Supporting Information

Silver-Mediated Oxidative Functionalization of Alkylsilanes

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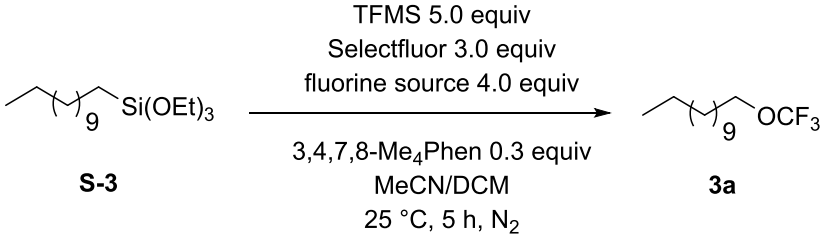
Materials and Methods

MeCN, EA, DCE, DMA, 1,4-dioxane, Et_2O, HMPA, DMSO and DCM were dried by distillation over CaH_2. THF and toluene were dried by distillation over sodium/benzophenone. $CDCl_3$ was purchased from Sigma-Aldrich. Selectfluor was purchased from Energy and recrystallized from MeCN/Et_2O before use. CsF was purchased from TCI. AgF was purchased from Strem. Karstedt's catalyst was purchased from J&K and Aladdin. $AgSCF_3$ was prepared according to the reported literature [1]. "OCF_3" reagents was prepared according to the reported literatures [2]. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). Preparative TLC was performed on silica gel Xinnuo $HSGF_{254}$ preparative TLC plates. Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Varian NMR 400 (400MHz, 101MHz and 376MHz). Signal positions were recorded in ppm with the abbreviations s, d, t, q, dd, dt and m denoting singlet, doublet, triplet, quadruplet, doublet of doublets, doublet of triplets and multiplet respectively. All NMR chemical shifts were referenced to residual solvent peaks or to $Si(CH_3)_4$ as an internal standard. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm, $Si(CH_3)_4$ = δ 0 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm. Mass spectra were acquired on Agilent 6520 Q-TOF LC/MS, Bruker APEX II FT-ICR-MS and Waters GCT Premier. Semipreparative HPLC was performed on an UltiMate 3000 liquid chromatography with a Thermo HG–C18, 21.2 mm × 15 cm column.

Experimental Data

Optimization of the reaction condition for the trifluoromethoxylation

Effect of fluorine sources on the reaction

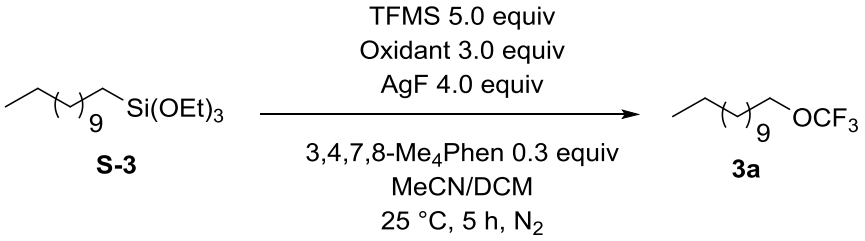


In a glovebox, to a mixture of fluorine source (0.800 mmol F^-, 4.00 equiv F^-), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 μL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S1.

Table S1: Effect of fluorine sources on the reaction

Fluorine salt	Yield [%] (^{19}F NMR)	Fluorine salt	Yield [%] (^{19}F NMR)
AgF	61	KHF_2	0
CsF	0	FeF_3	0
KF	0	TBAF	0
NaF	0	Py·HF	0
LiF	0	$Et_3N·3HF$	0

Effect of oxidants on the reaction

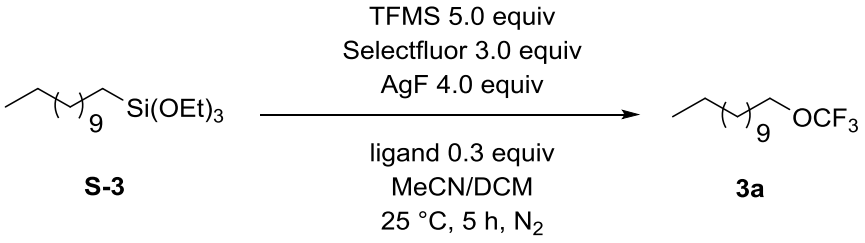


In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and oxidant (0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 μL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S2.

Table S2: Effect of oxidants on the reaction

Oxidant	Yield [%] (^{19}F NMR)	Oxidant	Yield [%] (^{19}F NMR)
NFSI	0	DDQ	0
$[FTMP]BF_4$	0	PhIO	0
Selectfluor	61	$PhI(OAc)_2$	0
Oxone	7	DTBP	0
$K_2S_2O_8$	6	$NaIO_4$	22

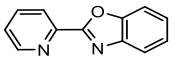
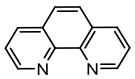
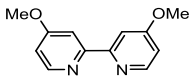
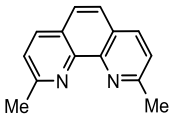
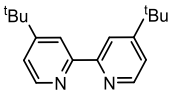
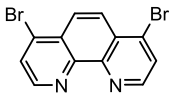
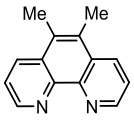
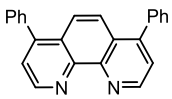
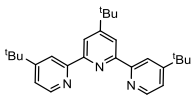
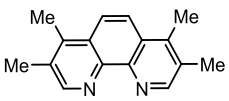
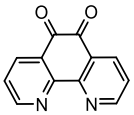
Effect of ligands on the reaction



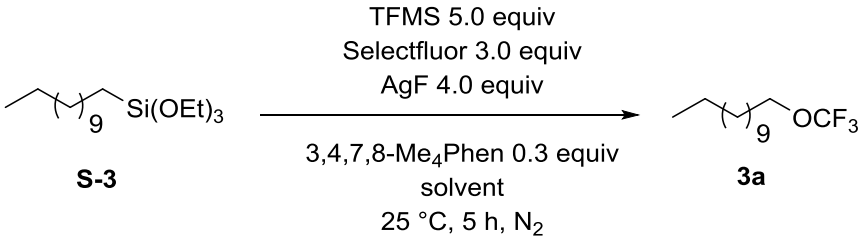
S-3 **3a**

In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), ligand (0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 µL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S3.

Table S3: Effect of ligands on the reaction

Ligand 0.30 equiv	Yield [%] (^{19}F NMR)	Ligand 0.30 equiv	Yield [%] (^{19}F NMR)
no	10		8
	45		60
	8		56
	8		58
	52		6
	61		2

Effect of solvents on the reaction



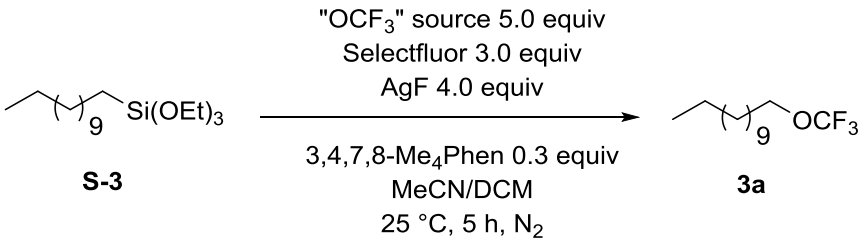
In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added solvent (3.6 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv) and dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) (When using MeCN/co-solvent as the solvent, the procedure was as follows: In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and oxidant (0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added co-solvent (0.8 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.8 mL)). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 μL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S4.

Table S4: Effect of solvents on the reaction

Solvent (3.6 mL)	Yield [%] (^{19}F NMR)	Solvent (MeCN/co-solvent = 2.8 mL/0.8 mL)	Yield [%] (^{19}F NMR)
MeCN	56	MeCN/DCM	61
DCM	0	MeCN/EA	60
EA	0	MeCN/DCE	58
DCE	0	MeCN/DMC	58
DMC	0	MeCN/1,4-dioxane	56
1,4-dioxane	0	MeCN/THF	53
THF	0	MeCN/DMA	0
DMA	0	MeCN/DMSO	0

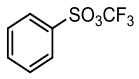
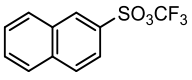
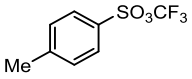
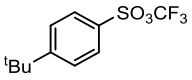
DMSO	0	MeCN/Et_2O	56
Et_2O	0	MeCN/HMPA	0
HMPA	0	MeCN/toluene	61
toluene	0		

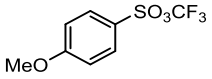
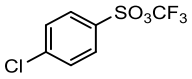
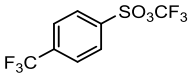
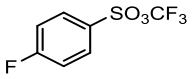
Effect of "OCF_3" sources on the reaction



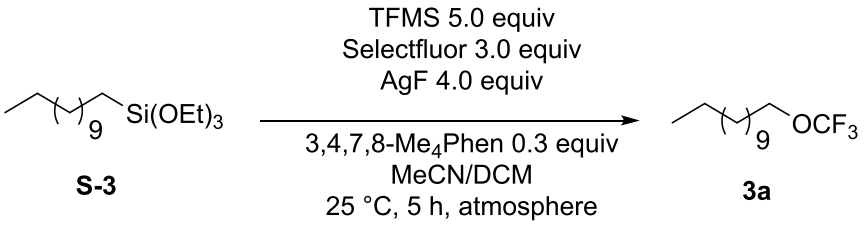
In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), "OCF_3" source (1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 μL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S5.

Table S5: Effect of "OCF_3" sources on the reaction

"OCF_3" sources	Yield [%] (^{19}F NMR)
	61
	37
	61
	61

	61
	43
	14
	44

Effect of atmospheres on the reaction

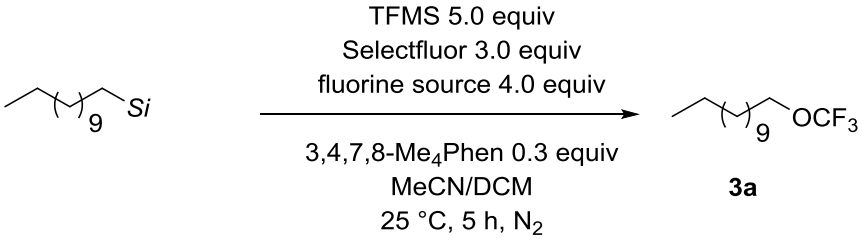


In different atmosphere, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 µL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S6.

Table S6: Effect of atmospheres on the reaction

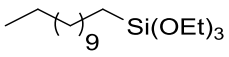
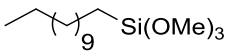
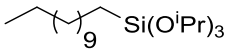
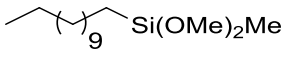
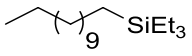
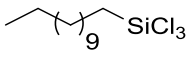
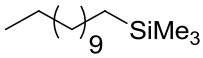
Atmosphere	Yield [%] (^{19}F NMR)
N_2 (glovebox)	61
O_2 (balloon)	29
air	43

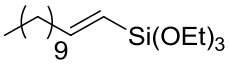
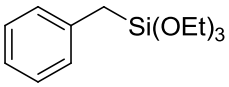
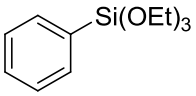
Effect of silanes on the reaction



In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) and Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), silane (0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 µL, 0.814 mmol) was added. The yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S7.

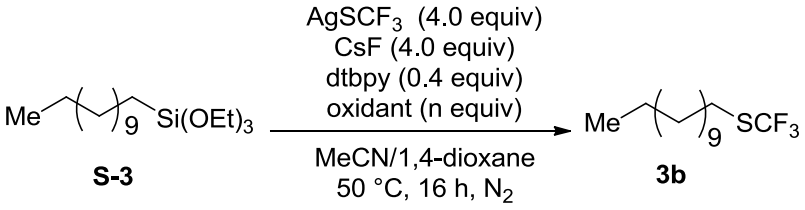
Table S7: Effect of silanes on the reaction

Silanes	Yield [%] (^{19}F NMR)
	61
	13
	49
	36
	0
	0
	0

	0
	12
	0

Optimization of the reaction condition for the trifluoromethylthiolation

Effect of oxidants on the reaction

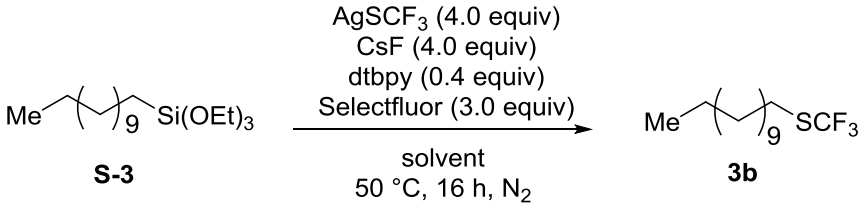


In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), oxidant, dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, benzotrifluoride (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S8.

Table S8: Effect of oxidants on the reaction

Oxidant	Yield [%] (^{19}F NMR)	Oxidant	Yield [%] (^{19}F NMR)
Selectfluor (2.0 equiv)	42	$NaIO_4$ (3.0 equiv)	0
Selectfluor (3.0 equiv)	78	$PhI(OAc)_2$ (3.0 equiv)	12
Selectfluor (4.0 equiv)	28	Oxone (3.0 equiv)	0
Selectfluor(OTf) (3.0 equiv)	66	$(PhCO_2)_2$ (3.0 equiv)	0
Selectfluor(PF_6) (3.0 equiv)	64	$K_2S_2O_8$ (3.0 equiv)	0
Selectfluor(II) (3.0 equiv)	63	BQ (3.0 equiv)	0

Effect of solvents on the reaction

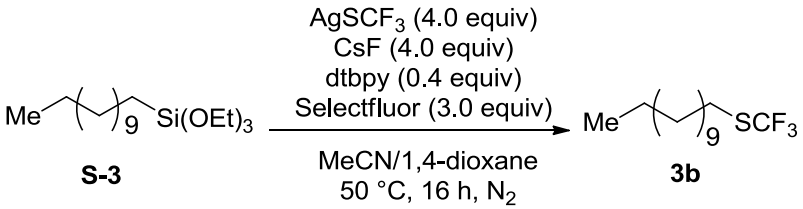


In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL solvent at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S9.

Table S9: Effect of solvents on the reaction

Solvent (0.05 M)	Yield [%] (^{19}F NMR)	Solvent (0.05 M)	Yield [%] (^{19}F NMR)
MeCN	62	DMF	19
1,4-dioxane	41	DME	13
DCE	0	MeCN/THF	0
EtOAc	53	MeCN/1,4-dioxane (1:1)	80
THF	0	EtOAc/1,4-dioxane (1:1)	59
toluene	19	DCE/1,4-dioxane (1:1)	37

Effect of reaction concentration on the reaction



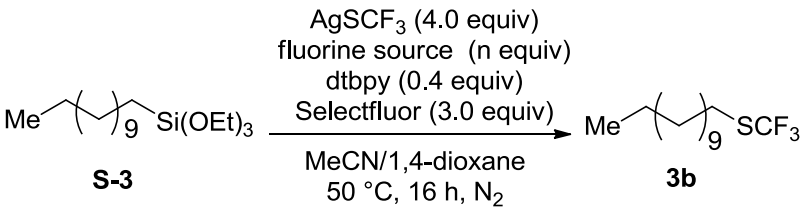
In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in n mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by

comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S10.

Table S10: Effect of reaction concentration on the reaction

Concentration (M)	Yield [%] (^{19}F NMR)
0.25	72
0.125	74
0.0625	75
0.05	80

Effect of fluorine sources on the reaction



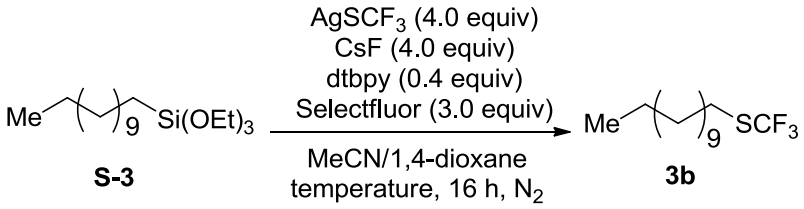
In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence fluorine source (0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S11.

Table S11: Effect of fluorine sources on the reaction

Fluorine source	Yield [%] (^{19}F NMR)
CsF (F^- 4.0 equiv)	80
CsF (F^- 6.0 equiv)	70
CsF (F^- 2.0 equiv)	34
KHF_2 (F^- 4.0 equiv)	6
LiF (F^- 4.0 equiv)	6

NaF (F^- 4.0 equiv)	8
KF (F^- 4.0 equiv)	69
RbF (F^- 4.0 equiv)	5
AgF (F^- 4.0 equiv)	52
FeF_3 (F^- 4.0 equiv)	0
SbF_3 (F^- 4.0 equiv)	0
no	0

Effect of temperatures on the reaction

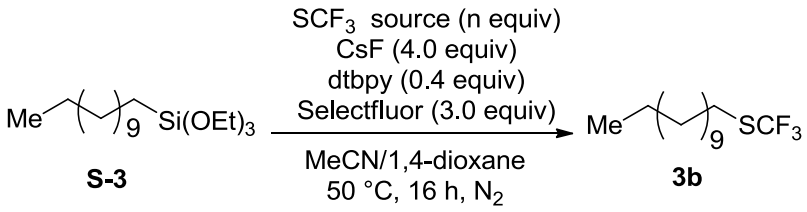


In a glovebox, to a solution of dodecyltriethoxysilane (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at different temperatures, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S12.

Table S12: Effect of temperatures on the reaction

Temperature	Yield [%] (^{19}F NMR)
0 °C	63
25 °C	74
50 °C	78
75 °C	60
100 °C	44

Effect of "SCF_3" sources on the reaction

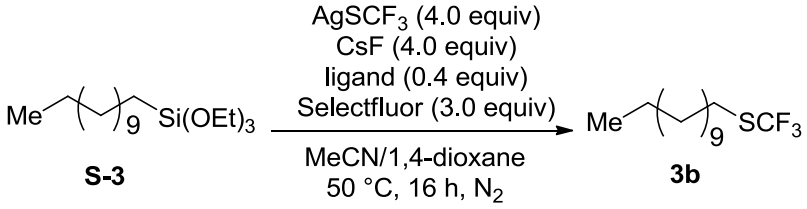


In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and "SCF_3 source". After stirring for 16.0 h at 50 ^{o}C, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S13.

Table S13: Effect of SCF_3 sources on the reaction

SCF_3 source	additive	Yield [%] (^{19}F NMR)
$AgSCF_3$ (4.0 equiv)	-	77
$AgSCF_3$ (2.0 equiv)	-	32
$AgSCF_3$ (6.0 equiv)	-	45
$AgSCF_3$ (4.0 equiv)	TBAI (4.0 equiv)	0
[*n*-Bu_4N][SCF_3] (4.0 equiv)	-	0
[*n*-Bu_4N][SCF_3] (4.0 equiv)	AgOTf (4.0 equiv)	0
$CsSCF_3$ (4.0 equiv)	-	0
$CsSCF_3$ (4.0 equiv)	AgOTf (4.0 equiv)	0
$CuSCF_3$ (4.0 equiv)	-	32

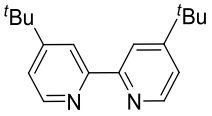
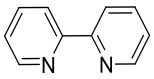
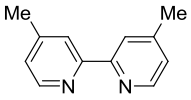
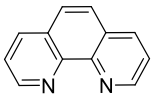
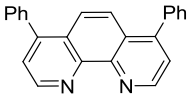
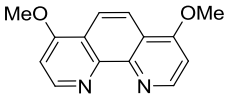
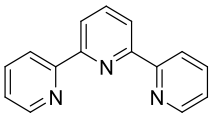
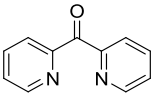
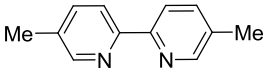
Effect of ligands on the reaction



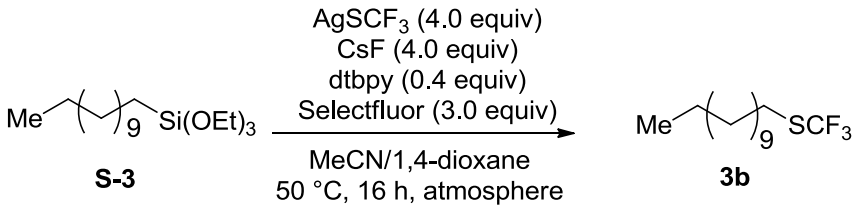
S-3 **3b**

In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), ligand (0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 °C, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S14.

Table S14: Effect of ligands on the reaction

ligand	Yield [%] (^{19}F NMR)	ligand	Yield [%] (^{19}F NMR)
	78		68
	60		40
	63		50
	64		58
	74	no	23

Effect of atmospheres on the reaction

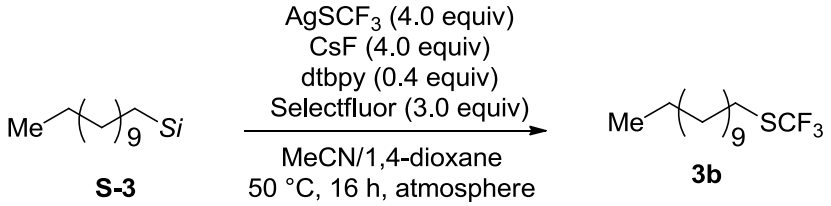


In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (16.6 mg, 0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 °C, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S15.

Table S15: Effect of atmospheres on the reaction

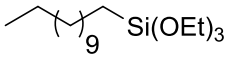
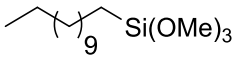
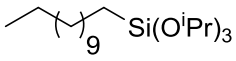
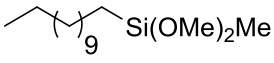
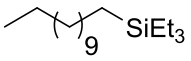
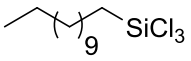
Atmosphere	Yield [%] (^{19}F NMR)
N_2 (glovebox)	80
O_2 (balloon)	0
air	64

Effect of different silanes on the reaction



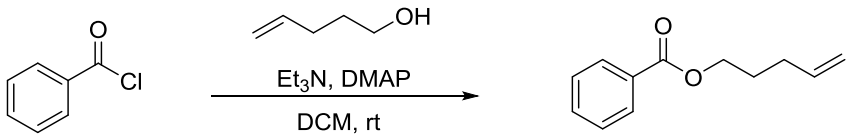
In a glovebox, to a solution of silane (0.0500 mmol, 1.00 equiv) in 1.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (30.4 mg, 0.200 mmol, 4.00 equiv), Selectfluor (53.1 mg, 0.150 mmol, 3.00 equiv), dtbpy (5.4 mg, 0.0200 mmol, 0.400 equiv) and $AgSCF_3$ (41.8 mg, 0.200 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). Yields are reported in Table S16.

Table S16: Effect of different silanes on the reaction

Silanes	Yield [%] (^{19}F NMR)
	80
	67
	38
	0
	0
	0

Experimental Procedures and Compound Characterization

Pent-4-en-1-yl benzoate (X-4)



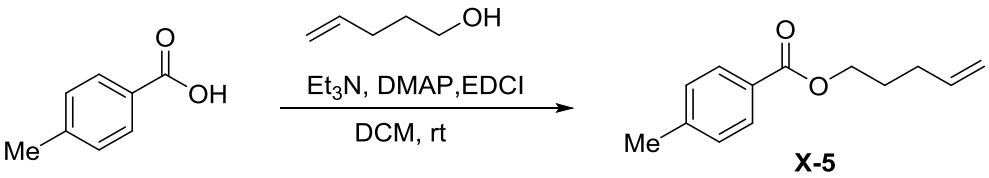
X-4

To a solution of pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (2.42 g, 24.0 mmol, 1.20 equiv) in CH_2Cl_2 (50.0 mL) at 0 °C was added benzoyl chloride (2.80 g, 20.0 mmol, 1.00 equiv). The reaction mixture was warmed to room temperature and stirred for 5 h before quenching with H_2O (10.0 mL) and extracting 3 times with CH_2Cl_2 (20.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 3.70 g pent-4-en-1-yl benzoate (**X-4**) as a colorless liquid (97% yield).

R_f = 0.56 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.04 (m, 2H), 7.61 – 7.52 (m, 1H), 7.48 – 7.41 (m, 2H), 5.91 – 5.80 (m, 1H), 5.10 – 5.00 (m, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.94 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 137.6, 133.0, 130.6, 129.7, 128.5, 115.5, 64.5, 30.3, 28.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{15}O_2$ $[M + H]^+$, 191.1072. Found, 191.1068.

IR (neat): υ (cm^{-1}): 3074, 2956, 2849, 1721, 1644, 1608, 1452, 1314, 1273, 1113, 1070, 1026, 914, 866, 711.

Pent-4-en-1-yl 4-methylbenzoate (X-5)

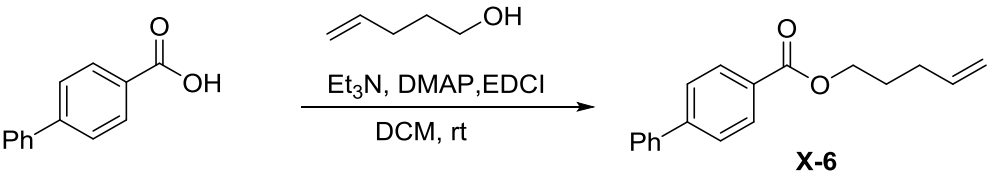


X-5

To a solution of 4-methylbenzoic acid (2.72 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 3.86 g pent-4-en-1-yl 4-methylbenzoate (**X-5**) as a colorless liquid (94% yield).

R_f = 0.35 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.90 – 5.80 (m, 1H), 5.10 – 5.00 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.26 – 2.18 (m, 2H), 1.93 – 1.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.6, 137.7, 129.7, 129.2, 127.8, 115.5, 64.3, 30.3, 28.1, 21.8. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{17}O_2$ $[M + H]^+$, 205.1229. Found, 205.1222. IR (neat): υ (cm^{-1}): 3039, 2923, 2866, 1718, 1645, 1612, 1455, 1386, 1273, 1177, 1107, 912, 804, 752.

Pent-4-en-1-yl 4-phenylbenzoate (X-6)

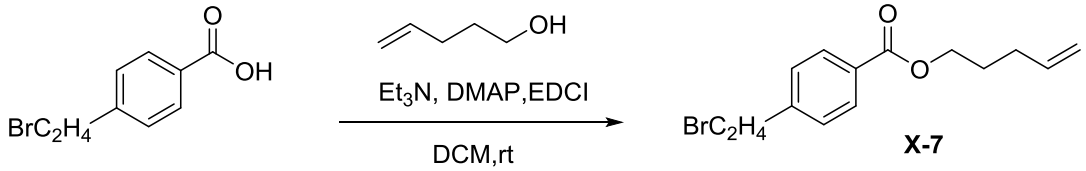


X-6

To a solution of 4-phenylbenzoic acid (3.96 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 3.74 g pent-4-en-1-yl 4-phenylbenzoate (**X-6**) as a colorless liquid (70% yield).

R_f = 0.50 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H), 7.71 – 7.66 (m, 2H), 7.65 – 7.62 (m, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.38 (m, 1H), 5.93 – 5.83 (m, 1H), 5.13 – 5.07 (m, 1H), 5.06 – 5.02 (m, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 2.31 – 2.22 (m, 2H), 1.94 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 145.7, 140.1, 137.6, 130.2, 129.3, 129.0, 128.2, 127.4, 127.2, 115.5, 64.5, 30.3, 28.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{19}O_2$ $[M + H]^+$, 267.1385. Found, 267.1383. IR (neat): υ (cm^{-1}): 3061, 2956, 2849, 1716, 1641, 1608, 1486, 1404, 1275, 1178, 1111, 1107, 914, 858, 747.

Pent-4-en-1-yl 4-(2-bromoethyl)benzoate (X-7)

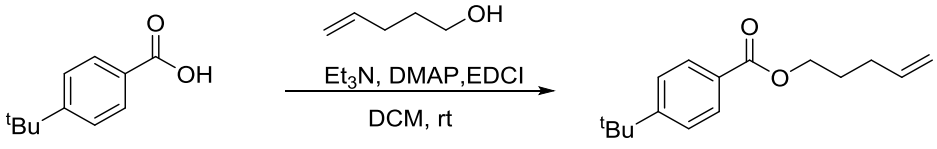


X-7

To a solution of 4-(2-bromoethyl)benzoic acid (4.60 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 3.79 g pent-4-en-1-yl 4-(2-bromoethyl)benzoate (**X-7**) as a colorless liquid (64% yield).

R_f = 0.45 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 6.7 Hz, 2H), 5.96 – 5.63 (m, 1H), 5.11 – 5.00 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.22 (t, *J* = 6.7 Hz, 2H), 2.26 – 2.19 (m, 2H), 1.93 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.1, 137.6, 130.0, 129.2, 128.8, 115.5, 64.4, 39.2, 32.3, 30.3, 28.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}BrO_2$ $[M + H]^+$, 297.0490. Found, 297.0481. IR (neat): υ (cm^{-1}): 3075, 2957, 2849, 1716, 1644, 1612, 1455, 1416, 1275, 1178, 1112, 1019, 914, 765.

Pent-4-en-1-yl 4-(*tert*-butyl)benzoate (X-9)



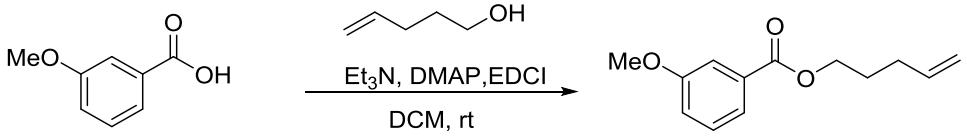
X-9

To a solution of 4-(tert-butyl)benzoic acid (3.56 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (244 mg, 2.00 mmol, 0.100 equiv) and Et_3N (6.07 g, 60.0 mmol, 3.00 equiv) in CH_2Cl_2 (20.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (5.75 g, 30.0 mmol, 1.50

equiv) and pent-4-en-1-ol (2.58 g, 30.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (20.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 3.84 g pent-4-en-1-yl 4-(*tert*-butyl)benzoate (**X-9**) as a colorless liquid (78% yield).

R_f = 0.43 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.47 – 7.45 (m, 2H), 5.90 – 5.80 (m, 1H), 5.11 – 5.00 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.25 – 2.20 (m, 2H), 1.91 – 1.84 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 156.4, 137.5, 129.5, 127.7, 125.3, 115.4, 64.1, 35.1, 31.2, 30.2, 28.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{23}O_2$ $[M + H]^+$, 247.1696. Found, 247.1698. IR (neat): υ (cm^{-1}): 3077, 2963, 2869, 1720, 1645, 1464, 1275, 1188, 1102, 1017, 913, 854, 775.

Pent-4-en-1-yl 3-methoxybenzoate (X-10)

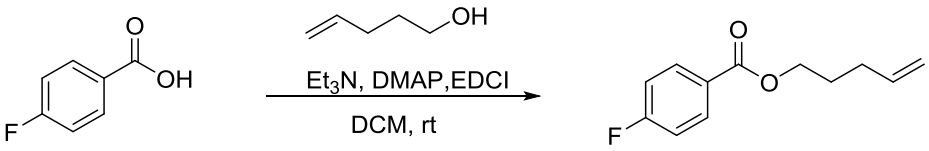


X-10

To a solution of 3-methoxybenzoic acid (3.56 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (244 mg, 2.00 mmol, 0.100 equiv) and Et_3N (6.07 g, 60.0 mmol, 3.00 equiv) in CH_2Cl_2 (20.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (5.75 g, 30.0 mmol, 1.50 equiv) and pent-4-en-1-ol (2.58 g, 30.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (20.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 3.70 g pent-4-en-1-yl 3-methoxybenzoate (**X-10**) as a colorless liquid (84% yield).

R_f = 0.48 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 1H), 7.57 – 7.56 (m, 1H), 7.37 – 7.33 (m, 1H), 7.11 – 7.08 (m, 1H), 5.90 – 5.80 (m, 1H), 5.10 – 5.00 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 2.25 – 2.19 (m, 2H), 1.91 – 1.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.6, 137.5, 131.8, 129.4, 122.0, 119.3, 115.5, 114.2, 64.5, 55.5, 30.3, 28.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{16}NaO_3$ $[M + Na]^+$, 243.0997. Found, 243.0989. IR (neat): υ (cm^{-1}): 3077, 2958, 2837, 1719, 1645, 1606, 1587, 1488, 1453, 1432, 1277, 1228, 1104, 1044, 916, 754.

Pent-4-en-1-yl 4-fluorobenzoate (X-11)

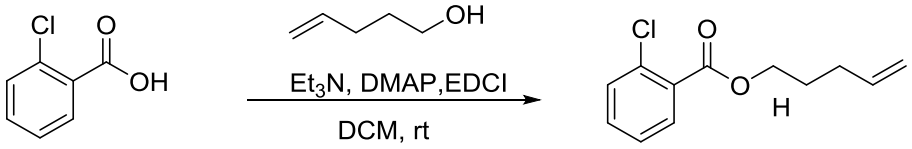


X-11

To a solution of 4-fluorobenzoic acid (2.80 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (244 mg, 2.00 mmol, 0.100 equiv) and Et_3N (6.07 g, 60.0 mmol, 3.00 equiv) in CH_2Cl_2 (20.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (5.75 g, 30.0 mmol, 1.50 equiv) and pent-4-en-1-ol (2.58 g, 30.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (20.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 3.69 g pent-4-en-1-yl 4-fluorobenzoate (**X-11**) as a colorless liquid (89% yield).

R_f = 0.38 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H), 7.12 – 7.08 (m, 2H), 5.90 – 5.79 (m, 1H), 5.09 – 5.00 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.90 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (d, *J* = 253.5 Hz), 165.6, 137.5, 132.1 (d, *J* = 9.2 Hz), 115.6, 115.4 (d, *J* = 5.5 Hz), 64.6, 30.2, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.90. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{14}FO_2$ $[M + H]^+$, 209.0978. Found, 209.0975. IR (neat): υ (cm^{-1}): 3079, 2956, 2850, 1717, 1644,. 1507, 1433, 1274, 1238, 1153, 1115, 1090, 915, 854, 767.

Pent-4-en-1-yl 2-chlorobenzoate (X-12)



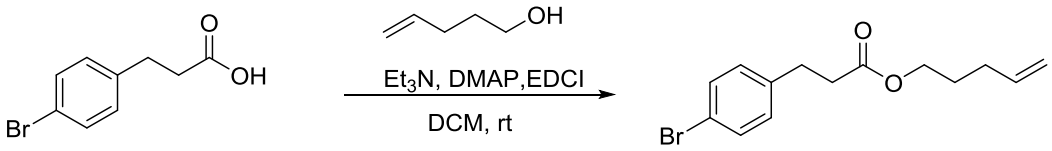
X-12

To a solution of 2-chlorobenzoic acid (1.57 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (122 mg, 1.00 mmol, 0.100 equiv) and Et_3N (3.04 g, 30.0 mmol, 3.00 equiv) in CH_2Cl_2 (10.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (2.88 g, 15.0 mmol, 1.50 equiv) and pent-4-en-1-ol (1.29 g, 15.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (10.0 mL) and extracting 3 times with CH_2Cl_2 (15.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 1.42 g pent-4-en-1-yl 2-chlorobenzoate (**X-12**) as a colorless liquid 63% yield).

R_f = 0.36 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.45 – 7.38 (m, 2H), 7.32 – 7.28 (m, 1H), 5.88 – 5.78 (m, 1H), 5.09 – 5.00 (m, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 2H), 1.90 – 1.83 (m, 2H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 165.9, 137.4, 133.7, 132.5, 131.4, 131.1, 130.5, 126.6, 115.5, 65.0, 30.2, 27.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}ClO_2$ $[M + H]^+$, 225.0682. Found, 225.0674. IR (neat): υ (cm^{-1}): 3077, 2957, 2850, 1731, 1645, 1593, 1471, 1436, 1292, 1251, 1120, 1050, 914, 747.

Pent-4-en-1-yl 3-(4-bromophenyl)propanoate (X-13)

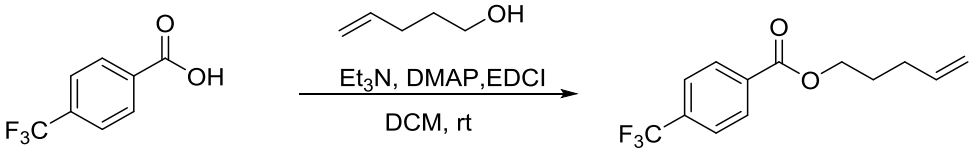


X-13

To a solution of 3-(4-bromophenyl)propanoic acid (4.58 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (244 mg, 2.00 mmol, 0.100 equiv) and Et_3N (6.07 g, 60.0 mmol, 3.00 equiv) in CH_2Cl_2 (20.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (5.75 g, 30.0 mmol, 1.50 equiv) and pent-4-en-1-ol (2.58 g, 30.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (20.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.75 g pent-4-en-1-yl 3-(4-bromophenyl)propanoate (**X-13**) as a colorless liquid (46% yield).

R_f = 0.45 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.08 – 7.06 (m, 2H), 5.83 – 5.72 (m, 1H), 5.04 – 4.97 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.90 (t, *J* =7.7 Hz, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.72 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 139.5, 137.5, 131.6, 130.2, 120.1, 115.4, 64.0, 35.7, 30.4, 30.1, 27.8. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}BrO_2$ $[M + H]^+$, 297.0490. Found, 297.0479. IR (neat): υ (cm^{-1}): 3078, 2954, 2868, 1733, 1641, 1488, 1361, 1292, 1255, 1175, 1072, 1011, 914, 814.

Pent-4-en-1-yl 4-trifluoromethylbenzoate (X-14)



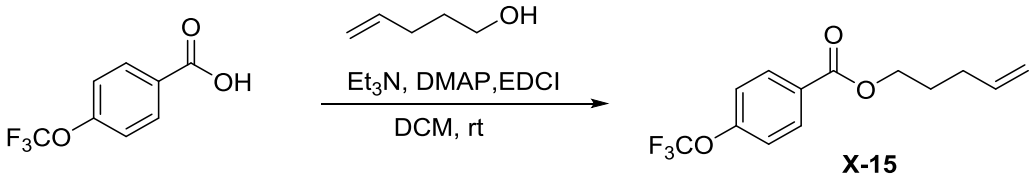
X-14

To a solution of 4-trifluoromethylbenzoic acid (3.80 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (244 mg, 2.00 mmol, 0.100 equiv) and Et_3N (6.07 g, 60.0 mmol, 3.00 equiv) in CH_2Cl_2 (20.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (5.75 g, 30.0 mmol, 1.50 equiv) and pent-4-en-1-ol (2.58 g, 30.0 mmol, 1.50 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (20.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting

with PE/EtOAc 50:1 (v/v) to afford 4.67 g pent-4-en-1-yl 4-trifluoromethylbenzoate (**X-14**) as a colorless liquid (90% yield).

R_f = 0.21 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 5.89 – 5.79 (m, 1H), 5.09 – 5.00 (m, 2H), 4.37 (t, *J* = 6.6 Hz, 2H), 2.25 – 2.19 (m, 2H), 1.92 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 137.4, 134.5 (q, *J* = 32.3 Hz), 133.8, 130.1, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 273.7 Hz), 115.6, 65.0, 30.2, 27.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.03. **X-14** is a known compound and spectral data match the reported literature values [3]. IR (neat): υ (cm^{-1}): 3081, 2959, 2851, 1727, 1642, 1515, 1412, 1326, 1276, 1169, 1131, 1101, 1018, 916, 862, 775.

Pent-4-en-1-yl 4-(trifluoromethoxy)benzoate (X-15)

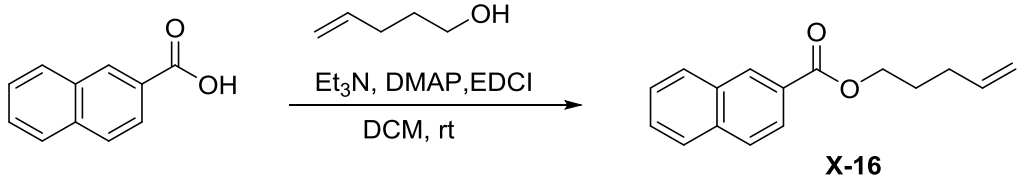


X-15

To a solution of 4-(trifluoromethoxy)benzoic acid (4.12 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 6.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 4.29 g pent-4-en-1-yl 4-(trifluoromethoxy)benzoate (**X-15**) as a colorless liquid (78% yield).

R_f = 0.59 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 5.90 – 5.80 (m, 1H), 5.10 – 5.00 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.25 – 2.19 (m, 2H), 1.95 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 152.7, 137.5, 131.7, 129.0, 120.4 (q, *J* = 258.4 Hz), 120.4, 115.6, 64.8, 30.3, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.36. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_8H_4F_3O_2$ $[M - C_5H_9O]^+$, 189.0163. Found, 189.0165. IR (neat): υ (cm^{-1}): 3061, 2959, 2853, 1724, 1645, 1608, 1474, 1258, 1220, 1167, 1113, 1018, 920, 863, 769.

Pent-4-en-1-yl 2-naphthoate (X-16)



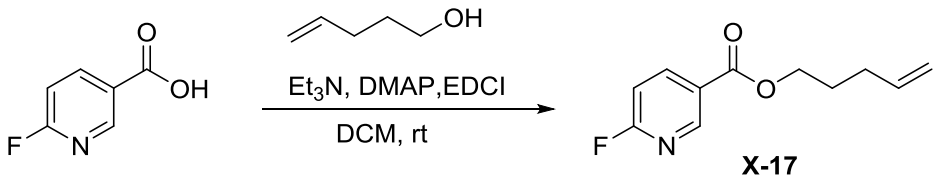
X-16

To a solution of 2-naphthoic acid (3.44 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol,

2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 3.19 g pent-4-en-1-yl 2-naphthoate (**X-16**) as a colorless liquid (66% yield).

R_f = 0.35 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.89 – 7.85 (m, 2H), 7.60 – 5.51 (m, 2H), 5.95 – 5.85 (m, 1H), 5.15 – 5.04 (m, 2H), 4.41 (t, *J* = 6.6 Hz, 2H), 2.36 – 2.28 (m, 2H), 2.00 – 1.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 137.5, 135.5, 132.5, 131.0, 129.4, 128.2, 128.2, 127.8, 127.7, 126.7, 125.3, 115.5, 64.6, 30.3, 28.0. HRMS-ESI (m/z): Calcd for $C_{16}H_{16}NaO_2$ $[M + Na]^+$, 263.1048. Found, 263.1048. IR (neat): υ (cm^{-1}): 3042, 2958, 2888, 1713, 1641, 1599, 1462, 1390, 1353, 1284, 1227, 1195, 1129, 1096, 986, 913, 865, 778.

Pent-4-en-1-yl 6-fluoronicotinate (X-17)

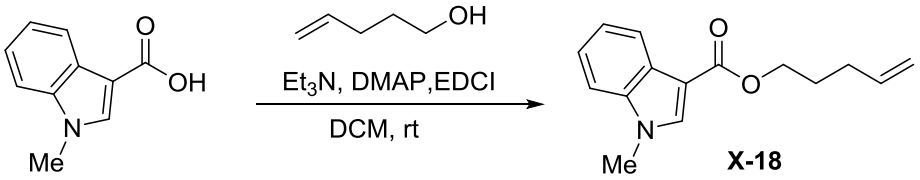


X-17

To a solution of 6-fluoronicotinic acid (2.82 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 2.70 g pent-4-en-1-yl 6-fluoronicotinate (**X-17**) 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 8.87 (d, *J* = 2.4 Hz, 1H), 8.41 – 8.37 (m, 1H), 7.00 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.87 – 5.77 (m, 1H), 5.08 – 4.98 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.23 – 2.17 (m, 2H), 1.93 – 1.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 245.5 Hz), 164.3, 150.4 (d, *J* = 16.6 Hz), 142.7 (d, *J* = 9.3 Hz), 137.3, 124.8 (d, *J* = 4.4 Hz), 115.7, 109.6 (d, *J* = 37.5 Hz), 66.1, 30.2, 27.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.53. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{13}FNO_2$ $[M + H]^+$, 210.0930. Found, 210.0930. IR (neat): υ (cm^{-1}): 3078, 2942, 2850, 1726, 1642, 1595, 1483, 1380, 1269, 1115, 1020, 915, 844, 777.

Pent-4-en-1-yl 1-methyl-1H-indole-3-carboxylate (X-18)

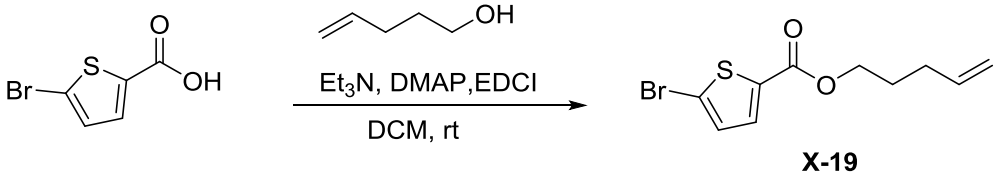


X-18

To a solution of 1-methyl-1H-indole-3-carboxylic acid (3.50 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 3.26 g pent-4-en-1-yl 1-methyl-1H-indole-3-carboxylate (**X-18**) as a colorless liquid (67% yield).

R_f = 0.08 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 7.78 (s, 1H), 7.38 – 7.27 (m, 3H), 5.94 – 5.84 (m, 1H), 5.13 – 5.02 (m, 2H), 4.36 (t, *J* = 6.6 Hz, 2H), 3.82 (s, 3H), 2.29 – 2.24 (m, 2H), 1.96 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 137.8, 137.3, 135.3, 126.7, 122.8, 121.9, 121.7, 115.3, 109.9, 107.2, 63.2, 33.5, 30.4, 28.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{18}NO_2$ $[M + H]^+$, 244.1338. Found, 244.1332. IR (neat): υ (cm^{-1}): 3056, 2941, 2848, 1696, 1640, 1536, 1467, 1400, 1372, 1268, 1223, 1152, 1103, 1013, 913, 774.

Pent-4-en-1-yl 5-bromothiophene-2-carboxylate (X-19)



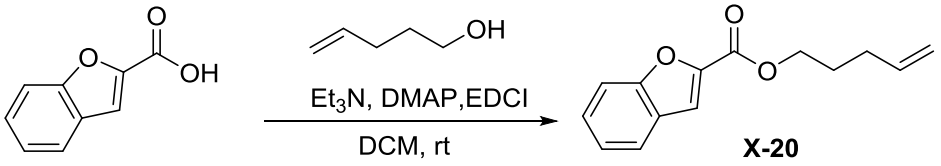
X-19

To a solution of 5-bromothiophene-2-carboxylic acid (4.14 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 25:1 (v/v) to afford 4.70 g pent-4-en-1-yl 5-bromothiophene-2-carboxylate (**X-19**) as a colorless liquid (81% yield).

R_f = 0.54 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.09 – 5.00 (m, 2H),

4.28 (t, *J* = 6.6 Hz, 2H), 2.22 – 2.14 (m, 2H), 1.90 – 1.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 137.4, 135.1, 133.7, 131.0, 120.2, 115.6, 64.9, 30.2, 27.9. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{10}H_{11}BrO_2S$ $[M]^+$, 273.9663. Found, 273.9666. IR (neat): υ (cm^{-1}): 3080, 2955, 2894, 1706, 1644, 1559, 1507, 1418, 1280, 1251, 1124, 1095, 915, 810, 745.

Pent-4-en-1-yl benzofuran-2-carboxylate (X-20)

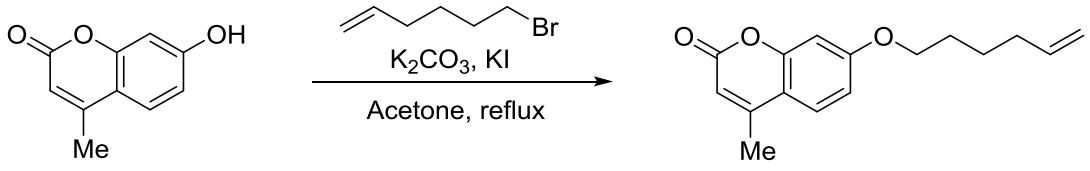


X-20

To a solution of benzofuran-2-carboxylic acid (3.24 g, 20.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (4.55 g, 45.0 mmol, 2.25 equiv) in CH_2Cl_2 (50.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (7.66 g, 40.0 mmol, 2.00 equiv) and pent-4-en-1-ol (1.90 g, 22.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 3.19 g pent-4-en-1-yl benzofuran-2-carboxylate (**X-20**) as a colorless liquid (69% yield).

R_f = 0.48 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 1H), 7.60 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.53 (d, *J* = 0.9 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.30 – 7.27 (m, 1H), 5.90 – 5.80 (m, 1H), 5.11 – 5.00 (m, 2H) , 4.39 (t, *J* = 6.7 Hz, 2H), 2.28 – 2.19 (m, 2H), 1.95 – 1.85 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 155.8, 145.7, 137.4, 127.7, 127.1, 123.9, 122.9, 115.6, 113.9, 112.5, 65.0, 30.1, 27.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{15}O_3$ $[M + H]^+$, 231.1021. Found, 231.1020. IR (neat): υ (cm^{-1}): 3075, 2957, 1730, 1641, 1564, 1447, 1295, 1178, 1097, 915, 749.

7-(Hex-5-en-1-yloxy)-4-methyl-2H-chromen-2-one (X-21)



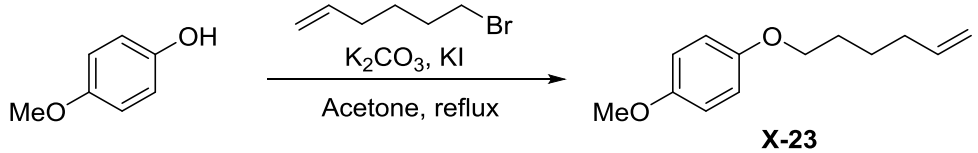
X-21

Under N_2 atmosphere, to a solution of 7-hydroxy-4-methyl-2H-chromen-2-one (3.52 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and

concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 4.60 g 7-(hex-5-en-1-yloxy)-4-methyl-2H-chromen-2-one (**X-21**) as a colorless liquid (89% yield).

R_f = 0.59 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 1H), 6.82 – 6.78 (m, 1H), 6.74 – 6.70 (m, 1H), 6.06 (s, 1H), 5.84 – 5.73 (m, 1H), 5.04 – 4.92 (m, 2H), 3.97 (t, *J* = 6.2 Hz, 2H), 2.34 (s, 3H), 2.14 – 2. 08 (m, 2H), 1.83 – 1.76 (m, 2H), 1.58 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.3, 155.2, 152.6, 138.3, 125.5, 114.9, 113.4, 112.6, 111.8, 101.3, 68.4, 33.4, 28.4, 25.2, 18.7. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{19}O_3$ $[M + H]^+$, 259.1334. Found, 259.1328. IR (neat): υ (cm^{-1}): 3018, 2896, 2793, 1724, 1710, 1611, 1388, 1281, 1200, 1147, 1070, 992, 911, 847.

1-(Hex-5-en-1-yloxy)-4-methoxybenzene (X-23)

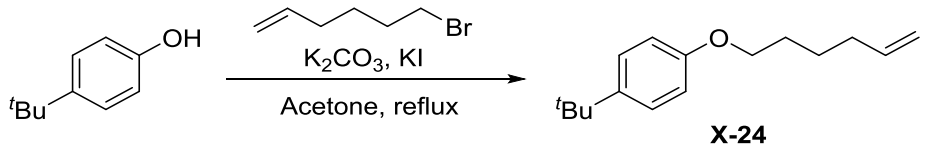


X-23

Under N_2 atmosphere, to a solution of 4-methoxyphenol (2.48 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 3.83 g 1-(hex-5-en-1-yloxy)-4-methoxybenzene (**X-23**) as a colorless liquid (93% yield).

R_f = 0.49 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 – 6.77 (m, 4H), 5.88 – 5.78 (m, 1H), 5.06 – 4.96 (m, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 2.17 – 2.09 (m, 2H), 1.83 – 1.75 (m, 2H), 1.60 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 153.4, 138.7, 115.5, 114.8, 114.7, 68.5, 55.9, 33.6, 29.0, 25.5. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{18}O_2$ $[M]^+$, 206.1307. Found, 206.1301. IR (neat): υ (cm^{-1}): 3078, 2937, 2834, 1640, 1616, 1508, 1469, 1231, 1106, 1041, 911, 744.

1-(Hex-5-en-1-yloxy)-4-(*tert*-butyl)benzene (X-24)



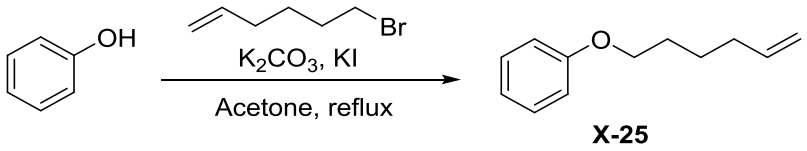
X-24

Under N_2 atmosphere, to a solution of 4-(*tert*-butyl)phenol (3.00 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to

afford 4.24 g 1-(hex-5-en-1-yloxy)-4-(*tert*-butyl)benzene (**X-24**) as a colorless liquid (91% yield).

R_f = 0.53 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 6.88 – 6.81 (m, 2H), 5.90 – 5.79 (m, 1H), 5.07 – 4.97 (m, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.84 – 1.77 (m, 2H), 1.62 – 1.54 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 143.3, 138.7, 126.3, 114.8, 114.0, 67.8, 34.2, 33.6, 31.7, 29.0, 25.5. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{16}H_{24}O$ $[M]^+$, 232.1827. Found, 232.1827. IR (neat): υ (cm^{-1}): 3076, 2961, 2867, 1644, 1610, 1513, 1473, 1246, 1183, 1035, 909, 827.

(Hex-5-en-1-yloxy)benzene (X-25)

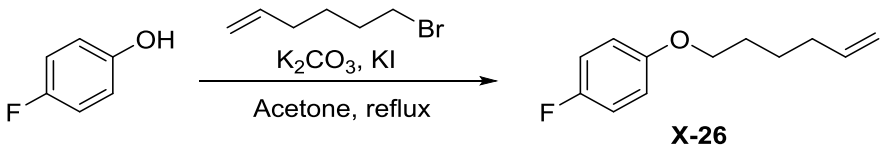


X-25

Under N_2 atmosphere, to a solution of phenol (1.88 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 3.13 g (hex-5-en-1-yloxy)benzene (**X-25**) as a colorless liquid (89% yield).

R_f = 0.53 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 6.98 – 6.88 (m, 3H), 5.90 – 5.80 (m, 1H), 5.08 – 4.97 (m, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.19 – 2.10 (m, 2H), 1.86 – 1.78 (m, 2H), 1.64 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 138.7, 129.5, 120.6, 114.9, 114.6, 67.7, 33.6, 28.9, 25.5. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{16}O$ $[M]^+$, 176.1201. Found, 176.1203. IR (neat): υ (cm^{-1}): 3047, 2965, 2881, 1640, 1600, 1495, 1469, 1300, 1244, 1171, 1036, 910, 752.

1-(Hex-5-en-1-yloxy)-4-fluorobenzene (X-26)

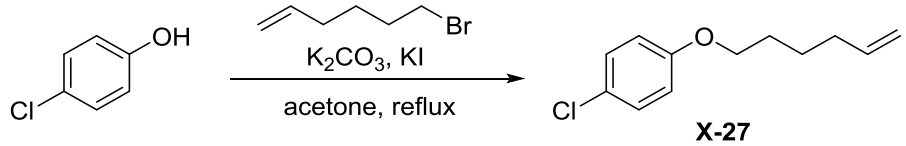


X-26

Under N_2 atmosphere, to a solution of 4-fluorophenol (2.24 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue

was purified by chromatography on silica gel, eluting with hexanes to afford 3.66 g 1-(hex-5-en-1-yloxy)-4-fluorobenzene (**X-26**) as a colorless liquid (94% yield).
R_f = 0.54 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.92 (m, 2H), 6.86 – 6.79 (m, 2H), 5.88 – 5.78 (m, 1H), 5.07 – 4.96 (m, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.08 (m, 2H), 1.84 – 1.73 (m, 2H), 1.63 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 237.7 Hz), 155.3 (d, *J* = 1.8 Hz), 138.6, 115.9 (d, *J* = 23.0 Hz), 115.5 (d, *J* = 8.0 Hz), 114.9, 68.5, 33.6, 28.9, 25.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.49. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{15}FO$ $[M]^+$, 194.1107. Found, 194.1105. IR (neat): υ (cm^{-1}): 3078, 2938, 2866, 1640, 1506, 1473, 1292, 1247, 1219, 1096, 1032, 912, 827, 757.

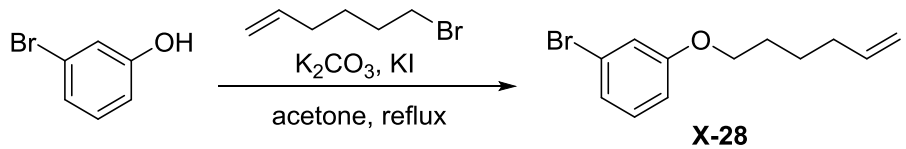
1-(Hex-5-en-1-yloxy)-4-chlorobenzene (X-27)



X-27

Under N_2 atmosphere, to a solution of 4-chlorophenol (2.57 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 3.97 g 1-(hex-5-en-1-yloxy)-4-chlorobenzene (**X-27**) as a colorless liquid (94% yield).
R_f = 0.59 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.86 – 6.79 (m, 2H), 5.89 – 5.79 (m, 1H), 5.06 – 4.97 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.83 – 1.76 (m, 2H), 1.63 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 138.6, 129.4, 125.4, 115.8, 114.9, 68.2, 33.5, 28.7, 25.4. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{15}ClO$ $[M]^+$, 210.0811. Found, 210.0812. IR (neat): υ (cm^{-1}): 3076, 2940, 2867, 1640, 1597, 1492, 1390, 1285, 1244, 1169, 1092, 1005, 911, 823.

1-(Hex-5-en-1-yloxy)-3-bromobenzene(X-28)



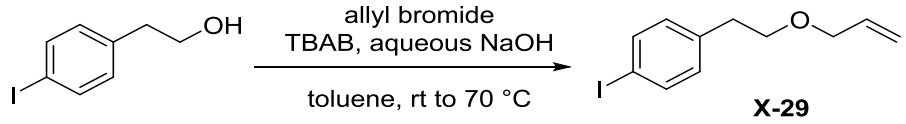
X-28

Under N_2 atmosphere, to a solution of 3-bromophenol (3.46 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue

was purified by chromatography on silica gel, eluting with hexanes to afford 4.66 g 1-(hex-5-en-1-yloxy)-3-bromobenzene (**X-28**) as a colorless liquid (91% yield).

R_f = 0.63 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 1H), 7.08 – 7.05 (m, 2H), 6.87 – 6.81 (m, 1H), 5.89 – 5.77 (m, 1H), 5.08 – 4.96 (m, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.84 – 1.74 (m, 2H), 1.63 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 138.6, 130.6, 123.7, 122.9, 117.8, 115.0, 113.7, 68.1, 33.5, 28.7, 25.4. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{15}BrO$ $[M]^+$, 254.0306. Found, 254.0311. IR (neat): υ (cm^{-1}): 3075, 2939, 2871, 1640, 1590, 1424, 1389, 1283, 1227, 1064, 992, 911, 862, 840, 764.

Allyl-(4-iodophenethyl)-ether (X-29)

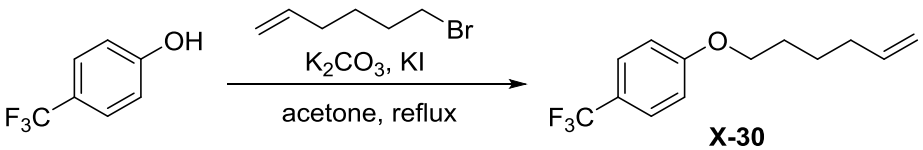


X-29

Under air atmosphere, to a solution of 2-(4-iodophenyl)ethanol (4.96 g, 20.0 mmol, 1.00 equiv) in toluene (12.0 mL) at room temperature were added TBAB (300 mg, 0.931 mmol, 0.0465 equiv) and aqueous NaOH (50 weight%, 2.30 g, 28.8 mmol, 1.44 equiv). The reaction mixture was stirred for 30 min at room temperature. Allyl bromide (3.03 g, 25.0 mmol, 1.25 equiv) was added into the mixture and the reaction mixture was then heated at 70 ºC for 10 h. After cooling to room temperature, the reaction mixture was diluted with water (20 mL) and extracting three times with EtOAc (40 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 4.40 g allyl-(4-iodophenethyl)-ether (**X-29**) as a colorless liquid (76% yield).

R_f = 0.46 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 7.62 – 7.59 (m, 2H), 7.00 – 6.98 (m, 2H), 5.94 – 5.84 (m, 1H), 5.28 – 5.14 (m, 2H), 3.98 (dt, *J* = 5.5 Hz, 1.2 Hz, 2H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, *δ*): 138.8, 137.5, 134.8, 131.1, 117.1, 91.5, 72.0, 70.8, 36.0. Mass Spectrometry: Calcd for HRMS-EI (m/z): Calcd for $C_{11}H_{13}IO$ $[M]^+$, 288.0011. Found, 288.0010. IR (neat): υ (cm^{-1}): 3017, 2919, 2856, 1640, 1600, 1507, 1484, 1399, 1346, 1100, 1060, 1006, 995, 923, 807.

1-(Hex-5-en-1-yloxy)-4-(trifluoromethyl)benzene (X-30)



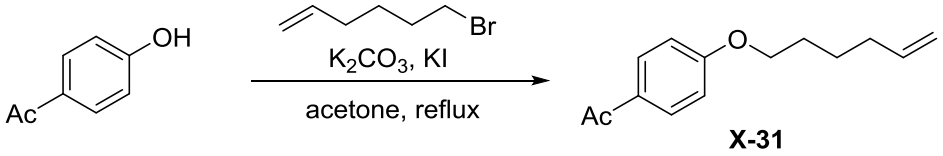
X-30

Under N_2 atmosphere, to a solution of 4-trifluoromethylphenol (3.26 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room

temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 4. 53 g 1-(hex-5-en-1-yloxy)-4-(trifluoromethyl)benzene (**X-30**) as a colorless liquid (93% yield).

R_f = 0.44 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.89 – 5.79 (m, 1H), 5.08 – 4.98 (m, 2H), 4.00 (t, J = 6.4 Hz, 2H), 2.17 – 2.12 (m, 2H), 1.87 – 1.78 (m, 2H), 1.65 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 161.7, 138.5, 127.0 (q, J = 3.9 Hz), 124.6 (q, J = 272.0 Hz), 122.8 (q, J = 32.7 Hz), 115.0, 114.5, 68.1, 33.5, 28.7, 25.4. ^{19}F NMR (376 MHz, $CDCl_3$, δ) -62.90. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{15}F_3O$ $[M]^+$, 244.1075. Found, 244.1073. IR (neat): υ (cm^{-1}): 3079, 2941, 2875, 1640, 1616, 1599, 1519, 1330, 1257, 1161, 1110, 1068, 995, 910, 835.

1-(4-(Hex-5-en-1-yloxy)phenyl)ethanone (X-31)

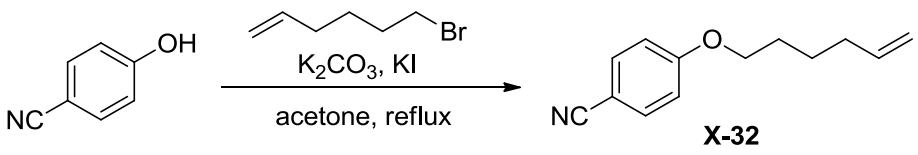


X-31

Under N_2 atmosphere, to a solution of 1-(4-hydroxyphenyl)ethanone (2.72 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 4.21 g 1-(4-(hex-5-en-1-yloxy)phenyl)ethanone (**X-31**) as a colorless liquid (97% yield).

R_f = 0.24 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 6.94 – 6.86 (m, 2H), 5.87 – 5.76 (m, 1H), 5.06 – 4.94 (m, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.54 (s, 3H), 2.17 – 2.07 (m, 2H), 1.85 – 1.78 (m, 2H), 1.62 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.1, 138.4, 130.7, 130.2, 115.0, 114.2, 68.1, 33.5, 28.6, 26.4, 25.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{19}O_2$ $[M + H]^+$, 219.1385. Found, 219.1383. IR (neat): υ (cm^{-1}): 3075, 2940, 2871, 1678, 1640, 1601, 1509, 1358, 1256, 1171, 1021, 995, 834.

4-(Hex-5-en-1-yloxy)benzonitrile (X-32)



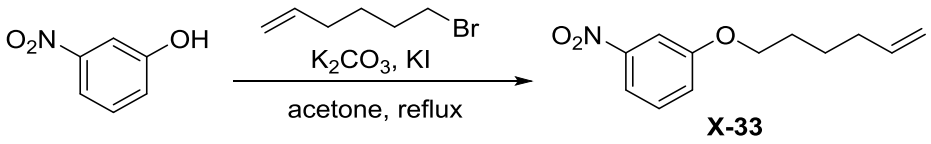
X-32

Under N_2 atmosphere, to a solution of 4-hydroxybenzonitrile (2.38 g, 20.0 mmol, 1.00 equiv)

and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 2.75 g 4-(hex-5-en-1-yloxy)benzonitrile (**X-32**) as a colorless liquid (86% yield).

R_f = 0.36 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 6.94 – 6.91 (m, 2H), 5.86 – 5.78 (m, 1H), 5.06 – 4.96 (m, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.15 – 2.10 (m, 2H), 1.86 – 1.78 (m, 2H), 1.61 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 138.4, 134.1, 119.4, 115.3, 115.1, 103.7, 68.3, 33.4, 28.5, 25.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{16}NO$ $[M + H]^+$, 202.1232. Found, 202.1229. IR (neat): υ (cm^{-1}): 3076, 2939, 2873, 2224, 1640, 1606, 1508, 1428, 1301, 1258, 1171, 1020, 997, 912, 835, 743, 703.

1-(Hex-5-en-1-yloxy)-3-nitrobenzene (X-33)

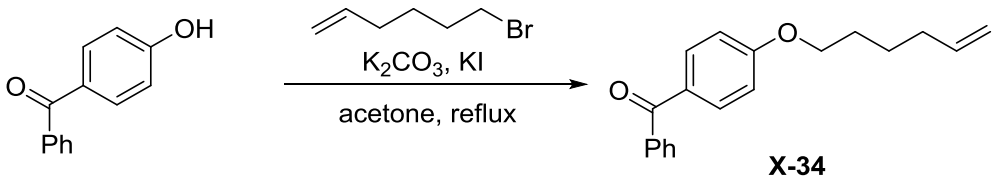


X-33

Under N_2 atmosphere, to a solution of 3-nitrophenol (2.80 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 4.03 g 1-(hex-5-en-1-yloxy)-3-nitrobenzene (**X-33**) as a yellow liquid (91% yield).

R_f = 0.48 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 1H), 7.70 (t, *J* = 2.3 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 5.87 – 5.77 (m, 1H), 5.06 – 4.96 (m, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.87 – 1.80 (m, 2H), 1.65 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.3, 138.4, 130.0, 121.8, 115.7, 115.1, 108.7, 68.6, 33.4, 28.5, 25.3. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{15}NO_3$ $[M]^+$, 221.1052. Found, 221.1053. IR (neat): υ (cm^{-1}): 3078, 2940, 2871, 1641, 1619, 1580, 1530, 1484, 1449, 1350, 1286, 1246, 1032, 995, 910, 812, 737.

(4-(Hex-5-enyloxy)phenyl)(phenyl)methanone (X-34)

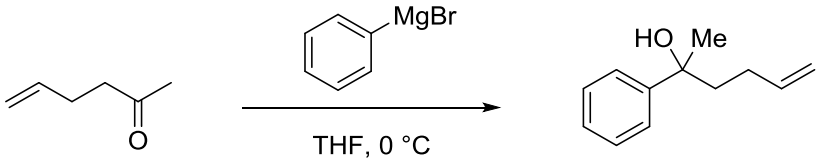


X-34

Under N_2 atmosphere, to a solution of (4-hydroxyphenyl)(phenyl)methanone (3.96 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 25:1 (v/v) to afford 5.04 g (4-(hex-5-enyloxy)phenyl)(phenyl)methanone (**X-34**) as a colorless liquid (90% yield).

R_f = 0.48 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.46 (m, 1H), 7.41 – 7.38 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.83 – 5.73 (m, 1H), 5.03 – 4.94 (m, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.57 – 1.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 162.6, 138.1, 132.3, 131.6, 129.7, 129.5, 128.0, 114.7, 113.8, 67.8, 33.2, 28.4, 25.1. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{19}H_{20}NaO_2$ $[M + Na]^+$, 303.1361. Found, 303.1358. IR (neat): υ (cm^{-1}): 3072, 2939, 2870, 1650, 1600, 1577, 1507, 1469, 1419, 1391, 1315, 1280, 1254, 1172, 1148, 1114, 1072, 1027, 998, 920, 844, 792.

2-Phenylhex-5-en-2-ol (X-36)

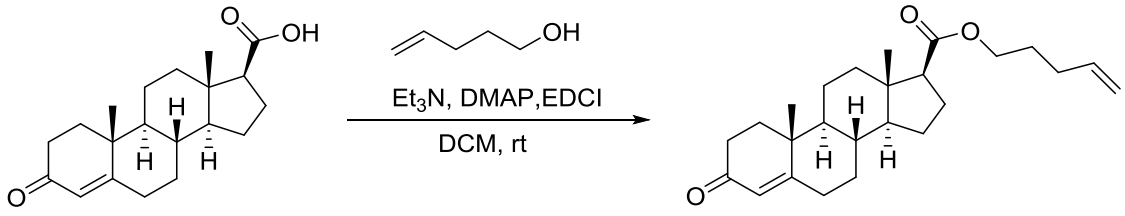


X-36

Under N_2 atmosphere, to a solution of hex-5-en-2-one (1.96 g, 20.0 mmol, 1.00 equiv) in dried THF (30.0 mL) at 0 °C was added dropwise phenylmagnesium bromide in THF (3M, 10.0 mL, 1.50 equiv). After stirring at 0 ºC for 5 h, the reaction mixture was quenching with H_2O (30.0 mL) and extracting 3 times with EtOAc (30.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 1.54 g 2-phenylhex-5-en-2-ol (**X-36**) as a colorless liquid (44% yield).

R_f = 0.18 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.37 – 7.31 (m, 2H), 7.28 – 7.20 (m, 1H), 5.84 – 5.74 (m, 1H), 4.99 – 4.86 (m, 2H), 2.10 – 1.82 (m, 5H), 1.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 138.9, 128.3, 126.7, 124.9, 114.7, 74.9, 43.2, 30.5, 28.7. HRMS-EI (m/z): Calcd for $C_{12}H_{14}$ $[M – H_2O]^+$, 158.1096. Found, 158.1095. IR (neat): υ (cm^{-1}): 3413, 3078, 2976, 2854, 1649, 1493, 1446, 1372, 1282, 1069, 995, 855, 763.

Pent-4-en-1-yl androst-4-en-3-one-17β-carboxylate (X-39)

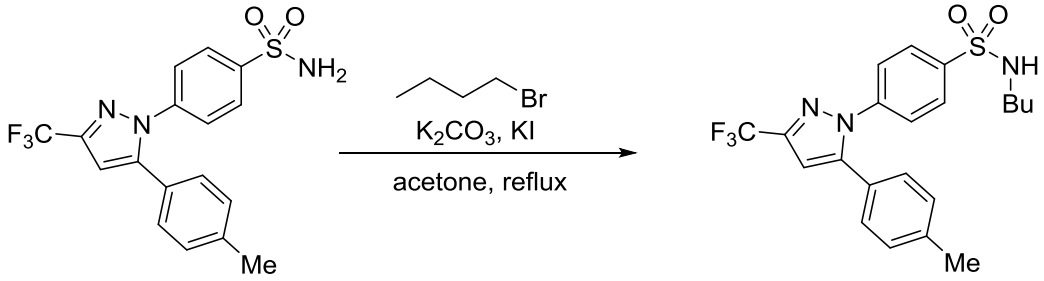


X-39

To a solution of 4-androsten-3-one-5-ene-17-carboxylic acid (3.15 g, 10.0 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (245 mg, 2.00 mmol, 0.200 equiv) and Et_3N (2.25 g, 22.5 mmol, 2.25 equiv) in CH_2Cl_2 (25.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (3.83 g, 20.0 mmol, 2.00 equiv) and pent-4-en-1-ol (0.95 g, 11.0 mmol, 1.10 equiv). The reaction mixture was stirred at room temperature for 3.0 h before quenching with H_2O (15.0 mL) and extracting 3 times with CH_2Cl_2 (15.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 2.50 g pent-4-en-1-yl androst-4-en-3-one-17β-carboxylate (**X-39**) as a colorless liquid (65% yield).

R_f = 0.18 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.71 (m, 1H), 5.68 (s, 1H), 5.02 – 4.93 (m, 2H), 4.10 – 3.97 (m, 2H), 2.45 – 2.19 (m, 5H), 2.15 – 1.96 (m, 5H), 1.87 – 1.61 (m, 6H), 1.61 – 1.20 (m, 5H), 1.14 (s, 3H), 1.12 – 0.87 (m, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 173.9, 171.0, 137.5, 123.9, 115.3, 63.5, 55.3, 55.2, 53.7, 43.9, 38.6, 38.1, 35.7, 35.7, 34.0, 32.8, 31.9, 30.2, 28.0, 24.4, 23.5, 20.9, 17.4, 13.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{25}H_{36}NaO_3$ $[M + Na]^+$, 407.2562. Found, 407.2560. IR (neat): υ (cm^{-1}): 3078, 2941, 2877, 1726, 1676, 1450, 1383, 1268, 1188, 1165, 1049, 995, 910.

***N*-butyl-Celecoxib (X-40')**



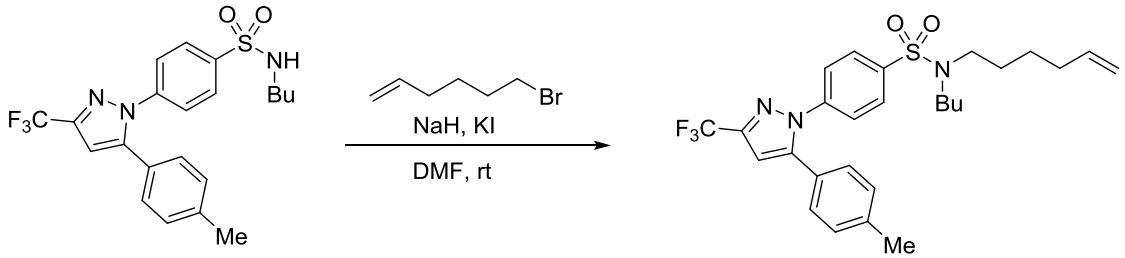
X-40'

Under N_2 atmosphere, to a solution of Celecoxib (3.81 g, 10.0 mmol, 1.00 equiv) and 1-Bromobutane (2.03 g, 15.0 mmol, 1.50 equiv) in acetone (25.0 mL) were added KI (1.66 g, 10.0 mmol, 1.00 equiv) and K_2CO_3 (2.76 g, 20.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction

mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 8:1 (v/v) to afford 3.10 g *N*-butyl-Celecoxib (**X-40'**) as a white solid (71% yield).

R_f = 0.41 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.1 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 4.37 (t, *J* = 6.0 Hz, 1H), 2.95 (q, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 1.50 – 1.38 (m, 2H), 1.33 – 1.24 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.2 (q, *J* = 38.7 Hz), 142.6, 139.9, 139.7, 129.9, 128.8, 128.2, 125.8, 125.7, 121.2 (q, *J* = 269.9 Hz), 106.4, 43.1, 31.7, 21.4, 19.8, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.13. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{23}F_3N_3O_2S$ $[M + H]^+$, 438.1463. Found, 438.1464. IR (neat): υ (cm^{-1}): 2978, 2913, 2886, 1590, 1499, 1449, 1407, 1373, 1342, 1281, 1236, 1176, 1115, 1096, 1020, 842, 766.

***N*-butyl-*N*-(hex-5-enyl)-Celecoxib (X-40)**

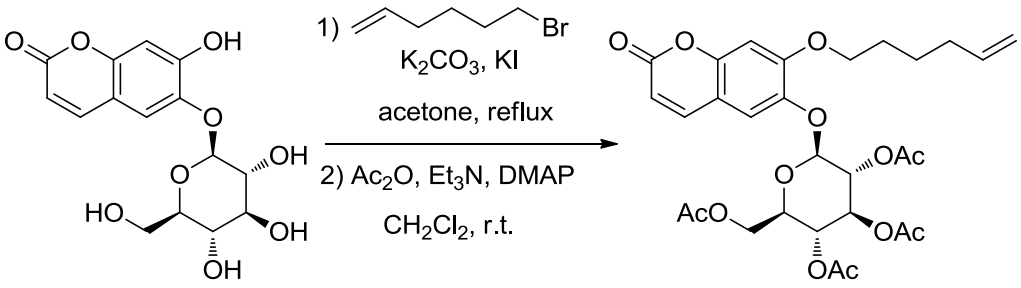


X-40' **X-40**

Under N_2 atmosphere, to a solution of *N*-butyl-Celecoxib (**X-40'**) (2.19 g, 5.00 mmol, 1.00 equiv) in dry DMF (10.0 mL) were added KI (830 mg, 5.00 mmol, 1.00 equiv) and NaH (300 mg, 7.50 mmol, 1.50 equiv) at 0 ºC. The reaction mixture was stirred at 0 ºC for 0.5 h. Then added 6-bromo-1-hexene (1.63 g, 10.0 mmol, 2.00 equiv) and stirred for 12.0 h at room temperature before quenching with H_2O (10.0 mL) and extracting 3 times with EtOAc (20.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 2.36 g *N*-butyl-*N*-(hex-5-enyl)-Celecoxib (**X-40**) as a white solid (91% yield).

R_f = 0.52 (hexanes/EtOAc 6:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 5.80 – 5.70 (m, 1H), 5.03 – 4.93 (m, 2H), 3.13 – 3.07 (m, 4H), 2.37 (s, 3H), 2.04 (q, *J* = 7.1 Hz, 2H), 1.58 – 1.43 (m, 4H), 1.40 – 1.21 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.2 (q, *J* = 38.3 Hz), 142.3, 139.9, 138.3, 129.8, 128.8, 128.2, 125.8, 125.6, 121.2 (q, *J* = 269.5 Hz), 115.1, 106.3, 48.1, 33.3, 30.7, 28.0, 26.0, 21.4, 20.0, 13.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.07. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{27}H_{33}F_3N_3O_2S$ $[M + H]^+$, 520.2246. Found, 520.2244. IR (neat): υ (cm^{-1}): 3036, 2960, 2929, 2886, 1638, 1597, 1498, 1449, 1407, 1373, 1342, 1268, 1236, 1159, 1135, 1096, 1018, 974, 911, 842, 766.

7-*O*-(hex-5-enyl)-Esculin tetracetate (X-41)

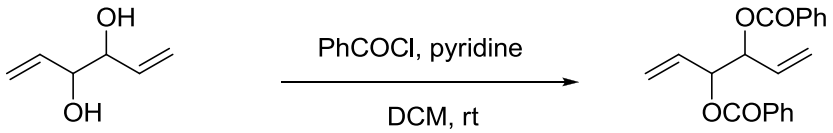


X-41

Under N_2 atmosphere, to a solution of 3-nitrophenol (6.80 g, 20.0 mmol, 1.00 equiv) and 6-bromo-1-hexene (6.52 g, 40.0 mmol, 2.00 equiv) in acetone (40.0 mL) were added KI (3.32 g, 20.0 mmol, 1.00 equiv) and K_2CO_3 (5.53 g, 40.0 mmol, 2.00 equiv) at room temperature. The reaction mixture was then refluxed for 12.0 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue obtained above was then solved in 50 mL CH_2Cl_2. DMAP (4-dimethylaminepyridine) (489 mg, 4.00 mmol, 0.200 equiv) and Et_3N (12.1 g, 120.0 mmol, 6.00 equiv) was added at room temperature. And Ac_2O (10.1 g, 10.0 mmol, 5.0 equiv) was added dropwise at 0 ºC. The reaction mixture was stirred at room temperature for 2 h before quenching with H_2O (30.0 mL) and extracting 3 times with CH_2Cl_2 (50.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 3:1 (v/v) to afford 8.14 g *7-O*-(hex-5-enyl)-Esculin tetracetate (**X-41**) as a white solid (69% yield).

R_f = 0.20 (hexanes/EtOAc 3:1(v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.5 Hz, 1H), 7.16 (s, 1H), 6.78 (s, 1H), 6.24 (d, *J* = 9.5 Hz, 1H), 5.85 – 5.75 (m, 1H), 5.31 – 5.20 (m, 2H), 5.16 – 5.10 (m, 1H), 5.04 – 4.95 (m, 3H), 4.25 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.77 – 3.73 (m, 1H), 2.11 (dd, *J* = 14.2, 7.1 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 6H), 1.87 – 1.75 (m, 2H), 1.61 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.3, 169.5, 169.2, 161.1, 153.7, 152.1, 143.2, 142.3, 138.2, 118.5, 115.2, 113.7, 111.4, 101.2, 100.1, 72.6, 72.1, 71.1, 69.1, 68.4, 61.8, 33.3, 28.4, 25.1, 20.8, 20.7, 20.7. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{29}H_{35}O_{13}$ $[M + H]^+$, 591.2078. Found, 591.2083. IR (neat): υ (cm^{-1}): 3077, 2996, 2947, 1754, 1738, 1728, 1640, 1619, 1563, 1512, 1440, 1381, 1285, 1233, 1068, 1043, 908, 823, 759.

Hexa-1,5-diene-3,4-diyl dibenzoate (X-48)



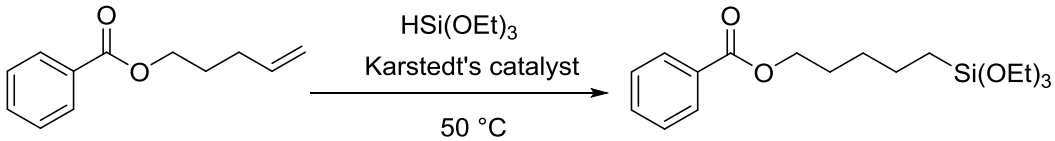
X-48

Under N_2 atmosphere, to a solution of 1,5-hexadiene-3,4-diol (1.14 g, 10.0 mmol, 1.00 equiv)

and pyridine (5.0 mL) in dry DCM (30.0 mL) was added dropwise benzoyl chloride (2.81 g, 20.0 mmol, 2.00 equiv) at 0 ºC. The reaction mixture was warmed to room temperature and stirred for 16.0 h. The reaction was then quenched with H_2O (25.0 mL) and extracted 3 times with DCM (25.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.98 g hexa-1,5-diene-3,4-diyl dibenzoate (**X-48**) as a colorless liquid (92% yield).

R_f = 0.37 (PE/EtOAc 20:1(v/v)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 4H), 7.56 (q, *J* = 8.0 Hz, 2H), 7.46 – 7.41 (m, 4H), 6.07 – 5.94 (m, 2H), 5.84 – 5.83 (m, 2H), 5.50 (d, *J* = 8.6 Hz, 2H), 5.38 (t, *J* = 10.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 165.4, 133.2, 132.1, 131.7, 130.0, 129.9, 129.7, 129.7, 128.5, 119.8, 119.7, 75.4, 75.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{19}O_4$ $[M + H]^+$, 323.1283. Found, 323.1294. IR (neat): υ (cm^{-1}): 3091, 3063, 3032, 2991, 2936, 1719, 1647, 1601, 1583. 1490, 1424, 1412, 1333, 1314, 1271, 1176, 1107, 1069, 1026, 985, 935, 883, 803, 758.

5-(Triethoxysilyl)pentyl benzoate (S-4)

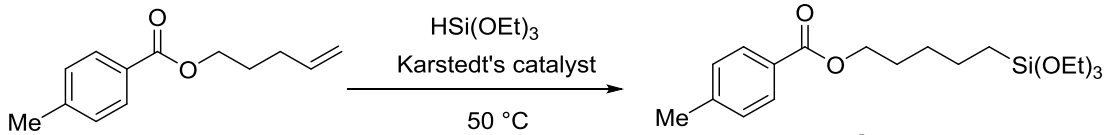


X-4 **S-4**

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl benzoate (**X-4**) (1.90 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.78 g 5-(triethoxysilyl)pentyl benzoate (**S-4**) as a colorless liquid (79% yield).

R_f = 0.38 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.81 – 1.74 (m, 2H), 1.54 – 1.46 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.69 – 0.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 132.9, 130.7, 129.7, 128.4, 65.2, 58.5, 29.7, 28.6, 22.7, 18.4, 10.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{34}NO_5Si$ $[M + NH_4]^+$, 372.2206. Found, 372.2202. IR (neat): υ (cm^{-1}): 2974, 2928, 2886, 1721, 1619, 1453, 1389, 1314, 1274, 1167, 1109, 1079, 1027, 957, 789.

5-(Triethoxysilyl)pentyl 4-methylbenzoate (S-5)



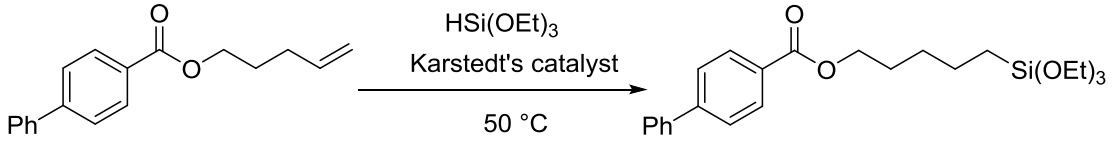
X-5 **S-5**

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 4-methylbenzoate (**X-5**) (2.04 g,

10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.10 g 5-(triethoxysilyl)pentyl 4-methylbenzoate (**S-5**) as a colorless liquid (57% yield).

R_f = 0.31 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.28 (t, *J* = 6.5 Hz, 2H), 3.81 (q, *J* = 6.9 Hz, 6H), 2.40 (s, 3H), 1.81 – 1.69 (m, 2H), 1.53 – 1.43 (m, 4H), 1.22 (t, *J* = 6.9 Hz, 9H), 0.71 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.5, 129.7, 129.1, 127.9, 65.0, 58.5, 29.6, 28.6, 22.7, 21.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{32}NaO_5Si$ $[M + Na]^+$, 391.1917. Found, 391.1917. IR (neat): υ (cm^{-1}): 2973, 2926, 2885, 1720, 1612, 1453, 1390, 1274, 1177, 1106, 1079, 1021, 957, 840, 780, 754.

5-(Triethoxysilyl)pentyl [1,1'-biphenyl]-4-carboxylate (S-6)

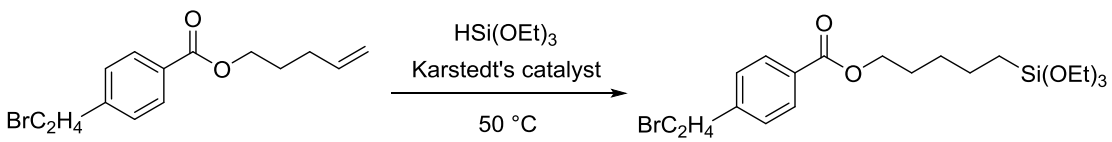


X-6 **S-6**

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl [1,1'-biphenyl]-4-carboxylate (**X-6**) (2.66 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.29 g 5-(triethoxysilyl)pentyl [1,1'-biphenyl]-4-carboxylate (**S-6**) as a colorless liquid (53% yield).

R_f = 0.19 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.67 – 7.61 (m, 4H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 1.80 (m, 2H), 1.56 – 1.48 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.72 – 0.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.6, 140.2, 130.2, 129.4, 129.0, 128.2, 127.4, 127.1, 65.2, 58.5, 29.7, 28.6, 22.8, 18.5, 10.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{24}H_{35}O_5Si$ $[M + H]^+$, 431.2254. Found, 431.2251. IR (neat): υ (cm^{-1}): 2982, 2882, 1720, 1609, 1485, 1450, 1404, 1389, 1276, 1166, 1103, 1078, 957, 858, 782, 748.

5-(Triethoxysilyl)pentyl 4-(2-bromoethyl)benzoate (S-7)

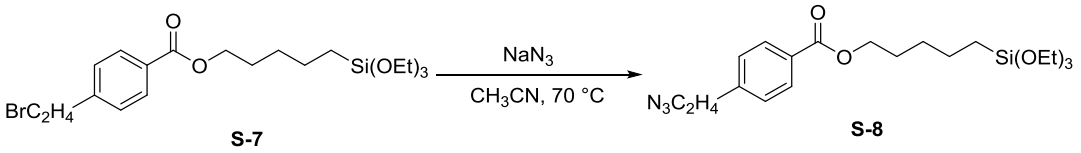


X-7 **S-7**

Under nitrogen atmosphere, to a mixture of pent-4-enyl 4-(2-bromoethyl)benzoate (**X-7**) (2.97 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.95 g 5-(triethoxysilyl)pentyl 4-(2-bromoethyl)benzoate (**S-7**) as a colorless liquid (64% yield).

R_f = 0.14 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.59 (t, *J* = 7.4 Hz, 2H), 3.22 (t, *J* = 7.4 Hz, 2H), 1.80 – 1.74 (m, 2H), 1.53 – 1.46 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 144.0, 130.0, 129.4, 128.8, 65.2, 58.5, 39.2, 32.4, 29.6, 28.5, 22.7, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{34}BrO_5Si$ $[M + H]^+$, 461.1359. Found, 461.1354. IR (neat): υ (cm^{-1}): 2926, 2864, 1735, 1601, 1488, 1389, 1284, 1212, 1165, 1076, 1076, 1011, 956, 780.

5-(Triethoxysilyl)pentyl 4-(2-azidoethyl)benzoate (S-8)

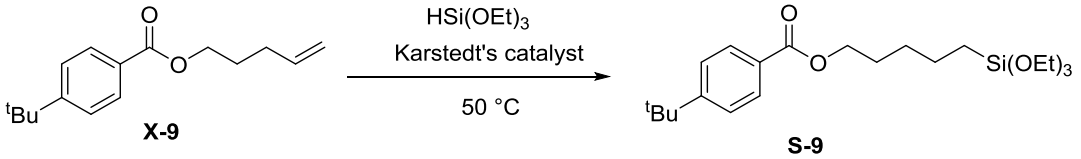


S-7 **S-8**

Under nitrogen atmosphere, to a solution of 5-(triethoxysilyl)pentyl 4-(2-bromoethyl)benzoate (**S-7**) (1.38 g, 3.00 mmol, 1.00 equiv) in 15.0 mL MeCN at room temperature was added NaN_3 (487 mg, 7.50 mmol, 2.50 equiv). The reaction mixture was then heated to 70 ºC and stirred for 48 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad, concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 1.12 g 5-(triethoxysilyl)pentyl 4-(2-azidoethyl)benzoate (**S-8**) as a colorless liquid (88% yield).

R_f = 0.11 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 3.54 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.51 – 1.46 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.4, 130.1, 128.9, 65.2, 58.5 52.2, 35.5, 29.6, 28.6, 22.7, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{34}N_3O_5Si$ $[M + H]^+$, 424.2268. Found, 424.2265. IR (neat): υ (cm^{-1}): 2974, 2886, 2099, 1729, 1680, 1601, 1554, 1494, 1444, 1277, 1176, 1115, 1019, 1000, 953, 855, 762.

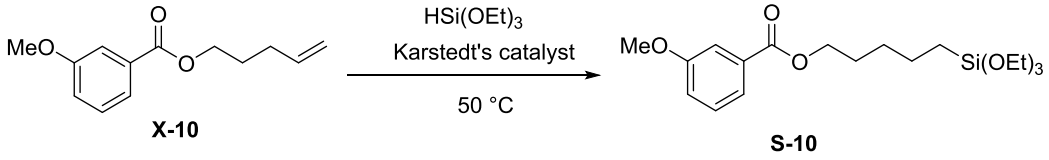
5-(Triethoxysilyl)pentyl 4-(*tert*-butyl)benzoate (S-9)



X-9 S-9

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 4-(*tert*-butyl)benzoate (**X-9**) (1.23 g, 5.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.150 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (1.34 g, 8.13 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 1.39 g 5-(triethoxysilyl)pentyl 4-(*tert*-butyl)benzoate (**S-9**) as a colorless liquid (68% yield).
R_f = 0.35 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.9 7 – 7.93 (m, 2H), 7.43 – 7.41 (m, 2H), 4.28 (t, *J* = 8.0 Hz, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 1.78 – 1.71 (m, 2H), 1.50 – 1.45 (m, 2H), 1.31 (s, 9H), 1.20 (t, *J* = 8.0 Hz, 9H), 0.66 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 156.3, 129.4, 127.8, 125.3, 64.8, 58.3, 35.0, 31.1, 29.6, 28.5, 22.6, 18.3, 10.4. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{22}H_{38}O_5Si$ $[M]^+$, 410.2489. Found, 410.2489. IR (neat): υ (cm^{-1}): 2970, 2928, 2886, 1720, 1610, 1442, 1389, 1275, 1187, 1103, 1079, 957, 775.

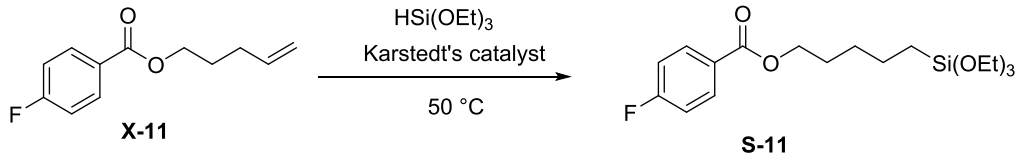
5-(Triethoxysilyl)pentyl 3-methoxybenzoate (S-10)



X-10 S-10

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 3-methoxybenzoate (**X-10**) (2.20 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.43 g 5-(triethoxysilyl)pentyl 3-methoxybenzoate (**S-10**) as a colorless liquid (63% yield).
R_f = 0.25 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 1H), 7.56 (s, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.09 – 7.07 (m, 1H), 4.31 (t, *J* = 8.0 Hz, 2H), 3.84 – 3.79 (m, *J* = 9H), 1.79 – 1.76 (m, 2H), 1.51 – 1.49 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.67 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 159.5, 131.7, 129.2, 121.8, 119.1, 114.0, 65.0, 58.2, 55.2, 29.4, 28.4, 22.5, 18.2, 10.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{36}NO_6Si$ $[M + NH_4]^+$, 402.2312. Found, 402.2304. IR (neat): υ (cm^{-1}): 2973, 2886, 1720, 1601, 1587, 1488, 1454, 1389, 1277, 1228, 1166, 1103, 1078, 1046, 957, 780.

5-(Triethoxysilyl)pentyl 4-fluorobenzoate (S-11)

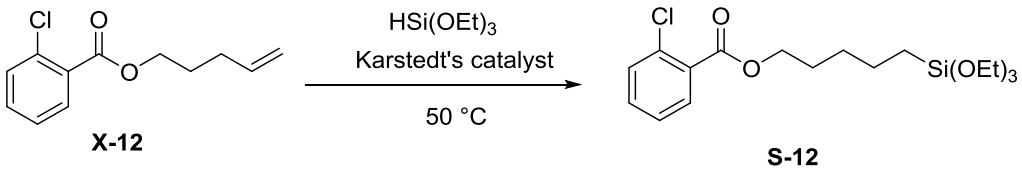


X-11 S-11

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 4-fluorobenzoate (**X-11**) (2.08 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.25 g 5-(triethoxysilyl)pentyl 4-fluorobenzoate (**S-11**) as a colorless liquid (60% yield).

R_f = 0.35 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.12 – 7.08 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.81 (q, *J* = 8.0 Hz, 6H), 1.80 – 1.73 (m, 2H), 1.49 – 1.47 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.66 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (d, *J* = 254.4 Hz), 165.7, 132.1 (d, *J* = 92.7 Hz), 126.8 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 21.8 Hz), 65.2, 58.4, 29.5, 28.5, 22.7, 18.3, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.01. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{33}FNO_5Si$ $[M + NH_4]^+$, 390.2112. Found, 390.2102. IR (neat): υ (cm^{-1}): 2973, 2927, 2885, 1720, 1603, 1508, 1433, 1389, 1274, 1238, 1153, 1108, 1079, 957, 854, 768.

5-(Triethoxysilyl)pentyl 2-chlorobenzoate (S-12)

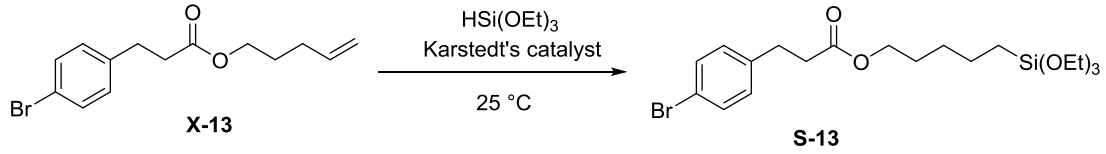


X-12 S-12

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 4-fluorobenzoate (**X-11**) (1.12 g, 5.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.150 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (1.34 g, 8.13 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 1.17 g 5-(triethoxysilyl)pentyl 2-chlorobenzoate (**S-12**) as a colorless liquid (60% yield).

R_f = 0.31 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 1H), 7.46 – 7.38 (m, 2H), 7.33 – 7.29 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.82 – 1.75 (m, 2H), 1.52 – 1.48 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 133.6, 132.4, 131.4, 131.1, 130.6, 126.6, 65.7, 58.4, 29.5, 28.4, 22.6, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{33}ClNO_5Si$ $[M + NH_4]^+$, 406.1817. Found, 406.1812. IR (neat): υ (cm^{-1}): 2927, 2886, 1729, 1611, 1592, 1435, 1390, 1292, 1249, 1169, 1105, 1078, 956, 780.

5-(Triethoxysilyl)pentyl 3-(4-bromophenyl)propanoate (S-13)

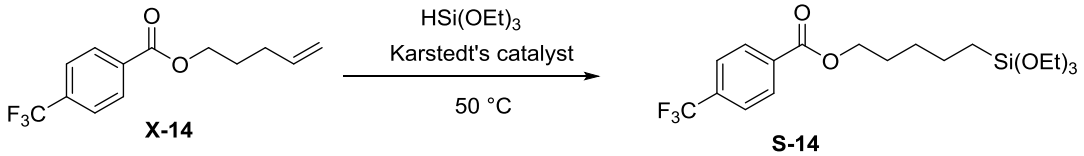


X-13 S-13

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 3-(4-bromophenyl)propanoate (**X-13**) (2.37 g, 8.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.240 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.14 g, 13.0 mmol, 1.63 equiv). After stirring at 25 ºC for 12.0 h, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.84 g 5-(triethoxysilyl)pentyl 3-(4-bromophenyl)propanoate (**S-13**) as a colorless liquid (77% yield).

R_f = 0.22 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (m, 2H), 7.04 – 7.02 (m, 2H), 4.00 (t, *J* = 6.7 Hz, 2H), 3.77 (q, *J* = 7.0 Hz, 6H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.43 – 1.27 (m, 4H), 1.17 (t, *J* = 7.0 Hz, 9H), 0.62 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 139.5, 131.5, 130.1, 120.0, 64.6, 58.3, 35.6, 30.3, 29.3, 28.3, 22.5, 18.3, 10.3. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{20}H_{33}BrO_5Si$ $[M]^+$, 460.1281. Found, 460.1271. IR (neat): υ (cm^{-1}): 2972, 2927, 2886, 1734, 1601, 1488, 1457, 1388, 1362, 1293, 1165, 1102, 1076, 1011, 956, 790, 733.

5-(Triethoxysilyl)pentyl 4-(trifluoromethyl)benzoate (S-14)

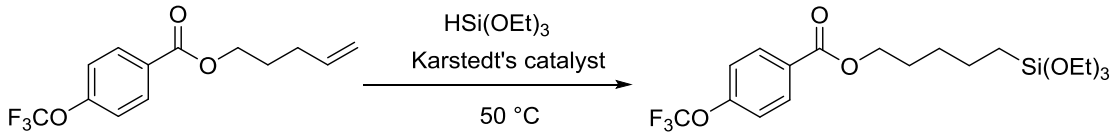


X-14 S-14

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 3-(4-bromophenyl)propanoate (**X-14**) (2.58 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 3.05 g 5-(triethoxysilyl)pentyl 4-(trifluoromethyl)benzoate (**S-14**) as a colorless liquid (72% yield).

R_f = 0.21 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.79 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.73 (m, 2H), 1.48-1.46 (m, 4H), 1.19 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 134.4 (q, *J* = 33.3 Hz), 133.8, 130.0, 125.4 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 273.7 Hz), 65.7, 58.4, 29.5, 28.4, 22.7, 18.4, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.09. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{33}F_3NO_5Si$ $[M + NH_4]^+$, 440.2080. Found, 440.2080. IR (neat): υ (cm^{-1}): 2975, 2887, 1728, 1601, 1444, 1412, 1390, 1326, 1276, 1168, 1102, 1079, 1018, 957, 863, 776.

5-(Triethoxysilyl)pentyl 4-(trifluoromethoxy)benzoate (S-15)

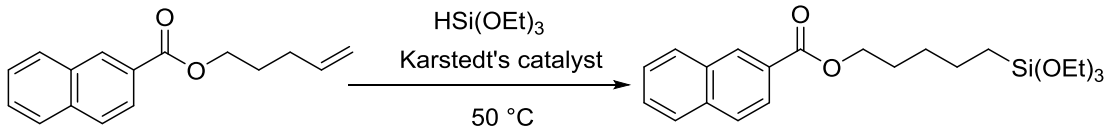


X-15 **S-15**

Under nitrogen atmosphere, to a mixture of pent-4-en-1-yl 4-(trifluoromethoxy)benzoate (**X-15**) (2.74 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 3.32 g 5-(triethoxysilyl)pentyl 4-(trifluoromethoxy)benzoate (**S-15**) as a colorless liquid (76% yield).

R_f = 0.24 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.30 – 7.23 (m, 2H), 4.32 (t, *J* = 6.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.81 – 1.74 (m, 2H), 1.53 – 1.47 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 152.7 (q, *J* = 1.5 Hz), 131.7, 129.1, 120.4 (q, *J* = 258.5 Hz), 120.4, 65.5, 58.5, 29.6, 28.5, 22.7, 18.4, 10.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.64. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{30}F_3O_6Si$ $[M + H]^+$, 439.1764. Found, 439.1760. IR (neat): υ (cm^{-1}): 2975, 2887, 1726, 1607, 1506, 1458, 1390, 1258, 1222, 1167, 1104, 1080, 1018, 957, 863, 770.

5-(Triethoxysilyl)pentyl 2-naphthoate (S-16)



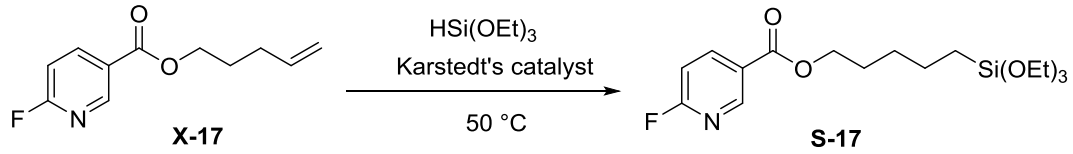
X-16 **S-16**

Under nitrogen atmosphere, to a mixture of pent-4-enyl 2-naphthoate (**X-16**) (2.40 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 1.89 g 5-(triethoxysilyl)pentyl 2-naphthoate (**S-16**) as a colorless liquid (47% yield).

R_f = 0.25 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.06 – 8.03 (m, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.55 – 7.47 (m, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.88 – 1.76 (m, 2H), 1.57 – 1.47 (m, 4H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 135.4, 132.5, 130.9, 129.3, 128.1, 128.0, 127.7, 126.5, 125.2, 65.2, 58.3, 29.5, 28.5, 22.6, 18.3, 10.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{33}O_5Si$ $[M + H]^+$, 405.2097.

Found, 405.2090. IR (neat): υ (cm^{-1}): 3066, 2973, 2885, 1715, 1631, 1468, 1390, 1284, 1227, 1196, 1100, 1079, 957, 779.

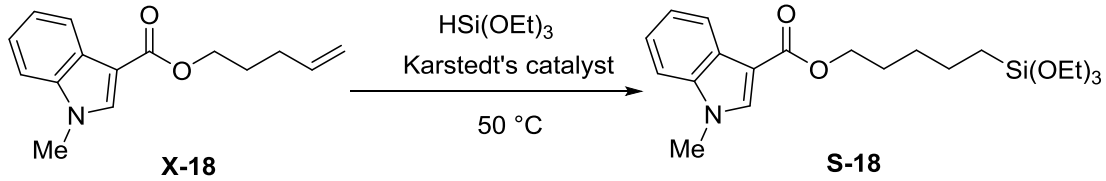
5-(Triethoxysilyl)pentyl 6-fluoronicotinate (S-17)



Under nitrogen atmosphere, to a mixture of pent-4-enyl 6-fluoronicotinate (**X-17**) (2.09 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 8:1 (v/v) to afford 2.66 g 5-(triethoxysilyl)pentyl 6-fluoronicotinate (**S-17**) as a colorless liquid (71% yield).

R_f = 0.09 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.4 Hz, 1H), 8.41 – 8.34 (m, 1H), 6.99 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.33 (t, *J* = 6.7 Hz,2H), 3.80 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.73 (m, 2H), 1.52 – 1.45 (m, 4H), 1.20 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 245.3 Hz), 164.4, 150.4 (d, *J* = 16.3 Hz), 142.6 (d, *J* = 9.3 Hz), 124.9 (d, *J* = 4.4 Hz), 109.6 (d, *J* = 37.4 Hz), 65.8, 58.5, 29.5, 28.4, 22.7, 18.4, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{29}FNO_5Si$ $[M + H]^+$, 374.1799. Found, 374.1791. IR (neat): υ (cm^{-1}): 2974, 2928, 2886, 1727, 1595, 1483, 1380, 1271, 1252, 1166, 1114, 1079, 1020, 957, 843, 778.

5-(Triethoxysilyl)pentyl 1-methyl-1H-indole-3-carboxylate (S-18)

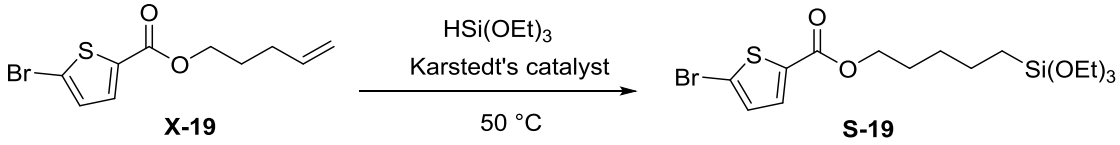


Under nitrogen atmosphere, to a mixture of pent-4-enyl 1-methyl-1H-indole-3-carboxylate (**X-18**) (2.40 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 3.19 g 5-(triethoxysilyl)pentyl 1-methyl-1H-indole-3-carboxylate (**S-18**) as a colorless liquid (78% yield).

R_f = 0.61 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 1H), 7.77 (s, 1H), 7.36 – 7.25 (m, 3H), 4.32 (t, *J* = 6.7 Hz, 2H), 3.82 (q, *J* = 7.0 Hz,

6H), 3.82 (s, 3H), 1.83 – 1.77 (m, 2H), 1.54 – 1.50 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 137.3, 135.3, 126.7, 122.8, 121.9, 121.8, 109.8, 107.3, 63.9, 58.4, 33.5, 29.8, 28.8, 22.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{34}NO_5Si$ $[M + H]^+$, 408.2206. Found, 408.2205. IR (neat): υ (cm^{-1}): 2958, 2884, 1703, 1611, 1534, 1466, 1383, 1267, 1221, 1152, 1104, 1078, 956, 776.

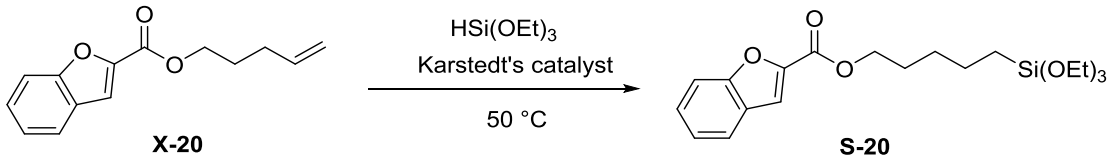
5-(Triethoxysilyl)pentyl 5-bromothiophene-2-carboxylate (S-19)



Under nitrogen atmosphere, to a mixture of pent-4-enyl 5-bromothiophene-2-carboxylate (**X-19**) (2.75 g, 10.0 mmol,1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.60 g 5-(triethoxysilyl)pentyl 5-bromothiophene-2-carboxylate (**S-19**) as a colorless liquid (57% yield).

R_f = 0.21 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.77 – 1.68 (m, 2H), 1.52 – 1.40 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 135.3, 133.6, 131.0, 120.1, 65.6, 58.5, 29.5, 28.5, 22.7, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{28}BrO_5SSi$ $[M + H]^+$, 439.0610. Found, 439.0597. IR (neat): υ (cm^{-1}): 2987, 2858, 1719, 1622, 1532, 1418, 1389, 1278, 1256, 1166, 1102, 1085, 956, 794, 746.

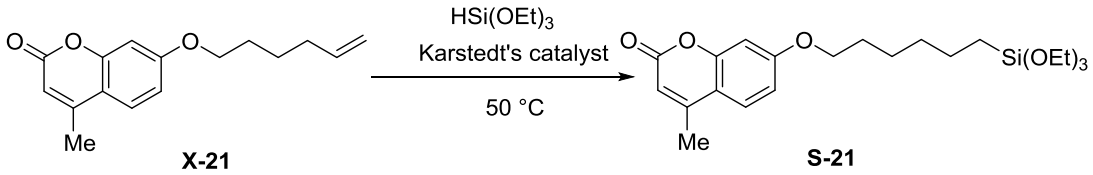
5-(Triethoxysilyl)pentyl benzofuran-2-carboxylate (S-20)



Under nitrogen atmosphere, to a mixture of pent-4-enyl benzofuran-2-carboxylate (**X-20**) (2.30 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 2.45 g 5-(triethoxysilyl)pentyl benzofuran-2-carboxylate (**S-20**) as a colorless liquid (62% yield).

R_f = 0.15 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.52 (d, *J* = 0.9 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.33 – 7.27 (m, 1H), 4.38 (t, *J* = 6.7 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.86 – 1.76 (m, 2H), 1.56 – 1.46 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.70 – 0.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 155.8, 145.8, 127.6, 127.1, 123.8, 122.9, 113.8, 112.4, 65.6, 58.4, 29.4, 28.5, 22.7, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{31}O_6Si$ $[M + H]^+$, 395.1890. Found, 395.1888. IR (neat): υ (cm^{-1}): 2950, 2886, 1735, 1614, 1563, 1476, 1389, 1295, 1223, 1210, 1178, 1079, 958, 885, 750.

4-Methyl-7-(6-(triethoxysilyl)hexyloxy)-2H-chromen-2-one (S-21)

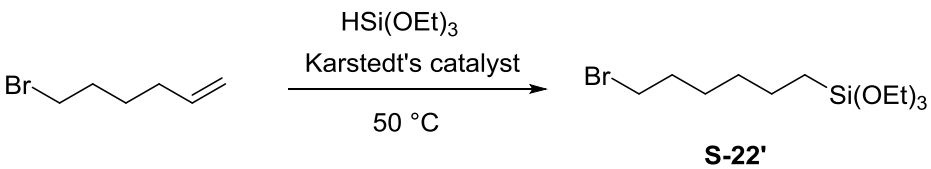


X-21 S-21

Under nitrogen atmosphere, to a mixture of 7-(hex-5-enyloxy)-4-methyl-2H-chromen-2-one (**X-21**) (2.58 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 6:1 (v/v) to afford 2.14 g 4-methyl-7-(6-(triethoxysilyl)hexyloxy)-2H-chromen-2-one (**S-21**) as a colorless liquid (51% yield).

R_f = 0.63 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 6.77 (s, 1H), 6.10 (s, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 2.37 (s, 3H), 1.83 – 1.74 (m, 2H), 1.51 – 1.36 (m, 6H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 161.4, 155.4, 152.7, 125.6, 113.5, 112.8, 111.9, 101.4, 68.7, 58.4, 32.9, 29.0, 25.7, 22.8, 18.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{35}O_6Si$ $[M + H]^+$, 423.2203. Found, 423.2195. IR (neat): υ (cm^{-1}): 2955, 2895, 1730, 1614, 1556, 1510, 1442, 1388, 1293, 1147, 1103, 1072, 1015, 957, 849, 791.

Bromo-6-(triethoxysilyl)hexane (S-22')



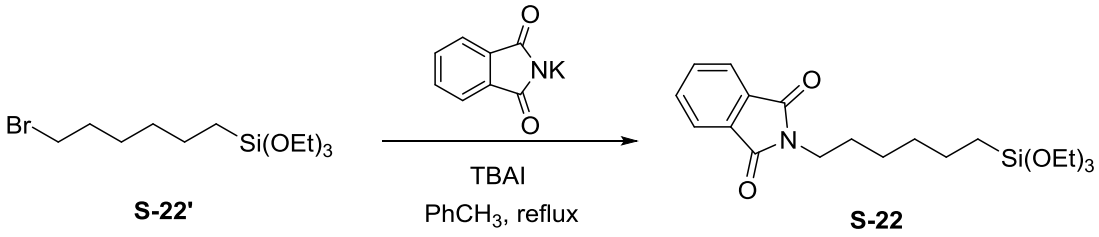
S-22'

Under nitrogen atmosphere, to a mixture of 6-bromo-1-hexene (3.26 g, 20.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.600 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature,

the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 5.31 g 1-bromo-6-(triethoxysilyl)hexane (**S-22'**) as a colorless liquid (81% yield).

R_f = 0.11 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (q, *J* = 7.0 Hz, 6H), 3.39 (t, *J* = 6.9 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.50 – 1.31 (m, 6H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.4, 34.1, 32.8, 32.3, 27.9, 22.7, 18.4, 10.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{28}BrO_3Si$ $[M + H]^+$, 327.0991. Found, 327.0988. IR (neat): υ (cm^{-1}): 2954, 2896, 2863, 1447, 1283, 1165, 1104, 1080.

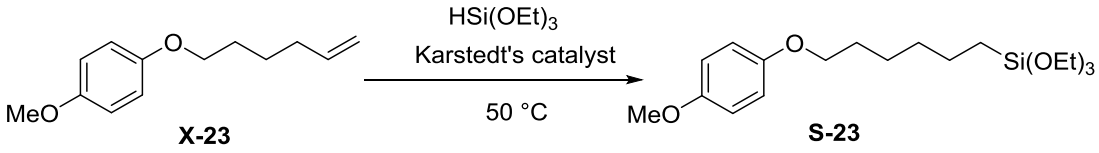
2-(6-(Triethoxysilyl)hexyl)isoindoline-1,3-dione (S-22)



Under N_2 atmosphere, to a solution of potassium phthalimide (1.48 g, 8.00 mmol, 2.00 equiv) and TBAI (0.296 g, 0.800 mmol, 0.200 equiv) in $PhCH_3$ (20.0 mL) were added 1-bromo-6-(triethoxysilyl)hexane (**S-22'**) (1.31 g, 4.00 mmol, 1.00 equiv) at room temperature. The reaction mixture was then refluxed for 18 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 1.15 g 1-(hex-5-en-1-yloxy)-4-(trifluoromethyl)benzene (**X-30**) as a colorless liquid (73% yield).

R_f = 0.27 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.72 – 7.66 (m, 2H), 3.79 (q, *J* = 7.0 Hz, 6H), 3.68 – 3.62 (m, 2H), 1.69 – 1.59 (m, 2H), 1.43 – 1.28 (m, 6H), 1.20 (t, *J* = 7.0 Hz, 9H), 0.61 – 0.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 133.9, 132.3, 123.2, 58.4, 38.2, 32.8, 28.7, 26.7, 22.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{32}NO_5Si$ $[M + H]^+$, 394.2050. Found, 394.2043. IR (neat): υ (cm^{-1}): 2973, 2927, 2861, 1715, 1614, 1466, 1395, 1367, 1248, 1166, 1102, 1078, 957, 791, 720.

Triethoxy(6-(4-methoxyphenoxy)hexyl)silane (S-23)

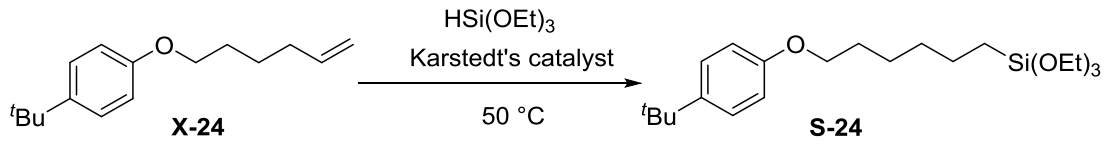


Under nitrogen atmosphere, to a mixture of 1-(hex-5-en-1-yloxy)-4-methoxybenzene (**X-23**) (2.06 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol,

1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.49 g triethoxy(6-(4-methoxyphenoxy)hexyl)silane (**S-23**) as a colorless liquid (67% yield).

R_f = 0.39 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.79 (m, 4H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.76 (s, 3H), 1.79 – 1.70 (m, 2H), 1.50 – 1.36 (m, 6H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 153.4, 115.5, 114.7, 68.8, 58.4, 55.9, 33.0, 29.4, 25.8, 22.9, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{35}O_5Si$ $[M + H]^+$, 371.2254. Found, 371.2254. IR (neat): υ (cm^{-1}): 2973, 2926, 1591, 1508, 1468, 1390, 1289, 1232, 1166, 1103, 1078, 956, 824, 746.

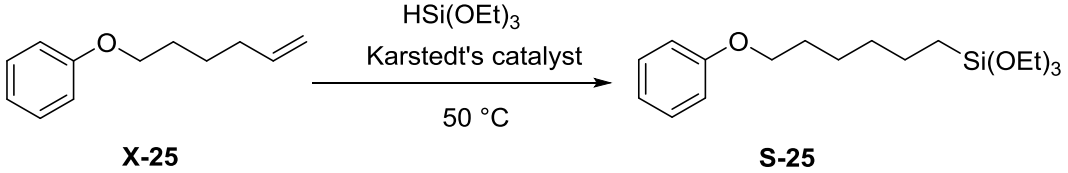
(6-(4-(Tert-butyl)phenoxy)hexyl)triethoxysilane (S-24)



Under nitrogen atmosphere, to a mixture of 1-(tert-butyl)-4-(hex-5-en-1-yloxy)benzene(**X-24**) (2.32 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 40:1 (v/v) to afford 2.70 g (6-(4-(tert-butyl)phenoxy)hexyl)triethoxysilane (**S-24**) as a colorless liquid (68% yield).

R_f = 0.58 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.86 – 6.81 (m, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.81 – 1.72 (m, 2H), 1.51 – 1.36 (m, 6H), 1.30 (s, 9H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 143.2, 126.3, 114.0, 68.0, 58.4, 34.2, 33.0, 31.7, 29.4, 25.9, 22.9, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{41}O_4Si$ $[M + H]^+$, 397.2774. Found, 397.2763. IR (neat): υ (cm^{-1}): 2969, 2866, 1611, 1580, 1513, 1468, 1390, 1294, 1183, 1104, 1079, 956, 828, 789.

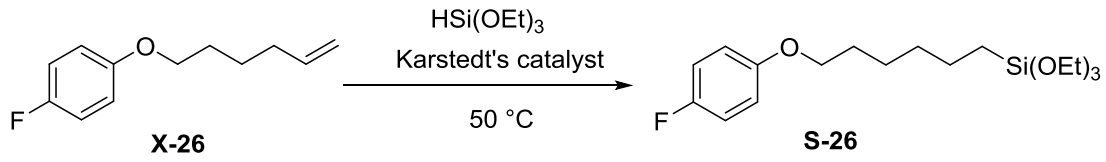
Triethoxy(6-phenoxyhexyl)silane (S-25)



Under nitrogen atmosphere, to a mixture of (hex-5-en-1-yloxy)benzene (**X-25**) (1.76 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 40:1 (v/v) to afford 2.45 g triethoxy(6-phenoxyhexyl)silane (**S-25**) as a colorless liquid (72% yield).

R_f = 0.63 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.96 – 6.86 (m, 3H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.82 – 1.72 (m, 2H), 1.50 – 1.37 (m, 6H), 1.23 (t, *J* = 7.0 Hz, 9H), 0.71 – 0.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 129.5, 120.6, 114.6, 68.0, 58.5, 33.0, 29.3, 25.8, 22.9, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{33}O_4Si$ $[M + H]^+$, 341.2148. Found, 341.2142. IR (neat): υ (cm^{-1}): 2974, 2928, 1601, 1497, 1391, 1246, 1170, 1104, 1080, 957, 789, 753.

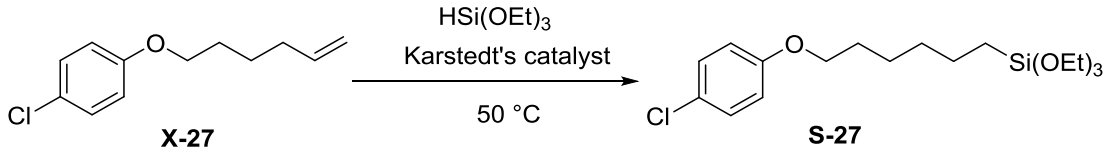
Triethoxy(6-(4-fluorophenoxy)hexyl)silane (S-26)



Under nitrogen atmosphere, to a mixture of 1-fluoro-4-(hex-5-en-1-yloxy)benzene (**X-26**) (1.94 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 40:1 (v/v) to afford 2.68 g triethoxy(6-(4-fluorophenoxy)hexyl)silane (**S-26**) as a colorless liquid (75% yield).

R_f = 0.50 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 – 6.90 (m, 2H), 6.84 – 6.78 (m, 2H), 3.89 (t, *J* = 6.5 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.70 (m, 2H), 1.50 – 1.38 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.69 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (d, *J* = 237.6 Hz), 115.8 (d, *J* = 23.0 Hz), 115.5 (d, *J* = 7.8 Hz), 68.7, 58.4, 33.0, 29.3, 25.8, 22.9, 18.4, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.38 – -125.60. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{32}FO_4Si$ $[M + H]^+$, 359.2054. Found, 359.2046. IR (neat): υ (cm^{-1}): 2977, 2885, 1600, 1507, 1473, 1390, 1293, 1248, 1211, 1103, 1079, 957, 827, 790.

(6-(4-Chlorophenoxy)hexyl)triethoxysilane (S-27)

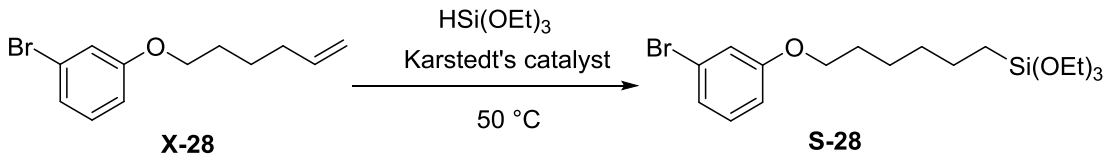


X-27 **S-27**

Under nitrogen atmosphere, to a mixture of 1-chloro-4-(hex-5-en-1-yloxy)benzene (**X-27**) (2.10 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 40:1 (v/v) to afford 2.09 g (6-(4-chlorophenoxy)hexyl)triethoxysilane (**S-27**) as a colorless liquid (56% yield).

R_f = 0.51 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 6.84 – 6.77 (m, 2H), 3.90 (t, *J* = 6.5 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.71 (m, 2H), 1.49 – 1.36 (m, 6H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.67 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 129.2, 125.2, 115.7, 68.3, 58.3, 32.8, 29.1, 25.6, 22.7, 18.3, 10.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{32}ClO_4Si$ $[M + H]^+$, 375.1758. Found, 375.1752. IR (neat): υ (cm^{-1}): 2960, 2927, 2886, 1603, 1490, 1387, 1286, 1167, 1102, 1079, 955, 823, 787.

(6-(3-Bromophenoxy)hexyl)triethoxysilane (S-28)

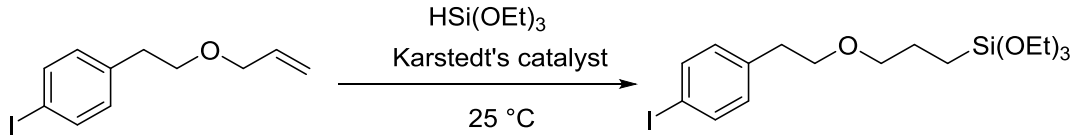


X-28 **S-28**

Under nitrogen atmosphere, to a mixture of 1-bromo-3-(hex-5-en-1-yloxy)benzene (**X-28**) (2.55 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 1.74 g (6-(3-bromophenoxy)hexyl)triethoxysilane (**S-28**) as a colorless liquid (42% yield).

R_f = 0.51 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.82 (q, *J* = 6.9 Hz, 6H), 1.81 – 1.72 (m, 2H), 1.50 – 1.36 (m, 6H), 1.23 (t, *J* = 6.9 Hz, 9H), 0.69 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 130.6, 123.7, 122.9, 117.8, 113.7, 68.3, 58.4, 32.9, 29.2, 25.7, 22.9, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{32}BrO_4Si$ $[M + H]^+$, 419.1253. Found, 419.1243. IR (neat): υ (cm^{-1}): 2971, 2883, 1590, 1469, 1390, 1284, 1228, 1166, 1103, 1079, 956, 859, 792, 773.

Triethoxy(3-(4-iodophenethoxy)propyl)silane (S-29)

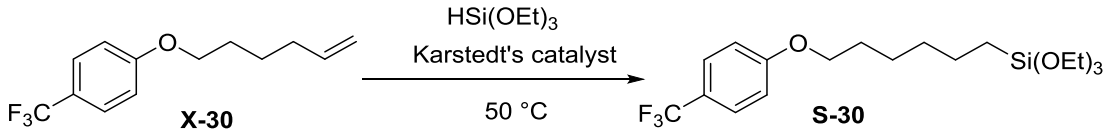


X-29 **S-29**

Under nitrogen atmosphere, to a mixture of 1-(2-(allyloxy)ethyl)-4-iodobenzene (**X-29**) (2.88 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was stirred for 12.0 h at 25 ºC. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 40:1 (v/v) to afford 3.39 g triethoxy(3-(4-iodophenethoxy)propyl)silane (**S-29**) as a colorless liquid (75% yield).

R_f = 0.23 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 6.99 – 6.95 (m, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.81 (t, *J* = 6.9 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.4, 131.2, 91.4, 73.3, 71.3, 58.5, 36.0, 23.1, 18.4, 6.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{30}IO_4Si$ $[M + H]^+$, 453.0958. Found, 453.0948. IR (neat): υ (cm^{-1}): 2973, 2881, 1600, 1485, 1390, 1364, 1228, 1166, 1105, 1079, 1006, 955, 793, 770.

Triethoxy(6-(4-(trifluoromethyl)phenoxy)hexyl)silane (S-30)

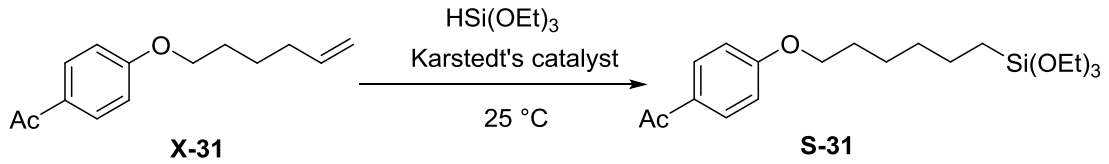


X-30 **S-30**

Under nitrogen atmosphere, to a mixture of 1-(hex-5-en-1-yloxy)-4-(trifluoromethyl)benzene (**X-30**) (2.44 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.54 g triethoxy(6-(4-(trifluoromethyl)phenoxy)hexyl)silane (**S-30**) as a colorless liquid (62% yield).

R_f = 0.48 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.82 – 1.76 (m, 2H), 1.51 – 1.36 (m, 6H), 1.23 (t, *J* = 6.9 Hz, 9H), 0.66 – 0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 127.0 (q, *J* = 3.5 Hz), 124.6 (q, *J* = 271.2 Hz), 122.7 (q, *J* = 32.7 Hz), 114.6, 68.4, 58.5, 32.9, 29.1, 25.8, 22.9, 18.5, 10.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.44. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{32}F_3O_4Si$ $[M + H]^+$, 409.2022. Found, 409.2019. IR (neat): υ (cm^{-1}): 2974, 2884, 1616, 1589, 1519, 1390, 1329, 1257, 1162, 1109, 1079, 956, 836, 789.

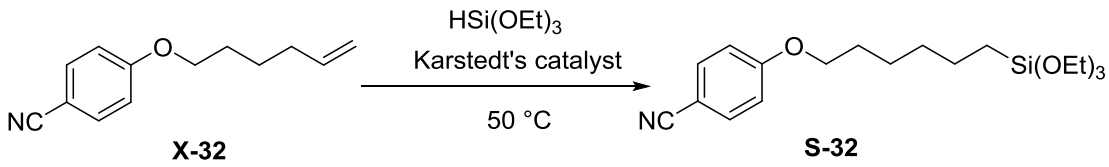
Triethoxy(6-(4-(trifluoromethyl)phenoxy)hexyl)silane (S-31)



X-31 S-31

Under nitrogen atmosphere, to a mixture of 1-(4-(hex-5-en-1-yloxy)phenyl)ethanone (**X-31**) (1.09 g, 5.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.150 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (1.34 g, 8.15 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 25:1 (v/v) to afford 0.801 g triethoxy(6-(4-(trifluoromethyl)phenoxy)hexyl)silane (**S-31**) as a colorless liquid (42% yield).
R_f = 0.08 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.81 (q, *J* = 6.9 Hz, 6H), 2.55 (s, 3H), 1.84 – 1.74 (m, 2H), 1.51 – 1.37 (m, 6H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.68 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 163.2, 130.7, 130.3, 114.3, 68.4, 58.5, 32.9, 29.1, 26.5, 25.7, 22.9, 18.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{35}O_5Si$ $[M + H]^+$, 383.2254. Found, 383.2243. IR (neat): υ (cm^{-1}): 2973, 2884, 1680, 1601, 1509, 1390, 1358, 1304, 1257, 1170, 1102, 1079, 1020, 956, 834, 795.

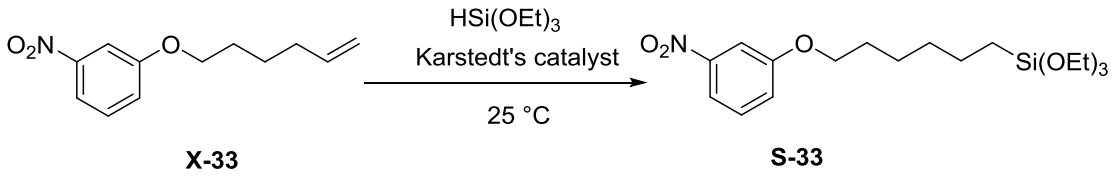
4-((6-(Triethoxysilyl)hexyl)oxy)benzonitrile (S-32)



X-32 S-32

Under nitrogen atmosphere, to a mixture of 4-(hex-5-en-1-yloxy)benzonitrile (**X-32**) (2.01 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 12:1 (v/v) to afford 2.02 g 4-((6-(triethoxysilyl)hexyl)oxy)benzonitrile (**S-32**) as a colorless liquid (56% yield).
R_f = 0.10 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 6.94 – 6.88 (m, 2H), 3.97 (t, *J* = 6.5 Hz, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 1.83 – 1.73 (m, 2H), 1.49 – 1.36 (m, 6H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 134.0, 119.4, 115.3, 103.7, 68.5, 58.4, 32.8, 29.0, 25.7, 22.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{32}NO_4Si$ $[M + H]^+$, 366.2101. Found, 366.2098. IR (neat): υ (cm^{-1}): 2972, 2884, 2224, 1606, 1508, 1389, 1300, 1258, 1173, 1110, 1077, 955, 792.

Triethoxy(6-(3-nitrophenoxy)hexyl)silane (S-33)

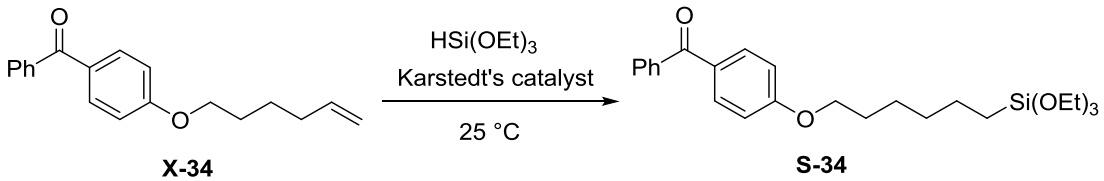


X-33 **S-33**

Under nitrogen atmosphere, to a mixture of 1-(hex-5-en-1-yloxy)-3-nitrobenzene (**X-33**) (2.21 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 30:1 (v/v) to afford 2.17 g triethoxy(6-(3-nitrophenoxy)hexyl)silane (**S-33**) as a yellow liquid (56% yield).

R_f = 0.24 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.69 (s, 1H), 7.39 (t, *J* = 8.2 Hz, 1H), 7.19 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 6H), 1.84 – 1.75 (m, 2H), 1.52 – 1.36 (m, 6H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.66 – 0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 149.3, 129.9, 121.8, 115.6, 108.8, 68.8, 58.4, 32.9, 29.0, 25.7, 22.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{32}NO_6Si$ $[M + H]^+$, 386.1999. Found, 386.1994. IR (neat): υ (cm^{-1}): 2962, 2907, 2854, 1618, 1579, 1532, 1467, 1389, 1286, 1166, 1103, 1079, 957, 862, 789, 737.

5-Phenyl(4-(6-(triethoxysilyl)hexyloxy)phenyl)methanone (S-34)



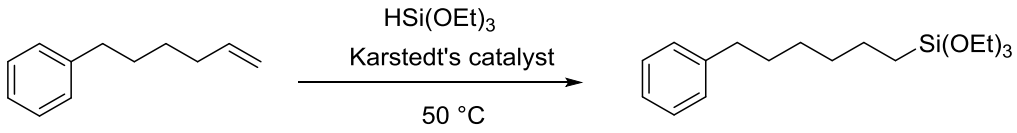
X-34 **S-34**

Under nitrogen atmosphere, to a mixture of (4-(hex-5-enyloxy)phenyl)(phenyl)methanone (**X-34**) (2.80 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h, the reaction mixture was then concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 2.25 g 5-phenyl(4-(6-(triethoxysilyl)hexyloxy)phenyl)methanone (**S-34**) as a colorless liquid (51% yield).

R_f = 0.24 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.39 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.79 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.73 (m,

2H), 1.44 – 1.33 (m, 6H), 1.19 (t, J = 7.0 Hz, 9H), 0.64 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 162.8, 138.3, 132.5, 131.8, 129.8, 129.6, 128.1, 114.0, 68.2, 58.3, 32.7, 29.0, 25.6, 22.7, 18.3, 10.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{25}H_{36}NaO_5Si$ [M + Na]$^+$, 467.2230. Found, 467.2228. IR (neat): υ (cm^{-1}): 2927, 2840, 1755, 1654, 1599, 1560, 1509, 1305, 1171, 1103, 1018, 955, 799.

Triethoxy(6-phenylhexyl)silane (S-35)

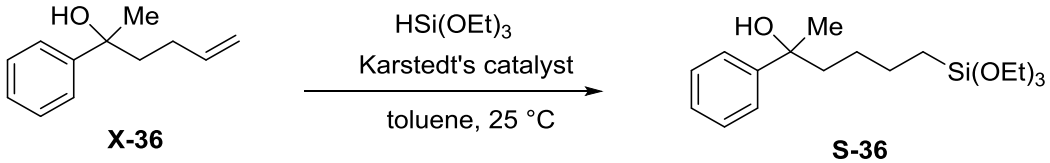


S-35

Under nitrogen atmosphere, to a mixture of hex-5-en-1-ylbenzene (3.21 g, 20.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.600 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (5.36 g, 32.6 mmol, 1.63 equiv). The reaction mixture was then heated to 50 ºC and stirred for 12.0 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting first with PE/EtOAc 100:1 (v/v) then with PE/EtOAc 50:1 (v/v) to afford 4.54 g triethoxy(6-phenylhexyl)silane (**S-35**) as a colorless liquid (70% yield).

R_f = 0.24 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 2H), 7.17 – 7.13 (m, 3H), 3.81 (q, J = 7.0 Hz, 6H), 2.59 (t, J = 7.8 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.42 – 1.34 (m, 6H), 1.22 (t, J = 7.1 Hz, 9H), 0.64 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 128.5, 128.3, 125.6, 58.4, 36.1, 33.1, 31.5, 29.0, 22.8, 18.4, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{33}O_3Si$ [M + H]$^+$, 325.2199. Found, 325.2193. IR (neat): υ (cm^{-1}): 2971, 2885, 1618, 1602, 1571, 1389, 1294, 1260, 1166, 1103, 1079, 957, 793, 749.

2-Phenyl-6-(triethoxysilyl)hexan-2-ol (S-36)

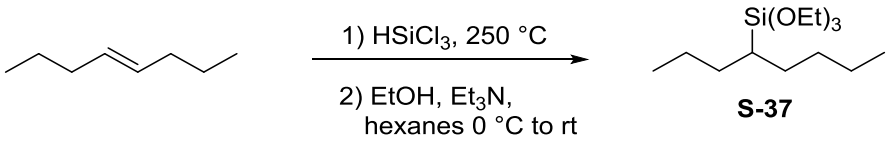


X-36 **S-36**

Under nitrogen atmosphere, to a solution of 2-phenylhex-5-en-2-ol (**X-36**) (1.41 g, 8.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.240 mL) in 4.00 mL toluene at room temperature was added dropwise $HSi(OEt)_3$ (2.14 g, 13.0 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 1.04 g 2-phenyl-6-(triethoxysilyl)hexan-2-ol (**S-36**) as a colorless liquid (38% yield).

R_f = 0.66 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 6H), 1.89 – 1.76 (m, 3H), 1.54 (s, 3H), 1.40 – 1.16 (m, 13H), 0.60 – 0.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 128.2, 126.6, 124.9, 74.7, 58.4, 43.9, 30.3, 27.5, 23.2, 18.4, 10.4. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{32}NaO_4Si$ $[M + Na]^+$, 363.1968. Found, 363.1968. IR (neat): υ (cm^{-1}): 3468, 2974, 2885, 1602, 1493, 1446, 1389, 1295, 1166, 1103, 1079, 954, 781, 765.

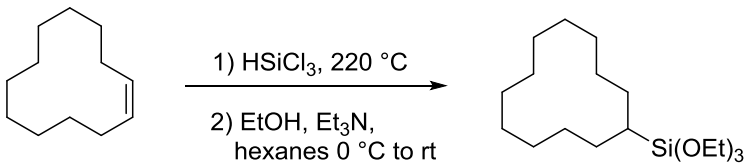
Triethoxy(octan-4-yl)silane (S-37)



S-37

In a glovebox, to (*E*)-oct-4-ene (5.00 g, 44.6 mmol, 1.00 equiv) in a dried 150 mL stainless-steel autoclave at room temperature was added $HSiCl_3$ (10.0 mL). The pressure vial was then sealed and taken out from the glovebox. The reaction mixture was then heated to 250 ºC and stirred for 4 h. (CAUTION: This reaction was carried out behind a blast shield. Extreme caution is necessary because of the high reaction pressure under high temperature). After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was then dissolved in 50 mL anhydrous DCM. The mixture was cooled to 0 ºC and added dropwise Et_3N (20.0 mL) and EtOH (20.0 mL). After stirring at room temperature for 2 h, 50 mL hexanes was added to the reaction mixture and the resulting white suspension was filtered through a Celite pad. Evaporation of volatiles afforded a colorless oil. The oil was purified by flash chromatography on silica gel, eluting with hexanes to afford 10.7 g triethoxy(octan-4-yl)silane (**S-37**) as a colorless liquid (87% yield).
R_f = 0.53 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (q, *J* = 7.0 Hz, 6H), 1.50 – 1.28 (m, 10H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.90 – 0.85(m, 6H), 0.81 – 0.75 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.5, 24.4, 24.3, 23.9, 23.8, 23.7, 23.6, 18.5, 14.6, 14.2. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{33}O_3Si$ $[M + H]^+$, 277.2199. Found, 277.2198. IR (neat): υ (cm^{-1}): 2958, 2860, 1460, 1389, 1294, 1166, 1105, 1082, 955, 775, 727.

Cyclododecyltriethoxysilane (S-38)



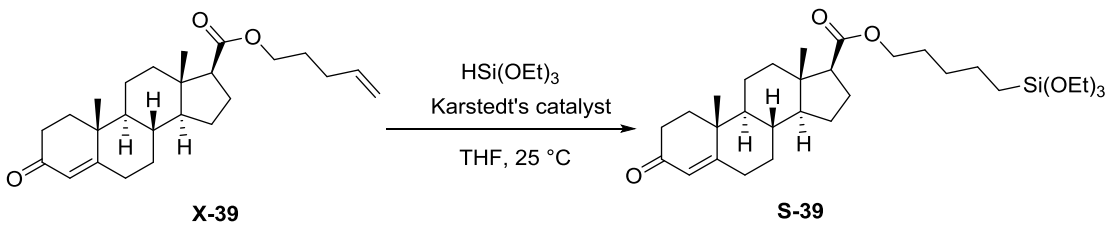
S-38

In a glovebox, to cyclododecene (832 mg,5.00 mmol,1.00 equiv) in a dried 15.0 mL glass pressure vial at room temperature was added $HSiCl_3$ (2.0 mL). The pressure vial was then sealed and taken out from the glovebox. The reaction mixture was then heated to 220 ºC and

stirred for 4 h. (CAUTION: This reaction was carried out behind a blast shield. Extreme caution is necessary because of the high reaction pressure under high temperature. We have also tried to use a safer stainless-steel autoclave instead of the glass pressure vial, only trace amount of product could be gained). After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was then dissolved in 20 mL anhydrous hexanes. The mixture was cooled to 0 ºC and added dropwise EtOH (1.50 mL)and Et_3N (3.00 mL). The reaction mixture was then warmed to room temperature and stirred for 2 h. The resulting white suspension was filtered through a Celite pad. Evaporation of volatiles afforded a colorless oil. The oil was purified by flash chromatography on silica gel, eluting with PE/EtOAc 50:1 (v/v) to afford 1.47g cyclododecyltriethoxysilane (**S-38**) as a colorless liquid (89% yield).

R_f = 0.52 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (q, *J* = 7.0 Hz, 6H), 1.50 – 1.33 (m, 22H), 1.21 (t, *J* = 7.0 Hz, 9H), 0.92 – 0.86 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.5, 24.4, 24.3, 23.9, 23.8, 23.7, 23.6, 18.5, 18.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{18}H_{39}O_3Si$ $[M + H]^+$, 331.2668. Found, 331.2667. IR (neat): υ (cm^{-1}): 2960, 2886, 1473, 1389, 1279, 1171, 1103, 1082, 954, 770.

5-(Triethoxysilyl)pentyl androst-4-en-3-one-17β-carboxylate (S-39)

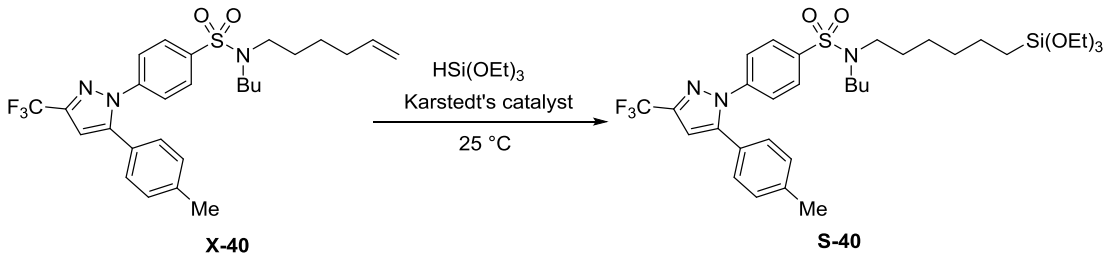


X-39 **S-39**

Under nitrogen atmosphere, to a solution of pent-4-en-1-yl androst-4-en-3-one-17β-carboxylate **(X-39)** (3.85 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in 5.00 mL THF at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 8:1 (v/v) to afford 3.15 g 5-(triethoxysilyl)pentyl androst-4-en-3-one-17β-carboxylate (**S-39**) as a colorless liquid (57% yield).

R_f = 0.19 (PE/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 1H), 4.13 – 3.95 (m, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 3.68 (s, 1H), 2.45 – 2.23 (m, 5H), 2.17 – 2.07 (m, 1H), 2.06 – 1.99 (m, 2H), 1.89 – 1.48 (m, 9H), 1.48 – 1.24 (m, 8H), 1.21 (t, *J* = 7.0 Hz, 9H), 1.17 (s, 3H), 1.12 – 0.91 (m, 3H), 0.69 (s, 3H), 0.63 – 0.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 174.1, 171.2, 124.0, 67.2, 64.3, 58.4, 55.4, 55.3, 53.9, 44.0, 38.7, 38.2, 35.8, 34.1, 32.9, 32.0, 29.6, 28.5, 24.5, 23.6, 22.6, 21.0, 18.4, 17.5, 13.5, 10.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{31}H_{52}NaO_6Si$ $[M + Na]^+$, 571.3431. Found, 571.3428. IR (neat): υ (cm^{-1}): 2970, 2930, 1728, 1680, 1643, 1554, 1453, 1382, 1258, 1187, 1113, 1019, 855, 763.

***N*-butane-*N*-(6-(triethoxysilyl)hexyl)-Celecoxib (S-40)**

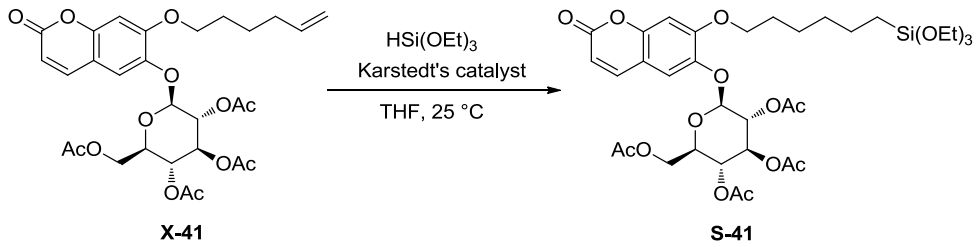


X-40 S-40

Under nitrogen atmosphere, to a solution of *N*-butyl-*N*-(hex-5-enyl)-Celecoxib (**X-40**) (1.56 g, 3.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.100 mL) in 2.00 mL THF at room temperature was added dropwise $HSi(OEt)_3$ (0.890 g, 5.43 mmol, 1.81 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 10:1 (v/v) to afford 1.23 g *N*-butane-*N*-(6-(triethoxysilyl)hexyl)-Celecoxib (**S-40**) as a colorless liquid (60% yield).

R_f = 0.53 (PE/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 3.79 (q, *J* = 7.0 Hz, 6H), 3.10 – 3.04 (m, 4H), 2.36 (s, 3H), 1.55 – 1.42 (m, 4H), 1.42 – 1.23 (m, 8H), 1.20 (t, *J* = 7.0 Hz, 9H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.63 – 0.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.1 (q, *J* = 38.7 Hz), 142.2, 139.8, 139.8, 129.8, 128.8, 128.1, 125.8, 125.6, 121.2 (q, *J* = 269.1 Hz), 106.2, 58.4, 48.3, 48.0, 32.8, 30.7, 28.6, 26.4, 22.8, 21.4, 20.0, 18.4, 13.8, 10.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ 63.00. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{33}H_{49}F_3N_3O_3SSi$ $[M + H]^+$, 684.3114. Found, 684.3117. IR (neat): υ (cm^{-1}): 2962, 2928, 2860, 1597, 1471, 1373, 1344, 1261, 1159, 1097, 1021, 975, 802.

***7-O*-(6-(triethoxysilyl)hexyl)-Esculin tetracetate (S-41)**

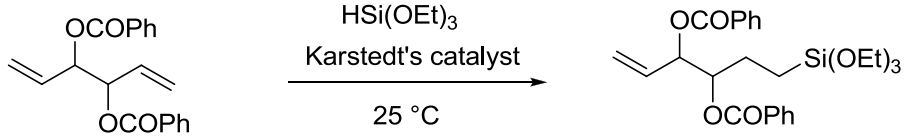


X-41 S-41

Under nitrogen atmosphere, to a solution of ***7-O*-(hex-5-enyl)-Esculin tetracetate (X-41)** (5.90 g, 10.0 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.300 mL) in 10.0 mL THF at room temperature was added dropwise $HSi(OEt)_3$ (2.67 g, 16.3 mmol, 1.63 equiv). The reaction mixture was stirred at 25 ºC for 12.0 h. Then the reaction mixture was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel,

eluting with PE/EtOAc 3:1 (v/v) to afford 6.71 g *7-O*-(6-(triethoxysilyl)hexyl)-Esculin tetracetate (**S-41**) as a colorless liquid (89% yield).
R_f = 0.20 (PE/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.5 Hz, 1H), 7.13 (s, 1H), 6.74 (s, 1H), 6.19 (d, *J* = 9.5 Hz, 1H), 5.26 – 5.18 (m, 2H), 5.14 – 5.06 (m, 1H), 4.98 – 4.90 (m, 1H), 4.22 (dd, *J* = 12.3, 4.9 Hz, 1H), 4.10 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.94 (t, *J* = 6.7 Hz, 2H), 3.74 (q, *J* = 7.0 Hz, 6H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (s, 6H), 1.82 – 1.70 (m, 2H), 1.46 – 1.29 (m, 6H), 1.15 (t, *J* = 7.0 Hz, 9H), 0.63 – 0.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.1, 169.4, 169.1, 161.0, 153.7, 152.0, 143.2, 142.2, 118.3, 113.5, 111.2, 101.1, 100.0, 72.5, 72.0, 71.0, 69.2, 68.3, 61.7, 58.2, 32.7, 28.7, 25.4, 22.7, 20.7, 20.7, 20.5, 18.7, 10.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{35}H_{51}O_{16}Si$ $[M + H]^+$, 755.2946. Found, 755.2946. IR (neat): υ (cm^{-1}): 2926, 2886, 1754, 1613, 1561, 1512, 1437, 1382, 1230, 1170, 1103, 1073, 1042, 856, 777.

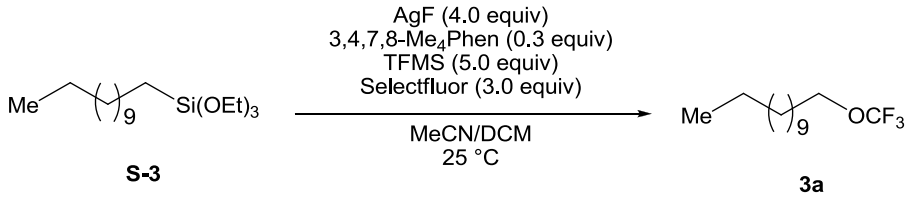
6-(Triethoxysilyl)hex-1-ene-3,4-diyl dibenzoate (S-48)



X-48 **S-48**

Under nitrogen atmosphere, to a mixture of hexa-1,5-diene-3,4-diyl dibenzoate (**X-48**) (1.61 g, 5.00 mmol, 1.00 equiv) and Karstedt's catalyst (in xylene, Pt ~2%, 0.150 mL) in a dried Schlenk tube at room temperature was added dropwise $HSi(OEt)_3$ (821 mg, 5.00 mmol, 1.00 equiv). The reaction mixture was stirred at 25 ºC for 40 min, the reaction mixture was then concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with PE/EtOAc 20:1 (v/v) to afford 491 mg 6-(triethoxysilyl)hex-1-ene-3,4-diyl dibenzoate (**S-48**) as a colorless liquid (20% yield).
R_f = 0.20 (PE/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.39 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.79 (q, *J* = 7.0 Hz, 6H), 1.80 – 1.73 (m, 2H), 1.44 – 1.33 (m, 6H), 1.19 (t, *J* = 7.0 Hz, 9H), 0.64 – 0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.5, 133.2, 133.1, 133.1, 132.7, 132.1, 130.3, 130.2, 129.8, 128.5, 119.8, 119.5, 76.4, 76.1, 75.7, 75.1, 58.5, 24.1, 23.5, 18.3, 6.2, 5.9. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{34}NaO_7Si$ $[M + Na]^+$, 509.1971. Found, 509.1958. IR (neat): υ (cm^{-1}): 3068, 2974, 2891, 1722, 1660, 1601, 1451, 1338, 1265, 1175, 1106, 956, 910, 778.

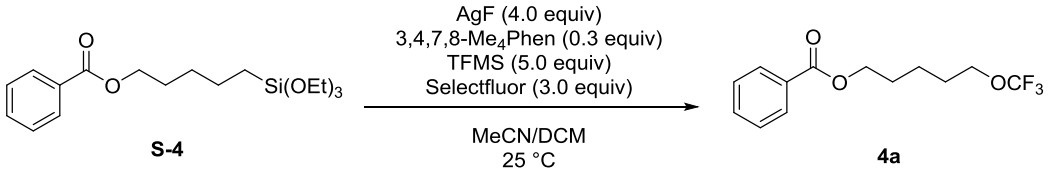
Dodecyl trifluoromethyl ether (3a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was cooled to 0°C and added Br_2 (0.100 mL) to remove the byproduct dodecene. After reacting for 5.0 min, 10.0 mL saturated Na_2SO_3 was added to quench the unreacted Br_2. The reaction mixture was filtrated and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes to afford 72.8 mg dodecyl trifluoromethyl ether (**3a**) as a colorless liquid (57% yield).

R_f = 0.91 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 – 3.93 (t, J = 6.6 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.38 – 1.27 (m, 18H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.9 (q, J = 254.4 Hz), 67.7 (q, J = 3.1 Hz), 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 28.9, 25.6, 22.9, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.54. **3a** is a known compound and spectral data match the reported literature values [4]. IR (neat): υ (cm^{-1}): 2977, 2873, 1488, 1467, 1269, 1207, 1173, 854, 768.

5-(Trifluoromethoxy)pentyl benzoate (4a)

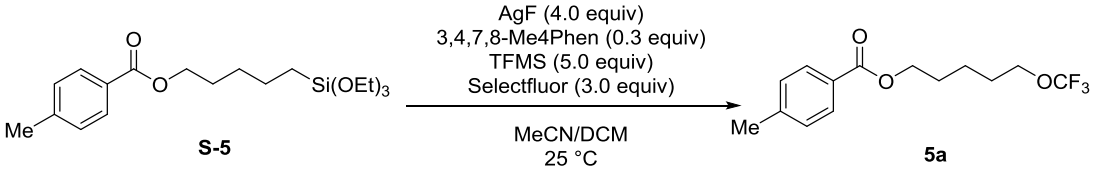


In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl benzoate (**S-4**) (177 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 79.9 mg 5-(trifluoromethoxy)pentyl benzoate (**4a**) as a colorless liquid (58% yield).

R_f = 0.39 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ

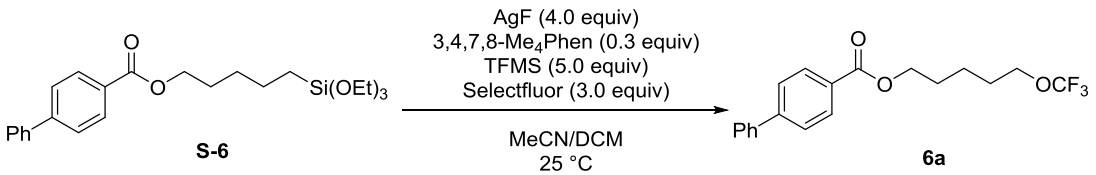
8.05 – 8.04 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 4.34 (t, J = 6.5 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 1.85 – 1.74 (m, 4H), 1.61–1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 133.0, 130.5, 129.6, 128.5, 121.8 (q, J = 254.7 Hz), 67.3 (q, J = 3.1 Hz), 64.7, 28.5, 28.3, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.69. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{16}F_3O_3$ $[M + H]^+$, 277.1052. Found, 277.1045. IR (neat): υ (cm^{-1}): 2962, 2929, 2863, 1722, 1572, 1479, 1273, 1139, 1070, 1026, 801, 711.

5-(Trifluoromethoxy)pentyl 4-methylbenzoate (5a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-methylbenzoate (**S-5**) (184 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 91.7 mg 5-(trifluoromethoxy)pentyl 4-methylbenzoate (**5a**) as a colorless liquid (63% yield).
R_f = 0.38 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.24 – 7.22 (m, 2H), 4.32 (t, J = 6.5 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 2.40 (s, 3H), 1.84 – 1.73 (m, 4H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.7, 129.6, 129.1, 127.7, 121.8 (q, J = 254.6 Hz), 67.2 (q, J = 3.1 Hz), 64.5, 28.4, 28.3, 22.2, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.70. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}F_3O_3$ $[M + H]^+$, 291.1199. Found, 291.1208. IR (neat): υ (cm^{-1}): 2953, 2872, 1717, 1612, 1408, 1273, 1178, 1138, 1108, 1021, 841, 754.

5-(Trifluoromethoxy)pentyl [1,1'-biphenyl]-4-carboxylate (6a)

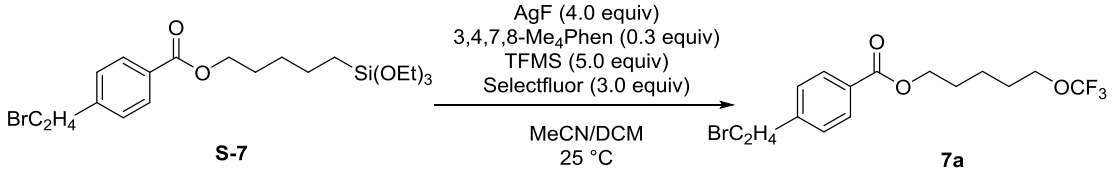


In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl [1,1'-biphenyl]-4-carboxylate (**S-6**) (215 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed

and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 99.1 mg 5-(trifluoromethoxy)pentyl [1,1'-biphenyl]-4-carboxylate (**6a**) as a pale yellow liquid (63% yield).

R_f = 0.31 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 7.68 – 7.62 (m, 4H), 7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 4.01 (t, *J* = 6.4 Hz, 2H), 1.88 – 1.78 (m, 4H), 1.63 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 145.7, 140.1, 130.2, 129.2, 129.0, 128.2, 127.4, 127.1, 121.8 (q, *J* = 254.8 Hz), 67.3 (q, *J* = 3.1 Hz), 64.7, 28.5, 28.3, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.58. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{20}F_3O_3$ $[M + H]^+$, 353.1365. Found, 353.1364. IR (neat): υ (cm^{-1}): 2960, 2873, 1722, 1711, 1609, 1407, 1268, 1137, 858, 748.

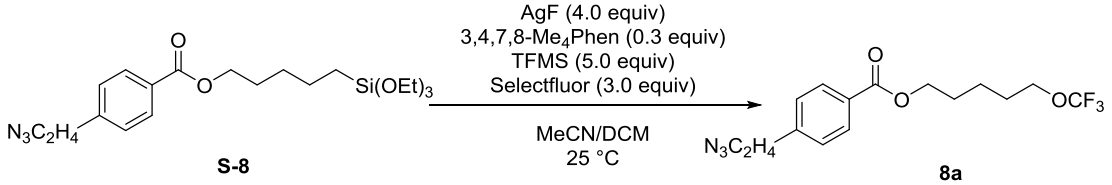
5-(Trifluoromethoxy)pentyl 4-(2-bromoethyl)benzoate (7a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-(2-bromoethyl)benzoate (**S-7**) (230 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 114 mg 5-(trifluoromethoxy)pentyl 4-(2-bromoethyl)benzoate (**7a**) as a colorless liquid (59% yield).

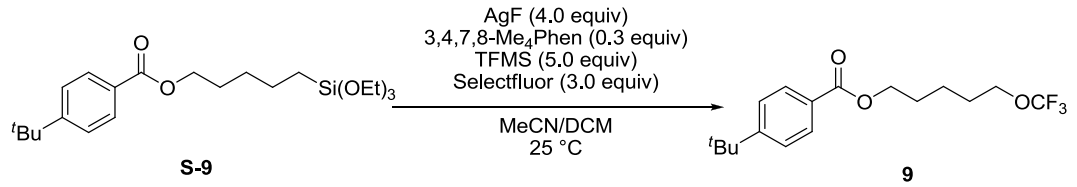
R_f = 0.27 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.99 (m, 2H), 7.30 – 7.28 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.58 (t, *J* = 7.6 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H), 1.84 – 1.73 (m, 4H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 144.1, 129.9, 129.1, 128.8, 121.7 (q, *J* = 253.8 Hz), 67.2 (q, *J* = 3.1 Hz), 64.6, 39.1, 32.3, 28.4, 28.3, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.37. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{19}F_3BrO_3$ $[M + H]^+$, 383.0470. Found, 383.0457. IR (neat): υ (cm^{-1}): 2947, 2914, 2850, 1717, 1685, 1610, 1542, 1458, 1271, 1179, 1134, 856, 764.

5-(Trifluoromethoxy)pentyl 4-(2-bromoethyl)benzoate (8a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-(2-azidoethyl)benzoate (**S-8**) (212 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 102 mg 5-(trifluoromethoxy)pentyl 4-(2- azidoethyl)benzoate (**8a**) as a colorless liquid (59% yield).
R_f = 0.21 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.52 (t, *J* = 7.1 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 1.84 – 1.72 (m, 4H), 1.59 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 143.5, 129.9, 129.0, 128.9, 121.7 (q, *J* = 254.7 Hz), 67.2 (q, *J* = 2.9 Hz), 64.6, 52.0, 35.3, 28.4, 28.2, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.52. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{19}F_3N_3O_3$ $[M + H]^+$, 346.1379. Found, 346.1378. IR (neat): υ (cm^{-1}): 2953, 2912, 2850, 2096, 1727, 1712, 1602, 1554, 1494, 1402, 1268, 1179, 1132, 1103, 847, 703.

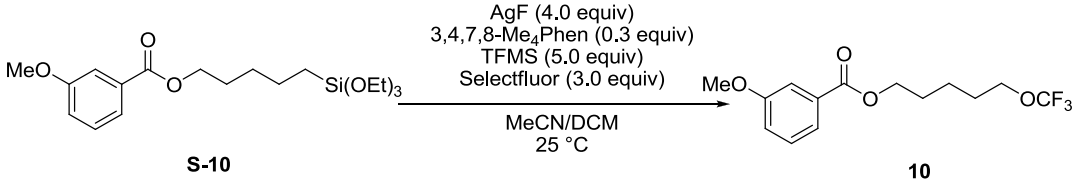
5-(Trifluoromethoxy)pentyl 4-(*tert*-butyl)benzoate (9)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-(*tert*-butyl)benzoate (**S-9**) (205 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 110 mg 5-(trifluoromethoxy)pentyl 4-(*tert*-butyl)benzoate (**9**) as a colorless liquid (66% yield).
R_f = 0.41 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 2H), 7.48 – 7.45 (m, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H),

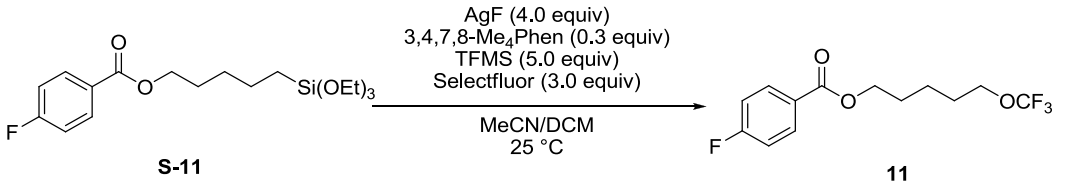
1.85 – 1.74 (m, 4H), 1.61 – 1.55 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 156.6, 129.5, 127.6, 125.4, 121.8 (q, J = 254.7 Hz), 67.3 (q, J = 3.1 Hz), 64.4, 35.1, 31.2, 28.4, 28.3, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.69. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{24}F_3O_3$ $[M + H]^+$, 333.1678. Found, 333.1678. IR (neat): υ (cm^{-1}): 2961, 2870, 1721, 1712, 1611, 1408, 1272, 1187, 1133, 1016, 854, 774.

5-(Trifluoromethoxy)pentyl 3-methoxybenzoate (10)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 3-methoxybenzoate (**S-10**) (192 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 102 mg 5-(trifluoromethoxy)pentyl 3-methoxybenzoate (**10**) as a colorless liquid (66% yield).
R_f = 0.27 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1H), 7.56 – 7.55 (m, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.10 – 7.07 (m, 1H), 4.32 (t, J = 6.5 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.83 (s, 3H), 1.83 – 1.72 (m, 4H), 1.59 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 159.6, 131.7, 129.5, 121.9, 121.8 (q, J = 254.7 Hz), 119.3, 114.1, 67.2 (q, J = 3.1 Hz), 64.7, 55.4, 28.4, 28.2, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.62. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}F_3O_4$ $[M + H]^+$, 307.1157. Found, 307.1151. IR (neat): υ (cm^{-1}): 2954, 2839, 1717, 1588, 1488, 1455, 1278, 1228, 1138, 1074, 1046, 844, 756.

5-(Trifluoromethoxy)pentyl 4-fluorobenzoate (11)

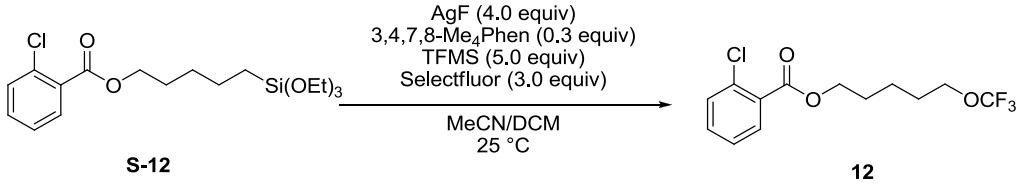


In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-fluorobenzoate (**S-11**) (136 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken

out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 86.3 mg 5-(trifluoromethoxy)pentyl 4-fluorobenzoate (**11**) as a colorless liquid (59% yield).

R_f = 0.27 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.12 – 7.06 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.84 – 1.72 (m, 4H), 1.59 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 254.6 Hz), 165.7, 132.2 (d, *J* = 9.3 Hz), 126.7 (d, *J* = 2.9 Hz), 121.8 (q, *J* = 254.6 Hz), 115.6 (d, *J* = 22.1 Hz), 67.2 (q, *J* = 3.1 Hz), 64.8, 28.4, 28.3, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.89, -106.00. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{15}F_4O_3$ $[M + H]^+$, 295.0957. Found, 295.0958. IR (neat): υ (cm^{-1}): 2955, 2868, 1716, 1604, 1507, 1270, 1239, 1137, 854, 767.

5-(Trifluoromethoxy)pentyl 2-chlorobenzoate (12)

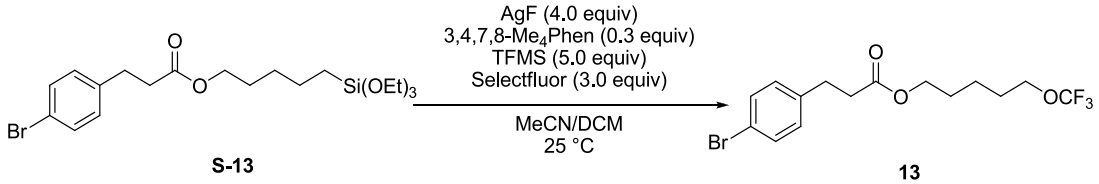


S-12 **12**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 2-chlorobenzoate (**S-12**) (136 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 94.2 mg 5-(trifluoromethoxy)pentyl 2-chlorobenzoate (**12**) as a colorless liquid (61% yield).

R_f = 0.27 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.45 – 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 4.34 (t, *J* = 6.5 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.84 – 1.71 (m, 4H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 133.6, 132.6, 131.4, 131.1, 130.4, 126.7, 121.8 (q, *J* = 254.7 Hz), 67.2 (q, *J* = 3.2 Hz), 65.2, 28.4, 28.1, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.67. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{15}ClF_3O_3$ $[M + H]^+$, 311.0662. Found, 311.0652. IR (neat): υ (cm^{-1}): 2962, 2871,1729, 1592, 1469, 1439, 1291, 1259, 1135, 1050, 800, 745.

5-(Trifluoromethoxy)pentyl 3-(4-bromophenyl)propanoate (13)

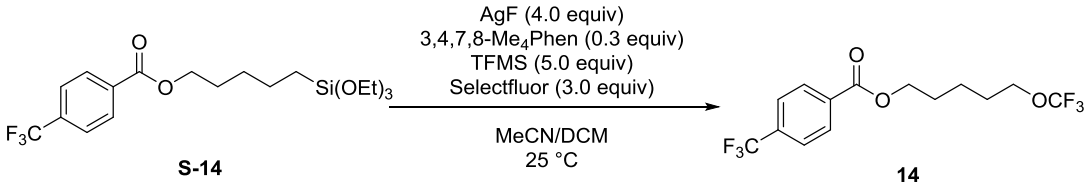


S-13 **13**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 3-(4-bromophenyl)propanoate (**S-13**) (231 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 114 mg 5-(trifluoromethoxy)pentyl 3-(4-bromophenyl)propanoate (**13**) as a colorless liquid (59% yield).

R_f = 0.27 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.08 – 7.06 (m, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.58 (m, 4H), 1.43 – 1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 139.5, 131.6, 130.2, 121.7 (q, *J* = 254.8 Hz), 120.1, 67.2 (q, *J* = 3.1 Hz), 64.2, 35.6, 30.4, 28.3, 28.1, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.62. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{22}BrF_3NO_3$ $[M + NH_4]^+$, 400.0735. Found, 400.0722. IR (neat): υ (cm^{-1}): 2960, 2856, 1734, 1592, 1488, 1390, 1287, 1173, 1105, 1079, 854, 767.

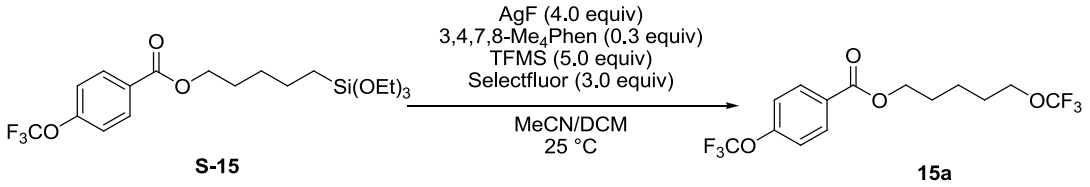
5-(Trifluoromethoxy)pentyl 4-(trifluoromethyl)benzoate (14)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-(trifluoromethyl)benzoate (**S-14**) (211 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 96.6 mg 5-(trifluoromethoxy)pentyl 4-(trifluoromethyl)benzoate (**14**) as a colorless liquid (56% yield).

R_f = 0.31 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (t, *J* = 7.9 Hz, 2H), 7.69 (t, *J* = 8.0 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 1.86 – 1.75 (m, 4H), 1.61 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 134.6 (q, *J* = 32.7 Hz), 133.7, 130.1, 125.5 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 273.5 Hz), 121.8 (q, *J* = 254.6 Hz), 67.2 (q, *J* = 2.8 Hz), 65.3, 28.5, 28.3, 22.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.68, -63.06. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{14}F_6O_3$ $[M]^+$, 344.0847. Found, 344.0859. IR (neat): υ (cm^{-1}): 2955, 2857. 1724, 1602, 1551, 1480, 1326, 1273, 1130, 1066, 1018, 863, 775.

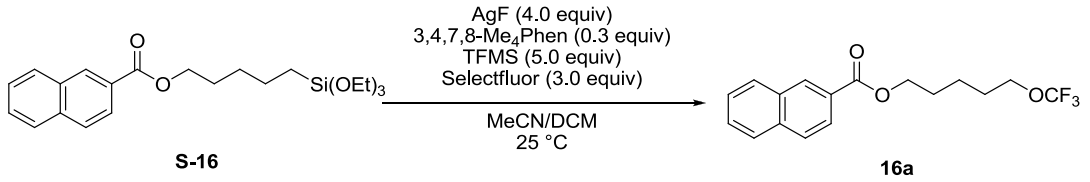
5-(Trifluoromethoxy)pentyl 4-(trifluoromethoxy)benzoate (15a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-(trifluoromethoxy)benzoate (**S-15**) (219 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 97.8 mg 5-(trifluoromethoxy)pentyl 4-(trifluoromethoxy)benzoate (**15a**) as a colorless liquid (54% yield).

R_f = 0.39 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 2H), 7.28 – 7.26 (m, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 1.86 – 1.74 (m, 4H), 1.61 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 152.7, 131.6, 128.9, 121.8 (q, *J* = 254.5 Hz), 120.5 (q, *J* = 259.3 Hz), 120.4, 67.2 (q, *J* = 3.2 Hz), 65.0, 28.4, 28.3, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.33, -60.39. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}F_6NO_4$ $[M + NH_4]^+$, 378.1140. Found, 378.1127. IR (neat): υ (cm^{-1}): 2957, 2871, 1723, 1607, 1411, 1258, 1219, 1166, 1139, 1018, 856, 769.

5-(Trifluoromethoxy)pentyl 2-naphthoate (16a)

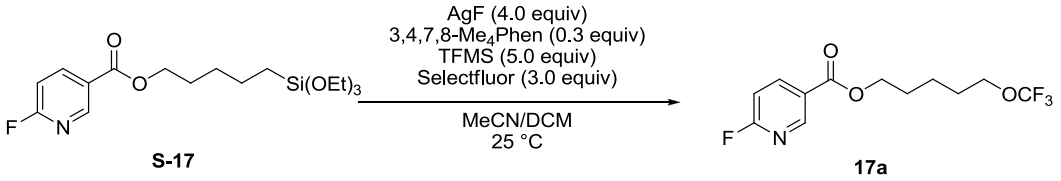


In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 2-naphthoate (**S-16**) (202 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 99.2 mg 5-(trifluoromethoxy)pentyl 2-naphthoate (**16a**) as a colorless liquid (61% yield).

R_f = 0.26 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.09 – 8.07 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.60 – 7.52 (m, 2H), 4.40 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 1.89 – 1.75 (m, 4H), 1.63 – 1.56 (m,

2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 135.6, 132.6, 131.0, 129.4, 128.3, 128.2, 127.8, 127.6, 126.7, 125.3, 121.8 (q, *J* = 254.7 Hz), 67.3 (q, *J* = 3.1 Hz), 64.8, 28.4, 28.3, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.34. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{18}F_3O_3$ $[M + H]^+$, 327.1208. Found, 327.1200. IR (neat): υ (cm^{-1}): 3037, 3011, 2941, 2888, 1717, 1632, 1602, 1507, 1458, 1391, 1353, 1285, 1228, 1186, 1117, 957, 857, 788, 758.

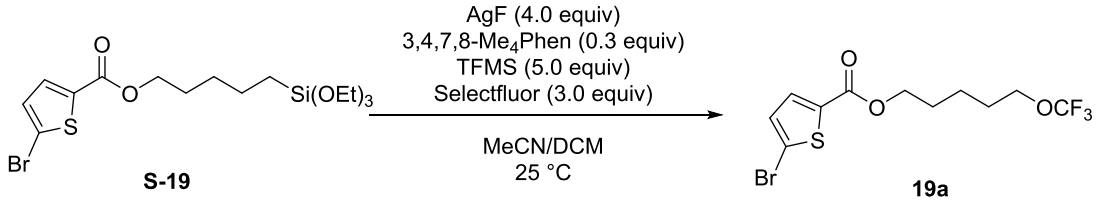
5-(Trifluoromethoxy)pentyl 6-fluoronicotinate (17a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 6-fluoronicotinate (**S-17**) (187 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 15:1 (v/v) to afford 81.0 mg 5-(trifluoromethoxy)pentyl 6-fluoronicotinate (**17a**) as a colorless liquid (61% yield).

R_f = 0.30 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.4 Hz, 1H), 8.38 – 8.33 (m, 1H), 6.97 (dd, *J* = 8.5 Hz, 2.8 Hz, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.3 Hz, 2H), 1.82 – 1.70 (m, 4H), 1.56 – 1.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (d, *J* = 246.3 Hz), 164.2, 150.3 (d, *J* = 16.6 Hz), 142.6 (d, *J* = 9.4 Hz), 124.6 (d, *J* = 4.5 Hz), 121.7 (q, *J* = 254.6 Hz), 109.6 (d, *J* = 37.7 Hz), 67.1 (q, *J* = 3.1 Hz), 65.2, 28.3, 28.1, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.77, -61.52. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}F_4NO_3$ $[M + H]^+$, 296.0910. Found, 296.0904. IR (neat): υ (cm^{-1}): 2959, 2873, 1726, 1596, 1483, 1381, 1286, 1134, 1021, 845, 777.

5-(Trifluoromethoxy)pentyl 5-bromothiophene-2-carboxylate (19a)

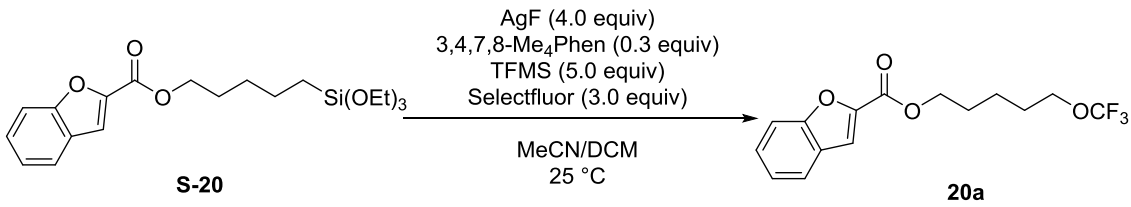


In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 5-bromothiophene-2-carboxylate (**S-19**) (220 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then

sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 113 mg 5-(trifluoromethoxy)pentyl 5-bromothiophene-2-carboxylate (**19a**) as a colorless liquid (62% yield).

R_f = 0.39 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.81 – 1.71 (m, 4H), 1.56 – 1.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 135.0 133.7, 131.0, 121.8 (q, *J* = 254.8 Hz), 120.3, 67.2 (q, *J* = 3.1 Hz), 65.1, 28.4, 28.2, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.68. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{11}H_{13}BrF_3O_3S$ $[M + H]^+$, 360.9721. Found, 360.9708. IR (neat): υ (cm^{-1}): 2956, 2873, 1713, 1612, 1554, 1469, 1418, 1328, 1253, 1139, 1091, 1047, 974, 856, 745.

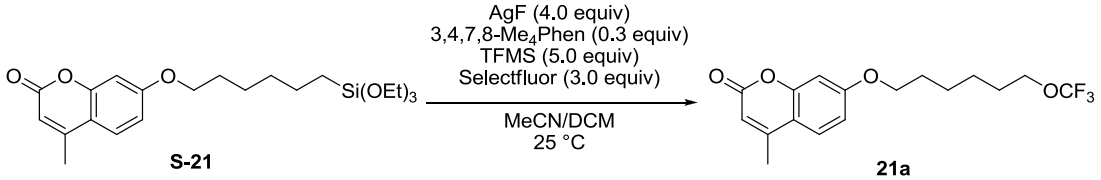
5-(Trifluoromethoxy)pentyl benzofuran-2-carboxylate (20a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl benzofuran-2-carboxylate (**S-20**) (197 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 88.6 mg 5-(trifluoromethoxy)pentyl benzofuran-2-carboxylate (**20a**) as a colorless liquid (56% yield).

R_f = 0.39 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 1H), 7.59 – 7.57 (m, 1H), 7.52 (d, *J* = 0.84 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.31 – 7.27 (m, 1H), 4.38 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.86 – 1.73 (m, 4H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 155.7, 145.5, 127.6, 126.9, 123.8, 122.8, 121.7 (q, *J* = 254.8 Hz), 113.8, 112.3, 67.1 (q, *J* = 3.1 Hz), 65.0, 28.3, 28.1, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.66. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{16}F_3O_4$ $[M + H]^+$, 317.1001. Found, 317.0996. IR (neat): υ (cm^{-1}): 2947, 2871, 1727, 1692, 1572, 1554, 1295, 1258, 1210, 1177, 1143, 1096, 885, 749.

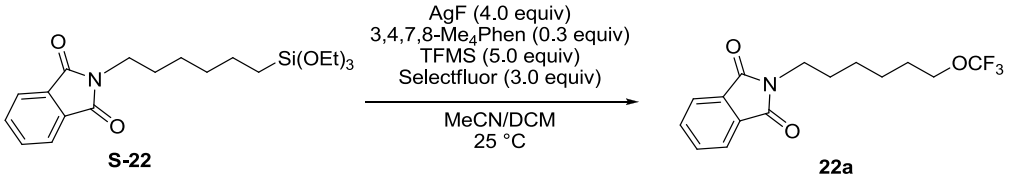
4-Methyl-7-((6-(trifluoromethoxy)hexyl)oxy)-2H-chromen-2-one (21a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 4-methyl-7-((6-(triethoxysilyl)hexyl)oxy)-2H-chromen-2-one (**S-21**) (211 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 5:1 (v/v) to afford 88.0 mg 4-methyl-7-((6-(trifluoromethoxy)hexyl)oxy)-2H-chromen-2-one (**21a**) as a colorless liquid (51% yield).

