Supporting Online Material for

Silver-Mediated Fluorination of Alkyl Iodide with $TMSCF_3$ as the Fluorinating Agent

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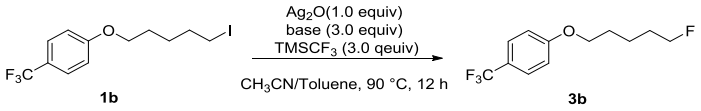
Materials and Methods

All reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless otherwise noted. CH_3CN used in reactions was dried by distillation over CaH_2. Toluene was dried by distillation over sodium/benzophenone. Other solvents were purified according to the purification handbook *Purification of Laboratory Chemicals* before using. Ag_2O (brownish black powder) and CaF_2 were purchased from Alfa and stored in the glovebox. $TMSCF_3$ (Trimethyl(trifluoromethyl)silane) (98%) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) (98%) were purchased from J&K. Deuterated solvents were purchased from Sigma-Aldrich. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). 200-300 mesh silica gel was purchased from Qingdao Haiyang Chemical Co., China. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. The data for NMR spectra (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) were recorded at 293 K on a Bruker AVANCE AV 400 (400MHz, 101MHz and 376MHz) and chemical shifts were recorded relative to the solvent resonance. Signal positions were recorded in ppm and the following abbreviations are used singularly or in combination to indicate the multiplicity of signals: s singlet, d doublet, t triplet, q quartet, m multiplet, Hz Hertz. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm. Mass spectra were obtained on Agilent 6520 Q-TOF LC/MS and Aligent 7890/5975C-GS/MSD. HRMS were obtained on Varian 7.0T FTMS (ESI) and GCT Premier (EI).

Experimental Data

Experimental Procedures and Compound Characterization

Effect of bases on the reaction

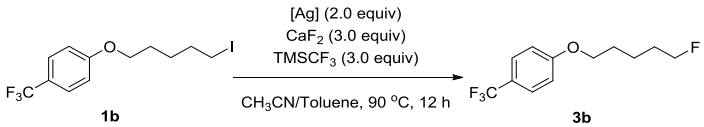


In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), base (0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) was added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S1.

Table S1: Effect of bases on the reaction

Bases	Yield [%] (^{1}HNMR)	Bases	Yield [%] (^{1}HNMR)
none	none	CaO	none
Et_3N	none	$NaHCO_3$	none
CaF_2	17	K_2CO_3	none
$CaCO_3$	7	NaOH	none
Cs_2CO_3	none	KO^{t}Bu	none

Effect of silver salts on the reaction



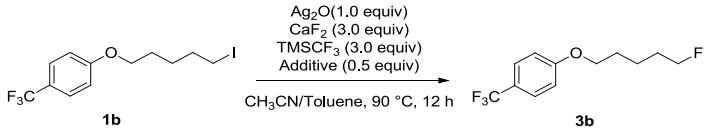
In an N_2 glovebox, to silver salt (0.100 mmol, 2.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) was added to the reaction and the resulting mixture was stirred for 12 h at 90 ^oC. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of

1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S2.

Table S2: Effect of silver salts on the reaction

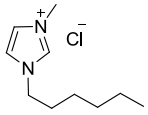
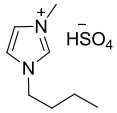
Silver salt	Yield [%] (^{1}HNMR)	Silver salt	Yield [%] (^{1}HNMR)
none	none	AgSCN	none
Ag_2SO_4	6	Ag_2O	17
Ag_2CO_3	none	$AgNO_3$	none
AgOTf	none	AgOBz	none

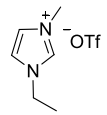
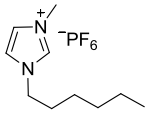
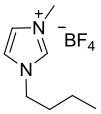
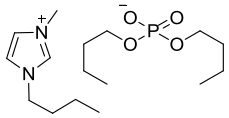
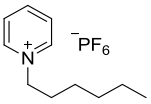
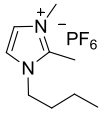
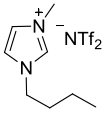
Effect of additives on the reaction



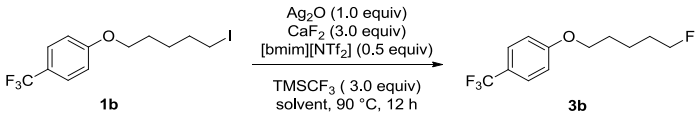
In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). Additive (0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^{1}H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S3.

Table S3: Effect of additives on the reaction

Additives	Yield [%] (^{1}HNMR)
18-crown-6	15
15-crown-5	14
	none
	2

	15
	81
	47
	1
	50
	13
	82
none	17

Effect of solvents on the reaction

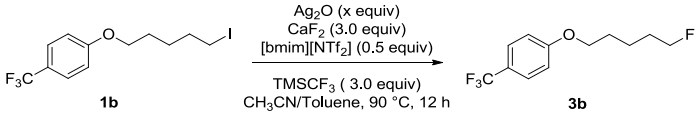


In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added solvent (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S4.

Table S4: Effect of solvents on the reaction

Solvent (0.1 M)	Yield [%] (^{1}HNMR)	Solvent (0.1 M)	Yield [%] (^{1}HNMR)
CH_3CN	77	Dioxane	none
DMSO	none	DCE	4
DMF	none	Toluene	5
THF	none	CH_3CN/Toluene 4:1(v:v)	83

Effect of Ag_2O amount on the reaction

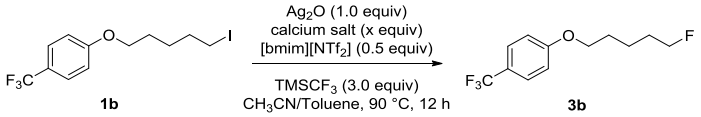


In an N_2 glovebox, to Ag_2O, CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^{1}H NMR resonance of 1-((5-fluorope ntyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S5.

Table S5: Effect of Ag_2O amount on the reaction

Amount of Ag_2O (equiv)	Yield [%] (^{1}H NMR)
0.0	0
0.5	40
1.0	83
2.0	65
3.0	47

Effect of calcium salts amount on the reaction



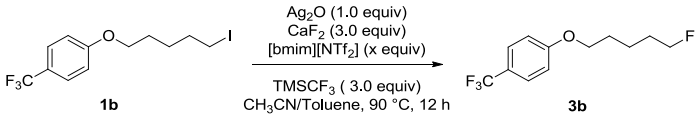
In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), calcium salt in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluorope ntyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S6.

Table S6: Effect of calcium salts amount on the reaction

Amount of calcium salt (equiv)	Yield [%] (^1H NMR)
CaF_2 (0.0 equiv)	0
CaF_2 (1.0 equiv)	40
CaF_2 (3.0 equiv)	83
CaF_2 (5.0 equiv)	76
$CaCO_3$ (1.0 equiv)	1
$CaCO_3$ (3.0 equiv)	5
$CaCO_3$ (5.0 equiv)	11
$CaCO_3$ (10.0 equiv)	21

$CaCO_3$ (milled once; 3.0 equiv)[a]	15
$CaCO_3$ (milled once; 5.0 equiv)	33
$CaCO_3$ (milled once; 10.0 equiv)	22
$CaCO_3$ (milled twice; 3.0 equiv)	18
CaO (3.0 equiv)	5
CaO (5.0 equiv)	5

Effect of [bmim][NTf_2] amount on the reaction



In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluorope ntyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S7.

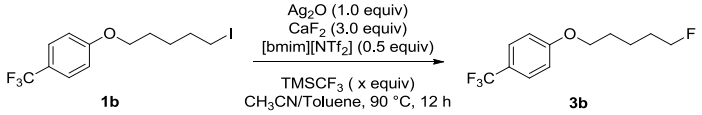
Table S7: Effect of [bmim][NTf_2] amount on the reaction

Amount of [bmim][NTf_2] (equiv)	Yield [%] (^1H NMR)
0.25	80
0.50	83

[a] Milled by QM-3SP2 planetary ball mill (Nanjing NanDa Instrument Plant)

1.00	80

Effect of $TMSCF_3$ amount on the reaction

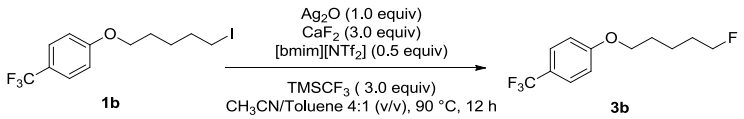


In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S8.

Table S8: Effect of $TMSCF_3$ amount on the reaction

Amount of $TMSCF_3$ (equiv)	Yield [%] (^1H NMR)
1.0	63
3.0	83
5.0	83

Effect of concentration on the reaction



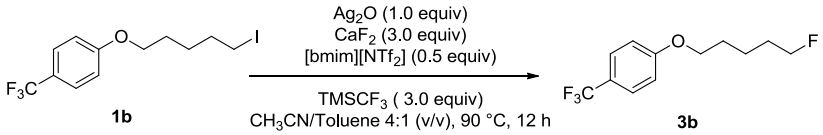
In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol , 3.00 equiv) in a 2.00 mL sealed vial were added solvent (CH_3CN/toluene = 4:1 (v/v)). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction

mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^{1}H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S9.

Table S9: Effect of concentration on the reaction

Concentration	Yield [%] (^{1}H NMR)
0.05 M (in 1.00 mL)	78
0.10 M (in 0.50 mL)	83
0.20 M (in 0.25 mL)	81

Effect of concentration on the reaction



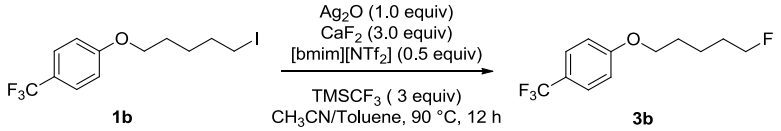
In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added solvent (CH_3CN/toluene = 4:1 (v/v)). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (179 mg, 0.500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, styrene (60.0 µL, 0.524 mmol). The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^{1}H NMR resonance of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S10.

Table S10: Effect of concentration on the reaction

Concentration	Yield [%] (^{1}H NMR)
0.10 M (in 5.00 mL)	80

0.20 M (in 2.50 mL)	83
0.40 M (in 1.25 mL)	70

Effect of CaF_2 surface area

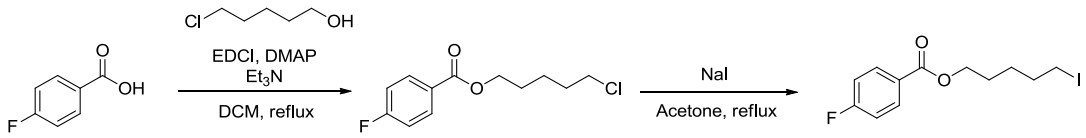


In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 (11.7 mg, 0.150 mmol, 3.00 equiv) in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (22.5 µL, 0.150 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, styrene (6.00 µL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluorope ntyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S11.

Table S11: Effect of CaF_2 surface area

CaF_2 (source)	BET results Surface area (m^2/g)	Yield [%] (^1H NMR)
Alfa (99.99%)	26.3	83
Aladdin (99.99%)	20.4	81
Fluorite (milled twice)	13.6	70
Fluorite (milled once)	8.4	29
Alfa (99.5%) (milled once)	10.7	41
Alfa (99.5%)	2.8	10
Fluorite	---	0

5-Iodopentyl 4-fluorobenzoate (1a)



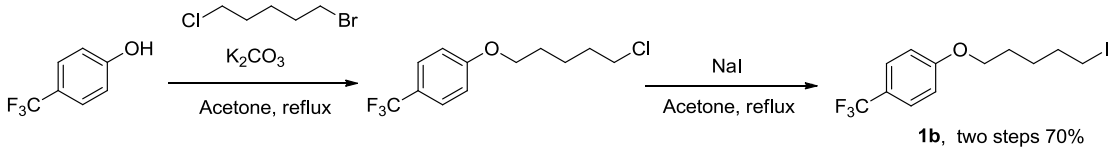
1a, two steps 80%

To a solution of 4-fluorobenzoic acid (1.40 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (610 mg, 5.00 mmol, 0.500 equiv) and Et_3N (4.17 mL, 30.0 mmol, 3.00 equiv) in dry DCM (15.0 mL) at 23 ^oC under N_2 were added EDCI (2.88 g, 15.0 mmol, 1.50 equiv) and 5-chloropentan-1-ol (2.31 mL, 30.0 mmol, 3.00 equiv). The reaction was refluxed for 12 h before diluted with DCM (10.0 mL) and quenched with H_2O (10.0 mL). The mixture was stirred for 15 min and extracted 3 times with DCM (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was dissolved with DCM (2.00 ml), passed through a pad of silica gel, washed with hexanes/EtOAc 5:1 (v/v), the filtrate was concentrated *in vacuo* and the crude product 5-chloropentyl 4-fluorobenzoate was used for next step directly.

The crude 5-chloropentyl 4-fluorobenzoate was dissolved with dry acetone (15.0 mL), sodium iodide (4.50 g, 30.0 mmol, 3.00 equiv) was added at 23 ^oC. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.68 g 5-iodopentyl 4-fluorobenzoate **(1a)** as a colorless liquid (80% yield).

R_f =0.3 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.15 – 7.08 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 6.9 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.84 – 1.75 (m, 2H), 1.61 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 253.7 Hz), 165.9, 132.4 (d, *J* = 9.3 Hz), 126.9 (d, *J* = 3.1 Hz), 115.8 (d, *J* = 22.0 Hz), 65.1, 33.3, 28.0, 27.3, 6.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5 – -105.6 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}FIO_2Na$ $[M+Na]^+$, 358.9920. Found, 358.9918.

1-((5-Iodopentyl)oxy)-4-(trifluoromethyl)benzene (1b)



1b, two steps 70%

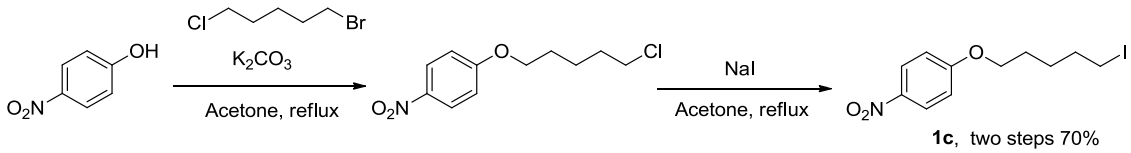
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-trifluoromethylphenol (1.62 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-(trifluoromethyl)benzene was taken on to the next reaction without

further purification.

The crude 1-((5-chloropentyl)oxy)-4-(trifluoromethyl)benzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 2.50 g 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene **(1b)** as a colorless liquid (70% yield).

R_f = 0.4 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.87 – 1.79 (m, 2H), 1.64 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 127.2 (q, *J* = 3.7 Hz), 124.8 (q, *J* = 271.1 Hz), 123.1 (q, *J* = 33.2 Hz), 114.7, 68.1, 33.4, 28.4, 27.4, 6.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.4 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{14}F_3IO$ [M], 358.0041. Found, 358.0045.

1-((5-Iodopentyl)oxy)-4-nitrobenzene (1c)

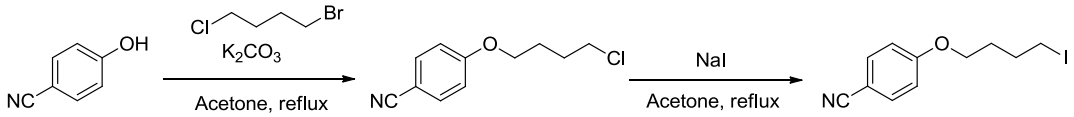


Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-nitrophenol (1.39 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-nitrobenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-nitrobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 2.34 g 1-((5-iodopentyl)oxy)-4-nitrobenzene **(1c)** as a white solid (70% yield).

R_f = 0.2 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.15 (m, 2H), 6.99 – 6.88 (m, 2H), 4.06 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 1.96 – 1.79 (m, 4H), 1.67 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 141.7, 126.3, 114.7, 68.8, 33.3, 28.3, 27.3, 6.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{14}INO_3Na$ $[M+Na]^+$, 357.9916. Found, 357.9916.

4-(4-Iodobutoxy)benzonitrile (1d)



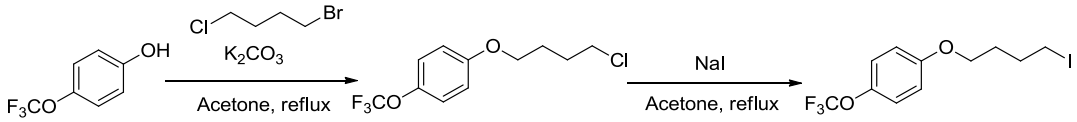
1d, two steps 83%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-hydroxybenzonitrile (1.19 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 4-(4-chlorobutoxy)benzonitrile was taken on to the next reaction without further purification.

The crude 4-(4-chlorobutoxy)benzonitrile was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 2.50 g 4-(4-iodobutoxy)benzonitrile **(1d)** as a white solid (83% yield).

R_f = 0.2 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 6.96 – 6.89 (m, 2H), 4.03 (t, *J* = 5.9 Hz, 2H), 3.26 (t, *J* = 6.7 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.98 – 1.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 134.3, 119.5, 115.4, 104.3, 67.4, 30.2, 30.2, 6.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{12}INONa$ $[M+Na]^+$, 323.9861. Found, 323.9859.

1-(4-Iodobutoxy)-4-(trifluoromethoxy)benzene (1e)



1e, two steps 53%

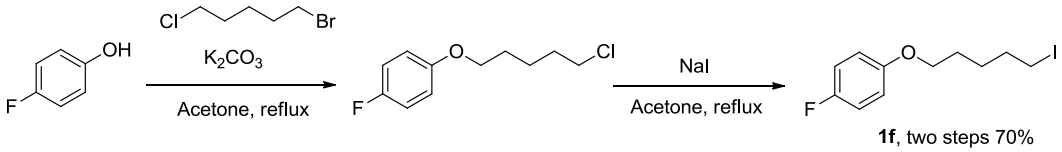
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-(trifluoromethoxy)phenol (1.78 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-(4-chlorobutoxy)-4-(trifluoromethoxy)benzene was taken on to the next reaction without further purification.

The crude 1-(4-chlorobutoxy)-4-(trifluoromethoxy)benzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and

concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 1.91 g 1-(4-iodobutoxy)-4-(trifluoromethoxy)benzene **(1e)** as a colorless liquid (53% yield).

R_f = 0.25 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 6.89 – 6.84 (m, 2H), 3.97 (t, *J* = 6.0 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.08 – 2.00 (m, 2H), 1.96 – 1.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 143.0, 122.8, 120.9 (q, *J* = 256.0 Hz), 115.5, 67.4, 30.4, 30.4, 6.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4 (s, 3F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{12}F_3IO_2$, [M] 359.9834. Found, 359.9850.

1-((5-Iodopentyl)oxy)-4-fluorobenzene (1f)



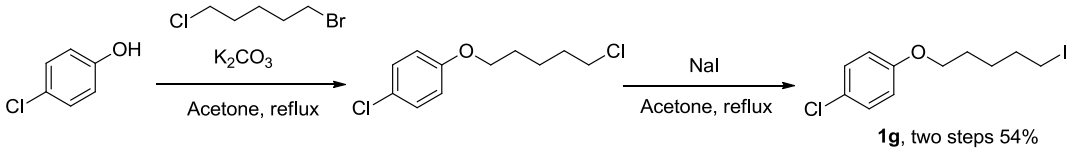
1f, two steps 70%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-fluorophenol (1.12 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-fluorobenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-fluorobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.15 g 1-((5-iodopentyl)oxy)-4-fluorobenzene **(1f)** as a colorless liquid (70% yield).

R_f = 0.25 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.92 (m, 2H), 6.85 – 6.78 (m, 2H), 3.92 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.84 (m, 2H), 1.83 – 1.75 (m, 2H), 1.63 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (d, *J* = 238.0 Hz), 155.4 (d, *J* = 1.3 Hz), 116.1 (d, *J* = 23.0 Hz), 115.7 (d, *J* = 7.9 Hz), 68.5, 33.5, 28.5, 27.4, 7.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.2 – -124.3 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}FIO$ [M], 308.0073. Found, 308.0077.

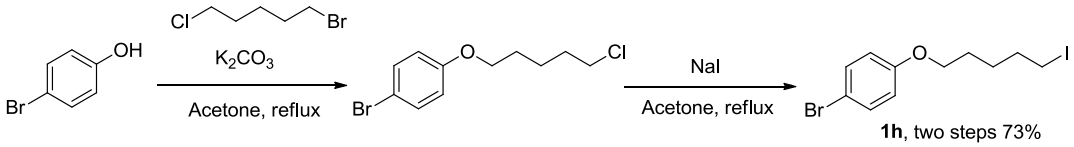
1-((5-Iodopentyl)oxy)-4-chlorobenzene (1g)



Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-chlorophenol (1.28 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-chlorobenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-chlorobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 1.75 g 1-((5-iodopentyl)oxy)-4-chlorobenzene **(1g)** as a colorless liquid (54% yield). R_f = 0.25 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 6.84 – 6.79 (m, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.86 (m, 2H), 1.84 – 1.76 (m, 2H), 1.62 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 129.6, 125.7, 116.0, 68.2, 33.5, 28.5, 27.4, 7.0. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}ClIO$ [M], 323.9778. Found, 323.9773.

1-((5-Iodopentyl)oxy)-4-bromobenzene (1h)



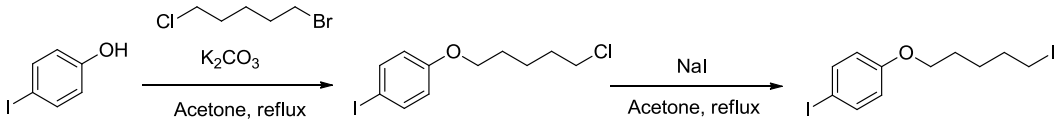
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-bromophenol (1.72 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-bromobenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-bromobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the

reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.70 g 1-((5-iodopentyl)oxy)-4-bromobenzene **(1h)** as a colorless liquid (73% yield).

R_f = 0.3 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 6.79 – 6.74 (m, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.86 (m, 2H), 1.84 – 1.76 (m, 2H), 1.62 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 132.5, 116.6, 113.0, 68.1, 33.4, 28.4, 27.4, 7.0. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}BrIO$ [M], 367.9273. Found, 367.9275.

1-((5-Iodopentyl)oxy)-4-iodobenzene (1i)



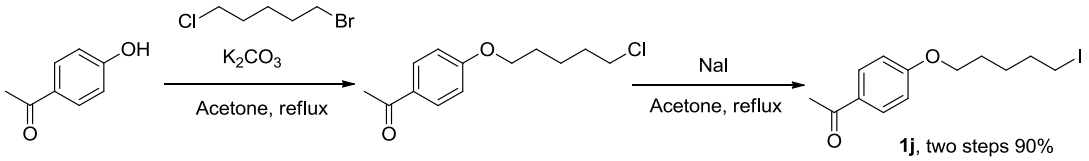
1i, two steps 50%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-iodophenol (2.20 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-iodobenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-iodobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.10 g 1-((5-iodopentyl)oxy)-4-iodobenzene **(1i)** as a white solid (50% yield).

R_f = 0.2 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 6.70 – 6.63 (m, 2H), 3.92 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.84 – 1.75 (m, 2H), 1.62 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 138.5, 117.2, 82.4, 68.0, 33.4, 28.4, 27.4, 7.0. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}I_2O$ [M], 415.9134. Found, 415.9138.

1-(4-((5-Iodopentyl)oxy)phenyl)ethanone (1j)

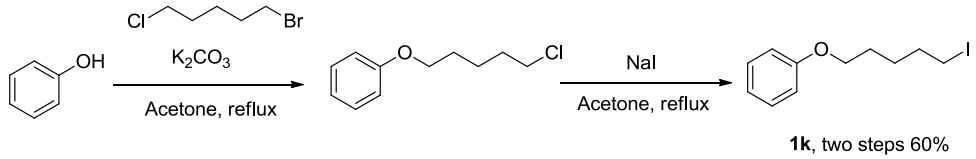


Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 1-(4-hydroxyphenyl)ethanone (1.36 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-(4-((5-chloropentyl)oxy)phenyl)ethanone was taken on to the next reaction without further purification.

The crude 1-(4-((5-chloropentyl)oxy)phenyl)ethanone was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 3.00 g 1-(4-((5-iodopentyl)oxy)phenyl)ethanone **(1j)** as a white solid (90% yield).

R_f = 0.2 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 6.94 – 6.89 (m, 2H), 4.03 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 6.9 Hz, 2H), 2.56 (s, 3H), 1.95 – 1.79 (m, 4H), 1.65 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 163.2, 130.9, 130.5, 114.4, 68.1, 33.4, 28.3, 27.3, 26.6, 6.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{18}IO_2$ $[M+H]^+$, 333.0351. Found, 333.0350.

((5-Iodopentyl)oxy)benzene (1k)



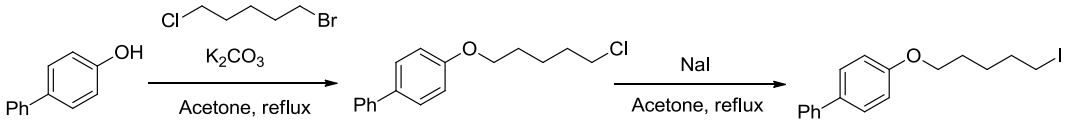
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), phenol (940 mg, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product ((5-chloropentyl)oxy)benzene was taken on to the next reaction without further purification.

The crude ((5-chloropentyl)oxy)benzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction

mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 1.73 g ((5-iodopentyl)oxy)benzene **(1k)** as a colorless liquid (60% yield).

R_f = 0.35 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.97 – 6.86 (m, 3H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.85 – 1.76 (m, 2H), 1.64 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 129.8, 120.9, 114.8, 67.7, 33.5, 28.5, 27.5, 7.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{15}IO$ [M], 290.0168. Found, 290.0169.

4-((5-Iodopentyl)oxy)-1,1'-biphenyl (1l)

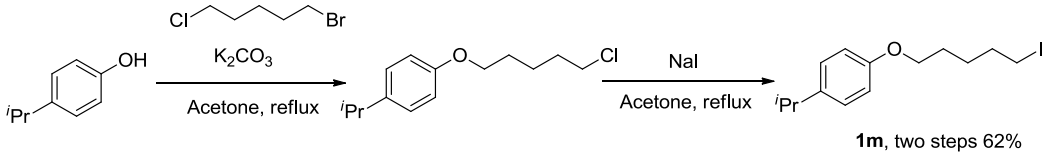


Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), [1,1'-biphenyl]-4-ol (1.70 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 4-((5-chloropentyl)oxy)-1,1'-biphenyl was taken on to the next reaction without further purification.

The crude 4-((5-chloropentyl)oxy)-1,1'-biphenyl was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.96 g 4-((5-iodopentyl)oxy)-1,1'-biphenyl **(1l)** as a white solid (81% yield).

R_f = 0.25 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 4H), 7.44 – 7.38 (m, 2H), 7.32 – 7.27 (m, 1H), 6.98 – 6.94 (m, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.88 – 1.80 (m, 2H), 1.66 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 141.1, 134.0, 129.1, 128.5, 127.0, 127.0, 115.1, 67.9, 33.5, 28.6, 27.5, 7.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{17}H_{19}IO$ [M], 366.0481, Found, 366.0483.

1-((5-Iodopentyl)oxy)-4-isopropylbenzene (1m)

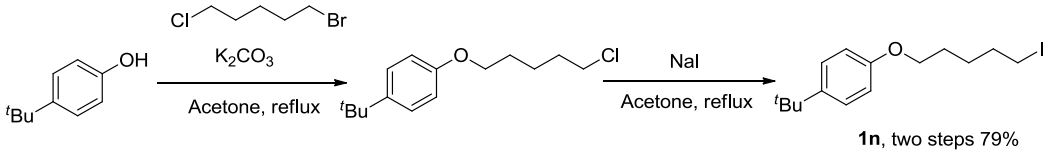


Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-isopropylphenol (1.36 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-isopropylbenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-isopropylbenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.06 g 1-((5-iodopentyl)oxy)-4-isopropylbenzene **(1m)** as a colorless liquid (62% yield).

R_f = 0.3 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 6.85 – 6.80 (m, 2H), 3.95 (t, *J* = 6.3 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 2.91 – 2.80 (m, 1H), 1.95 – 1.86 (m, 2H), 1.84 – 1.76 (m, 2H), 1.62 – 1.54 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 141.3, 127.5, 114.6, 67.8, 33.6, 33.5, 28.6, 27.5, 24.6, 7.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{21}IO$ [M], 332.0637. Found, 332.0633.

1-(*tert*-Butyl)-4-((5-iodopentyl)oxy)benzene (1n)



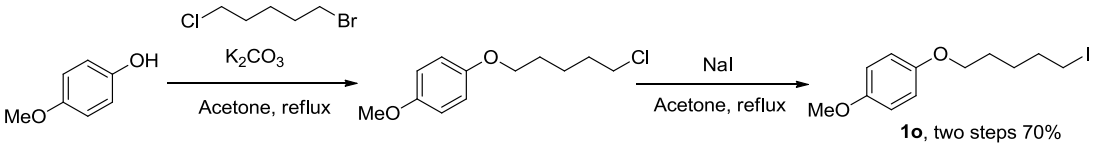
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-(*tert*-butyl)phenol (1.50 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-(*tert*-butyl)-4-((5-chloropentyl)oxy)benzene was taken on to the next reaction without

further purification.

The crude 1-(*tert*-butyl)-4-((5-chloropentyl)oxy)benzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 2.73 g 1-(*tert*-butyl)-4-((5-iodopentyl)oxy)benzene **(1n)** as a colorless liquid (79% yield).

R_f = 0.25 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 6.88 – 6.83 (m, 2H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.86 – 1.78 (m, 2H), 1.64 – 1.55 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 143.6, 126.5, 114.2, 67.8, 34.4, 33.5, 31.9, 28.6, 27.5, 7.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{23}IONa$ $[M+Na]^+$, 369.0691, Found, 369.0688.

1-((5-Iodopentyl)oxy)-4-methoxybenzene (1o)



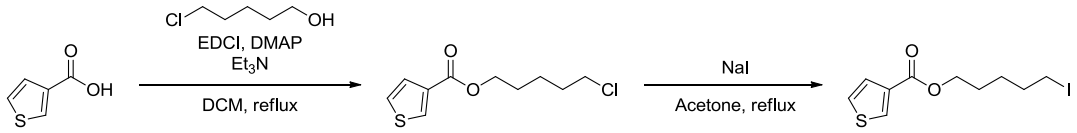
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-methoxyphenol (1.24 g, 10.0 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (1.32 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 1-((5-chloropentyl)oxy)-4-methoxybenzene was taken on to the next reaction without further purification.

The crude 1-((5-chloropentyl)oxy)-4-methoxybenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 2.25 g 1-((5-iodopentyl)oxy)-4-methoxybenzene **(1o)** as a colorless liquid (70% yield).

R_f = 0.25 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.83 – 1.73 (m, 2H), 1.63 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 153.4,

115.7, 114.9, 68.5, 56.0, 33.5, 28.6, 27.5, 7.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{17}IO_2$ [M], 320.0273. Found, 320.0271.

5-Iodopentyl thiophene-3-carboxylate (1p)

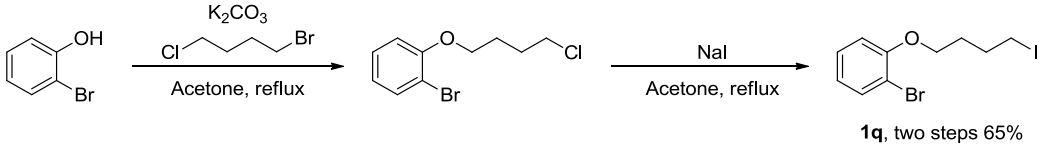


To a solution of thiophene-3-carboxylic acid (1.28 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (610 mg, 5.00 mmol, 0.50 equiv) and Et_3N (4.17 mL, 30.0 mmol, 3.00 equiv) in dry DCM (15.0 mL) at 23 °C under N_2 were added EDCI (2.88 g, 15.0 mmol, 1.50 equiv) and 5-chloropentan-1-ol (2.31 mL, 30.0 mmol, 3.00 equiv). The reaction was refluxed for 12 h before diluted with DCM (10.0 mL) and quenched with H_2O (10.0 mL). The mixture was stirred for 15 min and extracted 3 times with DCM (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was dissolved with DCM (2.00 ml), passed through a pad of silica gel, washed with hexanes/EtOAc 5:1 (v/v), the filtrate was concentrated *in vacuo* and the crude product 5-chloropentyl thiophene-3-carboxylate was used for next step directly.

The crude 5-chloropentyl thiophene-3-carboxylate was dissolved with dry acetone (15.0 mL), sodium iodide (4.50 g, 30.0 mmol, 3.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 1.86 g 5-iodopentyl thiophene-3-carboxylate **(1p)** as a light yellow liquid (80% yield).

R_f =0.3 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.53 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.31 (dd, *J* = 5.0, 3.1 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 3.21 (t, *J* = 6.9 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.81 – 1.72 (m, 2H), 1.60 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 134.1, 132.9, 128.2, 126.3, 64.6, 33.3, 28.0, 27.3, 6.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{10}H_{13}IO_2SNa$ $[M+Na]^+$, 346.9579. Found, 346.9578.

2-(4-Iodobutoxy)- 1-bromobenzene (1q)



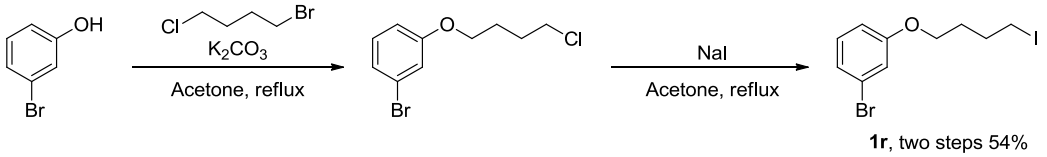
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 2-bromophenol (1.73 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water

(30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 2-(4-chlorobutoxy)-1-bromobenzene was taken on to the next reaction without further purification.

The crude 2-(4-chlorobutoxy)-1-bromobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 30:1 (v/v) to afford 2.29 g 2-(4-iodobutoxy)-1-bromobenzene **(1q)** as a colorless liquid (65% yield).

R_f = 0.35 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.28 – 7.22 (m, 1H), 6.90 – 6.80 (m, 2H), 4.05 (t, *J* = 5.9 Hz, 2H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.13 – 2.05 (m, 2H), 2.00 – 1.92 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 133.6, 128.7, 122.2, 113.4, 112.5, 68.1, 30.4, 30.2, 7.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{12}BrIO$ [M], 353.9116. Found, 353.9117.

3-(4-Iodobutoxy)- 1-bromobenzene (1r)



1r, two steps 54%

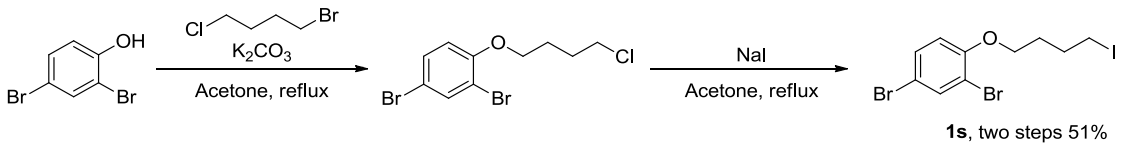
Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 3-bromophenol (1.73 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 3-(4-chlorobutoxy)-1-bromobenzene was taken on to the next reaction without further purification.

The crude 3-(4-chlorobutoxy)-1-bromobenzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v) to afford 1.91 g 3-(4-iodobutoxy)-1-bromobenzene **(1r)** as a colorless liquid (54% yield).

R_f = 0.3 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 3H), 6.85 – 6.78 (m, 1H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.07 – 1.97 (m, 2H), 1.94 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 130.9, 124.1, 123.1, 118.0, 113.8, 67.2, 30.3, 30.3, 6.7. Mass Spectrometry: HRMS-EI (m/z): Calcd for

$C_{10}H_{12}BrIO$ [M], 353.9116. Found, 353.9115.

2,4-Dibromo-1-(4-iodobutoxy)benzene (1s)



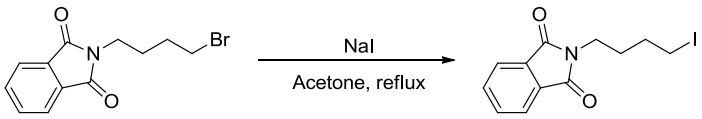
1s, two steps 51%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 2,4-dibromophenol (2.51 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 2,4-dibromo-1-(4-chlorobutoxy)benzene was taken on to the next reaction without further purification.

The crude 2,4-dibromo-1-(4-chlorobutoxy)benzene was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 2.20 g 2,4-dibromo-1-(4-iodobutoxy)benzene **(1s)** as a colorless liquid (51% yield).

R_f = 0.3 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 4.01 (t, *J* = 5.9 Hz, 2H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.12 – 2.02 (m, 2H), 2.00 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 135.8, 131.5, 114.5, 113.4, 113.3, 68.5, 30.4, 30.1, 6.9. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{11}Br_2IO$ [M], 431.8221. Found, 431.8227.

2-(4-Iodobutyl)isoindoline-1,3-dione (1t)



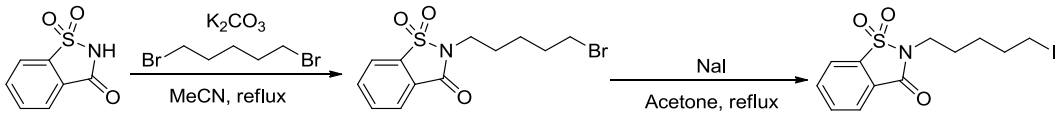
1t, 93%

2-(4-Bromobutyl)isoindoline-1,3-dione was dissolved with dry acetone (15.0 mL), sodium iodide (4.50 g, 30.0 mmol, 3.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 8:1 (v/v) to afford 3.05 g 2-(4-iodobutyl)isoindoline-1,3-dione **(1t)** as a white solid (93% yield).

R_f = 0.3 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87

– 7.82 (m, 2H), 7.75 – 7.69 (m, 2H), 3.72 (t, *J* = 6.7 Hz, 2H), 3.22 (t, *J* = 6.6 Hz, 2H), 1.92 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 134.4, 132.4, 123.6, 37.1, 30.9, 29.9, 5.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{13}INO_2$ $[M+H]^+$, 329.9991. Found, 329.9987.

***N*-(5-iodopentyl)saccharine (1u)**



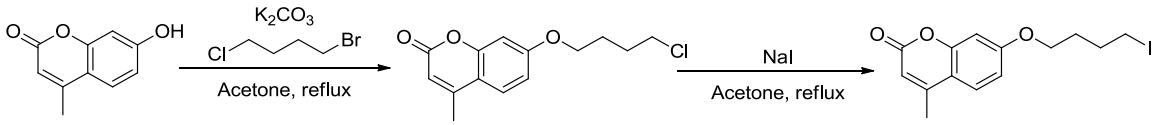
1u, two steps 33%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry MeCN (15.0 mL), saccharin (1.82 g, 10.0 mmol, 1.00 equiv) and 1,5-dibromopentane (2.72 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with hexanes/DCM 1:1 (v/v), to afford 1.50 g N-(5-bromopentyl)saccharine as a white solid (45% yield).

N-(5-Bromopentyl)saccharine was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v) to afford 1.25 g *N*-(5-iodopentyl)saccharine **(1u)** as a white solid (33% yield).

R_f = 0.2 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 1H), 7.95 – 7.80 (m, 3H), 3.79 (t, *J* = 7.4 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 1.95 – 1.82 (m, 4H), 1.60 – 1.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 137.9, 135.1, 134.7, 127.7, 125.5, 121.3, 39.4, 33.1, 28.0, 27.7, 6.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}INO_3SNa$ $[M+Na]^+$, 401.9637. Found, 401.9635.

7-(4-Iodobutoxy)-4-methyl-2H-chromen-2-one (1v)



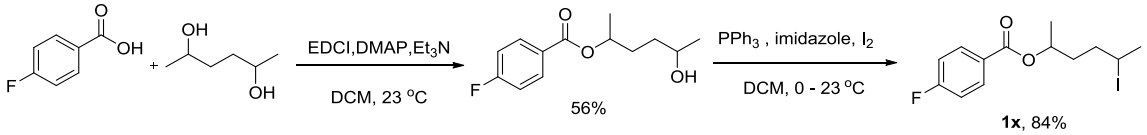
1v, two steps 60%

Potassium carbonate (2.76 g, 20.0 mmol, 2.00 equiv) was suspended in dry acetone (15.0 mL), 4-methylumbelliferone (1.76 g, 10.0 mmol, 1.00 equiv) and 1-bromo-4-chlorobutane (1.15 ml, 10.0 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product 7-(4-chlorobutoxy)-4-methyl-2H-chromen-2-one was taken on to the next reaction without further purification.

The crude 7-(4-chlorobutoxy)-4-methyl-2H-chromen-2-one was dissolved with dry acetone (15.0 mL), sodium iodide (6.00 g, 40.0 mmol, 4.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v) to afford 2.14 g 7-(4-iodobutoxy)-4-methyl-2H-chromen-2-one **(1v)** as a white solid (60% yield).

R_f = 0.4 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.14 (s, 1H), 4.05 (t, *J* = 6.0 Hz, 2H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 2.09 – 2.00 (m, 2H), 1.99 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.6, 155.5, 152.9, 125.9, 113.9, 112.9, 112.3, 101.6, 67.6, 30.3, 30.2, 19.0, 6.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{16}IO_3$ $[M+H]^+$, 359.0144. Found, 359.0138.

5-Iodohexan-2-yl 4-fluorobenzoate (1x)



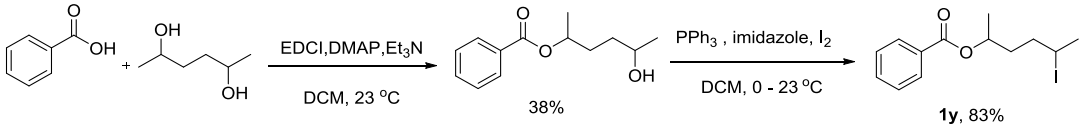
To a solution of 4-fluorobenzoic acid (700 mg, 5.00 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (305 mg, 2.50 mmol, 0.50 equiv) and Et_3N (1.74 mL, 12.5 mmol, 2.50 equiv) in dry DCM (15.0 mL) at 23 °C under N_2 were added EDCI (1.92 g, 10.0 mmol, 2.00 equiv) and hexane-2,5-diol (0.92 mL, 7.50 mmol, 1.50 equiv). The reaction mixture was stirred and monitored by TLC. When completed, the reaction was diluted with DCM (10.0 mL) and quenched with H_2O (10.0 mL). The mixture was stirred for 15 min and extracted three times with DCM (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo* .The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v) to afford 672 mg 5-hydroxyhexan-2-yl 4-fluorobenzoate as a light yellow liquid (56% yield).

5-Hydroxyhexan-2-yl 4-fluorobenzoate (672 mg, 2.80 mmol, 1.00 equiv) was dissolved with dry DCM (10.0 mL), to which was added sequentially triphenylphosphine (808 mg, 3.08 mmol, 1.10 equiv), imidazole (229 mg, 3.36 mmol, 1.20 equiv), and iodine (599 mg, 3.36 mmol, 1.20 equiv) in three portions. The reaction was stirred overnight, in the dark, at room temperature. The reaction was quenched by the addition of a saturated solution of sodium thiosulfate and extracted three times with DCM (20.0 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 823 mg 5-iodohexan-2-yl 4-fluorobenzoate **(1x)** as a light yellow liquid (84% yield).

R_f =0.2 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.16 – 7.05 (m, 2H), 5.23 – 5.11 (m, 1H), 4.25 – 4.13 (m, 1H), 2.00 – 1.63 (m, 7H), 1.36 (dd, *J* = 6.3, 0.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.5, 166.1 (d, *J* = 253.8 Hz), 132.4 (d, *J* = 9.4 Hz), 127.2 (d, *J* = 2.9 Hz), 127.1 (d, *J* = 2.9 Hz), 115.8 (d, *J* =

21.9 Hz), 71.5, 71.0, 39.1, 38.8, 36.6, 36.5, 29.8, 29.8, 29.3, 29.3, 20.6, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.7 – -105.9 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{16}F_3O_2$ [M-I], 223.1134. Found, 223.1135.

5-Iodohexan-2-yl benzoate (1y)

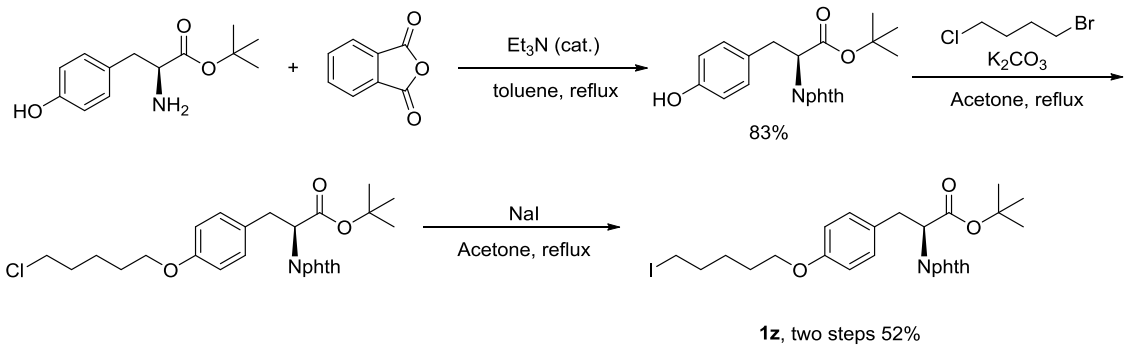


To a solution of benzoic acid (611 mg, 5.00 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (305 mg, 2.50 mmol, 0.50 equiv) and Et_3N (1.74 mL, 12.5 mmol, 2.50 equiv) in dry DCM (15.0 mL) at 23 °C under N_2 were added EDCI (1.92 g, 10.0 mmol, 2.00 equiv) and hexane-2,5-diol (0.92 mL, 7.50 mmol, 1.50equiv). The reaction mixture was stirred and monitored by TLC. When completed, the reaction was diluted with DCM (10.0 mL) and quenched with H_2O (10.0 mL). The mixture was stirred for 15 min and extracted three times with DCM (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo* .The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 8:1 (v/v) to afford 211 mg 5-hydroxyhexan-2-yl benzoate as a light yellow liquid (38% yield).

5-Hydroxyhexan-2-yl benzoate (211 mg, 1.90 mmol, 1.00 equiv) was dissolved with dry DCM (10.0 mL), to which was added sequentially triphenylphosphine (548 mg, 2.09 mmol, 1.10 equiv), imidazole (155 mg, 2.28 mmol, 1.20 equiv), and iodine (579 mg, 2.28 mmol, 1.20 equiv) in three portions. The reaction was stirred overnight, in the dark, at room temperature. The reaction was quenched by the addition of a saturated solution of sodium thiosulfate and extracted three times with DCM (20.0 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 524 mg 5-iodohexan-2-yl benzoate **(1y)** as a light yellow liquid (83% yield).

R_f =0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.25 – 5.13 (m, 1H), 4.26 – 4.13 (m, 1H), 2.01 – 1.66 (m, 7H), 1.37 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.4, 133.2, 130.9, 130.9, 129.9, 128.7, 71.3, 70.8, 39.2, 38.8, 36.7, 36.5, 30.0, 29.9, 29.4, 29.3, 20.6, 20.5. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{17}O_2$ [M-I], 205.1229. Found, 205.1227.

(S)-*tert*-Butyl-2-(1,3-dioxoisoindolin-2-yl)-3-(4-((5-iodopentyl)oxy)phenyl)propanoate (1z)



In a round-bottom flask fitted with Dean-stark apparatus and a reflux condenser, phthalic acid anhydride (1.48 g, 10 mmol, 1.00 equiv) and *tert*-butyl L-tyrosinate (2.37g, 10 mmol, 1.00 equiv) were refluxed in toluene (25.0 mL) in the presence of 0.1 mL triethylamine overnight. Afterwards the cooled mixture was concentrated *in vacuo*. Water was added to this oily mass and extracted three times with EtOAc (50.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v) to afford 3.08 g (S)-*tert*-butyl-2-(1,3-dioxoisoindolin-2-yl)-3-(4-hydroxyphenyl)propanoate as a white solid (83% yield).

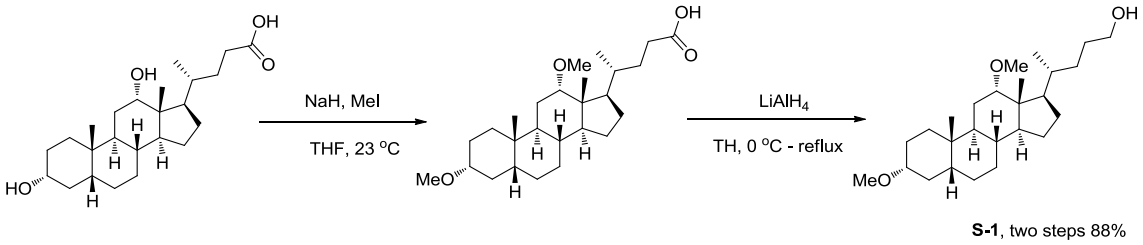
Potassium carbonate (1.38 g, 10.0 mmol, 2.00 equiv) was suspended in dry acetone (10.0 mL), (S)-*tert*-butyl-2-(1,3-dioxoisoindolin-2-yl)-3-(4-hydroxyphenyl)propanoate (1.54 g, 5.00 mmol, 1.00 equiv) and 1-bromo-5-chloropentane (0.66 ml, 5.00 mmol, 1.00 equiv) were added. Subsequently, the reaction mixture was refluxed for 12 h. Afterwards the cooled mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with 1 M aqueous NaOH solution (30.0 ml), water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product (S)-*tert*-butyl-3-(4-((5-chloropentyl)oxy)phenyl)-2-(1,3-dioxoisoindolin-2-yl)propanoate was taken on to the next reaction without further purification.

The crude (S)-*tert*-butyl-3-(4-((5-chloropentyl)oxy)phenyl) -2-(1,3-dioxoisoindolin-2-yl)propanoate was dissolved with dry acetone (10.0 mL), sodium iodide (3.00 g, 20.0 mmol, 4.00 equiv) was added at 23 ^{o}C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 10:1 (v/v) to afford 1.46 g (S)-*tert*-butyl-2-(1,3-dioxoisoindolin-2-yl)-3-(4-((5-iodopentyl)oxy)phenyl)propanoate **(1z)** as a colorless oily liquid (52% yield).

R*f* = 0.3 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.71 – 7.64 (m, 2H), 7.09 – 7.02 (m, 2H), 6.73 – 6.67 (m, 2H), 5.01 (dd, *J* = 10.0, 6.7 Hz, 1H), 3.90 – 3.80 (m, 2H), 3.51 – 3.43 (m, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.78 – 1.68 (m, 2H), 1.58 – 1.49 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 167.9, 167.6, 157.7, 134.0, 131.6, 129.8, 129.0, 123.4, 114.5, 82.7, 67.4, 54.3, 33.8, 33.2, 28.2, 27.9, 27.1, 6.8. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{30}INO_5Na$ $[M+Na]^+$, 586.1066. Found, 586.1065.

3,12-Dimethoxy cholan-24-iodo (1aa)

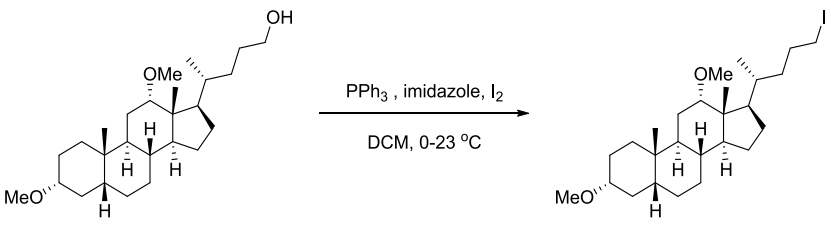


S-1, two steps 88%

To a suspension of NaH (684 mg of a 60 % suspension in mineral oil, 17.09 mmol, 3.40 equiv) in 40.0 mL of dry THF at 0 ℃, was added deoxycholic acid (1.96 g, 5.00 mmol, 1.00 equiv) in portions. The resulting solution was stirred at 0 ℃ for 10 min, and then was added methyl iodide (0.49 mL, 7.80 mmol, 1.56 equiv). The reaction mixture was stirred for 18 h at ambient temperature and then was added a second portion of NaH (557 mg, 13.9 mmol, 2.78 equiv), followed by more methyl iodide (0.40 mL, 6.50 mmol, 1.30 equiv). The reaction was stirred for an additional 36 h at ambient temperature. The reaction mixture was quenched by slow addition of methanol then concentrated *in vacuo*. The resulting mixture was diluted with ethyl acetate (50.0 mL) and poured on water (40.0 mL). The aqueous layer was then extracted three times with EtOAc (25.0 mL). The combined organics were washed with brine (25.0 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product di-*O*-methyl deoxycholic acid was taken on to the next reaction without further purification.

Crude di-*O*-methyl deoxycholic acid was dissolved with THF (15.0 mL) at 0 °C, to which was added $LiAlH_4$ (570 mg, 15.0 mmol, 3.00 equiv) in three portions with vigorous stirring under nitrogen atmosphere. The reaction mixture was then heated to reflux with stirring for overnight. Upon completion, the reaction was carefully quenched with the same amount of water (0.57 mL) as $LiAlH_4$ at 0°C, subsequently aqueous NaOH solution (0.57 mL), water (0.57 mL×3) were added, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 4:1 (v/v) to afford 1.80 g 3,12-dimeth oxycholan-24-ol (**S-1**) as a white solid (88% yield).

R_f = 0.5 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, *J* = 6.5 Hz, 2H), 3.39 (s, 1H), 3.33 (s, 3H), 3.25 (s, 3H), 3.19 – 3.09 (m, 1H), 1.91 – 1.68 (m, 8H), 1.67 – 1.51 (m, 4H), 1.47 – 0.98 (m, 14H), 0.95 – 0.88 (m, 6H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.6, 80.8, 63.9, 56.0, 55.8, 49.2, 47.0, 46.6, 42.4, 36.3, 35.7, 35.6, 34.8, 33.8, 32.9, 32.1, 29.8, 27.9, 27.7, 27.1, 26.4, 24.0, 23.6, 22.2, 18.0, 13.0. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{26}H_{46}O_3$ [M], 406.3447. Found, 406.3458

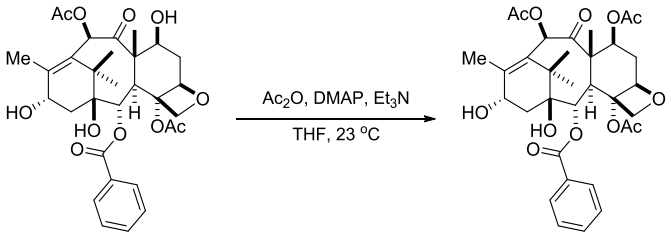


1aa, 90%

3,12-Dimethoxy cholan-24-ol (**S-1**) (1.90 g, 4.16 mmol, 1.00 equiv) was dissolved with dry DCM (10.0 mL), to which was added sequentially triphenylphosphine (1.20 g, 4.58 mmol, 1.10 equiv), imidazole (340 mg, 4.99 mmol, 1.20 equiv), and iodine (1.27 g, 4.99 mmol, 1.20 equiv) in portions. The reaction was stirred overnight, in the dark, at room temperature. The reaction was quenched by the addition of a saturated solution of sodium thiosulfate and extracted three times with DCM (20.0 m). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v) to afford 1.94 g 3,12-dimethoxy cholan-24-iodo **(1aa)** as a white solid (90% yield).

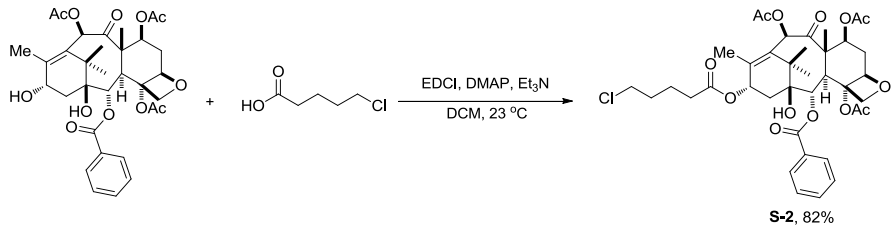
R_f = 0.2 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (s, 1H), 3.34 (s, 3H), 3.25 (s, 3H), 3.22 – 3.09 (m, 3H), 1.92 – 1.65 (m, 10H), 1.62 – 1.58 (m, 1H), 1.55 – 1.52 (m, 1H), 1.47 – 0.95 (m, 14H), 0.94-0.86 (m, 6H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.5, 80.8, 56.0, 55.9, 49.1, 46.9, 46.6, 42.4, 37.1, 36.3, 35.6, 35.2, 34.8, 33.8, 32.9, 30.7, 27.9, 27.6, 27.1, 26.4, 24.0, 23.6, 22.2, 18.1, 13.0, 8.3. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{26}H_{45}IO_2$ [M], 516.2464. Found, 516.2468.

7-*O*-acetyl-13-*O*-(5-iodopentanoate)baccatine III (1bb)



7-*O*-acetyl baccatine III, 90%

To a solution of baccatine III (200 mg, 0.341 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (20.8 mg, 0.17 mmol, 0.500 equiv) and Et_3N (187 µL, 1.71 mmol, 4.00 equiv) in dry THF (4.00 mL) at 23 °C under N_2 were added acetic anhydride (64.2 µL 0.684 mmol, 2.00 equiv). The reaction mixture was stirred and monitored by TLC. When completed, the reaction was diluted with EtOAc (50.0 mL) and quenched with H_2O (20.0 mL). The mixture was stirred for 15 min, and the aqueous fraction was separated and extracted three times with EtOAc (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 1:1 (v/v), to afford 203 mg 7-*O*-acetyl baccatine III[1] as a white solid (90% yield).

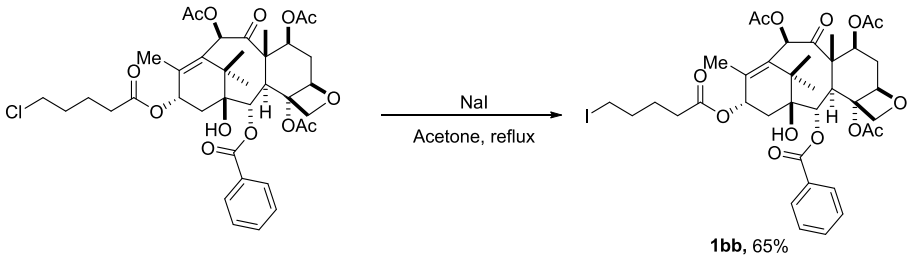


S-2, 82%

To a solution of 5-chloropentanoic acid (114 µL, 0.972 mmol, 3.00 equiv), DMAP (4-dimethylaminepyridine) (118 mg, 0.972 mmol, 3.00 equiv) and Et_3N (225 µL, 1.62 mmol, 5.00 equiv) in dry THF (4.00 mL) at 23 °C under N_2 were added EDCI (186 mg, 0.972 mmol, 3.00 equiv) and 7-*O*-acetyl baccatine III (203 mg, 0.324 mmol, 1.00 equiv). The reaction was

stirred for 20 h before diluted with EtOAc (50.0 mL) and quenched with H_2O (10.0 mL). The mixture was stirred for 15 min and extracted three times with EtOAc (25.0 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 3:1 (v/v), to afford 186 mg 7-*O*-acetyl-13-*O*-(5-chloropentanoate)baccatine III (**S-2**) as a white solid (82% yield).

R_f = 0.6 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.25 (s, 1H), 6.19 (t, *J* = 8.7 Hz, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 5.58 (dd, *J* = 10.5, 7.1 Hz, 1H), 4.96 (d, *J* = 8.6 Hz, 1H), 4.31 (d, *J* = 8.3 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.94 (d, *J* = 6.9 Hz, 1H), 3.58 (t, *J* = 5.5 Hz, 2H), 2.65 – 2.40 (m, 3H), 2.33 (s, 3H), 2.27 – 2.19 (m, 2H), 2.17 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.91 – 1.84 (m, 4H), 1.84 – 1.81 (m, 1H), 1.79 (s, 3H), 1.71 (s, 1H), 1.21 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 172.9, 170.8, 169.8, 169.2, 167.2, 141.7, 134.1, 132.8, 130.4, 129.4, 129.0, 84.3, 81.2, 79.1, 76.6, 75.7, 74.7, 71.7, 69.8, 56.4, 47.5, 44.7, 43.5, 35.8, 33.9, 33.7, 32.1, 26.7, 22.9, 22.5, 21.5, 21.1, 21.0, 15.2, 11.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{38}H_{51}ClNO_{13}$ $[M+NH_4]^+$, 764.3049. Found, 764.3043.

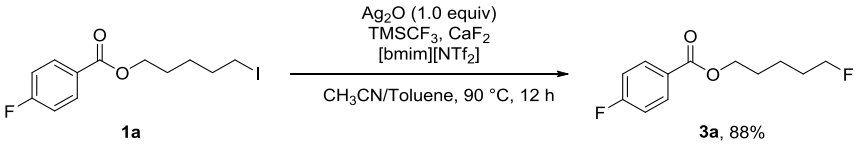


1bb, 65%

7-*O*-acetyl-13-*O*-(5-chloropentanoate)baccatine III (**S-2**) (186 mg, 0.266 mmol, 1.00 equiv) was dissolved with dry acetone (5.00 mL), sodium iodide (120 mg, 0.800 mmol, 3.00 equiv) was added at 23 °C. Subsequently, the reaction mixture was refluxed for 24 h. Afterwards the cooled mixture was filtrated and concentrated *in vacuo*. The residue was dissolved in EtOAc (50.0 mL) and washed successively with water (30.0 mL) and a saturated solution of sodium chloride (30.0 mL). The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 3:1 (v/v) to afford 145 mg 7-*O*-acetyl-13-*O*-(5-iodopentanoate)baccatine III **(1bb)** as a white solid (65% yield).

R_f = 0.6 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 6.26 (s, 1H), 6.20 (t, *J* = 8.3 Hz, 1H), 5.66 (d, *J* = 6.9 Hz, 1H), 5.59 (dd, *J* = 10.6, 7.1 Hz, 1H), 4.97 (d, *J* = 8.5 Hz, 1H), 4.33 (d, *J* = 8.5 Hz, 1H), 4.15 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 7.0 Hz, 1H), 3.22 (t, *J* = 6.6 Hz, 2H), 2.65 – 2.38 (m, 3H), 2.34 (s, 3H), 2.24 (d, *J* = 8.3 Hz, 2H), 2.18 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.94 – 1.81 (m, 5H), 1.80 (s, 3H), 1.65 (s, 1H), 1.22 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 172.5, 170.5, 169.5, 168.9, 166.9, 141.3, 133.8, 132.5, 130.1, 129.1, 128.7, 84.0, 80.9, 78.8, 76.3, 75.4, 74.4, 71.4, 69.5, 56.0, 47.2, 43.2, 35.5, 33.4, 33.2, 32.7, 26.4, 25.7, 22.6, 21.1, 20.8, 20.7, 14.9, 10.8, 5.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{38}H_{51}INO_{13}$ $[M+NH_4]^+$, 856.2405. Found, 856.2398.

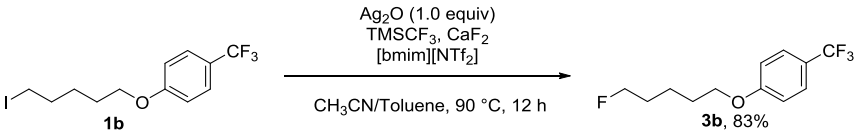
5-Fluoropentyl 4-fluorobenzoate (3a)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 5-iodopentyl 4-fluorobenzoate (**1a**) (168 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 4:1 (v/v) to afford 103 mg 5-fluoropentyl 4-fluorobenzoate (**3a**) as a colorless liquid (88% yield).

R_f = 0.20 (hexanes/toluene 3:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.15 – 7.07 (m, 2H), 4.48 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.70 (m, 4H), 1.64 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 253.7 Hz), 166.0, 132.4 (d, *J* = 9.3 Hz), 126.9 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.0 Hz), 84.2 (d, *J* = 164.7 Hz), 65.2, 30.4 (d, *J* = 19.7 Hz), 28.7, 22.3 (d, *J* = 5.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.8 – -105.9 (m, 1F), -218.4 – -218.9 (m, 1F) . Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}F_2O_2Na$ $[M+Na]^+$, 251.0860. Found, 251.0858.

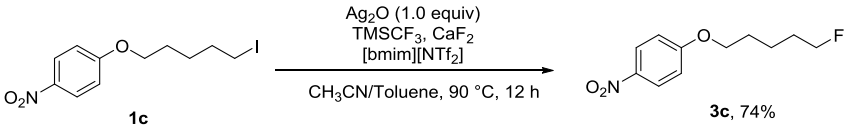
1-((5-Fluoropentyl)oxy)-4-(trifluoromethyl)benzene (3b)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (179 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 104 mg 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) as a colorless liquid (83% yield).

R_f = 0.50 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.49 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 1.90 – 1.71 (m, 4H), 1.66 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 126.9 (q, *J* = 3.6 Hz), 124.5 (q, *J* = 271.0 Hz), 122.7 (q, *J* = 32.7 Hz), 114.4, 83.9 (d, *J* = 164.6 Hz), 67.9, 30.1 (d, *J* = 19.7 Hz), 28.8, 22.0 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.4 (s, 3F), -218.3 – -218.8 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{14}F_4O$ [M], 250.0981. Found, 250.0978.

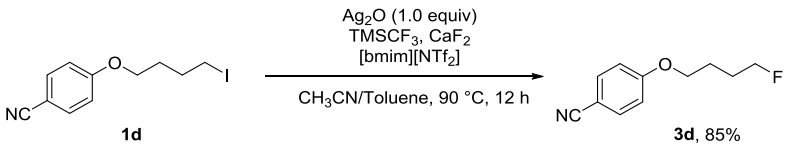
1-((5-Fluoropentyl)oxy)-4-nitrobenzene (3c)



In an N_2 glovebox, to Ag_2O (139 mg, 0.600 mmol, 1.20 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-nitrobenzene (**1c**) (168 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene/acetone 5:3:0.2 (v/v/v) to afford 84.4 mg 1-((5-fluoropentyl)oxy)-4-nitrobenzene (**3c**) as a colorless liquid (74% yield).

R_f = 0.20 (hexanes/toluene/acetone 5:3:0.2 (v/v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.16 (m, 2H), 6.97 – 6.89 (m, 2H), 4.49 (dt, *J* = 47.2, 5.9 Hz, 2H), 4.07 (t, *J* = 6.3 Hz, 2H), 1.93 – 1.70 (m, 4H), 1.66 – 1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 141.6, 126.2, 114.7, 84.1 (d, *J* = 164.6 Hz), 68.8, 30.3 (d, *J* = 19.7 Hz), 28.9, 22.2 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.9 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}FNO_3$ [M], 227.0958. Found, 227.0961.

4-(4-Fluorobutoxy)benzonitrile (3d)

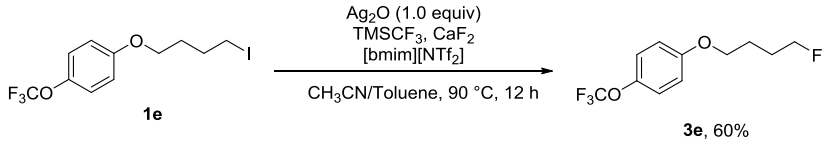


In an N_2 glovebox, to Ag_2O (139 mg, 0.600 mmol, 1.20 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 4-(4-iodobutoxy)benzonitrile (**1d**) (150 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was

stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene/acetone 1:1:0.015 (v/v/v) to afford 82.6 mg 4-(4-fluorobutoxy)benzonitrile (**3d**) as a white solid (85% yield).

R_f = 0.30 (hexanes/toluene/acetone 1:1:0.02 (v/v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 6.97 – 6.88 (m, 2H), 4.53 (dt, *J* = 47.6, 5.6 Hz, 2H), 4.05 (t, *J* = 6.0 Hz, 2H), 2.01 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 134.3, 119.6, 115.5, 104.2, 83.9 (d, *J* = 165.1 Hz), 68.0, 27.4 (d, *J* = 20.0 Hz), 25.4 (d, *J* = 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.6 – -219.0 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{12}FNO$ [M], 193.0903. Found, 193.0901.

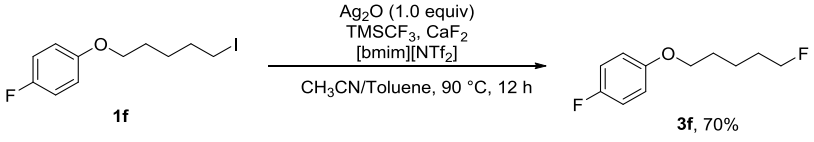
1-(4-Fluorobutoxy)-4-(trifluoromethoxy)benzene (3e)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-(4-iodobutoxy)-4-(trifluoromethoxy)benzene (**1e**) (180 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 75.1 mg 1-(4-fluorobutoxy)-4-(trifluoromethoxy)benzene (**3e**) as a colorless liquid (60% yield).

R_f = 0.40 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.10 (m, 2H), 6.90 – 6.84 (m, 2H), 4.53 (dt, *J* = 48.0, 5.5 Hz, 1H), 3.99 (t, *J* = 5.9 Hz, 2H), 1.97 – 1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 143.0, 122.8, 120.9 (q, *J* = 256.0 Hz), 115.5, 84.1 (d, *J* = 164.7 Hz), 68.0, 27.5 (d, *J* = 20.0 Hz), 25.6 (d, *J* = 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4 (s, 3F), -218.5 – -218.9 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{12}F_4O_2$ [M], 252.0773. Found, 252.0774.

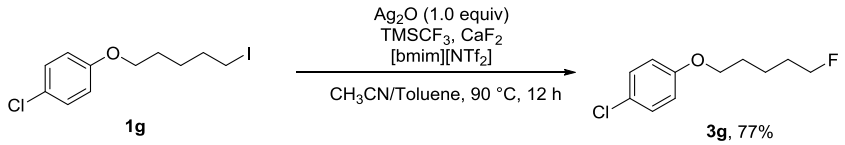
1-((5-Fluoropentyl)oxy)-4-fluorobenzene (3f)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-fluorobenzene (**1f**) (154 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 10:1 (v/v) to afford 70.1 mg 1-((5-fluoropentyl)oxy)-4-fluorobenzene (**3f**) as a colorless liquid (70% yield).

R_f = 0.2 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.92 (m, 2H), 6.86 – 6.79 (m, 2H), 4.48 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 1.90 – 1.69 (m, 4H), 1.64 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (d, *J* = 237.8 Hz), 155.5 (d, *J* = 2.0 Hz), 116.1 (d, *J* = 23.0 Hz), 115.7 (d, *J* = 8.0 Hz), 84.3 (d, *J* = 164.5 Hz), 68.6, 30.5 (d, *J* = 19.6 Hz), 29.2, 22.3 (d, *J* = 5.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.3 – -124.4 (m, 1F), -218.2 – -218.7 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}F_2O$ [M], 200.1013. Found, 200.1016.

1-((5-Fluoropentyl)oxy)-4-chlorobenzene (3g)

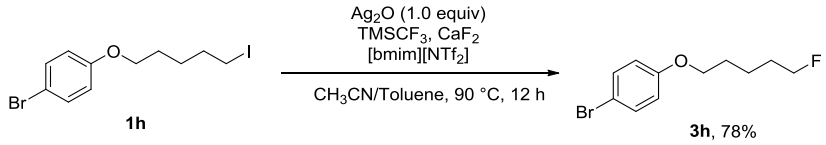


In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-chlorobenzene (**1g**) (162 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 83.1 mg 1-((5-fluoropentyl)oxy)-4-chlorobenzene (**3g**) as a colorless liquid (77% yield).

R_f = 0.4 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.85 – 6.77 (m, 2H), 4.48 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.94 (t, *J* = 6.3 Hz, 2H), 1.89 – 1.68 (m, 4H), 1.64 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 129.6, 125.7, 116.0, 84.3 (d, *J* = 164.5 Hz), 68.2, 30.5 (d, *J* = 19.6 Hz), 29.1, 22.2 (d, *J* = 5.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.3 – -218.7 (m, 1F). Mass Spectrometry: HRMS-EI (m/z):

Calcd for $C_{11}H_{14}ClFO$ [M], 216.0717. Found, 216.0719.

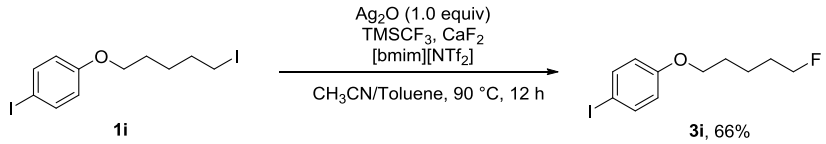
1-((5-Fluoropentyl)oxy)-4-bromobenzene (3h)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-bromobenzene (**1h**) (184 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/DCM 15:1 (v/v) to afford 102 mg 1-((5-fluoropentyl)oxy)-4-bromobenzene (**3h**) as a colorless liquid (78% yield).

R_f = 0.15 (hexanes/DCM 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 6.80 – 6.74 (m, 2H), 4.48 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.70 (m, 4H), 1.63 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 132.5, 116.6, 113.0, 84.2 (d, *J* = 164.6 Hz), 68.2, 30.4 (d, *J* = 19.7 Hz), 29.1, 22.2 (d, *J* = 5.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.3 – -218.7 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}BrFO$ [M], 260.0212. Found, 260.0214.

1-((5-Fluoropentyl)oxy)-4-iodobenzene (3i)

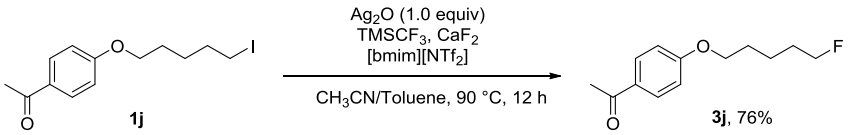


In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-iodobenzene (**1i**) (208 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 8:1 (v/v) to afford 101 mg 1-((5-fluoropentyl)oxy)-4-iodobenzene (**3i**) as a colorless liquid (66%

yield).

R_f = 0.2 (hexanes/toluene 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 6.70 – 6.63 (m, 2H), 4.47 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.70 (m, 4H), 1.63 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 138.5, 117.2, 84.2 (d, *J* = 164.6 Hz), 82.9, 68.1, 30.4 (d, *J* = 19.7 Hz), 29.1, 22.2 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.0 – -218.8 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{14}FIO$ [M], 308.0073. Found, 308.0076.

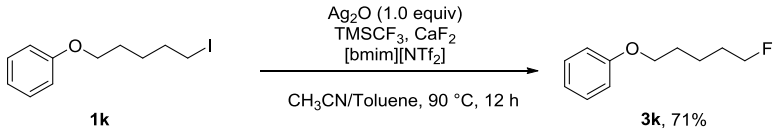
1-(4-((5-Fluoropentyl)oxy)phenyl)ethanone (3j)



In an N_2 glovebox, to Ag_2O (139 mg, 0.600 mmol, 1.20 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-(4-((5-iodopentyl)oxy)phenyl)ethanone (**1j**) (166 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene/acetone 5:3:0.2 (v/v/v) to afford 85.0 mg 1-(4-((5-fluoropentyl)oxy)phenyl)ethanone (**3j**) as a colorless liquid (76% yield).

R_f = 0.2 (hexanes/toluene/acetone 5:3:0.2 (v/v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 6.94 – 6.88 (m, 2H), 4.48 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 2H), 2.55 (s, 3H), 1.90 – 1.71 (m, 4H), 1.66 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 163.3, 130.9, 130.5, 114.4, 84.2 (d, *J* = 164.6 Hz), 68.2, 30.4 (d, *J* = 19.7 Hz), 29.0, 26.7, 22.2 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.3 – -218.7 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{17}FO_2Na$ $[M+Na]^+$, 247.1110. Found, 247.1110.

((5-Fluoropentyl)oxy)benzene (3k)

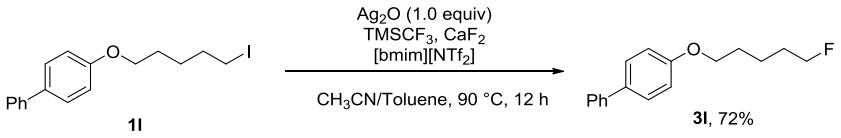


In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), ((5-iodopentyl)oxy)benzene (**1k**) (145 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C,

$TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 64.5 mg ((5-fluoropentyl)oxy)benzene (**3k**) as a colorless liquid (71% yield).

R_f = 0.4 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 6.98 – 6.86 (m, 3H), 4.48 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.89 – 1.70 (m, 4H), 1.65 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 129.8, 120.9, 114.8, 84.3 (d, *J* = 164.4 Hz), 67.8, 30.5 (d, *J* = 19.8 Hz), 29.3, 22.3 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.2 – -218.6 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{15}FO$ [M], 182.1107. Found, 182.1109.

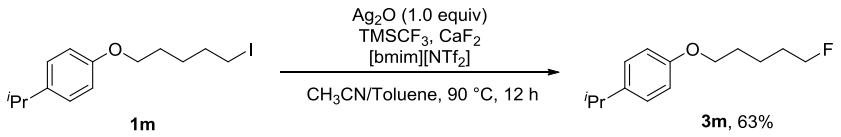
4-((5-Fluoropentyl)oxy)-1,1'-biphenyl (3l)



In an N_2 glovebox, to Ag_2O (139 mg, 0.600 mmol, 1.20 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 4-((5-iodopentyl)oxy)-1,1'-biphenyl (**1l**) (183 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 10:1 (v/v) to afford 92.9 mg 4-((5-fluoropentyl)oxy)-1,1'-biphenyl (**3l**) as a white solid (72% yield).

R_f = 0.2 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.45 – 7.38 (m, 2H), 7.34 – 7.30 (m, 1H), 7.00 – 6.93 (m, 2H), 4.49 (dt, *J* = 47.3, 5.9 Hz, 2H), 4.02 (t, *J* = 6.3 Hz, 2H), 1.93 – 1.72 (m, 4H), 1.67 – 1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 141.2, 134.0, 129.1, 128.5, 127.1, 127.0, 115.1, 84.3 (d, *J* = 164.7 Hz), 68.1, 30.5 (d, *J* = 19.7 Hz), 29.3, 22.3 (d, *J* = 5.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.2 – -218.6 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{17}H_{19}FO$ [M], 258.1420. Found, 258.1421.

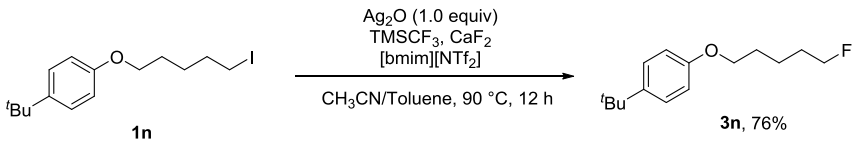
1-((5-Fluoropentyl)oxy)-4-isopropylbenzene (3m)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-isopropylbenzene (**1m**) (166 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 10:1 (v/v) to afford 70.0 mg 1-((5-fluoropentyl)oxy)-4-isopropylbenzene (**3m**) as a colorless liquid (63% yield).

R_f = 0.2 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 6.86 – 6.80 (m, 2H), 4.48 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.96 (t, *J* = 6.3 Hz, 2H), 2.92 – 2.81 (m, 1H), 1.87 – 1.70 (m, 4H), 1.64 – 1.55 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 141.3, 127.6, 114.6, 84.4 (d, *J* = 164.3 Hz), 67.9, 33.6, 30.5 (d, *J* = 19.6 Hz), 29.3, 24.6, 22.3 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.1 – -218.6 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{21}FO$ [M], 224.1576. Found, 224.1577.

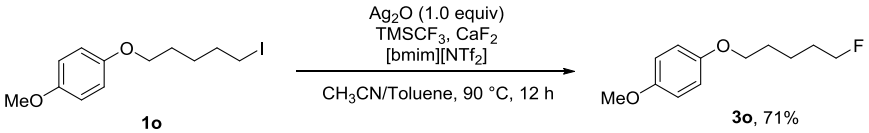
1-(*tert*-Butyl)-4-((5-fluoropentyl)oxy)benzene (3n)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-(*tert*-butyl)-4-((5-iodopentyl)oxy)benzene (**1n**) (173 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 10:1 (v/v) to afford 90.1 mg 1-(*tert*-butyl)-4-((5-fluoropentyl)oxy)benzene (**3n**) as a colorless liquid (76% yield).

R_f = 0.2 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.87 – 6.80 (m, 2H), 4.48 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.96 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.70 (m, 4H), 1.64 – 1.58 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 143.3, 126.2, 113.9, 84.0 (d, *J* = 164.5 Hz) , 67.6, 34.1, 31.6, 30.2 (d, *J* = 19.6 Hz), 29.0, 22.0 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.1 – -218.6 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{15}H_{23}FO$ [M], 238.1733, Found, 238.1733.

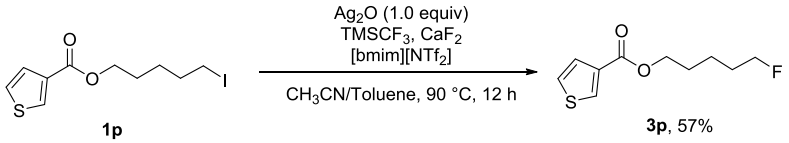
1-((5-Fluoropentyl)oxy)-4-methoxybenzene (3o)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-methoxybenzene (**1o**) (160 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^{o}C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^{o}C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 1:1 (v/v) to afford 74.8 mg 1-((5-fluoropentyl)oxy)-4-methoxybenzene (**3o**) as a colorless liquid (71% yield).

R_f = 0.15 (hexanes/toluene 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 4H), 4.48 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 1.85 – 1.70 (m, 4H), 1.64 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 153.5, 115.7, 115.0, 84.3 (d, *J* = 164.4 Hz), 68.6, 56.1 30.5 (d, *J* = 19.5 Hz), 29.3, 22.3 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.1 – -218.6 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{17}FO_2$ [M], 212.1213. Found, 212.1214.

5-Fluoropentyl thiophene-3-carboxylate (3p)

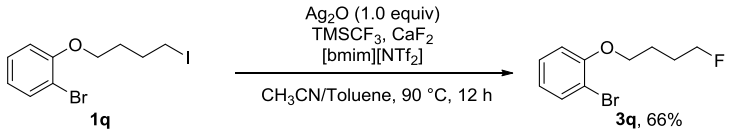


In an N_2 glovebox, to Ag_2O (139 mg, 0.600 mmol, 1.20 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 5-iodopentyl thiophene-3-carboxylate (**1p**) (162 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^{o}C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^{o}C for a further 12 h. After cooling to room temperature, the mixture was

diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 1:1 (v/v) to afford 61.6 mg 5-fluoropentyl thiophene-3-carboxylate (**3p**) as a colorless liquid (57% yield).

R_f = 0.1 (hexanes/toluene 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.52 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.31 (dd, *J* = 5.1, 3.1 Hz, 1H), 4.47 (dt, *J* = 47.3, 6.0 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.69 (m, 4H), 1.61 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 134.2, 132.9, 128.2, 126.3, 84.2 (d, *J* = 164.8 Hz), 64.8, 30.4 (d, *J* = 19.7 Hz), 28.7, 22.3 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.8 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{10}H_{13}FO_2SNa$ $[M+Na]^+$, 239.0518. Found, 239.0514.

