Electronic Supplementary Material (ESI) for ChemComm.

Supporting Online Material for

Silver-Catalyzed Meerwein Arylation: Intermolecular and Intramolecular Fluoroarylation of Styrenes

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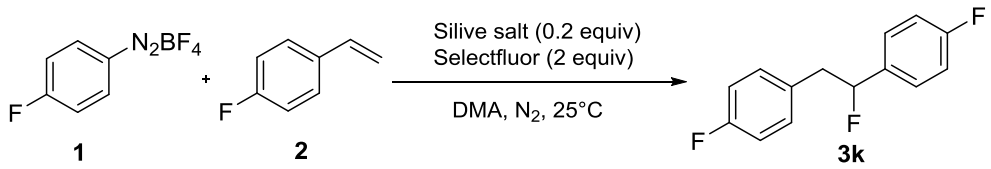
Materials and Methods

Unless otherwise noted, all fluorination reactions were performed in flame-dried apparatus under a nitrogen atmosphere using dry and deoxygenated solvents. A glove box was used to handle extremely air-sensitive and moisture-sensitive reagents and reactions under a nitrogen atmosphere (oxygen and moisture levels were maintained at 0–2 ppm at all times). The materials were purchased from commercial suppliers and used without further purification. DMA, DMF and DCM were dried by distillation over CaH_2. THF, Toluene was dried by distillation over sodium/benzophenone. H_2O and acetone were distilled. AgOTf was purchased from Alfa Aesar and Aladdin. Selectfluor, $CDCl_3$ and Acetone-d^6 were purchased from Sigma-Aldrich. TLC was performed on silica gel Huanghai $HSGF_{254}$ plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm). Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., China. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a Bruker AVANCE AV 400 (400MHz, 101MHz and 376MHz). Signal positions were recorded in ppm with the abbreviations s, d, t and m denoting singlet, doublet, triplet, and multiplet respectively. All NMR chemical shifts were reported with the solvent resonance as internal standard. For ^{1}H NMR: $CDCl_3$ = δ 7.26 ppm, Acetone-d^6 =δ 2.05 ppm. For ^{13}C NMR: $CDCl_3$ = δ 77.1 ppm, Acetone-d^6 =δ 29.9 ppm, δ 206.6 ppm . Mass spectra were acquired on Agilent 6520 Q-TOF LC/MS, Varian 7.0T FTMS and Aligent 7890/5975C-GS/MSD.

Experimental Data

Effect of silive salts on the reaction



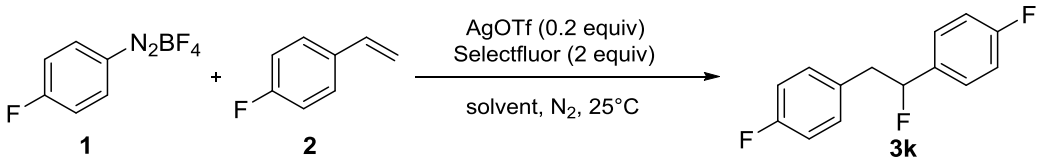
To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and silver salt (0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed 4-fluoro-1- chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S1.

Table S1: Effect of silver salts on the reaction

Silver salts	Yield [%] (^{19}FNMR)
-	56
Ag_2O	68
$AgBF_4$	65
AgOTf	69
Ag_2CO_3	65
$AgNO_3$	63
$AgSbF_4$	59
Ag_2SO_4	59
AgO	68

$AgN(OTf)_2$	52
AgOAc	56
AgSCN	55
AgF_2	59

Effect of solvents on the reaction



To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added solvent (0.240 mL) and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S2.

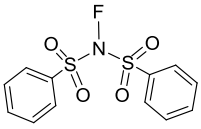
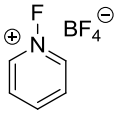
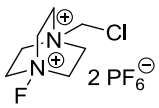
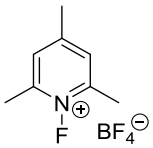
Table S2: Effect of solvents on the reaction

Solvent	Yield [%] (^{19}FNMR)	Solvent 10:1 (v/v)	Yield [%] (^{19}FNMR)
Dioxane	0	Dioxane /H_2O	19
DMF	54	DMF /H_2O	35
DCM	0	DCM /H_2O	trace
Acetone	0	Acetone/H_2O	14
DMA	68	DMA /H_2O	66
MeCN	4	MeCN/H_2O	5

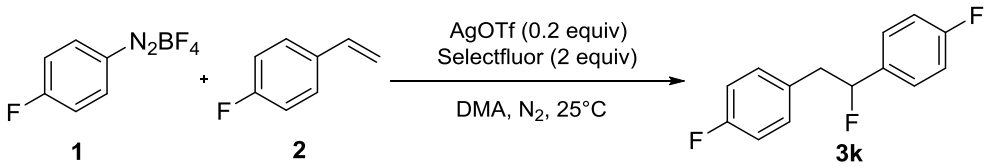
Effect of fluorinating reagents on the reaction

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 µL, 0.300 mmol, 5.00 equiv), then followed fluorinating reagent (0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 µL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S3.

Table S3: Effect of fluorinating reagents on the reaction

Fluorinating reagent	Yield [%] (^{19}FNMR)	Fluorinating reagent	Yield [%] (^{19}FNMR)
	0	AgF	0
	0	KF	0
	68	$Et_3N \cdot 3HF$	0
	50	TBAF	0
	0	$BF_3 \cdot Et_2O$	0
CsF	0	Pyridine • HF	0

Effect of ratios of the Starting materials on the reaction



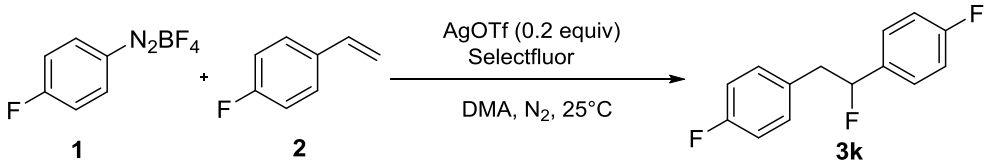
1 2 3k

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (X equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (Y equiv), then followed 4-fluoro-1- chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) **(3k)** was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S4.

Table S4: Effect of ratios of the Starting materials on the reaction

X:Y	Yield [%] (^{19}FNMR)
1:5	68
1:3	60
1:1	43
3:1	51
5:1	40

Effect of fluorinating reagent amount on the reaction



1 2 3k

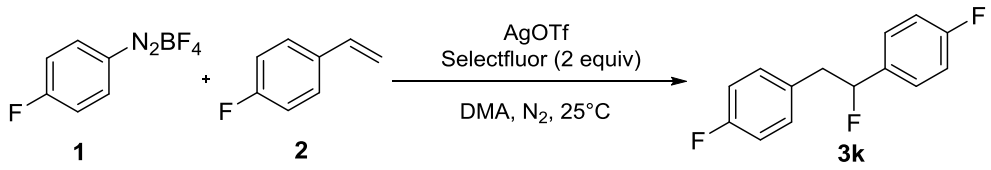
To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1- chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL,

0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S5.

Table S5: Effect of fluorinating reagent amount on the reaction

Amount of fluorination reagent (equiv)	Yield [%] (^{19}FNMR)
1.0	27
1.5	40
2.0	68
2.5	68
3.0	69
3.5	70

Effect of silive reagent amount on the reaction

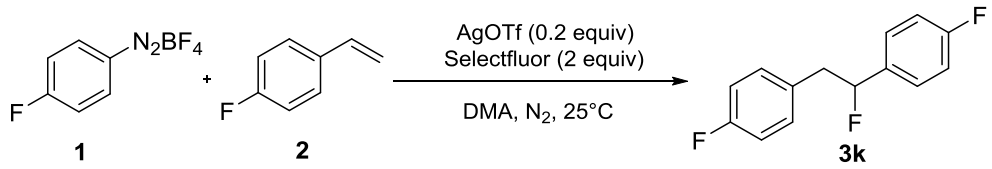


To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 µL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1- chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 µL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S6.

Table S6: Effect of silver reagent amount on the reaction

Amount of silver reagent (equiv)	Yield [%] (^{19}FNMR)
0.1	61
0.15	60
0.2	68
0.25	62
0.4	69
0.6	63
0.8	66
1.0	65

Effect of concentration on the reaction



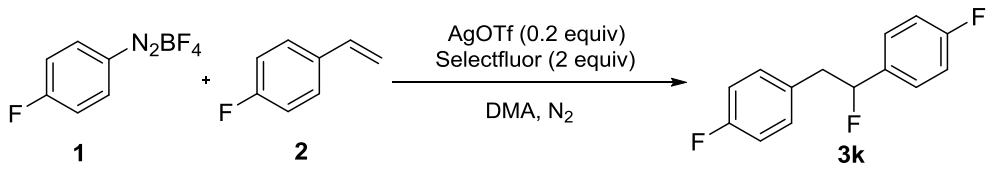
To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.060 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S7.

Table S7: Effect of concentration on the reaction

Concentration of reaction system (mol/L)	Yield [%] (^{19}FNMR)

1.00	23
0.500	60
0.250	68
0.167	61
0.125	65
0.100	63
0.0833	57
0.0500	46

Effect of temperature on the reaction



To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and Silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1- chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr in a sealed vial. Then 1-fluoro-3-nitrobenzene (5.00 μL, 0.0470 mmol) was added to the reaction mixture. The yield of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) was determined by comparing the integration of the ^{19}F NMR resonance of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) (-171.6 ppm) with that of 1-fluoro-3-nitrobenzene (-112.0 ppm). Yields are reported in Table S8.

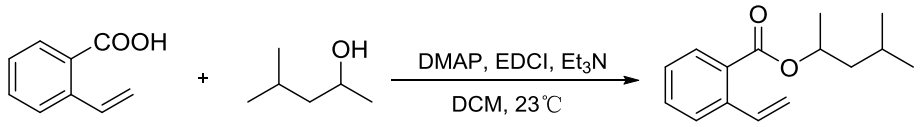
Table S8: Effect of temperature on the reaction

Temperature	Yield [%] (^{19}FNMR)
25 ^{o}C	68

35 °C	56
45 °C	46
60 °C	40
80 °C	23

General procedure and Compound Characterization

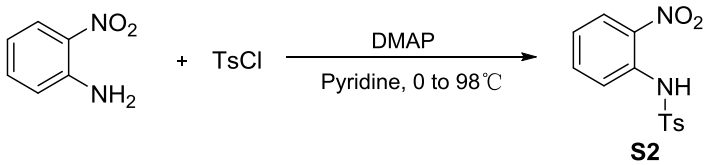
4-methylpentan-2-yl-2-vinylbenzoate[1] (S1)



S1

To a solution of 2-vinyl-benzoic acid (0.150 g, 1.00 mmol, 1.00 equiv), DMAP (4-dimethylaminepyridine) (6.60 mg, 0.0200 mmol, 0.200 equiv) and Et_3N (0.280 mL, 2.14 mmol, 2.14 equiv) in CH_2Cl_2 (5.00 mL) at 23 °C were added EDCI (1-ethyl-(3-(3-dimethylamino)propyl)-carbodiimide hydrochloride) (0.316 g, 2.00 mmol, 2.00 equiv) and 4-methylpentan-2-ol (0.280 ml, 1.00 mmol, 1.00 equiv). The reaction mixture was warmed to 23 °C and stirred for 6 hr before quenched with H_2O (10.0 mL) and extracted 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 hexanes/EtOAc 50:1 (v/v) to afford 0.210 g 4-methylpentan-2-yl-2-vinylbenzoate (**S1**) as a colourless oil (89% yield). R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.7 Hz, 1H), 7.63 – 7.52 (m, 1H), 7.48 (dd, *J* = 17.2, 4.0 Hz, 2H), 7.30 (s, 1H), 5.65 (d, *J* = 17.4 Hz, 1H), 5.33 (t, *J* = 11.9 Hz, 1H), 5.27 (m, 1H), 1.73 (m, 2H), 1.39 (m, 1H), 1.35 (d, *J* = 4.8 Hz, 3H), 0.96 (d, *J* = 4.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 139.5, 136.0, 131.8, 130.1, 129.5, 127.4, 127.2, 116.2, 70.3, 45.3, 24.9, 22.9, 22.4, 20.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$, 255.1361. Found, 255.1358.

4-methyl-N-(2-nitrophenyl)benzene sulfonamide[2] (S2)



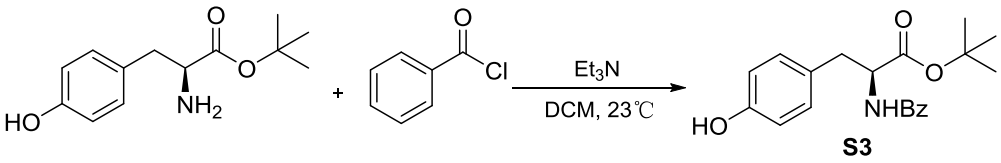
S2

4-methylbenzenesulfonyl chloride (11.4 g, 60.0 mmol, 1.20 equiv) was added to a solution of 2-nitroaniline (6.90 g, 50.0 mmol, 1.00 equiv) and 4-(dimethylamino)pyridine (0.610 g, 5.00 mmol,

0.100 equiv) in pyridine (60.0 ml) under a nitrogen atmosphere at 0 ℃. The reaction mixture was slowly warmed to 98 ℃ and stirred for 36 h. The reaction mixture was concentrated by removing the solvent under reduced pressure, diluted with ethyl acetate (120 ml) and sequentially washed with hydrochloric acid (2 M, 2 × 200 ml), aqueous sodium hydroxide (2 M, 2 × 250 ml). The combined aqueous extracts were slowly acidified with concentrated hydrochloric acid at 0 ℃ until pH 2 to obtain a bright yellow precipitate which was extracted with ethyl acetate (300 ml). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness to obtain 4-methyl-N-(2-nitrophenyl)benzene sulfonamide (**S2**) as brilliant yellow needles (9.60 g, 66%).

R_f = 0.5 (hexanes/EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 13.3 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.8, 135.9, 135.6, 133.8, 130.1, 127.3, 126.2, 123.8, 120.8, 21.6. The spectroscopic data (NMR) matched those reported in the literature for 4-methyl-N-(2-nitrophenyl)benzenesulfonamide.

tert-butyl benzoyl-L-tyrosinate[3] **(S3)**

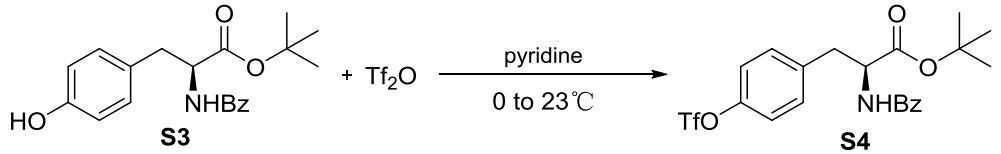


S3

To a solution of tert-butyl L-tyrosinate (2.40 g, 10.2 mmol, 1.00 equiv), Et_3N (1.98 mL, 24.2 mmol, 2.38 equiv) in CH_2Cl_2 (50.0 mL) were added benzoyl chloride (1.30 ml, 11.2 mmol, 1.10 equiv) at 0 ^{o}C stirred for 0.5 hr. The reaction mixture was warmed to 23 ^{o}C and stirred for 12 hr before quenched with H_2O (10.0 mL) and extracted 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 hexanes/EtOAc 5:1 (v/v) to afford 2.60 g tert-butyl benzoyl-L-tyrosinate (**S3**) as a colorless solid (75% yield).

R_f = 0.5 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, Acetone) δ 8.34 (s, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.47 (m, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.73 (dd, *J* = 14.3, 6.9 Hz, 1H), 3.13 (d, *J* = 8.6 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Acetone) δ 171.7, 167.4, 157.1, 135.4, 132.1, 131.2, 129.2, 128.9, 128.1, 116.0, 81.6, 55.8, 37.3, 28.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{20}H_{22}NO_4$ [M -H], 340.1549. Found, 340.1549.

tert-butyl (S)-2-benzamido-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate[4] **(S4)**

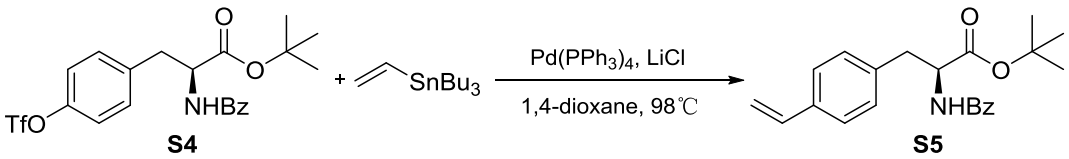


S3 **S4**

To a solution of tert-butyl benzoyl-L-tyrosinate (**S3**) (1.60 g, 4.69 mmol,1.00 equiv) in 10.0 mL of pyridine at 0 ℃ was slowly added trifluoromethanesulfonic anhydride (0.940 mL, 5.59 mmol, 1.20 equiv). The resulting mixture was stirred at 0 ℃ for 5 min and then allowed to warm to 23 ℃ and stirred at this temperature for 25 h. The resulting mixture was poured into water and extracted with ethyl ether. The ether extract was washed sequentially with water (20.0 ml), 10% aqueous hydrochloric acid solution (100 ml), water (20.0 ml), and a concentrated sodium chloride solution, dried ($MgSO_4$), and concentrated to yield an oil. Chromatography (flash column, hexanes-EtOAc 10:l) afforded tert-butyl (S)-2-benzamido-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (**S4**) as a colorless oil (1.21 g, 55%).

R_f = 0.5 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 6.9 Hz, 1H), 4.94 (dd, *J* = 12.8, 6.0 Hz, 1H), 3.27 (d, *J* = 5.9 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 166.8, 148.6, 137.2, 133.9, 132.0, 131.4, 128.8, 127.0, 121.3, 118.6 (m, $J_{(C-F)}$= 210.3 Hz), 83.2, 53.9, 37.6, 28.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.8 (m, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{22}F_3NO_6SNa$ [M + Na]$^+$, 496.1018. Found, 496.1018.

tert-butyl (S)-2-benzamido-3-(4-vinylphenyl)propanoate[4] **(S5)**

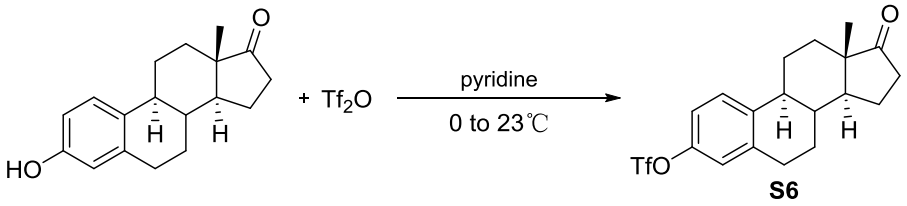


To a solution of tert-butyl (S)-2-benzamido-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (**S4**) (1.00 g, 2.10 mmol, 1.00 equiv) in 11 mL of 1,4-dioxane were added tri-n-butylethenylstannane (680 mg, 2.10 mmol, 1.00 equiv), LiCl (264 mg, 5.94 mmol, 2.80 equiv), $Pd(PPh_3)_4$ (48.0 mg, 0.0400 mmol, 0.0200 equiv), and a few crystals of 2,6-di-tert-butyl-4-methyl-phenol. The resulting suspension was heated to reflux (98 ℃) for 4 h, cooled to room temperature, and treated with 1.00 mL of pyridine and 2.00 mL of pyridinium fluoride (1.40 M solution in THF, 2.80 mmol). The resulting mixture was stirred at 23 ℃ for 16 h. The mixture was diluted with diethyl ether, filtered through a small pad of Celite, and washed with water, 10% HCI, water, and a concentrated sodium chloride solution. The solution was dried ($MgSO_4$) and concentrated to yield an oil. Chromatography (flash column, hexanes-EtOAc 20: 1) afforded tert-butyl (S)-2-benzamido-3-(4-vinylphenyl)propanoate (**S5**) as a colorless oil, which solidified on standing (273 mg, 37%).

R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 6.7 Hz, 2H), 7.26 (d, *J* = 1.7 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.75 – 6.67 (m, 1H), 6.65 (s, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.7 Hz, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 3.31 – 3.14 (m, 1H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 166.5, 136.5, 136.3, 135.9, 134.1, 131.8, 129.9, 128.7,

127.1, 126.3, 113.7, 82.8, 53.9, 37.7, 28.1. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{25}NO_3Na$ $[M + Na]^+$, 374.1732. Found, 374.1728.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate[4] **(S6)**

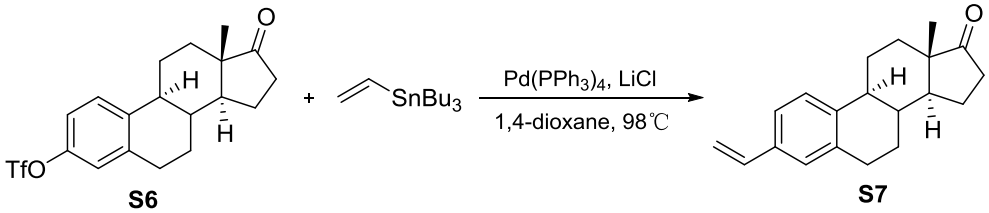


S6

To a solution of 1,3,5(10)-Estratrien-3-ol-17-one (2.70 g, 10.0 mmol, 1.00 equiv) in 25.0 mL of pyridine at 0 ℃ was slowly added trifluoromethanesulfonic anhydride (1.88 mL, 11.2 mmol, 1.10 equiv). The resulting mixture was stirred at 0 ℃ for 5 min and then allowed to warm to 23 ℃ and stirred at this temperature for 25 h. The resulting mixture was poured into water and extracted with ethyl ether. The ether extract was washed sequentially with water (50.0 ml), 10% aqueous hydrochloric acid solution (200 ml), water, and a concentrated sodium chloride solution, dried ($MgSO_4$), and concentrated to yield an oil. Chromatography (flash column, hexanes-EtOAc 20:l) afforded (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (**S6**) as a colorless solid (3.61 g, 90%).

R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 1H), 7.05 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.01 (d, *J* = 6.4 Hz, 1H), 2.94 (dt, *J* = 22.6, 11.5 Hz, 2H), 2.59 – 2.46 (m, 1H), 2.45 – 2.36 (m, 1H), 2.36 – 2.25 (m, 1H), 2.18 (dd, *J* = 18.5, 9.4 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.99 (dd, *J* = 8.7, 6.3 Hz, 1H), 1.72 – 1.60 (m, 2H), 1.57 – 1.44 (m, 4H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.2, 147.4, 140.2, 139.2, 127.2, 121.2, 119.6 (m, $J_{(C-F)}$= 212.3 Hz), 118.2, 50.3, 47.8, 44.1, 37.8, 35.7, 31.4, 29.4, 26.1, 25.7, 21.6, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.2 (m, 3F). The spectroscopic data (NMR) matched those reported in the literature[5] for (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate.

(8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one[4] **(S7)**



S6 **S7**

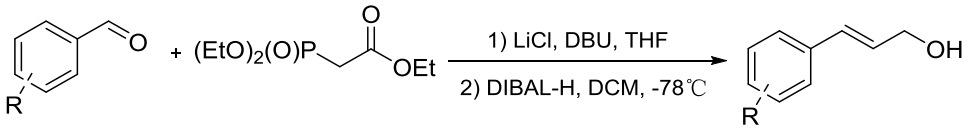
To a solution of (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-

cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (**S6**) (3.61 g, 9.00 mmol, 1.00 equiv) in 25.0 mL of 1,4-dioxane were added tri-n-butylethenylstannane (2.93 mg, 9.00 mmol, 1.00 equiv), LiCl (1.13 g, 25.4 mmol, 2.80 equiv), $Pd(PPh_3)_4$ (207 mg, 0.360 mmol, 0.0200 equiv), and a few crystals of 2,6-di-tert-butyl-4-methyl-phenol. The resulting suspension was heated to reflux (98 ℃) for 4 h, cooled to room temperature, and treated with 4.50 mL of pyridine and 2.00 mL of pyridinium fluoride (1.40 M solution in THF, 12.8 mmol). The resulting mixture was stirred at 23 ℃ for 16 h. The mixture was diluted with diethyl ether, filtered through a small pad of Celite, and washed with water, 10% HCI, water, and a concentrated sodium chloride solution. The solution was dried ($MgSO_4$) and concentrated to yield an oil. Chromatography (flash column, hexanes-EtOAc 25: 1) afforded (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**S7**) as a colorless oil, which solidified on standing (2.00 g, 75%).

R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 12.7 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.14 (s, 1H), 6.67 (dd, *J* = 17.2, 11.1 Hz, 1H), 5.71 (d, *J* = 17.8 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 2.92 (d, *J* = 4.2 Hz, 2H), 2.51 (dd, *J* = 18.7, 7.9 Hz, 1H), 2.43 (d, *J* = 11.4 Hz, 1H), 2.30 (m, 1H), 2.21 – 2.12 (m, 1H), 2.12 – 2.00 (m, 2H), 1.97 (d, *J* = 9.7 Hz, 1H), 1.62 (dd, *J* = 20.7, 10.0 Hz, 2H), 1.58 – 1.41 (m, 4H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 139.4, 136.5, 135.5, 135.3, 126.9, 125.5, 123.6, 113.1, 50.5, 48.0, 44.5, 38.1, 35.9, 31.6, 29.4, 26.5, 25.7, 21.6, 13.9. The spectroscopic data (NMR) matched those reported in the literature[6] for (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one.

General procedure for Preparation of Allylic Alcohols

The Allylic Alcohols were prepared according to literature reports[7] or through the following routes:



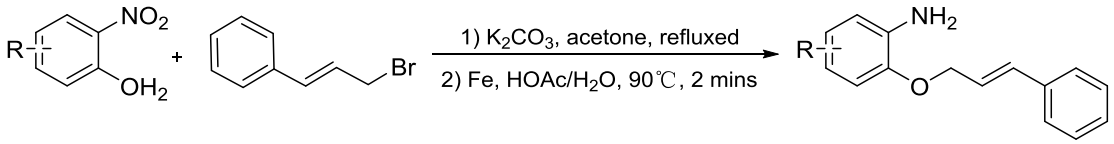
At room temperature, a flame-dried Schlenk flask is charged with LiCl (1.20 equiv) and dry THF under inert atmosphere, followed by addition of neat triethylphosphonoacetate (1.20 equiv). Prior to the addition of DBU (1.10 equiv), the reaction mixture is maintained for 15 min at this temperature. The neat aldehyde (1.00 equiv) is then added to the white suspension, which is allowed to stir for another 2 h at room temperature. After completion of reaction (TLC monitoring), the reaction mixture is quenched by pouring over ice. Standard work-up affords the crude α,β-unsaturated esters in good yields, which are used without further purification. Cinnamic bromide (E:Z > 99:1) is commercially available.

In a flame-dried Schlenk flask pre-cooled to –78 ℃ containing solution of DIBAL–H (1M in cyclohexane, 2.10 equiv) in CH_2Cl_2 is slowly added a solution of the crude α,β-unsaturated ester (1.00 equiv) in dry CH_2Cl_2. After completion (TLC monitoring), the reaction mixture is

carefully quenched with 2 M HCl solution, and standard work-up furnishes the allylic alcohols in almost quantitative yields after purification by flash column chromatography on silica gel. Characterization data in accordance to Heather E. Burks et al.

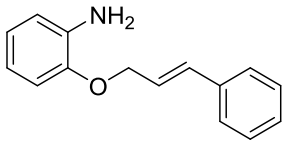
General procedure for Preparation of 2-(cinnamyloxy)aniline

The 2-(cinnamyloxy)aniline were prepared according to literature reports[11,12] or through the following routes:



(**Method A**): To a solution of 2- nitrophenol (1.00 equiv) and K_2CO_3 (1.00 equiv) in anhydrous acetone was added dropwise Cinnamic bromide (1.00 equiv) at 0 ℃. The mixture was warmed to reflux and stirred for 20 h. The reaction was washed with water and extracted with EtOAc. The organic phase was washed with a saturated NaCl and then dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography, furnishing the desired compound.
To nitrobenzene (1.00 g) and iron (2.44 g) were added AcOH (14.0 mL) and H_2O (1.40 mL), The reaction mixture was stirred untill it was heated to 90 ^oC for 3mins. After cooling slowly, the reaction mixture was filtered through Celite and washed with EtOAc, the system was adjusted by aqueous saturated $NaHCO_3$ to 8～9, then extracted with EtOAc. The organic phase was washed with aqueous saturated NaCl and then dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography, furnishing the desired compound.

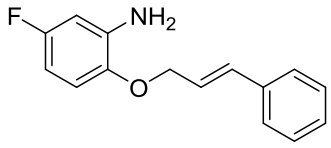
2-(cinnamyloxy)aniline (S8)



Compound 2-(cinnamyloxy)aniline was prepared following (**Method A**) from 2- Nitrophenol (1.39 g, 10.0 mmol) yielding it as a pale white solid (1.81 g, 80 %).

R_f = 0.40 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 9.3 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.23 (d, *J* = 6.4 Hz, 1H), 6.81 (d, *J* = 7.0 Hz, 2H), 6.75 – 6.58 (m, 3H), 6.40 (dt, *J* = 15.3, 5.1 Hz, 1H), 4.65 (d, *J* = 4.9 Hz, 2H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 136.5, 136.4, 132.8, 128.6, 127.9, 126.5, 124.7, 121.4, 118.4, 115.2, 112.1, 69.0. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{15}NONa$ $[M+Na]^+$, 248.1051. Found, 248.1048.

2-(cinnamyloxy)-5-fluoroaniline (S9)

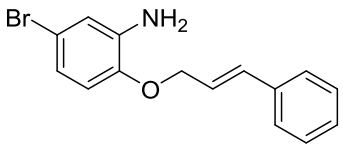


Compound 2-(cinnamyloxy)-5-fluoroaniline was prepared

following (**Method A**) from 4-fluoro-2-nitrophenol (1.57 g, 10.0 mmol) yielding it as a pale yellow solid (1.68 g, 69 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 10.6 Hz, 2H), 7.31 (dd, *J* = 14.1, 8.0 Hz, 2H), 7.26 (d, *J* = 6.3 Hz, 2H), 6.70 (t, *J* = 12.0 Hz, 2H), 6.51 – 6.28 (m, 2H), 4.65 (d, *J* = 4.3 Hz, 2H), 3.93 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (d, $J_{(C-F)}$= 200.4 Hz), 142.3 (d, $J_{(C-F)}$= 10.3 Hz), 138.0 (d, $J_{(C-F)}$= 13.6 Hz), 136.3 (d, $J_{(C-F)}$= 10.7 Hz), 133.1, 128.7, 128.0, 126.6, 124.6, 112.9 (d, $J_{(C-F)}$= 12.5 Hz), 103.4 (d, $J_{(C-F)}$= 21.3 Hz), 102.2, 69.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.2 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{14}FNO$, 242.0981. Found, 242.0988. The spectroscopic data (NMR) matched those reported in the literature[10] for 2-(cinnamyloxy)-5-fluoroaniline.

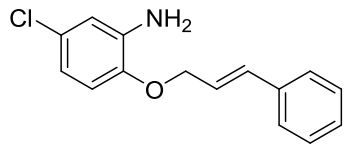
5-bromo-2-(cinnamyloxy)aniline (S10)



Compound 5-bromo-2-(cinnamyloxy)aniline was prepared following (**Method A**) from 4-bromo-2-nitrophenol (2.17 g, 10.0 mmol) yielding it as a yellow solid (1.73 g, 57 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.33 (s, 2H), 7.29 – 7.21 (m, 1H), 6.90 – 6.74 (m, 2H), 6.68 (t, *J* = 9.1 Hz, 2H), 6.41 (dd, *J* = 25.5, 16.9 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 2H), 3.88 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 138.1, 136.3, 133.4, 128.7, 128.1, 126.7, 124.1, 120.6, 117.4, 113.7, 113.4, 68.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{14}BrNO$, 303.0259. Found, 303.0213.

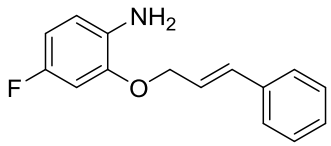
5-chloro-2-(cinnamyloxy)aniline (S11)



Compound 5-chloro-2-(cinnamyloxy)aniline was prepared following (**Method A**) from 4-chloro-2-nitrophenol (1.73 g, 10.0 mmol) yielding it as a pale yellow solid (1.83 g, 71 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.78 – 6.58 (m, 4H), 6.39 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.66 (d, *J* = 5.7 Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 137.7, 136.3, 133.3, 128.7, 127.9, 126.7, 126.2, 124.3, 117.7, 114.6, 112.8, 68.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{14}ClNO$, 259.0764. Found, 259.0740.

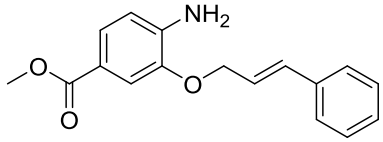
2-(cinnamyloxy)-4-fluoroaniline (S12)



Compound 2-(cinnamyloxy)-4-fluoroaniline was prepared following (**Method A**) from 5-fluoro-2-nitrophenol (1.57 g, 10.0 mmol) yielding it as a pale yellow solid (1.46 g, 60 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.8 Hz, 2H), 7.27 (d, *J* = 16.8 Hz, 2H), 7.24 (d, *J* = 5.4 Hz, 1H), 6.73 – 6.52 (m, 3H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.32 (dd, *J* = 22.8, 15.8 Hz, 1H), 4.57 (d, *J* = 4.4 Hz, 2H), 3.77 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (d, $J_{(C-F)}$= 212.9 Hz), 146.7 (d, $J_{(C-F)}$= 17.6 Hz), 136.1 (d, $J_{(C-F)}$= 51.3 Hz), 133.4, 132.3 (d, $J_{(C-F)}$= 17.4 Hz), 128.7, 128.1, 126.6 (d, $J_{(C-F)}$= 28.5 Hz), 124.0, 114.8 (d, $J_{(C-F)}$= 44.2 Hz), 106.9, 100.3, 69.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.9 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{14}FNO$, 243.1059. Found, 243.1028.

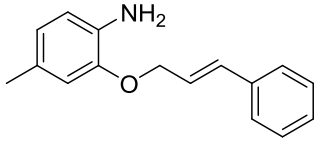
methyl 4-amino-3-(cinnamyloxy)benzoate (S13)



Compound methyl methyl 4-amino-3-(cinnamyloxy)benzoate was prepared following (**Method A**) from methyl 3-hydroxy-4-nitrobenzoate (1.97 g, 1.00 mmol) yielding it as a white solid (2.18 g, 77 %).

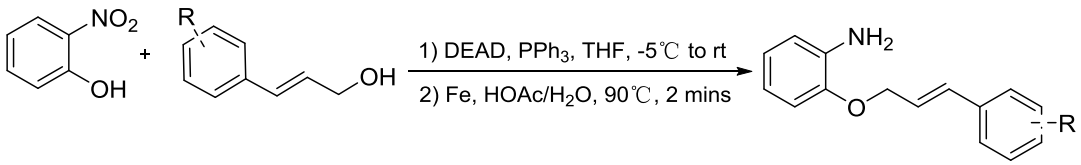
R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 30.3, 16.2 Hz, 2H), 7.38 (t, *J* = 11.0 Hz, 2H), 7.30 (d, *J* = 15.8 Hz, 2H), 7.26 (d, *J* = 6.0 Hz, 1H), 6.68 (dd, *J* = 17.0, 12.5 Hz, 2H), 6.49 – 6.28 (m, 1H), 4.72 (d, *J* = 4.8 Hz, 2H), 4.30 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 144.9, 141.3, 136.3, 133.5, 128.7, 128.0, 126.6, 124.3, 124.1, 119.4, 113.3, 112.5, 68.6, 51.2. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{17}NO_3Na$ $[M+Na]^+$, 306.1106. Found, 306.1105.

2-(cinnamyloxy)-4-methylaniline (S14)



Compound 2-(cinnamyloxy)-4-methylaniline was prepared following (**Method A**) from 5-methyl-2-nitrophenol (1.53 g, 1.00 mmol) yielding it as a yellow solid (1.36 g, 57%).

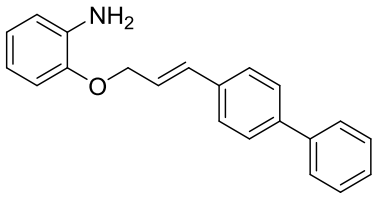
R_f = 0.40 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.28 (d, *J* = 17.5 Hz, 2H), 7.24 (d, *J* = 4.8 Hz, 1H), 6.77 – 6.53 (m, 4H), 6.49 – 6.31 (m, 1H), 4.65 (d, *J* = 4.1 Hz, 2H), 3.67 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.5, 133.8, 132.7, 128.6, 127.9, 127.7, 126.6, 124.9, 121.6, 115.2, 113.1, 68.6, 20.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{17}NONa$ $[M+Na]^+$, 262.1208. Found, 262.1209.



(**Method B**): 2-Nitrophenol (1.00 equiv) and triphenylphosphine (1.00 equiv) were dissolved in dry tetrahydrofuran. Allylic Alcohols (1.00 equiv) was added and the mixture cooled to 0 ℃. Diethyl azodicarboxylate (1.00 equiv) was added dropwise over 15 min. The mixture was stirred for 2 h and then more diethyl azodicarboxylate (0.500 equiv) was added before stirring for 12 h. The reaction mixture was evaporated to dryness, dissolved in ethyl acetate and washed with water, aqueous sodium hydroxide and aqueous hydrochloric acid. The organic phase was then dried over $MgSO_4$ and evaporated to dryness before purifying by column chromatography to give the desired compound.

To nitrobenzene (1.00 g) and iron (2.44 g) were added AcOH (14.0 mL) and H_2O (1.40 mL), The reaction mixture was stirred untill it was heated to 90 ^oC for 3mins. After cooling slowly, the reaction mixture was filtered through Celite and washed with EtOAc, the system was adjusted by aqueous saturated $NaHCO_3$ to 8～9, then extracted with EtOAc. The organic phase was washed with aqueous saturated NaCl and then dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography, furnishing the desired compound.

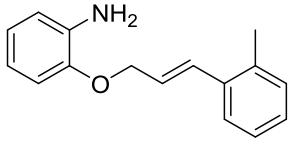
(E)-2-((3-([1,1'-biphenyl]-4-yl)allyl)oxy)aniline (S15)



Compound (E)-2-((3-([1,1'-biphenyl]-4-yl)allyl)oxy)aniline was prepared following (**Method B**) from 2-nitrophenol (1.39 g, 10.0 mmol) yielding it as a yellow solid (1.59 mg, 53 %).

R_f = 0.40 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 22.9, 13.2 Hz, 4H), 7.47 (dd, *J* = 30.4, 16.6 Hz, 4H), 7.37 (d, *J* = 6.3 Hz, 1H), 6.86 (dd, *J* = 20.7, 7.2 Hz, 2H), 6.78 (d, *J* = 14.7 Hz, 3H), 6.51 (d, *J* = 15.7 Hz, 1H), 4.76 (d, *J* = 4.6 Hz, 2H), 3.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 140.7, 140.5, 136.6, 135.5, 132.4, 128.9, 127.5, 127.4, 127.1, 127.0, 124.9, 121.6, 118.5, 115.3, 112.3, 68.7. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{19}NO$ Na $[M+Na]^+$, 324.1364. Found, 324.1362.

(E)-2-((3-(o-tolyl)allyl)oxy)aniline (S16)

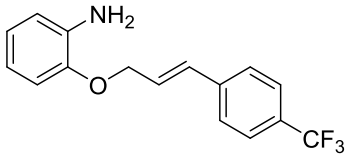


Compound (E)-2-((3-(o-tolyl)allyl)oxy)aniline was prepared following (**Method B**) from 2-nitrophenol (1.39 g, 10.0 mmol) yielding it as a white solid (0.740 g, 31 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^1H NMR

(400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 10.7 Hz, 1H), 7.27 (dd, *J* = 19.8, 7.0 Hz, 3H), 7.00 (t, *J* = 12.9 Hz, 1H), 6.90 (dt, *J* = 18.6, 9.7 Hz, 2H), 6.81 (d, *J* = 7.3 Hz, 2H), 6.40 (dt, *J* = 11.7, 5.6 Hz, 1H), 4.80 (d, *J* = 5.5 Hz, 2H), 3.90 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 136.6, 135.5, 130.9, 130.4, 128.4, 127.8, 126.2, 126.1, 125.8, 121.5, 118.4, 115.0, 112.3, 69.4, 19.8. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{17}NONa$ $[M+Na]^+$, 262.1208. Found, 262.1204.

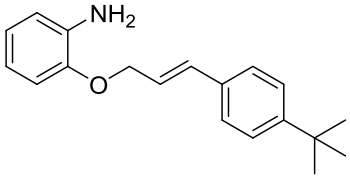
(E)-2-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)aniline (S17)



Compound (E)-2-((3-(4-(trifluoromethyl)phenyl)allyl)oxy)aniline was prepared following (**Method B**) from 2-nitrophenol (1.39 g, 10.0 mmol) yielding it as a pale white solid (1.38 g, 47 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 6.84 (dd, *J* = 17.1, 9.5 Hz, 2H), 6.80 – 6.67 (m, 3H), 6.55 (d, *J* = 15.8 Hz, 1H), 4.76 (d, *J* = 4.8 Hz, 2H), 3.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 139.9, 136.4, 131.1, 129.4 (d, $J_{(C-F)}$= 75.4 Hz), 127.4, 126.7, 125.4, 122.8 (m, $J_{(C-F)}$= 275.4 Hz), 121.7, 118.5, 115.1, 112.2, 68.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 (m, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{15}F_3NO$ $[M+H]^+$, 294.1106. Found, 294.1105.

(E)-2-((3-(4-(tert-butyl)phenyl)allyl)oxy)aniline (S18)

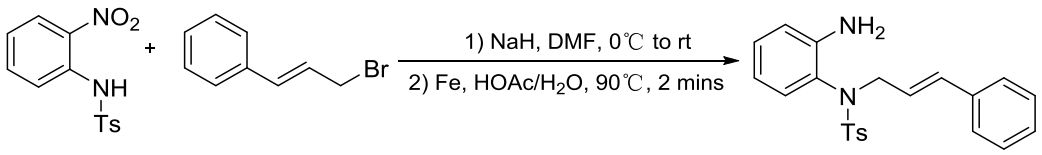


Compound (E)-2-((3-(4-(tert-butyl)phenyl)allyl)oxy)aniline was prepared following (**Method B**) from 2-nitrophenol (1.39 g, 10.0 mmol) yielding it as a pale yellow solid (1.21 g, 43 %).

R_f = 0.30 (hexanes/ EtOAc 10:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, 4H), 6.87 (dd, *J* = 19.3, 7.6 Hz, 2H), 6.76 (t, *J* = 10.8 Hz, 3H), 6.53 – 6.37 (m, 1H), 4.75 (d, *J* = 4.6 Hz, 2H), 3.87 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 146.3, 136.6, 133.7, 132.8, 126.4, 125.6, 124.0, 121.4, 118.5, 115.3, 112.2, 69.0, 34.6, 31.3. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{24}NO$ $[M+H]^+$, 282.1858. Found, 282.1863.

General procedure for Preparation of N-(2-aminophenyl)-N-cinnamyl-4-methylbenzenesulfonamide

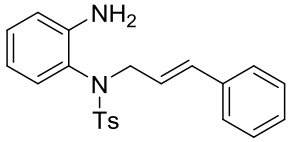
The N-(2-aminophenyl)-N-cinnamyl-4-methylbenzenesulfonamide were prepared according to literature reports[11,12] or through the following routes:



(**Method C**): NaH (1.50 equiv) (60 % dispersion in mineral oil) was added portionwise to a solution of N-(2-nitrophenyl)benzenesulfonamide (1.00 equiv) in anhydrous DMF and then was stirred for 1.5 hour at room temperature. Cinnamic bromide (1.50 equiv) was added dropwise to the previous solution at 0 ℃ and then stirred for 20 hours at room temperature. The reaction was quenched by NH_4Cl (sat), extracted by of diethyl ether, washed with brine, dried over $MgSO_4$, and then concentrated to give a crude product which was purified under silica gel chromatography with (elution with hexanes / EtOAc: 5 / 1) to give the desired compound.

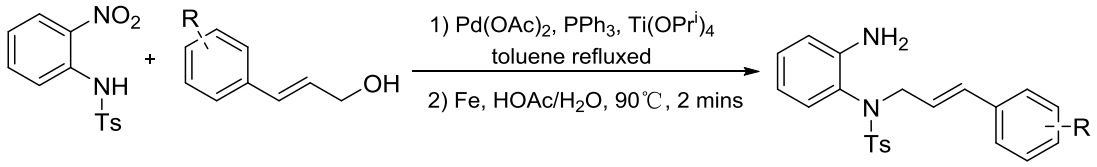
To nitrobenzene (1.00 g) and iron (2.44 g) were added AcOH (14.0 mL) and H_2O (1.40 mL), The reaction mixture was stirred untill it was heated to 90 ^oC for 3mins. After cooling slowly, the reaction mixture was filtered through Celite and washed with EtOAc, the system was adjusted by aqueous saturated $NaHCO_3$ to 8～9, then extracted with EtOAc. The organic phase was washed with aqueous saturated NaCl and then dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography, furnishing the desired compound.

N-(2-aminophenyl)-N-cinnamyl-4-methylbenzenesulfonamide (S19)



Compound N-(2-aminophenyl)-N-cinnamyl-4-methylbenzenesulfonamide was prepared following (**Method C**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (2.98 g, 79 %).

R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.7 Hz, 2H), 7.34 – 7.10 (m, 7H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.48 (dd, *J* = 12.5, 11.2 Hz, 1H), 6.44 – 6.26 (m, 2H), 6.20 – 6.01 (m, 1H), 4.52 (d, *J* = 13.4 Hz, 1H), 4.12 (s, 2H), 4.04 (d, *J* = 7.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 143.7, 136.5, 135.7, 134.1, 129.6, 129.4, 128.8, 128.5, 128.1, 127.8, 126.5, 124.7, 123.8, 117.9, 116.7, 54.0, 21.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{22}N_2O_2SNa$ $[M+Na]^+$, 401.1300. Found, 401.1298.

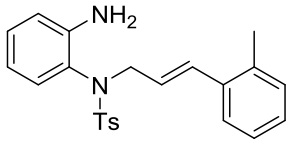


(**Method D**): A mixture of 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (1.00 equiv), allyl alcohol (1.20 equiv), $Pd(OAc)_2$ (0.0100 equiv), PPh_3 (0.0400 equiv), $Ti(OPr^i)_4$ (0.250 equiv), and

anhydrous toluene was refluxed under nitrogen for 3 h. After cooling, the reaction mixture was filtered through Celite and the solvent was distilled under reduced pressure. Column chromatography (n-hexane/EtOAc 5 : 1) of the residue afforded the desired benzenesulfonamide compound.

To nitrobenzene (1.0 g) and iron (2.44 g) were added AcOH (14.0 mL) and H_2O (1.40 mL), The reaction mixture was stirred untill it was heated to 90 ^oC for 3mins. After cooling slowly, the reaction mixture was filtered through Celite and washed with EtOAc, the system was adjusted by aqueous saturated $NaHCO_3$ to 8～9, then extracted with EtOAc. The organic phase was washed with aqueous saturated NaCl and then dried over anhydrous $MgSO_4$. The crude product was purified by flash column chromatography, furnishing the desired compound.

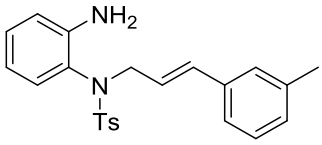
(E)-N-(2-aminophenyl)-4-methyl-N-(3-(o-tolyl)allyl)benzenesulfonamide (S20)



Compound (E)-N-(2-aminophenyl)-4-methyl-N-(3-(o-tolyl)allyl)benzenesulfonamide was prepared following (**Method D**) from (4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (2.55 g, 65 %).

R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.37 – 7.15 (m, 3H), 7.07 (d, *J* = 16.2 Hz, 4H), 6.67 (d, *J* = 49.8 Hz, 1H), 6.48 (t, *J* = 19.8 Hz, 2H), 6.38 (s, 1H), 5.97 (s, 1H), 4.57 (d, *J* = 11.3 Hz, 1H), 4.18 (s, 2H), 4.01 (m, 1H), 2.43 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.7, 135.9, 135.6, 135.4, 132.8, 130.1, 129.6, 129.4, 128.7, 128.1, 127.7, 126.1, 126.0, 124.9, 124.6, 117.8, 116.7, 54.1, 21.6, 19.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{24}N_2O_2SNa$ $[M+Na]^+$, 415.1456. Found, 415.1455.

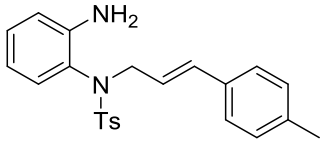
(E)-N-(2-aminophenyl)-4-methyl-N-(3-(m-tolyl)allyl)benzenesulfonamide (S21)



Compound (E)-N-(2-aminophenyl)-4-methyl-N-(3-(m-tolyl)allyl)benzenesulfonamide was prepared following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a colorless oil (2.04 g, 52 %).

R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.2 Hz, 2H), 7.23 (t, *J* = 18.6 Hz, 2H), 7.17 – 7.08 (m, 1H), 7.03 (s, 4H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.56 – 6.45 (m, 1H), 6.45 – 6.37 (m, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.20 – 6.02 (m, 1H), 4.52 (d, *J* = 13.6 Hz, 1H), 4.19 (s, 2H), 4.09 – 3.97 (m, 1H), 2.38 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 143.6, 137.9, 136.3, 135.6, 134.1, 129.4, 129.3, 128.7, 128.5, 128.3, 128.0, 127.2, 124.6, 123.6, 123.4, 117.7, 116.6, 54.0, 21.5, 21.2. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{24}N_2O_2SNa$ $[M+Na]^+$, 415.1456. Found, 415.1456.

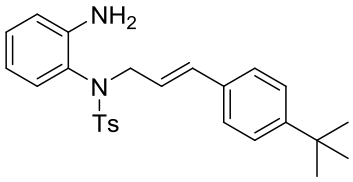
(E)-N-(2-aminophenyl)-4-methyl-N-(3-(p-tolyl)allyl)benzenesulfonamide (S22)



Compound (E)-N-(2-aminophenyl)-4-methyl-N-(3-(p-tolyl)allyl)benzenesulfonamide was prepared following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (2.35 g, 60 %).

R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 10.4 Hz, 2H), 7.08 – 6.96 (m, 3H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.48 (d, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.04 (dd, *J* = 15.0, 7.0 Hz, 1H), 4.50 (d, *J* = 13.6 Hz, 1H), 4.11 (s, 2H), 4.02 (dd, *J* = 13.2, 7.5 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.7, 137.7, 135.8, 134.1, 133.7, 129.5, 129.4, 129.2, 128.9, 128.1, 126.4, 124.7, 122.7, 117.8, 116.7, 54.1, 21.6, 21.2. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{24}N_2O_2SNa$ $[M+Na]^+$, 415.1456. Found,415.1454.

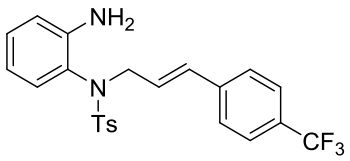
(E)-N-(2-aminophenyl)-N-(3-(4-(tert-butyl)phenyl)allyl)-4-methylbenzenesulfonamide (S23)



Compound (E)-N-(2-aminophenyl)-N-(3-(4-(tert-butyl)phenyl)allyl)-4-methylbenzenesulfonamide was prepared following (**Method D**) from4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (2.60 g, 60 %).

R_f = 0.40 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.24 (dd, *J* = 23.1, 10.1 Hz, 4H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.54 – 6.42 (m, 1H), 6.42 – 6.33 (m, 1H), 6.31 (s, 1H), 6.06 (dd, *J* = 14.9, 7.3 Hz, 1H), 4.52 (d, *J* = 13.7 Hz, 1H), 4.17 (s, 2H), 4.07 – 3.93 (m, 1H), 2.42 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 146.8, 143.7, 135.7, 134.0, 133.8, 129.5, 129.4, 128.8, 128.1, 126.3, 125.4, 124.7, 122.9, 117.8, 116.7, 54.1, 34.5, 31.3, 21.6. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{30}N_2O_2SNa$ $[M+Na]^+$, 457.1926. Found, 457.1922.

(E)-N-(2-aminophenyl)-4-methyl-N-(3-(4-(trifluoromethyl)phenyl)allyl)benzenesulfonamide (S24)

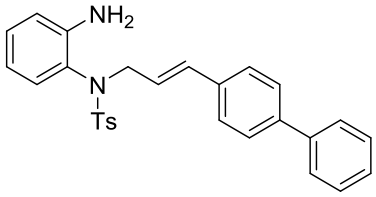


Compound (E)-N-(2-aminophenyl)-4-methyl-N-(3-(4-(trifluoromethyl)phenyl)allyl)benzenesulfonamide was prepared

following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a white solid (3.17g, 71 %).

R_f = 0.40 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 19.2 Hz, 2H), 7.29 (dd, *J* = 17.5, 8.8 Hz, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.52 (t, *J* = 7.1 Hz, 1H), 6.40 (t, *J* = 12.0 Hz, 2H), 6.28 – 6.15 (m, 1H), 4.58 (d, *J* = 13.1 Hz, 1H), 4.18 (s, 2H), 4.02 (dd, *J* = 13.4, 7.0 Hz, 1H), 2.43 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 143.9, 140.0 (d, $J_{(C-F)}$= 12.0 Hz), 135.5, 132.6, 129.8, 129.6, 129.2 (m, $J_{(C-F)}$= 212.0 Hz), 128.7, 128.1, 127.6, 126.7, 125.5, 124.7, 118.6, 118.0, 116.8, 53.4, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (m, 3F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{21}F_3N_2O_2SNa$ $[M+Na]^+$, 469.1174. Found, 469.1174.

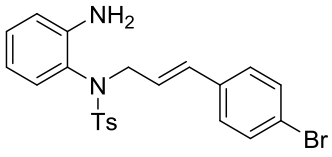
(E)-N-(3-([1,1'-biphenyl]-4-yl)allyl)-N-(2-aminophenyl)-4-methylbenzenesulfonamide (S25)



Compound (E)-N-(3-([1,1'-biphenyl]-4-yl)allyl)-N-(2-aminophenyl)-4-methylbenzenesulfonamide was prepared following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale yellow solid (1.91 g, 42 %).

R_f = 0.30 (hexanes/ EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (t, *J* = 7.0 Hz, 2H), 7.52 (dd, *J* = 16.3, 7.0 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.43 – 7.35 (m, 2H), 7.35 – 7.22 (m, 5H), 6.73 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.72 (dt, *J* = 10.7, 5.3 Hz, 1H), 6.54 – 6.48 (m, 1H), 6.43 – 6.36 (m, 2H), 6.16 (dt, *J* = 15.7, 6.8 Hz, 1H), 4.55 (dd, *J* = 14.2, 6.1 Hz, 1H), 4.19 (s, 2H), 4.04 (dd, *J* = 14.2, 7.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 143.8, 140.6, 140.5, 135.7, 135.5, 133.7, 129.6, 129.5, 128.8, 128.1, 127.6, 127.4, 127.2, 127.0, 126.9, 124.8, 123.9, 117.9, 116.7, 54.0, 21.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{28}H_{26}N_2O_2SNa$ $[M+Na]^+$, 477.1613. Found, 477.1609.

(E)-N-(2-aminophenyl)-N-(3-(4-bromophenyl)allyl)-4-methylbenzenesulfonamide (S26)

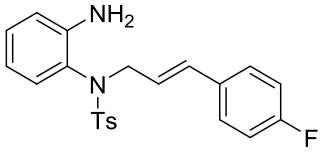


Compound (E)-N-(2-aminophenyl)-N-(3-(4-bromophenyl)allyl)-4-methylbenzenesulfonamide was prepared following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (2.37 g, 52 %).

R_f = 0.30 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 11.6 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 19.3, 7.7 Hz, 3H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 7.2 Hz, 1H), 6.42 – 6.34 (m, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 6.18 – 6.04 (m, 1H), 4.52 (d, *J* = 13.4 Hz, 1H), 4.17 (s, 2H), 4.05 – 3.93 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 143.8, 135.6, 135.5, 132.8, 131.6, 129.6, 129.5, 128.8,

128.3, 128.1, 128.0, 124.7, 121.6, 118.0, 116.8, 53.9, 21.5. Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{21}BrN_2O_2SNa$ $[M+Na]^+$, 479.0405. Found, 479.0405.

(E)-N-(2-aminophenyl)-N-(3-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide (S27)

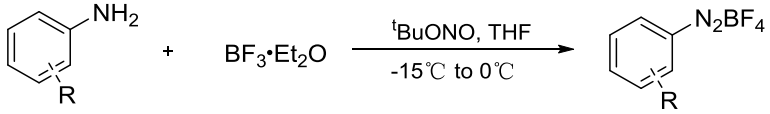


Compound (E)-N-(2-aminophenyl)-N-(3-(4-fluorophenyl)allyl)-4-methylbenzenesulfonamide was prepared following (**Method D**) from 4-methyl-N-(2-nitrophenyl)benzenesulfonamide (2.92 g, 10.0 mmol) yielding it as a pale white solid (1.94 g, 49 %).

R_f = 0.40 (hexanes/ EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 12.6 Hz, 2H), 7.26 (dd, *J* = 15.4, 9.3 Hz, 2H), 7.19 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.03 (dd, *J* = 19.6, 11.9 Hz, 1H), 6.93 (t, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.51 (t, *J* = 7.6 Hz, 1H), 6.36 (dd, *J* = 14.1, 8.7 Hz, 1H), 6.31 (s, 1H), 6.09 – 5.94 (m, 1H), 4.53 (dd, *J* = 14.1, 6.0 Hz, 1H), 4.19 (s, 2H), 3.99 (dd, *J* = 14.2, 7.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{(C-F)}$= 224.8 Hz), 146.8, 143.8, 135.6 (d, $J_{(C-F)}$= 14.1 Hz), 132.9, 132.7, 129.6, 129.5, 128.8, 128.1, 128.0, 124.8 (d, $J_{(C-F)}$= 21.7 Hz), 123.6, 118.0, 116.7, 115.5 (d, $J_{(C-F)}$= 21.7 Hz), 53.9, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{21}FN_2O_2S$ Na $[M+Na]^+$, 419.1205. Found, 419.1206

General procedure for Preparation of Aryldiazonium salts

The Aryldiazonium salts were prepared according to literature reports.[13]



To boron trifluoride etherate (1.06 g, 7.50 mmol, 1.50 equiv) contained in a three-neck round-bottom flask fitted with two addition funnels and a reflux condenser connected to a gas buret was added 5.00 mmol of the aromatic amine in a minimal volume of the anhydrous solvent, usually 10.0 mL. Prior to addition of the amine, the boron trifluoride etherate was cooled at -15 ℃ in an ice-acetone bath. If a solid amine-BF_3 complex had formed, additional solvent or ethyl ether was added to produce a homogeneous solution. tert-Butyl nitrite (0.618 g, 6.00 mmol, 1.20 equiv) in 5.00 mL of the same solvent was added dropwise to the rapidly stirred reaction solution over a 10 min period. Following complete addition. the temperature of the reaction solution was maintained at -15 ℃ for 10 min and then allowed to warm to 5 ℃ in an ice-water bath over a 20 min period. A crystalline precipitate usually formed during the addition of tert-butyl nitrite, and following the 20 min period at 5 ℃ precipitation was complete. n-Hexane (40.0 mL) was then added to the reaction solution, and the solid was suction filtered, washed with cold ether (2 × 10.0 mL), then dissolved in acetone (5.00 mL) and subsequently poured onto cold diethyl ether (50.0

mL). The resultant precipitate was carefully filtered under nitrogen to give the desired aryldiazonium tetrafluoroborate. The fluorination reactions were immediately carried out when aryldiazonium tetrafluoroborates were gained.

2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzoic acid (3a)

1 **2a** **3a** 61% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (189 mg, 0.900 mmol, 3.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 2-vinyl-benzoic acid (**2a**) (44.5 mg, 0.300 mmol, 1.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 10:1 (v/v), to afford 47.8 mg 2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzoic acid (**3a**) as a white solid (61% yield). R_f = 0.40 (hexanes/EtOAc 8:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.51 – 7.41 (m, 1H), 7.26 (t, *J* = 6.9 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.54 (ddd, *J* = 49.1, 8.3, 2.3 Hz, 1H), 3.37 – 3.19 (m, 1H), 3.00 (ddd, *J* = 22.6, 14.6, 8.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 161.7 (d, $J_{(C-F)}$= 268.6 Hz), 143.9 (d, $J_{(C-F)}$= 19.9 Hz), 134.0, 133.2 (d, $J_{(C-F)}$= 3.2 Hz), 131.7, 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 128.0, 126.2 (d, $J_{(C-F)}$= 14.3 Hz), 125.2 (d, $J_{(C-F)}$= 4.4 Hz), 115.2 (d, $J_{(C-F)}$= 21.2 Hz), 92.2 (d, $J_{(C-F)}$= 172.6 Hz), 43.3 (d, $J_{(C-F)}$= 23.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5 (m, 1F), -181.7 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{12}F_2O_2$, 262.0805. Found, 262.0767.

1-bromo-2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (3b)

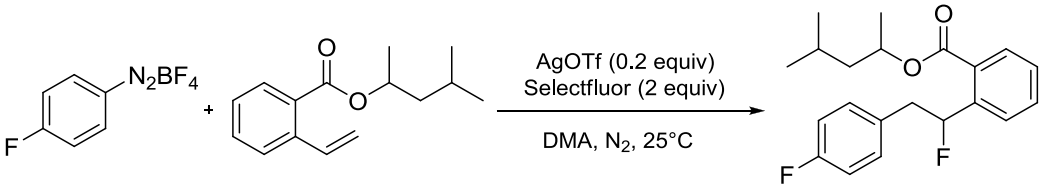
1 **2b** **3b** 60% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 1-bromo-2-vinylbenzene (**2b**) (275 mg, 1.500 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The

combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v), to afford 53.2 mg 1-bromo-2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3b**) as a colorless oil (60% yield).

R_f = 0.30 (hexanes/EtOAc 100:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 (dd, *J* = 10.8, 4.2 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.04 – 6.94 (m, 2H), 5.91 (ddd, *J* = 46.8, 8.2, 3.1 Hz, 1H), 3.23 (ddd, *J* = 32.8, 14.7, 3.0 Hz, 1H), 3.04 (ddd, *J* = 22.8, 14.8, 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, $J_{(C-F)}$= 211.0 Hz), 139.1 (d, $J_{(C-F)}$= 21.8 Hz), 132.7, 132.4 (d, $J_{(C-F)}$= 2.7 Hz), 131.1 (d, $J_{(C-F)}$= 8.0 Hz), 129.7, 127.8, 127.0 (d, $J_{(C-F)}$= 10.3 Hz), 120.6 (d, $J_{(C-F)}$= 6.0 Hz), 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 93.2 (d, $J_{(C-F)}$= 124.5 Hz), 41.6 (d, $J_{(C-F)}$= 23.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2 (m, 1F), -182.7 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{11}BrF_2$, 296.0012. Found, 296.0. Elemental Analysis: Calcd for C:56.59%, H:3.73%. Found, C:56.48%, H:3.94%.

4-methylpentan-2-yl-2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzoate (3c)



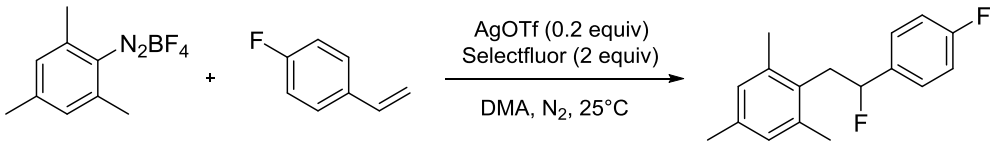
1 **2c** **3c** 59% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (189 mg, 0.900 mmol, 3.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-methylpentan-2-yl-2-vinylbenzoate (**2c**) (69.7 mg, 0.300 mmol, 1.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v), to afford 60.8 mg 4-methylpentan-2-yl-2-(1-fluoro-2-(4-fluorophenyl)ethyl)benzoate (**3c**) as a colorless oil (59% yield).

R_f = 0.40 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.59 (dd, *J* = 13.9, 6.0 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 (dd, *J* = 14.1, 8.2 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.50 (dd, *J* = 49.1, 8.5 Hz, 1H), 5.33 – 5.19 (m, 1H), 3.29 (dd, *J* = 35.9, 14.6 Hz, 1H), 3.09 – 2.84 (m, 1H), 1.82 – 1.63 (m, 2H), 1.47 – 1.38 (m, 1H), 1.35 (t, *J* = 6.3 Hz, 3H), 1.05 – 0.86 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (d, $J_{(C-F)}$= 24.2 Hz), 161.5 (d, $J_{(C-F)}$= 180.4 Hz), 142.7 (d, $J_{(C-F)}$= 28.8 Hz), 133.3 (d, $J_{(C-F)}$= 19.9 Hz), 132.5, 131.2 (d, $J_{(C-F)}$= 7.9 Hz), 130.4, 127.7 (d, $J_{(C-F)}$= 14.3 Hz), 125.9 (d, $J_{(C-F)}$= 13.7 Hz), 115.1 (d, $J_{(C-F)}$= 21.1 Hz), 92.0 (d, $J_{(C-F)}$= 130.6 Hz), 70.6 (d, $J_{(C-F)}$= 12.6 Hz), 45.1 (d, $J_{(C-F)}$= 14.3 Hz), 43.1 (dd, $J_{(C-F)}$= 62.9, 14.2 Hz), 25.0 (d, $J_{(C-F)}$= 28.8 Hz), 23.1 (d, $J_{(C-F)}$= 7.6 Hz), 22.4

(d, $J_{(C-F)}$= 7.3 Hz), 20.7 (d, $J_{(C-F)}$= 6.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.8 (m, 1F), -181.6 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{21}H_{24}F_2O_2Na$ $[M+Na]^+$, 369.1642. Found, 369.1640.

2-(2-fluoro-2-(4-fluorophenyl)ethyl)-1,3,5-trimethylbenzene (3d)

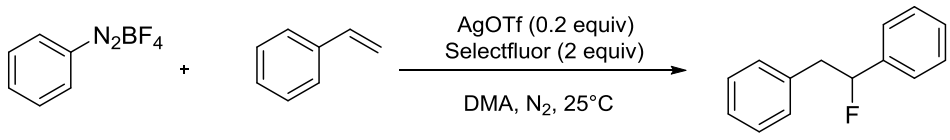


1d **2** **3d** 22% yield

To 2,4,6-trimethylbenzenediazonium tetrafluoroborate (**1d**) (70.2 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 °C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 17.1 mg 2-(2-fluoro-2-(4-fluorophenyl)ethyl)-1,3,5-trimethylbenzene (**3d**) as a yellow oil (22% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.85 (s, 2H), 5.53 (ddd, *J* = 47.0, 8.0, 5.3 Hz, 1H), 3.31 (td, *J* = 14.2, 8.4 Hz, 1H), 3.10 – 2.93 (m, 1H), 2.26 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{(C-F)}$= 226.3 Hz), 137.2, 136.5 (d, $J_{(C-F)}$= 20.8 Hz), 136.3, 130.3, 129.2, 127.2, 115.4 (d, $J_{(C-F)}$= 21.5 Hz), 93.6 (d, $J_{(C-F)}$= 193.4 Hz), 37.7 (d, $J_{(C-F)}$= 25.1 Hz), 20.9, 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7 (m, 1F), -173.3 (m, 1F). Mass Spectrometry: GS- Mass (EI) (m/z): Calcd for $C_{17}H_{18}F_2$, 260.1377. Found, 260.1. Elemental Analysis: Calcd for C:78.43%, H:6.97%. Found, C:78.29%, H:6.85%.

(1-fluoroethane-1,2-diyl)dibenzene (3e)



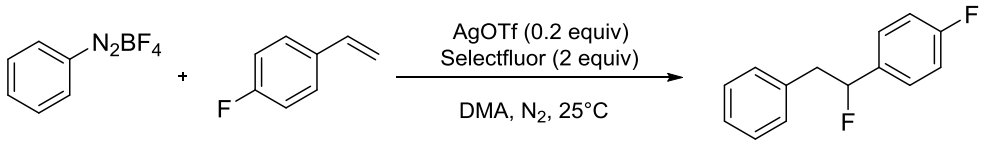
1e **2e** **3e** 67% yield

To benzenediazonium tetrafluoroborate (**1e**) (57.6 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and styrene (**2e**) (170 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 °C in a sealed vial. The reaction was

diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 40.0 mg (1-fluoroethane-1,2-diyl)dibenzene (**3e**) as a colorless solid (67% yield).

R_f = 0.40 (hexanes/EtOAc 100:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.32 – 7.25 (m, 4H), 7.23 (t, *J* = 5.1 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 5.61 (ddd, *J* = 47.4, 8.1, 4.8 Hz, 1H), 3.27 (ddd, *J* = 17.5, 14.3, 8.1 Hz, 1H), 3.10 (ddd, *J* = 28.7, 14.2, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (d, $J_{(C-F)}$= 5.3 Hz), 139.8, 136.8 (d, $J_{(C-F)}$= 9.7 Hz), 129.6, 128.5, 126.8, 125.8, 125.7 (d, $J_{(C-F)}$= 6.9 Hz), 94.7 (d, $J_{(C-F)}$= 123.1 Hz), 44.0 (d, $J_{(C-F)}$= 21.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.2 (m, 1F). The spectroscopic data (NMR) matched those reported in the literature[14] for (1-fluoroethane-1,2-diyl)dibenzene.

1-fluoro-4-(1-fluoro-2-phenylethyl)benzene (3f)

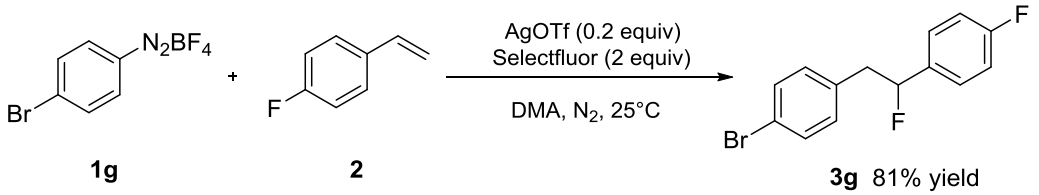


1e **2** **3f** 59% yield

To benzenediazonium tetrafluoroborate (**1e**) (57.6 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 38.4 mg 1-fluoro-4-(1-fluoro-2-phenylethyl)benzene (**3f**) as a colorless solid (59% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.21 (m, 3H), 7.14 (d, *J* = 6.8 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 5.60 (ddd, *J* = 47.0, 7.7, 5.3 Hz, 1H), 3.27 (ddd, *J* = 17.4, 14.2, 7.8 Hz, 1H), 3.09 (ddd, *J* = 26.7, 14.1, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, $J_{(C-F)}$= 172.2 Hz), 136.3 (d, $J_{(C-F)}$= 8.2 Hz), 135.5 (d, $J_{(C-F)}$= 26.4 Hz), 129.5, 128.5, 127.6 (d, $J_{(C-F)}$= 24.2 Hz), 126.9, 115.4 (d, $J_{(C-F)}$= 21.5 Hz), 93.9 (d, $J_{(C-F)}$= 162.0 Hz), 43.9 (d, $J_{(C-F)}$= 33.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 (m, 1F), -170.9 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{12}F_2$, 218.0907. Found, 218.1. Elemental Analysis: Calcd for C:77.05%, H:5.54%. Found, C:76.80%, H:5.84%.

1-bromo-4-(2-fluoro-2-(4-fluorophenyl)ethyl)benzene (3g)

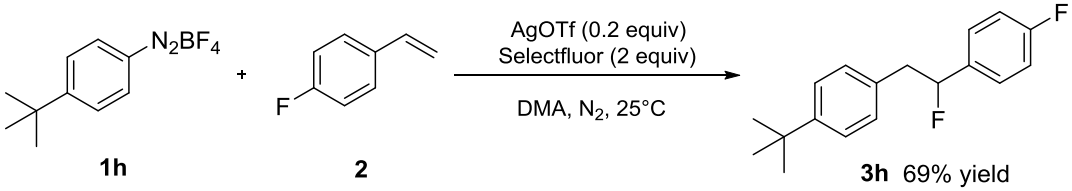


1g **2** **3g** 81% yield

To 4-bromobenzenediazonium tetrafluoroborate (**1g**) (81.2 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 72.6 mg 1-bromo-4-(2-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3g**) as a colorless solid (81% yield).

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 12.9, 5.0 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 5.56 (ddd, *J* = 46.9, 7.3, 5.4 Hz, 1H), 3.19 (ddd, *J* = 18.1, 14.3, 7.6 Hz, 1H), 3.05 (ddd, *J* = 26.2, 14.2, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, $J_{(C-F)}$= 249.2 Hz), 135.2 (d, $J_{(C-F)}$= 4.4 Hz), 135.1 (d, $J_{(C-F)}$= 6.8 Hz), 131.6, 131.4, 127.6 (d, $J_{(C-F)}$= 7.8 Hz), 120.9, 115.5 (d, $J_{(C-F)}$= 21.7 Hz), 93.5 (d, $J_{(C-F)}$= 167.4 Hz), 43.1 (d, $J_{(C-F)}$= 34.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (m, 1F), -171.5 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{11}BrF_2$, 296.0012. Found, 296.0. Elemental Analysis: Calcd for C:56.59%, H:3.73%. Found, C:56.89%, H:3.59%.

1-(tert-butyl)-4-(2-fluoro-2-(4-fluorophenyl)ethyl)benzene (3h)



1h **2** **3h** 69% yield

To 4-tert-butylbenzenediazonium tetrafluoroborate (**1h**) (74.4 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to

afford 57.0 mg 1-(tert-butyl)-4-(2-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3h**) as a colorless solid (69% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (m, 2H),7.13 (d, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.60 (ddd, *J* = 47.2, 8.2, 4.8 Hz, 1H), 3.25 (ddd, *J* = 17.1, 14.4, 8.2 Hz, 1H), 3.05 (ddd, *J* = 27.1, 14.1, 5.2 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, $J_{(C-F)}$= 148.7 Hz), 149.7, 135.8 (d, $J_{(C-F)}$= 14.5 Hz), 133.4 (d, $J_{(C-F)}$= 13.4 Hz), 129.2, 127.7 (d, $J_{(C-F)}$= 8.2 Hz), 125.4, 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 94.1 (d, $J_{(C-F)}$= 159.3 Hz), 43.2 (d, $J_{(C-F)}$= 44.8 Hz), 34.3, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 (m, 1F), -170.7 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{18}H_{20}F_2$, 274.1533. Found, 274.2. Elemental Analysis: Calcd for C:78.80%, H:7.35%. Found, C:78.75%, H:7.83%.

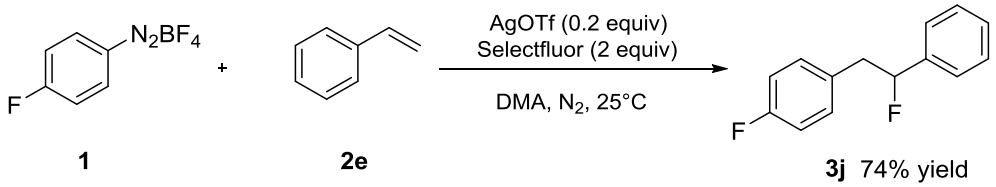
1-fluoro-4-(1-fluoro-2-(p-tolyl)ethyl)benzene (3i)

1i **2** **3i** 73% yield

To 4-methylbenzenediazonium tetrafluoroborate (**1i**) (61.8 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 50.9 mg 1-fluoro-4-(1-fluoro-2-(p-tolyl)ethyl)benzene (**3i**) as a colorless solid (73% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 3.6 Hz, 2H), 7.24 (d, *J* = 5.7 Hz,1H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 8.3 Hz, 3H), 5.56 (ddd, *J* = 47.0, 7.7, 5.3 Hz, 1H), 3.22 (ddd, *J* = 17.2, 14.2, 7.8 Hz, 1H), 3.04 (ddd, *J* = 26.7, 14.1, 5.3 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, $J_{(C-F)}$= 197.2 Hz), 136.4 (d, $J_{(C-F)}$= 10.8 Hz), 135.6 (d, $J_{(C-F)}$= 26.9 Hz), 133.1, 129.5, 129.2, 127.6 (d, $J_{(C-F)}$= 20.5 Hz), 115.4 (d, $J_{(C-F)}$= 21.6 Hz), 94.3 (d, $J_{(C-F)}$= 129.9 Hz), 43.4 (d, $J_{(C-F)}$= 30.1 Hz), 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.6 (m, 1F), -170.7 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{14}F_2$, 232.1064. Found, 232.1. Elemental Analysis: Calcd for C:77.57%, H:6.08%. Found, C:77.65%, H:6.17%.

1-fluoro-4-(2-fluoro-2-phenylethyl)benzene (3j)

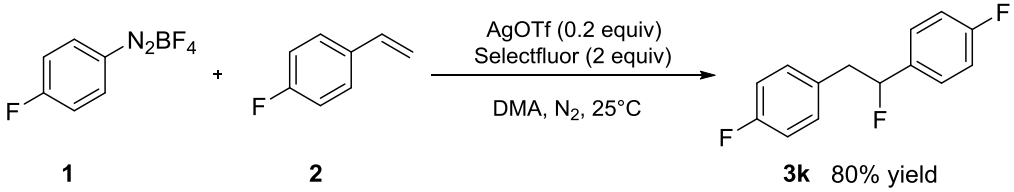


1 **2e** **3j** 74% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and styrene (**2e**) (170 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 °C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 48.1 mg 1-fluoro-4-(2-fluoro-2-phenylethyl)benzene (**3j**) as a colorless solid (74% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.11 (dd, *J* = 8.3, 5.6 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 5.57 (ddd, *J* = 47.3, 7.8, 4.9 Hz, 1H), 3.22 (ddd, *J* = 18.2, 14.4, 7.9 Hz, 1H), 3.08 (ddd, *J* = 27.7, 14.3, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{(C-F)}$= 233.6 Hz), 139.6 (d, $J_{(C-F)}$= 20.0 Hz), 132.3 (d, $J_{(C-F)}$= 3.6 Hz), 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 128.5, 128.5, 125.7 (d, $J_{(C-F)}$= 6.7 Hz), 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 94.4 (d, $J_{(C-F)}$= 101.6 Hz), 43.1 (d, $J_{(C-F)}$= 24.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3 (m, 1F), -173.7 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{12}F_2$, 218.0907. Found, 218.1. Elemental Analysis: Calcd for C:77.05%, H:5.54%. Found, C:77.10%, H:5.50%.

4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (3k)

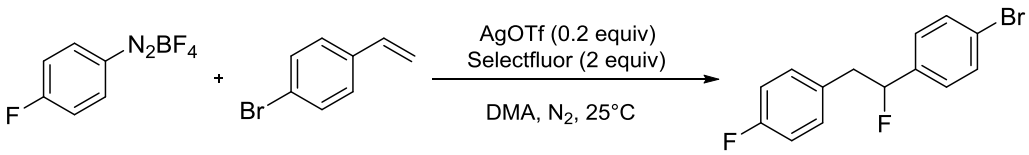


1 **2** **3k** 80% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 °C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 56.7 mg 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) as a colorless solid (80% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 2H), 7.12 – 7.05 (m, 3H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.96 (t, *J* = 8.7 Hz, 2H), 5.56 (ddd, *J* = 46.9, 7.4, 5.4 Hz, 1H), 3.22 (ddd, *J* = 17.2, 8.4, 5.2 Hz, 1H), 3.06 (ddd, *J* = 26.1, 14.3, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, $J_{(C-F)}$= 56.6 Hz), 161.0 (d, $J_{(C-F)}$= 58.2 Hz), 135.2 (d, $J_{(C-F)}$= 31.0 Hz), 131.8 (d, $J_{(C-F)}$= 20.1 Hz), 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 127.5 (d, $J_{(C-F)}$= 48.1 Hz), 115.5 (d, $J_{(C-F)}$= 14.7 Hz), 115.3 (d, $J_{(C-F)}$= 14.3 Hz), 93.9 (d, $J_{(C-F)}$= 174.2 Hz), 43.1 (d, $J_{(C-F)}$= 24.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.3 (m, 1F), -116.1 (m, 1F), -171.6 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{11}F_3$, 236.0813. Found, 236.1. Elemental Analysis: Calcd for C:71.18%, H:4.69%. Found, C:71.31%, H:4.54%.

1-bromo-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (3l)

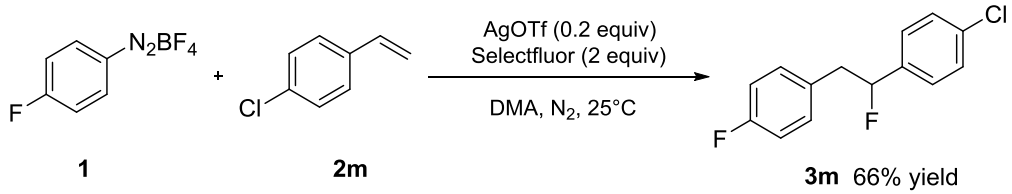


1 **2l** **3l** 72% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 1-bromo-4-vinylbenzene (**2l**) (196.5 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 °C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 64.0 mg 1-bromo-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3l**) as a colorless solid (72% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.11 (dd, *J* = 9.0, 6.3 Hz, 2H), 7.12 – 7.05 (m, 2H), 7.00 – 6.91 (m, 2H), 5.55 (ddd, *J* = 46.9, 7.4, 5.2 Hz, 1H), 3.20 (ddd, *J* = 18.8, 14.3, 7.5 Hz, 1H), 3.07 (ddd, *J* = 26.0, 14.3, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, $J_{(C-F)}$= 165.6 Hz), 138.4 (d, $J_{(C-F)}$= 18.8 Hz), 131.8, 131.6, 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 127.4 (d, $J_{(C-F)}$= 6.8 Hz), 122.2 (d, $J_{(C-F)}$= 35.9 Hz), 115.3 (d, $J_{(C-F)}$= 21.3 Hz), 93.7 (d, $J_{(C-F)}$= 192.5 Hz), 43.0 (d, $J_{(C-F)}$= 24.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0 (m, 1F), -174.4 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{11}BrF_2$, 296.0012. Found, 296.0. Elemental Analysis: Calcd for C:56.59%, H:3.73%. Found, C:56.42%, H:3.85%.

1-chloro-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (3m)

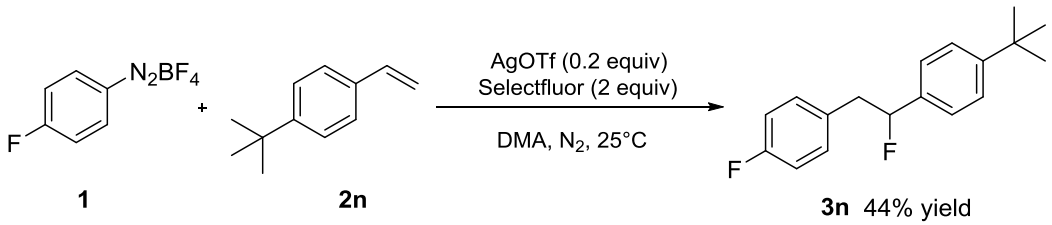


1 **2m** **3m** 66% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 1-chloro-4-vinylbenzene (**2m**) (180 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 50.0 mg 1-chloro-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3m**) as a white solid (66% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 13.7, 5.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.09 (dd, *J* = 8.2, 5.7 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 5.56 (ddd, *J* = 46.9, 7.3, 5.3 Hz, 1H), 3.20 (ddd, *J* = 18.7, 14.3, 7.5 Hz, 1H), 3.07 (ddd, *J* = 26.0, 14.3, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, $J_{(C-F)}$= 176.7 Hz), 137.9 (d, $J_{(C-F)}$= 15.5 Hz), 134.3 (d, $J_{(C-F)}$= 18.6 Hz), 131.8, 131.1 (d, $J_{(C-F)}$= 8.0 Hz), 128.7, 127.1 (d, $J_{(C-F)}$= 6.7 Hz), 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 93.6 (d, $J_{(C-F)}$= 144.4 Hz), 43.0 (d, $J_{(C-F)}$= 24.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0 (m, 1F), -173.5 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{14}H_{11}ClF_2$, 252.0517. Found, 252.1. Elemental Analysis: Calcd for C:66.55%, H:4.39%. Found, C:66.42%, H:4.25%.

1-(tert-butyl)-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (3n)



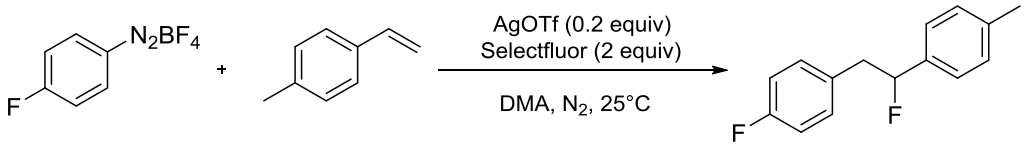
1 **2n** **3n** 44% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 1-(tert-butyl)-4-vinylbenzene (**2n**) (275 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the

residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 36.0 mg 1-(tert-butyl)-4-(1-fluoro-2-(4-fluorophenyl)ethyl)benzene (**3n**) as a colorless solid (44% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.14 (dt, *J* = 16.3, 8.2 Hz, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 5.54 (ddd, *J* = 47.5, 8.4, 4.3 Hz, 1H), 3.23 (ddd, *J* = 17.3, 14.6, 8.5 Hz, 1H), 3.06 (ddd, *J* = 27.2, 14.2, 5.6 Hz,, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, $J_{(C-F)}$= 168.7 Hz), 151.6 (d, $J_{(C-F)}$= 16.5 Hz), 136.5 (d, $J_{(C-F)}$= 17.7 Hz), 132.8, 131.0 (d, $J_{(C-F)}$= 7.9 Hz), 125.6 (d, $J_{(C-F)}$= 6.3 Hz), 125.5, 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 94.8 (d, $J_{(C-F)}$= 173.3 Hz), 43.0 (d, $J_{(C-F)}$= 24.6 Hz), 34.7, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4 (m, 1F), -172.1 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{18}H_{20}F_2$, 274.1533. Found, 274.2. Elemental Analysis: Calcd for C:78.80%, H:7.35%. Found, C:78.47%, H:7.70%.

1-fluoro-4-(2-fluoro-2-(p-tolyl)ethyl)benzene (3o)

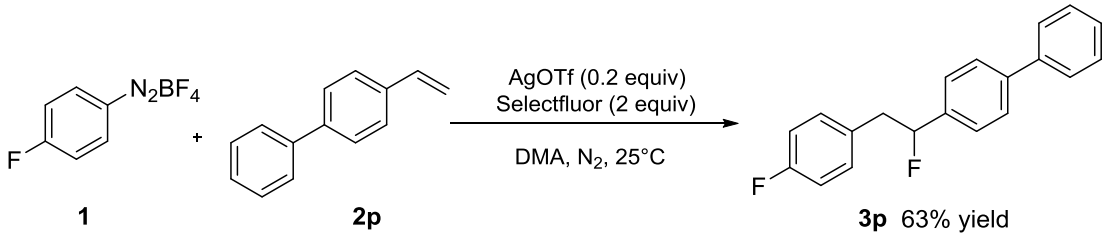


1 **2o** **3o** 85% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 1-methyl-4-vinylbenzene (**2o**) (197 μL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 °C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 59.4 mg 1-fluoro-4-(2-fluoro-2-(p-tolyl)ethyl)benzene (**3o**) as a white solid (85% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 4H), 7.12 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.01 – 6.93 (m, 2H), 5.54 (ddd, *J* = 47.3, 7.9, 4.9 Hz, 1H), 3.23 (ddd, *J* = 17.6, 14.4, 8.0 Hz, 1H), 3.07 (ddd, *J* = 27.7, 14.3, 4.9 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (d, $J_{(C-F)}$= 207.5 Hz), 138.4 (d, $J_{(C-F)}$= 1.9 Hz), 136.6, 132.5 (d, $J_{(C-F)}$= 3.6 Hz), 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 129.2, 125.8 (d, $J_{(C-F)}$= 6.4 Hz), 115.2 (d, $J_{(C-F)}$= 21.2 Hz), 94.1 (d, $J_{(C-F)}$= 190.6 Hz), 43.1 (d, $J_{(C-F)}$= 24.9 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5 (m, 1F), -171.7 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{14}F_2$, 232.1064. Found, 232.1. Elemental Analysis: Calcd for C:77.57%, H:6.08%. Found, C:77.55%, H:6.28%.

4-(1-fluoro-2-(4-fluorophenyl)ethyl)-1,1'-biphenyl (3p)

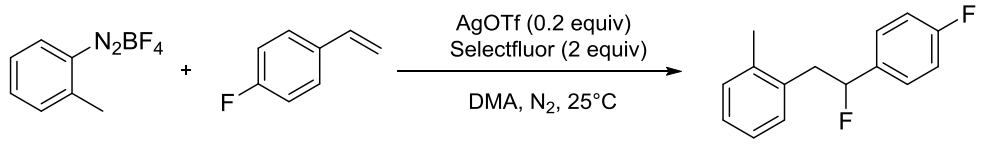


1 **2p** **3p** 63% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-vinyl-1,1'-biphenyl (**2p**) (270 mg, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 55.6 mg 4-(1-fluoro-2-(4-fluorophenyl)ethyl)-1,1'-biphenyl (**3p**) as a white solid (63% yield).

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.52 – 7.44 (m, 2H), 7.42 – 7.32 (m, 3H), 7.14 (t, *J* = 15.5 Hz, 2H), 7.05 – 6.93 (m, 2H), 5.66 (ddd, *J* = 47.5, 7.7, 4.2 Hz, 1H), 3.30 (ddd, *J* = 17.4, 8.2, 5.4 Hz, 1H), 3.15 (ddd, *J* = 27.7, 14.2, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{(C-F)}$= 221.5 Hz), 141.4 (d, $J_{(C-F)}$= 10.7 Hz), 140.5 (d, $J_{(C-F)}$= 23.0 Hz), 138.6, 138.4, 132.2, 131.1 (d, $J_{(C-F)}$= 7.9 Hz), 128.9, 127.6, 127.2 (d, $J_{(C-F)}$= 4.6 Hz), 126.2, 115.3 (d, $J_{(C-F)}$= 21.2 Hz), 94.4 (d, $J_{(C-F)}$= 162.8 Hz), 43.1 (d, $J_{(C-F)}$= 24.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2 (m, 1F), -173.2 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{20}H_{16}F_2$, 294.1220. Found, 294.1. Elemental Analysis: Calcd for C:81.61%, H:5.48%. Found, C:81.79%, H:5.56%.

1-(2-fluoro-2-(4-fluorophenyl)ethyl)-2-methylbenzene (3q)



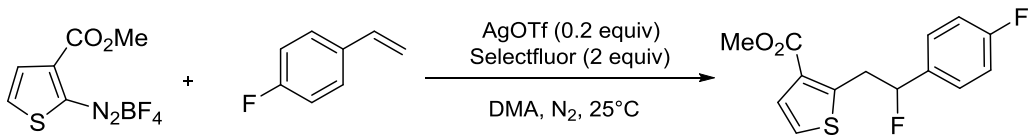
1q **2** **3q** 82% yield

To 2-methylbenzenediazonium tetrafluoroborate (**1q**) (61.8 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the

residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 57 mg 1-(2-fluoro-2-(4-fluorophenyl)ethyl)-2-methylbenzene (**3q**) as a colorless solid (82% yield).

R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 7.15 (dd, *J* = 5.4, 1.7 Hz, 2H), 7.12 (s, 1H), 7.12 – 7.06 (m, 1H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.59 (ddd, *J* = 46.8, 7.7, 5.4 Hz, 1H), 3.27 (ddd, *J* = 16.2, 14.3, 7.8 Hz, 1H), 3.07 (ddd, *J* = 26.6, 14.3, 5.3 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $J_{(C-F)}$= 190.6 Hz), 136.7 (d, $J_{(C-F)}$= 8.5 Hz), 135.8, 134.6 (d, $J_{(C-F)}$= 10.8 Hz), 130.4, 127.5 (d, $J_{(C-F)}$= 6.7 Hz), 127.4, 127.0, 126.1, 115.4 (d, $J_{(C-F)}$= 21.6 Hz), 93.8 (d, $J_{(C-F)}$= 157.5 Hz), 41.0 (d, $J_{(C-F)}$= 47.7 Hz), 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 (m, 1F), -171.6 (m, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{14}F_2$, 232.1064. Found, 232.1. Elemental Analysis: Calcd for C:77.57%, H:6.08%. Found, C:77.39%, H:6.25%.

Methyl-2-(2-fluoro-2-(4-fluorophenyl)ethyl)thiophene-3-carboxylate (3r)

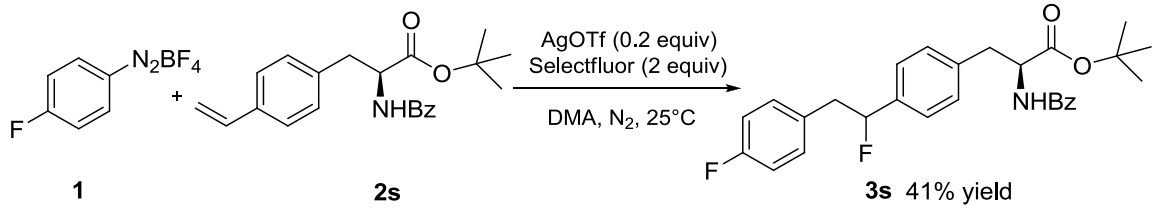


1r **2** **3r** 34% yield

To 2-((tetrafluoroboranyl)diazenyl)thiophene-3-carboxylate (**1r**) (76.8 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and 4-fluorostyrene (**2**) (179 µL, 1.50 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 50:1 (v/v), to afford 33 mg Methyl-2-(2-fluoro-2-(4-fluorophenyl)ethyl)thiophene-3-carboxylate (**3r**) as a colorless solid (34% yield).

R_f = 0.30 (hexanes/EtOAc 25:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 5.0 Hz, 1H), 7.36 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.11 – 6.99 (m, 2H), 6.97 (t, *J* = 8.9 Hz, 1H), 5.70 (ddd, *J* = 47.6, 8.8, 3.8 Hz, 1H), 3.87 (s, 3H), 3.65 (ddd, *J* = 18.0, 14.6, 4.3 Hz, 1H), 3.48 (ddd, *J* = 16.5, 14.2, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 162.6 (d, $J_{(C-F)}$= 196.7 Hz), 145.2 (d, $J_{(C-F)}$= 2.7 Hz), 135.8 (d, $J_{(C-F)}$= 16.7 Hz), 131.8, 130.5, 127.7, 127.3 (d, $J_{(C-F)}$= 8.6 Hz), 115.4 (d, $J_{(C-F)}$= 21.7 Hz), 93.6 (d, $J_{(C-F)}$= 173.9 Hz), 52.0, 37.8 (d, $J_{(C-F)}$= 98 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8 (m, 1F), -174.7 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{14}H_{12}F_2O_2SNa$ $[M+Na]^+$, 305.0424. Found, 305.0420.

tert-butyl (2S)-2-benzamido-3-(4-(1-fluoro-2-(4-fluorophenyl)ethyl)phenyl)propanoate (3s)

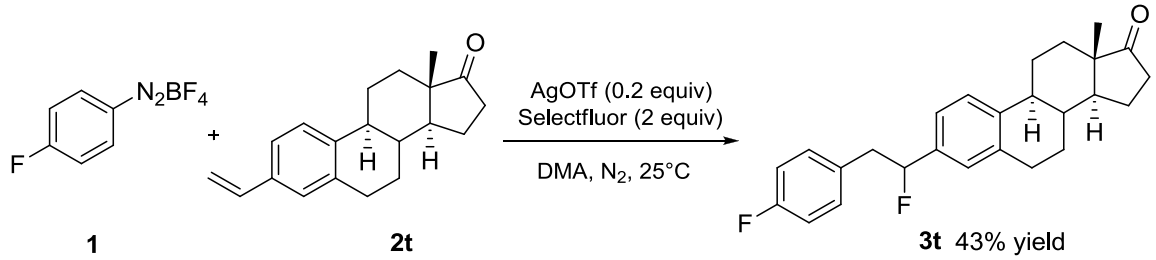


1 **2s** **3s** 41% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (31.5 mg, 0.150 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and tert-butyl (S)-2-benzamido-3-(4-vinylphenyl)propanoate (**2s**) (158 mg, 0.450 mmol, 3.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 28.8 mg tert-butyl (2S)-2-benzamido-3-(4-(1-fluoro-2-(4-fluorophenyl)ethyl)phenyl)propanoate (**3s**) as a colorless solid (41% yield).

R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.17 (s, 4H), 7.06 (s, 2H), 6.93 (t, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 6.2 Hz, 1H), 5.55 (ddd, *J* = 47.2, 7.8, 5.6 Hz, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 3.39 – 3.14 (m, 3H), 3.12 – 2.92 (m, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.7, 161.8 (d, $J_{(C-F)}$= 196.2 Hz), 138.2 (d, $J_{(C-F)}$= 31.9 Hz), 136.6, 134.1, 131.8, 131.1 (d, $J_{(C-F)}$= 9.3 Hz), 129.8, 128.6 (d, $J_{(C-F)}$= 16.0 Hz), 127.0, 125.8 (d, $J_{(C-F)}$= 6.2 Hz), 115.1 (d, $J_{(C-F)}$= 15.2 Hz), 94.3 (d, $J_{(C-F)}$= 136.1 Hz), 82.8, 53.9, 43.0 (d, $J_{(C-F)}$= 24.3 Hz), 37.8, 31.0, 28.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1 (m, 1F), -173.6 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{28}H_{29}F_2NO_3Na$ $[M+Na]^+$, 488.2013. Found, 488.2010.

(8R,9S,13S,14S)-3-(1-fluoro-2-(4-fluorophenyl)ethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3t)



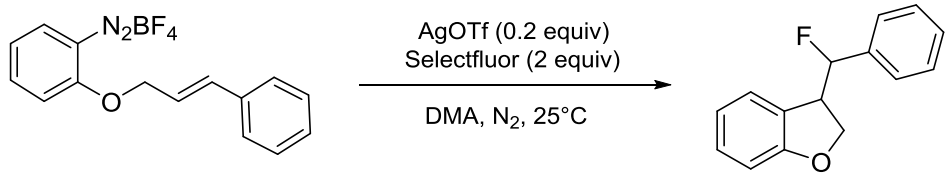
1 **2t** **3t** 43% yield

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (63.0 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (1.20 mL) and (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**2t**) (420 mg, 1.50 mmol, 5.00 equiv), then followed by 4-

fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 10 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 51.1 mg (8R,9S,13S,14S)-3-(1-fluoro-2-(4-fluorophenyl)ethyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3t**) as a colorless solid (43 % yield).

R_f = 0.5 (hexanes/EtOAc 20:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 5.7 Hz, 1H), 7.16 (dd, *J* = 17.0, 11.4 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 5.51 (ddd, *J* = 47.5, 8.4, 4.3 Hz, 1H), 3.22 (td, *J* = 15.8, 8.8 Hz, 1H), 3.14 – 2.97 (m, 1H), 2.92 (d, *J* = 5.1 Hz, 2H), 2.59 – 2.47 (m, 1H), 2.47 – 2.40 (m, 1H), 2.33 (d, *J* = 9.1 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.11 – 1.91 (m, 3H), 1.63 (ddd, *J* = 17.8, 10.5, 6.8 Hz, 2H), 1.57 – 1.40 (m, 4H), 0.95 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 162.0 (d, $J_{(C-F)}$= 214.2 Hz), 140.1 (d, $J_{(C-F)}$= 15.2 Hz), 137.1 (d, $J_{(C-F)}$= 8.2 Hz), 136.8, 132.7 (d, $J_{(C-F)}$= 7.4 Hz), 131.0 (d, $J_{(C-F)}$= 7.2 Hz), 126.5, 125.6 (d, $J_{(C-F)}$= 5.6 Hz), 123.2, 115.2 (d, $J_{(C-F)}$= 13.5 Hz), 94.6 (d, $J_{(C-F)}$= 149.6 Hz), 50.5, 47.8, 44.4, 42.9 (d, $J_{(C-F)}$= 20.3 Hz), 38.0, 35.9, 31.6, 29.4, 26.4, 25.7, 21.5, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4 (m, 1F), -172.5 (m, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{28}F_2ONa$ $[M+Na]^+$, 417.2006. Found, 417.2008.

3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (5a)



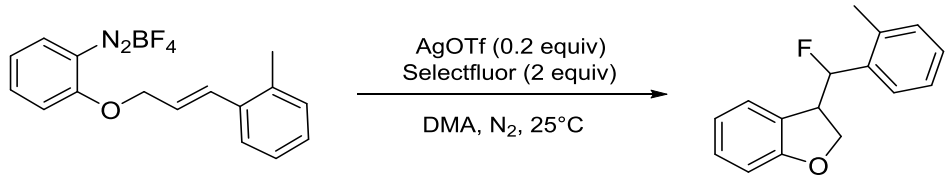
4a **5a** 81% yield (dr=14:1)

To 2-cinnamyloxybenzenediazonium tetrafluoroborate (**4a**) (97.2 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.0600 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 55.6 mg 3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (**5a**) as a colorless solid (81% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 3H), 7.32 (d, *J* = 3.9 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.66 (t, *J*

= 7.5 Hz, 1H), 6.29 (d, *J* = 7.4 Hz, 1H), 5.39 (dd, *J* = 47.3, 8.7 Hz, 1H), 4.80 (dd, *J* = 9.3, 4.6 Hz, 1H), 4.66 (t, *J* = 9.1 Hz, 1H), 4.07 – 3.86 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 137.3, 129.3 (d, $J_{(C-F)}$= 2.2 Hz), 129.3, 128.6, 127.3 (d, $J_{(C-F)}$= 5.9 Hz), 125.9, 124.6 (d, $J_{(C-F)}$= 9.2 Hz), 120.2, 109.8, 95.2 (d, $J_{(C-F)}$= 186.8 Hz), 73.7 (d, $J_{(C-F)}$= 2.7 Hz), 48.6 (d, $J_{(C-F)}$= 26.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -170.1 (dd, *J* = 47.3, 13.4 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{13}FONa$ $[M+Na]^+$, 251.0848. Found, 251.0843.

3-(fluoro(o-tolyl)methyl)-2,3-dihydrobenzofuran (5b)

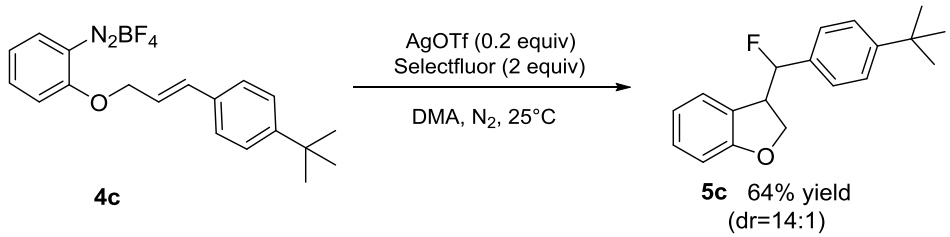


4b **5b** 71% yield (dr=7:1)

To 2-(E)-(o-tolyl)allyloxybenzenediazonium tetrafluoroborate (**4b**) (101 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 51.5 mg 3-(fluoro(o-tolyl)methyl)-2,3-dihydrobenzofuran (**5b**) as a colorless solid (71% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 1H), 7.36 – 7.25 (m, 2H), 7.18 – 7.05 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 7.4 Hz, 1H), 5.65 (dd, *J* = 47.0, 9.0 Hz, 1H), 4.86 (dd, *J* = 9.4, 3.9 Hz, 1H), 4.69 – 4.58 (m, 1H), 3.90 (dtd, *J* = 12.8, 8.6, 4.0 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 136.2 (d, $J_{(C-F)}$= 5.1 Hz), 135.9 (d, $J_{(C-F)}$= 18.9 Hz), 130.5, 129.3, 128.9, 126.6 (d, $J_{(C-F)}$= 6.4 Hz), 126.5, 125.6, 124.4 (d, $J_{(C-F)}$= 9.9 Hz), 120.4, 109.8, 91.4 (d, $J_{(C-F)}$= 119.1 Hz), 74.0 (d, $J_{(C-F)}$= 1.4 Hz), 48.3 (d, $J_{(C-F)}$= 45.1 Hz), 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.8 (dd, *J* = 47.0, 13.5 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{16}H_{15}FONa$ $[M+Na]^+$, 265.1005. Found, 265.0994.

3-((4-(tert-butyl)phenyl)fluoromethyl)-2,3-dihydrobenzofuran (5c)



4c **5c** 64% yield (dr=14:1)

To 2-(E)-4-(tert-butyl)-allyloxybenzenediazonium tetrafluoroborate (**4c**) (114 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 54.2 mg 3-((4-(tert-butyl)phenyl)fluoromethyl)-2,3-dihydrobenzofuran (**5c**) as a colorless solid (64% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 2H), 7.12 (t, *J* = 7.0 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 6.7 Hz, 1H), 6.33 (d, *J* = 6.8 Hz, 1H), 5.37 (dd, *J* = 47.3, 8.0 Hz, 1H), 4.74 (t, *J* = 15.0 Hz, 1H), 4.66 (t, *J* = 8.6 Hz, 1H), 3.98 (d, *J* = 4.8 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 152.5, 134.5 (d, $J_{(C-F)}$= 19.9 Hz), 129.2, 127.0 (d, $J_{(C-F)}$= 5.6 Hz), 125.8, 125.6, 124.8 (d, $J_{(C-F)}$= 9.2 Hz), 120.2, 109.8, 95.4 (d, $J_{(C-F)}$= 174.8 Hz), 73.6 (d, $J_{(C-F)}$= 2.1 Hz), 48.3 (t, $J_{(C-F)}$= 30.2 Hz), 34.5, 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.1 (dd, *J* = 47.3, 13.5 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{19}H_{21}FONa$ $[M+Na]^+$, 307.1474. Found, 307.1471.