R_f = 0.27 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 1H), 6.83 – 6.81 (m, 1H), 6.76 (d, *J* = 1.6 Hz, 1H), 6.09 (s, 1H), 4.01 – 3.94 (m, 4H), 2.36 (s, 3H), 1.85 – 1.78 (m, 2H), 1.75 – 1.68 (m, 2H), 1.53 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.4, 155.3, 152.7, 125.6, 121.8 (q, *J* = 254.8 Hz), 113.5, 112.6, 111.9, 101.4, 68.4, 67.4 (q, *J* = 3.1 Hz), 28.9, 28.7, 25.6, 25.3, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.60. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{20}F_3O_4$ $[M + H]^+$, 345.1314. Found, 345.1310. IR (neat): υ (cm^{-1}): 2944, 2864, 1730, 1614, 1554, 1432, 1388, 1369, 1277, 1201, 1138, 1070, 1015, 848.

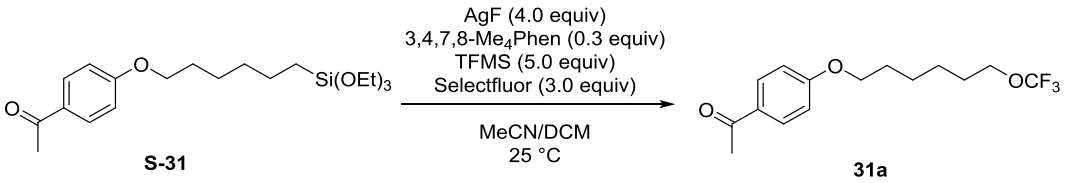
2-(6-(Trifluoromethoxy)hexyl)isoindoline-1,3-dione (22a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 2-(6-(triethoxysilyl)hexyl)isoindoline-1,3-dione (**S-22**) (197 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 15:1 (v/v) to afford 102 mg 2-(6-(trifluoromethoxy)hexyl)isoindoline-1,3-dione (**22a**) as a white solid (65% yield).

R_f = 0.25 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.71 – 7.67 (m, 2H), 3.92 (t, J = 6.5 Hz, 2H), 3.66 (t, J = 7.3 Hz, 2H), 1.71 – 1.63 (m, 4H), 1.46 – 1.32 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 134.0, 132.2, 123.3, 121.7 (q, *J* = 254.6 Hz), 67.4 (q, *J* = 3.1 Hz), 37.9, 28.6, 28.5, 26.4, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.63. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{17}F_3NO_3$ $[M + H]^+$, 316.1161. Found, 316.1155. IR (neat): υ (cm^{-1}): 2939, 2860, 1772, 1714, 1396, 1265, 1135, 1054, 719.

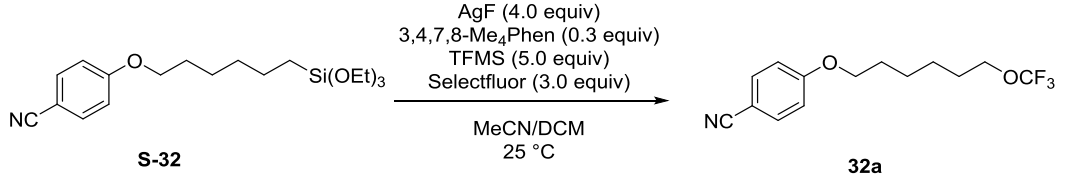
1-(4-((6-(Trifluoromethoxy)hexyl)oxy)phenyl)ethan-1-one (31a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 1-(4-((6-(triethoxysilyl)hexyl)oxy)phenyl)ethan-1-one (**S-31**) (191 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 63.0 mg 1-(4-((6-(trifluoromethoxy)hexyl)oxy)phenyl)ethan-1-one (**31a**) as a colorless liquid (41% yield).

R_f = 0.13 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 2H), 6.91 – 6.88 (m, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.95 (t, J = 6.4 Hz, 2H), 2.53 (s, 3H), 1.84 – 1.77 (m, 2H), 1.74 – 1.67 (m, 2H), 1.54 – 1.41 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.1, 130.6, 130.2, 121.8 (q, *J* = 254.6 Hz), 114.2, 68.0, 67.4 (q, *J* = 3.1 Hz), 29.0, 28.7, 26.4, 25.6, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.65. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{20}F_3O_3$ $[M + H]^+$, 305.1365. Found, 305.1365. IR (neat): υ (cm^{-1}): 2944, 2868, 1678, 1601, 1419, 1359, 1255, 1171, 1136, 1019, 834.

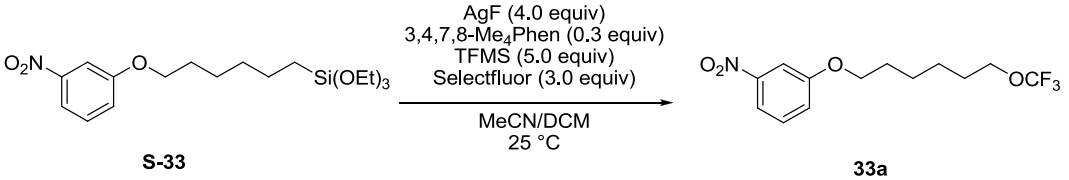
4-((6-(Trifluoromethoxy)hexyl)oxy)benzonitrile (32a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600

mg, 2.50 mmol, 5.00 equiv), 4-((6-(triethoxysilyl)hexyl)oxy)benzonitrile (**S-32**) (183 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 15:1 (v/v) to afford 77.7 mg 4-((6-(trifluoromethoxy)hexyl)oxy)benzonitrile (**32a**) as a colorless liquid (54% yield).
R_f = 0.22 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 4.01 – 3.94 (m, 4H), 1.84 – 1.70 (m, 4H), 1.54 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 134.0, 121.8 (q, *J* = 254.7 Hz), 119.3, 115.3, 103.8, 68.2, 67.4 (q, *J* = 3.0 Hz), 28.9, 28.7, 25.5, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.63. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{17}F_3NO_2$ $[M + H]^+$, 288.1211. Found, 288.1209. IR (neat): υ (cm^{-1}): 2947, 2879, 2261, 1605, 1494, 1258, 1171, 1135, 1016, 834, 737.

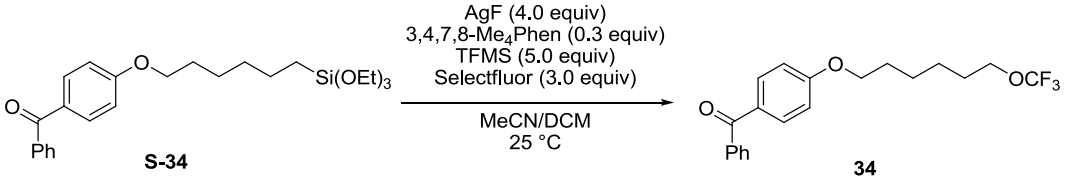
1-Nitro-3-((6-(trifluoromethoxy)hexyl)oxy)benzene (33a)



S-33 **33a**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), triethoxy(6-(3-nitrophenoxy)hexyl)silane (**S-33**) (193 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 100:1 (v/v) to afford 98.8 mg 1-nitro-3-((6-(trifluoromethoxy)hexyl)oxy)benzene (**33a**) as a colorless liquid (64% yield).
R_f = 0.26 (hexanes/EtOAc 100:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.70 (t, J = 2.3 Hz, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 4.03 (t, J = 6.4 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.76 – 1.70 (m, 2H), 1.57 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.3, 130.0, 121.8 (q, *J* = 254.7 Hz), 121.7, 115.7, 108.7, 68.5, 67.4 (q, *J* = 3.1 Hz), 28.9, 28.7, 25.6, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.62. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{20}F_3N_2O_4$ $[M + NH_4]^+$, 325.1375. Found, 325.1368. IR (neat): υ (cm^{-1}): 2902, 2885, 1619, 1580, 1473, 1407, 1350, 1287, 1245, 1139, 1027, 860, 759.

Phenyl(4-((6-(trifluoromethoxy)hexyl)oxy)phenyl)methanone (34)

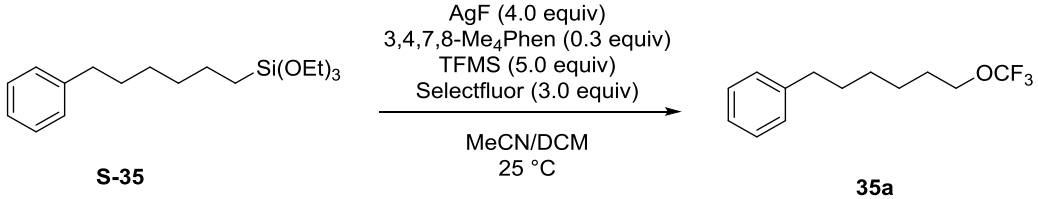


S-34 **34**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), phenyl(4-((6-(triethoxysilyl)hexyl)oxy)phenyl)methanone (**S-34**) (222 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 20:1 (v/v) to afford 100 mg phenyl(4-((6-(trifluoromethoxy)hexyl)oxy)phenyl)methanone (**34**) as a white solid (55% yield).

R_f = 0.19 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 2H), 7.75 – 7.73 (m, 2H), 7.57 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 6.95 – 6.92 (m, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.75 – 1.69 (m, 2H), 1.55 – 1.47 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 162.8, 138.4, 132.6, 131.9, 130.0, 129.7, 128.2, 121.8 (q, *J* = 254.6 Hz), 114.0, 68.0, 67.4 (q, *J* = 3.1 Hz), 29.0, 28.6, 25.6, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.66. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{22}F_3O_3$ $[M + H]^+$, 367.1521. Found, 367.1521. IR (neat): υ (cm^{-1}): 2943, 2870, 1657, 1599, 1279, 1255, 1171, 1145, 1022, 792, 700.

(6-(Trifluoromethoxy)hexyl)benzene (35a)



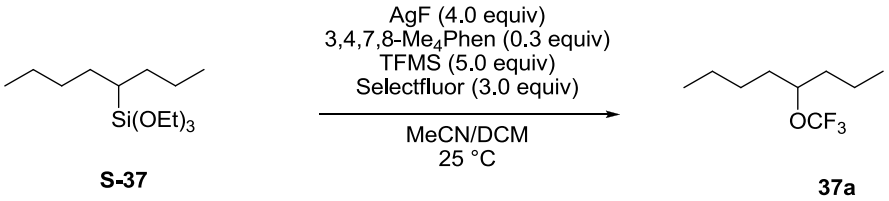
S-35 **35a**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), triethoxy(6-phenylhexyl)silane (**S-35**) (162 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes to afford 74.8 mg (6-(trifluoromethoxy)hexyl)benzene (**35a**) as a

colorless liquid (61% yield).

R_f = 0.57 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 3.91 (t, J = 6.6 Hz, 2H), 2.60 (t, J = 7.8 Hz, 2H), 1.68 – 1.58 (m, 4H), 1.43 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 128.5, 128.4, 125.8, 121.9 (q, J = 254.5 Hz), 67.6 (q, J = 3.1 Hz), 35.9, 31.4, 28.8, 28.8, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.42. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{17}F_3O$ $[M]^+$, 246.1231. Found, 246.1232. IR (neat): υ (cm^{-1}): 2917, 2849, 1622, 1555, 1538, 1415, 1264, 1148, 1023, 856, 795.

4-(Trifluoromethoxy)octane (37a)

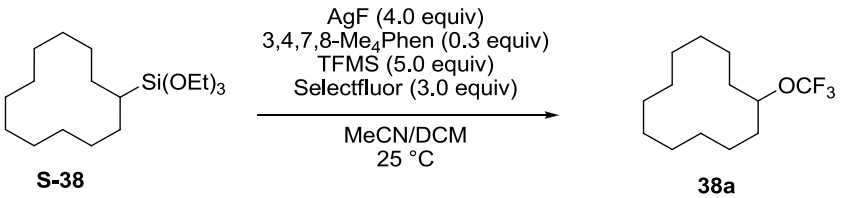


S-37 **37a**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), triethoxy(octan-4-yl)silane (**S-37**) (138 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (50.0 µL, 0.407 mmol) was added. The ^{19}F NMR yield of the volatile 4-(trifluoromethoxy)octane (**37a**) was determined by comparing the integration of the ^{19}F NMR (376 MHz, CDCl3) resonance of benzotrifluoride (-207.53 ppm) with that of 4-(trifluoromethoxy)octane (-57.26 ppm). (12% ^{19}F NMR Yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.26.

(Trifluoromethoxy)cyclododecane (38a)

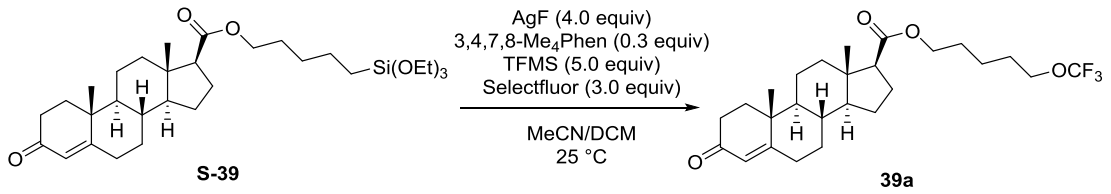


S-38 **38a**

In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), cyclododecyltriethoxysilane (**S-38**) (165 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (50.0 µL, 0.407 mmol) was added. The ^{19}F NMR yield of the volatile (trifluoromethoxy)cyclododecane (**38a**) was determined by comparing the integration of the ^{19}F NMR (376 MHz, $CDCl_3$) resonance of benzotrifluoride (-62.8 ppm) with that of (trifluoromethoxy)cyclododecane (-57.73 ppm). (9% ^{19}F NMR Yield).

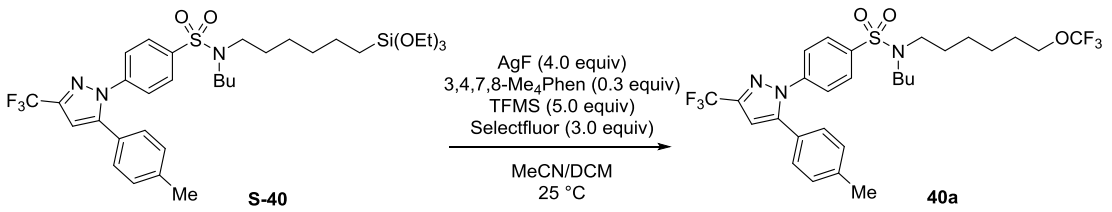
NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.73.
38a is a known compound and spectral data match the reported literature values [5].

5-(Trifluoromethoxy)pentyl androst-4-en-3-one-17β-carboxylate (39a)



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl androst-4-en-3-one-17β-carboxylate (**S-39**) (274 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 5:1 (v/v) to afford 147 mg 5-(trifluoromethoxy)pentyl androst-4-en-3-one-17β-carboxylate (**39a**) as a white solid (62% yield).
R_f = 0.17 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 1H), 4.11 – 3.98 (m, 2H), 3.93 (t, J = 6.3 Hz, 2H), 2.43 – 2.22 (m, 5H), 2.15 – 2.06 (m, 1H) , 2.01 – 1.98 (m, 2H), 1.84 – 1.19 (m, 17H), 1.14 (s, 3H), 1.11 – 0.89 (m, 3H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 174.0, 171.1, 123.9, 121.7 (q, J = 254.9 Hz), 67.2 (q, J = 2.9 Hz), 63.8, 55.4, 55.2, 53.8, 44.0, 38.7, 38.2, 35.8, 34.0, 32.9, 32.0, 28.3, 28.3, 24.5, 23.6, 22.2, 20.9, 17.4, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.52. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{38}F_3O_4$ $[M + H]^+$, 471.2722. Found, 471.2720. IR (neat): υ (cm^{-1}): 2942, 2856, 1734, 1685, 1663, 1559, 1448, 1270, 1139, 1052, 868.

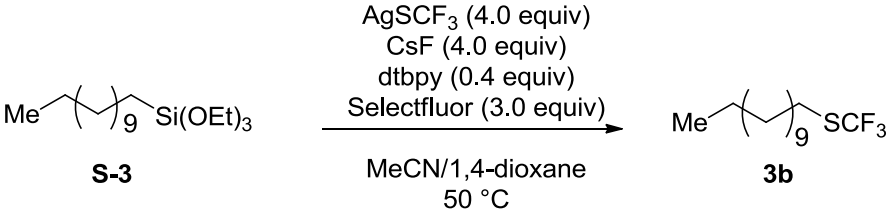
***N*-butane-*N*-(6-(trifluoromethoxy)hexyl)-Celecoxib (40a)**



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), tmph (35.4 mg, 0.150 mmol, 0.300 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at

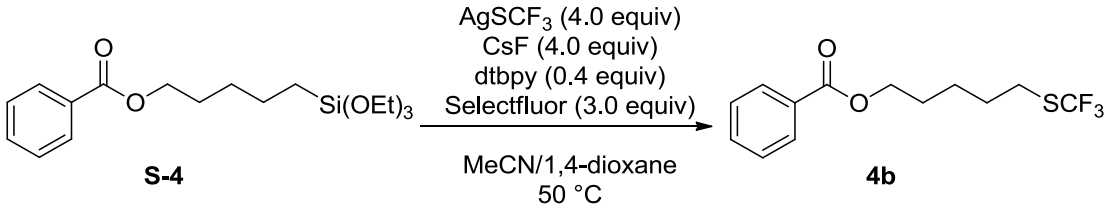
room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), *N*-butane-*N*-(6-(triethoxysilyl)hexyl)-Celecoxib (**S-40**) (274 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 15:1 (v/v) to get a crude product, which was then purified by preparative TLC, eluting with hexanes/DCM 2:1 (v/v) to afford 96.6 mg *N*-butane-*N*-(6-(trifluoromethoxy)hexyl)-Celecoxib (**40a**) as a white solid (32% yield).
R_f = 0.33 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.17 – 7.15 (m, 2H), 7.10 – 7.08 (m, 2H), 6.74 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 4H), 2.37 (s, 3H), 1.70 – 1.63 (m, 2H), 1.57 – 1.23 (m, 10H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.1 (q, *J* = 38.7 Hz), 142.3, 139.9, 139.8, 129.8, 128.8, 128.1, 125.8, 125.6, 121.8 (q, *J* = 254.6 Hz), 121.2 (q, *J* = 269.8 Hz), 106.3, 67.4 (q, *J* = 2.9 Hz), 48.1, 30.7, 28.7, 28.6, 26.2, 25.2, 21.4, 20.0, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.65, -62.42. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{28}H_{34}F_6N_3NaO_3S$ $[M + Na]^+$, 628.2045. Found, 628.2040. IR (neat): υ (cm^{-1}): 2961, 2938, 2866, 1622, 1588, 1472, 1373, 1340, 1263, 1237, 1160, 1136, 1024, 975, 804.

Dodecyl(trifluoromethyl)sulfane (3b)



In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes to afford 108 mg dodecyl(trifluoromethyl)sulfane (**3b**) as a colorless liquid (80% yield).
R_f = 0.75 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.43 – 1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4 (q, *J* = 305.6 Hz), 32.1, 30.0 (q, *J* = 1.8 Hz), 29.9, 29.7, 29.6, 29.6, 29.5, 29.1, 28.7, 22.9, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.56. **3b** is a known compound and spectral data match the reported literature values [6]. IR (neat): υ (cm^{-1}): 2926, 2856, 1473, 1283, 1154, 1119, 756.

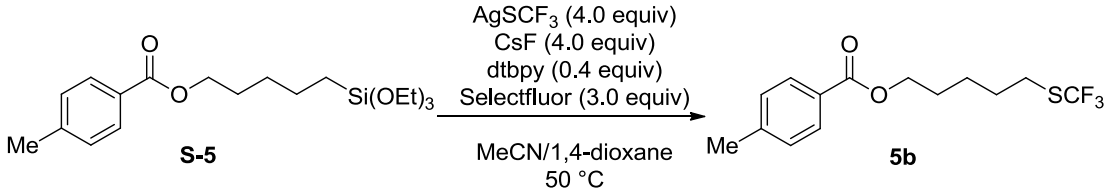
5-((Trifluoromethyl)thio)pentyl benzoate (4b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl benzoate (**S-4**) (177 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 12:1 (v/v) to afford 98.4 mg 5-((trifluoromethyl)thio)pentyl benzoate (**4b**) as a colorless liquid (67% yield).

R_f = 0.49 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.62 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 4.33 (t, J = 6.5 Hz, 2H), 2.91 (t, J = 7.3 Hz, 2H), 1.84 – 1.74 (m, 4H), 1.61 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 131.3 (q, J = 305.6 Hz), 130.4, 129.7, 128.5, 64.7, 29.8 (q, J = 1.9 Hz), 29.3, 28.3, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.40. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{13}H_{16}F_3O_2S$ $[M + H]^+$, 293.0823. Found, 293.0814. IR (neat): υ (cm^{-1}): 2950, 2866, 1720, 1602, 1585, 1452, 1315, 1276, 1147, 1114, 1070, 1026, 755.

5-((Trifluoromethyl)thio)pentyl 4-methylbenzoate (5b)

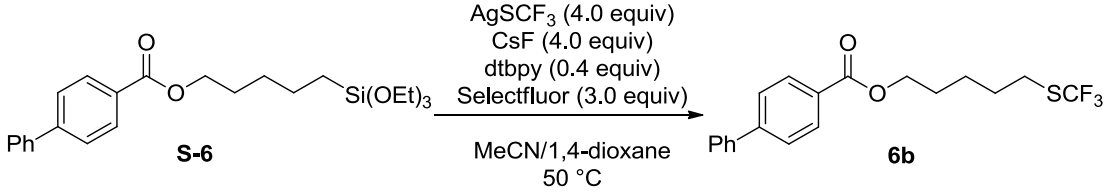


In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 4-methylbenzoate (**S-5**) (184 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM

12:1 (v/v) to afford 107 mg 5-((trifluoromethyl)thio)pentyl 4-methylbenzoate (**5b**) as a colorless liquid (70% yield).

R_f = 0.42 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.22 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.74 – 1.64 (m, 4H), 1.51 – 1.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.7, 131.2 (q, *J* = 305.6 Hz), 129.6, 129.2, 127.7, 64.4, 29.8 (q, *J* = 1.9 Hz), 29.2, 28.3, 25.2, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.40. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{18}F_3O_2S$ $[M + H]^+$, 307.0980. Found, 307.0969. IR (neat): υ (cm^{-1}): 2953, 2866, 1718, 1613, 1459, 1375, 1276, 1178, 1112, 1020, 841, 754.

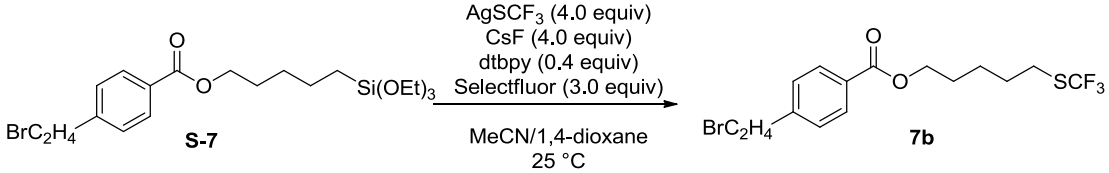
5-((Trifluoromethyl)thio)pentyl [1,1'-biphenyl]-4-carboxylate (6b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl [1,1'-biphenyl]-4-carboxylate (**S-6**) (215 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 12:1 (v/v) to afford 78.6 mg 5-((trifluoromethyl)thio)pentyl [1,1'-biphenyl]-4-carboxylate (**6b**) as a colorless liquid (43% yield).

R_f = 0.35 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 4.25 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.77 (m, 4H), 1.64 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 144.6, 138.9, 130.1 (q, *J* = 305.7 Hz), 129.0, 128.0, 127.9, 127.1, 126.2, 126.0, 63.5, 28.7 (q, *J* = 1.7 Hz), 28.1, 27.2, 24.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.43. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{20}F_3O_2S$ $[M + H]^+$, 369.1136. Found, 369.1126. IR (neat): υ (cm^{-1}): 2947, 2864, 1715, 1609, 1487, 1450, 1405, 1311, 1278, 1114, 1007, 858, 783, 748.

5-((Trifluoromethyl)thio)pentyl 4-(2-bromoethyl)benzoate (7b)

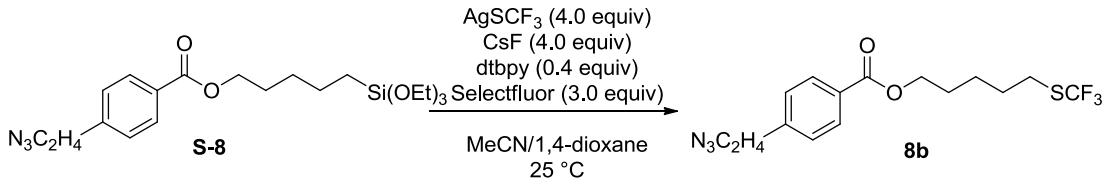


In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 4-(2-bromoethyl)benzoate (**S-7**) (231

mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 10:1 (v/v) to afford 128 mg 5-((trifluoromethyl)thio)pentyl 4-(2-bromoethyl)benzoate (**7b**) as a colorless liquid (64% yield).

R_f = 0.30 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 2H), 3.59 (t, *J* = 7.4 Hz, 2H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.84 – 1.74 (m, 4H), 1.60 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 144.2, 131.2 (q, *J* = 305.8 Hz), 130.0, 129.1, 128.9, 64.7, 39.2, 32.3, 29.8 (q, *J* = 2.1 Hz), 29.3, 28.3, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.49. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{19}BrF_3O_2S$ $[M + H]^+$, 399.0241. Found, 399.0226. IR (neat): υ (cm^{-1}): 2946, 2861, 1715, 1611, 1415, 1308, 1276, 1179, 1114, 1020, 756.

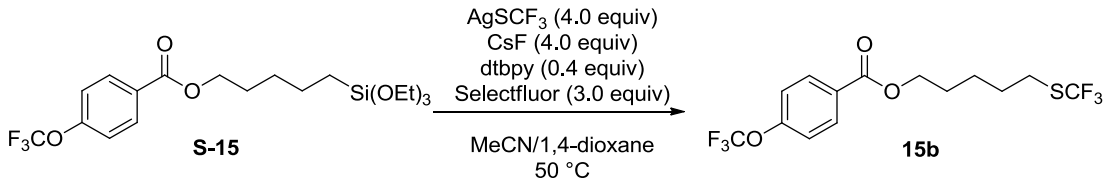
5-((Trifluoromethyl)thio)pentyl 4-(2-azidoethyl)benzoate (8b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 4-(2-azidoethyl)benzoate (**S-8**) (212 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 25:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 12:1 (v/v) to afford 112 mg 5-((trifluoromethyl)thio)pentyl 4-(2-azidoethyl)benzoate (**8b**) as a colorless liquid (62% yield).

R_f = 0.24 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 3.53 (t, *J* = 7.1 Hz, 2H), 2.97 – 2.88 (m, 4H), 1.85 – 1.75 (m, 4H), 1.62 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 143.5, 131.2 (q, *J* = 305.9 Hz), 130.0, 129.0, 128.9, 64.6, 52.0, 35.4, 29.8 (q, *J* = 1.3 Hz), 29.2, 28.2, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.20. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{19}F_3N_3O_2S$ $[M + H]^+$, 362.1150. Found, 362.1142. IR (neat): υ (cm^{-1}): 2946, 2869, 2097. 1722, 1612, 1415, 1276, 1179, 1147, 1114, 1020, 852.

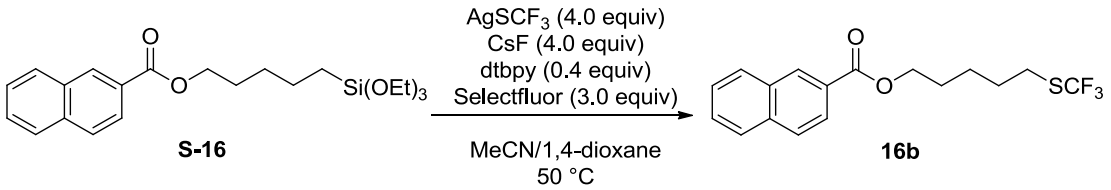
5-((Trifluoromethyl)thio)pentyl 4-(trifluoromethoxy)benzoate (15b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 4-(trifluoromethoxy)benzoate (**S-15**) (219 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 12:1 (v/v) to afford 99.7 mg 5-((trifluoromethyl)thio)pentyl 4-(trifluoromethoxy)benzoate (**15b**) as a colorless liquid (53% yield).

R_f = 0.41 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.85 – 1.75 (m, 4H), 1.61 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 152.8 (q, *J* = 1.6 Hz), 131.7, 131.3 (q, *J* = 305.7 Hz), 128.8, 120.4 (q, *J* = 258.5 Hz), 120.4, 65.0, 29.8 (q, *J* = 1.8 Hz), 29.2, 28.2, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.11, -57.60. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{14}F_6NaO_3S$ $[M + Na]^+$, 399.0466. Found, 399.0465. IR (neat): υ (cm^{-1}): 2958, 2869, 1720, 1605, 1561, 1460, 1375, 1263, 1158, 1116, 1018, 858, 769.

5-((Trifluoromethyl)thio)pentyl 2-naphthoate (16b)

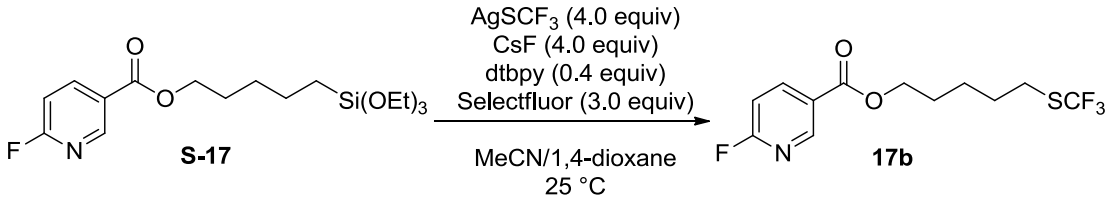


In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 2-naphthoate (**S-16**) (202 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 12:1 (v/v) to afford 112 mg 5-((trifluoromethyl)thio)pentyl 2-naphthoate (**16b**) as a colorless liquid (65% yield).

R_f = 0.40 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.62 (s, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.62 – 7.53 (m, 2H), 4.39 (t, J = 6.5 Hz, 2H), 2.92 (t, J = 7.4 Hz, 2H), 1.88 – 1.76 (m, 4H), 1.63 – 1.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 135.6, 132.6, 131.3 (d, J = 305.8 Hz), 131.1, 129.4, 128.3, 128.2, 127.8, 127.6, 126.7, 125.3, 64.8, 29.8 (q, J = 1.6 Hz), 29.2, 28.3, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.41. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{18}F_3O_2S$ $[M + H]^+$, 343.0980. Found, 343.0978. IR (neat): υ (cm^{-1}): 3062, 2947, 2864, 1718, 1632, 1599, 1507, 1466, 1389, 1353, 1285, 1228, 1196, 1116, 957, 866, 827, 779, 762.

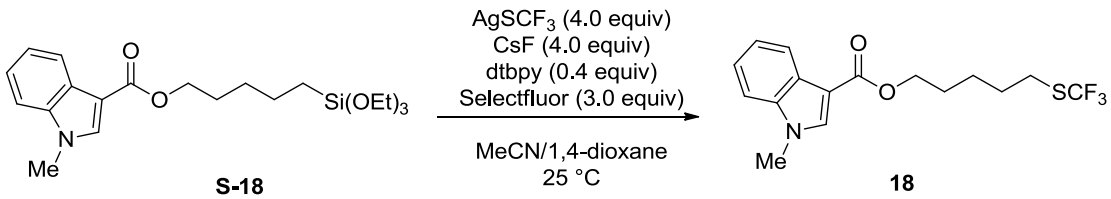
5-((Trifluoromethyl)thio)pentyl 6-fluoronicotinate (17b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 6-fluoronicotinate (**S-17**) (187 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 10:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 2:1 (v/v) to afford 83.0 mg 5-((trifluoromethyl)thio)pentyl 6-fluoronicotinate (**17b**) as a colorless liquid (53% yield).

R_f = 0.18 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 2.4 Hz, 1H), 8.40 – 8.36 (m, 1H), 6.99 (dd, J = 8.5, 2.8 Hz, 1H), 4.35 (t, J = 6.5 Hz, 2H), 2.89 (t, J = 7.3 Hz, 2H), 1.84 – 1.73 (m, 4H), 1.59 – 1.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0 (d, J = 245.7 Hz), 164.3, 150.4 (d, J = 16.4 Hz), 142.6 (d, J = 8.9 Hz), 131.2 (q, J = 305.3 Hz), 124.7 (d, J = 4.5 Hz), 109.6 (d, J = 37.3 Hz), 65.3, 29.8 (q, J = 1.9 Hz), 29., 28.2, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.40, -61.64. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{12}H_{14}F_4NO_2S$ $[M + H]^+$, 312.0681. Found, 312.0680. IR (neat): υ (cm^{-1}): 2949, 2866, 1725, 1595, 1483, 1381, 1282, 1114, 1020, 844, 777.

5-((Trifluoromethyl)thio)pentyl 1-methyl-1H-indole-3-carboxylate (18)

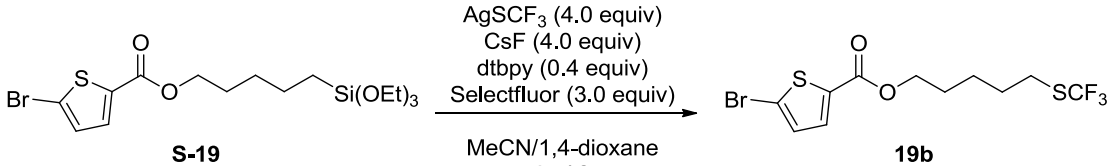


In a glovebox, to a solution of 5-(triethoxysilyl)pentyl1-methyl-1H-indole-3- carboxylate (**S-18**) (204 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531

mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 4:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 1:3 (v/v) to afford 70.5 mg 5-((trifluoromethyl)thio)pentyl 1-methyl-1H-indole-3-carboxylate (**18**) as a colorless liquid (41% yield).

R_f = 0.33 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 7.77 (s, 1H), 7.35 – 7.26 (m, 3H), 4.34 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.75 (m, 4H), 1.63 – 1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 137.2, 135.2, 131.3 (q, *J* = 305.6 Hz), 126.7, 122.9, 122.0, 121.7, 109.9, 107.1, 63.4, 33.5, 29.9 (q, *J* = 1.9 Hz), 29.3, 28.5, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.33. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{19}F_3NO_2S$ $[M + H]^+$, 346.1089. Found, 346.1082. IR (neat): υ (cm^{-1}): 3121, 3055, 2946, 2865, 1695, 1616, 1575, 1468, 1424, 1401, 1378, 1268, 1223, 1151, 1104, 1012, 775.

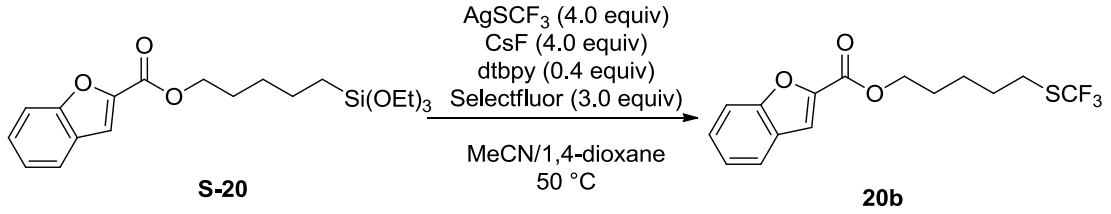
5-((Trifluoromethyl)thio)pentyl 5-bromothiophene-2-carboxylate (19b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 5-bromothiophene-2- carboxylate (**S-19**) (220 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 25:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 10:1 (v/v) to afford 112 mg 5-((trifluoromethyl)thio)pentyl 5-bromothiophene-2-carboxylate (**19b**) as a colorless liquid (60% yield).

R_f = 0.46 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 1H), 4.27 (t, *J* = 6.5 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.79 – 1.72 (m, 4H), 1.57 – 1.49 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 135.0, 133.7,131.2 (q, *J* = 305.8 Hz), 131.0, 120.3, 65.1, 29.8 (q, *J* = 1.9 Hz), 29.2, 28.2, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.11. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{11}H_{12}BrF_3O_2S_2$ [M]+, 375.9414. Found, 375.9413. IR (neat): υ (cm^{-1}): 2946, 2863, 1718, 1532, 1418, 1328, 1282, 1251, 1148, 1116, 1047, 973, 810, 745.

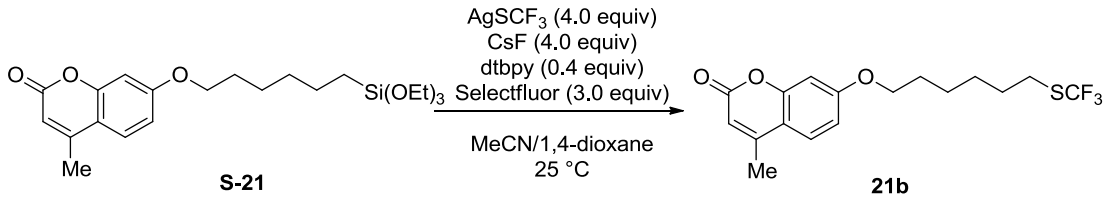
5-((Trifluoromethyl)thio)pentyl benzofuran-2-carboxylate (20b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl benzofuran-2-carboxylate (**S-20**) (197 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 25:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 8:1 (v/v) to afford 108 mg 5-((trifluoromethyl)thio)pentyl benzofuran-2-carboxylate (**20b**) as a colorless liquid (65% yield).

R_f = 0.31 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.33 – 7.27 (m, 1H), 4.39 (t, *J* = 6.6 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.74 (m, 4H), 1.61 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 155.9, 145.6, 131.3 (q, *J* = 305.8 Hz), 127.7, 127.1, 123.9, 122.9, 114.0, 112.5, 65.1, 29.8 (q, *J* = 1.9 Hz), 29.2, 28.2, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.40. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{16}F_3O_3S$ $[M + H]^+$, 333.0772. Found, 333.0769. IR (neat): υ (cm^{-1}): 3067, 2947, 2864, 1733, 1614, 1589, 1475, 1448, 1348, 1296, 1258, 1180, 1146, 1117, 955, 885, 857, 750.

4-Methyl-7-((6-((trifluoromethyl)thio)hexyl)oxy)-2H-chromen-2-one (21b)

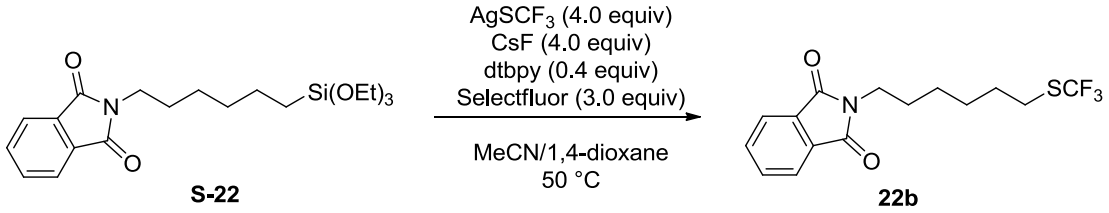


In a glovebox, to a solution of 4-methyl-7-((6-(triethoxysilyl)hexyl)oxy)-2H- chromen-2-one (**S-21**) (211 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 5:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 1:2 (v/v) to afford 111 mg 4-methyl-7-((6-((trifluoromethyl)thio)hexyl)oxy)-2H-chromen-2-one (**21b**) as a colorless

liquid (62% yield).

R_f = 0.57 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 6.08 (d, *J* = 1.4 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.84 – 1.75 (m, 2H), 1.72 – 1.68 (m, 2H), 1.54 – 1.45 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 161.3, 155.3, 152.7, 131.2 (q, *J* = 305.9 Hz), 125.6, 113.5, 112.6, 111.9, 101.4, 68.3, 29.8 (q, *J* = 3.0 Hz), 29.4, 28.9, 28.2, 25.5, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.42. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{20}F_3O_3S$ $[M + H]^+$, 361.1085. Found, 361.1080. IR (neat): υ (cm^{-1}): 2942, 2862, 1734, 1718, 1616, 1559, 1498, 1465, 1387, 1146, 1116, 1070, 856, 777.

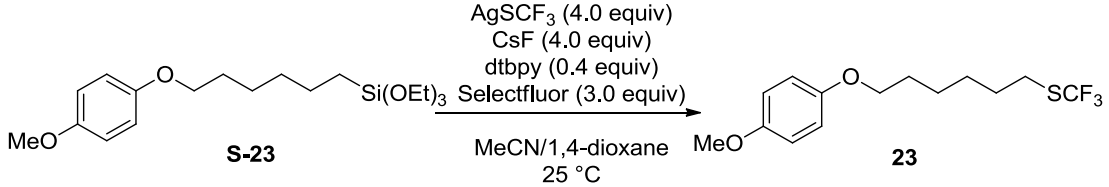
2-(6-((Trifluoromethyl)thio)hexyl)isoindoline-1,3-dione (22b)



In a glovebox, to a solution of 2-(6-(triethoxysilyl)hexyl)isoindoline-1,3-dione (**S-22**) (197 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 10:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 3:1 (v/v) to afford 103 mg 2-(6-((trifluoromethyl)thio)hexyl)isoindoline-1,3-dione (**22b**) as a colorless liquid (61% yield).

R_f = 0.16 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 7.70 – 7.67 (m, 2H), 3.64 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.76 – 1.54 (m, 4H), 1.49 – 1.26 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 133.9, 132.1, 131.2 (q, *J* = 305.8 Hz), 123.2, 37.8, 29.8 (q, *J* = 1.8 Hz), 29.3, 28.4, 28.0, 26.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.38. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{17}F_3NO_2S$ $[M + H]^+$, 332.0932. Found, 332.0927. IR (neat): υ (cm^{-1}): 2939. 2861, 1713, 1599, 1467, 1437, 1396, 1370, 1178, 1116, 1048, 755, 719.

(6-(4-Methoxyphenoxy)hexyl)(trifluoromethyl)sulfane (23)

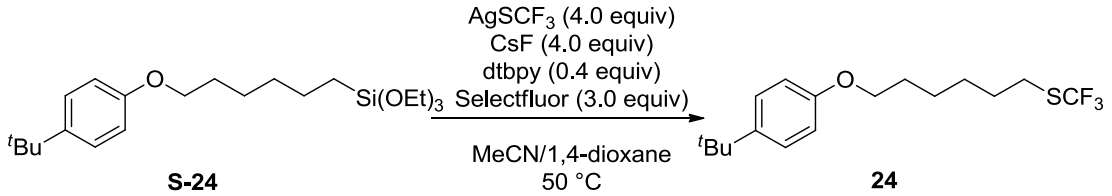


In a glovebox, to a solution of triethoxy(6-(4-methoxyphenoxy)hexyl)silane (**S-23**) (185 mg,

0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 8:1 (v/v) afford 95.1 mg (6-(4-methoxyphenoxy)hexyl)(trifluoromethyl)sulfane (**23**) as a colorless liquid (62% yield).

R_f = 0.39 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 – 6.80 (m, 4H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.77 (s, 3H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.81 – 1.70 (m, 4H), 1.54 – 1.45 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 153.3, 131.5 (q, *J* = 305.6 Hz), 115.6, 114.8, 68.5, 55.9, 29.9 (q, *J* = 1.9 Hz), 29.5, 29.3, 28.4, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.59. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{19}F_3O_2S$ $[M]^+$, 308.1058. Found, 308.1057. IR (neat): υ (cm^{-1}): 2939, 2861, 2835, 1601, 1508, 1468, 1232, 1146, 1116, 1039, 824.

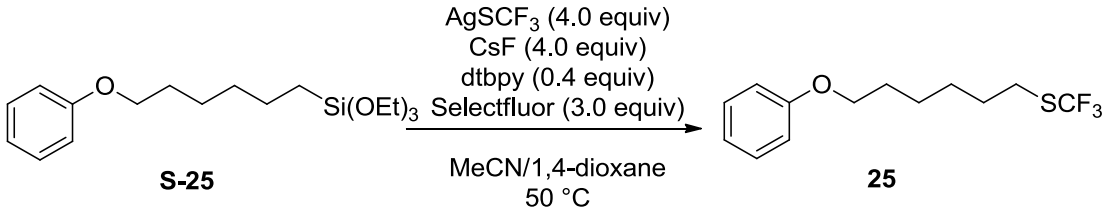
(6-(4-(*Tert*-butyl)phenoxy)hexyl)(trifluoromethyl)sulfane (24)



In a glovebox, to a solution of (6-(4-(*tert*-butyl)phenoxy)hexyl)triethoxysilane (**S-24**) (198 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 113 mg (6-(4-(*tert*-butyl)phenoxy)hexyl)(trifluoromethyl)sulfane (**24**) as a colorless liquid (68% yield).

R_f = 0.49 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.97 (t, *J* = 6.3 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.72 (m, 4H), 1.56 – 1.46 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 143.4, 131.3 (q, *J* = 305.7 Hz), 126.3, 114.0, 67.7, 34.2, 31.7, 29.9 (q, *J* = 1.9 Hz), 29.5, 29.3, 28.4, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.20. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{17}H_{25}F_3OS$ $[M]^+$, 334.1578. Found, 334.1580. IR (neat): υ (cm^{-1}): 3039, 2949, 2865, 1611, 1581, 1513, 1462, 1391, 1364, 1294, 1247, 1183, 1149, 1116, 1077, 828.

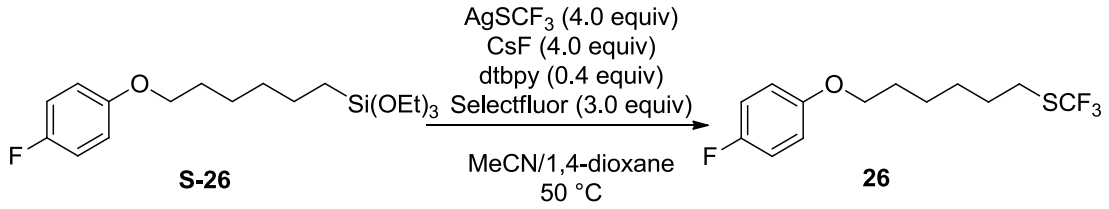
(6-Phenoxyhexyl)(trifluoromethyl)sulfane (25)



In a glovebox, to a solution of triethoxy(6-phenoxyhexyl)silane (**S-25**) (170 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 101 mg (6-phenoxyhexyl)(trifluoromethyl)sulfane (**25**) as a colorless liquid (73% yield).

R_f = 0.51 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 6.99 – 6.91 (m, 3H), 3.98 (t, *J* = 6.2 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.71 (m, 4H), 1.58 – 1.48 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 131.3 (q, *J* = 305.5 Hz), 129.6, 120.7, 114.6, 67.6, 29.9 (q, *J* = 1.8 Hz), 29.5, 29.2, 28.4, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.02. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{17}F_3OS$ $[M]^+$, 278.0952. Found, 278.0952. IR (neat): υ (cm^{-1}): 2936, 2863, 1618, 1586, 1498, 1246, 1150, 1119, 755.

(6-(4-Fluorophenoxy)hexyl)(trifluoromethyl)sulfane (26)

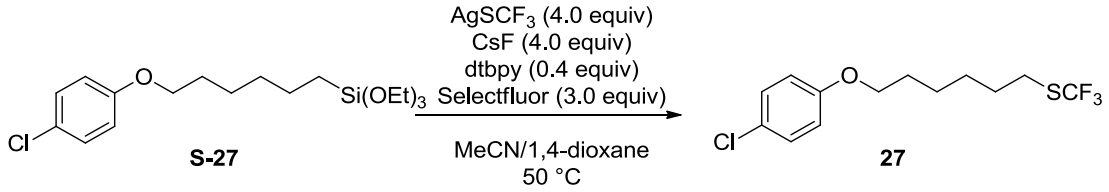


In a glovebox, to a solution of triethoxy(6-(4-fluorophenoxy)hexyl)silane (**S-26**) (179 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 92.0 mg (6-(4-fluorophenoxy)hexyl)(trifluoromethyl)sulfane (**26**) as a colorless liquid (63% yield).

R_f = 0.48 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.94 (m, 2H), 6.85 – 6.80 (m, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 1.82 – 1.70 (m, 4H), 1.54 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 237.8 Hz), 155.3 (d, *J* = 2.1 Hz), 131.3 (q, *J* = 305.7 Hz), 115.9 (d, *J* = 23.0 Hz), 115.5 (d, *J* = 7.9

Hz), 68.4, 29.9 (q, J = 2.0 Hz), 29.5, 29.2, 28.4, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.13, -124.27. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{16}F_4OS$ $[M]^+$, 296.0858. Found, 296.0859. IR (neat): υ (cm^{-1}): 2944, 2864, 1600, 1507, 1475, 1390, 1248, 1220, 1117, 828, 758, 722.

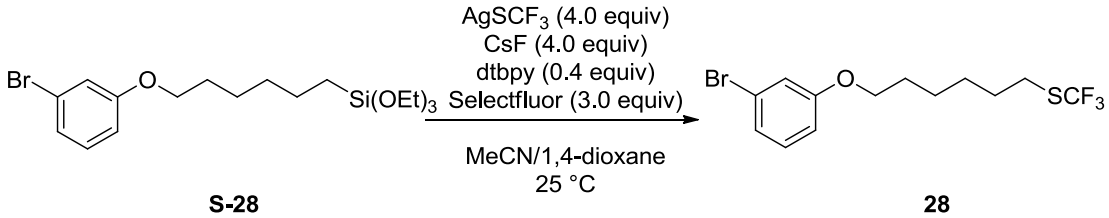
(6-(4-Chlorophenoxy)hexyl)(trifluoromethyl)sulfane (27)



In a glovebox, to a solution of (6-(4-chlorophenoxy)hexyl)triethoxysilane (**S-27**) (188 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 99.8 mg (6-(4-chlorophenoxy)hexyl)(trifluoromethyl)sulfane (**27**) as a colorless liquid (64% yield).

R_f = 0.53 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 6.84 – 6.80 (m, 2H), 3.92 (t, J = 6.4 Hz, 2H), 2.90 (t, J = 7.4 Hz, 2H), 1.82 – 1.70 (m, 4H), 1.54 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 131.3 (q, J = 305.5 Hz), 129.4, 125.5, 115.9, 68.1, 29.9 (q, J = 1.3 Hz), 29.5, 29.1, 28.4, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.32. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{16}ClF_3OS$ $[M]^+$, 312.0562. Found, 312.0566. IR (neat): υ (cm^{-1}): 2943, 2860, 1597, 1579, 1492, 1473, 1390, 1285, 1244, 1147, 1116, 1005, 824, 755.

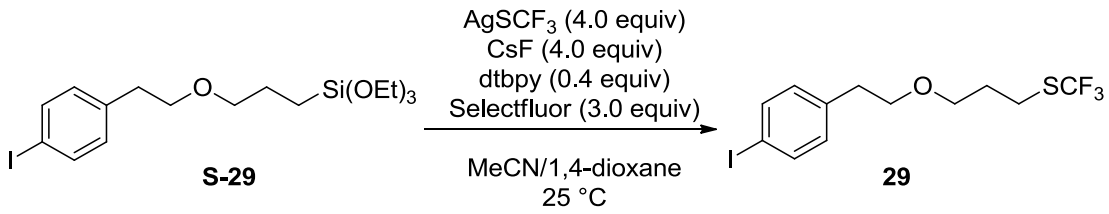
(6-(3-Bromophenoxy)hexyl)(trifluoromethyl)sulfane (28)



In a glovebox, to a solution of (6-(3-bromophenoxy)hexyl)triethoxysilane (**S-28**) (210 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 103 mg (6-(3-bromophenoxy)hexyl)(trifluoromethyl)sulfane (**28**) as a colorless liquid (58% yield).

R_f = 0.59 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 8.0 Hz, 1H), 7.08 – 7.03 (m, 2H), 6.83 – 6.80 (m, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.83 – 1.69 (m, 4H), 1.53 – 1.45 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 131.3 (q, *J* = 305.6 Hz), 130.7, 123.8, 122.9, 117.8, 113.7, 68.0, 29.9 (q, *J* = 1.9 Hz), 29.5, 29.1, 28.3, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.46. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{16}BrF_3OS$ $[M]^+$, 356.0057. Found, 356.0058. IR (neat): υ (cm^{-1}): 2964, 2882, 1589, 1572, 1478, 1468, 1284, 1244, 1147,1103, 1025, 861, 766.

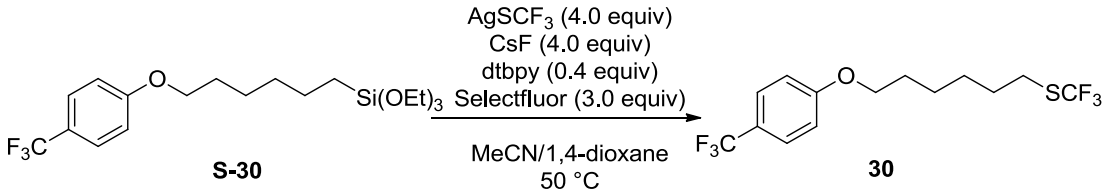
(3-(4-Iodophenethoxy)propyl)(trifluoromethyl)sulfane (29)



In a glovebox, to a solution of triethyl(3-(4-iodophenethoxy)propyl)silane (**S-29**) (226 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to afford 118 mg (3-(4-iodophenethoxy)propyl)(trifluoromethyl)sulfane (**29**) as a colorless liquid (61% yield).

R_f = 0.34 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.51 (t, *J* = 5.8 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.82 (t, *J* = 6.7 Hz, 2H), 1.96 – 1.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.5, 131.3 (q, *J* = 305.8 Hz), 131.1, 91.5, 71.5, 68.4, 35.9, 29.7, 26.9 (q, *J* = 1.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.52. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{14}F_3IOS$ $[M]^+$, 389.9762. Found, 389.9760. IR (neat): υ (cm^{-1}): 2930, 2863, 1584, 1484, 1248, 1146, 1112, 1006, 807, 754.

(Trifluoromethyl)(6-(4-(trifluoromethyl)phenoxy)hexyl)sulfane (30)

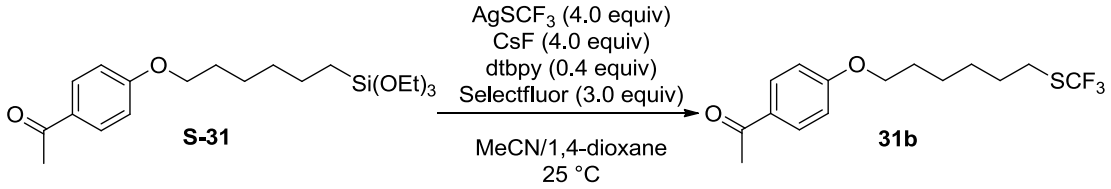


In a glovebox, to a solution of triethoxy(6-(4-(trifluoromethyl)phenoxy)hexyl)silane (**S-30**) (237 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531

mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 118 mg (trifluoromethyl)(6-(4-(trifluoromethyl)phenoxy)hexyl)sulfane (**30**) as a colorless liquid (68% yield).

R_f = 0.55 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.70 (m, 4H), 1.56 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 131.3 (q, *J* = 305.6 Hz), 127.0 (q, *J* = 3.7 Hz), 124.7 (q, *J* = 271.0 Hz), 122.8 (q, *J* = 32.7 Hz), 114.5, 68.0, 29.9 (q, *J* = 1.9 Hz), 29.5, 29.0, 28.3, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.27, -61.49. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{16}F_6OS$ $[M]^+$, 346.0826. Found, 346.0826. IR (neat): υ (cm^{-1}): 2944, 2864, 1616, 1590, 1519, 1469, 1424, 1330, 1311, 1259, 1158, 1110, 1067, 1009, 836, 755.

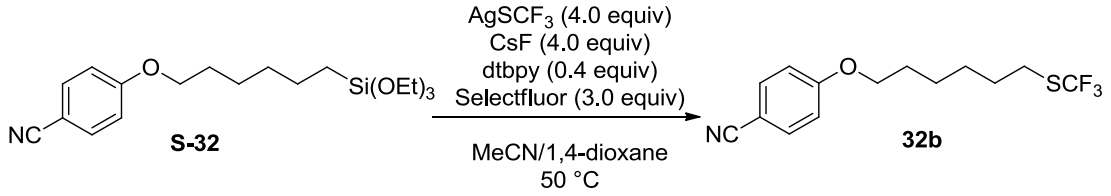
1-(4-((6-((Trifluoromethyl)thio)hexyl)oxy)phenyl)ethanone (31b)



In a glovebox, to a solution of 1-(4-((6-(triethoxysilyl)hexyl)oxy)phenyl)ethanone (**S-31**) (191 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 10:1 (v/v) to give a crude product, which was then purified by preparative TLC, eluting with hexanes/DCM 4:1 (v/v) to afford 102 mg 1-(4-((6-((trifluoromethyl)thio)hexyl)oxy)phenyl)ethanone (**31b**) as a colorless liquid (64% yield).

R_f = 0.11 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.55 (s, 3H), 1.86 – 1.78 (m, 2H), 1.77 – 1.70 (m, 2H), 1.54 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 163.1, 131.3 (q, *J* = 305.6 Hz), 130.7, 130.4, 114.2, 68.1, 29.9 (q, *J* = 1.9 Hz), 29.5, 29.0, 28.3, 26.5, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.42. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{20}F_3O_2S$ $[M + H]^+$, 321.1136. Found, 321.1135. IR (neat): υ (cm^{-1}): 2902, 2844, 1677, 1601, 1511, 1422, 1358, 1306, 1255, 1171, 1116, 954, 835, 756.

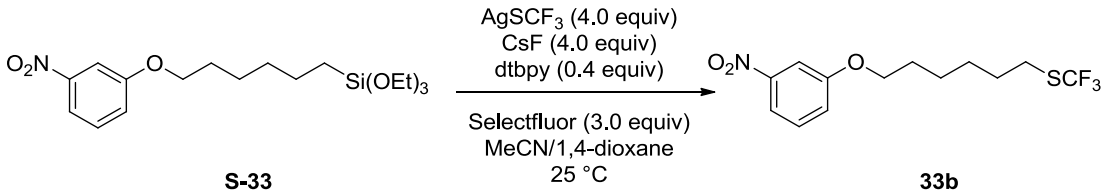
4-((6-((Trifluoromethyl)thio)hexyl)oxy)benzonitrile (32b)



In a glovebox, to a solution of 4-((6-(triethoxysilyl)hexyl)oxy)benzonitrile (**S-32**) (183 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 15:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 5:1 (v/v) to afford 89.5 mg 4-((6-((trifluoromethyl)thio)hexyl)oxy)benzonitrile (**32b**) as a colorless liquid (53% yield).

R_f = 0.19 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.78 (m, 2H), 1.77 – 1.69 (m, 2H), 1.54 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 134.1, 131.3 (q, *J* = 305.7 Hz), 119.4, 115.3, 103.9, 68.2, 29.9 (q, *J* = 1.4 Hz), 29.4, 28.9, 28.6, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.43. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{17}F_3NOS$ $[M + H]^+$, 304.0983. Found, 304.0977. IR (neat): υ (cm^{-1}): 2941, 2862, 2224, 1606, 1572, 1509, 1467, 1422, 1302, 1260, 1171, 1116, 1079, 834, 755.

(6-(3-Nitrophenoxy)hexyl)(trifluoromethyl)sulfane (33b)

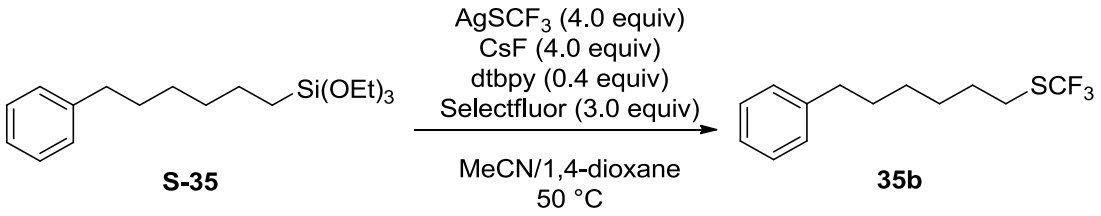


In a glovebox, to a solution of triethoxy(6-(3-nitrophenoxy)hexyl)silane (**S-33**) (193 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 30:1 (v/v) to afford 115 mg (6-(3-nitrophenoxy)hexyl)(trifluoromethyl)sulfane (**33b**) as a yellow liquid (71% yield).

R_f = 0.31 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.69 (t, *J* = 2.3 Hz, 1H), 7.40 (t, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.02 (t, *J* = 6.3 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.77 – 1.69 (m, 2H), 1.56 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 149.2, 131.3 (q, *J* =

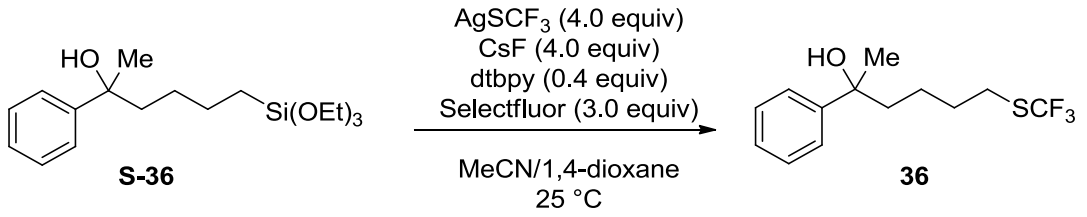
305.7 Hz), 130.0, 121.7, 115.7, 108.7, 68.5, 29.9 (q, J = 1.9 Hz), 29.4, 28.9, 28.3, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.50. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{16}F_3NO_3S$ $[M]^+$, 323.0803. Found, 323.0808. IR (neat): υ (cm^{-1}): 2940, 2861, 1618, 1578, 1527, 1482, 1439, 1389, 1320, 1246, 1115, 1049, 1027, 874, 860, 813, 795, 737.

(6-Phenylhexyl)(trifluoromethyl)sulfane (35b)



In a glovebox, to a solution of triethoxy(6-phenylhexyl)silane (**S-35**) (162 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 78.5 mg (6-phenylhexyl)(trifluoromethyl)sulfane (**35b**) as a colorless liquid (58% yield).
R_f = 0.83 (hexanes/EtOAc 40:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 2.87 (t, J = 7.4 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 1.73 – 1.59 (m, 4H), 1.49 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 131.3 (q, J = 305.5 Hz), 128.5, 128.4, 125.7, 35.8, 31.2, 30.0 (q, J = 2.0 Hz), 29.3, 28.6, 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.50. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{17}F_3S$ $[M]^+$, 262.1003. Found, 262.1003. IR (neat): υ (cm^{-1}): 2930, 2860, 2840, 1604, 1572, 1451, 1260, 1149, 1116, 1026, 746.

2-Phenyl-6-((trifluoromethyl)thio)hexan-2-ol (36b)

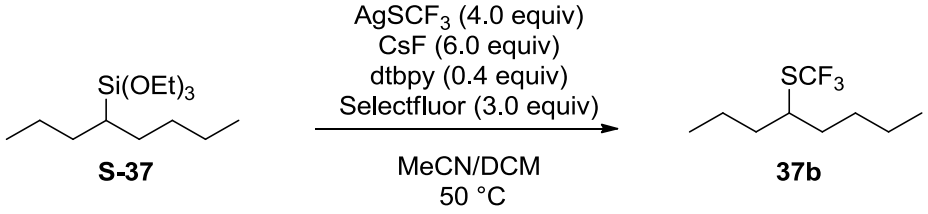


In a glovebox, to a solution of 2-phenyl-6-(triethoxysilyl)hexan-2-ol (**S-36**) (170 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 8:1 (v/v) to get a crude product, which was then purified by preparative TLC, eluting with hexanes/DCM 2:1 (v/v) to

afford 53.4 mg 2-phenyl-6-((trifluoromethyl)thio)hexan-2-ol (**36b**) as a colorless liquid (38% yield).

R_f = 0.11 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 1.85 – 1.72 (m, 3H), 1.67 – 1.59 (m, 2H),1.57 (s, 3H), 1.45 – 1.34 (m, 1H), 1.30 – 1.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 131.3 (q, *J* = 305.6 Hz), 128.4, 126.8, 124.8, 74.6, 43.6, 30.4, 29.9, 29.8 (q, *J* = 1.8 Hz), 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.07. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{13}H_{15}F_3S$ $[M - H_2O]^+$, 260.0847. Found, 260.0857. IR (neat): υ (cm^{-1}): 3423, 2972, 2866, 1600, 1572, 1445, 1263, 1116, 1028, 833, 765.

Octan-4-yl(trifluoromethyl)sulfane (37b)

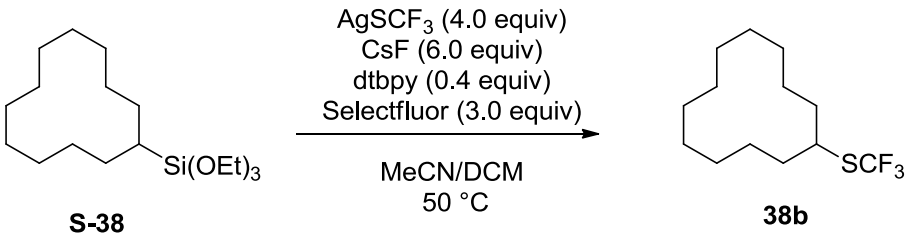


In a glovebox, to a solution of triethoxy(octan-4-yl)silane (**S-37**) (138 mg, 0.500 mmol, 1.00 equiv) in 4.00 mL MeCN/DCM 1:1 (v/v) at room temperature were added in sequence CsF (456 mg, 3.00 mmol, 6.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 1.96 mmol) was added to the reaction mixture. The ^{19}F NMR yield of the volatile octan-4-yl(trifluoromethyl)sulfane (**37b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-39.39 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). (25% ^{19}F NMR Yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.39.

37b is a known compound and spectral data match the reported literature values [7].

Cyclododecyl(trifluoromethyl)sulfane (38b)



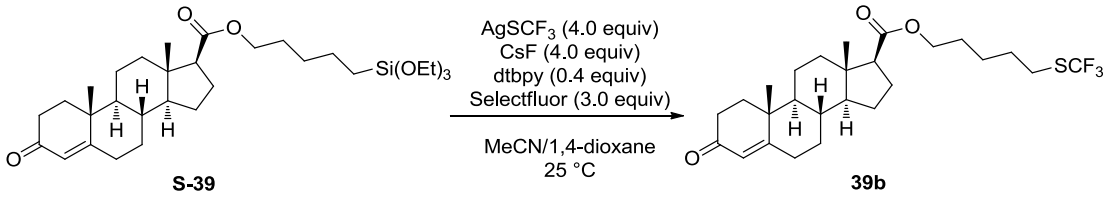
In a glovebox, to a solution of cyclododecyltriethoxysilane (**S-38**) (165 mg, 0.500 mmol, 1.00 equiv) in 4.00 mL MeCN/DCM 1:1(v/v) at room temperature were added in sequence CsF (456 mg, 3.00 mmol, 6.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 1.96 mmol) was added to the reaction mixture. The ^{19}F NMR yield of the volatile cyclododecyl(trifluoromethyl)sulfane (**38b**) was determined by comparing the integration of the ^{19}F NMR resonance of

dodecyl(trifluoromethyl)sulfane (-39.43 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm). (27% ^{19}F NMR Yield).

NMR Spectroscopy: ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.43.

38b is a known compound and spectral data match the reported literature values [7].

5-((Trifluoromethyl)thio)pentyl androst-4-en-3-one-17β-carboxylate (39b)

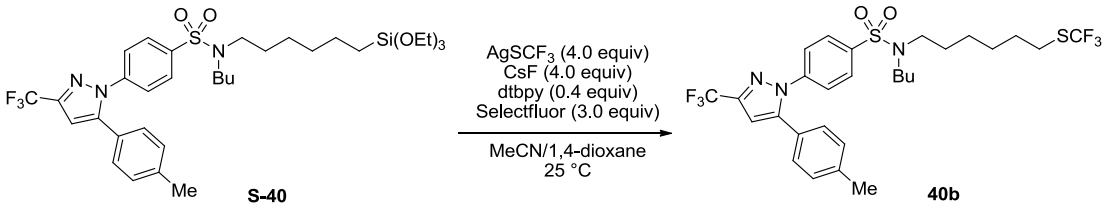


S-39 **39b**

In a glovebox, to a solution of 5-(triethoxysilyl)pentyl androst-4-en-3-one-17β-carboxylate (**S-39**) (274 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 6:1 (v/v) to give a crude product, then the residue was purified by preparative TLC, eluting with hexanes/DCM 2:1 (v/v) to afford 168 mg 5-((trifluoromethyl)thio)pentyl androst-4-en-3-one-17β-carboxylate (**39b**) as a colorless oil (69% yield).

R_f = 0.30 (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 4.12 – 3.98 (m, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.21 (m, 5H), 2.15 – 2.06 (m, 1H), 2.00 (d, *J* = 11.8 Hz, 2H), 1.87 – 1.34 (m, 13H), 1.31 – 1.21 (m, 2H), 1.15 (s, 3H), 1.10 – 1.00 (m, 2H), 0.96 – 0.89 (m, 1H), 0.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 173.9, 171.0, 131.2 (q, *J* = 305.7 Hz), 124.0, 63.7, 55.4, 55.2, 53.8, 43.9, 38.7, 38.2, 35.6, 34.0, 32.8, 32.0, 29.8 (q, *J* = 1.2 Hz), 29.1, 28.2, 25.1, 24.5, 23.6, 20.9, 17.4, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.02. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{37}F_3NaO_3S$ $[M + Na]^+$, 509.2313. Found, 509.2313. IR (neat): υ (cm^{-1}): 2978, 2886, 1720, 1672, 1617, 1450, 1436, 1384, 1350, 1227, 1112, 956, 866, 755.

***N*-butane-*N*-(6-(trifluoromethylthio)hexyl)-Celecoxib (40b)**



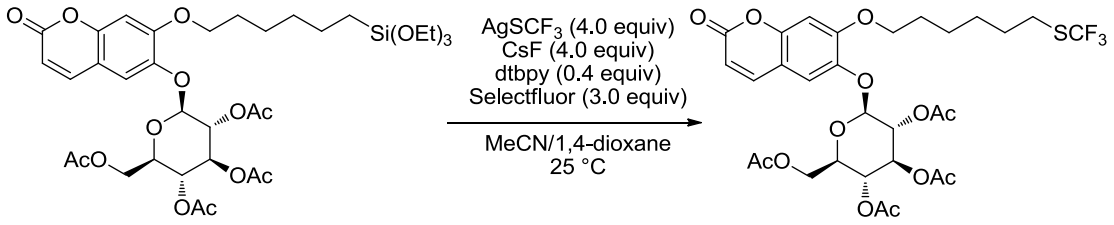
S-40 **40b**

In a glovebox, to a solution of *N*-butane-*N*-(6-(triethoxysilyl)hexyl)-Celecoxib (**S-40**) (342 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*.

The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 8:1 (v/v) to get a crude product, which was then purified by preparative TLC, eluting with hexanes/DCM 2:1 (v/v) to afford 168 mg *N*-butane-*N*-(6-(trifluoromethylthio)hexyl)-Celecoxib (**40b**) as a white solid (57% yield).

R_f = 0.59 (hexanes/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H),7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.73 (s, 1H), 3.12 – 3.06 (m, 4H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.71 – 1.63 (m, 2H), 1.58 – 1.35 (m, 6H), 1.33 – 1.22 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.1 (q, *J* = 38.5 Hz), 142.3, 139.8, 139.6, 131.2 (q, *J* = 305.8 Hz), 129.8, 128.8, 128.1, 125.7, 125.6, 121.2 (q, *J* = 269.2 Hz), 106.3 (q, *J* = 1.8 Hz), 48.1, 48.1, 30.7, 29.8 (q, *J* = 1.8 Hz), 29.4, 28.5, 28.1, 26.1, 21.4, 20.0, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.76, -63.01. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{28}H_{34}F_6N_3O_2S_2$ $[M + H]^+$, 622.1997. Found, 622.1999. IR (neat): υ (cm^{-1}): 2936, 2868, 1597, 1497, 1472, 1374, 1341, 1271, 1237, 1160, 1118, 975, 843, 768.

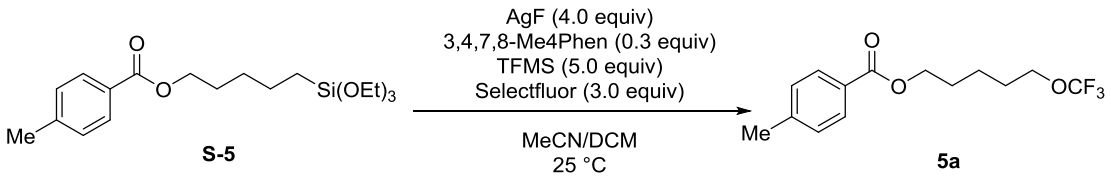
***7-O*-(6-(trifluoromethylthio)hexyl)-Esculin tetracetate (41)**



In a glovebox, to a solution of *7-O*-(6-(triethoxysilyl)hexyl)-Esculin tetracetate (**S-41**) (377 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 20 mL EtOAc and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 3:1 (v/v) to get a crude product, which was then purified by preparative TLC, eluting with DCM/MeOH 100:3 (v/v) to afford 204 mg *7-O*-(6-(trifluoromethylthio)hexyl)-Esculin tetracetate (**41**) as a white solid (59% yield).

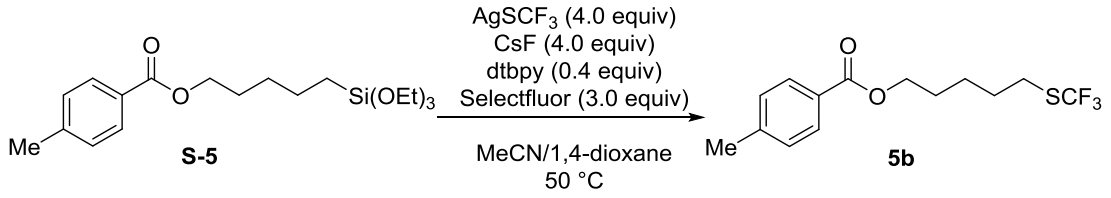
R_f = 0.20 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 9.5 Hz, 1H), 7.13 (s, 1H), 6.75 (s, 1H), 6.21 – 6.18 (m, 1H), 5.26 – 5.19 (m, 2H), 5.15 – 5.09 (m, 1H), 4.99 – 4.93 (m, 1H), 4.23 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.11 (d, *J* = 12.3 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.78 – 3.73 (m, 1H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.01 (s, 3H), 2.01 (s, 3H), 1.98 (s, 6H), 1.83 – 1.75 (m, 2H), 1.75 – 1.67 (m, 2H), 1.55 – 1.40 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 170.1, 169.3, 169.0, 160.9, 153.4, 151.8, 143.1, 142.3, 135.7, 135.7, 131.13 (q, *J* = 305.9 Hz), 117.7, 113.6, 111.3, 101.1, 99.9, 72.4, 72.0, 71.0, 69.0, 68.2, 61.7, 29.7, 29.2, 28.8 – 28.6 (m), 28.1, 25.3, 20.6, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.66. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{30}H_{36}F_3O_{12}S$ $[M + H]^+$, 693.1829. Found, 693.1825. IR (neat): υ (cm^{-1}): 2935, 2865, 1730, 1606, 1572, 1460,1377, 1258, 1179, 1115, 1026, 859, 755.

Gram scale synthesis of 5-(trifluoromethoxy)pentyl 4-methylbenzoate (5a)



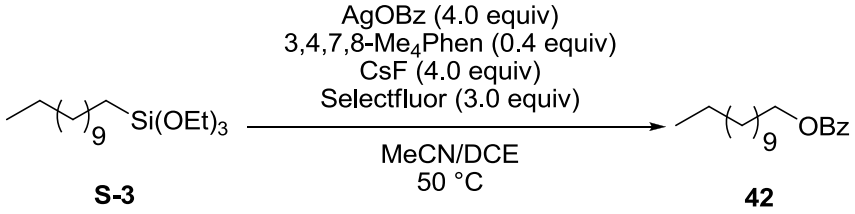
In a glovebox, to a mixture of AgF (1.52 g, 12.0 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (213 mg, 0.900 mmol, 0.300 equiv) and Selectfluor (3.19 g, 9.00 mmol, 3.00 equiv) in a 100 mL round flask at room temperature were sequentially added DCM (12.0 mL), TFMS (3.60 g, 15.0 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl 4-methylbenzoate (**S-5**) (1.11 g, 3.00 mmol, 1.00 equiv) and MeCN (42.0 mL). The round flask was then sealed, taken out from the glovebox and added an N_2 balloon. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 20 mL H_2O and extracting three times with DCM (50 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by by chromatography on silica gel, eluting with hexanes/DCM 12:1 (v/v) to get a crude product, which was then purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford afford 387 mg 5-(trifluoromethoxy)pentyl 4-methylbenzoate (**5a**) as a colorless liquid (44% yield).

Gram-scale synthesis of 5-((Trifluoromethyl)thio)pentyl 4-methylbenzoate (5b)



In a glovebox, to a solution of 5-(triethoxysilyl)pentyl 4-methylbenzoate (**S-5**) (1.11 g, 3.00 mmol, 1.00 equiv) in 60.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (1.82 g, 12.00 mmol, 4.00 equiv), Selectfluor (3.19 g, 9.00 mmol, 3.00 equiv), dtbpy (321 mg, 1.20 mmol, 0.400 equiv) and $AgSCF_3$ (2.51 g, 12.0 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 60 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v) to give a crude product , then the residue was purified by chromatography on silica gel, eluting with hexanes/DCM 12:1 (v/v) to afford 634 mg 5-((trifluoromethyl)thio)pentyl 4-methylbenzoate (**5b**) as a colorless liquid (69% yield).

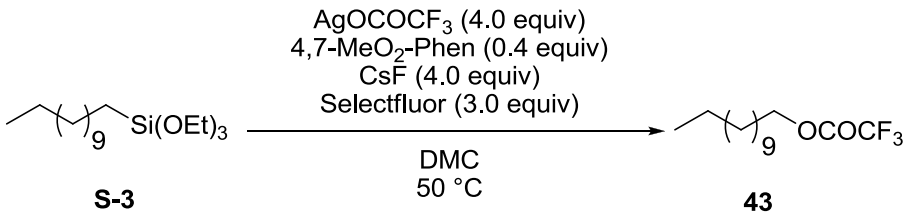
Dodecyl benzoate (42)



In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) in 4.0 mL MeCN/DCE 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), 3,4,7,8-Me_4Phen (47.2 mg, 0.20 mmol, 0.400 equiv) and AgOBz (458 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to afford 88 mg dodecyl benzoate (**42**) as a colorless liquid (61% yield).

R_f = 0.15 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 4.31 (t, J = 6.7 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.48 – 1.40 (m, 2H), 1.40 – 1.22 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.9, 130.7, 129.7, 128.5, 65.3, 32.1, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 28.9, 26.2, 22.8, 14.3. **42** is a known compound and spectral data match the reported literature values [8]. IR (neat): υ (cm^{-1}): 2924, 2853, 1721, 1461, 1433, 1313, 1271, 1250, 1175, 1111, 1069, 1026, 710.

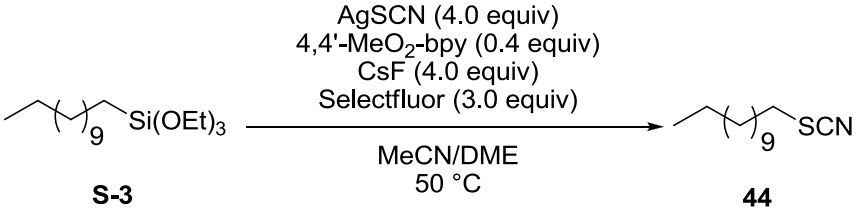
Dodecyl 2,2,2-trifluoroacetate (43)



In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) in 4.0 mL DMC at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), 4,7-MeO_2-Phen (48.0 mg, 0.20 mmol, 0.400 equiv) and $AgOCOCF_3$ (440 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 86 mg dodecyl 2,2,2-trifluoroacetate (**43**) as a colorless liquid (61% yield).

R_f = 0.65 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (t, J = 6.7 Hz, 2H), 1.77 – 1.70 (m, 2H) , 1.42 – 1.20 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (q, J = 42.0 Hz), 114.7 (q, J = 285.6 Hz), 68.5, 32.1, 29.8, 29.7, 29.6, 29.5, 29.2, 28.3, 25.7, 22.8, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.15. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{14}H_{25}F_3O_2$ $[M]^+$, 282.1807. Found, 282.1811. IR (neat): υ (cm^{-1}): 2925, 2855, 1744, 1461, 1453, 1365, 1237, 1168, 1039.

1-Thiocyanatododecane (44)

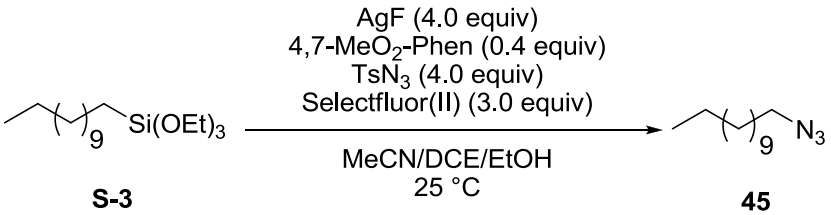


S-3 **44**

In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) in 4.0 mL MeCN:DME 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), 4,4'-MeO_2-bpy (43.2 mg, 0.20 mmol, 0.400 equiv) and AgSCN (332 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 50 mg 1-thiocyanatododecane (**44**) as a colorless liquid (43% yield).

R_f = 0.15 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (t, *J* = 7.3 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.48 – 1.30 (m, 2H), 1.35 – 1.22 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 112.6, 34.2, 32.0, 30.0, 29.7, 29.6, 29.5, 29.5, 29.0, 28.1, 22.8, 14.3. **44** is a known compound and spectral data match the reported literature values [9]. IR (neat): υ (cm^{-1}): 2925, 2854, 2155, 1465, 1376, 1282, 1242.

1-Azidododecane (45)



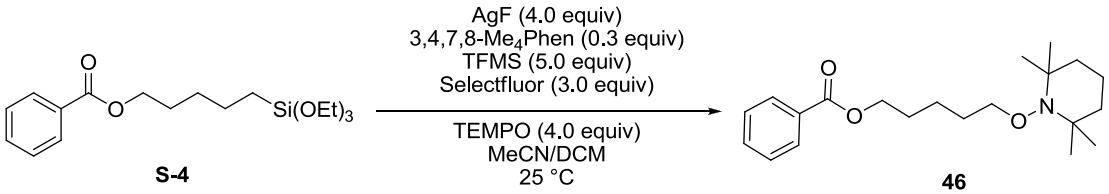
S-3 **45**

In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (166 mg, 0.500 mmol, 1.00 equiv) in 1.1 mL MeCN:DCE:EtOH 5:5:1 (v/v) at room temperature were added in sequence AgF (254 mg, 2.00 mmol, 4.00 equiv), Selectfluor(II) (480 mg, 1.50 mmol, 3.00 equiv), 4,4'-MeO_2Phen (48.0 mg, 0.200 mmol, 0.400 equiv) and TsN_3 (394 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 25 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes to afford 64 mg 1-azidododecane (**45**) as a colorless liquid (61% yield).

R_f = 0.72 (hexanes). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (t, *J* = 7.0 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.40 – 1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 51.6, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 26.9, 22.8, 14.3. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{12}H_{25}N_3$ $[M]^+$, 211.2048. Found, 211.2039. IR (neat): υ (cm^{-1}): 2925, 2854, 2094, 1465, 1348, 1288, 1252, 1209.

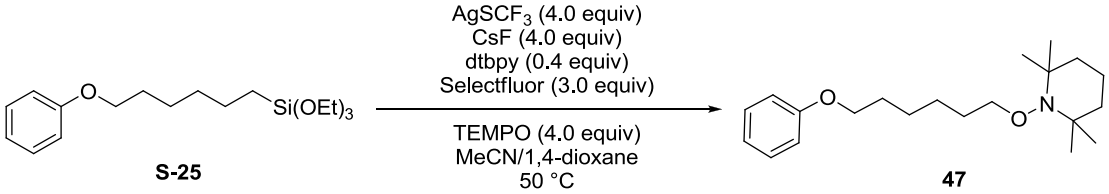
Mechanism Studies

Mechanism studies by radical-trapping reaction



In a glovebox, to a mixture of AgF (253 mg, 2.00 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (35.4 mg, 0.150 mmol, 0.300 equiv) , TEMPO (313 mg, 2.00 mmol, 4.00 equiv) and Selectfluor (531 mg, 1.50 mmol, 3.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (2.00 mL), TFMS (600 mg, 2.50 mmol, 5.00 equiv), 5-(triethoxysilyl)pentyl benzoate (**S-4**) (177 mg, 0.500 mmol, 1.00 equiv) and MeCN (7.00 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, the reaction mixture was quenching with 10 mL H_2O and extracting three times with DCM (10 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 50:1 (v/v) to afford 45.8 mg 5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentyl benzoate (**46**) as a colorless liquid (25% yield).

R_f = 0.12 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.75 (t, *J* = 6.2 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.63 – 1.42 (m, 8H), 1.36 – 1.25 (m, 2H), 1.14 (s, 6H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 132.9, 130.6, 129.7, 128.4, 76.5, 65.1, 59.8, 39.7, 33.2, 28.9, 28.5, 23.2, 20.2, 17.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{34}NO_3$ $[M + H]^+$, 348.2539. Found, 348.2540. IR (neat): υ (cm^{-1}): 2936, 2855, 1726, 1598, 1442, 1386, 1275, 1109, 1027, 802, 711.

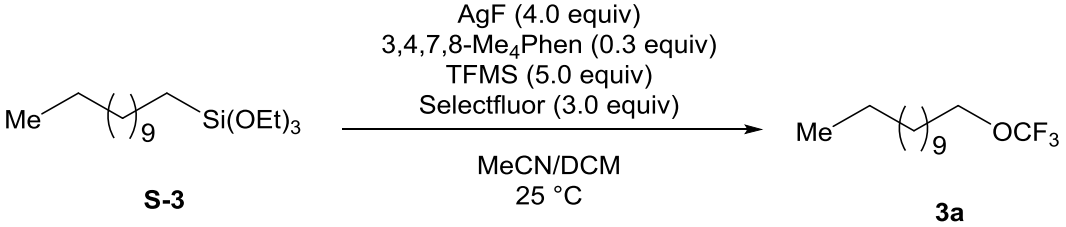


In a glovebox, to a solution of triethoxy(6-phenoxyhexyl)silane (**S-25**) (170 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv), $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv) and TEMPO (313 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by preparative TLC, eluting with hexanes/EtOAc 40:1 (v/v) to to afford 63.3 mg 2,2,6,6-tetramethyl-1-(6-phenoxyhexyloxy)piperidine (**47**) as a colorless liquid (38% yield).

R_f = 0.22 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.6 Hz, 2H), 6.94 – 6.88 (m, 3H), 3.95 (t, *J* = 6.2 Hz, 2H), 3.74 (t, *J* = 6.1 Hz, 2H),

1.83 – 1.76 (m, 2H), 1.57 – 1.41 (m, 11H), 1.34 – 1.28 (m, 1H), 1.15 (s, 6H), 1.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 129.5, 120.6, 114.6, 76.8, 67.9, 59.8, 39.7, 33.2, 29.4, 28.8, 26.4, 26.3, 20.3, 17.3. Mass Spectrometry: HRMS-EI (m/z): Calcd for $C_{21}H_{35}NO_2$ $[M]^+$, 333.2668. Found, 333.2661. IR (neat): υ (cm^{-1}): 2978, 2936, 2873, 1599, 1493, 1245, 1172, 1133, 1045, 753.

Mechanism studies using radical inhibitor

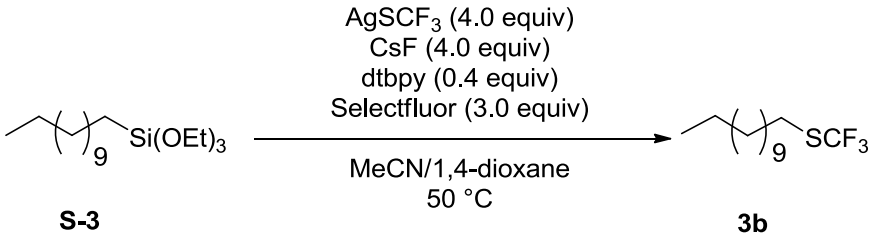


S-3 **3a**

In a glovebox, to a mixture of AgF (102 mg, 0.800 mmol, 4.00 equiv), 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv), Selectfluor (213 mg, 0.600 mmol, 3.00 equiv) and radical inhibitor (BHT or 1,1-diphenylethylene) (2.00 mmol, 4.00 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (50.0 μL, 0.407 mmol) was added. The ^{19}F NMR yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). Yields are reported in Table S17.

Table S17: Effect of radical inhibitors on the reaction

Radical inhibitors	Yield [%] (^{19}F NMR)
BHT	0
1,1-diphenylethylene	0



S-3 **3b**

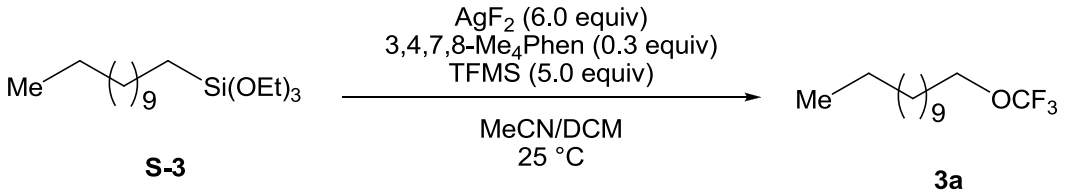
In a glovebox, to a solution of dodecyltriethoxysilane (**S-3**) (66.4 mg, 0.200 mmol, 1.00 equiv) in 4.00 mL MeCN/1,4-dioxane 1:1 (v/v) at room temperature were added in sequence CsF (121.6 mg, 0.800 mmol, 4.00 equiv), radical inhibitor (BHT or 1,1-diphenylethylene), Selectfluor (212.4 mg, 0.600 mmol, 3.00 equiv), dtbpy (21.4 mg, 0.0800 mmol, 0.400 equiv) and $AgSCF_3$ (167.2 mg, 0.800 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, (trifluoromethyl)benzene (25.0 *u*L, 0.203 mmol) was added to the reaction mixture. The yield

of dodecyl(trifluoromethyl)sulfane (**3b**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl(trifluoromethyl)sulfane (-41.56 ppm) with that of (trifluoromethyl)benzene (-62.80 ppm).

Table S18: Effect of radical inhibitors on the reaction

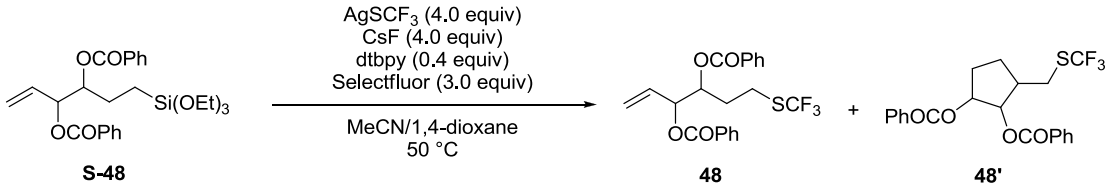
Radical inhibitors	Yield [%] (^{19}F NMR)
BHT (4.0 equiv)	39
BHT (6.0 equiv)	24
BHT (8.0 equiv)	9
1,1-diphenylethylene (4.0 equiv)	39

Mechanism studies using AgF_2



In a glovebox, to a mixture of AgF_2 (175 mg, 1.20 mmol, 6.00 equiv) and 3,4,7,8-Me_4Phen (14.2 mg, 0.0600 mmol, 0.300 equiv) in a polypropylene vial at room temperature were sequentially added DCM (0.800 mL), TFMS (240 mg, 1.00 mmol, 5.00 equiv), dodecyltriethoxysilane (**S-3**) (66.5 mg, 0.200 mmol, 1.00 equiv) and MeCN (2.80 mL). The polypropylene vial was then sealed and taken out from the glovebox. After stirring at 25 ºC for 5.0 h, benzotrifluoride (100 µL, 0.814 mmol) was added. The ^{19}F NMR yield of dodecyl trifluoromethyl ether (**3a**) was determined by comparing the integration of the ^{19}F NMR resonance of dodecyl trifluoromethyl ether (**3a**) (-60.54 ppm) with that of benzotrifluoride (-62.80 ppm). (28% ^{19}F NMR Yield).

Mechanism studies of radical cyclization



In a glovebox, to a solution of 6-(Triethoxysilyl)hex-1-ene-3,4-diyl dibenzoate (**S-48**) (243 mg, 0.500 mmol, 1.00 equiv) in 10.0 mL MeCN/1,4-dioxane 1:1(v/v) at room temperature were added in sequence CsF (304 mg, 2.00 mmol, 4.00 equiv), Selectfluor (531 mg, 1.50 mmol, 3.00 equiv), dtbpy (53.6 mg, 0.200 mmol, 0.400 equiv) and $AgSCF_3$ (418 mg, 2.00 mmol, 4.00 equiv). After stirring for 16.0 h at 50 ºC, the reaction mixture was concentrated *in vacuo*. The residue was then added 10 mL DCM and filtered. The organic layer was concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with

hexanes/EtOAc 20:1 (v/v) to give crude product **48** and **48'**. Further purification was carried through preparative HPLC (3 mL/min, detector UV λmax 200 nm, MeCN/H_2O=75/25) to yield **48** (38 min, 20.7 mg) and **48'** (26 min, 11.8 mg).

48 (^{19}F NMR yield: 37%). R_f = 0.33 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 4H), 7.63 – 7.52 (m, 2H), 7.50 – 7.38 (m, 4H), 6.03 – 5.89 (m, 1H), 5.82 – 5.73 (m, 1H), 5.60 – 5.48 (m, 2H), 5.39 (t, *J* = 11.4 Hz, 1H), 3.09 – 2.89 (m, 2H), 2.34 – 2.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 166.1, 165.5, 165.4, 133.6, 133.4, 131.9, 131.7, 131.0 (q, *J* = 306.3 Hz), 129.9, 129.9, 129.8, 129.8, 129.7, 129.6, 128.7, 128.6, 120.4, 120.2, 75.4, 75.1, 73.1, 72.7, 31.4, 30.4, 26.3 (q, *J* = 2.2 Hz), 26.1 (q, *J* = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.34. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{19}F_3NaO_4S$ $[M + Na]^+$, 447.0854. Found, 447.0839. IR (neat): υ (cm^{-1}): 3042, 2945, 2855, 1720, 1677, 1614, 1582, 1331, 1284, 1148, 1115, 1025, 766.

48' (^{19}F NMR yield: 12%). R_f = 0.21 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 5.77 – 5.73 (m, 1H), 5.56 – 5.49 (m, 1H), 3.18 (dd, *J* = 13.4, 7.3 Hz, 1H), 3.00 (dd, *J* = 13.3, 8.2 Hz, 1H), 2.68 – 2.57 (m, 1H), 2.38 – 2.30 (m, 1H), 2.20 – 2.04 (m , 2H), 1.96 – 1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.7, 133.5, 133.1, 131.1 (q, *J* = 306.2 Hz), 129.9, 129.8, 129.7, 128.7, 128.4, 75.1, 75.0, 40.4, 30.4 – 30.2 (m), 28.0, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.44. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{19}F_3NaO_4S$ $[M + Na]^+$, 447.0854. Found, 447.0842. IR (neat): υ (cm^{-1}): 3042, 2973, 2877, 1724, 1601, 1584, 1451, 1314, 1246, 1113, 1025, 759.

Reference

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7. Wu, H; Xiao, Z.-W; Wu, J.-H; Guo, Y; Xiao, J.-C; Liu, C; Chen, Q.-Y. *Angew. Chem. Int. Ed.* **2015**, *54*, 4070 – 4074.
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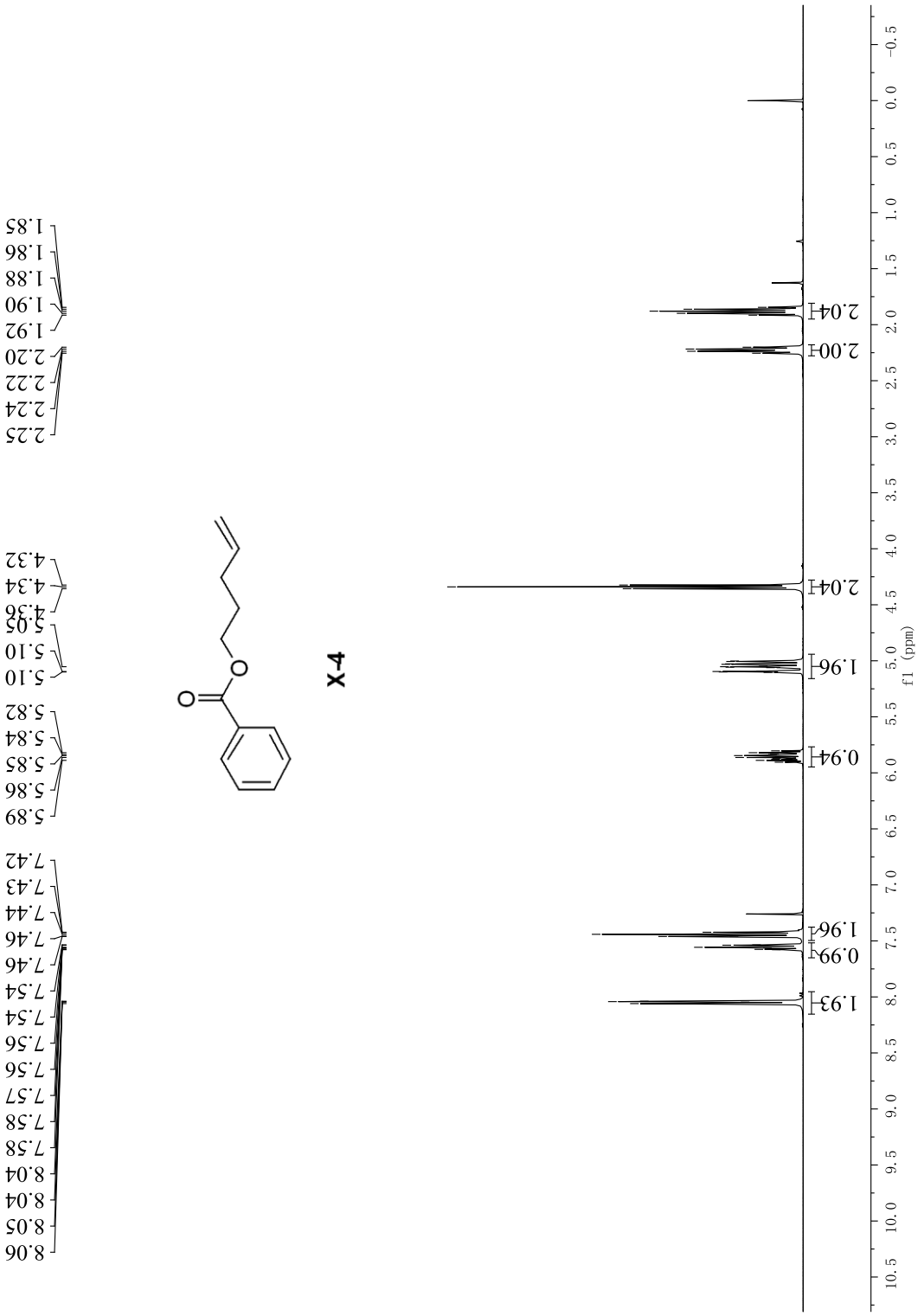
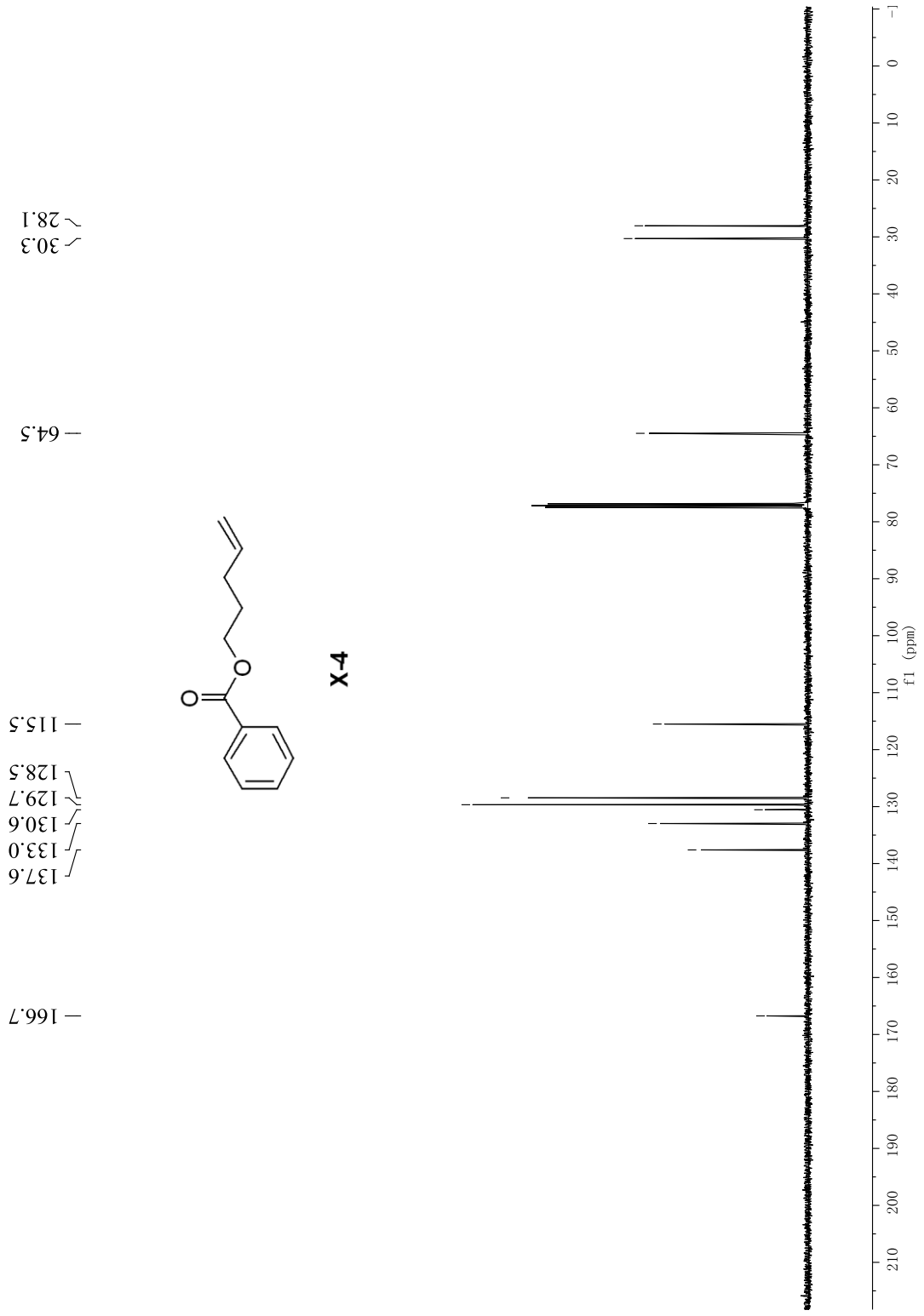
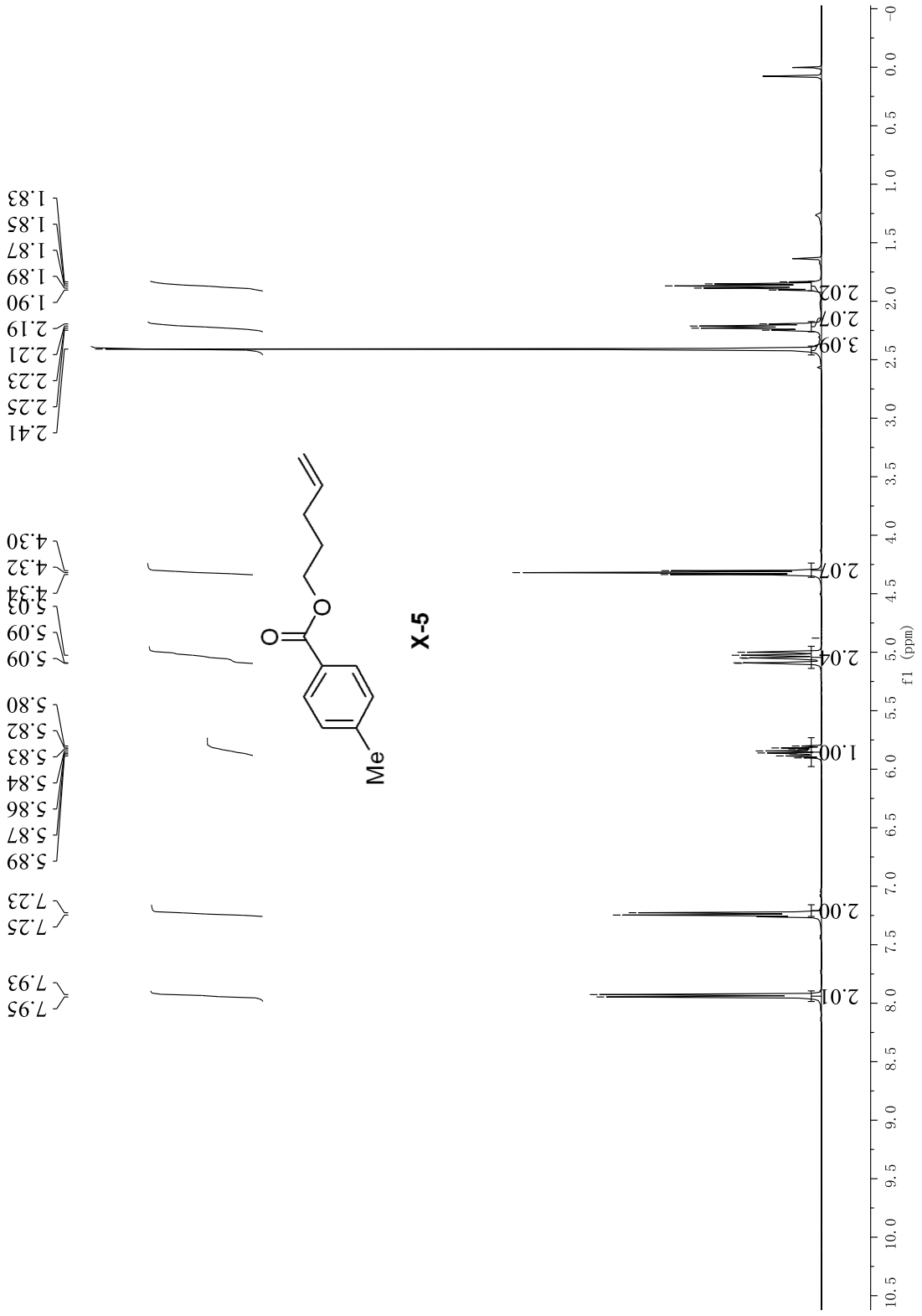
Spectrum Data



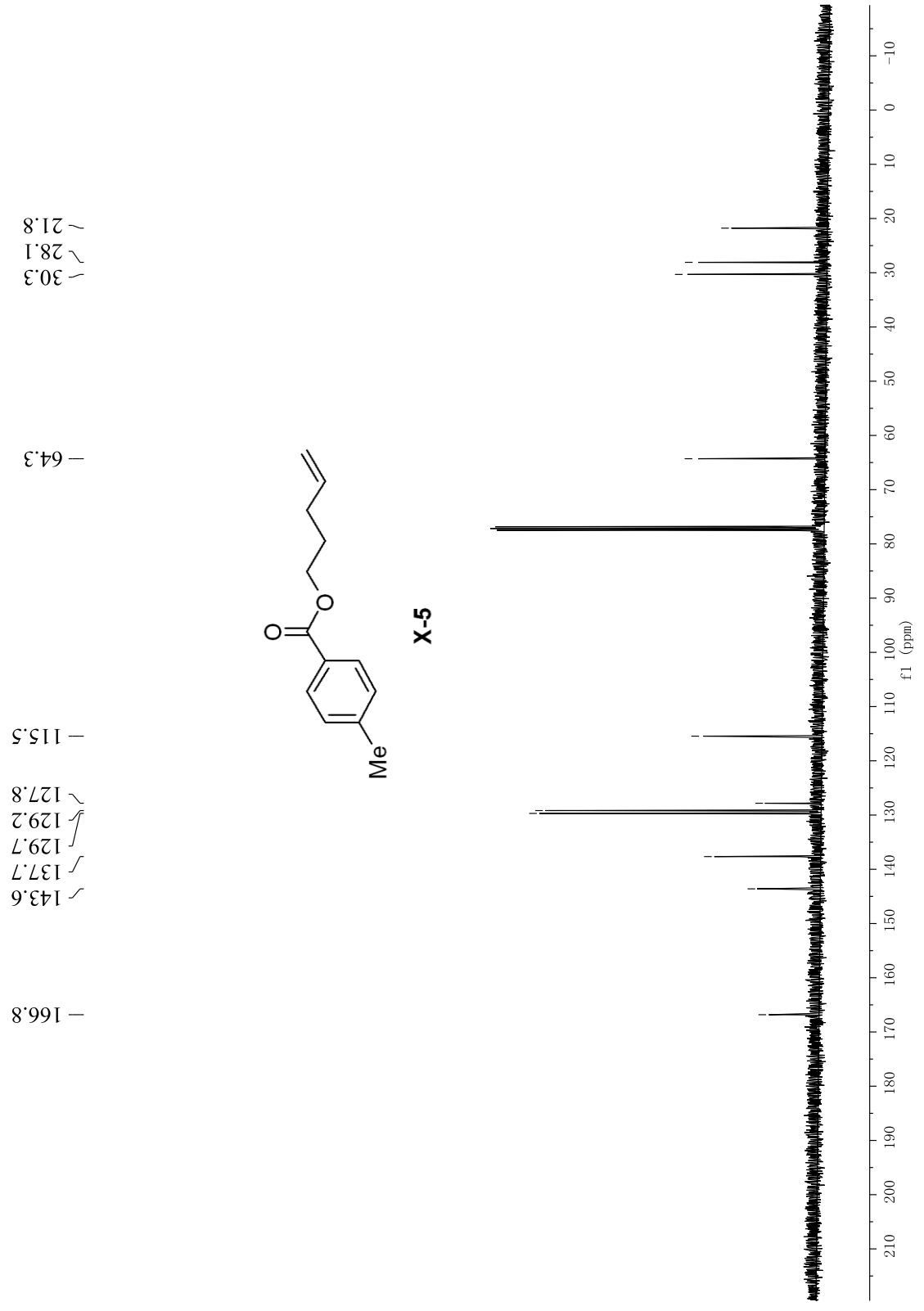
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-4**



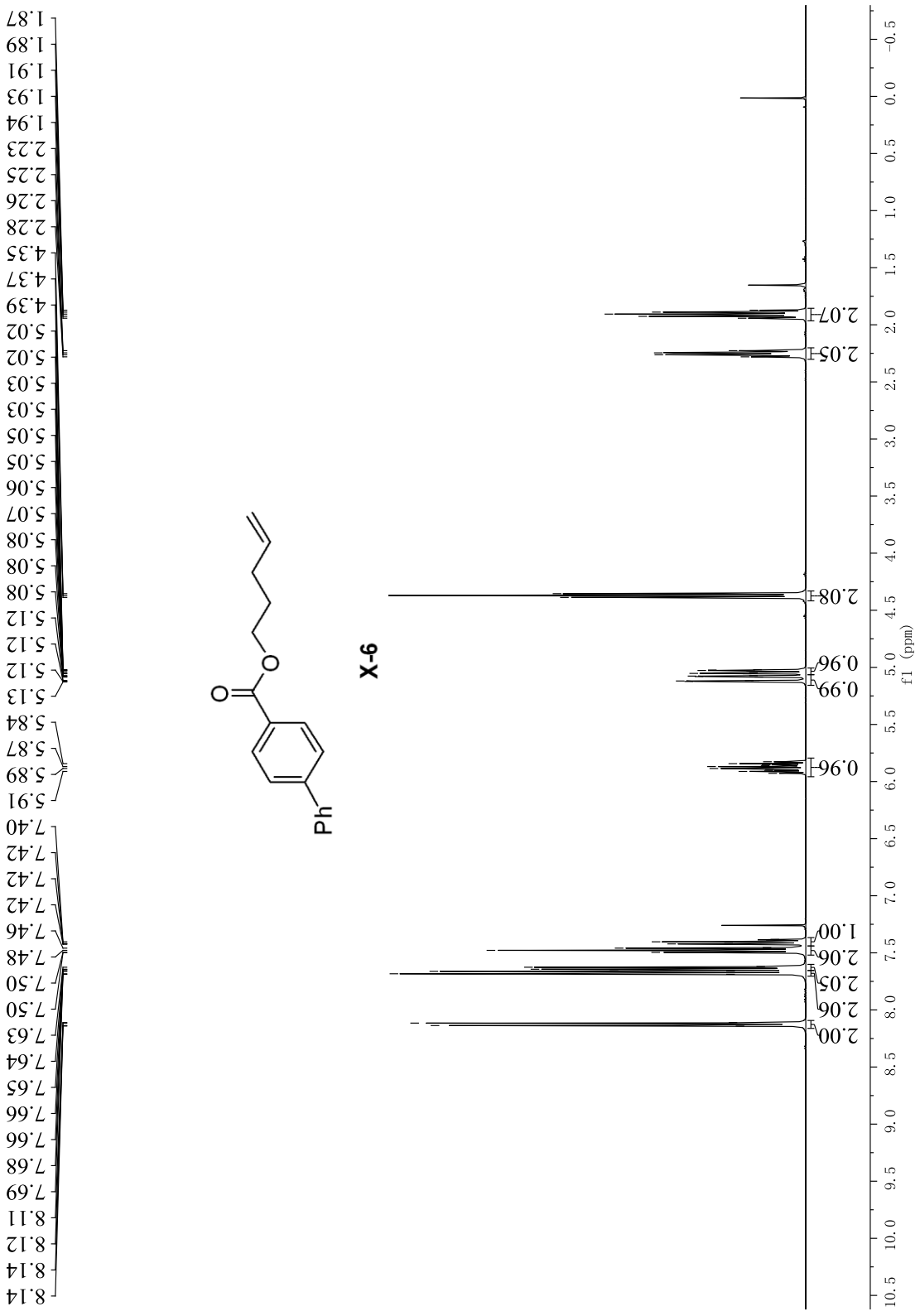
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-4**



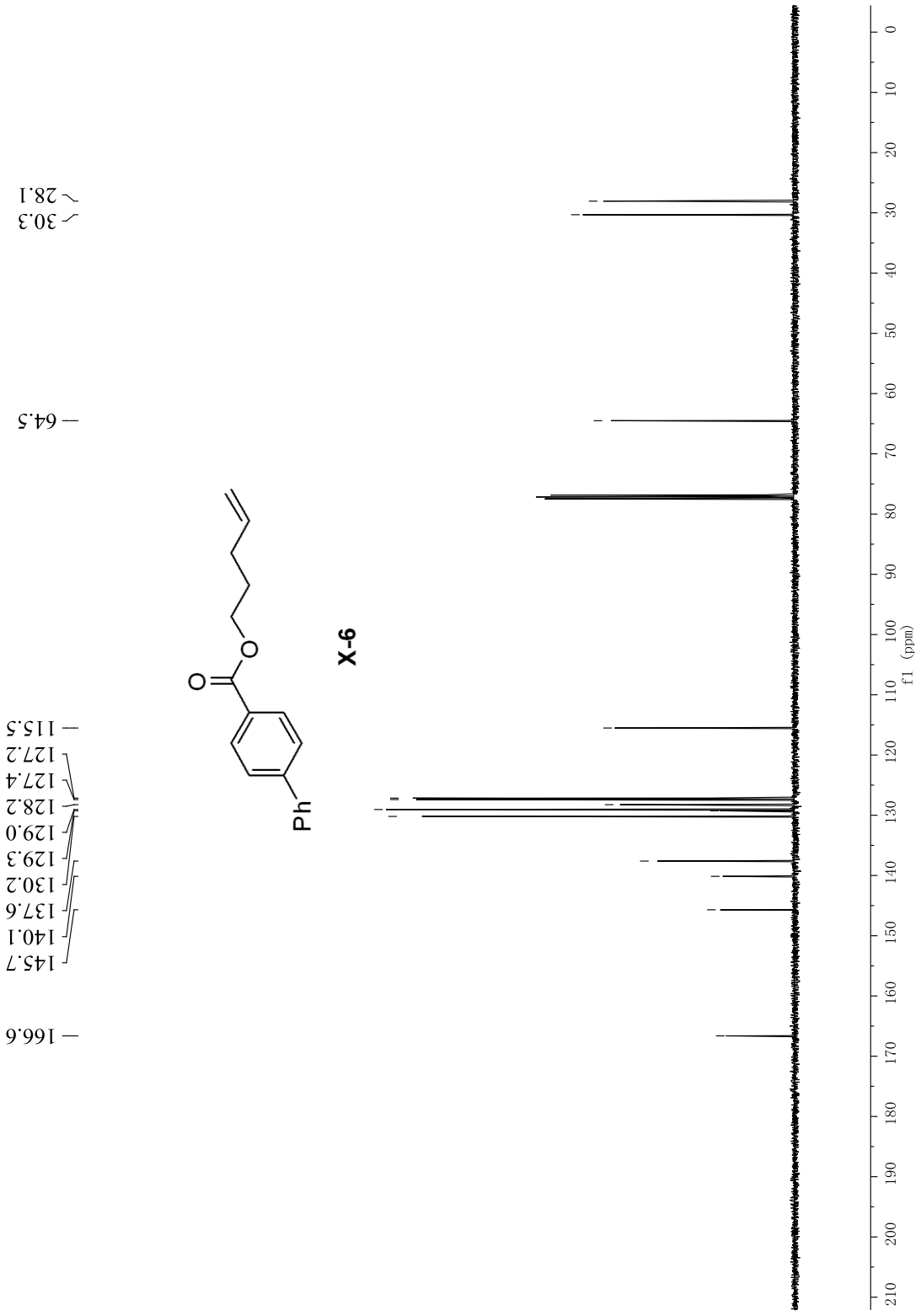
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-5**



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

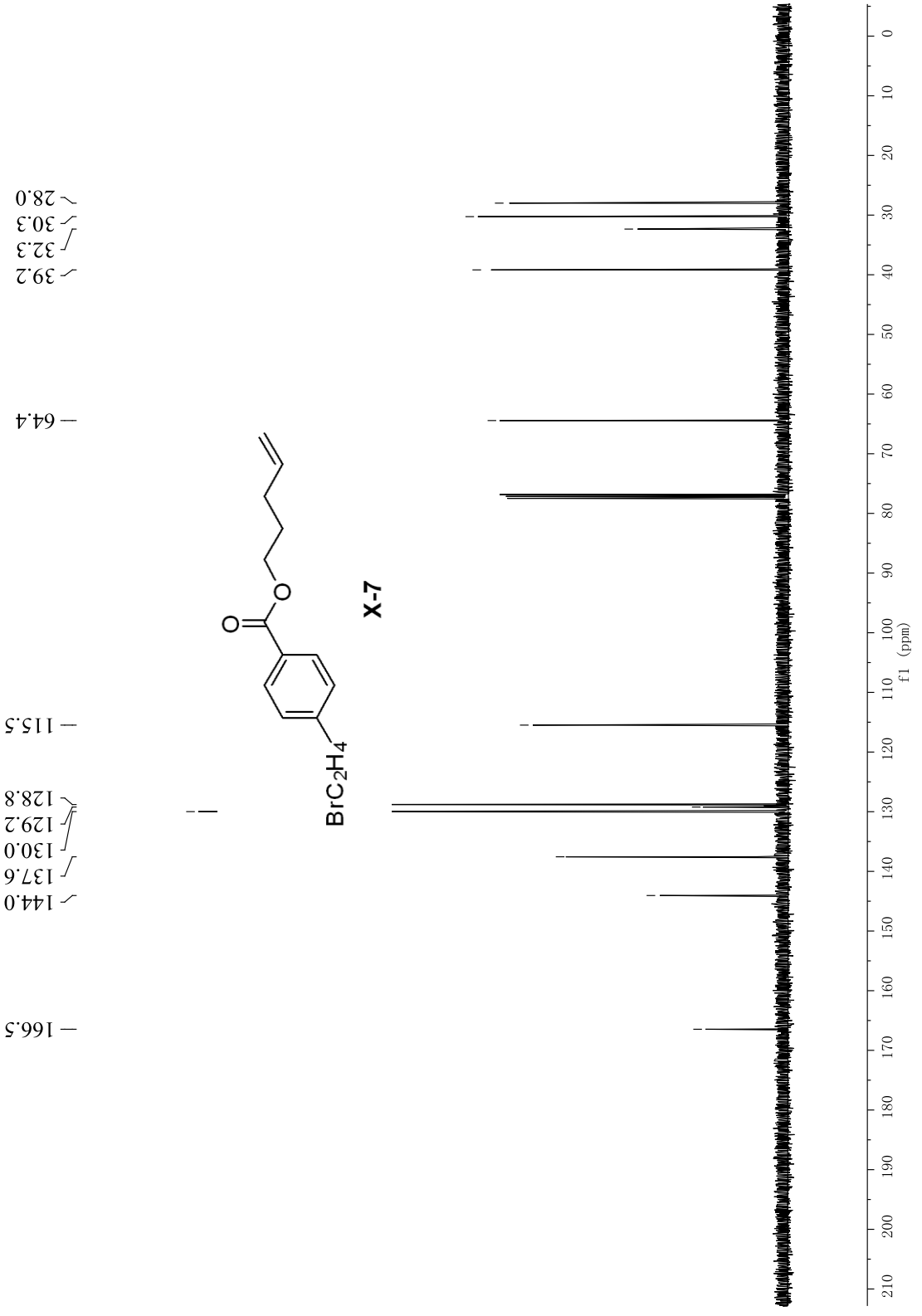


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-6**

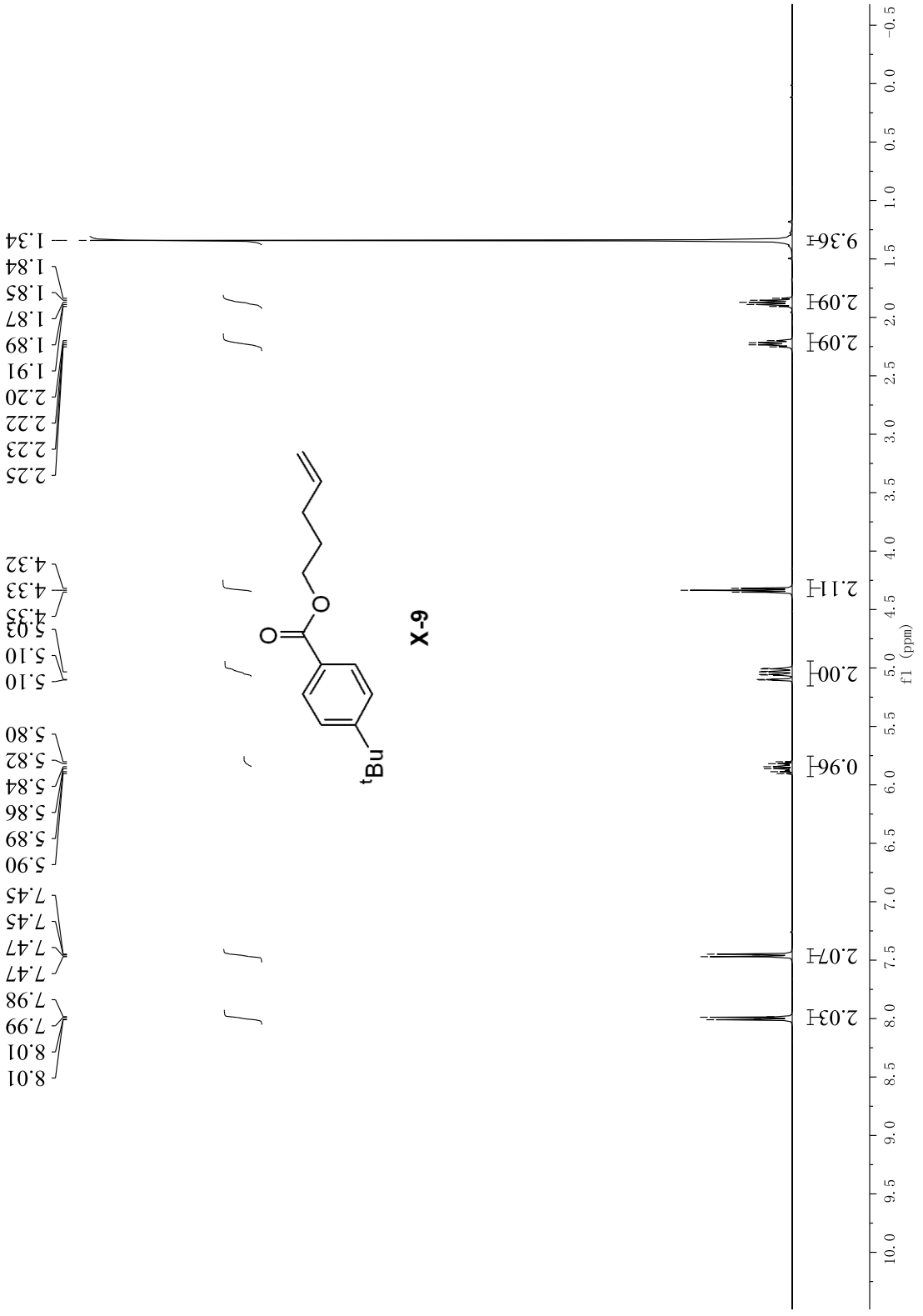


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-6**

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

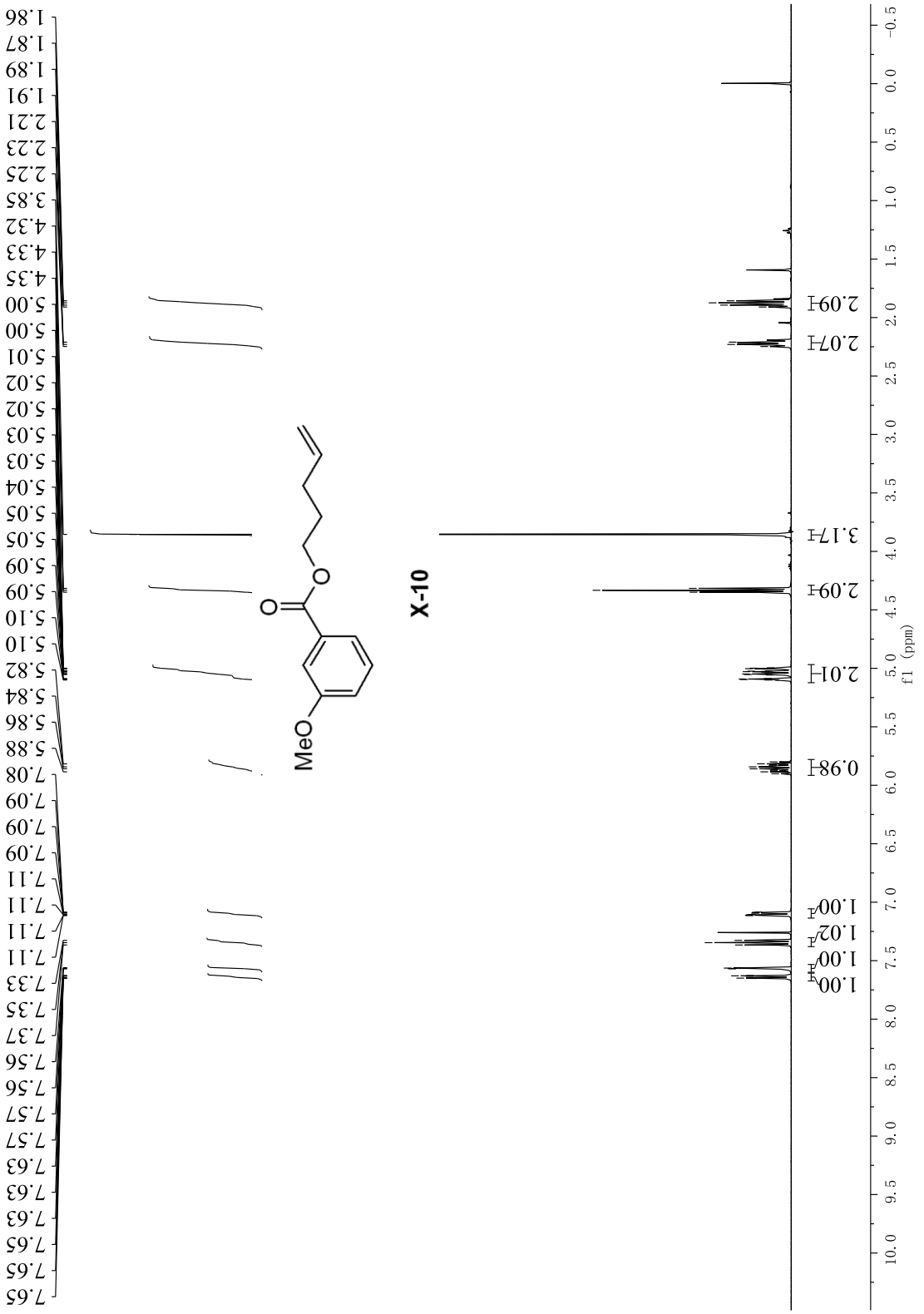


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-7**



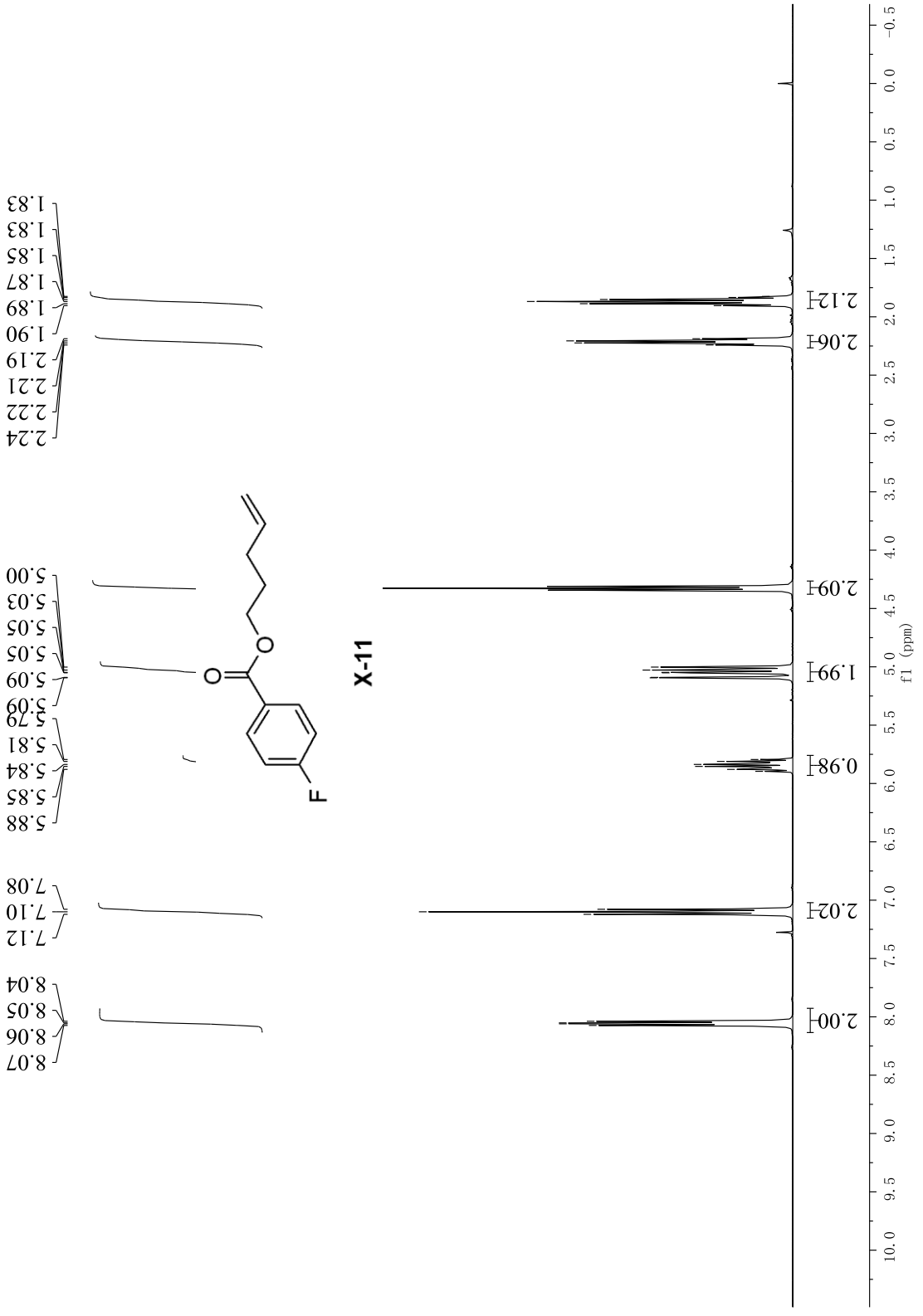
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-9**

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



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

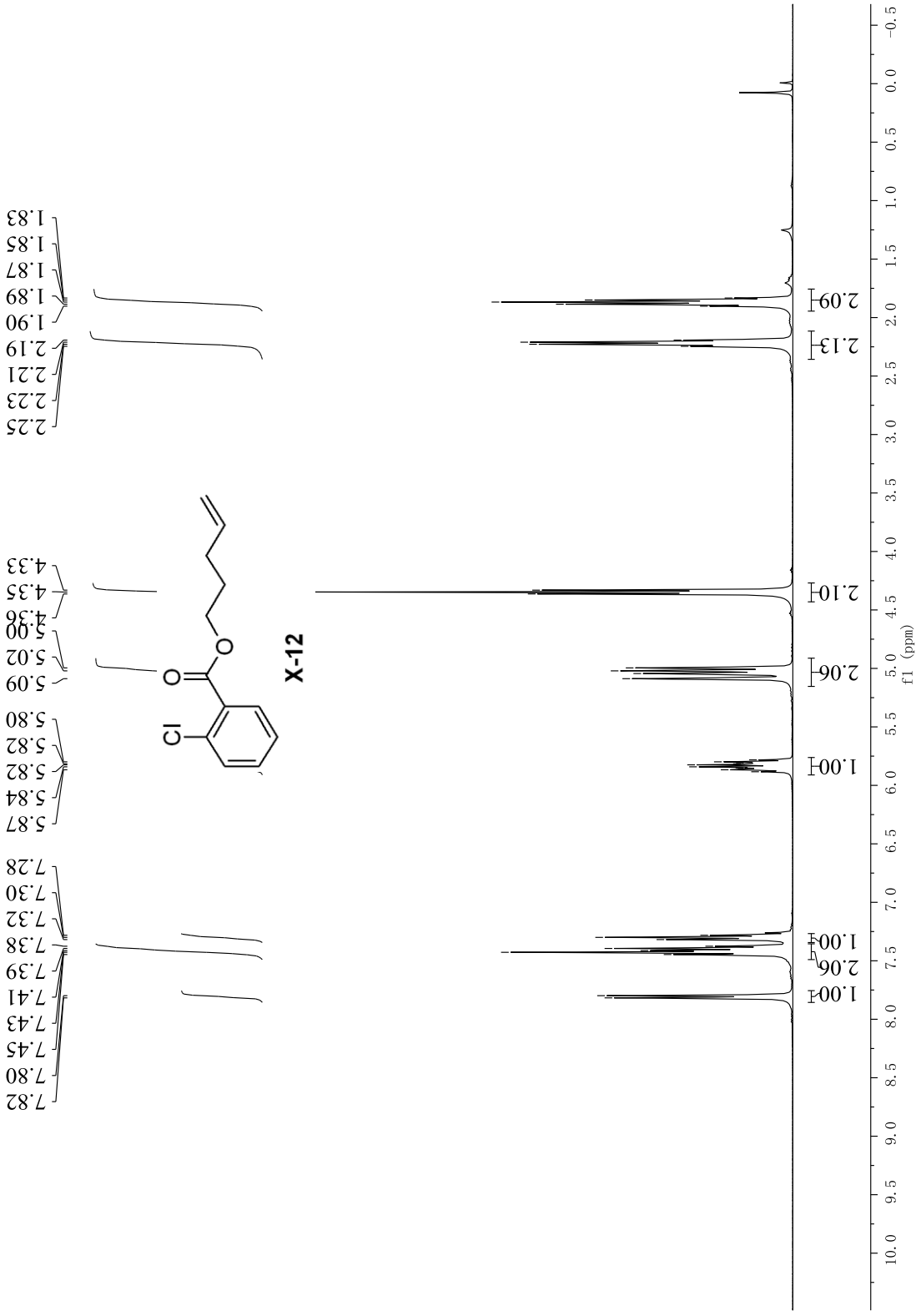
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-10**



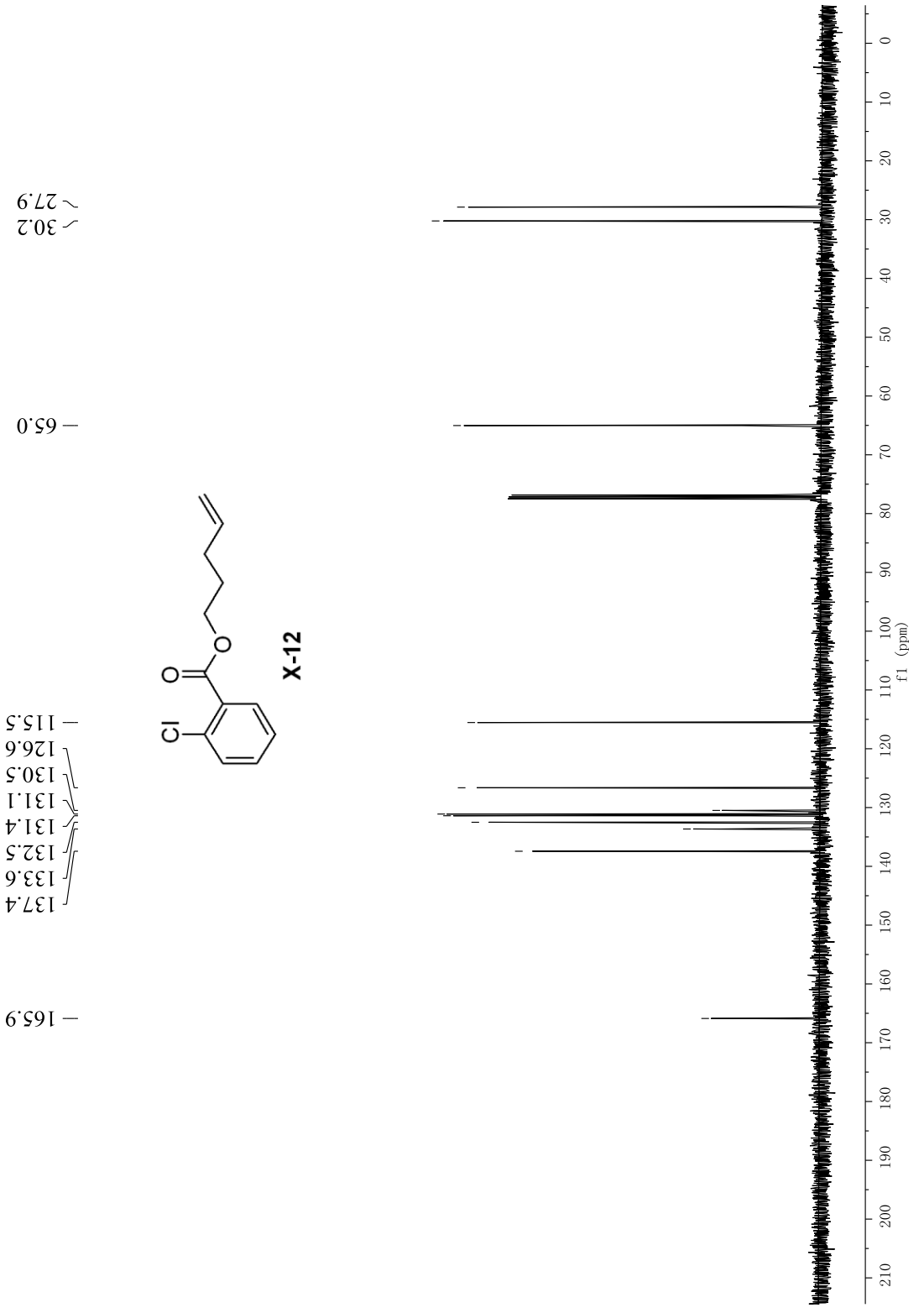
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-11**

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

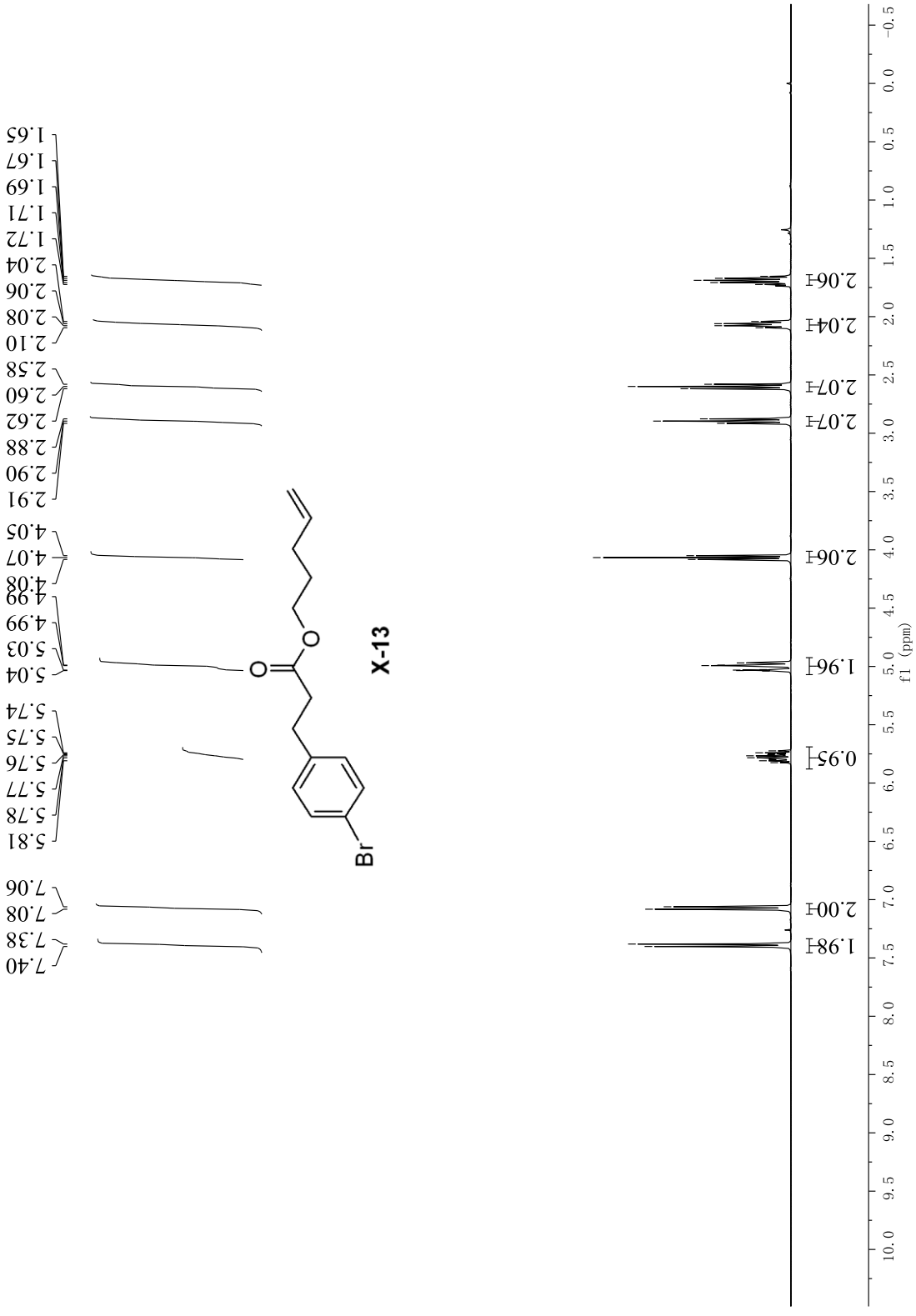
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-11**



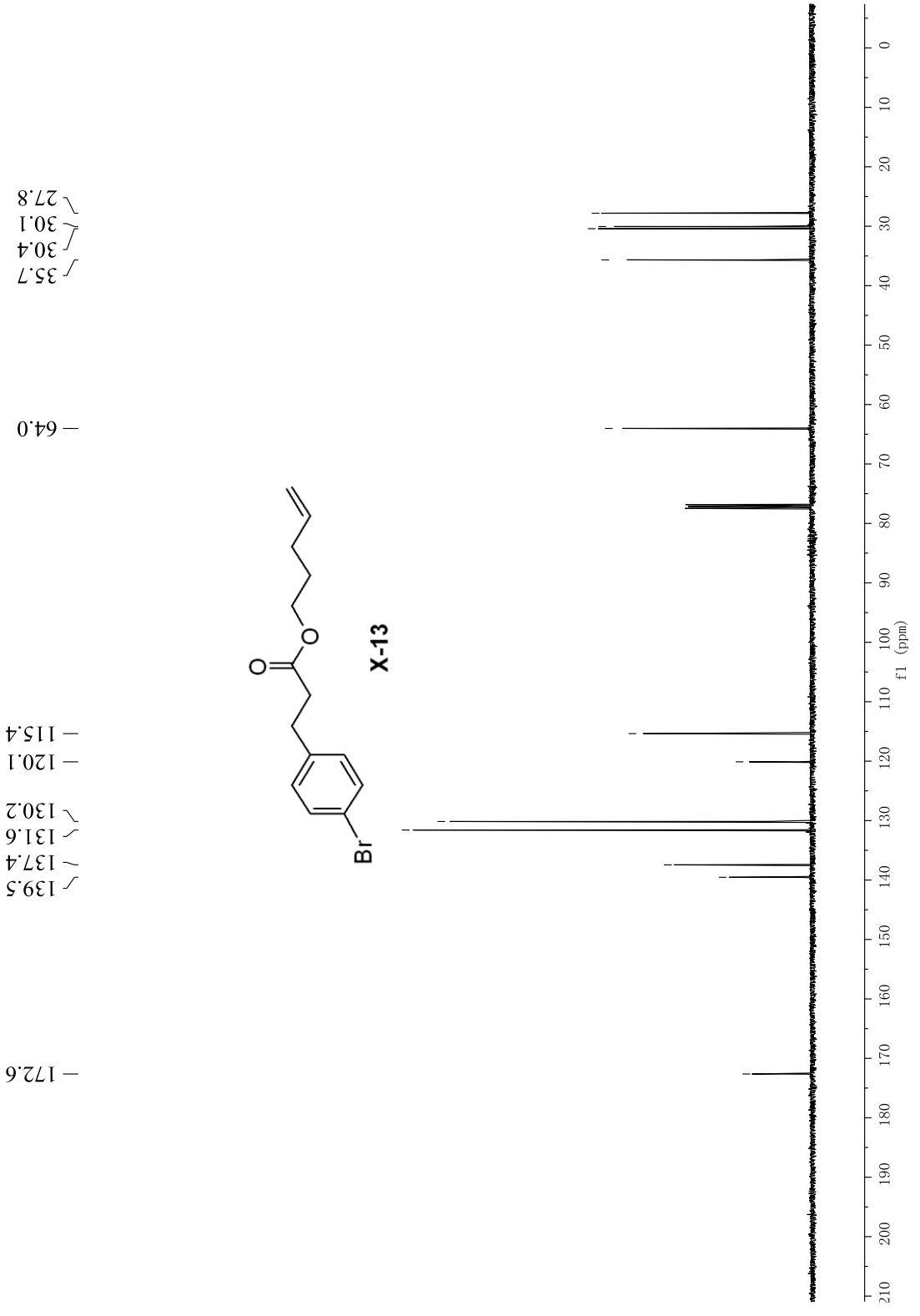
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-12**



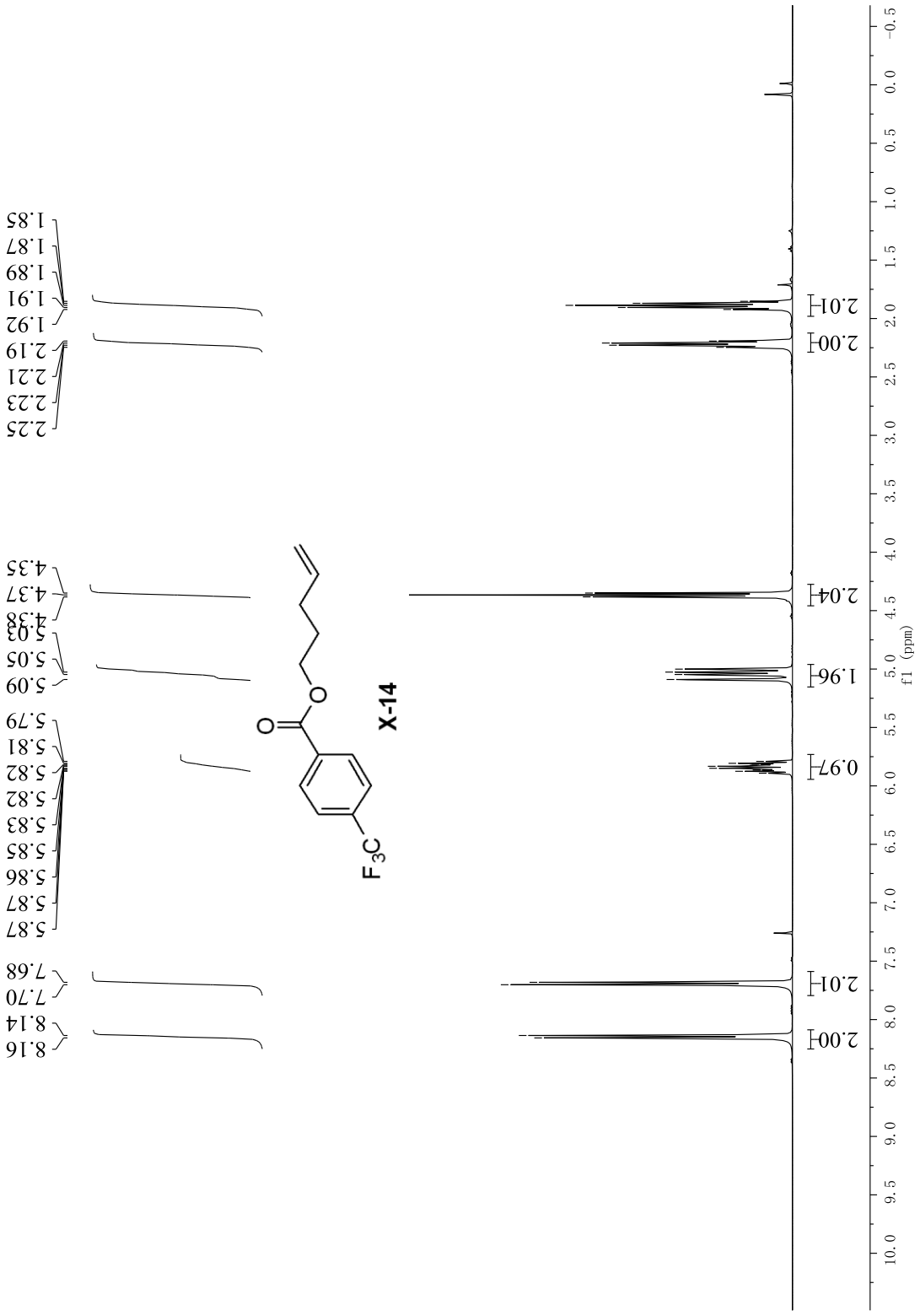
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-12**



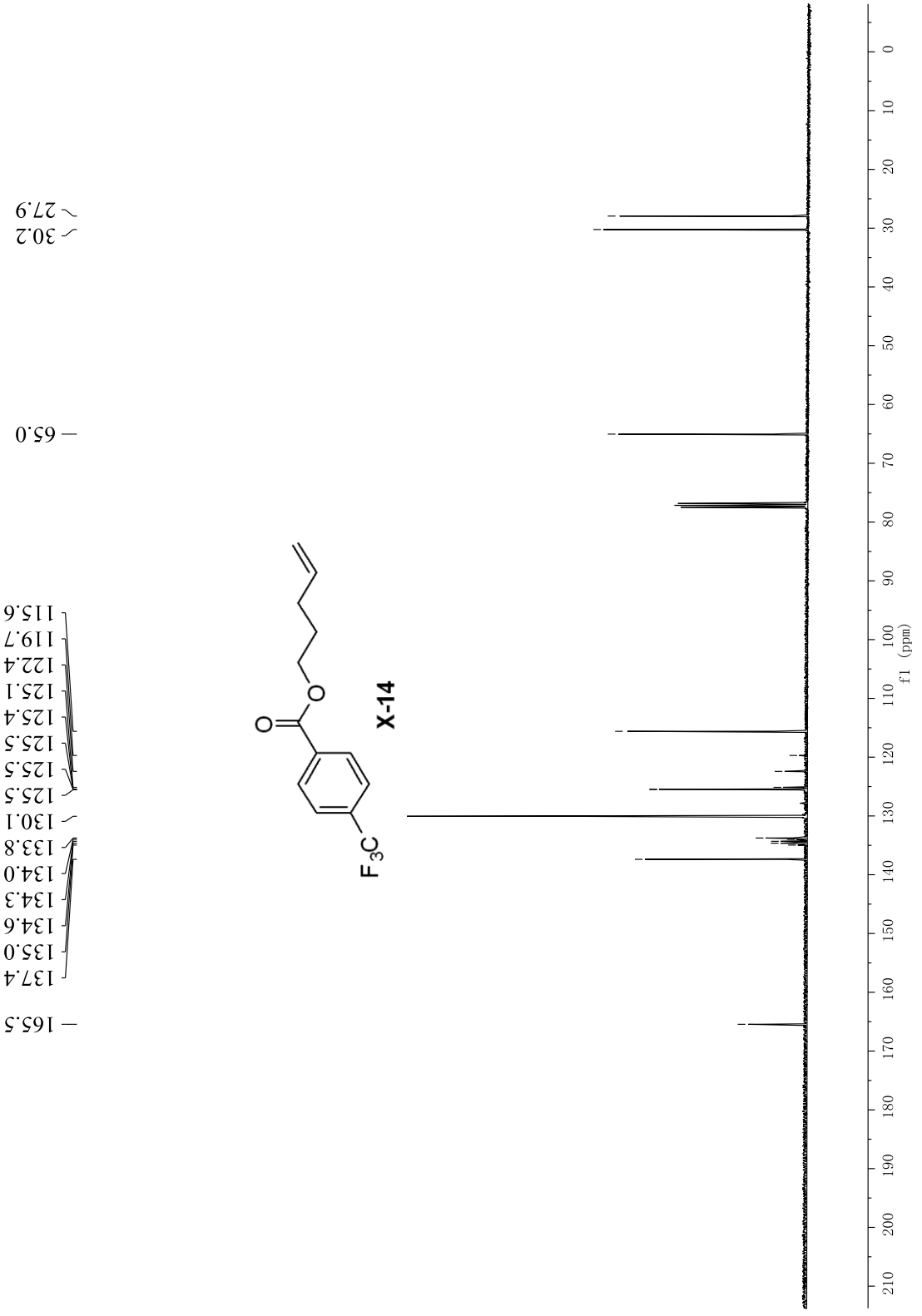
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-13**



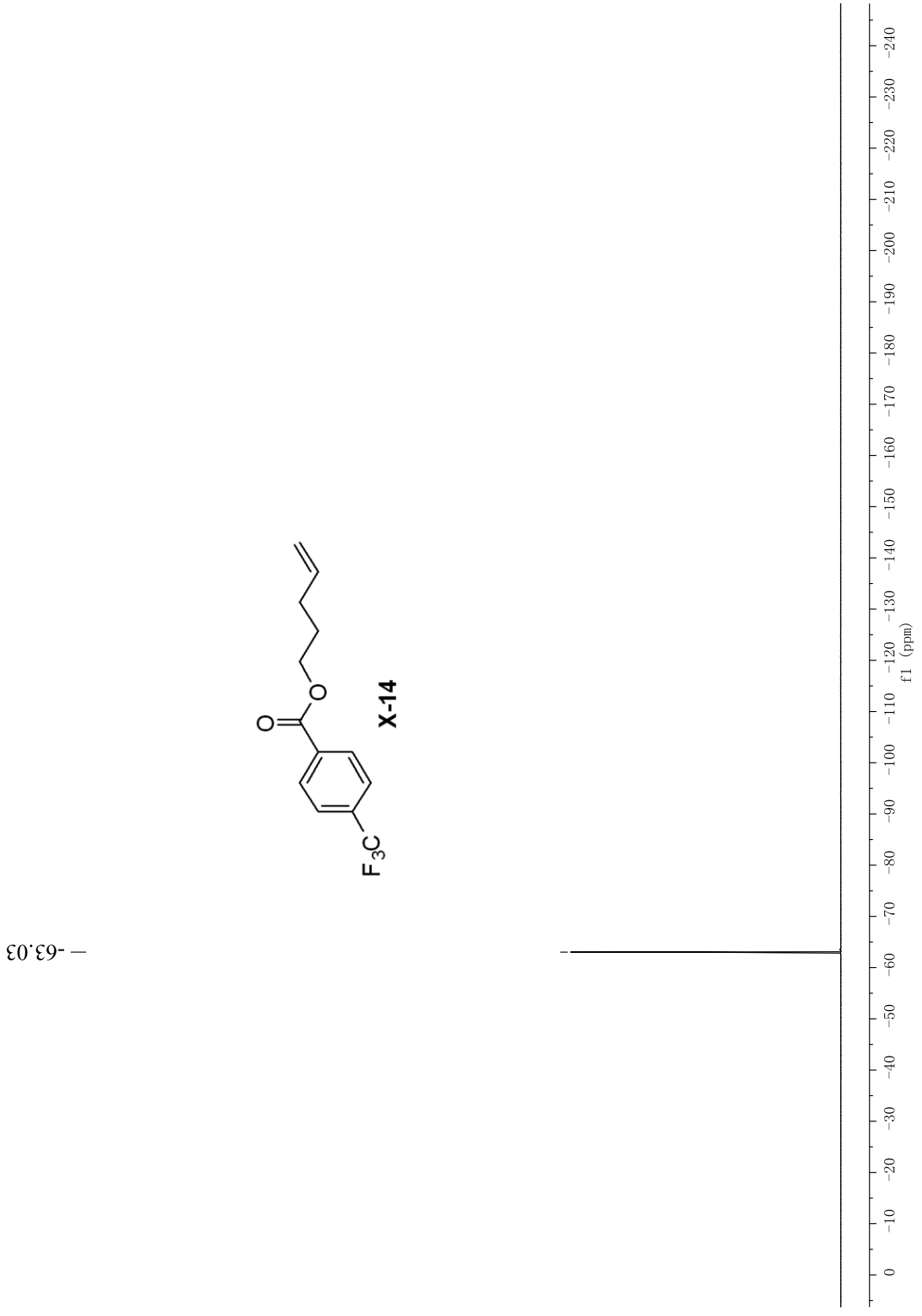
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-13**



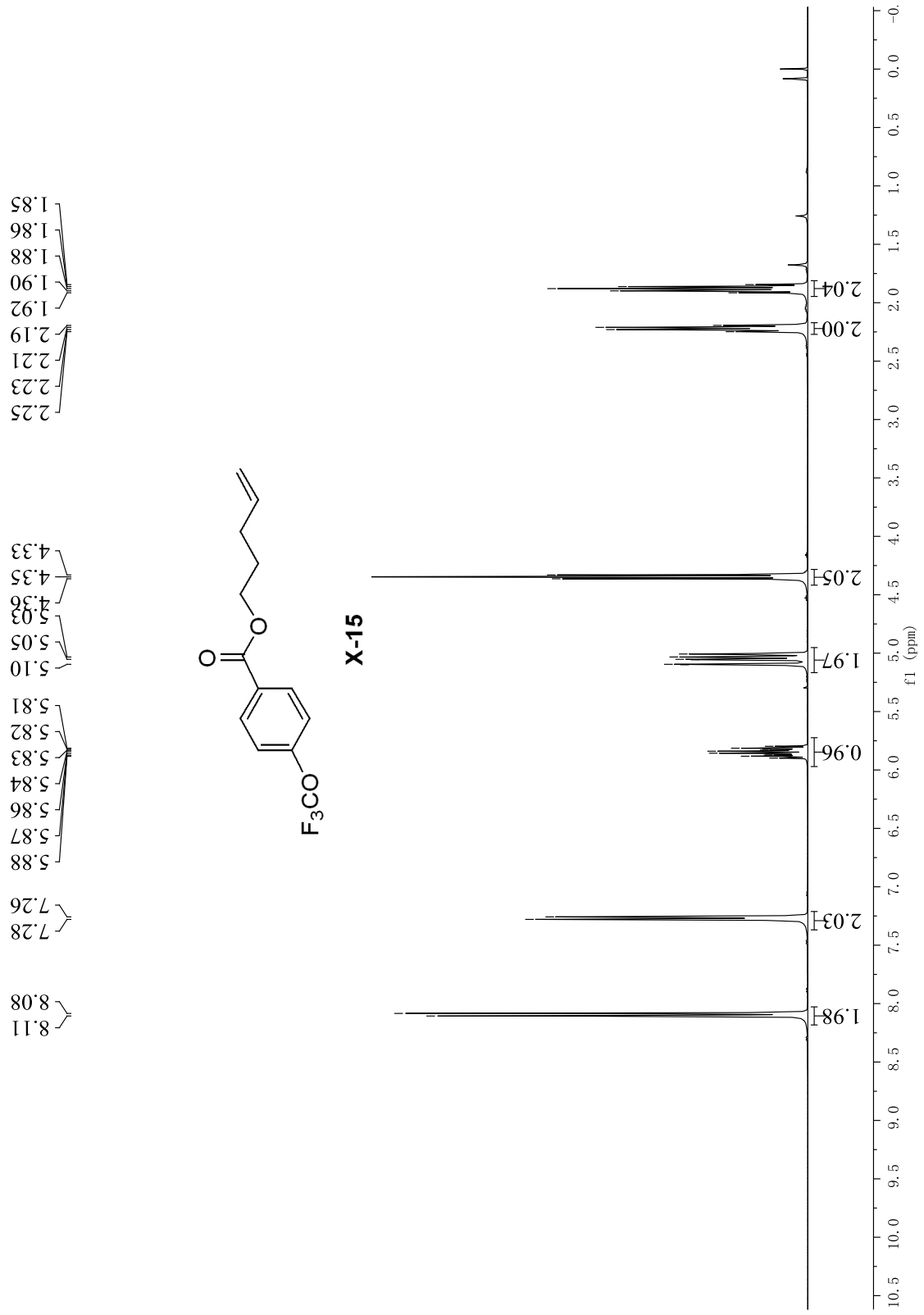
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-14**



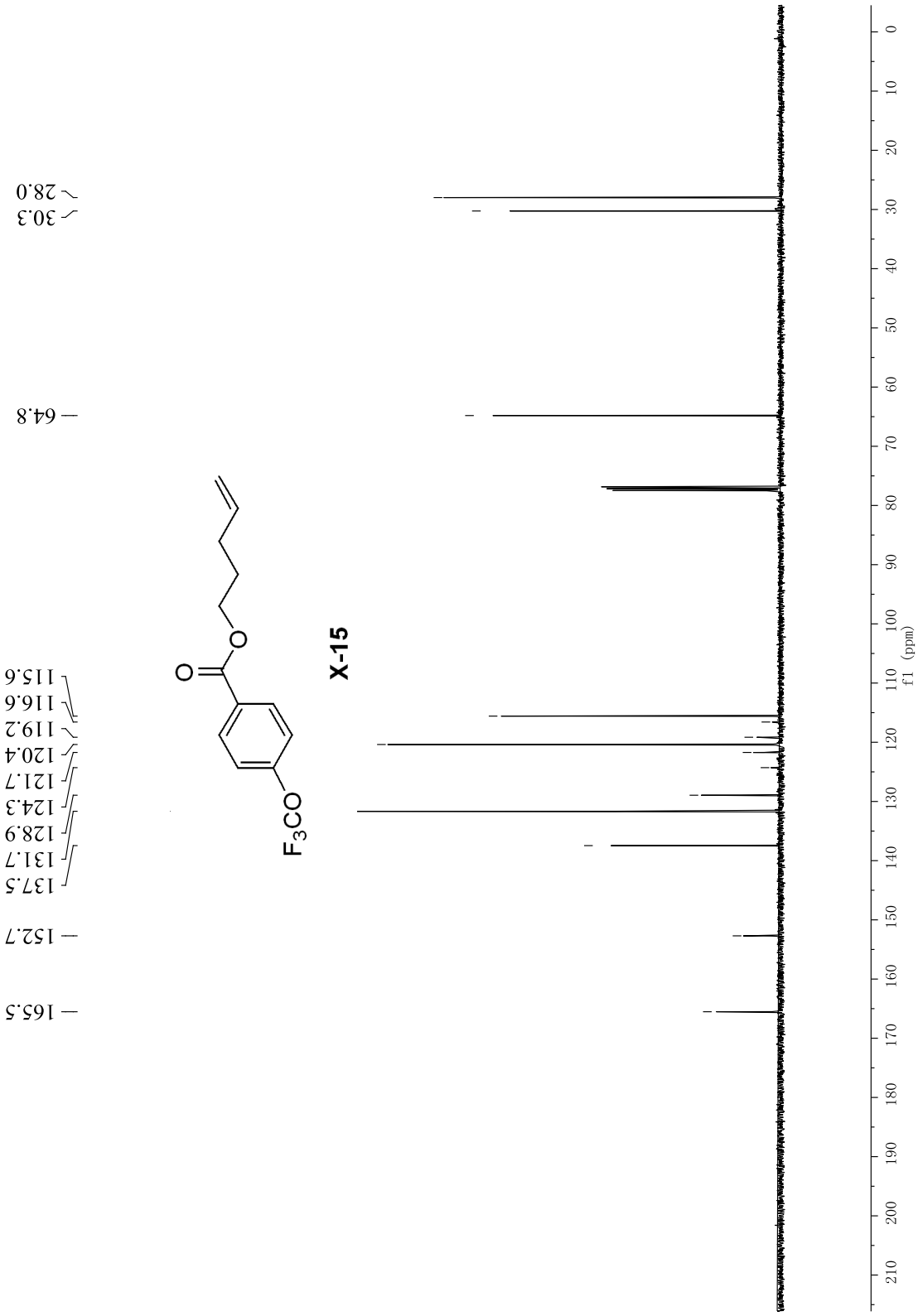
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-14**



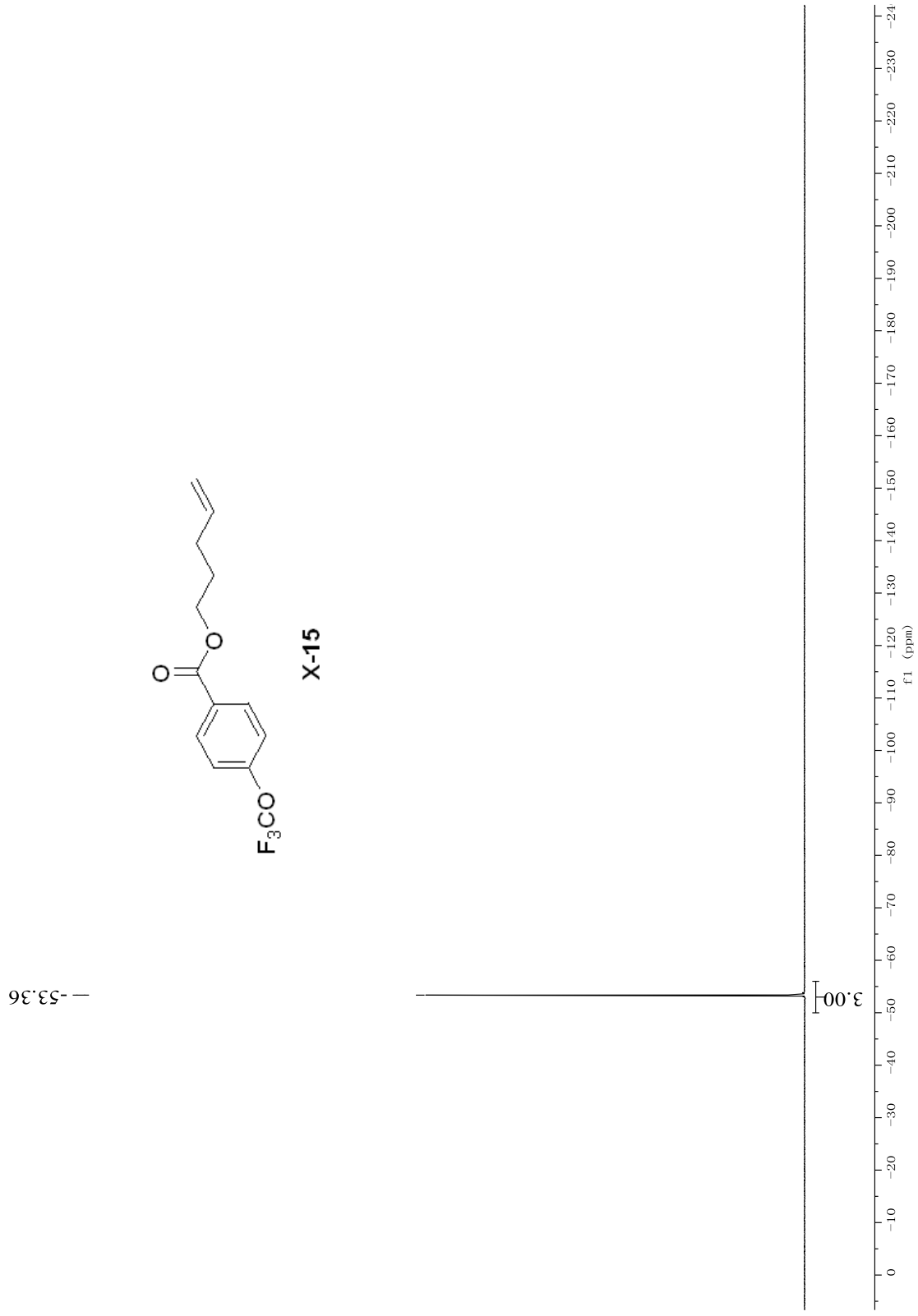
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-14**



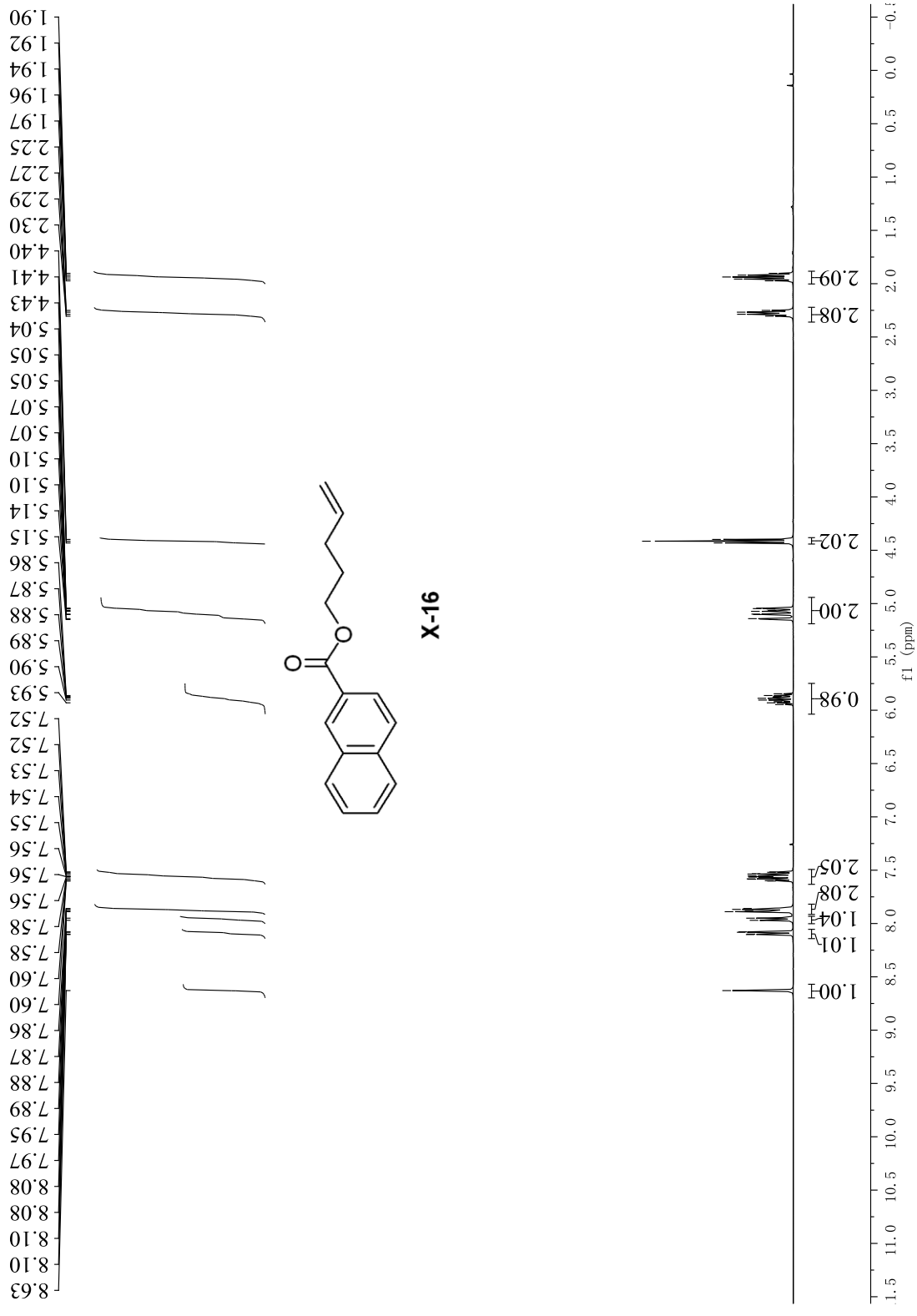
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-15**



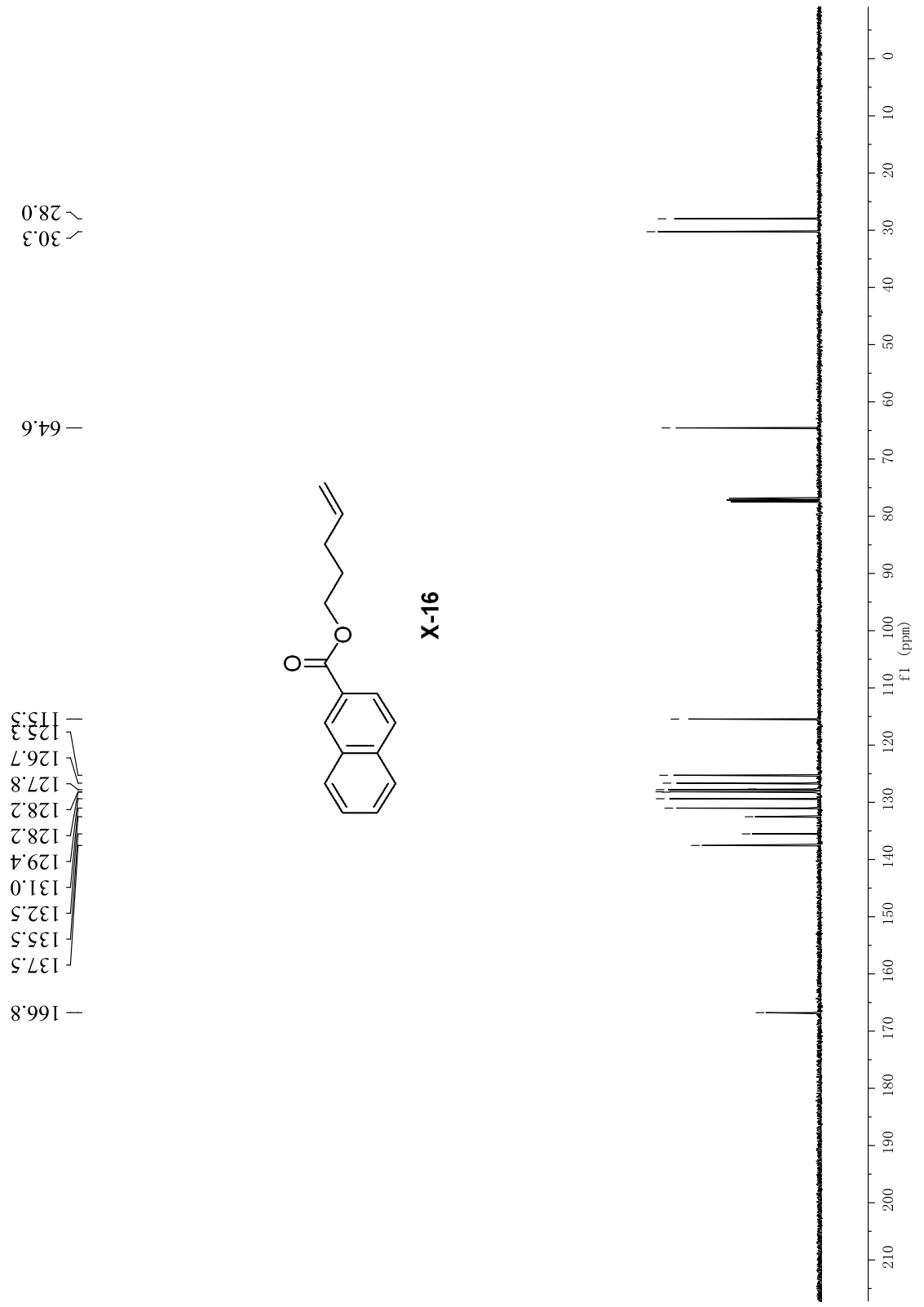
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-15**



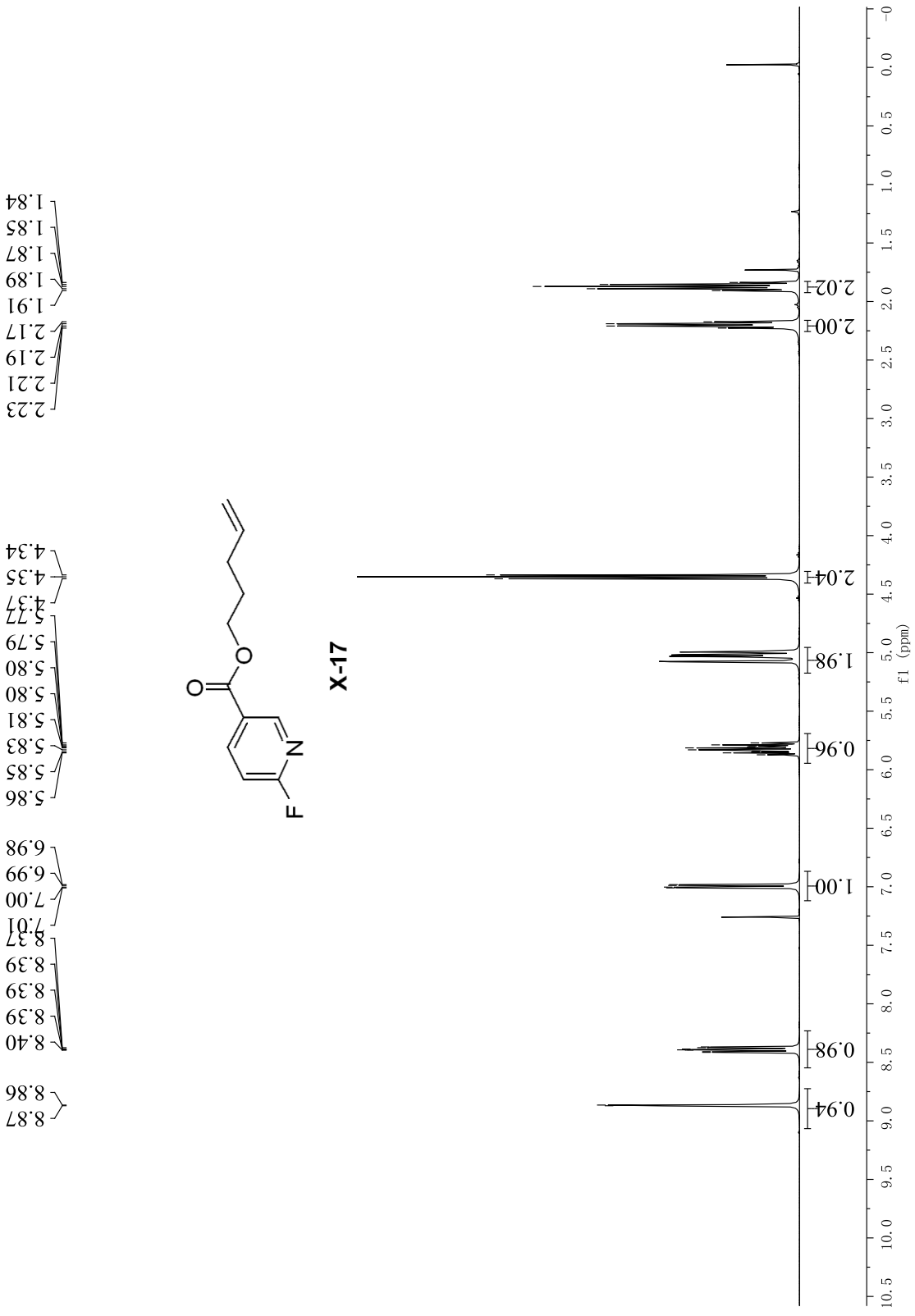
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-15**