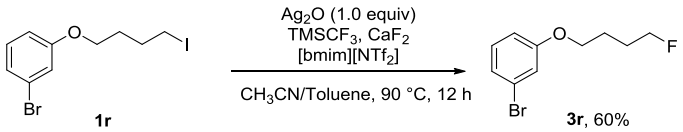
2-(4-Fluorobutoxy)-1-bromobenzene (3q)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 2-(4-iodobutoxy)-1-bromobenzene (**1q**) (178 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^{o}C, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^{o}C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 80.2 mg 2-(4-fluorobutoxy)-1-bromobenzene (**3q**) as a colorless liquid (66% yield).

R_f = 0.25 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.29 – 7.21 (m, 1H), 6.93 – 6.80 (m, 2H), 4.56 (dt, *J* = 46.7, 4.7 Hz, 2H), 4.08 (t, *J* = 5.4 Hz, 2H), 2.08 – 1.85 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 133.7, 128.8, 122.2, 113.5, 112.6, 84.2 (d, *J* = 164.4 Hz), 68.7, 27.6 (d, *J* = 19.9 Hz), 25.5 (d, *J* = 5.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.9 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{12}BrFO$ [M], 246.0056. Found, 246.0065.

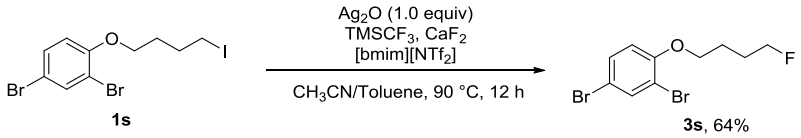
3-(4-Fluorobutoxy)-1-bromobenzene (3r)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 3-(4-iodobutoxy)-1-bromobenzene (**1r**) (178 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL , 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 73.3 mg 3-(4-fluorobutoxy)-1-bromobenzene (**3r**) as a colorless liquid (60% yield).

R_f = 0.4 (hexanes/toluene 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 1H), 7.09 – 7.03 (m, 2H), 6.84 – 6.80 (m, 1H), 4.52 (dt, *J* = 47.4, 5.6 Hz, 2H), 3.99 (t, *J* = 5.9 Hz, 2H), 1.97 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 130.9, 124.1, 123.1, 118.1, 113.8, 84.1 (d, *J* = 164.8 Hz), 67.8, 27.5 (d, *J* = 20.0 Hz), 25.5 (d, *J* = 5.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.9 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{12}BrFO$ [M], 246.0056. Found, 246.0052.

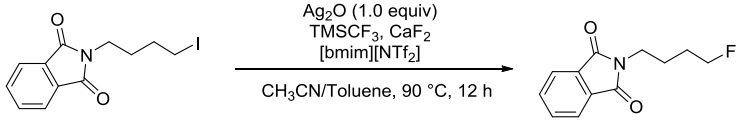
2,4-Dibromo-1-(4-fluorobutoxy)benzene (3s)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 2,4-dibromo-1-(4-iodobutoxy)benzene (**1s**) (217 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/toluene 15:1 (v/v) to afford 103 mg 2,4-dibromo-1-(4-fluorobutoxy)benzene (**3s**) as a colorless liquid (64% yield).

R_f = 0.3 (hexanes/toluene 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.4 Hz, 1H), 7.39 – 7.32 (m, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 4.55 (dt, *J* = 46.7, 5.1 Hz, 2H), 4.04 (t, *J* = 5.4 Hz, 2H), 2.03 – 1.85 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 135.8, 131.5, 114.5, 113.4, 113.2, 84.1 (d, *J* = 164.6 Hz), 69.1, 27.5 (d, *J* = 19.9 Hz), 25.5 (d, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.3 – -219.1 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{11}Br_2FO$ [M], 323.9161. Found, 323.9162.

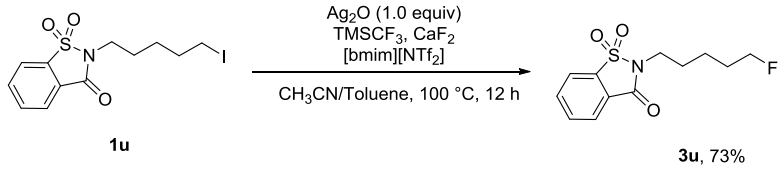
2-(4-Fluorobutyl)isoindoline-1,3-dione (3t)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 2-(4-iodobutyl)isoindoline-1,3-dione (**1t**) (165 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 12:1 (v/v) to afford 89.4 mg 2-(4-fluorobutyl)isoindoline-1,3-dione (**3t**) as a white solid (81% yield).

R_f = 0.35 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 4.48 (dt, *J* = 47.4, 5.7 Hz, 2H), 3.74 (t, *J* = 6.9 Hz, 2H), 1.87 – 1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 134.3, 132.4, 123.5, 83.7 (d, *J* = 165.2 Hz), 37.7, 28.1 (d, *J* = 20.1 Hz), 24.9 (d, *J* = 4.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.6 – -219.0 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{13}FNO_2$ $[M+H]^+$, 222.0930. Found, 222.0922.

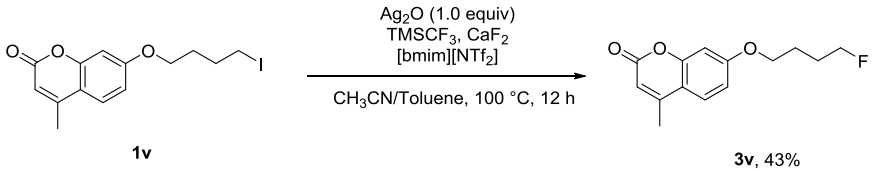
***N*-(5-fluoropentyl)saccharine (3u)**



In an N_2 glovebox, to Ag_2O (232 mg, 1.00 mmol, 2.00 equiv), CaF_2 (234 mg, 3.00 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), *N*-(5-iodopentyl)saccharine (**1u**) (190 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (225 μL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 100 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 10:1 (v/v) to afford 99.2 mg *N*-(5-fluoropentyl)saccharine (**3u**) as a colorless liquid (73% yield).

R_f = 0.2 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 1H), 7.94 – 7.90 (m, 1H), 7.90 – 7.80 (m, 2H), 4.45 (dt, *J* = 47.2, 6.0 Hz, 2H), 3.79 (t, *J* = 7.4 Hz, 2H), 1.95 – 1.85 (m, 2H), 1.84 – 1.69 (m, 2H), 1.59 – 1.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 138.0, 135.1, 134.7, 127.7, 125.5, 121.3, 84.1 (d, *J* = 164.7 Hz), 39.5, 30.1 (d, *J* = 19.8 Hz), 28.3, 22.9 (d, *J* = 5.3 Hz) . ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.8 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{15}FNO_3S$ $[M+H]^+$, 272.0757. Found, 272.0748.

7-(4-Fluorobutoxy)-4-methyl-2H-chromen-2-one (3v)

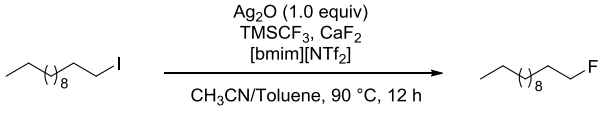


1v **3v**, 43%

In an N_2 glovebox, to Ag_2O (232 mg, 1.00 mmol, 2.00 equiv), CaF_2 (234 mg, 3.00 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 7-(4-iodobutoxy)-4-methyl-2H-chromen-2-one (**1v**) (179 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 100 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v) to afford 53.3 mg 7-(4-fluorobutoxy)-4-methyl-2H-chromen-2-one (**3v**) as a white solid (43% yield).

R_f = 0.3 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.13 (d, *J* = 0.7 Hz, 1H), 4.53 (dt, *J* = 48.0, 5.5 Hz, 2H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.39 (d, *J* = 0.9 Hz, 3H), 2.00 – 1.83 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.6, 155.5, 152.9, 125.8, 113.8, 112.8, 112.1, 101.6, 83.9 (d, *J* = 164.9 Hz), 68.1, 27.3 (d, *J* = 20.0 Hz), 25.4 (d, *J* = 4.9 Hz), 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.6 – -219.1 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{16}FO_3$ $[M+H]^+$, 251.1083. Found, 251.1081.

1-Fluorododecane (3w)



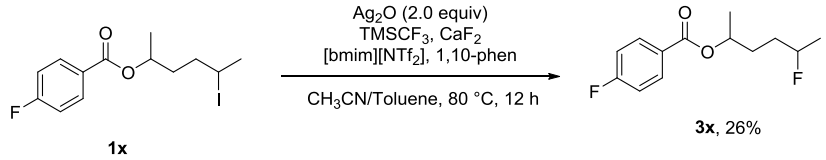
1w **3w**, 76%

In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 1.00 equiv), CaF_2 (117 mg, 1.50 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (2.00 mL) and toluene (0.500 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 1-iodododecane (**1w**) (148 mg, 0.500 mmol, 1.00 equiv) were added to

the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (225 µL, 1.50 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo* (< 20 °C). The residue was purified by chromatography on silica gel, eluting with pentane to afford 71.1 mg 1-fluorododecane (**3w**) as a colorless liquid (76% yield).

R_f = 0.8 (pentane). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (dt, *J* = 47.4, 6.2 Hz, 2H), 1.76 – 1.61 (m, 2H), 1.43 – 1.22 (m, 18H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.6 (d, *J* = 164.0 Hz), 32.3, 30.8 (d, *J* = 19.3 Hz), 30.0, 29.9, 29.9, 29.7, 29.6, 25.5 (d, *J* = 5.5 Hz), 23.0, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -217.7 – -218.2 (m, 1F). The spectroscopic data (NMR) matched those reported in the literature for 1-fluorododecane.[2]

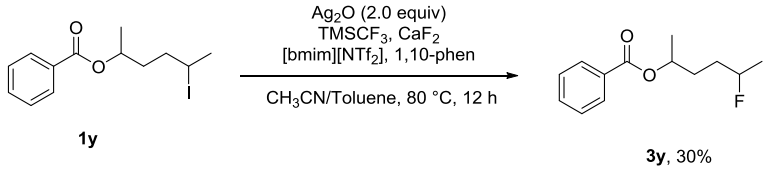
5-Fluorohexan-2-yl 4-fluorobenzoate (3x)



In an N_2 glovebox, to Ag_2O (232 mg, 1.00 mmol, 2.00 equiv), CaF_2 (234 mg, 3.00 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (4.00 mL) and toluene (1.00 mL). 1,10-phenanthroline (45.0 mg, 0.250 mmol, 0.500 equiv), [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 5-iodohexan-2-yl 4-fluorobenzoate (**1x**) (175 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 °C, $TMSCF_3$ (75.0 µL, 0.500 mmol, 1.00 equiv) was added and then the reaction mixture was stirred at 80 °C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 75:1 (v/v) to afford 32.0 mg 5-fluorohexan-2-yl 4-fluorobenzoate (**3x**) as a colorless liquid (26% yield).

R_f = 0.2 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.17 – 7.05 (m, 2H), 5.24 – 5.11 (m, 1H), 4.80 – 4.56 (m, 1H), 1.95 – 1.52 (m, 4H), 1.41 – 1.25 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, *J* = 253.6 Hz), 165.5, 165.5, 132.4 (d, *J* = 9.2 Hz), 127.2 (d, *J* = 2.6 Hz), 127.2 (d, *J* = 2.1 Hz), 115.8 (d, *J* = 22.0 Hz), 91.0 (d, *J* = 165.3 Hz), 90.7 (d, *J* = 165.1 Hz), 72.0, 71.6, 33.3 (d, *J* = 21.1 Hz), 33.0 (d, *J* = 21.0 Hz), 32.0 (d, *J* = 4.5 Hz), 31.8 (d, *J* = 4.5 Hz), 21.3 (d, *J* = 22.7 Hz), 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.8 – -106.0 (m, 1F), -172.9 – -173.8 (m, 1F) . Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{17}F_2O_2$ $[M+H]^+$, 243.1197. Found, 243.1191.

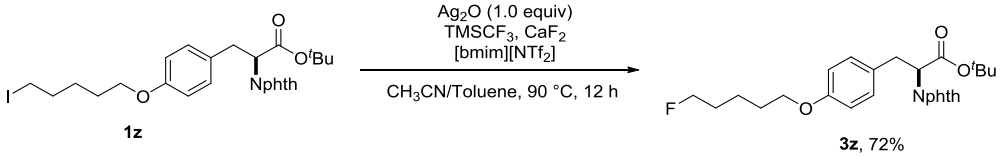
5-Fluorohexan-2-yl 4-fluorobenzoate (3y)



In an N_2 glovebox, to Ag_2O (232 mg, 1.00 mmol, 2.00 equiv), CaF_2 (234 mg, 3.00 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (4.00 mL) and toluene (1.00 mL). 1,10-phenanthroline (45.0 mg, 0.250 mmol, 0.500 equiv), [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (105 mg, 0.250 mmol, 0.500 equiv), 5-iodohexan-2-yl benzoate (**1y**) (166 mg, 0.500 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (75.0 μL, 0.500 mmol, 1.00 equiv) was added and then the reaction mixture was stirred at 80 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 75:1 (v/v) to afford 33.4 mg 5-fluorohexan-2-yl benzoate (**3y**) as a colorless liquid (30% yield).

R_f = 0.2 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.25 – 5.13 (m, 1H), 4.81 – 4.57 (m, 1H), 1.96 – 1.59 (m, 4H), 1.40 – 1.28 (m, 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.5, 133.2, 131.0, 131.0, 129.9, 128.7, 91.1 (d, *J* = 165.1 Hz), 90.7 (d, *J* = 165.2 Hz), 71.8, 71.3, 33.4 (d, *J* = 21.0 Hz), 33.0 (d, *J* = 21.0 Hz), 32.1 (d, *J* = 4.4 Hz), 31.8 (d, *J* = 4.4 Hz), 21.3 (d, *J* = 22.7 Hz), 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.4 – -173.5 (m) (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{18}FO_2$ $[M+H]^+$, 225.1291. Found, 225.1284.

(S)-*tert*-Butyl 2-(1,3-dioxoisoindolin-2-yl)-3-(4-((5-fluoropentyl)oxy)phenyl)propanoate (3z)

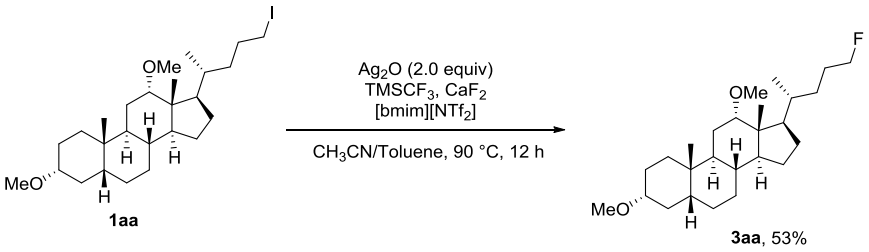


In an N_2 glovebox, to Ag_2O (58.0 mg, 0.250 mmol, 1.00 equiv), CaF_2 (58.5 mg, 0.750 mmol, 3.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (1.00 mL) and toluene (0.250 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (52.5 mg, 0.125 mmol, 0.500 equiv), (S)-*tert*-butyl 2-(1,3-dioxoisoindolin-2-yl)-3-(4-((5-iodopentyl)oxy)phenyl)propanoate (**1z**) (141 mg, 0.250 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (113 μL, 0.750 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 90 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and

washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc/DCM 20:1:1 (v/v/v) to afford 82.0 mg (S)-*tert*-butyl 2-(1,3-dioxoisoindolin-2-yl)-3-(4-((5-fluoropentyl)oxy)phenyl)propanoate (**3z**) as a colorless liquid (72% yield).

R_f = 0.2 (hexanes/EtOAc/DCM 20:1:1 (v/v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.70 – 7.64 (m, 2H), 7.08 – 7.02 (m, 2H), 6.72 – 6.66 (m, 2H), 5.07 – 4.94 (m, 1H), 4.43 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.91 – 3.80 (m, 2H), 3.50 – 3.40 (m, 2H), 1.80 – 1.65 (m, 4H), 1.57 – 1.48 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 168.0, 158.0, 134.3, 132.0, 130.1, 129.3, 123.7, 114.7, 84.2 (d, *J* = 164.4 Hz), 83.0, 67.8, 54.6, 34.1, 30.4 (d, *J* = 19.6 Hz), 29.1, 28.2, 22.2 (d, *J* = 5.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.4 – -218.9 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{30}FNO_5Na$ $[M+Na]^+$, 478.2006. Found, 478.2005.

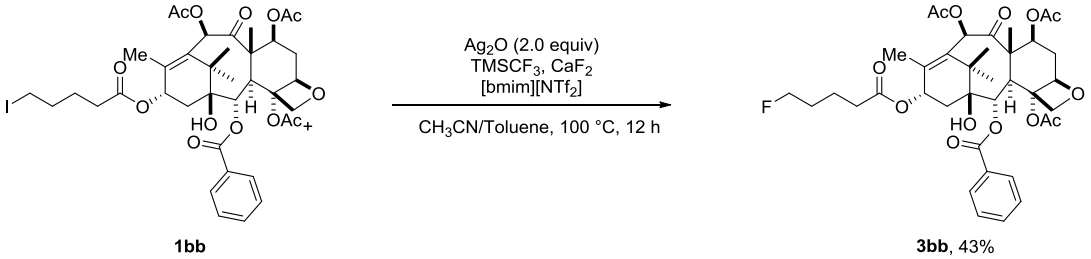
3,12-Dimethoxy cholan-24-fluoro (3aa)



In an N_2 glovebox, to Ag_2O (116 mg, 0.500 mmol, 2.00 equiv), CaF_2 (117 mg, 1.50 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (1.00 mL) and toluene (0.250 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (52.5 mg, 0.125 mmol, 0.500 equiv), 3,12-dimethoxy cholan-24-iodo (**1aa**) (129 mg, 0.250 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^{o}C, $TMSCF_3$ (113 μL, 0.750 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 100 ^{o}C for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 75:1 (v/v) to afford 54.0 mg 3,12-dimethoxy cholan-24-fluoro (**3aa**) as a colorless liquid (53% yield).

R_f = 0.4 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (dt, *J* = 47.4, 6.3 Hz, 2H), 3.39 (t, *J* = 2.4 Hz, 1H), 3.34 (s, 3H), 3.25 (s, 3H), 3.19 – 3.10 (m, 1H), 1.90 – 1.69 (m, 9H), 1.57 – 1.44 (m, 4H), 1.41 – 0.94 (m, 13H), 0.93 – 0.89 (m, 6H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.1 (d, *J* = 164.1 Hz), 82.6, 80.8, 56.0, 55.9, 49.2, 46.9, 46.6, 42.4, 36.3, 35.6, 35.5, 34.8, 33.9, 32.9, 31.4 (d, *J* = 5.2 Hz), 27.8, 27.7, 27.4 (d, *J* = 19.2 Hz), 27.1, 26.4, 24.0, 23.6, 22.3, 17.9, 13.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -217.0 – -217.4 (m, 1F). Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{26}H_{45}FO_2$ [M], 408.3404. Found, 408.3416.

7-*O*-acetyl-13-*O*-(5-fluoropentanoate)baccatine III (3bb)

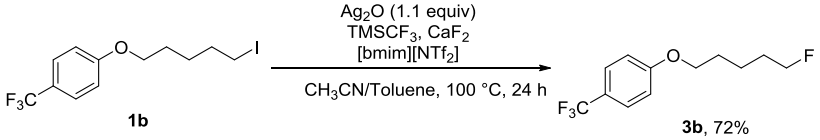


1bb **3bb**, 43%

In an N_2 glovebox, to Ag_2O (58.0 mg, 0.250 mmol, 2.00 equiv), CaF_2 (58.5 mg, 0.75 mmol, 6.00 equiv) in a 10.0 mL sealed vial were added CH_3CN (1.00 mL) and toluene (0.250 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (26.3mg, 0.0625 mmol, 0.500 equiv), 7-*O*-acetyl-13-*O*-(5-iodopentanoate)baccatine III (**1bb**) (105 mg, 0.125 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred for 30 min at 25 ^oC, $TMSCF_3$ (56.5 µL, 0.375 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 100 ^oC for a further 12 h. After cooling to room temperature, the mixture was diluted with EtOAc (10.0 mL) and quenched with H_2O (10.0 mL), filtrated and washed three times with EtOAc (10.0 mL). The filtrate was extracted three times with EtOAc (5.00 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 3:1 (v/v) to afford 39.2 mg 7-*O*-acetyl-13-*O*-(5-fluoropentanoate)baccatine III (**3bb**) as a white solid (43% yield).

R_f = 0.15 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.24 (s, 1H), 6.18 (t, *J* = 8.8 Hz, 1H), 5.64 (d, *J* = 6.9 Hz, 1H), 5.57 (dd, *J* = 10.4, 7.2 Hz, 1H), 4.95 (d, *J* = 9.2 Hz, 1H), 4.49 (dt, *J* = 47.6, 5.4 Hz, 2H), 4.30 (d, *J* = 8.4 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.94 (d, *J* = 6.9 Hz, 1H), 2.63 – 2.42 (m, 3H), 2.32 (s, 3H), 2.23 (dd, *J* = 8.8, 3.4 Hz, 2H), 2.16 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H), 1.88 – 1.72 (m, 5H), 1.78 (s, 3H), 1.76 (s, 1H), 1.20 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 173.0, 170.7, 169.9, 169.2, 167.2, 141.7, 134.1, 132.7, 130.4, 129.4, 129.0, 83.9 (d, *J* = 165.2 Hz), 84.3, 81.2, 79.0, 76.6, 75.7, 74.7, 71.7, 69.7, 56.3, 47.5, 43.4, 35.8, 34.1, 33.6, 30.0 (d, *J* = 19.8 Hz), 26.6, 22.8, 21.4, 21.3 (d, *J* = 4.6 Hz), 21.1, 21.0, 15.1, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.3 – -218.7 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{38}H_{51}FNO_{13}$ $[M+NH_4]^+$, 748.3344. Found, 748.3342.

Gram-scale synthesis of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (3b)



1b **3b**, 72%

In an N_2 glovebox, to Ag_2O (1.78 g, 7.70 mmol, 1.10 equiv), CaF_2 (1.64 g, 21.0 mmol, 3.00 equiv) in a 150 mL sealed vial were added CH_3CN (10.0 mL) and toluene (2.50 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (1.47 g, 3.50 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (2.51 g, 7.00 mmol, 1.00 equiv) were added to the reaction subsequently. The resulting mixture was stirred

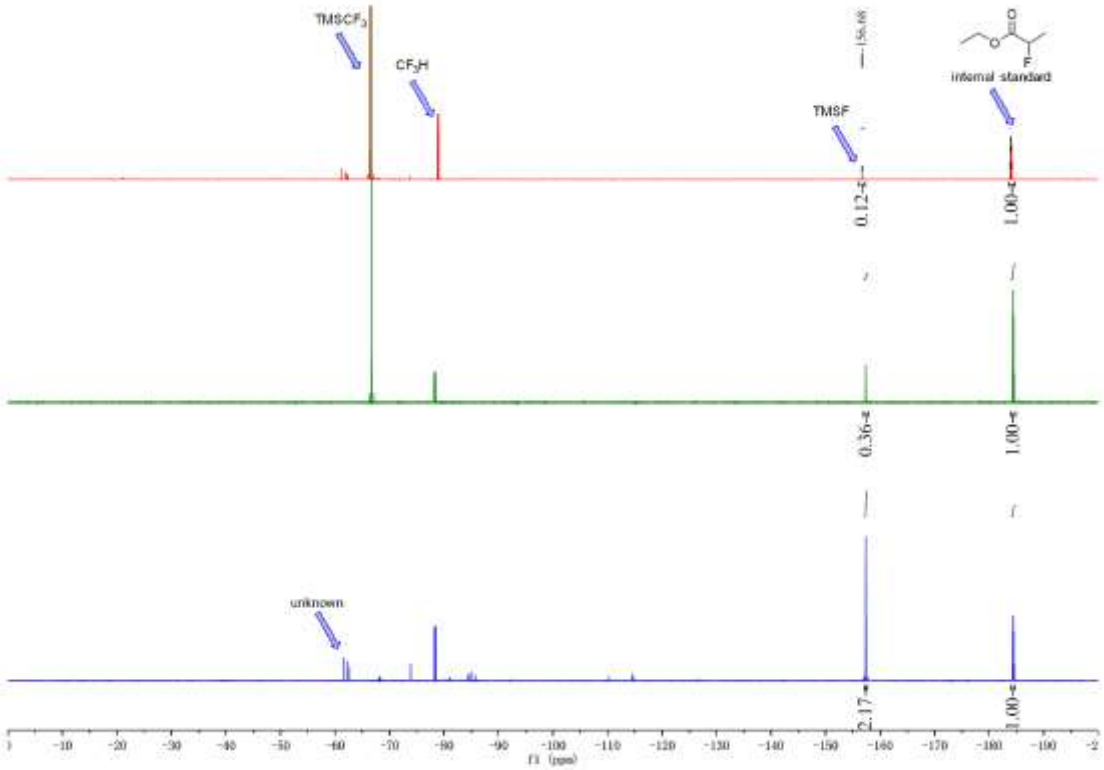
for 30 min at 25 °C, $TMSCF_3$ (3.15 mL, 21.0 mmol, 3.00 equiv) was added and then the reaction mixture was stirred at 100 °C for a further 24h. After cooling to room temperature, the mixture was diluted with EtOAc (50.0 mL) and quenched with H_2O (20.0 mL), filtrated and washed three times with EtOAc (20.0 mL). The filtrate was extracted three times with EtOAc (20.0 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to afford 1.26 g 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) as a colorless liquid (72% yield).

The study of Mechanism

The preparation of TMSF

A 25.0 mL three-necked, round-bottomed flask equipped with a magnetic stir bar, dropping funnel with pressure-equalizing side arm, distilling apparatus, 10.0 mL round-bottomed receiving flask, and was charged with AgF (10.0 g, 78.8 mmol, 4.55 equiv) followed by dry CH_3CN (2.00 mL). TMSCl (1.50 mL, 17.3 mmol, 1.00 equiv) was added drop wise at room tempreture. Meanwhile, the receiving flask was cooled to -78 ℃. After the addition was complete, dry CH_3CN (2.00 mL) was added to 1.05 g TMSF (65% yield) in 10 mL round-bottomed receiving flask, and stored at -20 °C. The spectroscopic data (NMR) matched those reported in the literature for TMSF.[3]

Figure 1S. NMR Spectra of Intermediates (TMSF)

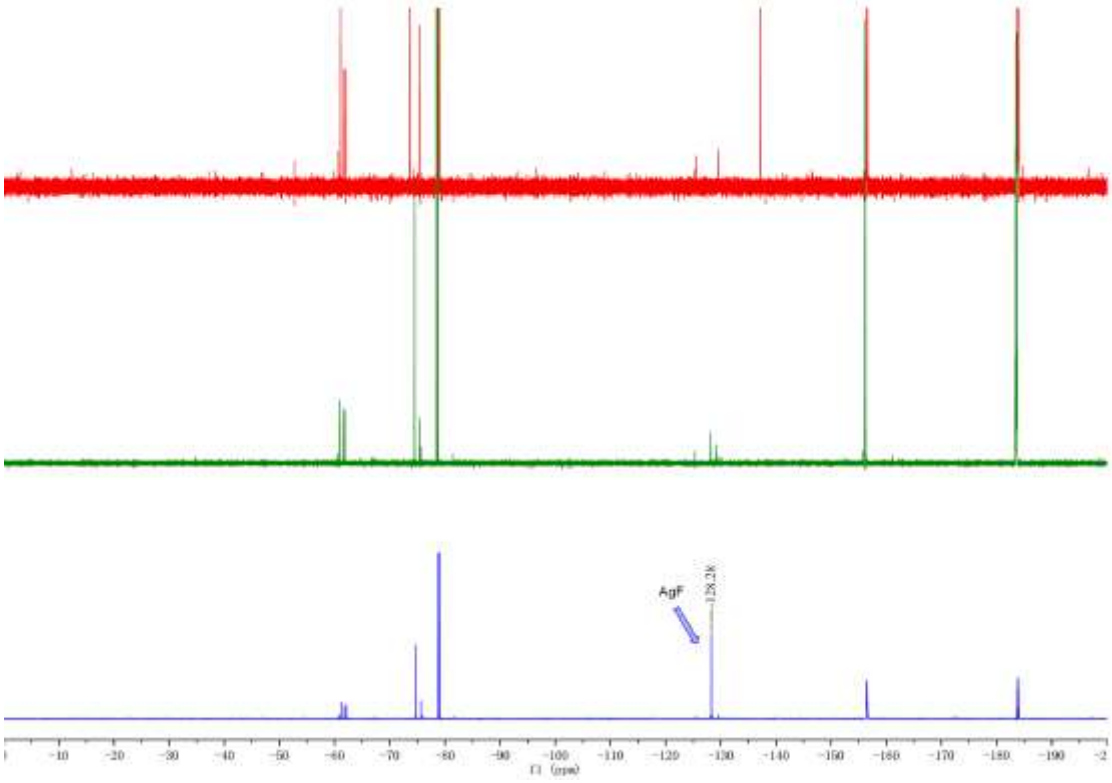


Top line: the mixture of 0.150 mmol $TMSCF_3$ and 0.0500 mmol Ag_2O in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (6.00 μL, 0.0500 mmol) was added as internal standard;

Middle line: the mixture of 0.150 mmol $TMSCF_3$ and 0.150 mmol CaF_2 in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (6.00 μL, 0.0500 mmol) was added as internal standard;

Bottom line: the mixture of 0.150 mmol $TMSCF_3$, 0.0500 mmol Ag_2O, and 0.150 mmol CaF_2 in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (6.00 μL, 0.050 mmol) was added as internal standard.

Figure 2S. NMR Spectra of Intermediates (AgF)



Top line: the mixture of 0.0500 mmol $TMSCF_3$, 0.0500 mmol Ag_2O, and 0.150 mmol CaF_2 in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (2.00 μL, 0.0167 mmol) was added as internal standard;

Middle line: the mixture of 0.0500 mmol $TMSCF_3$, 0.0500 mmol Ag_2O, and 0.150 mmol CaF_2 in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (2.00 μL, 0.0167 mmol) was added as internal standard, then water (50.0 μL) was added;

Bottom line: the mixture of 0.0500 mmol $TMSCF_3$, 0.0500 mmol Ag_2O, and 0.150 mmol CaF_2 in CH_3CN (0.400 mL) and toluene (0.100 mL) was stirred at 90°C for 10 h, after cooling to room temperature, ethyl 2-fluoropropanoate (2.00 μL, 0.0167 mmol) was added as internal standard, then aqueous AgF solution (50.0 μL) was added.

Effect of TMSF on the reaction

In an N_2 glovebox, to Ag_2O (11.6 mg, 0.0500 mmol, 1.00 equiv), CaF_2 in a 2.00 mL sealed vial were added CH_3CN (0.400 mL) and toluene (0.100 mL). [bmim][NTf_2] (1-Butyl-3-methylimidazoliumBis(trifluoromethanesulfonyl)) (10.5 mg, 0.0250 mmol, 0.500 equiv), 1-((5-iodopentyl)oxy)-4-(trifluoromethyl)benzene (**1b**) (17.9 mg, 0.0500 mmol, 1.00 equiv) were added to the reaction and the resulting mixture was stirred for 30 min at 25 °C, TMSF in CH_3CN (16.0 μL, 0.0500 mmol, 1.00 equiv) was added and then the reaction mixture was stirred at 90 °C for a further 12 h. After cooling to room temperature, styrene (6.00 μL, 0.0524 mmol), $CDCl_3$ (1.50 mL) was added to the reaction mixture. The yield of 1-((5-fluoropentyl)oxy)-4-(trifluoromethyl)benzene (**3b**) was determined by comparing the integration of the ^1H NMR resonance of 1-((5-fluorope ntyl)oxy)-4-(trifluoromethyl)benzene (4.54 ppm, t) with that of styrene (5.25 ppm, d). Yields are reported in Table S12.

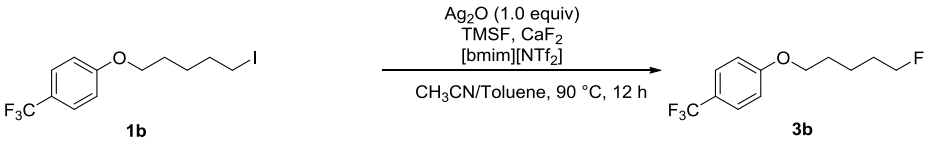


Table S12 Effect of TMSF on the reaction

Conditions	Yield [%] (^1H NMR)
TMSF (1.0 equiv), CaF_2 (1.0 equiv)	38
TMSF (1.0 equiv), CaF_2 (2.0 equiv)	43
TMSF (1.0 equiv)	7
CaF_2 (3.0 equiv)	8

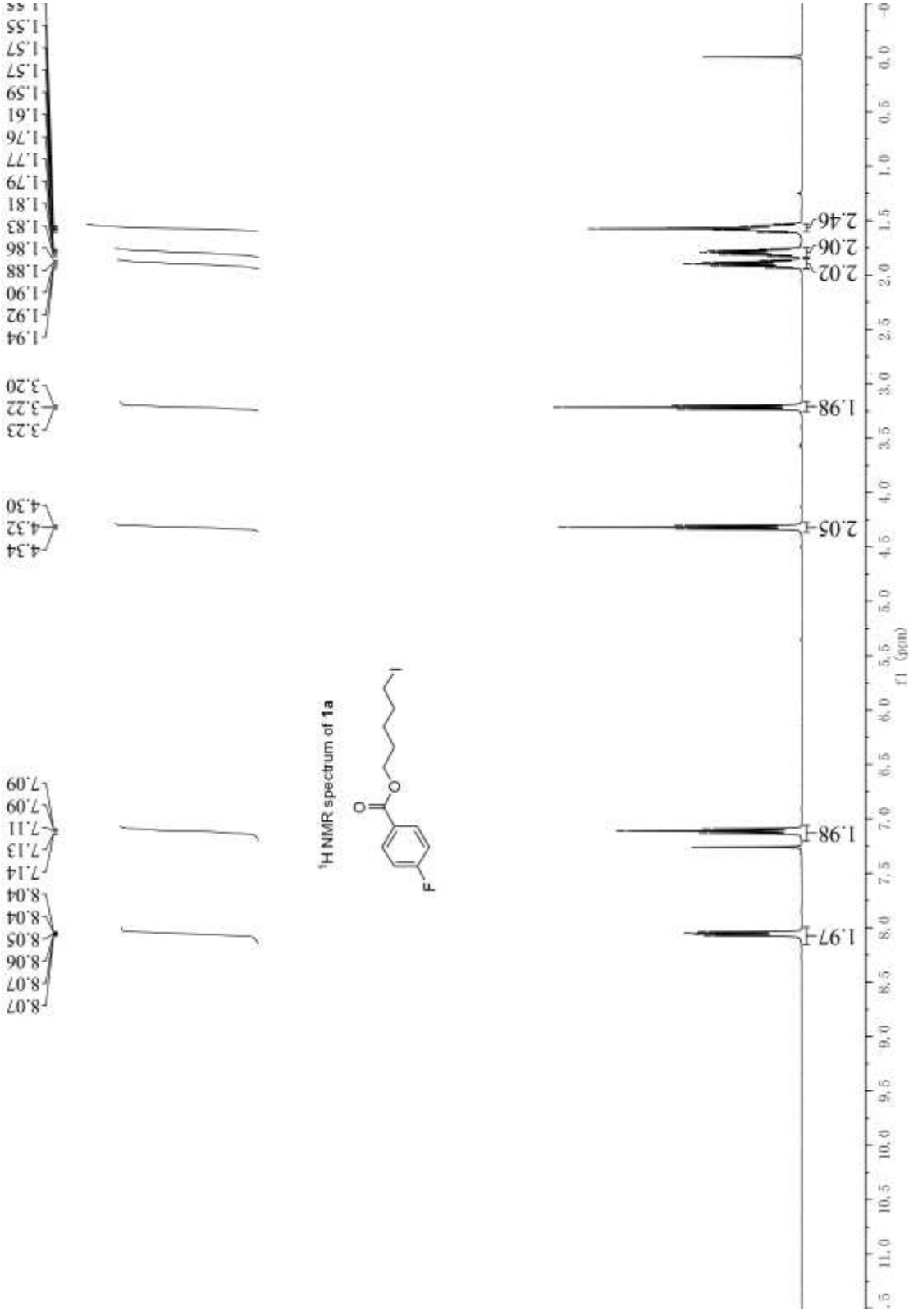
References

[1] Nawarathne, I. N.; Walker, K. D. *J. Nat. Prod.* **2010**, *73*, 151

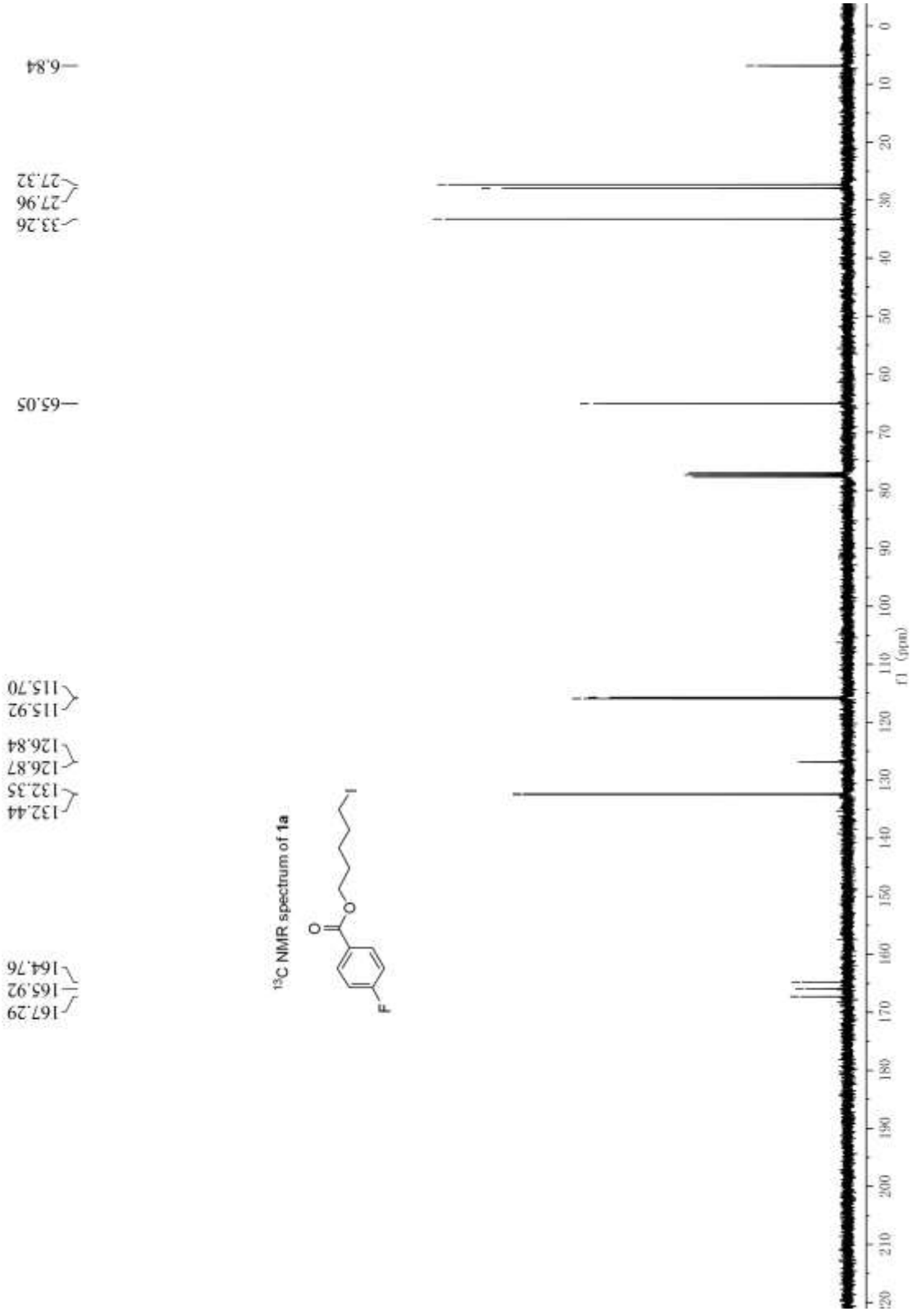
[2] Furuya, T.; Nomoto, T.; Fukuhara, T.; Hara, S. *J. Fluorine Chem.***2009**, *130*, 348.

[3] (a) Levin, V. V.; Dilman, A. D.; Belyakov, P. A.; Struchkova, M. I.; Tartakovsky, V. A. *J. Fluorine Chem.***2009**, *130*, 667.; (b) Rakita, P. E.; Worsham, L. S. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 547.

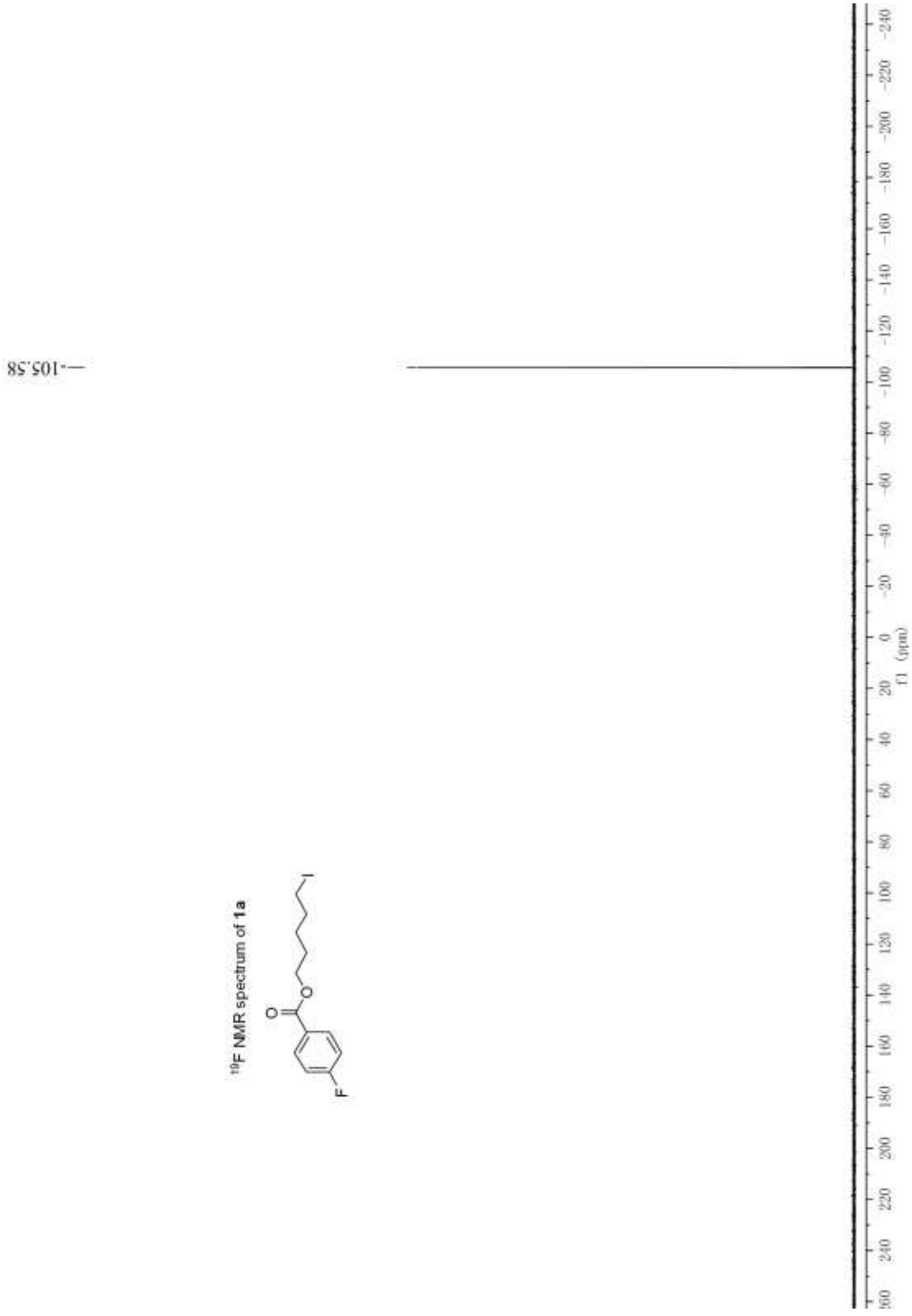
Spectroscopic Data



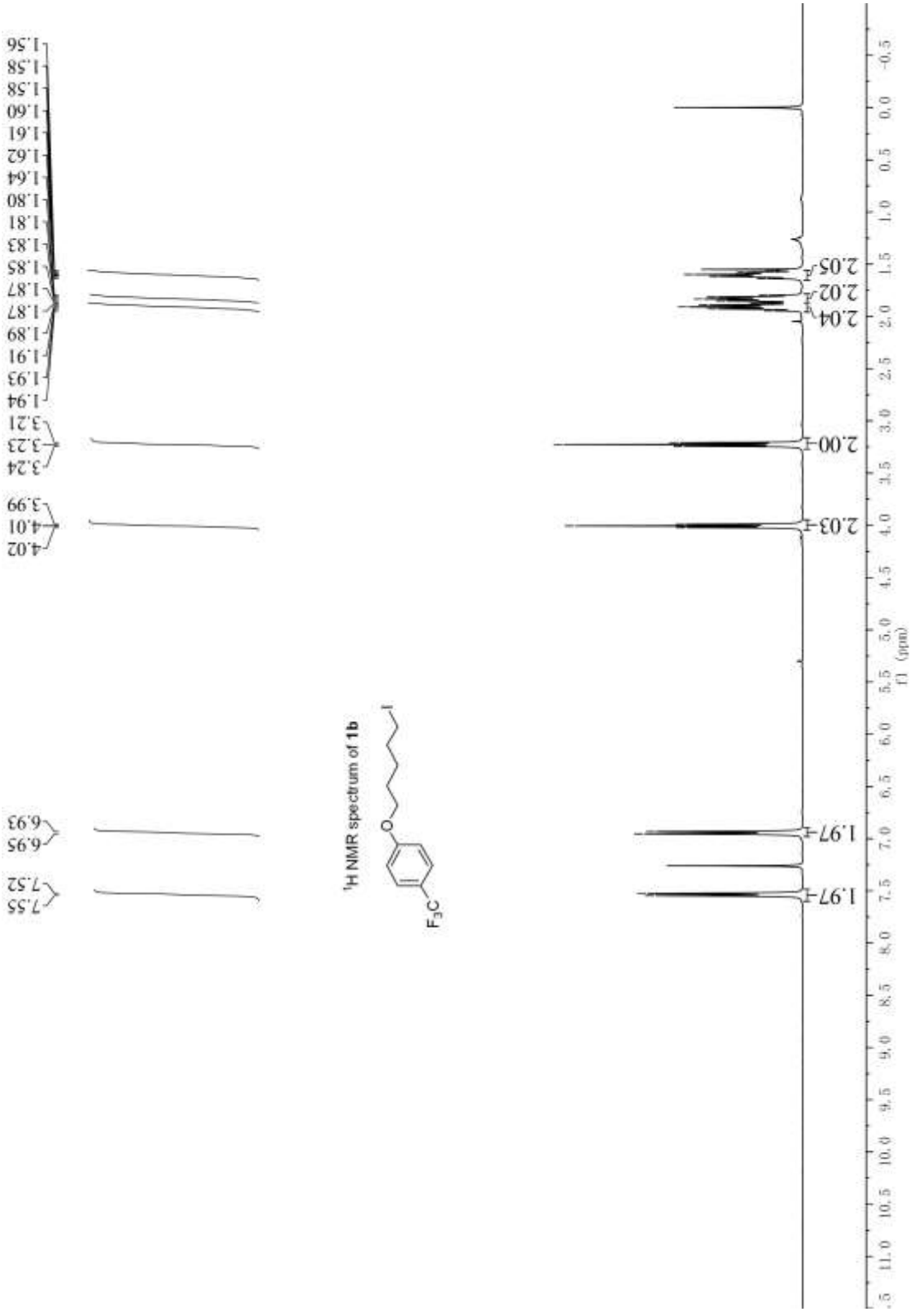
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**



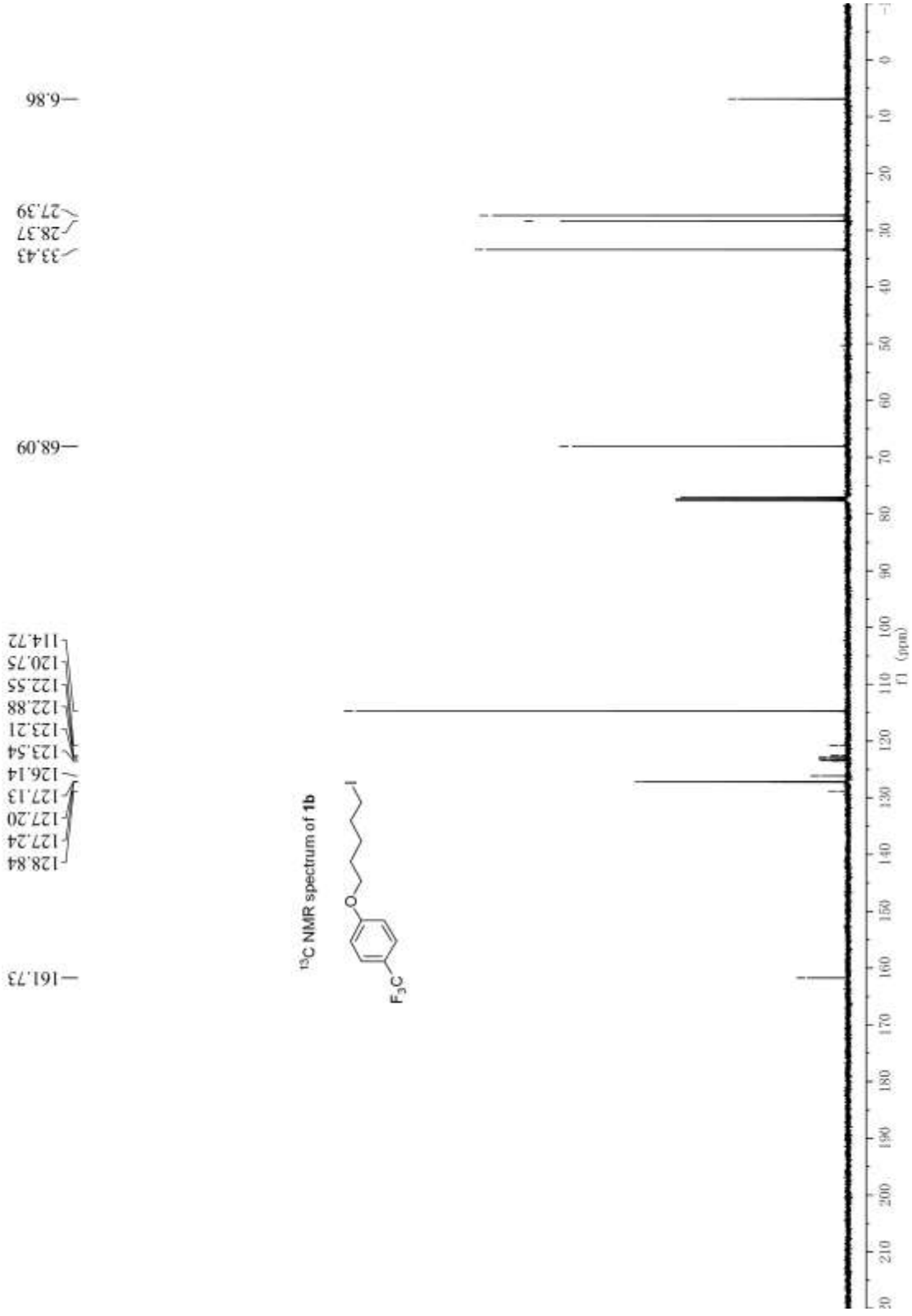
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1a**



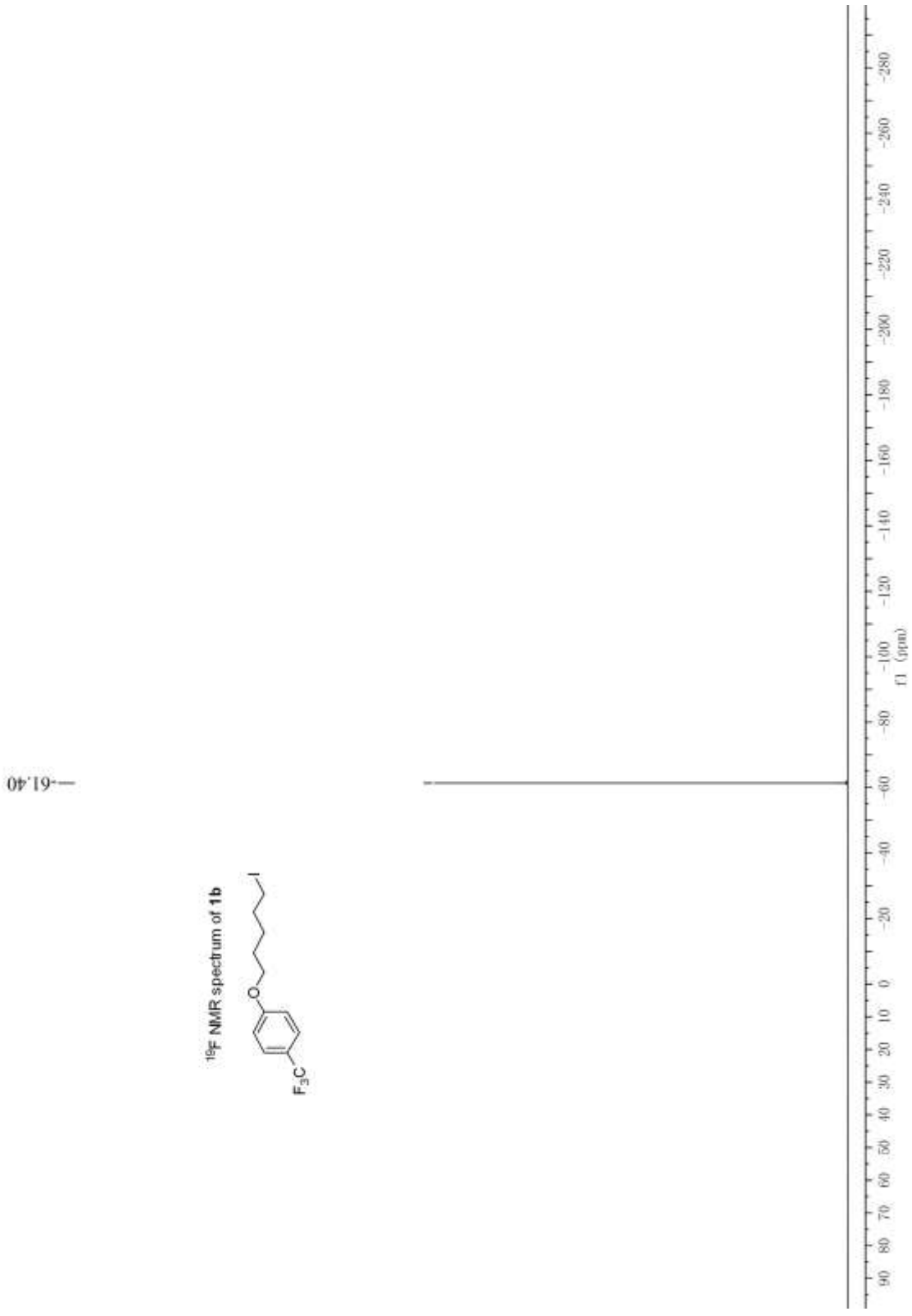
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **1a**



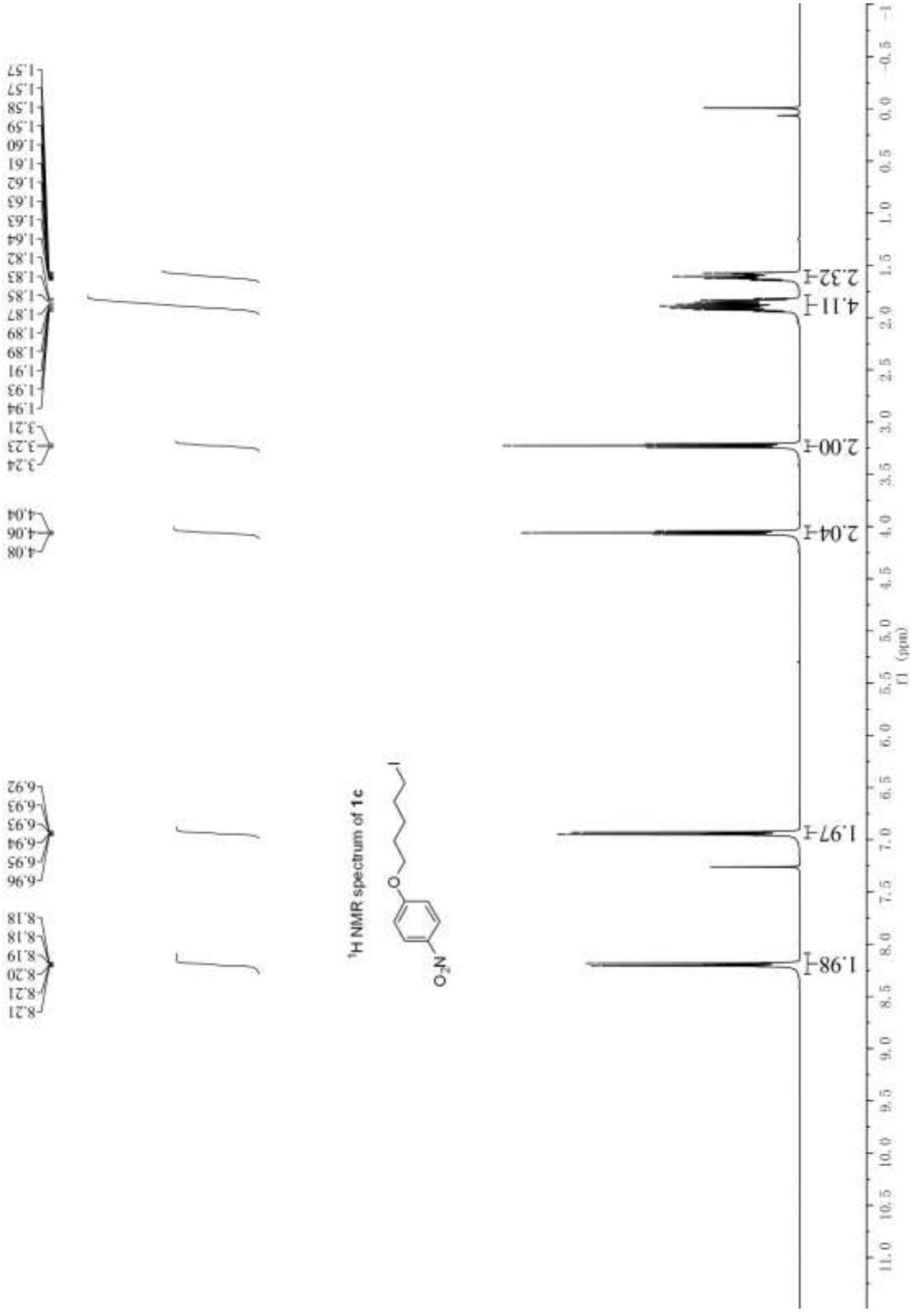
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**



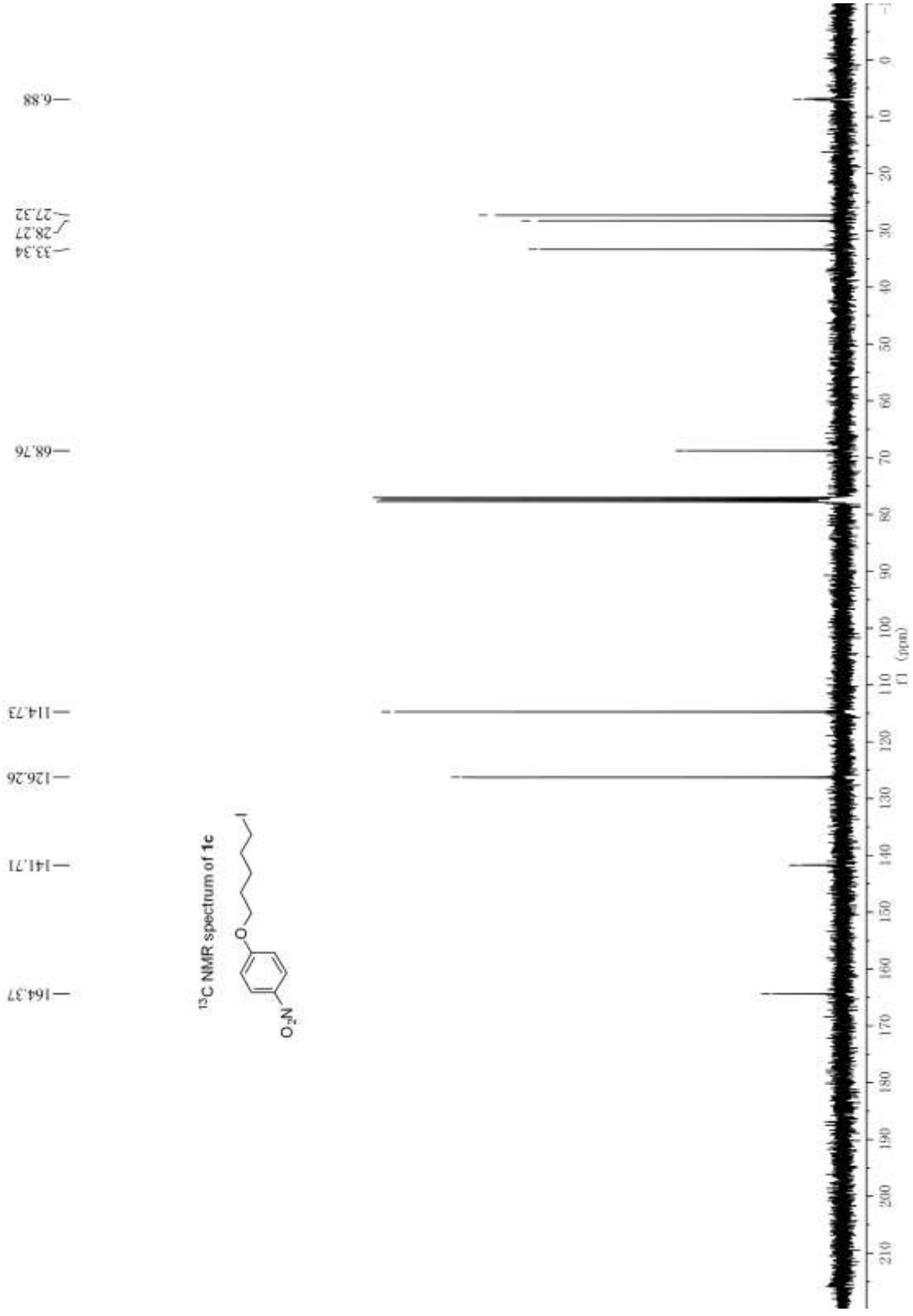
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1b**



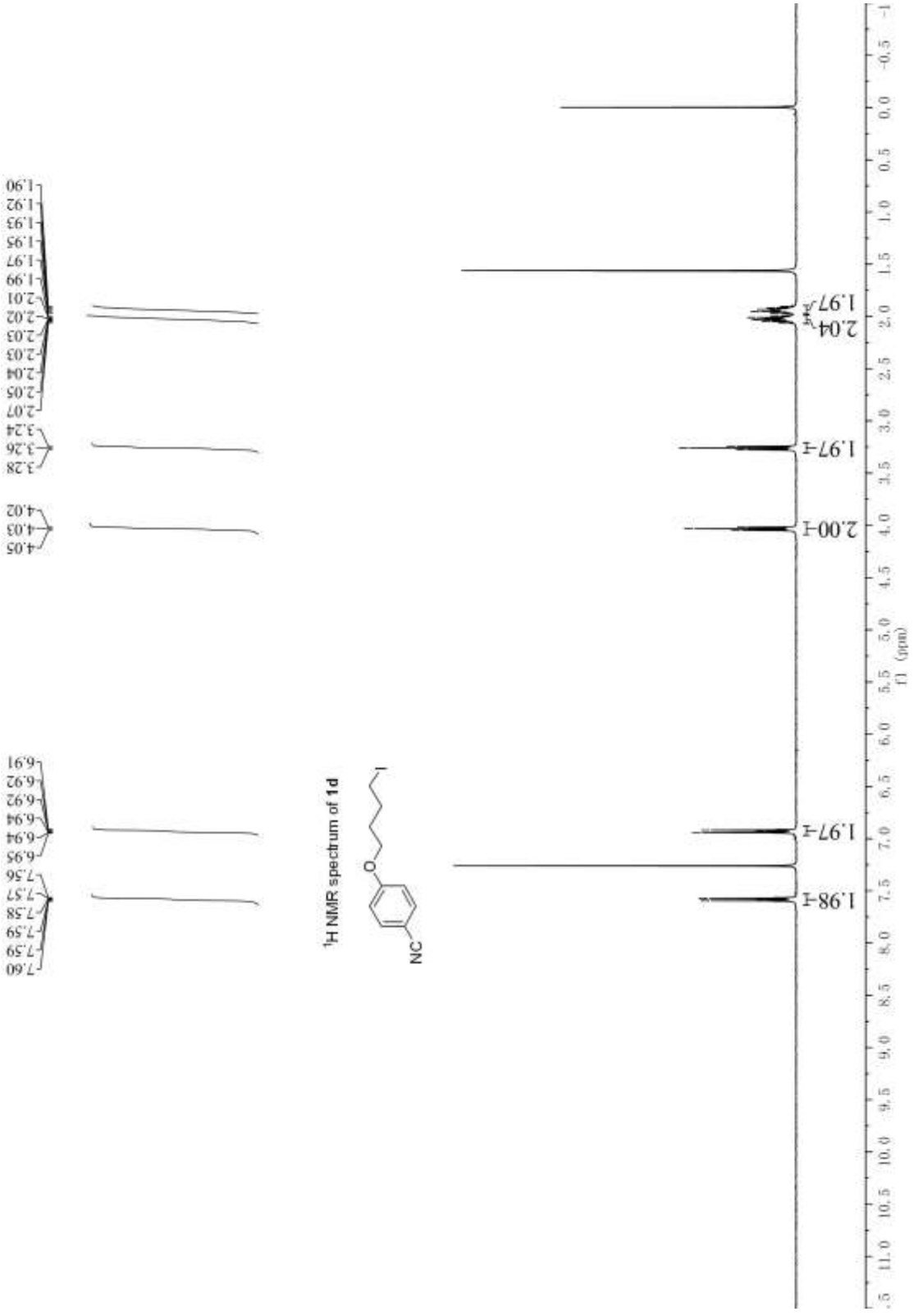
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **1b**



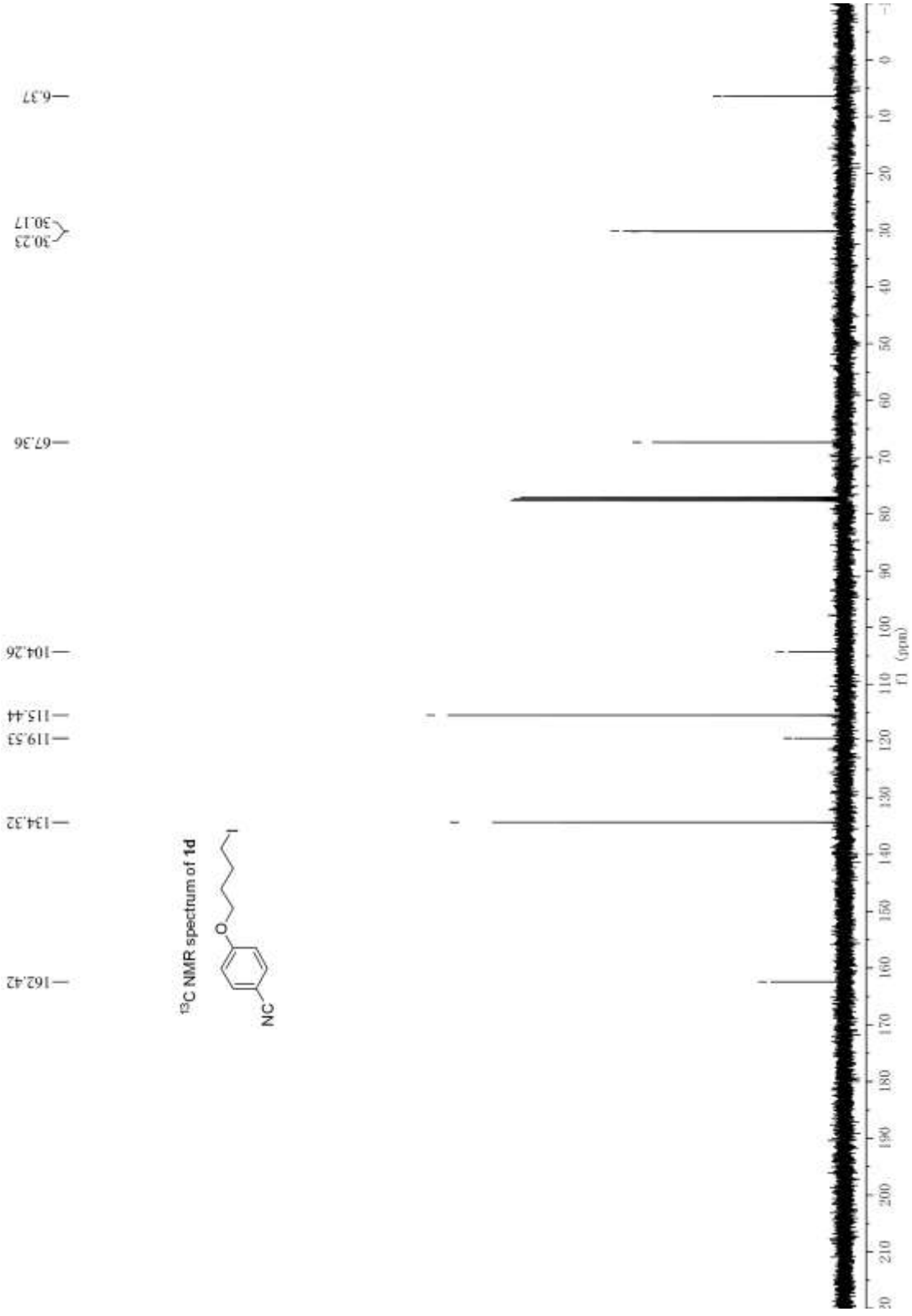
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1c**



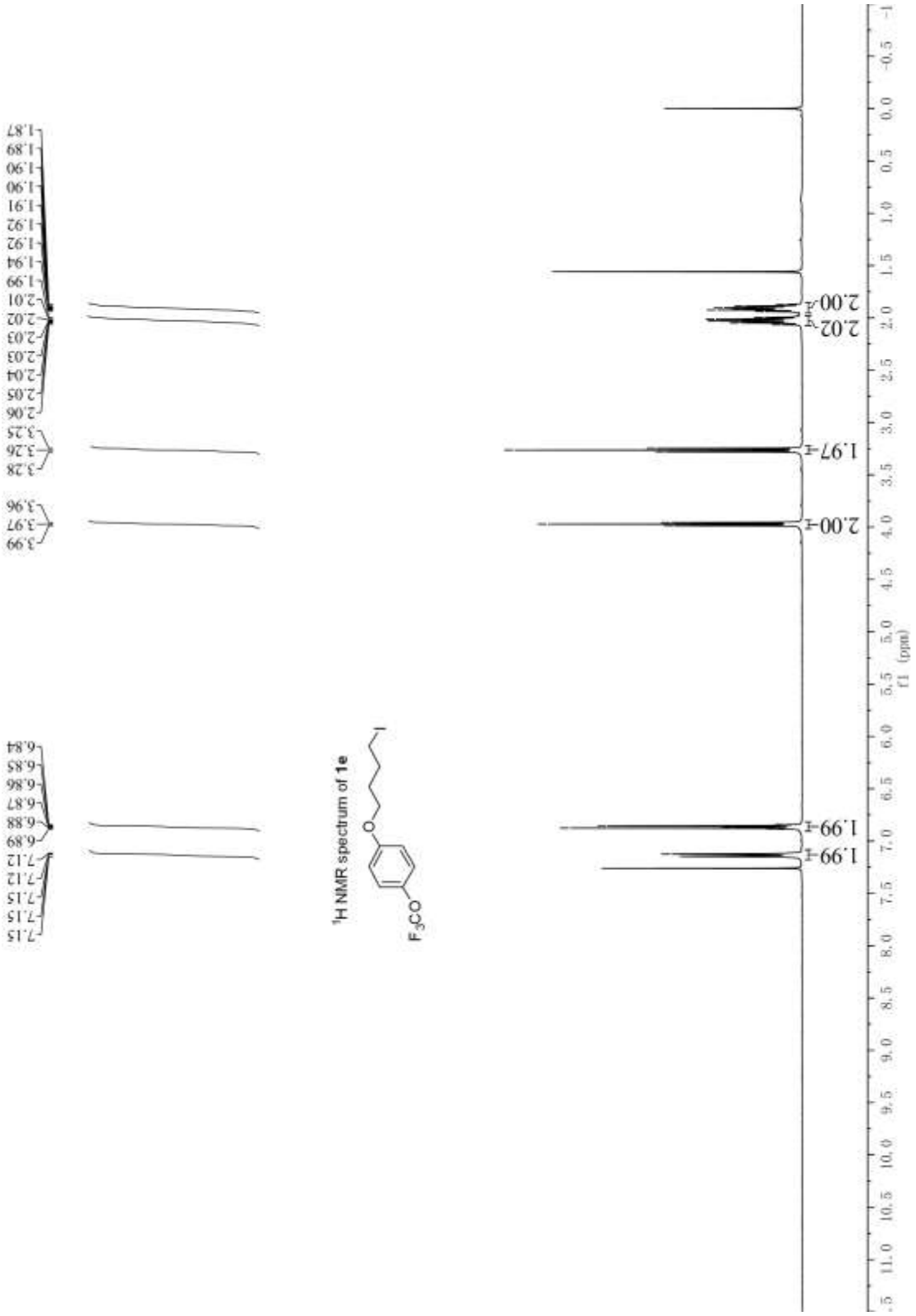
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1c**



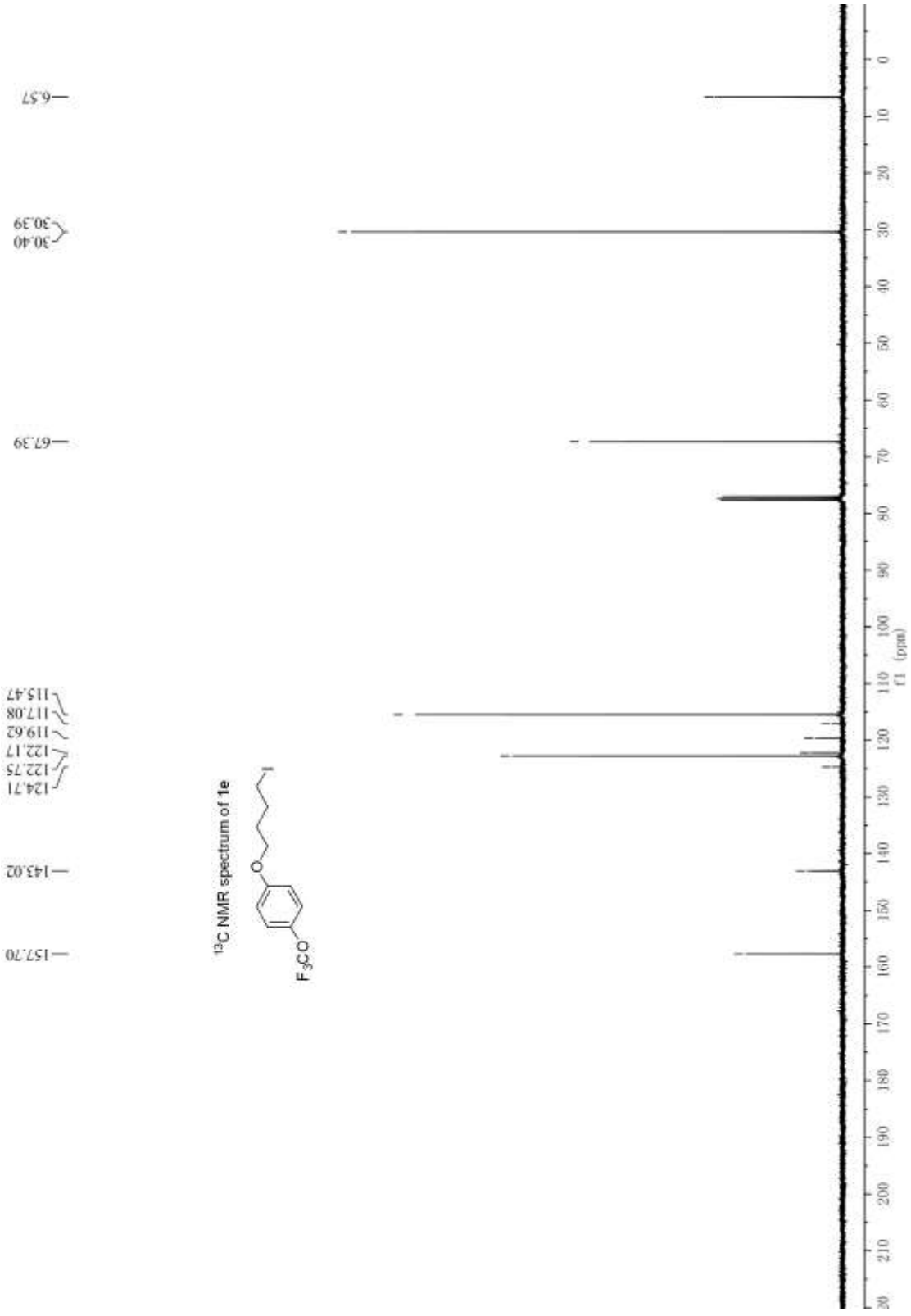
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1d**



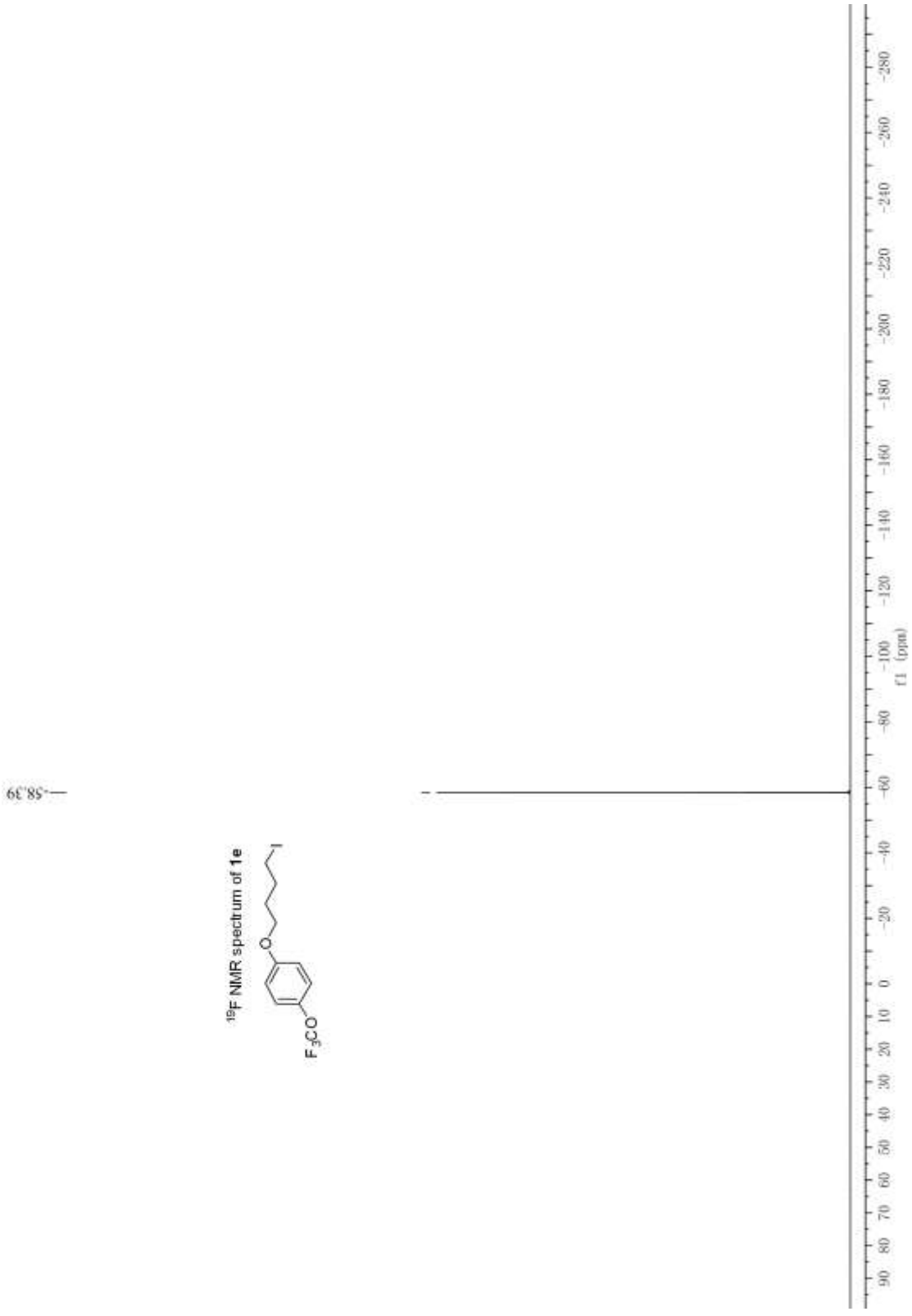
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1d**



