SUPPORTING INFORMATION

Lewis Acid-Catalyzed Tandem Cyclization of *in Situ* Generated *o*-Quinone Methides and Arylsulfonyl Hydrazides for a One-Pot Entry to 3-Sulfonylbenzofurans

Fan-Xiao Meng,[a] Ruo-Nan Wang,[a] Hong-Li Huang,[a] Shu-Wen Gong,[a] Qian-Li Li,[a] Shao-Liang Zhang,[a] Chun-Lin Ma,[a] Chen-Zhong Li,[b] and Ji-Yuan Du*[a]

[a]College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

[b]Nanobioengineering/Bioelectronics Laboratory, Department of Biomedical Engineering, Florida International University, Miami, USA

Contents

General

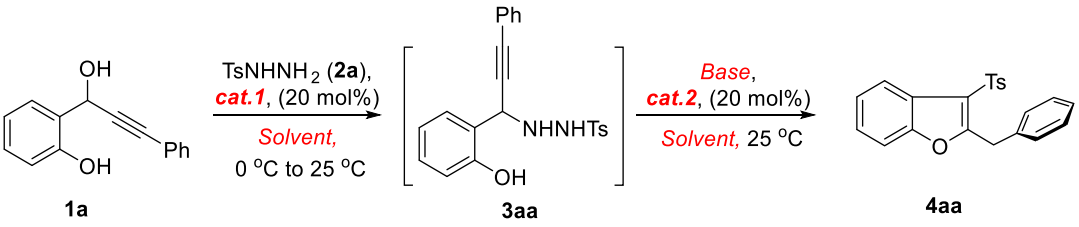
All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH_2Cl_2 (CaH_2), EtOAc (Na), toluene (Na), $ClCH_2CH_2Cl$ (CaH_2). The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Anhui Liangchen Silicon Material Company in China.

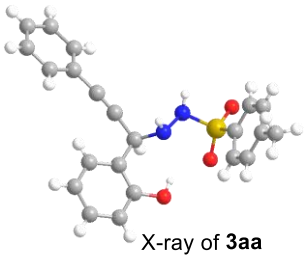
^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian 500 MHz instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent ($CDCl_3$ (7.27 ppm), DMSO-d_6 (2.50 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for ^1H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm), DMSO-d_6 (39.51 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for ^{13}C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. The MS data were obtained with ESI technique, and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. The X-ray single-crystal determination was performed on a Bruker Smart 1000 CCD X-ray single crystal diffractometer.

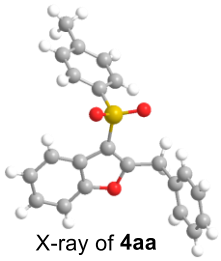
1. Optimization of the Reaction Conditions.

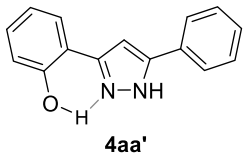
A mixture of **1a** (44.8 mg, 0.20 mmol) and **2a** (44.64 mg, 0.24 mmol) was dissolved in solvent (2.0 mL), to the solution was added **Cat.1** (0.04 mmol) at 0°C, after 0.5 h, the temperature recovered to 25 °C. Until **1a** was consumed, the **Cat.2** (0.04 mmol) and base (0.4 mmol) were successively for the indicated time. The solvent was removed and purified by flash column chromatography on silica gel to give the product **4aa**.

Table 1. Optimization of the Reaction Conditions[a]









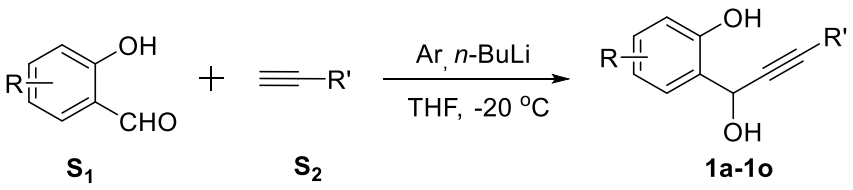
Entry	**Cat.1**	**Cat.2**	Base	Solvent	Time (h)	Yield (%)[b] **4aa/3aa/4aa′**
1	$TsOH·H_2O$	-	-	$CHCl_3$	3.5	0/80/0
2	(±) CSA	-	-	$CHCl_3$	2.5	0/85/0
3	$FeCl_3·6H_2O$	-	-	$CHCl_3$	2	-[c]
4	$AlCl_3$	-	-	$CHCl_3$	2	-[c]
5	AgOTf	-	-	$CHCl_3$	2	-[c]
6	$Sc(OTf)_3$	-	-	$CHCl_3$	2	-[c]
7	$BF_3·Et_2O$	-	-	$CHCl_3$	2	0/99/0
8	$BF_3·Et_2O$	-	K_2CO_3	$CHCl_3$	8	50/0/0
9	$BF_3·Et_2O$	-	Na_2CO_3	$CHCl_3$	14	42/0/0

10	$BF_3{\cdot}Et_2O$	-	K_3PO_4	$CHCl_3$	5	35/0/0
11	$BF_3{\cdot}Et_2O$	-	DBU	$CHCl_3$	6	45/0/0
12	$BF_3{\cdot}Et_2O$	-	DMAP	$CHCl_3$	6	20/0/0
13	$BF_3{\cdot}Et_2O$	-	Et_3N	$CHCl_3$	24	0/99/0
14	$BF_3{\cdot}Et_2O$	-	K_2CO_3	CH_3CN	8	60/0/0
15	$BF_3{\cdot}Et_2O$	Cu_2O	K_2CO_3	CH_3CN	3	60/0/15
16	$BF_3{\cdot}Et_2O$	CuI	K_2CO_3	CH_3CN	4	33/0/26
17	$BF_3{\cdot}Et_2O$	CuCl	K_2CO_3	CH_3CN	7	55/0/25
18	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	CH_3CN	4.5	78/0/5
19	$BF_3{\cdot}Et_2O$	$AgNO_3$	K_2CO_3	CH_3CN	8	62/0/19
20	$BF_3{\cdot}Et_2O$	AgOAc	K_2CO_3	CH_3CN	8	58/0/16
21	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	toluene	5	36/0/0
22	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	DCE	3	54/0/0
23	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	THF	3	35/0/0
24	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	DCM	3	23/0/0
25	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	DMF	21	0/0/0
26	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	1,4-dioxane	3	50/0/0
27	$BF_3{\cdot}Et_2O$	Ag_2O	K_2CO_3	chlorobenzene	3	46/0/0

[a]Unless otherwise noted, the reactions were performed with **1a** (0.20 mmol), **2a** (0.24 mmol), **cat.1** (20 mol%), in solvent (2.0 mL) at 25 °C until **1a** was consumed; and then base (0.40 mmol) and **cat. 2** (20 mol%) were added to the resulting mixture and stirred at 25 °C for the indicated time. [b]Yield of isolated product. [c]Only unidentified byproducts were obtained. (±) CSA = camphorsulfonic acid.

2. General Procedure for the Synthesis of *o*-hydroxyl-benzyl alcohol （*o*-HBAs）

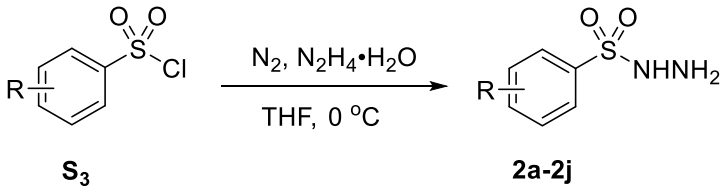
Compounds *o*-hydroxyl-benzyl alcohol (*o*-HBAs) **1a-1o** were prepared according to the reported literature.[1] General synthesis of *o*-HBAs are shown below.



S_1 S_2 **1a-1o**

To the solution of S_2 (2.2 mmol) in dry THF (10 mL) was slowly added *n*-BuLi (2.1 mmol, 2.5 M in THF) at –20 °C under argon. The reaction mixture was stirred at this temperature for 1 h, then a solution of the corresponding salicylaldehyde S_1 (1 mmol in 4 mL of THF) was added dropwise via cannula slowly. The reaction mixture was stirred at –20 °C for another 0.5 h until the disappearance of the starting material. Then the reaction mixture was quenched by the addition of saturated NH_4Cl. The aqueous phase was extracted with EtOAc. Combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. Crude products **1a-1o** were purified by column chromatography [gradient eluent: petroleum ether/EtOAc].

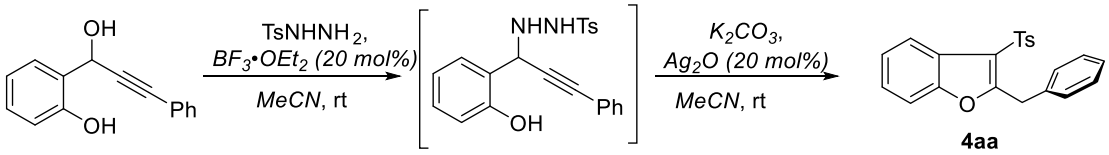
3. General Procedure for the Synthesis of Arylsulfonyl Hydrazides



S_3 **2a-2j**

Arylsulfonyl hydrazides **2a-2i** were prepared according to the literature procedure.[2] Hydrazine monohydrate (250 mg, 5.0 mmol) was added dropwise to a solution of an arylsulfonyl chloride (2.0 mmol) in tetrahydrofuran (10 mL) under nitrogen at 0 °C. During the addition the mixture became brown and a white precipitate of hydrazine hydrochloride was deposited. The mixture was stirred at 0 °C for 30 min, added ethyl acetate (60 mL), and washed with saturated brine (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, and added slowly to stirred hexane (12 mL) over 5 min. After being stirred for 10 min, the mixture was filtered, and the collected solid was dried in vacuum. The yields for the formation of arylsulfonyl hydrazides range from 68% to 91%.

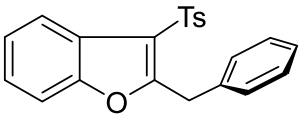
4. General Procedure for the Synthesis of 3-Sulfonylbenzofurans



4aa

For 0.2 mmol Scale:

A mixture of **1** (0.20 mmol) and **2** (0.24 mmol) was dissolved in MeCN (2.0 mL), to the solution was added catalyst BF_3•OEt_2 (4 μL, 0.04 mmol) at 0°C, after another 0.5 h, the temperature recovered to 25 °C. Until **1a** was consumed in 2 hours, then catalyst Ag_2O (9.2 mg, 0.04 mmol) and base K_2CO_3 (56.2 mg, 0.4 mmol) were added for another 2 hours. Then the solvent was removed and purified by flash column chromatography on silica gel to give the product **4aa.**

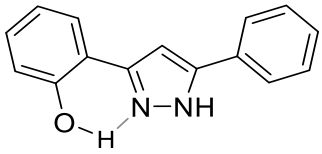


4aa

General procedure was followed, **4aa** (56.5 mg, 0.156 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4aa: (78% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], white crystal, mp. =188.2 ^{o}C).

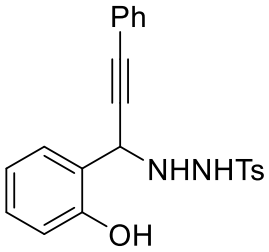
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 – 7.86 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.28 (m, 6H), 7.27 – 7.25 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 2H), 2.37 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.4, 153.4, 144.2, 139.3, 135.8, 129.8, 129.0, 128.7, 127.0, 126.8, 125.4, 124.3, 124.1, 120.5, 118.3, 111.4, 33.1, 21.5 ppm; **IR:** $\bar{\upsilon}$ = 3093,1568, 1315, 1153, 758cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{19}O_3SNa$: 385.0874; found: 385.0828 [*M* + Na]$^{+}$.



4aa'

Compound 4aa': (5% yield, *Rf* = 0.50 [8:1 petroleum ether/EtOAc], white solid, mp. = 109.6 ºC).

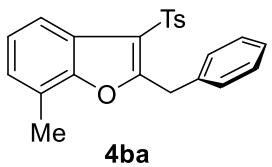
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.72 – 7.57 (m, 4H), 7.45 (m, 4H), 7.25 – 7.21 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.94 ppm (dt, *J* = 19.2, 6.8 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.9, 152.9, 143.2, 135.2, 129.6, 129.5, 127.3, 127.0, 126.6, 119.5, 117.2, 116.3, 99.8 ppm; **IR:** $\bar{\upsilon}$ = 3354, 1457, 1259, 971, 749 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{12}N_2OH$: 237.1026; found: 237.1028 $[M + H]^+$.



3aa

Compound 3aa: (99% yield, Rf=0.40 [10:1 petroleum ether / EtOAc], white crystal, mp. = 135.8 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.57 – 7.49 (m, 3H), 7.43 – 7.34 (m, 4H), 7.33 – 7.26 (m, 3H), 7.24 (s, 1H), 6.94 – 6.85 (m, 2H), 6.49 (s, 1H), 5.27 (s, 1H), 2.41 ppm(s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.9, 144.6, 135.1, 132.0, 130.6, 129.9, 129.2, 128.5, 128.2, 127.9, 121.6, 120.1, 120.0, 117.3, 89.4, 83.5, 56.1, 21.6 ppm; **IR**：$\bar{\upsilon}$ = 3268, 1487, 1320, 1155, 752 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{19}N_2O_3SNa$: 385.0874; found: 385.0828 $[M + Na]^+$.

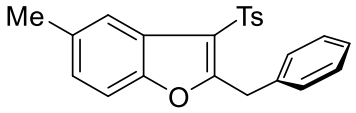


4ba

General procedure was followed, **4ba** (45.8 mg, 0.122 mmol) was from *o*-HBA **1b** (47.6 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ba: (61% yield, *Rf* = 0.54 [10:1 petroleum ether/EtOAc], off white solid, mp. = 119.3 ^{o}C).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.77 – 7.72 (m, 2H), 7.68 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.19 (dd, *J* = m, 3H), 7.09 (m, 1H), 4.59 (d, *J* = 2.8 Hz, 2H), 2.44 (s, 3H), 2.35 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.0, 152.5, 144.1, 139.4, 136.0, 129.7, 129.1, 128.7, 127.0, 126.9, 126.4, 124.4, 123.7, 121.8, 118.4, 118.0, 33.2, 21.5, 14.8 ppm; **IR**: $\bar{\upsilon}$ = 2923, 1566, 1333, 1148, 786 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_3SNa$: 399.1031; found: 399.0985 [*M* + Na]$^{+}$.

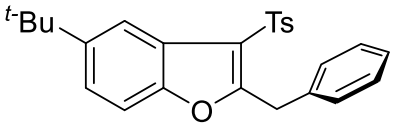


4ca

General procedure was followed, **4ca** (43.6 mg, 0.116 mmol) was from *o*-HBA **1c** (47.6 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ca: (56% yield, *Rf* = 0.50 [10:1 petroleum ether/EtOAc], off white solid, mp. = 121.1 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.67 (s, 1H), 7.33 – 7.25 (m, 6H), 7.22 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.55 (s, 2H), 2.44 (s, 3H), 2.36 ppm (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.5, 151.9, 144.2, 139.4, 135.9, 134.2, 129.8, 129.1, 128.7, 127.0, 126.8, 126.7, 124.2, 120.2, 117.9, 111.0, 33.2, 21.5, 21.5 ppm. **IR:** $\bar{\upsilon}$ = 3028, 2958, 1471, 1323, 831, 620 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_3SNa$: 399.1031; found: 399.0988 [*M* + Na]$^{+}$.

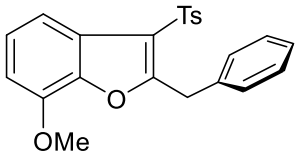


4da

General procedure was followed, **4da** (54.3 mg, 0.131 mmol) was from *o*-HBA **1d** (46.0 mg, 0.20 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4da: (65% yield, *Rf* = 0.51 [10:1 petroleum ether/EtOAc], off white solid, mp. = 119.7 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.25 (m, 7H), 7.22 (m, 2H), 4.57 (s, 2H), 2.36 (s, 3H), 1.35 ppm (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.5, 151.8, 147.7, 144.2, 139.4, 136.0, 129.8, 129.1, 128.7, 127.0, 127.0, 123.8, 123.4, 118.3, 116.7, 110.8, 34.9, 33.3, 31.8, 21.6. ppm; **IR:** $\bar{\upsilon}$ = 3056, 2958, 1471, 1323, 831,620 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{26}H_{26}O_3SNa$: 441.1500; found: 441.1465 [*M* + Na]$^{+}$.



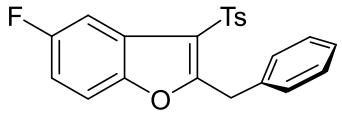
4ea

General procedure was followed, **4ea** (32.9 mg, 0.084 mmol) was from *o*-HBA **1e** (50.8 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ea: (42% yield, *Rf* = 0.46 [10:1 petroleum ether/EtOAc], off yellow solid, mp. = 133.8 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.44 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.16 (m, 4H), 6.81 (d, *J* = 8.0 Hz, 1H), 4.59 (s, 2H), 3.94 (s, 3H), 2.35 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.4, 145.2, 144.2, 142.9, 139.3, 135.9, 129.7, 129.1, 128.7, 127.0, 126.9, 126.0, 125.2, 118.6, 112.6,

107.7, 56.1, 33.2, 21.5 ppm; **IR**: $\bar{\upsilon}$ = 2924, 1492, 1278, 1147, 678 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_4SNa$: 415.0980; found: 415.0935 $[M + Na]^+$.

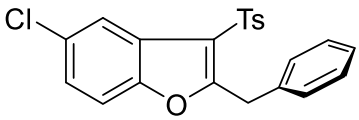


4fa

General procedure was followed, **4fa** (47.4 mg, 0.120 mmol) was from *o*-HBA **1f** (48.4 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4fa: (60% yield, *Rf* = 0.46 [10:1 petroleum ether/EtOAc], off white solid, mp. = 126.9 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.1 Hz, 2H), 7.55 (m, 1H), 7.37 – 7.27 (m, 6H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.01 (m, 1H), 4.56 (s, 2H), 2.38 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.0, 160.8, 158.9, 149.6, 144.5, 139.1, 135.5, 129.9, 129.1, 128.8, 127.2, 126.8, 113.5, 113.3, 112.4, 112.3, 106.7, 106.5, 33.3, 21.6 ppm; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −117.6 ppm; **IR:** $\bar{\upsilon}$ = 3105, 1569, 1327, 1166, 707 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}FO_3SNa$: 403.0780; found: 403.0756 $[M + Na]^+$.



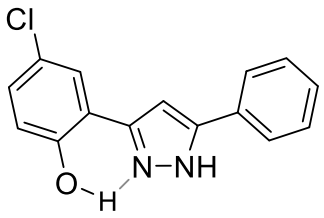
4ga

General procedure was followed, **4ga** (44.3 mg, 0.112 mmol) was from *o*-HBA **1g** (51.7 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ga: (56% yield, *Rf* = 0.48 [10:1 petroleum ether/EtOAc], off white solid, mp. = 127.8 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 2.1 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H),

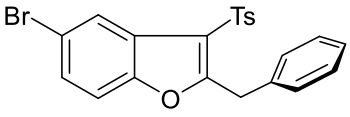
7.34 – 7.28 (m, 5H), 7.27 (m, 2H), 7.24 (m, 2H), 4.55 (s, 2H), 2.38 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.7, 151.8, 144.6, 139.1, 135.4, 130.3, 130.0, 129.1, 128.8, 127.2, 126.8, 125.9, 125.6, 120.3, 112.5, 118.2, 33.3, 21.6 ppm; **IR**: $\bar{\upsilon}$ = 3098, 1560, 1334, 1150, 716cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}ClO_3SNa$: 419.0485; found: 419.0449 $[M + Na]^+$.



4ga'

Compound 4ga': (32% yield, *Rf* = 0.49 [8:1 petroleum ether/EtOAc], off yellow white, mp. = 150.8 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 (m, 3H), 7.54 – 7.42 (m, 3H), 7.26 (s, 2H), 7.18 (m, 1H), 6.98 (dd, *J* = 8.9, 4.2 Hz, 1H), 6.89 ppm(d, *J* = 4.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.6, 152.0, 144.2, 129.4, 129.4, 129.2, 128.3, 126.1, 125.7, 124.1, 118.5, 117.7, 99.7 ppm; **IR:** $\bar{\upsilon}$ = 3378, 1454, 1257, 979, 752 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{11}ClN_2OH$: 271.0644; found: 271.0565 $[M + H]^+$.



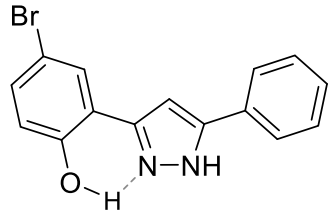
4ha

General procedure was followed, **4ha** (52.8 mg, 0.160 mmol) was from *o*-HBA **1h** (60.8 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ha: (60% yield, *Rf* = 0.49 [10:1 petroleum ether/EtOAc], off white solid, mp. = 114.9 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.40 (m, 1H), 7.31 – 7.27 (m, 6H), 7.24 (s, 2H), 4.55 (s, 2H), 2.38 ppm (s, 3H); **^{13}C**

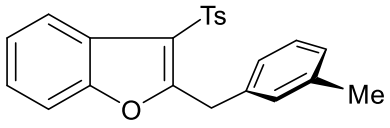
NMR (126 MHz, $CDCl_3$) δ = 162.6, 152.2, 144.6, 139.0, 135.3, 130.0, 129.1, 128.8, 128.6, 127.2, 126.8, 126.1, 123.3, 118.1, 117.7, 113.0, 33.2, 21.6 ppm; **IR**: $\bar{\upsilon}$ = 3088, 1568, 1328, 1151, 816cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}BrO_3SNa$: 462.9979; found: 462.9946 $[M + Na]^+$.



4ha'

Compound 4ha': (38% yield, *Rf* = 0.49 [8:1 petroleum ether/EtOAc], off yellow white, mp. = 138.8 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (m, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.54 – 7.41 (m, 4H), 7.31 (dt, *J* = 8.7, 2.1 Hz, 1H), 7.26 (s, 1H), 6.97 – 6.85 ppm (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.1, 150.8, 143.2, 131.1, 128.4, 128.3, 128.0, 127.3, 124.7, 118.0, 117.2, 110.2, 98.7 ppm; **IR:** $\bar{\upsilon}$ = 3378, 1560, 1450, 1256, 977, 758 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{11}BrN_2OH$: 315.0138; found: 315.0069 $[M + H]^+$.



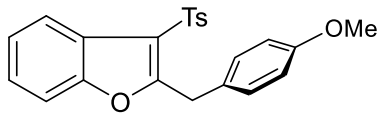
4ia

General procedure was followed, **4ia** (43.6 mg, 0.116 mmol) was from *o*-HBA **1i** (47.6 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ia: (64% yield, *Rf* = 0.45 [10:1 petroleum ether/EtOAc], off white solid, mp. = 91.3 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 – 7.87 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.07 – 7.03 (m, 2H), 4.53 (s, 2H), 2.36 (s, 3H), 2.28 ppm (s,

3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.6, 153.5, 144.2, 139.5, 138.4, 135.7, 129.8, 129.7, 128.6, 127.8, 126.9, 126.2, 125.4, 124.4, 124.3, 120.6, 118.4, 111.5, 33.1, 21.5, 21.3 ppm; **IR:** $\bar{\upsilon}$ = 2922, 1567, 1247,1150, 813 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_3SNa$: 399.1031; found: 399.0985 $[M + Na]^+$.

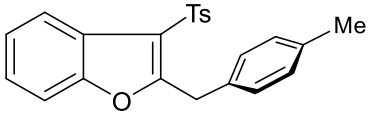


4ja

General procedure was followed, **4ja** (49.4 mg, 0.116 mmol) was from *o*-HBA **1j** (47.6 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition

Compound 4ja: (63% yield, *Rf* = 0.45 [10:1 petroleum ether/EtOAc], off white solid, mp. = 122.4 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.84 (m, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.31 – 7.27 (m, 3H), 7.25 – 7.21 (m, 3H), 6.86 – 6.80 (m, 2H), 4.50 (s, 2H), 3.78 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ =161.9, 158.8, 153.5, 144.2, 139.6, 130.2, 129.8, 127.9, 126.9, 125.4, 124.4, 124.3, 120.6, 118.1, 114.2, 111.5, 55.3, 32.4, 21.5 ppm; **IR**: $\bar{\upsilon}$ = 2925, 1564, 1315, 1151, 807 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_4SNa$: 415.0980; found: 415.0941 $[M + Na]^+$.

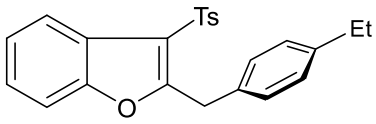


4ka

General procedure was followed, **4ka** (43.6 mg, 0.116 mmol) was from *o*-HBA **1k** (47.6 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ka: (58% yield, *Rf* = 0.56 [10:1 petroleum ether/EtOAc], off white solid, mp. = 172.3 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (m, 1H), 7.83 – 7.79 (m, 2H), 7.40 (m, 1H), 7.33 – 7.26 (m, 2H), 7.22 (m, 4H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.53 (s, 2H), 2.37 (s, 3H), 2.32 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 160.7, 152.5, 143.2, 138.4, 135.7, 131.7, 128.8, 128.4, 128.0, 125.8, 124.4, 123.3, 123.2, 119.5, 117.1, 110.4, 31.8, 20.5, 20.0 ppm; **IR**: $\bar{\upsilon}$ = 3022, 1567, 1151, 1052, 814, cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_3SNa$: 399.1031; found: 399.0986 $[M + Na]^+$.

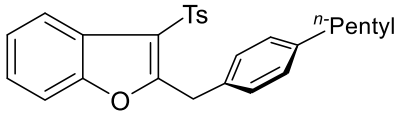


4la

General procedure was followed, **4la** (54.6 mg, 0.116 mmol) was from *o*-HBA **1l** (50.4 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4la: (70% yield, *Rf* = 0.51 [10:1 petroleum ether/EtOAc], off white solid, mp. = 121.9 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.85 (m, 1H), 7.79 (dd, *J* = m, 2H), 7.40 (dt, *J* = 7.6,2.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 (dd, *J* = 10.8, 8.0 Hz, 4H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.54 (s, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.22 ppm (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.8, 153.5, 144.2, 143.1, 139.5, 133.0, 129.8, 129.1, 128.2, 126.9, 125.4, 124.3, 124.3, 120.6, 118.2, 111.5, 32.8, 28.5, 21.5, 15.6 ppm. **IR:** $\bar{\upsilon}$ = 2923, 1567, 1452, 1195, 822 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{24}H_{22}O_3SNa$: 413.1187; found: 413.1149 $[M + Na]^+$.



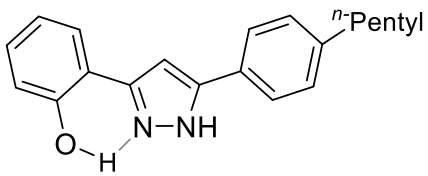
4ma

General procedure was followed, **4ma** (43.2 mg, 0.116 mmol) was from *o*-HBA **1m** (58.8 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure

condition.

Compound 4ma: (50% yield, *Rf* = 0.54 [10:1 petroleum ether/EtOAc], off white solid, mp. = 99.4 ^{o}C).

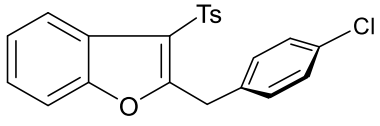
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (m, 1H), 7.78 (m, 2H), 7.40 (m, 1H), 7.29 (m, 2H), 7.22 (dd, *J* = 10.5, 8.0 Hz, 4H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.54 (s, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 1.59 (m, 2H), 1.32 (m, 4H), 0.89 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.8, 153.5, 144.2, 141.8, 139.4, 132.9, 129.8, 129.0, 128.7, 128.0, 126.9, 125.4, 124.3, 120.5, 118.1, 111.5, 35.5, 32.8, 31.5, 31.2, 22.5, 21.5, 14.0 ppm; **IR:** $\bar{\upsilon}$ = 2928, 1565, 1303, 1152, 846 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{27}H_{28}O_3SNa$: 455.1657; found: 455.1654 [*M* + Na]$^{+}$.



4ma'

Compound 4ma': (29% yield, *Rf* = 0.50 [8:1 petroleum ether/EtOAc], off white solid, mp. = 118.8 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 (m, 1H), 7.50 (t, *J* = 6.9 Hz, 2H), 7.24 (dd, *J* = 7.1, 3.9 Hz, 3H), 7.06 (t, *J* = 6.8 Hz, 1H), 6.94 (q, *J* = 6.9 Hz, 1H), 6.86 (m, 1H), 2.63 (q, *J* = 7.2 Hz, 2H), 1.63 (p, *J* = 7.3 Hz, 2H), 1.34 (dq, *J* = 7.1, 3.6, 3.2 Hz, 4H), 0.90 ppm(t, *J* = 6.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.9, 152.9, 144.3, 144.1, 129.4, 129.3, 126.6, 126.1, 125.6, 119.5, 117.1, 116.7, 99.1, 35.7, 31.5, 31.0, 22.6, 14.0 ppm; **IR:** $\bar{\upsilon}$ = 3376, 2927, 1589, 1309, 828 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{20}H_{22}N_2OH$: 307.1816; found: 307.1747 [*M* + H]$^{+}$.



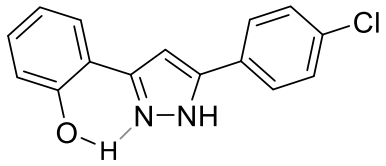
4na

General procedure was followed, **4na** (43.6 mg, 0.116 mmol) was from *o*-HBA **1n**

(51.7 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4na: (55% yield, *Rf* = 0.49 [10:1 petroleum ether/EtOAc], off yellow solid, mp. = 127.5 ºC).

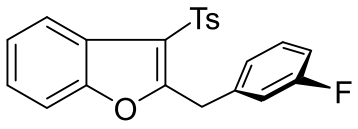
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 – 7.86 (m, 1H), 7.81 – 7.76 (m, 2H), 7.43 – 7.39 (m, 1H), 7.32 (m, 2H), 7.26 – 7.22 (m, 6H), 4.54 (s, 2H), 2.37 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 160.7, 153.5, 144.4, 139.2, 134.2, 133.0, 130.4, 129.9, 128.8, 126.8, 125.6, 124.5, 124.1, 120.6, 118.5, 111.5, 32.5, 21.6 ppm; **IR:** $\bar{\upsilon}$ =2921, 1566, 1300, 1153,803 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}ClO_3SNa$: 419.0485; found: 419.0431 $[M + Na]^+$.



4na'

Compound 4na': (29% yield, *Rf* = 0.47 [8:1 petroleum ether/EtOAc], off yellow solid, mp. = 187.8 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.97 – 6.87 ppm(m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 156.0, 153.1, 144.1, 129.5, 129.3, 129.2, 128.8, 126.6, 125.7, 119.4, 117.1, 116.5, 99.6. ppm; **IR:** $\bar{\upsilon}$ = 3345, 2923, 1456, 1260,971, 750 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{11}N_3O_3H$: 271.0644; found: 271.0565 $[M + H]^+$.



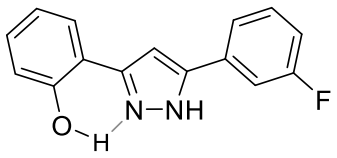
4oa

General procedure was followed, **4oa** (38.0 mg, 0.10 mmol) was from *o*-HBA **1o**

(48.4 mg, 0.2 mmol) and **2a** (44.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition

Compound 4oa: (50% yield, *Rf* = 0.48 [10:1 petroleum ether/EtOAc], off white solid, mp. = 176.2 ºC).

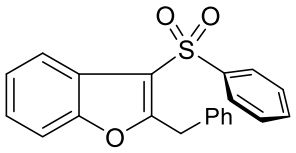
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 – 7.86 (m, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.32 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.01 – 6.92 (m, 2H), 4.57 (s, 2H), 2.37 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.9, 161.9, 160.4, 153.5, 144.4, 139.3, 138.1, 138.0, 130.2, 130.1, 129.9, 126.8, 125.7, 124.8, 124.8, 124.5, 124.1, 120.7, 118.8, 116.1, 116.0, 114.1, 114.0, 111.5, 32.9, 21.6 ppm; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = −112.7 ppm; **IR:** $\bar{\upsilon}$ = 3060, 1569, 1449, 1152, 759 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}FO_3SNa$: 403.0780; found: 403.0729 $[M + Na]^+$.



4oa'

Compound 4oa': (36% yield, *Rf* = 0.47 [8:1 petroleum ether/EtOAc], off yellow solid, mp. = 126.7 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.47 (td, *J* = 7.9, 5.7 Hz, 1H), 7.41 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.34 (dt, *J* = 9.4, 2.0 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 3H), 7.13 (m, 1H), 7.05 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.99 – 6.91 ppm(m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.9, 153.0, 144.1, 129.5, 129.3, 129.2, 128.7, 126.6, 125.7, 119.4, 117.1, 116.4, 99.6 ppm; **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -111.5 ppm; **IR:** $\bar{\upsilon}$ = 3393, 1589, 1462, 1153, 748 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{15}H_{11}FN_2OH$: 255.0939; found: 255.0856 $[M + H]^+$.

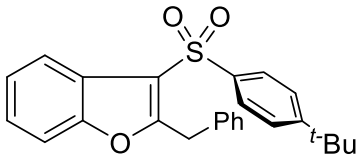


4ab

A mixture of **1a** (44.8 mg, 0.20 mmol) and **2b** (41.2 mg, 0.24 mmol) was dissolved in MeCN (2.0 mL), to the solution was added catalyst BF_3•OEt_2 (4 μL, 0.04 mmol) at 0 °C, after another 0.5 h , the temperature recover to 25 °C. Until **1a** disappeared, then catalyst Ag_2O (9.2 mg, 0.04 mmol) and base K_2CO_3 (56.2 mg, 0.4 mmol) was added at 15°C for another 2 hours. Then the solvent was removed and purified by flash column chromatography on silica gel to give the product **4ab** (42.3 mg, 0.122 mmol).

Compound 4ab: (61% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], white solid, mp. =163.2 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (m, 3H), 7.56 – 7.53 (m, 1H), 7.46 – 7.40 (m, 3H), 7.34 – 7.25 (m, 7H), 4.59 ppm (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.8, 153.5, 142.2, 135.7, 133.3, 129.2, 129.1, 128.7, 127.1, 126.8, 125.5, 124.5, 124.2, 120.6, 118.0, 111.5, 33.2 ppm; **IR**: $\bar{\upsilon}$ = 3258, 2925, 1448, 1155, 758 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{16}O_3SNa$: 371.0721; found: 371.0667 $[M + Na]^+$.



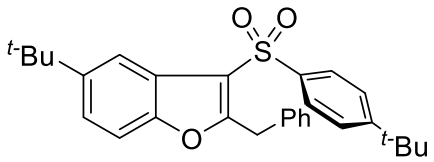
4ac

General procedure was followed, **4ac** (50.9 mg, 0.126 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2c** (43.0 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ac: (63% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], off yellow solid, mp. = 176.2 ^oC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95 – 7.90 (m, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.33 – 7.27 (m, 7H), 4.58 (s, 2H), 1.28 ppm (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.5, 157.2, 153.5, 139.2, 135.8, 129.1, 128.7, 127.0, 126.6, 126.2,

125.5, 124.4, 124.3, 120.7, 118.4, 111.5, 35.2, 33.2, 31.0 ppm; **IR:** $\bar{\upsilon}$ = 2963, 1567, 1323, 1149, 767 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{25}H_{24}O_3SNa$: 427.1344; found: 427.1302 $[M + Na]^+$.

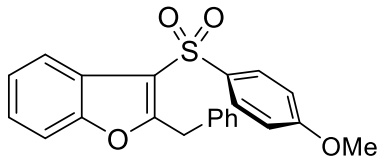


4dc

General procedure was followed, **4dc** (60.7 mg, 0.116 mmol) was from *o*-HBA **1d** (53.8 mg, 0.2 mmol) and **2c** (43.0 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4dc: (66% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], off white solid, mp. = 128.9 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (m, 3H), 7.43 (dd, *J* = 8.6, 3.6 Hz, 2H), 7.38 – 7.27 (m, 4H), 7.26 – 7.20 (m, 3H), 4.57 (d, *J* = 3.6 Hz, 2H), 1.35 (s, 9H), 1.28 ppm (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 161.6, 157.2, 151.8, 147.7, 139.4, 136.0, 129.0, 128.7, 127.0, 126.8, 126.1, 124.0, 123.3, 118.4, 116.8, 110.7, 35.2, 34.9, 33.3, 31.7, 31.0 ppm; **IR:** $\bar{\upsilon}$ = 2961, 1455, 1159, 898, 758 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{29}H_{32}O_3SNa$: 483.1970; found: 483.1945 $[M + Na]^+$.



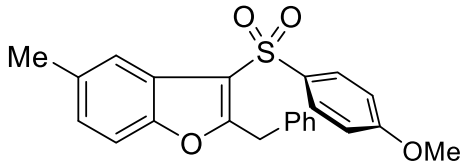
4ad

General procedure was followed, **4ad** (50.6 mg, 0.134 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2d** (48.4 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ad: (67% yield, *Rf* = 0.45 [10:1 petroleum ether/EtOAc], off yellow

solid, mp. = 150.8 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.86 (m, 1H), 7.83 (d, J = 9.0 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.35 – 7.28 (m, 6H), 7.27 – 7.25 (m, 1H), 6.88 (d, J = 8.9 Hz, 2H), 4.59 (s, 2H), 3.81 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.3, 160.0, 152.4, 134.8, 132.8, 128.0, 128.0, 127.7, 126.0, 124.4, 123.3, 123.1, 119.5, 117.6, 113.3, 110.4, 54.5, 32.1 ppm; **IR**: $\bar{\upsilon}$ = 3264, 1568, 1313, 1169, 759 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{18}O_4SNa$: 401.0823; found: 401.0778 [M + Na]$^+$.

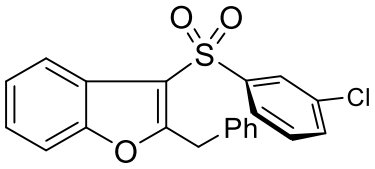


4cd

General procedure was followed, **4cd** (52.5 mg, 0.116 mmol) was from *o*-HBA **1c** (51.7 mg, 0.2 mmol) and **2d** (48.5 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition

Compound 4cd: (67% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], off white solid, mp. = 93.8 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (td, J = 6.7, 3.2 Hz, 2H), 7.67 (d, J = 5.2 Hz, 1H), 7.29 (m, 6H), 7.14 – 7.08 (m, 1H), 6.88 (m, 2H), 4.54 (s, 2H), 3.84 (s, 3 H), 2.45 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.4, 161.2, 152.0, 136.0, 134.2, 134.1, 129.0, 129.0, 128.7, 127.0, 126.7, 124.3, 120.3, 118.4, 114.3, 111.0, 55.6, 33.2, 21.5 ppm; **IR:** $\bar{\upsilon}$ = 3025, 2842, 1592, 1114,803 cm^{-1} **HRMS** (ESI): *m/z* calcd for $C_{23}H_{20}O_4SNa$: 415.0980; found: 415.0941 [M + Na]$^+$.



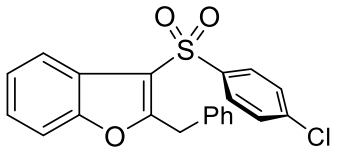
4ae

General procedure was followed, **4ae** (41.2 mg, 0.108 mmol) was from *o*-HBA **1a**

(44.8 mg, 0.2 mmol) and **2e** (52.9 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ae: (54% yield, *Rf* = 0.53 [10:1 petroleum ether/EtOAc], off white solid, mp. = 103.6 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.84 (m, 1H), 7.81 (m, 1H), 7.76 (m, 1H), 7.50 – 7.43 (m, 2H), 7.38 – 7.30 (m, 7H), 7.30 – 7.26 (m, 1H), 4.59 ppm (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.3, 153.5, 143.8, 135.5, 135.4, 133.4, 130.4, 129.0, 128.8, 127.3, 126.9, 125.7, 124.9, 124.7, 124.0, 120.4, 117.3, 111.6, 33.2 ppm; **IR:** $\bar{\upsilon}$ = 3093, 1560, 1345, 1155, 750 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{15}ClO_3SNa$: 405.0328; found: 405.0282 [*M* + Na]$^+$.

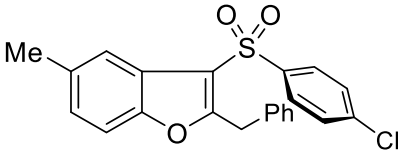


4af

General procedure was followed, **4af** (58.9 mg, 0.154 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2f** (53.1 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4af: (77% yield, *Rf* = 0.54 [10:1 petroleum ether/EtOAc], off white solid, mp. = 122.9 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.86 (m, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.35 – 7.31 (m, 6H), 7.27 (s, 1H), 7.25 (d, *J* = 4.6 Hz, 2H)， 4.57 ppm (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.0, 153.5, 140.6, 139.9, 135.6, 129.4, 129.0, 128.8, 128.2, 127.1, 125.7, 124.6, 124.0, 120.3, 117.6, 111.6, 33.2 ppm; **IR**: $\bar{\upsilon}$ = 2925, 1566, 1395, 1155, 759 cm^{-1} ; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{15}ClO_3SNa$: 405.0328; found: 405.0268 [*M* + Na]$^+$.

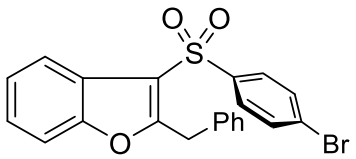


4cf

General procedure was followed, **4cf** (51.4 mg, 0.116 mmol) was from *o*-HBA **1c** (47.6 mg, 0.2 mmol) and **2f** (41.2 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4cf: (65% yield, *Rf* = 0.54 [10:1 petroleum ether/EtOAc], off white solid, mp. = 105.6 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.25 (m, 3H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.54 (s, 2H), 2.44 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.1, 152.0, 140.8, 139.8, 135.7, 134.5, 129.4, 129.0, 128.8, 128.2, 127.1, 127.0, 124.1, 120.1, 117.3, 111.1, 33.3, 21.5 ppm; **IR**: $\bar{\upsilon}$ = 3028, 1568, 1468, 1147, 806 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}ClO_3SK$: 435.0224; found: 435.0191 $[M + K]^+$.



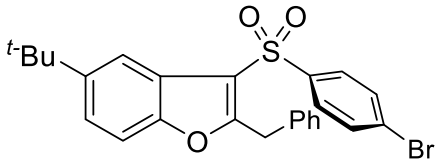
4ag

General procedure was followed, **4ag** (68.2 mg, 0.161 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2g** (64.08 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ag: (80% yield, *Rf* = 0.49 [10:1 petroleum ether/EtOAc], off white solid, mp. = 150.8 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 – 7.81 (m, 1H), 7.69 (m, 2H), 7.57 – 7.49 (m, 2H), 7.45 (m, 1H), 7.35 – 7.28 (m, 6H), 7.27 – 7.26 (m, 1H), 4.61 – 4.51 ppm (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.0, 153.5, 141.2, 135.6, 132.5, 129.0, 128.8,

128.5, 128.3, 127.2, 125.7, 124.6, 124.0, 120.4, 117.6, 111.6, 33.2 ppm; **IR:** $\bar{\upsilon}$ = 3083, 1569, 1318, 1152, 758 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{15}BrO_3SNa$: 448.9823; found: 448.9772 $[M + Na]^+$.

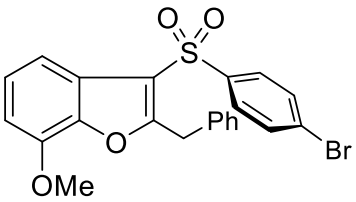


4dg

General procedure was followed, **4dg** (68.4 mg, 0.116 mmol) was from *o*-HBA **1d** (53.8 mg, 0.2 mmol) and **2g** (60.4mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4dg: (71% yield, *Rf* = 0.49 [10:1 petroleum ether/EtOAc], off white solid, mp. = 123.6 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.28 (d, *J* = 4.3 Hz, 5H), 4.55 (s, 2H), 1.36 ppm (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.1, 151.8, 148.0, 141.3, 135.8, 132.4, 129.5，129.0, 128.8, 128.4, 128.4, 127.1, 123.7, 117.5, 116.5, 110.9, 35.0, 33.3, 31.7 ppm; **IR:** $\bar{\upsilon}$ = 3085, 2960, 1572, 1328, 808 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{25}H_{23}BrO_3SK$: 521.0188; found: 521.0182 $[M + K]^+$.



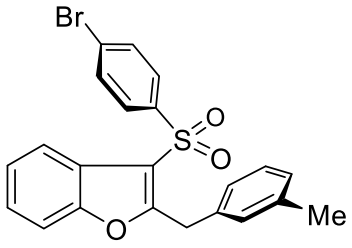
4eg

General procedure was followed, **4eg** (60.2 mg, 0.132 mmol) was from *o*-HBA **1e** (50.8 mg, 0.2 mmol) and **2g** (60.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4eg: (66% yield, *Rf* = 0.55 [10:1 petroleum ether/EtOAc], yellow solid,

mp. = 115.8 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.49 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.29 (d, *J* = 6.3 Hz, 4H), 7.23 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 1.3 Hz, 2H), 3.96 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.1, 145.3, 143.0, 141.1, 135.7, 132.4, 129.0, 128.8, 128.4, 128.3, 127.1, 125.7, 125.5, 117.8, 112.3, 107.8, 56.1, 33.2 ppm; **IR:** $\bar{\upsilon}$ = 3090, 2922, 1571, 1273, 779 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}B_rO_4SNa$: 478.9929; found: 478.9929 [*M* + Na]$^+$.

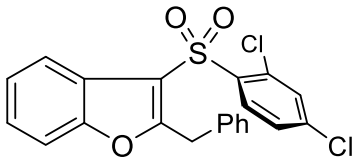


4ig

General procedure was followed, **4ig** (60.2 mg, 0.132 mmol) was from *o*-HBA **1i** (50.8 mg, 0.2 mmol) and **2g** (60.6 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ig: (70% yield, *Rf* = 0.50 [10:1 petroleum ether/EtOAc], white solid, mp. = 120.8 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 – 7.85 (m, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.36 – 7.30 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.00 (m, 3H), 4.52 (s, 2H), 2.28 ppm(s, 3H); **^{13}C NMR** (126 MHz, CDCl3) δ = 162.2, 153.5, 141.3, 138.5, 135.4, 132.4, 129.6, 128.7, 128.4, 128.3, 127.9, 126.1, 125.7, 124.6, 124.1, 120.4, 117.6, 111.7, 33.1, 21.3 ppm; **IR:** $\bar{\upsilon}$ = 2924, 1728, 1276, 1150, 762 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{17}BrO_3SNa$: 462.9979; found: 462.9937 [*M* + Na]$^+$.