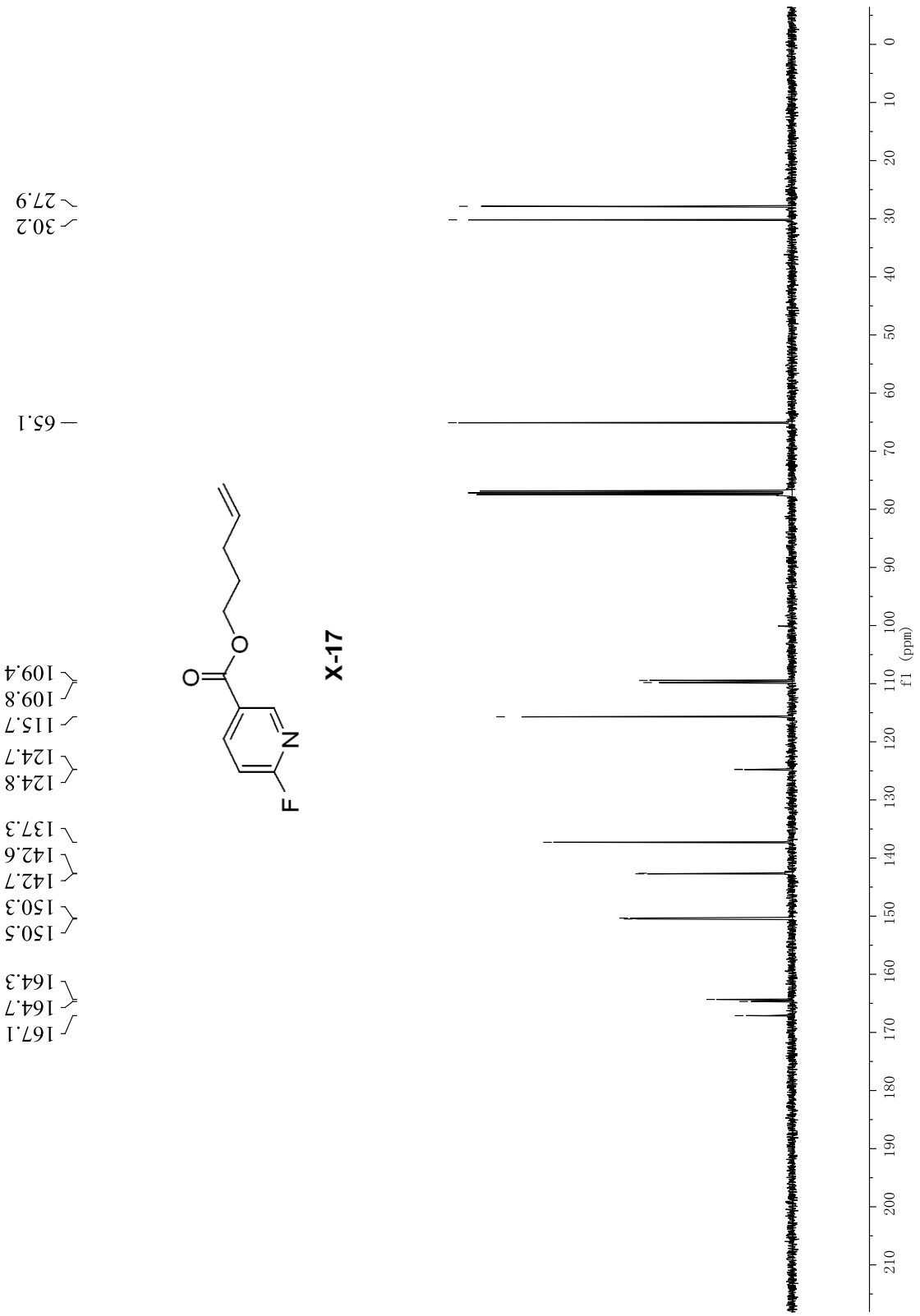
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-16**



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

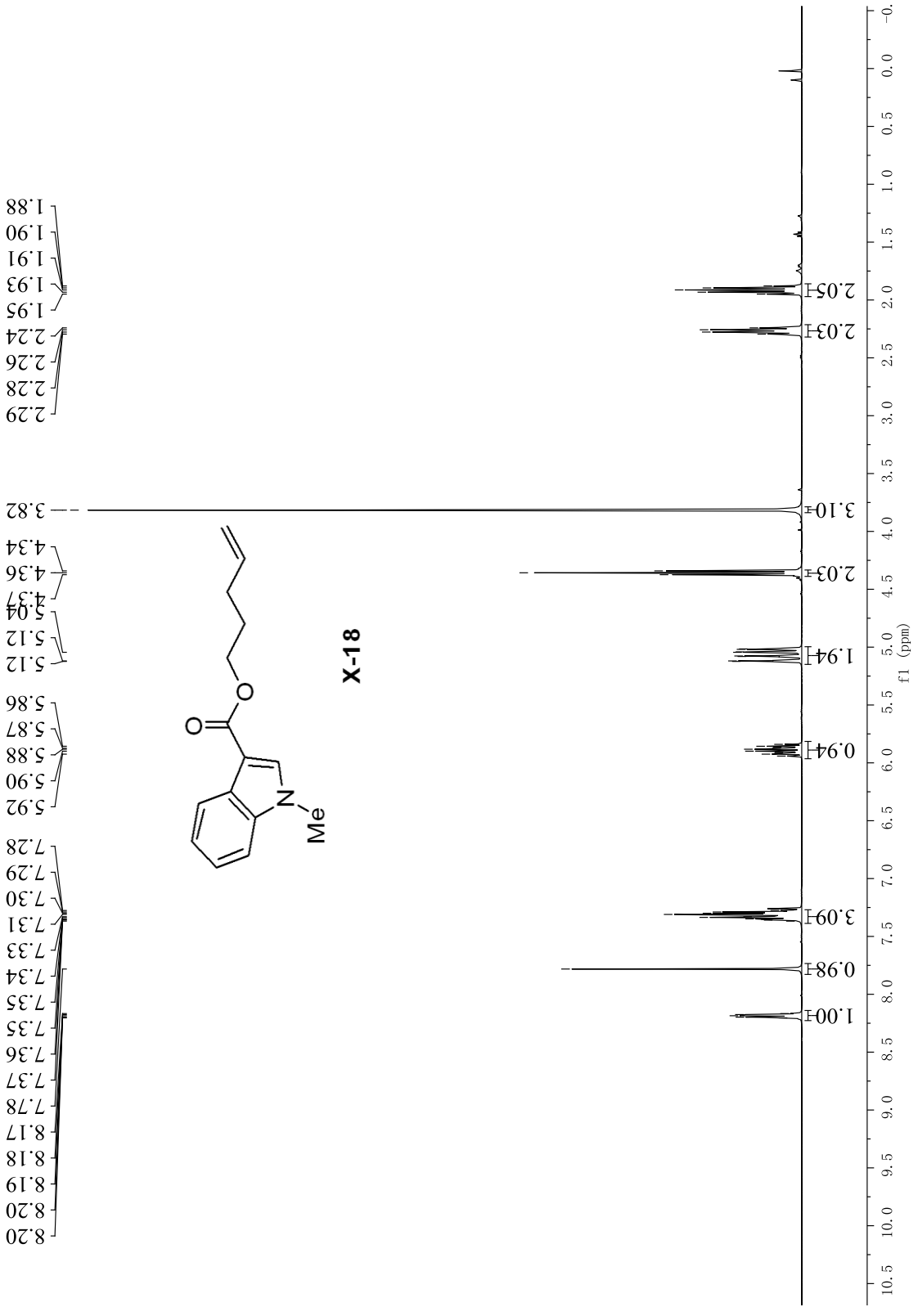


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-17**

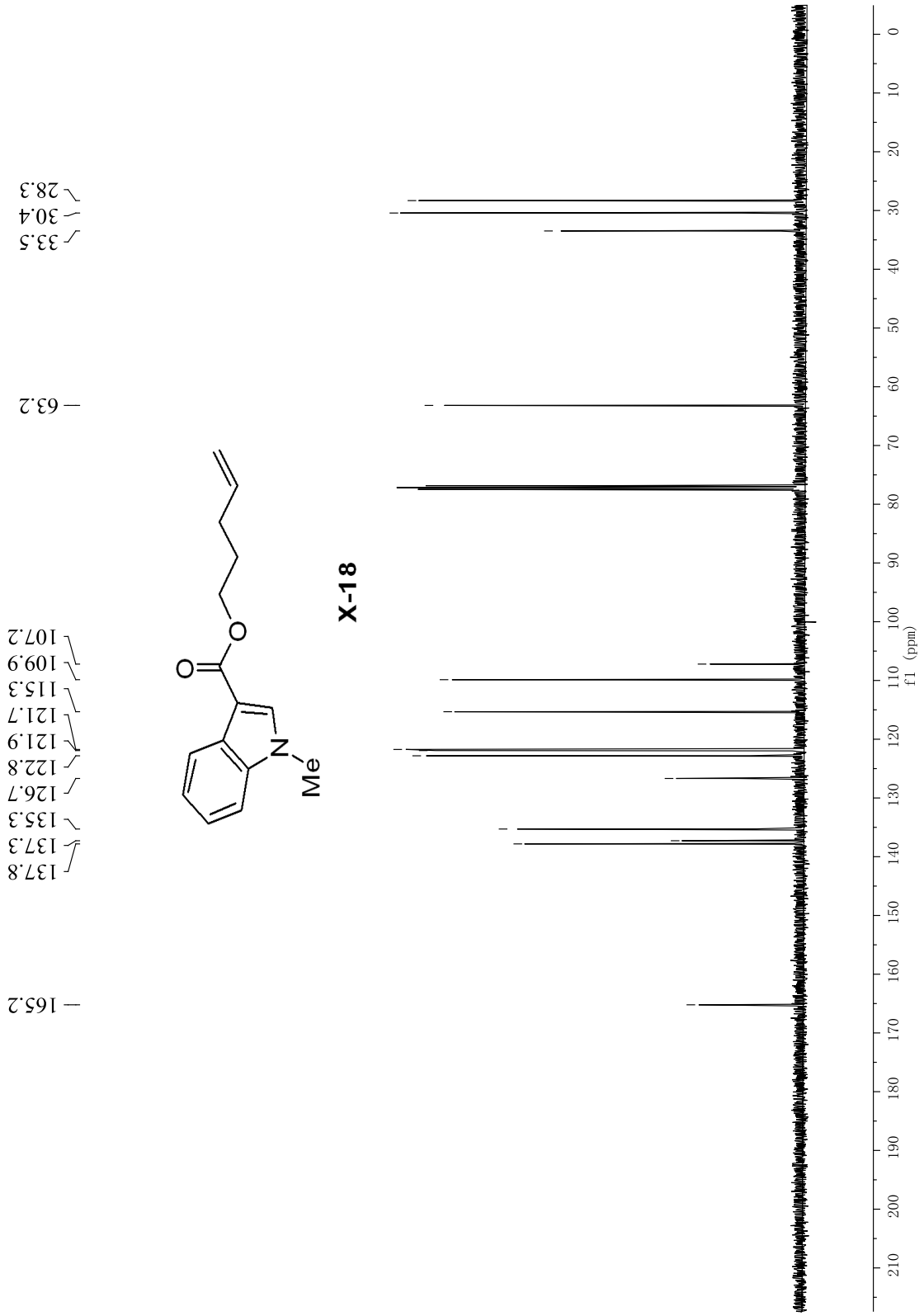


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-17**

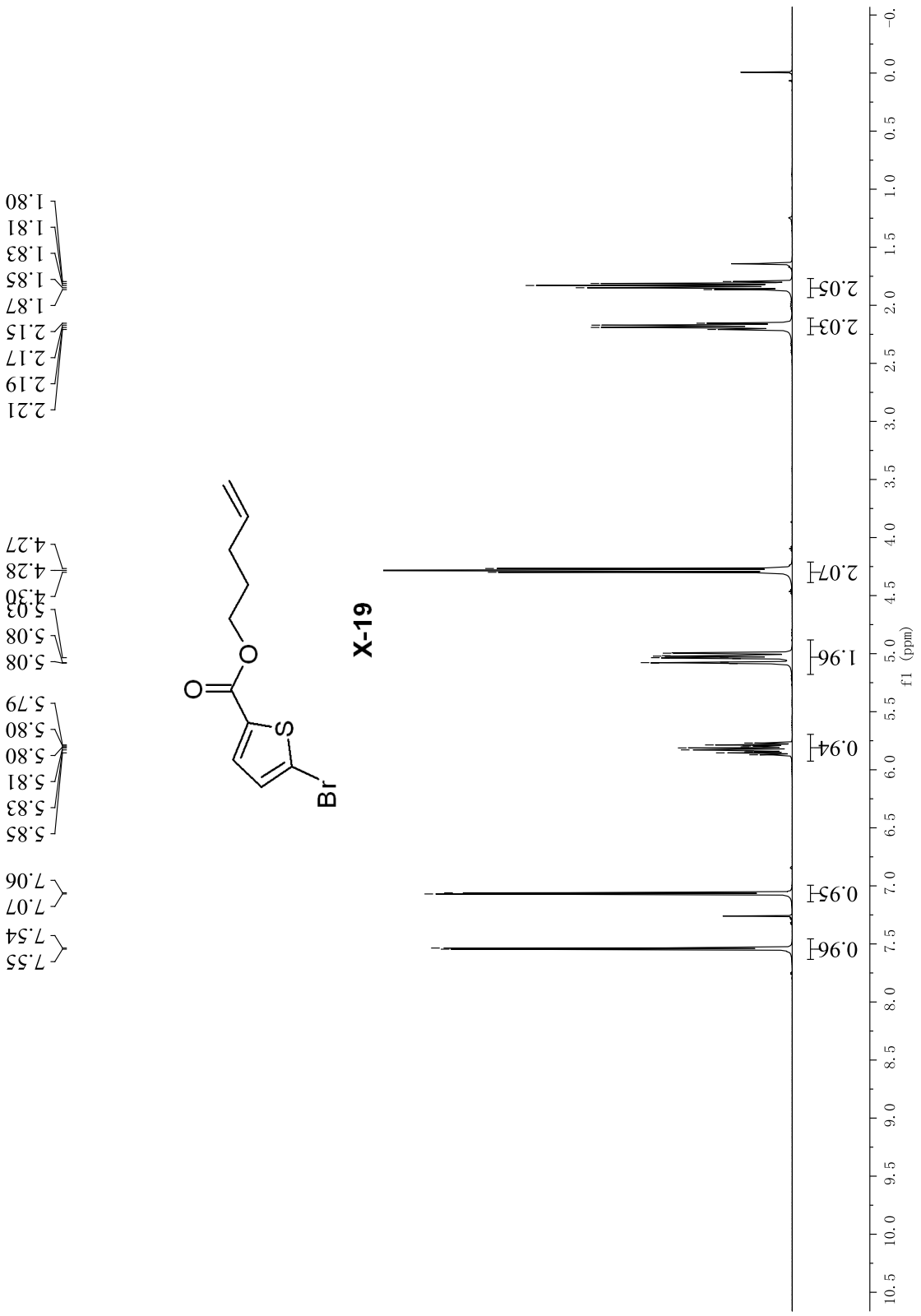
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-17**



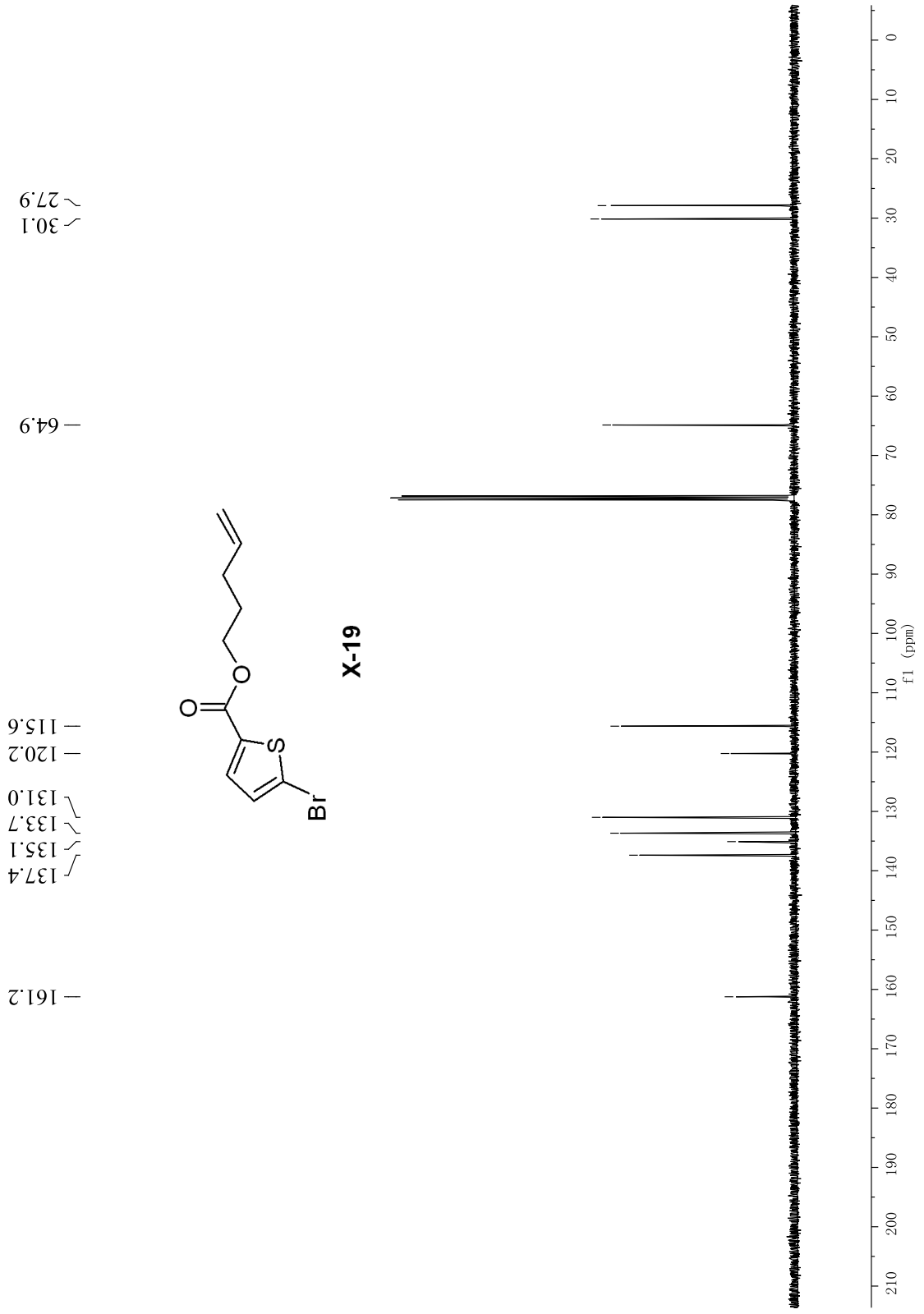
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-18**



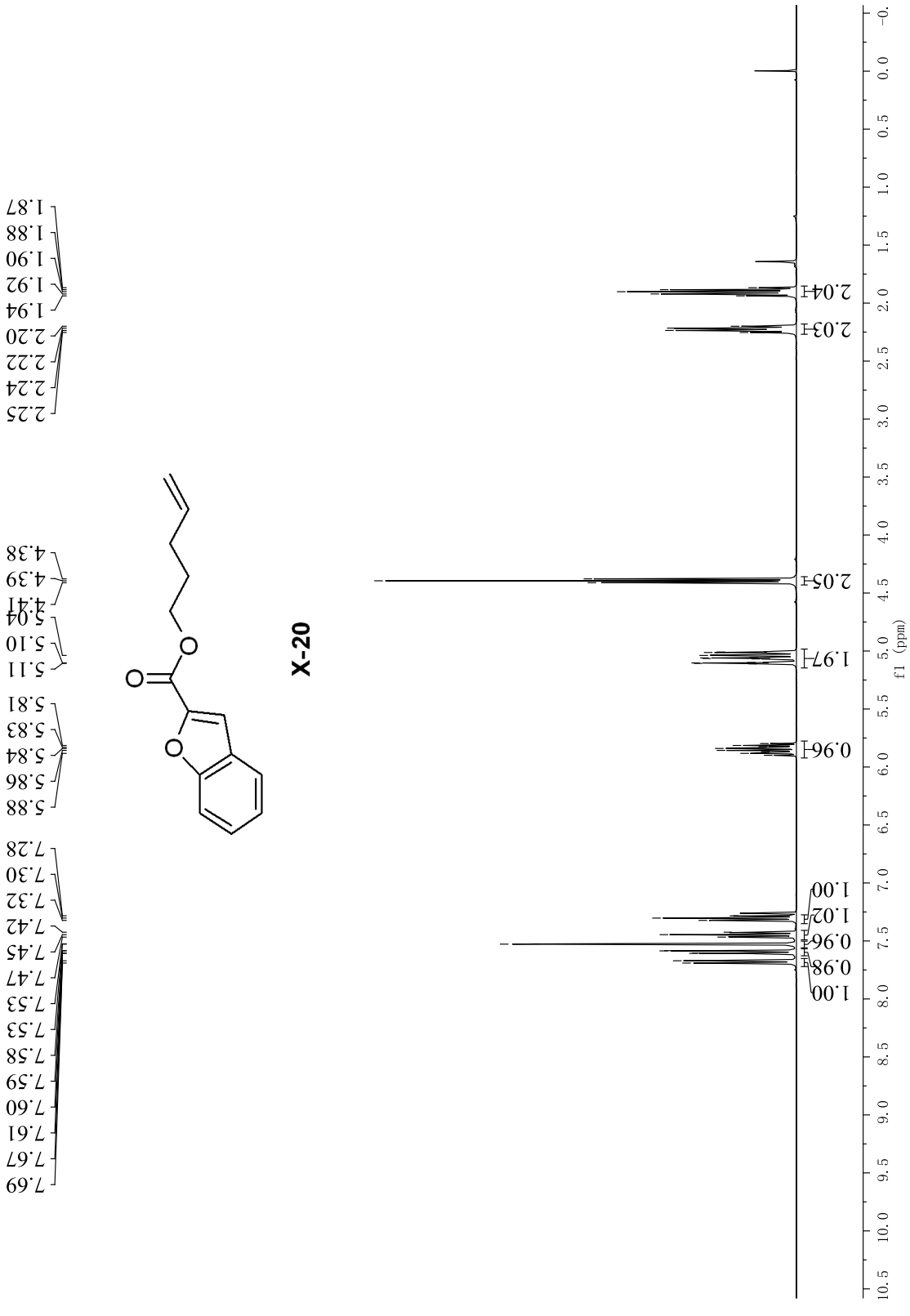
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-18**



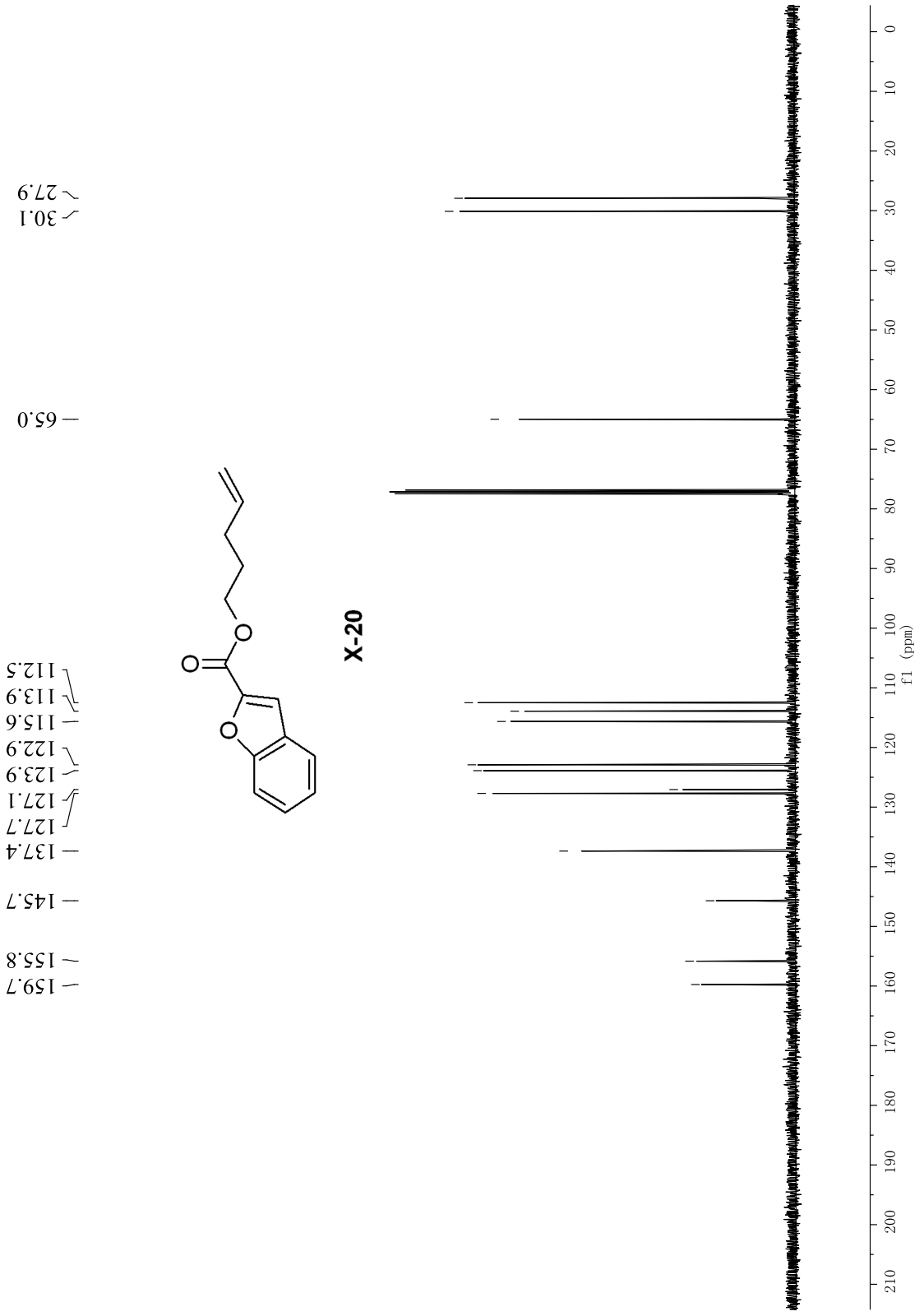
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-19**



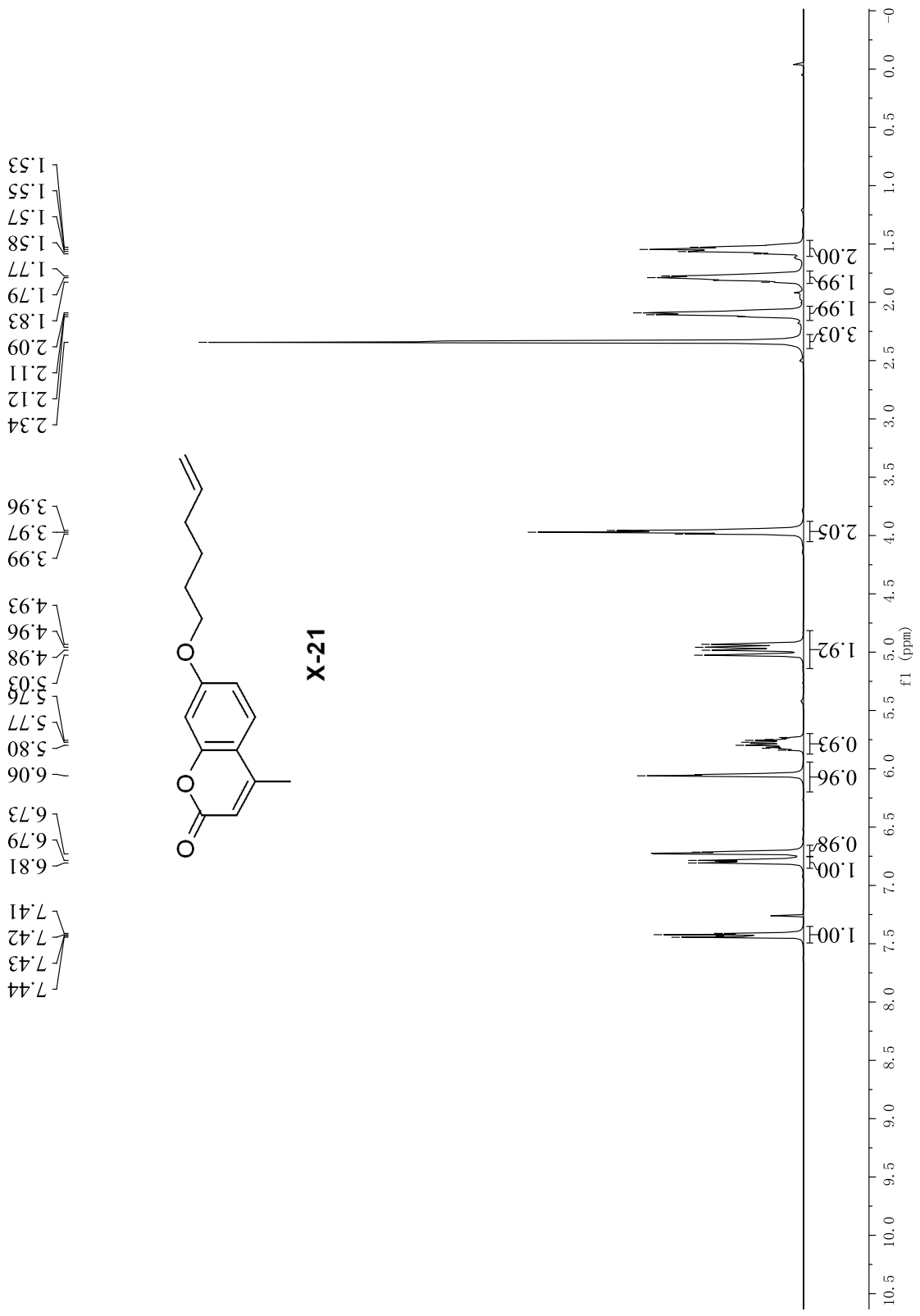
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-19**



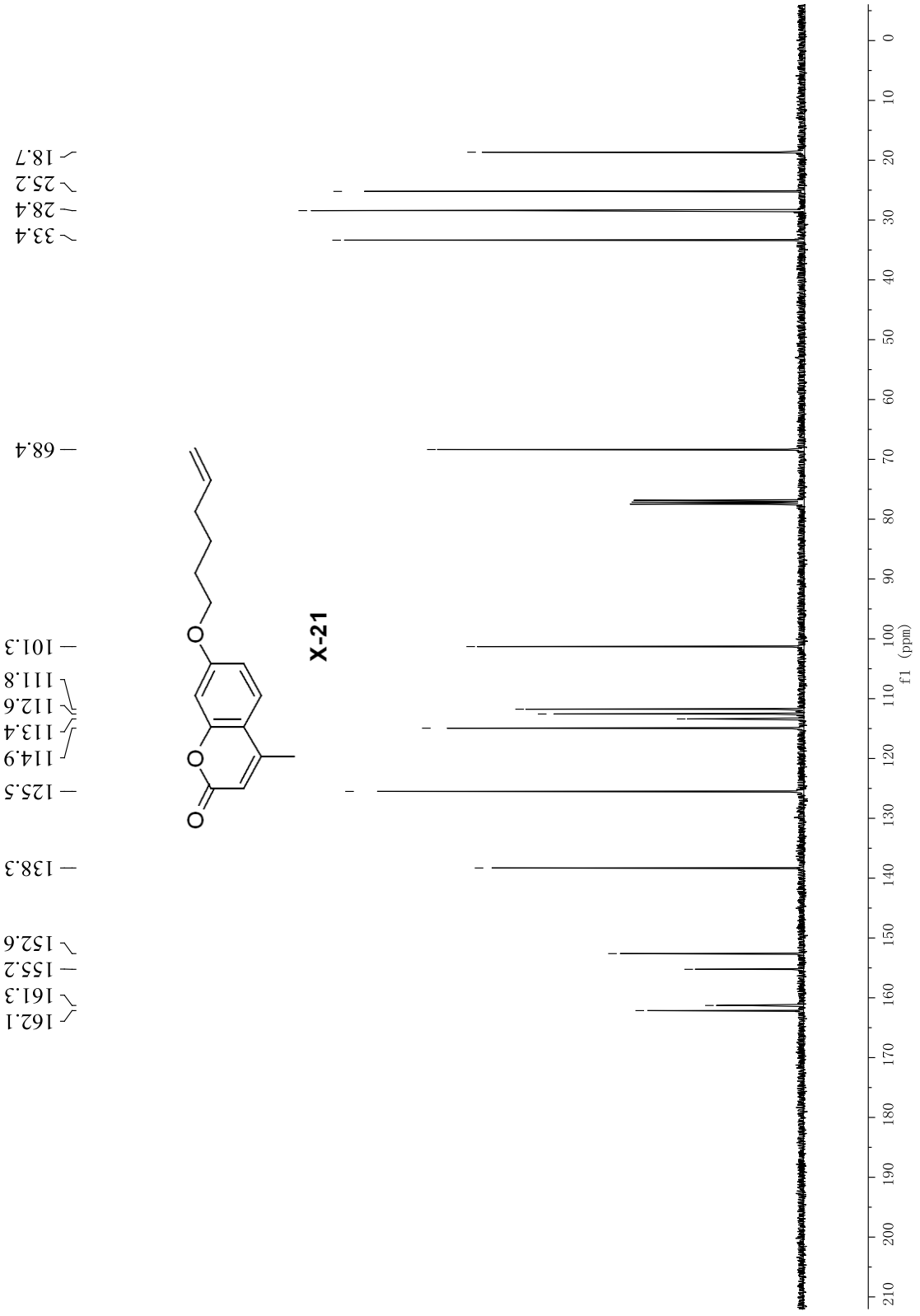
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-20**



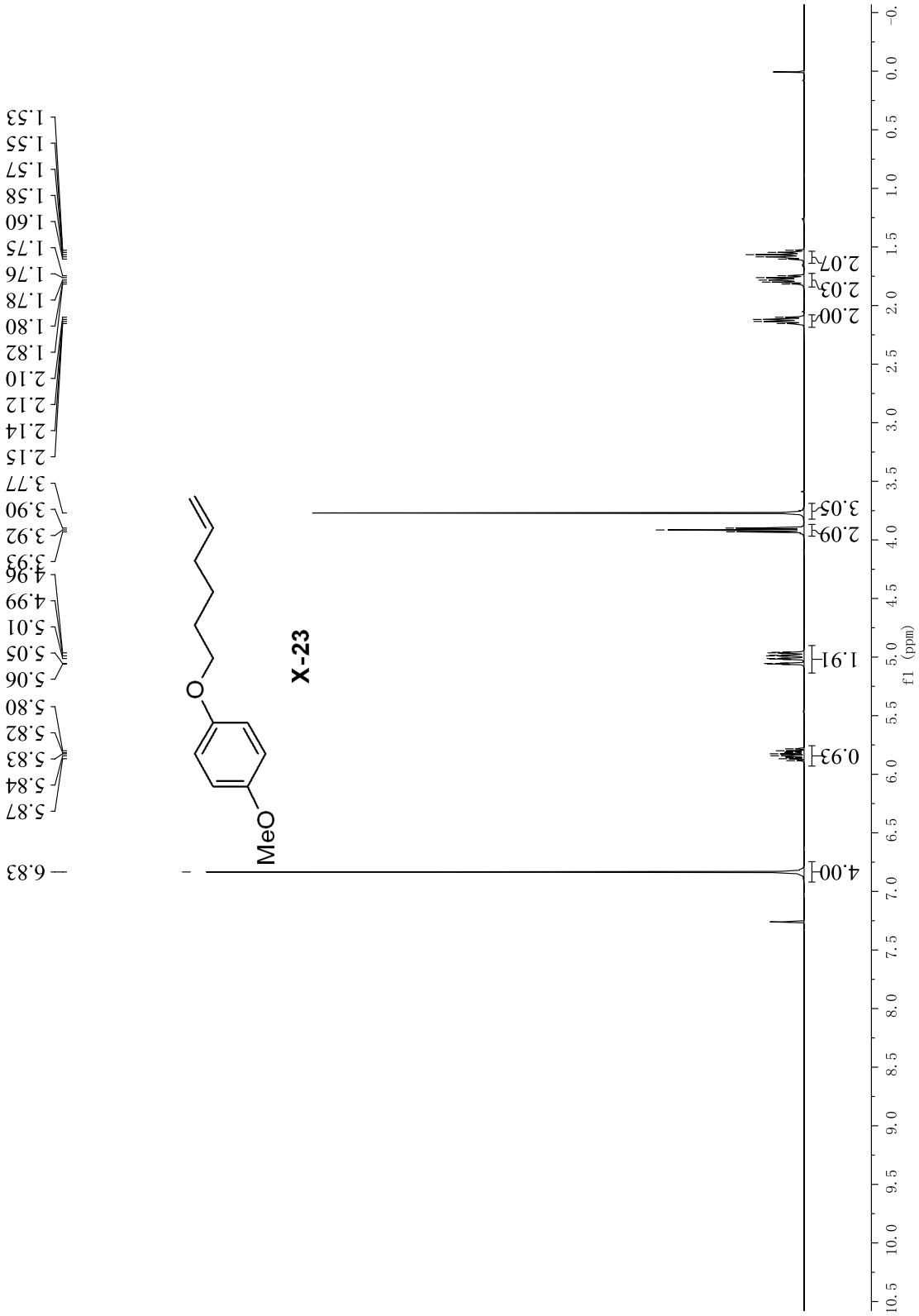
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-20**



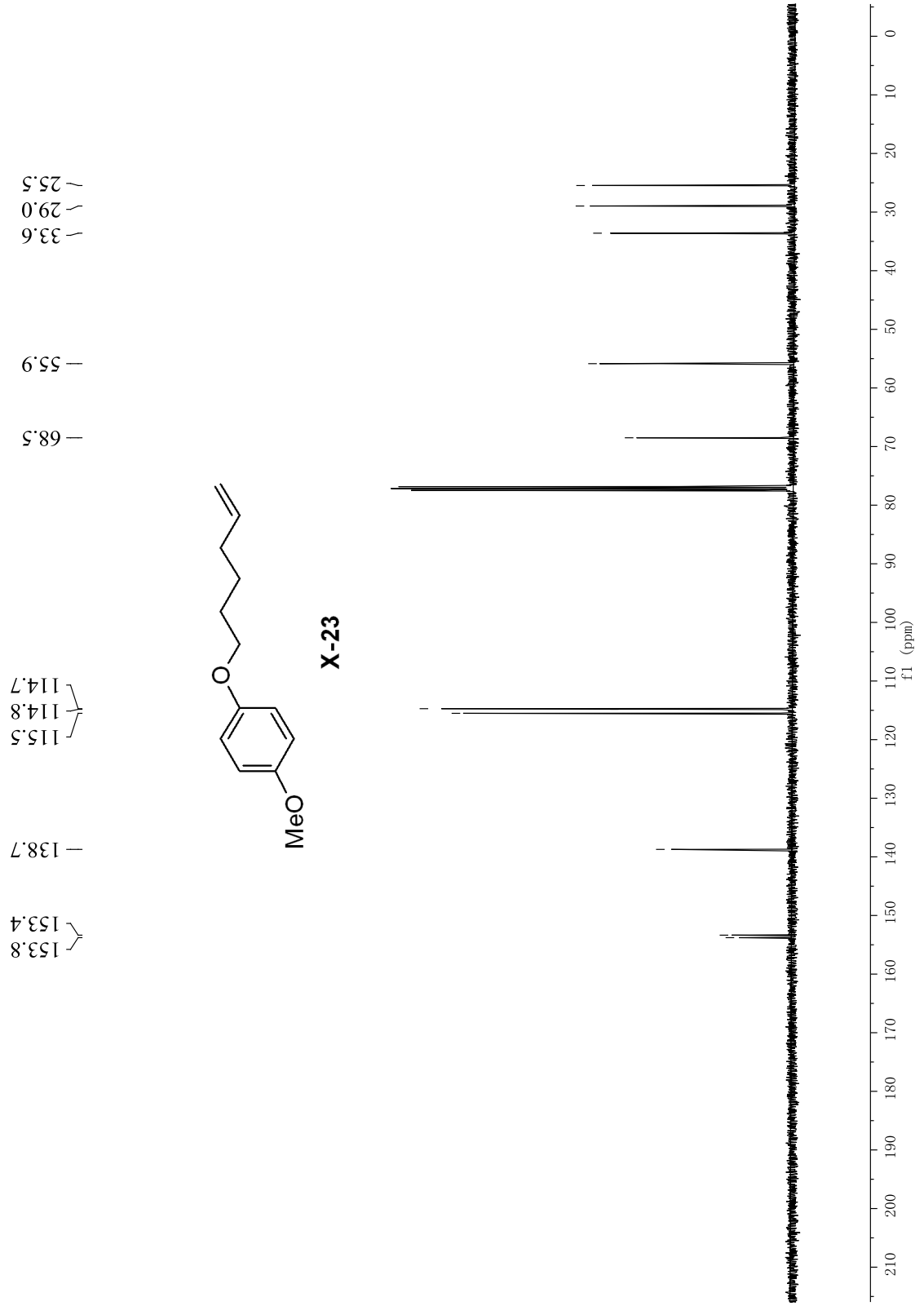
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-21**



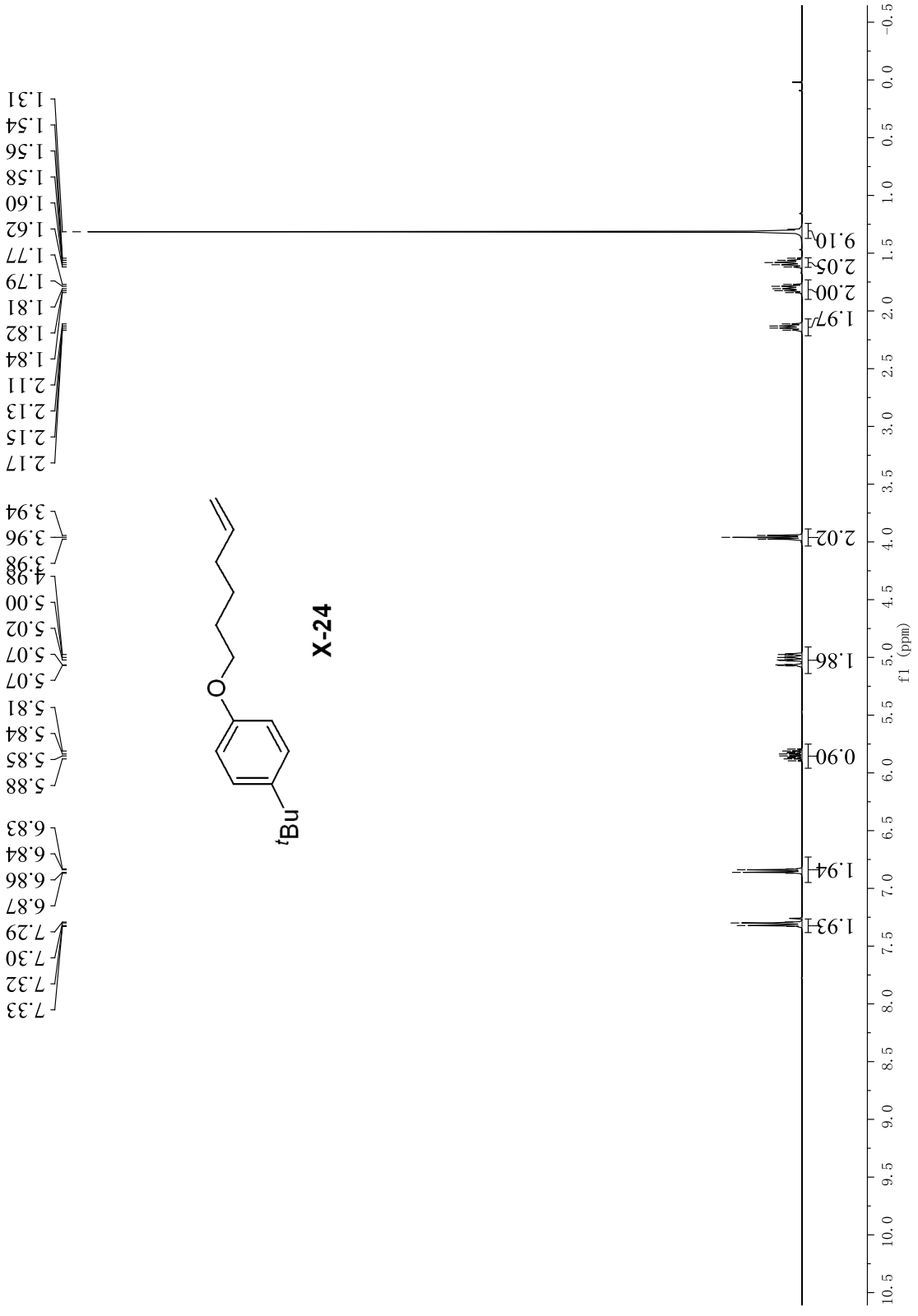
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-21**



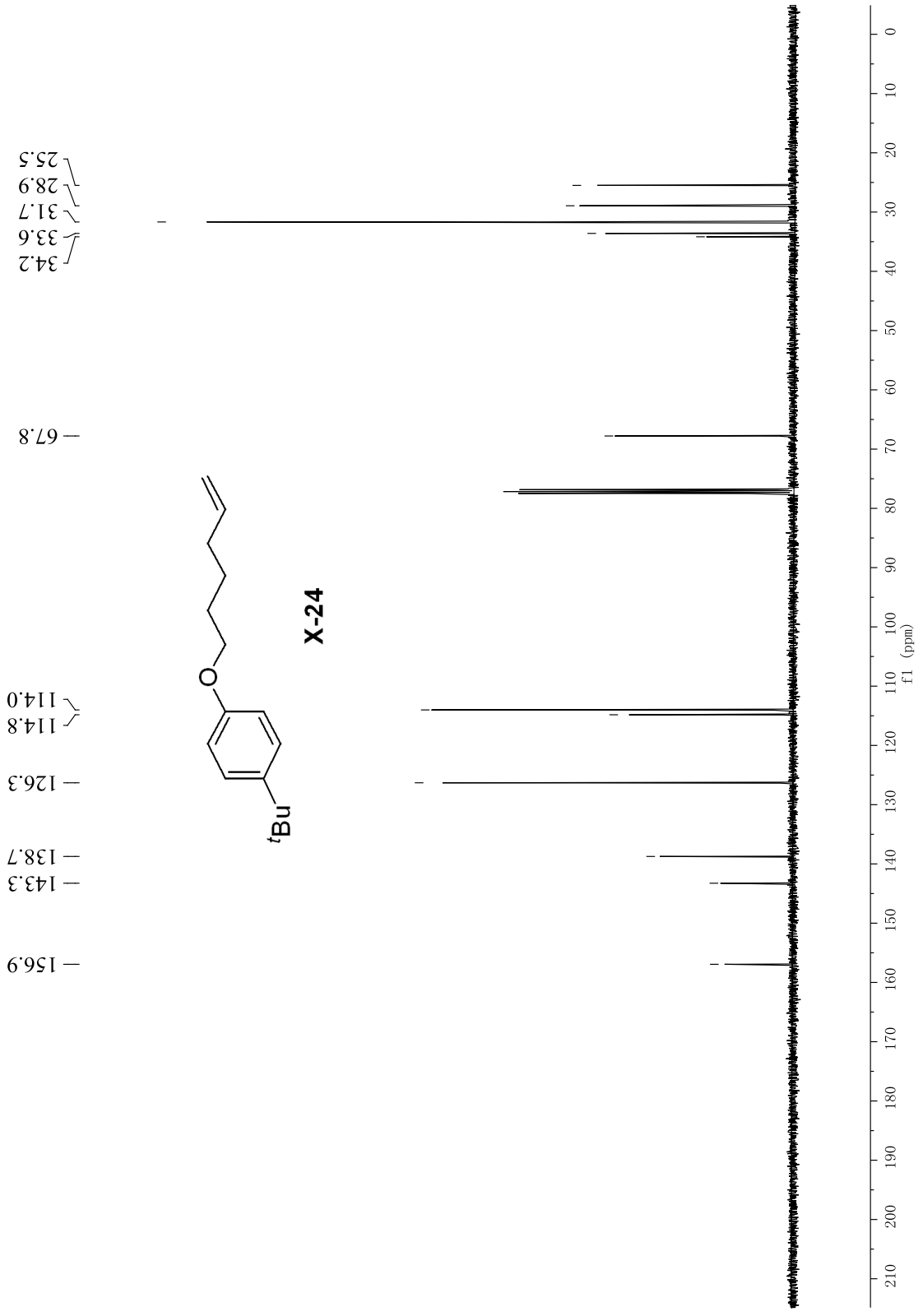
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-23**



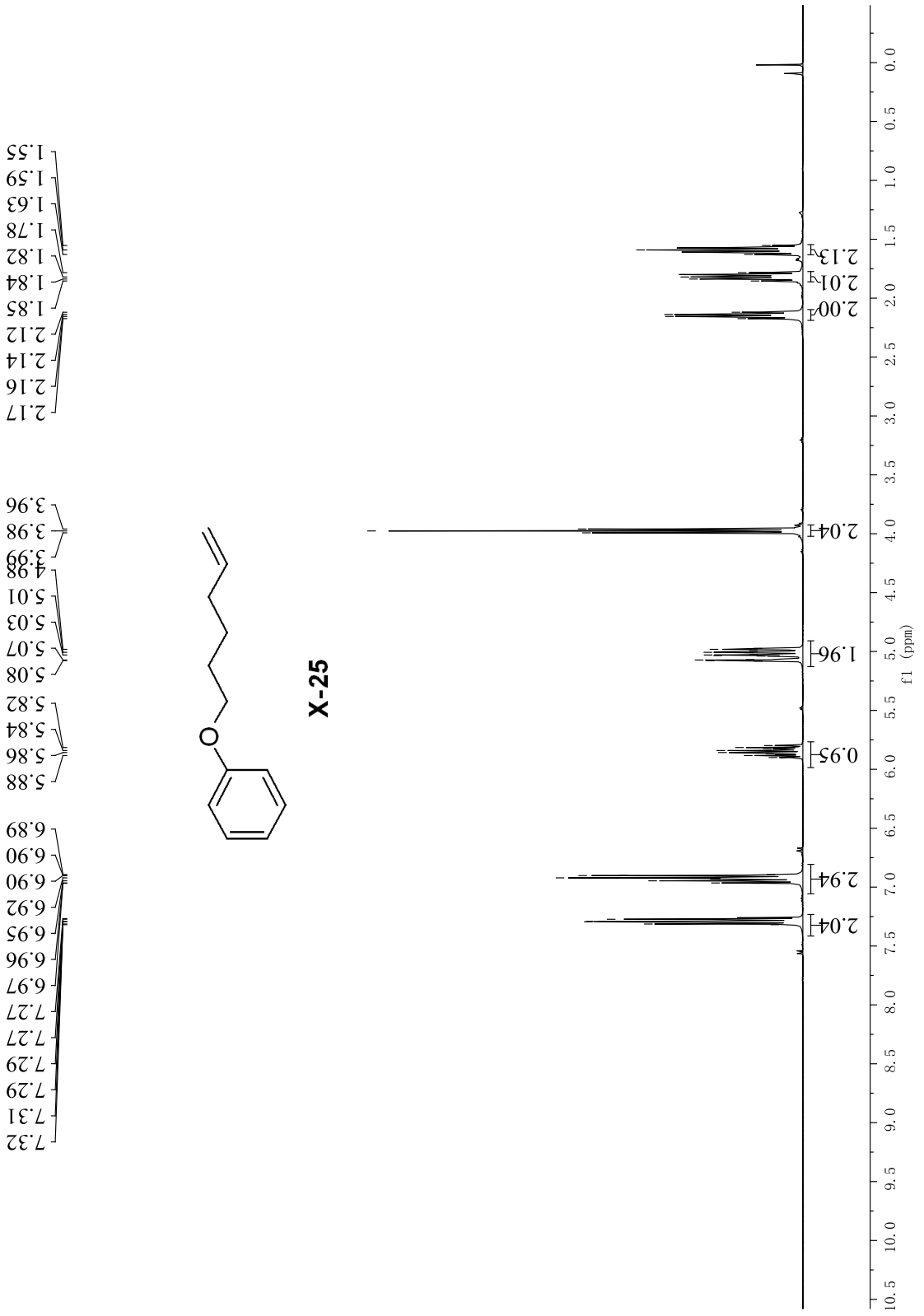
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-23**



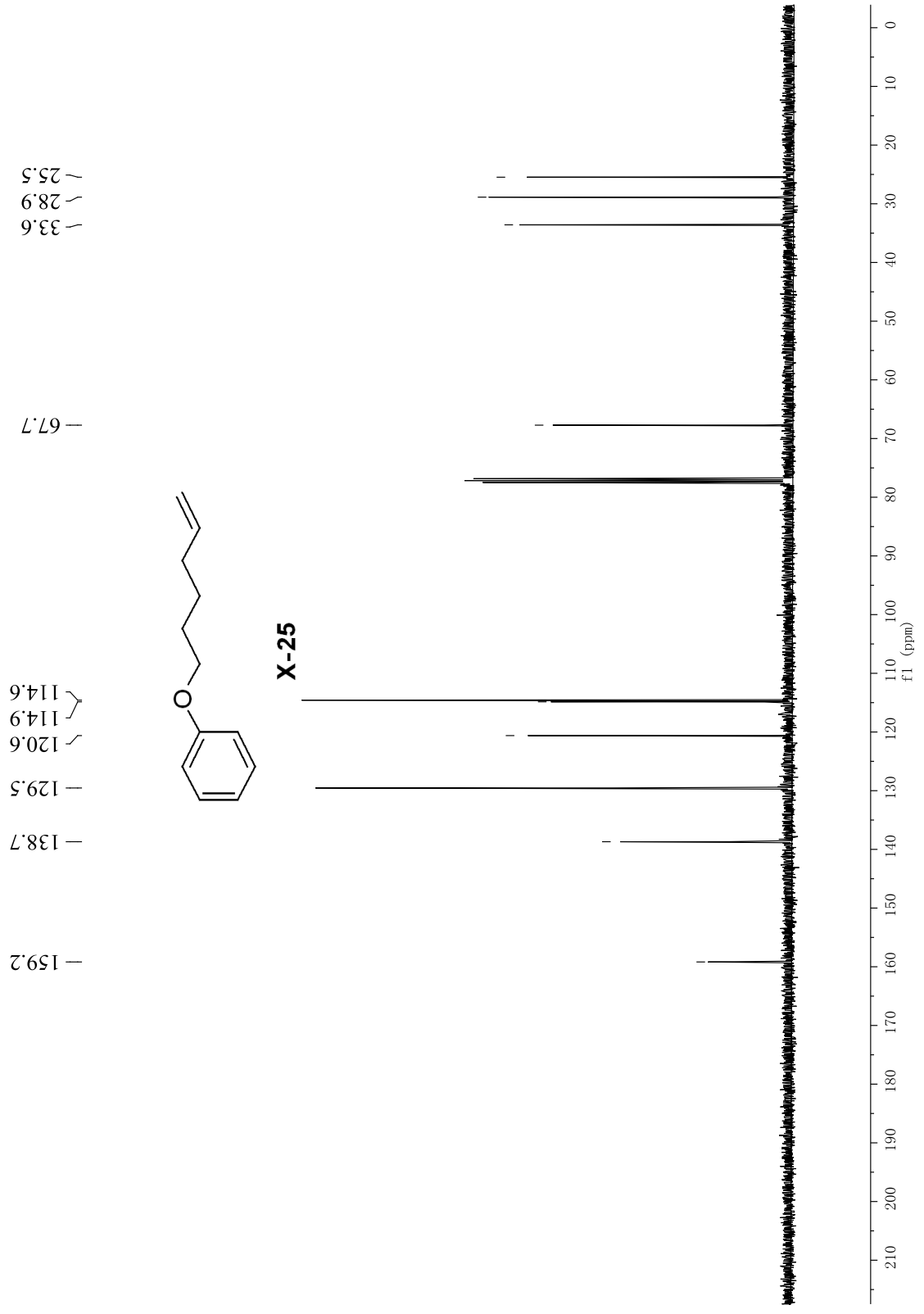
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-24**



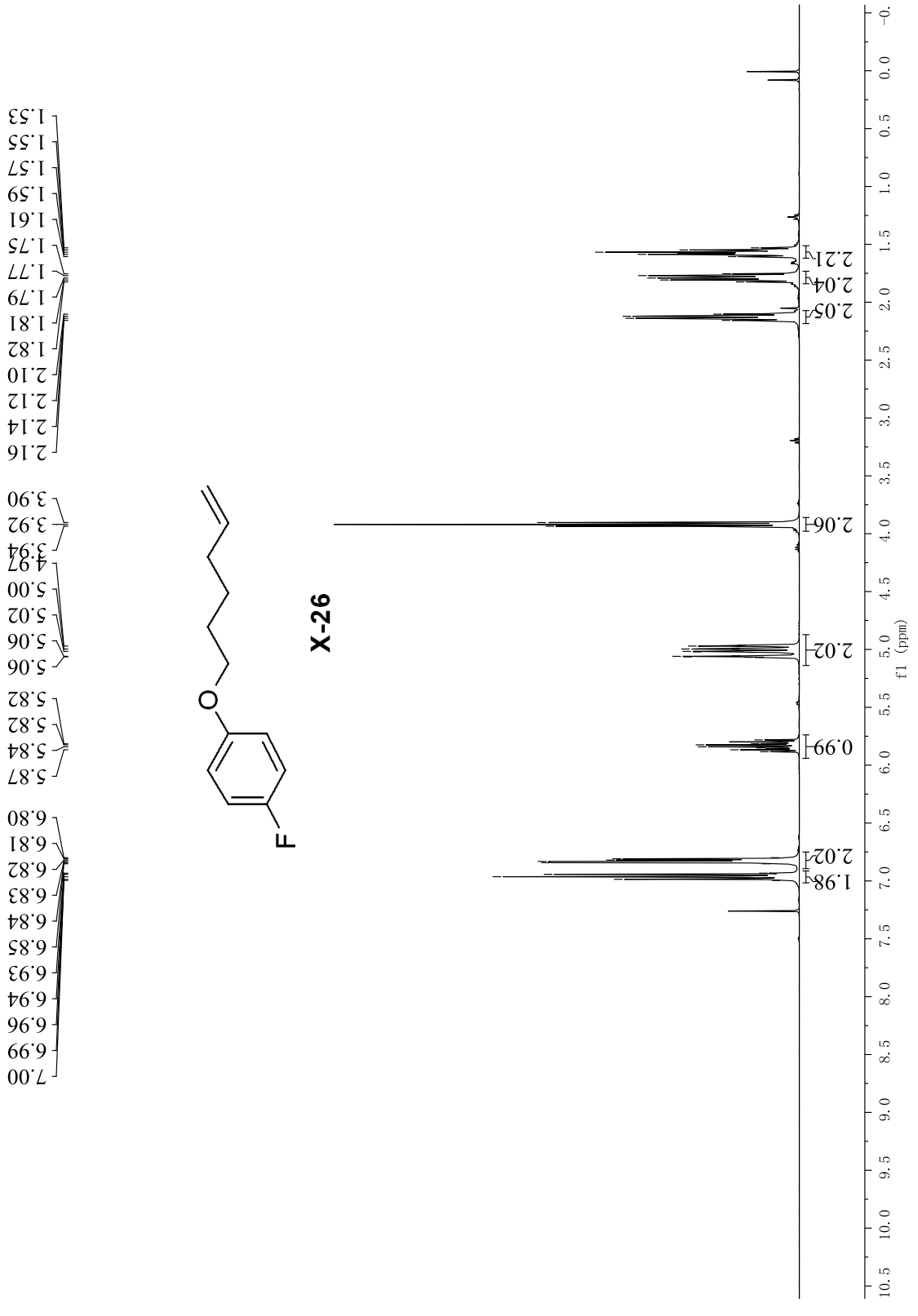
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-24**



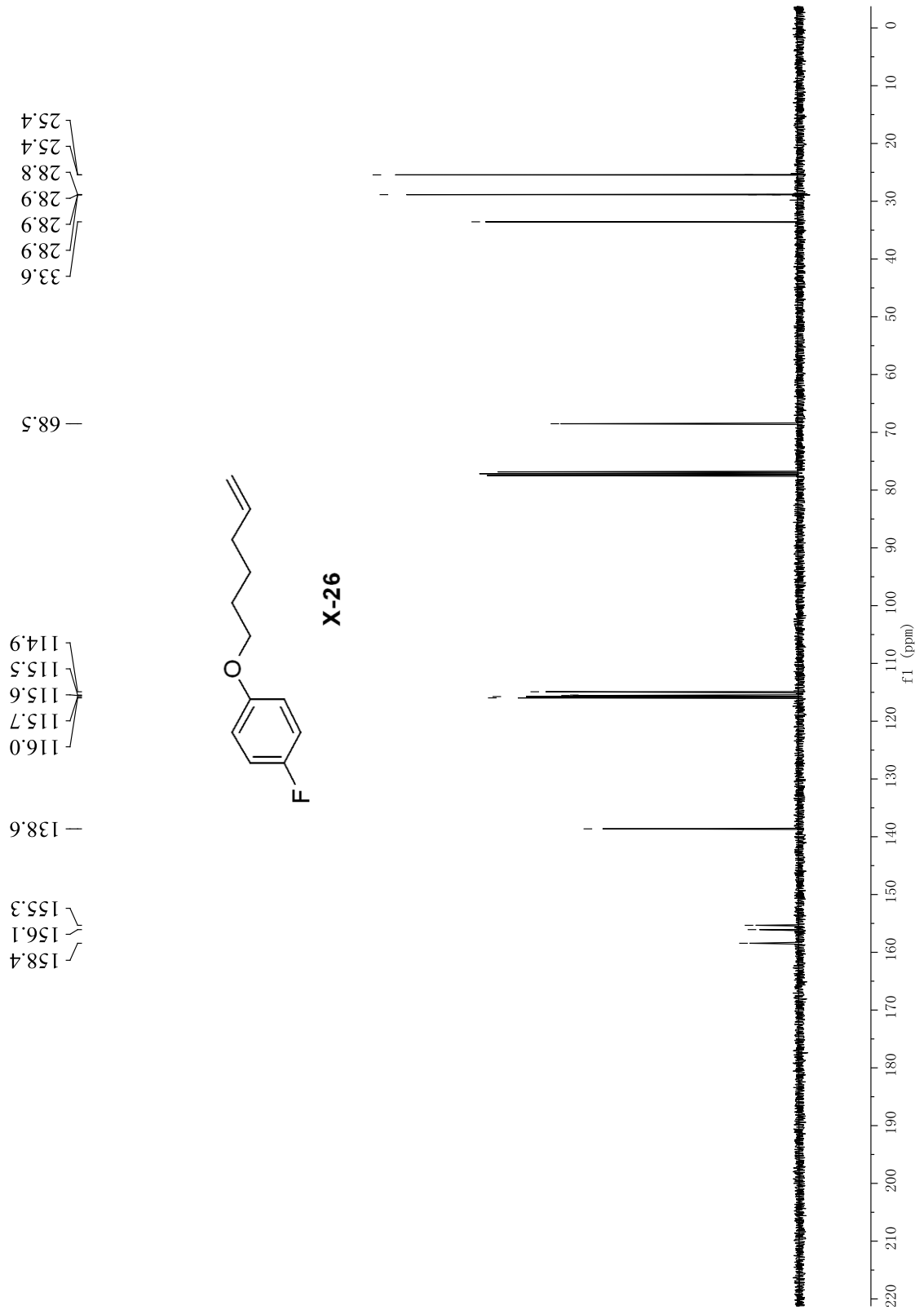
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-25**



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

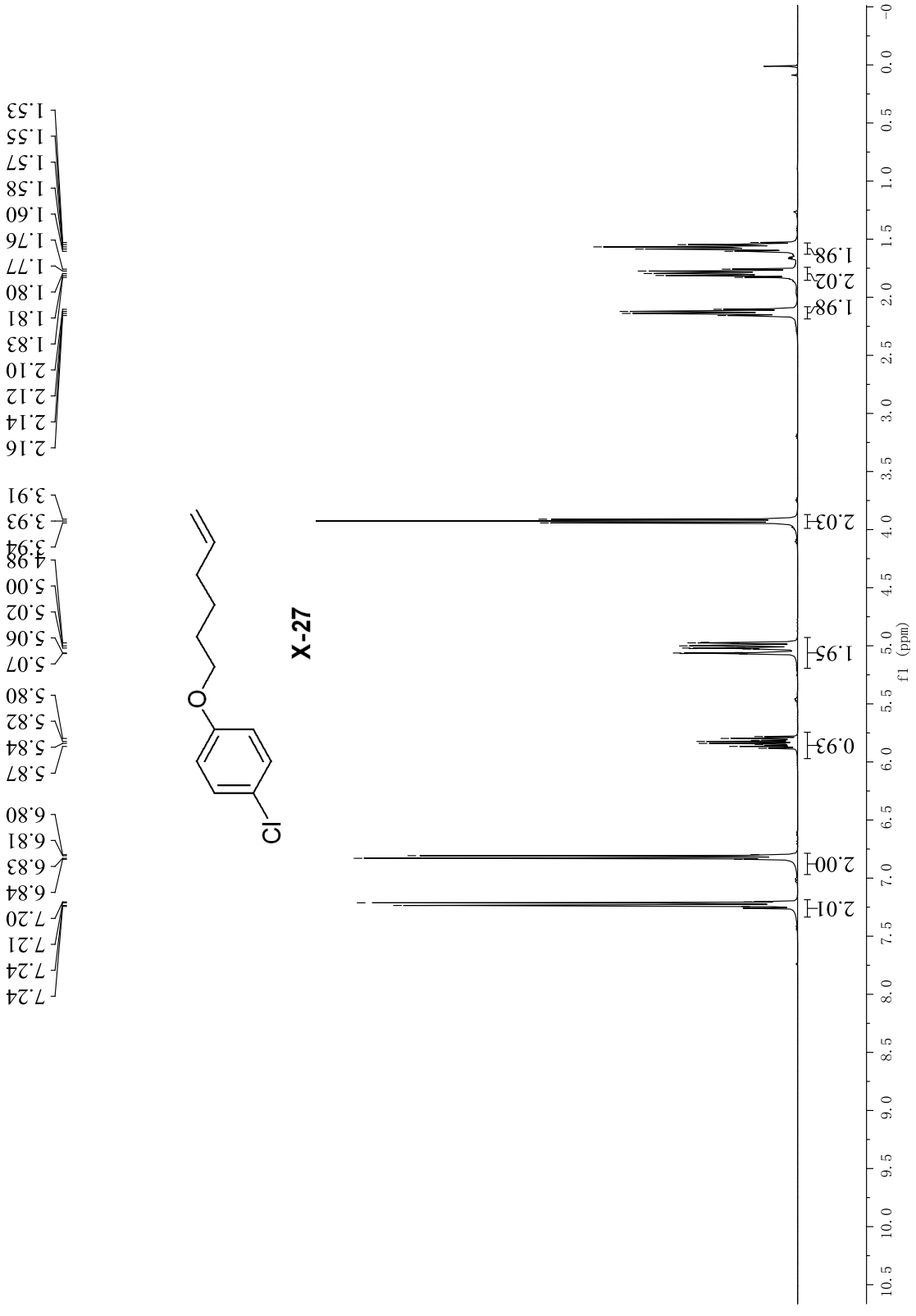


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-26**

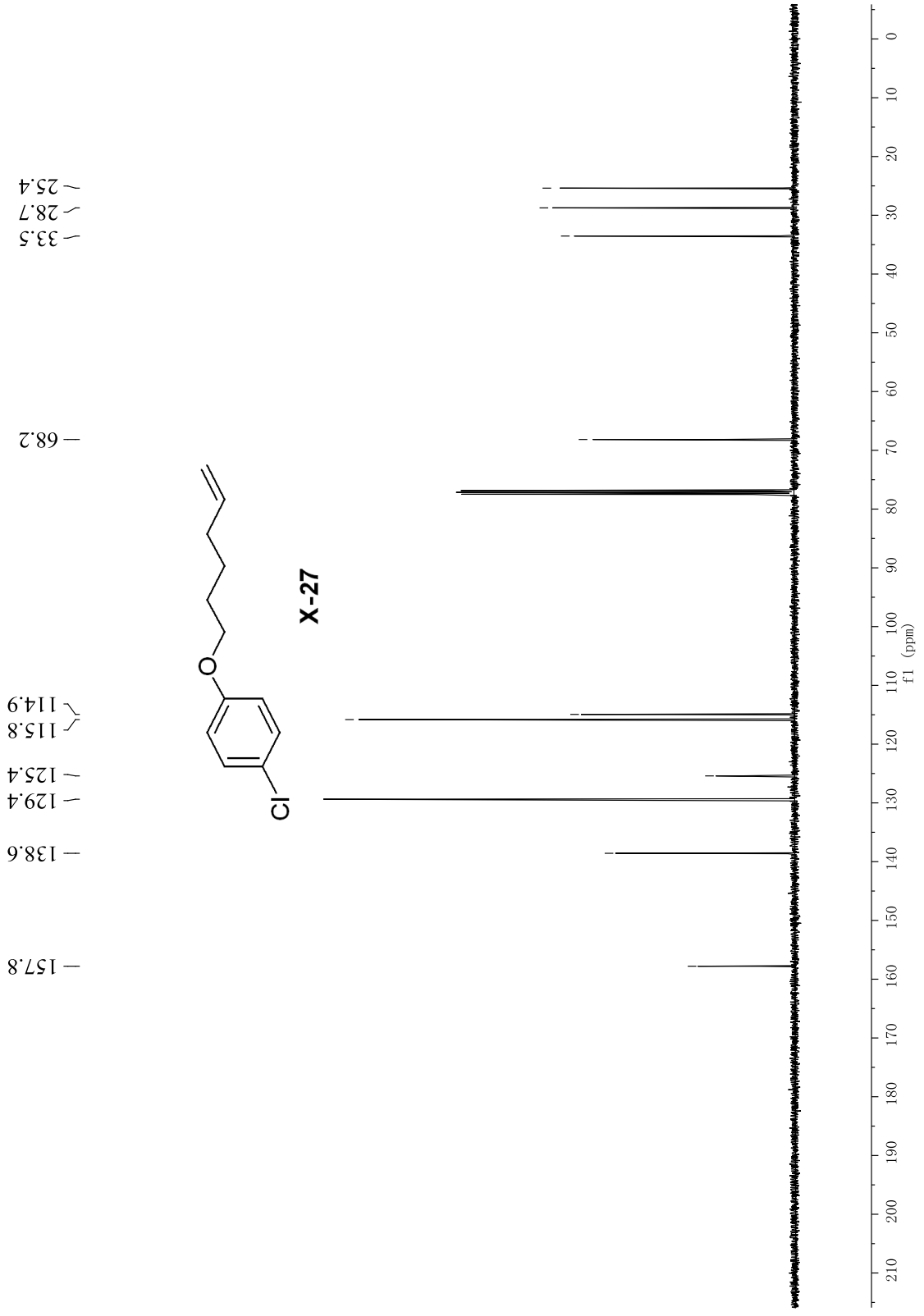


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-26**

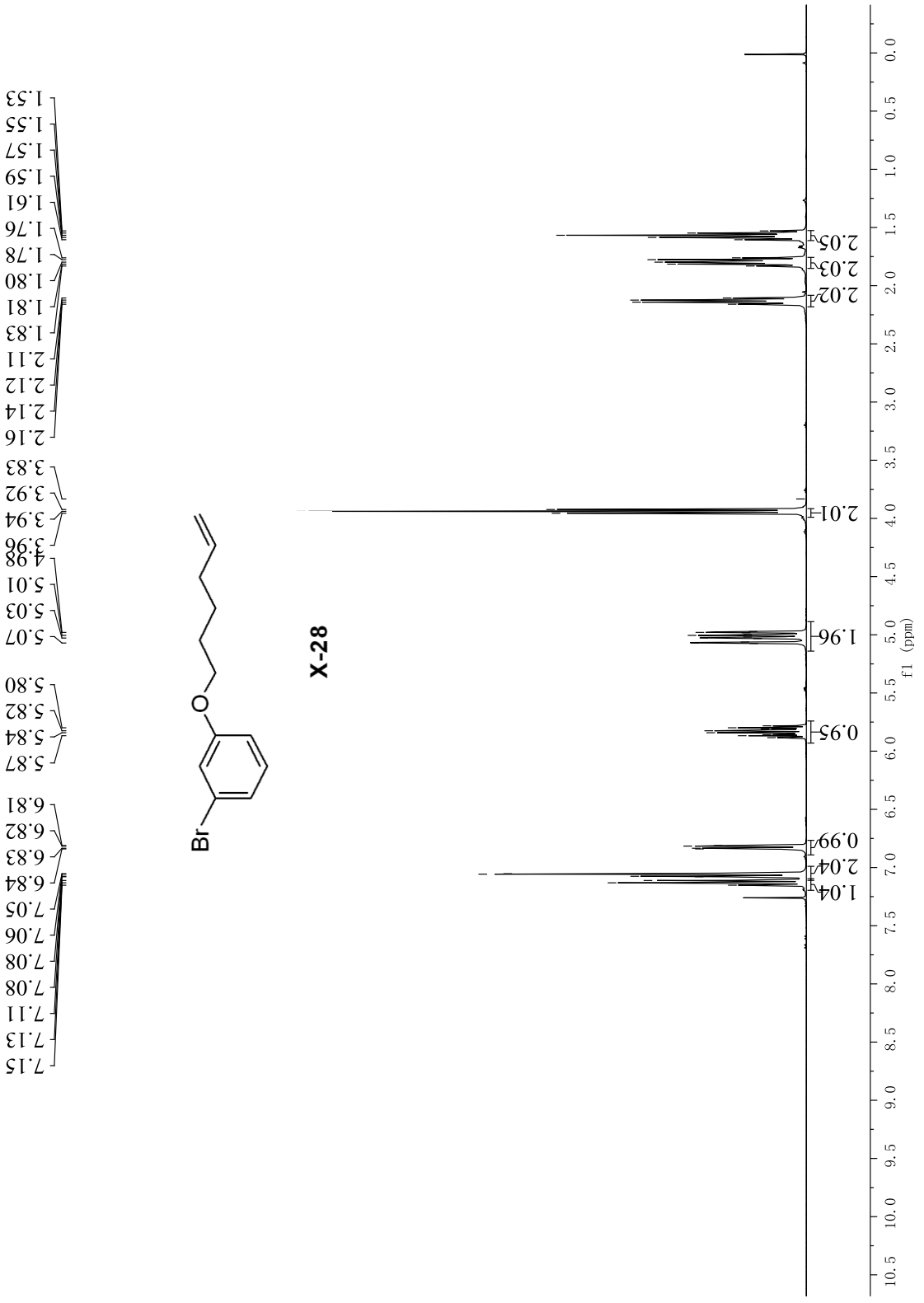
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-26**



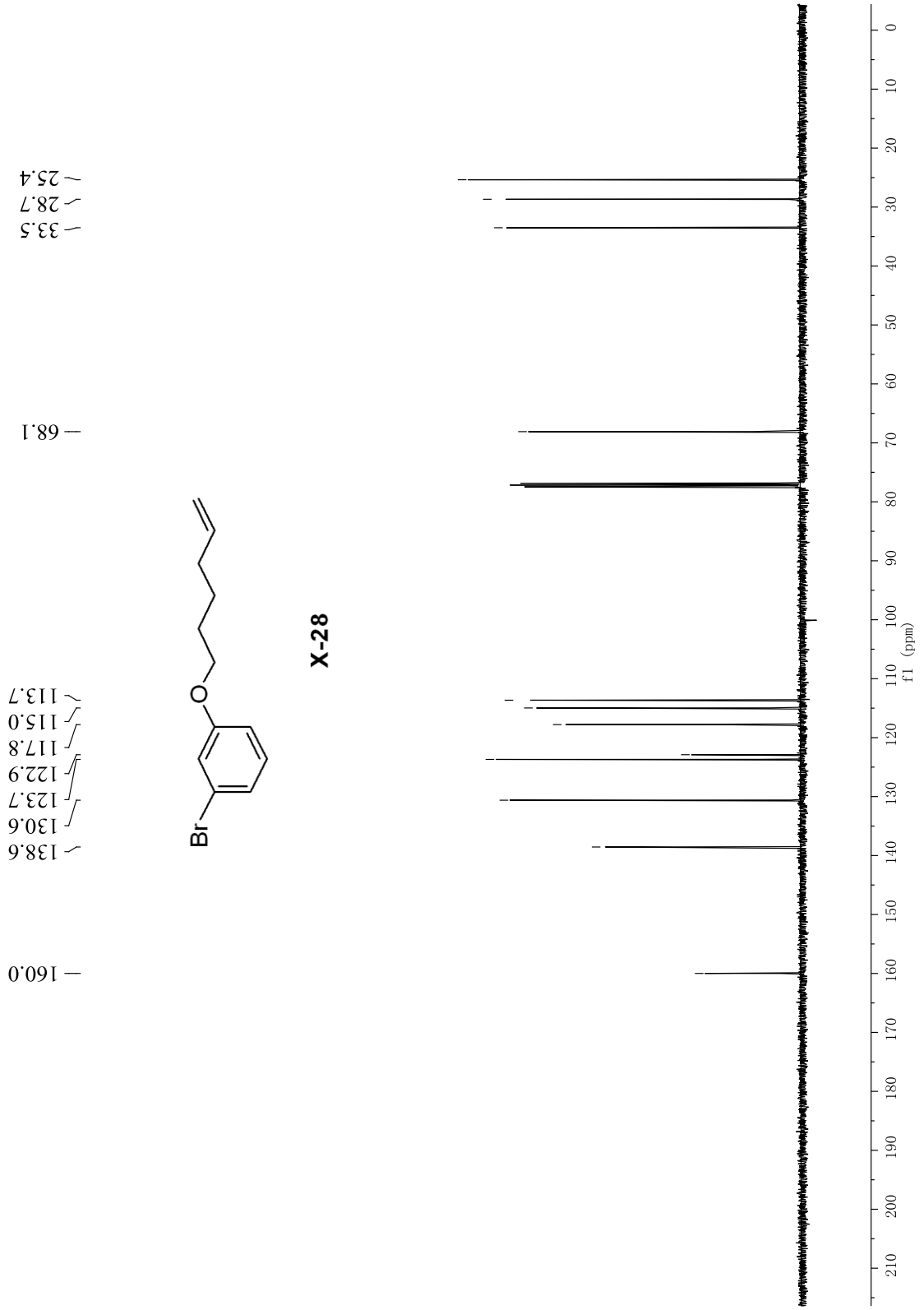
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-27**



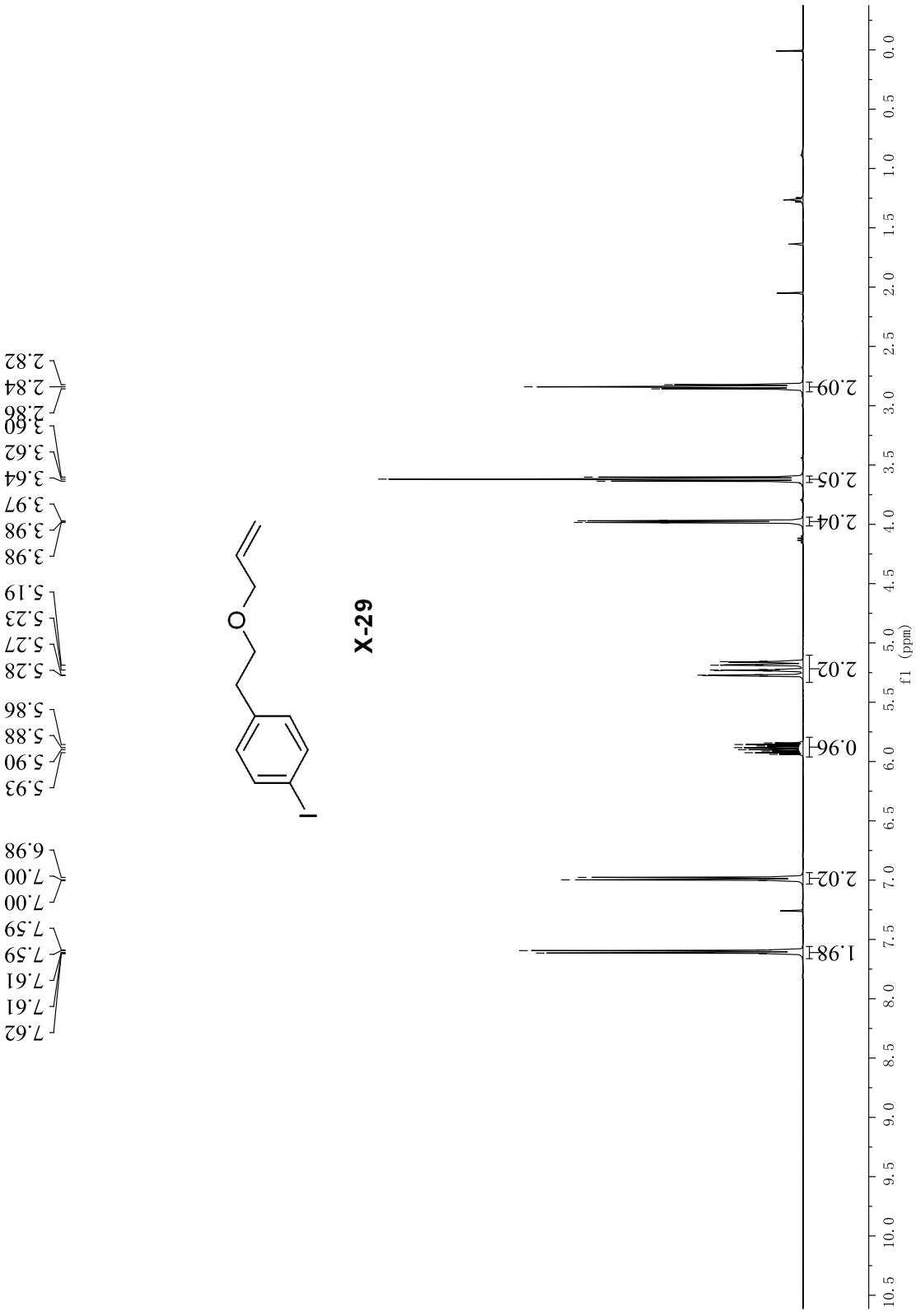
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-27**



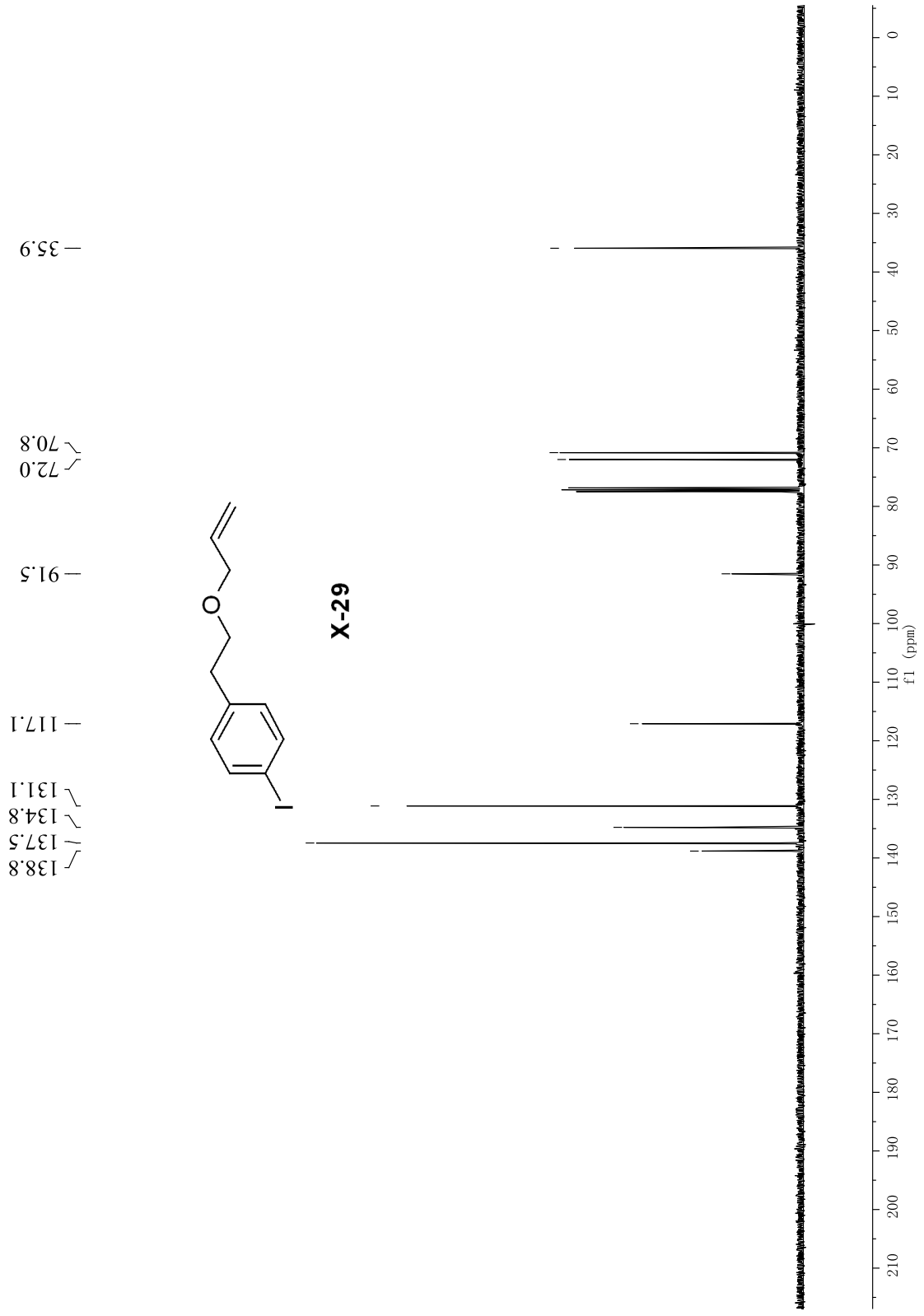
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-28**



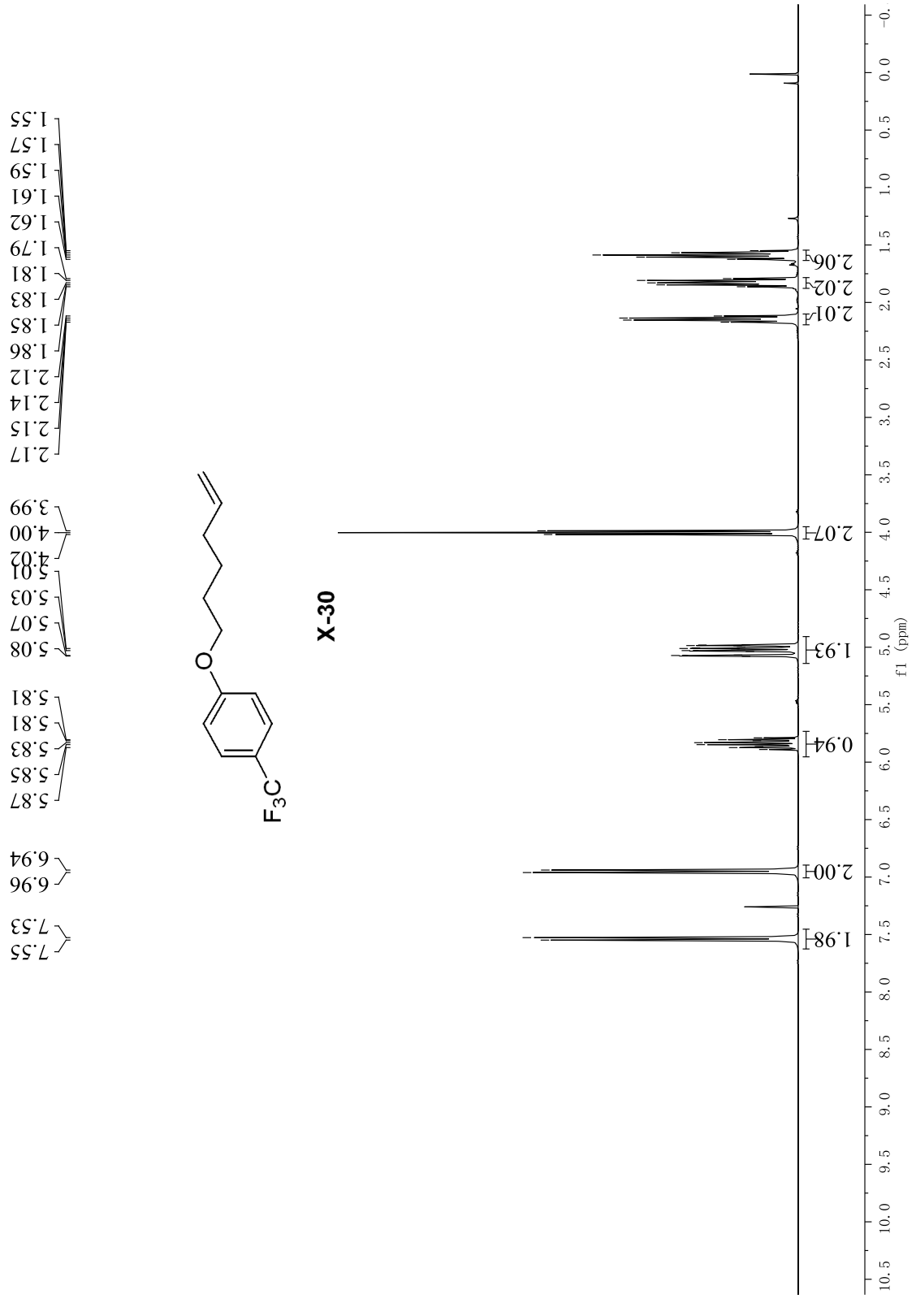
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-28**



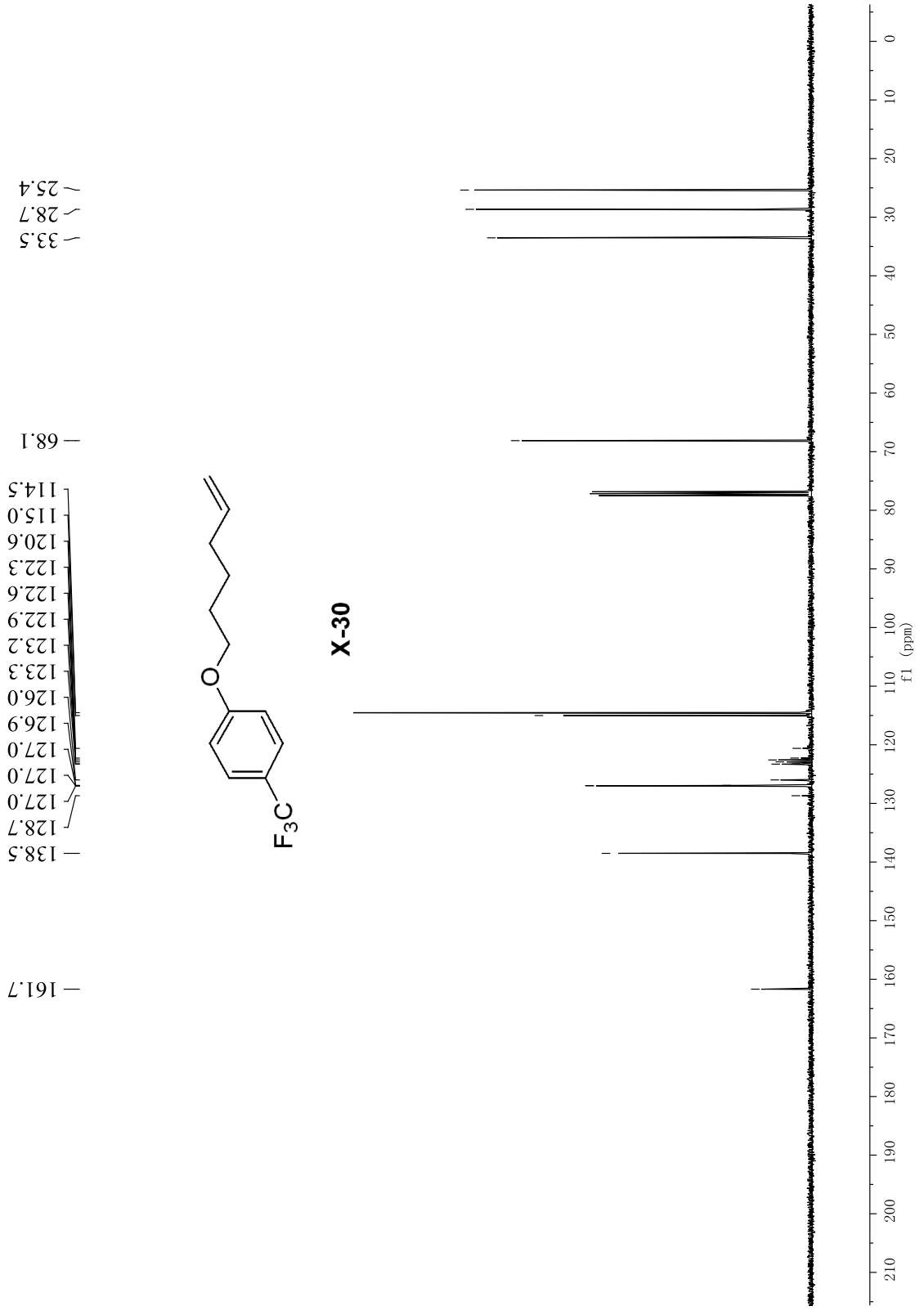
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-29**



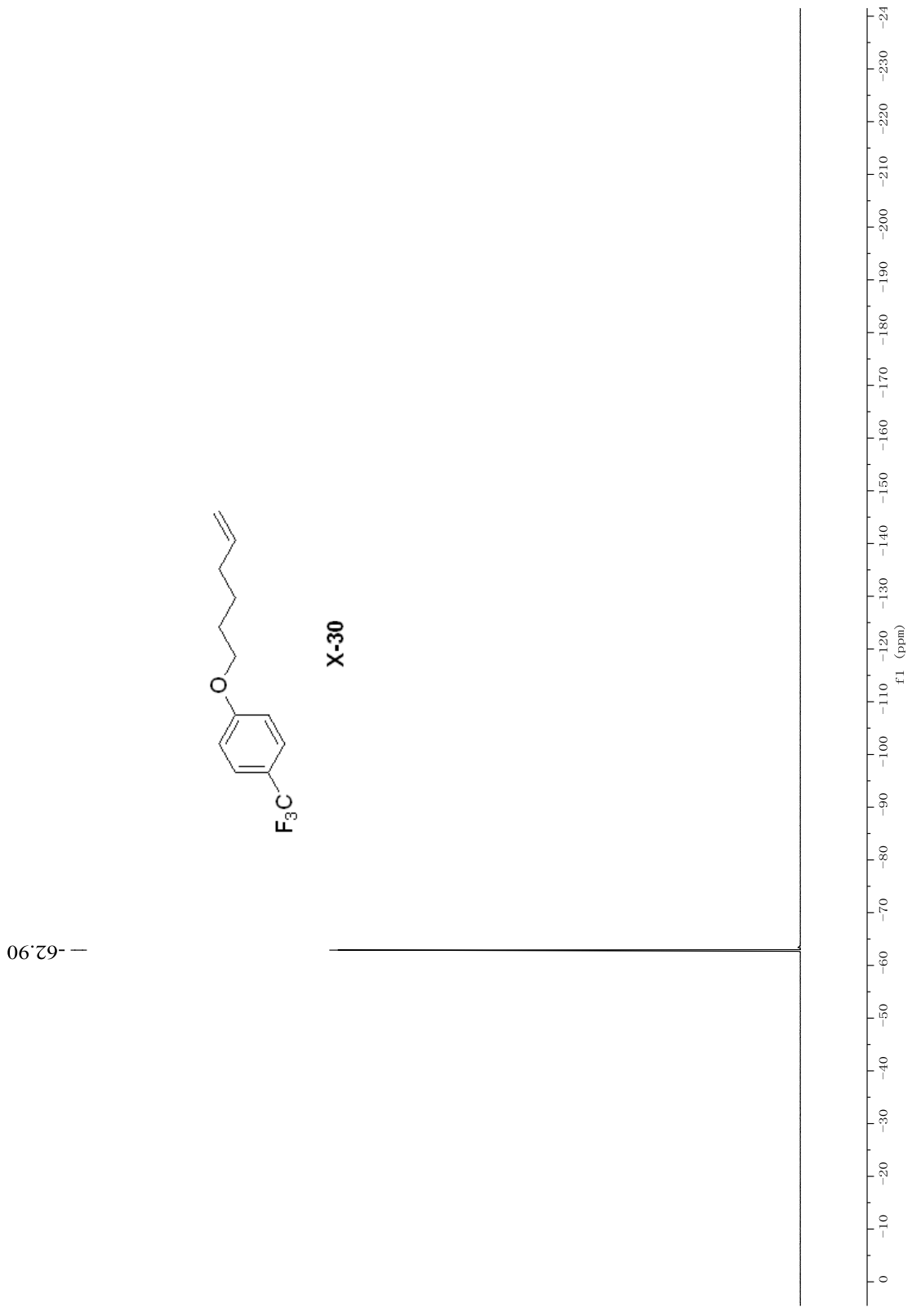
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-29**



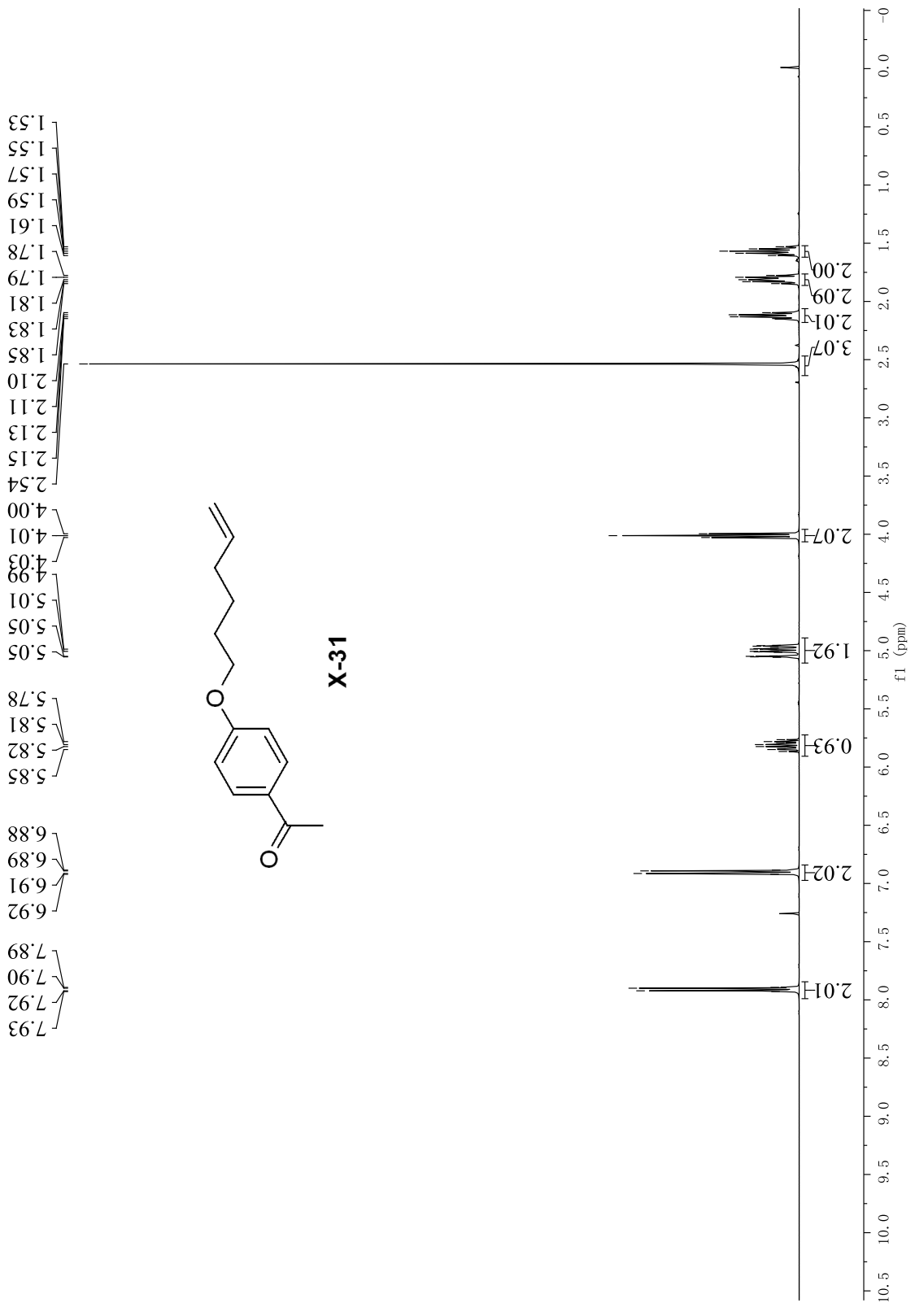
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-30**



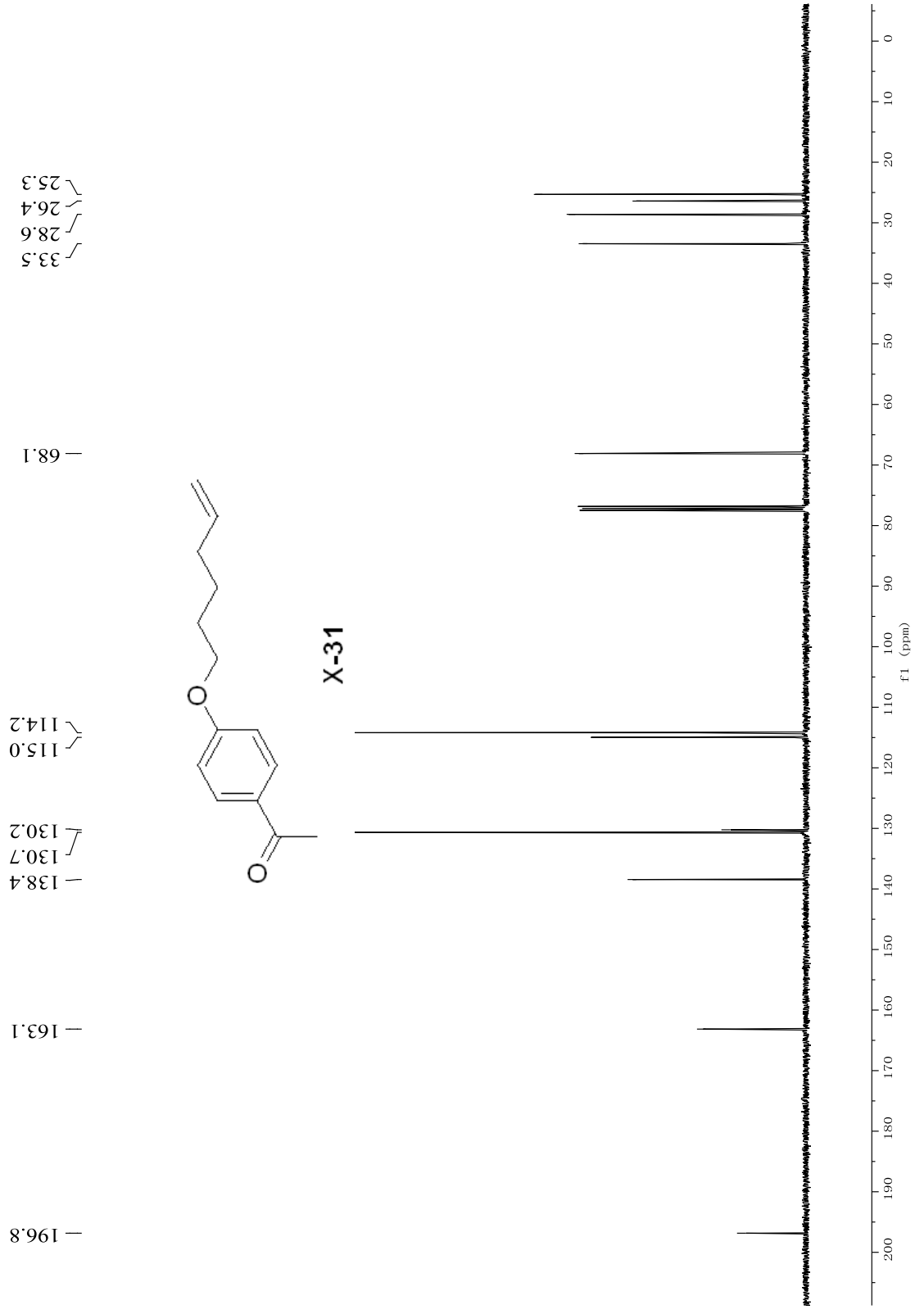
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-30**



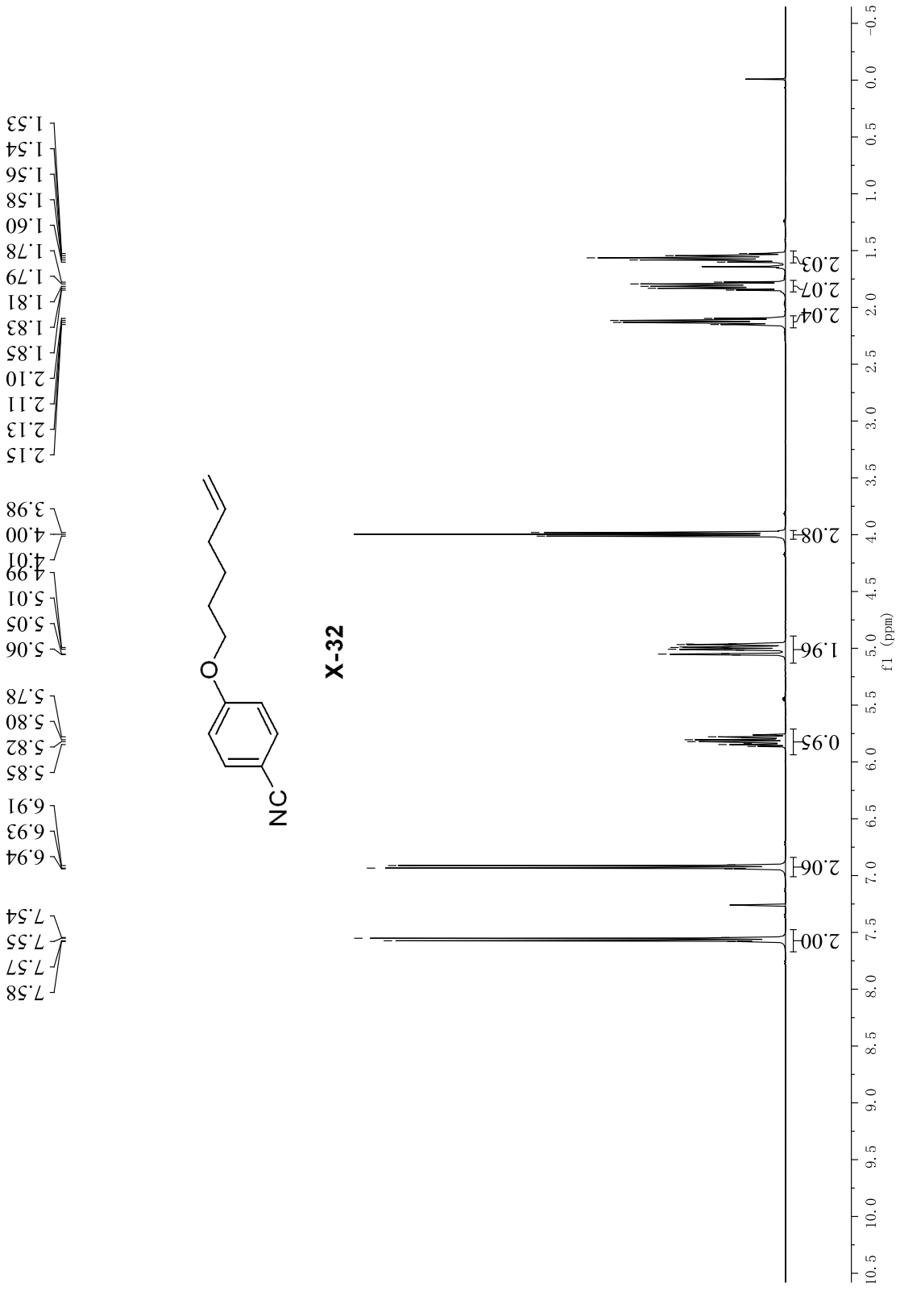
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-30**



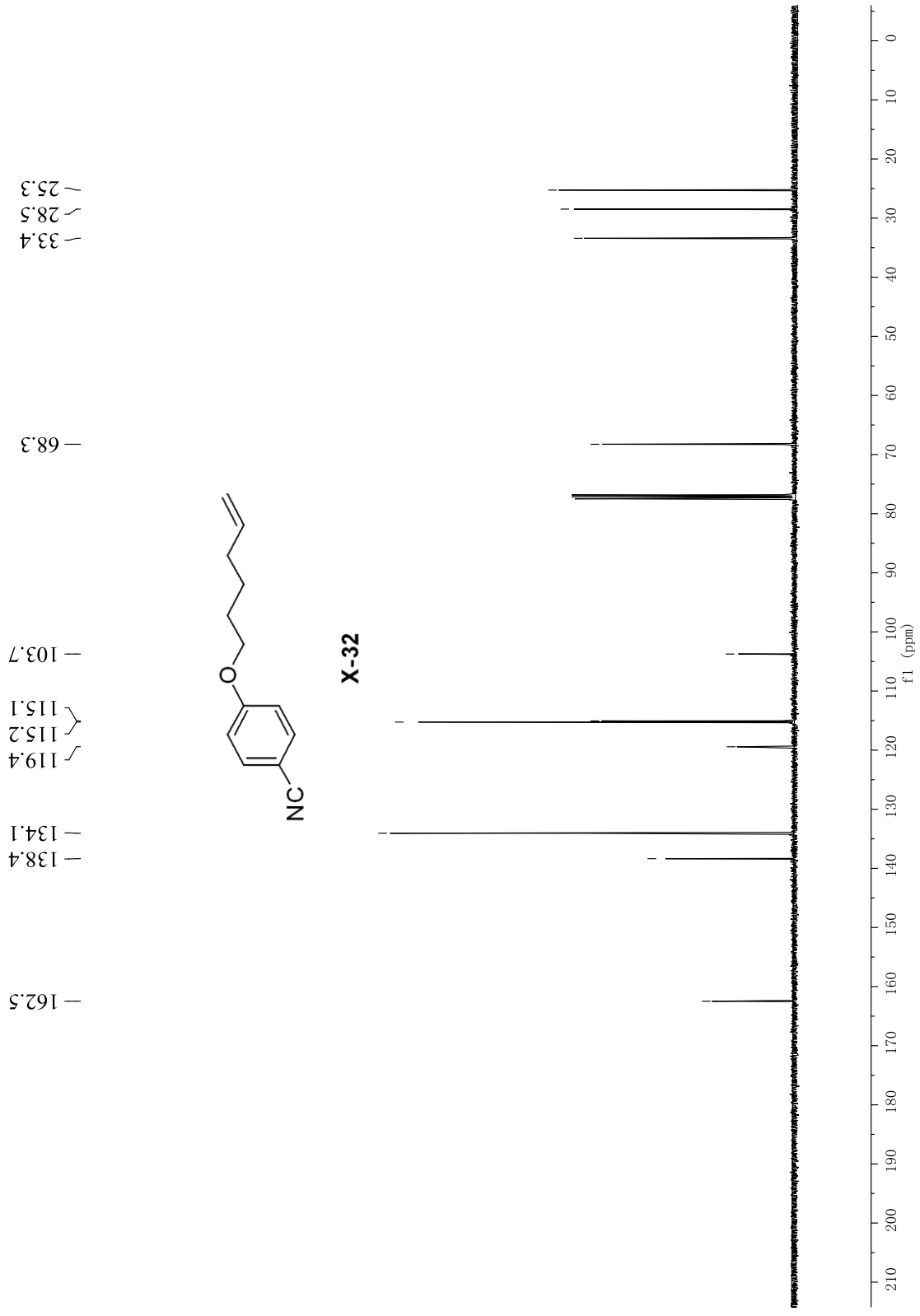
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-31**



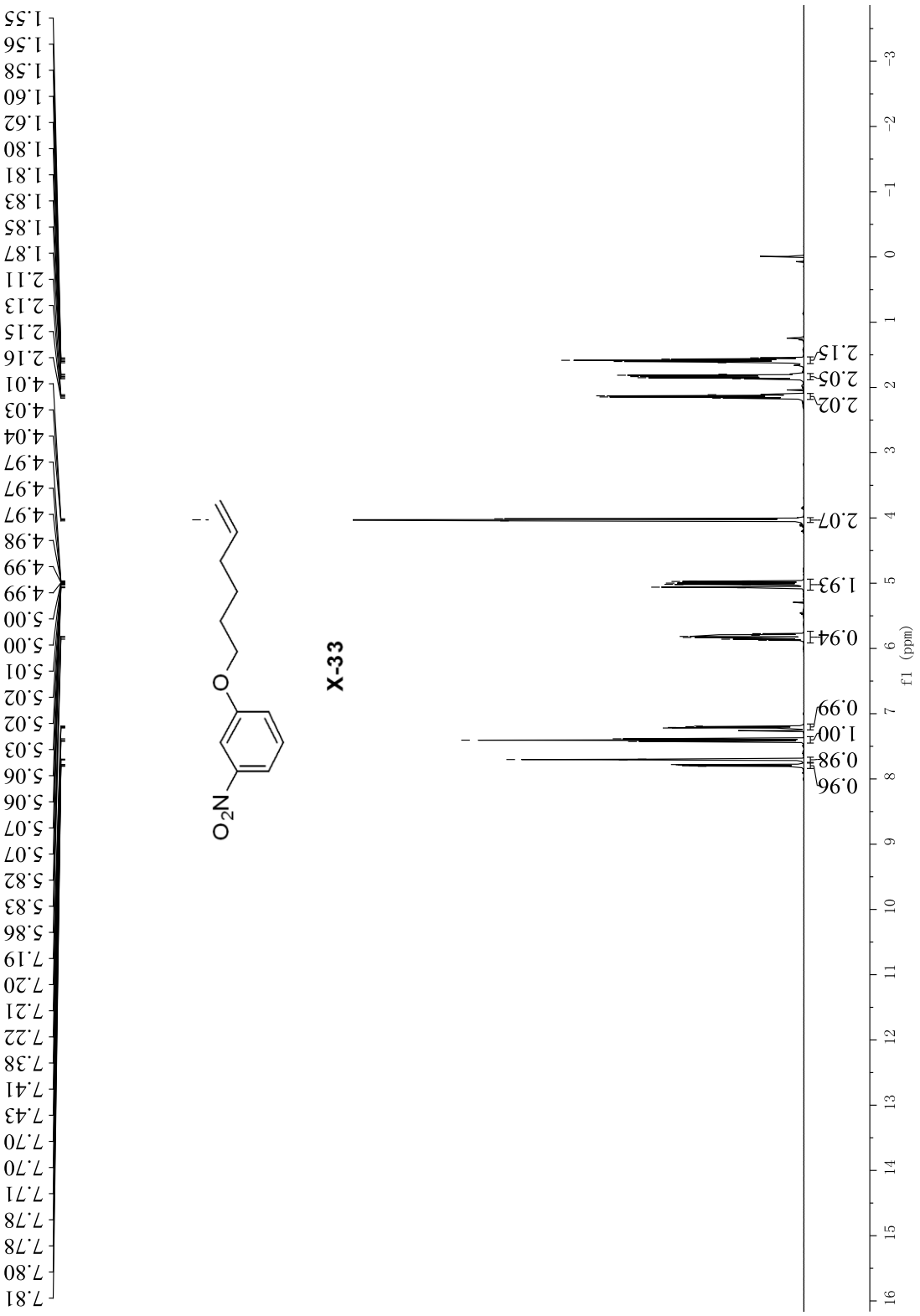
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-31**



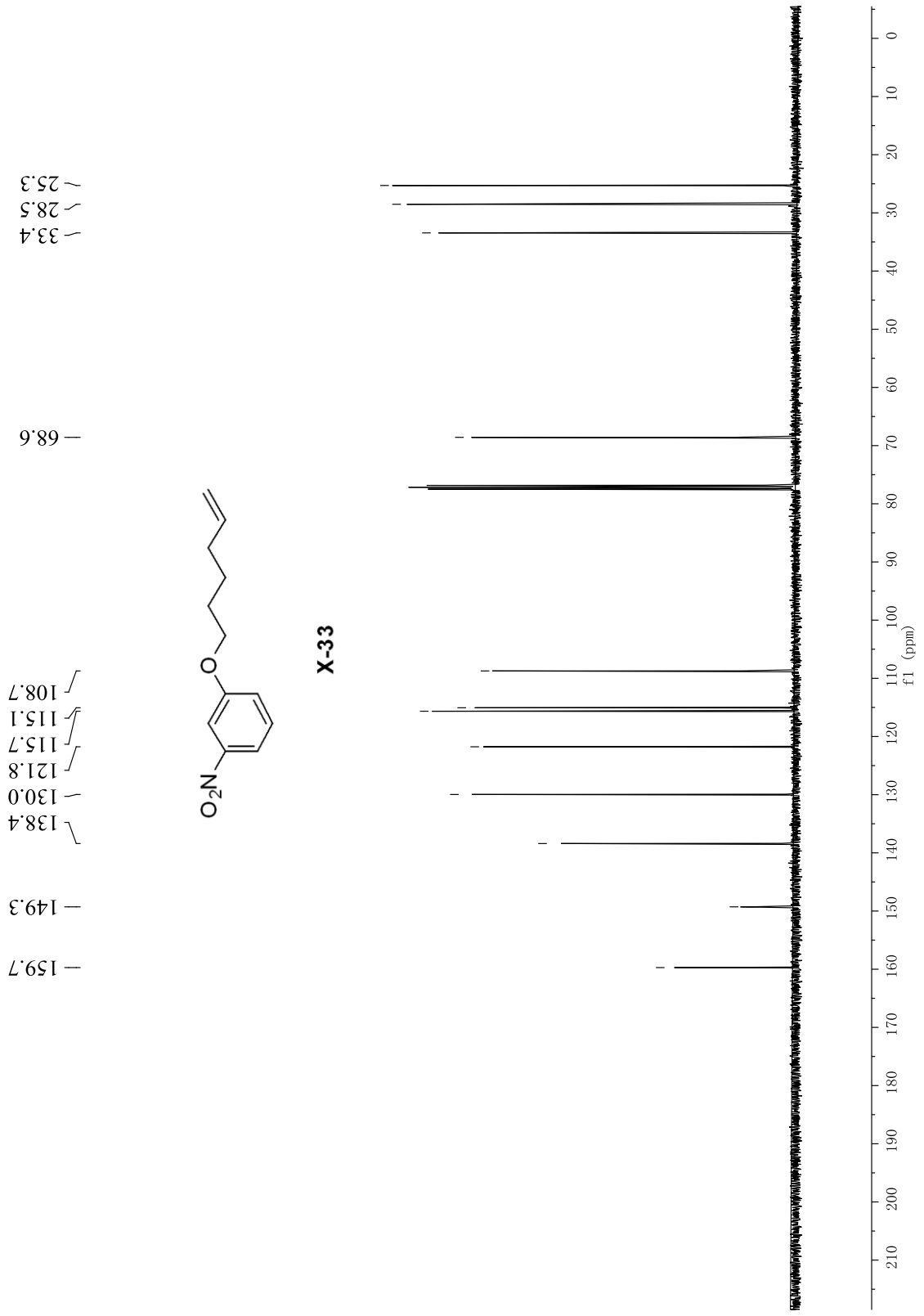
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-32**



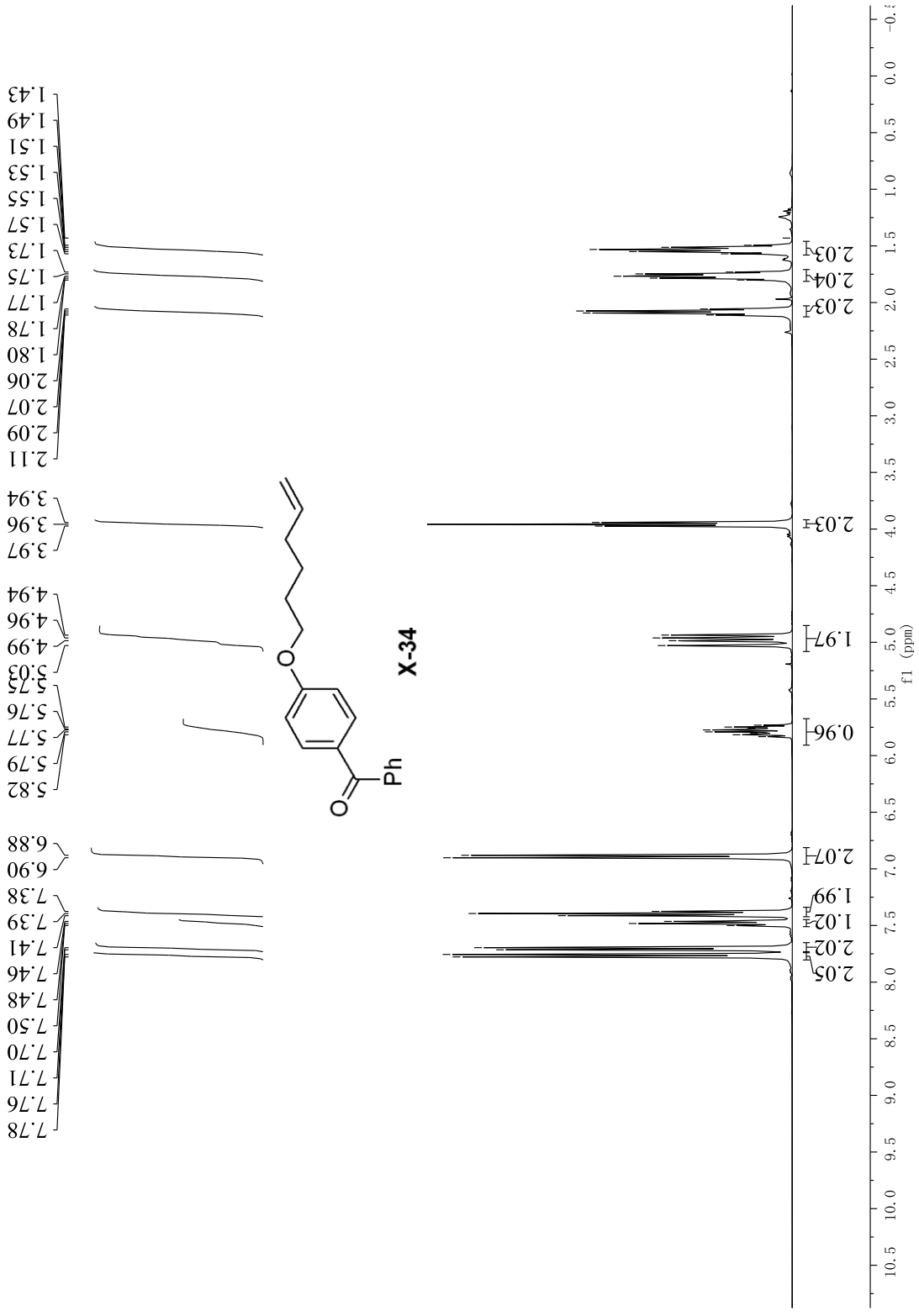
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-32**



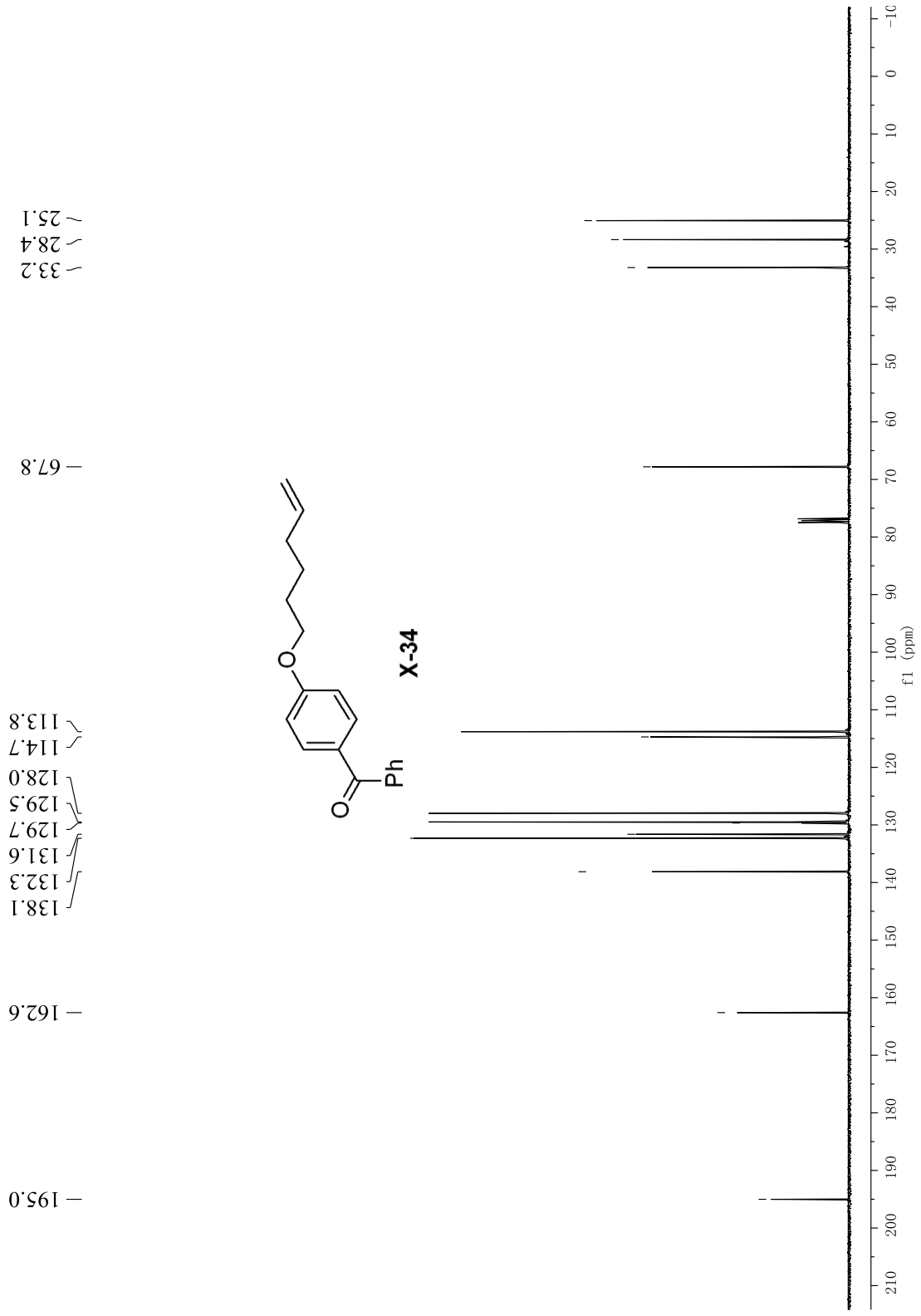
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-33**



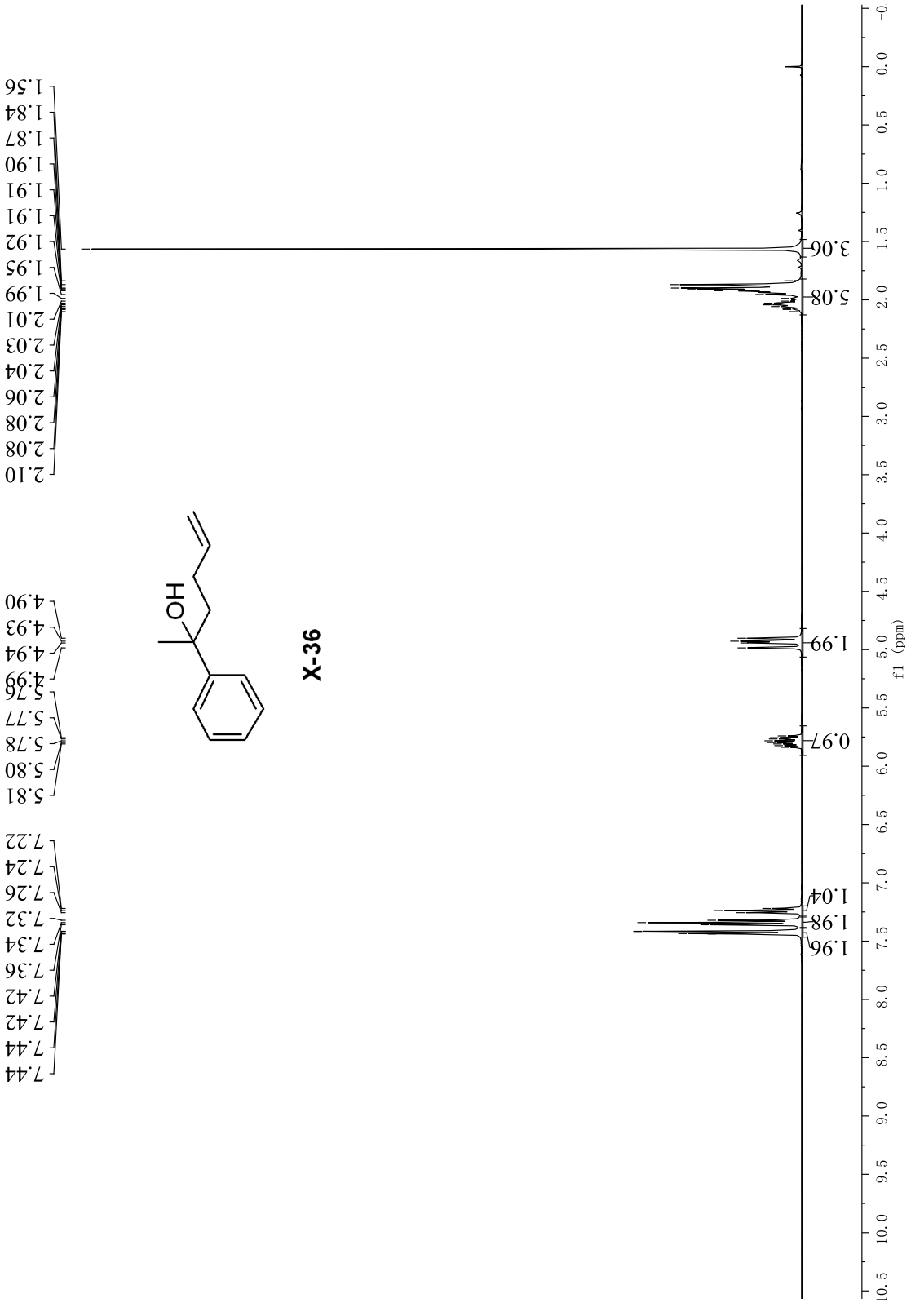
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-33**



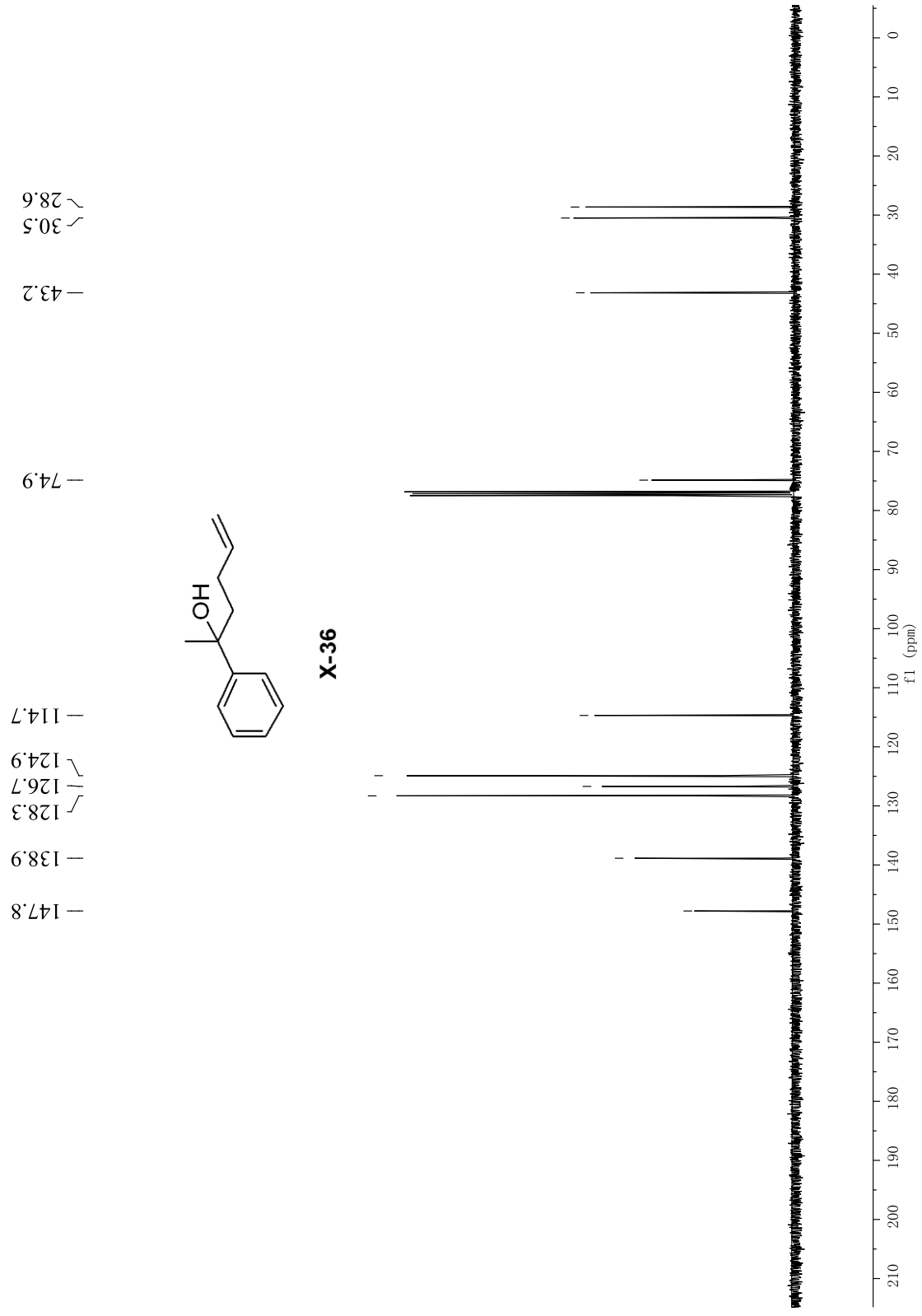
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-34**



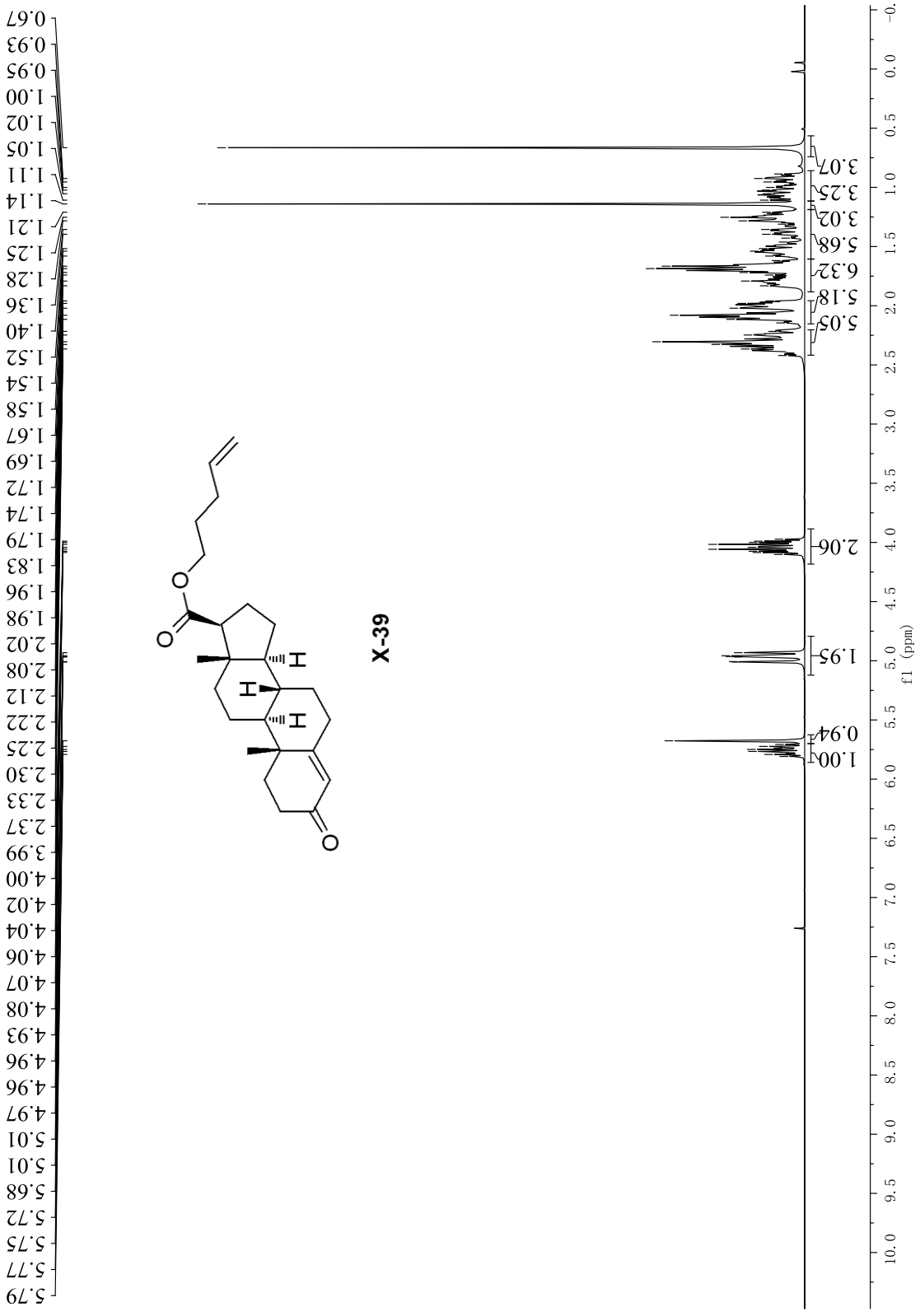
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-34**



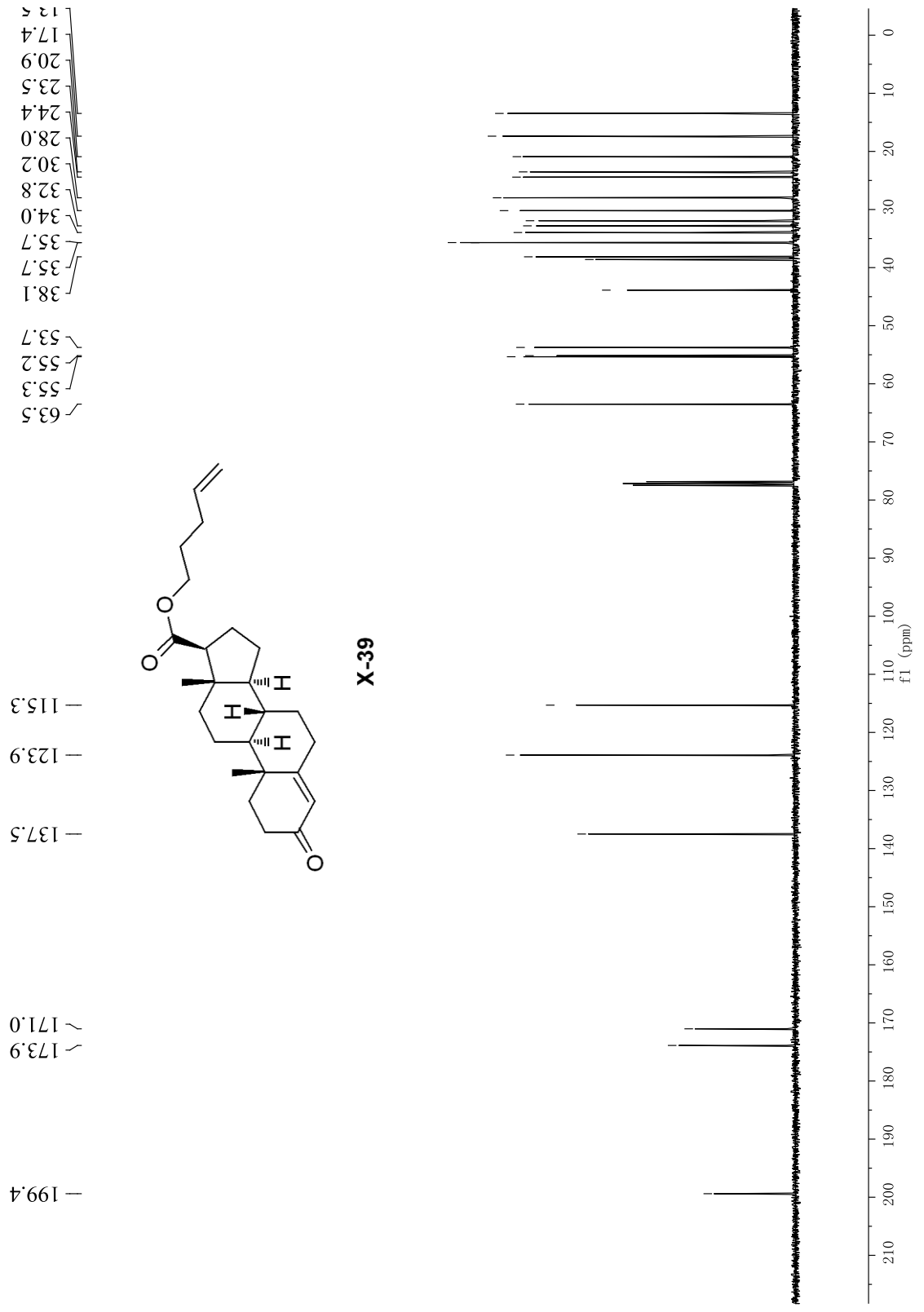
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-36**



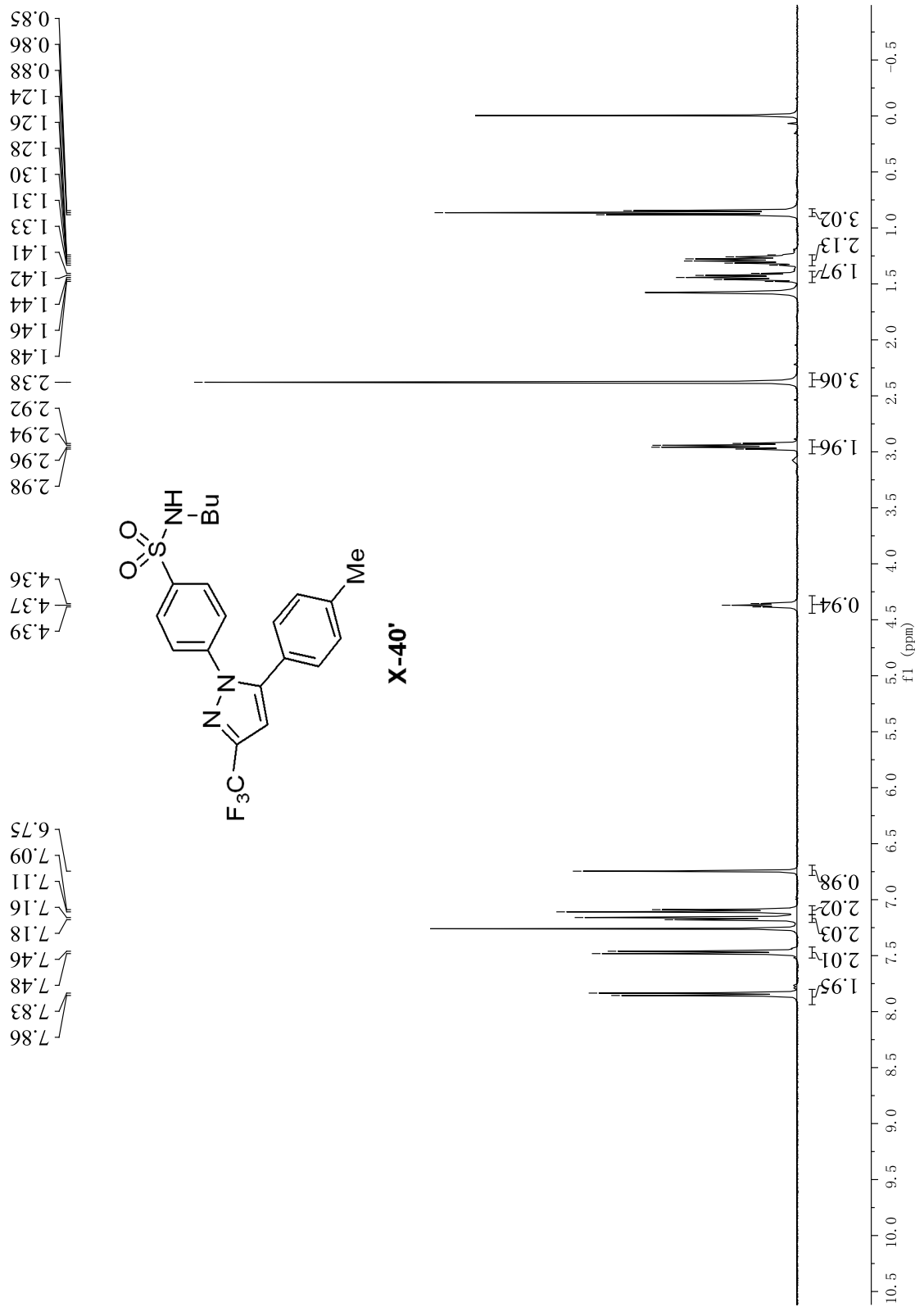
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-36**



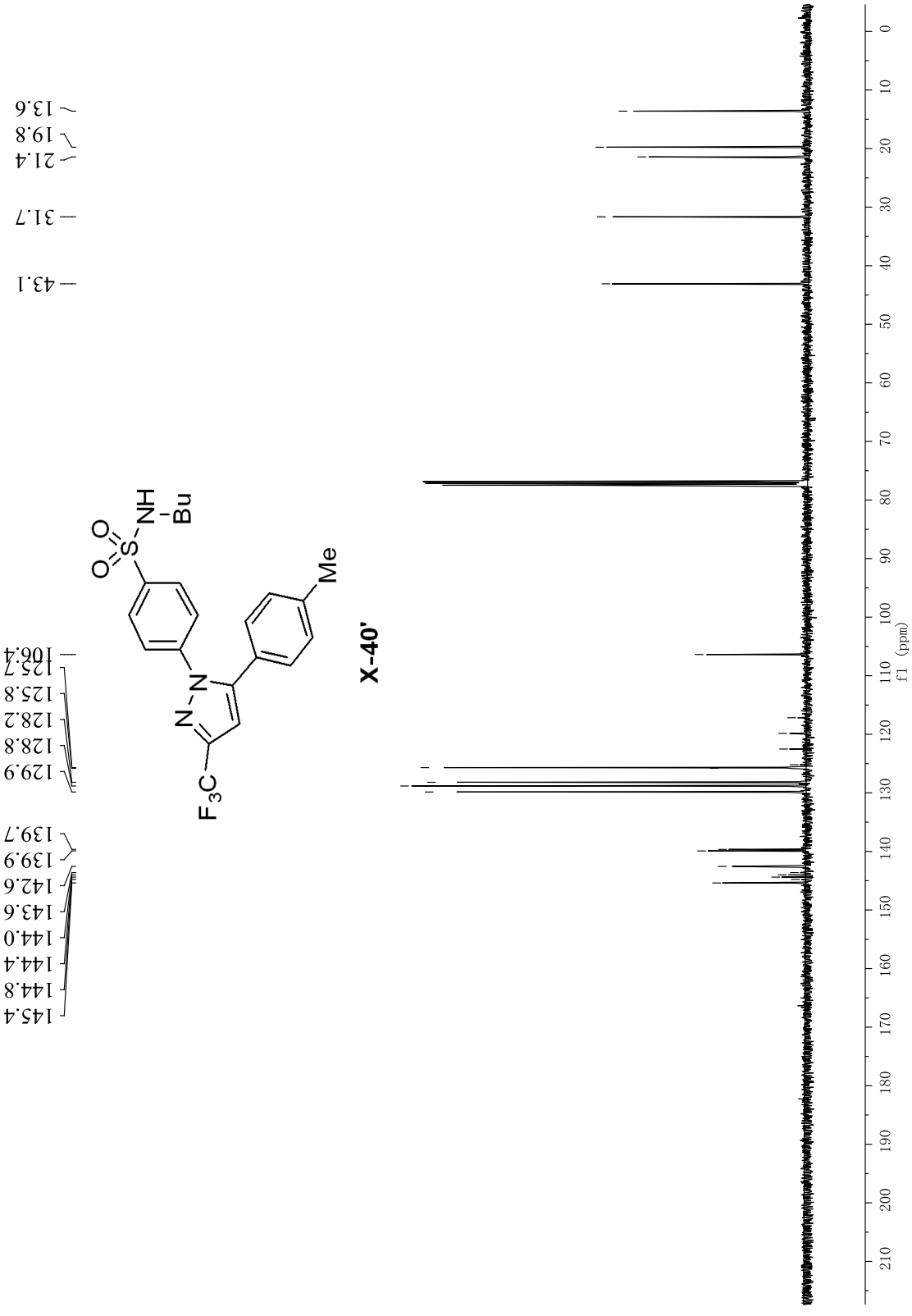
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-39**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-39**

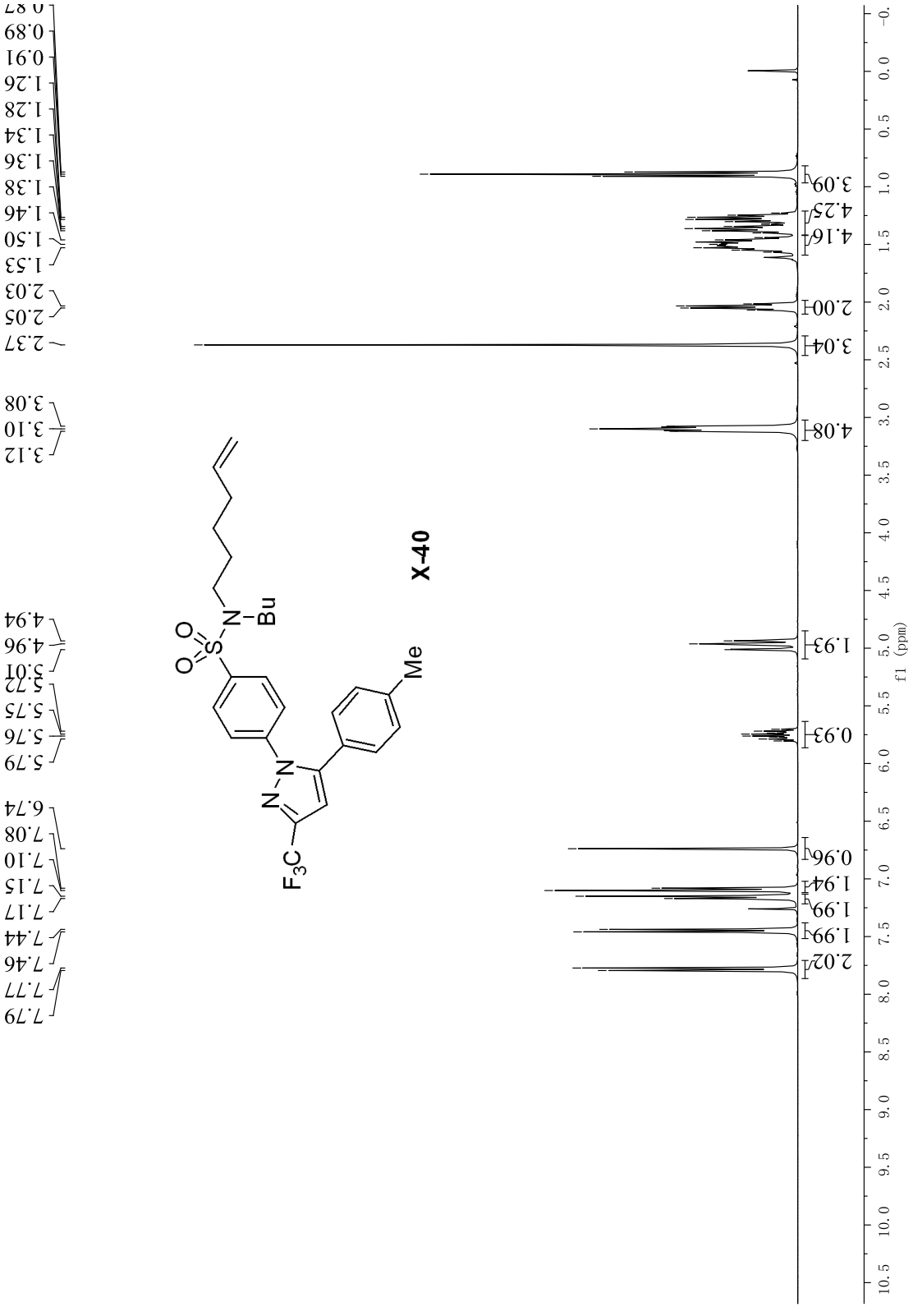


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-40'**

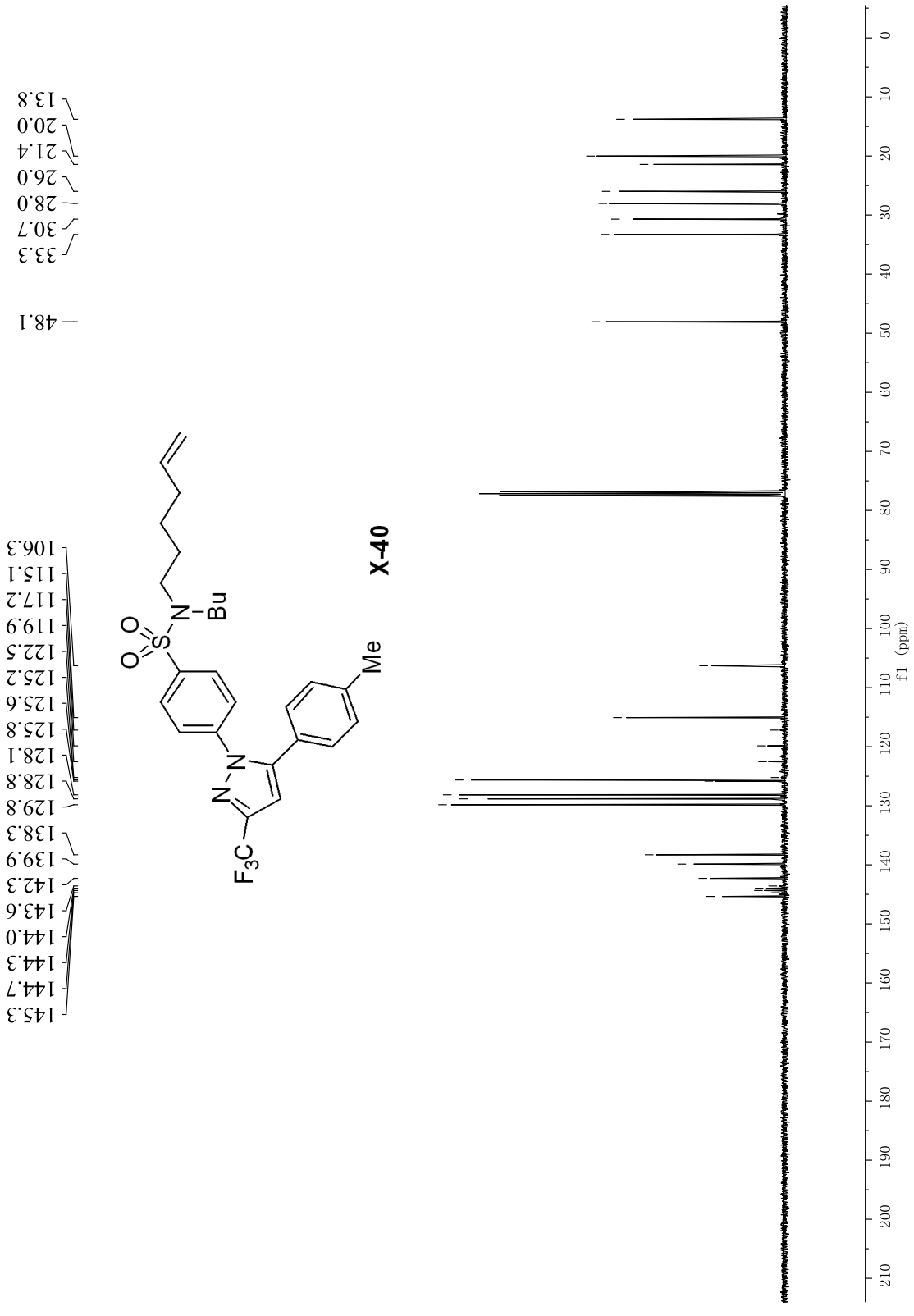


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-40'**

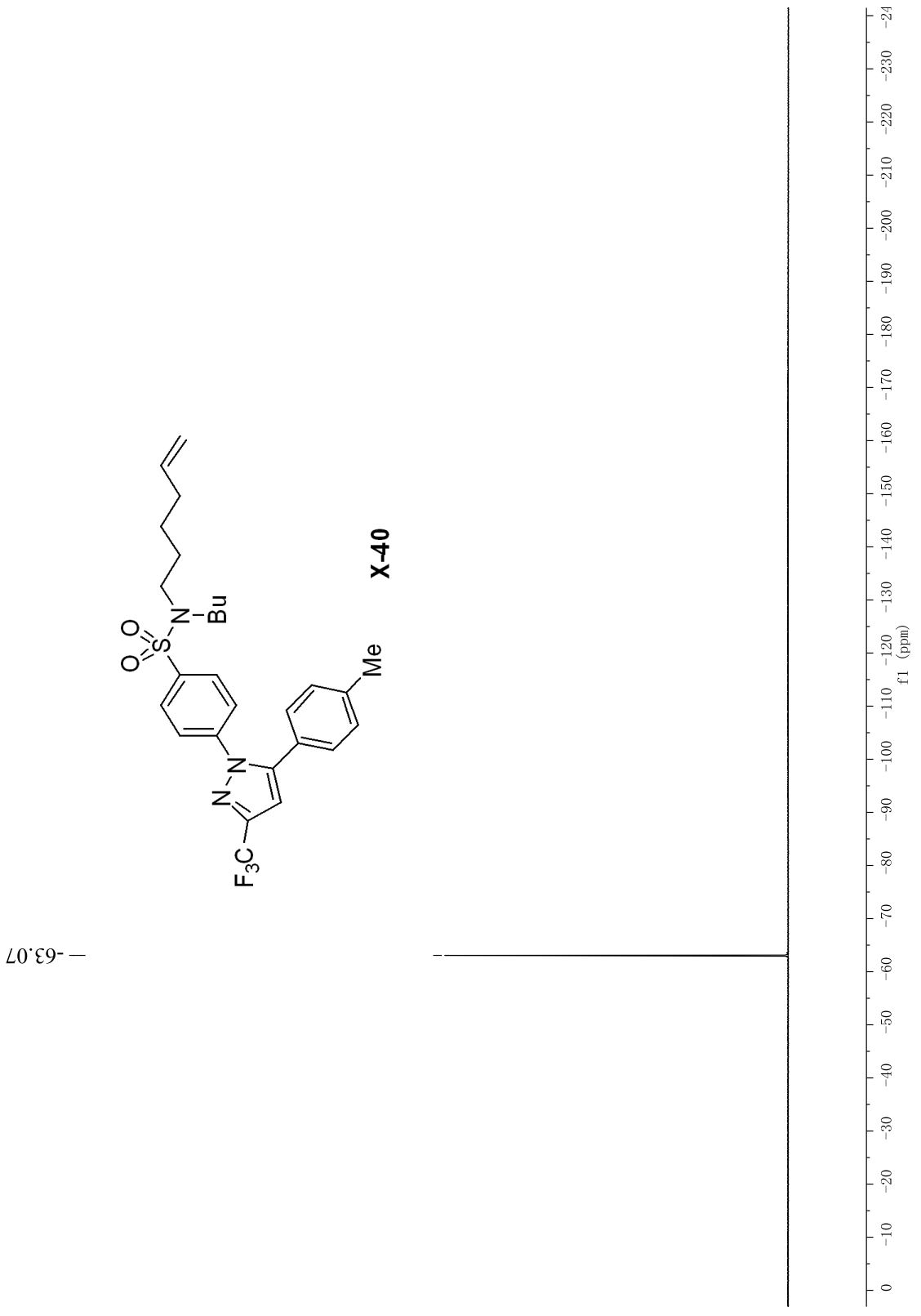
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-40'**



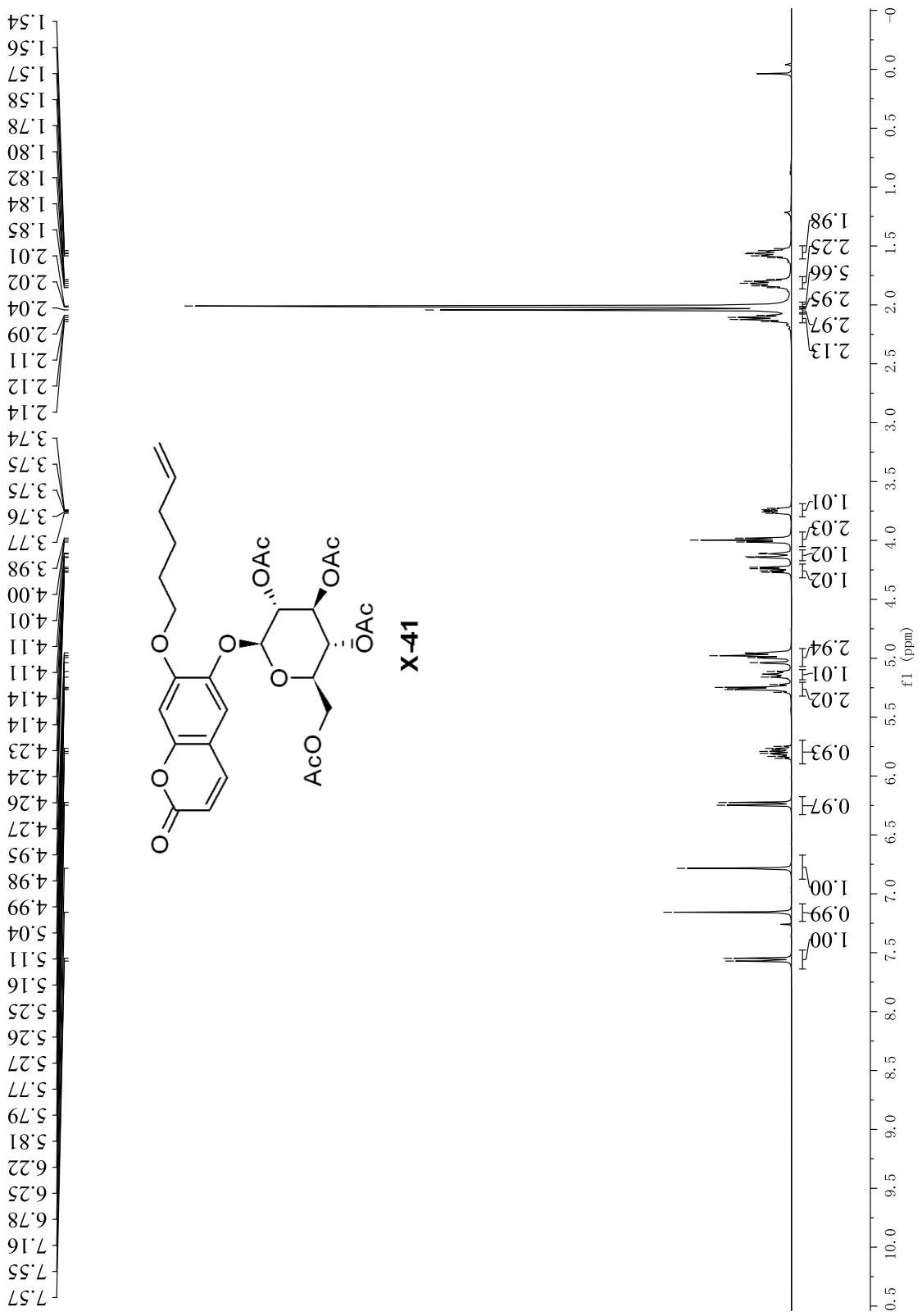
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-40**



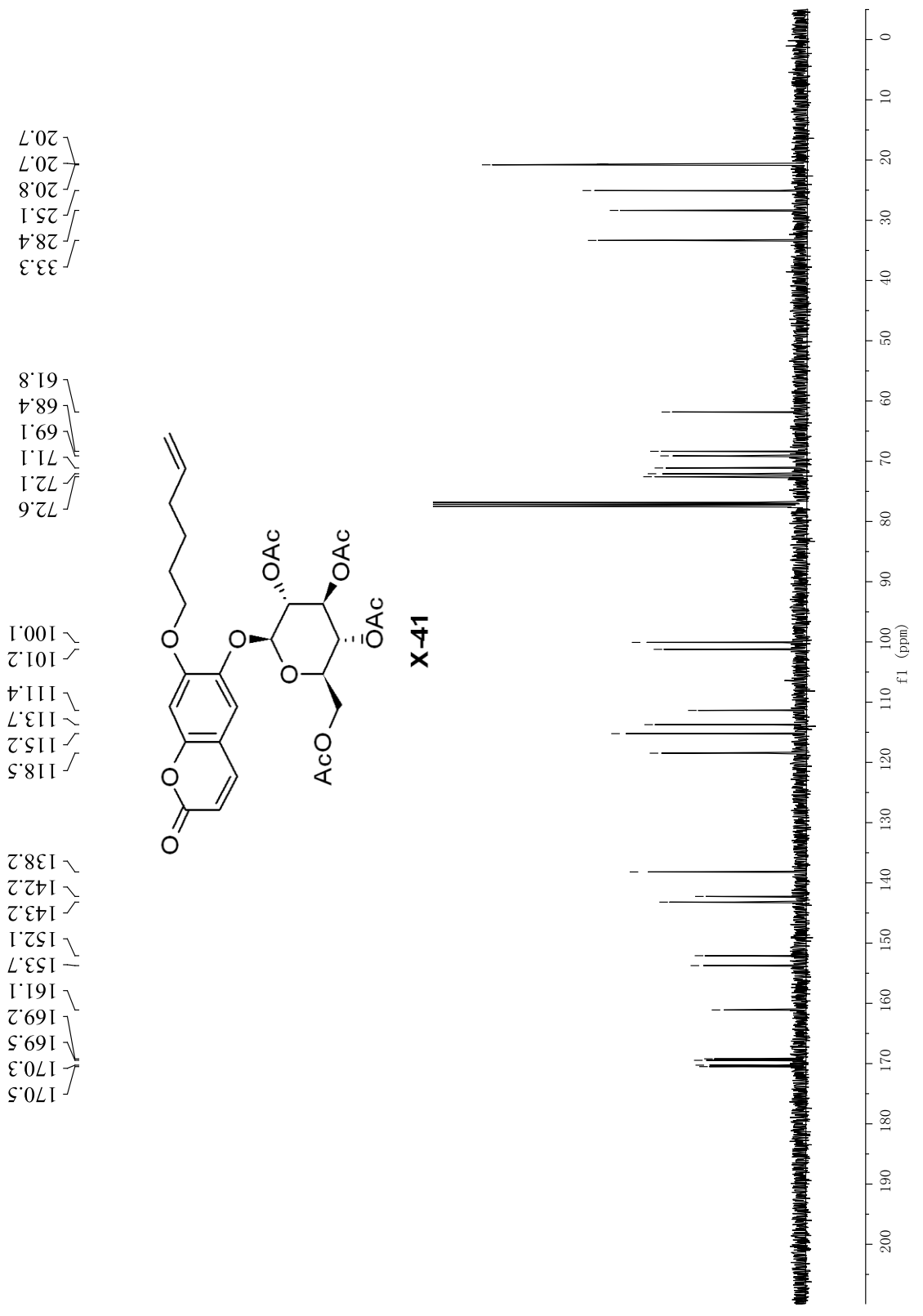
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-40**



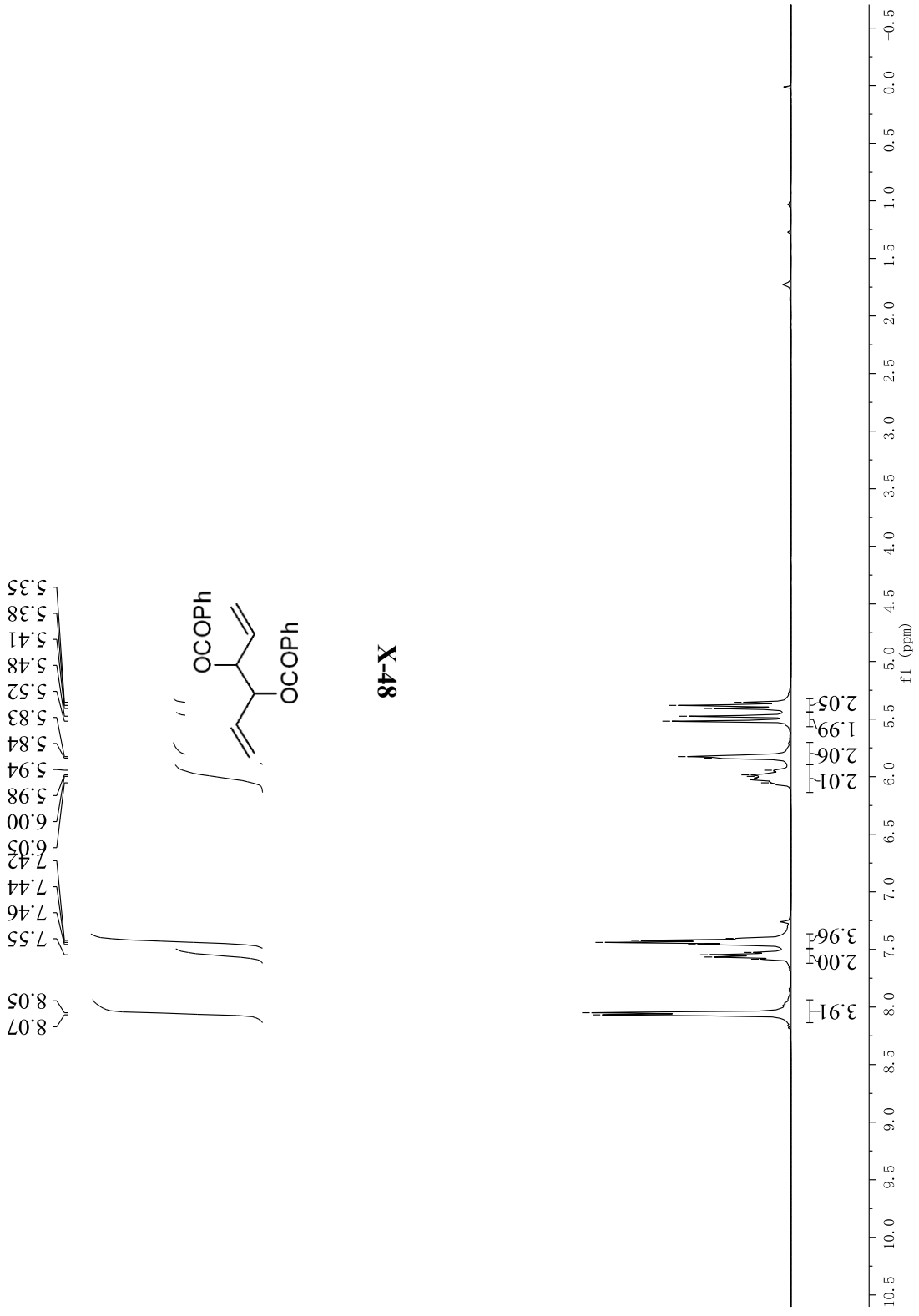
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **X-40'**



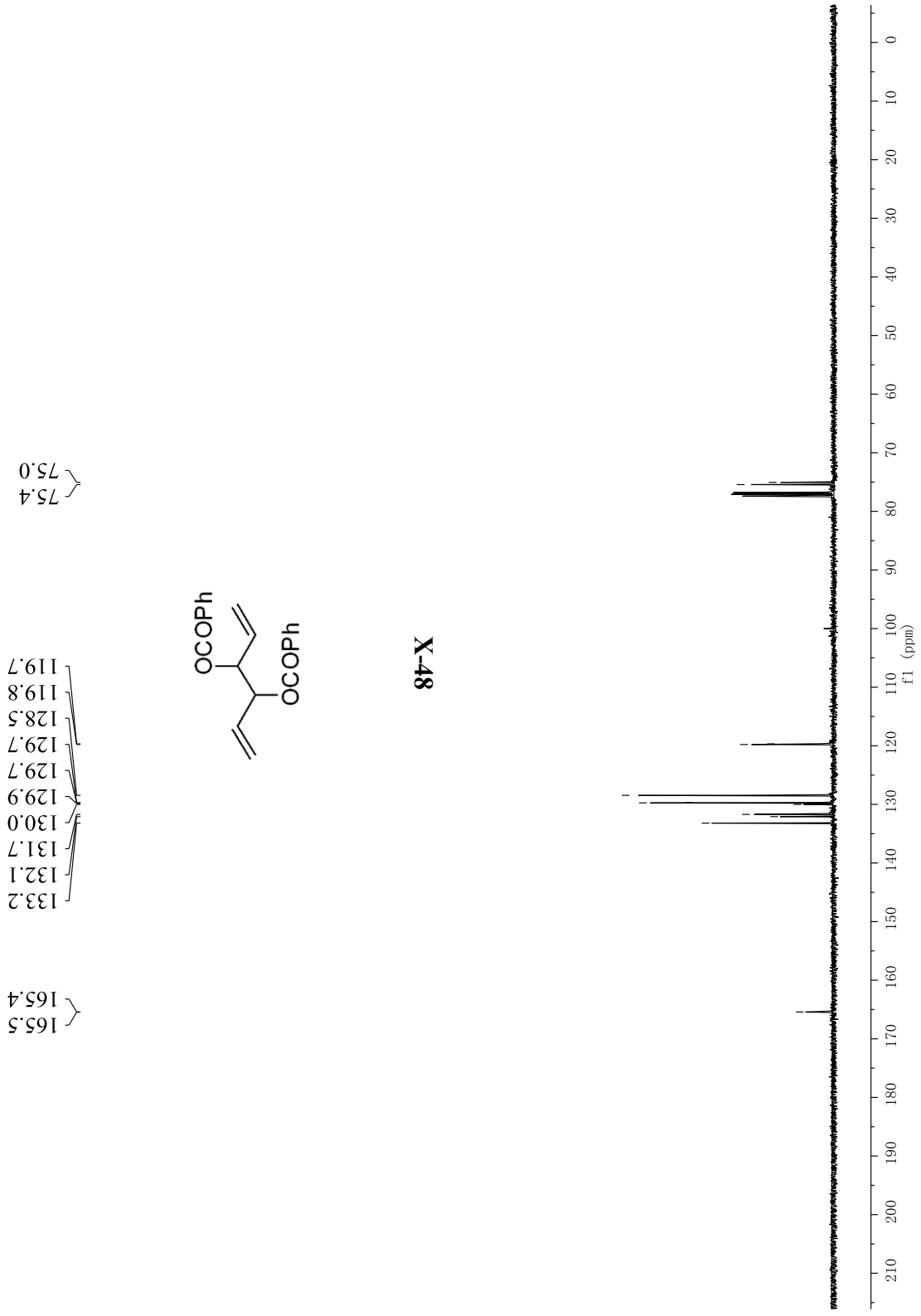
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-41**



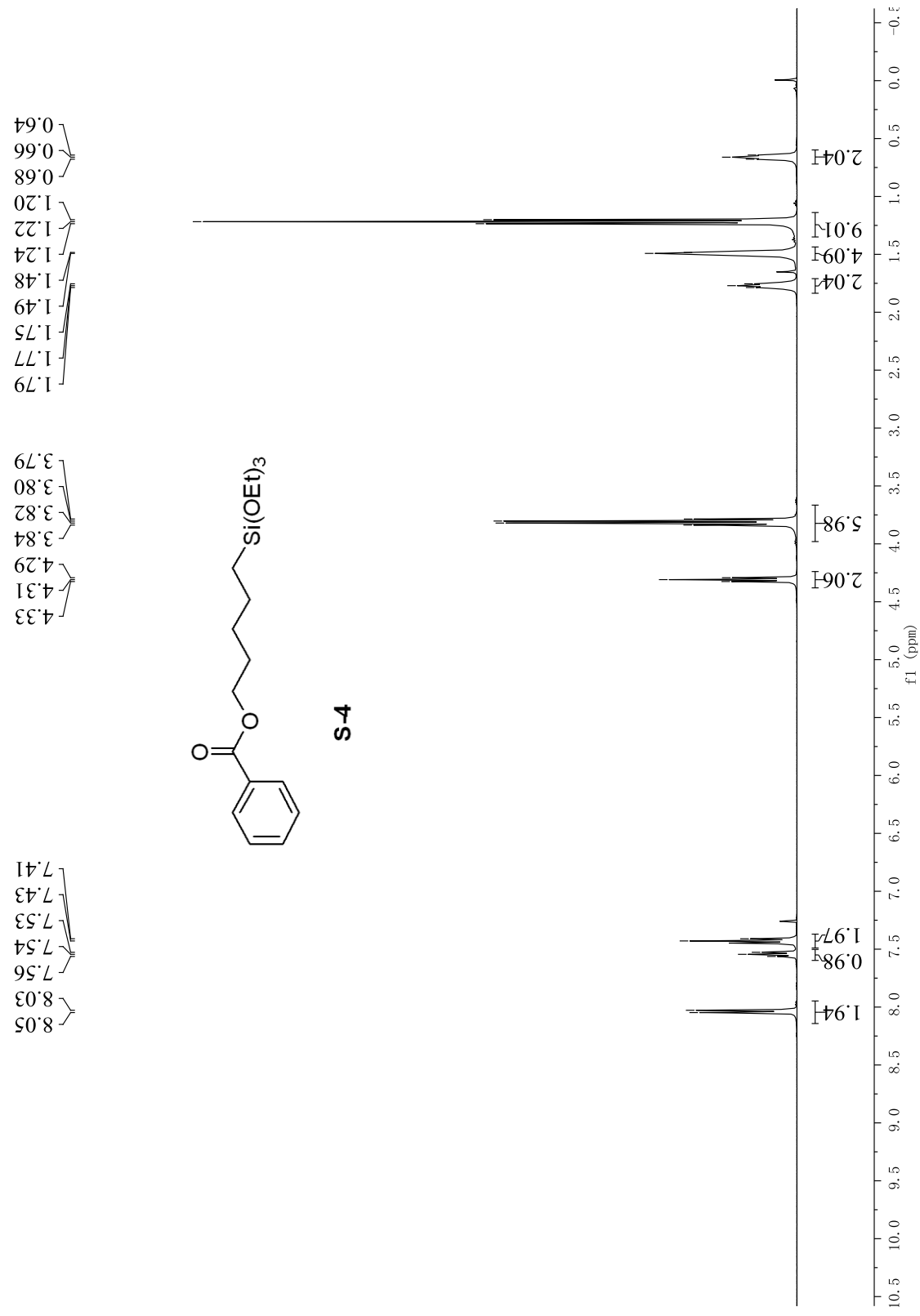
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-41**