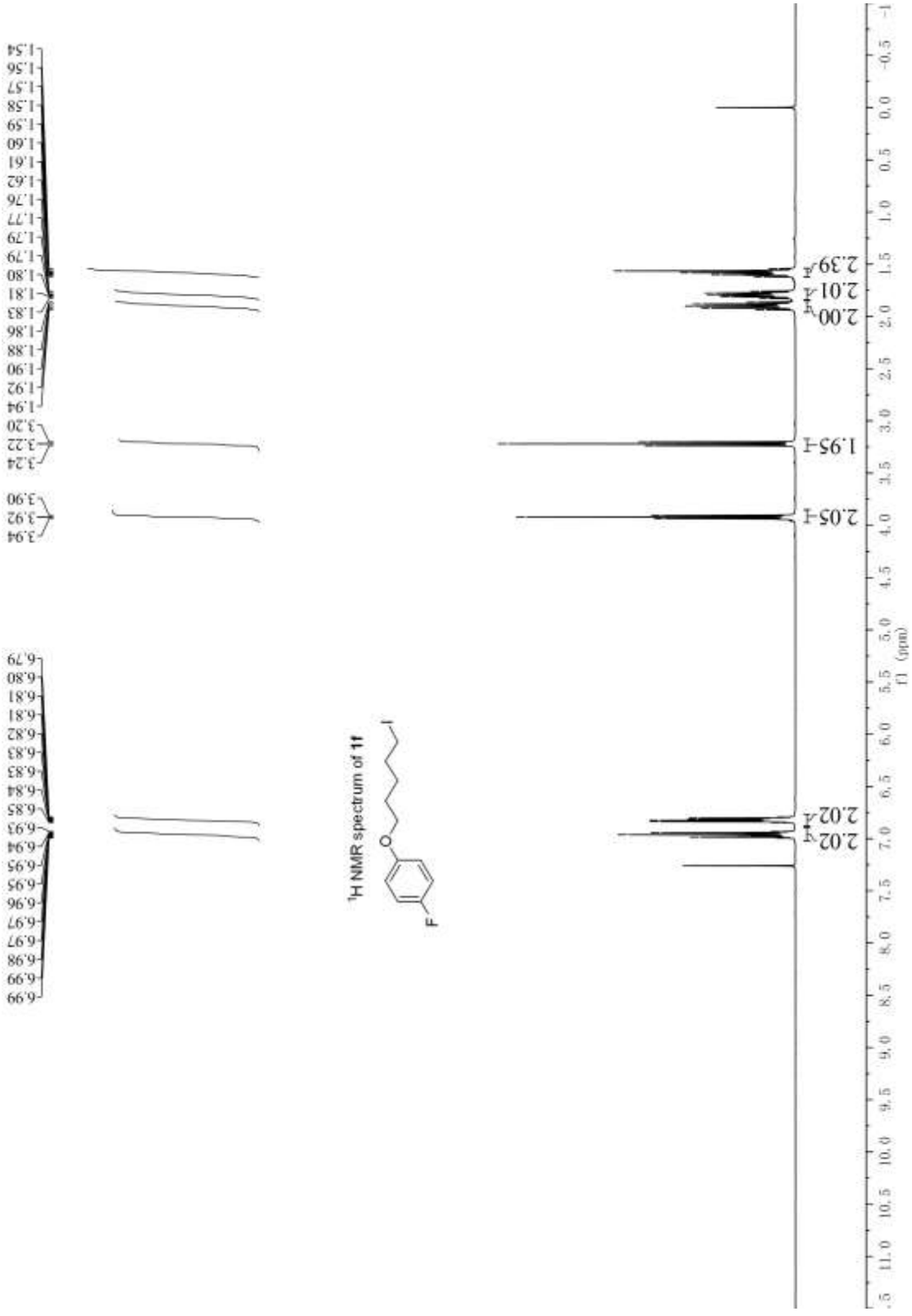
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1e**



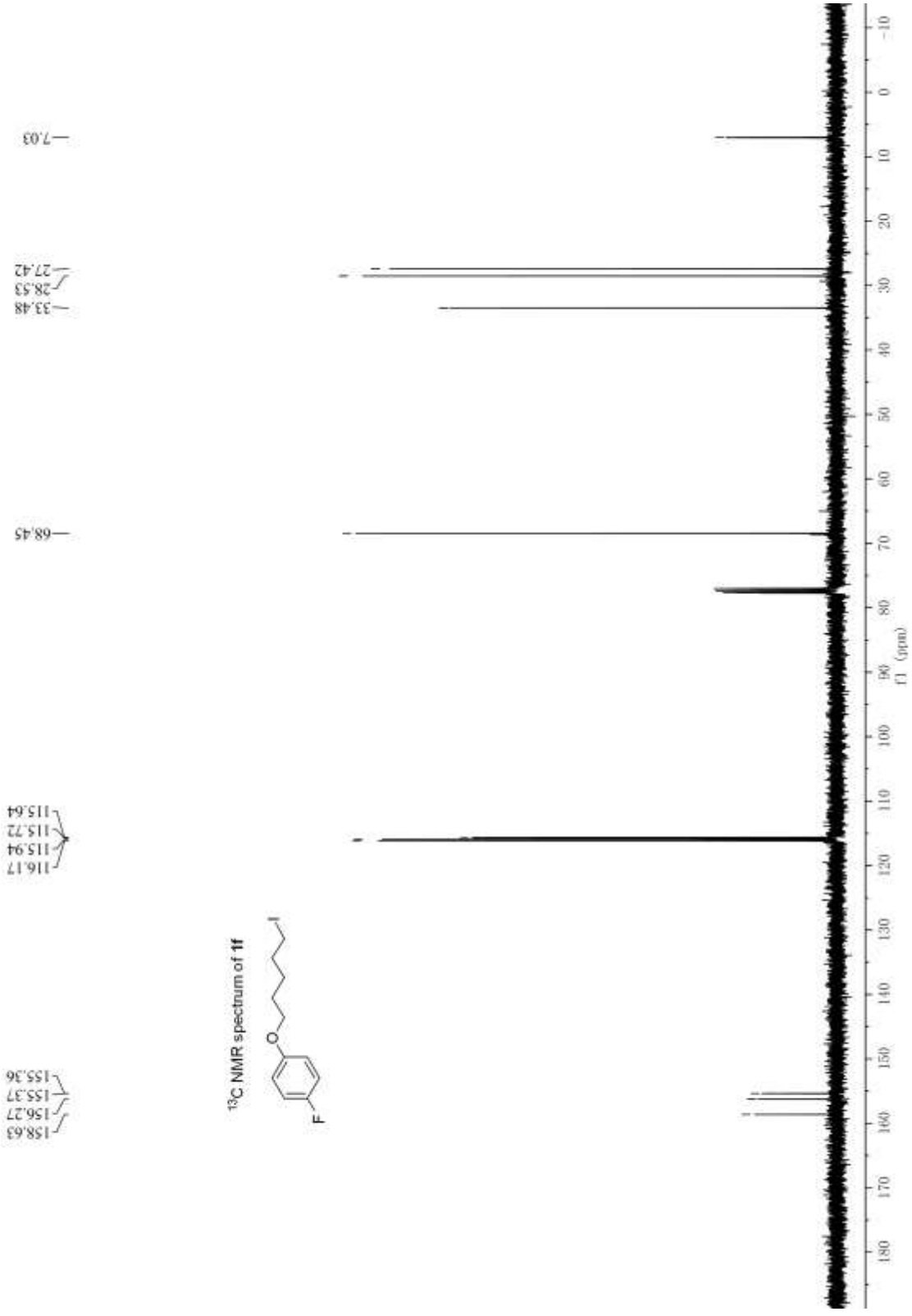
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1e**



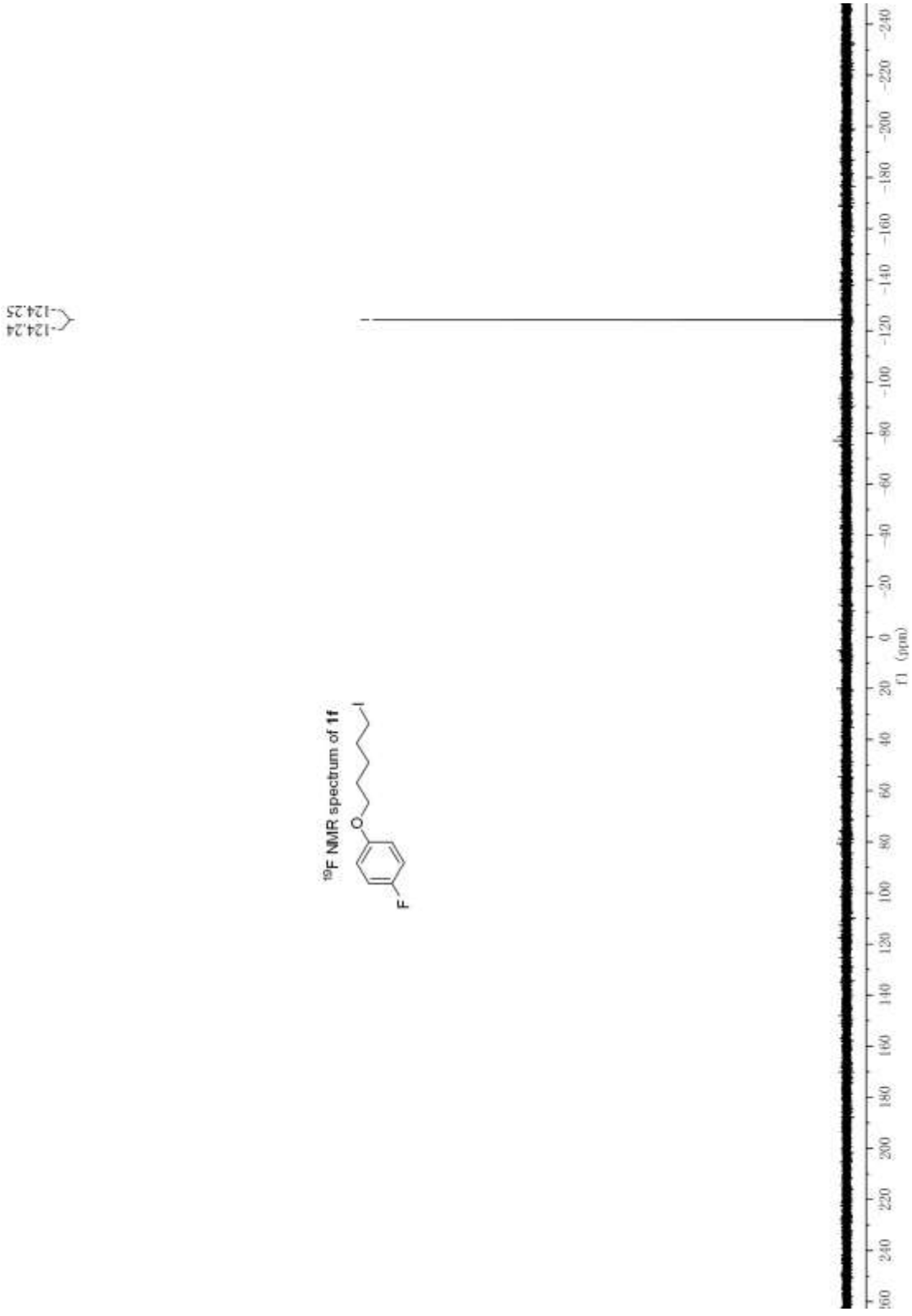
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **1e**



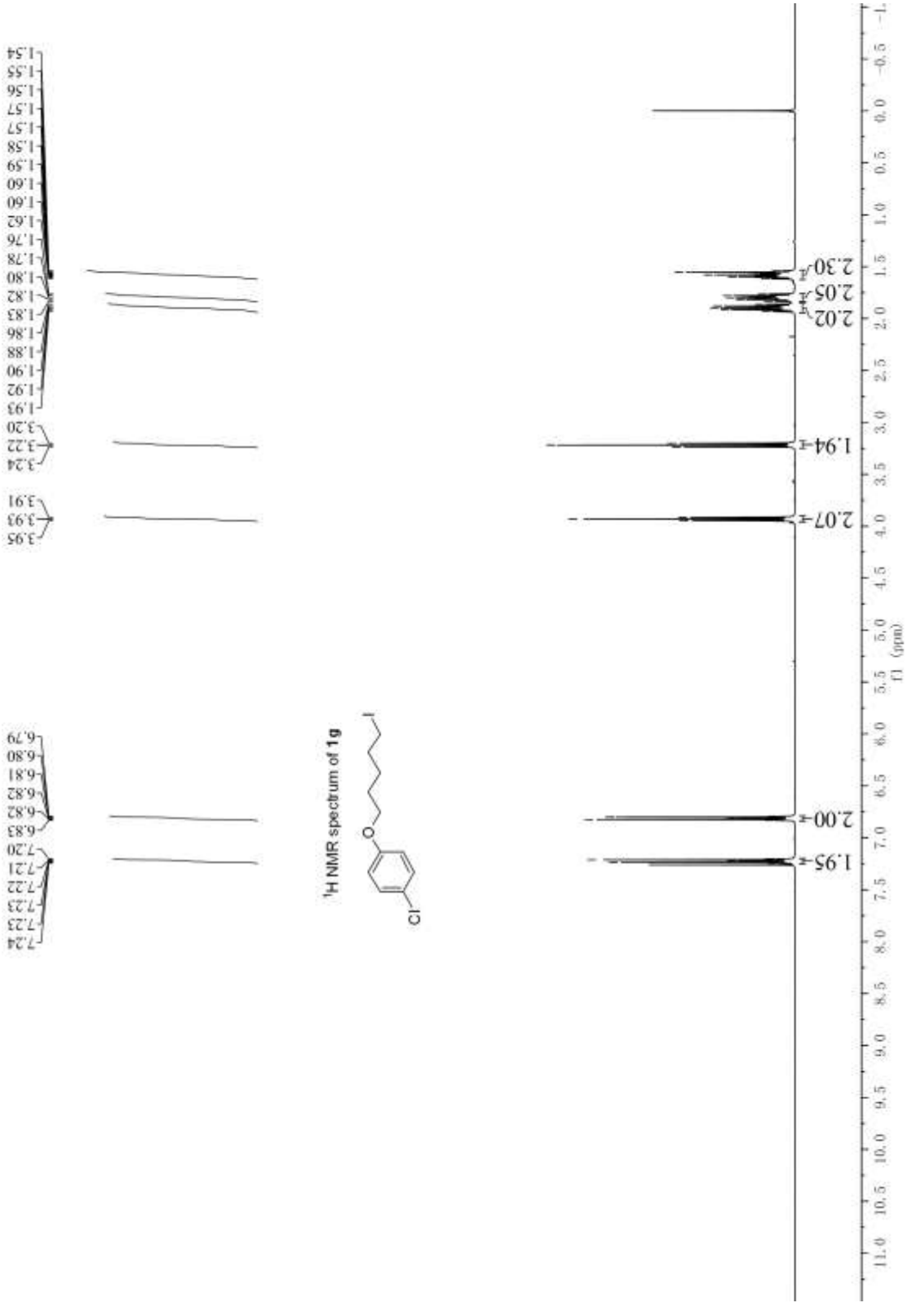
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1f**



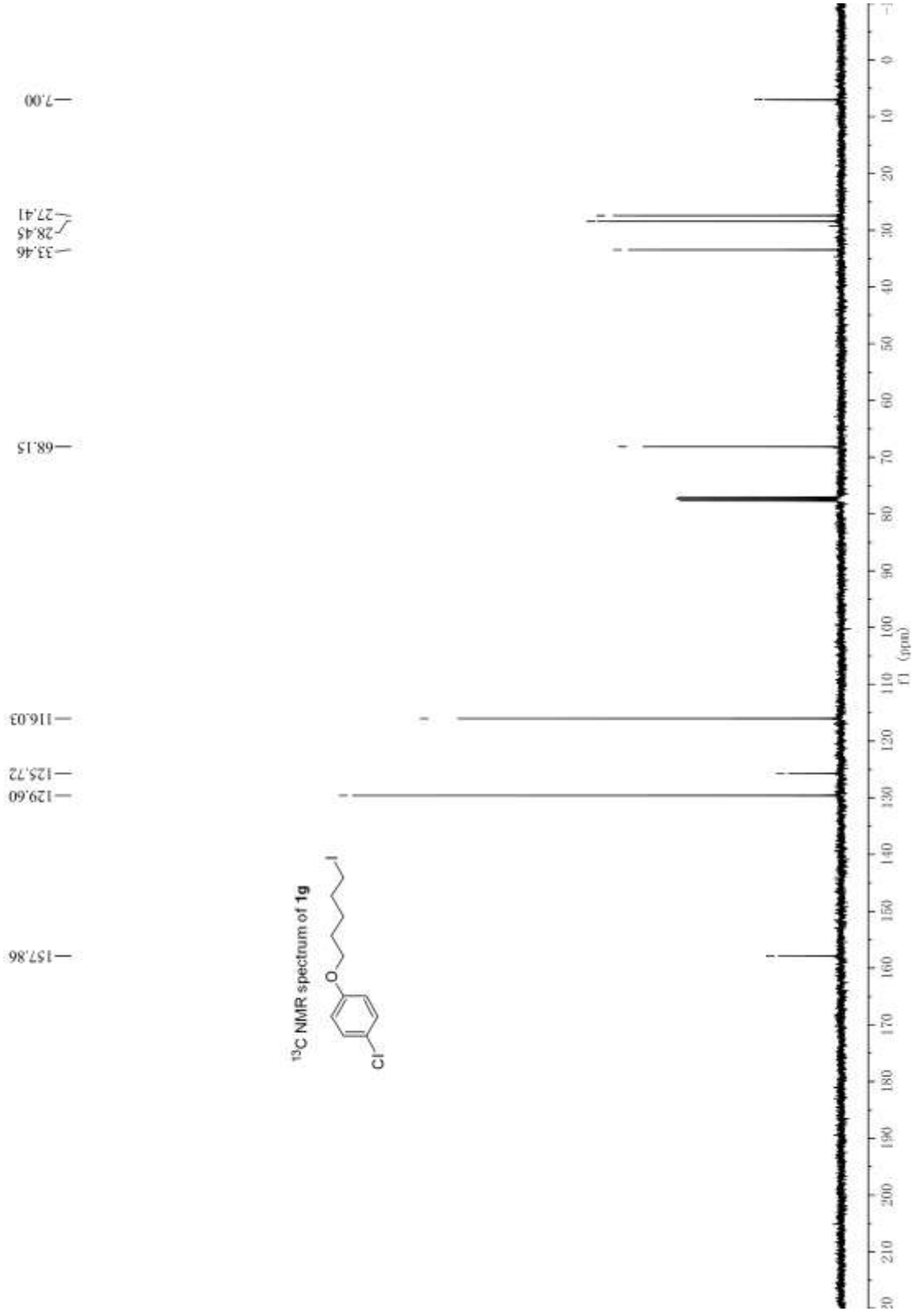
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1f**



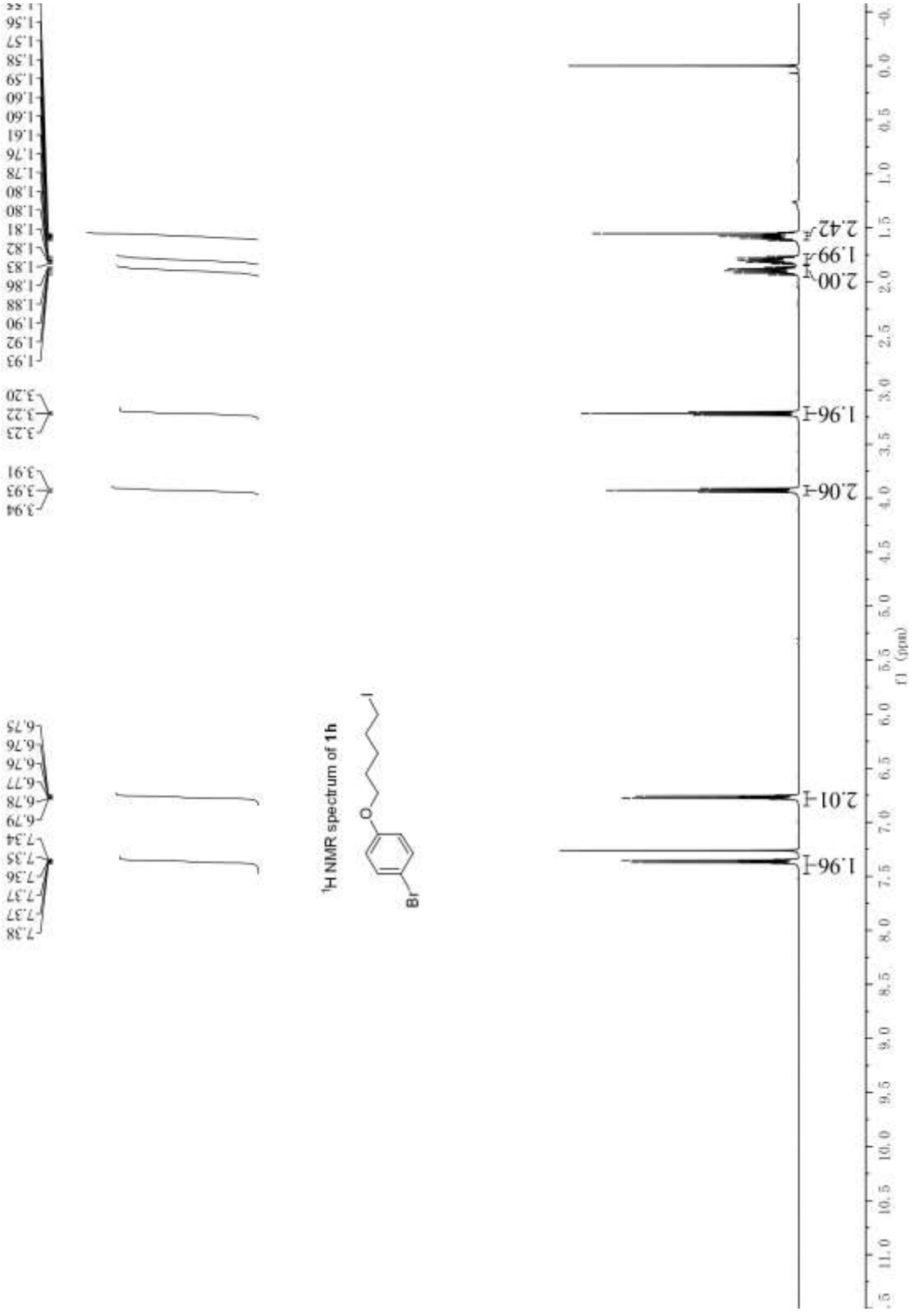
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **1f**



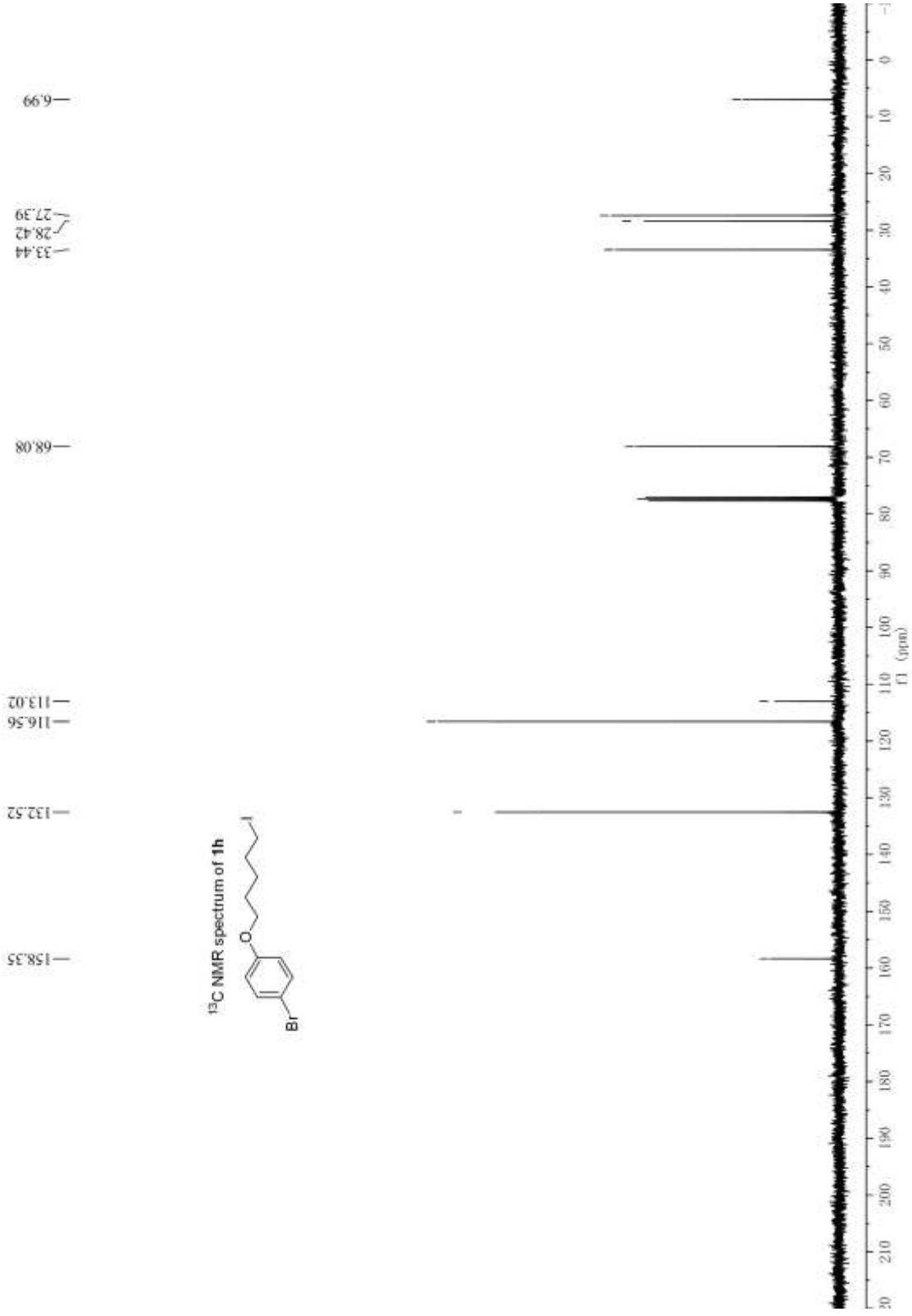
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1g**



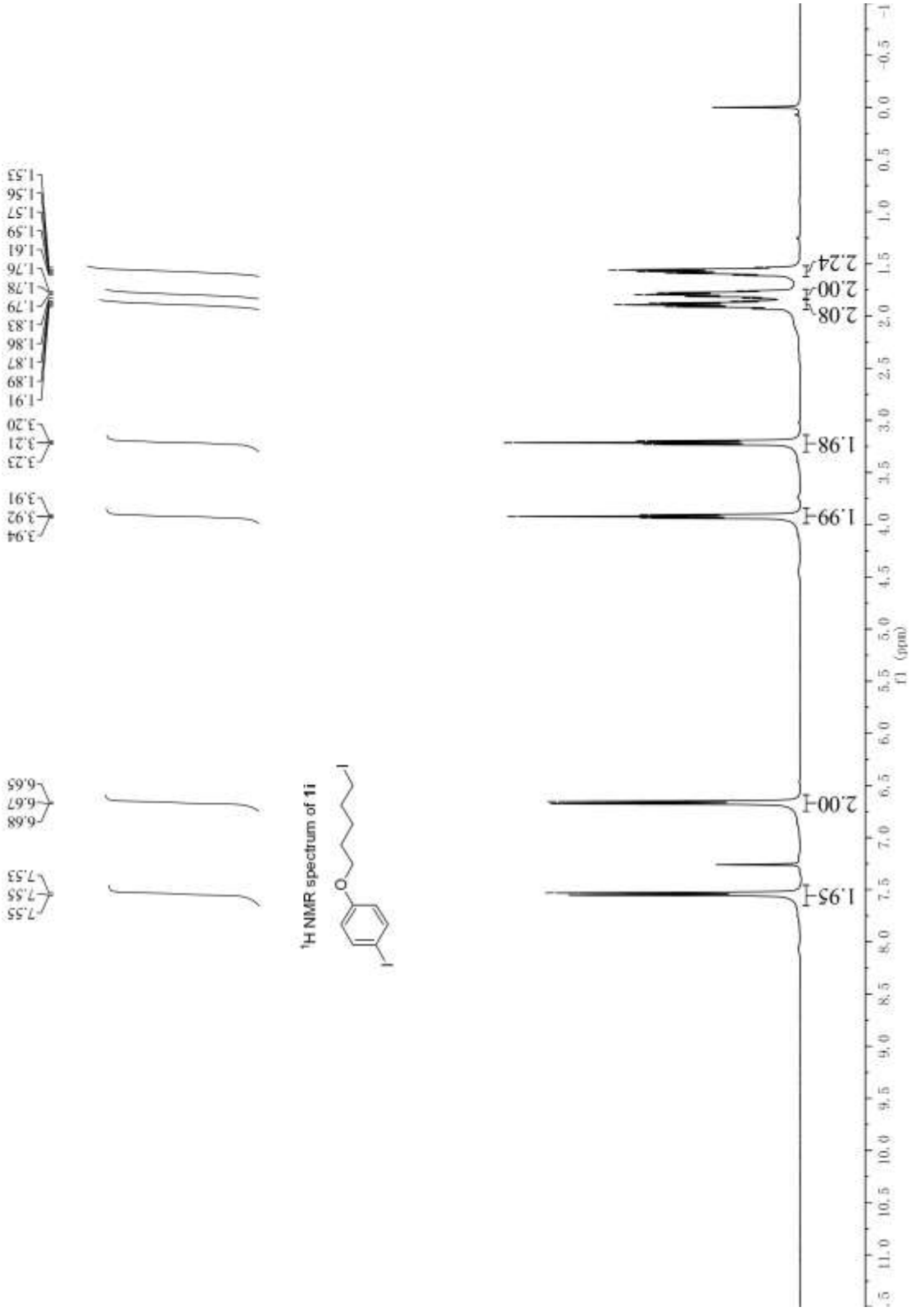
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1g**



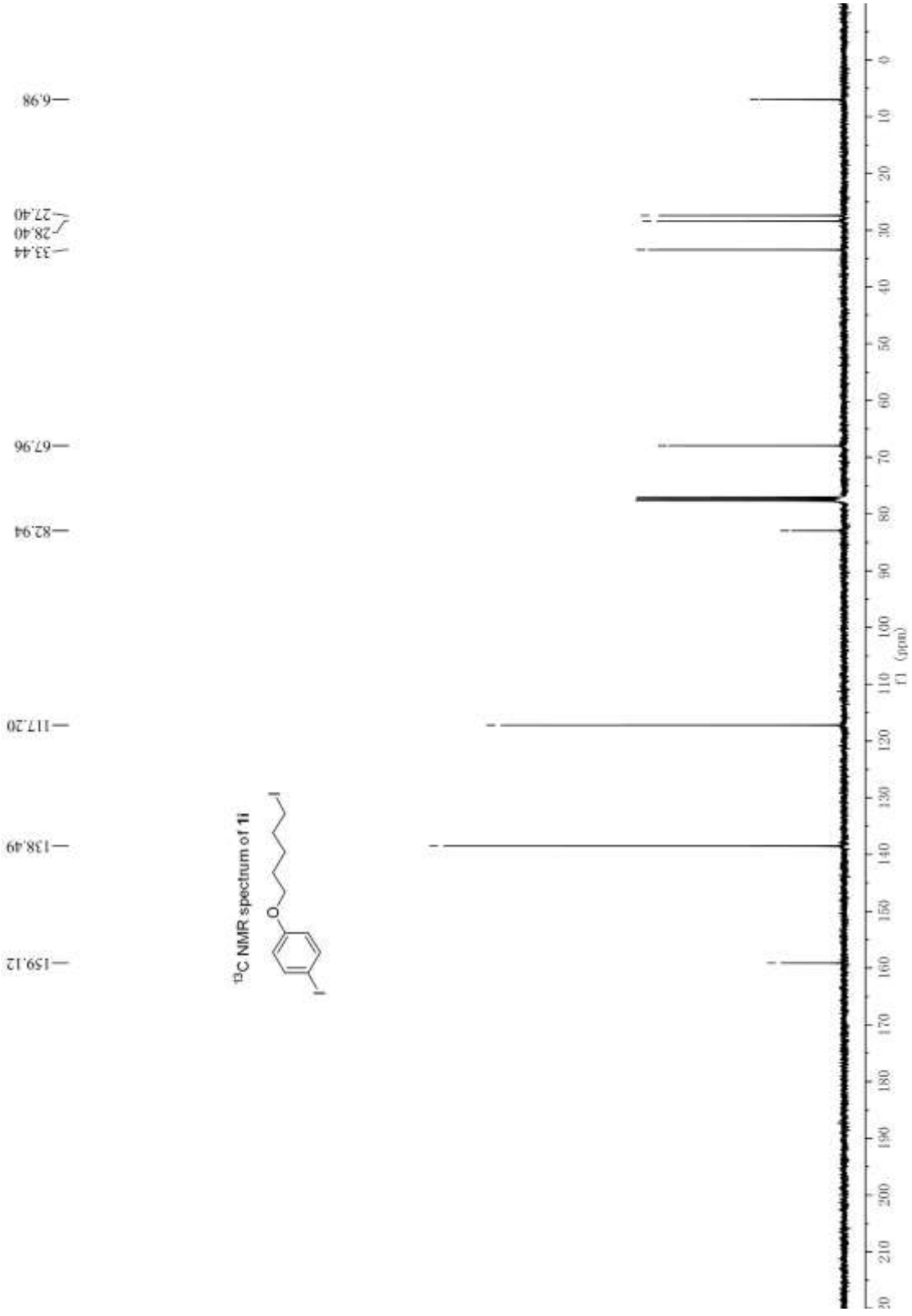
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1h**



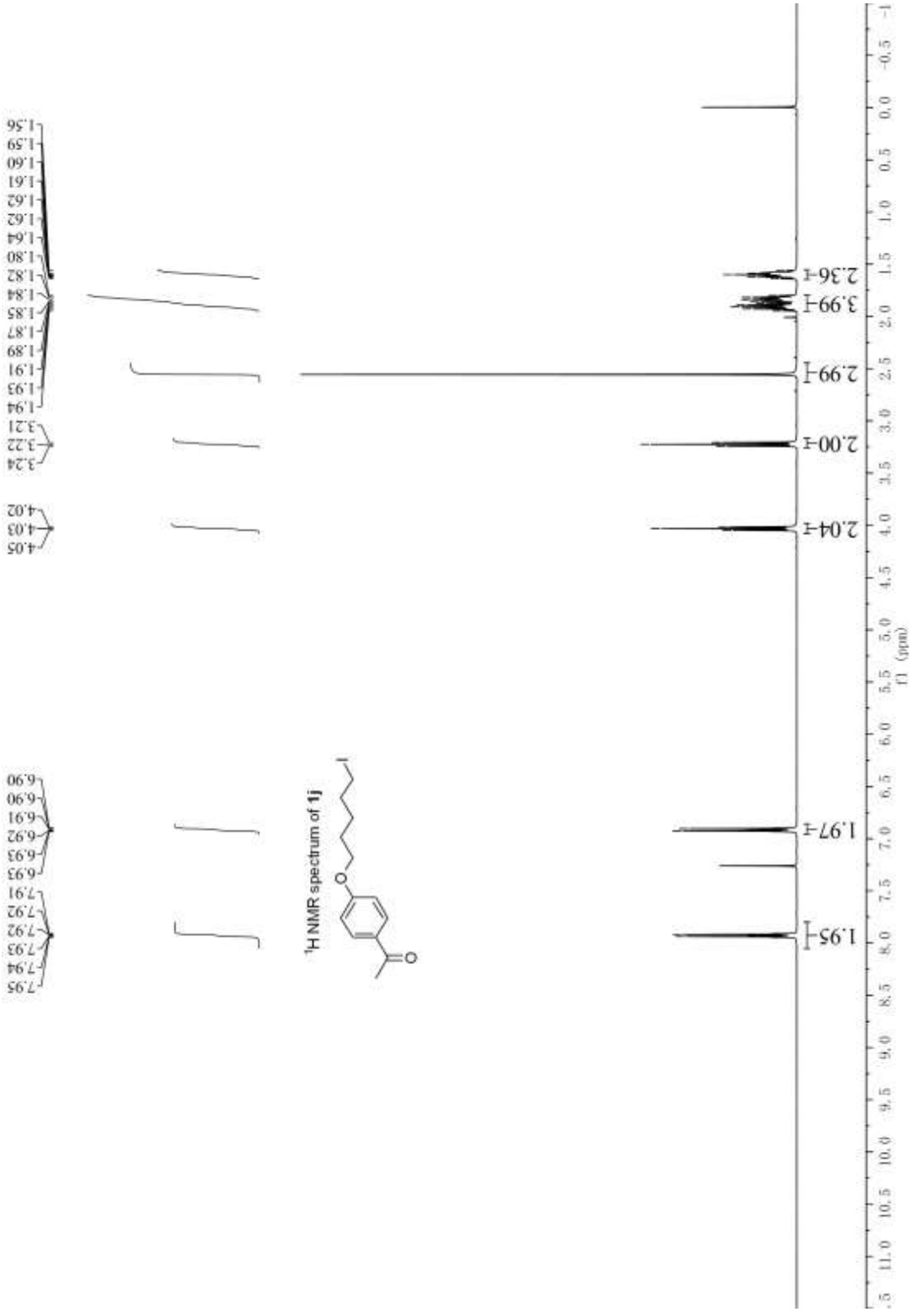
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1h**



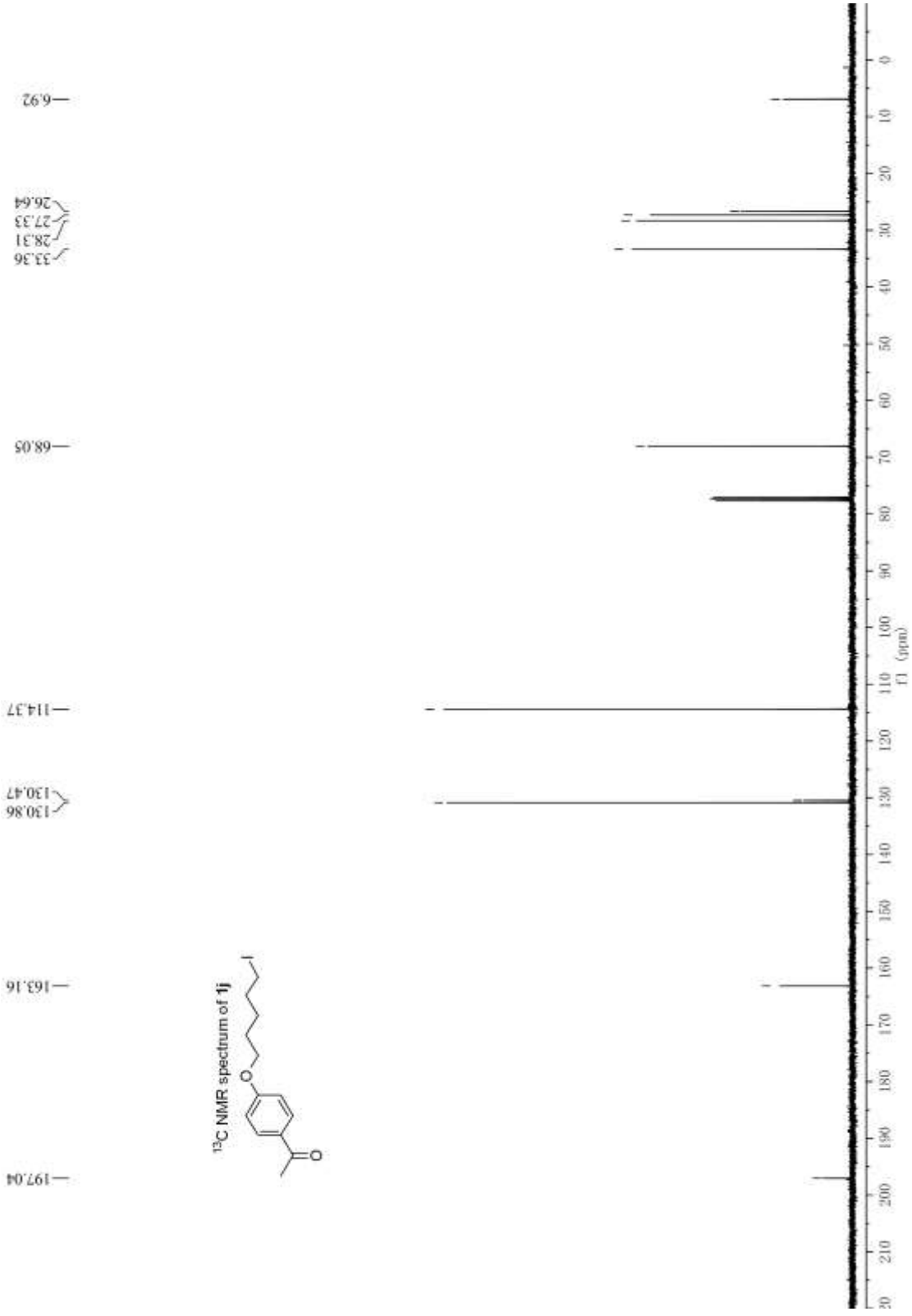
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1i**



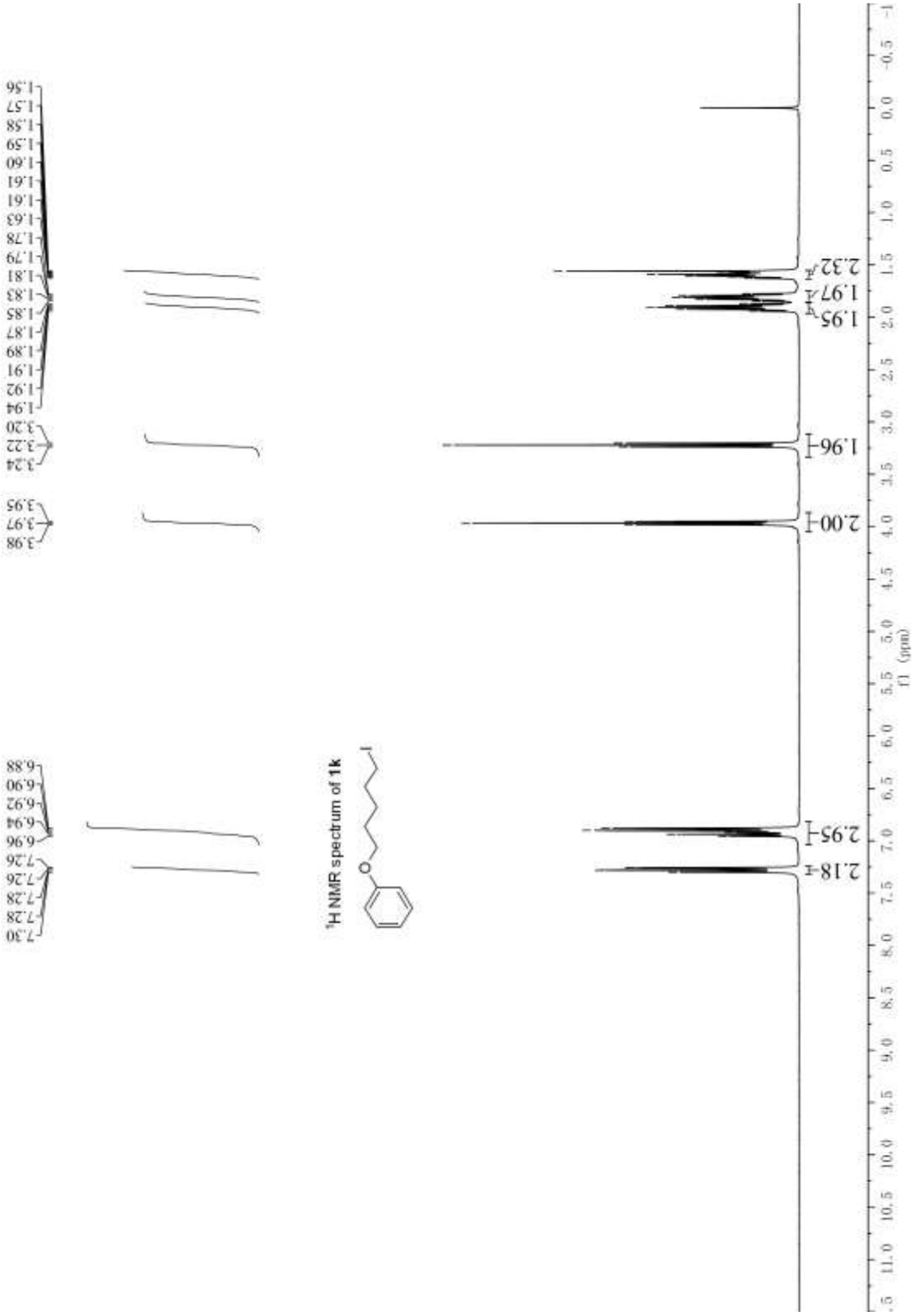
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1i**



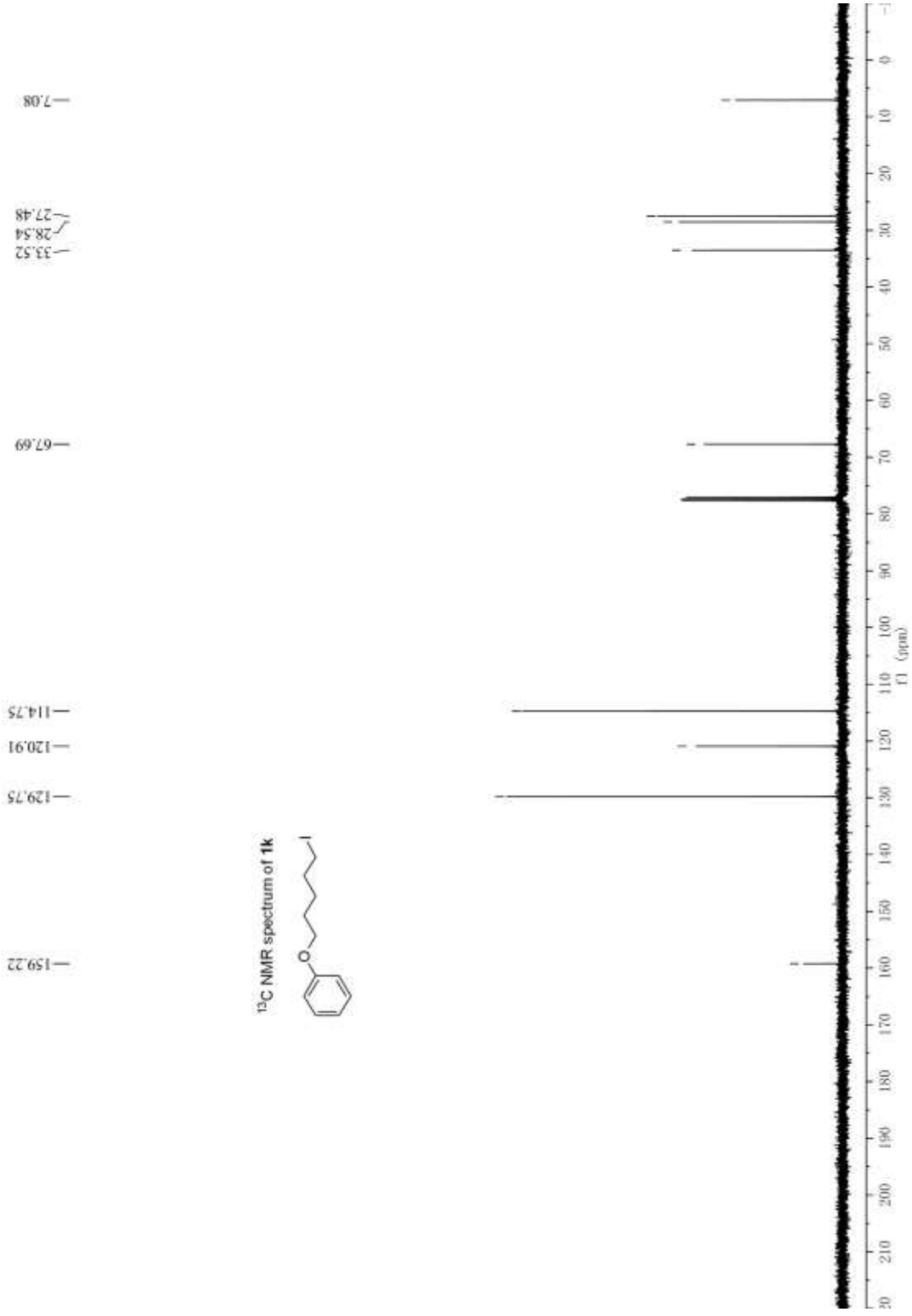
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1j**



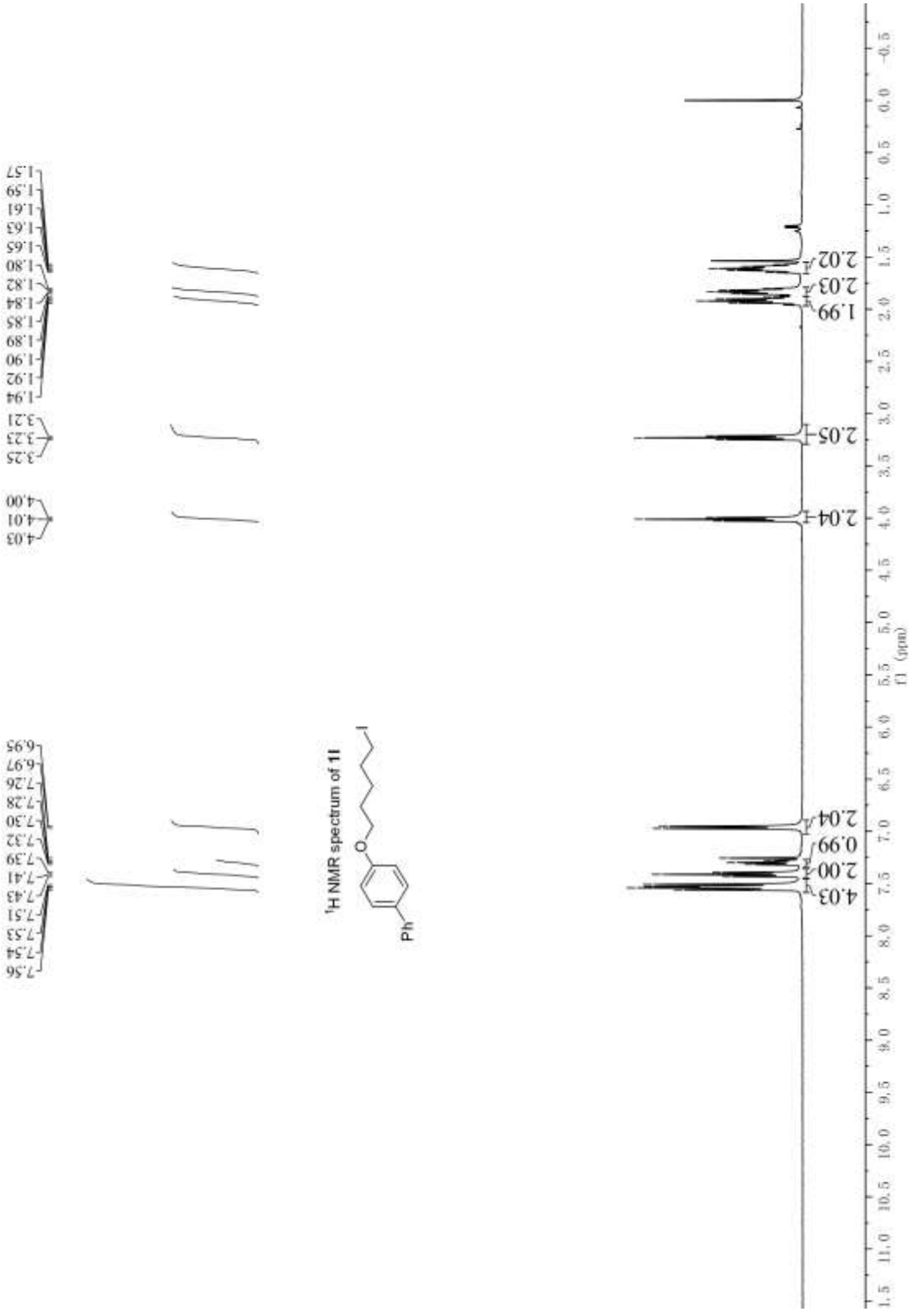
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1j**



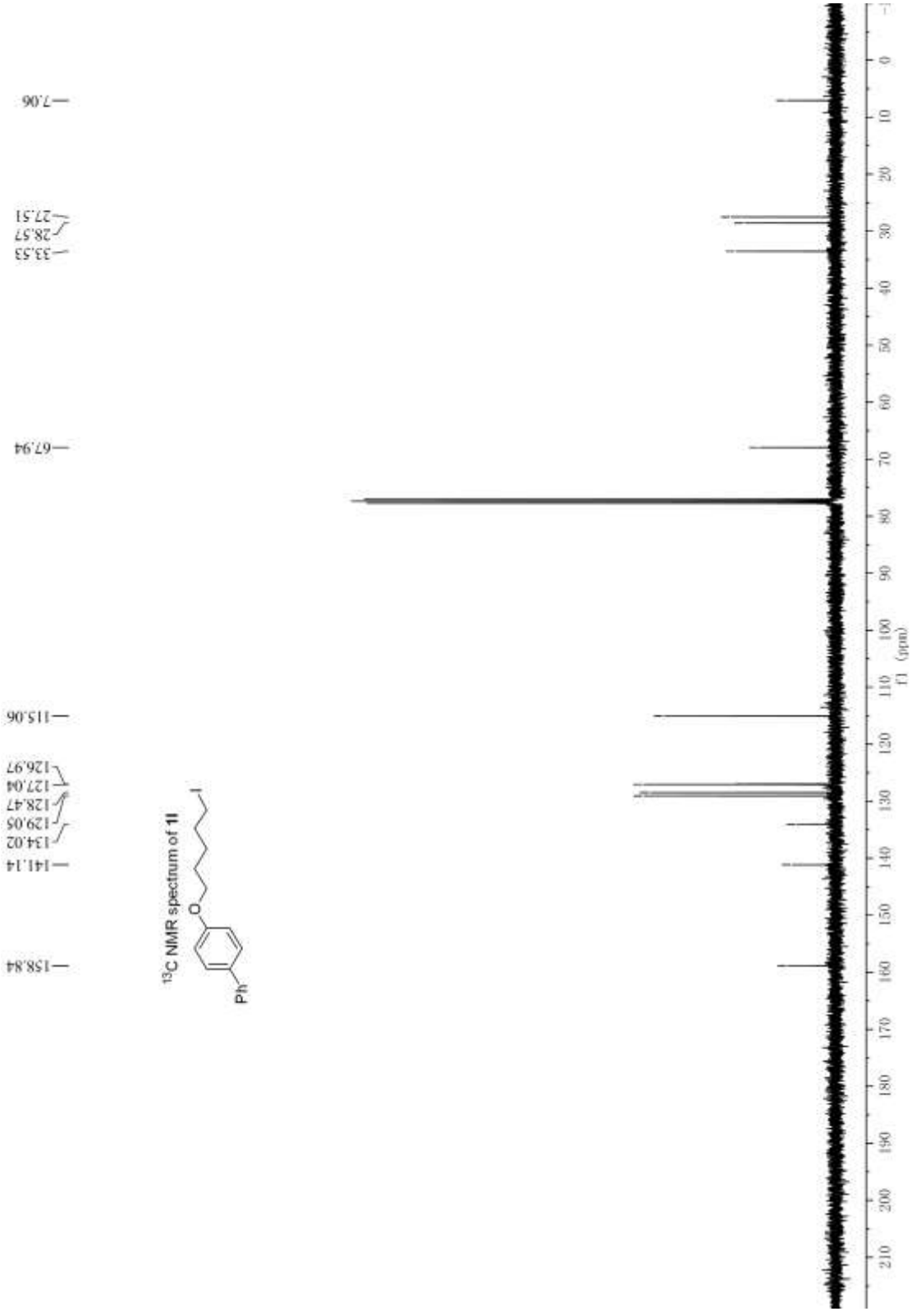
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1k**



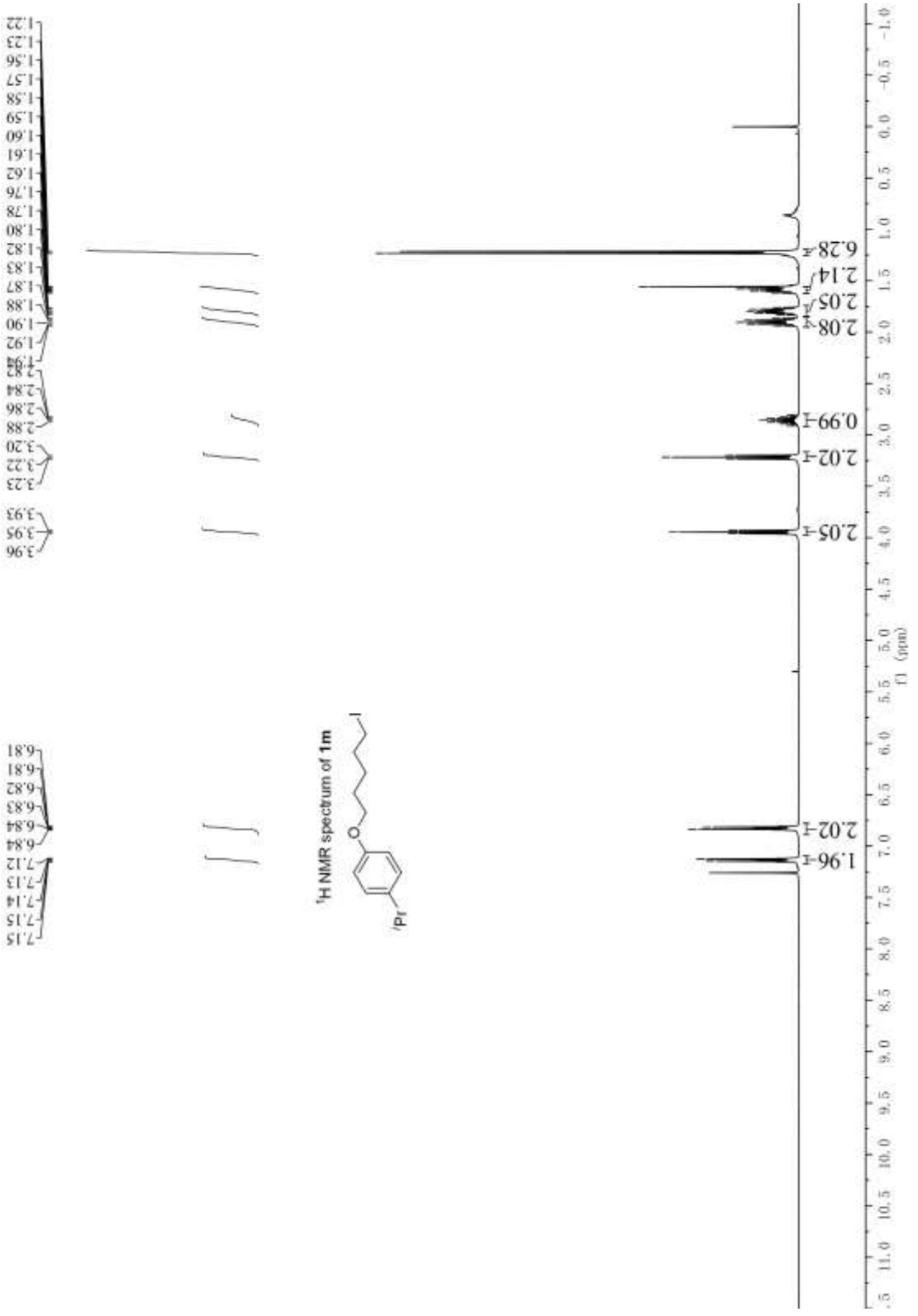
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1k**



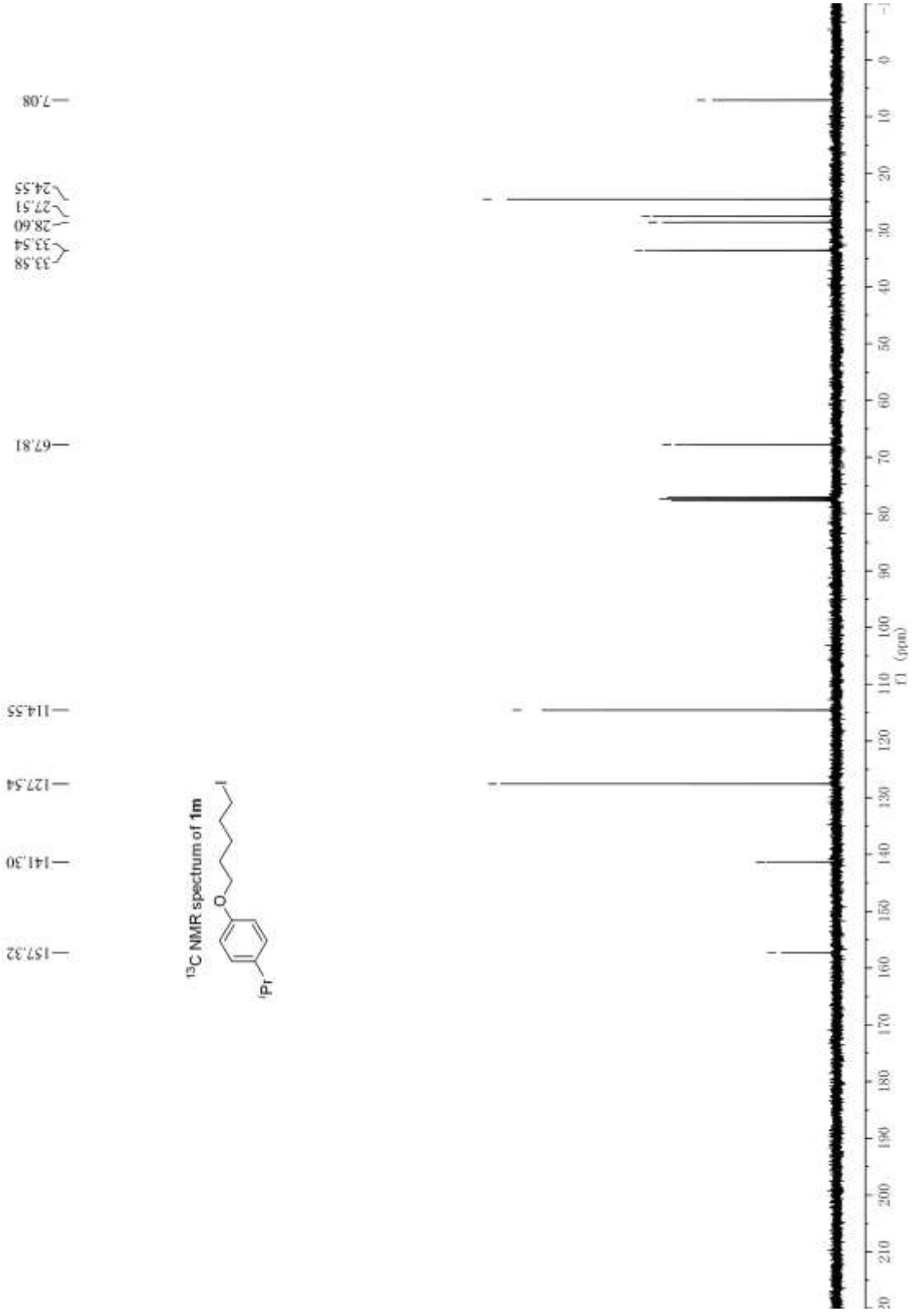
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1l**



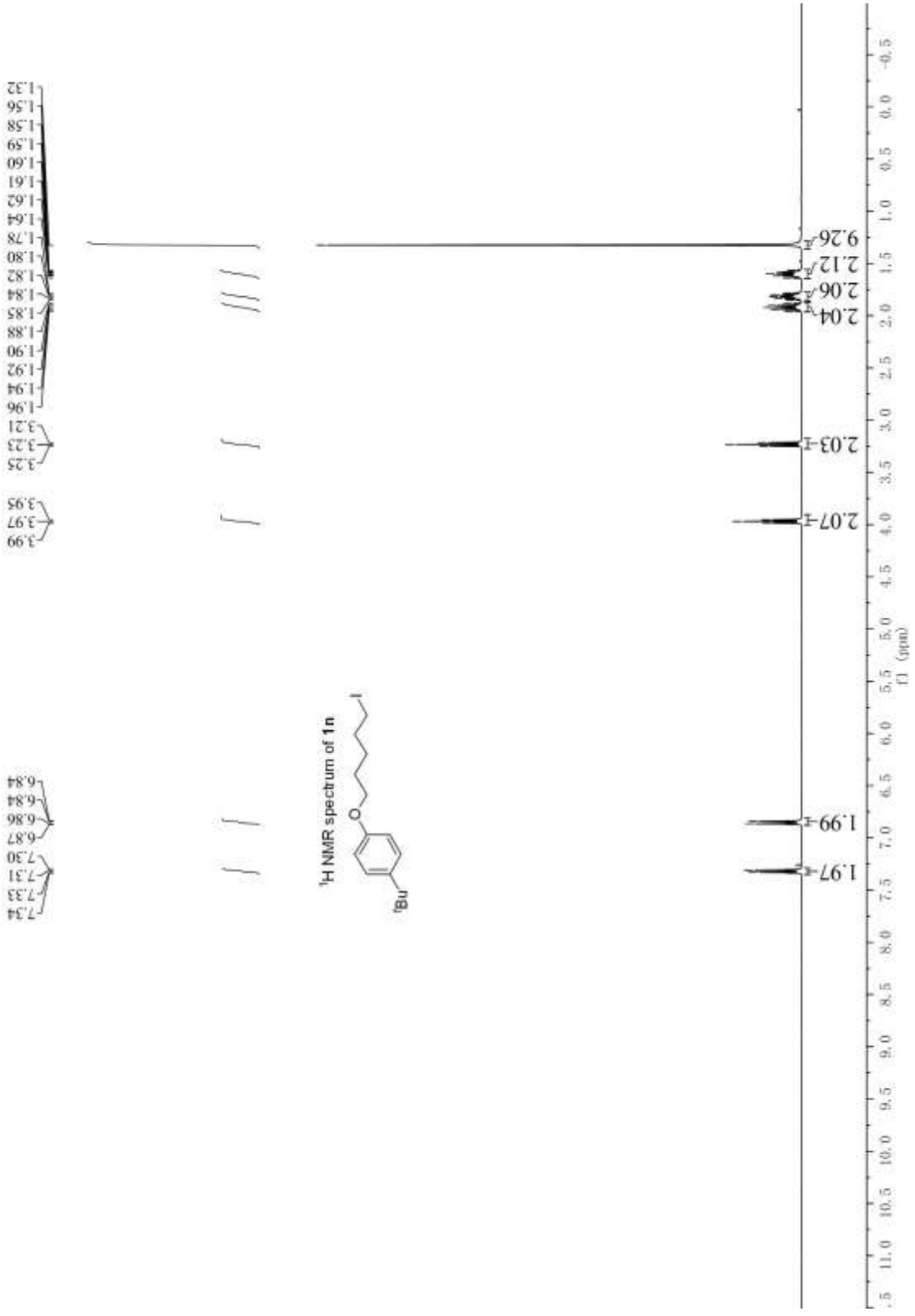
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1l**



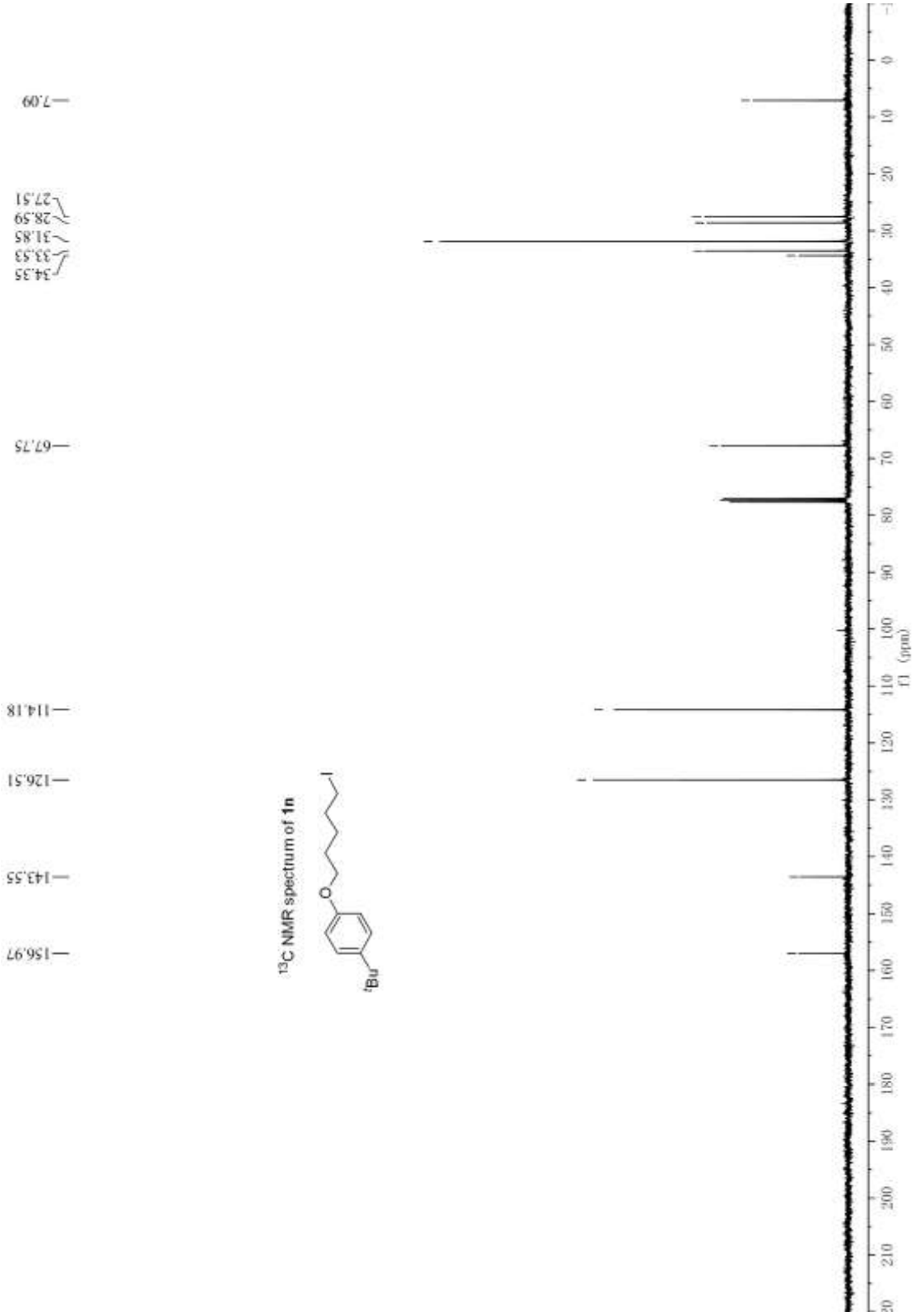
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1m**



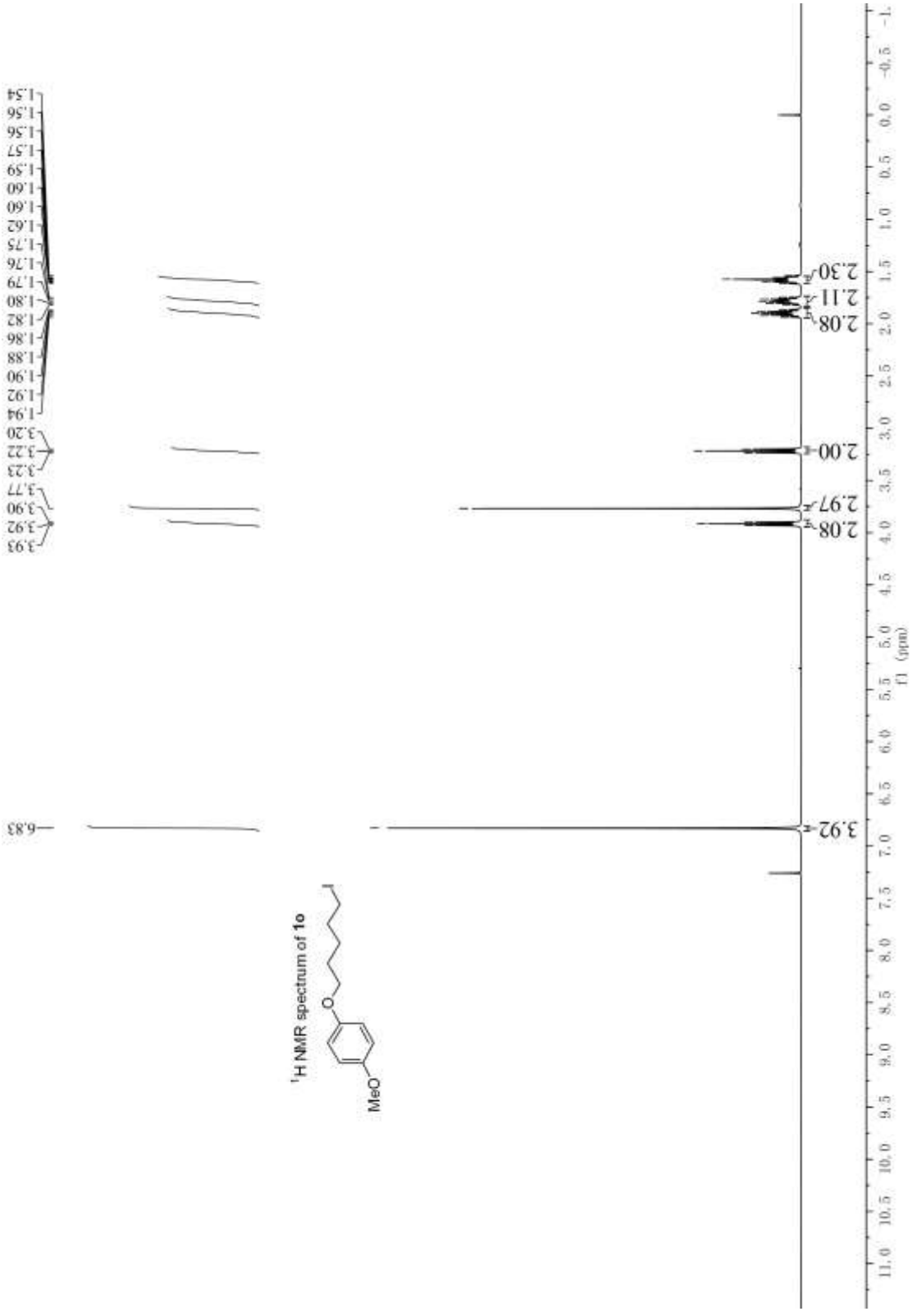
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1m**



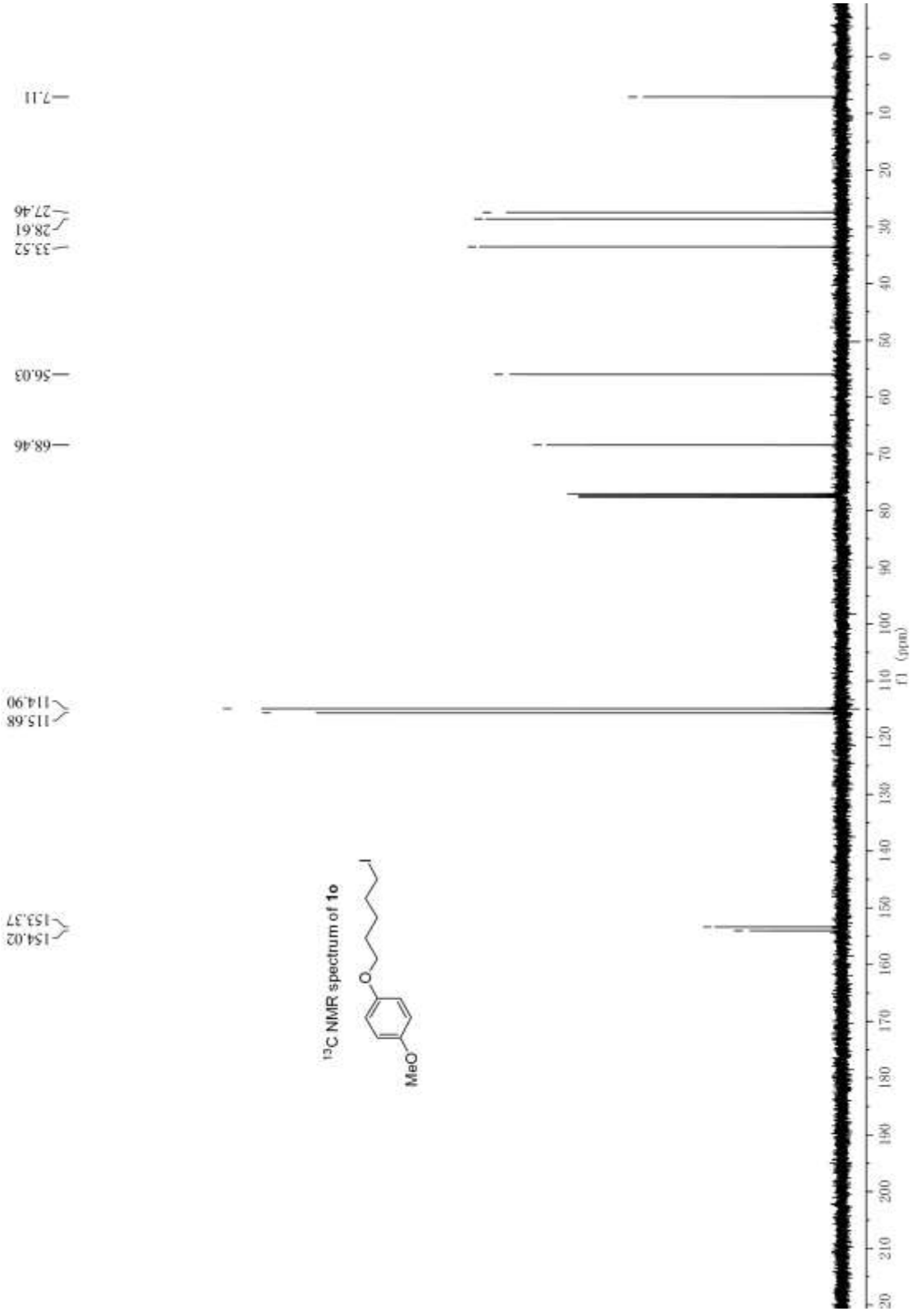
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1n**



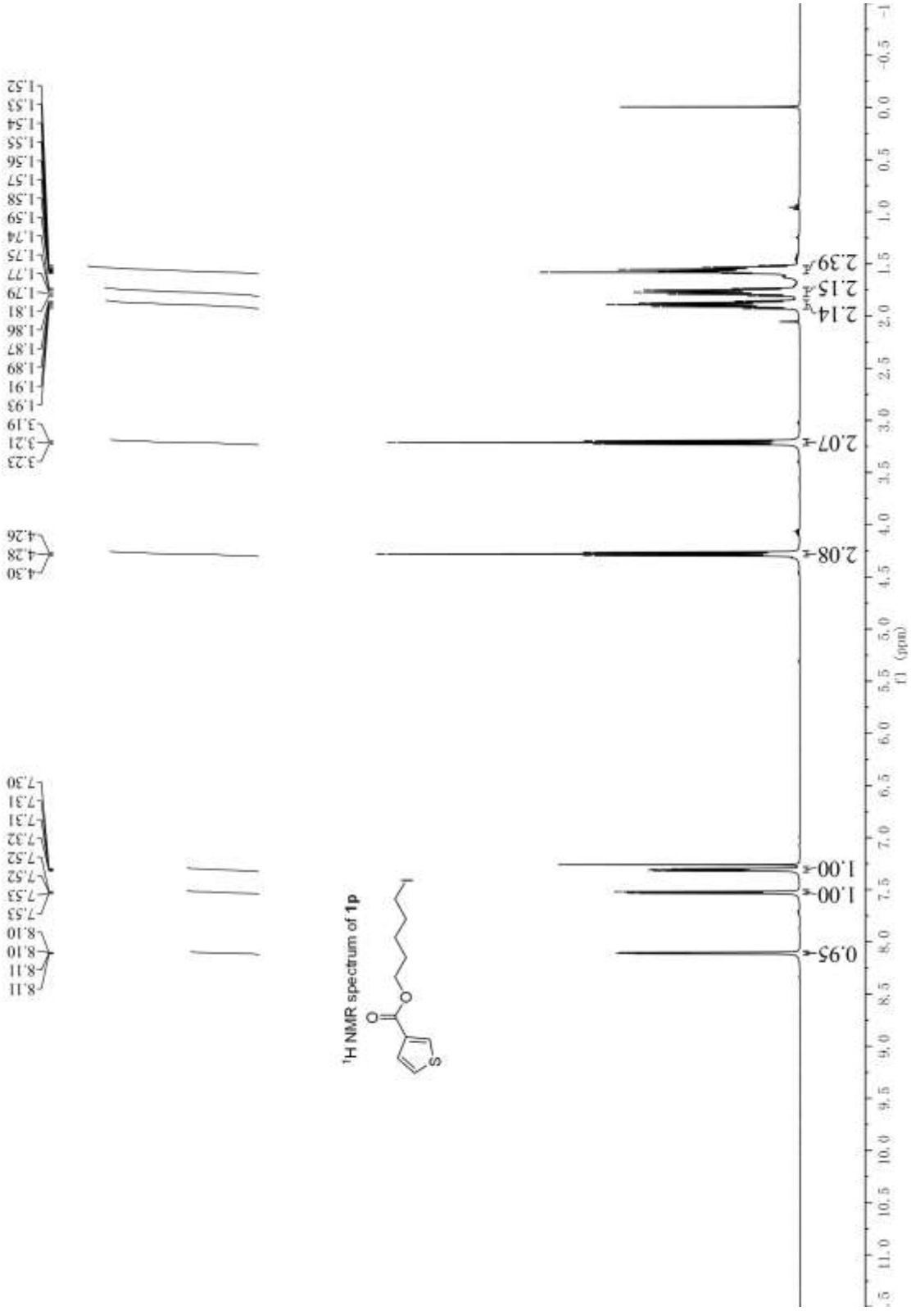
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1n**



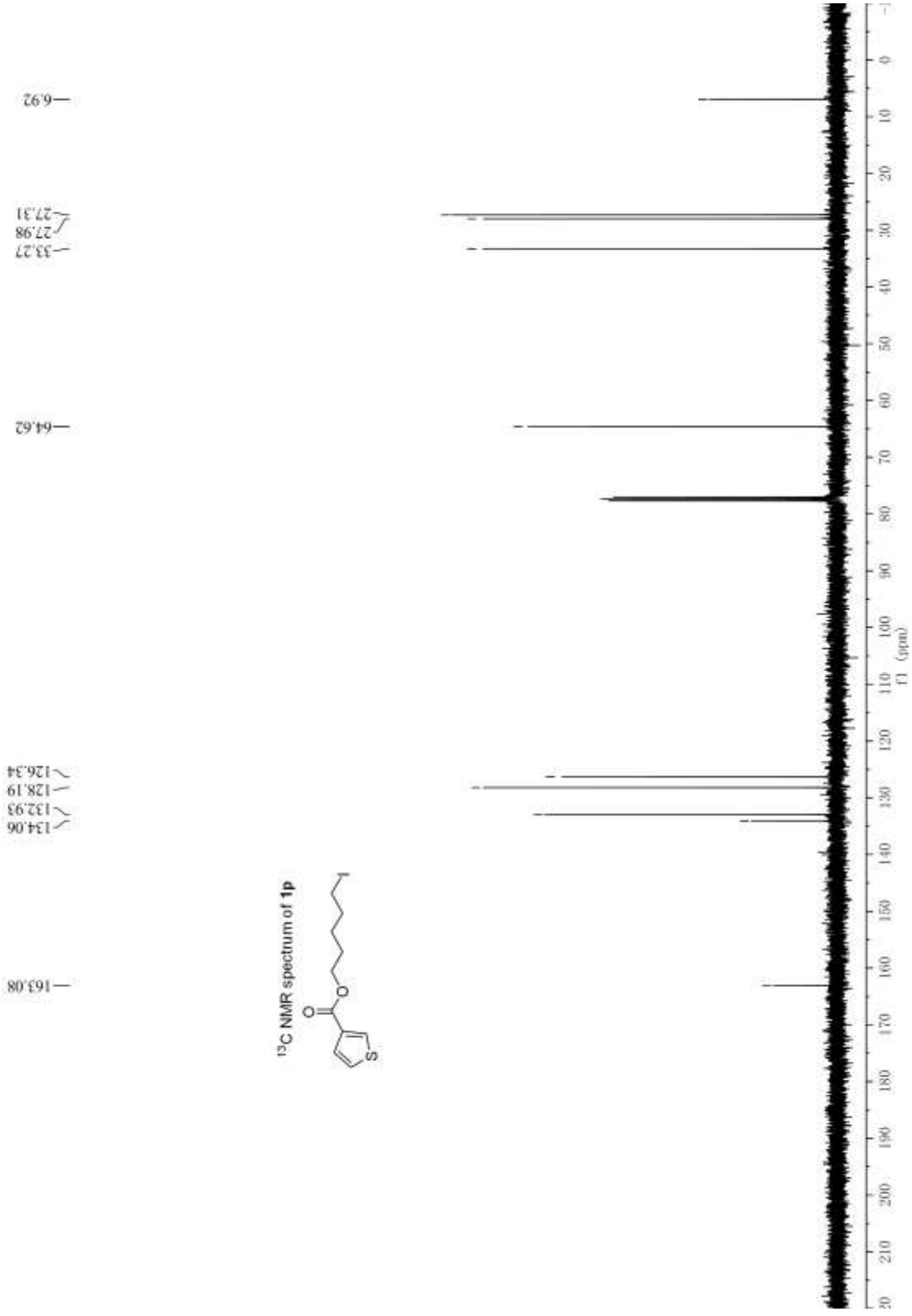
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1o**



