Three-Component Synthesis of β-Sulfonyl Enamines and Dienamines Enabled by Silver(I) Acetate

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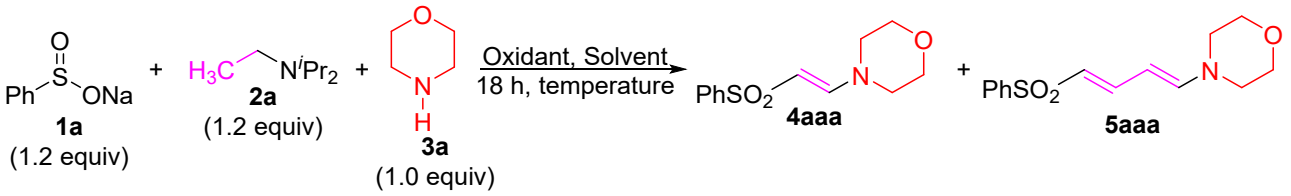
General Information

All reactions were carried out in a dry argon atmosphere. The progress of the reactions was monitored by thin-layer chromatography and ^{1}H NMR spectroscopy. NMR spectra were measured using an Agilent 400MR DD2 (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz) and JEOL 400 MHz YH (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz) spectrometer at 298 K. The multiplicities are reported as follows: (s) singlet, (br s) broad singlet, (d) dublet, (dd) dublet of dublets, (dt) doublet of triplets, (hept) heptet, (q) quartet, (t) triplet, and (m) multiplet. Mass spectra were measured using a Thermo Scientific LTQ Orbitrap Velos (Orbitrap mass analyzer). Dry and degassed THF was prepared using PureSolv MD7. Silica gel (Merck, silica gel 60, 40−63 μm or Merck, silica gel 60, 63−200 μm) was used for column chromatography. ^{n}BuLi (2.5 M solution in hexane) and other compounds were purchased from Sigma-Aldrich and Fluorochem. The concentration of ^{n}BuLi was determined by titration using menthol and 1,10-phenanthroline before use.

Optimization of reaction conditions

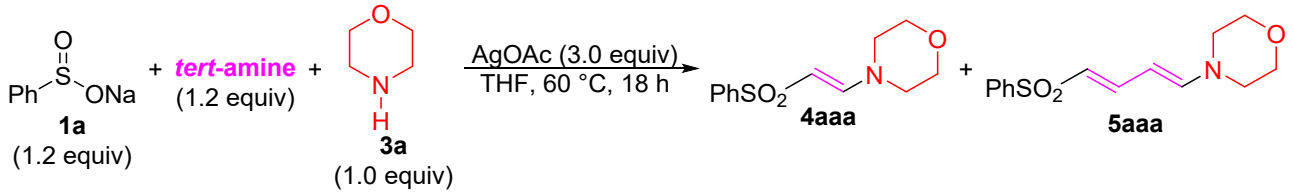


Entry	Oxidant (eq.)	Temperature [°C]	Solvent	**4aaa/5aaa** ^{1}H NMR yield [%]
1	Ag_2O (1.5)	100	1,4-Dioxane	24/3/0
2	Ag_3PO_4 (1.0)	100	1,4-Dioxane	12/14/0
3	AgI (3.0)	100	1,4-Dioxane	–
4	$AgNO_3$ (3.0)	100	1,4-Dioxane	–
5	AgTFA (3.0)	100	1,4-Dioxane	–
6	Ag_2CO_3 (1.5)	100	1,4-Dioxane	30/5/0
7	AgOAc	100	1,4-Dioxane	37/2/0
8	AgOAc (20 mol%), $K_2S_2O_8$ (3.0)	60	THF	0/0/3
9	AgOAc (20 mol%), $CuBr_2$ (20 mol%), air	60	THF	0/0/18
10	Ag_2CO_3 (1.0), $K_2S_2O_8$ (2.0)	60	THF	6/3/3
11	Ag_2CO_3 (20 mol%), NMMO (3.0)	60	THF	–
12	$Pb(OAc)_4$ (3.0)	60	THF	–
13	$SnCl_4$ (3.0)	60	THF	–
14	$FeCl_3$ (3.0)	60	THF	0/0/trace
15	I_2 (3.0)	60	THF	0/0/72
16	MnO_2 (3.0)	60	THF	–
17	$CuBr_2$ (1.5)	60	THF	0/0/trace
18[a]	I_2/TBHP	60	DMSO	0/0/34
19	CuI (3.0)	60	THF	–

Table S1 Optimization of the oxidizing agent used.

[a] Triethylamine was used instead of *N*,*N*-diisopropylethylamine.

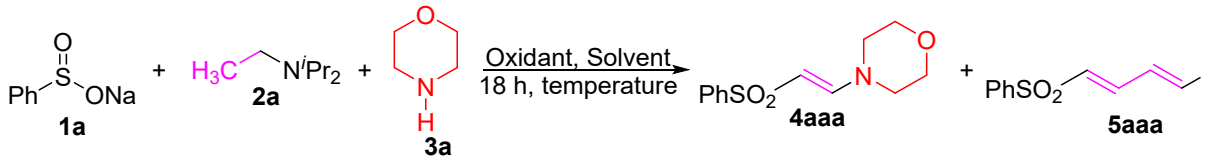
Table S2 Optimization of the tertiary amine used.



Entry	Tertiary amine	**4aaa** ^{1}H NMR yield [%]	**5aaa** ^{1}H NMR yield [%]
1	*N*,*N*-Diisopropylethylamine	63 (43%)[a]	2
2	Triethylamine	44	–
3	$PhNEt_2$	6	–
4	$BnNEt_2$	12	–
5	$(TMS)_2NEt$	–	–
6	Cy_2NEt	45	7
7	1-Ethyl-1*H*-indole	–	–
8	N-Ethylpiperidine	3	–
9	1-Et 2,2,6,6-tetramethylpiperidine	–	–
10	*N*-Ethylmorpholine	trace	–
11	DIPEA·HCl	30	10
12[b]	DIPEA·HCl	trace	14
13	Benzyltriethylammonium chloride	–	–

[a] Isolated yield. [b] A mixture of MeCN and EtOH (1:3, v/v) was used.

Table S3 Optimization of the equivalents of **1a**, **2a**, **3a**, as well as the solvent and temperature used.

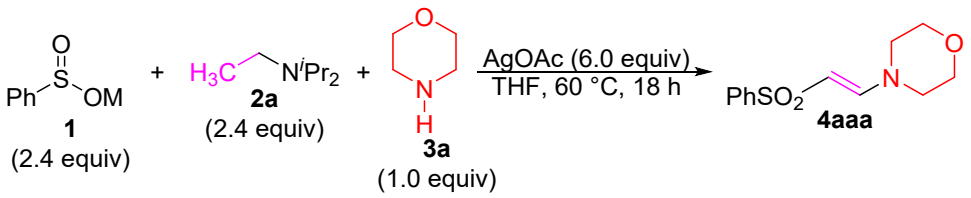


Entry	Sulfinate **1a** [equiv]	DIPEA [equiv]	AgOAc [equiv]	Temperature [°C]	Solvent	^{1}H NMR yield [%] **4aaa/5aaa**
1	1.2	1.2	1.5	100	1,4-Dioxane	15/2
2	3	1.2	1.5	100	1,4-Dioxane	12/5
[a]3	3	1.2	1.5	100	1,4-Dioxane	9/trace
4	3	1.2	3	100	1,4-Dioxane	31/5
5[b]	3	1	3	100	1,4-Dioxane	27/6
6	1.2	1.2	3	100	1,4-Dioxane	37/2
7	1.2	1.2	4	100	1,4-Dioxane	35/trace
8	1.2	3	3	100	1,4-Dioxane	40/4
9	1.2	1.2	3	80	1,4-Dioxane	33/5
10	1.2	1.2	3	60	1,4-Dioxane	44/ 6
11	1.2	1.2	3	40	1,4-Dioxane	–
12	1.2	1.2	3	60	THF	52/3
13	1.2	2.2	3	60	THF[c]	63/2
14[b]	1.2	2.2	3	60	THF[c]	36/trace
15	2.4	2.4	6	60	THF[c]	90(67)[d]/–
16	3.4	3.4	9	60	THF	67[d]
17	1.2	1.2	3	60	DMSO	14/3
18	1.2	1.2	3	60	DMF	14/0
19	1.2	1.2	3	100	Toluene	36/2
20	1.2	1.2	3	40	CH_2Cl_2	20/3
21	1.2	1.2	3	60	Toluene	22/4
22	1.2	1.2	3	60	CCl_4	6/0
23	1.2	1.2	3	60	CPME	11/trace
24	1.2	1.2	3	60	MeOH	0/10
25	1.2	1.2	3	60	$PhCF_3$	23/10
26	1.2	1.2	3	60	Hexane	–
27	1.2	1.2	3	60	1,3-Dioxolane	46/6
28	1.2	1.2	3	60	H_2O	–
29	1.2	1.2	3	60	BuOH	2/24
30	1.2	2.2	3	60	BuOH	2/26
31[e]	1.2	2.2	3	60	BuOH	1/25
32[e]	1.2	2.2	3	60	THF	50/6
33	1.2	4.2	3	60	BuOH	2/33
34	1.2	1.2	3	60	MeCN	24/24
35	1.2	2.2	3	60	MeCN	15/25
36	1.2	2.2	3	60	THF/BuOH (1:1)	17/27

37	1.2	2.2	3	60	MeCN/BuOH (1:1)	6/35
38	1.2	2.2	3	60	MeCN/BuOH (3:1)	10/36
39	1.2	2.2	3	60	^{i}PrOH	trace/25
40	1.2	2.2	3	60	PrOH	2/27
41	1.2	2.2	3	60	CF_3CH_2OH	–
42	1.2	2.2	3	60	EtOH	trace/30
43	1.2	2.2	3	60	MeCN/EtOH (1:1)	4/42
44	1.2	2.2	3	60	MeCN/EtOH (1:3)	2/41
45	1.2	4.2	3	60	MeCN/EtOH (1:3)	2/53 (22)[d]
46	2.4	4.2	6	60	MeCN/EtOH (1:3)	0/–(35)[d]
47	3.4	6	9	60	MeCN/EtOH (1:3)	0/–(35)[d]

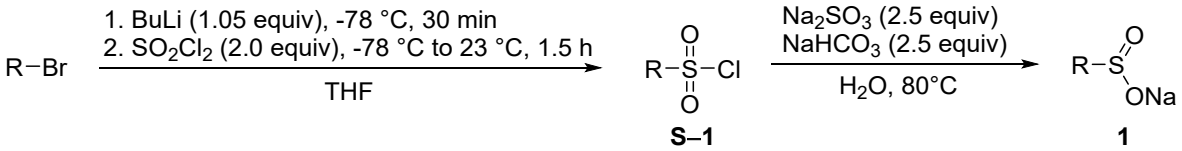
Reaction conditions: Sodium benzensulfinate (**1a**) and silver acetate was dissolved in a solvent (2 mL). Then *N*,*N*-diisopropylamine and morpholine (0.25 mmol) were added and the reaction mixture was stirred 18 h at indicated temperature. [a]Performed under air. [b]0.75 mmol of morpholine was used. [c]16 mL/mmol of THF was used. [d]Isolated yield. [e]CH_3COOH (1.0 equiv) was used.

Table S4 Optimization of benzensufinate salt used.



Entry	**1**	Isolated yield **4aaa** [%]
1	**1a**^{Li}	46
2	**1a**	67
3	**1a**^{K}	55

General procedure for the preparation of sulfinic acid salts 1 from sulfonyl chlorides (GP1)

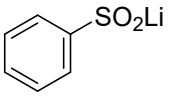


S–1 **1**

Halogen derivative (1.0 equiv) and THF (1 mL/mmol) were added to an argon-filled round bottom flask. To the solution was added buthyllithium (1.05 equiv) at -78 °C. The reaction was stirred for 30 minutes and sulfuryl chloride (2.0 equiv) was added at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. Then, it was poured into ice water and extracted with diethyl ether (100 mL). The organic layer was dried with anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure, and column chromatography (Silica gel) gave sulfonyl chloride **S–1**.

To the prepared sulfonyl chloride, sodium sulfite (2.5 equiv), sodium bicarbonate (2.5 equiv), and water (1.5 mL/mmol) were added. The reaction mixture was stirred overnight at 80 °C. Water was evaporated under reduced pressure. The residue was sonoficated for 30 minutes with ethanol (1 mL/mmol). The resulting suspension was filtered. The filtrate was evaporated, and the resulting sulfinic acid sodium salt **1** was washed with acetonitrile and diethyl ether and dried under vacuum.

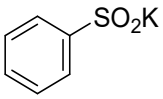
Benzenesulfinic acid lithium salt (**1a^{Li}**)



1a^{Li}, 84%

Bromobenzene (3.15 g, 20 mmol) and THF (20 mL) were placed in a round bottom flask filled with argon. The solution was cooled to -78 °C and buthylithium (8 mL, 2.50 M, 20 mmol) was added dropwise. The reaction mixture was stirred for 30 min at the same temperature, and liquid sulfur dioxide was added dropwise by syringe in excess. Sulfur dioxide was generated by adding conc. H_2SO_4 to an aqueous solution of Na_2SO_3 and condensed at -78 °C. The reaction mixture was warm up to 23°C and stirred for 30 min. The solvents were evaporated under reduced pressure, and the residue was washed with Et_2O (3 x 20 mL). The preparation afforded 2.48 g (84%) of benzenesulfinic acid lithium salt (**1a^{Li}**) as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.68–7.61 (m, 2H), 7.57–7.47 (m, 3H), in accordance with the data reported in the literature.[1]

Benzenesulfinic acid potassium salt (**1a^{K}**)

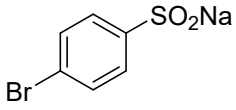


1a^{K}, 93%

Benzenesulfinic acid sodium salt (8.24 g, 50.2 mmol) was dissolved in 3 M HCl (50 mL), and the resulting solution was extracted by EtOAc (3 × 50 mL). Combined organic layers were dried over anhydrous Mg_2SO_4. The solvent was evaporated under reduced pressure, and the residue was dissolved in 30 mL water and 3 M aq. K_2CO_3 (20 mL) was added. After 20 minutes, water was evaporated under reduced pressure, and the residue was sonoficated 30 minutes with ethanol (50 mL). The resulting suspension was filtered, and the filtrate was evaporated to give 8.45 g (93%) of potassium salt **1a^{K}** as a white solid.

^{1}H NMR (400 MHz, D_2O) δ 7.70–7.65 (m, 2H), 7.60–7.52 (m, 3H), in accordance with the data reported in the literature.[2]

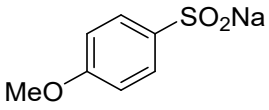
4-Bromobenzenesulfinic acid sodium salt (**1b**)



1b, 48%

Prepared according to GP1 from 4-bromobenzenesulfonyl chloride (4.12 g, 16 mmol), Na_2SO_3 (5.04 g, 40 mmol), $NaHCO_3$ (3.36 g, 40 mmol) and H_2O (24 mL) to give 1.85 g (48%) of the titled compound **1b** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), in accordance with the data reported in the literature.[3]

4-Methoxybenzenesulfinic acid sodium salt (**1c**)

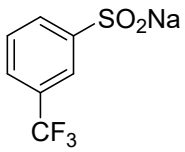


1c, 18%

4-Methoxybenzenesulfonyl chloride was prepared according to GP1 from 4-bromoanisole (3.74 g, 20 mmol), butyllithium (8.4 mL, 2.5 M, 21 mmol), sulfuryl chloride (3.2 mL, 40 mmol) and THF (20 mL). Column chromatography (Hexane/EtOAc, 4:1, R_f = 0.09) gave 1.81 g (44%) of 4-methoxybenzenesulfonyl chloride. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.1 Hz, 2H), 7.05 (d, *J* = 9.1 Hz, 2H), 3.93 (s, 3H), in accordance with the data reported in the literature.[4]

Isolated 4-methoxybenzenesulfonyl chloride (1.81 g, 8.8 mmol) was treated with Na_2SO_3 (2.77 g, 22 mmol), $NaHCO_3$ (1.85 g, 22 mmol) and H_2O (13 mL) to give 0.278 g (18%) of the titled compound **1c** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.57 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz, D_2O) δ 160.53, 145.90, 125.20, 114.35, 55.48, in accordance with the data reported in the literature.[3]

3-(Trifluoromethyl)benzenesulfinic acid sodium salt (**1d**)



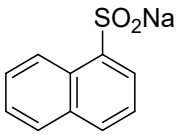
1d, 55%

3-(Trifluoromethyl)benzenesulfonyl chloride was prepared according to GP1 from 1-bromo-3-(trifluoromethyl)benzene (4.50 g, 20 mmol), butyllithium (8.4 mL, 2.5 M, 21 mmol), sulfuryl chloride (3.2 mL, 40 mmol) and THF (20 mL). Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.23) gave 1.44 g (29%) of 3-(trifluoromethyl)benzenesulfonyl chloride. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34–8.28 (m, 1H), 8.29–8.22 (m, 1H), 8.05–7.98 (m, 1H), 7.87–7.75 (m, 1H), in accordance with the data reported in the literature.[5]

Isolated 3-(trifluoromethyl)benzenesulfonyl chloride (1.44 g, 5.9 mmol) was treated with Na_2SO_3 (1.86 g, 14.8 mmol), $NaHCO_3$ (1.24 g, 14.8 mmol) and H_2O (9 mL) to give 0.75 g (55%) of the titled compound **1d** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.96–7.90 (m, 1H), 7.88–7.77 (m, 2H), 7.72–7.64 (m, 1H). **^{13}C NMR** (101 MHz, D_2O) δ 154.56, 130.44 (q, J_{C-F} = 32.3 Hz), 129.83, 127.29, 127.16 (q, J_{C-F} = 3.7 Hz),

123.97 (q, J_{C-F} = 272.0 Hz), 120.55 (q, J_{C-F} = 3.9 Hz). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.43. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_7H_4F_3NaO_2S$ 254.9674; Found 254.9675.

Naphthalene-1-sulfinic acid sodium salt (**1e**)

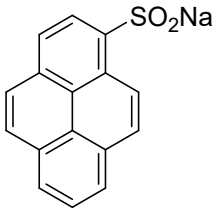


1e, 100%

1-Naphthalenesulfonyl chloride was prepared according to GP1 from 1-bromonaphthalene (6.21 g, 30 mmol), butyllithium (12.6 mL, 2.5 M, 31.5 mmol), sulfuryl chloride (4.8 mL, 60 mmol) and THF (30 mL). Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.15) gave 2.08 g (31%) of 1-naphthalenesulfonyl chloride. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.7 Hz, 1H), 8.38 (dd, *J* = 7.5, 1.1 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.86–7.77 (m, 1H), 7.74–7.67 (m, 1H), 7.65–7.58 (m, 1H) in accordance with the data reported in the literature.[6]

Isolated 1-naphthalenesulfonyl chloride (1.65 g, 7.3 mmol) was treated with Na_2SO_3 (2.31 g, 18.3 mmol), $NaHCO_3$ (1.54 g, 18.3 mmol) and H_2O (11 mL) to give 1.58 g (100%) of the titled compound **1e** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 8.52 (d, *J* = 8.2 Hz, 1H), 7.97–7.82 (m, 3H), 7.62–7.47 (m, 3H), in accordance with the data reported in the literature.[7]

Pyrene-1-sulfinic acid sodium salt (**1f**)

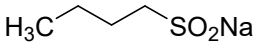


1f, 13%

Pyrene-1-sulfonyl chloride was prepared according to GP1 from 1-bromopyrene (5.63 g, 20 mmol), butyllithium (8.4 mL, 2.5 M, 21 mmol), sulfuryl chloride (3.2 mL, 40 mmol) and THF (20 mL). Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.10) gave 0.80 g (13%) of Pyrene-1-sulfonyl chloride as a yellow solid, mp = 172.3–173.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 9.4 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 8.48–8.37 (m, 3H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.21–8.12 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.69, 135.65, 131.90, 131.61, 130.82, 130.07, 128.48, 128.17, 128.09, 127.48, 126.99, 126.38, 125.21, 123.80, 123.67, 122.52.