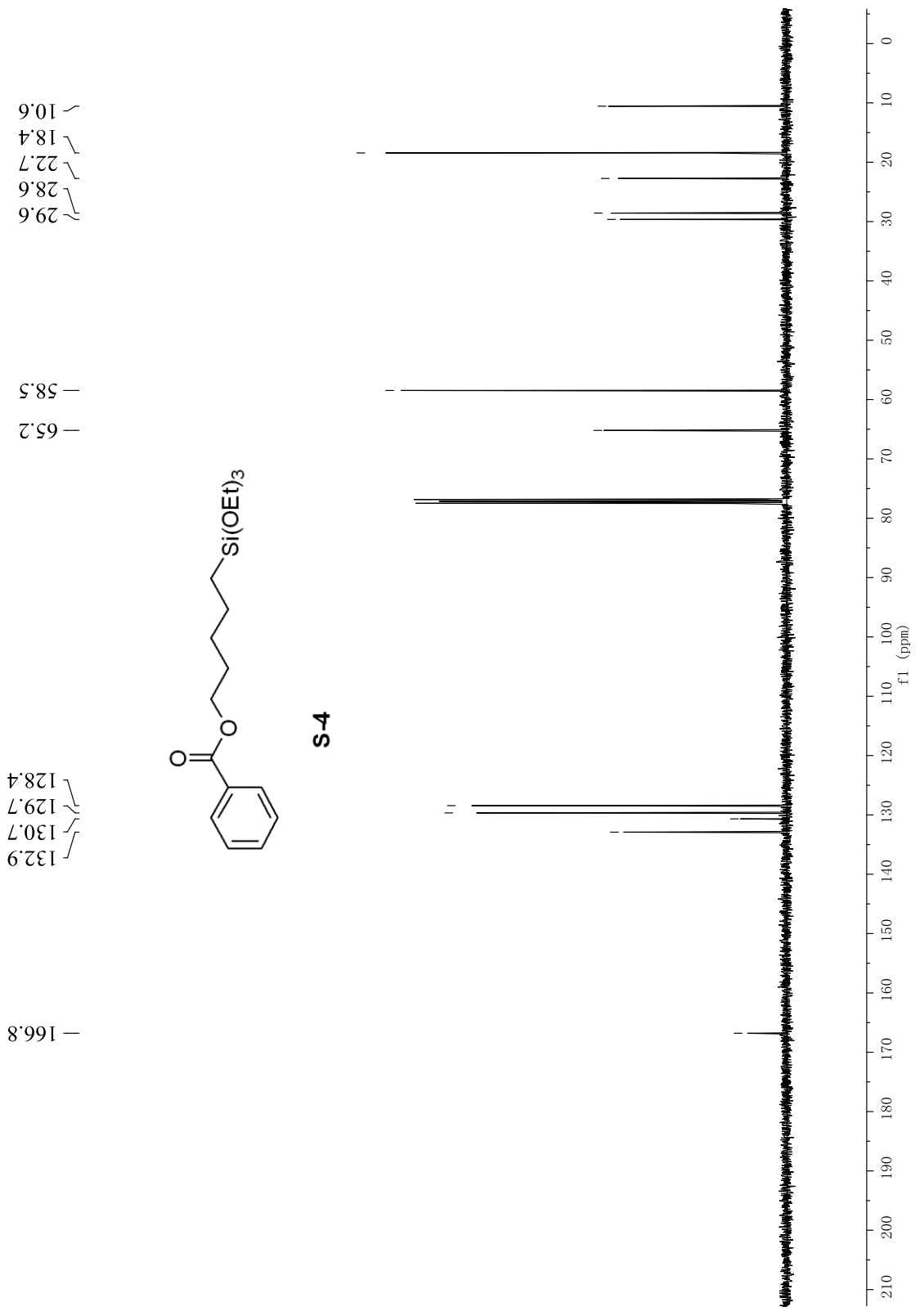
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **X-48**



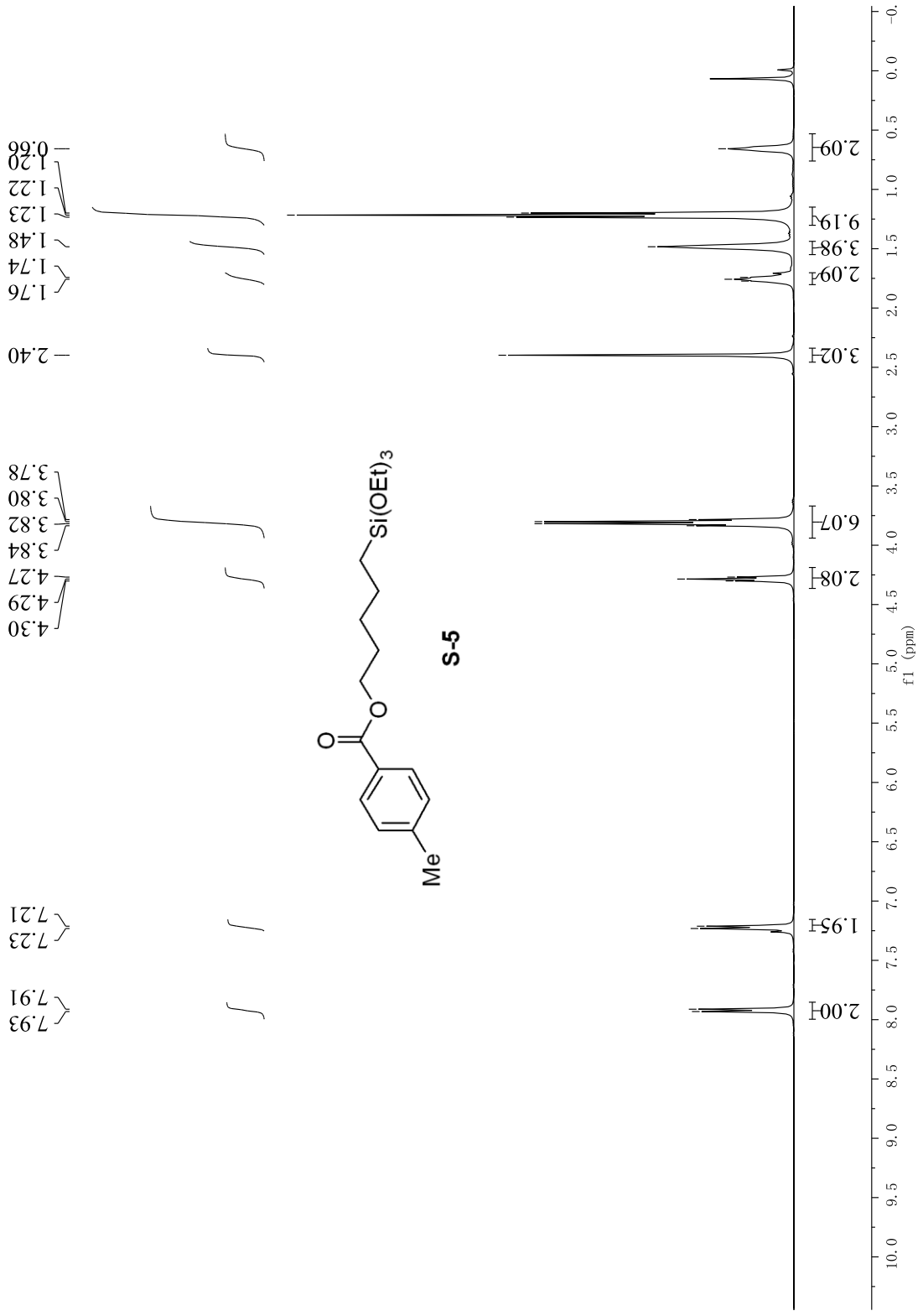
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **X-48**



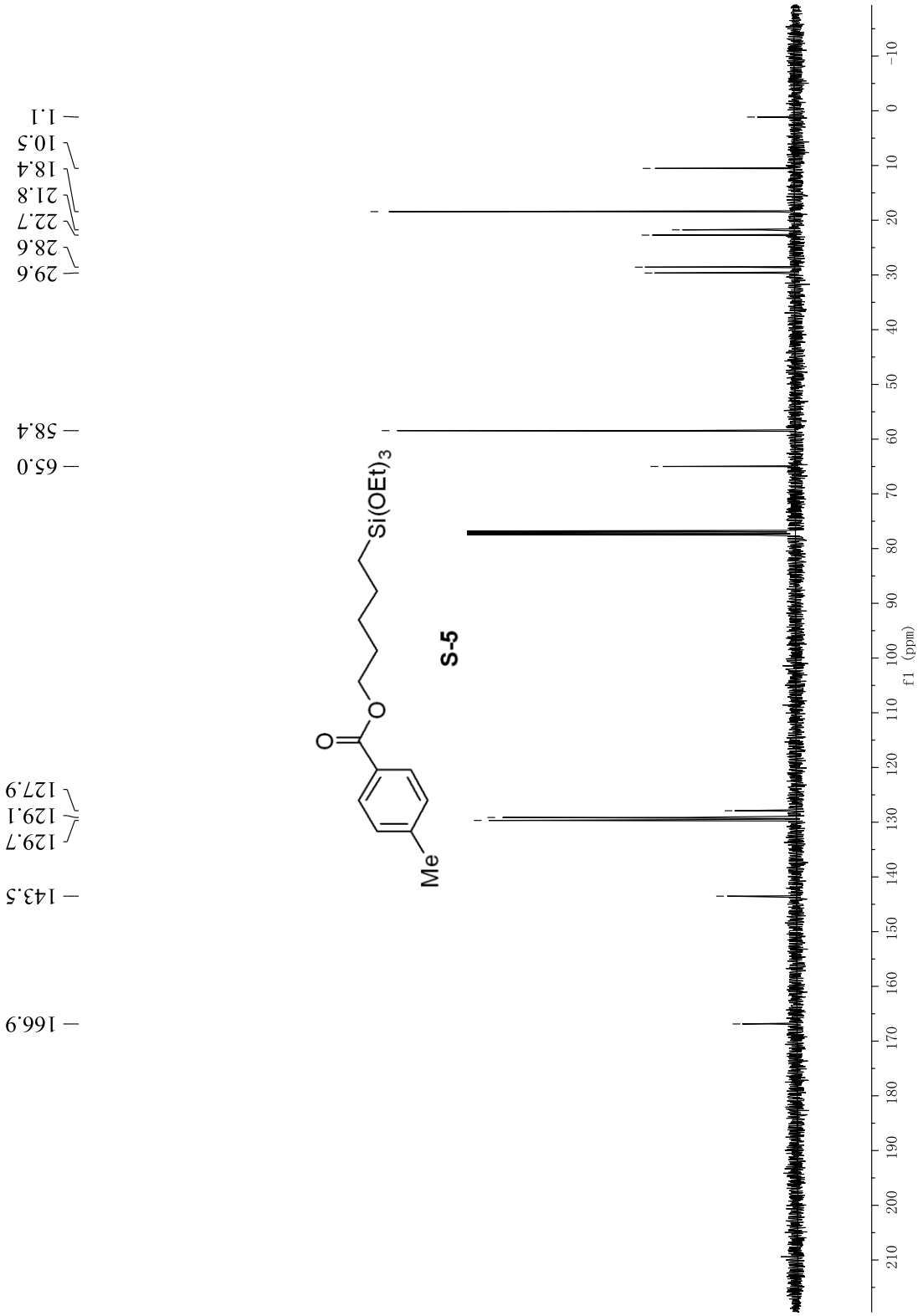
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-4**



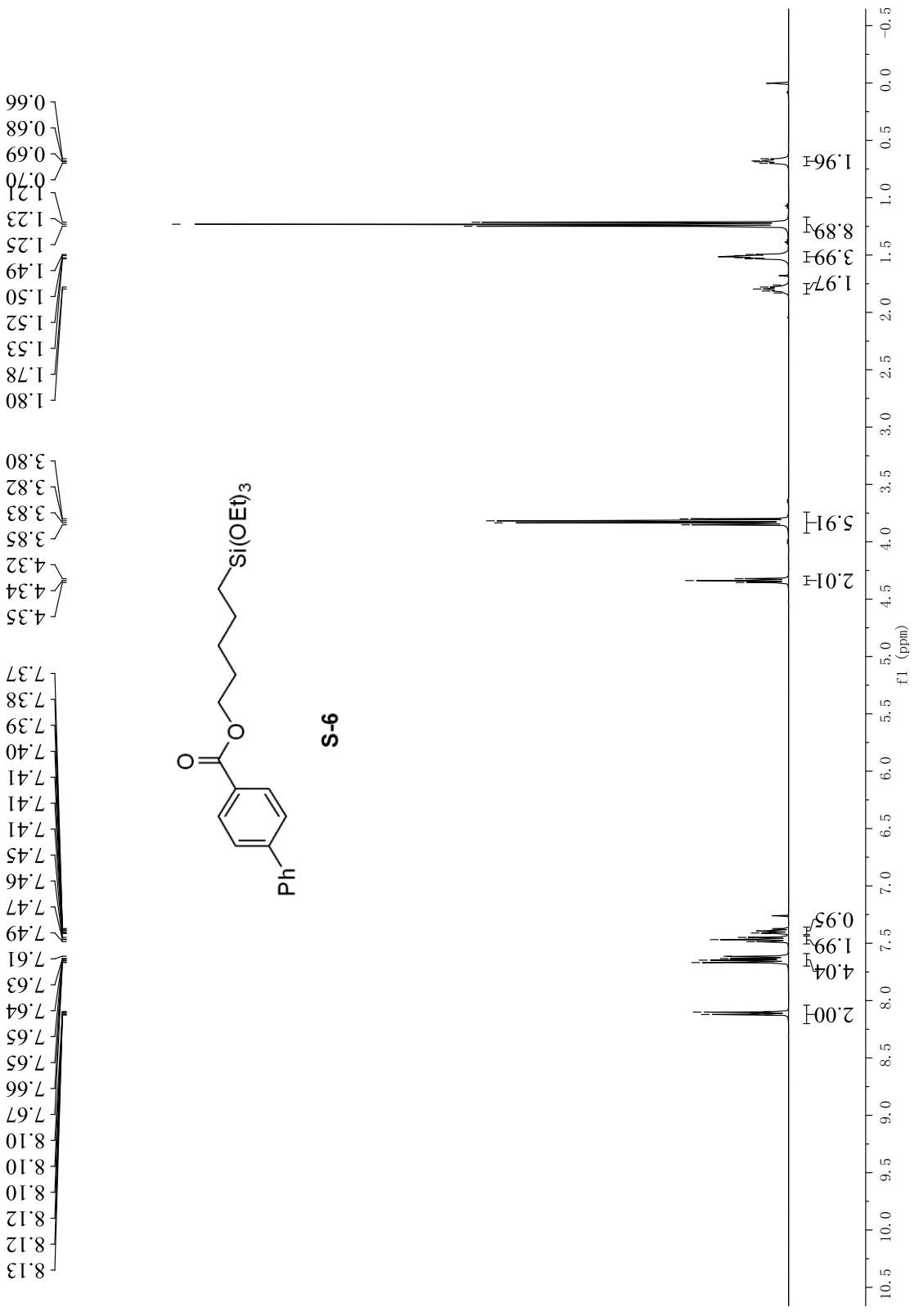
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-4**



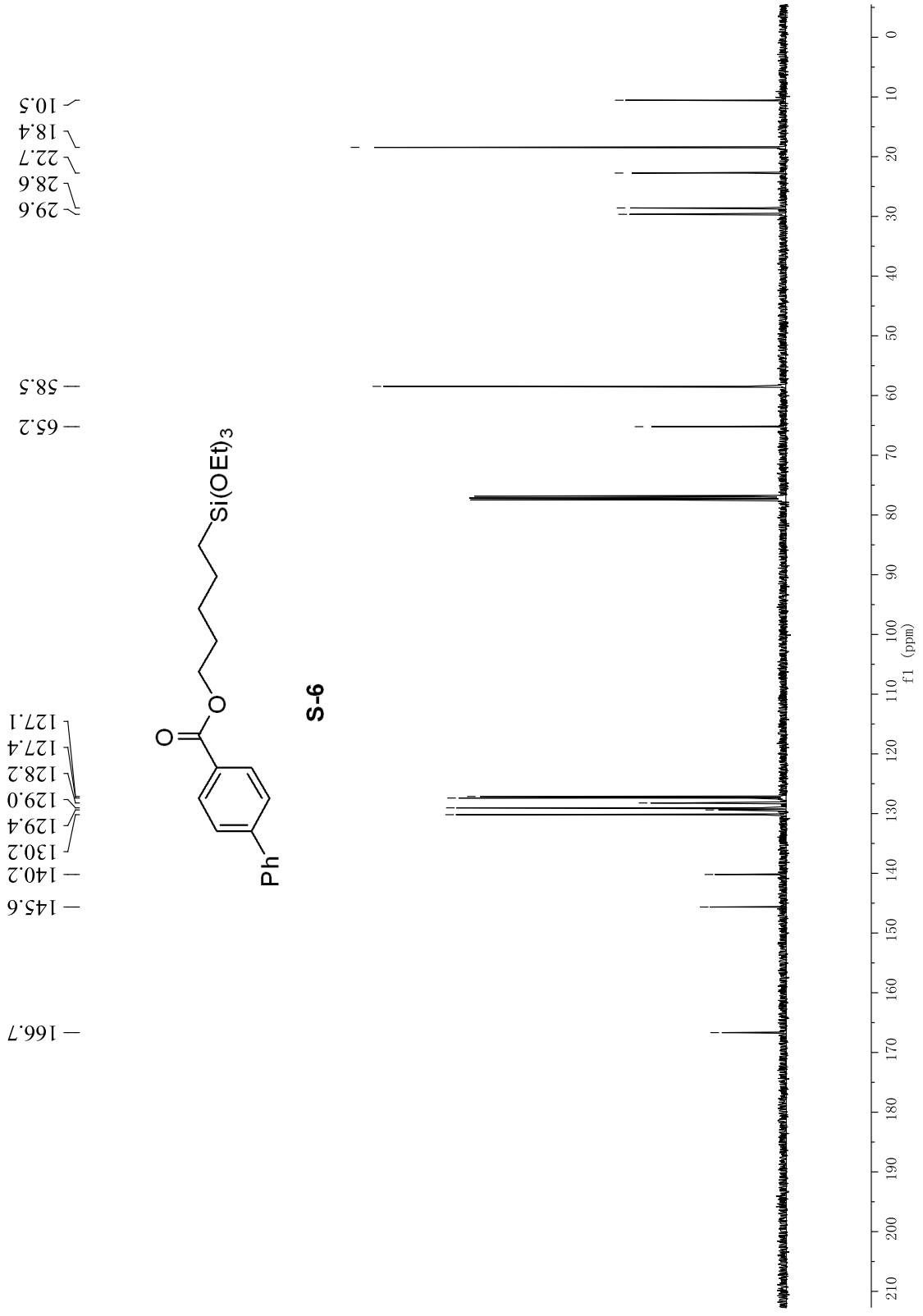
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-5**



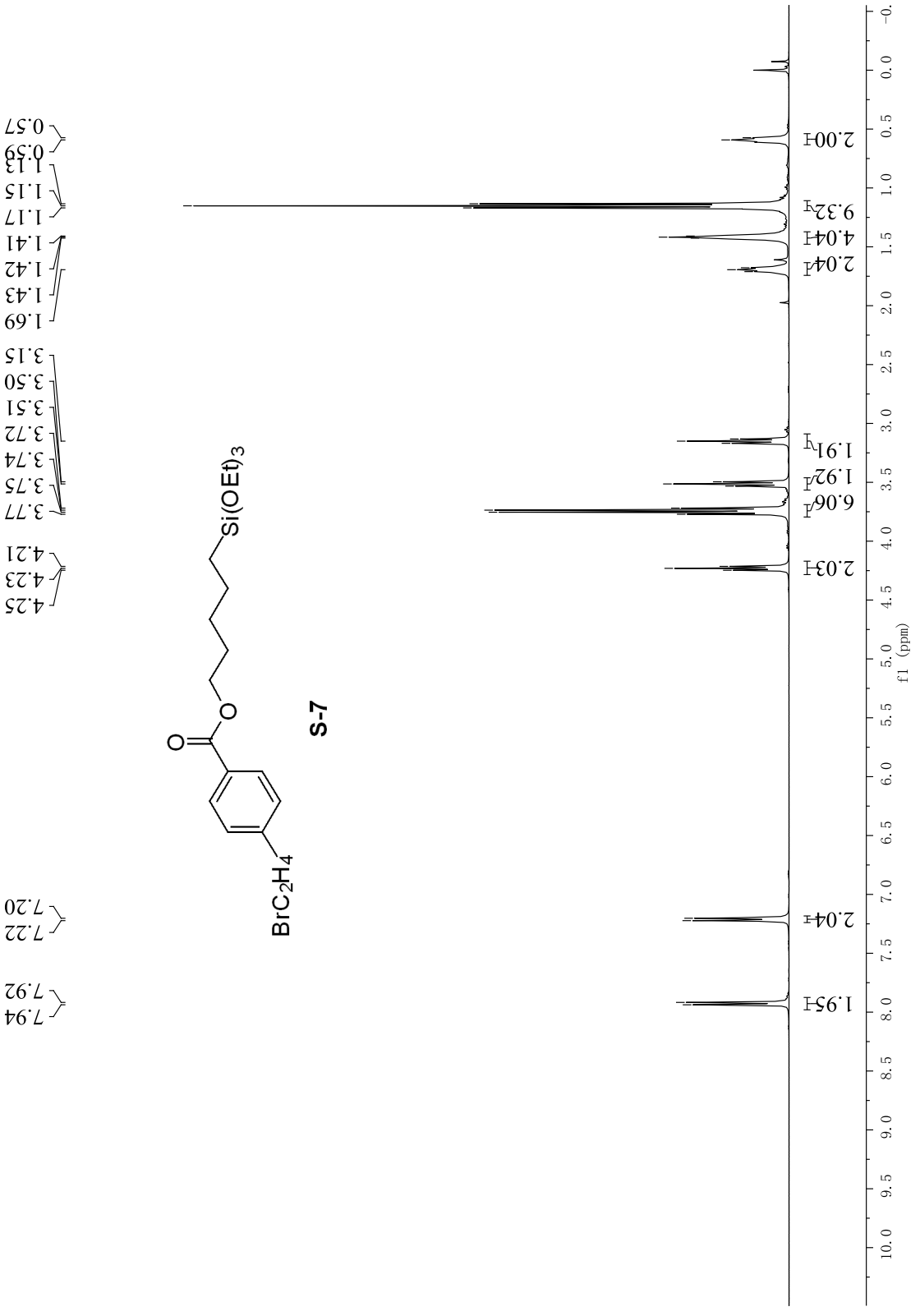
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-5**



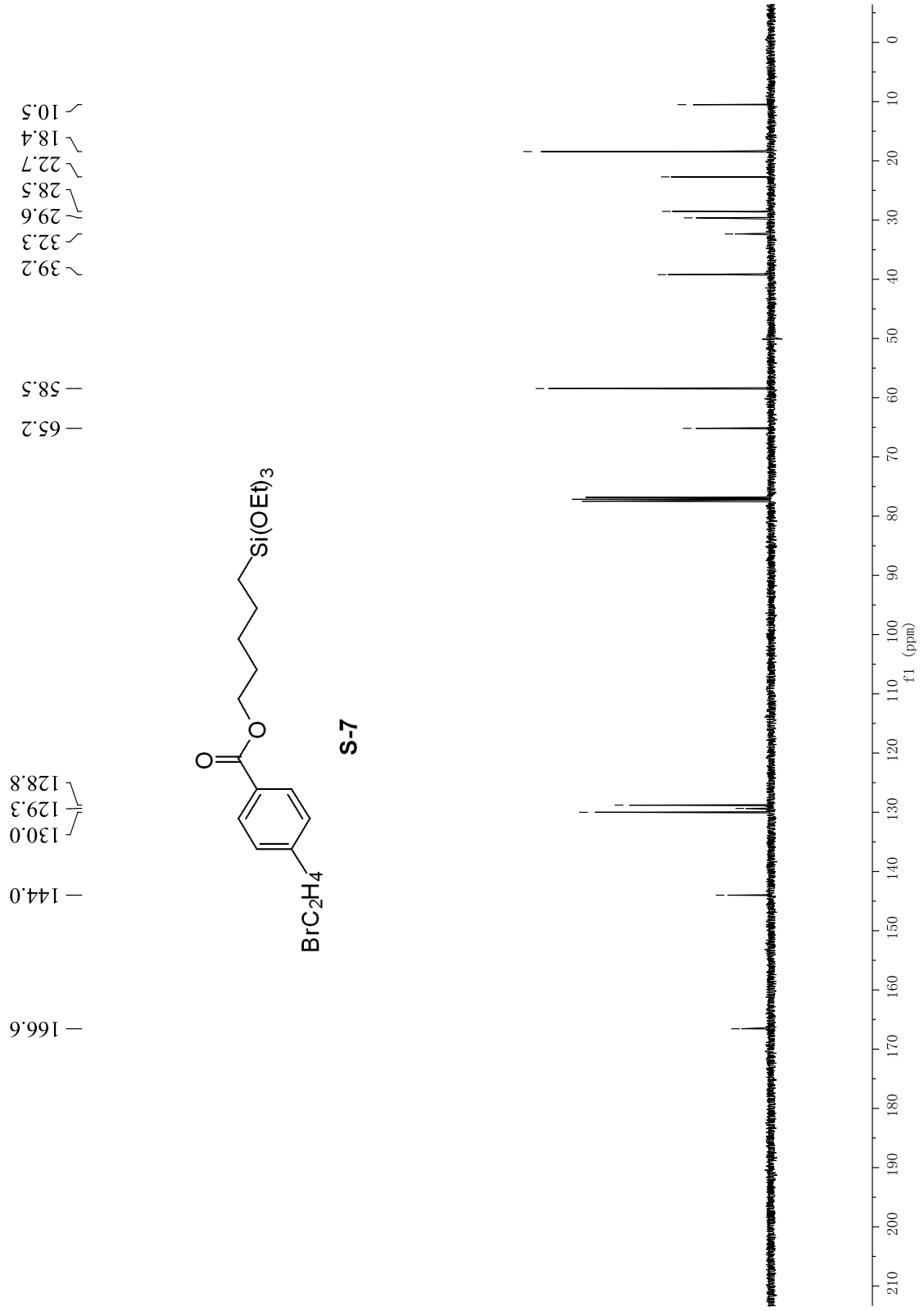
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-6**



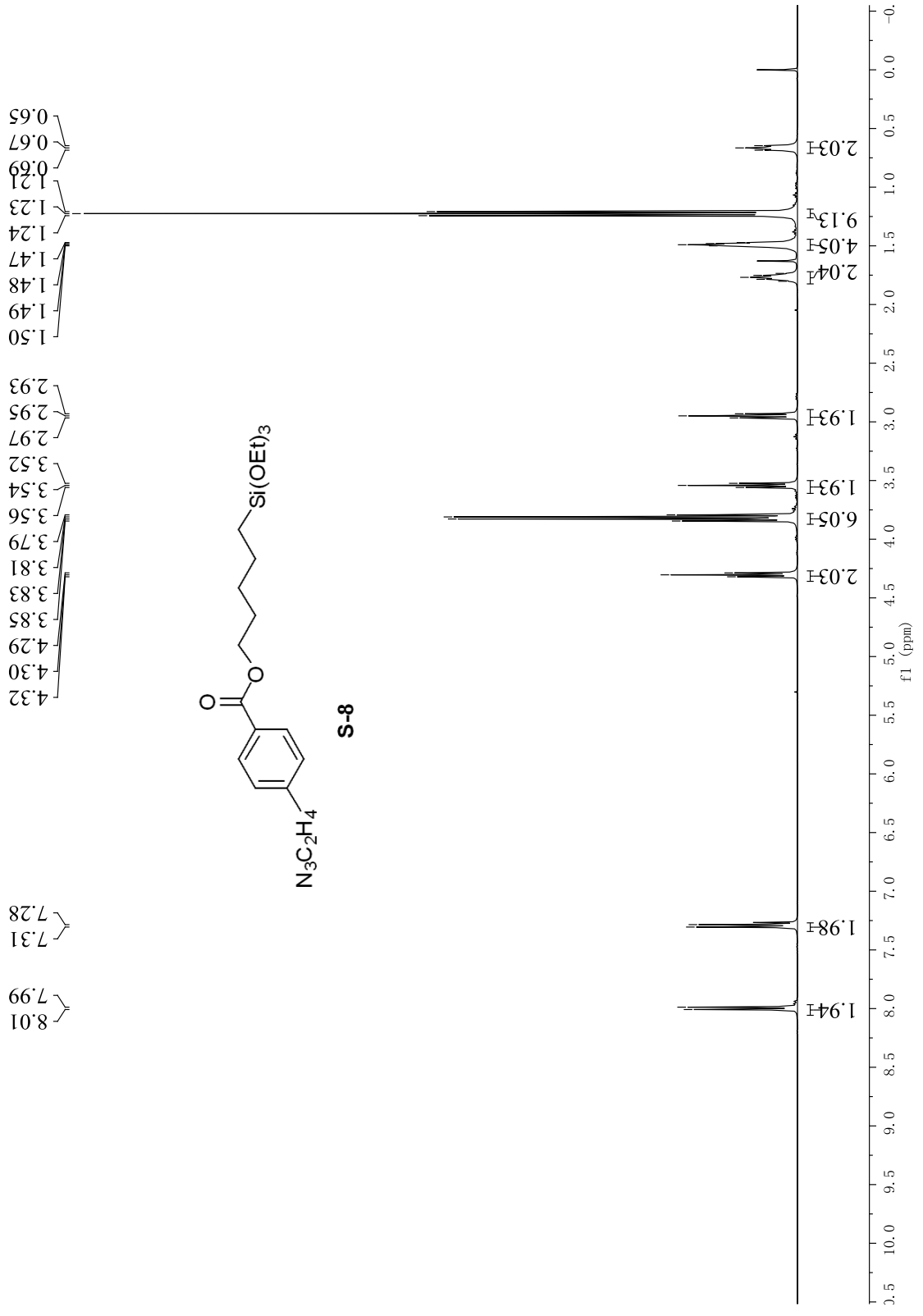
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-6**



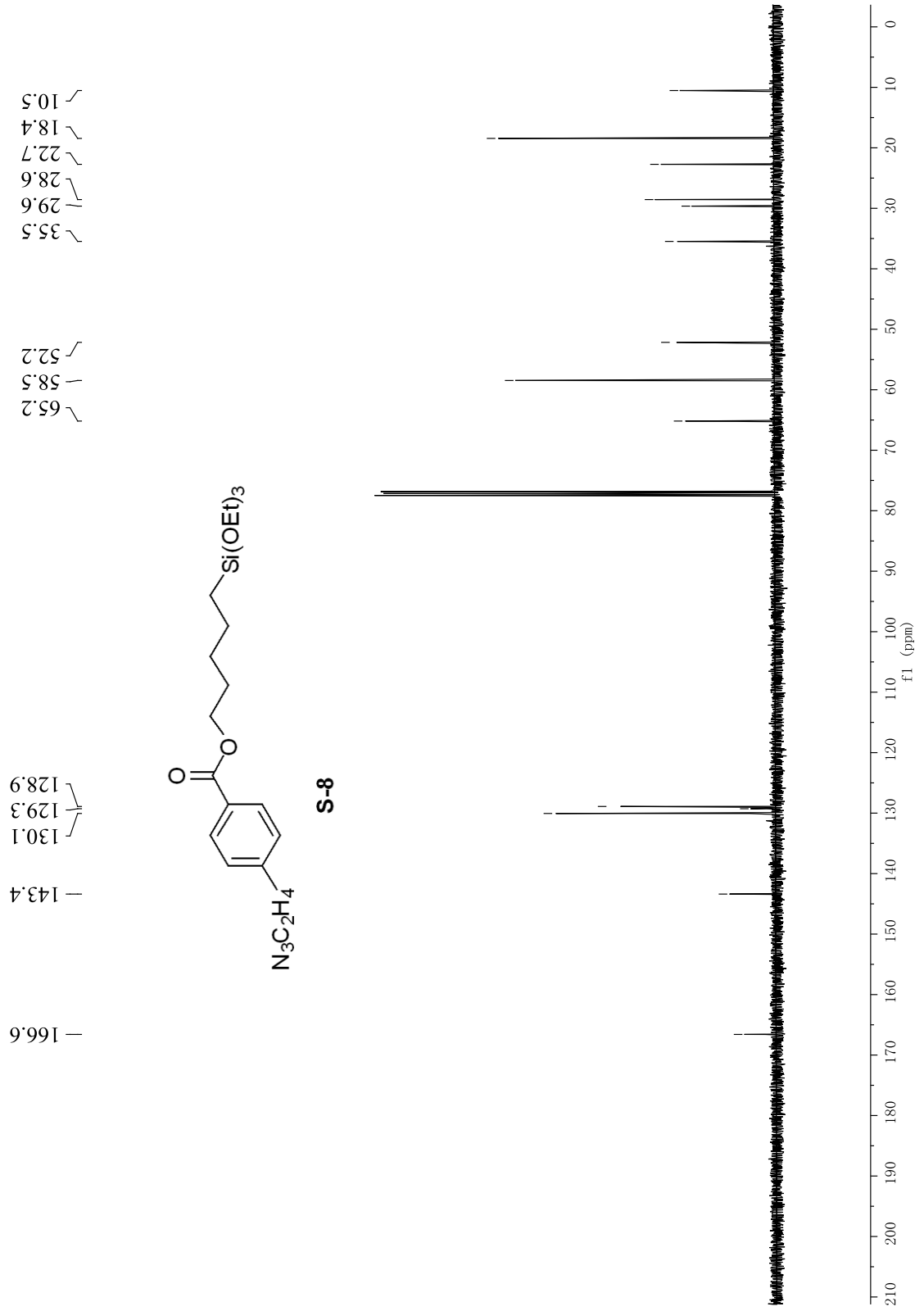
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-7**



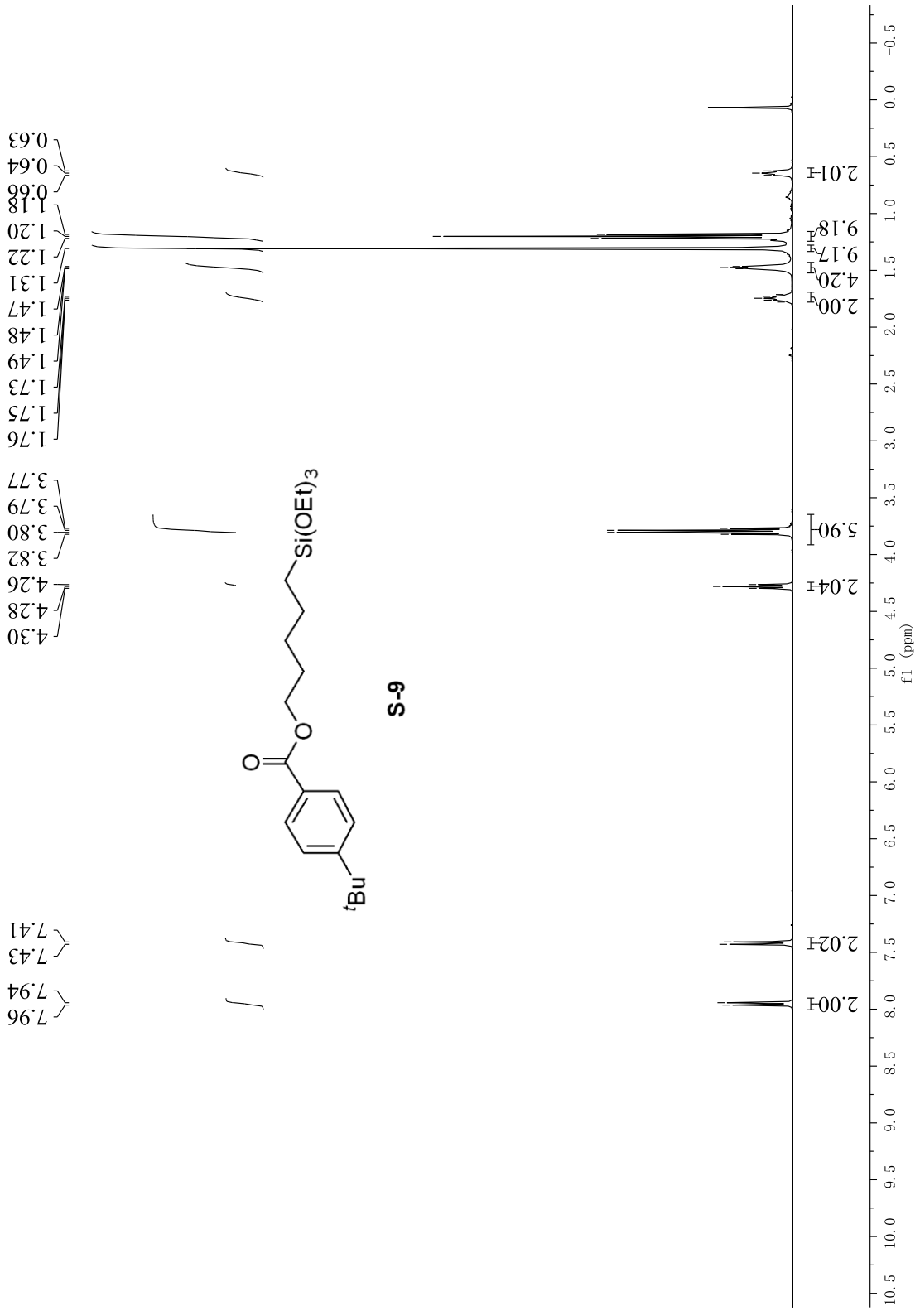
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-7**



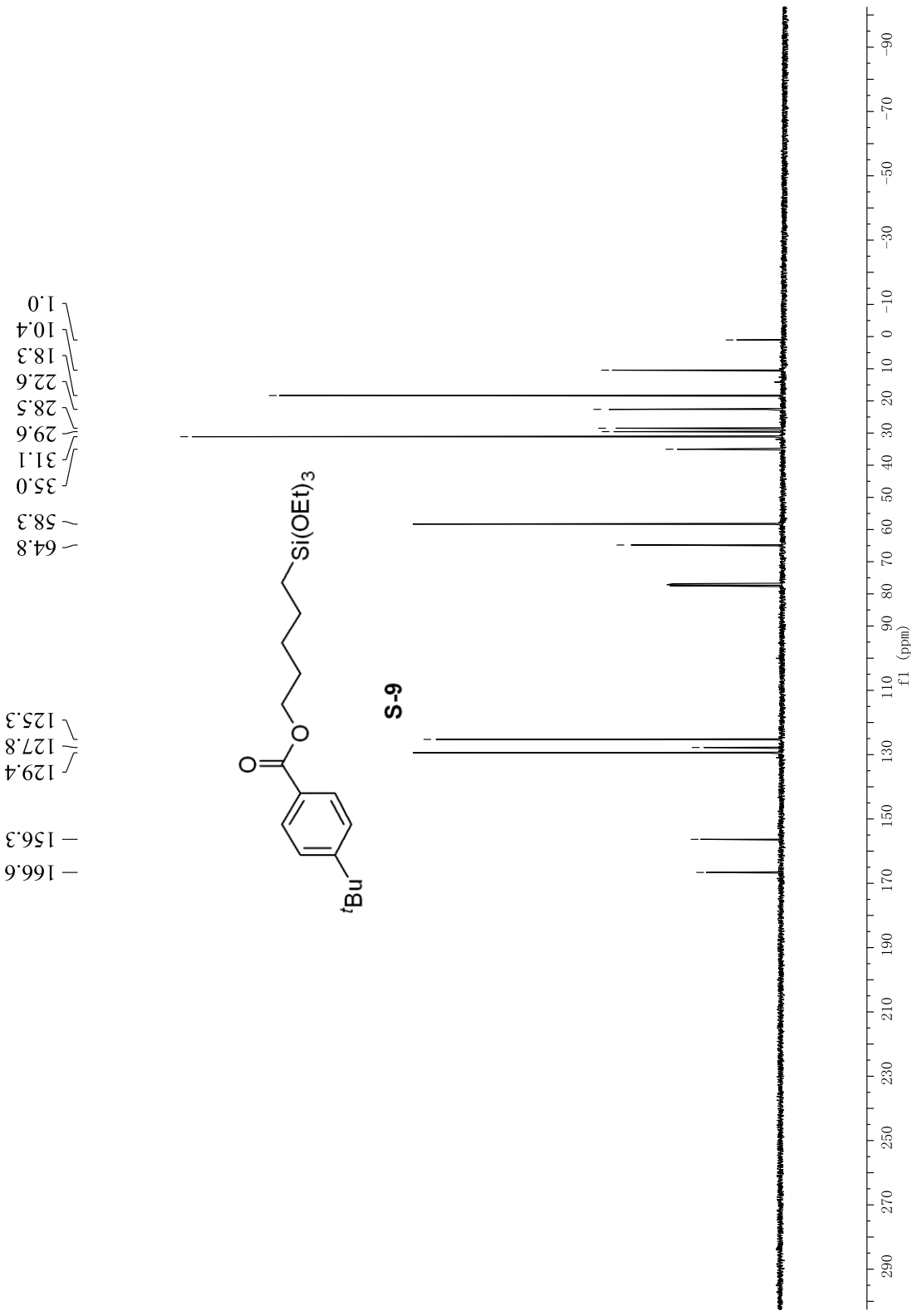
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-8**



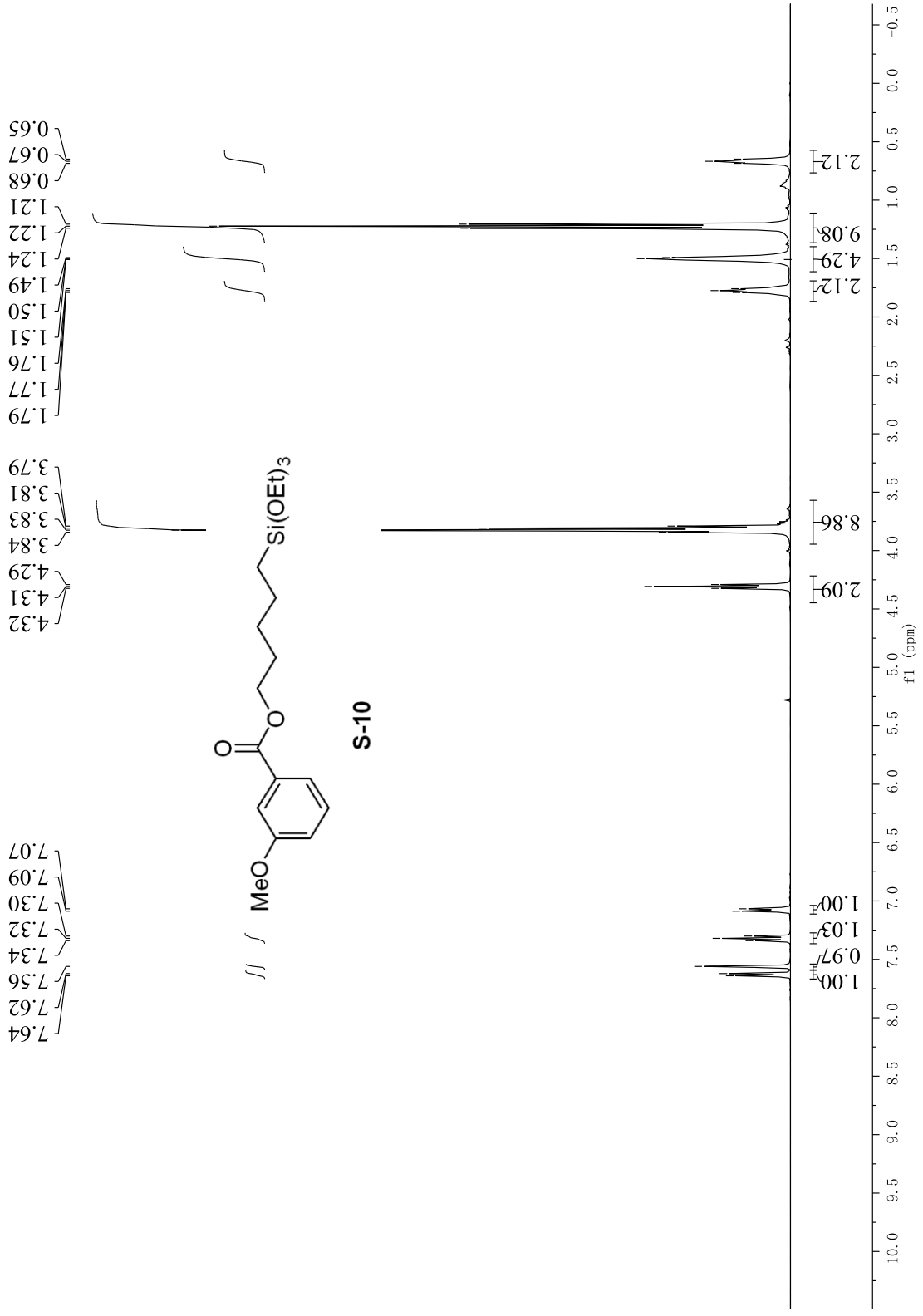
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-8**



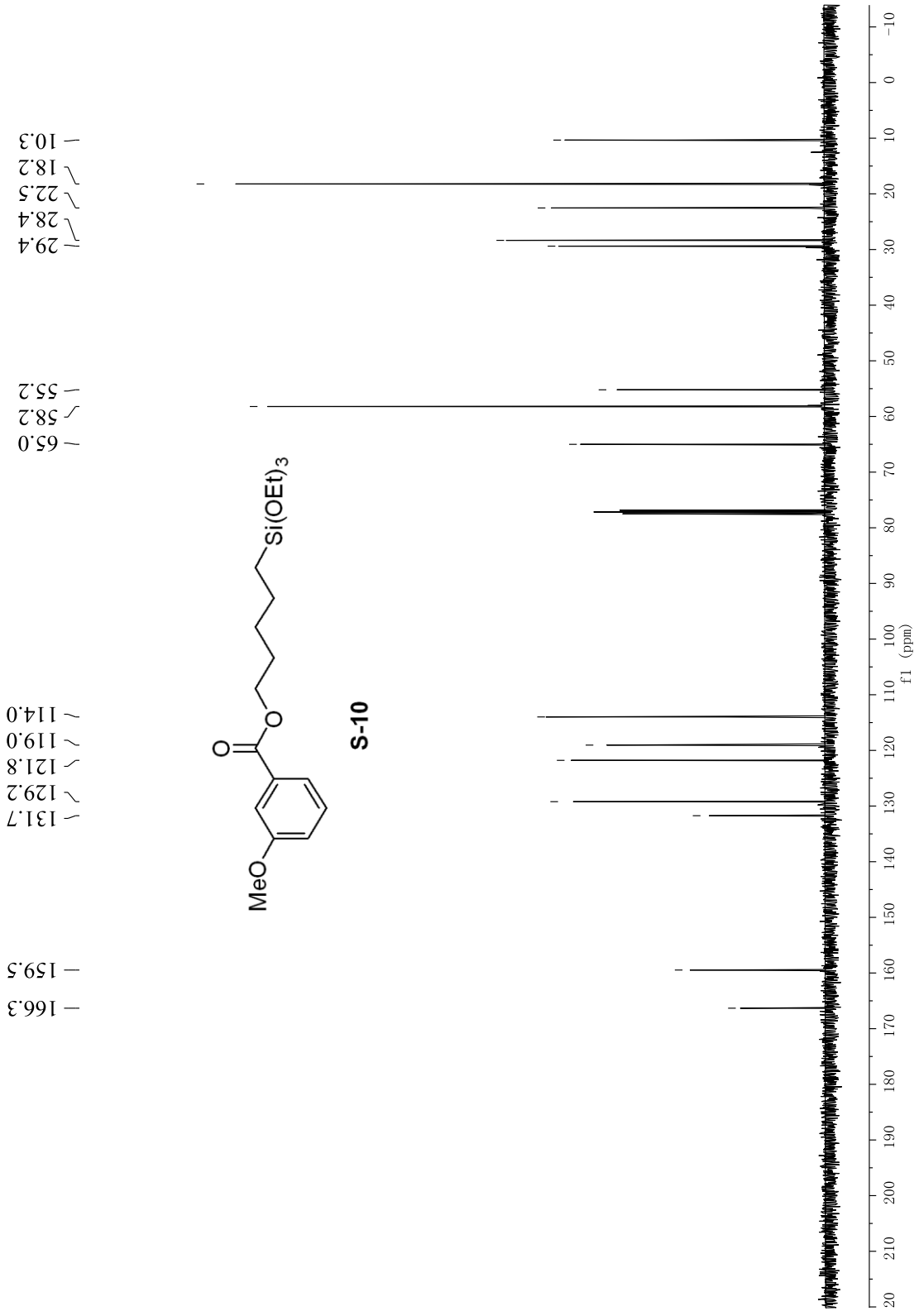
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-9**



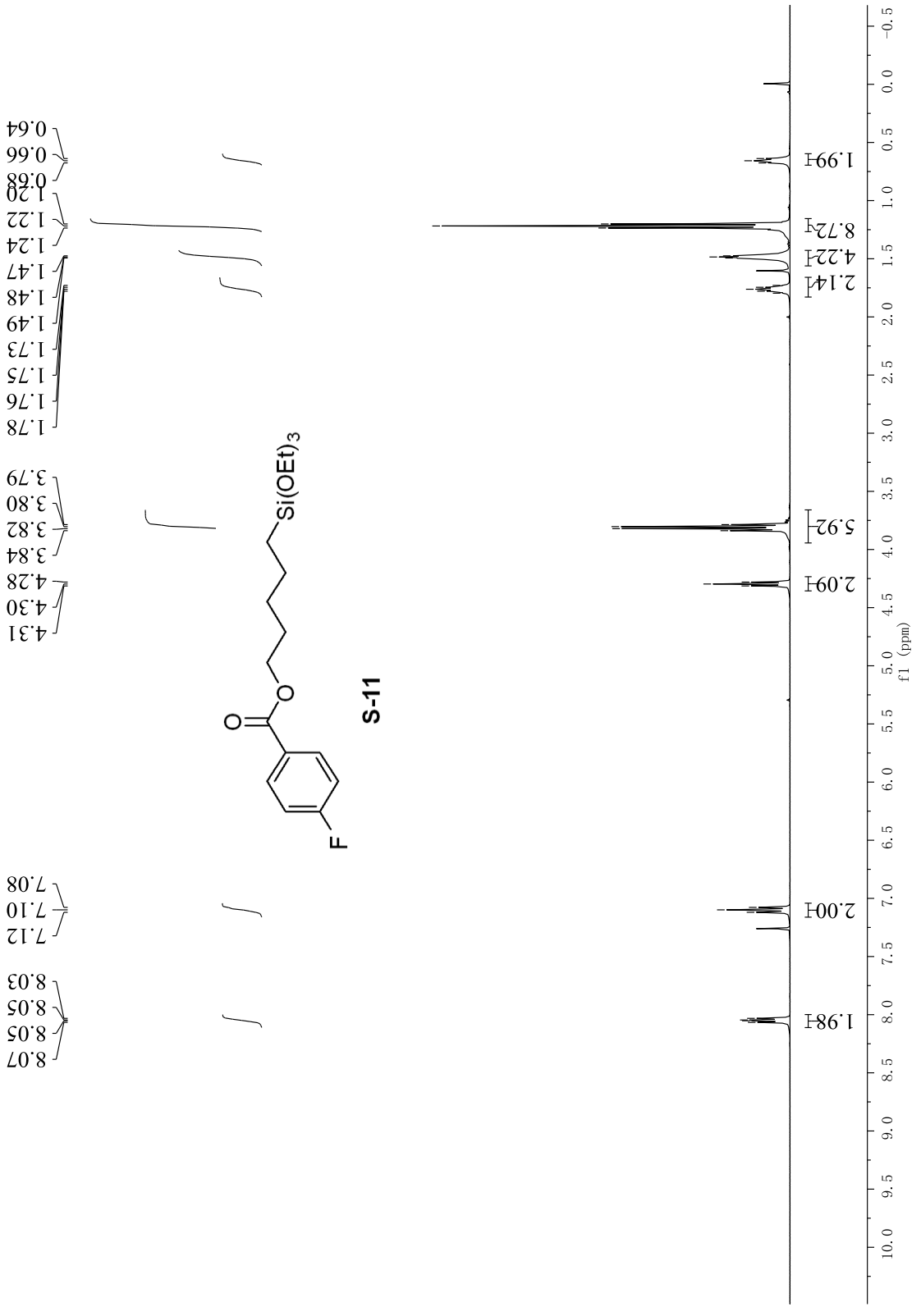
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-9**



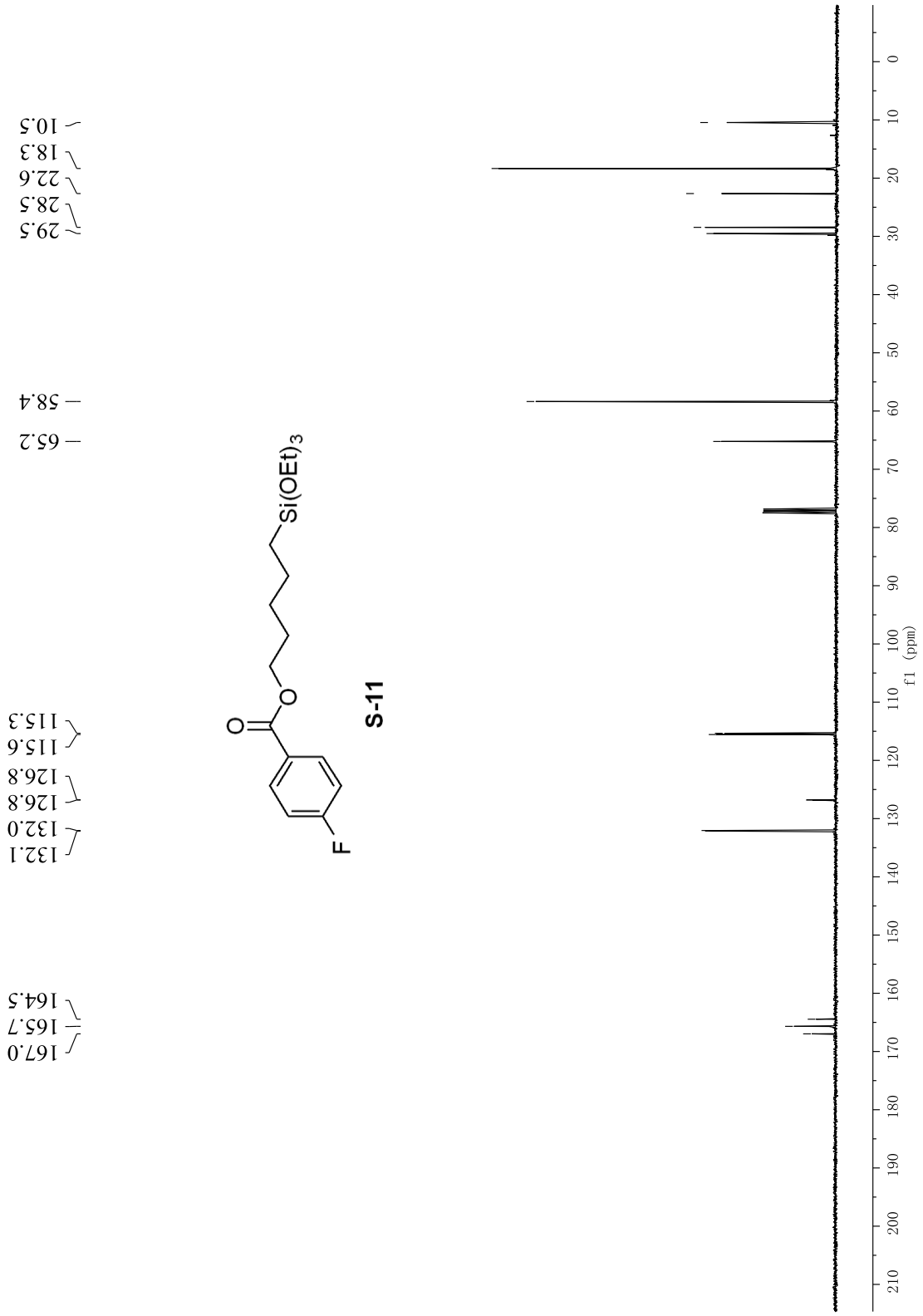
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-10**



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

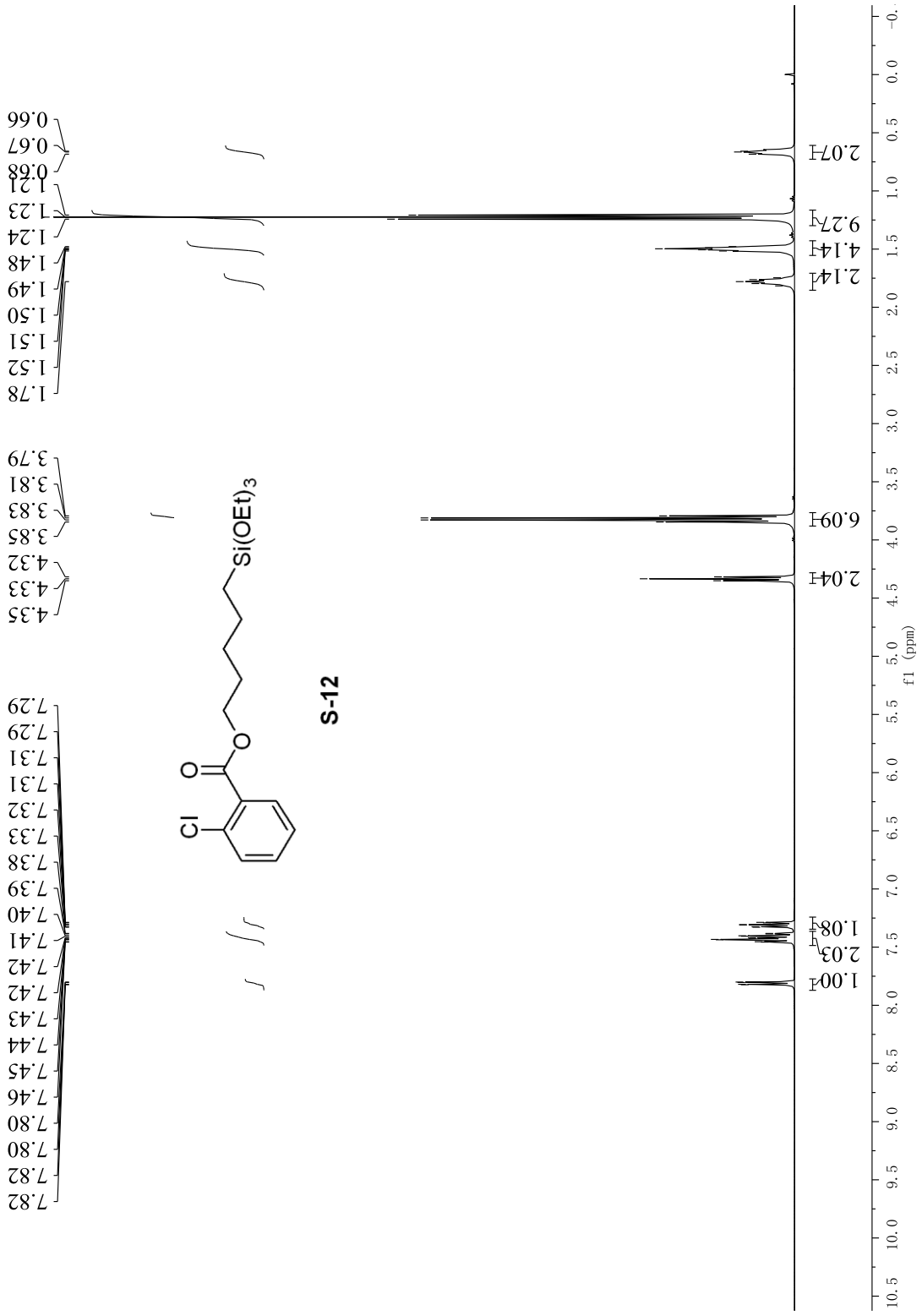


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-11**

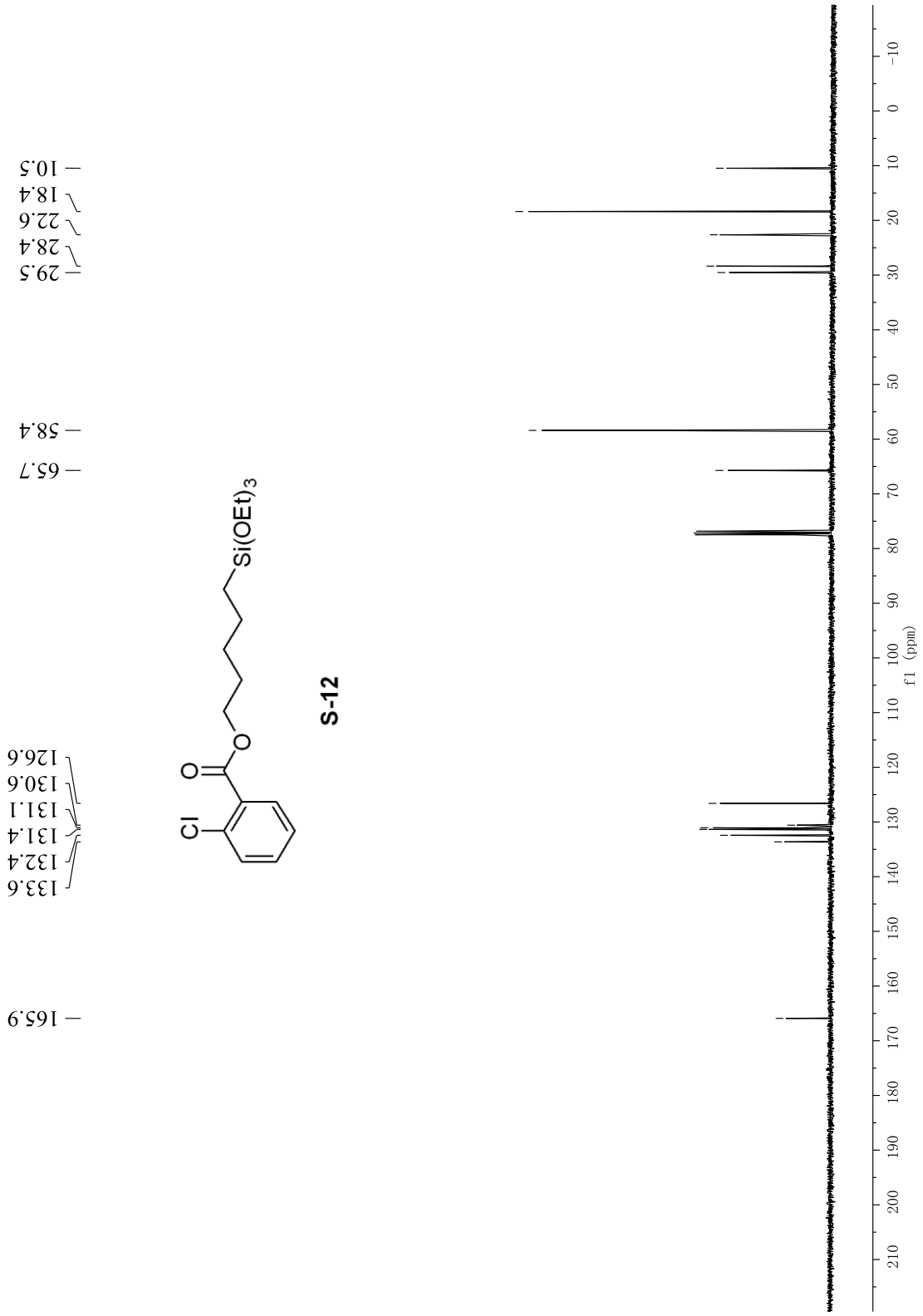


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-11**

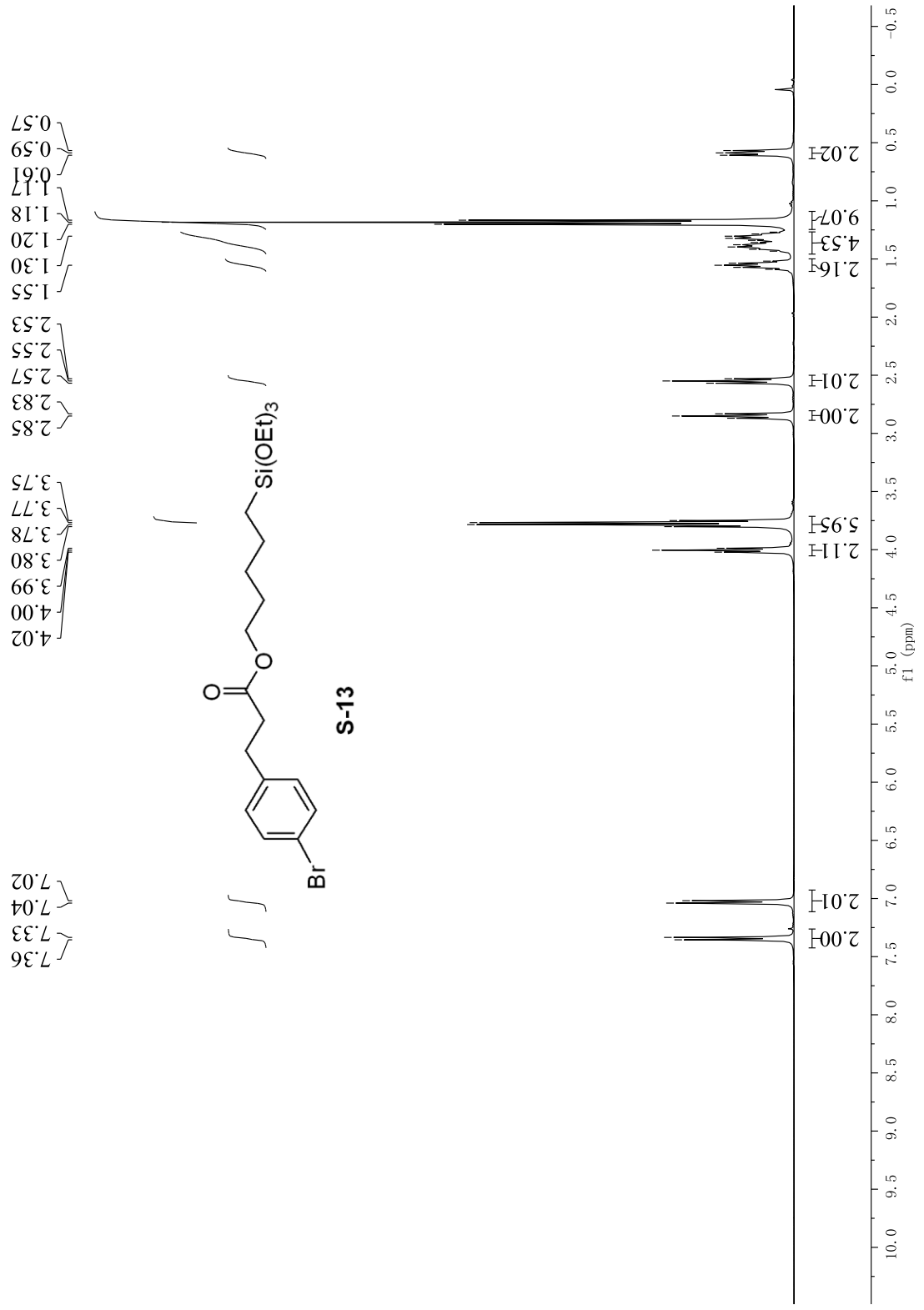
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-11**



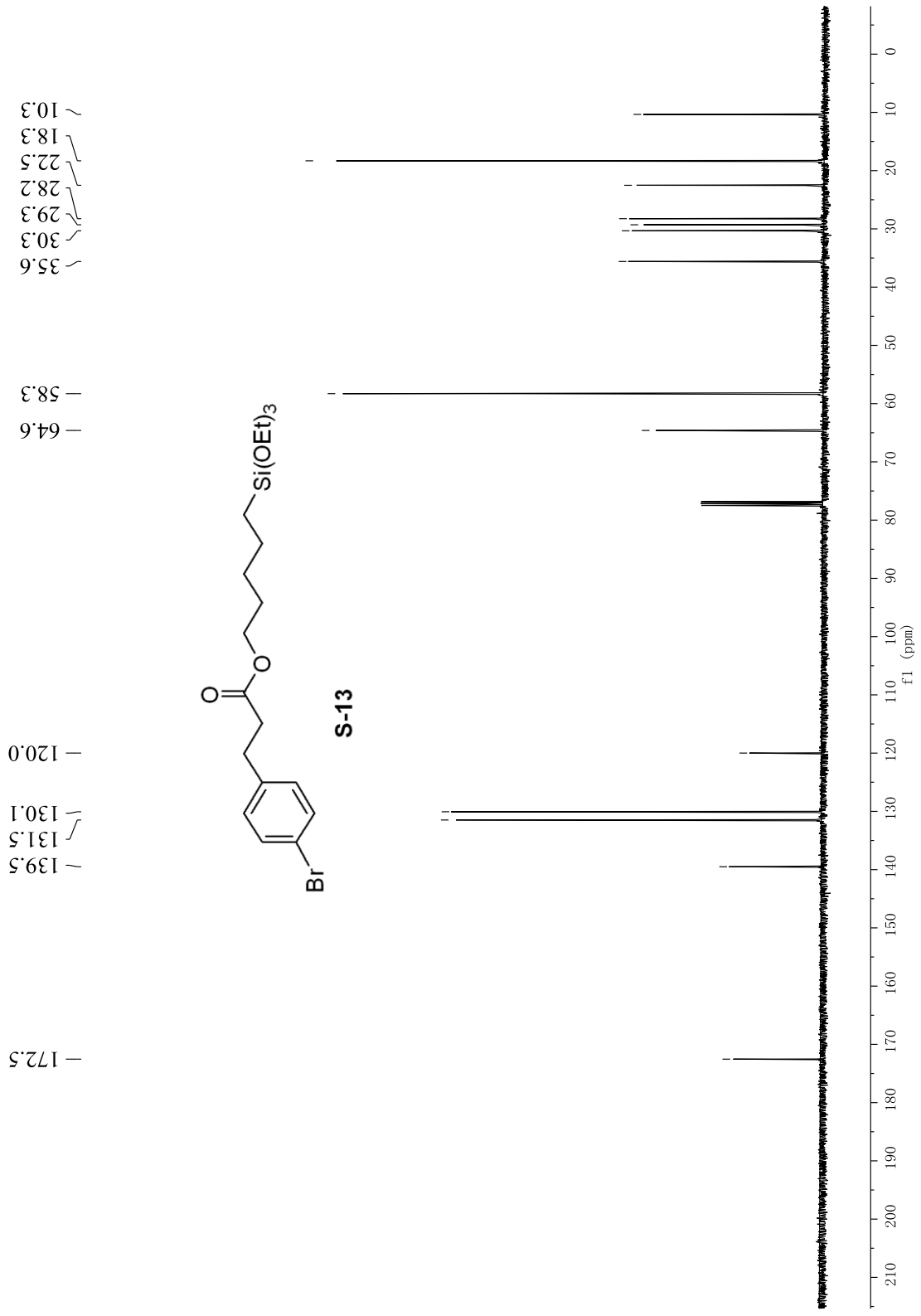
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-12**



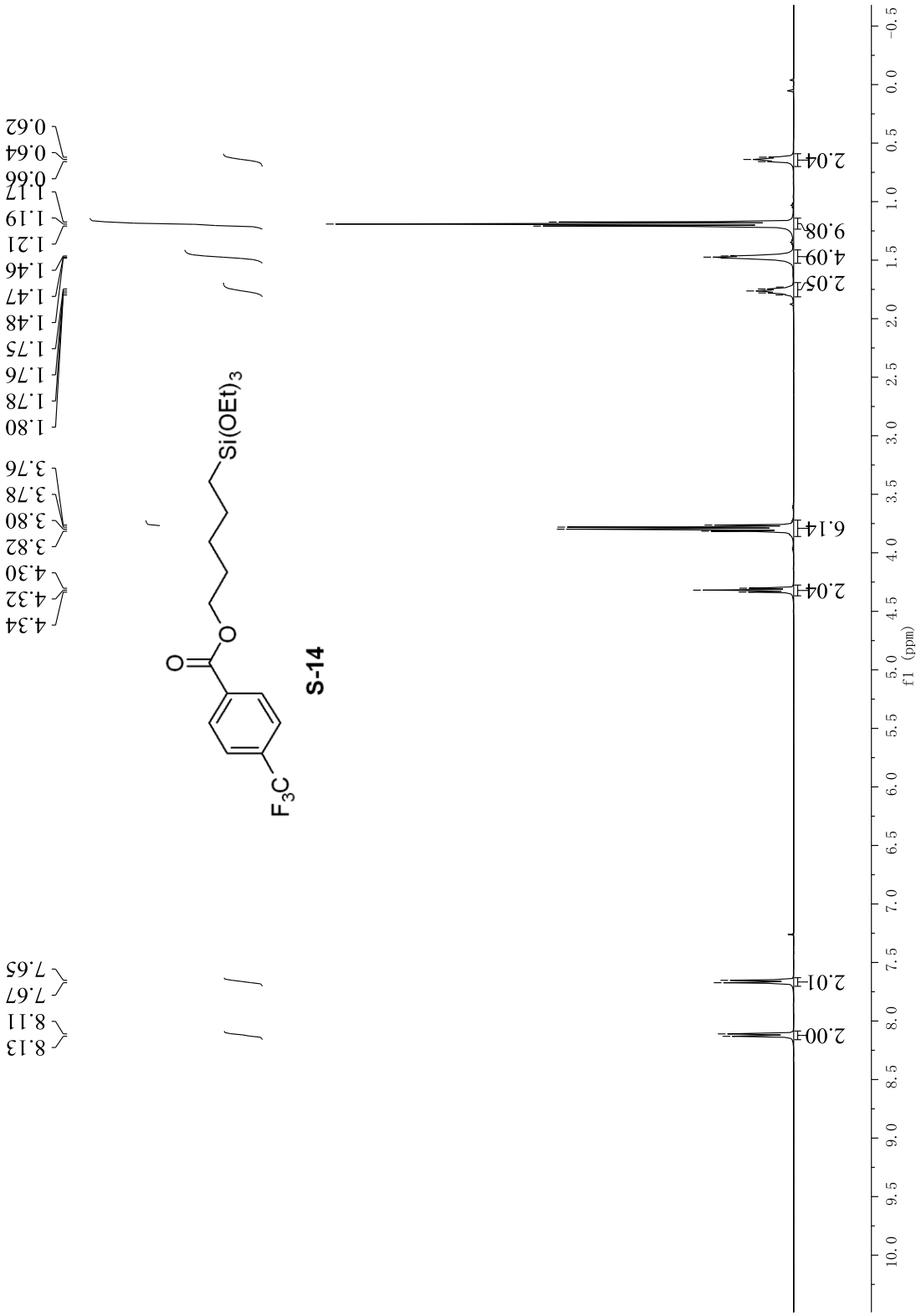
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-12**



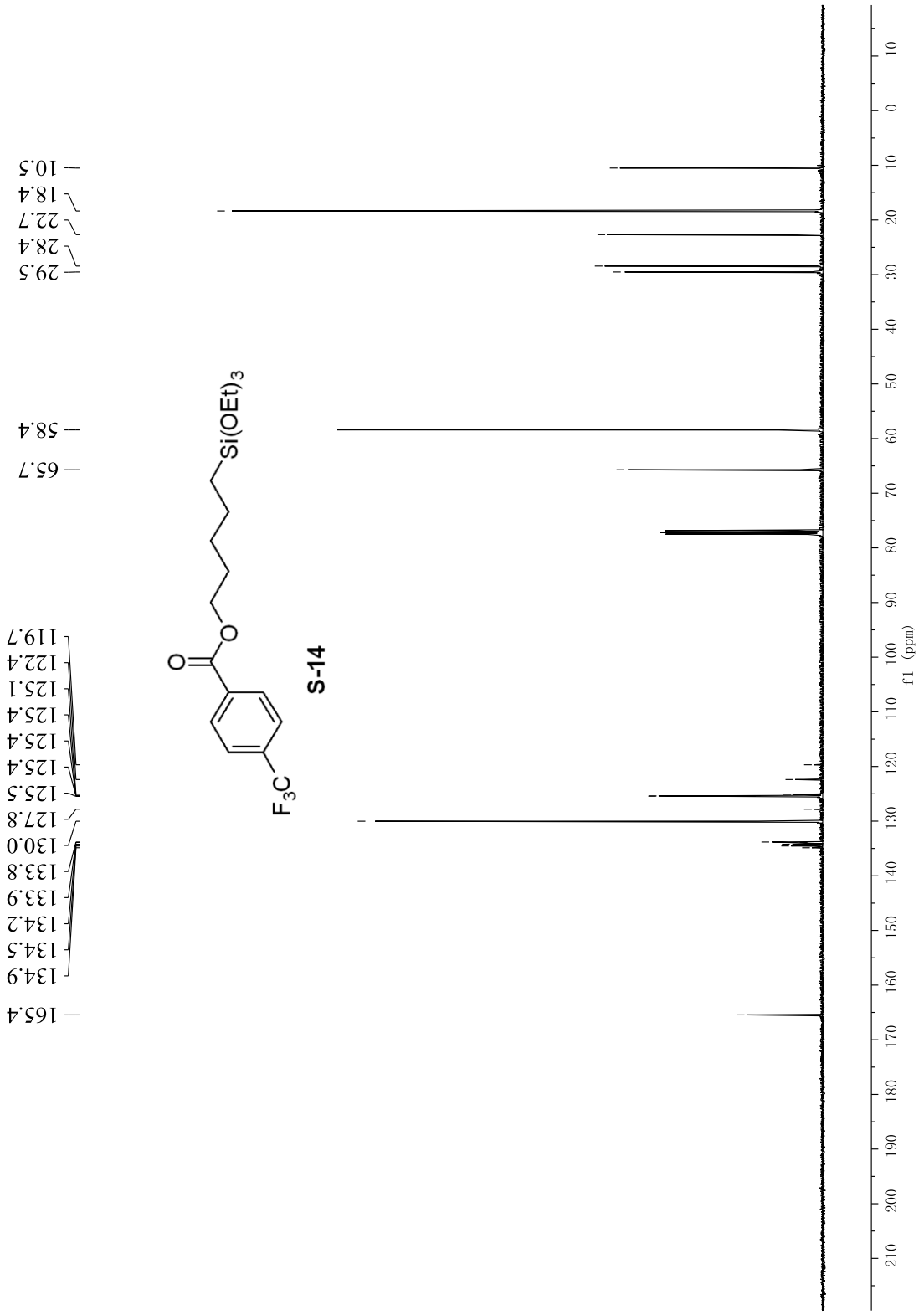
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-13**



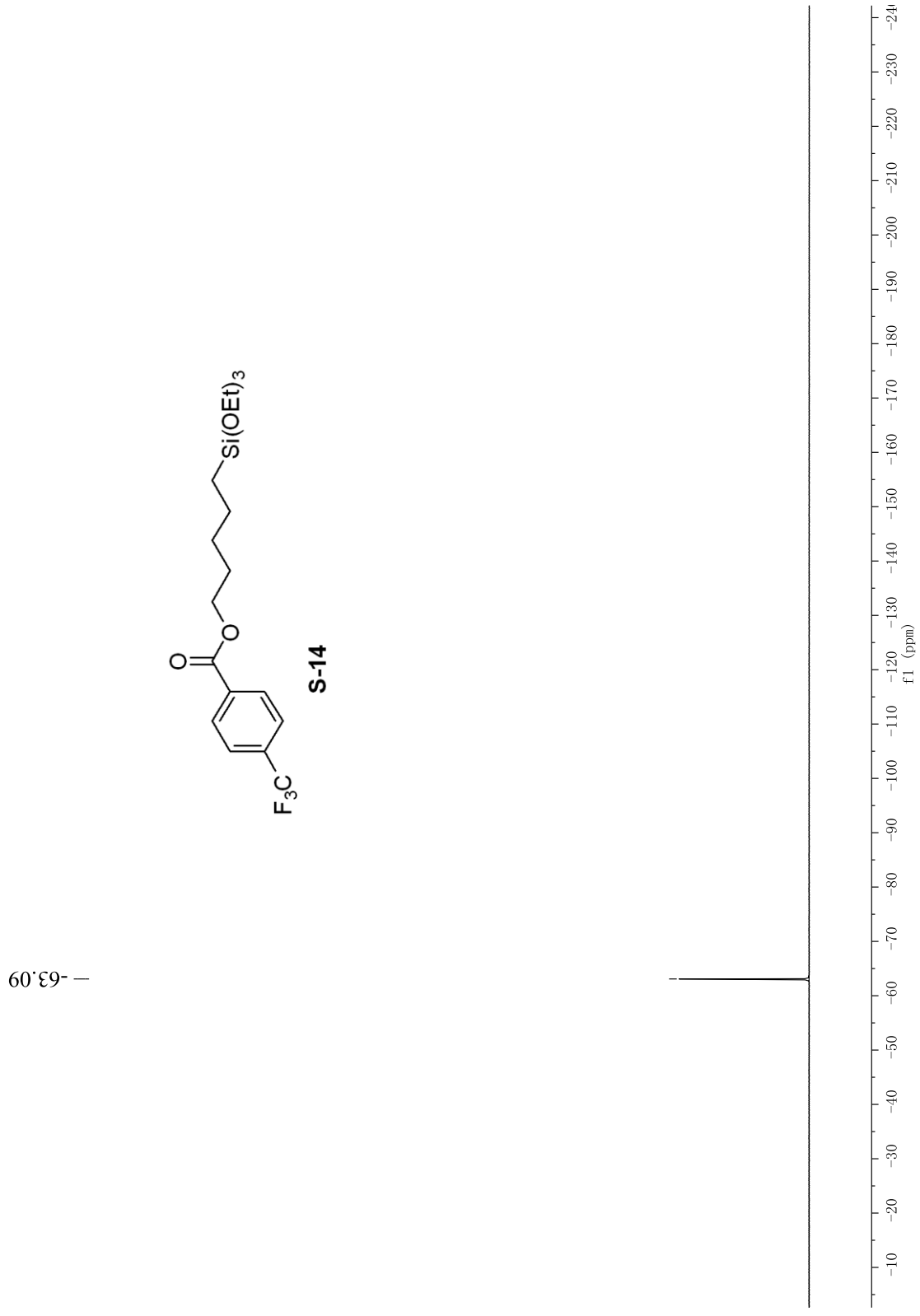
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-13**



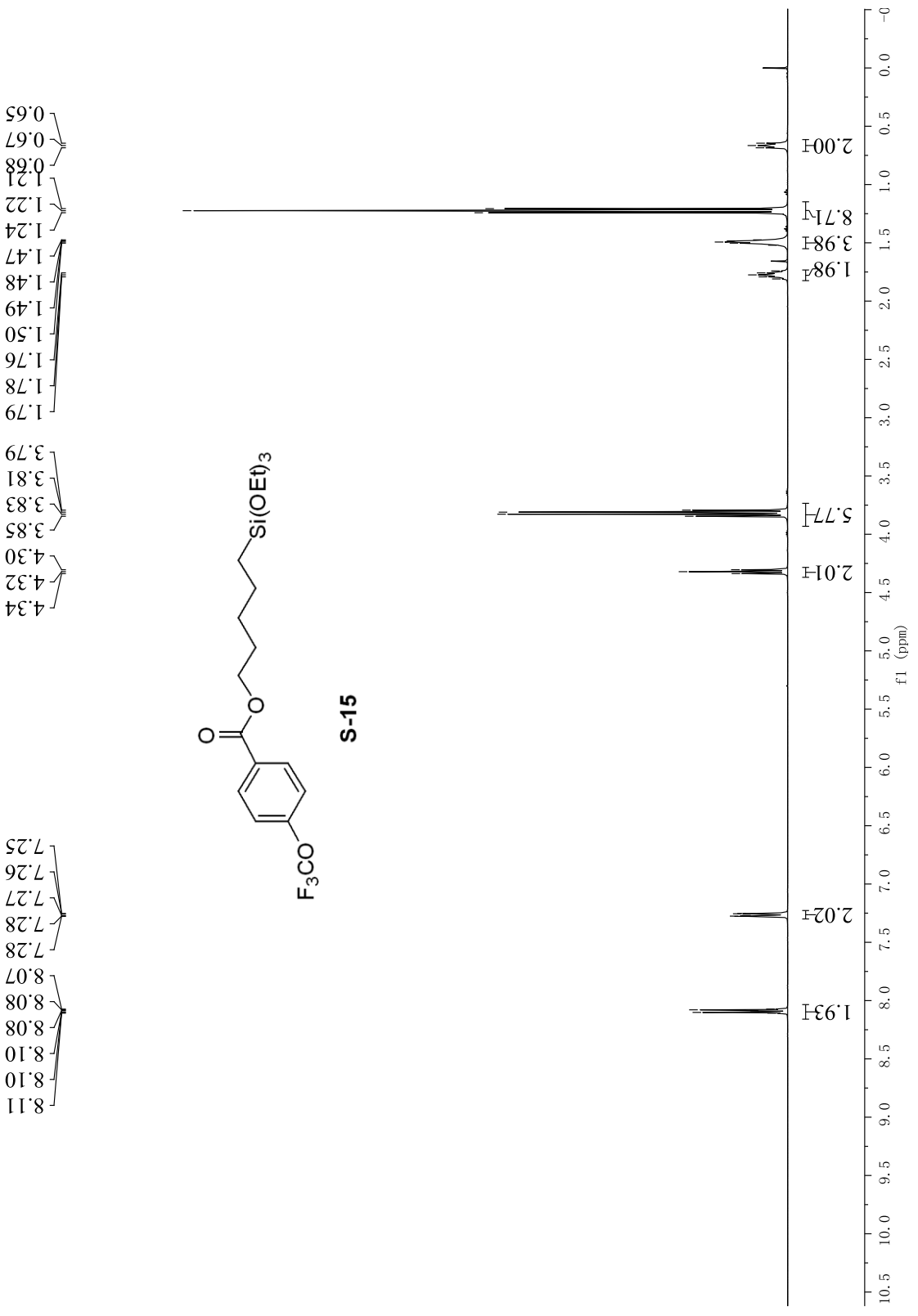
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-14**



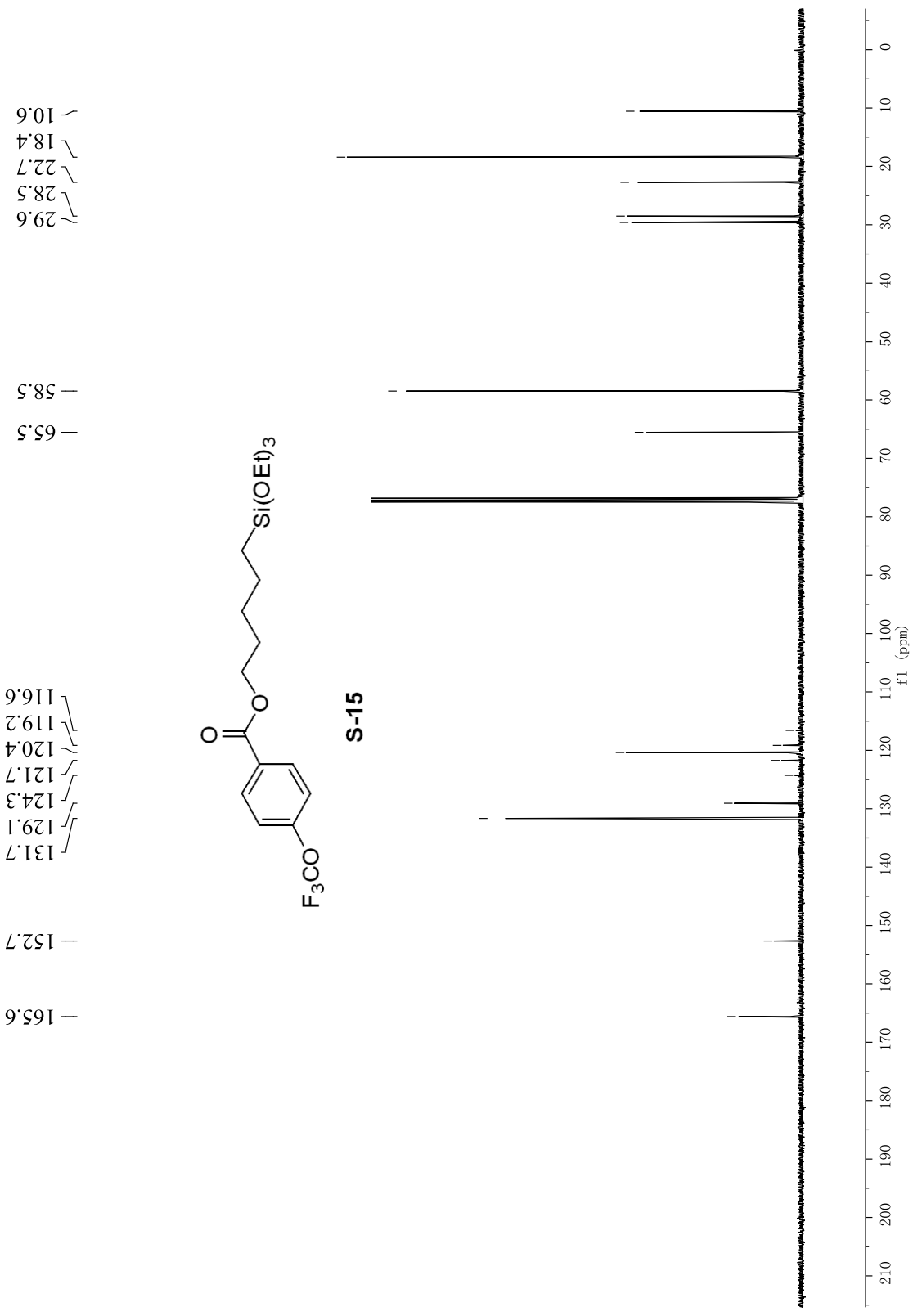
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-14**



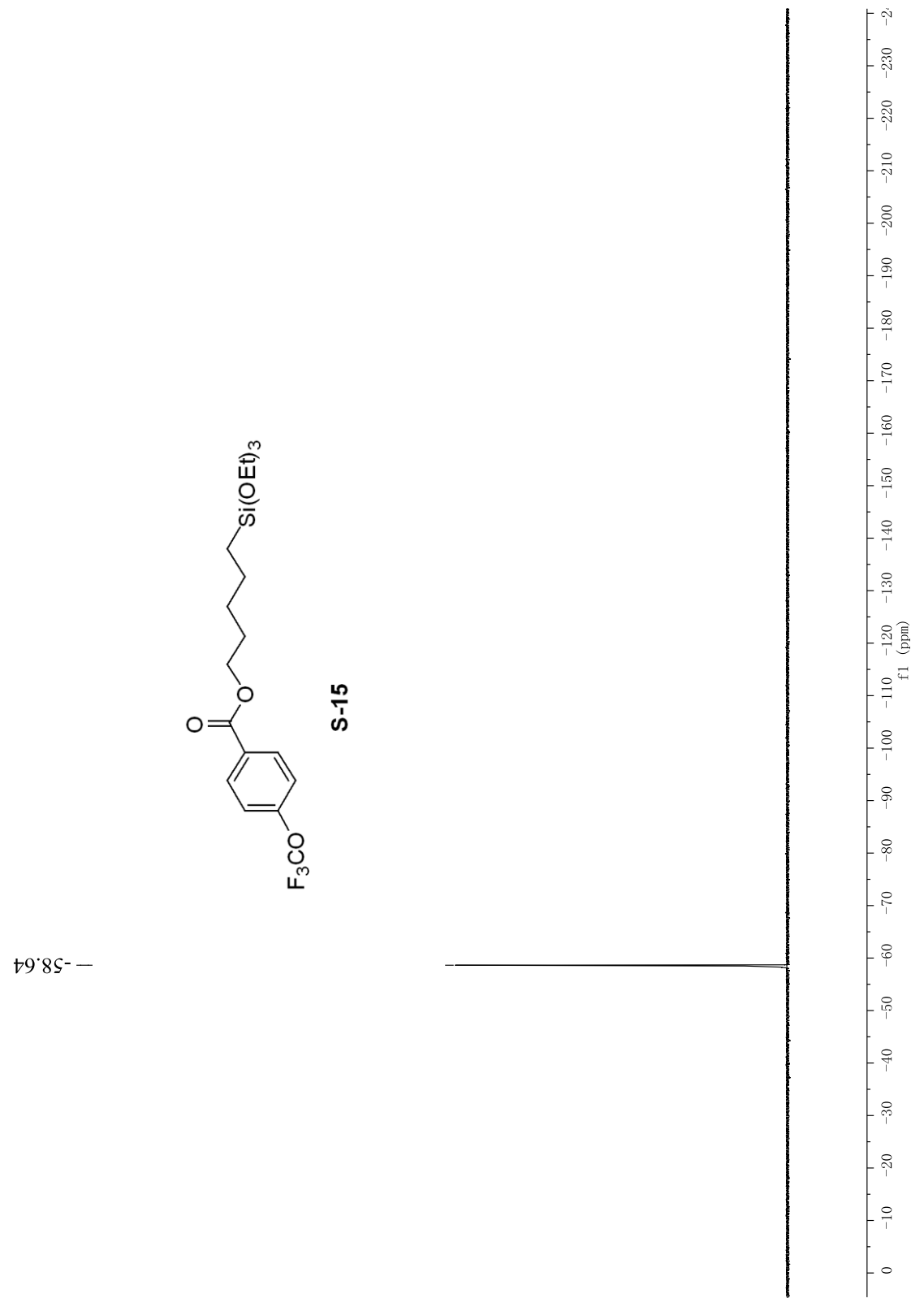
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-14**



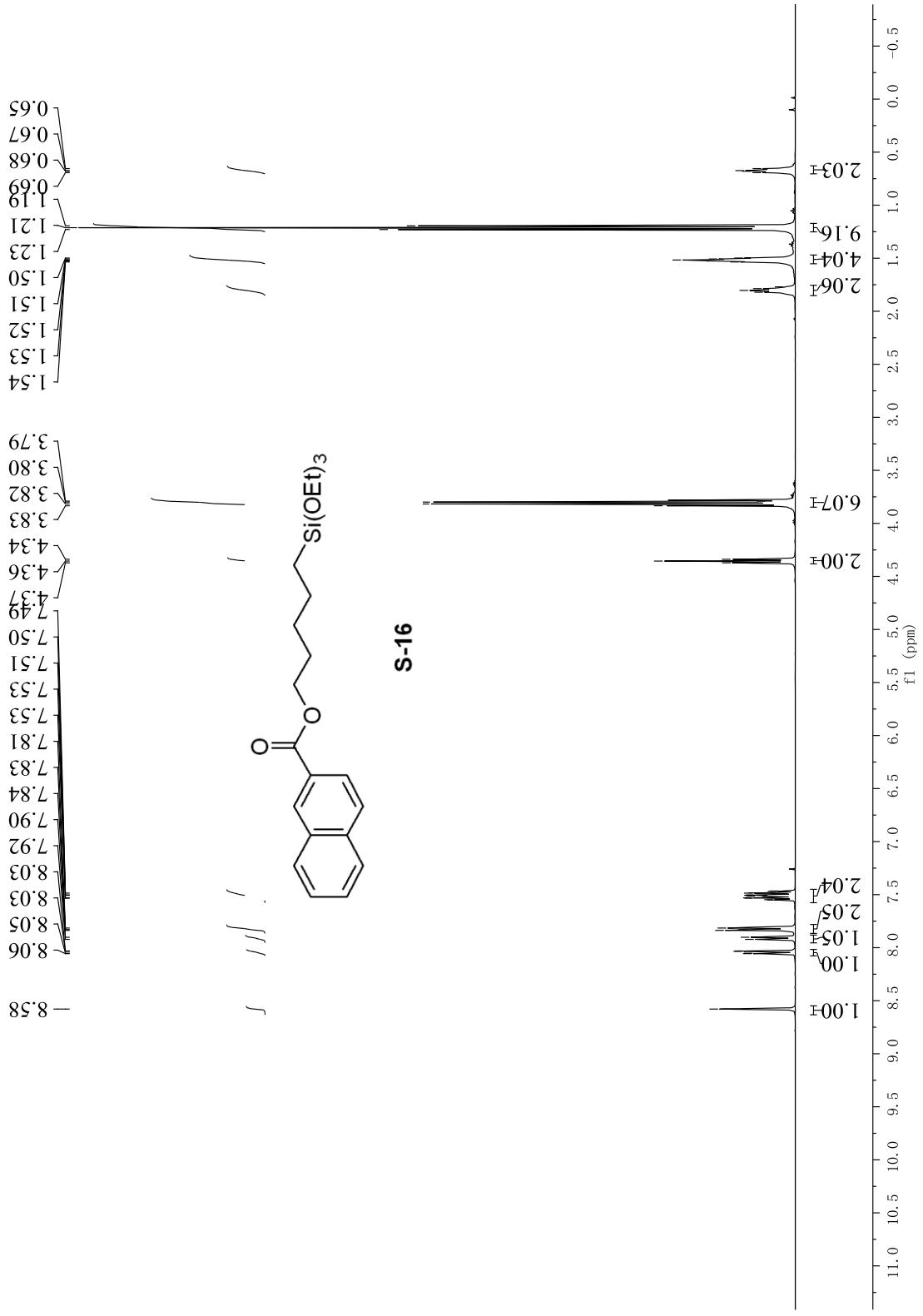
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-15**



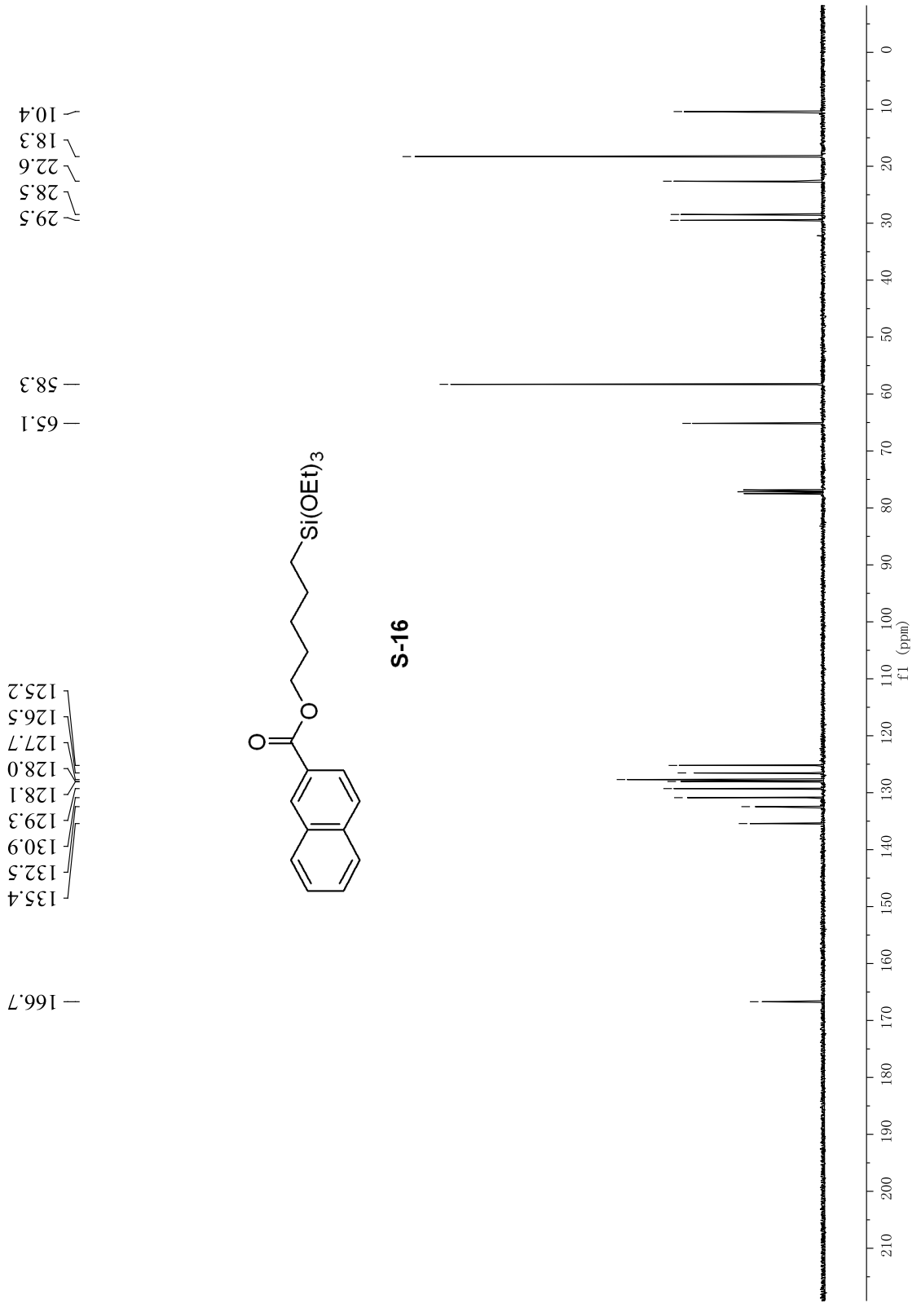
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-15**



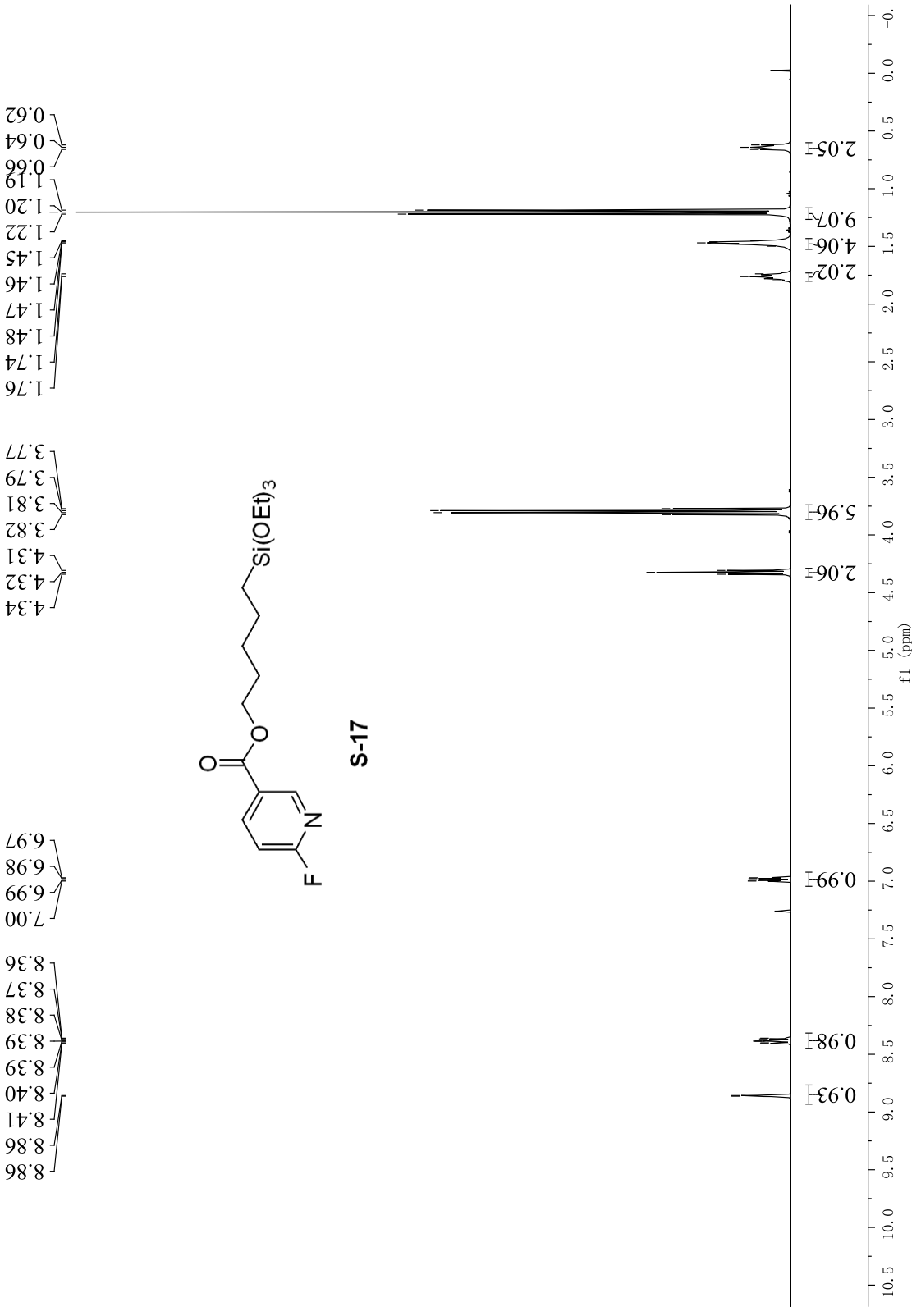
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-15**



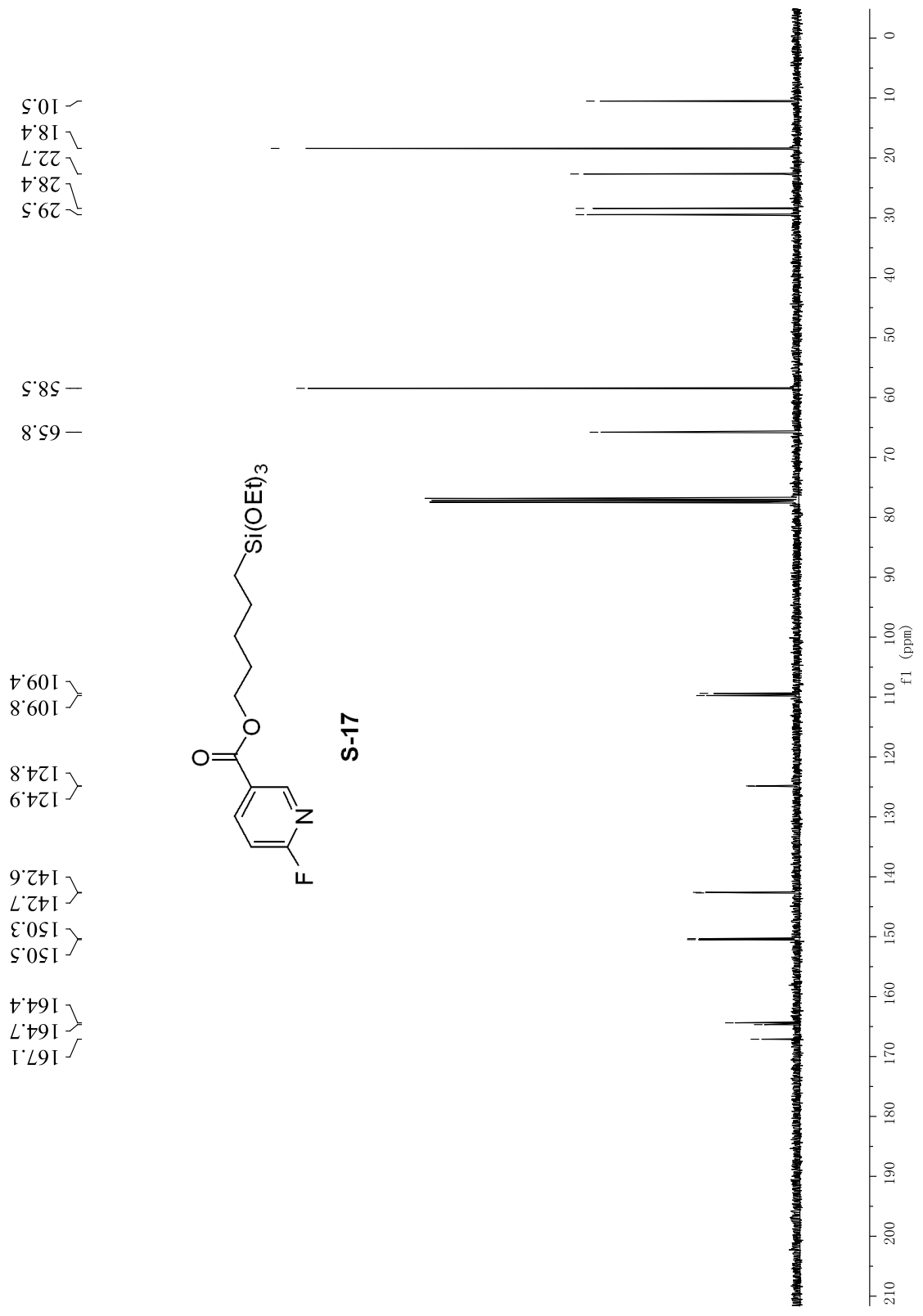
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-16**



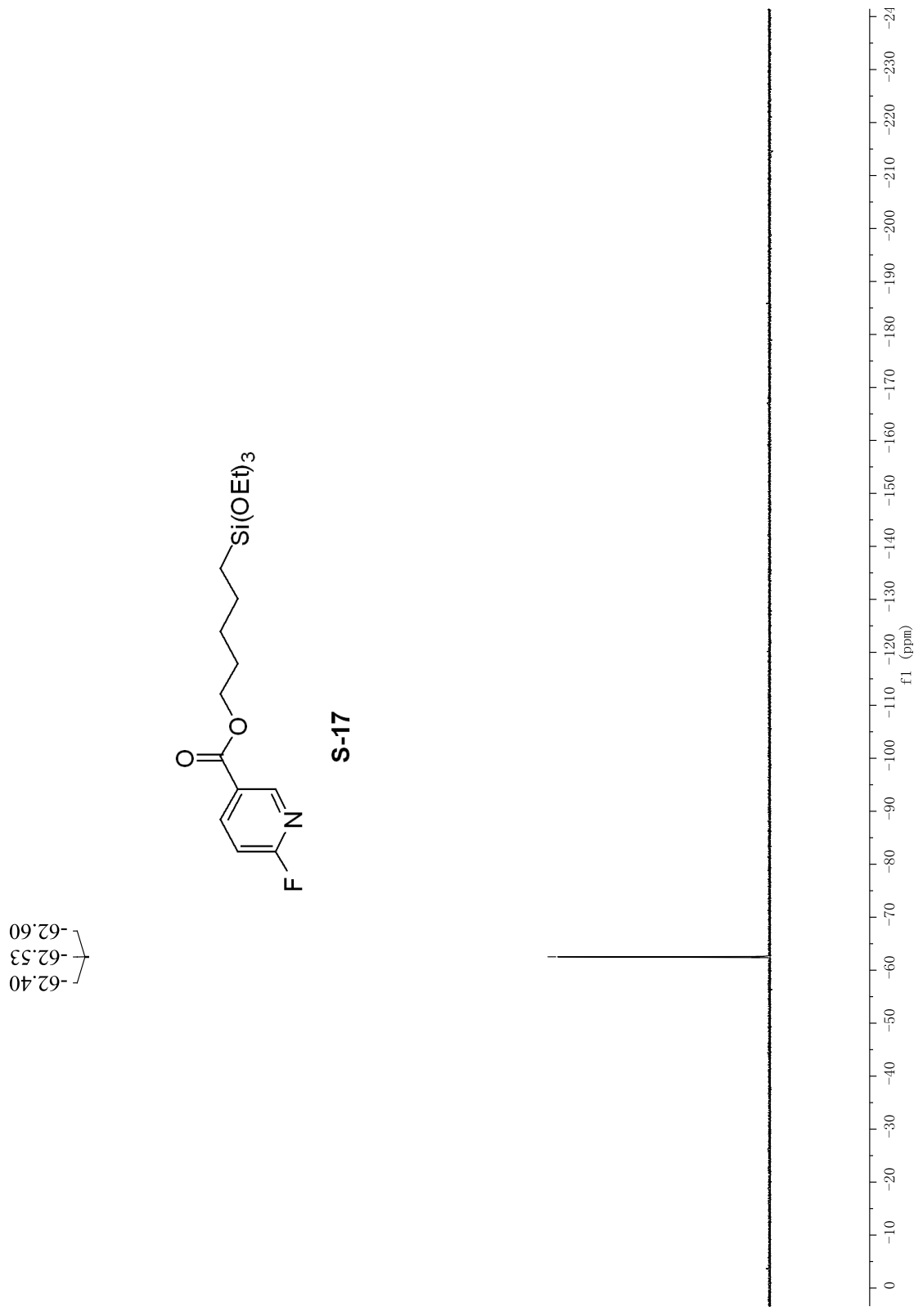
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-16**



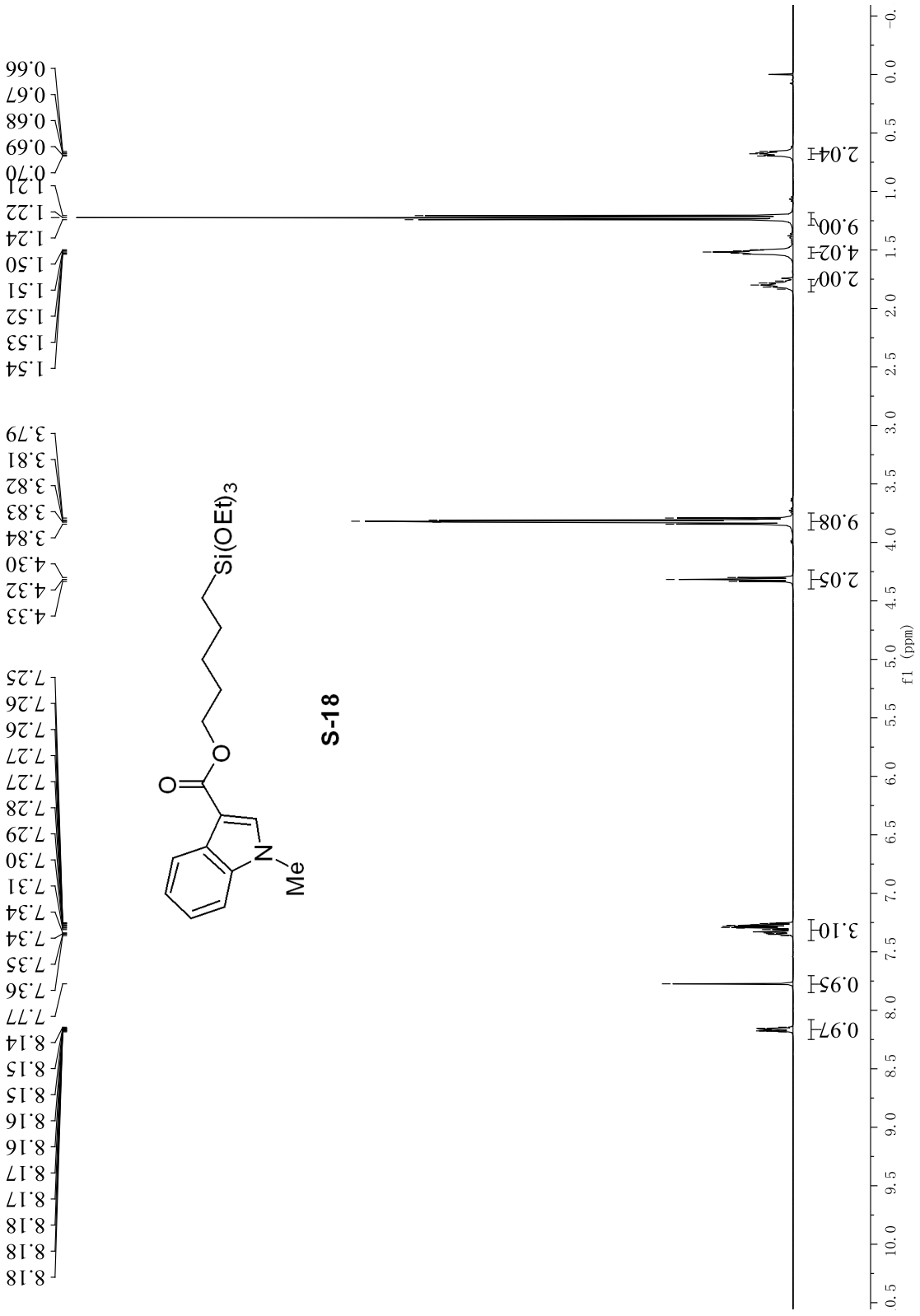
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-17**



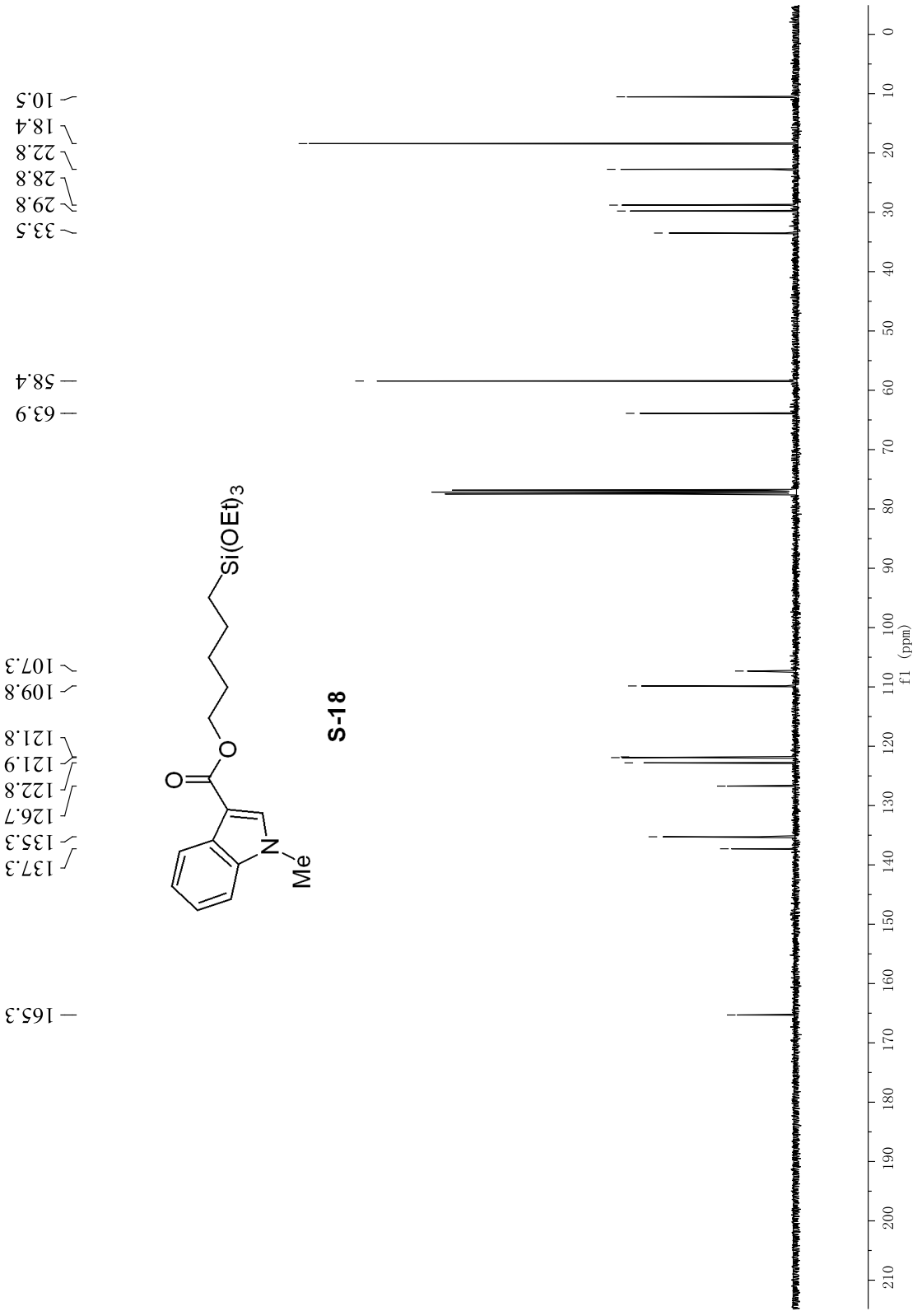
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-17**



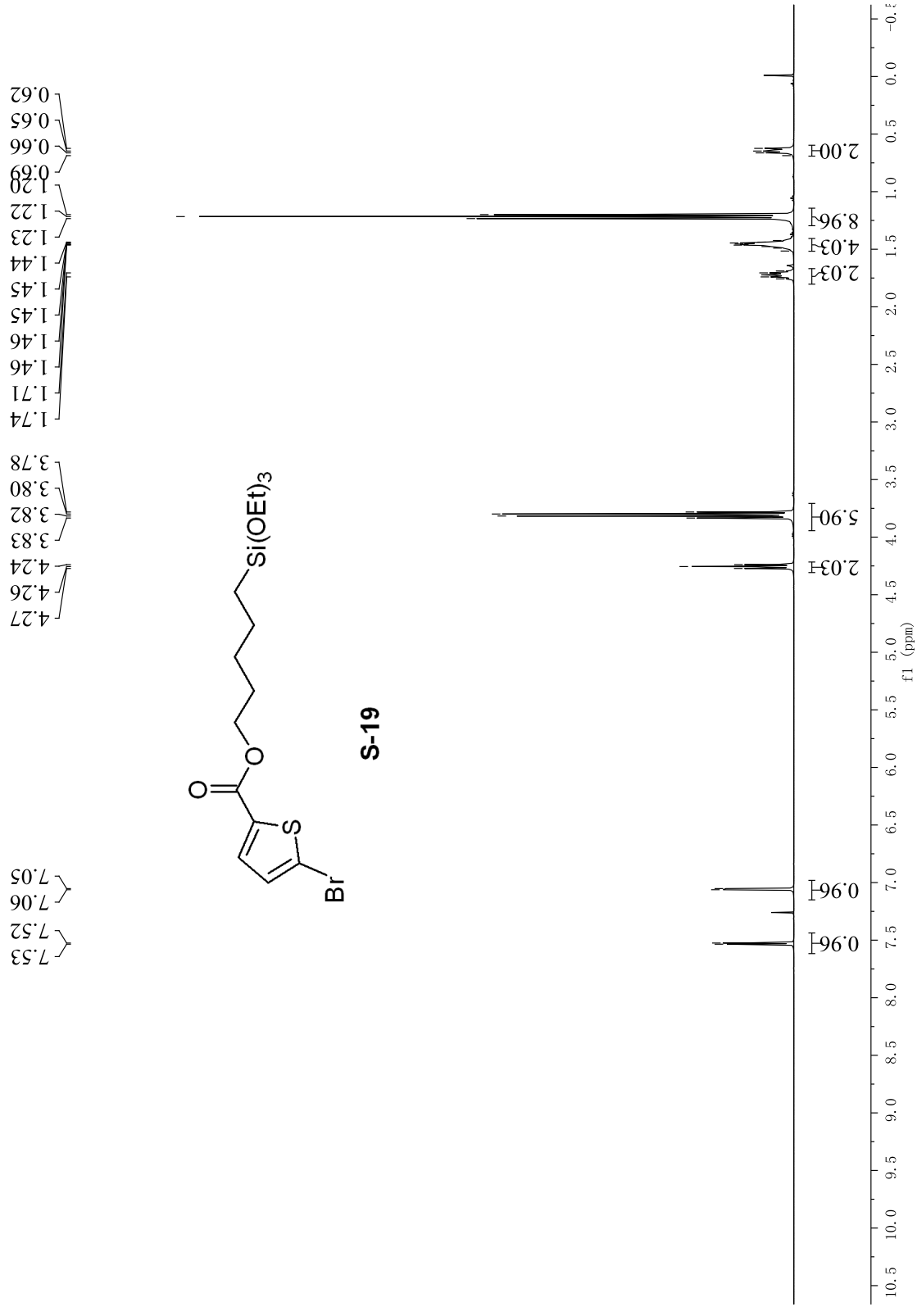
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-17**



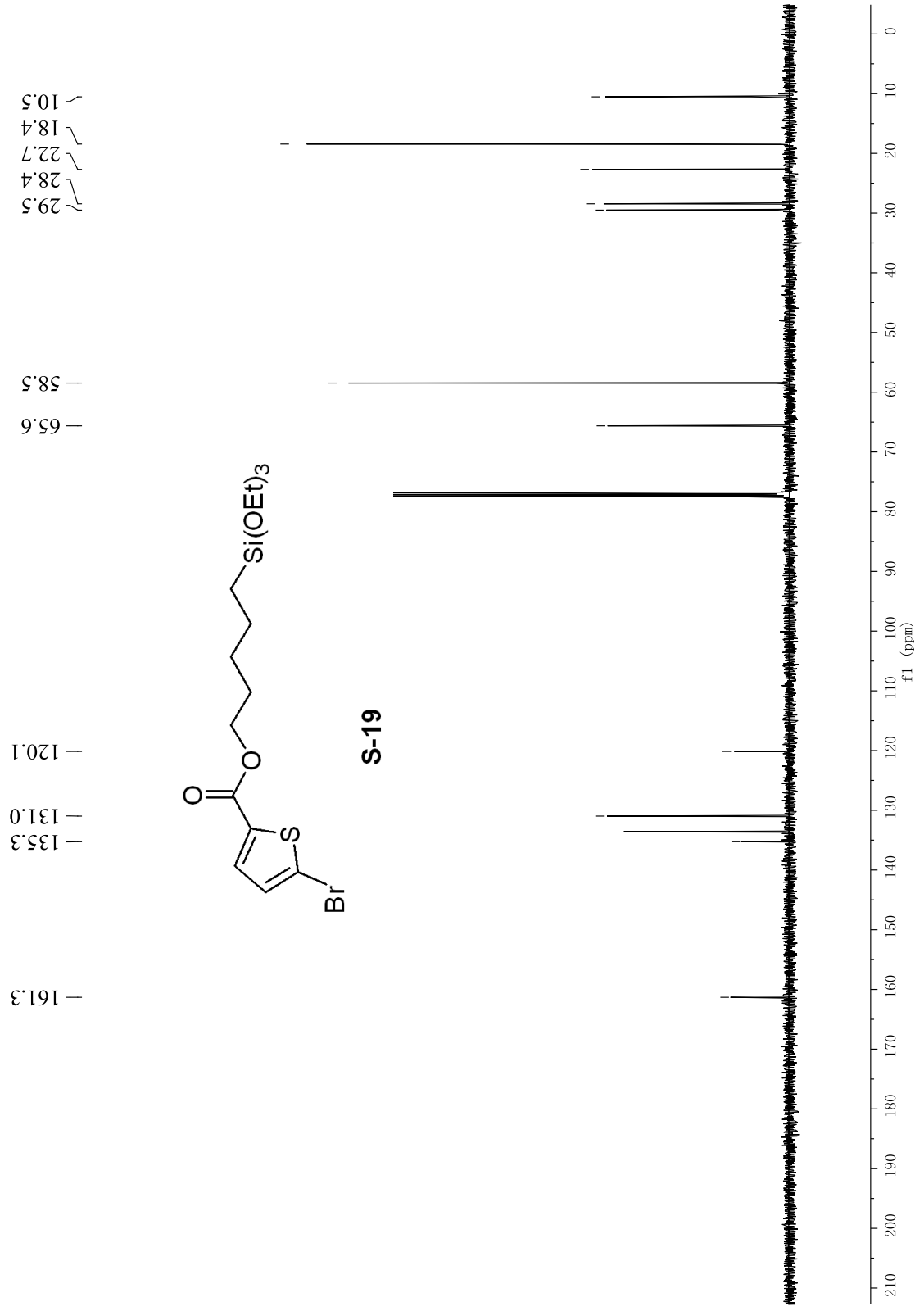
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-18**



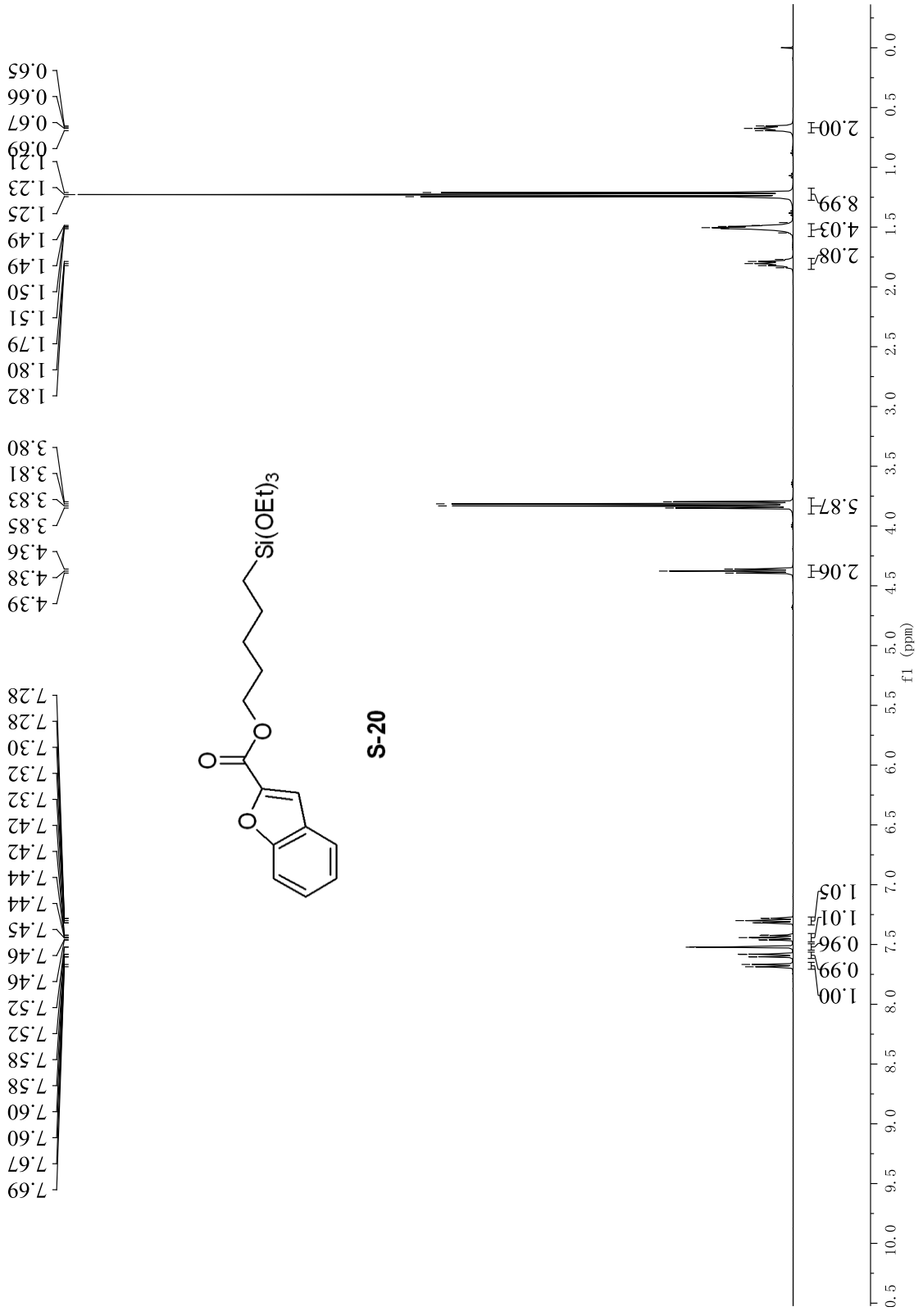
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-18**



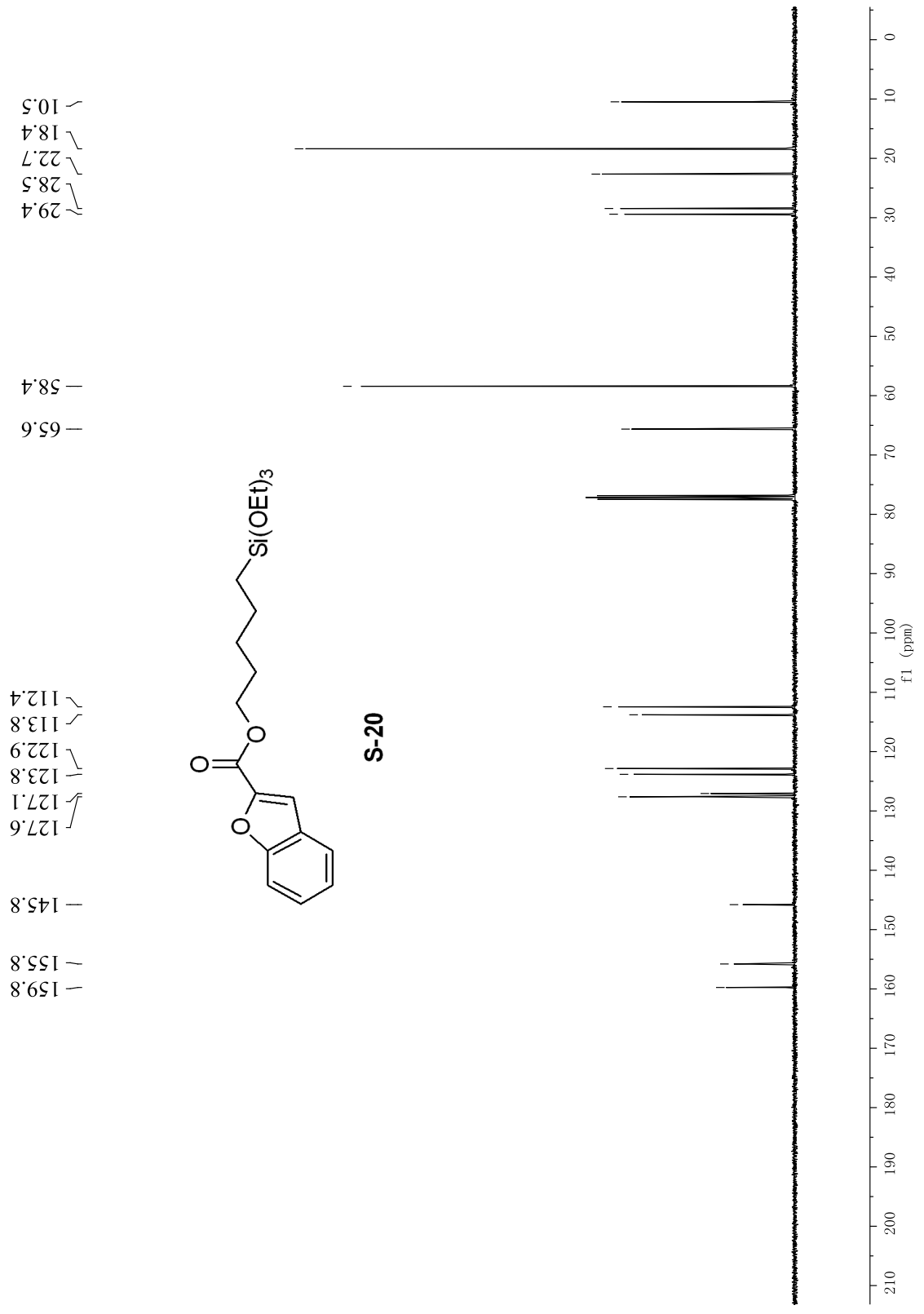
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-19**



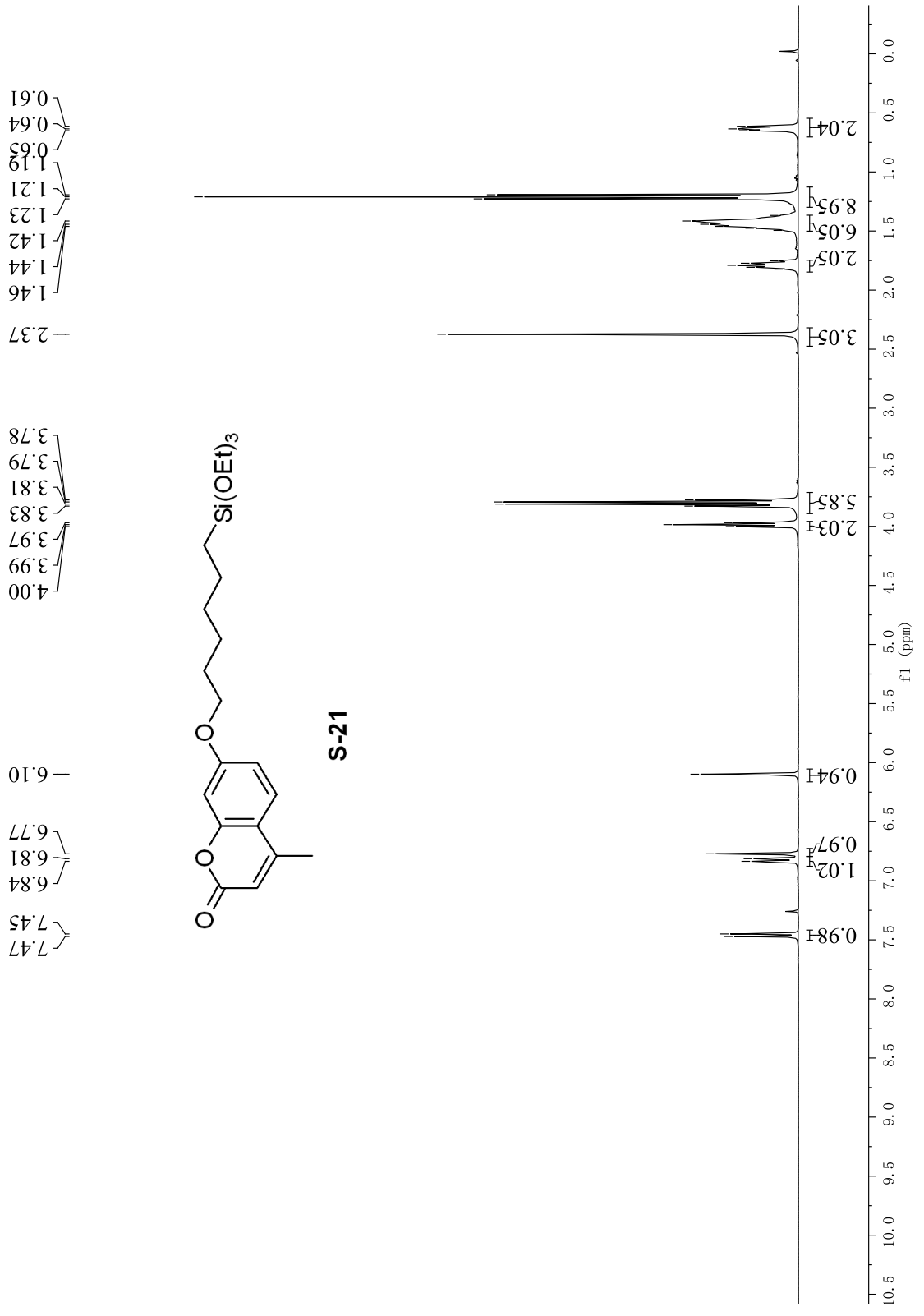
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-19**



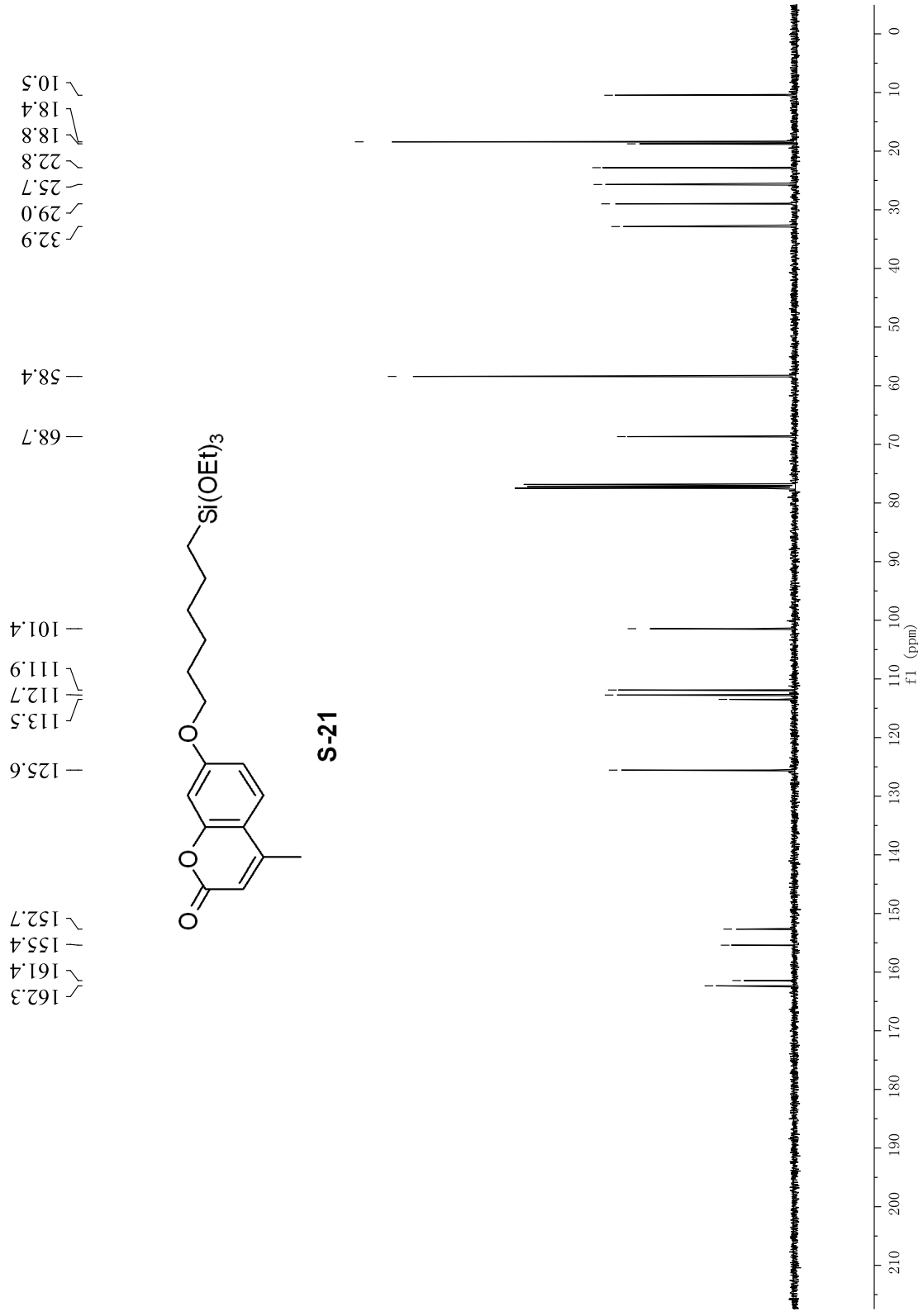
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-20**



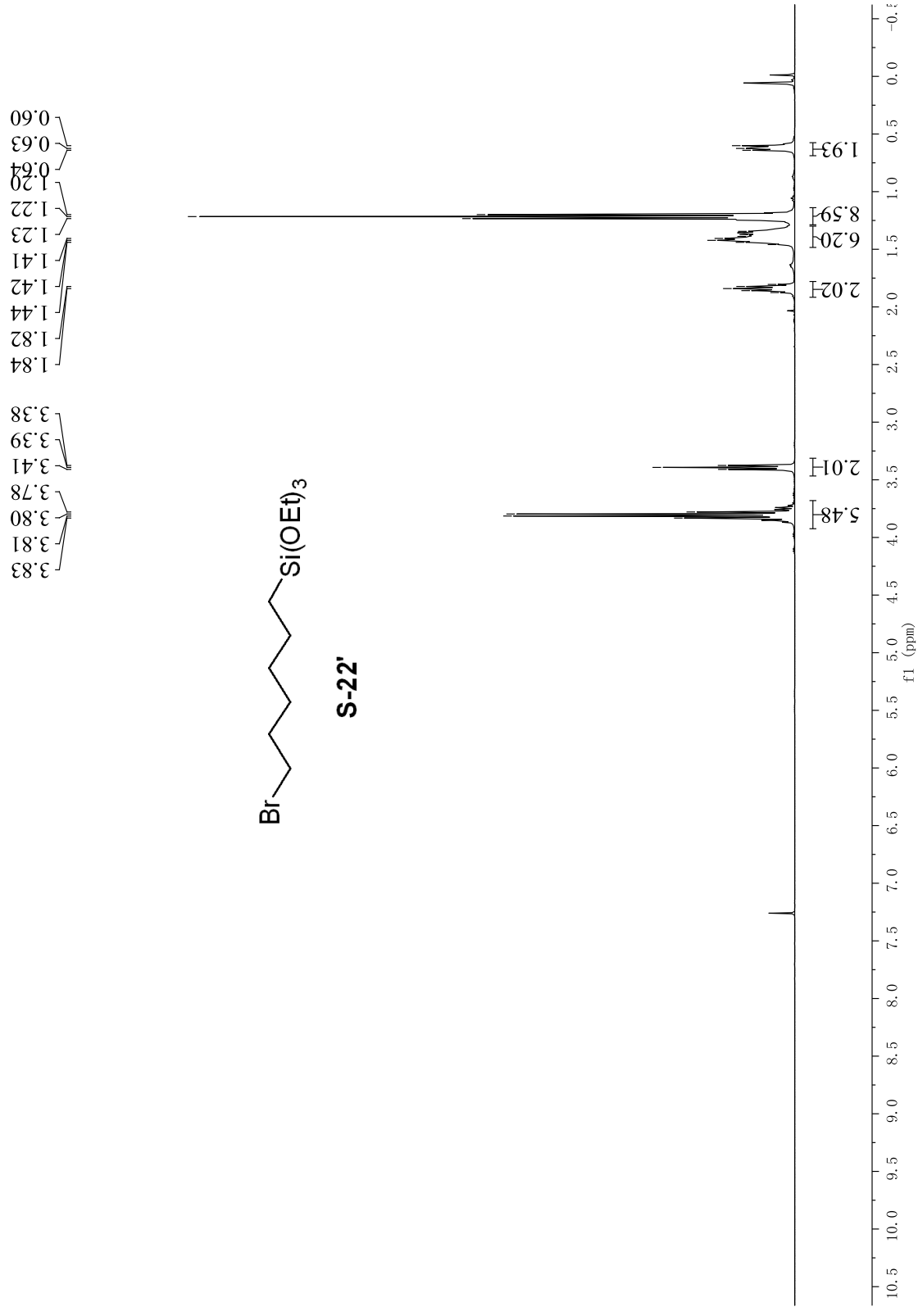
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-20**



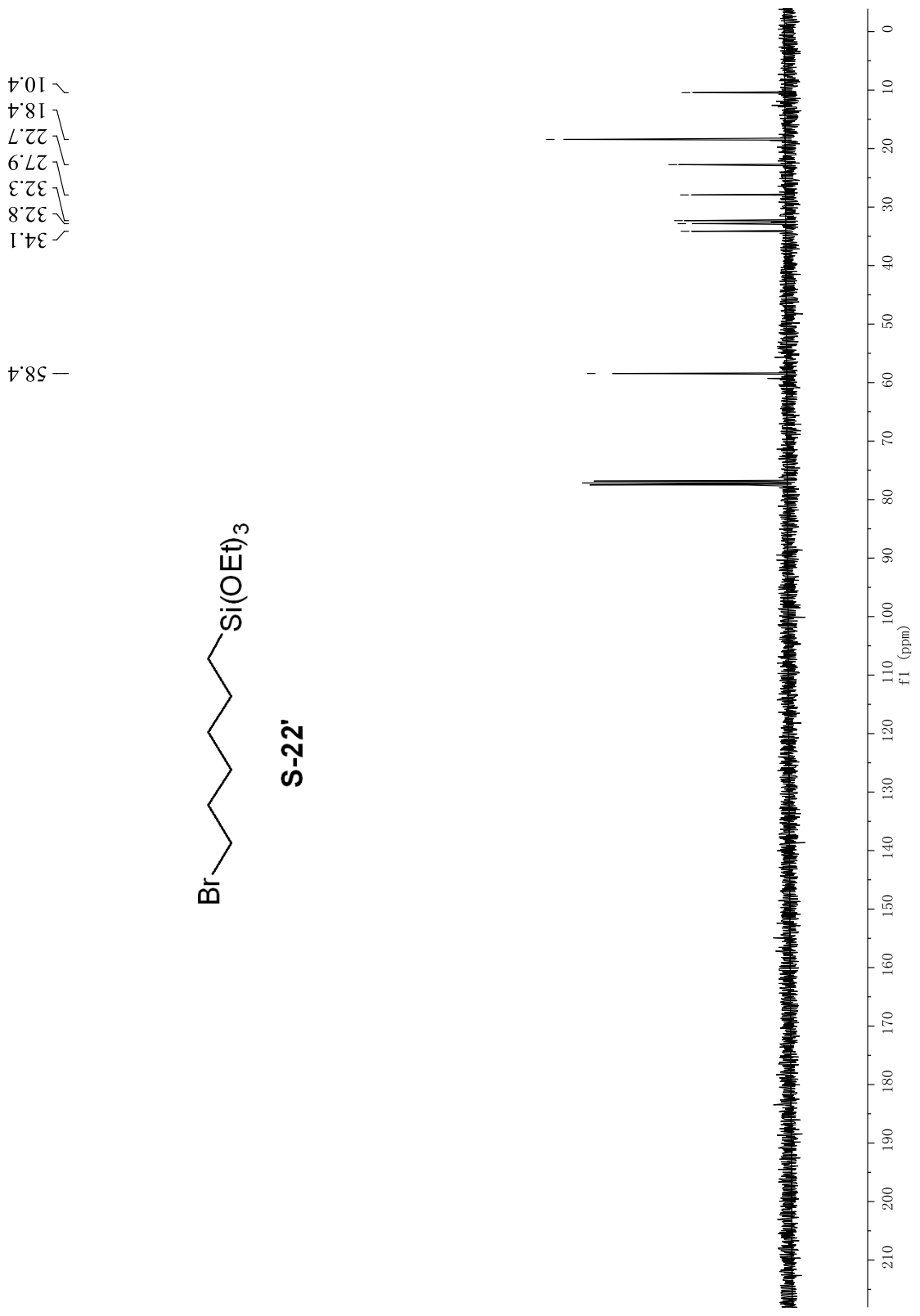
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-21**



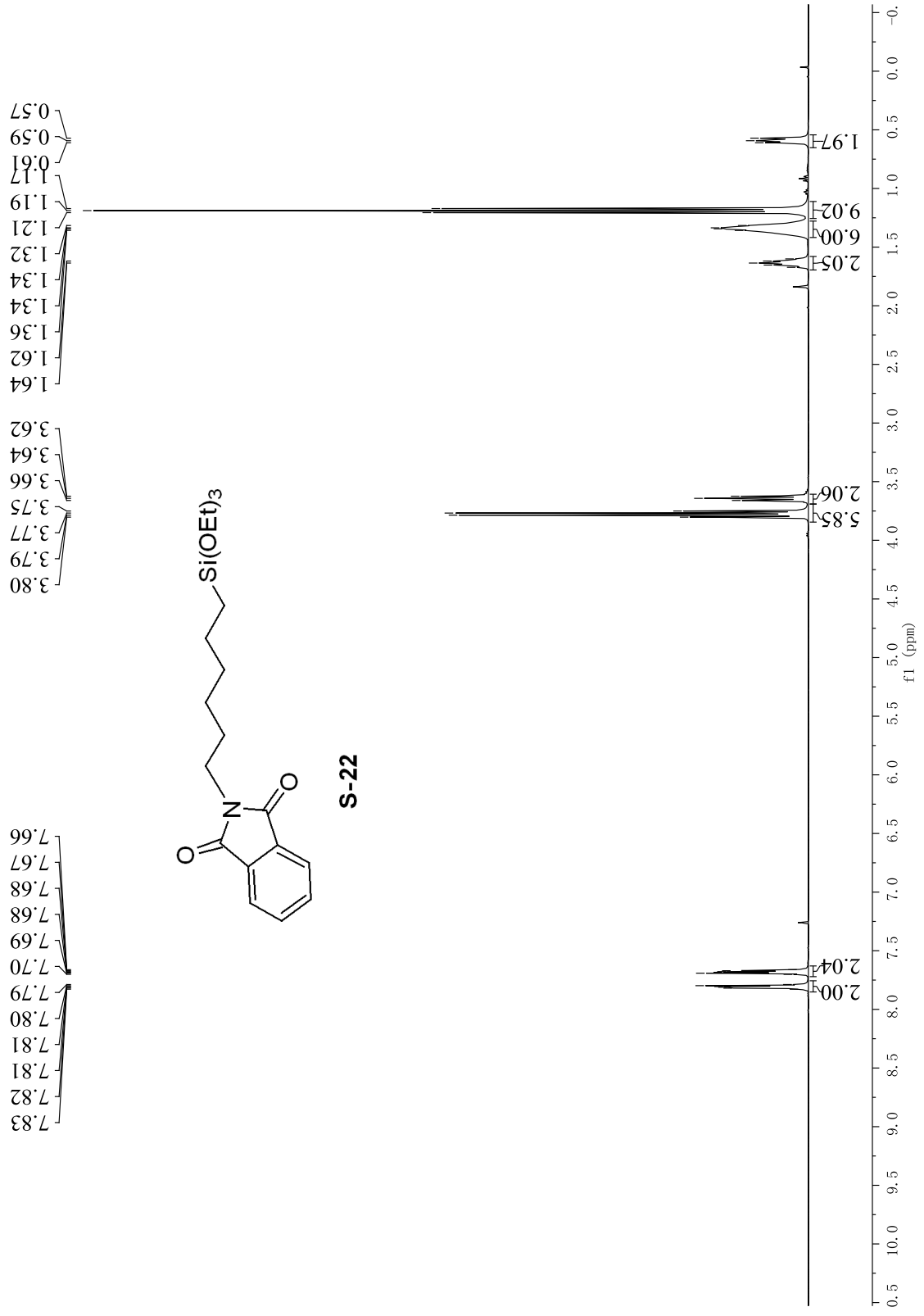
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-21**



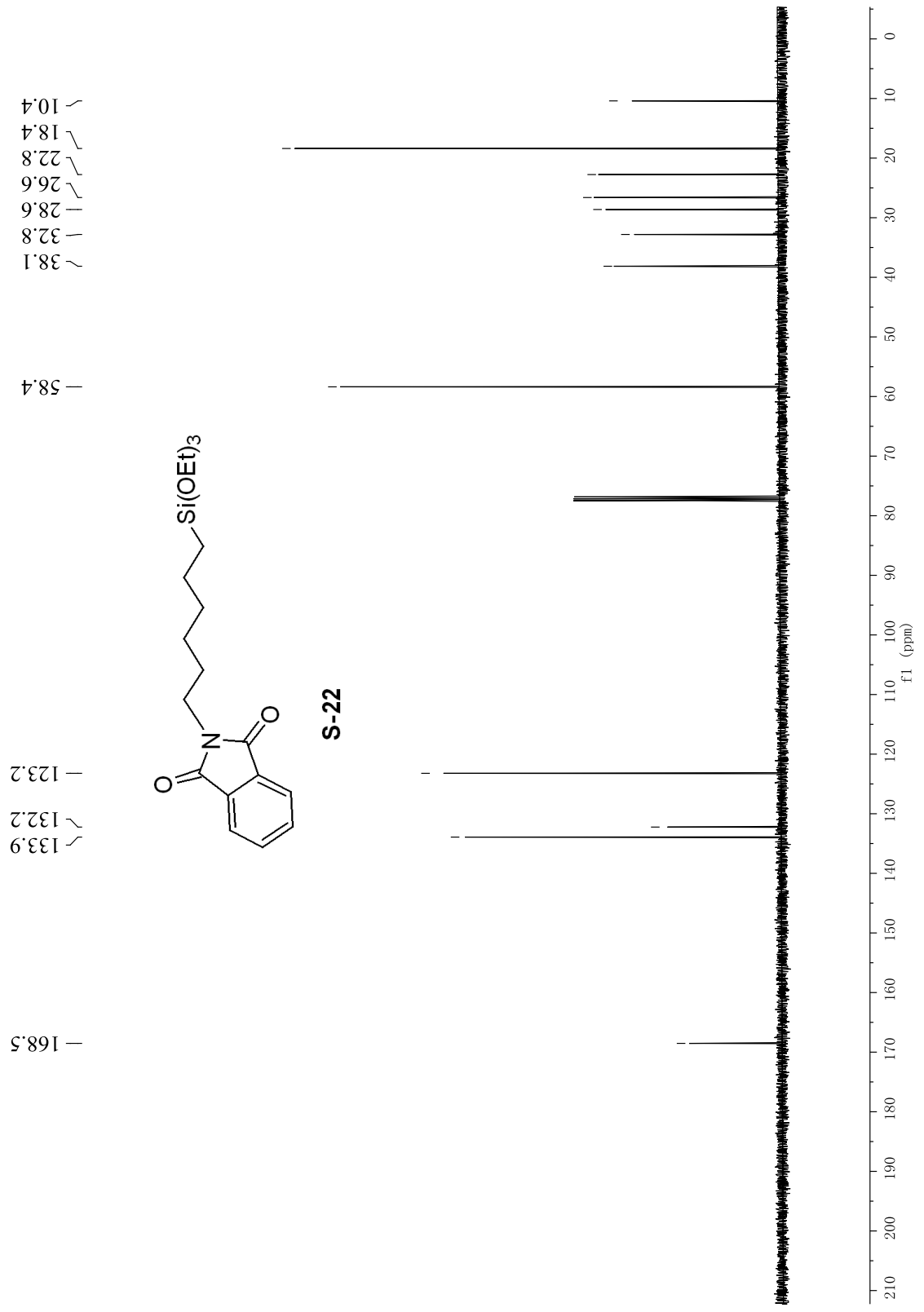
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-22'**



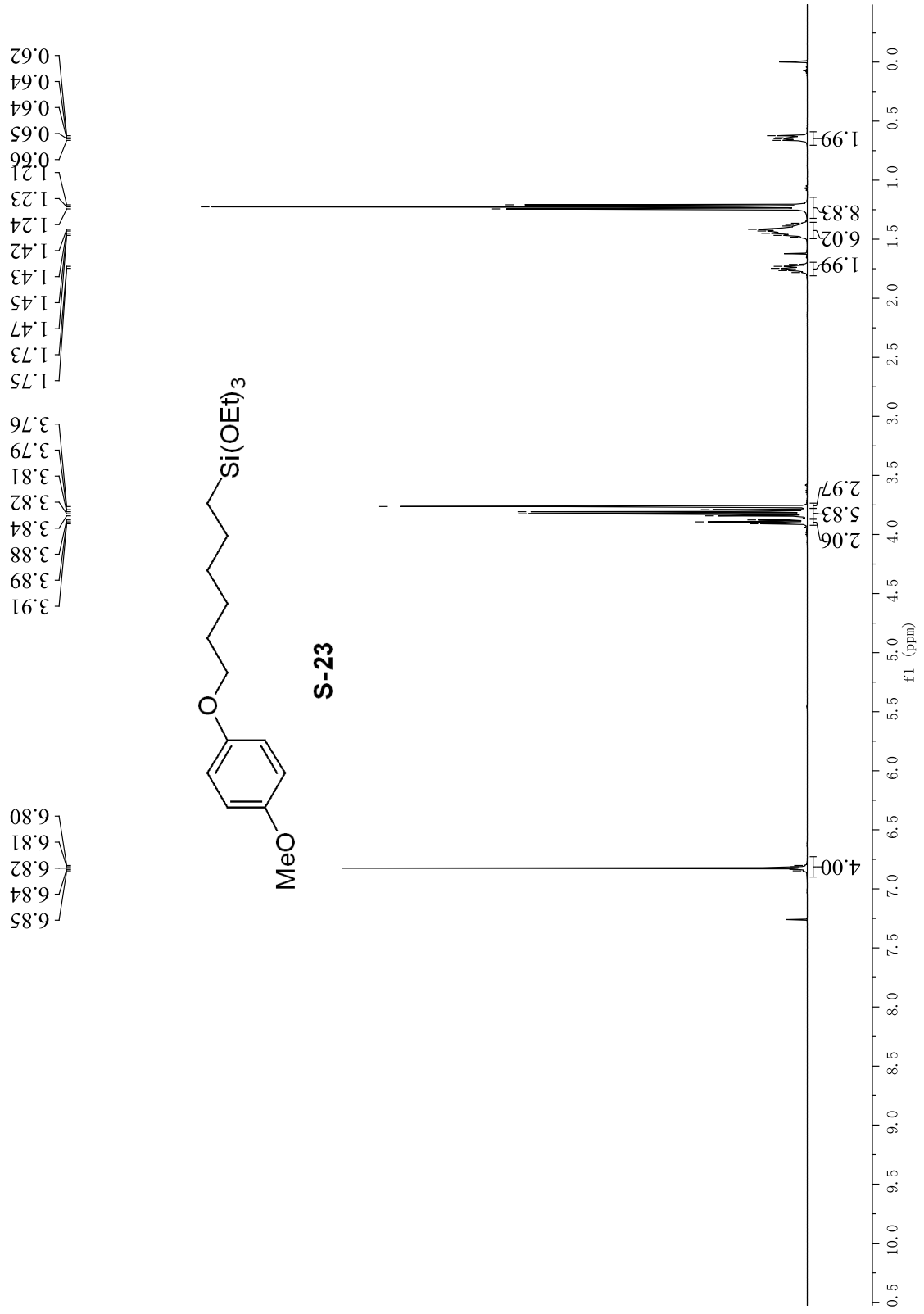
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-22'**



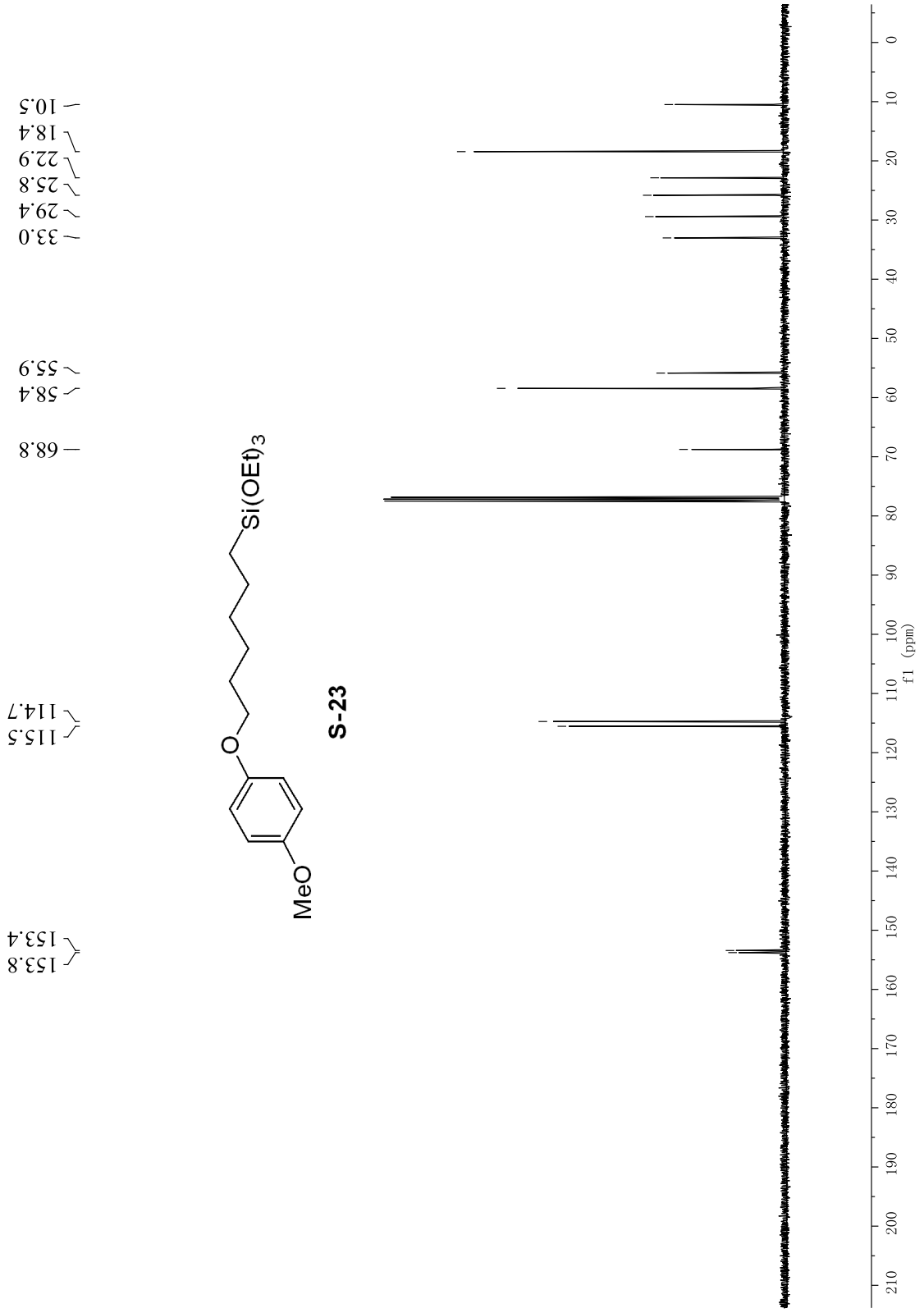
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-22**



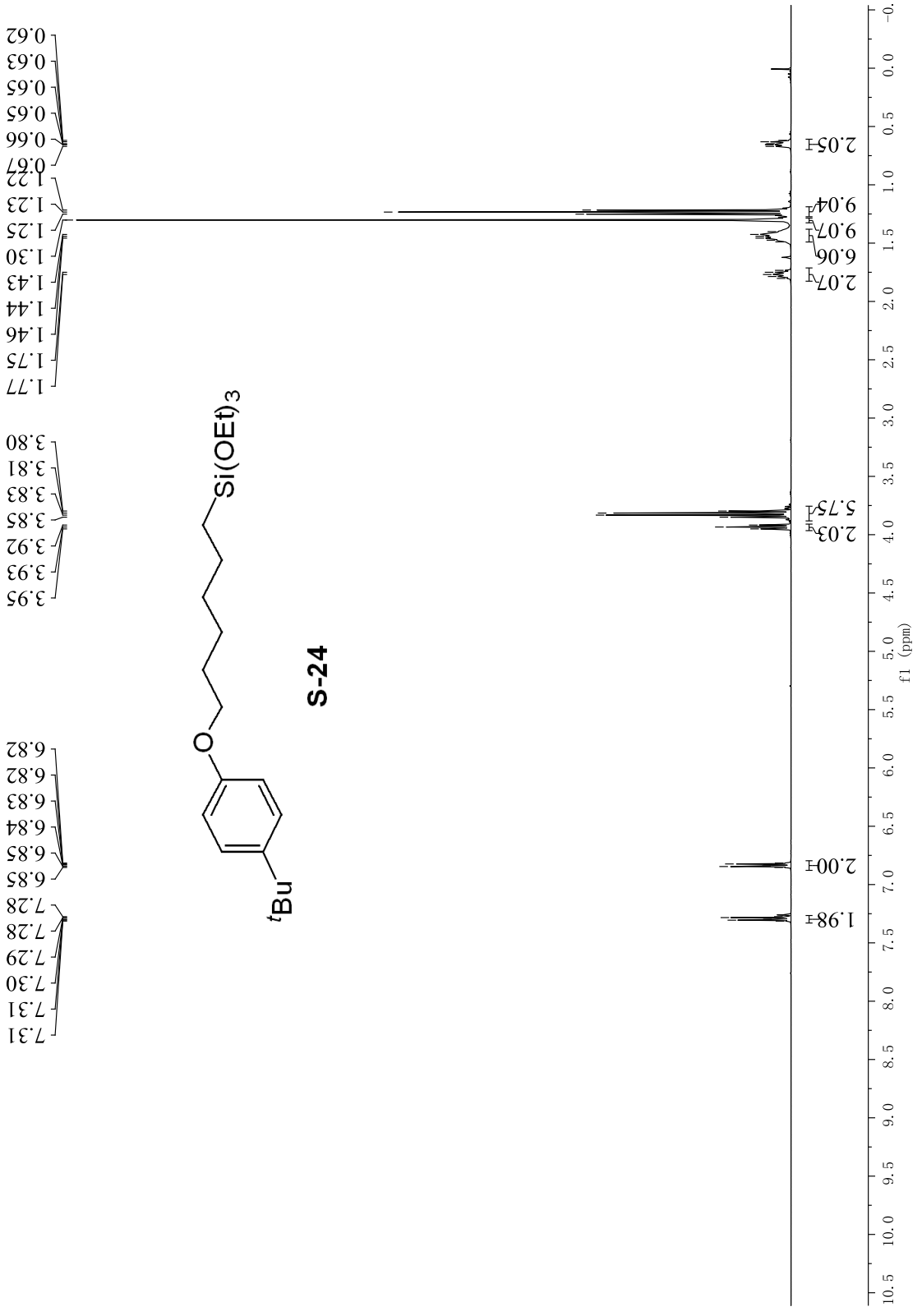
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-22**



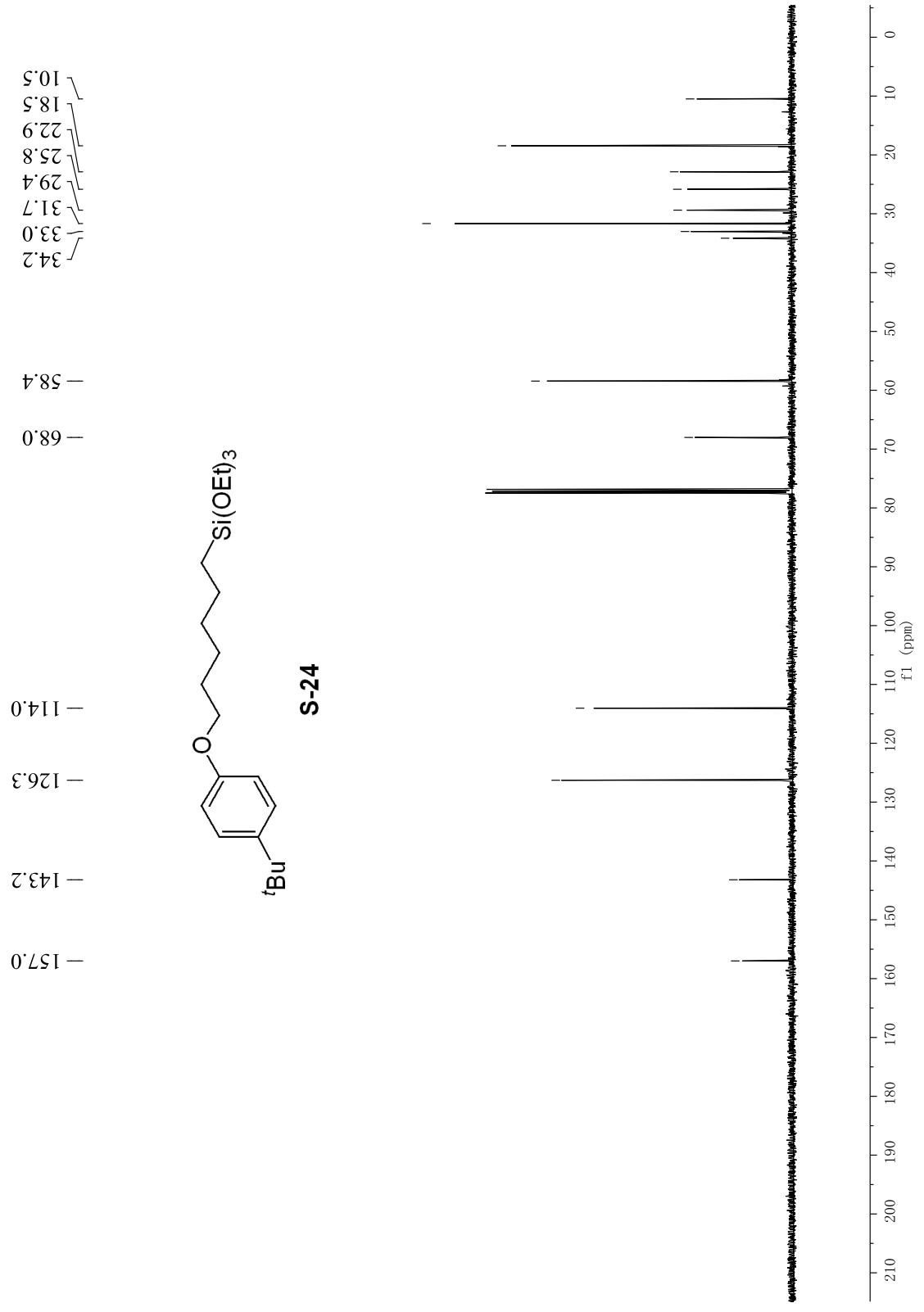
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-23**



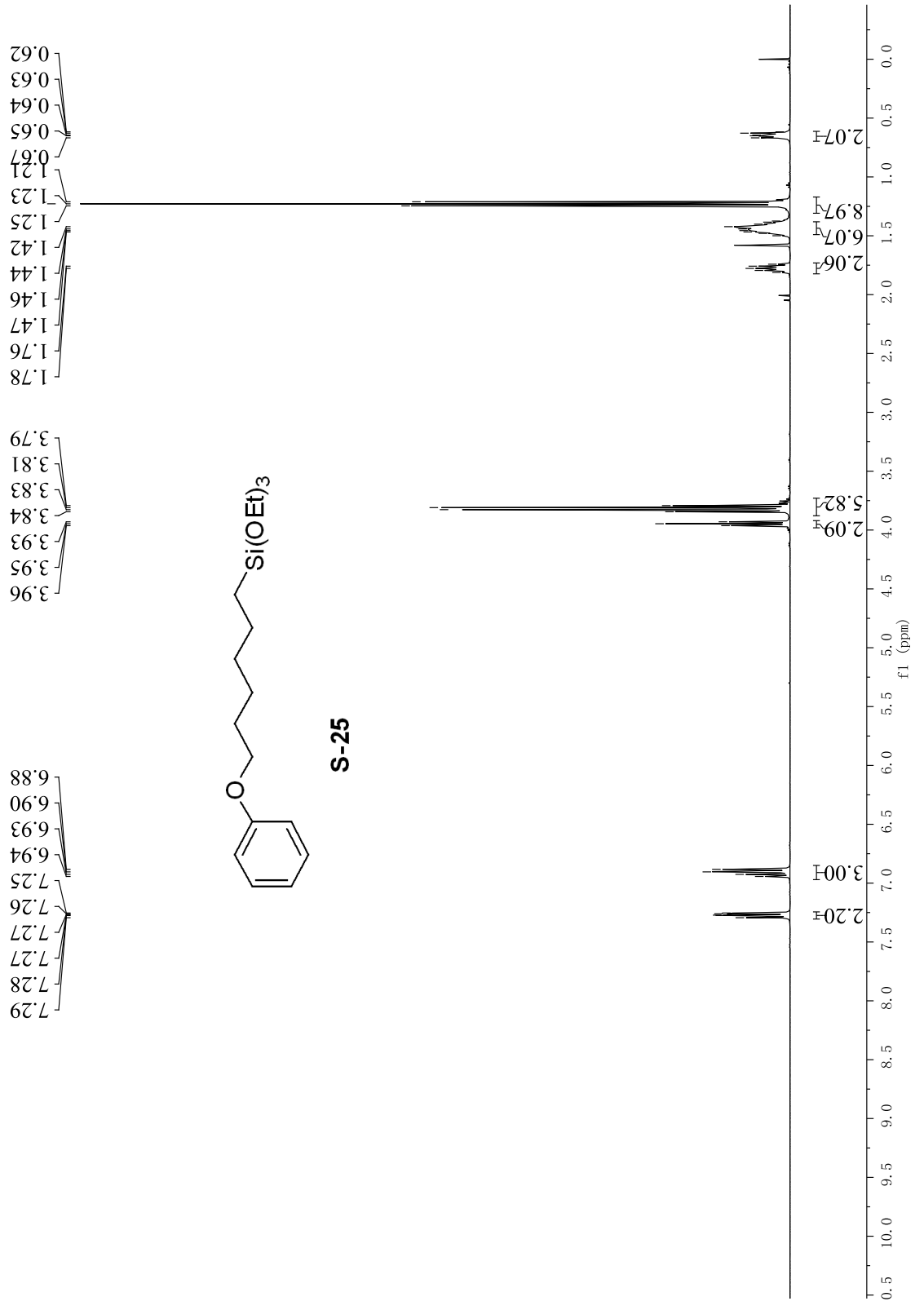
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-23**



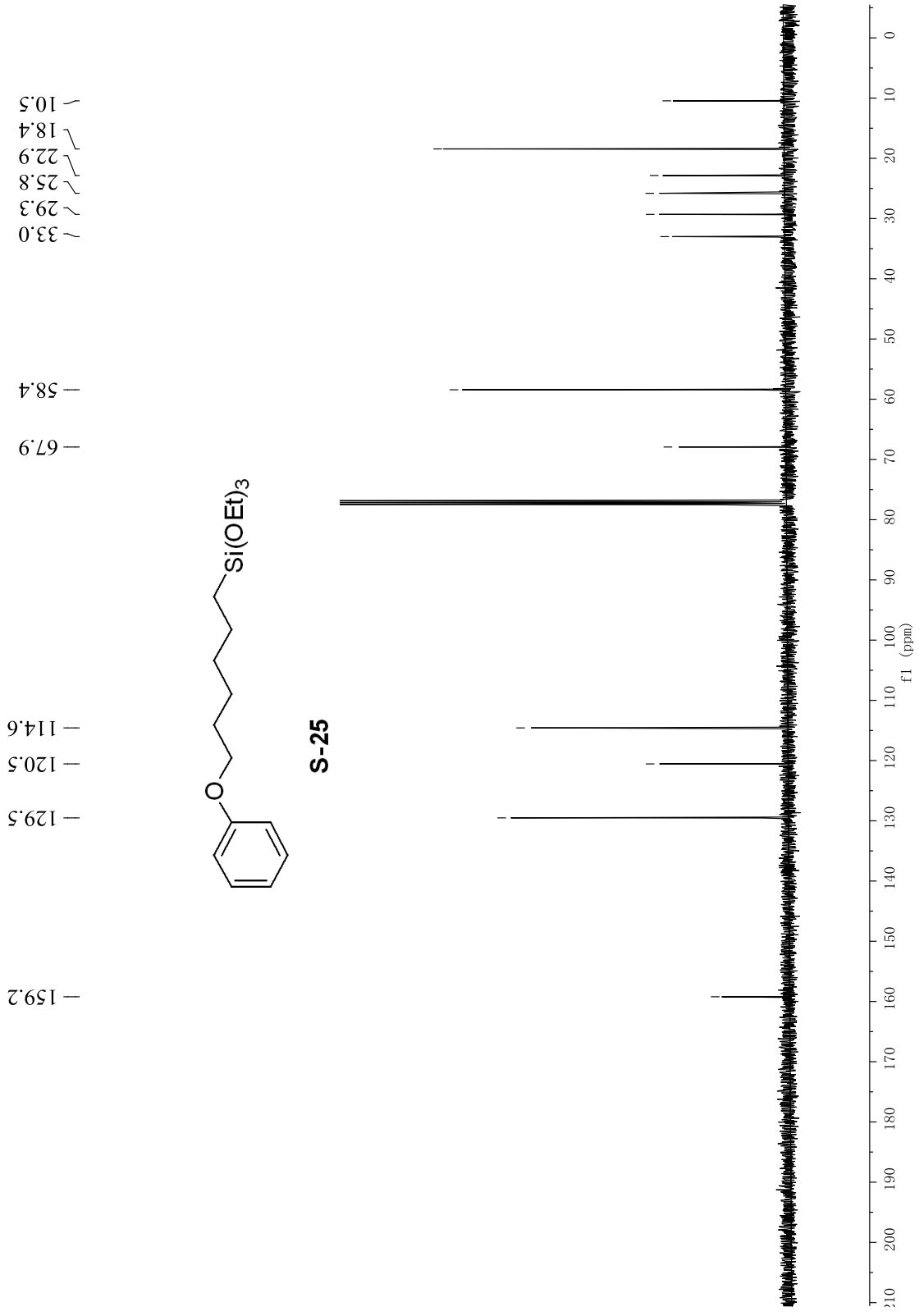
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-24**



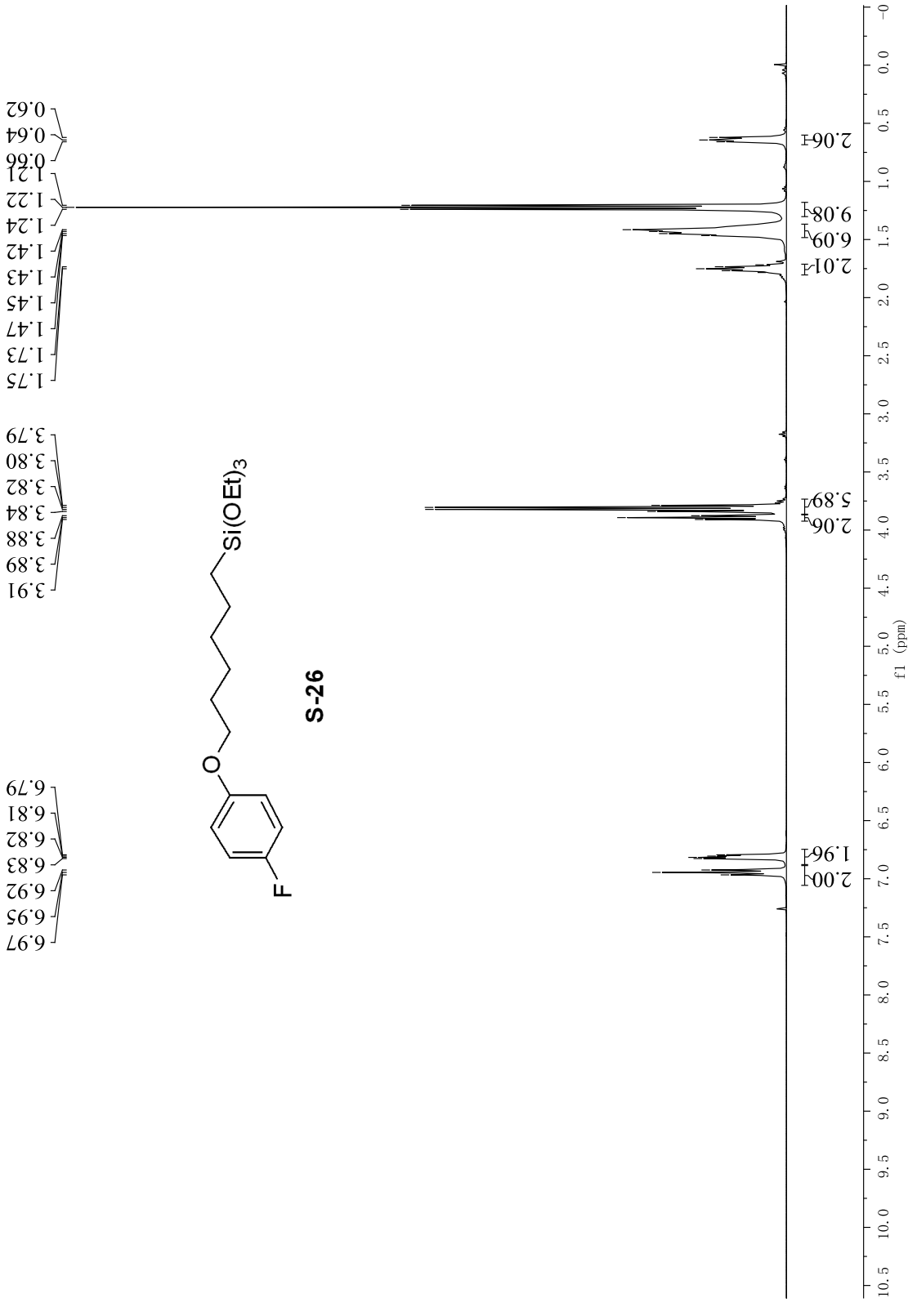
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-24**