3-(fluoro(4-(trifluoromethyl)phenyl)methyl)-2,3-dihydrobenzofuran (5d)

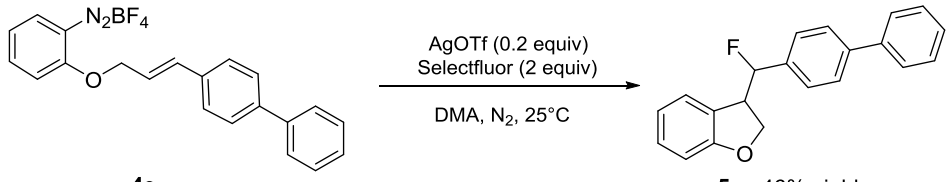
4d **5d** 56% yield (dr=13:1)

To 2-(E)-4-(trifluoromethyl)-allyloxybenzenediazonium tetrafluoroborate (**4d**) (118 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by

chromatography on silica gel, eluting with hexanes/EtOAc 75:1 (v/v), to afford 50 mg 3-(fluoro(4-(trifluoromethyl)phenyl)methyl)-2,3-dihydrobenzofuran (**5d**) as a white solid (56% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.2 Hz, 1H), 5.45 (dd, *J* = 47.0, 8.3 Hz, 1H), 4.78 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.62 (t, *J* = 9.0 Hz, 1H), 4.00 – 3.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 141.3 (d, $J_{(C-F)}$= 15.5 Hz), 132.4 (m, $J_{(C-F)}$= 15.5 Hz), 129.6, 127.4 (d, $J_{(C-F)}$= 6.3 Hz), 125.7, 125.6 (d, $J_{(C-F)}$= 7.5 Hz), 125.3, 124.0 (m, $J_{(C-F)}$= 218.7 Hz), 122.6, 120.4, 110.1, 94.4 (d, $J_{(C-F)}$= 177.8 Hz), 73.3 (d, $J_{(C-F)}$= 3.2 Hz), 48.7 (d, $J_{(C-F)}$= 25.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (m, 3F), -174.0 (dd, *J* = 47.0, 14.0 Hz, 1F). The X-ray Crystal data of the product was displayed in this information.

3-([1,1'-biphenyl]-4-ylfluoromethyl)-2,3-dihydrobenzofuran (5e)

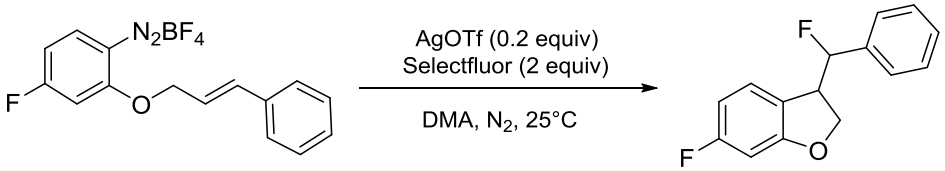


4e **5e** 46% yield (dr=13:1)

To 2-(E)-[1,1'-biphenyl]-4-yl-allyloxybenzenediazonium tetrafluoroborate (**4e**) (120 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 42.4 mg 3-([1,1'-biphenyl]-4-ylfluoromethyl)-2,3-dihydrobenzofuran (**5e**) as a colorless solid (46% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.5, 4.5 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 7.4 Hz, 1H), 5.43 (dd, *J* = 47.2, 8.7 Hz, 1H), 4.82 (dd, *J* = 9.4, 4.6 Hz, 1H), 4.69 (t, *J* = 9.1 Hz, 1H), 4.09 – 3.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 142.1, 140.4 (d, $J_{(C-F)}$= 15.1 Hz), 136.3 (d, $J_{(C-F)}$= 18.9 Hz), 129.3, 129.0, 127.8, 127.7, 127.3, 127.2, 125.9, 124.6 (d, $J_{(C-F)}$= 9.1 Hz), 120.3, 109.9, 95.3 (d, $J_{(C-F)}$= 175.8 Hz), 73.7 (d, $J_{(C-F)}$= 2.6 Hz), 48.6 (d, $J_{(C-F)}$= 26.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.7 (dd, *J* = 47.3, 13.3 Hz, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{21}H_{17}FO$, 304.1263. Found, 304.1. Elemental Analysis: Calcd for C:82.87%, H:5.63%. Found, C:82.87%, H:5.81%.

6-fluoro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (5f)

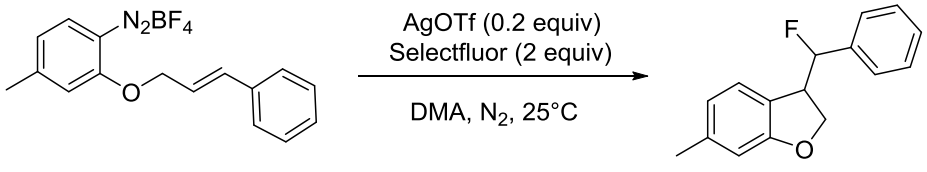


4f **5f** 71% yield (dr=7:1)

To 2-(cinnamyloxy)-4-fluorobenzenediazonium tetrafluoroborate (**4f**) (103 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 52.4 mg 6-fluoro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (**5f**) as a colorless oil(71% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 3H), 7.34 – 7.27 (m, 2H), 6.58 – 6.42 (m, 1H), 6.41 – 6.27 (m, 1H), 6.17 (dd, *J* = 8.2, 5.8 Hz, 1H), 5.34 (dd, *J* = 47.2, 8.7 Hz, 1H), 4.82 (dt, *J* = 28.0, 14.0 Hz, 1H), 4.71 (t, *J* = 9.1 Hz, 1H), 3.99 – 3.83 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (d, $J_{(C-F)}$= 196.4 Hz), 162.0 (d, $J_{(C-F)}$= 16.5 Hz), 137.0 (d, $J_{(C-F)}$= 25.5 Hz), 129.4 (d, $J_{(C-F)}$= 2.3 Hz), 128.7, 127.2 (d, $J_{(C-F)}$= 6.0 Hz), 126.2 (d, $J_{(C-F)}$= 10.5 Hz), 120.2 (d, $J_{(C-F)}$= 20.3 Hz), 106.9 (d, $J_{(C-F)}$= 22.8 Hz), 98.3 (d, $J_{(C-F)}$= 26.5 Hz), 95.2 (d, $J_{(C-F)}$= 163.5 Hz), 74.9 (d, $J_{(C-F)}$= 2.6 Hz), 47.9 (d, $J_{(C-F)}$= 26.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6 (m, 1F), -170.3 (dd, *J* = 47.2, 13.1 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{15}H_{12}F_2ONa$ $[M+Na]^+$, 269.0754. Found, 269.0750.

3-(fluoro(phenyl)methyl)-6-methyl-2,3-dihydrobenzofuran (5g)



4g **5g** 61% yield (dr=14:1)

To 2-(cinnamyloxy)-4-methylbenzenediazonium tetrafluoroborate (**4g**) (101 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The

reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 44.4 mg 3-(fluoro(phenyl)methyl)-6-methyl-2,3-dihydrobenzofuran (**5g**) as a white solid (61% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 3H), 7.31 (ddd, *J* = 5.2, 3.3, 2.1 Hz, 2H), 6.63 (s, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 7.6 Hz, 1H), 5.34 (dd, *J* = 47.3, 8.8 Hz, 1H), 4.78 (ddd, *J* = 9.4, 4.6, 0.7 Hz, 1H), 4.64 (t, *J* = 9.0 Hz, 1H), 3.99 – 3.85 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 139.5, 137.3 (d, $J_{(C-F)}$= 38.4 Hz), 129.3, 128.6, 127.3 (d, $J_{(C-F)}$= 5.9 Hz), 125.4, 121.5 (d, $J_{(C-F)}$= 7.6 Hz), 121.0, 110.5, 95.3 (d, $J_{(C-F)}$= 134.7 Hz), 74.0 (d, $J_{(C-F)}$= 2.5 Hz), 48.2 (d, $J_{(C-F)}$= 27.7 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.7 (dd, *J* = 47.3, 13.2 Hz, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{16}H_{15}FO$, 242.1107. Found, 242.1. Elemental Analysis: Calcd for C:76.32%, H:6.24%. Found, C:76.25%, H:6.25%.

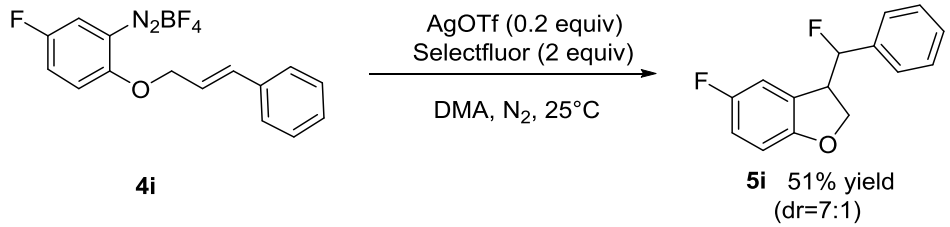
Methyl-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran-6-carboxylate (5h)

To Benzenediazonium 2-(cinnamyloxy)-4-benzoate tetrafluoroborate (**4h**) (115 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 25:1 (v/v), to afford 52.8 mg Methyl-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran-6-carboxylate (**5h**) as a colorless solid (62% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 11.6 Hz, 4H), 7.37 (s, 1H), 7.28 (s, 2H), 6.34 (d, *J* = 7.5 Hz, 1H), 5.39 (dd, *J* = 47.1, 8.4 Hz, 1H), 4.88 – 4.78 (m, 1H), 4.69 (t, *J* = 9.0 Hz, 1H), 3.96 (t, *J* = 15.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 160.9, 136.9 (d, $J_{(C-F)}$= 23.5 Hz), 131.4 (d, $J_{(C-F)}$= 23.8 Hz), 130.0, 129.5, 128.7, 127.1 (d, $J_{(C-F)}$= 5.9 Hz), 125.6, 122.1, 110.6, 94.7 (d, $J_{(C-F)}$= 158.5 Hz), 73.6 (d, $J_{(C-F)}$= 58.9 Hz), 52.3, 48.6 (d, $J_{(C-F)}$= 26.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.2 (dd, *J* = 47.1, 13.7 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{17}H_{15}FO_3Na$ $[M+Na]^{+}$,

309.0903. Found, 309.0899.

5-fluoro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (5i)



4i **5i** 51% yield (dr=7:1)

To 2-(cinnamyloxy)-5-fluorobenzenediazonium tetrafluoroborate (**4i**) (103 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 37.3 mg 5-fluoro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (**5i**) as a colorless solid (51% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.36 (m, 3H), 7.30 (d, *J* = 3.2 Hz, 2H), 6.80 (td, *J* = 8.8, 2.3 Hz, 1H), 6.69 (dd, *J* = 8.6, 4.1 Hz, 1H), 6.04 – 5.87 (m, 1H), 5.38 (dd, *J* = 47.1, 8.6 Hz, 1H), 4.79 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.67 (t, *J* = 9.1 Hz, 1H), 4.03 – 3.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (d, $J_{(C-F)}$= 139.4 Hz), 155.6 (d, $J_{(C-F)}$= 42.1 Hz), 136.9 (d, $J_{(C-F)}$= 25.8 Hz), 129.6 (d, $J_{(C-F)}$= 2.2 Hz), 128.8, 127.1 (d, $J_{(C-F)}$= 5.8 Hz), 126.02 (t, $J_{(C-F)}$= 9.0 Hz), 115.5 (d, $J_{(C-F)}$= 24.2 Hz), 112.9 (d, $J_{(C-F)}$= 25.3 Hz), 109.9 (d, $J_{(C-F)}$= 8.5 Hz), 94.9 (d, $J_{(C-F)}$= 162.5 Hz), 74.3 (d, $J_{(C-F)}$= 2.7 Hz), 48.6 (dd, $J_{(C-F)}$= 42.3, 37.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.2 (m, 1F), -170.5 (dd, *J* = 47.1, 13.4 Hz, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{12}F_2O$, 246.0856. Found, 246.1. Elemental Analysis: Calcd for C:73.16%, H:4.91%. Found, C:73.17%, H:5.10%.

5-chloro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (5j)

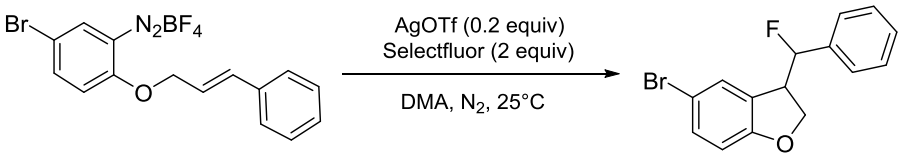
4j **5j** 53% yield (dr=9:1)

To 5-chloro-2-(cinnamyloxy)-benzenediazonium tetrafluoroborate (**4j**) (108 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added

anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 41.8 mg 5-chloro-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (**5j**) as a colorless solid (51% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 3H), 7.28 (t, *J* = 8.3 Hz, 2H), 7.07 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.26 (s, 1H), 5.38 (dd, *J* = 47.1, 8.3 Hz, 1H), 4.77 (dt, *J* = 26.2, 13.1 Hz, 1H), 4.65 (t, *J* = 9.1 Hz, 1H), 4.01 – 3.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 136.9 (d, $J_{(C-F)}$= 12.2 Hz), 129.5 (d, $J_{(C-F)}$= 12.7 Hz), 129.2, 128.8, 127.0 (d, $J_{(C-F)}$= 6.0 Hz), 126.6 (d, $J_{(C-F)}$= 8.8 Hz), 125.9, 124.9, 110.5, 94.7 (d, $J_{(C-F)}$= 160.2 Hz), 74.0 (d, $J_{(C-F)}$= 15.8 Hz), 48.5 (d, $J_{(C-F)}$= 47.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.1 (dd, *J* = 47.1, 14.1 Hz, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{12}ClFO$, 262.0561. Found, 262.1. Elemental Analysis: Calcd for C:68.58%, H:4.60%. Found, C:68.60%, H:4.83%.

5-bromo-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (5k)



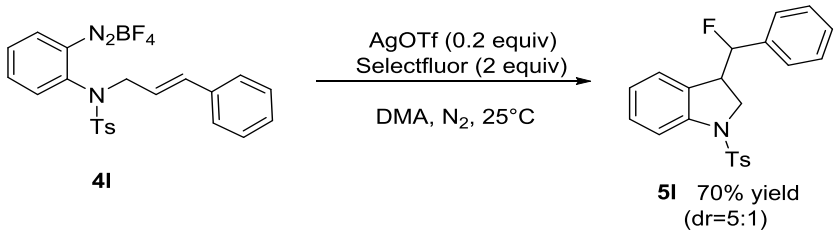
4k **5k** 41% yield (dr=11:1)

To 5-bromo-2-(cinnamyloxy)-benzenediazonium tetrafluoroborate (**4k**) (121 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford 37.3 mg 5-bromo-3-(fluoro(phenyl)methyl)-2,3-dihydrobenzofuran (**5k**) as a colorless solid (41% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.30 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 3H), 7.28 (s, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.40 (s, 1H), 5.38 (dd, *J* = 47.0, 7.1 Hz, 1H), 4.76 (m, 1H), 4.65 (d, *J* = 8.6 Hz, 1H), 3.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 137.0 (d, $J_{(C-F)}$= 14.3 Hz), 136.8, 132.1, 129.5, 128.8, 127.1 (d, $J_{(C-F)}$= 8.6 Hz), 127.0 (d, $J_{(C-F)}$= 5.9 Hz), 111.9, 111.4, 94.5 (d, $J_{(C-F)}$= 125.1 Hz), 73.8 (d, $J_{(C-F)}$= 47.3 Hz), 48.3

(d, $J_{(C-F)}$= 57.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.6 (dd, *J* = 47.0, 14.2 Hz, 1F). Mass Spectrometry: GS-Mass(EI) (m/z): Calcd for $C_{15}H_{12}BrFO$, 306.0056. Found, 306.0. Elemental Analysis: Calcd for C:58.65%, H:3.94%. Found, C:58.76%, H:4.04%.

3-(fluoro(phenyl)methyl)-1-tosylindoline (5l)

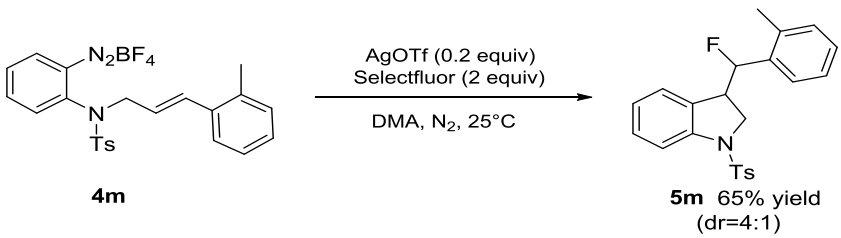


4l **5l** 70% yield (dr=5:1)

To Benzenediazonium 2-[cinnamyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4l**) (143 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 80.5 mg 3-(fluoro(phenyl)methyl)-1-tosylindoline (**5l**) as a colorless solid (70% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.0 Hz, 4H), 7.28 (s, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 6.6 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 7.5 Hz, 1H), 4.68 (dd, *J* = 47.0, 8.5 Hz, 1H), 4.23 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.97 (dd, *J* = 11.3, 8.9 Hz, 1H), 3.66 – 3.49 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.8, 137.0 (d, $J_{(C-F)}$= 19.7 Hz), 134.0 (d, $J_{(C-F)}$= 5.5 Hz), 129.8, 129.3, 129.2, 129.1, 128.6, 127.5, 127.0 (d, $J_{(C-F)}$= 6.0 Hz), 126.1, 123.4, 115.3, 94.6 (d, $J_{(C-F)}$= 152.1 Hz), 52.3 (d, $J_{(C-F)}$= 11.0 Hz), 46.7 (d, $J_{(C-F)}$= 31.5 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.9 (dd, *J* = 46.8, 13.9 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{20}FNO_2SNa$ $[M+Na]^+$, 404.1096. Found, 404.1095.

3-(fluoro(o-tolyl)methyl)-1-tosylindoline (5m)



4m **5m** 65% yield (dr=4:1)

To Benzenediazonium 2-[(o-tolyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4m**)

(147 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 77.6 mg 3-(fluoro(o-tolyl)methyl)-1-tosylindoline (**5m**) as a colorless solid (65% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 6.9 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 4H), 7.22 – 7.16 (m, 1H), 7.03 (d, *J* = 6.7 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.02 (d, *J* = 7.5 Hz, 1H), 4.97 (dd, *J* = 46.8, 9.1 Hz, 1H), 4.37 (dd, *J* = 11.5, 2.3 Hz, 1H), 3.98 (dd, *J* = 11.5, 8.5 Hz, 1H), 3.61 – 3.43 (m, 1H), 2.37 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.7, 135.9 (d, $J_{(C-F)}$= 5.2 Hz), 135.6, 135.4, 134.2, 130.3, 129.9, 129.1, 129.0 (d, $J_{(C-F)}$= 14.2 Hz), 127.5, 126.5, 126.4 (d, $J_{(C-F)}$= 7.6 Hz), 125.9, 123.5, 115.0 (d, $J_{(C-F)}$= 21.6 Hz), 91.0 (d, $J_{(C-F)}$= 152.2 Hz), 52.5 (d, $J_{(C-F)}$= 35.4 Hz), 46.7 (d, $J_{(C-F)}$= 38.6 Hz), 21.4, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.4 (dd, *J* = 46.9, 12.8 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{22}FNO_2SNa$ [M +Na]$^{+}$, 418.1253. Found, 418.1250.

3-(fluoro(m-tolyl)methyl)-1-tosylindoline (5n)

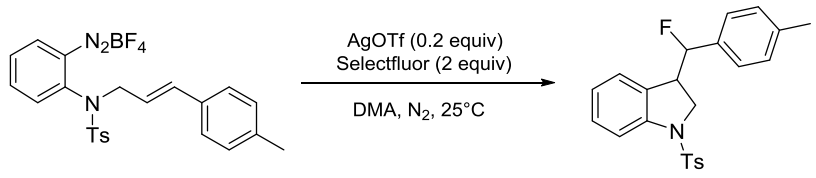
4n **5n** 61% yield (dr=4:1)

To Benzenediazonium 2-[(m-tolyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4n**) (147 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 72.6 mg 3-(fluoro(m-tolyl)methyl)-1-tosylindoline (**5n**) as a colorless solid (61% yield). Further purification by preparative TLC gave the *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 6.7 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.20 (dd, *J* = 15.5, 8.9 Hz, 3H),

6.89 (d, *J* = 13.6 Hz, 1H), 6.83 (t, *J* = 11.0 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 7.4 Hz, 1H), 4.68 (dd, *J* = 47.2, 8.3 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.97 (t, *J* = 10.1 Hz, 1H), 3.60 (d, *J* = 9.5 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 142.8, 138.3, 136.9 (d, $J_{(C-F)}$= 13.7 Hz), 134.1, 130.0, 129.8, 129.4 (d, $J_{(C-F)}$= 8.7 Hz), 129.0, 128.5, 127.6 (d, $J_{(C-F)}$= 6.3 Hz), 127.5, 126.1, 124.1 (d, $J_{(C-F)}$= 5.9 Hz), 123.4, 115.2, 94.7 (d, $J_{(C-F)}$= 148.2 Hz), 52.0 (d, $J_{(C-F)}$= 59.9 Hz), 46.7 (d, $J_{(C-F)}$= 25.7 Hz), 29.8, 21.6 (d, $J_{(C-F)}$= 14.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.9 (dd, *J* = 47.1, 14.2 Hz, 1H). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{22}FNO_2SNa$ $[M+Na]^+$, 418.1253. Found, 418.1253.

3-(fluoro(p-tolyl)methyl)-1-tosylindoline (5o)



4o **5o** 75% yield (dr=4:1)

To Benzenediazonium 2-[(p-tolyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4o**) (147 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 89.4 mg 3-(fluoro(p-tolyl)methyl)-1-tosylindoline (**5o**) as a colorless solid (75% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

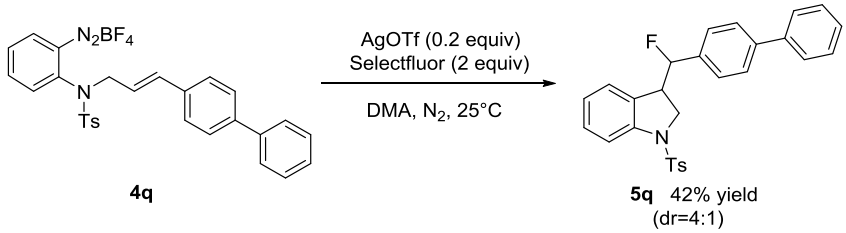
R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 5.4 Hz, 2H), 7.20 (t, *J* = 6.6 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.96 (d, *J* = 7.3 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.18 (d, *J* = 7.7 Hz, 1H), 4.64 (dd, *J* = 47.0, 8.6 Hz, 1H), 4.27 – 4.14 (m, 1H), 3.98 (dd, *J* = 11.4, 8.9 Hz, 1H), 3.65 – 3.52 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.3, 134.2 (d, $J_{(C-F)}$= 13.8 Hz), 134.0, 129.8, 129.5 (d, $J_{(C-F)}$= 8.8 Hz), 129.3, 129.0, 127.5, 127.3 (d, $J_{(C-F)}$= 7.8 Hz), 127.1, 126.2, 123.4, 115.3, 94.6 (d, $J_{(C-F)}$= 147.1 Hz), 52.1 (d, $J_{(C-F)}$= 80.7 Hz), 46.6 (d, $J_{(C-F)}$= 34.8 Hz), 21.6, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.8 (dd, *J* = 40.8, 20.6 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{22}FNO_2SNa$ $[M+Na]^+$, 418.1253. Found, 418.1250.

3-(fluoro(4-(trifluoromethyl)phenyl)methyl)-1-tosylindoline (5p)

To Benzenediazonium 2-[4-(trifluoromethyl)phenyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4p**) (164 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 77.0 mg 3-(fluoro(4-(trifluoromethyl)phenyl)methyl)-1-tosylindoline (**5p**) as a colorless solid (57% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 3H), 7.19 (d, *J* = 7.5 Hz, 2H), 6.81 (t, *J* = 6.2 Hz, 1H), 6.24 (d, *J* = 7.0 Hz, 1H), 4.85 (dd, *J* = 46.8, 7.7 Hz, 1H), 4.22 (d, *J* = 11.2 Hz, 1H), 3.92 (t, *J* = 9.8 Hz, 1H), 3.59 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 142.8, 140.8, 133.8, 129.8 (d, $J_{(C-F)}$= 10.4 Hz), 129.3, 128.5 (m, $J_{(C-F)}$= 15.7 Hz), 127.5, 127.4 (d, $J_{(C-F)}$= 3.1 Hz), 127.2, 126.9 125.9, 125.5 (m, $J_{(C-F)}$=216.3 Hz), 123.5, 115.2 (d, $J_{(C-F)}$= 9.7 Hz), 93.5 (d, $J_{(C-F)}$= 134.2 Hz), 52.0 (d, $J_{(C-F)}$= 3.3 Hz), 46.7 (d, $J_{(C-F)}$= 22.7 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 (m, 3F), -175.6 (dd, *J* = 46.6, 14.5 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{23}H_{19}F_4NO_2SNa$ $[M+Na]^+$, 472.0970. Found, 472.0968.

3-([1,1'-biphenyl]-4-ylfluoromethyl)-1-tosylindoline (5q)

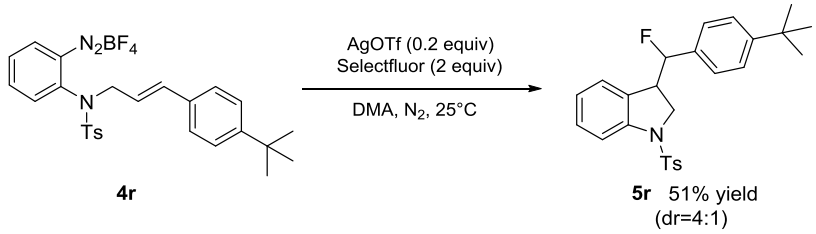


To Benzenediazonium 2-[([1,1'-biphenyl]-4-yl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4q**) (166 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-

fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 58.0 mg 3-([1,1'-biphenyl]-4-ylfluoromethyl)-1-tosylindoline (**5q**) as a colorless solid (42% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.59 (dd, *J* = 8.0 Hz, 4H), 7.44 (dd, *J* = 14.0, 6.6 Hz, 2H), 7.37 (d, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 7.3 Hz, 1H), 4.75 (dd, *J* = 46.9, 8.2 Hz, 1H), 4.22 (t, *J* = 14.9 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.61 (d, *J* = 30.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.8, 142.3, 140.3, 135.9 (d, $J_{(C-F)}$= 14.6 Hz), 134.1 (d, $J_{(C-F)}$= 9.5 Hz), 129.8, 129.1, 129.0, 127.8, 127.6, 127.5 (d, $J_{(C-F)}$= 4.7 Hz), 127.5, 127.3, 127.2, 126.2, 123.5, 115.3, 94.5 (d, $J_{(C-F)}$= 182.6 Hz), 52.1 (d, $J_{(C-F)}$= 46.9 Hz), 46.6 (d, $J_{(C-F)}$= 29.3 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.5 (dd, *J* = 40.6, 20.2 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{28}H_{24}FNO_2SNa$ $[M+Na]^+$, 480.1409. Found, 480.1408.

3-((4-(tert-butyl)phenyl)fluoromethyl)-1-tosylindoline (5r)



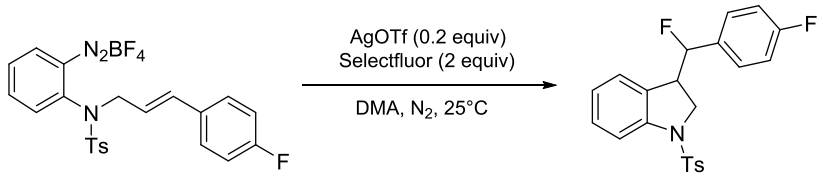
4r **5r** 51% yield (dr=4:1)

To Benzenediazonium 2-[4-(tert-butyl)phenyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4r**) (160 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 67.0 mg 3-((4-(tert-butyl)phenyl)fluoromethyl)-1-tosylindoline (**5r**) as a colorless solid (51% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 9.6 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.77 (t, *J* = 6.9 Hz, 1H), 6.22 (d, *J* = 7.1 Hz, 1H),

4.70 (dd, *J* = 47.0, 7.9 Hz, 1H), 4.18 (t, *J* = 12.8 Hz, 1H), 3.98 (t, *J* = 10.0 Hz, 1H), 3.60 (d, *J* = 6.0 Hz, 1H), 2.38 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 143.2, 134.1, 131.7, 129.8(d, $J_{(C-F)}$= 15.8 Hz), 129.6, 129.0, 127.5(d, $J_{(C-F)}$= 7.8 Hz), 127.0, 126.7 (d, $J_{(C-F)}$= 5.8 Hz), 126.0, 125.6, 123.4, 115.2, 94.4 (d, $J_{(C-F)}$= 142.5 Hz), 52.0 (d, $J_{(C-F)}$= 57.8 Hz), 46.5 (d, $J_{(C-F)}$= 28.1 Hz), 34.2, 31.4, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.6 (dd, *J* = 47.1, 14.3 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{26}H_{28}FNO_2SNa$ $[M+Na]^+$, 460.1722. Found, 460.1720.

3-(fluoro(4-fluorophenyl)methyl)-1-tosylindoline (5s)

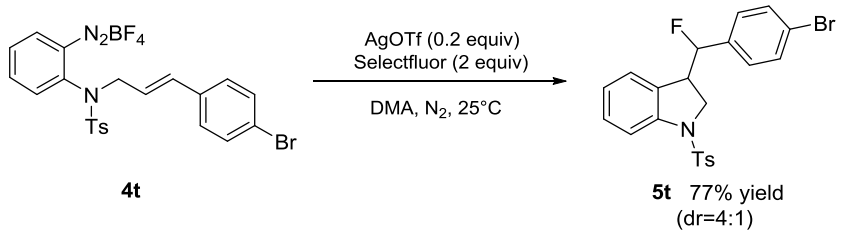


4s **5s** 77% yield (dr=3:1)

To Benzenediazonium 2-[(4-fluorophenyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4s**) (149 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA(2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 92.0 mg 3-(fluoro(4-fluorophenyl)methyl)-1-tosylindoline (**5s**) as a colorless solid (77% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 5.9 Hz, 1H), 7.04 (s, 2H), 7.02 (s, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 7.6 Hz, 1H), 4.68 (dd, *J* = 46.6, 8.7 Hz, 1H), 4.21 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.96 (dd, *J* = 11.4, 8.8 Hz, 1H), 3.57 (ddd, *J* = 18.1, 8.9, 4.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3 (d, $J_{(C-F)}$= 25.1 Hz), 142.5, 134.1, 129.8 (d, $J_{(C-F)}$= 7.2 Hz), 129.2, 129.0, 128.5 (d, $J_{(C-F)}$= 14.6 Hz), 127.5, 127.4, 126.7 (d, $J_{(C-F)}$= 9.2 Hz), 126.2, 123.8, 123.4, 115.9 (d, $J_{(C-F)}$= 24.8 Hz), 115.3, 114.8, 93.8 (d, $J_{(C-F)}$= 116.9 Hz), 52.3 (d, $J_{(C-F)}$= 18.4 Hz), 46.6 (d, $J_{(C-F)}$= 53.2 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8 (m, 1F), -169.5 (dd, *J* = 46.7, 12.0 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{19}F_2NO_2SNa$ $[M+Na]^+$, 422.1002. Found, 422.0999.

3-((4-bromophenyl)fluoromethyl)-1-tosylindoline (5t)

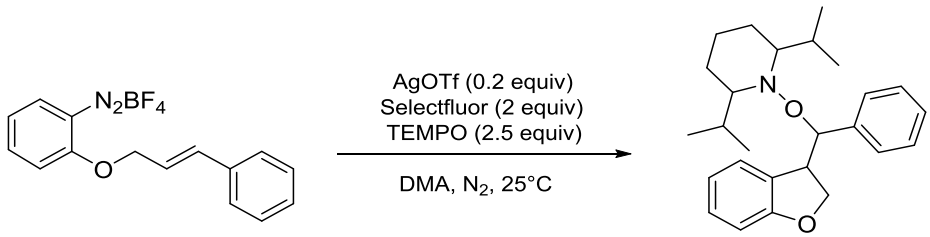


4t **5t** 77% yield (dr=4:1)

To Benzenediazonium 2-[(4-bromophenyl)allyl[(4-methylphenyl)sulfonyl]amino]-tetrafluoroborate (**4t**) (167 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20 hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 20:1 (v/v), to afford 106 mg 3-((4-bromophenyl)fluoromethyl)-1-tosylindoline (**5t**) as a colorless solid (77% yield). Further purification by preparative TLC gave the main *trans*-isomer for collecting data.

R_f = 0.40 (hexanes/EtOAc 15:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.26 (d, *J* = 7.4 Hz, 1H), 4.72 (dd, *J* = 46.7, 8.3 Hz, 1H), 4.21 (d, *J* = 11.4 Hz, 1H), 3.95 (t, *J* = 10.9, 9.2 Hz, 1H), 3.63 – 3.50 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 142.8, 135.9 (d, $J_{(C-F)}$= 16.0 Hz), 134.0, 131.8, 129.8, 129.3, 128.7, 128.6 (d, $J_{(C-F)}$= 6.0 Hz), 128.3 (d, $J_{(C-F)}$= 7.6 Hz), 127.5, 126.1, 123.5, 115.2, 93.9 (d, $J_{(C-F)}$= 177.0 Hz), 52.1 (d, $J_{(C-F)}$= 34.6 Hz), 46.5 (d, $J_{(C-F)}$= 25.1 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.2 (dd, *J* = 46.7, 13.7 Hz, 1F). Mass Spectrometry: HRMS-ESI (m/z): Calcd for $C_{22}H_{19}BrFNO_2SNa$ $[M+Na]^+$, 482.0202. Found, 482.0198.

The mechanism study



4a **5** 56% yield (dr=3:1)

To 2-cinnamyloxybenzenediazonium tetrafluoroborate (**4a**) (97.2 mg, 0.300 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (15.3 mg, 0.060 mmol, 0.200 equiv) were added anhydrous DMA (2.00 mL), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (212 mg, 0.600 mmol, 2.00 equiv). The reaction mixture was stirred for 20

hrs at 25 ^{o}C in a sealed vial. The reaction was diluted with H_2O (30.0 mL) and extracted 2 times with EtOAc (10.0 mL). The combined organic layer was dried over $MgSO_4$. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 100:1 (v/v), to afford the desire product (**5**) as a colorless oil (56% yield).

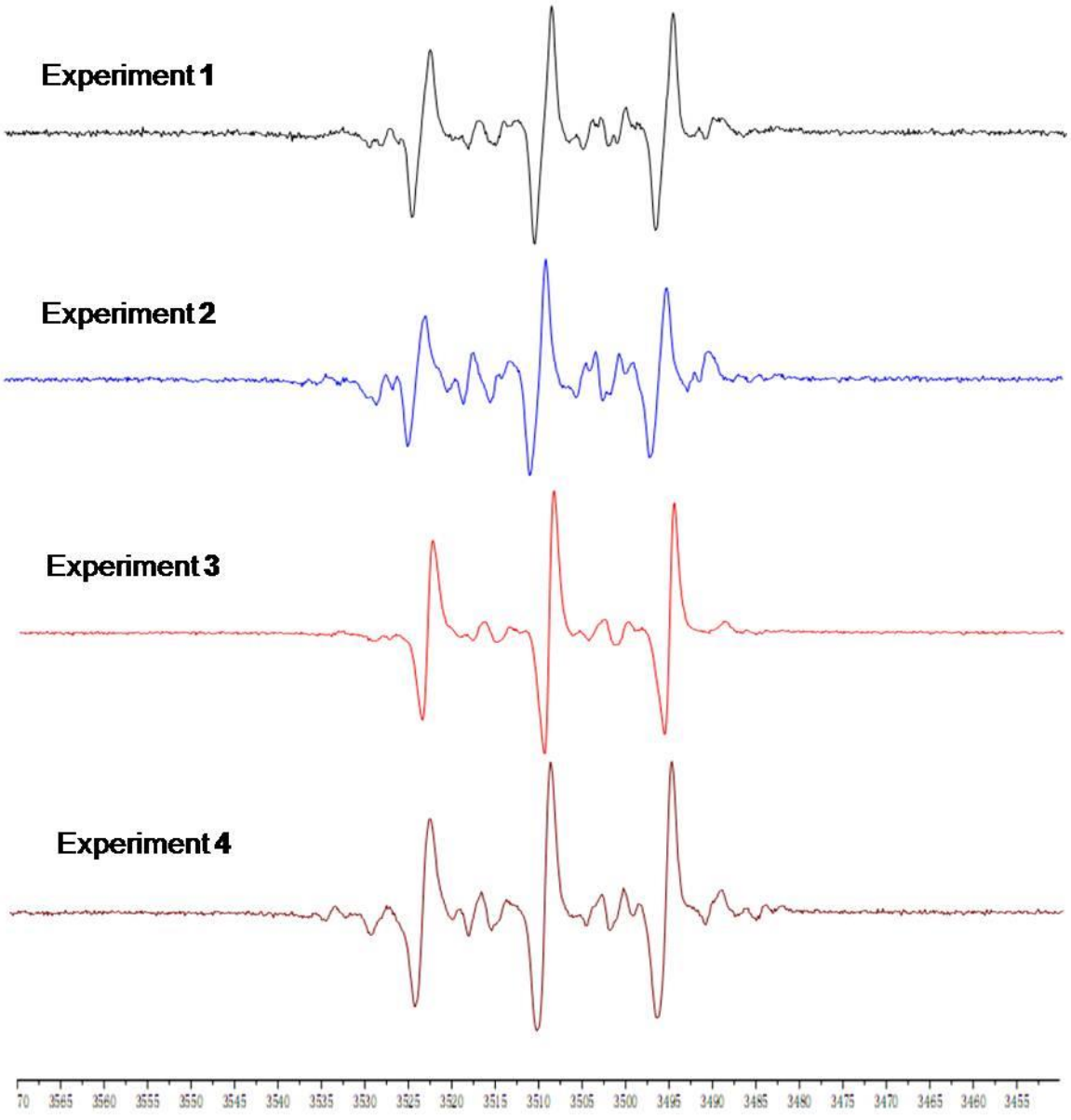
R_f = 0.40 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.4 Hz, 3H), 7.10 (d, *J* = 6.2 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.1 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 1H), 4.60 (d, *J* = 7.2 Hz, 2H), 4.35 – 4.16 (m, 1H), 1.46 (d, *J* = 11.9 Hz, 3H), 1.36 (d, *J* = 27.8 Hz, 4H), 1.29 (s, 7H), 1.01 (s, 4H), 0.88 (s, 1H), 0.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 139.2, 129.9, 128.5, 127.9, 127.5, 127.2, 126.4, 119.8, 109.3, 87.6, 73.7, 60.6, 46.1, 40.5, 34.0, 20.3, 17.1.

The EPR study

To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (12.6 mg, 0.0600 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (3.10 mg, 0.0120 mmol, 0.200 equiv) were added anhydrous DMA (0.240 mL) and 4-fluorostyrene (**2**) (35.8 μL, 0.300 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (42.3 mg, 0.120 mmol, 2. 00 equiv). The reaction mixture was stirred for 0.5 hr in a sealed vial. Then the reation system was added into the DMA solution of DMPO and detected by EPR spectrometer. The detial of reations are reported in Table S9.

Table S9: The EPR study on the reaction

Experiment Number	Reaction condition
1	Without **1** and **2**
2	Without **1**
3	Without **2**
4	With **1** and **2**



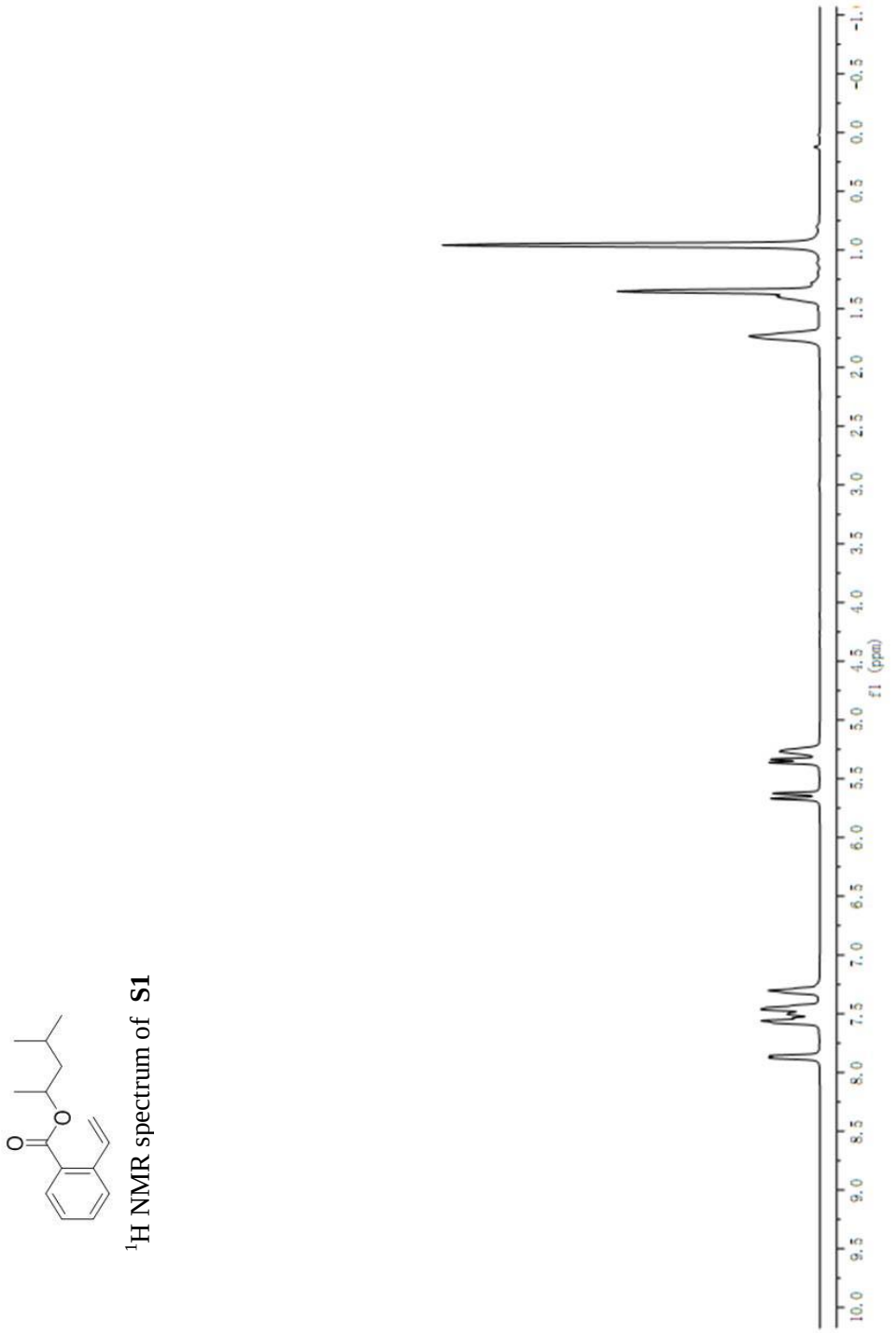
The result of EPR

Typical spectrometer parameters were: Receiver Gain = 2.00*105; Phase = 0 deg; Harmonic= 1; Mod. Frequency = 100 kHz; Mod. Amplitude = 1G; Center Field = 3510; Sweep width = 120; Resolution = 1024; Conversion = 163.84 ms; Time const = 40.96 m; Sweep time = 167.77s; power= 1 mw. DMPO (5,5-dimethyl-1-pyrroline N-oxide) was employed as the radical trapper.

Gram-scale synthesis of 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (3k)

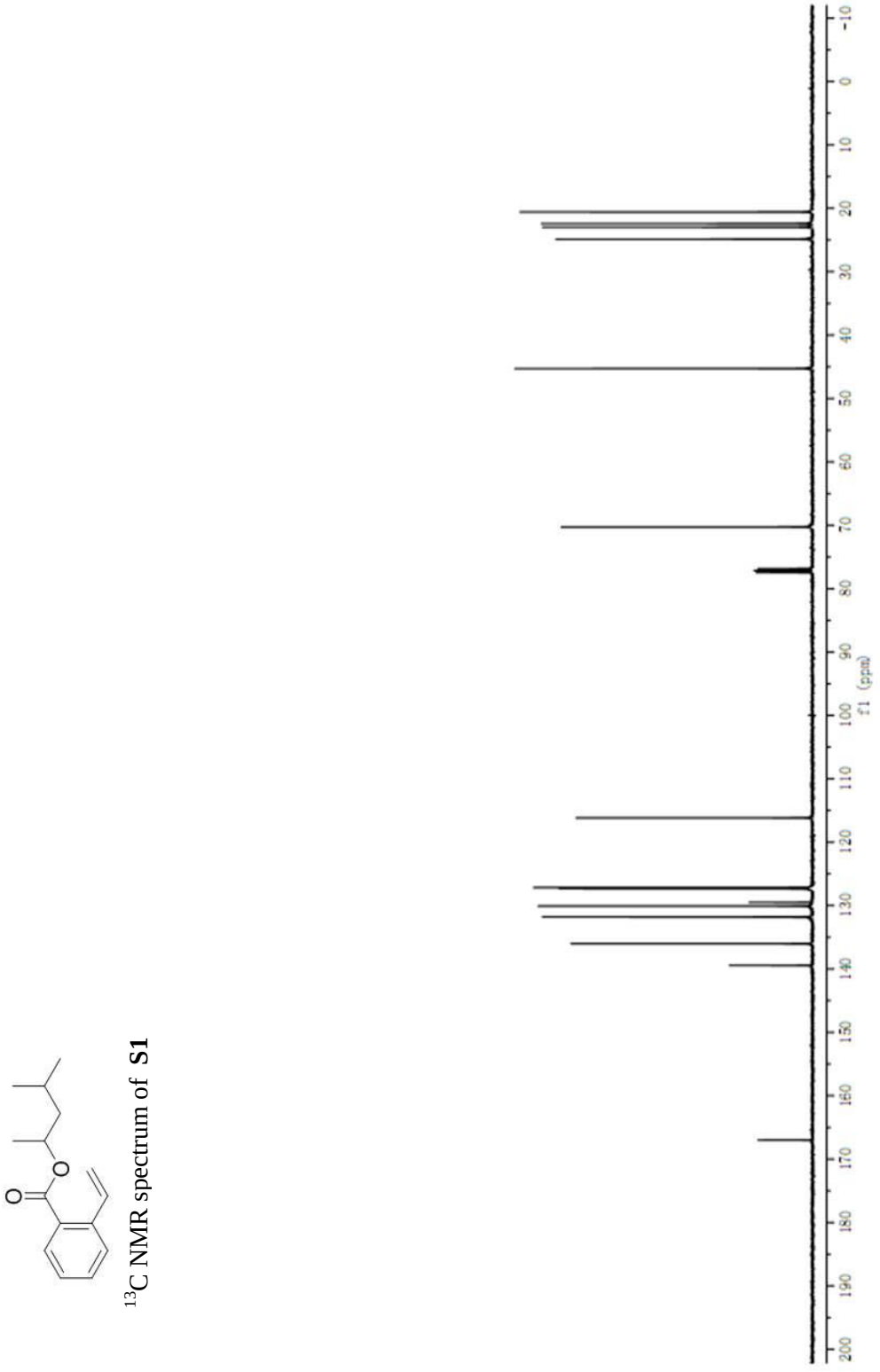
To 4-fluorobenzenediazonium tetrafluoroborate (**1**) (1.00 g, 4.76 mmol, 1.00 equiv) and silver trifluoromethanesulfonate (0.244 g, 0.952 mmol, 0.200 equiv) were added anhydrous DMA (19.0 mL) and 4-fluorostyrene (**2**) (2.84 mL, 23.8 mmol, 5.00 equiv), then followed by 4-fluoro-1-chloromethyl-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (3.37 g, 9.52 mmol, 2.00 equiv). The reaction mixture was stirred for 12 hr at 25 ^{o}C in a sealed vial. The reaction was washed with H_2O (100 mL) and extracted 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 hexanes/EtOAc 100:1 (v/v), to afford 692 mg 4,4'-(1-fluoroethane-1,2-diyl)bis(fluorobenzene) (**3k**) as a colorless solid (62% yield).

Spectroscopic Data



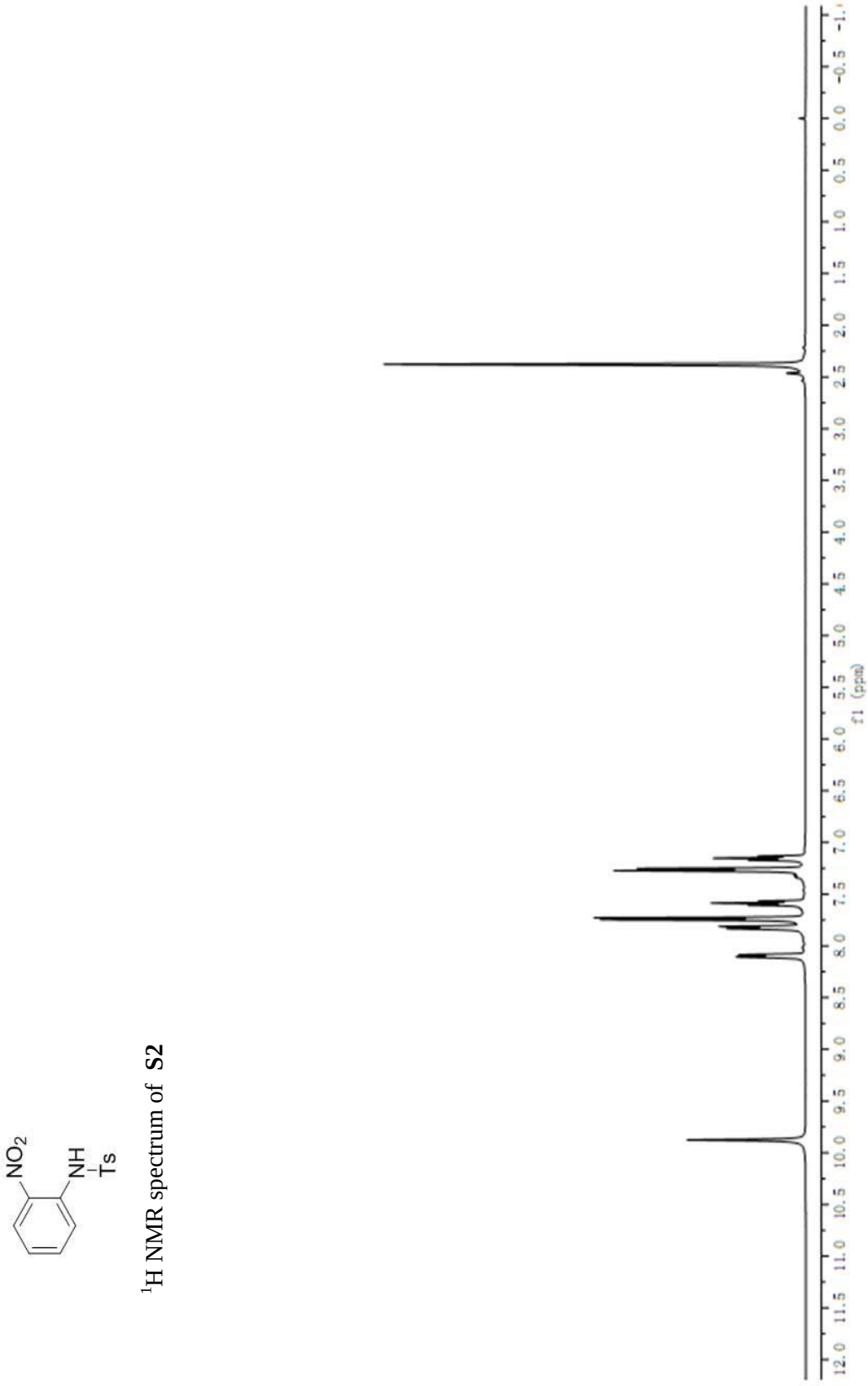
^{1}H NMR spectrum of **S1**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S1**



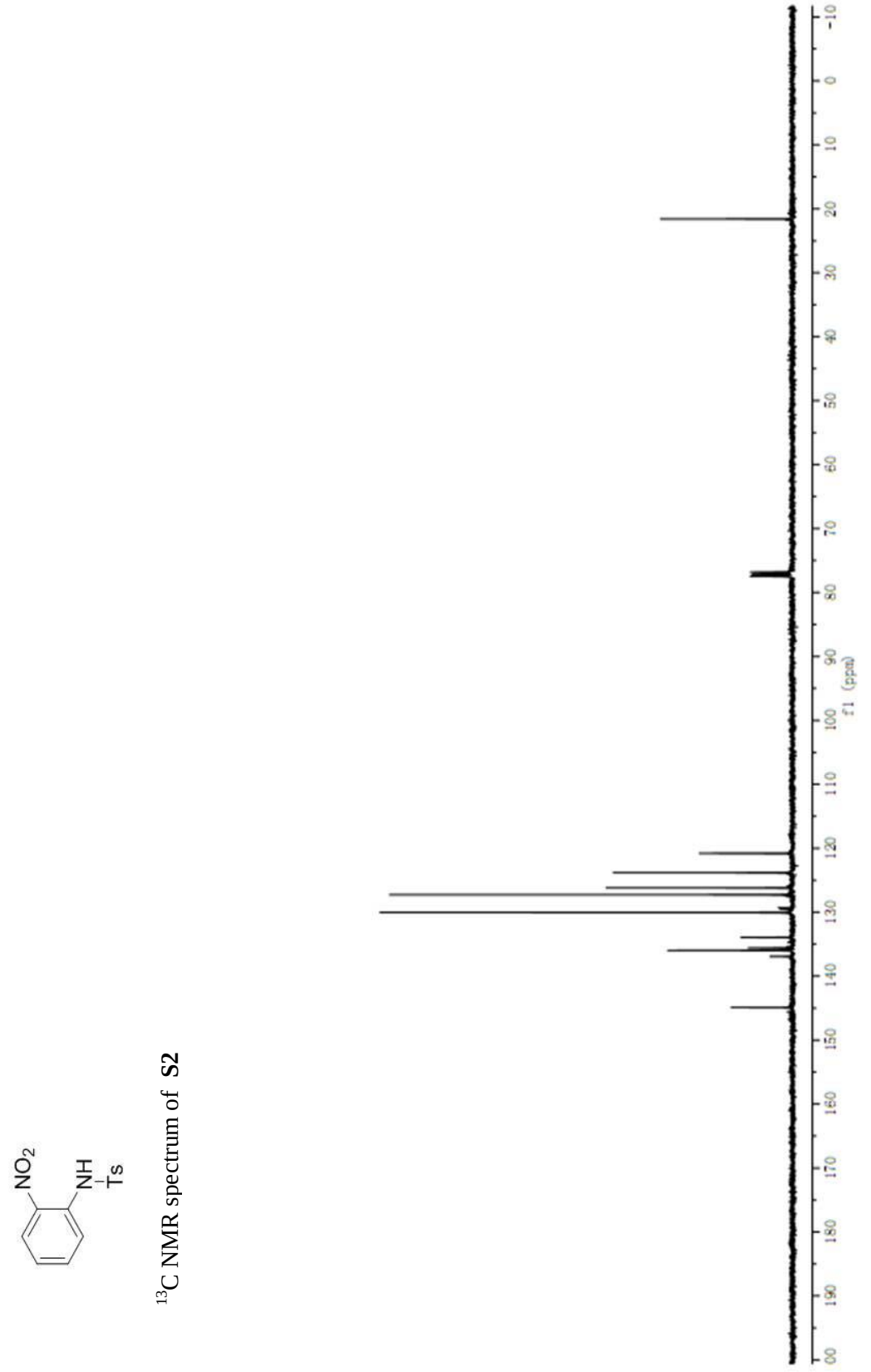
^{13}C NMR spectrum of **S1**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S1**



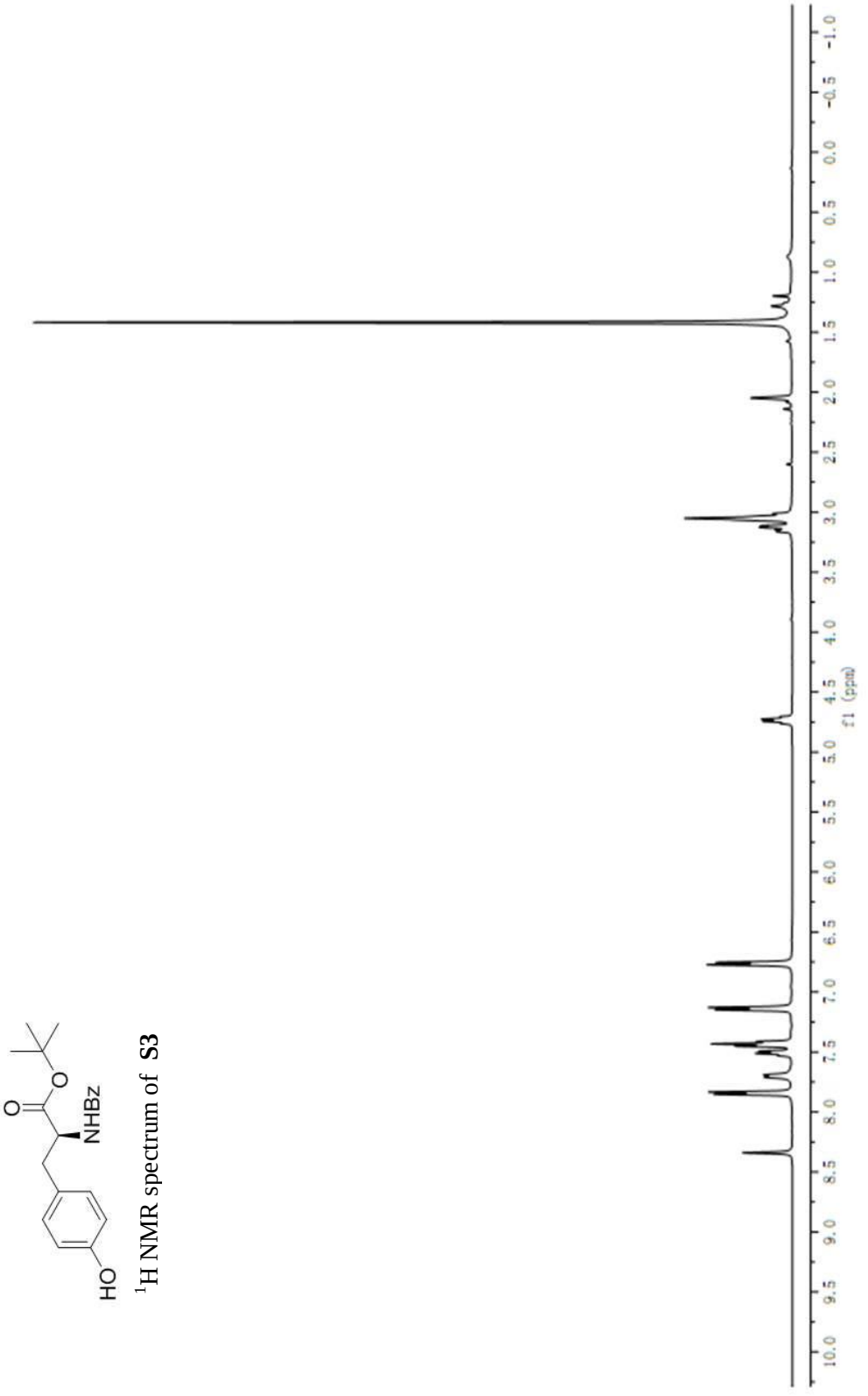
^{1}H NMR spectrum of **S2**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S2**



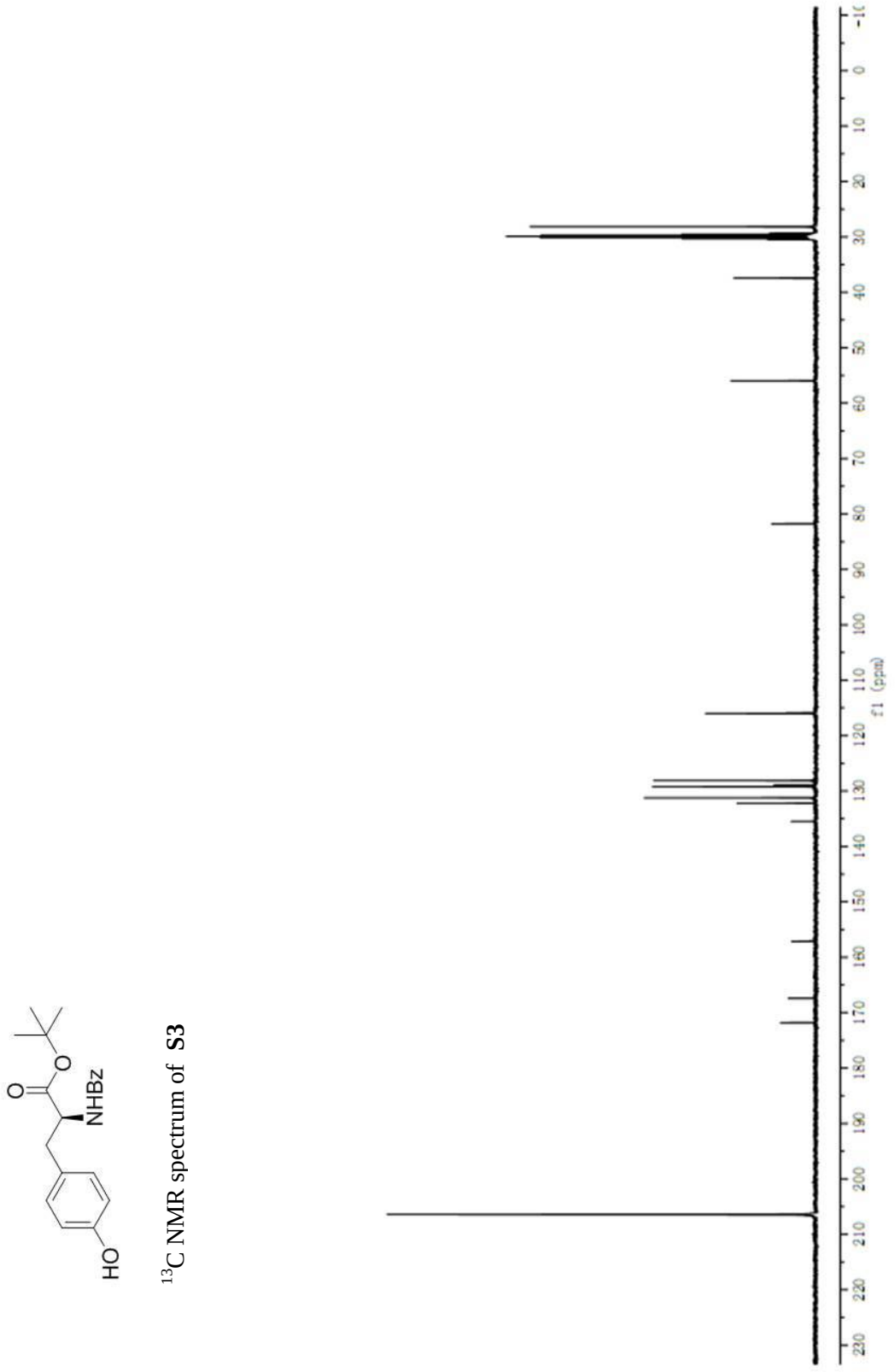
^{13}C NMR spectrum of **S2**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S2**



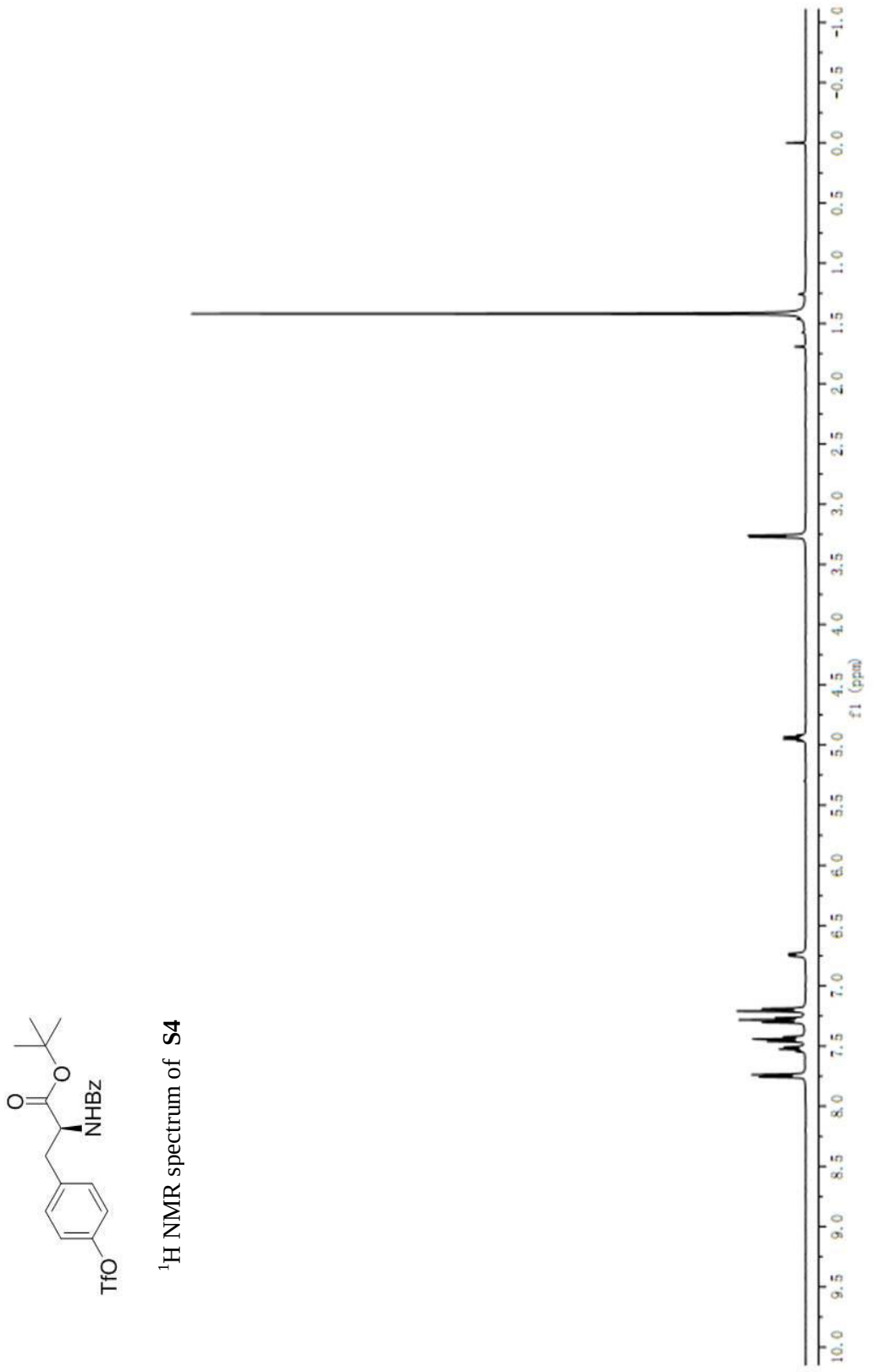
^{1}H NMR spectrum of **S3**

^{1}H NMR spectrum (400 MHz, Acetone-d^6, 23 ℃) of **S3**



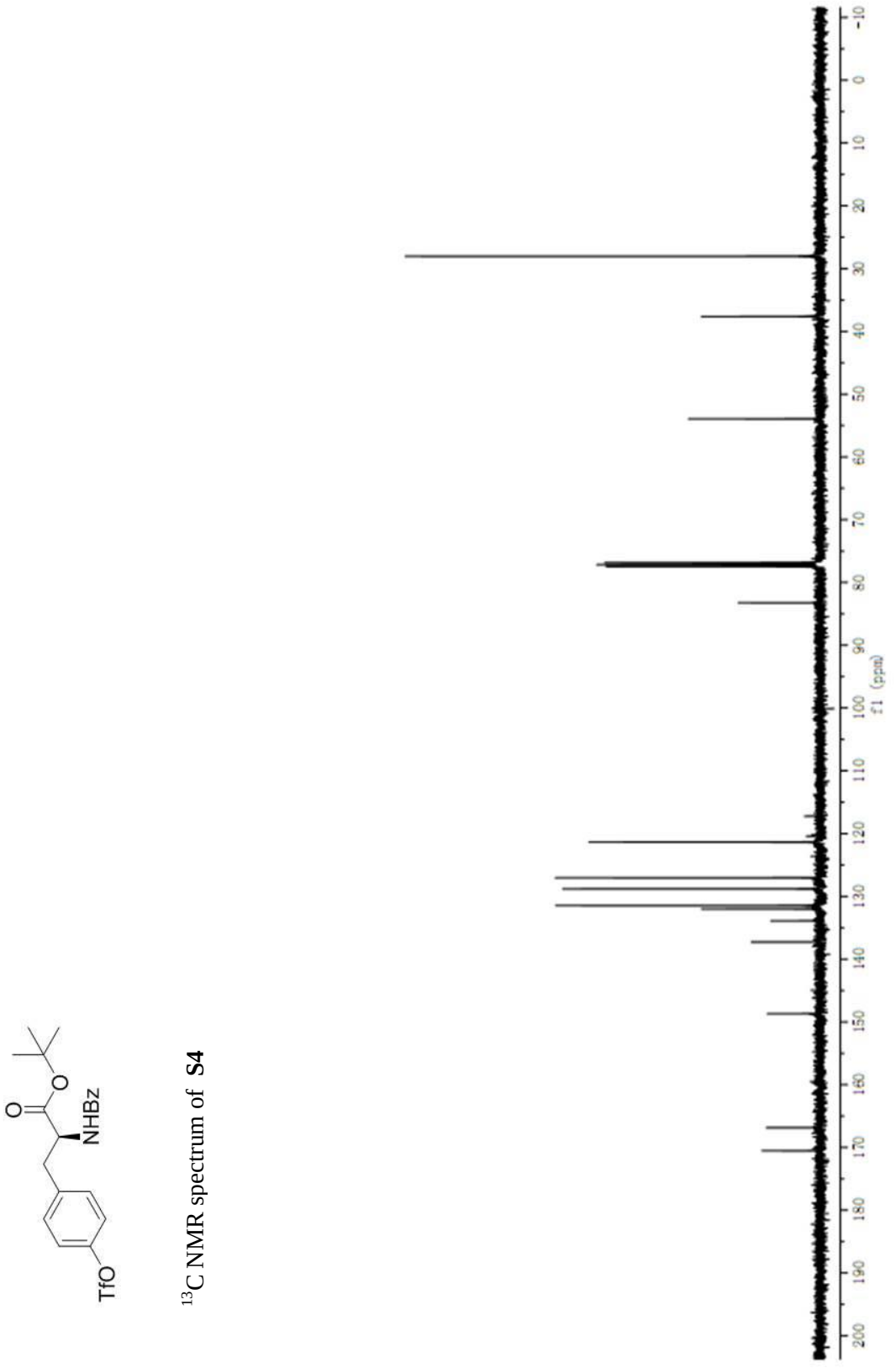
^{13}C NMR spectrum of **S3**

^{13}C NMR spectrum (101 MHz, Acetone-d^{6}, 23 ℃) of **S3**



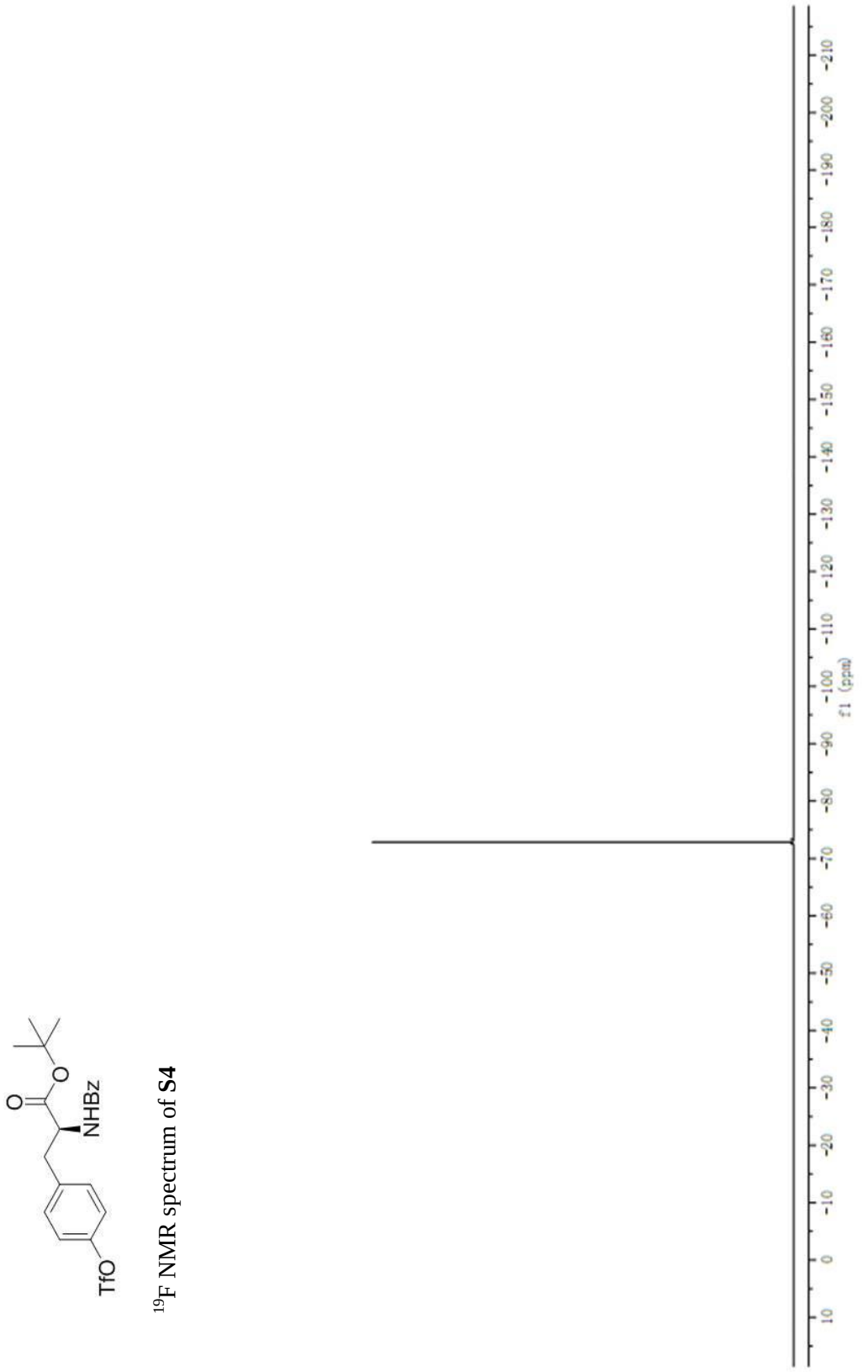
^{1}H NMR spectrum of **S4**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S4**



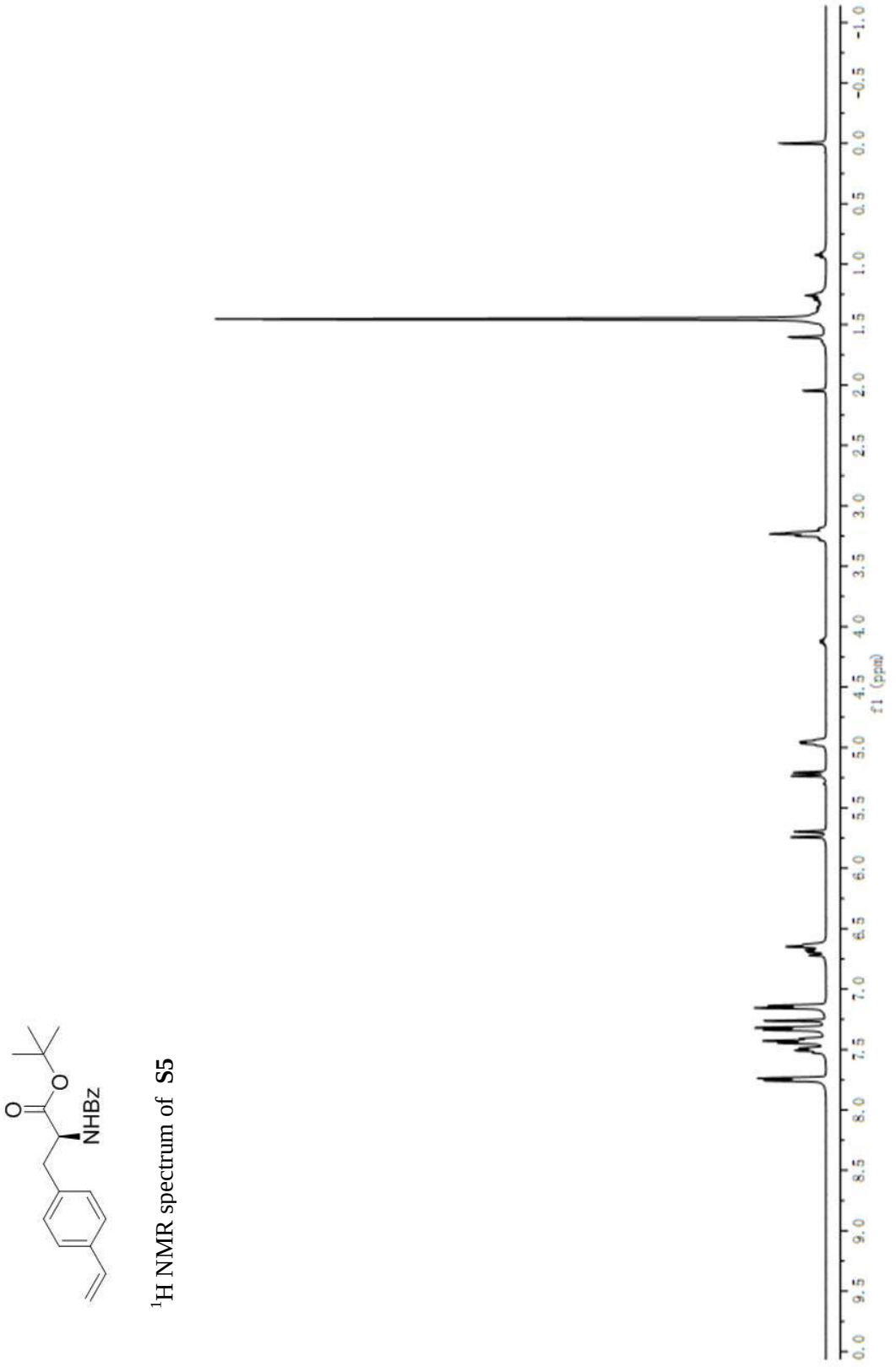
^{13}C NMR spectrum of **S4**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S4**



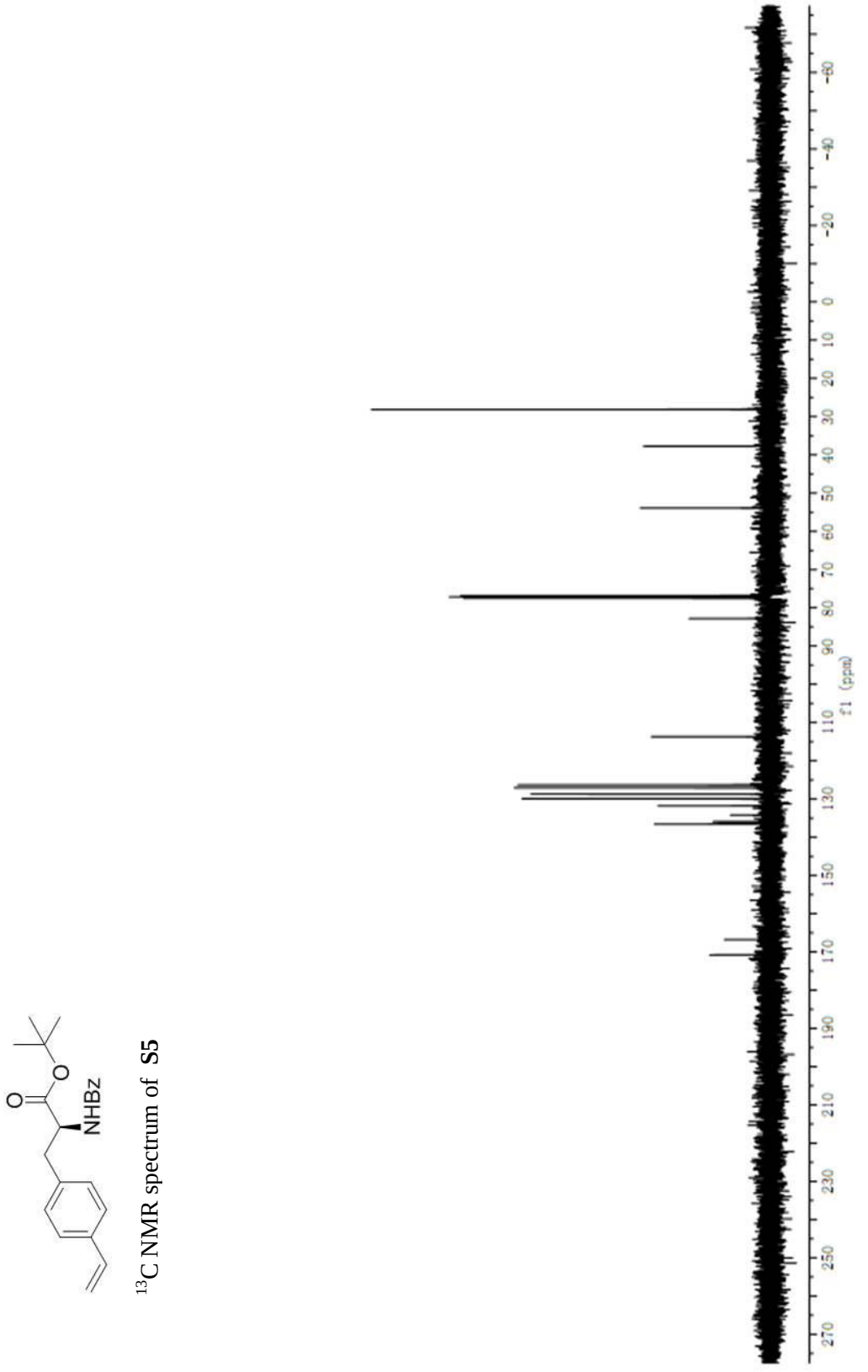
^{19}F NMR spectrum of **S4**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S4**



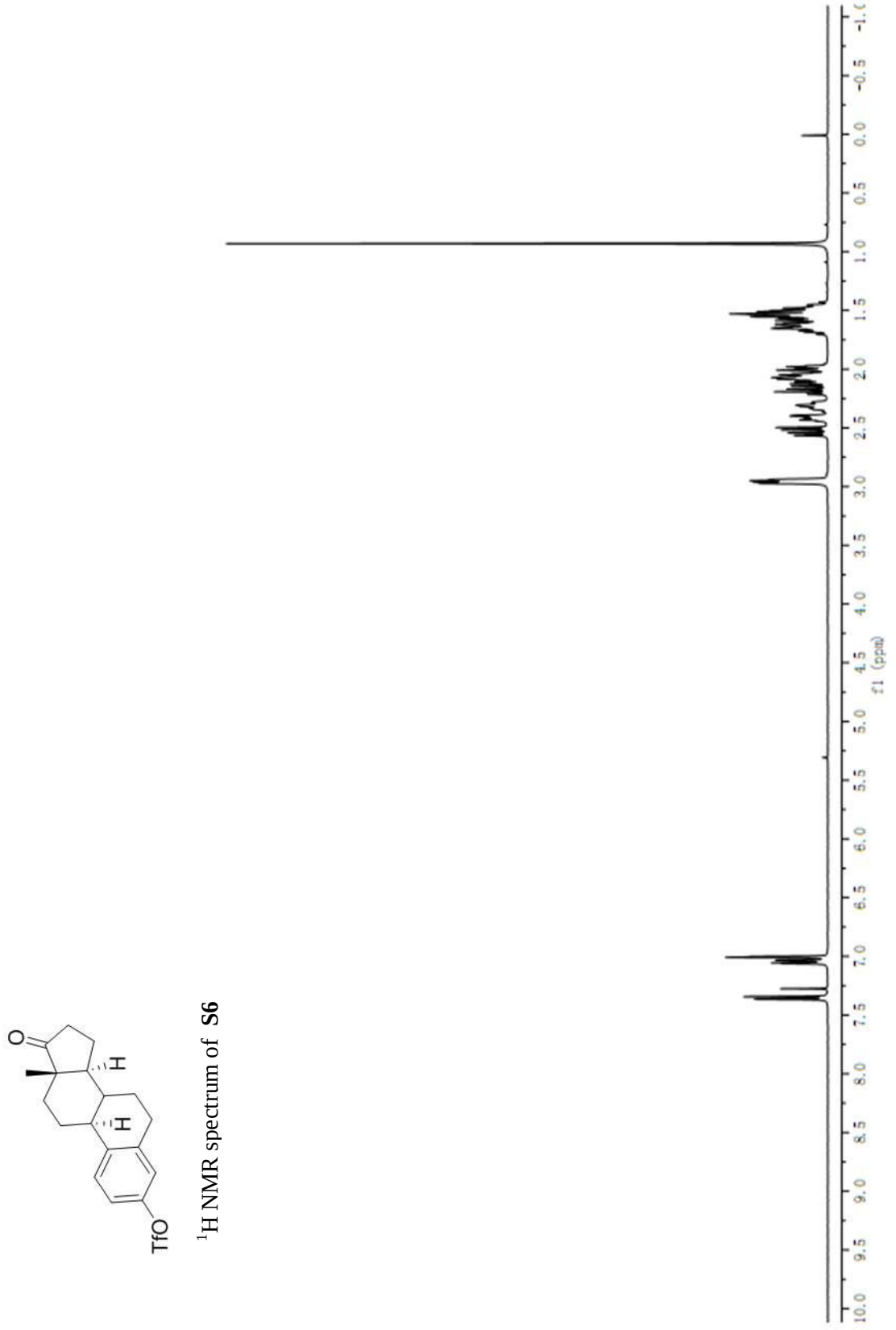
^{1}H NMR spectrum of **S5**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S5**



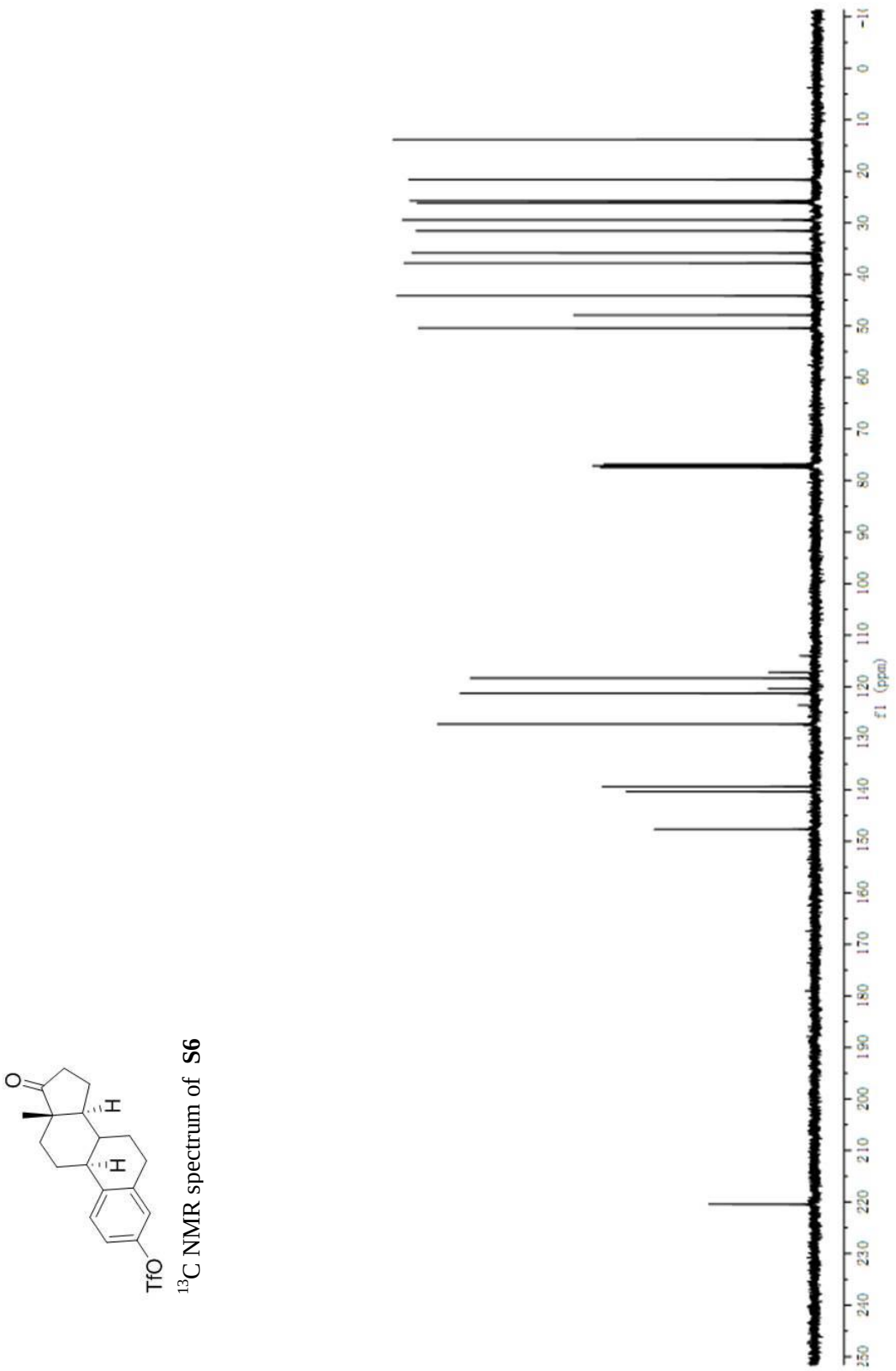
^{13}C NMR spectrum of **S5**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S5**



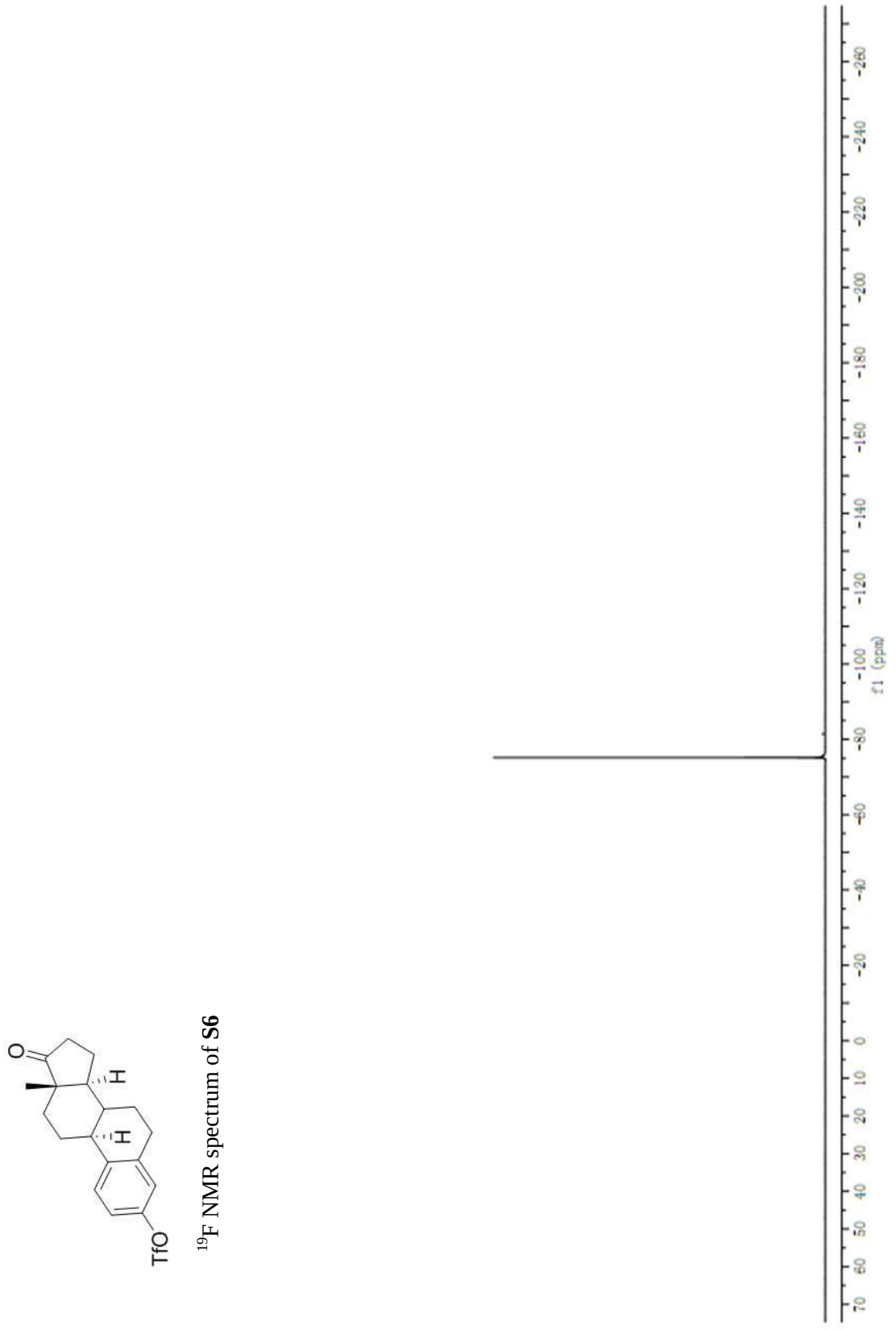
^{1}H NMR spectrum of **S6**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S6**



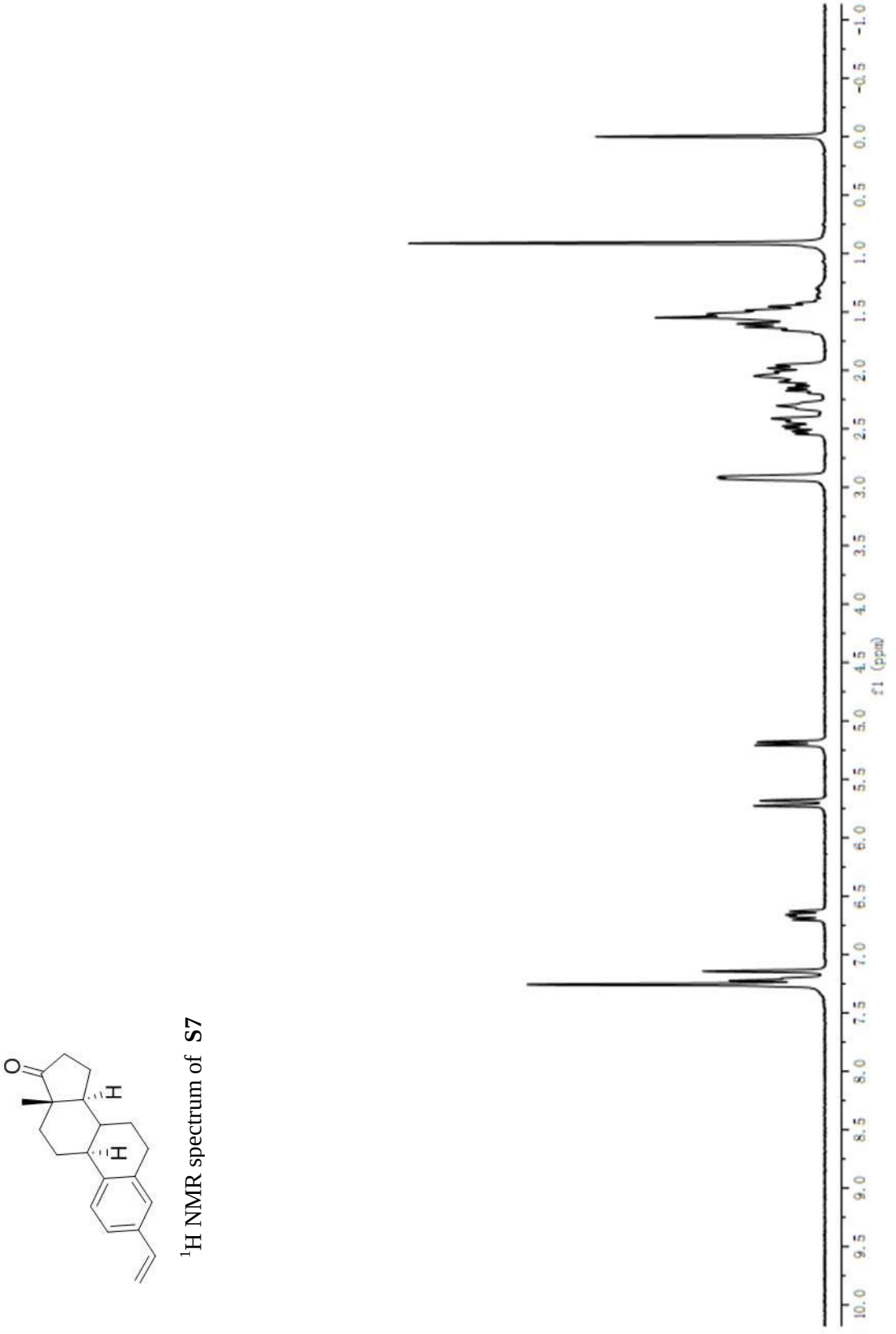
^{13}C NMR spectrum of **S6**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S6**



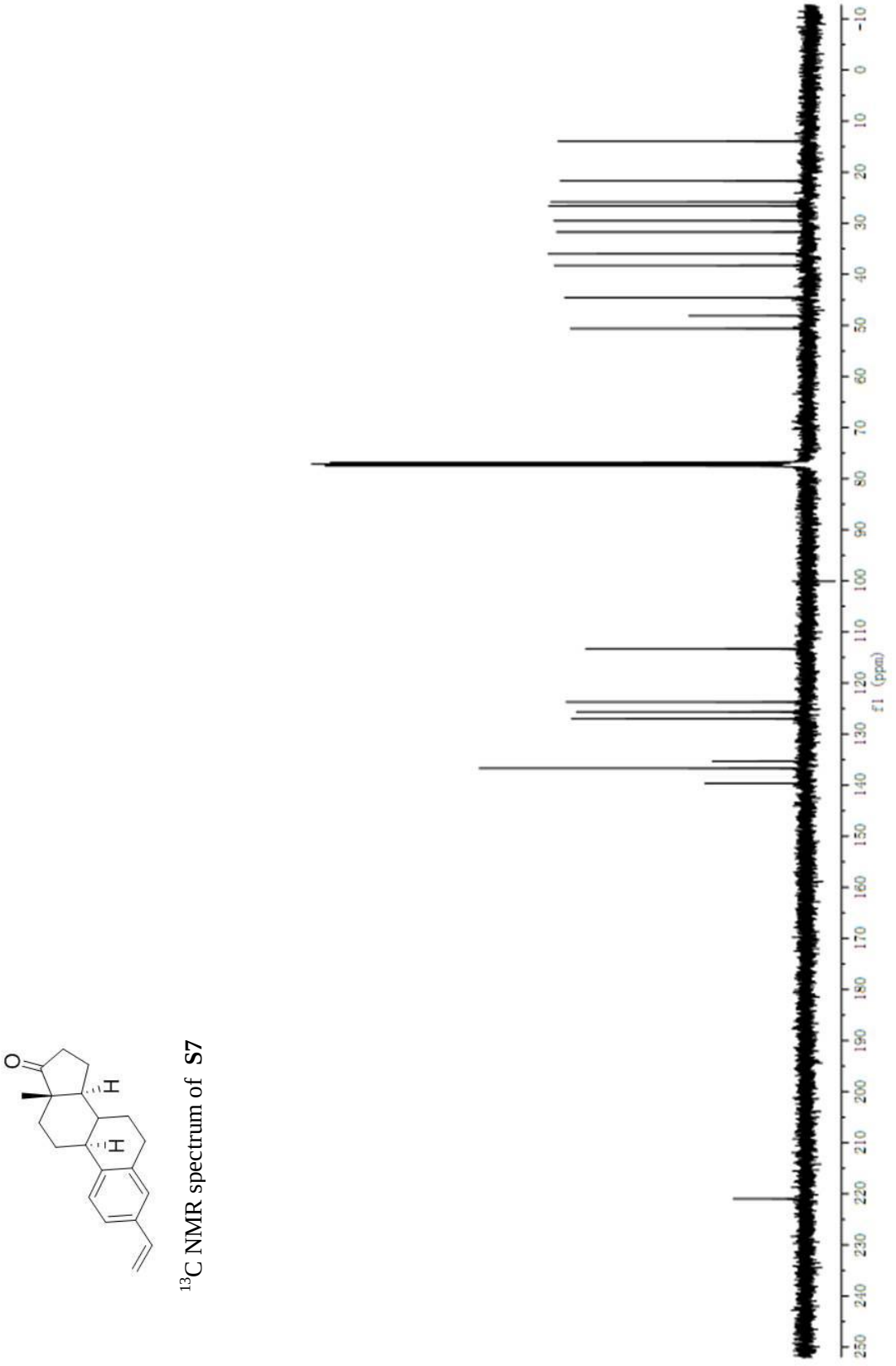
^{19}F NMR spectrum of **S6**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S6**



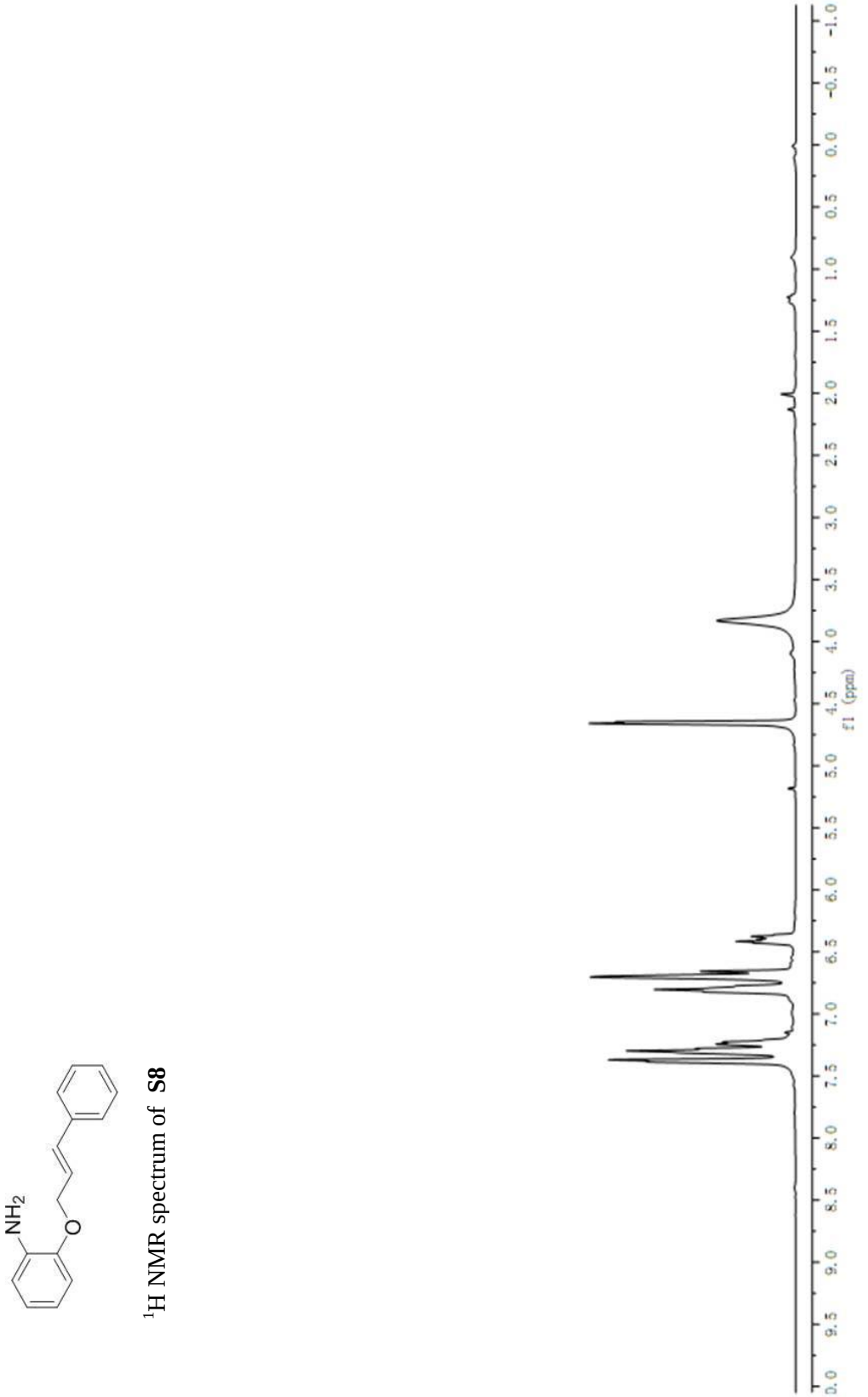
^{1}H NMR spectrum of **S7**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S7**