Isolated pyrene-1-sulfonyl chloride (0.78 g, 2.6 mmol) was treated with Na_2SO_3 (0.82 g, 6.5 mmol), $NaHCO_3$ (0.55 g, 6.5 mmol) and H_2O (4 mL) to give 0.478 g (64%) of the titled compound **1f** as a yellowish solid. **^{1}H NMR** (400 MHz, D_2O) δ 8.14 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.28–7.21 (m, 2H), 7.16–7.03 (m, 3H), 6.96–6.87 (m, 1H). **^{13}C NMR** (101 MHz, D_2O) δ 144.87, 131.57, 129.75, 129.19, 127.42, 127.35, 126.87, 126.27, 125.39, 124.96, 124.91, 124.67, 123.05, 122.72, 120.77, 118.35. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{16}H_9NaO_2S$ 311.0113; Found 311.0115.

Butan-1-sulfinic acid sodium salt (**1g**)

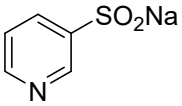


1g, 59%

Butane-1-sulfonyl chloride was prepared according to GP1 from butyllithium (8 mL, 2.5 M, 20 mmol), sulfuryl chloride (3.2 mL, 40 mmol) and THF (20 mL). Vacuum distillation gave 1.24 g (40%) of butane-1-sulfonyl chloride, bp = 82 °C at 9 torr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.71–3.63 (m, 2H), 2.10–1.98 (m, 2H), 1.62–1.47 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), in accordance with the data reported in the literature.[8]

Isolated butane-1-sulfonyl chloride (1.24 g, 7.9 mmol) was treated with Na_2SO_3 (2.50 g, 19.8 mmol), $NaHCO_3$ (1.66 g, 19.8 mmol) and H_2O (12 mL) to give 0.671 g (59%) of the titled compound **X** as a white solid. **^{1}H NMR** (400 MHz,D_2O) δ 2.40–2.30 (m, 2H), 1.58–1.47 (m, 2H), 1.44–1.33 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H), in accordance with the data reported in the literature.[9]

Pyridine-2-sulfinic acid sodium salt (**1h**)

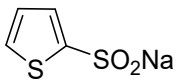


1h, 66%

3-Pyridinesulfonyl chloride was prepared according to GP1 from 3-bromopyridine (3.16 g, 20 mmol), butyllithium (8 mL, 2.5 M, 20 mmol), sulfuryl chloride (3.2 mL, 40 mmol) and Et_2O (40 mL). Column chromatography (Hexane/CH_2Cl_2, 1:2, R_f = 0.14) gave 1.03 g (29%) of the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.97 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.35–8.30 (m, 1H), 7.60 (ddt, *J* = 8.2, 4.9, 0.7 Hz, 1H), in accordance with the data reported in the literature.[10]

Isolated 3-pyridinesulfonyl chloride (1.03 g, 5.8 mmol) was treated with Na_2SO_3 (1.83 g, 14.5 mmol), $NaHCO_3$ (1.22 g, 14.5 mmol) and H_2O (9 mL) to give 0.628 g (66%) of the titled compound **1h** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 8.70–8.65 (m, 1H), 8.60–8.53 (m, 1H), 8.06–7.99 (m, 1H), 7.59–7.50 (m, 1H), in accordance with the data reported in the literature.[11]

Thiophene-2-sulfinic acid sodium salt (**1i**)

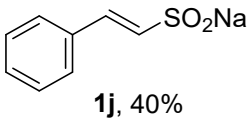


1i, 90%

Sulfuryl chloride (3.3 mL, 41 mmol) was added to DMF (2 mL, 26 mmol) at 0 °C and stirred for 30 minutes. Then, thiophene (2 mL, 20 mmol) was added at 0 °C and the reaction mixture was stirred for 1 h at 100 °C. The mixture was cooled down, poured to ice water, and extracted by CH_2Cl_2 (100 mL). The organic layer was washed with saturated $NaHCO_3$, water and dried with anhydrous $MgSO_4$. The solvent was evaporated, and vacuum distillation gave 2.154 g (59%) of the product, bp = 107 °C at 1 torr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1H NMR (400 MHz, cdcl3) δ 7.90 (dd, *J* = 4.0, 1.4, 1H), 7.83 (dd, *J* = 5.0, 1.4, 1H), 7.19 (dd, *J* = 5.0, 3.9, 1H), in accordance with the data reported in the literature.[12]

Isolated thiophene-2-sulfonyl chloride (2.154 g, 11.8 mmol) was treated with Na_2SO_3 (3.72 g, 29.5 mmol), $NaHCO_3$ (2.48 g, 29.5 mmol) and H_2O (18 mL) to give 1.81 g (90%) of the titled compound **1i** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.58 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.33 (dd, *J* = 3.6, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.6 Hz, 1H), in accordance with the data reported in the literature.[13]

(*E*)-2-Phenylethene-1-sulfinic acid sodium salt (**1j**)



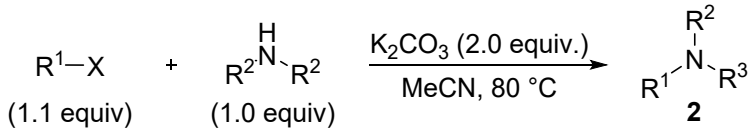
1j, 40%

Sulfuryl chloride (8.1 mL, 100 mmol) was added to DMF (8 mL) at 0 °C and stirred for 30 minutes at 23 °C. Then styrene (5.20 g, 50 mmol) was added at 0 °C and the reaction mixture was stirred for 2.5 h at 80 °C. The mixture was cooled down, poured to ice-water and extracted by Et_2O (100 mL). The organic layer was washed with water (2 x 50 mL) and dried with anhydrous $MgSO_4$. The mixture was concentrated under reduced pressure and then filtered through silica gel (Hexane/EtOAc 20:1, R_f = 0.36). The filtrate was concentrated under reduced pressure to afford 5.25 g (52%) of 2-phenylethenesulfonyl chloride as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.2 Hz, 1H), 7.59–7.45 (m, 5H), 7.24 (d, *J* = 15.1 Hz, 1H), in accordance with the data reported in the literature.[14]

Isolated 2-phenylethenesulfonyl chloride (5.25 g, 25.9 mmol) was treated with Na_2SO_3 (8.17 g, 64.8 mmol), $NaHCO_3$ (5.44 g, 64.8 mmol) and H_2O (39 mL) to give 1.99 g (40%) of the titled compound **1j** as a white solid. **^{1}H NMR** (400 MHz, D_2O) δ 7.61–7.51 (m, 2H), 7.48–7.36 (m, 3H), 7.05–6.96 (m, 1H), 6.91–6.83 (m, 1H). **^{13}C NMR** (101 MHz, D_2O) δ 141.67, 134.61, 133.98, 129.55, 129.05, 127.56. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd. for $C_8H_7NaO_2S$ 212.9957; Found 212.9957.

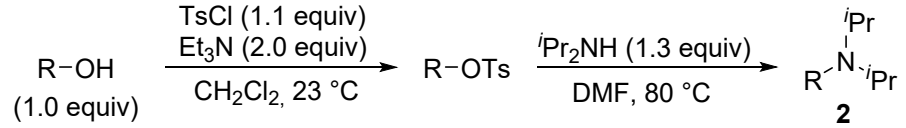
General procedures for the preparation of tertiary amines 2

– From organohalides (**GP2**)



The round bottom flask were placed K_2CO_3 (2.0 equiv) and MeCN (1 mL/mmol). To the resulting suspension, amine (1.0 equiv) and organohalide (1.1 equiv) were added. The reaction mixture was stirred overnight at 80 °C and concentrated under reduced pressure. The isolated residue was mixed with CH_2Cl_2 (5 mL/mmol) and the resulting suspension was filtered. The filtrate was washed with 1 M KOH (2 mL/mmol). The aqueous layer was extracted with CH_2Cl_2 (5 mL/mmol). Combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and pure amine **2** was obtained by vacuum distillation.

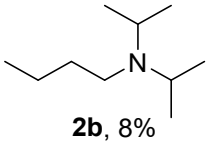
– From tosylates (**GP3**)



To the solution of TsCl (1.1 equiv) in CH_2Cl_2 (3 mL/mmol) were added Et_3N (2.0 equiv) and alcohol (1.0 equiv) at 23 °C. The reaction mixture was stirred for 16 h at the same temperature until saturated $NaHCO_3$ (5 mL/ mmol) was added. The organic layer was separated and washed with water (5 mL/ mmol), the aqueous layer was extracted with CH_2Cl_2 (5 mL/ mmol). The combined organic layers were dried over Na_2SO_4. The solvents were evaporated under reduced pressure, and column chromatography (Silica gel) or vacuum distillation gave the desire tosylate.

Diisopropylamine (1.3 equiv) was added to a solution of tosylate (1.0 equiv) in dry DMF (1 mL/mmol) under argon, and then the reaction mixture was stirred at 80 °C for 72 h. After cooling to ambient temperature, 3 M HCl was added to the mixture and washed with Et_2O (3 x 2 mL/ mmol). Then, the aqueous layer was made basic (pH = 8) by adding 10 M NaOH and extracted with Et_2O (3 x 2 mL/mmol). Combined organic layers were dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. Column chromatography (silica gel) or vacuum distillation gave the desired amine **2**.

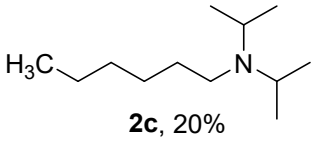
***N*,*N*-Diisopropylbutan-1-amine** (**2b**)



2b, 8%

Prepared according to **GP2** from diisopropylamine (5.08 g, 50.2 mmol), brombutane (6 mL, 55.2 mmol), K_2CO_3 (13.88 g, 100.4 mmol) and MeCN (50 mL). Vacuum distillation gave 0.598 g (8 %) of the amine **2b** as a colorless liquid, bp = 55 °C at 10 torr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.00 (hept, *J* = 6.6 Hz, 2H), 2.39–2.32 (m, 2H), 1.43–1.21 (m, 4H), 0.99 (d, *J* = 6.5 Hz, 12H), 0.90 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 48.64, 45.28, 34.07, 20.82, 20.76, 14.28. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{23}N$ 158.1903; Found 158.1903 in accordance with the data reported in the literature.[15]

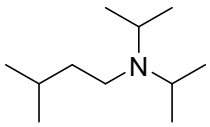
***N*,*N*-Diisopropylhexan-1-amine** (**2c**)



2c, 20%

Prepared according to **GP2** from diisopropylamine (10.08 g, 0.1 mol), bromhexane (15 mL, 0.11 mol), K_2CO_3 (27.64 g, 0.2 mol) and MeCN (100 mL). Vacuum distillation gave 3.63 g (20 %) of the amine **2c** as a colorless liquid, bp = 101 °C at 23 torr.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.00 (hept, *J* = 6.6 Hz, 2H), 2.41–2.32 (m, 2H), 1.42–1.21 (m, 8H), 0.99 (d, *J* = 6.6 Hz, 12H), 0.92–0.85 (m, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 48.68, 45.65, 32.03, 31.85, 27.33, 22.89, 20.82, 14.24. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{27}N$ 186.2216; Found 186.2214.

***N*,*N*-Diisopropyl-3-methylbutan-1-amine** (**2d**)



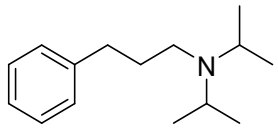
2d, 11%

Isoamyl tosylate was prepared according to **GP3** from isoamyl alcohol (2.65 g, 30 mmol), TsCl (6.29 g, 33 mmol), Et_3N (8.4 mL, 60 mmol) CH_2Cl_2 (90 mL). Column chromatography (Hexane/EtOAc, 2:1, R_f = 0.14) gave 6.20 g (85%) of the product. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37–7.33 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 1.77–1.61 (m, 1H), 1.52 (q, *J* = 6.7 Hz, 2H), 0.84 (d, *J* = 6.6 Hz, 6H) in accordance with the data reported in the literature.[16]

Isolated isoamyl tosylate (4.07 g, 16.8 mmol) was converted to the title compound according to **GP3** using diisopropylamine (3.1 mL, 21.8 mmol) and DMF (17 mL). Vacuum distillation gave 0.308 g (11%) of the product **2g** as a colorless liquid, bp = 70 °C at 13 torr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.00 (hept, *J* =

6.5 Hz, 2H), 2.43–2.34 (m, 2H), 1.61–1.48 (m, 1H), 1.35–1.24 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 12H), 0.89 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 48.74, 43.77, 41.06, 26.70, 23.00, 20.81.

***N*,*N*-diisopropyl-3-phenylpropan-1-amine** (**2e**)

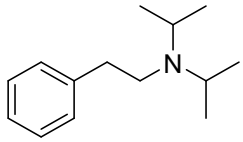


2e, 50%

3-Phenylpropyl 4-methylbenzenesulfonate was prepared according to **GP3** from 3-phenyl-1-propanol (4.04 g, 29.7 mmol), TsCl (6.23 g, 32.7 mmol), Et_3N (8.3 mL, 59.4 mmol) CH_2Cl_2 (90 mL) Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.34) gave 7.63 g (88 %) of the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37–7.32 (m, 2H), 7.26–7.21 (m, 2H), 7.20–7.14 (m, 1H), 7.09–7.04 (m, 2H), 4.03 (t, *J* = 6.2 Hz, 2H), 2.67–2.61 (m, 2H), 2.46 (s, 3H), 2.01–1.90 (m, 2H), in accordance with the data reported in the literature.[17]

Isolated 3-phenylpropyl 4-methylbenzenesulfonate (7.36 g, 25.3 mmol) was converted to the title compound according to **GP3** using diisopropylamine (4.6 mL, 32.9 mmol) and DMF (25 mL). Column chromatography (Hexane/EtOAc , 9:1, 1% Et_3N, R_f = 0.30) gave 2.76 g (50%) of the product **2e** as a colorless liquid **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.22 (m, 2H), 7.22–7.14 (m, 3H), 3.01 (hept, *J* = 6.6 Hz, 2H), 2.63–2.56 (m, 2H), 2.49–2.38 (m, 2H), 1.79–1.67 (m, 2H), 0.99 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.96, 128.50, 128.35, 125.65, 48.58, 45.07, 33.86, 33.10, 20.88, in accordance with the data reported in the literature.[18]

***N*-Isopropyl-*N*-phenethylpropan-2-amine** (**2f**)

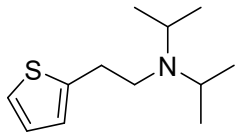


2f, 28%

2-Phenylethyl tosylate was prepared according to **GP3** from 2-phenylethanol (3.68 g, 30 mmol), TsCl (6.29 g, 33 mmol), Et_3N (8.4 mL, 60 mmol) CH_2Cl_2 (90 mL). Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.31) gave 7.25 g (87%) of the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.31–7.20 (m, 5H), 7.14–7.09 (m, 2H), 4.21 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), in accordance with the data reported in the literature.[19]

Isolated 2-phenylethyl tosylate (2.80 g, 15 mmol) was converted to the title compound according to **GP3** using diisopropylamine (2.7 mL, 19.5 mmol) and DMF (10 mL). Column chromatography (Hexane/EtOAc , 9:1, 1% Et_3N, R_f = 0.46) gave 0.862 g (28%) of the product **2f** as a colorless liquid **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.22–7.16 (m, 3H), 3.06 (hept, *J* = 6.6 Hz, 2H), 2.74–2.58 (m, 4H), 1.03 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.35, 128.90, 128.36, 125.93, 48.99, 48.20, 39.03, 20.90. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{23}N$ 206.1903; Found 206.1903.

***N*-isopropyl-*N*-(2-(thiophen-2-yl)ethyl)propan-2-amine** (**2g**)

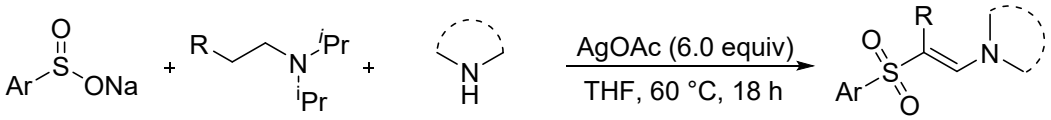


2g, 37%

2-(2-Thienyl)ethyl tosylate was prepared according to **GP3** from 2-thiopheneethanol (3.82 g, 30 mmol), TsCl (6.29 g, 33 mmol), Et_3N (8.4 mL, 60 mmol) CH_2Cl_2 (90 mL). Column chromatography (Hexane/EtOAc, 9:1, R_f = 0.31) gave 7.54 g (90%) of the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.34–7.29 (m, 2H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.81–6.78 (m, 1H), 4.21 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), in accordance with the data reported in the literature.[20]

Isolated 2-(2-thienyl)ethyl tosylate (5.67 g, 20 mmol) was converted to the title compound according to **GP3** using diisopropylamine (3.6 mL, 26 mmol) in DMF (20 mL). Column chromatography (Hexane/EtOAc , 9:1, 1% Et_3N, R_f = 0.39) gave 1.56 g (37%) of the product **2g** as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13–7.09 (m, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.82–6.78 (m, 1H), 3.05 (hept, *J* = 6.6 Hz, 2H), 2.93–2.86 (m, 2H), 2.73–2.65 (m, 2H), 1.03 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.58, 126.69, 124.44, 123.12, 48.95, 48.00, 32.76, 20.93. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{21}NS$ 212.1468; Found 212.1468.

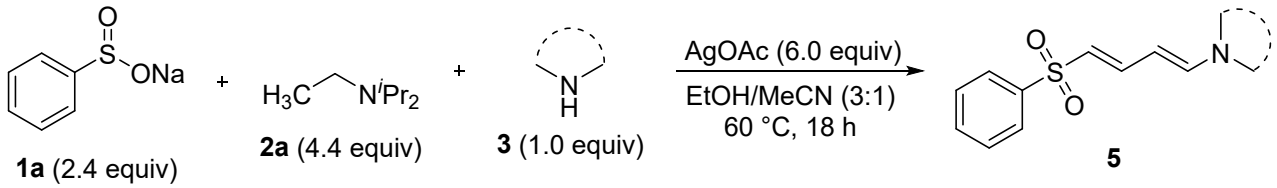
General procedure for the synthesis of *β*-arylsulfonyl enamines 4 (GP4)



1 (2.4 equiv) **2** (2.4 equiv) **3** (1.0 equiv) **4**

Silver acetate (6.0 equiv) and sulfinic acid sodium salt (2.4 equiv) were placed in a round-bottom flask. After flushing with argon, dry THF (16 mL/mmol) was added. Tertiary amine **2** (2.4 equiv) and secondary amine **3** (1.0 equiv) were added at 23 °C. The reaction mixture was stirred for 18 h at 60 °C. After cooling to ambient temperature, the reaction mixture was filtered and diluted with water (20 mL/mmol) and extracted with diethyl ether (40 mL/mmol). The organic layer was dried over anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure, and column chromatography (Silica gel) gave enamine **4**.

General procedure for the synthesis of *δ*-arylsulfonyl dienamines 5 (GP5)

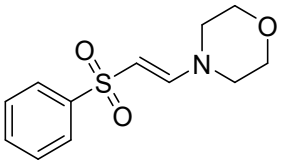


1a (2.4 equiv) **2a** (4.4 equiv) **3** (1.0 equiv) **5**

Silver acetate (6.0 equiv) and benzenesulfinic acid sodium salt **1a** (2.4 equiv) were added to a round-bottom flask. After flushing with argon, dry EtOH (6 mL/mmol) and dry MeCN (2 mL/mmol) were added. Tertiary amine **3** (4.4 equiv) and secondary amine **2a** (1.0 equiv) were added at 23 °C. The reaction mixture was stirred for 18 h at 60 °C. After cooling down, the reaction mixture was filtered and diluted with water (20 mL/mmol) and extracted with diethyl ether (40 mL/mmol). The organic

layer was dried over anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure, and column chromatography (Silica gel) gave dienamine **5**.

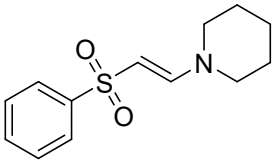
(*E*)-4-(2-(Phenylsulfonyl)vinyl)morpholine (**4aaa**)



4aaa, 67 %

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.20) gave 0.082 g (67%) of the title compound as a yellowish solid, mp = 160.0–161.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.77 (m, 2H), 7.58–7.37 (m, 3H), 7.27 (d, *J* = 12.8 Hz, 1H), 5.06 (d, *J* = 12.8 Hz, 1H), 3.81–3.58 (m, 4H), 3.20 (br s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.78, 144.56, 131.97, 129.03, 126.43, 94.55, 66.13. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}NO_3S$ 254.0845; Found 254.0843.