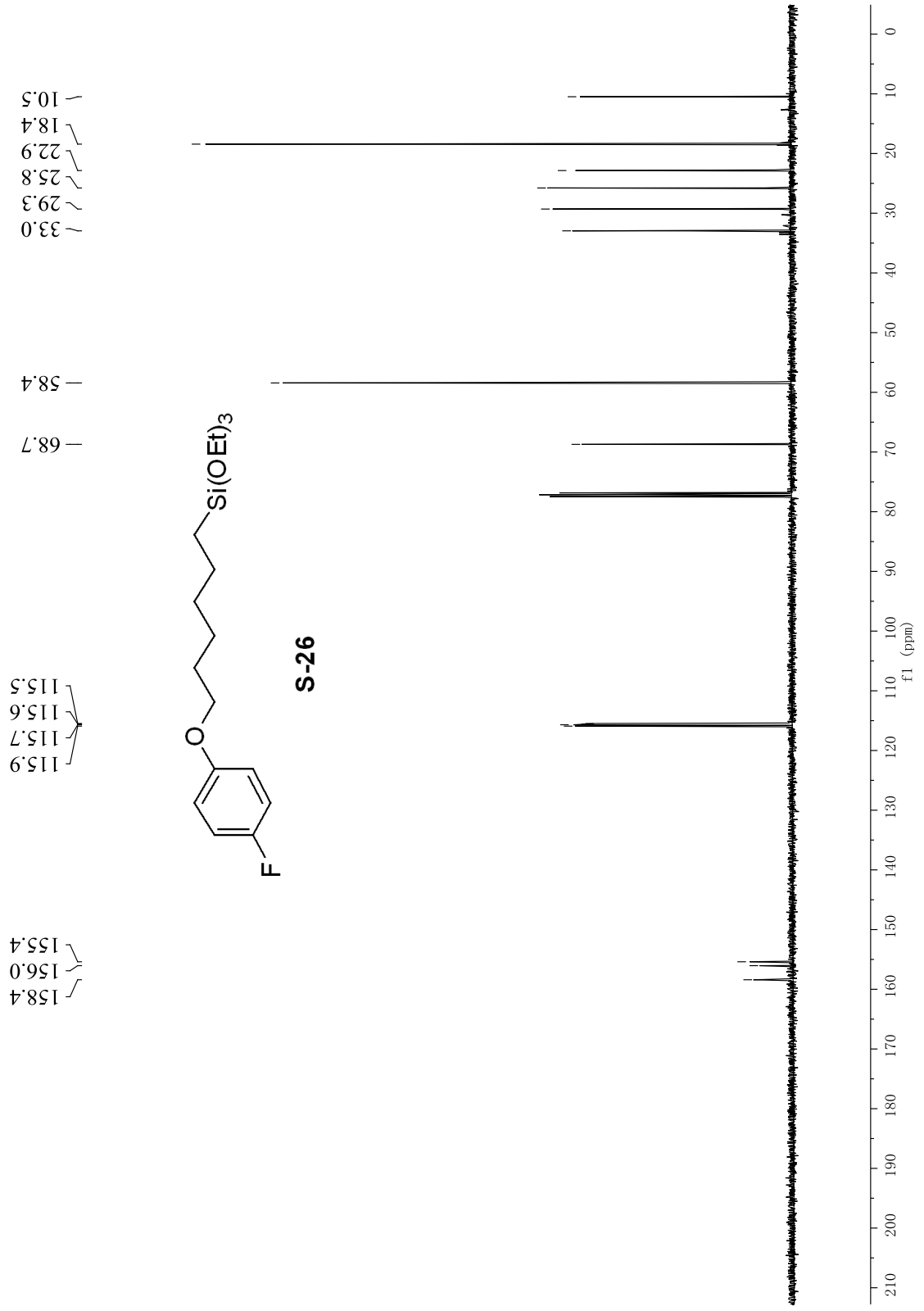
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-25**



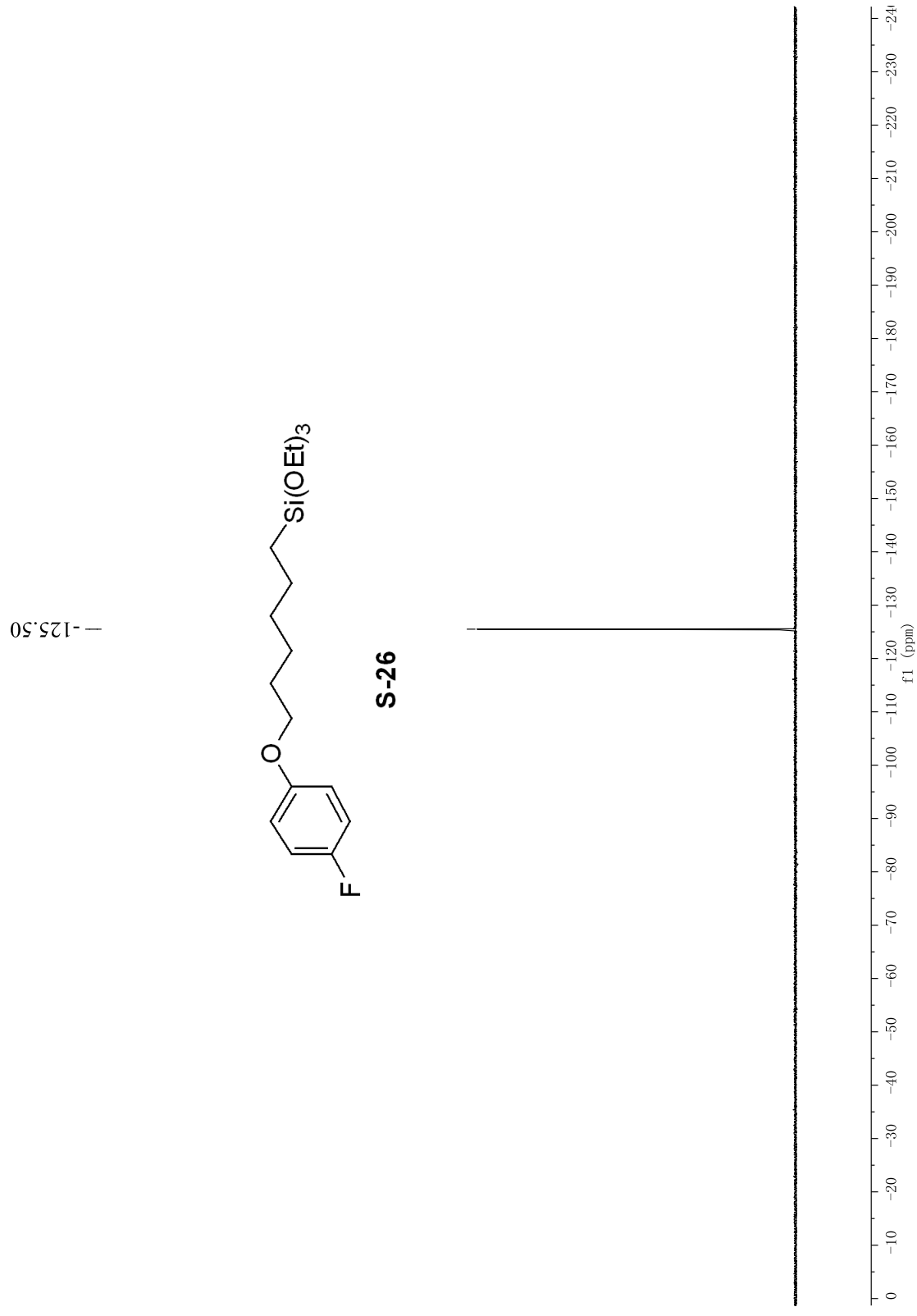
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-25**



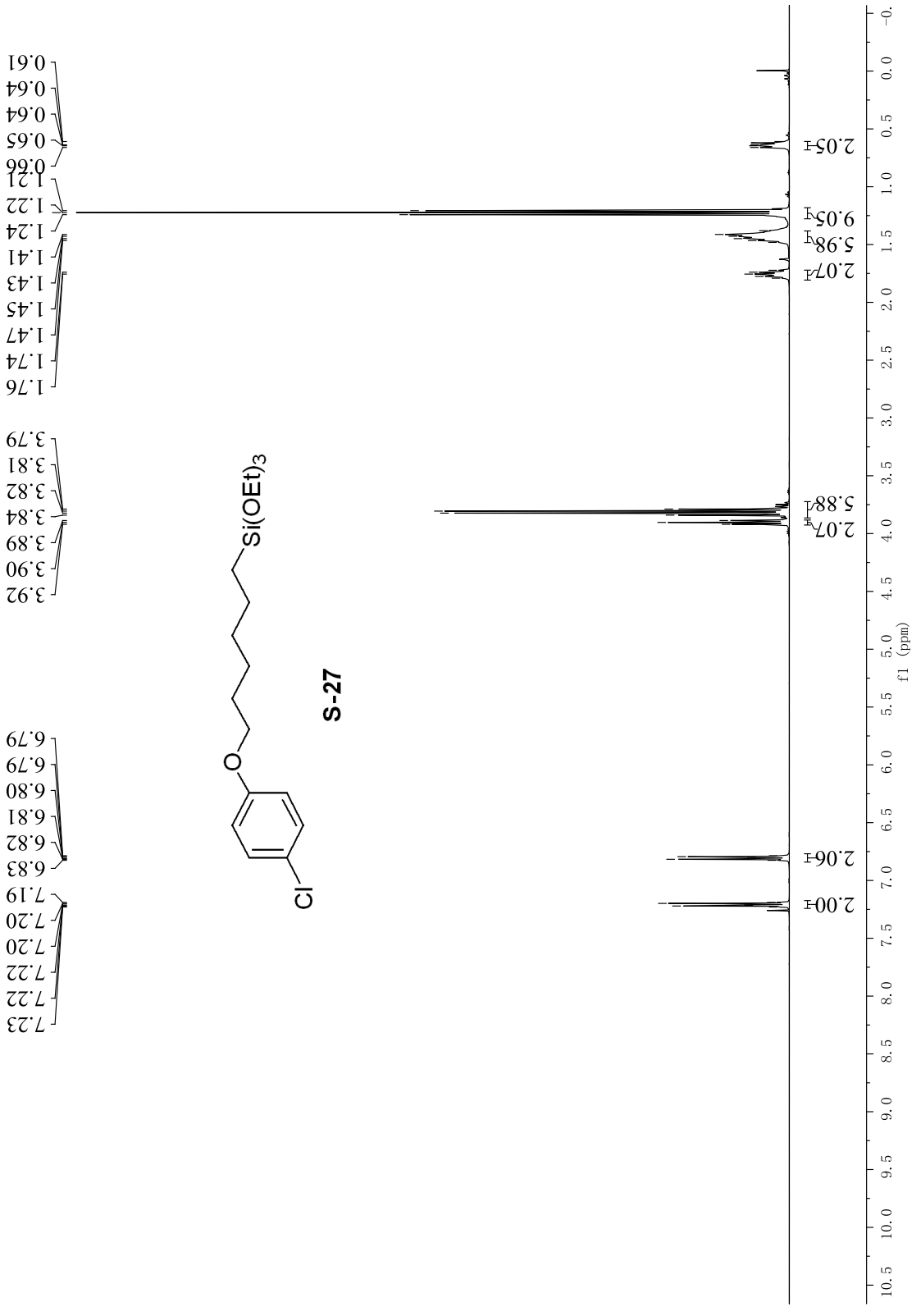
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-26**



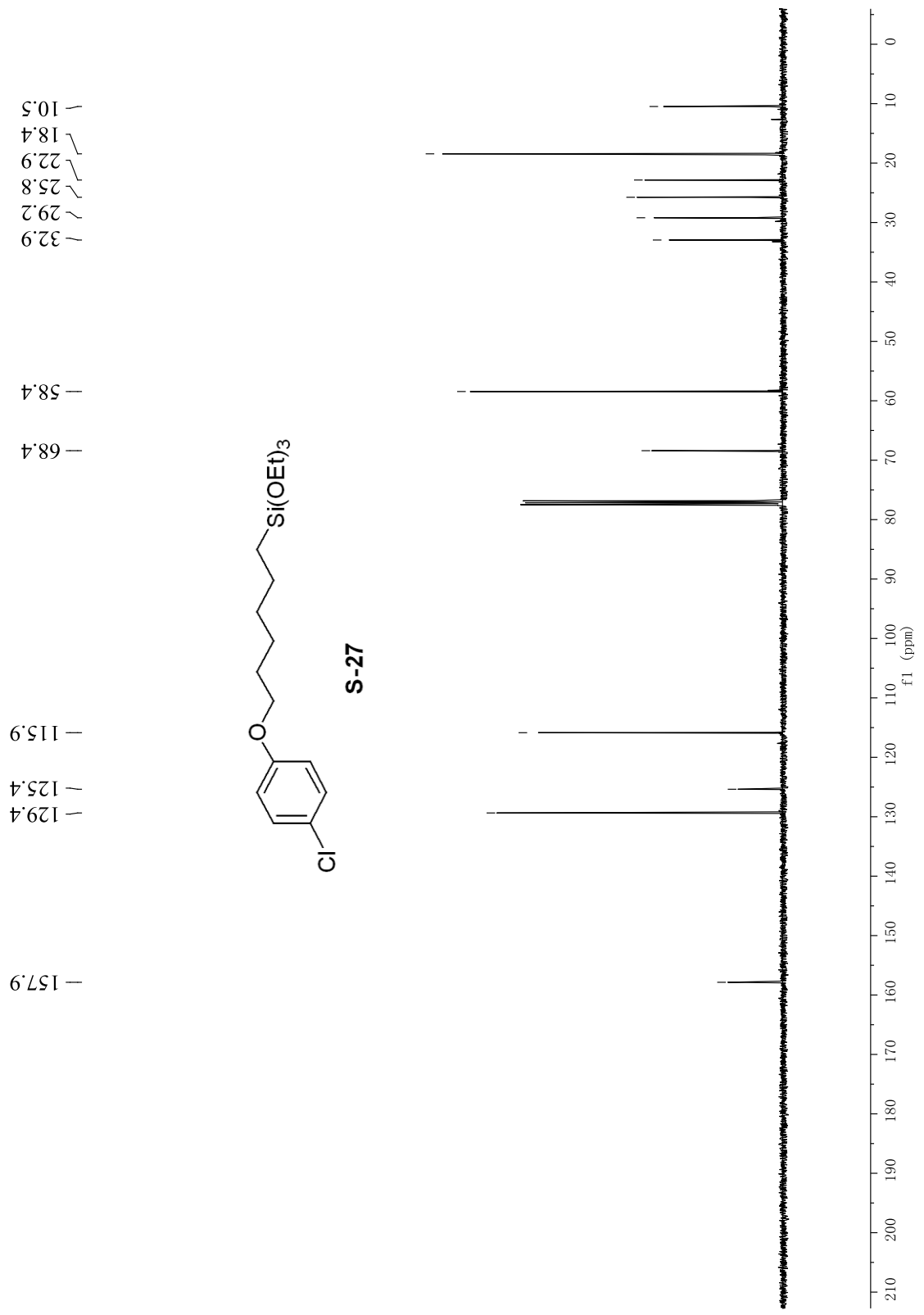
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-26**



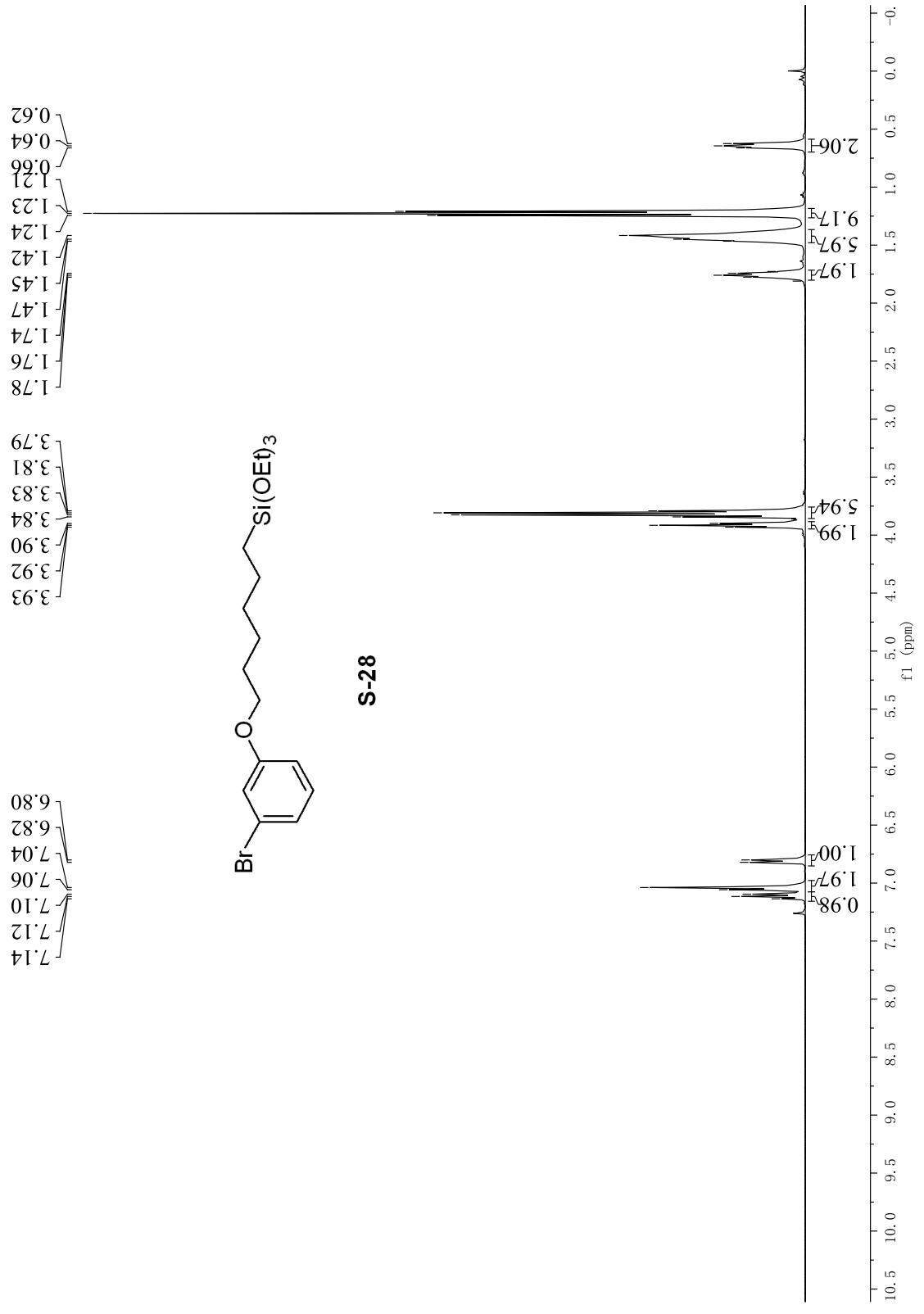
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-26**



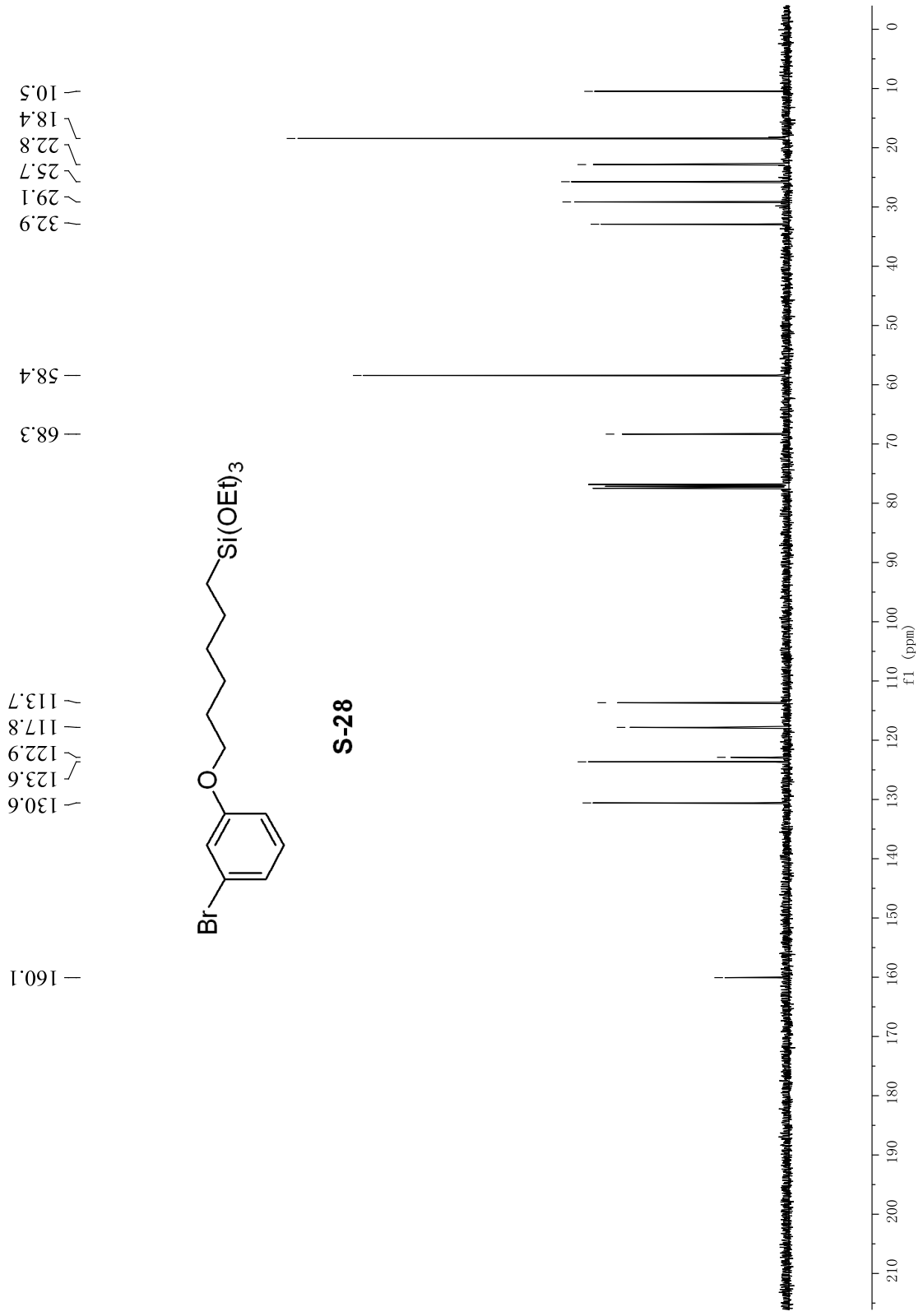
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-27**



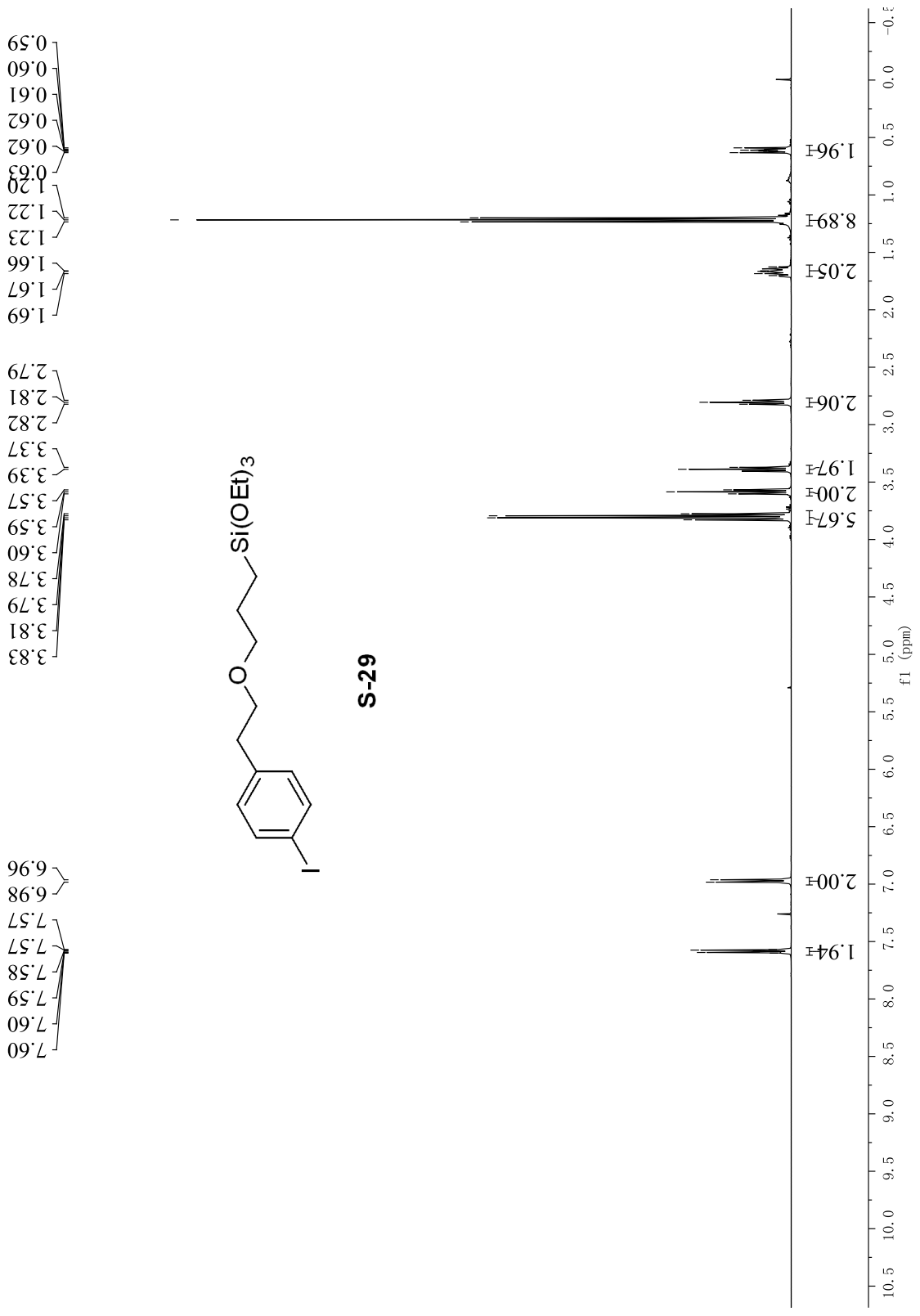
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-27**



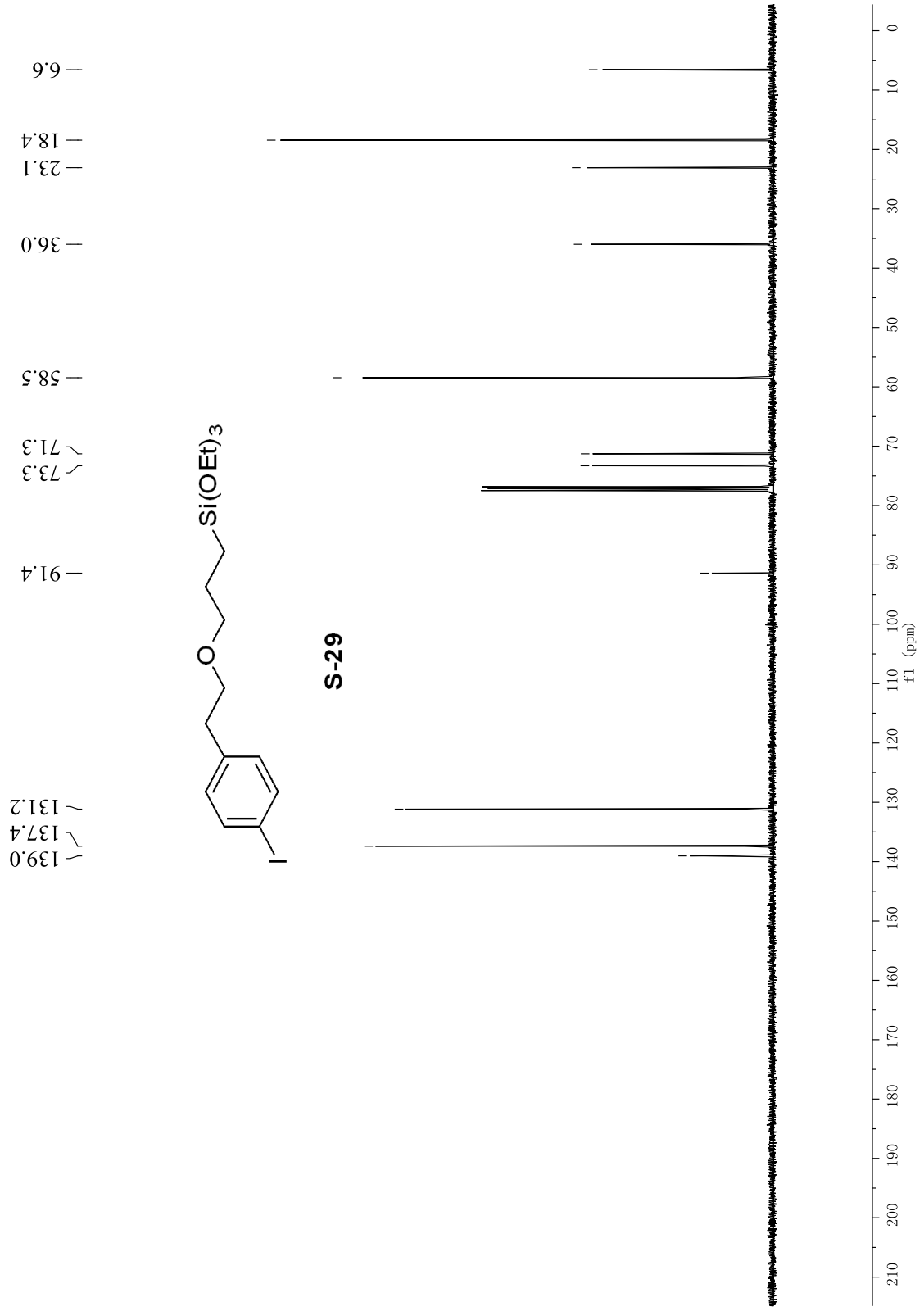
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-28**



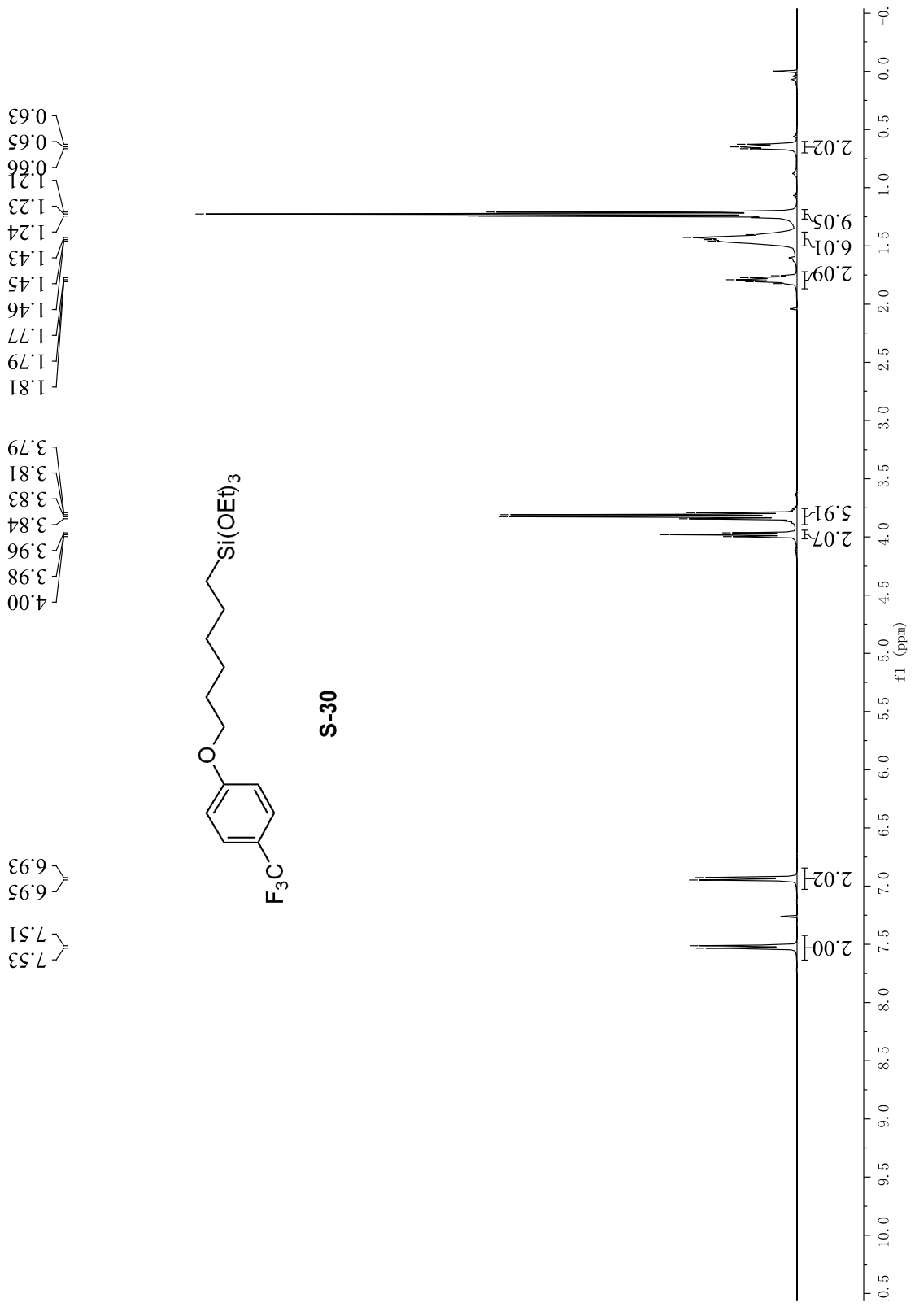
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-28**



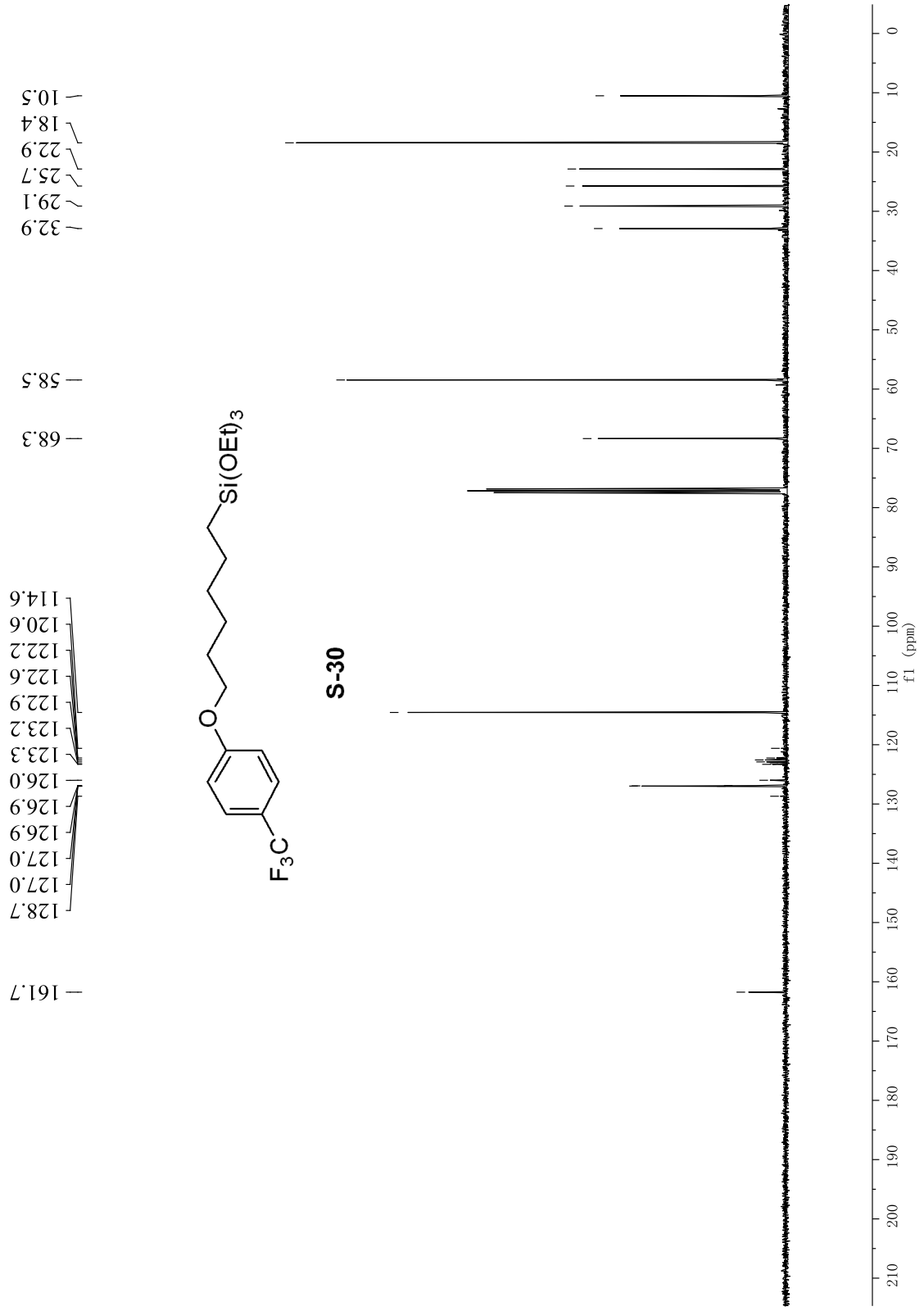
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-29**



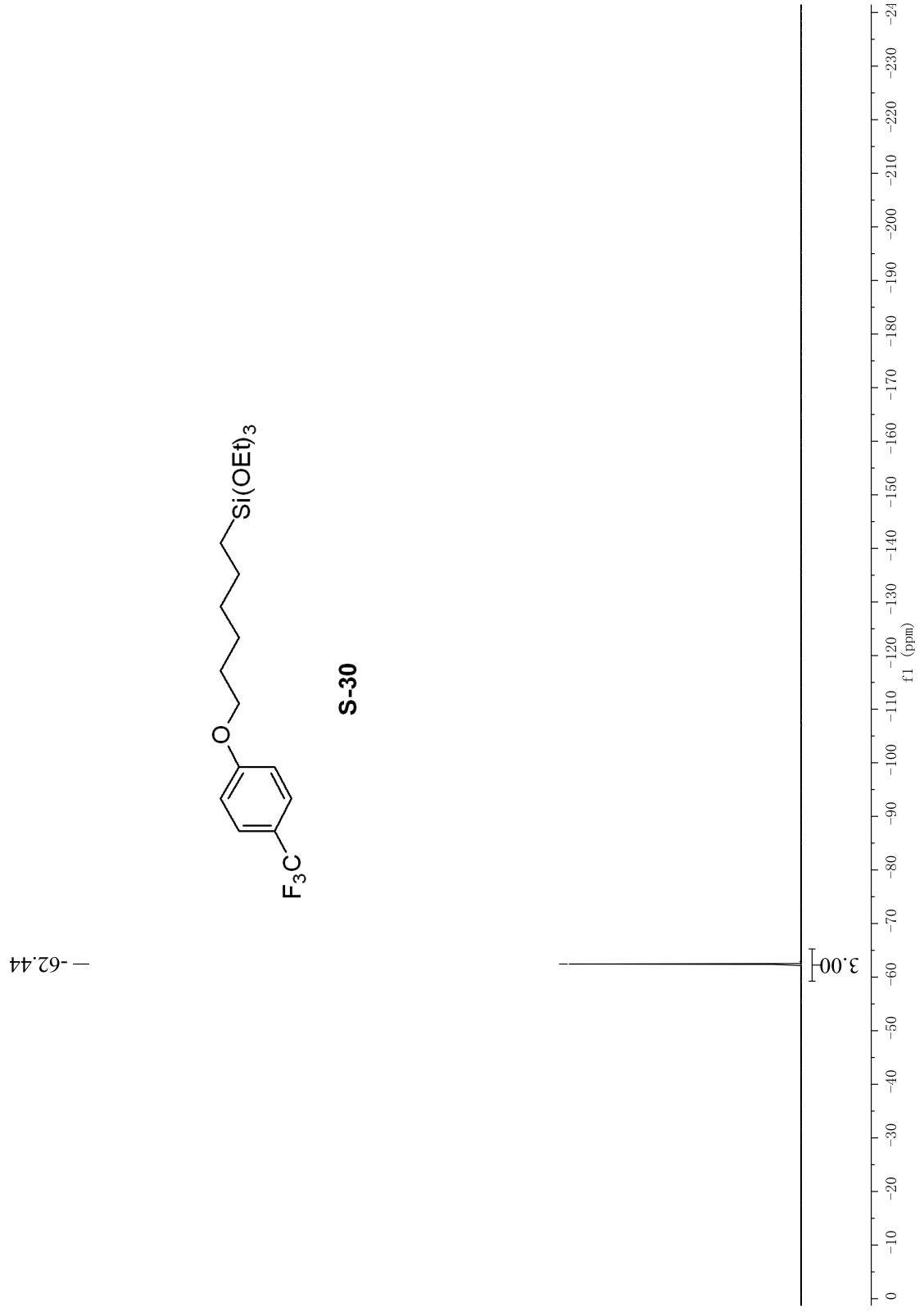
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-29**



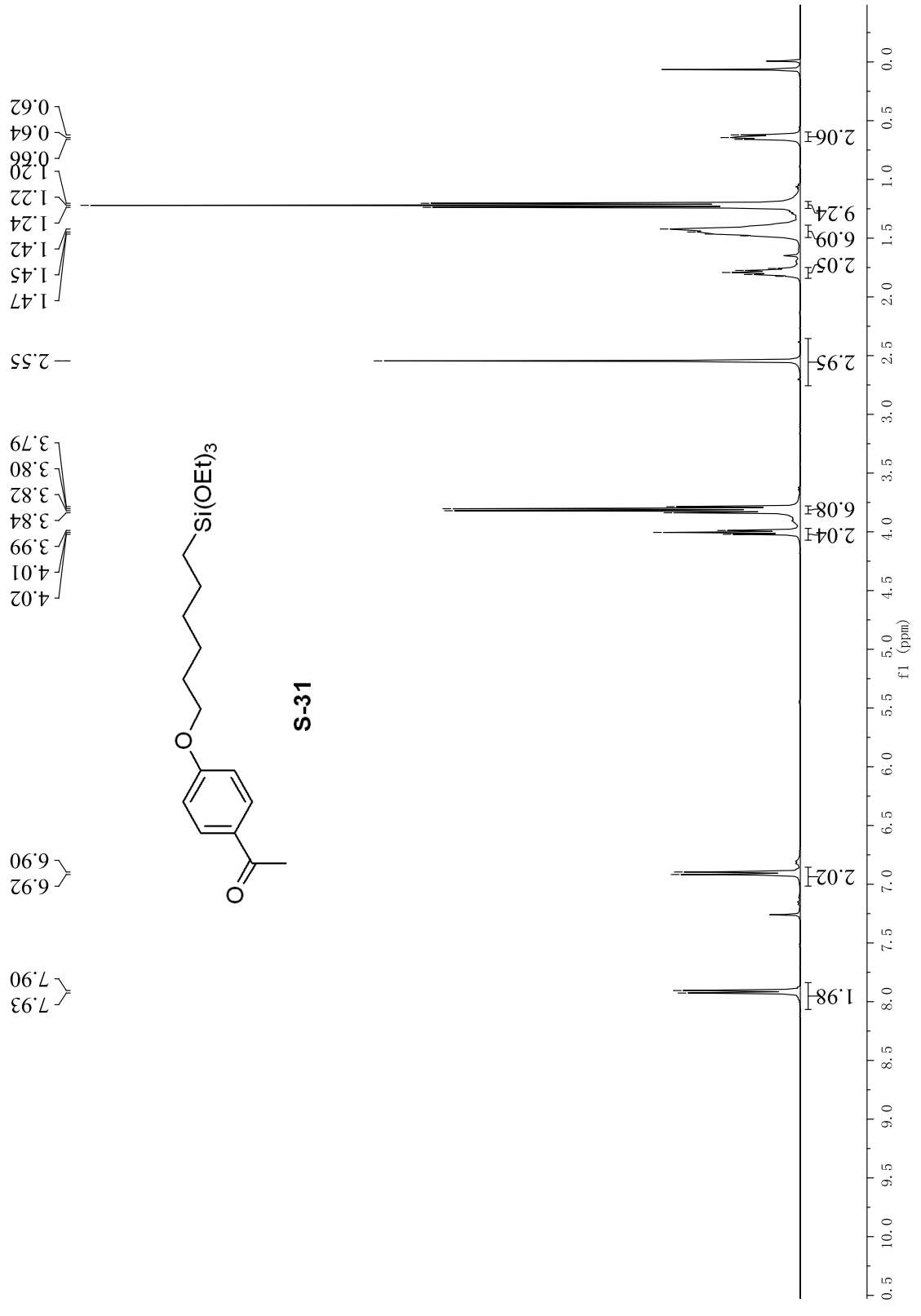
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-30**



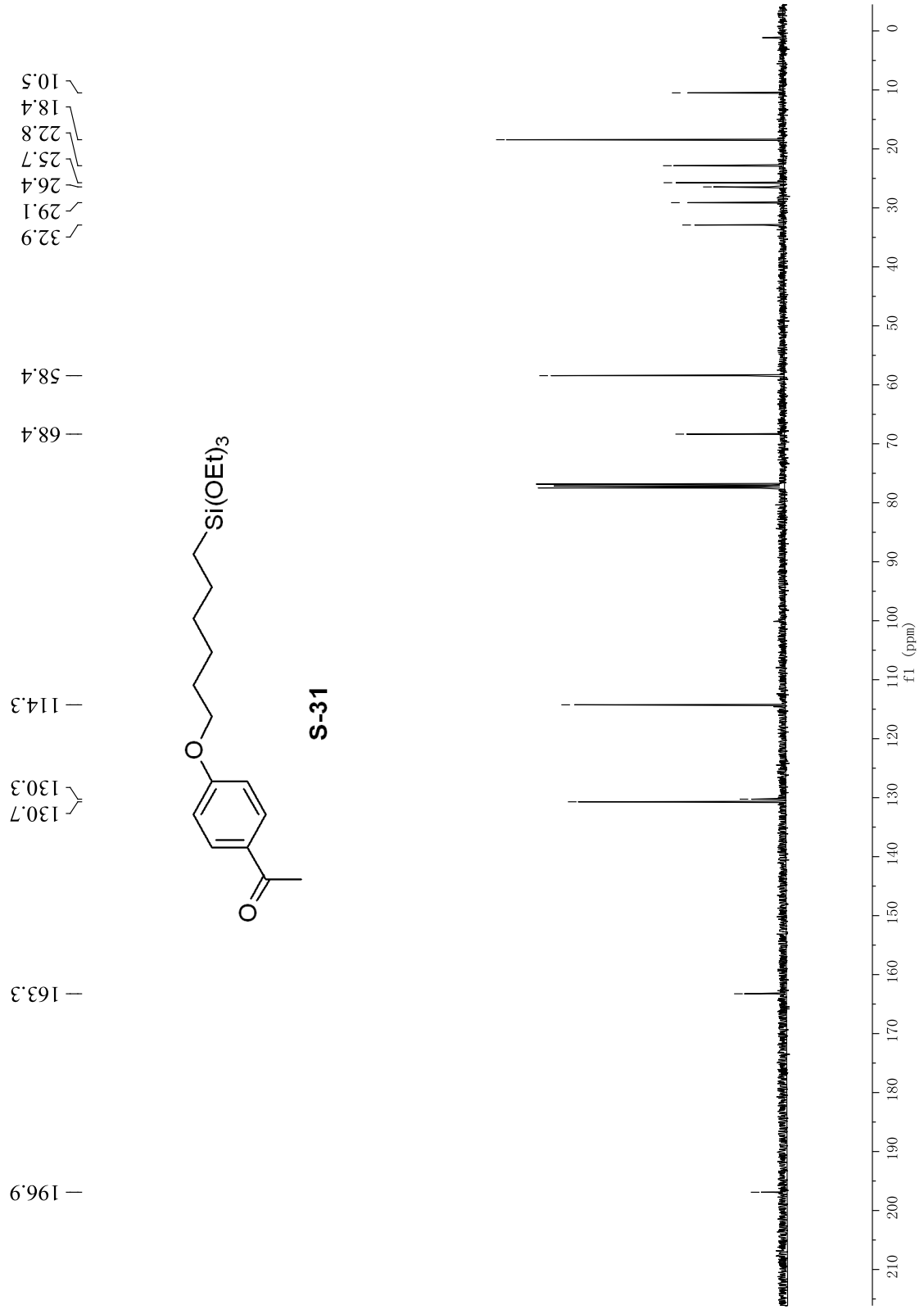
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-30**



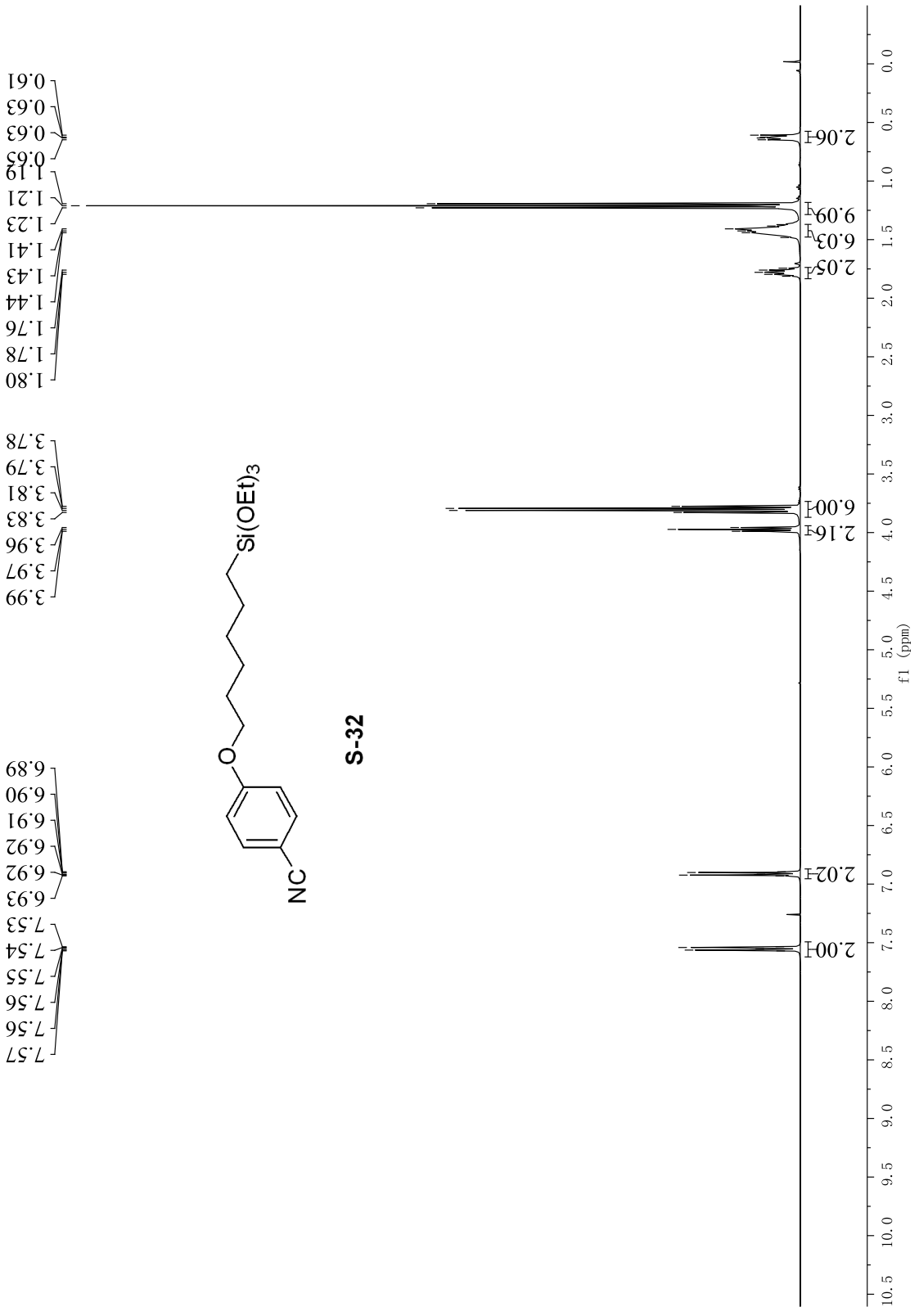
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-30**



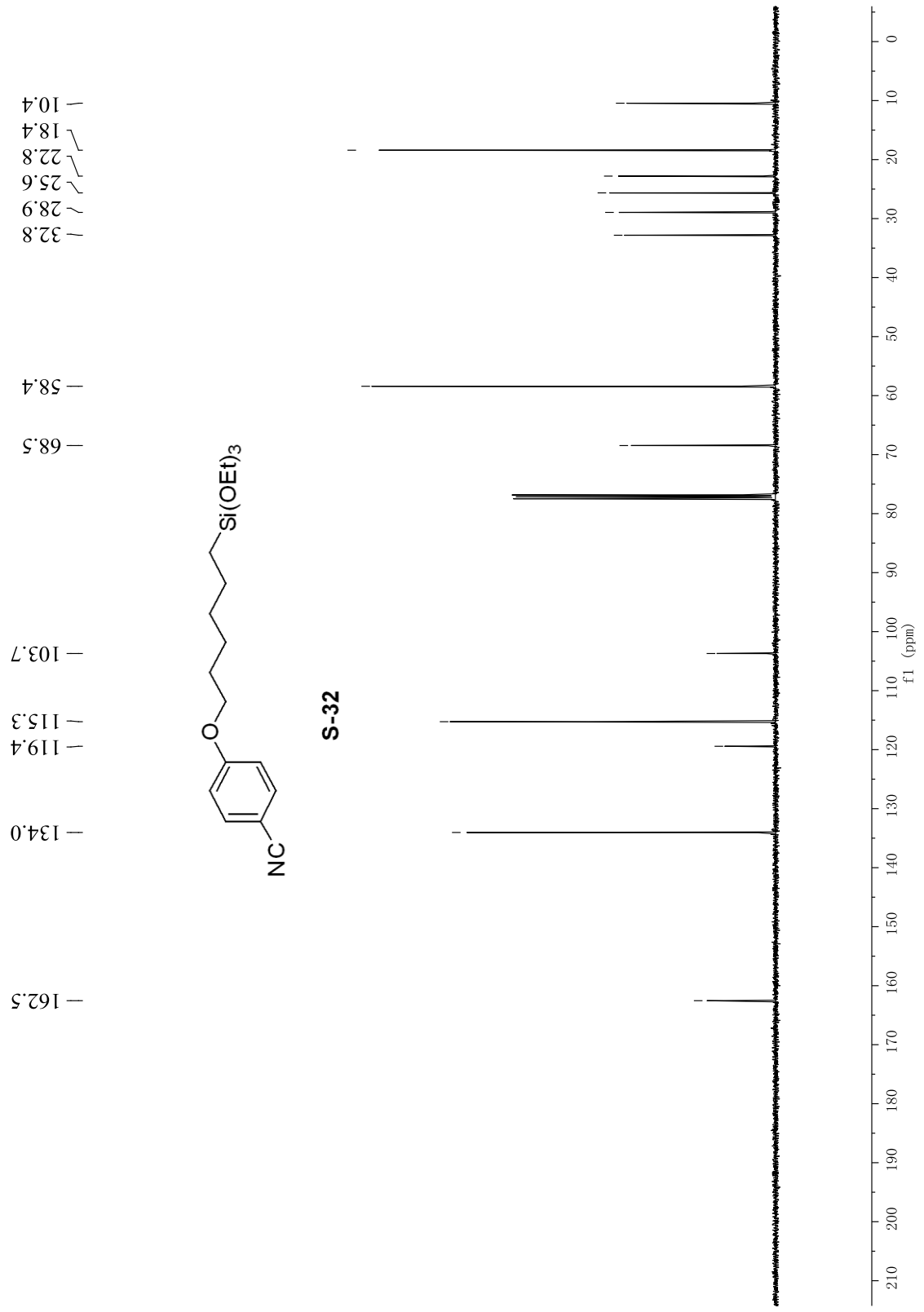
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-31**



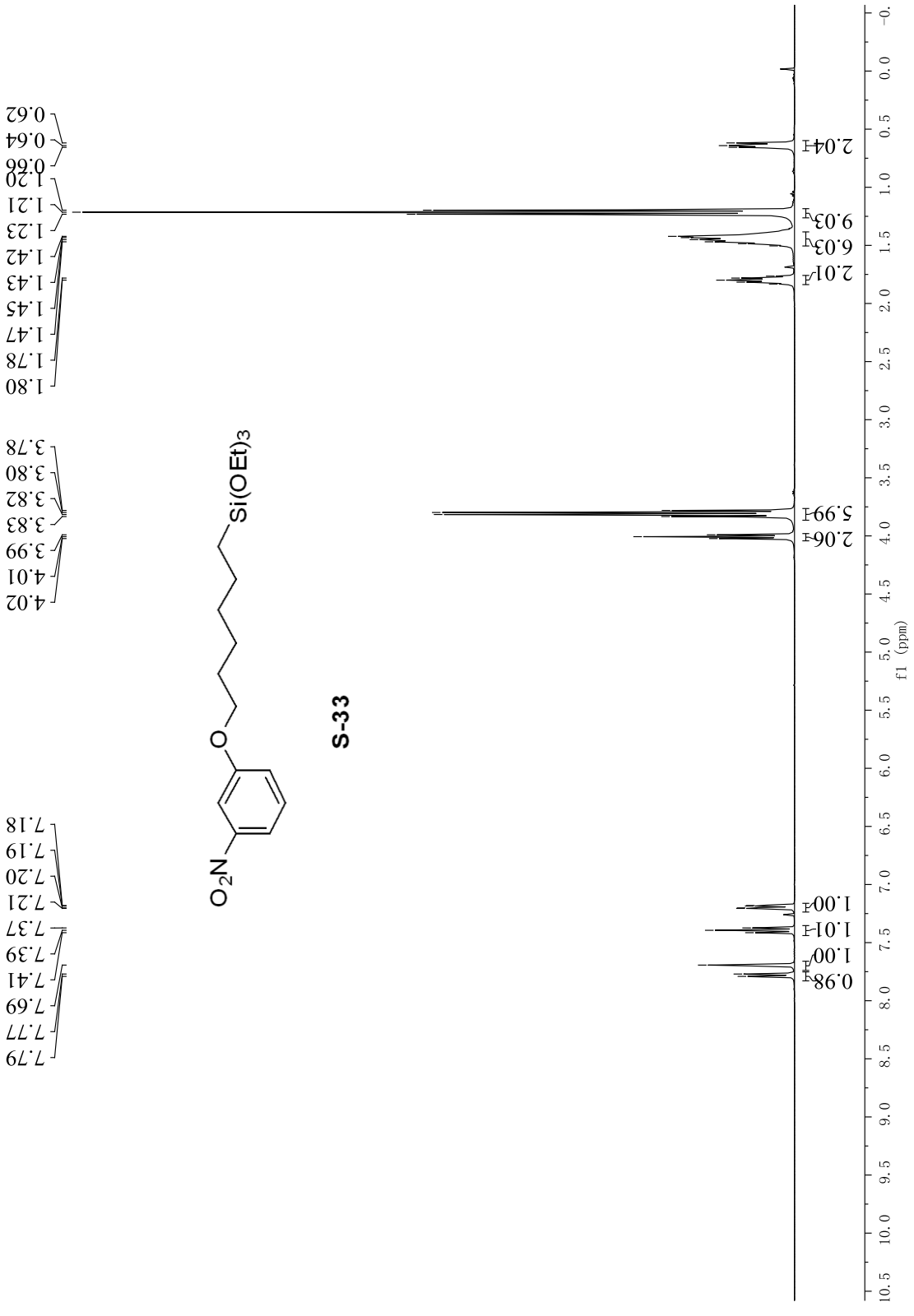
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-31**



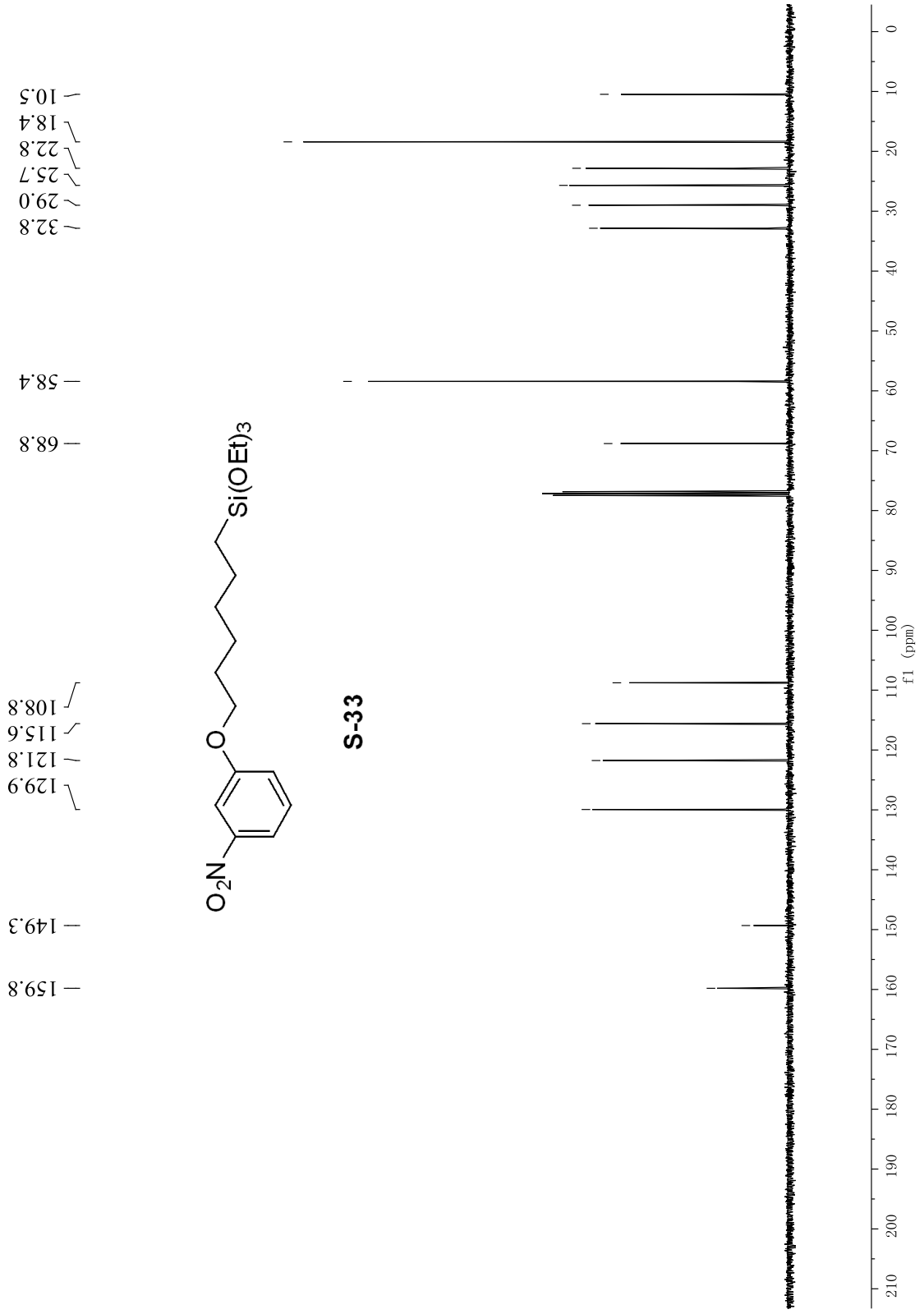
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-32**



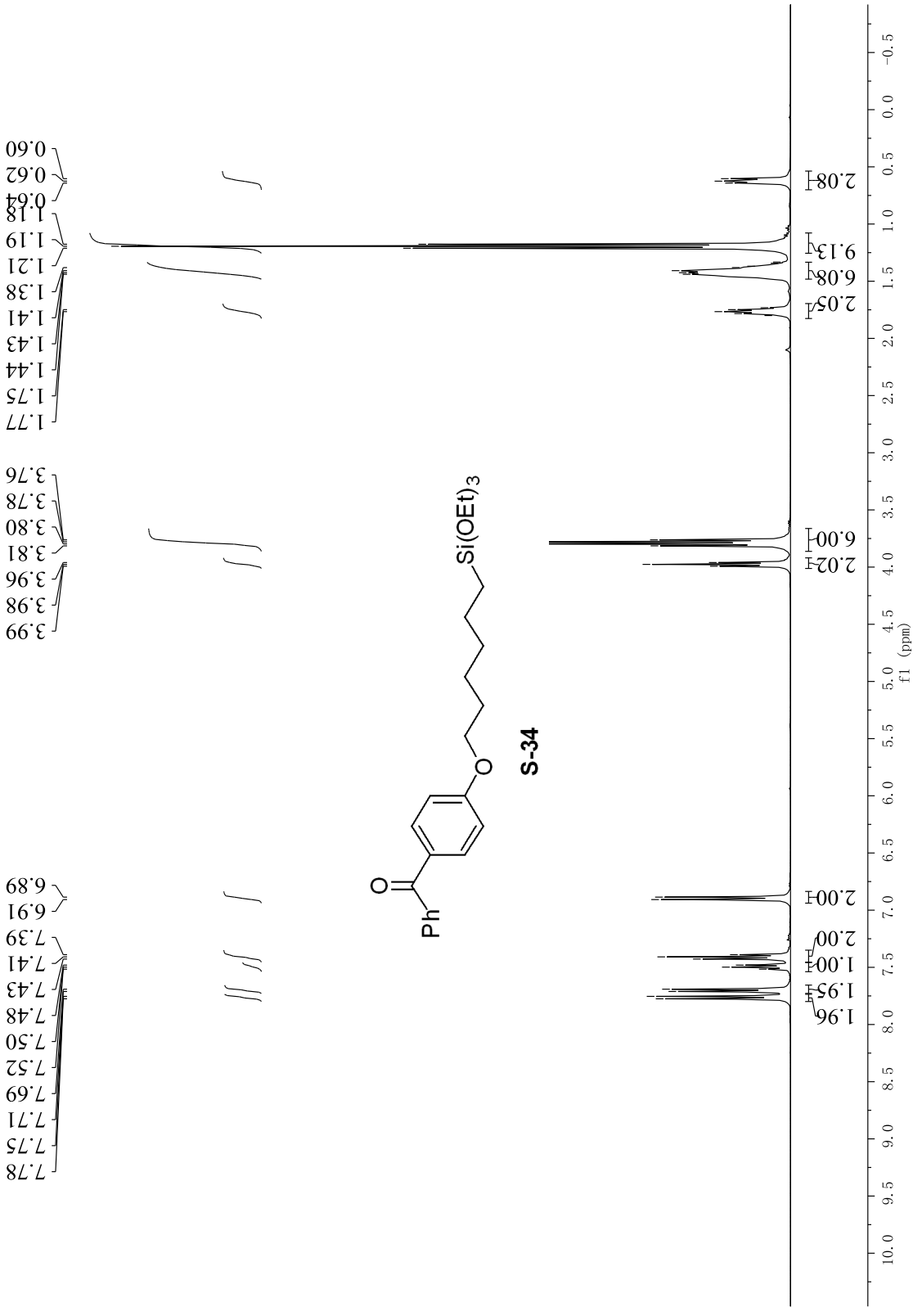
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-32**



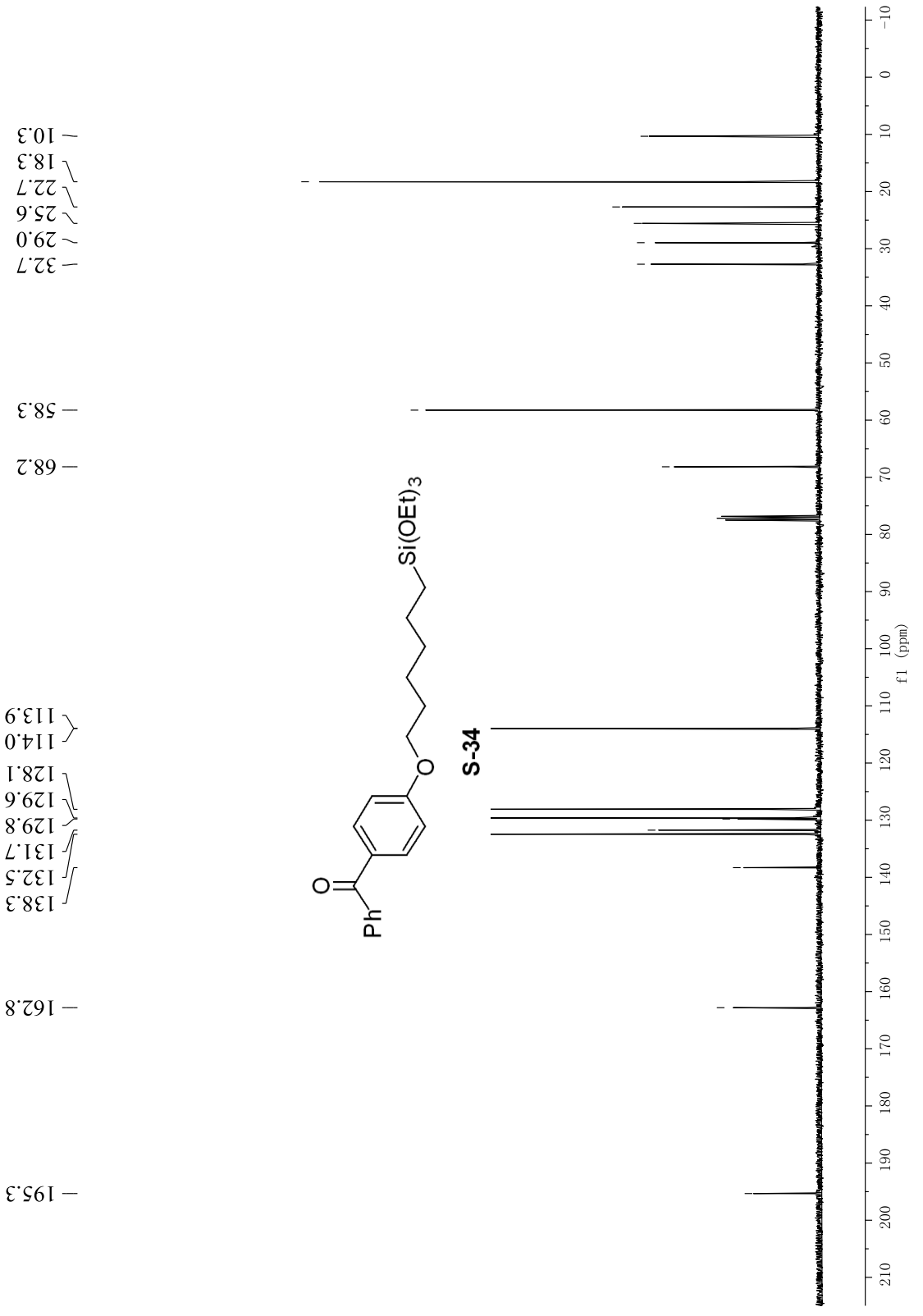
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-33**



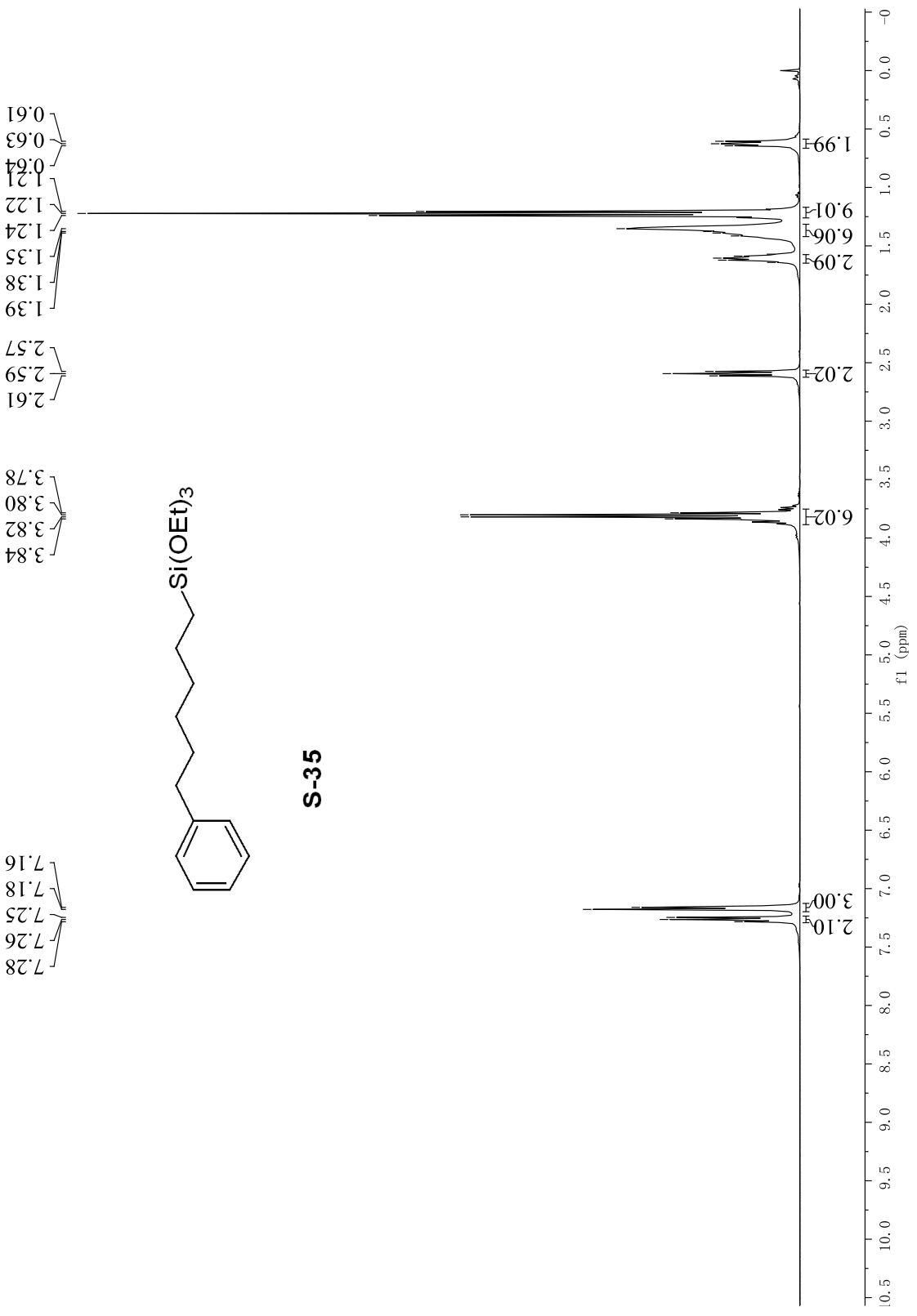
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-33**



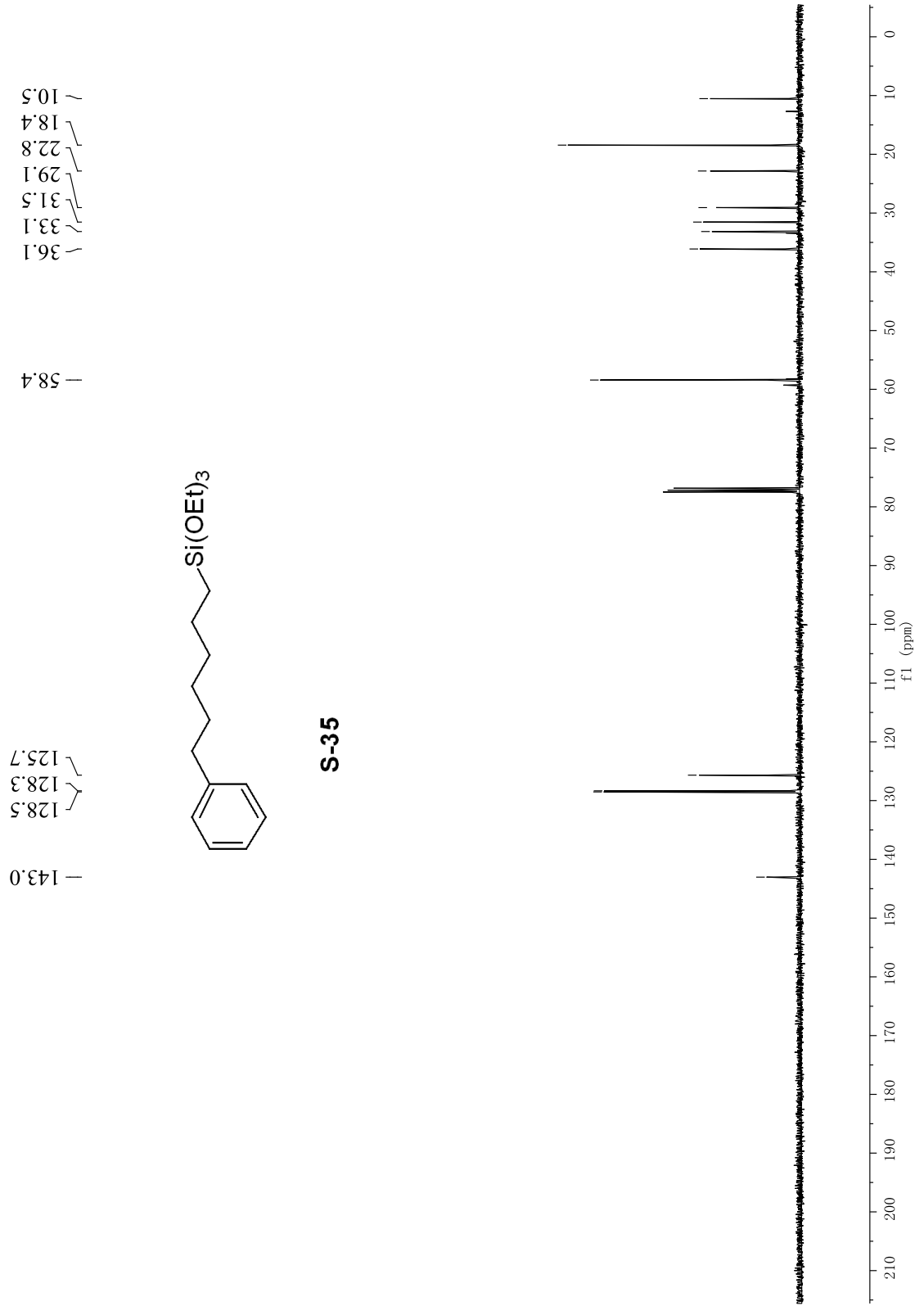
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-34**



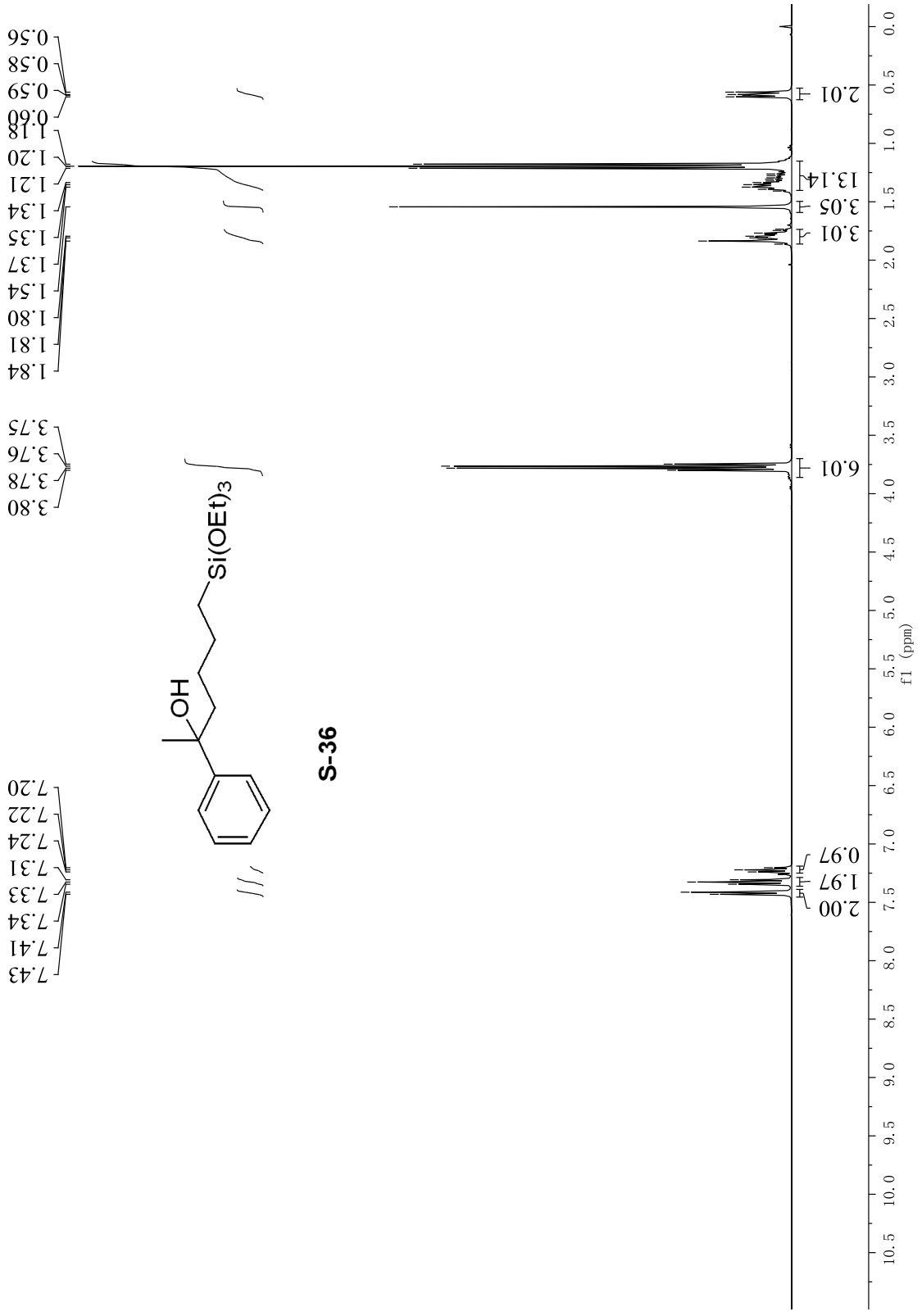
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-34**



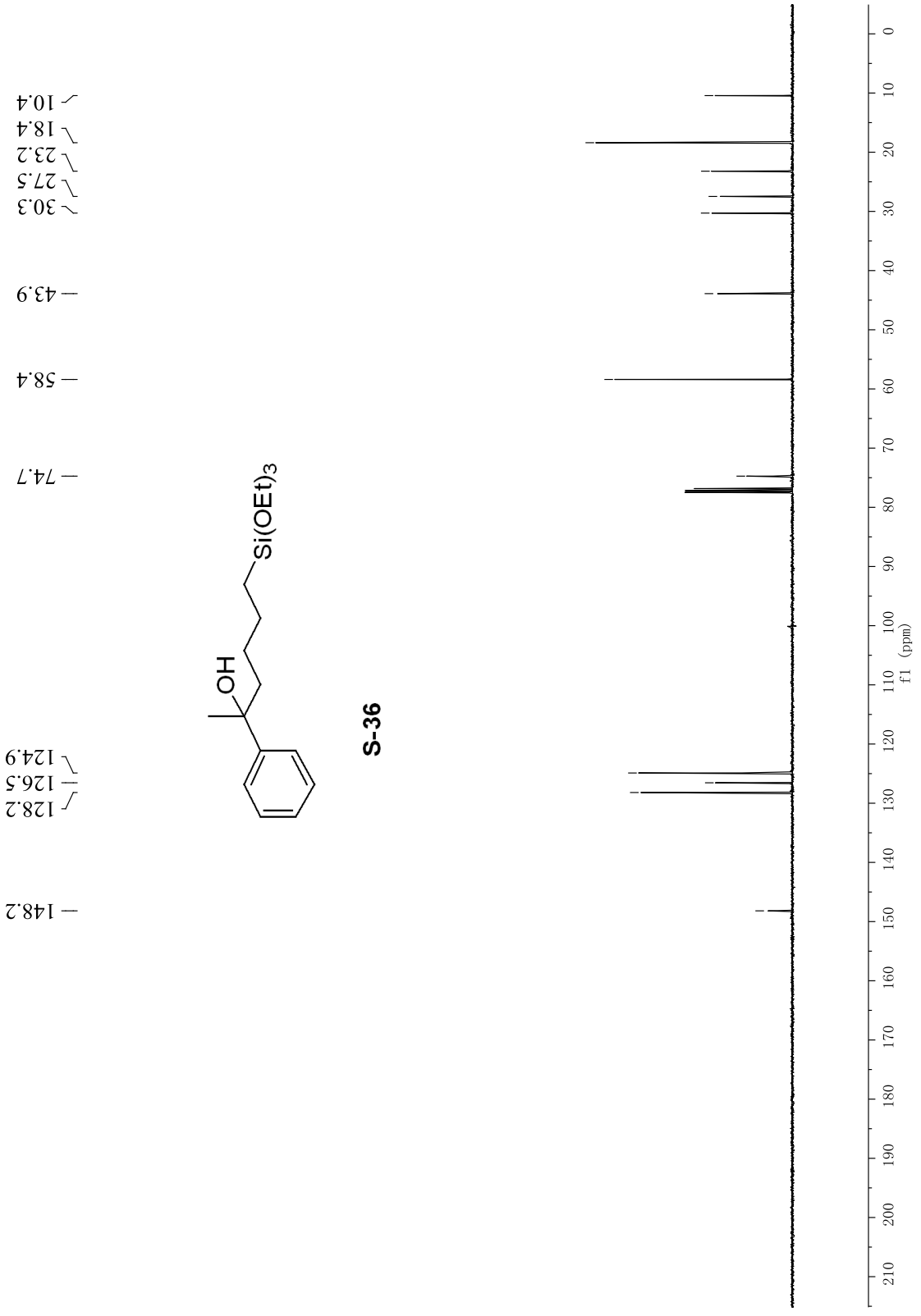
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-35**



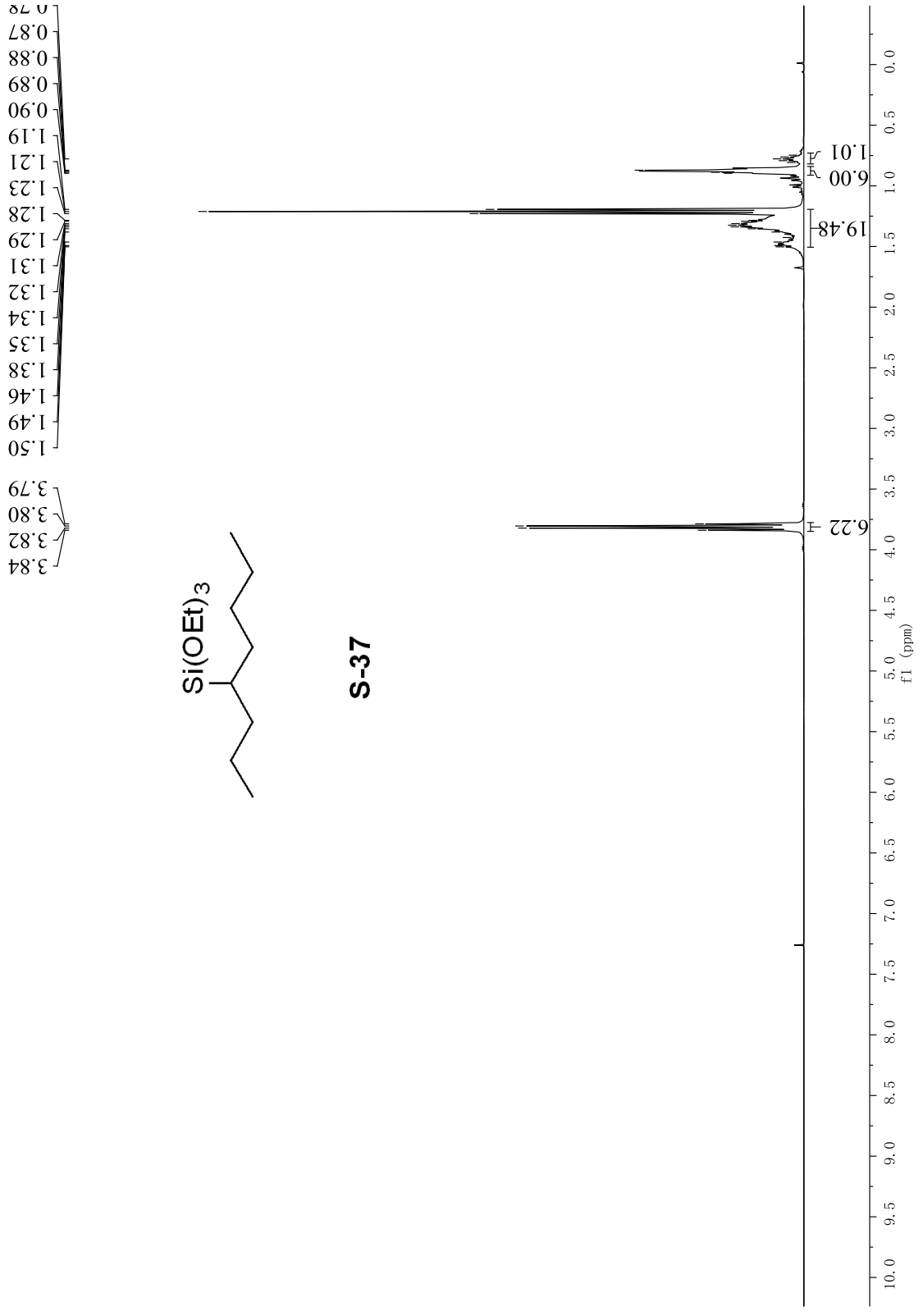
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-35**



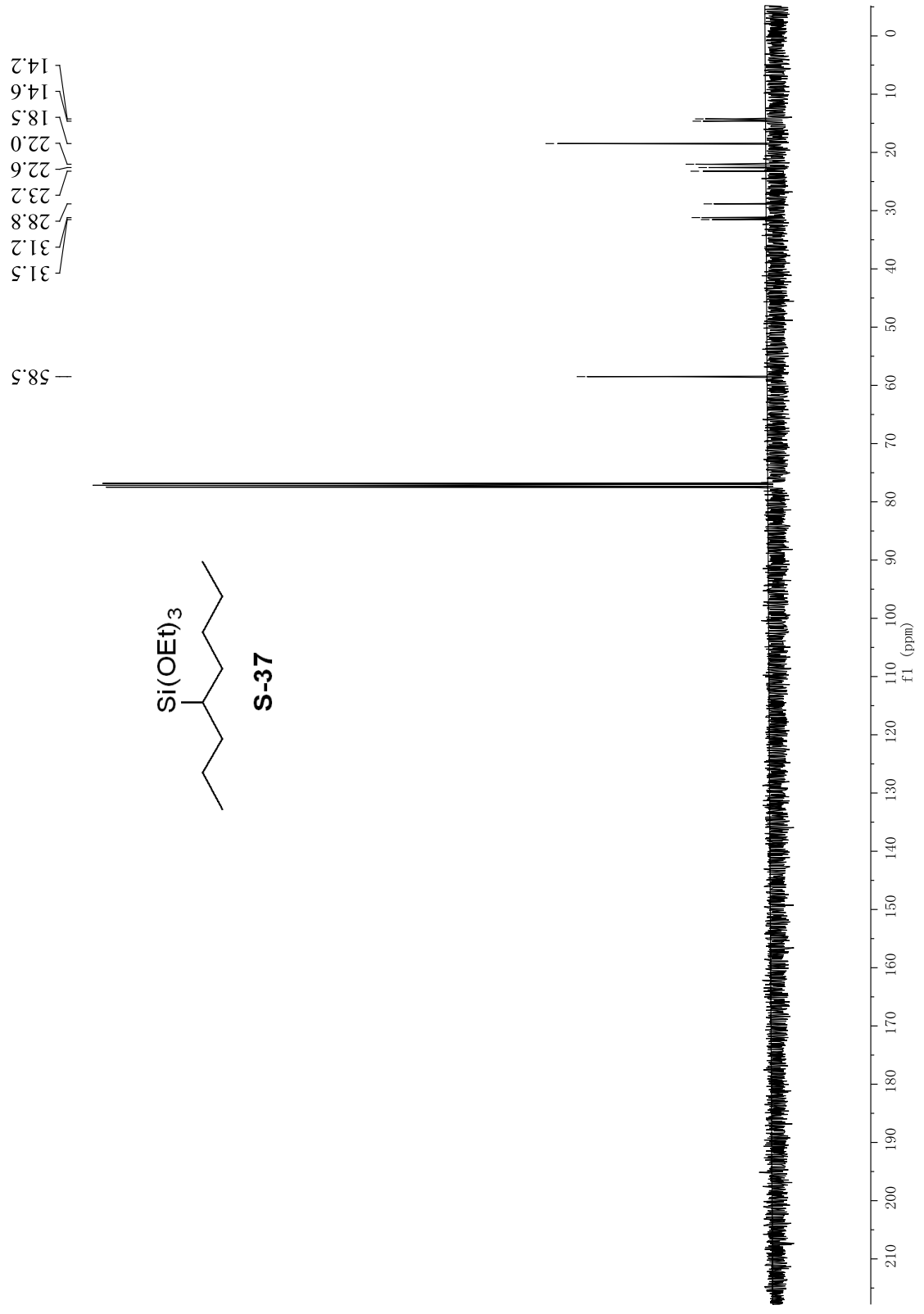
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-36**



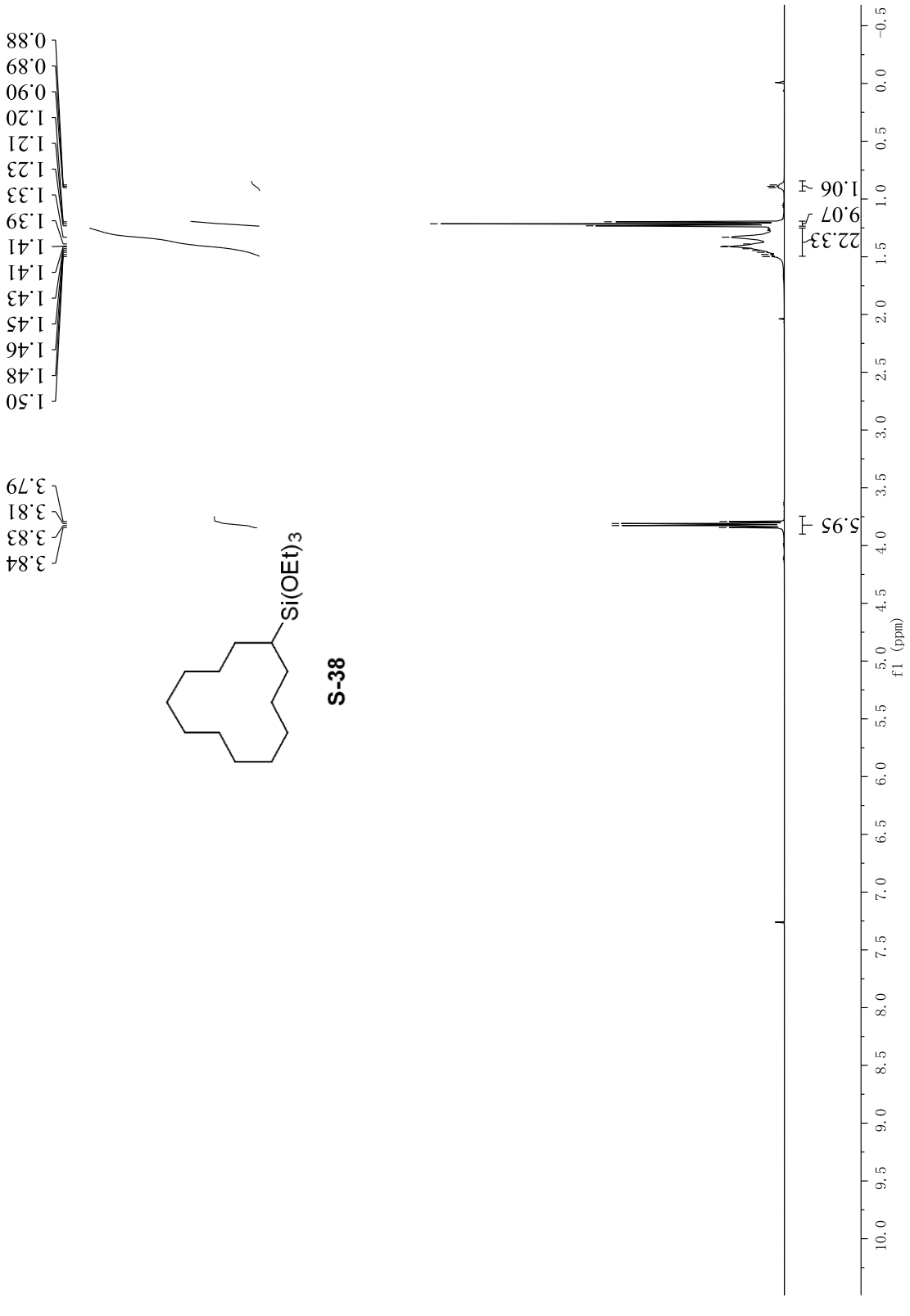
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-36**



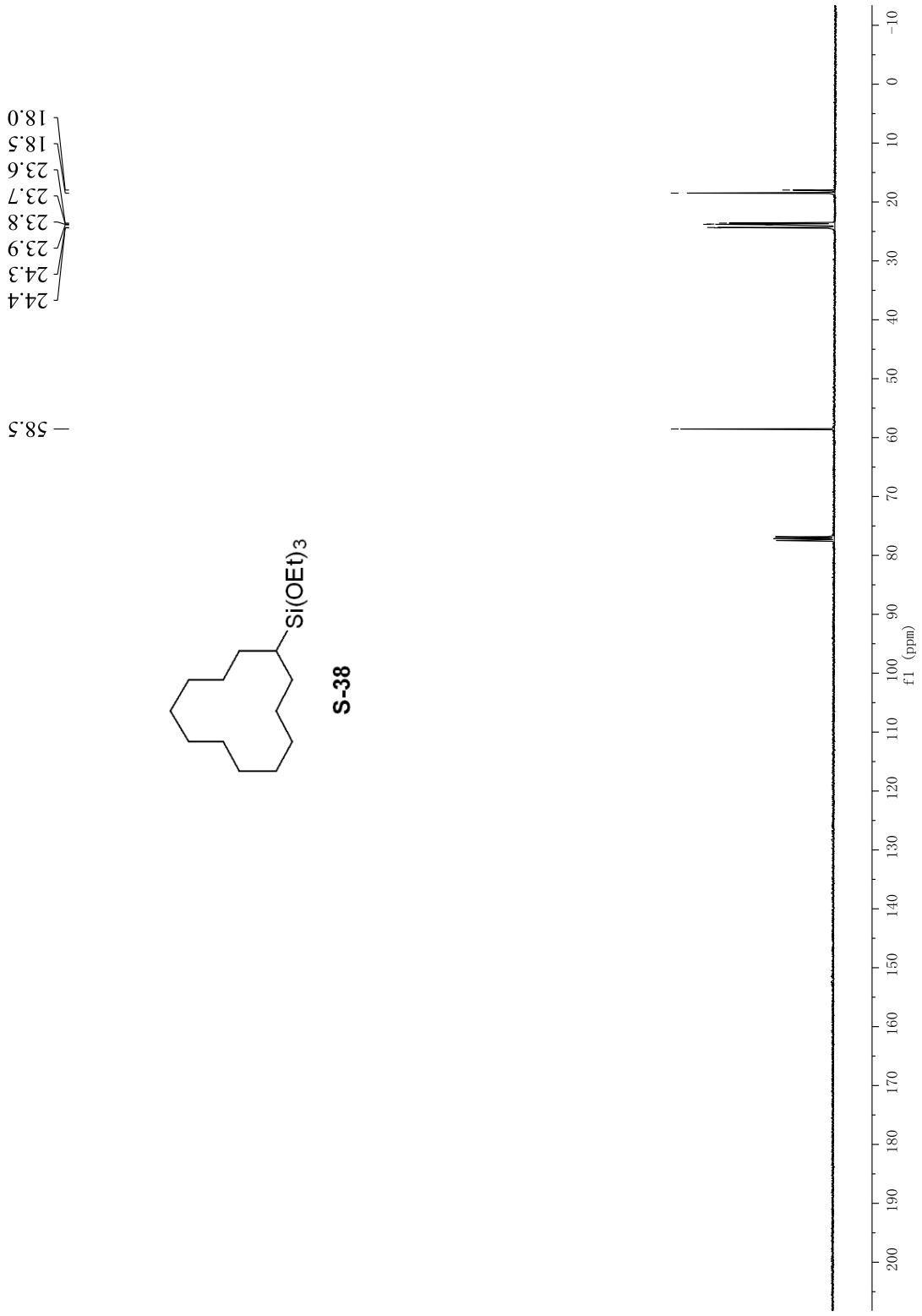
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-37**



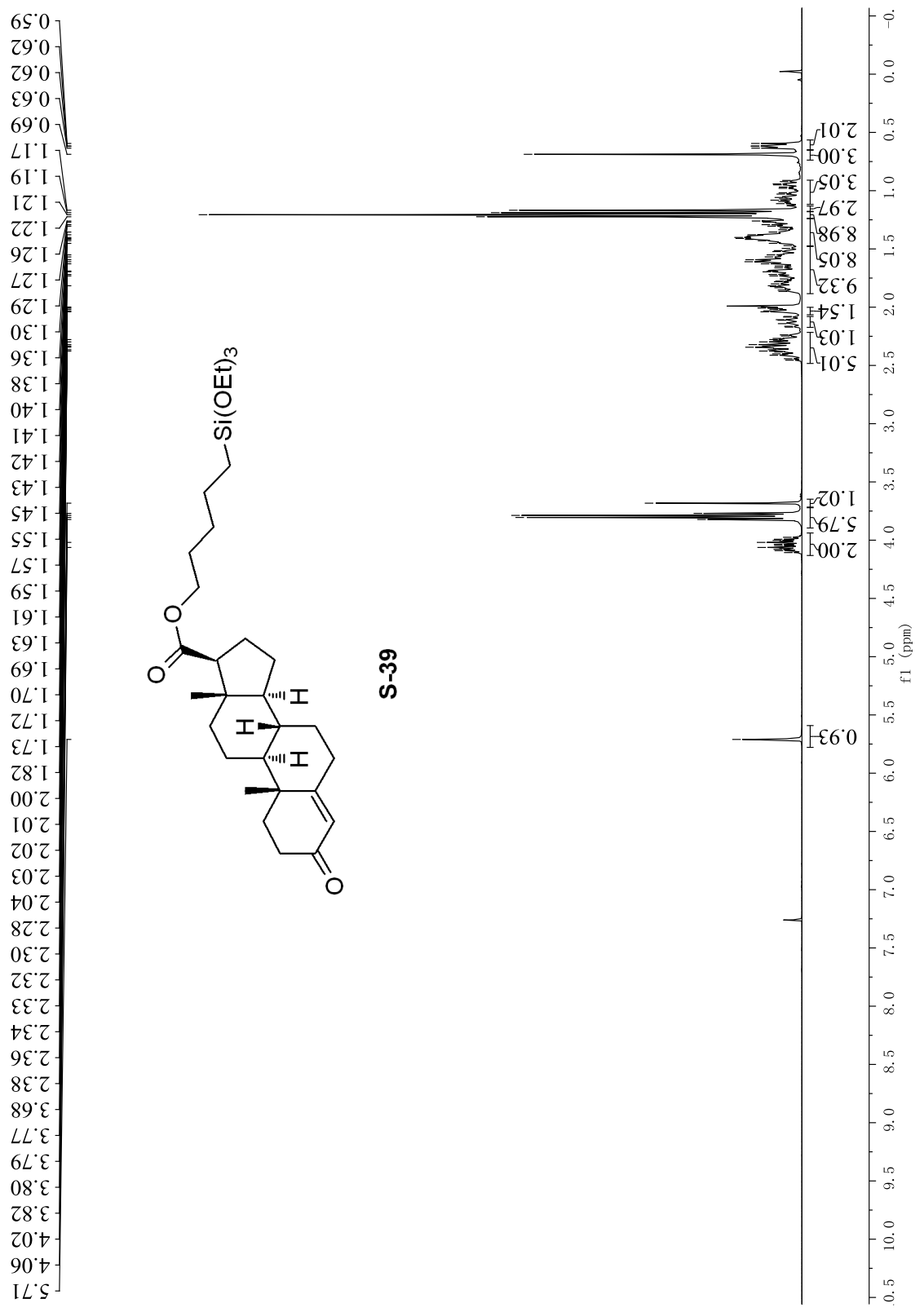
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-37**



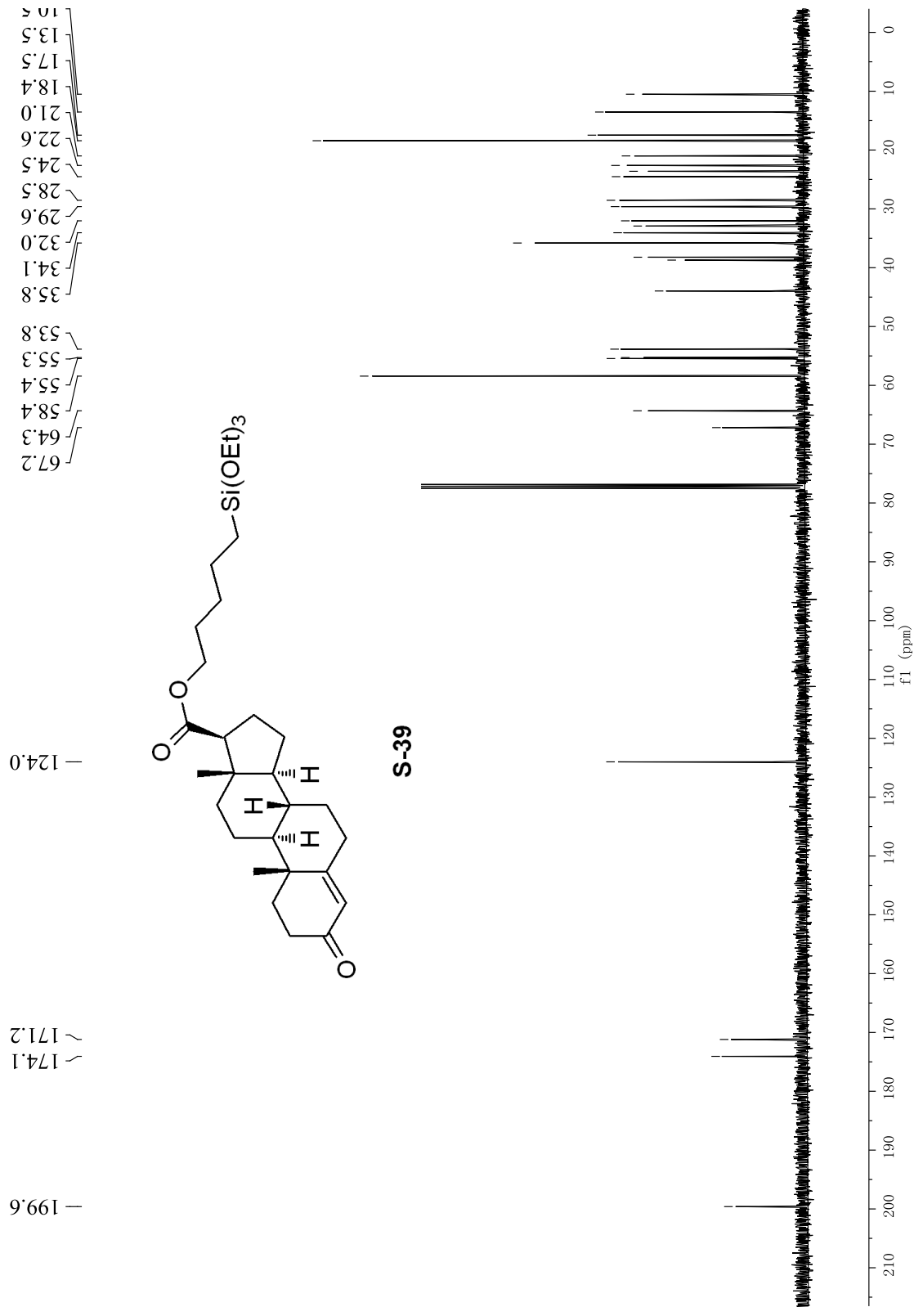
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-38**



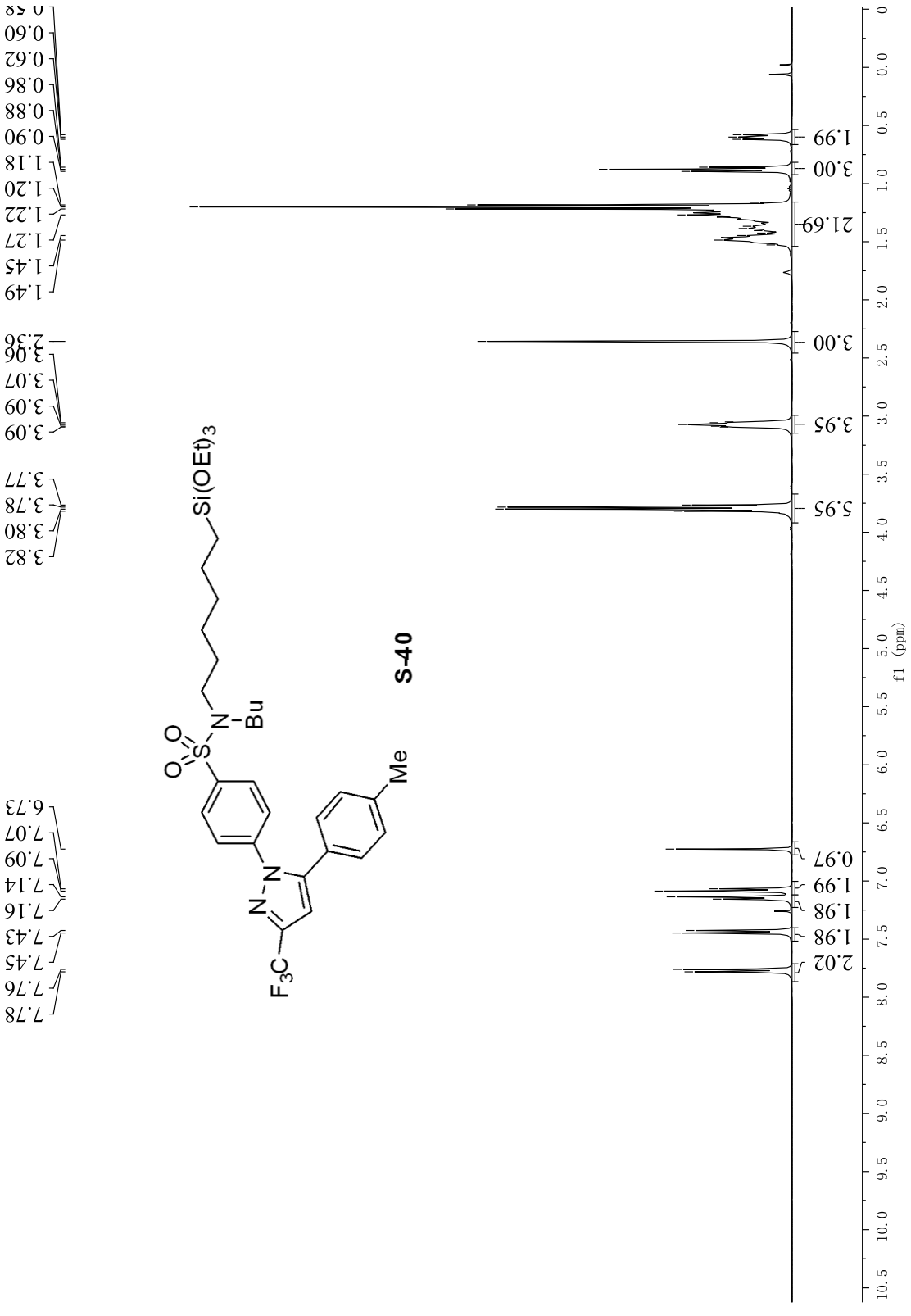
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-38**



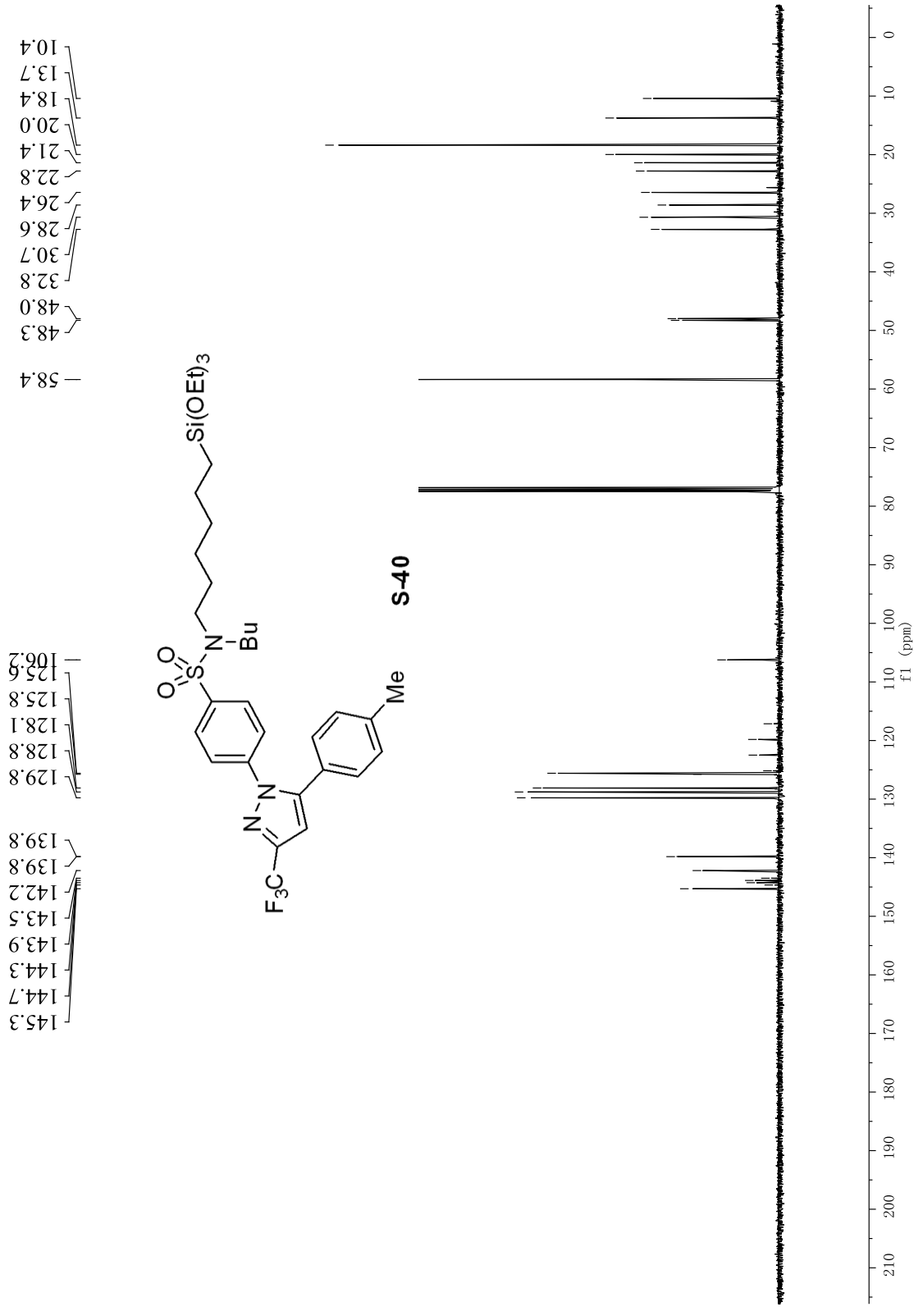
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-39**



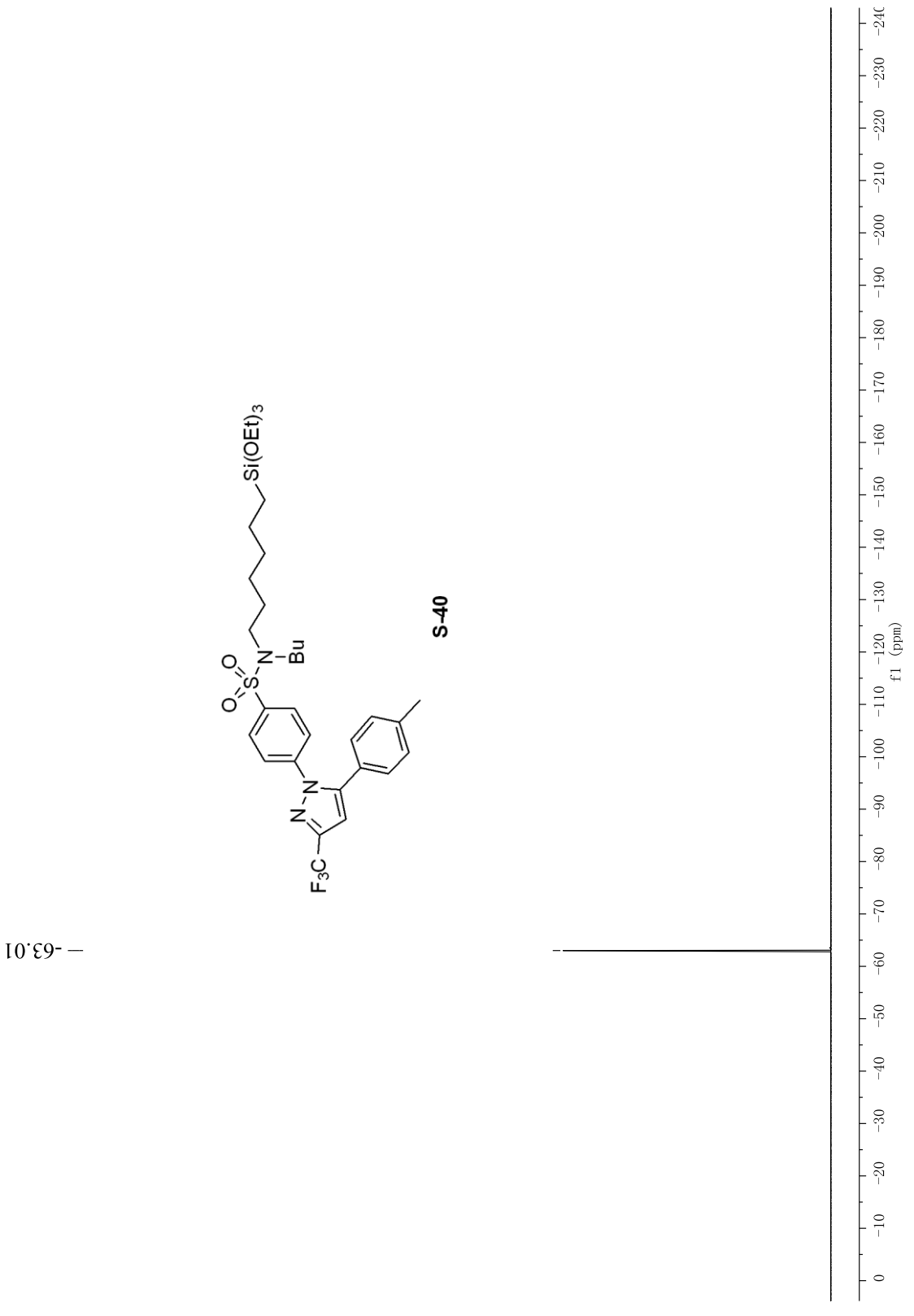
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-39**



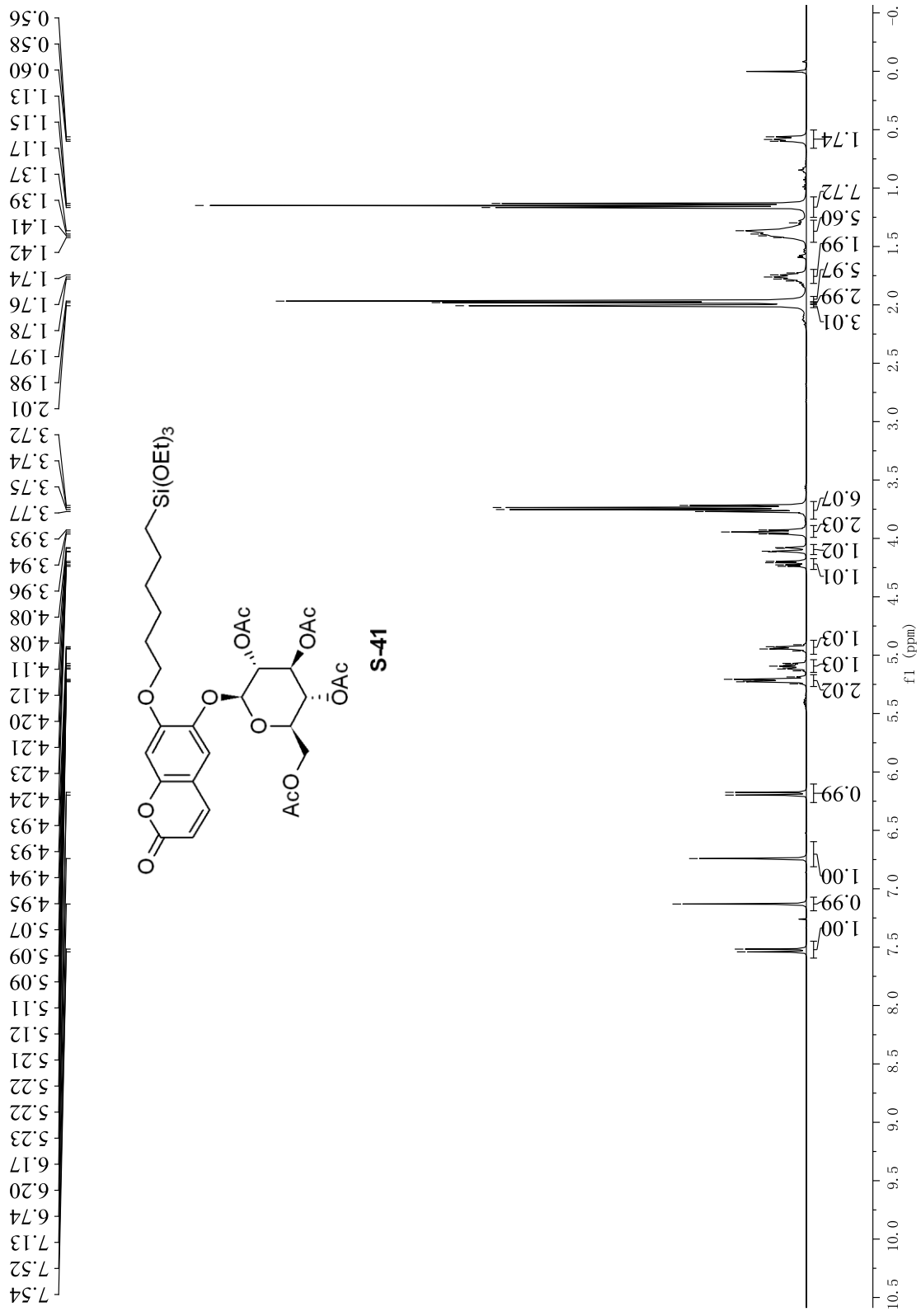
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-40**



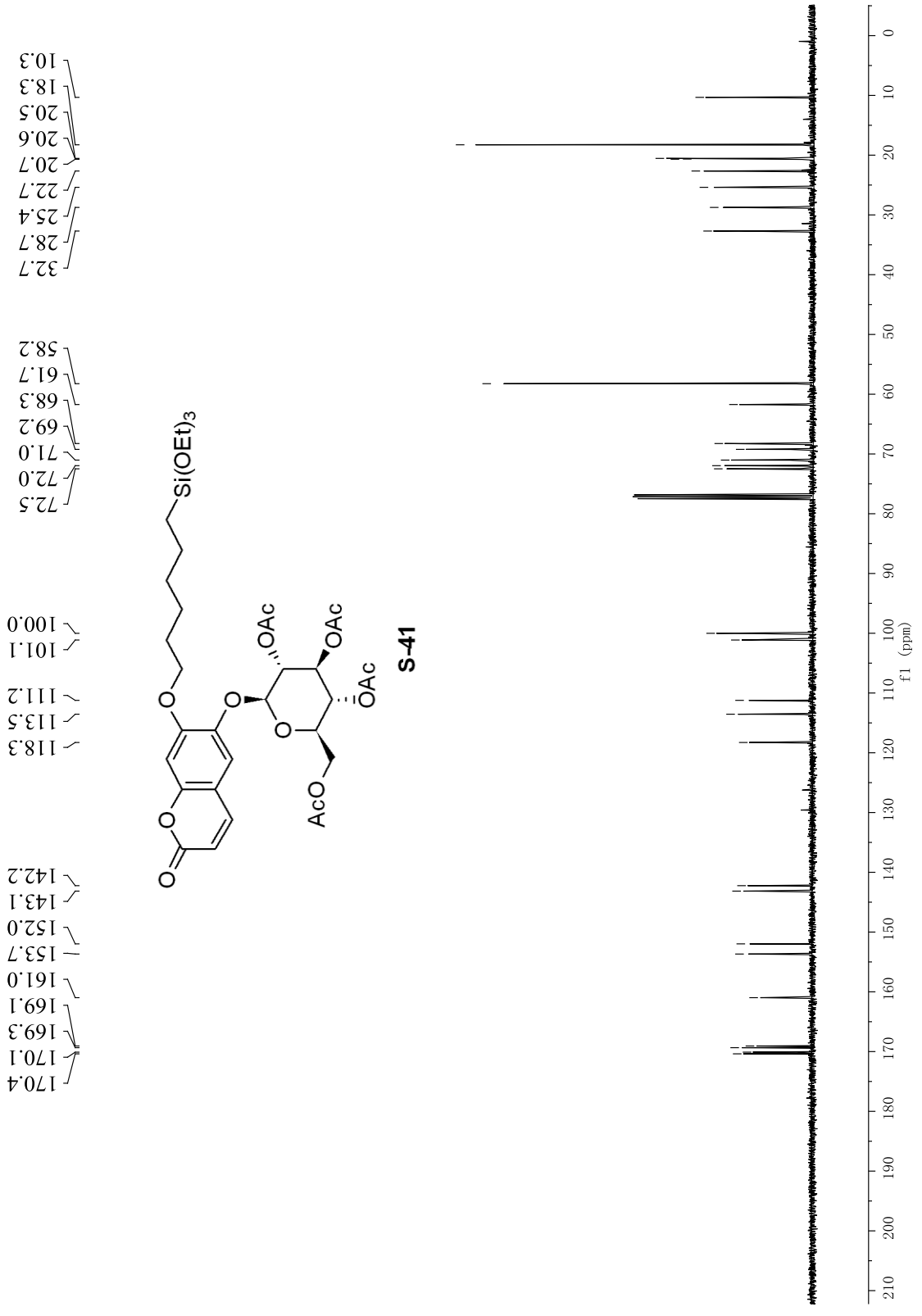
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-40**



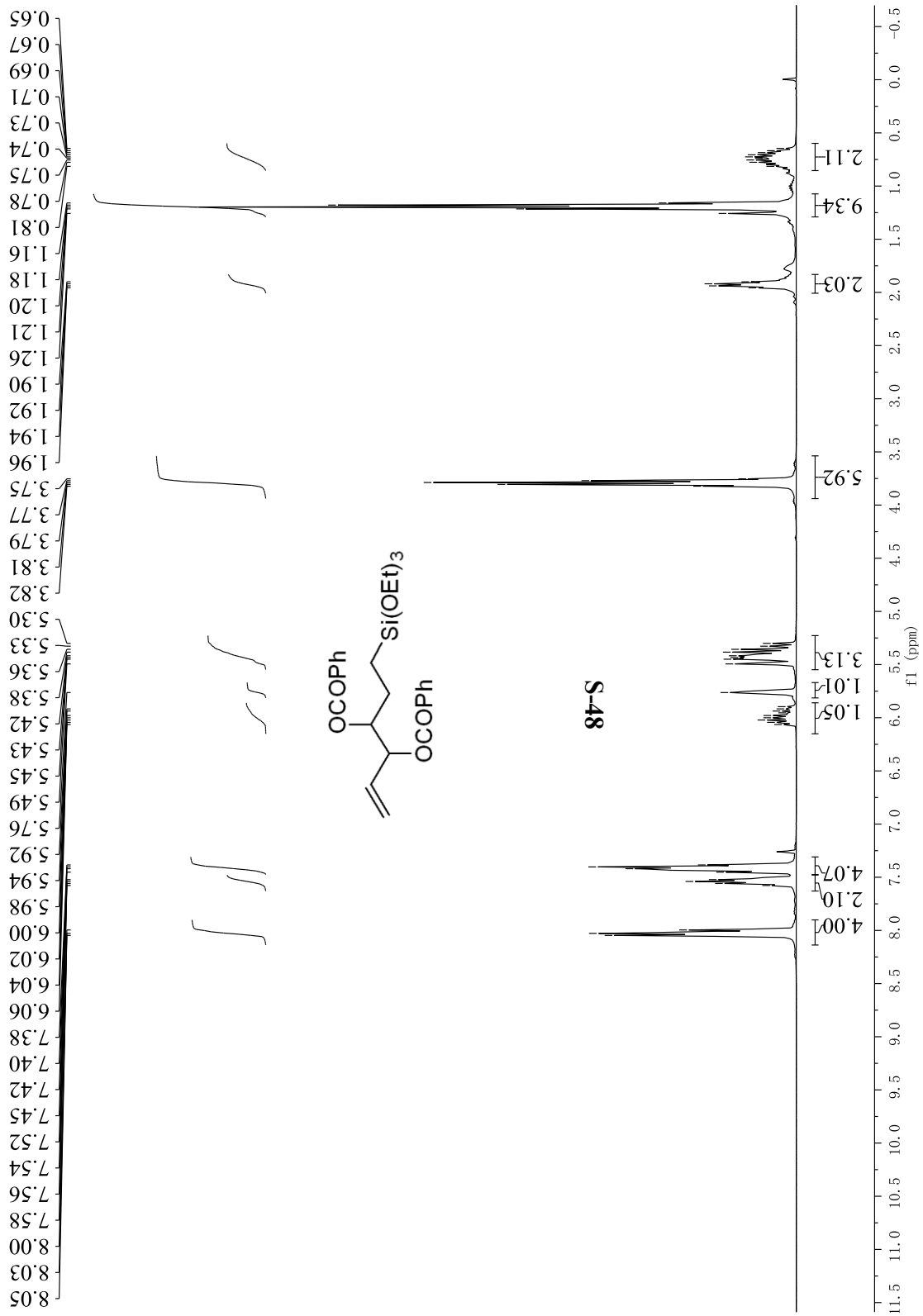
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **S-40**



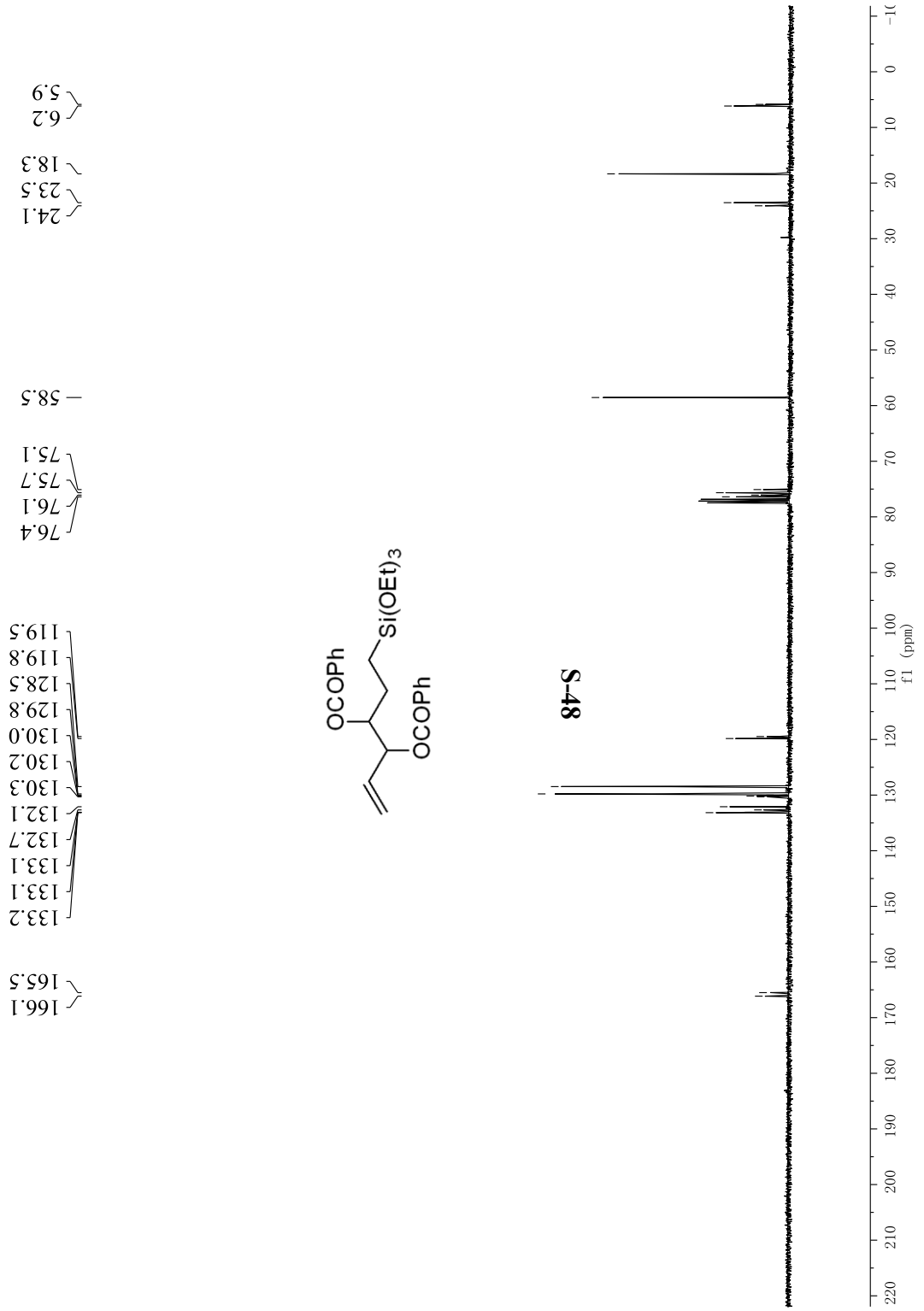
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-41**



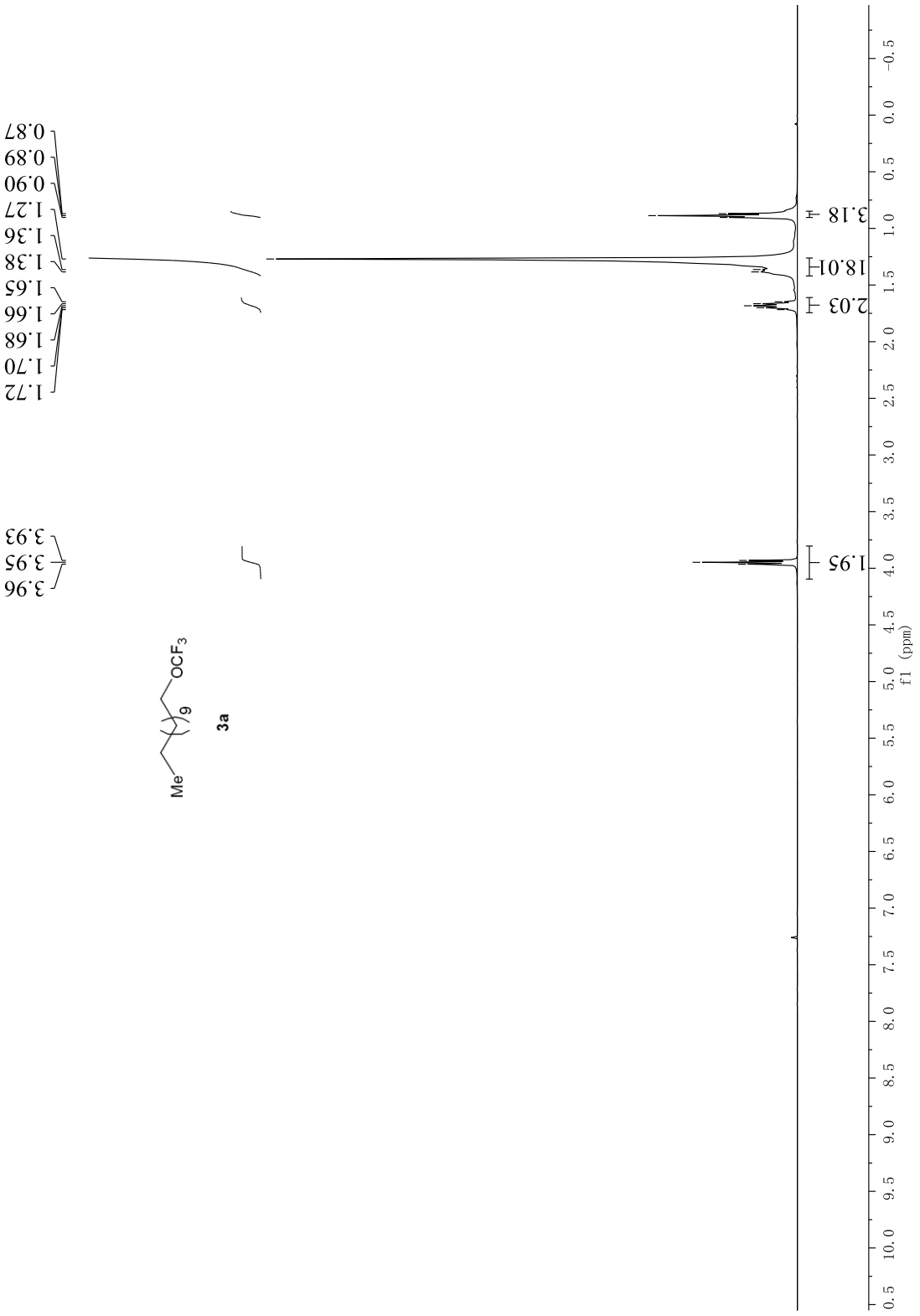
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-41**



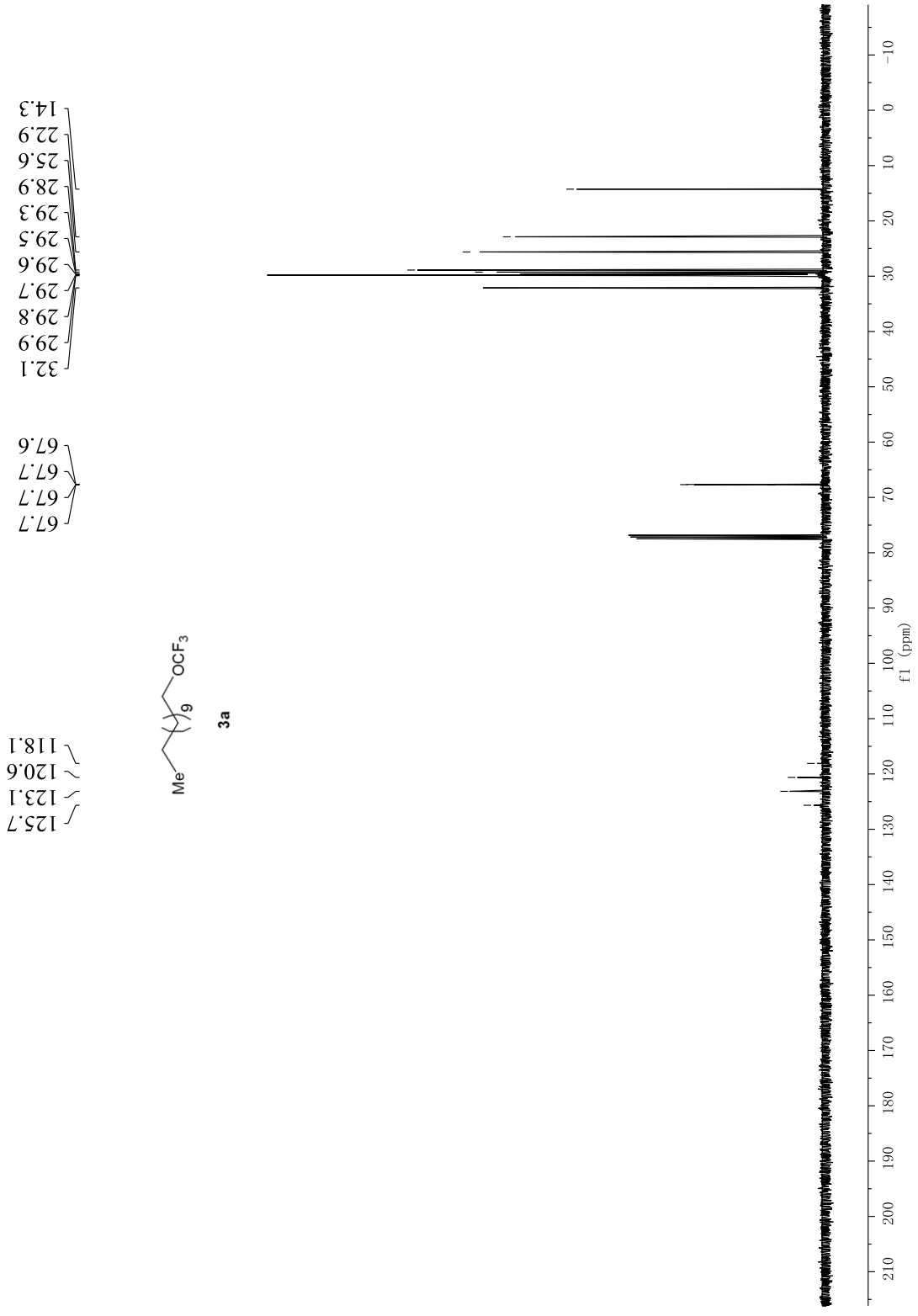
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **S-48**



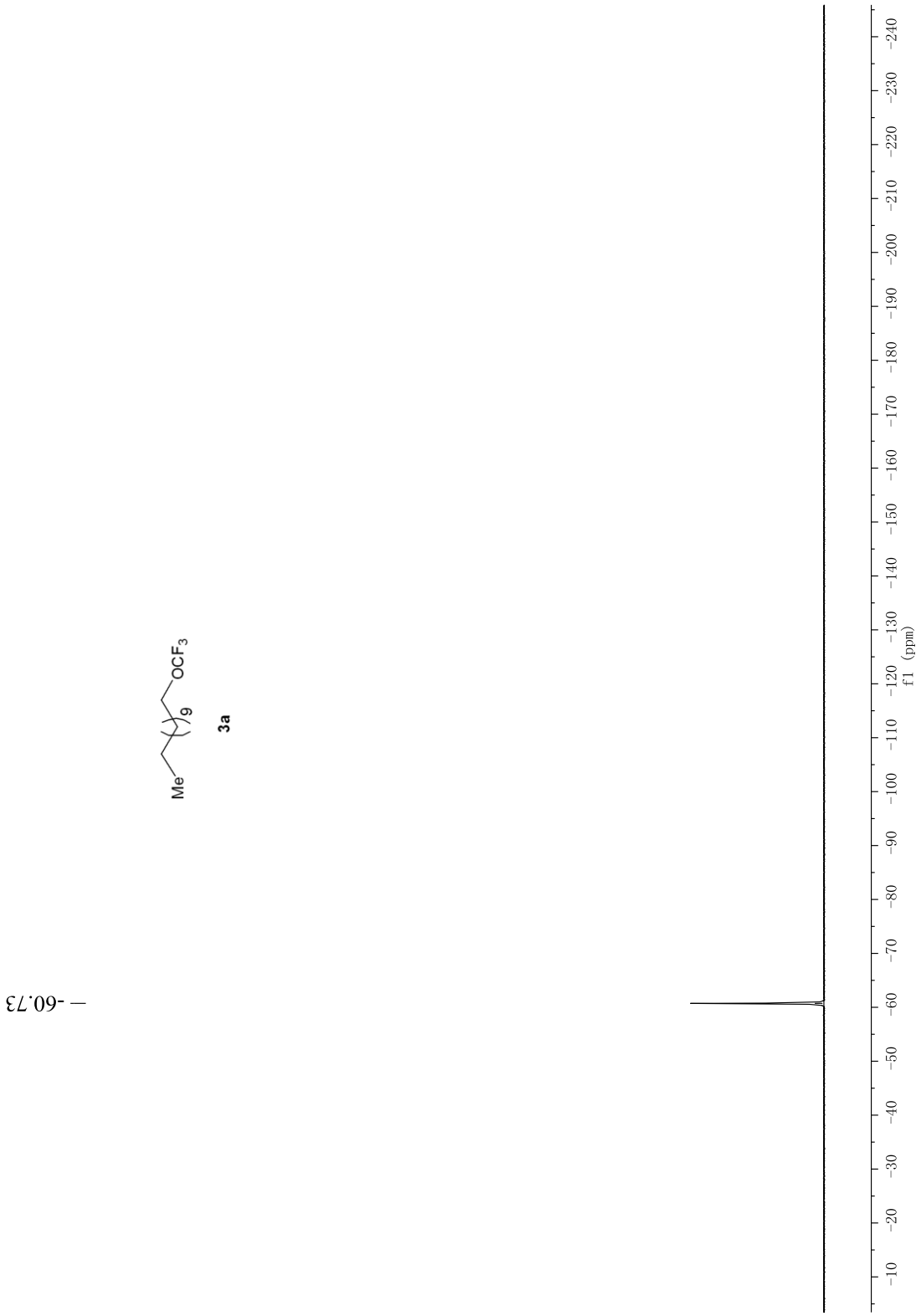
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **S-48**



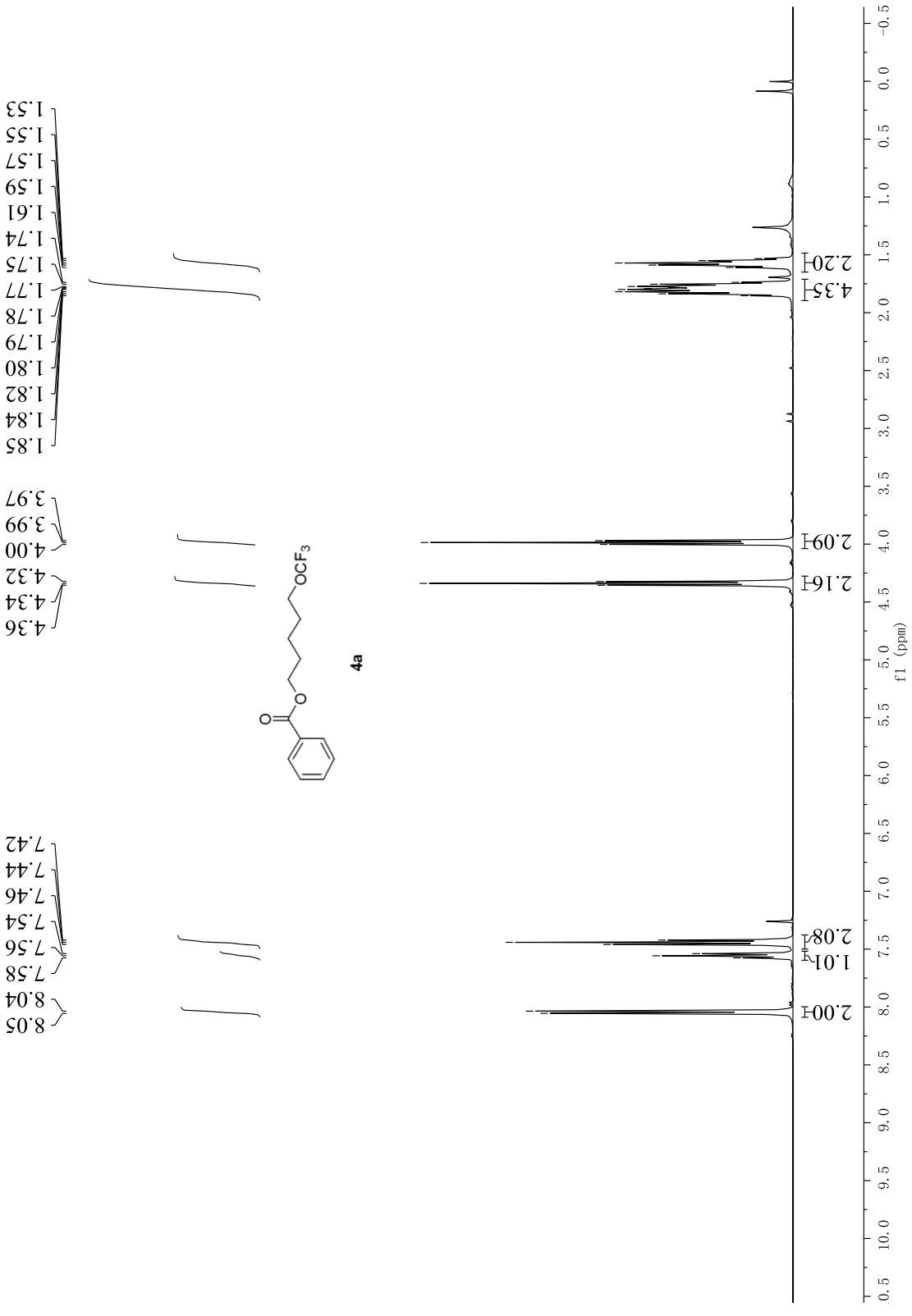
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



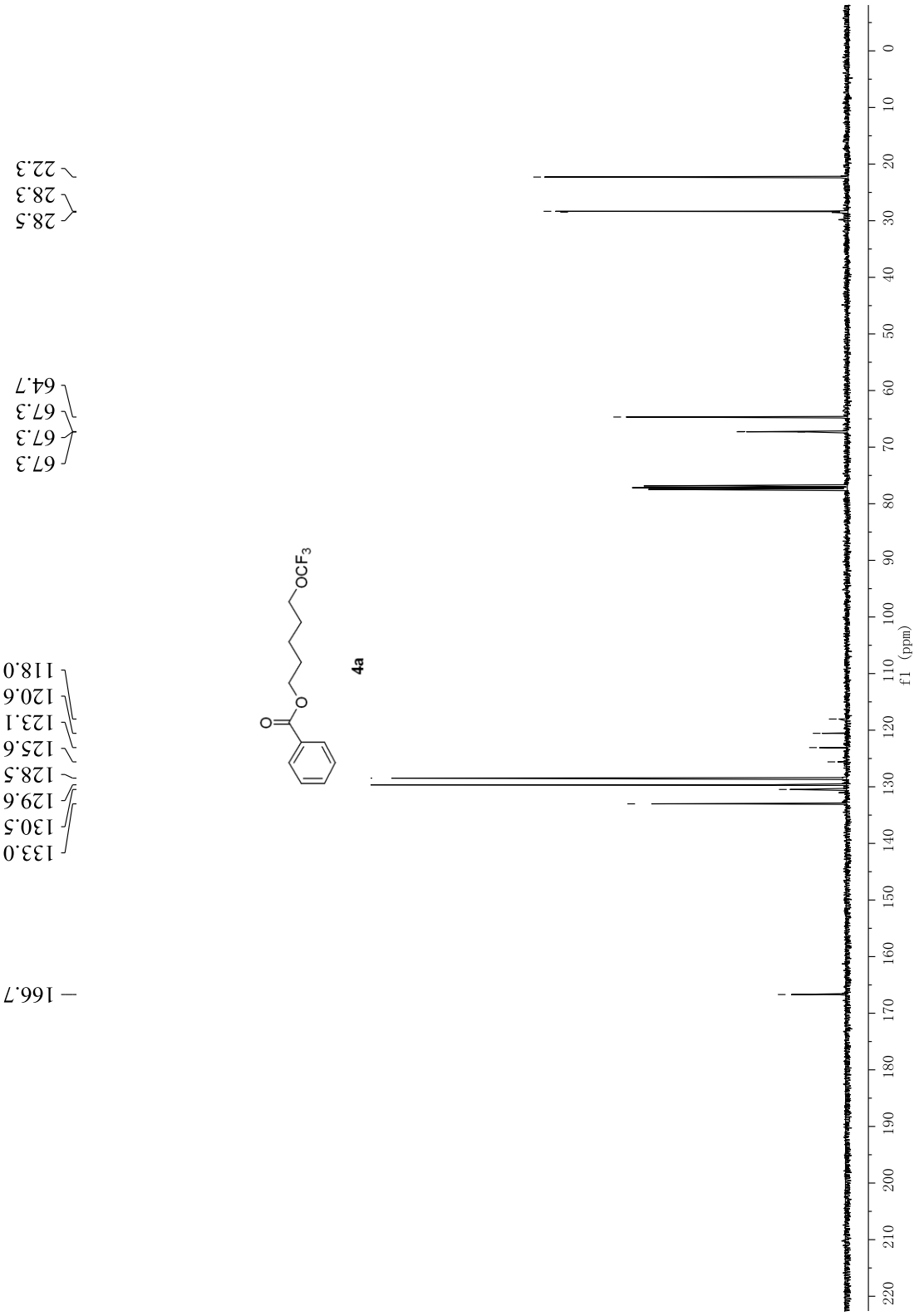
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3a**



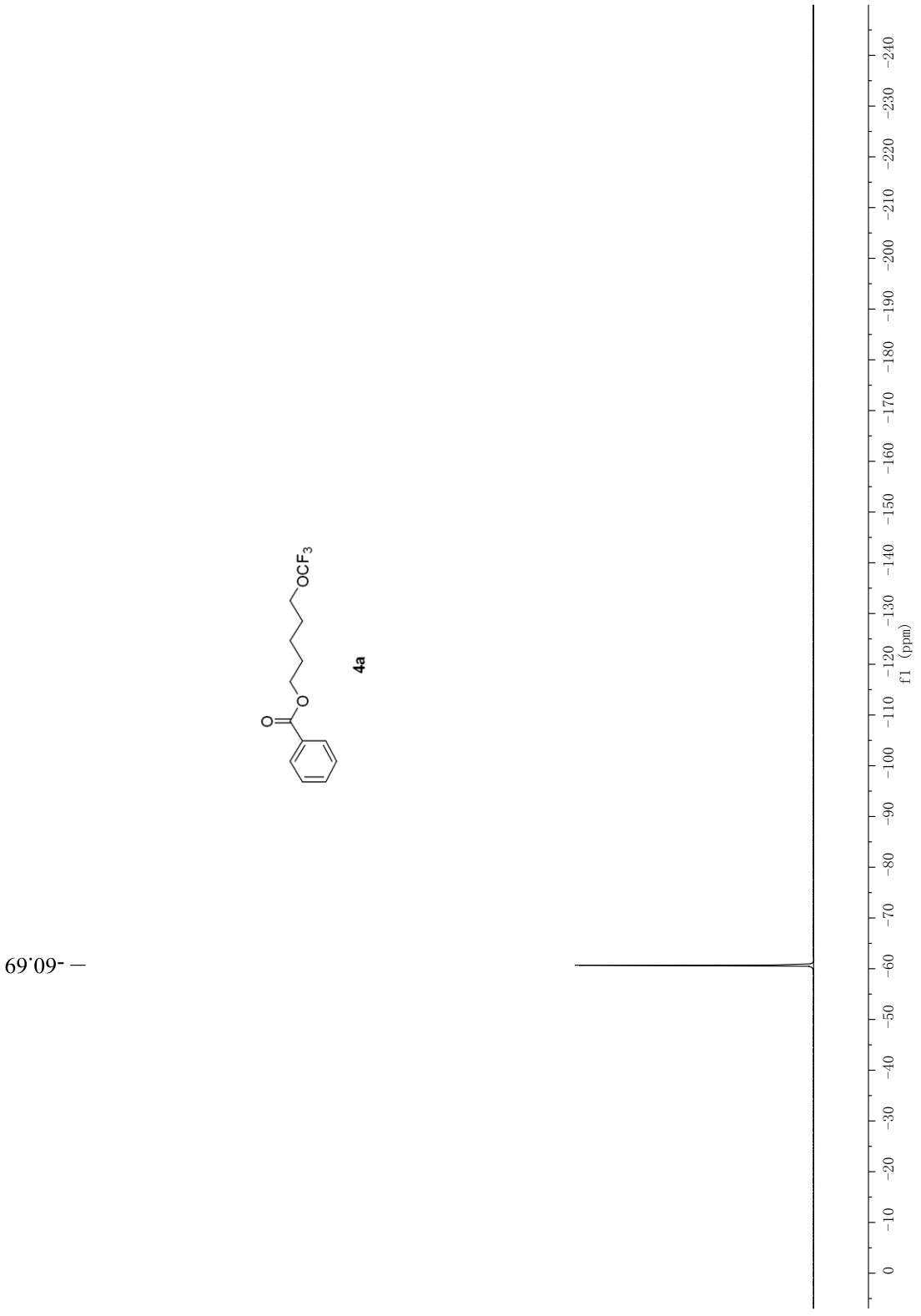
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3a**



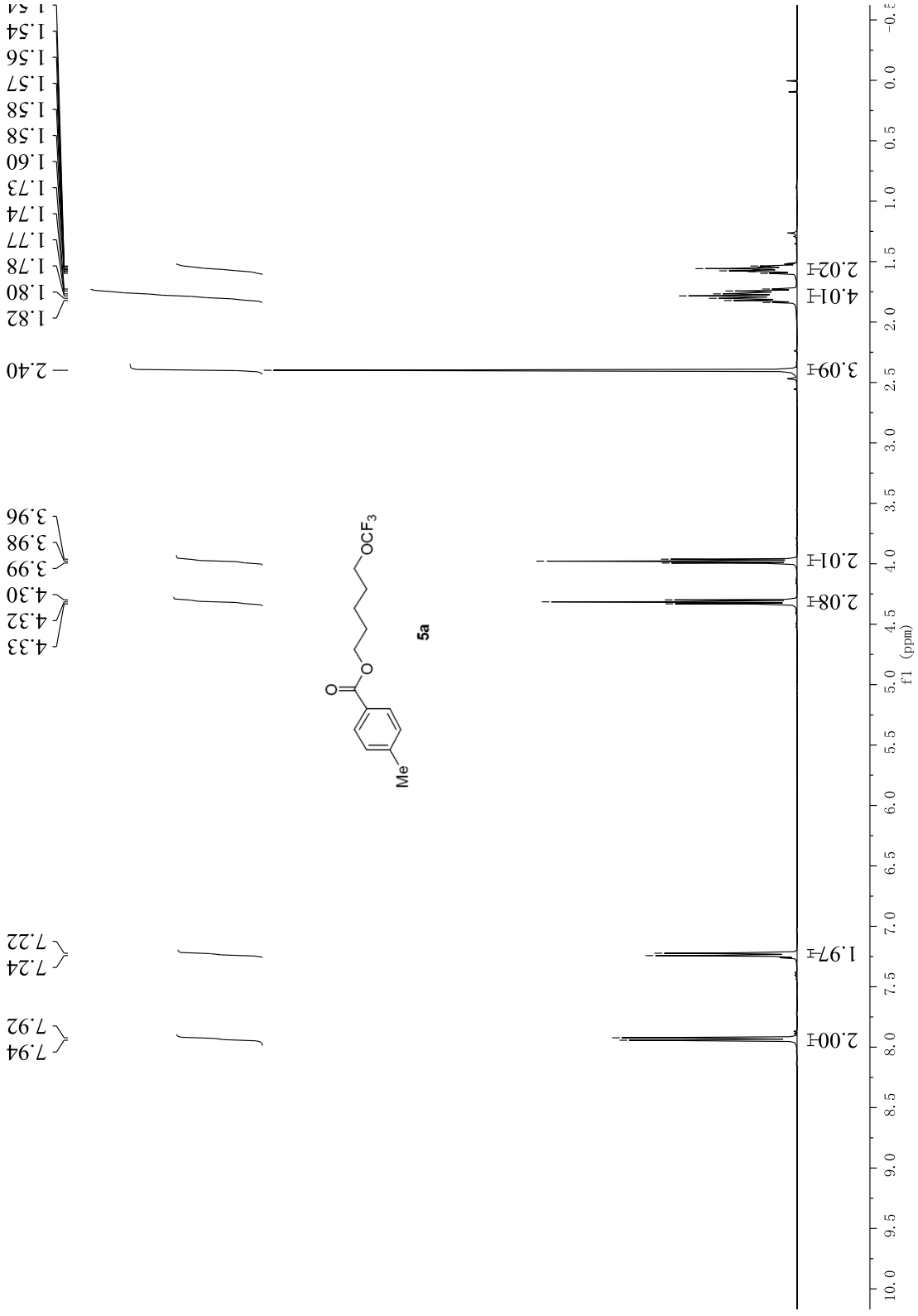
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**



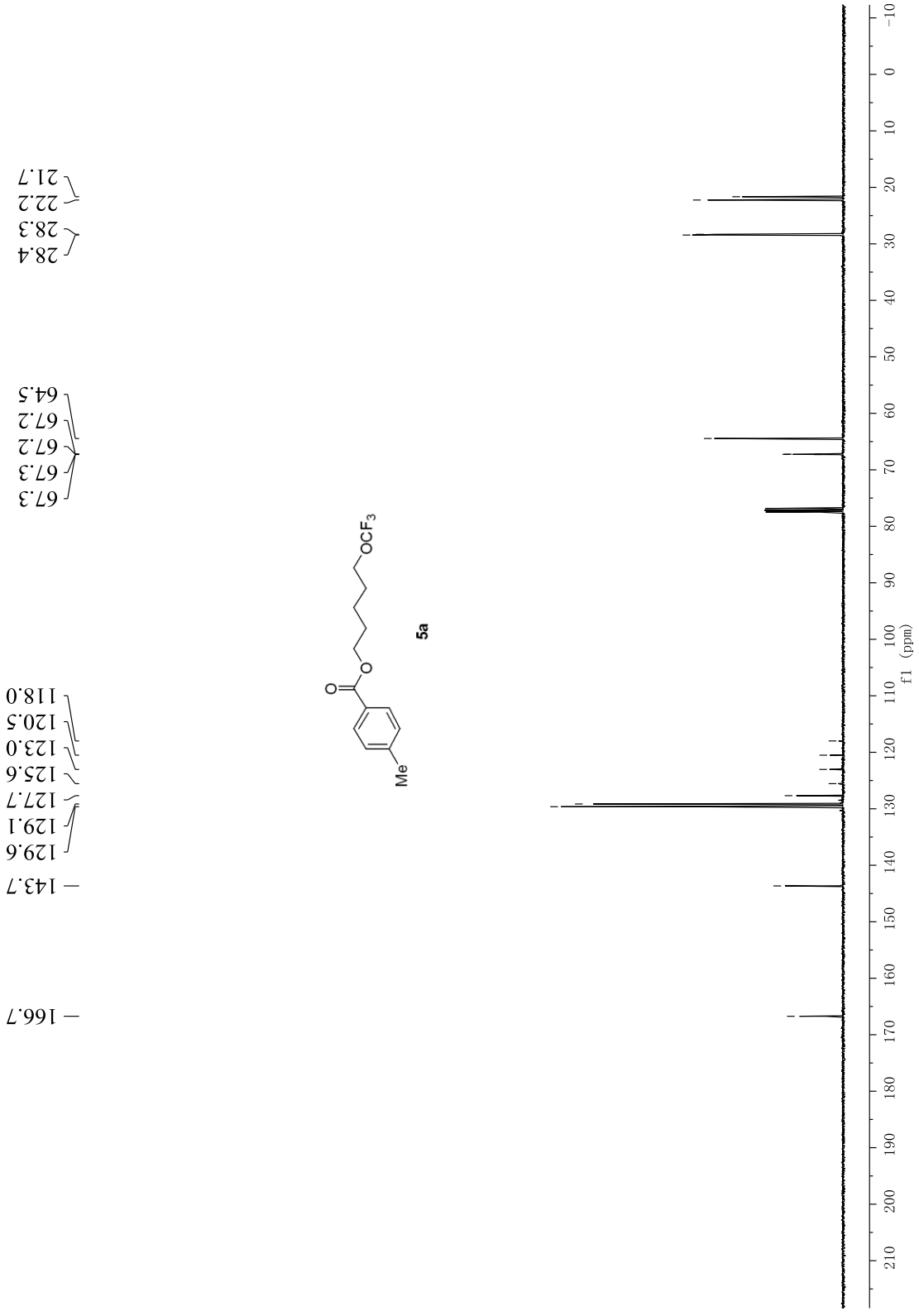
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4a**



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

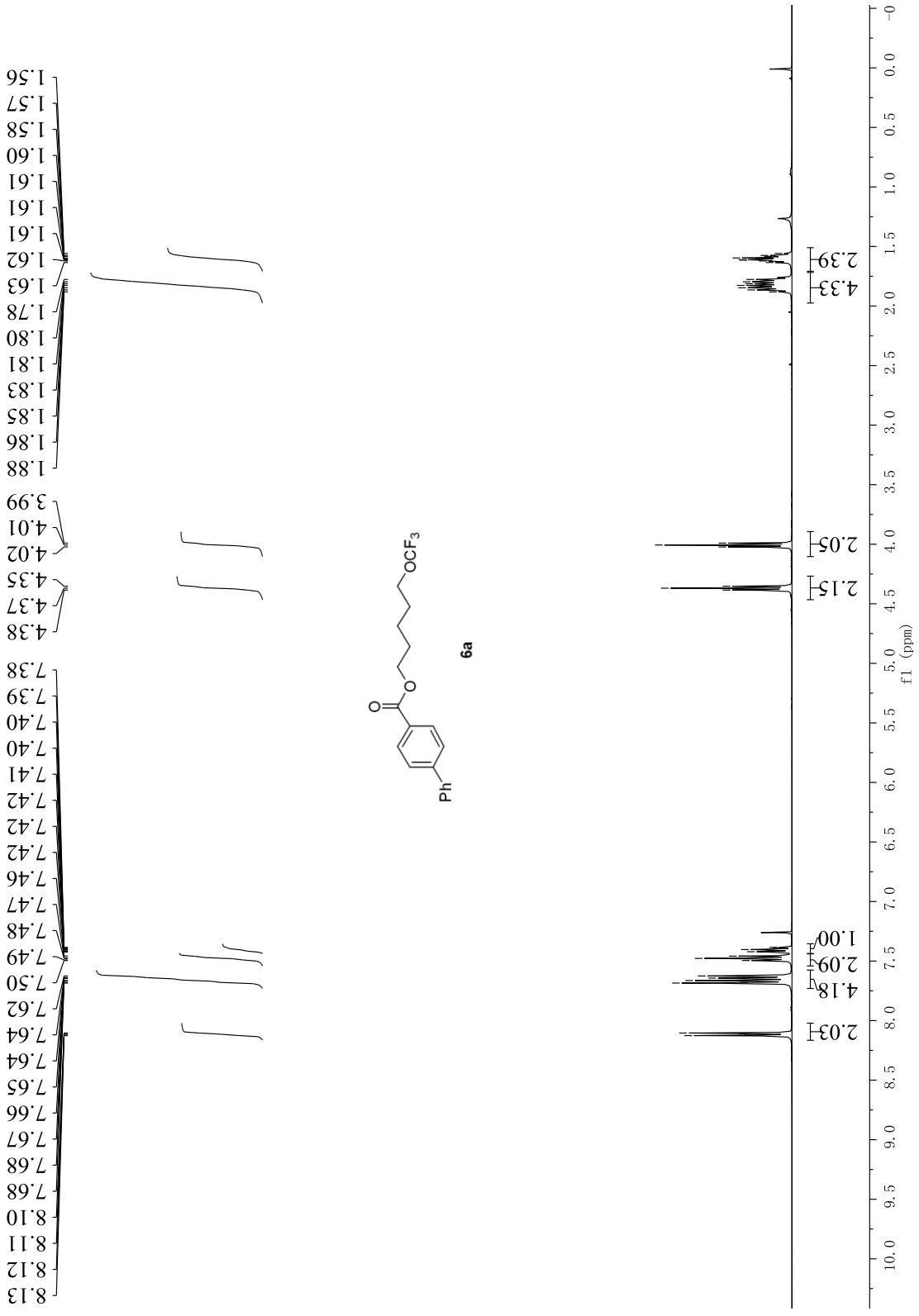


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a**

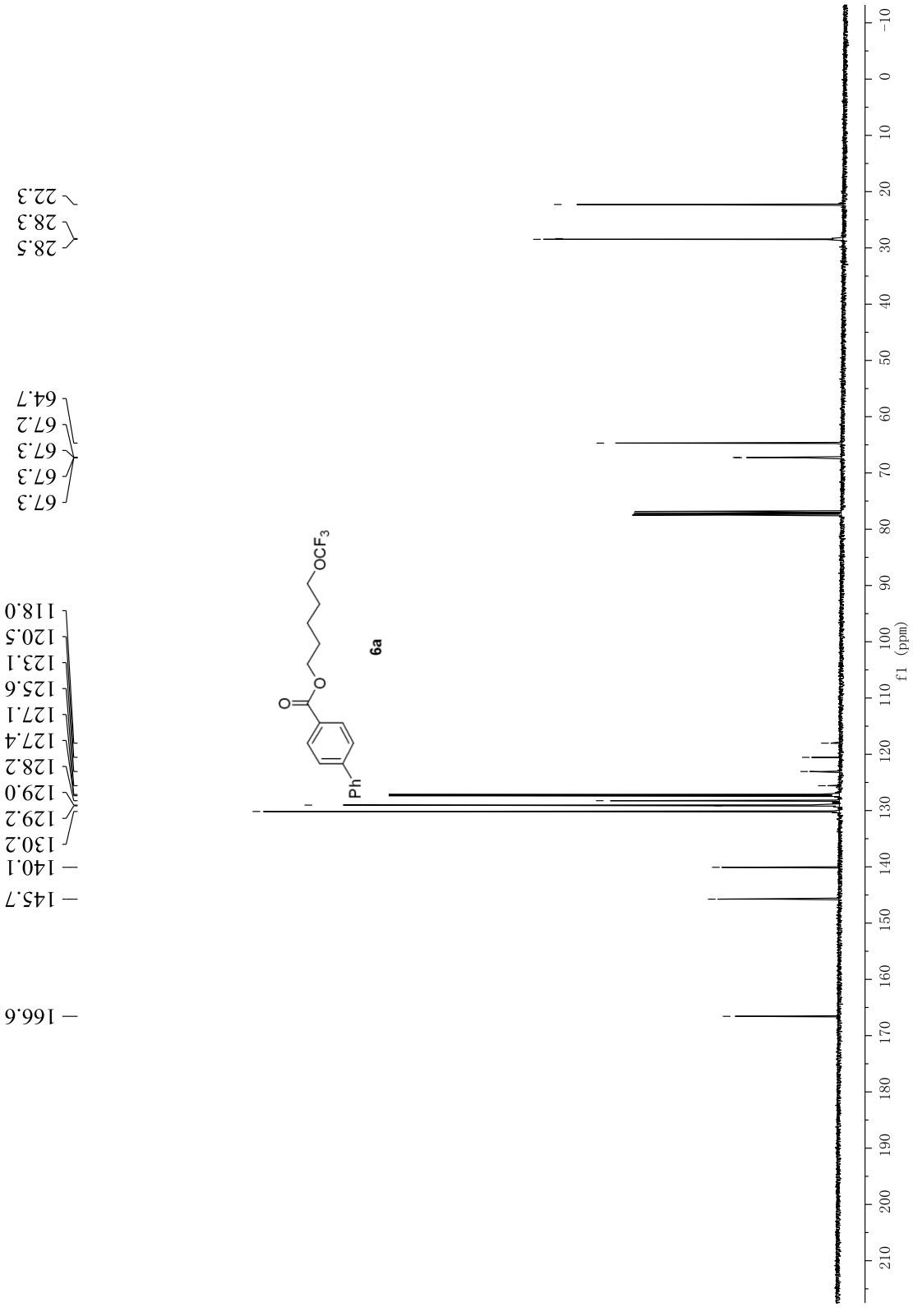


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a**

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

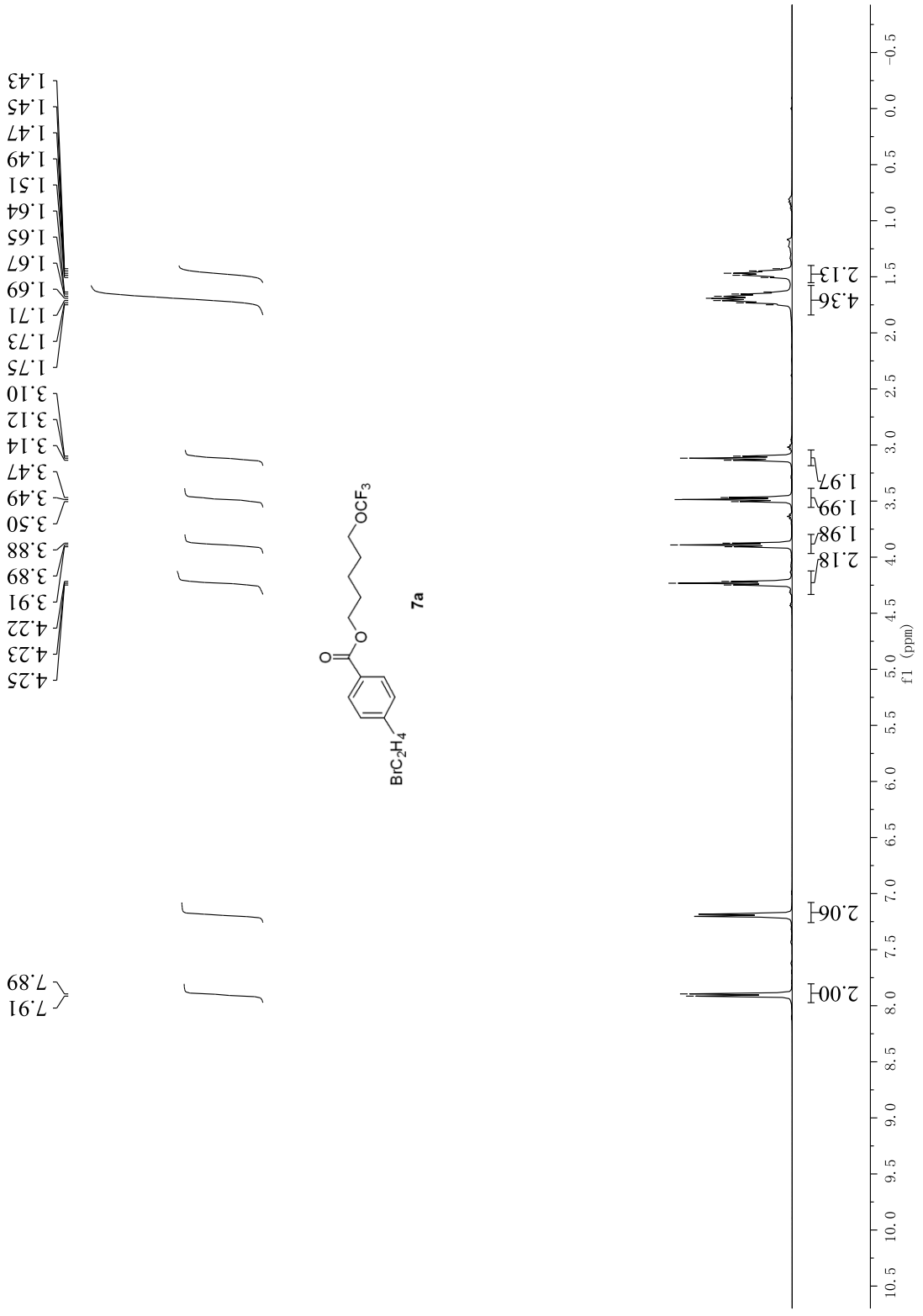


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6a**

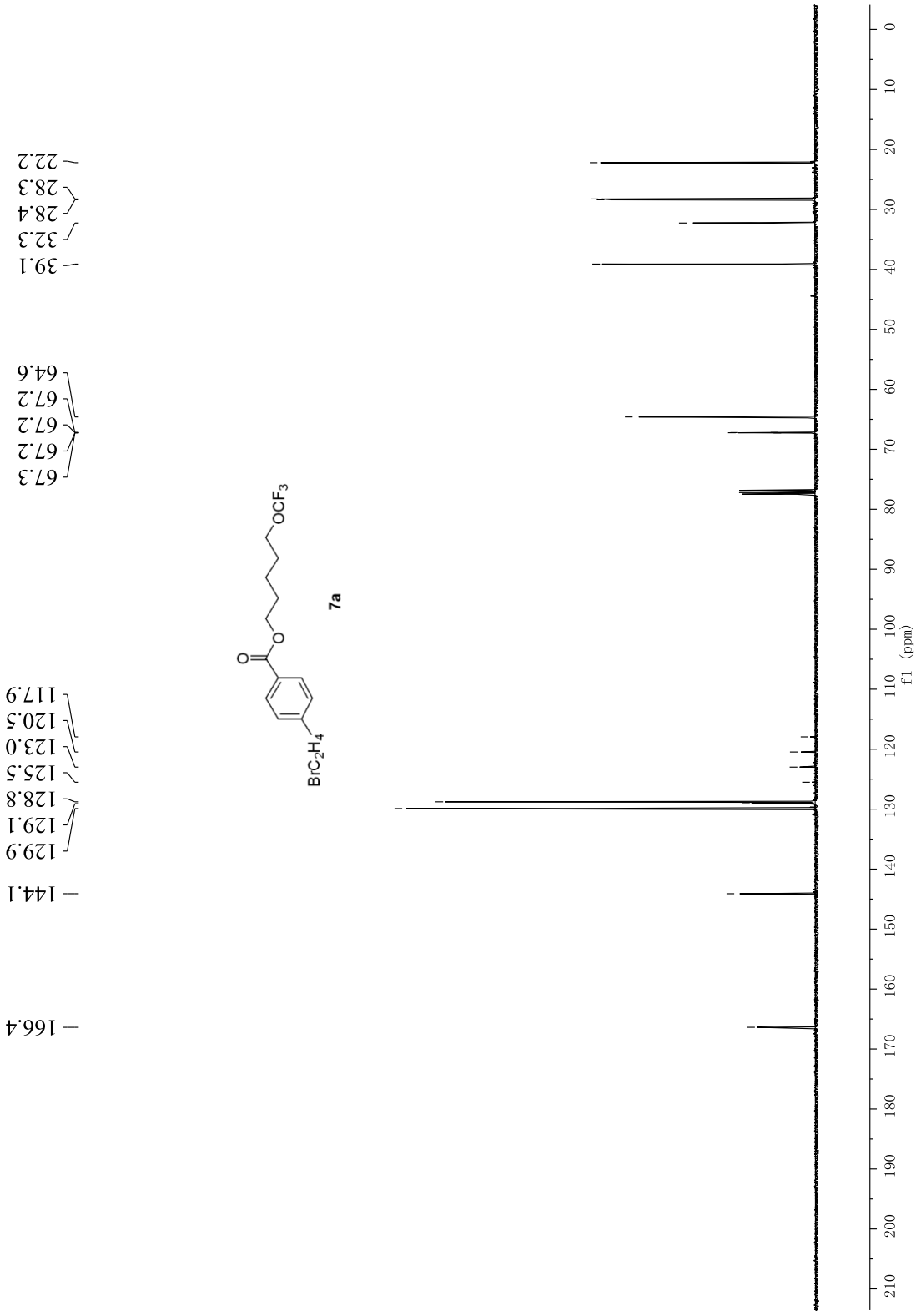


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6a**

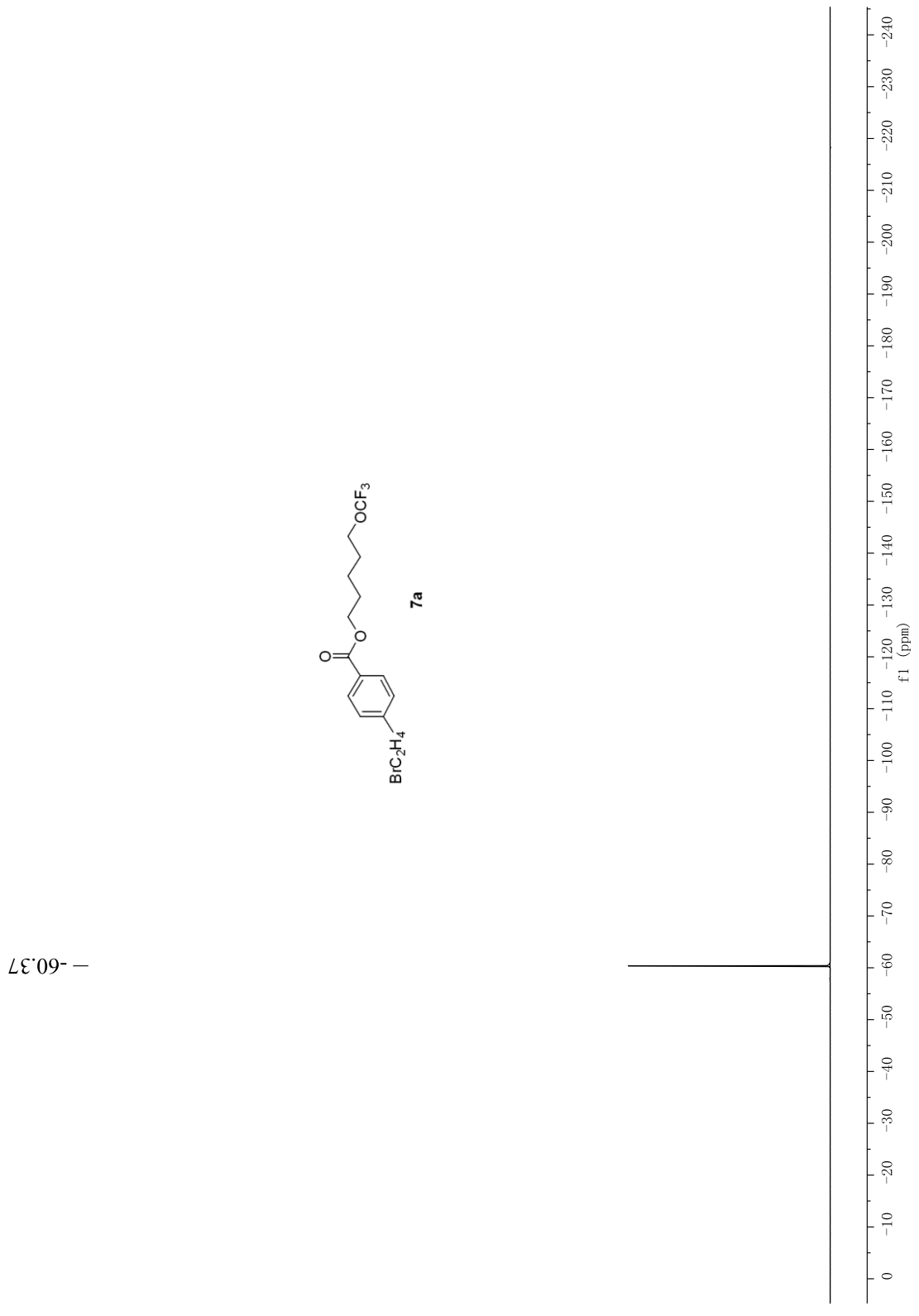
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6a**