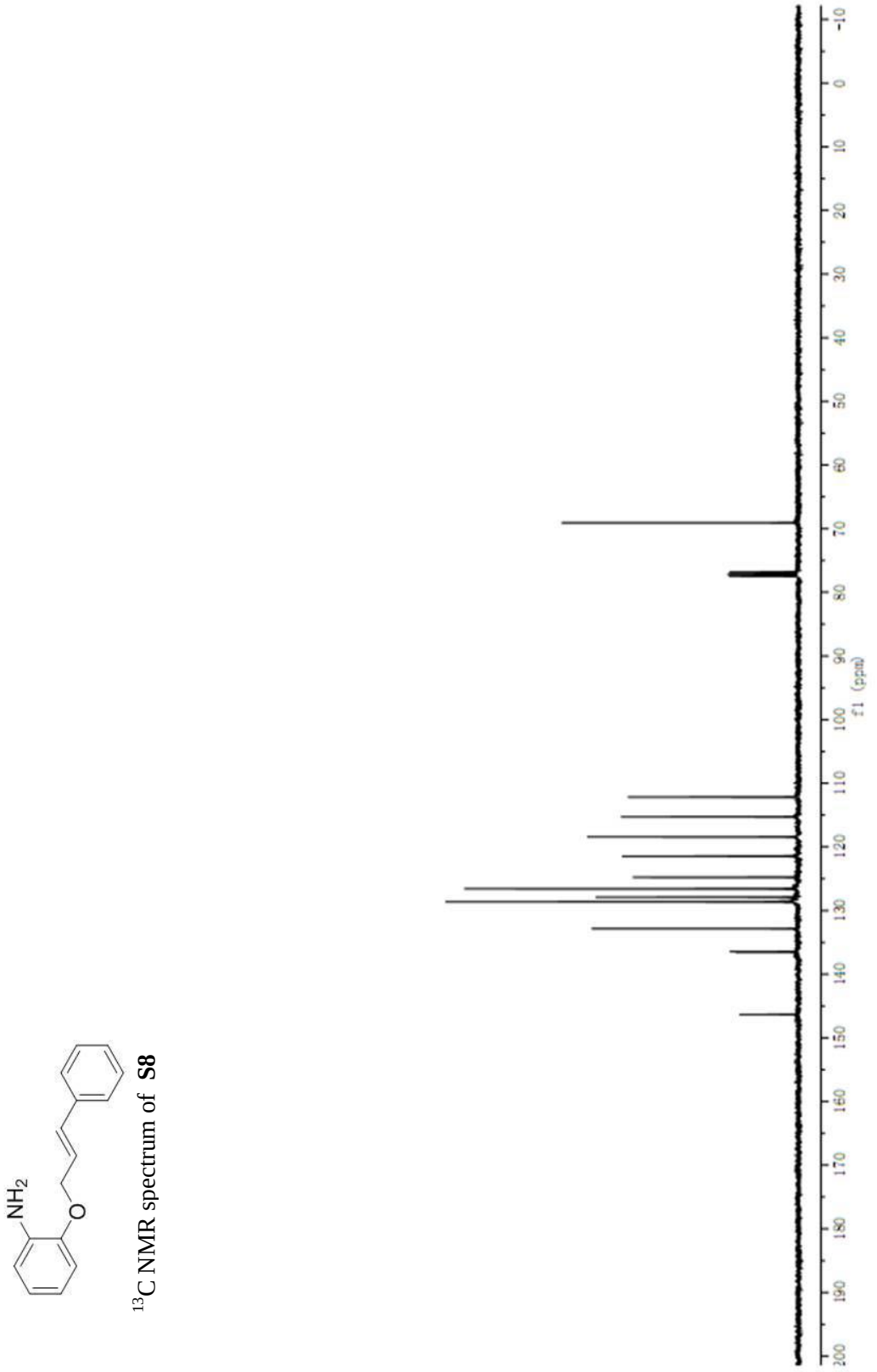
^{13}C NMR spectrum of **S7**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S7**



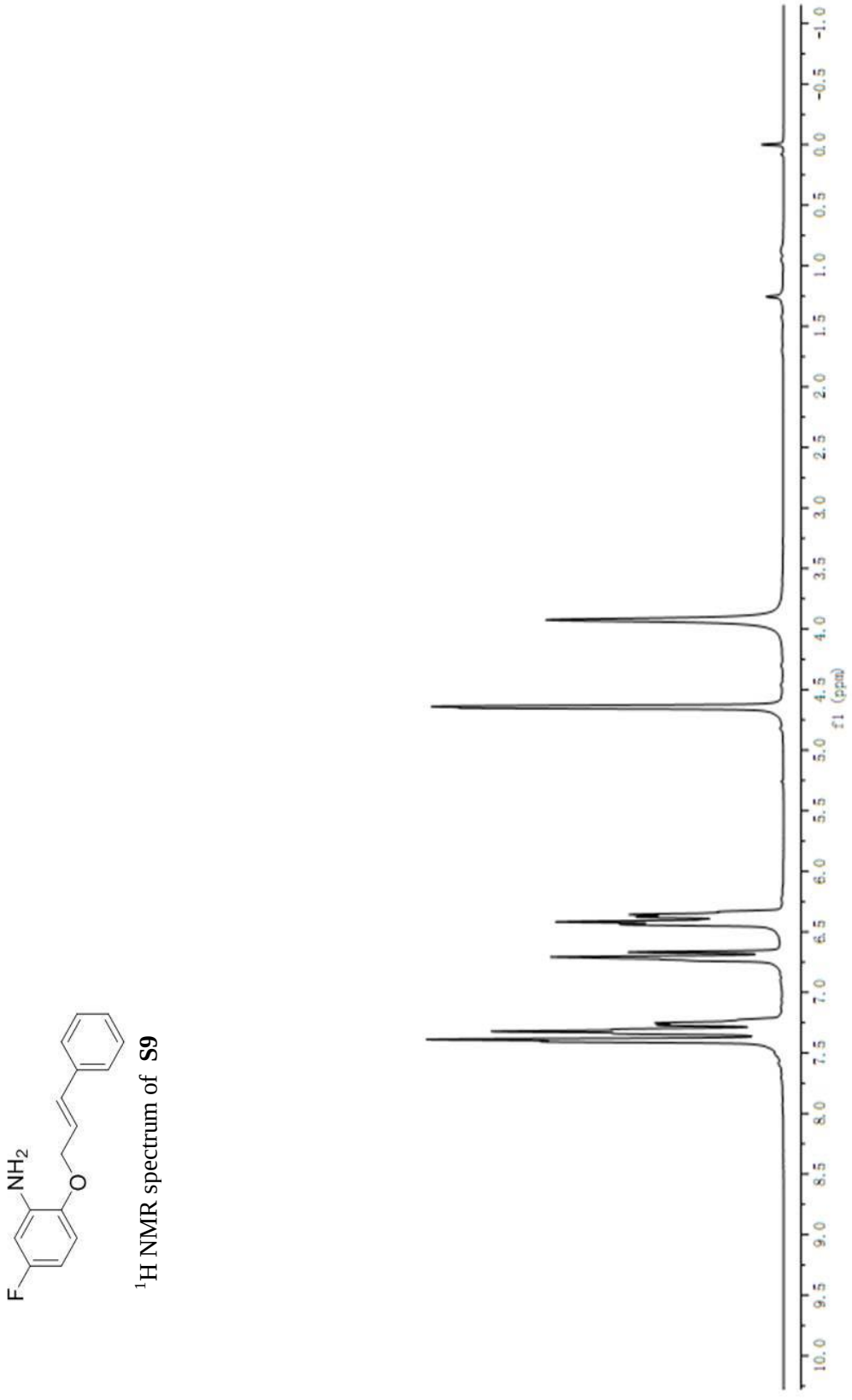
^{1}H NMR spectrum of **S8**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S8**



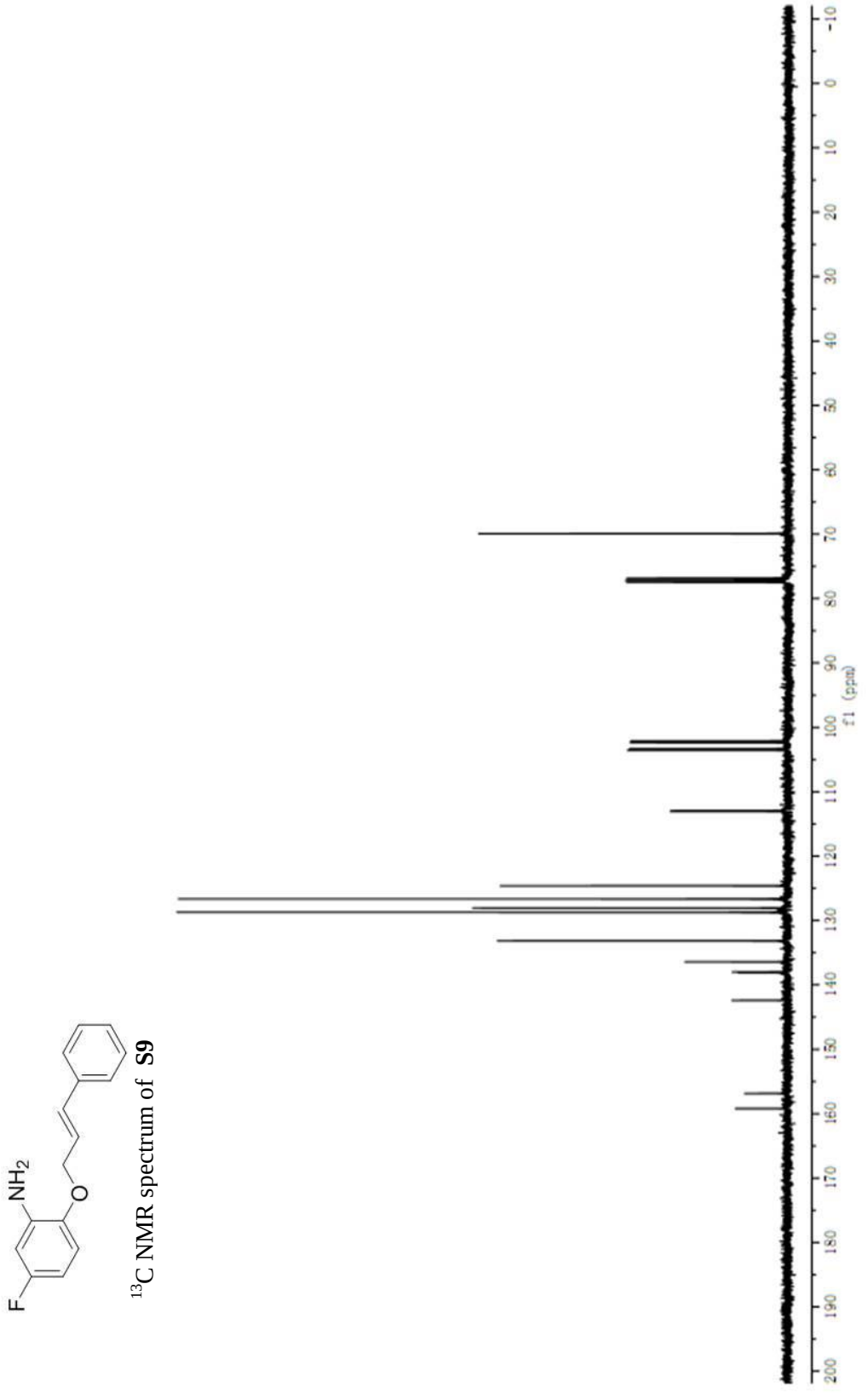
^{13}C NMR spectrum of **S8**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S8**



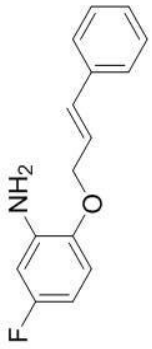
^{1}H NMR spectrum of **S9**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S9**

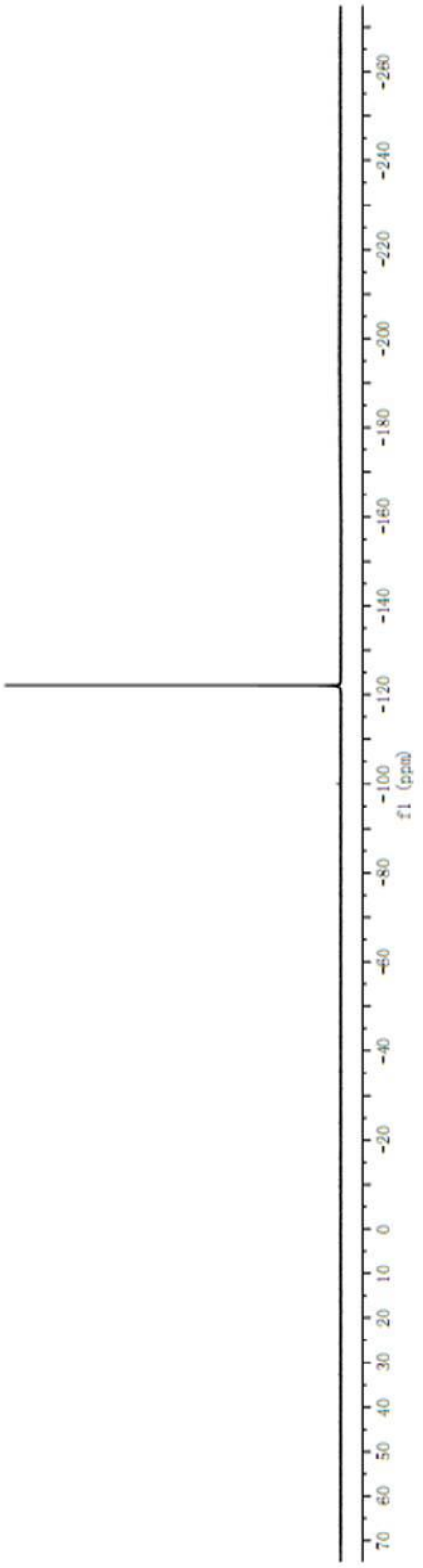


^{13}C NMR spectrum of **S9**

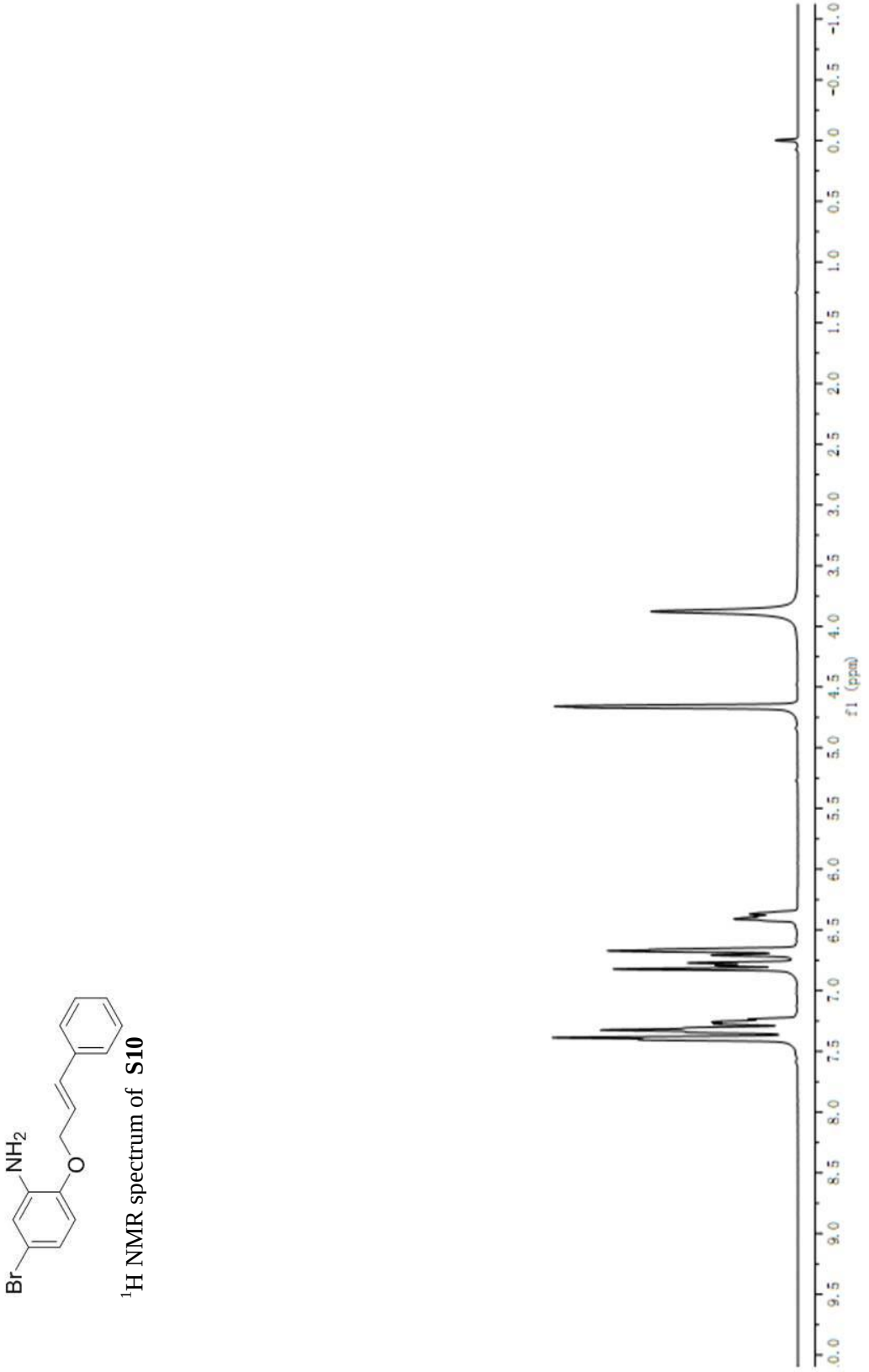
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S9**



^{19}F NMR spectrum of **S9**

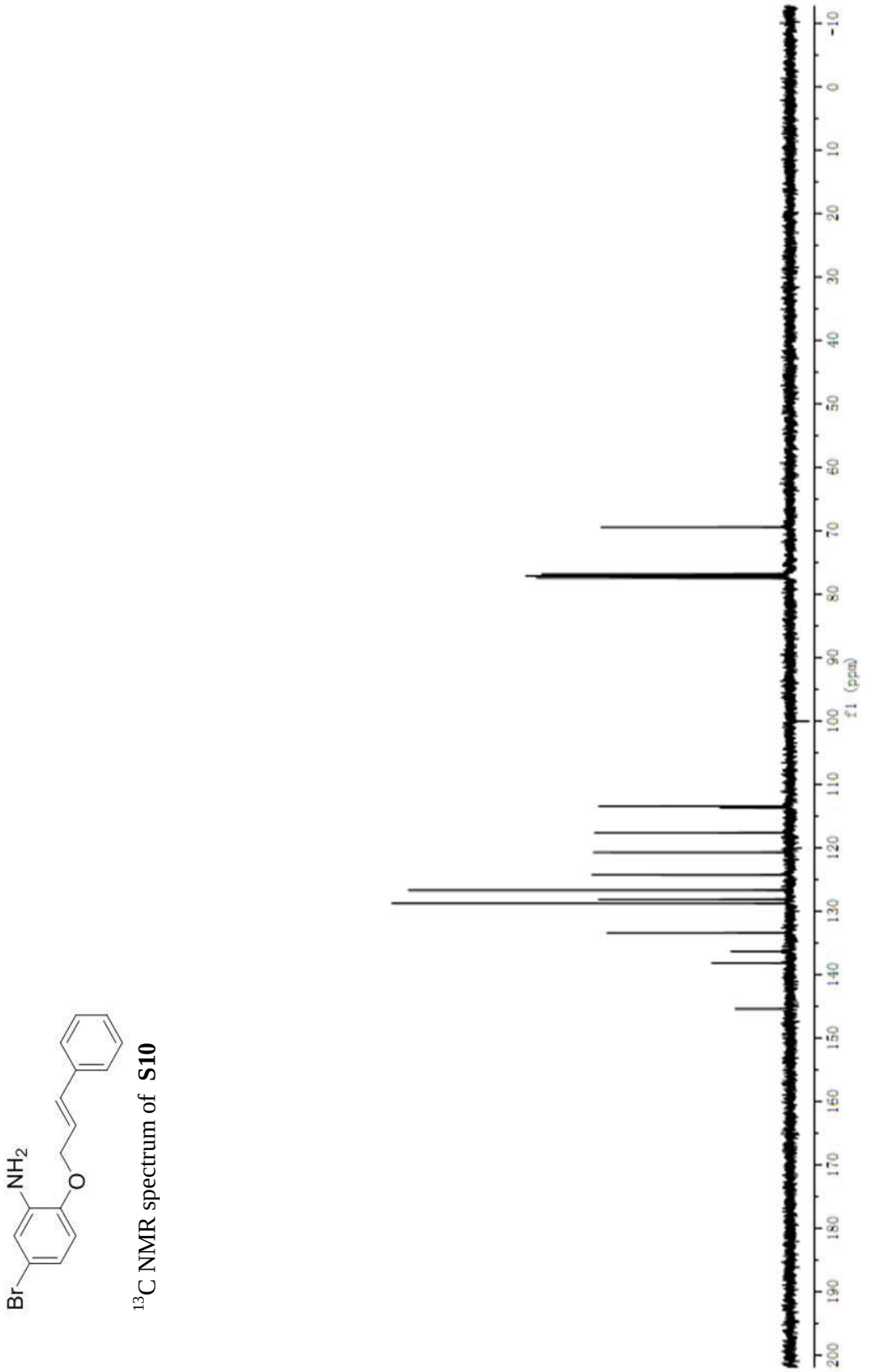


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S9**



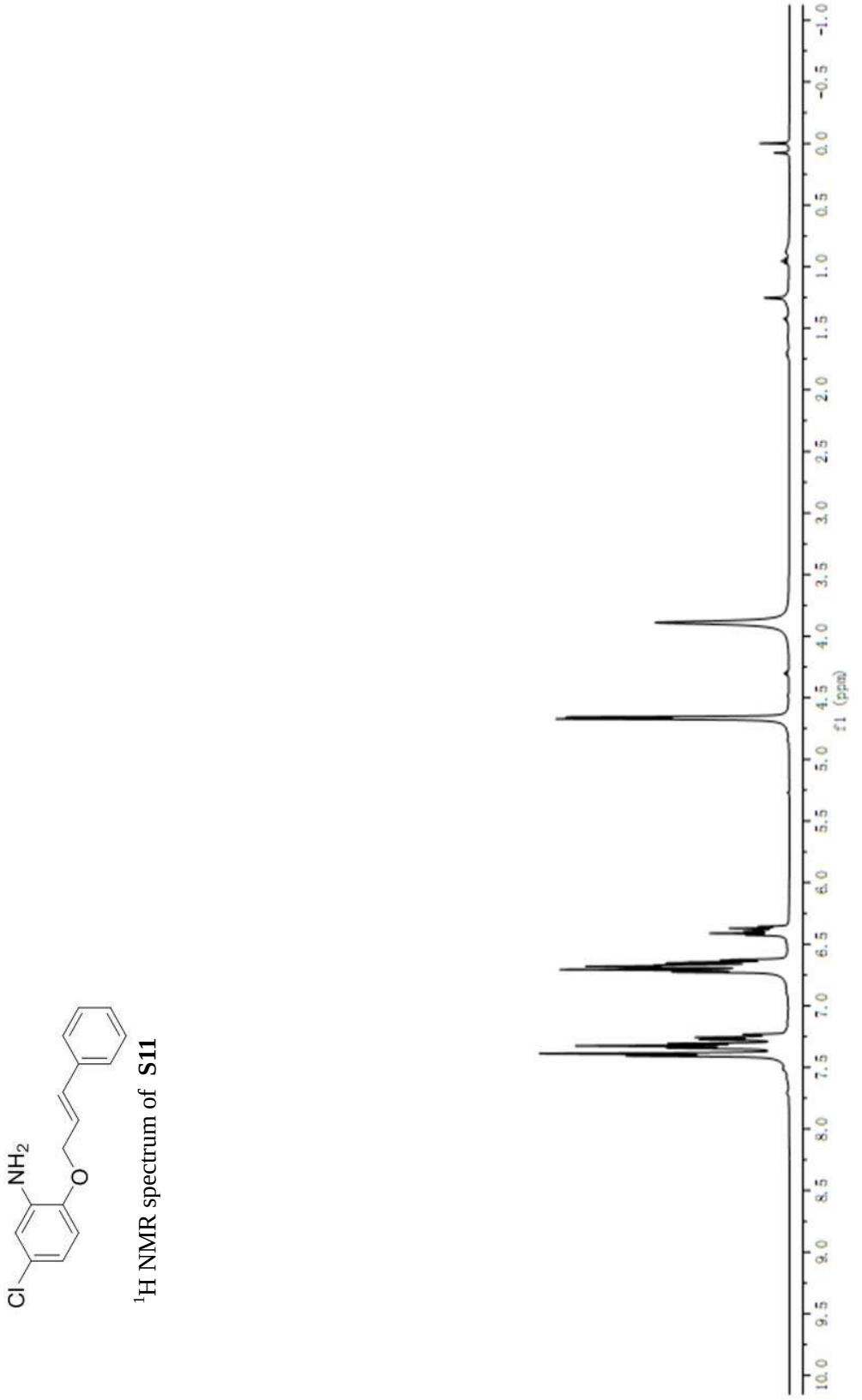
^{1}H NMR spectrum of **S10**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S10**



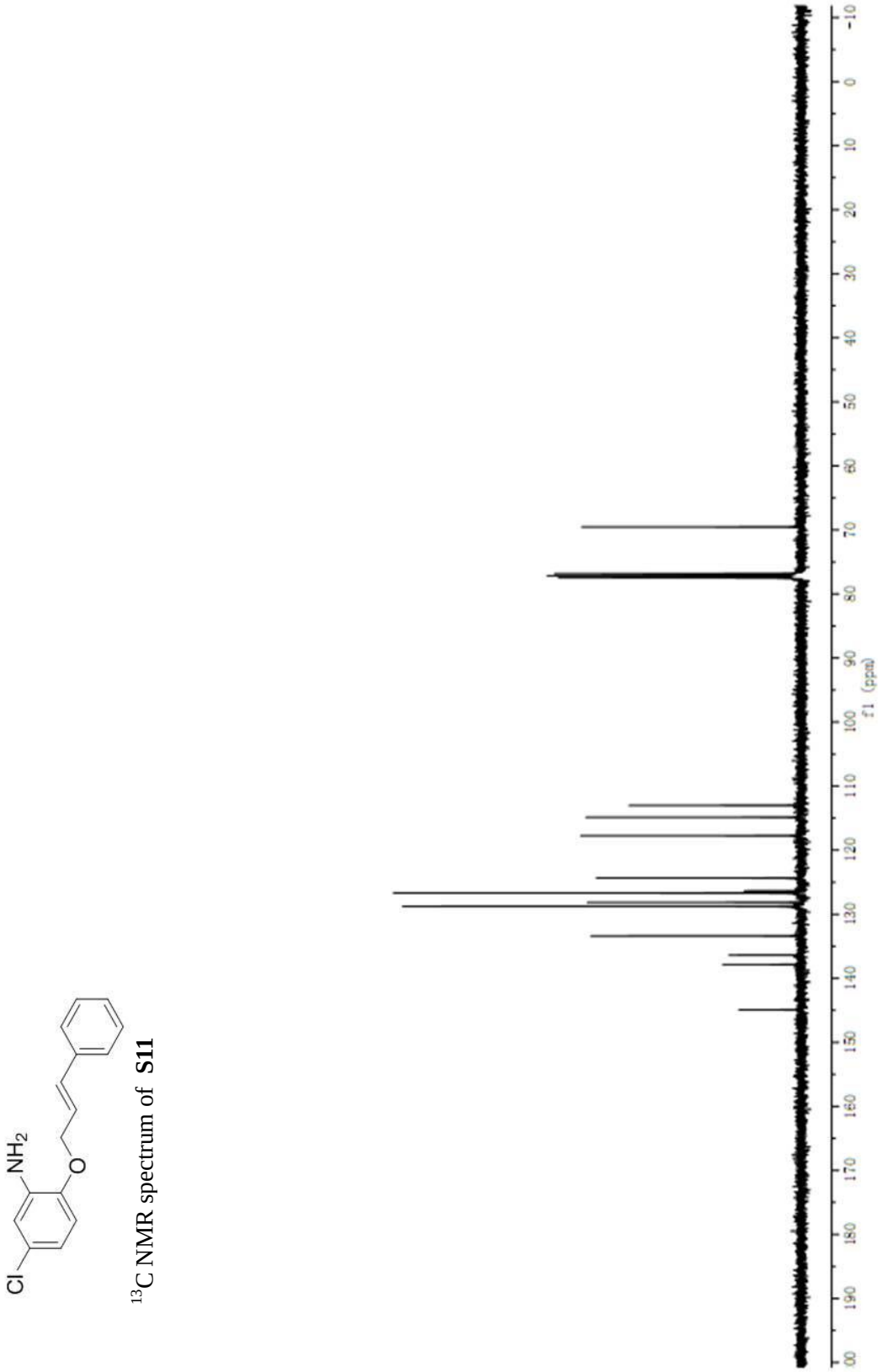
^{13}C NMR spectrum of **S10**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S10**



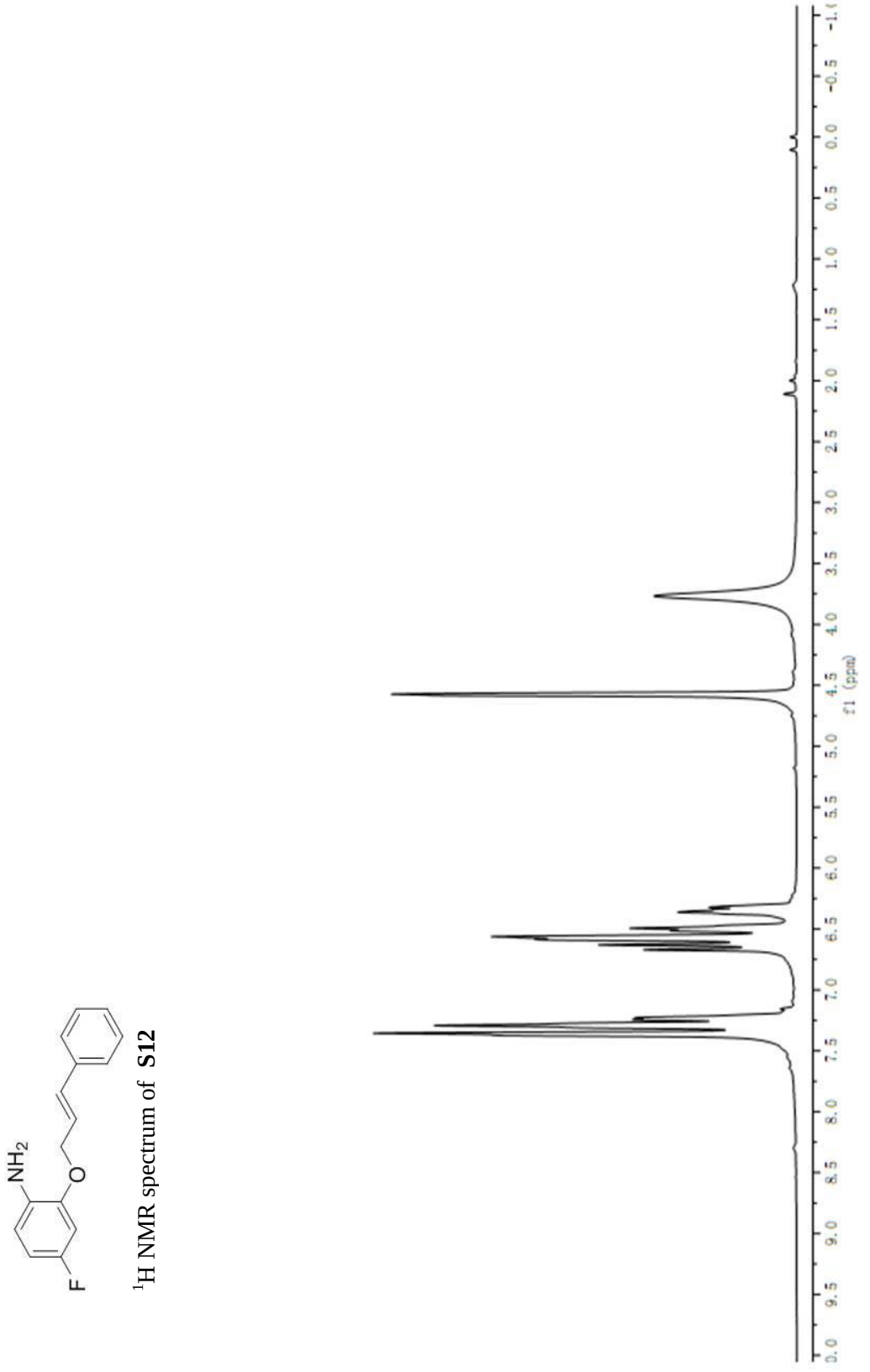
^{1}H NMR spectrum of **S11**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S11**



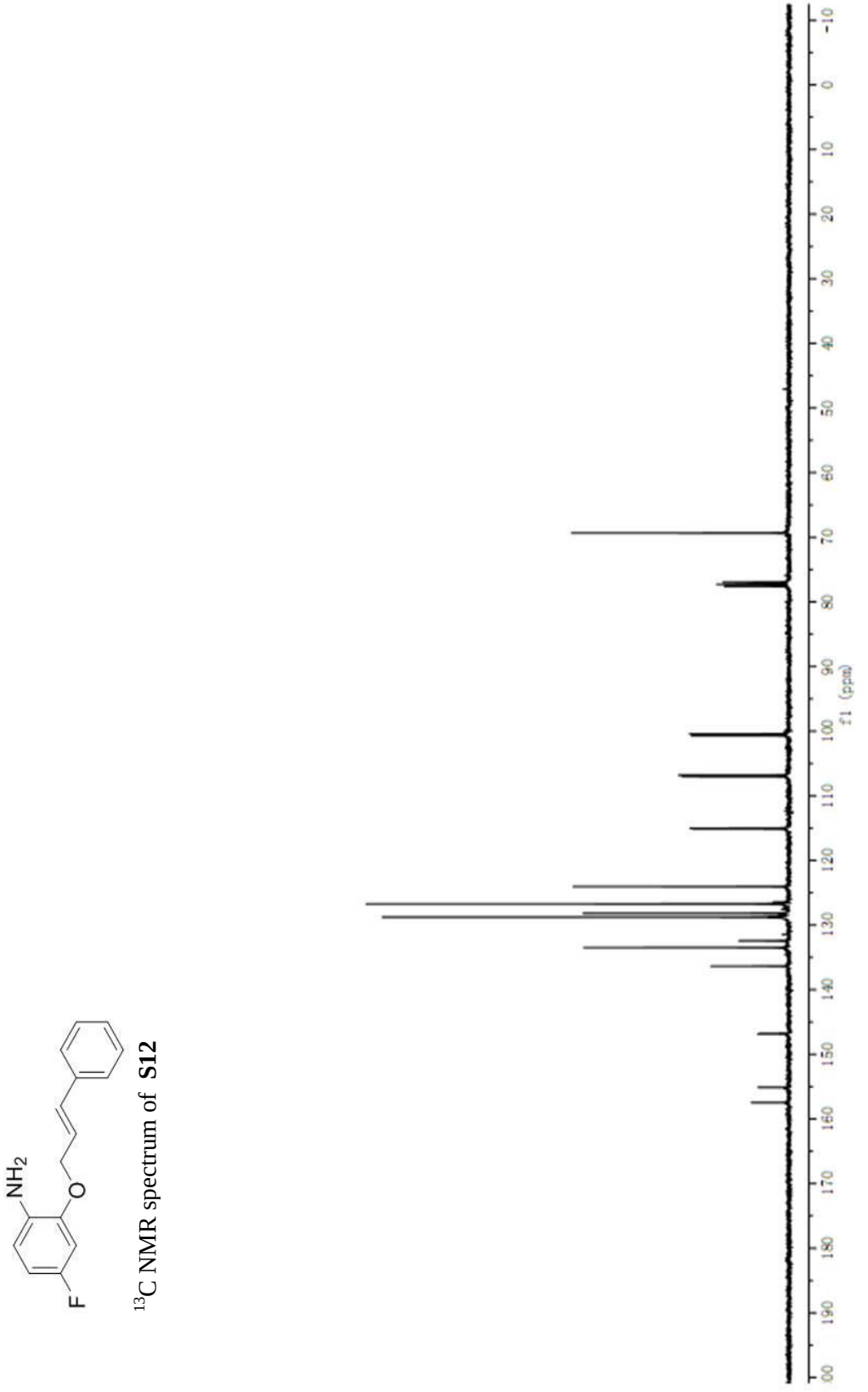
^{13}C NMR spectrum of **S11**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S11**



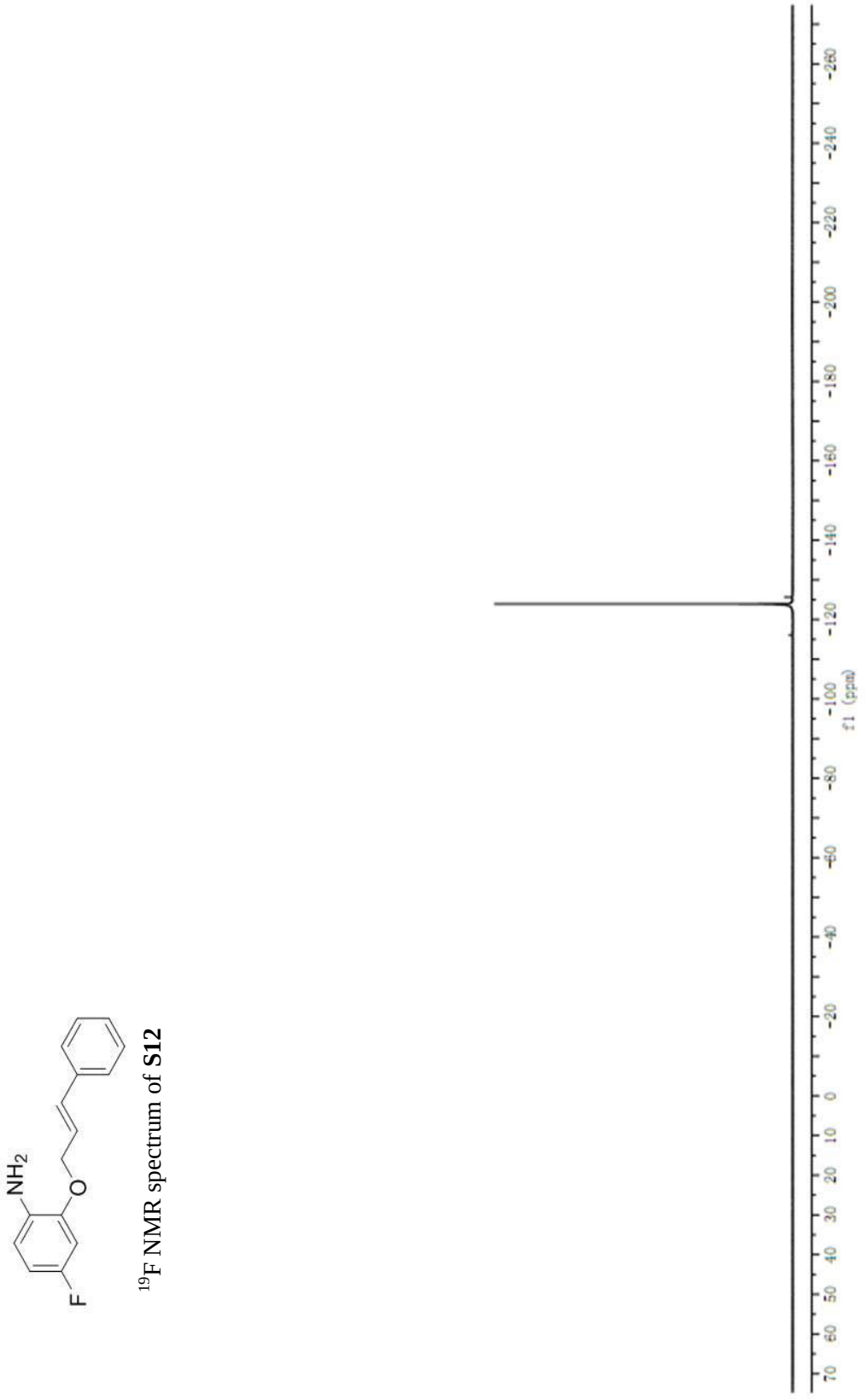
^{1}H NMR spectrum of **S12**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S12**



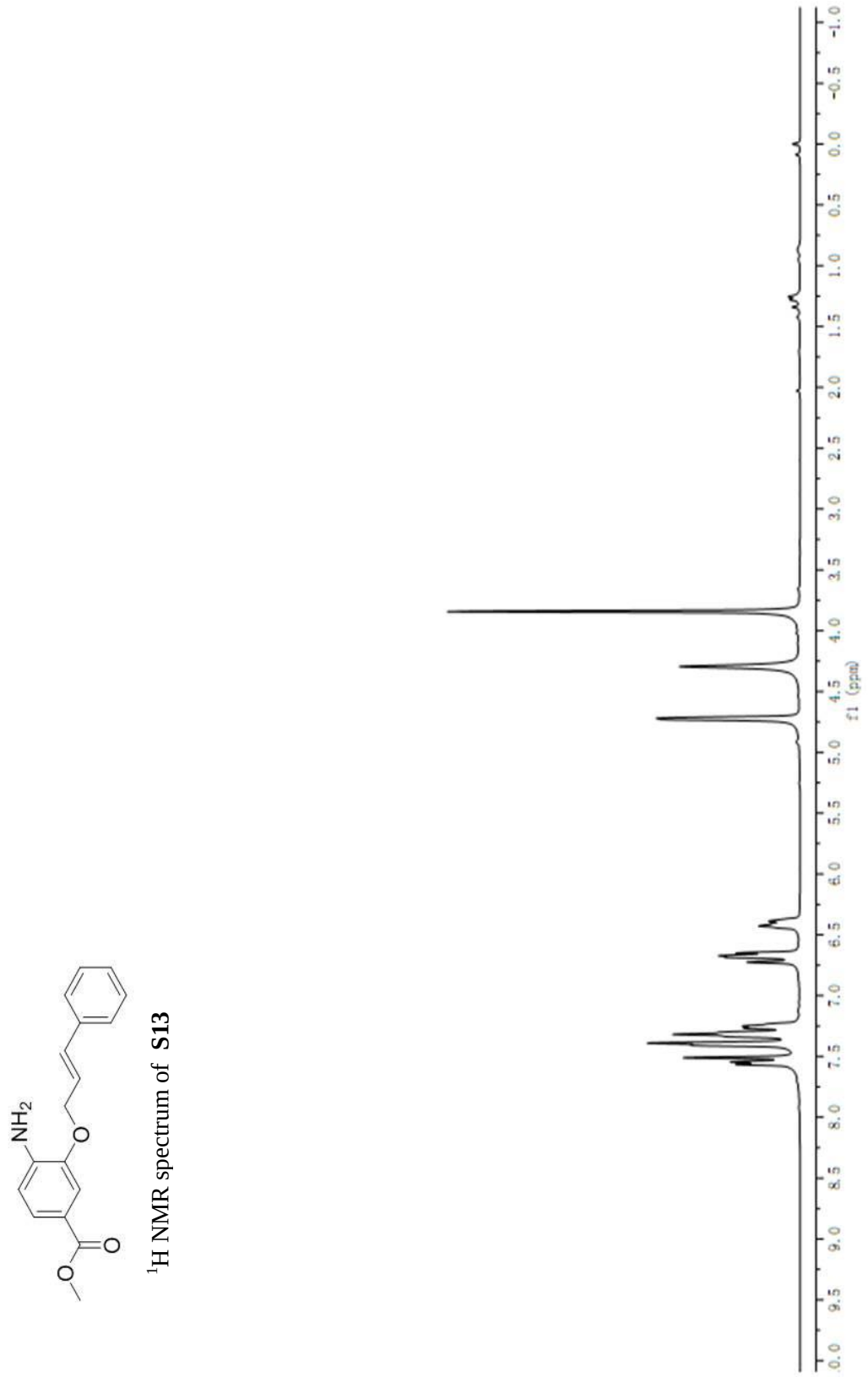
^{13}C NMR spectrum of **S12**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S12**



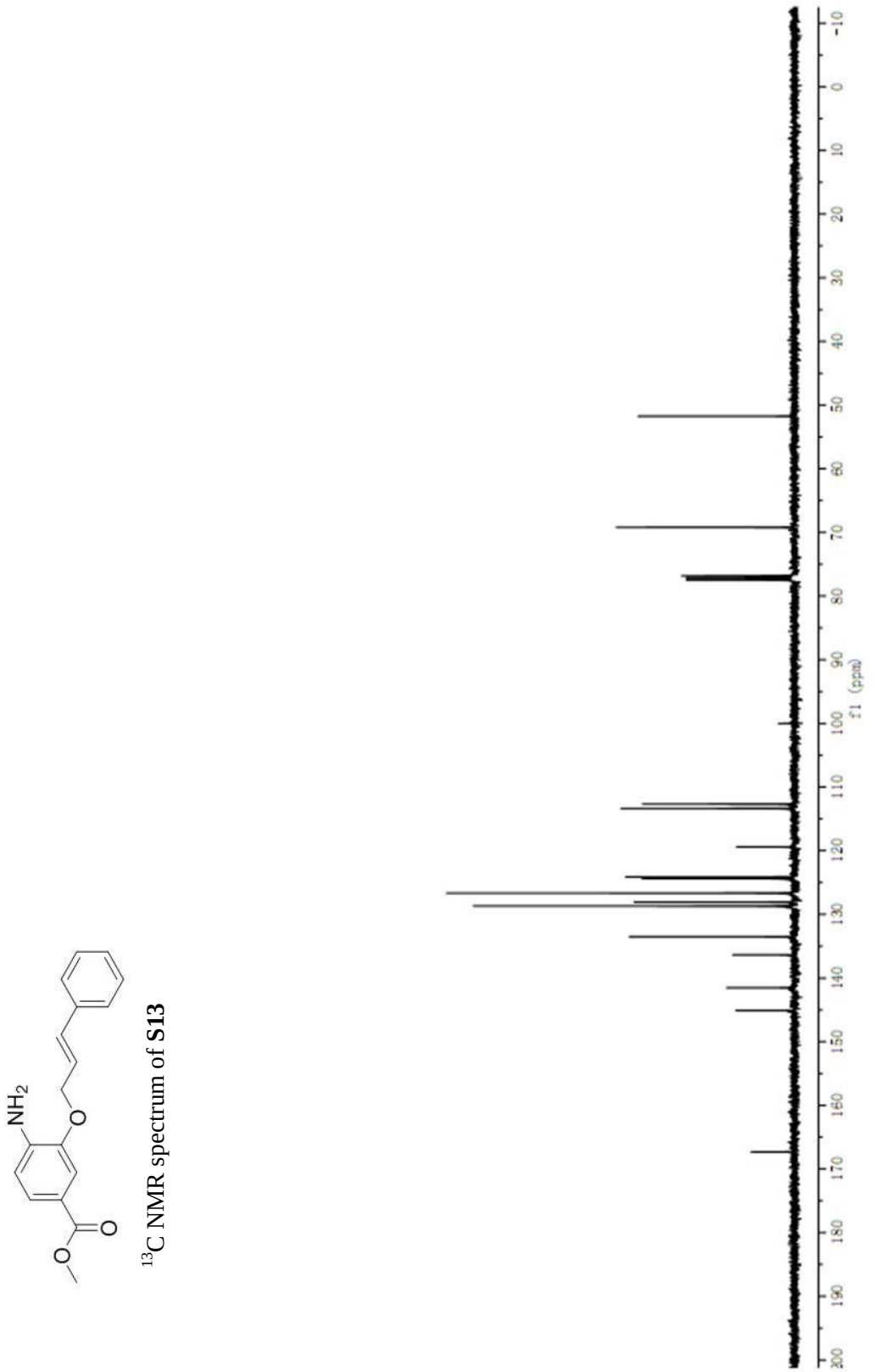
^{19}F NMR spectrum of **S12**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S12**



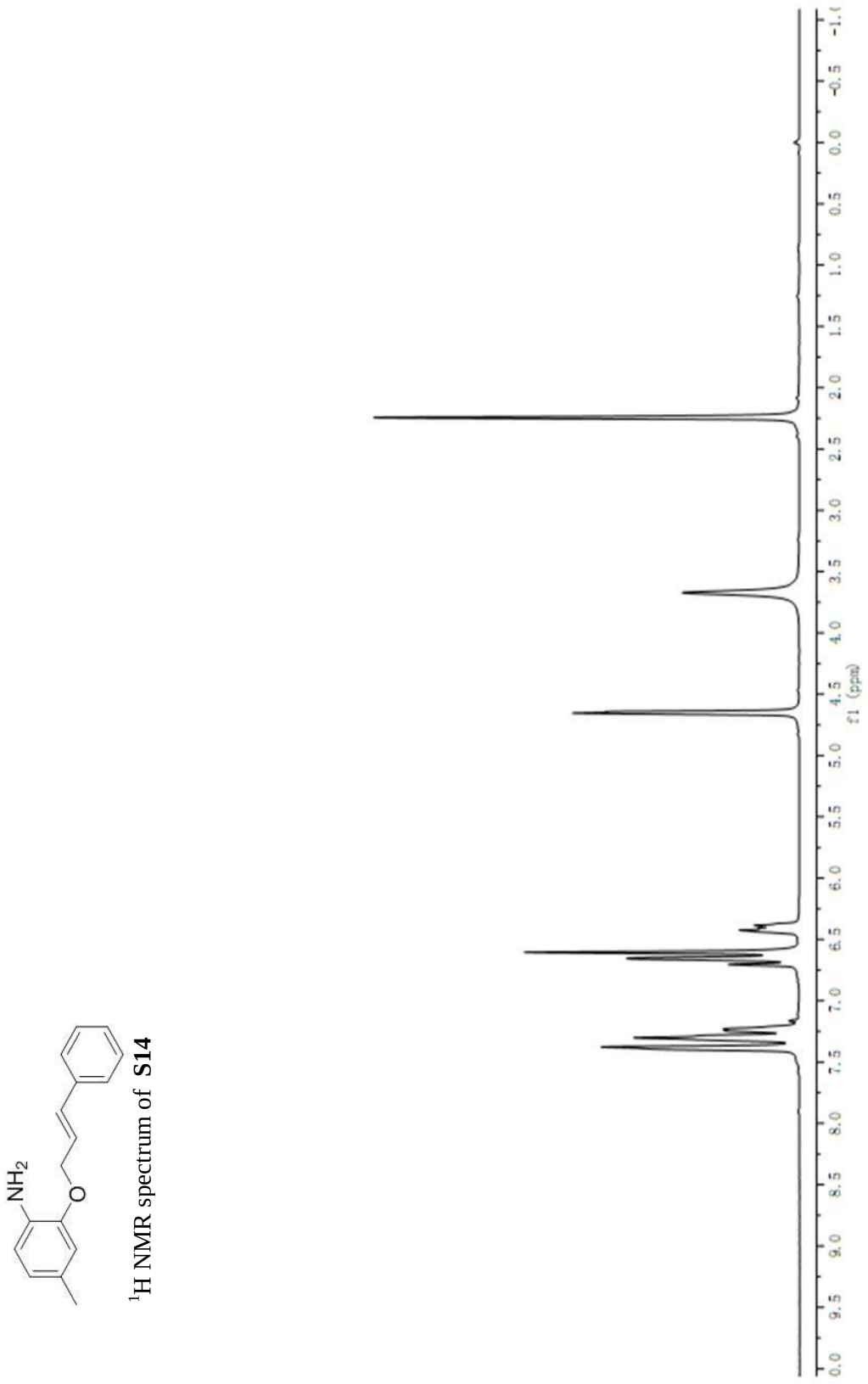
^{1}H NMR spectrum of **S13**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S13**



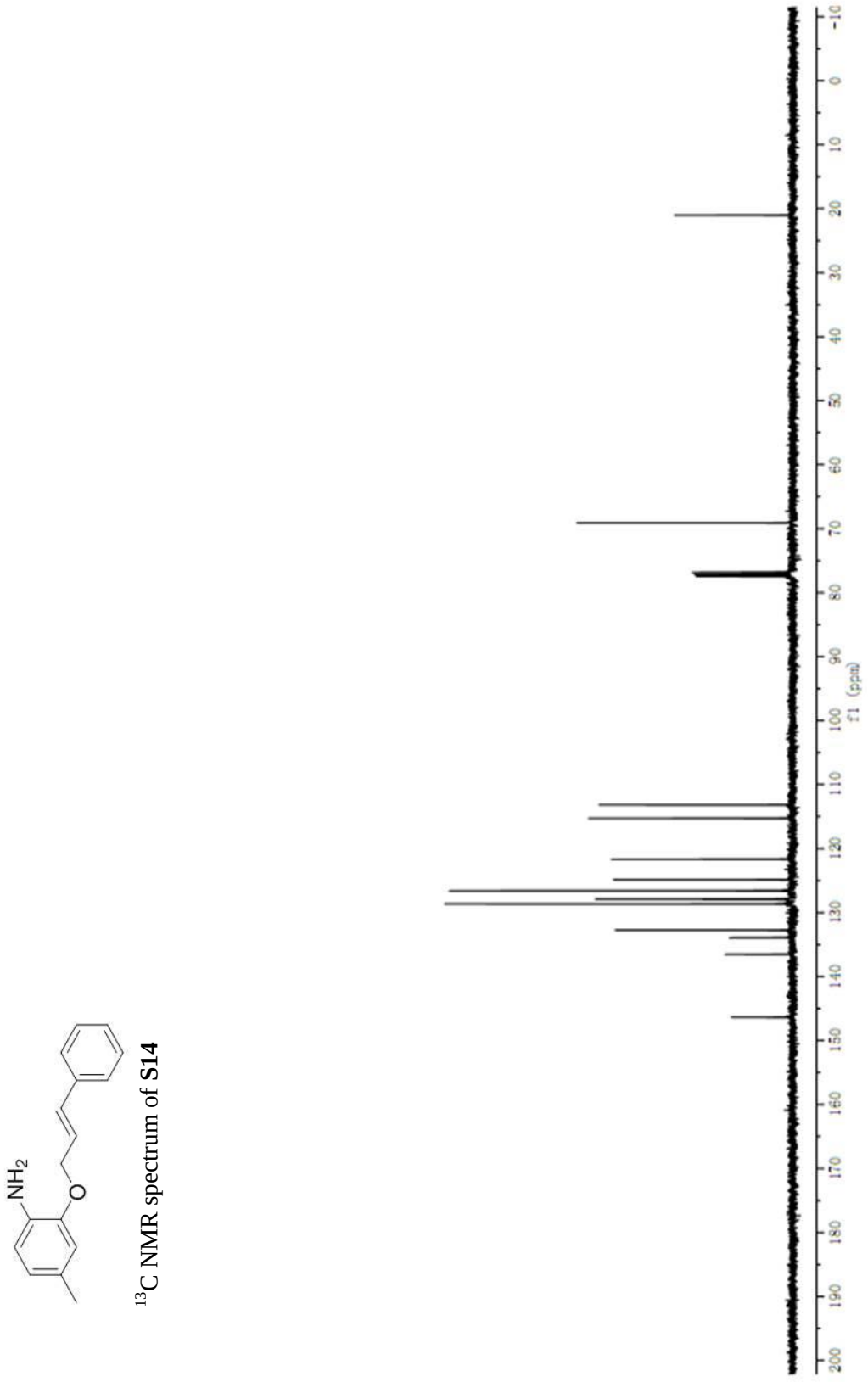
^{13}C NMR spectrum of **S13**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S13**



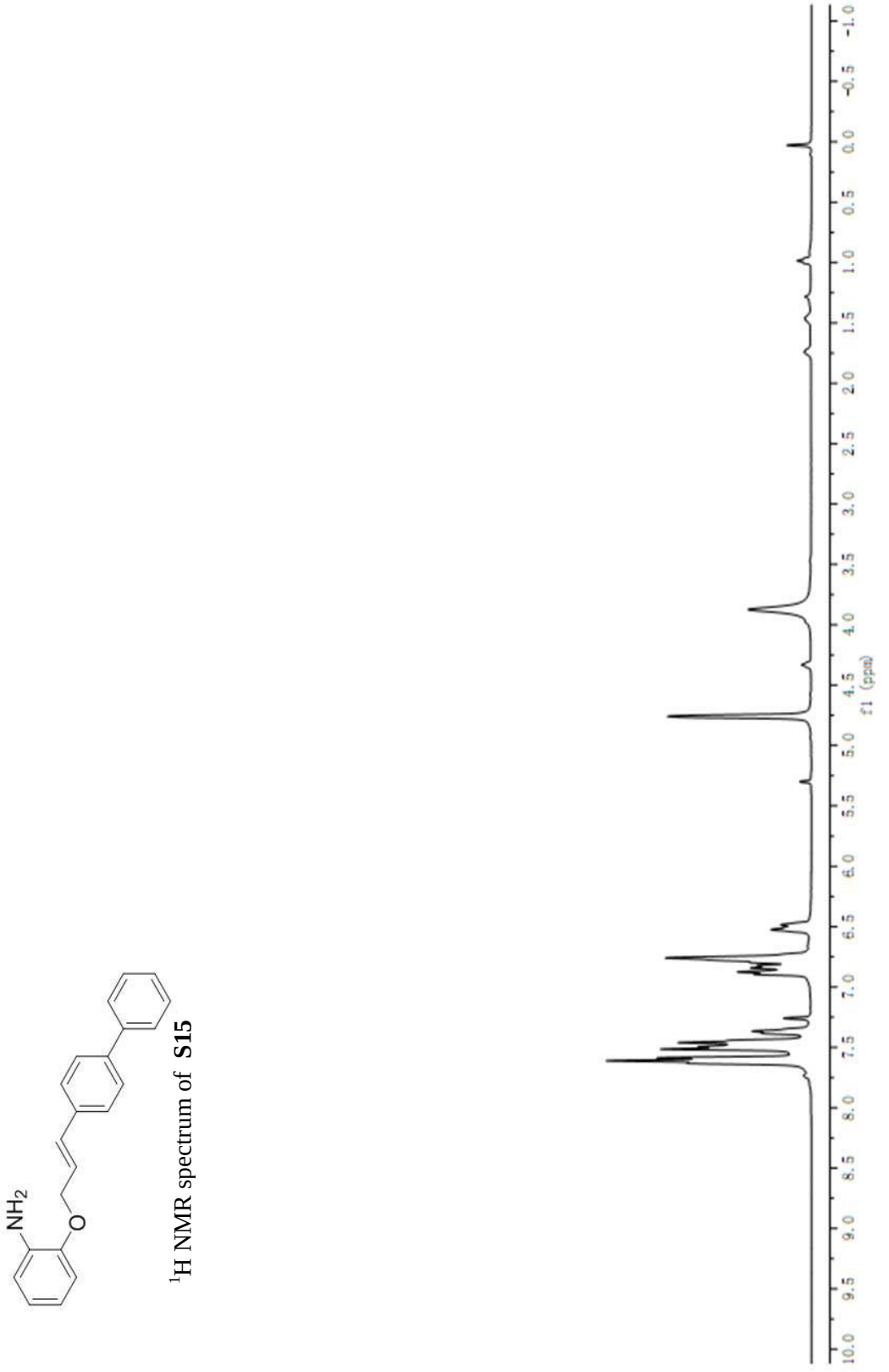
^{1}H NMR spectrum of **S14**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S14**



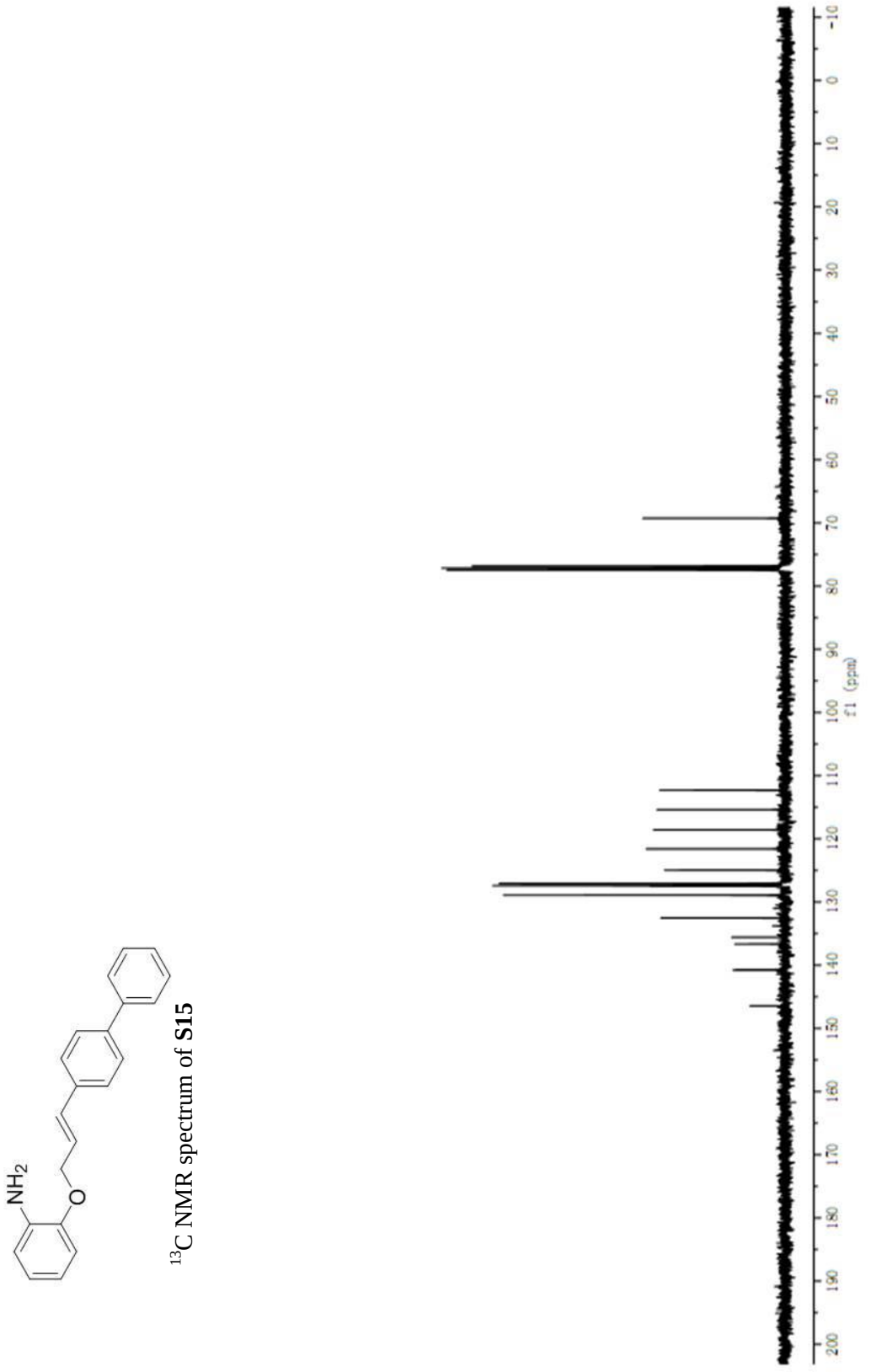
^{13}C NMR spectrum of **S14**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S14**



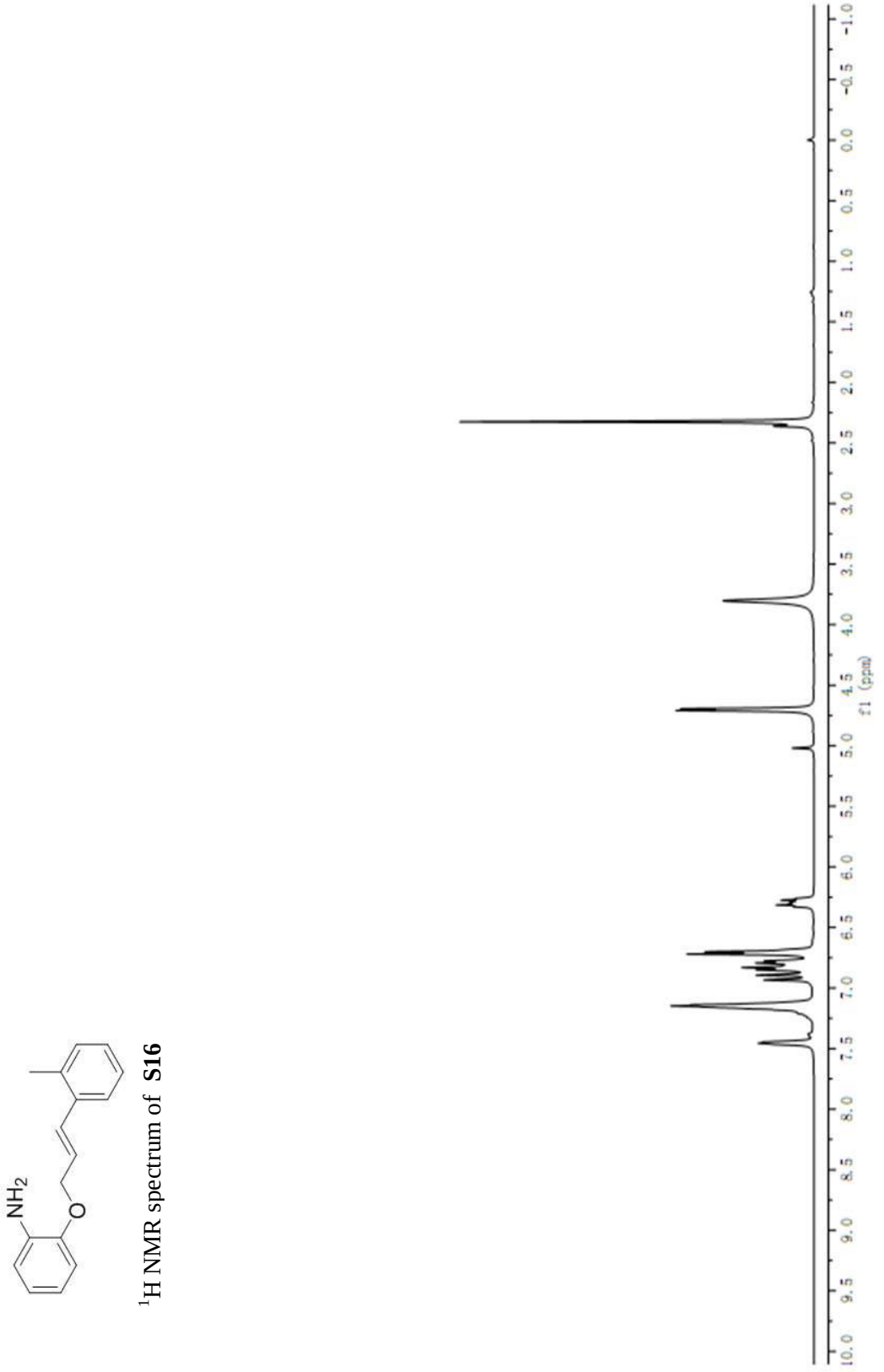
^{1}H NMR spectrum of **S15**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S15**



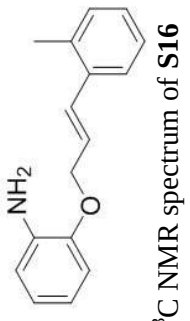
^{13}C NMR spectrum of **S15**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S15**

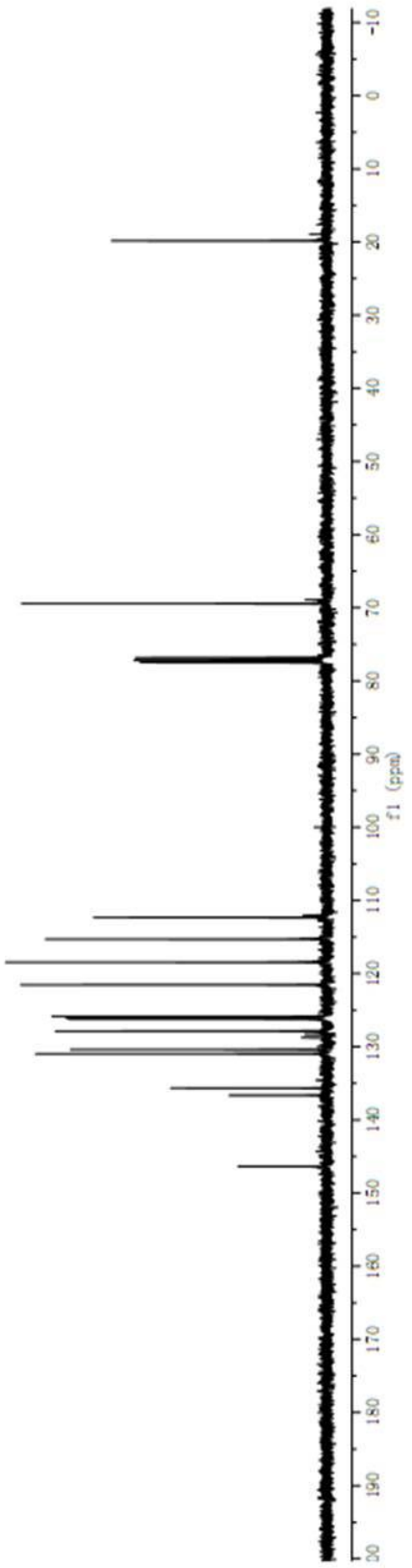


^{1}H NMR spectrum of **S16**

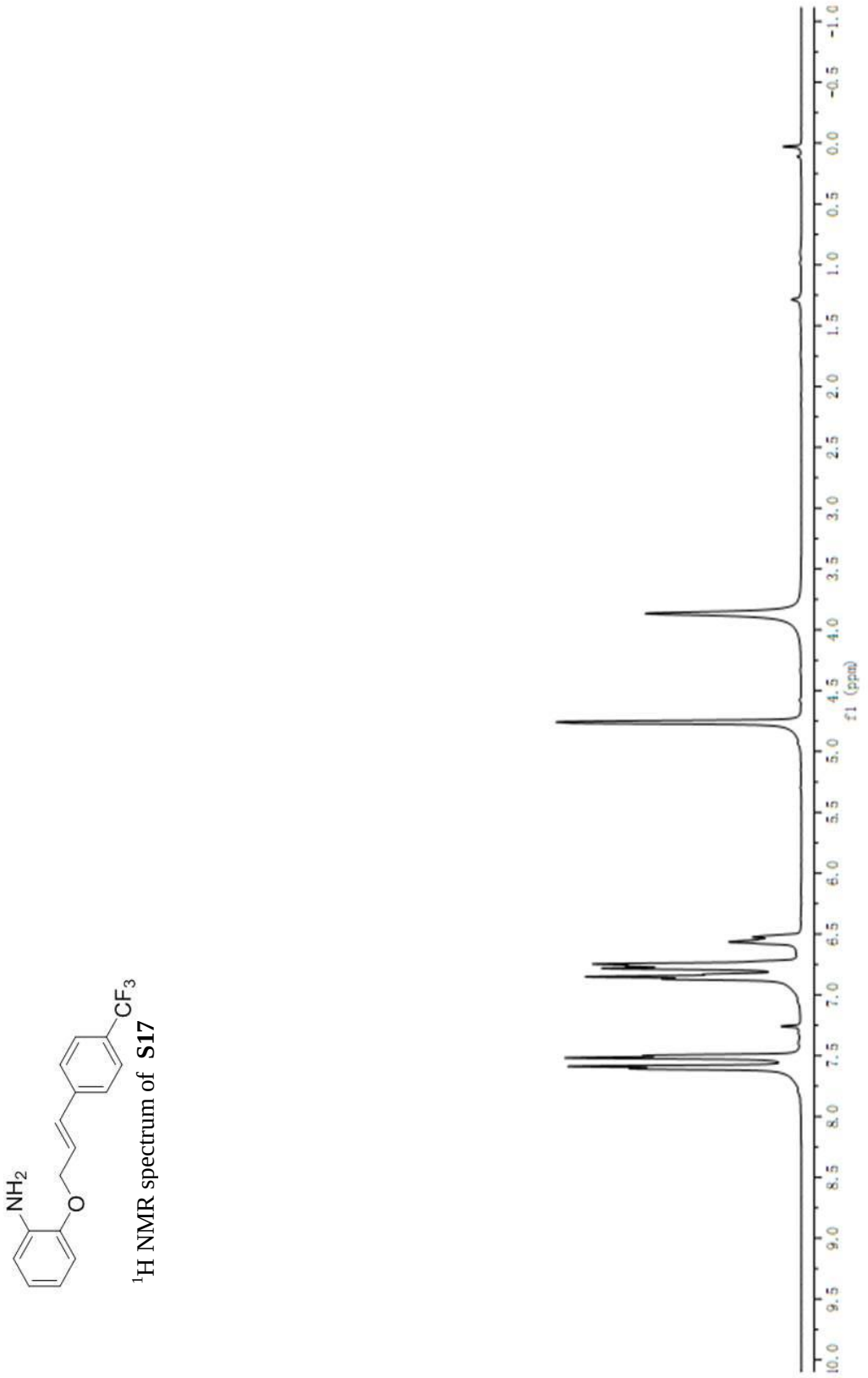
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S16**



^{13}C NMR spectrum of **S16**

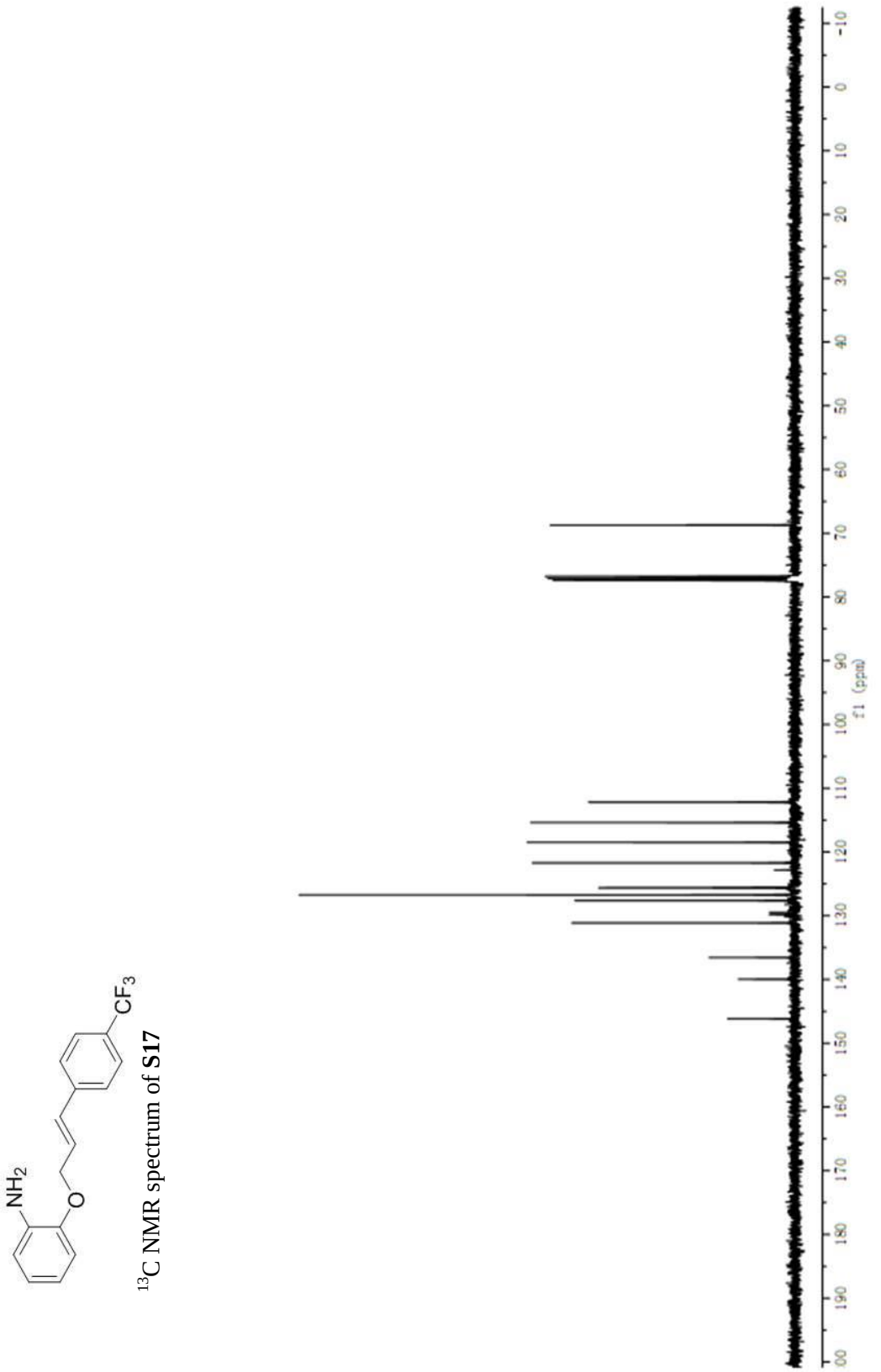


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S16**



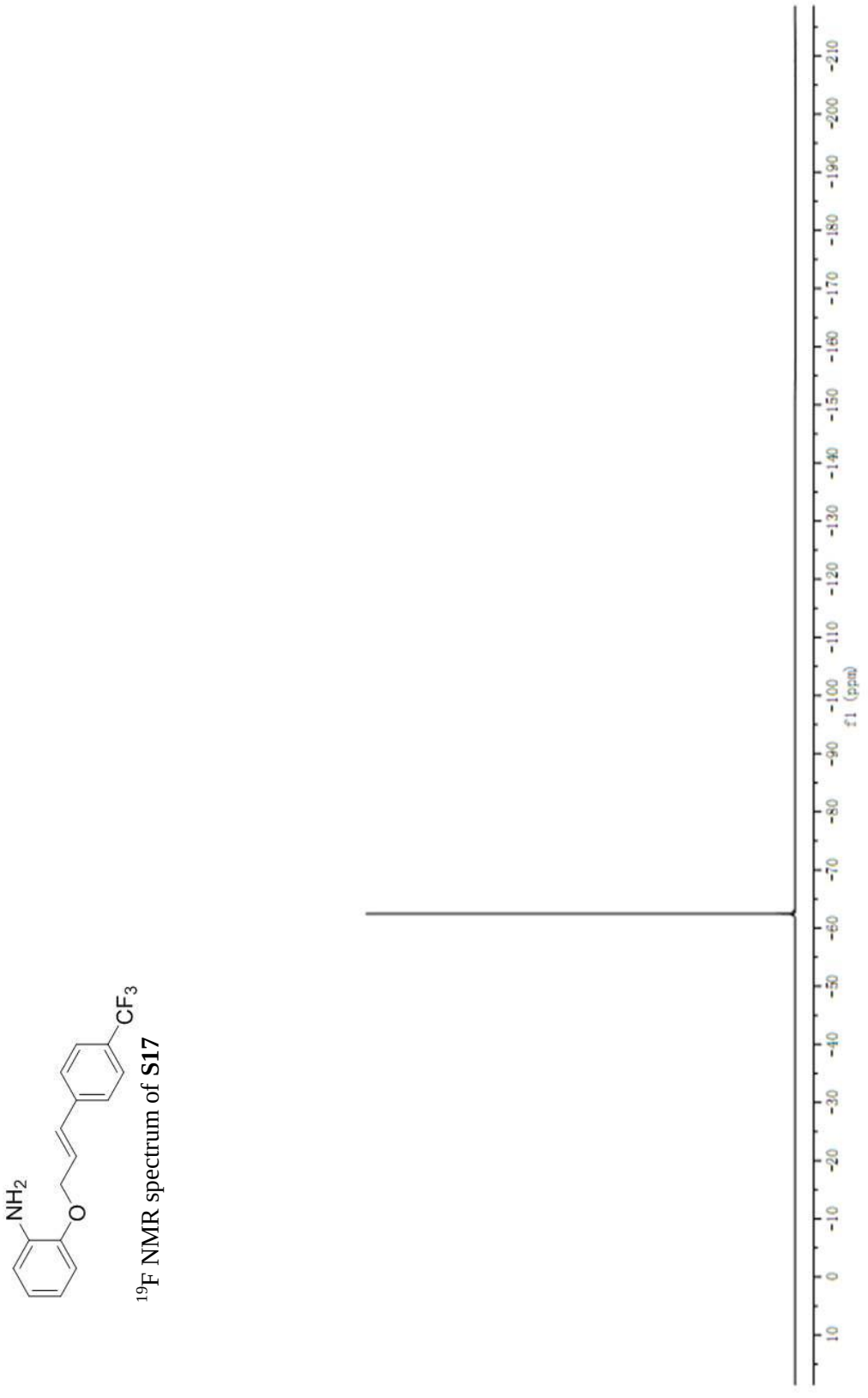
^{1}H NMR spectrum of **S17**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S17**



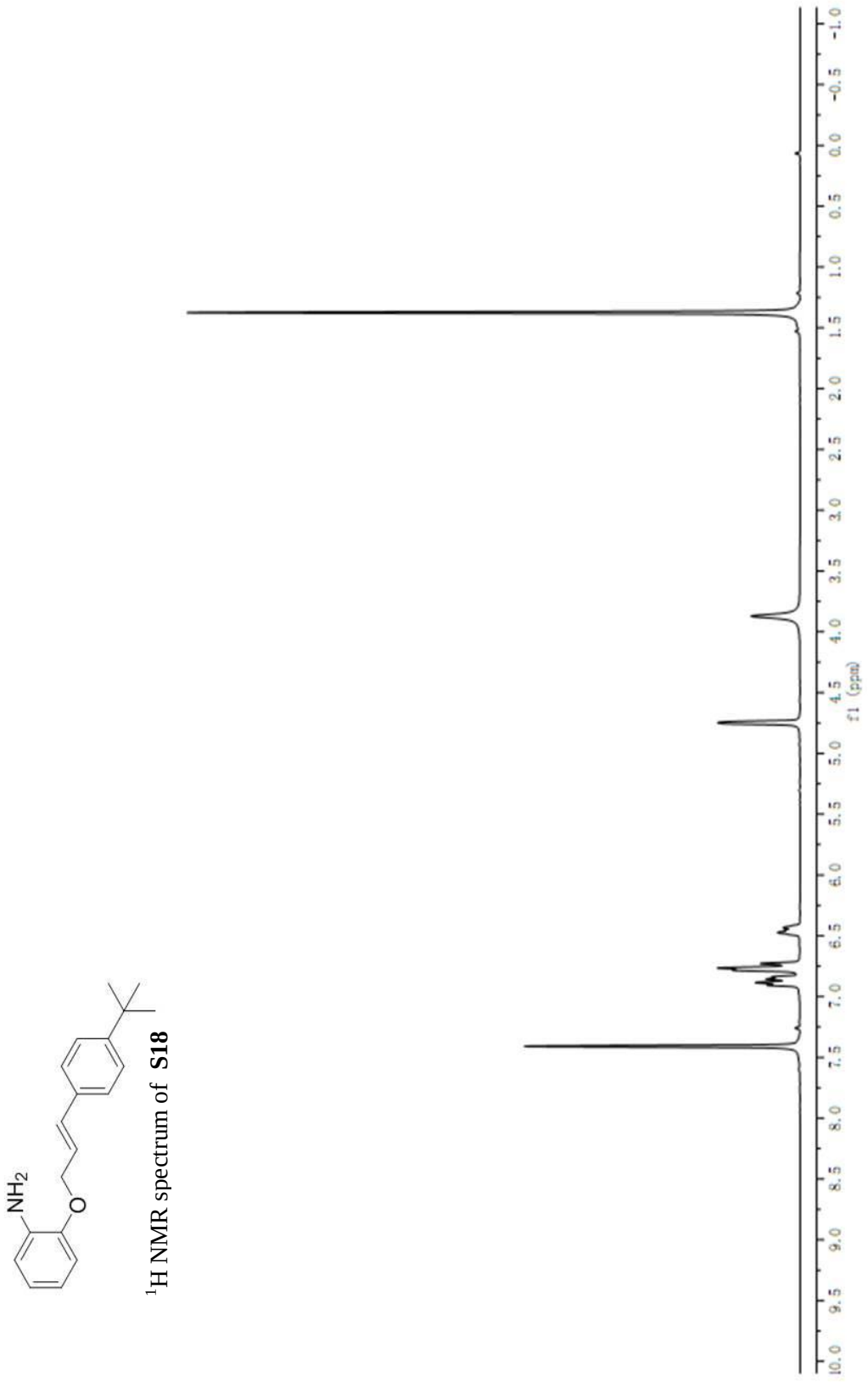
^{13}C NMR spectrum of **S17**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S17**



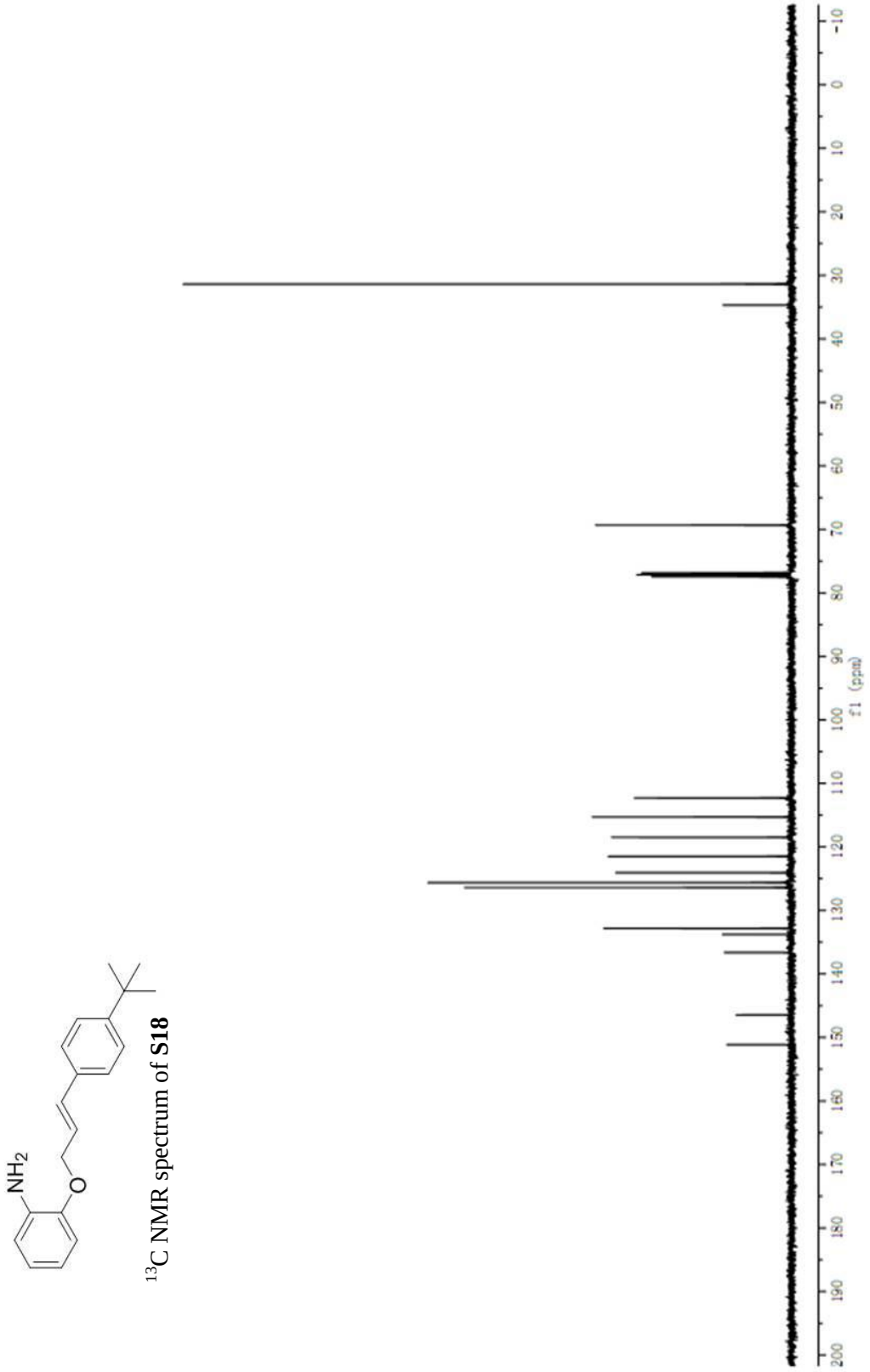
^{19}F NMR spectrum of **S17**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S17**



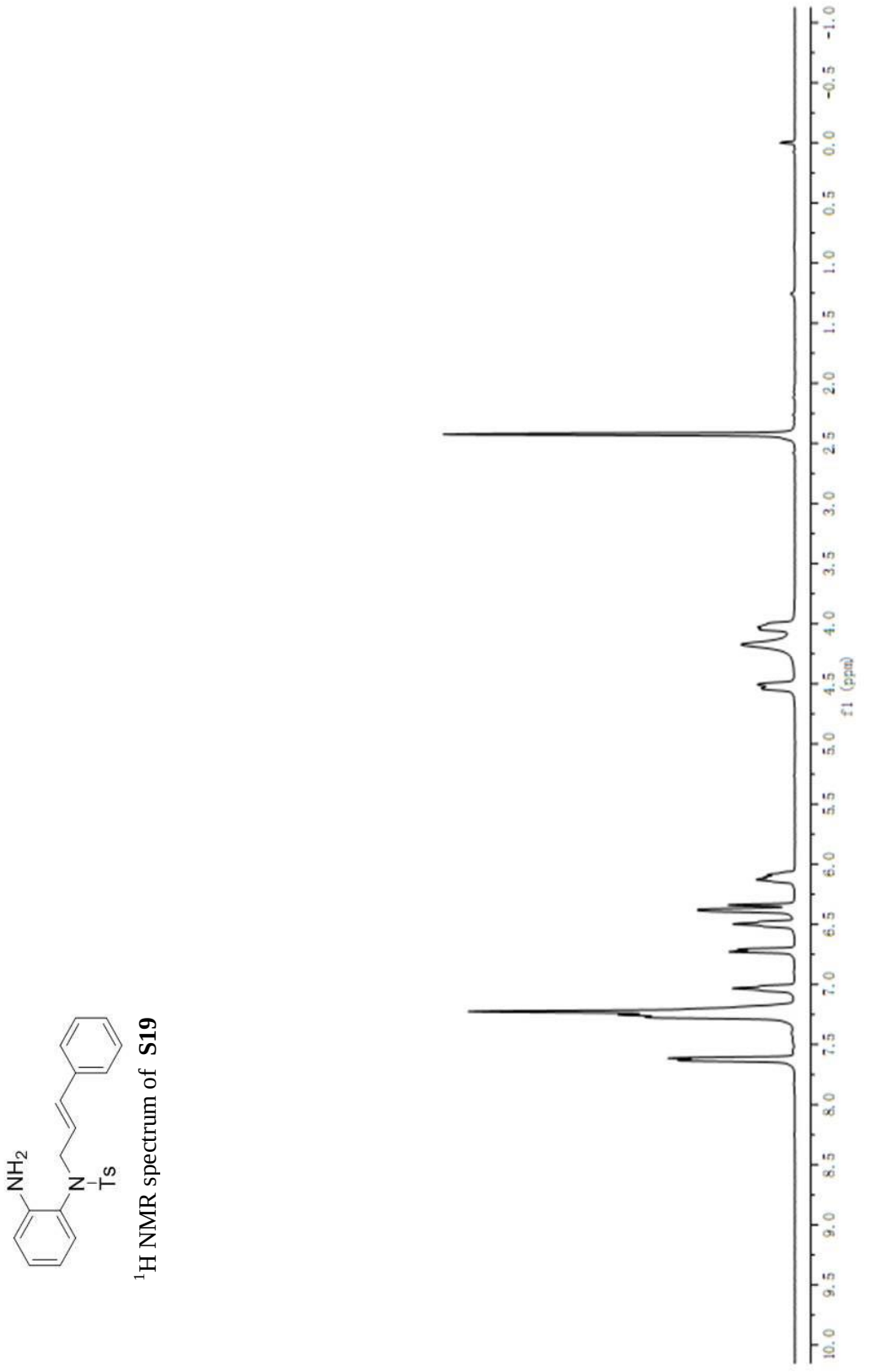
^{1}H NMR spectrum of **S18**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S18**



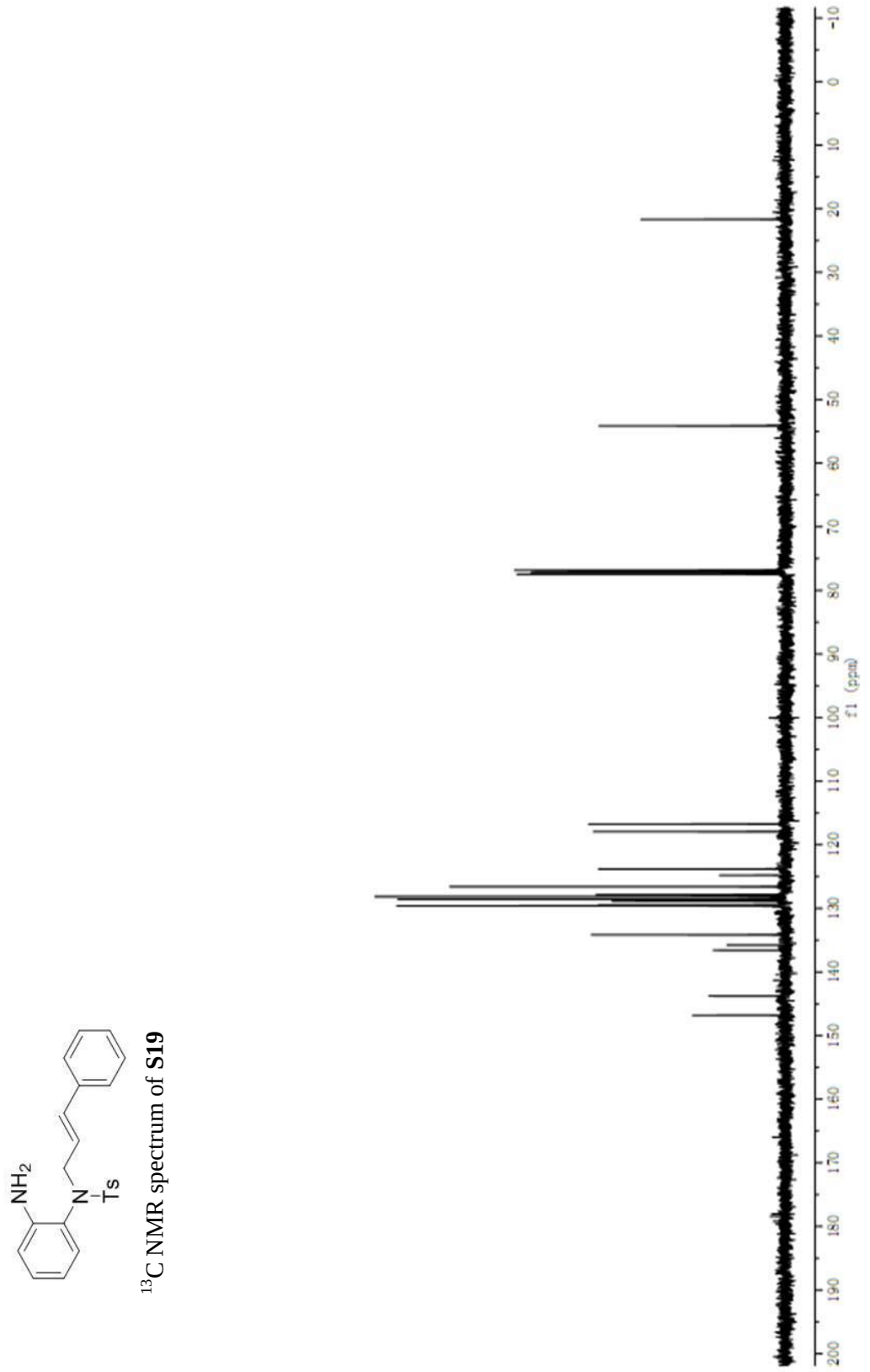
^{13}C NMR spectrum of **S18**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S18**



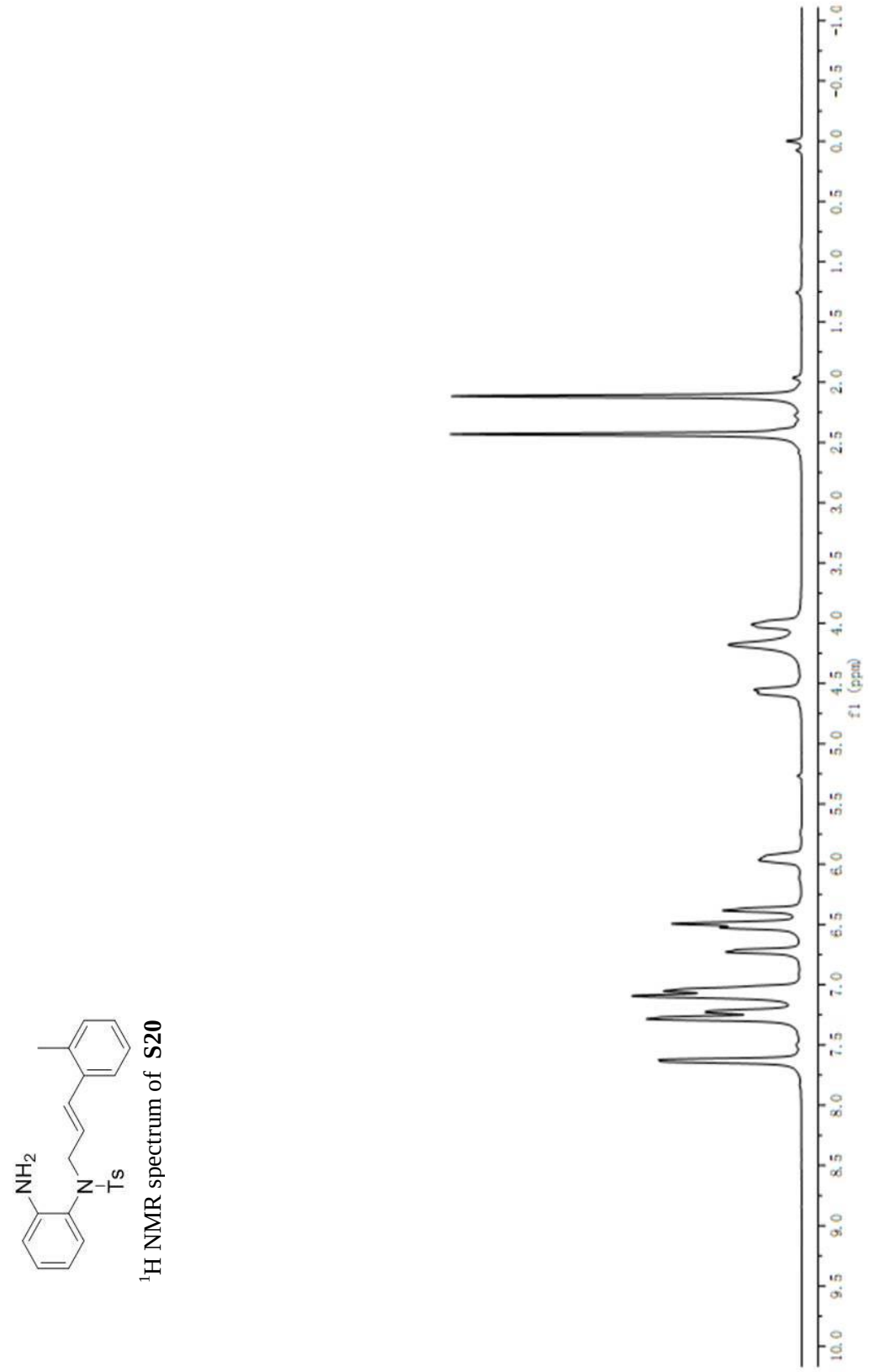
^{1}H NMR spectrum of **S19**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S19**



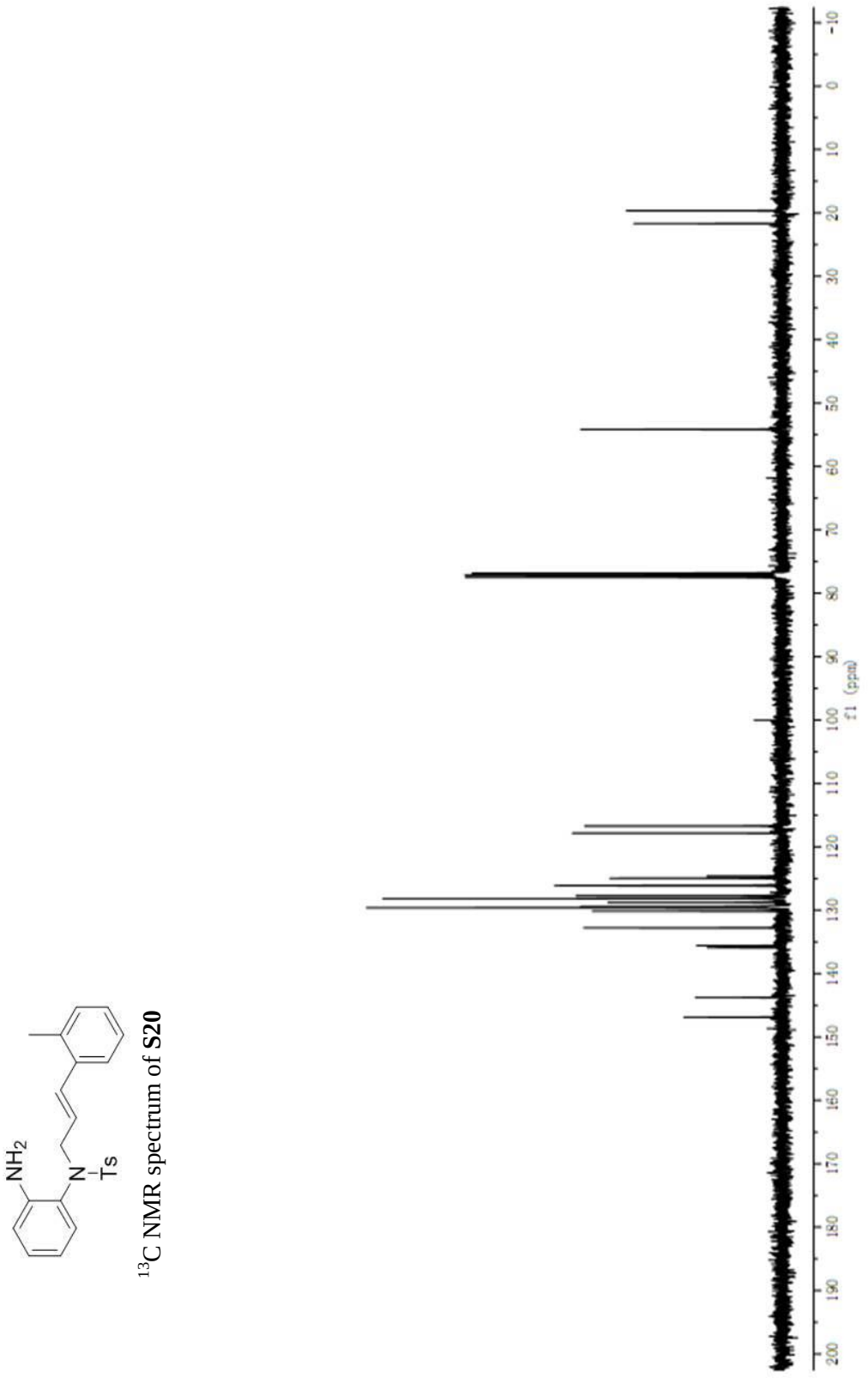
^{13}C NMR spectrum of **S19**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S19**



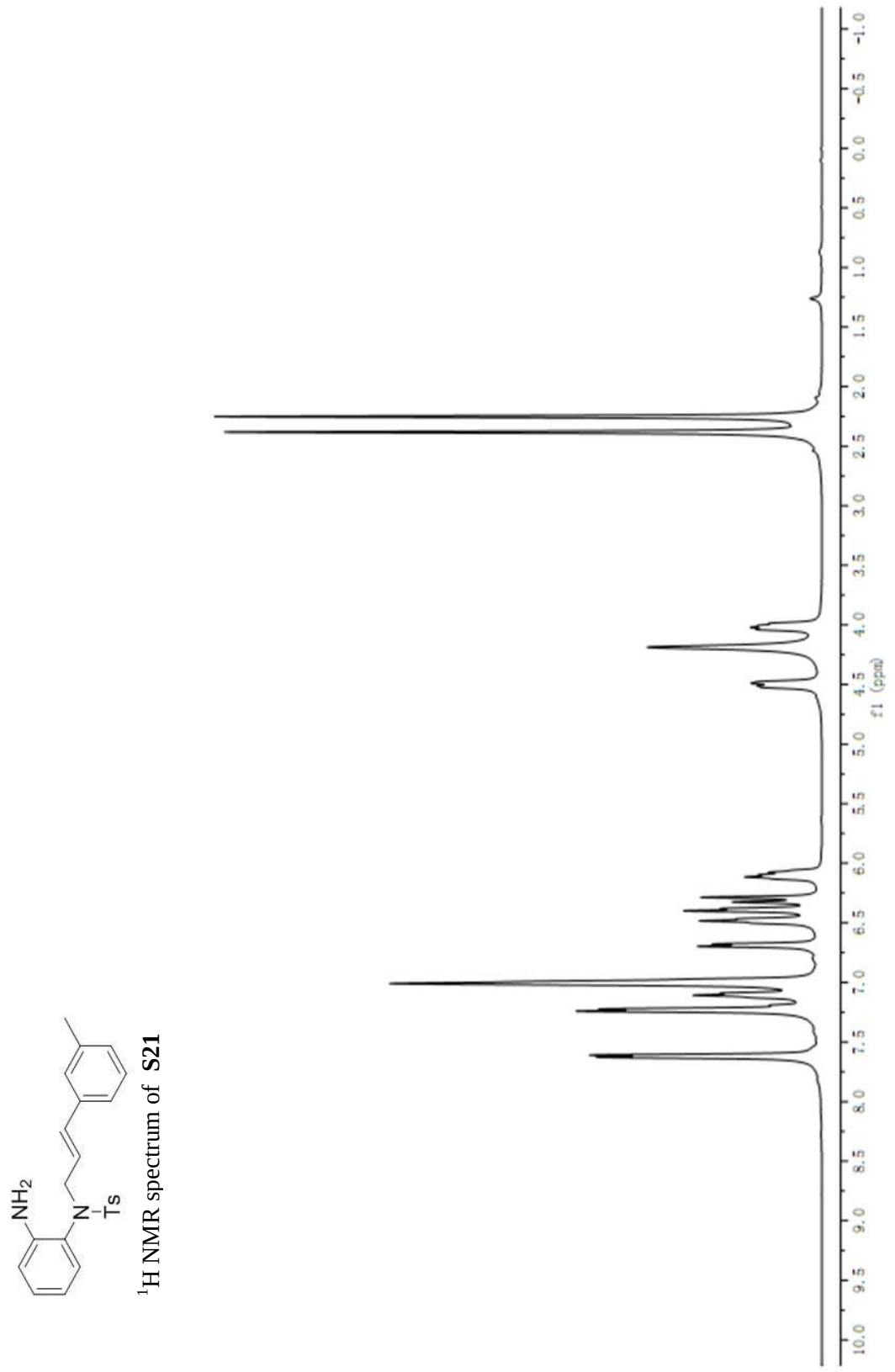
^{1}H NMR spectrum of **S20**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S20**