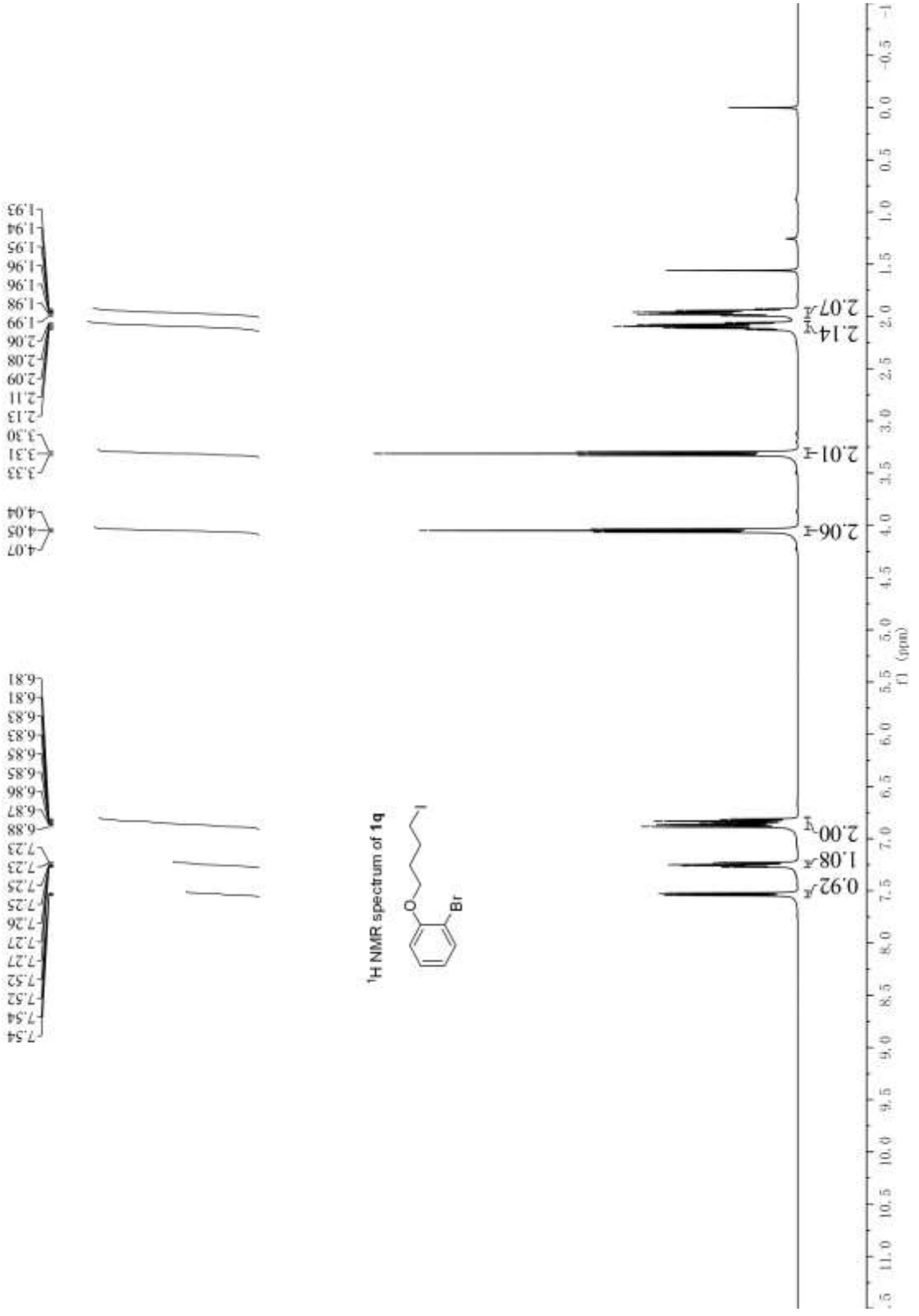
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1o**



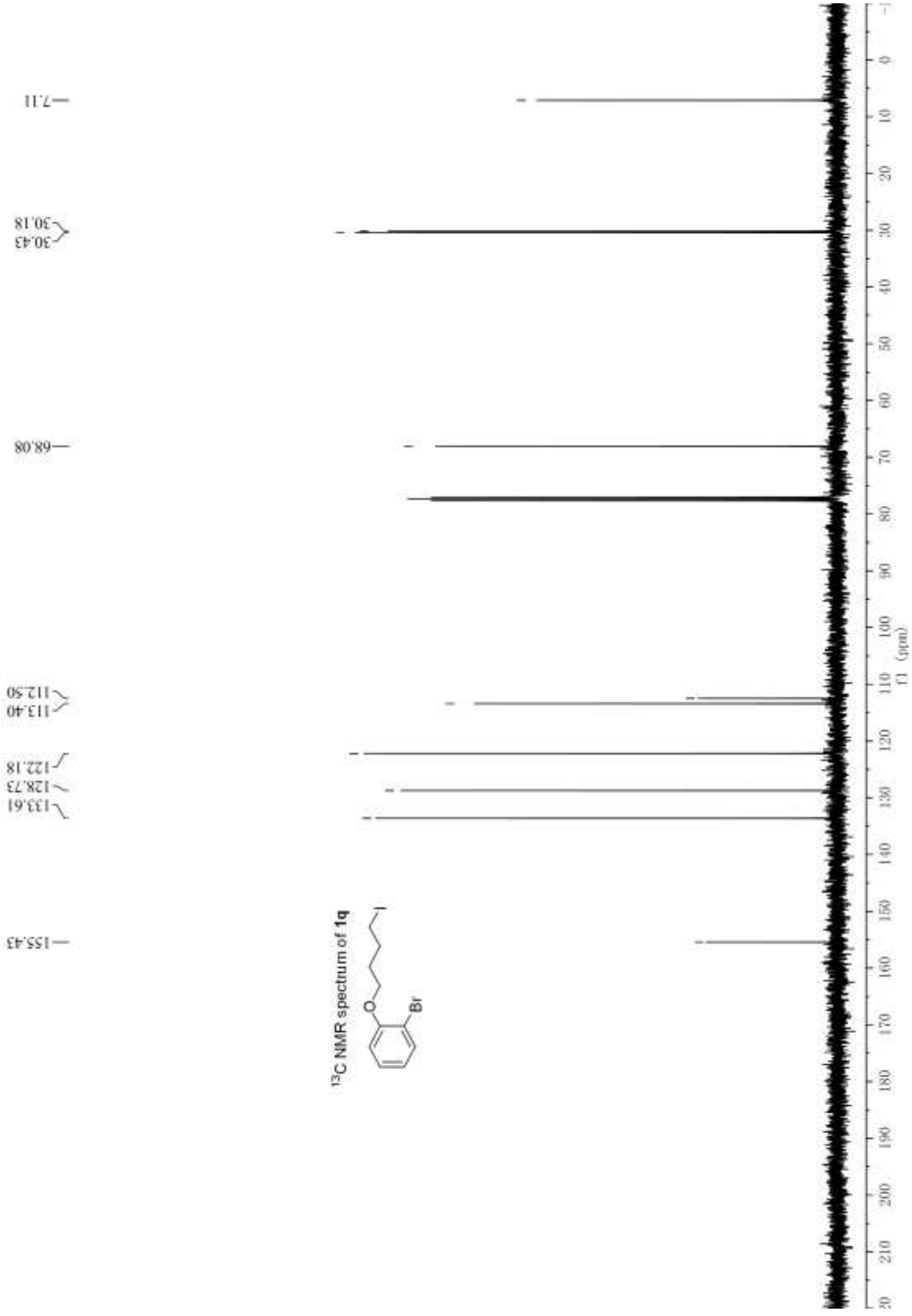
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1p**



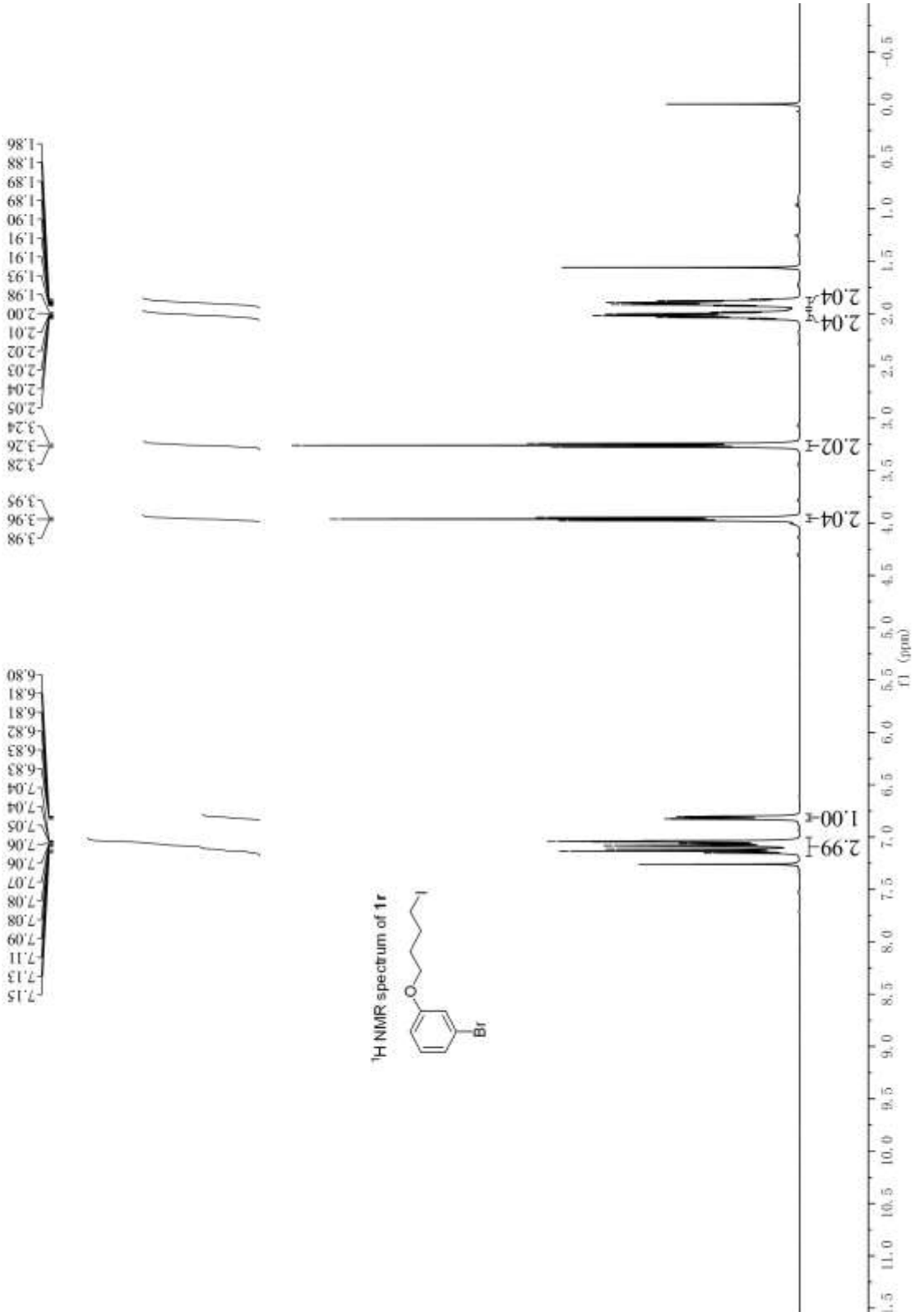
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1p**



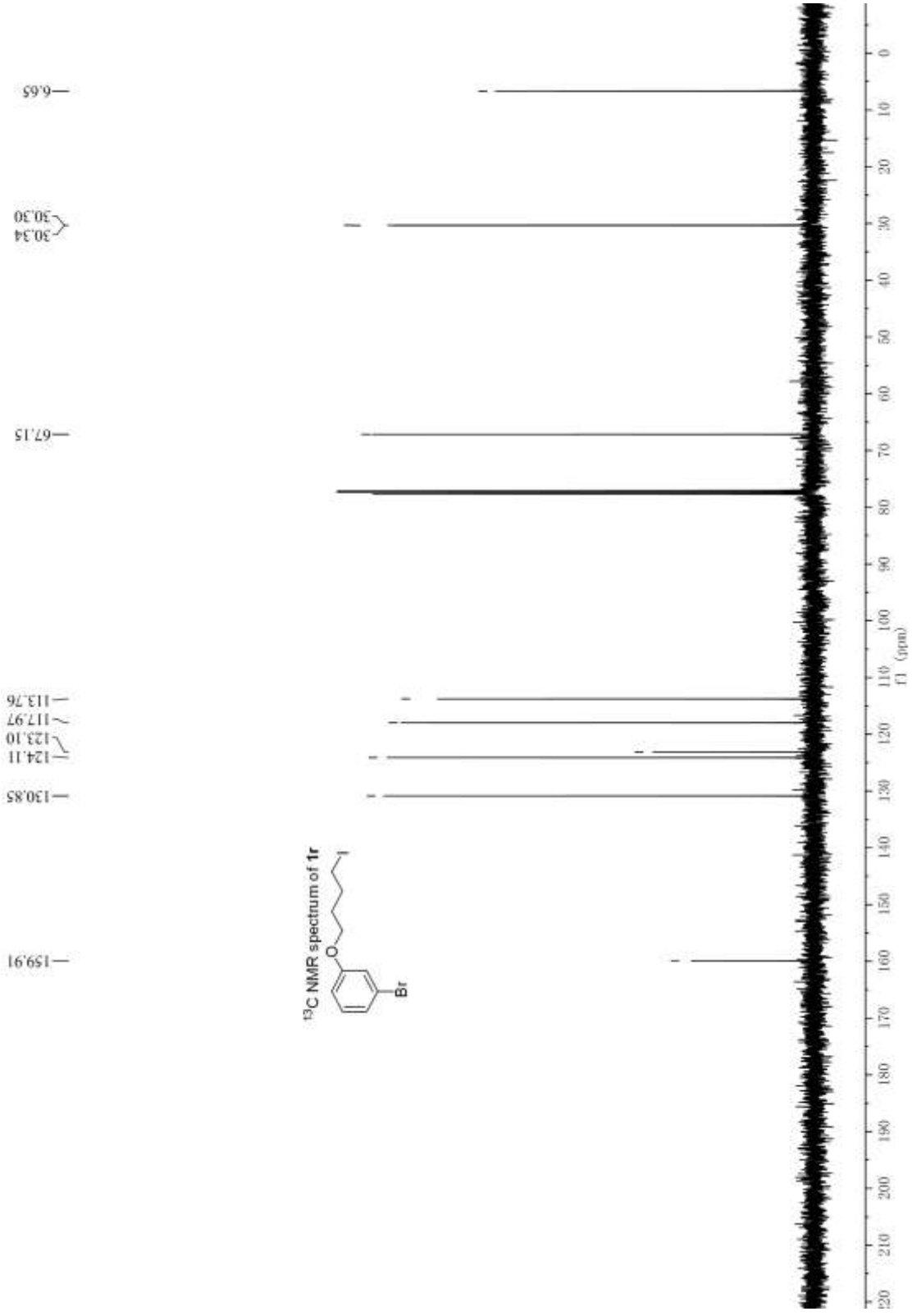
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1q**



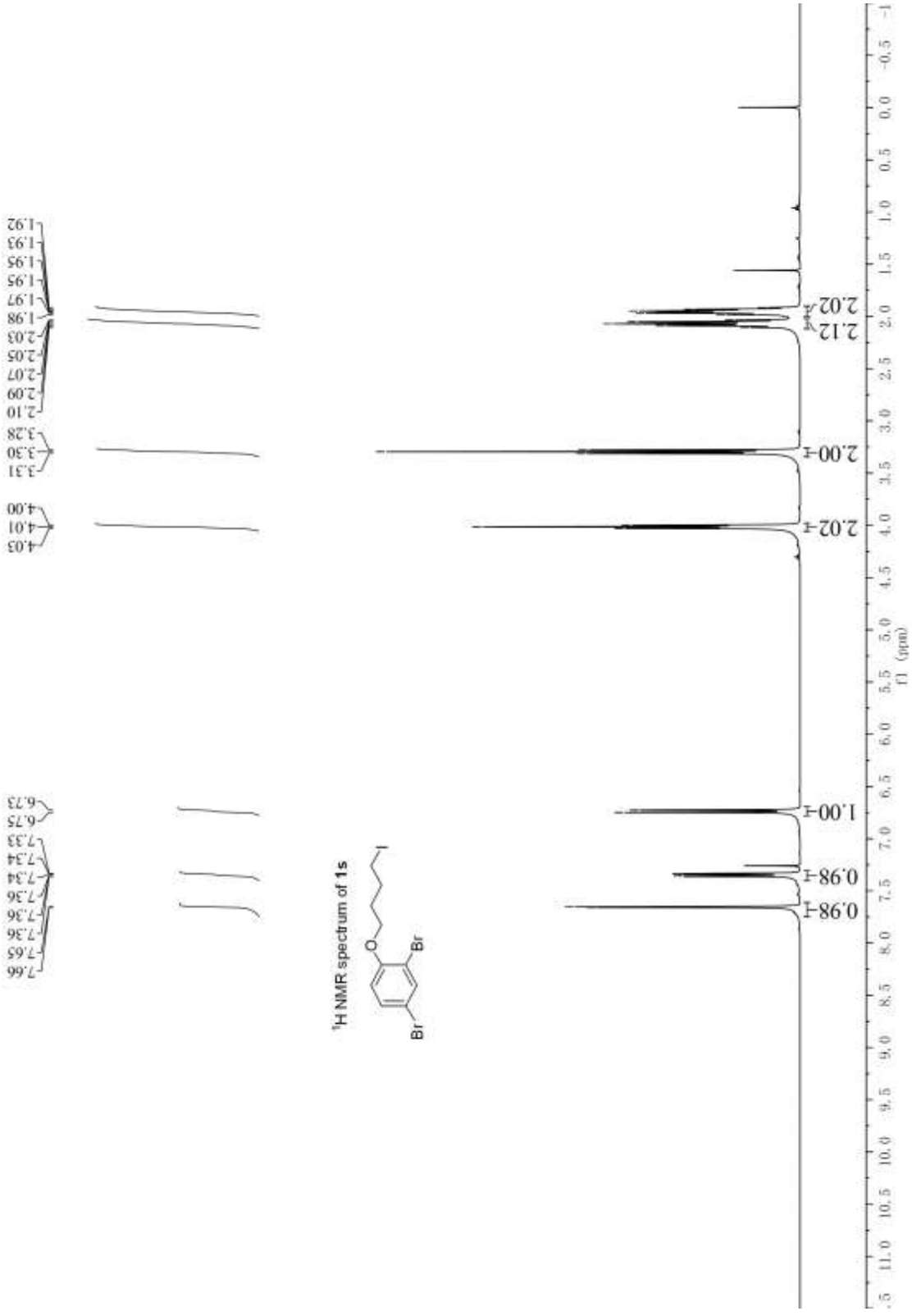
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1q**



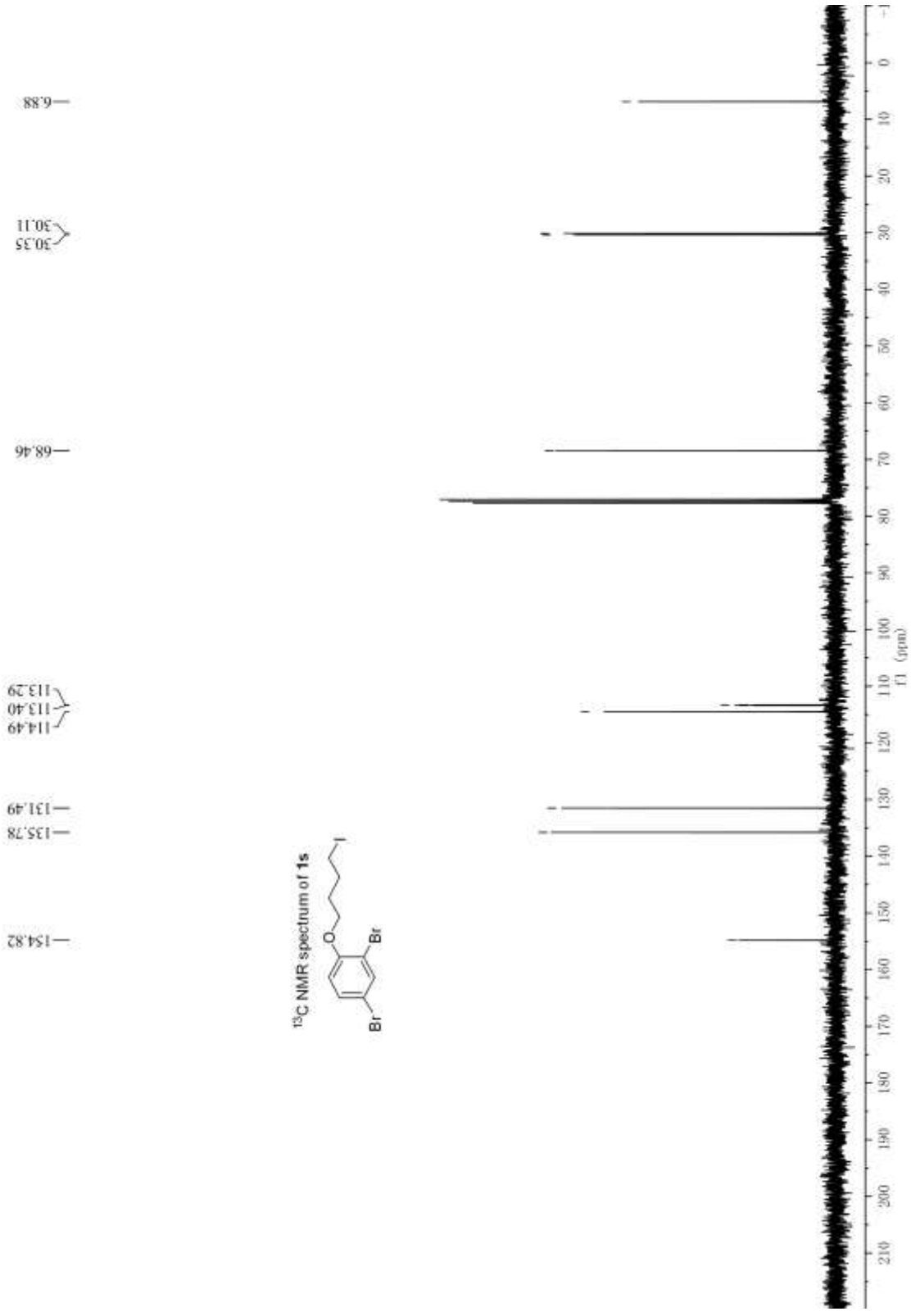
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1r**



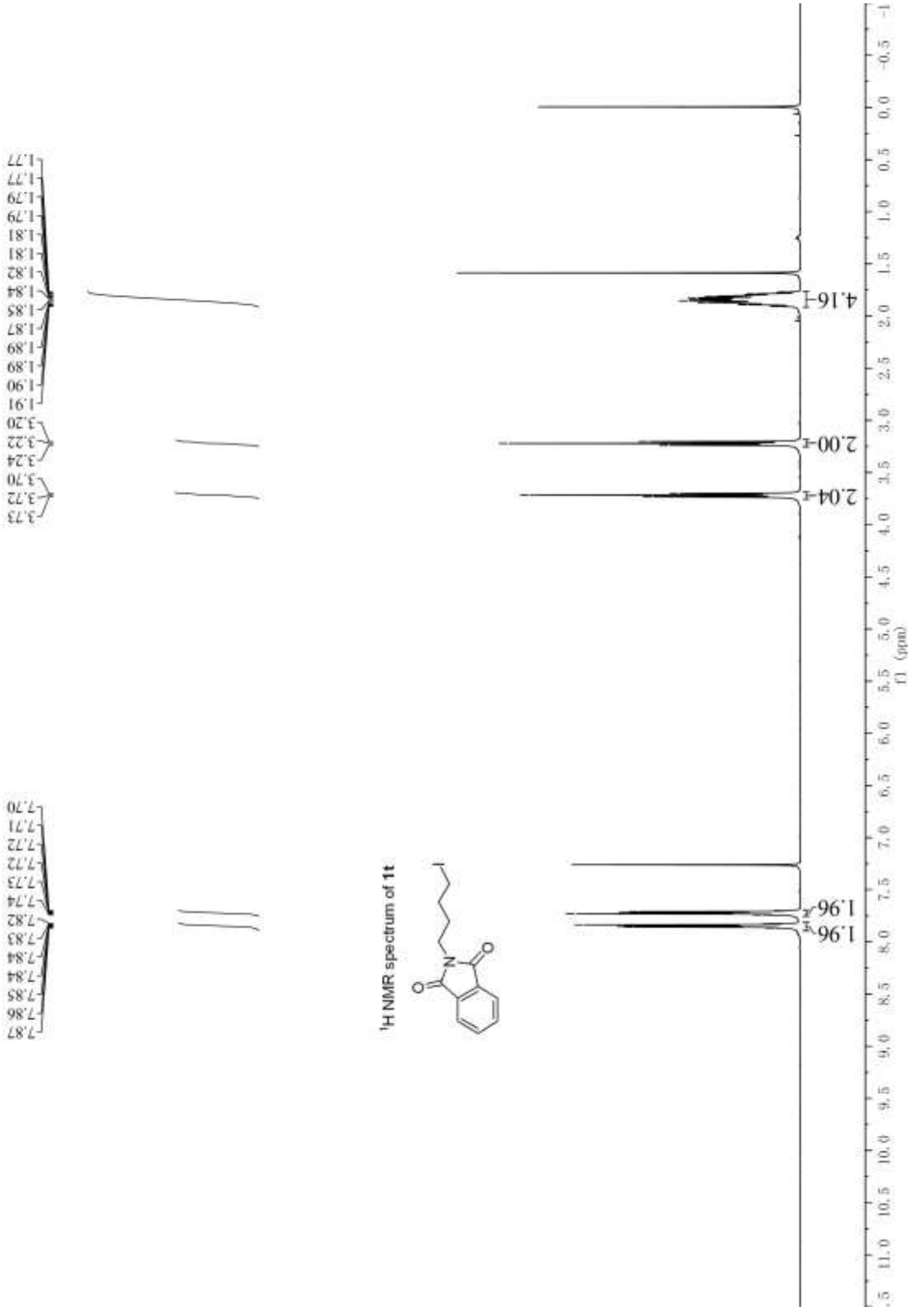
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1r**



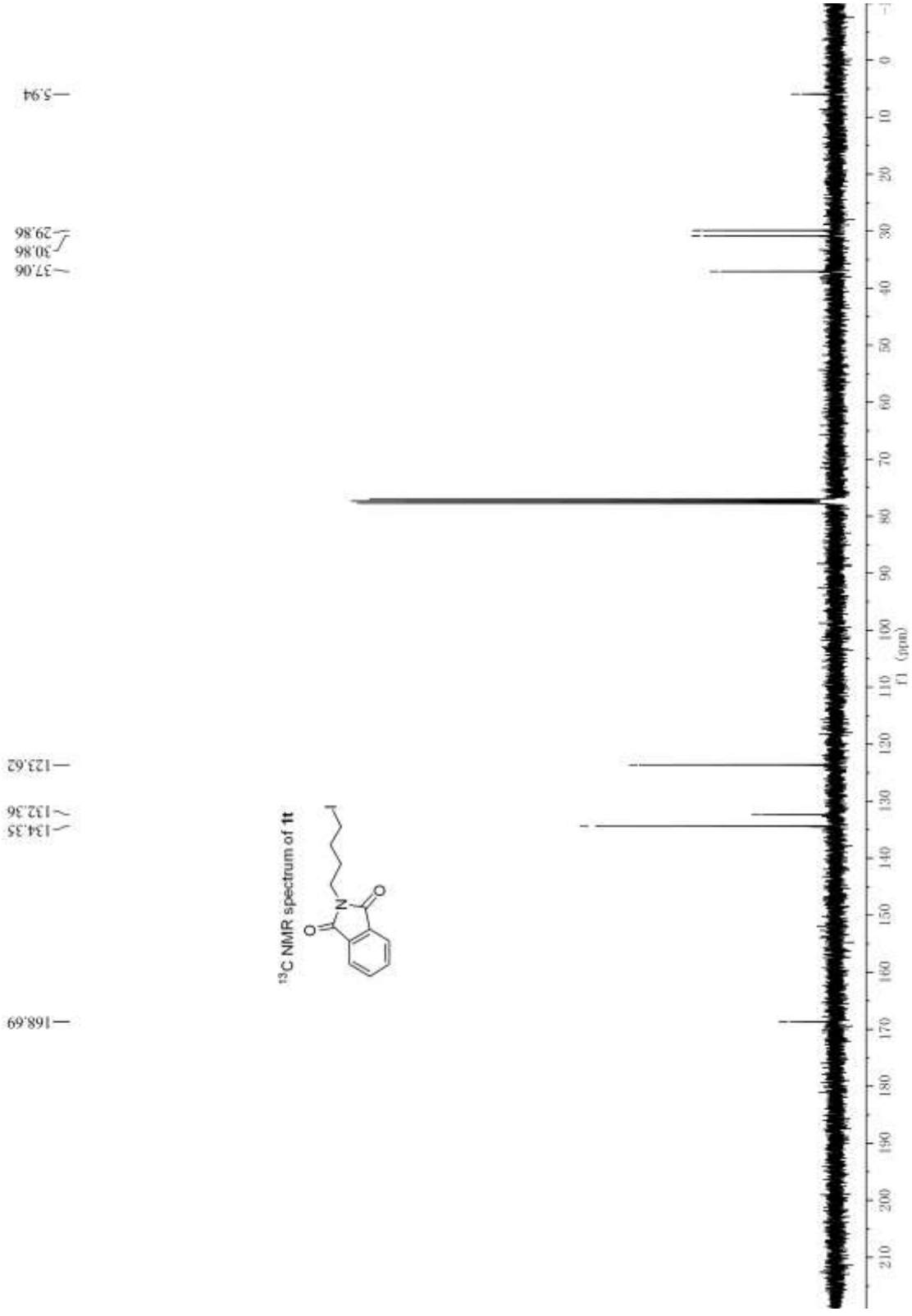
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1s**



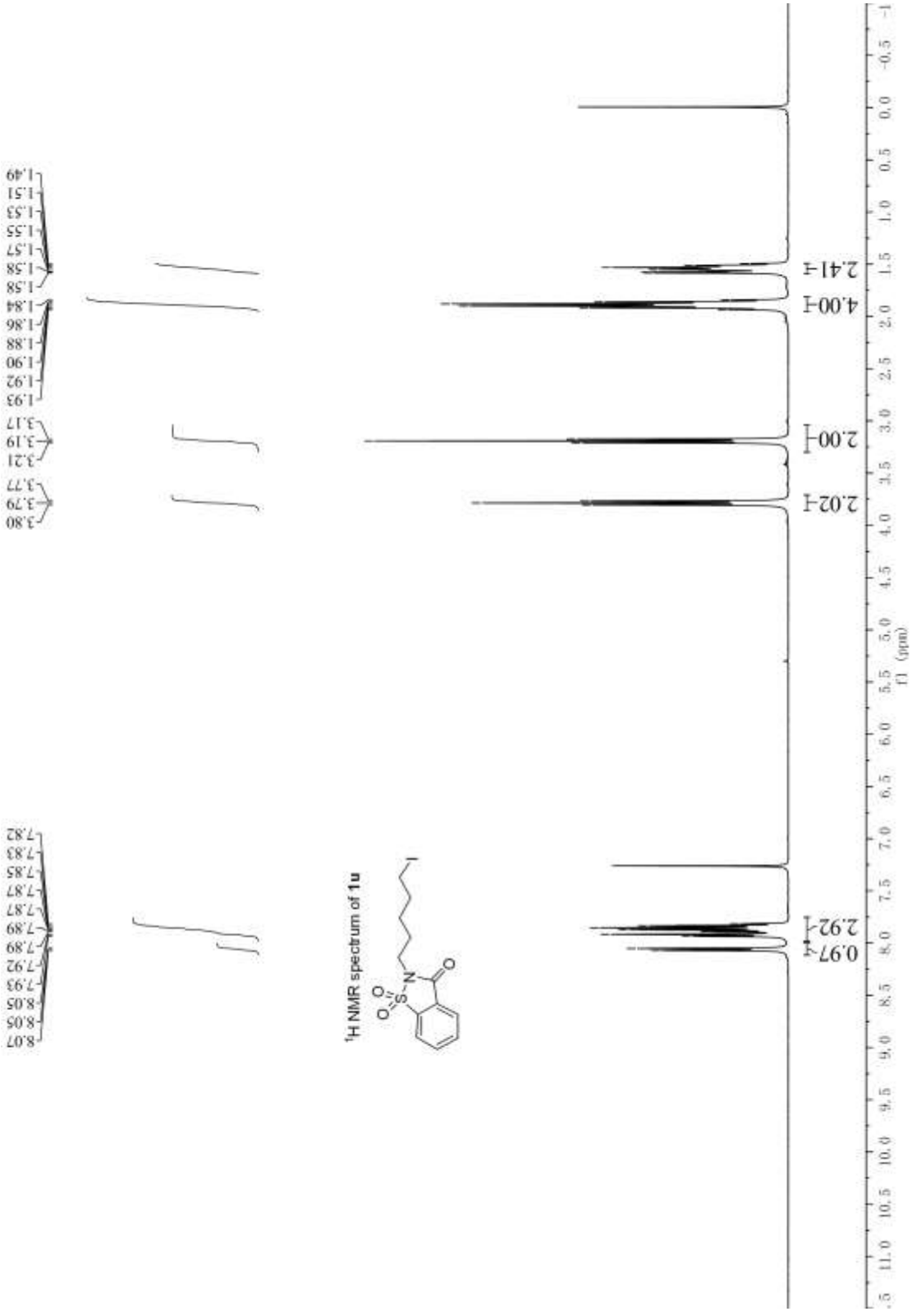
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1s**



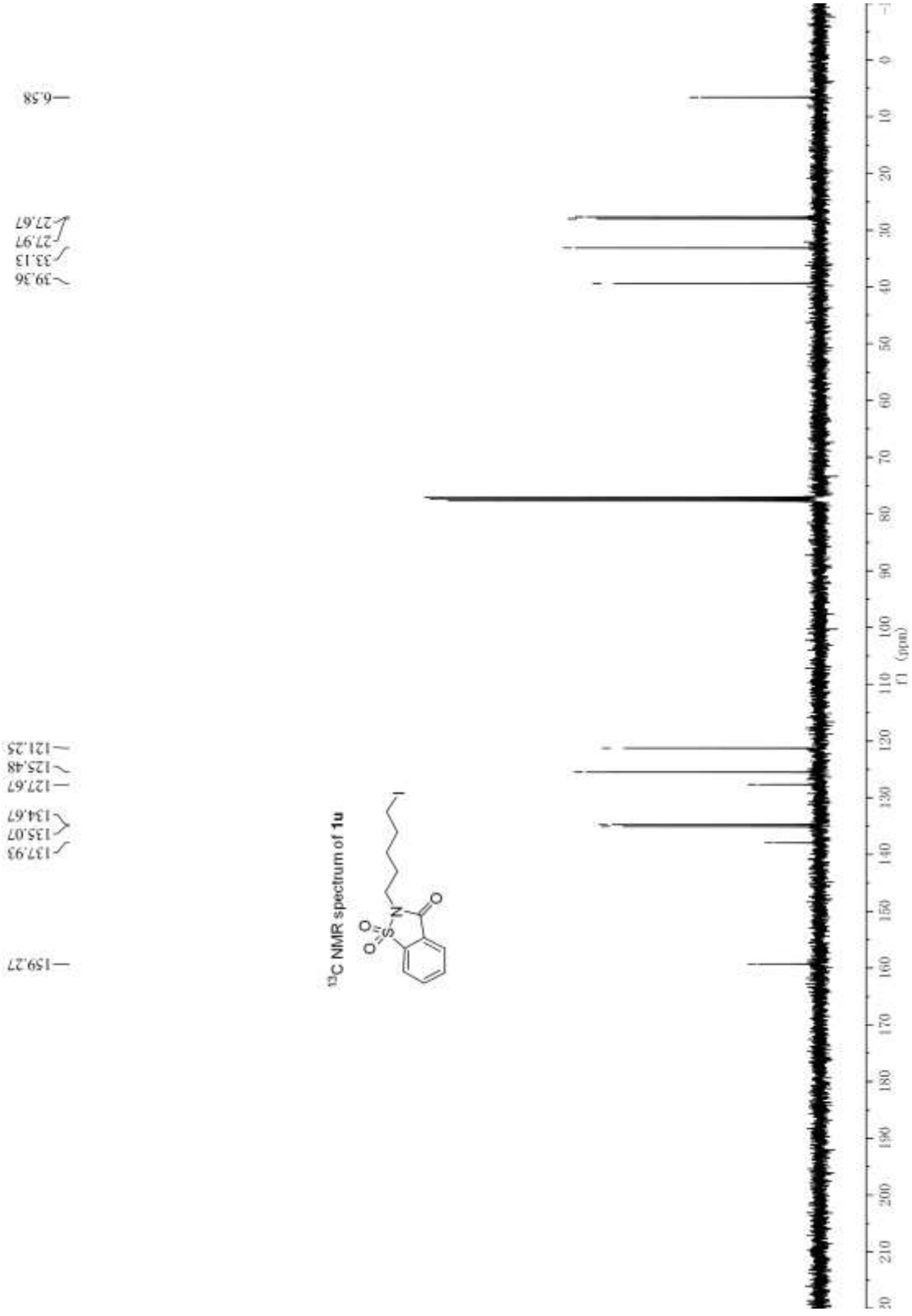
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1t**



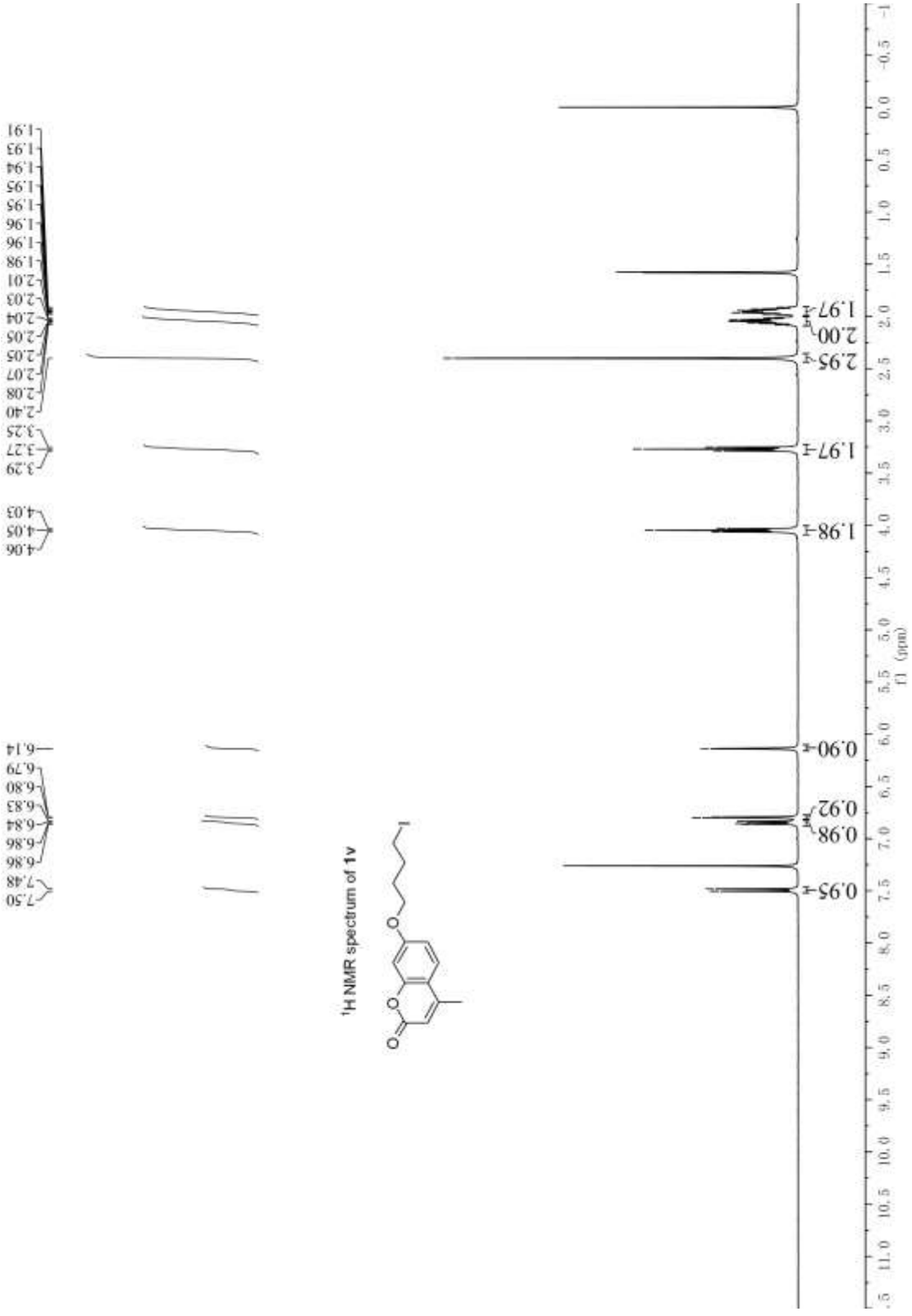
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1t**



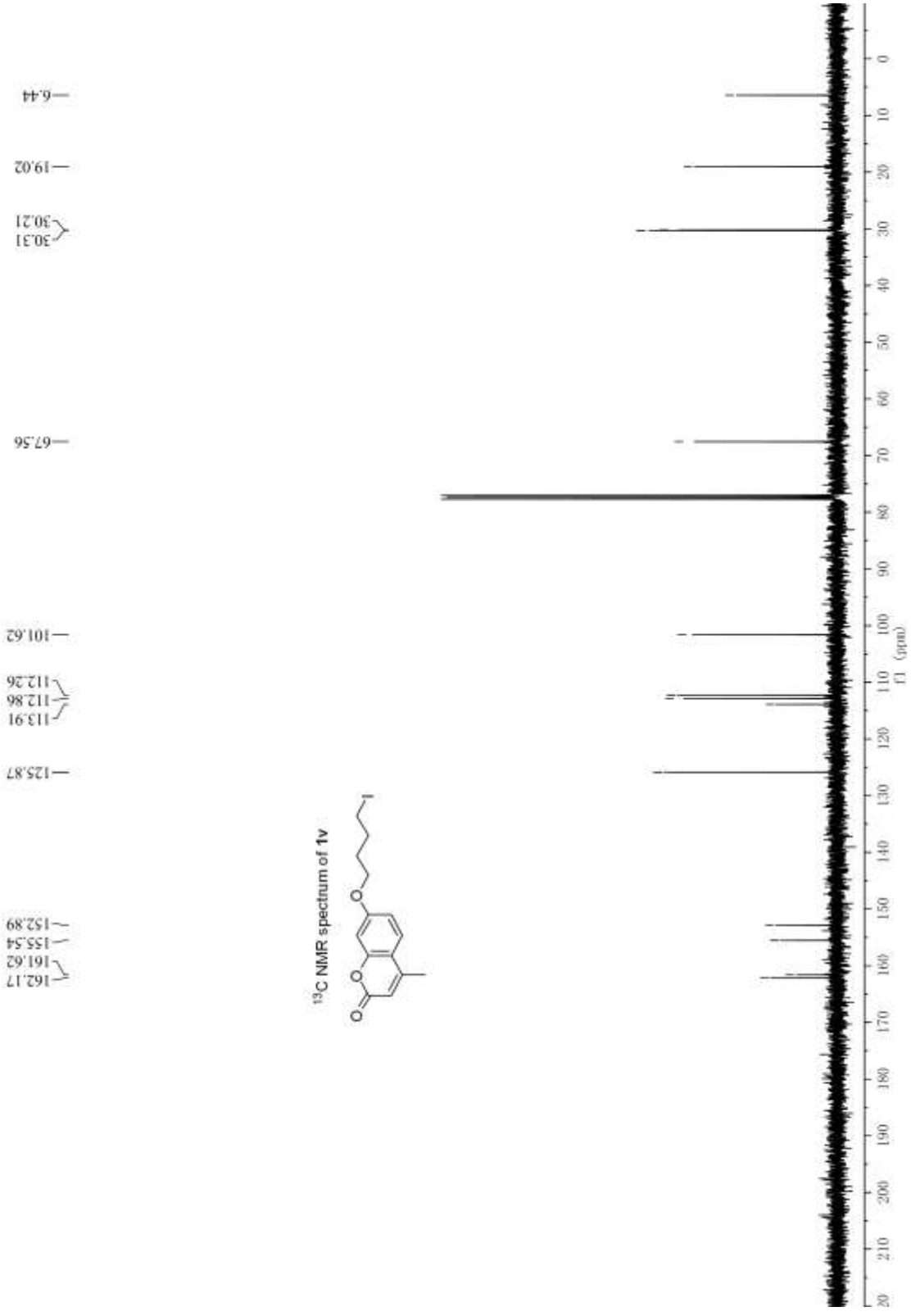
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1u**



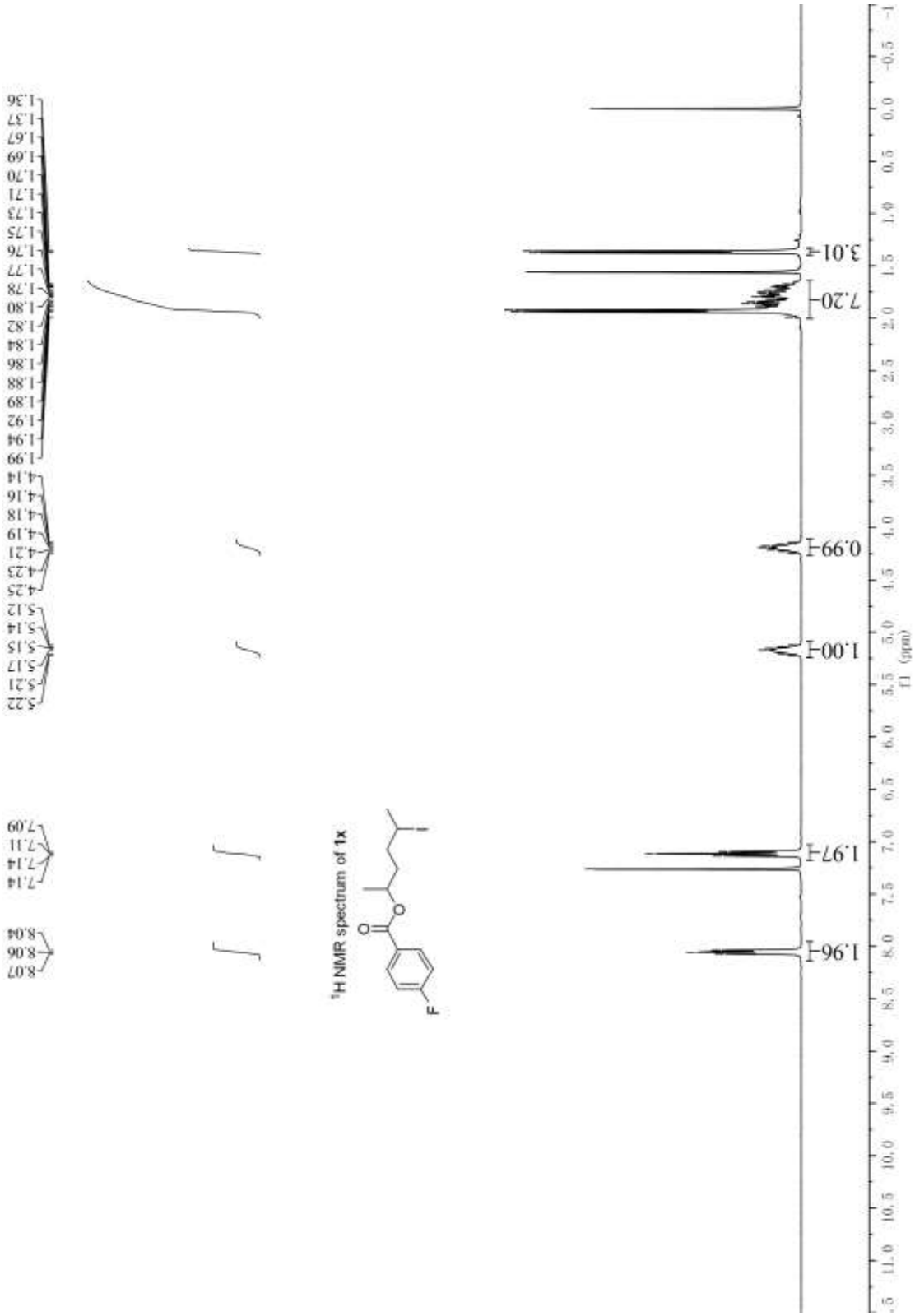
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1u**



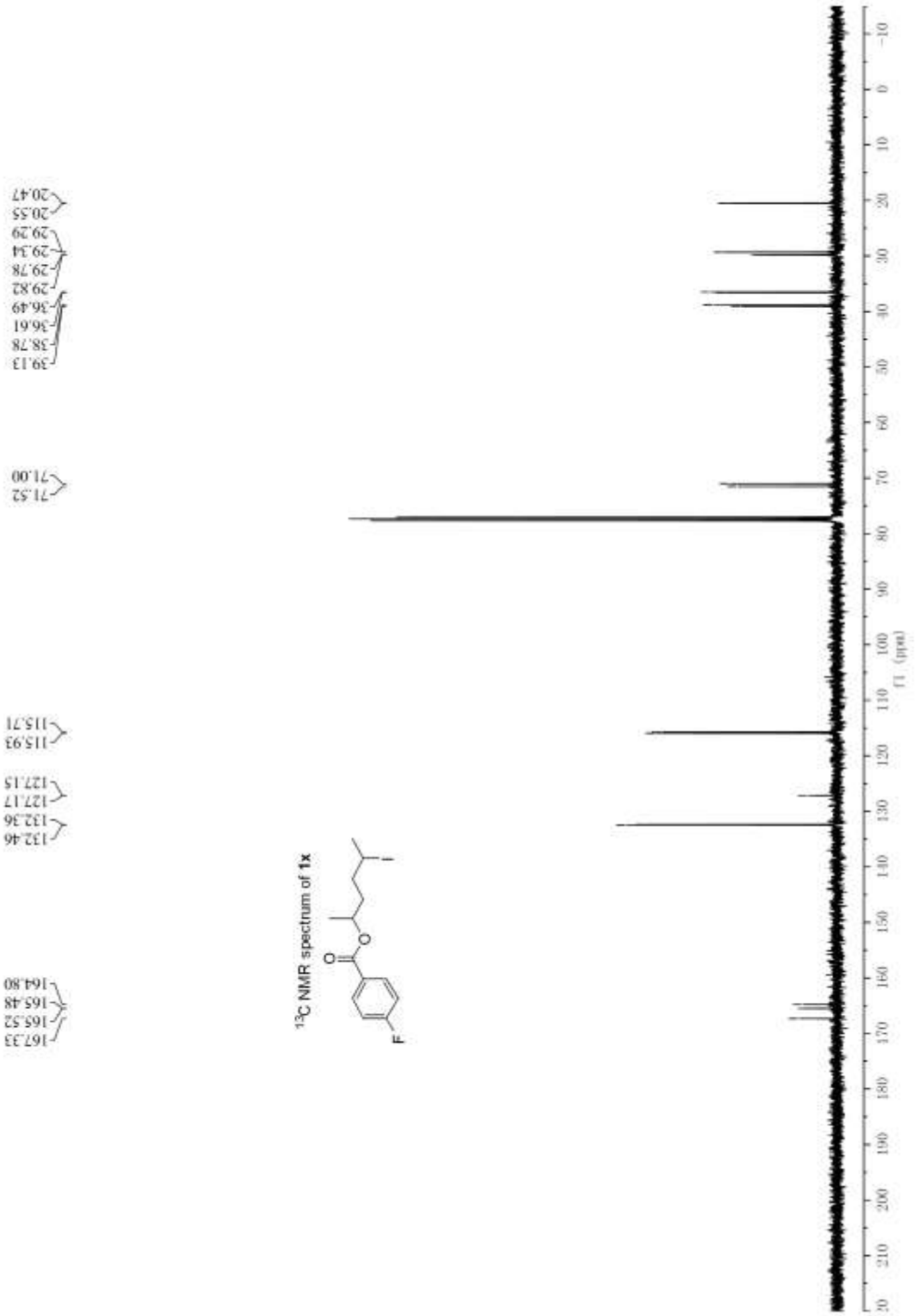
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1v**



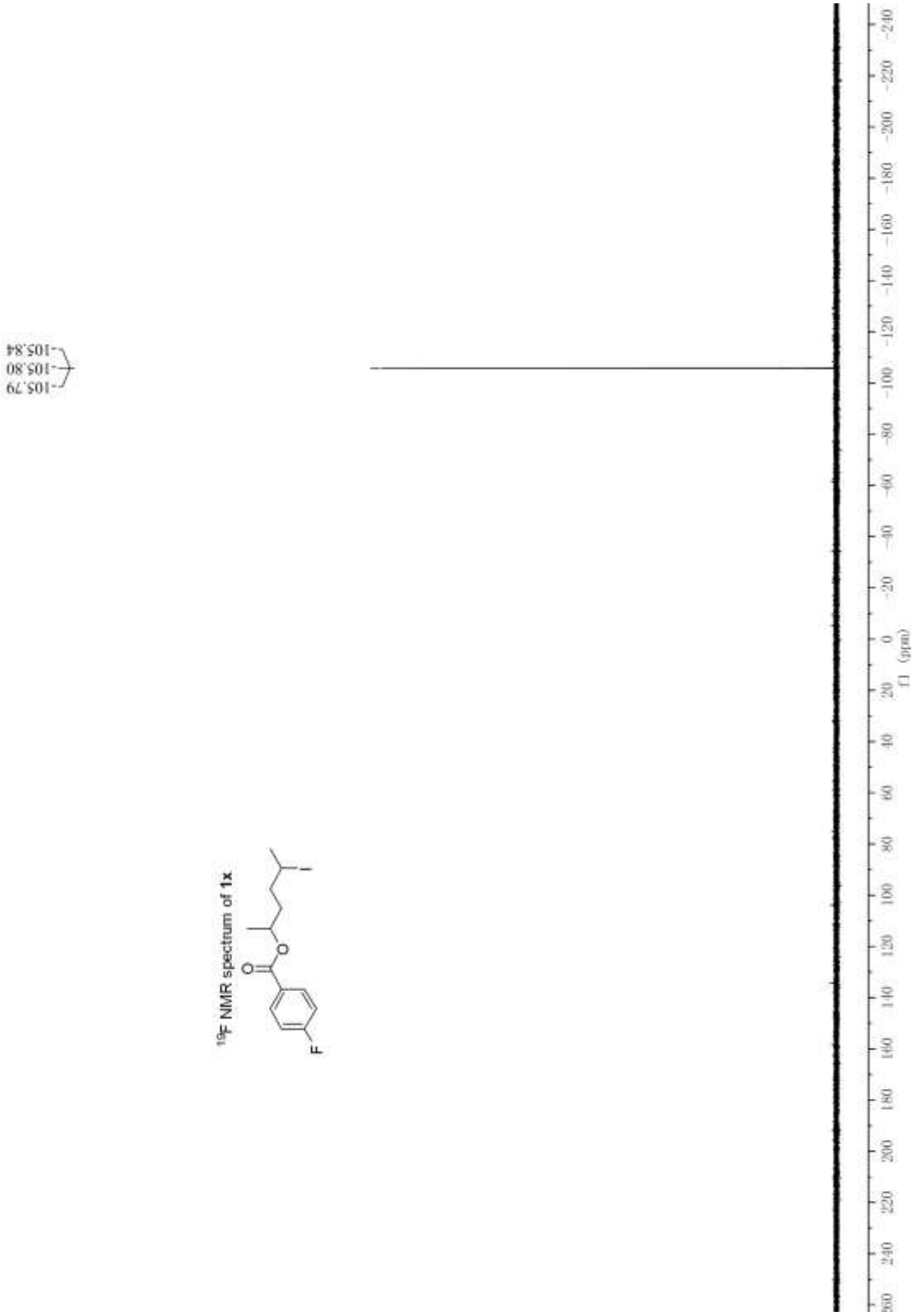
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1v**



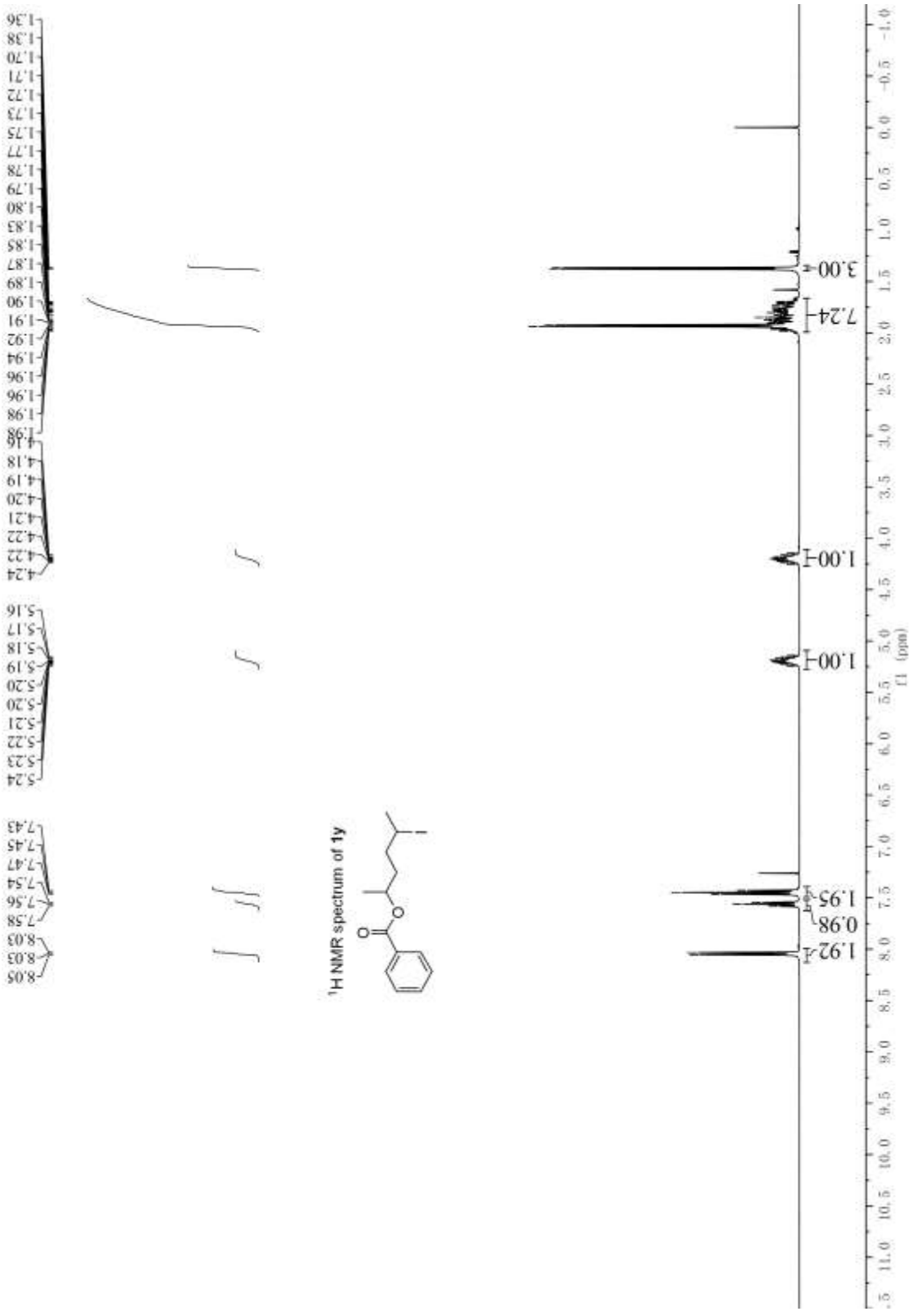
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1x**



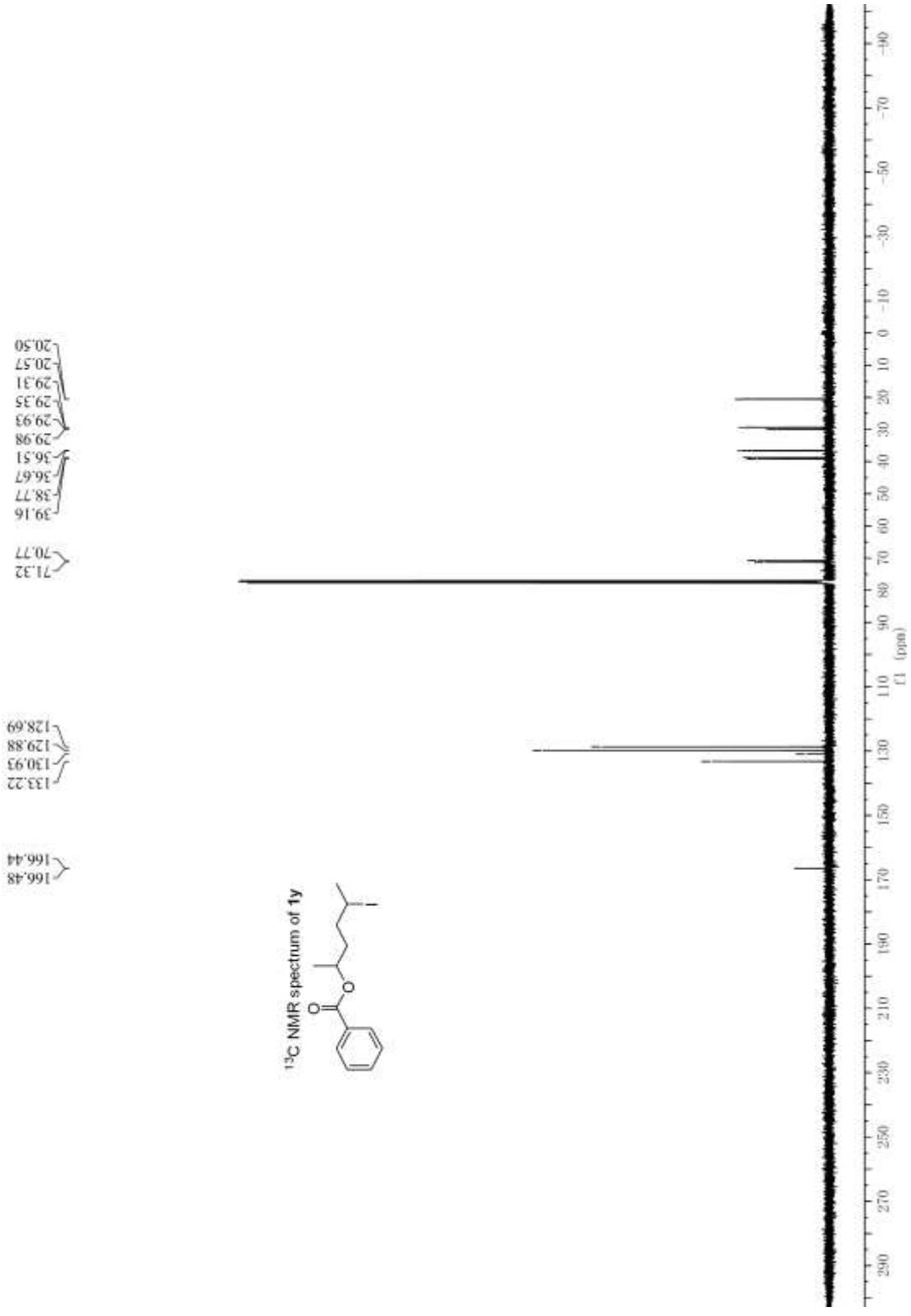
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1x**



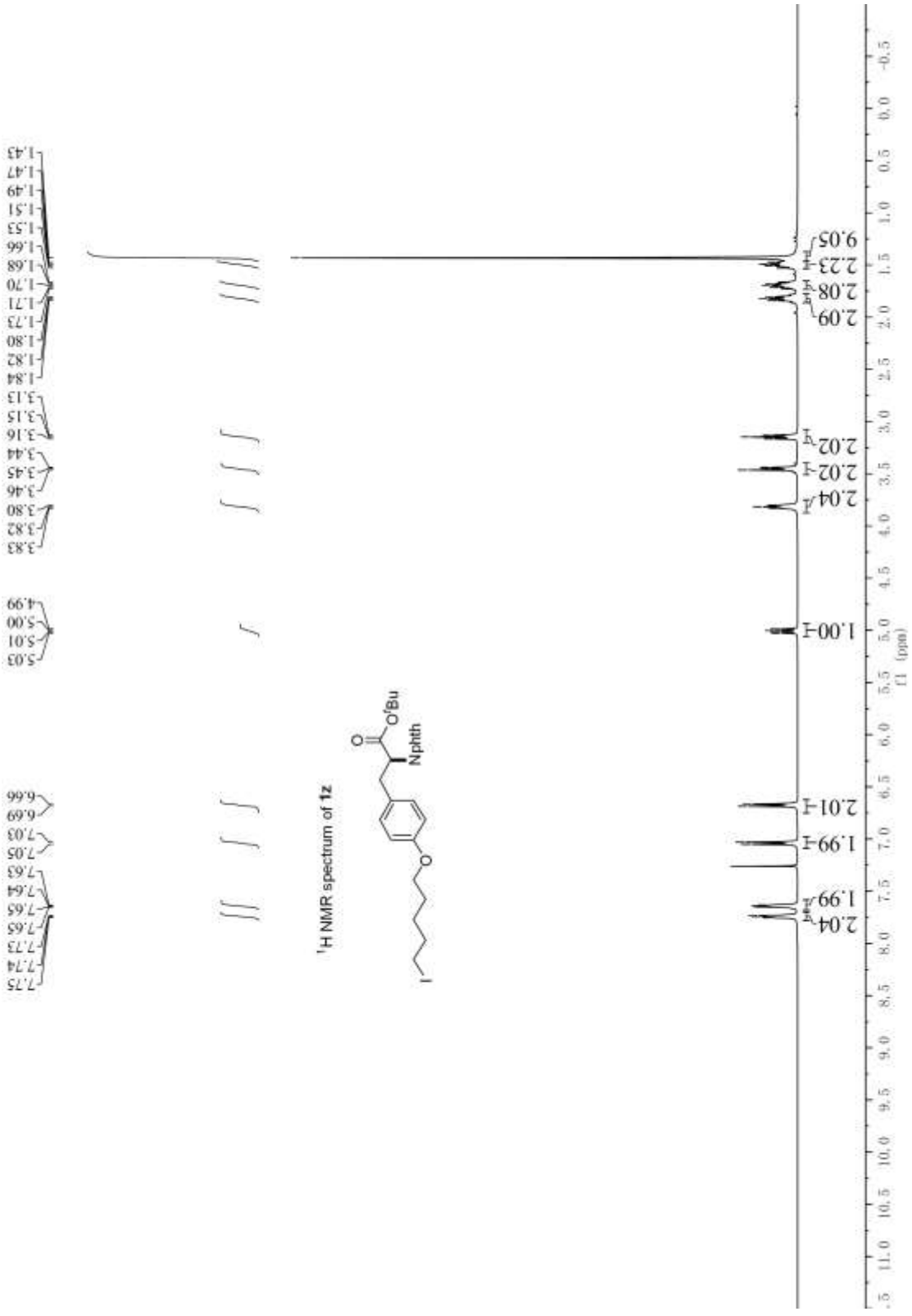
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **1x**



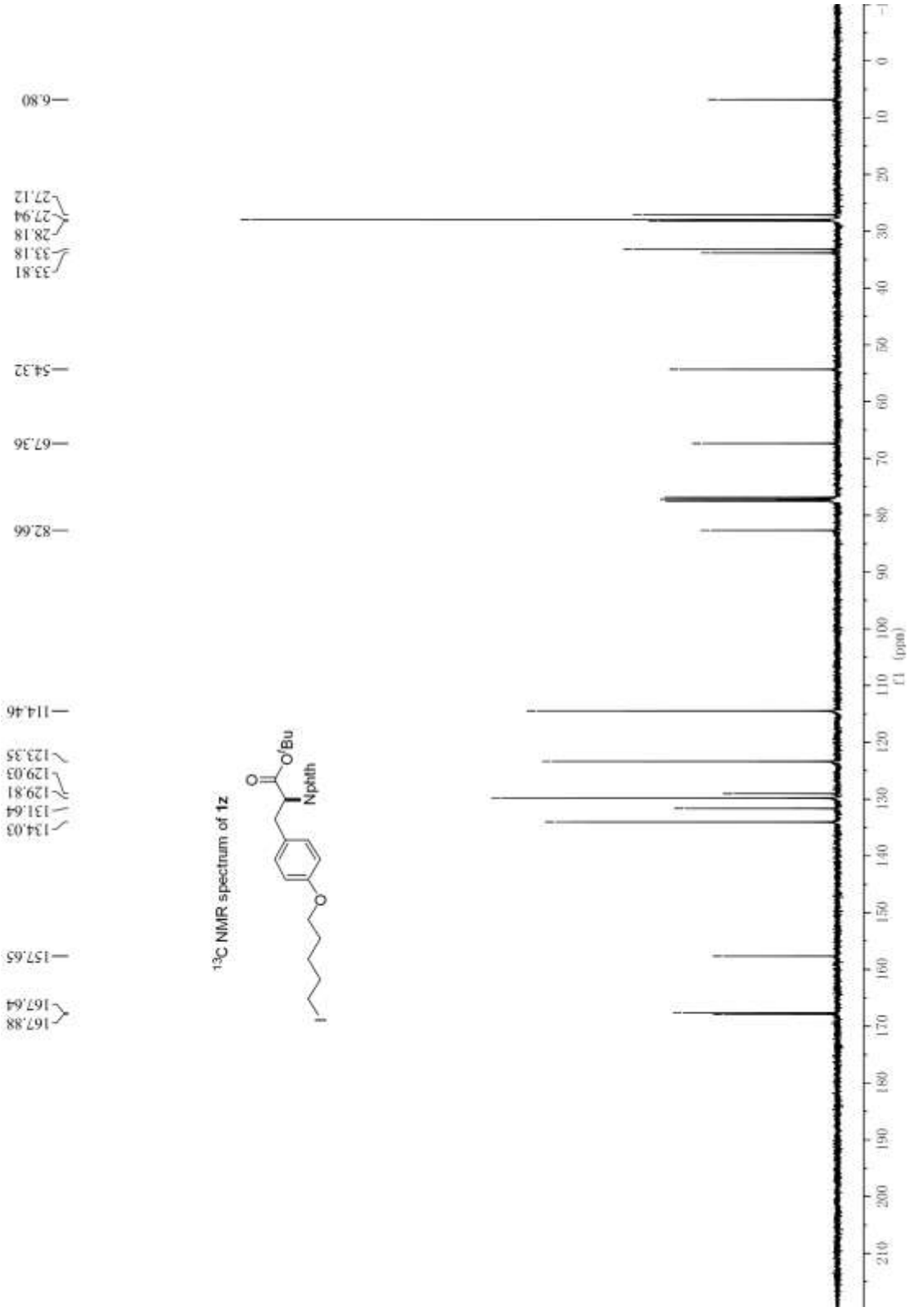
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1y**



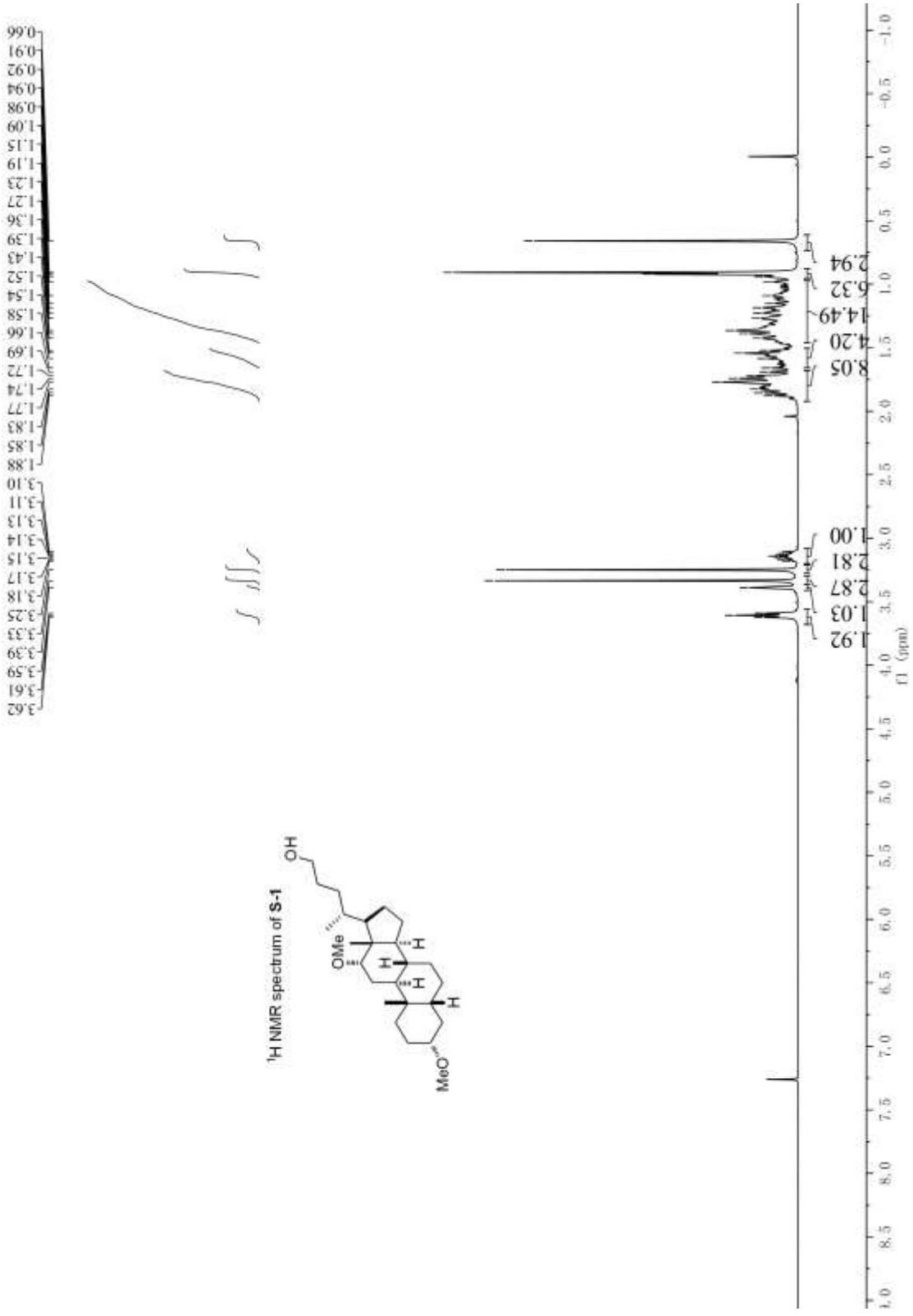
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1y**



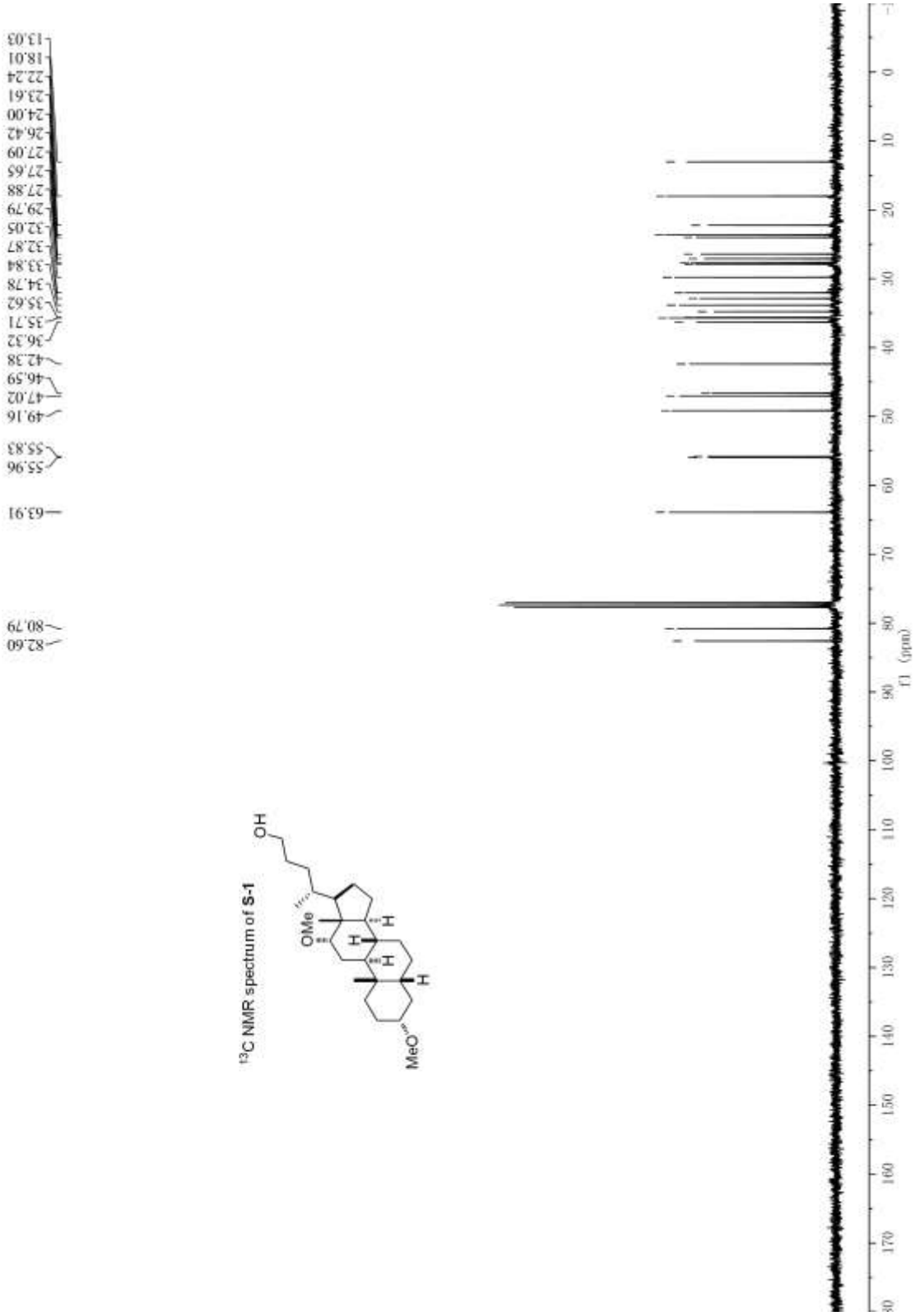
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1z**



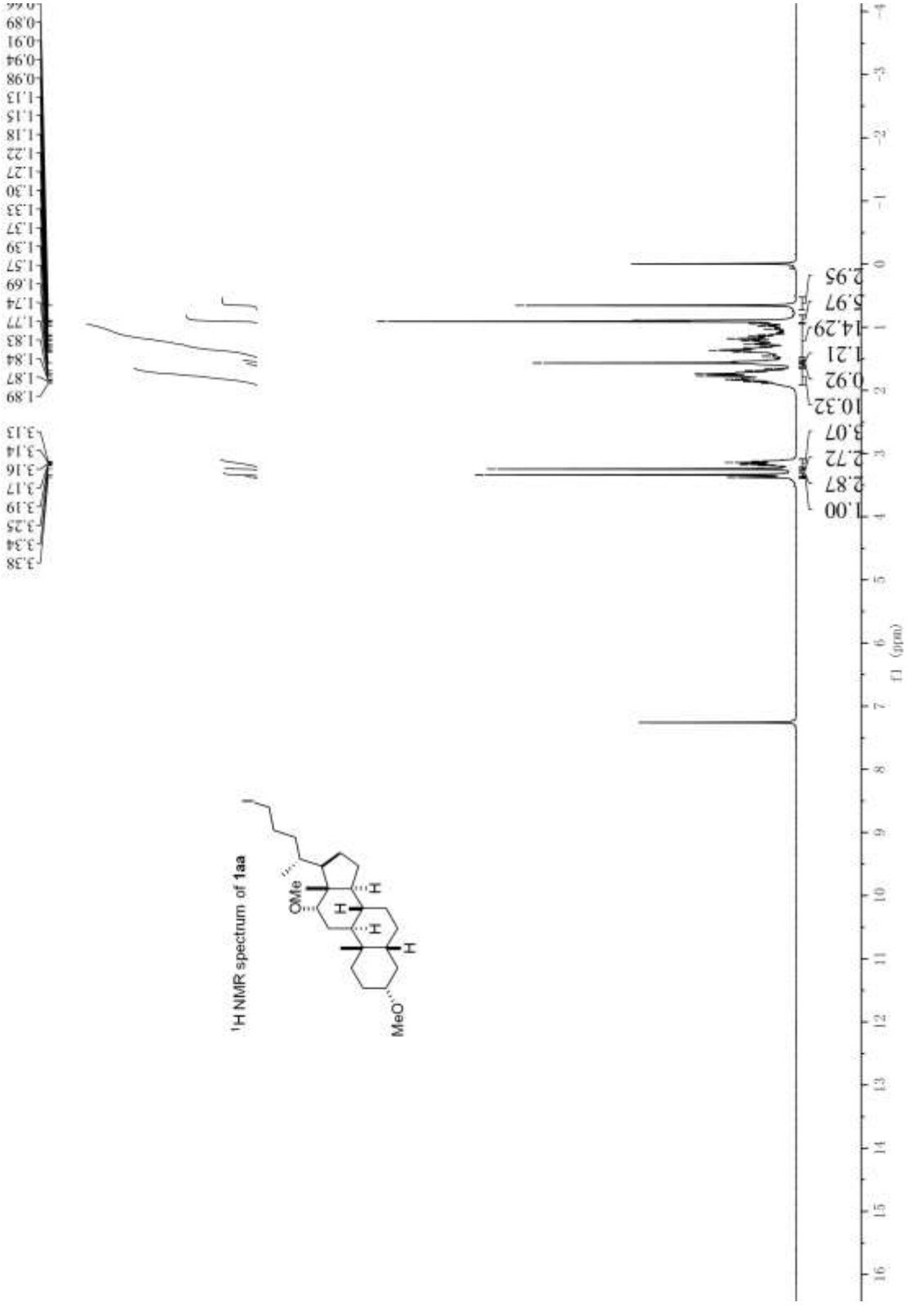
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1z**