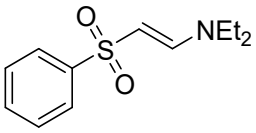
(*E*)-1-(2-(Phenylsulfonyl)vinyl)piperidine (**4aab**)



4aab, 48%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.21 mL, 1.2 mmol), piperidine (0.044 g, 0.52 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.14) gave 0.062 g (48%) of the title compound as a white solid, mp = 78–79°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.81 (m, 2H), 7.53–7.41 (m, 3H), 7.26 (d, *J* = 12.6 Hz, 1H), 4.95 (d, *J* = 12.7 Hz, 1H), 3.16 (br s, 4H), 1.70–1.47 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.99, 145.24, 131.63, 128.91, 126.25, 91.93, 25.45, 23.86. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}NO_2S$ 252.1053; Found 252.1054.

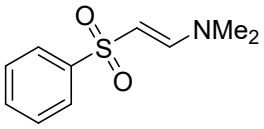
(*E*)-*N*,*N*-diethyl-2-(phenylsulfonyl)ethen-1-amine (**4aac**)



4aac, 62%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), diethylamine (0.035 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.18) gave 0.071 g (62%) of the title compoud as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.50–7.43 (m, 3H), 7.31 (d, *J* = 12.7 Hz, 1H), 4.90 (d, *J* = 12.7 Hz, 1H), 3.24 (br s, 2H), 3.11 (br s, 2H), 1.15 (br s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.12, 145.39, 131.53, 128.86, 126.13, 91.23, 50.13, 42.73, 14.80, 11.19, in accordance with the data reported in the literature.[21]

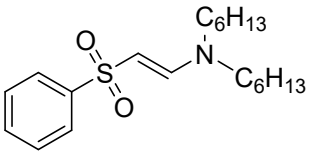
(*E*)-*N*,*N*-dimethyl-2-(phenylsulfonyl)ethen-1-amine (**4aad**)



4aad, 48%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.31 mL, 1.8 mmol), dimethylamine hydrochloride (0.042 g, 0.52 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.21) gave 0.053 g (48%) of the title compound as a yellowish solid, mp = 121.3–122.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 2H), 7.50–7.43 (m, 3H), 7.32 (d, *J* = 12.5 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 3.05 (br s, 3H), 2.73 (br s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.10, 145.16, 131.68, 128.92, 126.27, 92.44, 44.7, 37.3 in accordance with the data reported in the literature.[22]

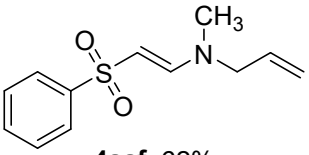
(*E*)-*N*-hexyl-*N*-(2-(phenylsulfonyl)vinyl)hexan-1-amine (**4aae**)



4aae, 46%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), DIPEA (0.21 mL, 1.2 mmol), dihexylamine (0.093 g, 0.50 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 9:1, 1% Et_3N, R_f = 0.27) gave 0.080 g (46%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.50–7.40 (m, 3H), 7.28 (d, *J* = 12.7 Hz, 1H), 4.84 (d, *J* = 12.7 Hz, 1H), 3.16 (br s, 2H), 2.97 (br s, 2H), 1.57–1.43 (m, 4H), 1.33–1.16 (m, 12H), 0.93–0.79 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.06, 145.49, 131.48, 128.84, 126.12, 91.04, 56.16, 48.72, 31.49, 29.21, 22.62, 14.05. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{33}NO_2S$ 352.2305; Found 352.2308.

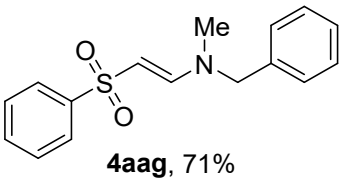
(*E*)-*N*-methyl-*N*-(2-(phenylsulfonyl)vinyl)prop-2-en-1-amine (**4aaf**)



4aaf, 62%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.21 mL, 1.2 mmol), *N*-allylmethylamine (0.036 g, 0.51 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.15) gave 0.074 g (62%) of the title compound as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 2H), 7.53–7.43 (m, 3H), 7.38 (d, *J* = 12.5 Hz, 1H), 5.74 (br s, 1H), 5.21 (dd, *J* = 23.2, 13.6 Hz, 2H), 4.93 (d, *J* = 12.5 Hz, 1H), 3.79 (br s, 2H), 2.69 (br s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.52, 145.07, 132.72, 131.70, 128.91, 126.27, 118.83, 93.00, 59.98, 35.35. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}NO_2S$ 238.0896; Found 238.0897.

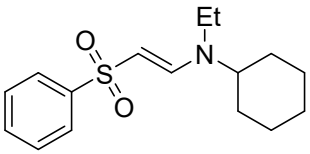
(*E*)-*N*-benzyl-*N*-methyl-2-(phenylsulfonyl)ethen-1-amine (**4aag**)



4aag, 71%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), DIPEA (0.21 mL, 1.2 mmol), *N*-benzylmethylamine (0.060 g, 50 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.14) gave 0.101 g (71%) of the title compound as a white solid, mp = 122.5–123.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.64–7.43 (m, 4H), 7.40–7.28 (m, 3H), 7.21–7.12 (m, 2H), 4.99 (d, *J* = 12.6 Hz, 1H), 4.37 (br s, 2H), 2.64 (br s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.89, 145.02, 135.98, 131.78, 129.05, 128.97, 128.27, 127.44, 126.33, 93.30, 61.46, 35.31. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}NO_2S$ 288.1053; Found 288.1056.

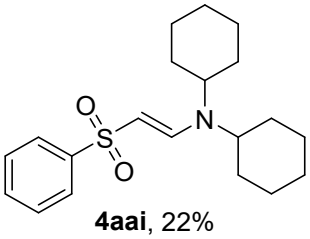
(*E*)-*N*-ethyl-*N*-(2-(phenylsulfonyl)vinyl)cyclohexanamine (**4aah**)



4aah, 43%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), DIPEA (0.21 mL, 1.2 mmol), *N*-ethylcyclohexylamine (0.063 g, 0.50 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.34) gave 0.063 g (43%) of the title compound as a white solid, mp = 99.6–100.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.50–7.42 (m, 3H), 7.38 (d, *J* = 12.6 Hz, 1H), 4.87 (d, *J* = 12.7 Hz, 1H), 3.18–2.97 (m, 3H), 1.89–1.77 (m, 4H), 1.71–1.61 (m, 1H), 1.49–1.03 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.65, 145.58, 131.50, 128.90, 126.18, 90.77, 65.13, 41.93, 32.67, 25.85, 25.32, 12.35. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{23}NO_2S$ 294.1522; Found 294.1525.

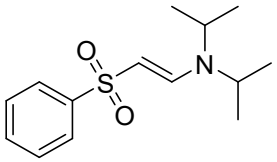
(*E*)-*N*-cyclohexyl-*N*-(2-(phenylsulfonyl)vinyl)cyclohexanamine (**4aai**)



4aai, 22%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), DIPEA (0.21 mL, 1.2 mmol), dicyclohexylamine (0.091 g, 0.50 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.46) gave 0.039 g (22%) of the title compound as a white solid, mp = 216.6–217.6°C. **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.88–7.81 (m, 2H), 7.53–7.43 (m, 3H), 7.41 (d, *J* = 12.7 Hz, 1H), 4.93 (d, *J* = 12.7 Hz, 1H), 3.15 (br s, 1H), 3.05 (br s, 1H), 1.89–1.76 (m, 4H), 1.76–1.61 (m, 6H), 1.54–1.37 (m, 4H), 1.31–1.22 (m, 4H), 1.18–1.05 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.06, 145.63, 131.42, 128.86, 126.19, 90.51, 58.52, 56.37, 34.33, 29.97, 26.10, 25.86, 25.43, 25.22, in accordance with the data reported in the literature.[23]

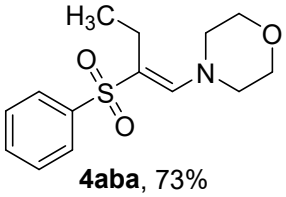
(*E*)-*N*-Isopropyl-*N*-(2-(phenylsulfonyl)vinyl)propan-2-amine (**4aaj**)



4aaj, 44%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.085 g, 0.52 mmol), AgOAc (0.260 g, 1.6 mmol), DIPEA (0.067 g, 0.52 mmol), diisopropylamine (0.053 g, 0.52 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.26) gave 0.061 g (44%) of the title compound as a white solid, mp = 106.2–107.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.79 (m, 2H), 7.50–7.42 (m, 3H), 7.39 (d, *J* = 12.8 Hz, 1H), 4.95 (d, *J* = 12.8 Hz, 1H), 3.58 (br s, 2H), 1.19 (br s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.55, 145.34, 131.46, 128.87, 126.16, 91.31, 49.37, 47.60, 23.56, 19.57, in accordance with the data reported in the literature.[24]

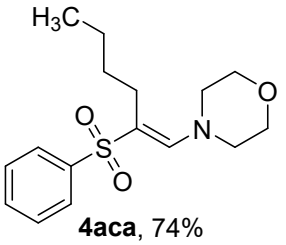
(*E*)-4-(2-(phenylsulfonyl)but-1-en-1-yl)morpholine (**4aba**)



4aba, 73%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), tributylamine (0.29 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.18) gave 0.099 g (73%) of the title compound as a white solid, mp = 120.5–121.5°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.55–7.45 (m, 3H), 7.25 (s, 1H), 3.76–3.71 (m, 4H), 3.43–3.37 (m, 4H), 2.28 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.27, 142.68, 132.06, 128.91, 127.42, 107.07, 66.74, 50.52, 19.02, 15.33. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{19}NO_3S$ 282.1158; Found 282.1161.

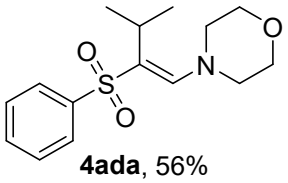
(*E*)-4-(2-(phenylsulfonyl)hex-1-en-1-yl)morpholine (**4aca**)



4aca, 74%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.181 g, 1.1 mmol), AgOAc (0.467 g, 2.8 mmol), *N*,*N*-diisopropylhexan-1-amine (**2c**) (0.204 g, 1.1 mmol), morpholine (0.041 g, 0.47 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.11) gave 0.109 g (74%) of the title compound as a white solid, mp = 74.5–75.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.81 (m, 2H), 7.55–7.44 (m, 3H), 7.25 (s, 1H), 3.76–3.69 (m, 4H), 3.41–3.35 (m, 4H), 2.25–2.15 (m, 2H), 1.37–1.12 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.31, 142.63, 132.04, 128.89, 127.40, 106.11, 66.72, 50.49, 32.82, 25.62, 22.70, 13.76. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{23}NO_3S$ 310.1471; Found 310.1476.

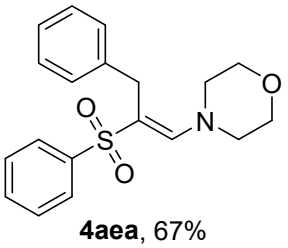
(*E*)-4-(3-methyl-2-(phenylsulfonyl)but-1-en-1-yl)morpholine (**4ada**)



4ada, 56%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), *N*,*N*-diisopropyl-3-methylbutan-1-amine (**2d**) (0.206 g, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.24) gave 0.079 g (56%) of the title compound as a yellowish solid, mp = 114.4–115.4 °C. **H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 2H), 7.53–7.43 (m, 3H), 7.32 (s, 1H), 3.80–3.70 (m, 4H), 3.46–3.39 (m, 4H), 2.91 (hept, *J* = 7.2 Hz, 1H), 1.05 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.62, 144.11, 131.83, 128.77, 126.98, 111.49, 66.70, 51.77, 26.35, 22.45. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{21}NO_3S$ 296.1315; Found 296.1317.

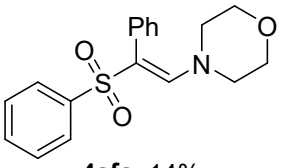
(*E*)-4-(3-phenyl-2-(phenylsulfonyl)prop-1-en-1-yl)morpholine (**4aea**)



4aea, 67%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), *N*,*N*-diisopropyl-3-phenylpropan-1-amine (**2e**) (0.263 g, 1.2 mmol), morpholine (0.043 g, 0.49 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.21) gave 0.113 g (67%) of the title compound as a yellowish solid, mp = 142.4–143.2°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.76 (m, 2H), 7.52 (s, 1H), 7.47–7.35 (m, 3H), 7.20–7.07 (m, 3H), 7.04–6.98 (m, 2H), 3.76 (s, 2H), 3.48–3.42 (m, 4H), 3.30–3.24 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.57, 142.57, 138.61, 131.97, 128.85, 128.55, 127.61, 127.35, 126.35, 102.37, 66.62, 50.61, 31.18. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{21}NO_3S$ 344.1315; Found 344.1321.

(*E*)-4-(2-phenyl-2-(phenylsulfonyl)vinyl)morpholine (**4afa**)

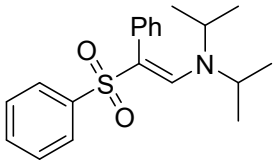


4afa, 14%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), *N*-isopropyl-*N*-phenethylpropan-2-amine (**2f**) (0.246 g, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.20 **4afa,** R_f = 0.66 4afj) gave 0.022 g (14%) of the enamine **4afa** as a white solid, mp = 166.0–167.0 °C and 0.072 g (25%) of the enamine **4afj** as a white solid, mp = 145.0–146.0 °C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.48 (s, 1H), 7.46–7.41 (m, 1H), 7.36–7.30 (m, 2H), 7.25–7.17 (m, 3H), 7.06–7.02 (m, 2H), 3.56–3.50 (m, 4H), 3.06–2.96 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.82, 141.87, 133.06, 131.93, 131.60,

128.49, 128.46, 128.29, 127.58, 108.12, 66.45, 50.50. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}NO_3S$ 330.1158; Found 330.1161.

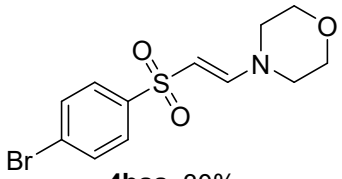
(*E*)-*N*-isopropyl-*N*-(2-phenyl-2-(phenylsulfonyl)vinyl)propan-2-amine (**4afj**)



4afj, 28%

Prepared according to **GP4** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), *N*-isopropyl-*N*-phenethylpropan-2-amine (**2f**) (0.246 g, 1.2 mmol), diisopropylamine (0.050 g, 0.49 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 6:1, 1% Et_3N, R_f = 0.33) gave 0.114 g (28%) of the title compound as a white solid, mp = 145.0–146.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.54–7.49 (m, 2H), 7.44–7.38 (m, 1H), 7.35–7.29 (m, 2H), 7.24–7.16 (m, 3H), 7.05–7.00 (m, 2H), 3.46 (hept, *J* = 6.8 Hz, 2H), 1.06 (br s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.73, 140.66, 133.04, 133.01, 131.45, 128.37, 128.16, 128.09, 127.37, 104.98, 47.31. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{25}NO_2S$ 344.1679; Found 344.1685.

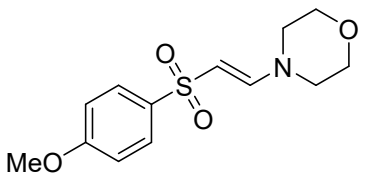
(*E*)-4-(2-((4-Bromophenyl)sulfonyl)vinyl)morpholine (**4baa**)



4baa, 30%

Prepared according to **GP4** from 4-bromobenzenesulfinic acid sodium salt (**1b**) (0.292 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 1:1, 1% Et_3N, R_f = 0.31) gave 0.048 g (30%) of the title compound as a yellowish solid, mp = 202.1–203.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73–7.69 (m, 2H), 7.63–7.59 (m, 2H), 7.25 (d, *J* = 12.8 Hz, 1H), 5.02 (d, *J* = 12.7 Hz, 1H), 3.75–3.66 (m, 4H), 3.29–3.14 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.03, 143.72, 132.27, 128.13, 126.77, 94.02, 66.22. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{14}BrNO_3S$ 331.9951; Found 331.9953.

(*E*)-4-(2-((4-Methoxyphenyl)sulfonyl)vinyl)morpholine (**4caa**)

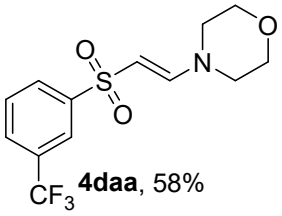


4caa, 38%

Prepared according to **GP4** from 4-methoxybenzenesulfinic acid sodium salt (**1c**) (0.193 g, 1.1 mmol), AgOAc (0.471 g, 2.8 mmol), DIPEA (0.20 mL, 1.1 mmol), morpholine (0.041 g, 0.47 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.10) gave 0.050 g (38%) of the title compound as an orange solid, mp = 156.3–156.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.23 (d, *J* = 12.8 Hz, 1H), 6.97–6.90 (m, 2H), 5.05 (d, *J* = 12.8 Hz, 1H), 3.84 (s, 3H), 3.73–3.65 (m, 4H),

3.24–3.10 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.46, 149.20, 136.40, 128.56, 114.18, 95.57, 66.15, 55.69. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}NO_4S$ 284.0951; Found 284.0953.

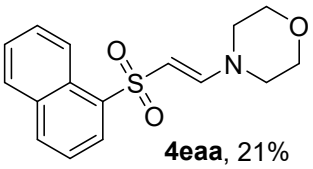
(*E*)-4-(2-((3-(Trifluoromethyl)phenyl)sulfonyl)vinyl)morpholine (**4daa**)



4daa, 58%

Prepared according to **GP4** from 3-(trifluoromethyl)benzenesulfinic acid sodium salt (**1d**) (0.279 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f =0.15) gave 0.089 g (58%) of the title compound as a yellowish solid, mp = 110.7–111.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13–8.09 (m, 1H), 8.06–8.01 (m, 1H), 7.79–7.74 (m, 1H), 7.65–7.58 (m, 1H), 7.29 (d, *J* = 12.7 Hz, 1H), 5.03 (d, *J* = 12.7 Hz, 1H), 3.78–3.64 (m, 4H), 3.23 (br s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.45, 145.92, 131.63 (q, *J* = 33.3 Hz), 129.82, 129.77, 128.59 (q, *J* = 3.6 Hz), 123.59 (q, *J* = 3.9 Hz), 123.50 (q, *J* = 273.1 Hz), 93.30, 66.11. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.26. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{14}F_3NO_3S$ 322.0719; Found 322.0721.

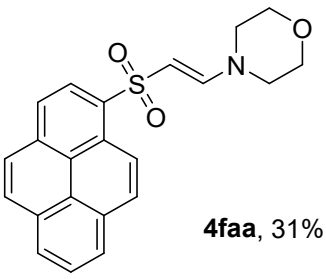
(*E*)-4-(2-(Naphthalen-1-ylsulfonyl)vinyl)morpholine (**4eaa**)



4eaa, 21%

Prepared according to **GP4** from naphthalene-1-sulfinic acid sodium salt (**1e**) (0.242 g, 1.1 mmol), AgOAc (0.471 g, 2.8 mmol), DIPEA (0.20 mL, 1.1 mmol), morpholine (0.041 g, 0.47 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f =0.12) gave 0.030 g (21%) of the title compound as a colorless viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72–8.66 (m, 1H), 8.28 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.96–7.90 (m, 1H), 7.69–7.63 (m, 1H), 7.62–7.50 (m, 2H), 7.36 (d, *J* = 12.8 Hz, 1H), 5.26 (d, *J* = 12.7 Hz, 1H), 3.73–3.62 (m, 4H), 3.18 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.03, 139.46, 134.38, 133.64, 129.16, 128.37, 128.00, 127.54, 126.70, 124.74, 124.65, 94.92, 66.13. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}NO_3S$ 304.1002; Found 304.1004.

(*E*)-4-(2-(Pyren-1-ylsulfonyl)vinyl)morpholine (**4faa**)

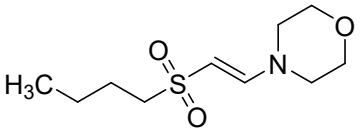


4faa, 31%

Prepared according to **GP4** from pyrene-1-sulfinic acid sodium salt (**X**) (0.326 g, 1.1 mmol), AgOAc (0.471 g, 2.8 mmol), DIPEA (0.20 mL, 1.1 mmol), morpholine (0.041 g, 0.47 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.08) gave 0.054 g (31%) of the enamine **X**

as a yellowish solid, mp = 224.6–225.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 9.3 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H), 8.31–8.24 (m, 3H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 9.0 Hz, 1H), 8.11–8.05 (m, 2H), 7.44 (d, *J* = 12.7 Hz, 1H), 5.38 (d, *J* = 12.7 Hz, 1H), 3.68–3.60 (m, 4H), 3.24–3.11 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.68, 136.15, 134.48, 131.12, 130.28, 129.88, 129.72, 127.83, 127.25, 126.81, 126.75, 126.70, 125.67, 125.31, 124.35, 124.33, 123.44, 95.88, 66.09. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{19}NO_3S$ 378.1158; Found 378.1167.