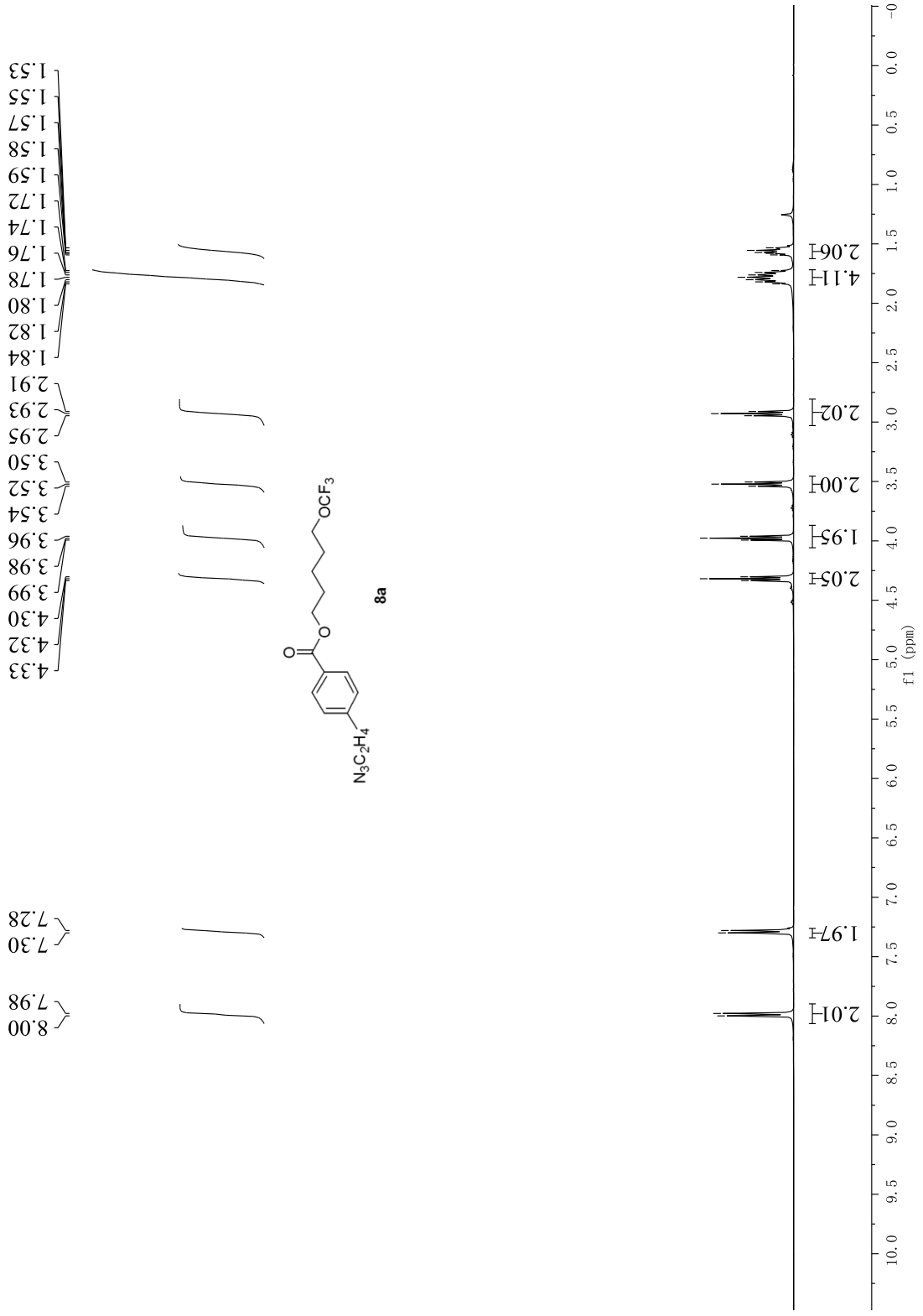
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a**



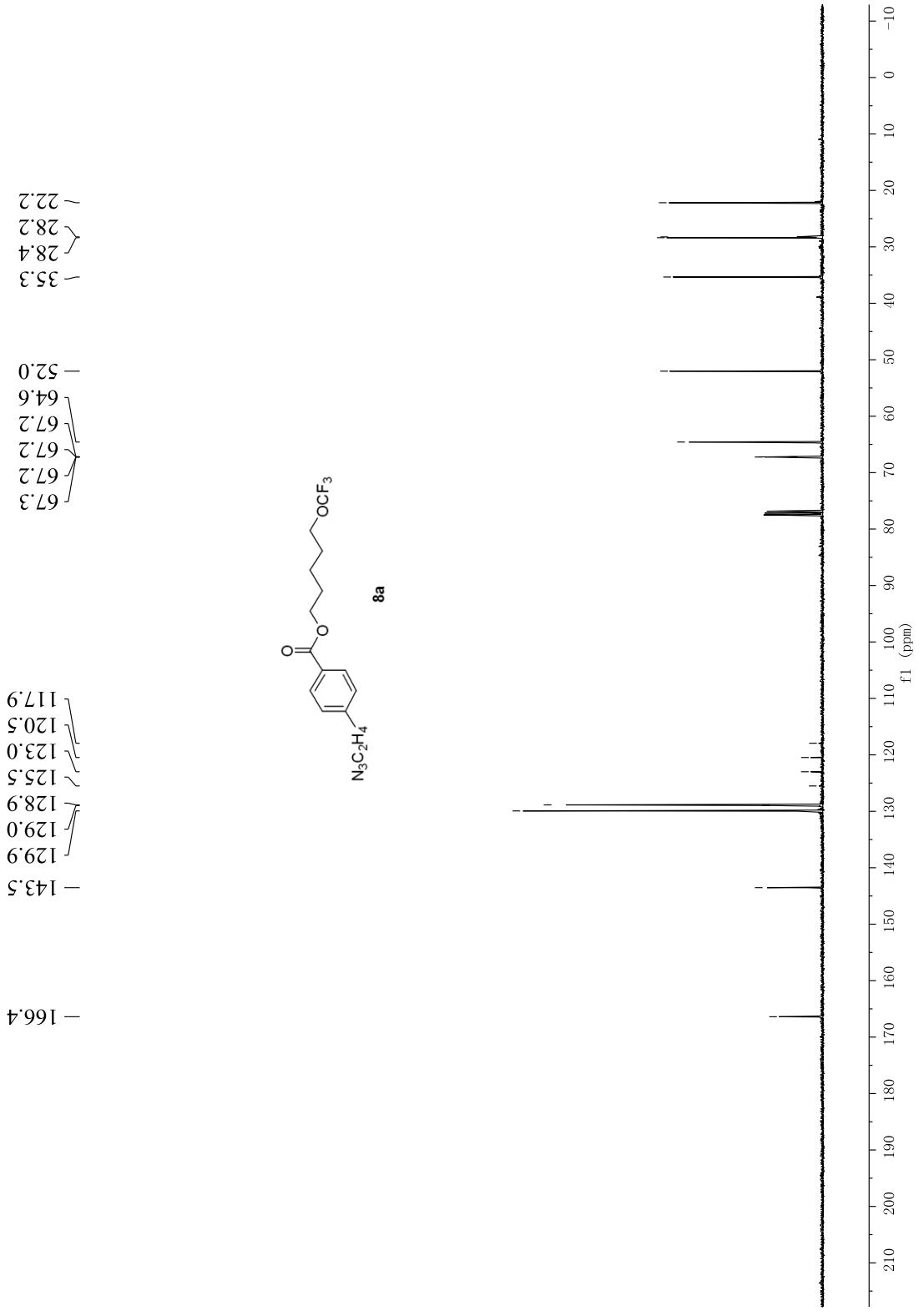
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7a**



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

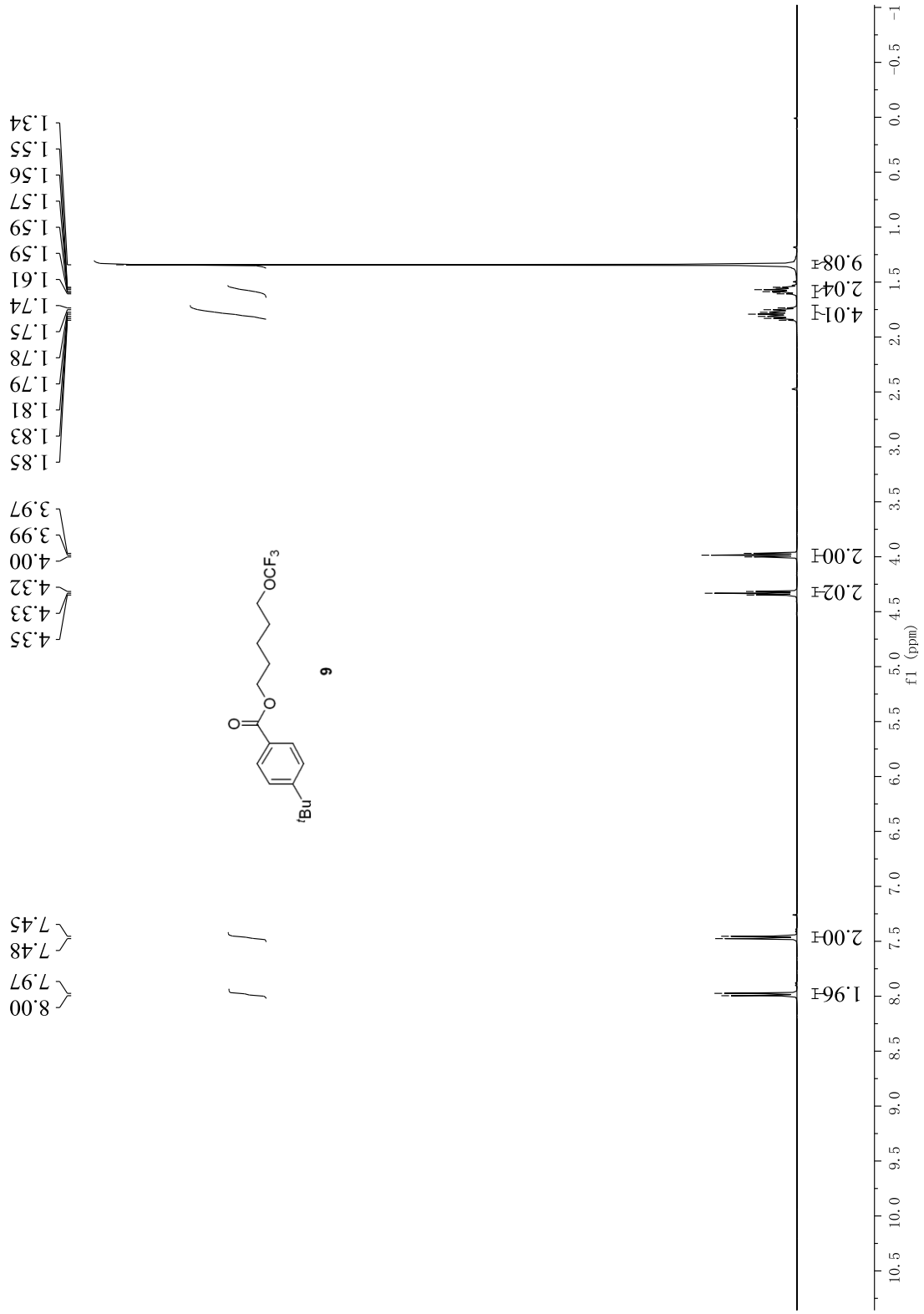


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8a**

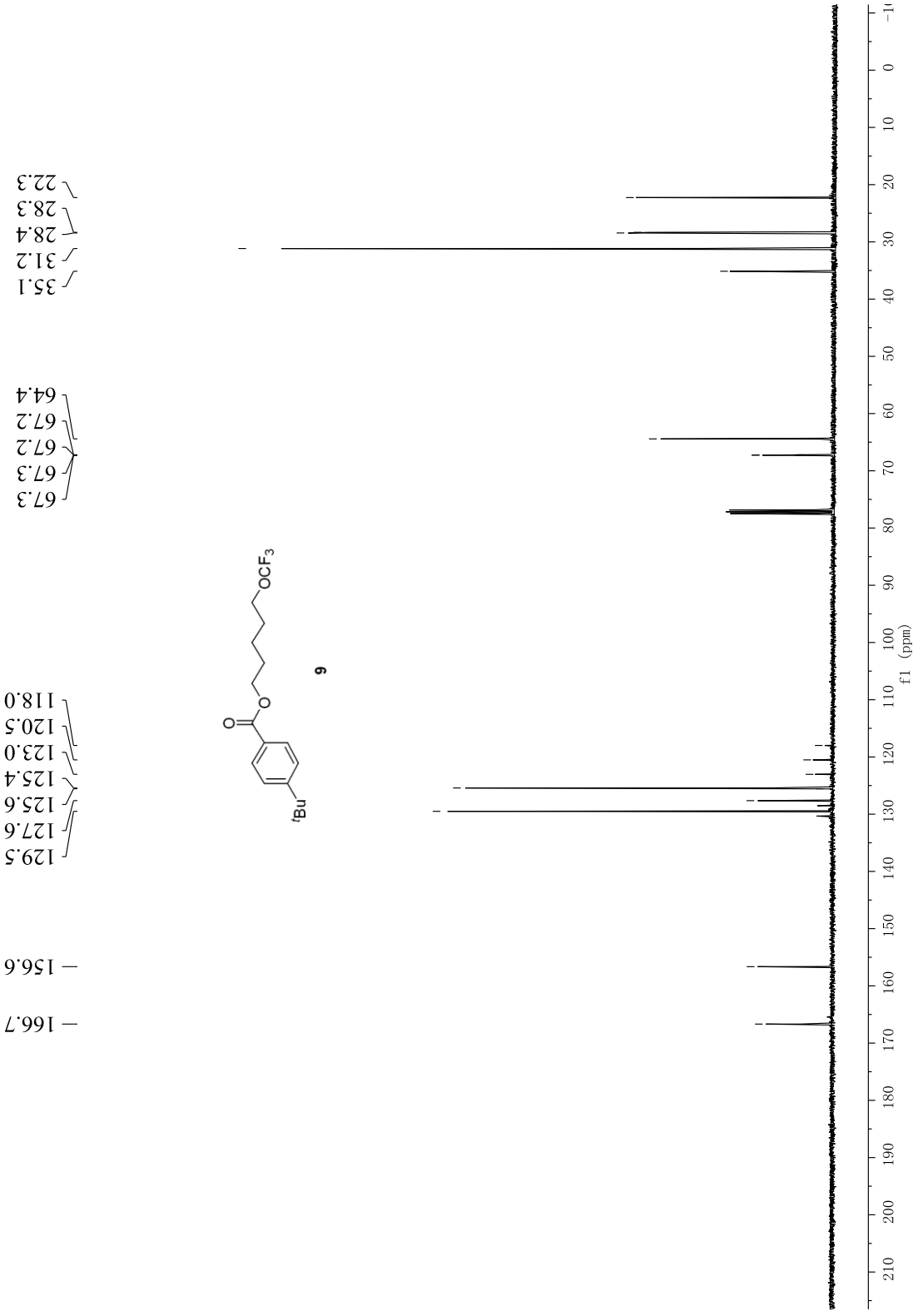


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **8a**

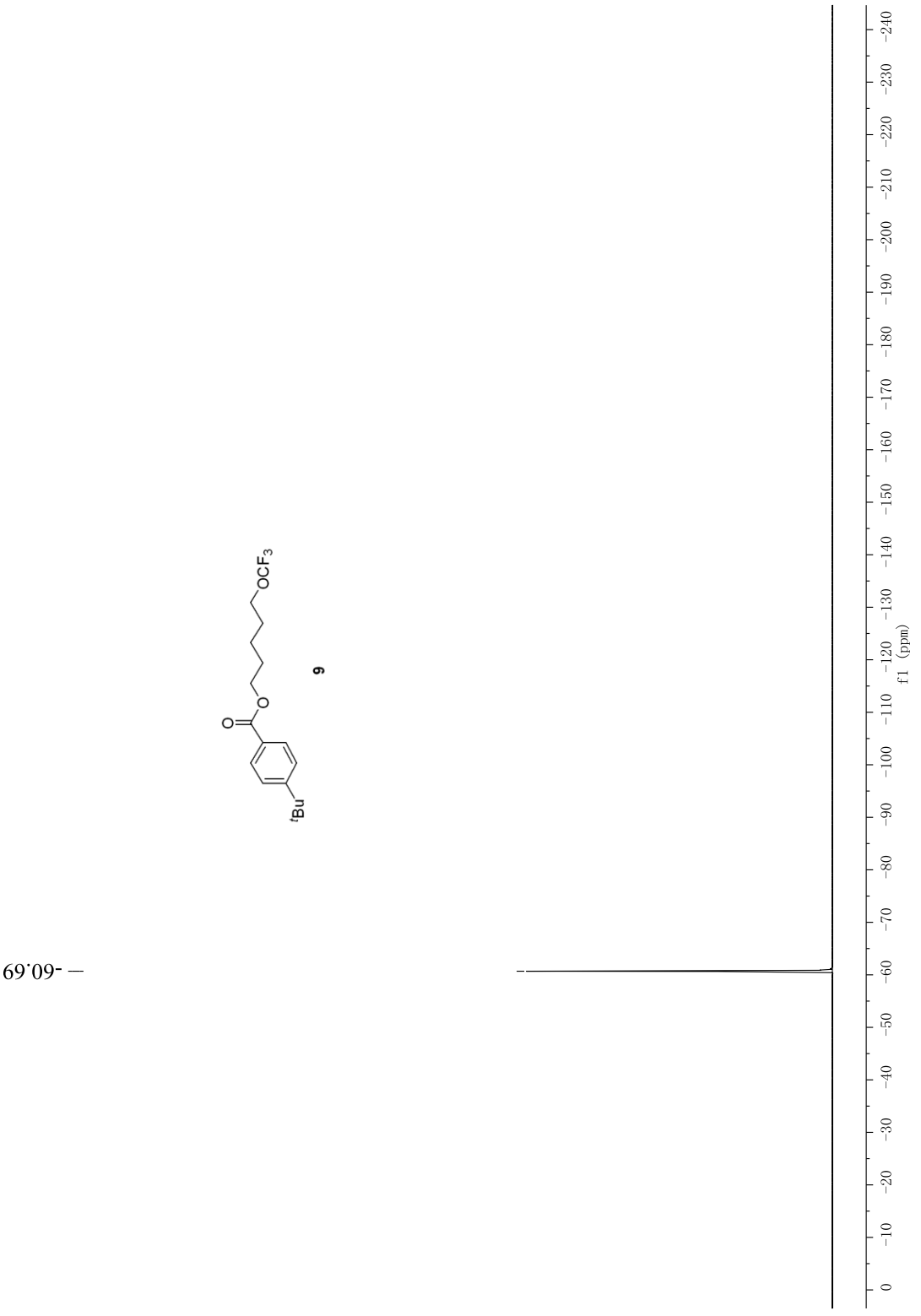
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **8a**



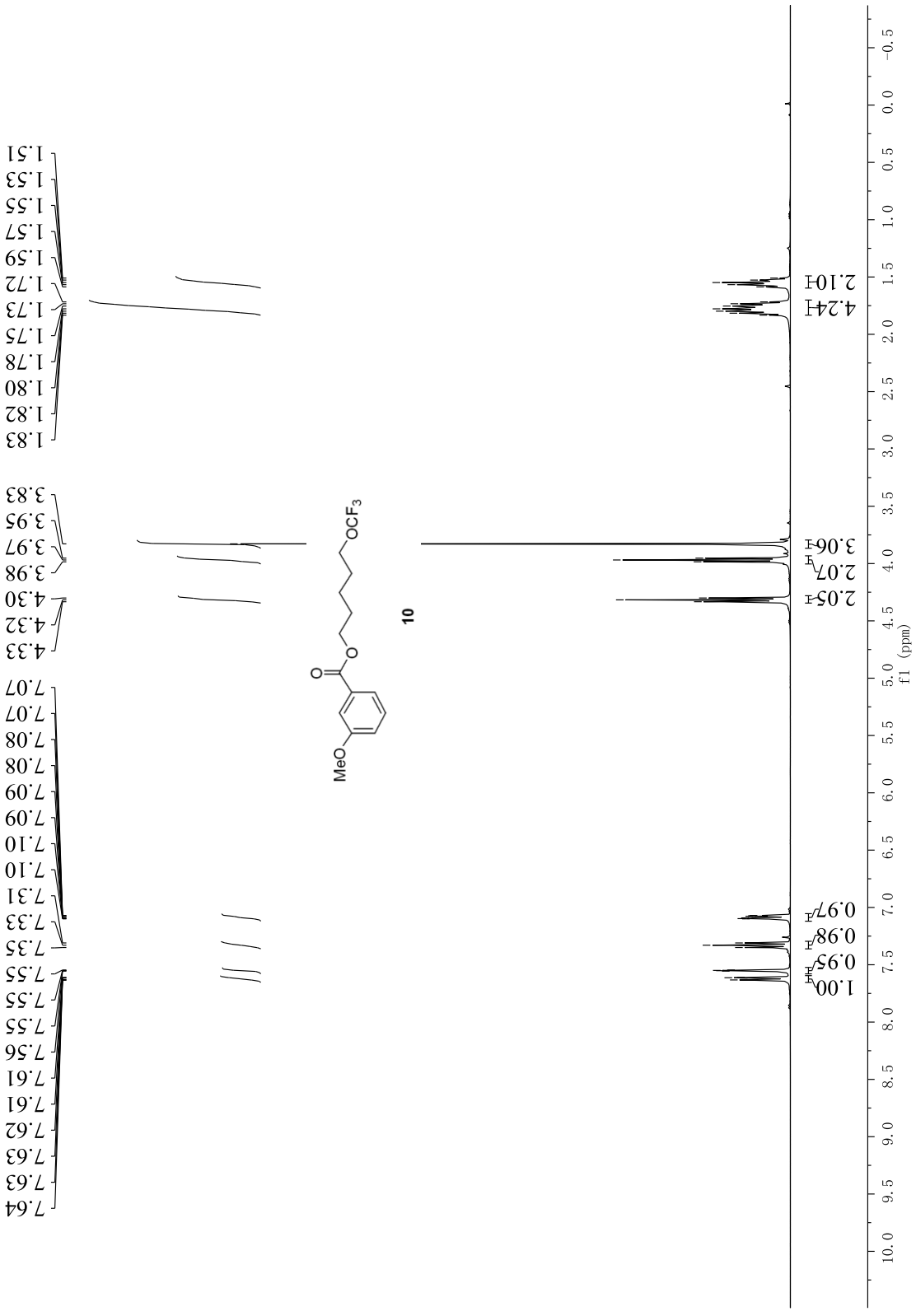
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9**



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

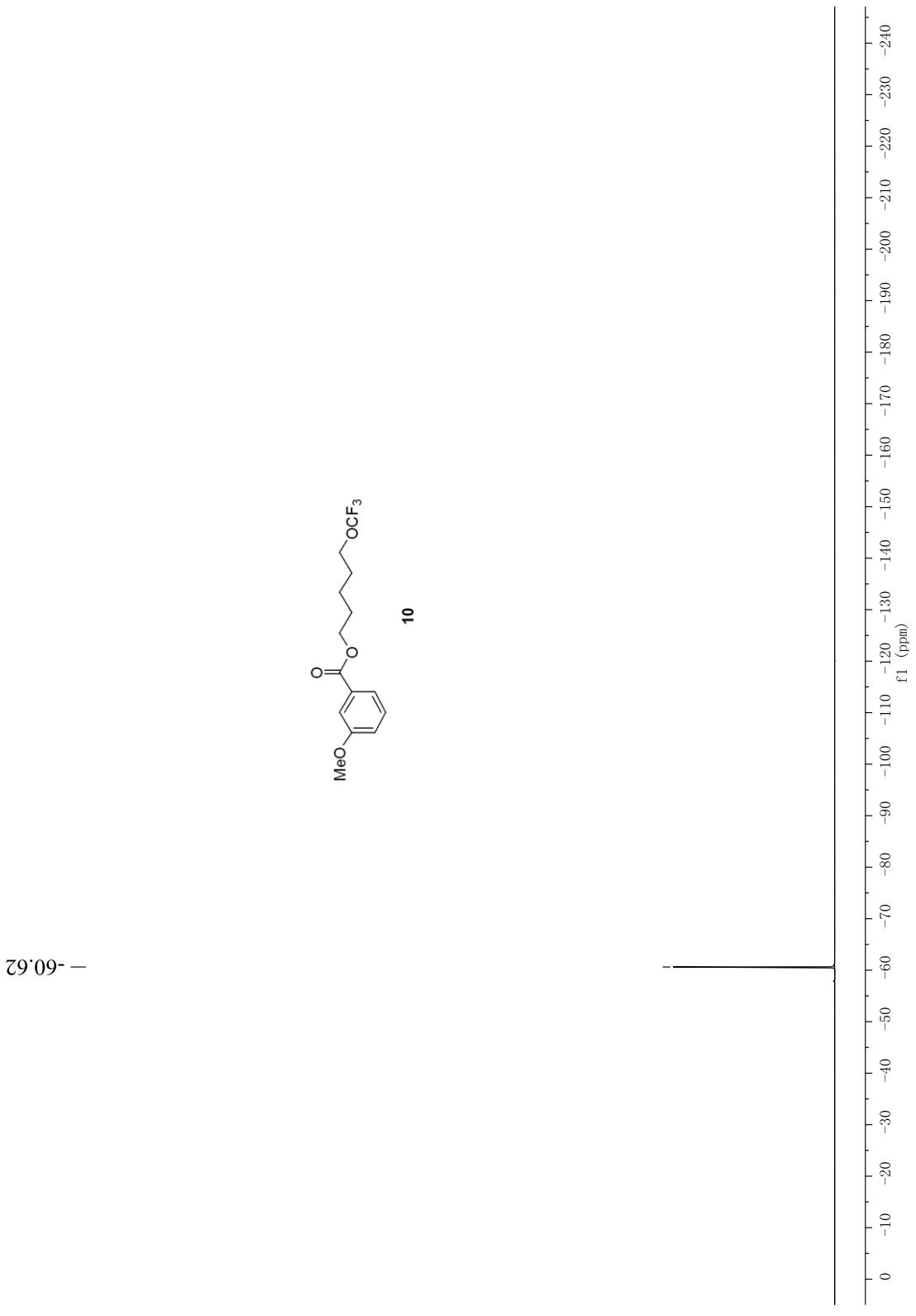


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **9**

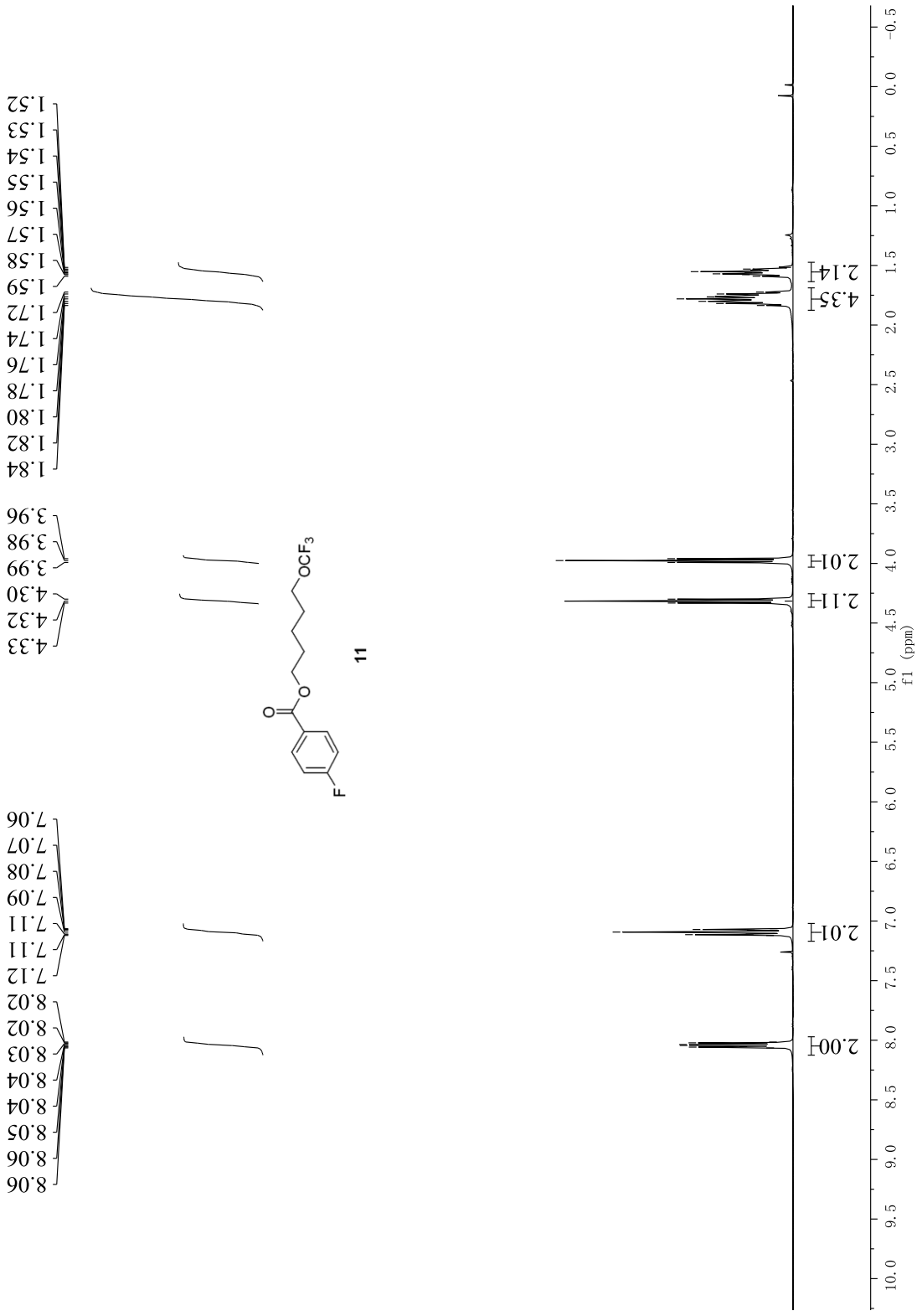


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **10**

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

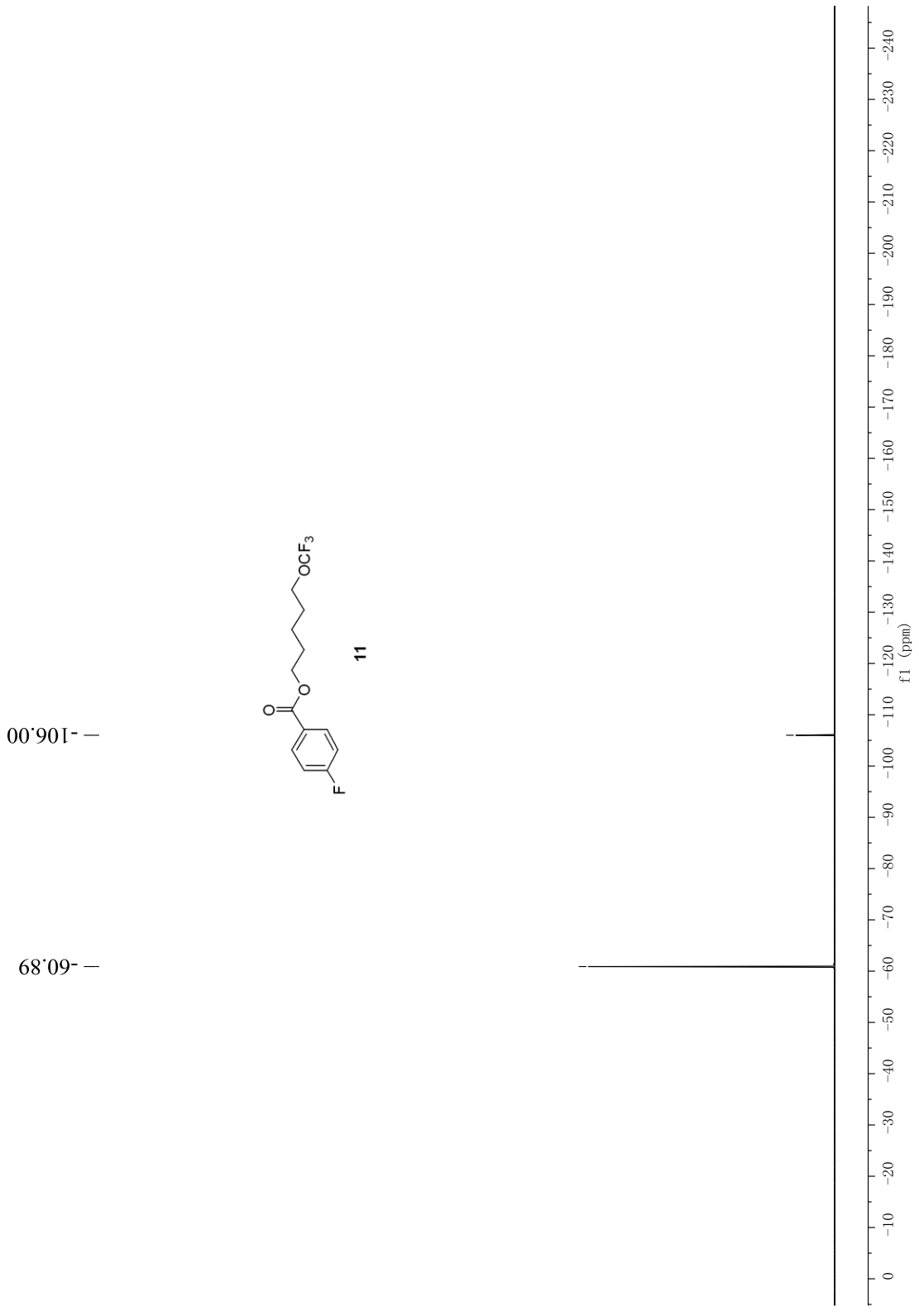


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **10**

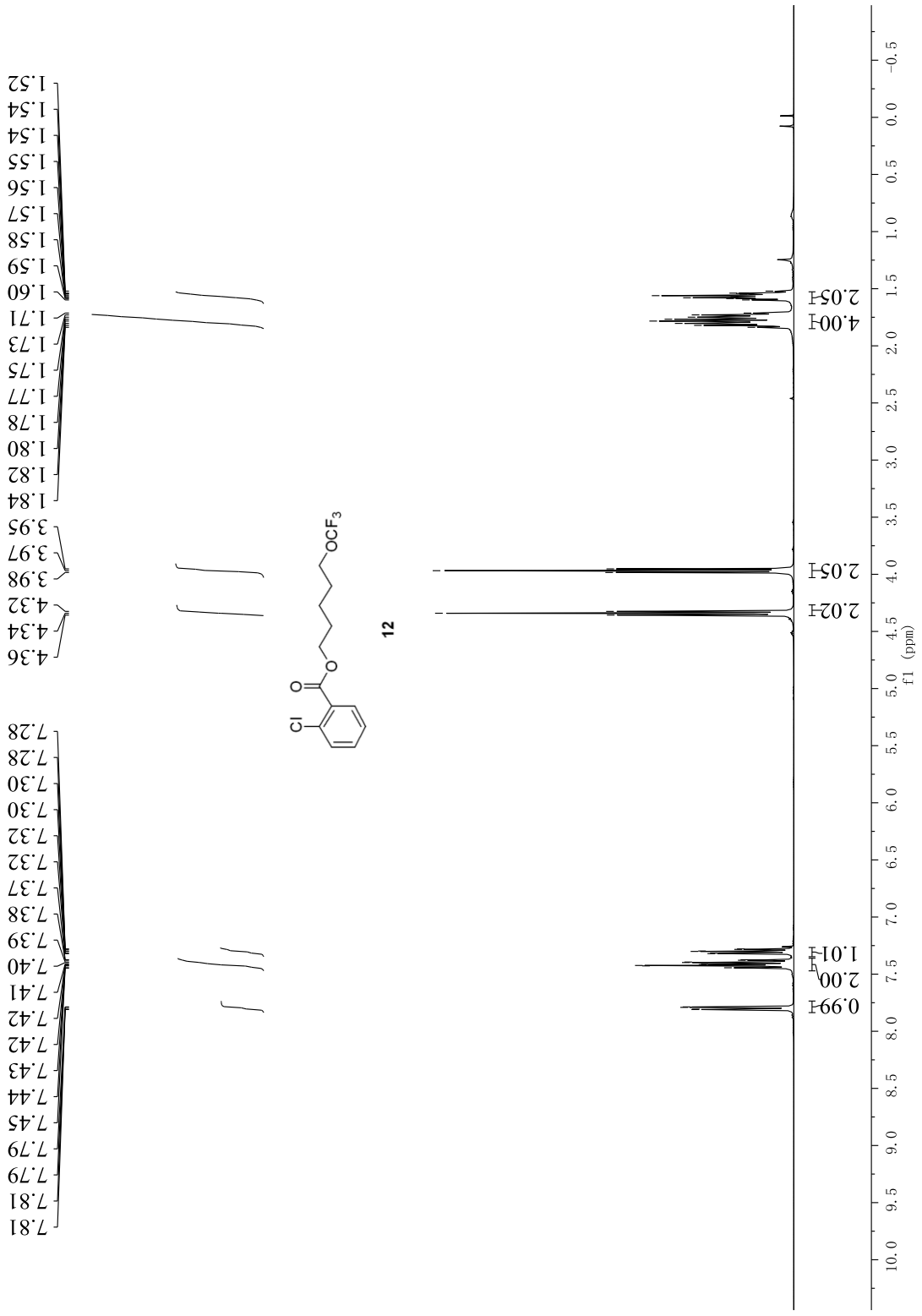


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11**

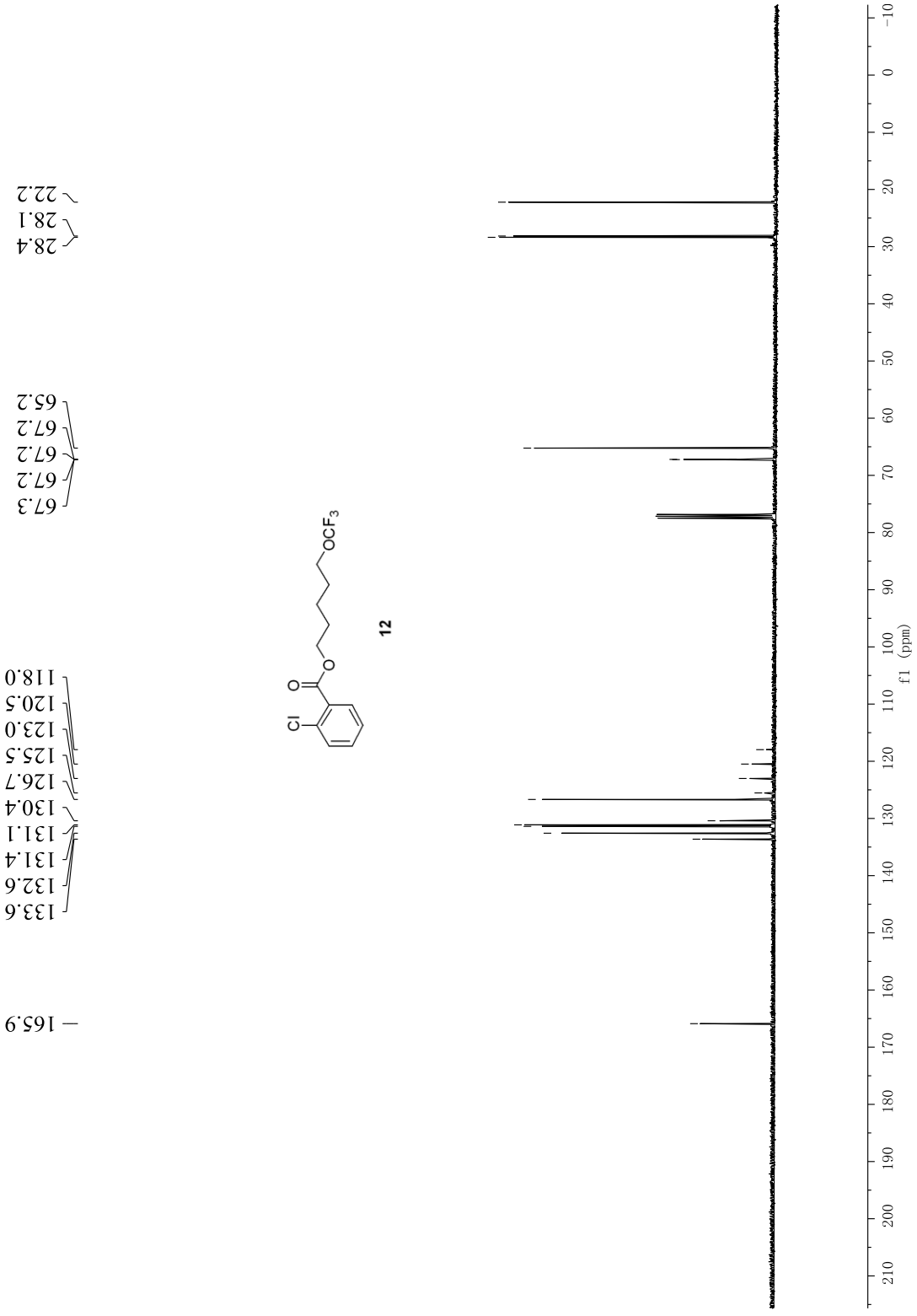
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **11**



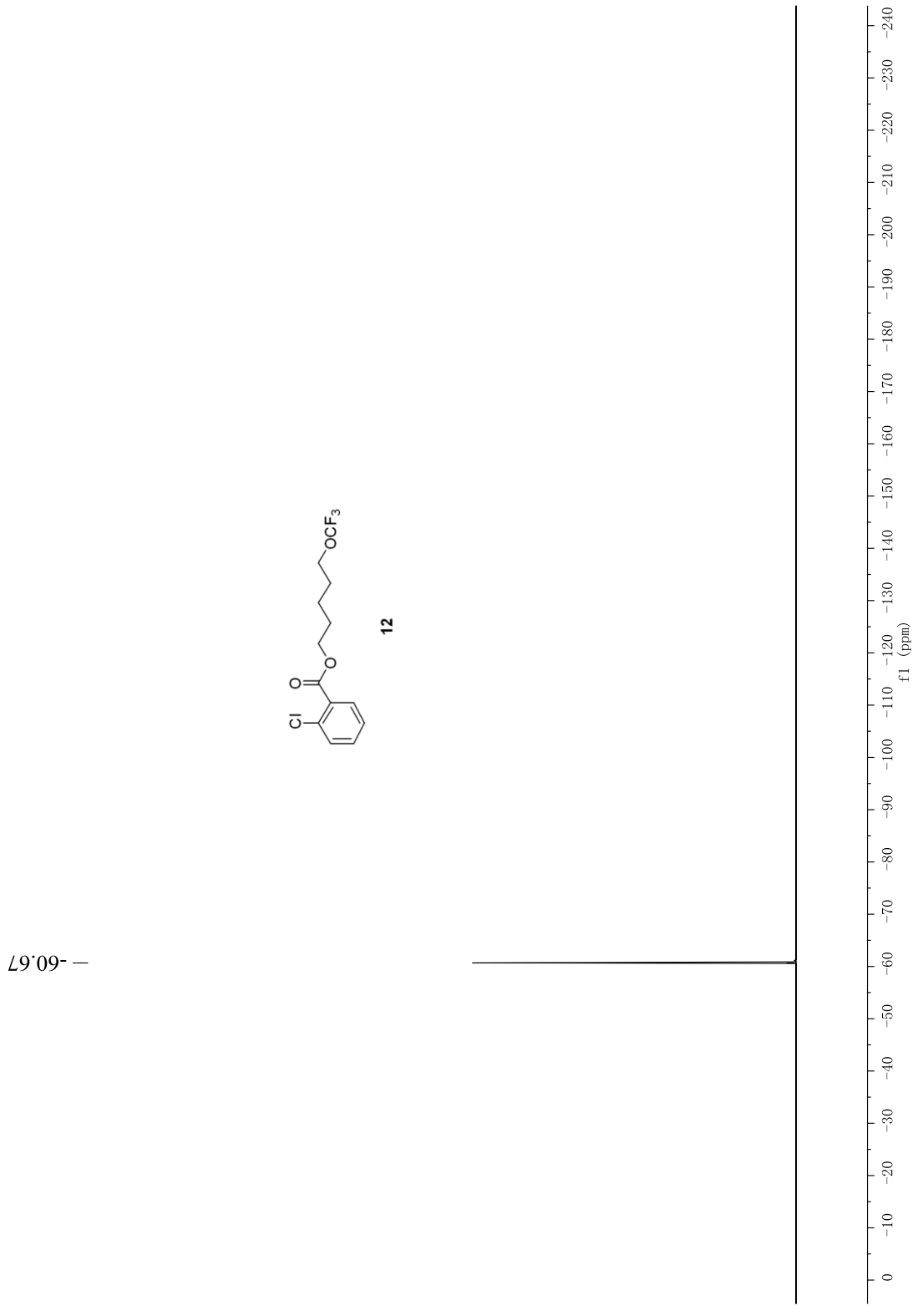
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **11**



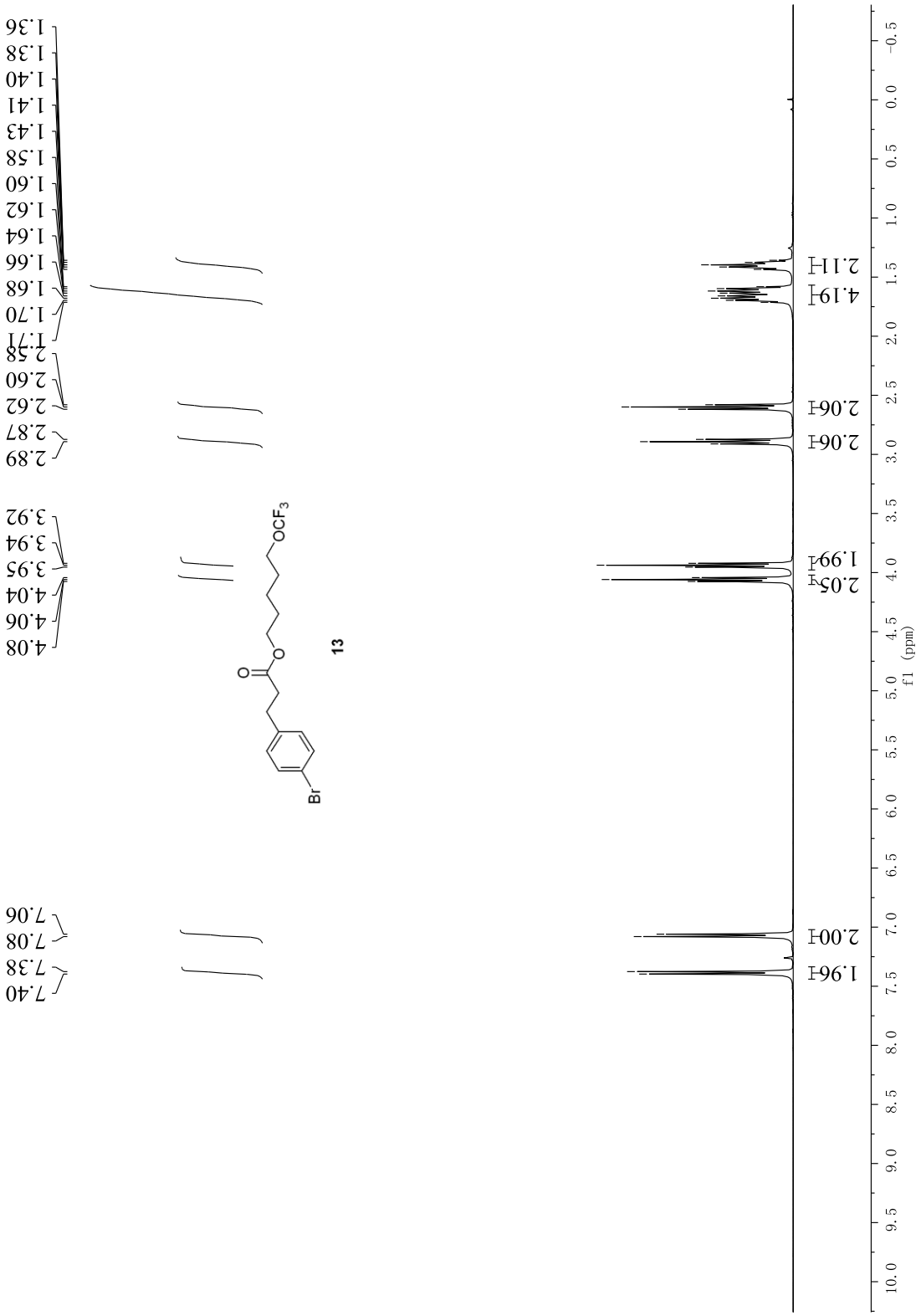
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **12**

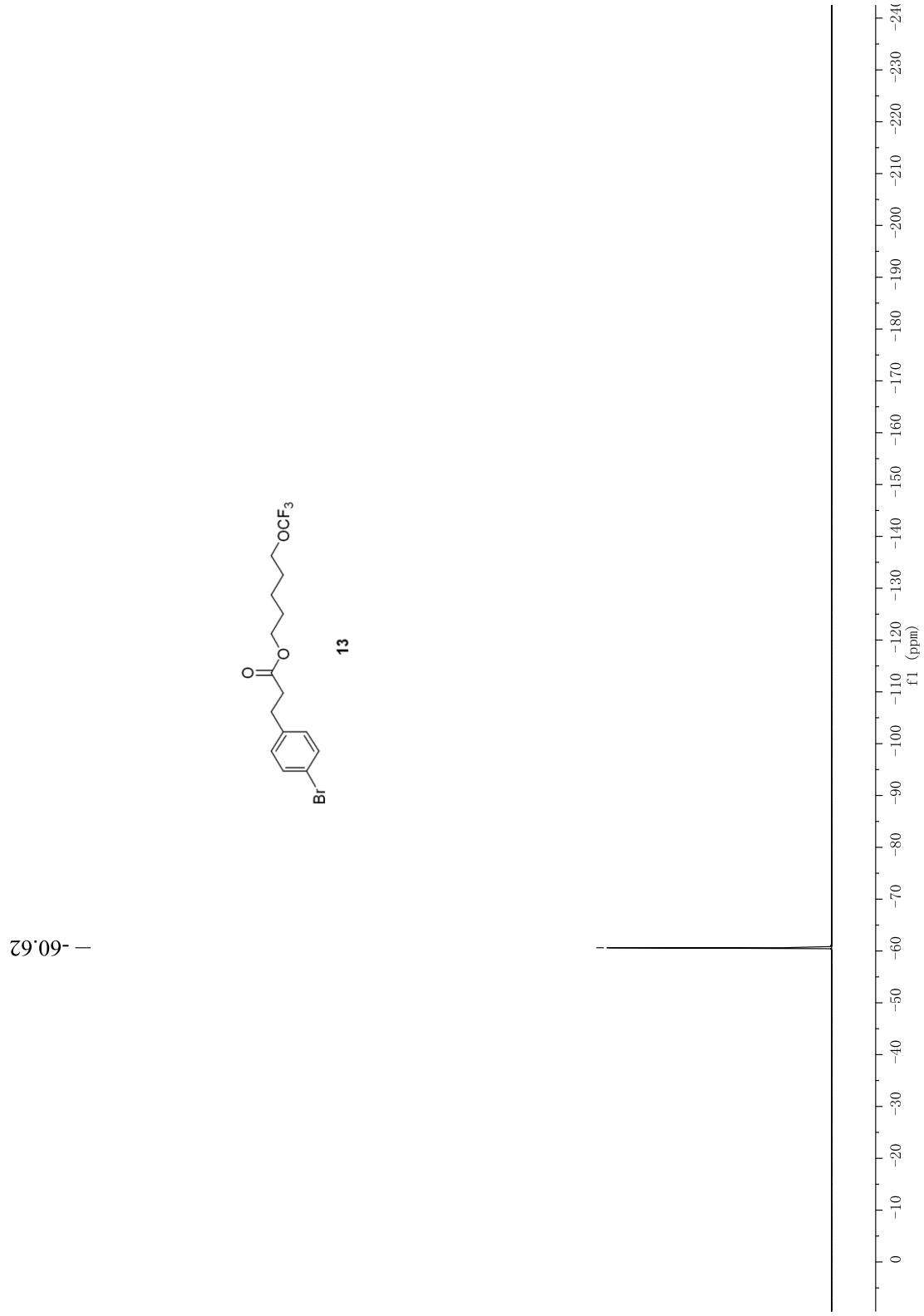


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **12**

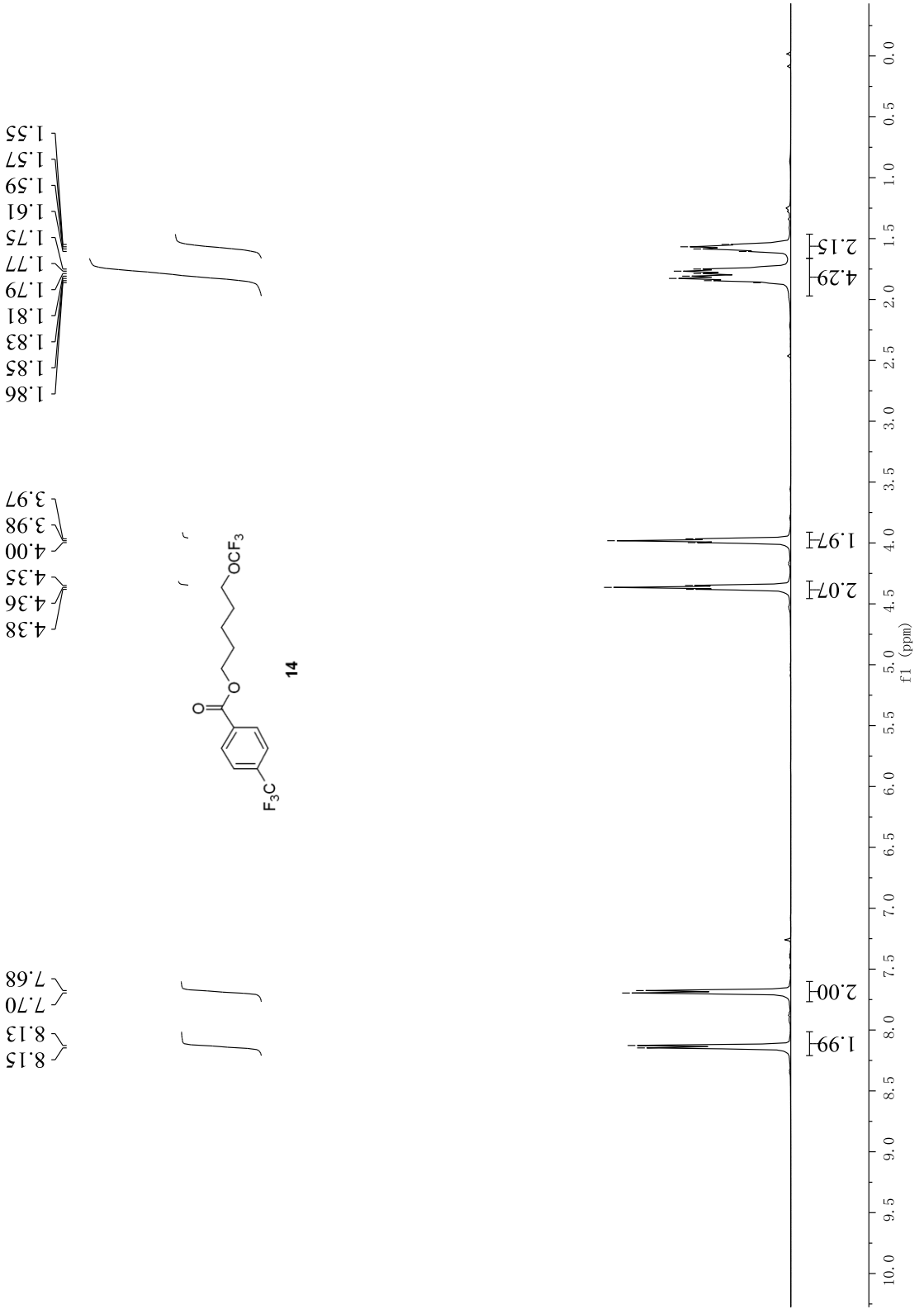


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13**

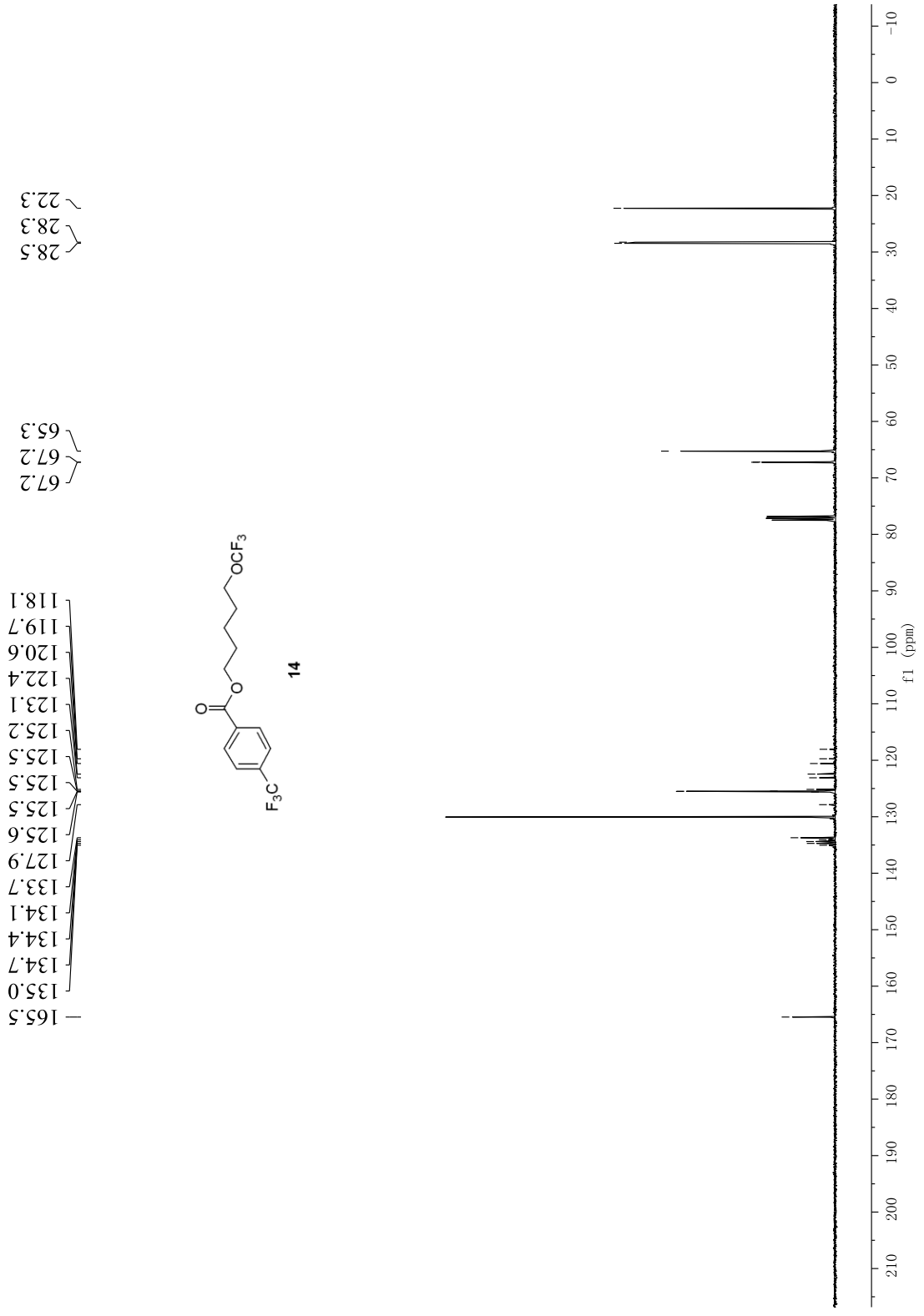
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **13**



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

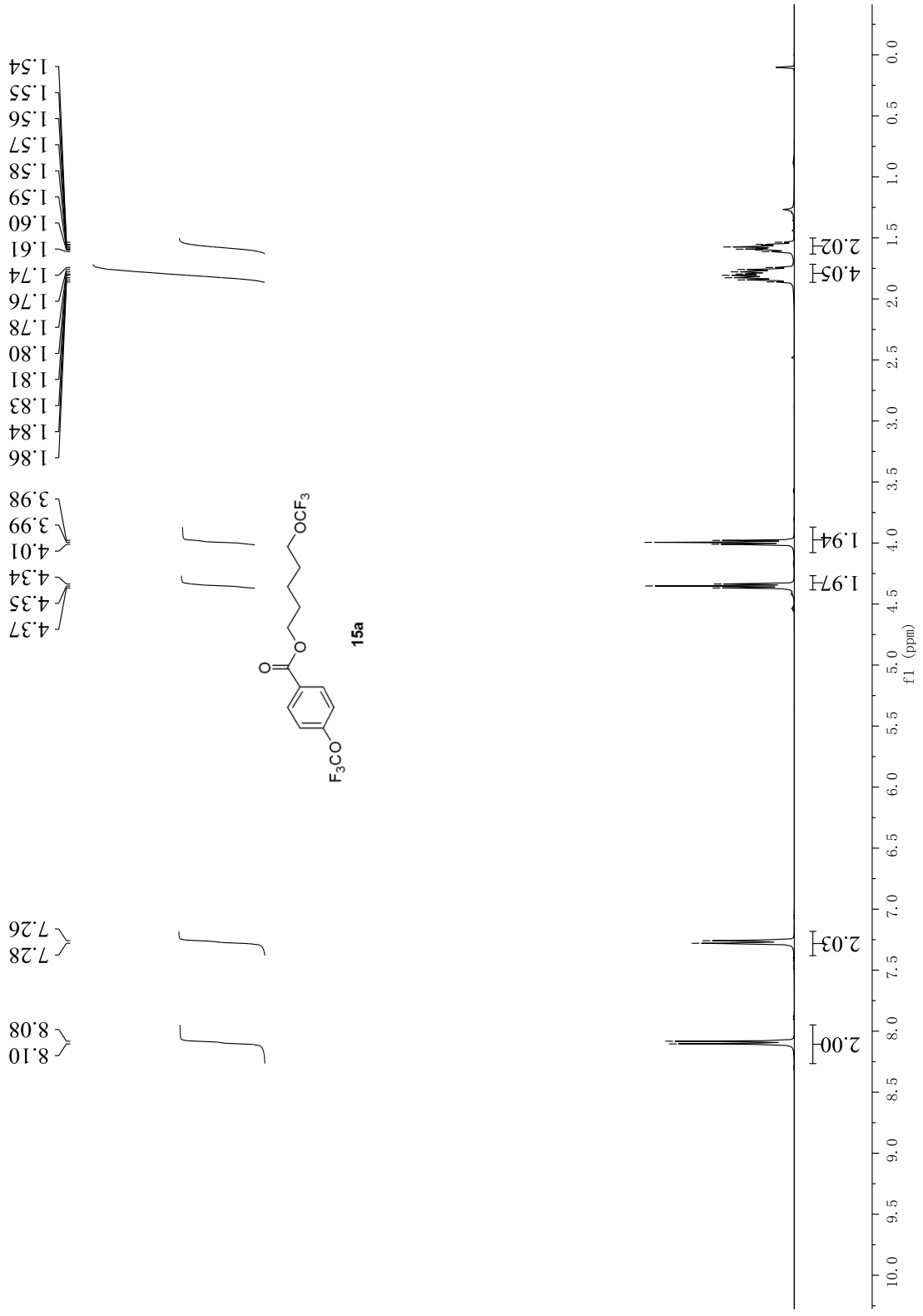


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14**

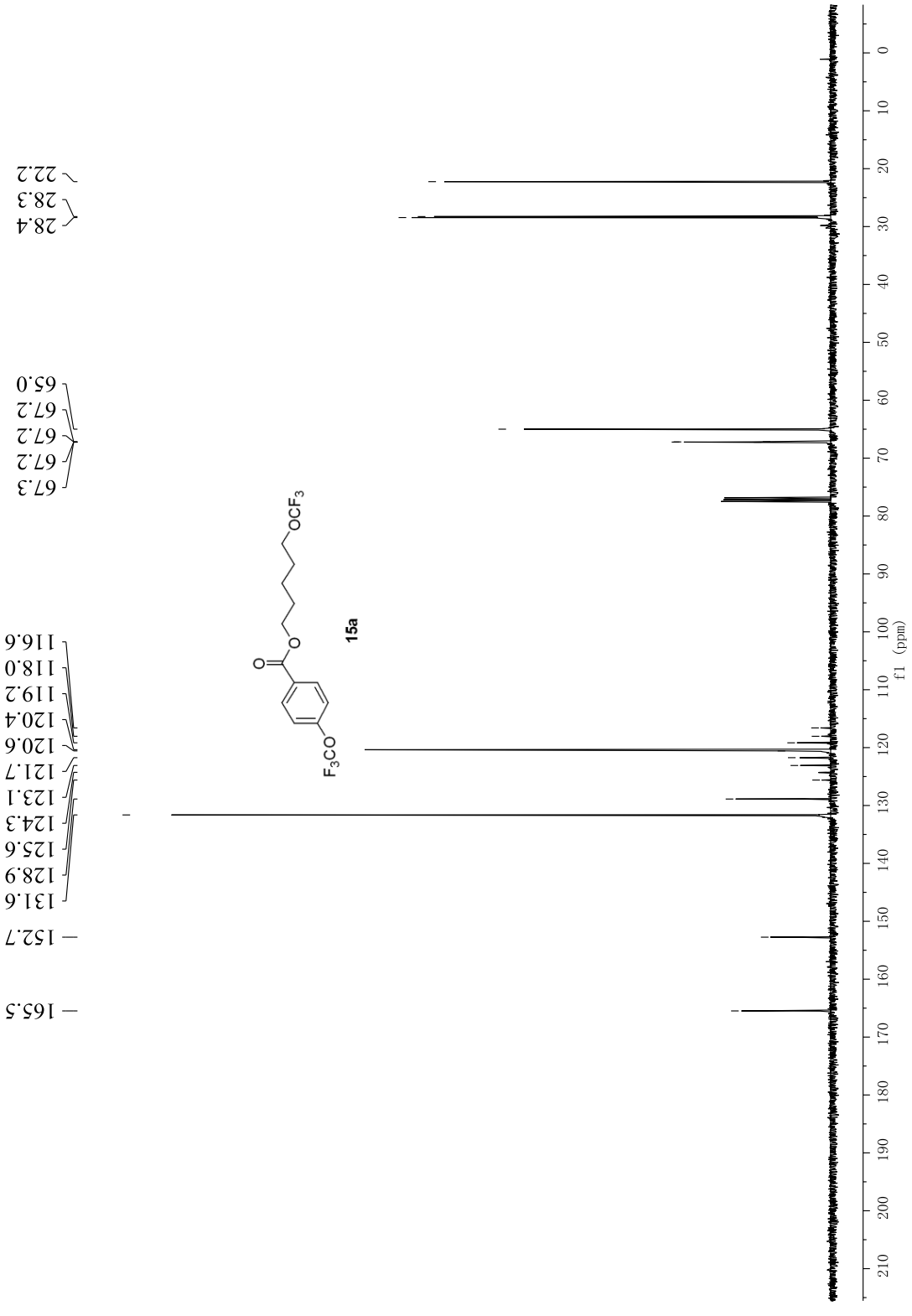


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **14**

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

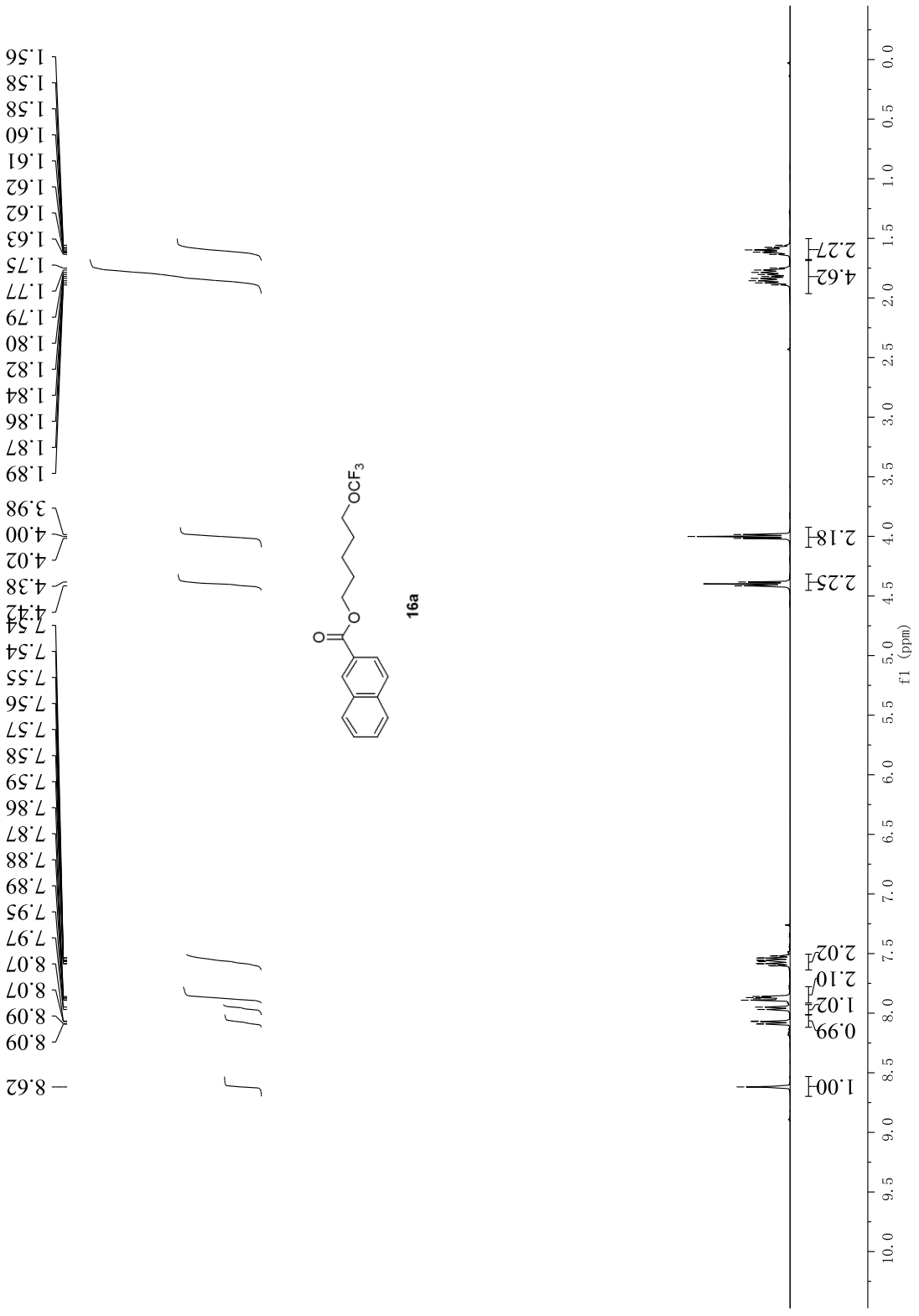


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **15a**

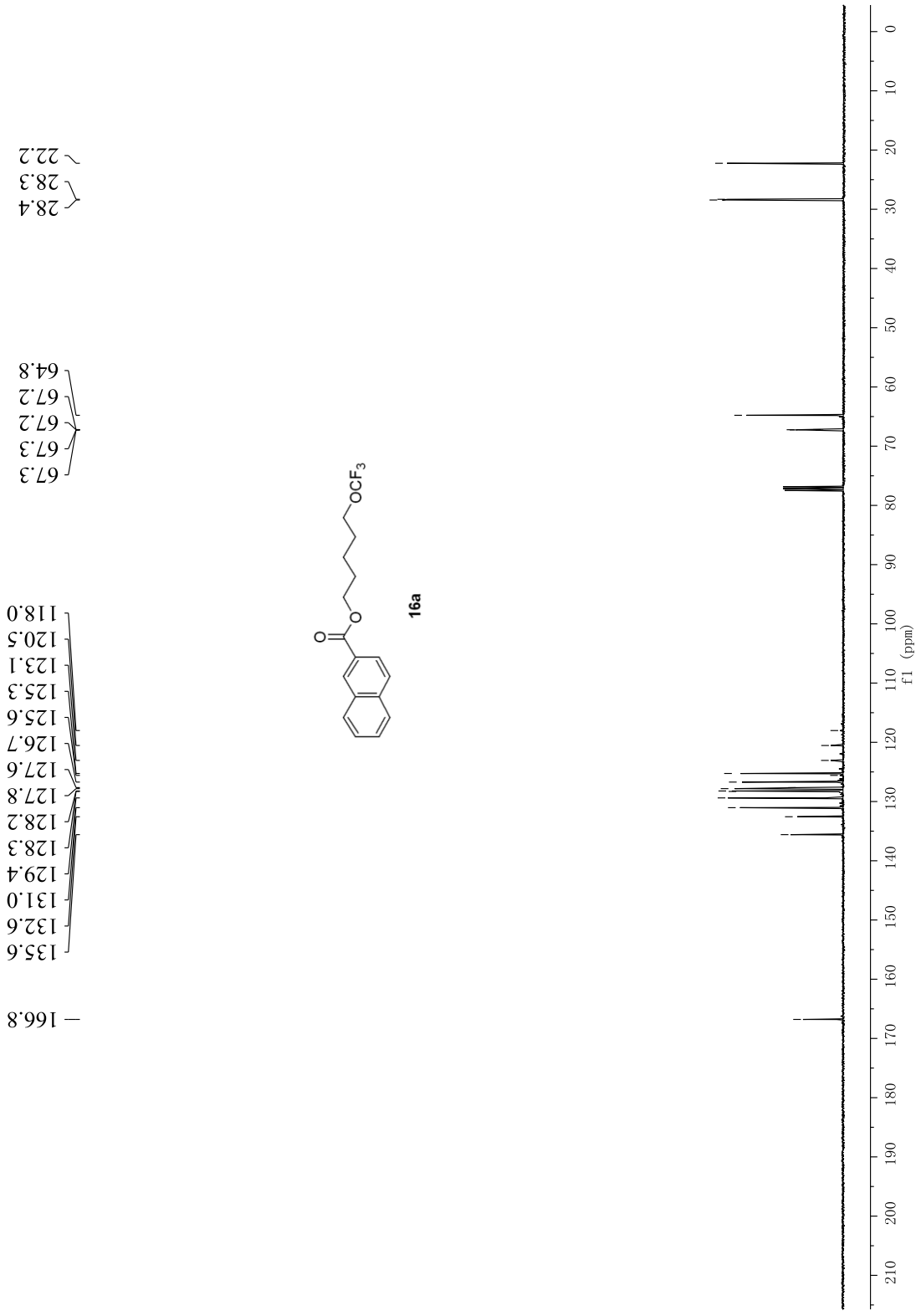


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **15a**

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

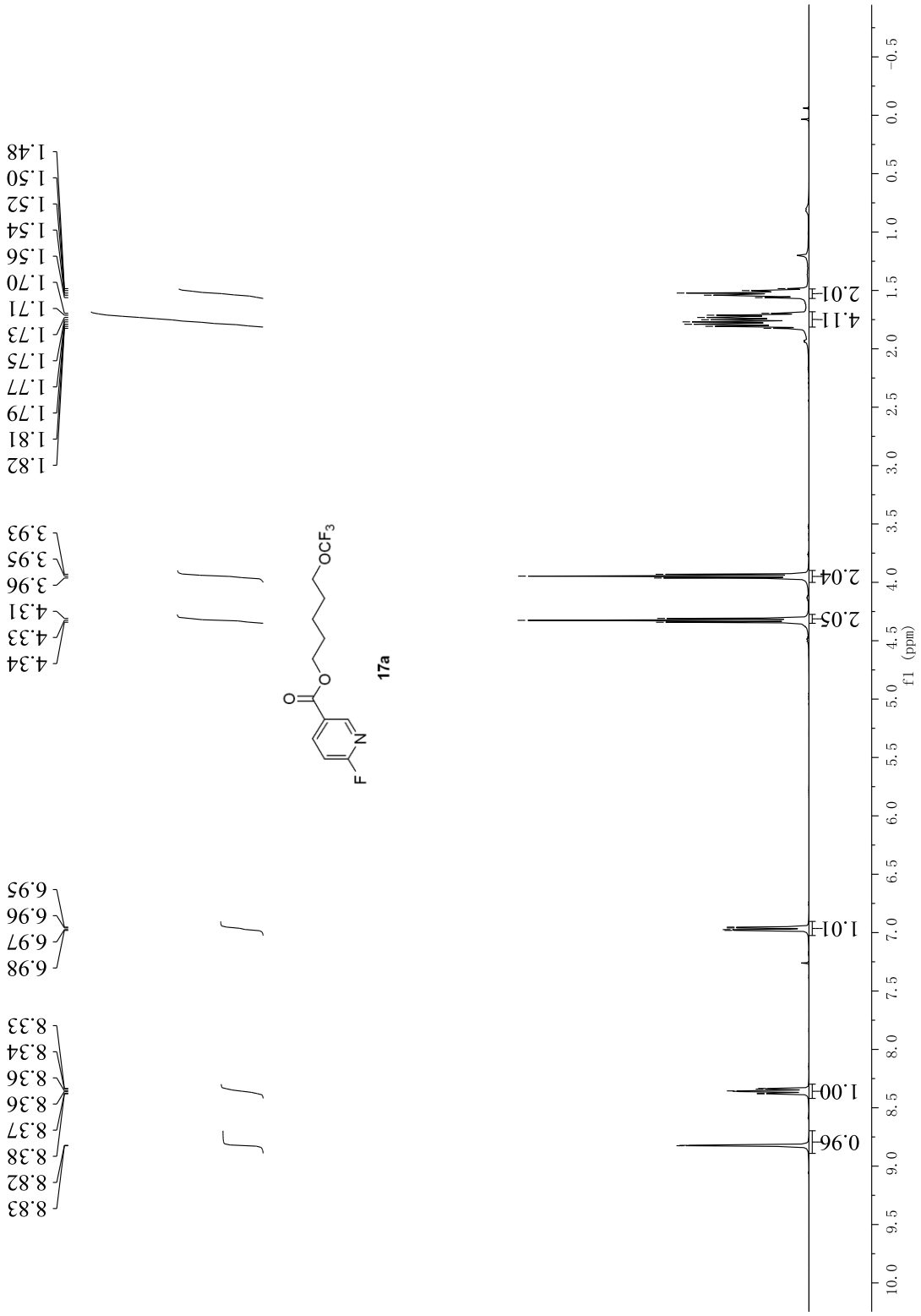


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16a**

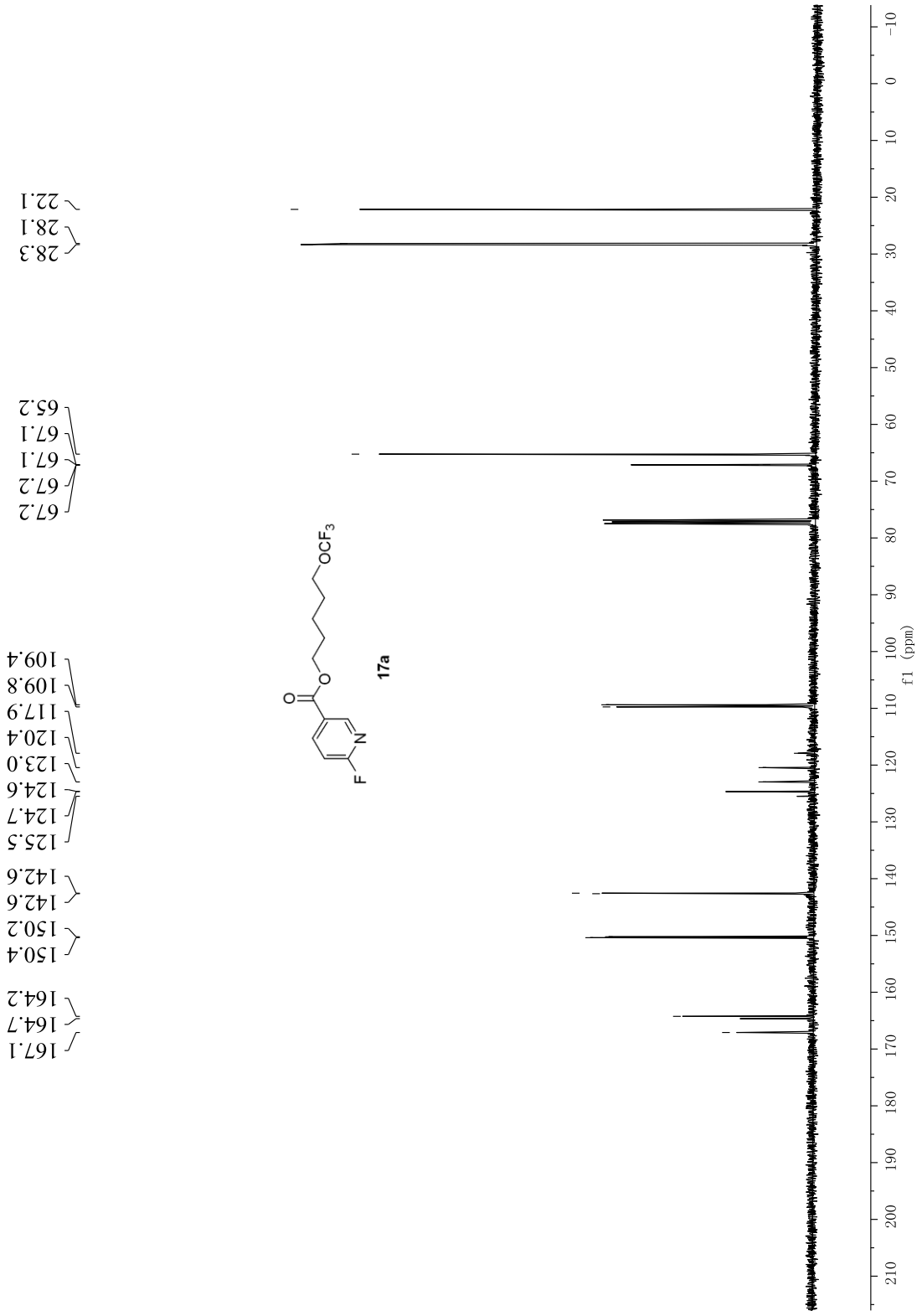


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16a**

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

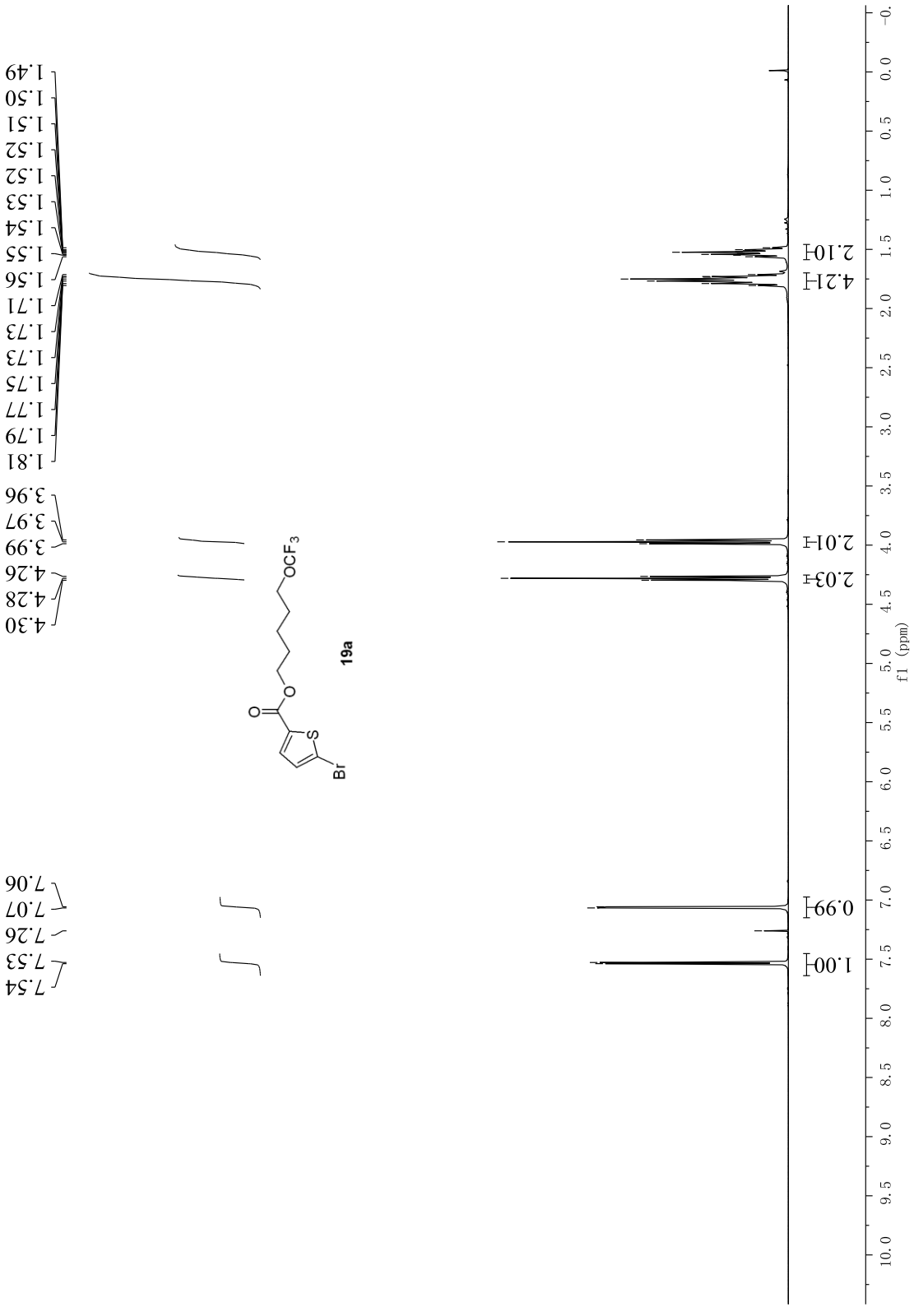


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **17a**

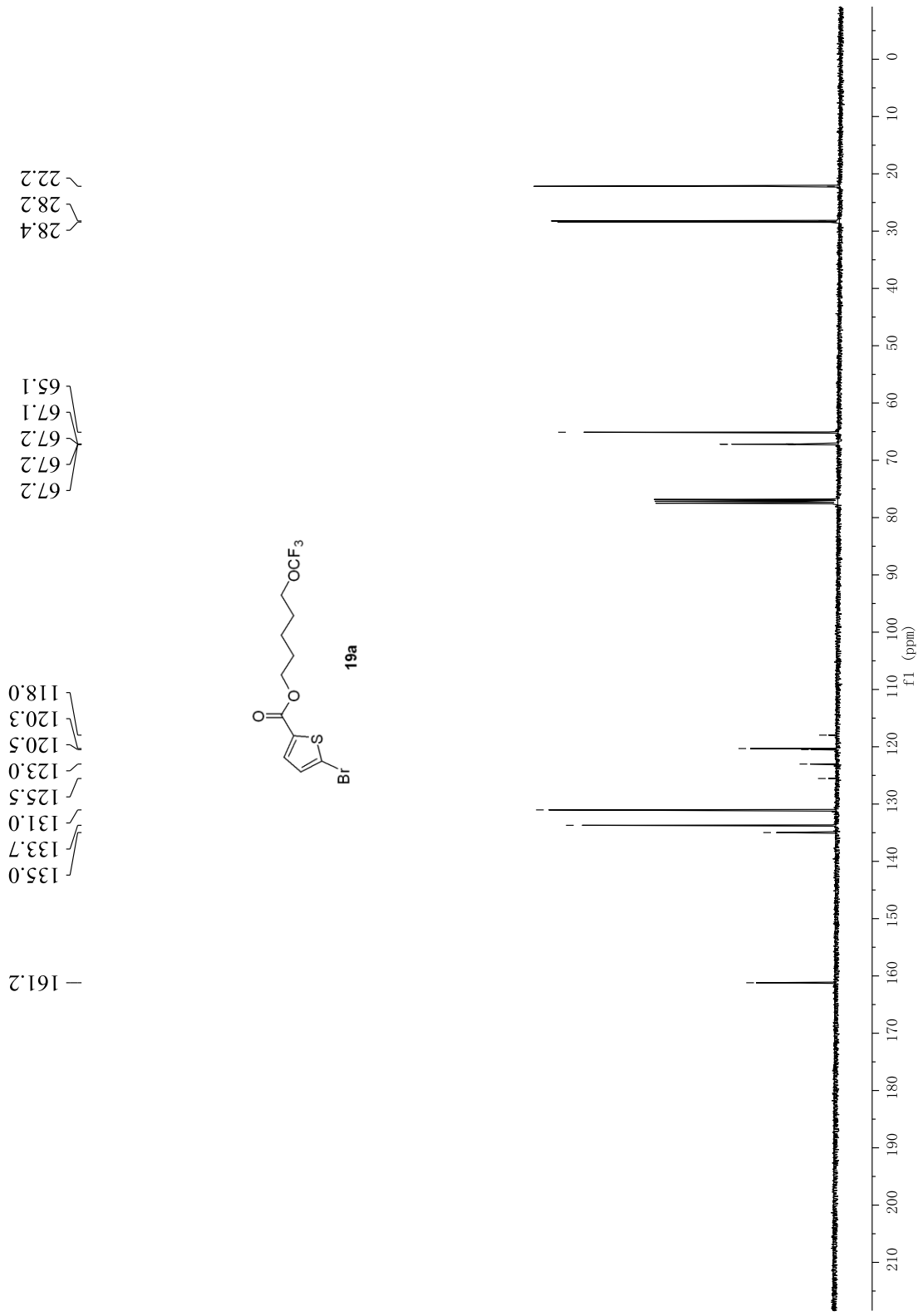


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **17a**

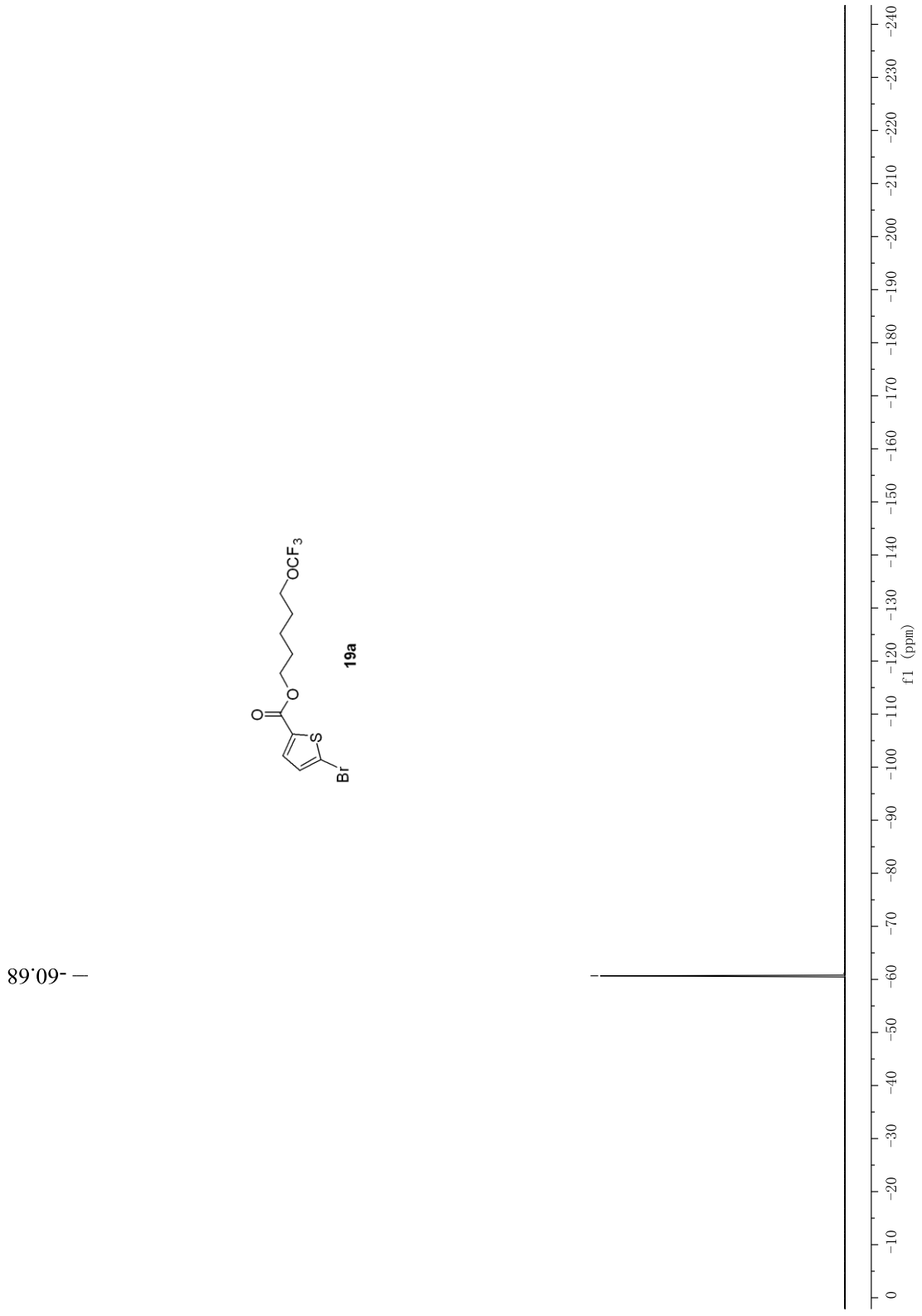
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **17a**



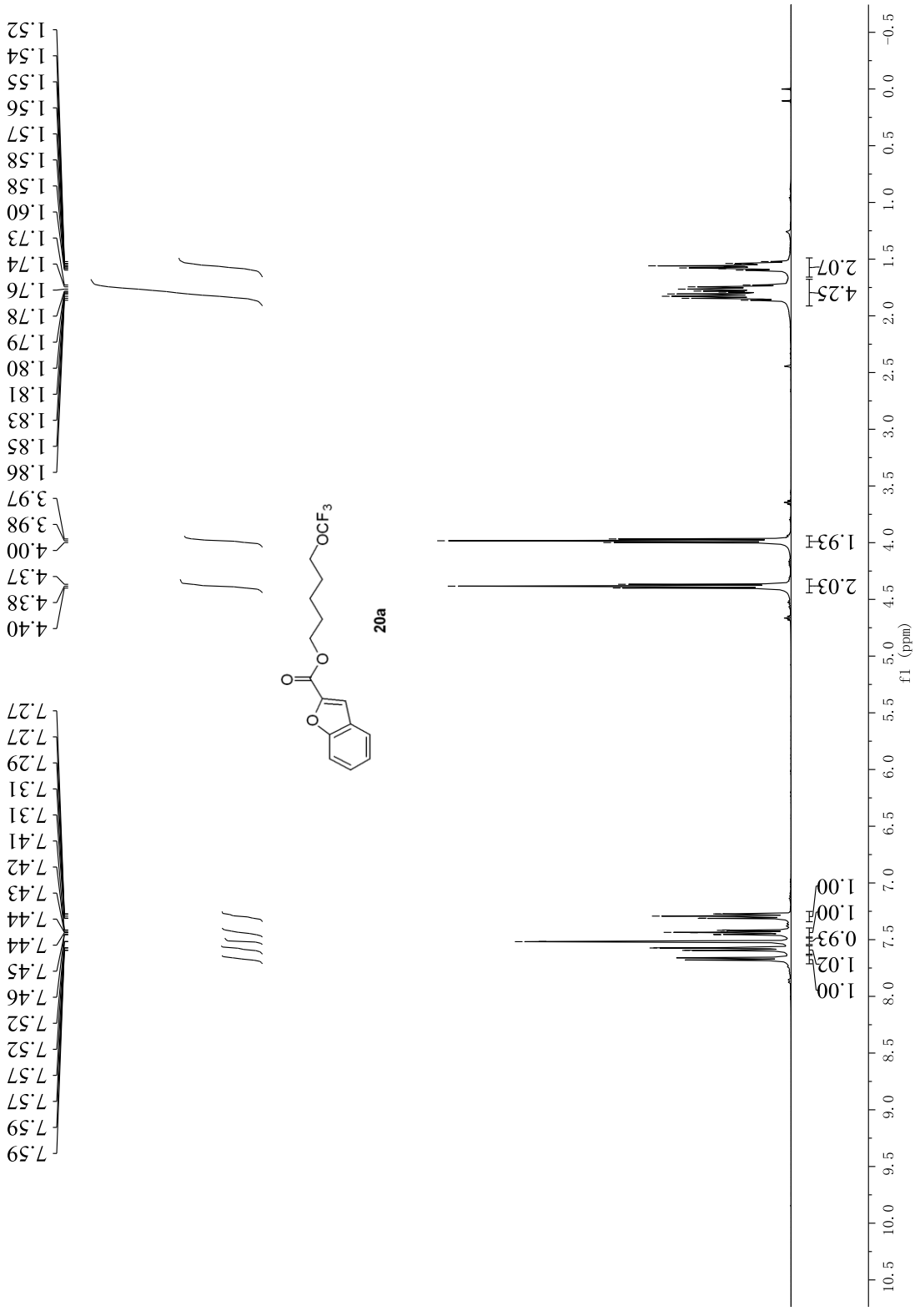
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **19a**



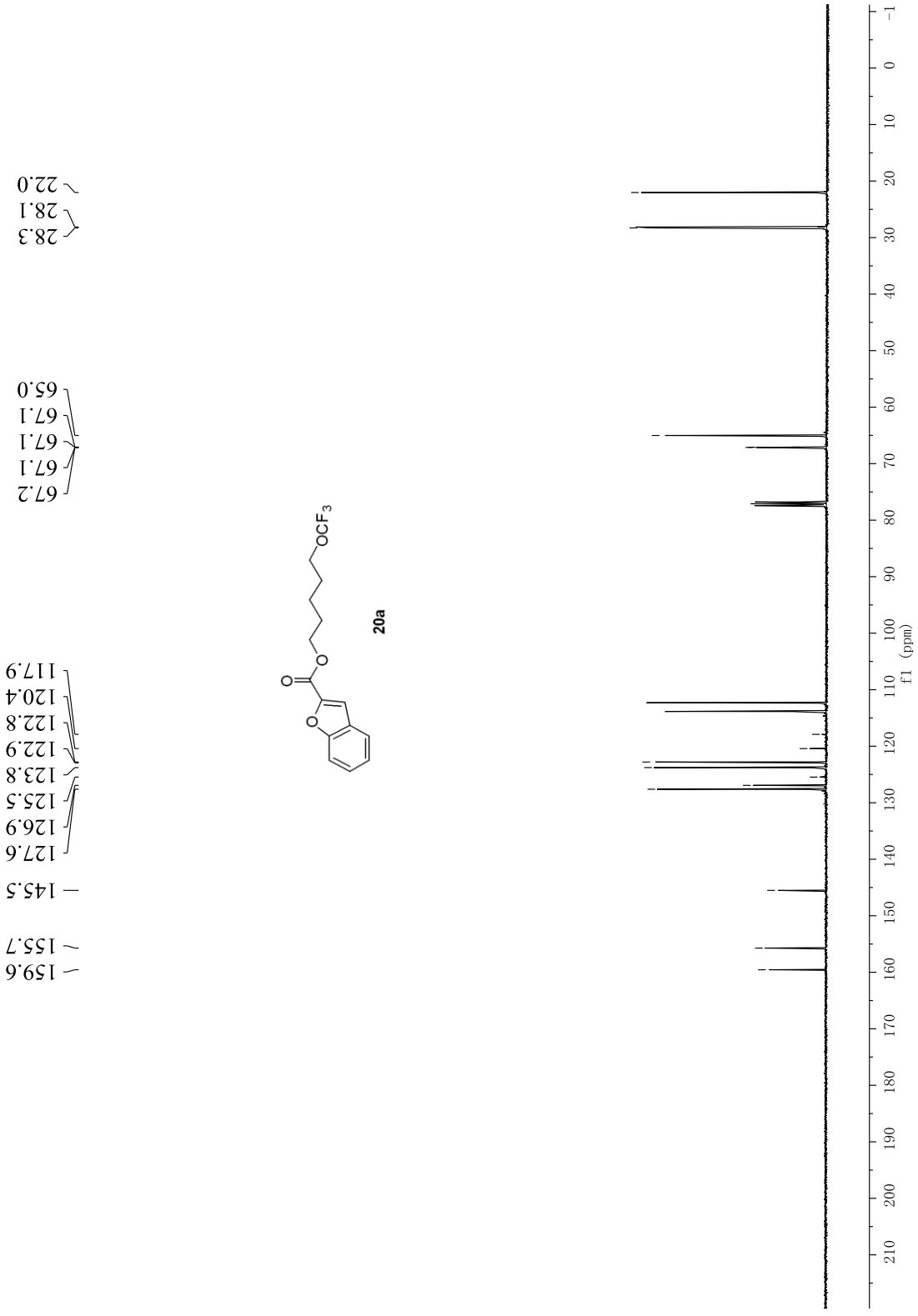
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **19a**



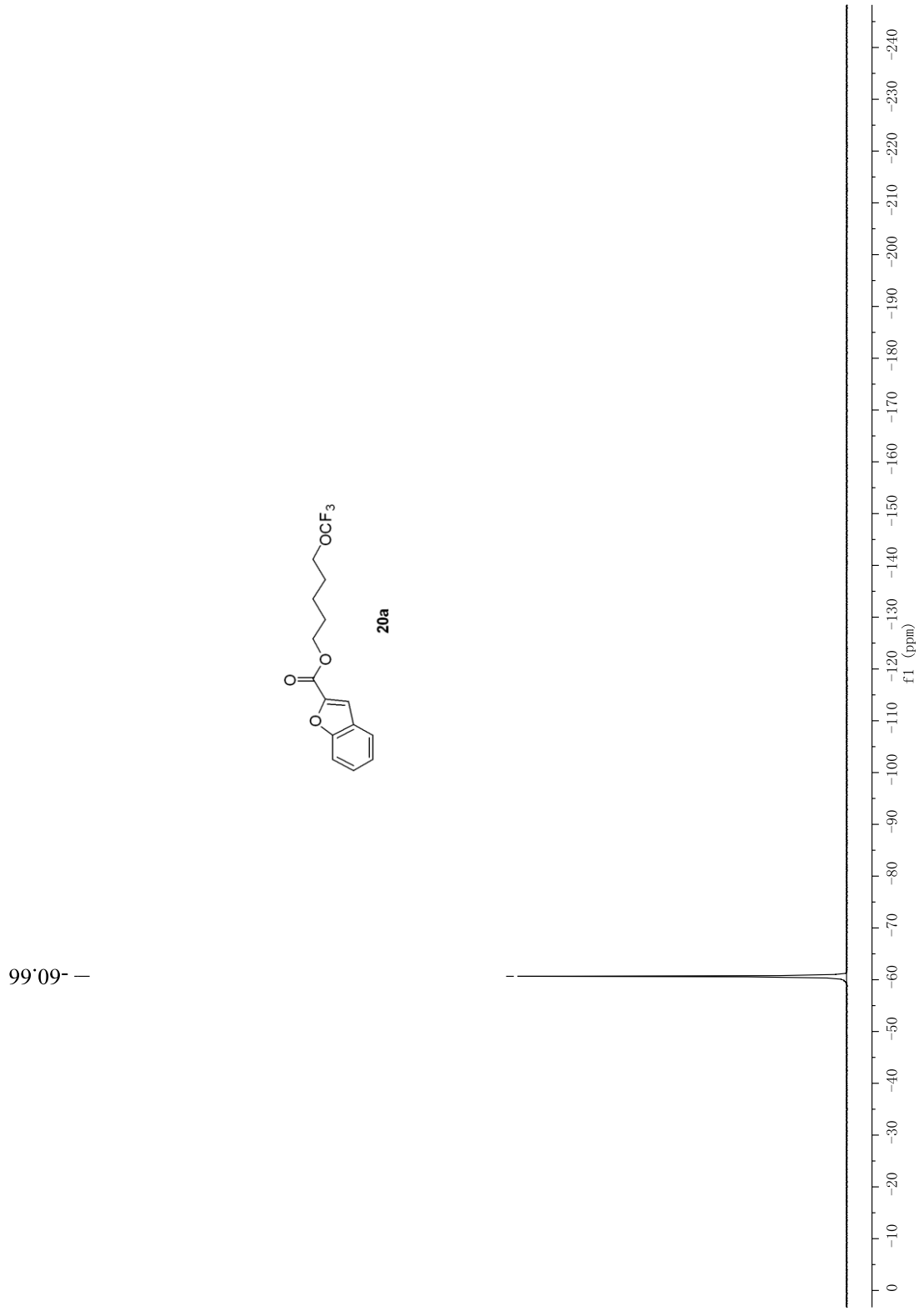
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **19a**



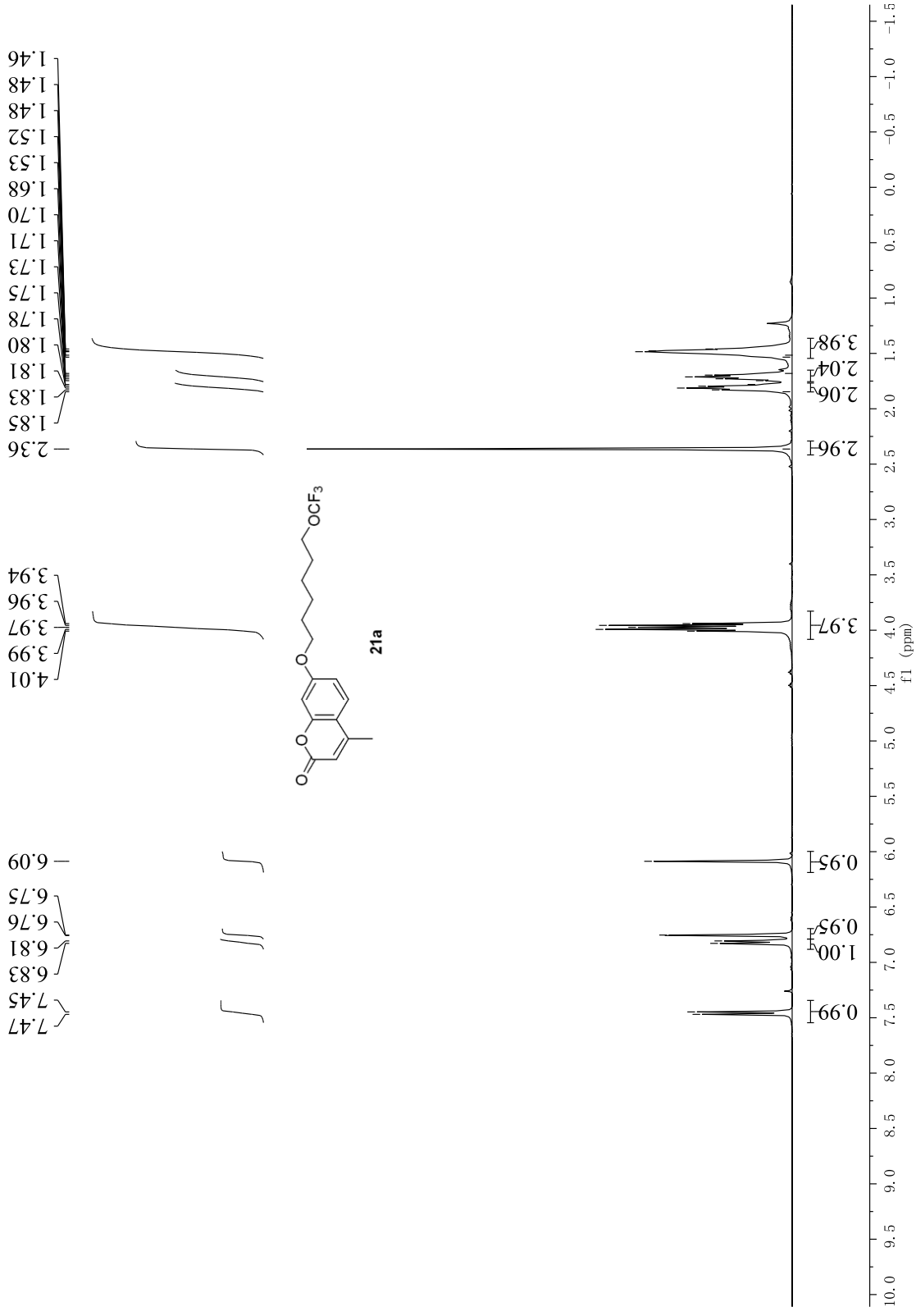
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20a**



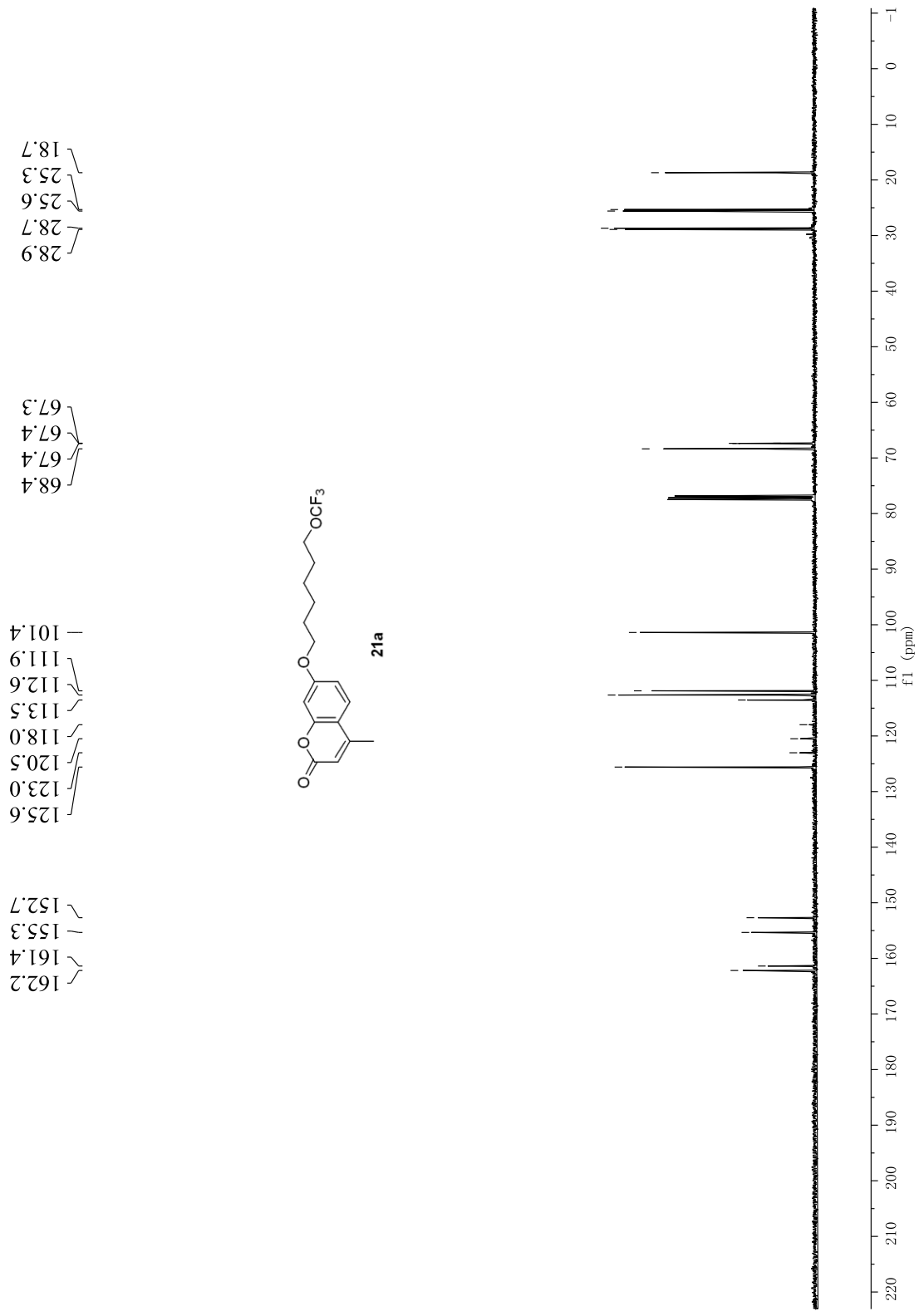
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **20a**



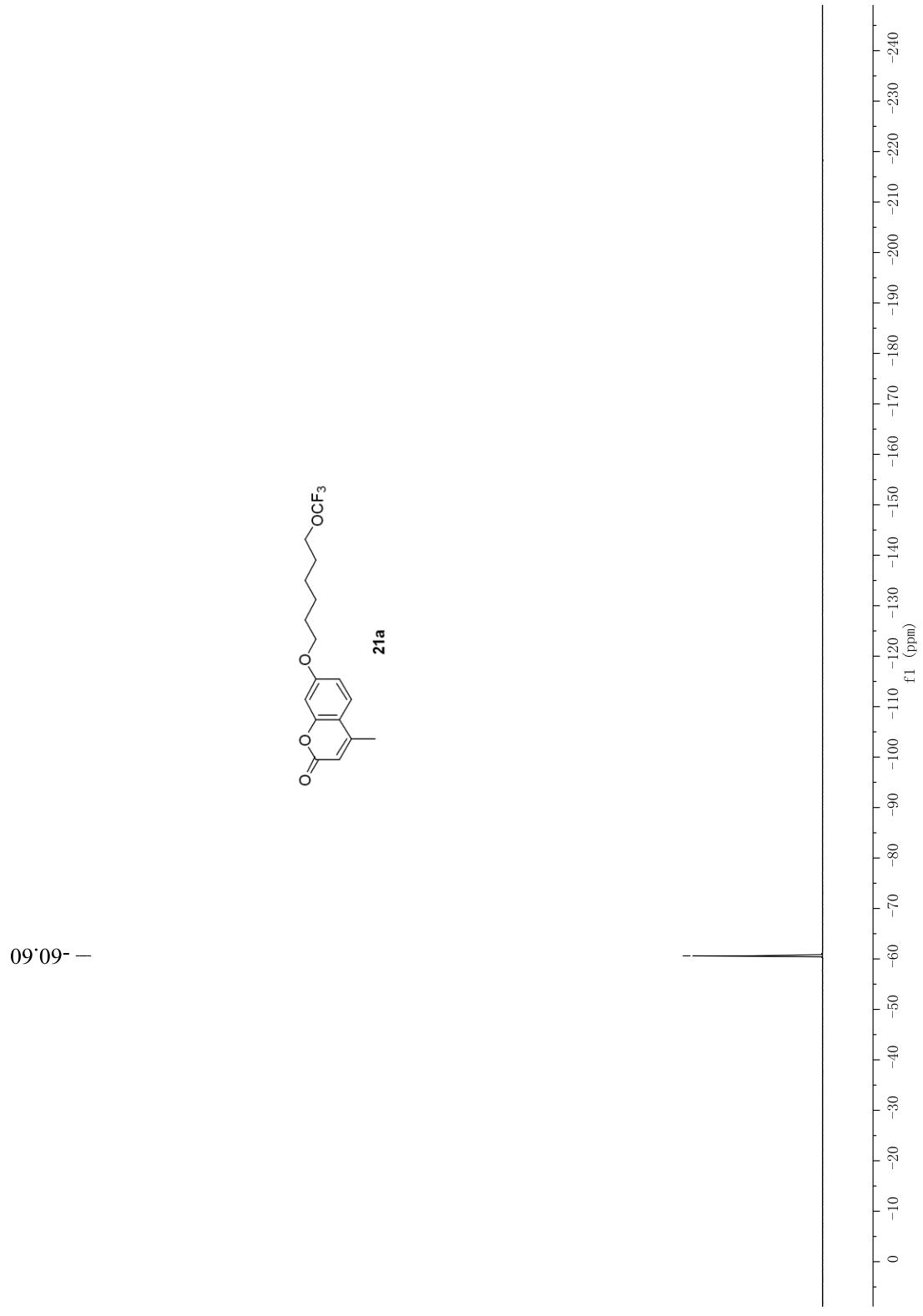
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **20a**



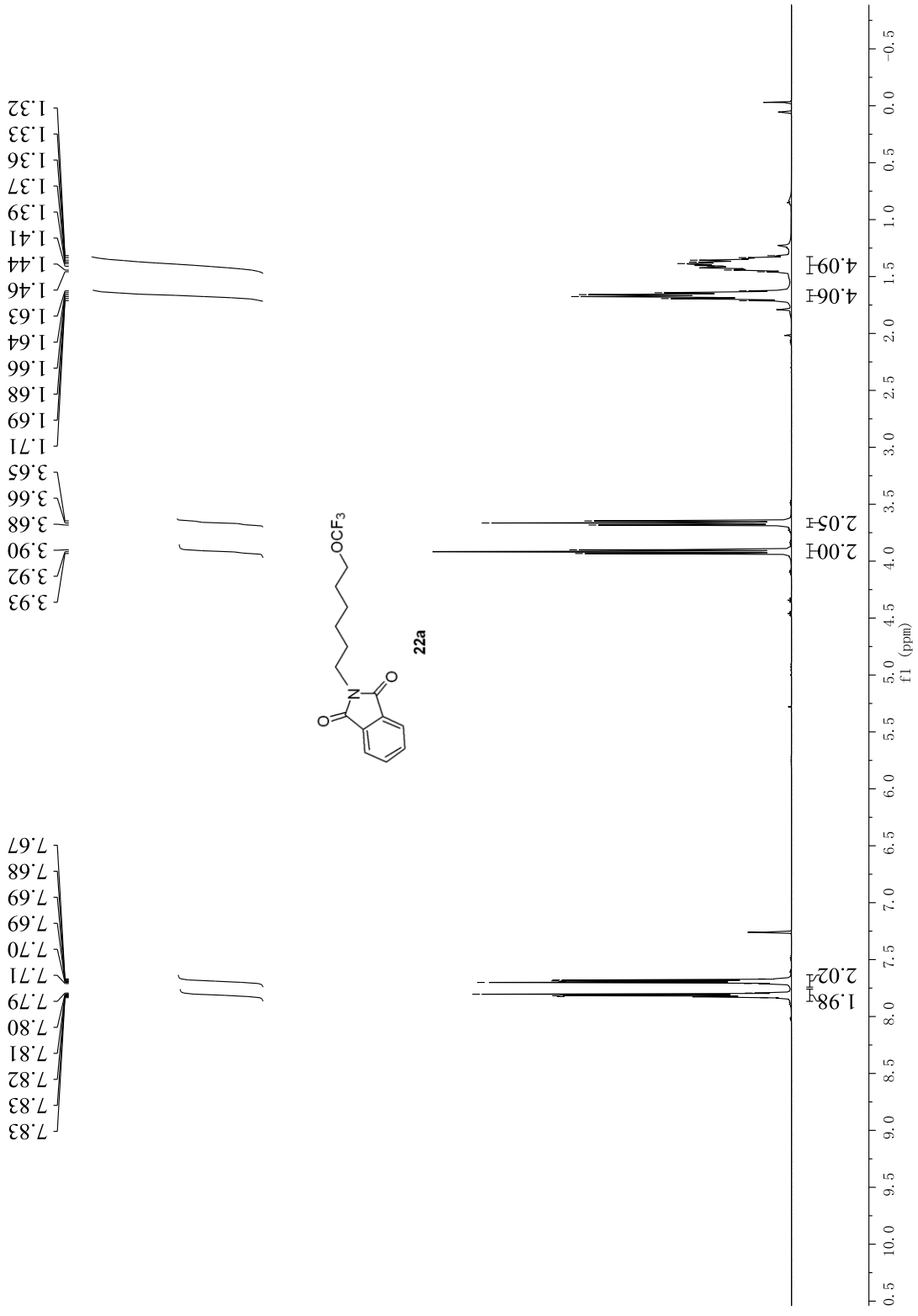
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **21a**



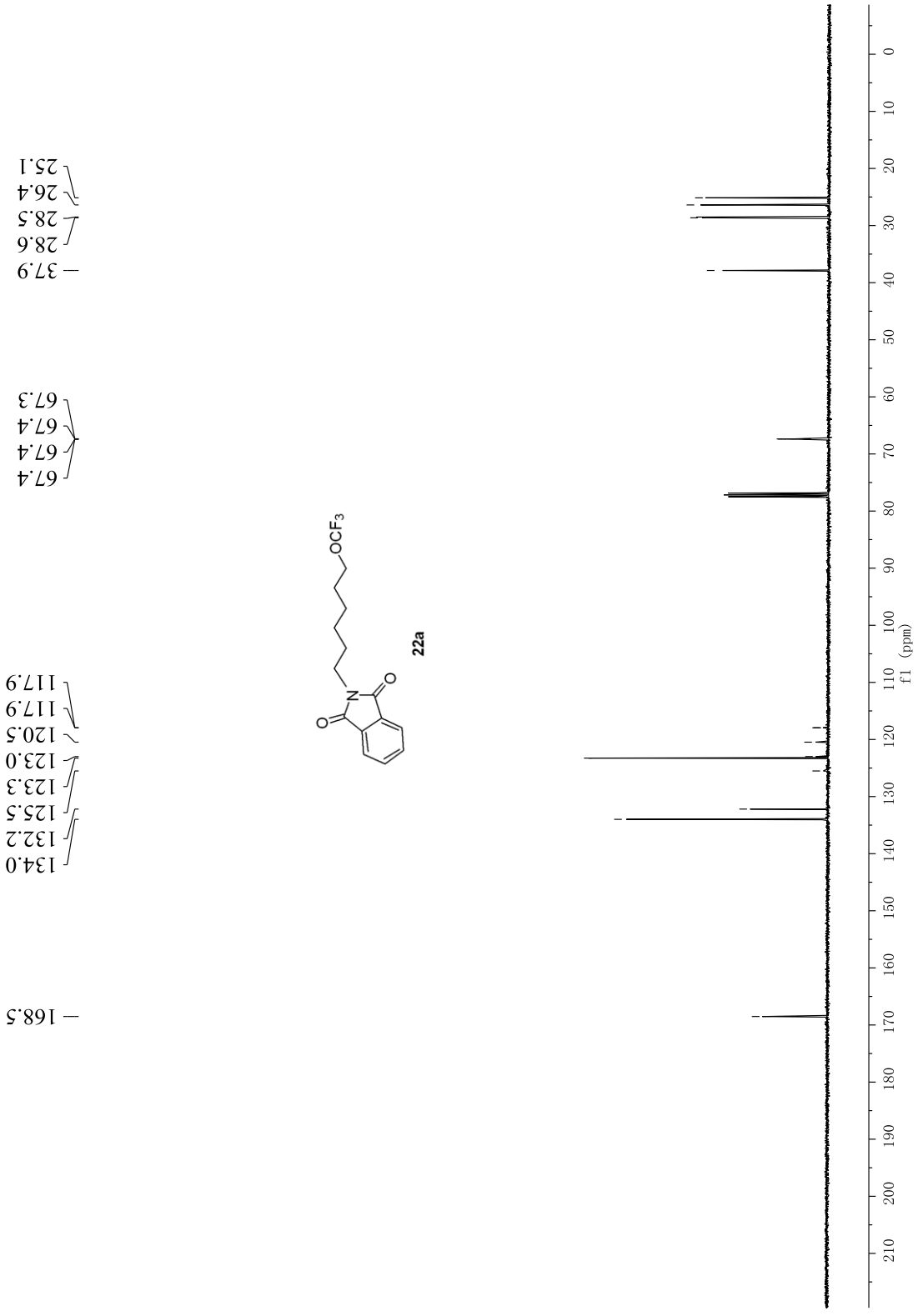
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **21a**



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

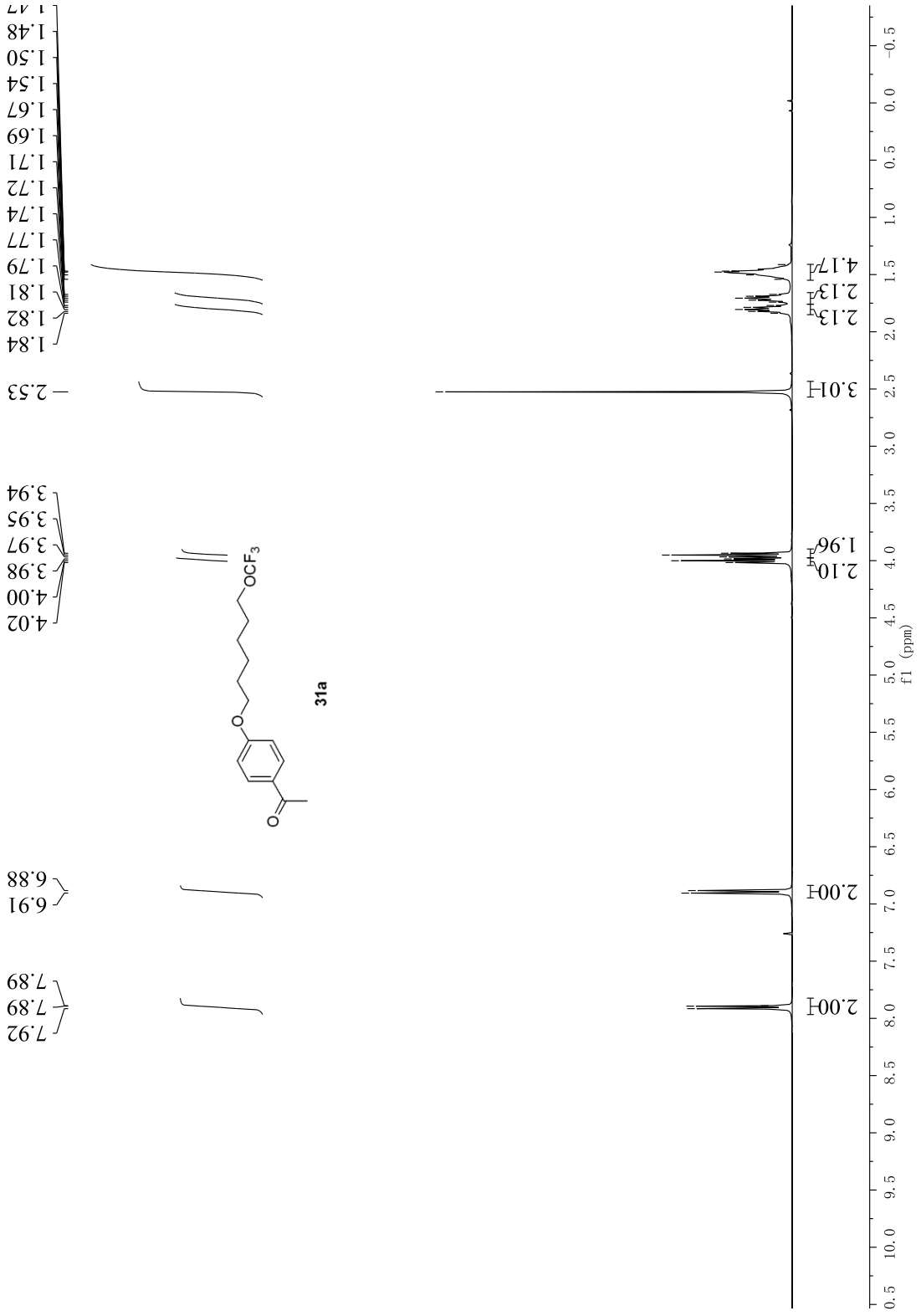


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **22a**

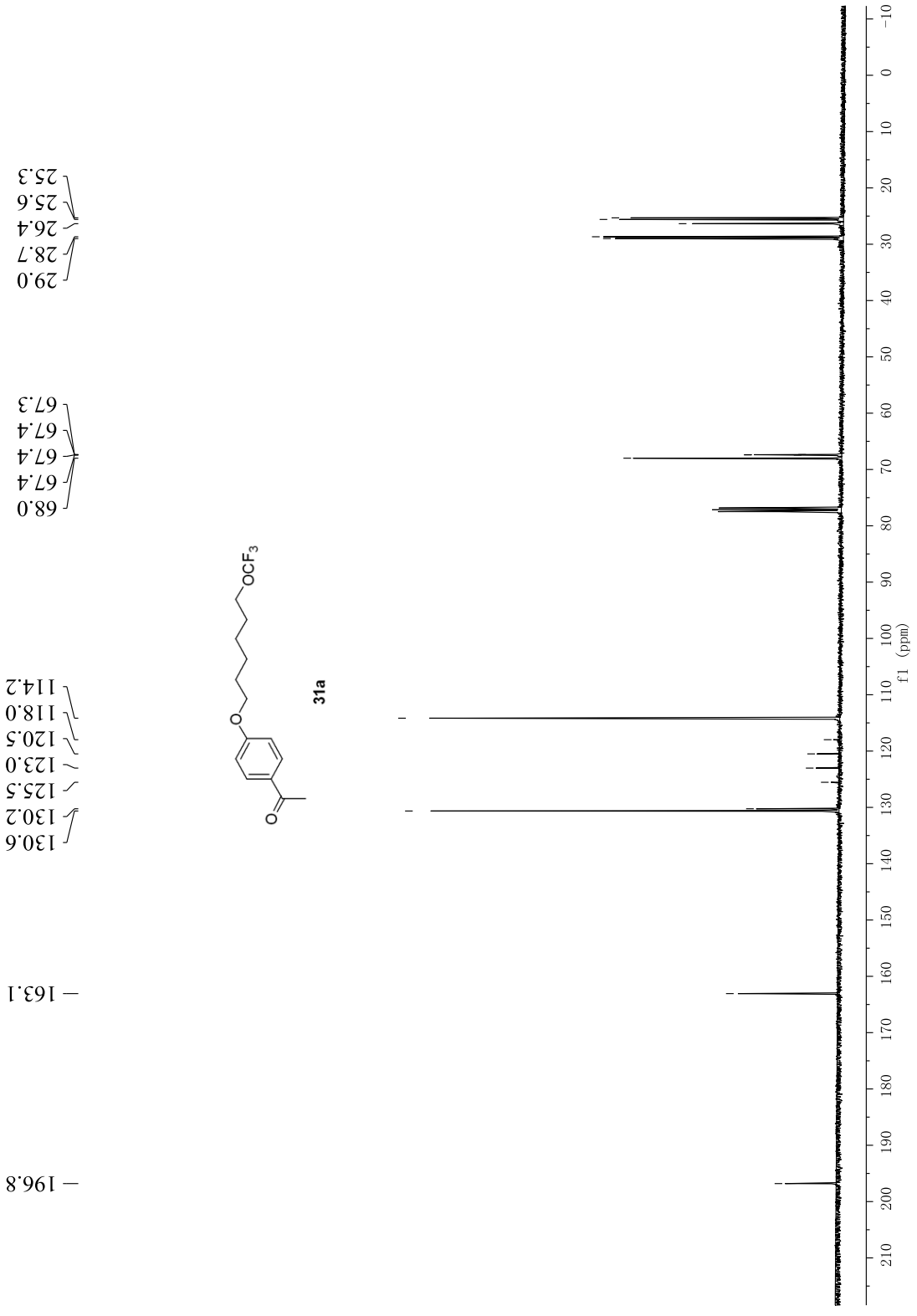


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **22a**

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

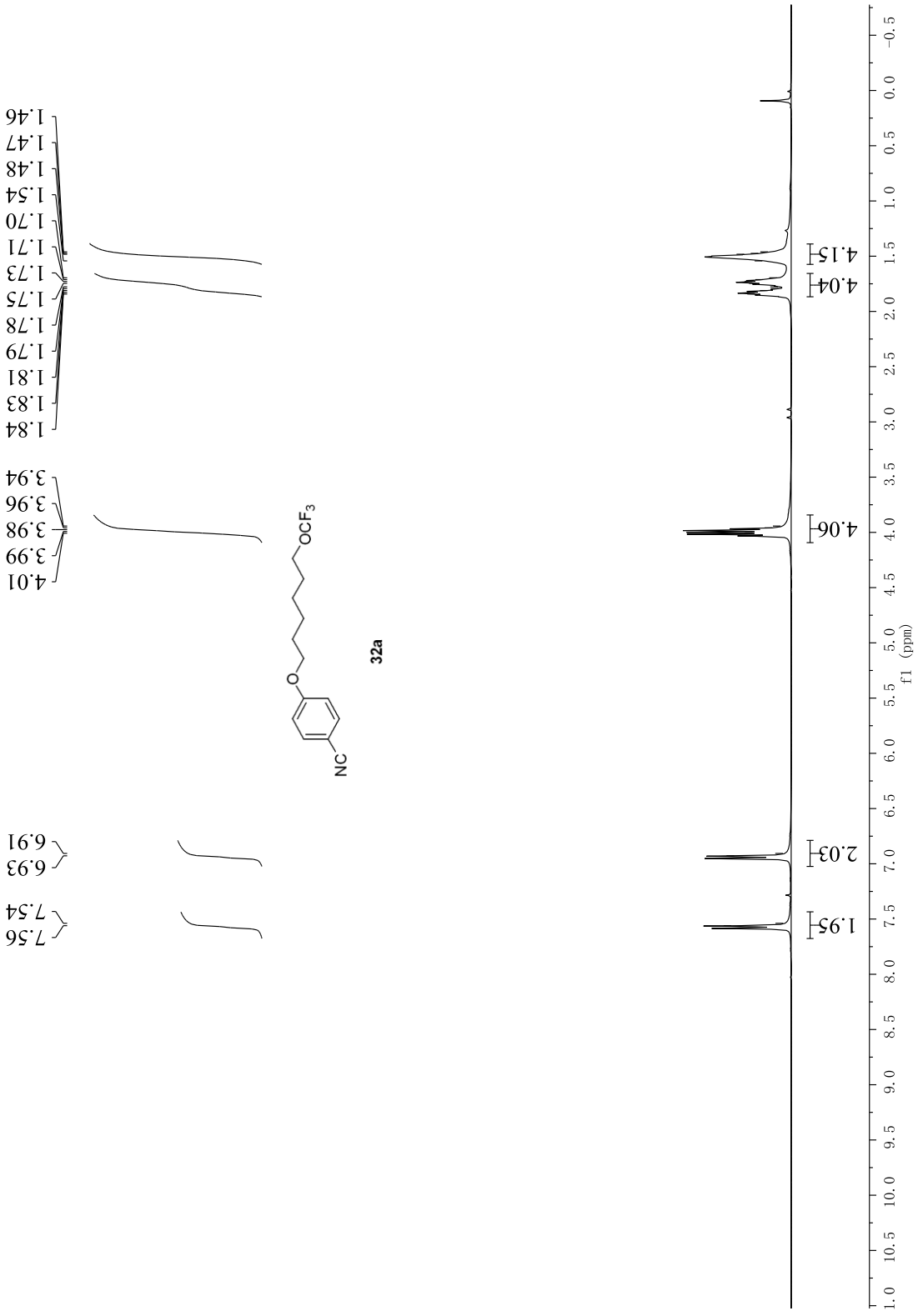


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **31a**

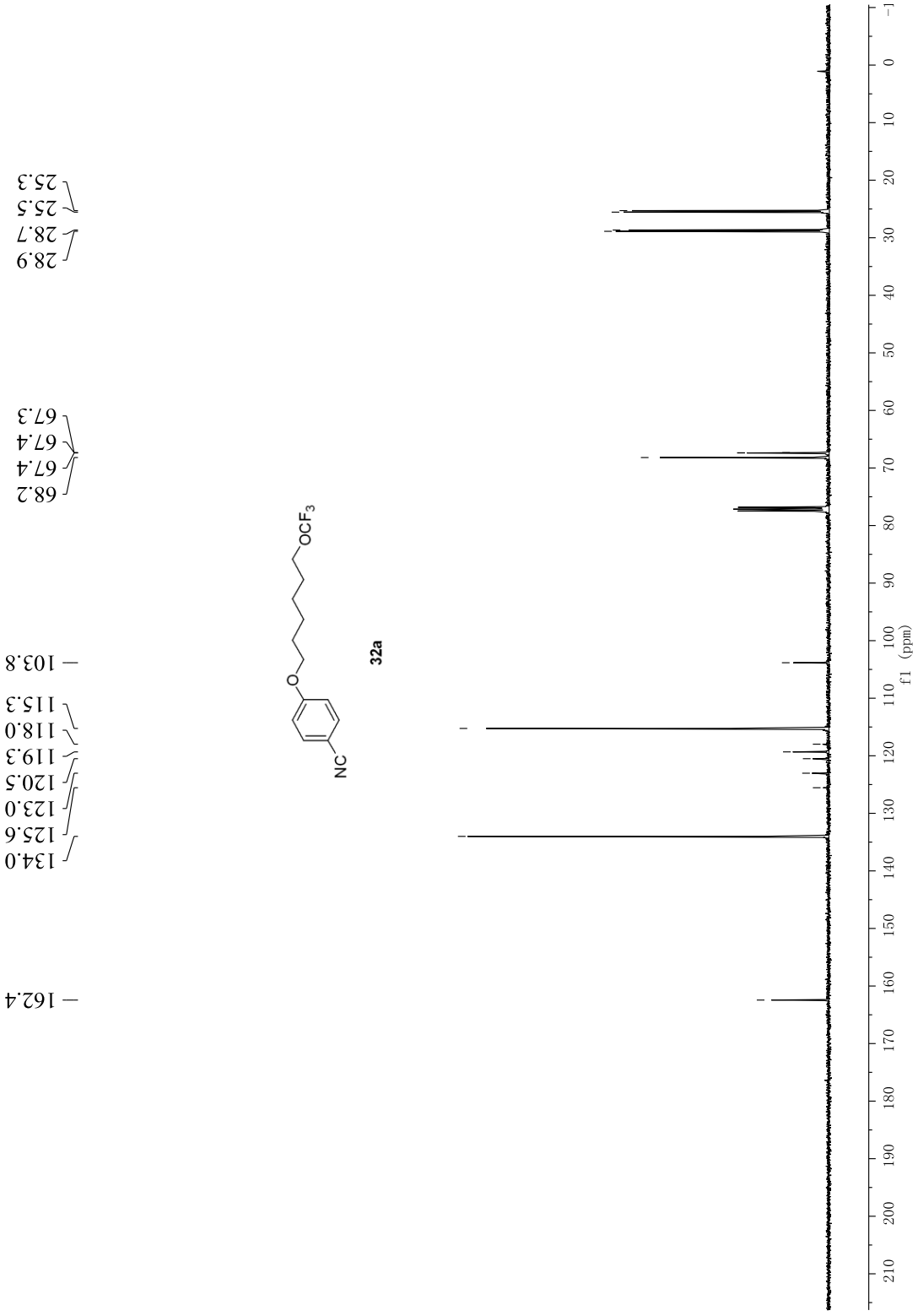


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **31a**

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

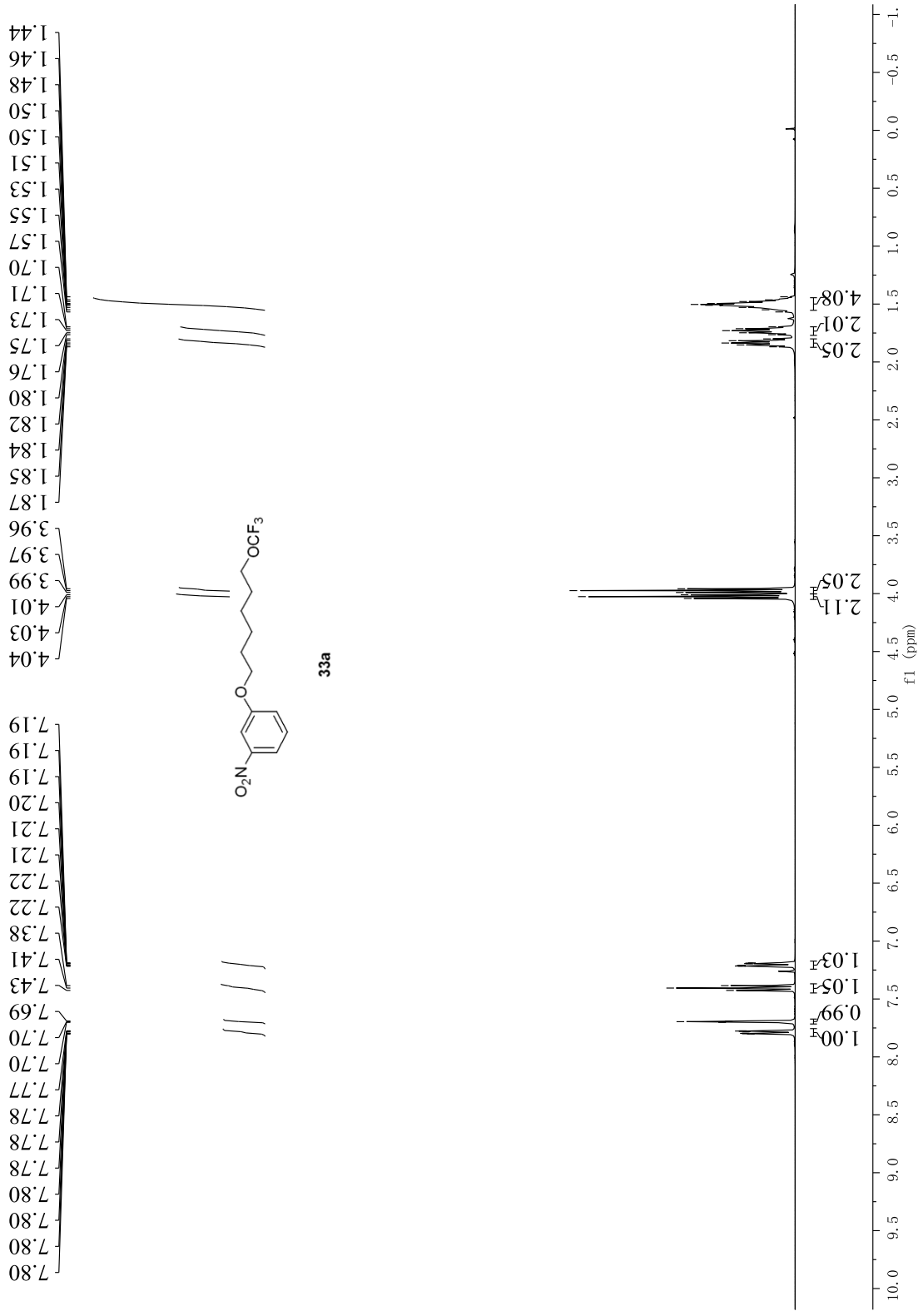


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **32a**

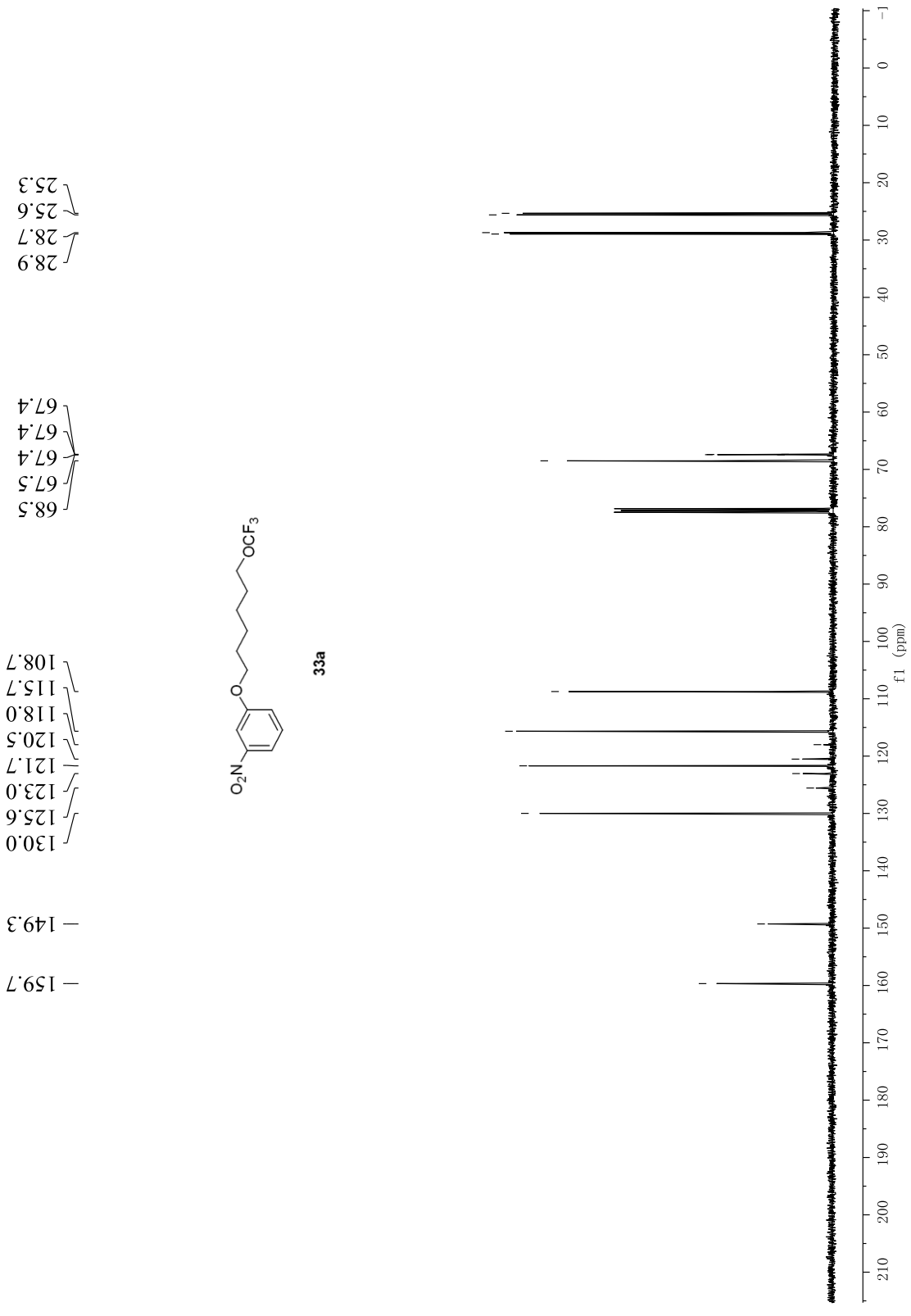


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **32a**

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

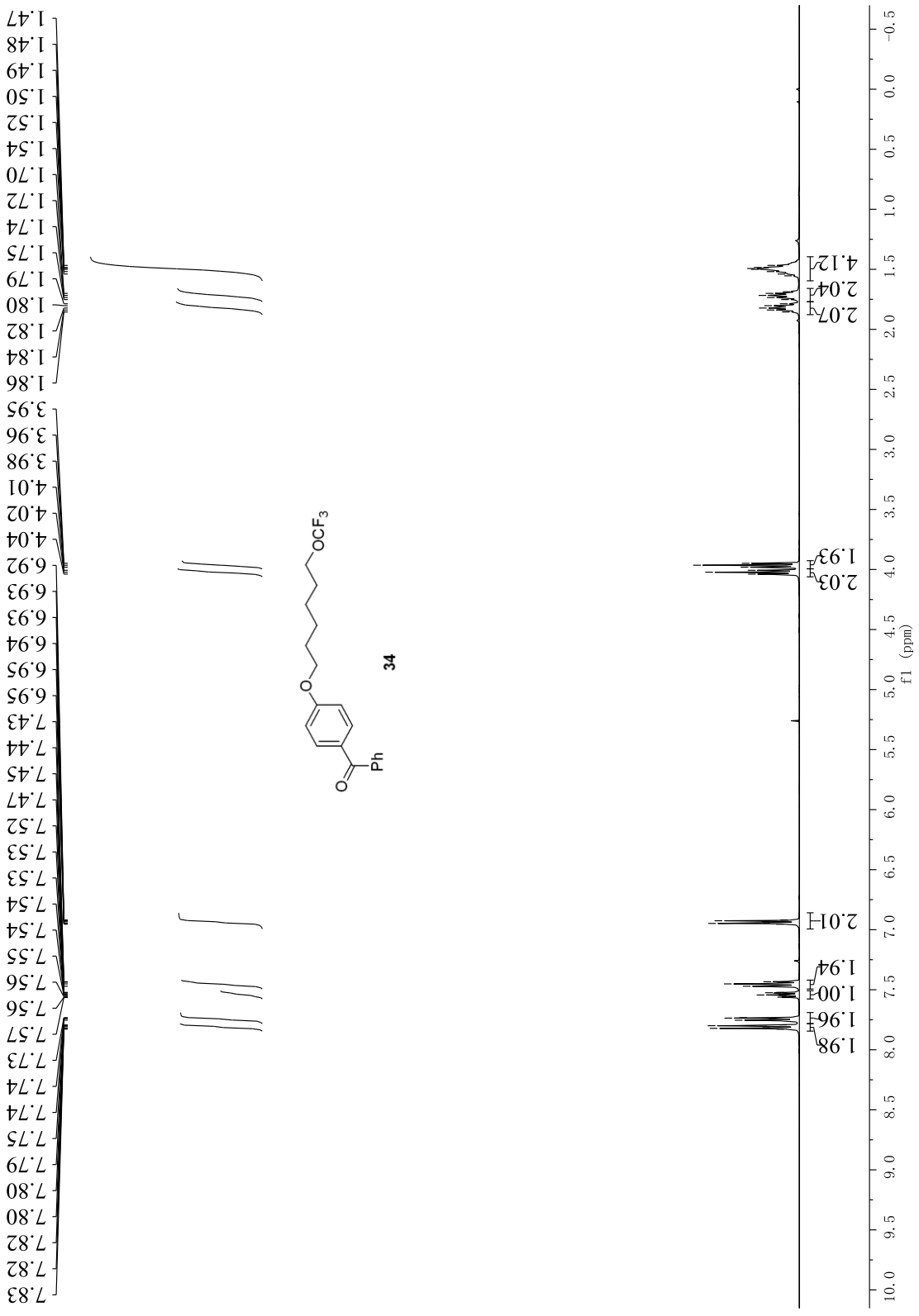


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **33a**

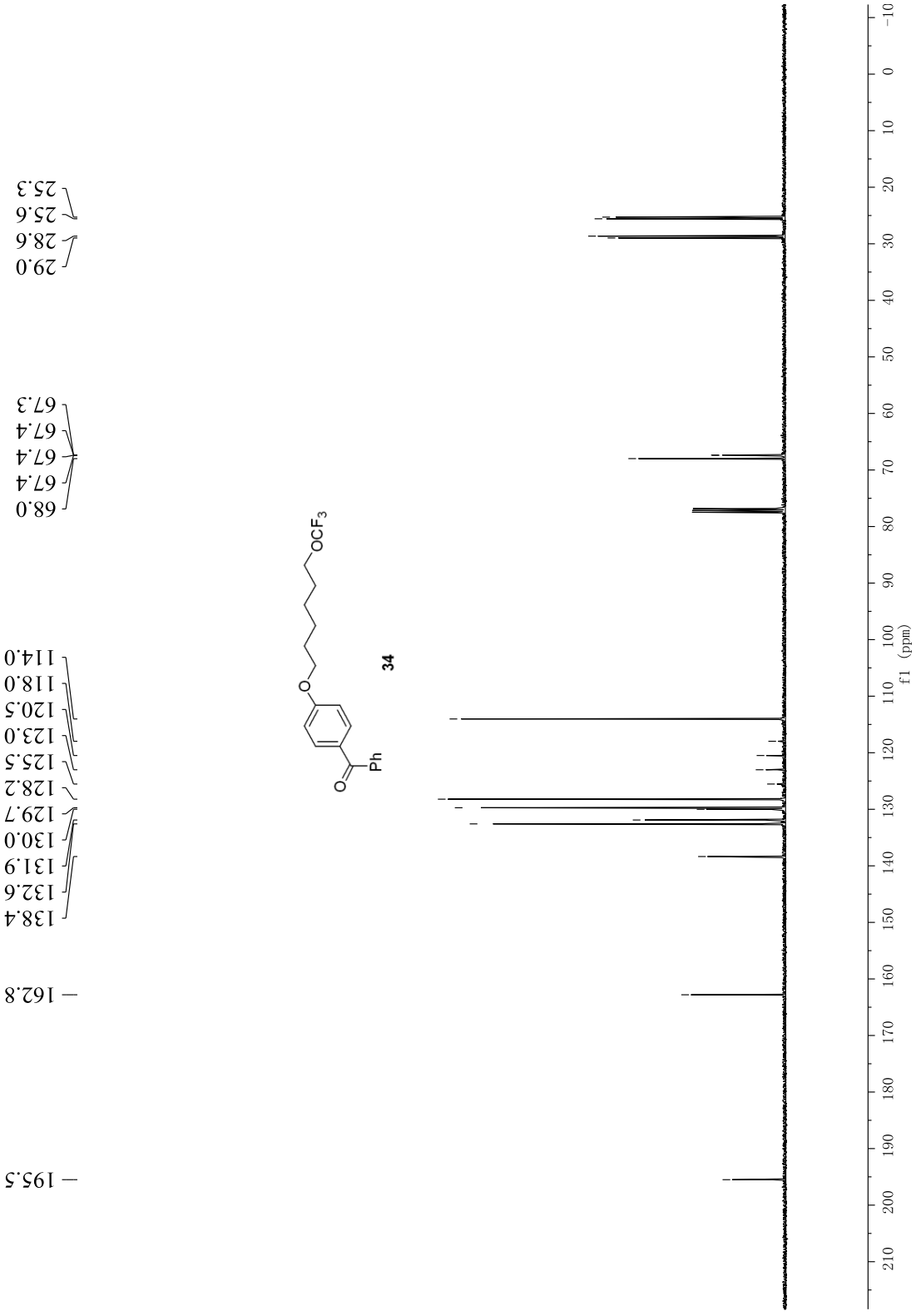


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **33a**

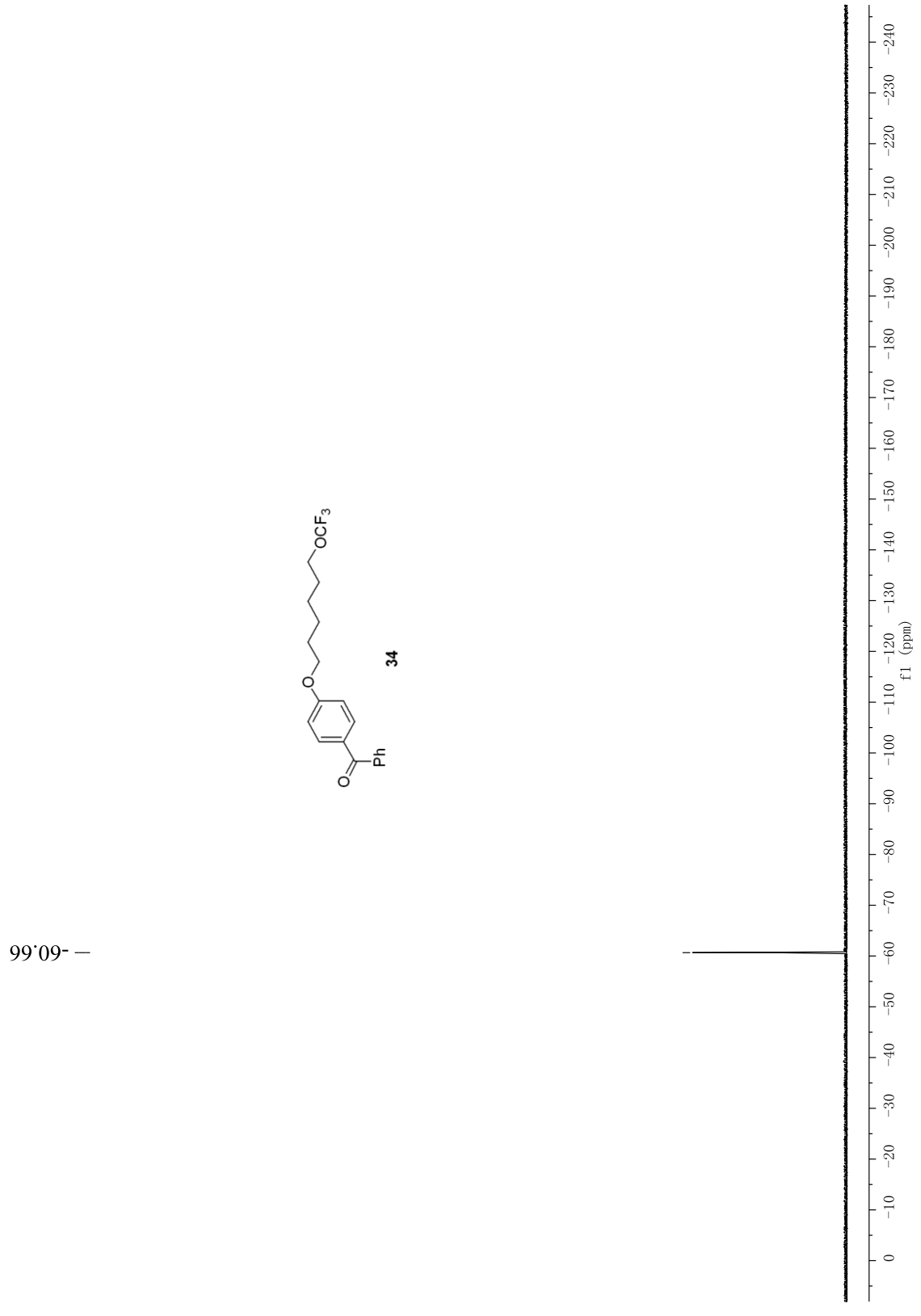
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **33a**



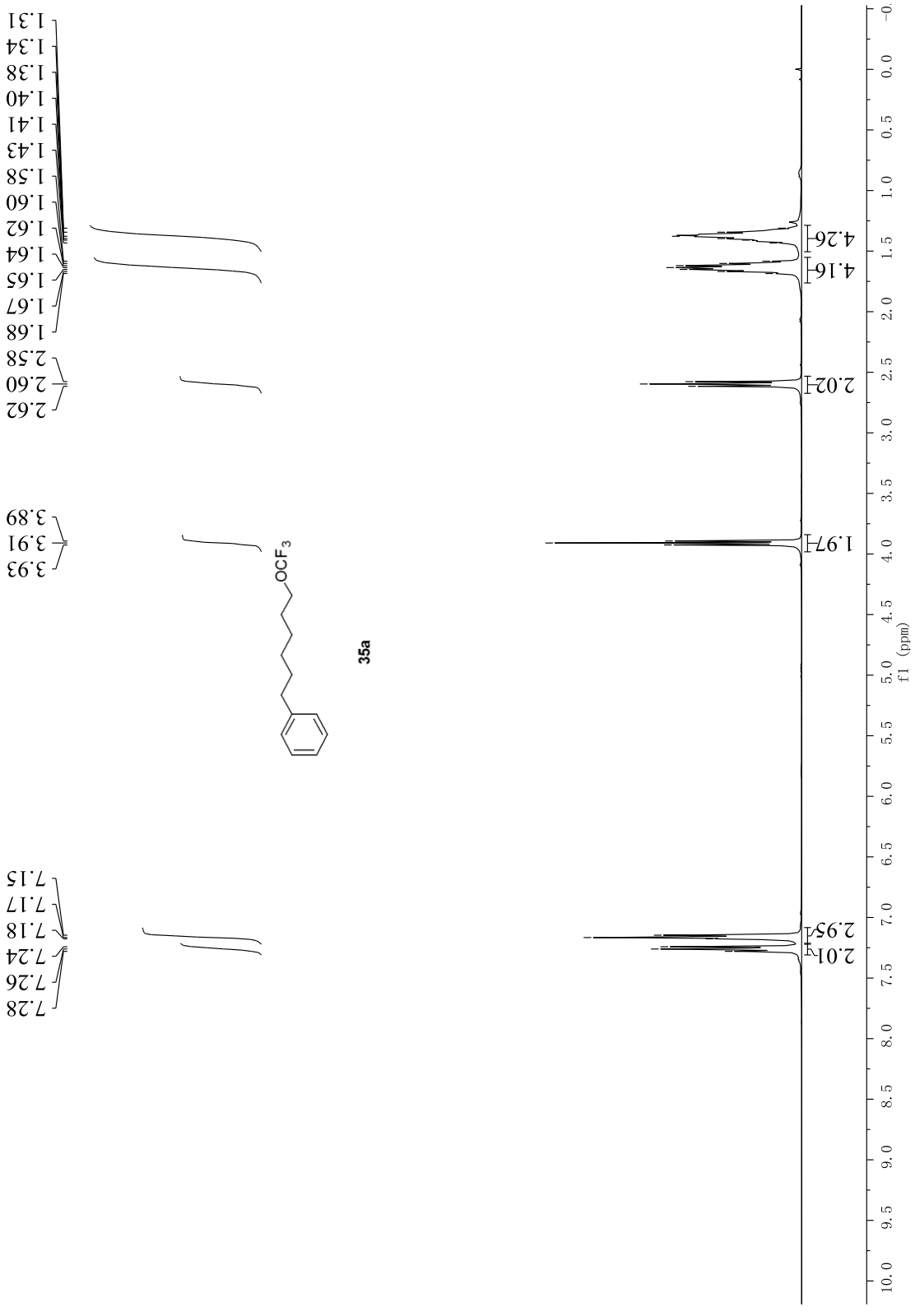
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **34**



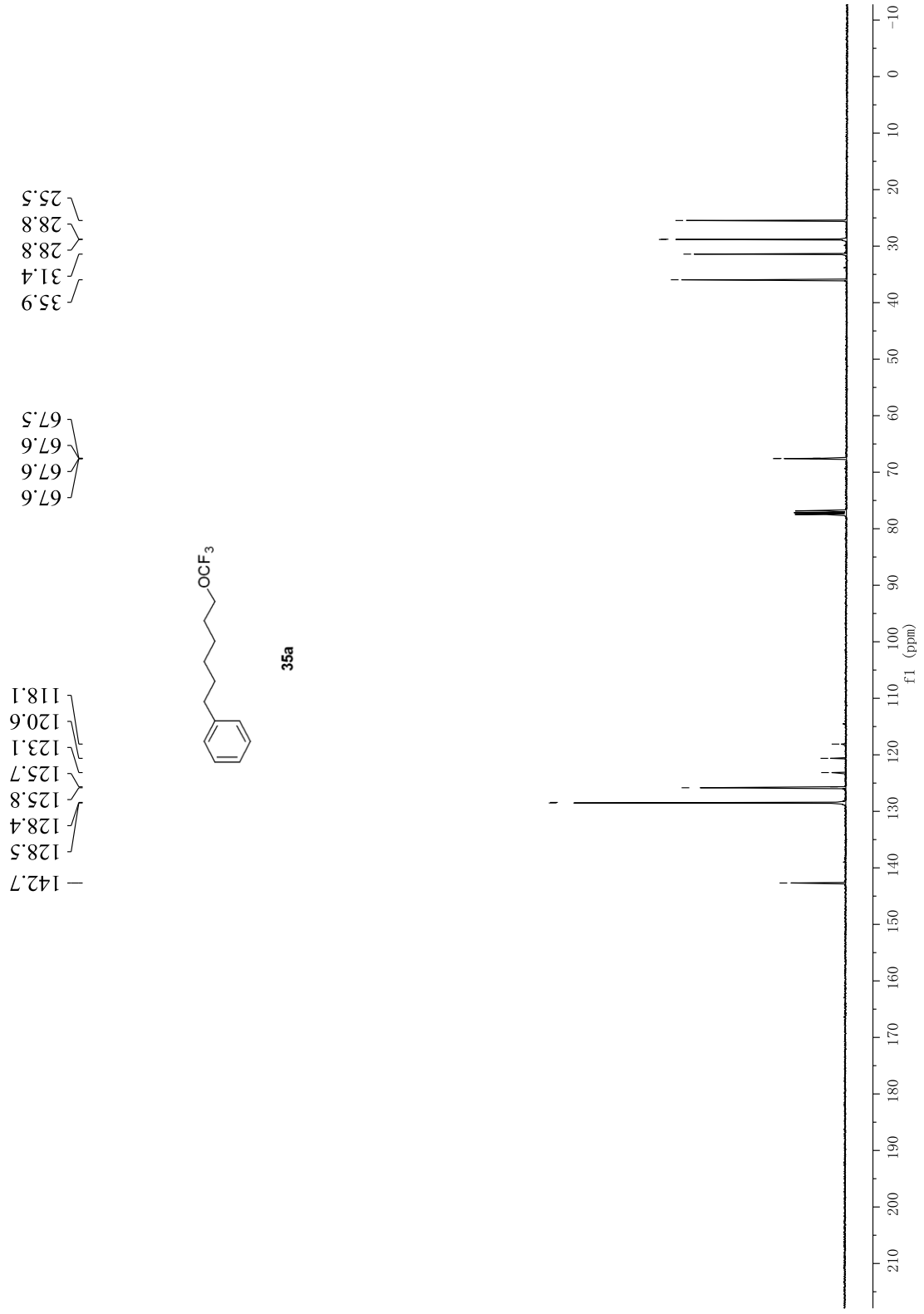
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **34**



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

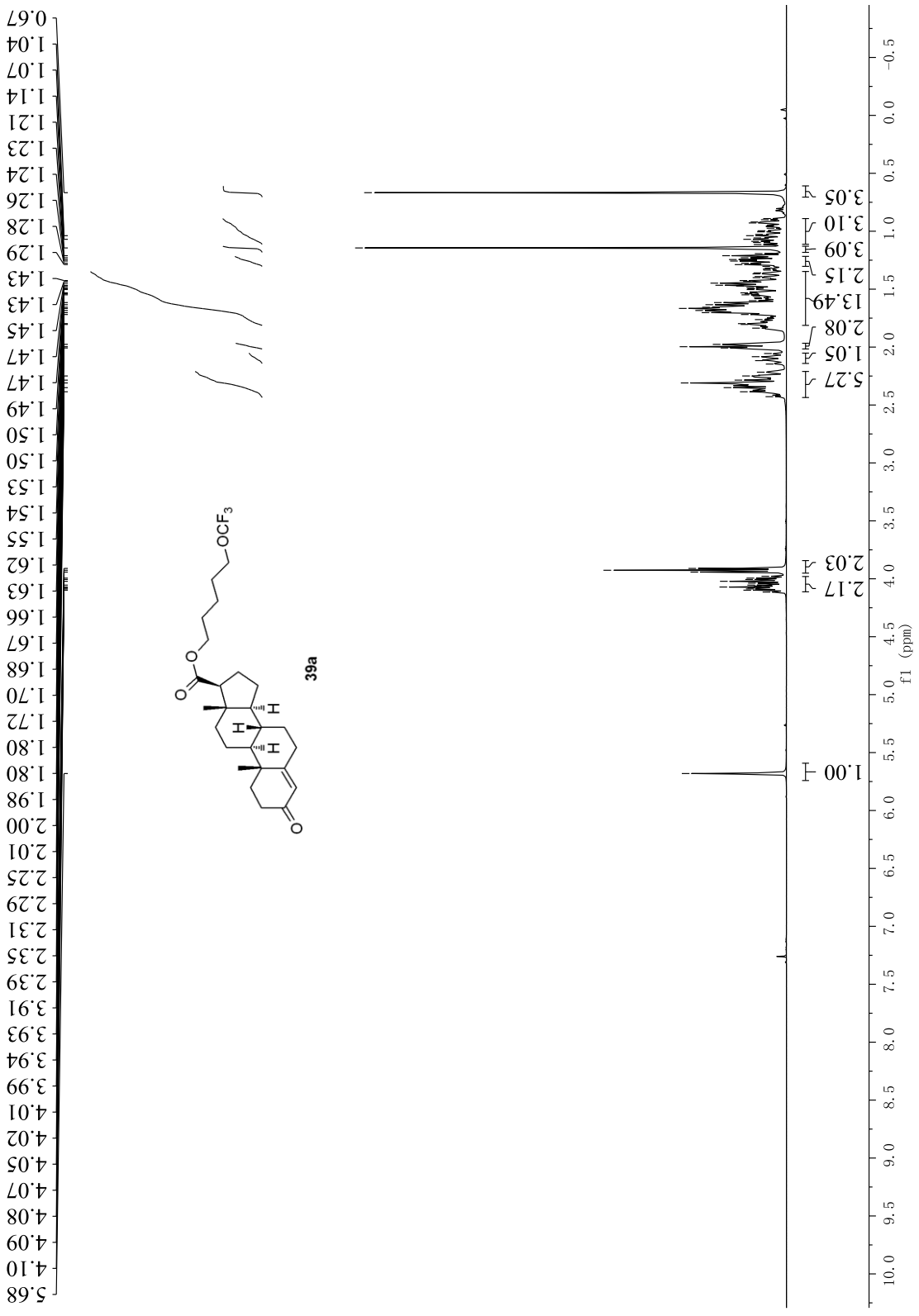


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **35a**

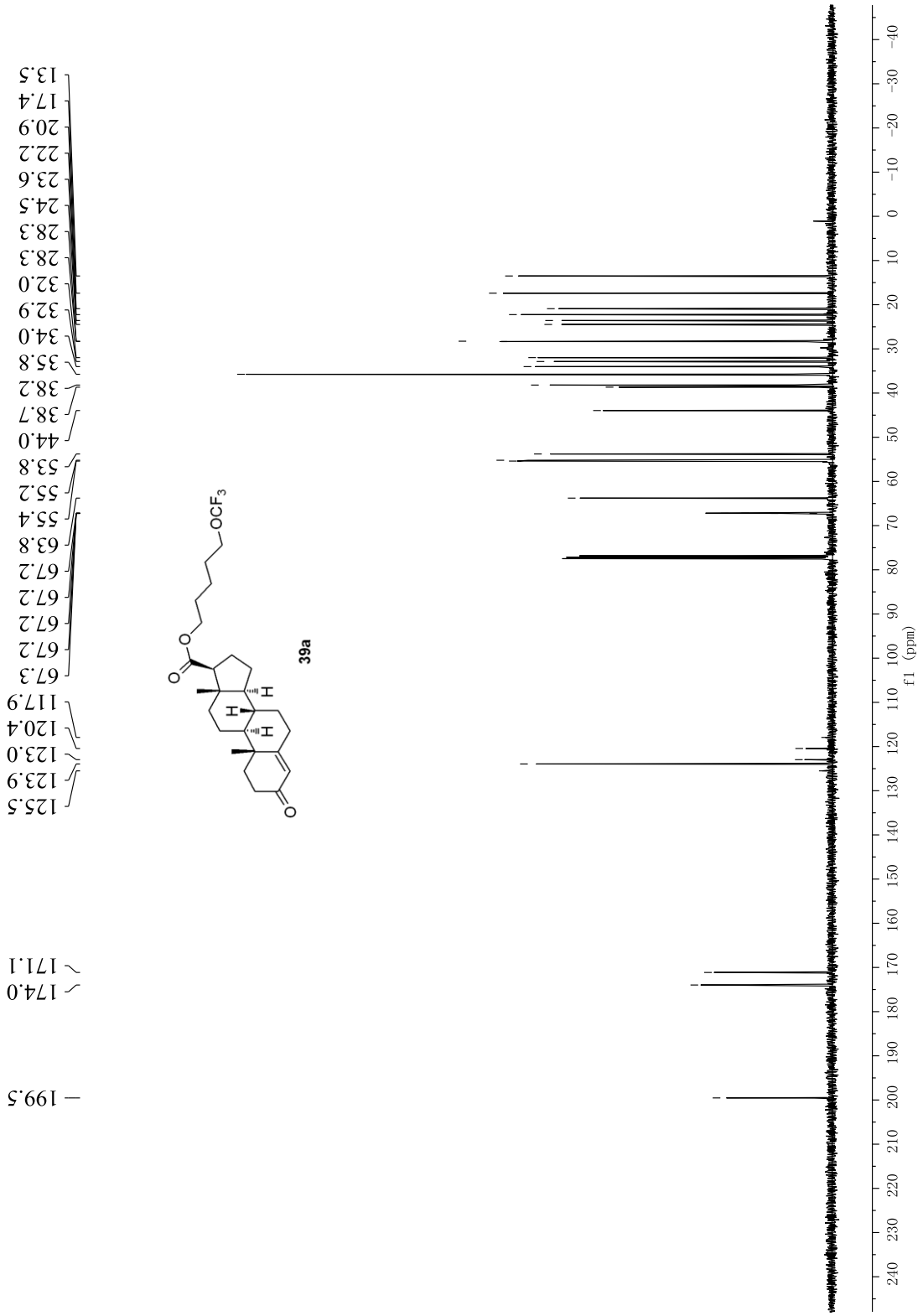


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **35a**

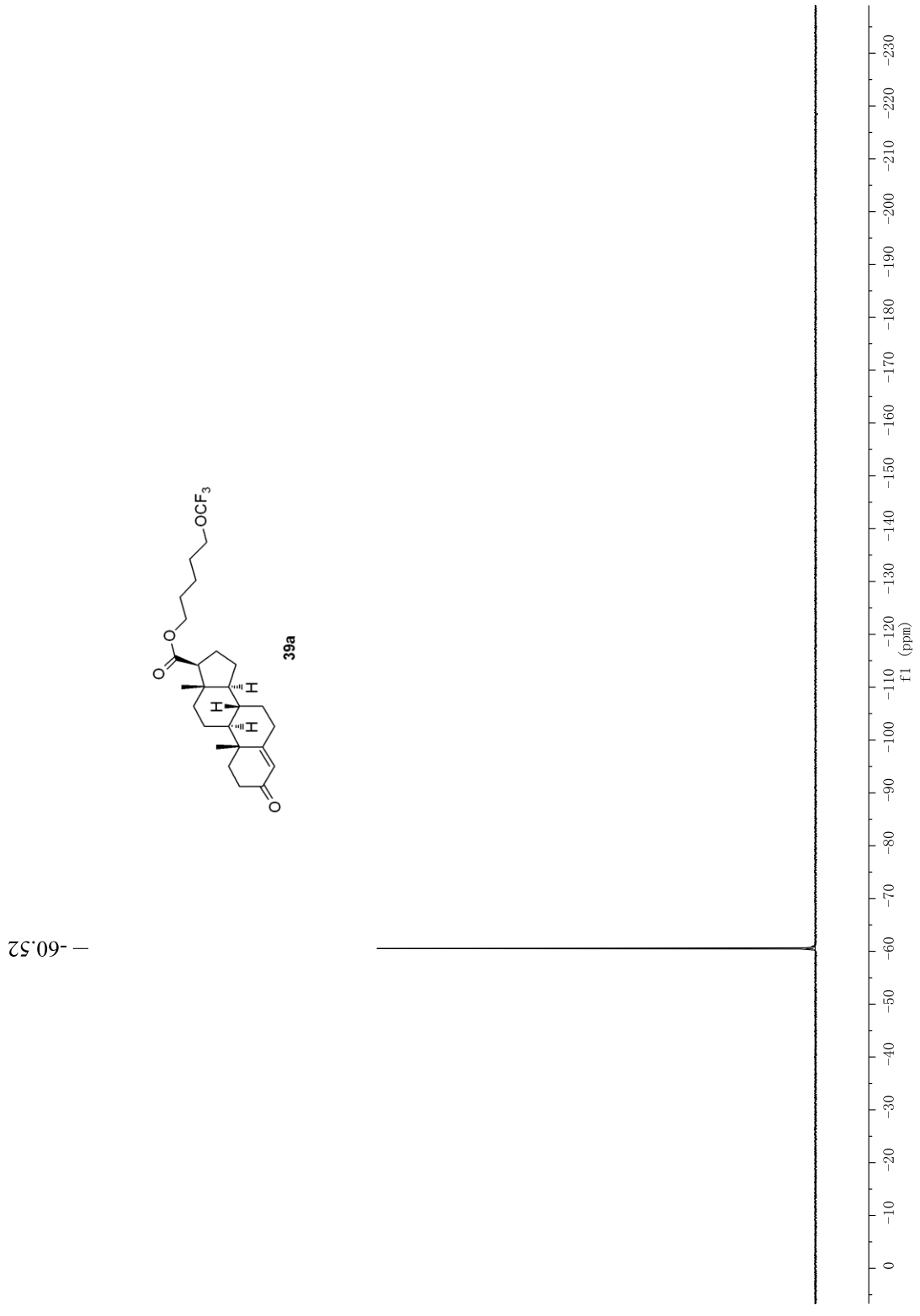
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **35a**



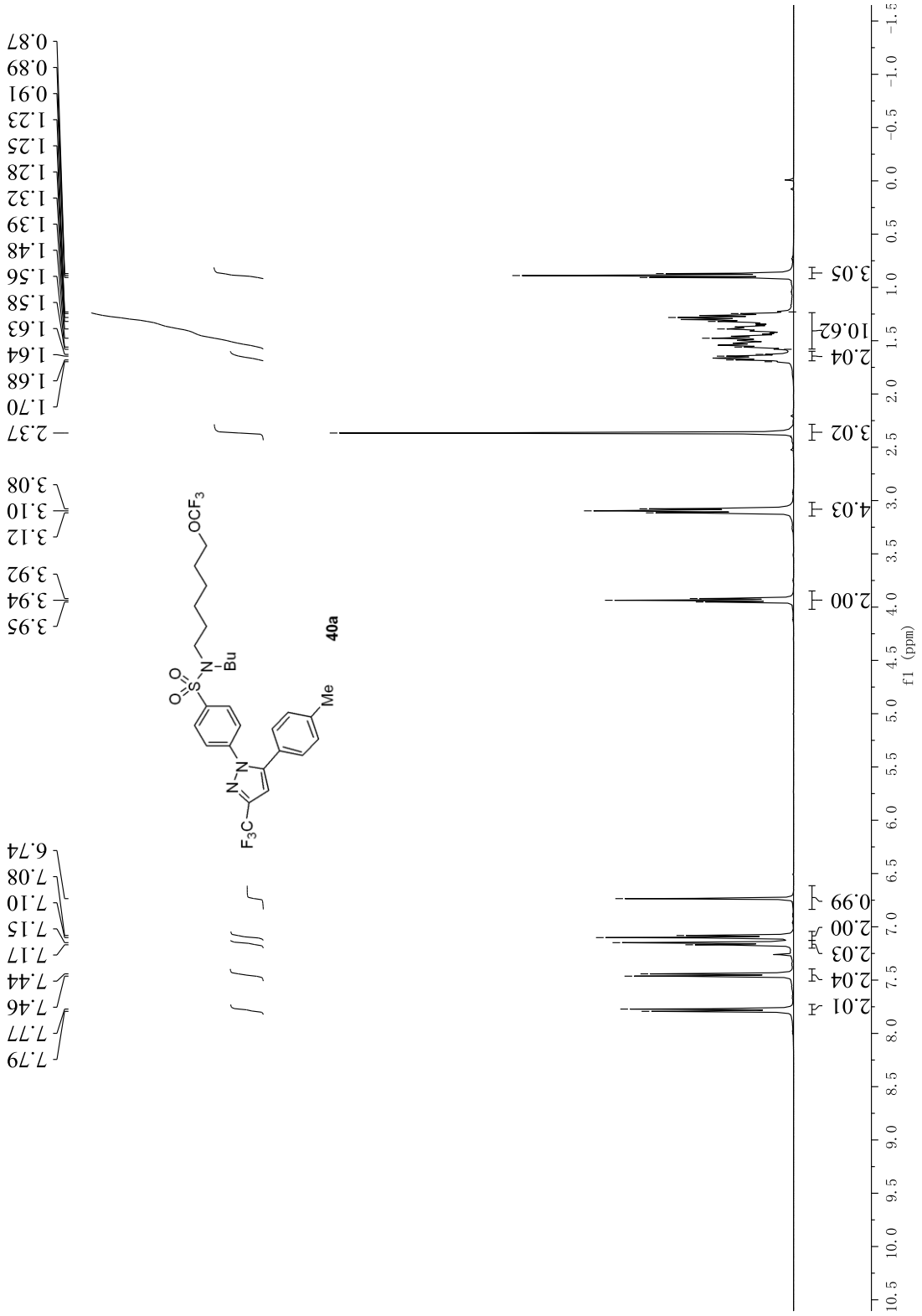
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **39a**