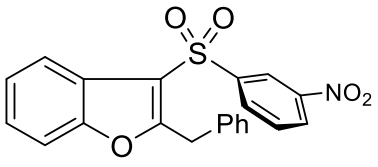


4ah

General procedure was followed, **4ah** (47.4 mg, 0.114 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2h** (61.44 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ah: (57% yield, *Rf* = 0.51 [10:1 petroleum ether/EtOAc], off white solid, mp. = 105.5 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.38 (m, 4H), 7.36 – 7.26 (m, 5H), 7.23 (m, 1H), 4.58 ppm (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.4, 153.4, 140.5, 137.4, 135.2, 134.2, 131.8, 131.7, 129.1, 128.7, 127.6, 127.1, 125.5, 124.4, 124.0, 120.2, 115.6, 111.6, 33.6 ppm; **IR:** $\bar{\upsilon}$ = 2924, 1565, 1453, 1157, 754 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{14}ClO_3SNa$: 438.9938; found: 438.9925 $[M + Na]^+$.



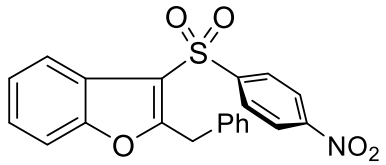
4ai

General procedure was followed, **4ai** (35.60 mg, 0.092 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2i** (61.44 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4ai: (45% yield, *Rf* = 0.52 [10:1 petroleum ether/EtOAc], off white solid, mp. = 117.3 ^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.69 (s, 1H), 8.33 (d, *J* = 8.3, 2.2 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.58 (m, 1H), 7.50 – 7.46 (m, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.26 (m, 4H), 7.24 (m, 1H), 4.61 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ

= 163.0, 153.5, 148.2, 144.1, 135.2, 132.2, 130.5, 128.9, 128.9, 127.7, 127.3, 126.0, 125.0, 123.8, 122.1, 120.2, 116.6, 111.8, 33.3 ppm; **IR:** $\bar{\upsilon}$ = 3069, 1567, 1356, 1160, 746 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{21}H_{15}NO_5SNa$: 416.0569; found: 416.0494 [*M* + Na]$^+$.



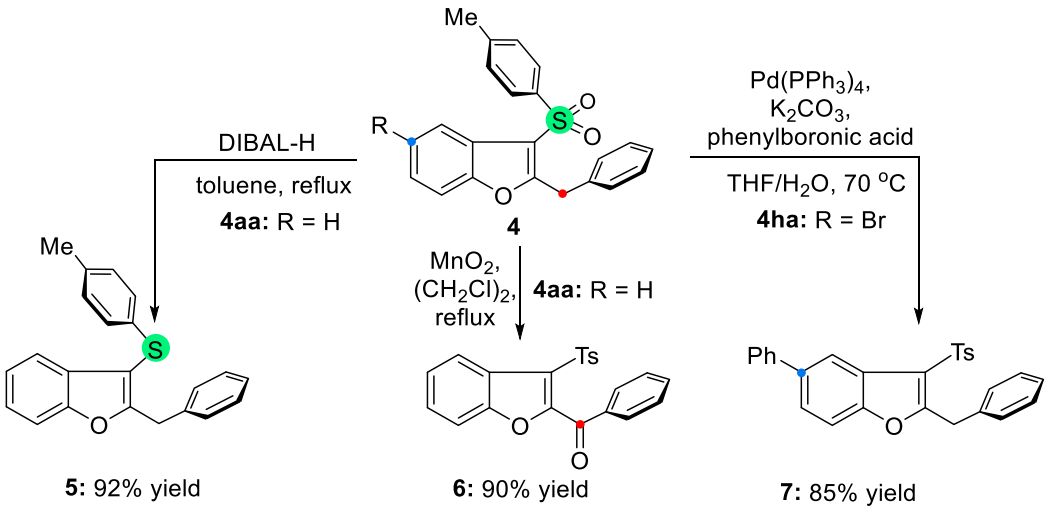
4aj

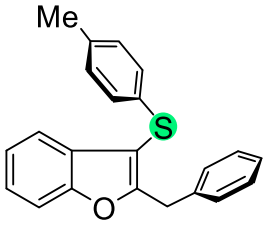
General procedure was followed, **4aj** (37.7 mg, 0.096 mmol) was from *o*-HBA **1a** (44.8 mg, 0.2 mmol) and **2j** (55.44 mg, 0.24 mmol), and purified using silica gel flash column chromatography [20:1 petroleum ether/EtOAc] under normal pressure condition.

Compound 4aj: (48% yield, *Rf* = 0.50 [10:1 petroleum ether/EtOAc], off white solid, mp. = 146.3 ºC)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.89 – 7.85 (m, 1H), 7.51 – 7.46 (m, 1H), 7.38 – 7.35 (m, 2H), 7.29 (s, 5H), 4.59 ppm (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 163.1, 153.5, 150.3, 147.5, 135.3, 129.0, 128.9, 128.0, 127.4, 126.0, 124.9, 124.4, 123.8, 120.2, 116.6, 111.8, 33.3 ppm; IR: $\bar{\upsilon}$ = 3267,1560, 1389, 1155, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{15}NO_5SNa$: 416.0569; found: 461.0589 [*M* + Na]$^+$

5. General Procedure for the Synthesis of Functionalized derivatives 5, 6 and 7.





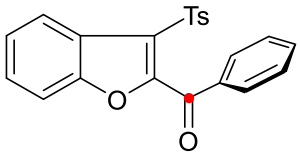
5

Under nitrogen atmosphere, compound **4aa** (36.2 mg, 0.1 mmol) was added to a 15 mL Schlenk tube, then added 2 mL toluene and 0.3 mL DIBAL-H. The solution was refluxed under a nitrogen atmosphere until the **3aa** was disappeared .The reaction mixture was poured into aqueous ammonium chloride and extracted with EtOAc. The combined organic layers were washed with a saturated salt solution, dried with magnesium sulfate, and evaporated. The residue was purified by chromatography to brown oil **5** (30.3 mg, 0.09 mmol).

Compound 5: (92% yield, *Rf* = 0.58 [10:1 petroleum ether/EtOAc], brown oil).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.31 (m, 3H), 7.23 – 7.14 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.36 (d, *J* = 7.3 Hz, 1H), 4.11 (s, 2H), 2.31 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.8, 155.0, 137.5,

137.3, 134.0, 129.8, 128.9, 128.6, 128.6, 126.8, 123.4, 122.5, 120.4, 110.9, 103.4, 35.0, 21.1 ppm; **IR:** $\bar{\upsilon}$ = 2922, 1454, 1253, 803, 750,703 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{18}OSH$: 331.1162; found: 331.1155 $[M + H]^+$

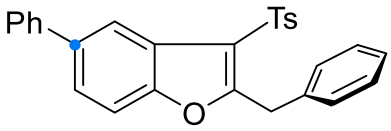


6

Compound **4aa** (36.2 mg, 0.1 mmol), MnO_2 (260mg, 0.3 mmol) was added to a 15 mL Schlenk tube, then added 2 mL DCE. The solution was refluxed until the **3aa** was disappeared. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography (ethyl acetate/petroleum ether) to give **6** (33.3 mg, 0.09 mmol).

Compound 6: (90% yield, *Rf* = 0.49 [10:1 petroleum ether/EtOAc], off brown solid, mp. = 114.8 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.21 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.97 – 7.91 (m, 2H), 7.70 – 7.64 (m, 1H), 7.58 – 7.44 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.41 ppm (s, 3H); **13C NMR** (126 MHz, $CDCl_3$) δ = 184.7, 153.7, 152.8, 144.8, 138.2, 135.6, 134.5, 130.3, 129.8, 128.8, 128.2, 127.8, 125.5, 125.4, 123.7, 122.3, 112.4, 21.7 ppm; **IR:** $\bar{\upsilon}$ = 2962, 1668, 1471, 1258, 798, 672 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{22}H_{16}O_4SNa$: 399.0667; found: 399.0619 $[M + Na]^+$..



7

Under nitrogen atmosphere, compound **4ha** (25.0 mg, 0.06 mmol), phenylboronic acid (14.6 mg, 2.0 equiv), K_2CO_3 (24 mg, 3.0 equiv), $Pd(PPh_3)_4$ (6.9 mg, 0.10 equiv), were successively added to a 15 mL Schlenk tube, followed by the addition of 2.0 mL of THF and 0.2 mL H_2O, the mixture was degassed and purged with N_2 and then heated to 70 °C for 6 h. After cooling to 25 °C, the solvent was removed and purified by chromatography to a white solid **7** (26.4 mg, 0.051 mmol).

Compound 7: (85% yield, *Rf* = 0.54 [10:1 petroleum ether/EtOAc], off white solid, mp. = 122.5 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.06 (d, J = 2.1 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.52 (d, J = 8.5 Hz, 1H), 7.46 (t, J = 7.4 Hz, 3H), 7.32 (m, 6H), 7.22 (d, J = 7.9 Hz, 2H), 4.59 (s, 2H), 2.36 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.0, 153.1, 144.3, 141.0, 139.4, 138.2, 135.8, 129.9, 129.1, 128.8, 128.7, 127.6, 127.3, 127.1, 126.9, 125.2, 124.8, 116.0, 119.0, 118.6, 33.3, 21.5 ppm; **IR:** $\bar{\upsilon}$ = 3056, 1492, 1323, 1150, 815 cm^{-1}; **HRMS** (ESI): *m/z* calcd for $C_{28}H_{22}O_3SNa$: 461.1187; found: 461.1158 $[M + Na]^+$.

6. Relative Configuration Assignment of 3aa, 4aa, and 4ha' by X-Ray Crystallographic Analysis

The single crystal of **3aa** which was used for the determination of its relative configurations via X-ray crystallography (see below), was recrystallized from ethyl acetate and petroleum ether. The intensity data were collected using graphite-monochromated Mo Kα radiation.

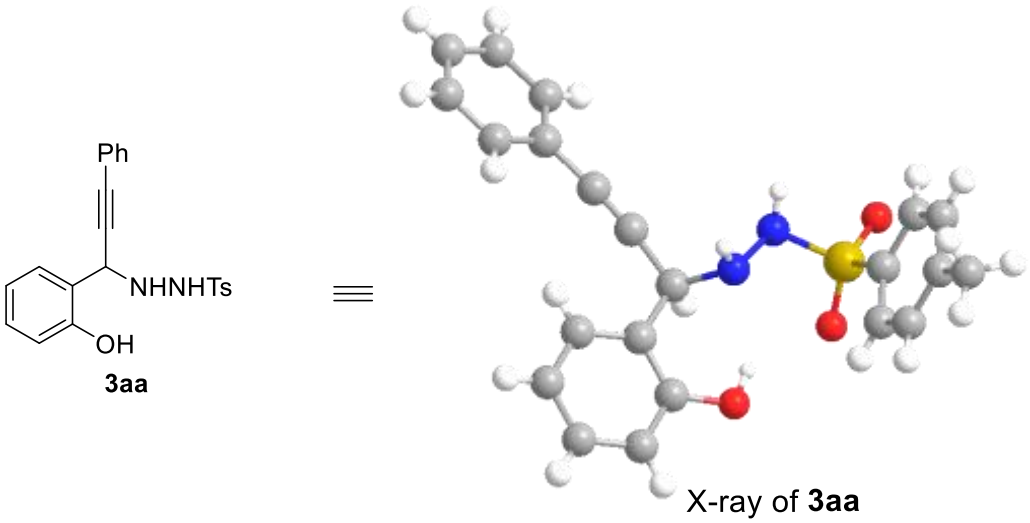
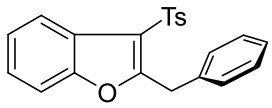


Table 2 Crystal data and structure refinement for 3aa.

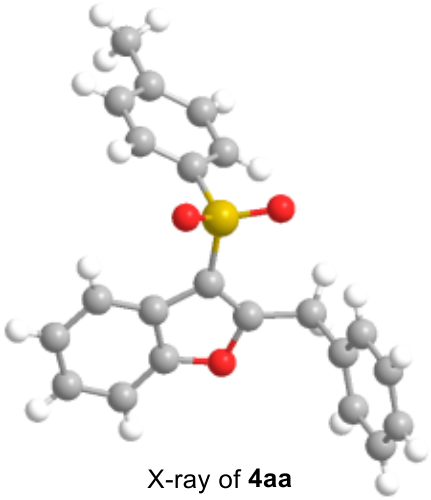
CCDC number	1942386
Identification code	**3aa**
Empirical formula	$C_{22}H_{20}N_2O_3S$
Formula weight	392.46
Temperature/K	293(2)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	20.9823(17)
b/Å	5.1771(3)
c/Å	18.9441(15)
α/°	90
β/°	105.594(3)
γ/°	90
Volume/Å^3	1982.1(3)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	1.659
F(000)	824.0
Crystal size/mm^3	0.37 × 0.08 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.75 to 132.092
Index ranges	$-24 \leq h \leq 22$, $-6 \leq k \leq 5$, $-22 \leq l \leq 22$
Reflections collected	6252
Independent reflections	3449 [R_{int} = 0.0466, R_{sigma} = 0.0761]
Data/restraints/parameters	3449/0/254
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.1095, wR_2 = 0.1292
Largest diff. peak/hole / e Å^{-3}	0.20/-0.24

The single crystal of **4aa** which was used for the determination of its relative configurations via X-ray crystallography (see below), was recrystallized from ethyl acetate and petroleum ether. The intensity data were collected using graphite-monochromated Mo Kα radiation.



4aa



X-ray of **4aa**

Table 3 Crystal data and structure refinement for 4aa.

CCDC number	1942385
Identification code	**4aa**
Empirical formula	$C_{22}H_{18}O_3S$
Formula weight	362.42
Temperature/K	298(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.6861(9)
b/Å	9.7446(7)
c/Å	18.3414(15)
α/°	90
β/°	105.015(3)
γ/°	90
Volume/Å^3	1844.7(3)
Z	4
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	0.194
F(000)	760.0
Crystal size/mm^3	0.4 × 0.3 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.75 to 50.04
Index ranges	$-12 \le h \le 11$, $-11 \le k \le 8$, $-19 \le l \le 21$
Reflections collected	8948
Independent reflections	3243 [R_{int} = 0.0329, R_{sigma} = 0.0383]
Data/restraints/parameters	3243/0/236
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.0993

Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1121
Largest diff. peak/hole / e Å^{-3}	0.18/-0.38

The single crystal of **4ha'** which was used for the determination of its relative configurations via X-ray crystallography (see below), was recrystallized from ethyl acetate and petroleum ether. The intensity data were collected using graphite-monochromated Mo Kα radiation.

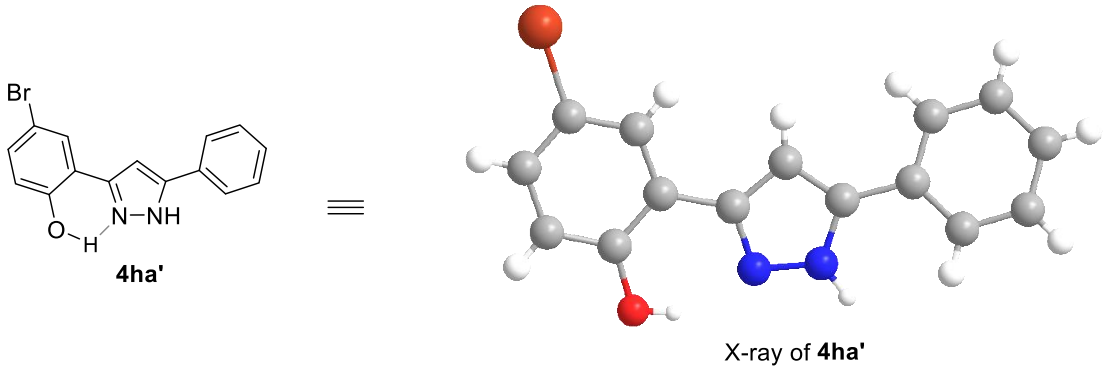


Table 4 Crystal data and structure refinement for 4ha'.

CCDC number	1942384
Identification code	**4ha'**
Empirical formula	$C_{15}H_{11}BrN_2O$
Formula weight	315.17
Temperature/K	298(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	3.9930(2)
b/Å	12.1484(11)
c/Å	26.691(2)
α/°	90.00
β/°	91.442(2)
γ/°	90.00
Volume/Å^3	1294.35(17)
Z	4
ρ_{calc}g/cm^3	1.617
μ/mm^{-1}	3.168
F(000)	632.0
Crystal size/mm^3	0.4 × 0.08 × 0.05

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.54 to 50.02
Index ranges	$-4 \leq h \leq 4$, $-11 \leq k \leq 14$, $-31 \leq l \leq 30$
Reflections collected	6312
Independent reflections	2282 [R_{int} = 0.0550, R_{sigma} = 0.0601]
Data/restraints/parameters	2282/0/172
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.0908
Final R indexes [all data]	R_1 = 0.0744, wR_2 = 0.0956
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.22

---

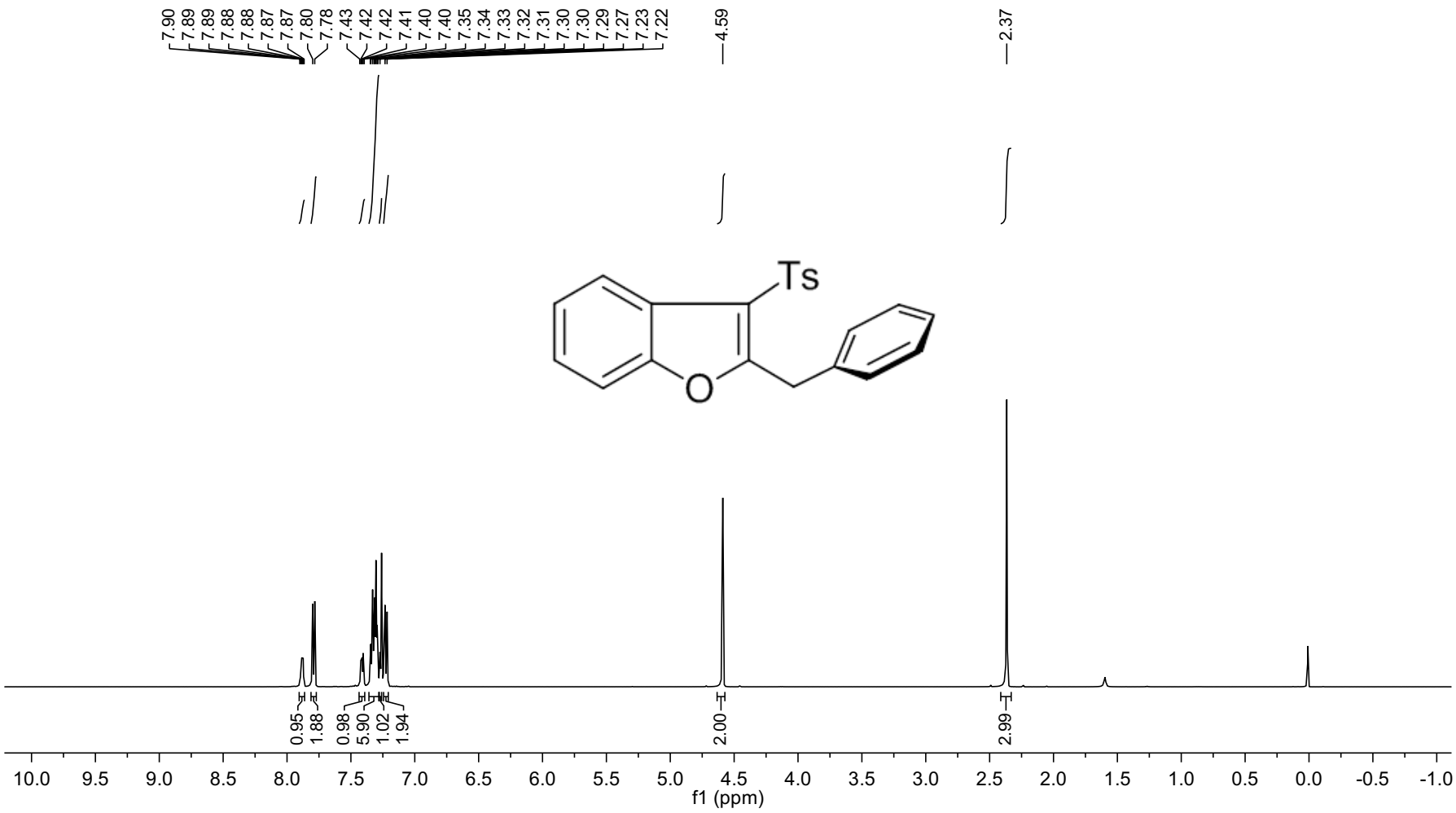
7. References

1. a) Saha, S.; Schneider, C. *Org. Lett.* **2015**, *17*, 648. b) Rajesh, M.; Thirupathi, N.; Jagadeshwar Reddy, T.; Kanojiya, S.; Sridhar Reddy, M., *J. Org. Chem.* **2015**, *80*, 12311c) Ranjith Kumar, G.; Kiran Kumar, Y.; Kant, R.; Sridhar Reddy, M., *Org. Biomol. Chem.* **2016**, *14*, 4077 d) Harkat, H.; Blanc, A.; Weibel, J.-M.; Pale, P *J. Org. Chem.* **2008**, *73*, 1620. e) Yoshida, M.; Fujino, Y.; Doi, T. *Org. Lett.* **2011**, *13*, 4526. f) Tian, T.; Li, L.; Xue, J.; Zhang, J.; Li, Y. *J. Org. Chem.* **2015**, *80*, 4189. g) Du, J.-Y.; Ma, Y.-H.; Meng, F.-X.; Chen, B.-L.; Zhang, S.-L.; Li, Q.-L.; Gong, S.-W.; Wang, D.-Q.; Ma, C.-L. *Org. Lett.* **2018**, *20*, 4371-4374. h) Du, J.-Y.; Ma, Y.-H.; Yuan, R.-Q.; Xin, N.; Nie, S.-Z.; Ma, C.-L.; Li, C.-Z.; Zhao, C.-Q. *Org. Lett.* **2018**, *20*, 477-480.

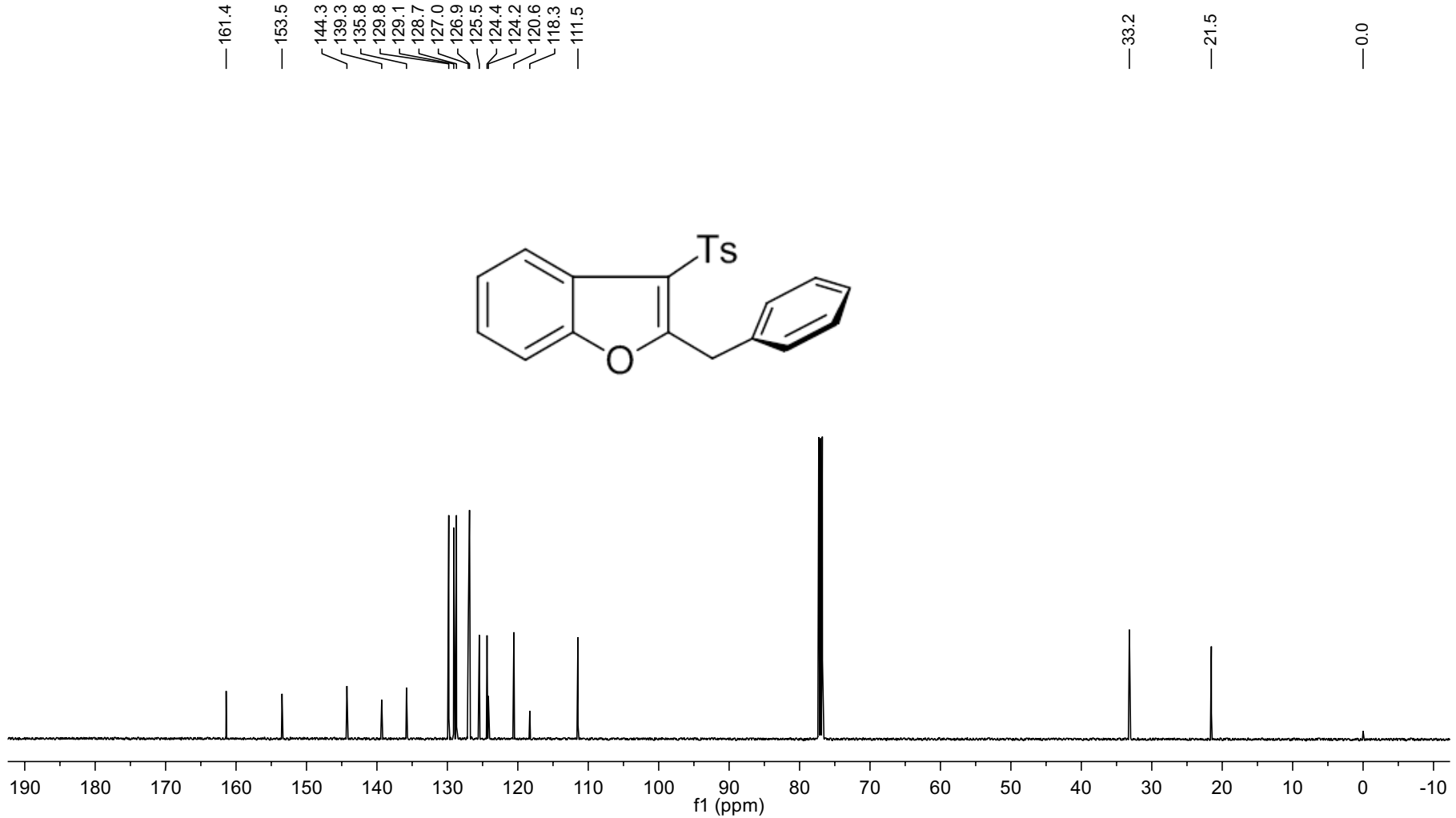
2. Yang, F.-L.; Ma, X.-T.; Tian, S.-K., *Chem. Eur. J.* **2012**, *18*, 1582.