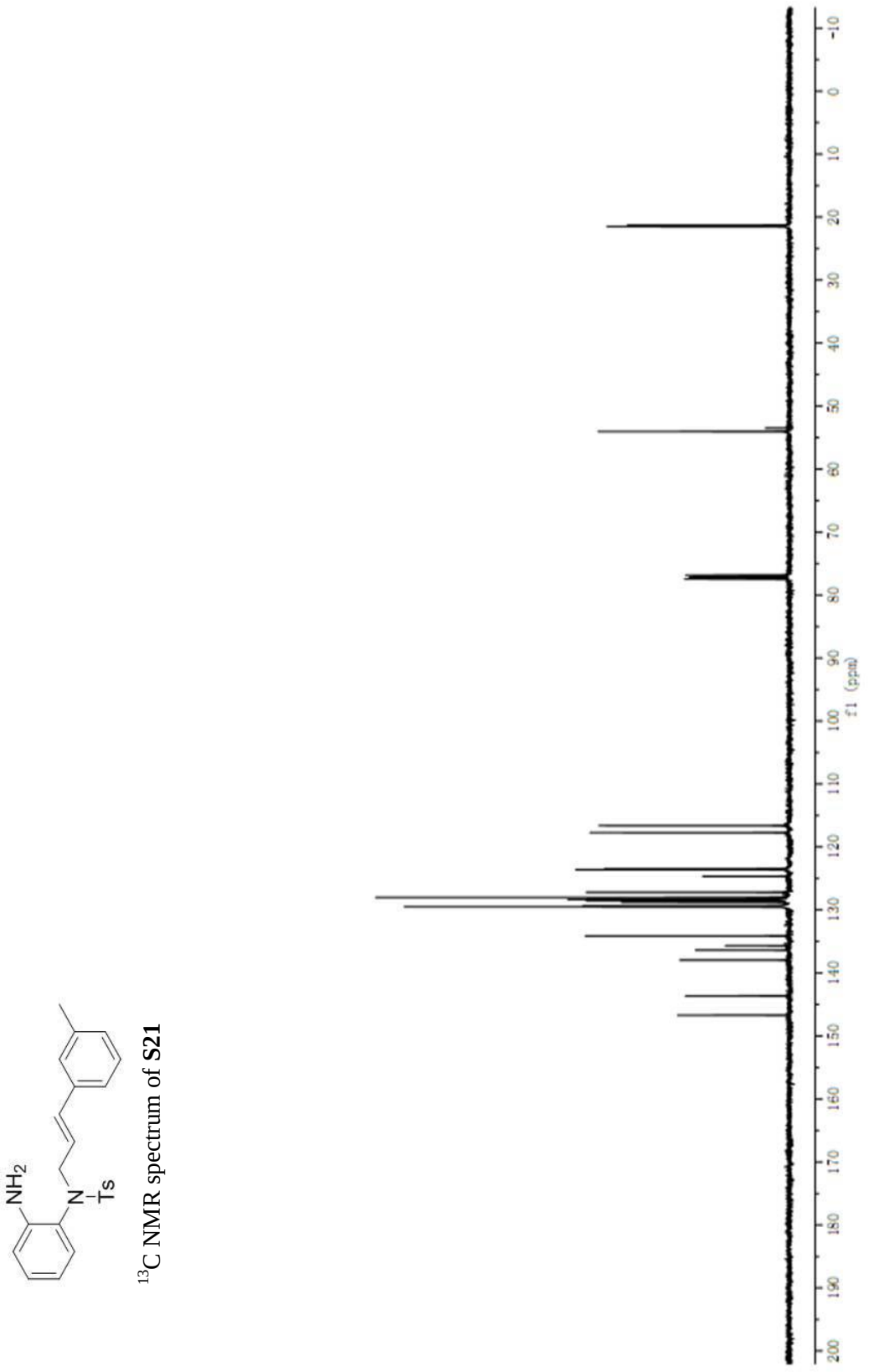
^{13}C NMR spectrum of **S20**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S20**



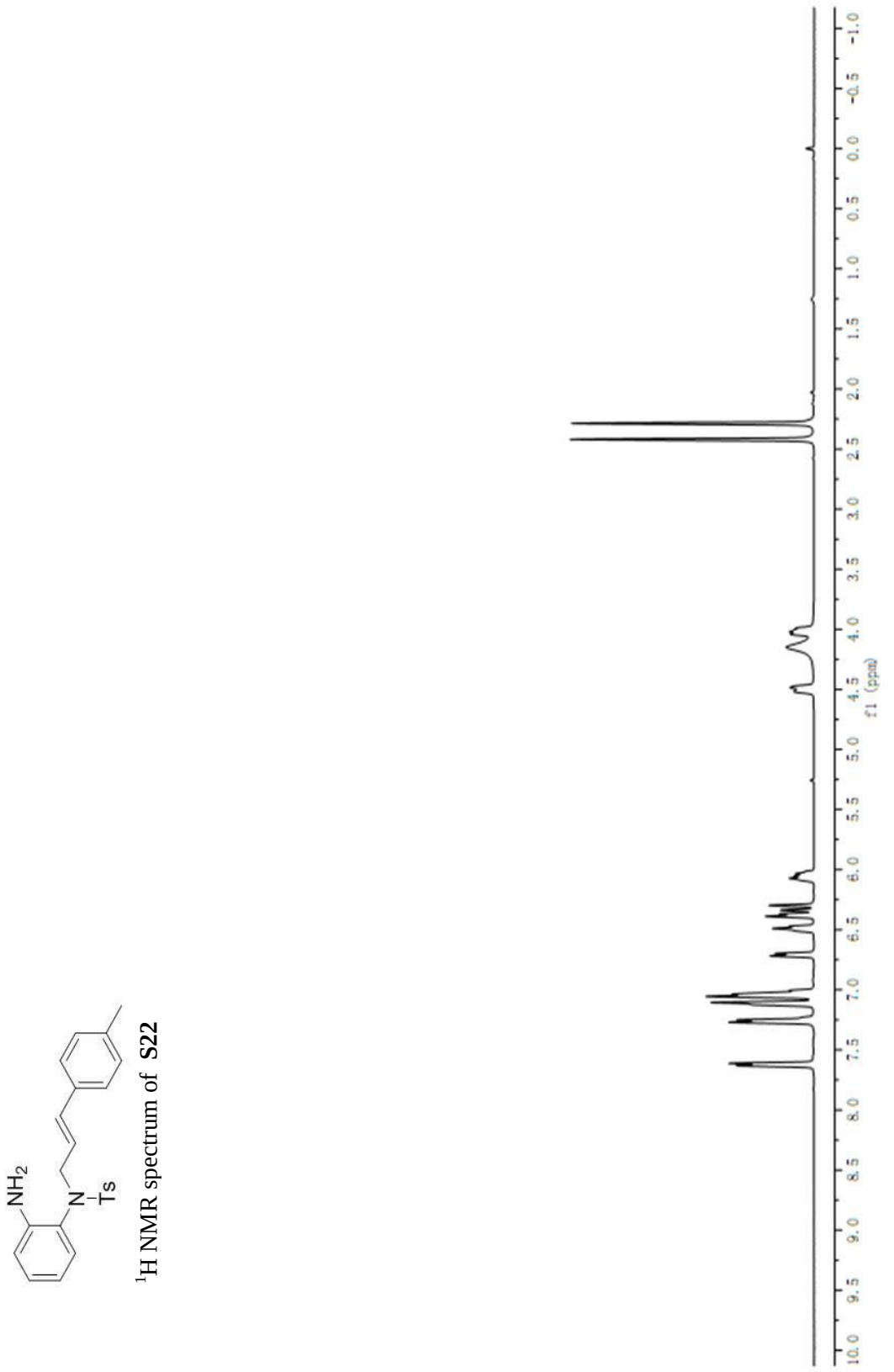
^{1}H NMR spectrum of **S21**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S21**



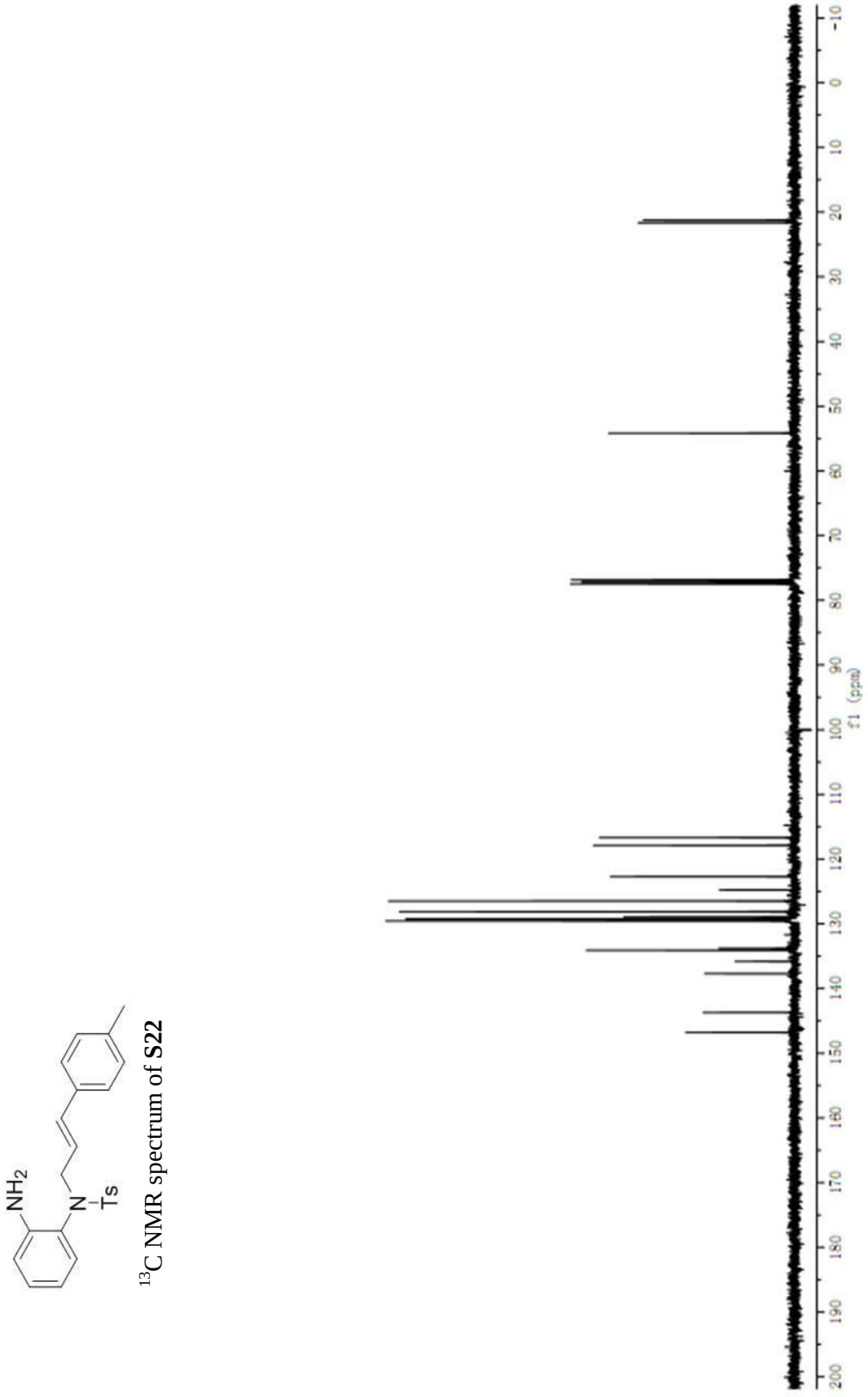
^{13}C NMR spectrum of **S21**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S21**



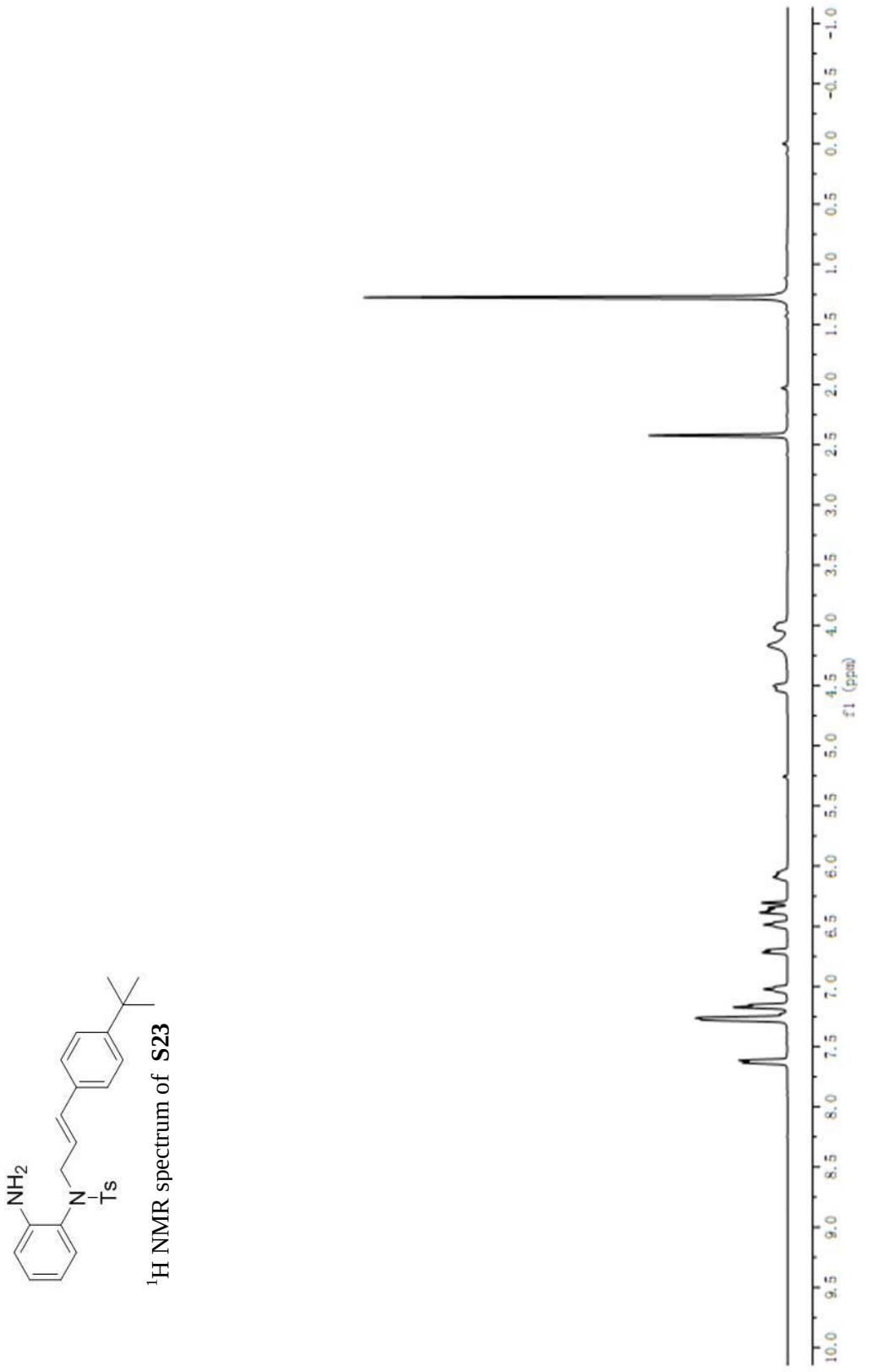
^{1}H NMR spectrum of **S22**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S22**



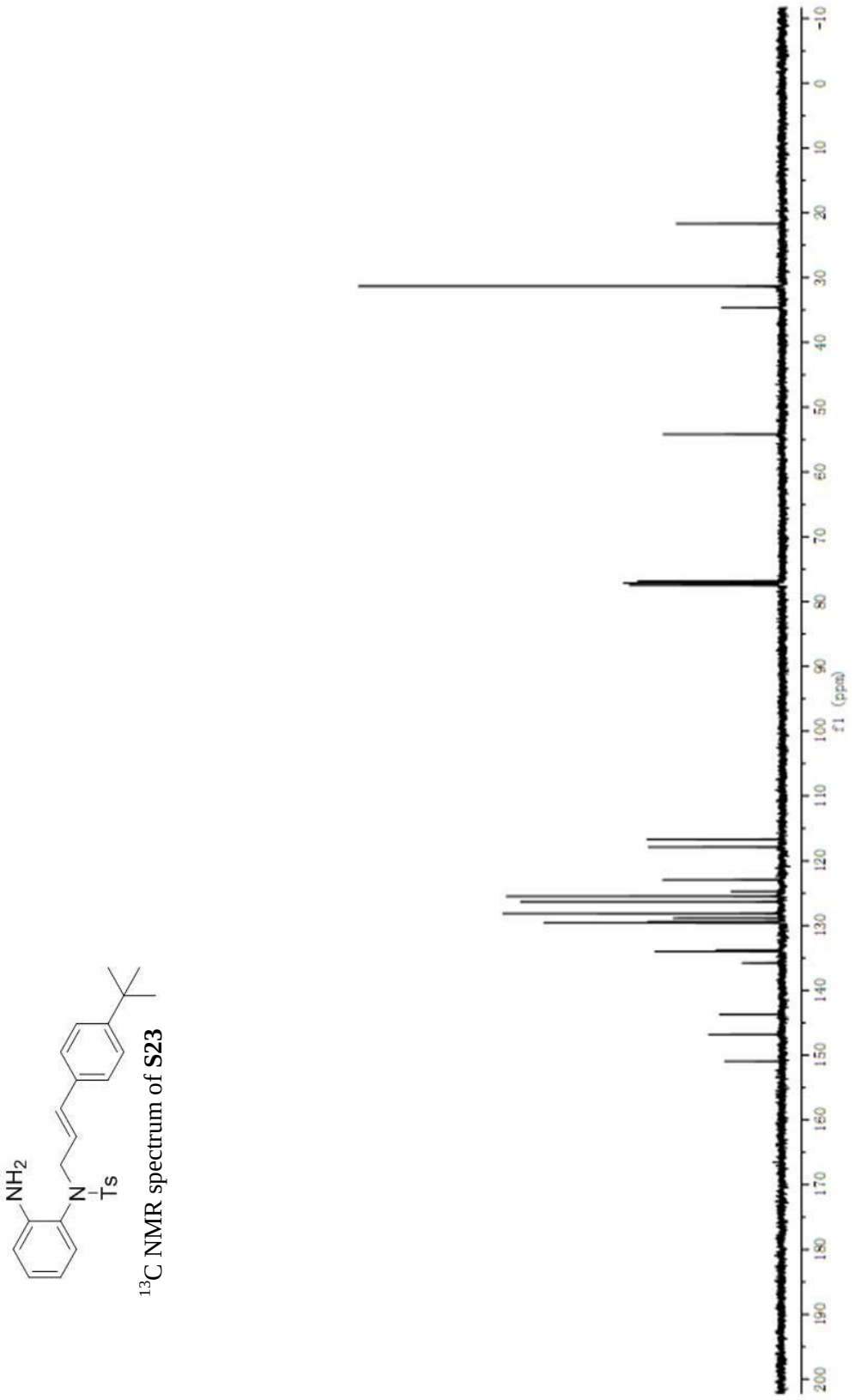
^{13}C NMR spectrum of **S22**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S22**



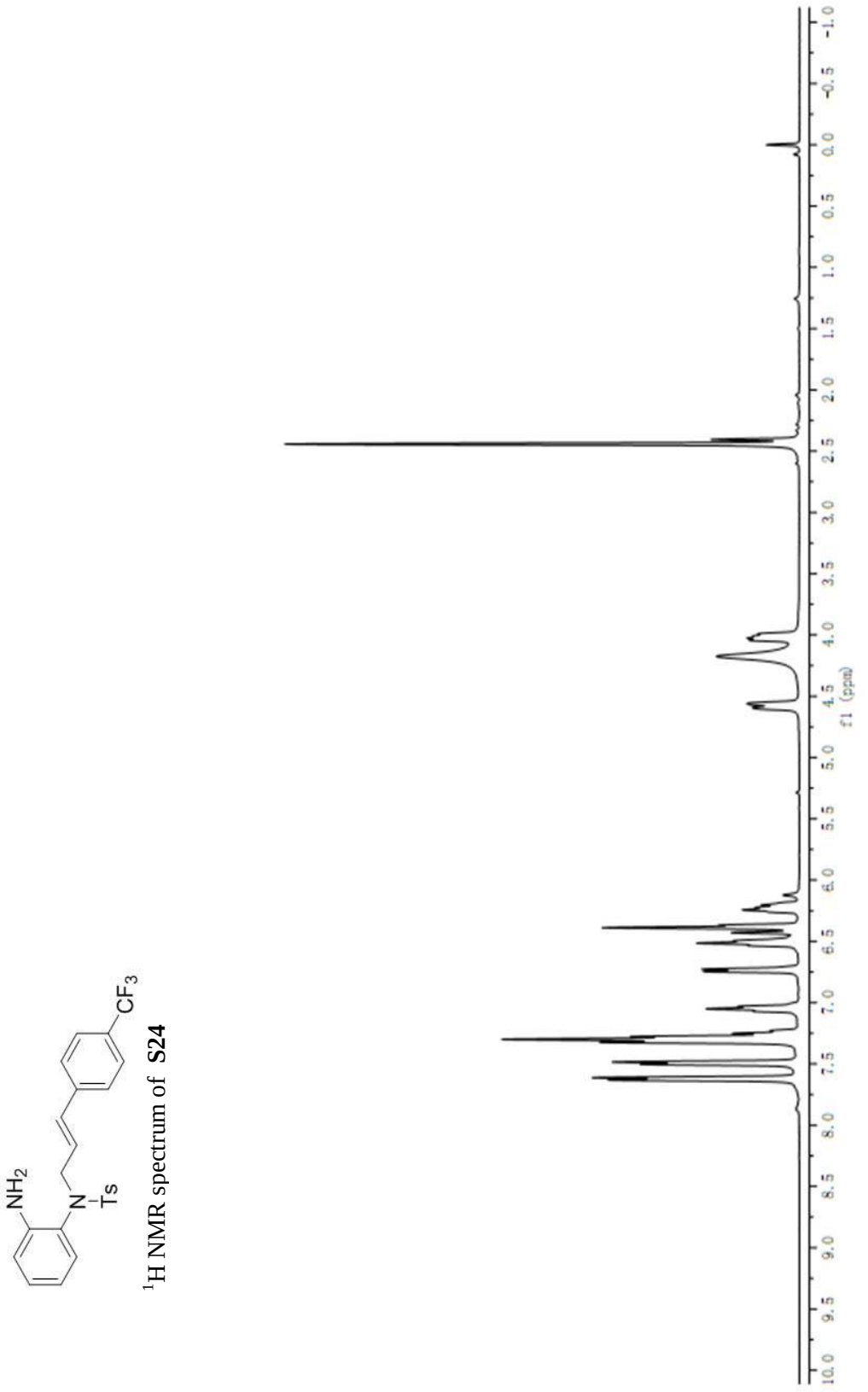
^{1}H NMR spectrum of **S23**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S23**



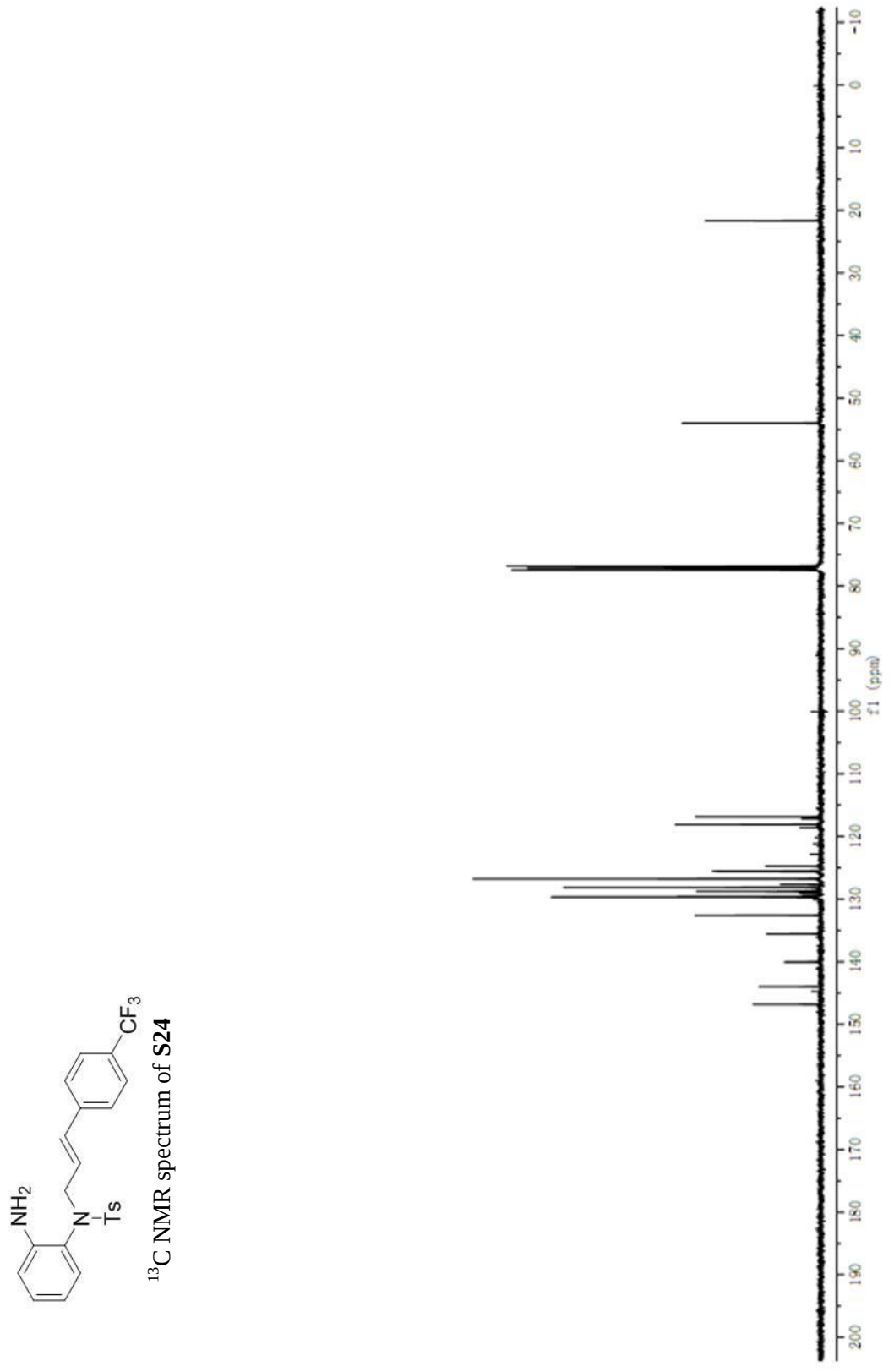
^{13}C NMR spectrum of **S23**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S23**



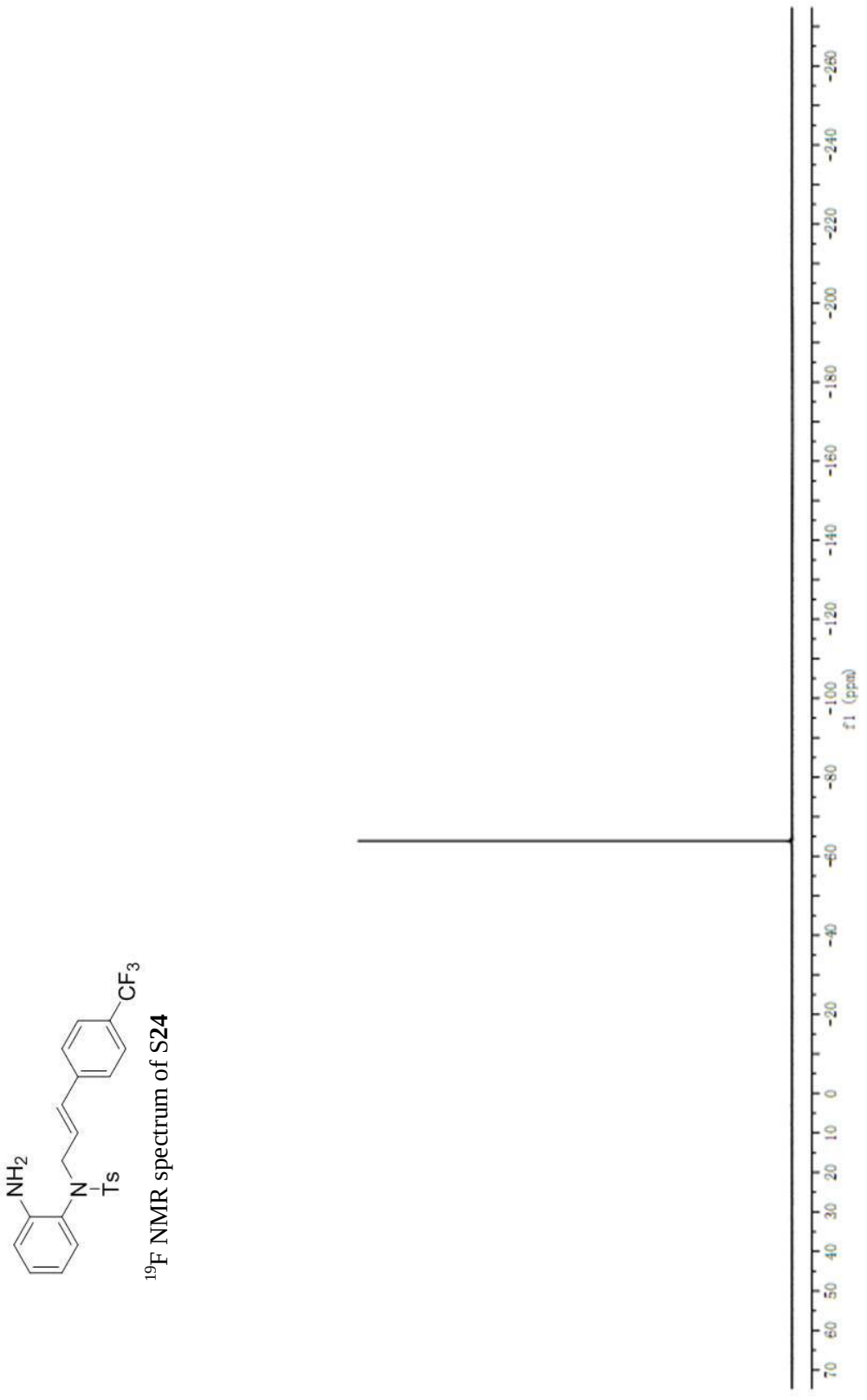
^{1}H NMR spectrum of **S24**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S24**



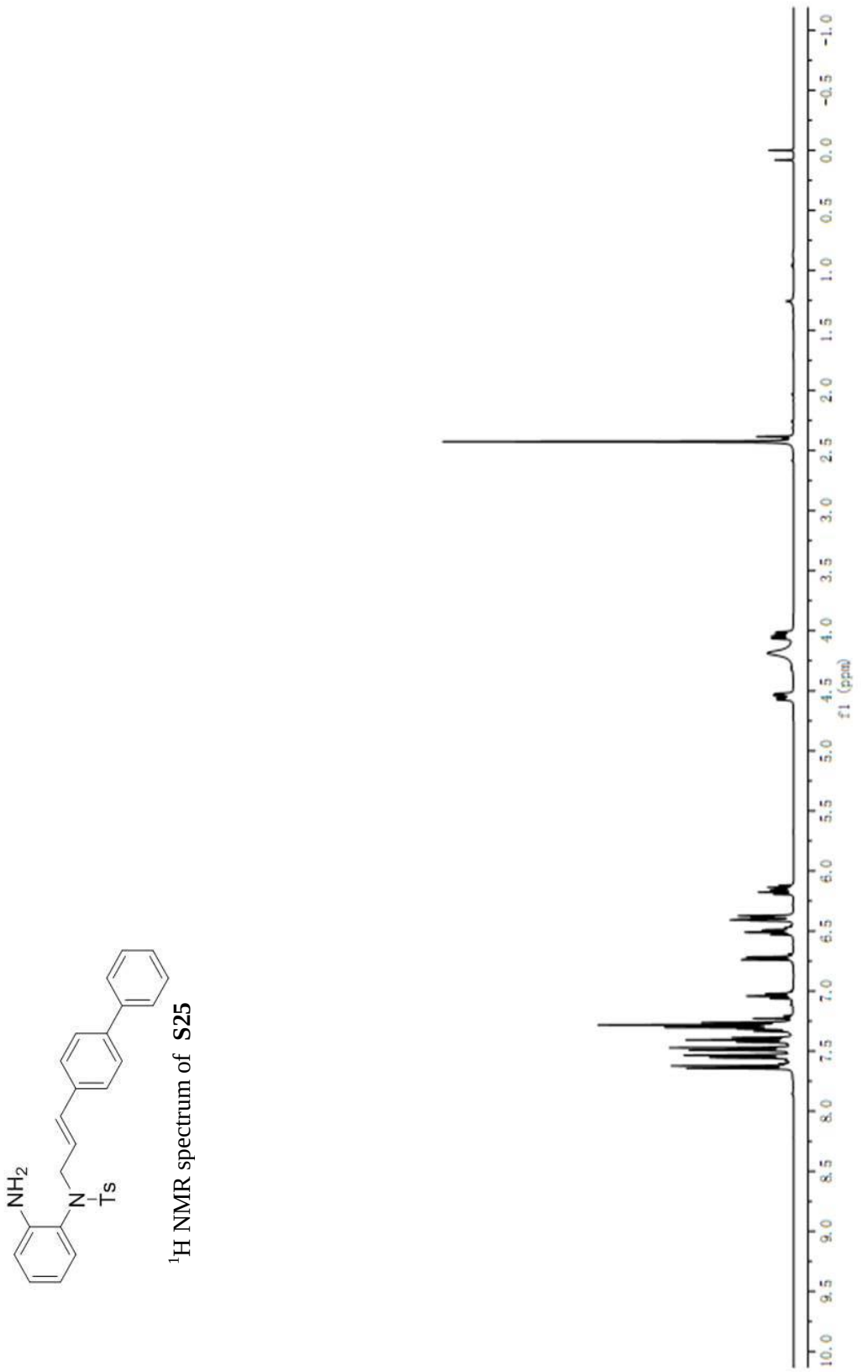
^{13}C NMR spectrum of **S24**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S24**



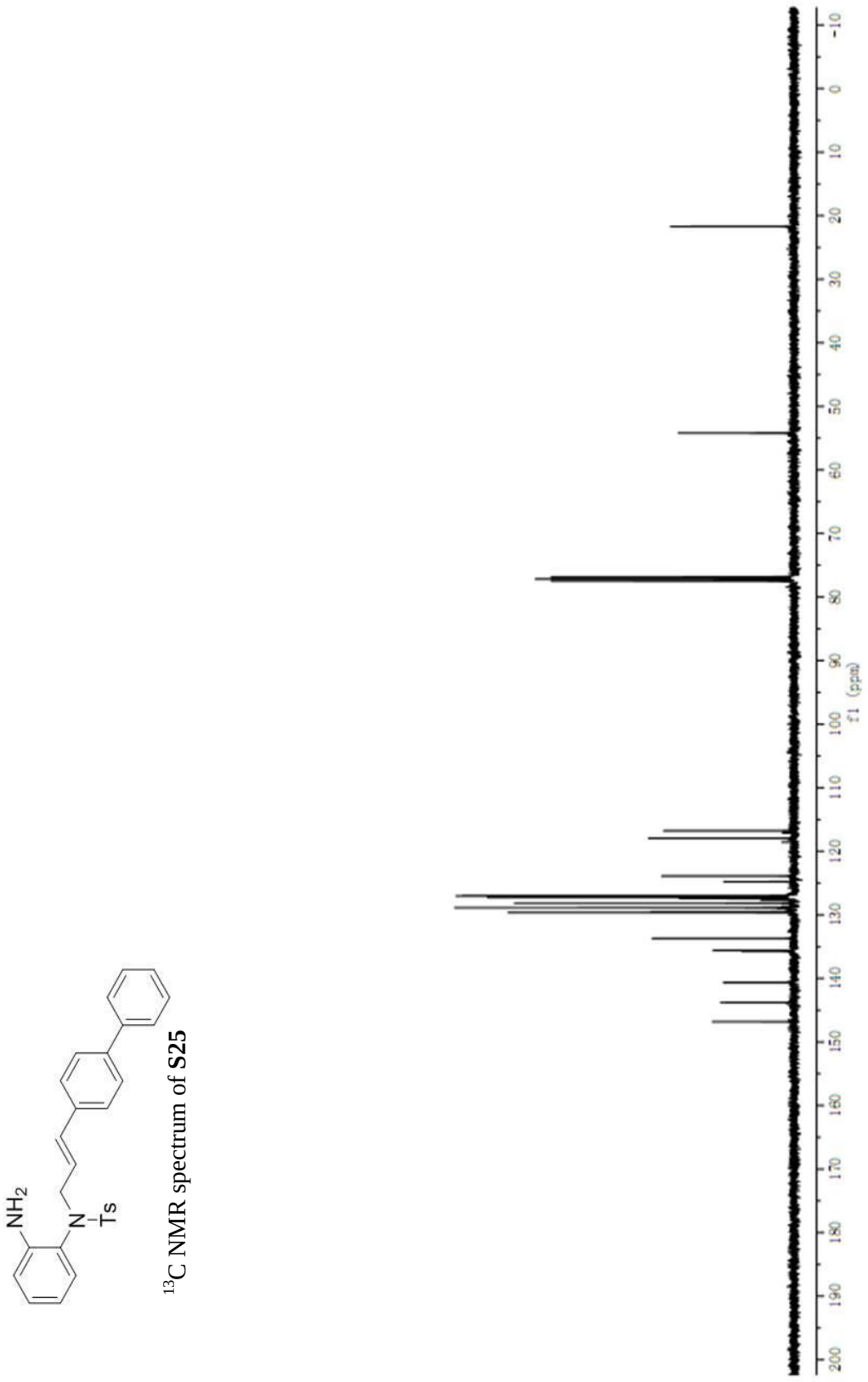
^{19}F NMR spectrum of S**24**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of S**24**



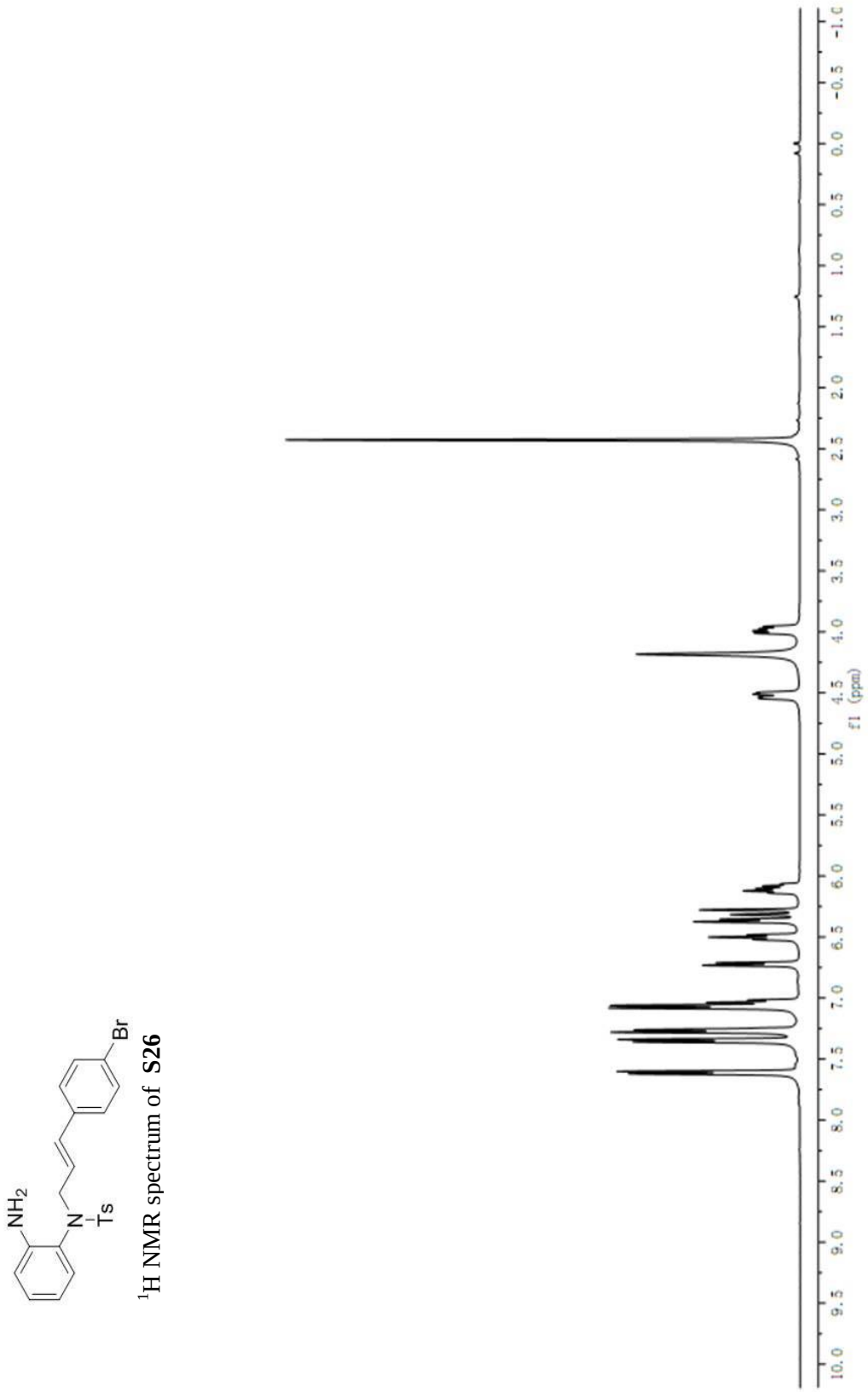
^{1}H NMR spectrum of **S25**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S25**



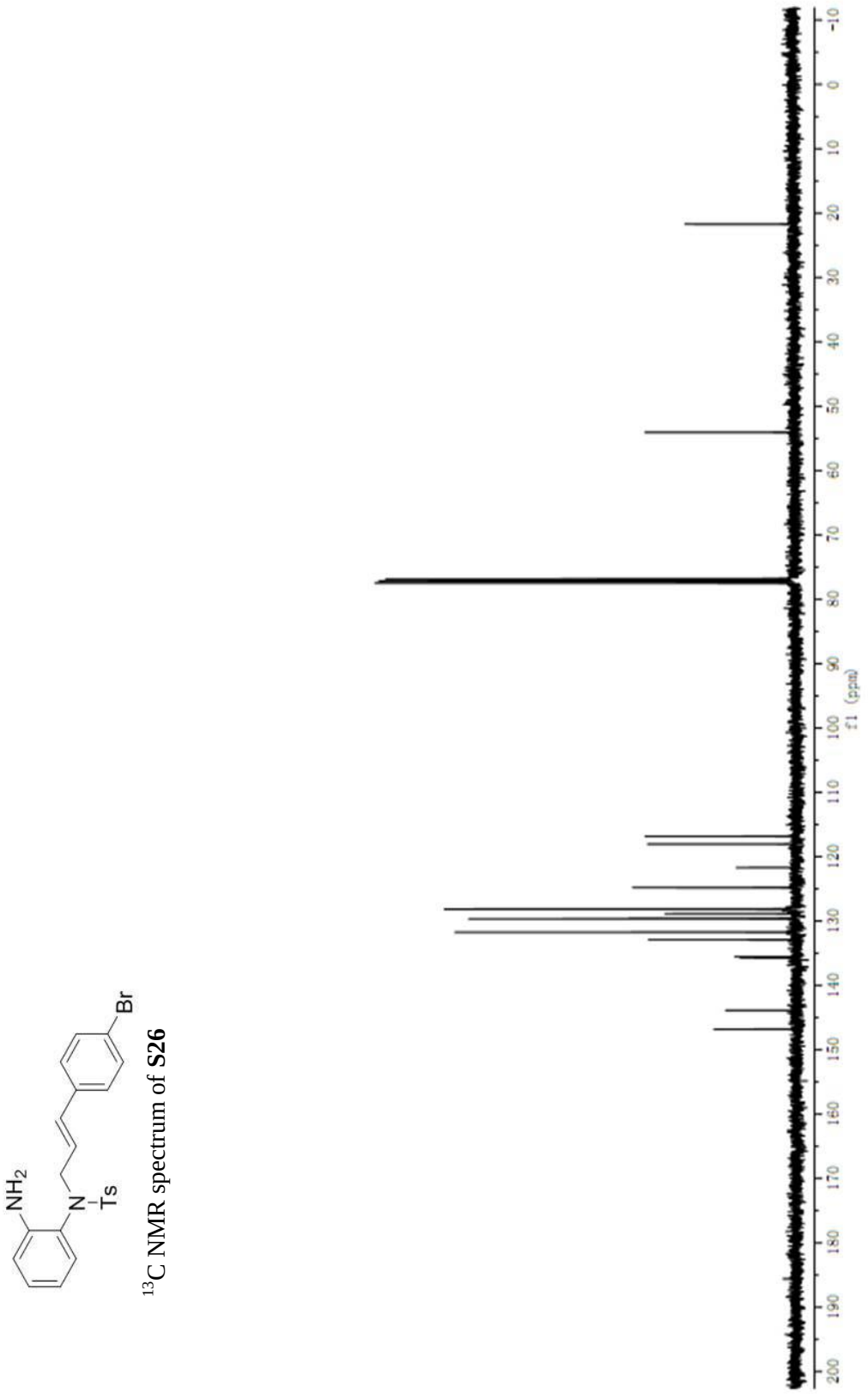
^{13}C NMR spectrum of **S25**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S25**



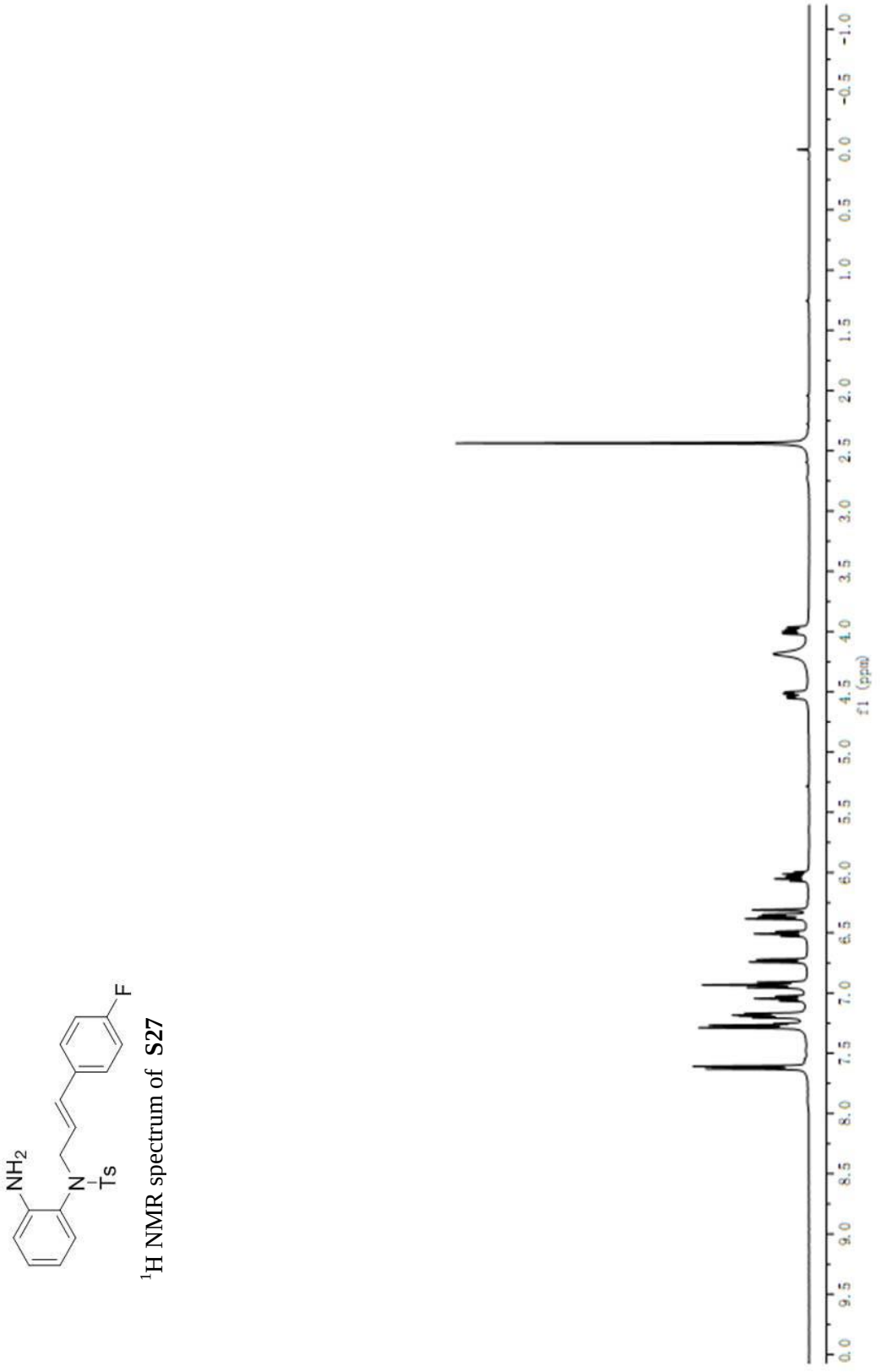
^{1}H NMR spectrum of **S26**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S26**



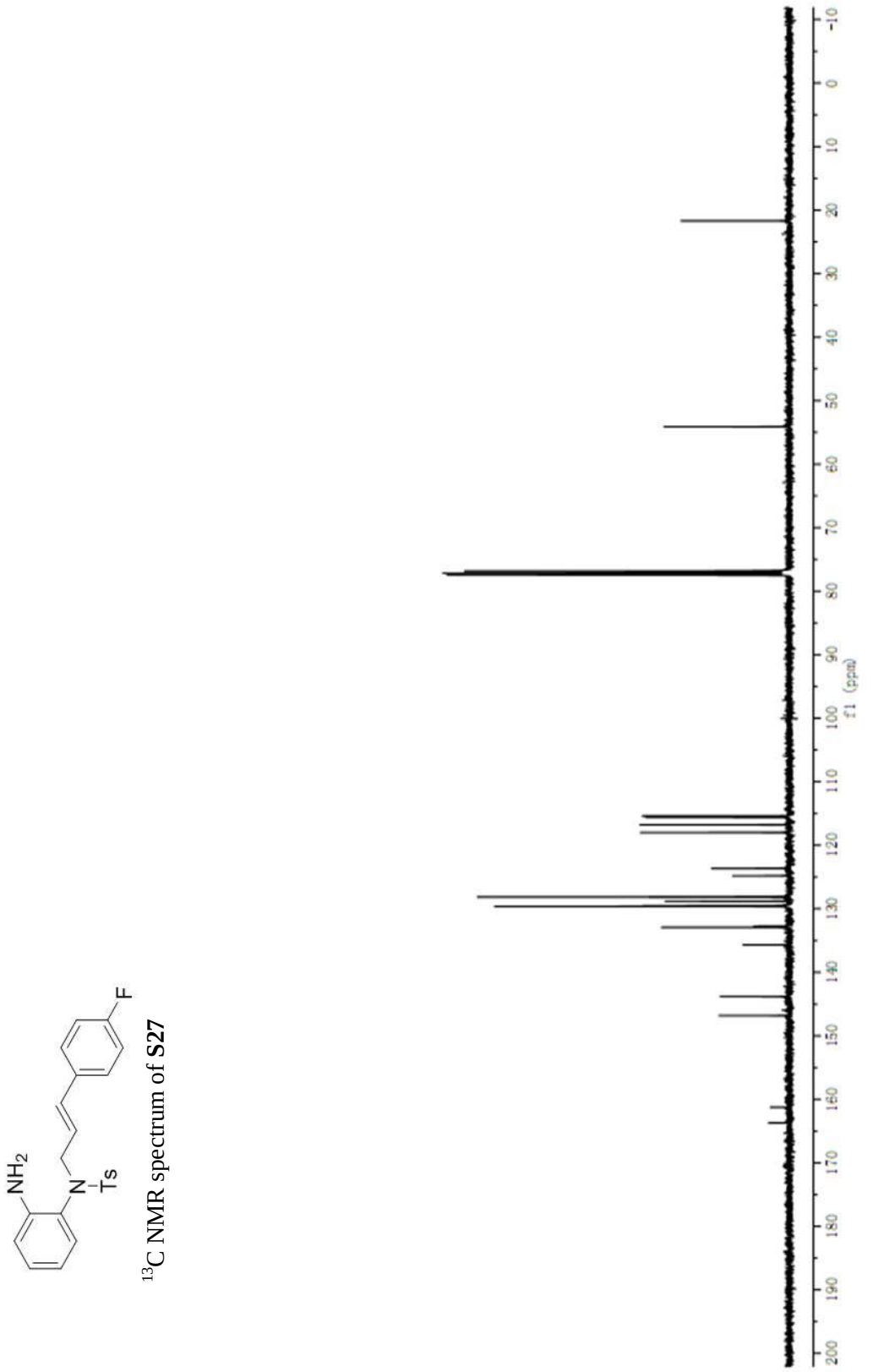
^{13}C NMR spectrum of **S26**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S26**



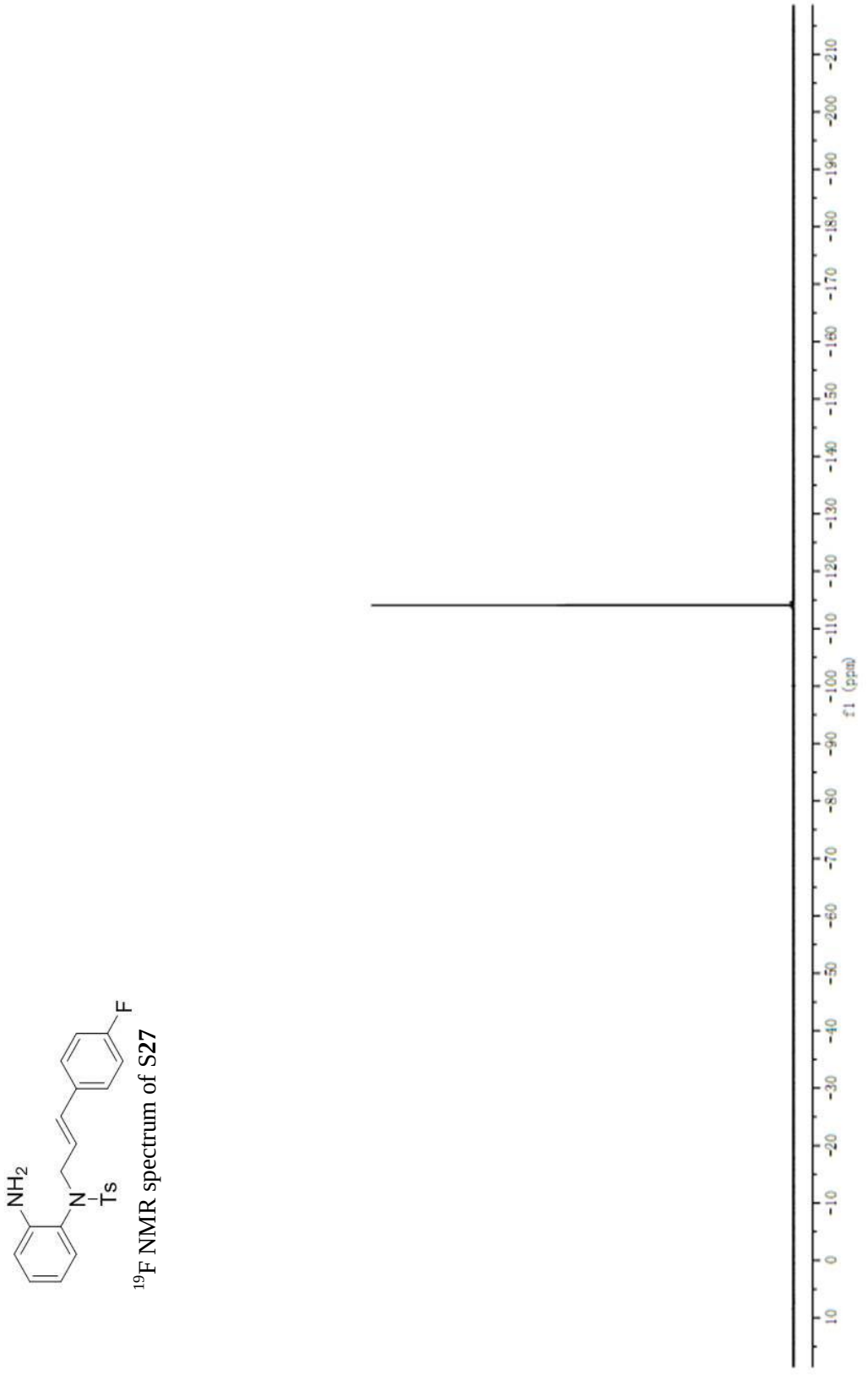
^{1}H NMR spectrum of **S27**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **S27**



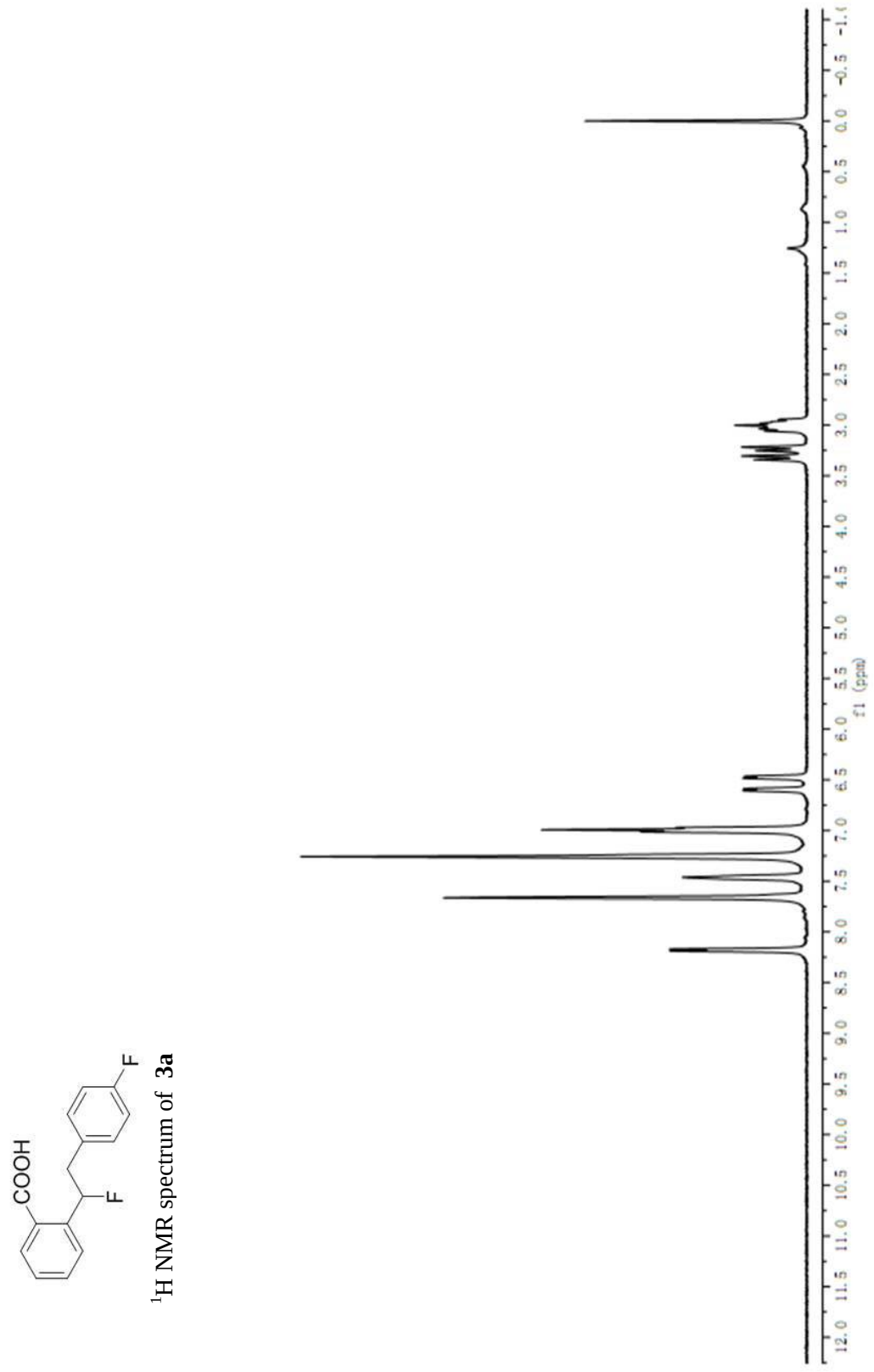
^{13}C NMR spectrum of **S27**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **S27**



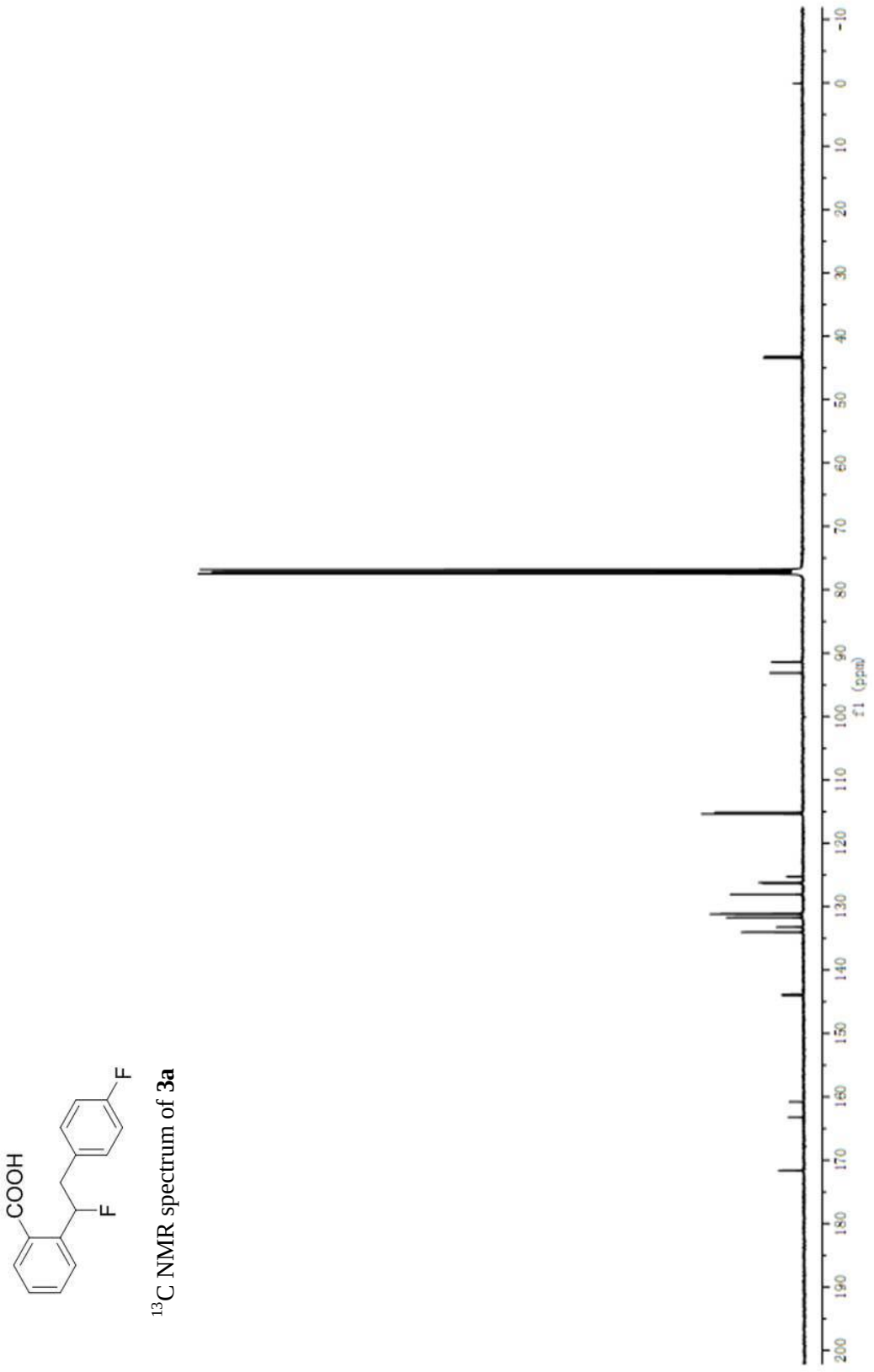
^{19}F NMR spectrum of **S27**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **S27**

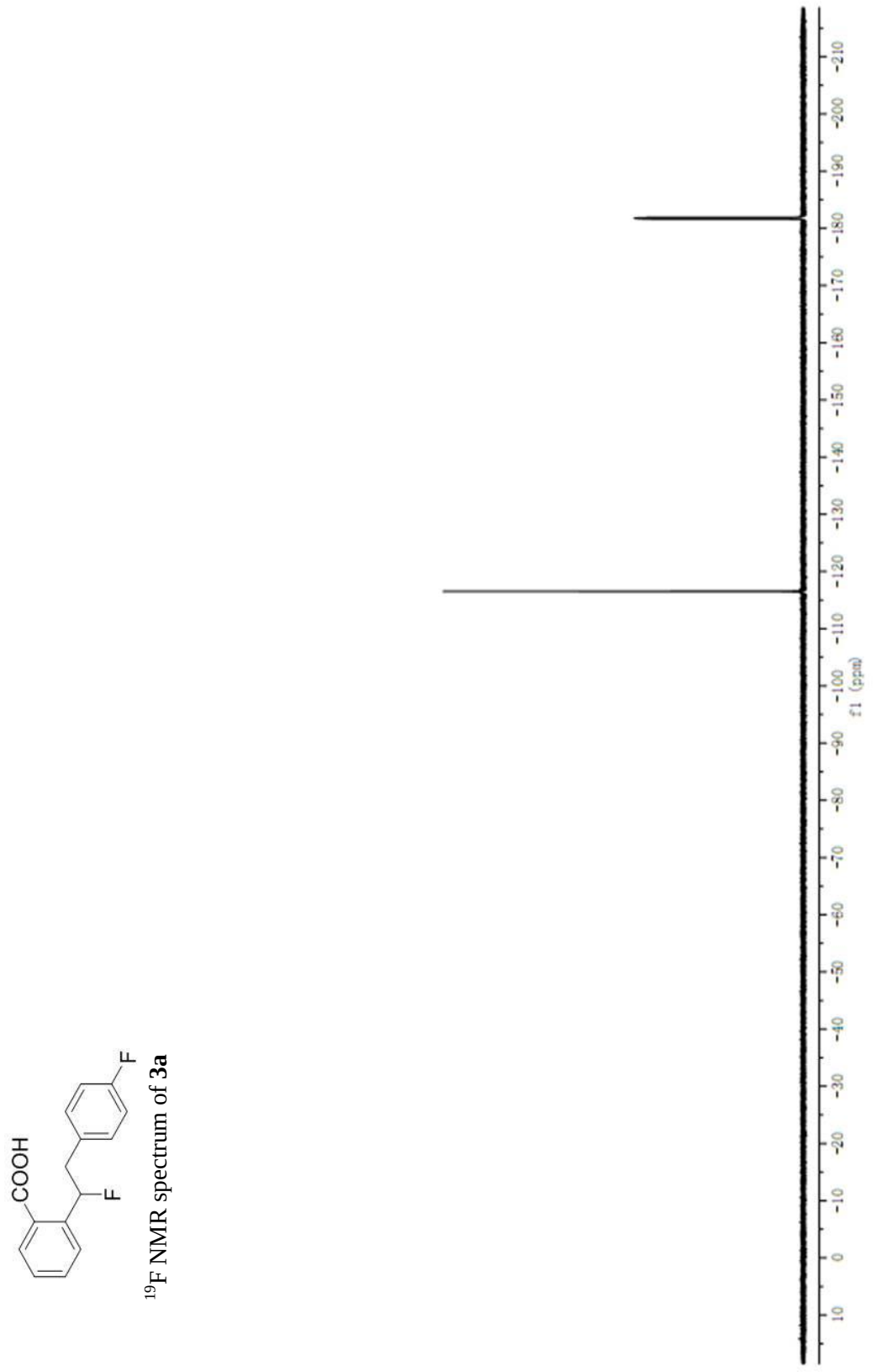


^{1}H NMR spectrum of **3a**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3a**

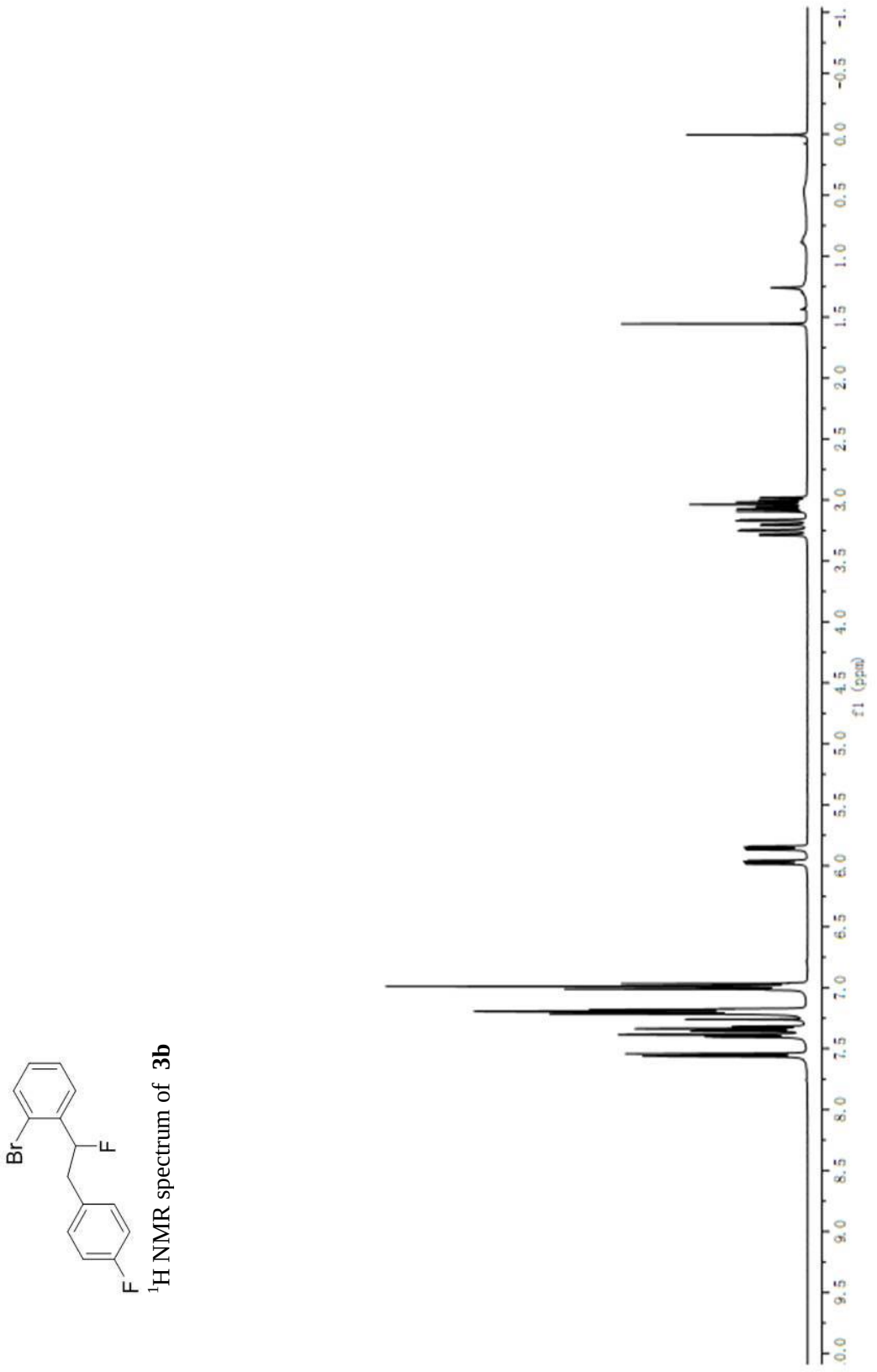


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3a**



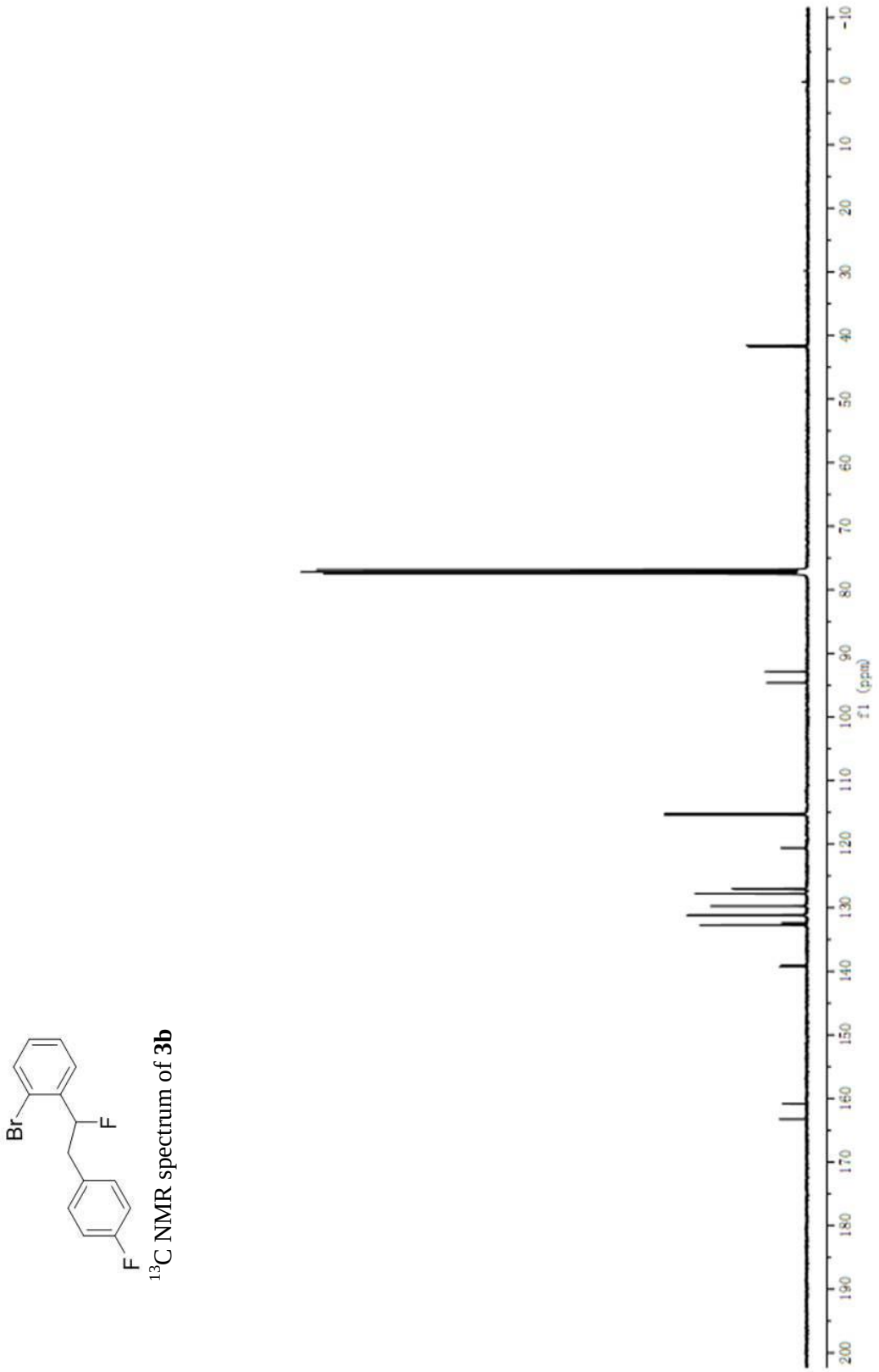
^{19}F NMR spectrum of **3a**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3a**



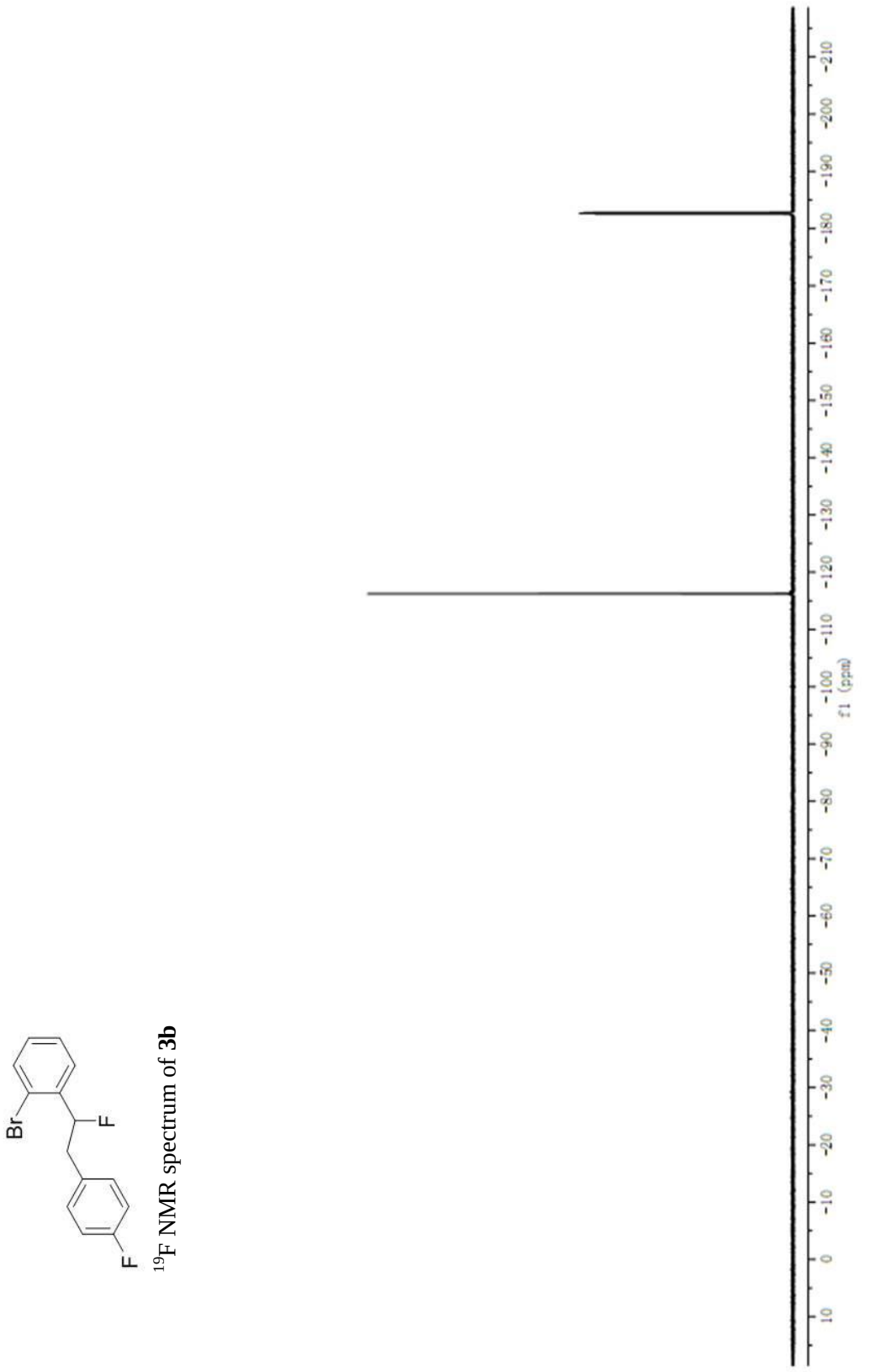
^{1}H NMR spectrum of **3b**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3b**



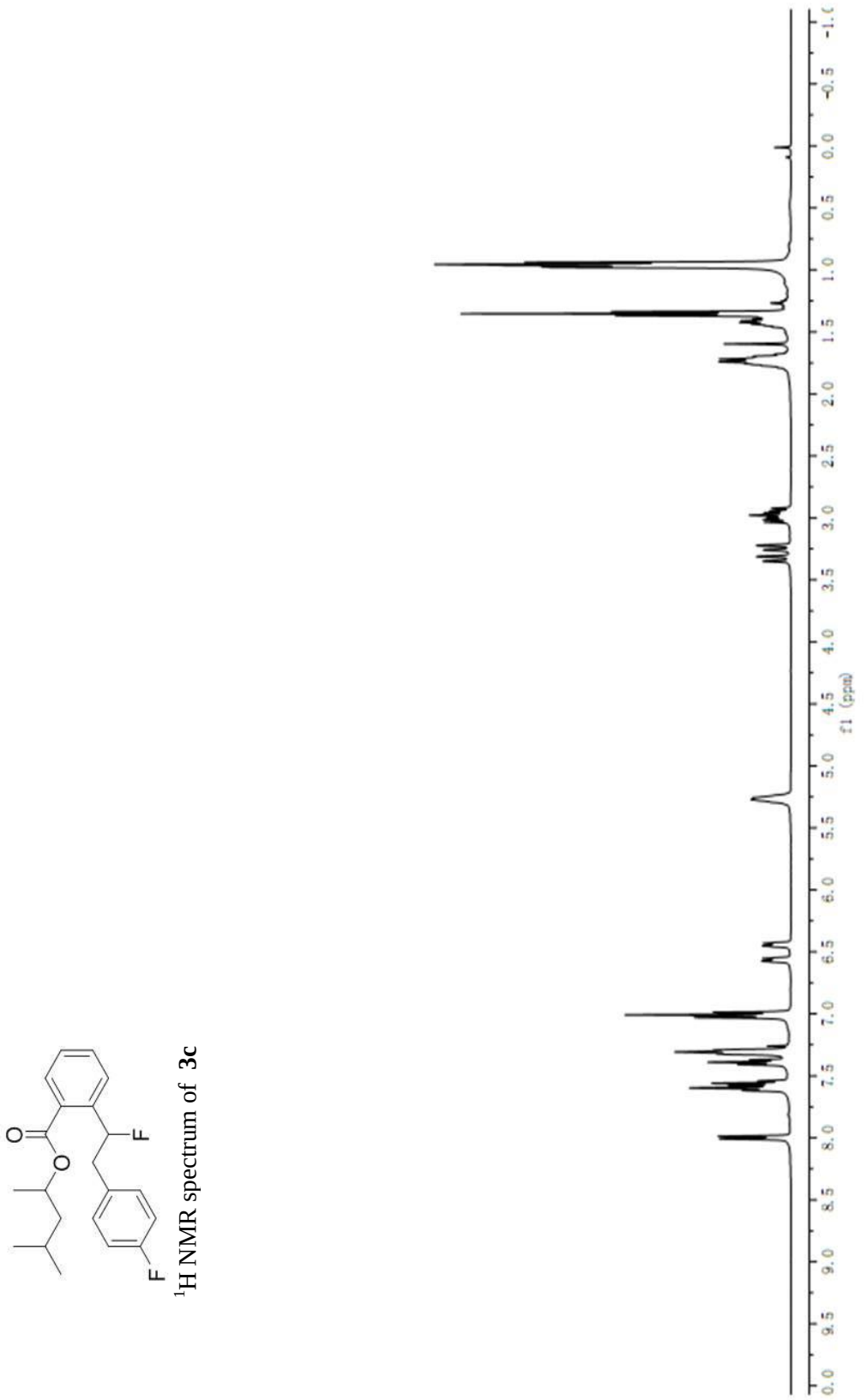
^{13}C NMR spectrum of **3b**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3b**



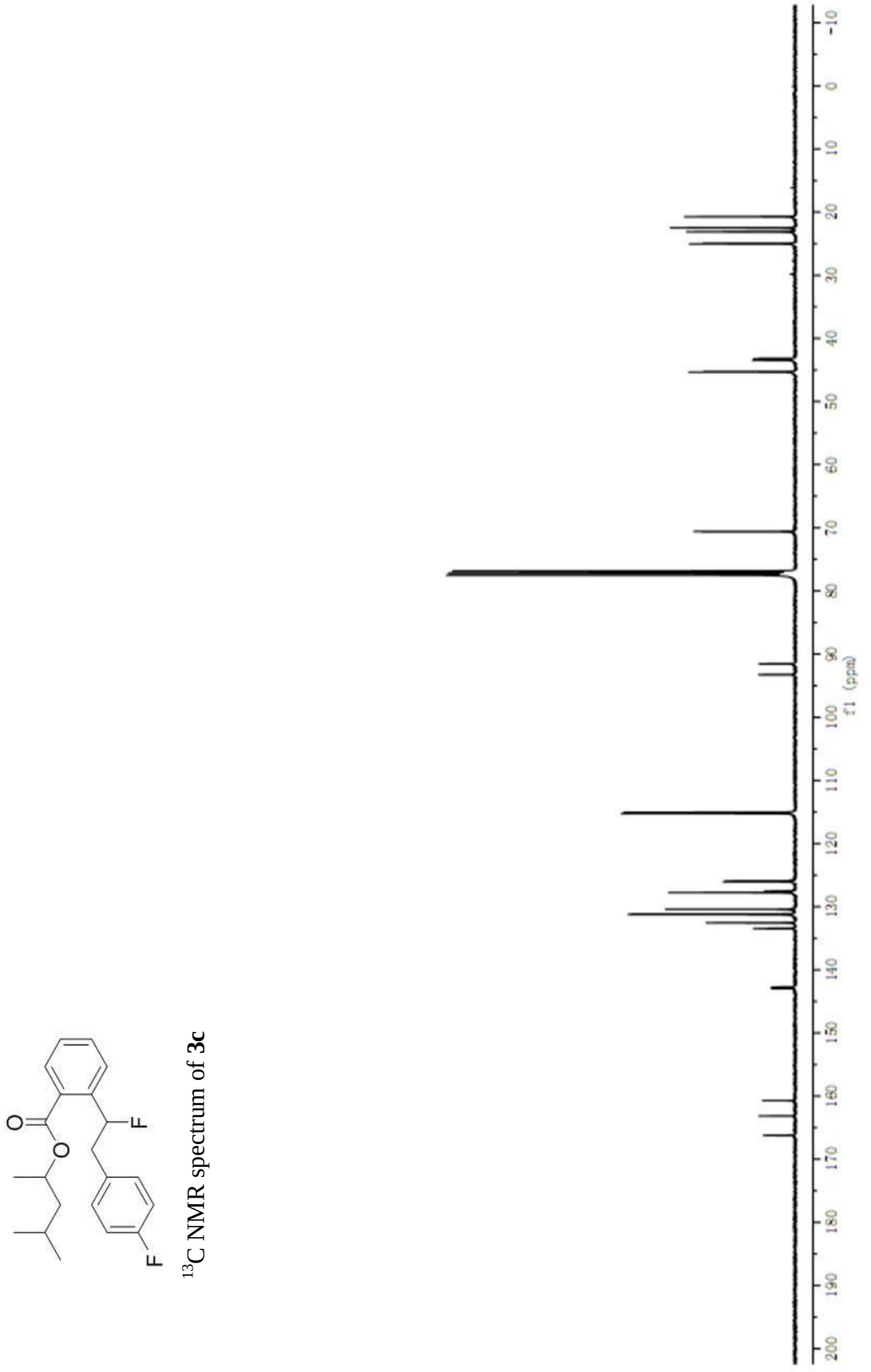
^{19}F NMR spectrum of **3b**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3b**



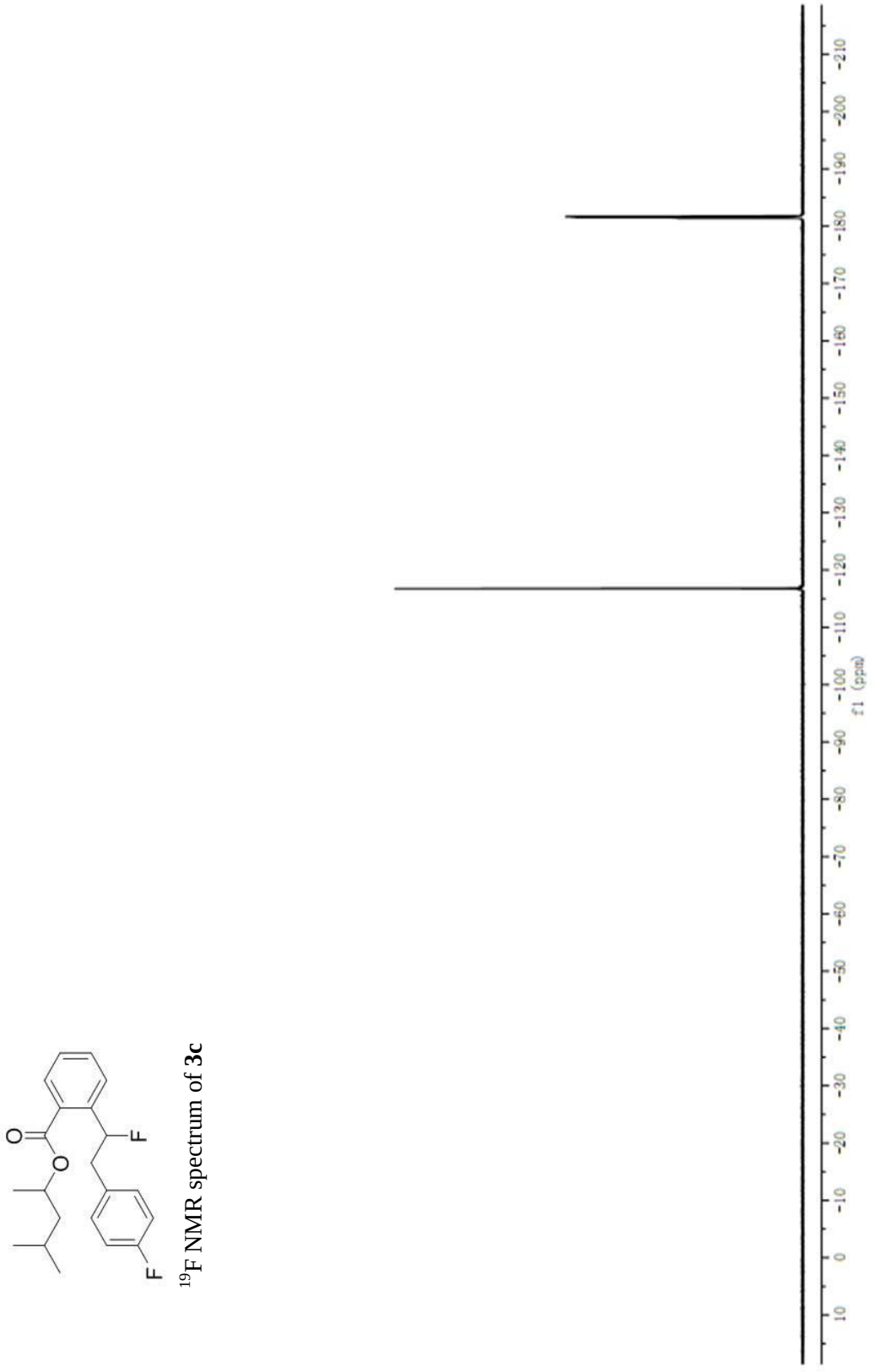
^{1}H NMR spectrum of **3c**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3c**



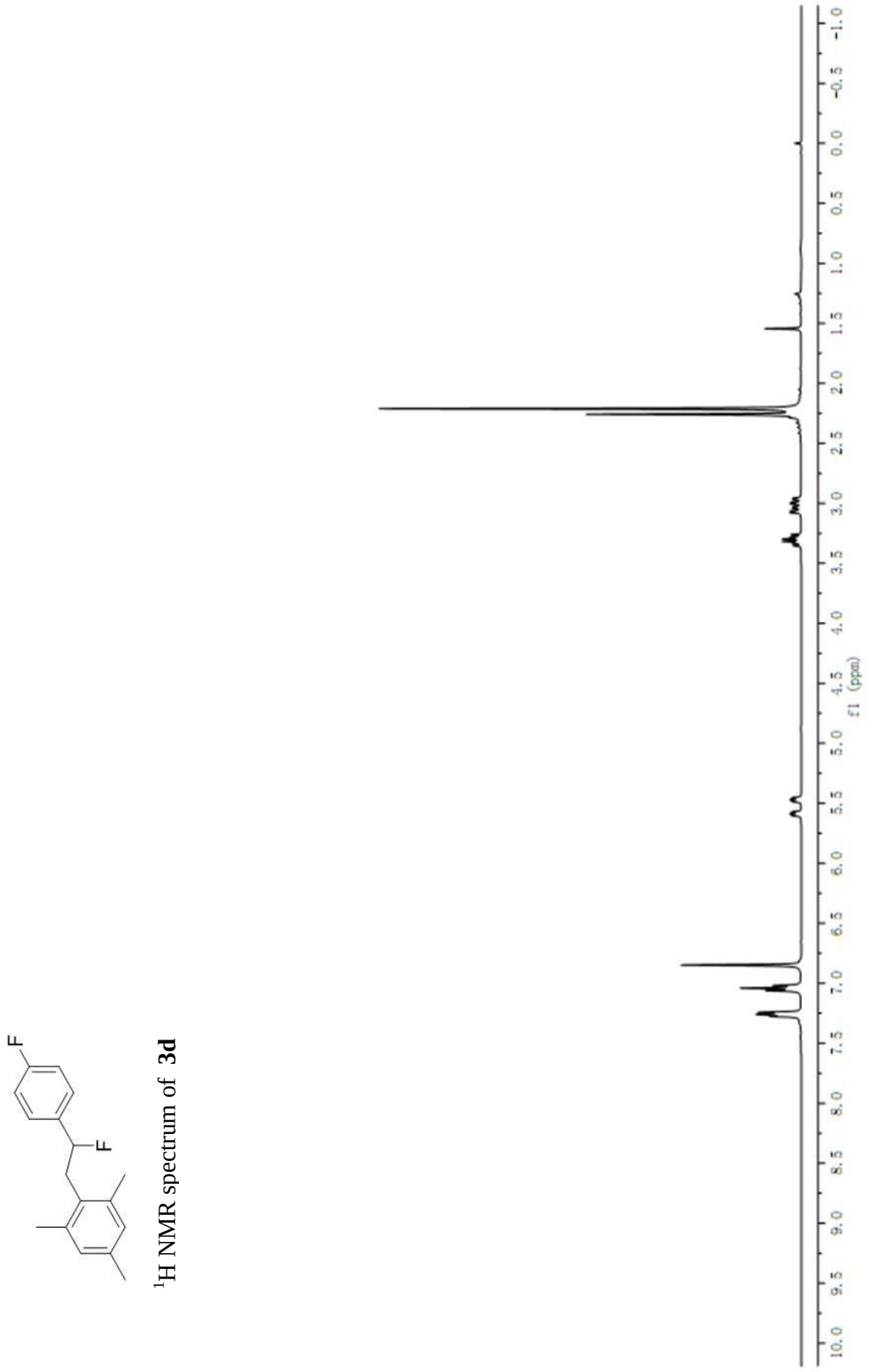
^{13}C NMR spectrum of **3c**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3c**

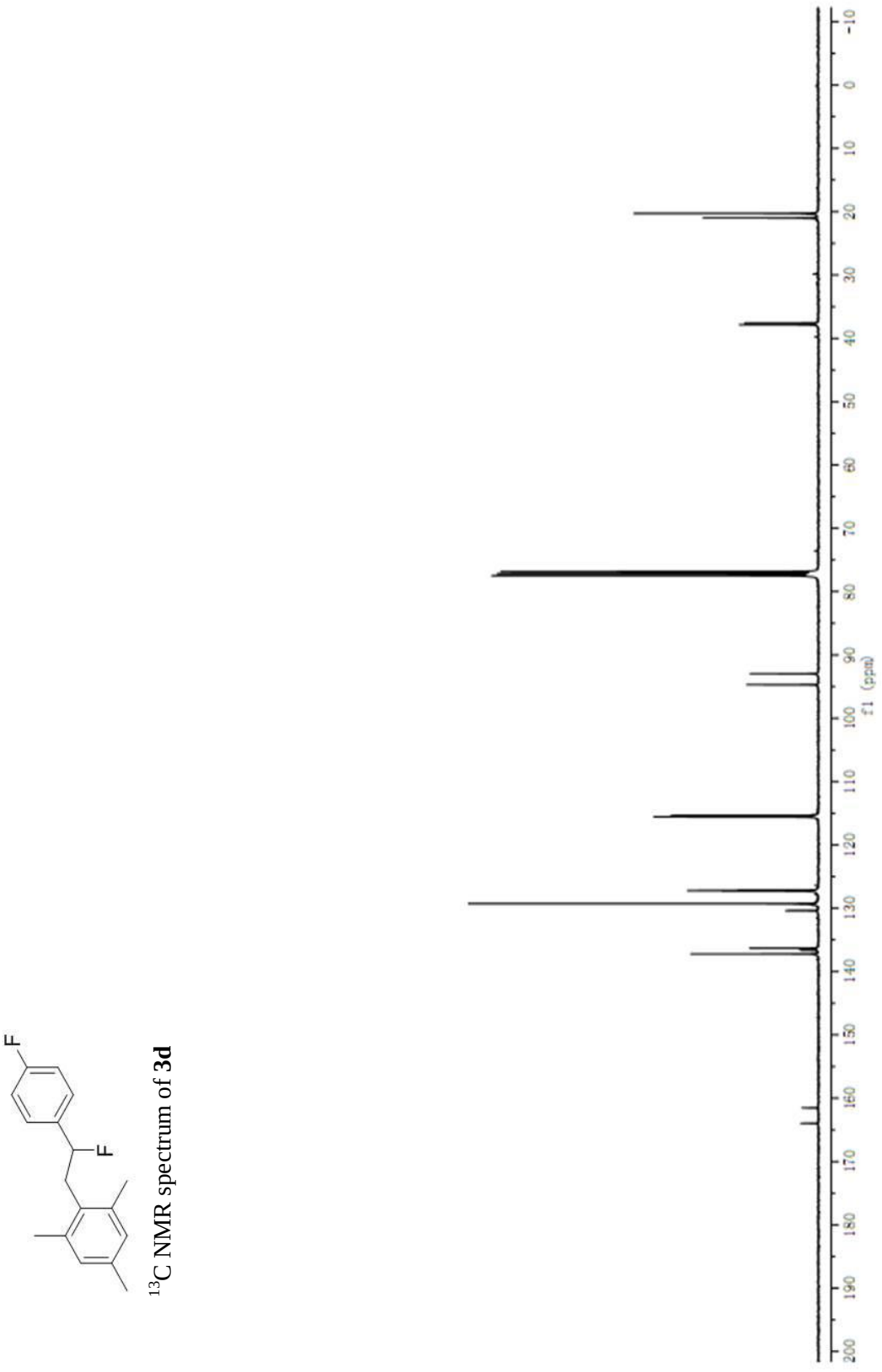


^{19}F NMR spectrum of **3c**

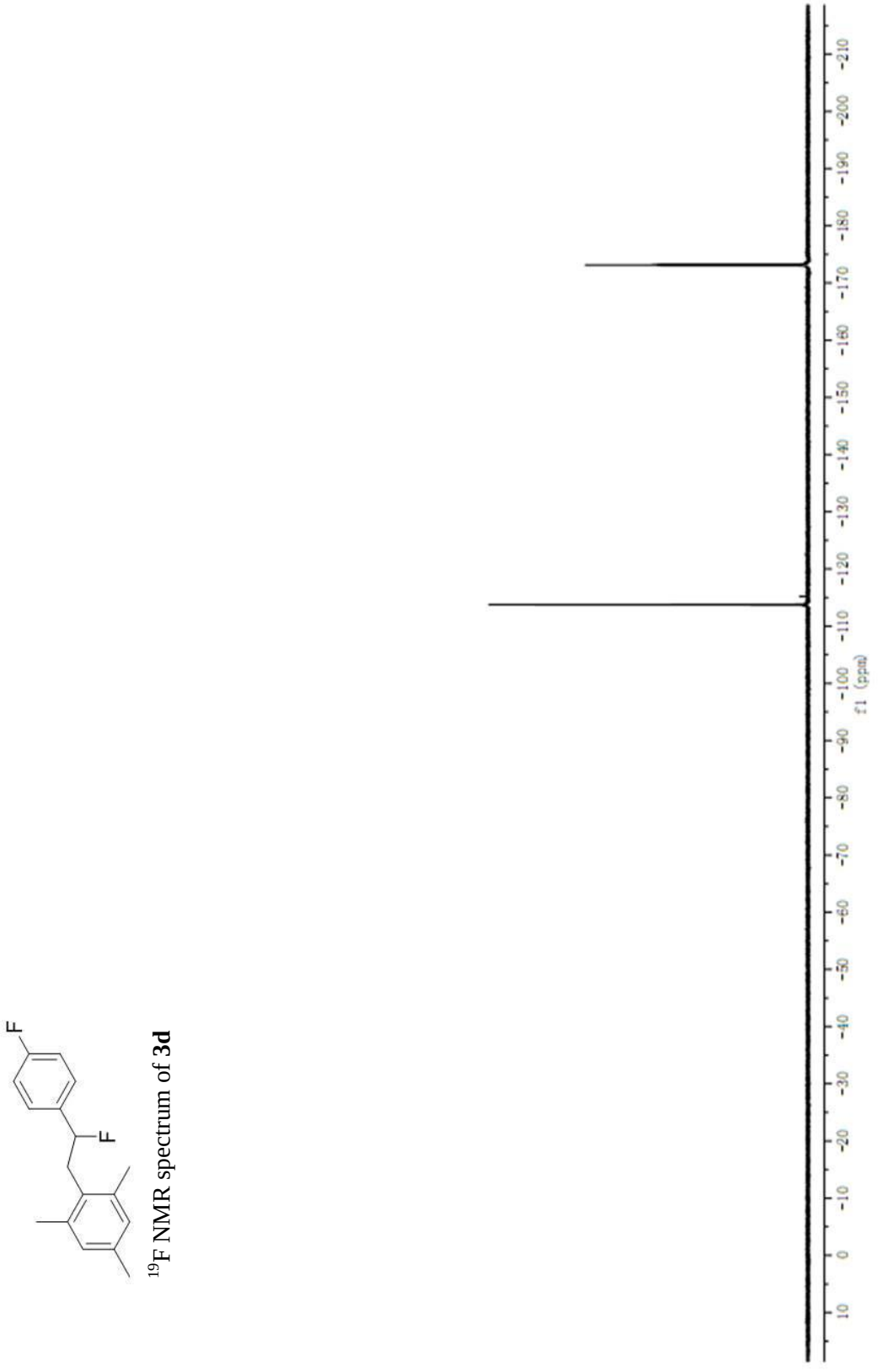
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3c**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3d**

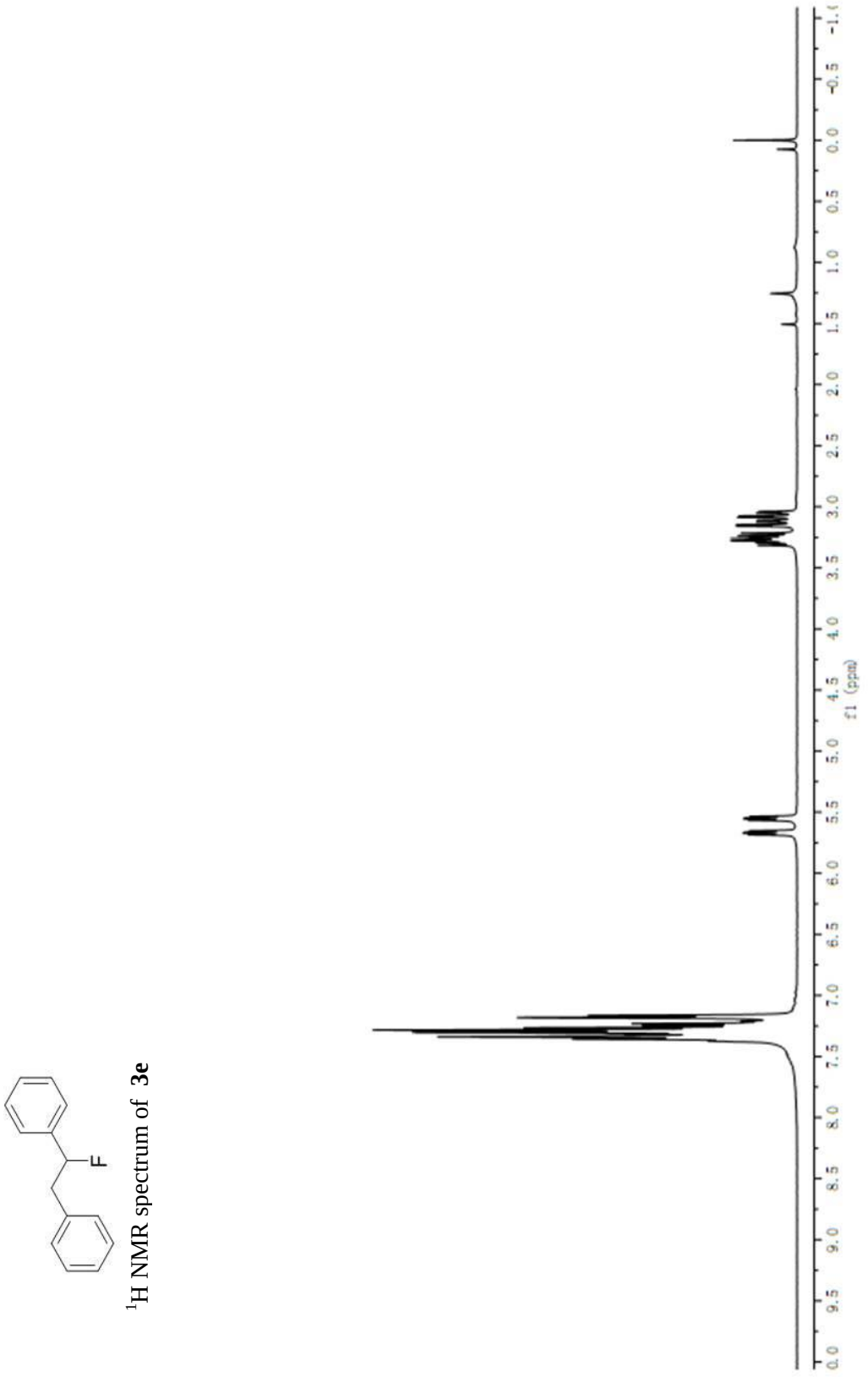


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3d**



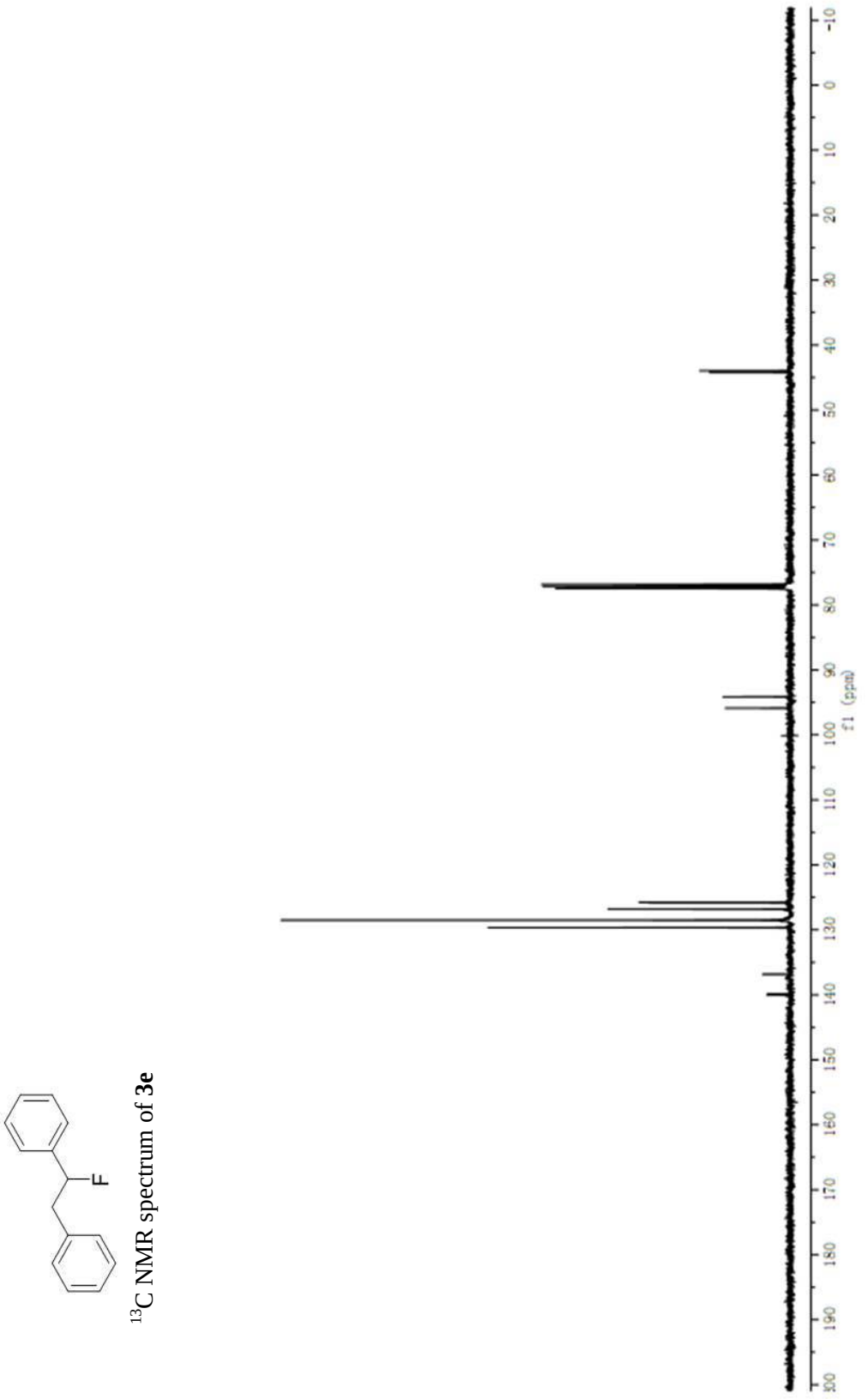
^{19}F NMR spectrum of **3d**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3d**