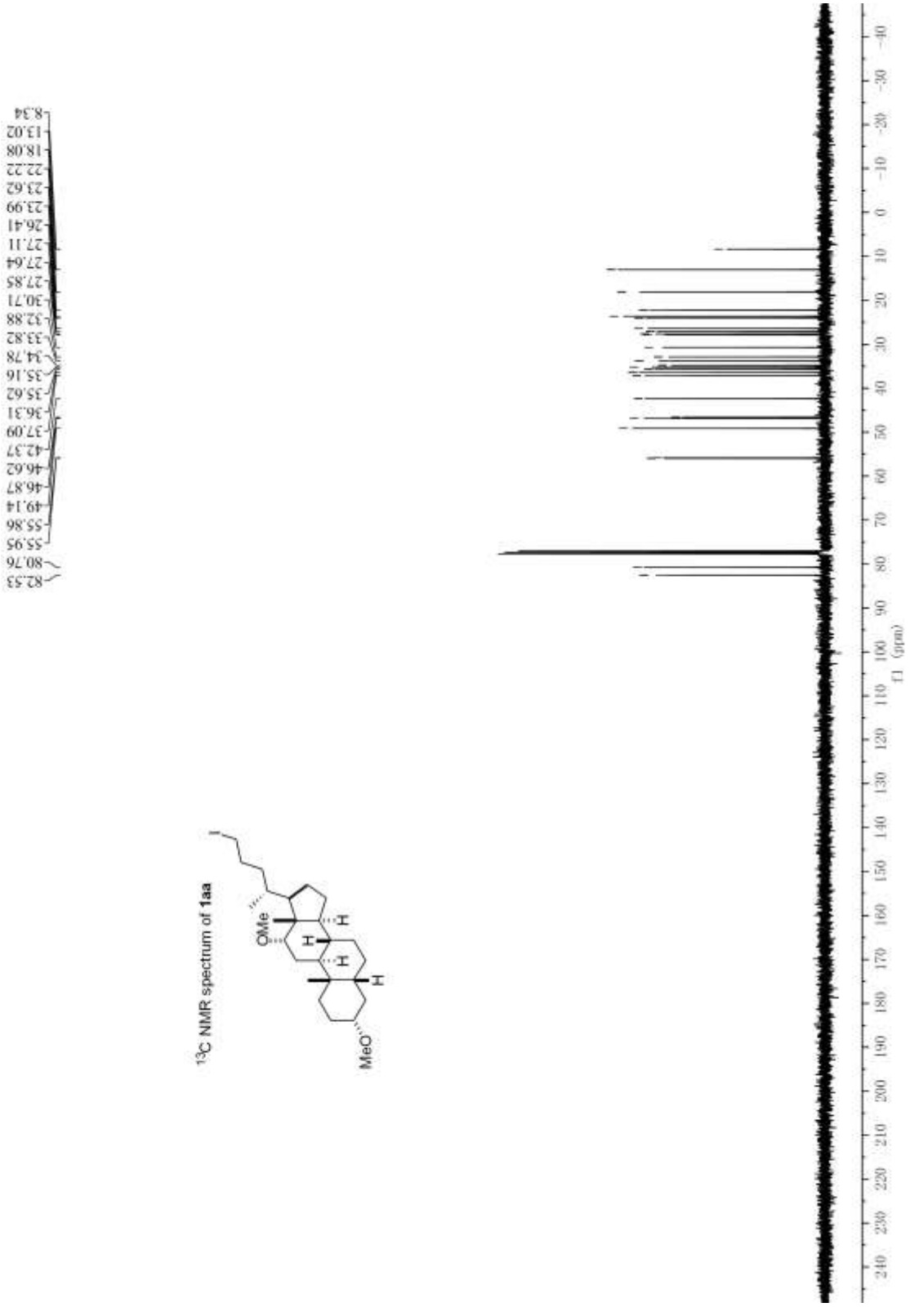
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-1**



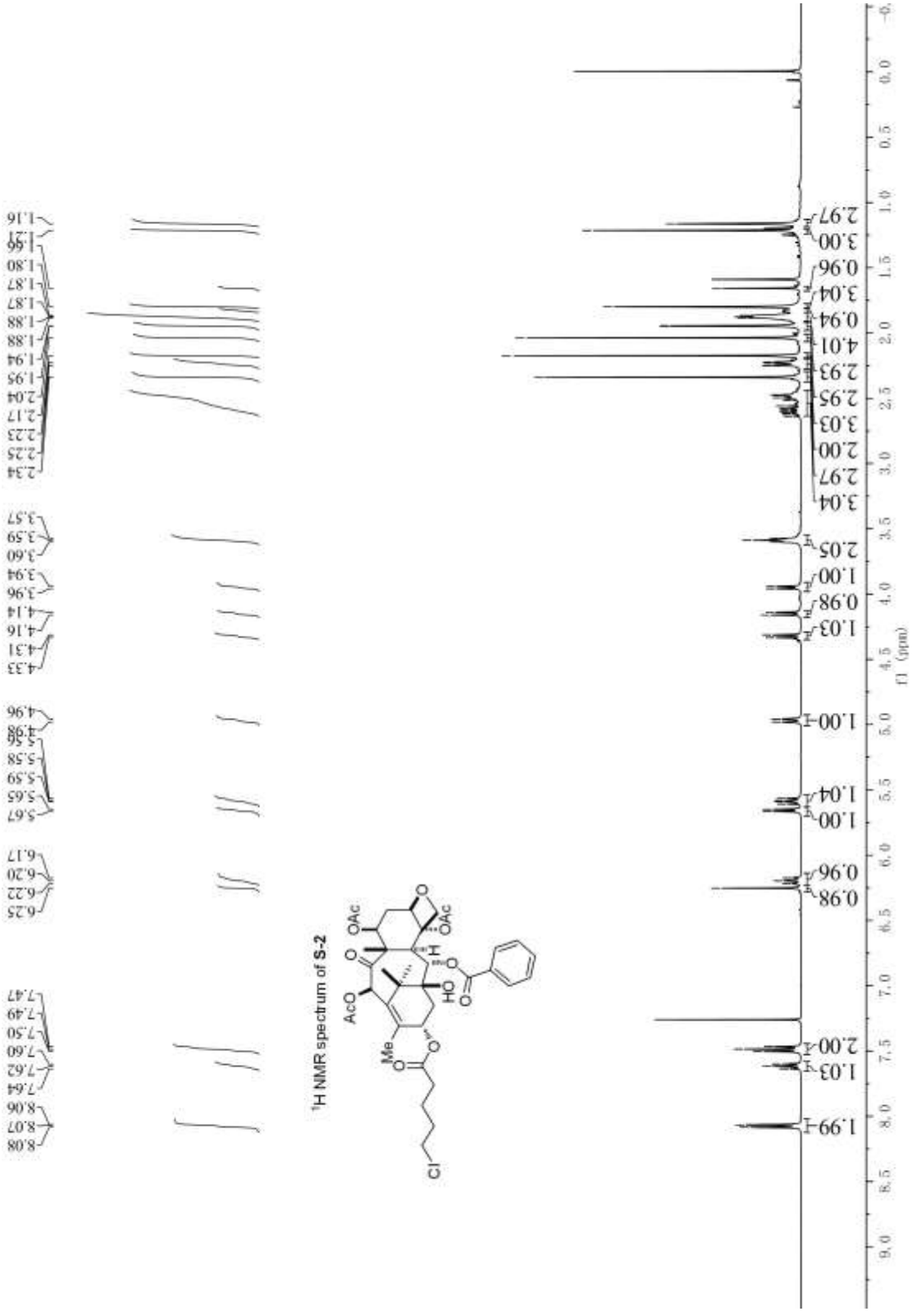
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-1**



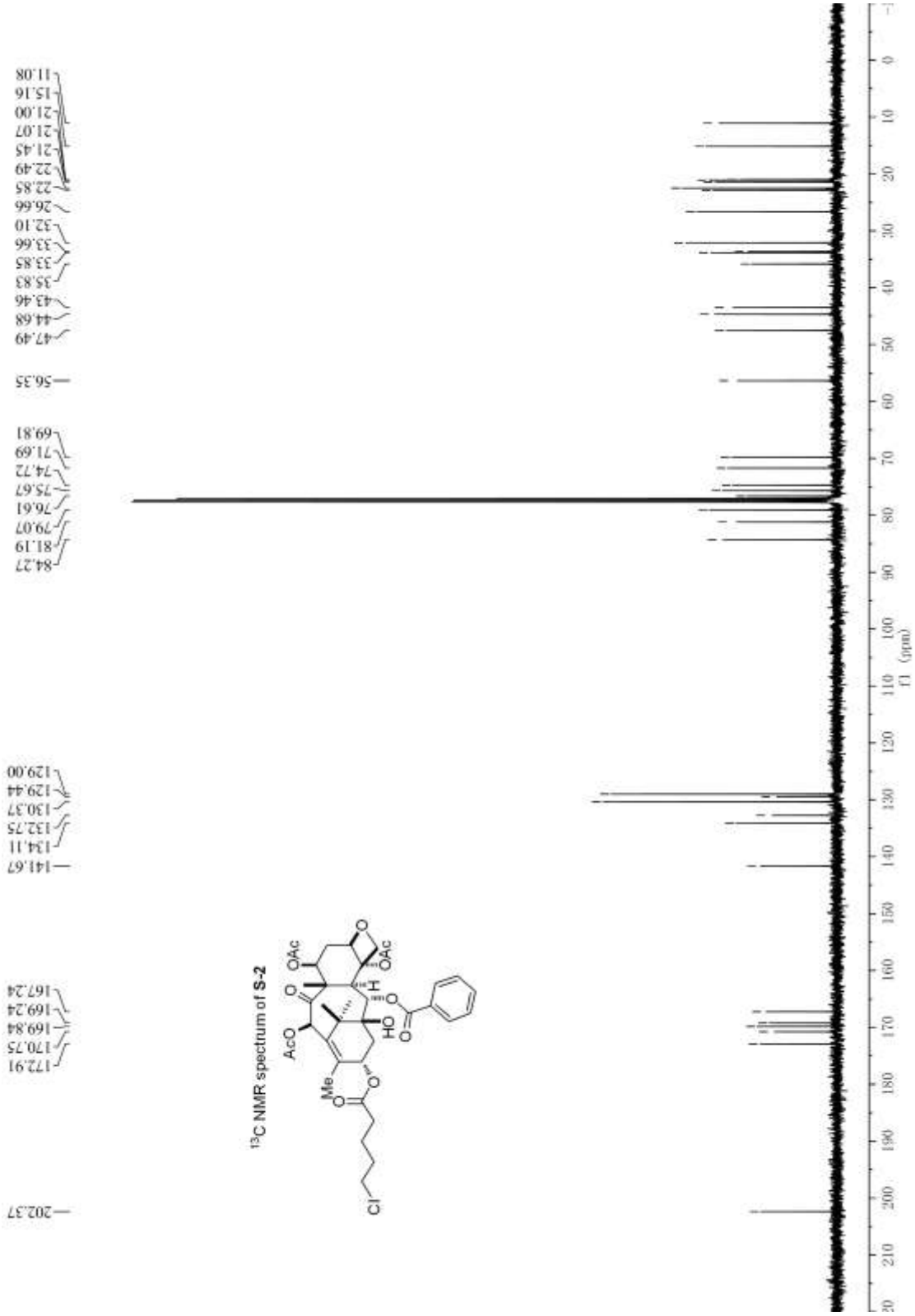
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1aa**



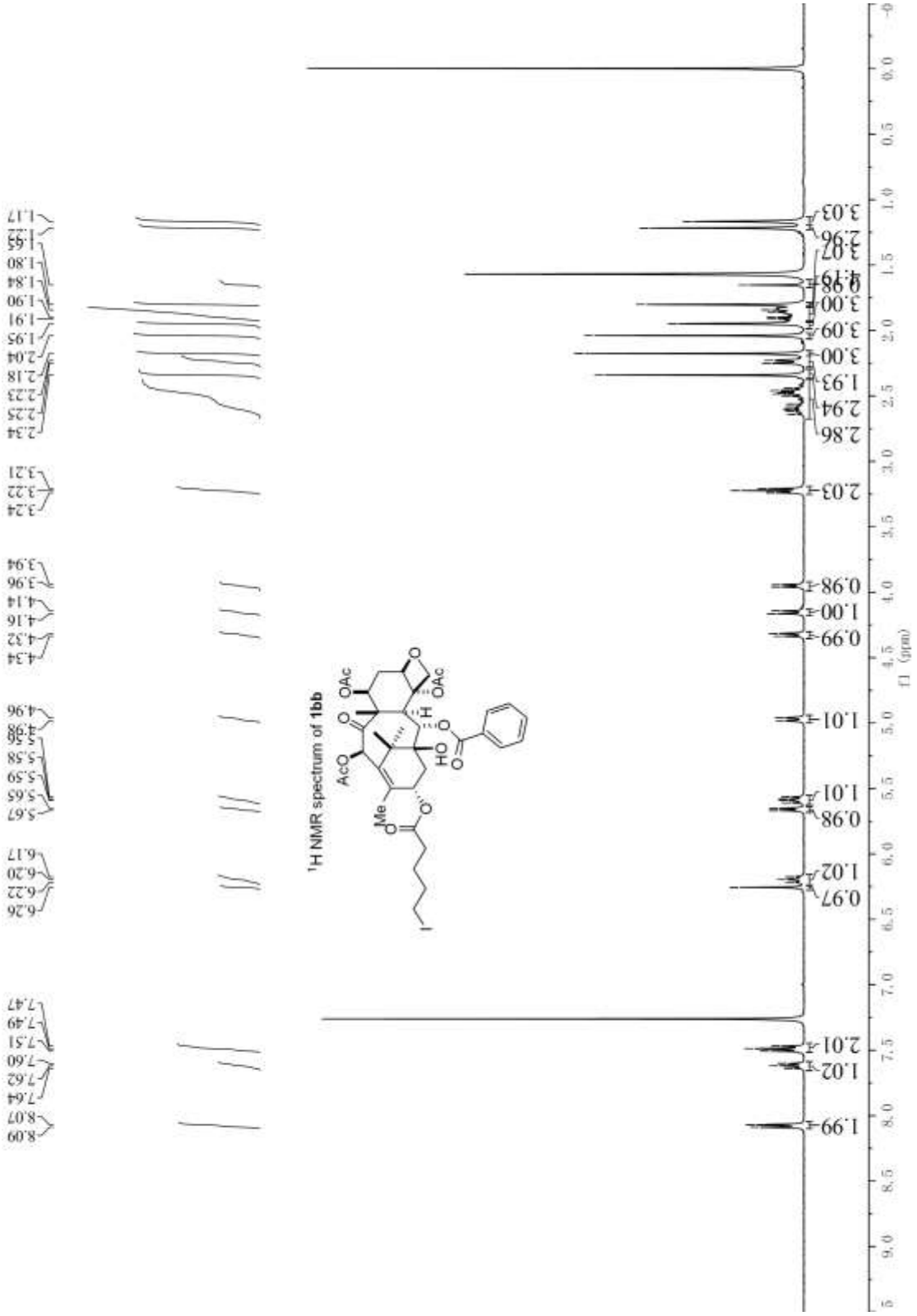
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1aa**



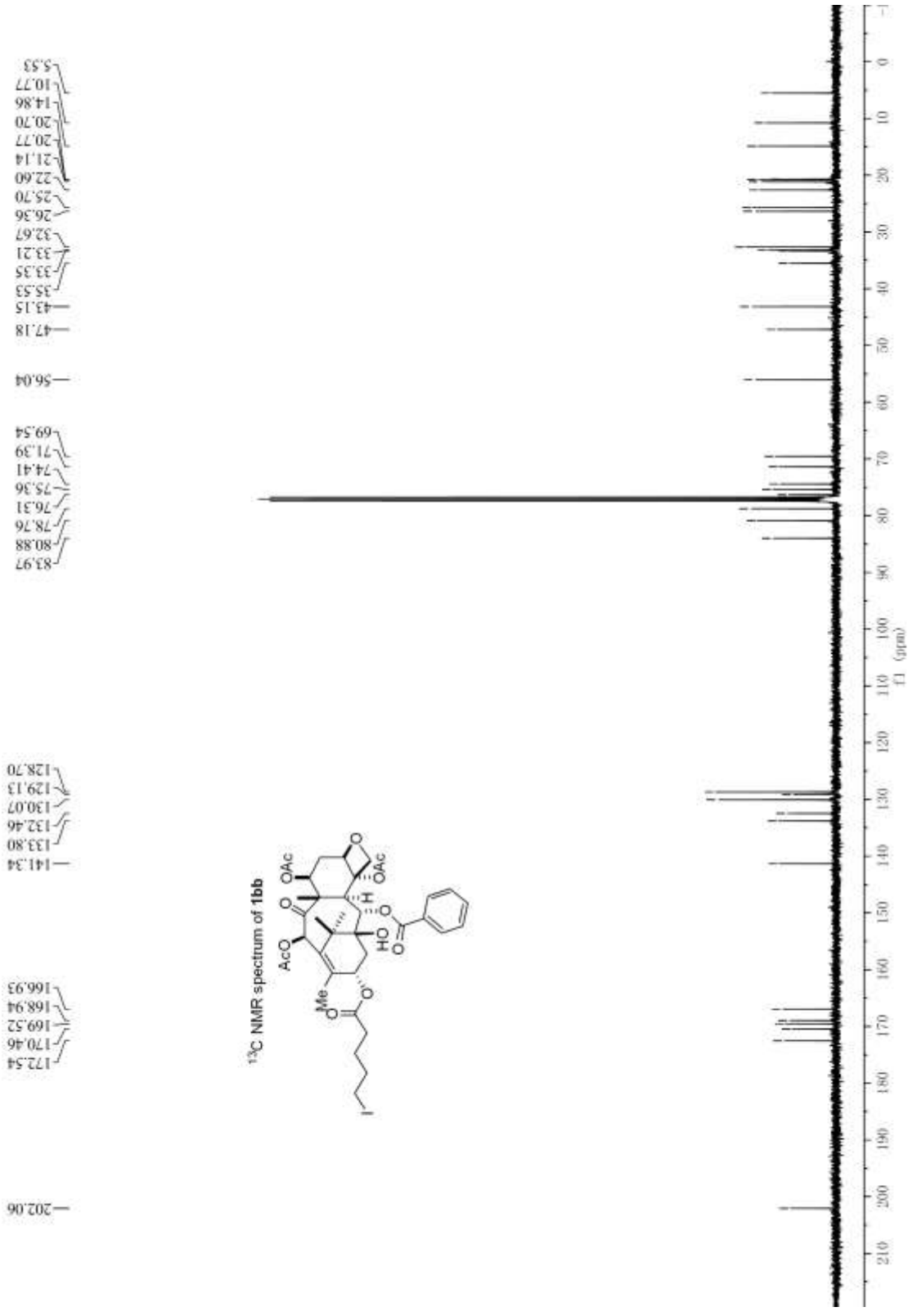
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-2**



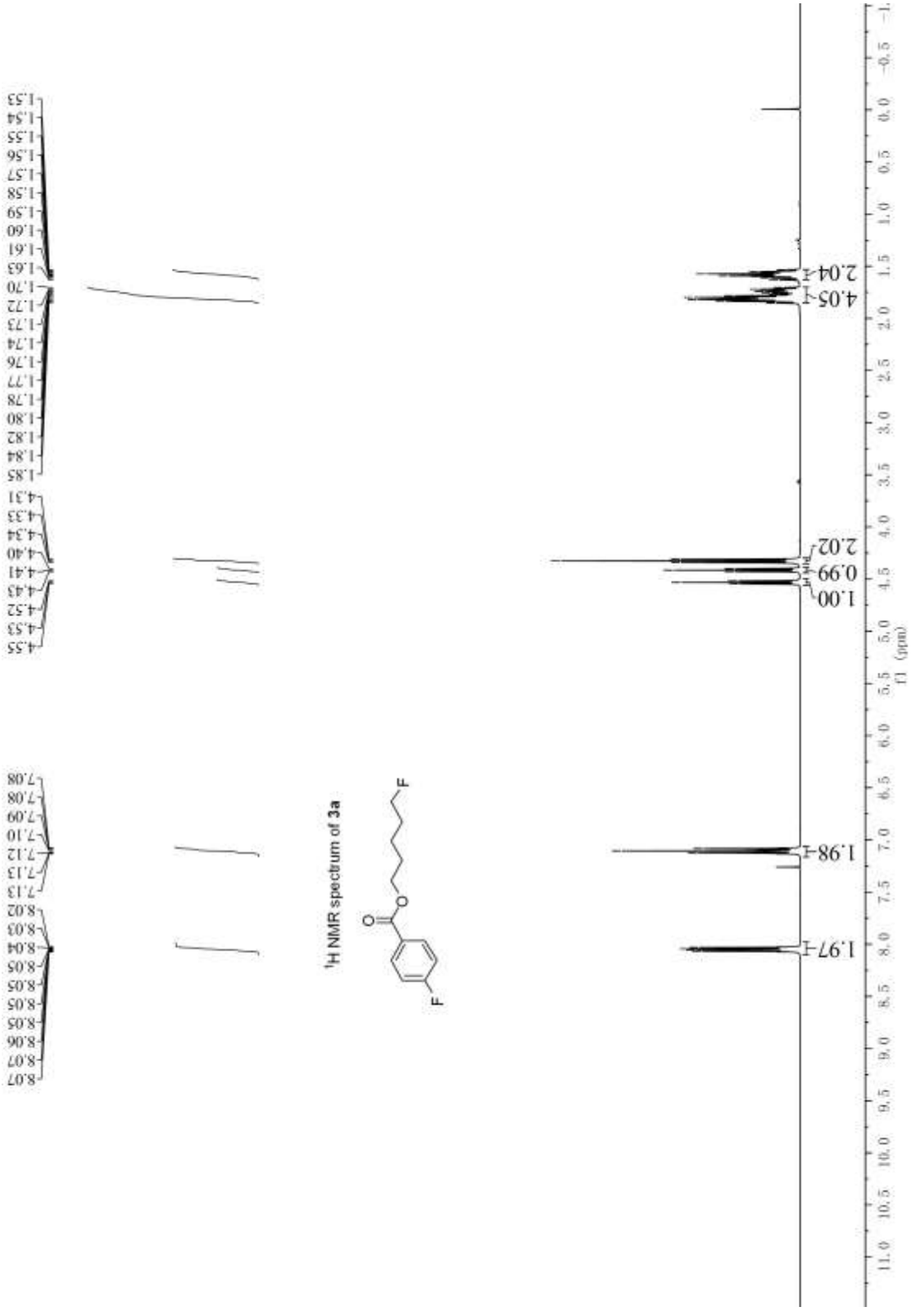
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-2**



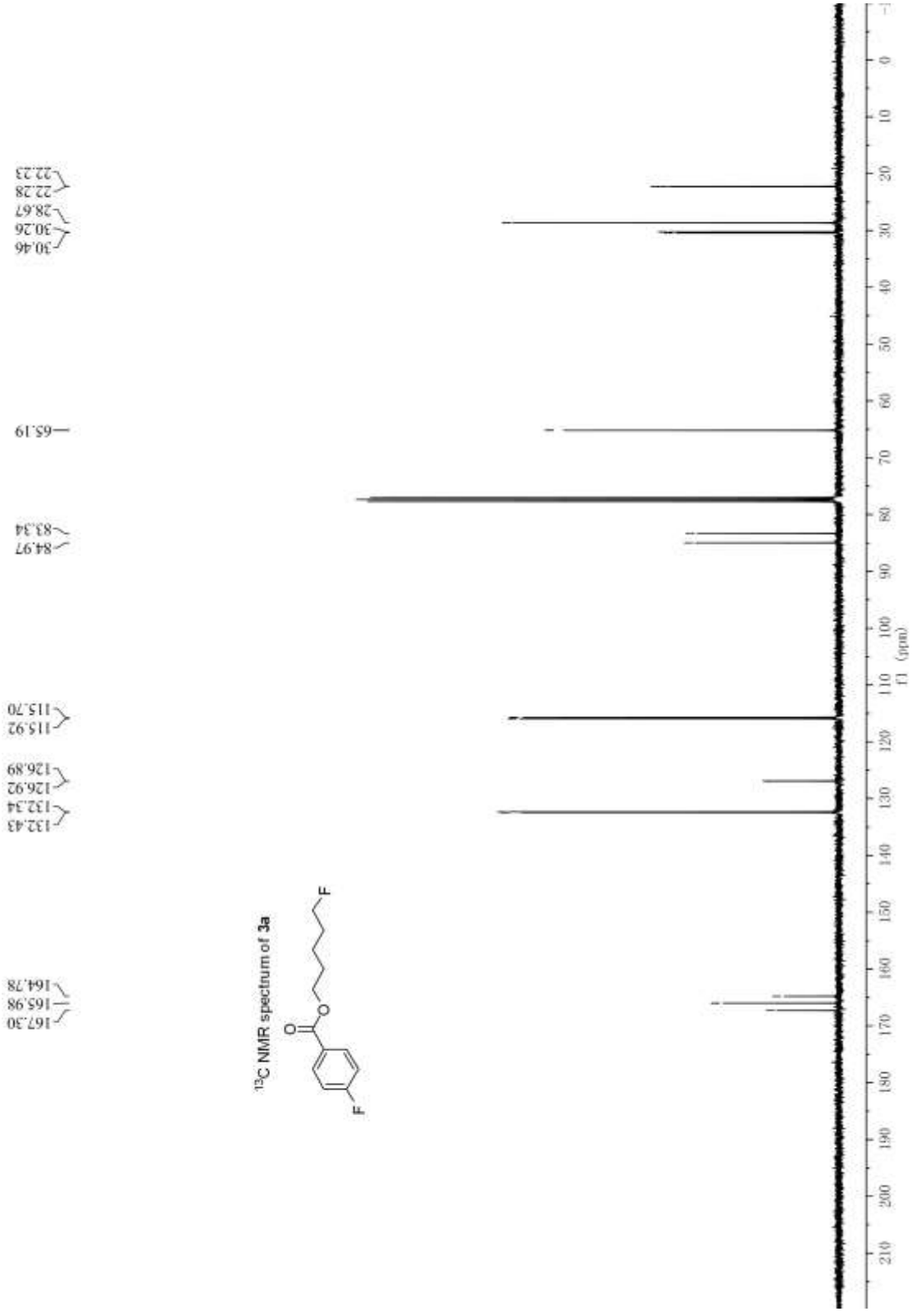
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1bb**



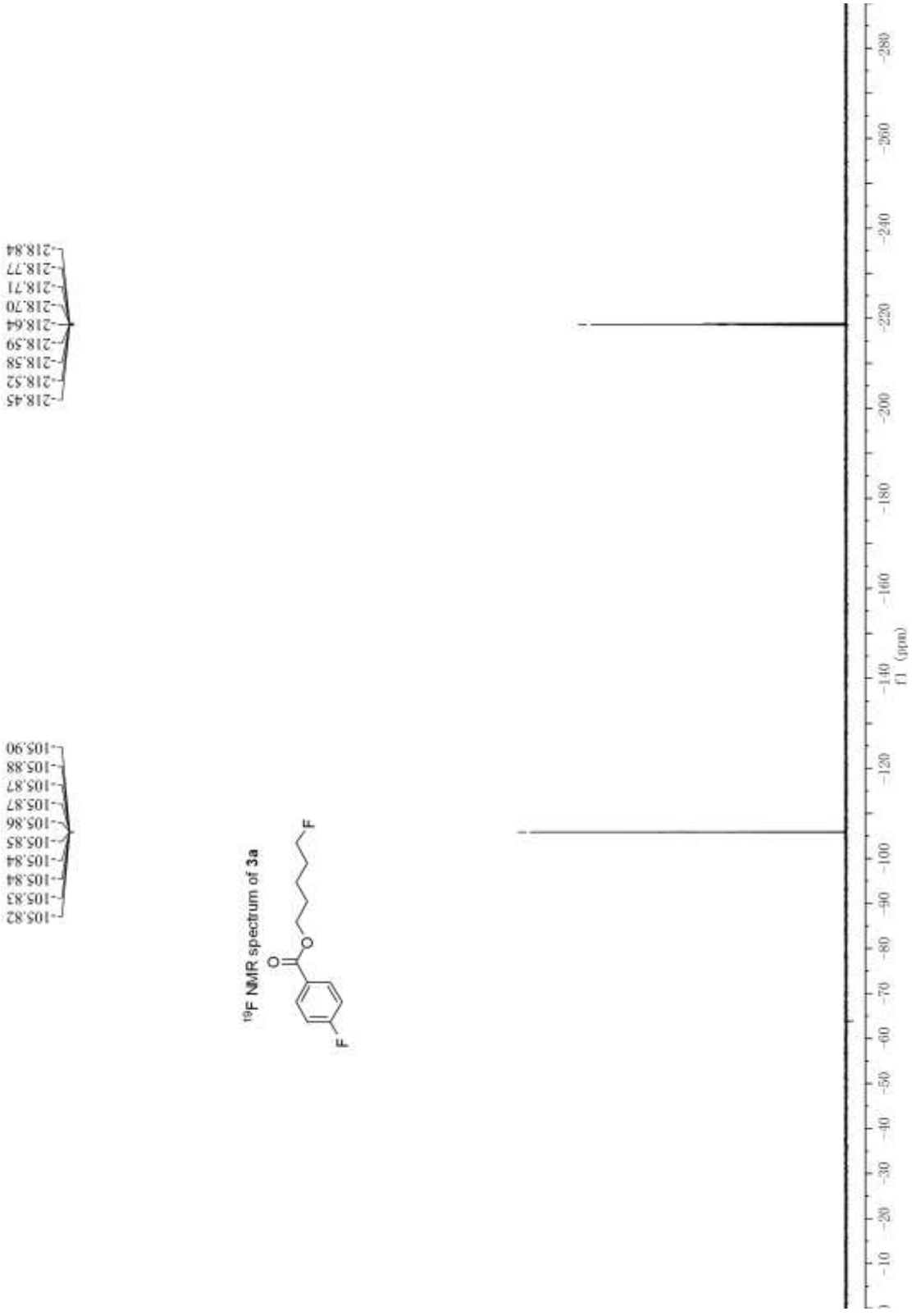
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1bb**



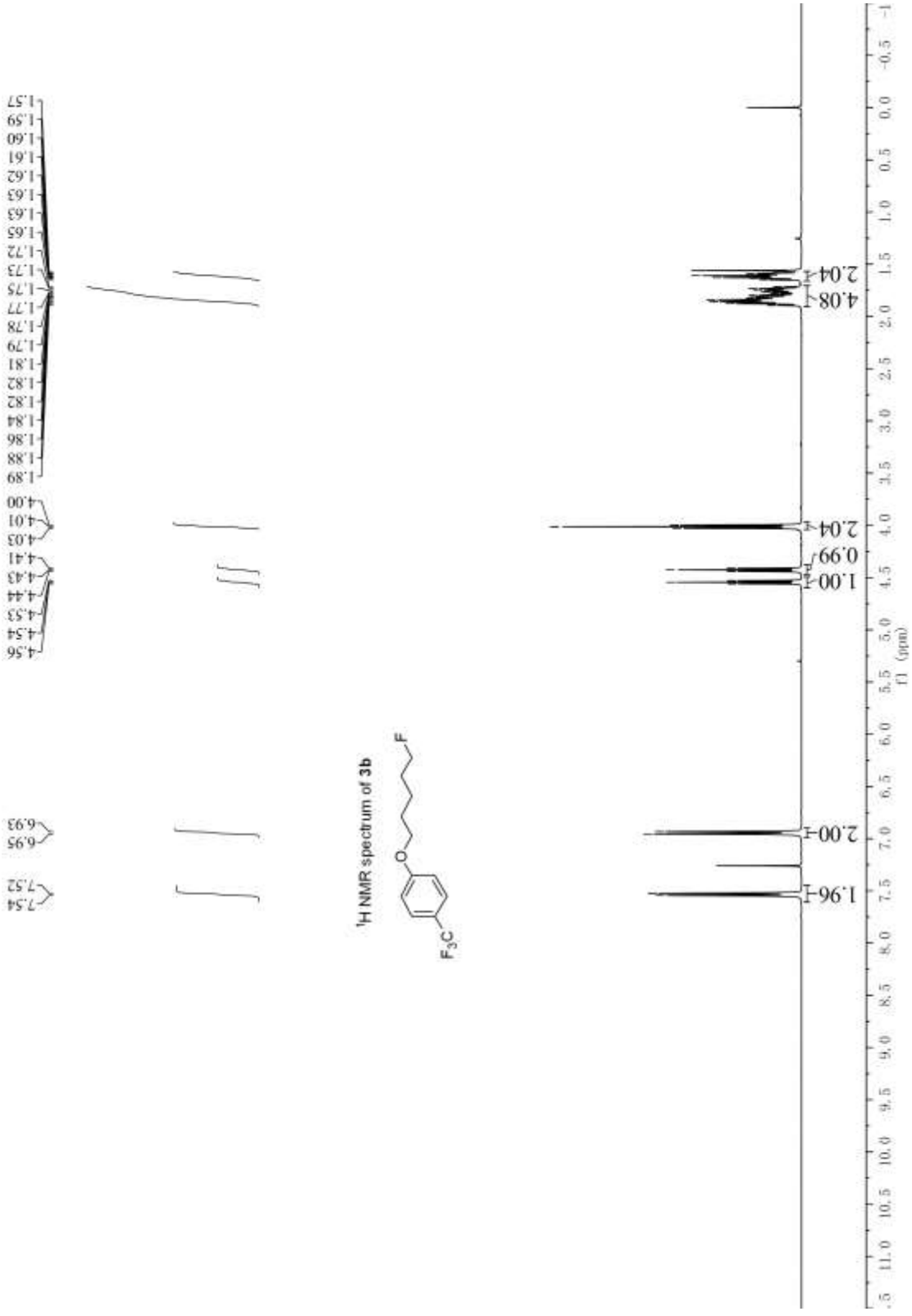
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



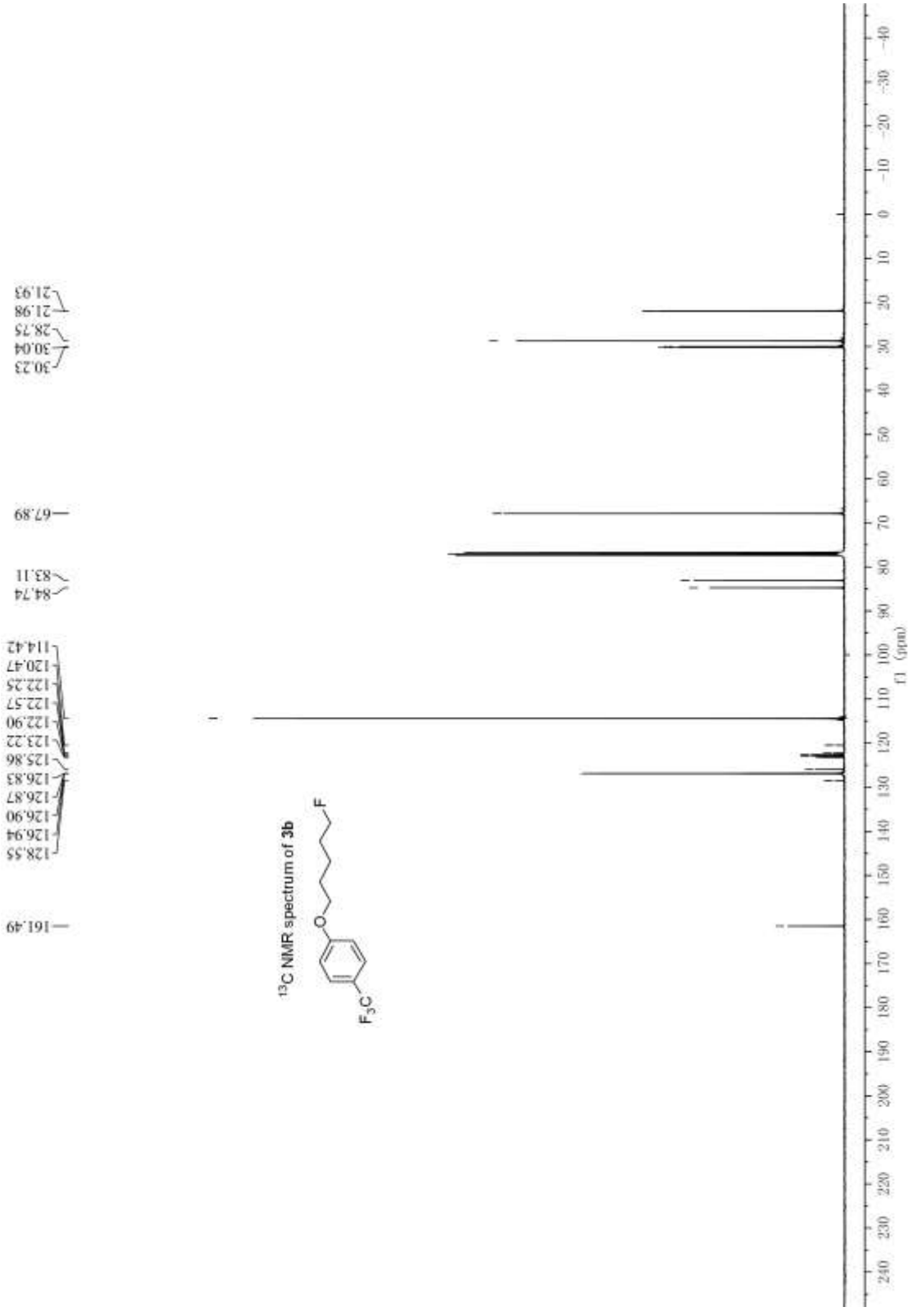
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3a**



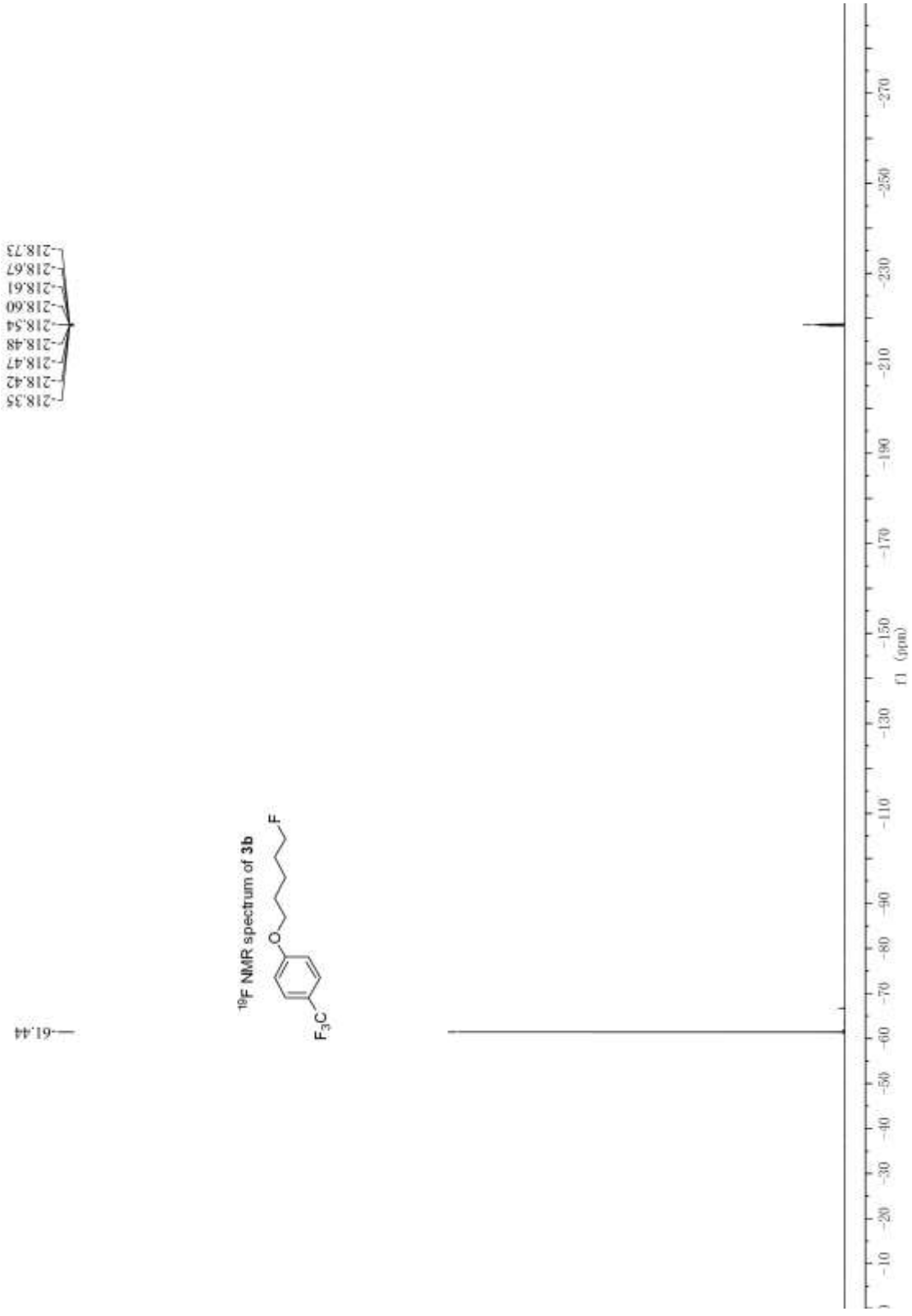
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3a**



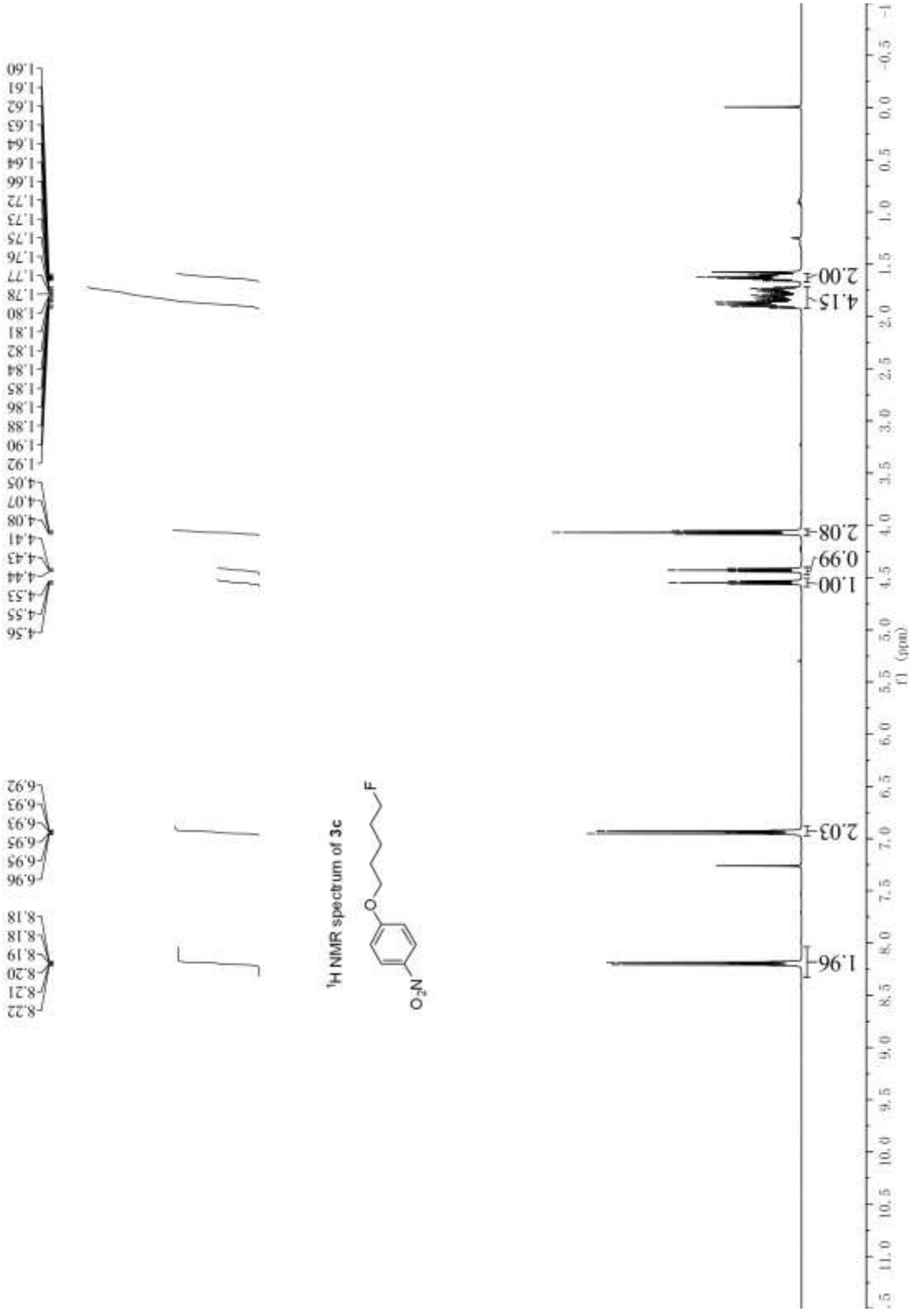
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



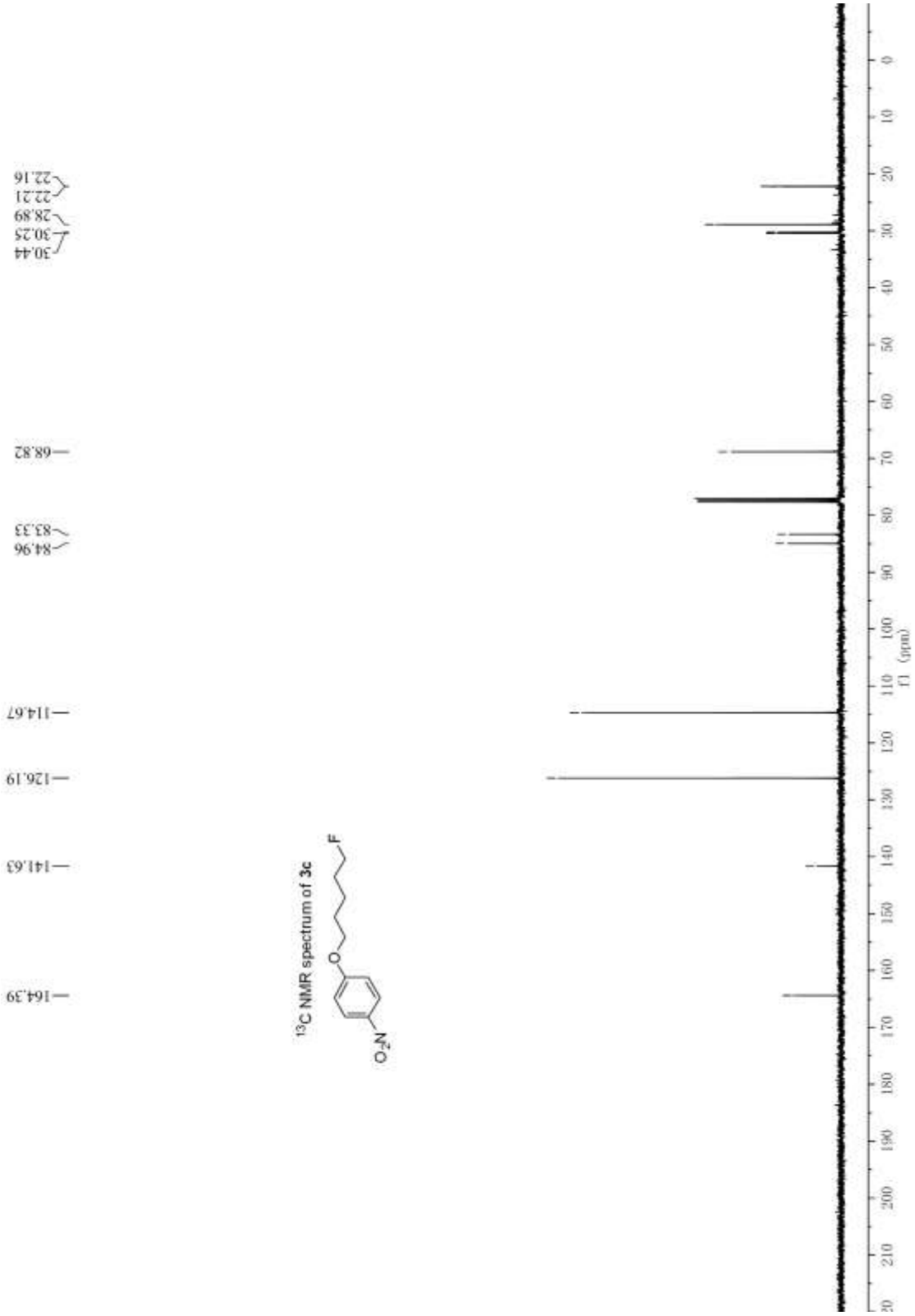
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3b**



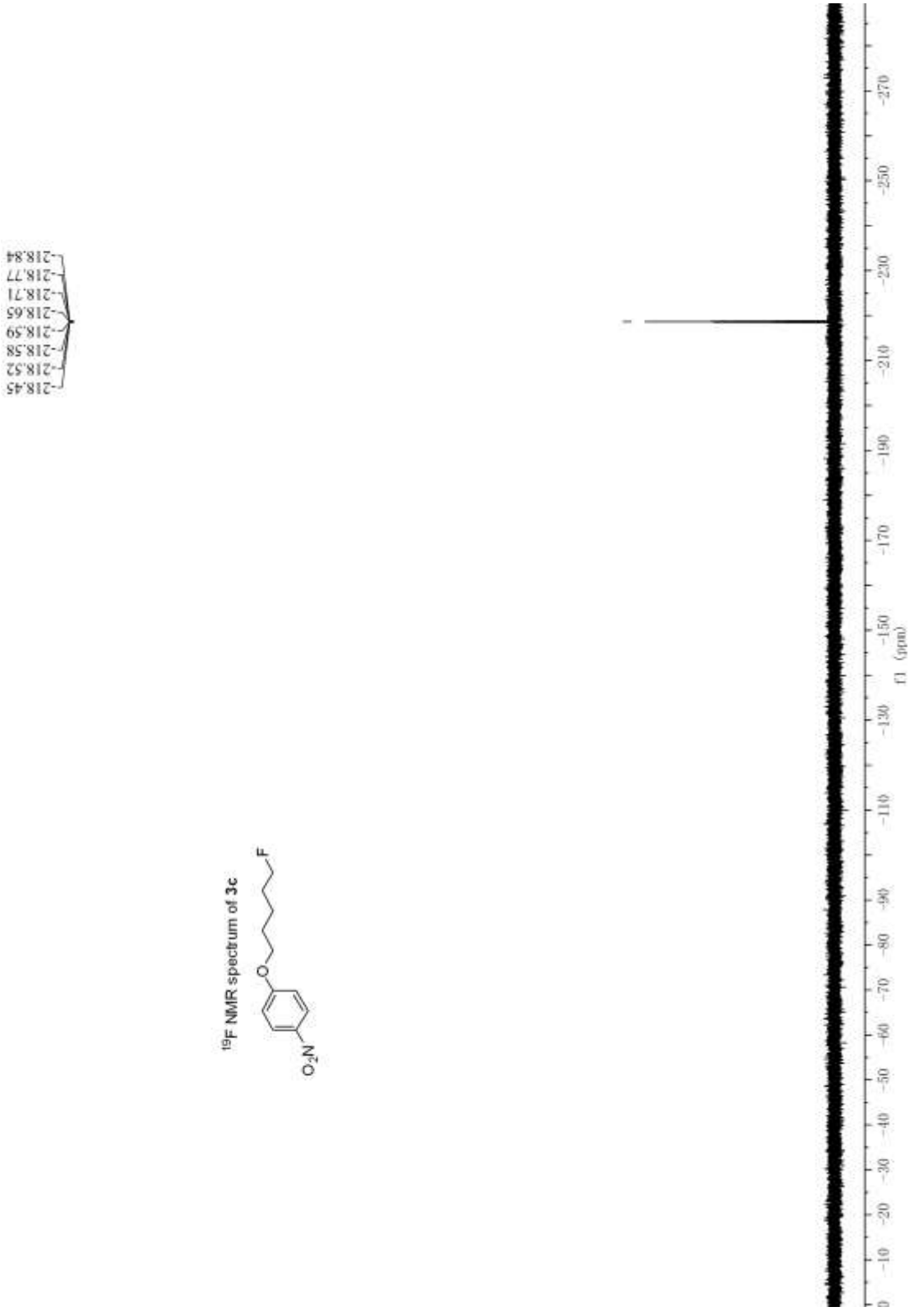
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3b**



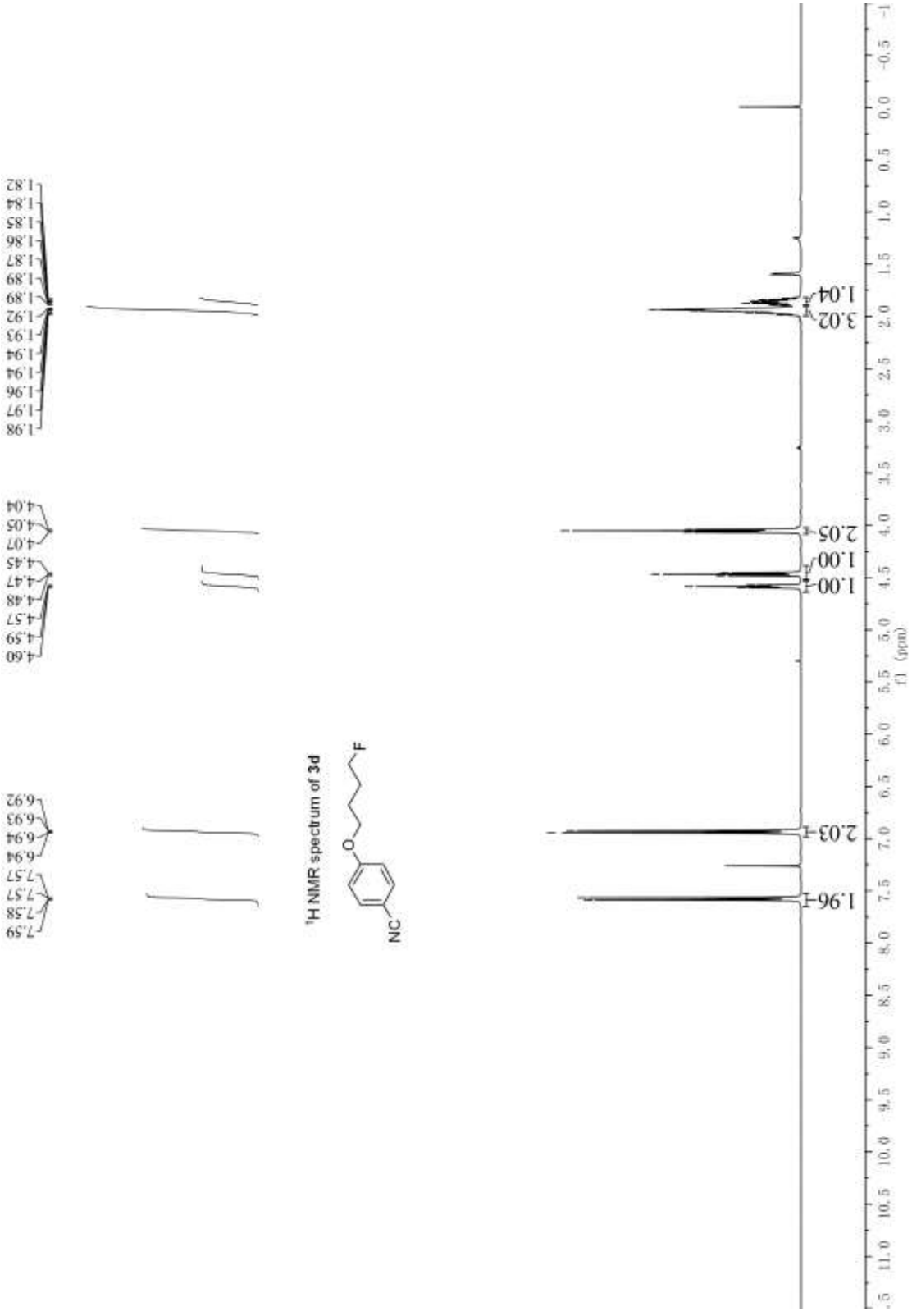
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**



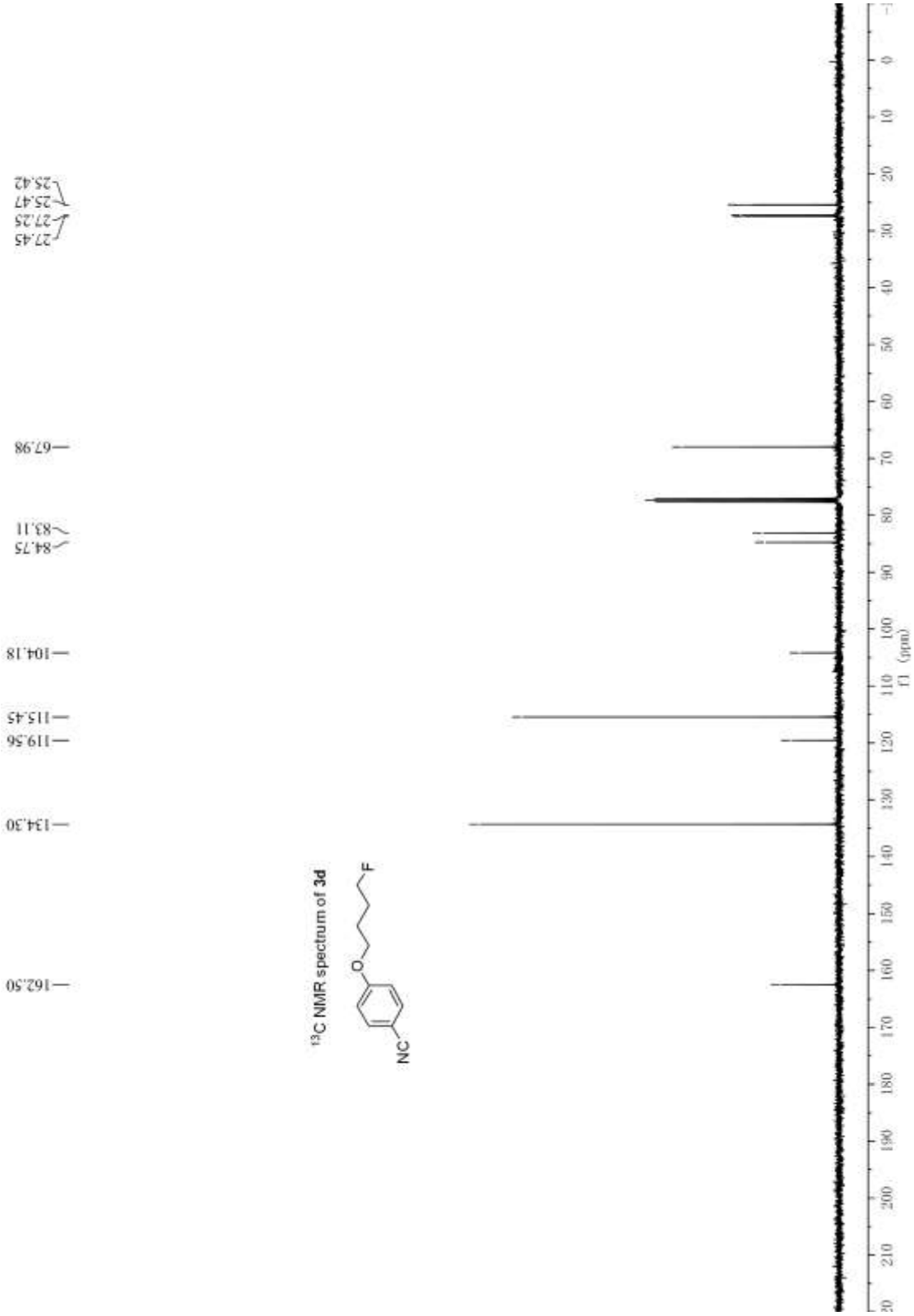
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3c**



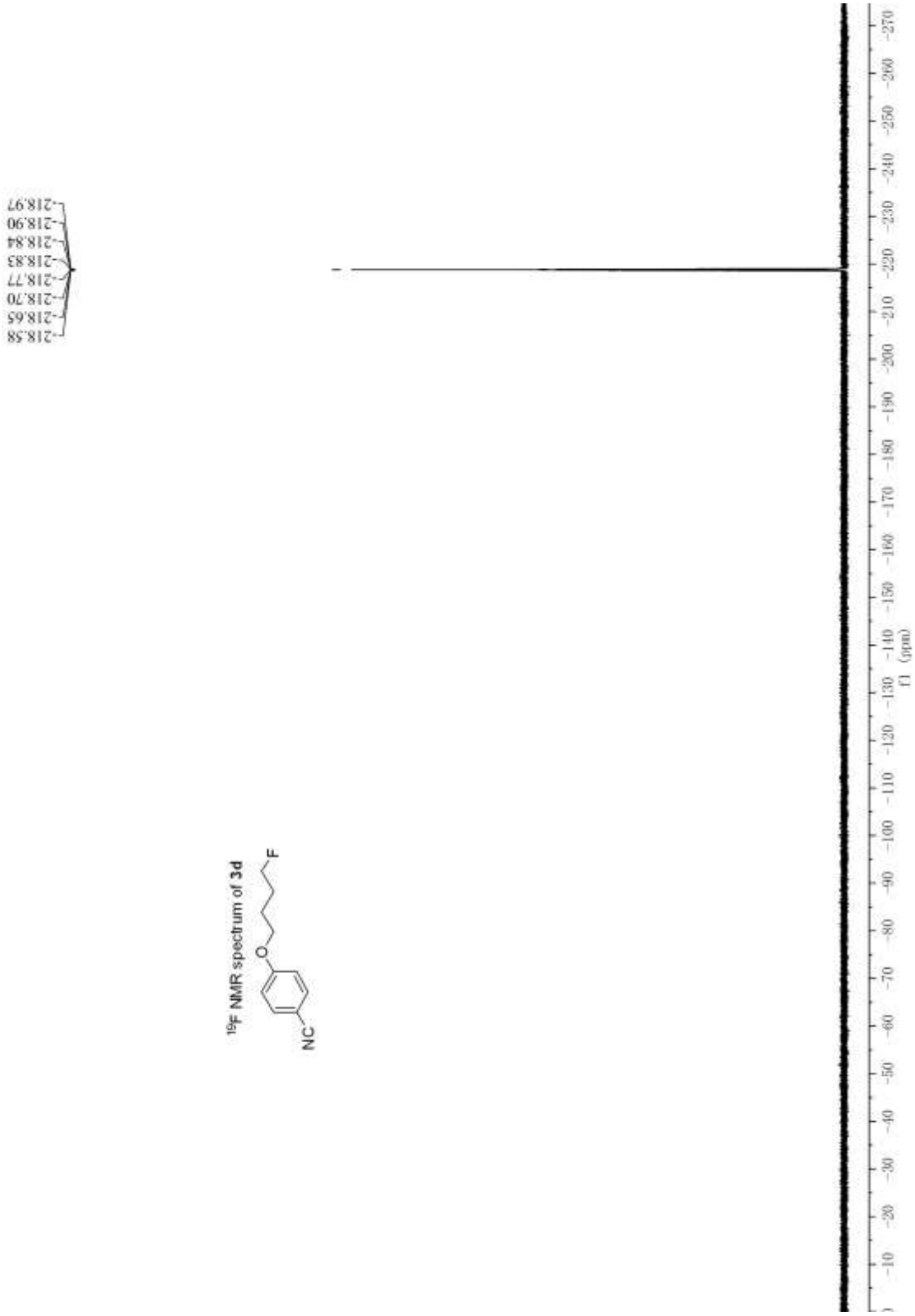
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3c**



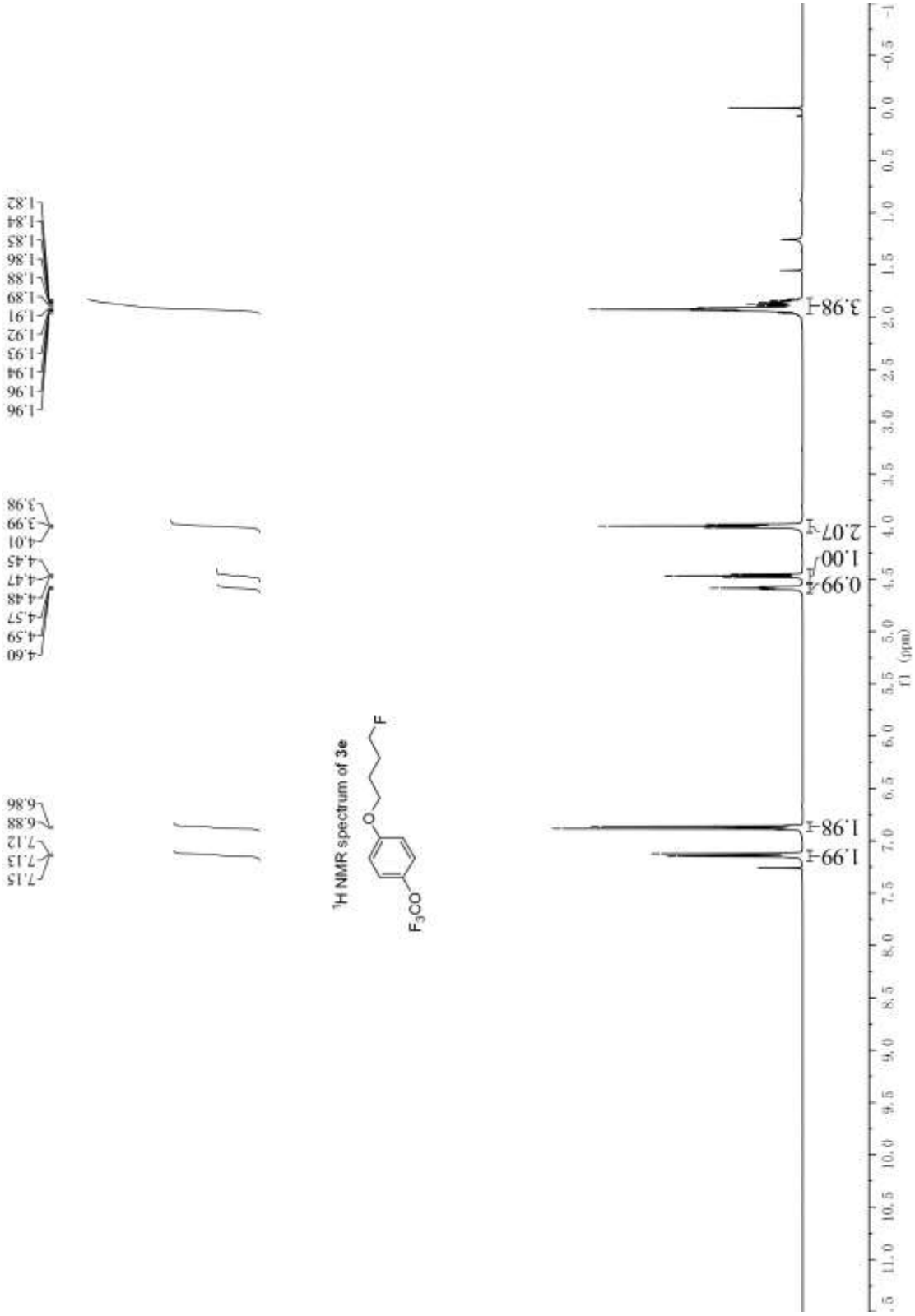
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**



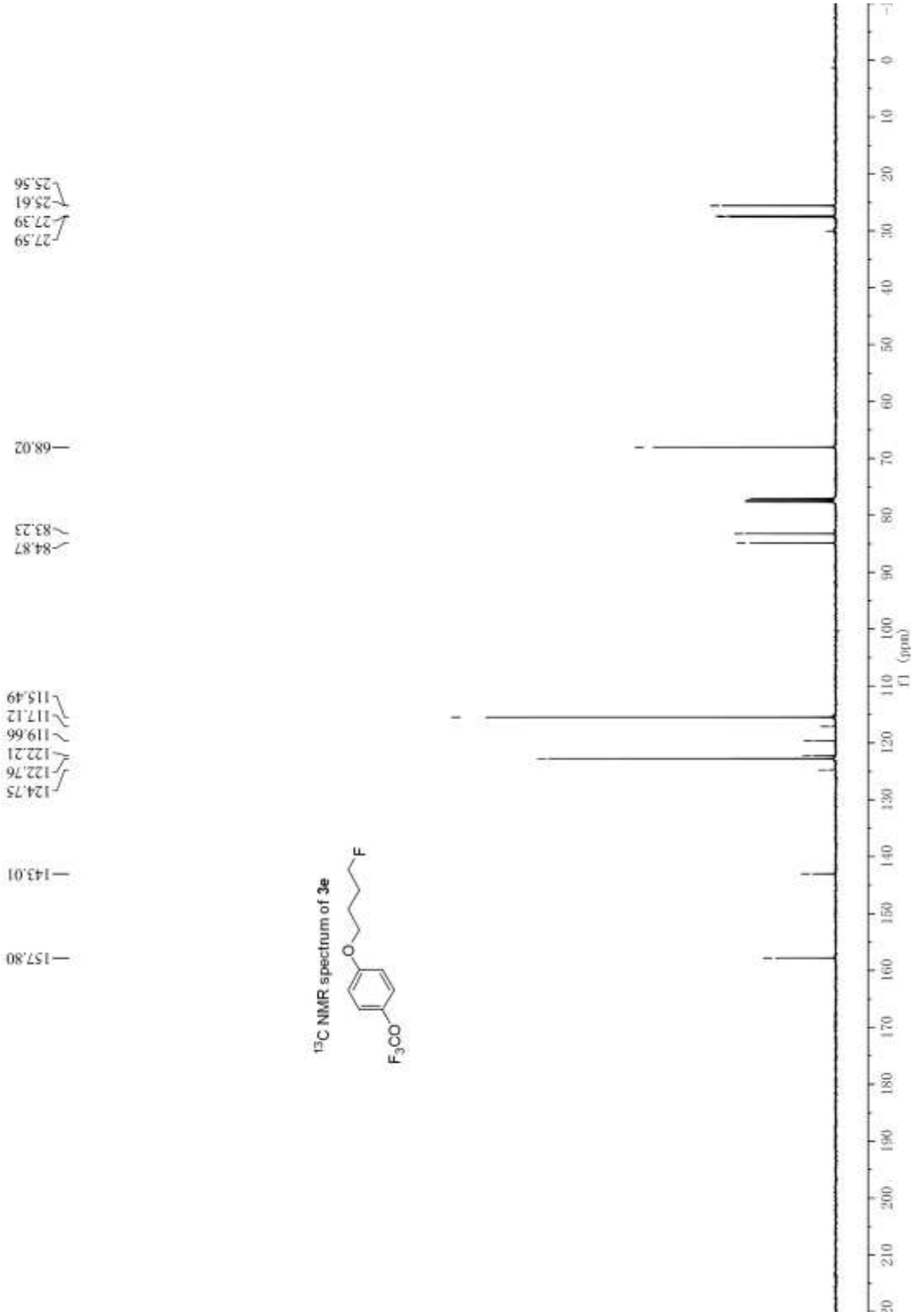
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3d**



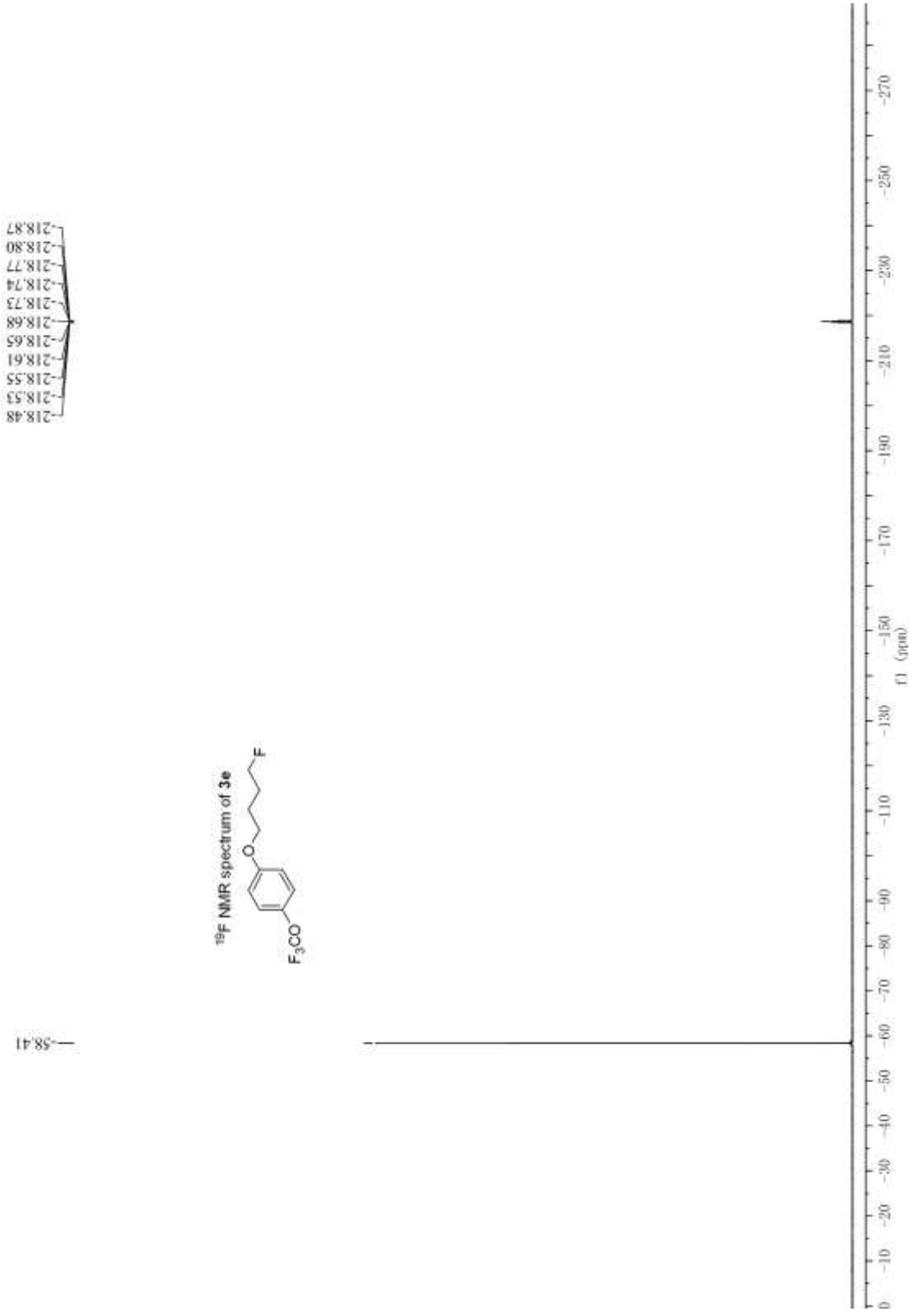
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3d**



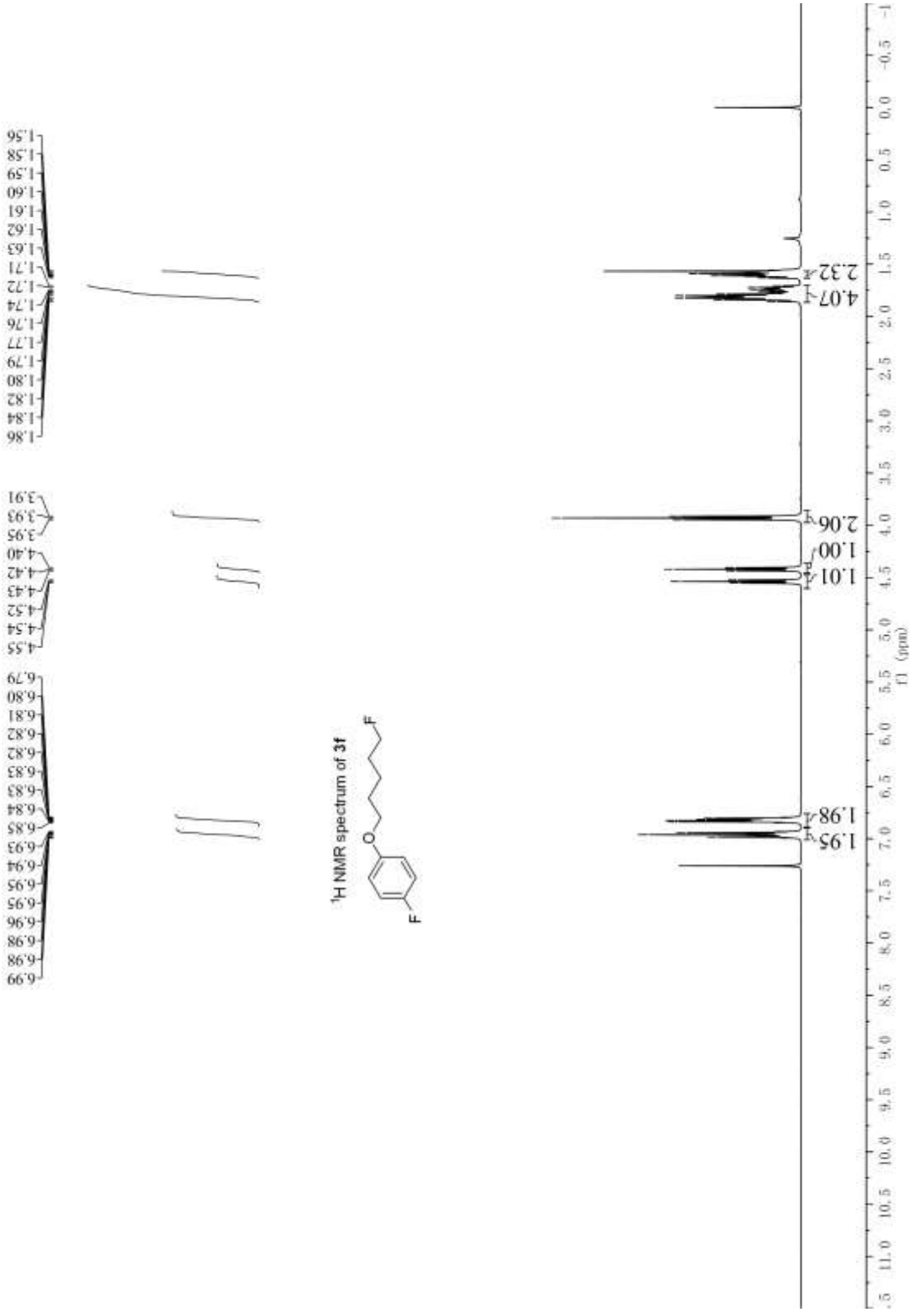
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**



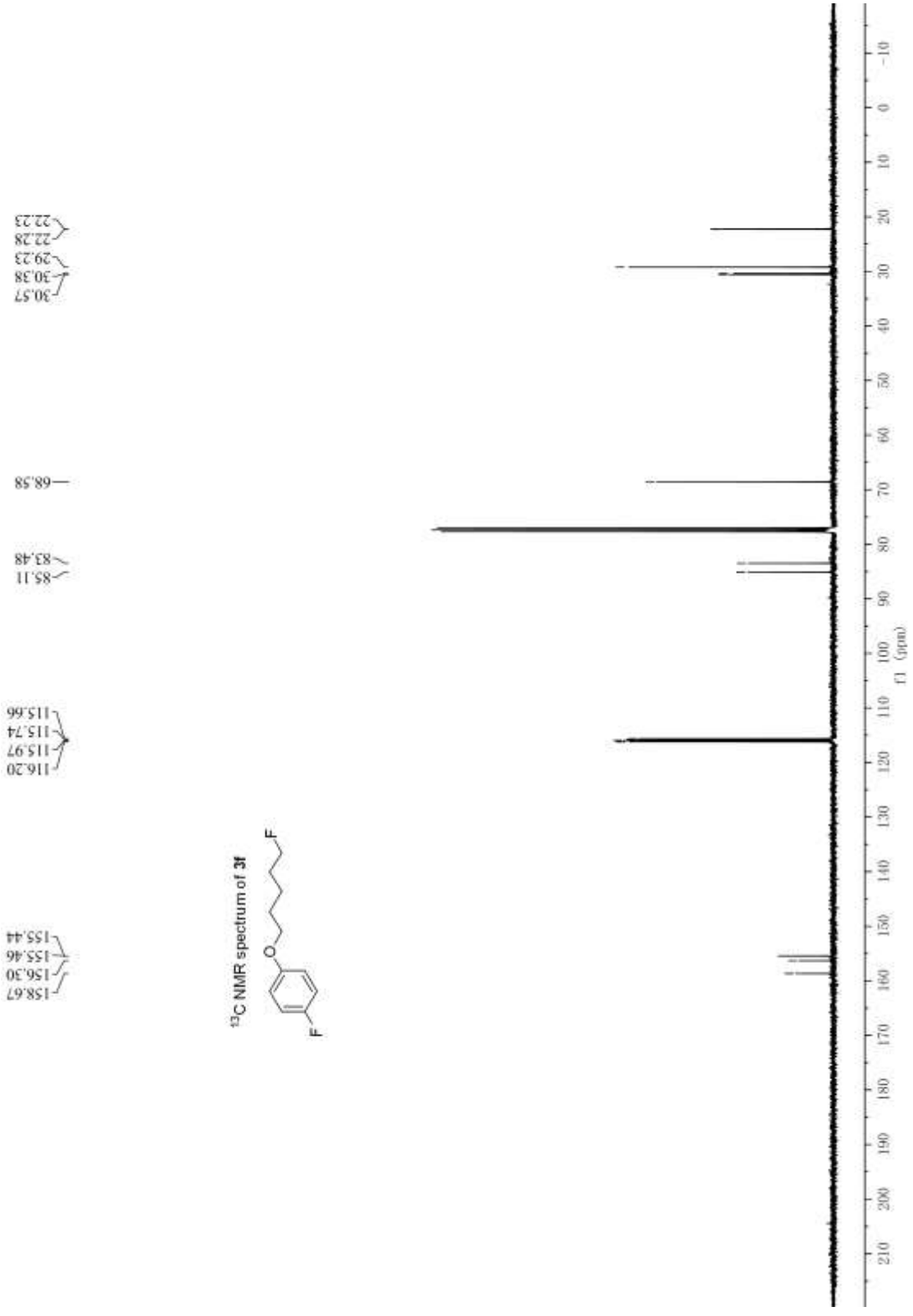
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3e**