8. Copies of NMR Spectra

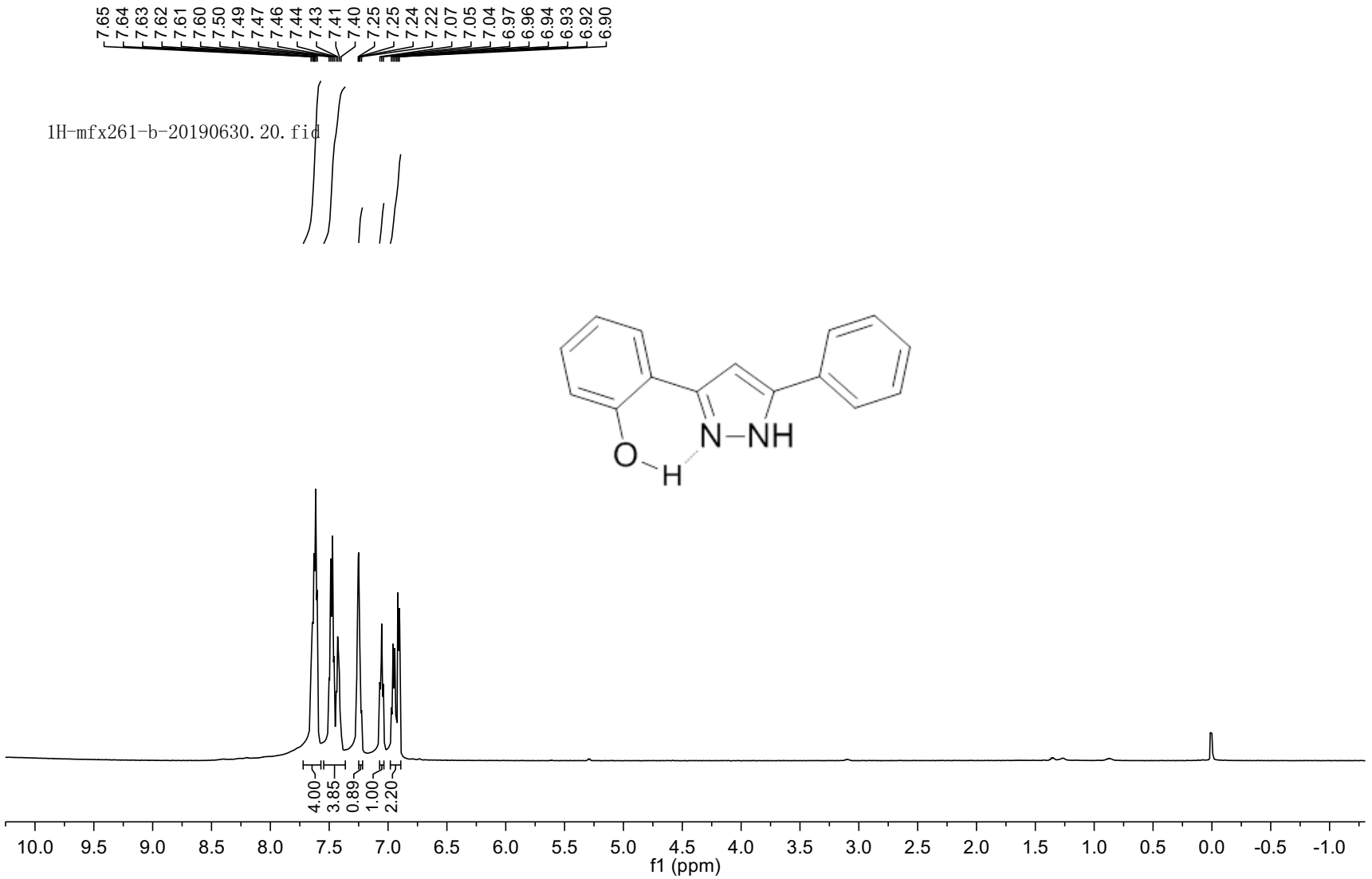
^{1}H NMR Spectroscopy of **4aa**



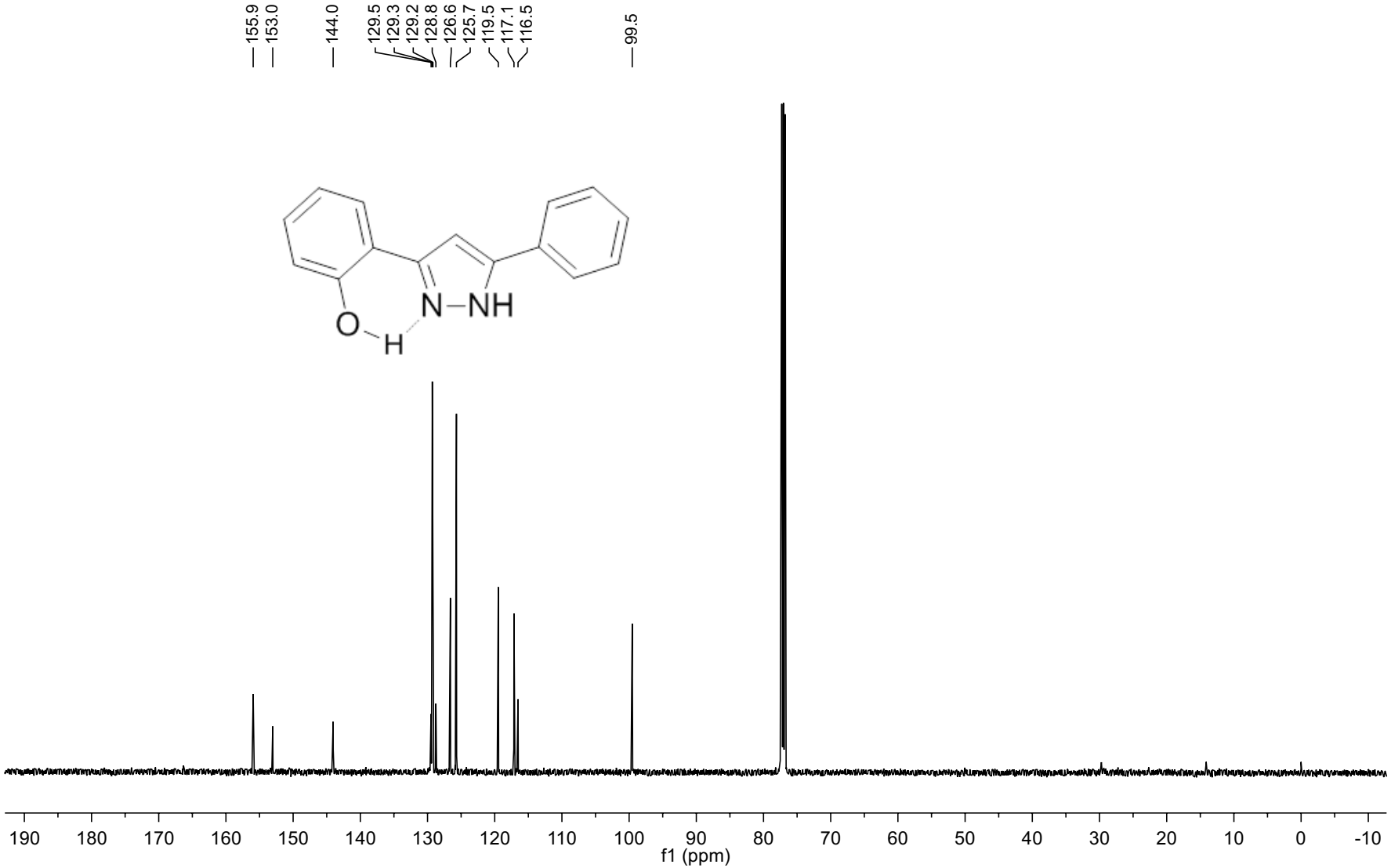
^{13}C NMR Spectroscopy of **4aa**



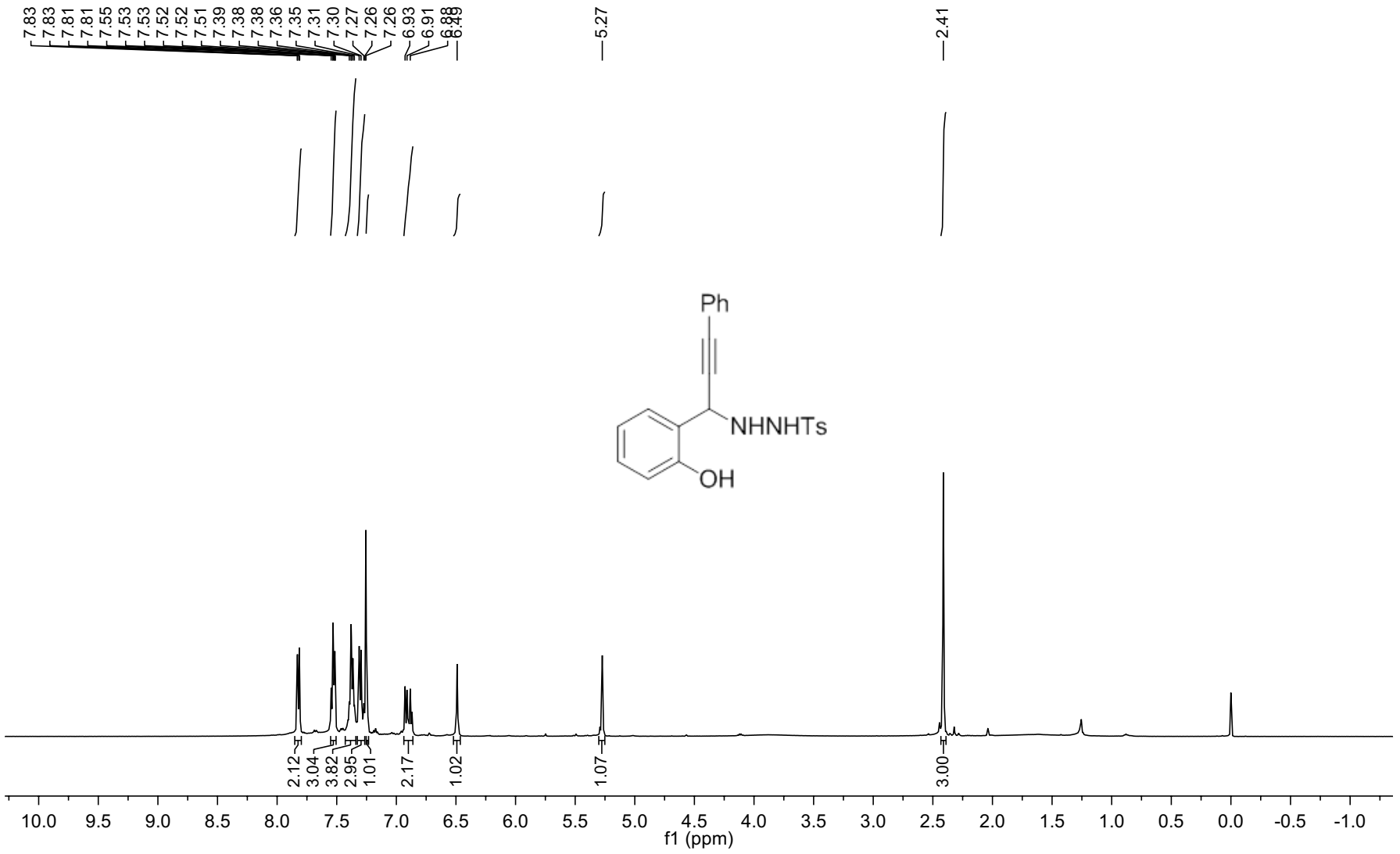
^{1}H NMR Spectroscopy of **4aa'**



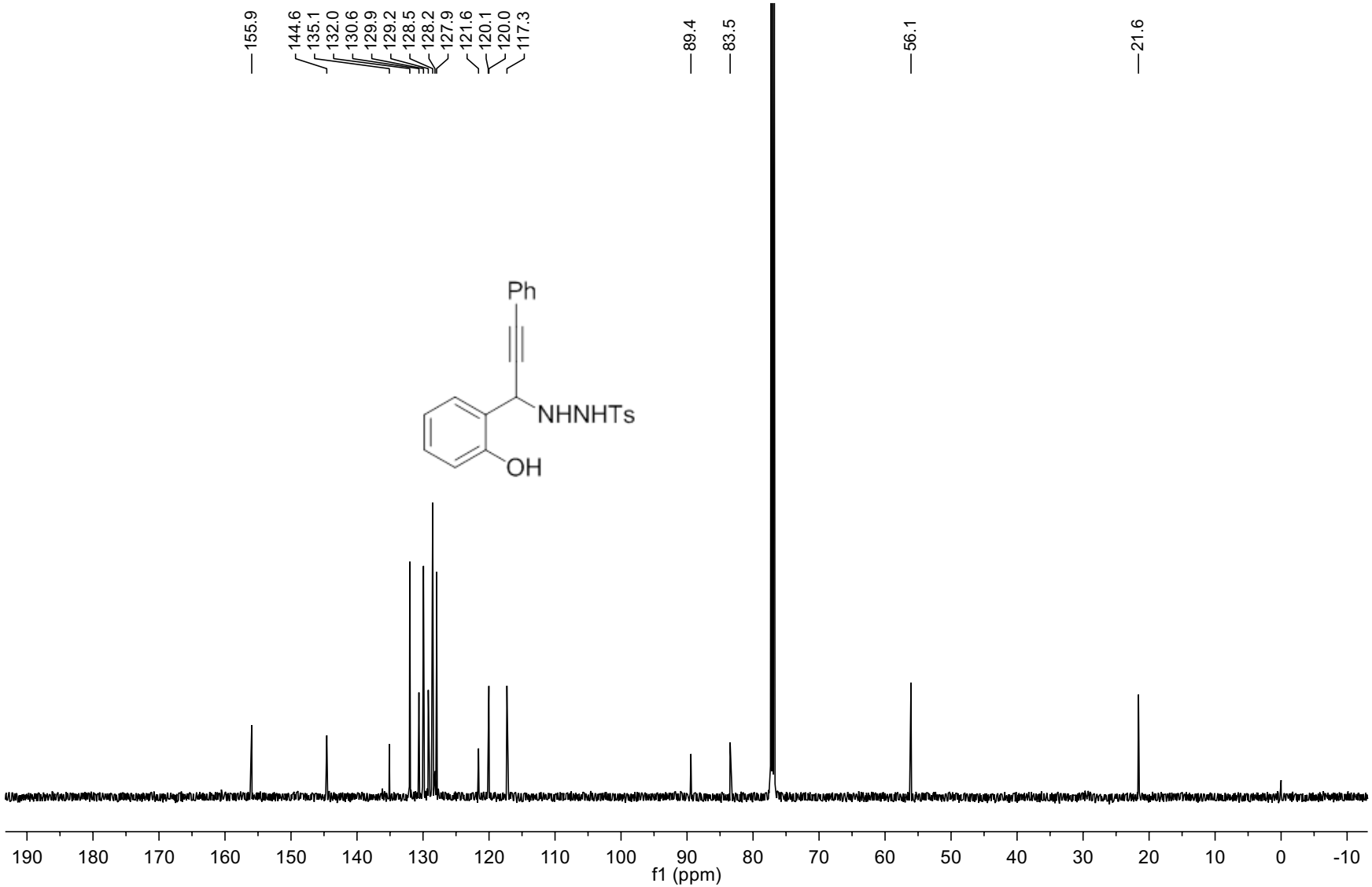
^{13}C NMR Spectroscopy of **4aa'**



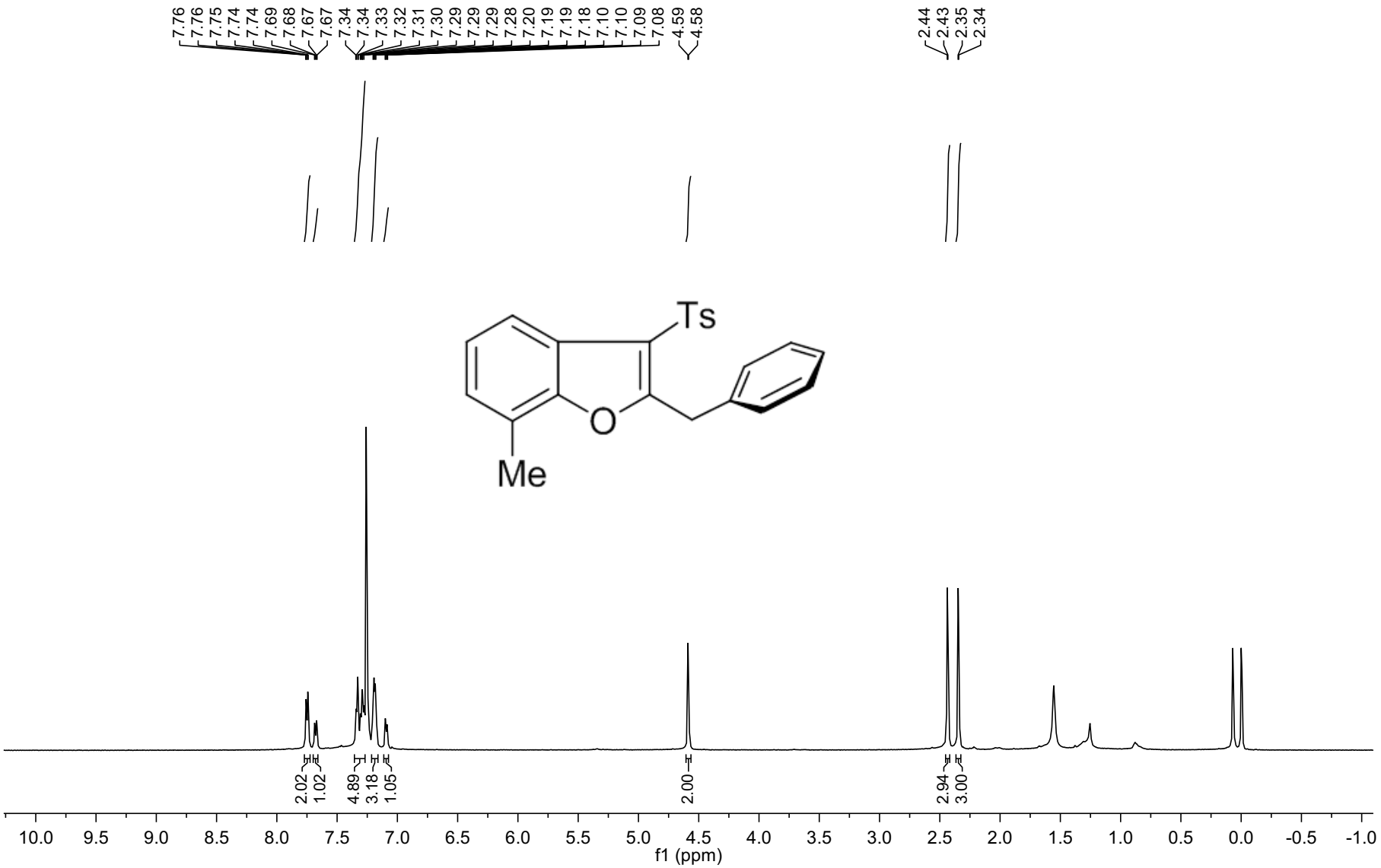
^{1}H NMR Spectroscopy of **3aa**



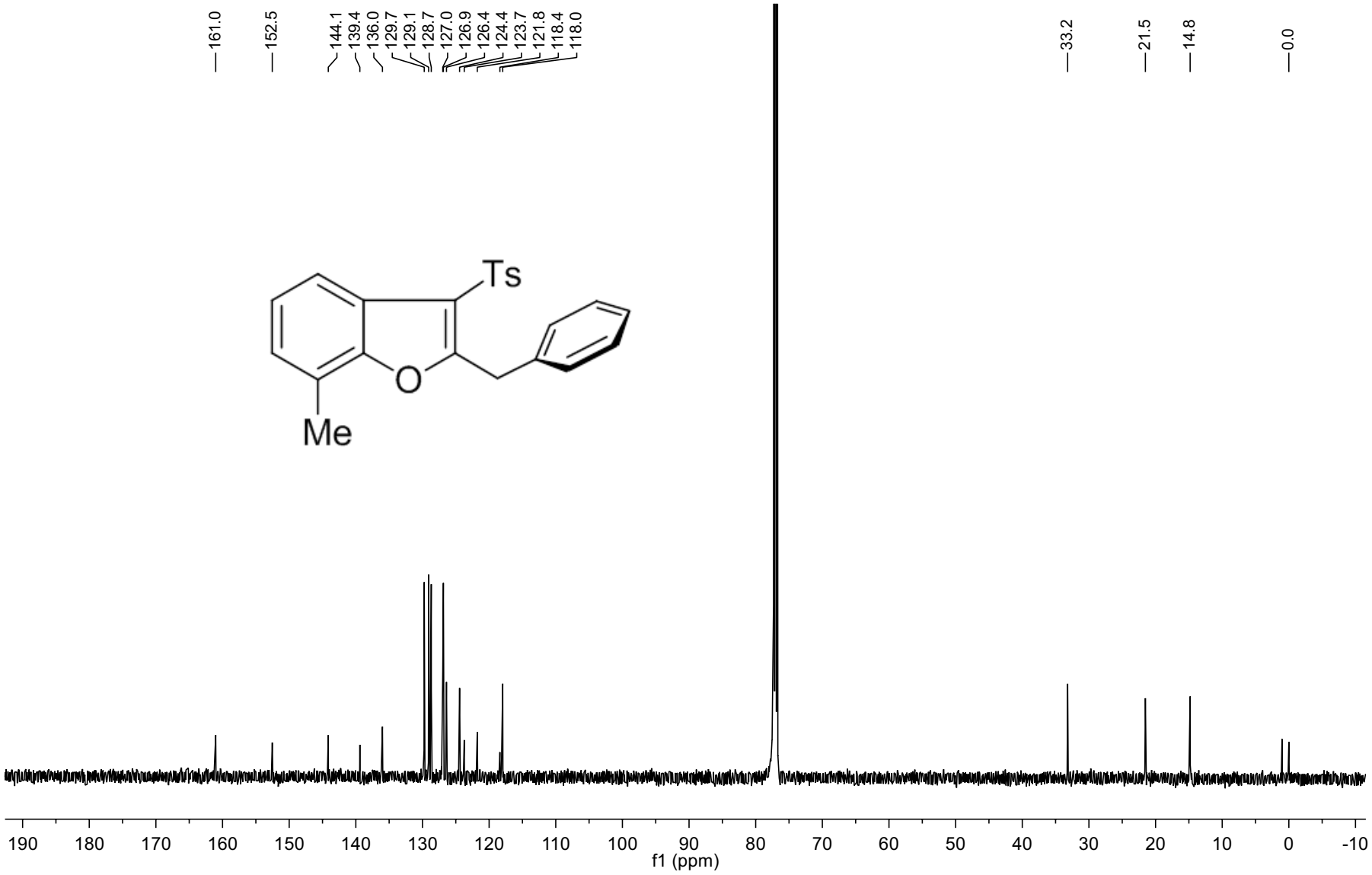
^{13}C NMR Spectroscopy of **3aa**



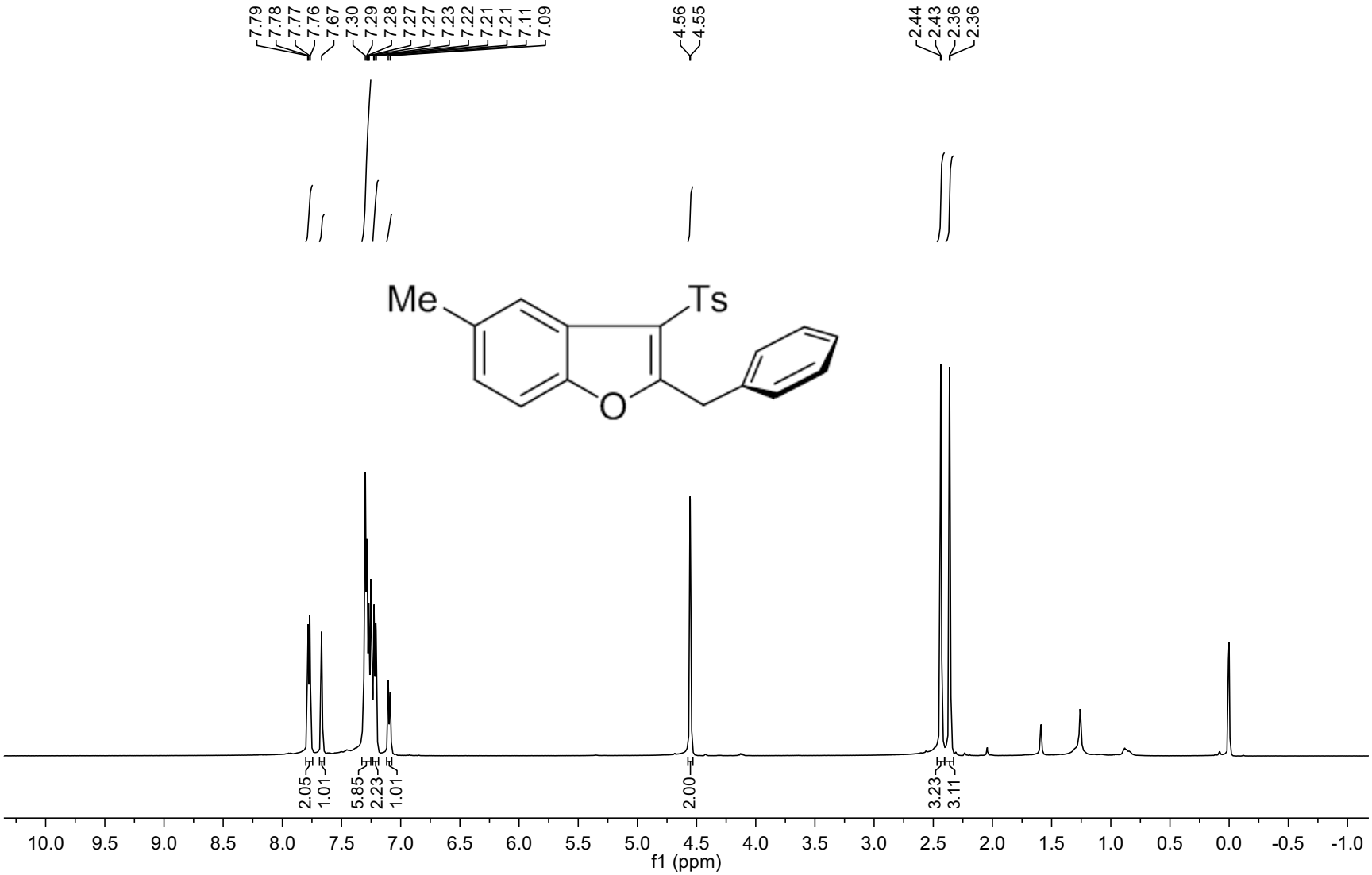
^{1}H NMR Spectroscopy of **4ba**



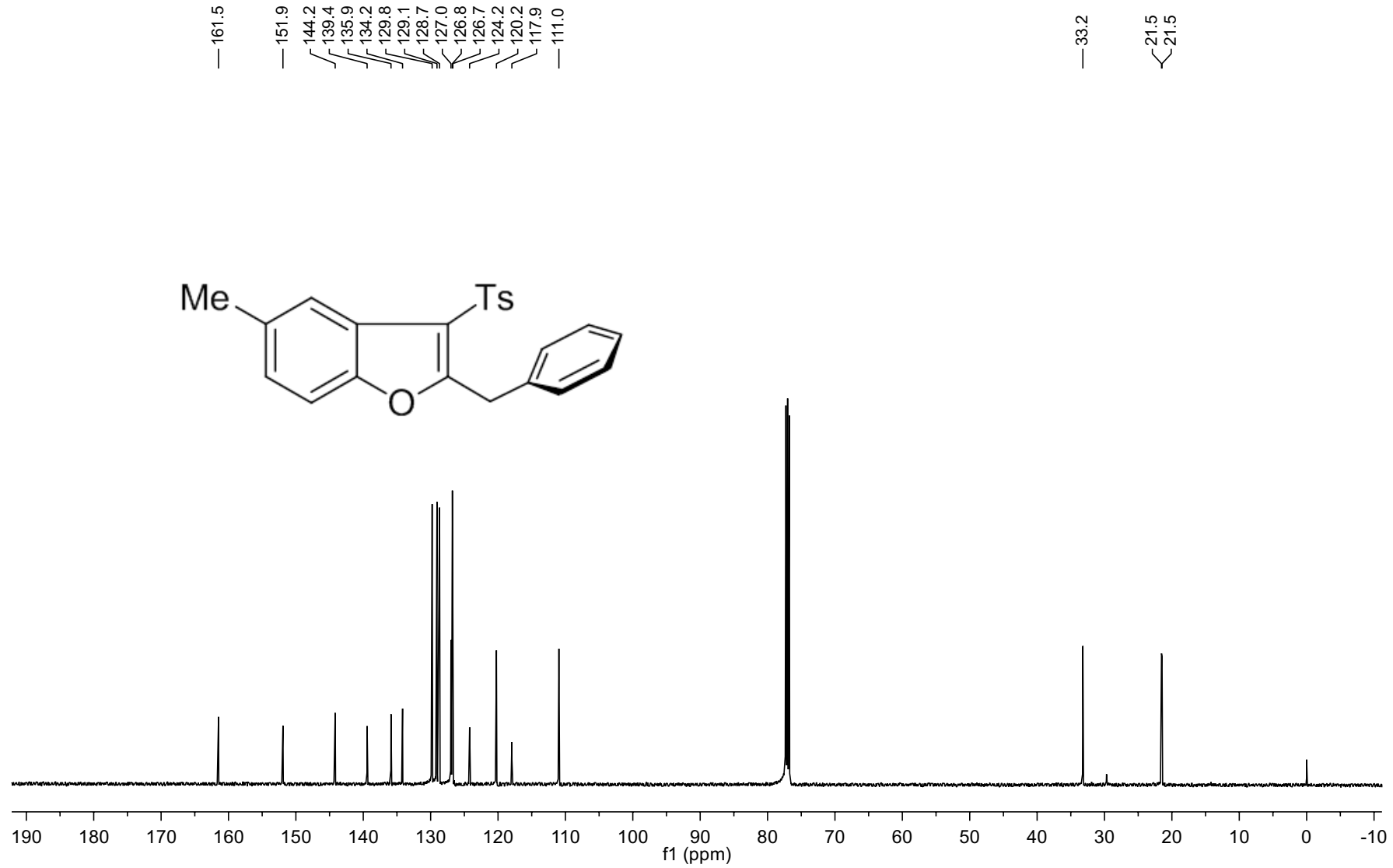
^{13}C NMR Spectroscopy of **4ba**



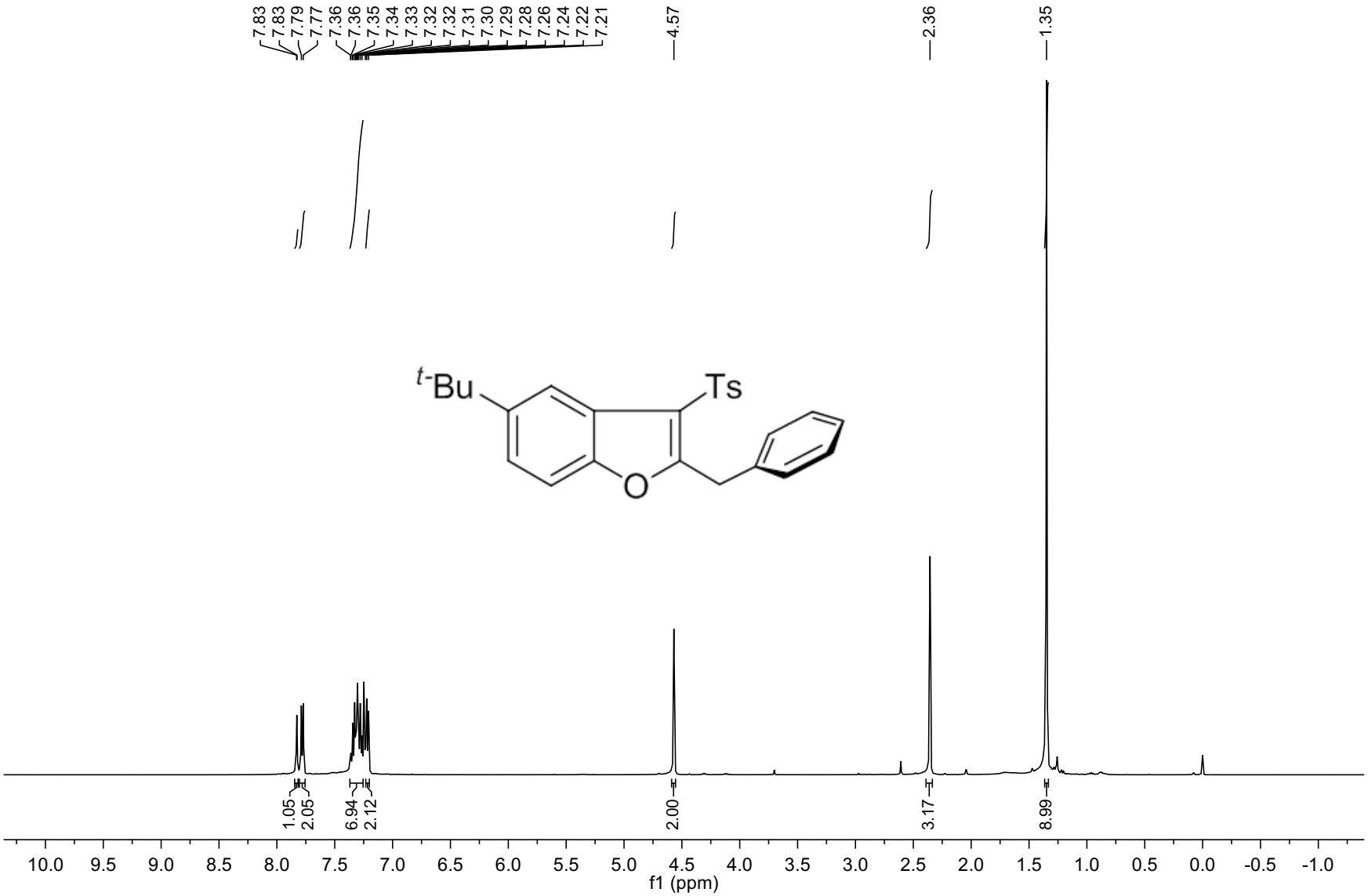
^{1}H NMR Spectroscopy of **4ca**



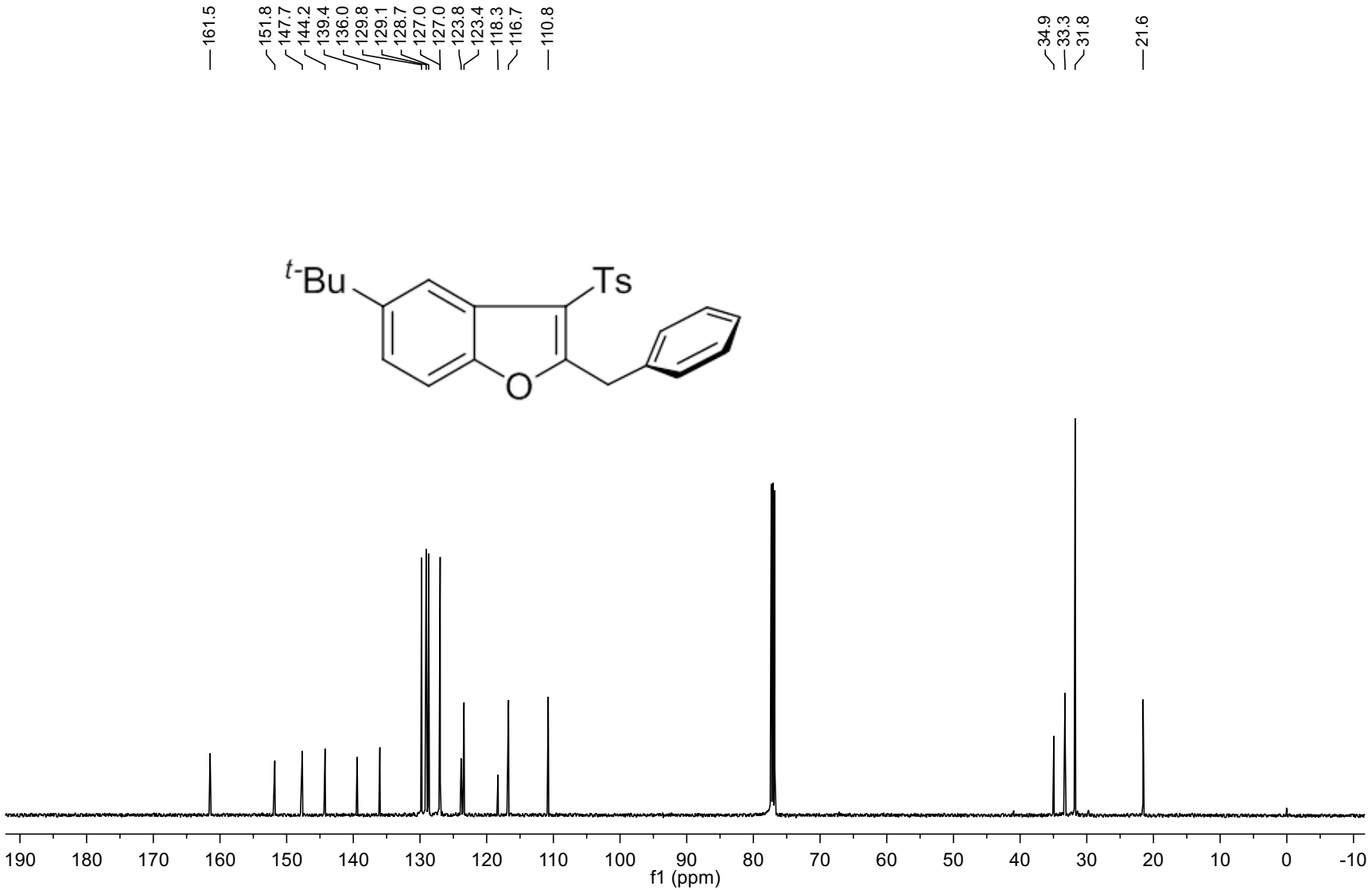
^{13}C NMR Spectroscopy of **4ca**



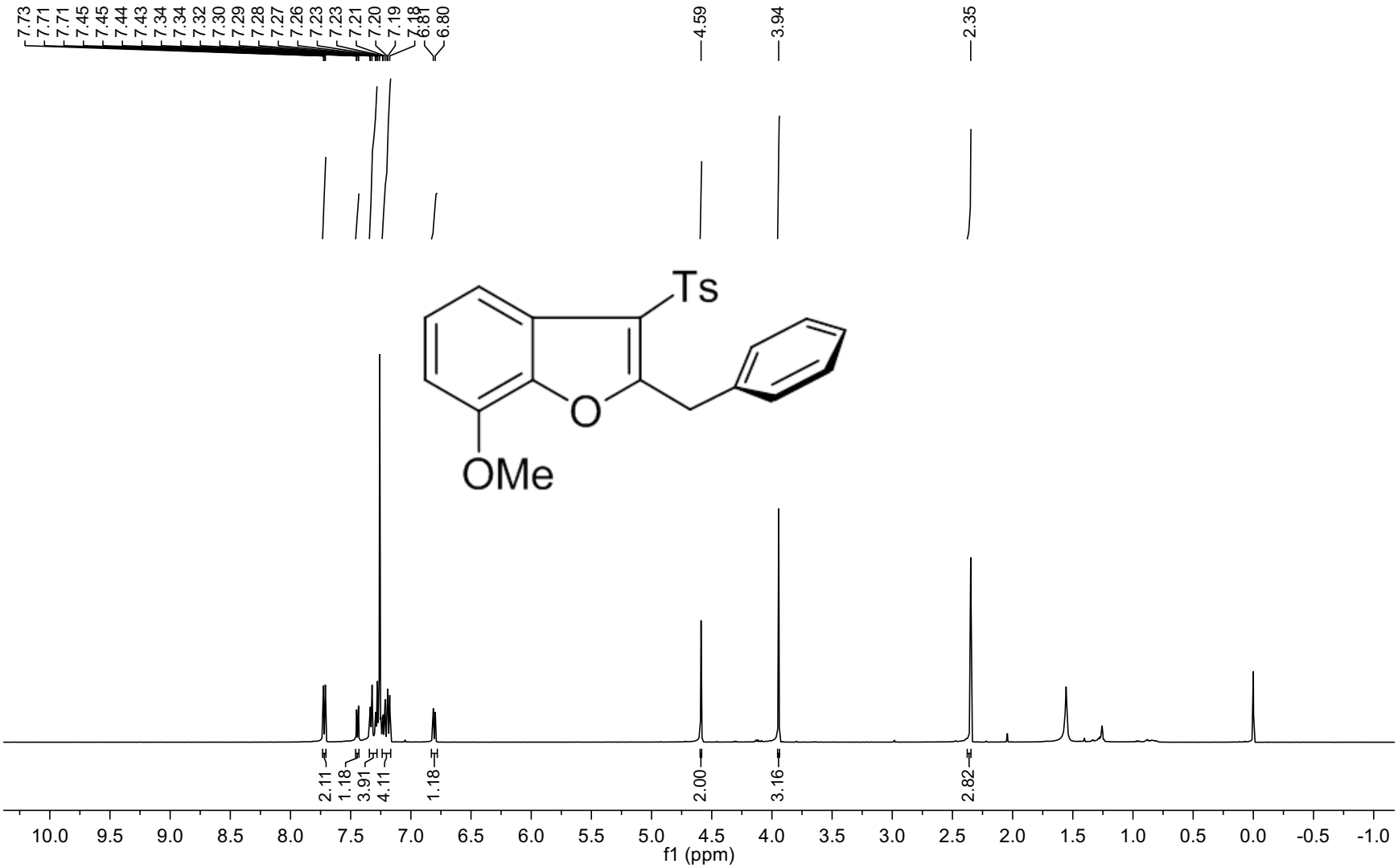
^{1}H NMR Spectroscopy of **4da**



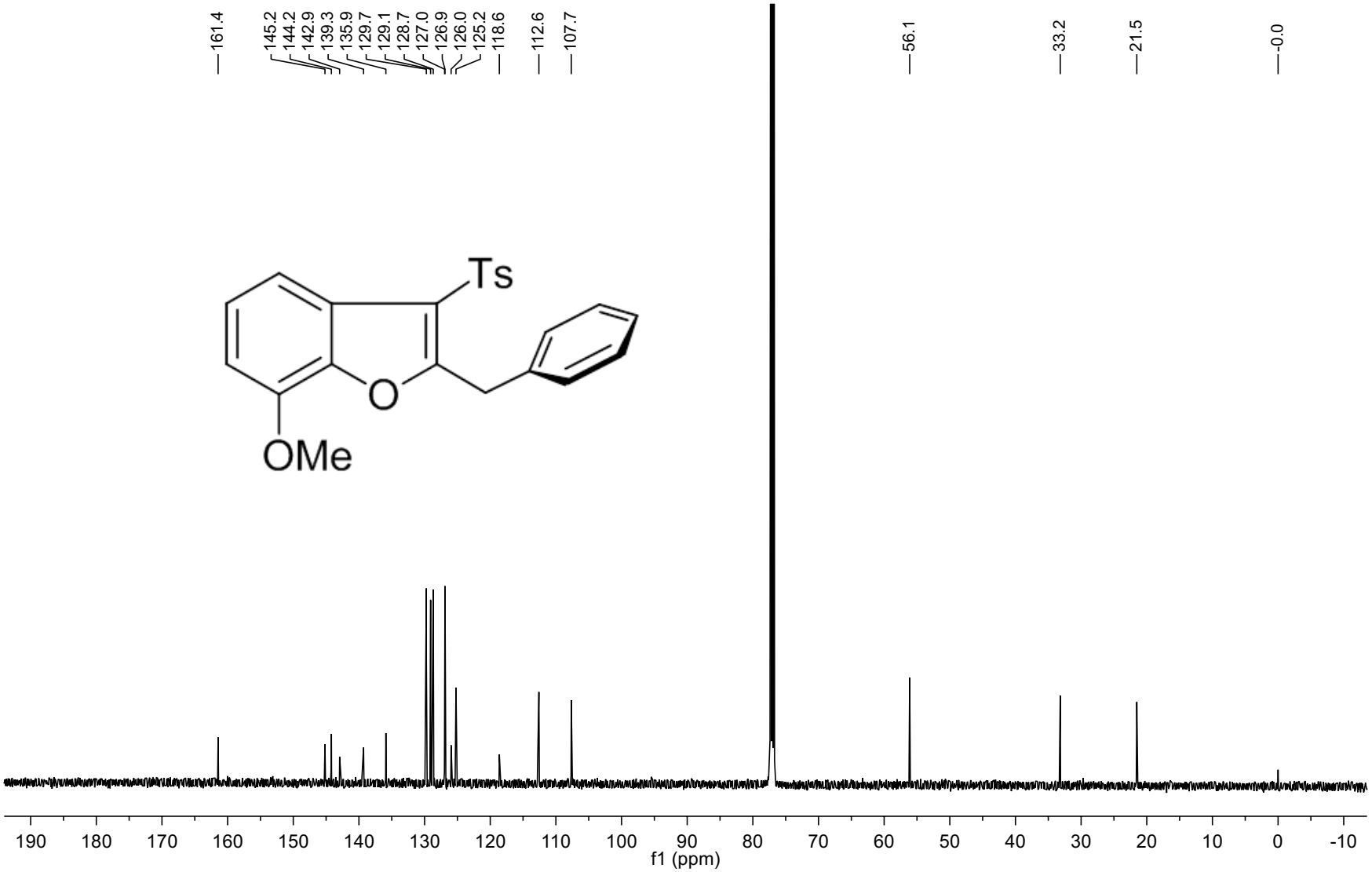
^{13}C NMR Spectroscopy of **4da**



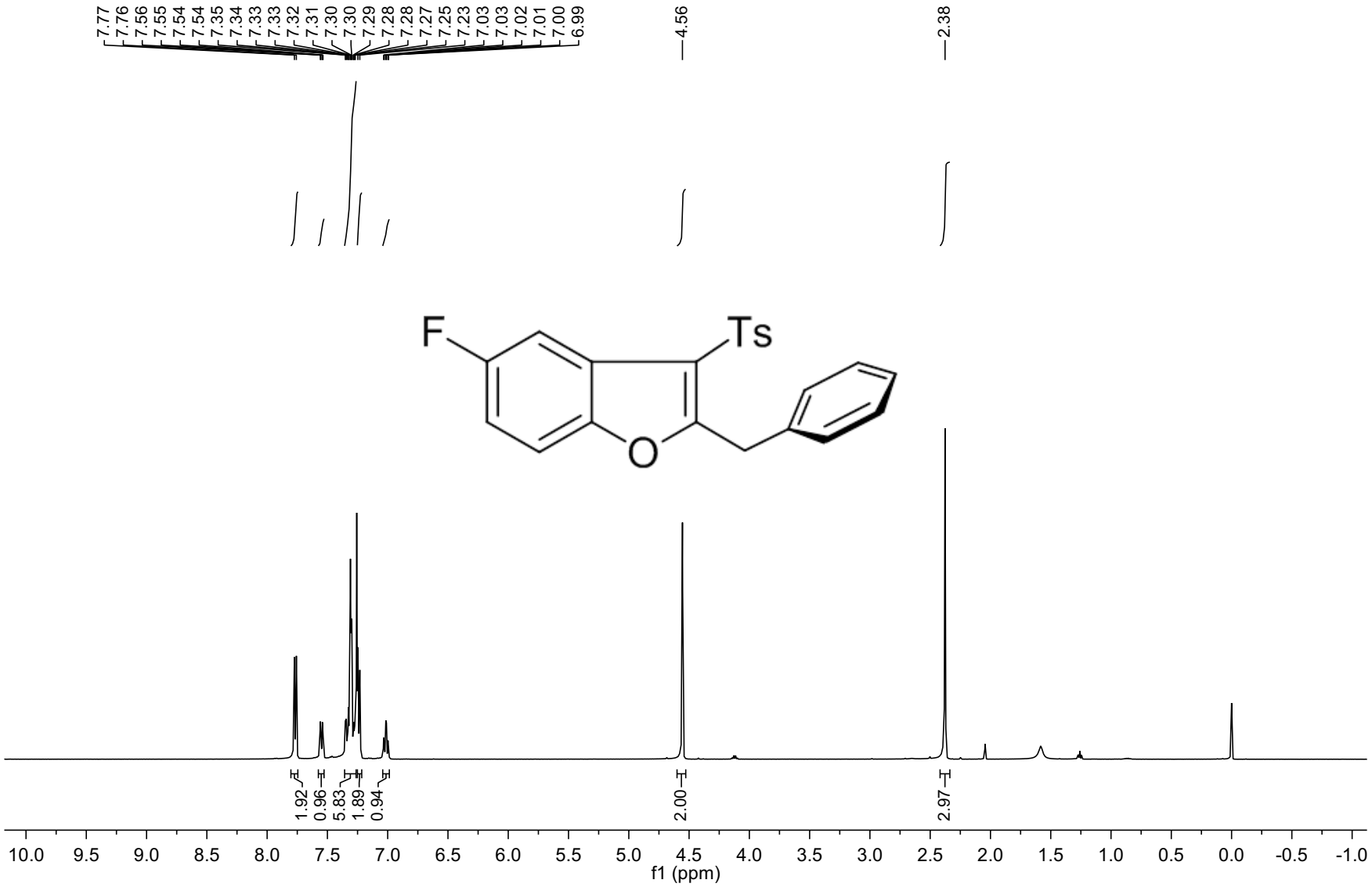
^{1}H NMR Spectroscopy of **4ea**



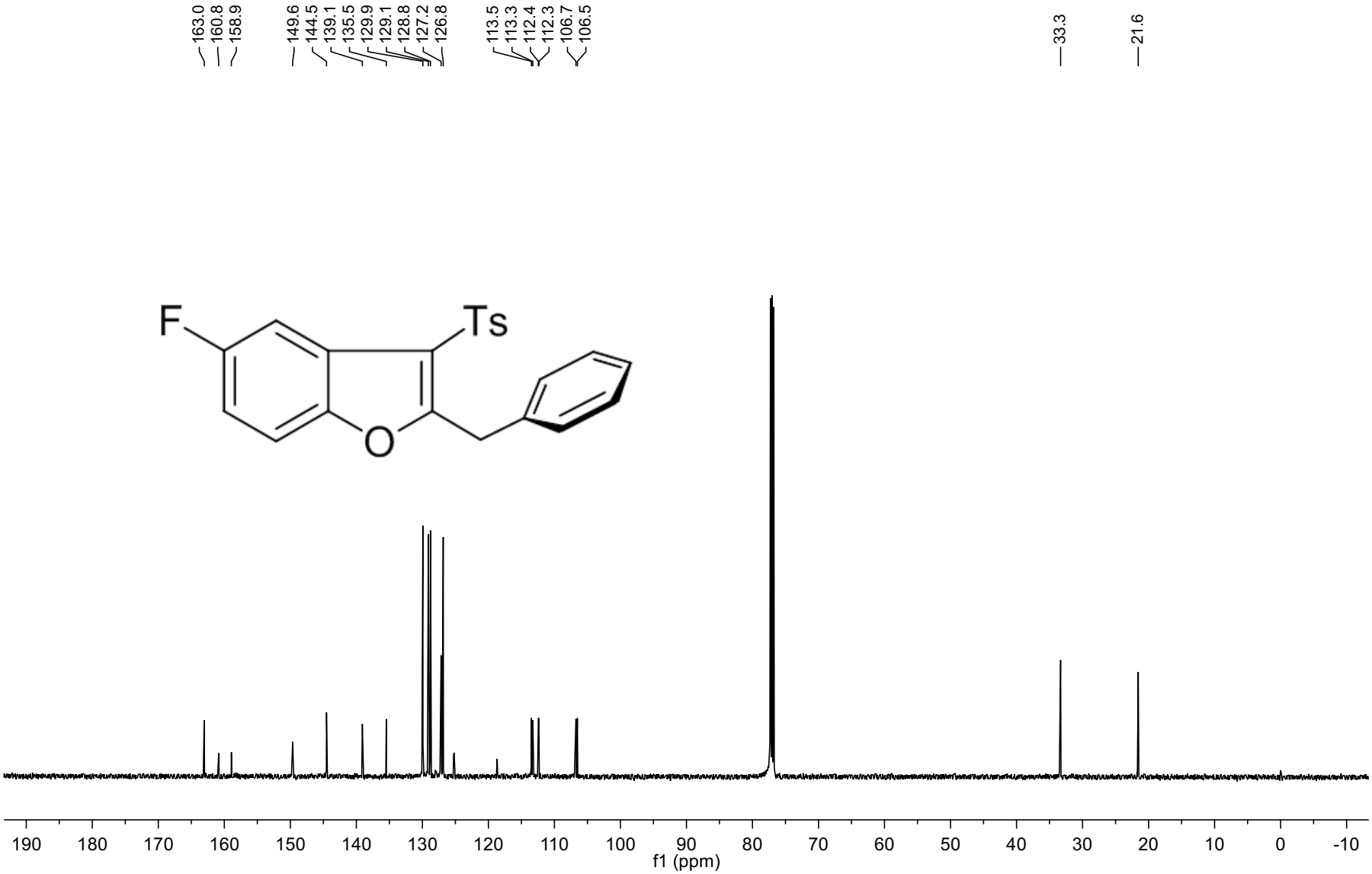