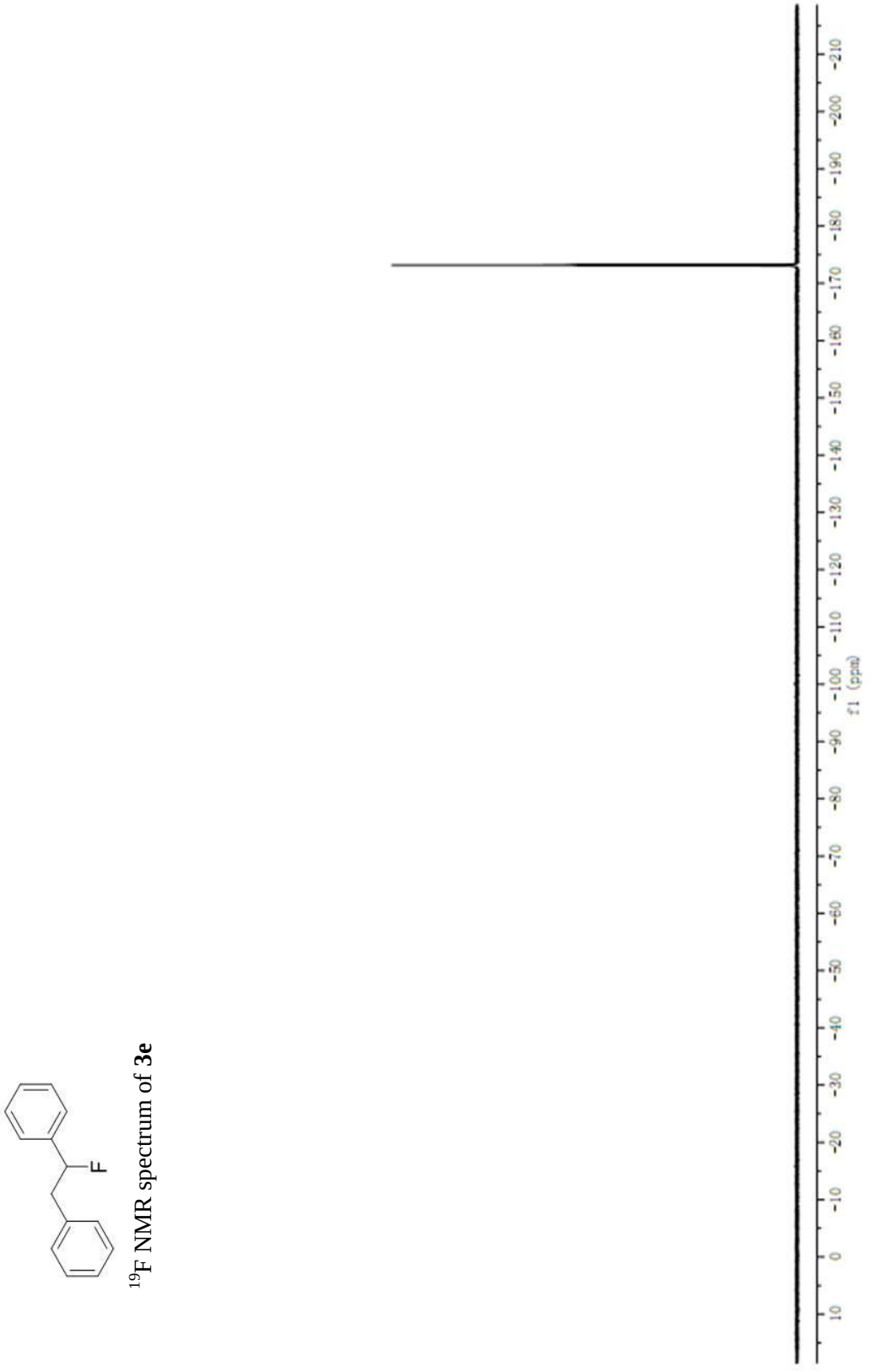


^{1}H NMR spectrum of **3e**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3e**

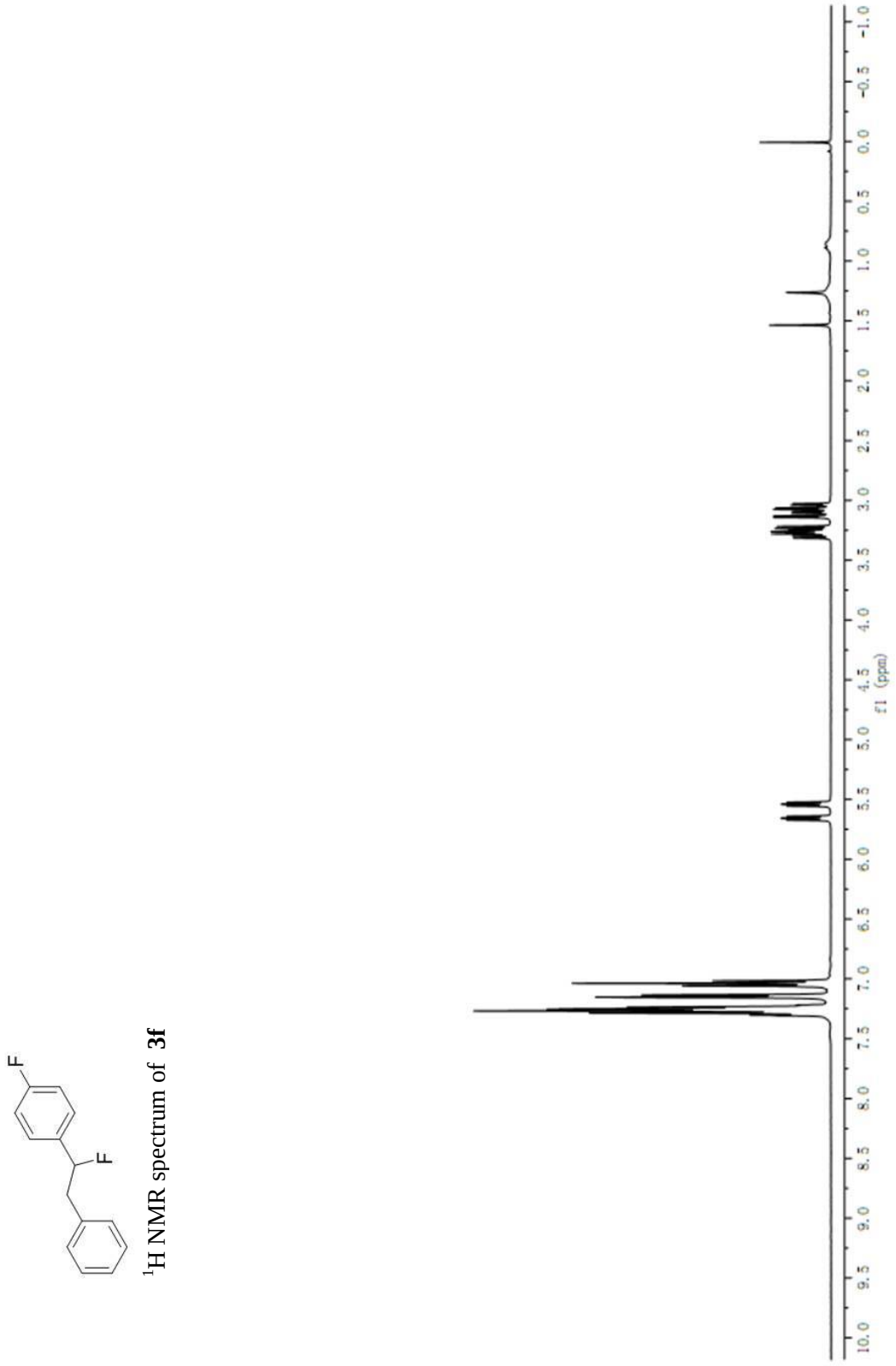


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3e**



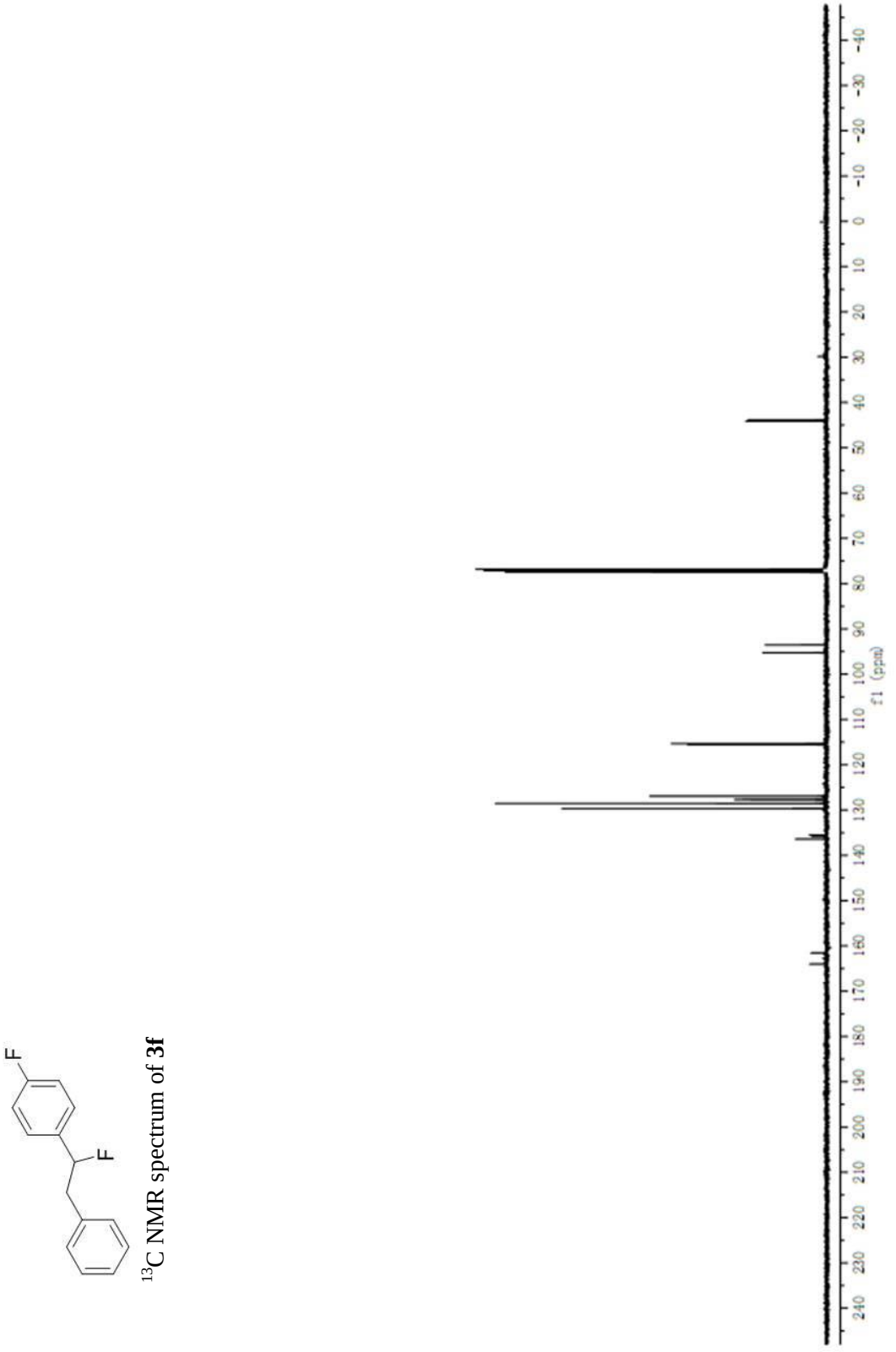
^{19}F NMR spectrum of **3e**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3e**

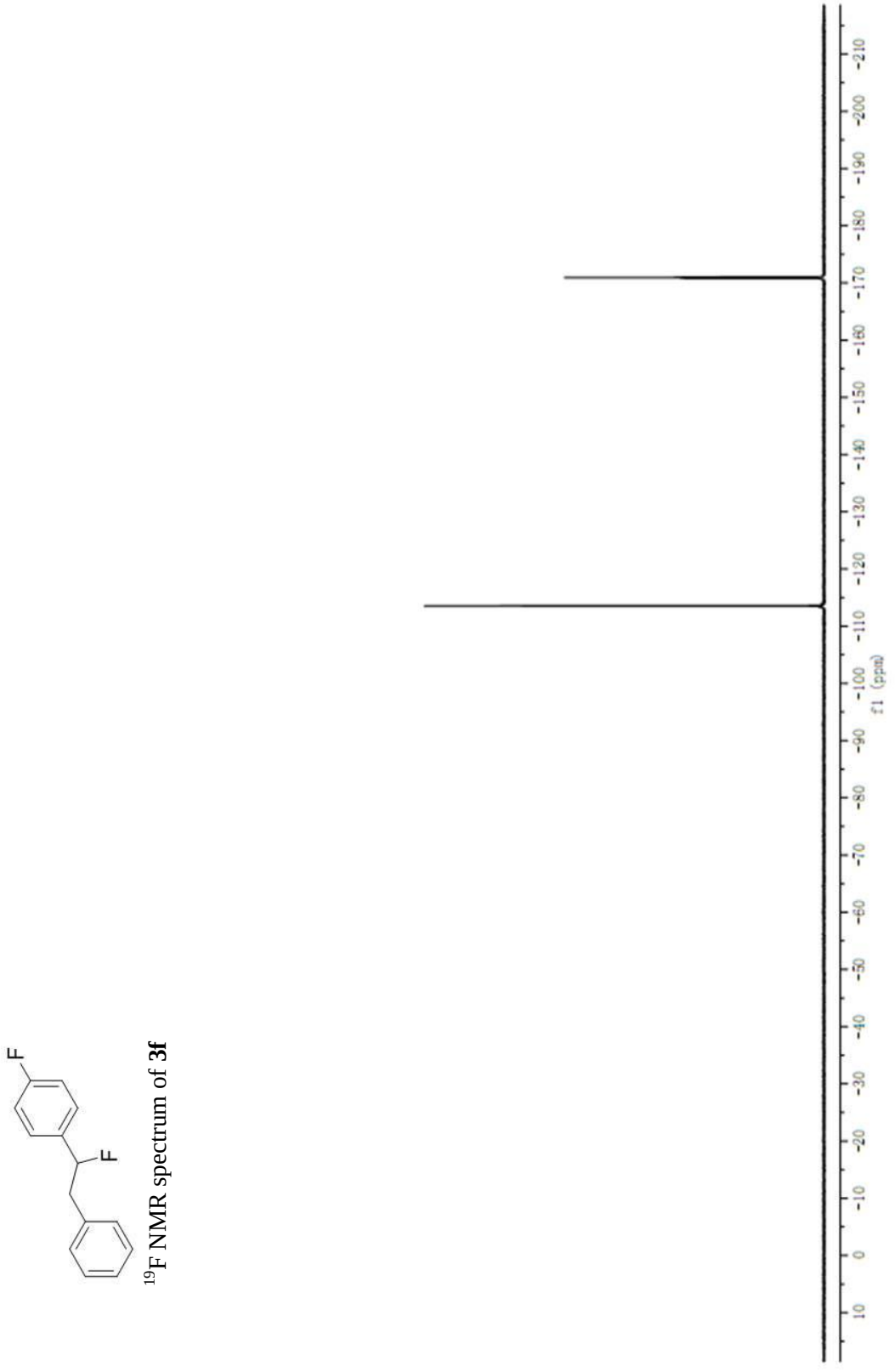


^{1}H NMR spectrum of **3f**

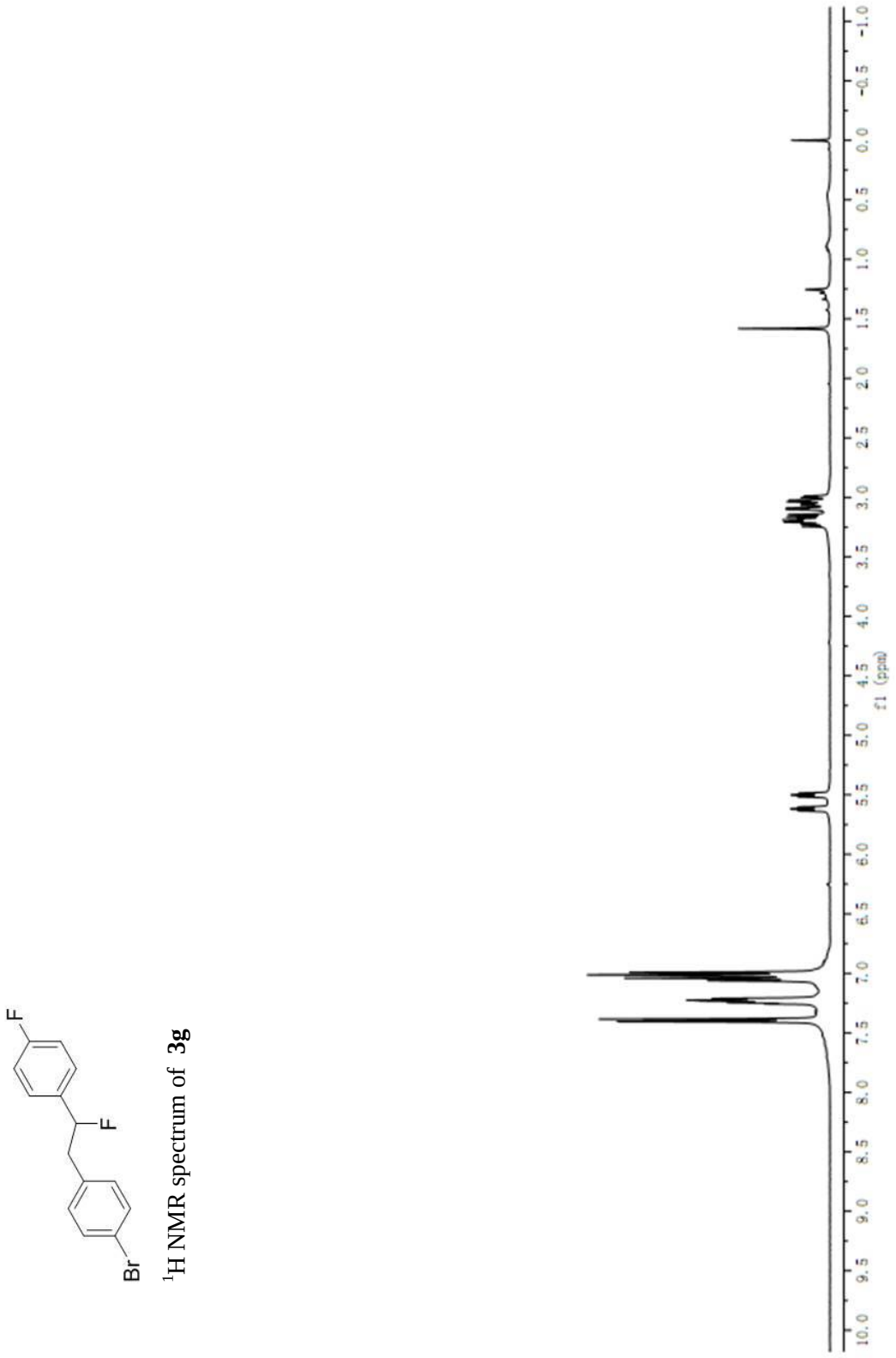
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3f**



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3f**

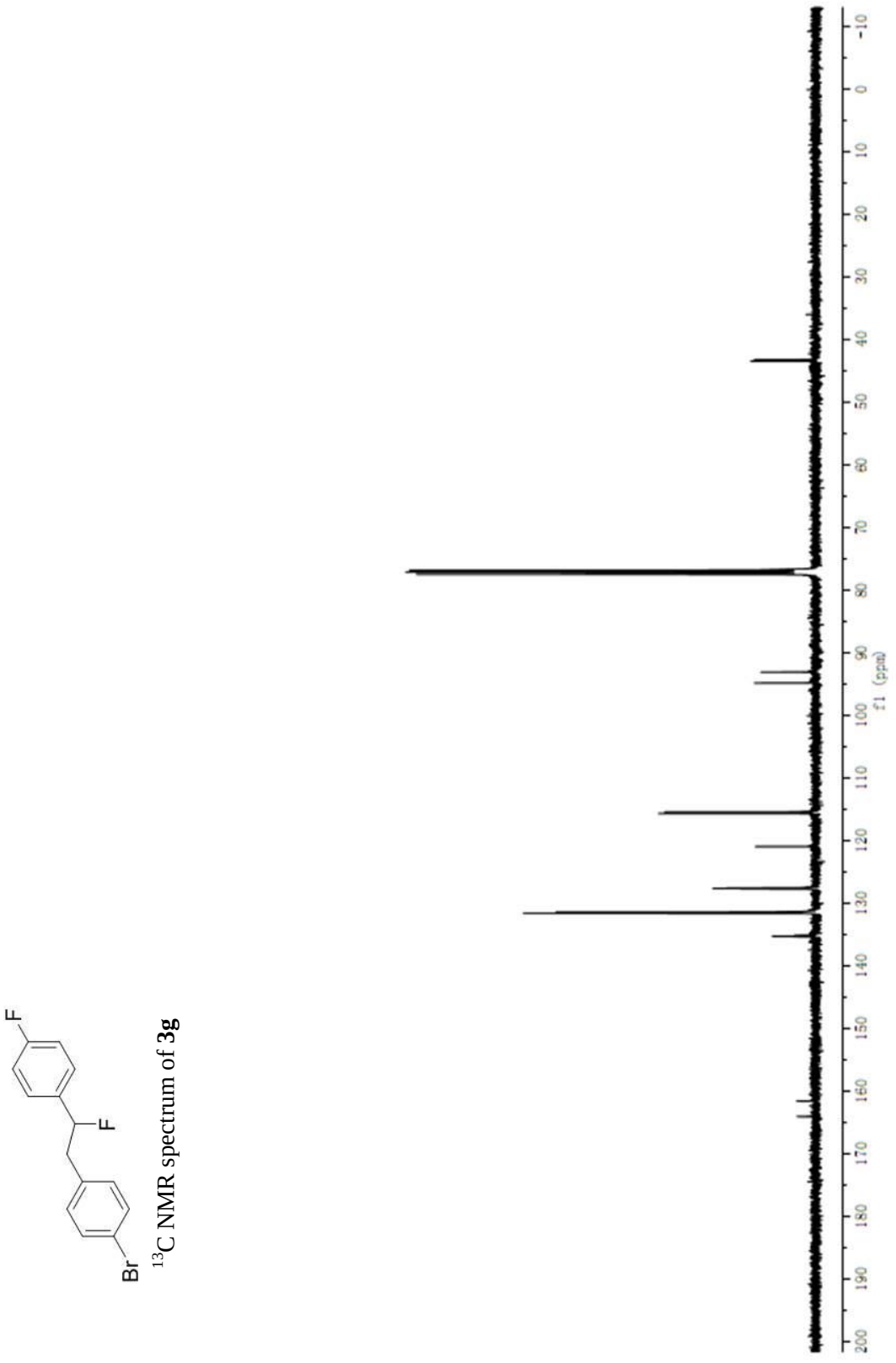


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3f**



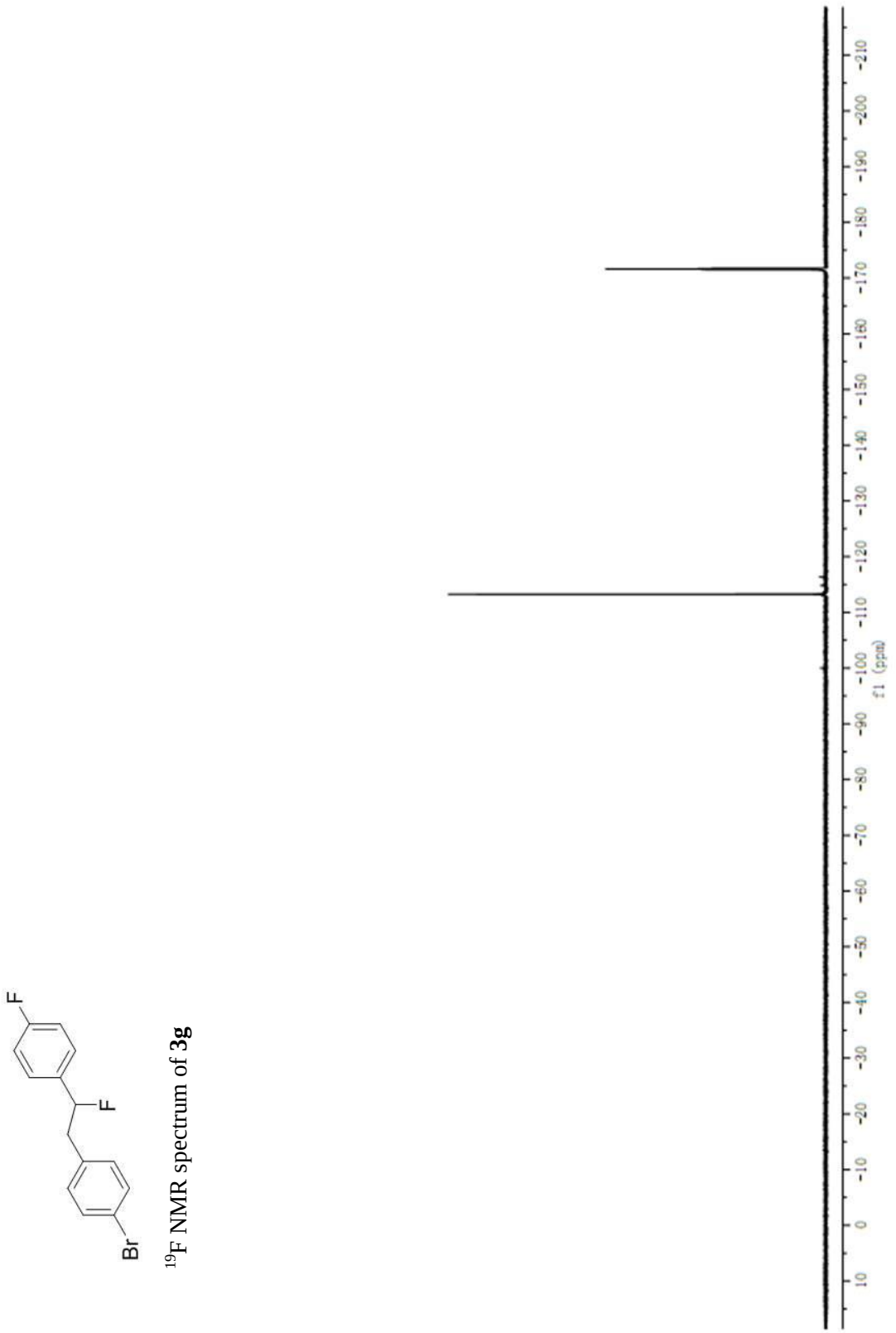
^{1}H NMR spectrum of **3g**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3g**



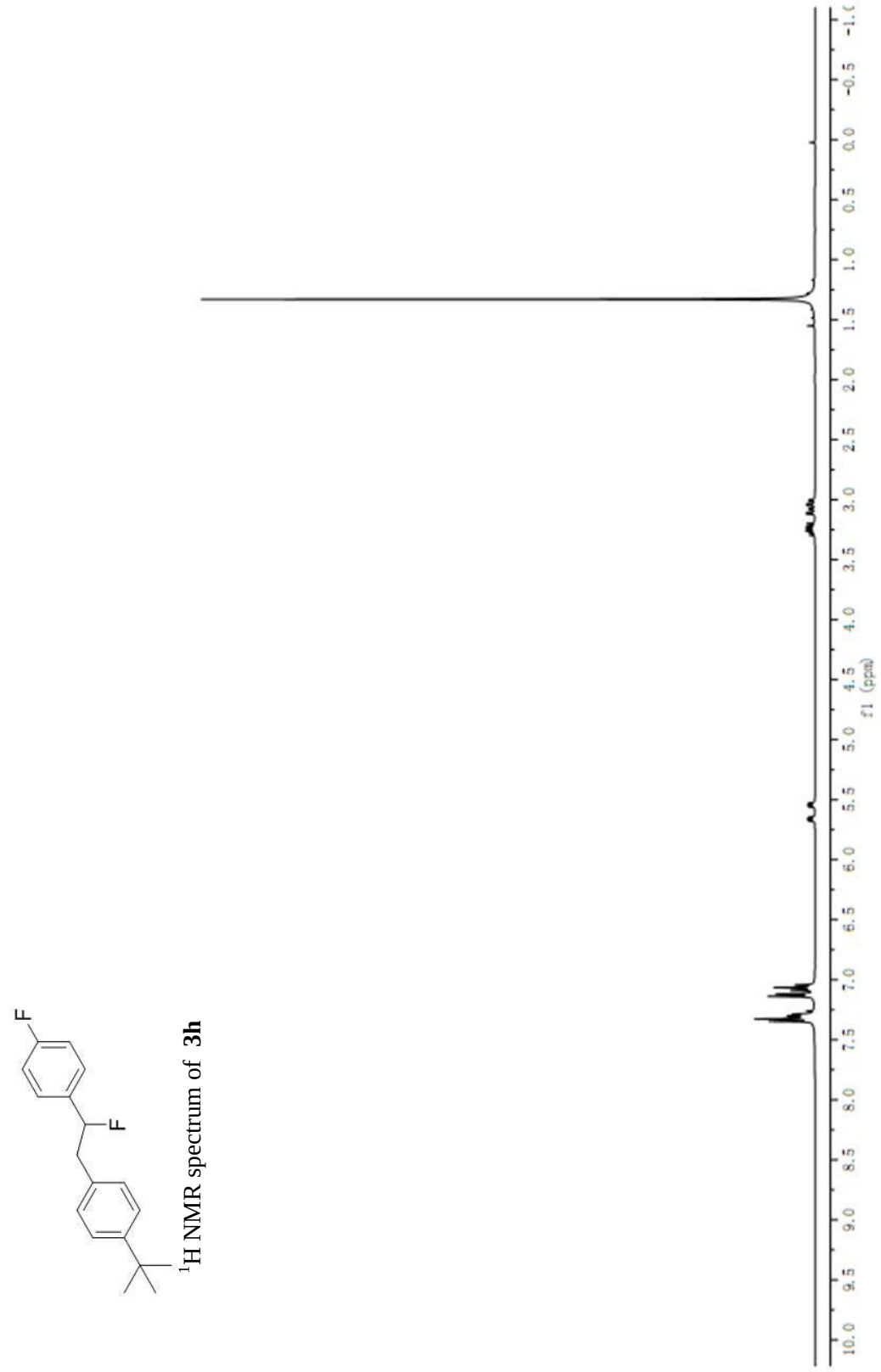
^{13}C NMR spectrum of **3g**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3g**



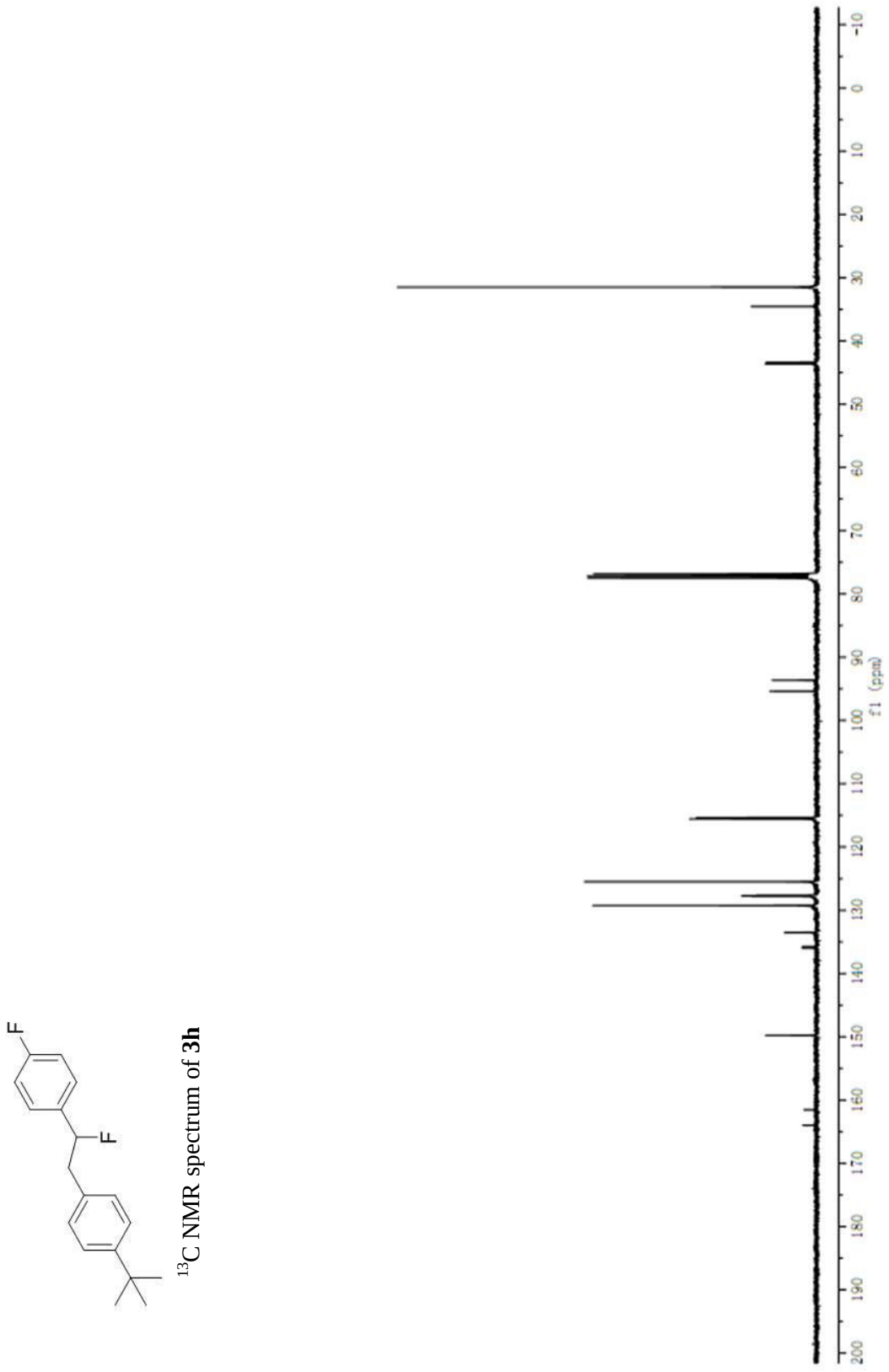
^{19}F NMR spectrum of **3g**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3g**

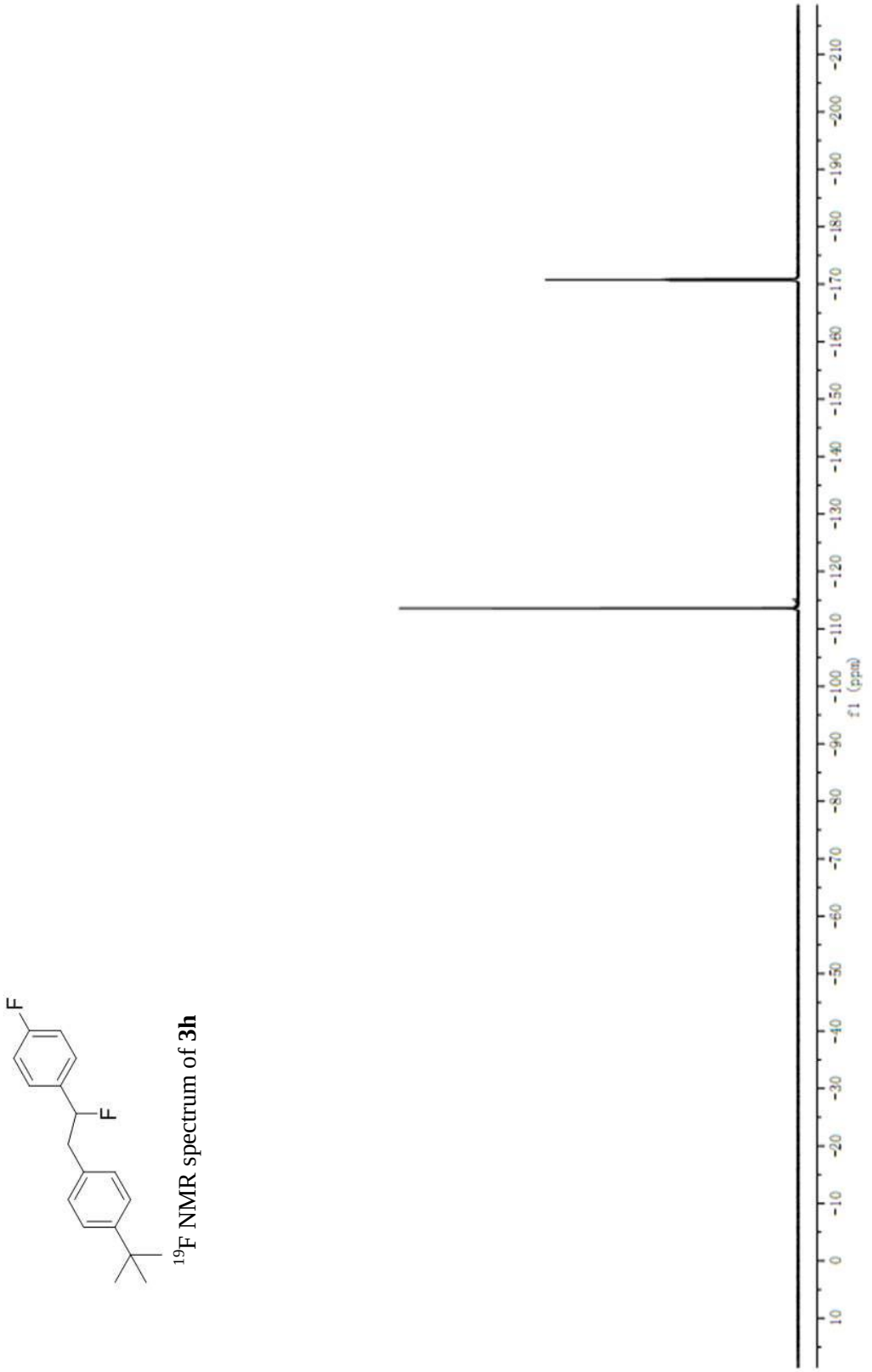


^{1}H NMR spectrum of **3h**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3h**

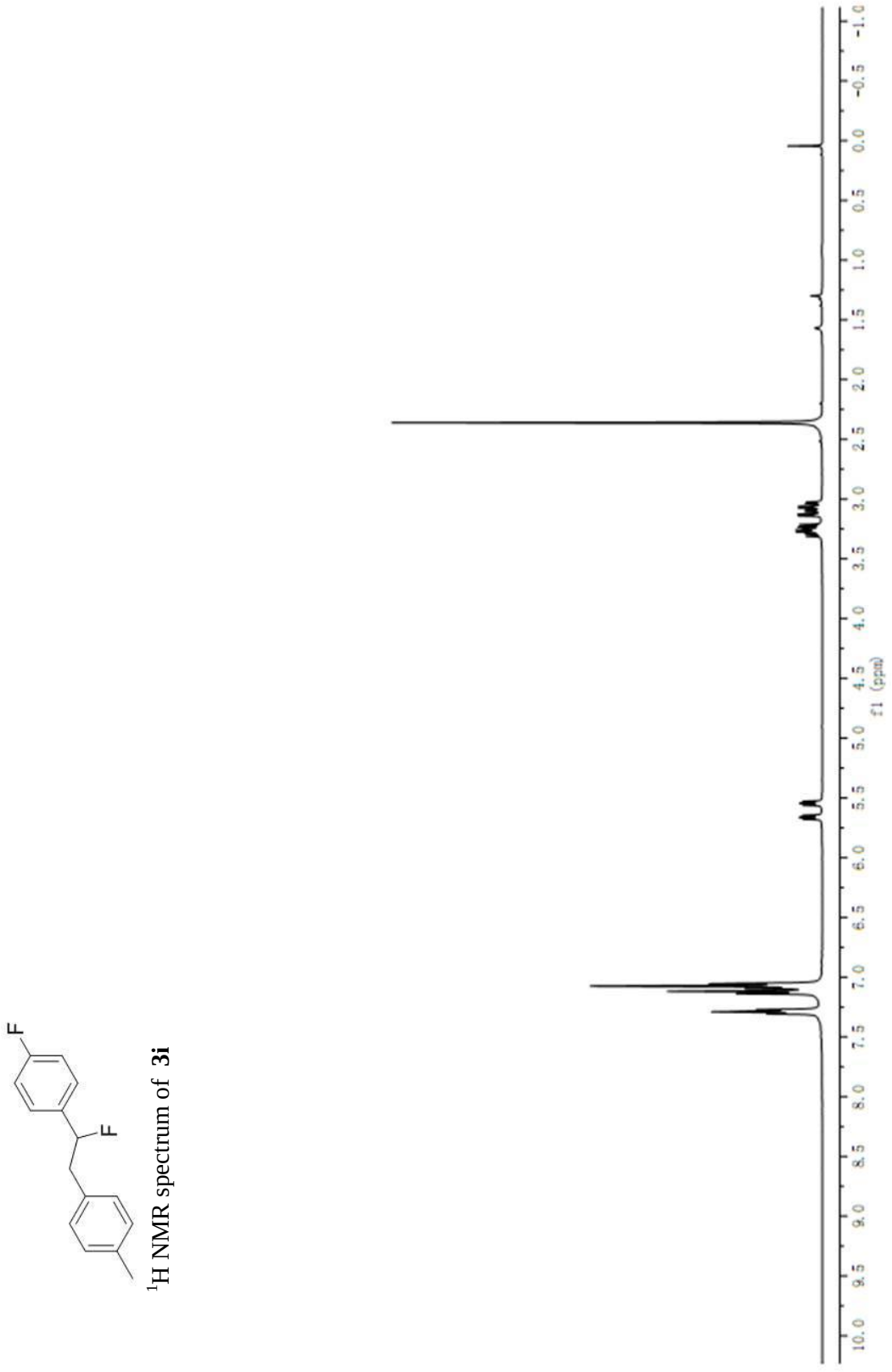


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3h**



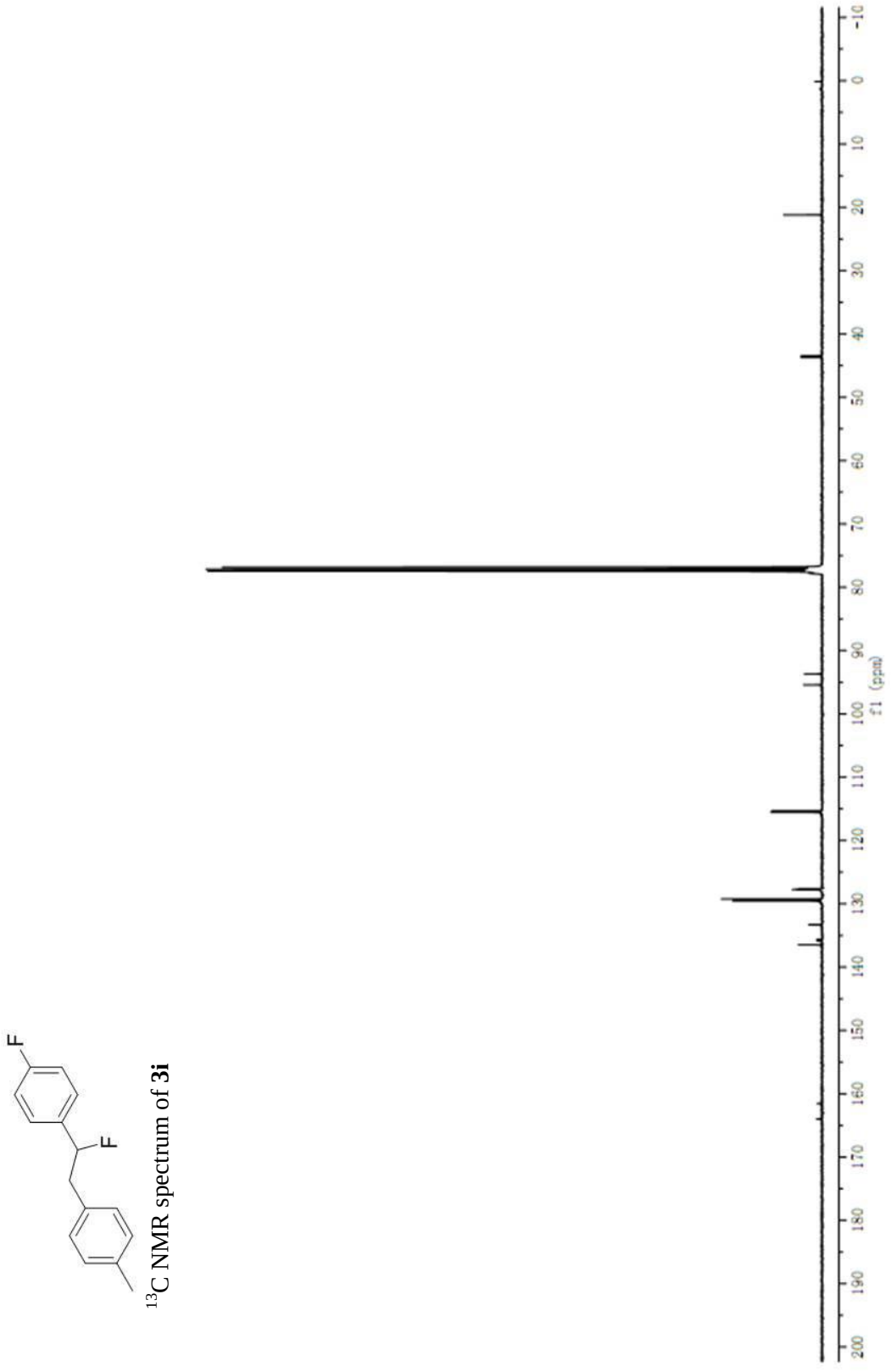
^{19}F NMR spectrum of **3h**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3h**

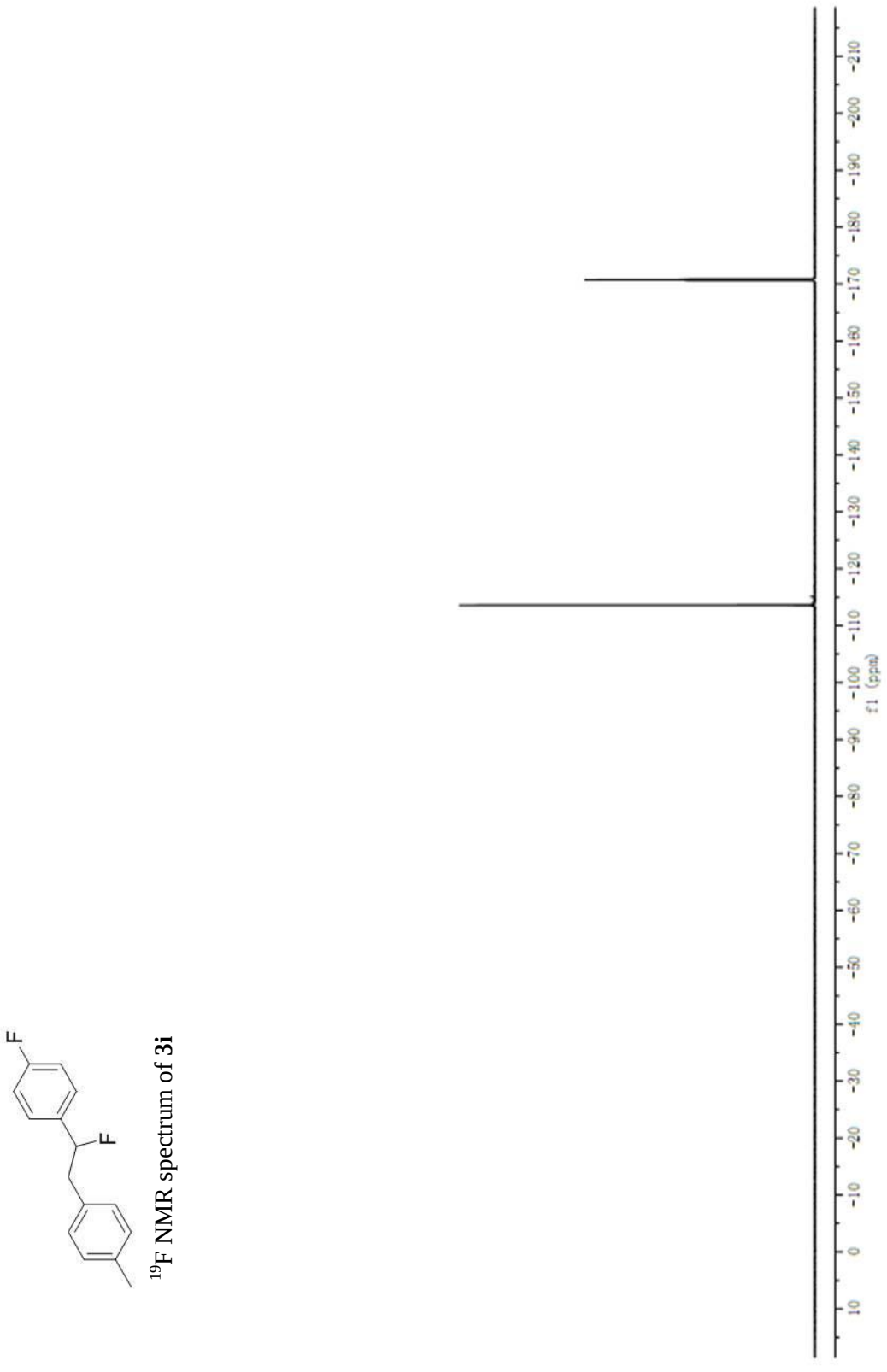


^{1}H NMR spectrum of **3i**

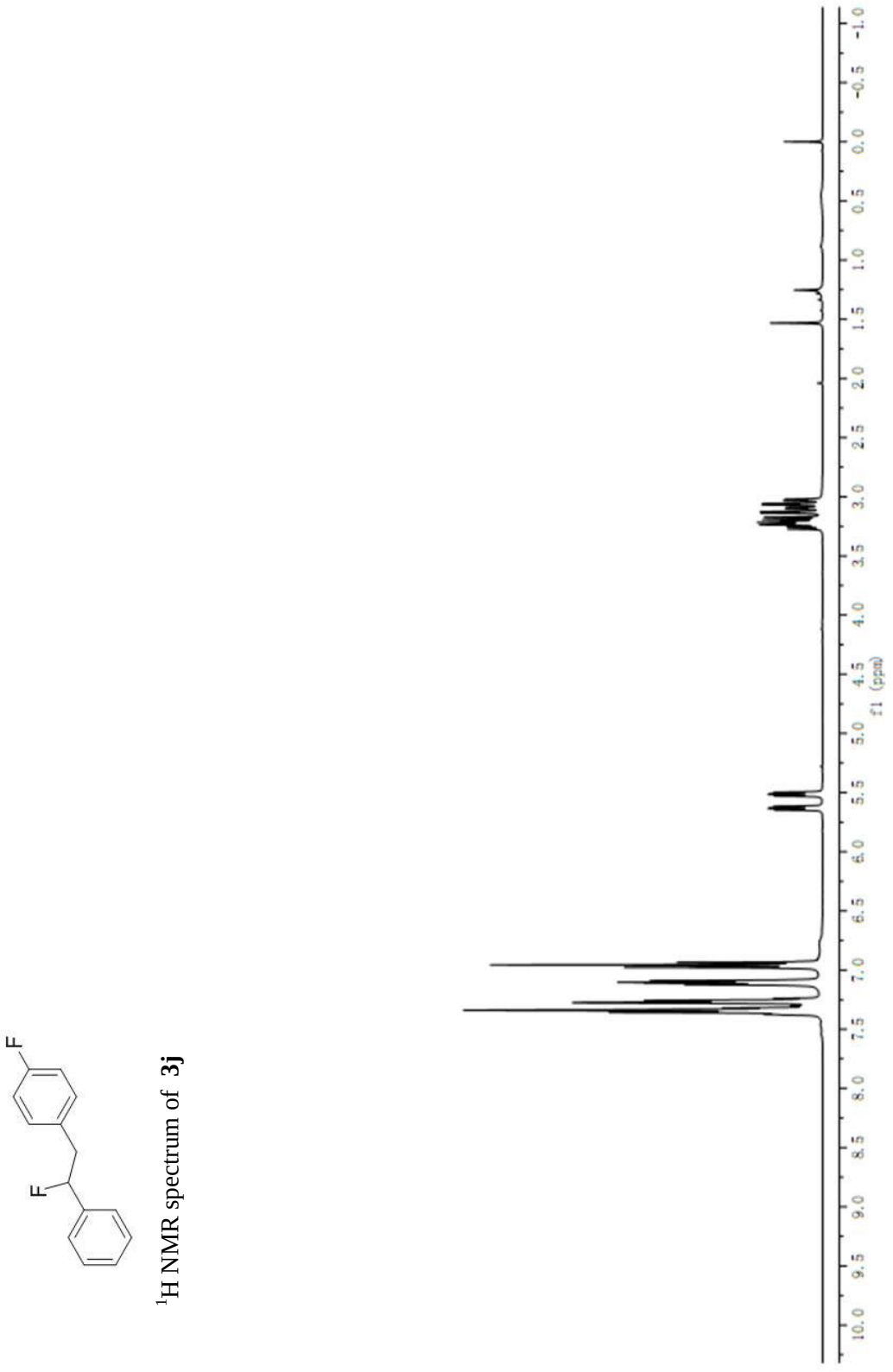
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3i**



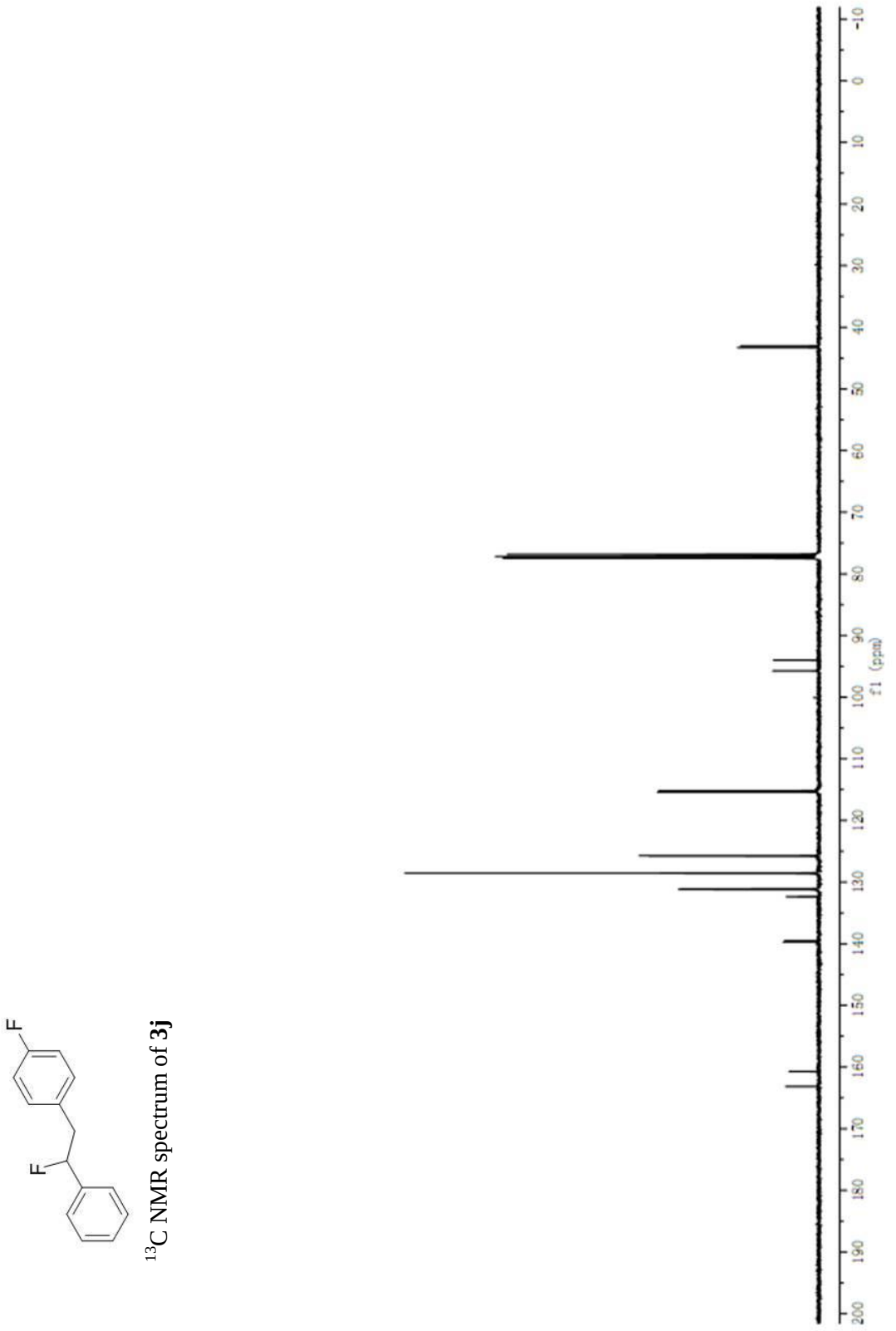
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3i**



^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3i**

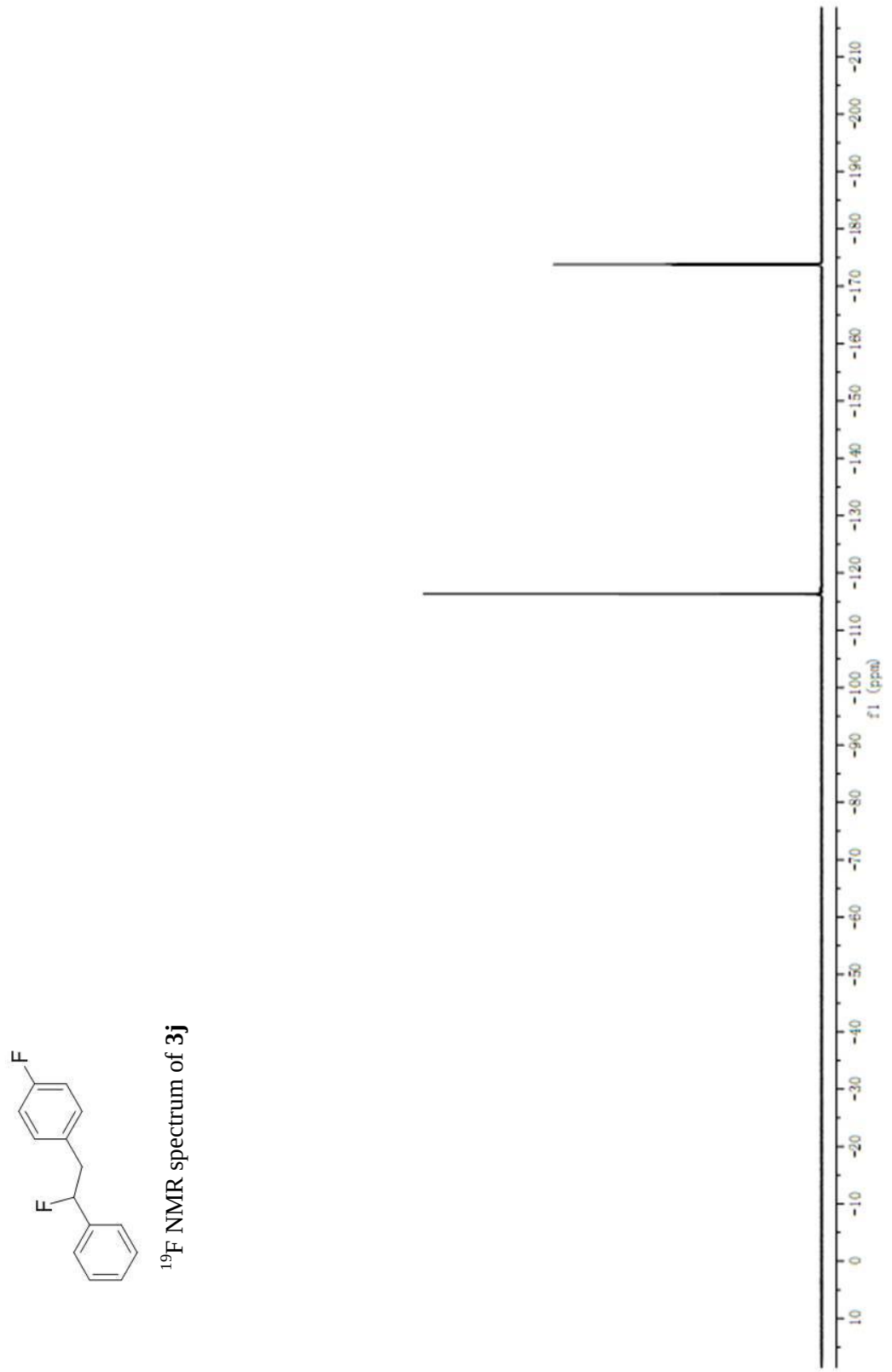


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3j**

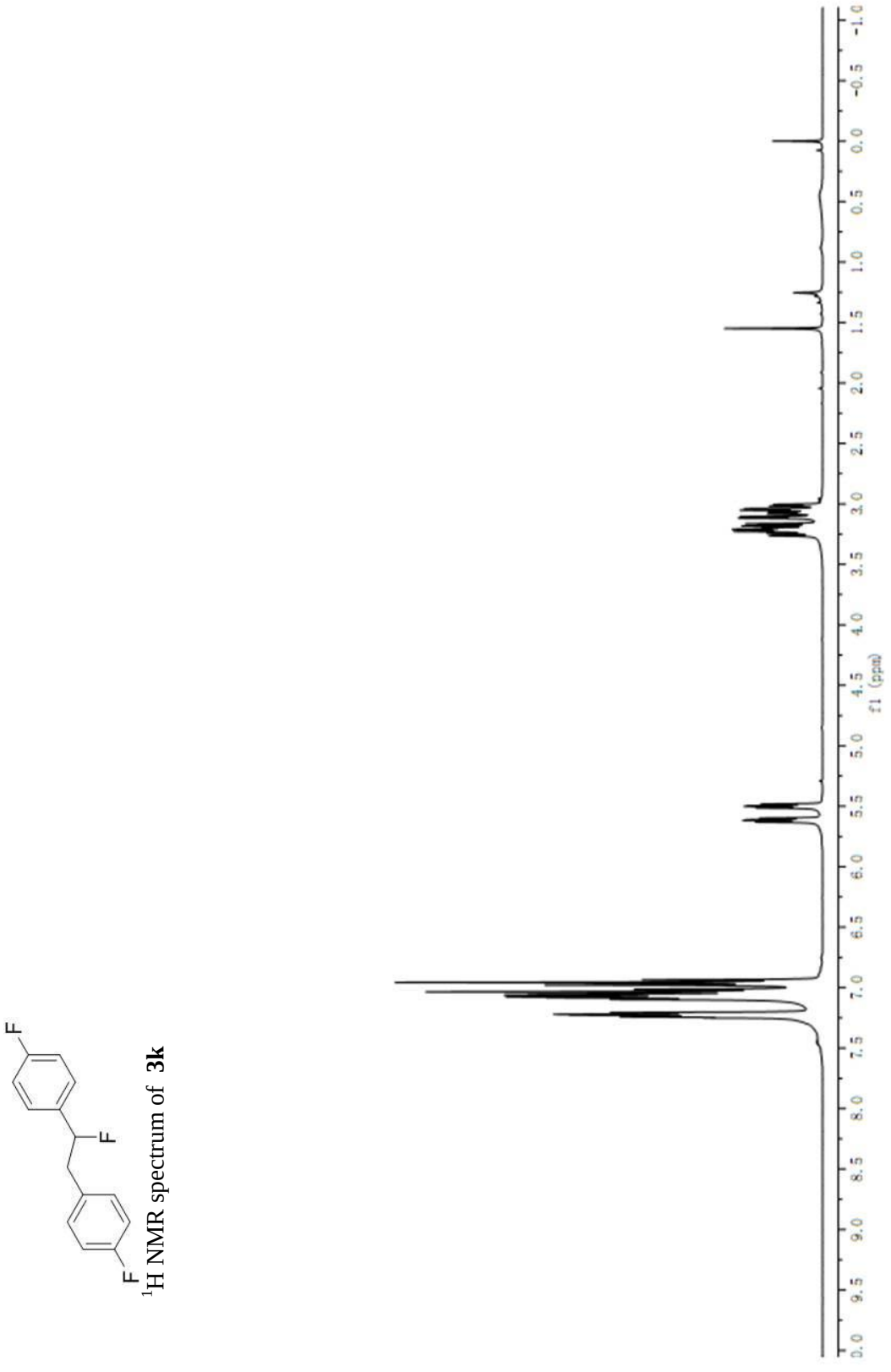


^{13}C NMR spectrum of **3j**

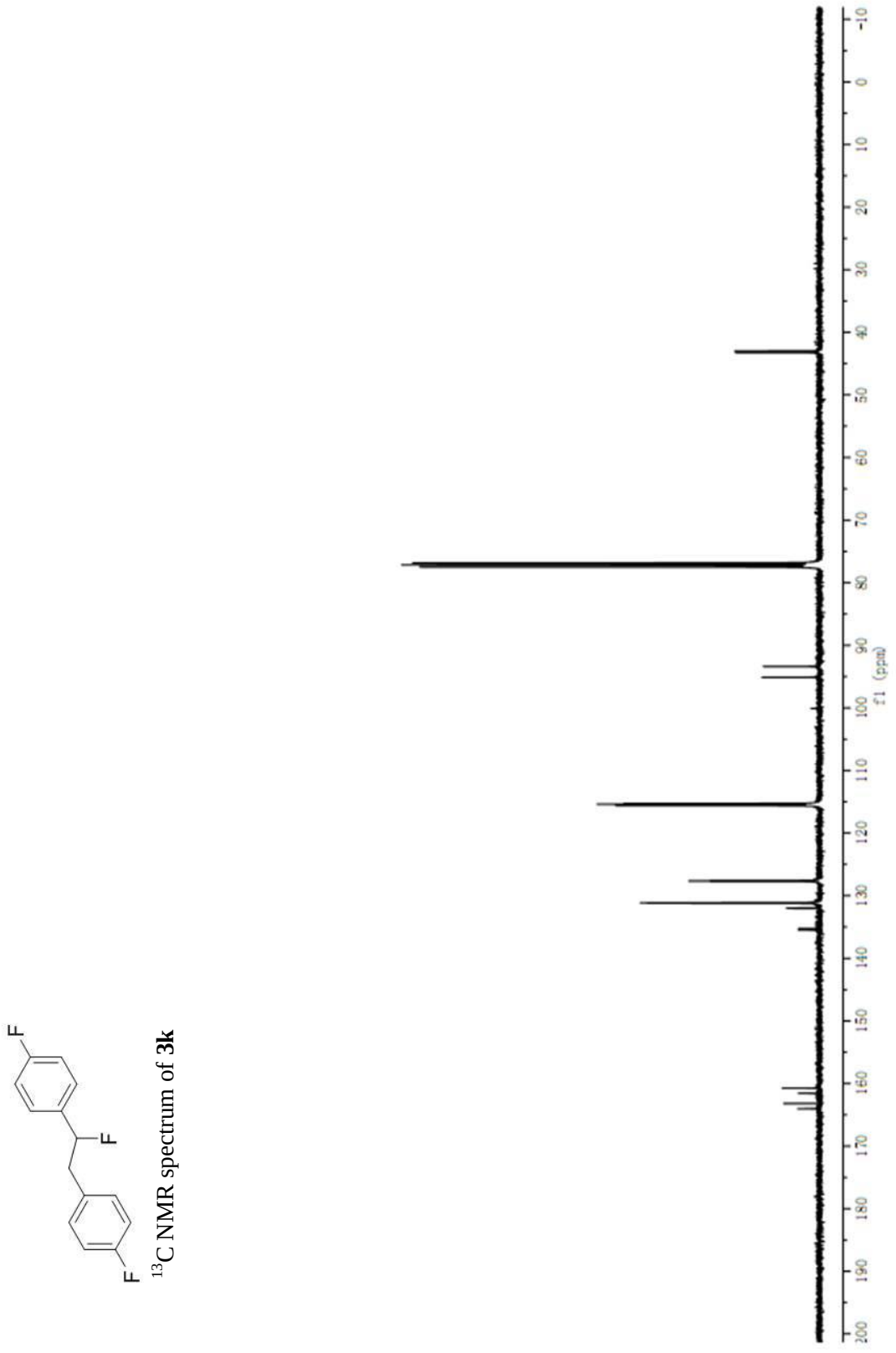
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3j**



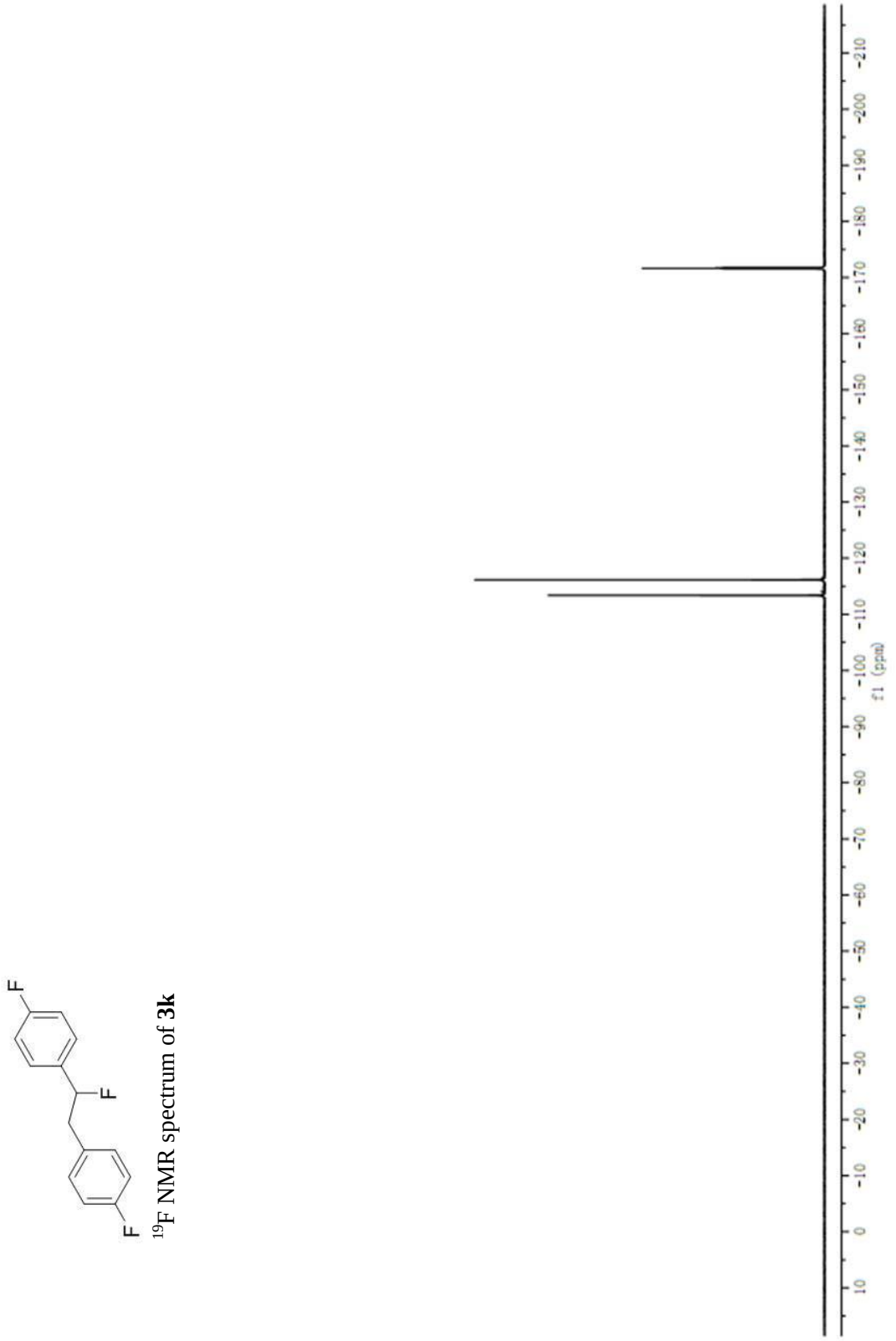
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3j**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3k**

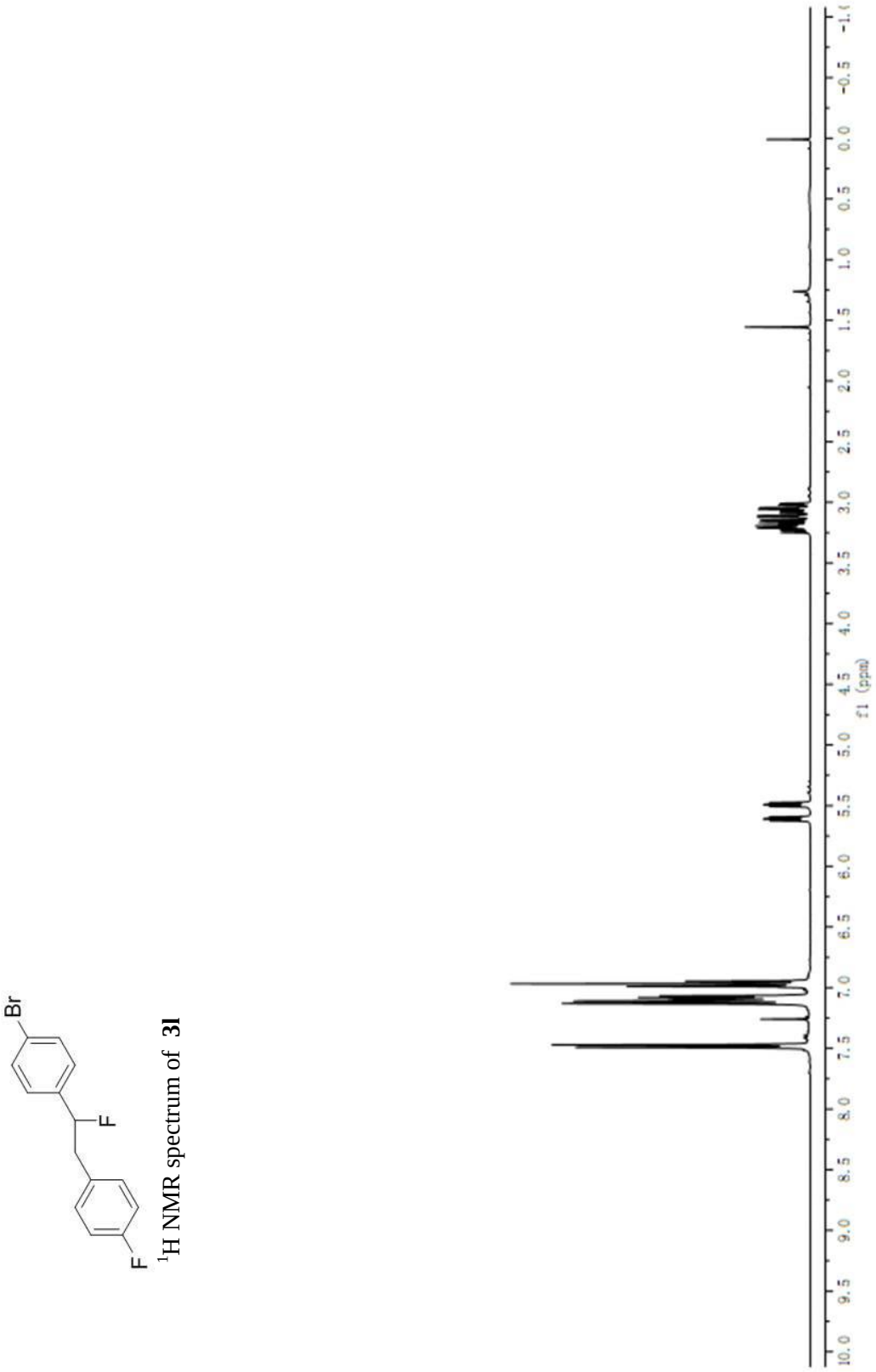


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3k**



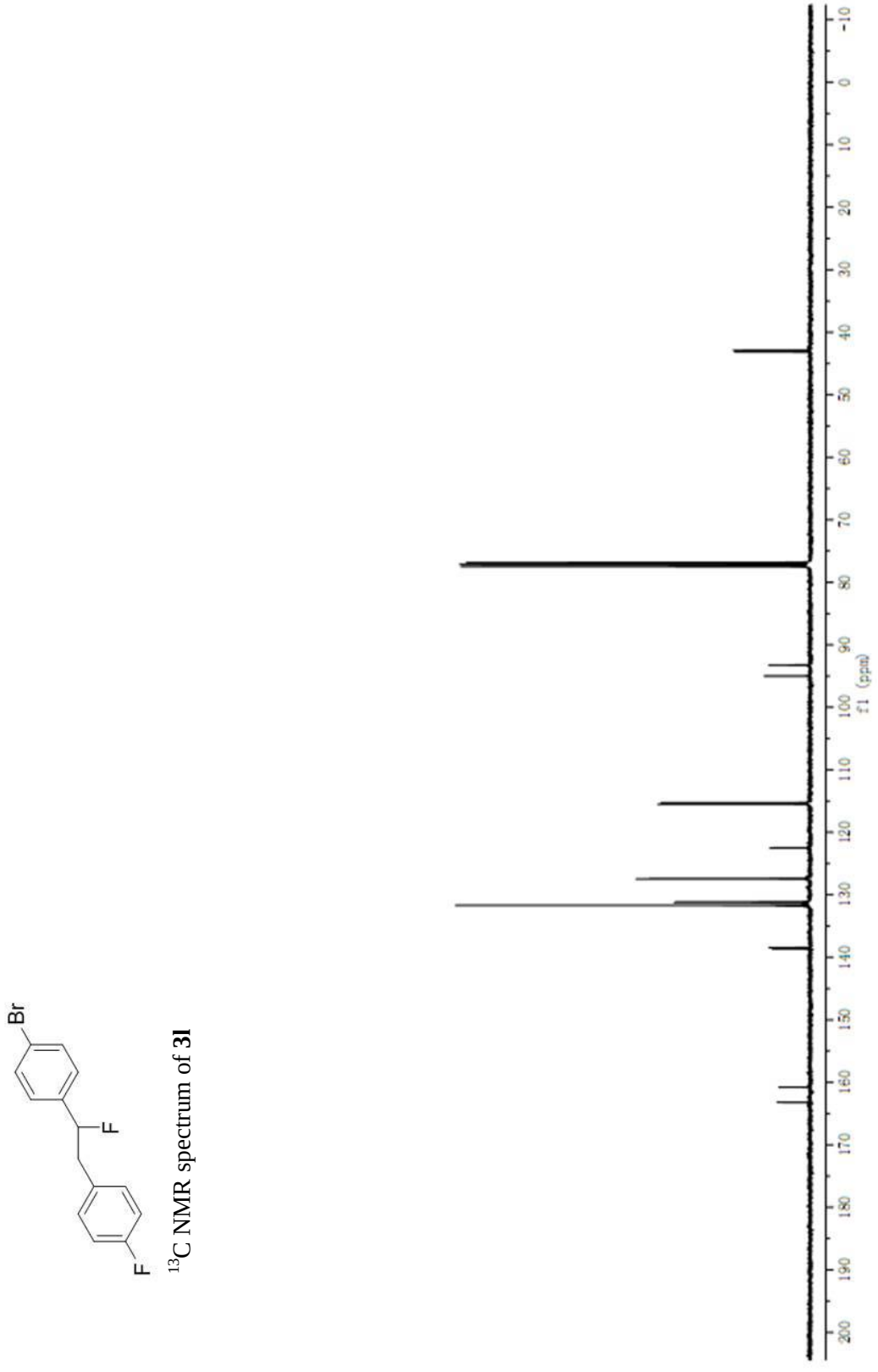
^{19}F NMR spectrum of **3k**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3k**

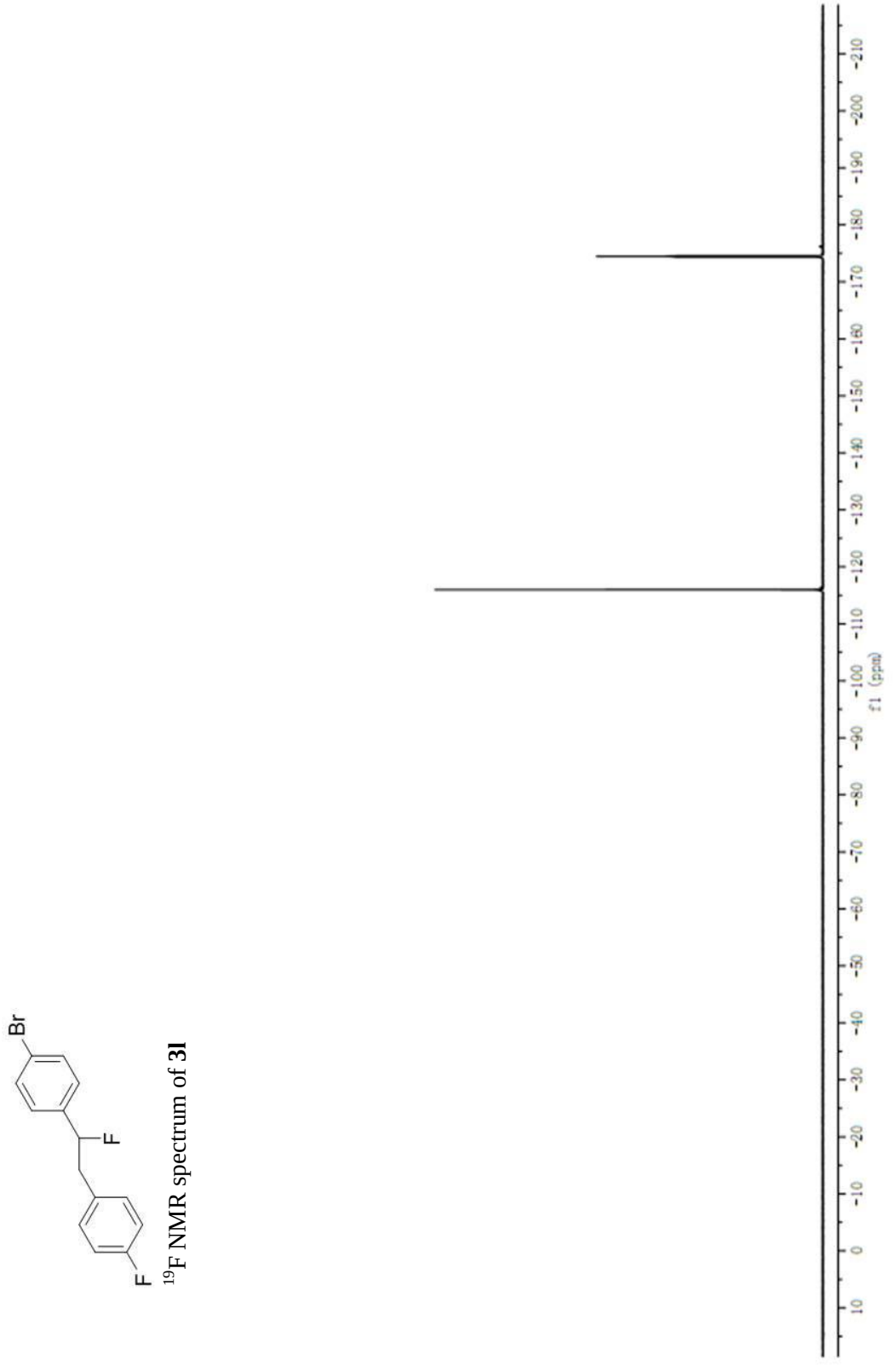


^{1}H NMR spectrum of **3l**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3l**

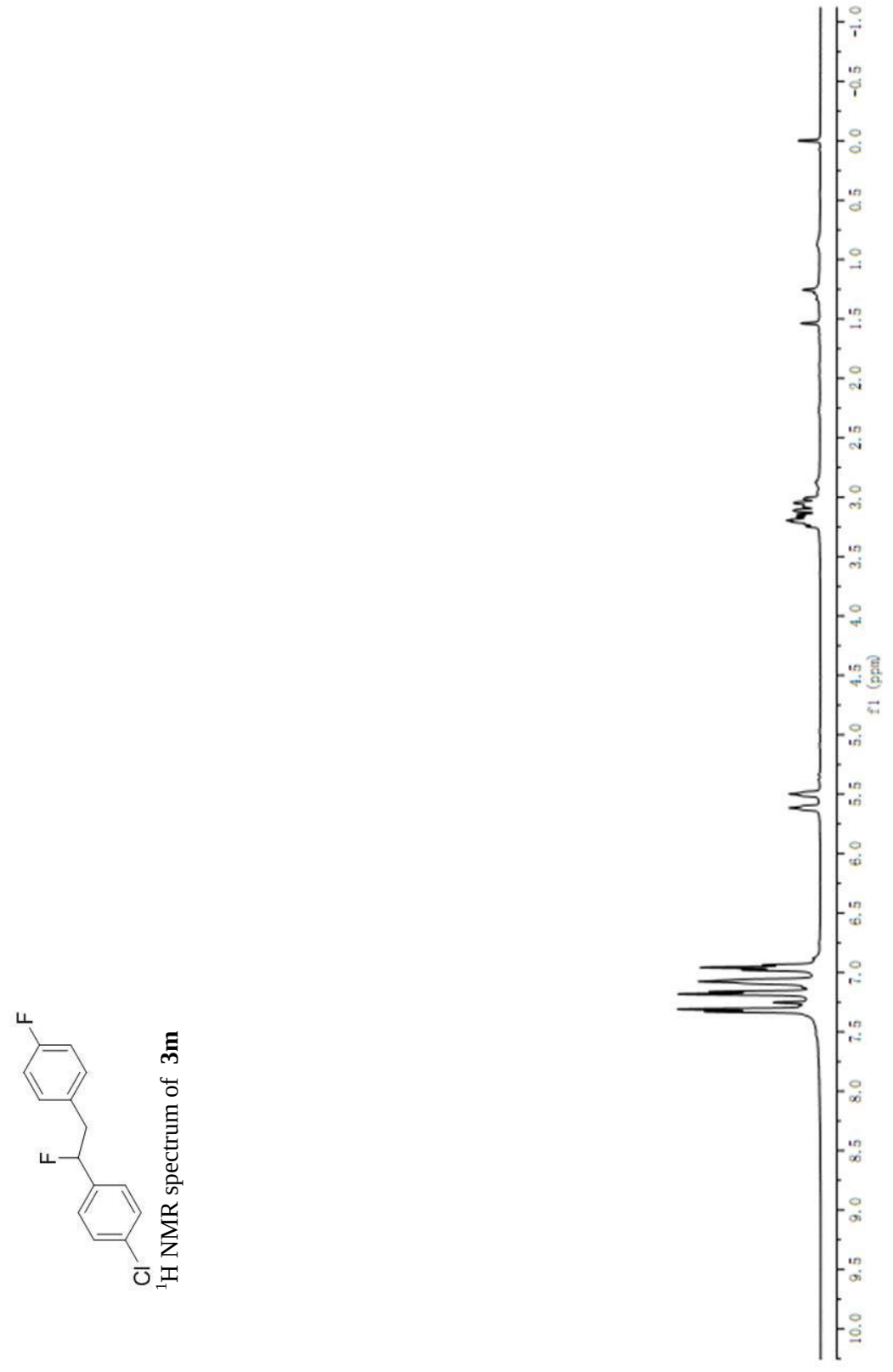


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3l**



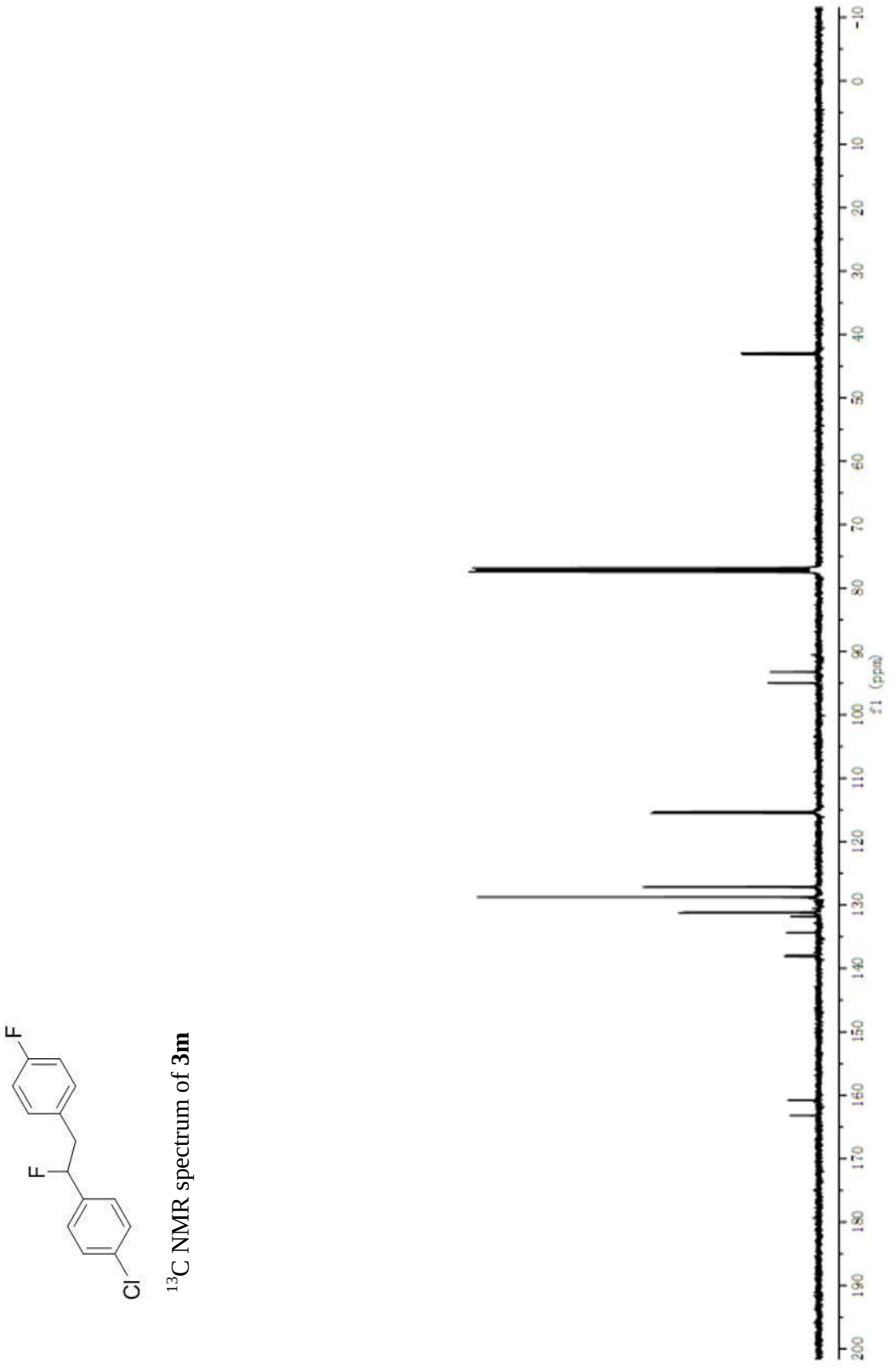
^{19}F NMR spectrum of **3l**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3l**



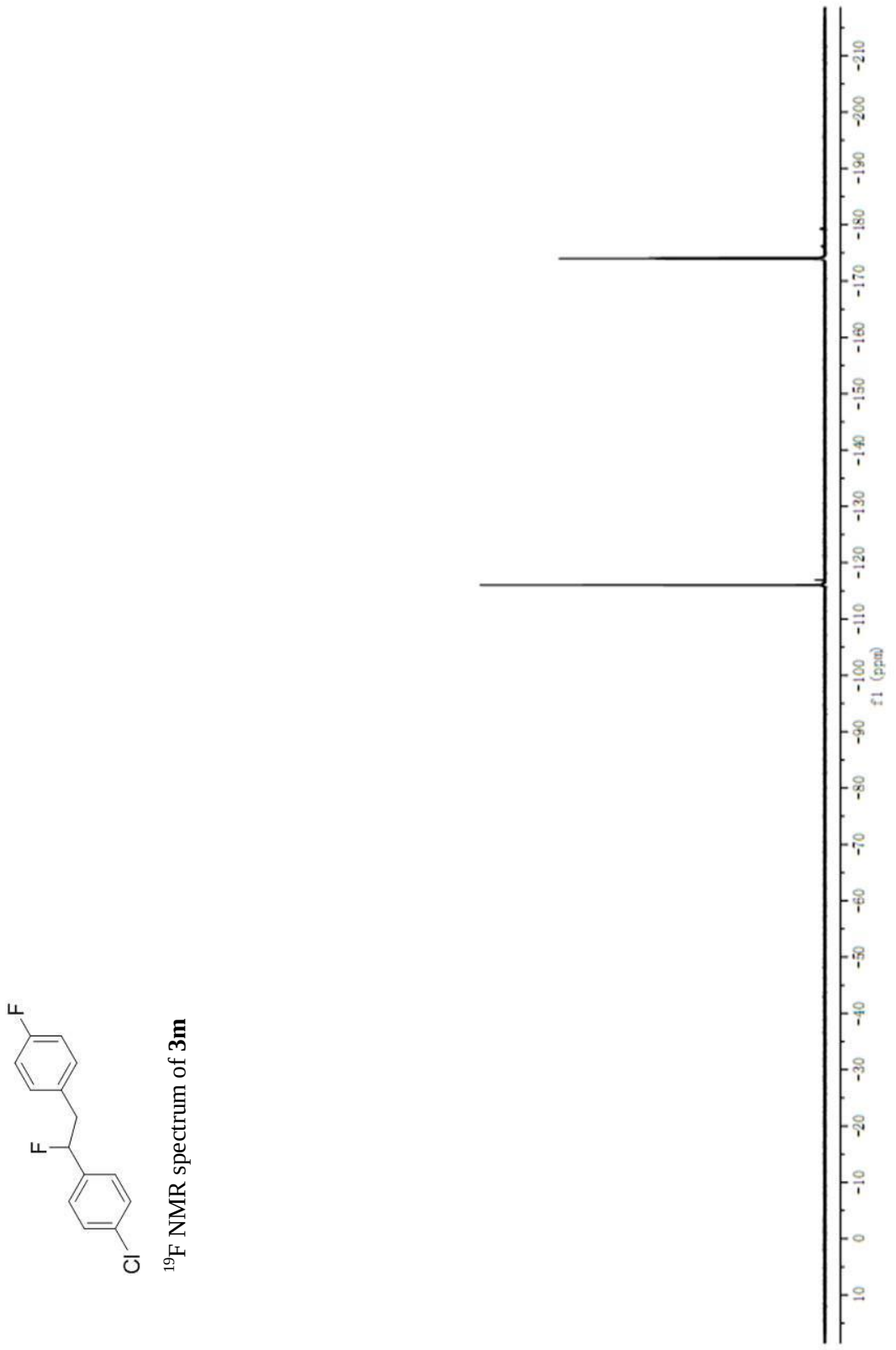
^{1}H NMR spectrum of **3m**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3m**

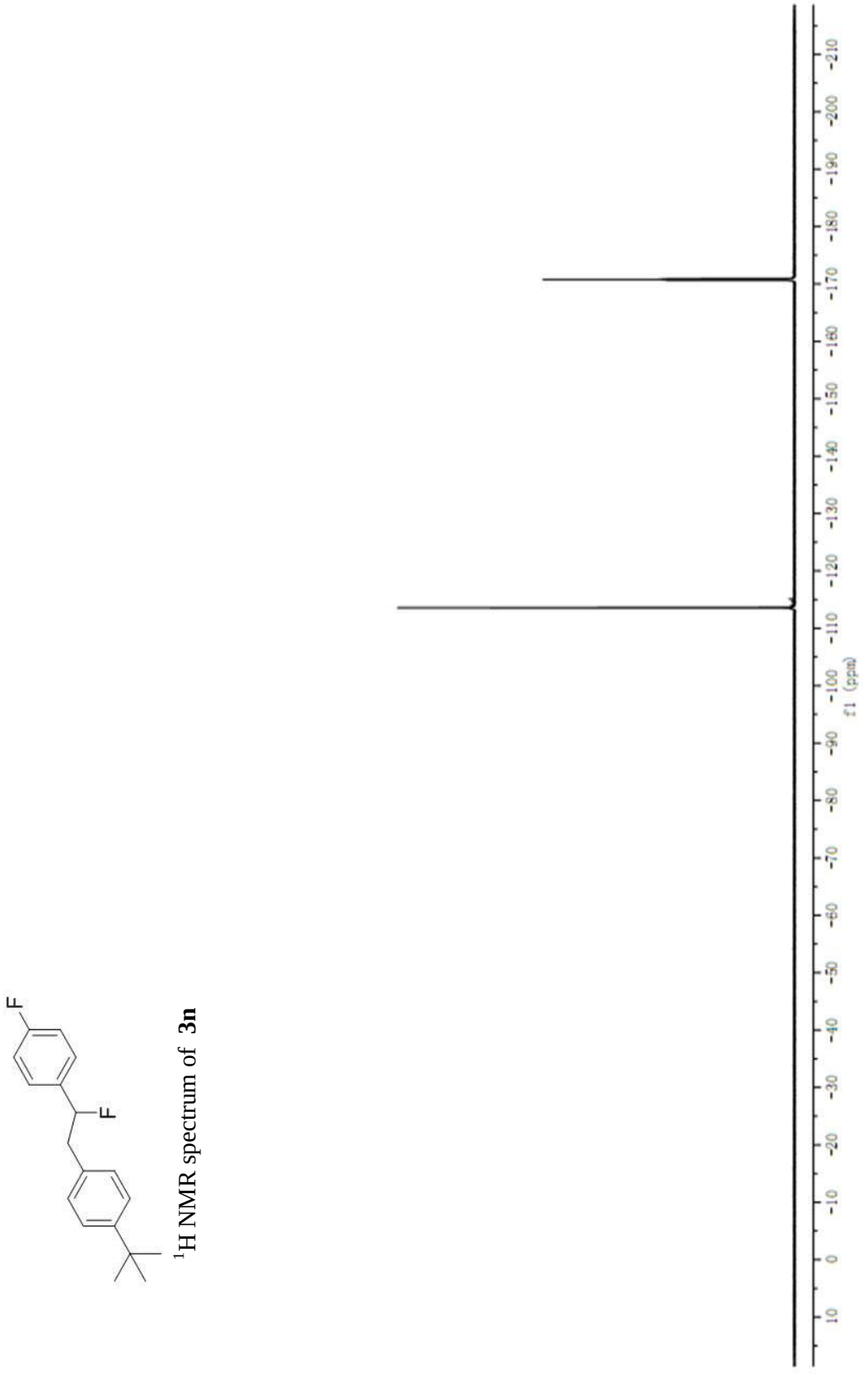


^{13}C NMR spectrum of **3m**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3m**

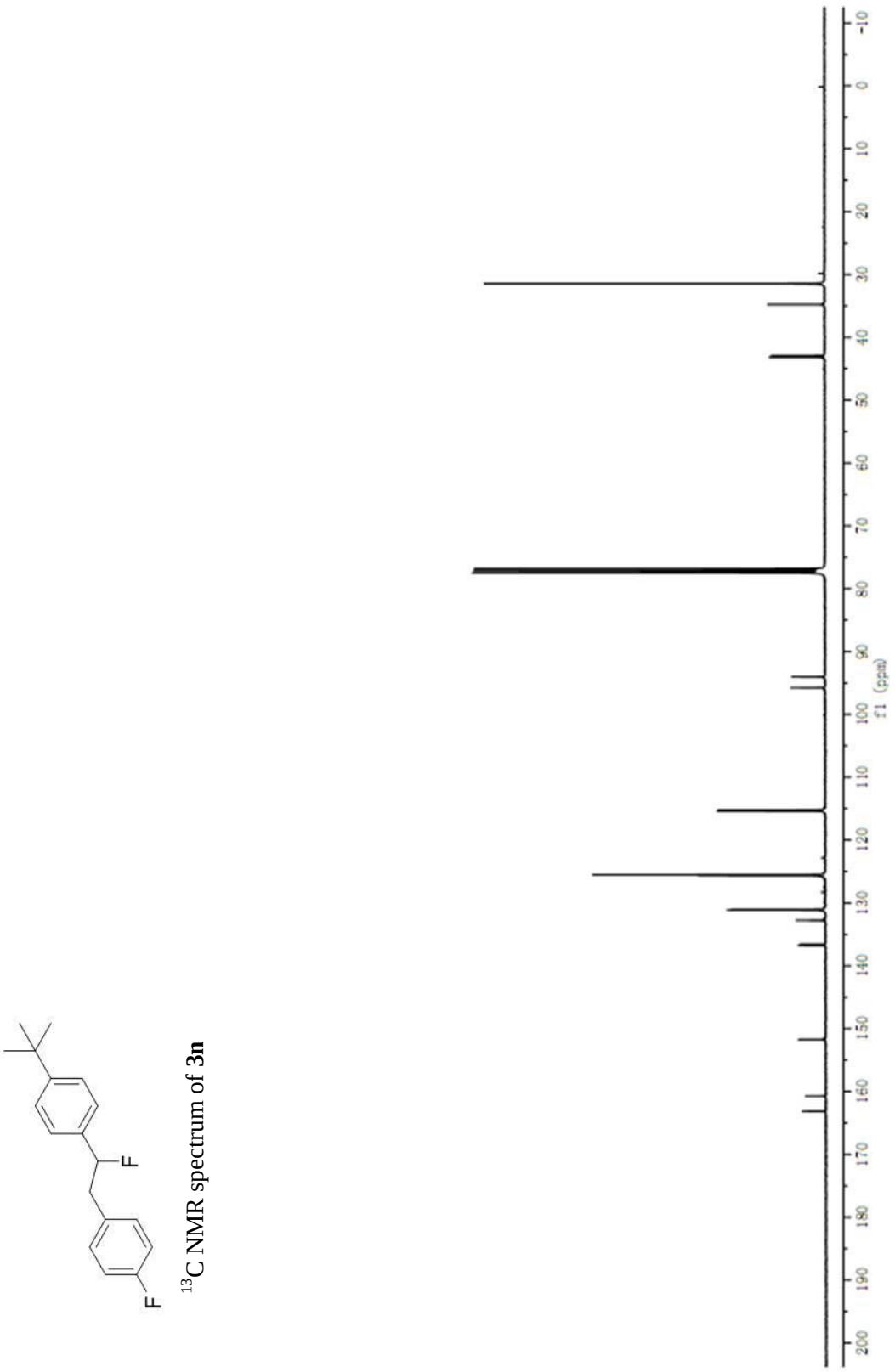


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3m**

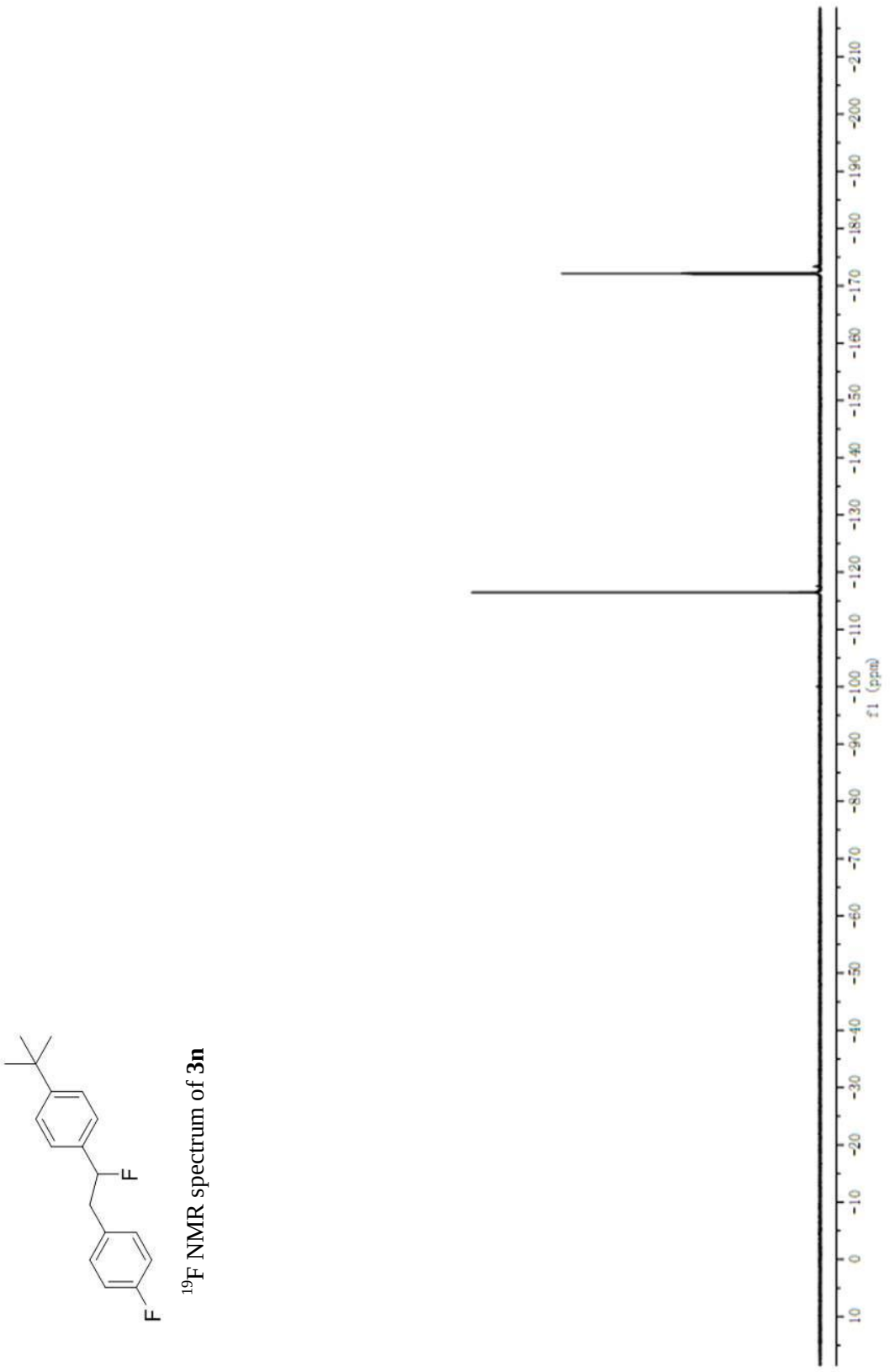


^{1}H NMR spectrum of **3n**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3n**