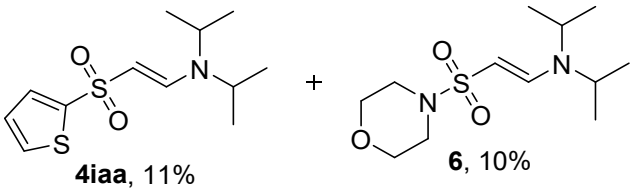
(*E*)-4-(2-(butylsulfonyl)vinyl)morpholine (**4gaa**)



4gaa, 9%

Prepared according to **GP4** from butan-1-sulfinic acid sodium salt (**1g**) (0.173 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.11) gave 0.010 g (9%) of the title compound as a yellowish viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 12.9 Hz, 1H), 4.95 (d, *J* = 12.9 Hz, 1H), 3.76–3.69 (m, 4H), 3.27–3.16 (m, 4H), 3.00–2.91 (m, 2H), 1.81–1.70 (m, 2H), 1.50–1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.74, 91.76, 56.89, 29.78, 25.33, 21.74, 13.74. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{19}NO_3S$ 234.1158; Found 234.1161.

(*E*)-*N*-isopropyl-*N*-(2-(thiophen-2-ylsulfonyl)vinyl)propan-2-amine (**4iaa**) **and (*E*)-*N*-isopropyl-*N*-(2-(morpholinosulfonyl)vinyl)propan-2-amine** (**6**)



4iaa, 11% **6**, 10%

Prepared according to **GP4** from thiophene-2-sulfinic acid sodium salt (**1i**) (0.204 g, 1.2 mmol), AgOAc (0.484 g, 2.9 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.042 g, 0.48 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.21 **4iaa**, 0.12 **6**) gave 0.015 g (11%) of the enamine **4iaa** as a yellowish solid, mp = 101.3–102.3 °C, and 0.013 g, (10%) of the enamine **6** as an off-white solid, mp = 92.0–93.0 °C.

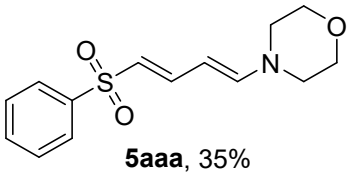
(*E*)-*N*-isopropyl-*N*-(2-(thiophen-2-ylsulfonyl)vinyl)propan-2-amine (**4iaa**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 3.7, 1.4 Hz, 1H), 7.46 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.42 (d, *J* = 12.7 Hz, 1H), 7.01 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.10 (d, *J* = 12.8 Hz, 1H), 3.61 (br s, 3H), 1.21 (br s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.48, 145.58, 130.38, 129.82, 127.15, 92.45, 23.54, 19.57. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{19}NO_2S_2$ 274.0930; Found 274.0932.

(*E*)-*N*-isopropyl-*N*-(2-(morpholinosulfonyl)vinyl)propan-2-amine (**6**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 12.9 Hz, 1H), 4.68 (d, *J* = 13.0 Hz, 1H), 3.81–3.73 (m, 4H), 3.61 (br s, 2H), 3.03–2.93 (m, 4H), 1.21 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.37, 82.31, 66.42, 46.09. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{24}N_2O_3S$ 277.1580; Found 277.1582.

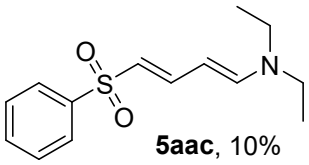
4-((1*E*,3*E*)-4-(Phenylsulfonyl)buta-1,3-dien-1-yl)morpholine (**5aaa**)



5aaa, 35%

Prepared according to **GP5** from benzenesulfinic acid sodium salt (0.181 g, 1.1 mmol), AgOAc (0.471 g, 2.8 mmol), DIPEA (0.35 mL, 2.0 mmol), morpholine (0.040 g, 0.46 mmol), EtOH (3 mL) and MeCN (1 mL). Column chromatography (Hexane/EtOAc, 1:1, 1% Et_3N, R_f = 0.26) gave 0.045 g (35%) of the title compound as an orange sticky solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.57–7.41 (m, 3H), 7.33–7.20 (m, 1H), 6.61 (d, *J* = 12.9 Hz, 1H), 5.84 (d, *J* = 14.2 Hz, 1H), 5.16 (dd, *J* = 12.9, 11.5 Hz, 1H), 3.74–3.67 (m, 4H), 3.21–3.14 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.93, 145.36, 143.27, 132.30, 129.08, 126.92, 115.79, 95.20, 66.24, 48.62. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}NO_3S$ 280.1001; Found 280.1004.

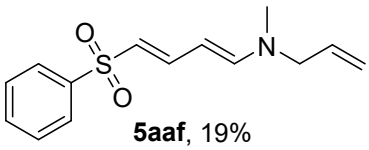
(1*E*,3*E*)-*N*,*N*-Diethyl-4-(phenylsulfonyl)buta-1,3-dien-1-amine (**5aac**)



5aac, 10%

Prepared according to **GP5** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.38 mL, 2.2 mmol), diethylamine (0.037 g, 0.51 mmol), EtOH (3 mL) and MeCN (1 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.14) gave 0.14 g (10%) of the title compound as an orange viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.83 (m, 2H), 7.52–7.42 (m, 3H), 7.26 (dd, *J* = 14.6, 11.1 Hz, 1H), 6.69 (d, *J* = 12.8 Hz, 1H), 5.71 (d, *J* = 14.1 Hz, 1H), 5.03 (dd, *J* = 12.7, 11.7 Hz, 1H), 3.18 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.46, 146.72, 143.98, 131.96, 128.99, 126.76, 112.01, 93.28. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{19}NO_2S$ 266.1209; Found 266.1211.

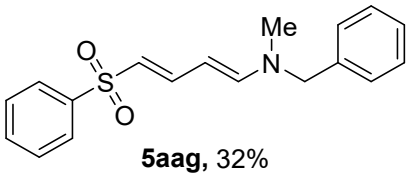
(1*E*,3*E*)-*N*-Allyl-*N*-methyl-4-(phenylsulfonyl)buta-1,3-dien-1-amine (**5aaf**)



5aaf, 19%

Prepared according to **GP5** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.38 mL, 2.2 mmol), *N*-allylmethylamine (0.036 g, 0.51 mmol), EtOH (3 mL) and MeCN (1 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.13) gave 0.025 g (19%) of the title compound as an orange viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.83 (m, 2H), 7.53–7.42 (m, 3H), 7.32–7.20 (m, 1H), 6.74 (d, *J* = 12.7 Hz, 1H), 5.85–5.65 (m, 2H), 5.28–5.12 (m, 2H), 5.03 (dd, *J* = 12.7, 11.6 Hz, 1H), 3.72 (dt, *J* = 5.7, 1.6 Hz, 2H), 2.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.57, 146.05, 143.67, 132.08, 129.00, 126.79, 118.32, 113.58, 94.23. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}NO_2S$ 264.1053; Found 264.1053.

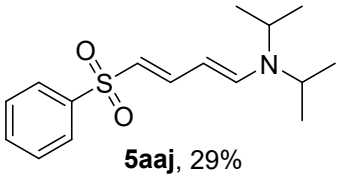
(1*E*,3*E*)-*N*-Benzyl-*N*-methyl-4-(phenylsulfonyl)buta-1,3-dien-1-amine (**5aag**)



5aag, 32%

Prepared according to **GP5** from benzenesulfinic acid sodium salt (0.200 g, 1.2 mmol), AgOAc (0.517 g, 3.1 mmol), DIPEA (0.38 mL, 2.2 mmol), *N*-benzylmethylamine (0.062 g, 0.51 mmol), EtOH (3 mL) and MeCN (1 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.18) gave 0.052 g (32%) of the title compound as an orange solid, mp = 114.4–115.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.54–7.45 (m, 3H), 7.39–7.27 (m, 4H), 7.19–7.14 (m, 2H), 6.90 (d, *J* = 12.7 Hz, 1H), 5.80 (d, *J* = 14.2 Hz, 1H), 5.15–5.05 (m, 1H), 4.32 (s, 2H), 2.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.88, 145.96, 143.62, 136.29, 132.13, 129.09, 129.04, 128.12, 127.37, 126.84, 114.00, 94.36. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}NO_2S$ 314.1209; Found 314.1211.

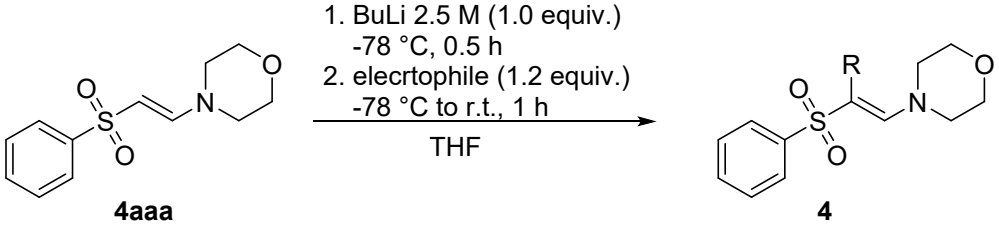
(1*E*,3*E*)-*N*,*N*-Diisopropyl-4-(phenylsulfonyl)buta-1,3-dien-1-amine (**5aaj**)



5aaj, 29%

Prepared according to **GP5** from benzenesulfinic acid sodium salt (0.080 g, 0.49 mmol), AgOAc (0.250 g, 1.5 mmol), DIPEA (0.129 g, 1.0 mmol), diisopropylamine (0.05 g, 0.49 mmol), EtOH (3 mL) and MeCN (1 mL). Column chromatography (Hexane/EtOAc, 4:1, 1% Et_3N, R_f = 0.33) gave 0.043 g (29%) of the title compound as a yellowish solid, mp = 120.3–121.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.52–7.42 (m, 3H), 7.30 (dd, *J* = 14.1, 11.6 Hz, 1H), 6.79 (d, *J* = 12.8 Hz, 1H), 5.69 (d, *J* = 14.0 Hz, 1H), 5.16 (dd, *J* = 12.8, 11.5 Hz, 1H), 3.67 (br s, 2H), 1.18 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.40, 147.03, 144.11, 131.88, 128.95, 126.69, 111.01, 93.34, 47.76, 21.71. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{23}NO_2S$ 294.1522; Found 294.1525.

General procedure for the modification in *β*-position of (*E*)-4-(2-(Phenylsulfonyl)vinyl)morpholine (**4aa**) **by lithiation and subsequent reaction with organohalide (GP6)**

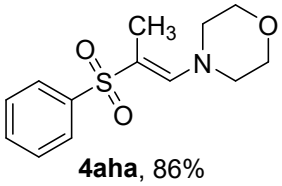


4aaa **4**

(*E*)-4-(2-(Phenylsulfonyl)vinyl)morpholine (**4aaa**) (1.0 equiv) was placed in a round-bottom flask. The flask was flushed with argon, and dry THF (5 mL/ mmol) was added. Butyllithium (1.0 equiv) was added dropwise to the solution cooled to -78 °C. After 30 minutes, the electrophile (1.2 equiv) was added dropwise at the same temperature. The reaction mixture was allowed to warm up to room temperature (23 °C) and it was stirred for 1 hour until saturated NH_4Cl (5 mL/ mmol) was added. The mixture was diluted by water (50 mL/ mmol) and extracted by diethyl ether (50 mL/mmol). The organic

layer was separated and dried over anhydrous $MgSO_4$. The solvents were evaporated under reduced pressure, and column chromatography (Silica gel) gave the desired product **4**.

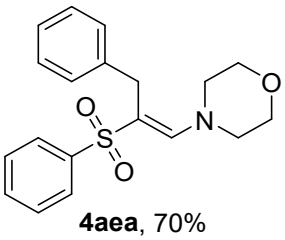
(*E*)-4-(2-(Phenylsulfonyl)prop-1-en-1-yl)morpholine (**4aha**)



4aha, 86%

Prepared according to **GP6** from enamine **4aaa** (0.051 g, 0.20 mmol), BuLi (0.08 mL, 2.50 M, 0.20 mmol), methyl iodide (0.02 mL, 0.24 mL) and THF (1 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.23) gave 0.046 g (86%) of the title compound as a yellowish solid, mp = 82.9–83.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 2H), 7.55–7.45 (m, 3H), 7.25 (s, 1H), 3.75–3.67 (m, 4H), 3.44–3.38 (m, 4H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.64, 141.90, 132.11, 128.95, 127.31, 101.02, 66.72, 50.40, 12.01. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}NO_3S$ 268.1002; Found 268.1004.

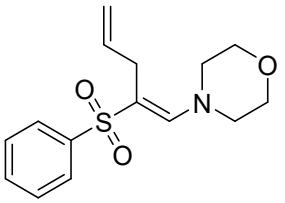
(*E*)-4-(3-Phenyl-2-(phenylsulfonyl)prop-1-en-1-yl)morpholine (**4aea**)



4aea, 70%

Prepared according to **GP6** from enamine **4aaa** (0.127 g, 0.50 mmol), BuLi (0.20 mL, 2.50 M, 0.50 mmol), benzyl bromide (0.71 mL, 0.60 mmol) and THF (2 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.20) gave 0.121 g (70%) of the title compound as a yellowish solid.

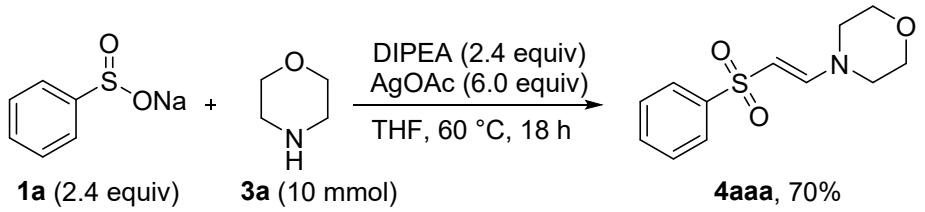
(*E*)-4-(2-(Phenylsulfonyl)penta-1,4-dien-1-yl)morpholine (**4aia**)



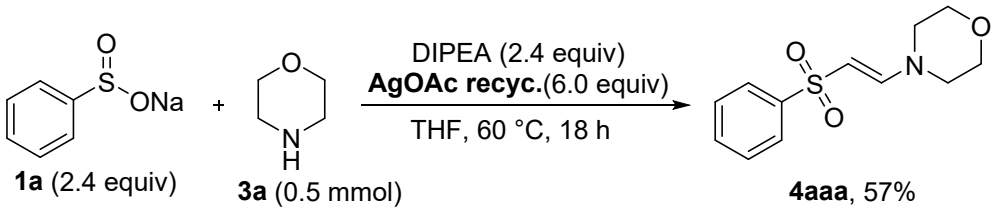
4aia, 74%

Prepared according to **GP6** from enamine **4aaa** (0.051 g, 0.20 mmol), BuLi (0.08 mL, 2.50 M, 0.20 mmol), allyl bromide (0.02 mL, 0.24 mmol) and THF (1 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f =0.21) gave 0.044 g (74%) of the title compound as a yellowish solid, mp = 101.9–102.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.52–7.42 (m, 3H), 7.41 (s, 1H), 5.70–5.58 (m, 1H), 4.98–4.80 (m, 2H), 3.71–3.62 (m, 4H), 3.43–3.34 (m, 4H), 3.11–3.03 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.50, 142.53, 135.42, 132.05, 128.88, 127.50, 116.13, 101.78, 66.88, 50.48, 29.37. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}NO_3S$ 294.1158; Found 294.1161.

Gram-scale synthesis of (*E*)-4-(2-(Phenylsulfonyl)vinyl)morpholine (4aaa) including Ag recycling



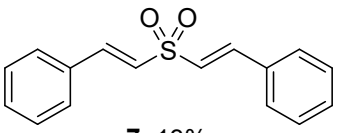
70% of AgOAc was recovered



Gram-scale synthesis was performed according to **GP4 f**rom benzenesulfinic acid sodium salt (3.82 g, 23.3 mmol), AgOAc (9.71 g, 58.2 mmol), DIPEA (4.1 mL, 23.3 mmol), morpholine (0.843 g, 9.7 mmol), and THF (160 mL). Column chromatography gave 1.71 g (70%) of enamine **4aaa**. Silver residue collected by filtration was dissolved in conc. HNO_3. The HNO_3 was then distilled off to produce crude $AgNO_3$. $AgNO_3$ was then dissolved in demi-water, and AgOAc was obtained by precipitation with a solution of NaOAc in demi-water. The precipitate was filtered, washed with water and acetone, and dried under a vacuum. This gave 6.80 g (70% recovery) of AgOAc.

The reaction with recycled $AgNO_3$ was performed according to **GP4** from benzenesulfinic acid sodium salt (0.181 g, 1.1 mmol), AgOAc (0.467 g, 2.8 mmol), DIPEA (0.20 mL, 1.1 mmol), morpholine (0.041 g, 0.47 mmol), and THF (8 mL). Column chromatography gave 0.068 g (57%) of enamine **4aaa**.

((1*E*,1'*E*)-sulfonylbis(ethene-2,1-diyl))dibenzene (7)



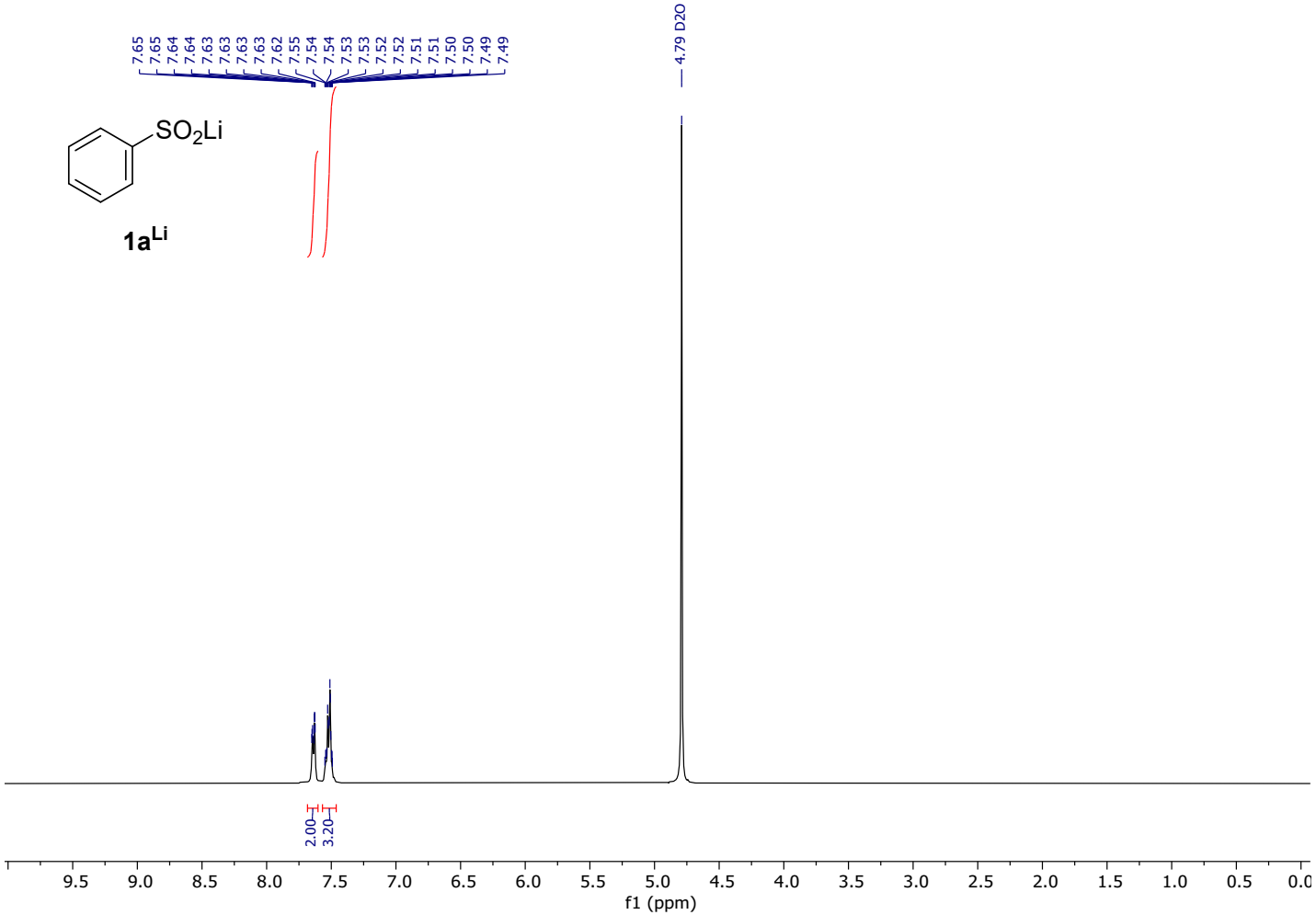
7, 13%

Prepared according to **GP4** from (*E*)-2-phenylethene-1-sulfinic acid sodium salt (**1j**) (0.228 g, 1.2 mmol), AgOAc (0.501 g, 3 mmol), DIPEA (0.21 mL, 1.2 mmol), morpholine (0.043 g, 0.49 mmol) and THF (8 mL). Column chromatography (Hexane/EtOAc, 2:1, 1% Et_3N, R_f = 0.21) gave 0.02 g (13%) of the title compound as a yellowish viscous liquid. **^{1}H NMR** (400 MHz, $CDCl_3$). δ 7.65 (d, *J* = 15.4 Hz, 2H), 7.54–7.49 (m, 4H), 7.45–7.38 (m, 6H), 6.86 (d, *J* = 15.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.63, 132.64, 131.42, 129.27, 128.71, 126.50.[25]