^{13}C NMR Spectroscopy of **4ea**



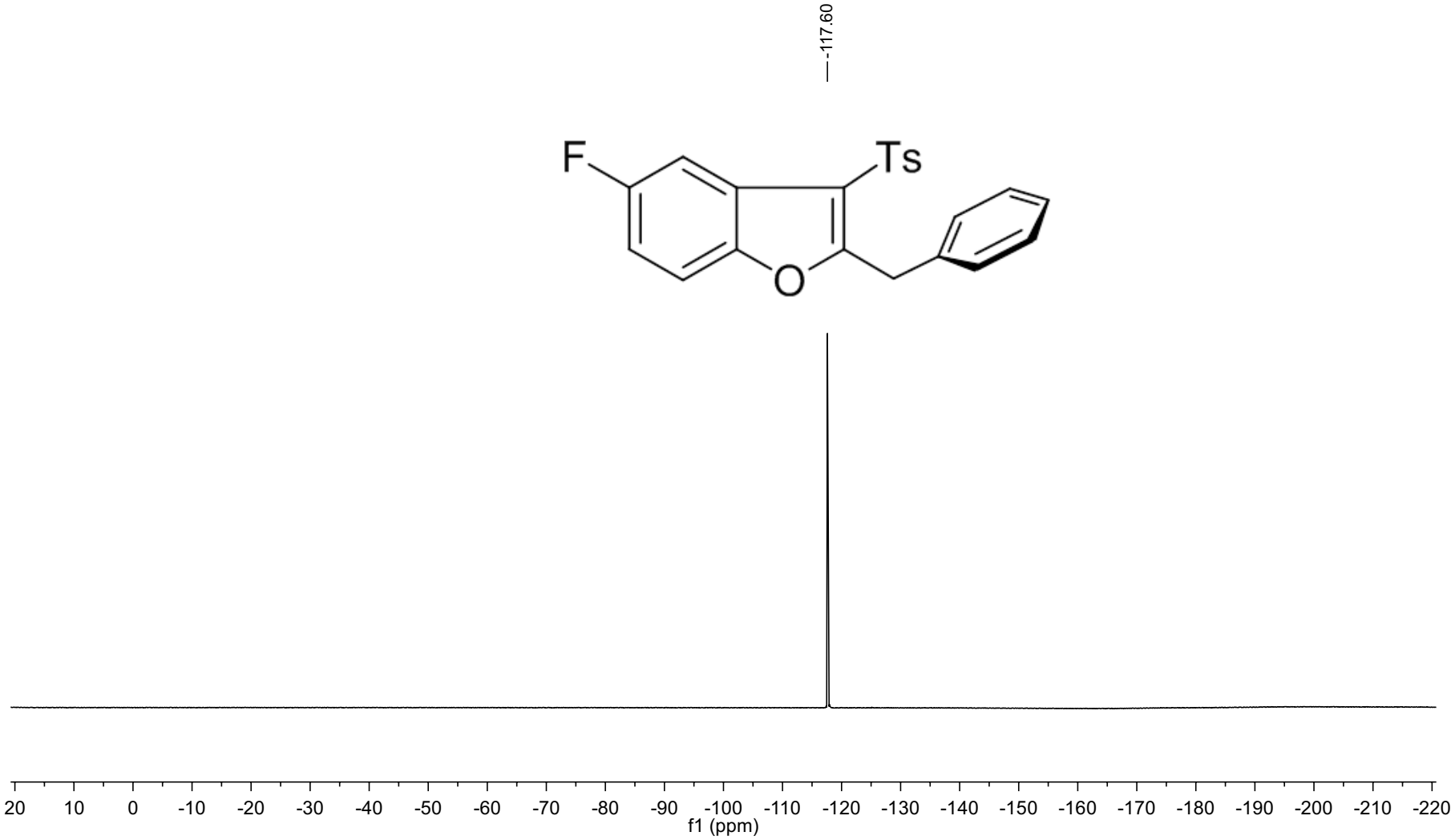
^{1}H NMR Spectroscopy of **4fa**



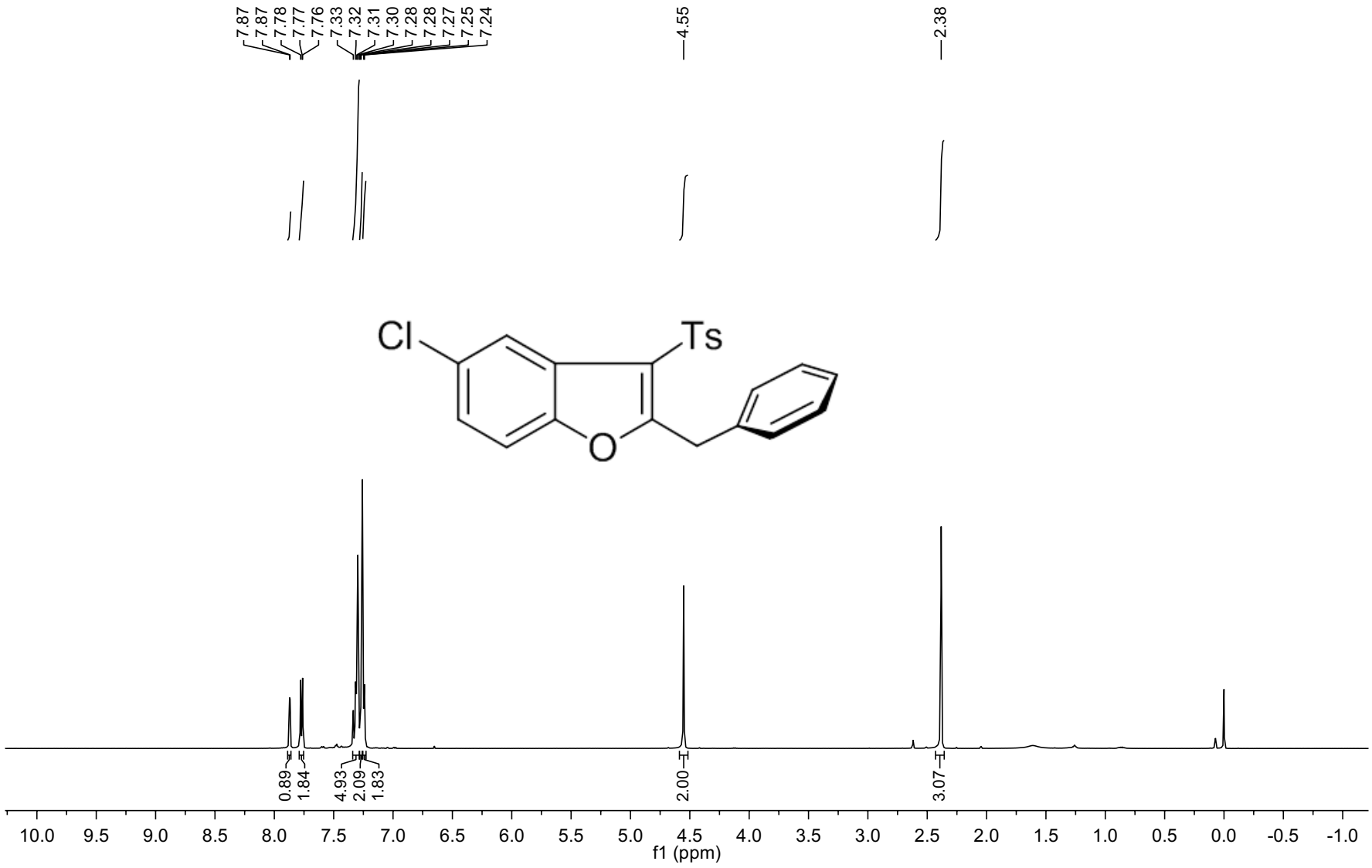
^{13}C NMR Spectroscopy of **4fa**



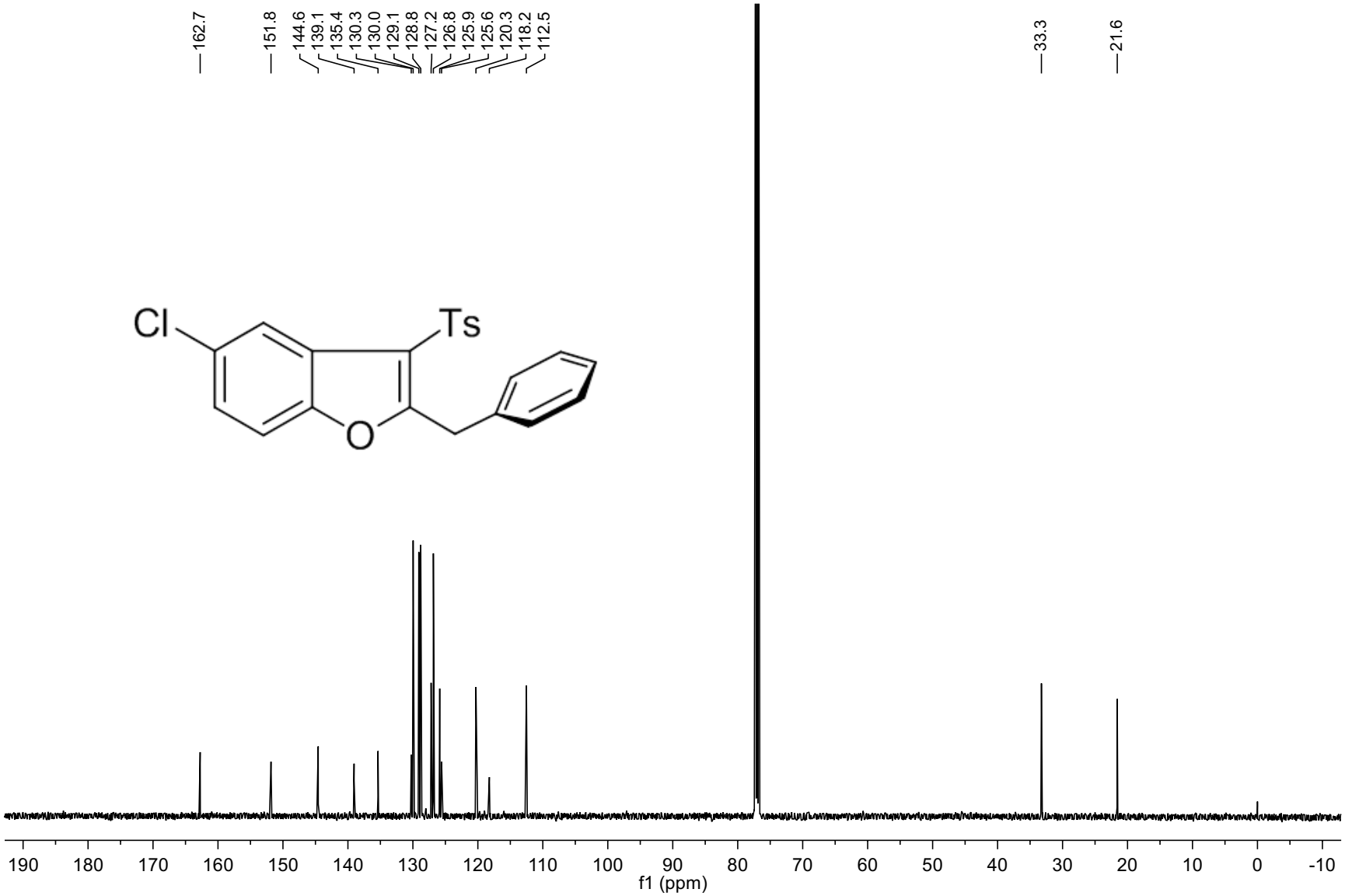
^{19}F NMR Spectroscopy of **4fa**



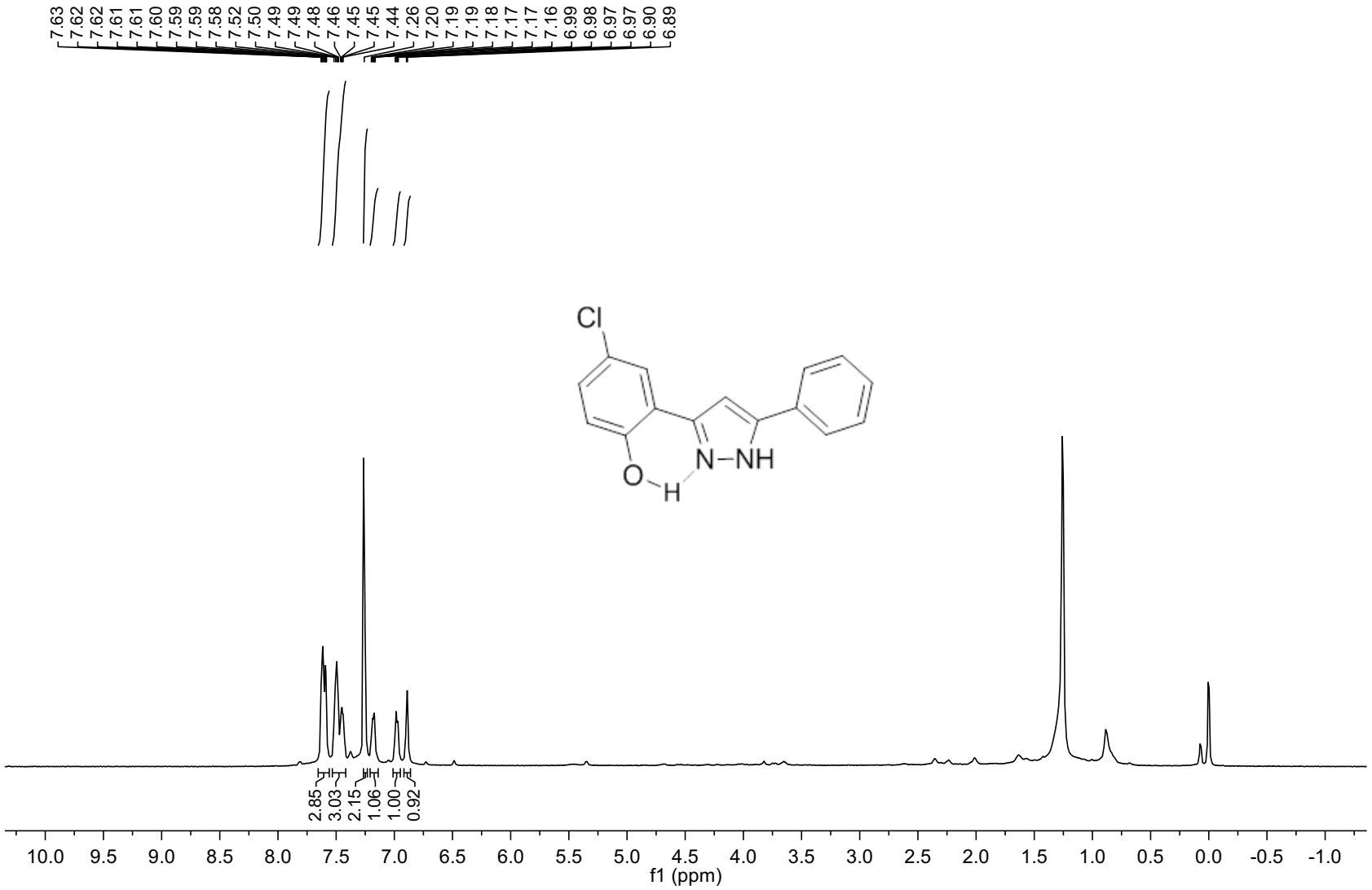
^{1}H NMR Spectroscopy of **4ga**



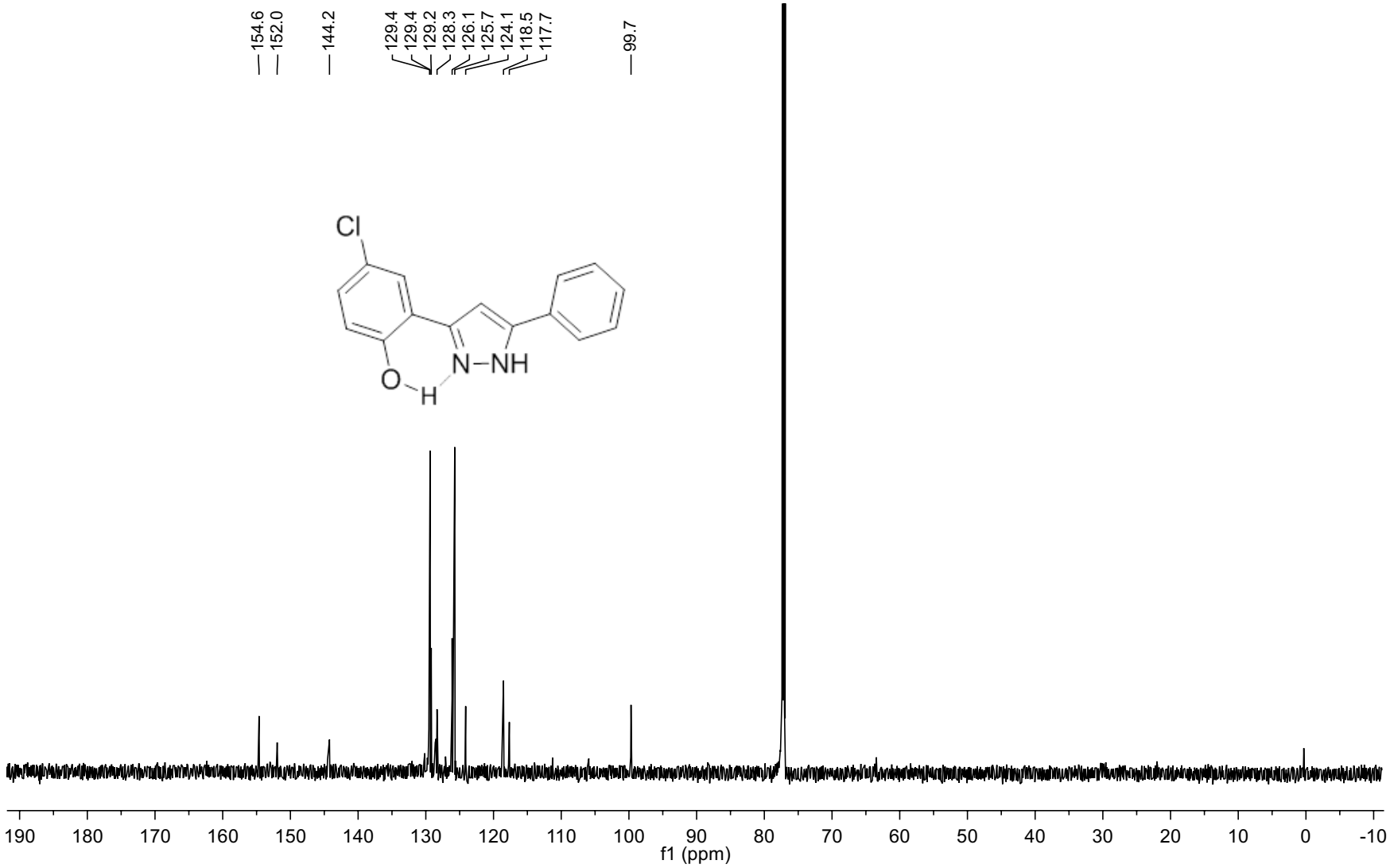
^{13}C NMR Spectroscopy of **4ga**



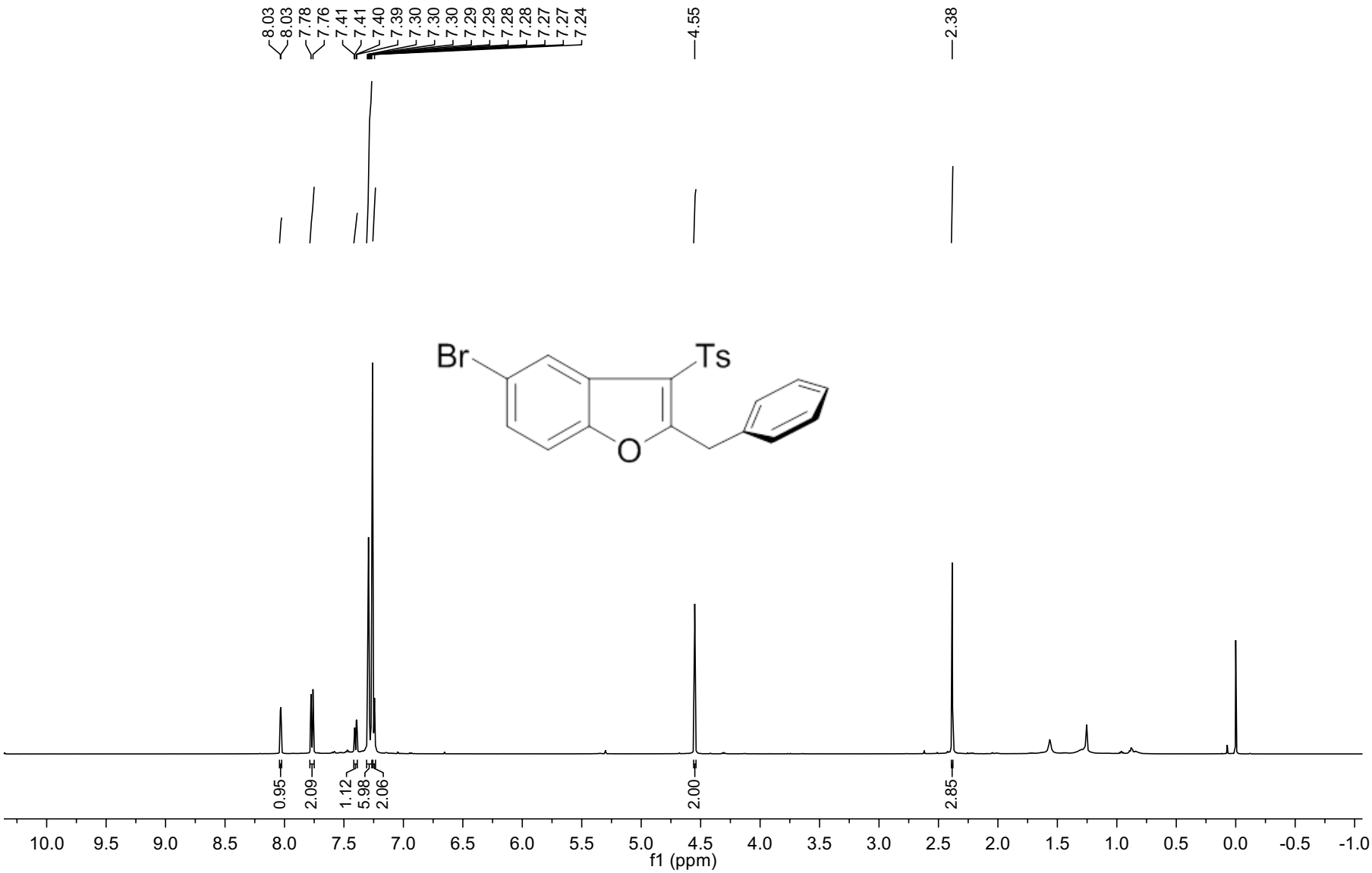
^{1}H NMR Spectroscopy of **4ga'**



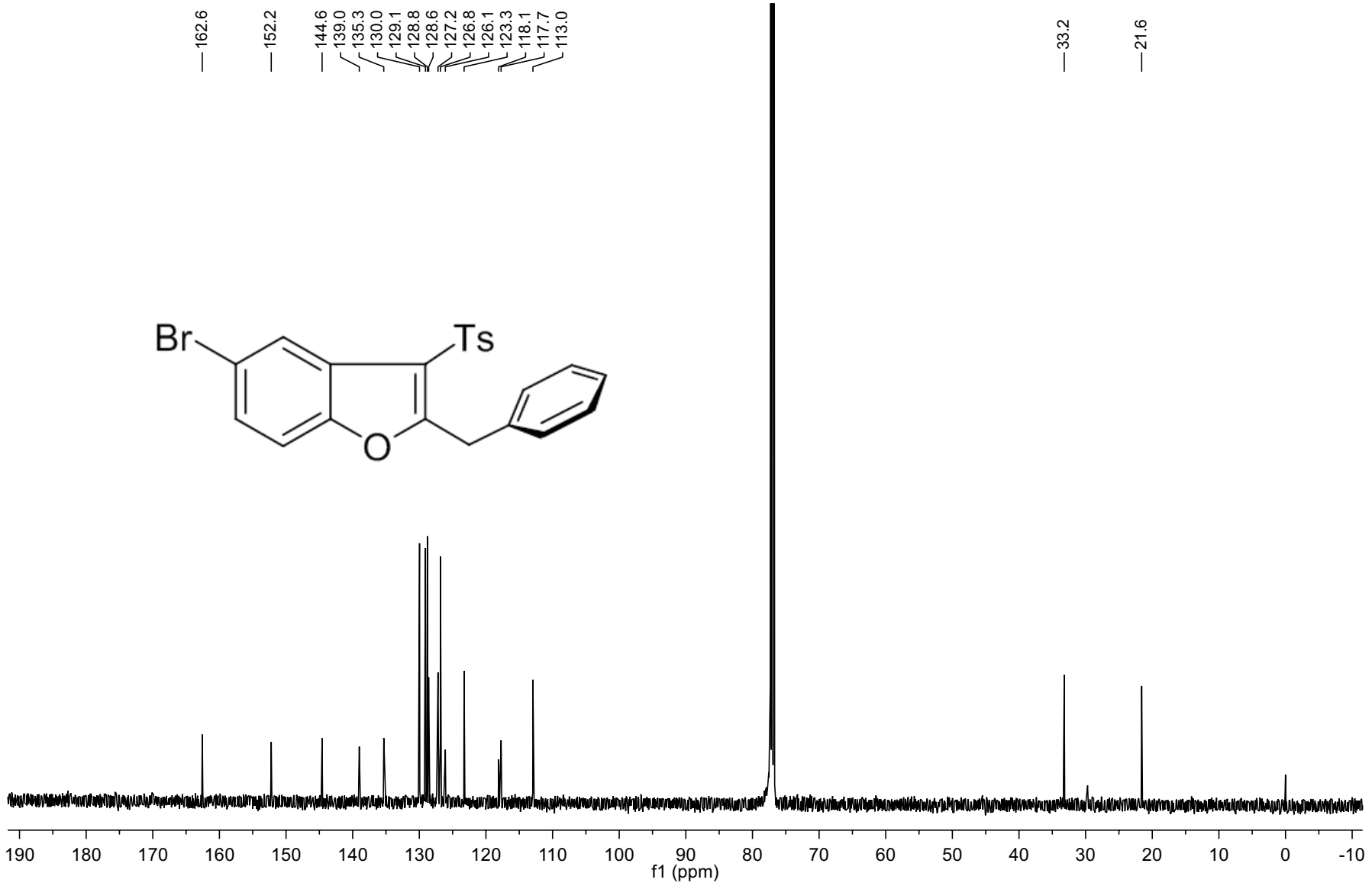
^{13}C NMR Spectroscopy of **4ga'**



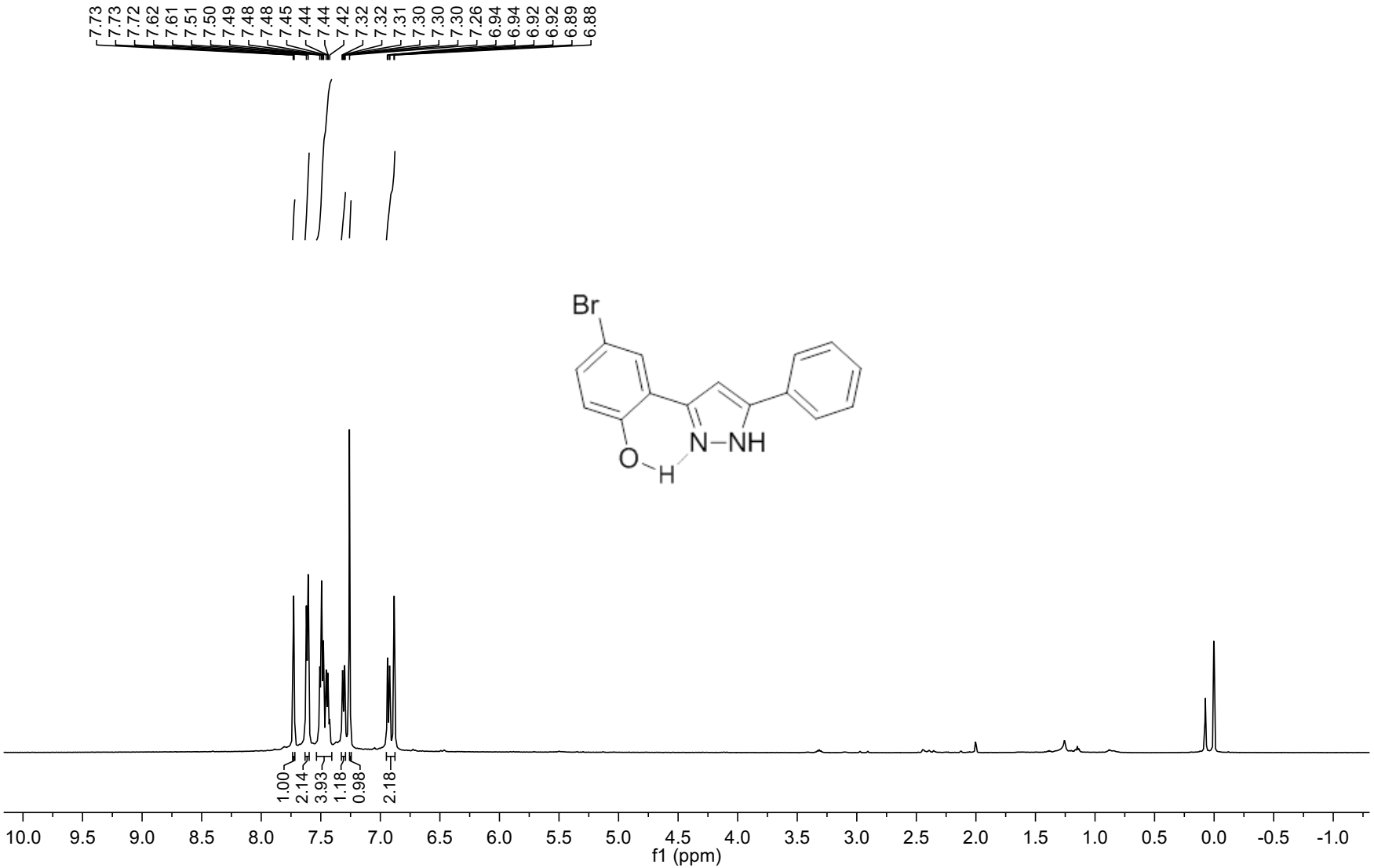
^{1}H NMR Spectroscopy of **4ha**



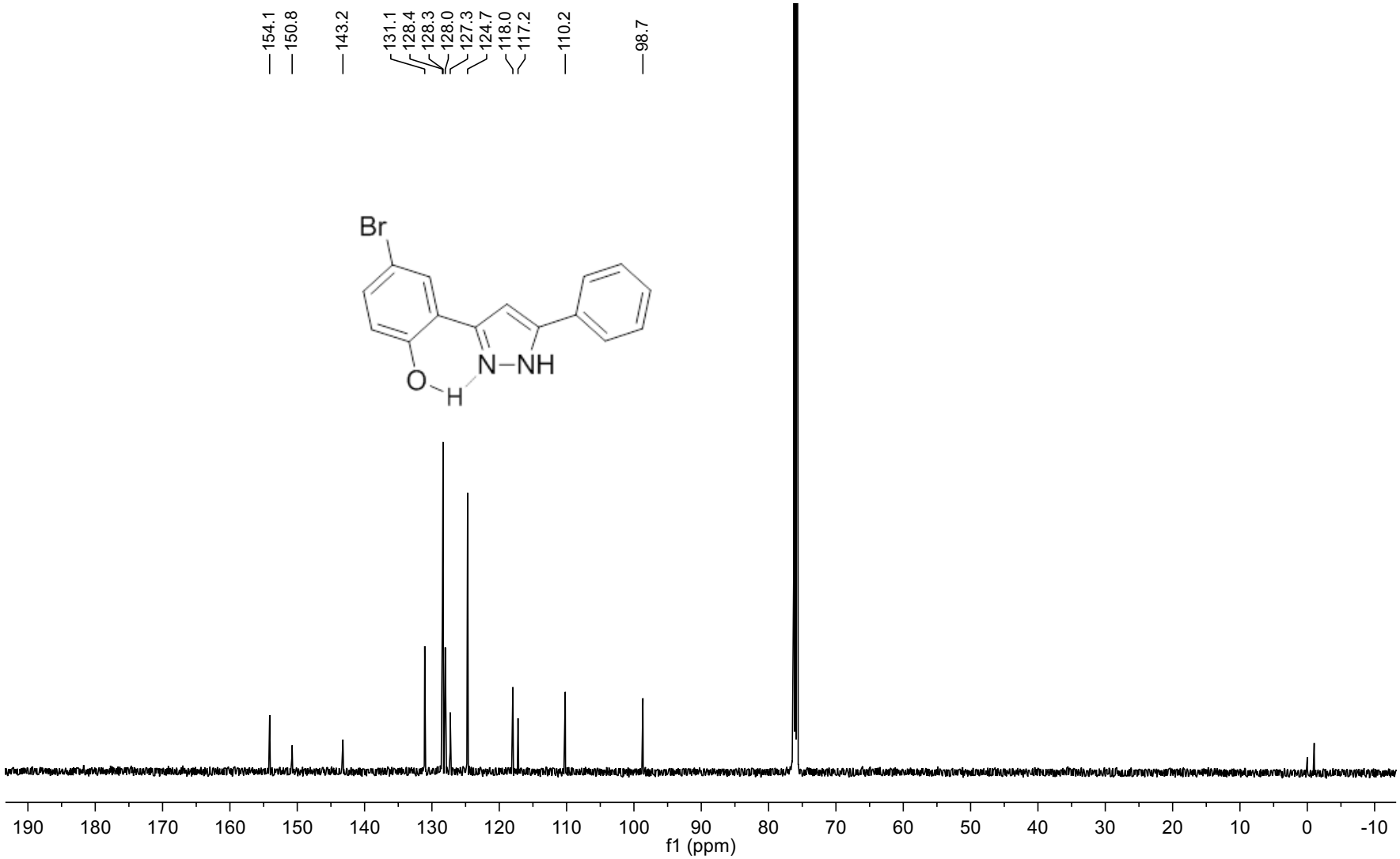
^{13}C NMR Spectroscopy of **4ha**



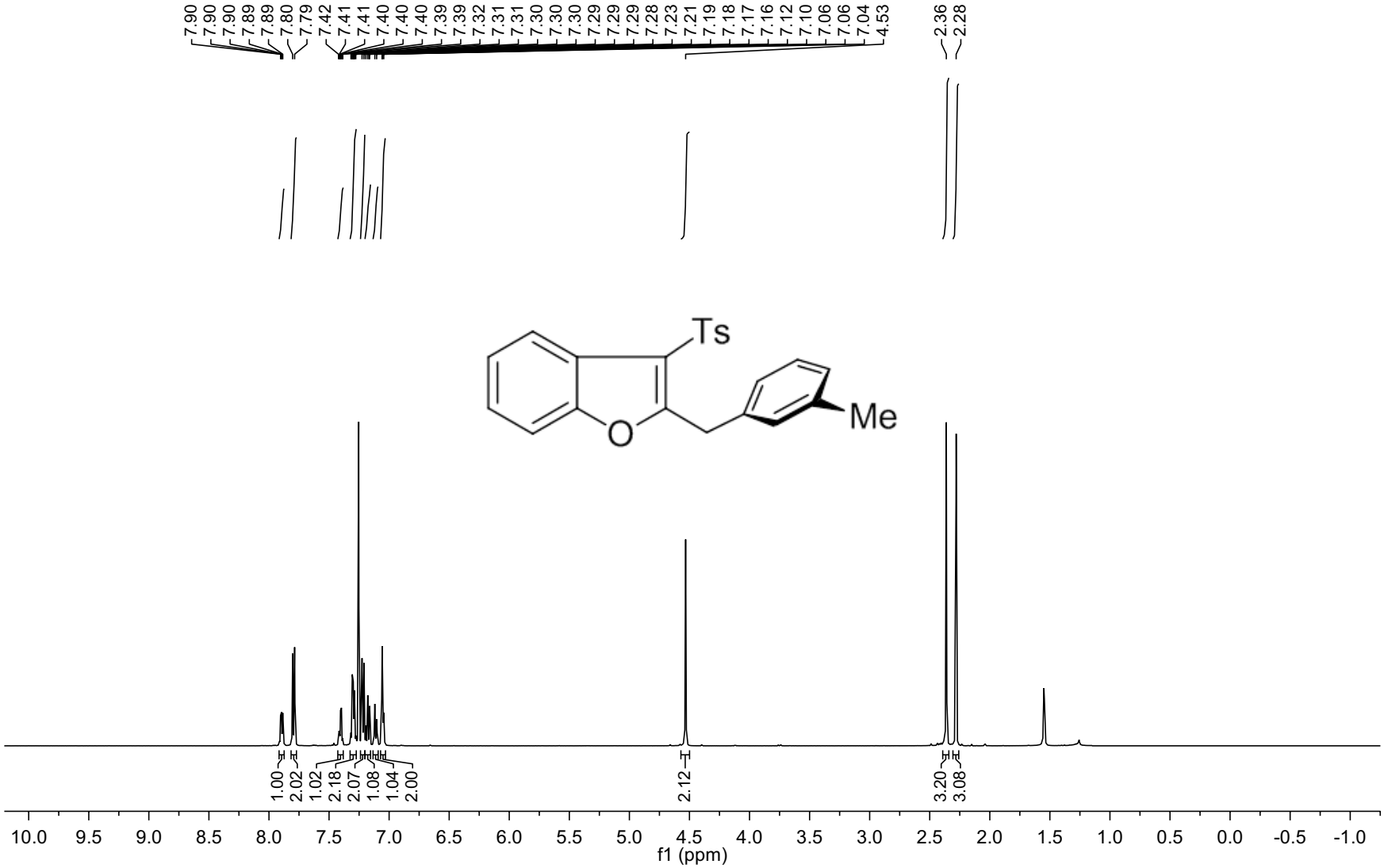
^{1}H NMR Spectroscopy of **4ha'**



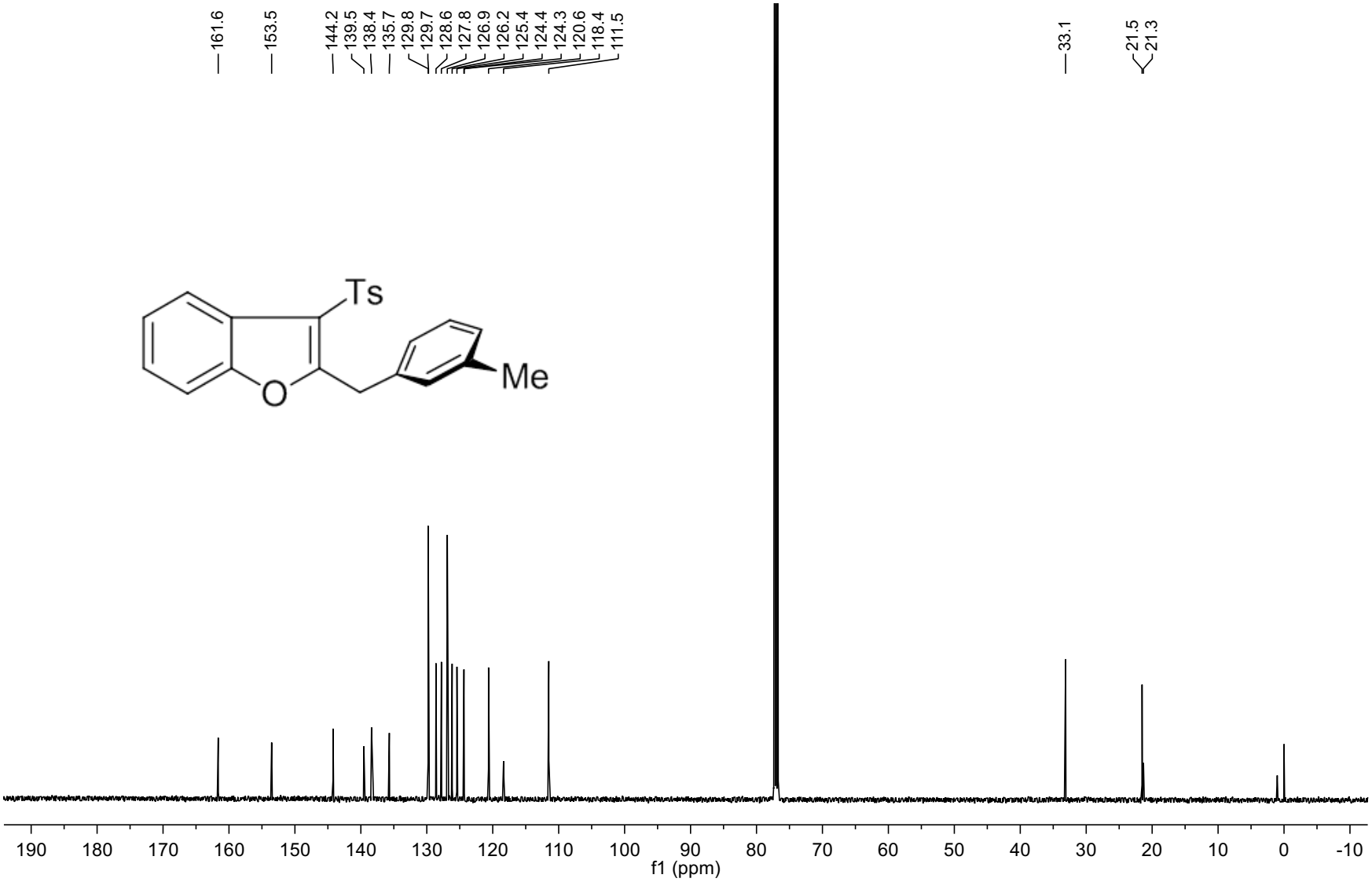
^{13}C NMR Spectroscopy of **4ha'**



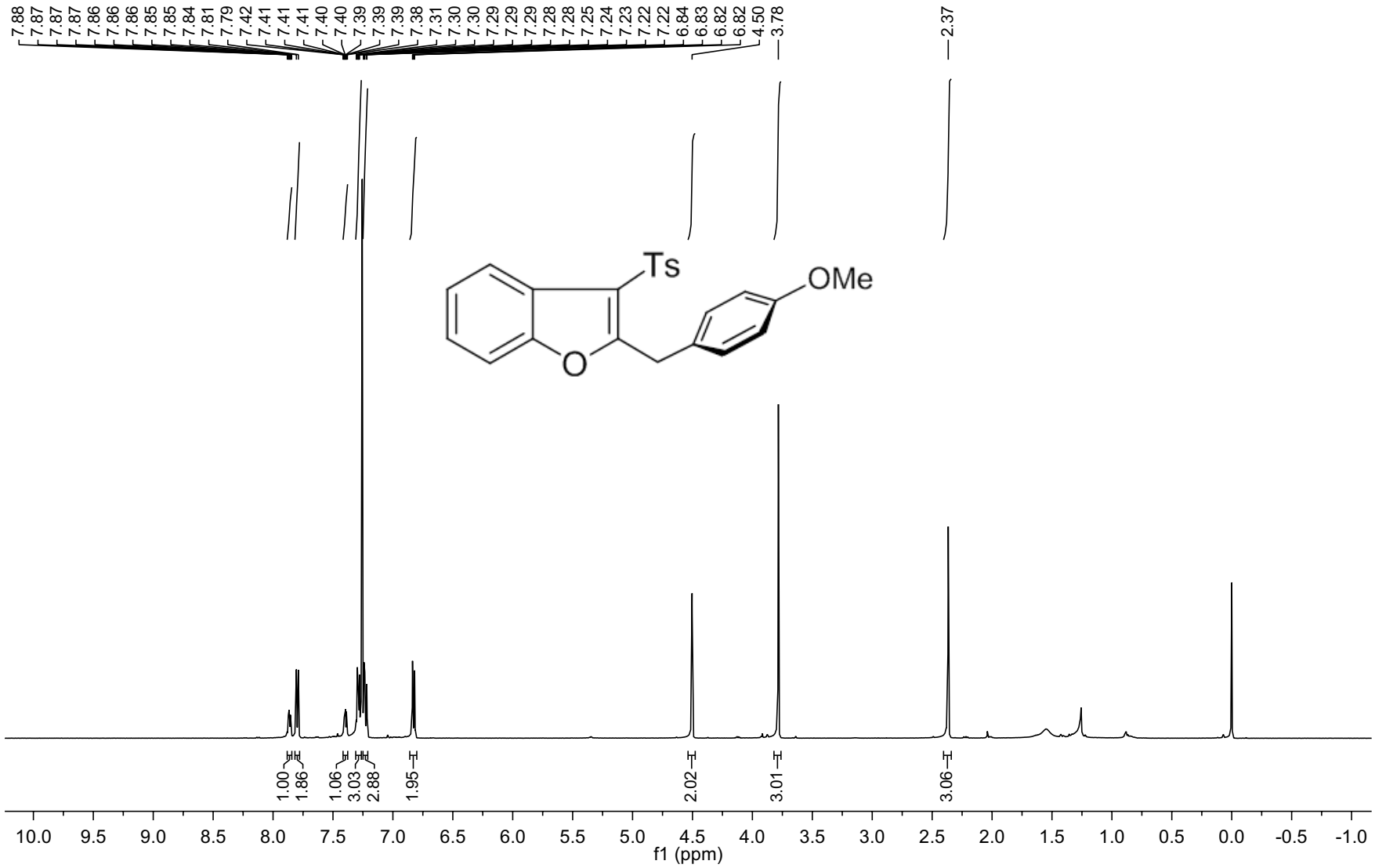
^{1}H NMR Spectroscopy of **4ia**



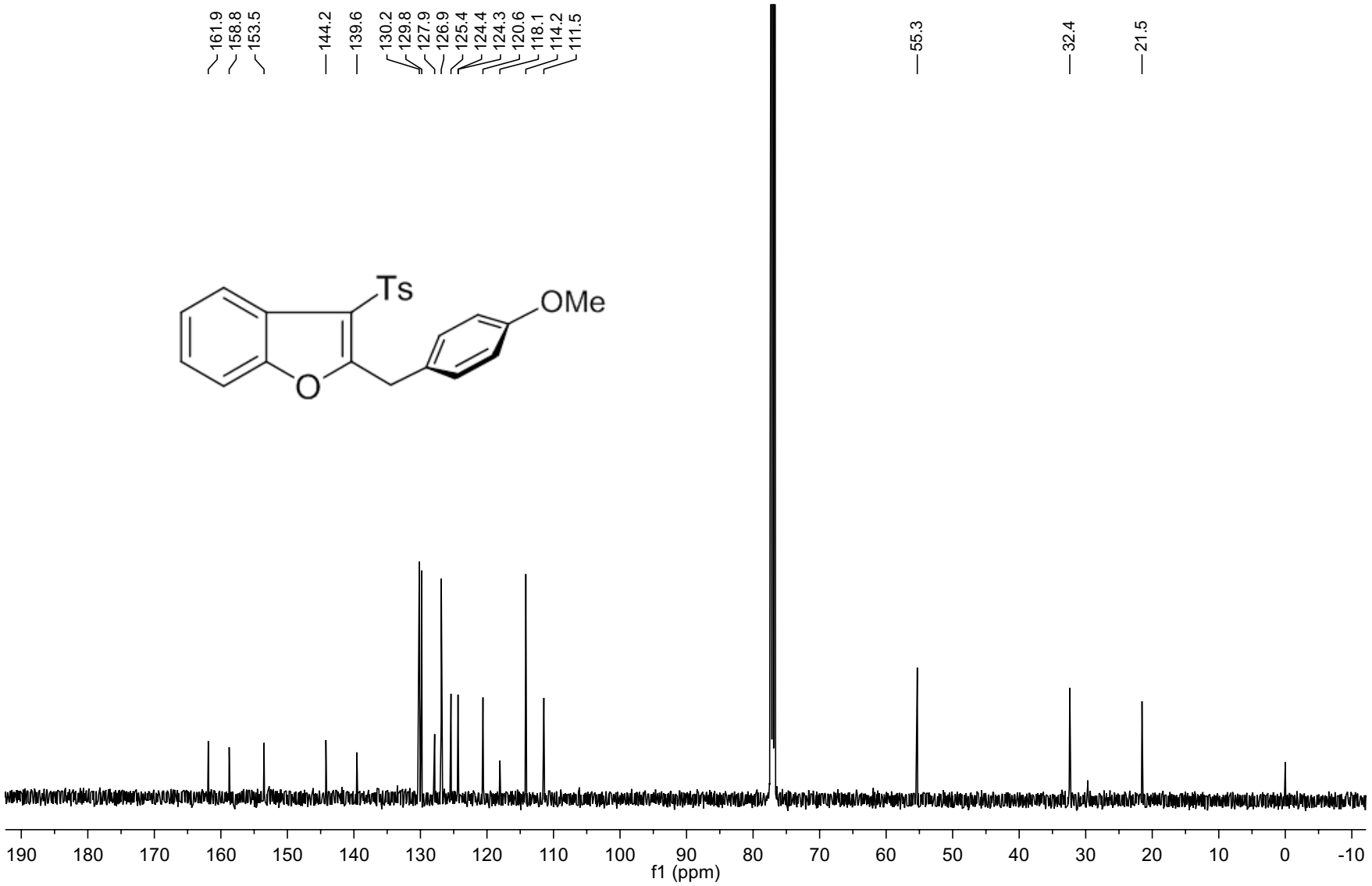
^{13}C NMR Spectroscopy of **4ia**