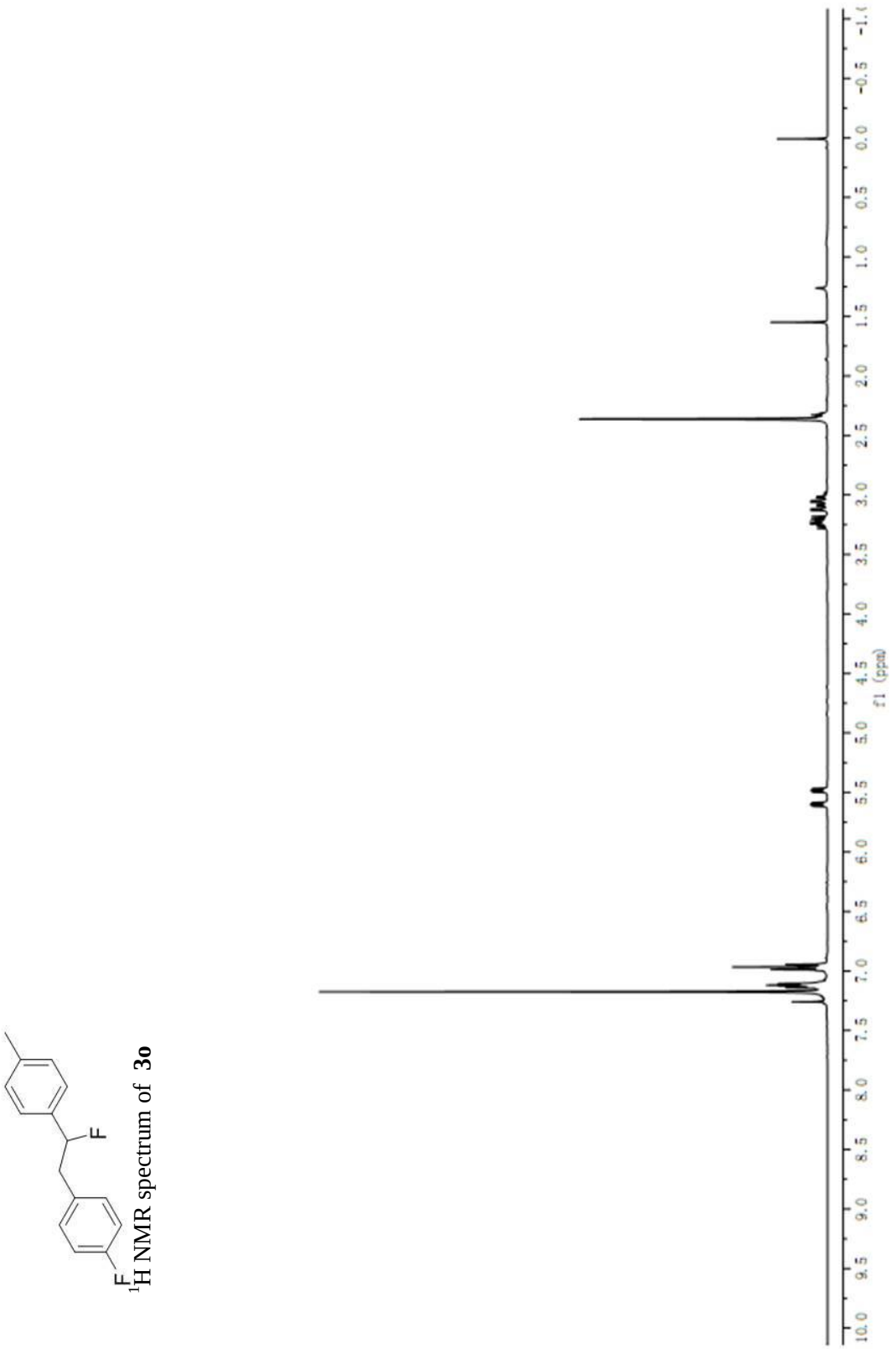


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3n**

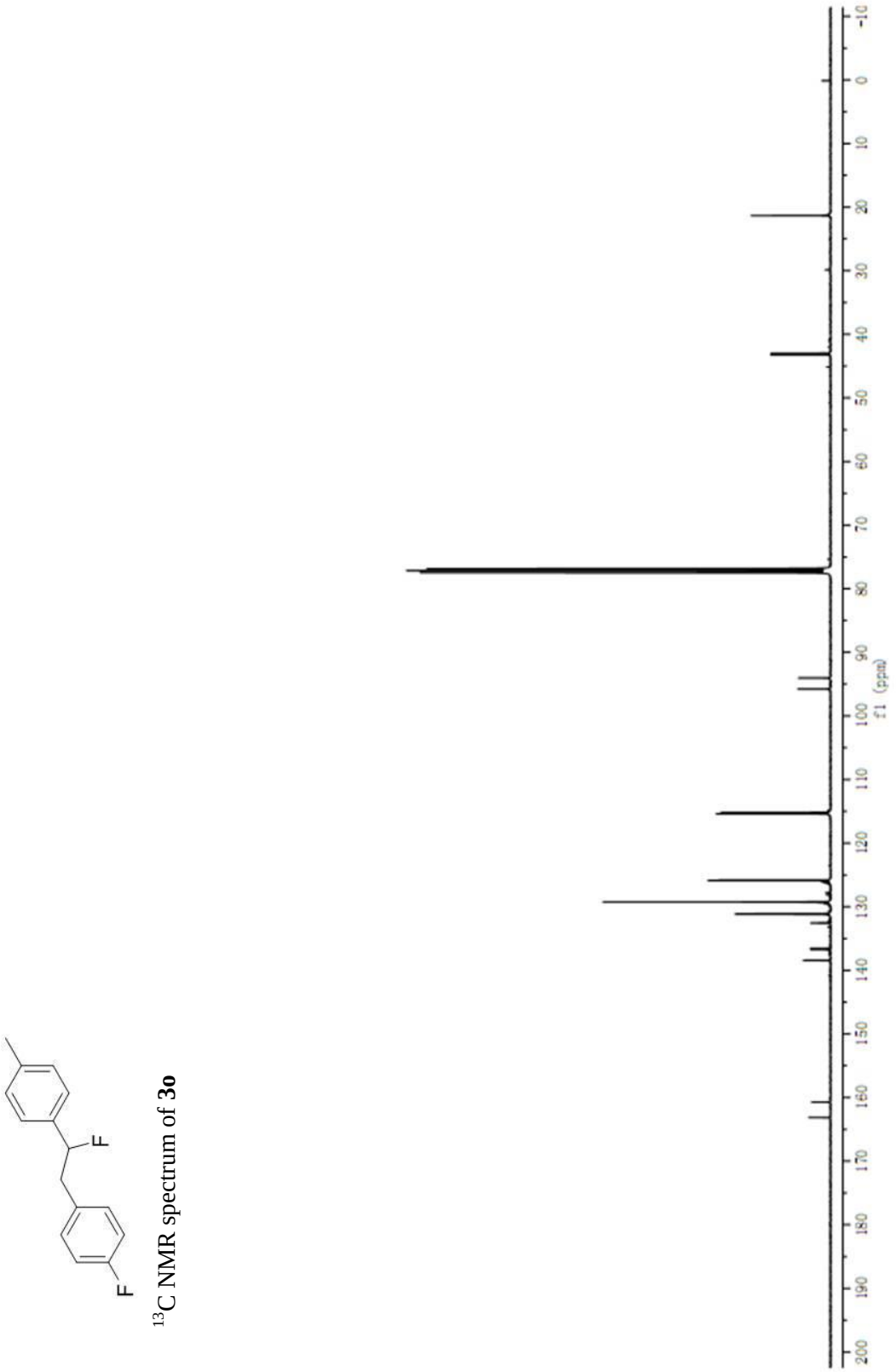


^{19}F NMR spectrum of **3n**

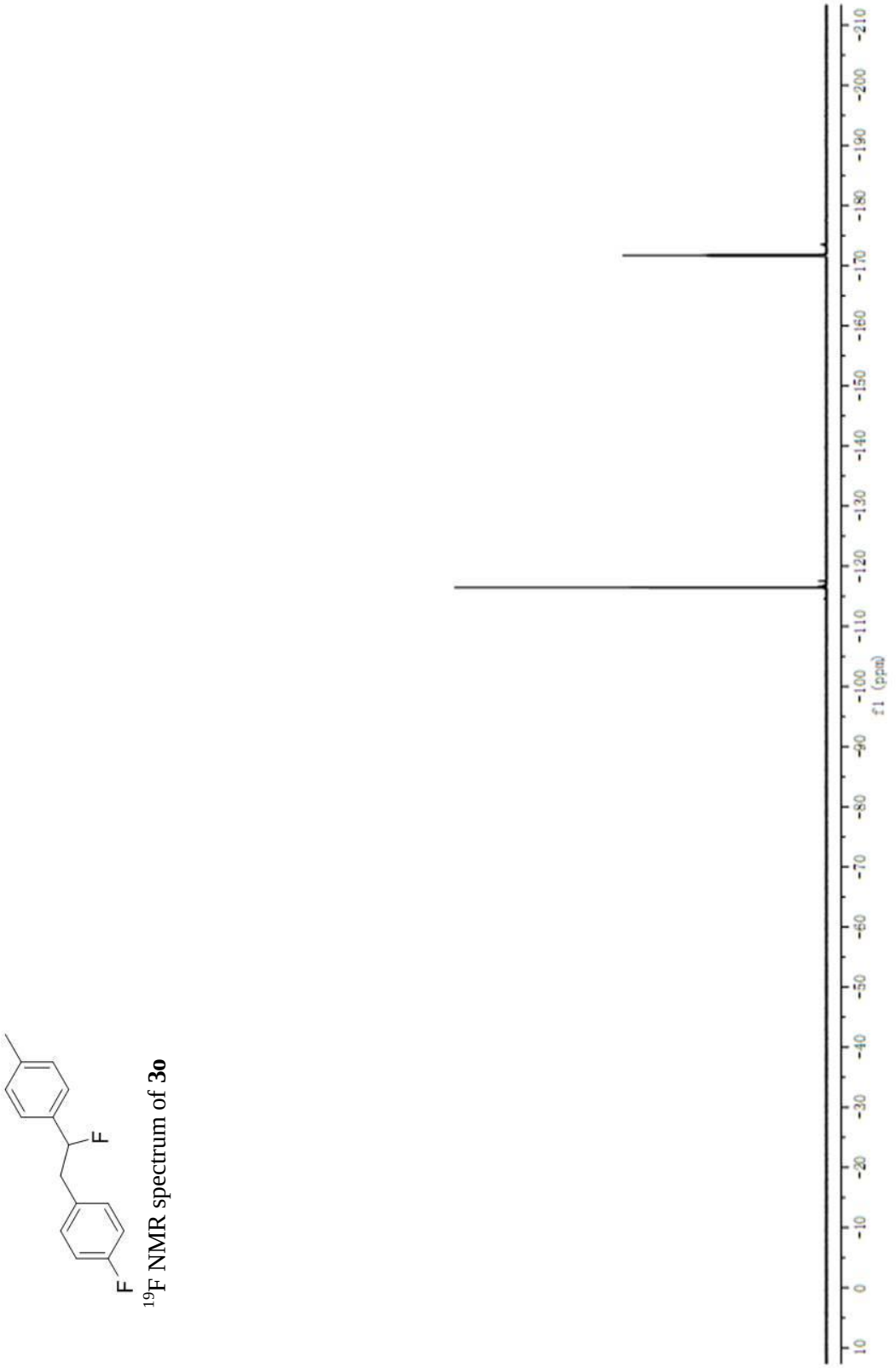
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3n**



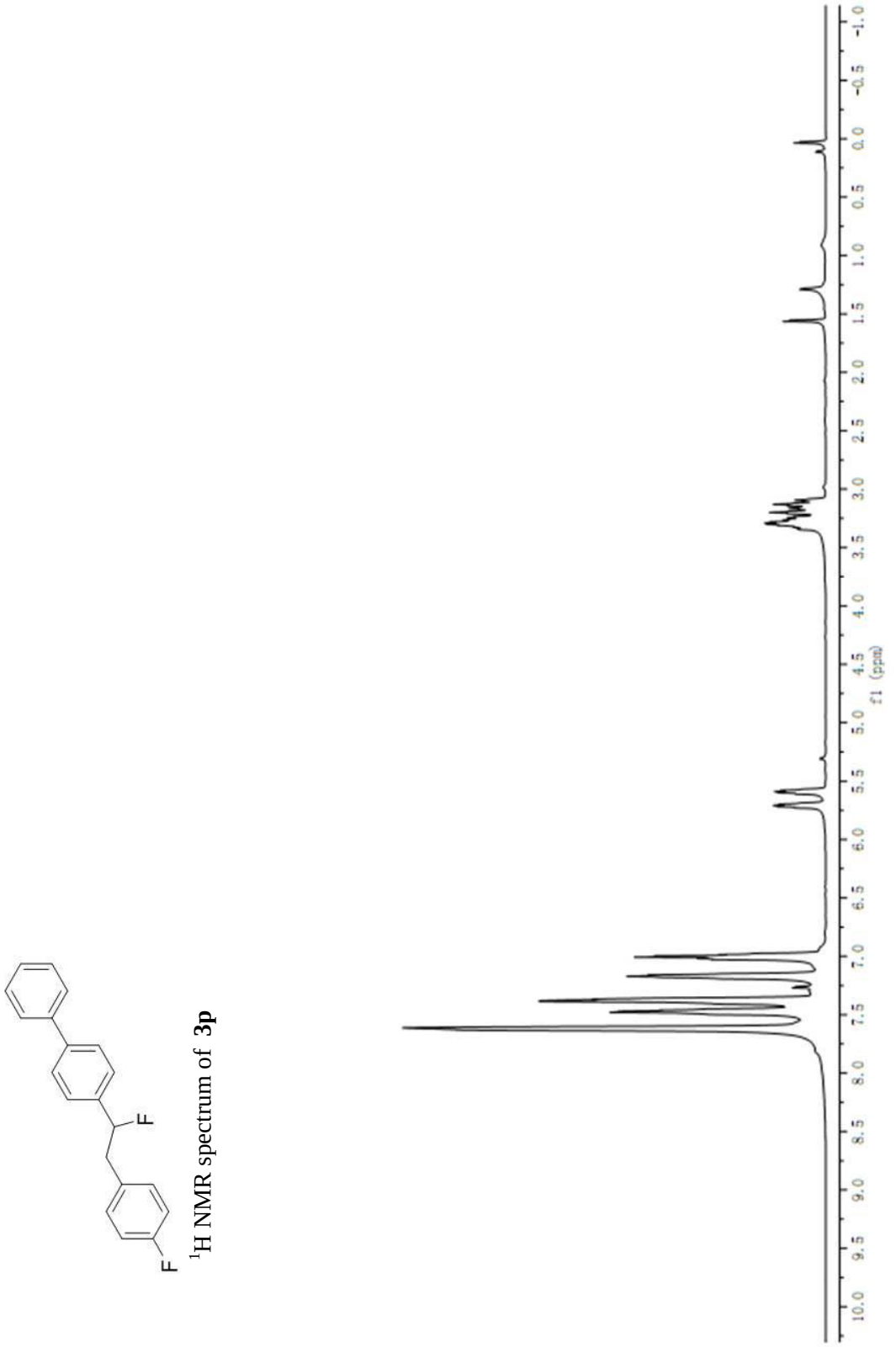
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3o**



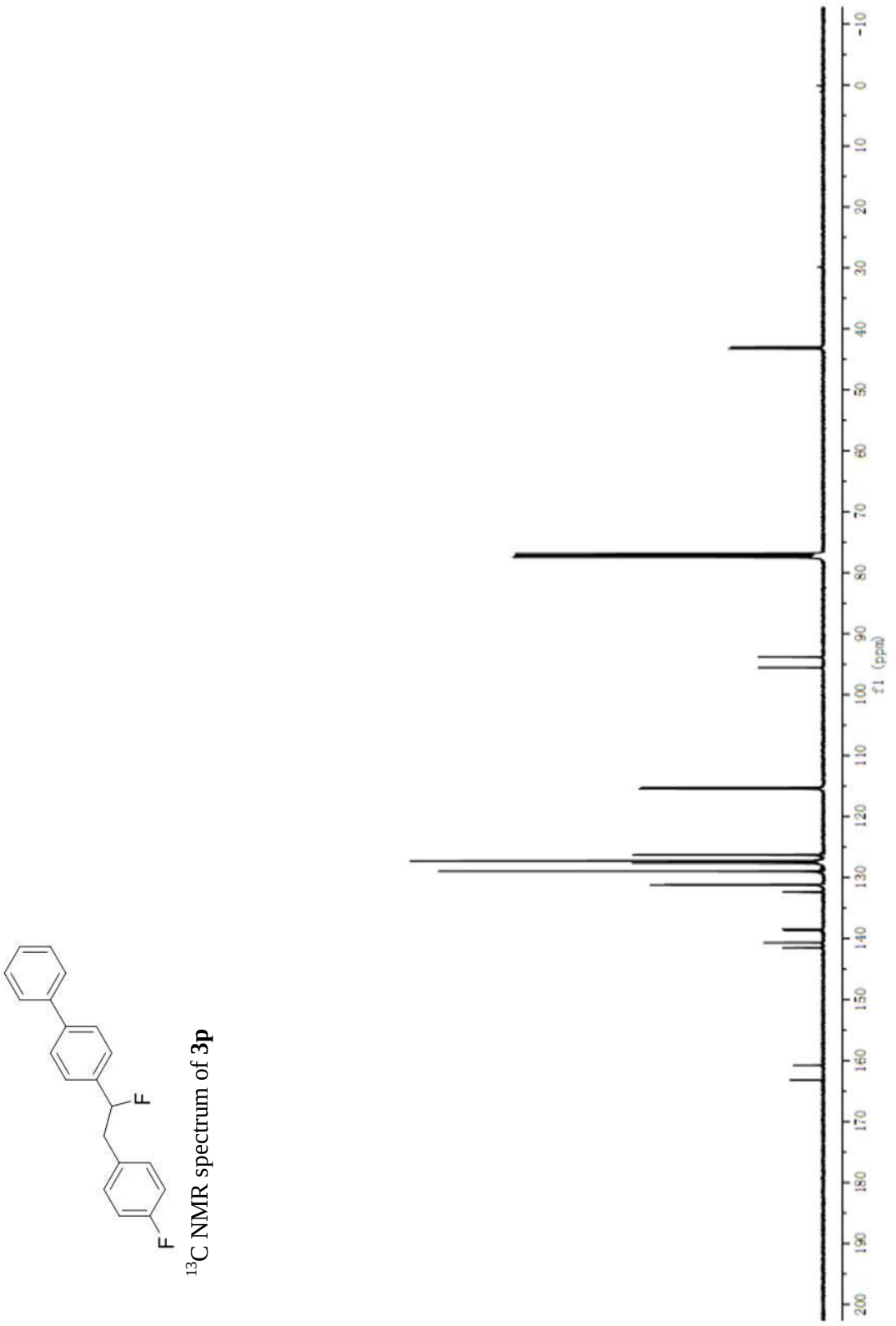
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3o**



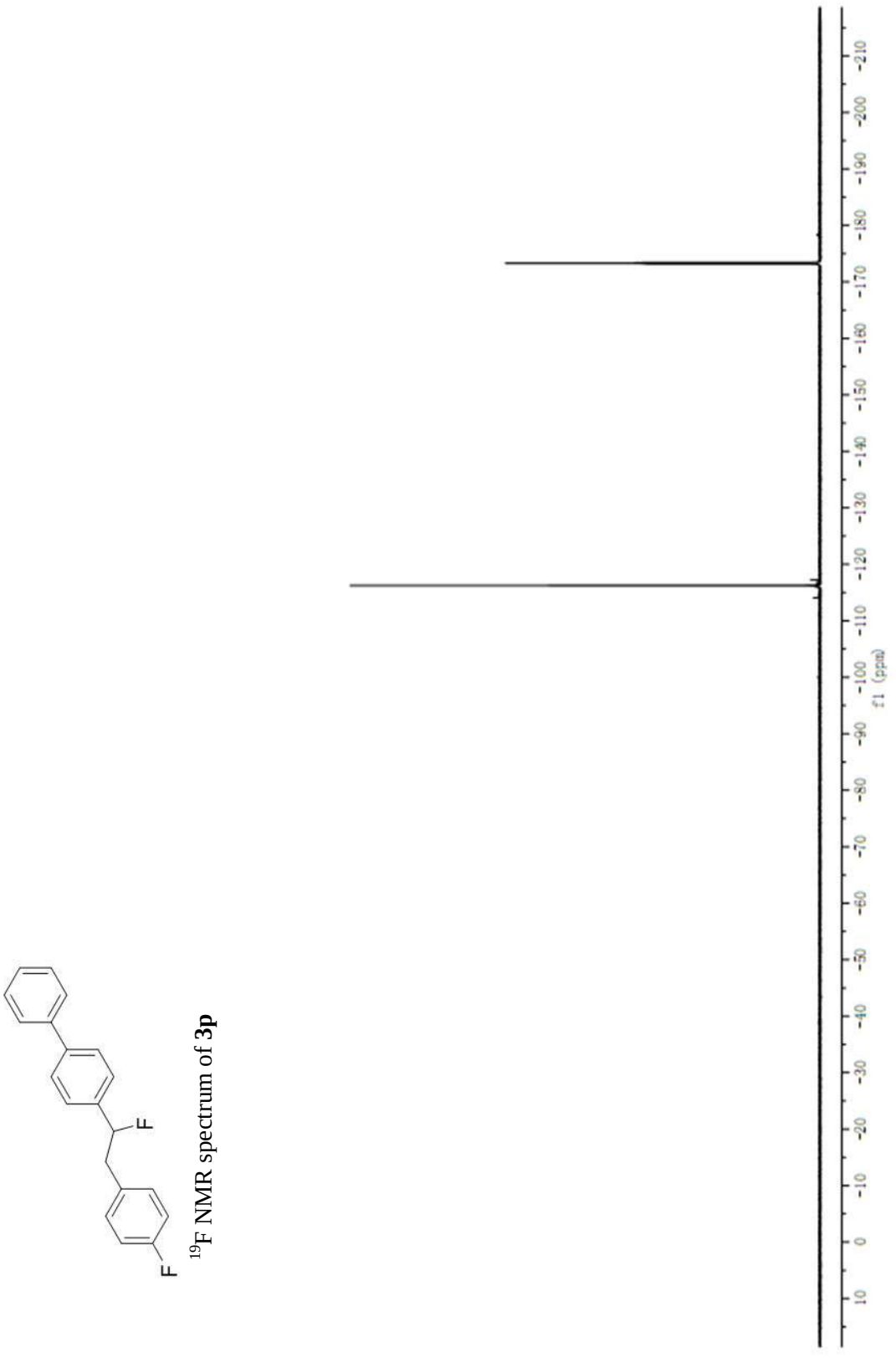
^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3o**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3p**

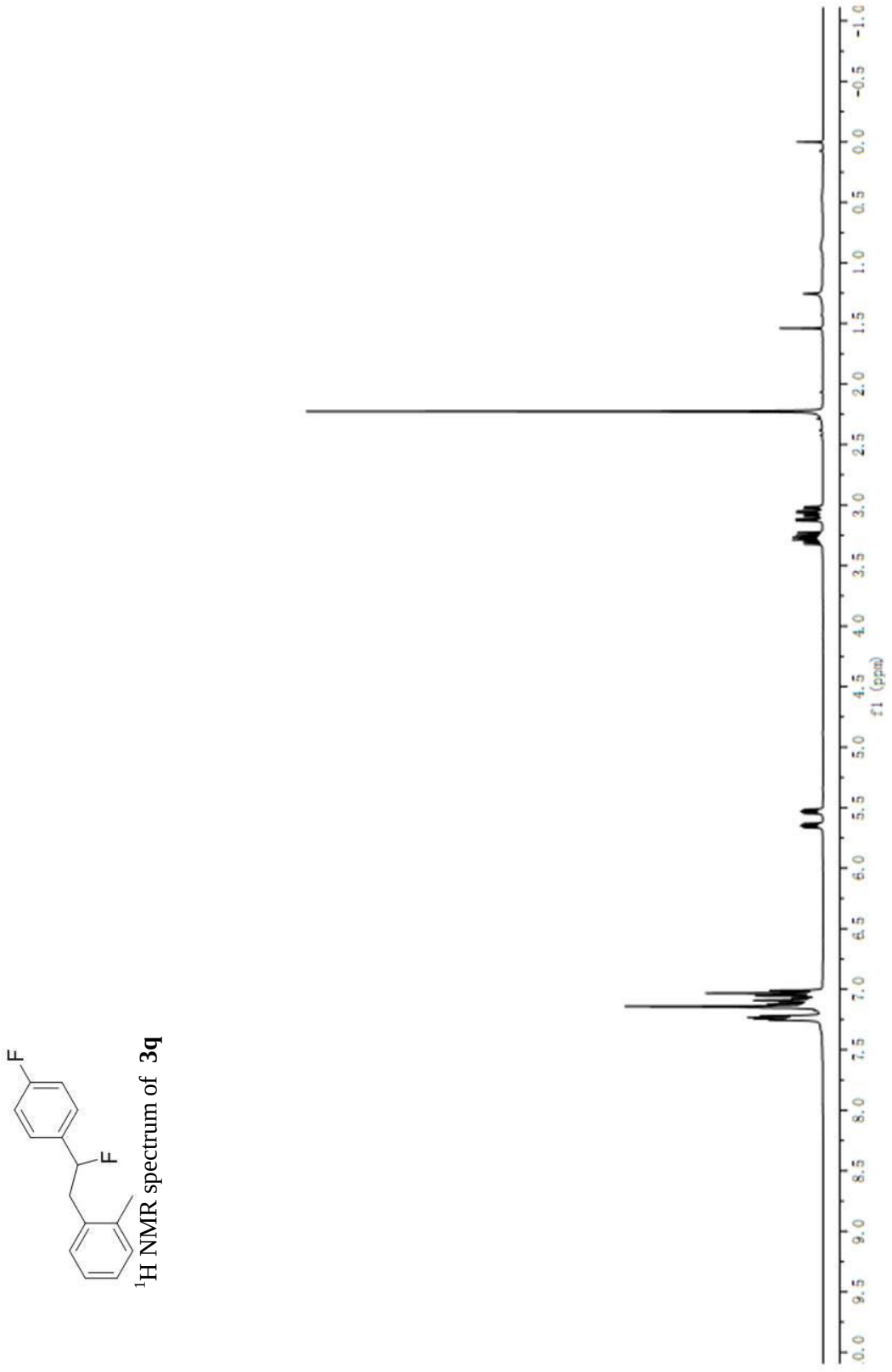


^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3p**



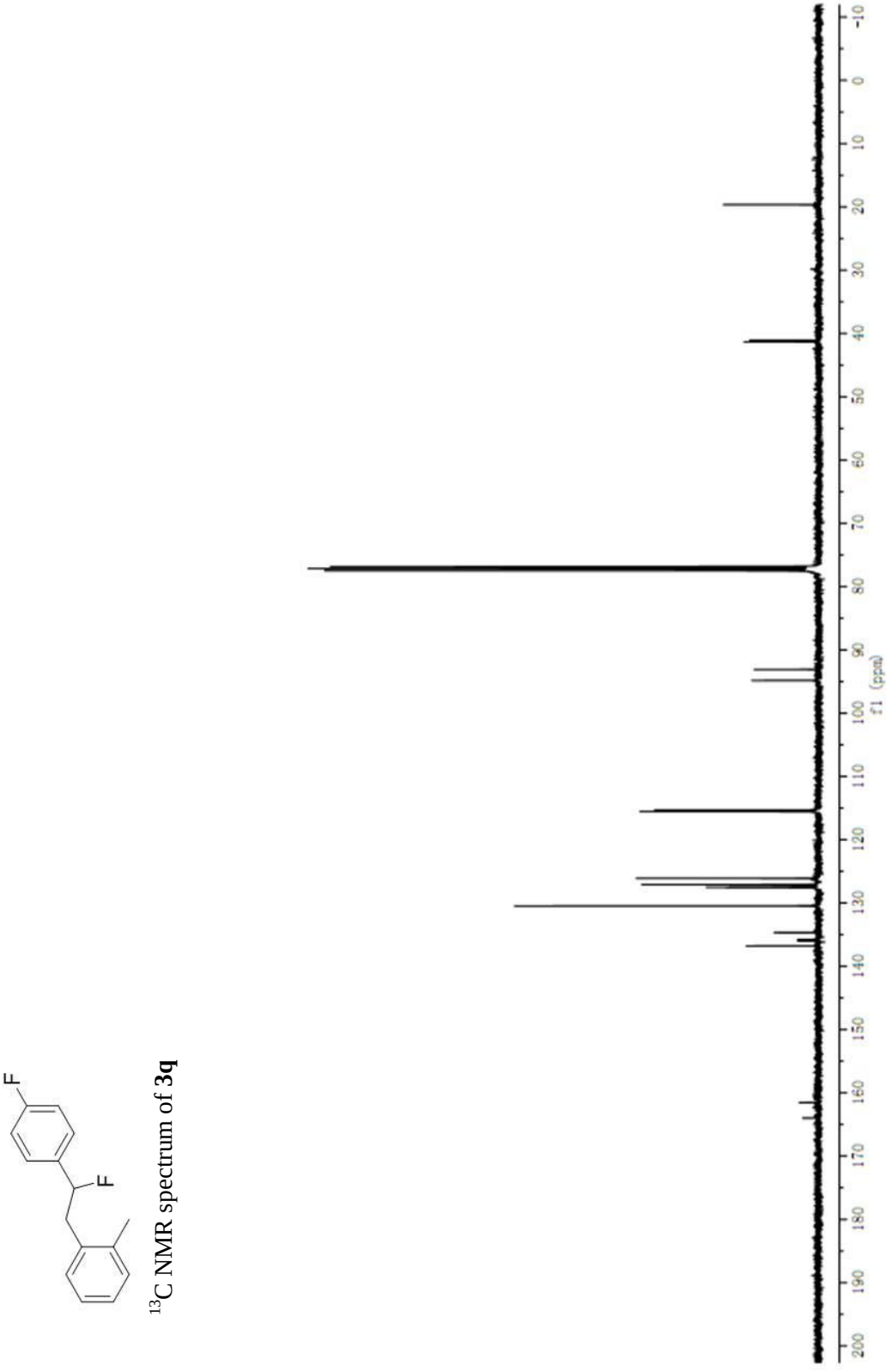
^{19}F NMR spectrum of **3p**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3p**

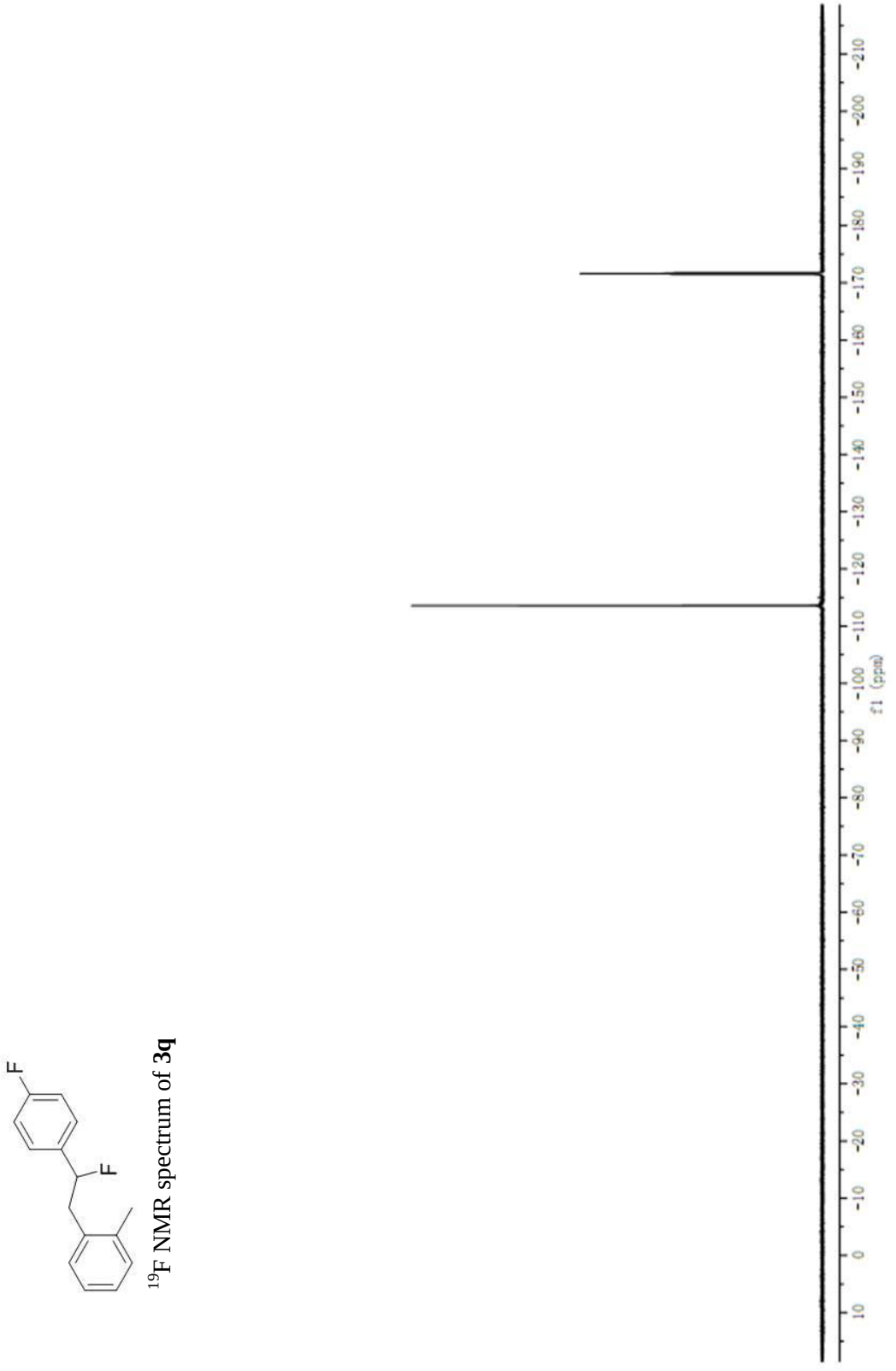


^{1}H NMR spectrum of **3q**

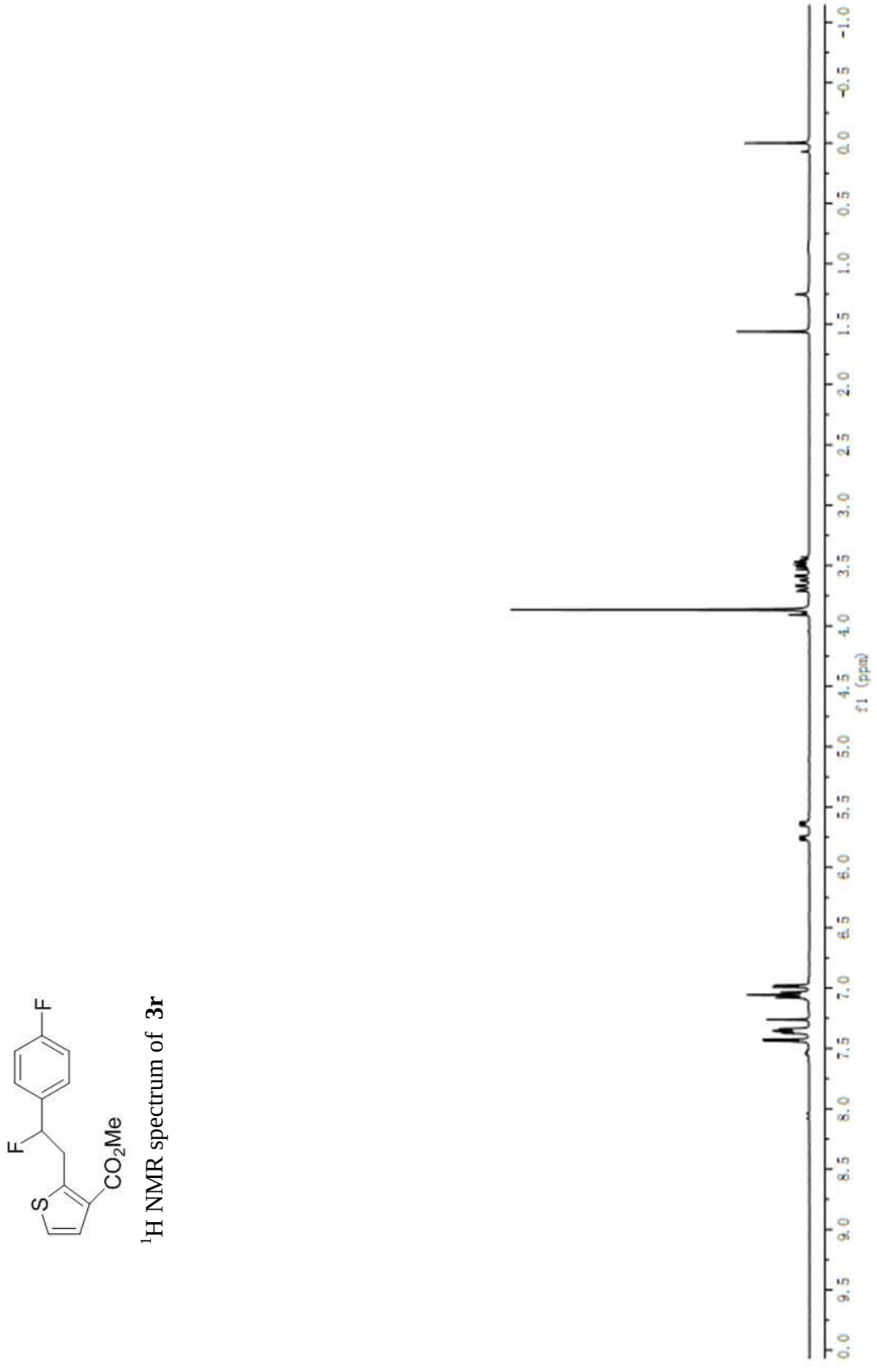
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3q**



^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3q**

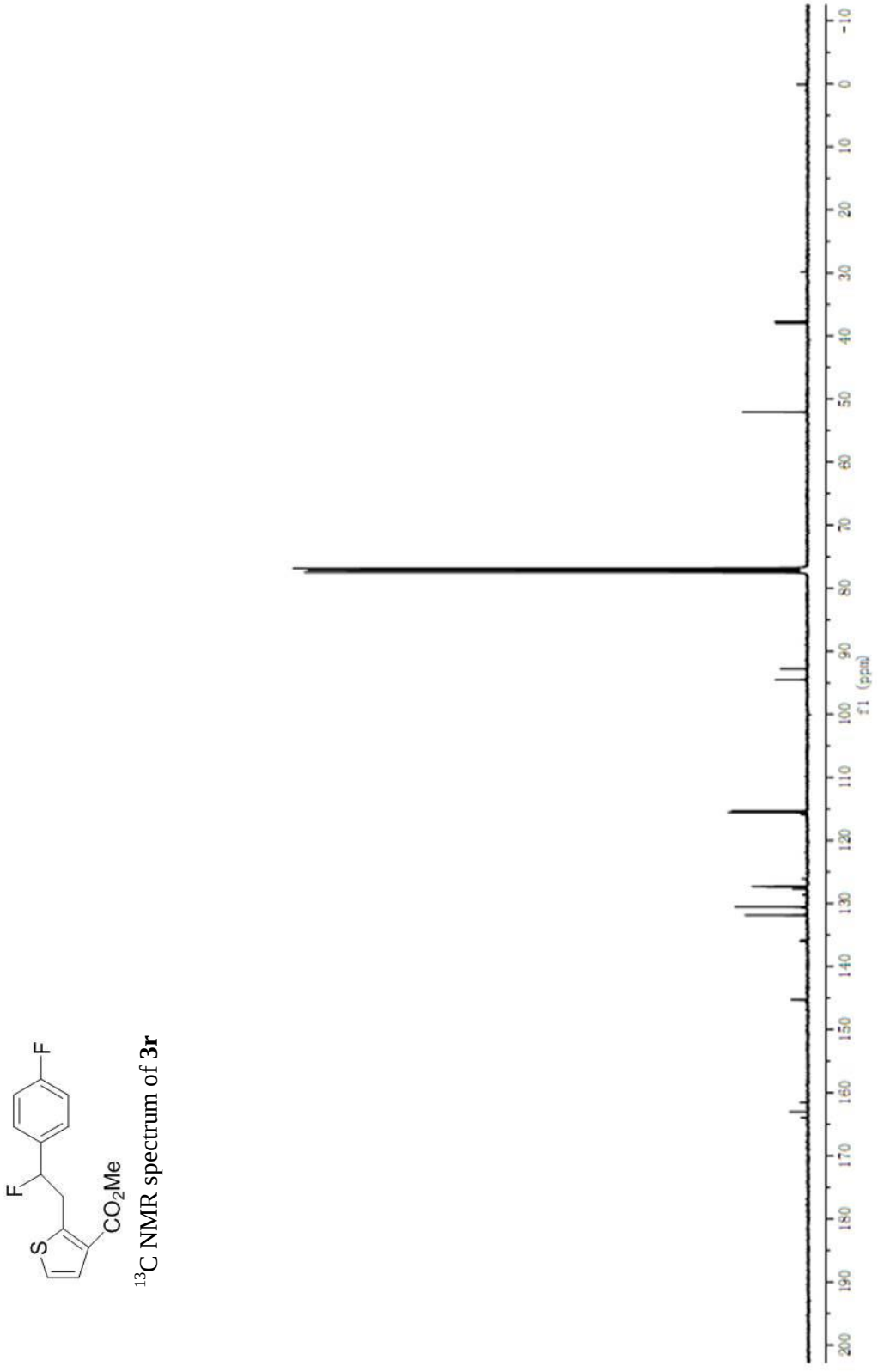


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3q**



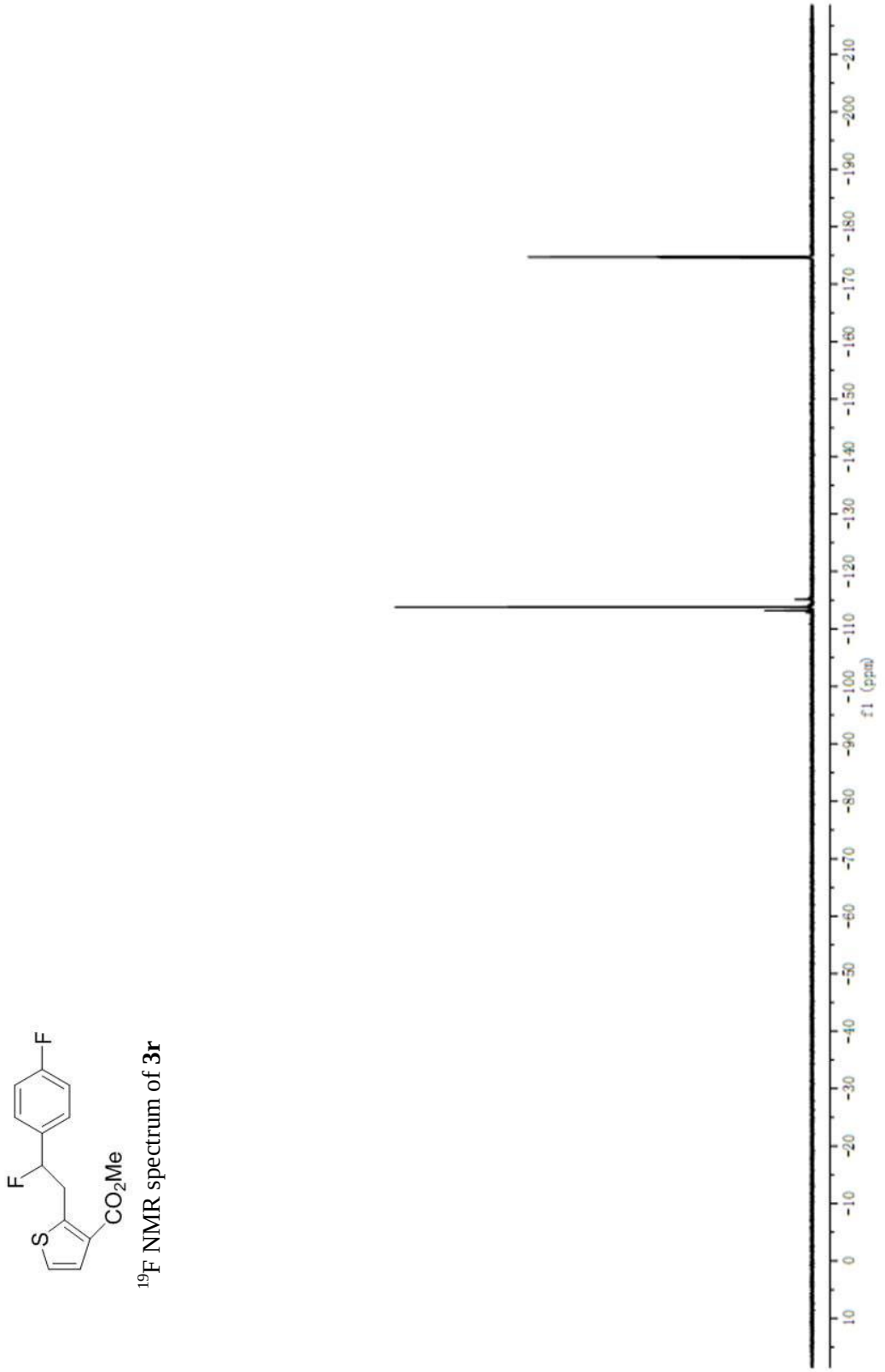
^{1}H NMR spectrum of **3r**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3r**



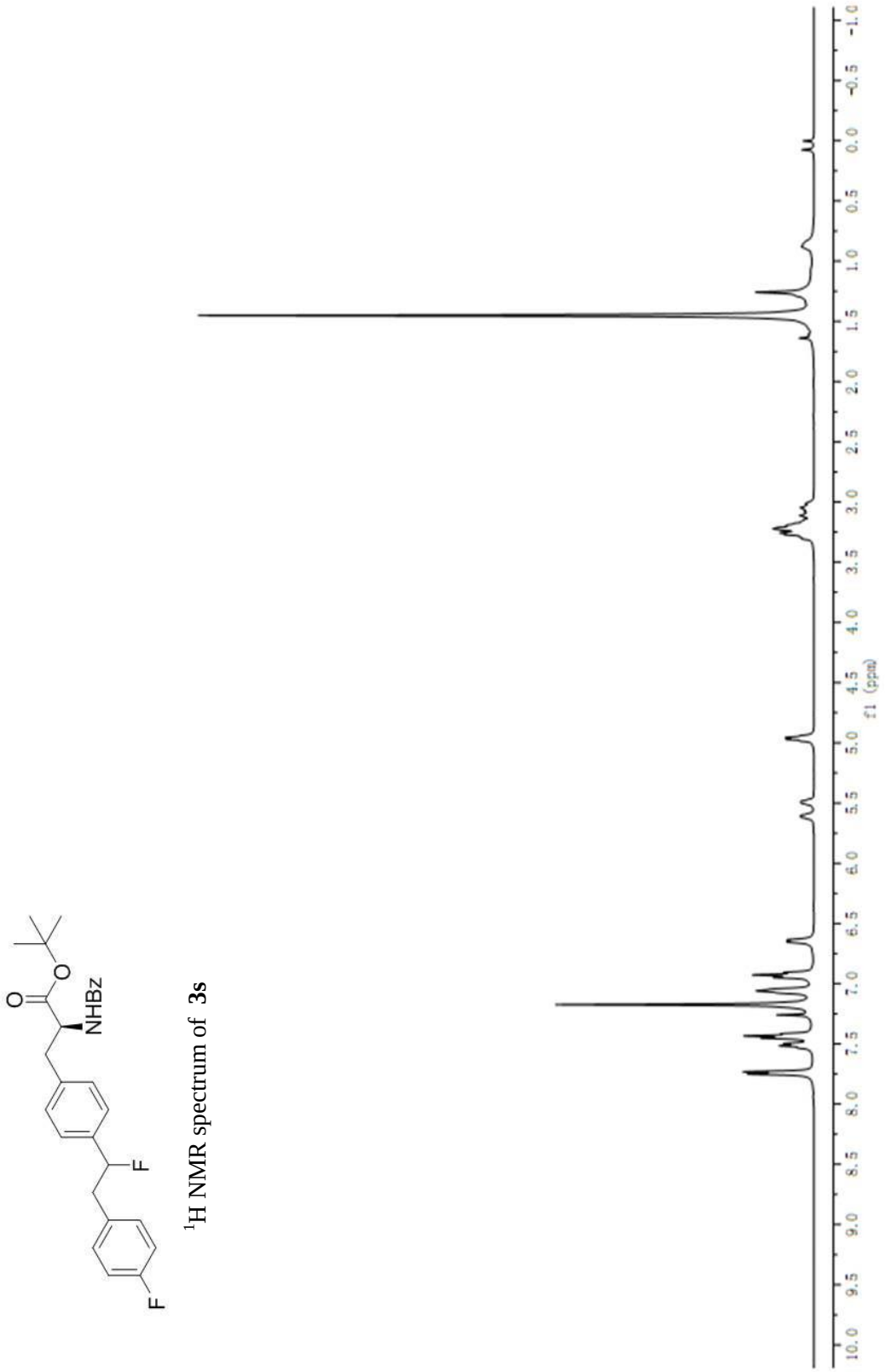
^{13}C NMR spectrum of **3r**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3r**



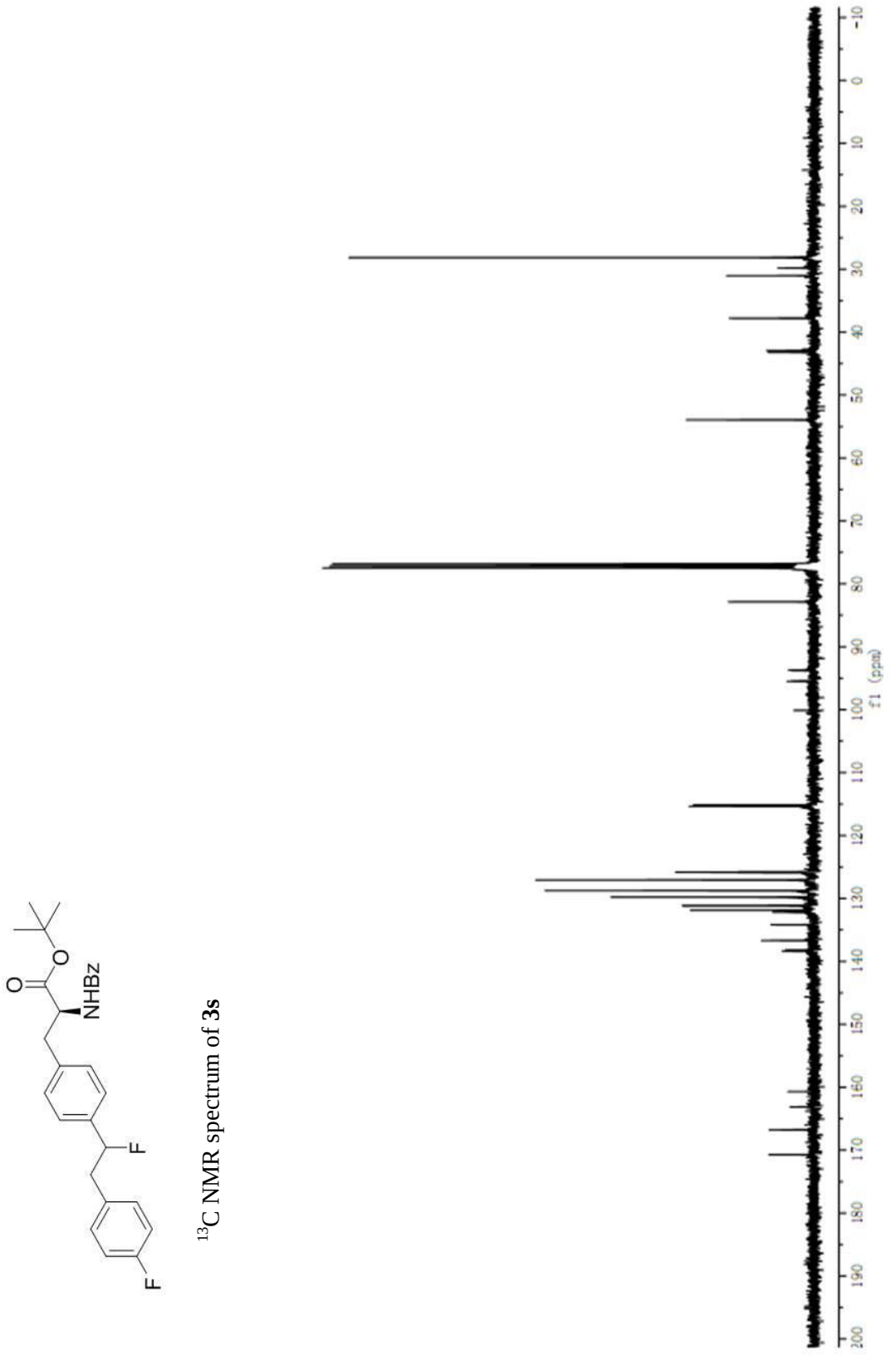
^{19}F NMR spectrum of **3r**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3r**



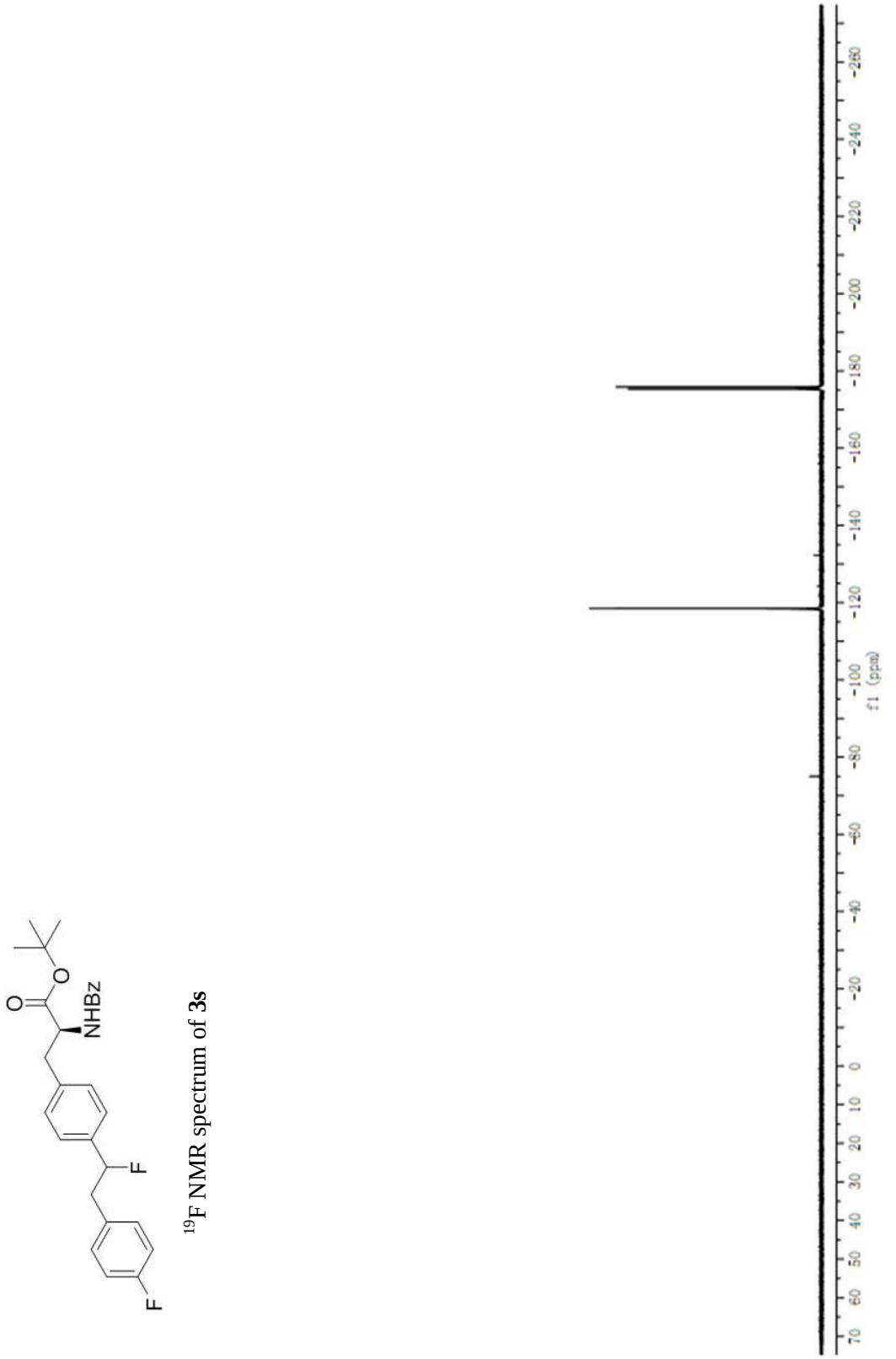
^{1}H NMR spectrum of **3s**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3s**



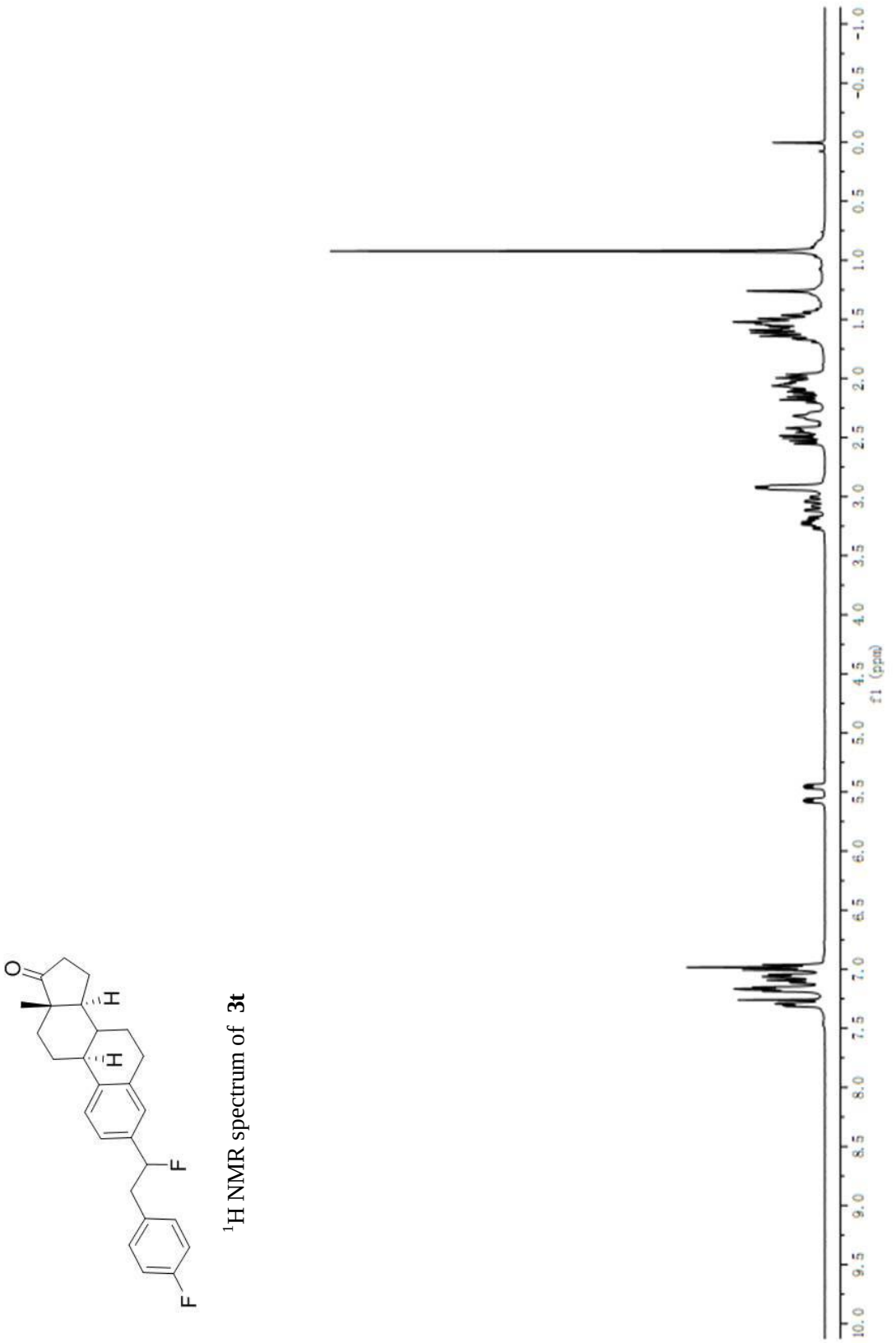
^{13}C NMR spectrum of **3s**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3s**



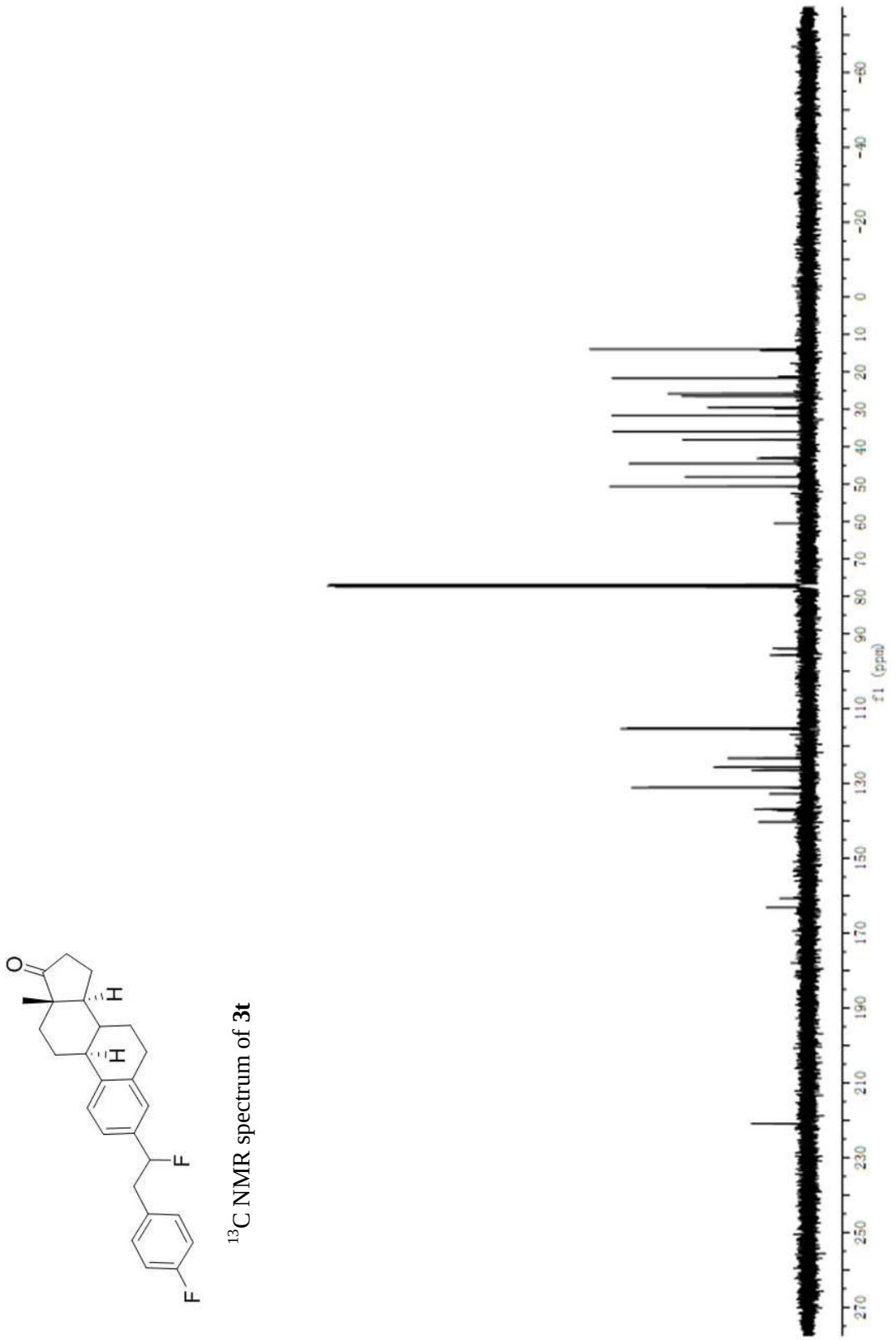
^{19}F NMR spectrum of **3s**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3s**



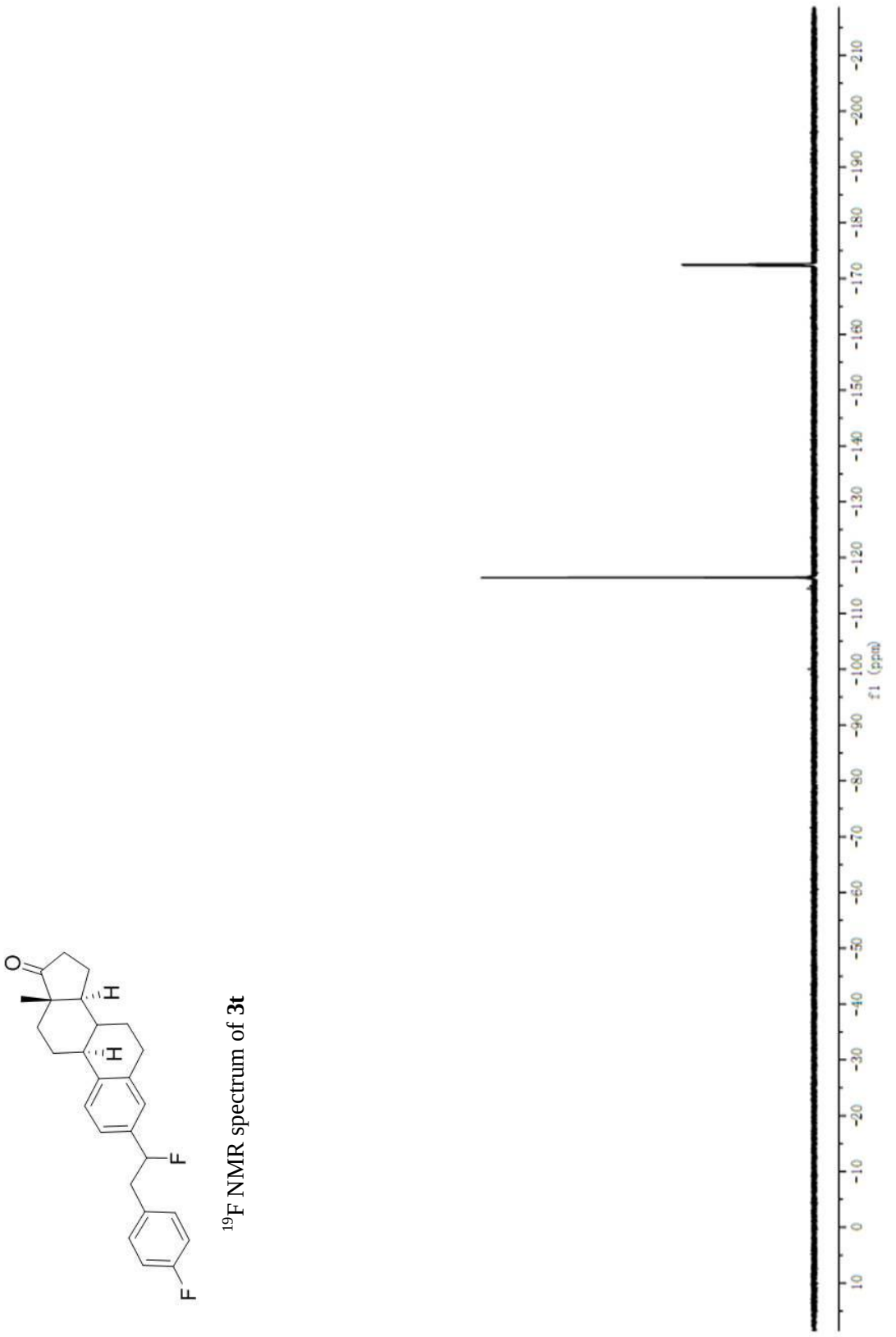
^{1}H NMR spectrum of **3t**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **3t**



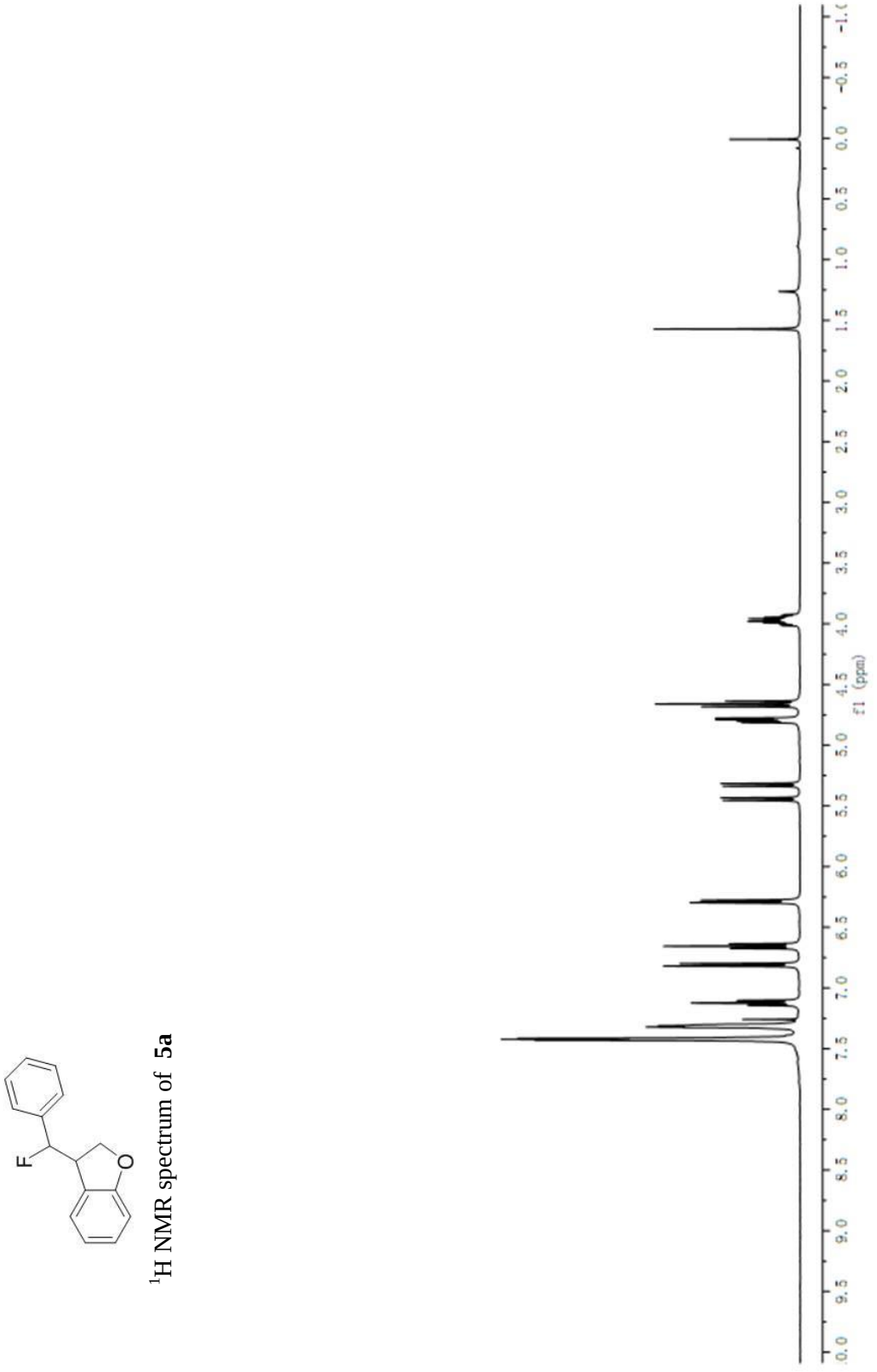
^{13}C NMR spectrum of **3t**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **3t**



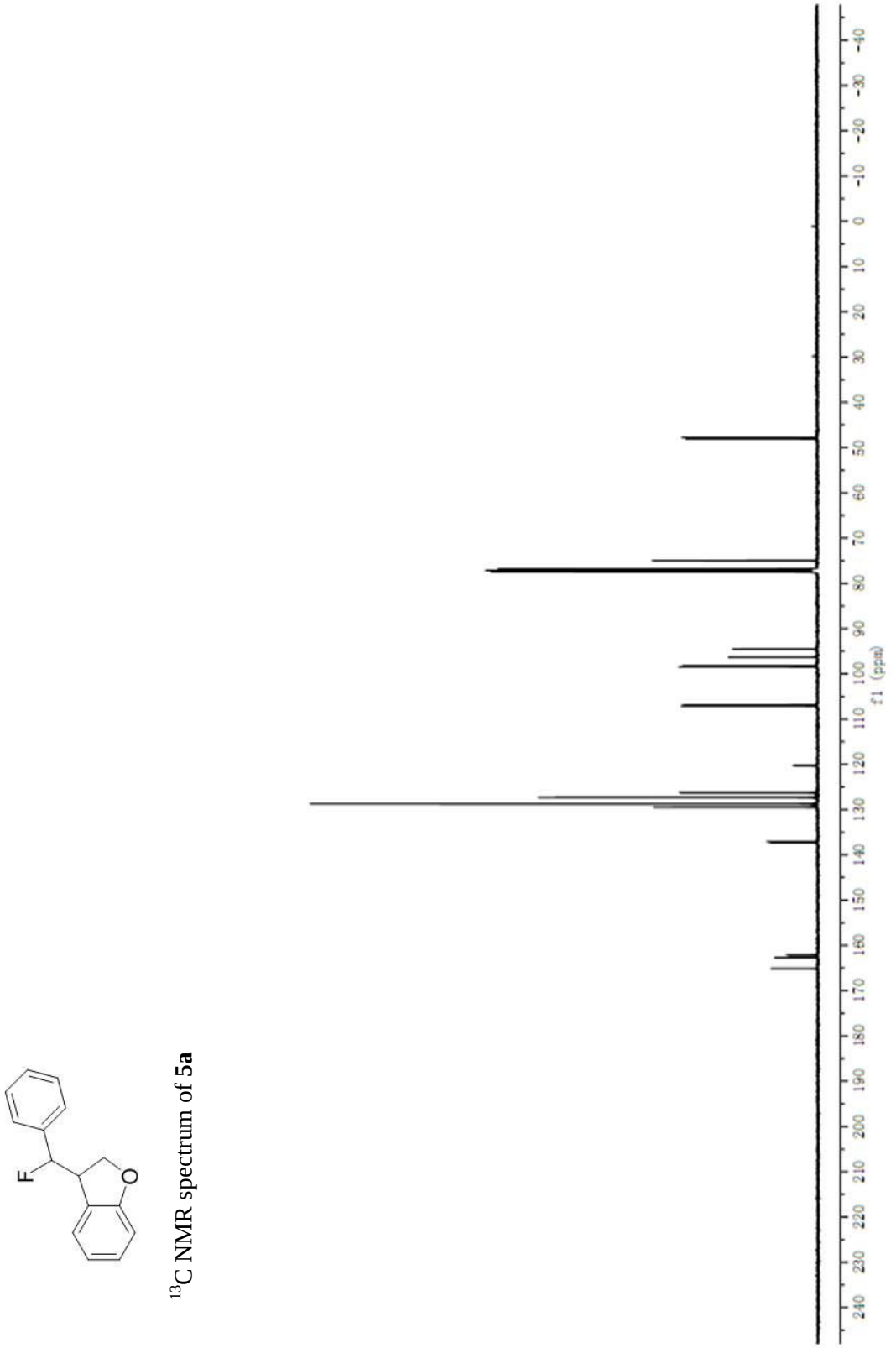
^{19}F NMR spectrum of **3t**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **3t**



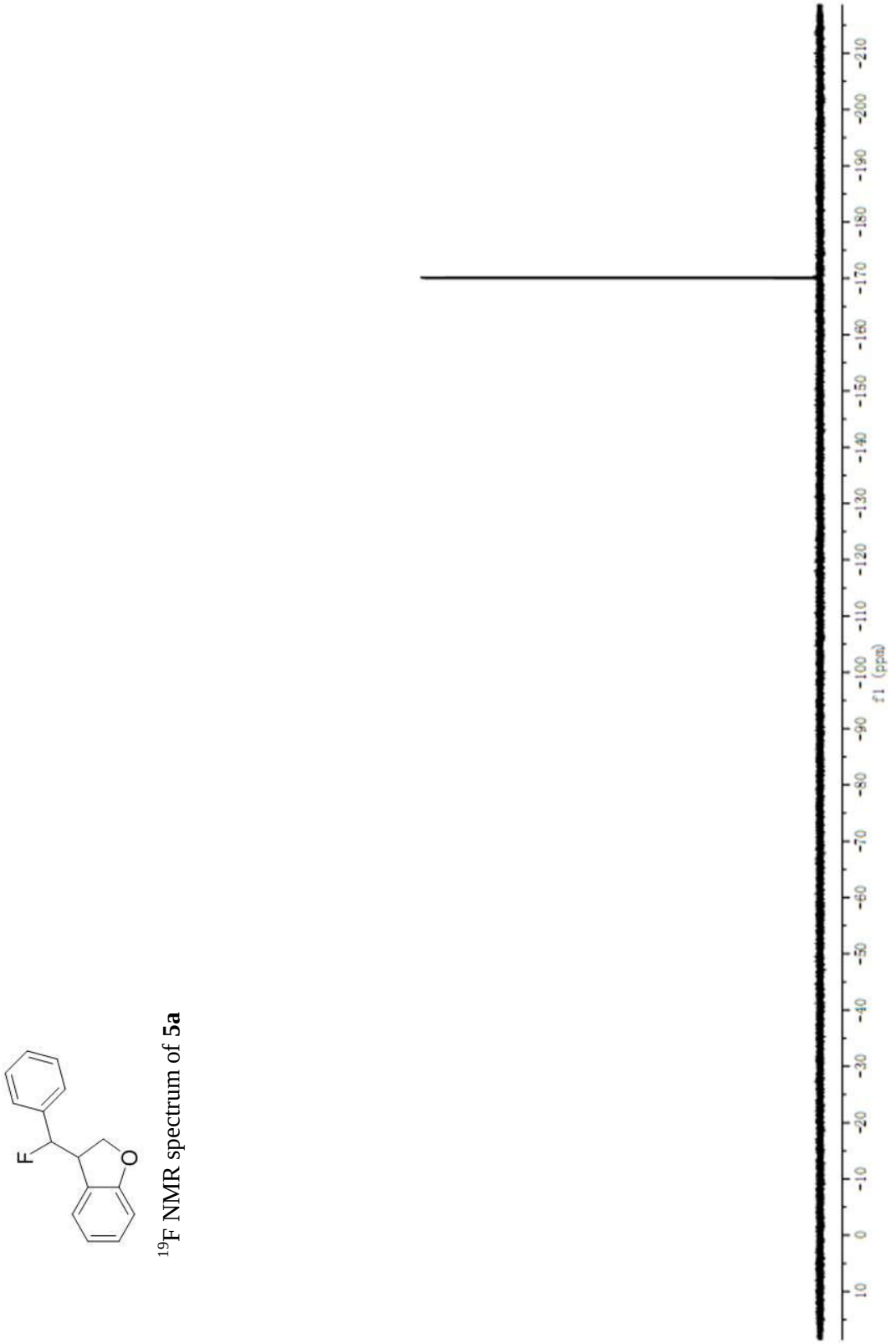
^{1}H NMR spectrum of **5a**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5a**



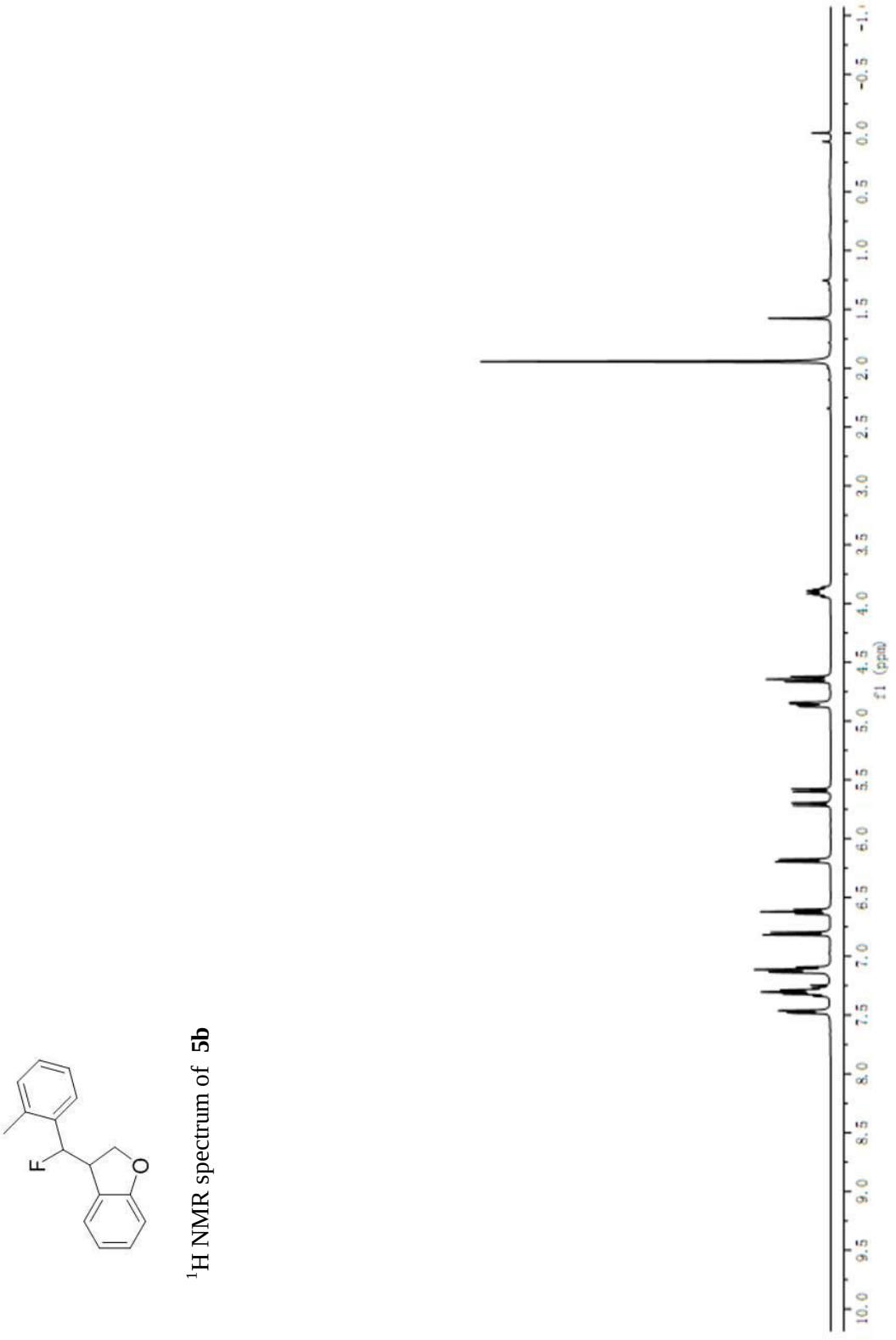
^{13}C NMR spectrum of **5a**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5a**



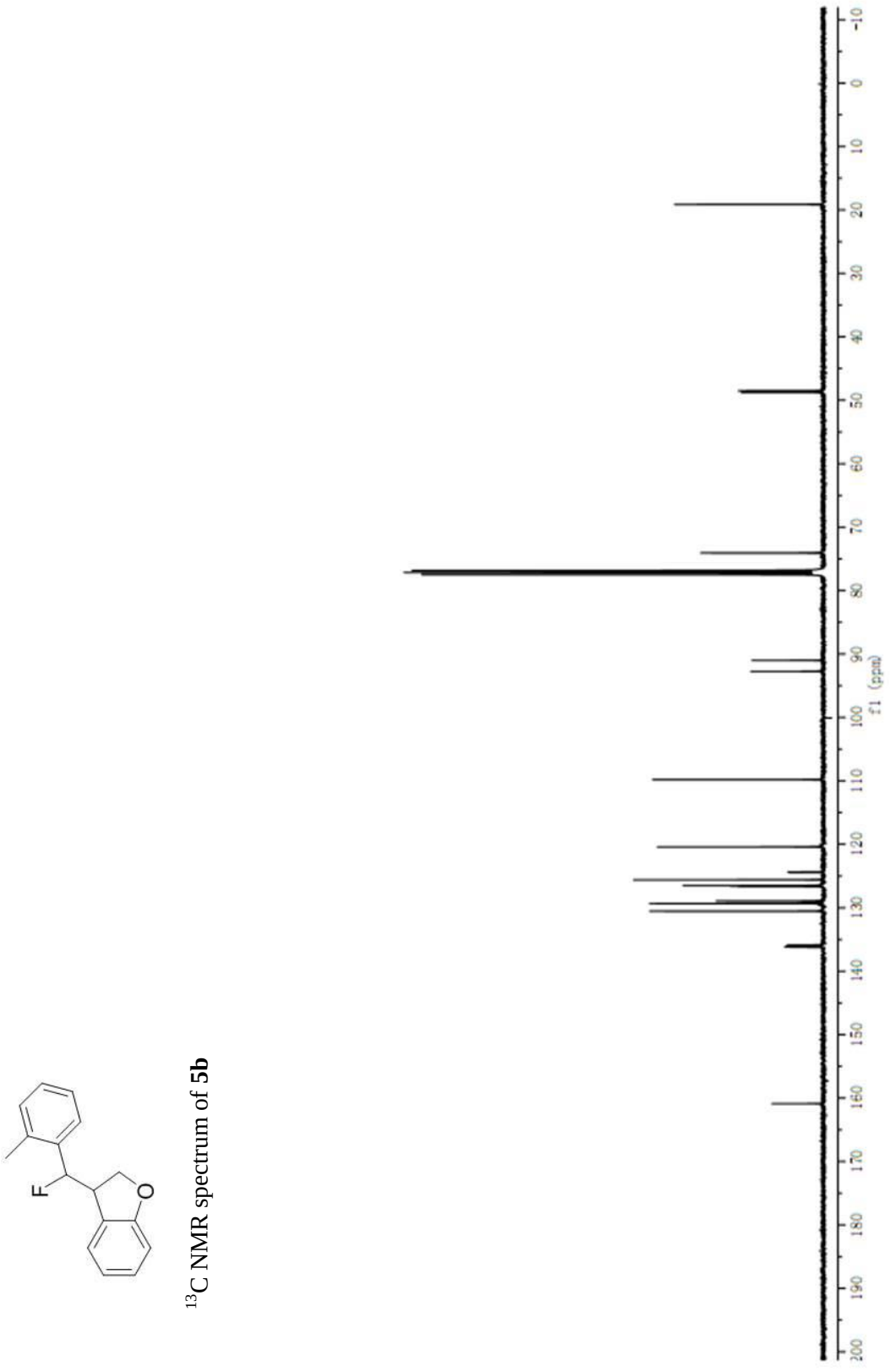
^{19}F NMR spectrum of **5a**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5a**



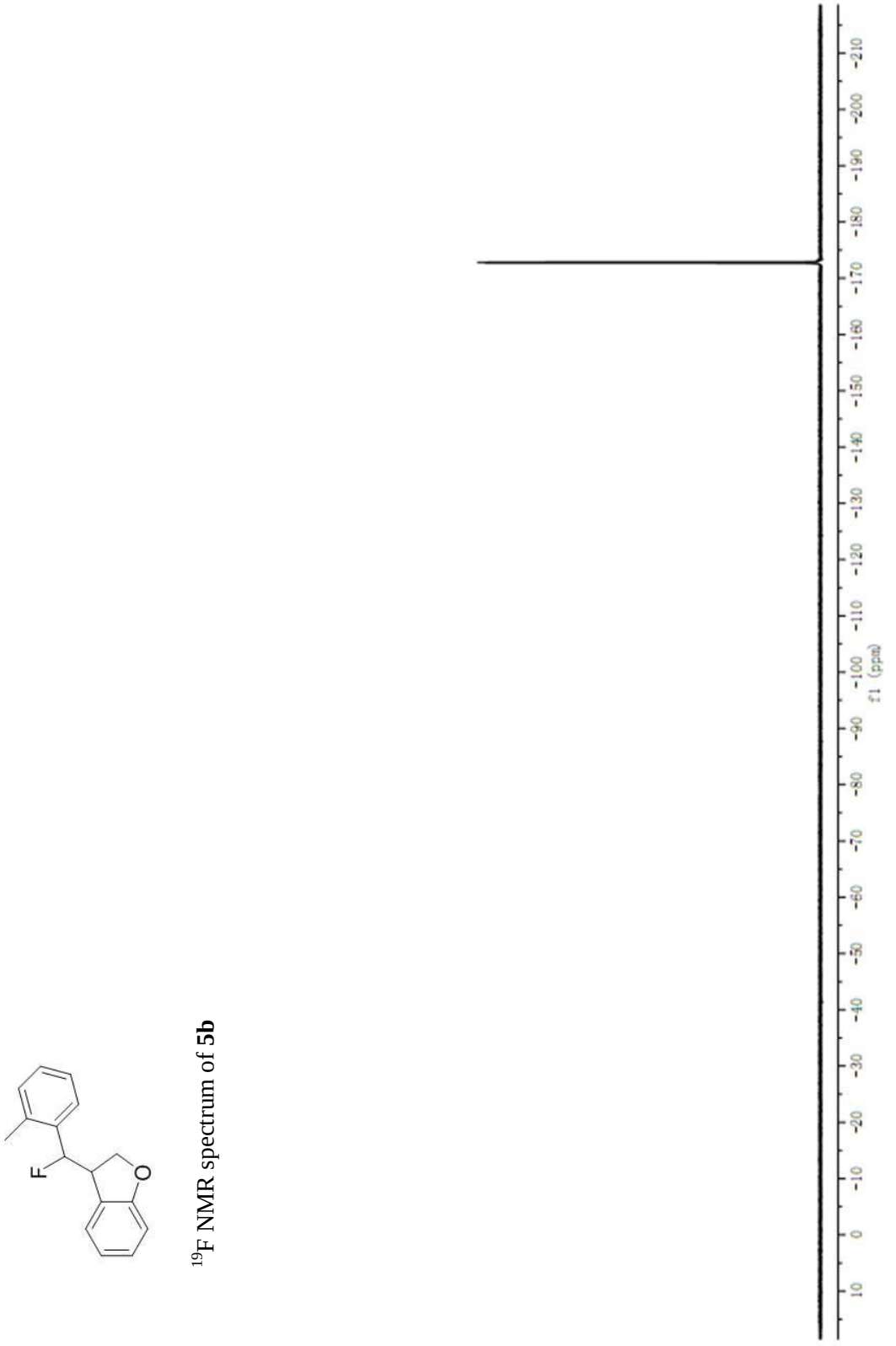
^{1}H NMR spectrum of **5b**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5b**



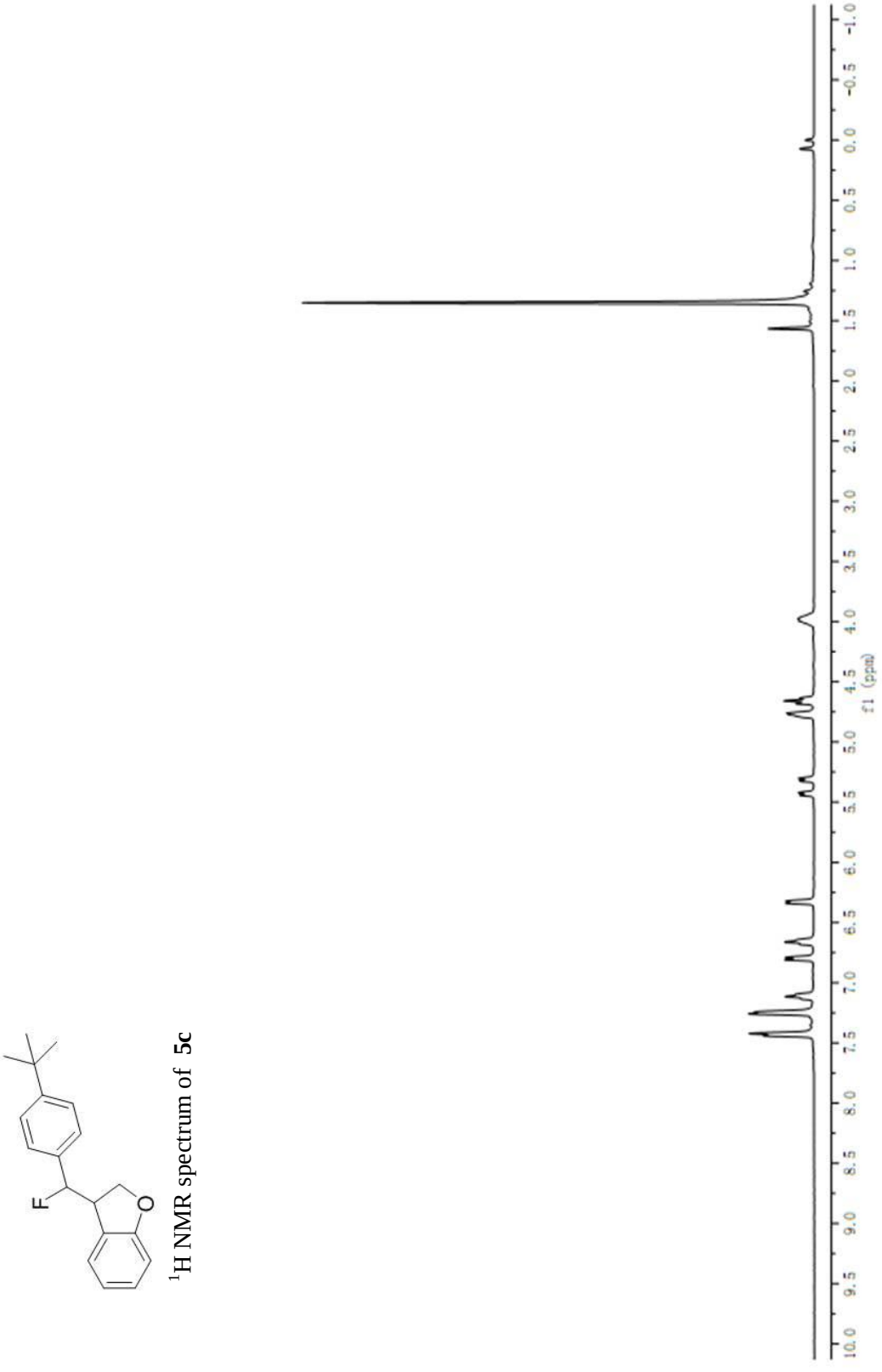
^{13}C NMR spectrum of **5b**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5b**



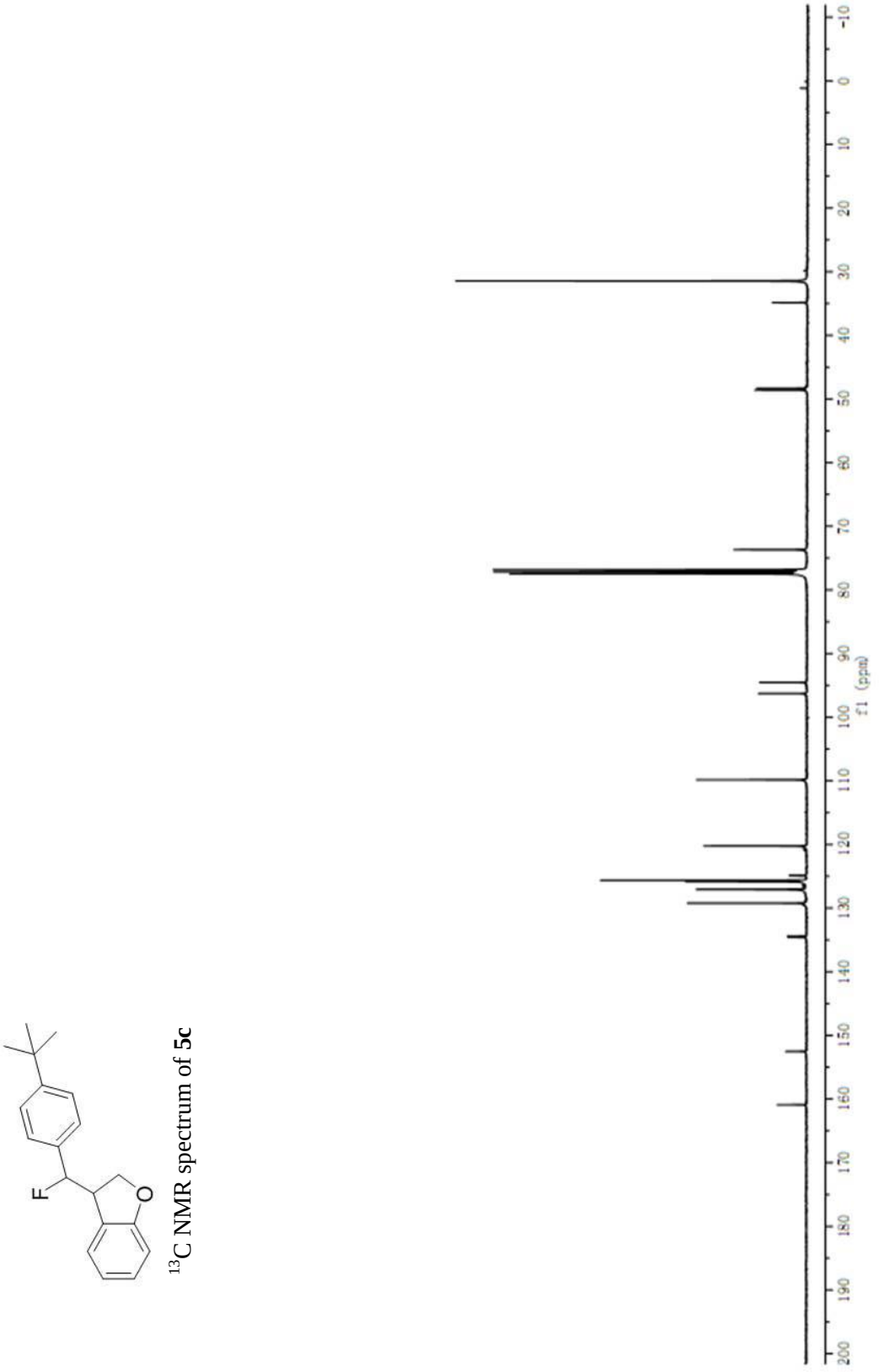
^{19}F NMR spectrum of **5b**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5b**



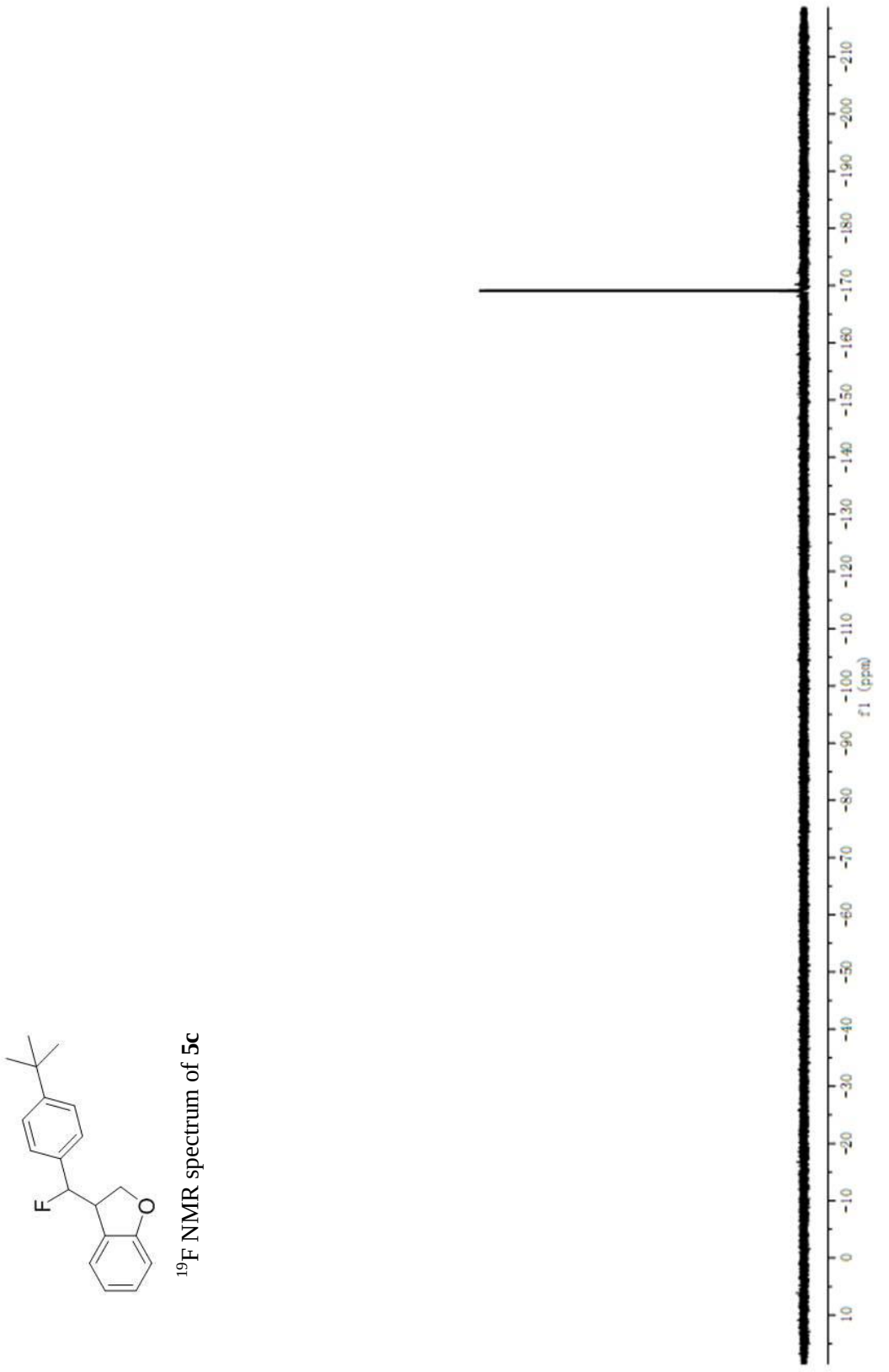
^{1}H NMR spectrum of **5c**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5c**