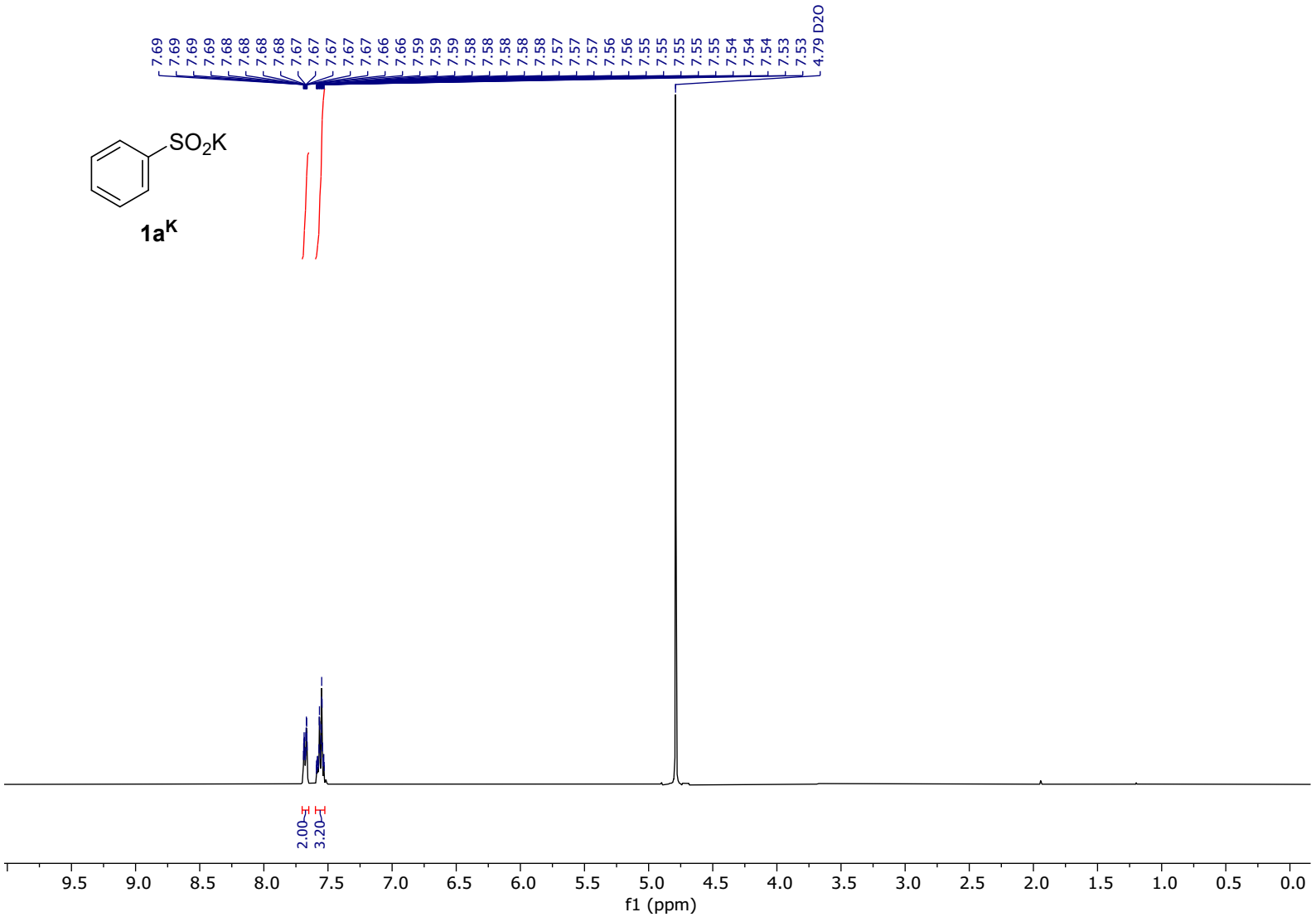
References:

(1) C. Martin, F. Sandrinelli, C. Perrio, S. Perrio and M.-C. Lasne, *J. Org. Chem.* 2006, **71**, 210.
(2) S. Waiba, A. Das, M. K. Barman and B. Maji, *ACS Omega* 2019, **4**, 7082.
(3) A. U. Meyer, S. Jäger, D. Prasad Hari and B. König, *Adv. Synth. Catal.* 2015, **357**, 2050.
(4) M. Kirihara, S. Naito, Y. Nishimura, Y. Ishizuka, T. Iwai, H. Takeuchi, T. Ogata, H. Hanai, Y. Kinoshita, M. Kishida, K. Yamazaki, T. Noguchi, S. Yamashoji, *Tetrahedron* 2014, **70**, 2464.
(5) M. Jereb and L. Hribernik, *Green Chem.* 2017, **19**, 2286.
(6) J. R. DeBergh, N. Niljianskul and S. L. Buchwald, *J. Am. Chem. Soc.* 2013, **135**, 10638.
(7) T. Chen, J. Lahbi, G. Broggini, A. Pradal and G. Poli, *Eur. J. Org. Chem.* 2023, **26**, e202201493.
(8) Z. Yang, Y. Zheng and J. Xu, *Synlett* 2013, **24**, 2165.
(9) A. U. Meyer, K. Straková, T. Slanina and B. König, *Chem. Eur. J.* 2016, **22**, 8694.
(10) U. Galli, O. Mesenzani, C. Coppo, G. Sorba, P. L. Canonico, G. C. Tron and A. A. Genazzani, *Eur. J. Med. Chem.* 2012, **55**, 58.
(11) J. Wei, H. Liang, C. Ni, R. Sheng and J. Hu, *Org. Lett.* 2019, **21**, 937.
(12) R. Chen, S. Xu, F. Shen, C. Xu, K. Wang, Z. Wang and L. Liu, *Molecules* **2021**, *26*, 5551.
(13) G. Bogonda, D. V. Patil, H. Y. Kim and K. Oh, *Org. Lett.* 2019, **21**, 3774.
(14) B. Shi, S. Merten, D. K. Y. Wong, J. C. K. Chu, L. L. Liu, S. K. Lam, A. Jäger, W.-T. Wong, P. Chiu and P. Metz, *Adv. Synth. Catal.* 2009, **351**, 3128.
(15) A. Alberti, F. Canè, P. Dembech, D. Lazzari, A. Ricci and G. Seconi, *J. Org. Chem.* 1996, **61**, 1677.
(16) Q. Lin, W. Tong, X.-Z. Shu and Y. Chen, *Org. Lett.* 2022, **24**, 8459.
(17) Z.-Q. Zhang, C.-T. Yang, L.-J. Liang, B. Xiao, X. Lu, J.-H. Liu, Y.-Y. Sun, T. B. Marder and Y. Fu, *Org. Lett.* 2014, **16**, 6342.
(18) S. Li, K. Huang, J. Zhang, W. Wu and X. Zhang, *Org. Lett.* 2013, **15**, 3078.
(19) K. Gulbe and M. Turks, *J. Org. Chem.* 2020, **85**, 5660.
(20) D.-T. D. Tang, K. D. Collins, J. B. Ernst and F. Glorius, *Angew. Chem. Int. Ed.* 2014, **53**, 1809.
(21) J. Lai, L. Chang and G. Yuan, *Org. Lett.* **2016**, *18*, 3194.
(22) N. Peša, C. J. Welch and A. N. Boa, *J. Heterocycl. Chem.* 2005, **42**, 599.
(23) H.-S. Kim and S. Lee, *Eur. J. Org. Chem.* 2019, 6951.
(24) H. Jiang, X. Tang, Z. Xu, H. Wang, K. Han, X. Yang, Y. Zhou, Y.-L. Feng, X.-Y. Yu and Q.Gui, *Org. Biomol. Chem.* 2019, **17**, 2715.
(25) M.-Y. Chang, Y.-S. Wu and Y.-T. Hsiao, *Synthesis* 2018, **50**, 4651.

Copies of ^{1}H and ^{13}NMR spectra



^{1}H NMR (400 MHz, D_2O) spectrum of compound **$1a^{Li}$**.



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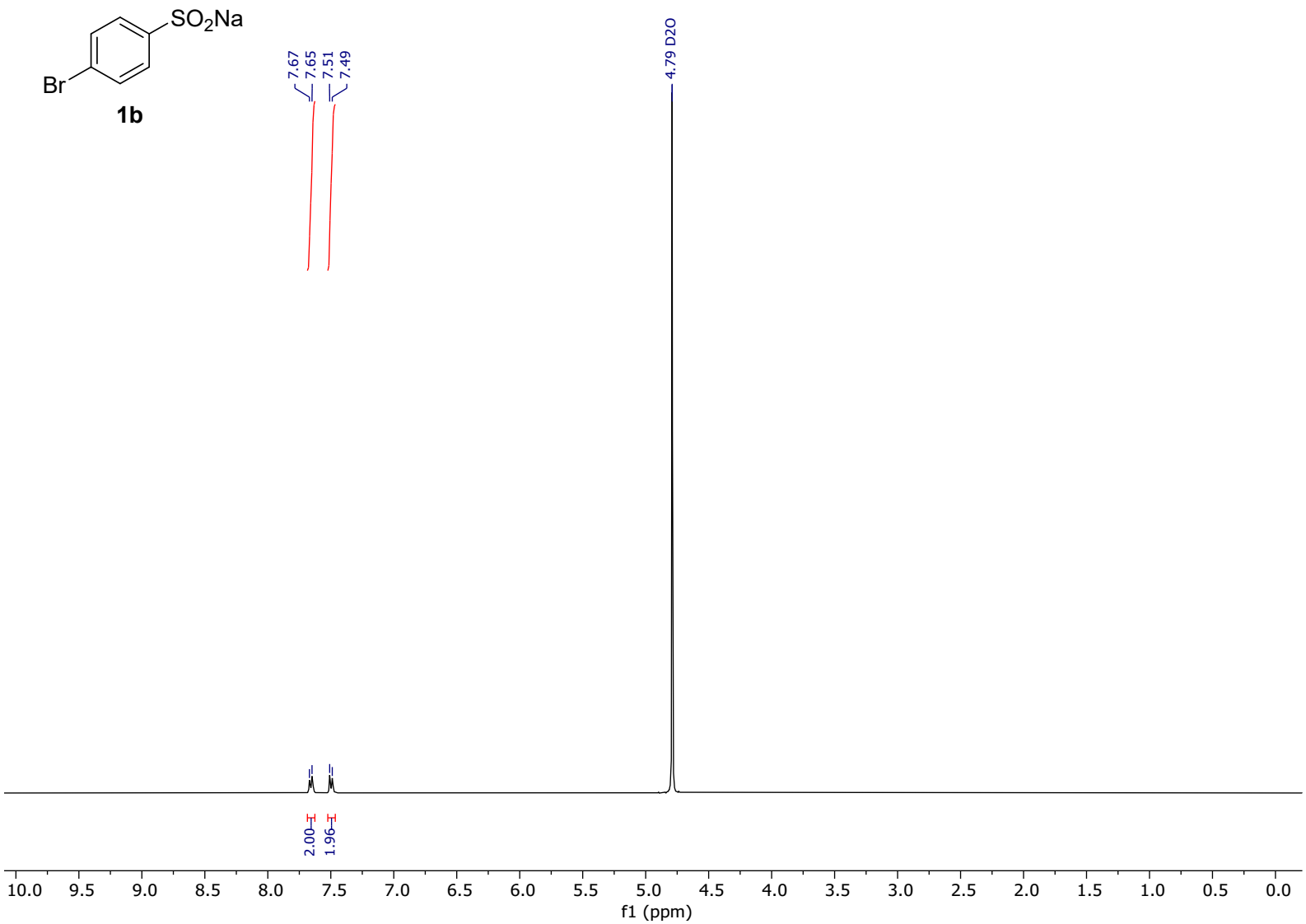
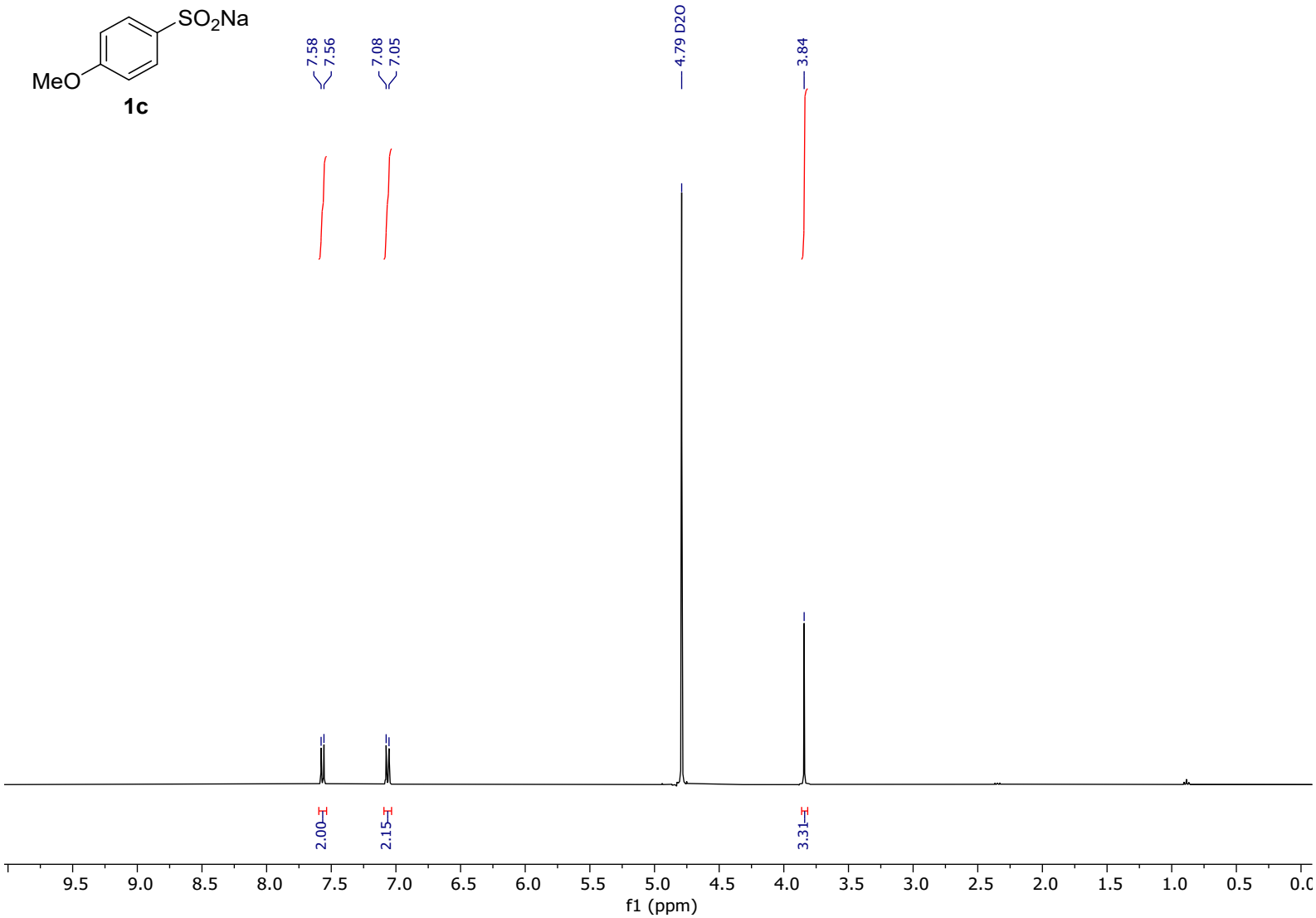


^{1}H NMR (400 MHz, D_2O) spectrum of compound **1b**.