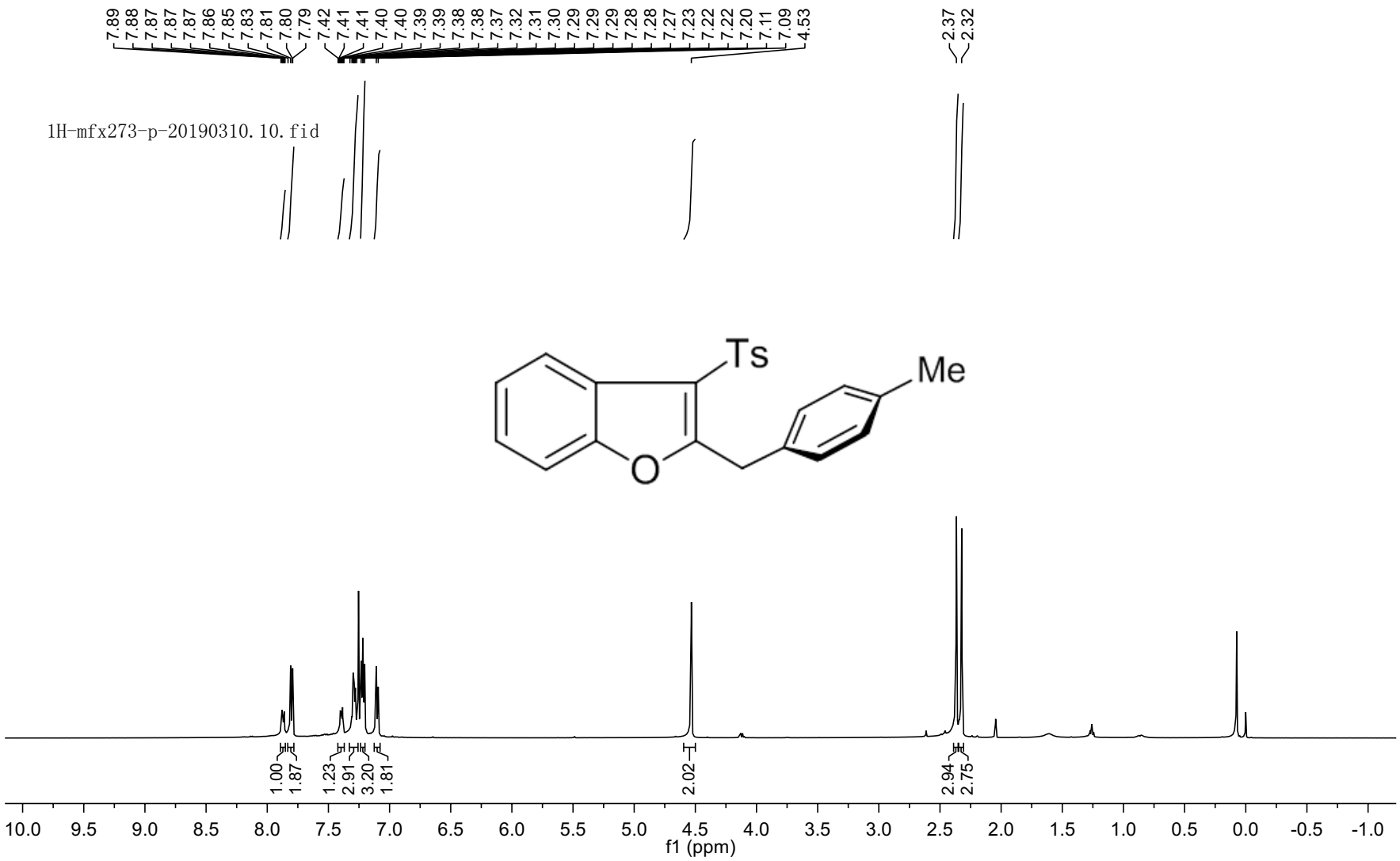
^{1}H NMR Spectroscopy of **4ja**



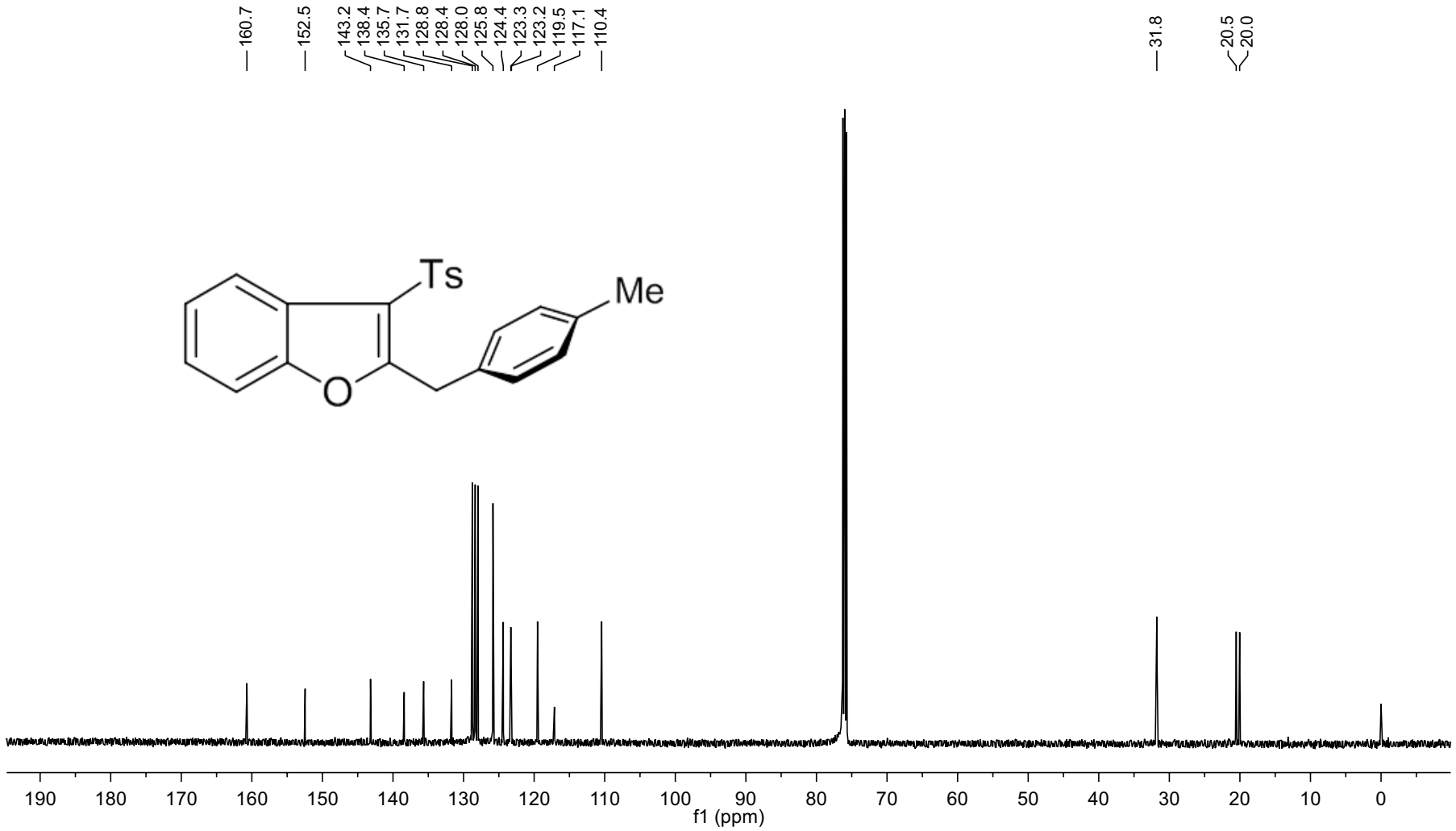
^{13}C NMR Spectroscopy of **4ja**



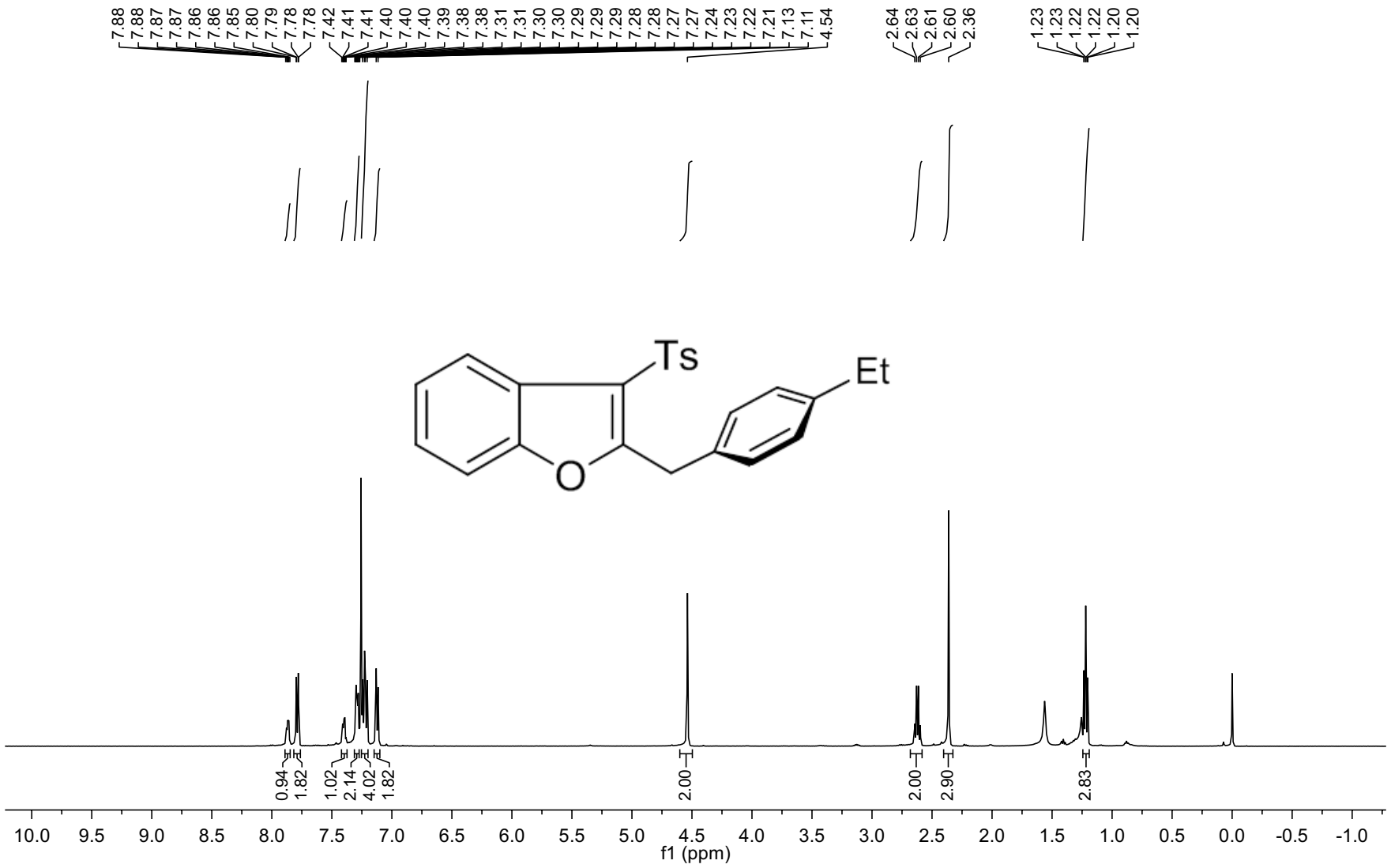
^{1}H NMR Spectroscopy of **4ka**



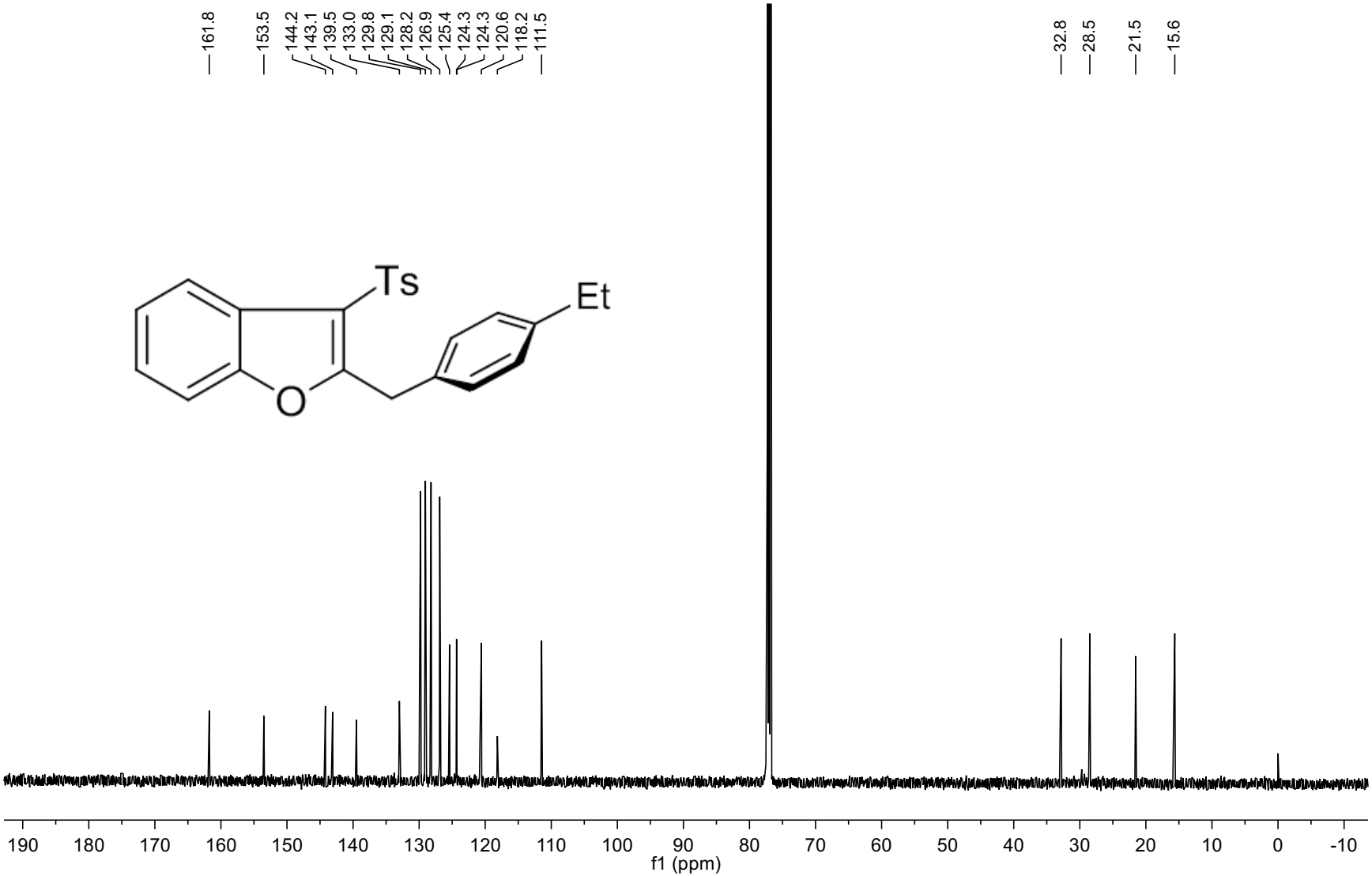
^{13}C NMR Spectroscopy of **4ka**



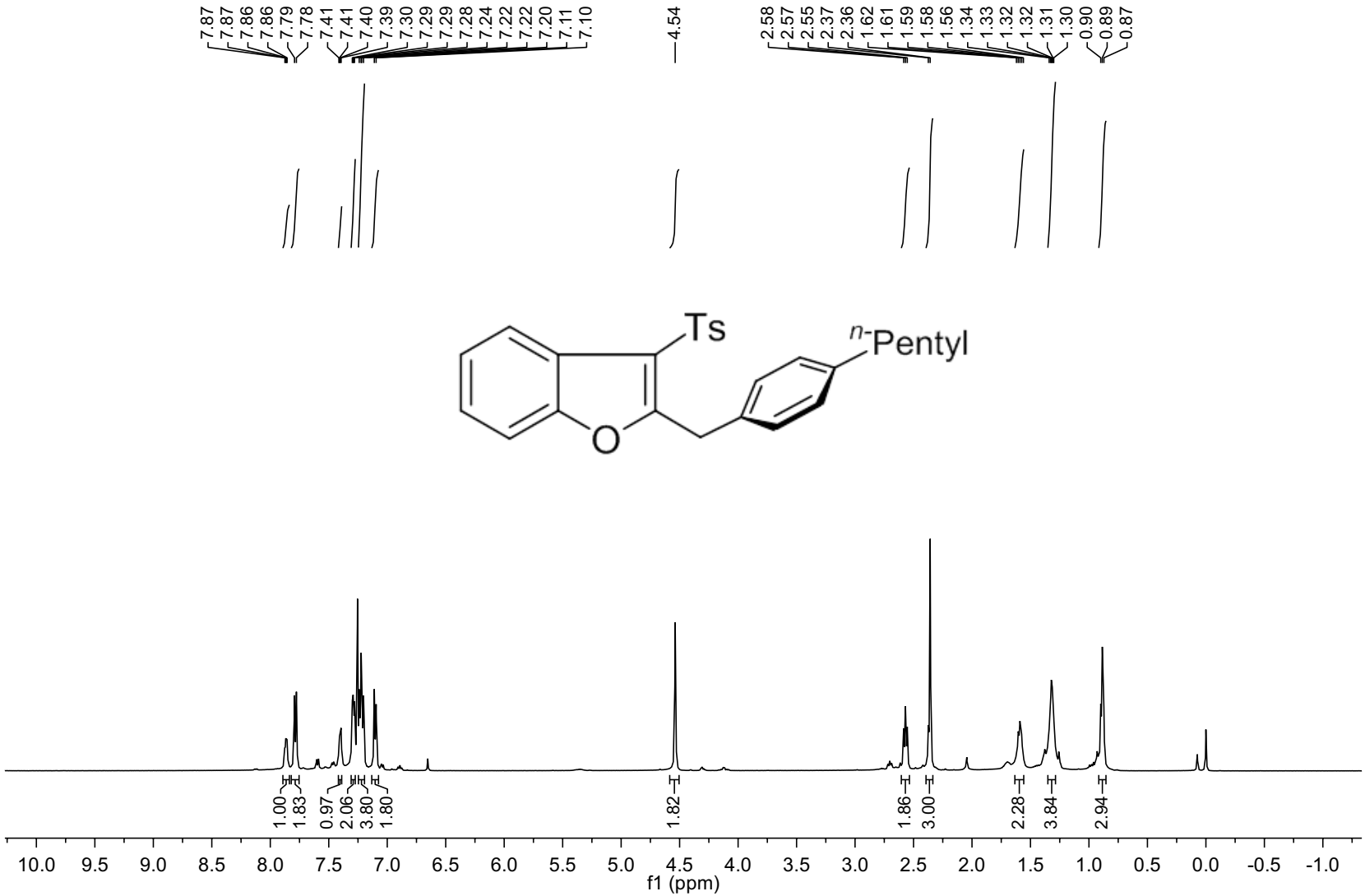
^{1}H NMR Spectroscopy of **4la**



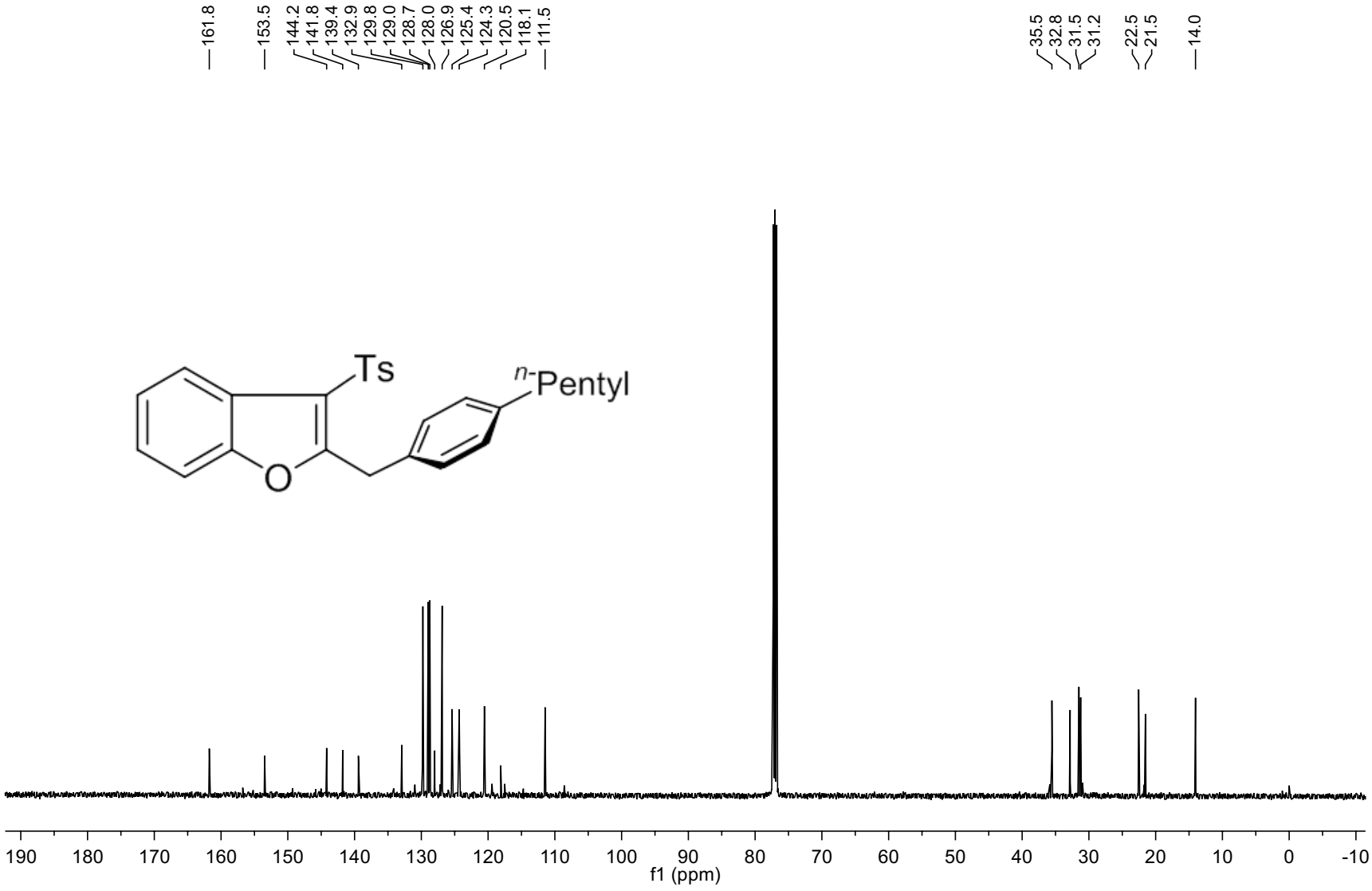
^{13}C NMR Spectroscopy of **4la**



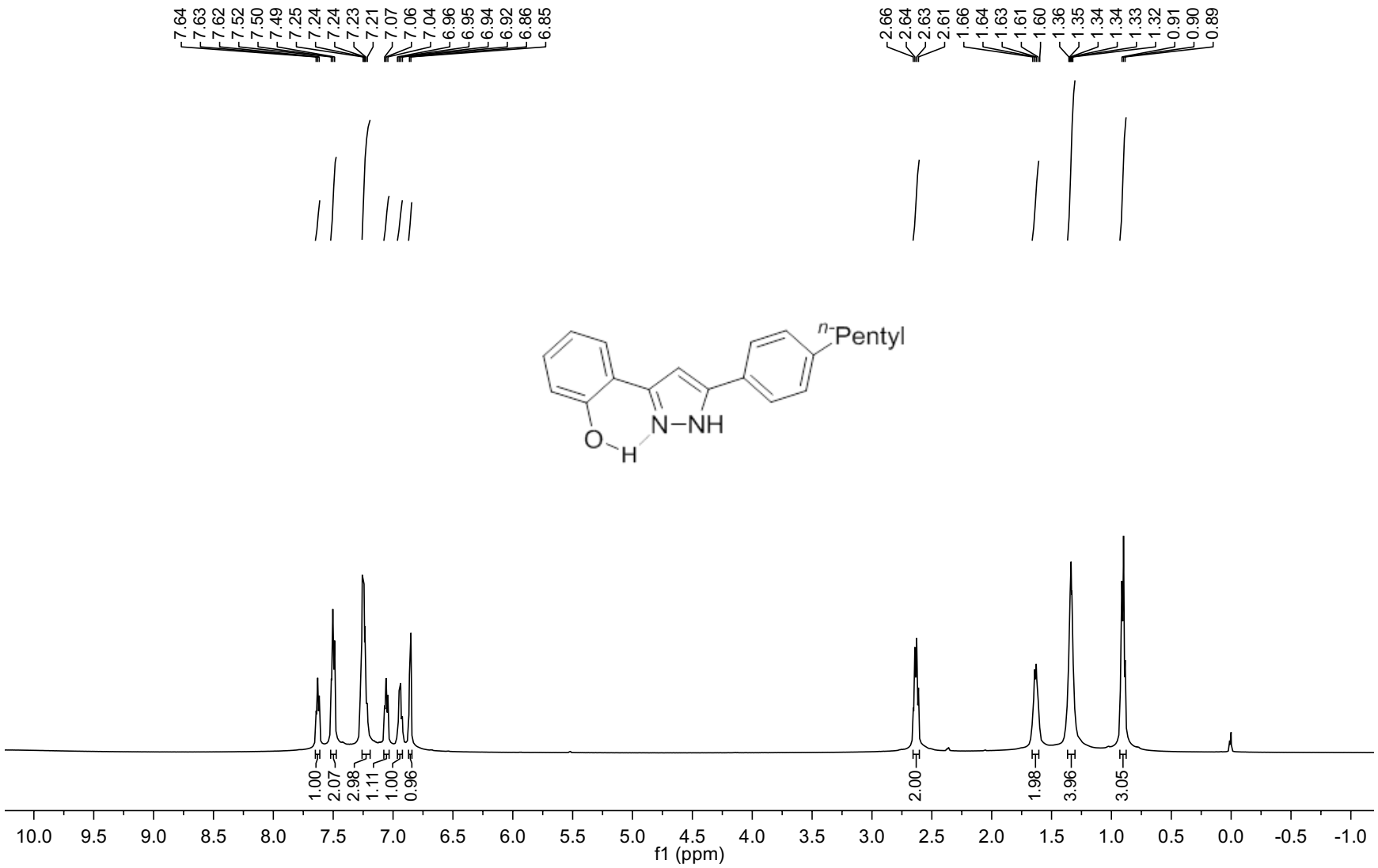
^{1}H NMR Spectroscopy of **4ma**



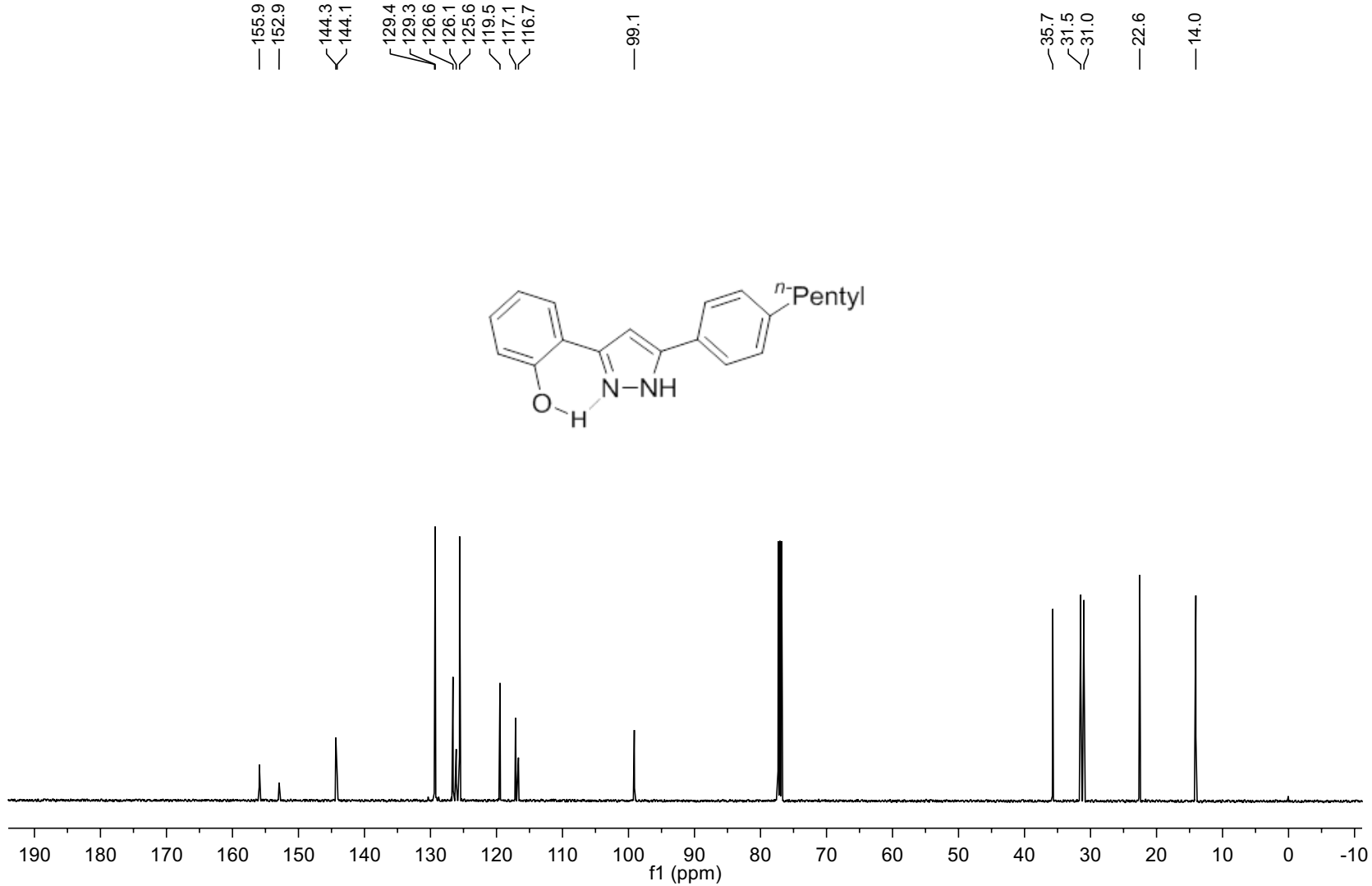
^{13}C NMR Spectroscopy of **4ma**



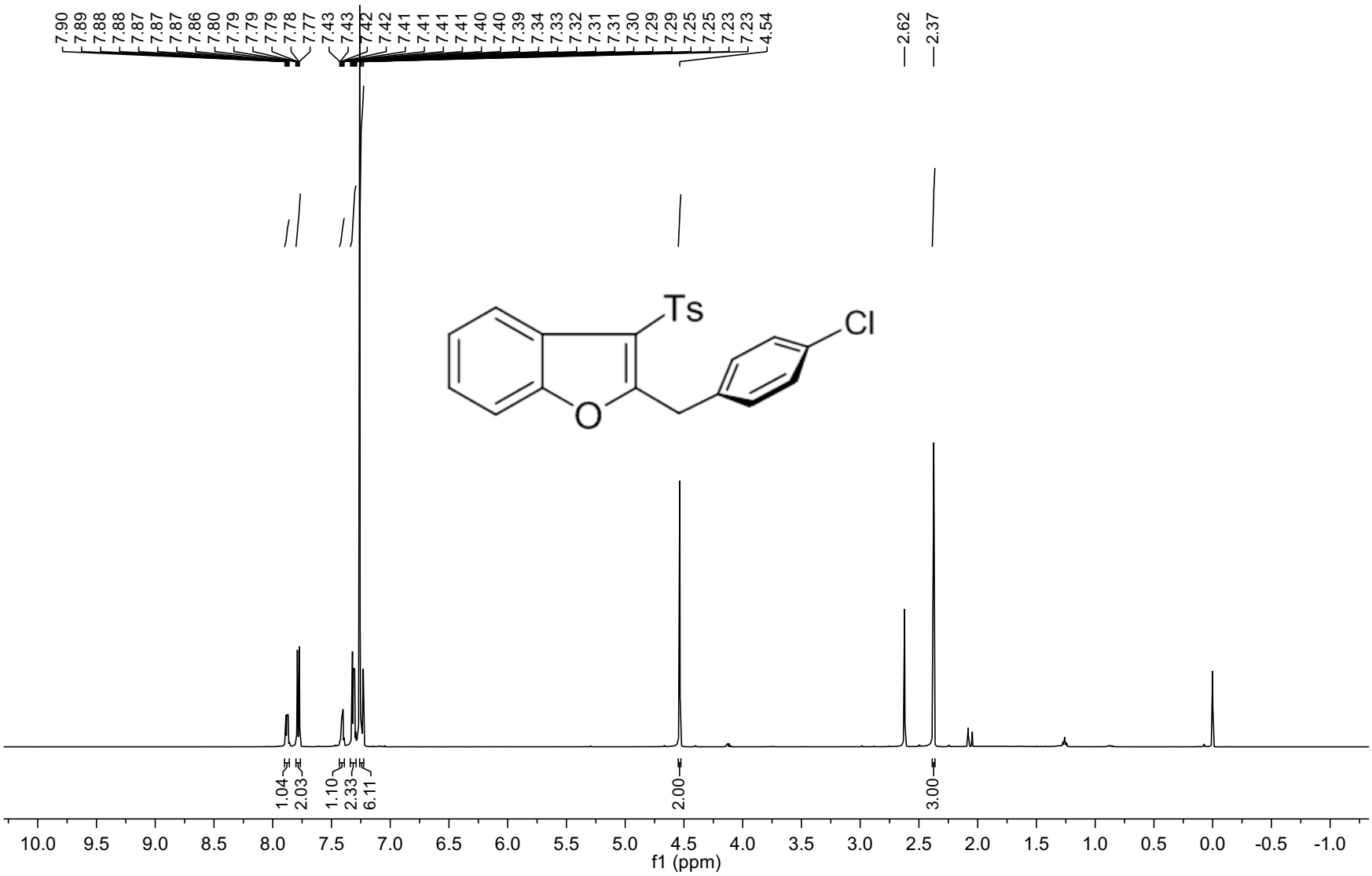
^{1}H NMR Spectroscopy of **4ma'**



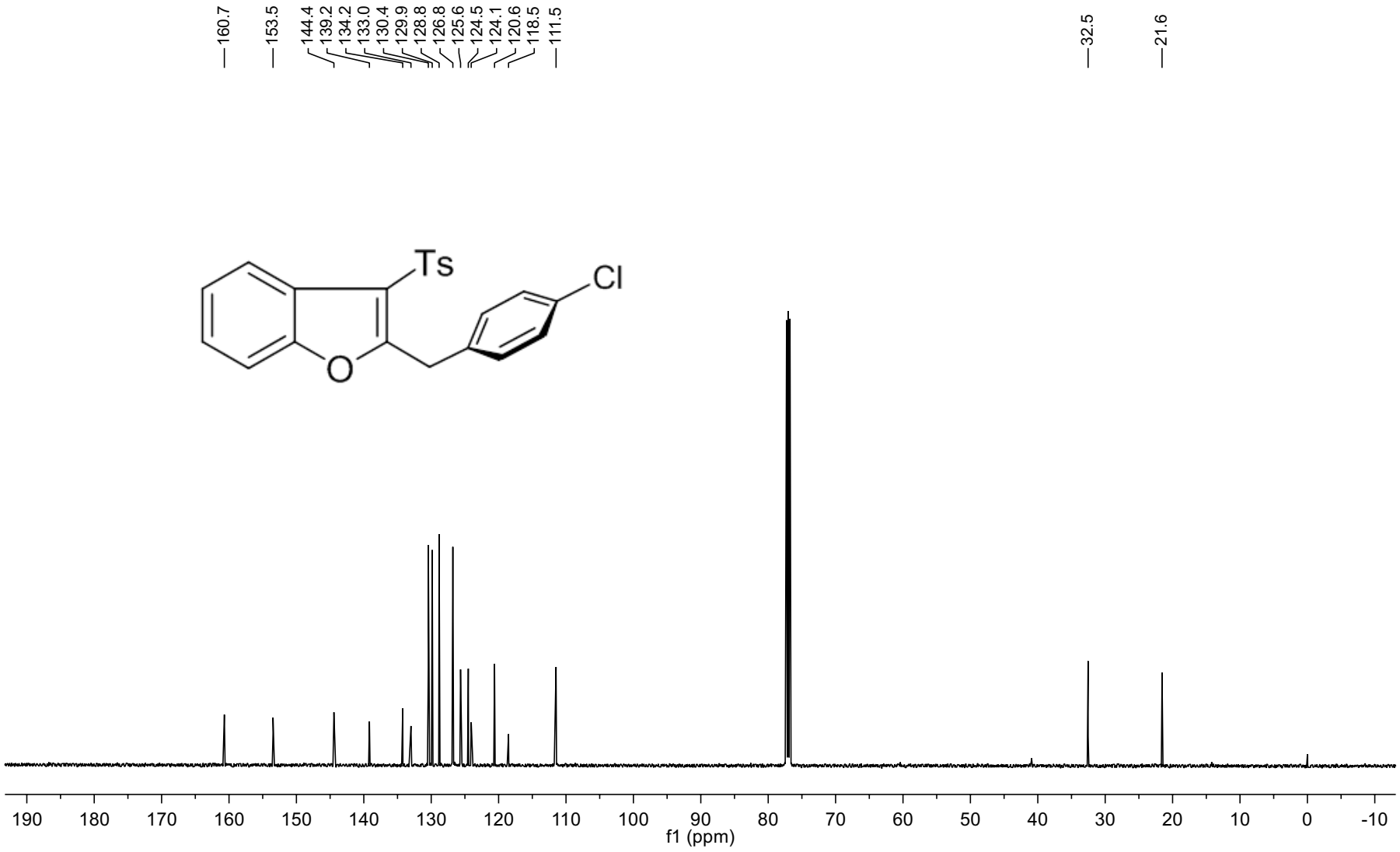
^{13}C NMR Spectroscopy of **4ma'**



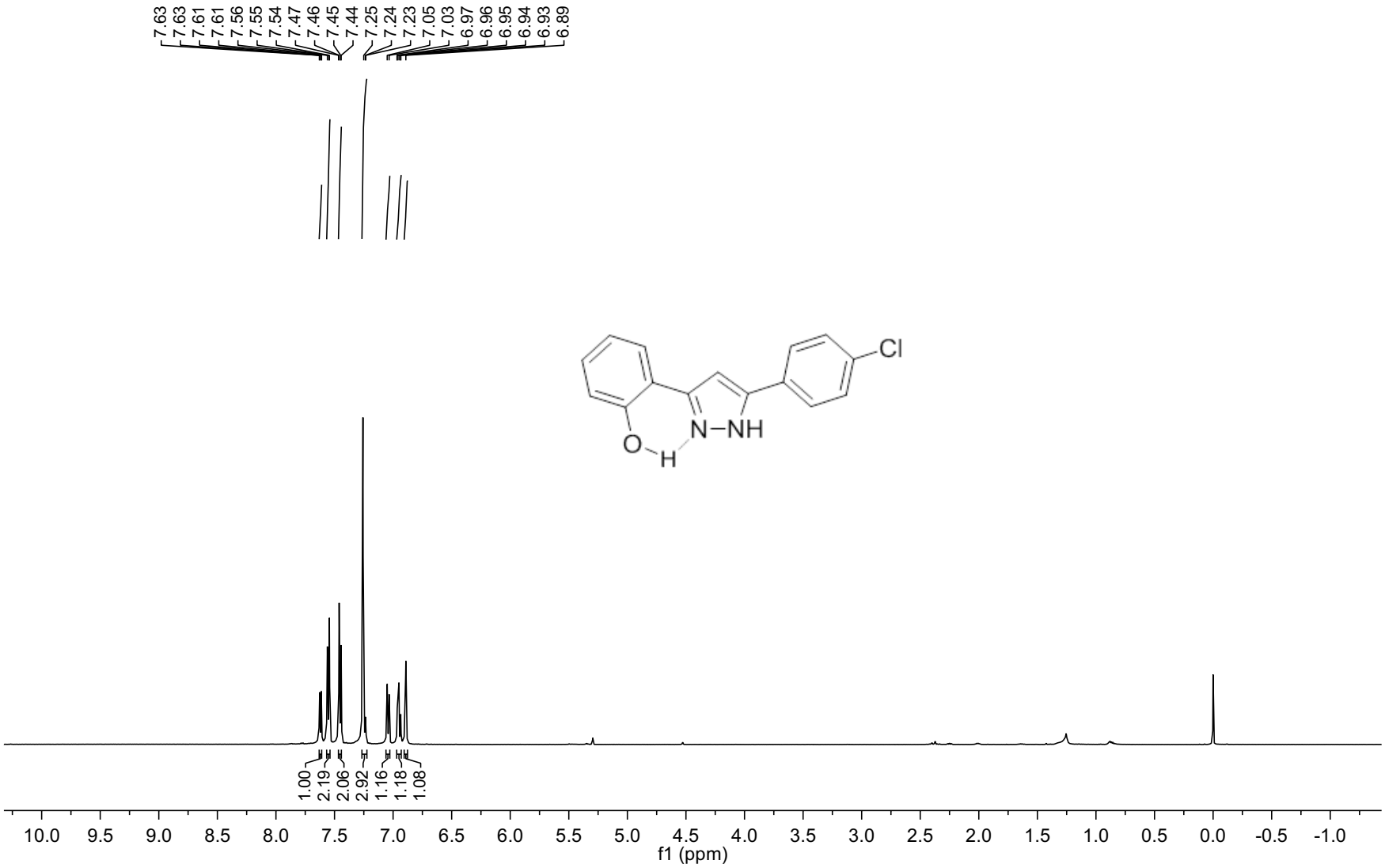
^{1}H NMR Spectroscopy of **4na**



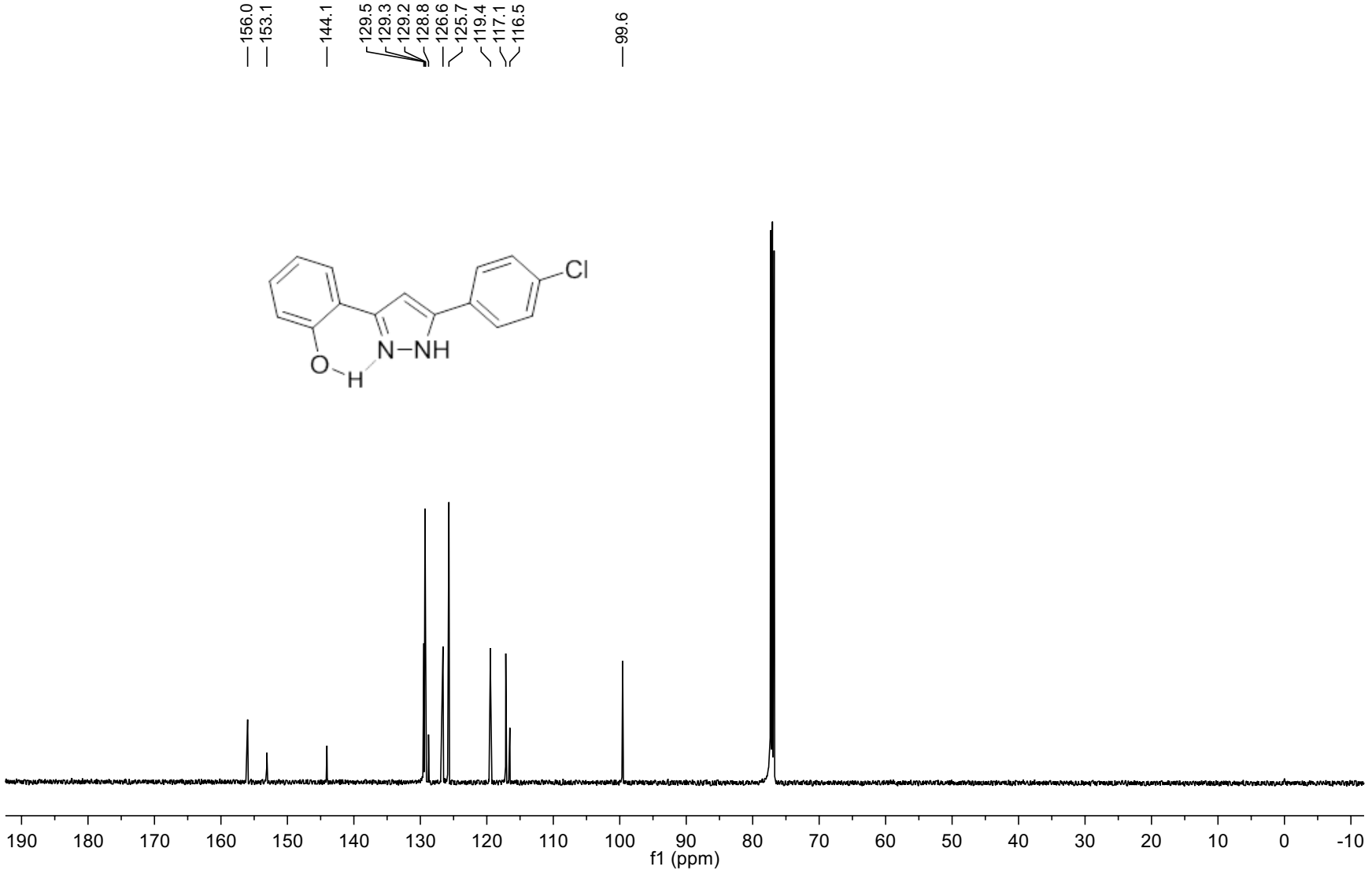
^{13}C NMR Spectroscopy of **4na**



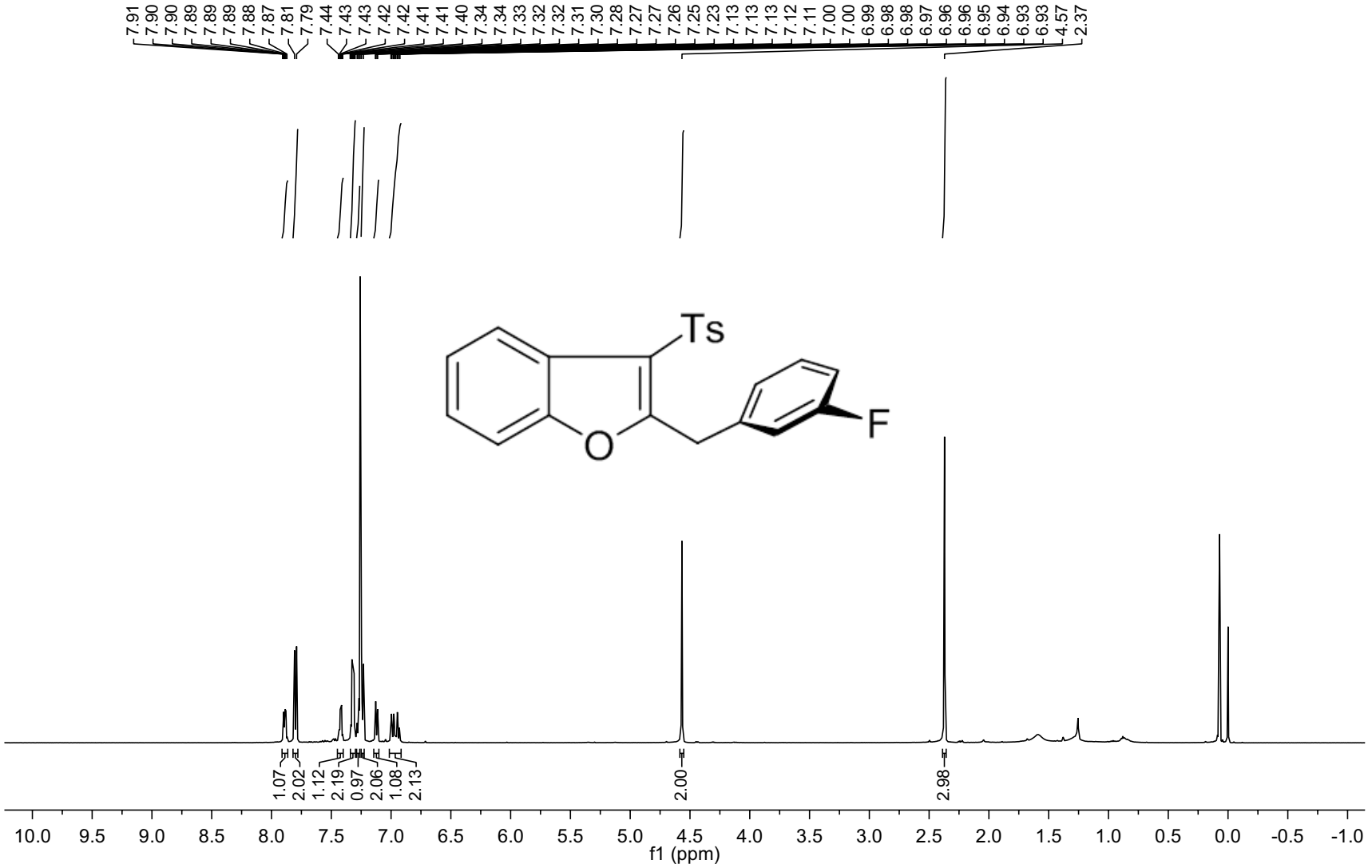
^{1}H NMR Spectroscopy of **4na'**



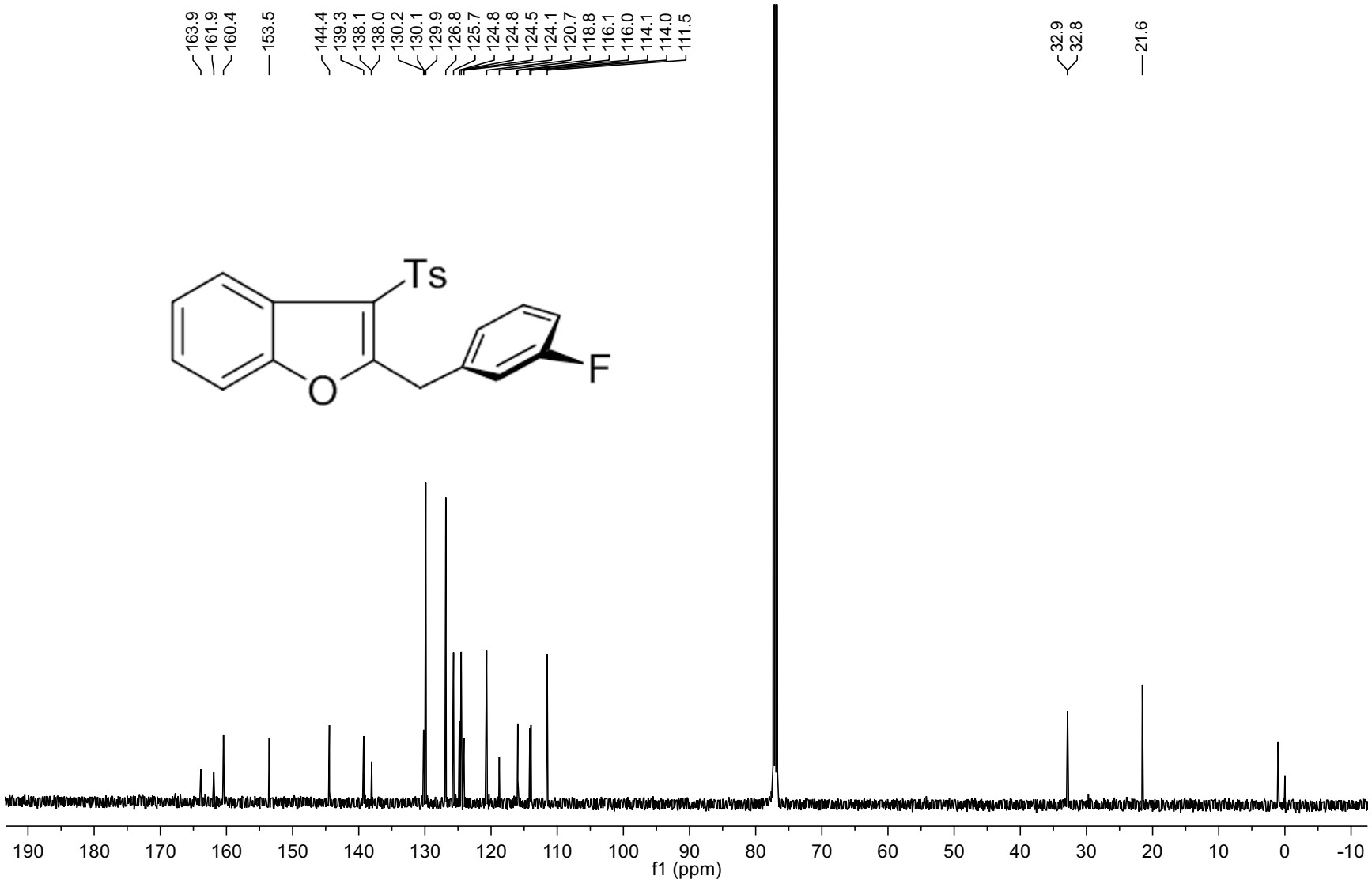