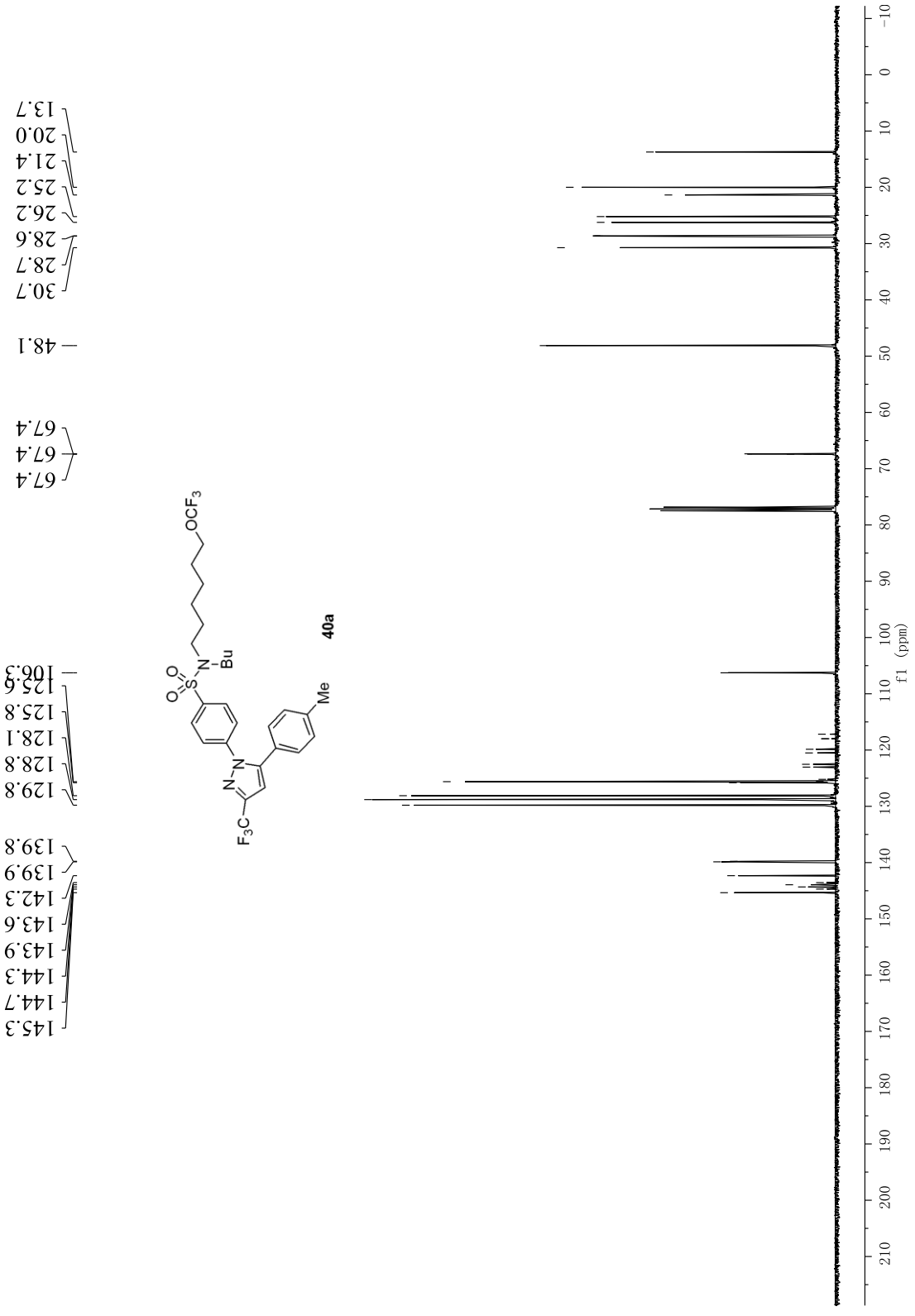
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **39a**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **39a**

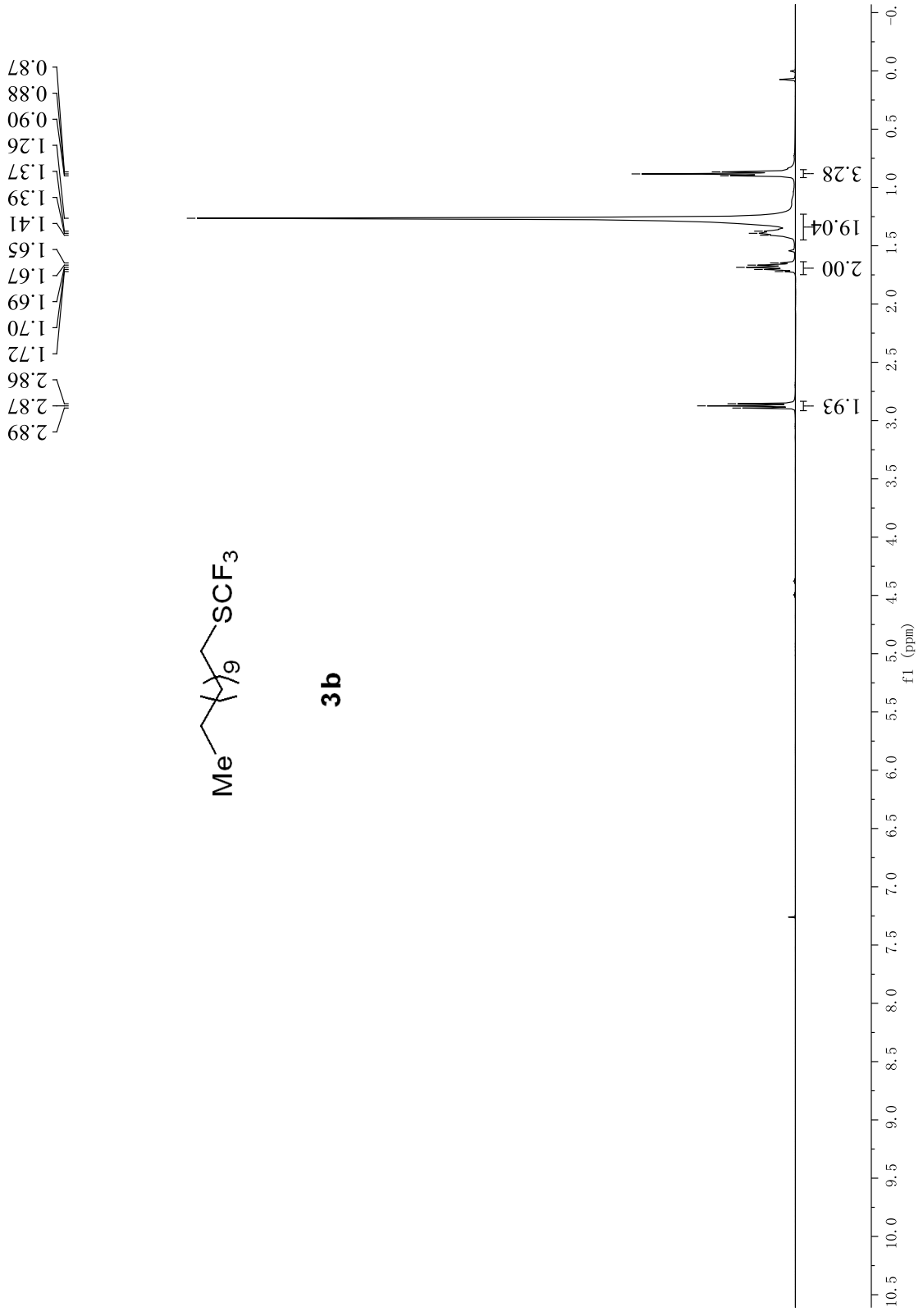


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **40a**

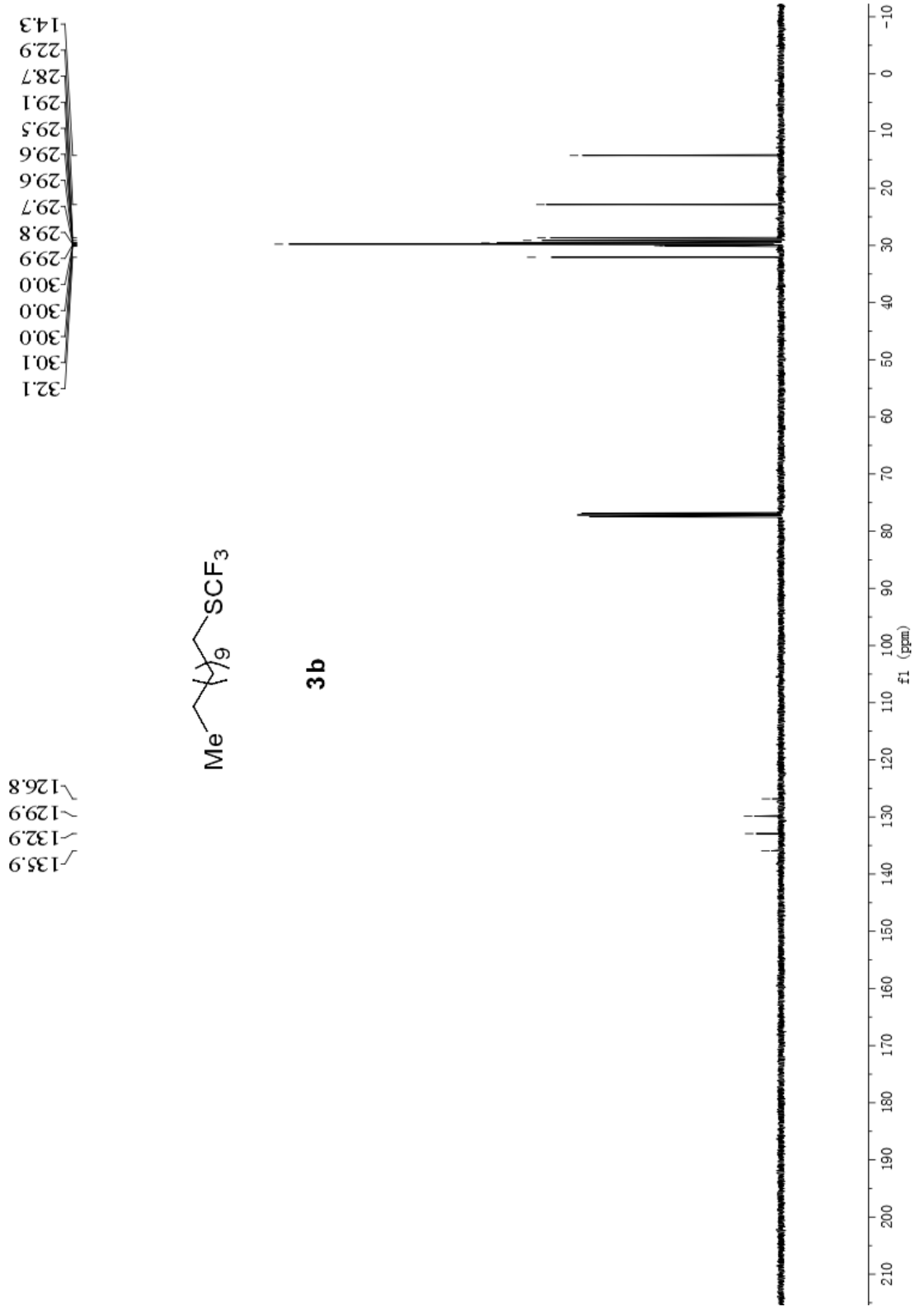


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **40a**

^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **40a**

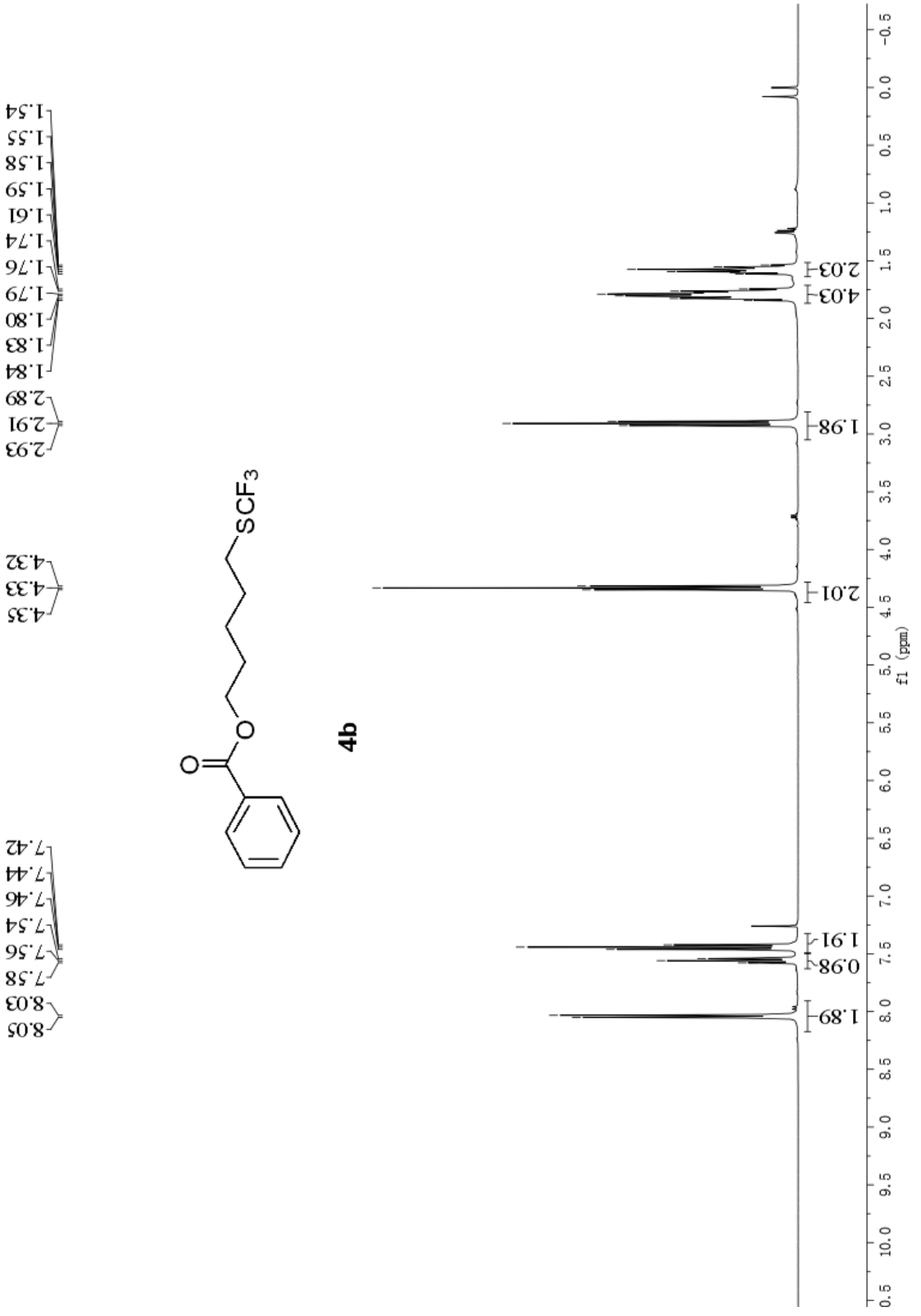


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**

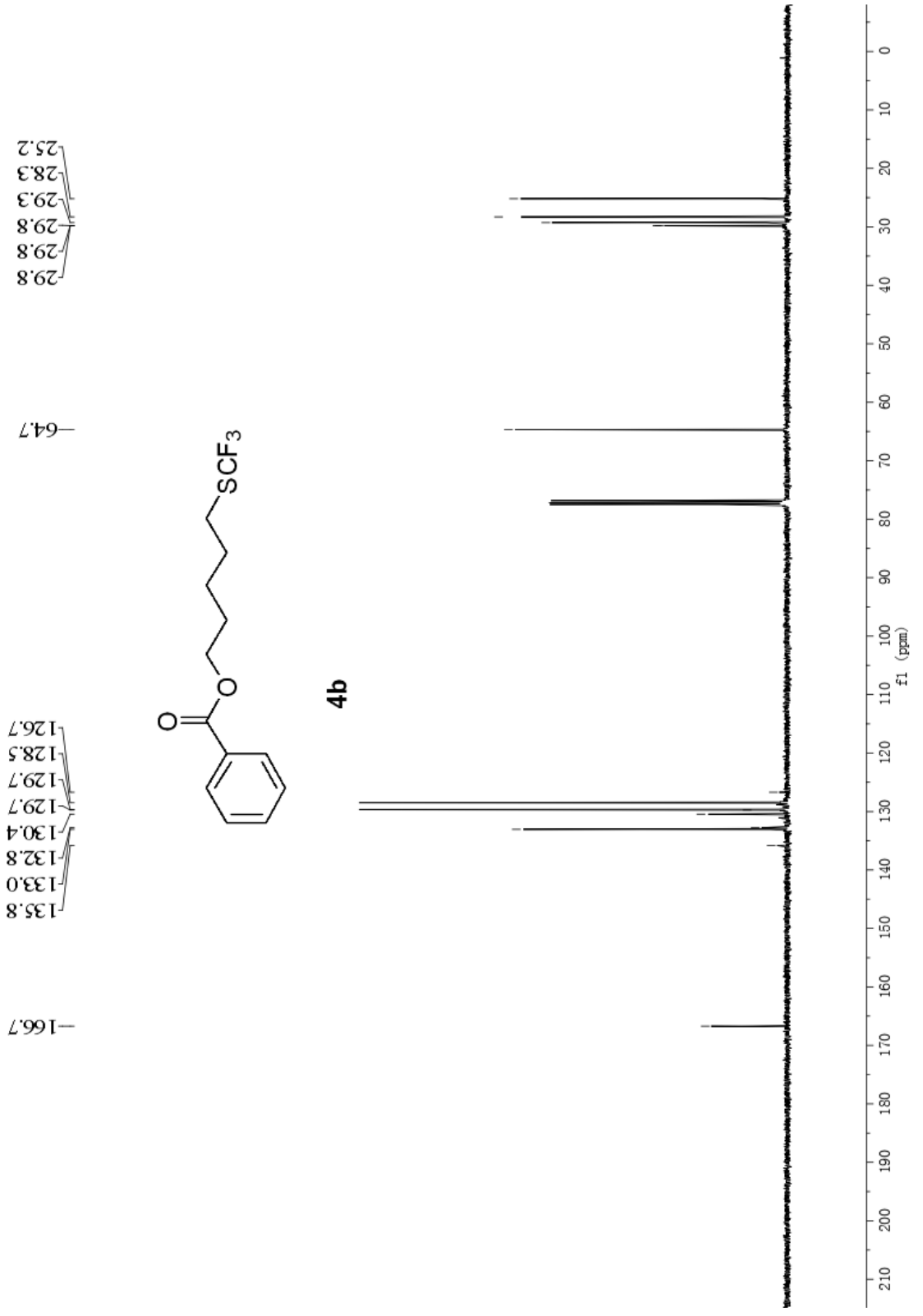


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3b**

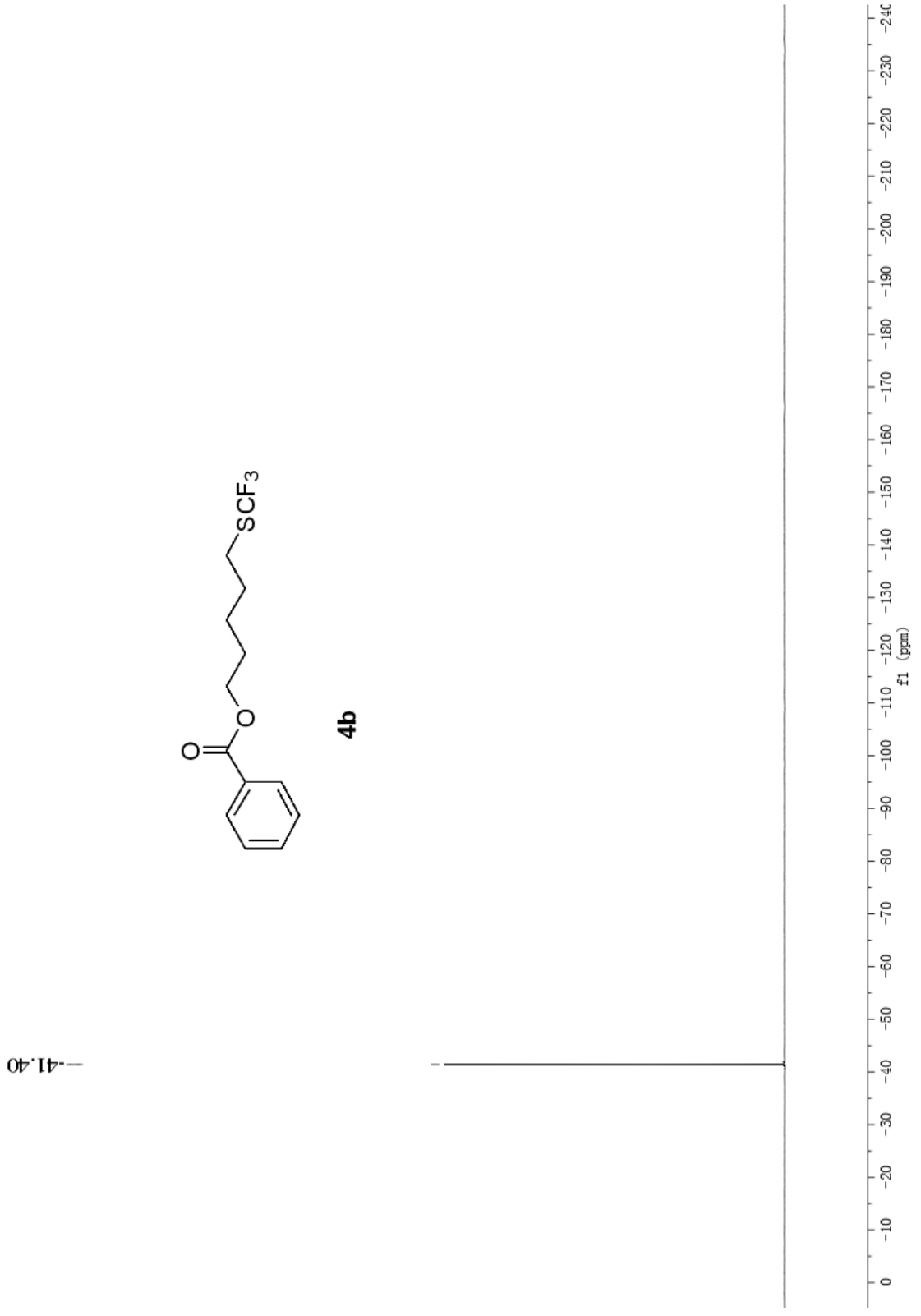
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **3b**



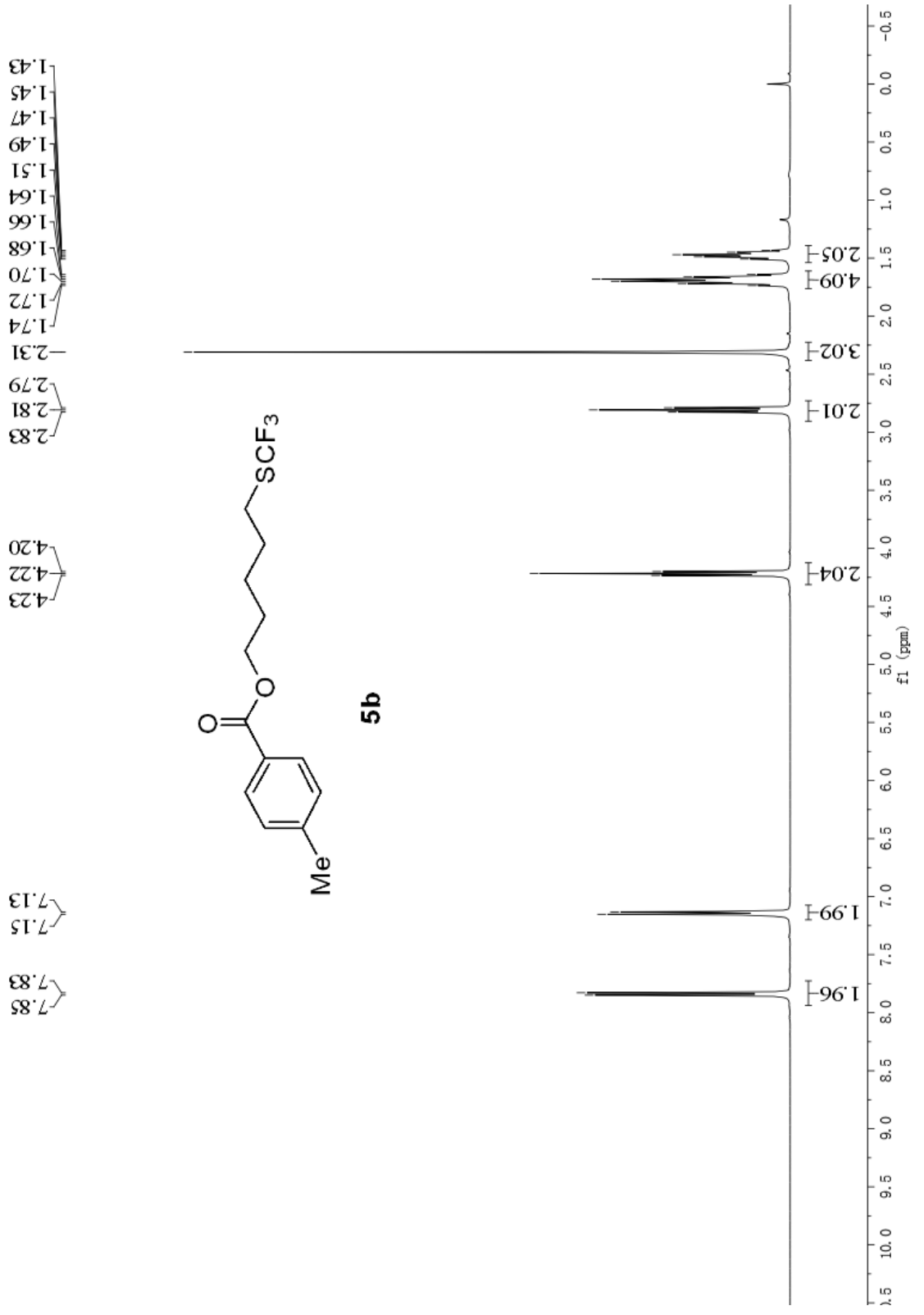
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**



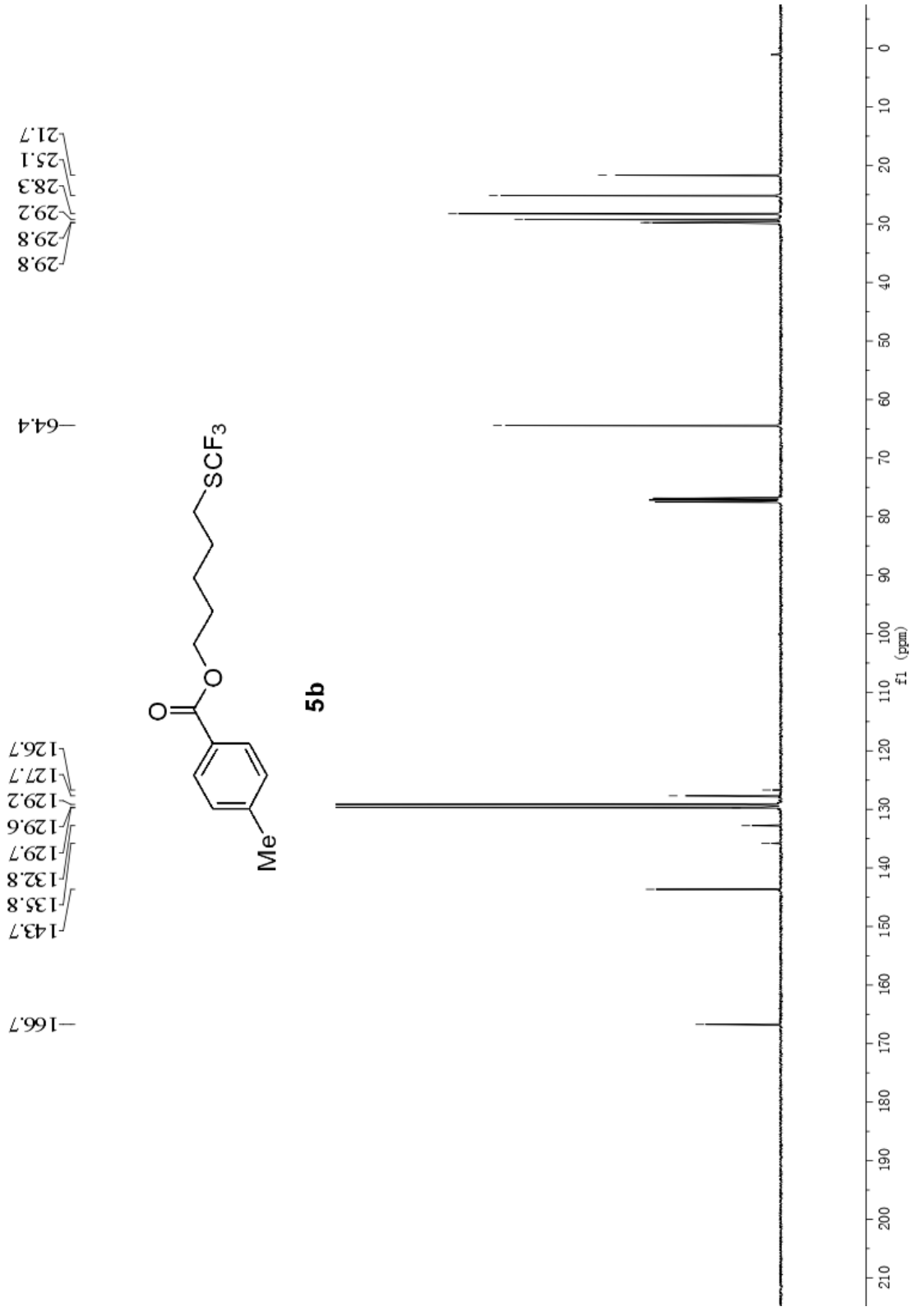
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4b**



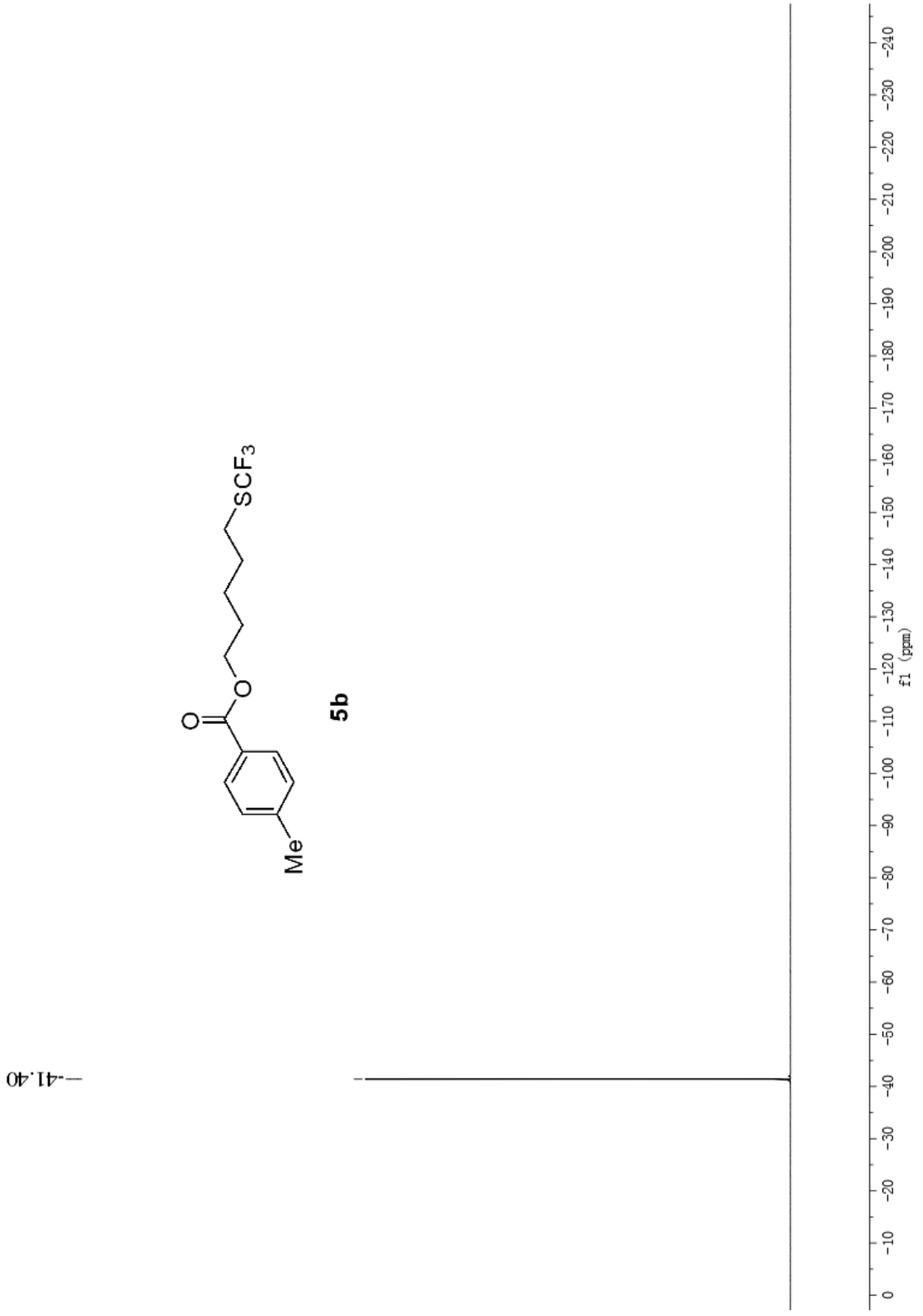
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **4b**



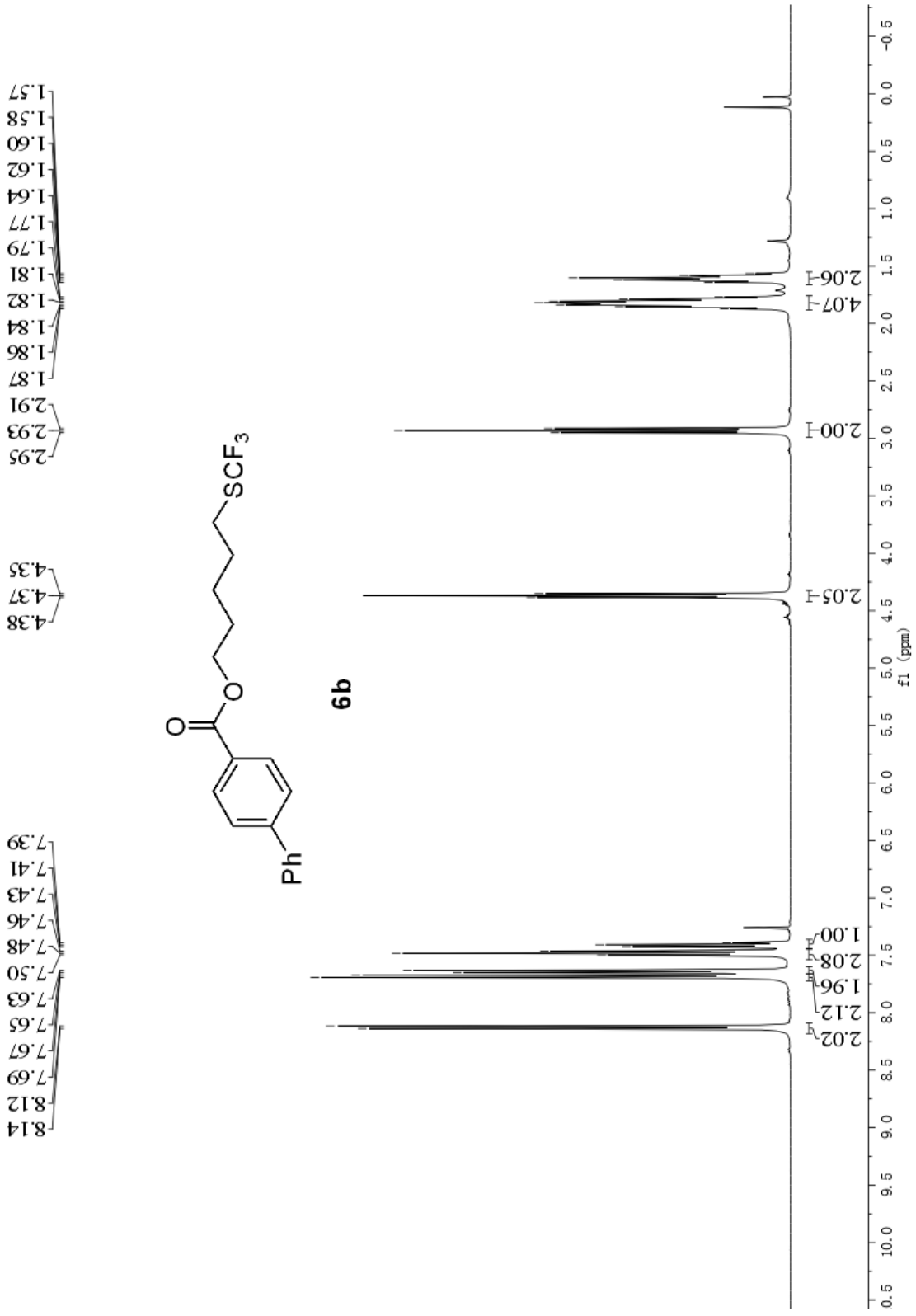
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**



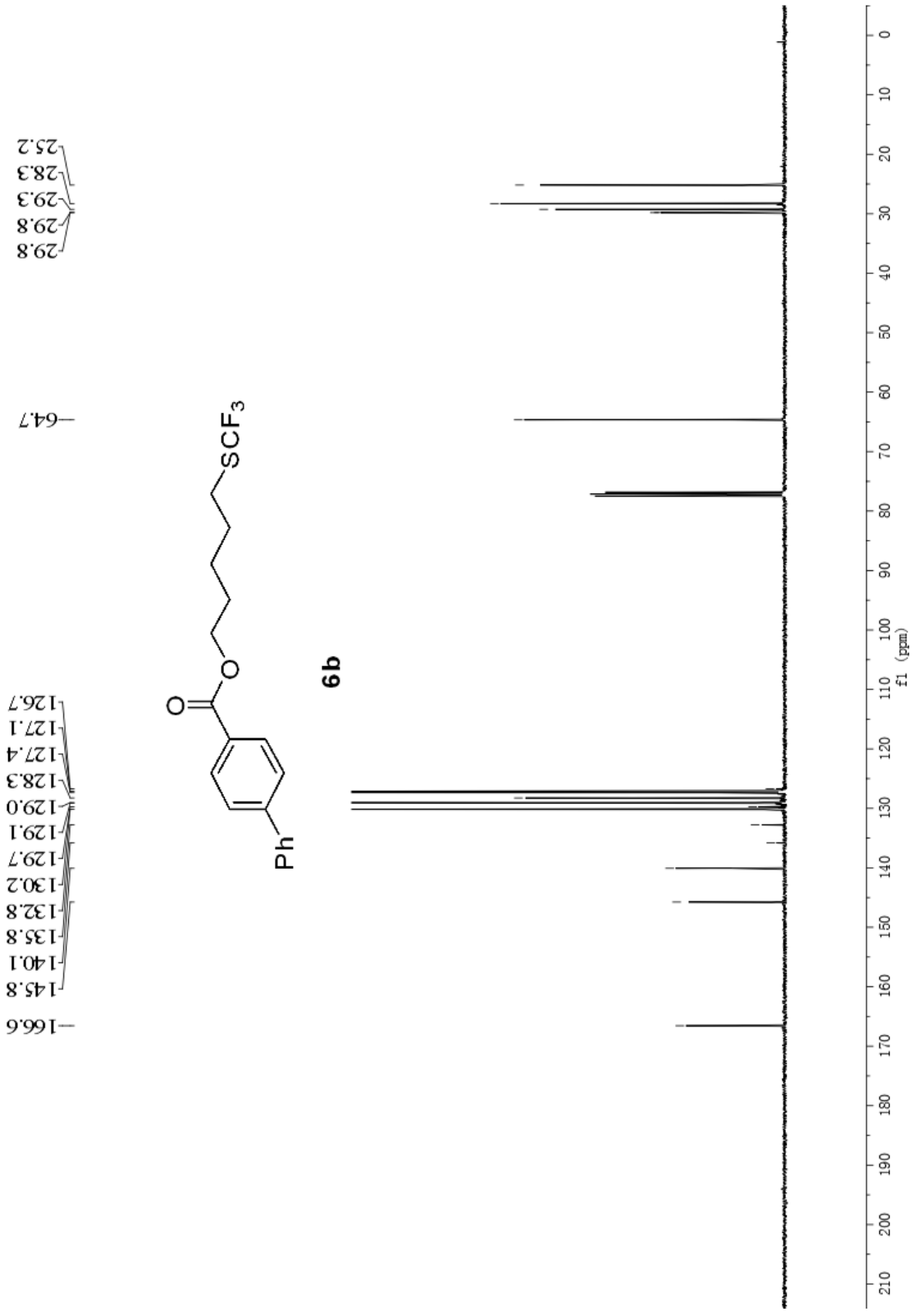
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b**



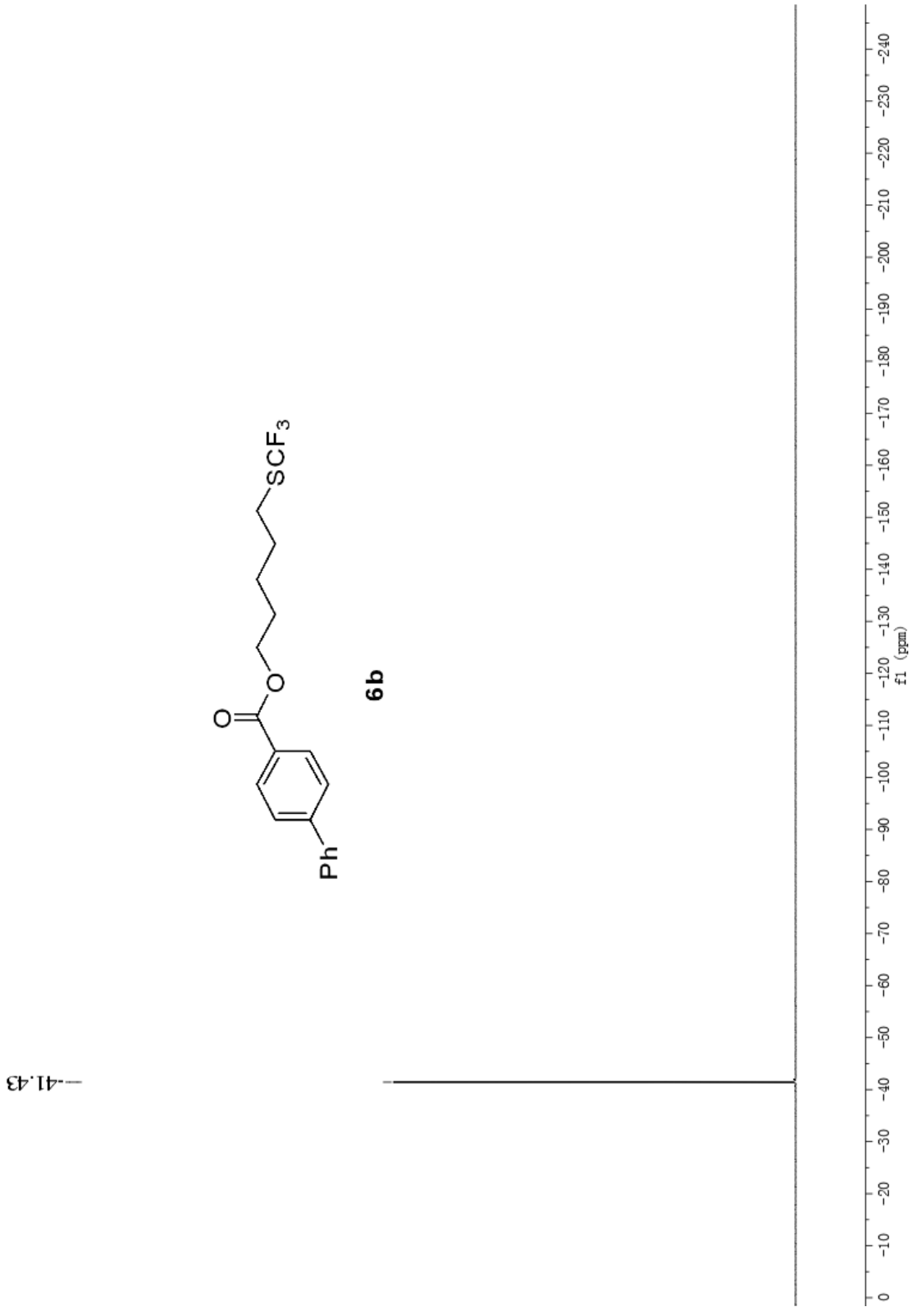
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5b**



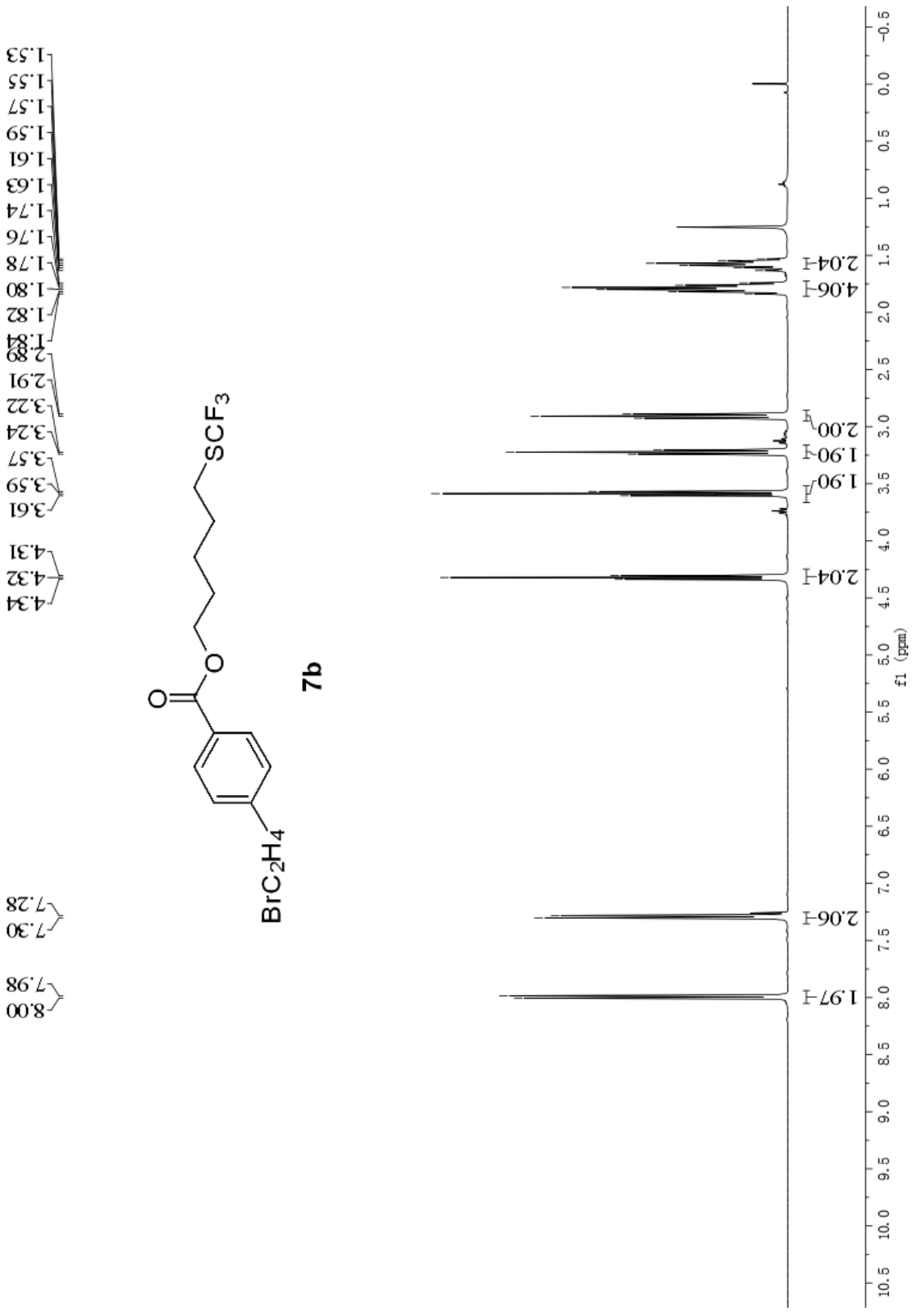
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6b**



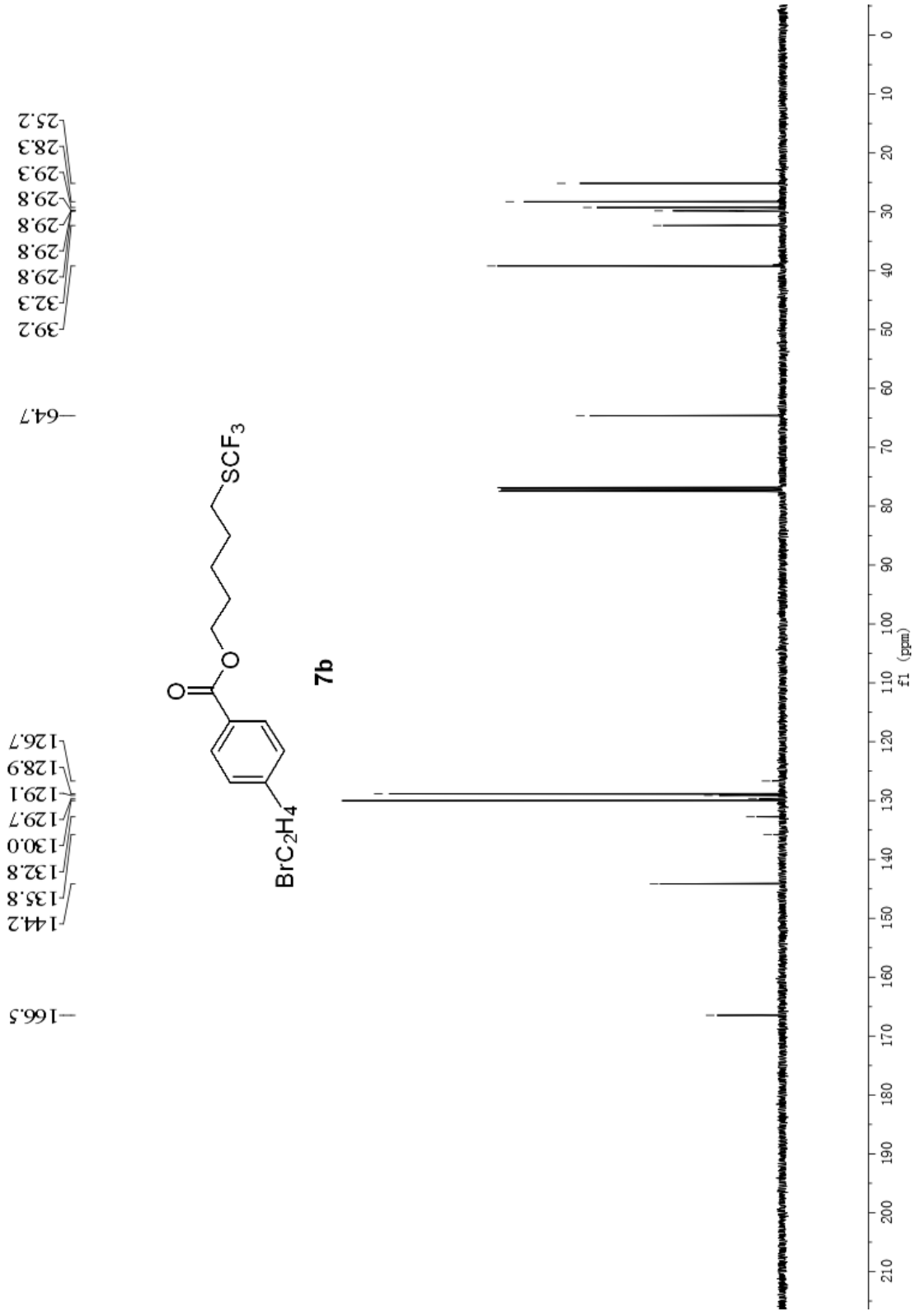
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6b**



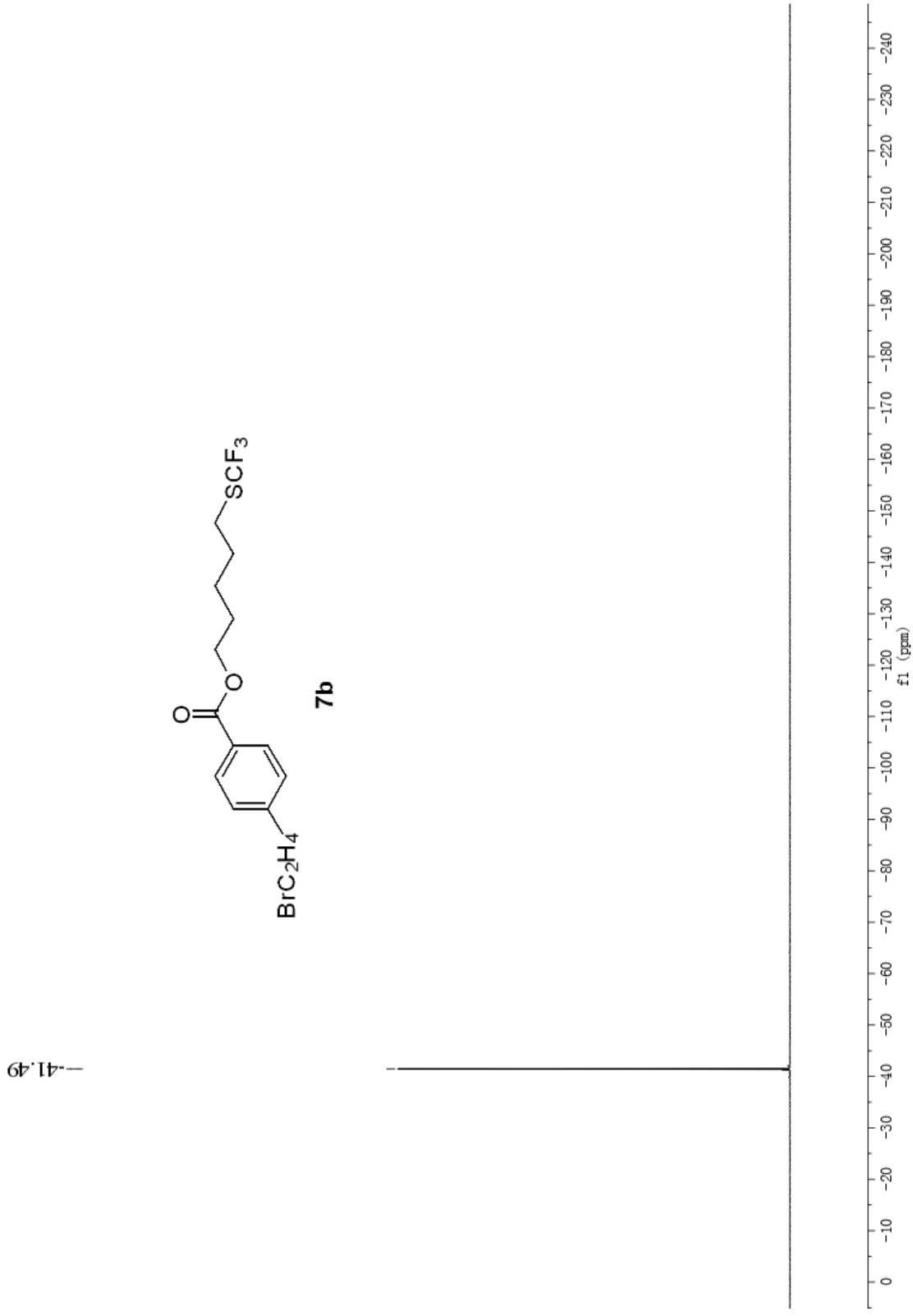
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6b**



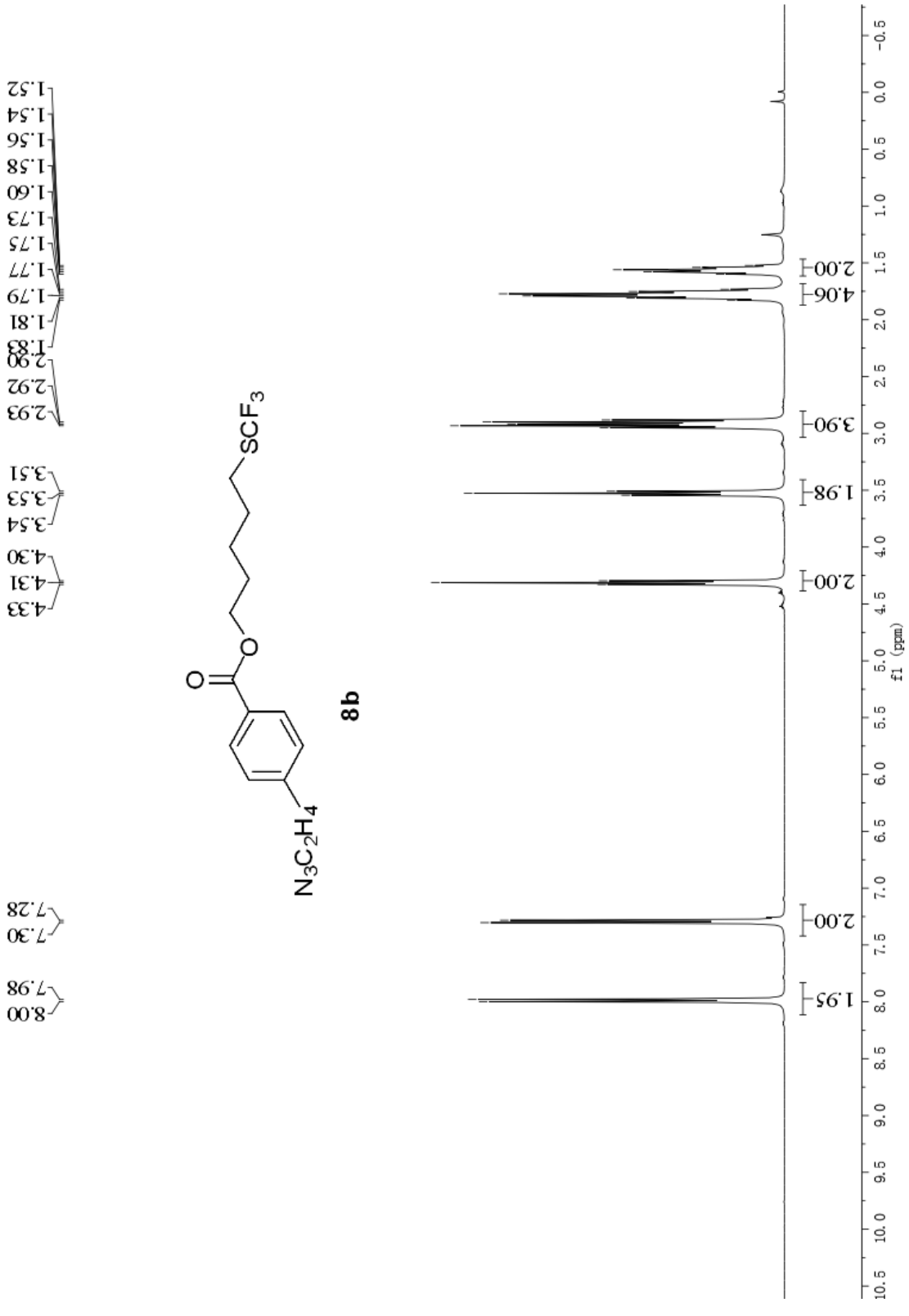
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7b**



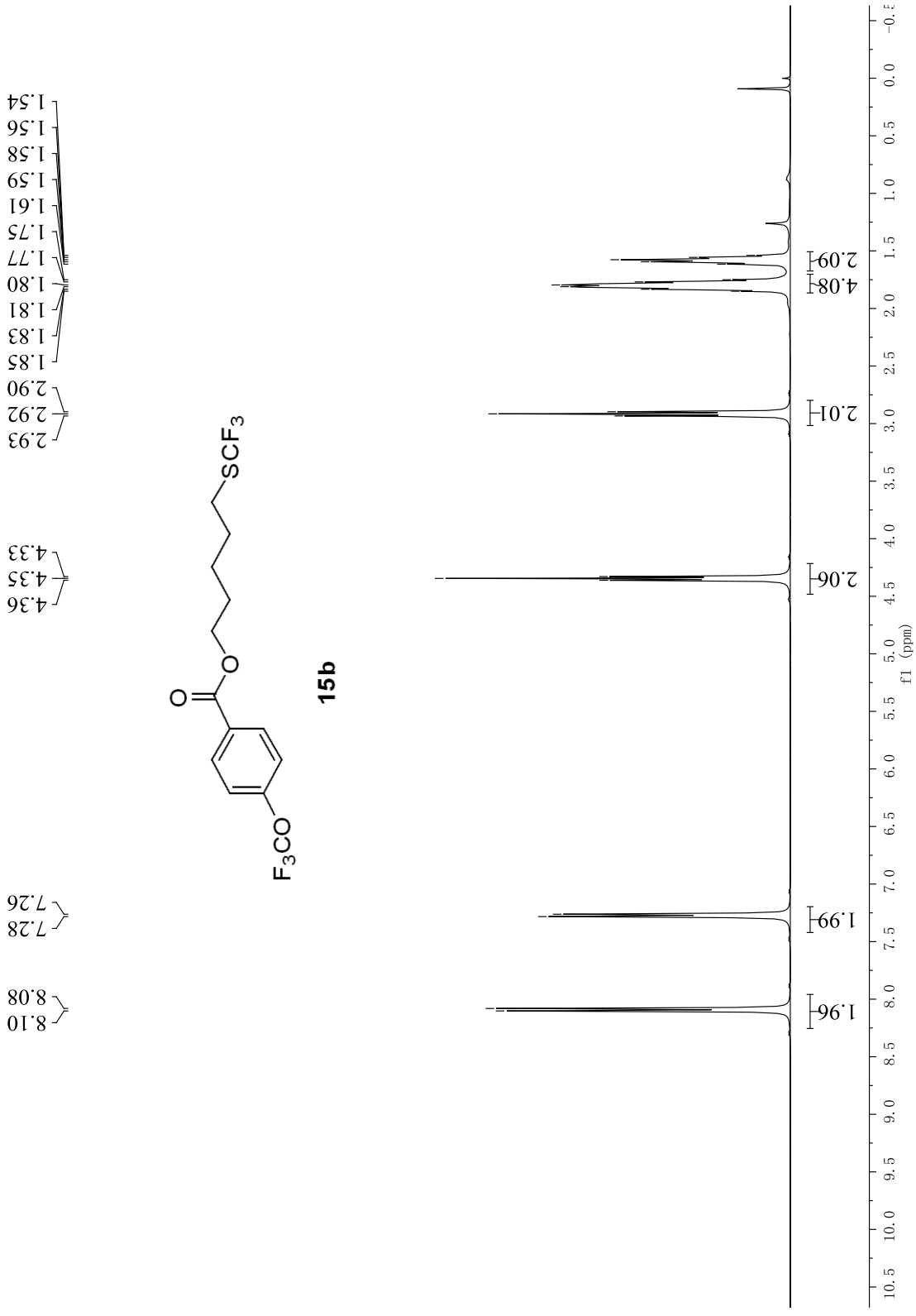
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7b**



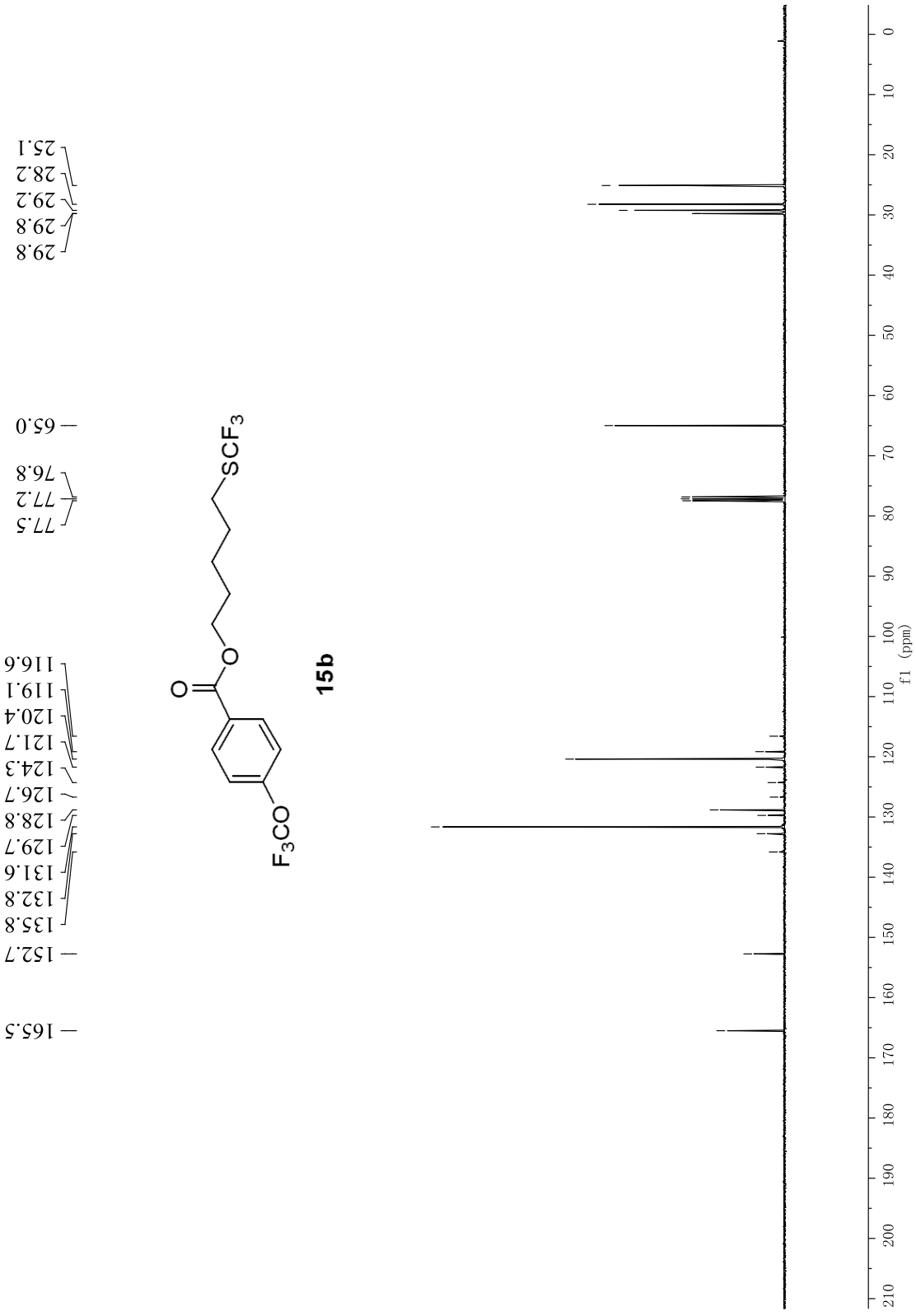
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **7b**



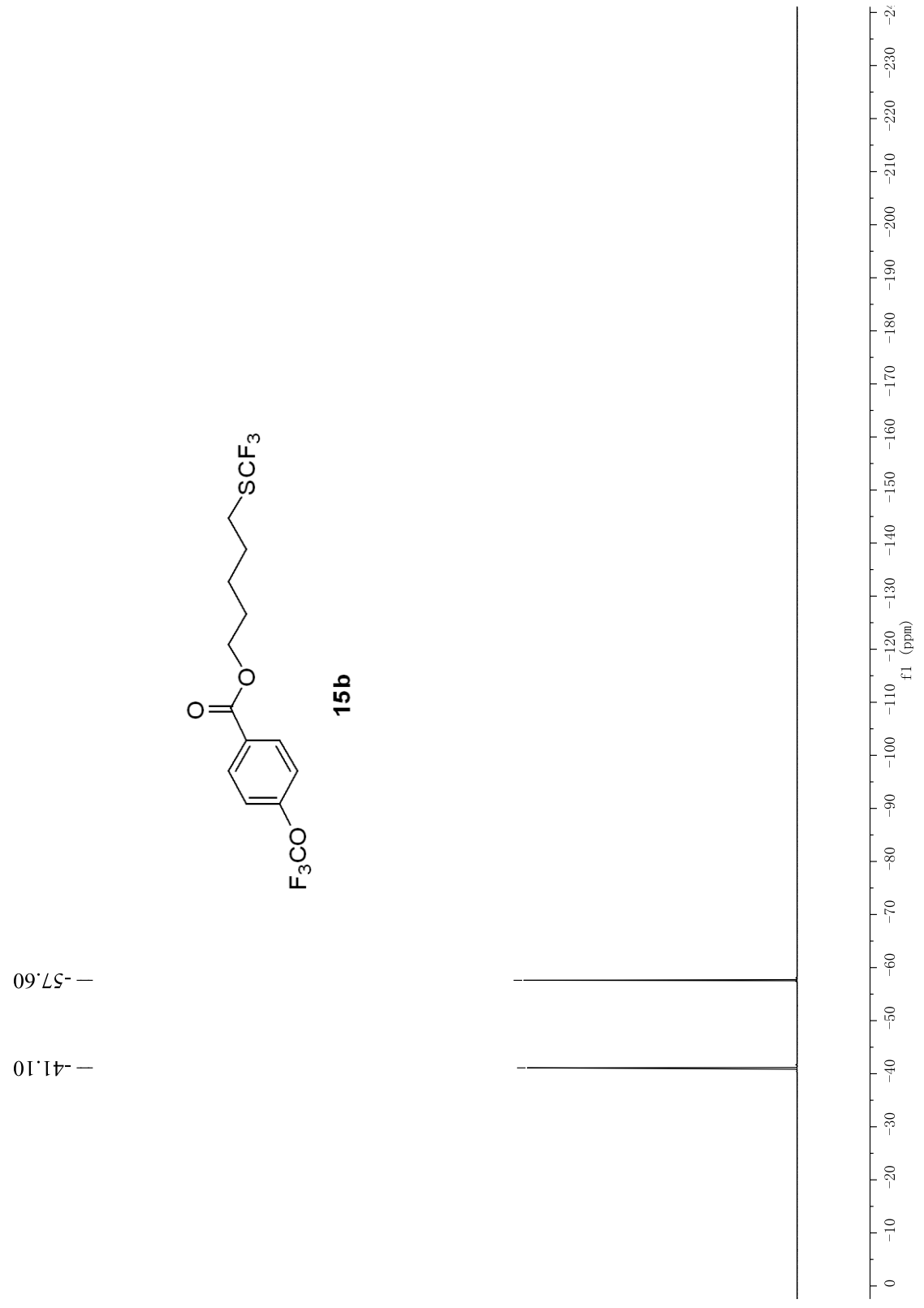
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8b**



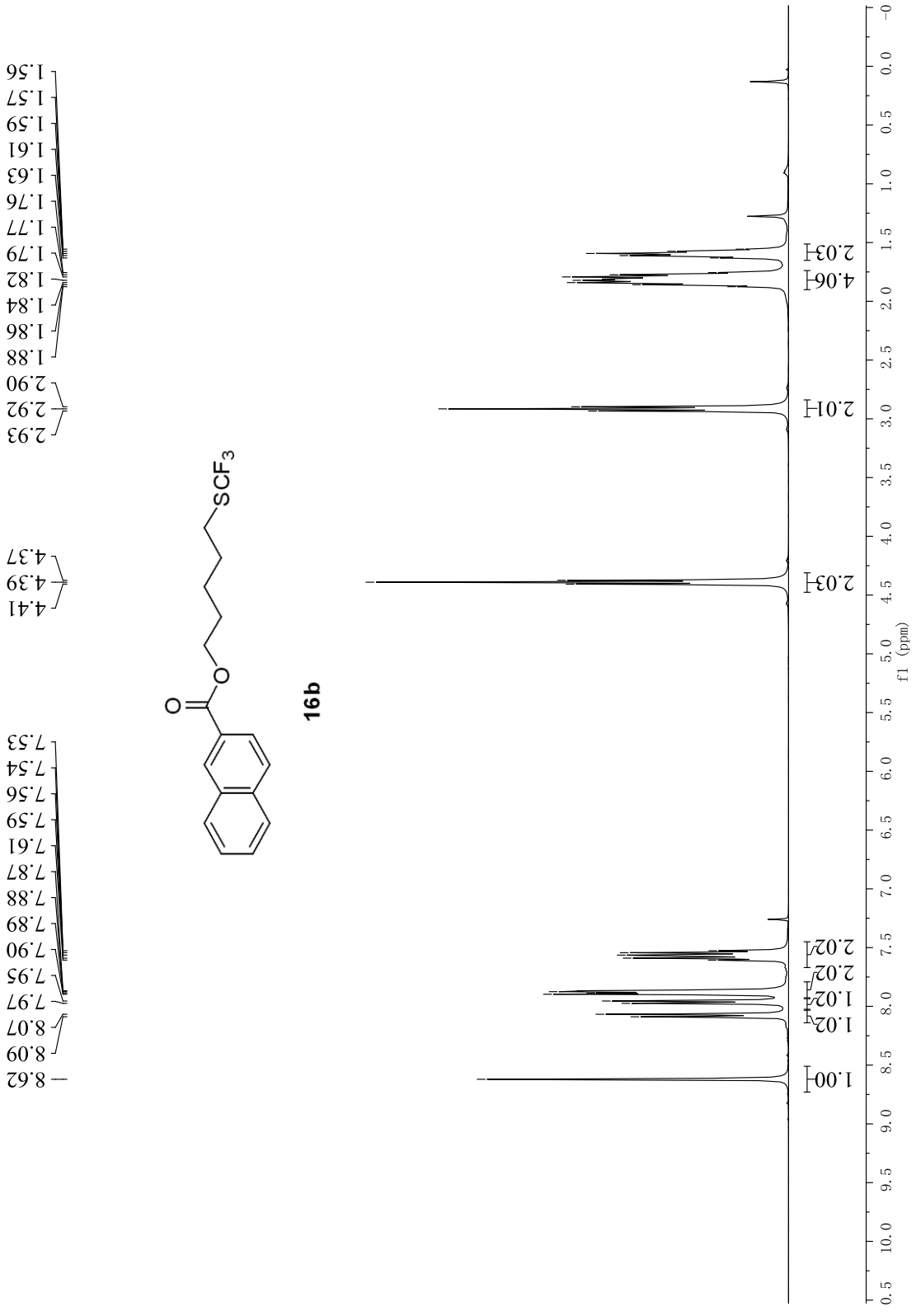
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **15b**



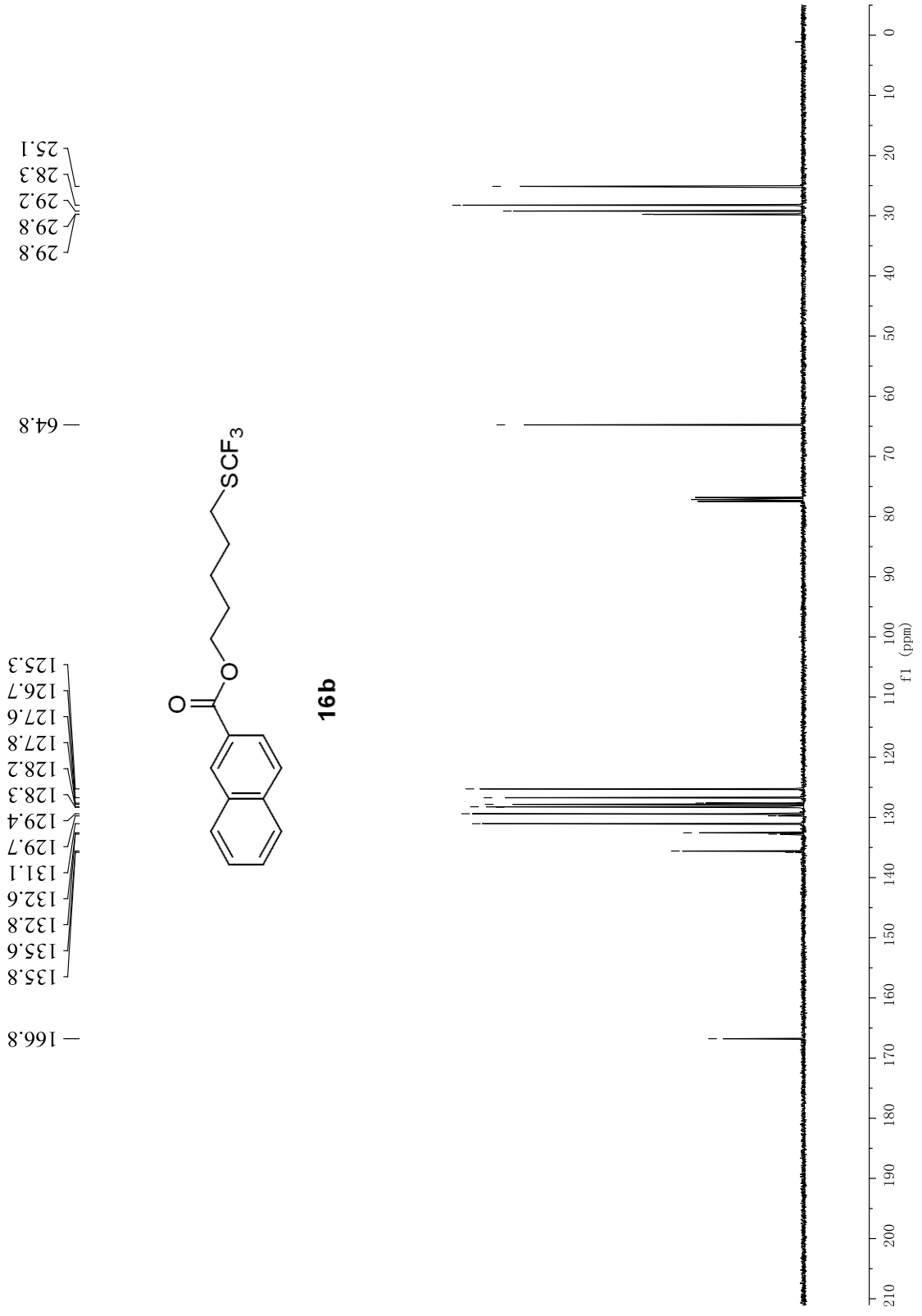
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **15b**



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

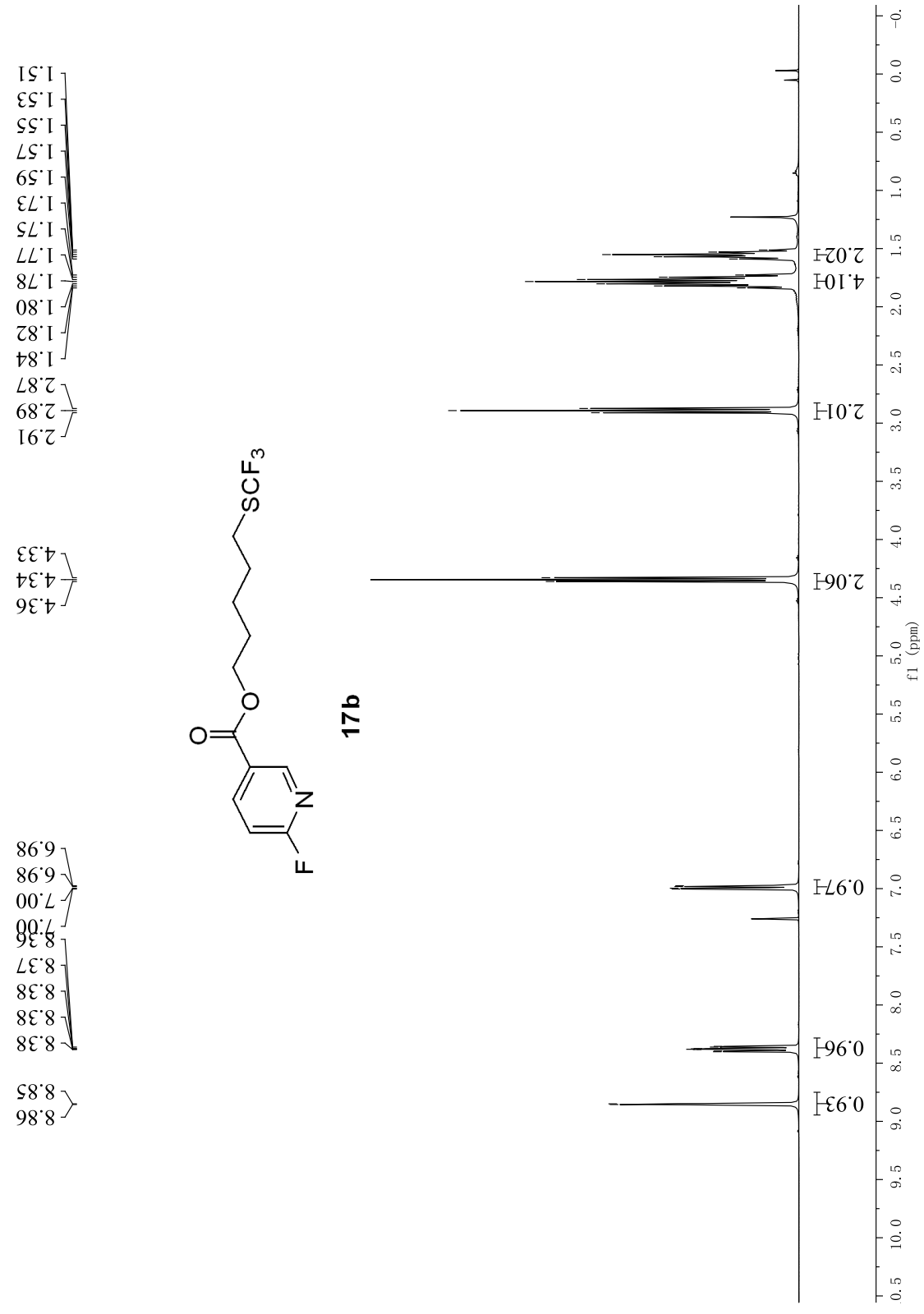


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16b**

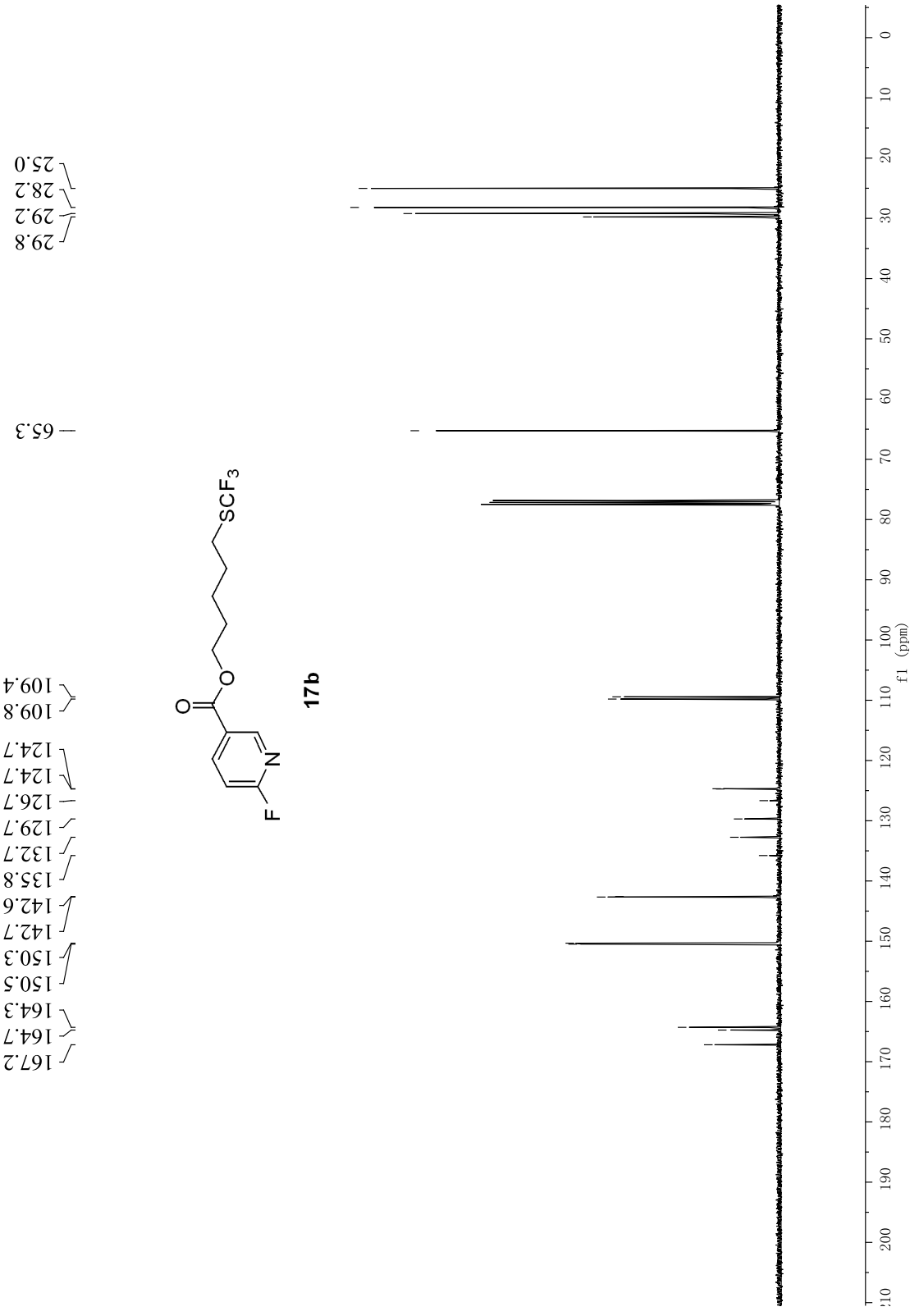


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16b**

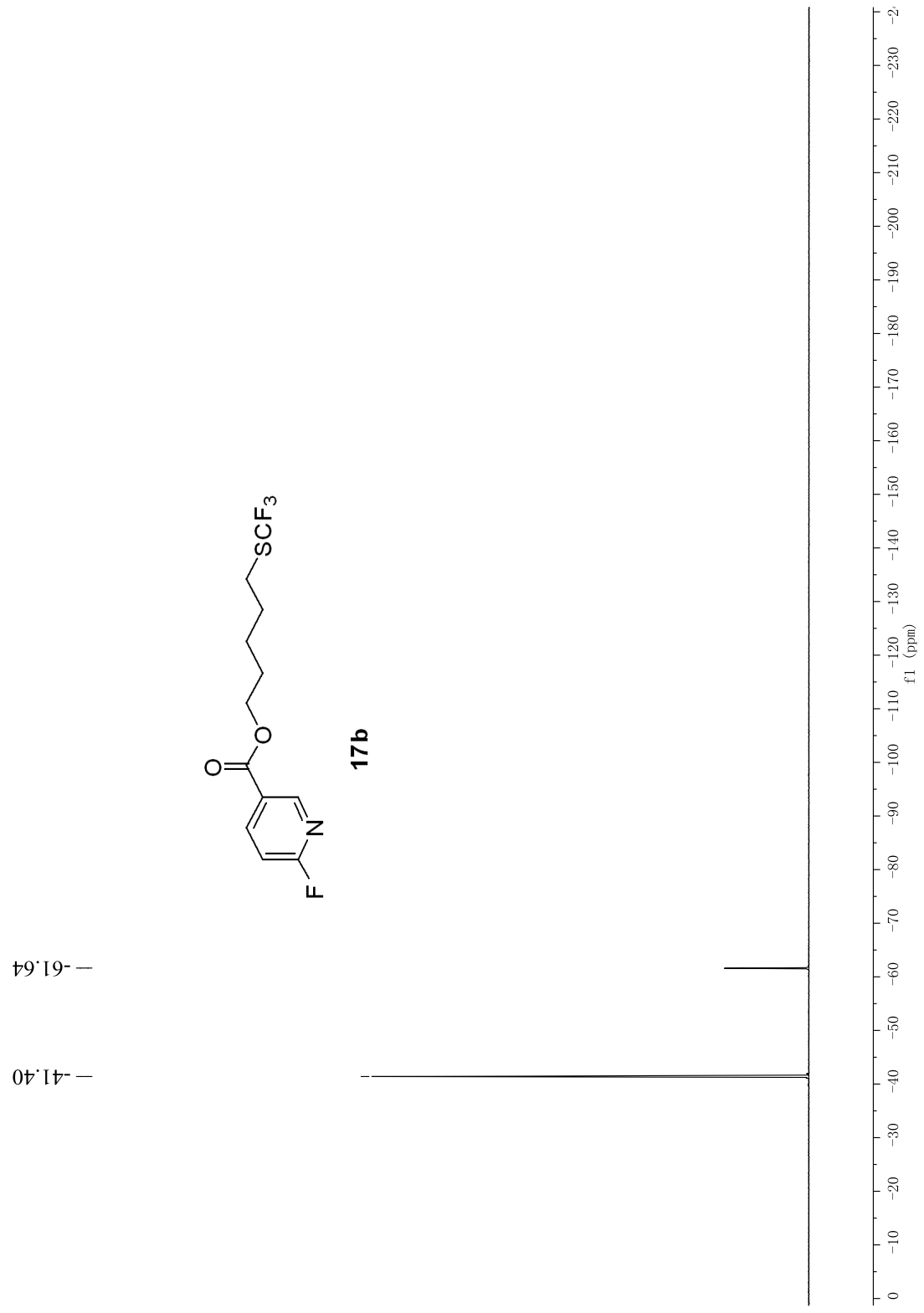
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **16b**



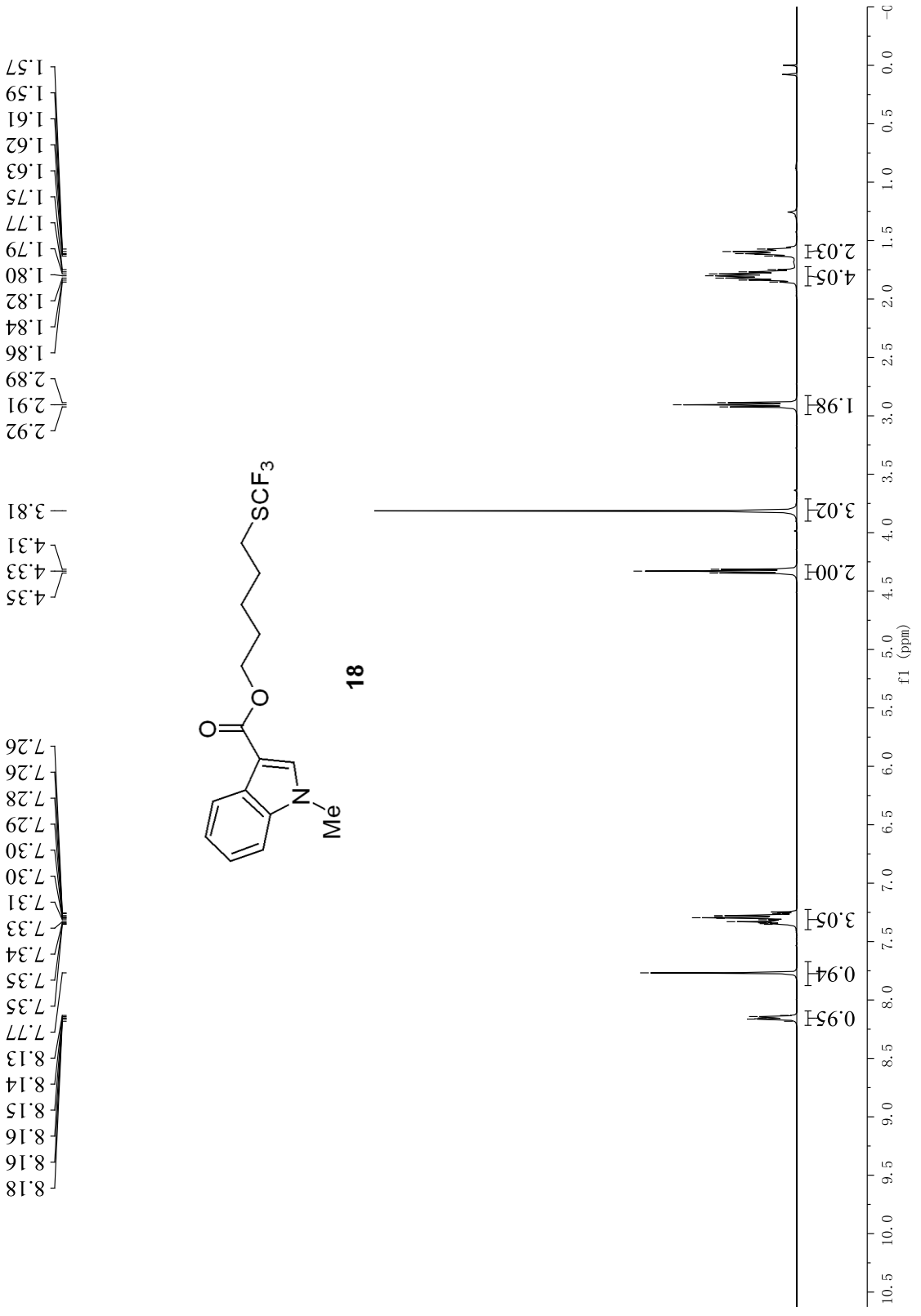
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **17b**



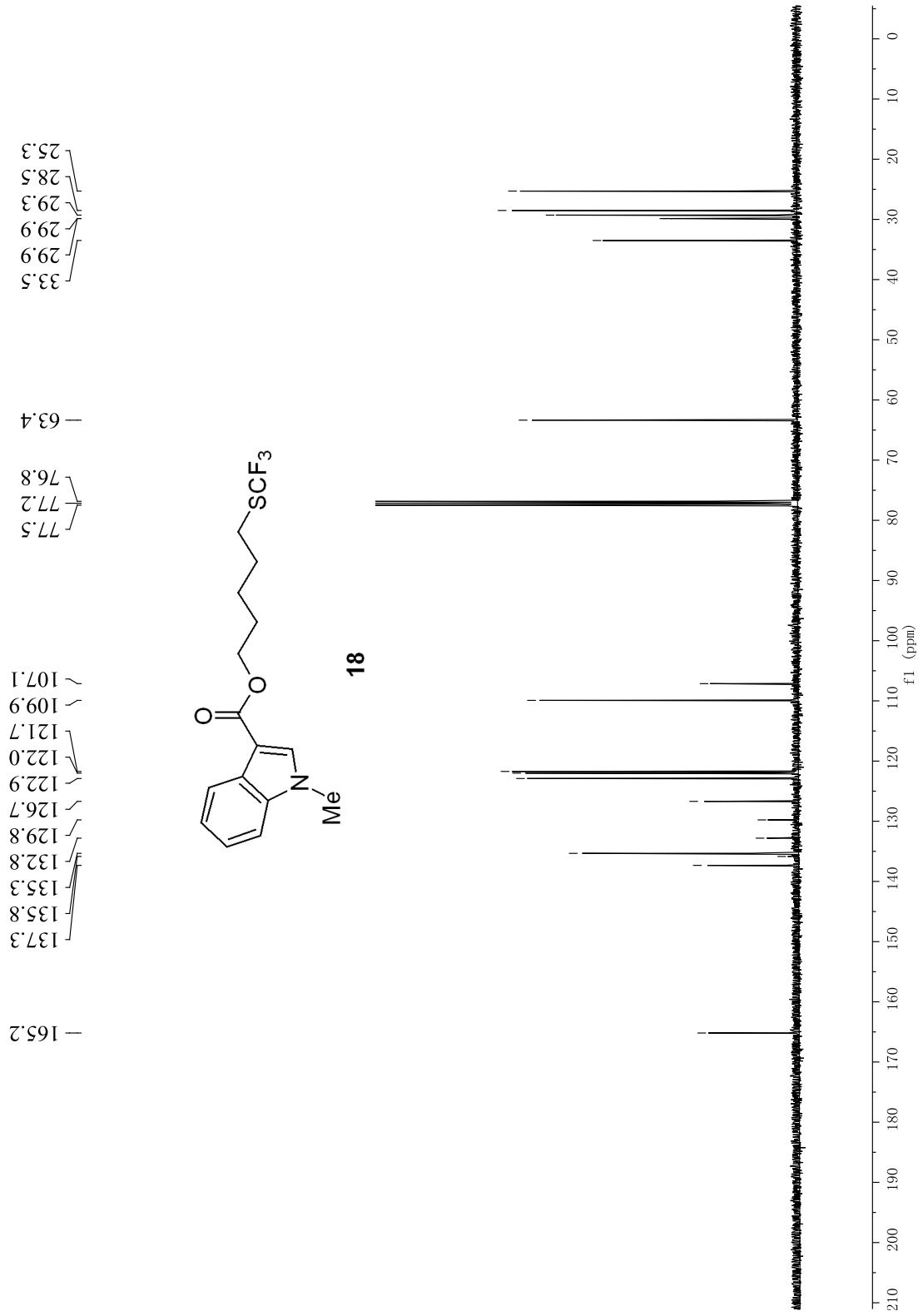
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **17b**



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

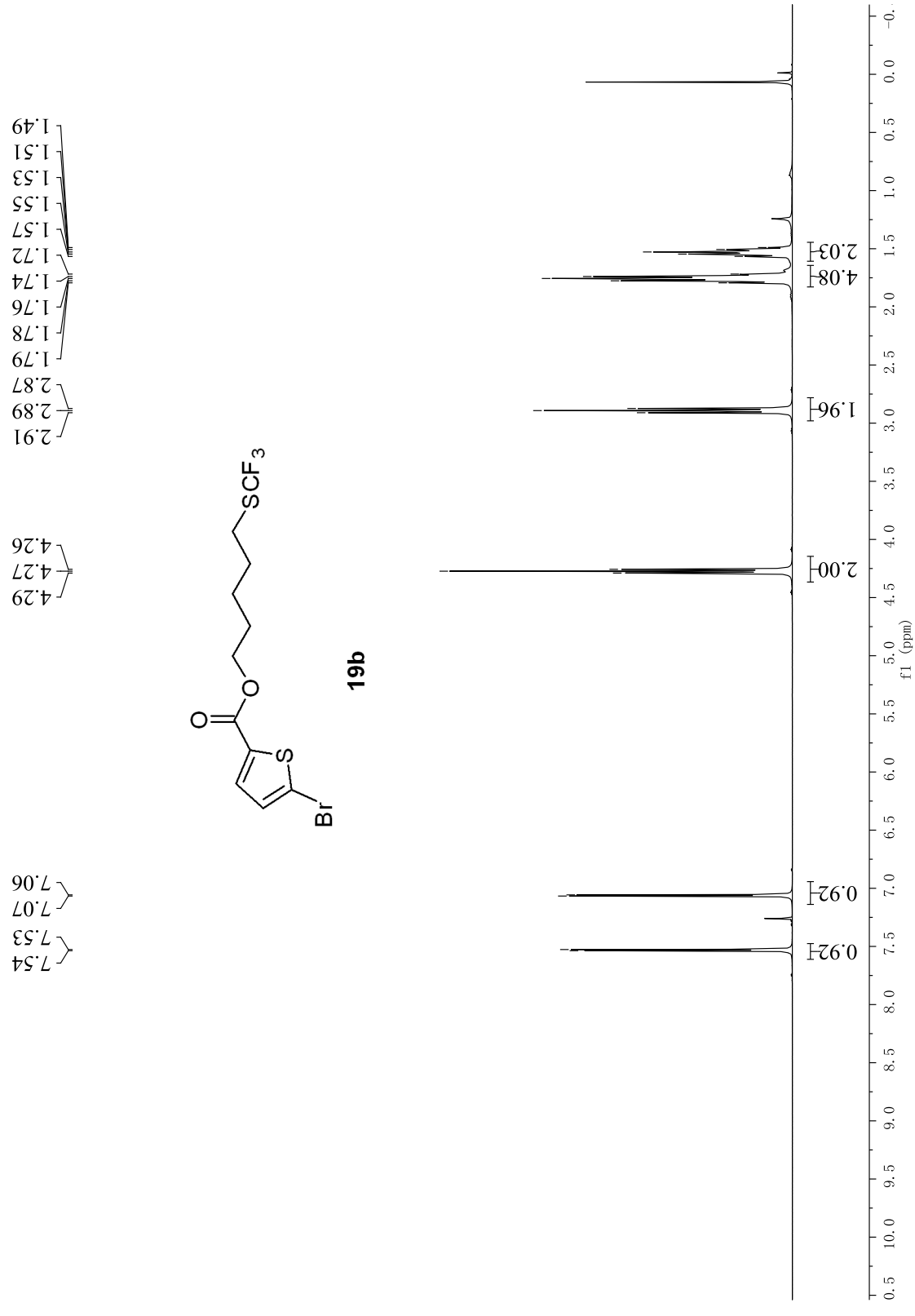


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **18**

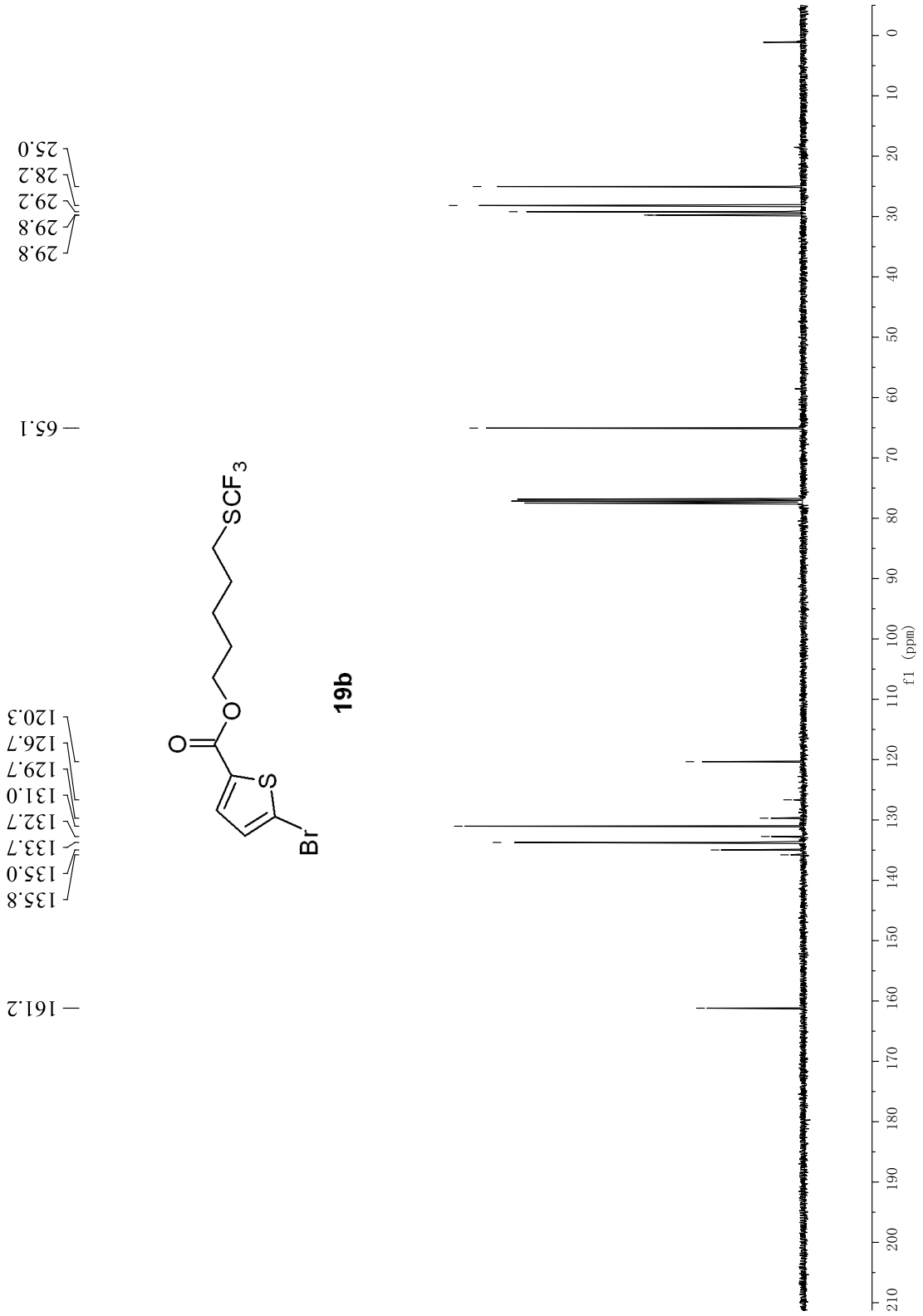


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **18**

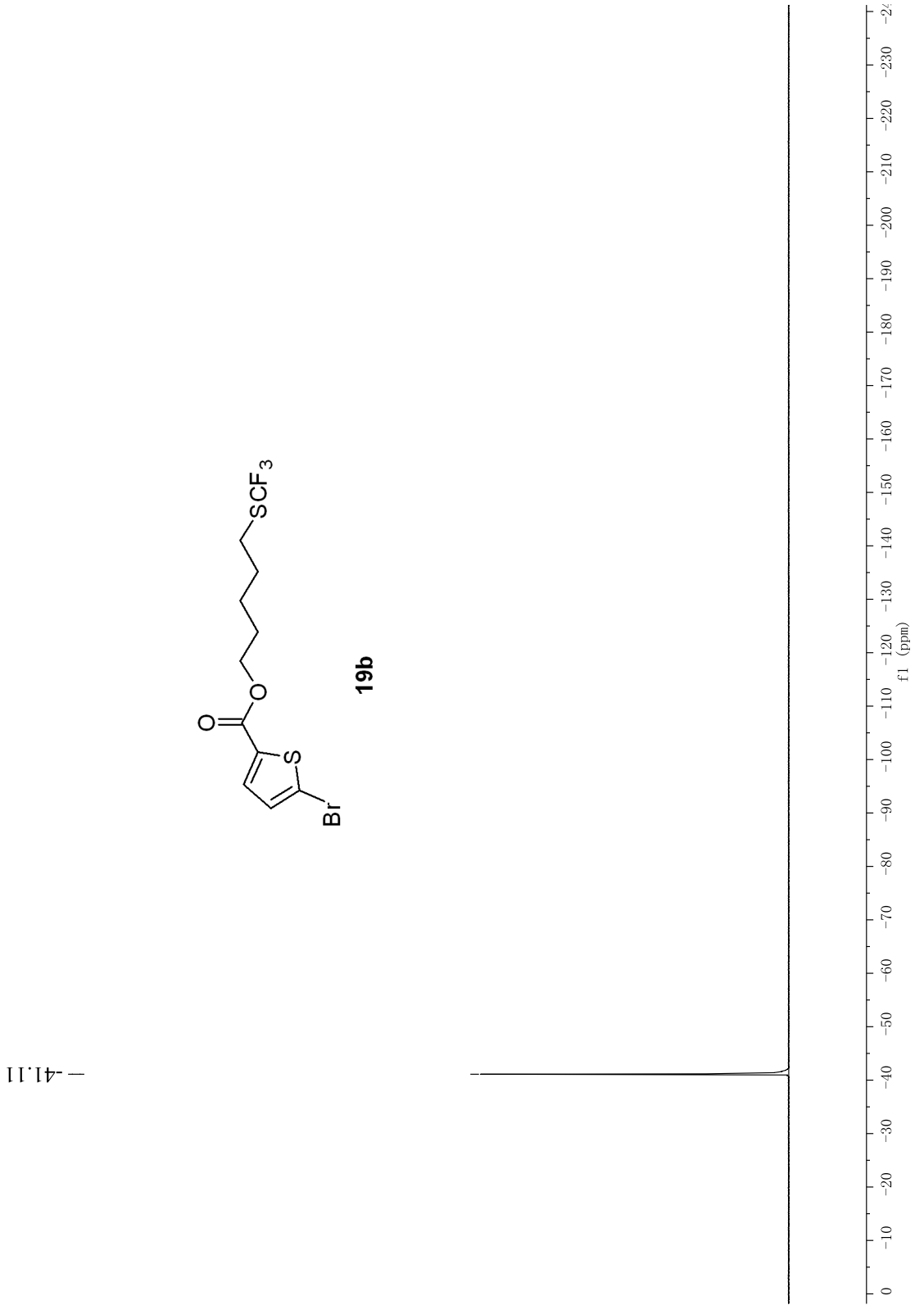
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **18**



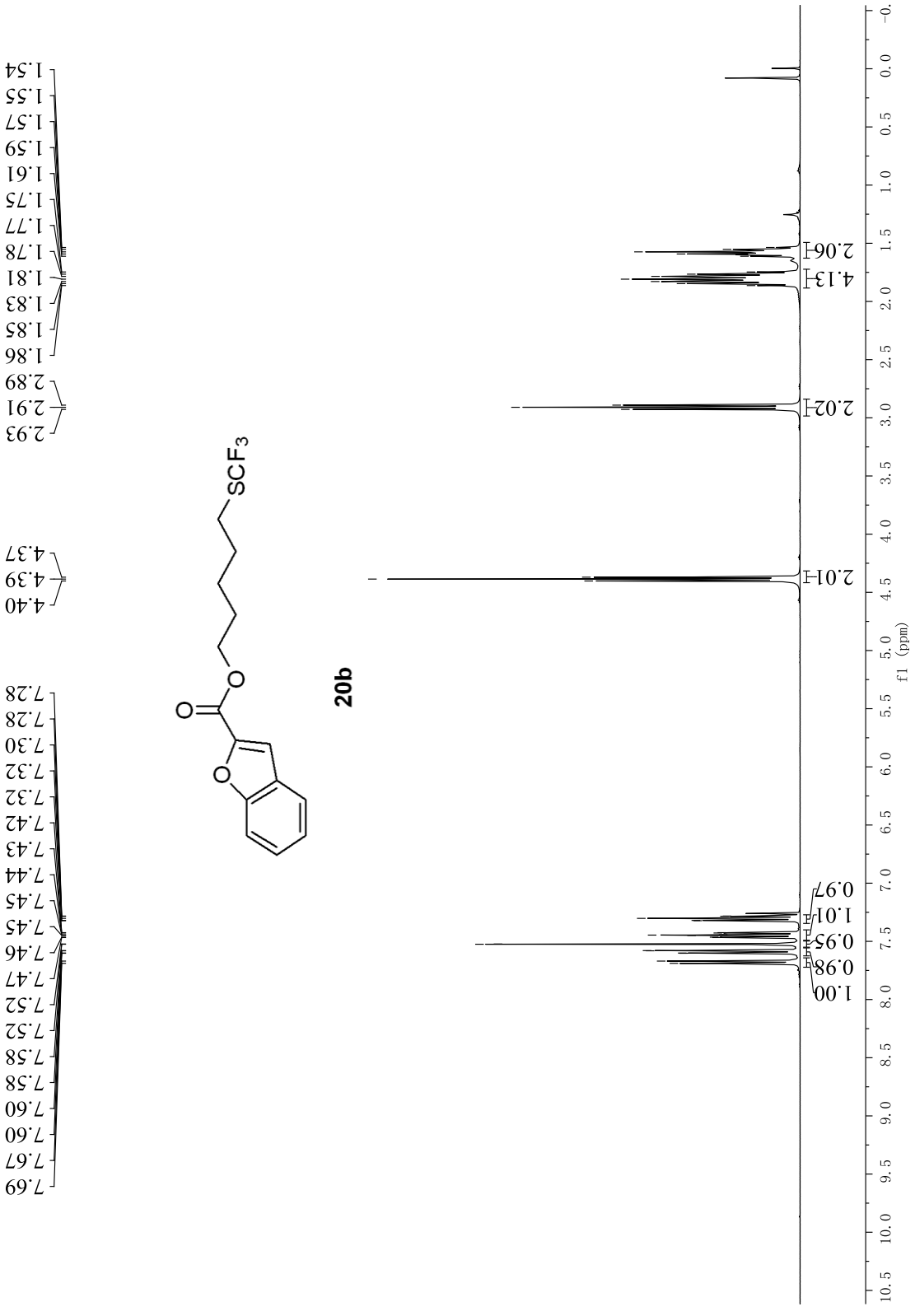
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **19b**



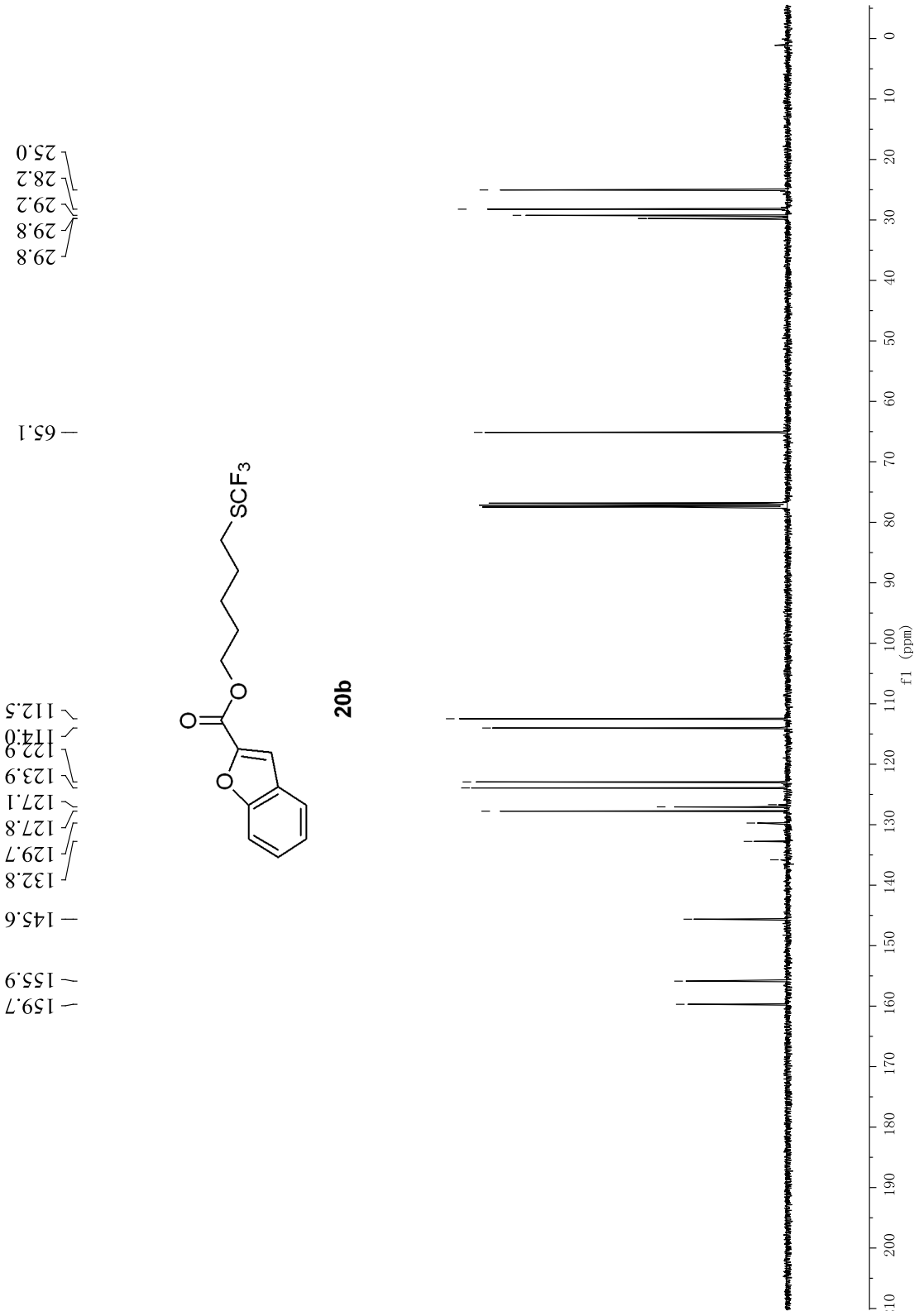
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **19b**



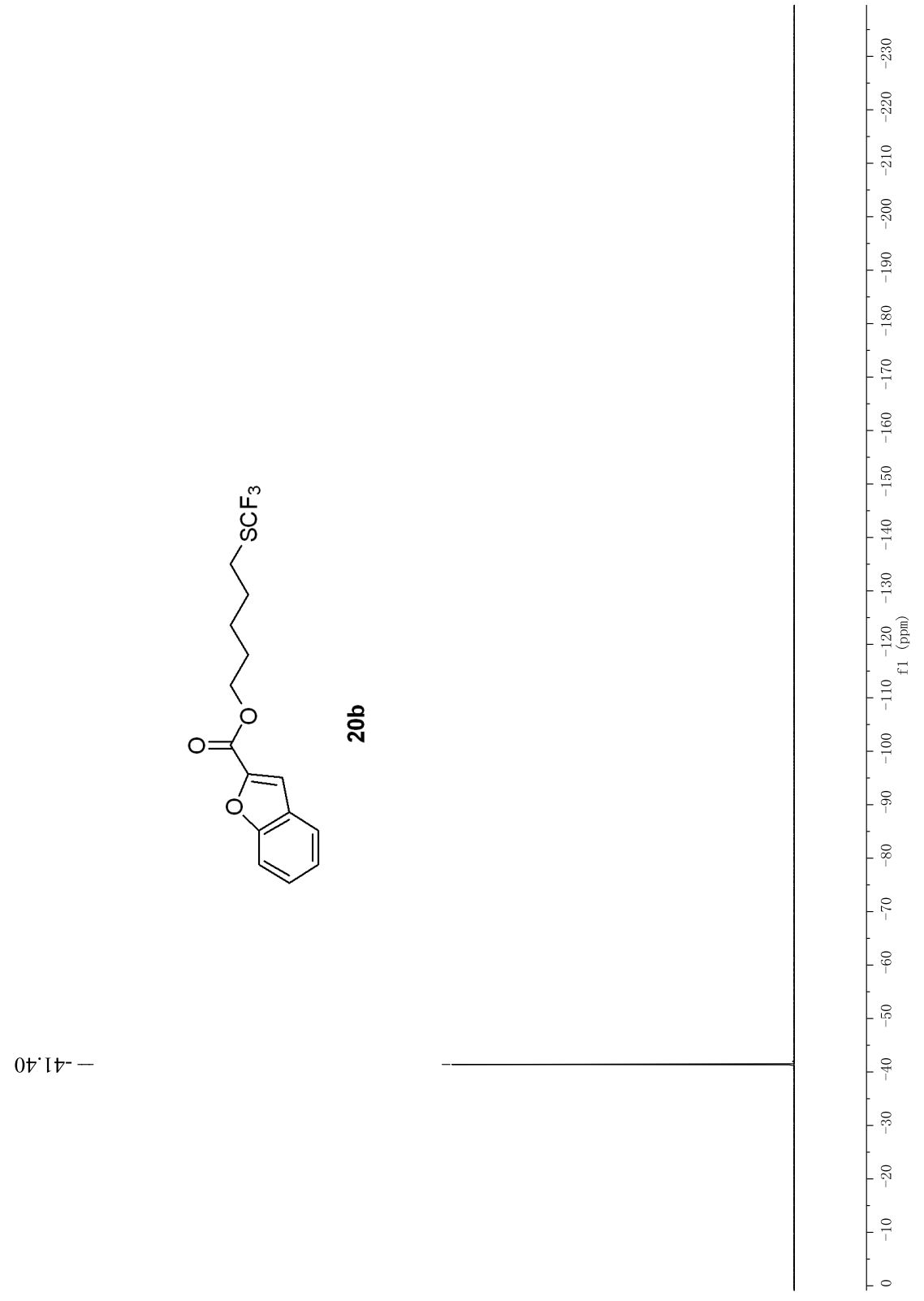
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **19b**



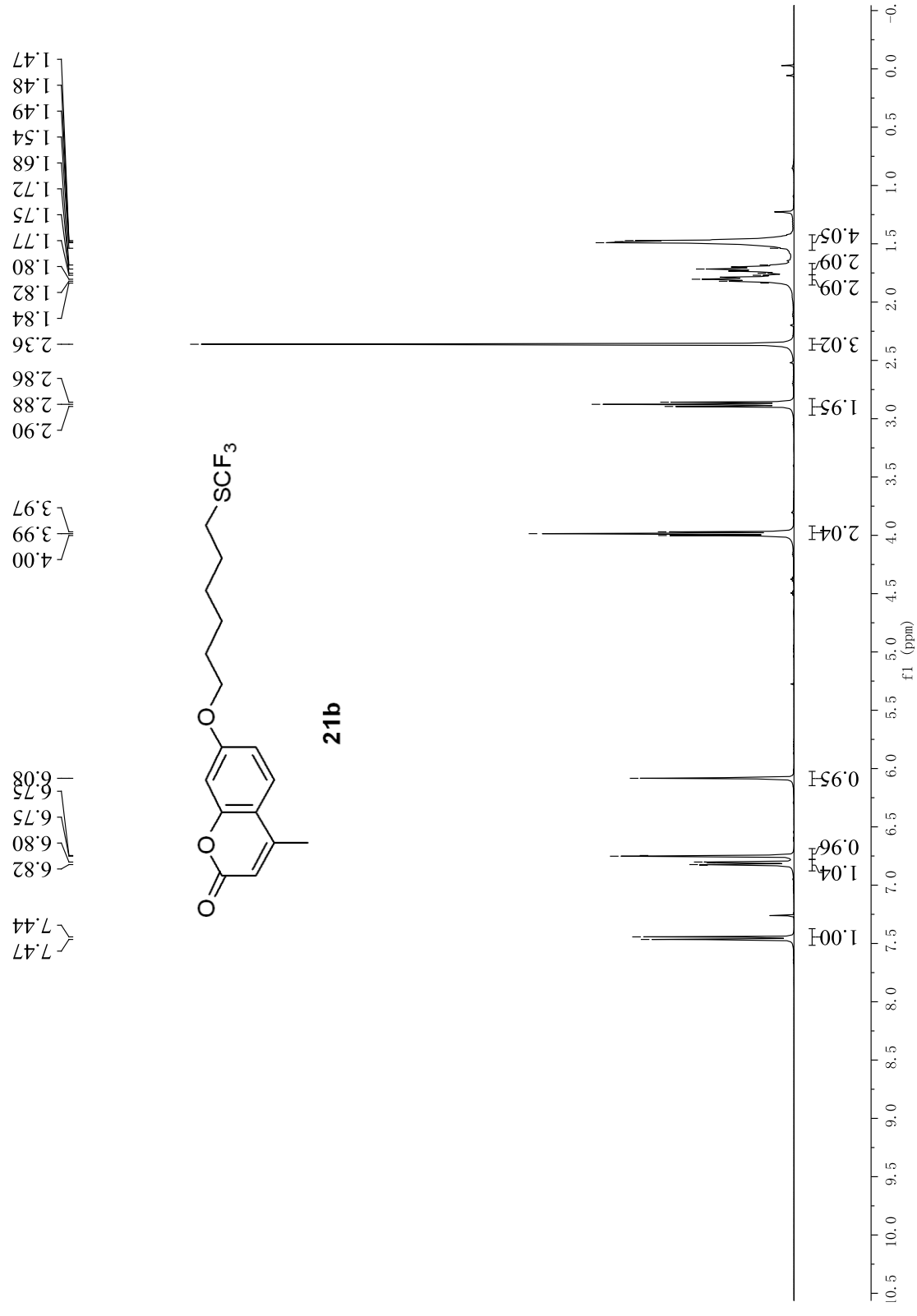
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20b**



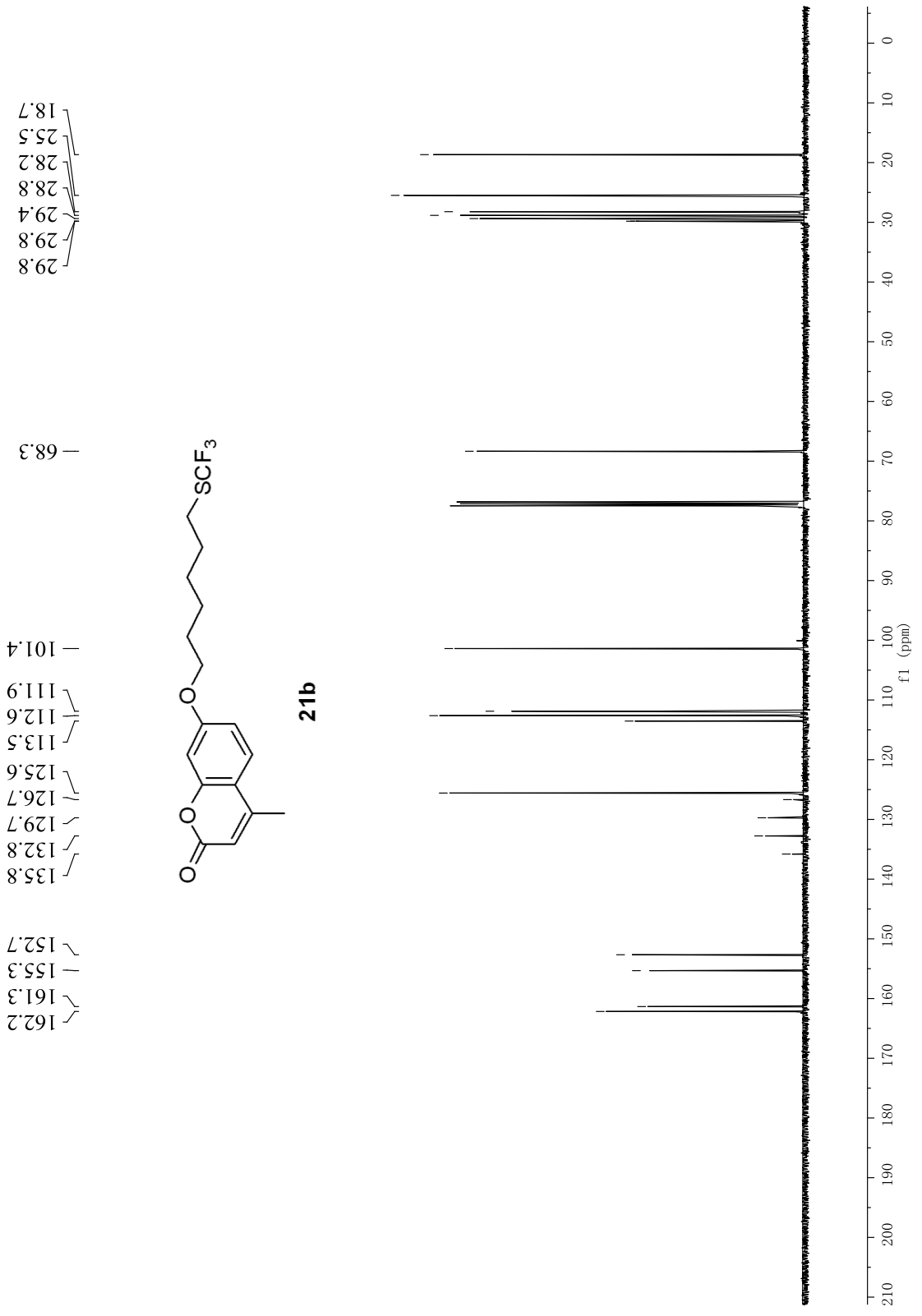
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **20b**



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

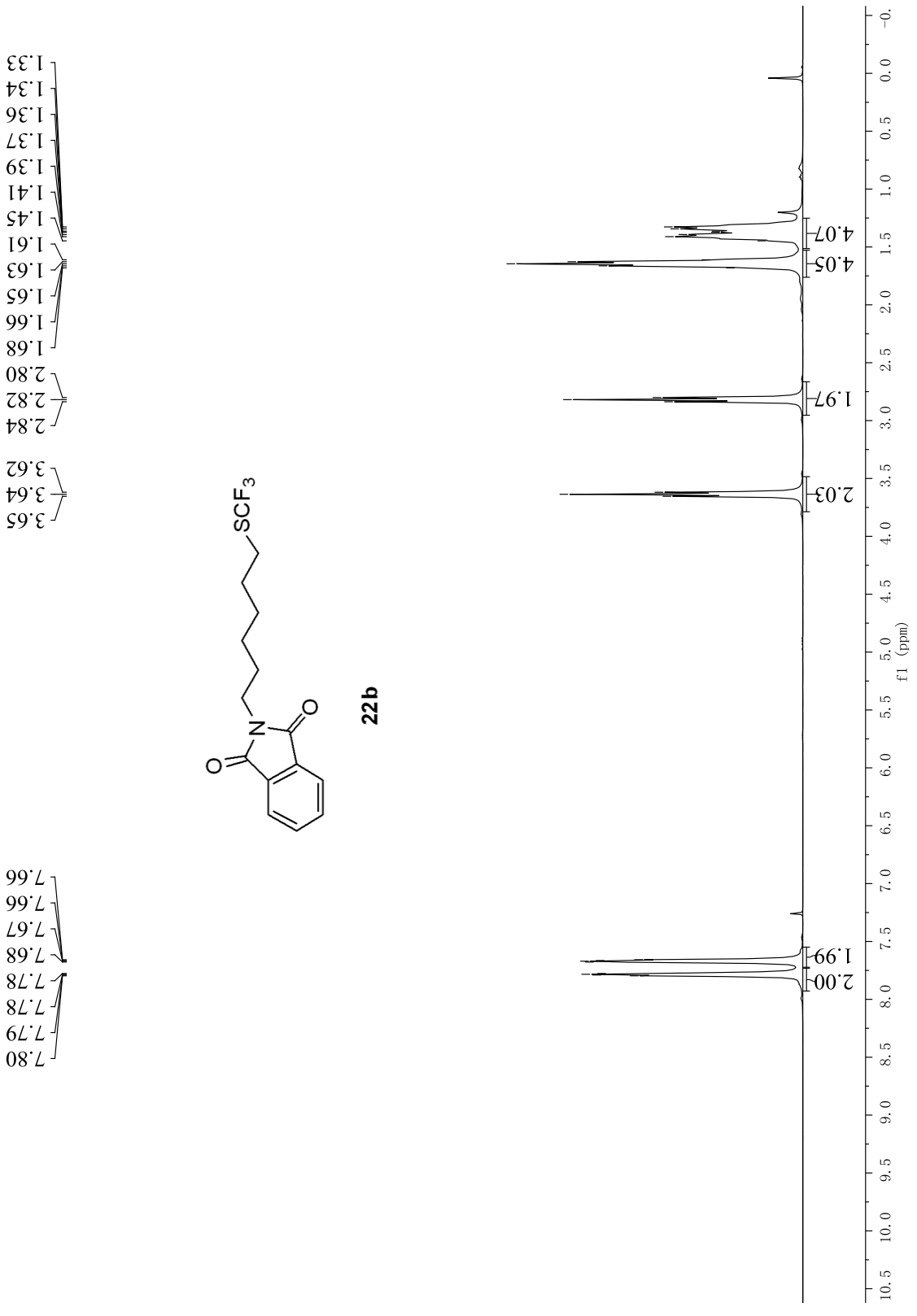


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **21b**

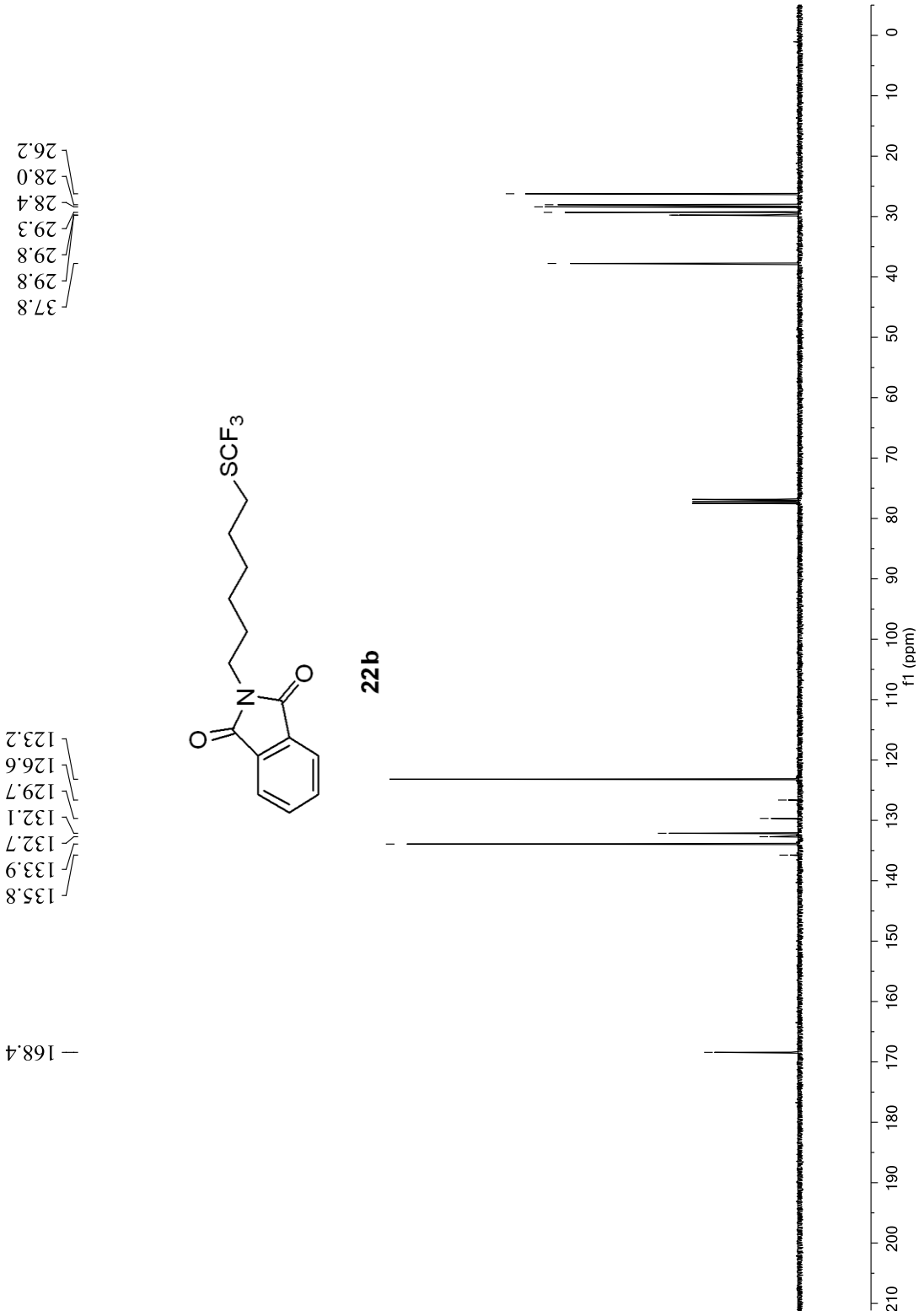


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **21b**

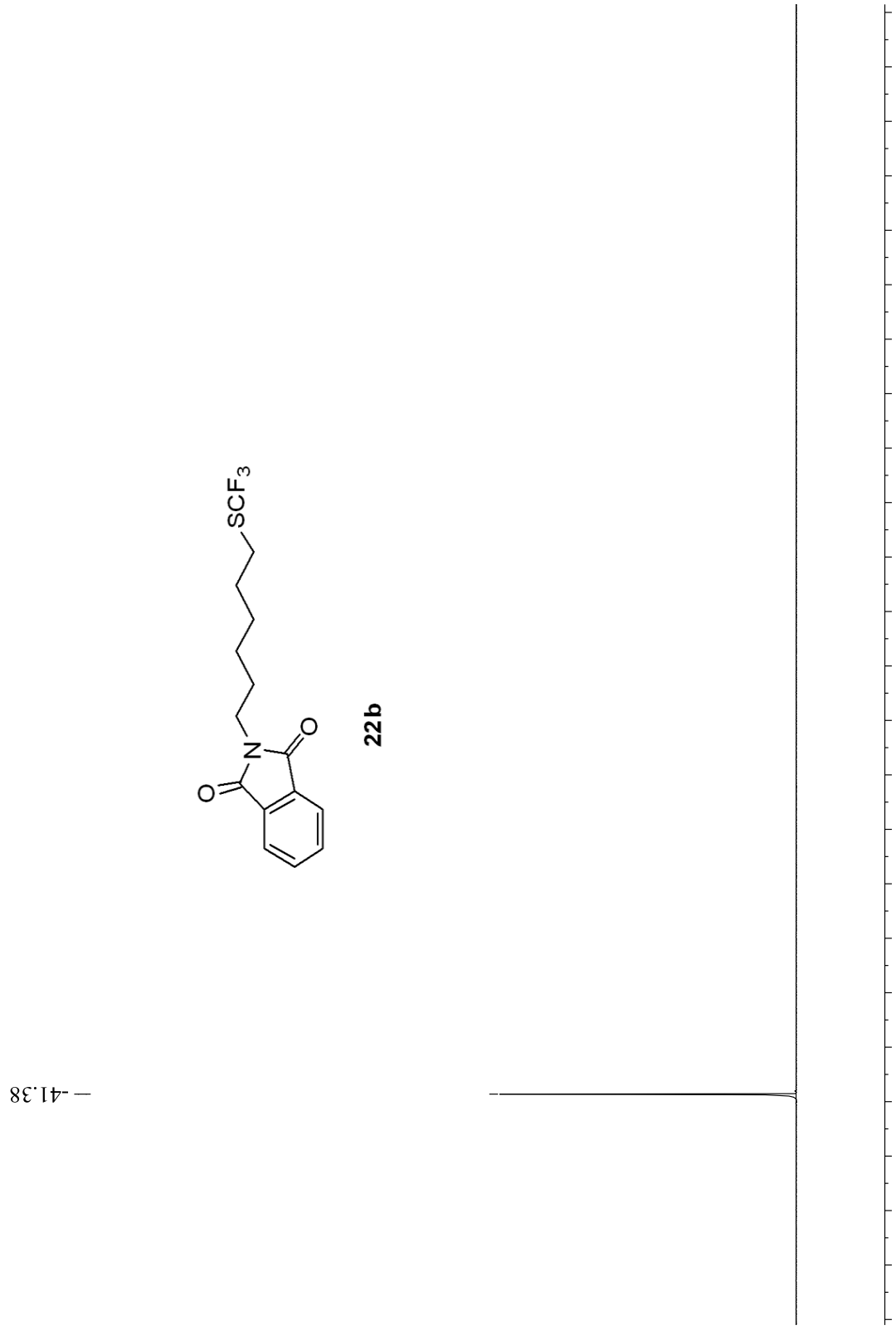
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **21b**



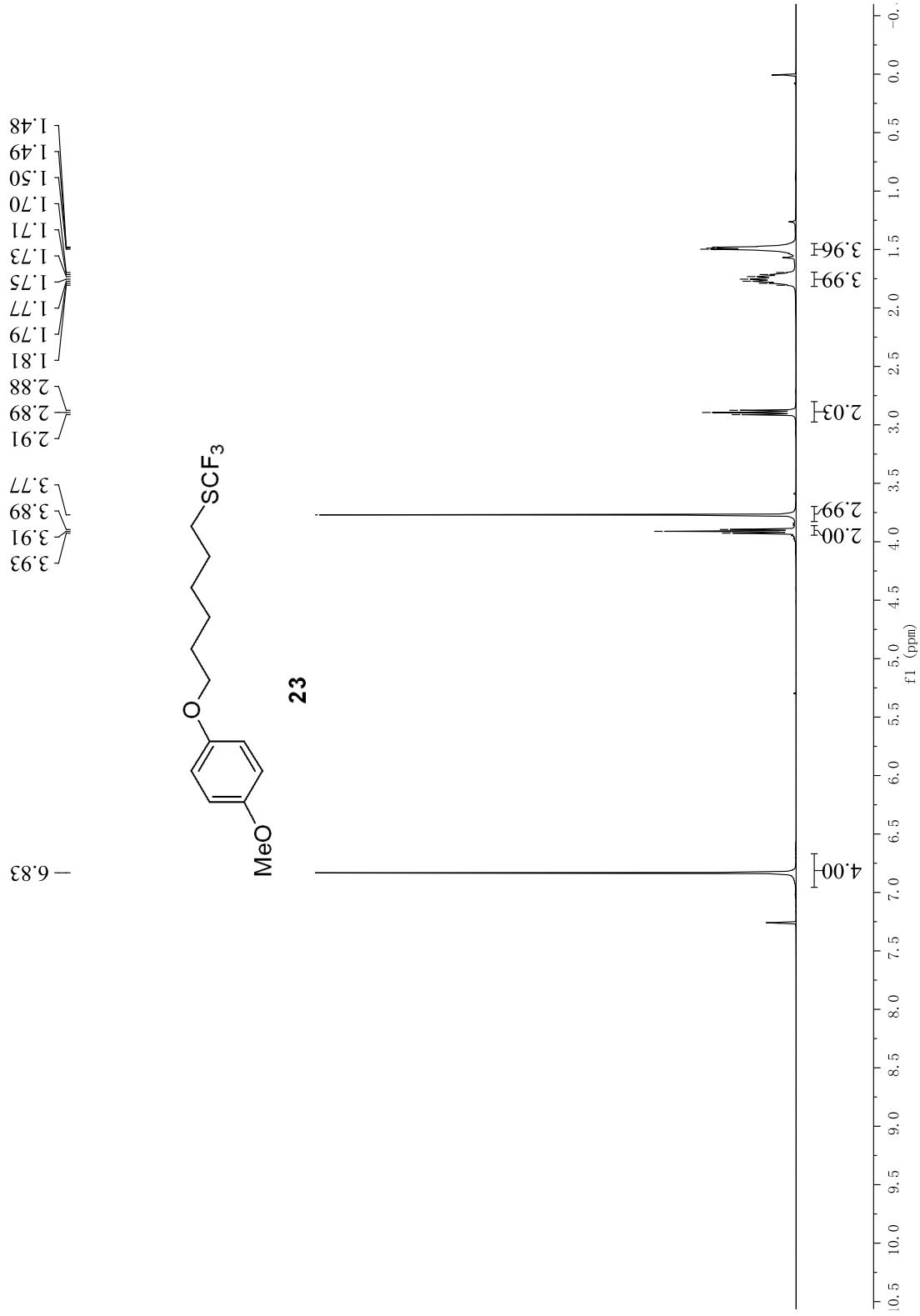
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **22b**



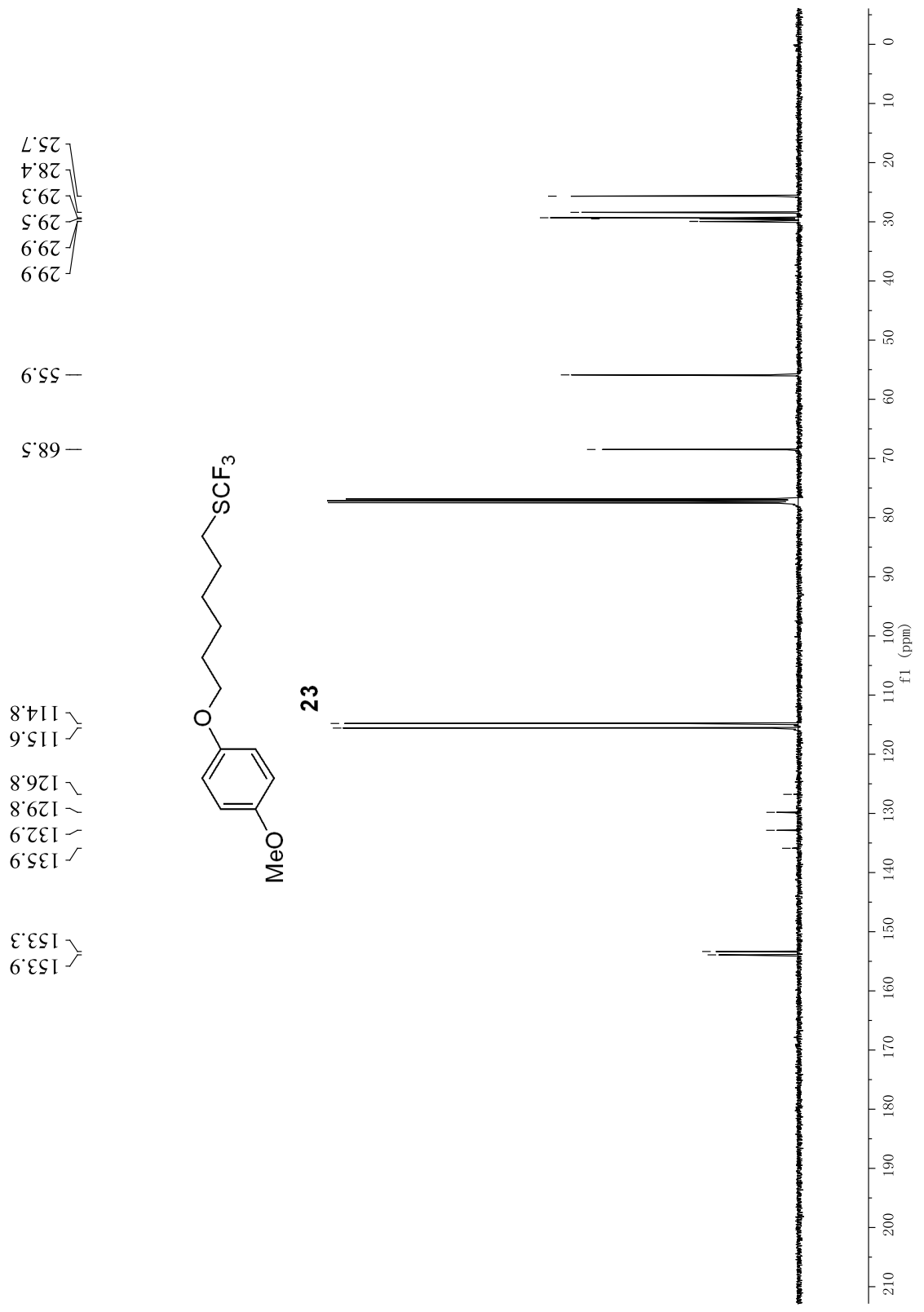
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **22b**



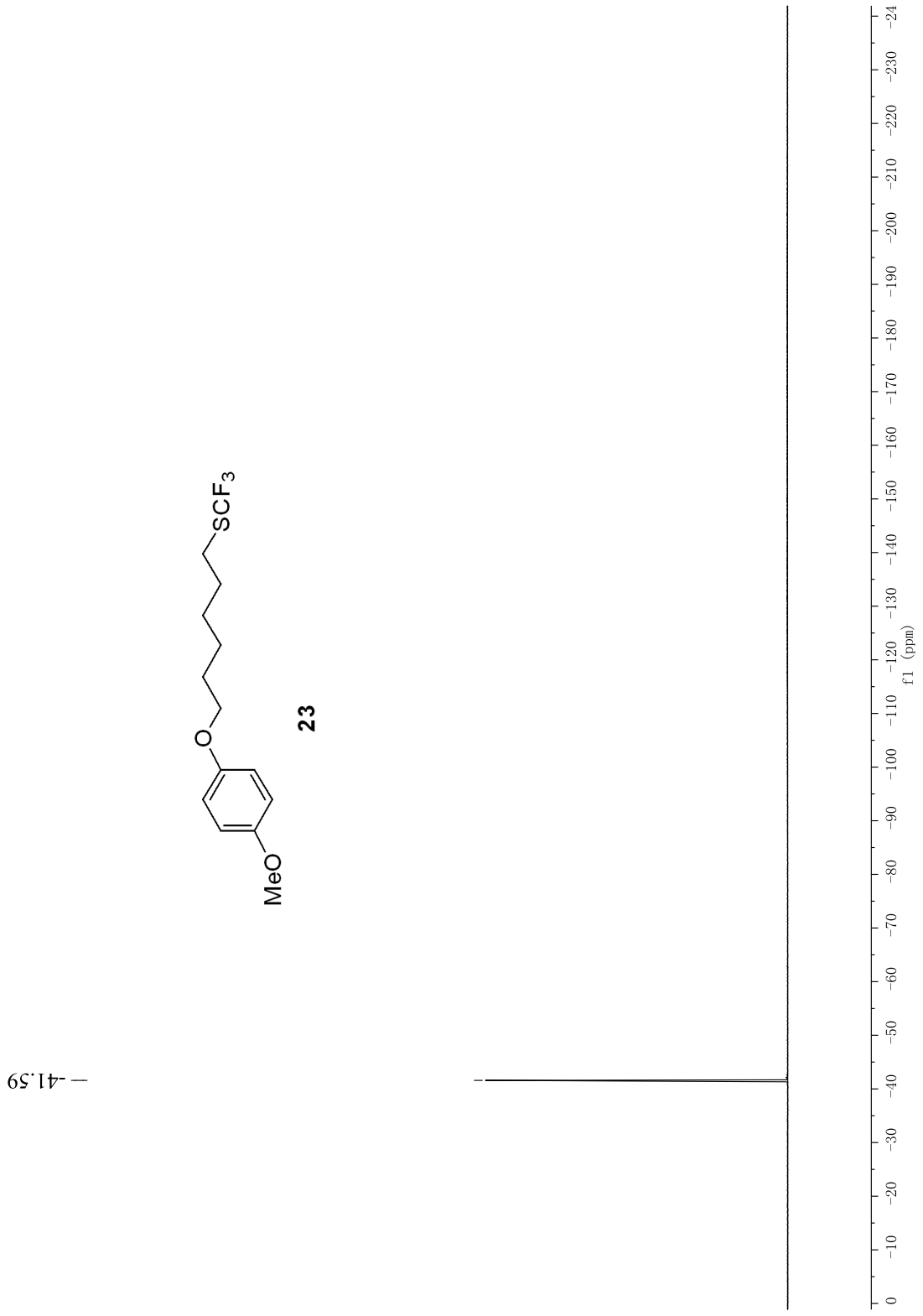
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **22b**



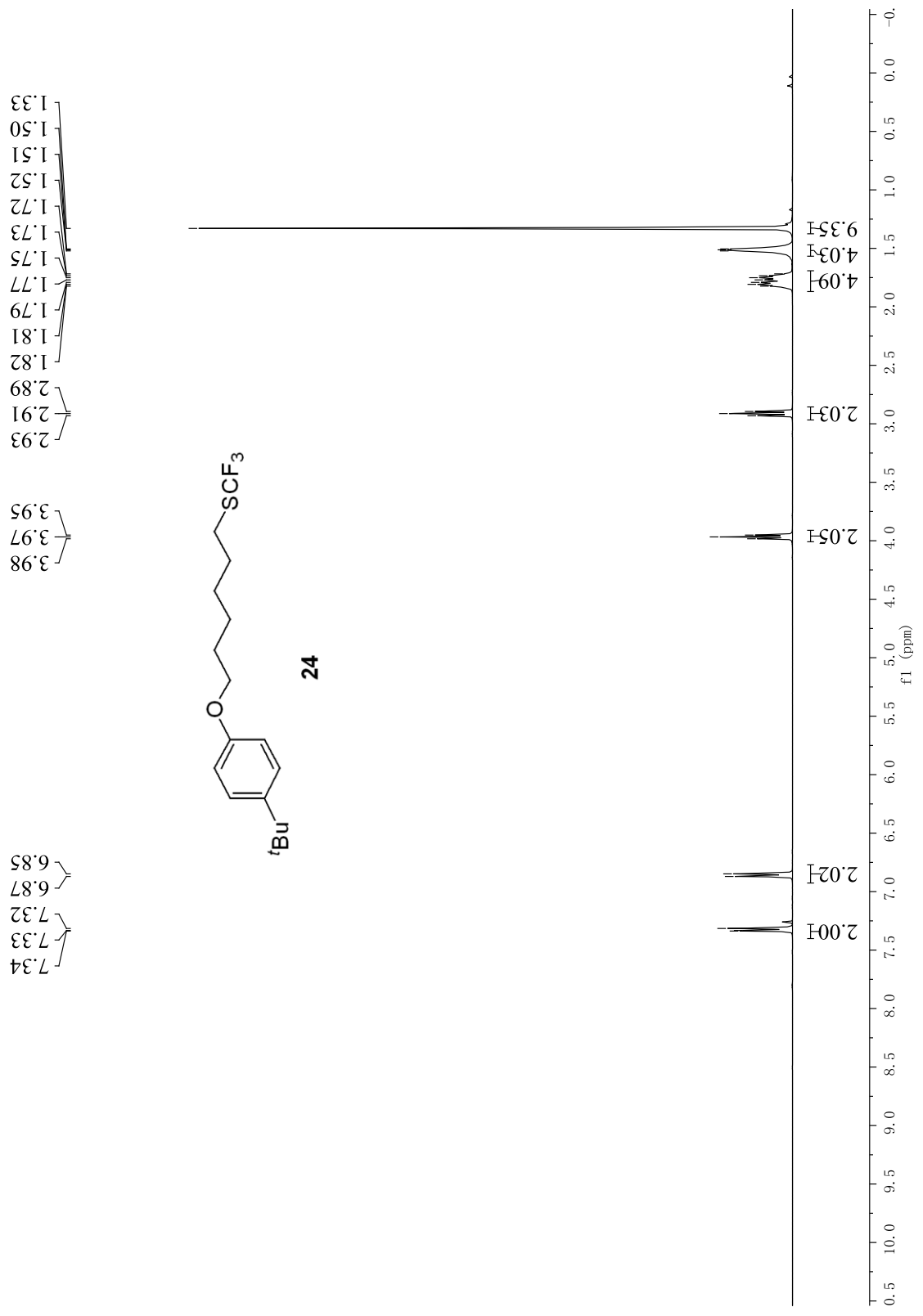
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **23**



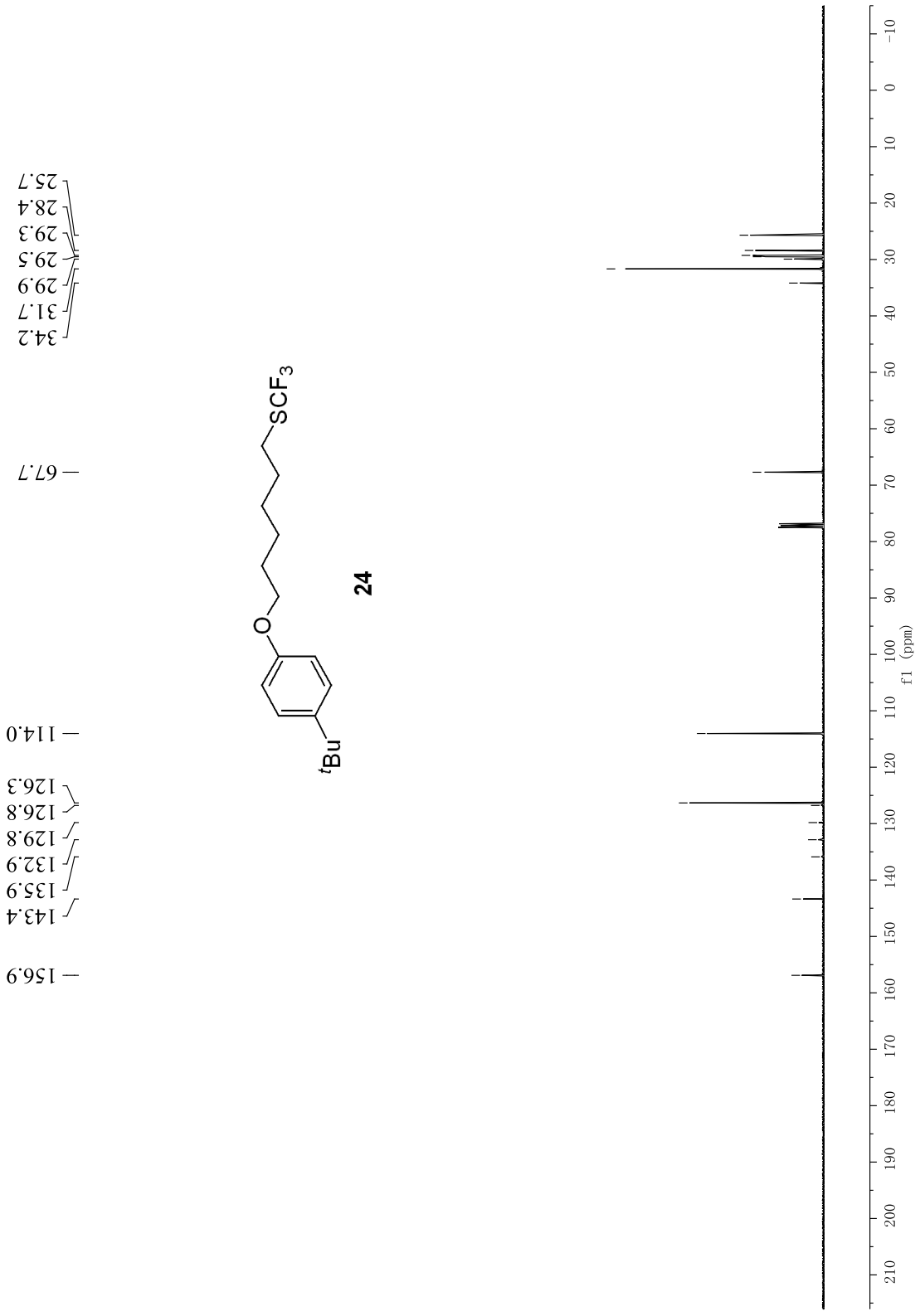
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **23**



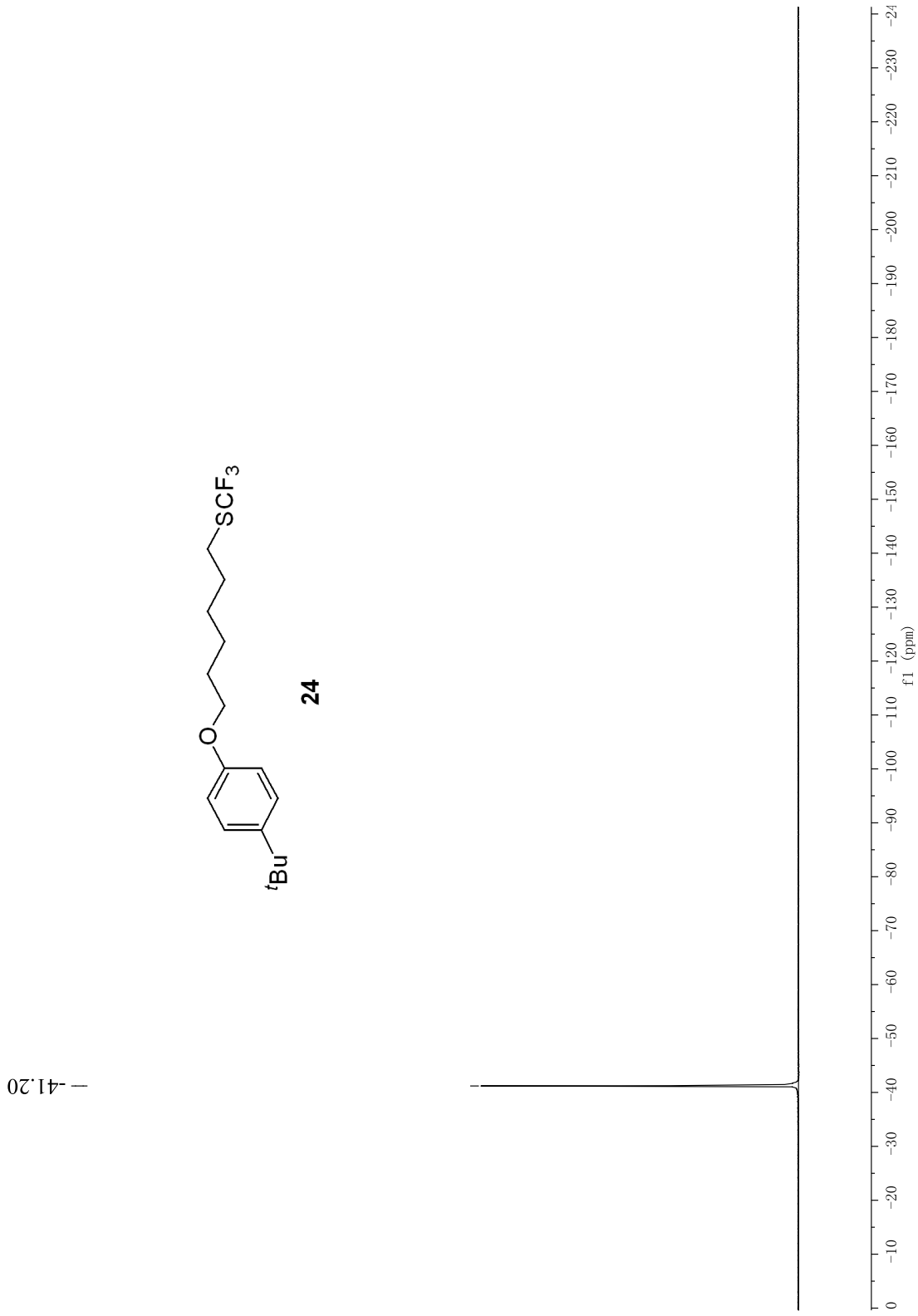
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **23**



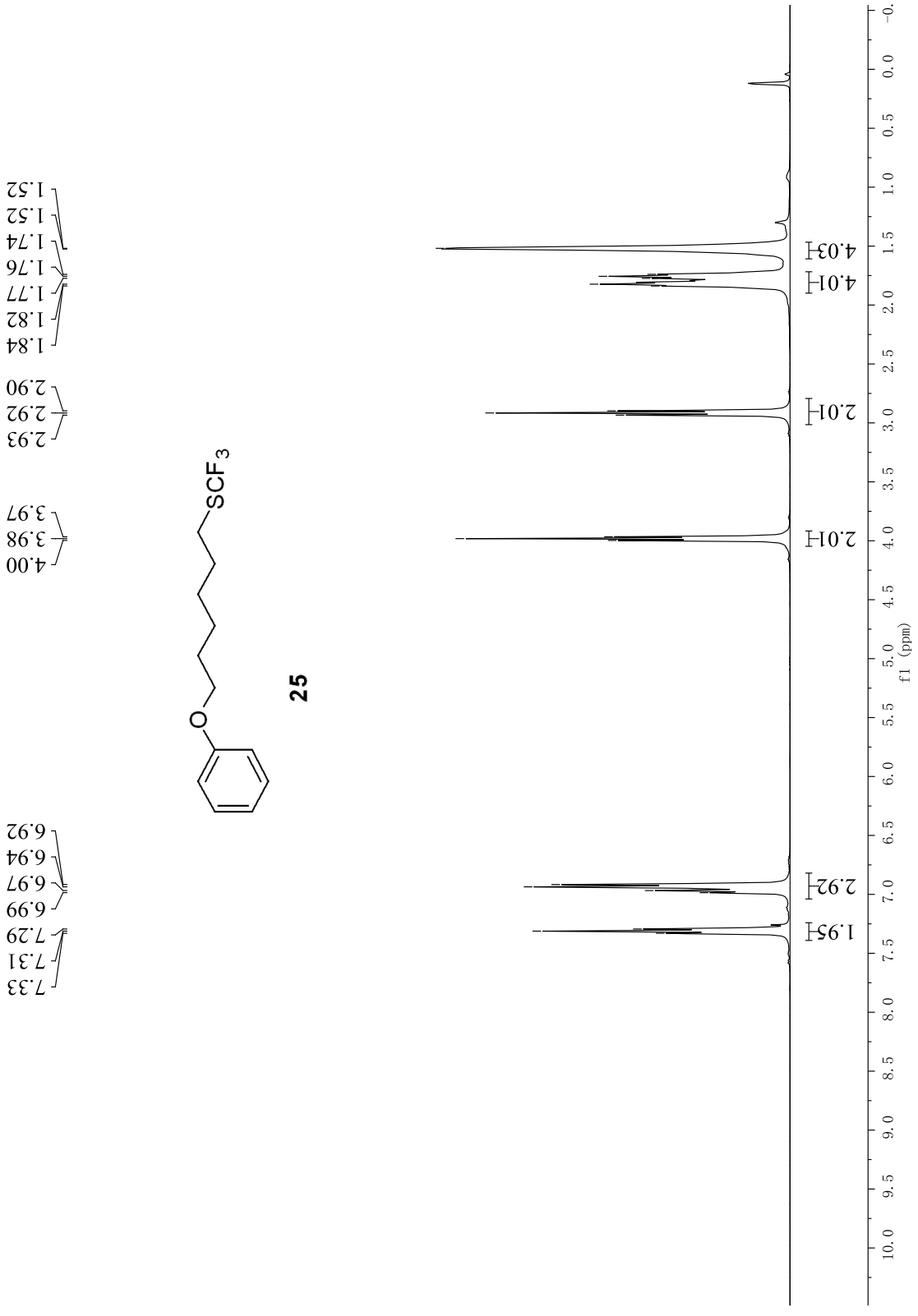
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **24**



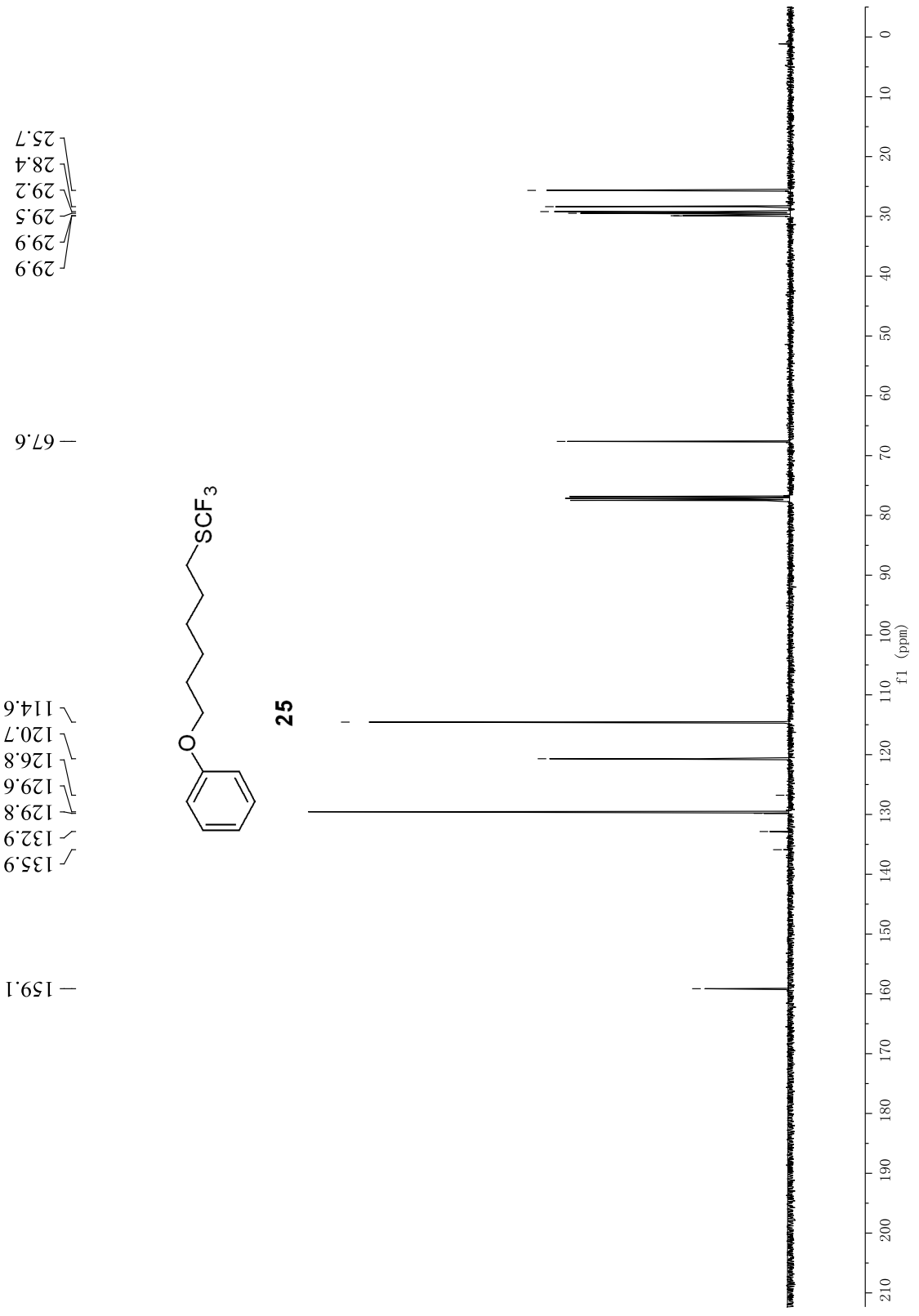
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **24**



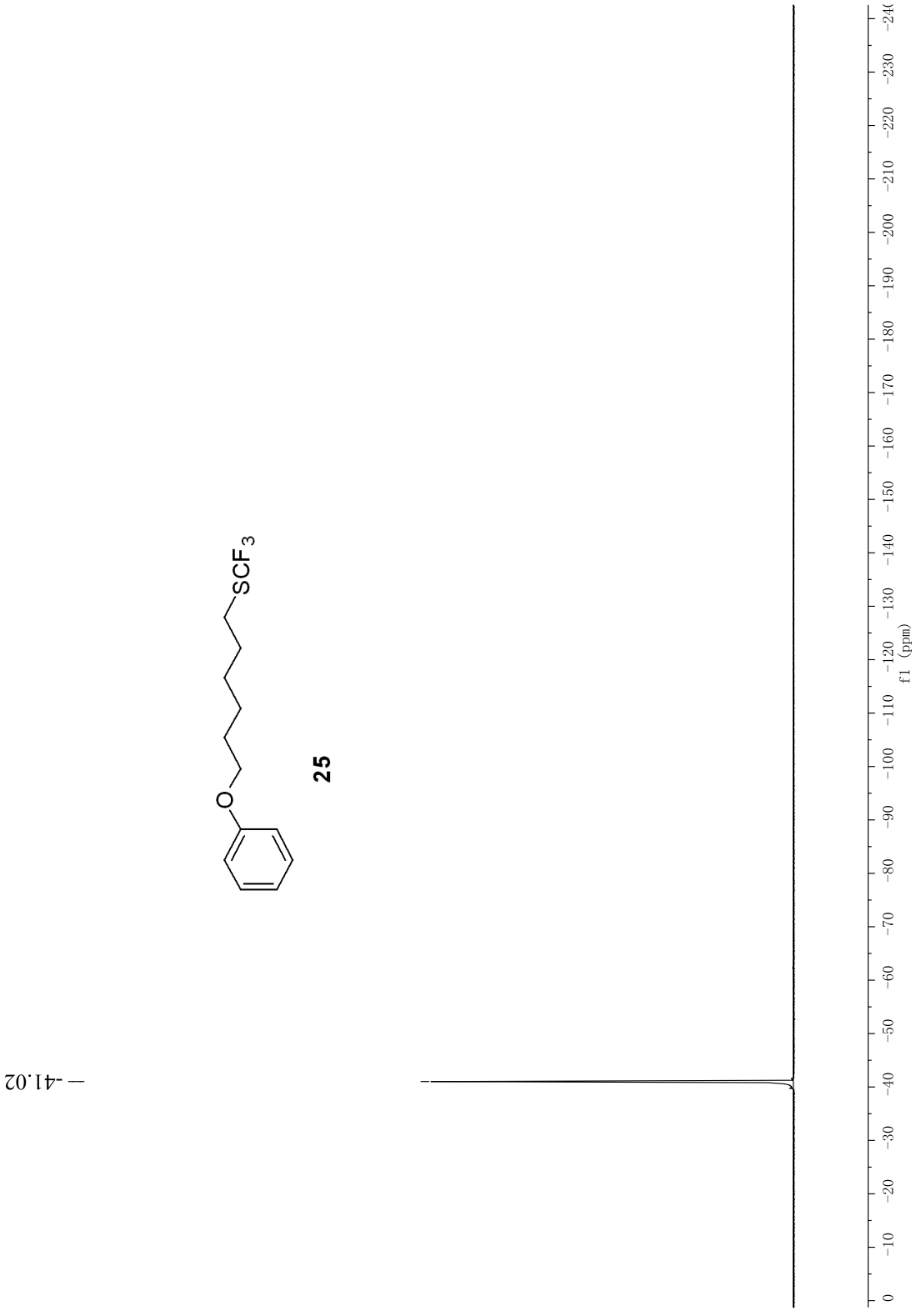
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **24**



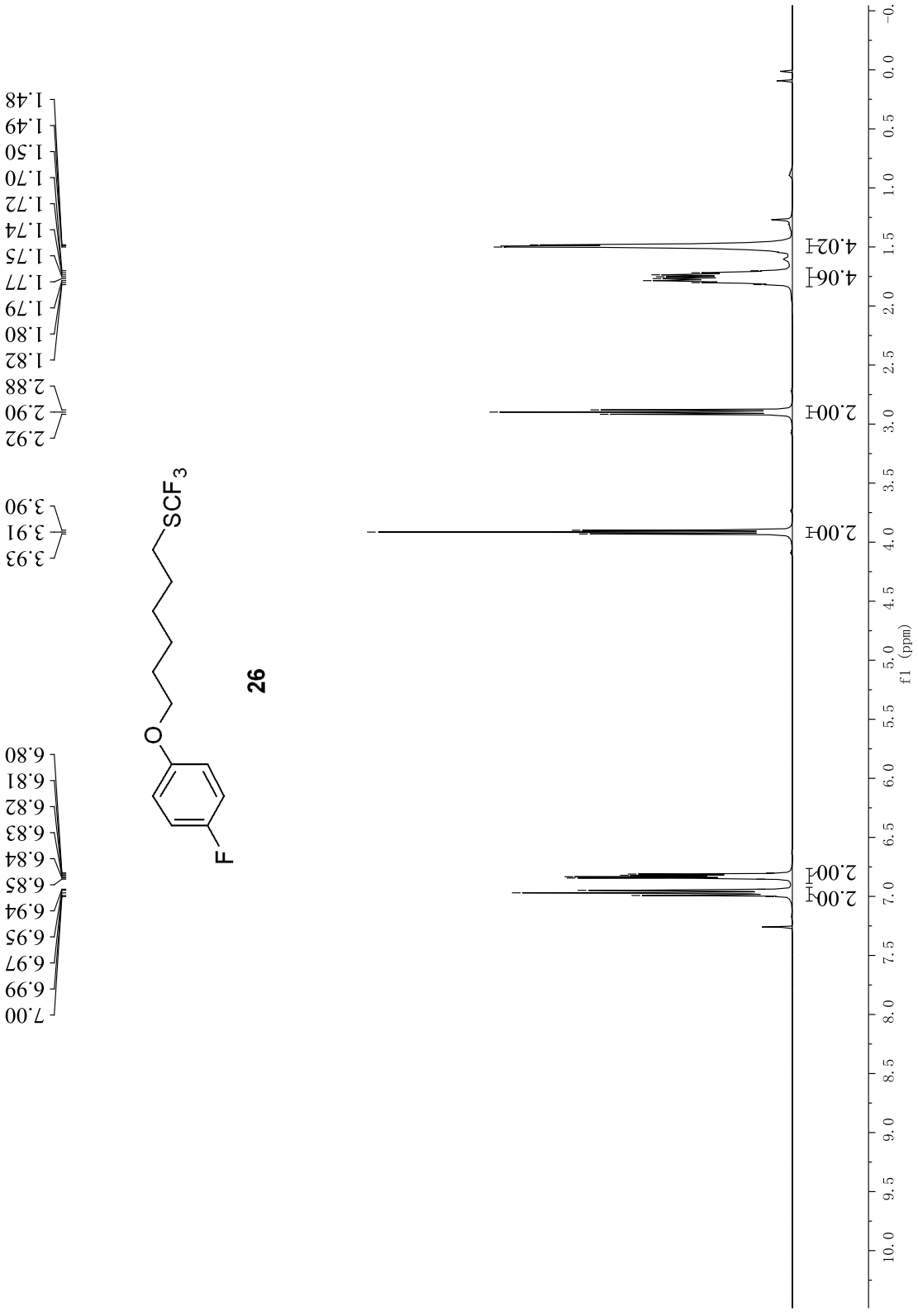
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **25**



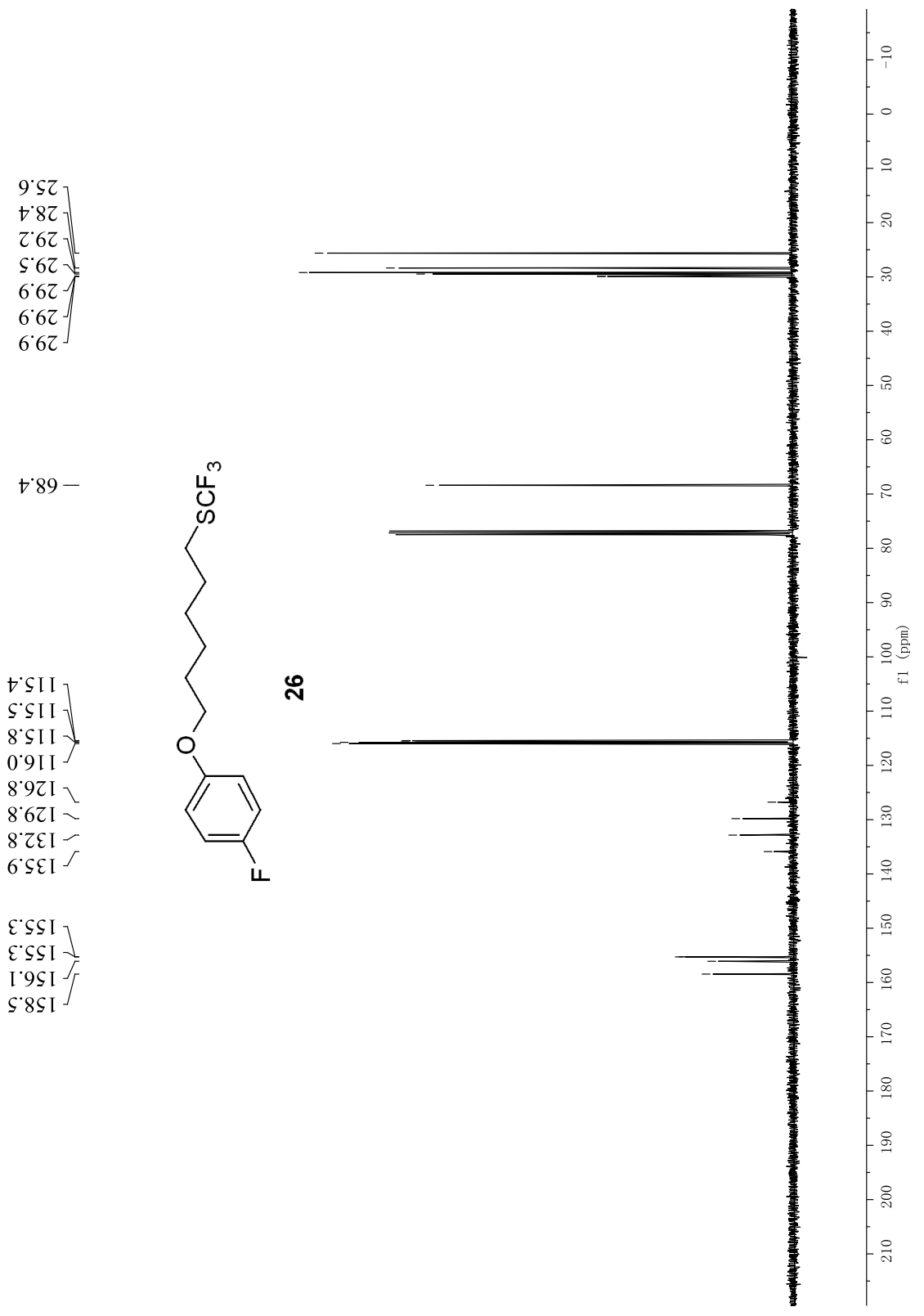
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **25**



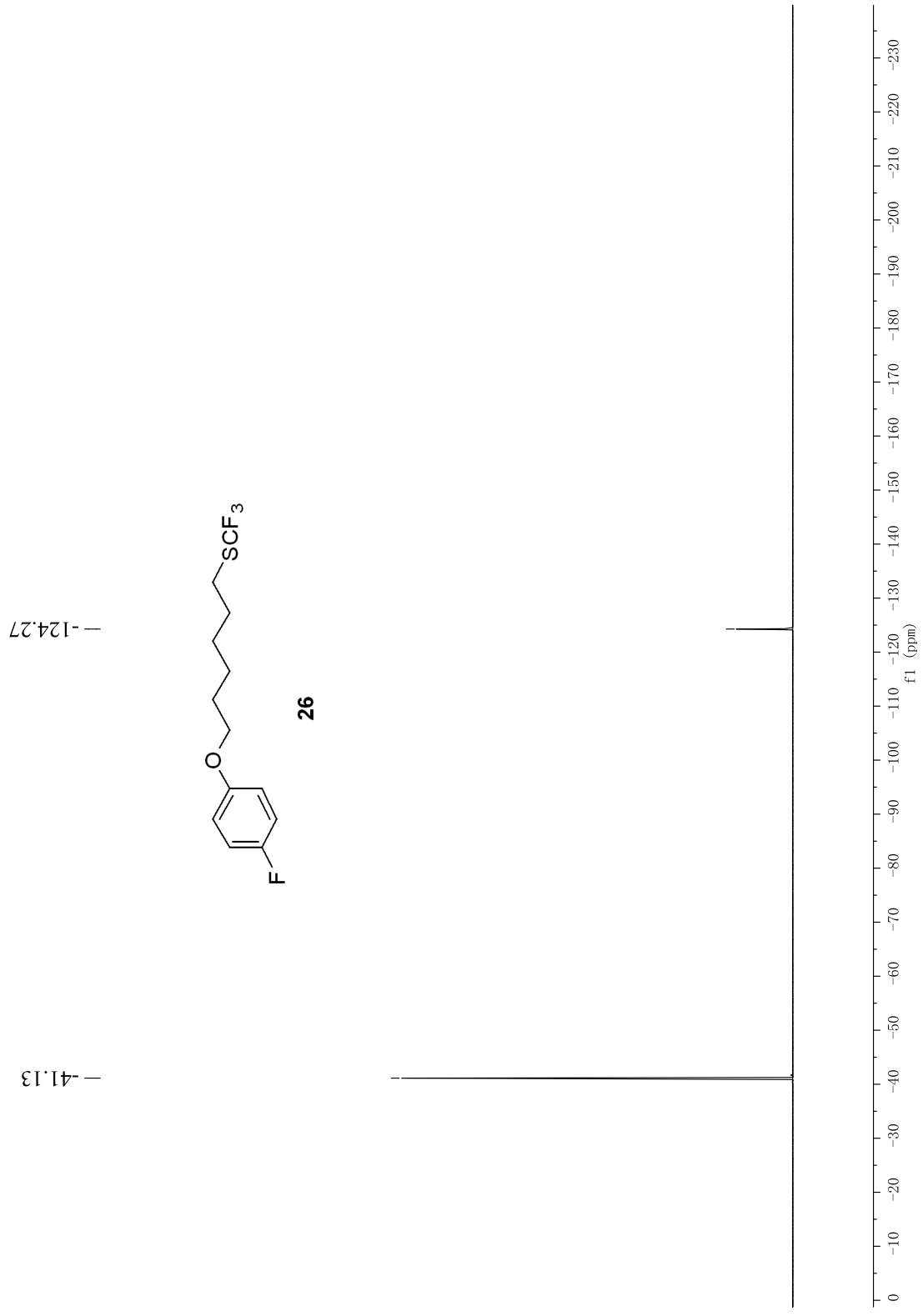
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **25**