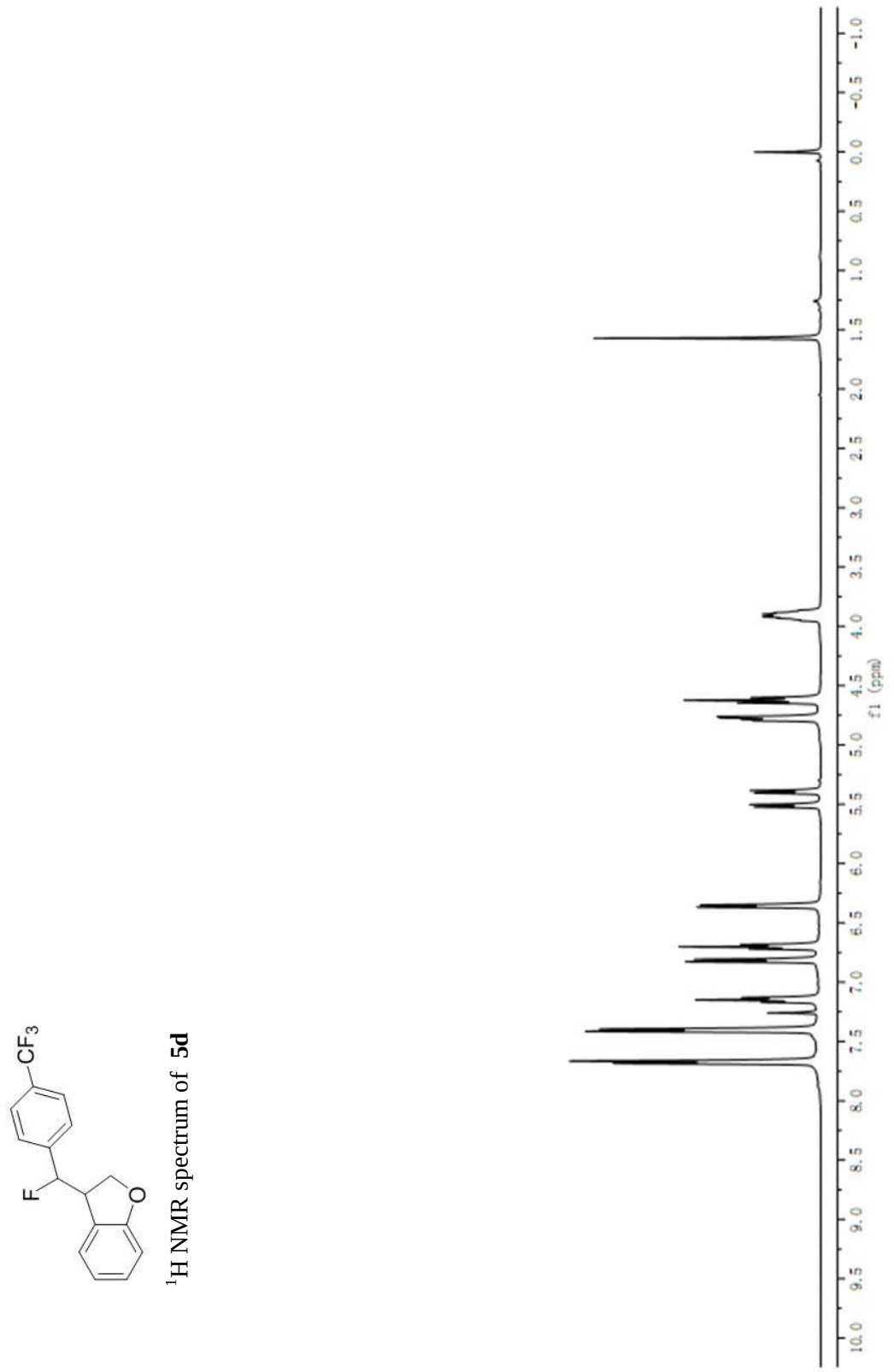
^{13}C NMR spectrum of **5c**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5c**



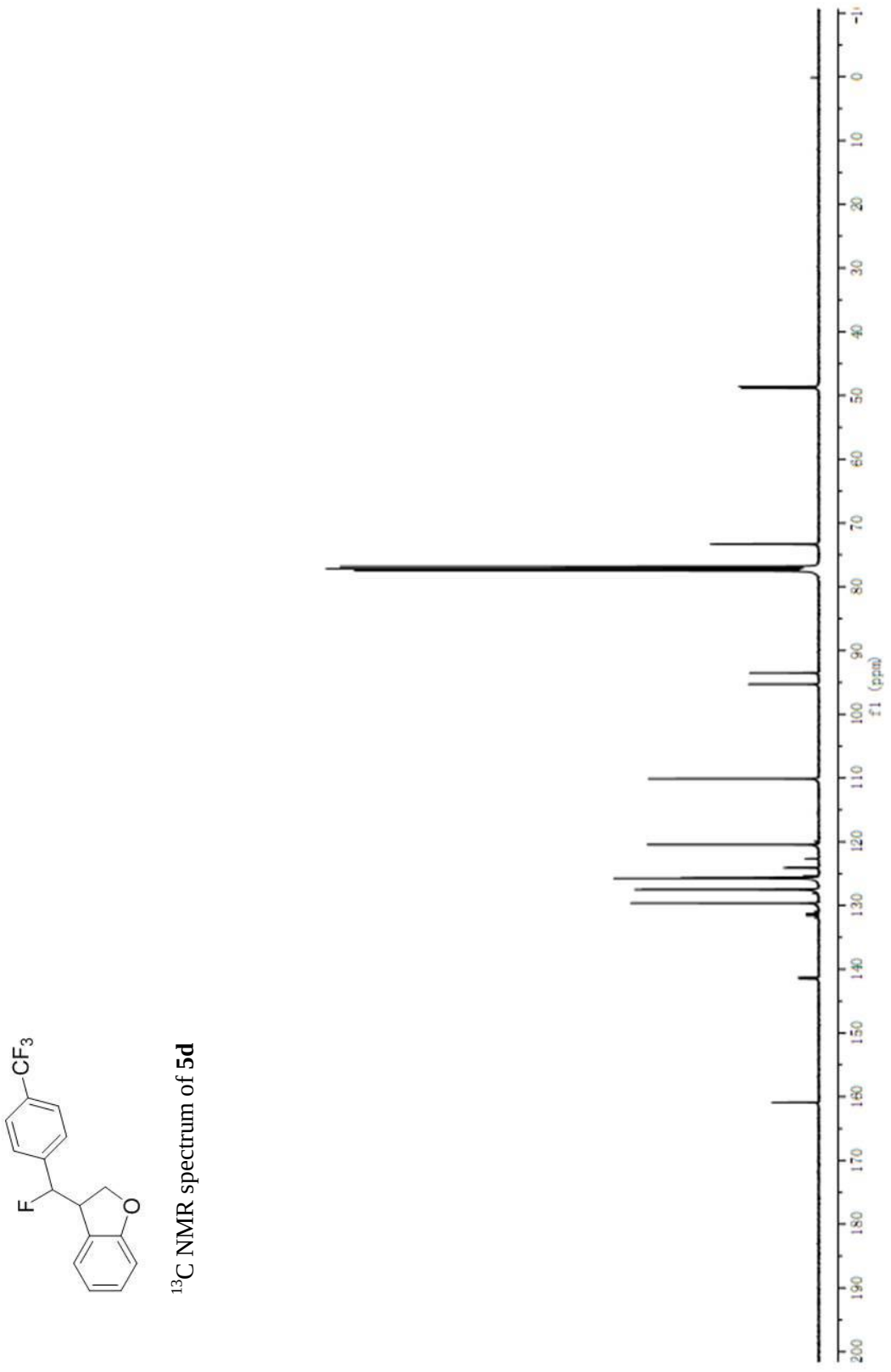
^{19}F NMR spectrum of **5c**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5c**



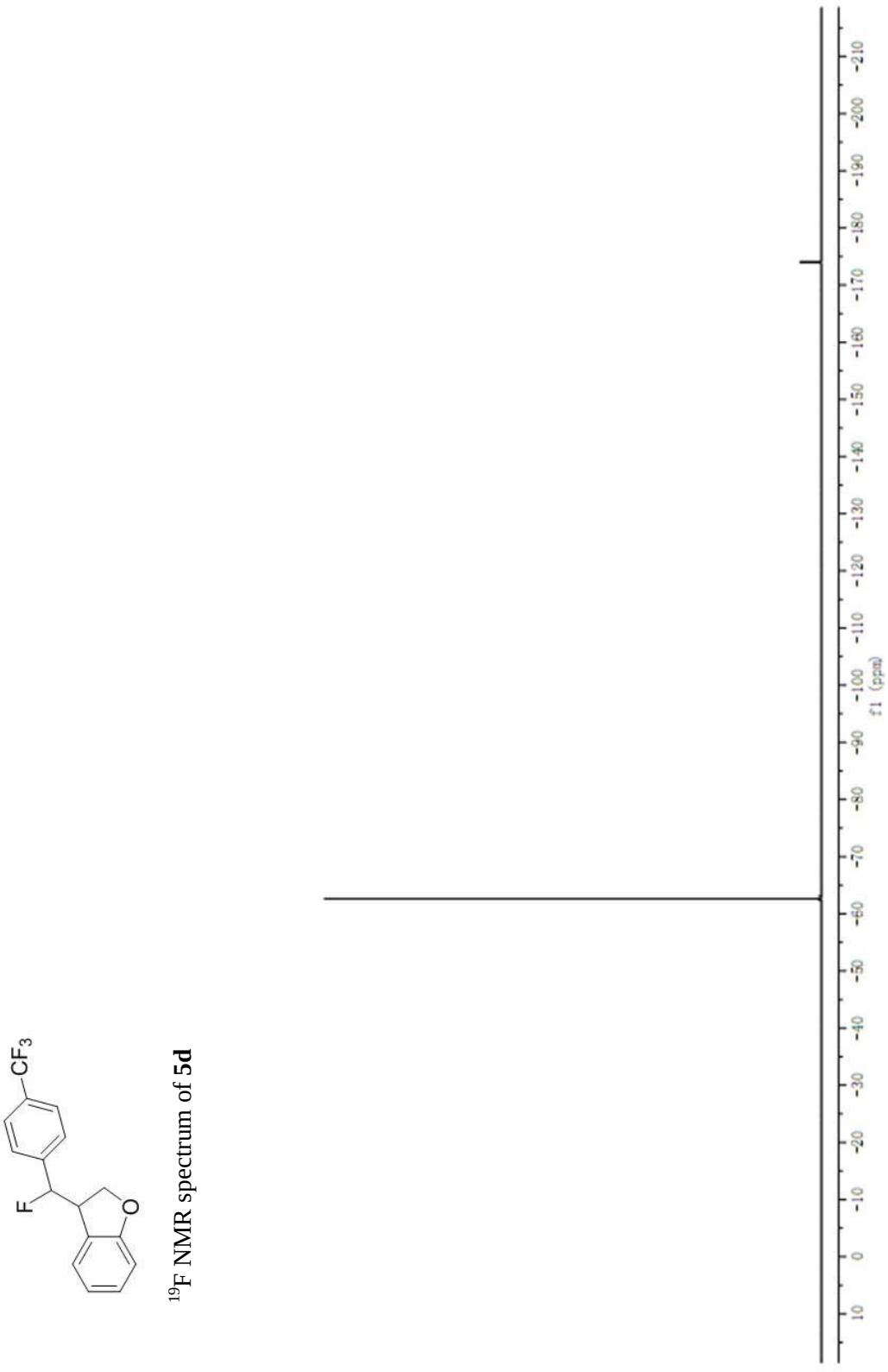
^{1}H NMR spectrum of **5d**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5d**



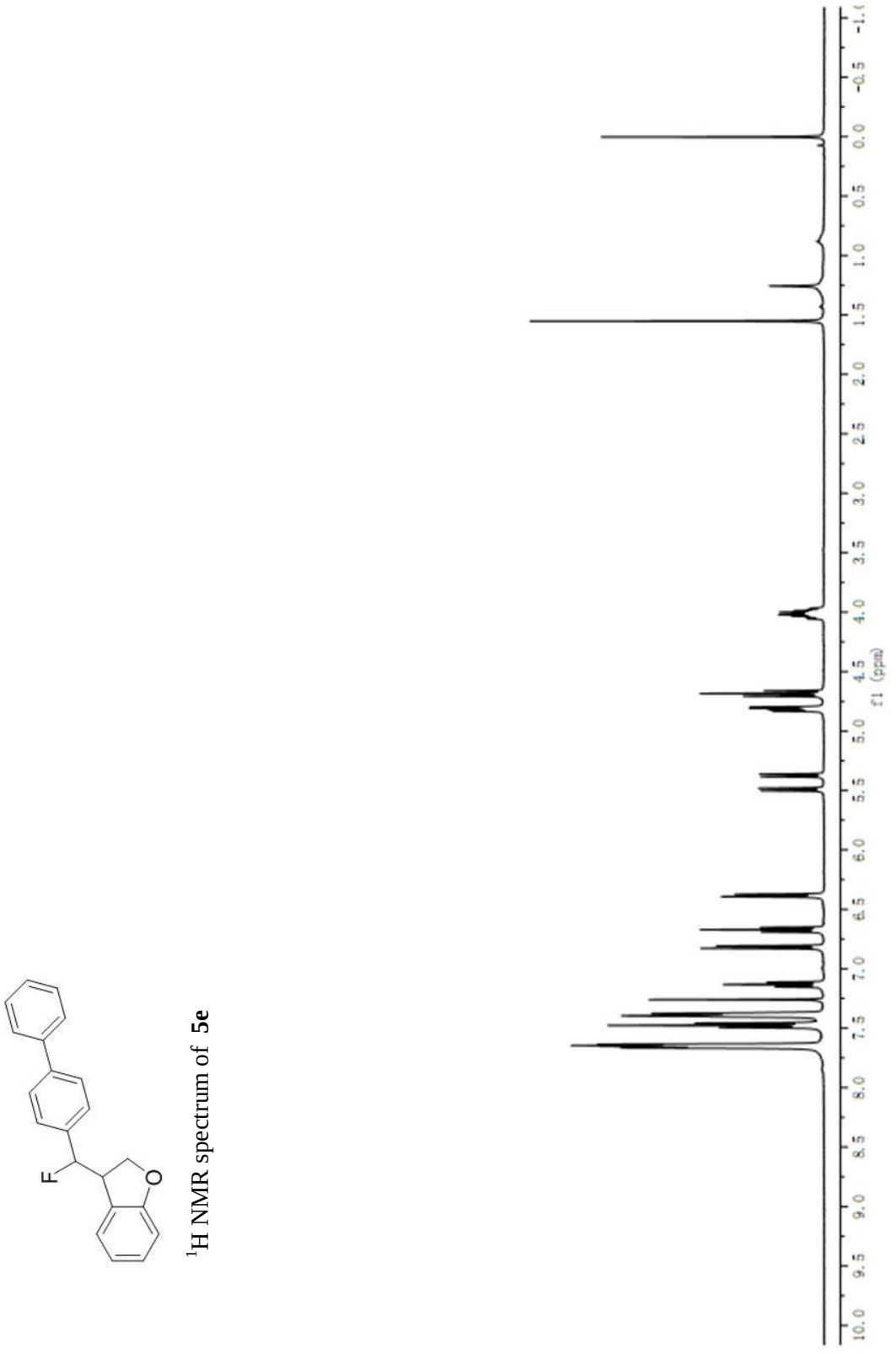
^{13}C NMR spectrum of **5d**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5d**



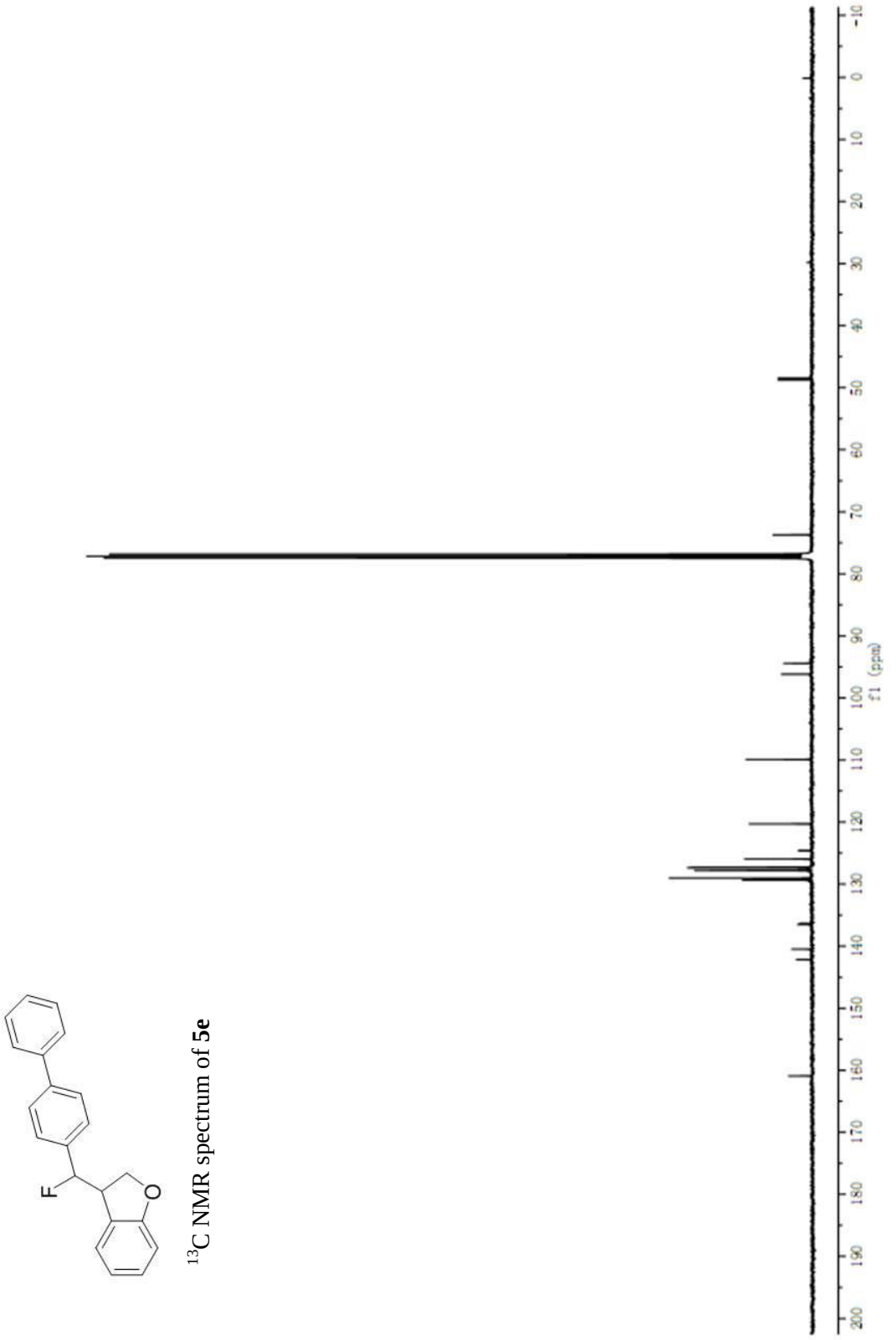
^{19}F NMR spectrum of **5d**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5d**



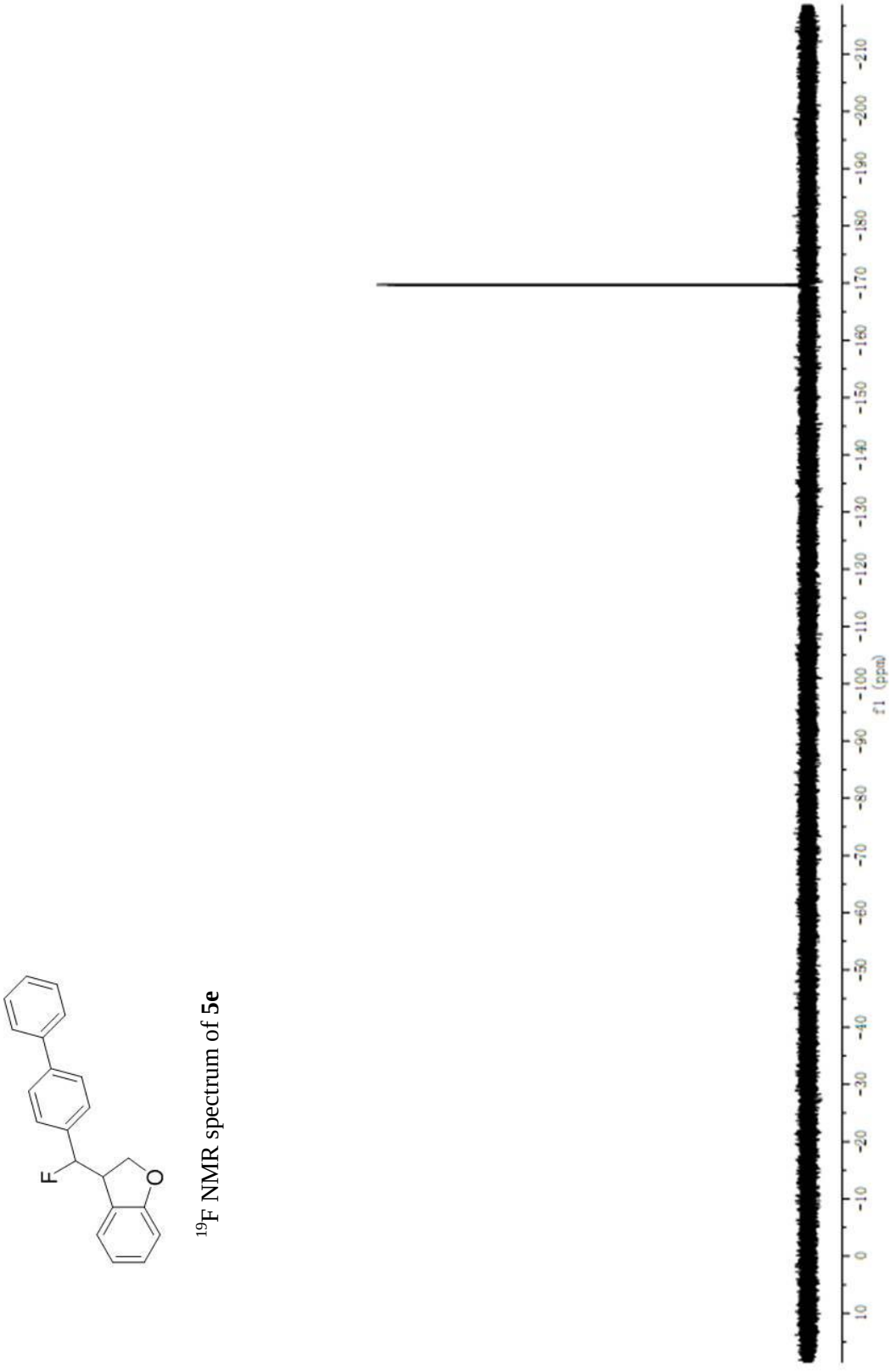
^{1}H NMR spectrum of **5e**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5e**



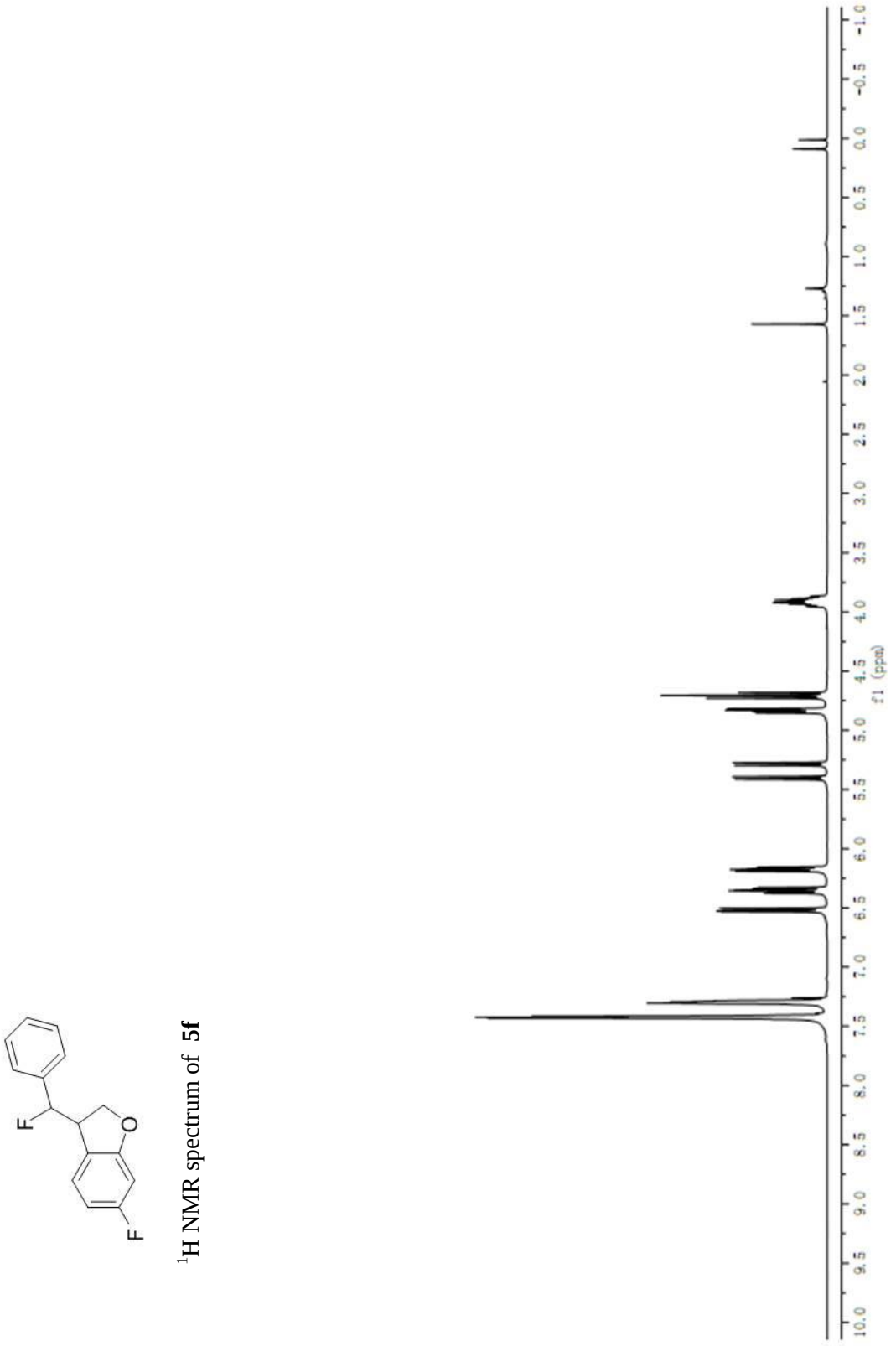
^{13}C NMR spectrum of **5e**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5e**



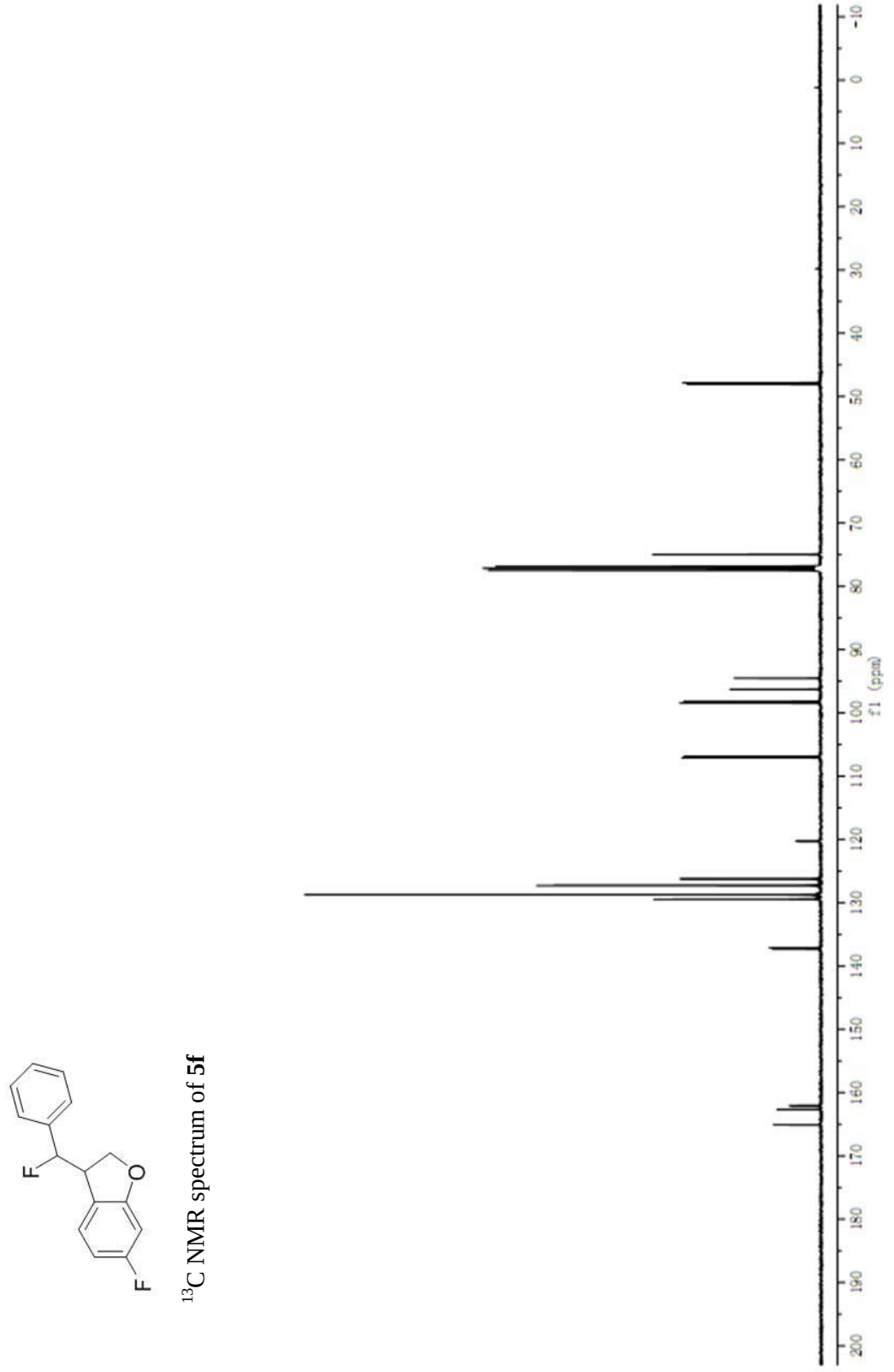
^{19}F NMR spectrum of **5e**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5e**



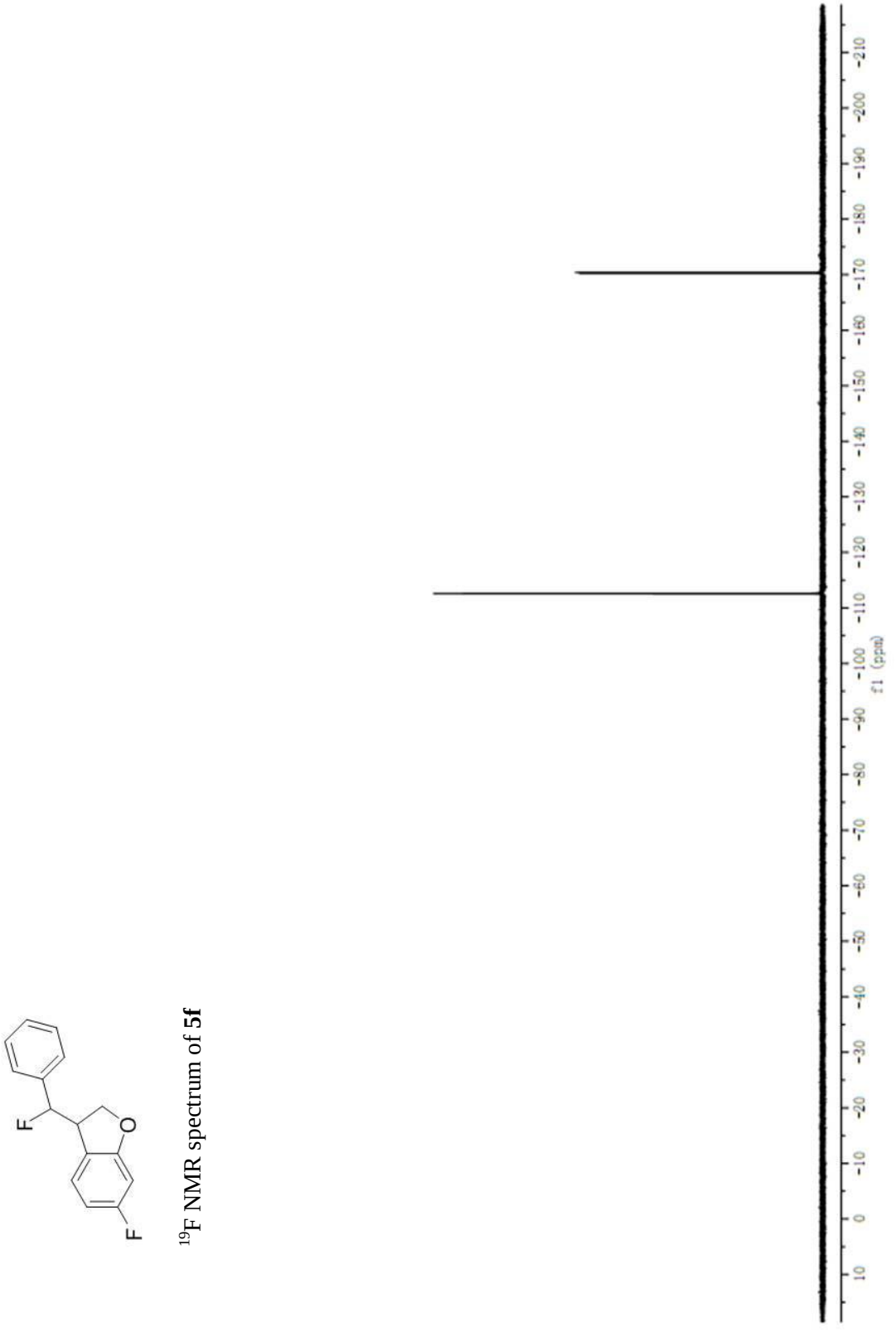
^{1}H NMR spectrum of **5f**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5f**



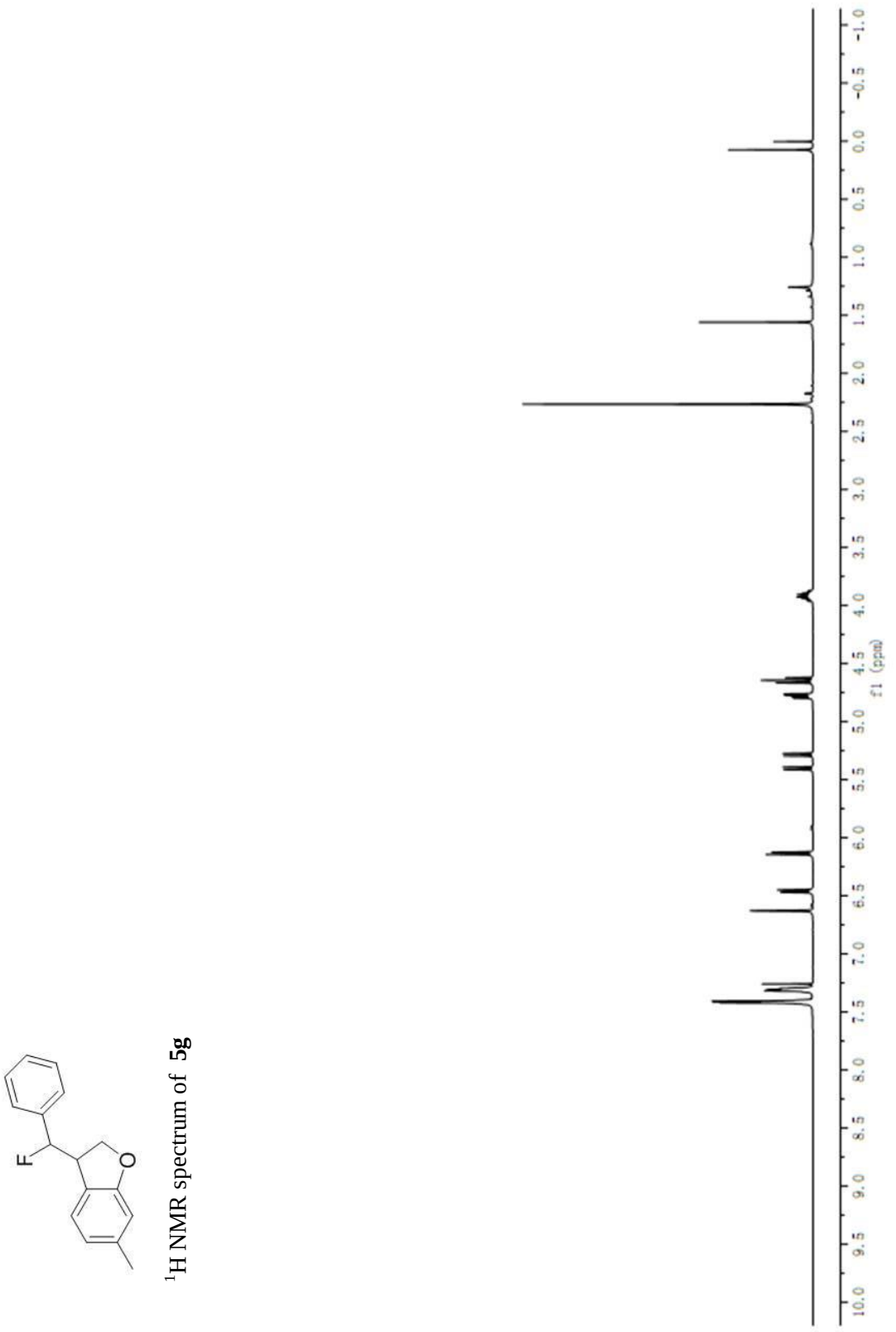
^{13}C NMR spectrum of **5f**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5f**



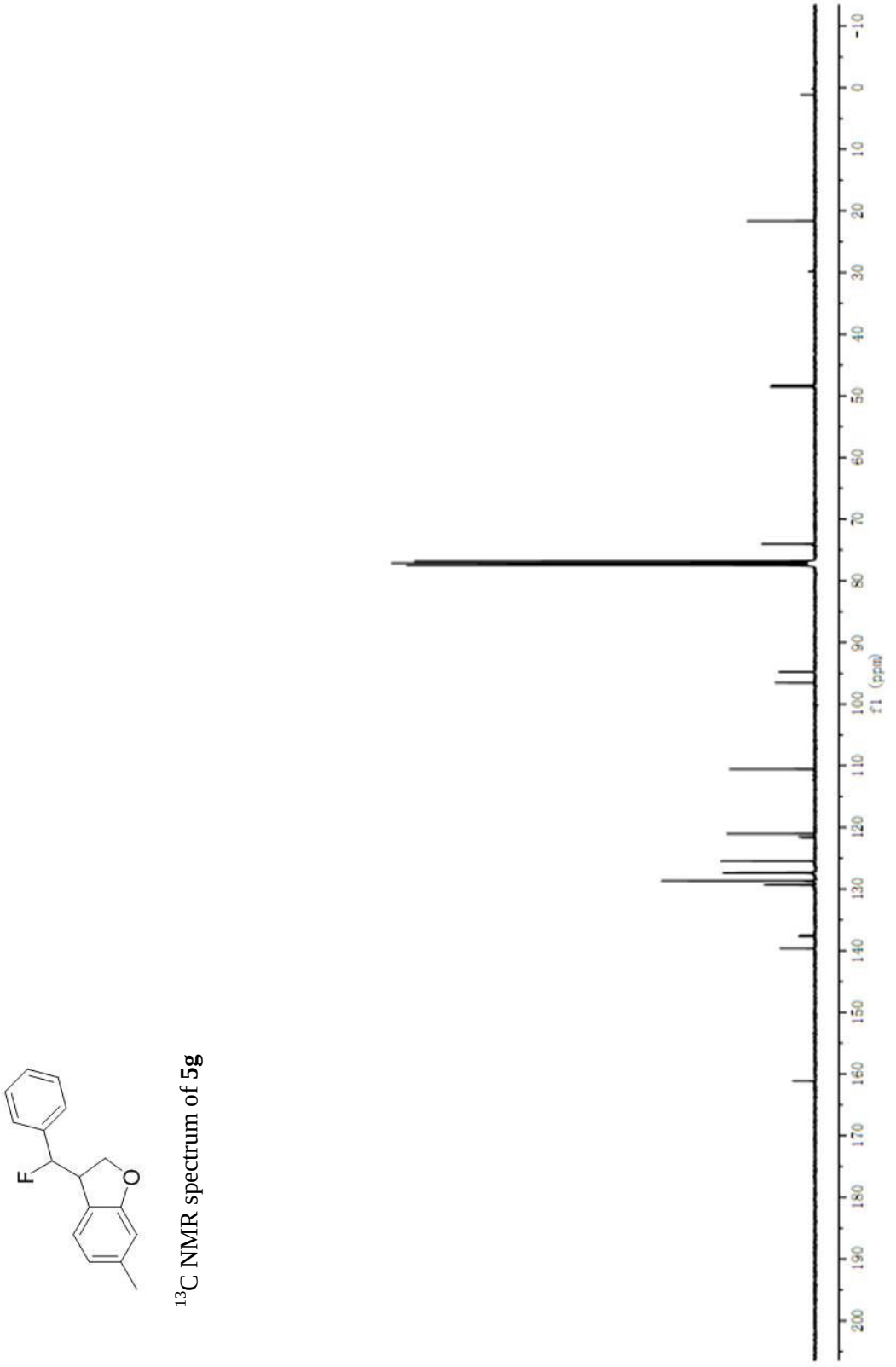
^{19}F NMR spectrum of **5f**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5f**



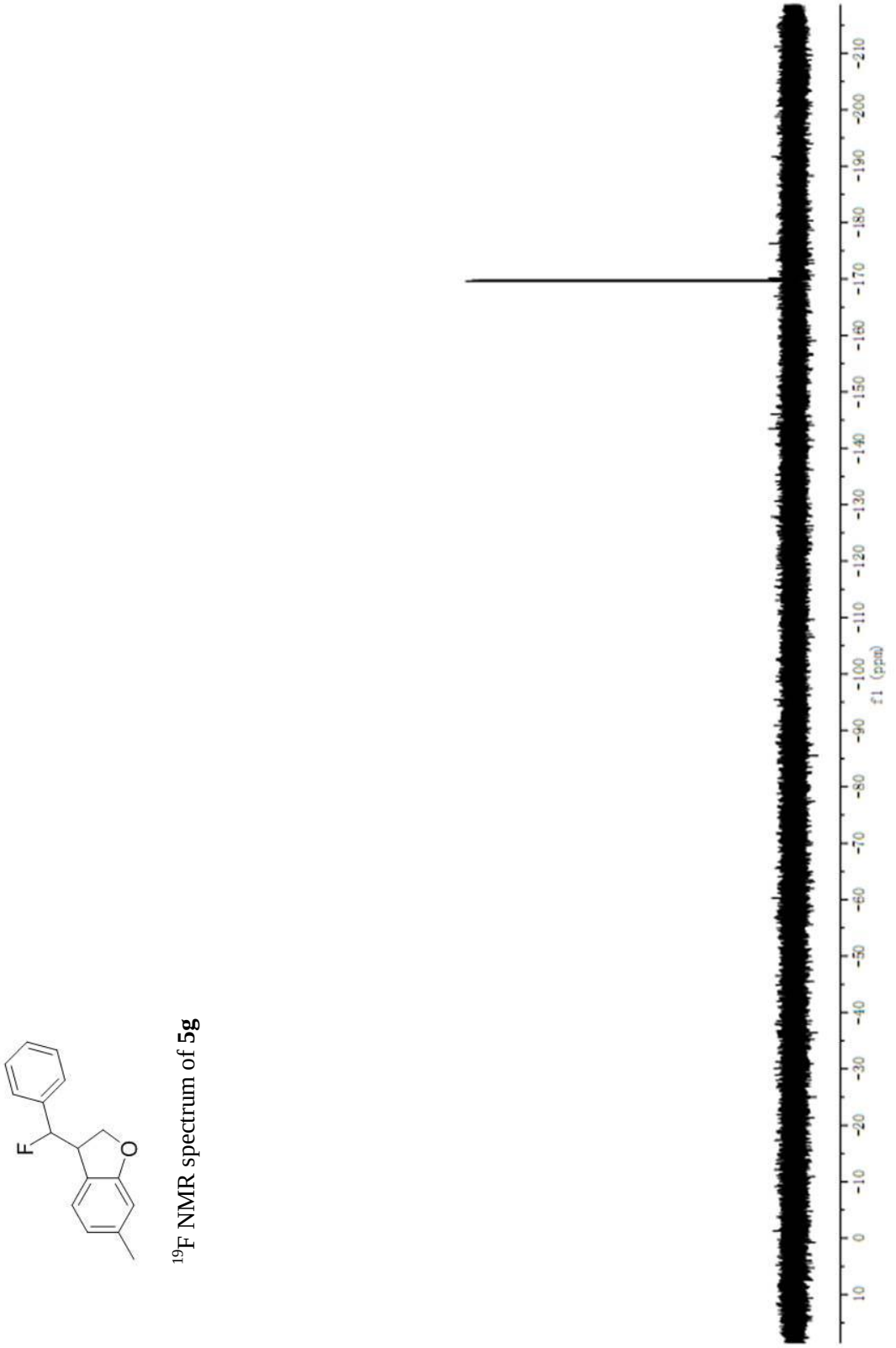
^{1}H NMR spectrum of **5g**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5g**



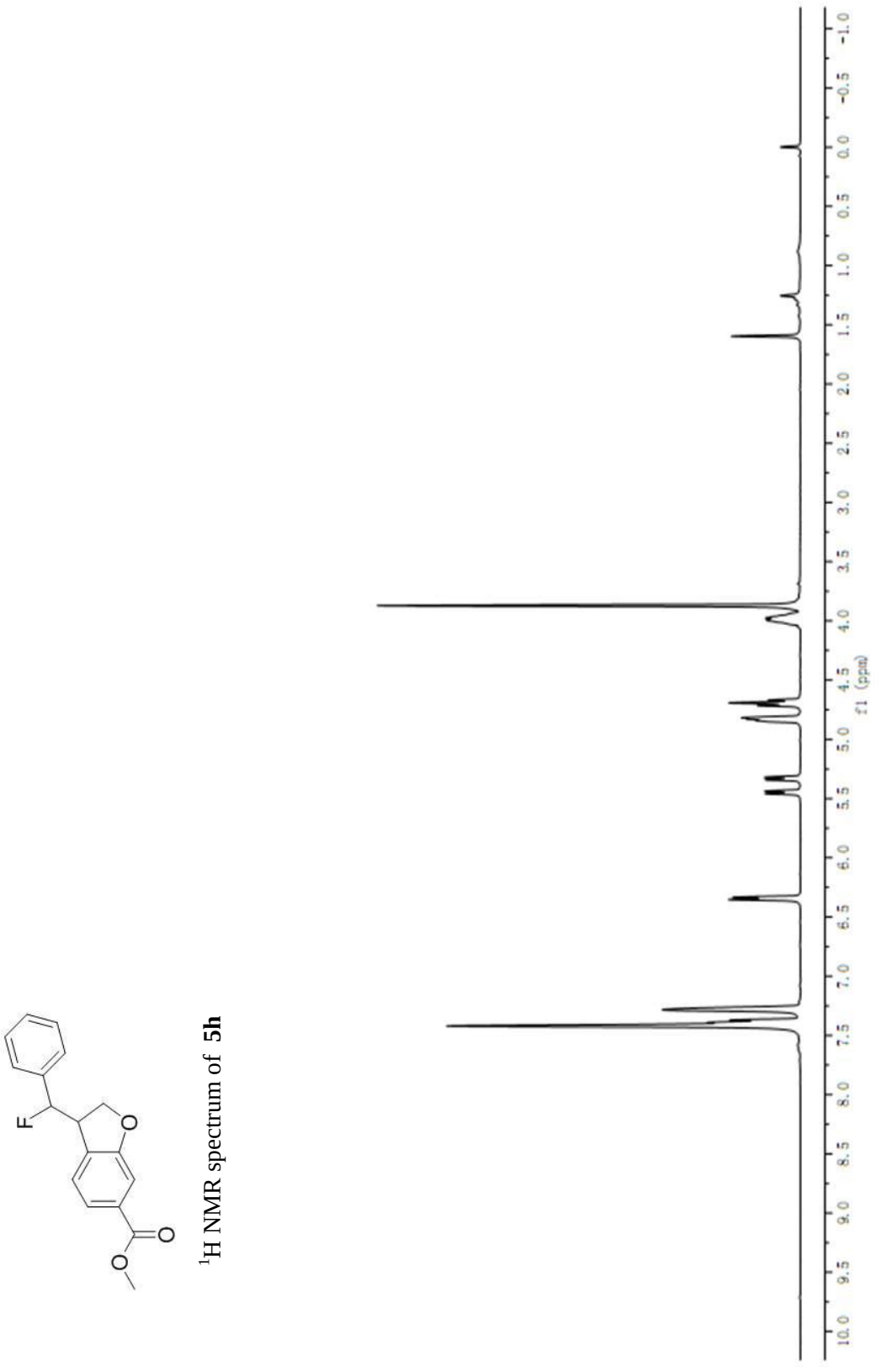
^{13}C NMR spectrum of **5g**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5g**



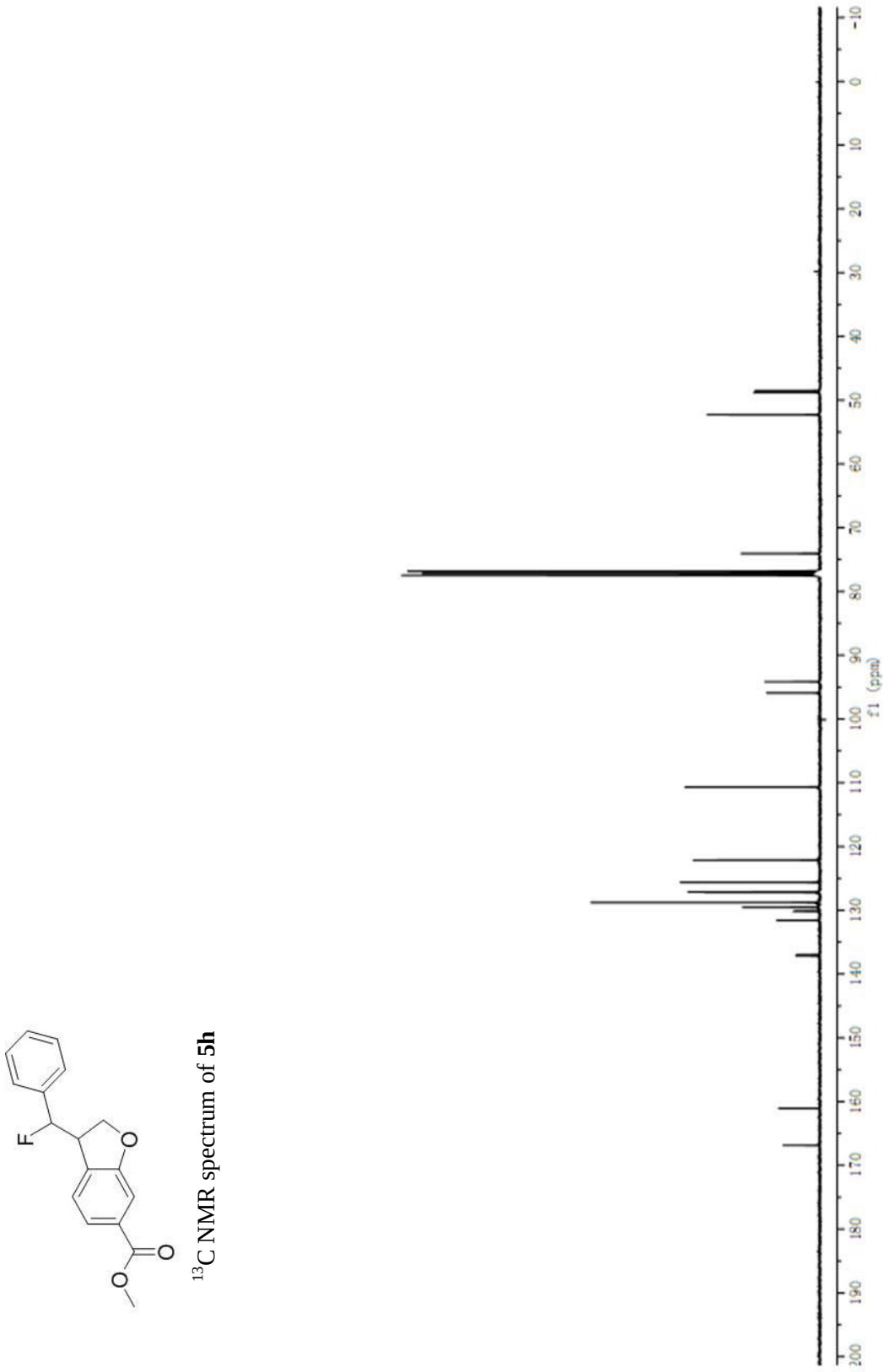
^{19}F NMR spectrum of **5g**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5g**



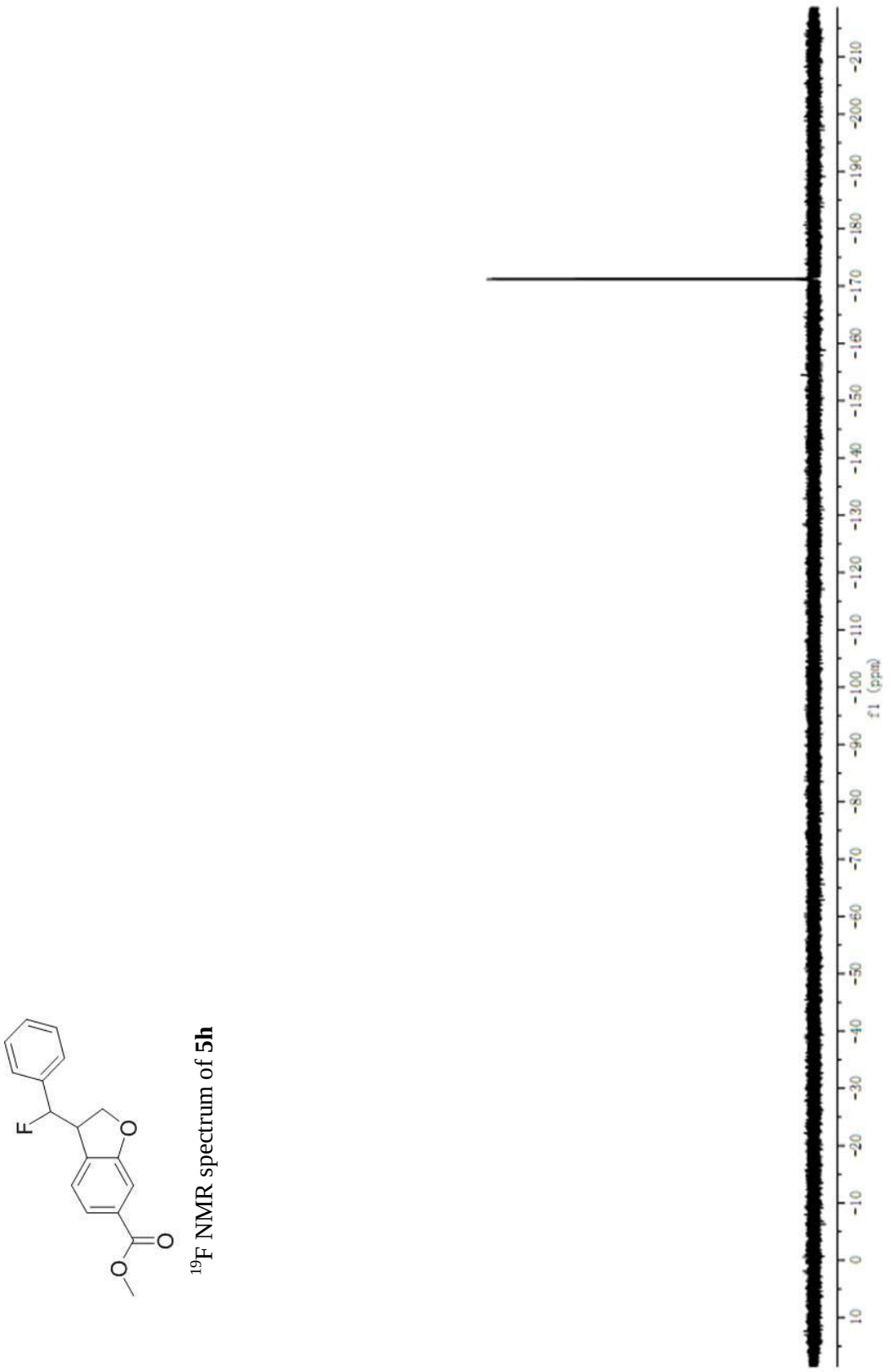
^{1}H NMR spectrum of **5h**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5h**



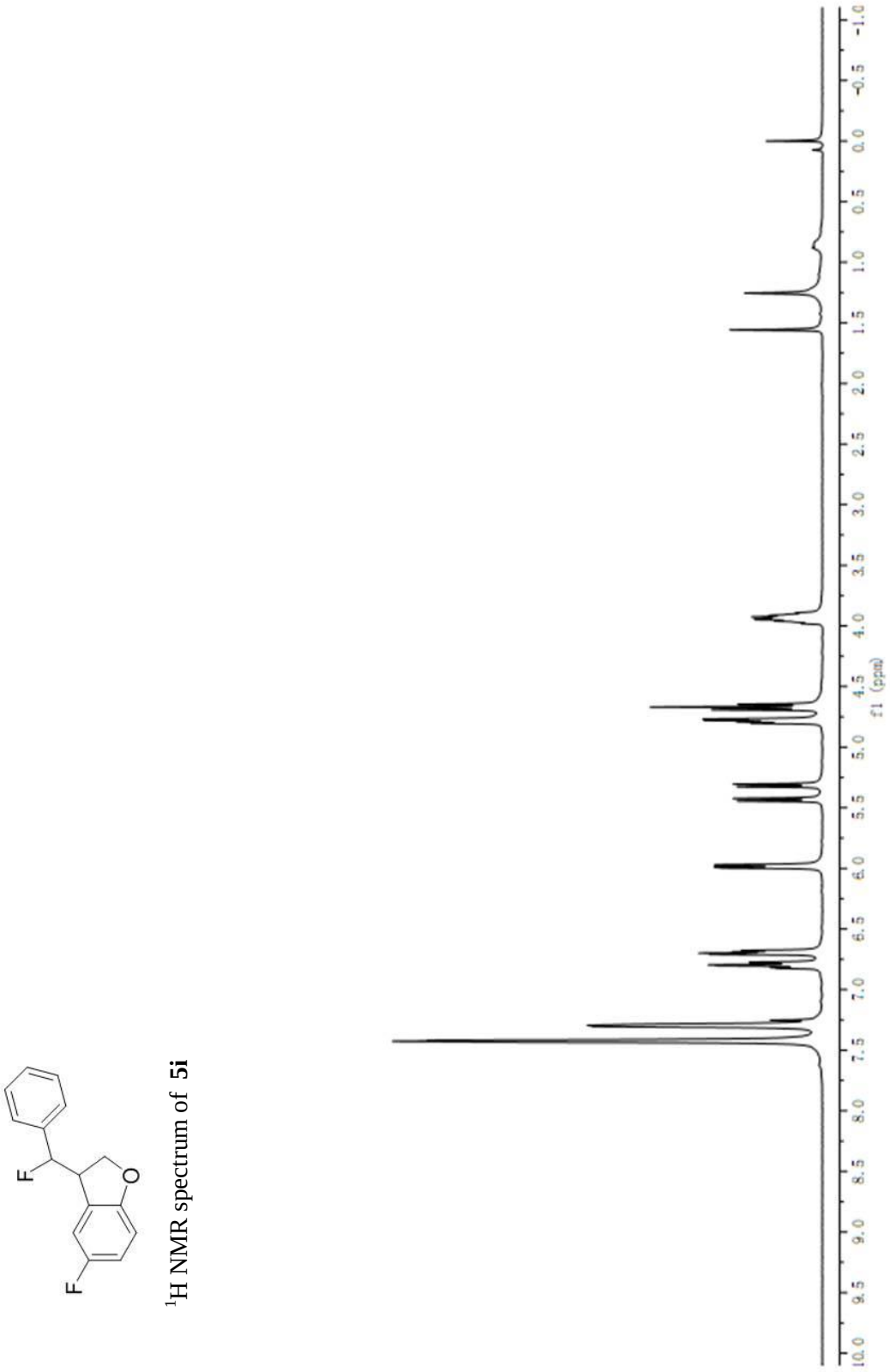
^{13}C NMR spectrum of **5h**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5h**



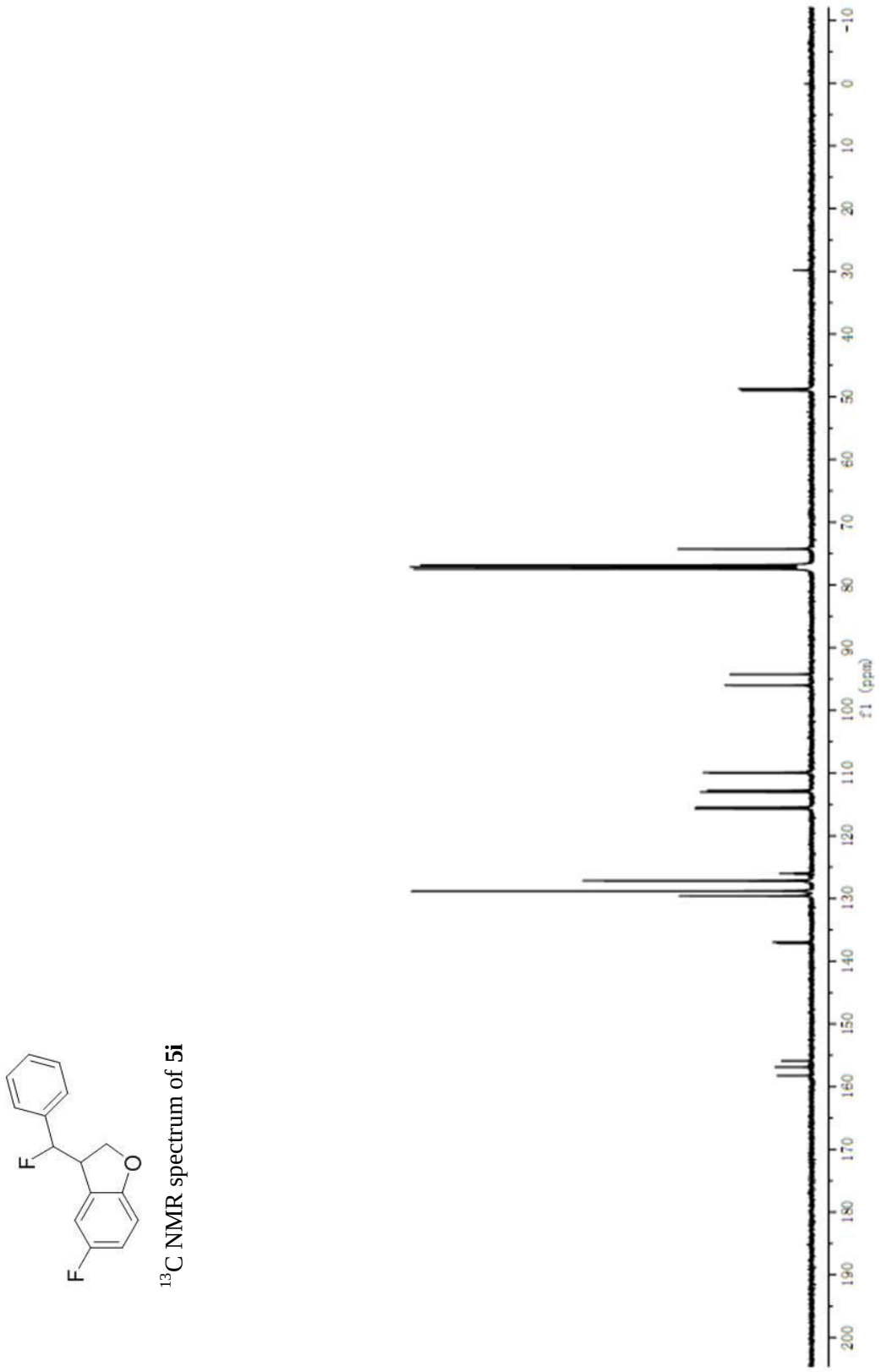
^{19}F NMR spectrum of **5h**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5h**



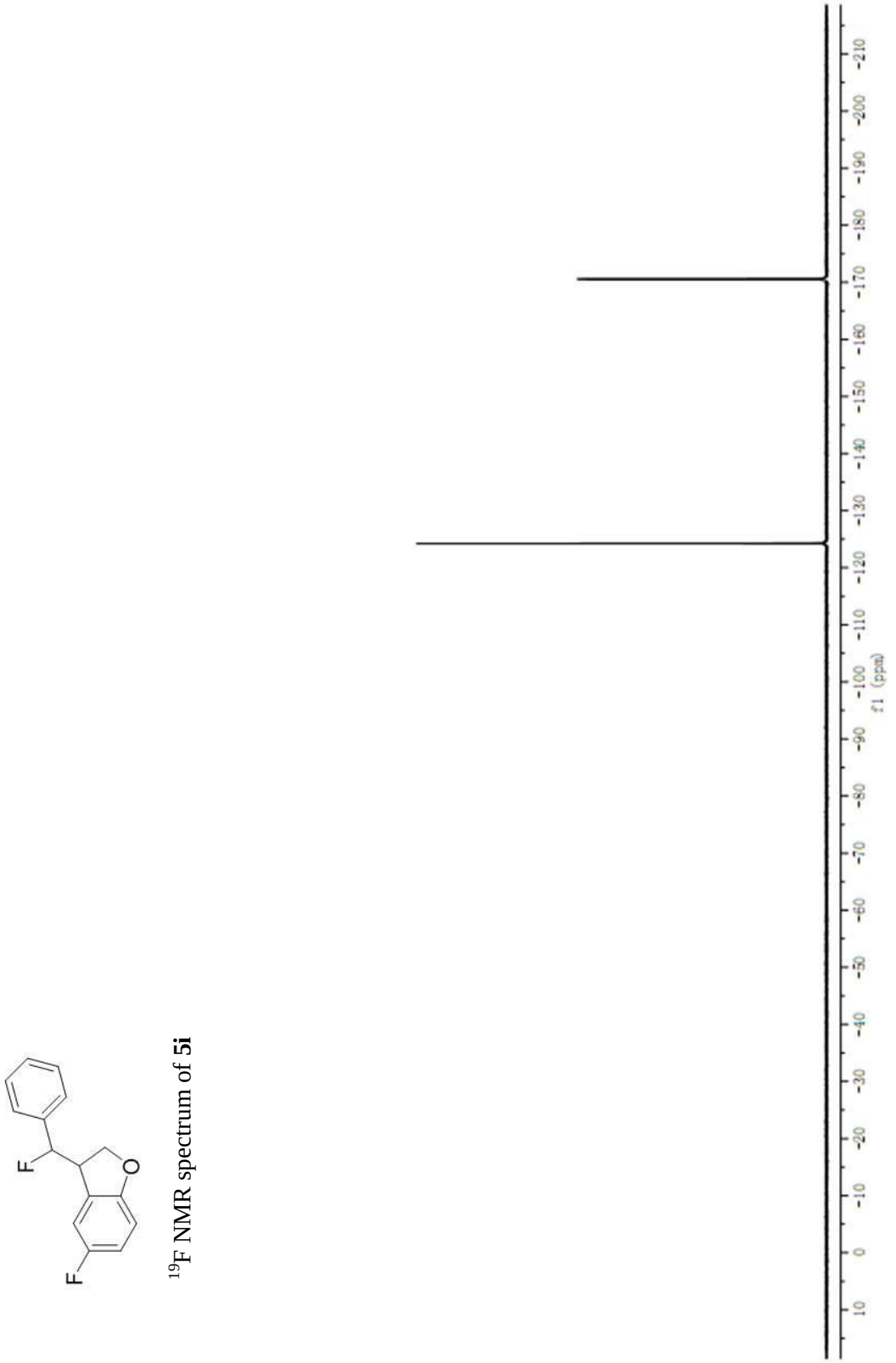
^{1}H NMR spectrum of **5i**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5i**

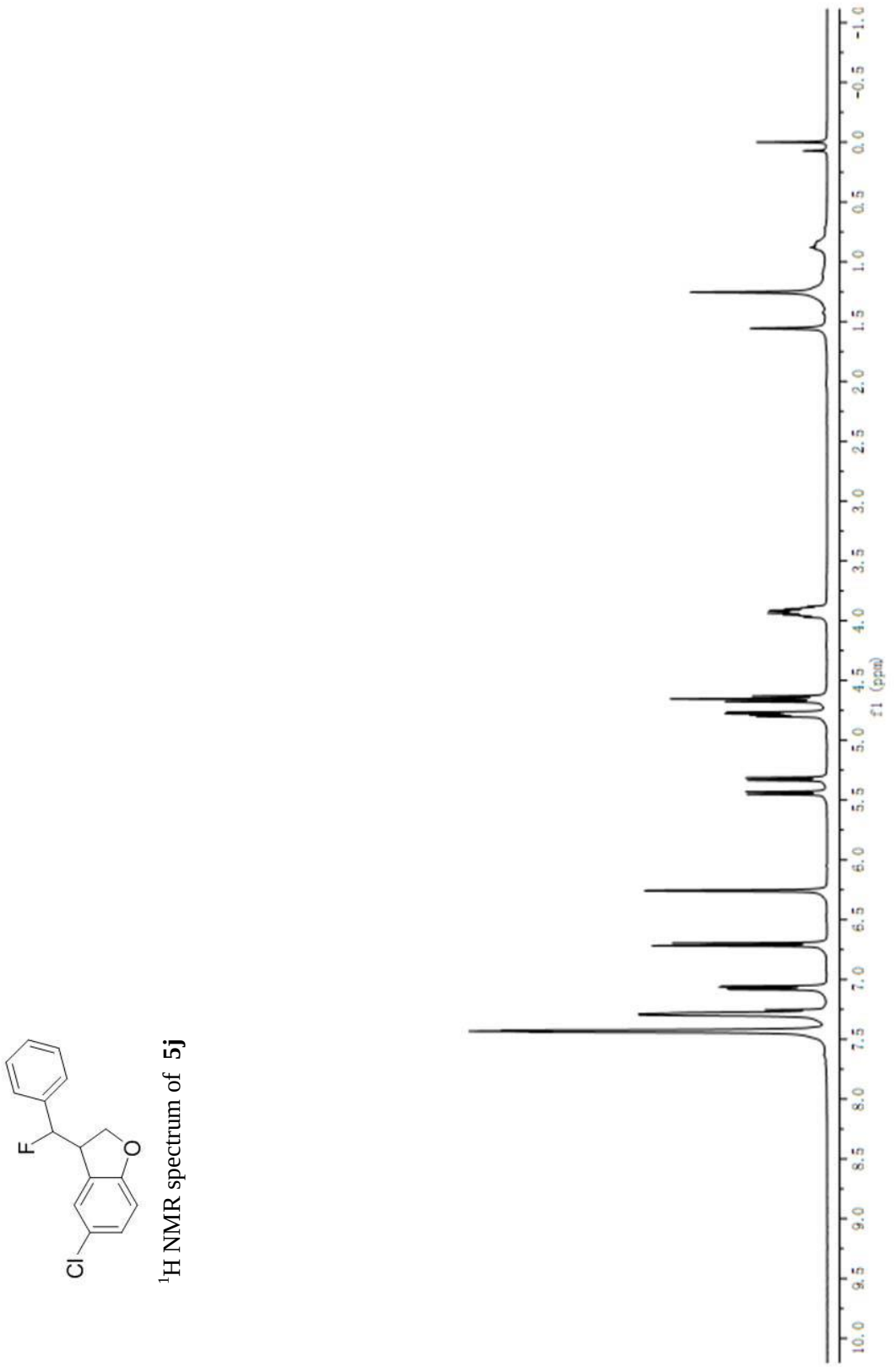


^{13}C NMR spectrum of **5i**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5i**

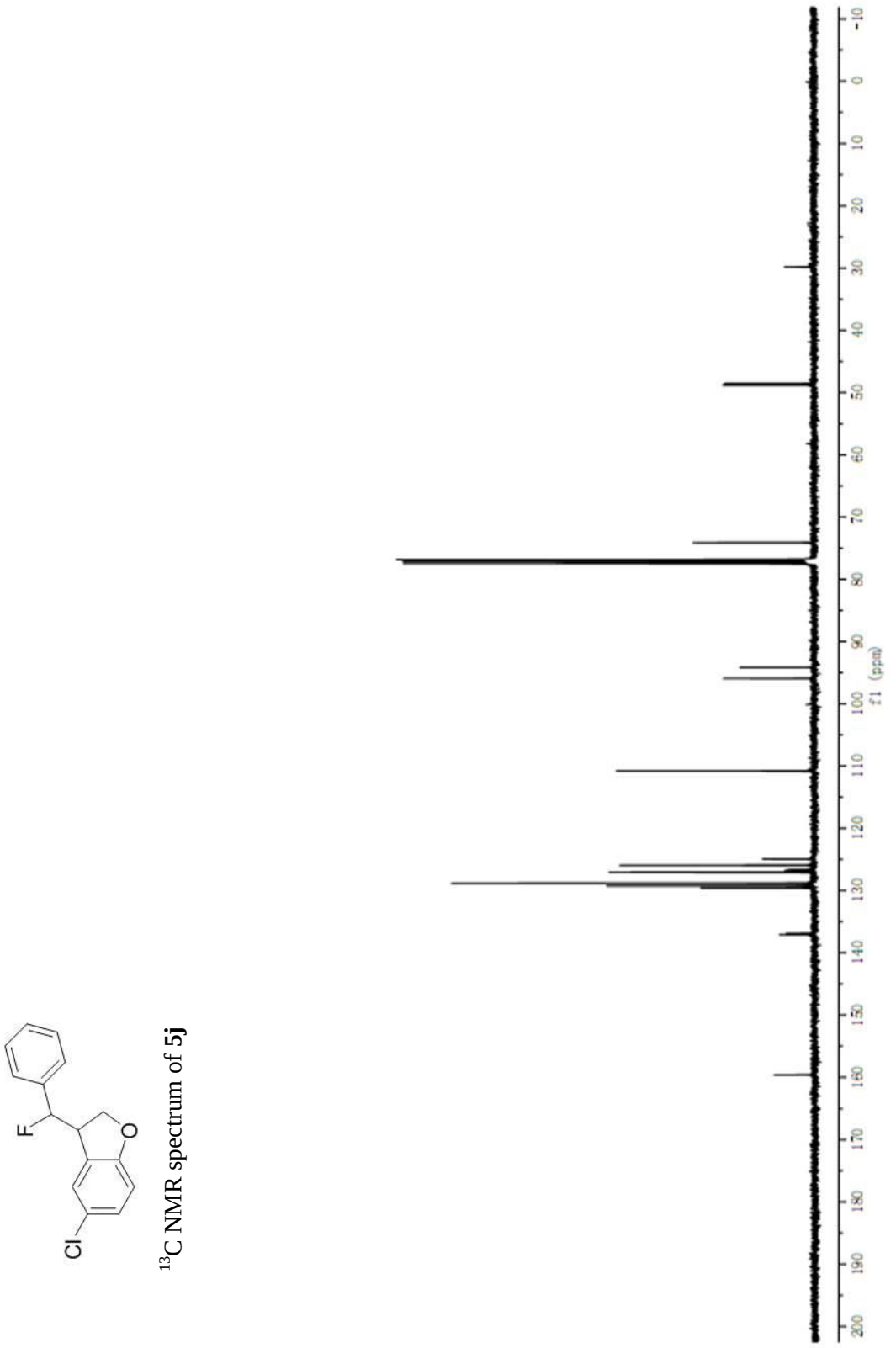


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5i**



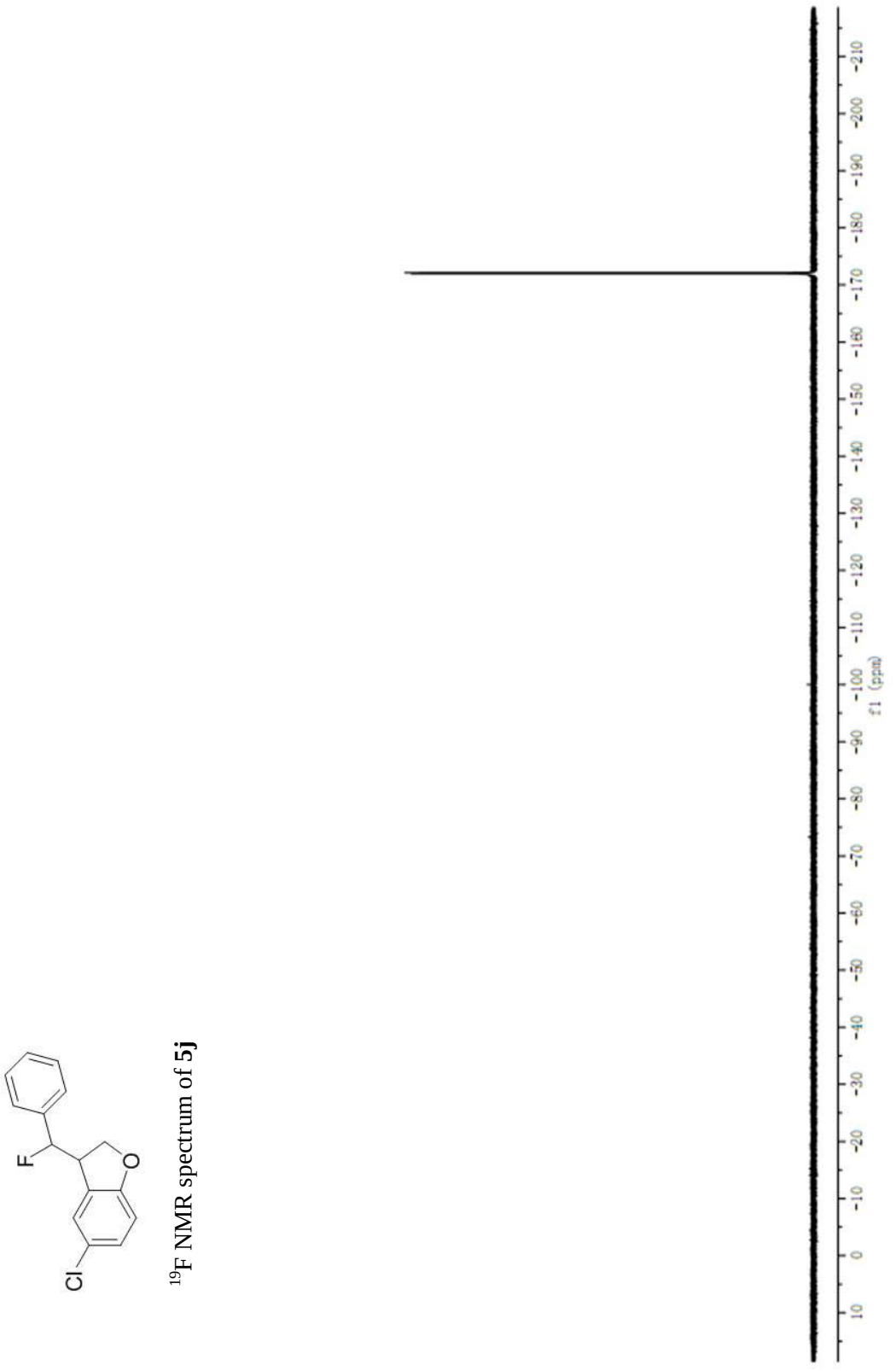
^{1}H NMR spectrum of **5j**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5j**



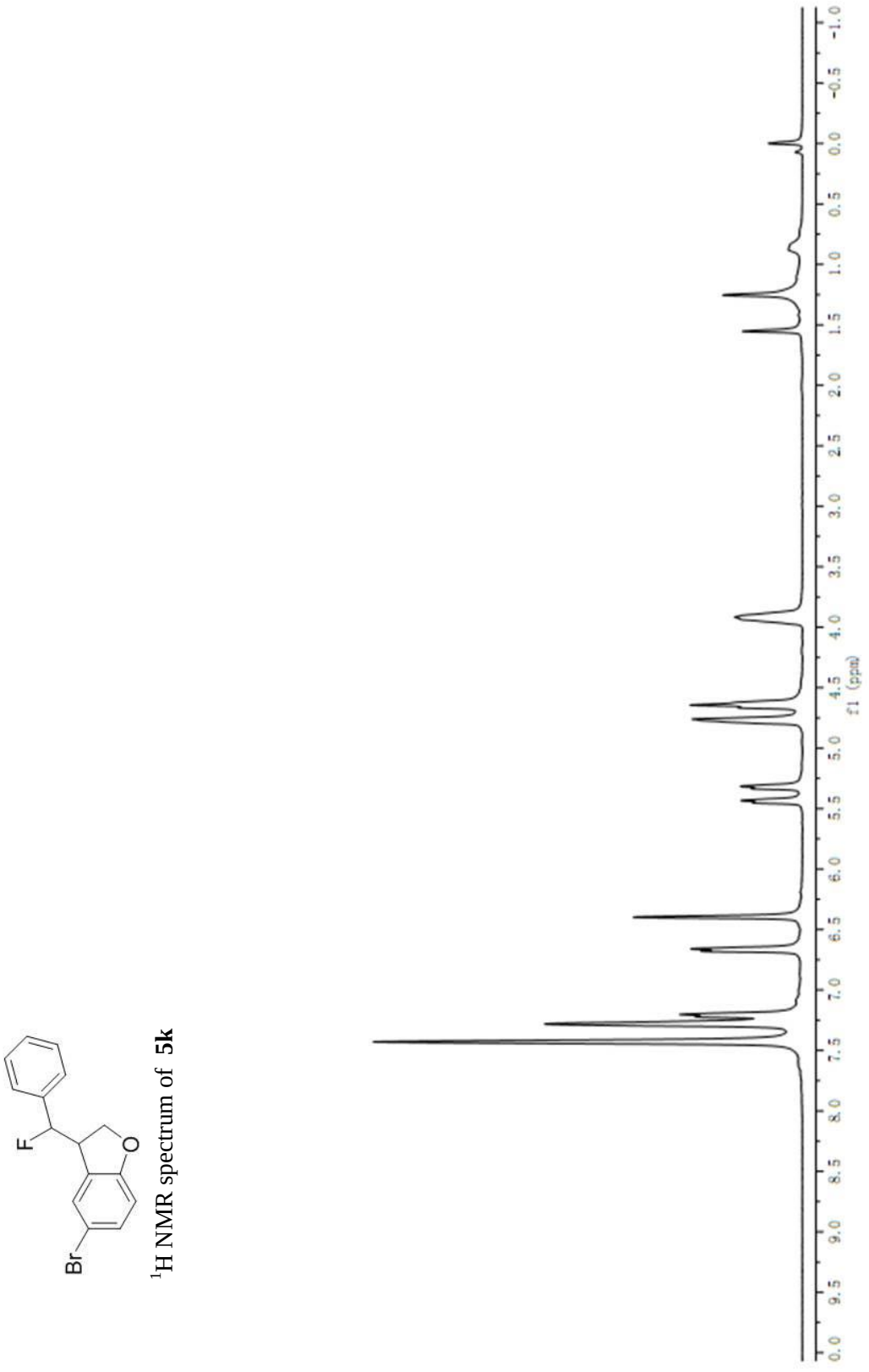
^{13}C NMR spectrum of **5j**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5j**



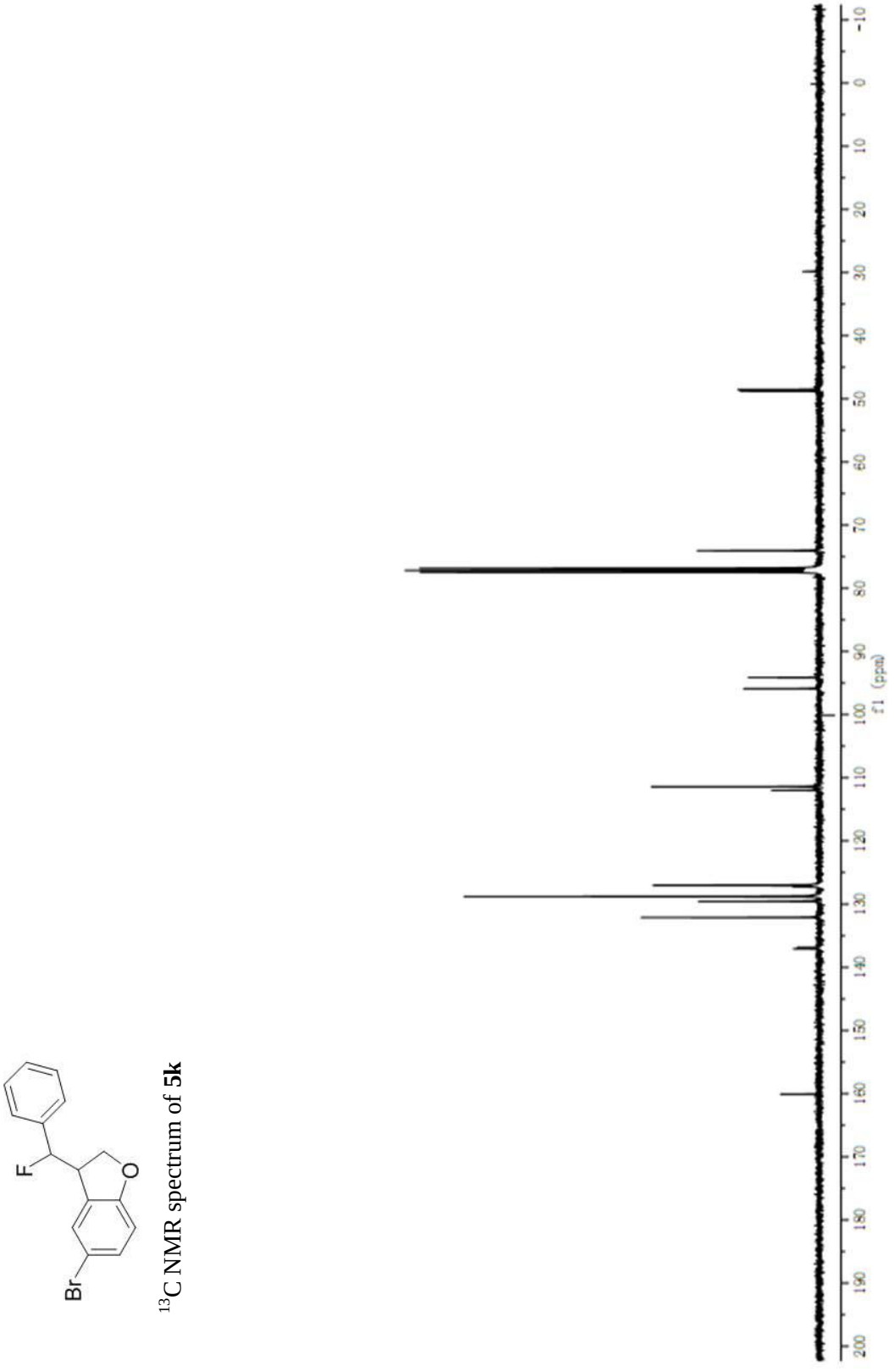
^{19}F NMR spectrum of **5j**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5j**



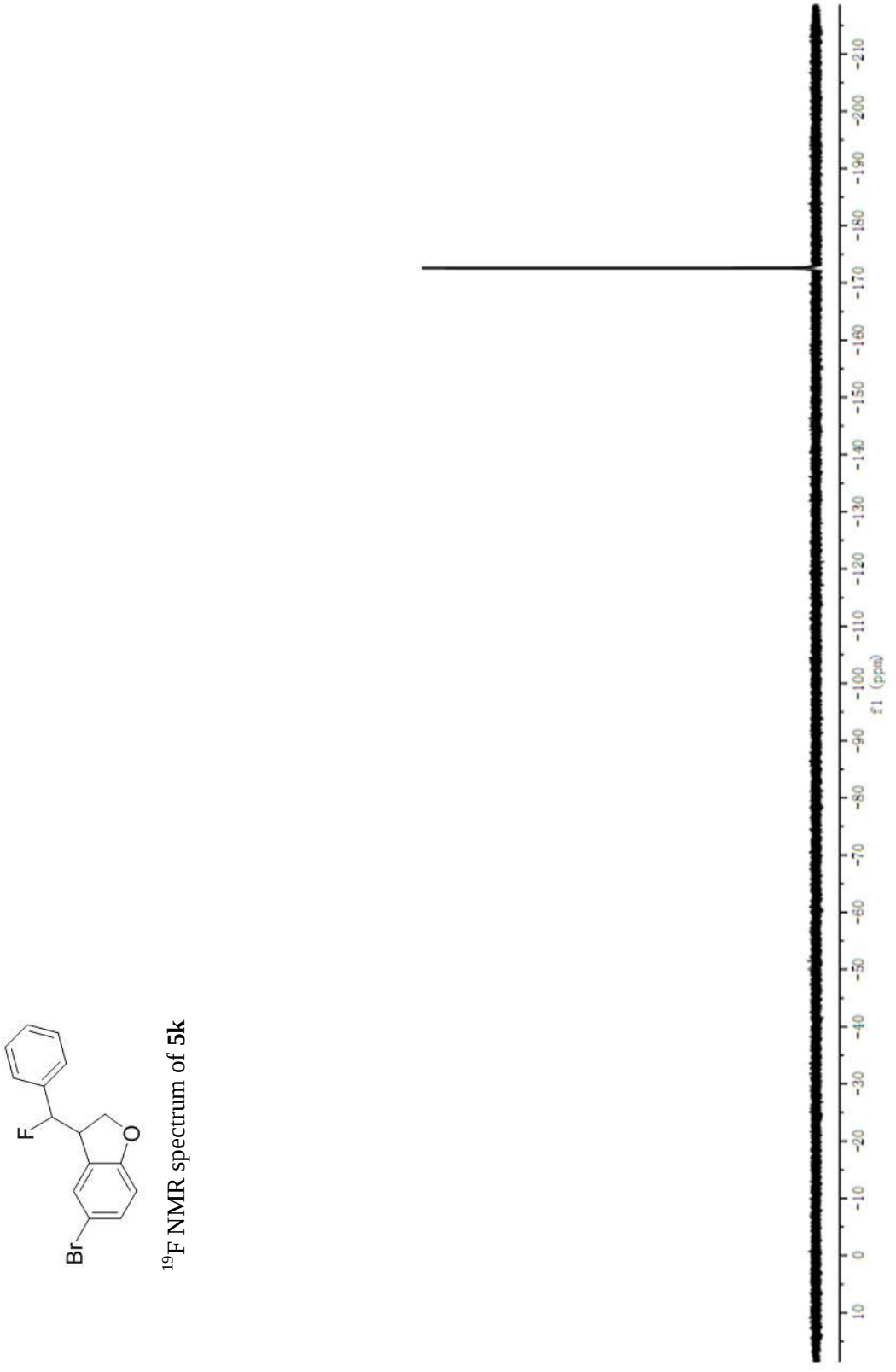
^{1}H NMR spectrum of **5k**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5k**



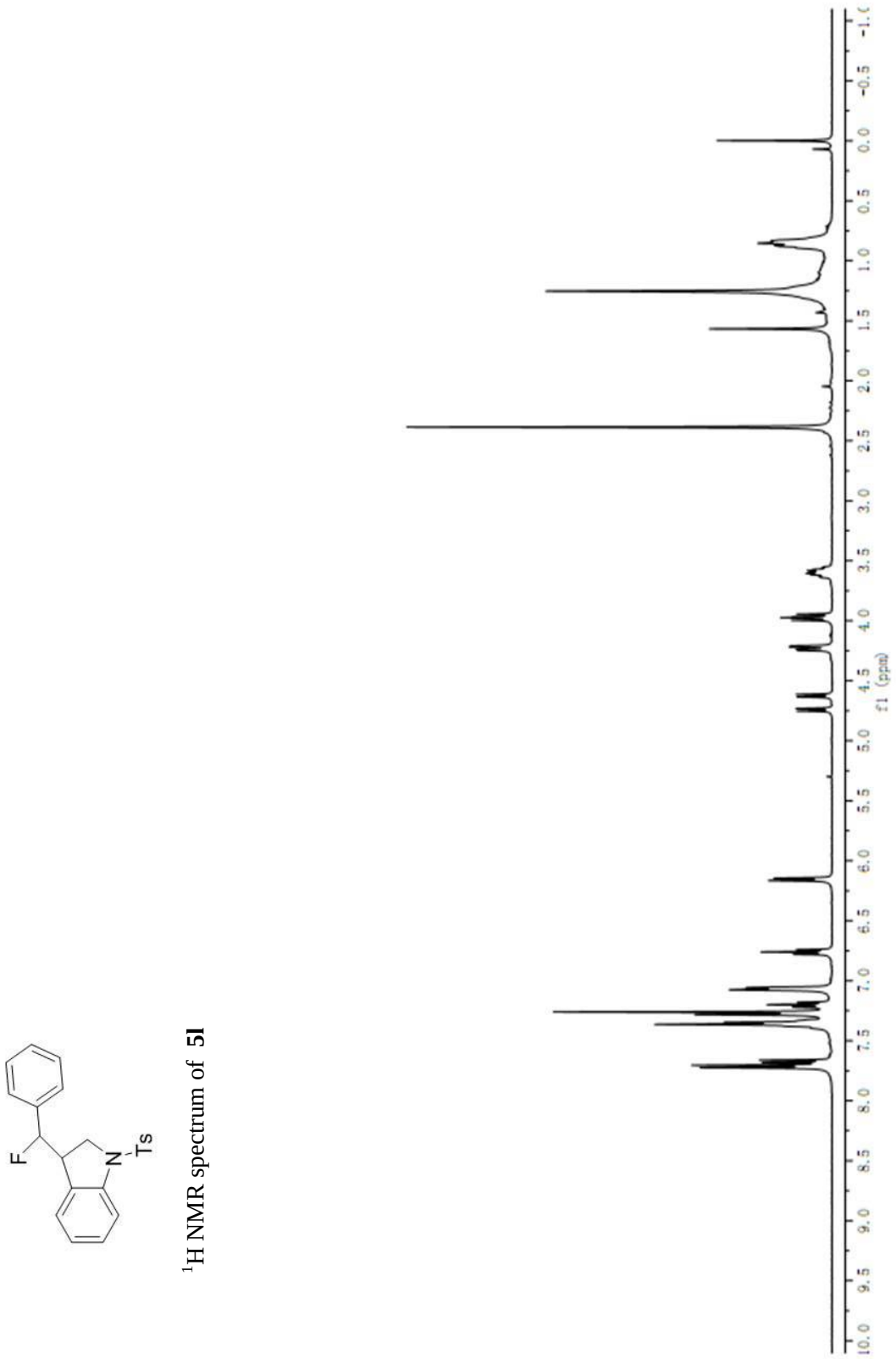
^{13}C NMR spectrum of **5k**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5k**



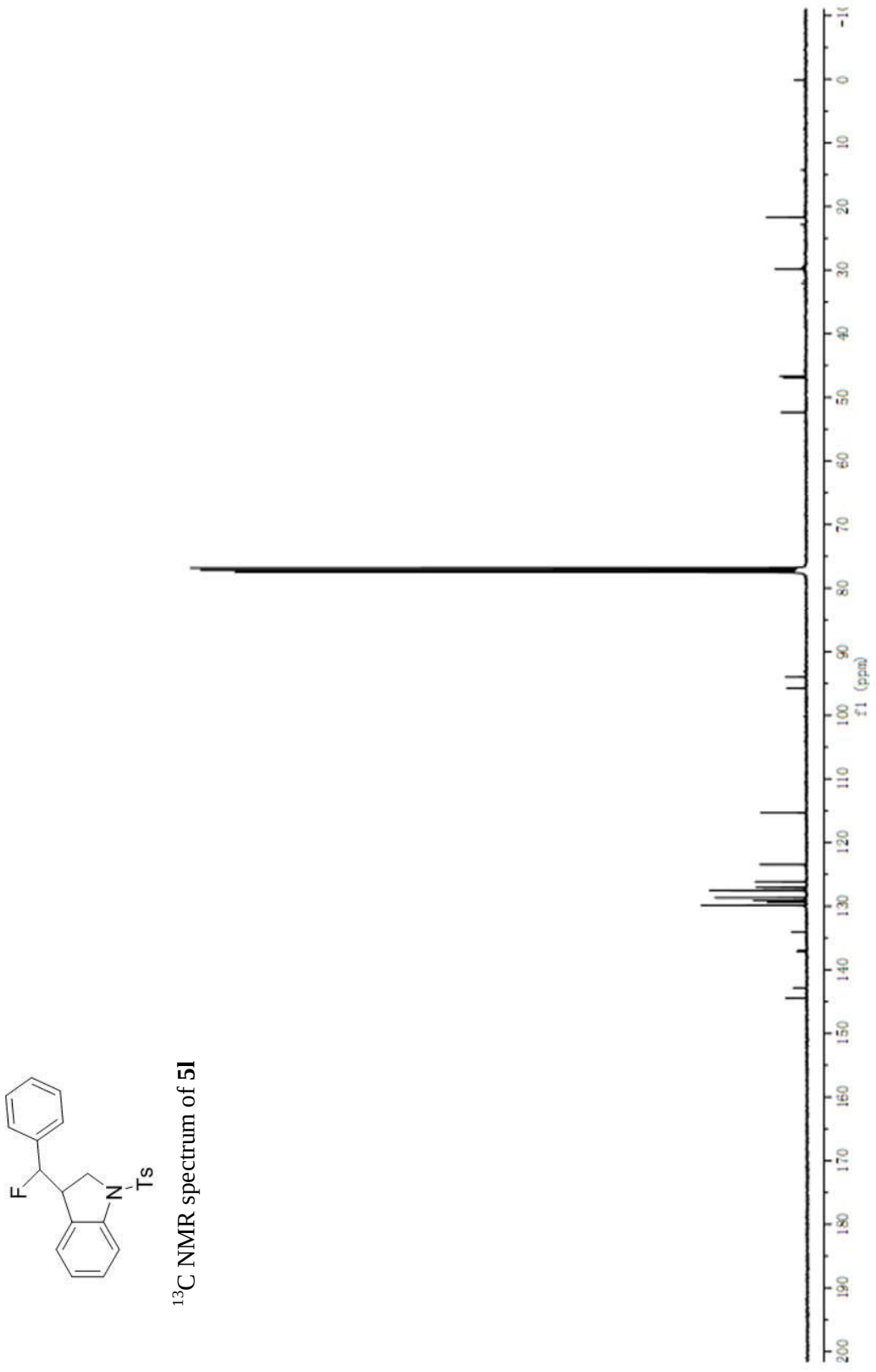
^{19}F NMR spectrum of **5k**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5k**



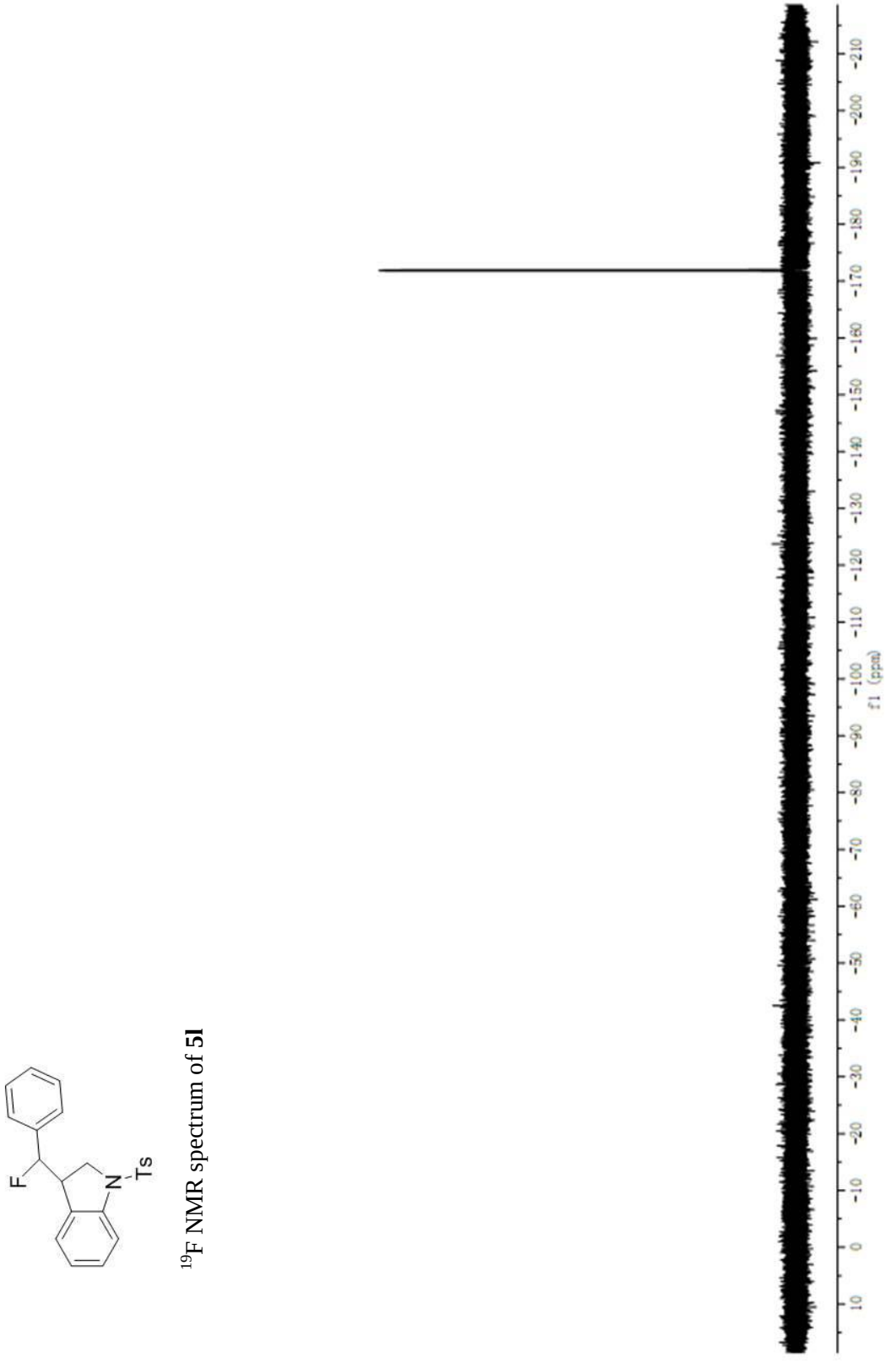
^{1}H NMR spectrum of **5l**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5l**



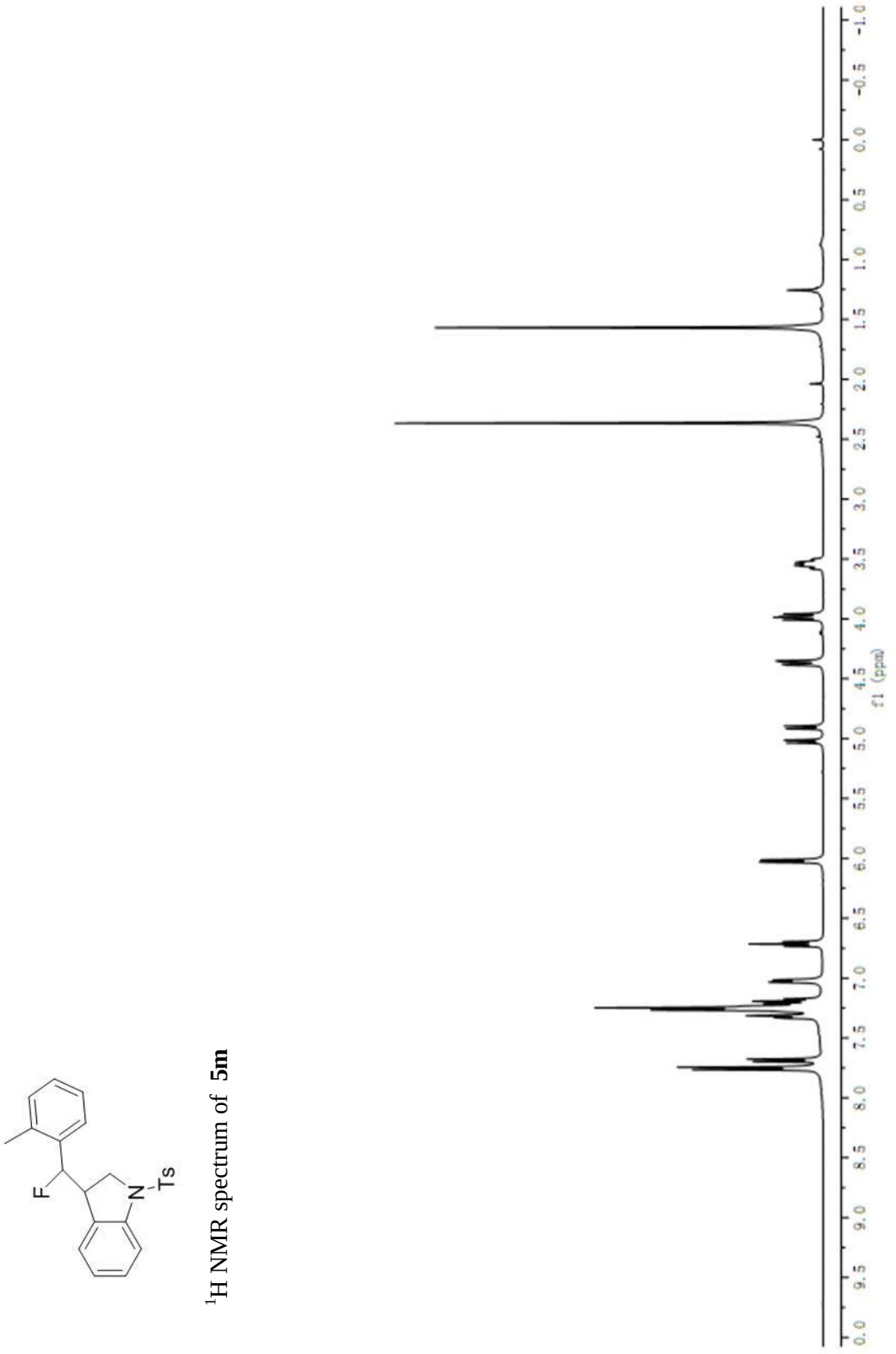
^{13}C NMR spectrum of **5l**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5l**