^{13}C NMR Spectroscopy of **4na'**



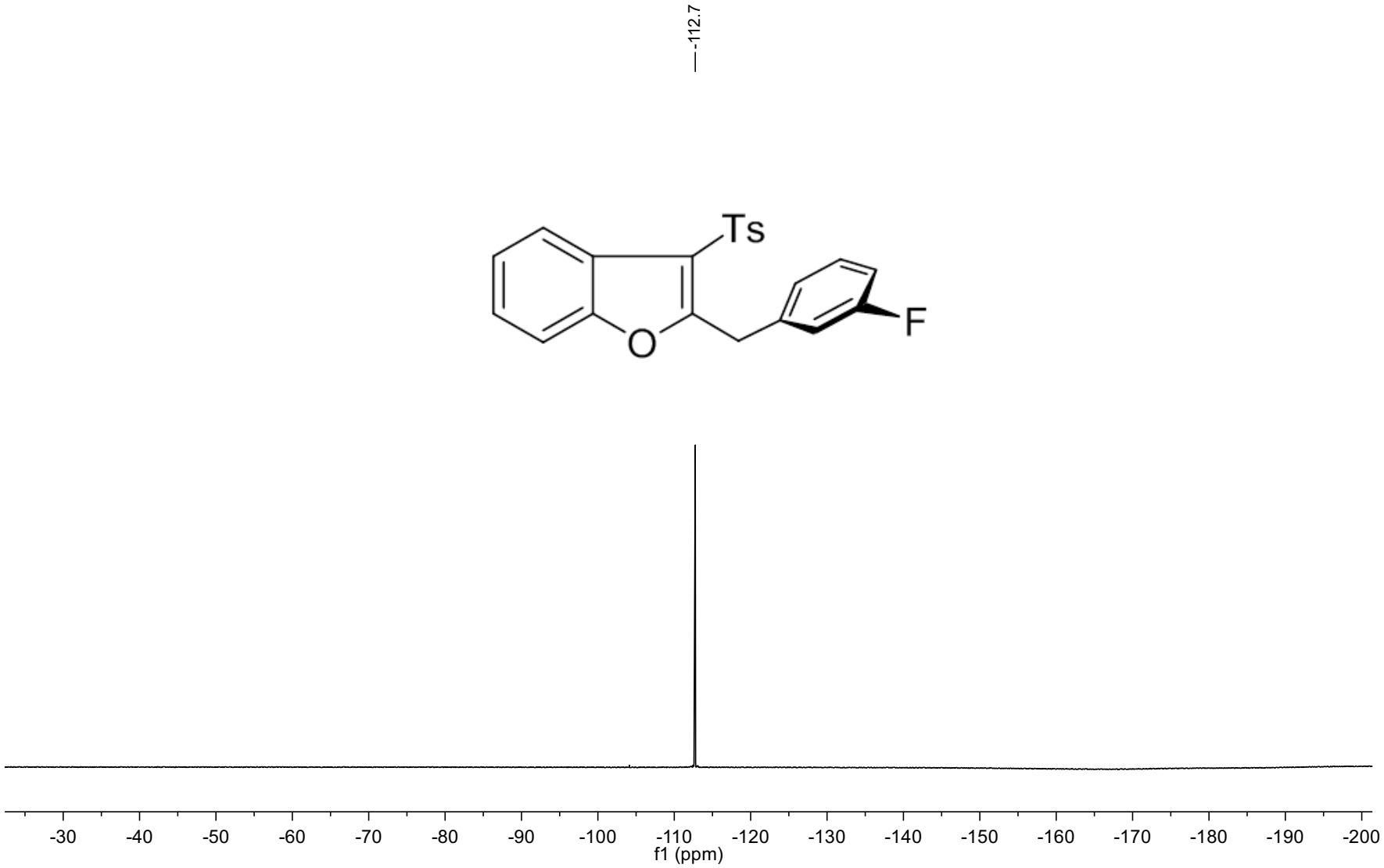
^{1}H NMR Spectroscopy of **4oa**



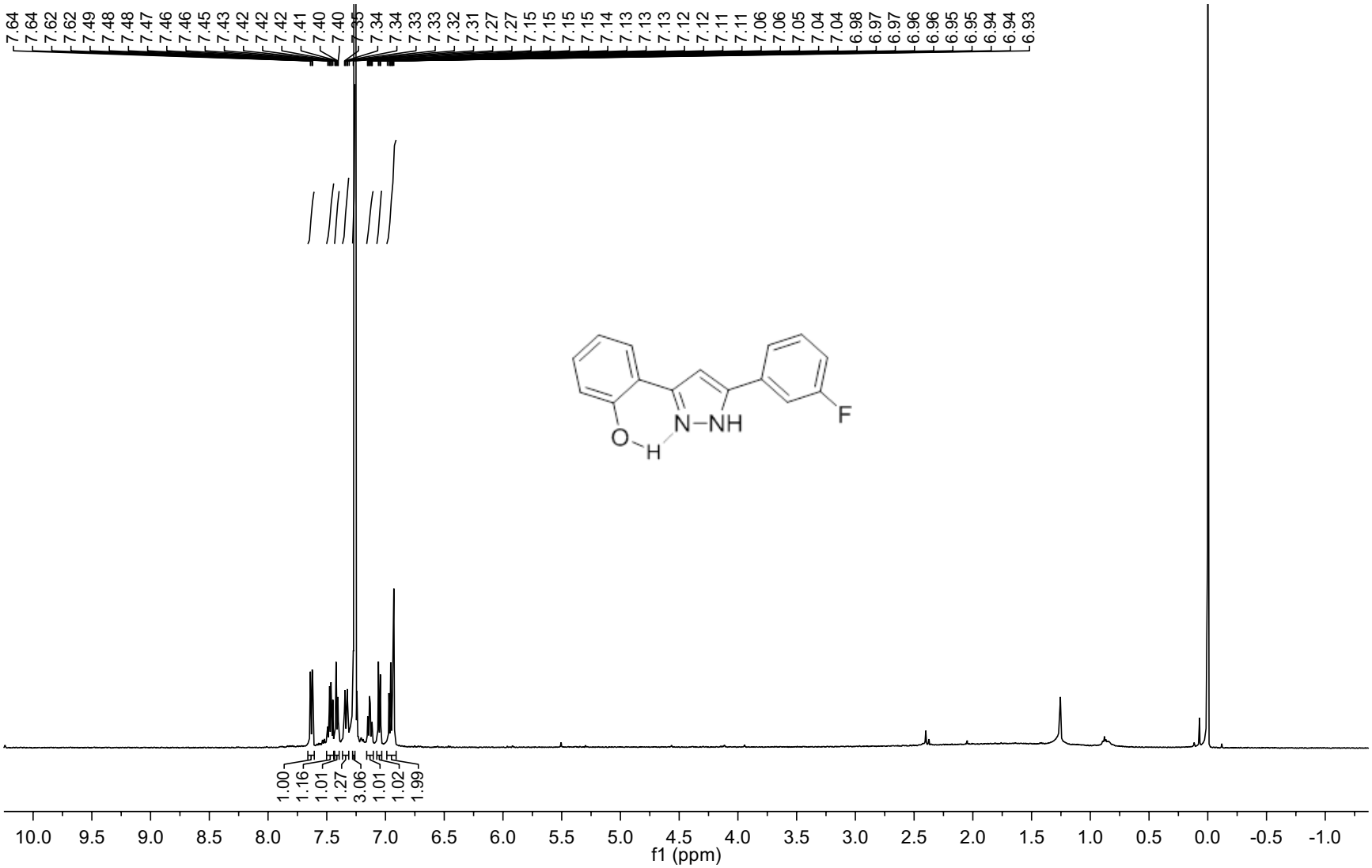
^{13}C NMR Spectroscopy of **4oa**



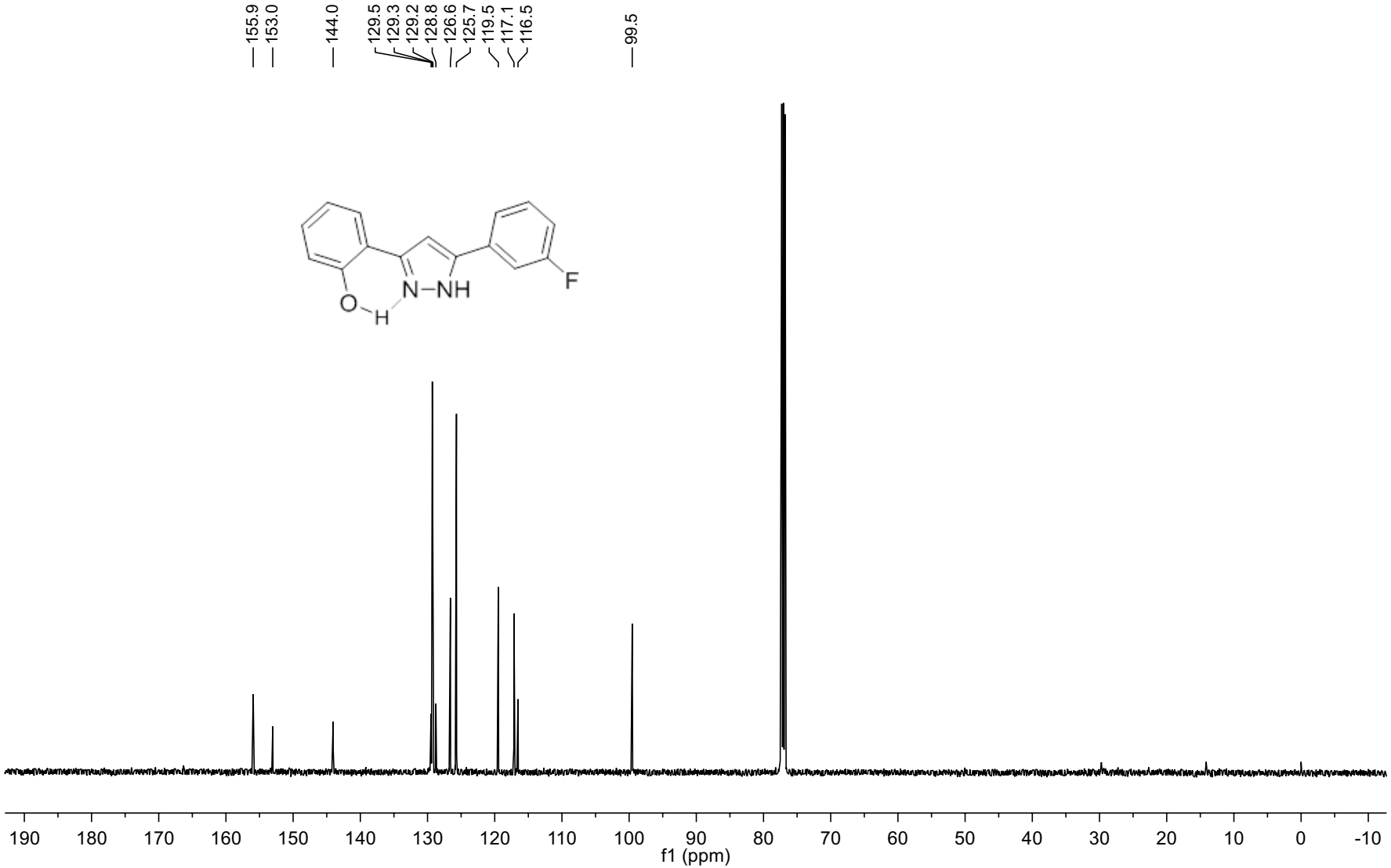
^{19}F NMR Spectroscopy of **4oa**



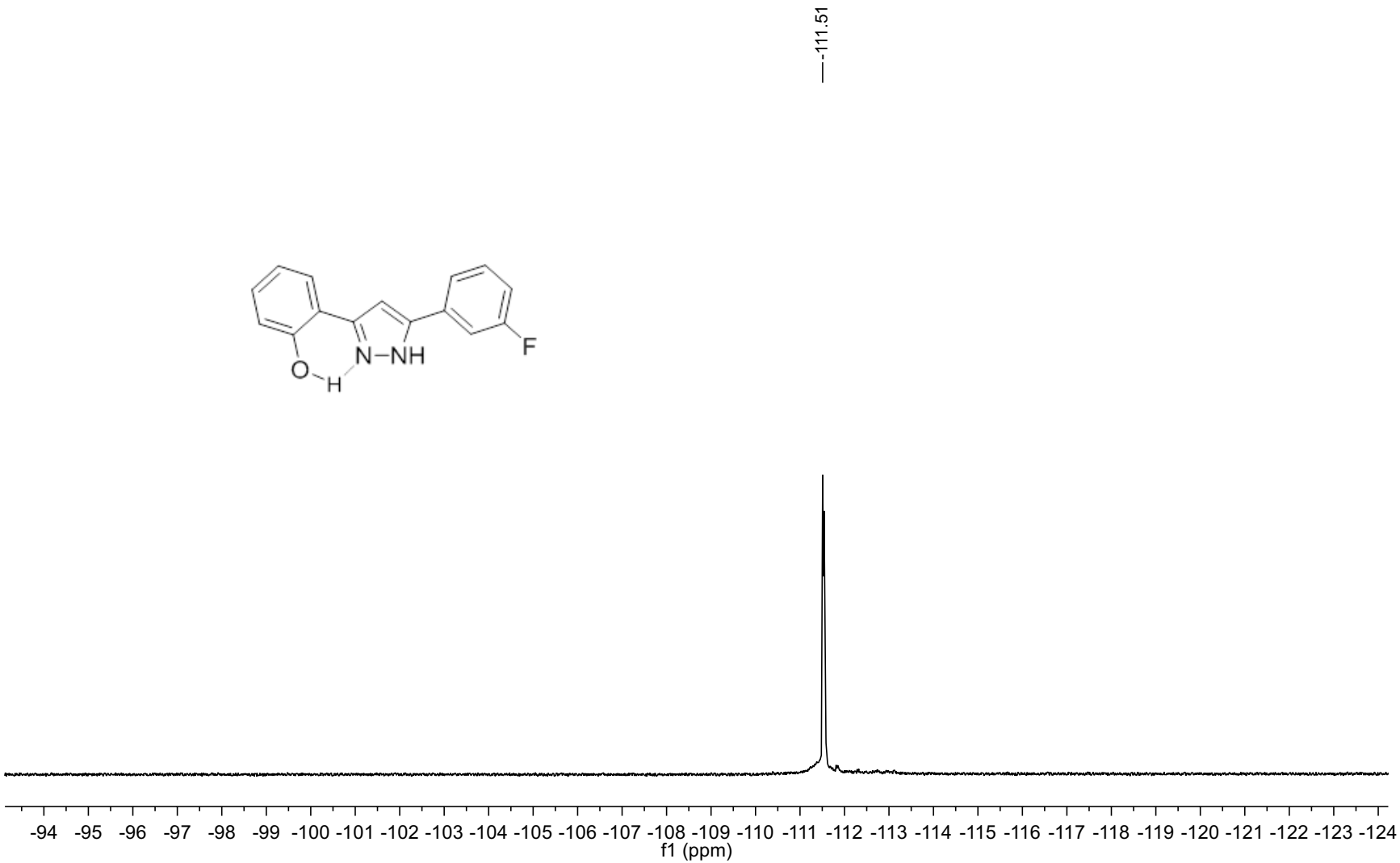
^{1}H NMR Spectroscopy of **4oa'**



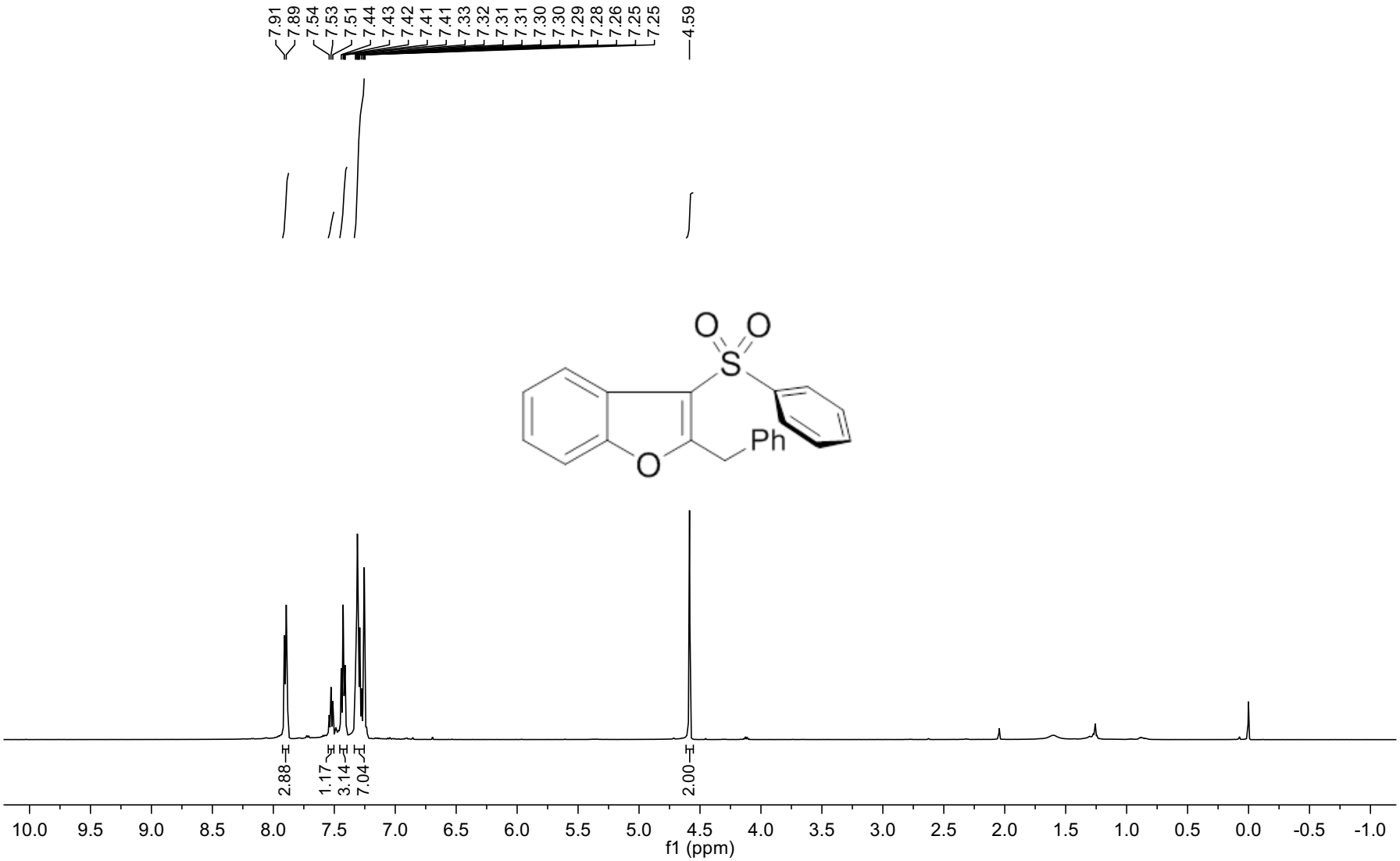
^{13}C NMR Spectroscopy of **4oa'**



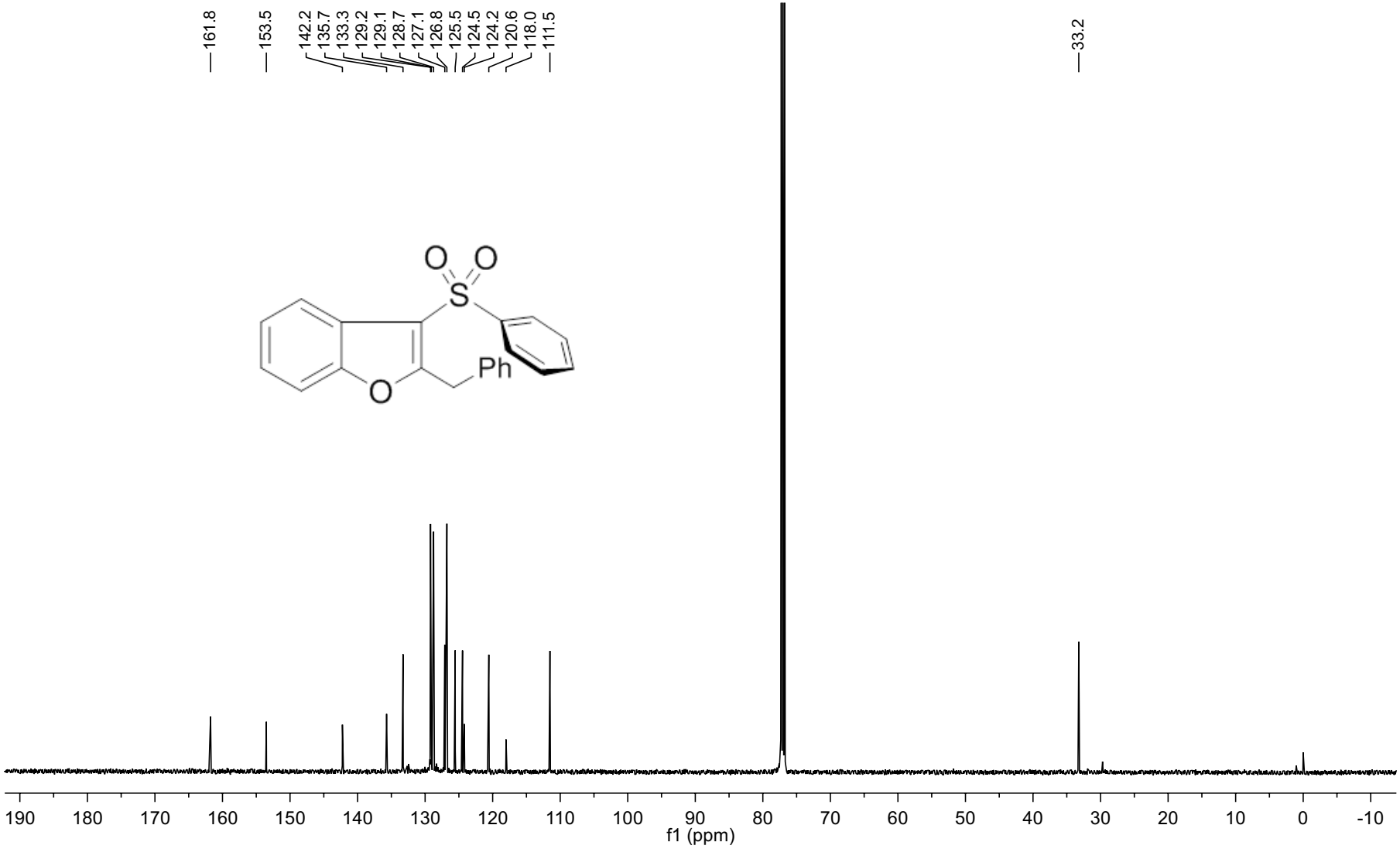
^{19}F NMR Spectroscopy of **4oa'**



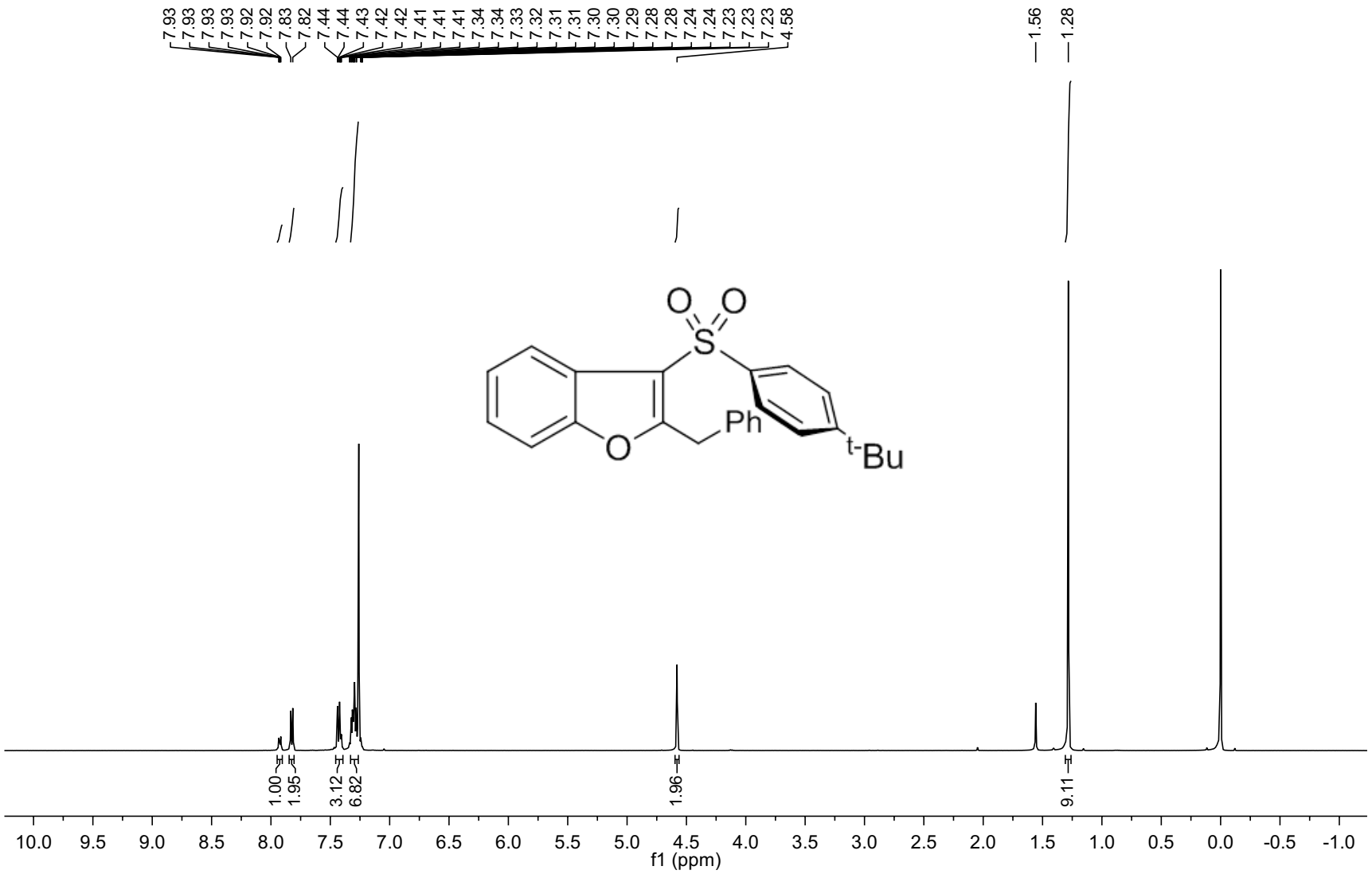
^{1}H NMR Spectroscopy of **4ab**



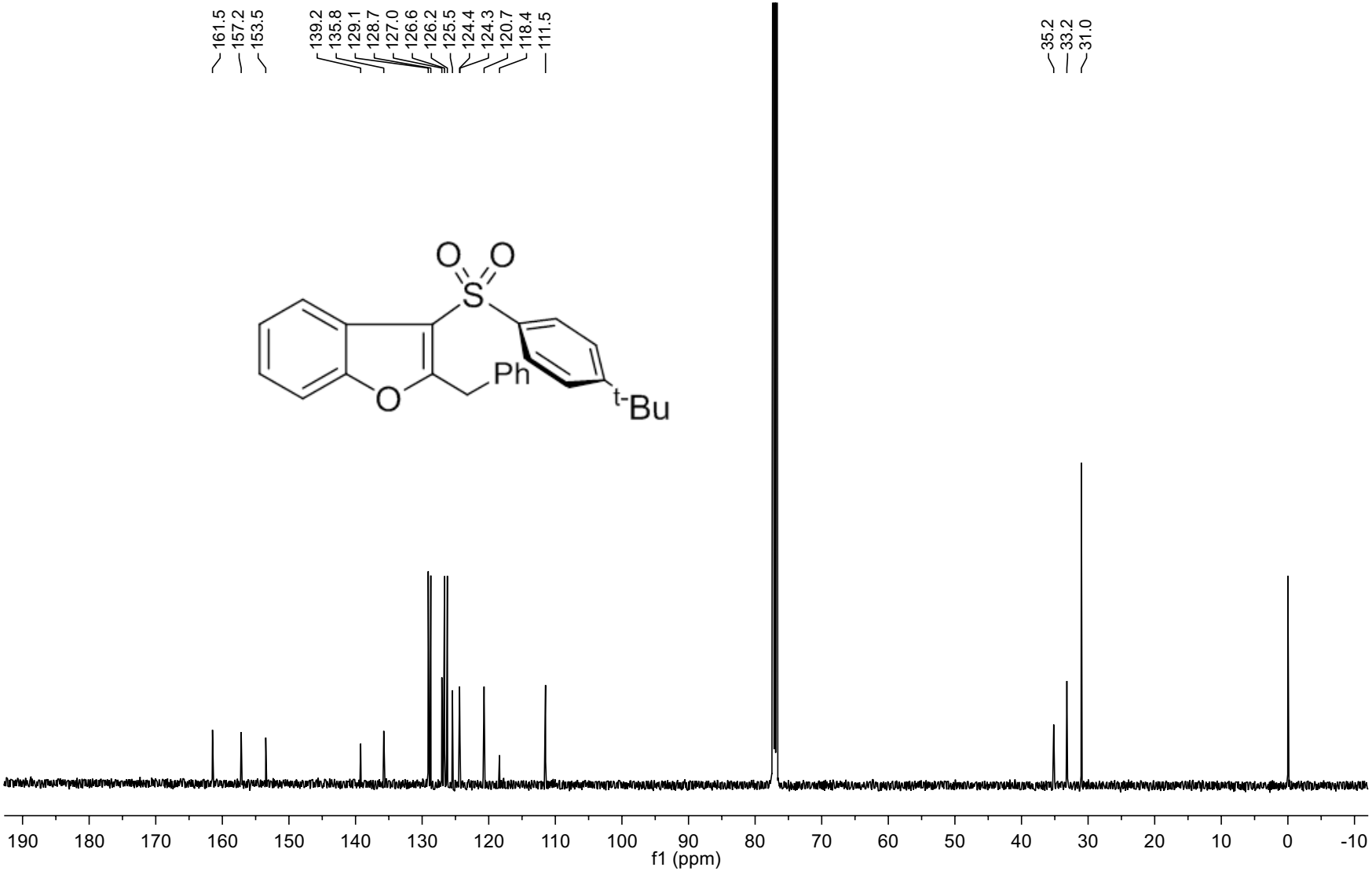
^{13}C NMR Spectroscopy of **4ab**



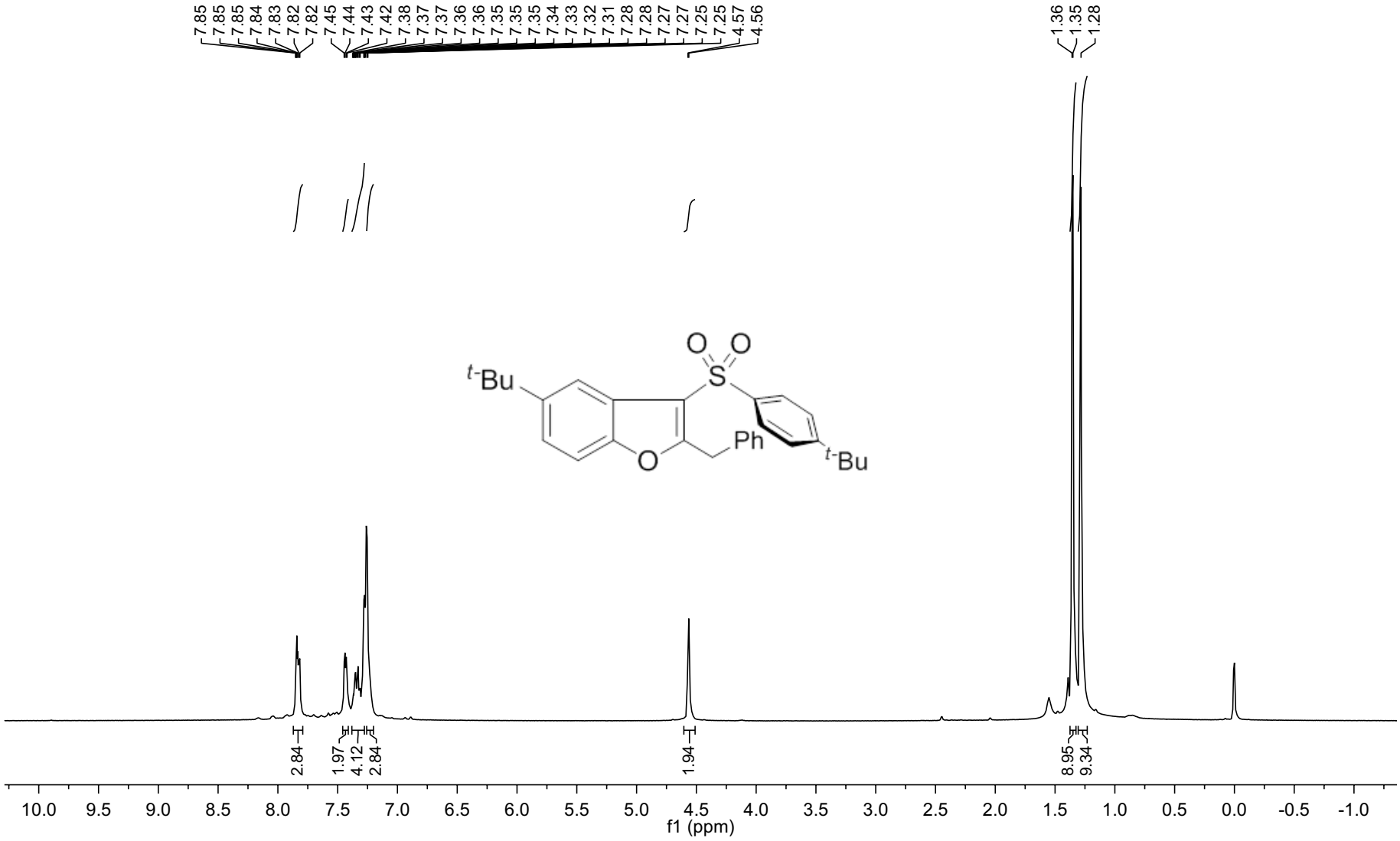
^{1}H NMR Spectroscopy of **4ac**



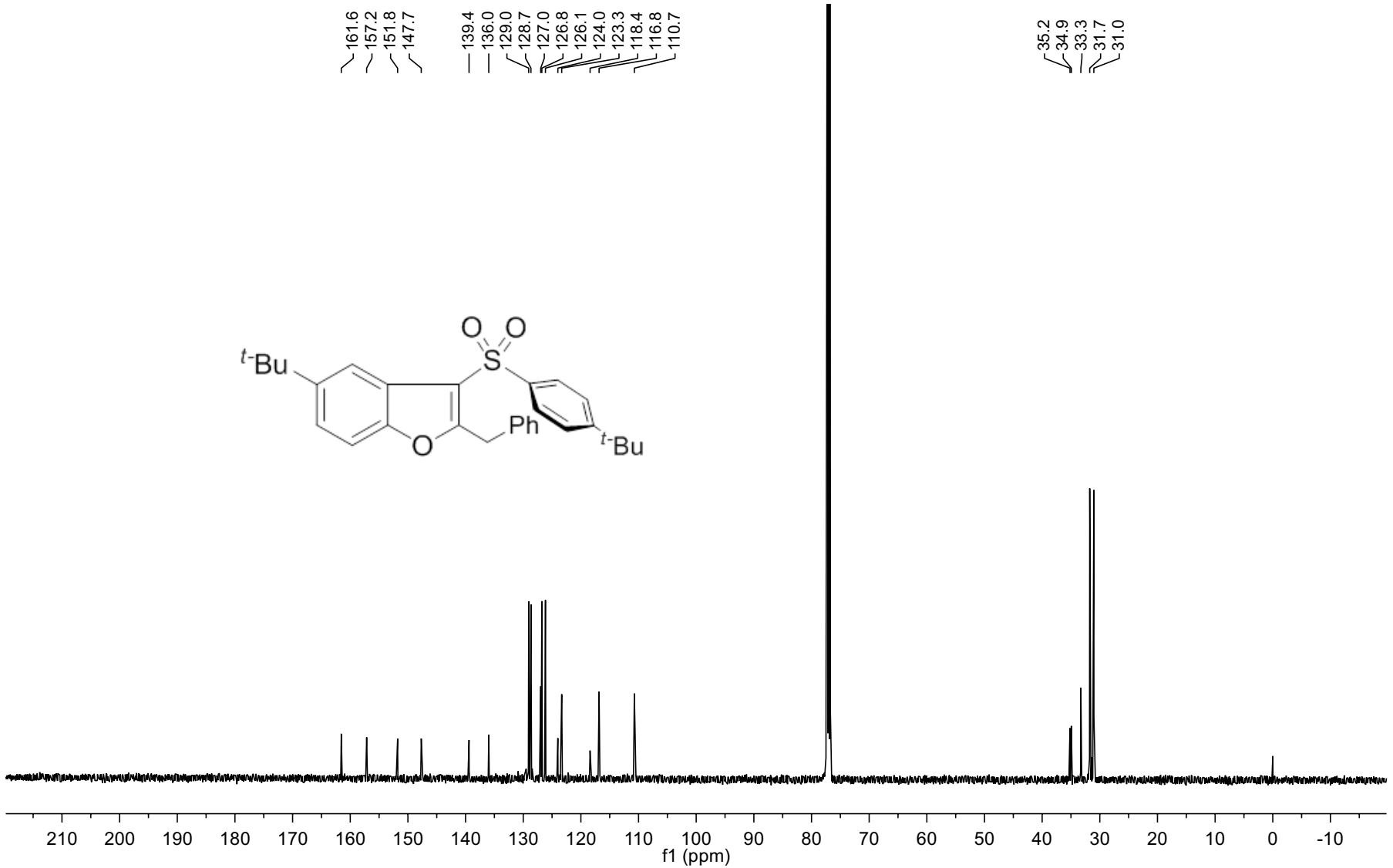
^{13}C NMR Spectroscopy of **4ac**



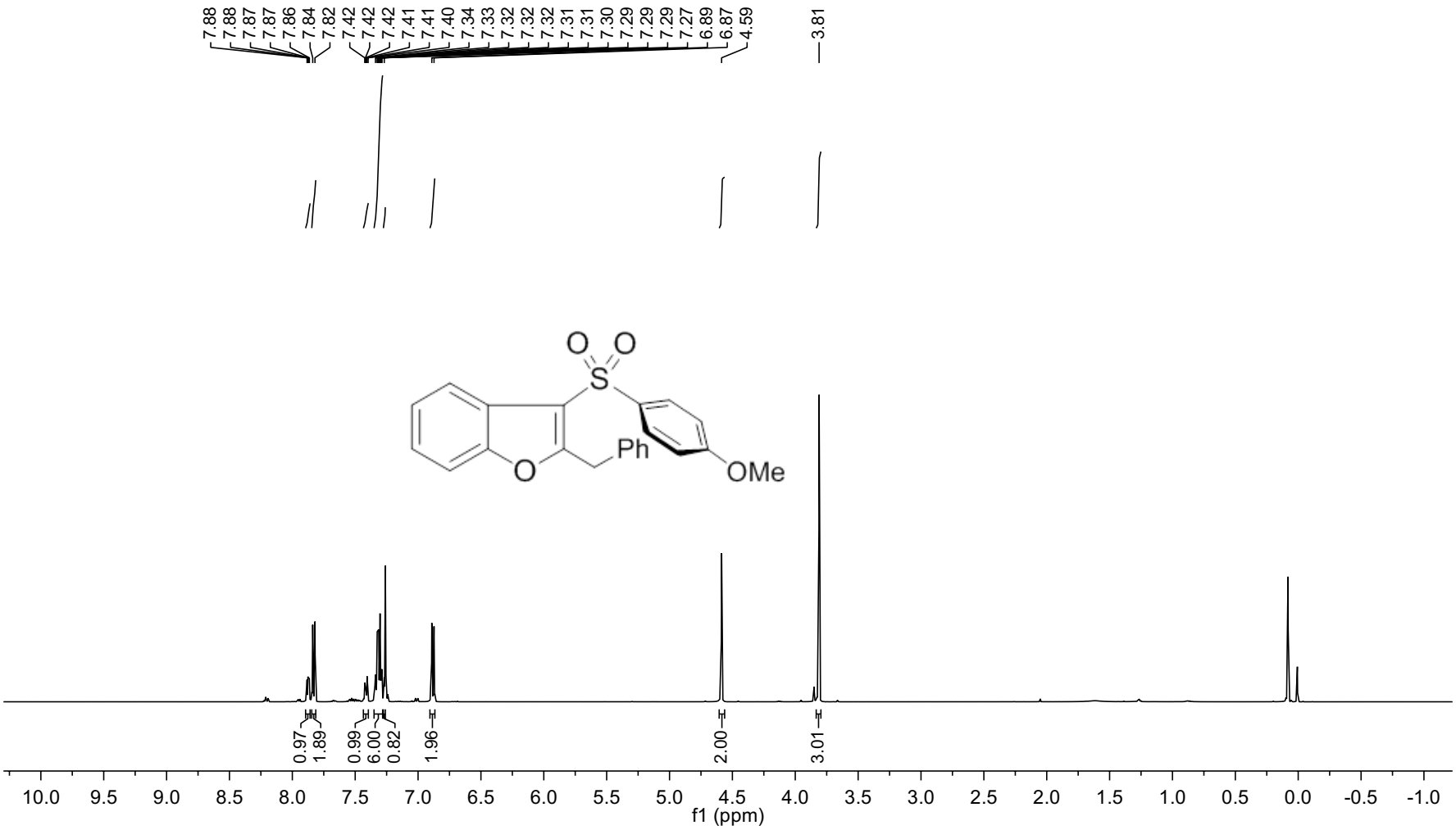
^{1}H NMR Spectroscopy of **4dc**



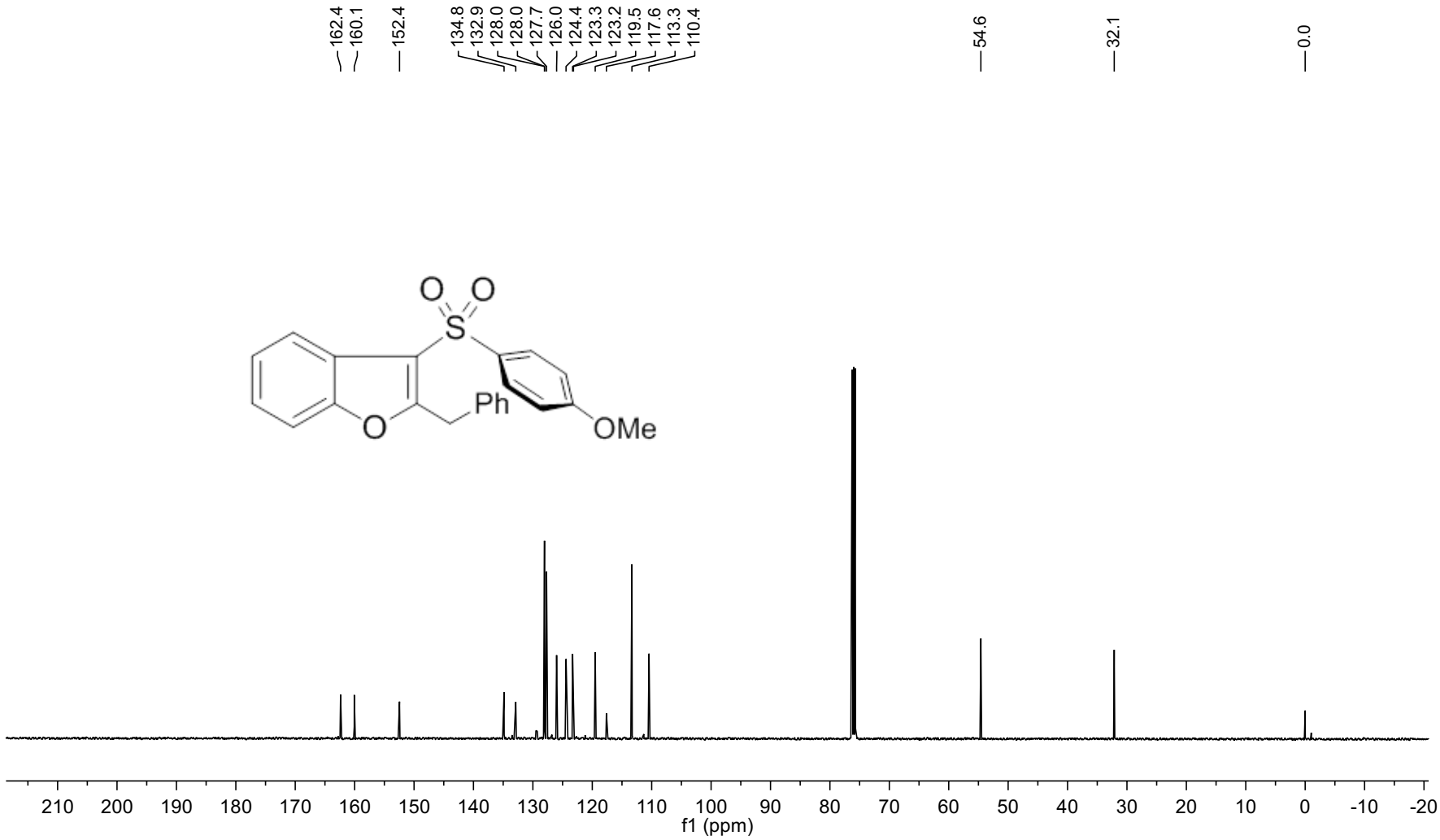
^{13}C NMR Spectroscopy of **4dc**



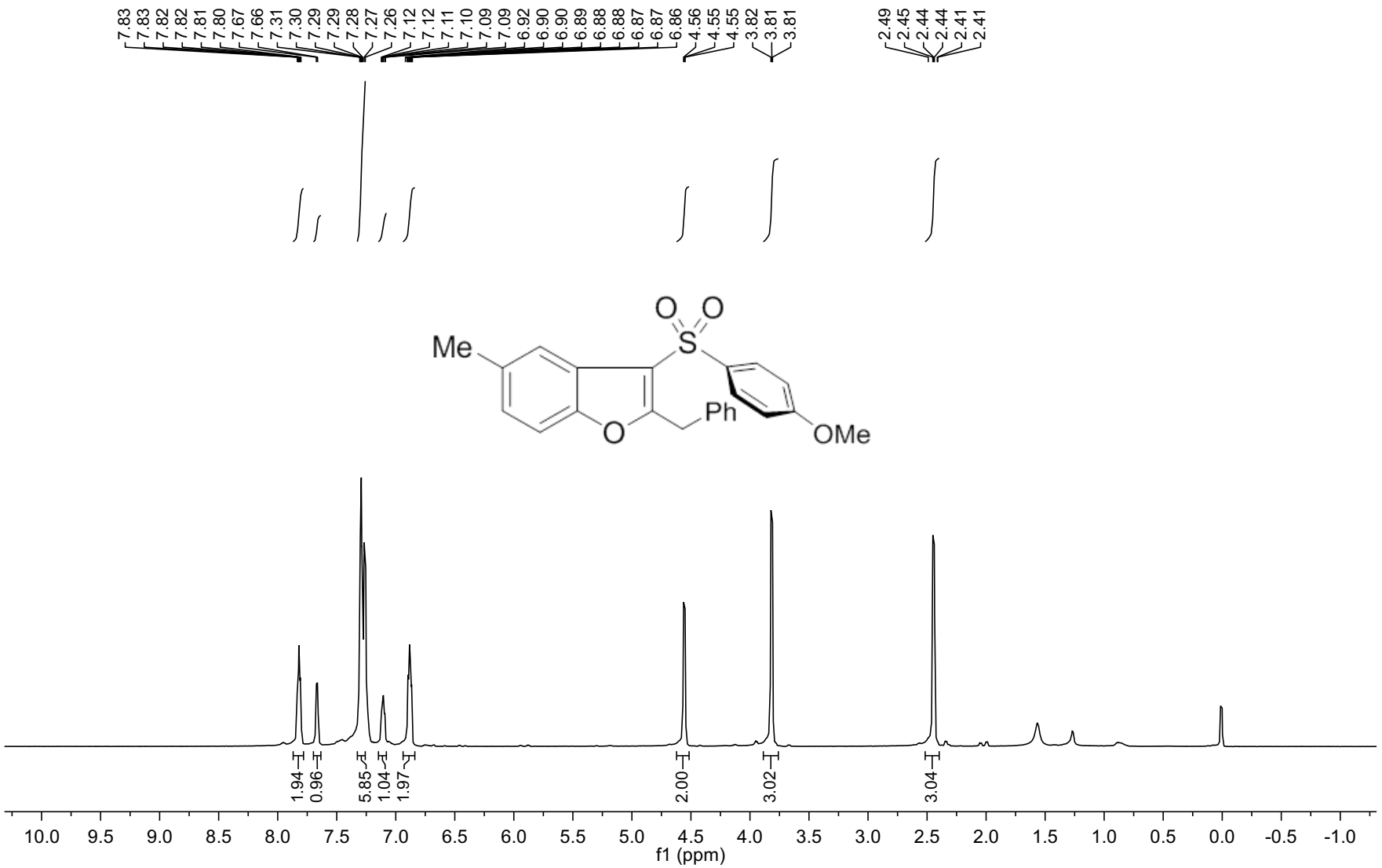
^{1}H NMR Spectroscopy of **4ad**