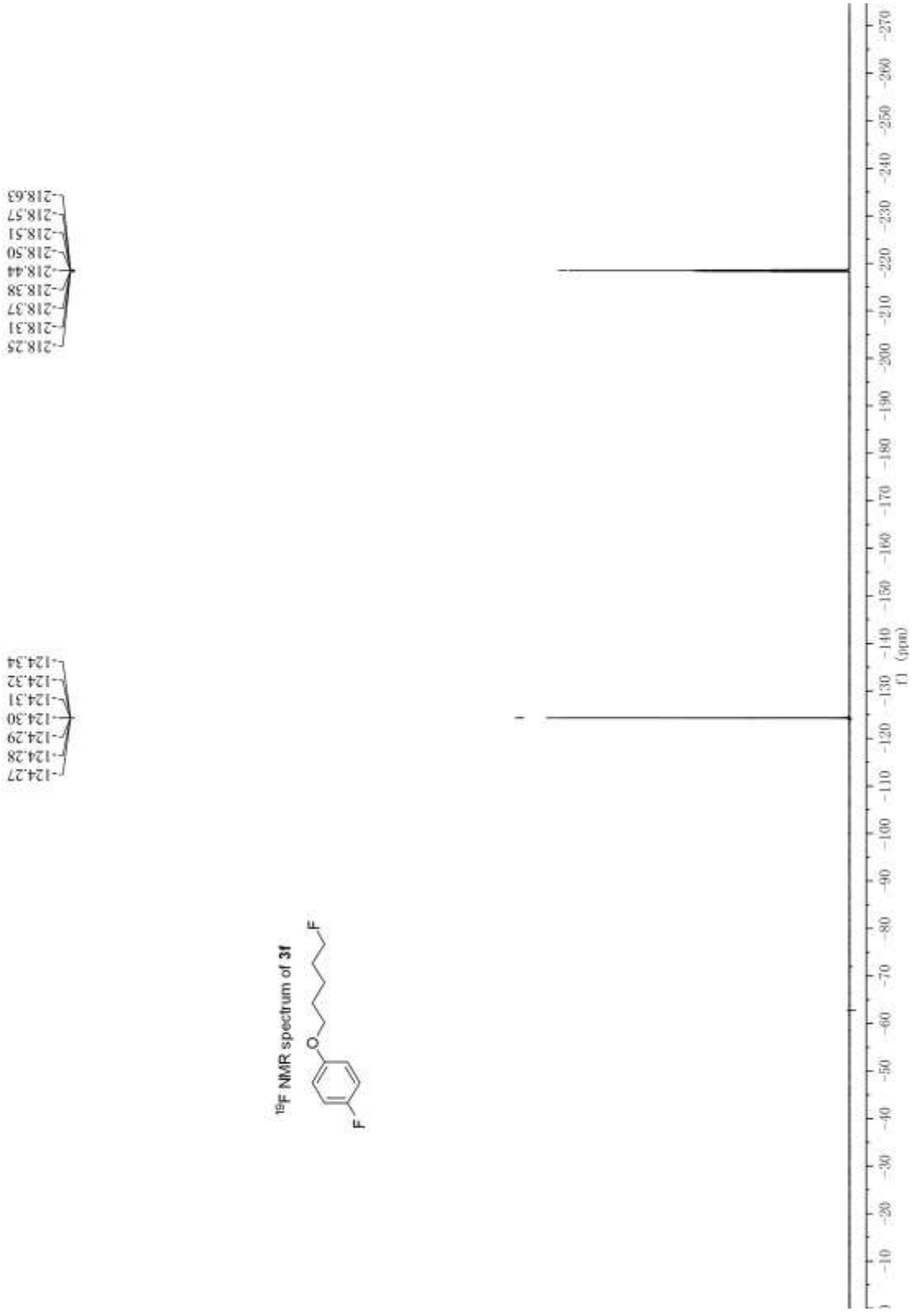
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3e**



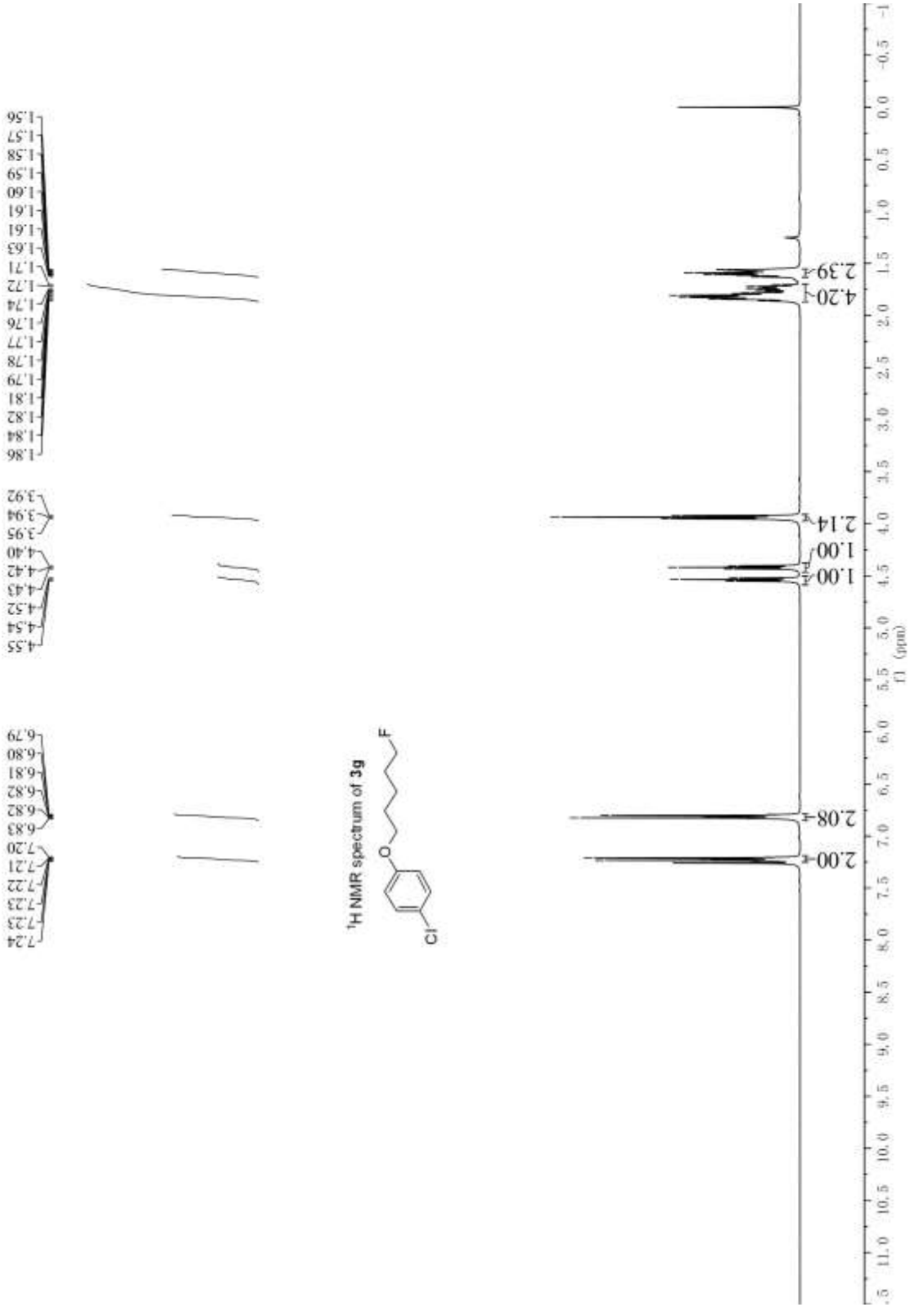
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3f**



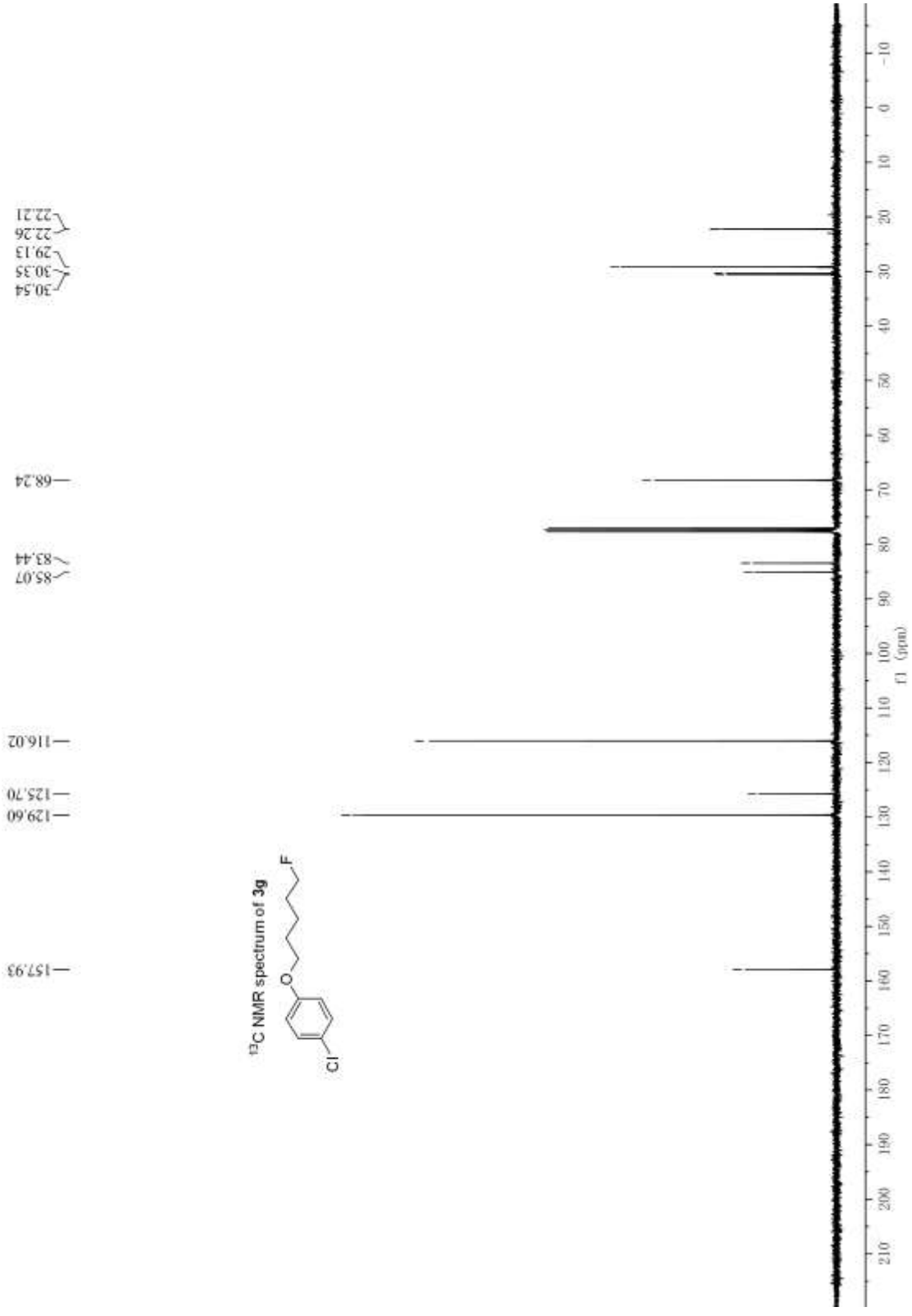
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3f**



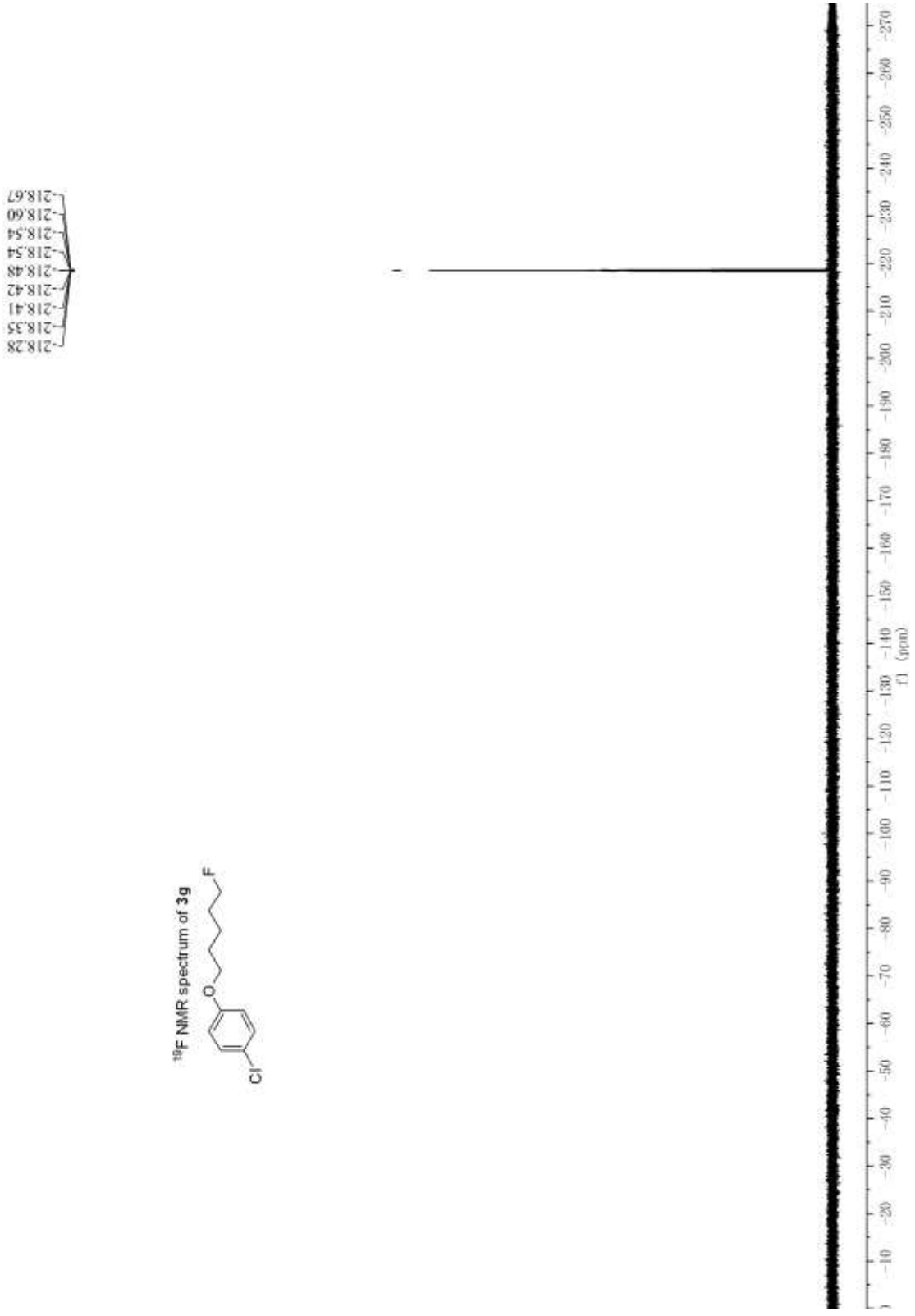
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3f**



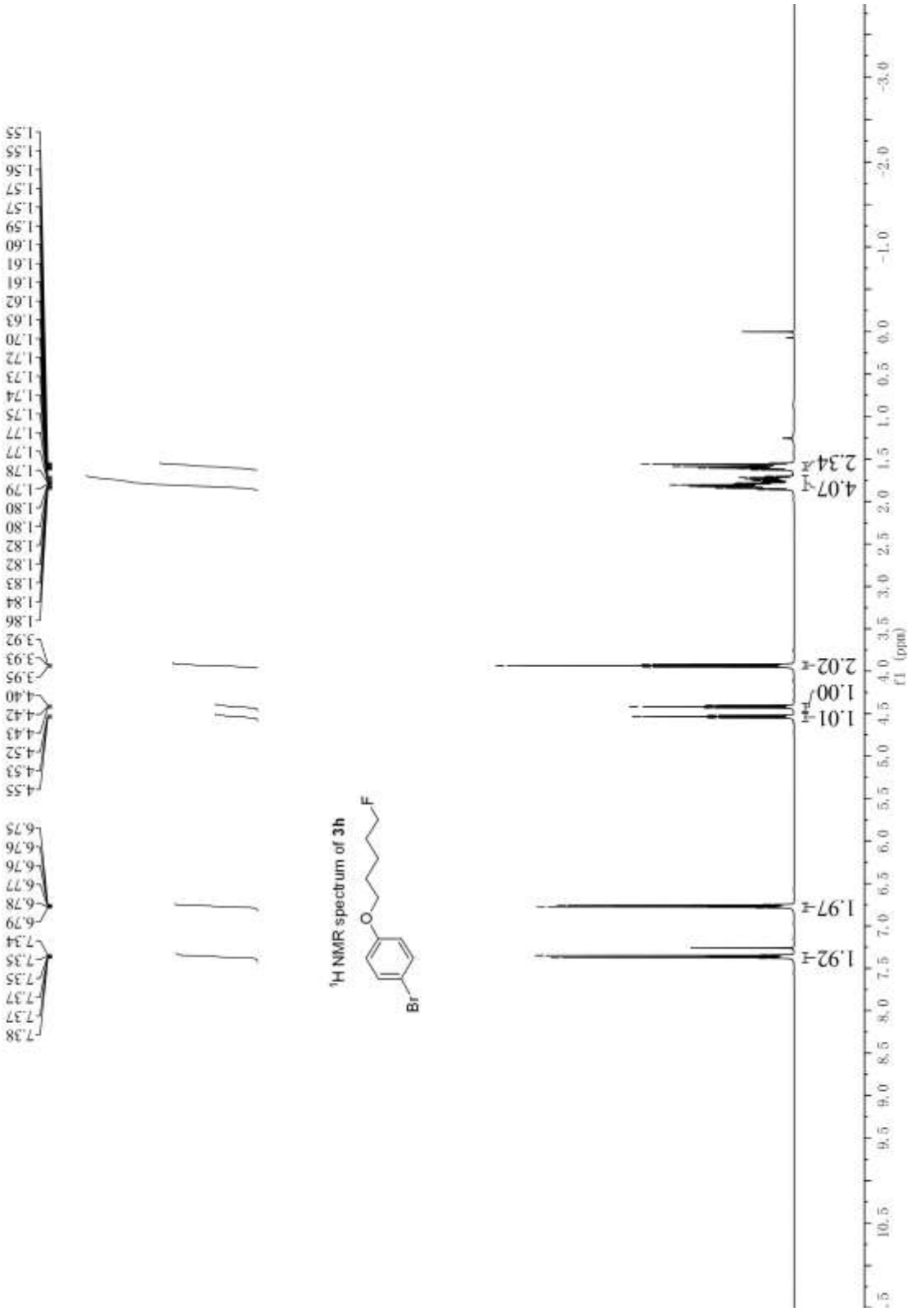
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3g**



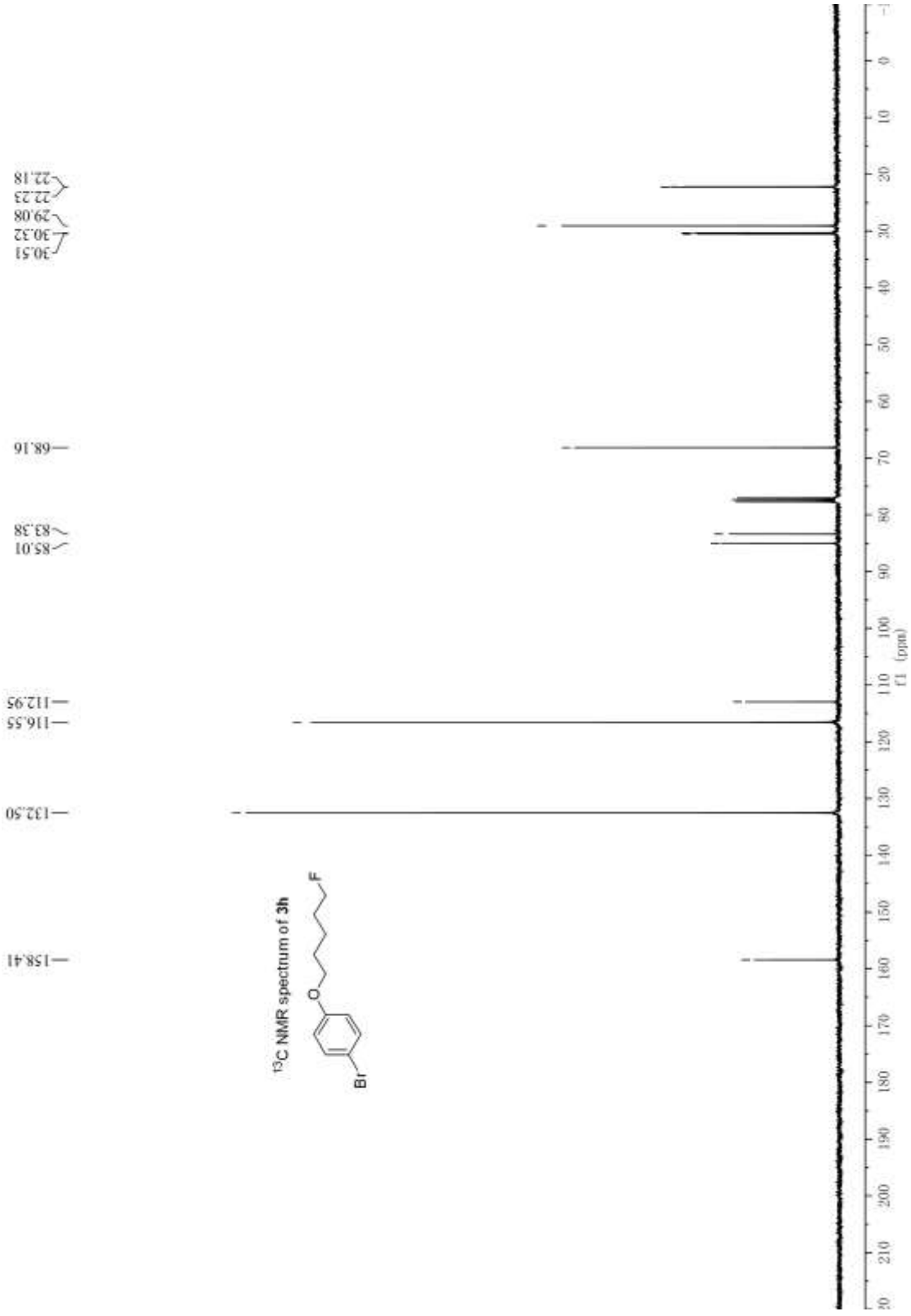
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3g**



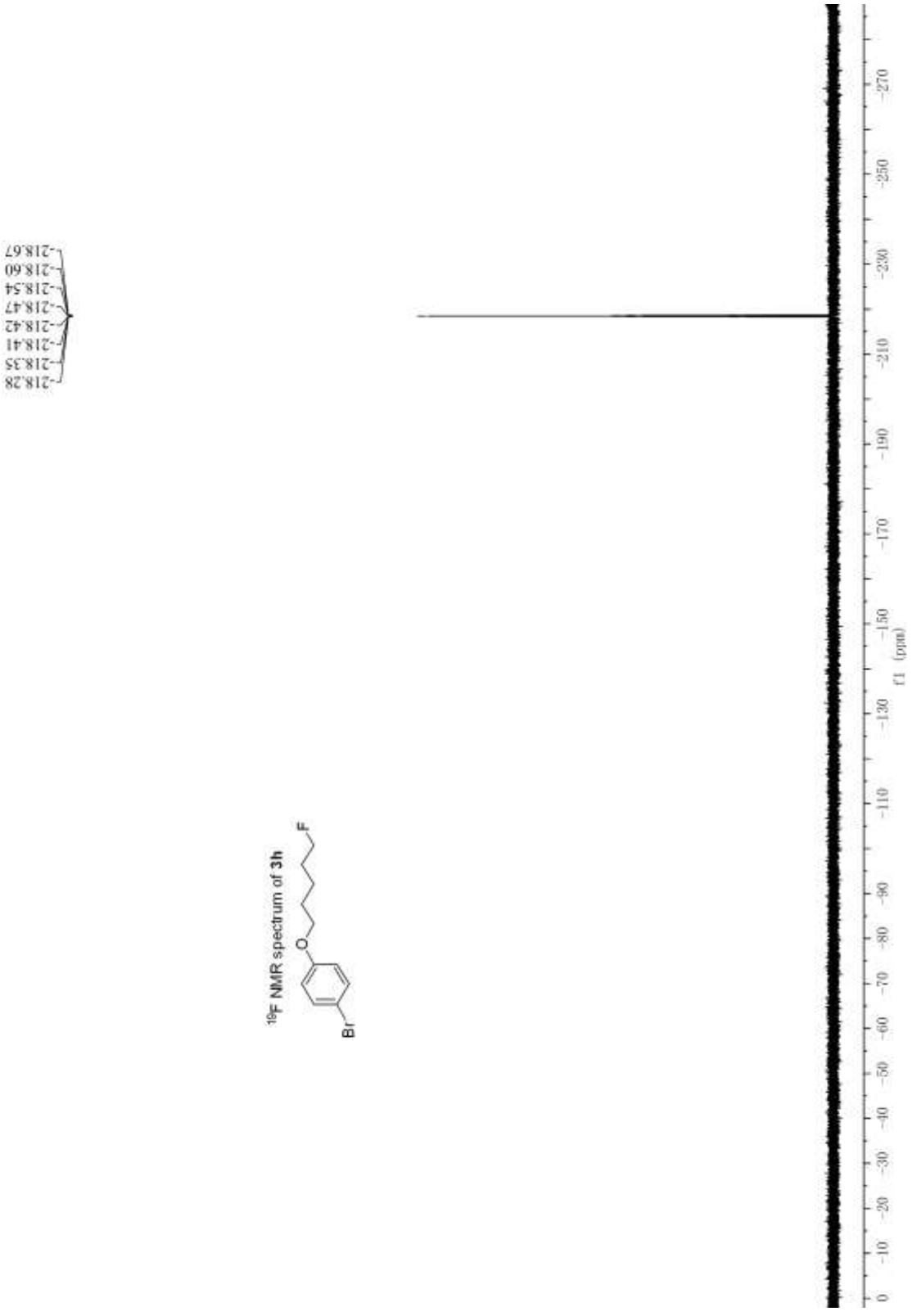
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3g**



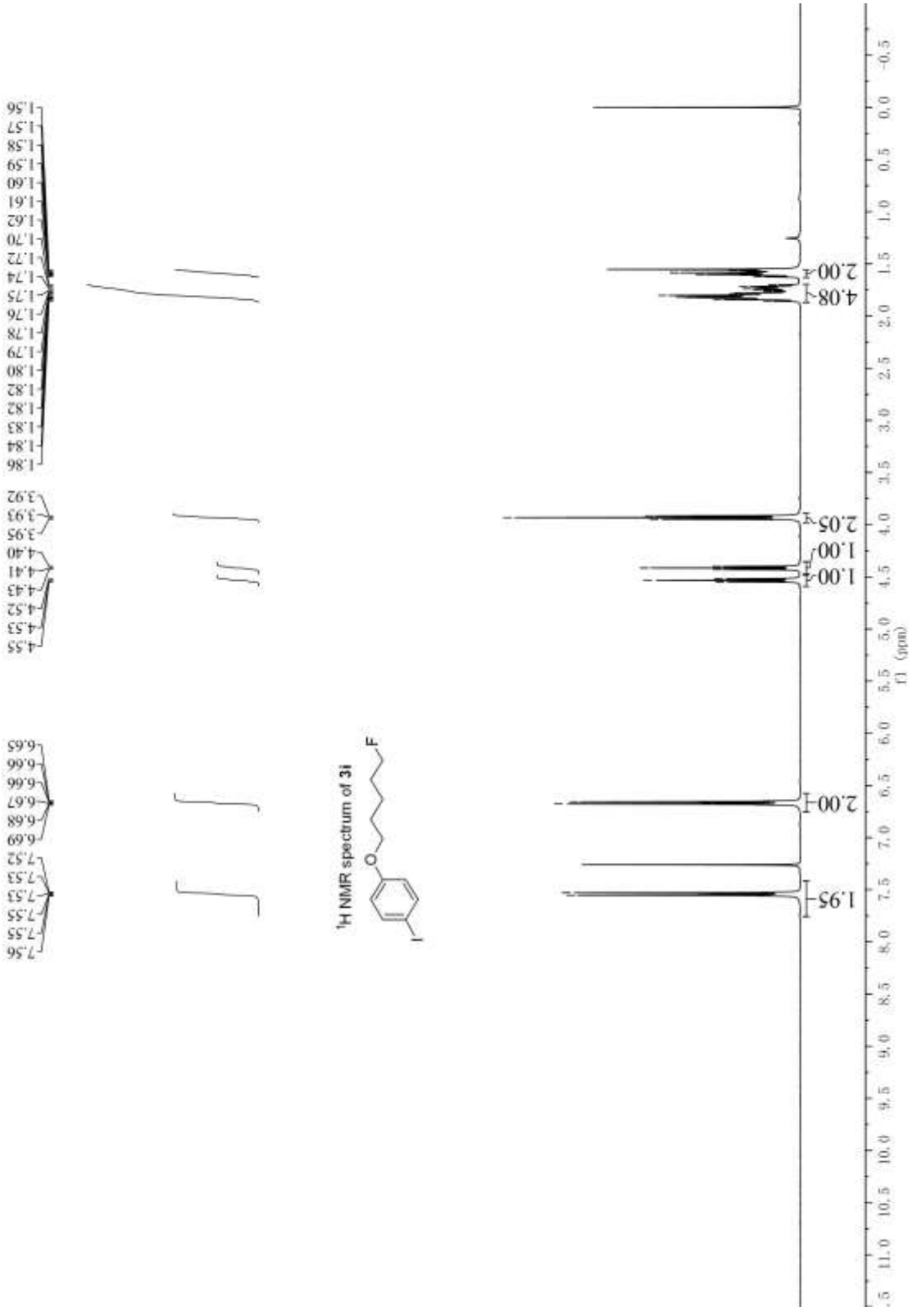
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3h**



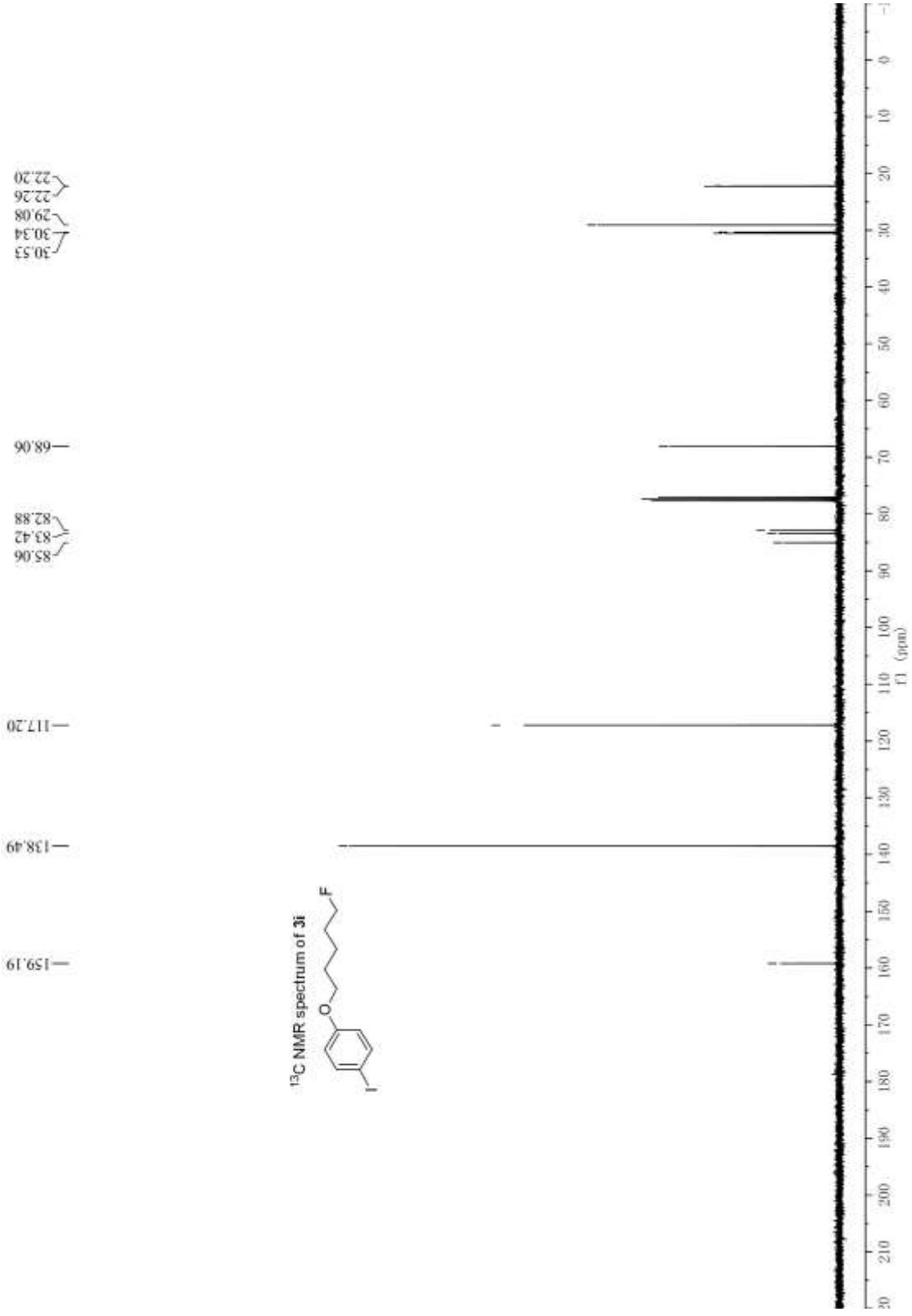
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3h**



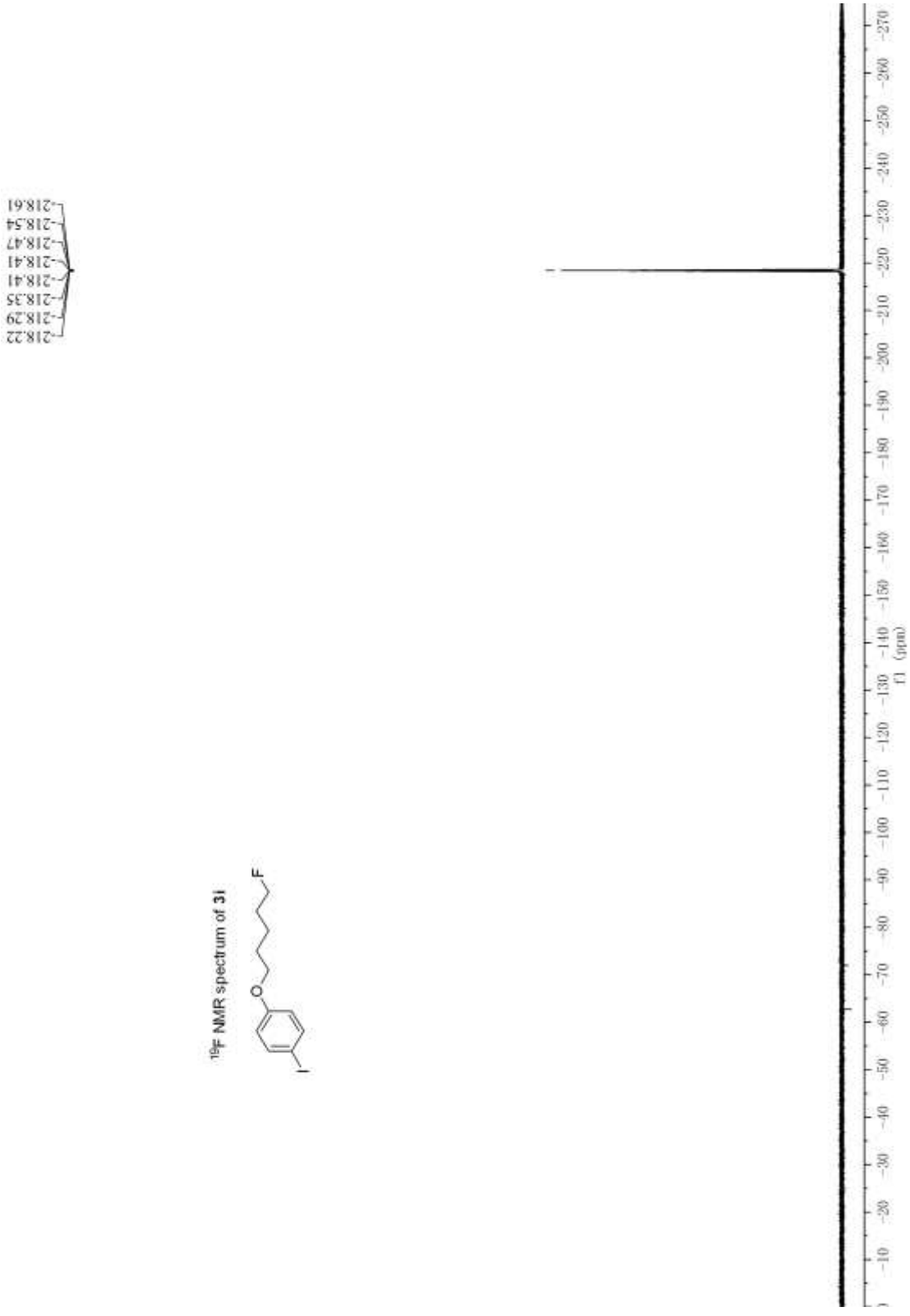
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3h**



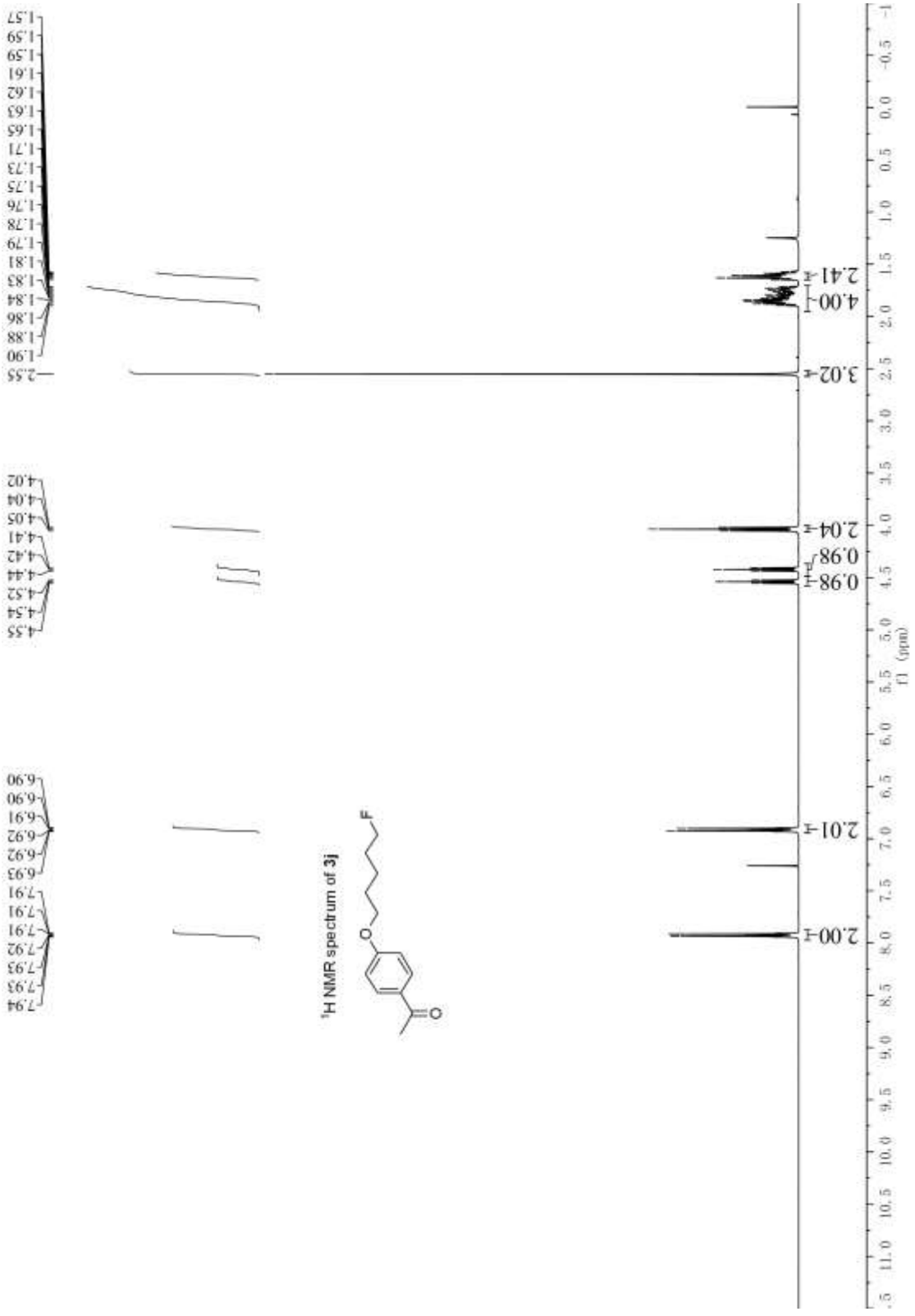
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3i**



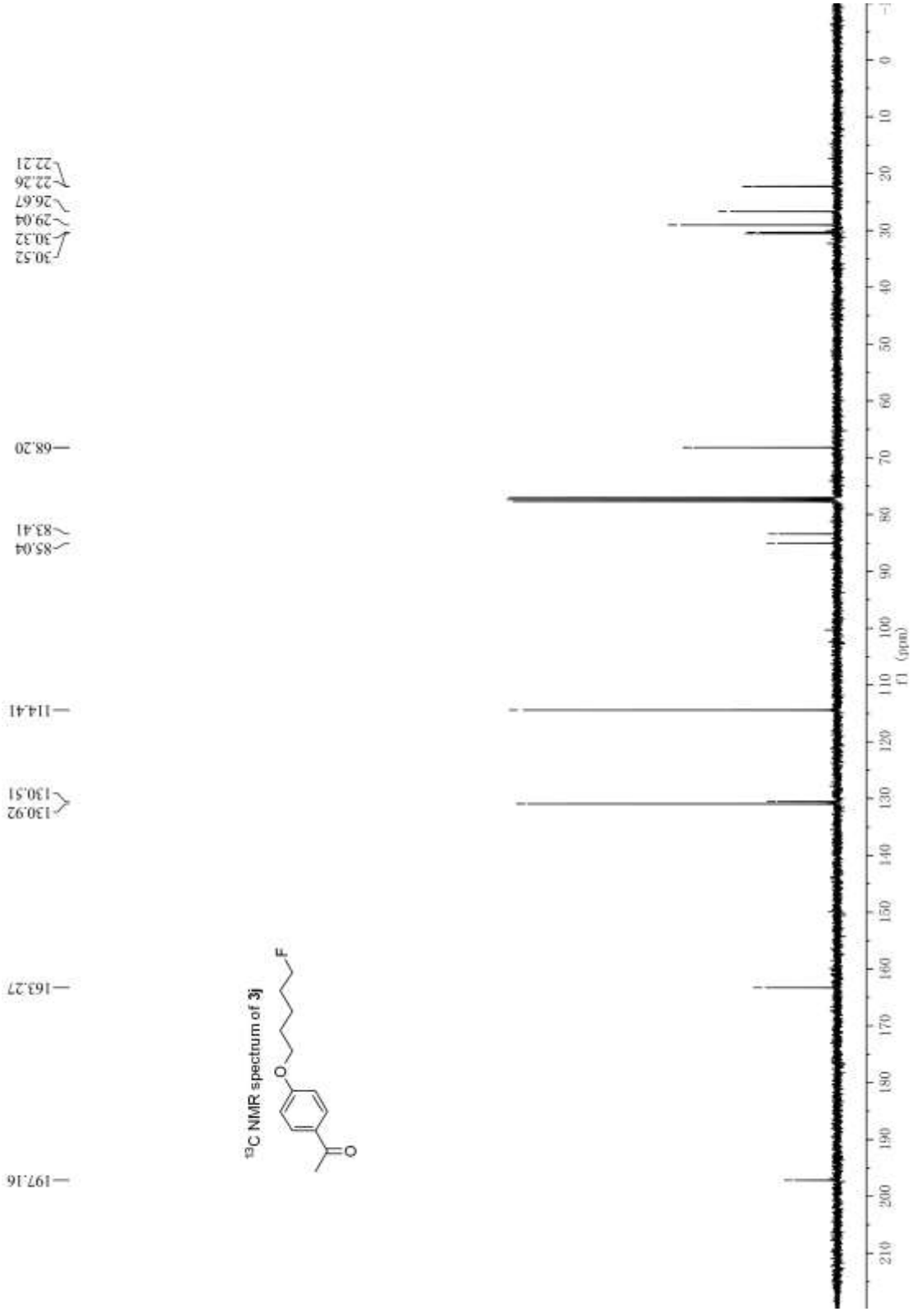
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3i**



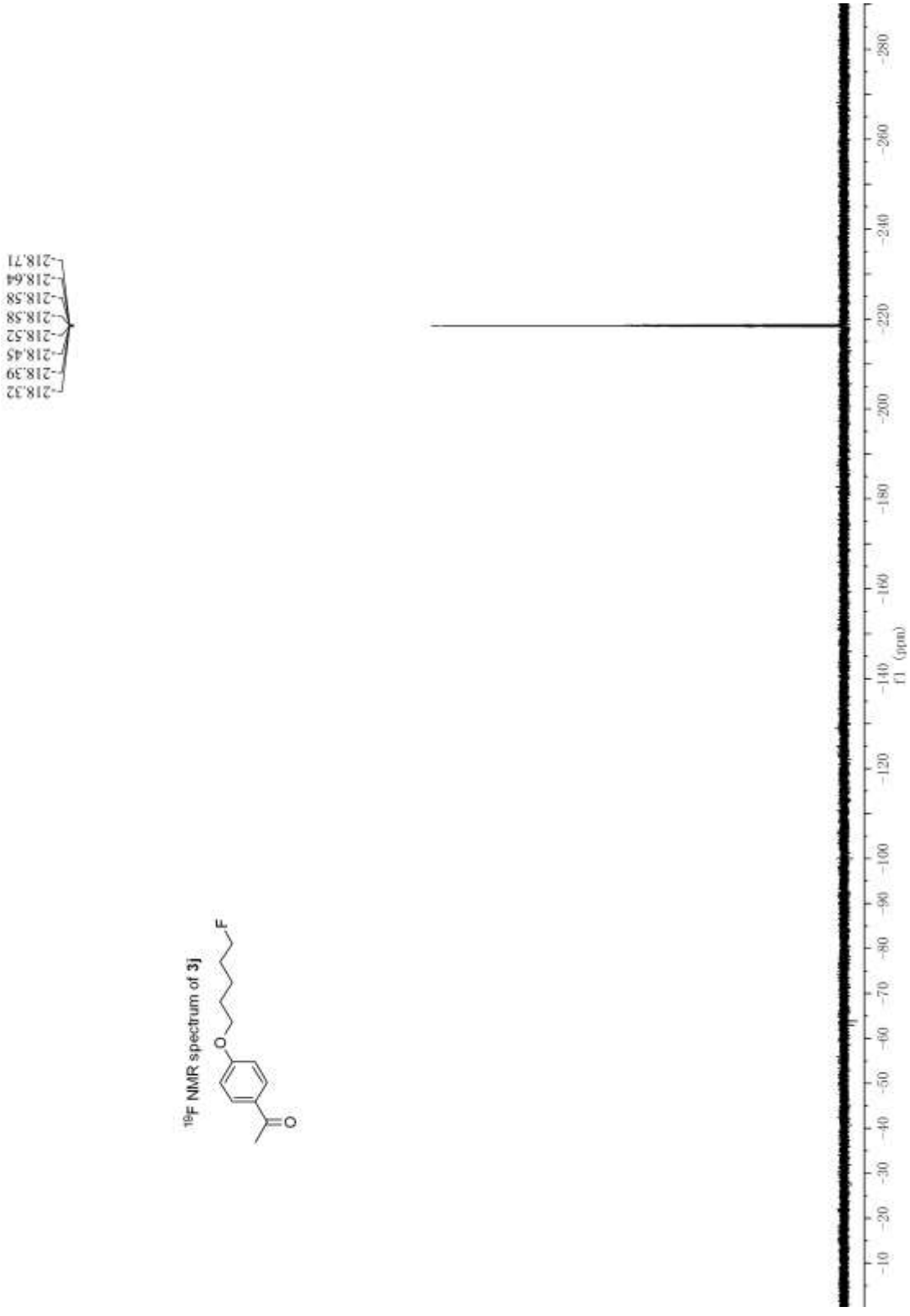
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3i**



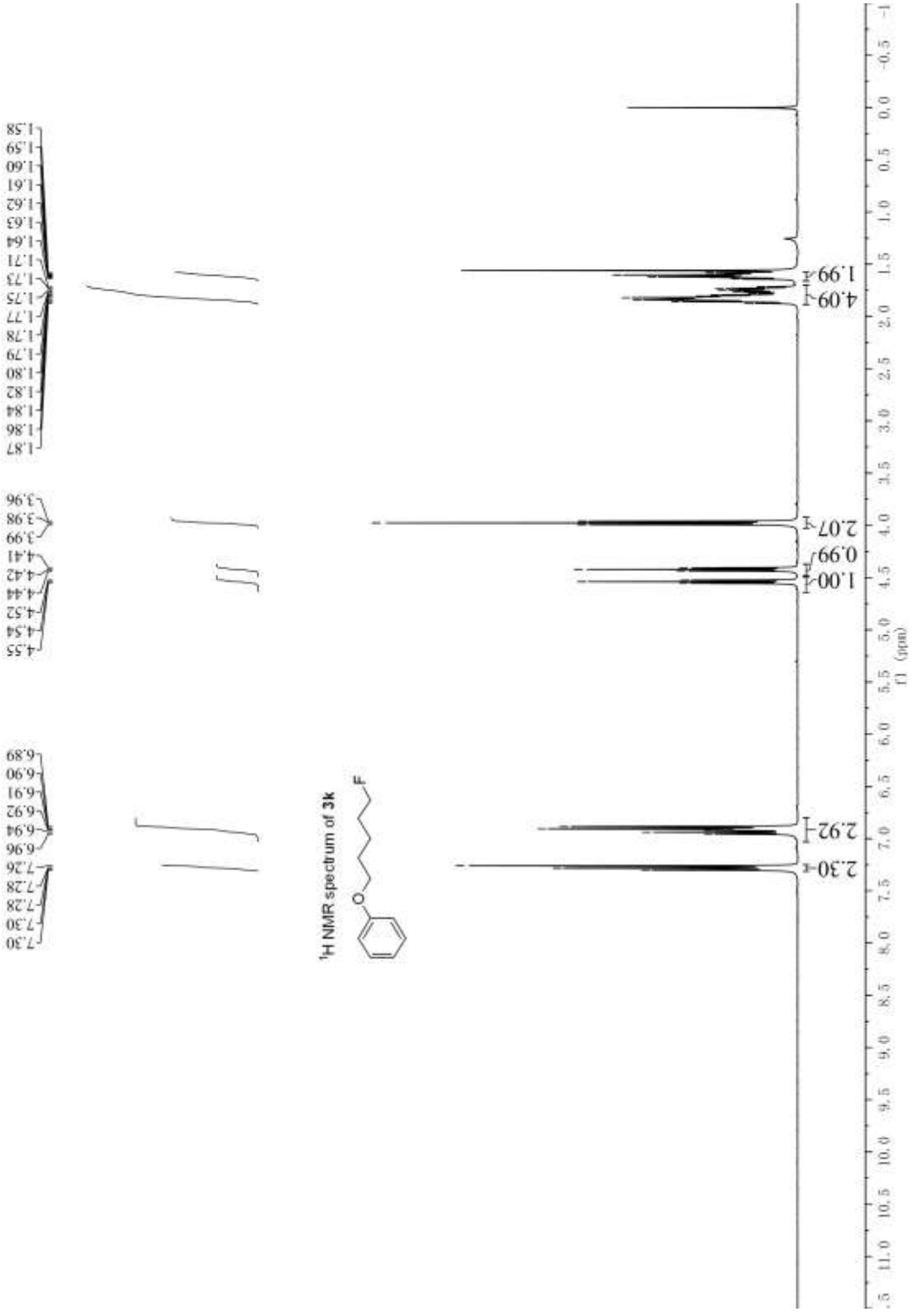
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3j**



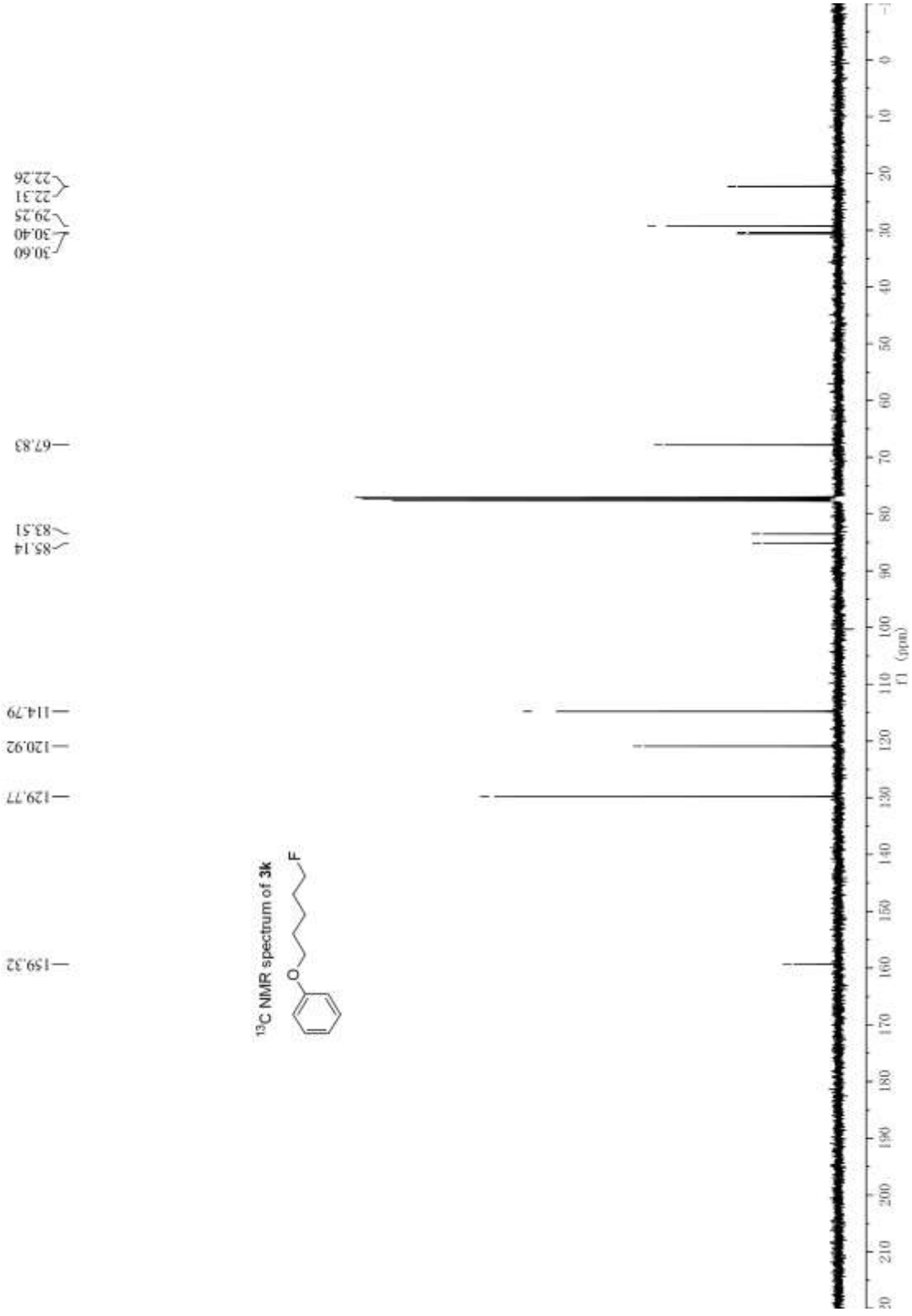
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3j**



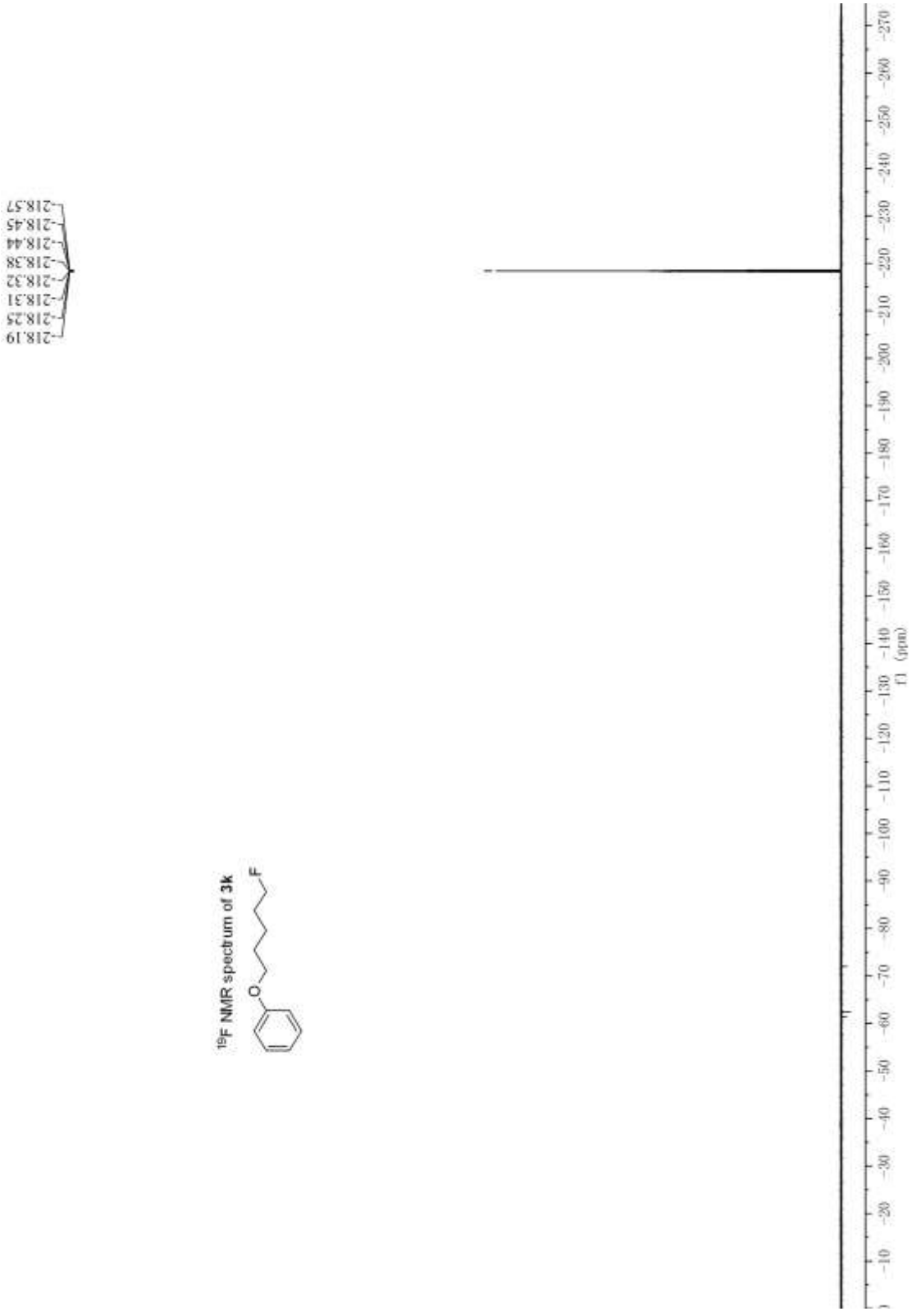
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3j**



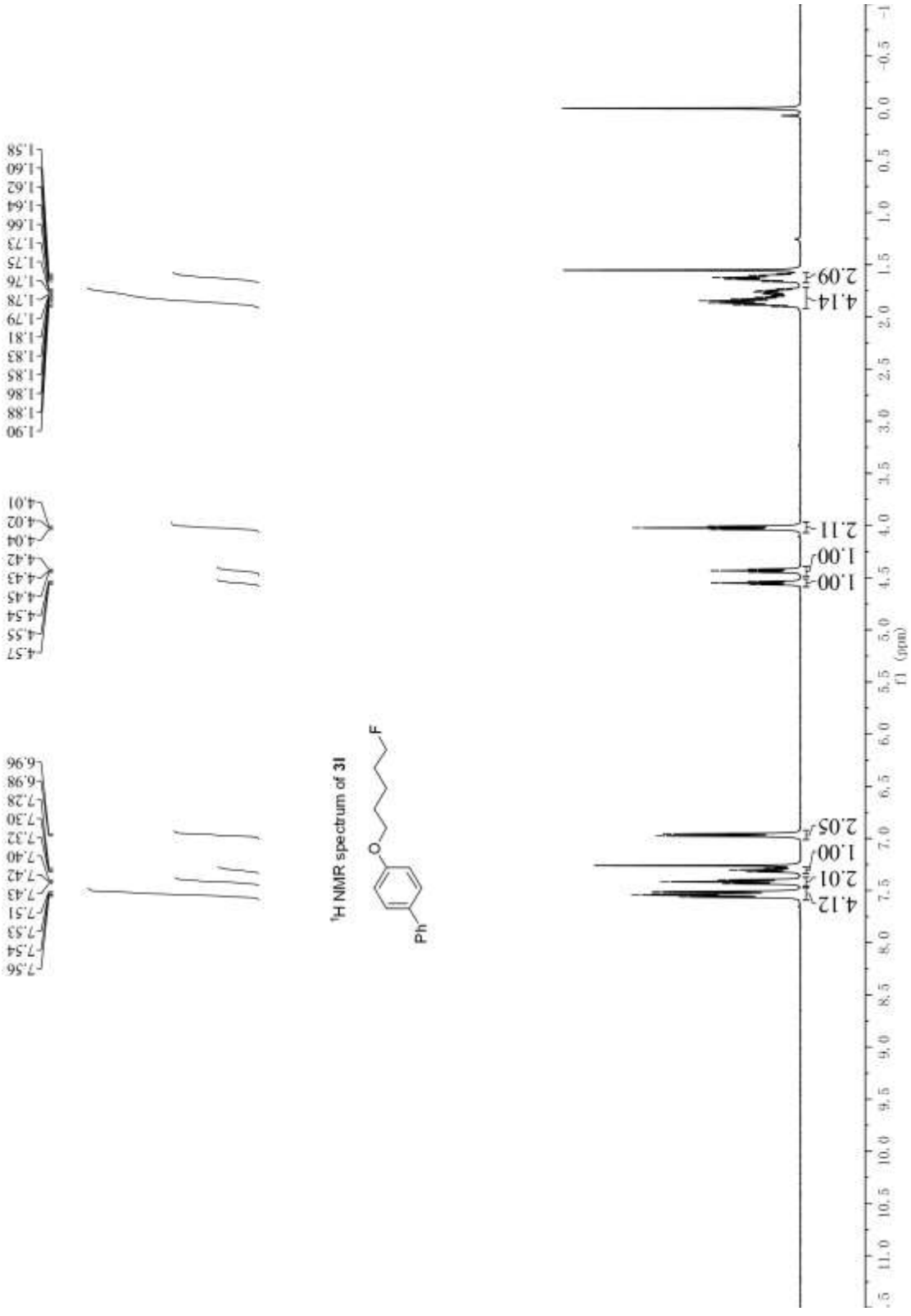
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3k**



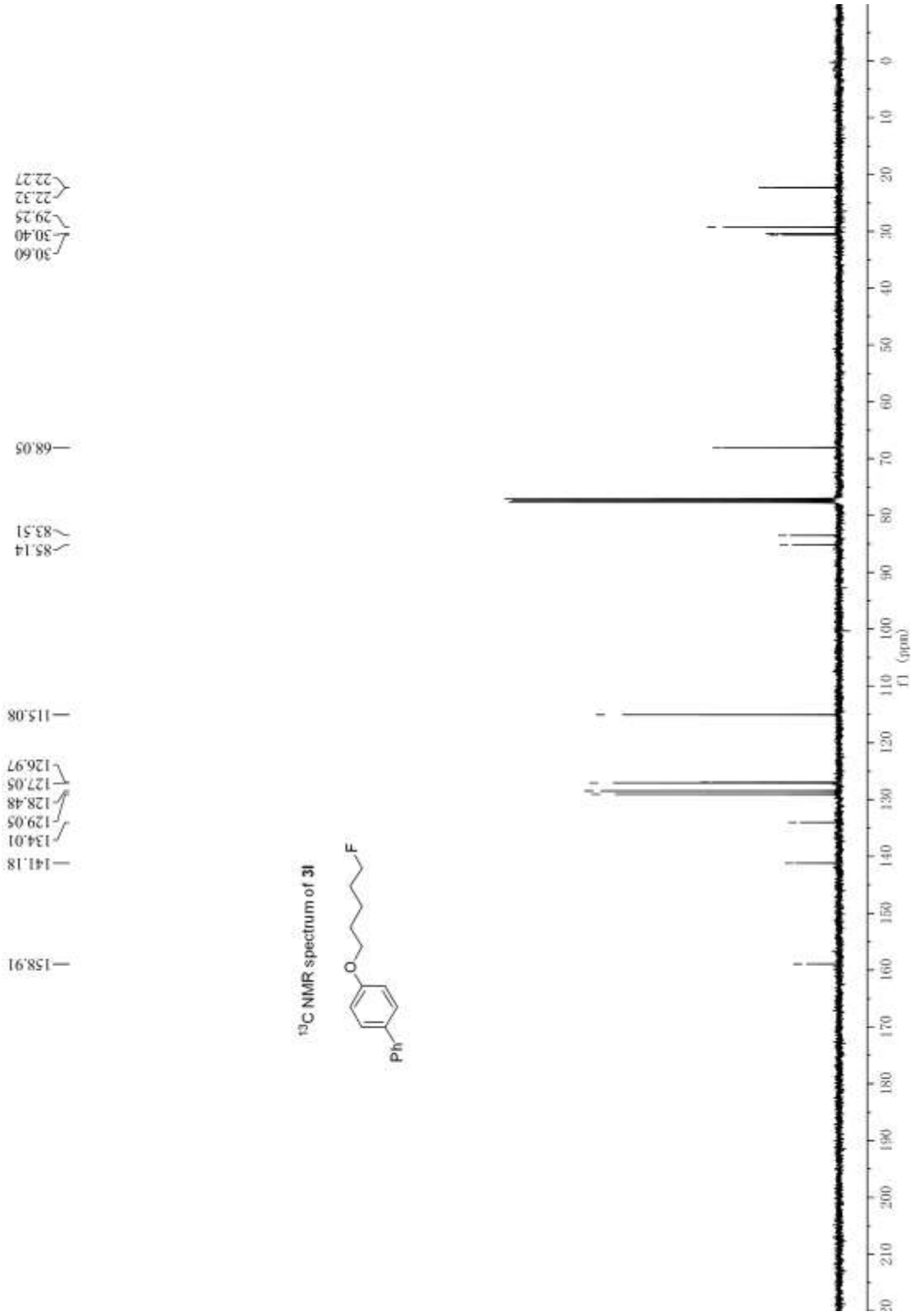
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3k**



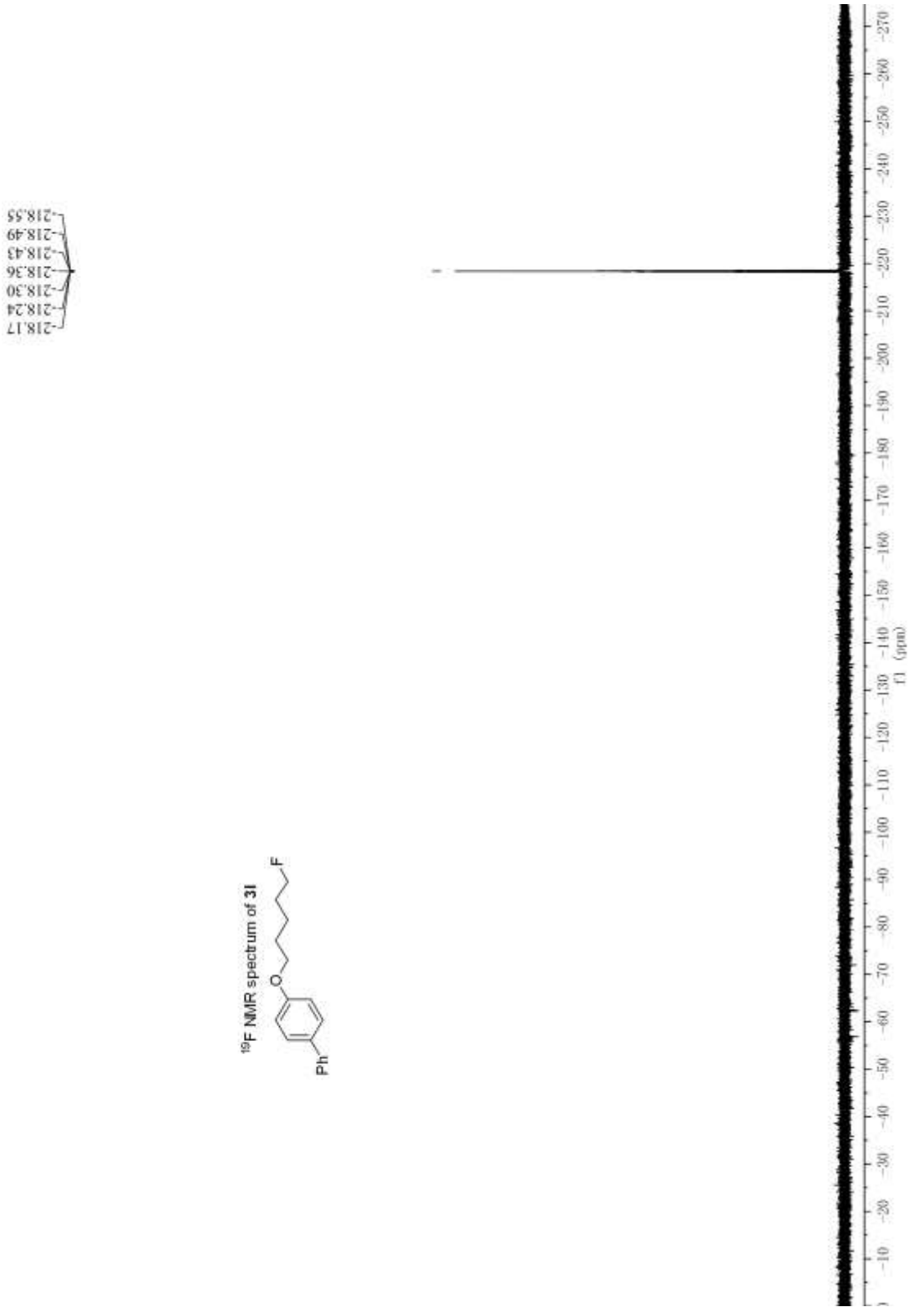
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3k**



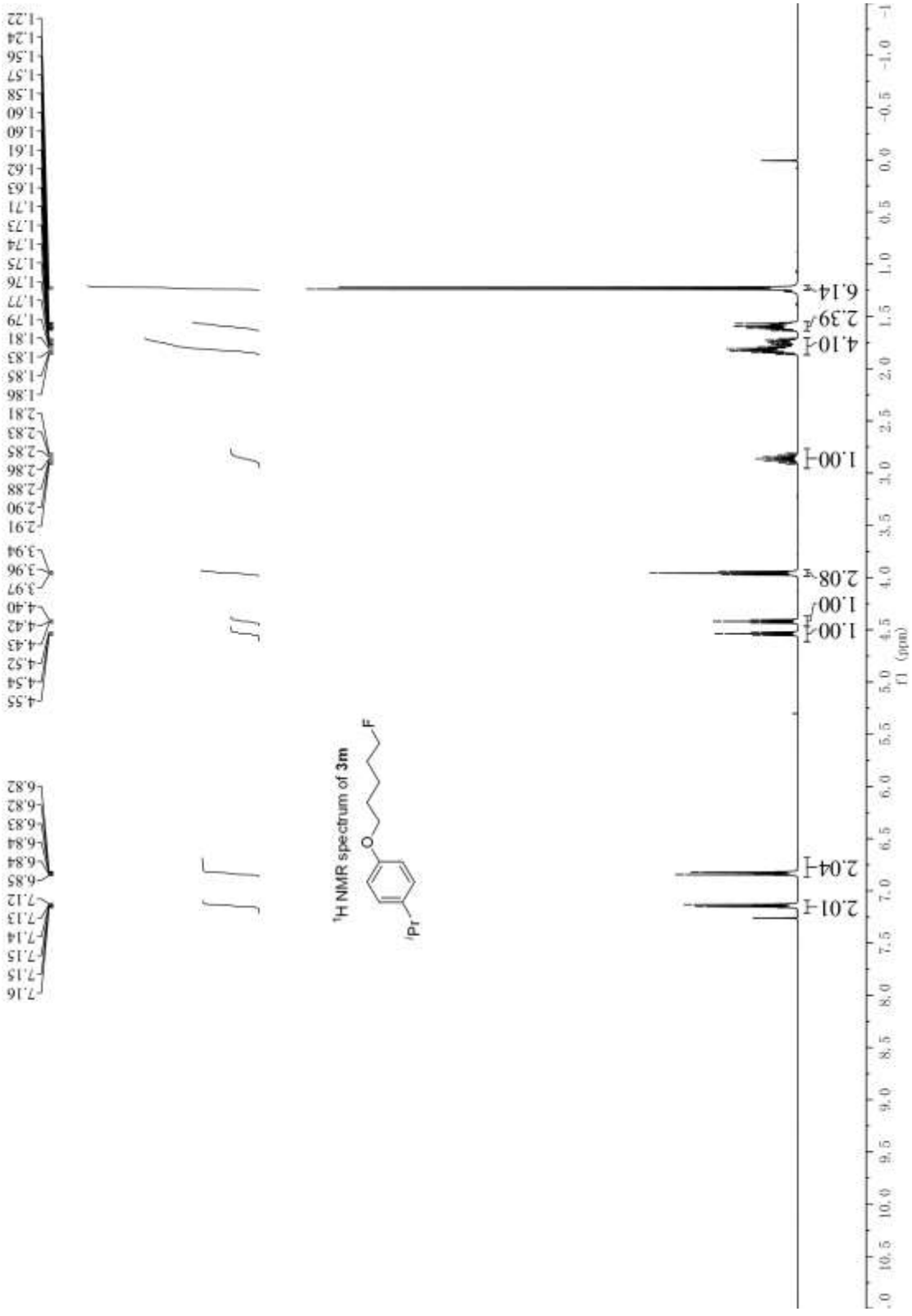
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3l**



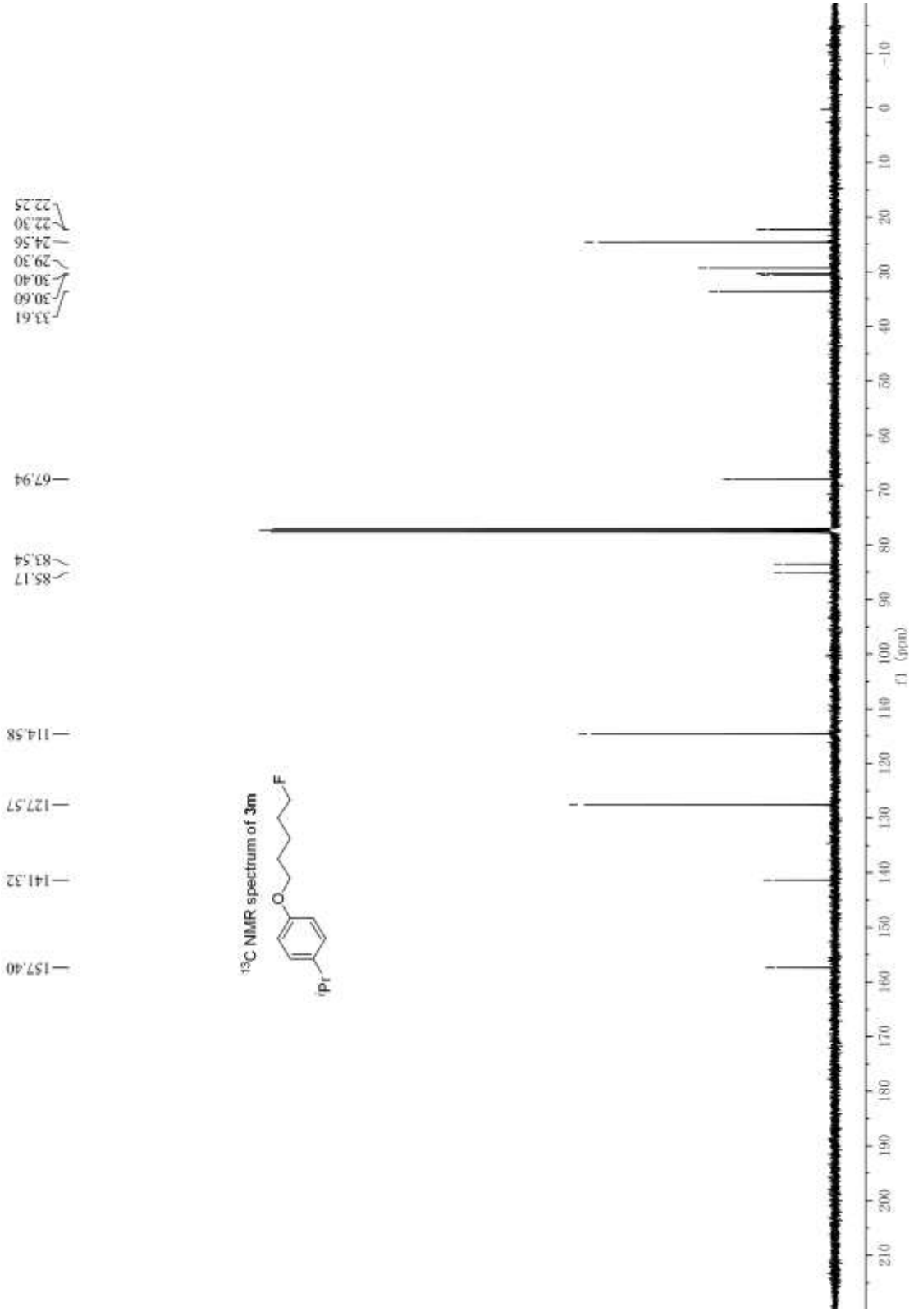
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3l**



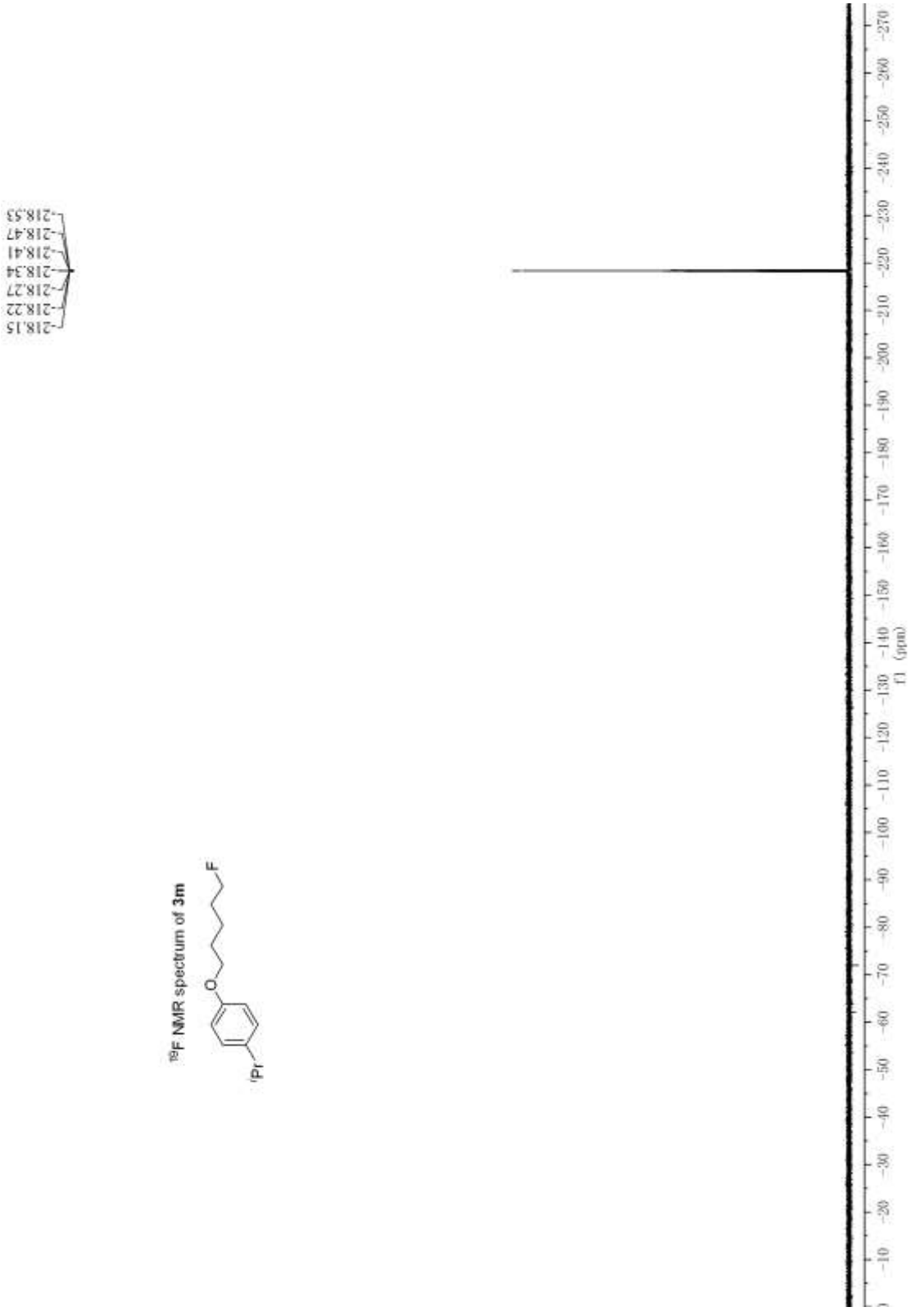
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3l**