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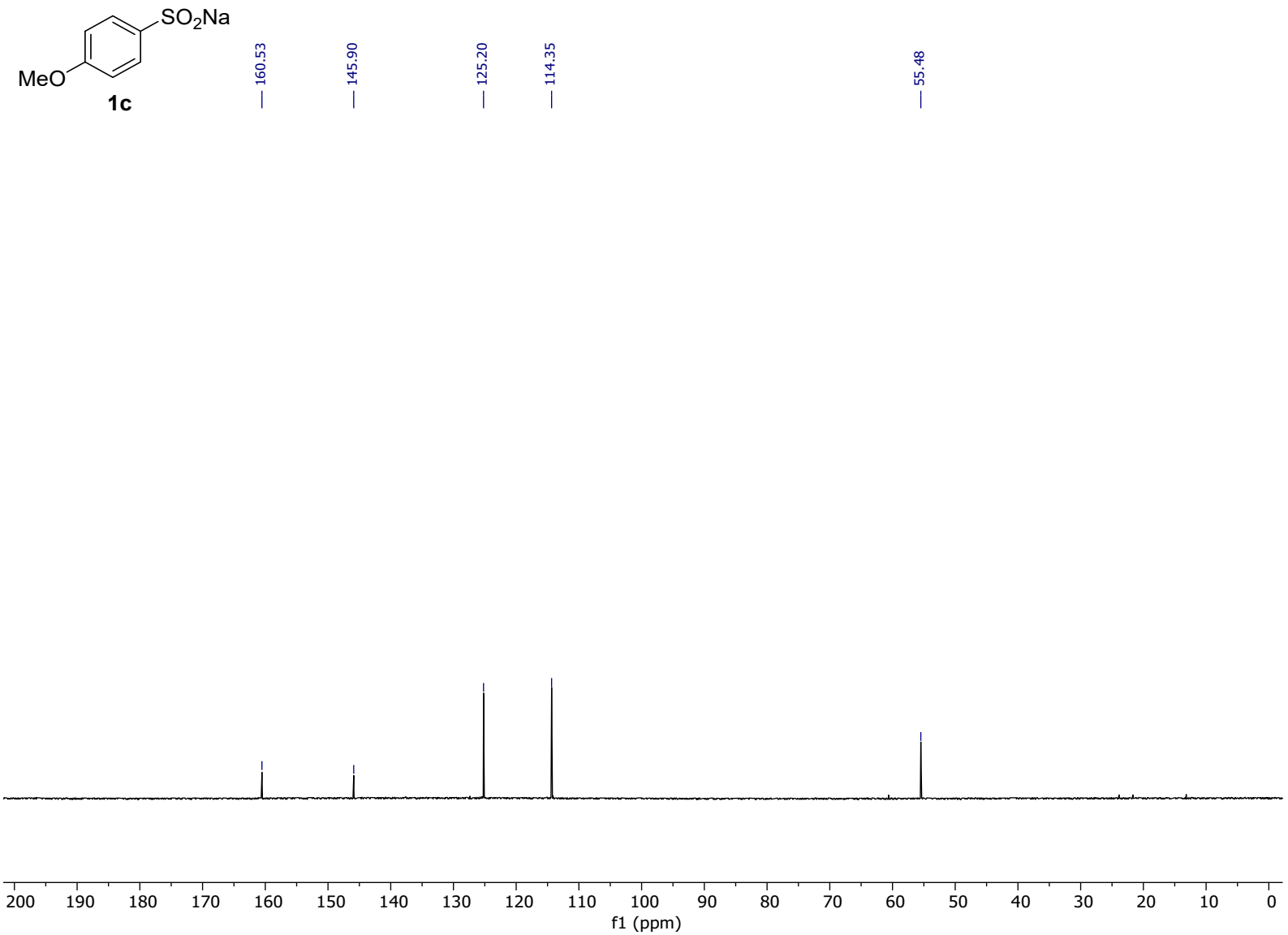
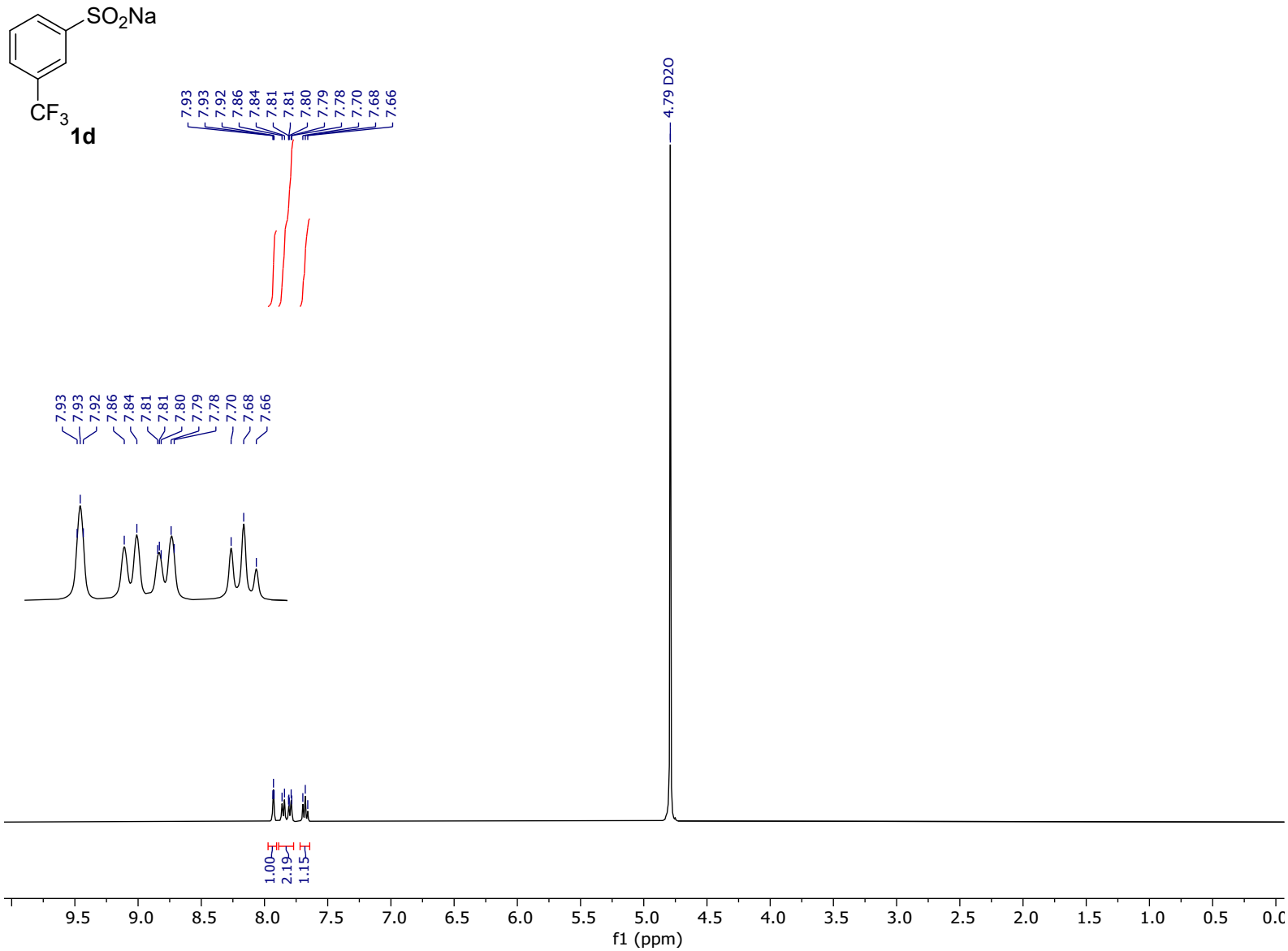
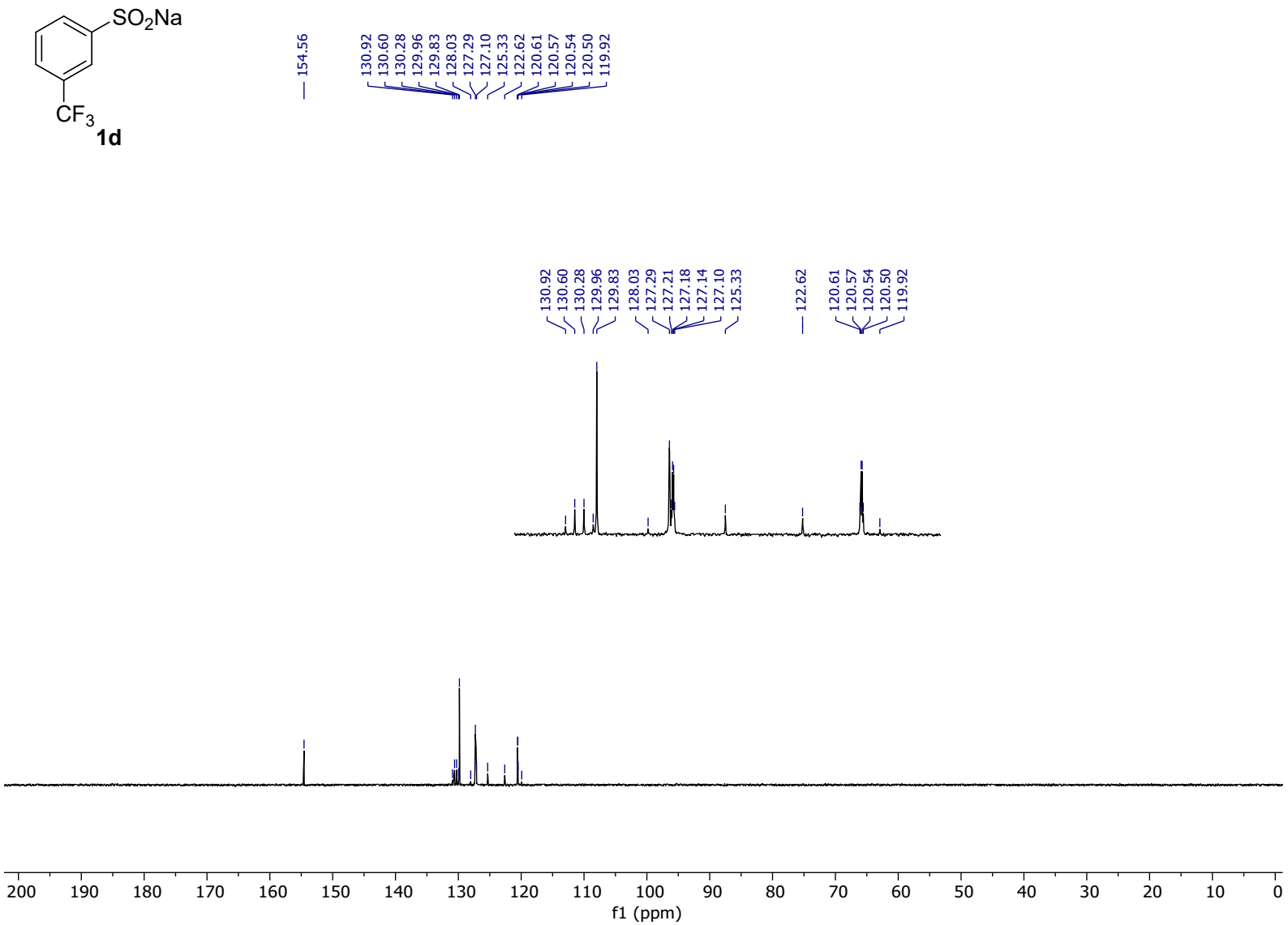


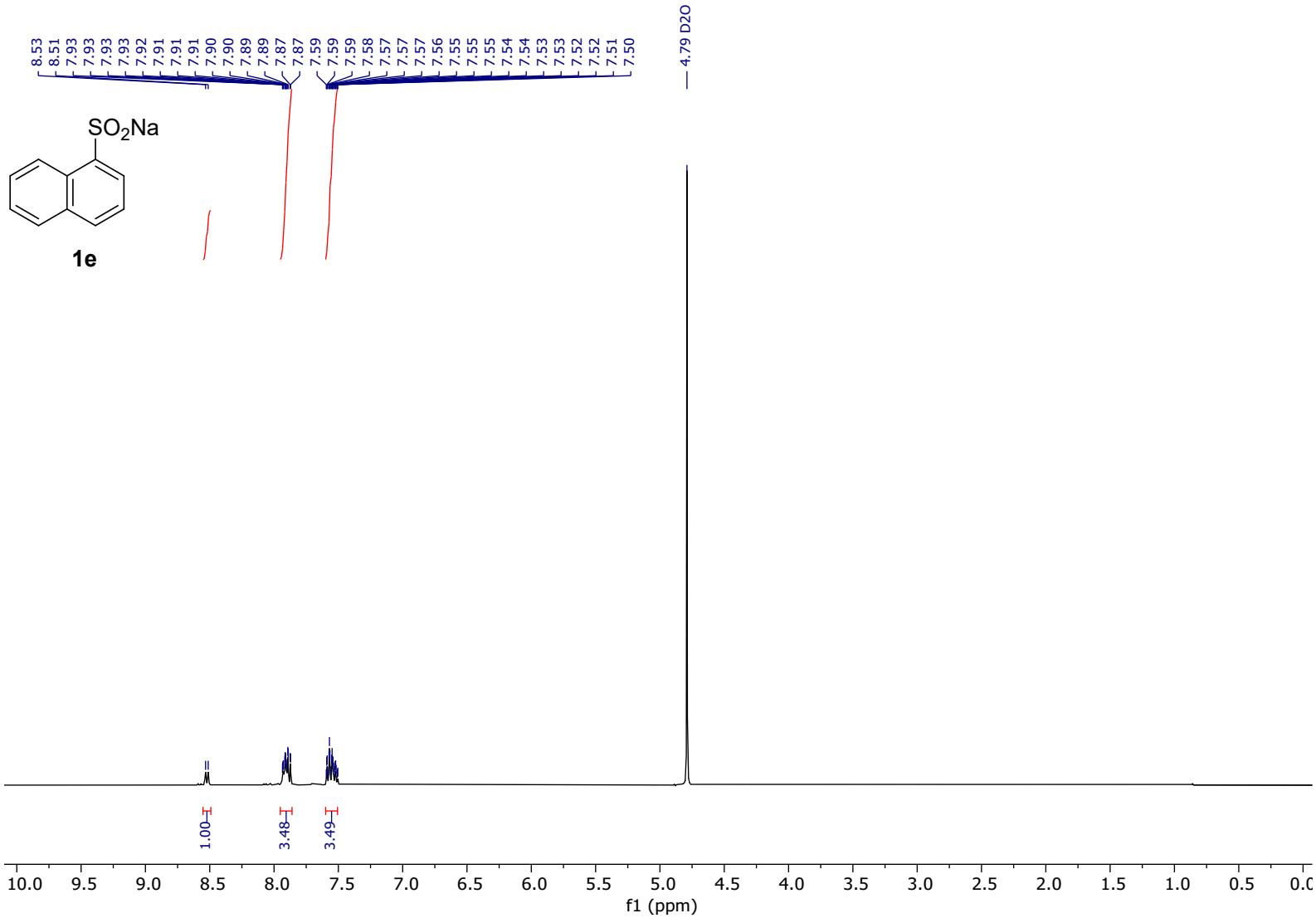
$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O) spectrum of compound **1c**.



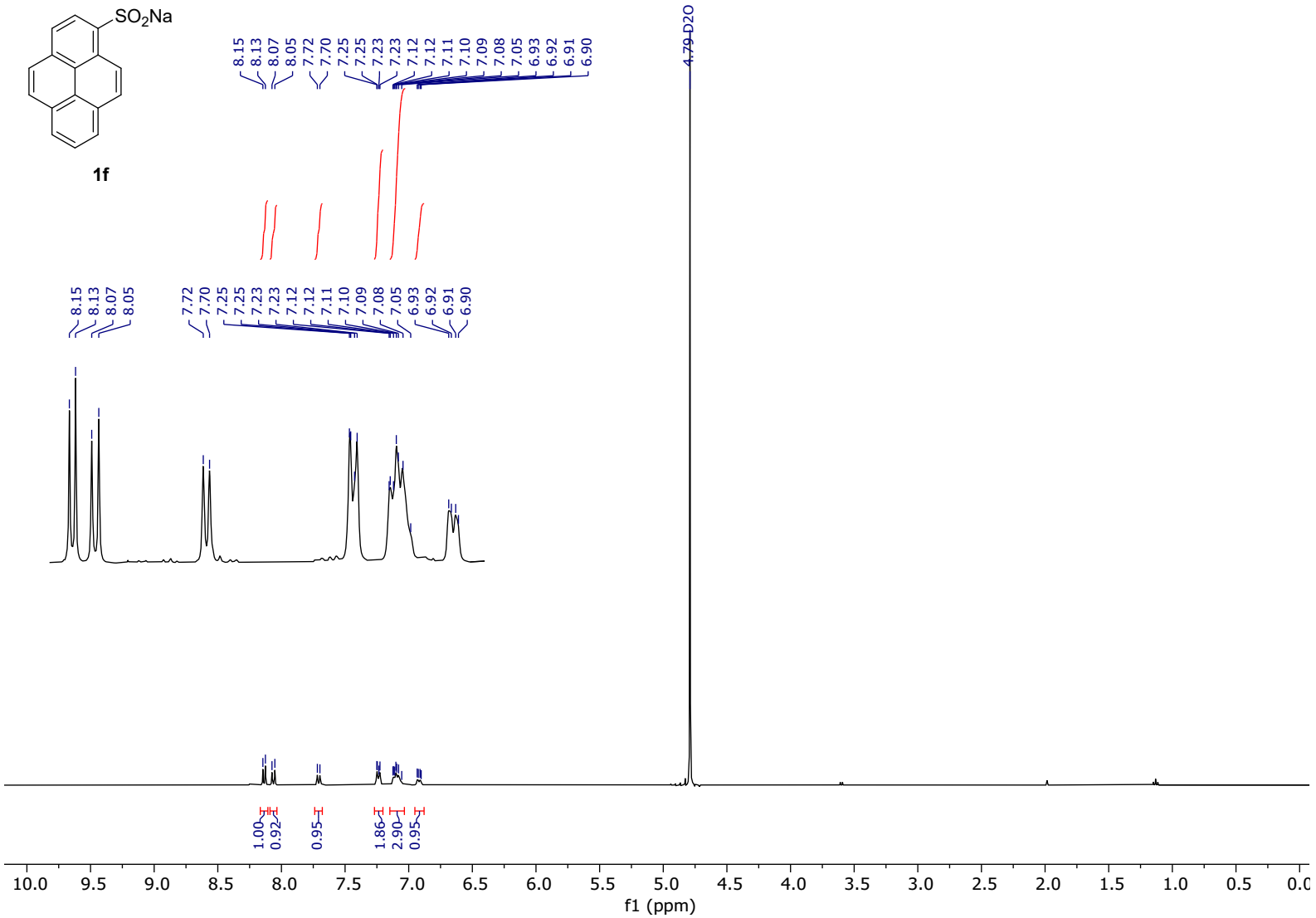
^{1}H NMR (400 MHz, D_2O) spectrum of compound **1d**.



$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O) spectrum of compound **1d**.



^{1}H NMR (400 MHz, D_2O) spectrum of compound **1e**.