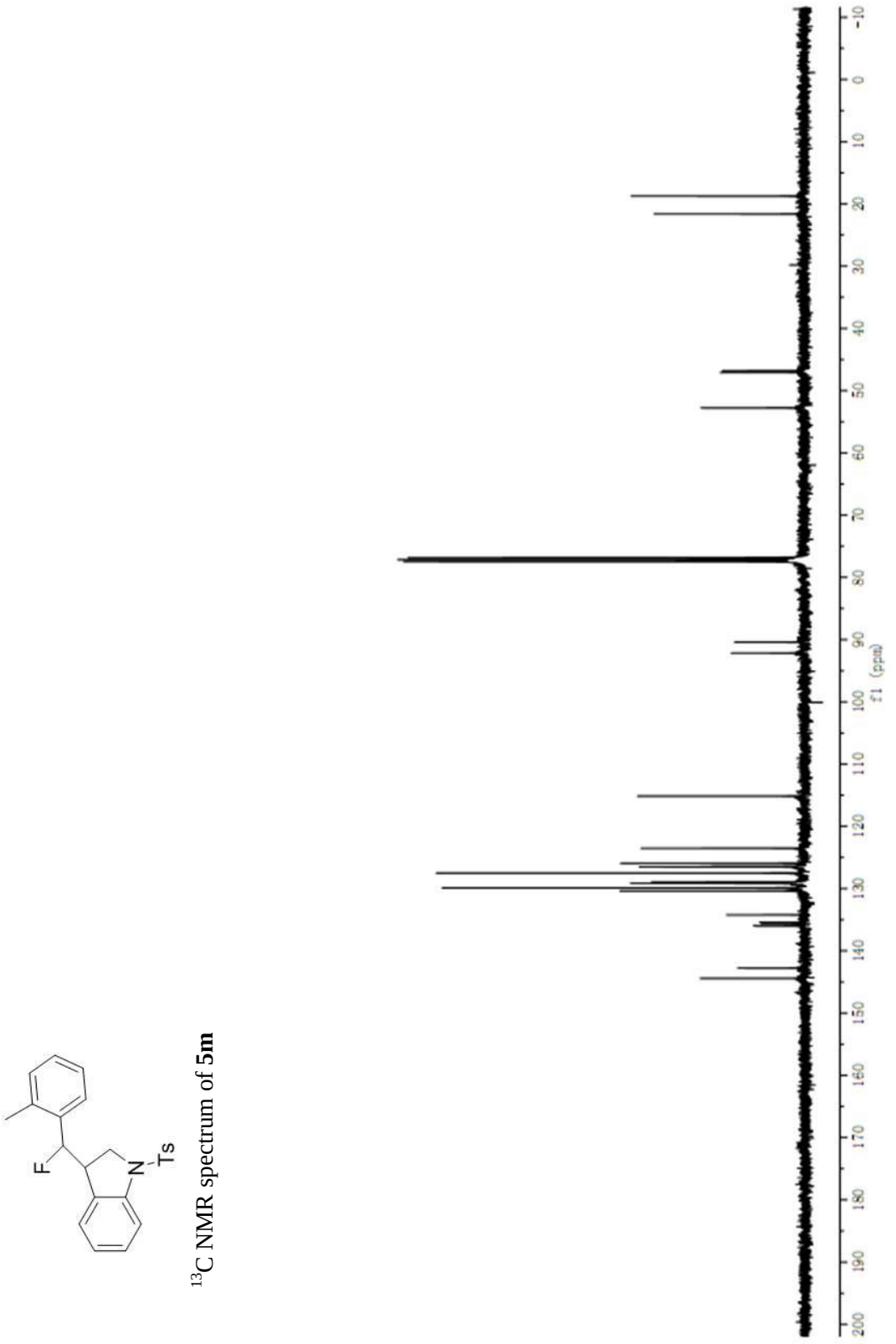
^{19}F NMR spectrum of **5l**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5l**



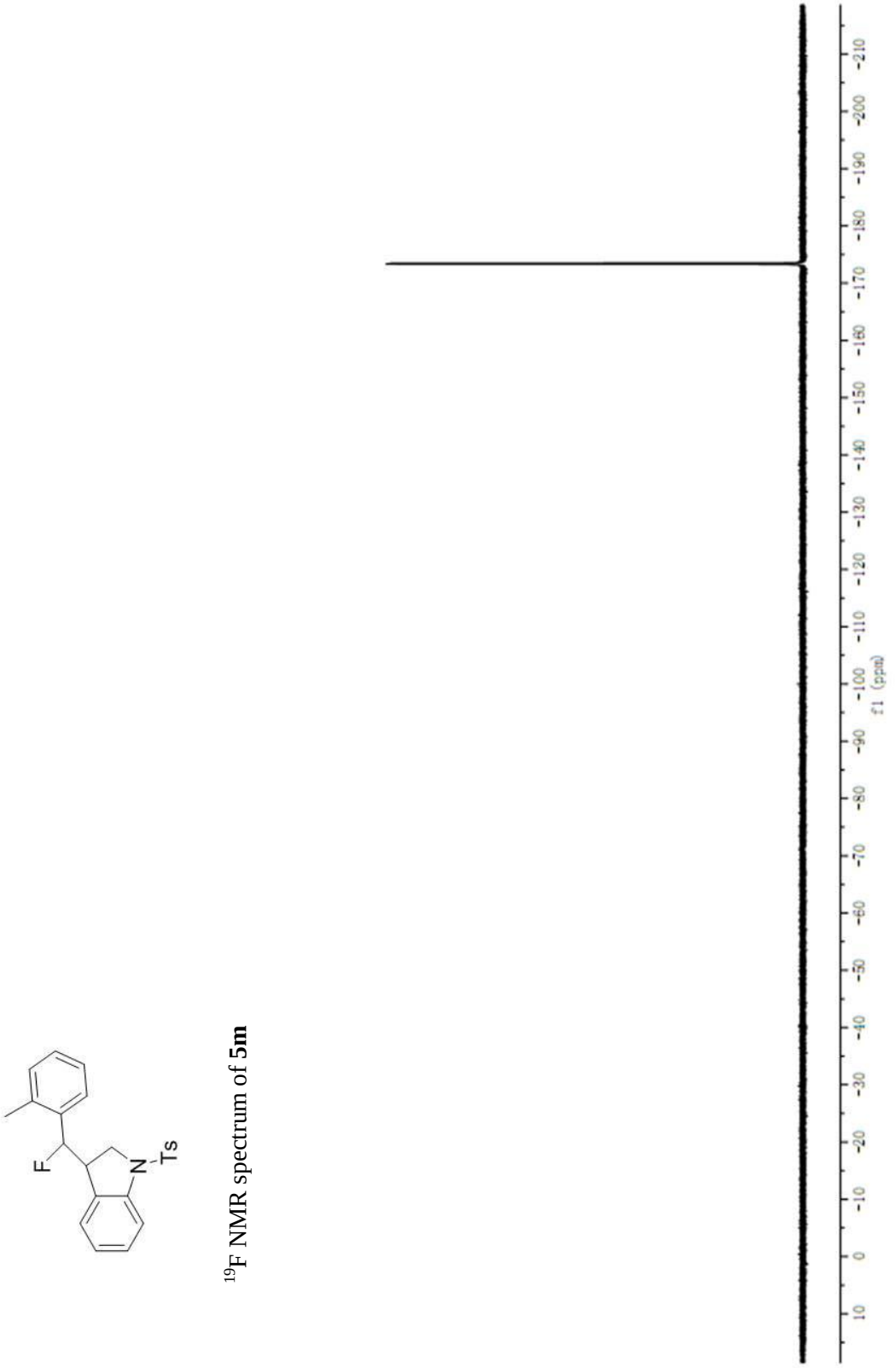
^{1}H NMR spectrum of **5m**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5m**



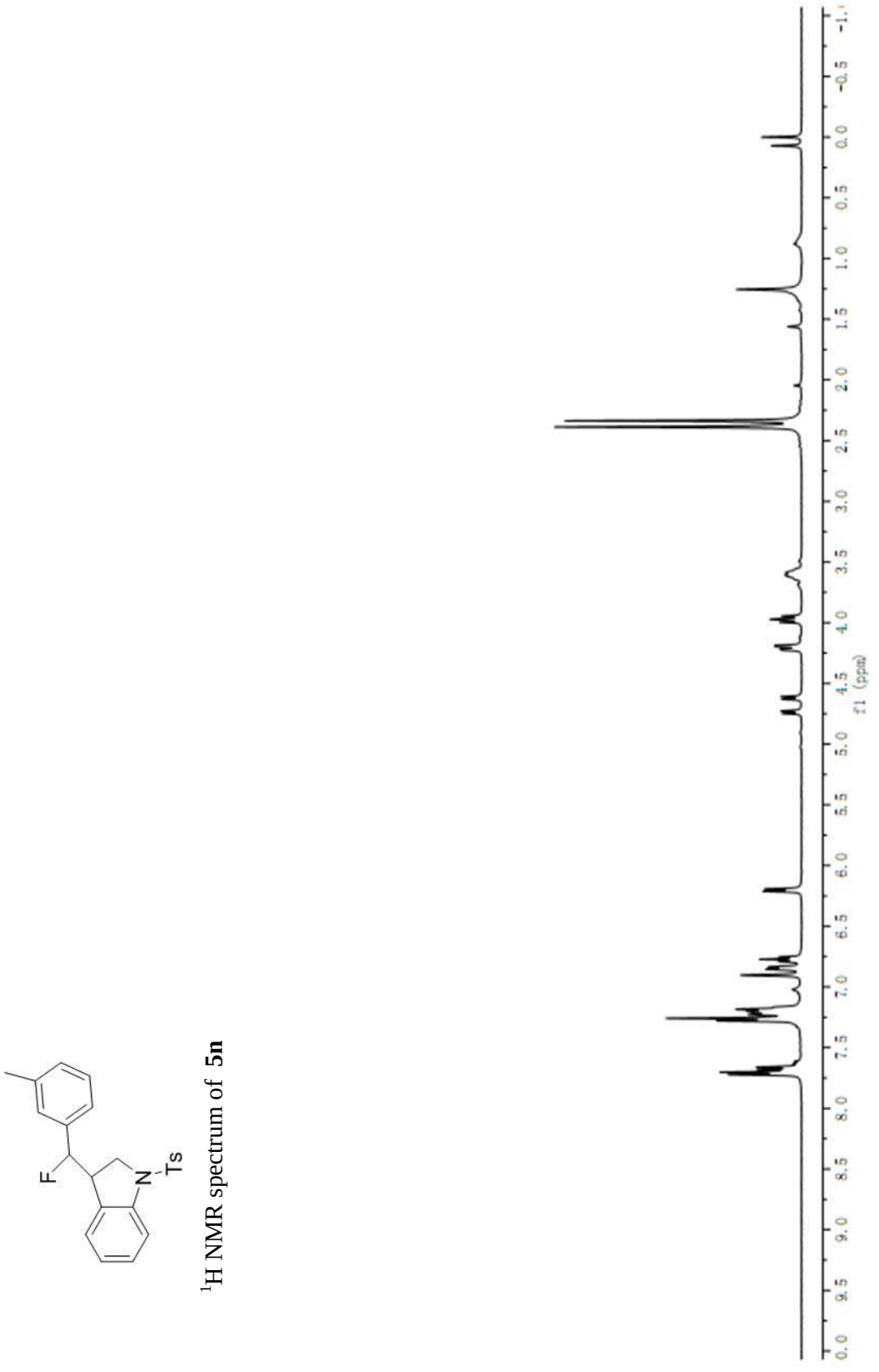
^{13}C NMR spectrum of **5m**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5m**



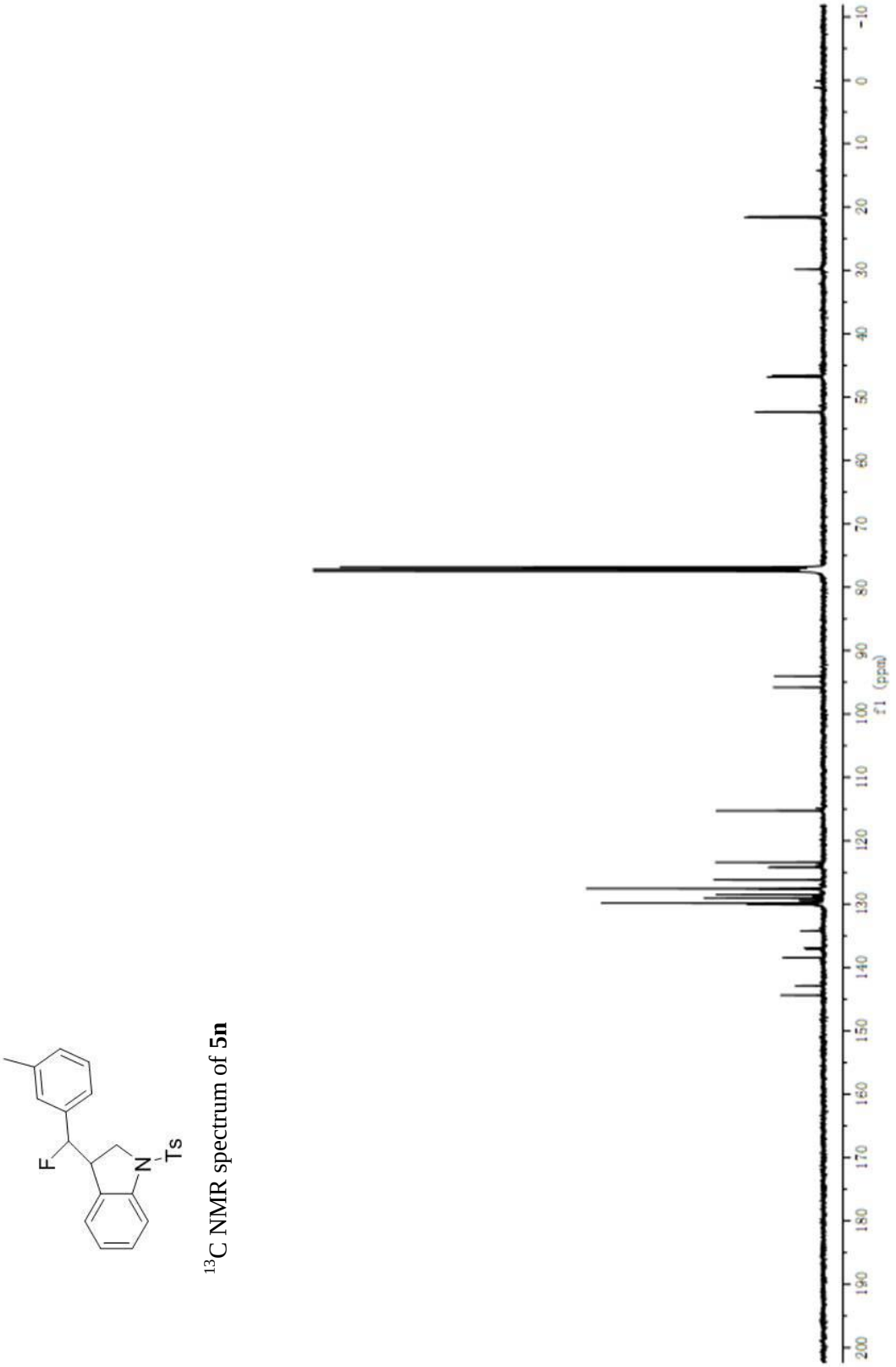
^{19}F NMR spectrum of **5m**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5m**



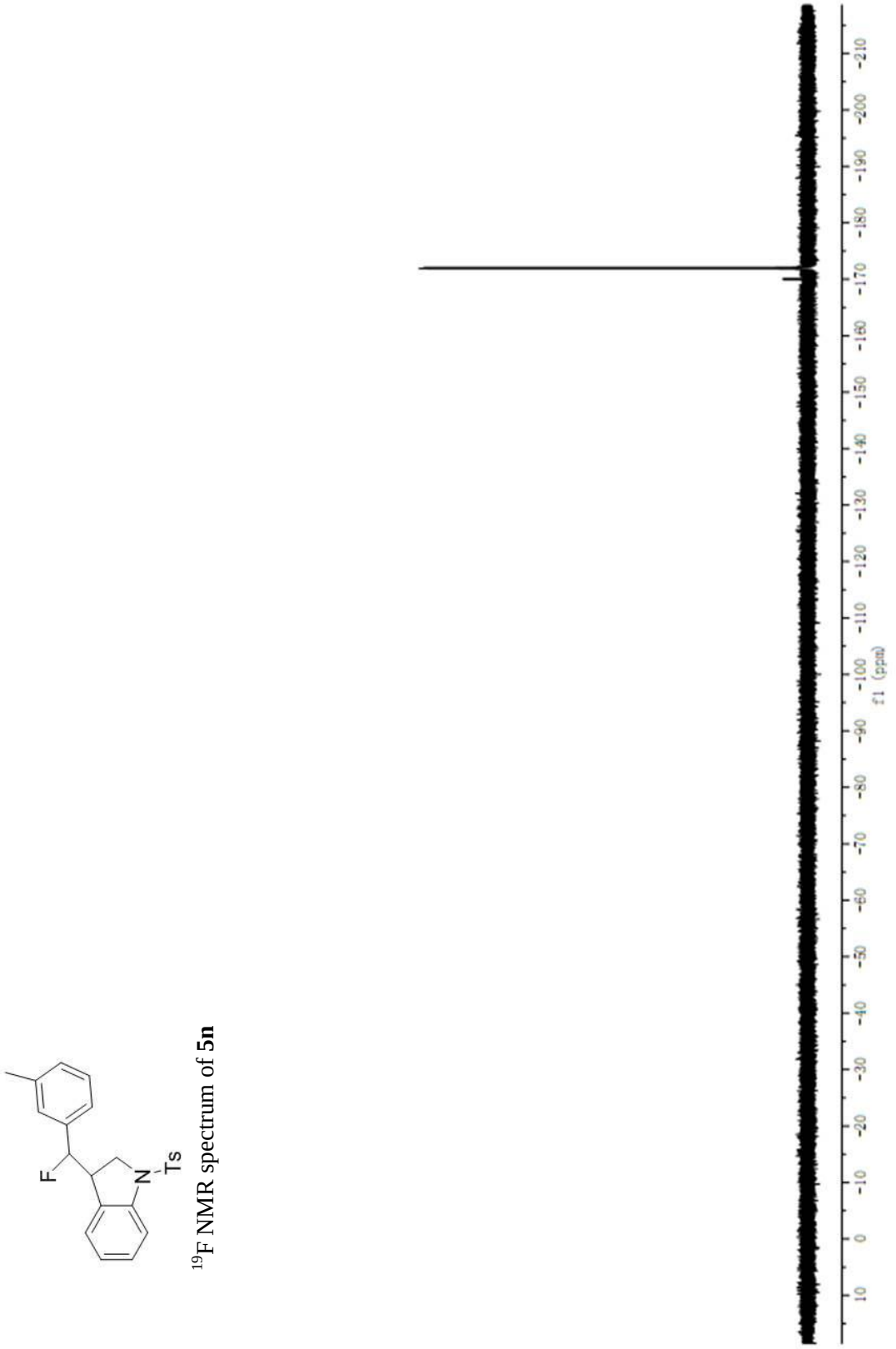
^{1}H NMR spectrum of **5n**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5n**



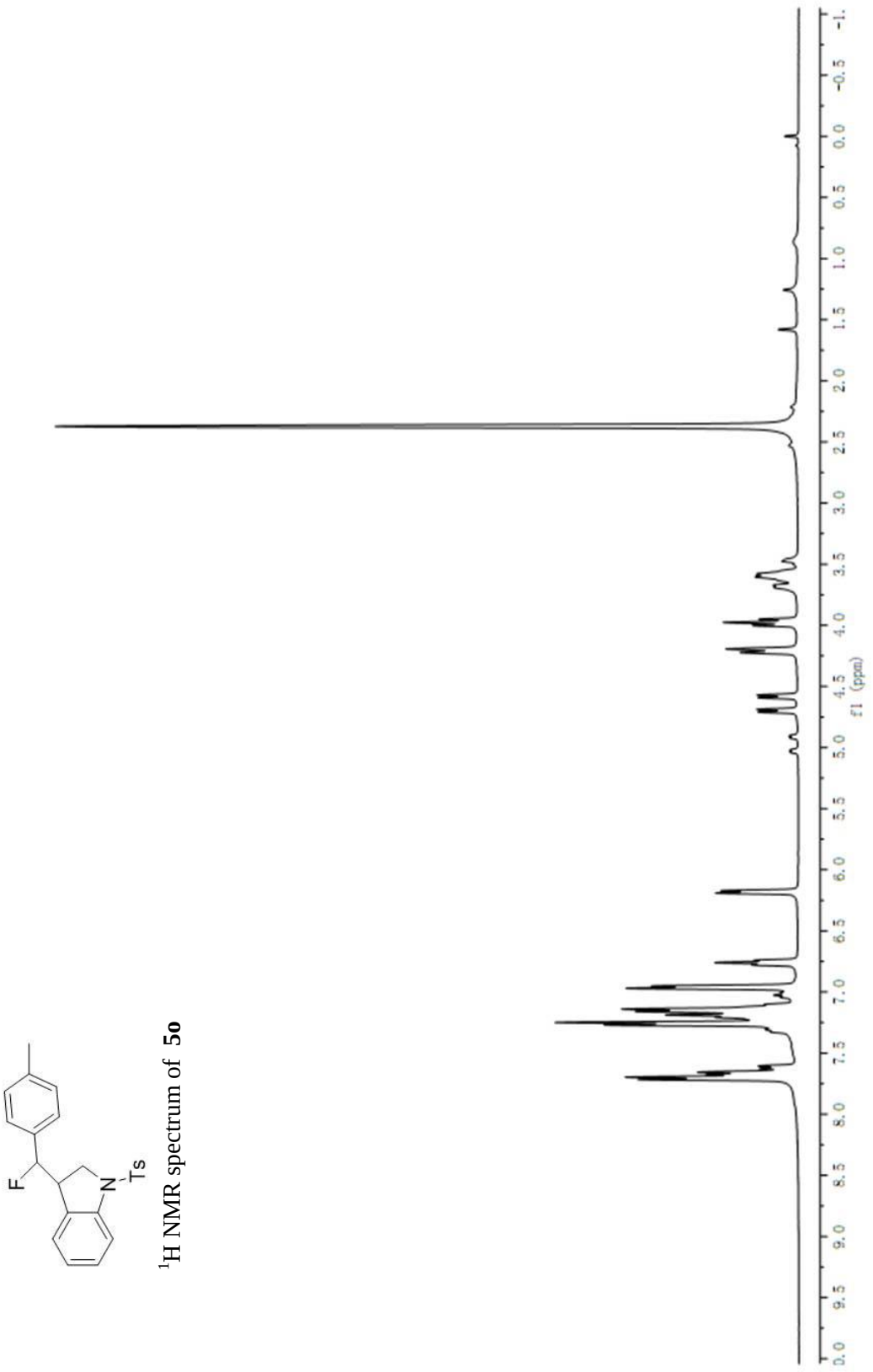
^{13}C NMR spectrum of **5n**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5n**



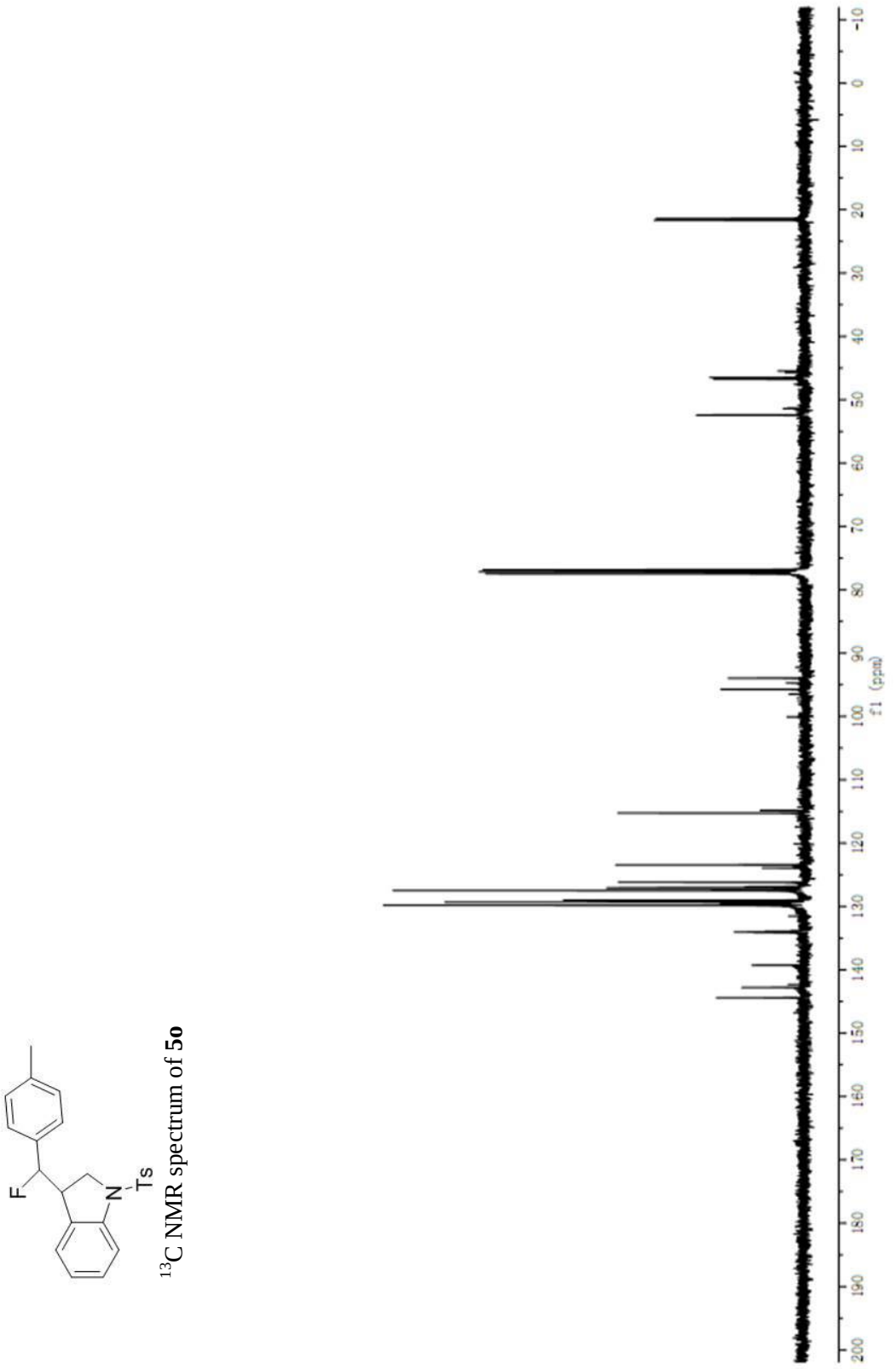
^{19}F NMR spectrum of **5n**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5n**



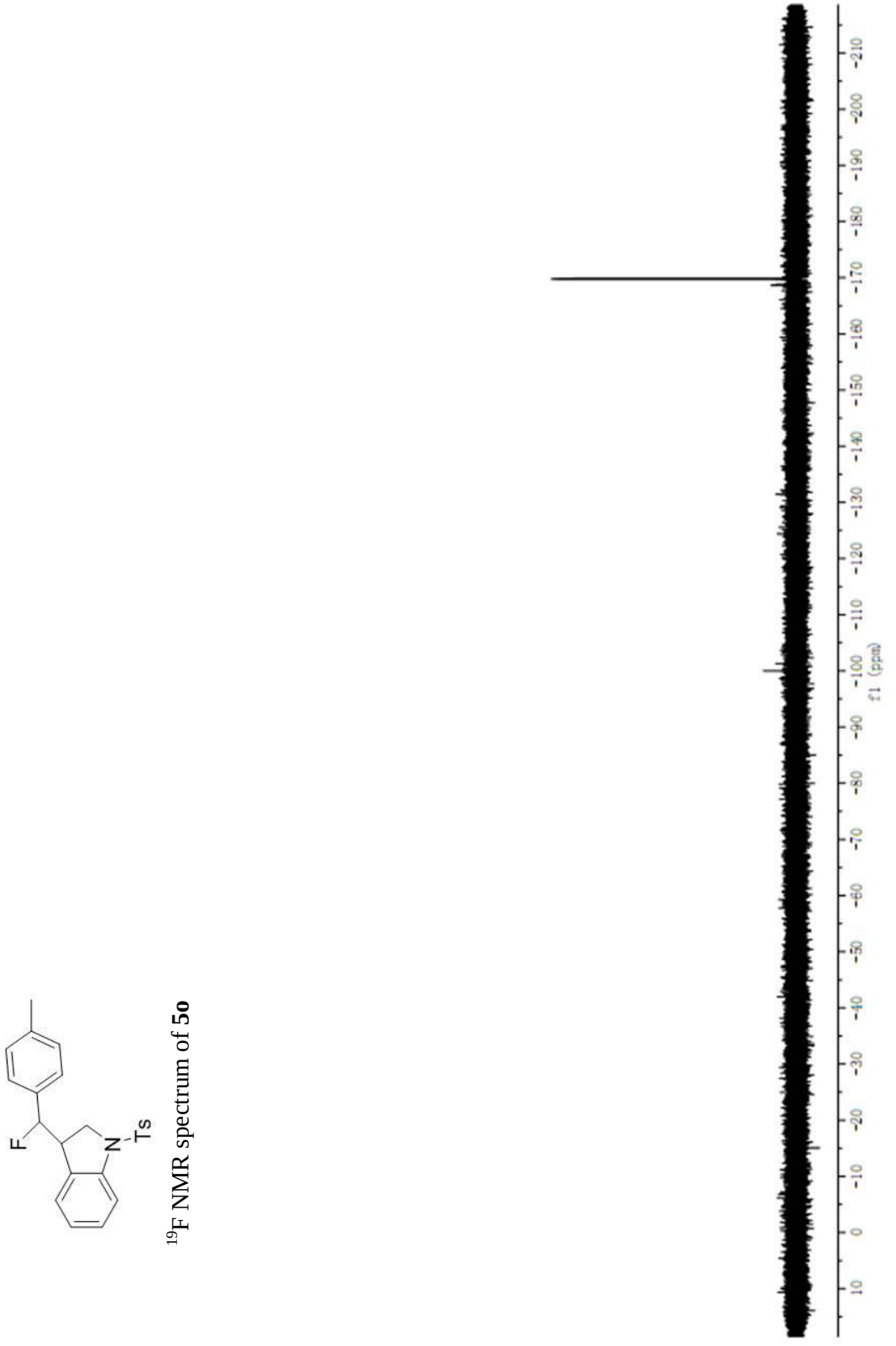
^{1}H NMR spectrum of **5o**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5o**



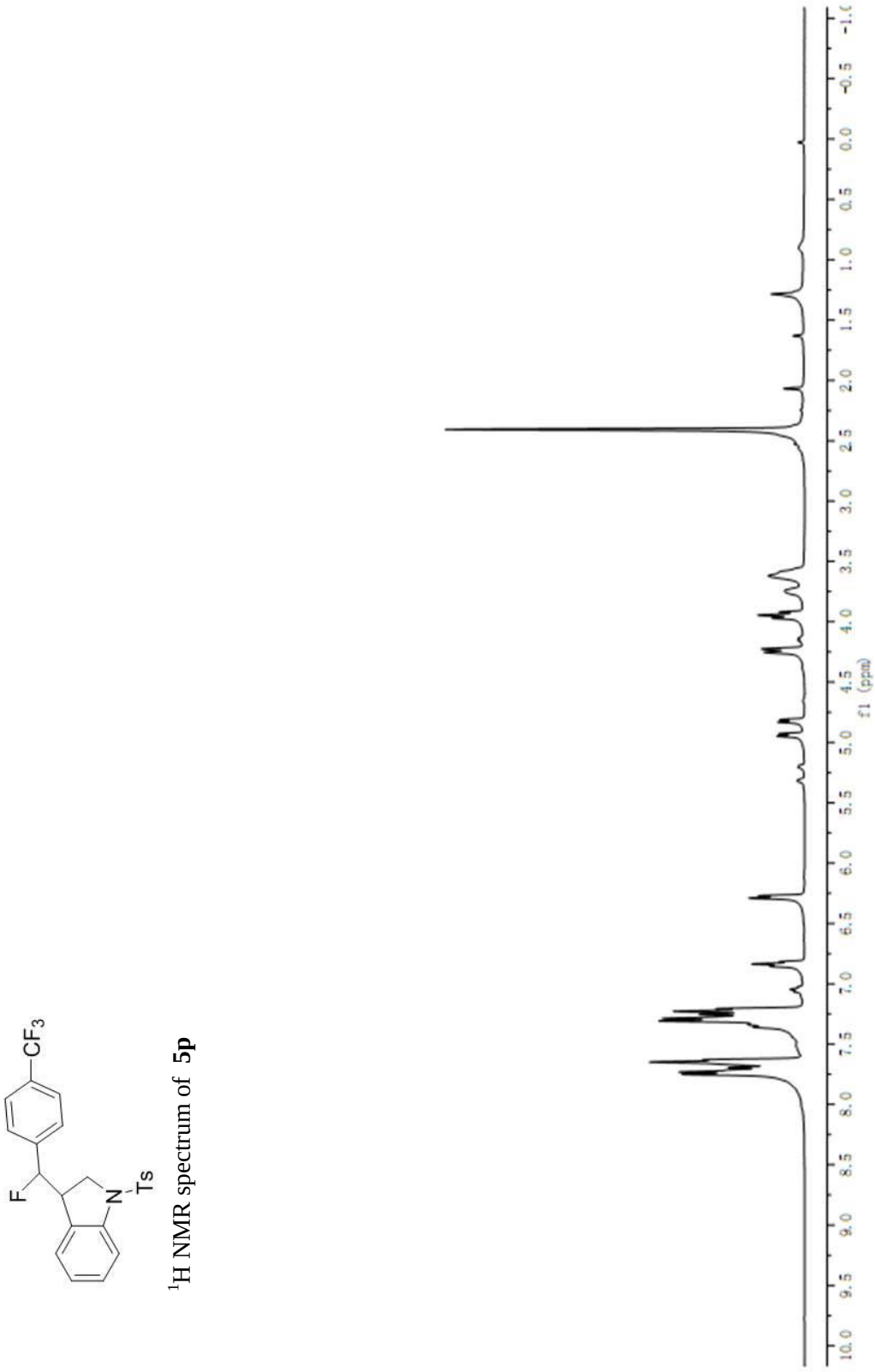
^{13}C NMR spectrum of **5o**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5o**



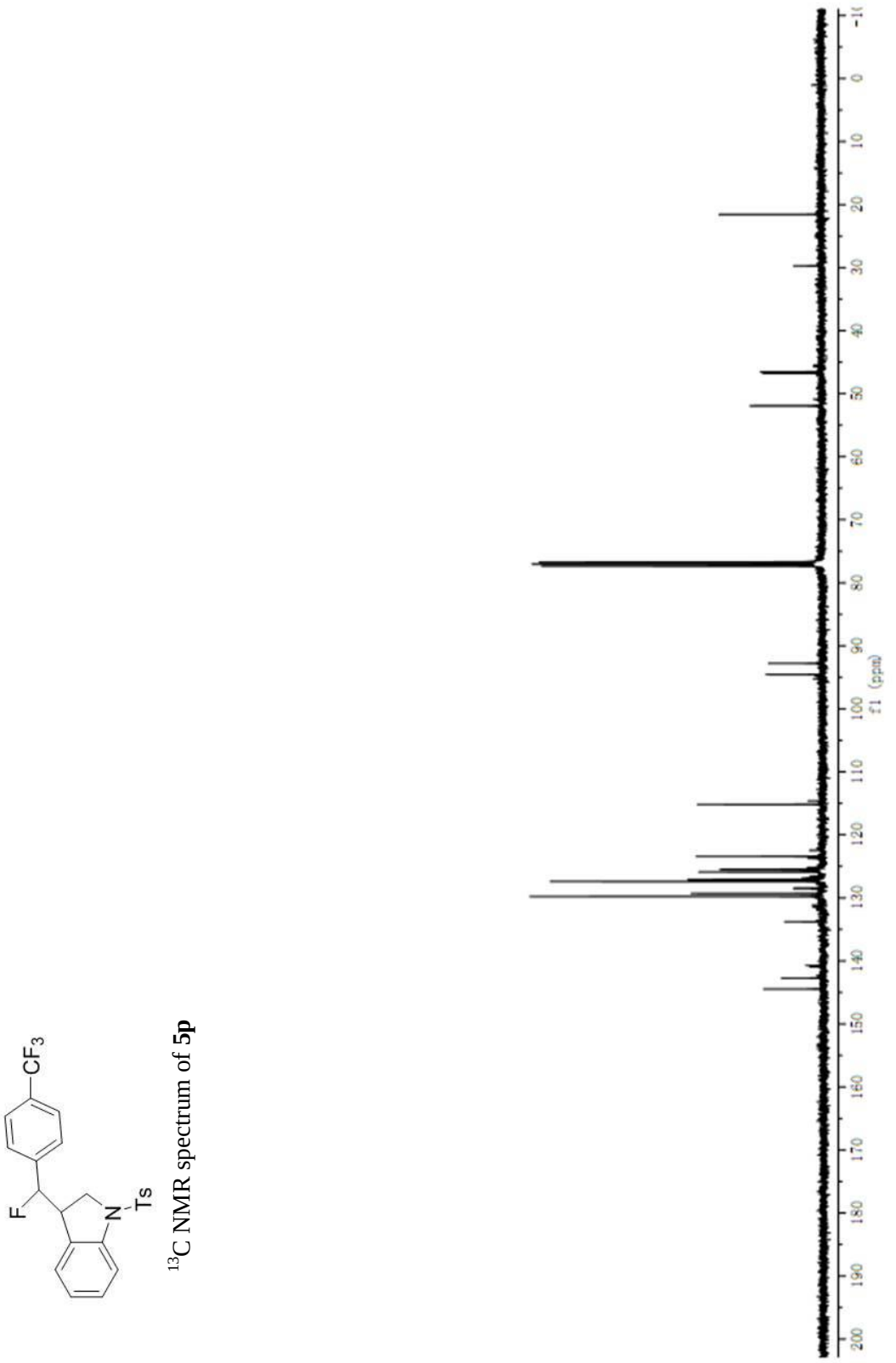
^{19}F NMR spectrum of **5o**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5o**



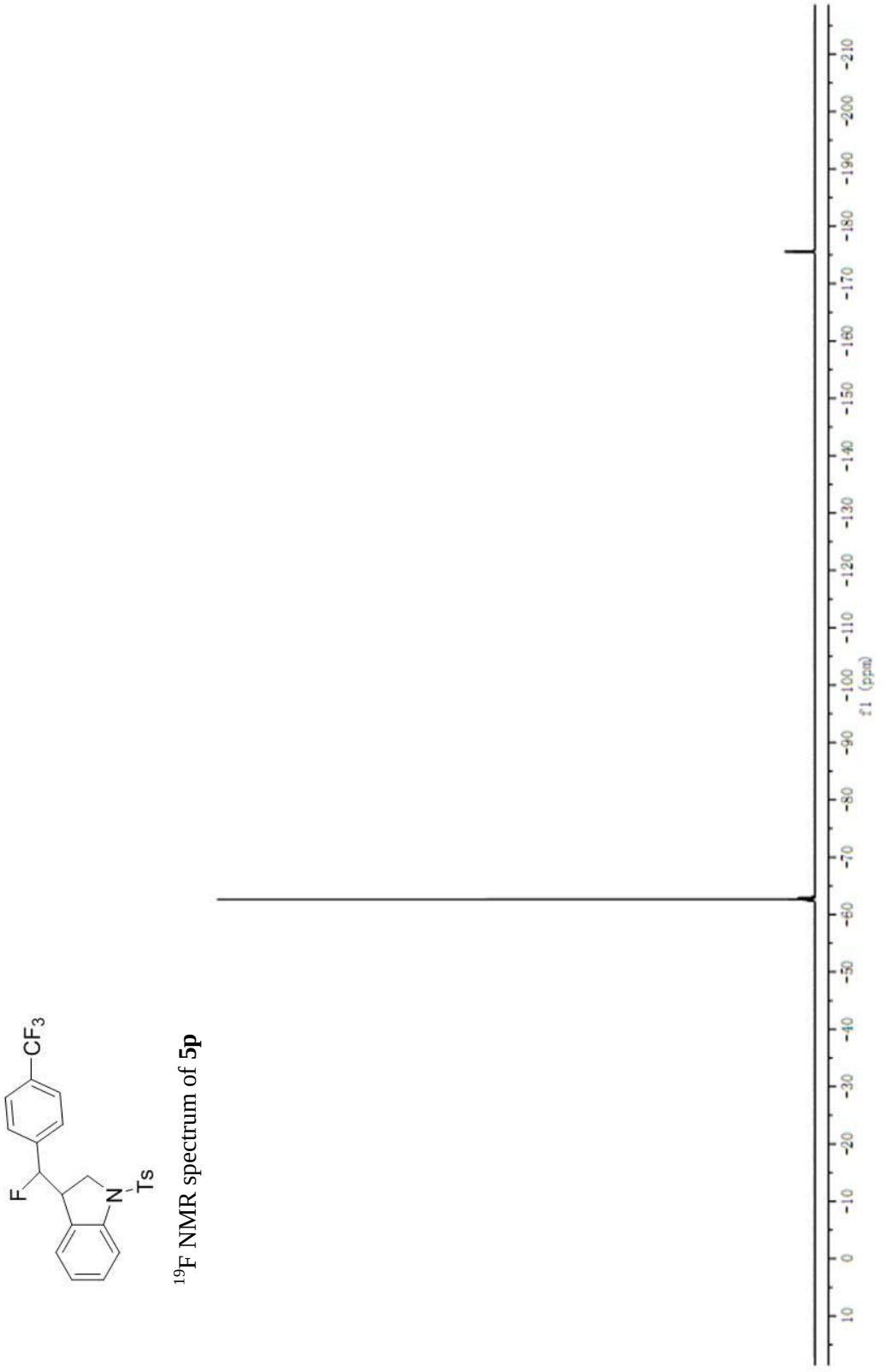
^{1}H NMR spectrum of **5p**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5p**



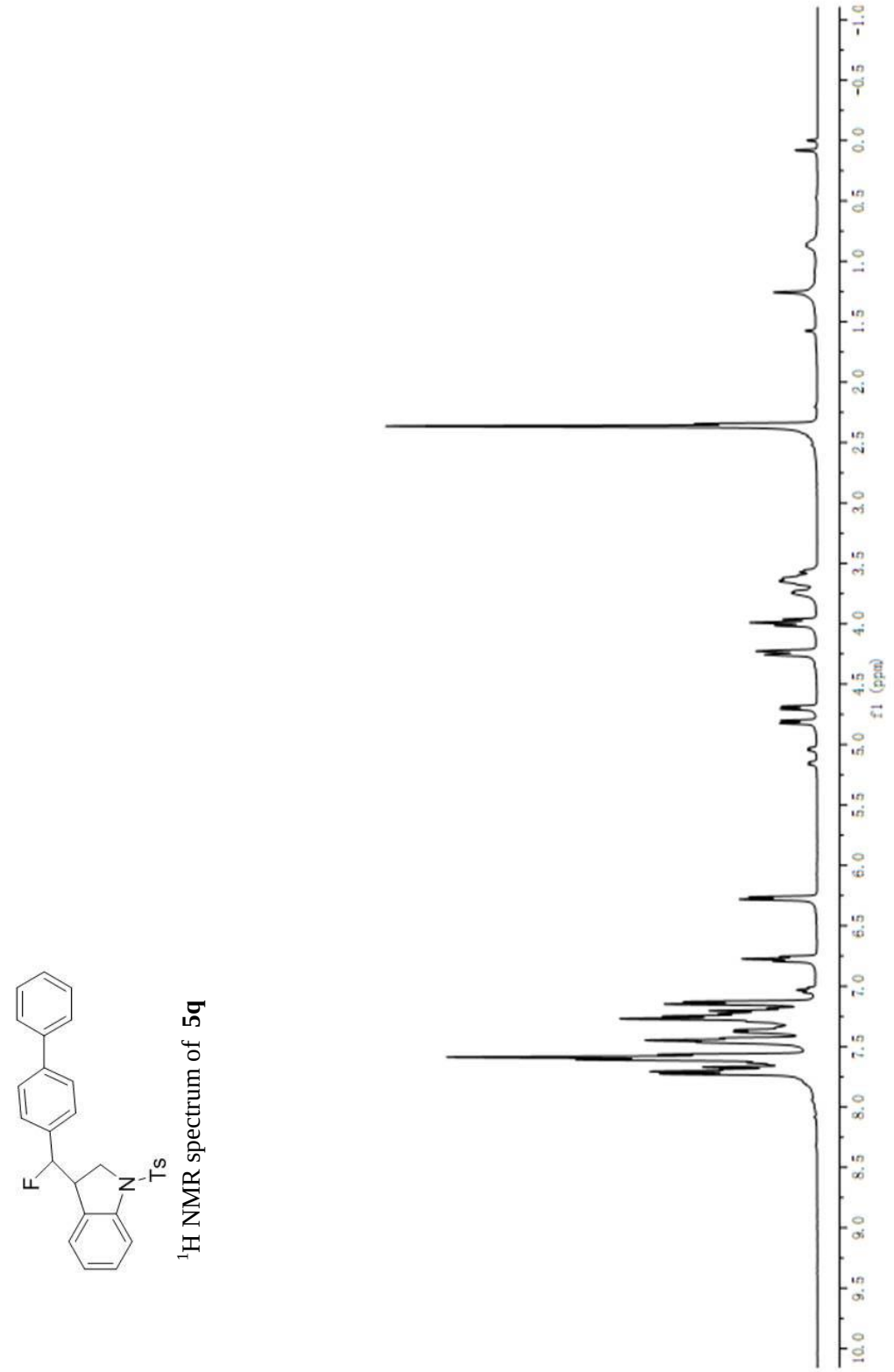
^{13}C NMR spectrum of **5p**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5p**



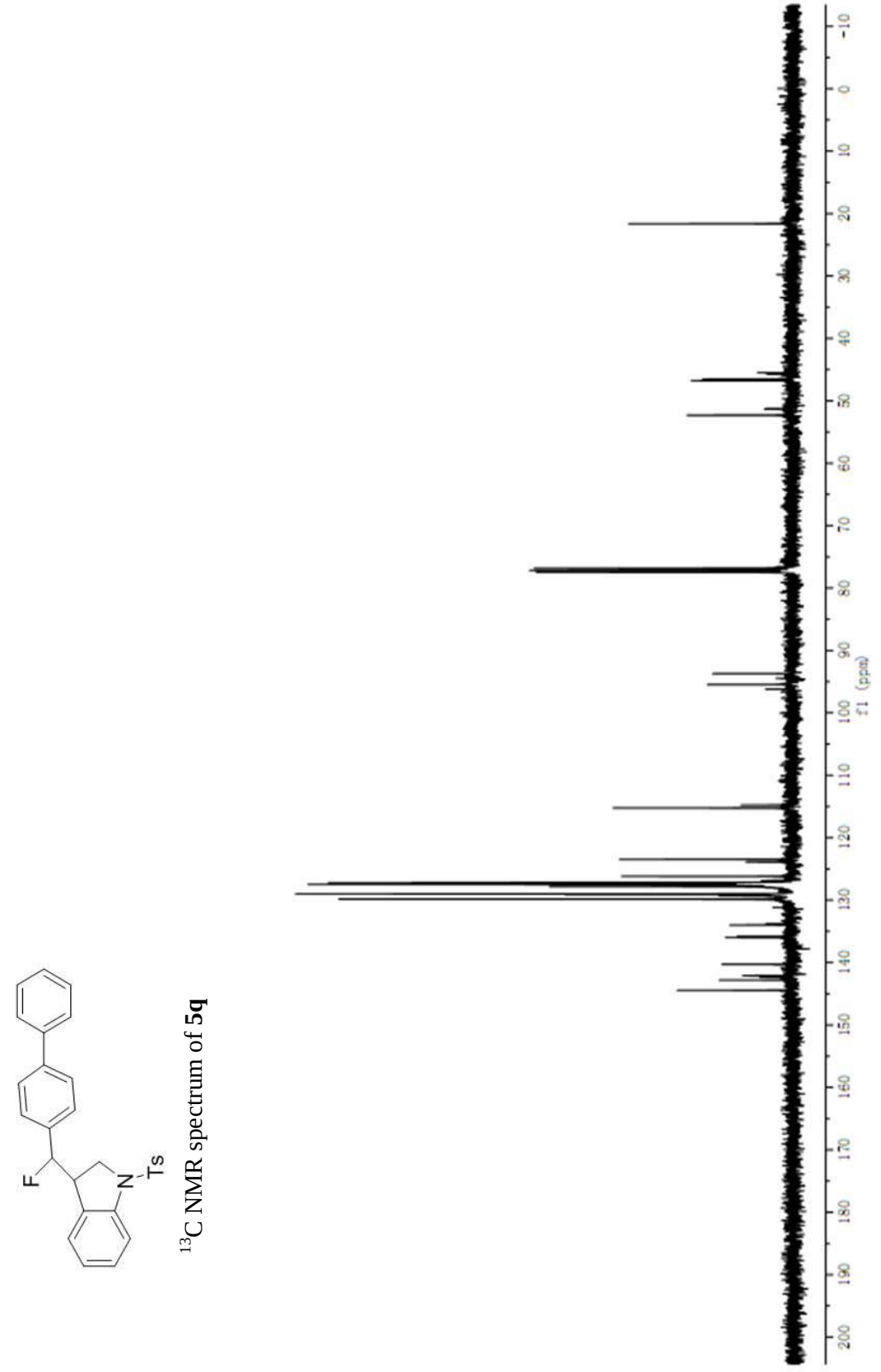
^{19}F NMR spectrum of **5p**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5p**



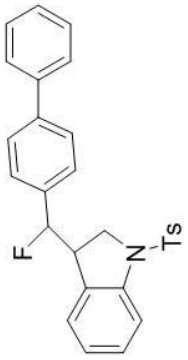
^{1}H NMR spectrum of **5q**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5q**

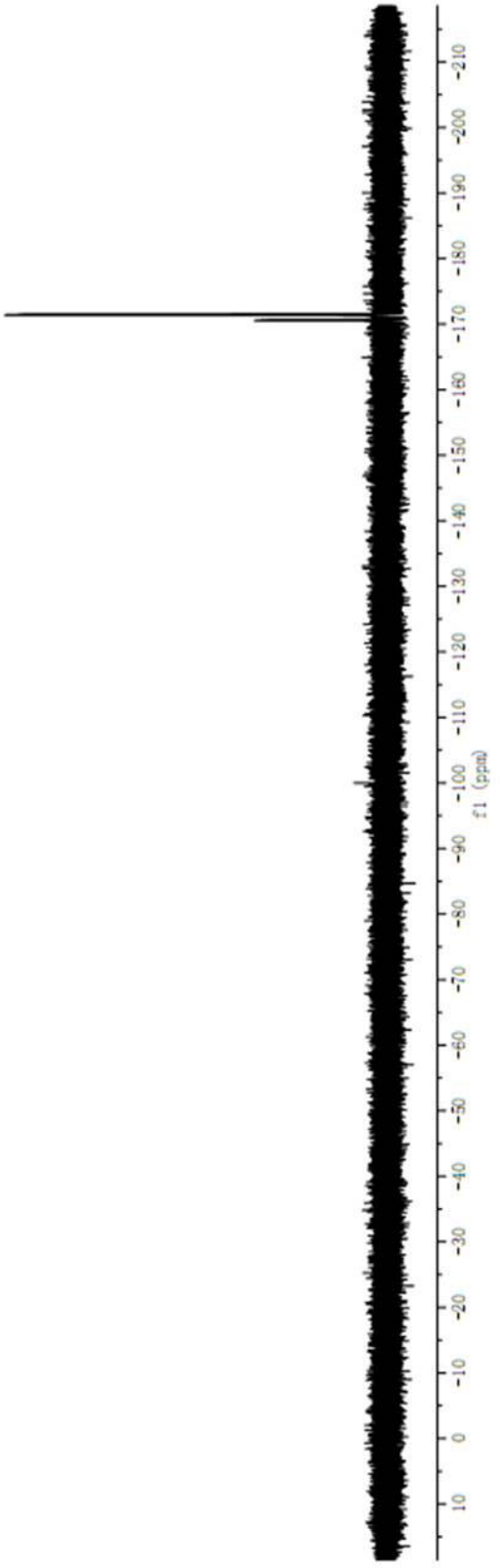


^{13}C NMR spectrum of **5q**

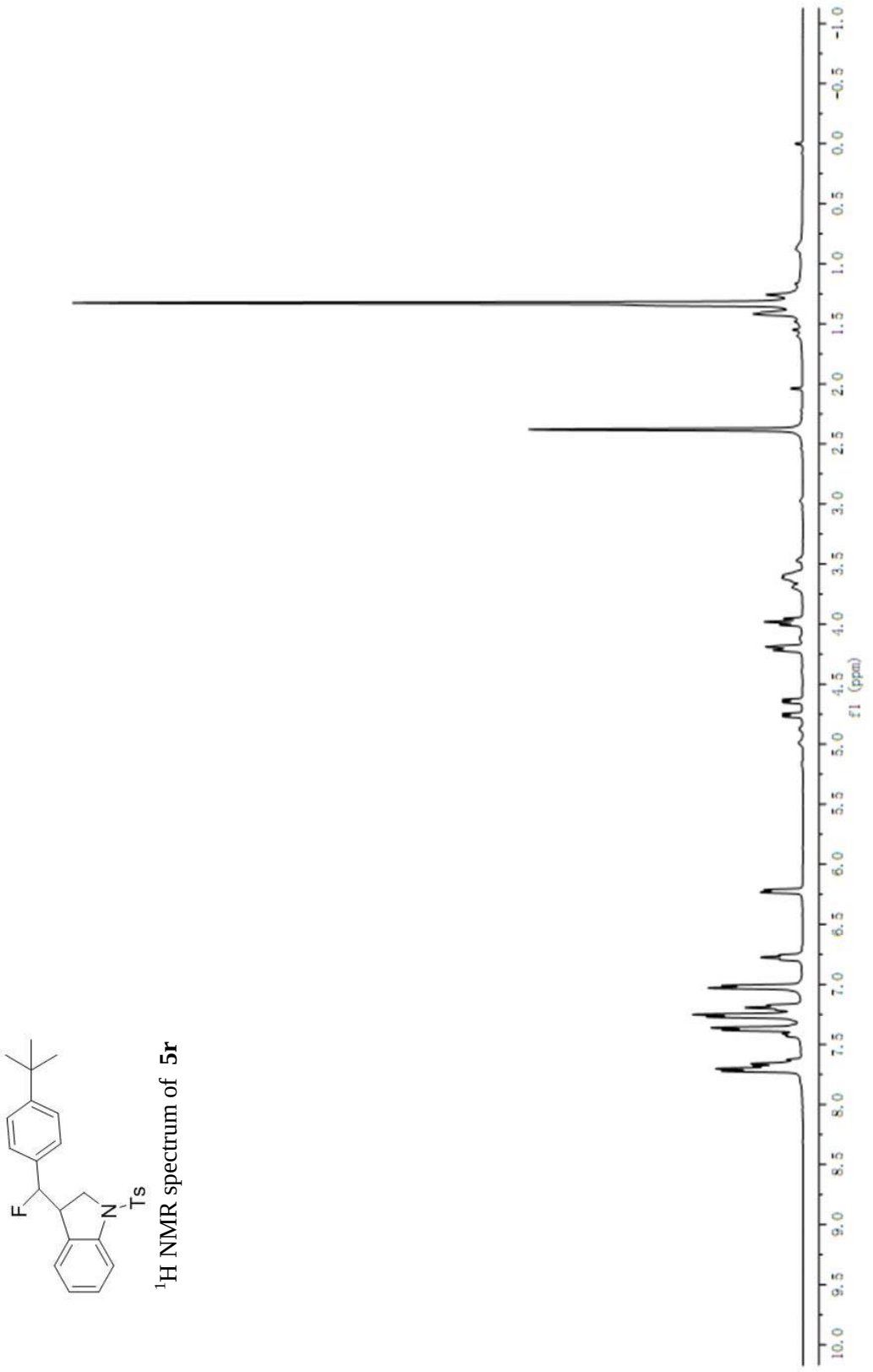
^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5q**



^{19}F NMR spectrum of **5q**

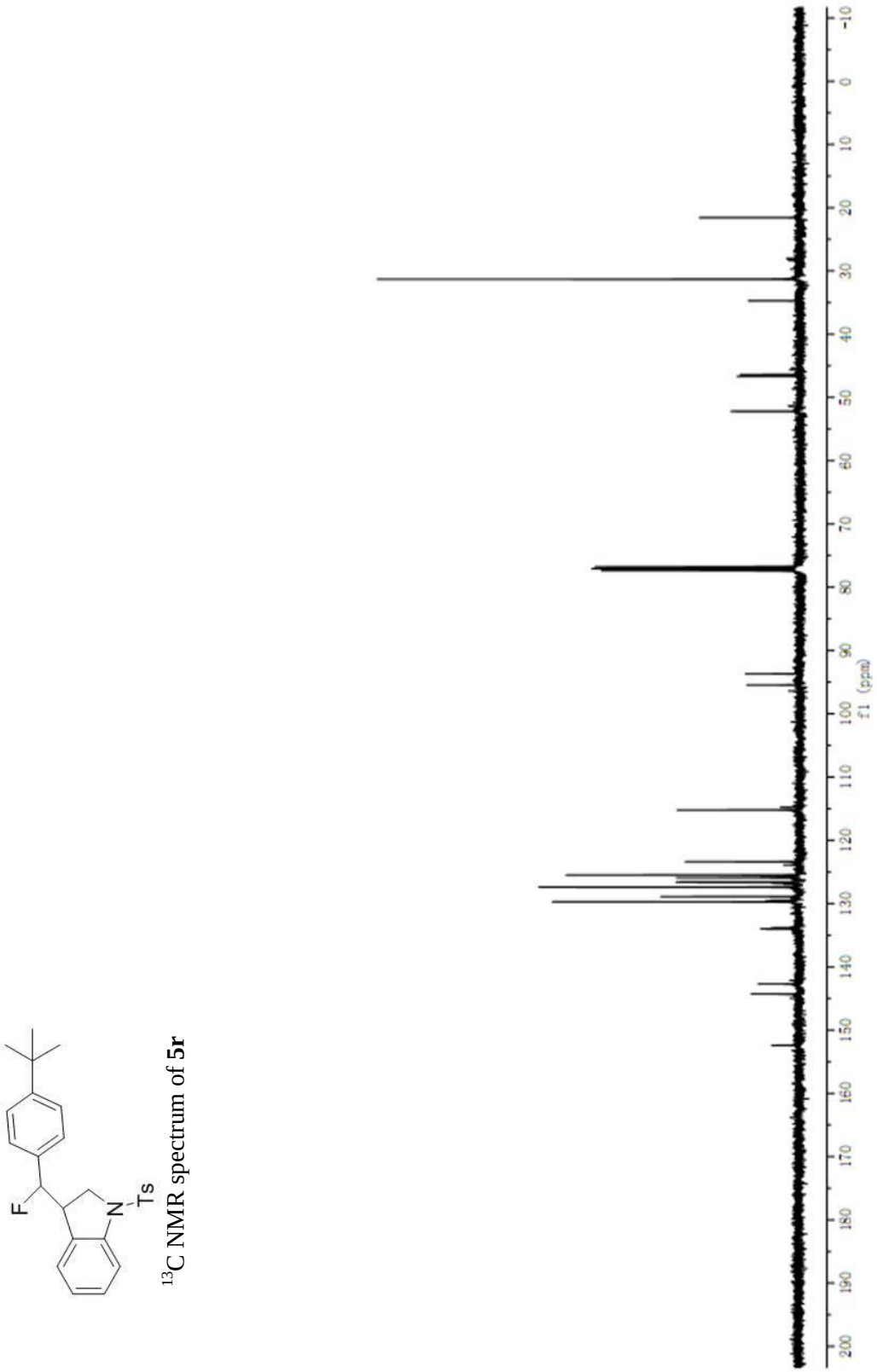


^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5q**



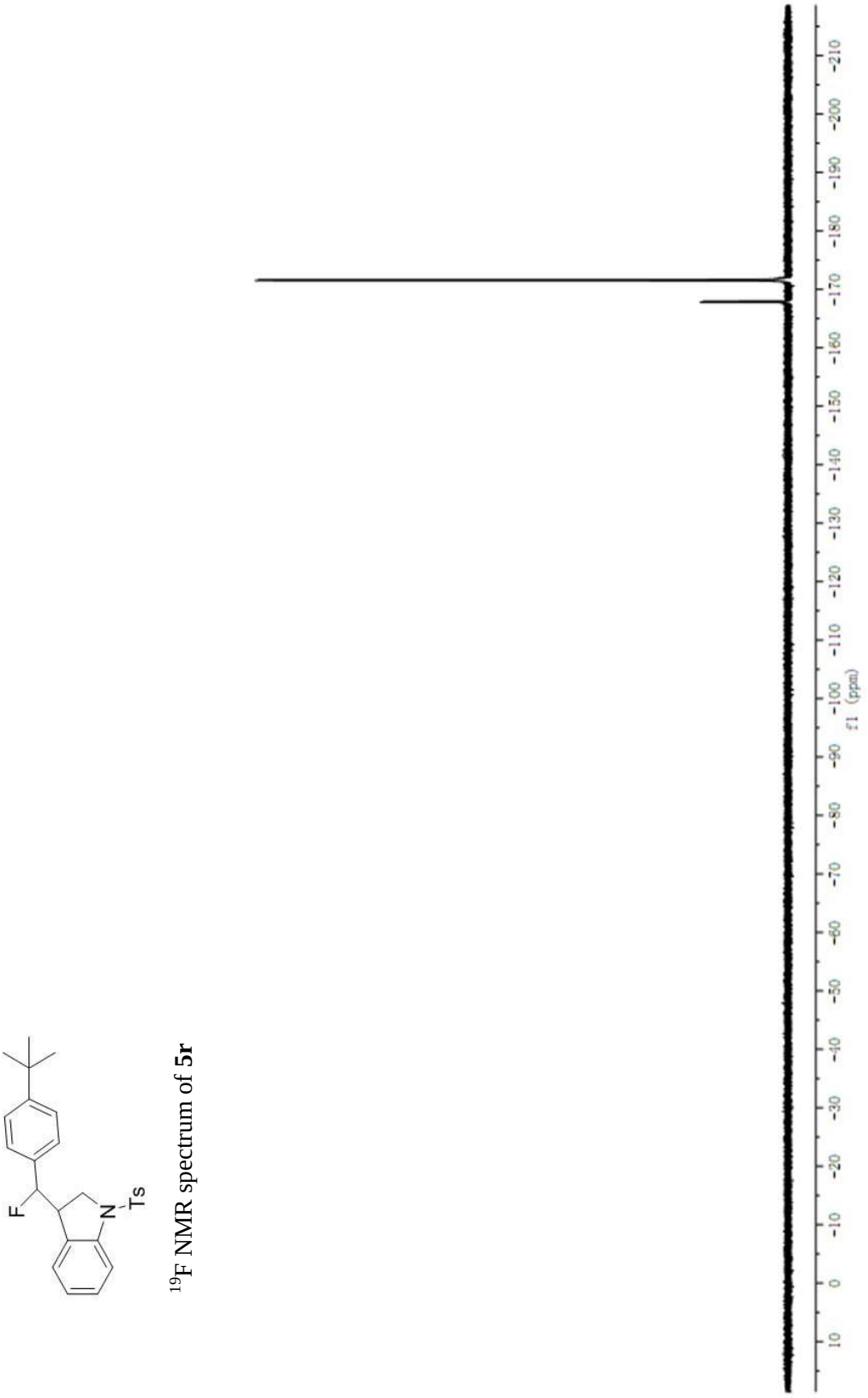
^{1}H NMR spectrum of **5r**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5r**



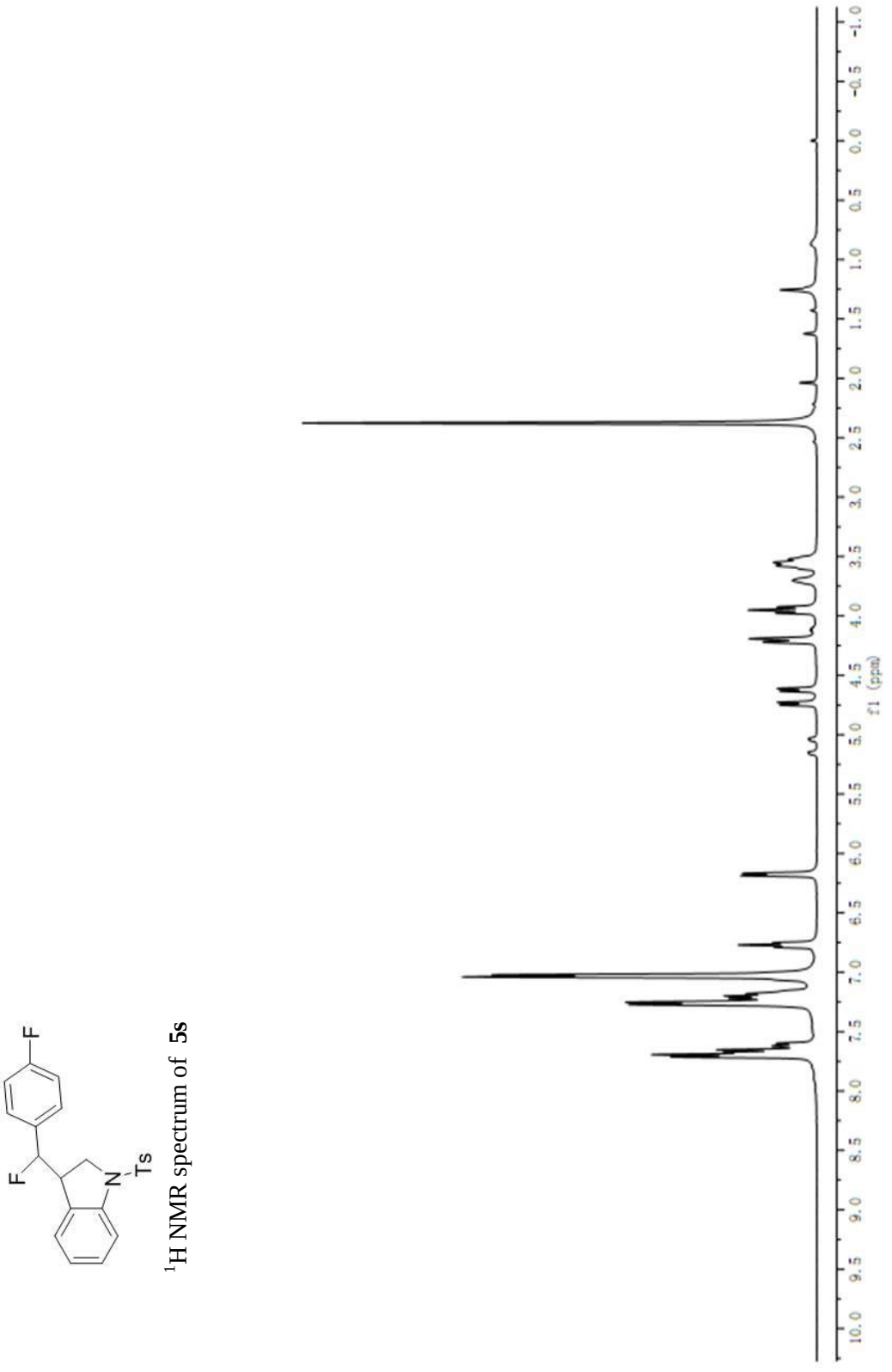
^{13}C NMR spectrum of **5r**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5r**



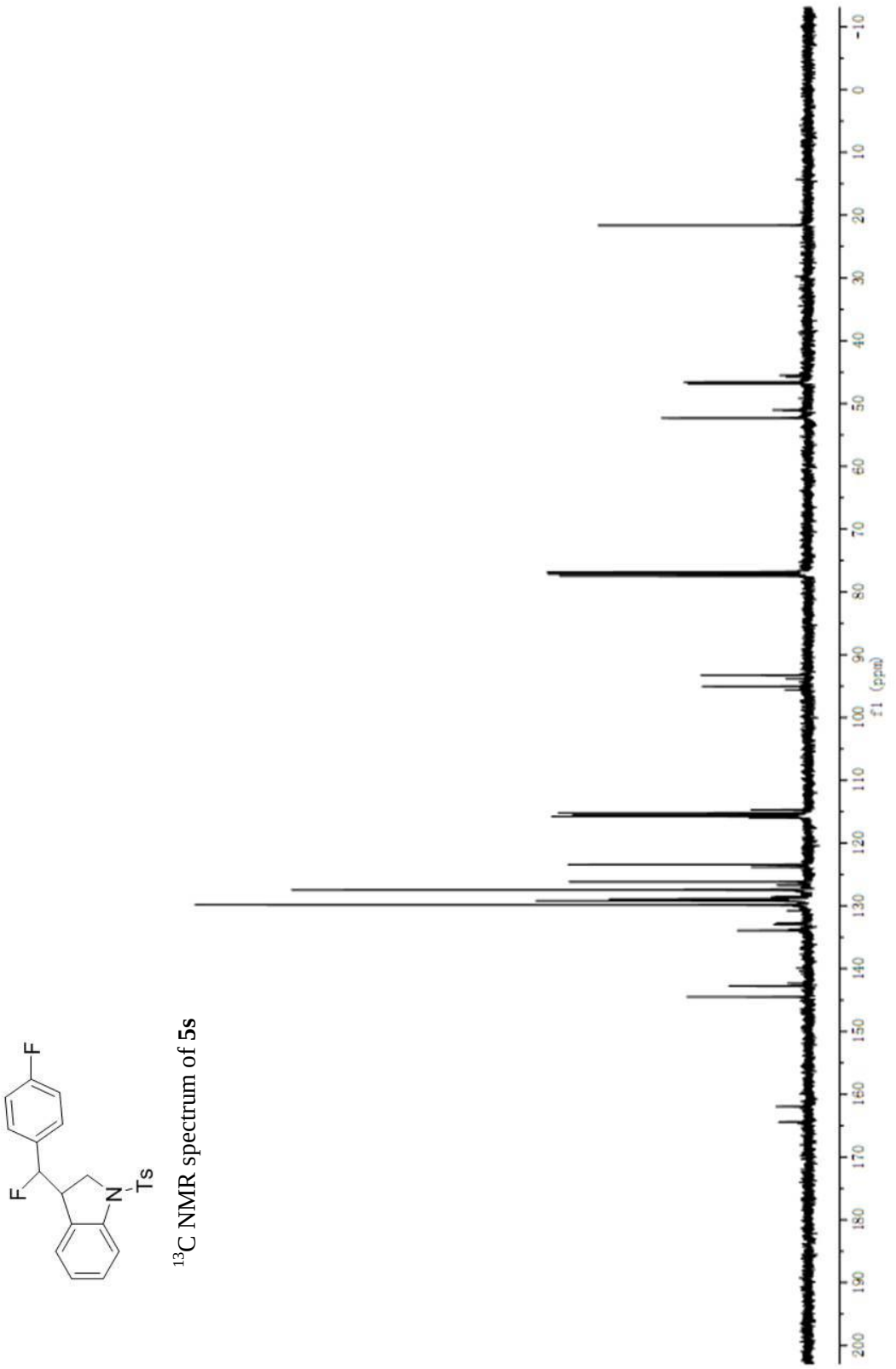
^{19}F NMR spectrum of **5r**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5r**



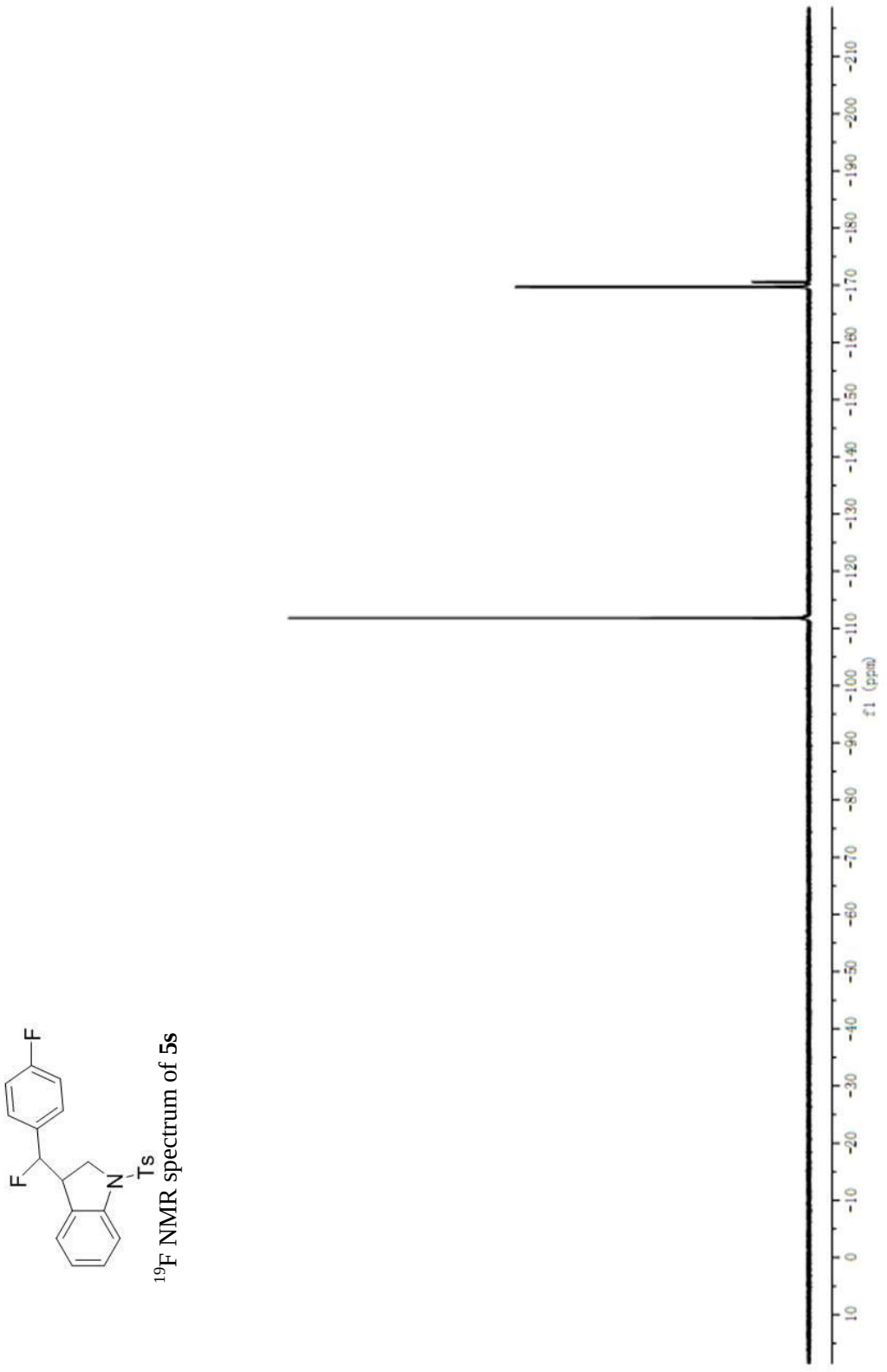
^{1}H NMR spectrum of **5s**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5s**



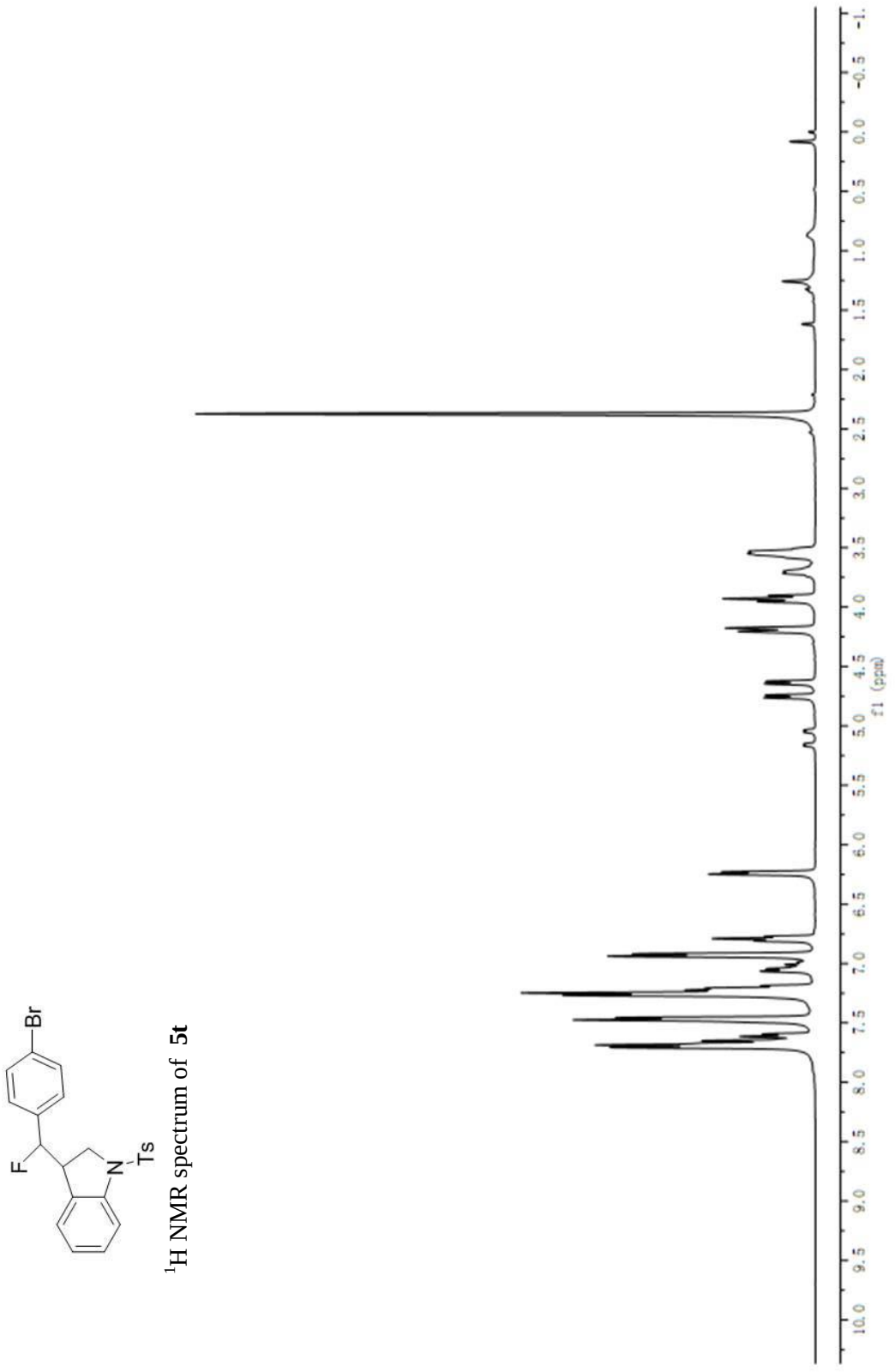
^{13}C NMR spectrum of **5s**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5s**



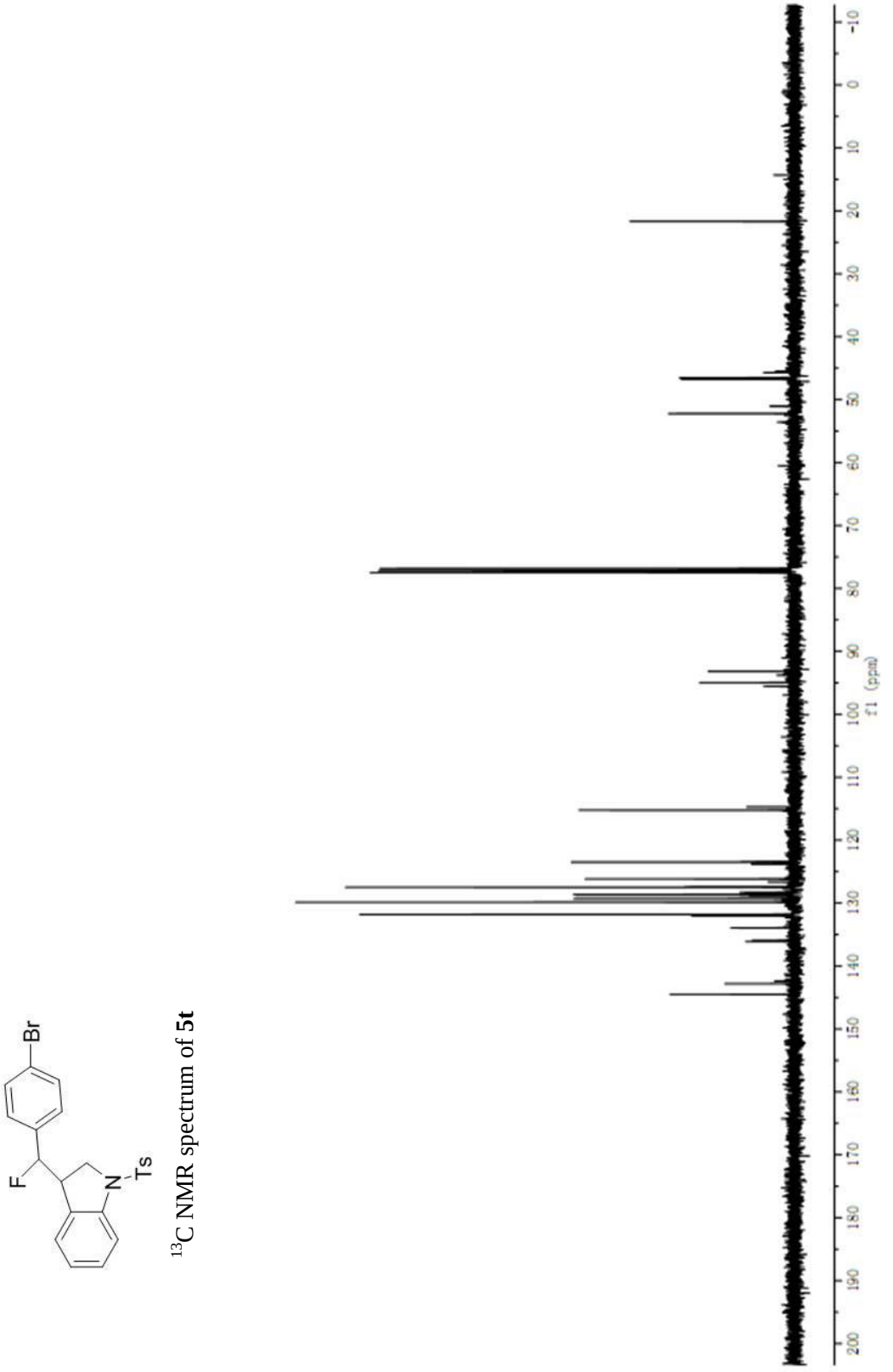
^{19}F NMR spectrum of **5s**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5s**



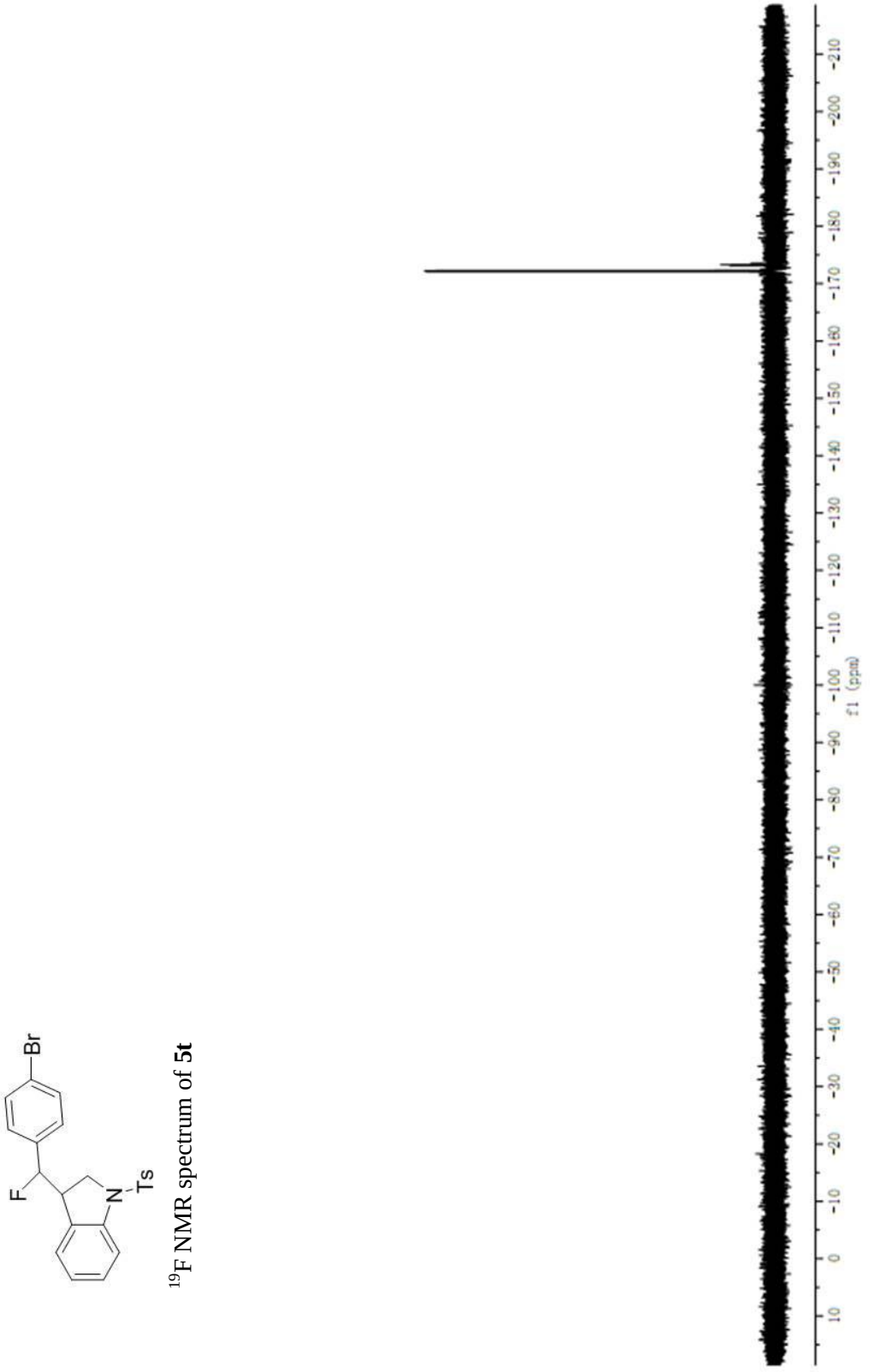
^{1}H NMR spectrum of **5t**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5t**



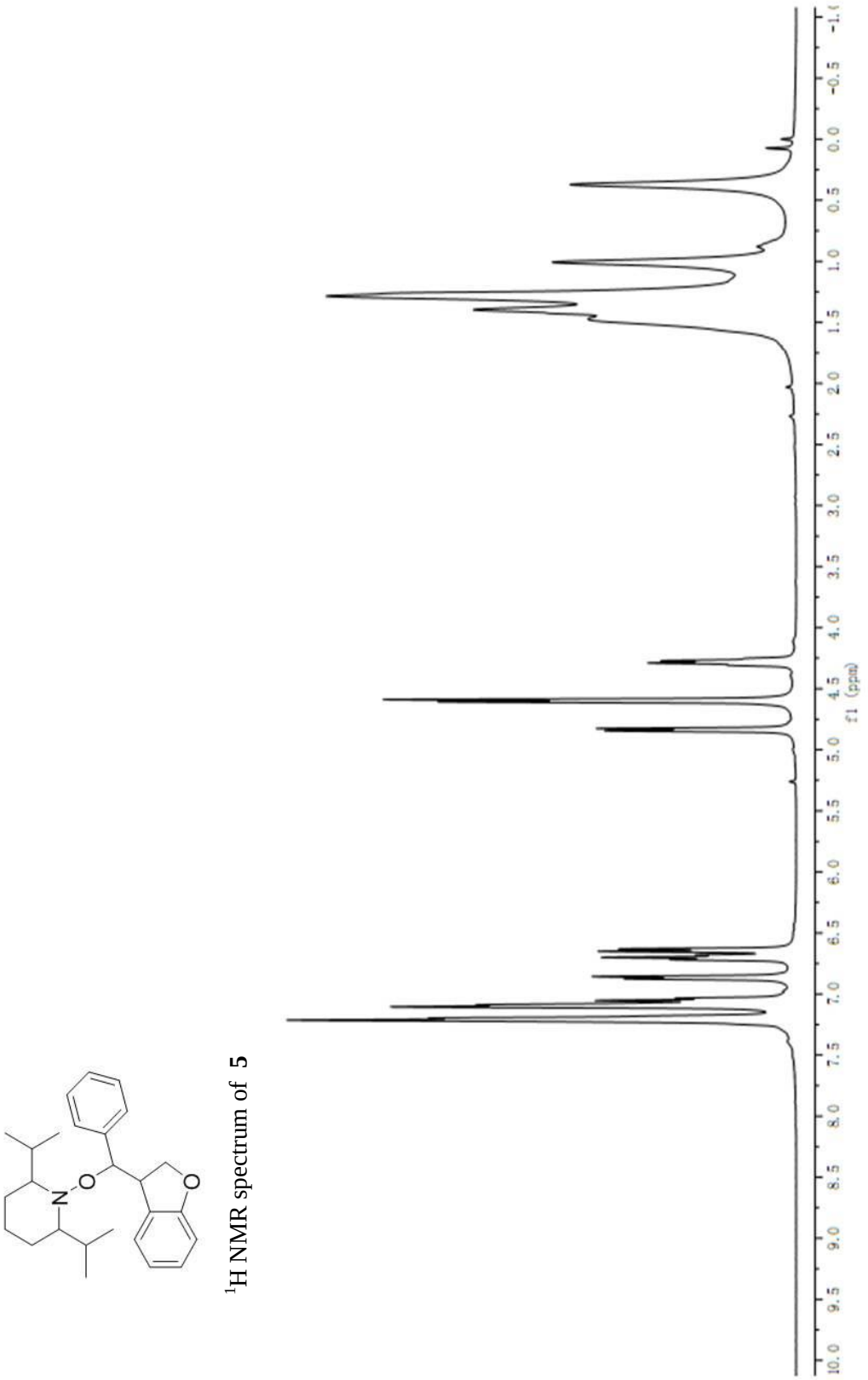
^{13}C NMR spectrum of **5t**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5t**



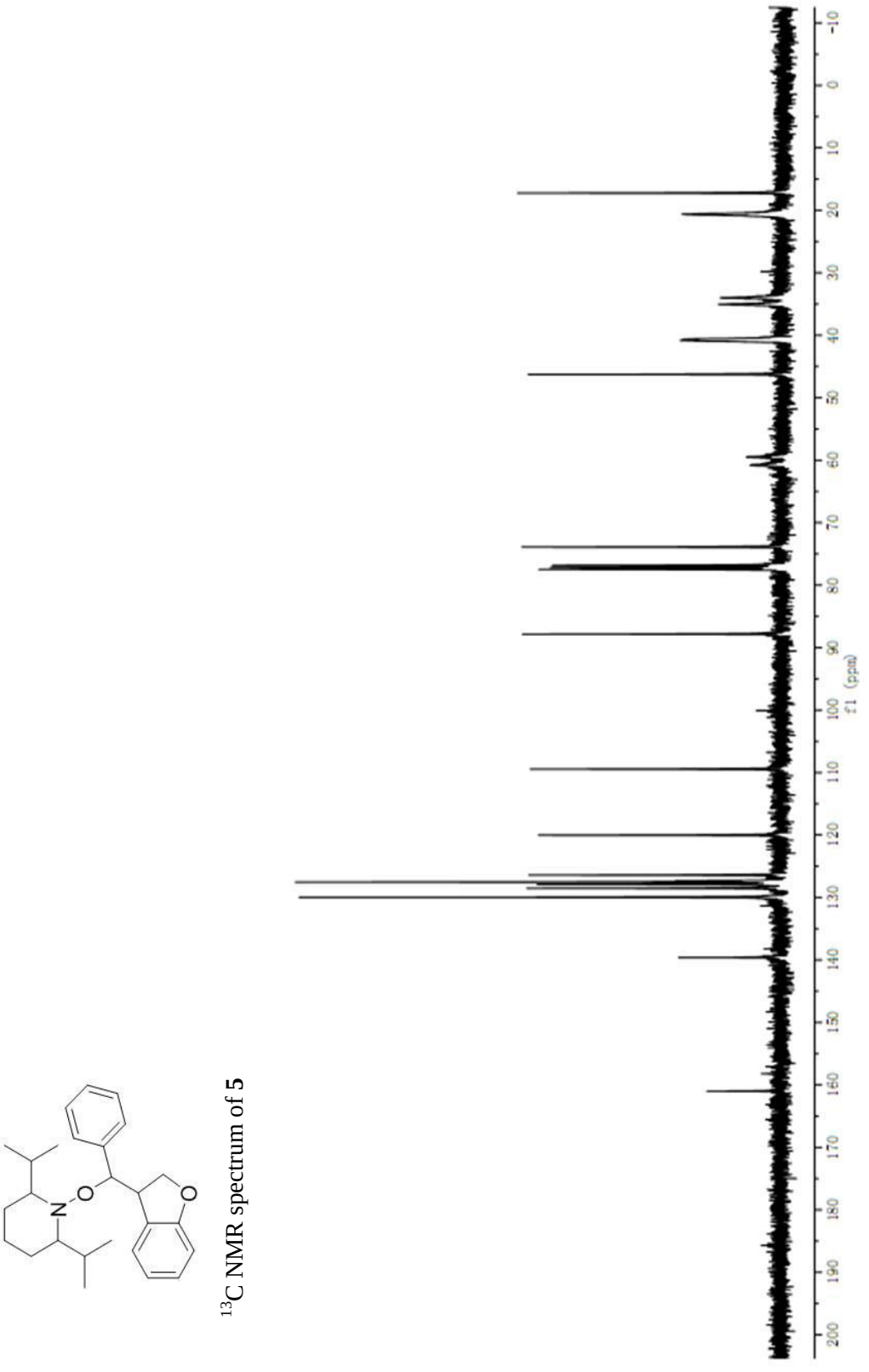
^{19}F NMR spectrum of **5t**

^{19}FNMR spectrum (375 MHz, $CDCl_3$, 23 ℃) of **5t**



^{1}H NMR spectrum of **5**

^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 ℃) of **5**



^{13}C NMR spectrum of **5**

^{13}C NMR spectrum (101 MHz, $CDCl_3$, 23 ℃) of **5**

X-ray Crystal Structure Data

X-ray Crystal Structure Data for 3-(fluoro(4-(trifluoromethyl)phenyl)methyl)-2,3-dihydrobenzofuran (5d)

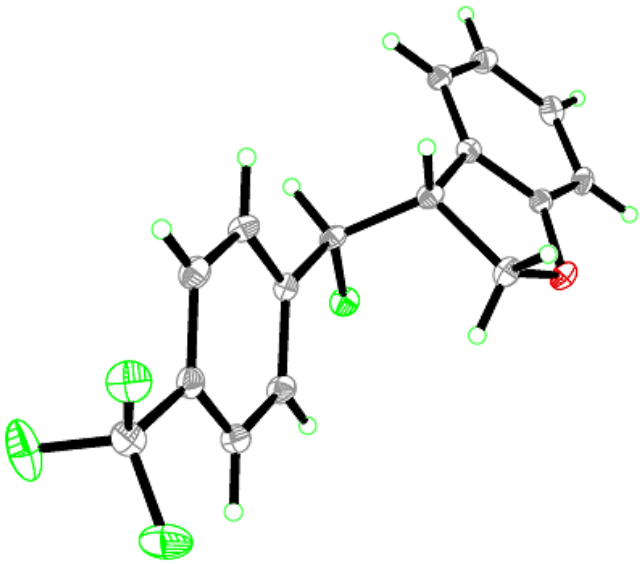


Table 10. Crystal data and structure refinement for shelx1.

Identification code	shelx1
Empirical formula	$C_{16}\,H_{12}\,F_4\,O$
Formula weight	296.26
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 22.639(5) A alpha = 90 deg.
	b = 5.0207(10) A beta = 93.54(3) deg.
	c = 11.438(2) A gamma = 90 deg.
Volume	1297.6(4) A^3
Z, Calculated density	2, 1.639 Mg/m^3
Absorption coefficient	0.137 mm^-1
F(000)	660
Crystal size	0.20 x 0.18 x 0.12 mm

Theta range for data collection	1.80 to 25.02 deg.
Limiting indices	-26<=h<=24, -5<=k<=5, -13<=l<=13
Reflections collected / unique	9216 / 2266 [R(int) = 0.1034]
Completeness to theta = 25.02	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9838 and 0.9731
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2266 / 0 / 191
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0656, wR2 = 0.1470
R indices (all data)	R1 = 0.0856, wR2 = 0.1617
Extinction coefficient	0.031(4)
Largest diff. peak and hole	0.387 and -0.332 e.A^-3

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2x 10^3) for shelxl. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	Y	Z	U(eq)
F(1)	4622(1)	-4727(4)	7089(2)	48(1)
F(2)	4706(1)	-2396(4)	5539(2)	58(1)
F(3)	4128(1)	-5782(4)	5486(1)	39(1)
F(4)	2573(1)	5032(3)	8189(1)	28(1)
O(1)	1626(1)	1759(4)	9677(1)	25(1)
C(1)	4316(1)	-3703(6)	6150(3)	32(1)
C(2)	3818(1)	-1939(5)	6477(2)	26(1)
C(3)	3325(1)	-1641(5)	5691(2)	28(1)
C(4)	2874(1)	51(5)	5959(2)	27(1)
C(5)	2907(1)	1481(5)	7007(2)	22(1)
C(6)	3405(1)	1191(6)	7784(2)	26(1)
C(7)	3857(1)	-543(6)	7519(2)	28(1)
C(8)	2396(1)	3277(5)	7266(2)	23(1)
C(9)	1851(1)	1739(5)	7632(2)	23(1)
C(10)	1342(1)	3582(5)	7874(2)	21(1)
C(11)	1004(1)	5293(5)	7150(2)	25(1)

C(12)	585(1)	6907(5)	7647(2)	28(1)
C(13)	507(1)	6801(5)	8843(2)	28(1)
C(14)	840(1)	5067(5)	9573(2)	25(1)
C(15)	1255(1)	3489(5)	9063(2)	21(1)
C(16)	1952(1)	287(6)	8821(2)	25(1)

Table 12. Bond lengths [A] and angles [deg] for shelxl.

F(1)-C(1)	1.343(3)
F(2)-C(1)	1.333(3)
F(3)-C(1)	1.344(3)
F(4)-C(8)	1.414(3)
O(1)-C(15)	1.371(3)
O(1)-C(16)	1.463(3)
C(1)-C(2)	1.499(4)
C(2)-C(7)	1.381(4)
C(2)-C(3)	1.396(4)
C(3)-C(4)	1.378(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.400(3)
C(5)-C(8)	1.510(3)
C(6)-C(7)	1.391(4)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(9)	1.536(3)
C(8)-H(8)	1.0000
C(9)-C(10)	1.517(3)
C(9)-C(16)	1.548(3)
C(9)-H(9)	1.0000
C(10)-C(15)	1.386(3)
C(10)-C(11)	1.389(3)
C(11)-C(12)	1.395(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.391(3)

C(12)-H(12)	0.9500
C(13)-C(14)	1.395(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(4)
C(14)-H(14)	0.9500
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(15)-O(1)-C(16)	107.18(18)
F(2)-C(1)-F(1)	106.4(2)
F(2)-C(1)-F(3)	106.4(2)
F(1)-C(1)-F(3)	106.5(2)
F(2)-C(1)-C(2)	111.9(2)
F(1)-C(1)-C(2)	112.7(2)
F(3)-C(1)-C(2)	112.6(2)
C(7)-C(2)-C(3)	120.5(2)
C(7)-C(2)-C(1)	120.4(2)
C(3)-C(2)-C(1)	119.0(2)
C(4)-C(3)-C(2)	119.7(3)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	120.5(2)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	119.3(2)
C(4)-C(5)-C(8)	118.4(2)
C(6)-C(5)-C(8)	122.3(2)
C(7)-C(6)-C(5)	120.1(3)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(2)-C(7)-C(6)	119.8(2)
C(2)-C(7)-H(7)	120.1
C(6)-C(7)-H(7)	120.1
F(4)-C(8)-C(5)	109.46(19)
F(4)-C(8)-C(9)	107.75(19)
C(5)-C(8)-C(9)	113.0(2)
F(4)-C(8)-H(8)	108.8
C(5)-C(8)-H(8)	108.8
C(9)-C(8)-H(8)	108.8
C(10)-C(9)-C(8)	112.1(2)
C(10)-C(9)-C(16)	101.53(19)

C(8)-C(9)-C(16)	113.5(2)
C(10)-C(9)-H(9)	109.8
C(8)-C(9)-H(9)	109.8
C(16)-C(9)-H(9)	109.8
C(15)-C(10)-C(11)	120.0(2)
C(15)-C(10)-C(9)	108.3(2)
C(11)-C(10)-C(9)	131.7(2)
C(10)-C(11)-C(12)	118.7(2)
C(10)-C(11)-H(11)	120.7
C(12)-C(11)-H(11)	120.7
C(13)-C(12)-C(11)	120.6(3)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(12)-C(13)-C(14)	121.1(3)
C(12)-C(13)-H(13)	119.5
C(14)-C(13)-H(13)	119.5
C(15)-C(14)-C(13)	117.4(3)
C(15)-C(14)-H(14)	121.3
C(13)-C(14)-H(14)	121.3
O(1)-C(15)-C(14)	123.8(2)
O(1)-C(15)-C(10)	113.9(2)
C(14)-C(15)-C(10)	122.3(2)
O(1)-C(16)-C(9)	107.3(2)
O(1)-C(16)-H(16A)	110.3
C(9)-C(16)-H(16A)	110.3
O(1)-C(16)-H(16B)	110.3
C(9)-C(16)-H(16B)	110.3
H(16A)-C(16)-H(16B)	108.5

Symmetry transformations used to generate equivalent atoms:

Table 13. Anisotropic displacement parameters (A^2 x 10^3) for shelxl. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12

F(1)	43(1)	47(1)	52(1)	-8(1)	-13(1)	17(1)
F(2)	49(1)	37(1)	92(2)	7(1)	40(1)	5(1)
F(3)	44(1)	31(1)	41(1)	-9(1)	1(1)	9(1)
F(4)	36(1)	23(1)	25(1)	-7(1)	1(1)	-3(1)
O(1)	34(1)	25(1)	17(1)	0(1)	2(1)	3(1)
C(1)	31(2)	28(2)	37(2)	1(1)	2(1)	0(1)
C(2)	27(2)	24(2)	27(2)	3(1)	5(1)	-2(1)
C(3)	34(2)	25(2)	23(2)	-2(1)	2(1)	0(1)
C(4)	29(2)	28(2)	23(2)	2(1)	-3(1)	3(1)
C(5)	25(1)	22(2)	20(1)	2(1)	4(1)	0(1)
C(6)	31(2)	27(2)	20(1)	-4(1)	1(1)	-1(1)
C(7)	27(2)	31(2)	26(2)	2(1)	0(1)	-2(1)
C(8)	30(2)	24(2)	14(1)	-4(1)	-1(1)	0(1)
C(9)	29(2)	20(2)	19(1)	-3(1)	0(1)	1(1)
C(10)	25(1)	16(2)	22(1)	-3(1)	1(1)	-2(1)
C(11)	27(2)	26(2)	21(1)	0(1)	0(1)	0(1)
C(12)	30(2)	26(2)	28(2)	2(1)	-1(1)	3(1)
C(13)	30(2)	22(2)	33(2)	0(1)	7(1)	0(1)
C(14)	30(2)	26(2)	21(1)	-2(1)	7(1)	-4(1)
C(15)	25(1)	18(2)	21(1)	1(1)	-1(1)	-3(1)
C(16)	33(2)	21(2)	21(2)	-1(1)	4(1)	3(1)

Table 14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for shelexl.

	x	y	z	U(eq)
H(3)	3301	-2603	4974	33
H(4)	2538	246	5426	32
H(6)	3434	2179	8494	31
H(7)	4192	-765	8053	34
H(8)	2282	4348	6550	27
H(9)	1722	432	7008	27
H(11)	1057	5363	6334	30
H(12)	350	8088	7164	33
H(13)	223	7929	9168	34
H(14)	785	4971	10388	30
H(16A)	1806	-1569	8756	30
H(16B)	2379	247	9065	30

Table 15. Torsion angles [deg] for shelexl.

F(2)-C(1)-C(2)-C(7)	-90.4(3)
F(1)-C(1)-C(2)-C(7)	29.4(4)
F(3)-C(1)-C(2)-C(7)	149.9(3)
F(2)-C(1)-C(2)-C(3)	87.0(3)
F(1)-C(1)-C(2)-C(3)	-153.2(3)
F(3)-C(1)-C(2)-C(3)	-32.7(4)
C(7)-C(2)-C(3)-C(4)	-0.2(4)
C(1)-C(2)-C(3)-C(4)	-177.6(2)
C(2)-C(3)-C(4)-C(5)	0.3(4)
C(3)-C(4)-C(5)-C(6)	0.3(4)
C(3)-C(4)-C(5)-C(8)	-179.1(2)
C(4)-C(5)-C(6)-C(7)	-1.1(4)
C(8)-C(5)-C(6)-C(7)	178.3(2)
C(3)-C(2)-C(7)-C(6)	-0.5(4)

C(1)-C(2)-C(7)-C(6)	176.8(2)
C(5)-C(6)-C(7)-C(2)	1.2(4)
C(4)-C(5)-C(8)-F(4)	-165.0(2)
C(6)-C(5)-C(8)-F(4)	15.6(3)
C(4)-C(5)-C(8)-C(9)	74.9(3)
C(6)-C(5)-C(8)-C(9)	-104.5(3)
F(4)-C(8)-C(9)-C(10)	59.5(3)
C(5)-C(8)-C(9)-C(10)	-179.4(2)
F(4)-C(8)-C(9)-C(16)	-54.8(3)
C(5)-C(8)-C(9)-C(16)	66.3(3)
C(8)-C(9)-C(10)-C(15)	-112.1(2)
C(16)-C(9)-C(10)-C(15)	9.3(3)
C(8)-C(9)-C(10)-C(11)	64.2(3)
C(16)-C(9)-C(10)-C(11)	-174.3(3)
C(15)-C(10)-C(11)-C(12)	0.5(4)
C(9)-C(10)-C(11)-C(12)	-175.5(2)
C(10)-C(11)-C(12)-C(13)	0.0(4)
C(11)-C(12)-C(13)-C(14)	-0.7(4)
C(12)-C(13)-C(14)-C(15)	0.9(4)
C(16)-O(1)-C(15)-C(14)	174.5(2)
C(16)-O(1)-C(15)-C(10)	-7.1(3)
C(13)-C(14)-C(15)-O(1)	177.9(2)
C(13)-C(14)-C(15)-C(10)	-0.4(4)
C(11)-C(10)-C(15)-O(1)	-178.7(2)
C(9)-C(10)-C(15)-O(1)	-1.9(3)
C(11)-C(10)-C(15)-C(14)	-0.3(4)
C(9)-C(10)-C(15)-C(14)	176.5(2)
C(15)-O(1)-C(16)-C(9)	12.9(3)
C(10)-C(9)-C(16)-O(1)	-13.3(2)
C(8)-C(9)-C(16)-O(1)	107.1(2)

Symmetry transformations used to generate equivalent atoms:

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