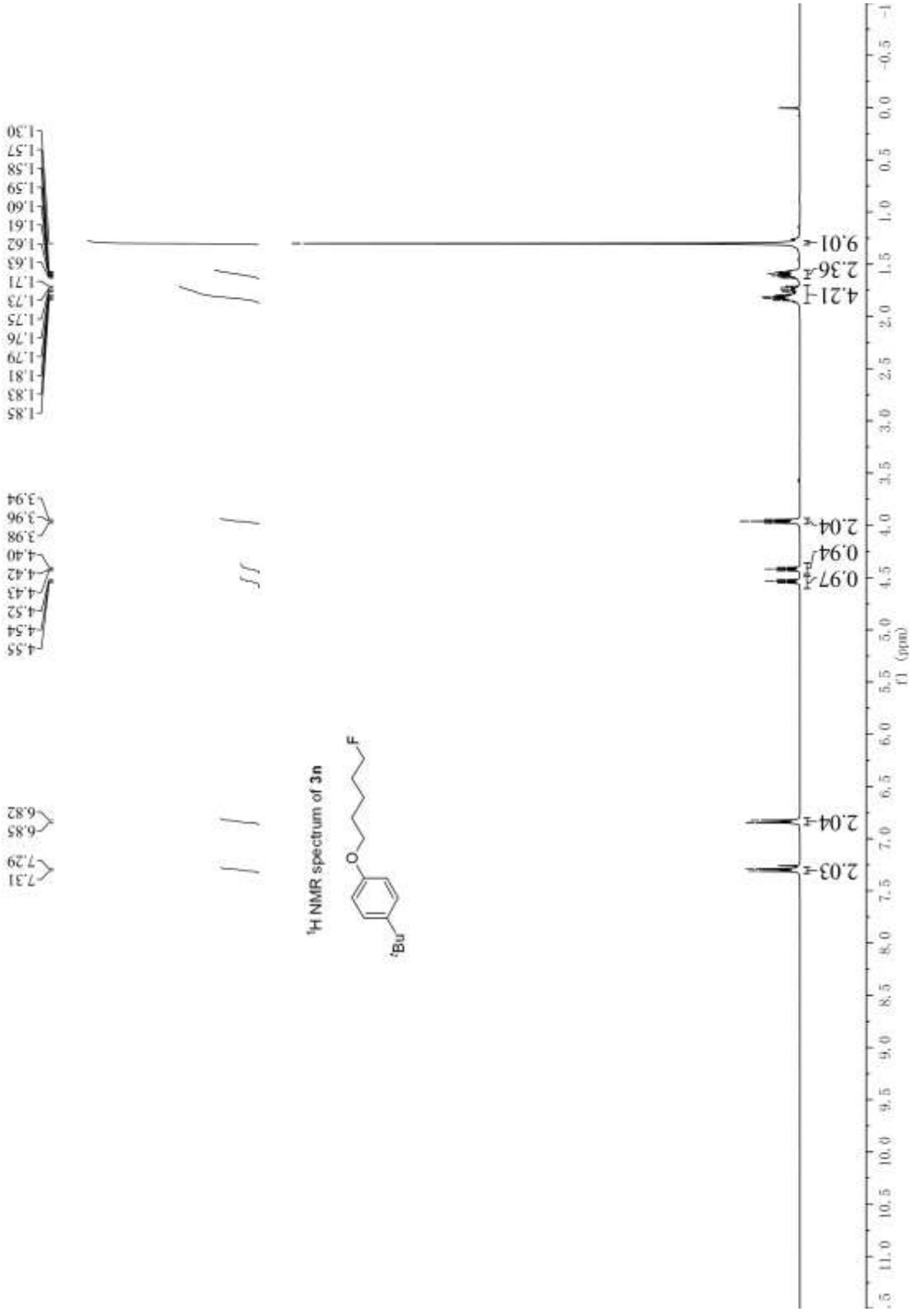
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3m**



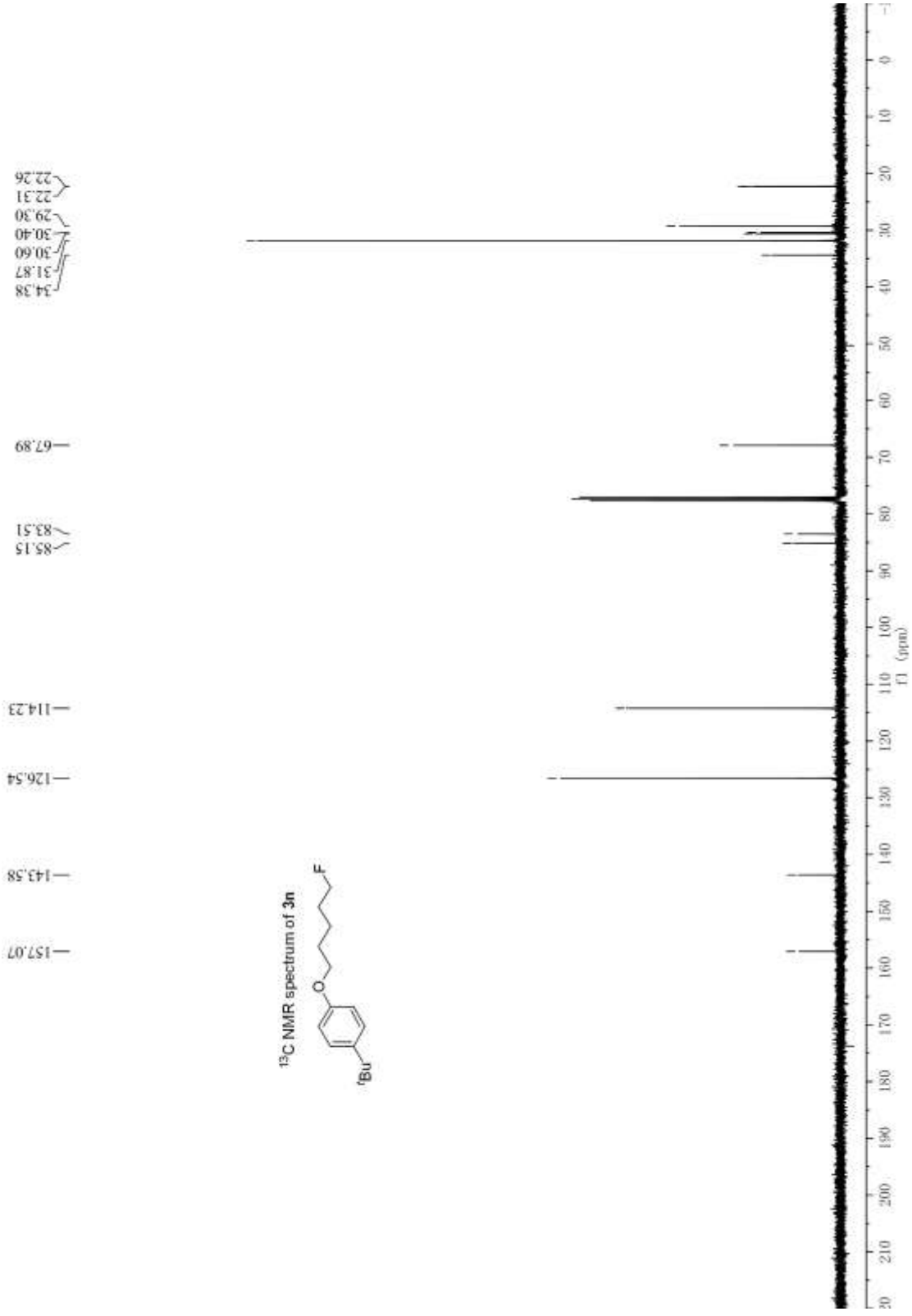
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3m**



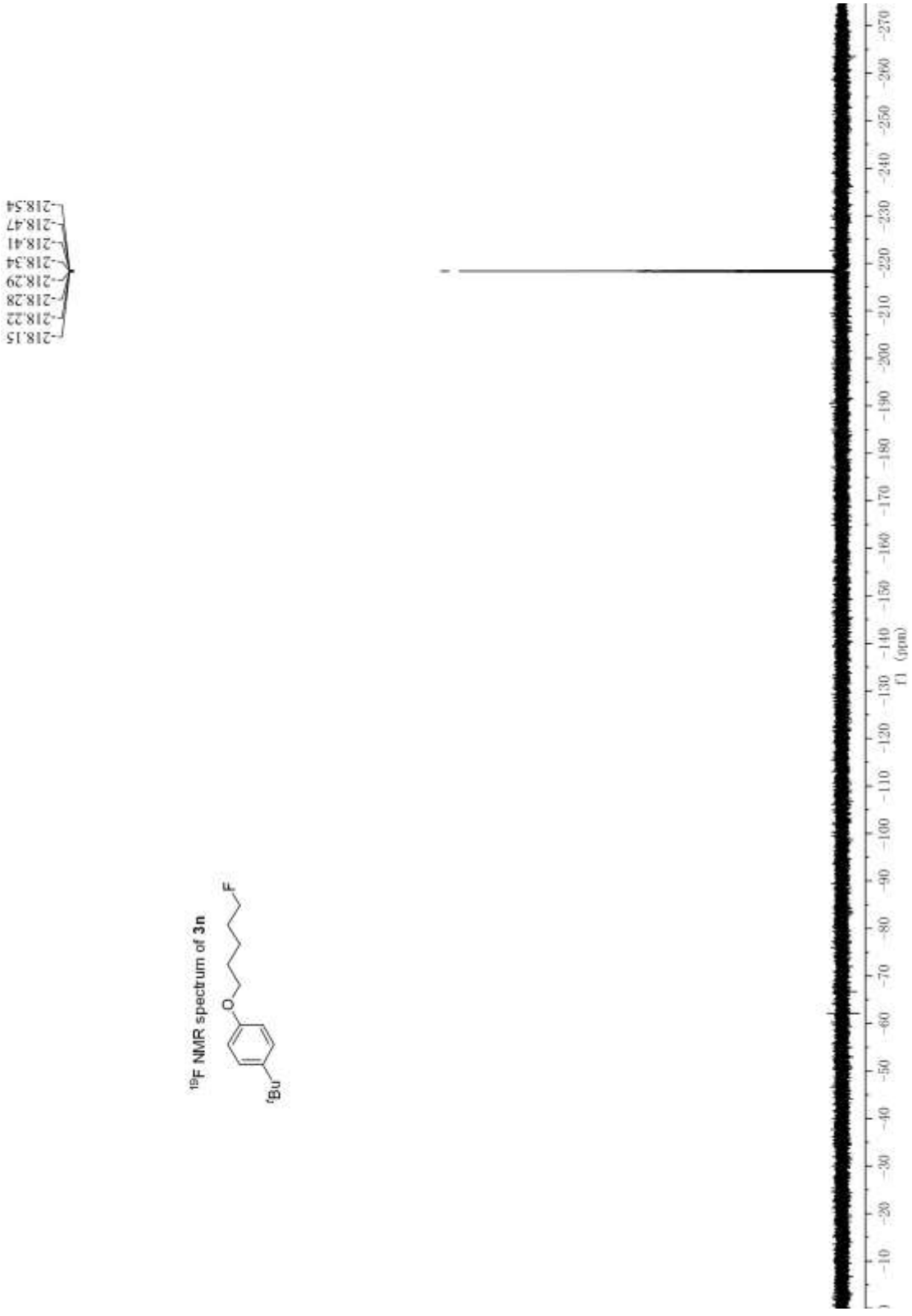
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3m**



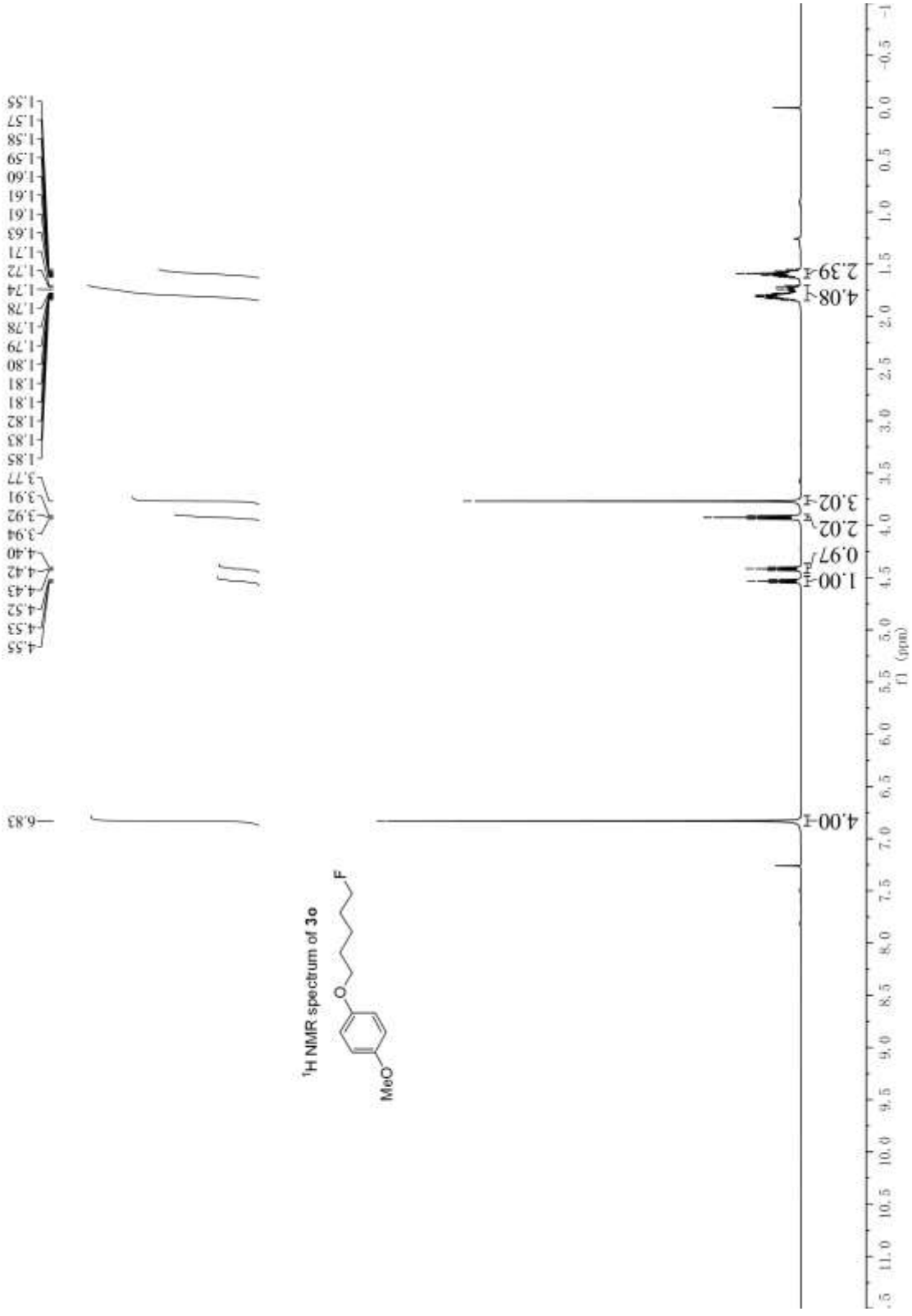
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3n**



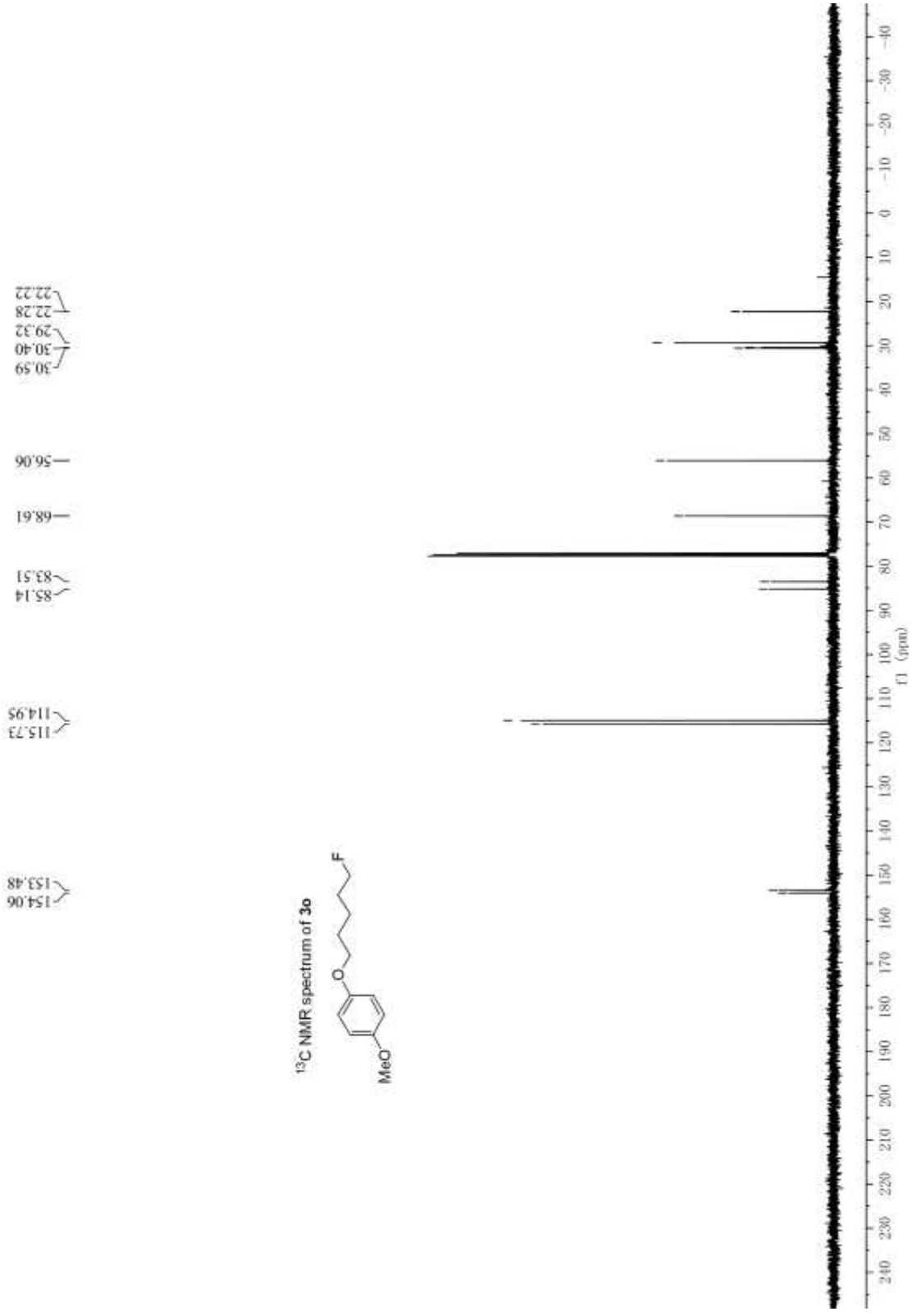
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3n**



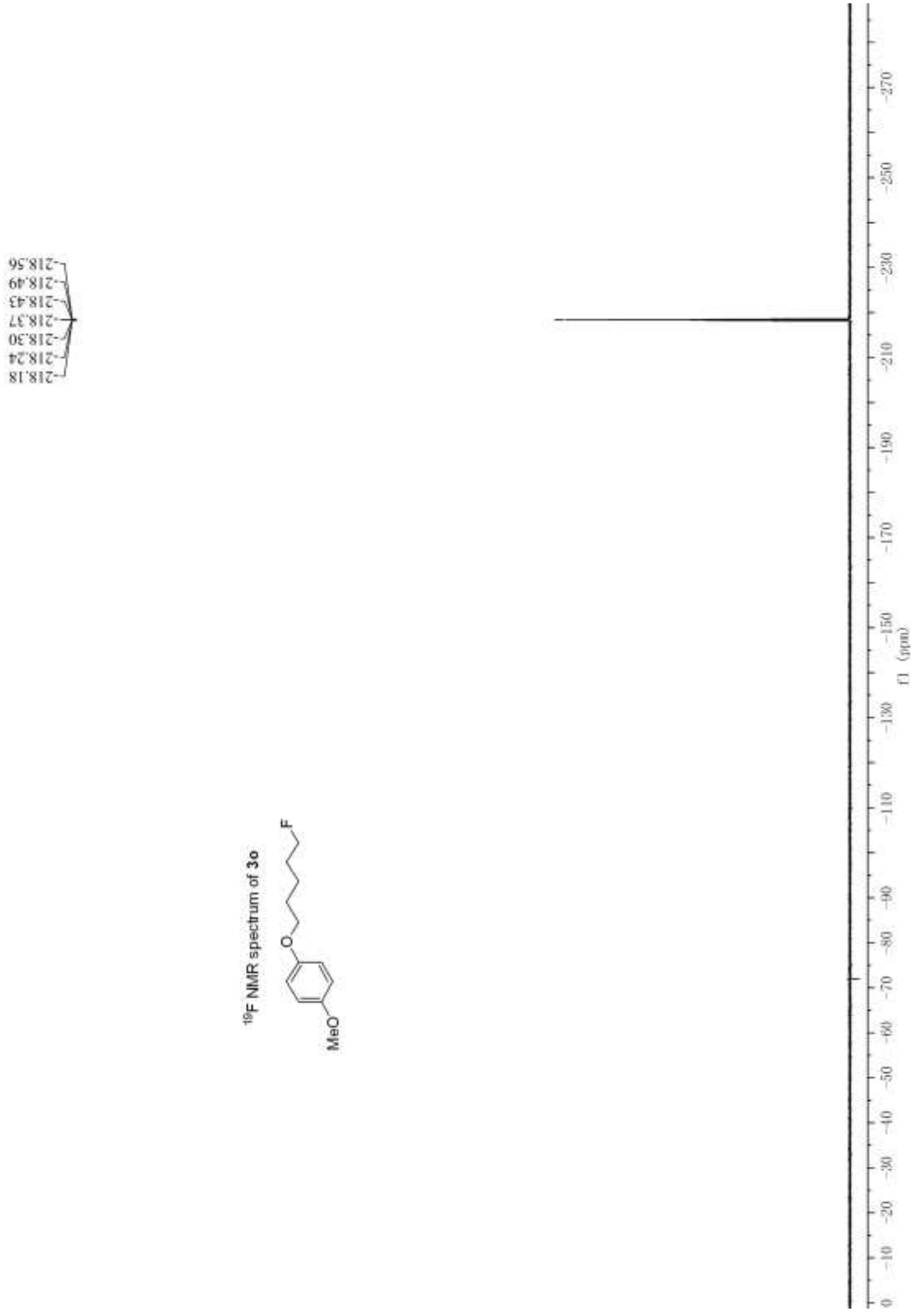
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3n**



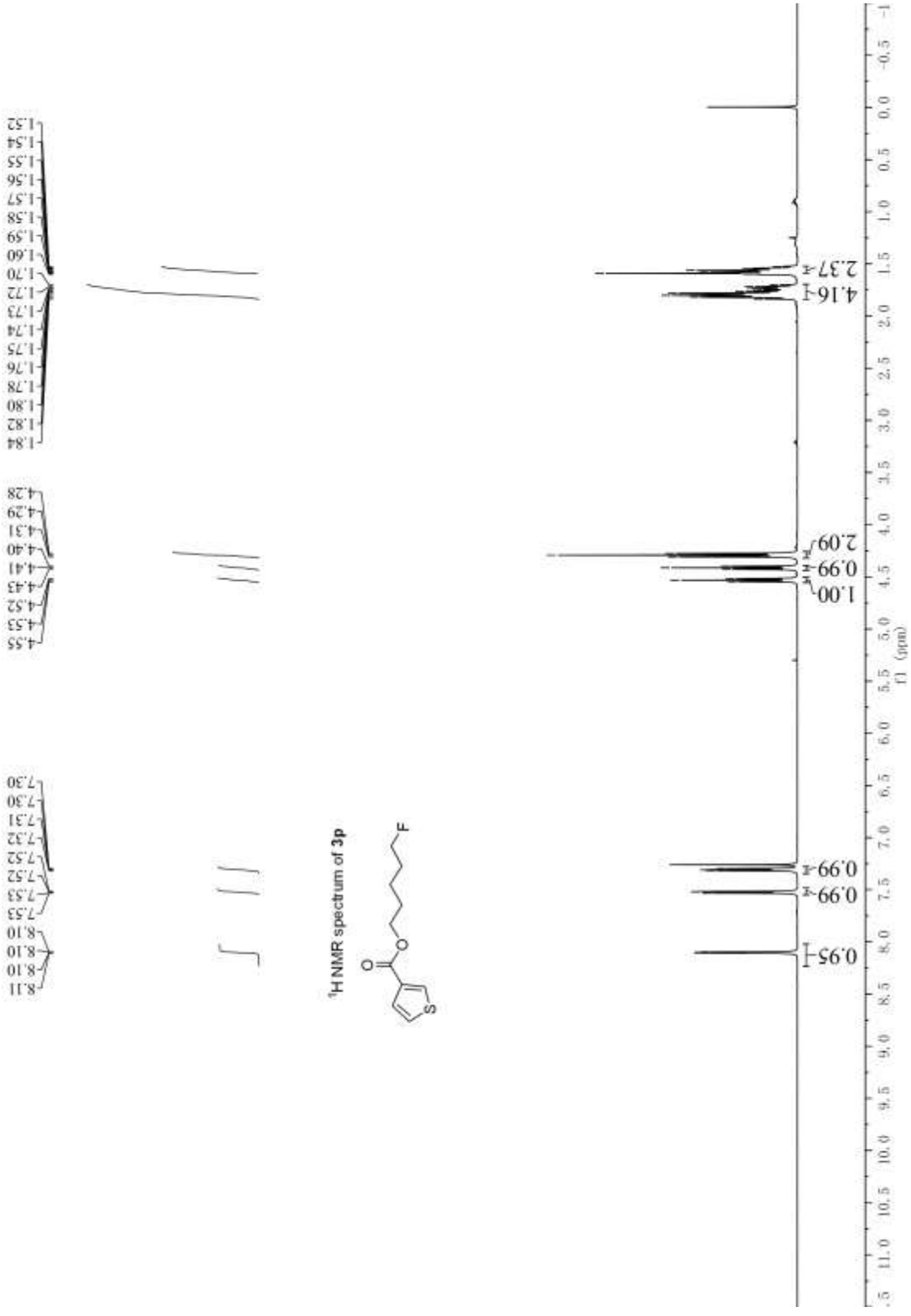
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3o**



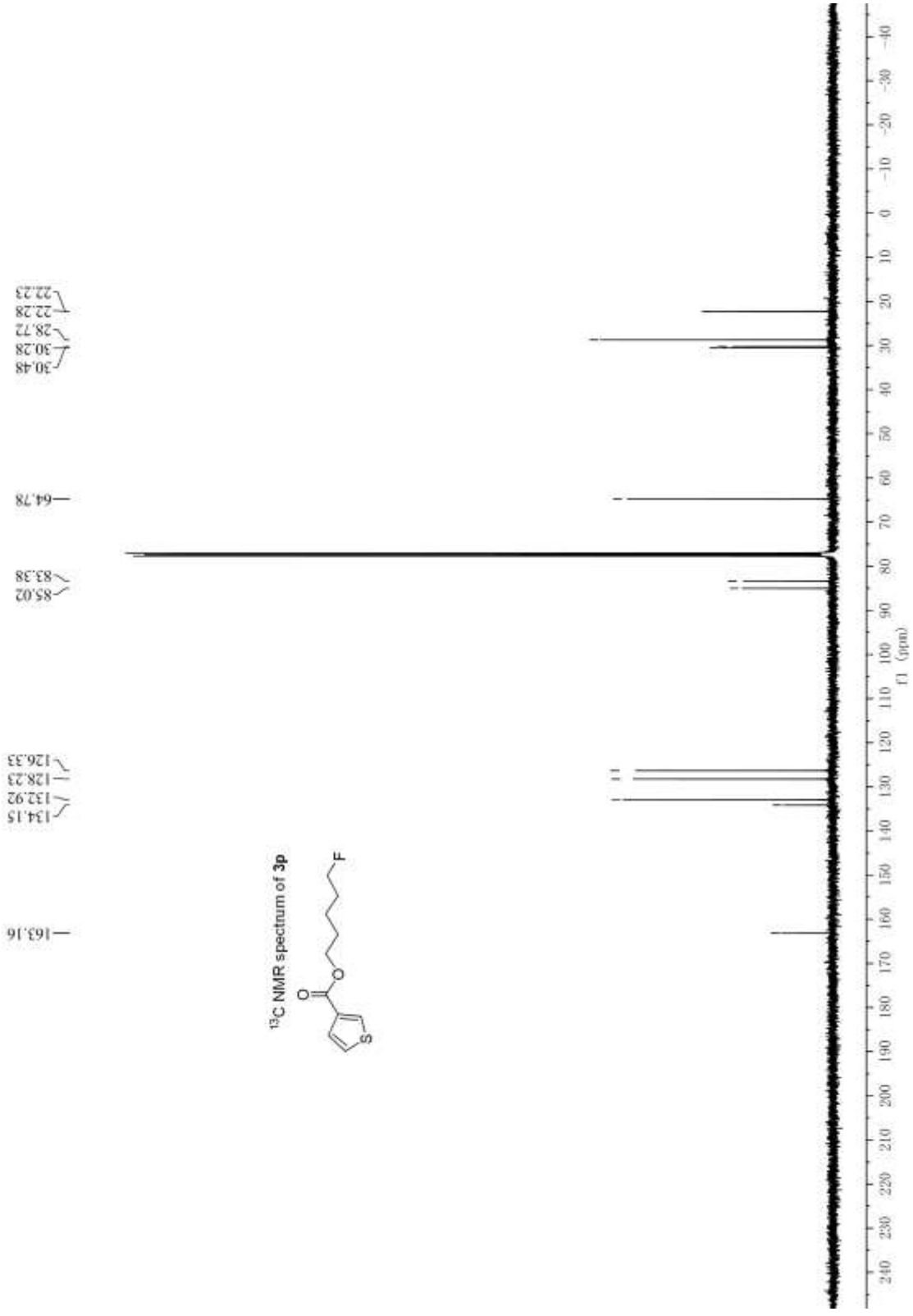
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3o**



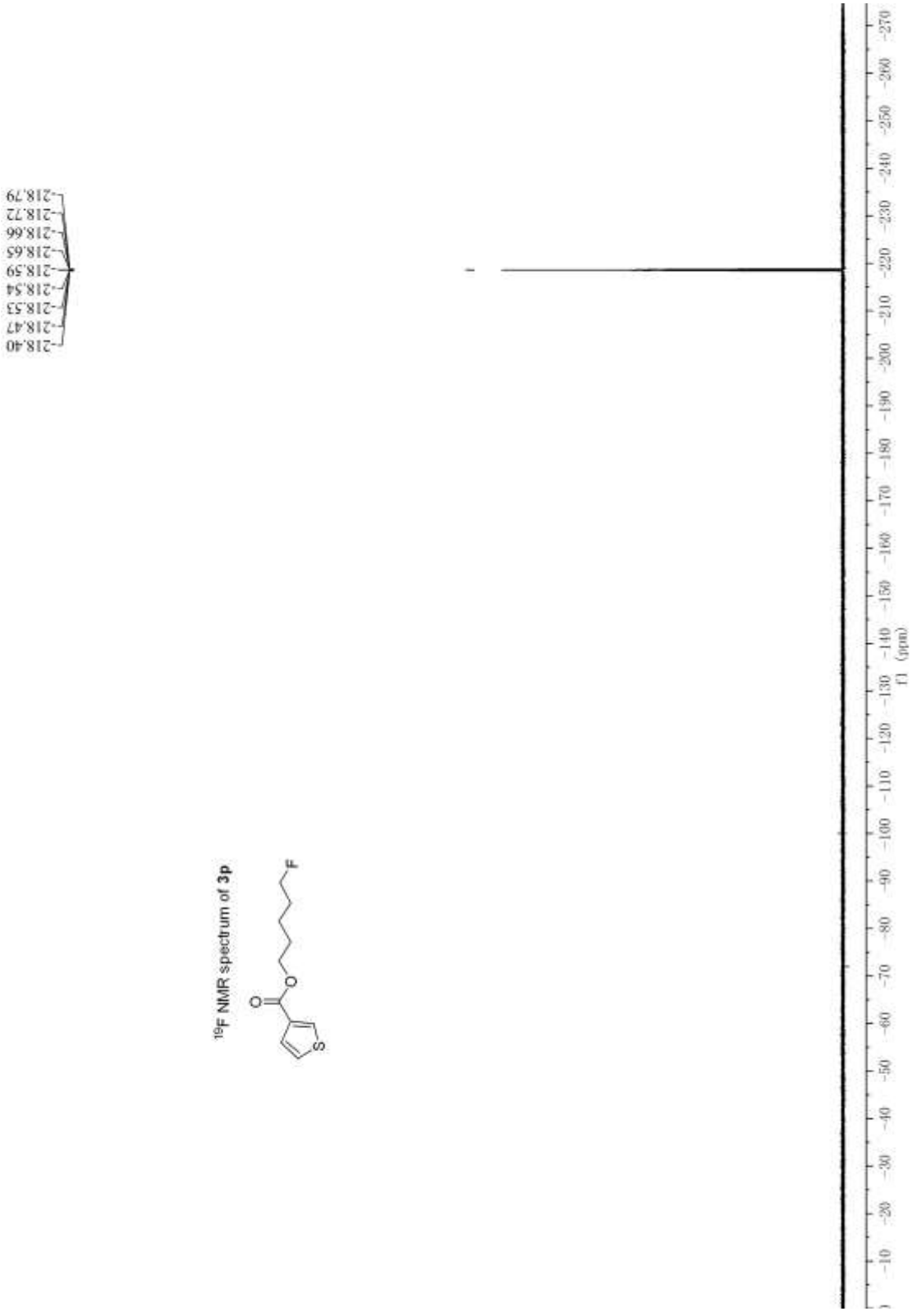
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3o**



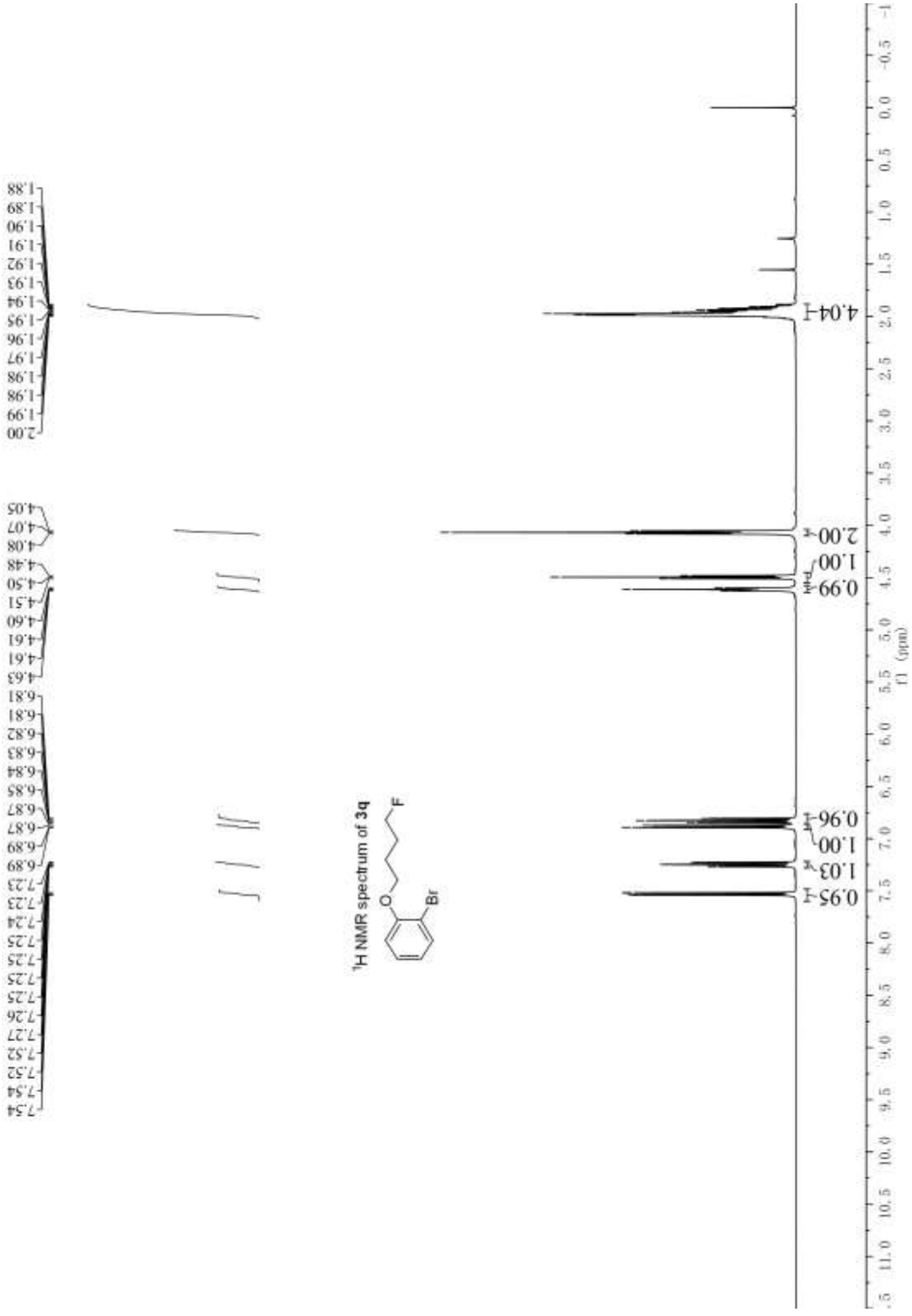
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3p**



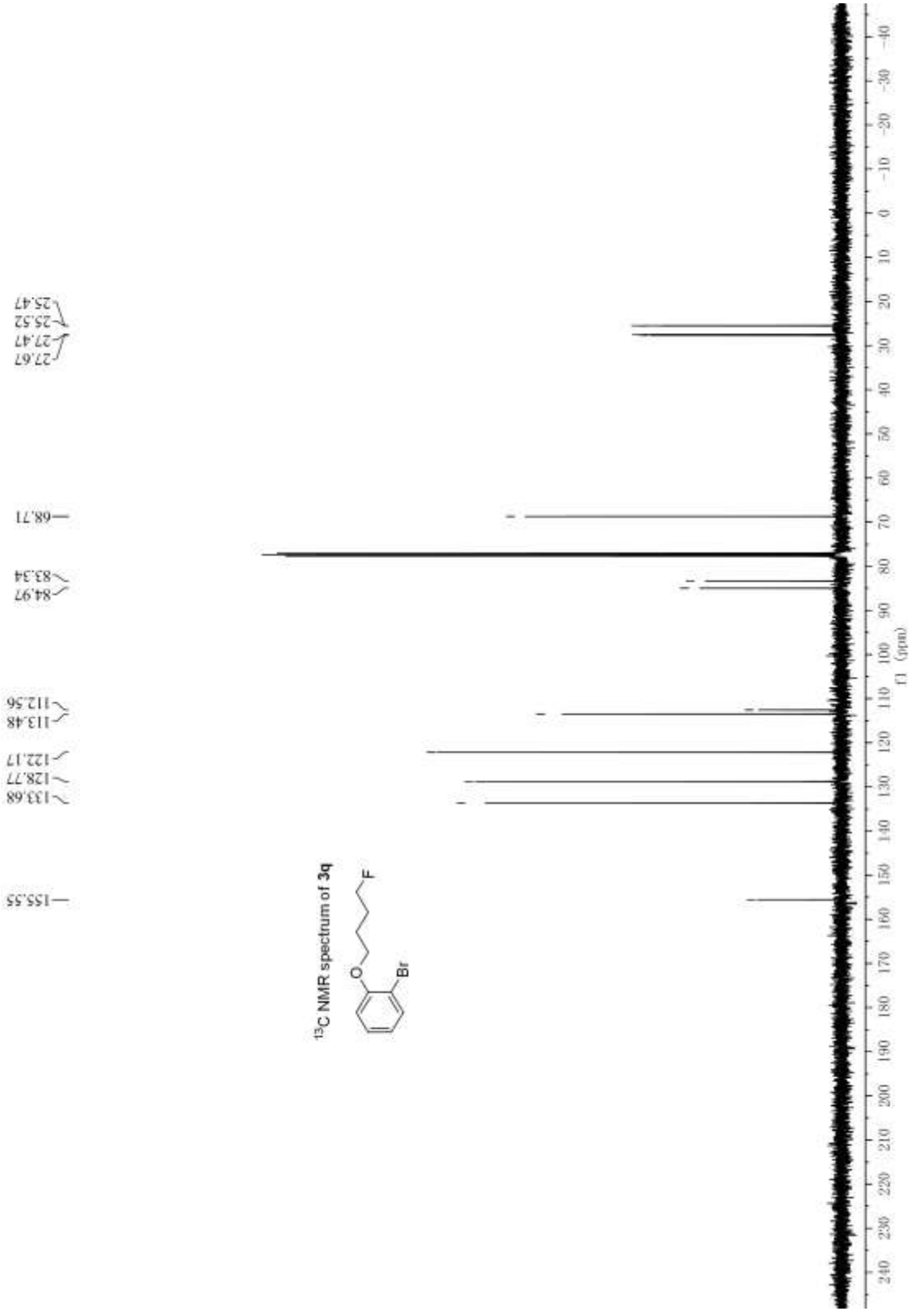
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3p**



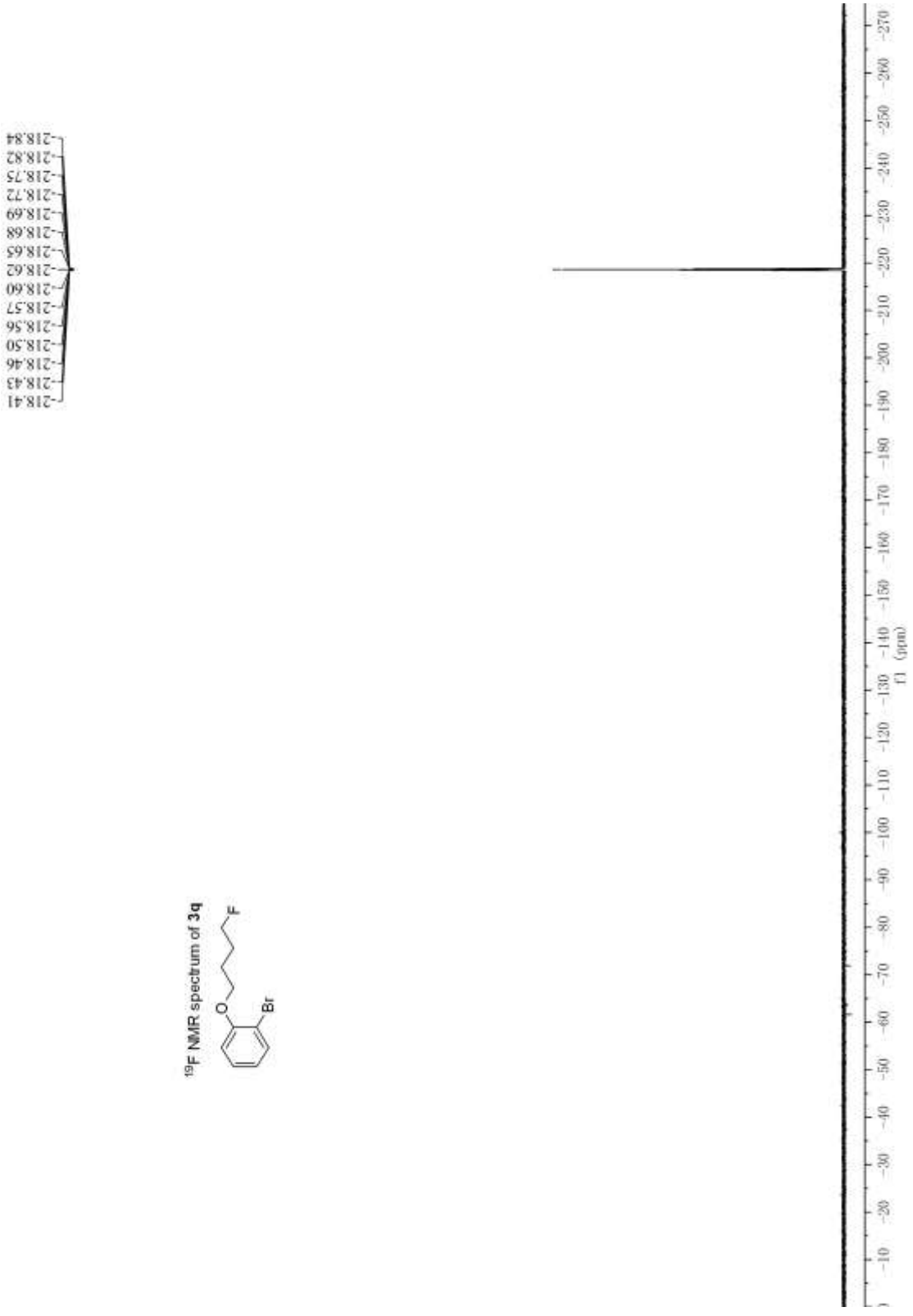
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3p**



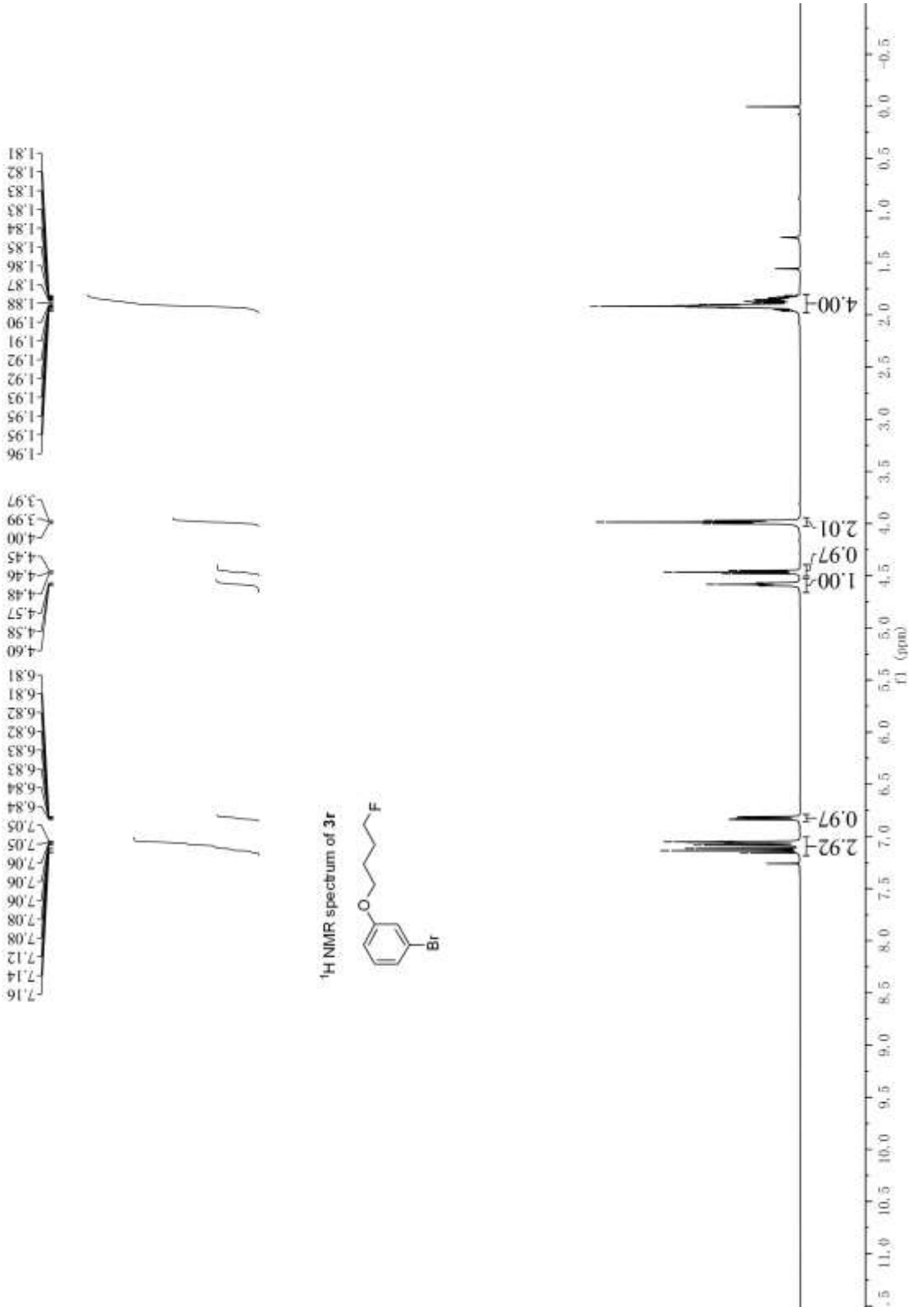
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3q**



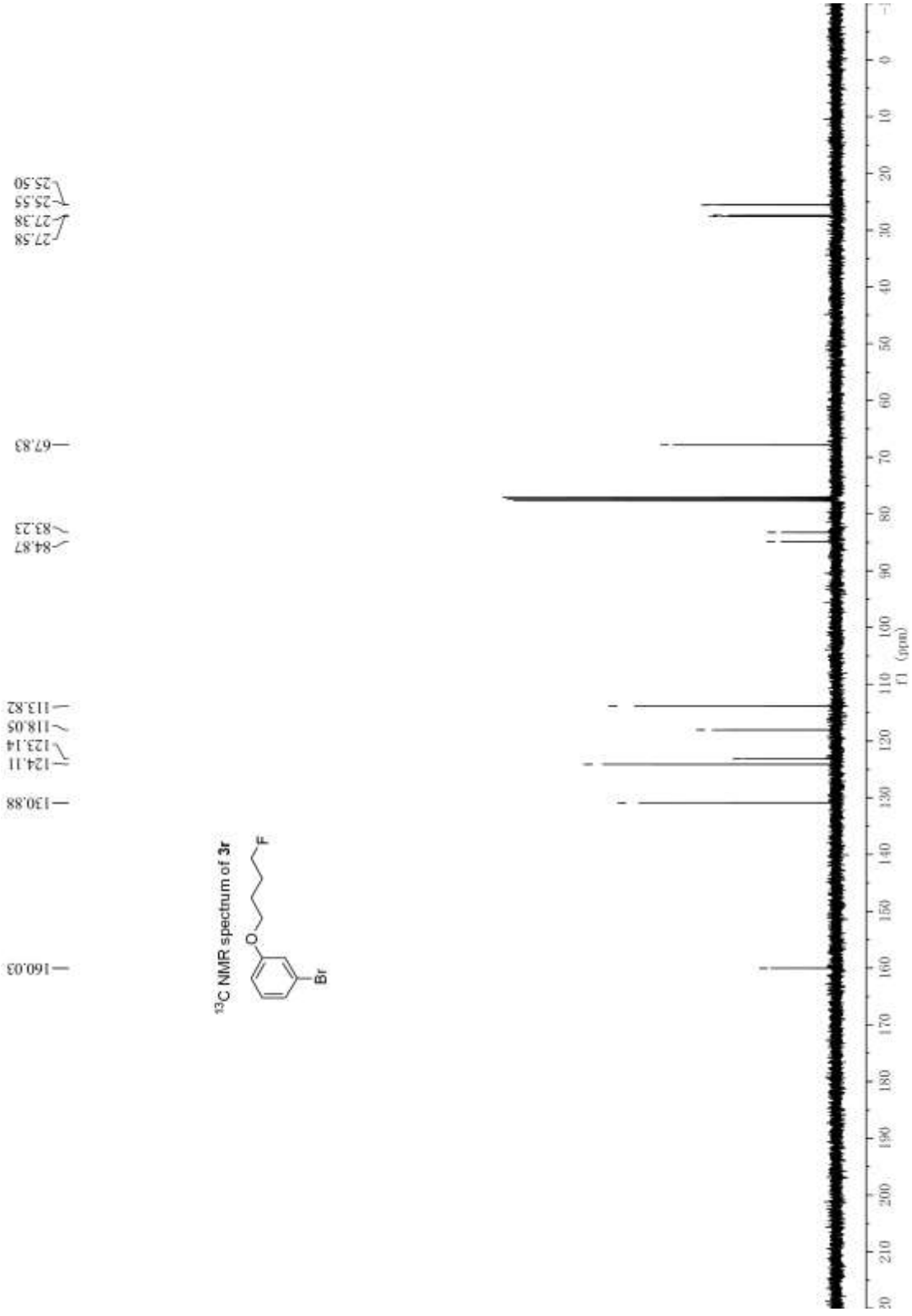
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3q**



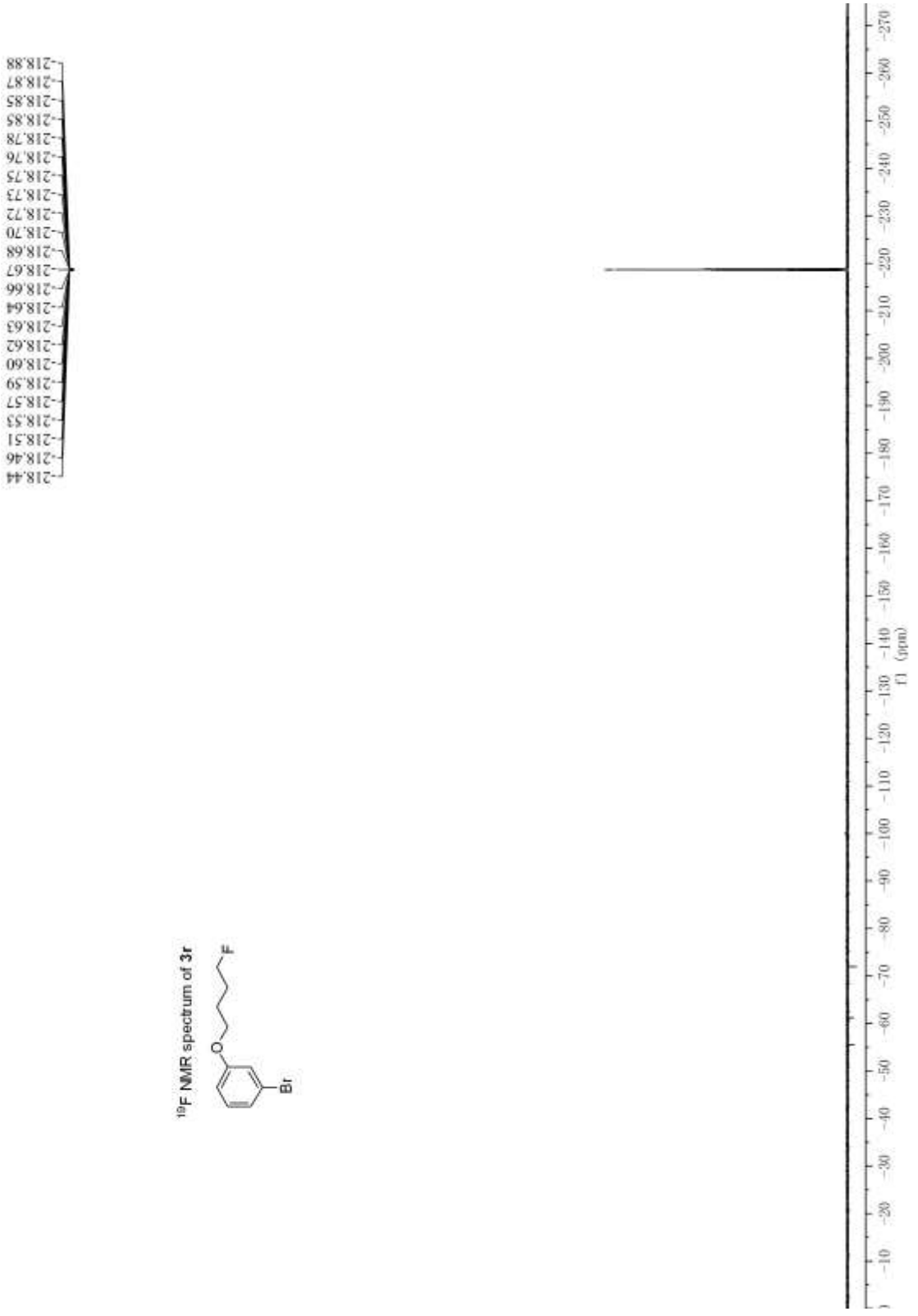
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3q**



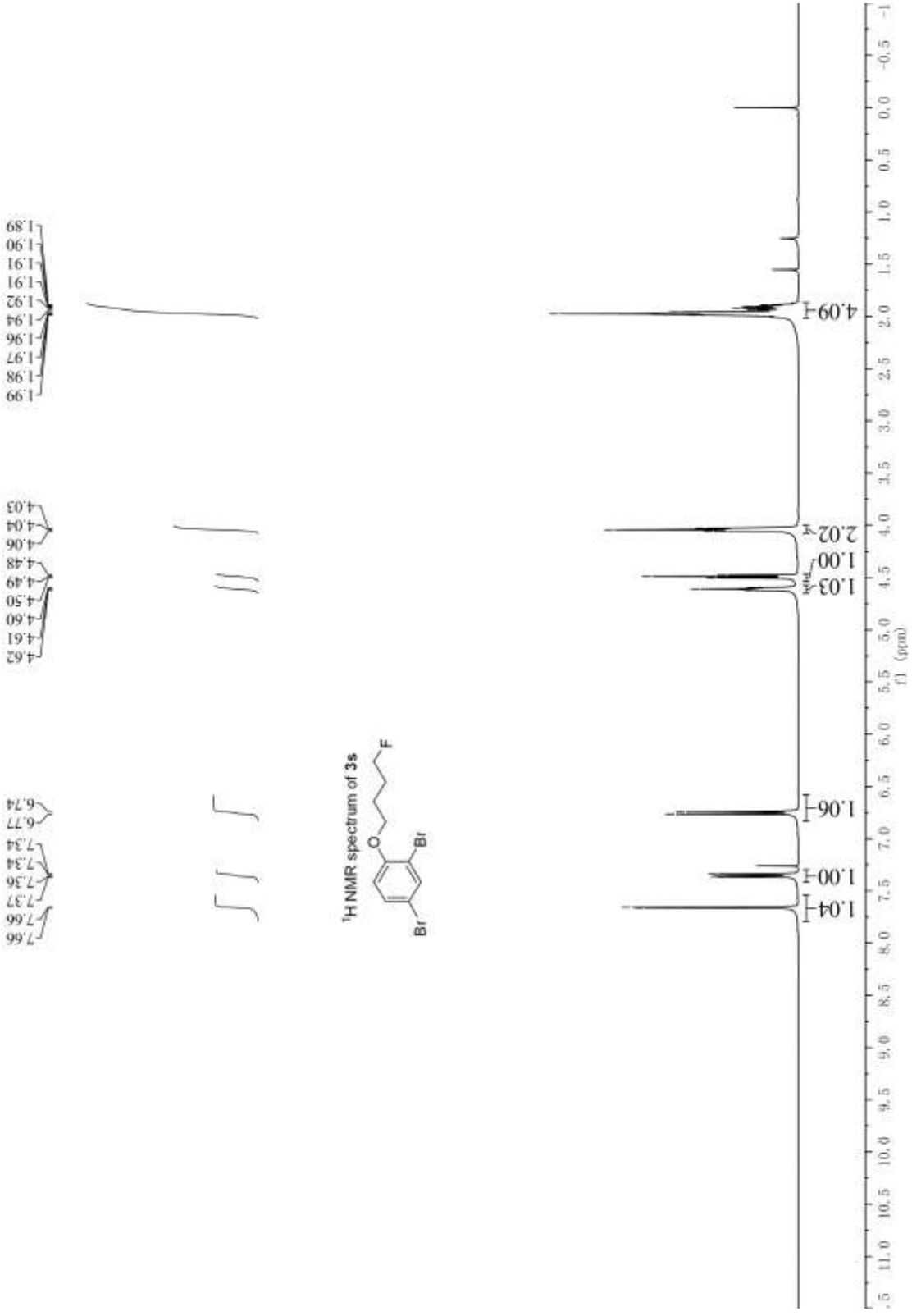
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3r**



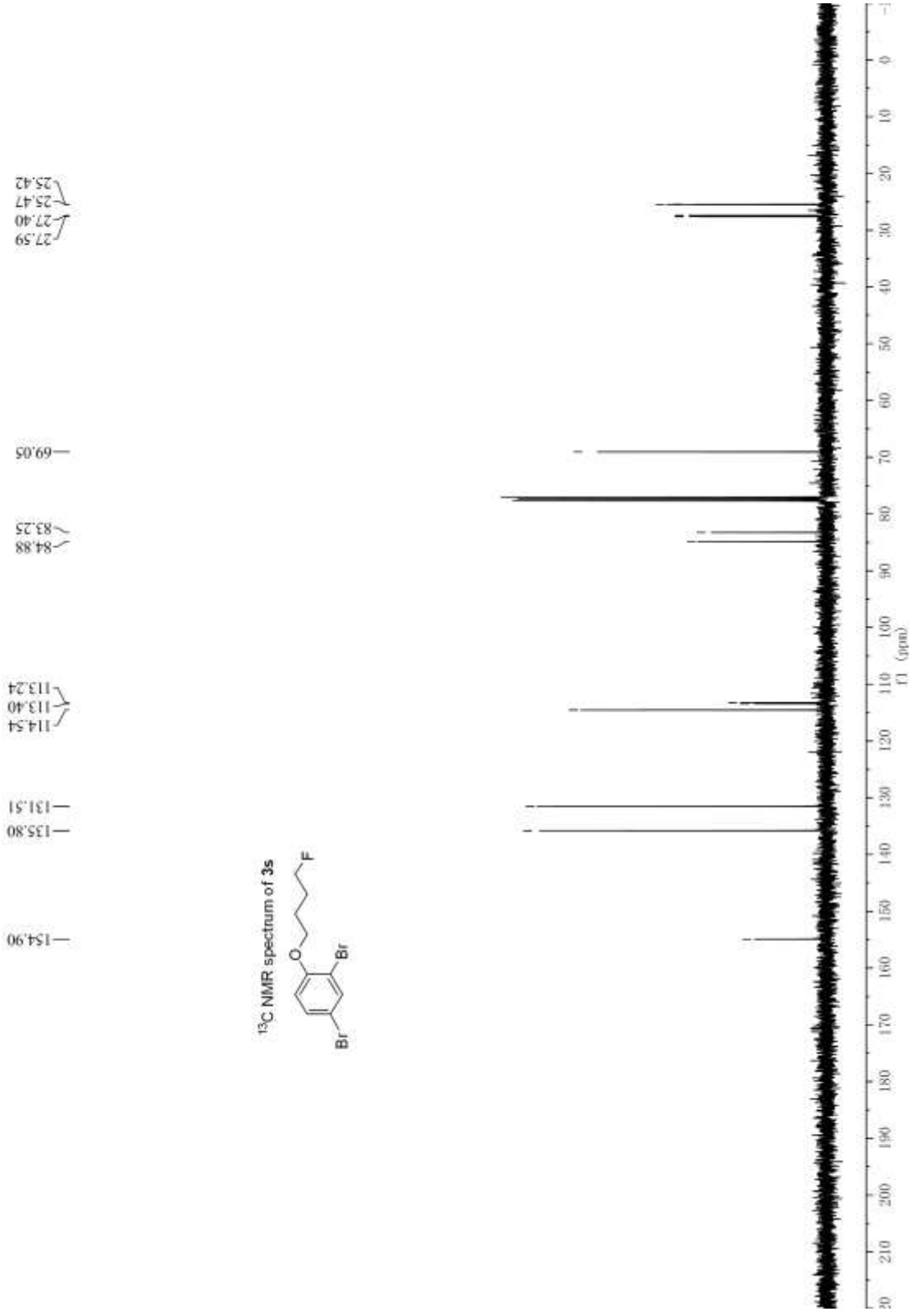
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3r**



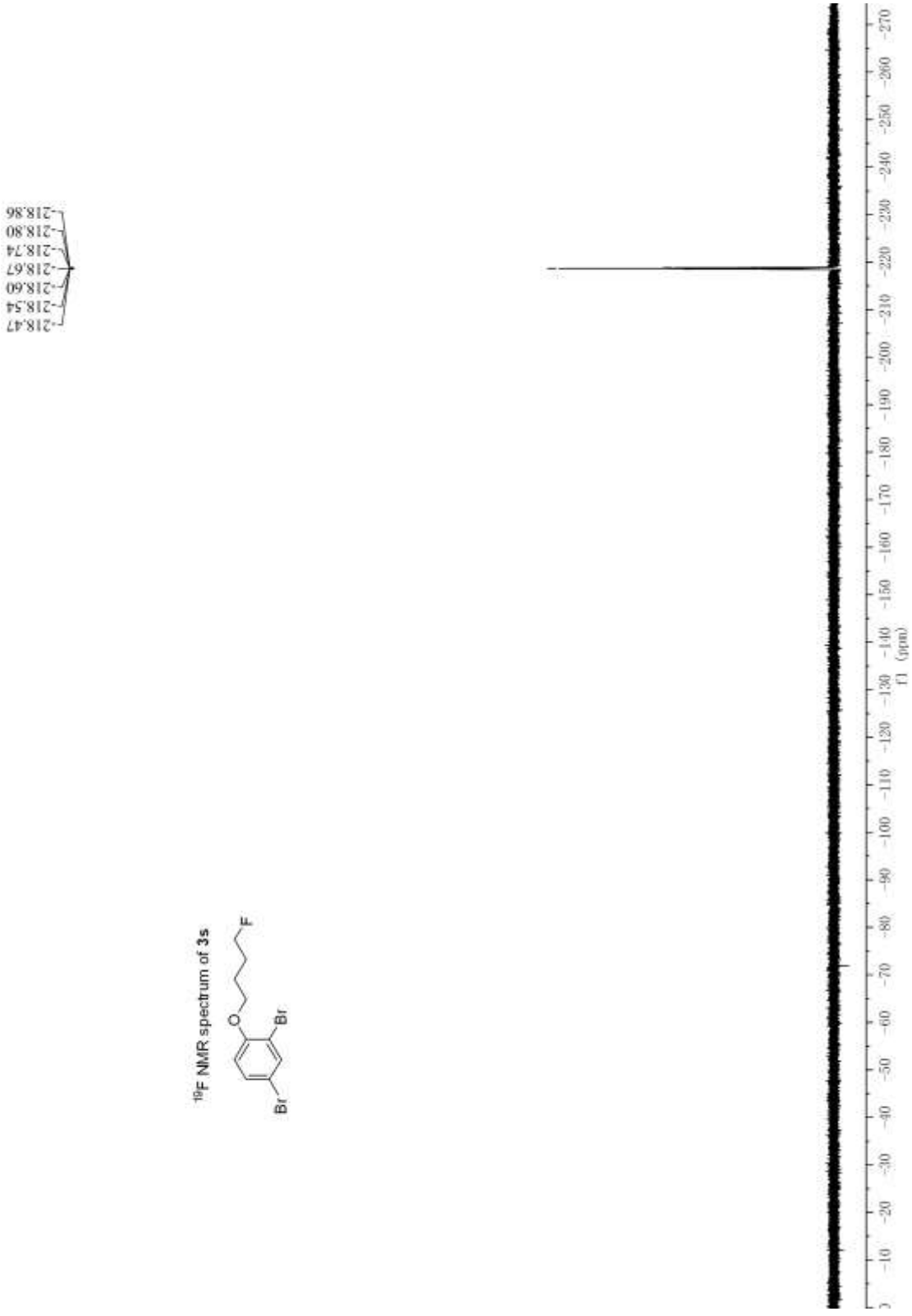
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3r**



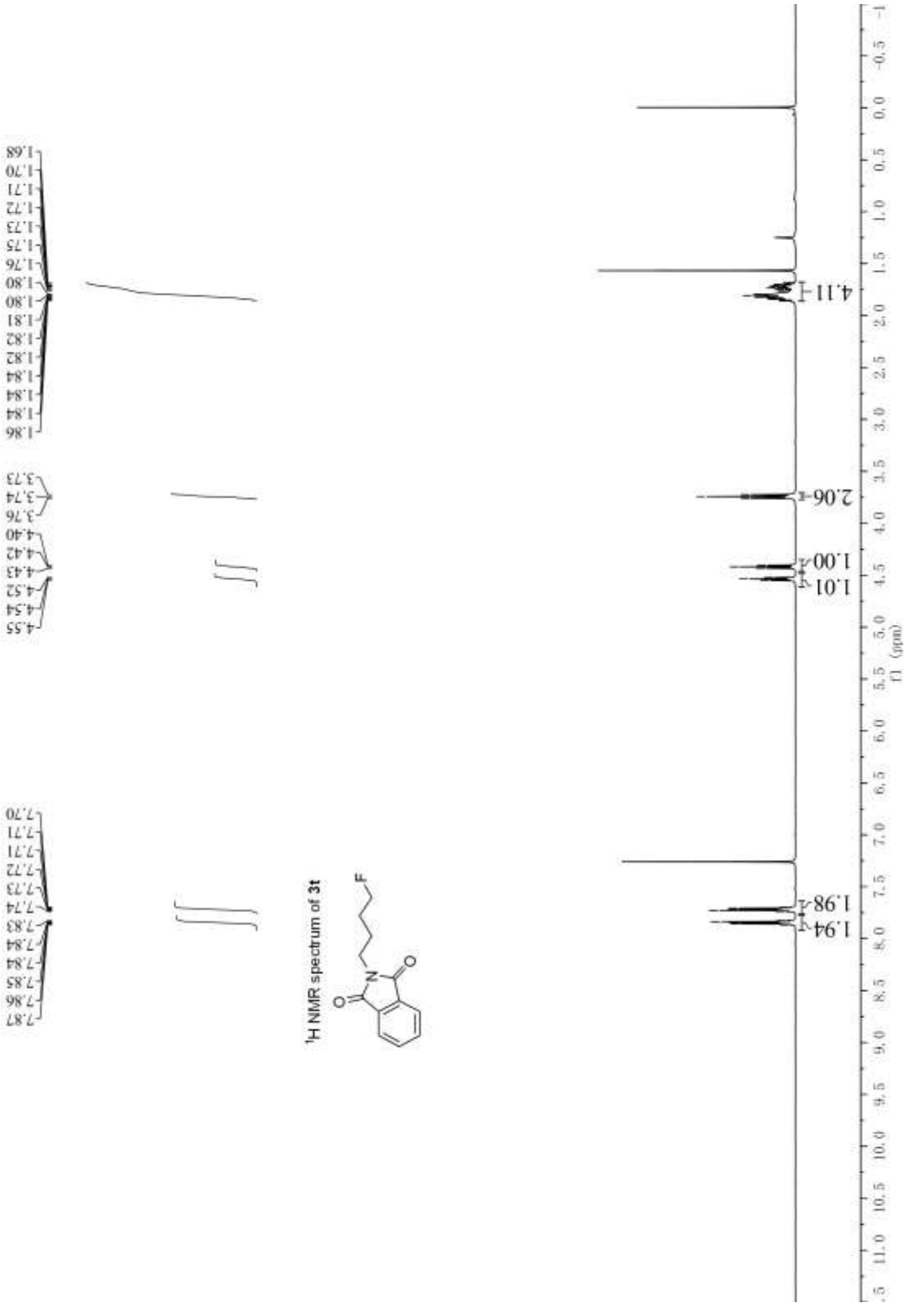
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3s**



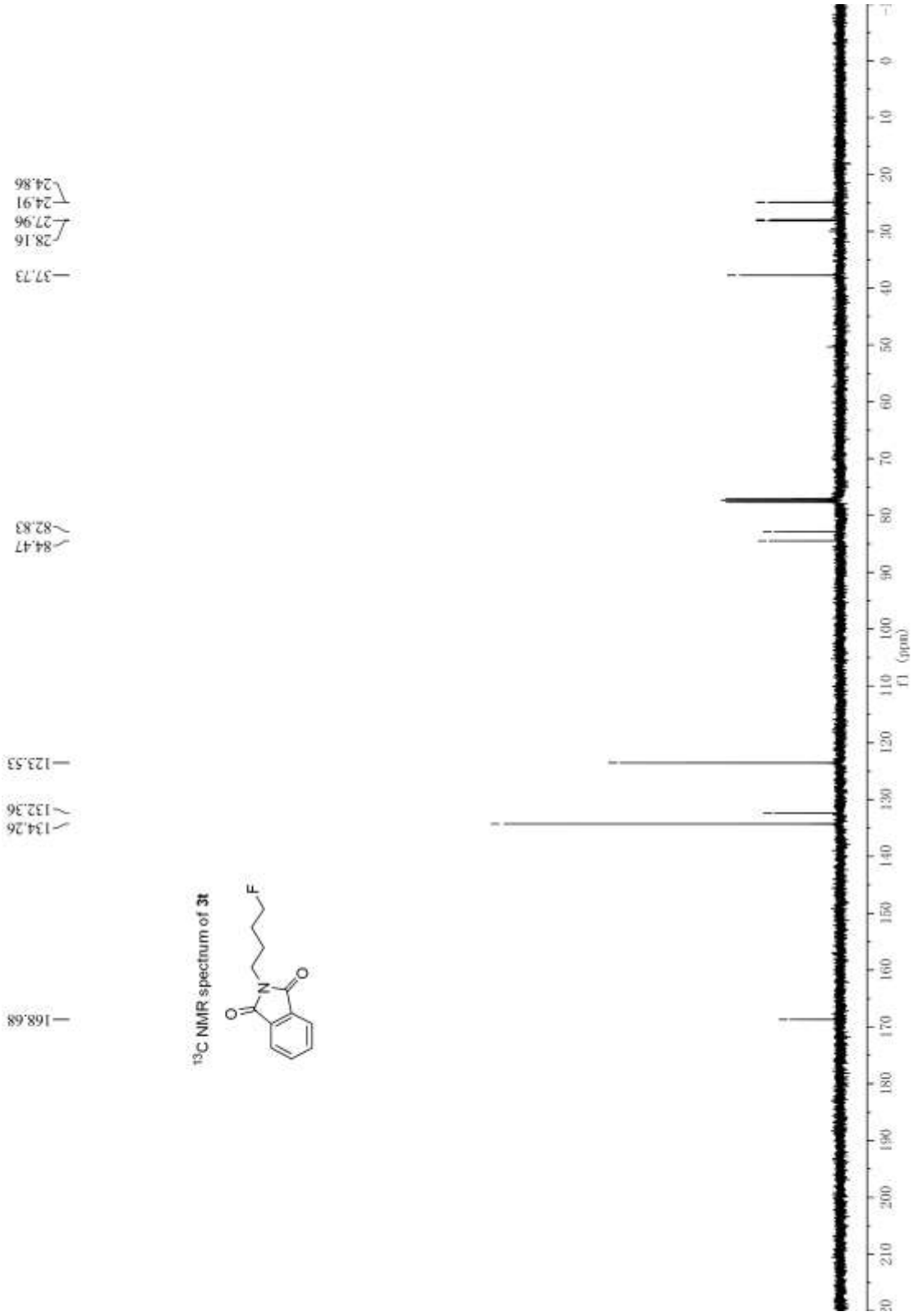
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3s**



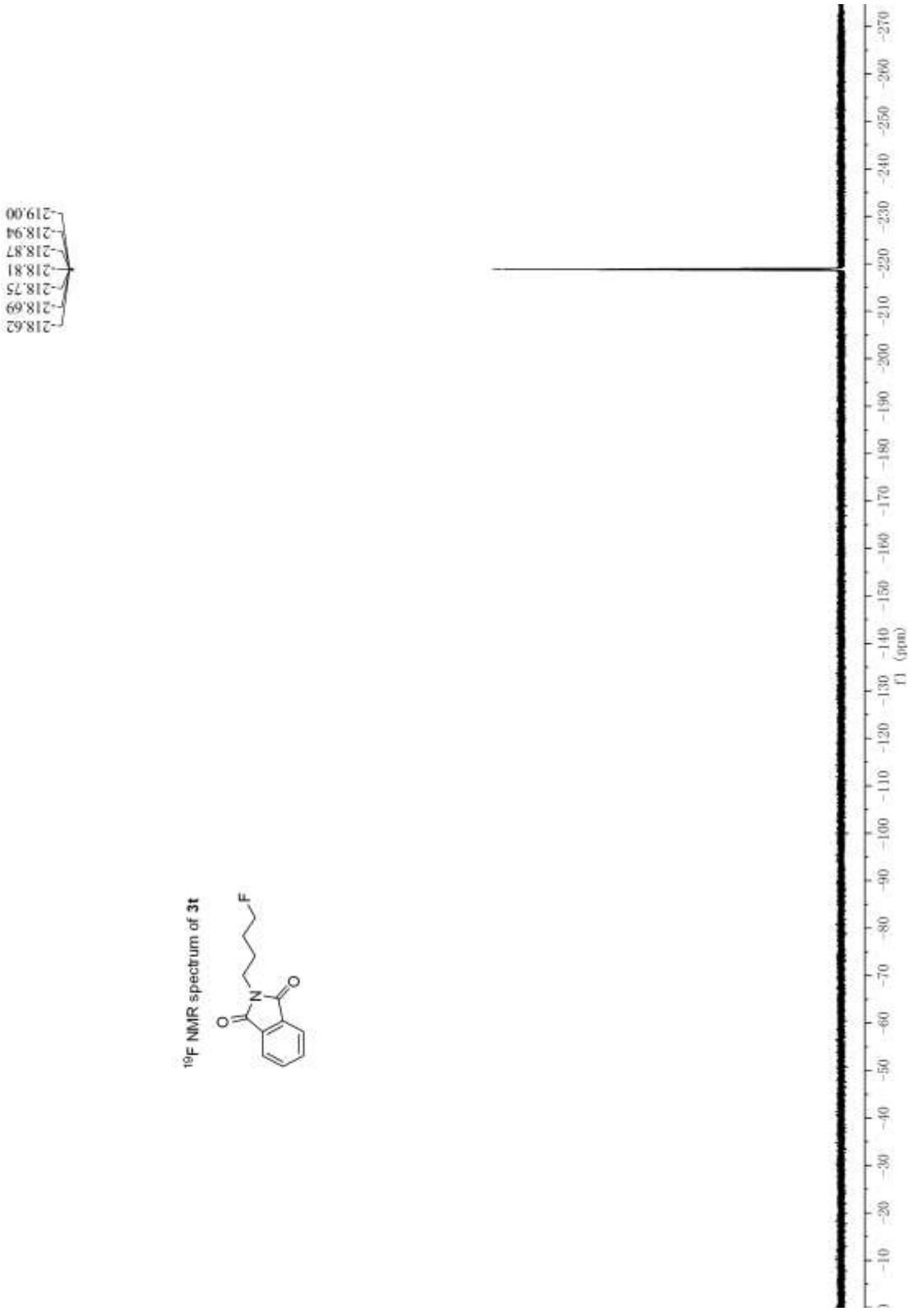
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3s**



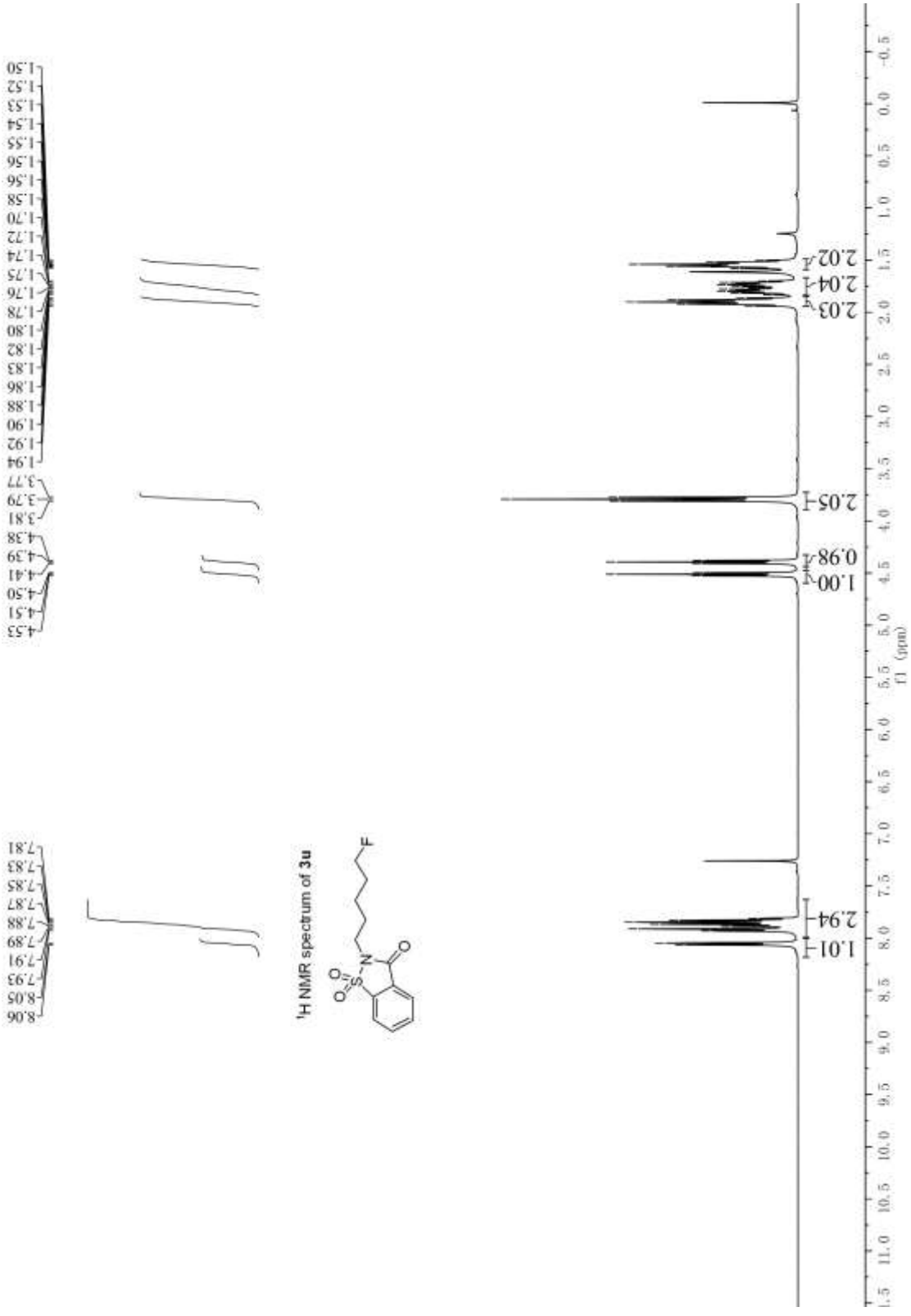
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3t**



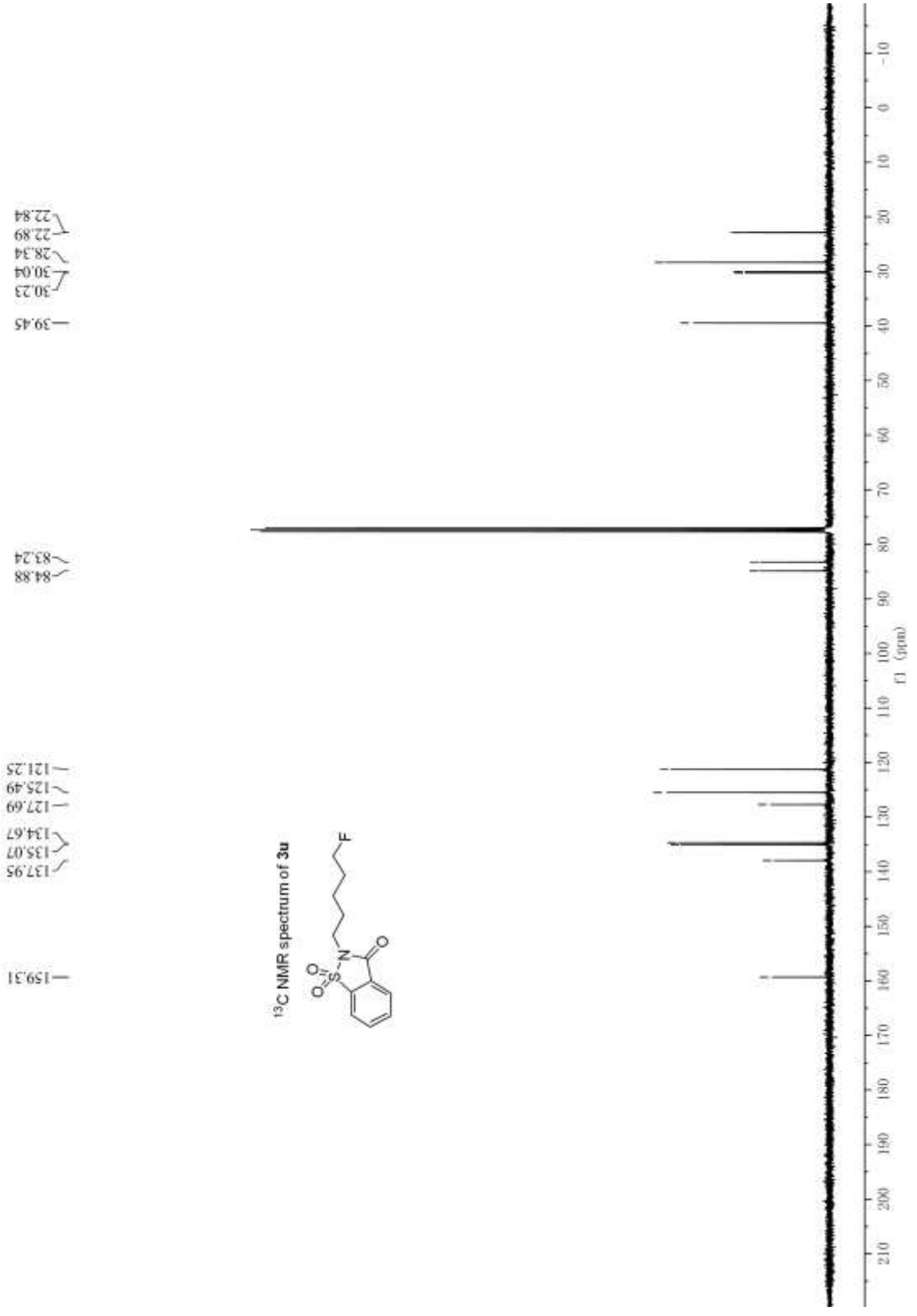
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3t**