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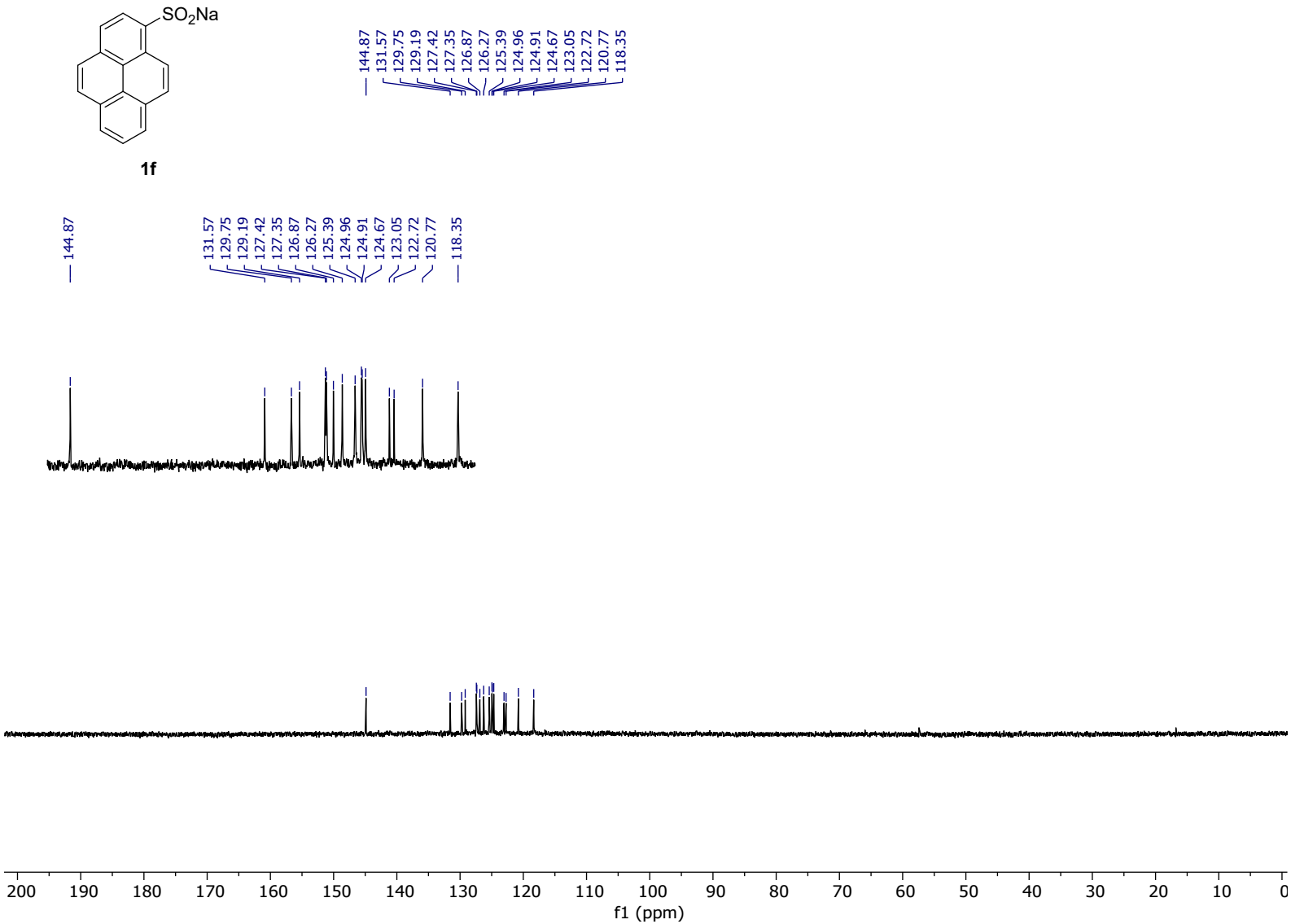
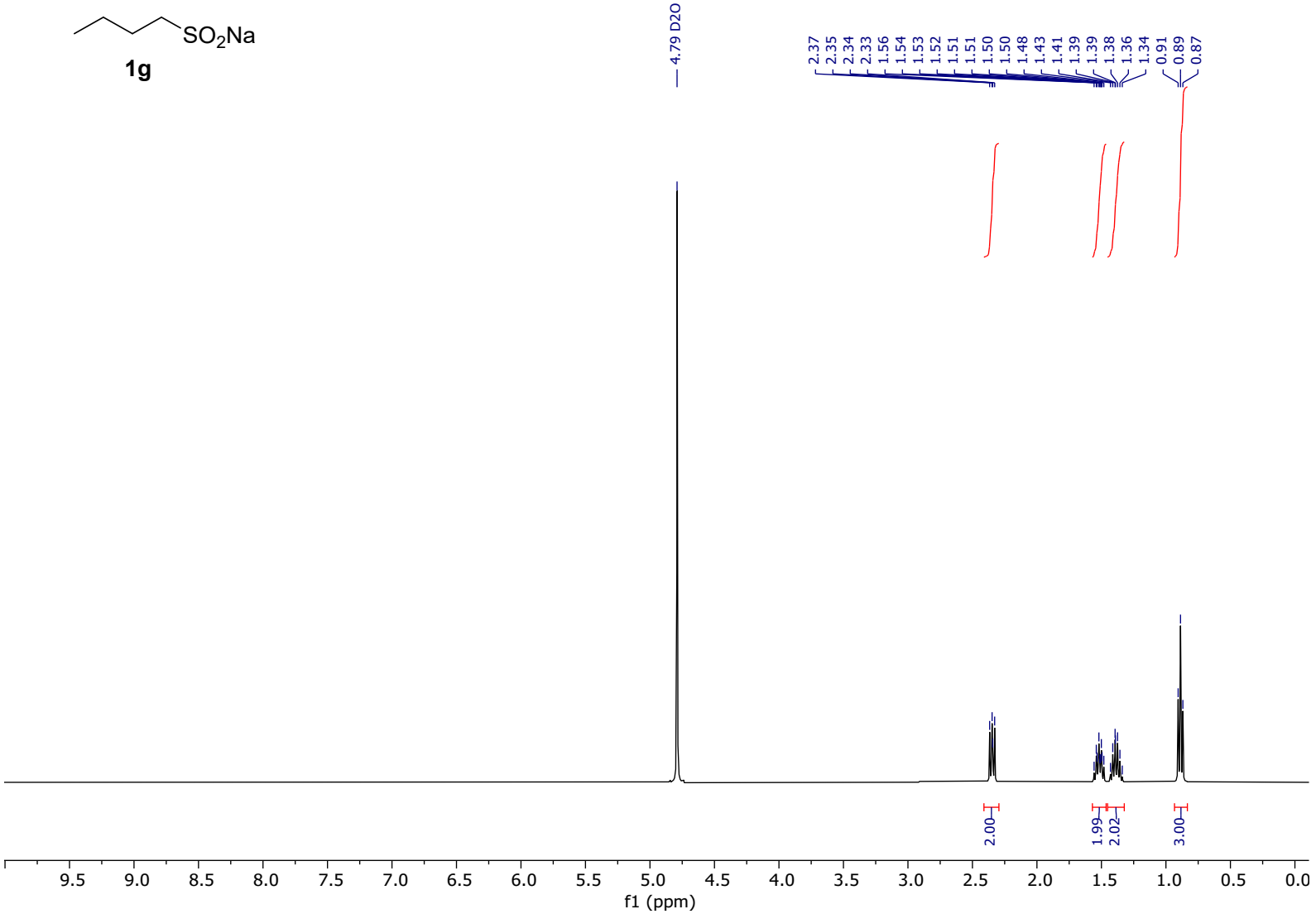
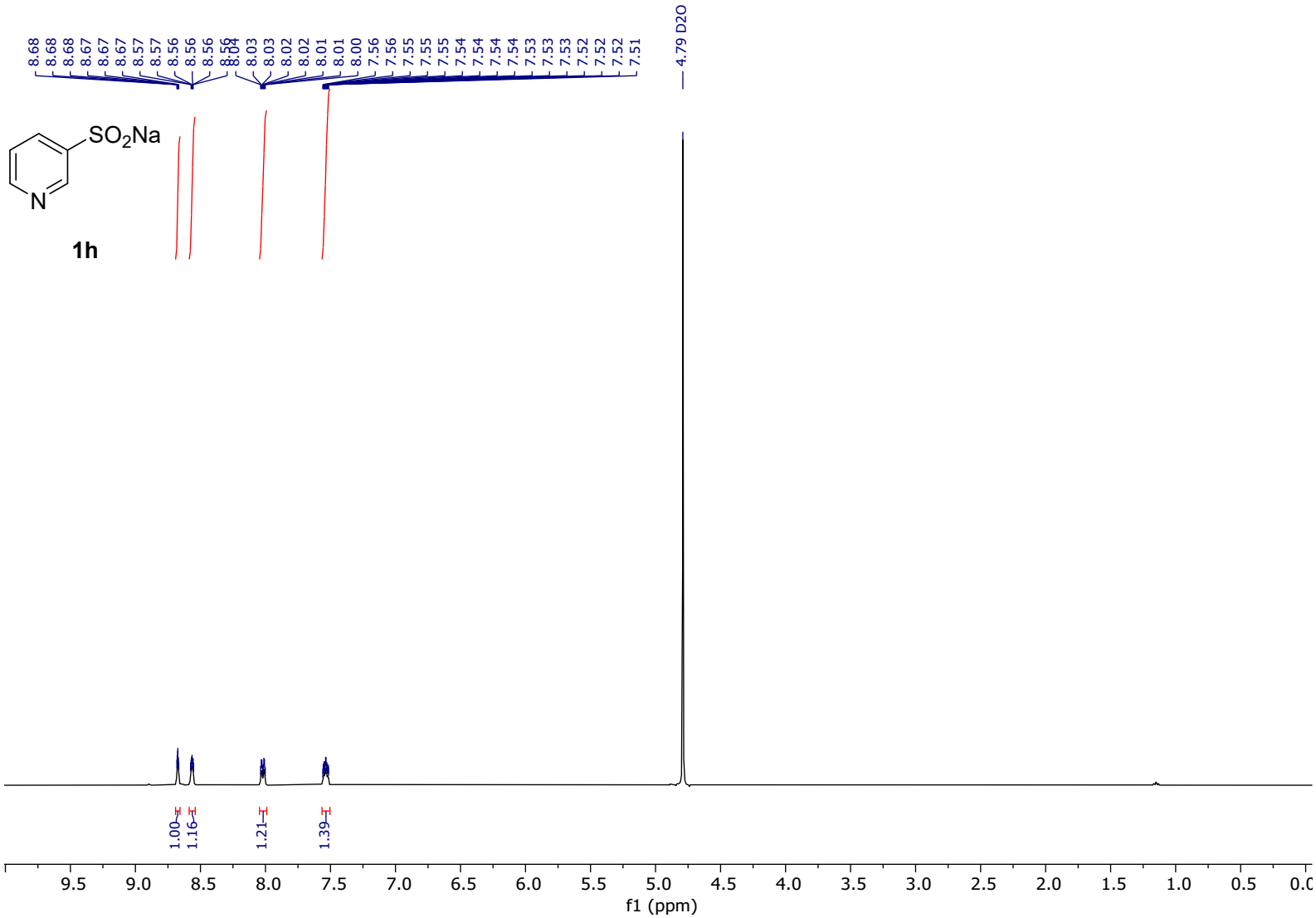


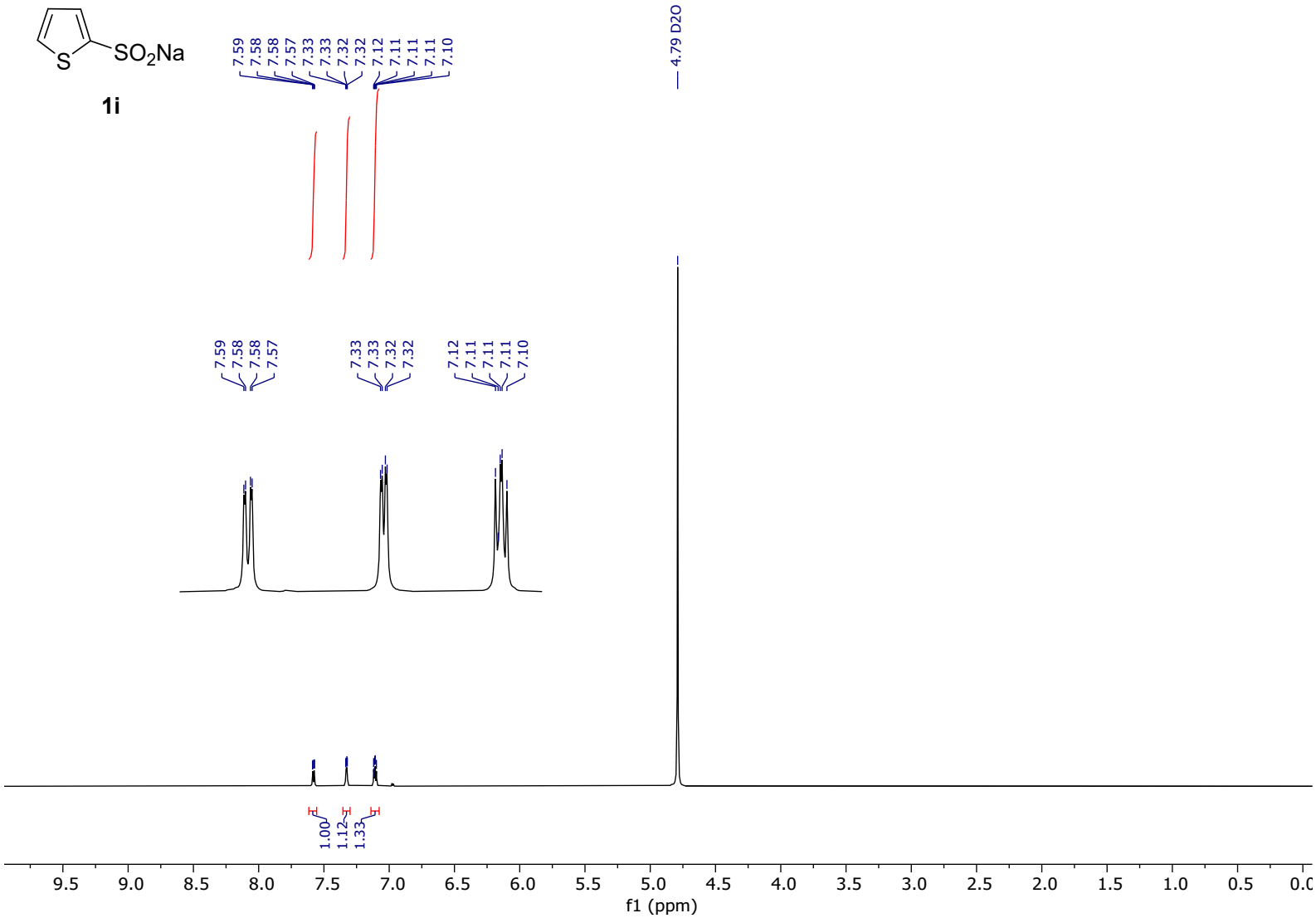
$^{13}C\{^{1}H\}$ NMR (101 MHz, D_2O) spectrum of compound **1f**.



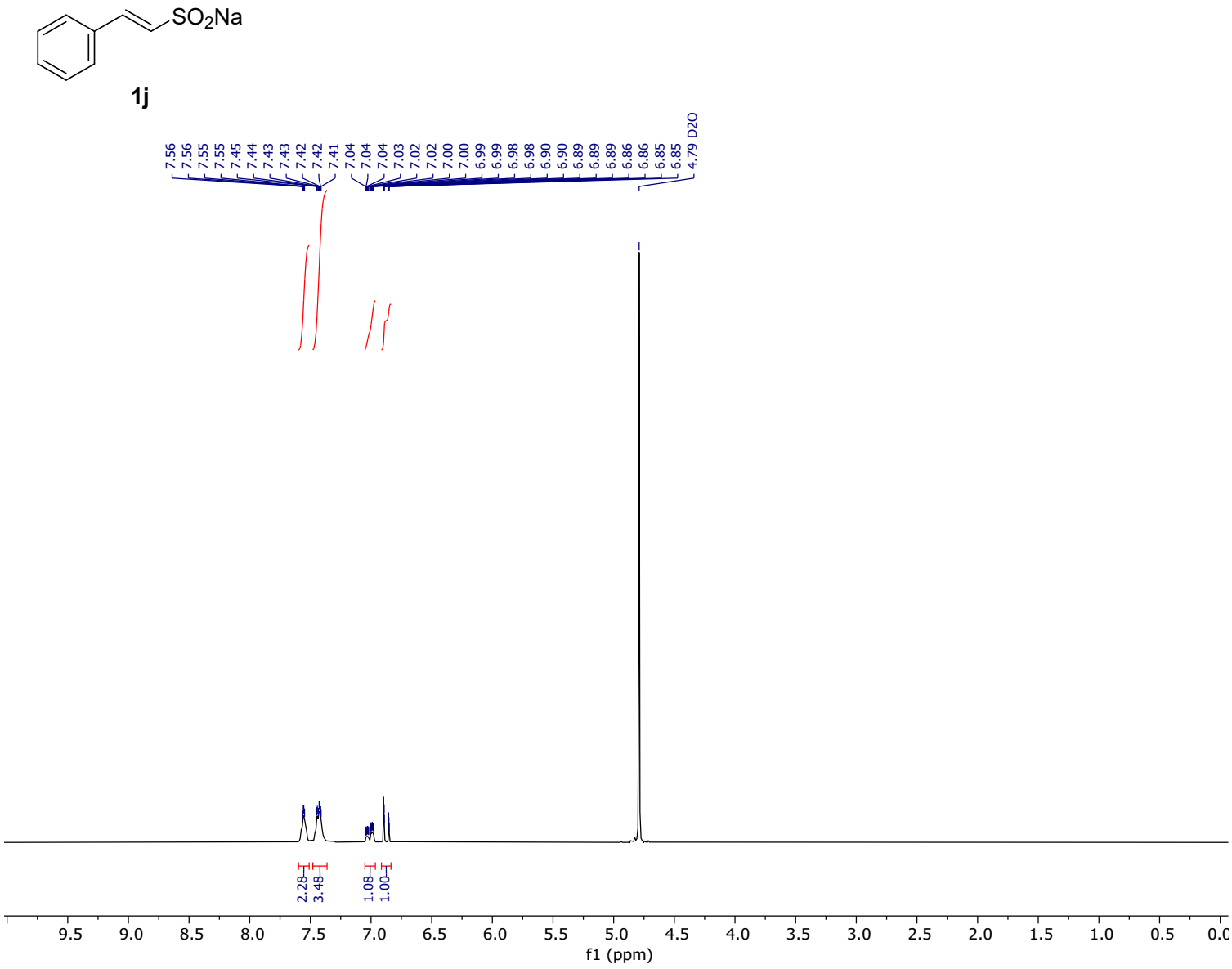
^{1}H NMR (400 MHz, D_2O) spectrum of compound **1g**.



^{1}H NMR (400 MHz, D_2O) spectrum of compound **1h**.



^{1}H NMR (400 MHz, D_2O) spectrum of compound **1i**.



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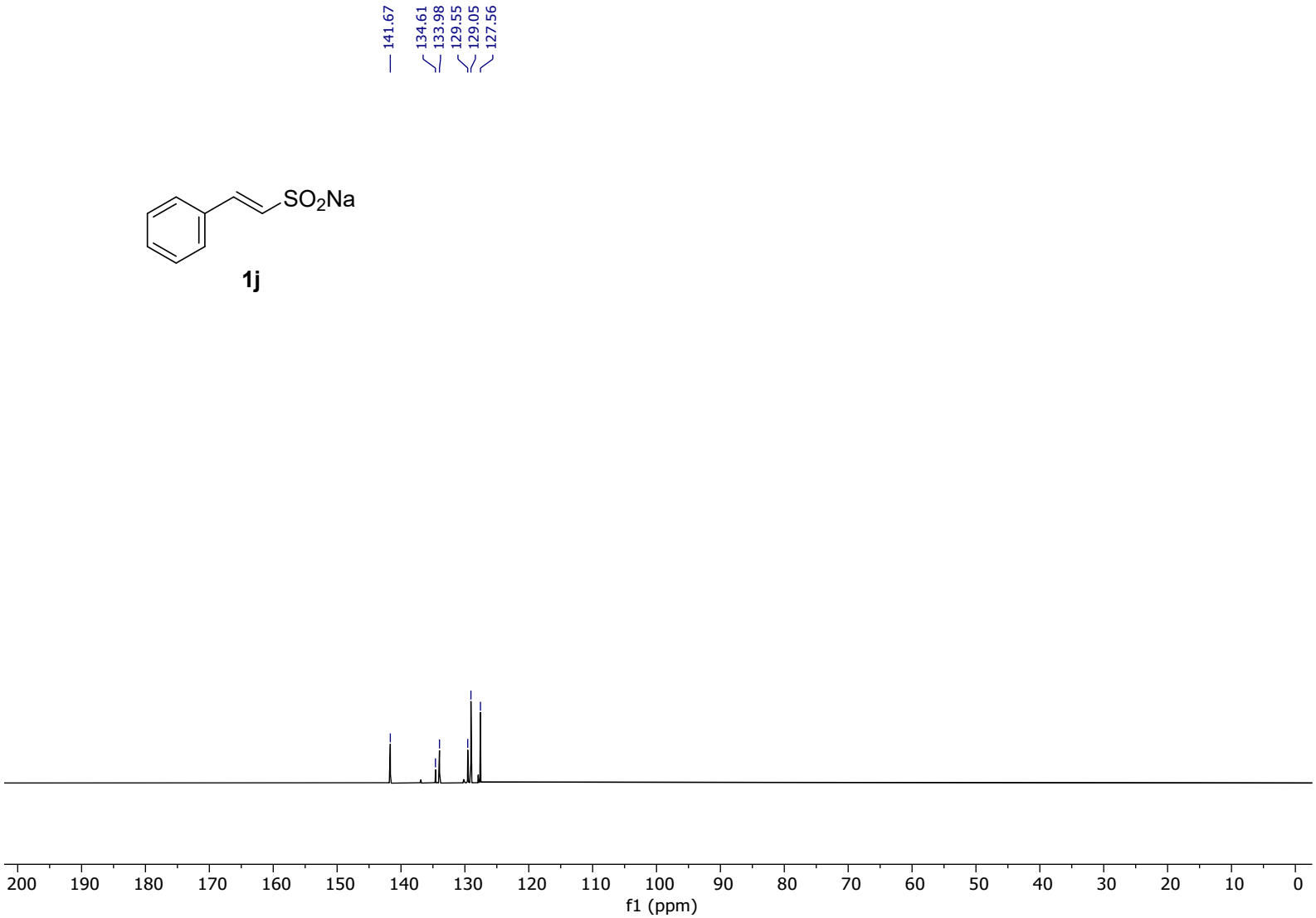