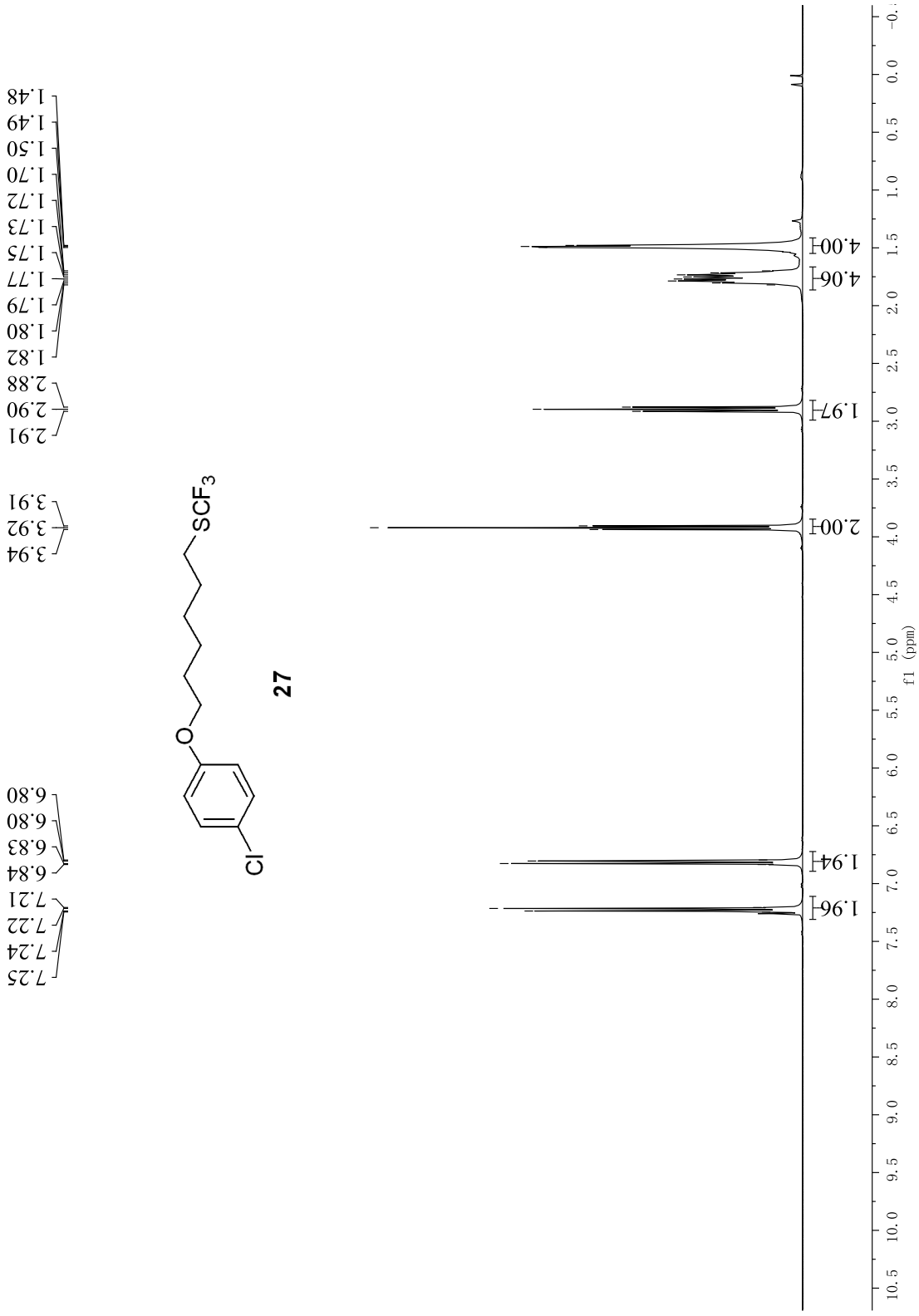
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **26**



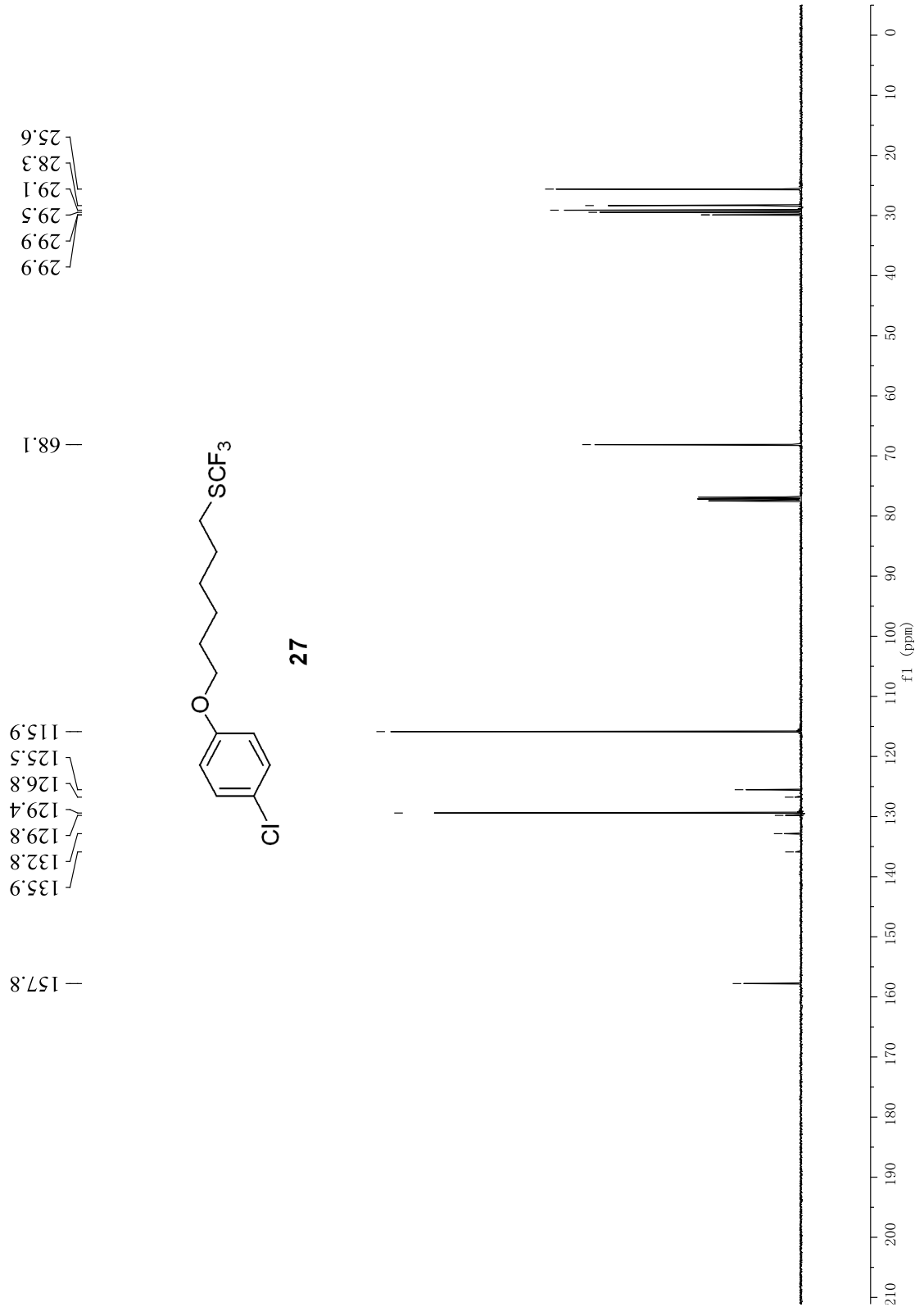
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **26**



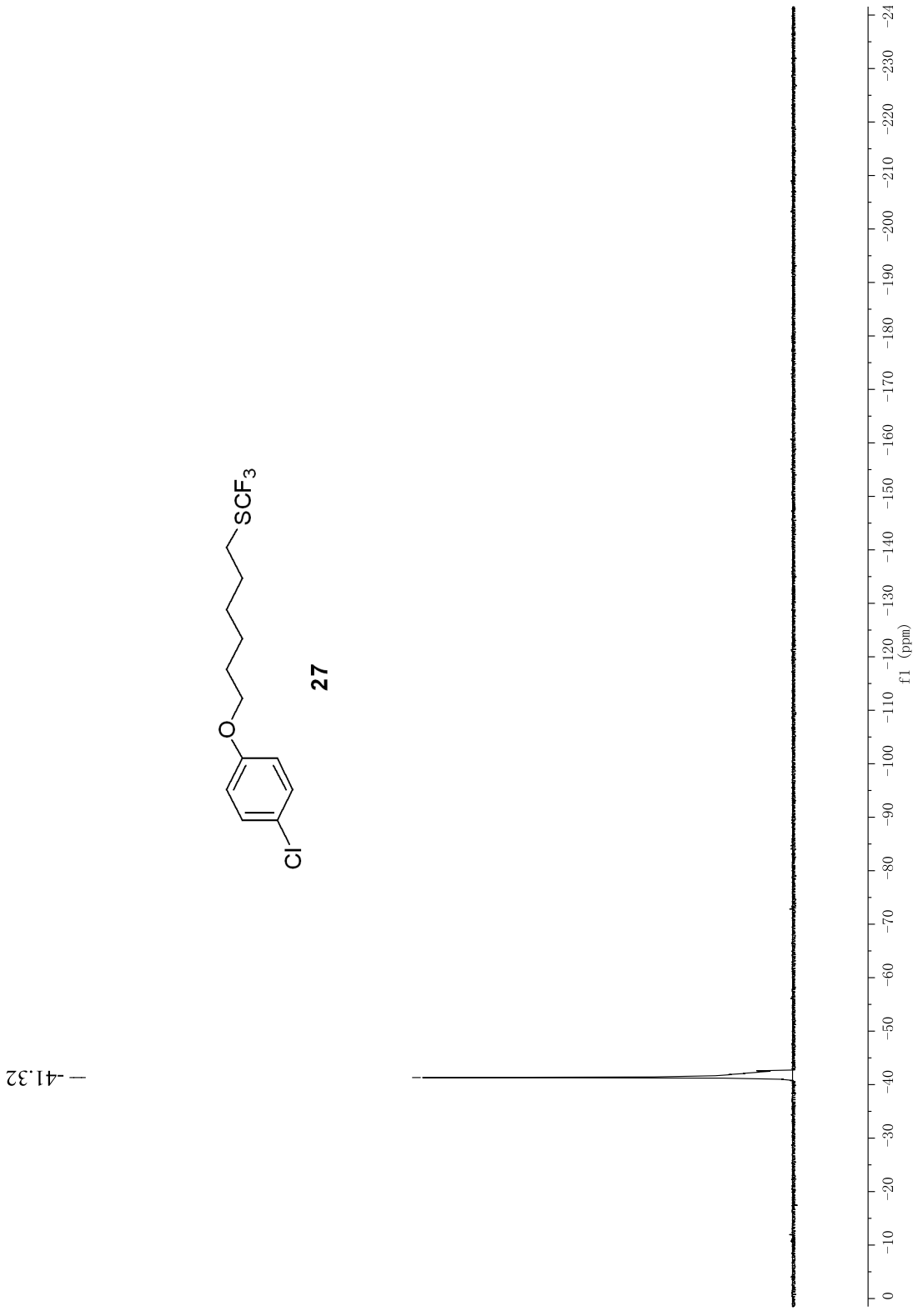
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **26**



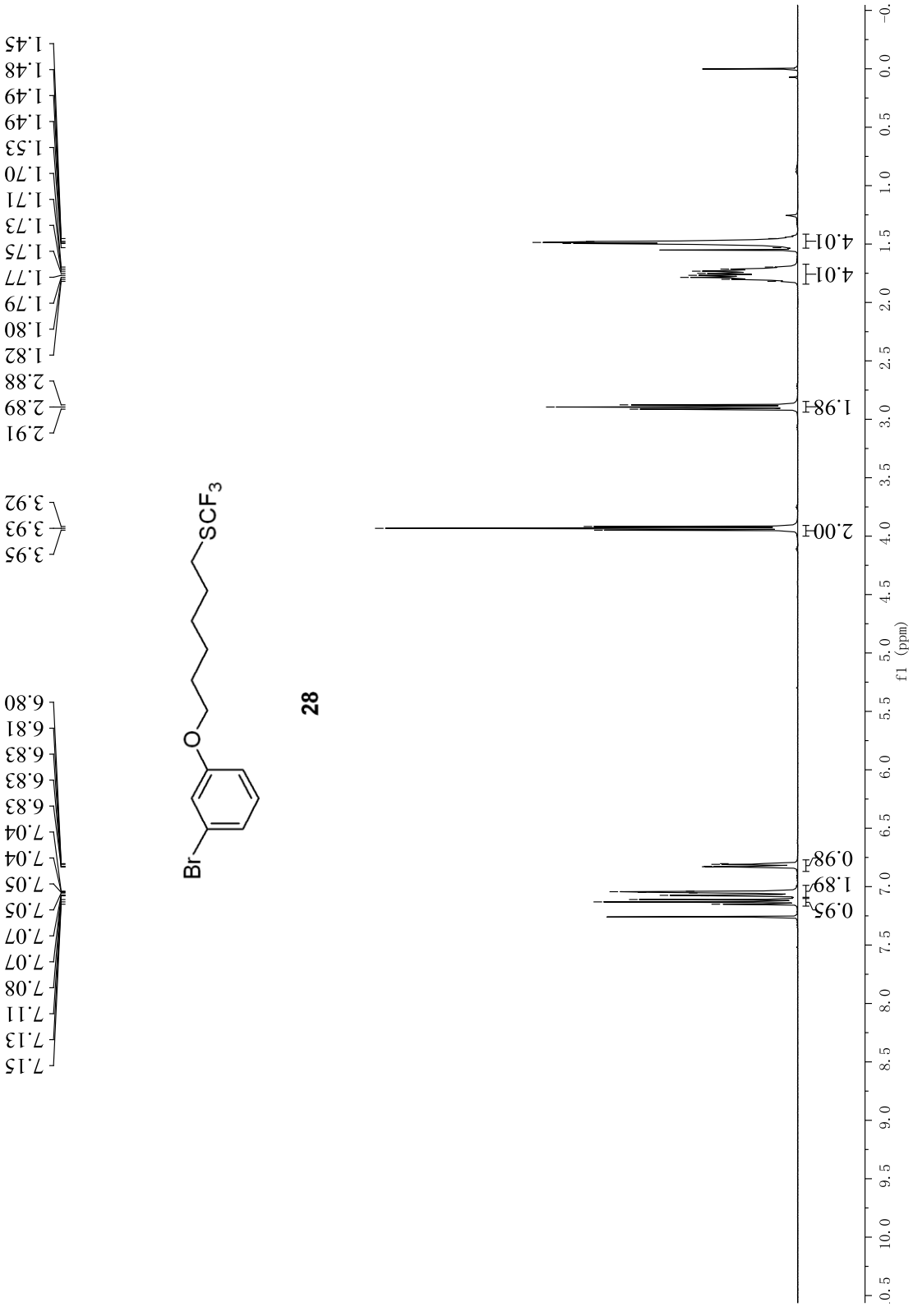
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **27**



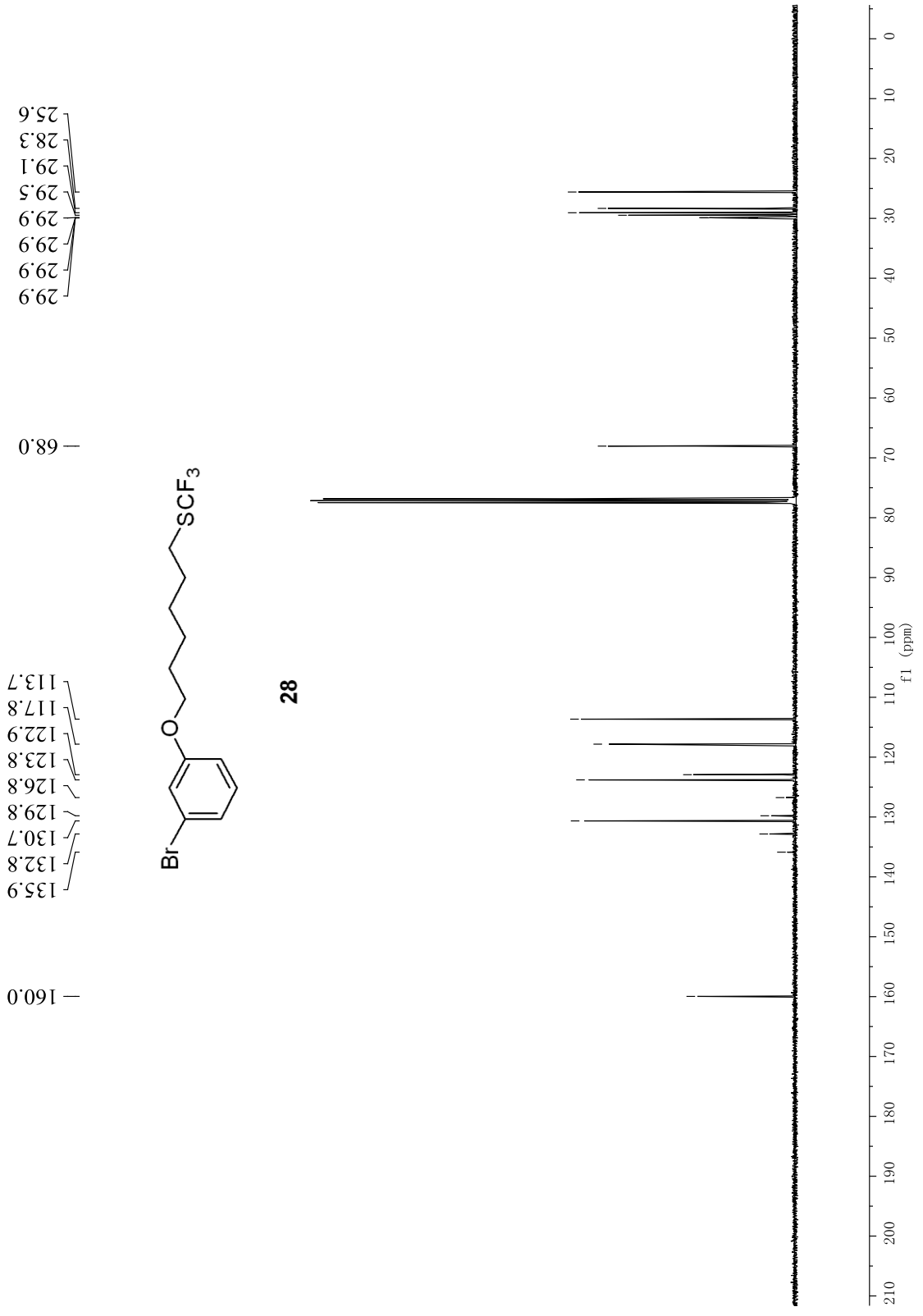
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **27**



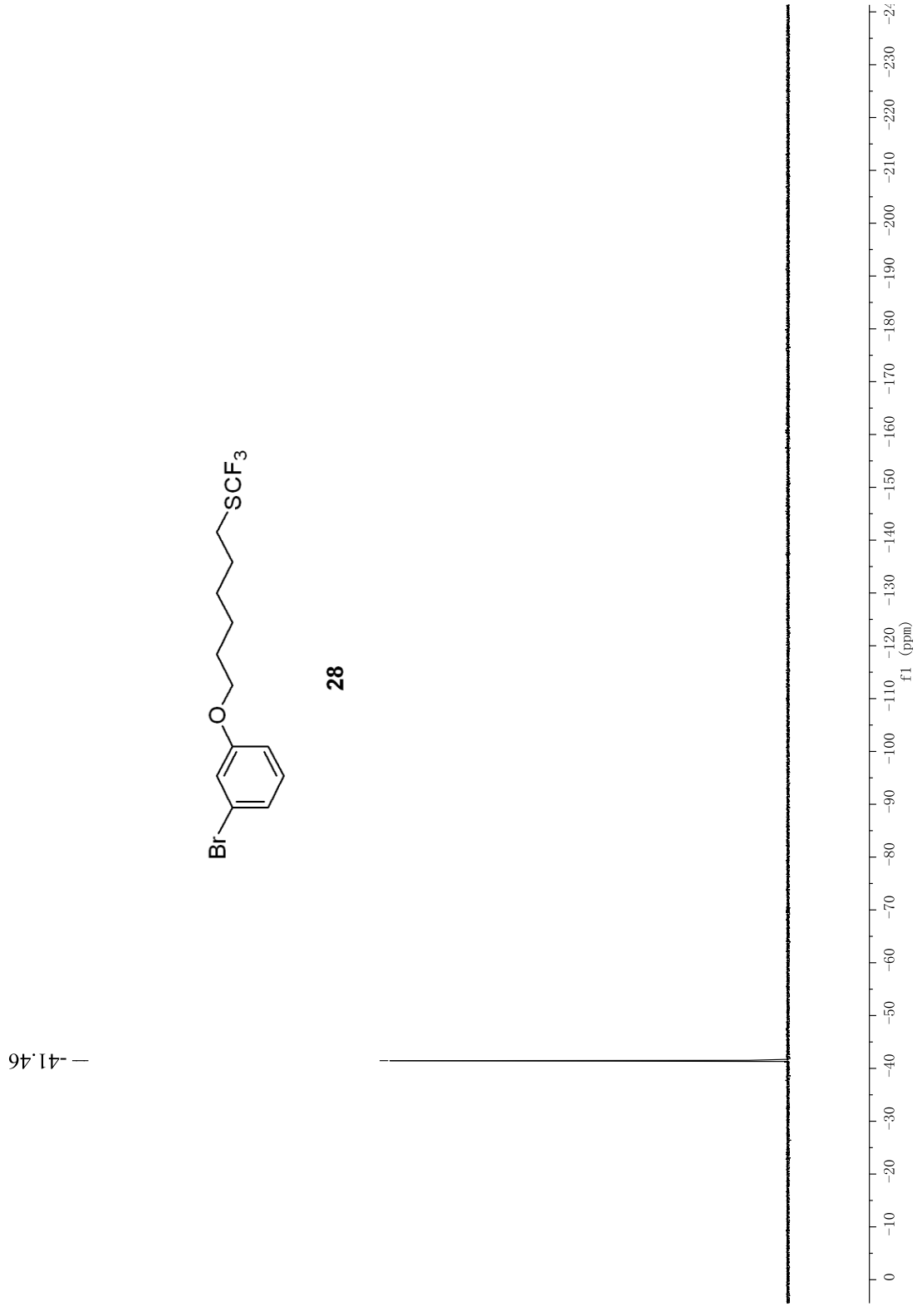
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **27**



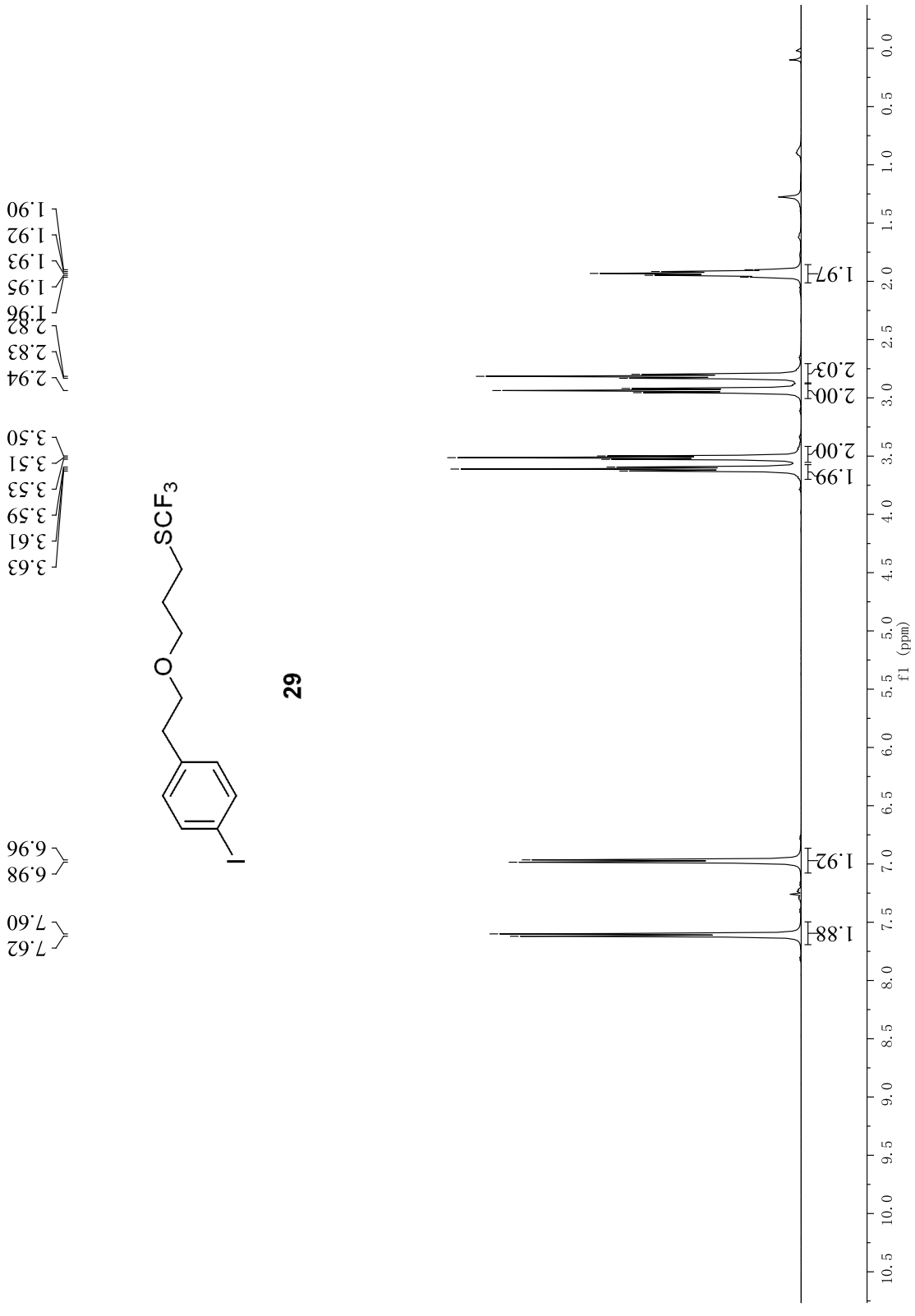
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **28**



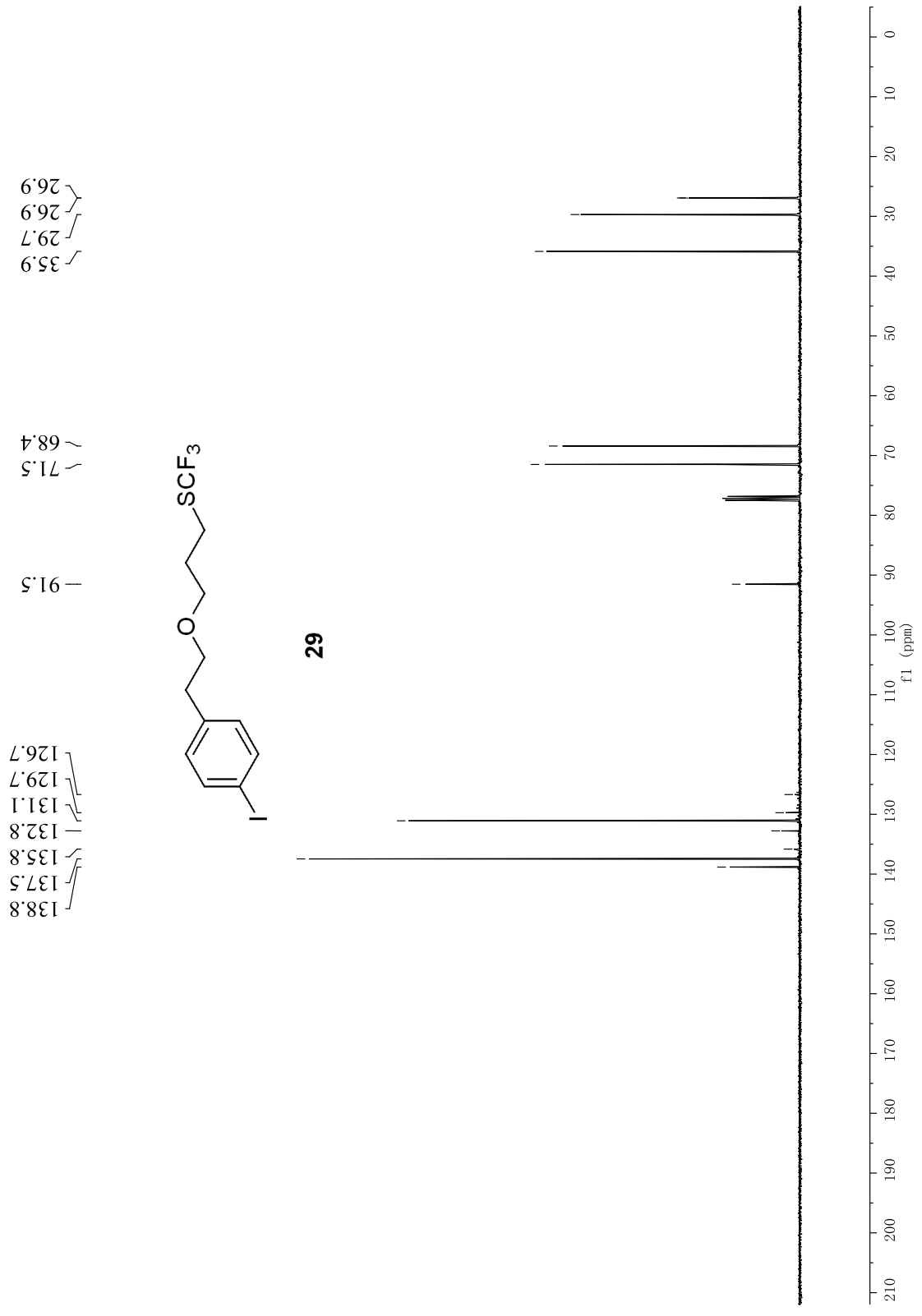
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **28**



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

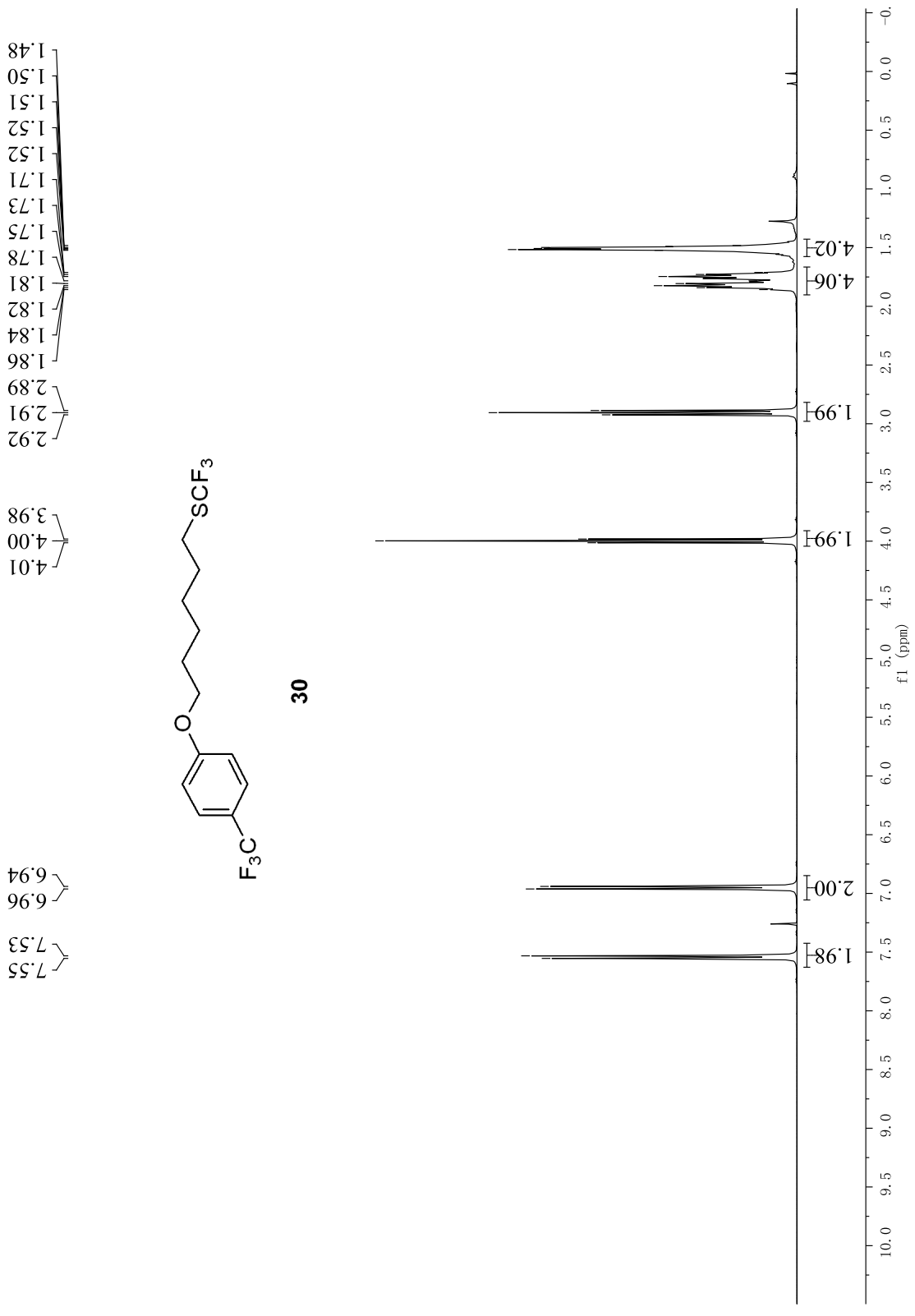


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **29**

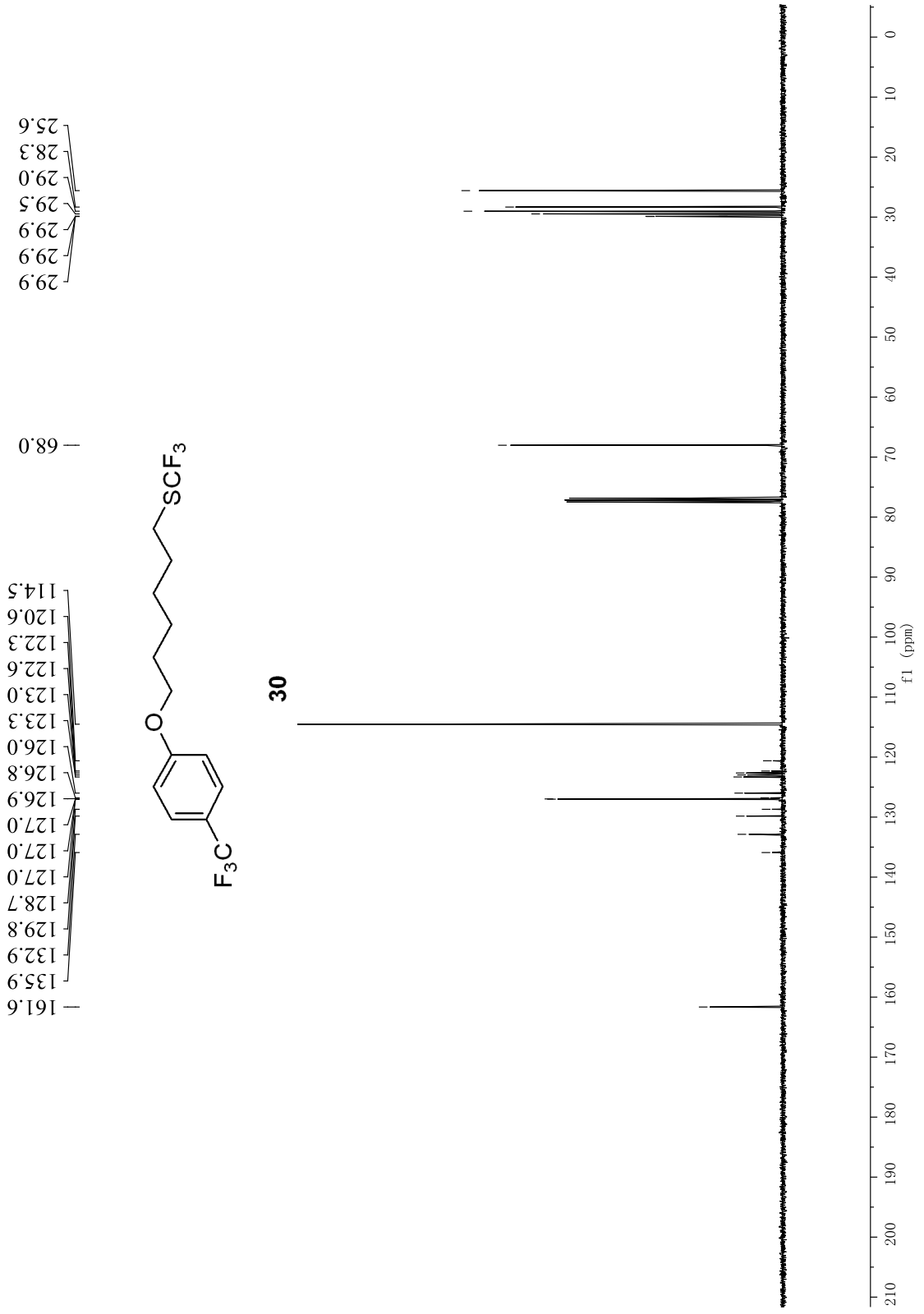


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **29**

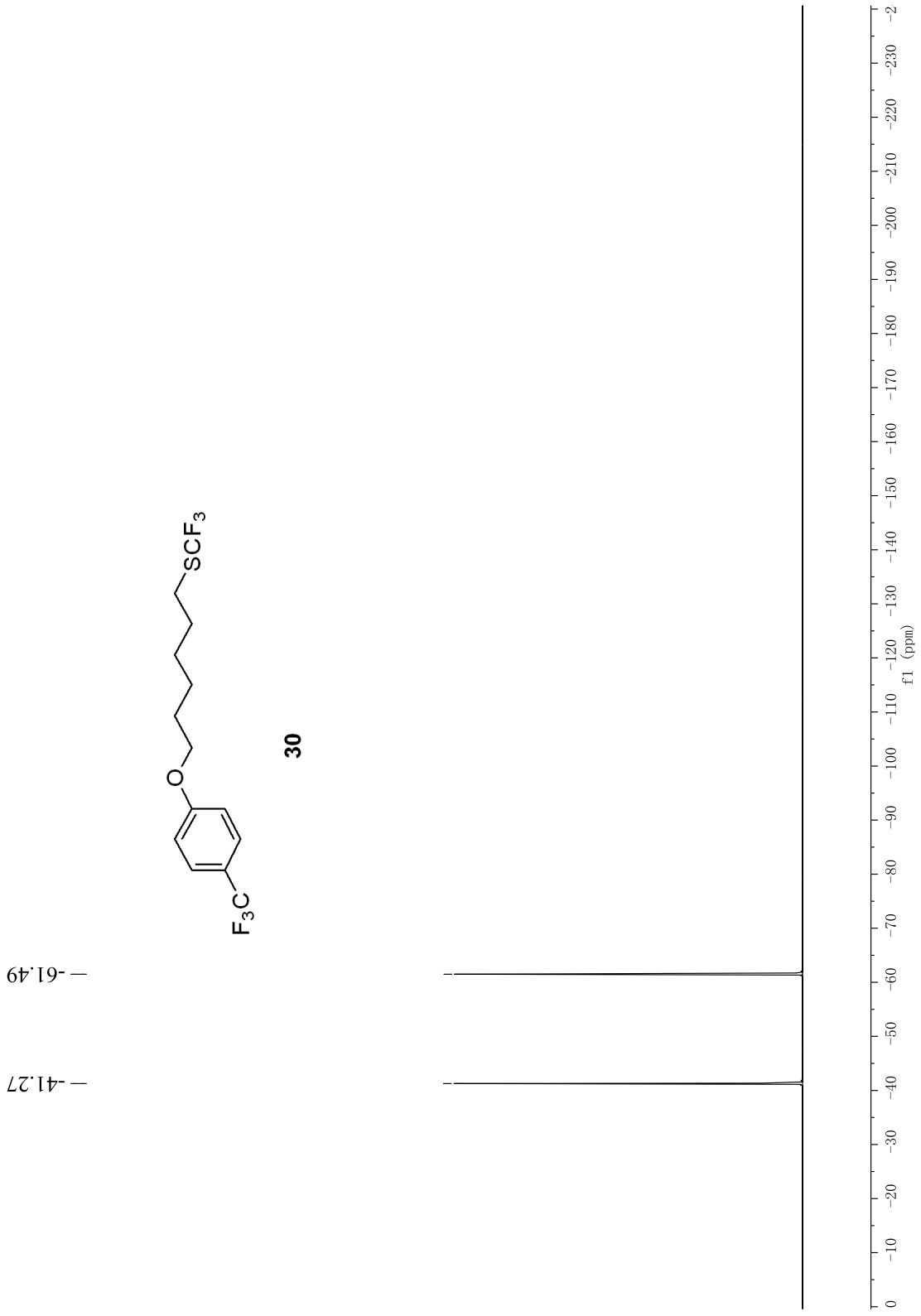
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **29**



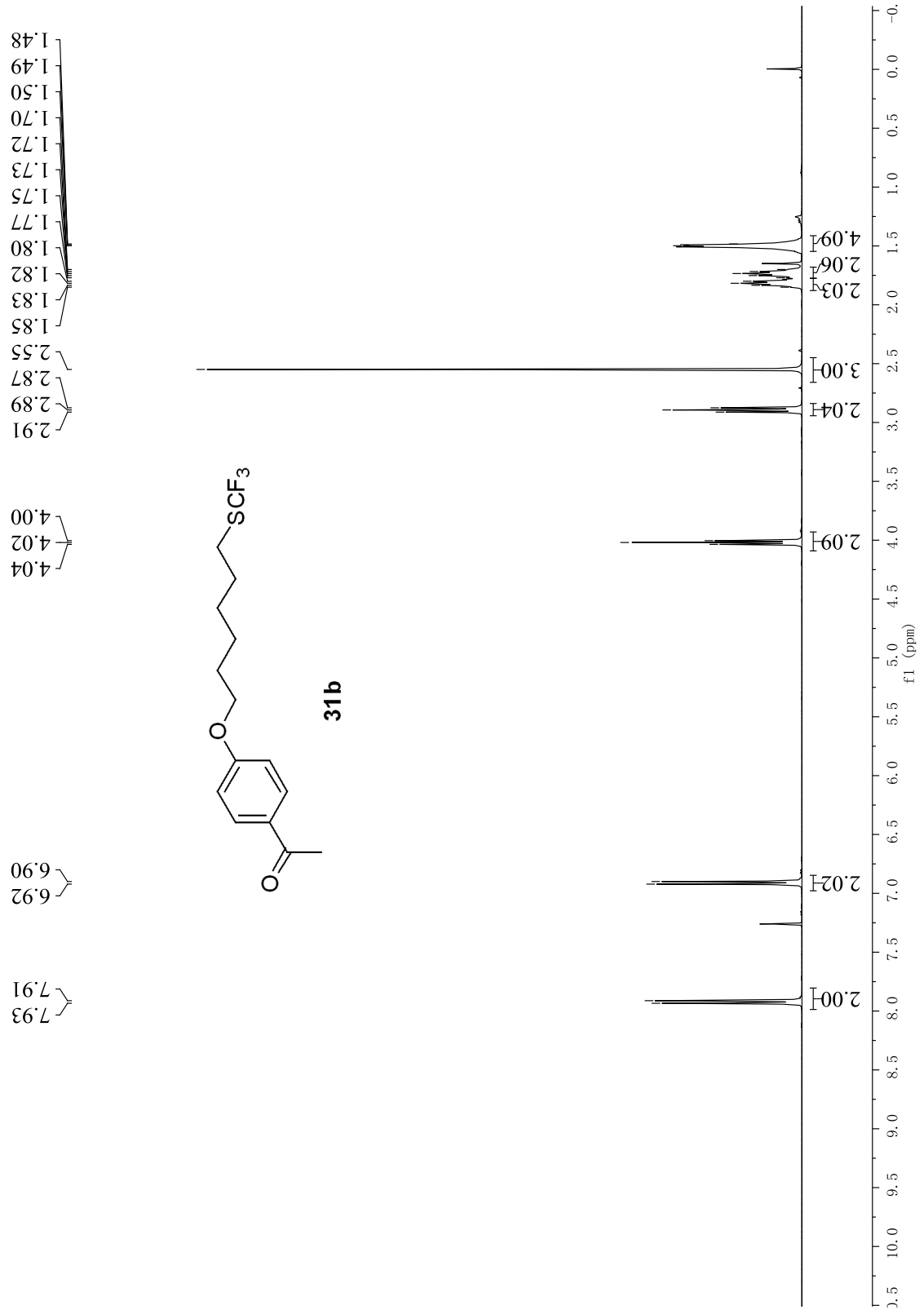
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **30**



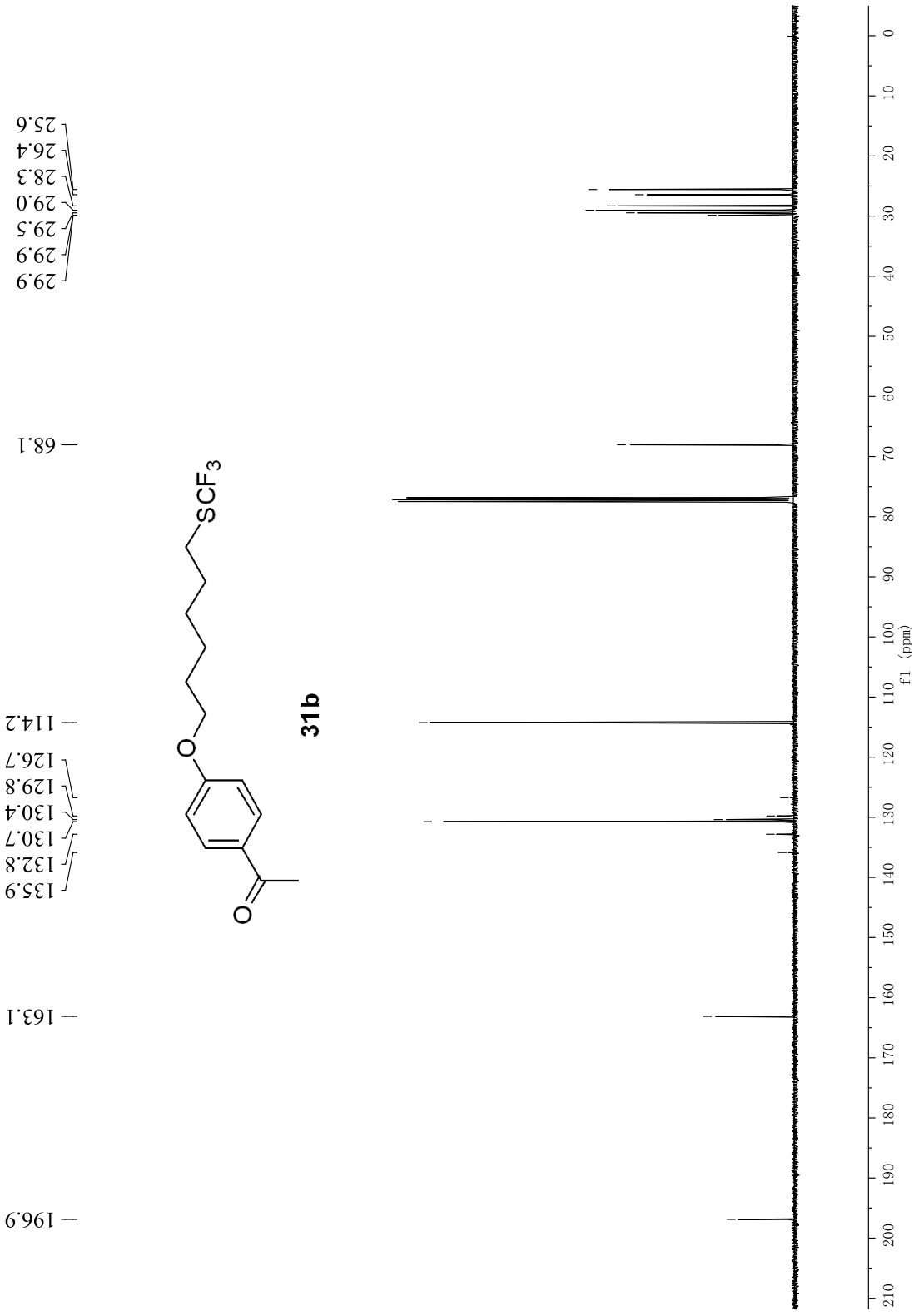
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **30**



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

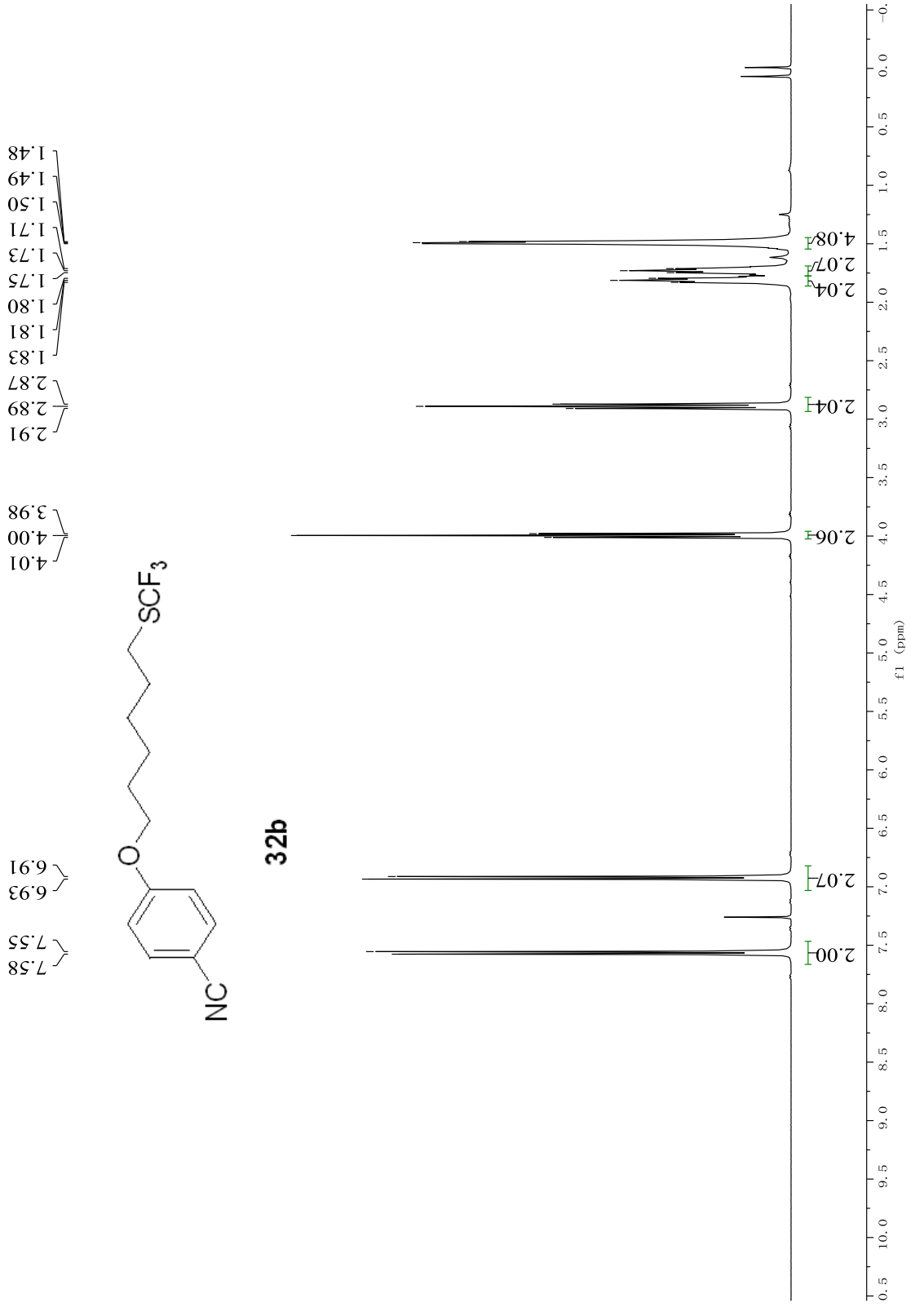


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **31b**

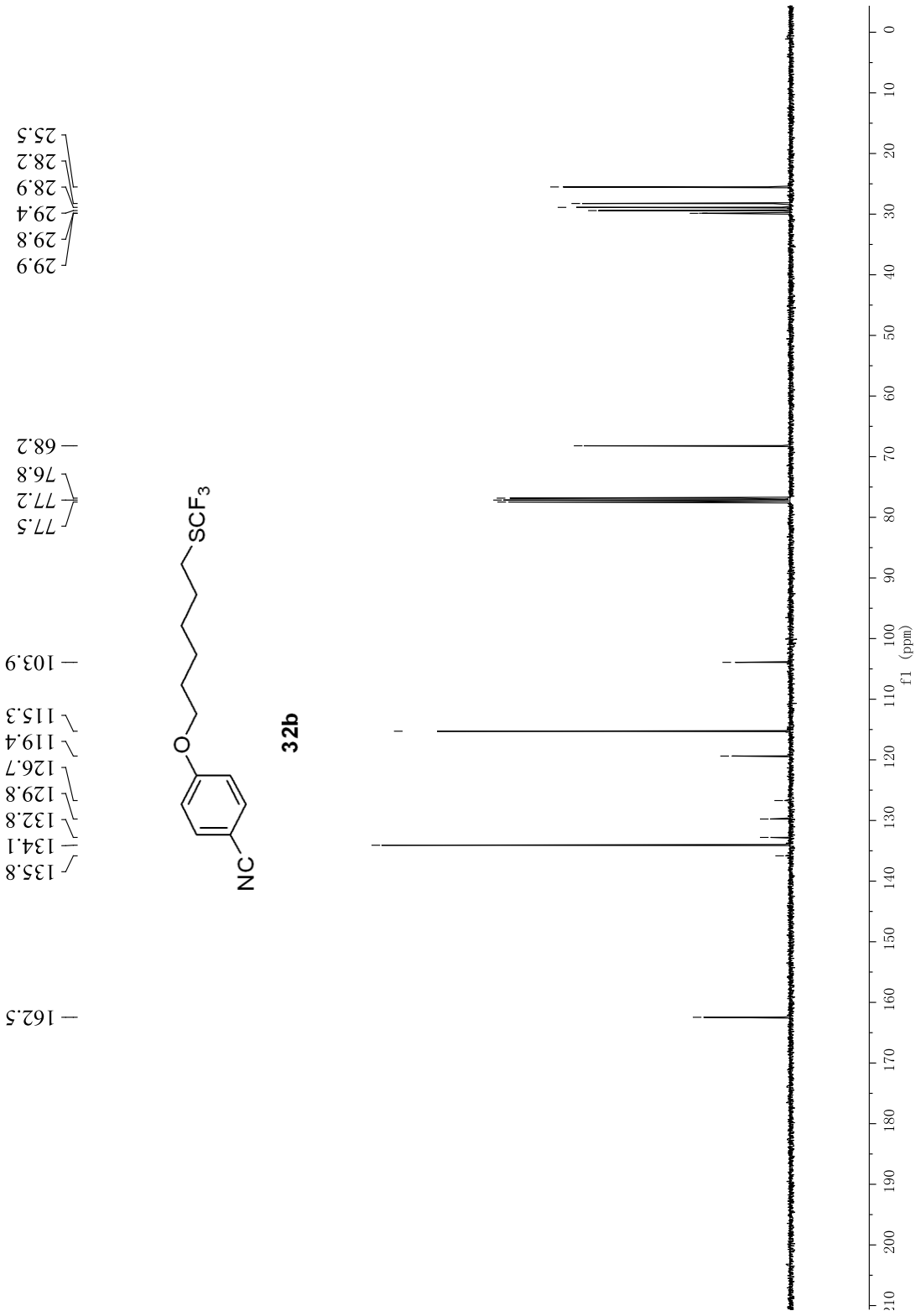


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **31b**

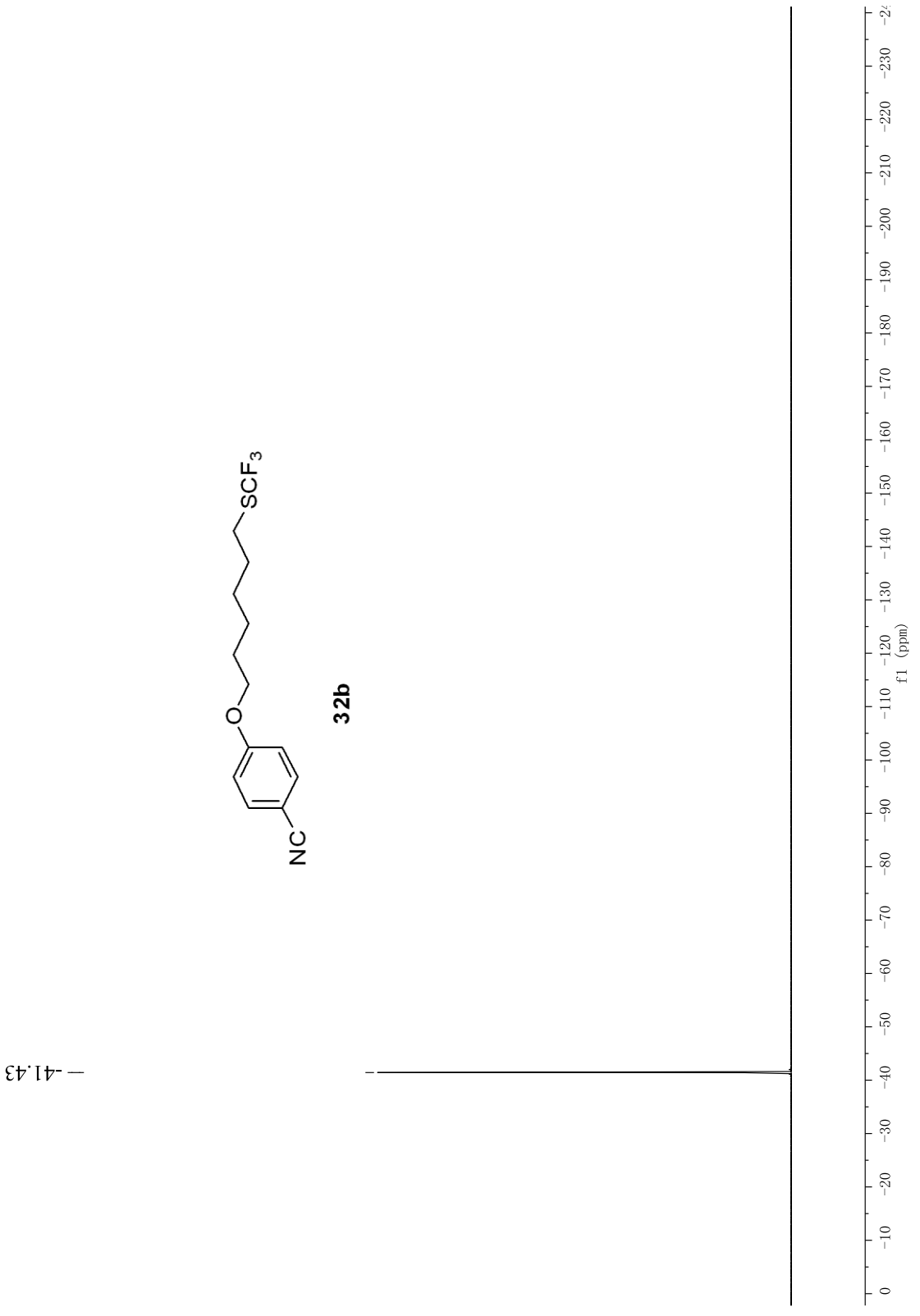
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **31b**



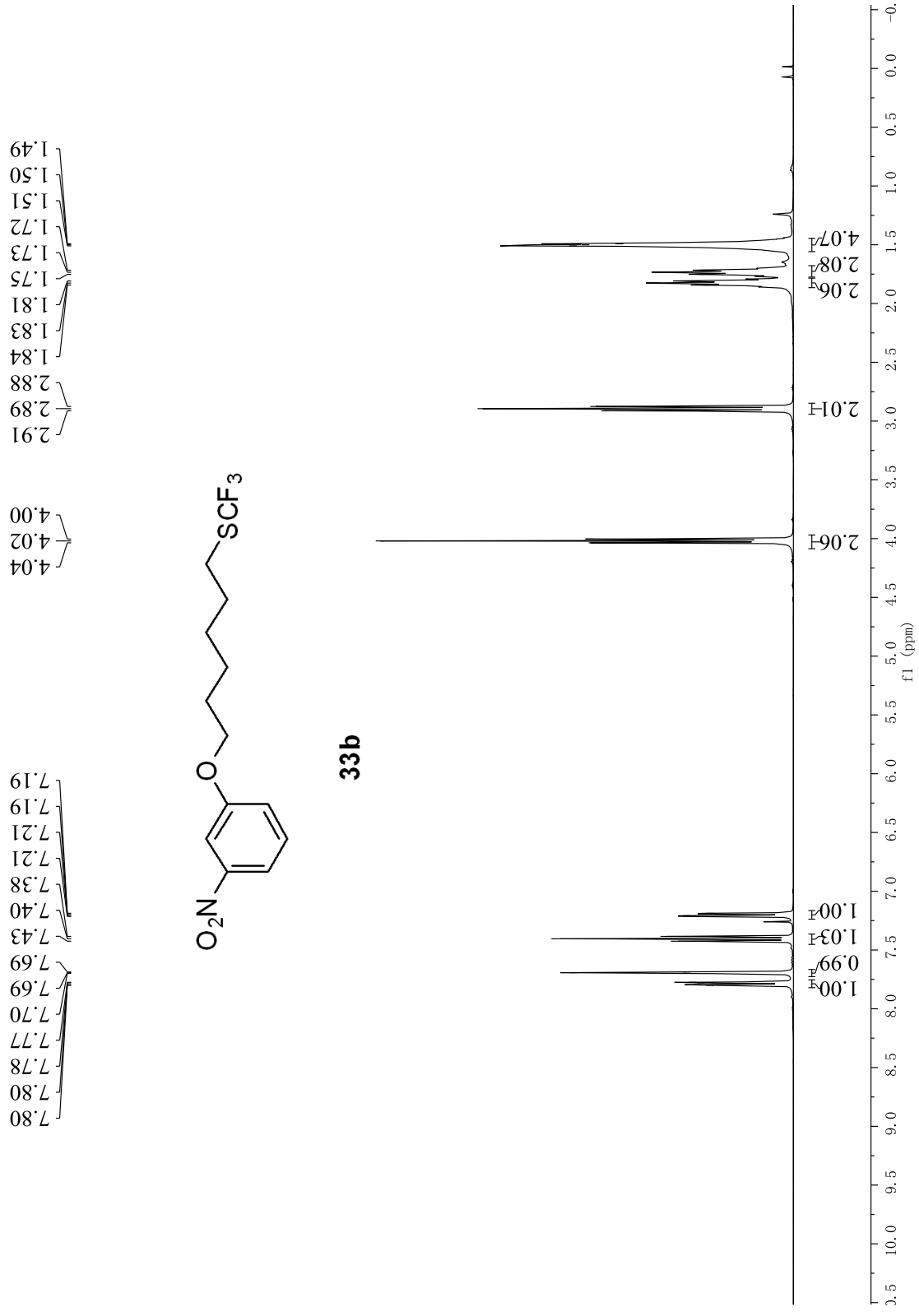
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **32b**



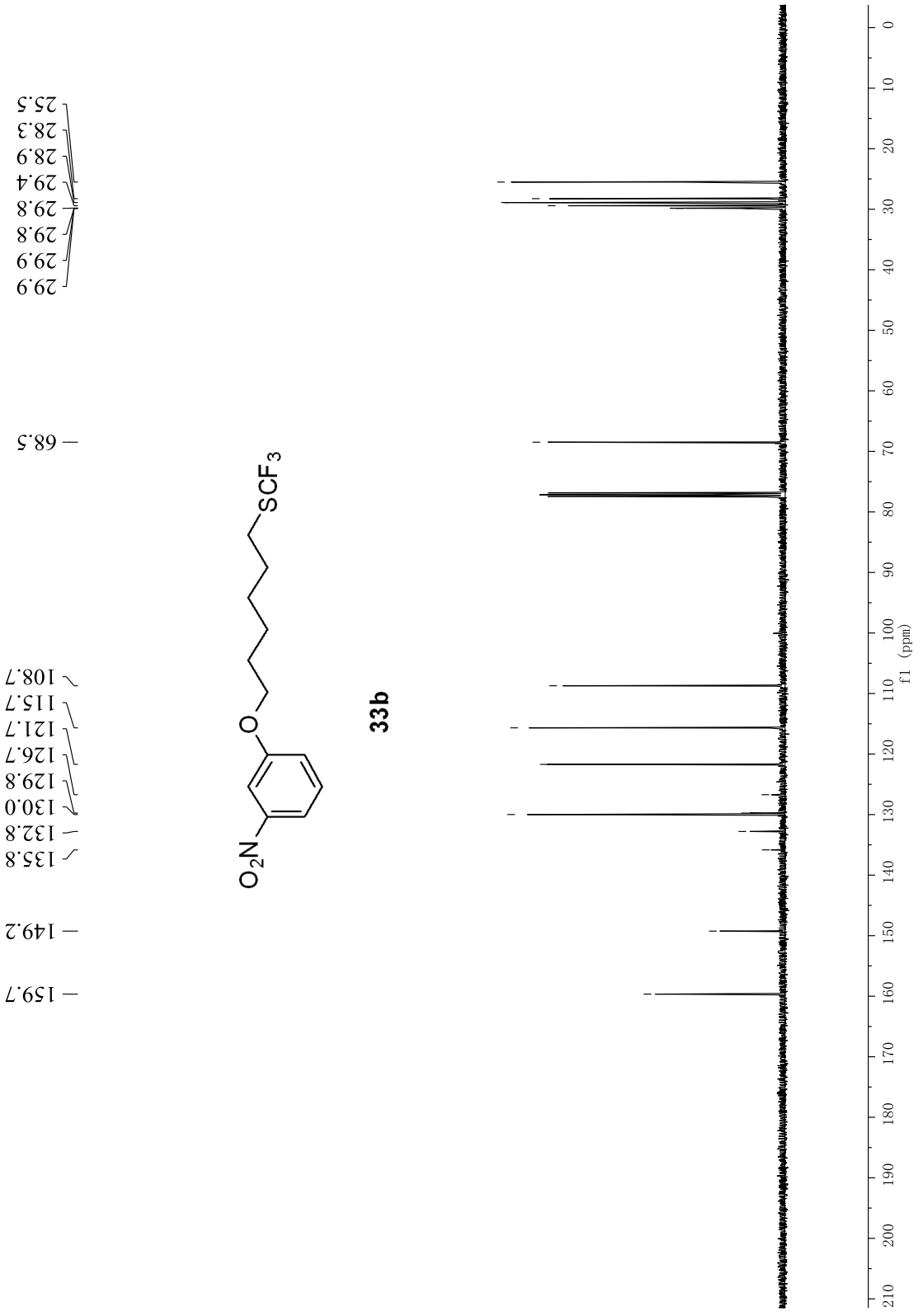
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **32b**



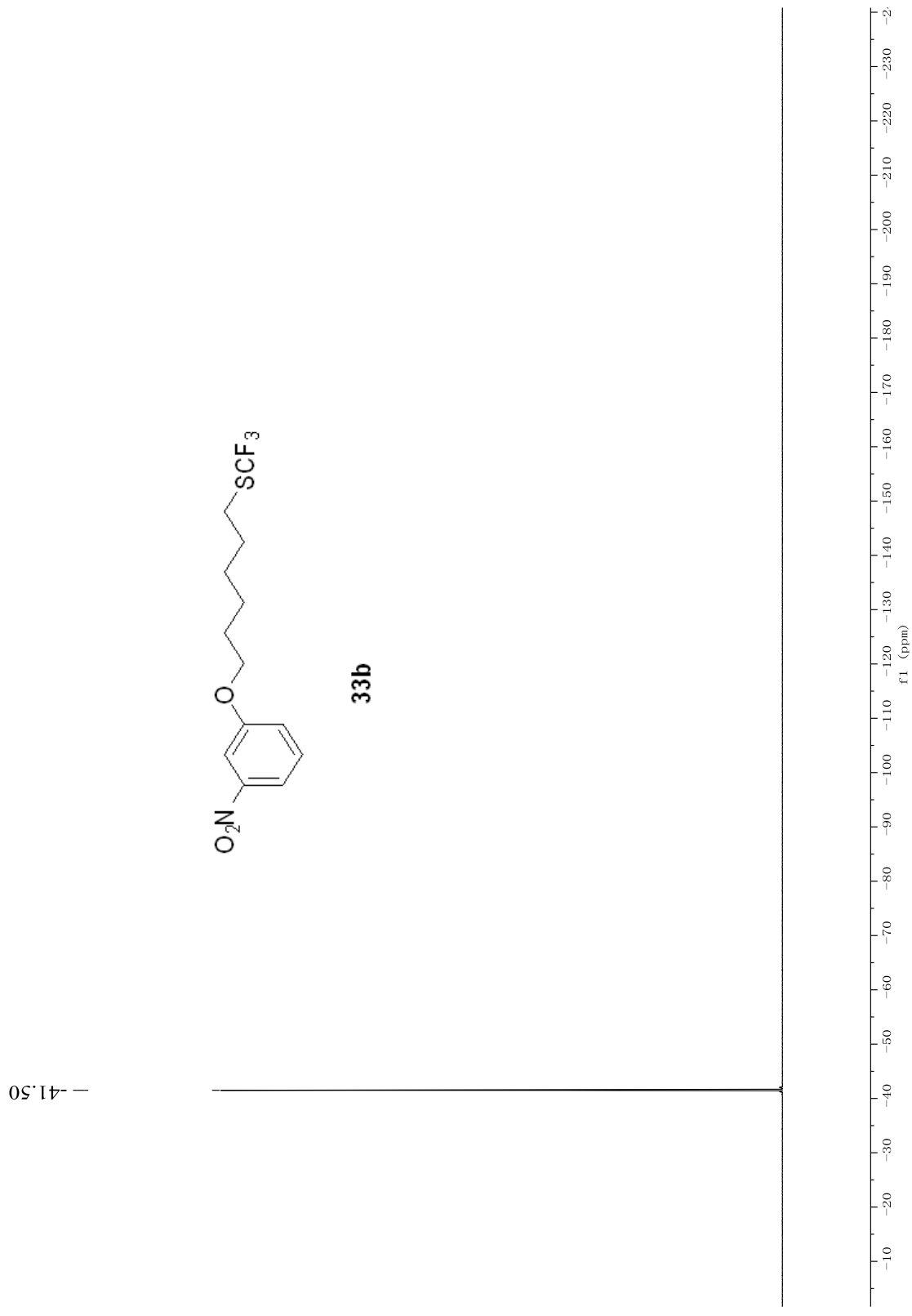
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **32b**



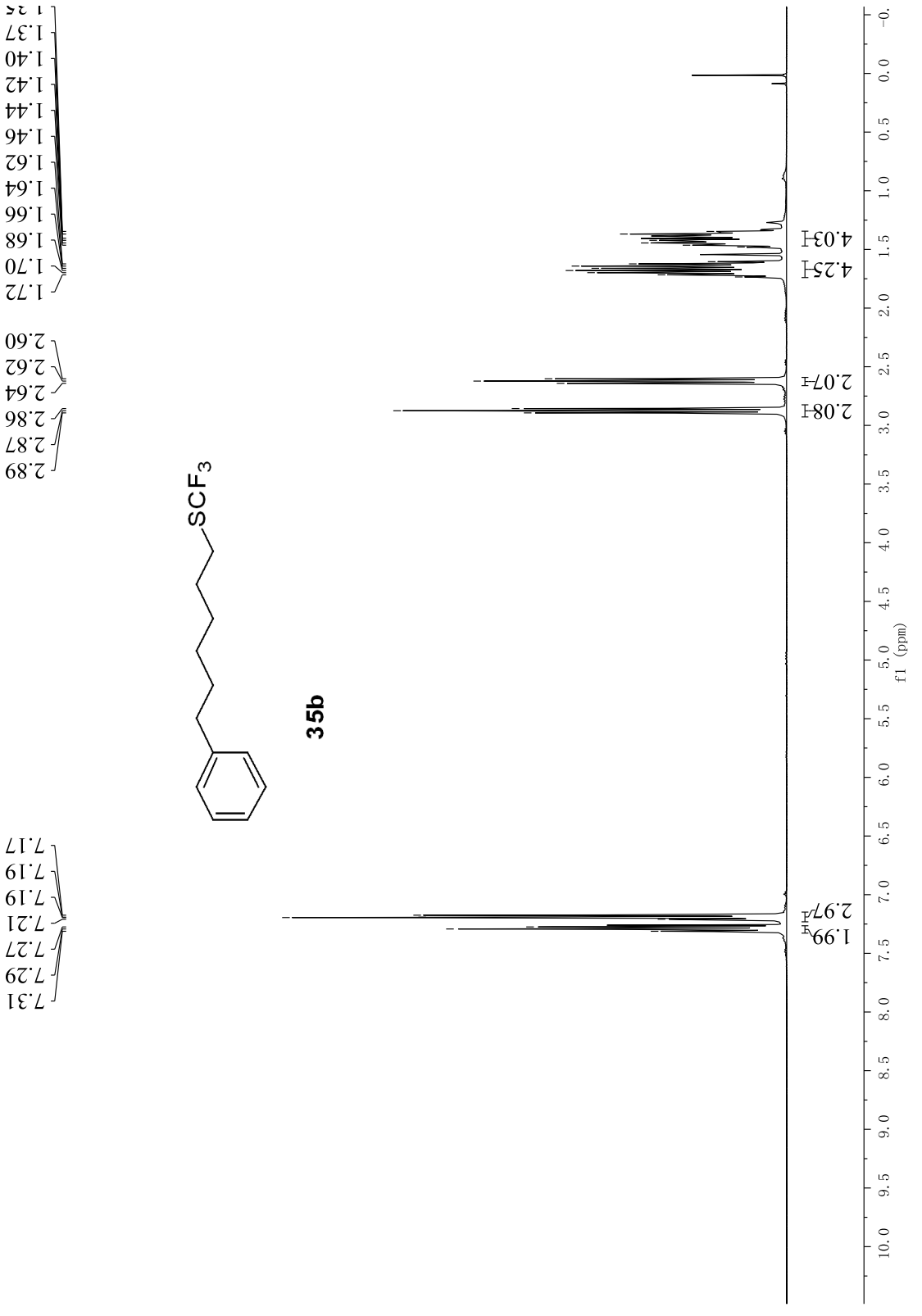
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **33b**



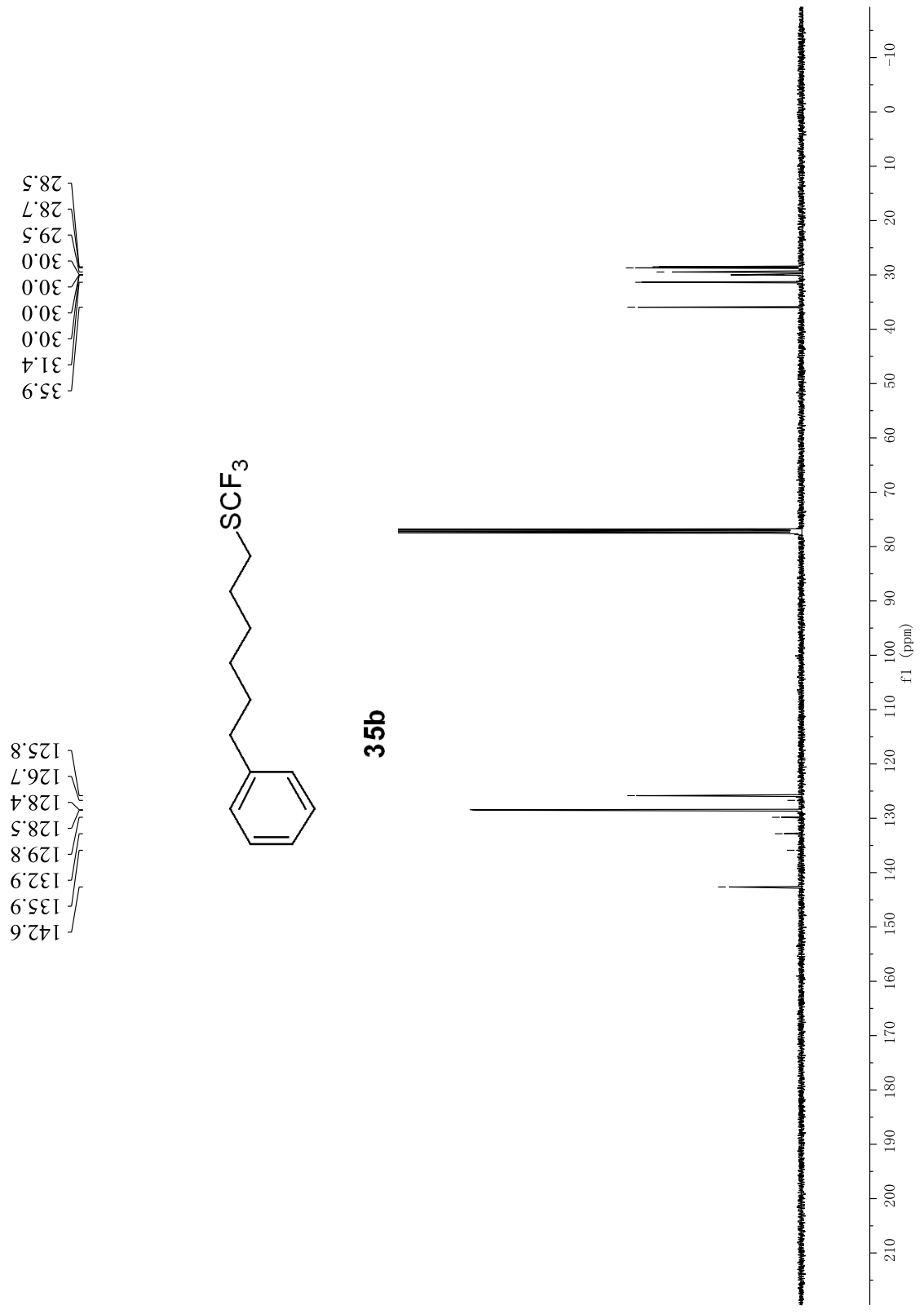
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **33b**



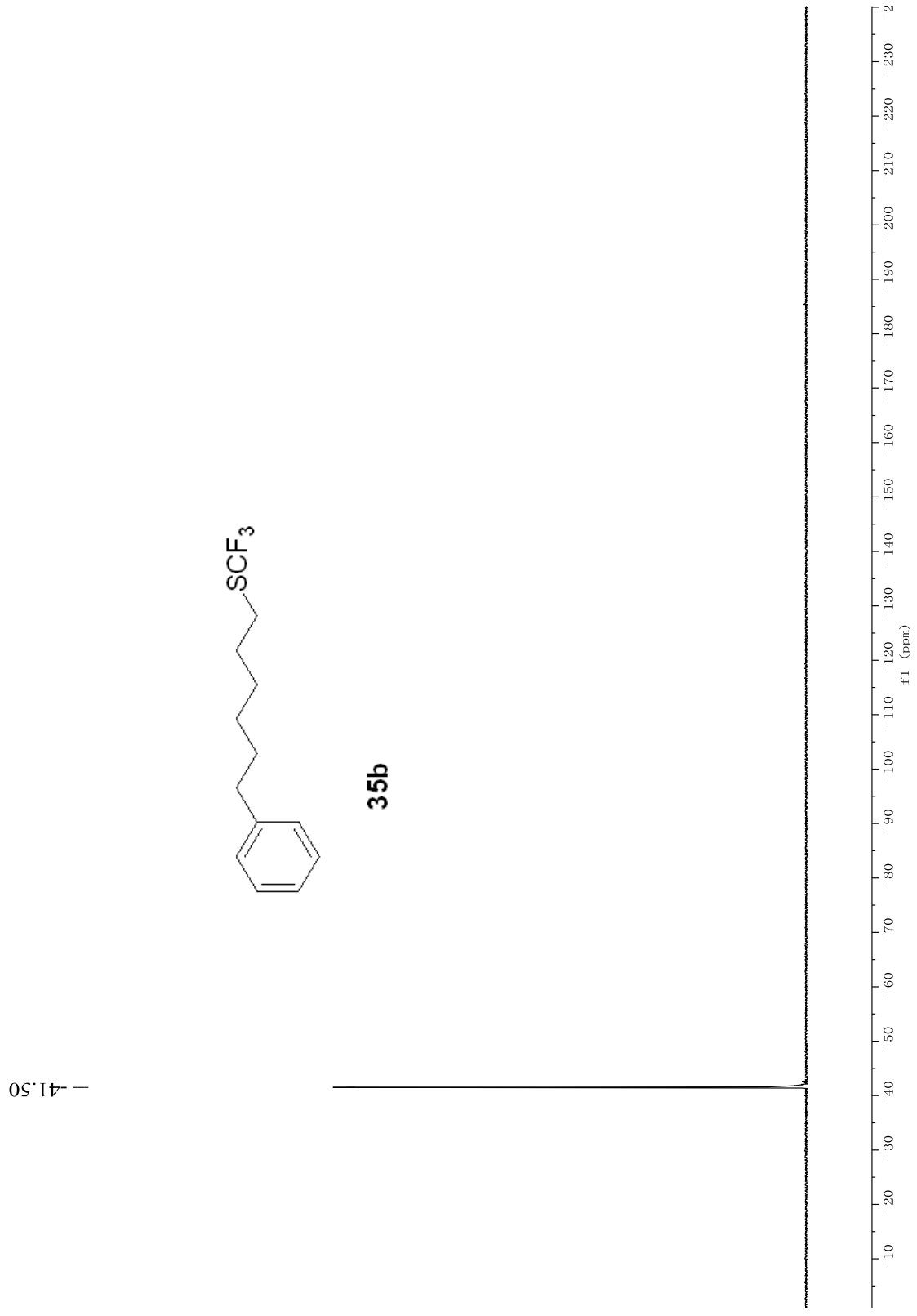
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **33b**



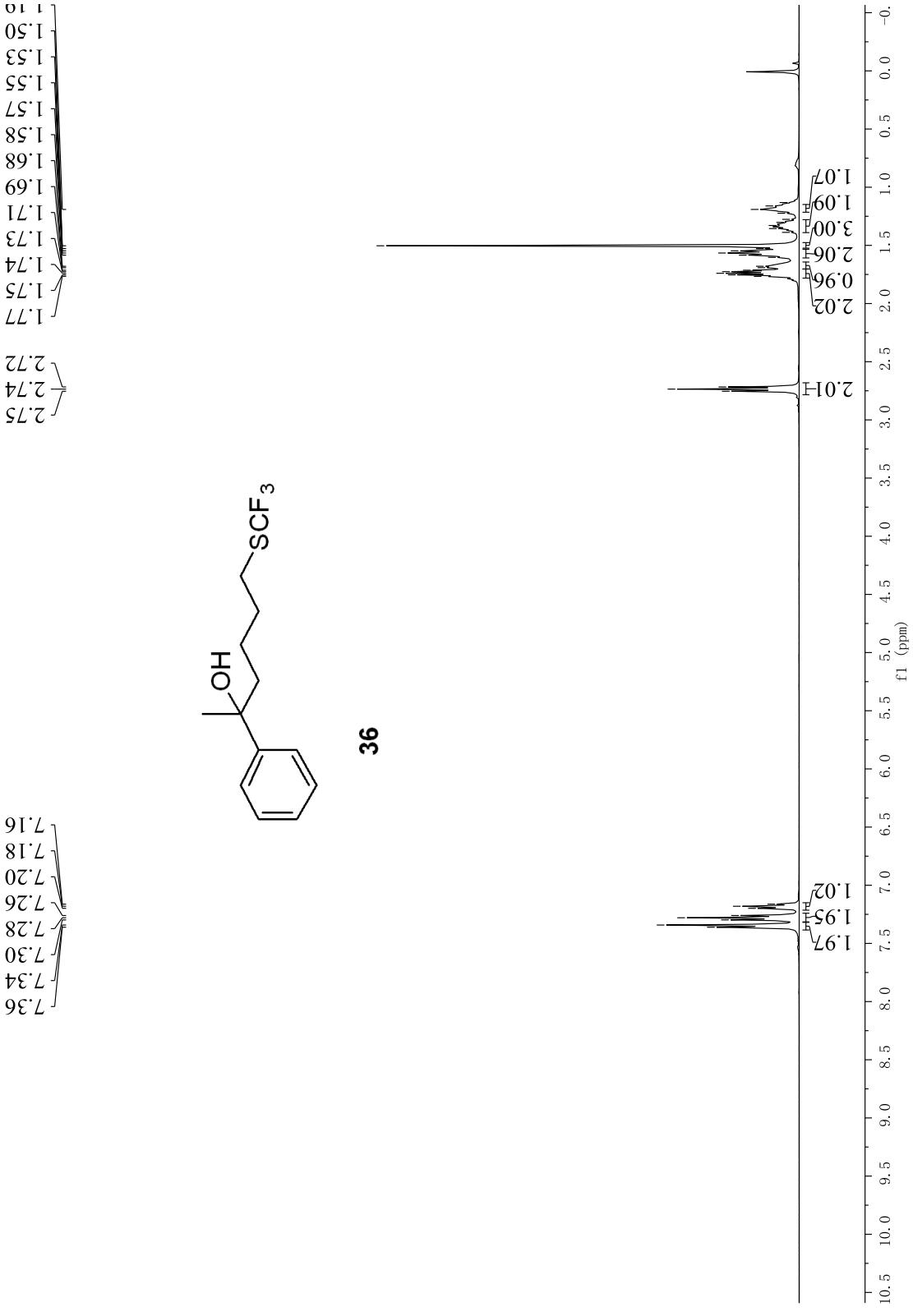
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **35b**



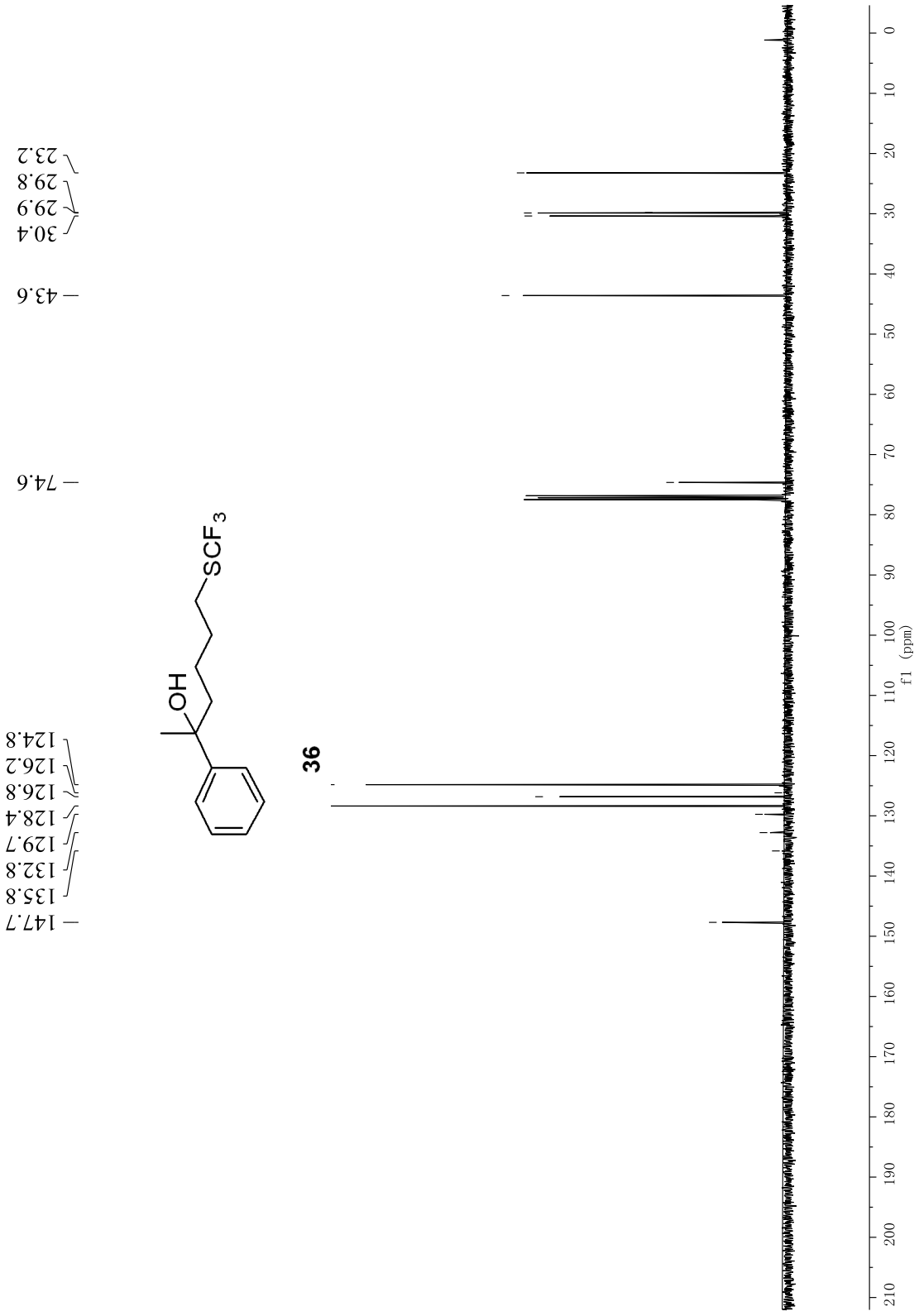
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **35b**



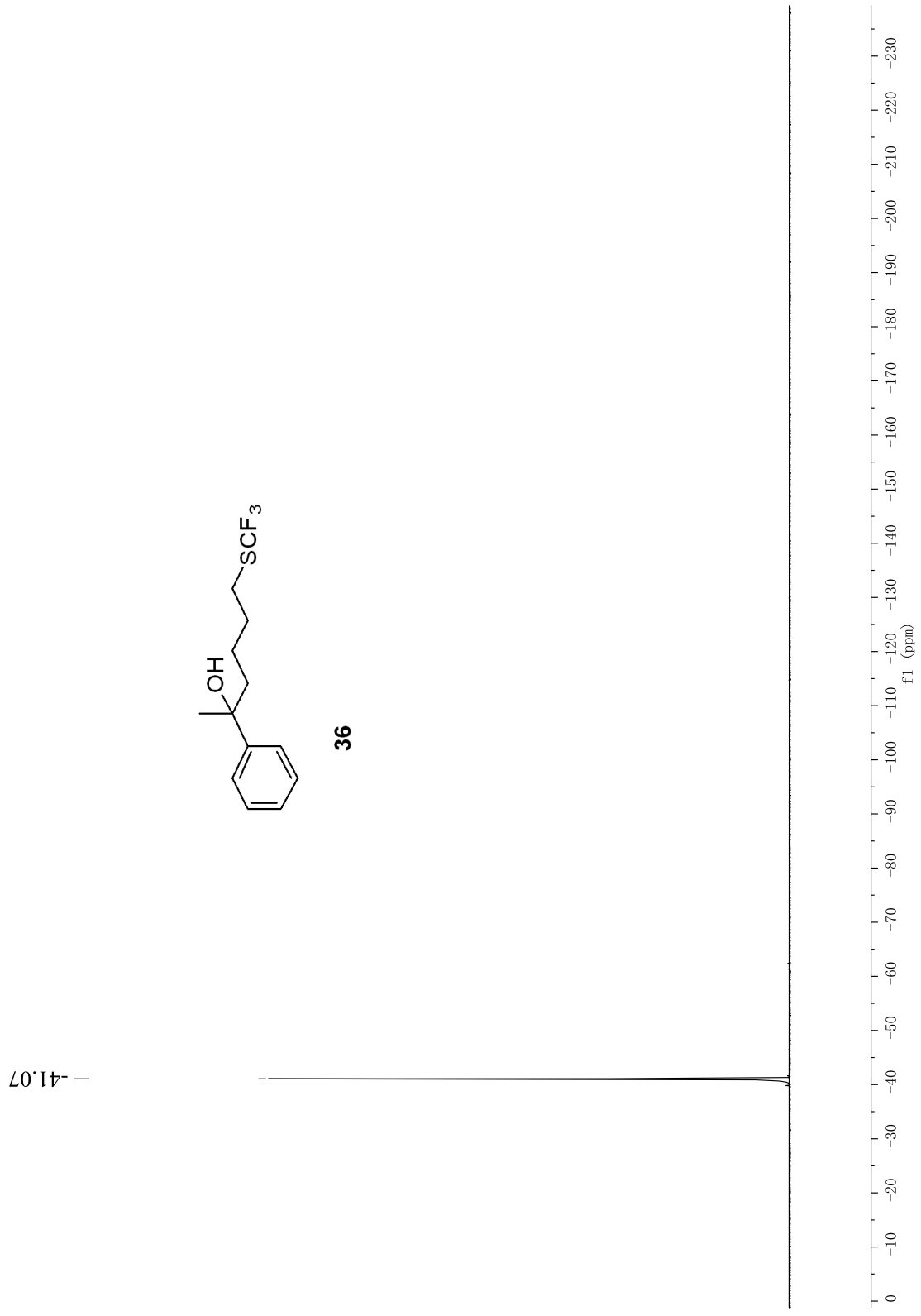
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **35b**



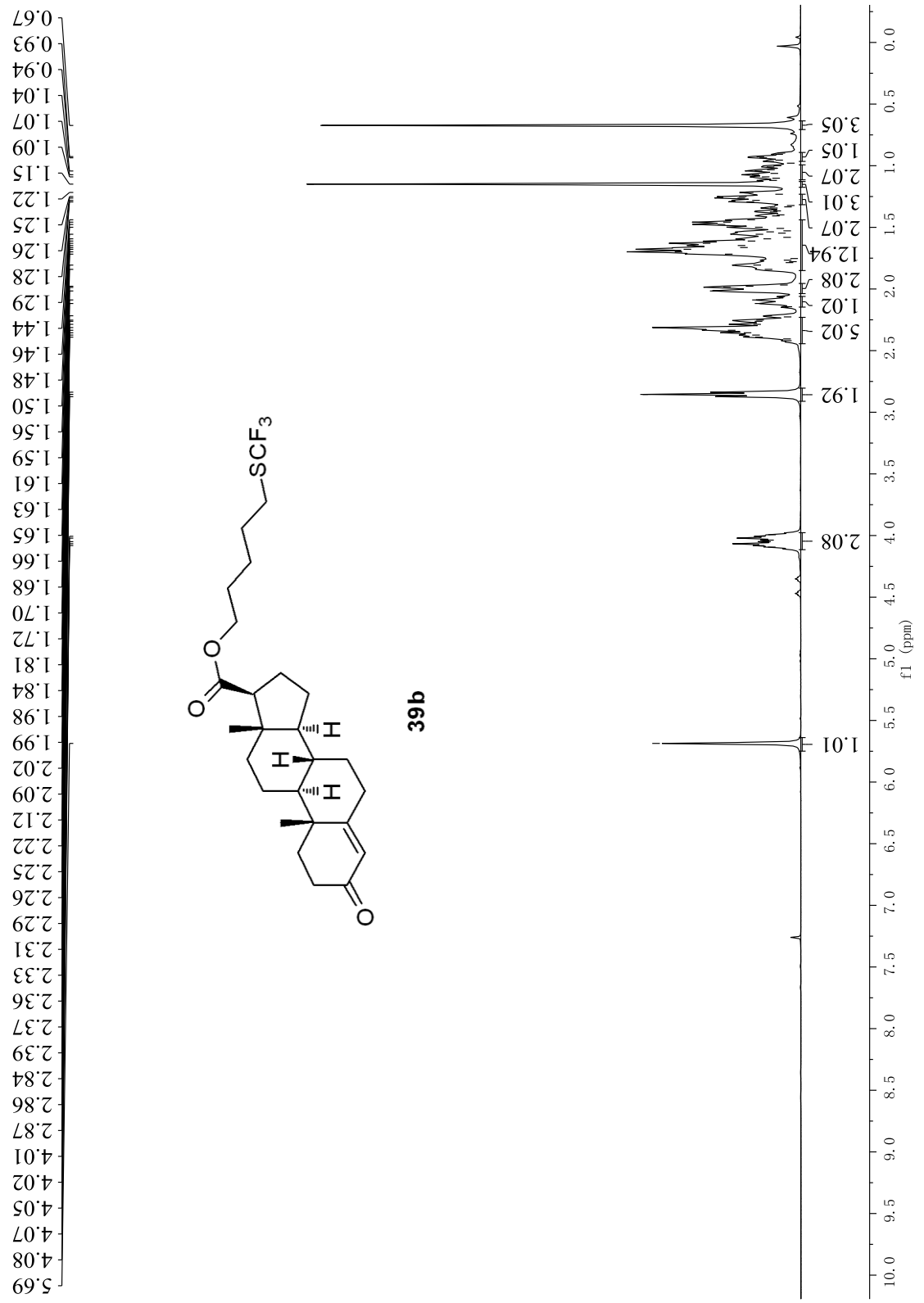
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **36**



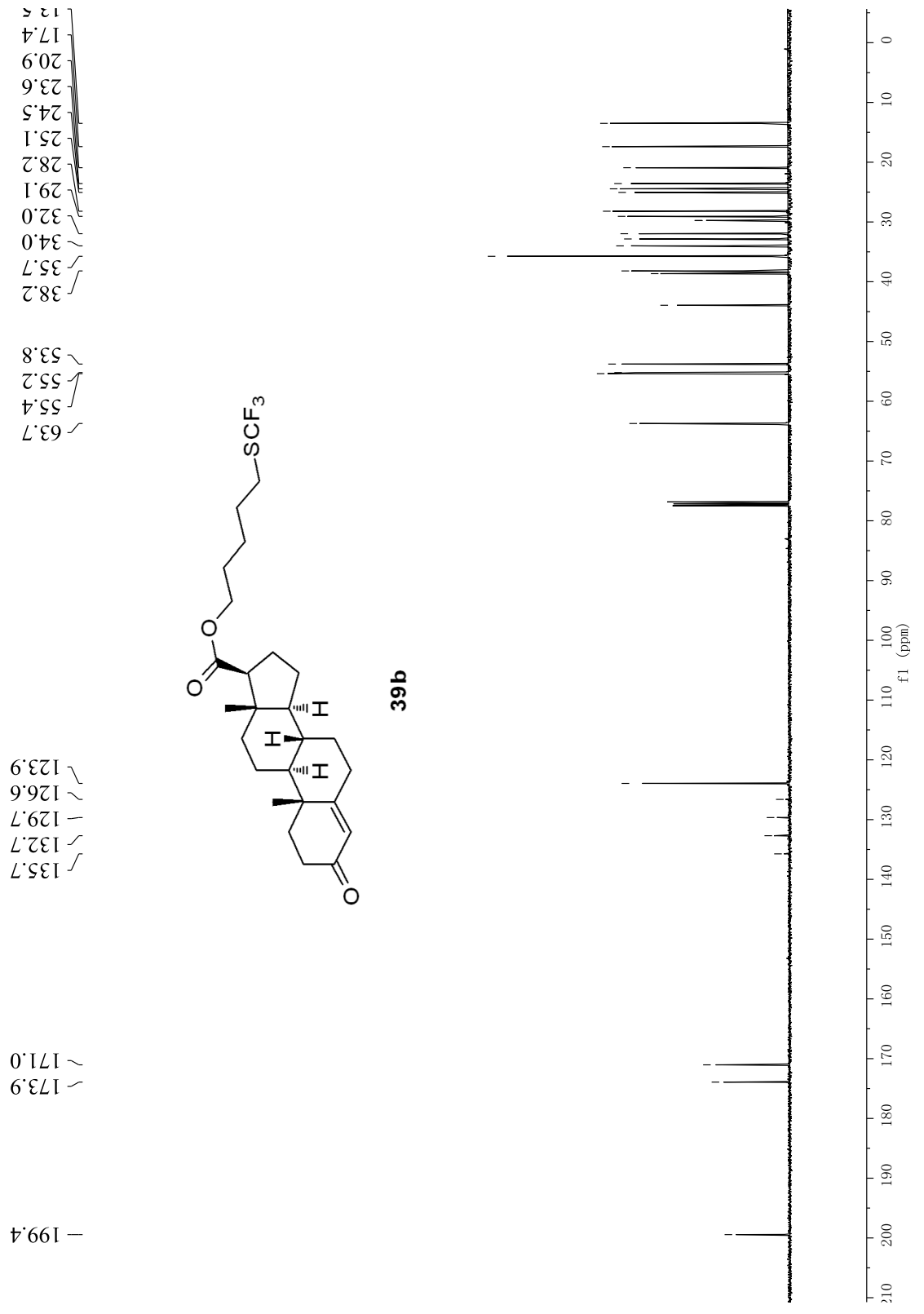
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **36**



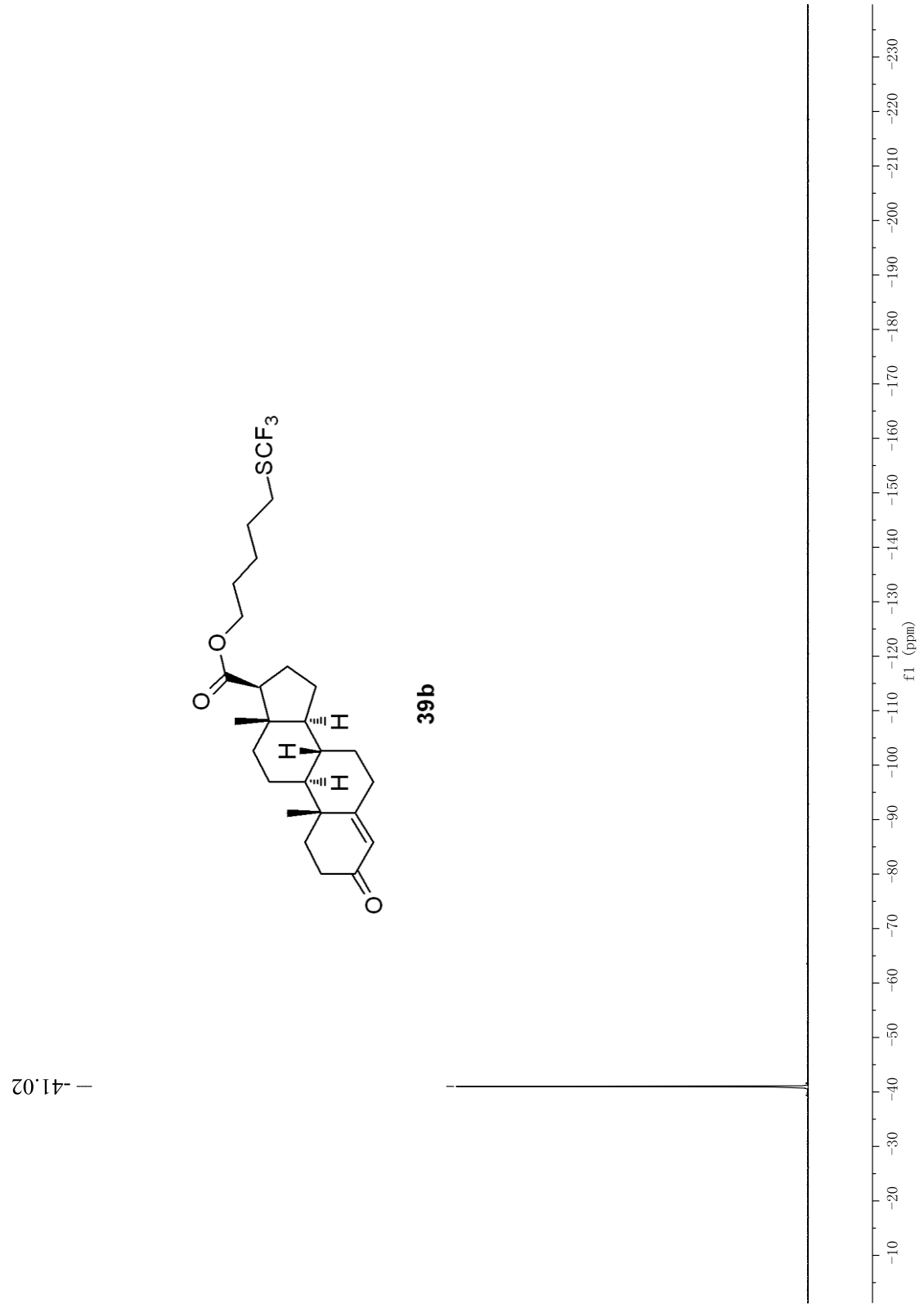
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **36**



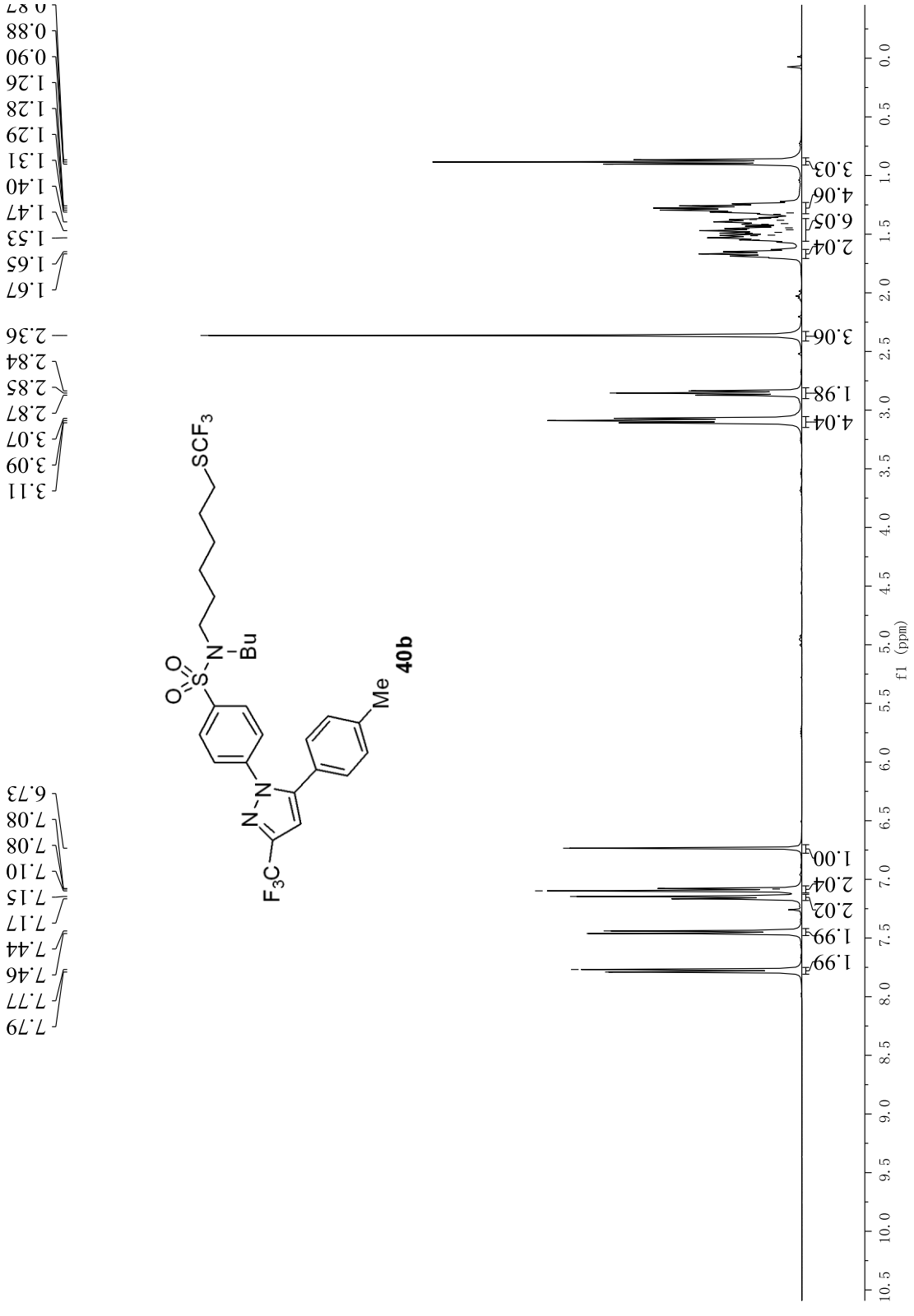
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **39b**



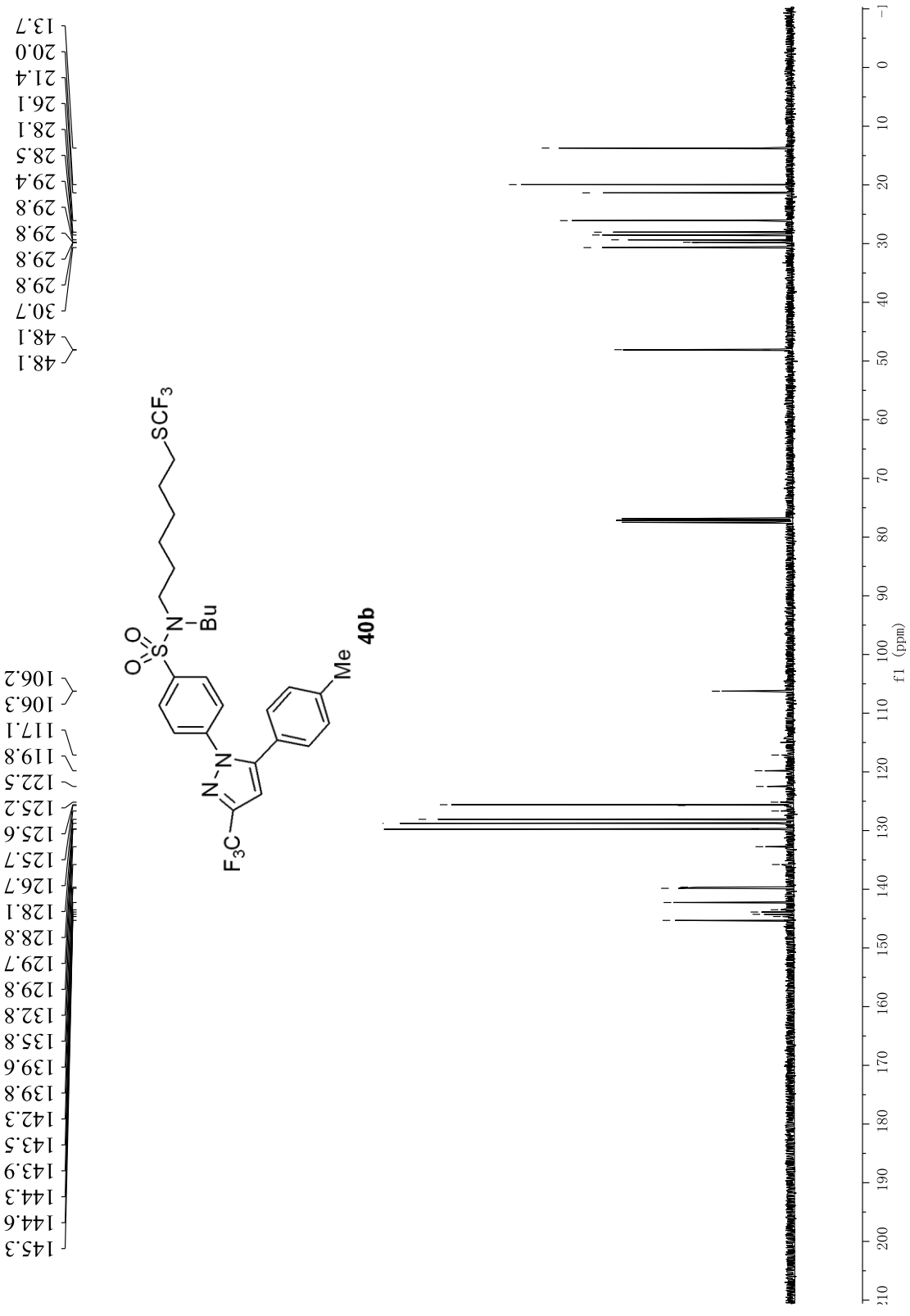
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **39b**



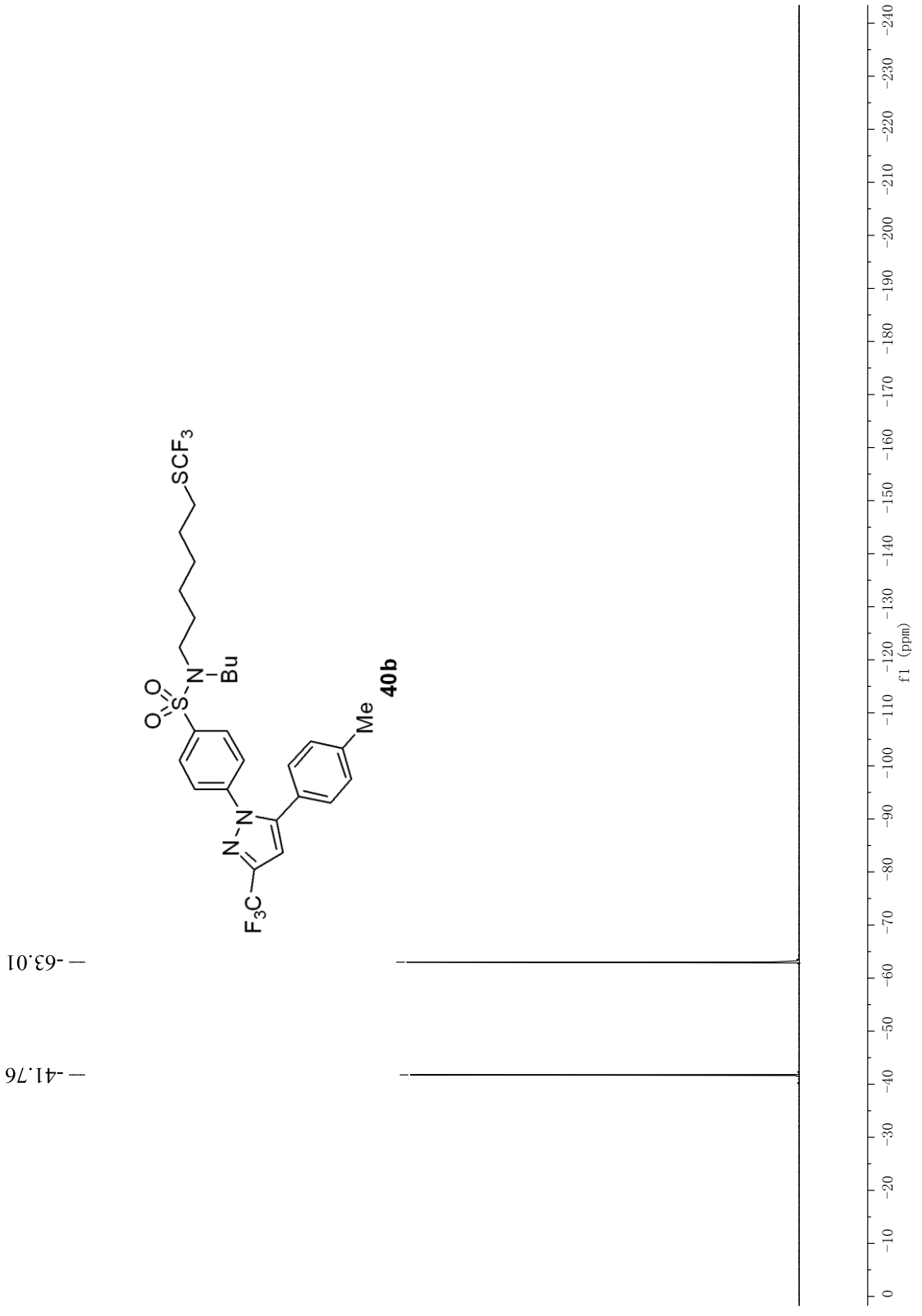
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **39b**



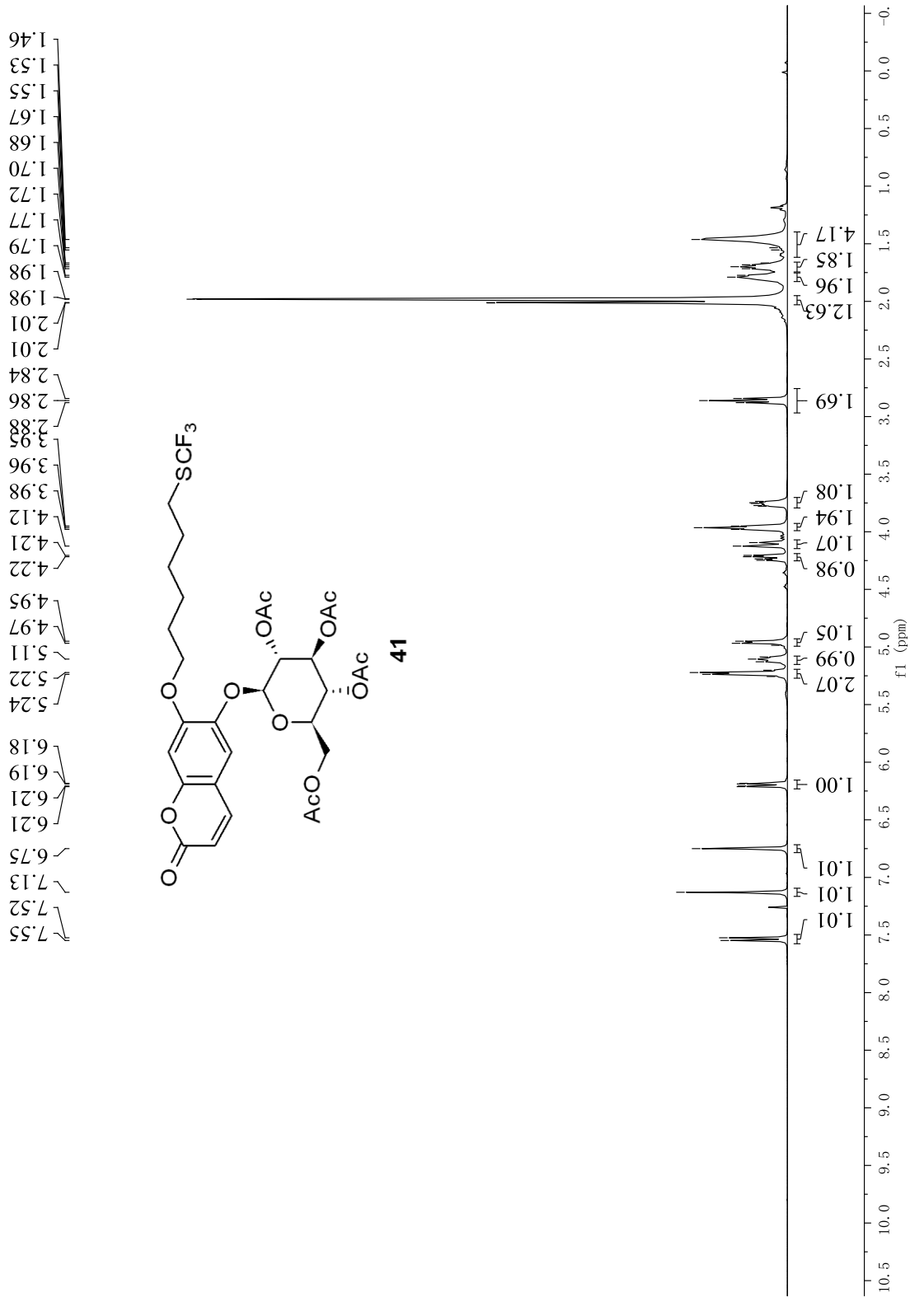
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **40b**



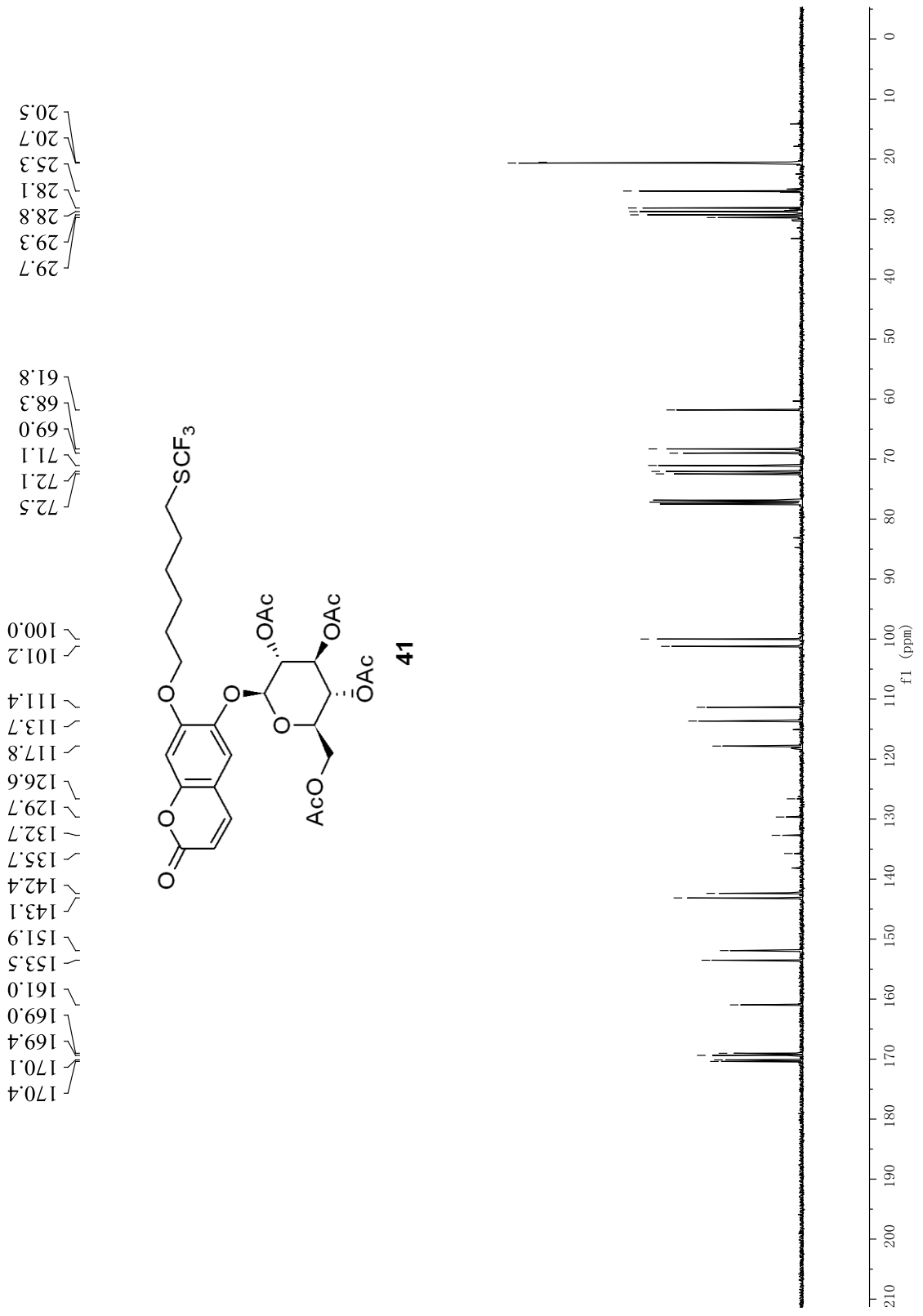
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **40b**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **40b**

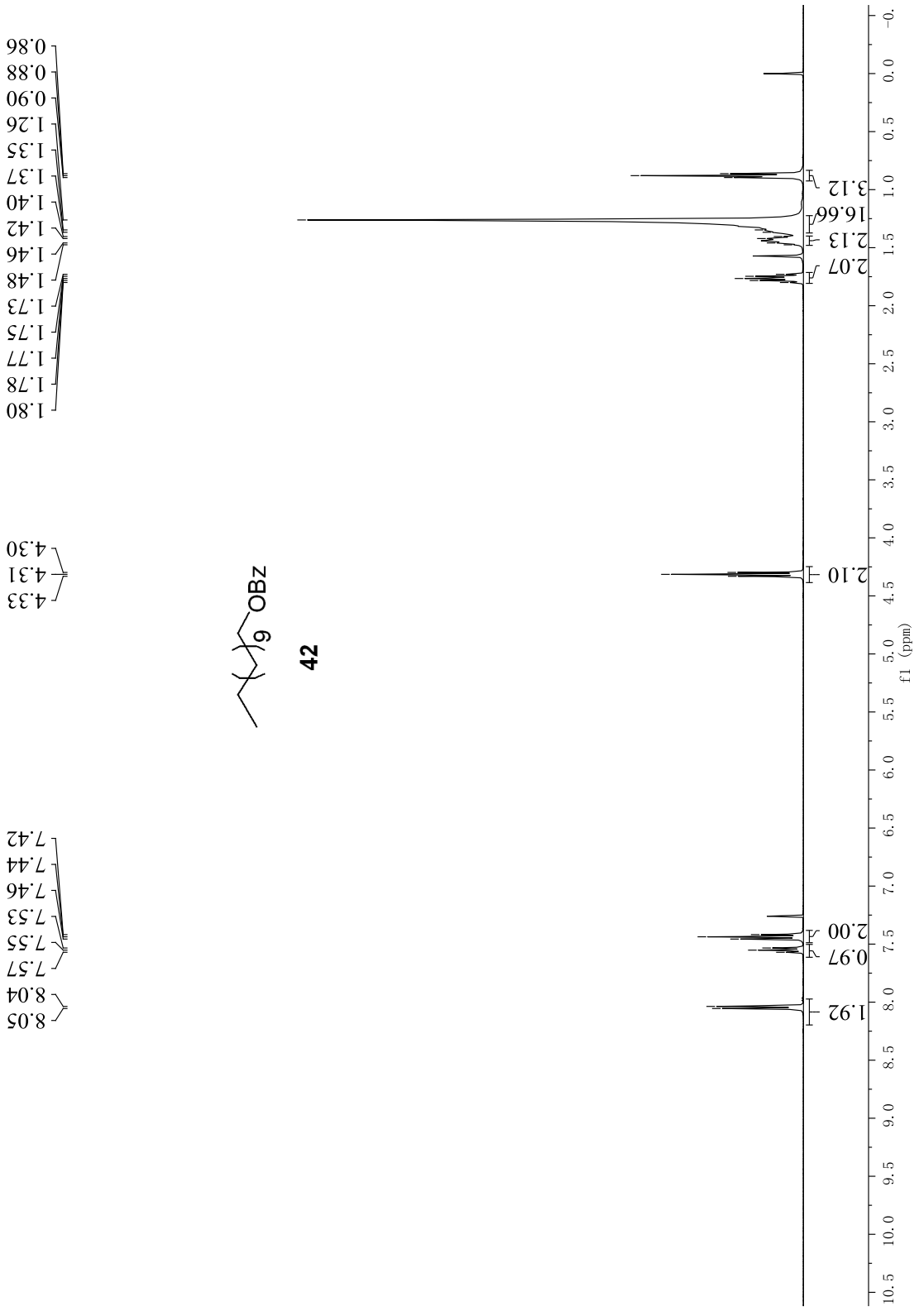


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **41**

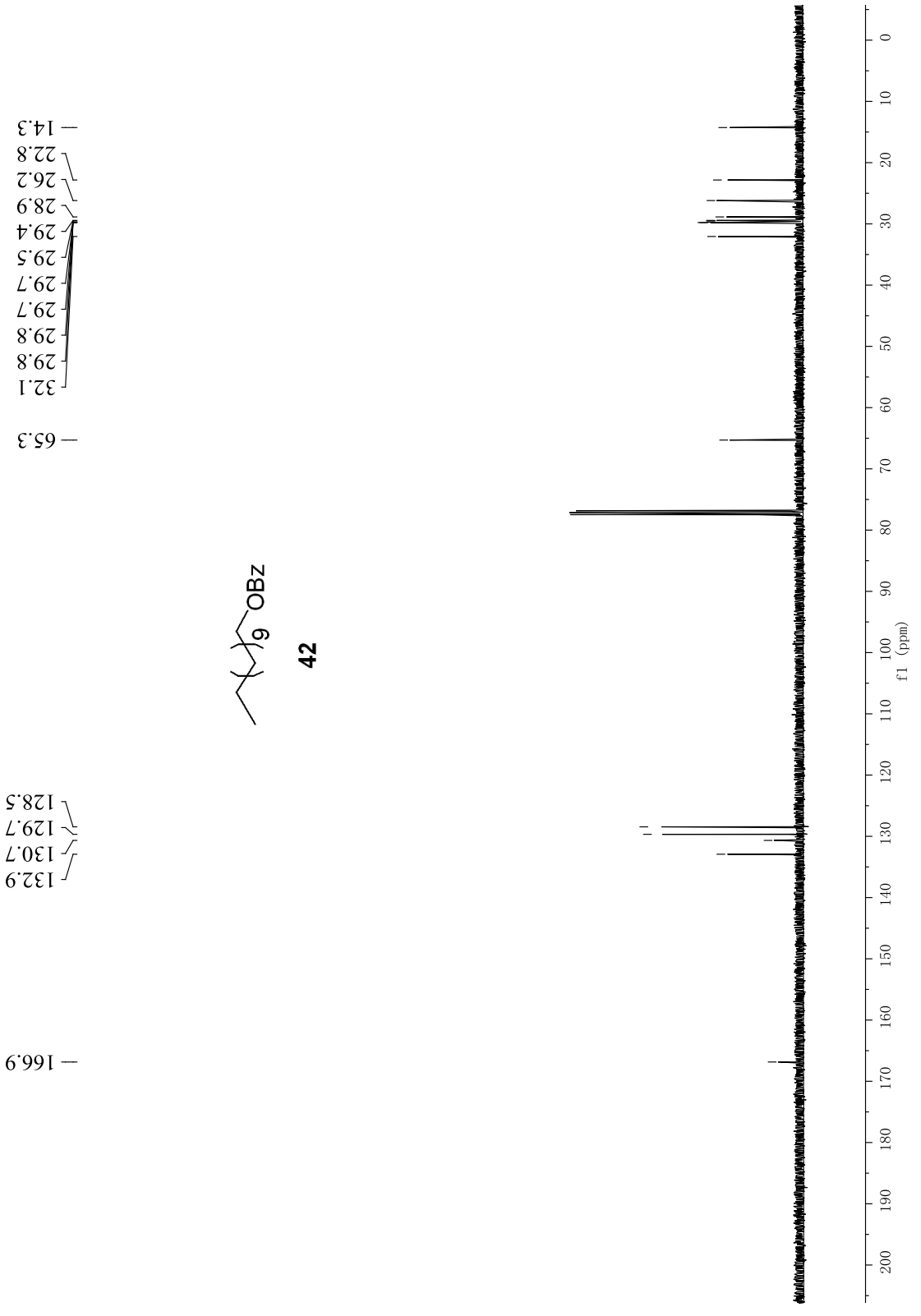


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **41**

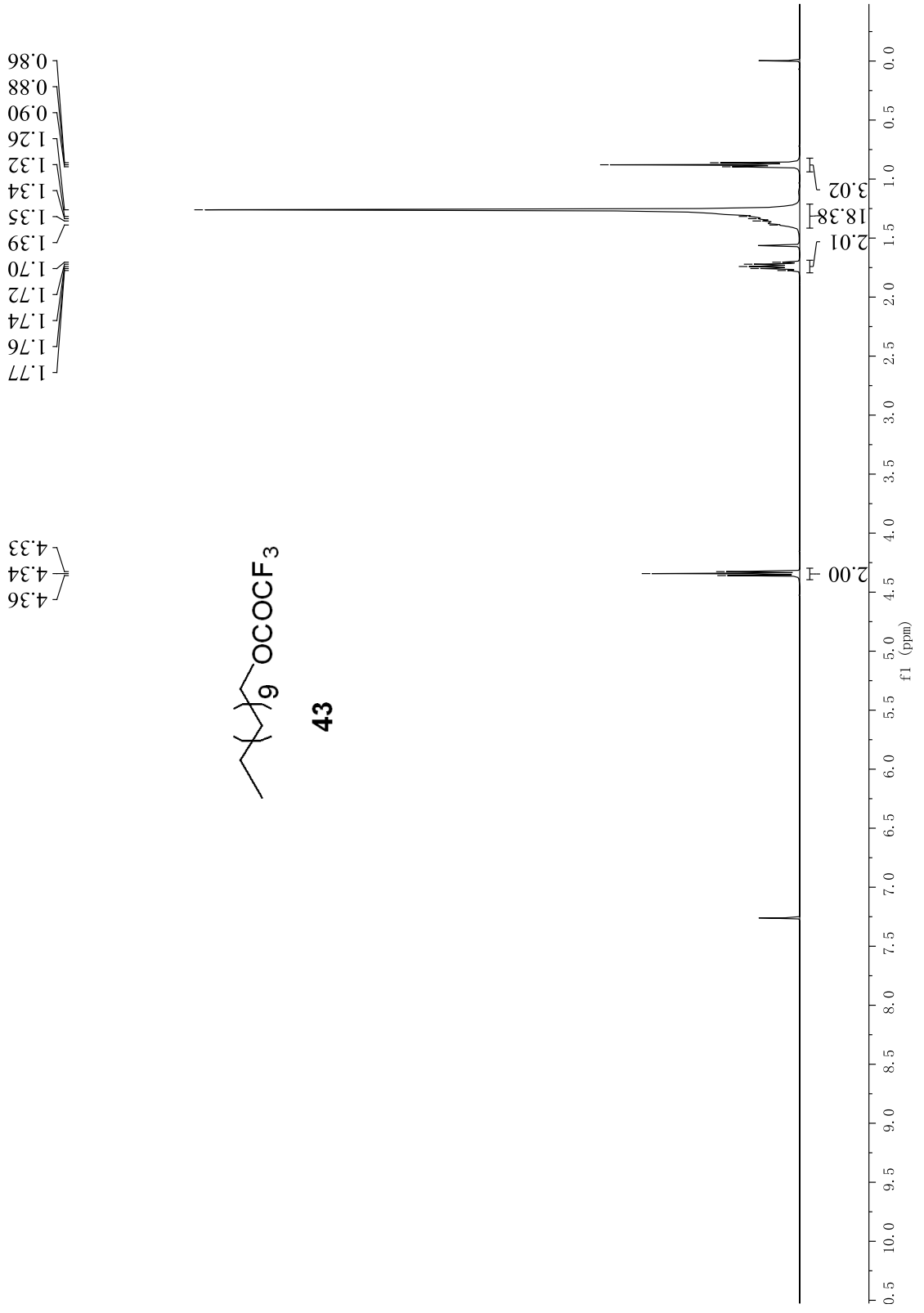
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **41**



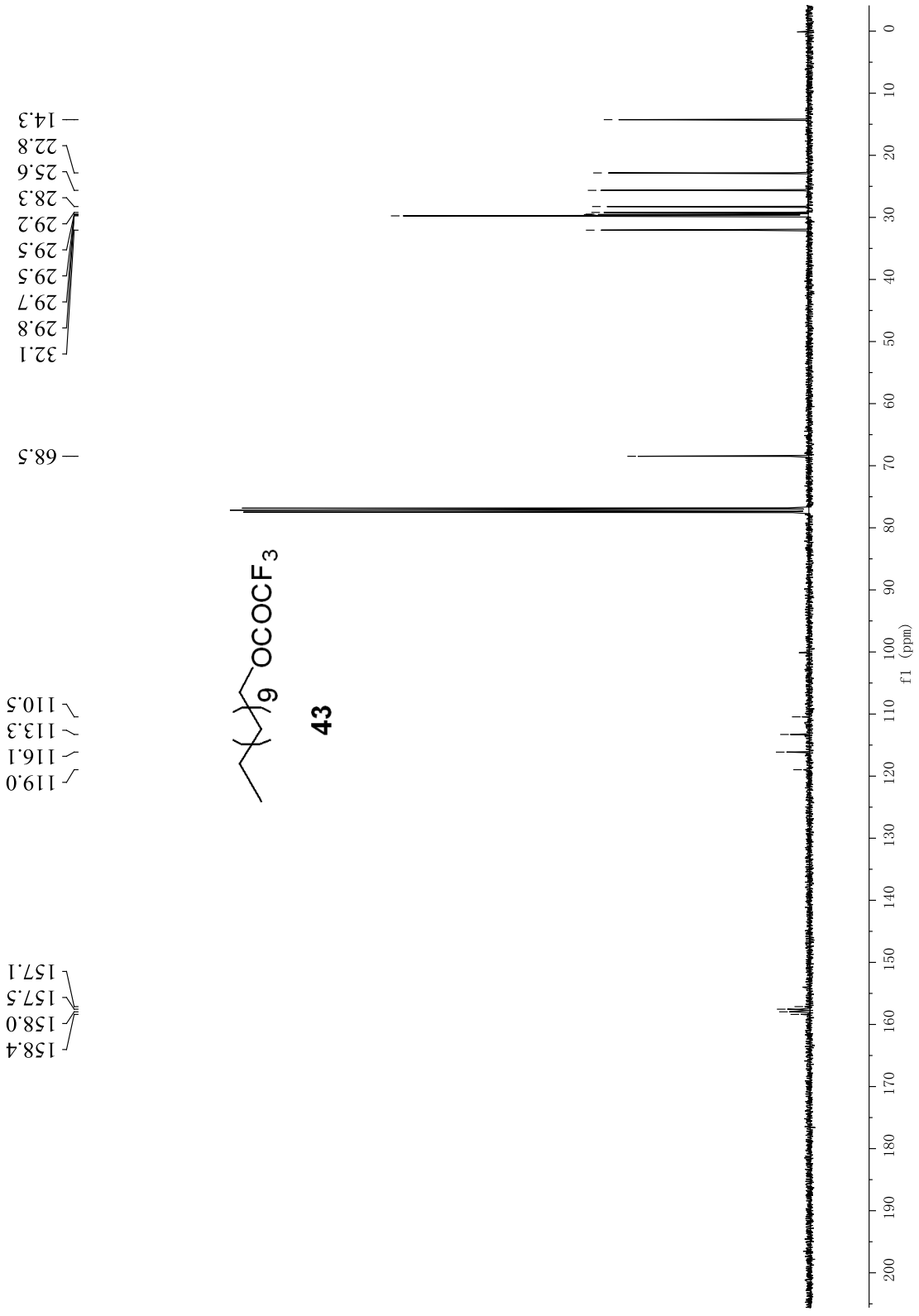
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **42**



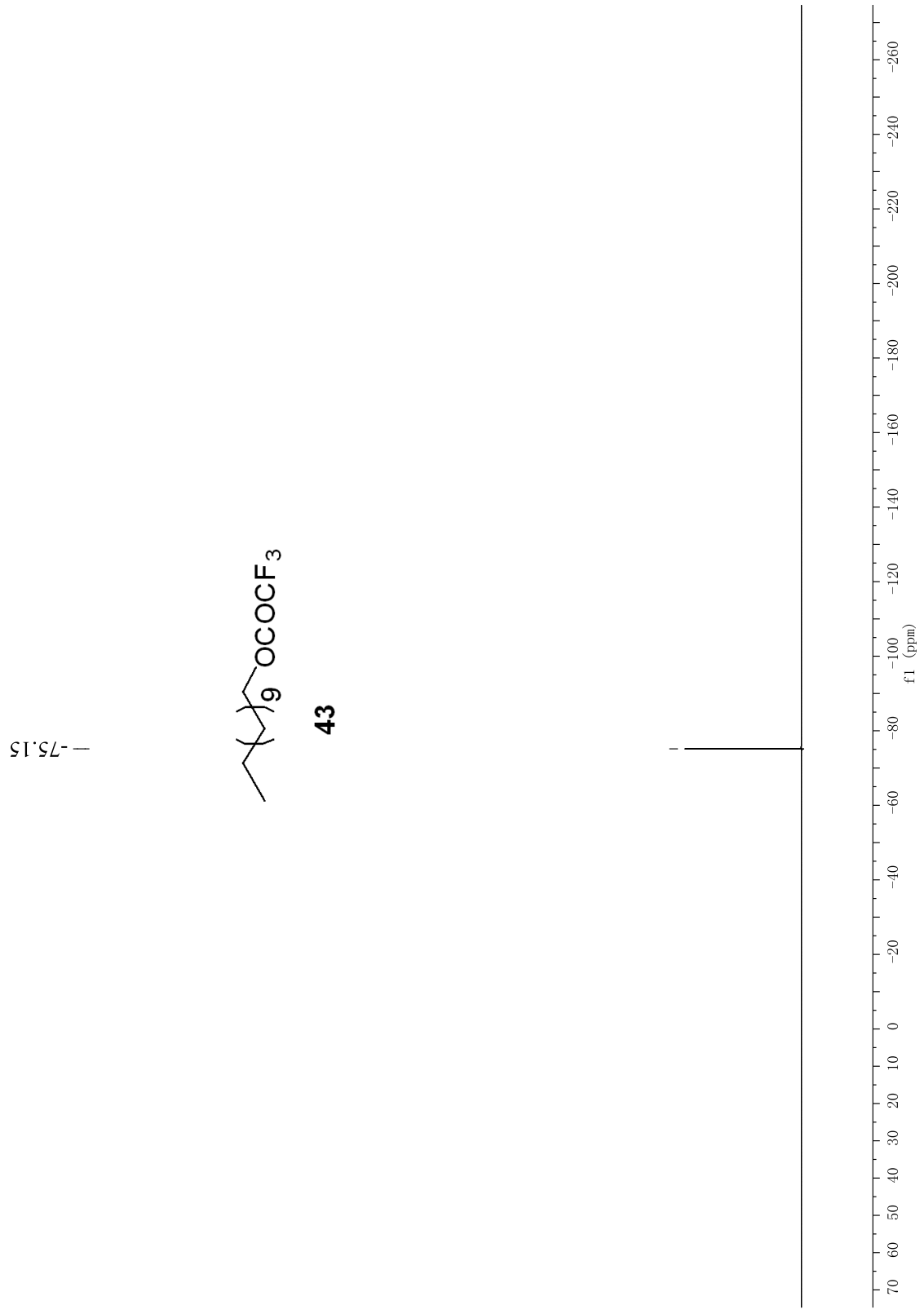
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **42**



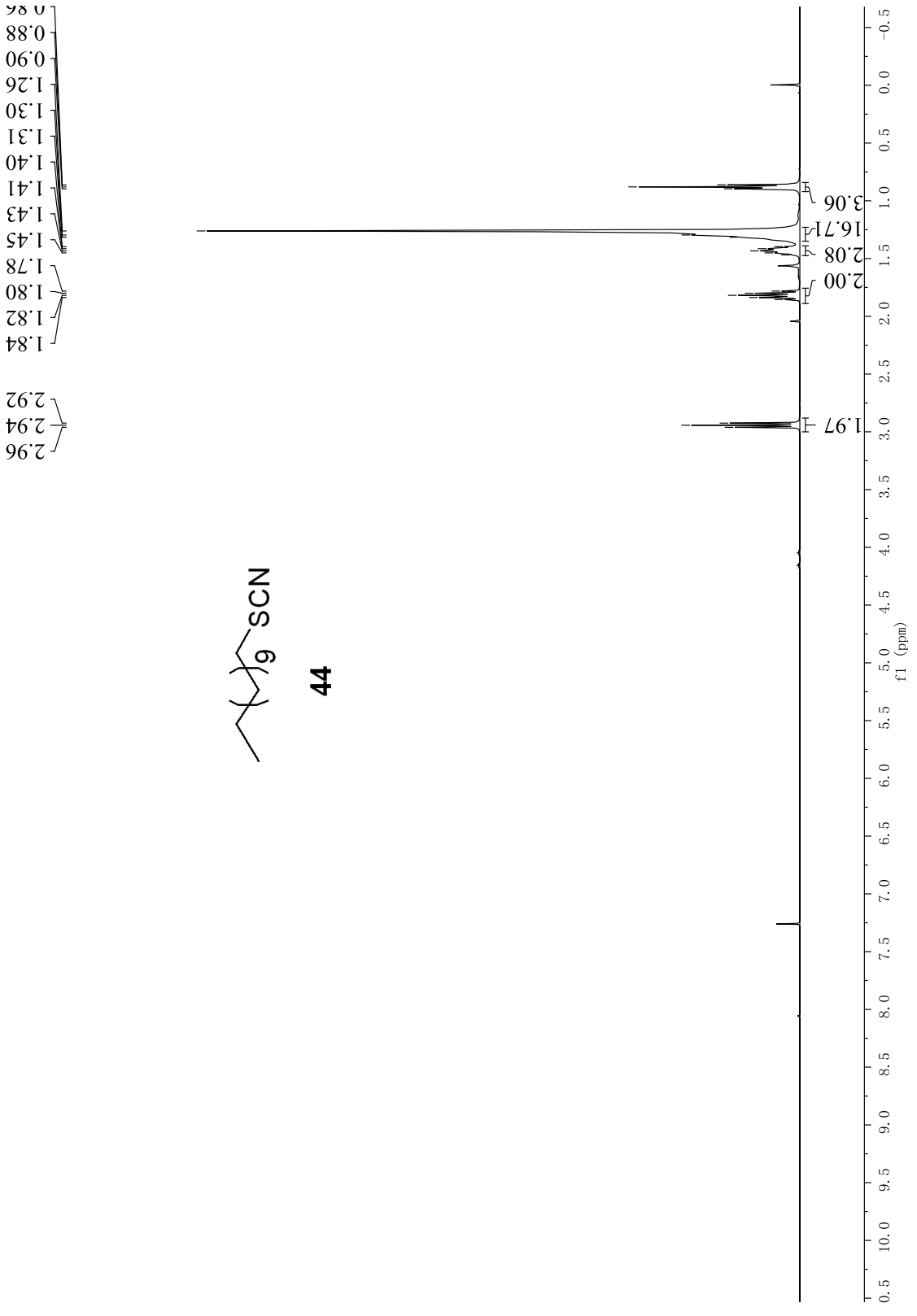
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **43**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **43**

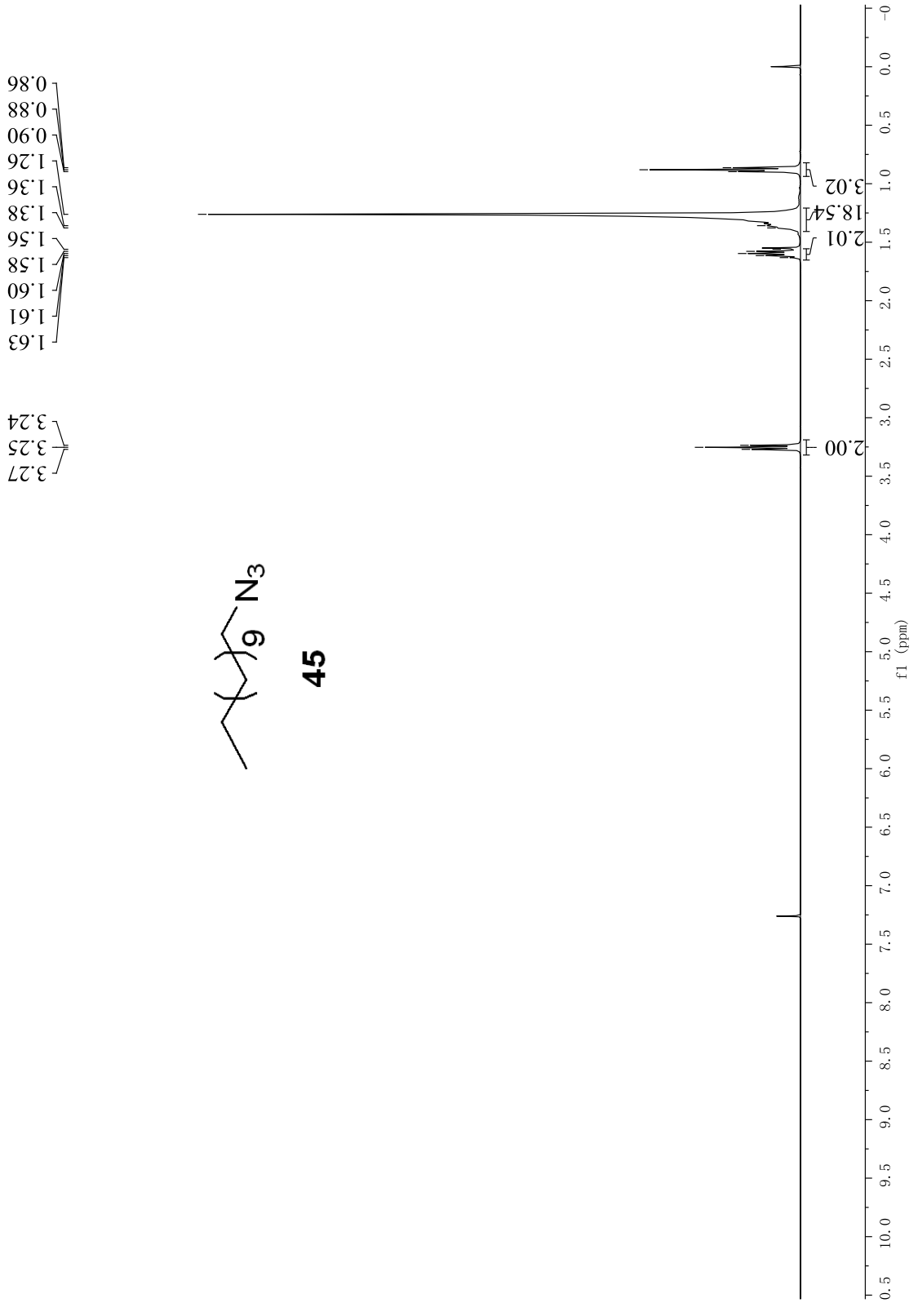


^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **43**

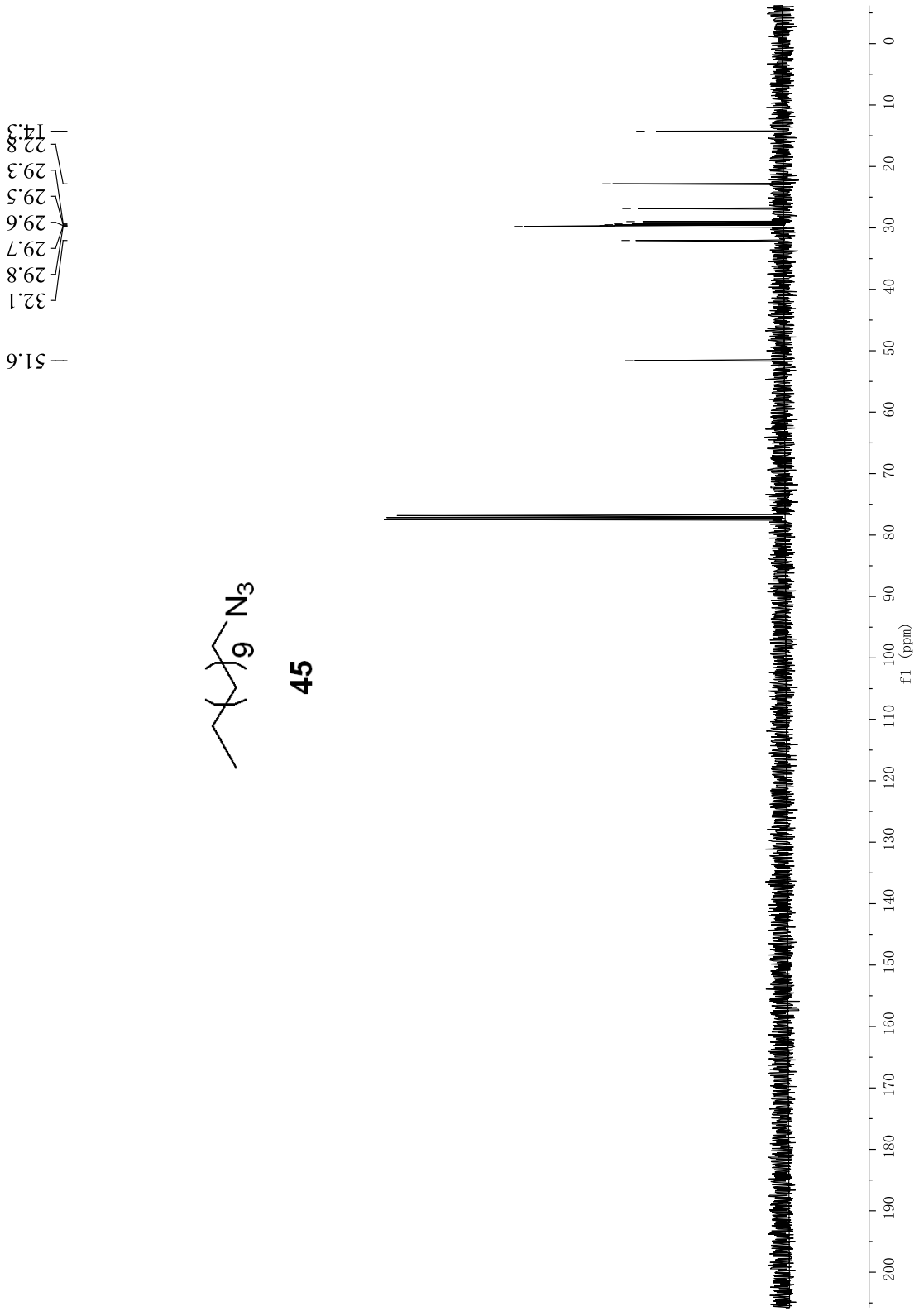


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **44**

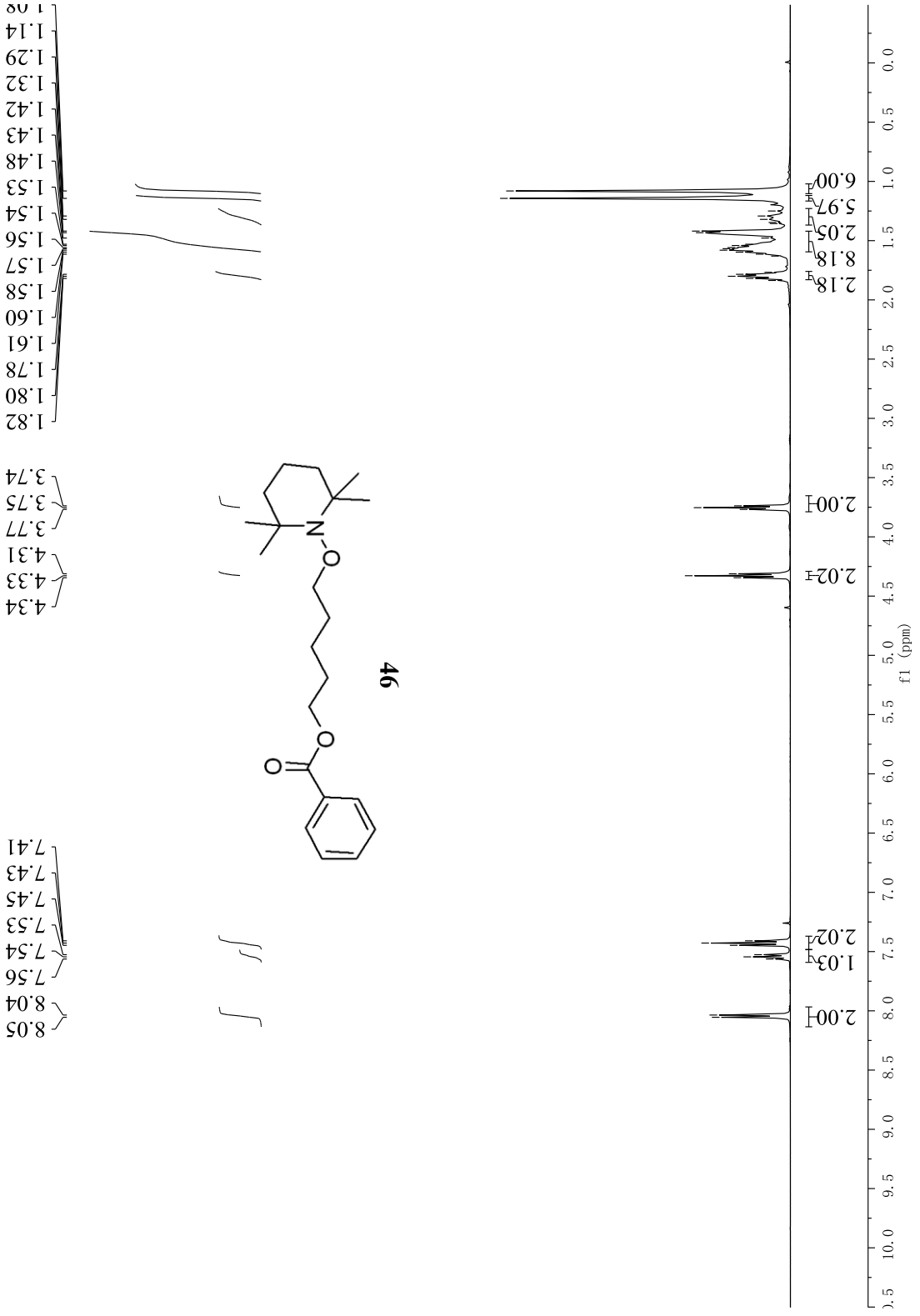
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **44**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **45**

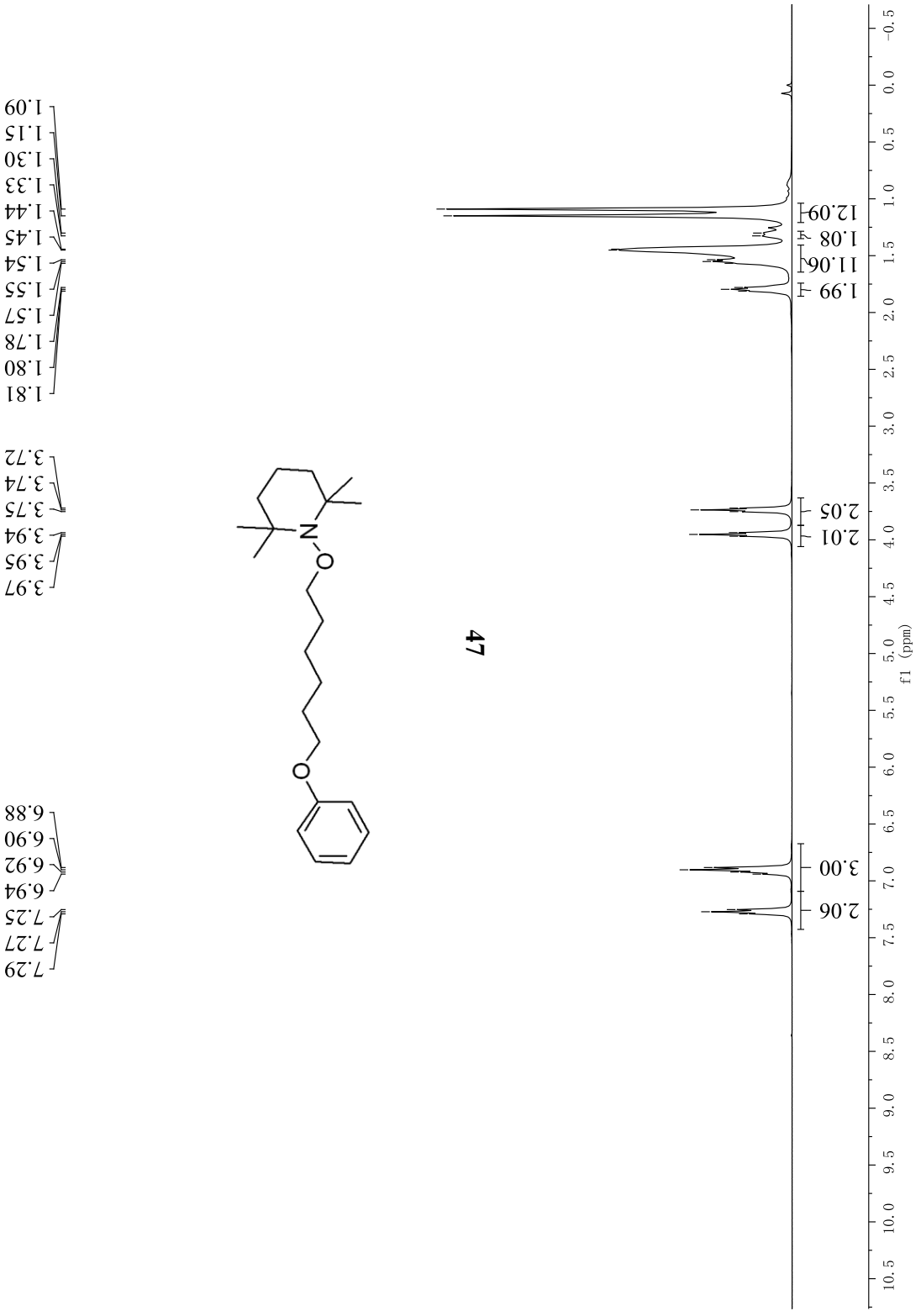


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **45**

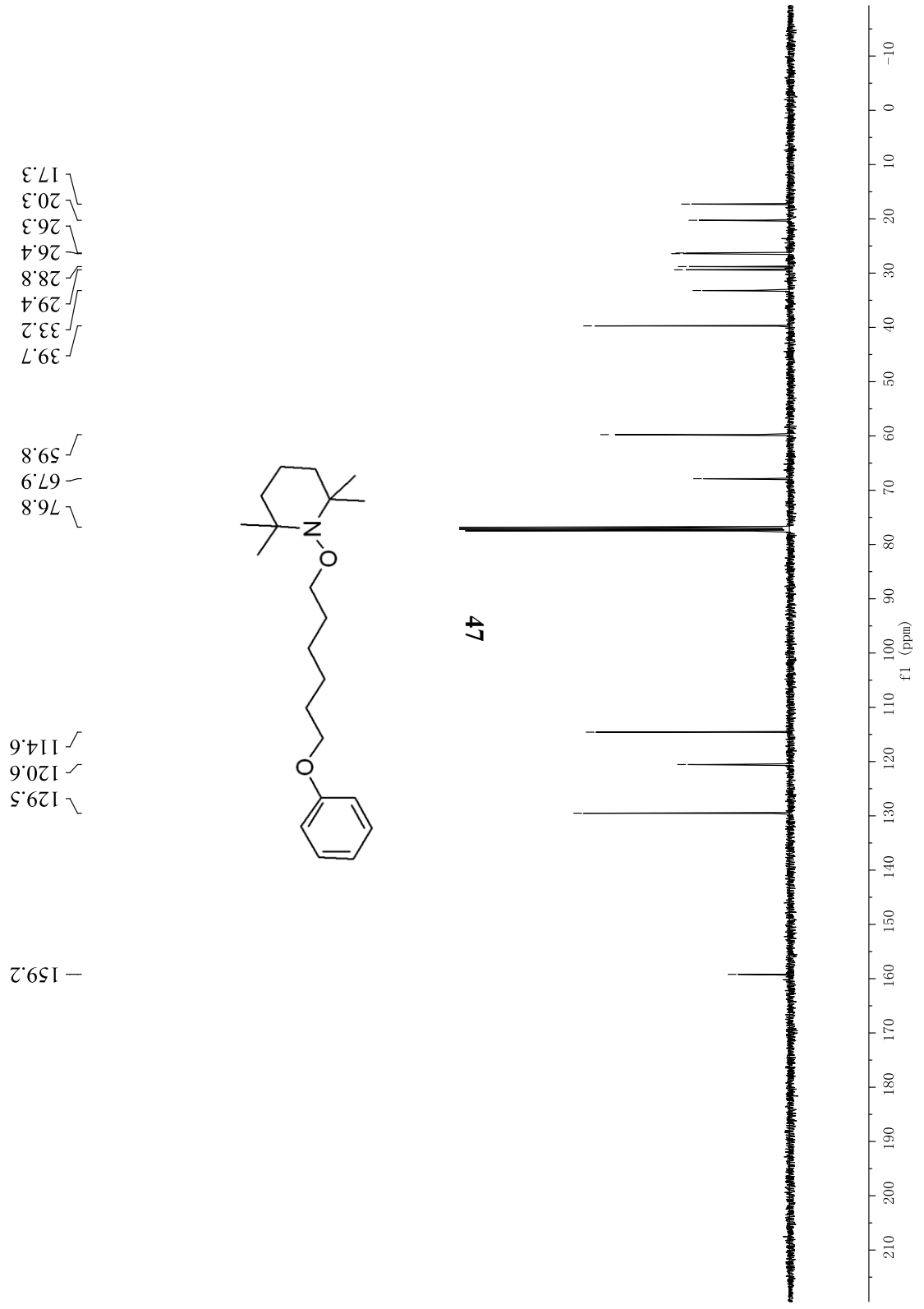


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **46**

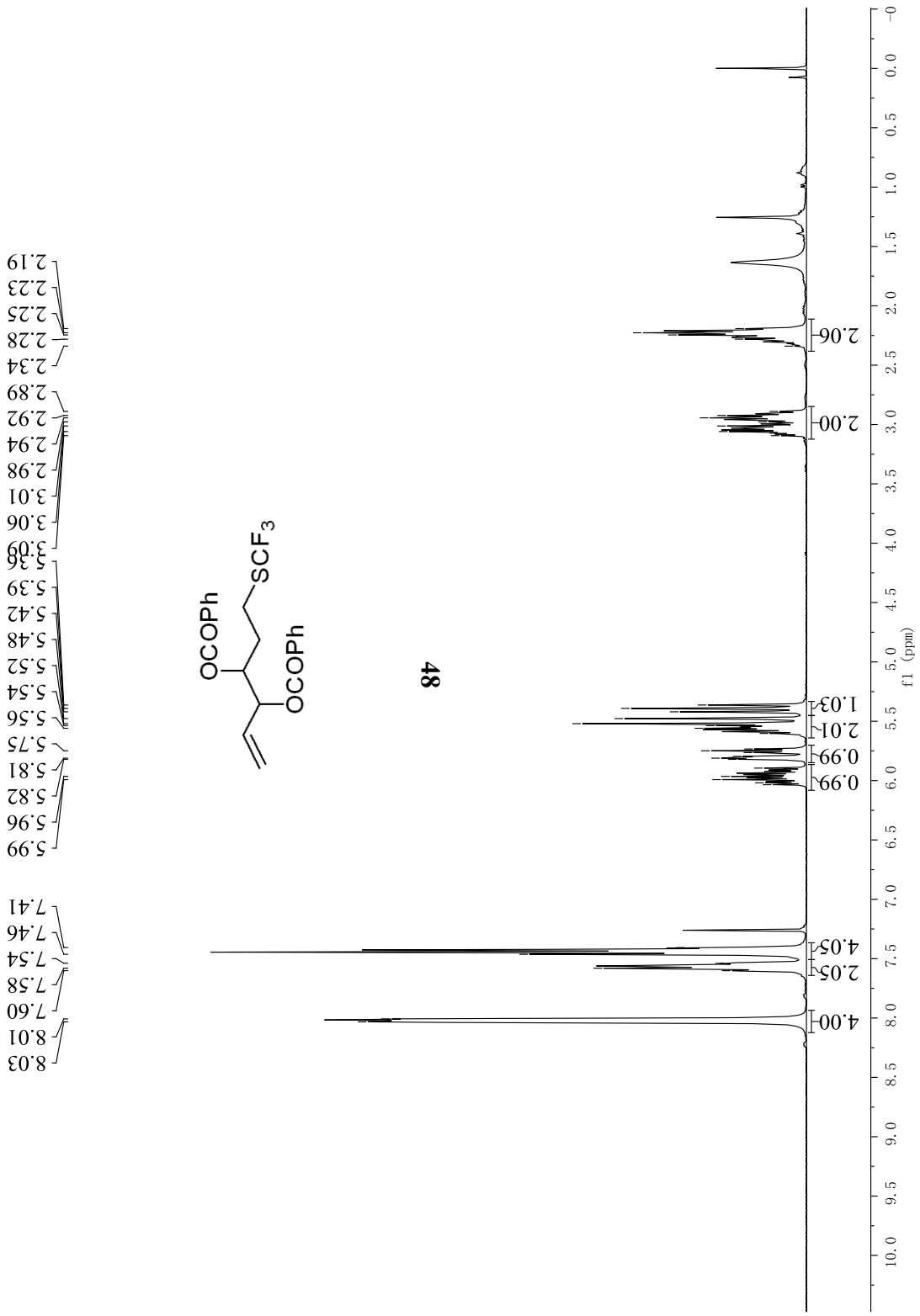
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **46**



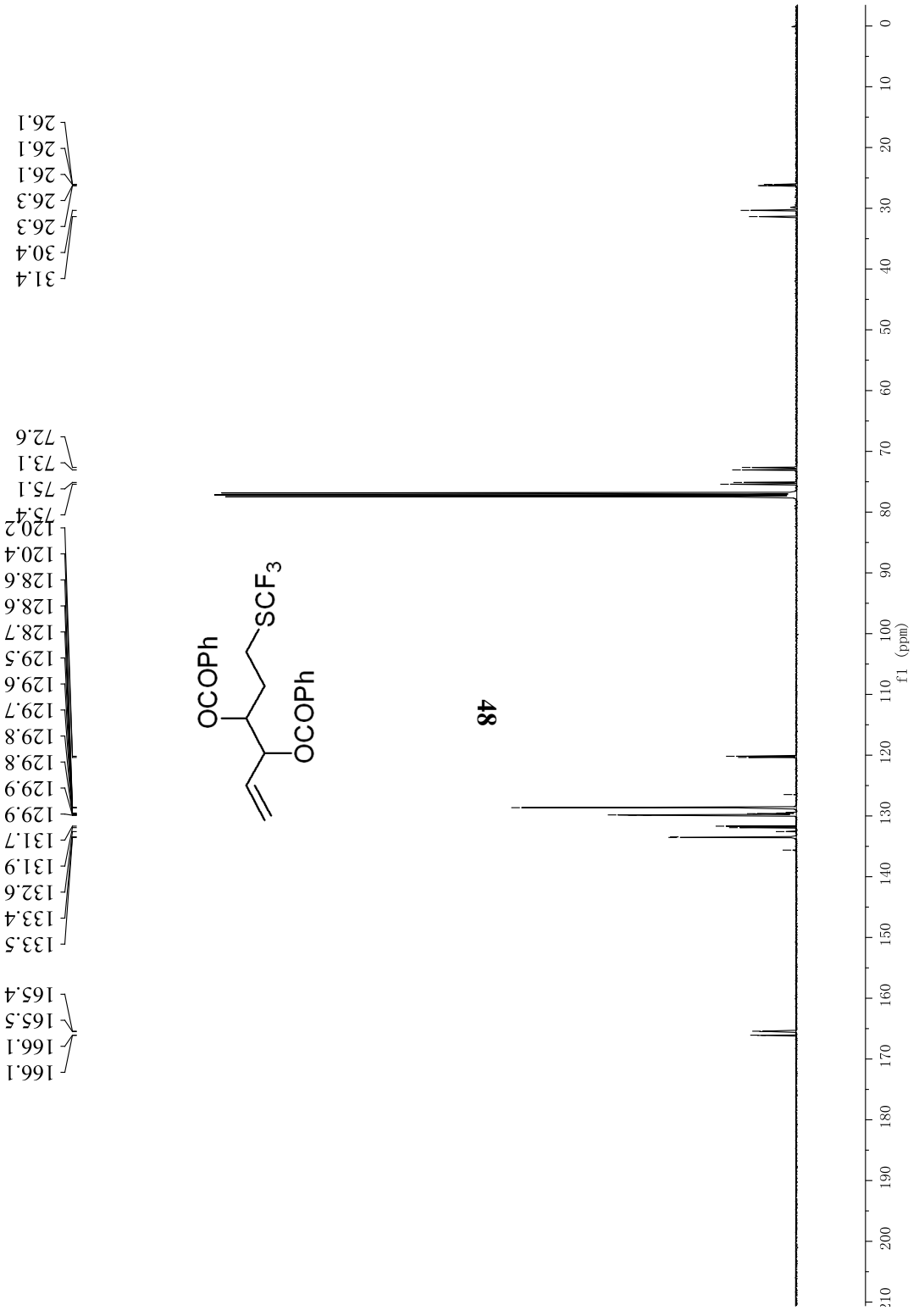
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **47**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **47**

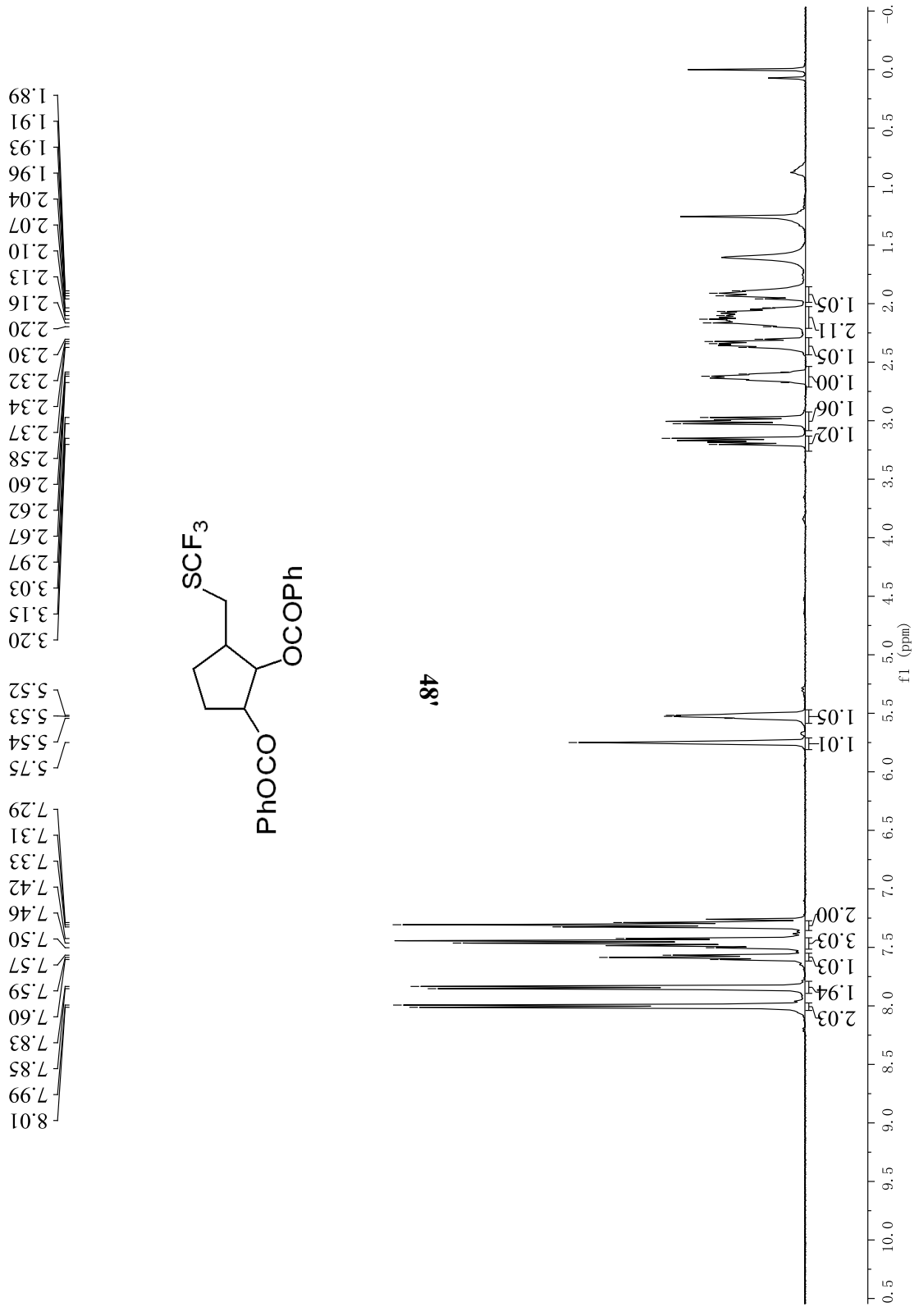


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **48**

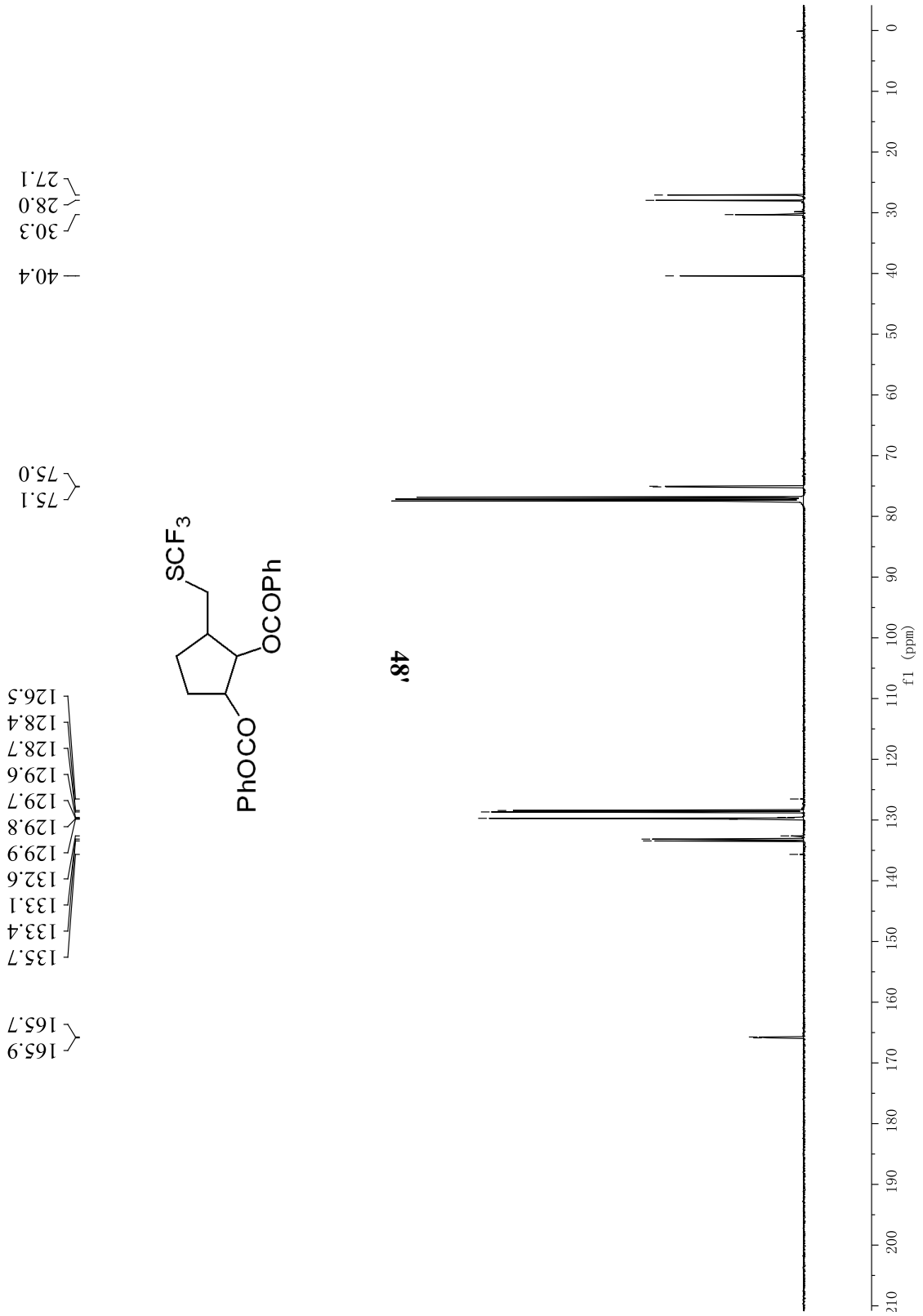


^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **48**

^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **48**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **48'**



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **48'**

^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **48'**