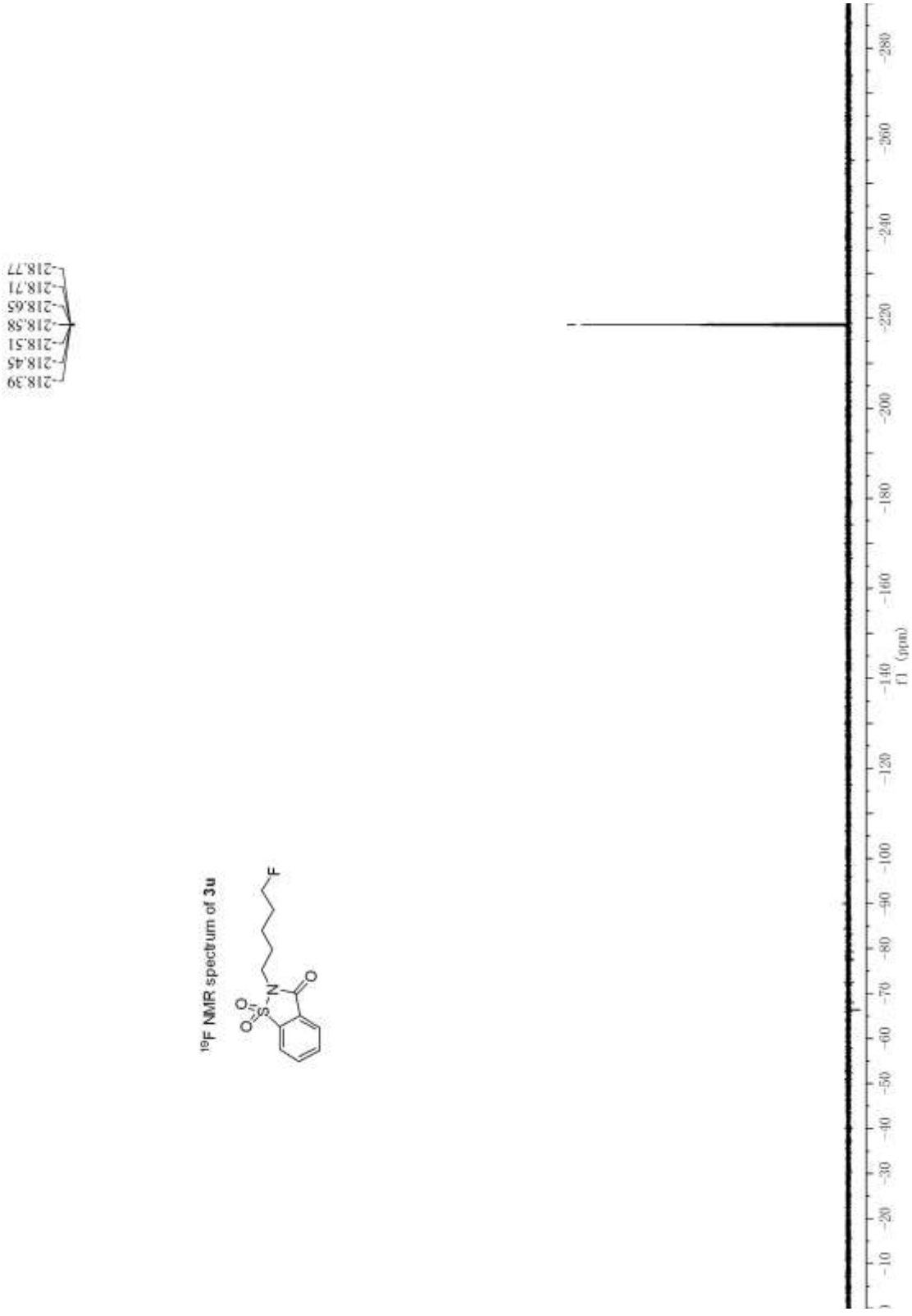
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3t**



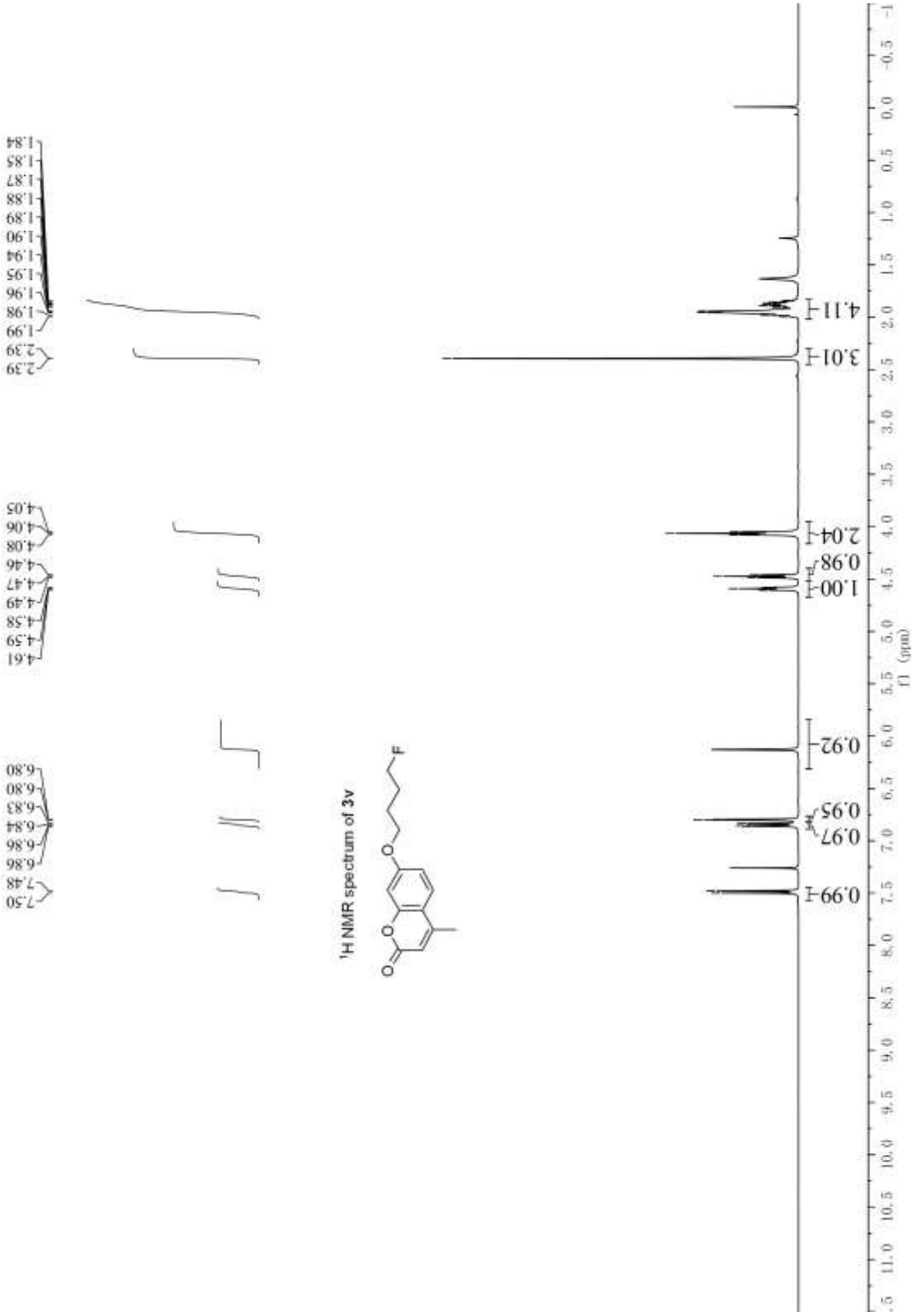
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3u**



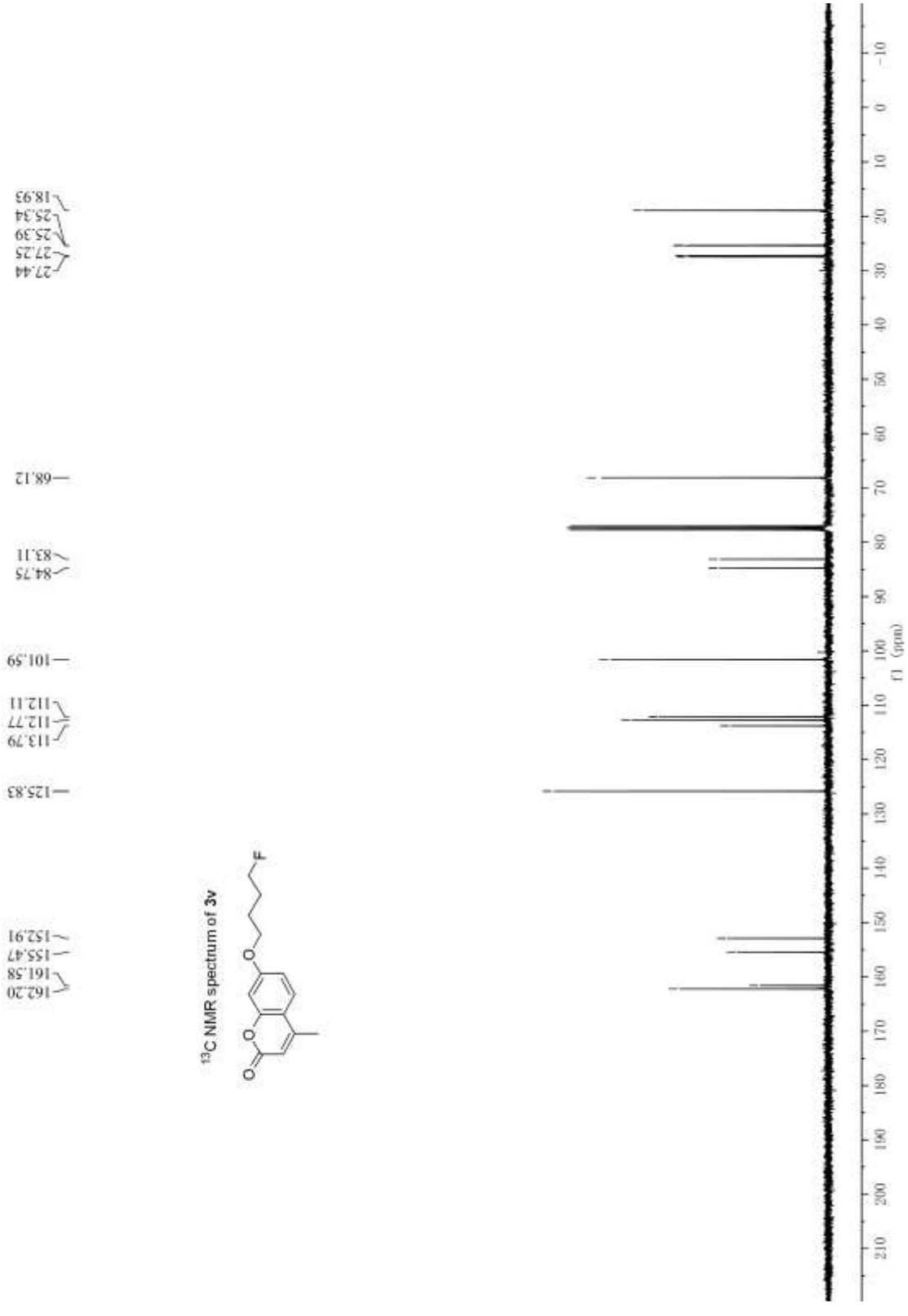
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3u**



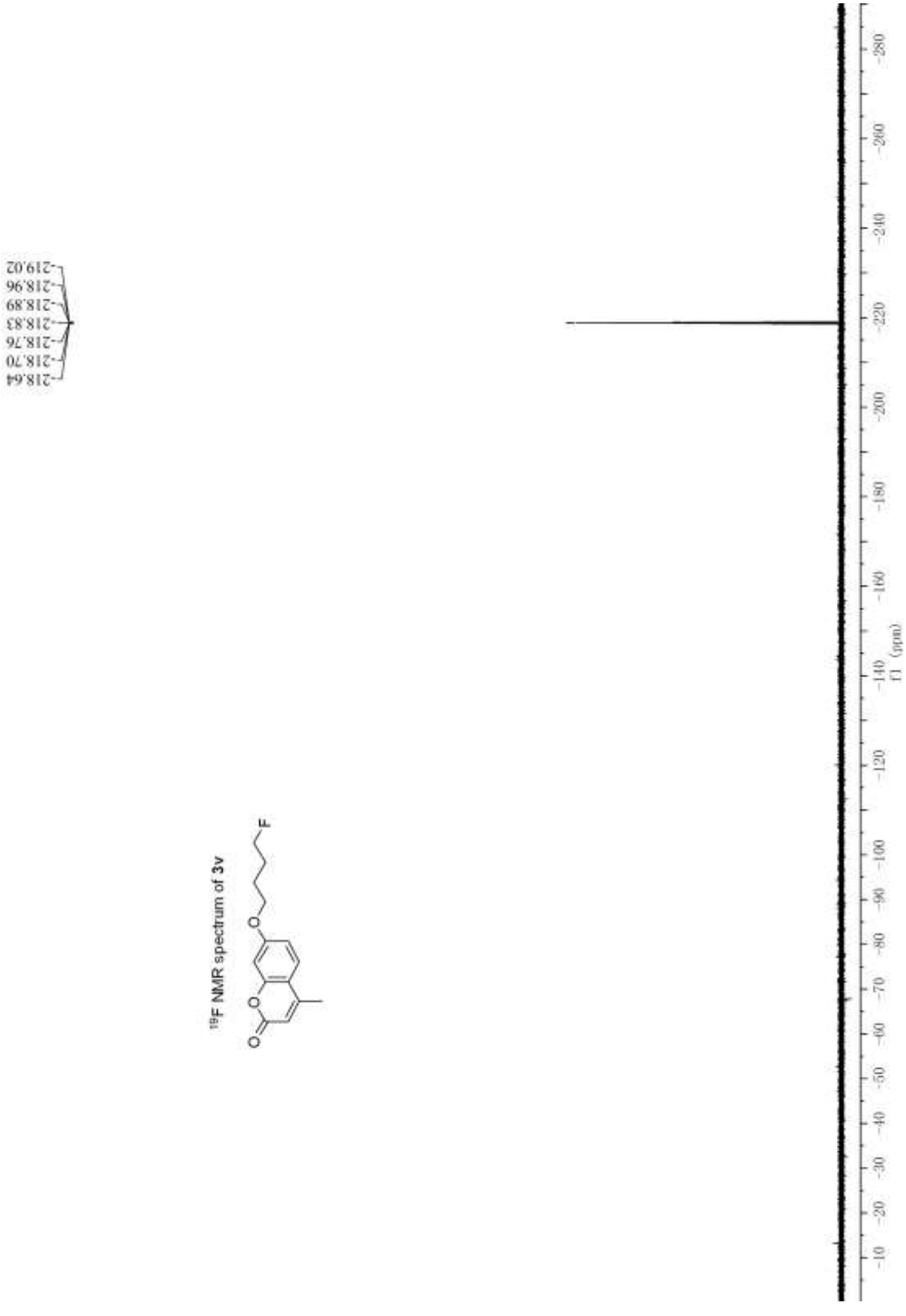
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3u**



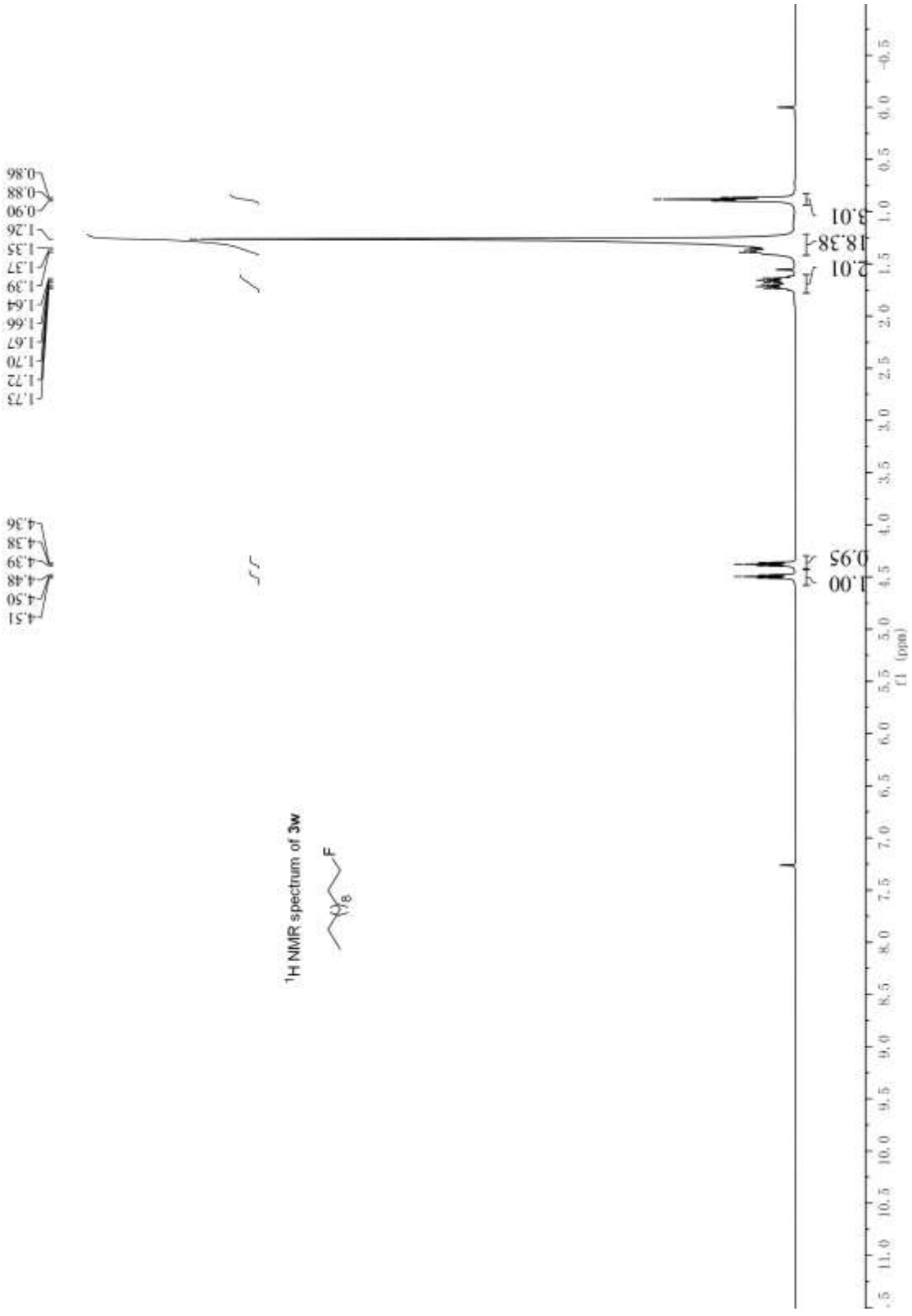
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3v**



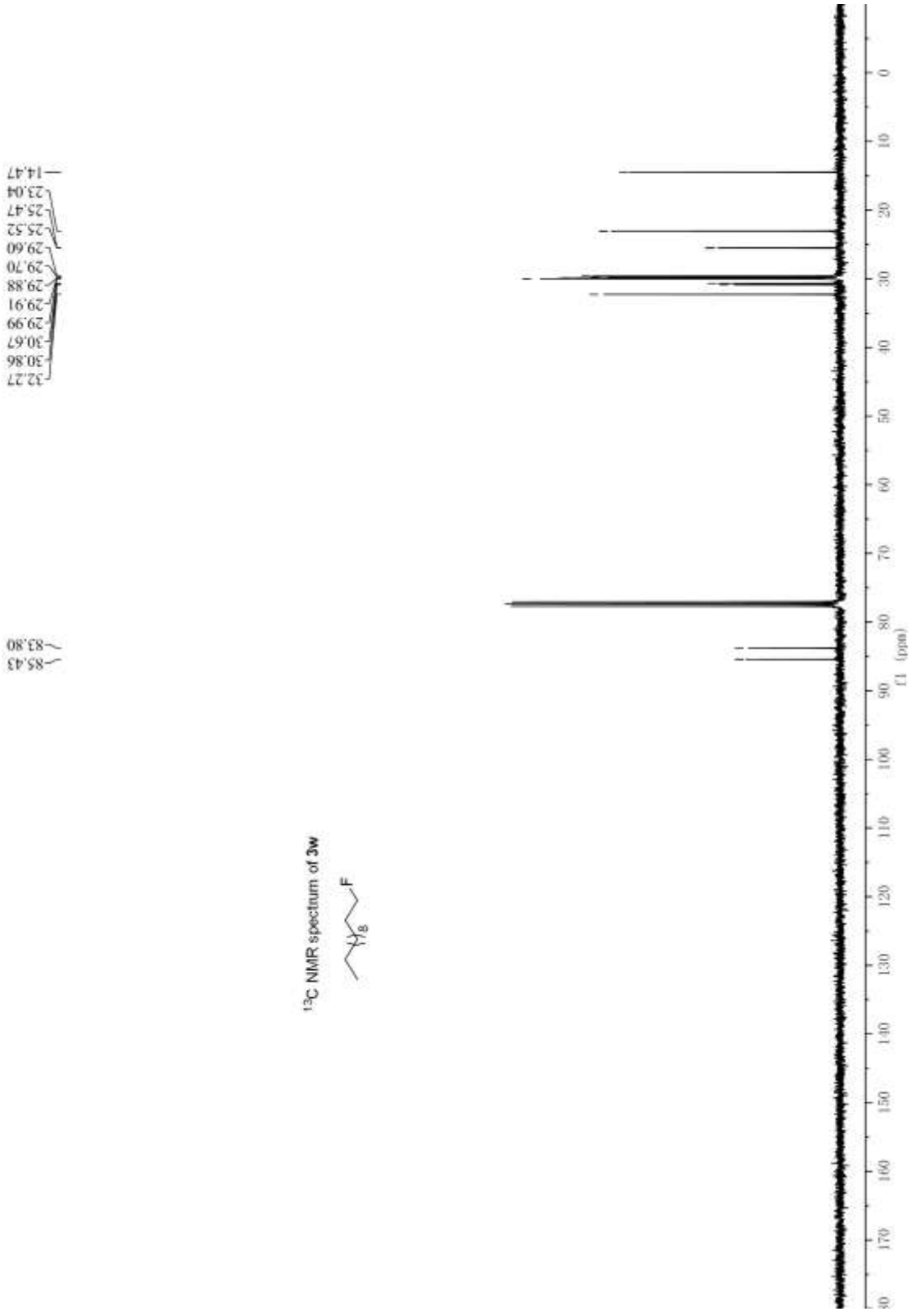
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3v**



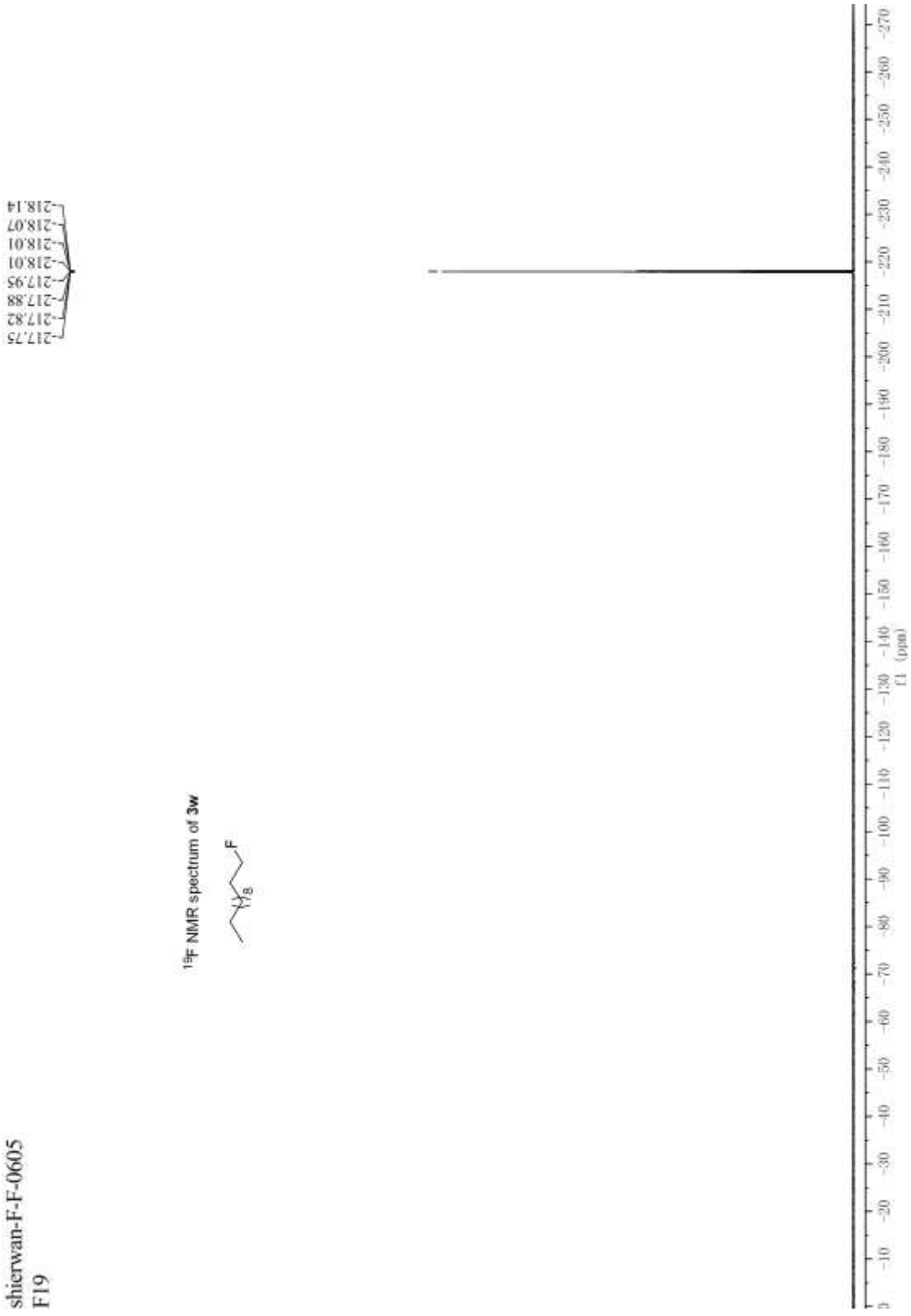
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3v**



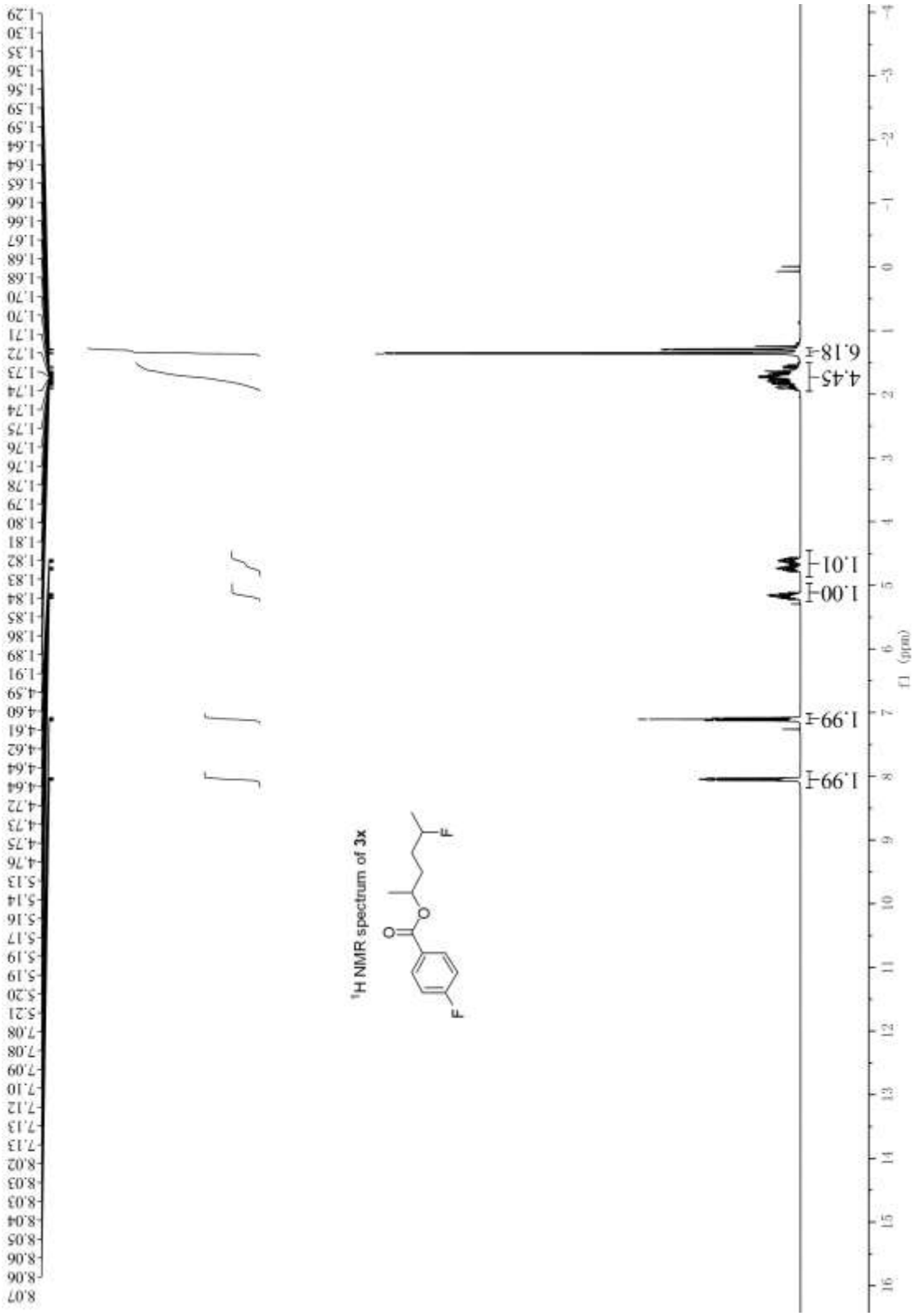
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3w**



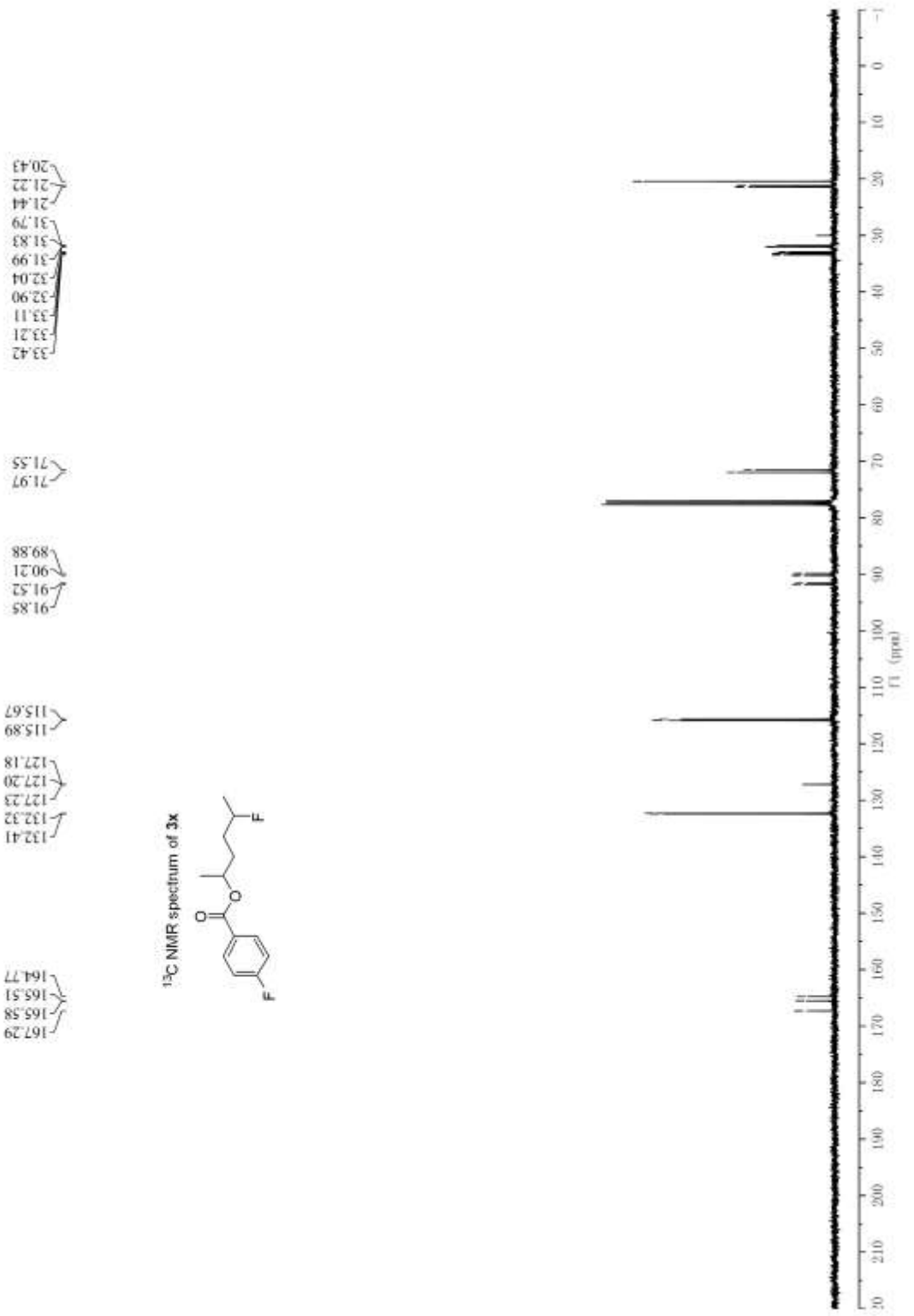
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3w**



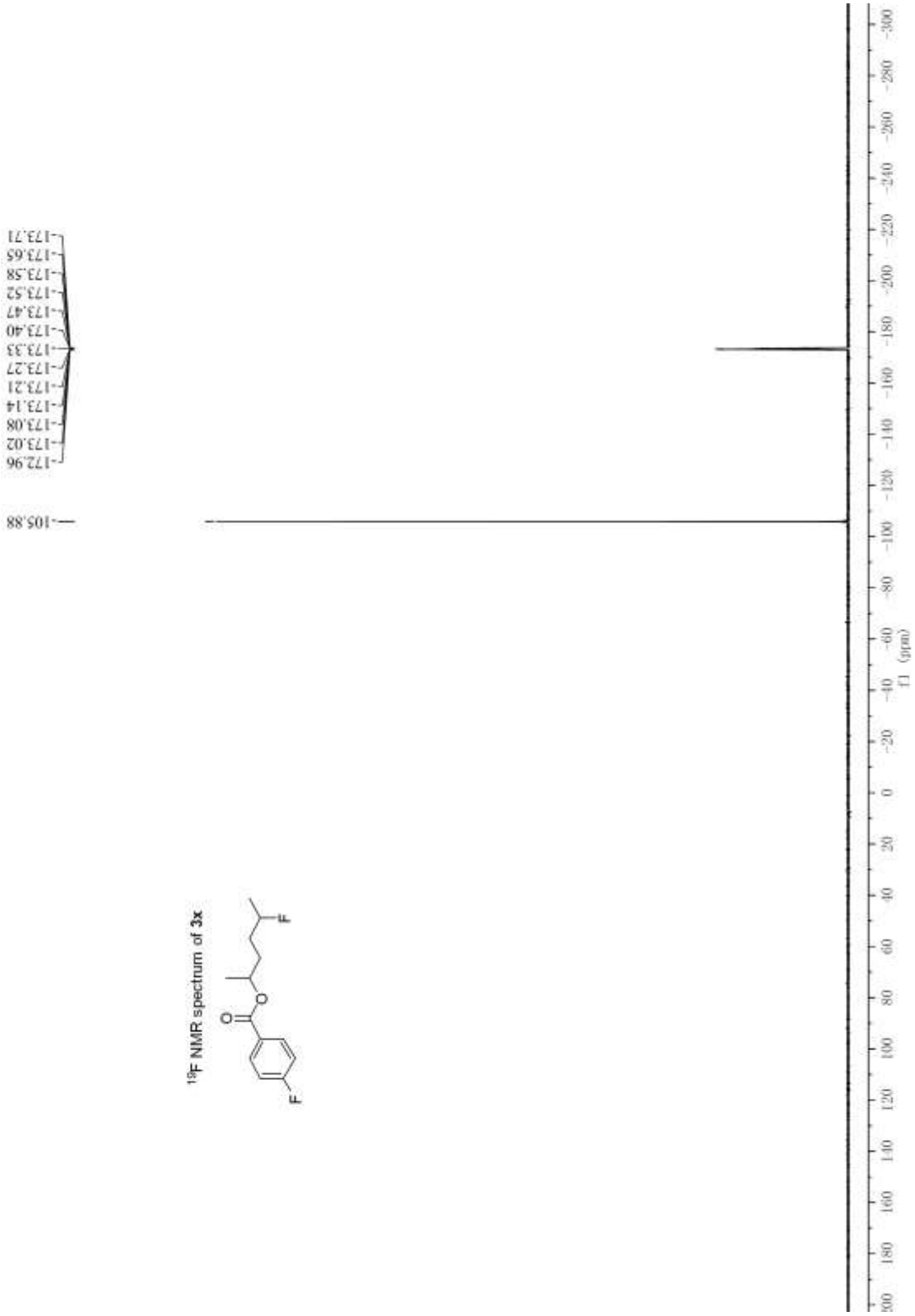
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3w**



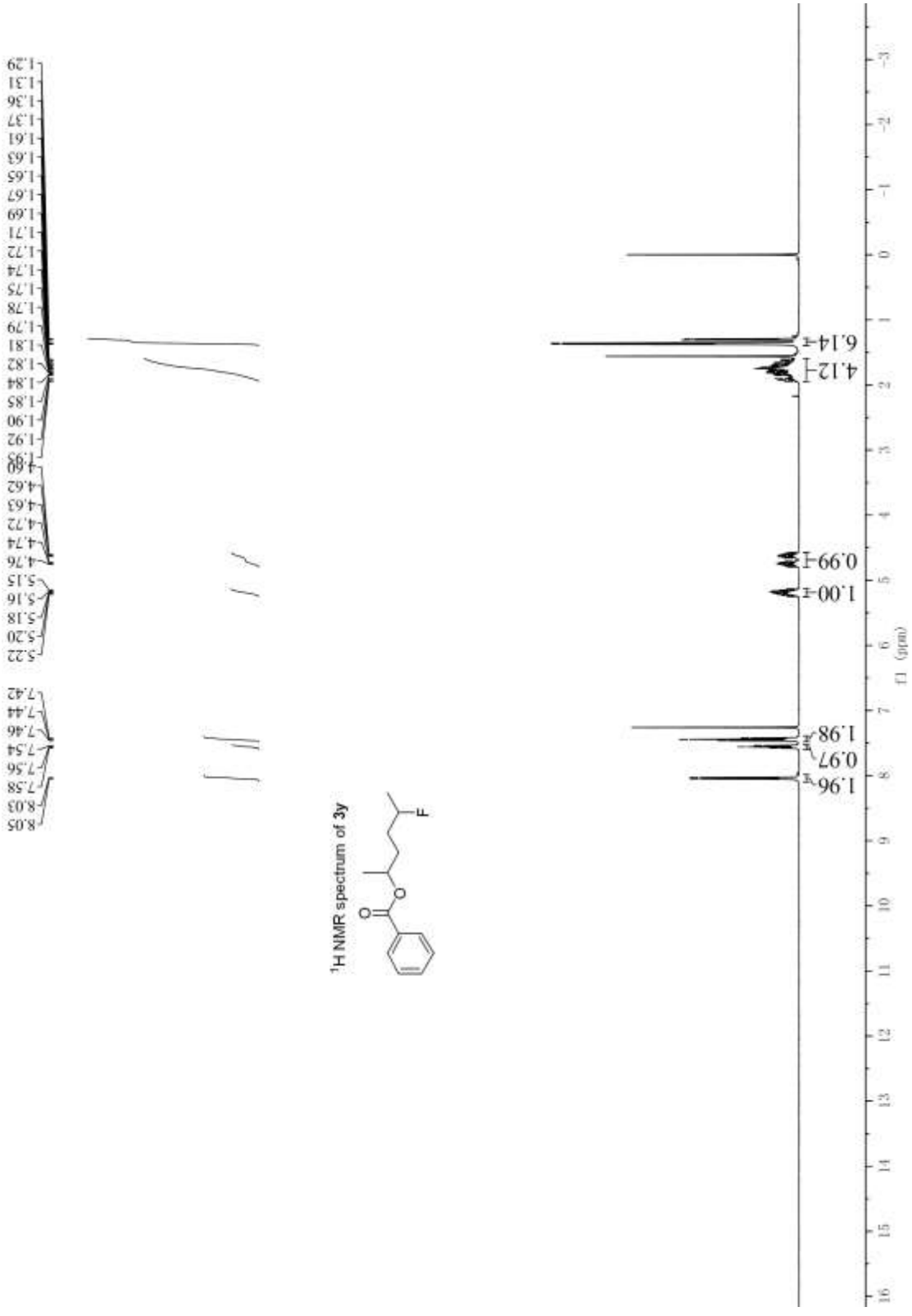
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3x**



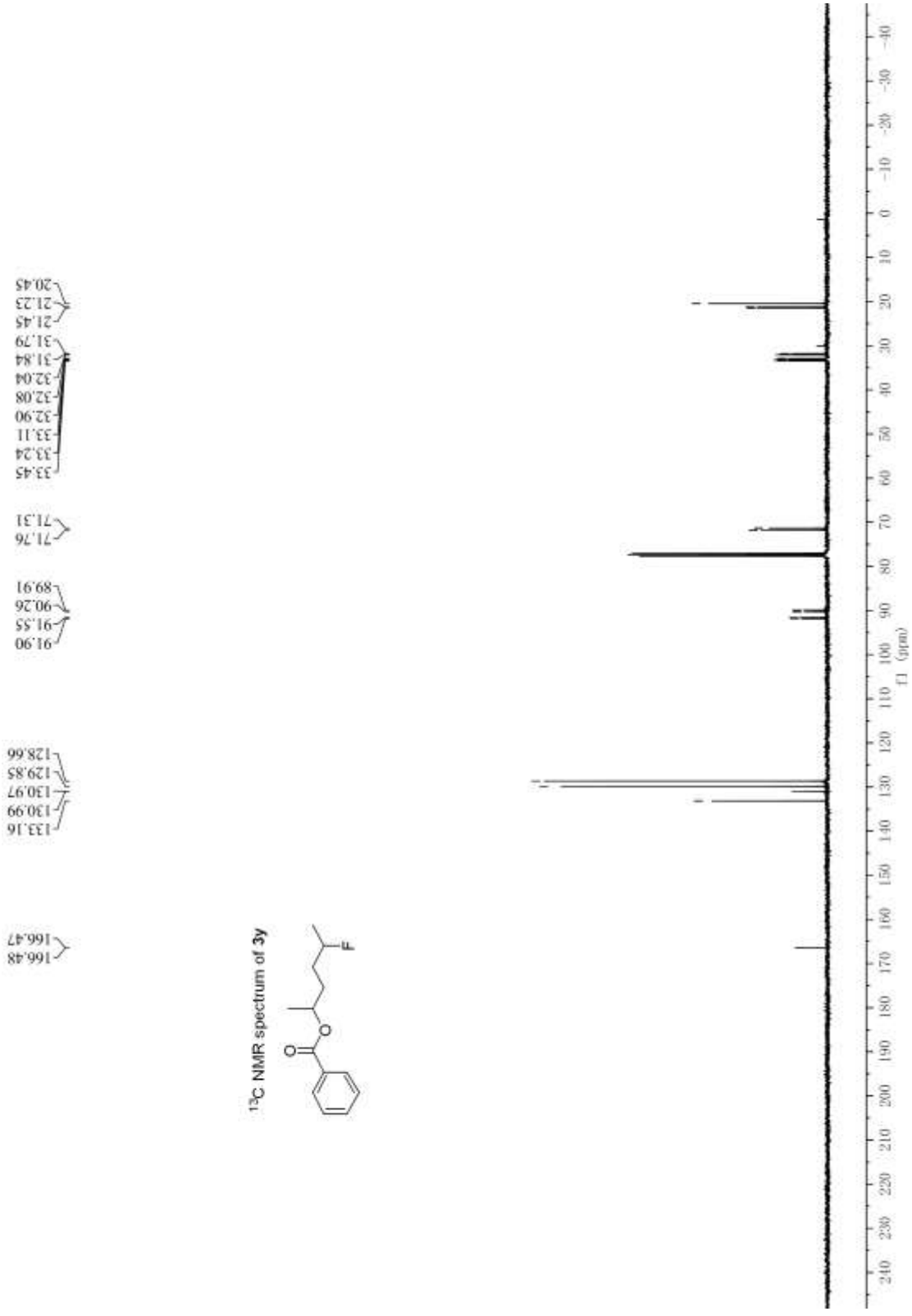
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3x**



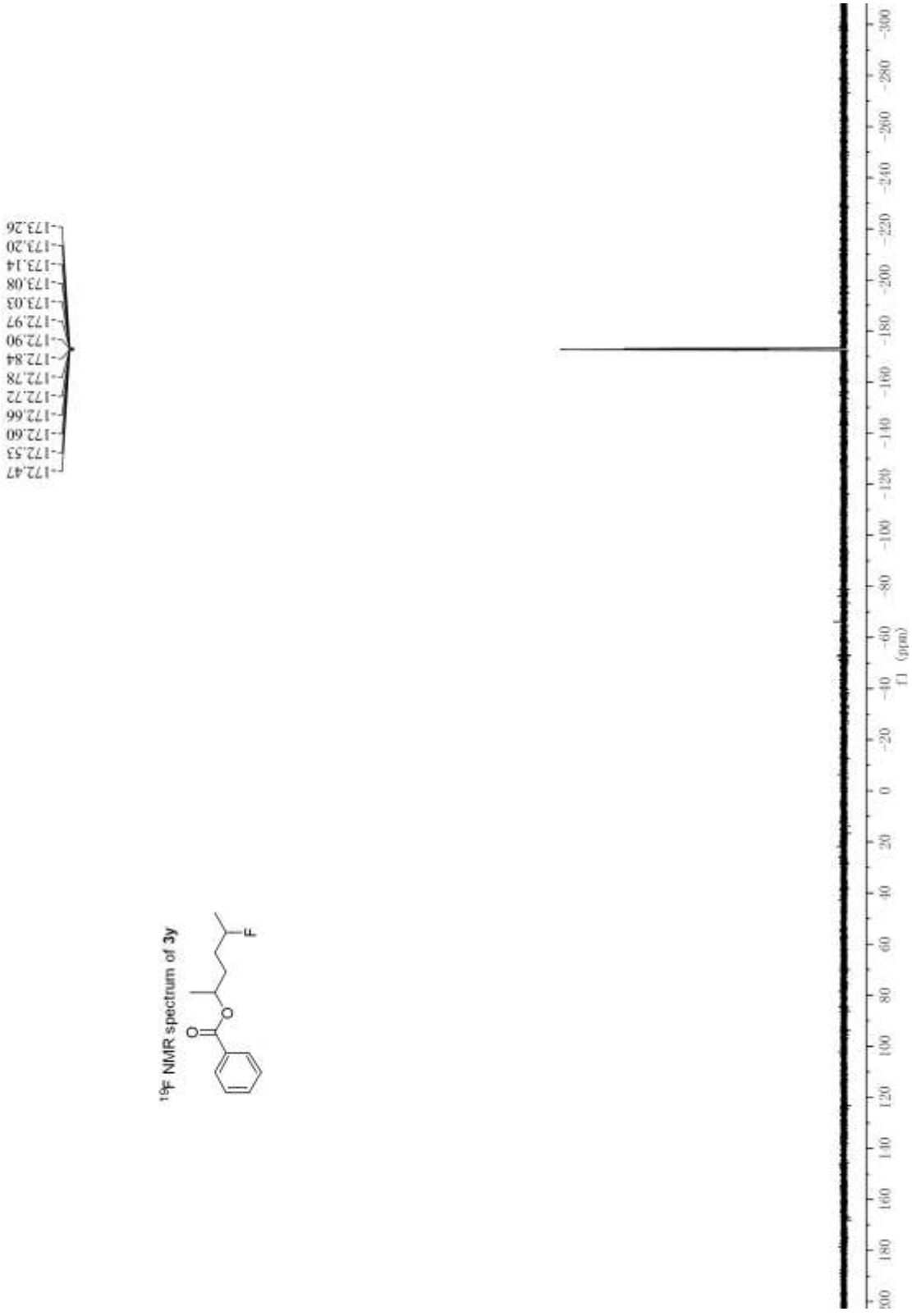
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3x**



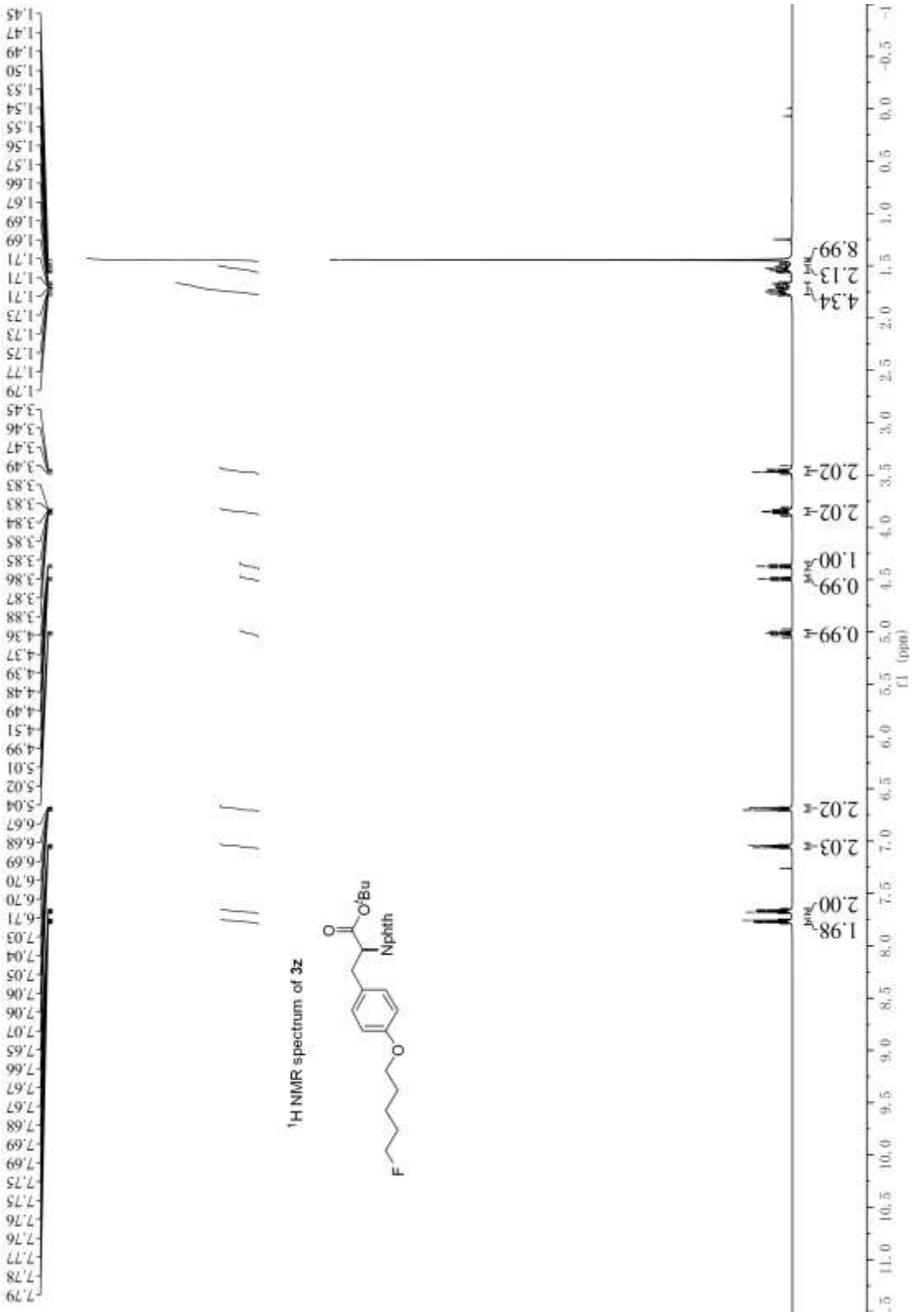
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3y**



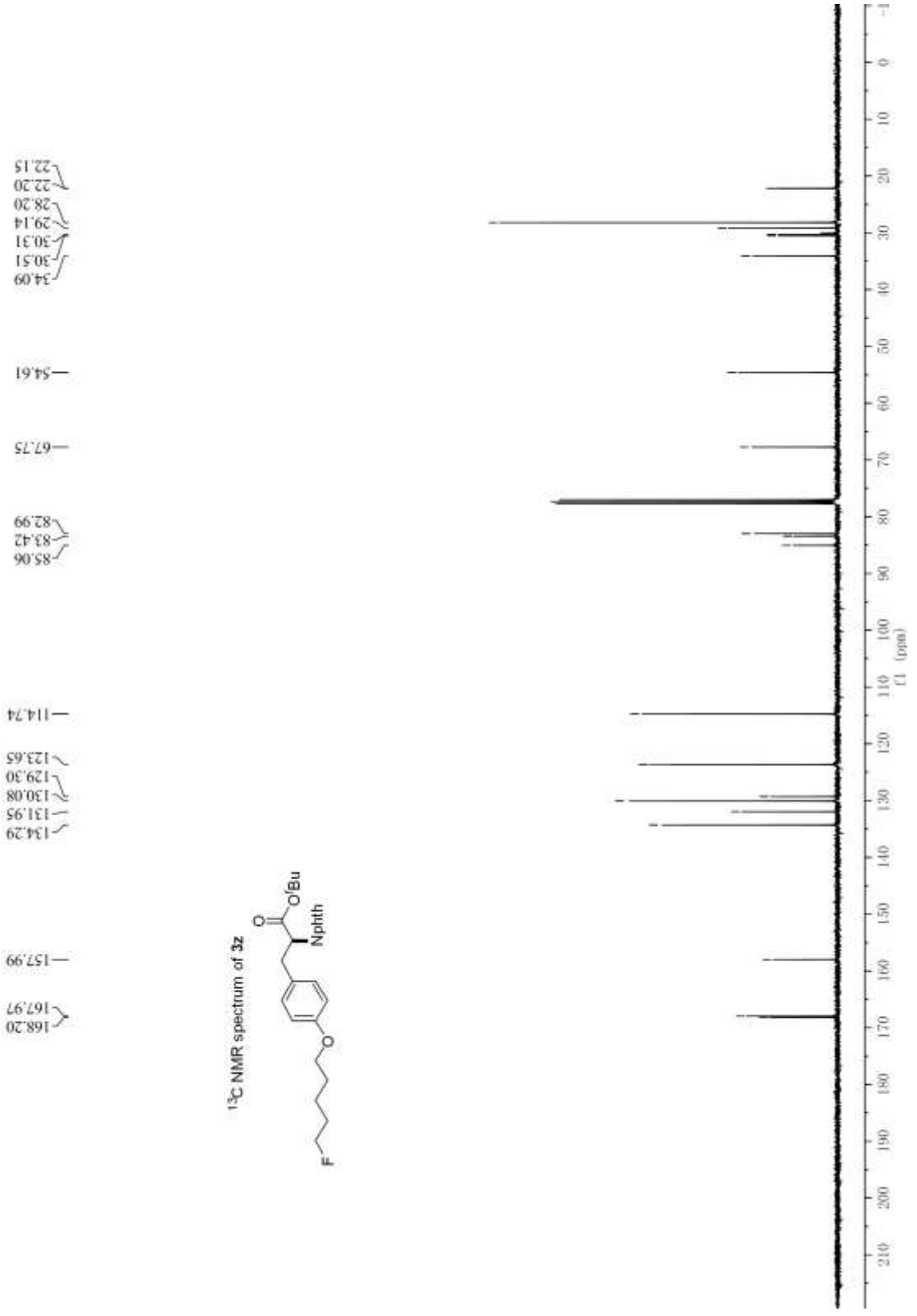
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3y**



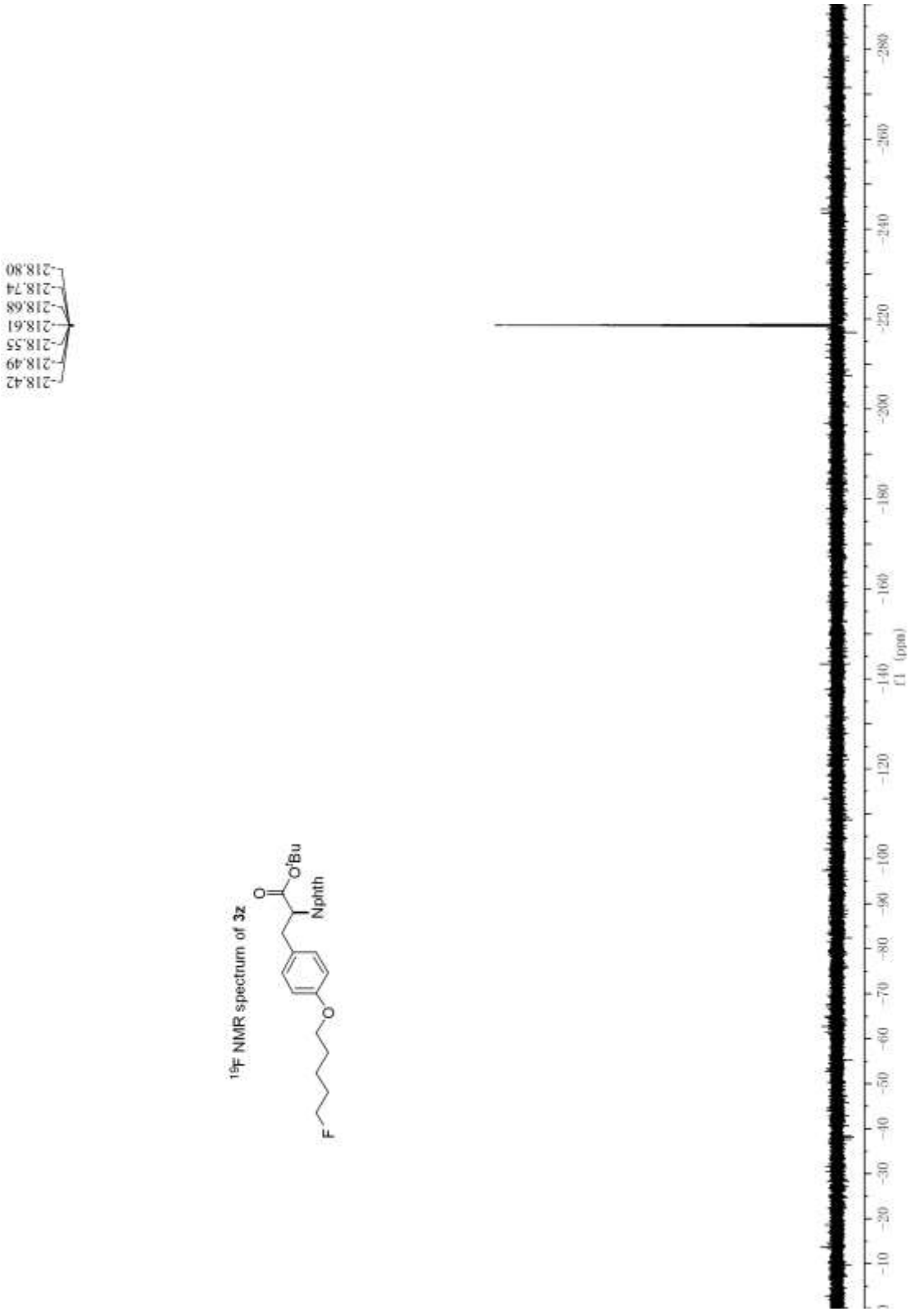
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3y**



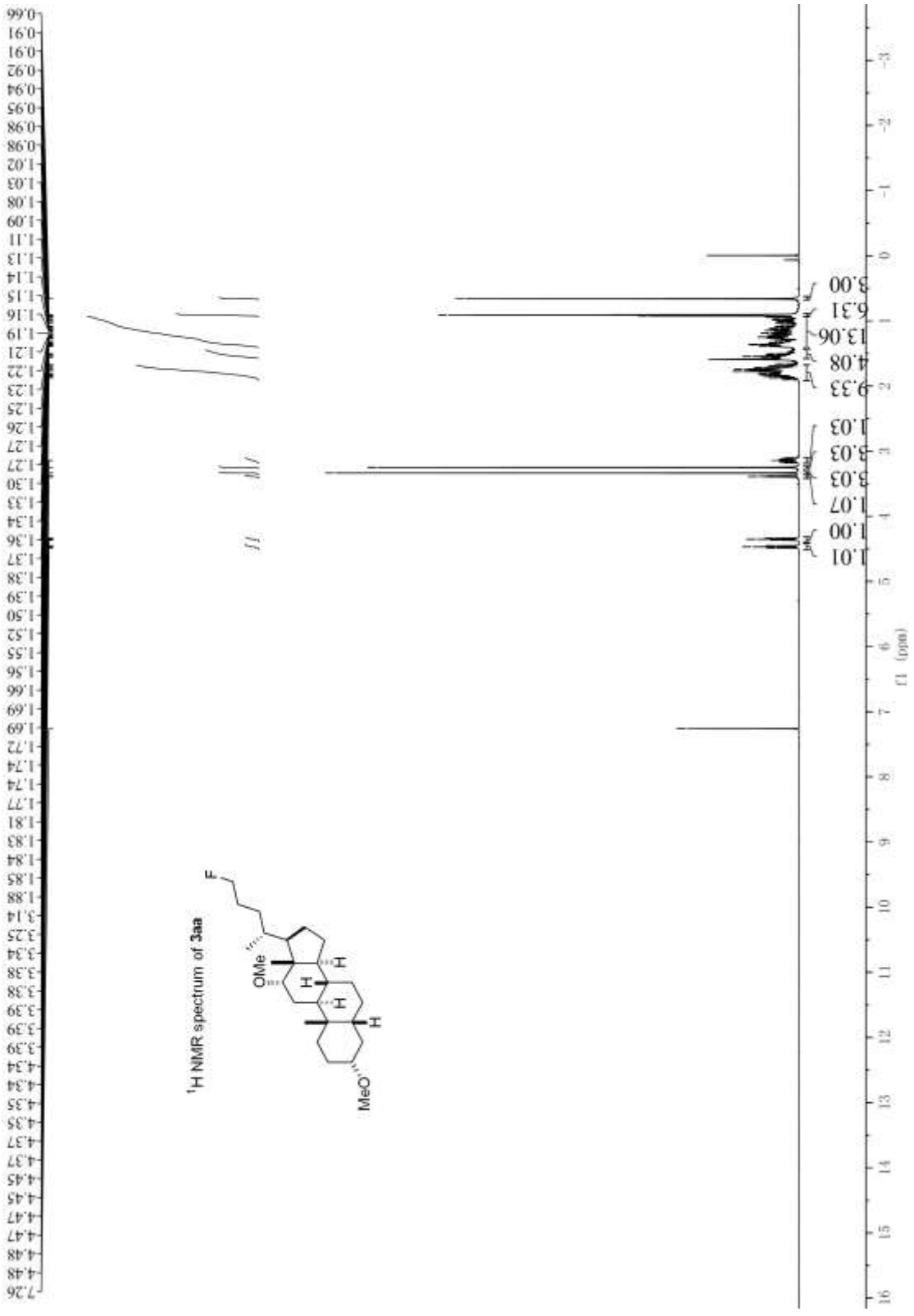
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3z**



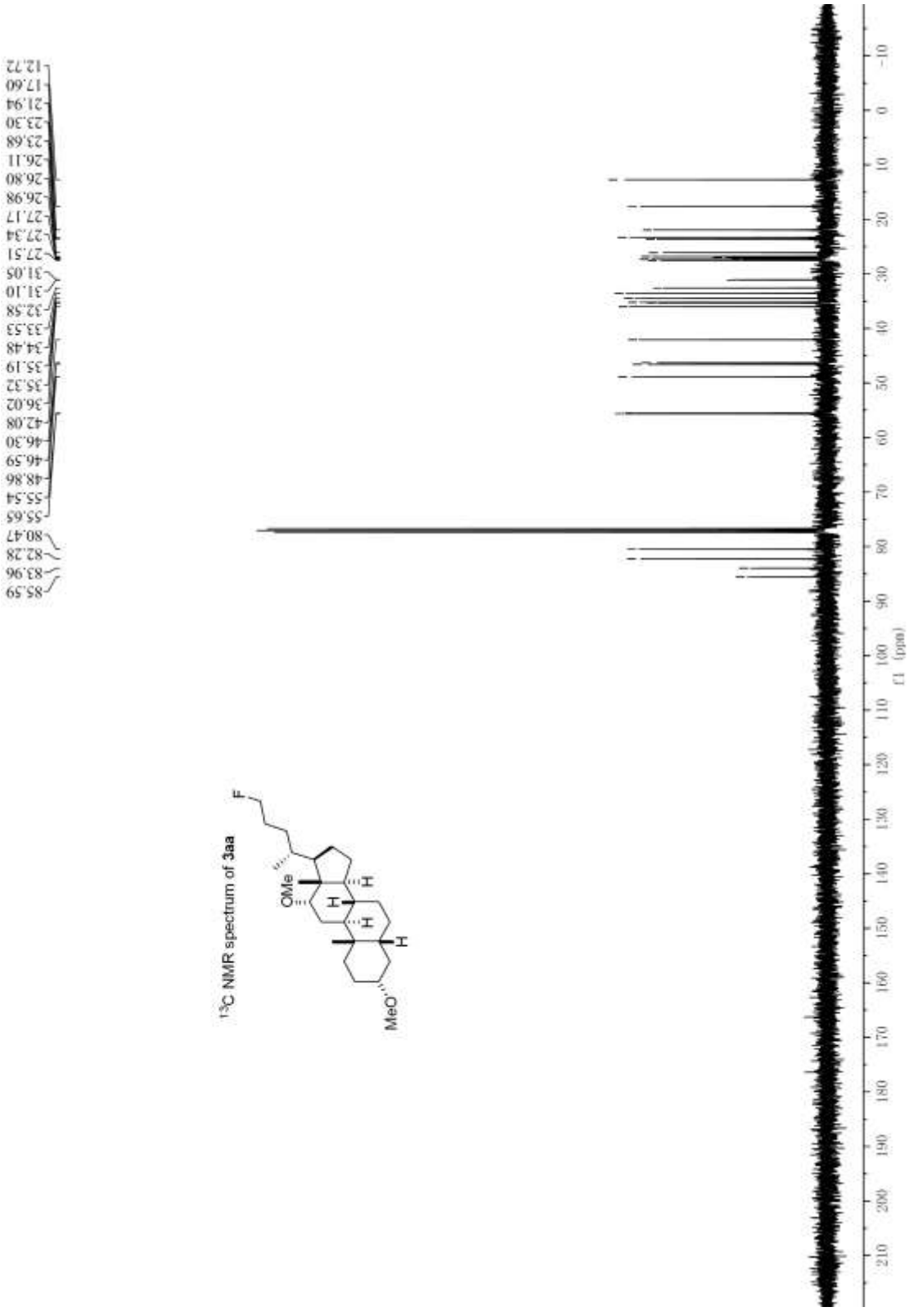
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3z**



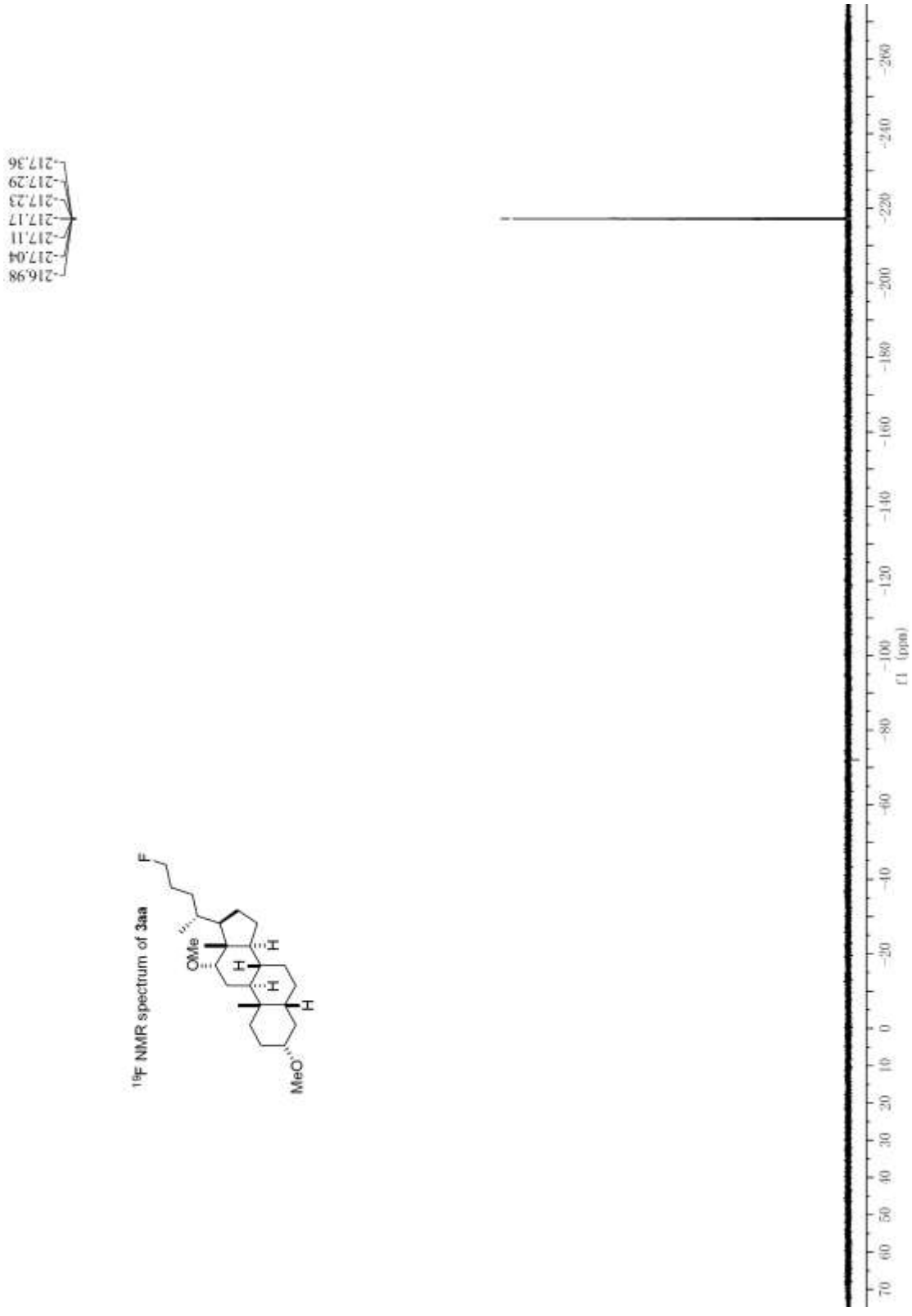
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3z**



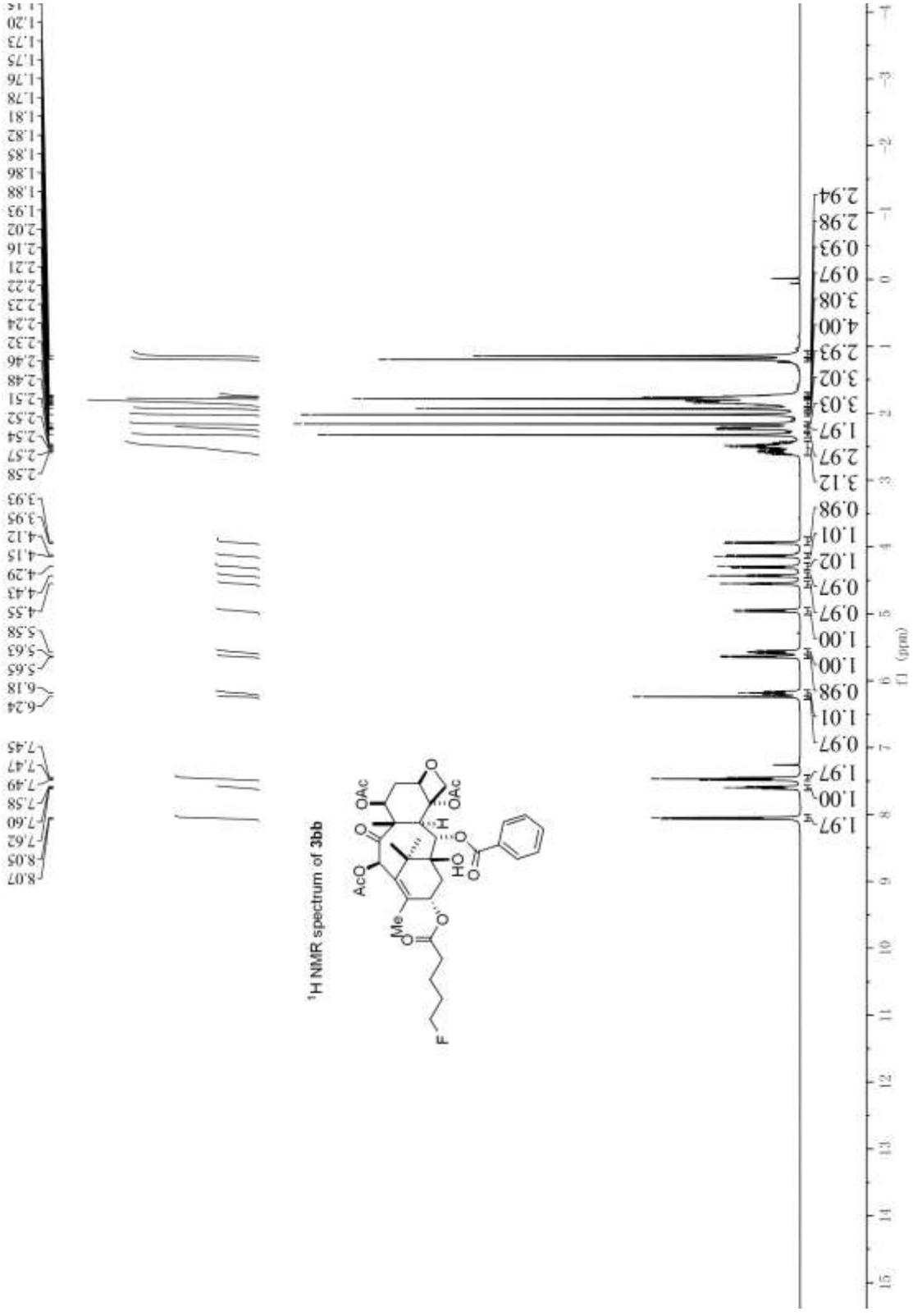
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3aa**



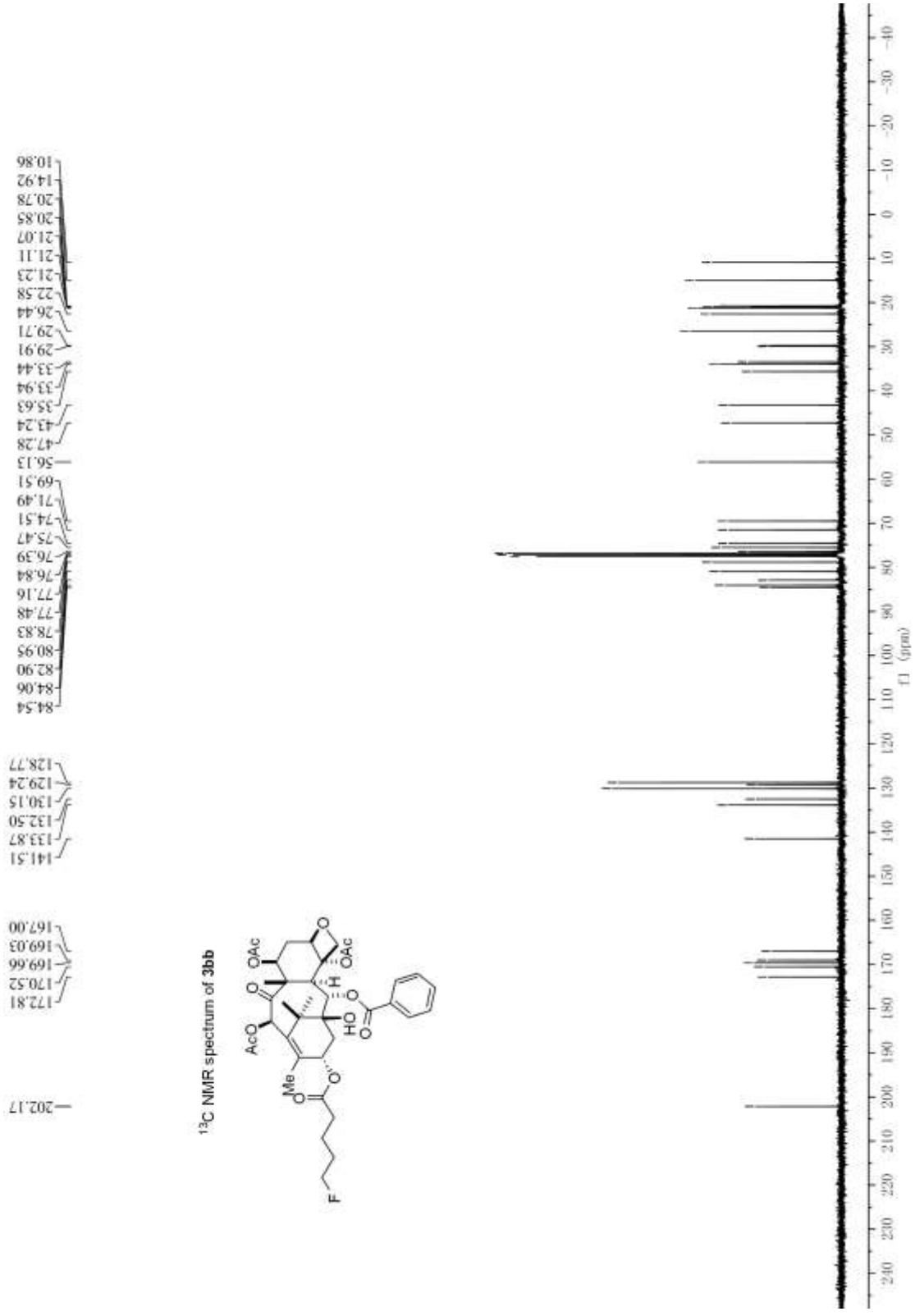
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3aa**



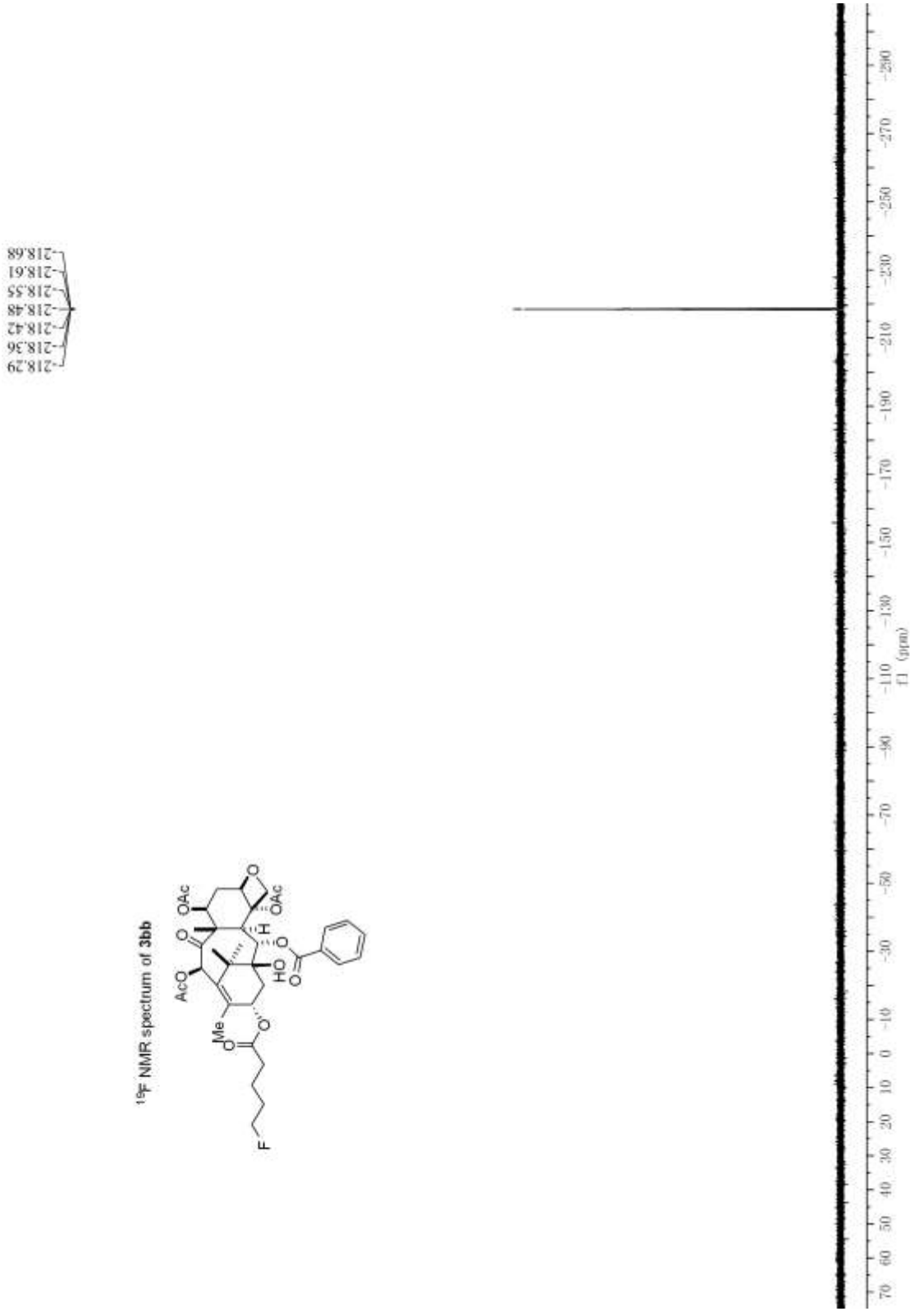
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3aa**



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



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3bb**



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