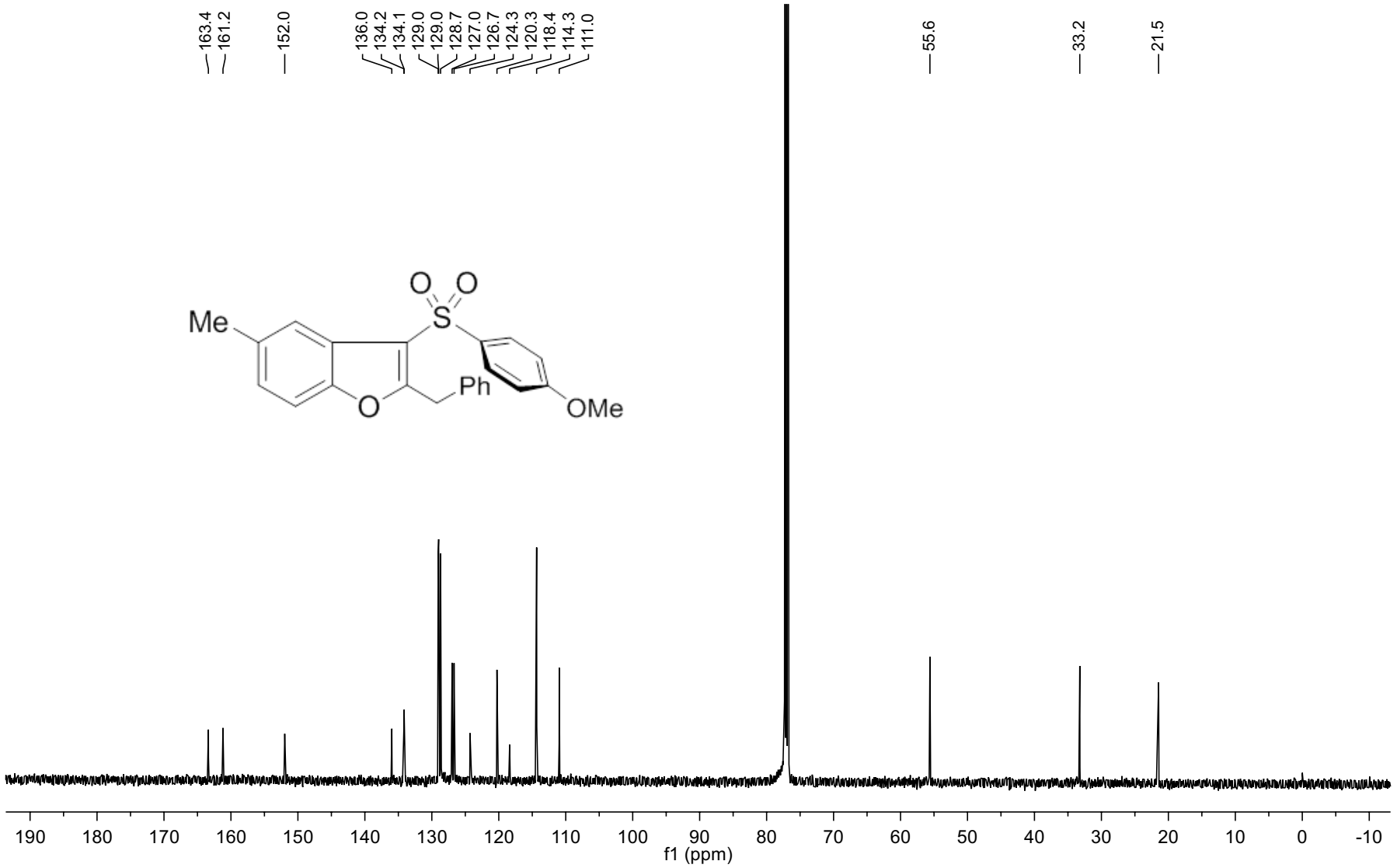
^{13}C NMR Spectroscopy of **4ad**



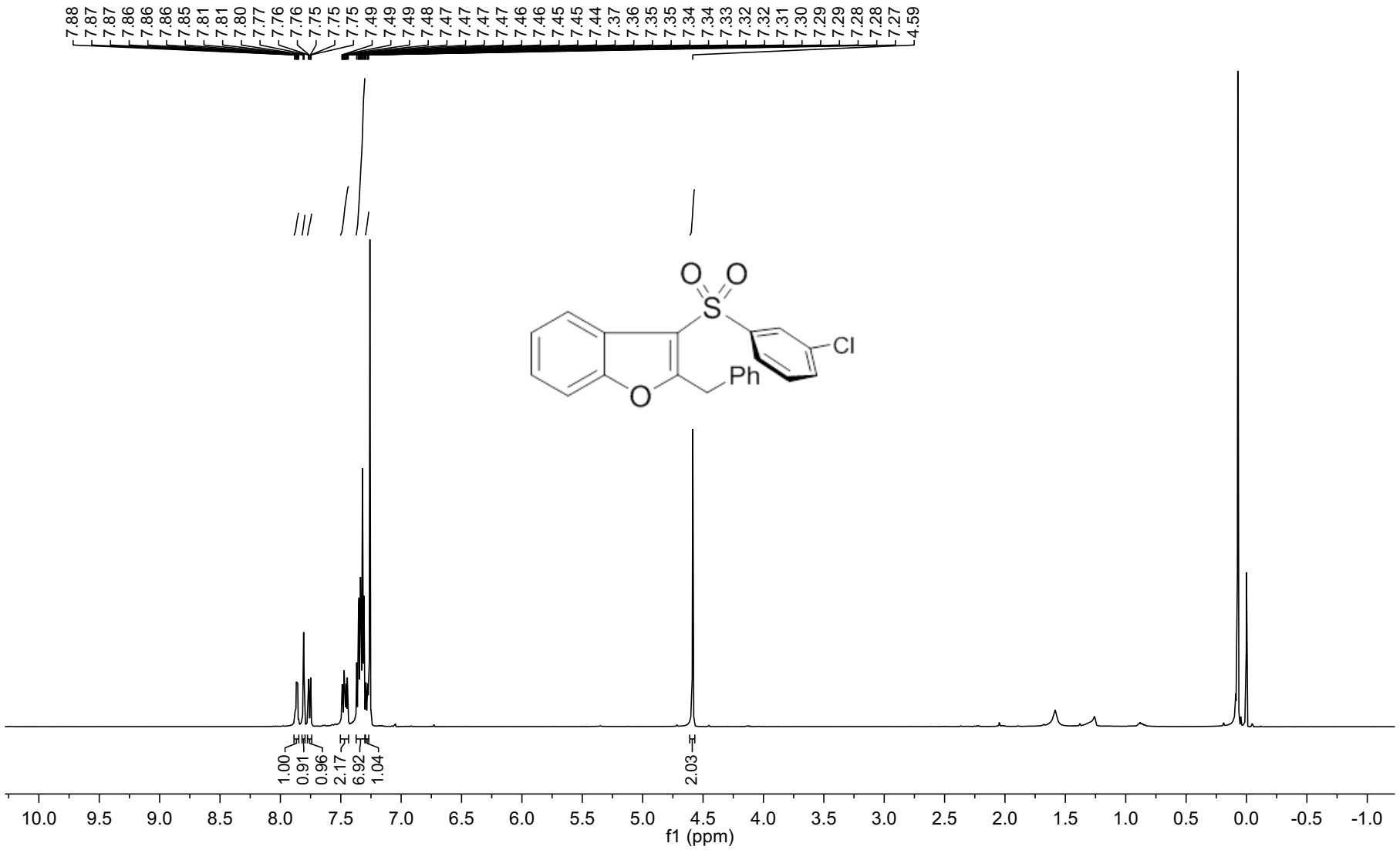
^{1}H NMR Spectroscopy of **4cd**



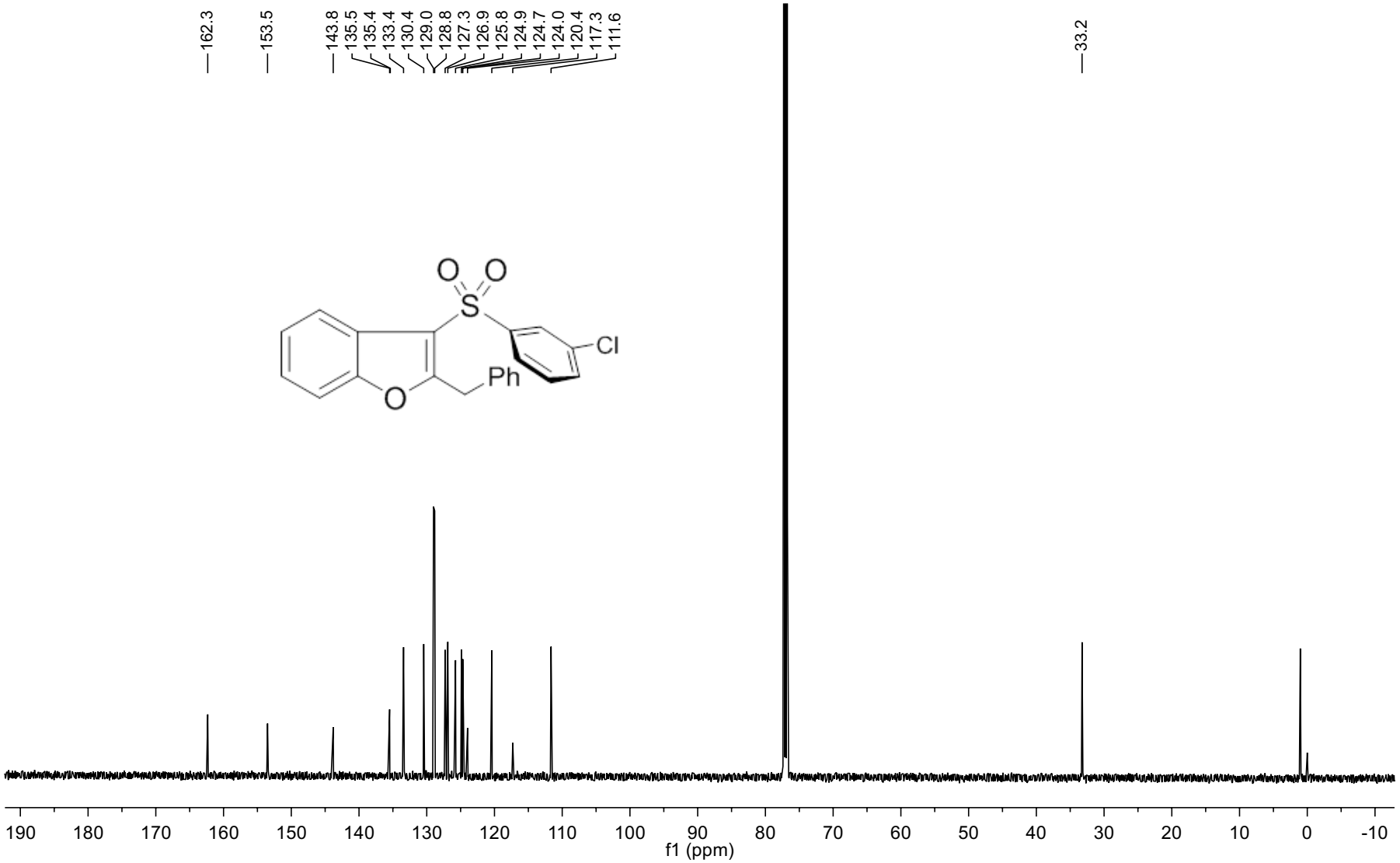
^{13}C NMR Spectroscopy of **4cd**



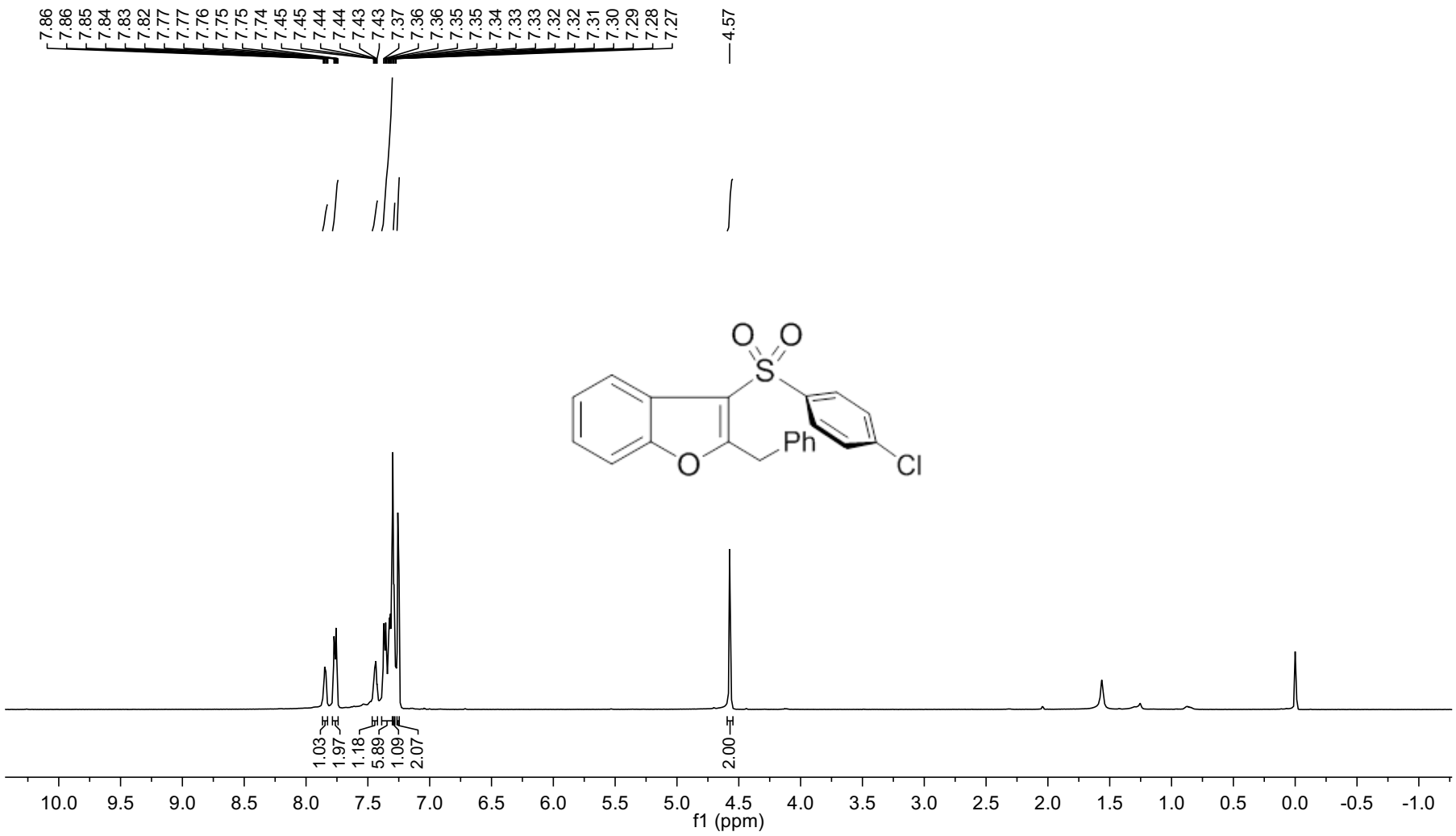
^{1}H NMR Spectroscopy of **4ae**



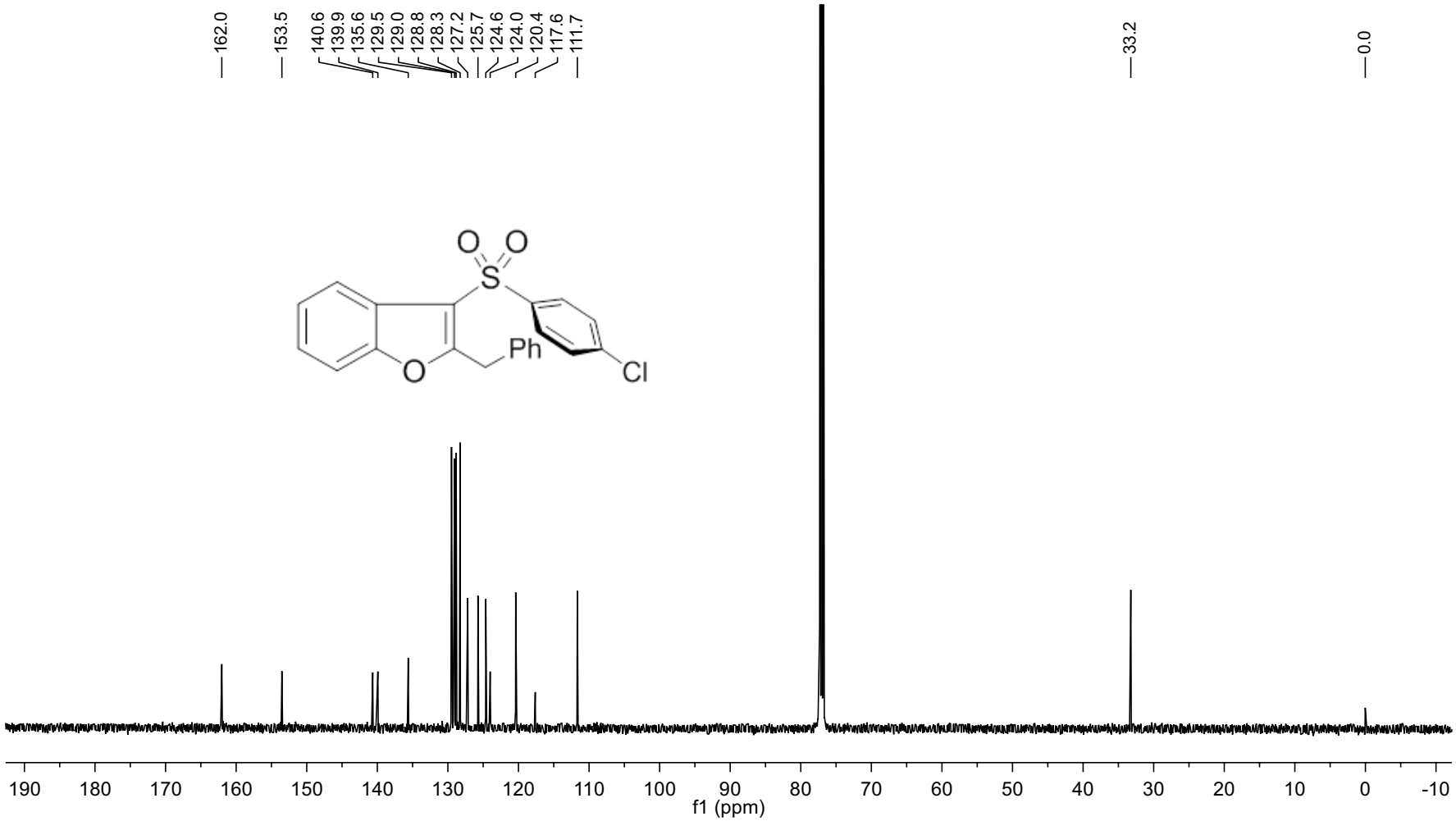
^{13}C NMR Spectroscopy of **4ae**



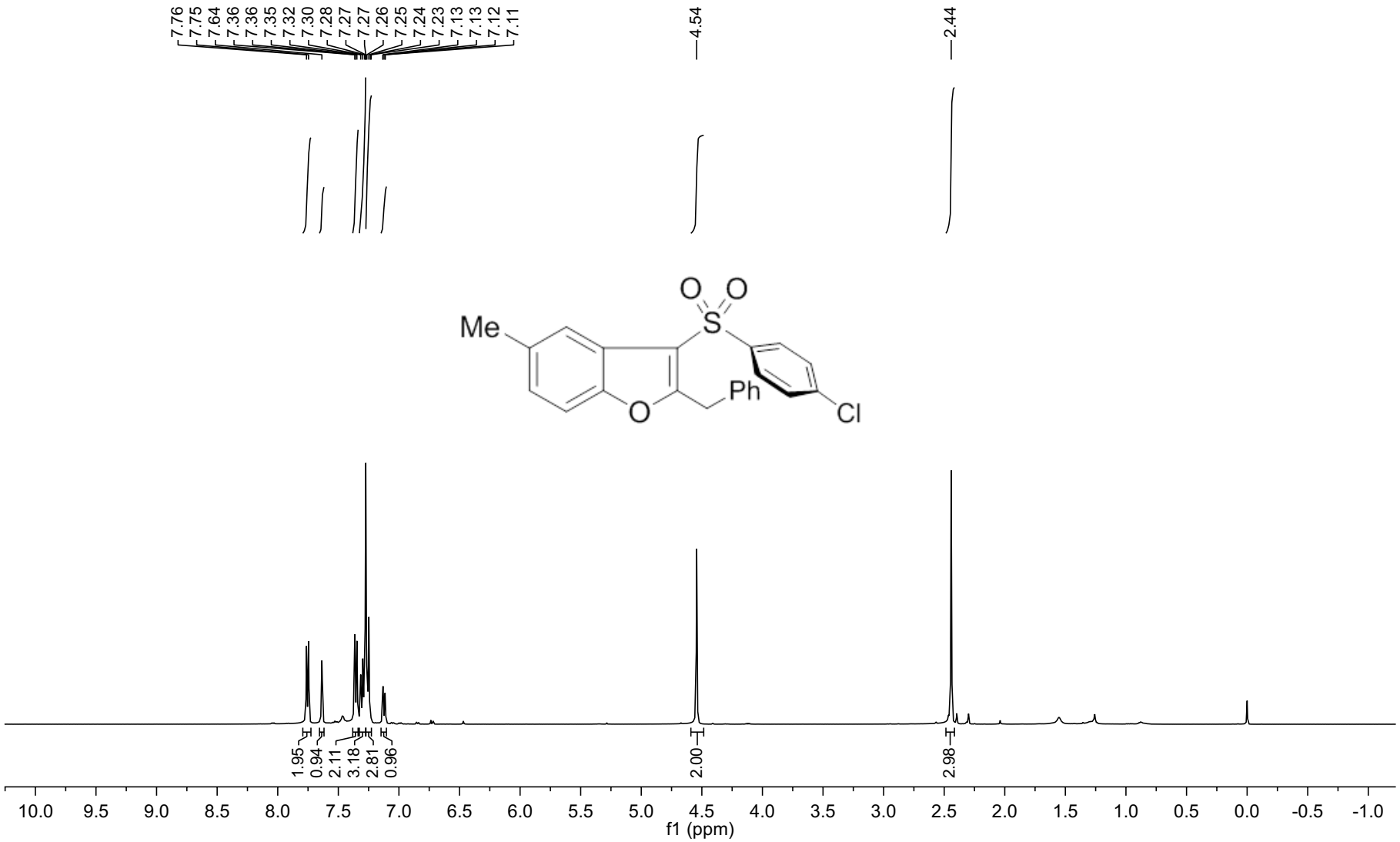
^{1}H NMR Spectroscopy of **4af**



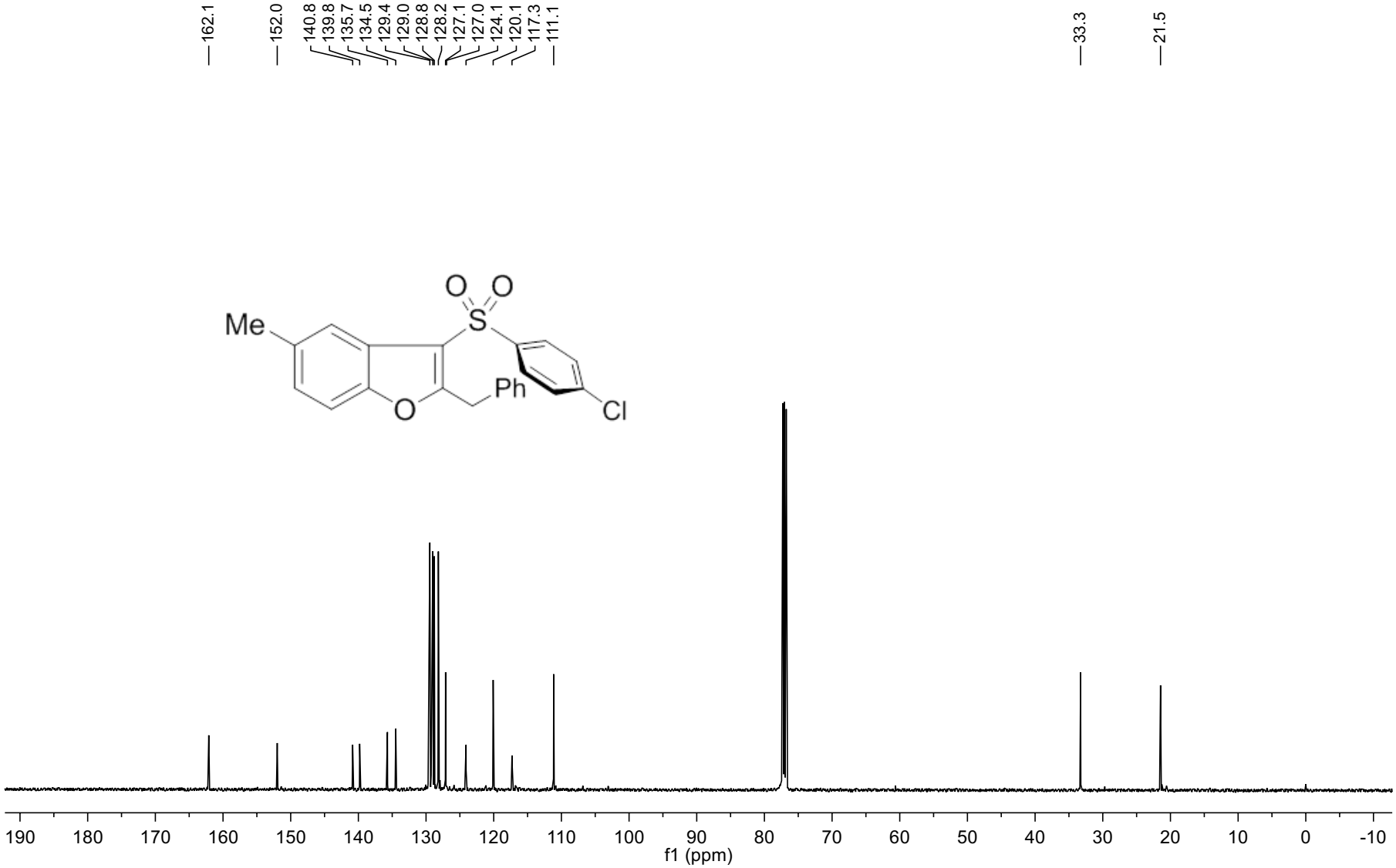
^{13}C NMR Spectroscopy of **4af**



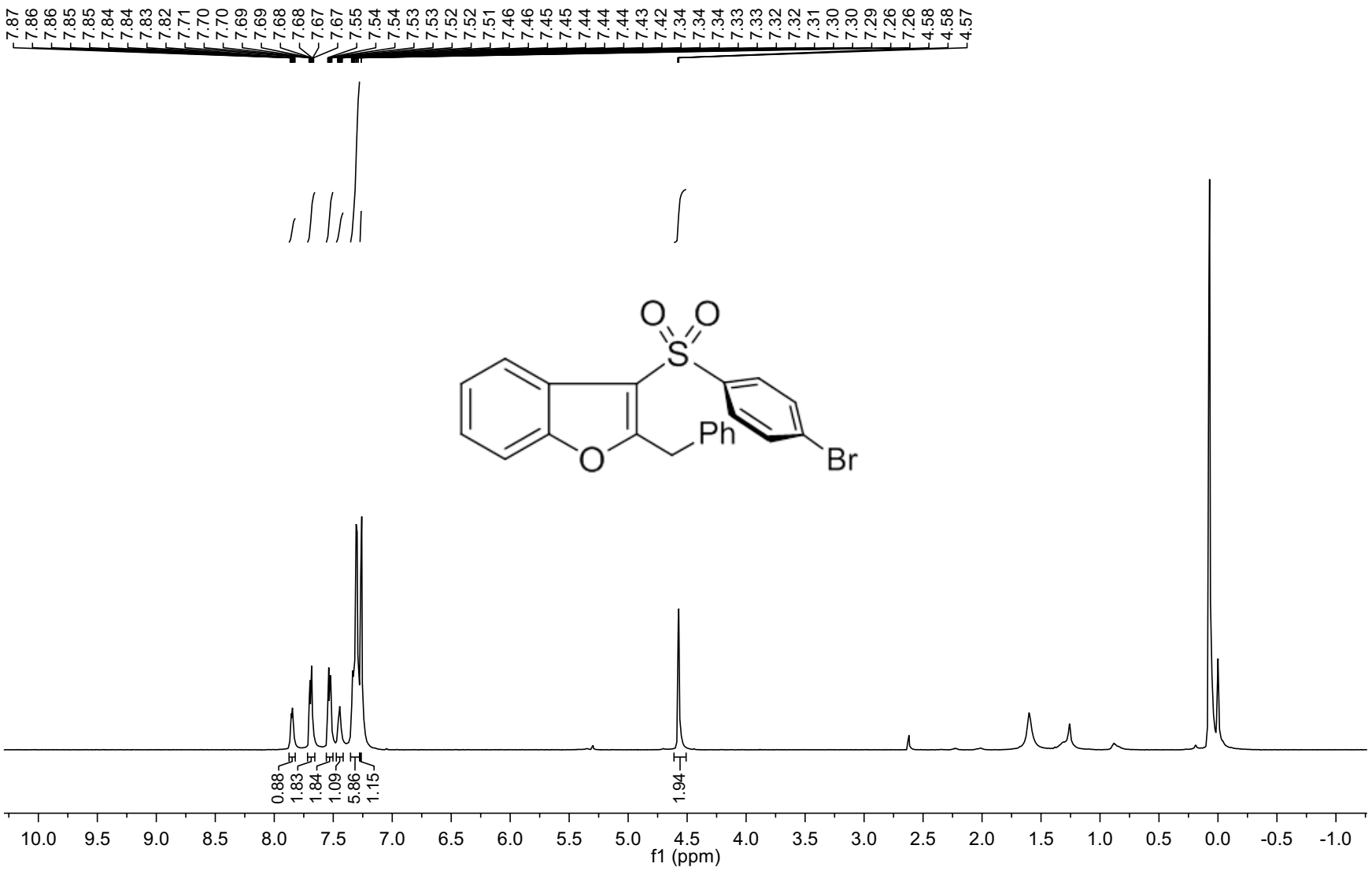
^{1}H NMR Spectroscopy of **4cf**



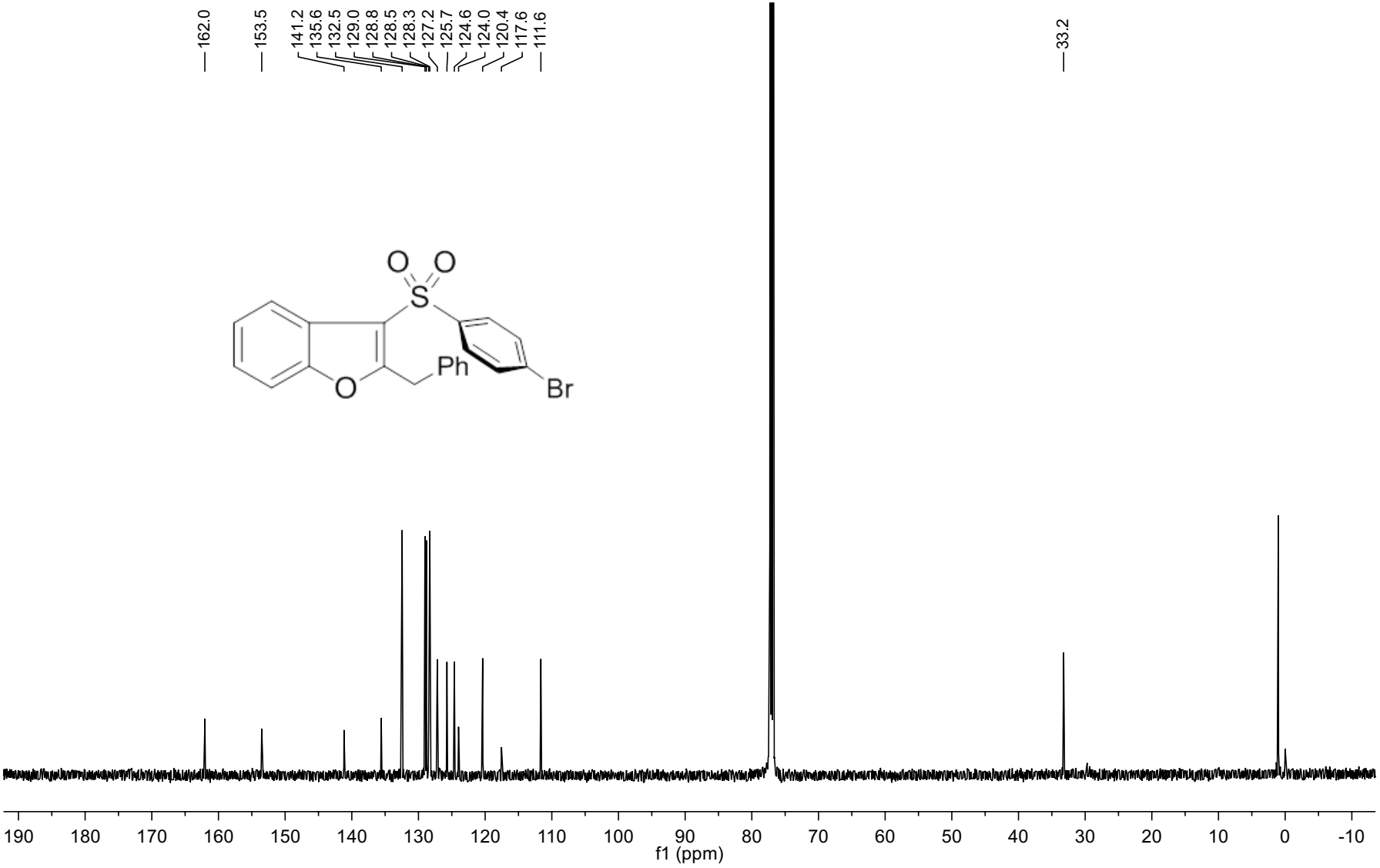
^{13}C NMR Spectroscopy of **4cf**



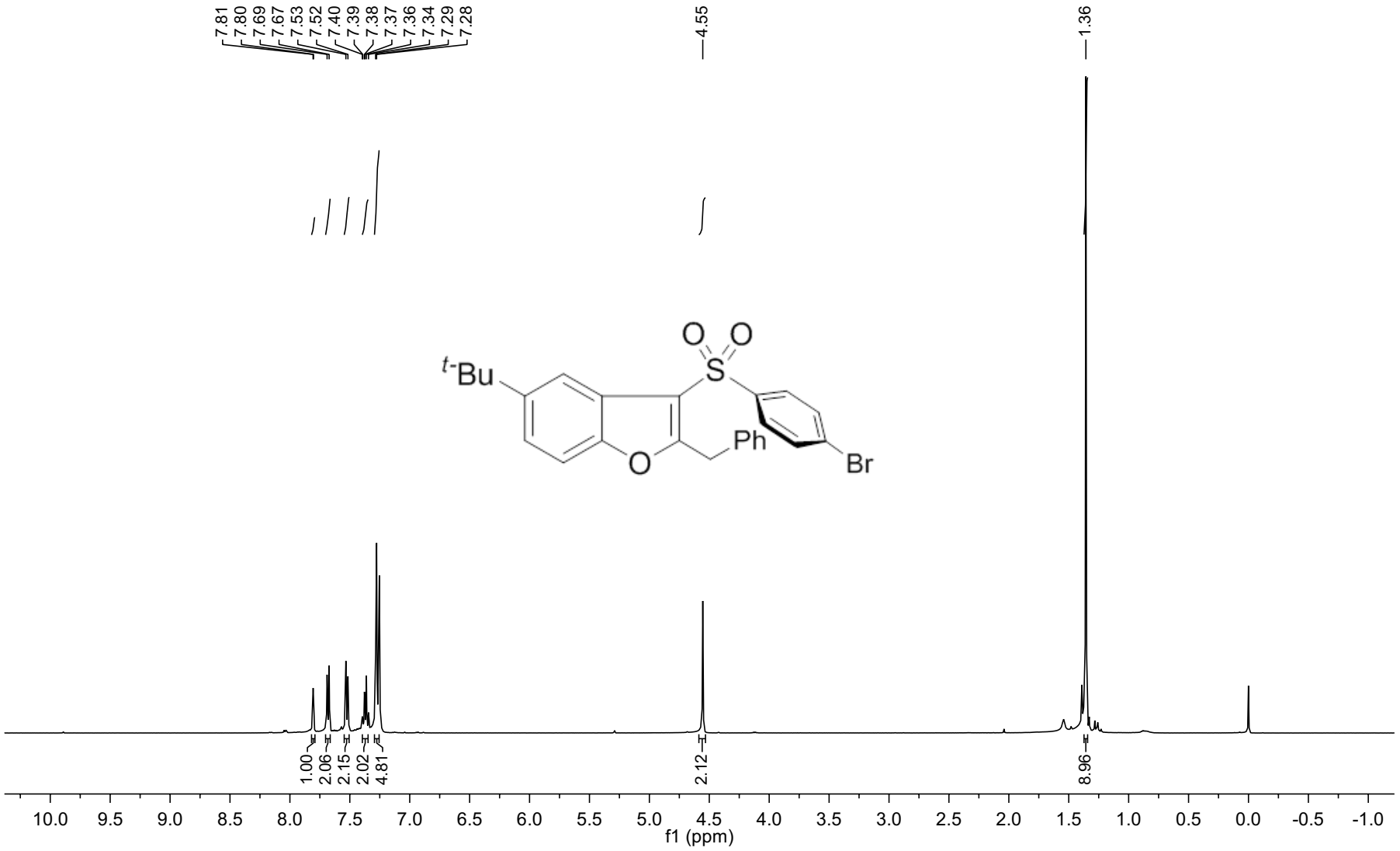
^{1}H NMR Spectroscopy of **4ag**



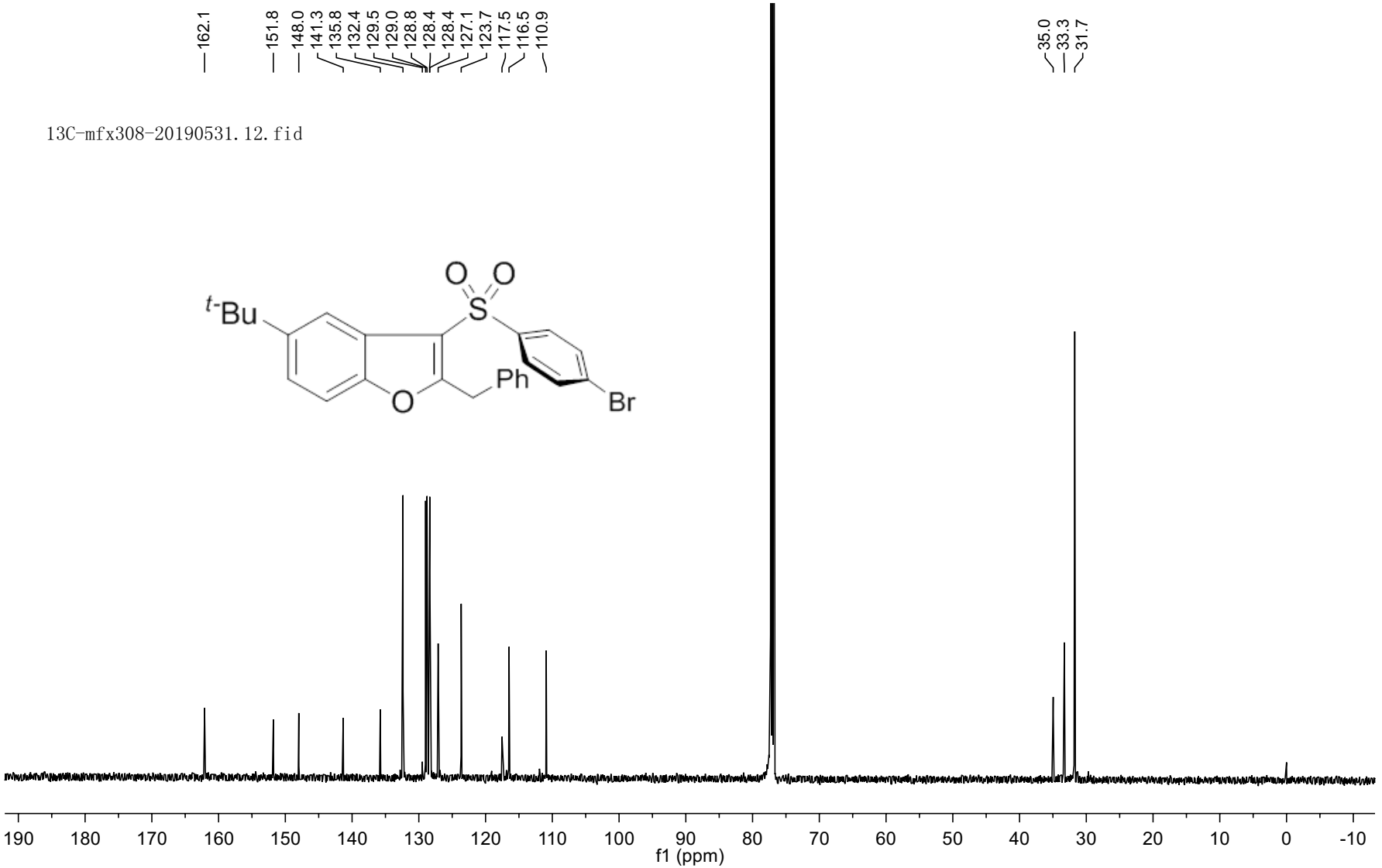
^{13}C NMR Spectroscopy of **4ag**



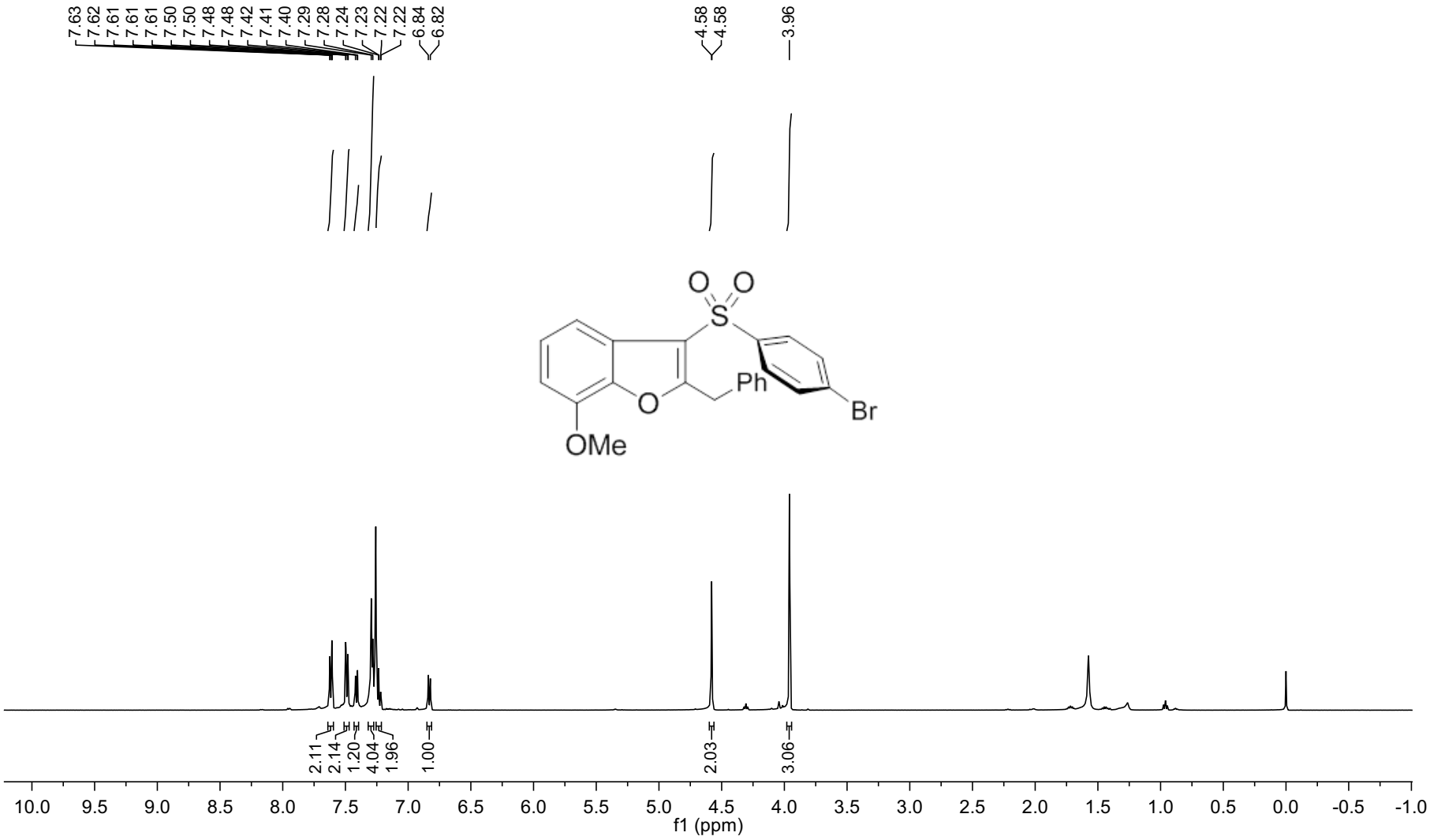
^{1}H NMR Spectroscopy of **4dg**



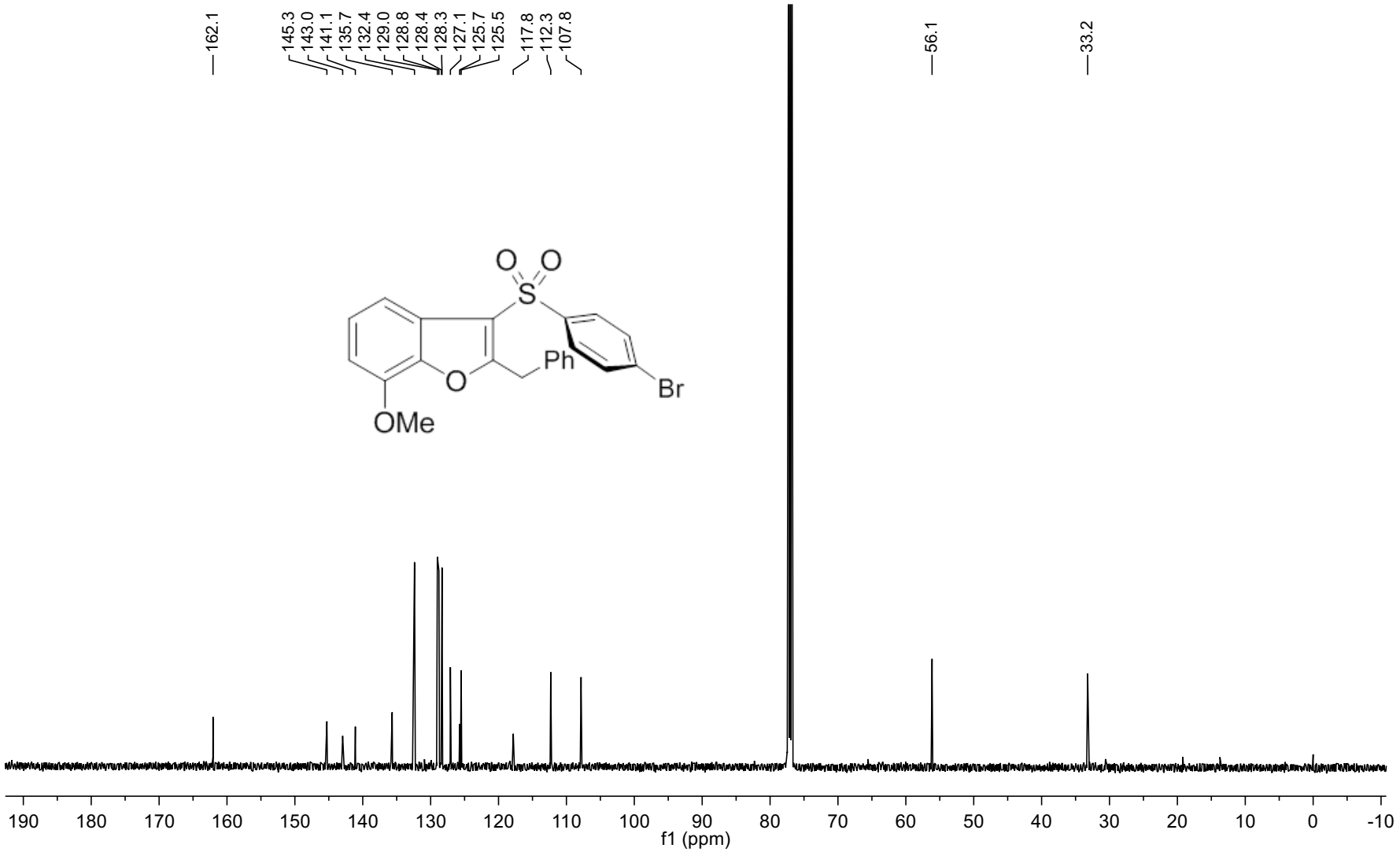
^{13}C NMR Spectroscopy of **4dg**



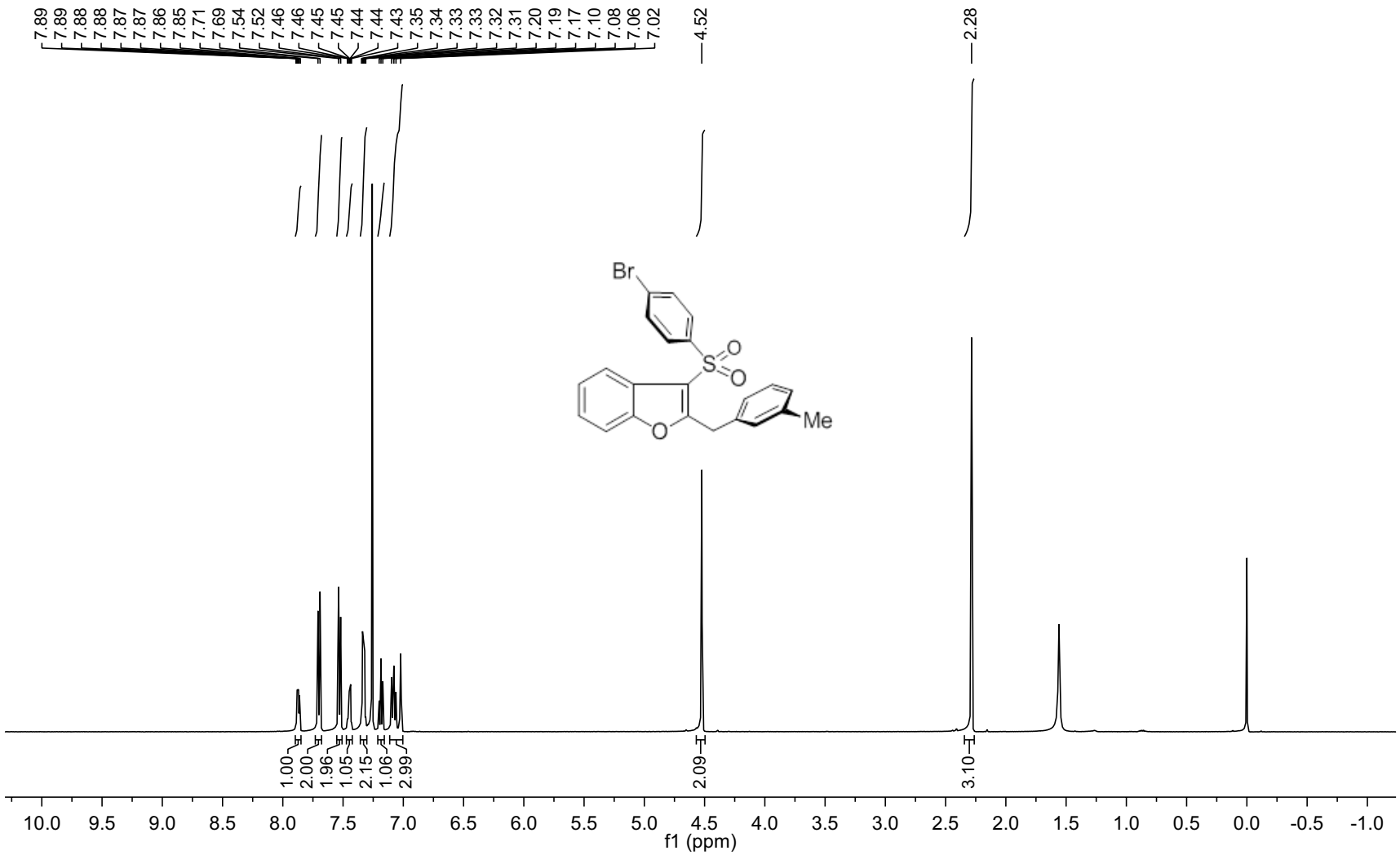
^{1}H NMR Spectroscopy of **4eg**



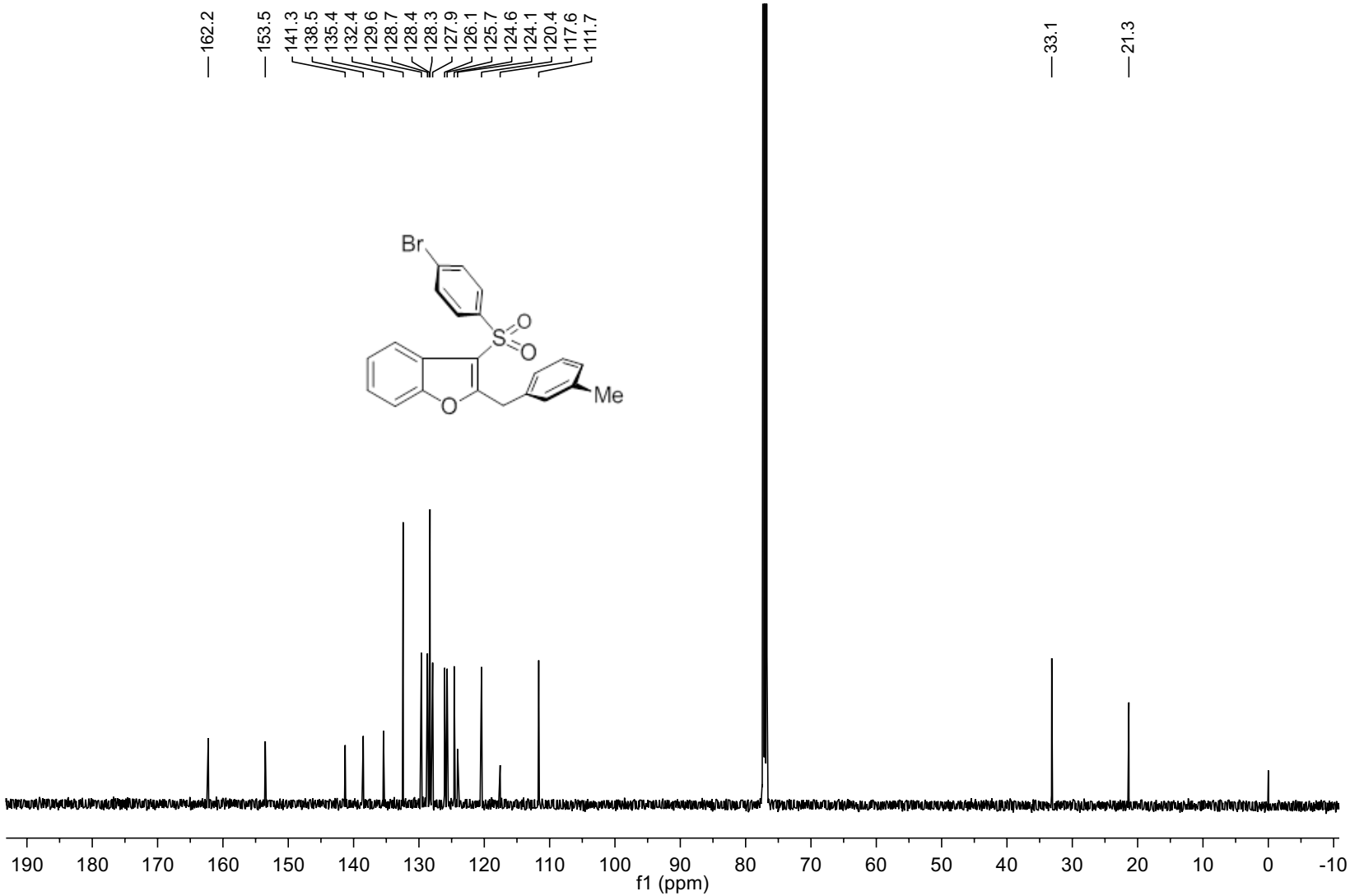
^{13}C NMR Spectroscopy of **4eg**



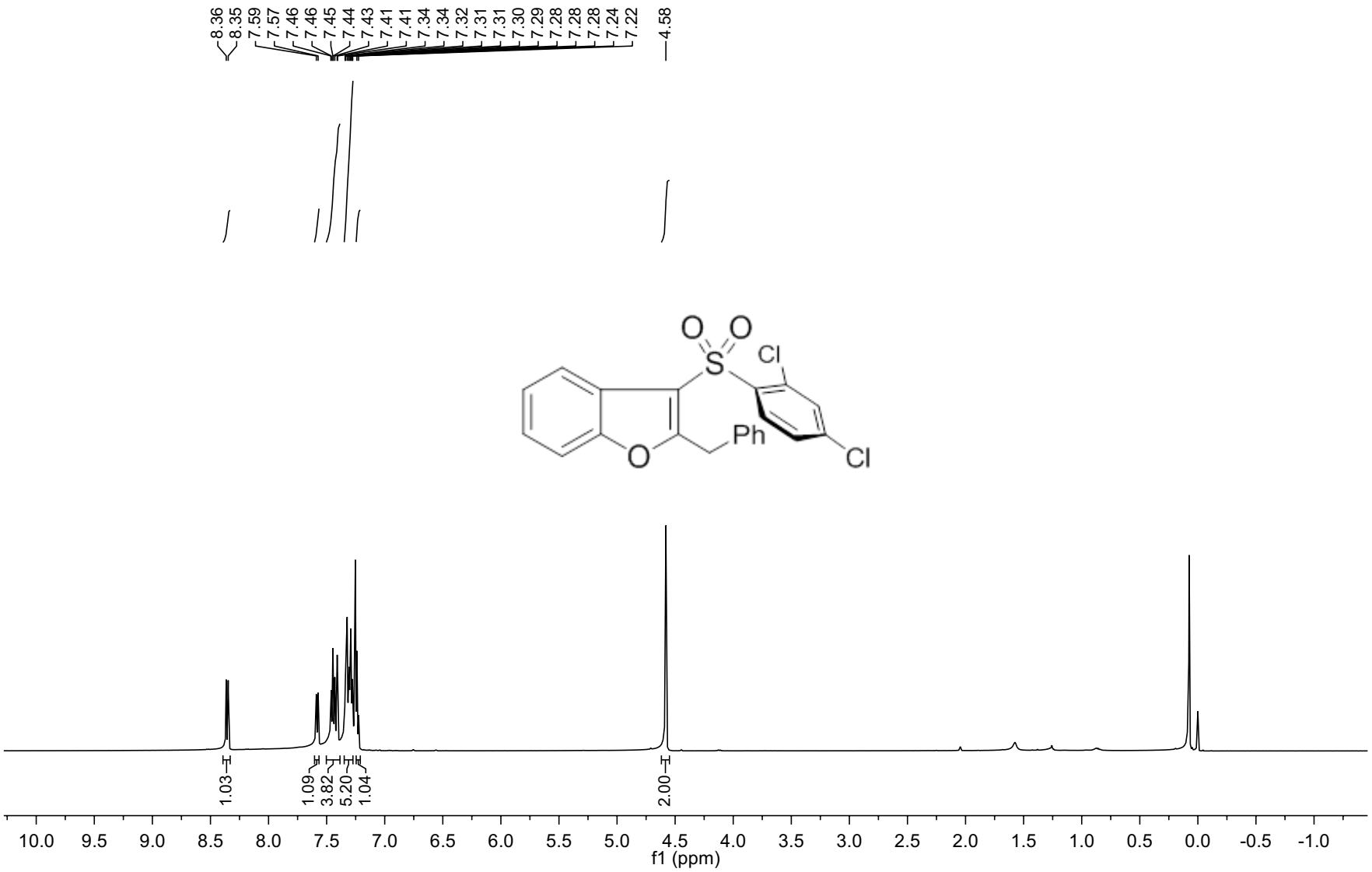
^{1}H NMR Spectroscopy of **4ig**



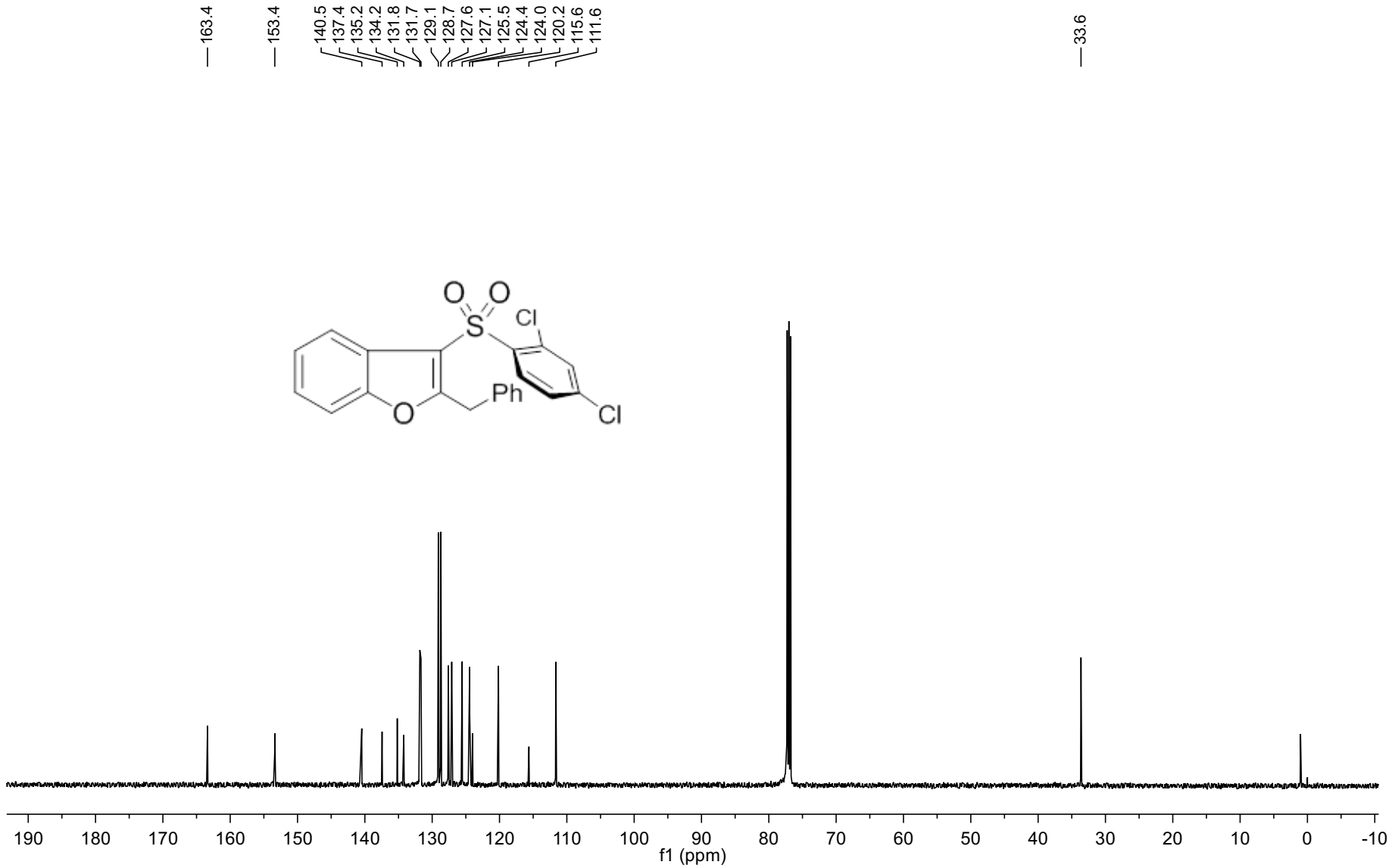
^{13}C NMR Spectroscopy of **4ig**



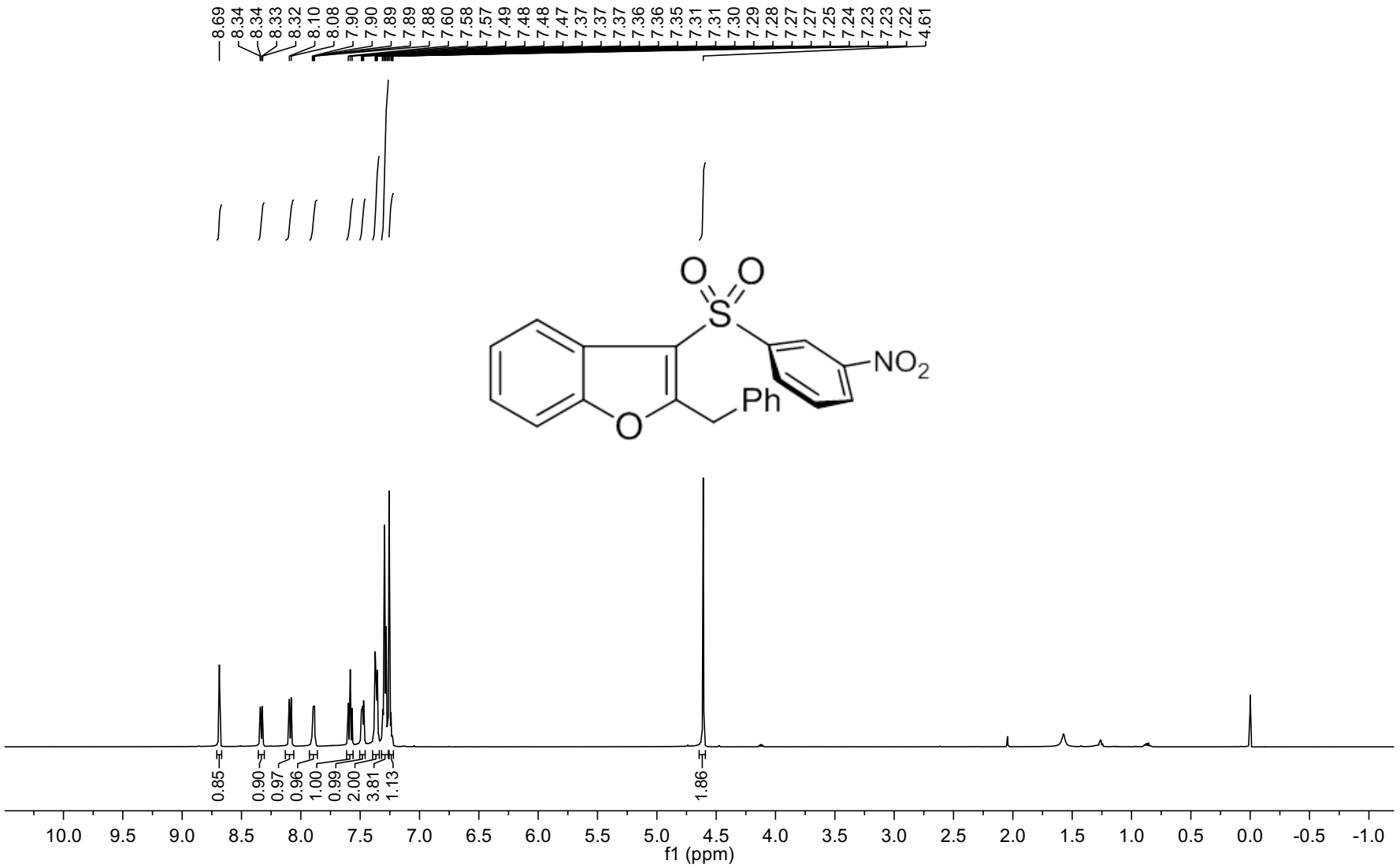
^{1}H NMR Spectroscopy of **4ah**



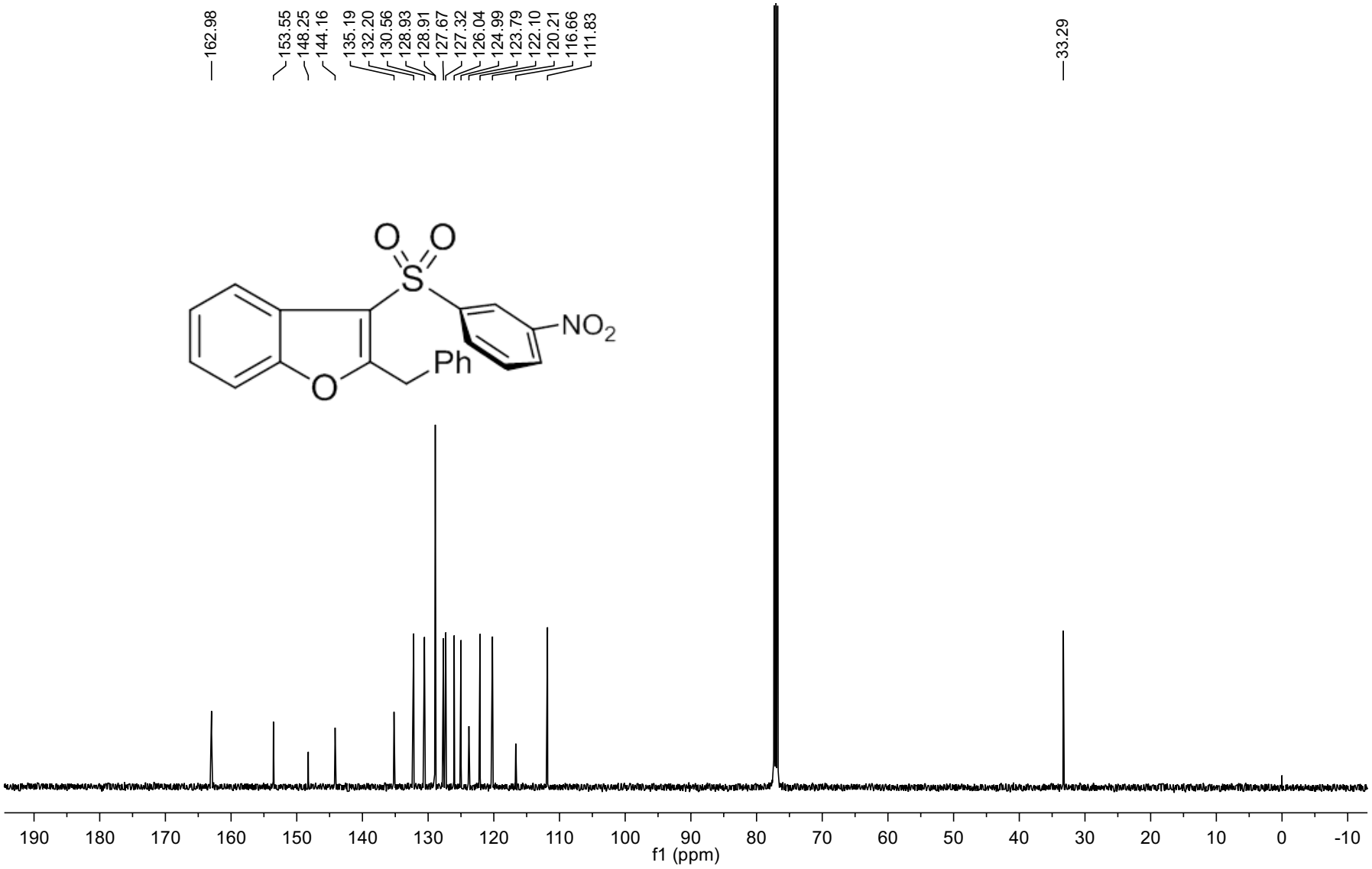
^{13}C NMR Spectroscopy of **4ah**



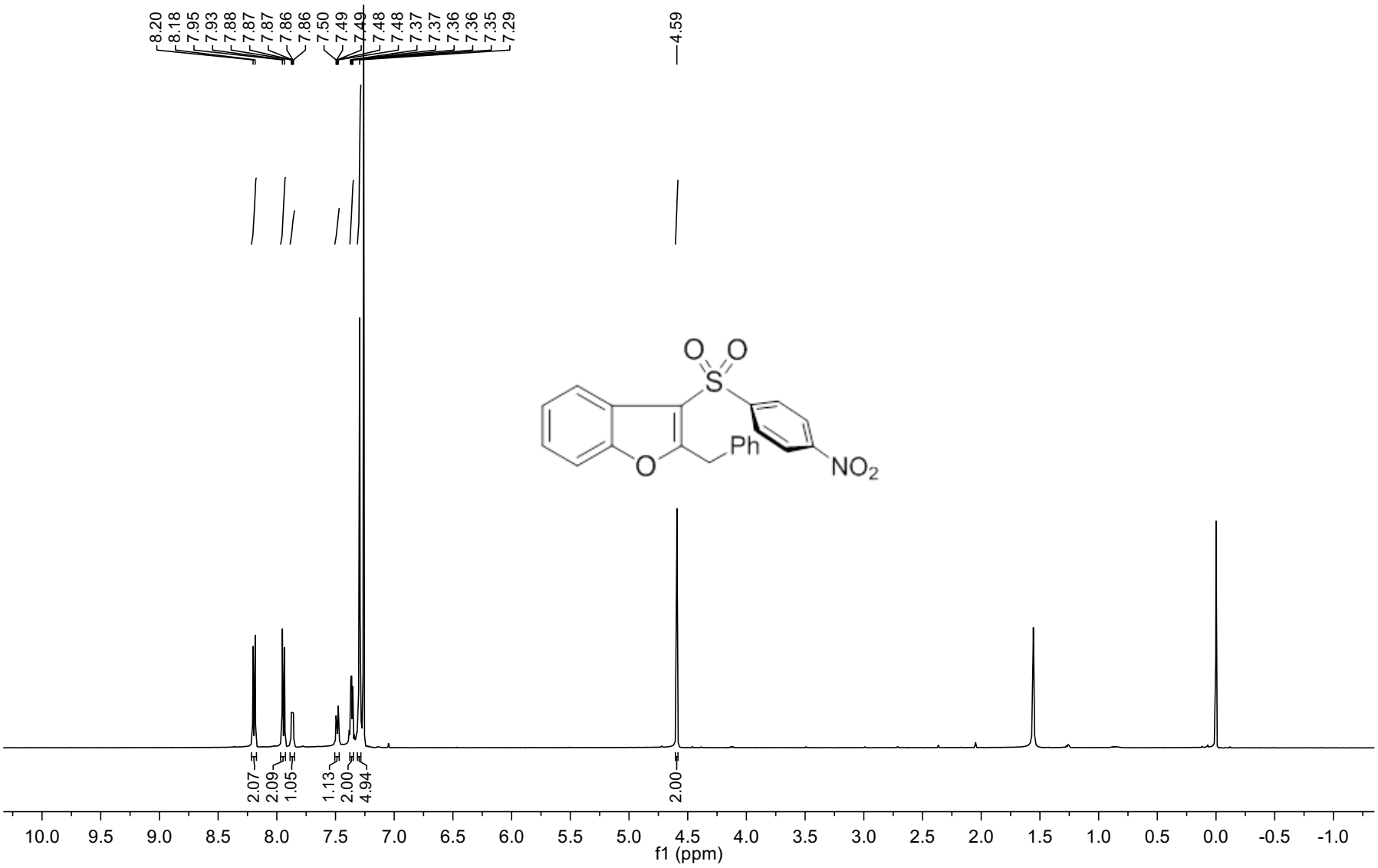
^{1}H NMR Spectroscopy of **4ai**



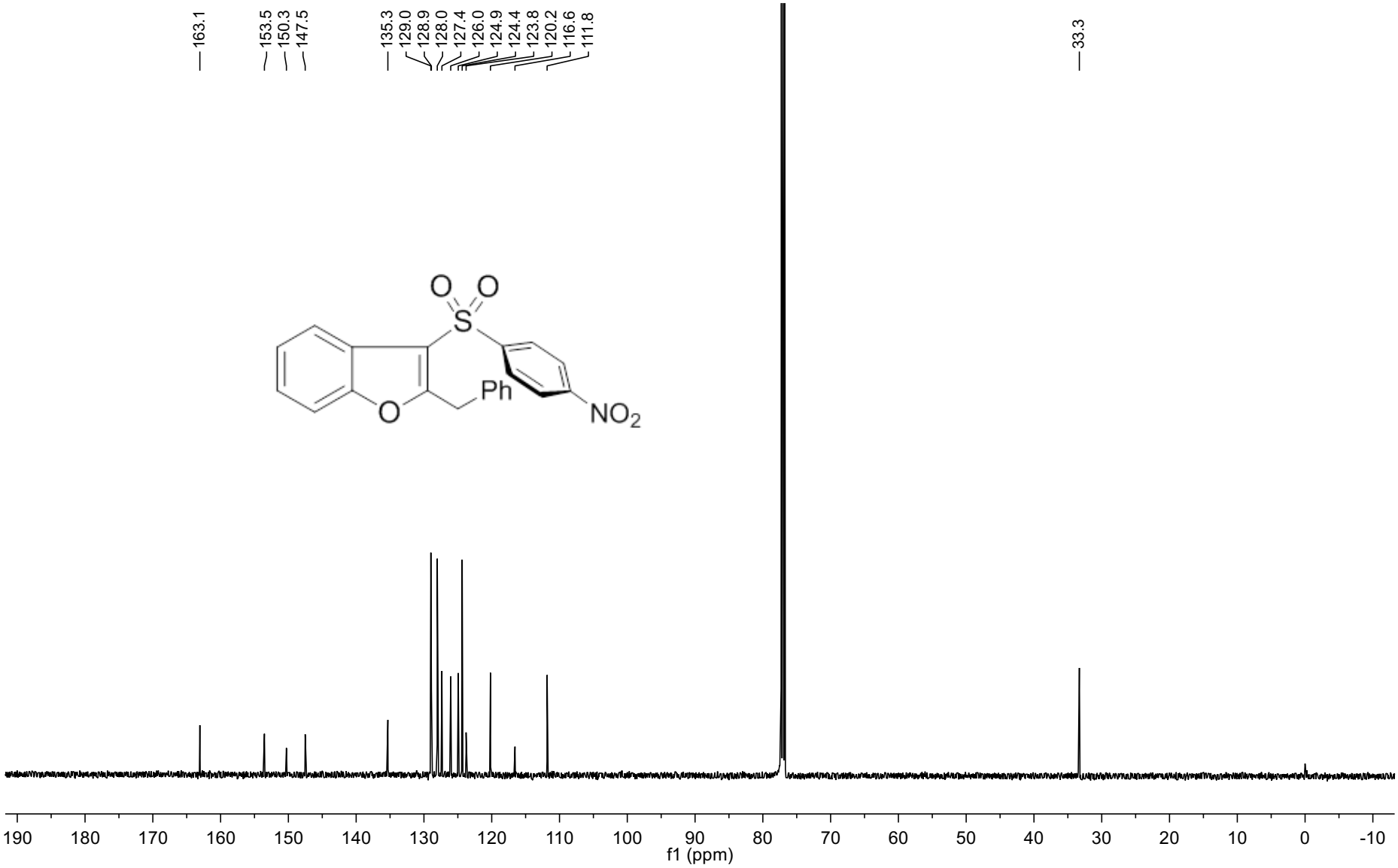
^{13}C NMR Spectroscopy of **4ai**



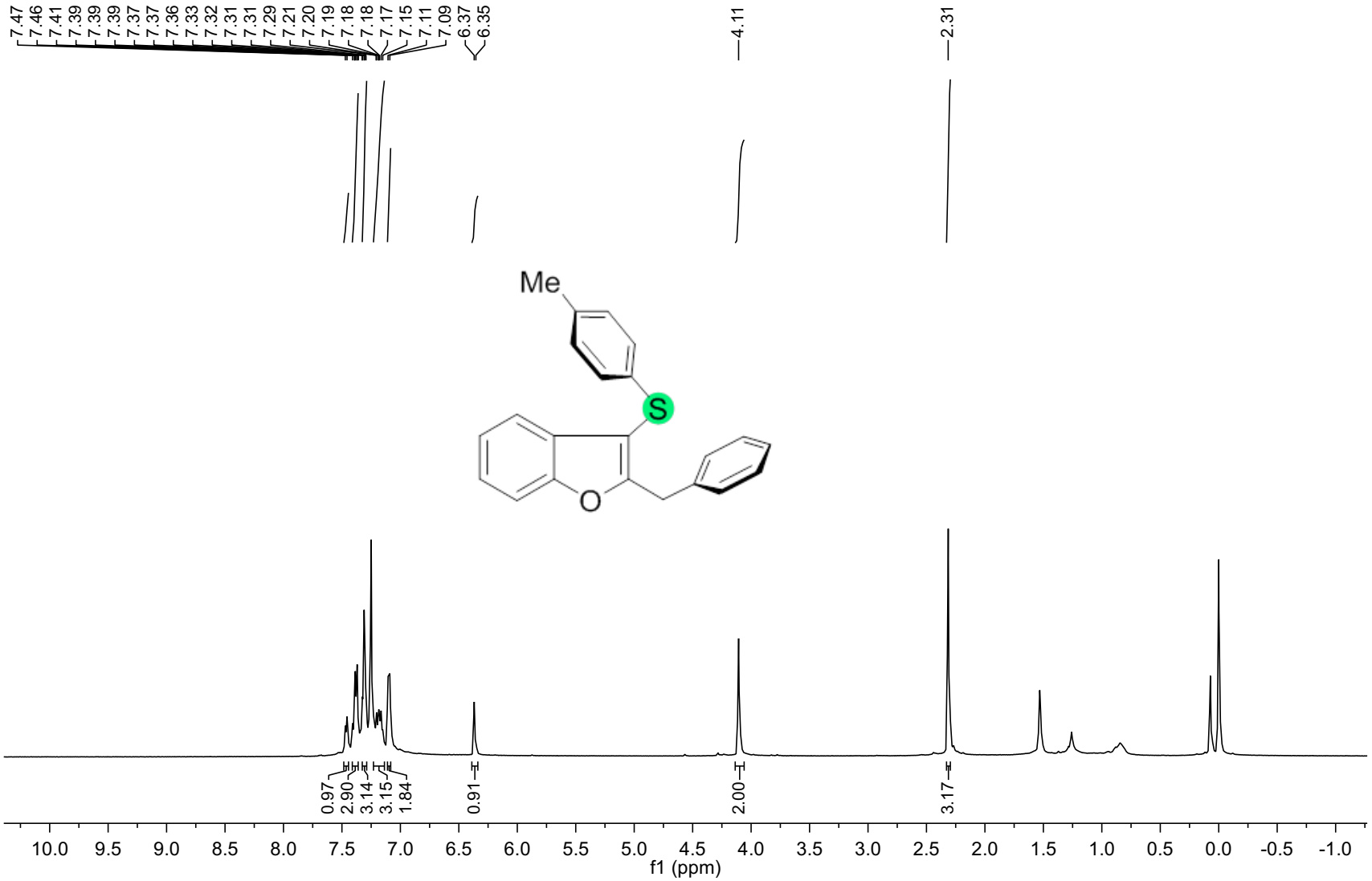
^{1}H NMR Spectroscopy of **4aj**



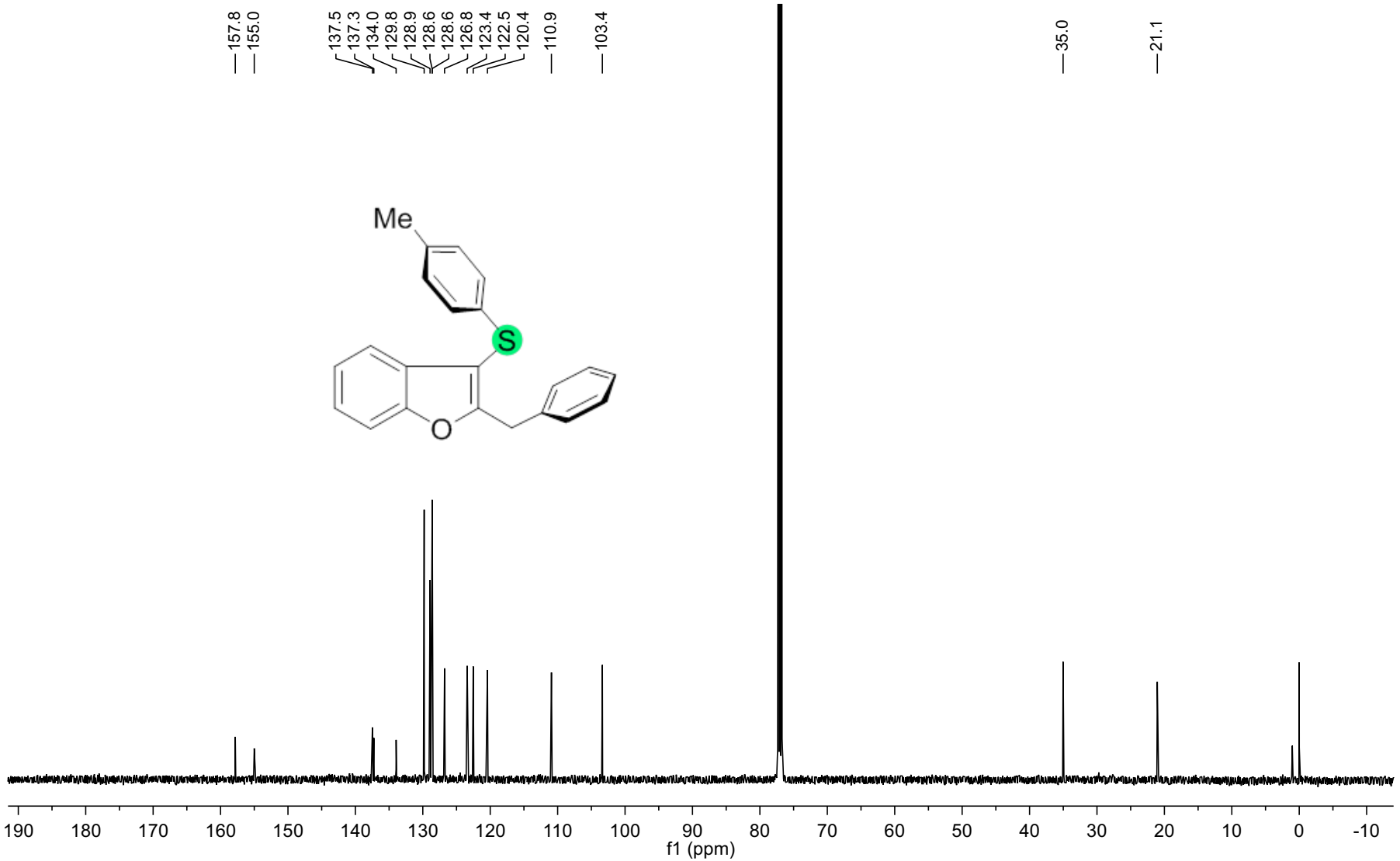
^{13}C NMR Spectroscopy of **4aj**



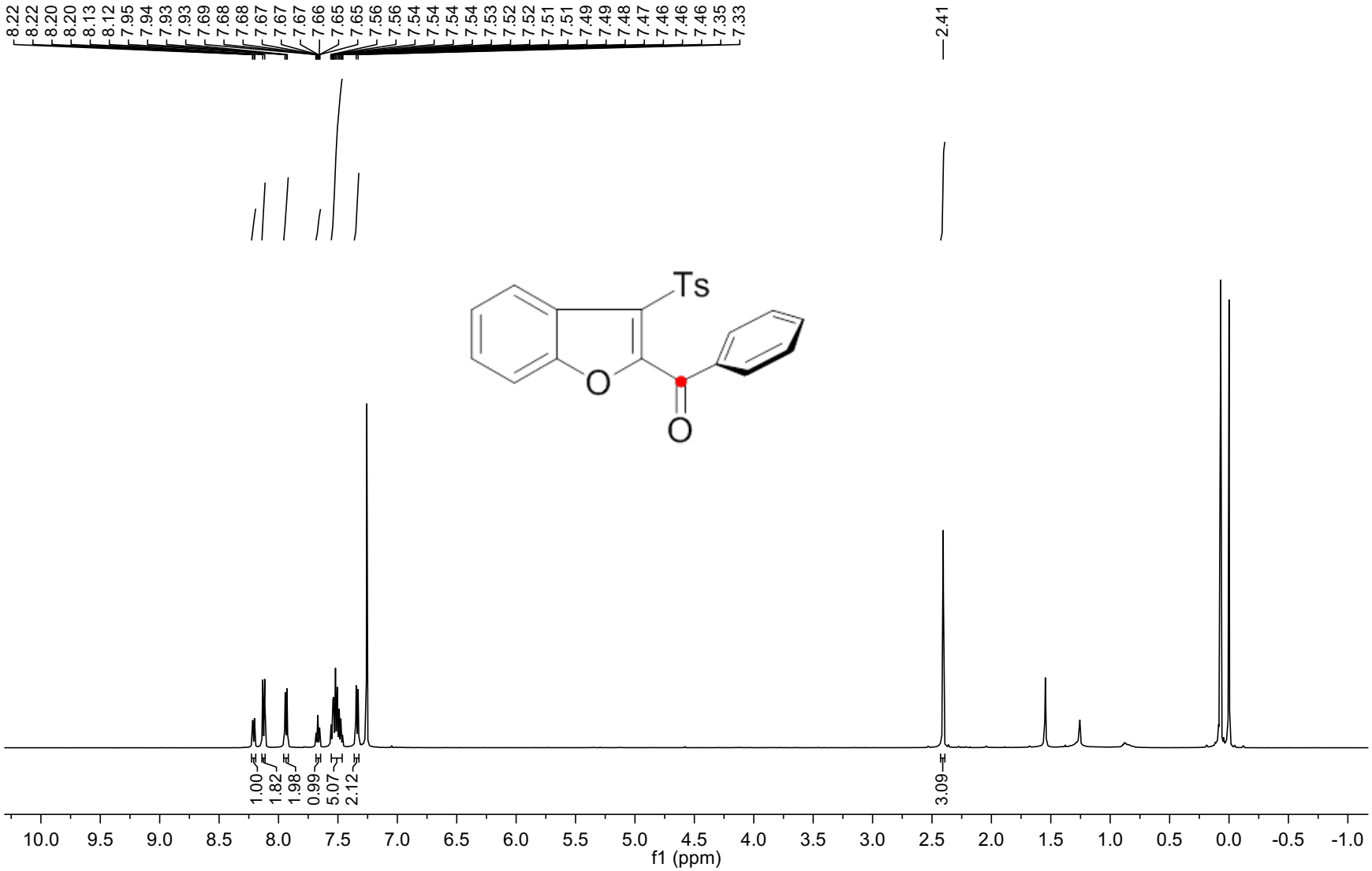
^{1}H NMR Spectroscopy of **5**



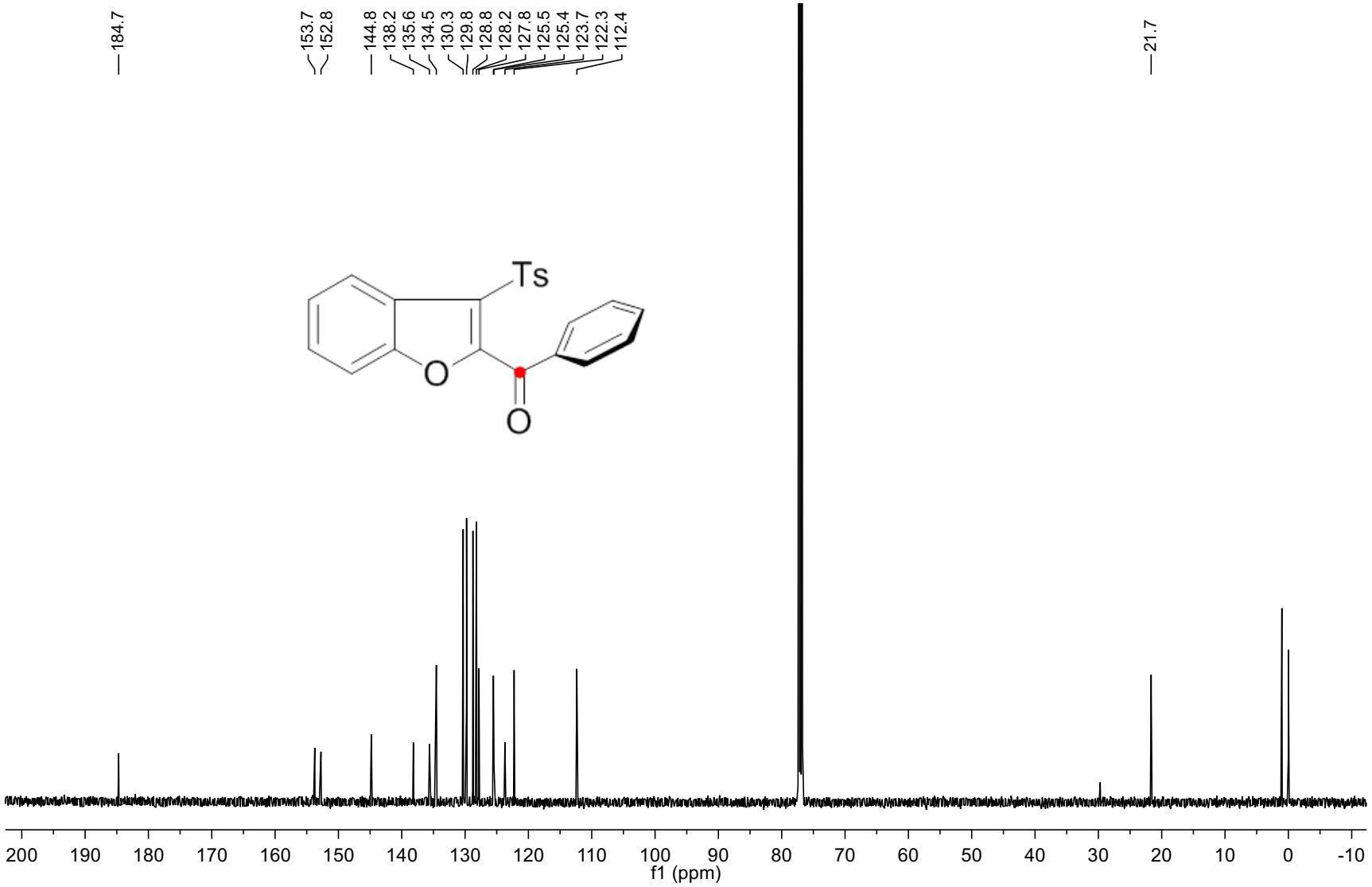
^{13}C NMR Spectroscopy of **5**



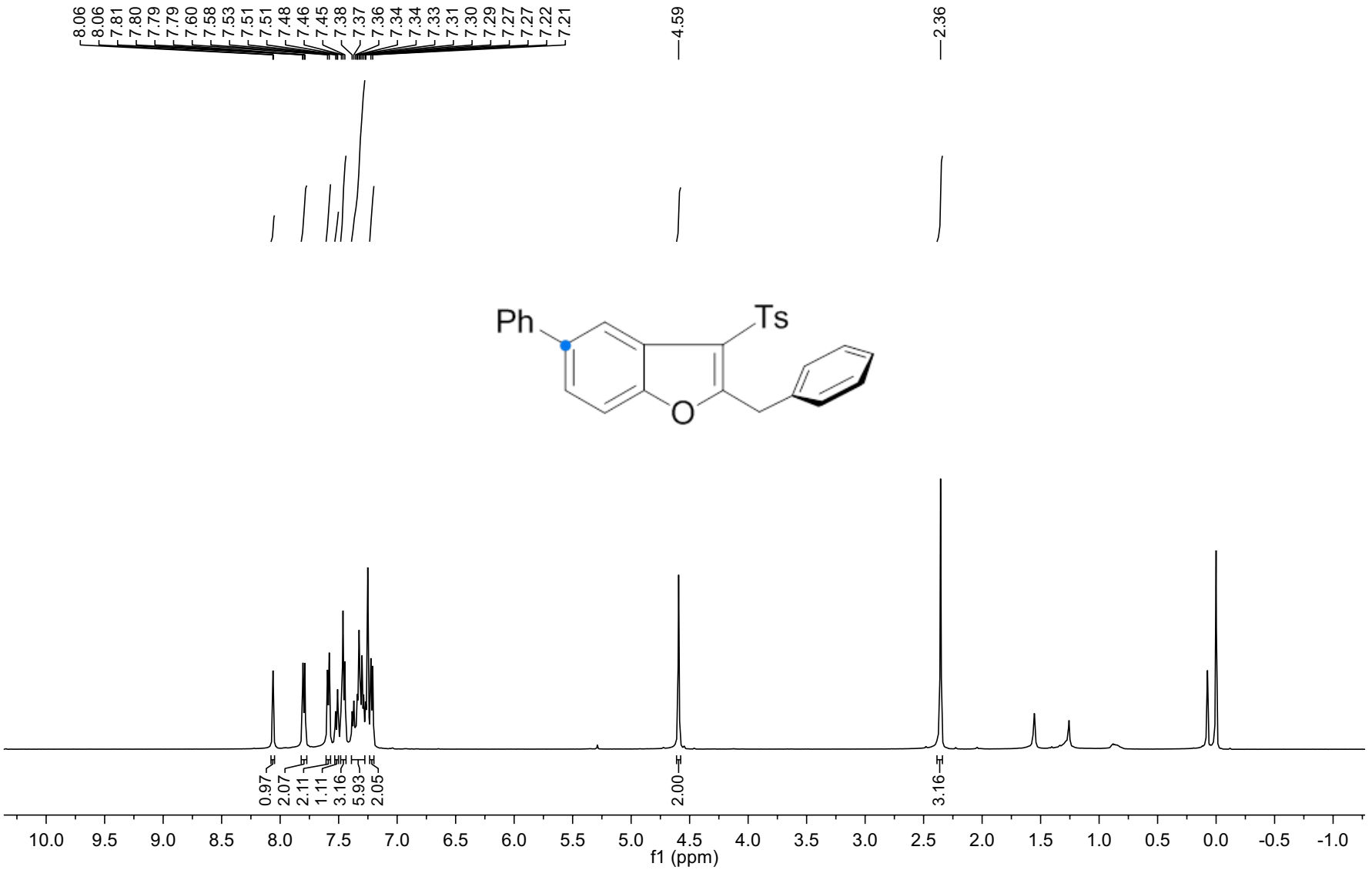
^{1}H NMR Spectroscopy of **6**



^{13}C NMR Spectroscopy of **6**



^{1}H NMR Spectroscopy of **7**



^{13}C NMR Spectroscopy of **7**