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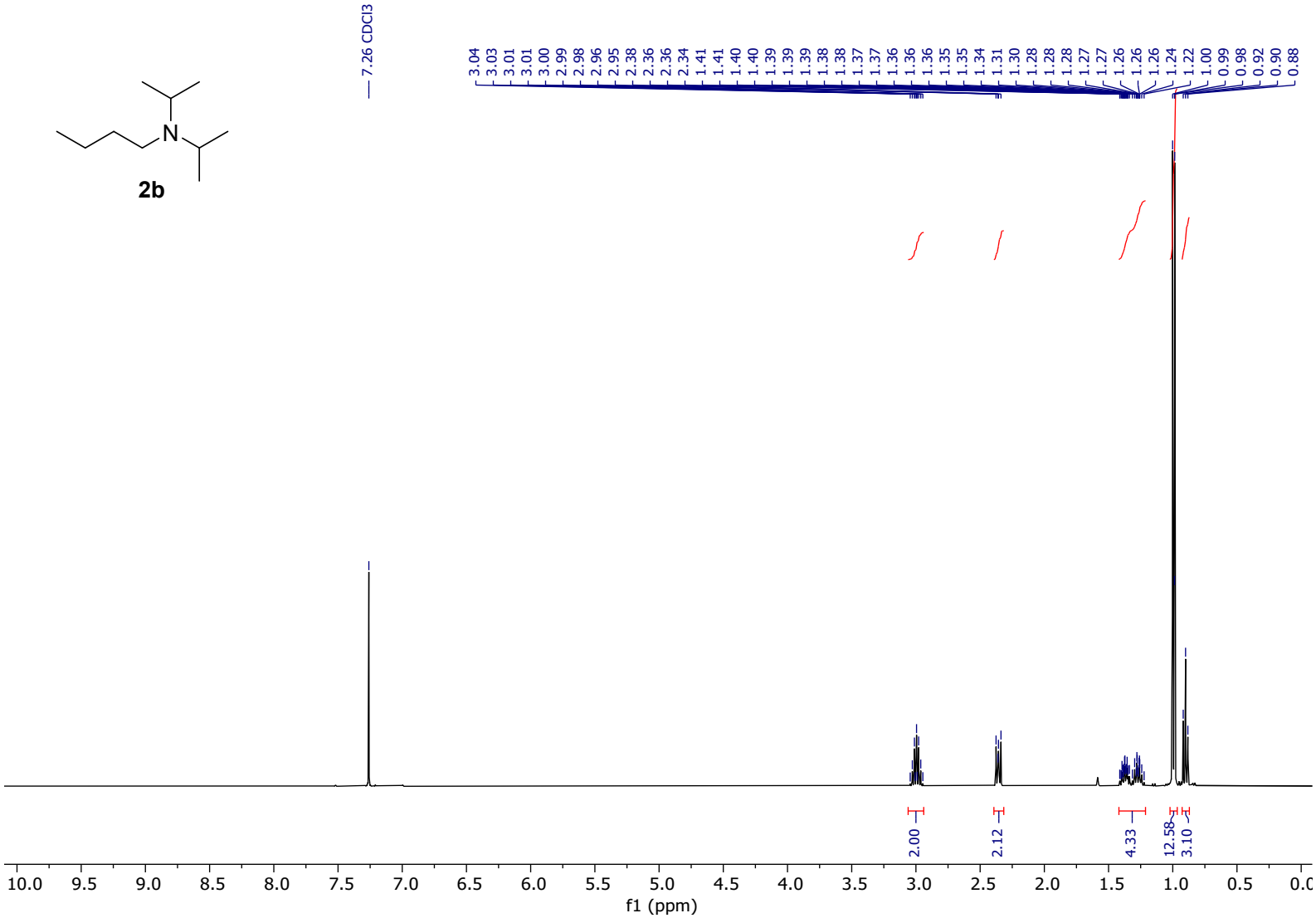
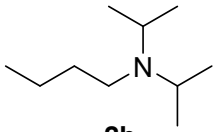
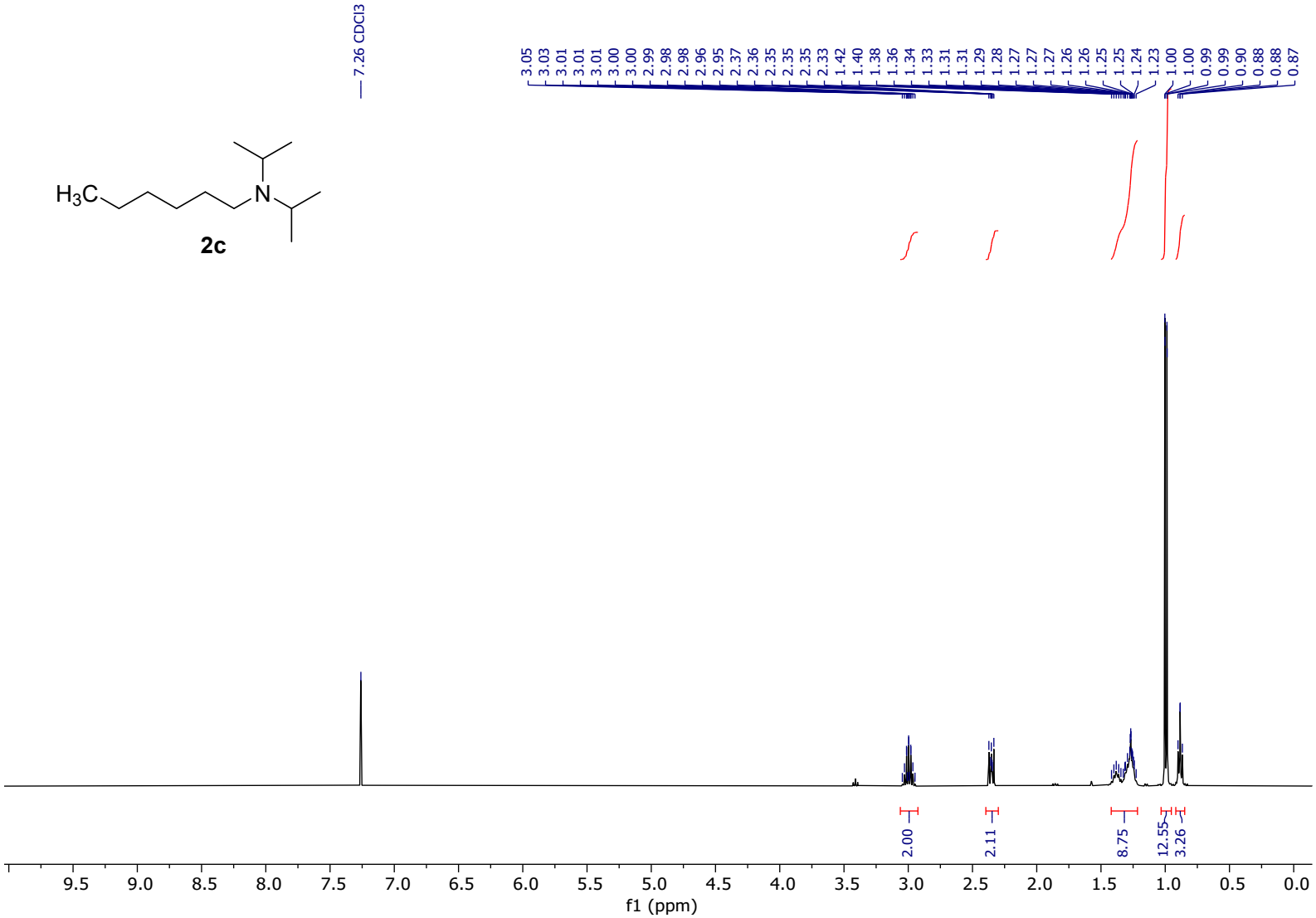


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2b**.



2b

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **2b**.



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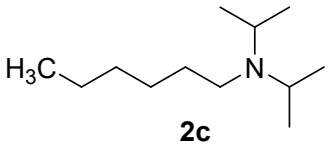

2c

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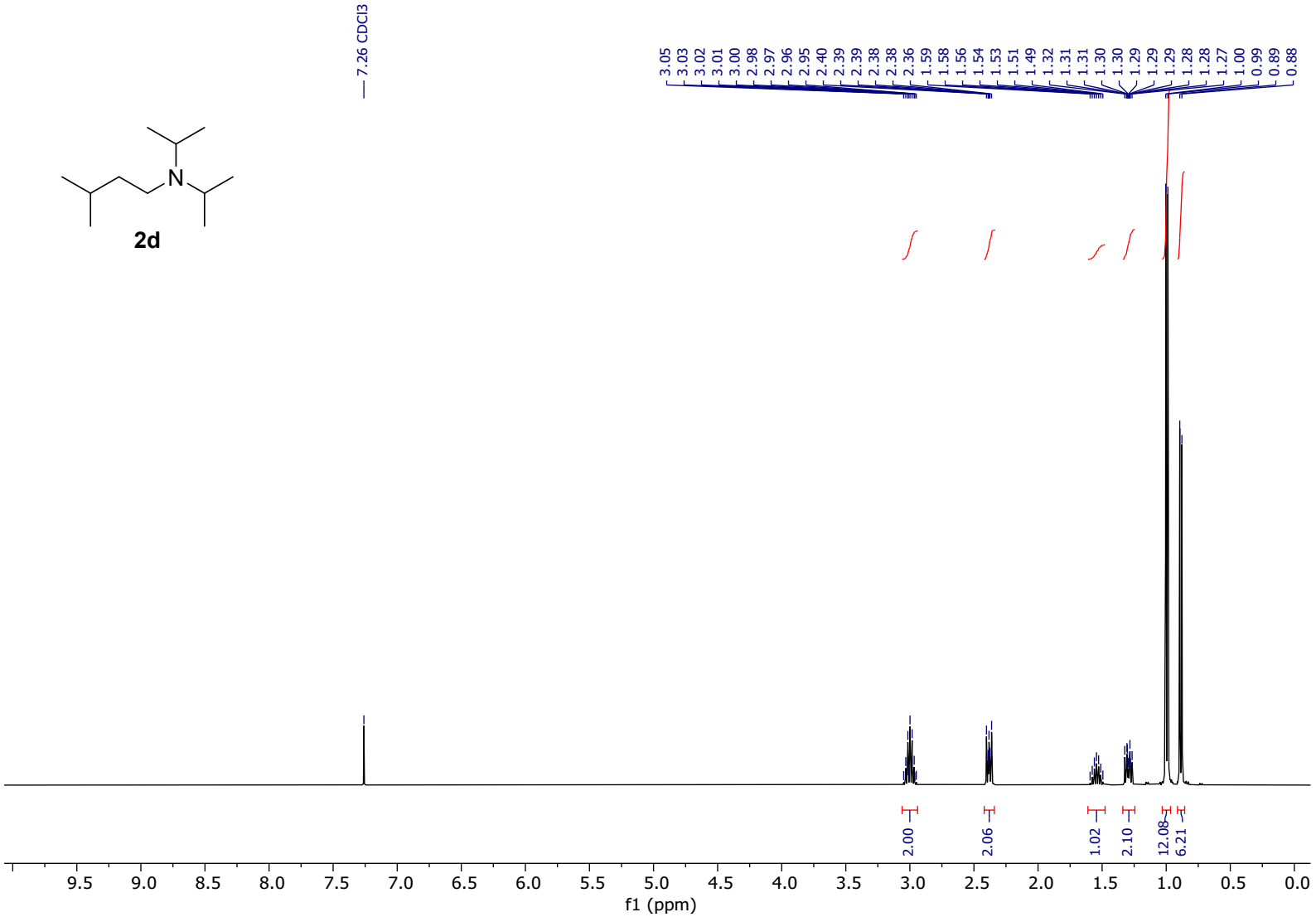

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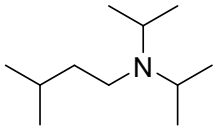
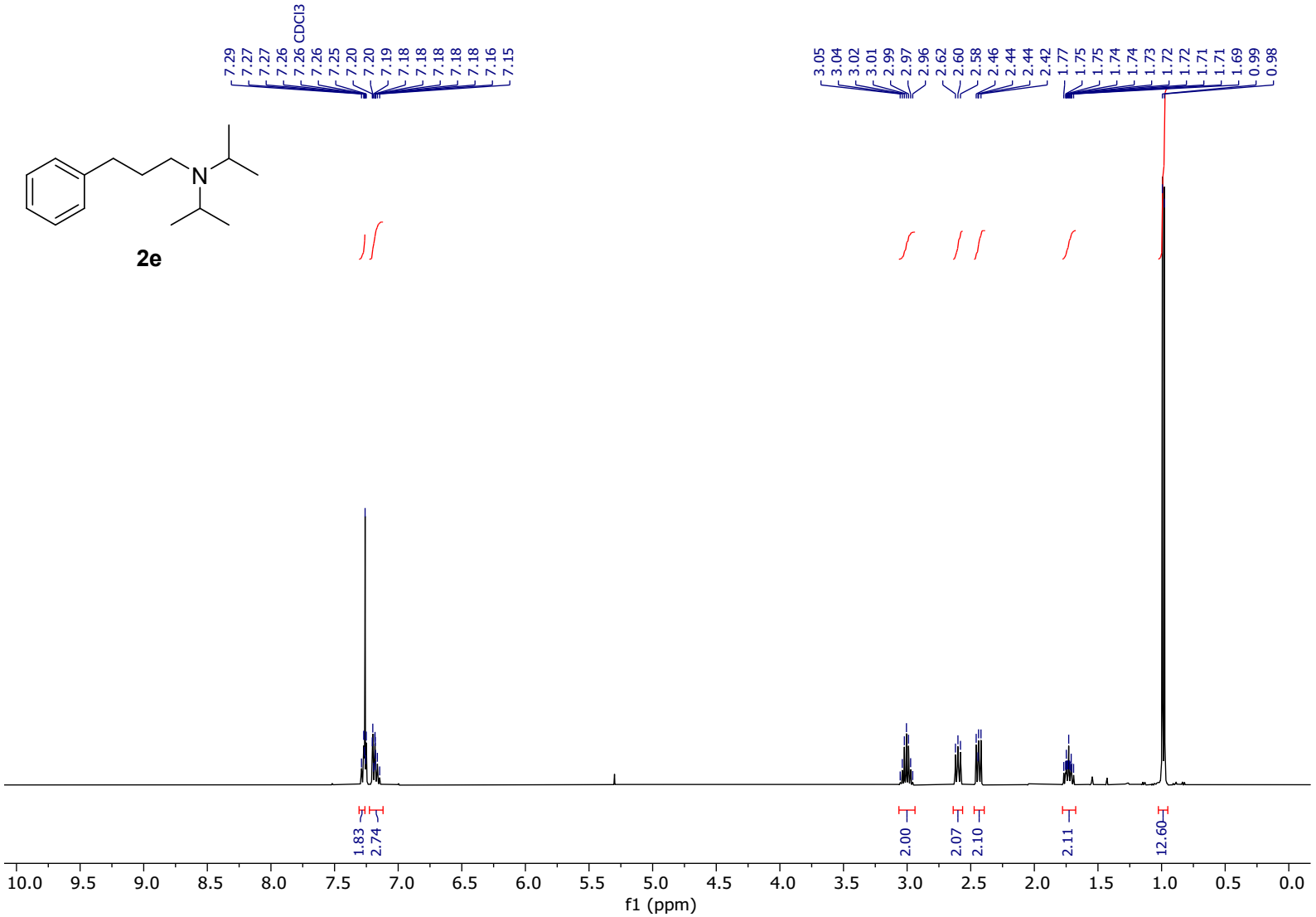


2d

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **2d**.



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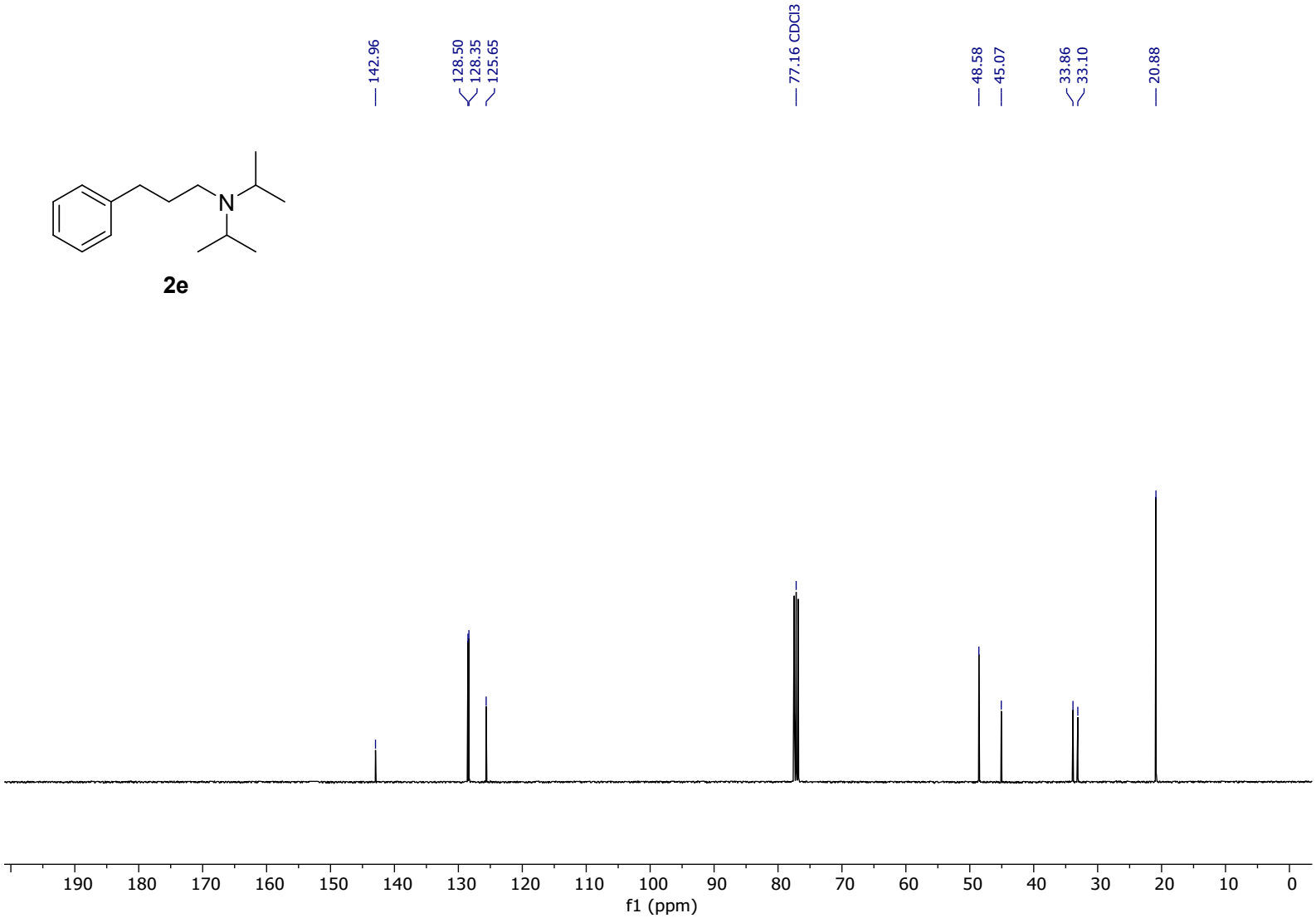

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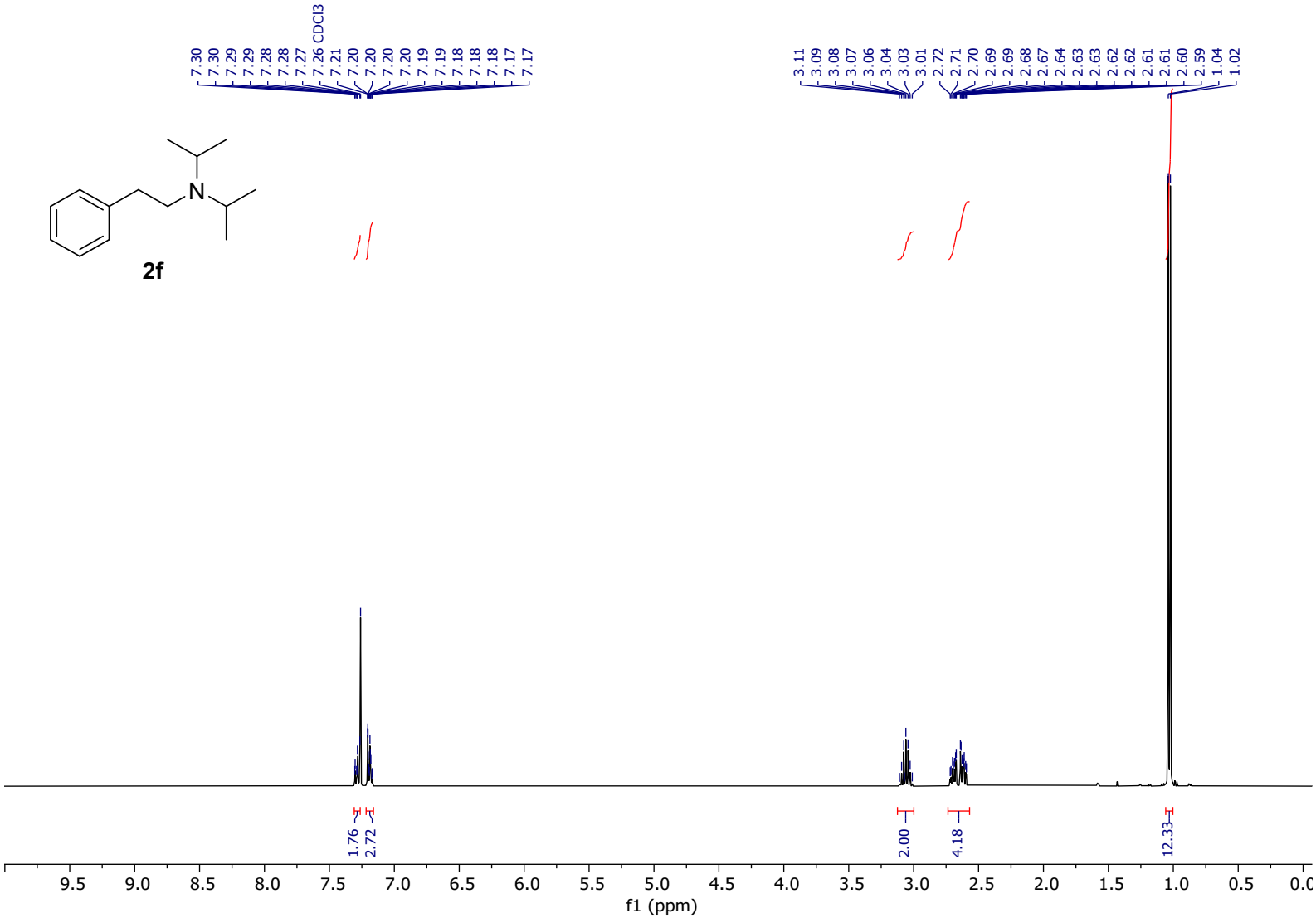

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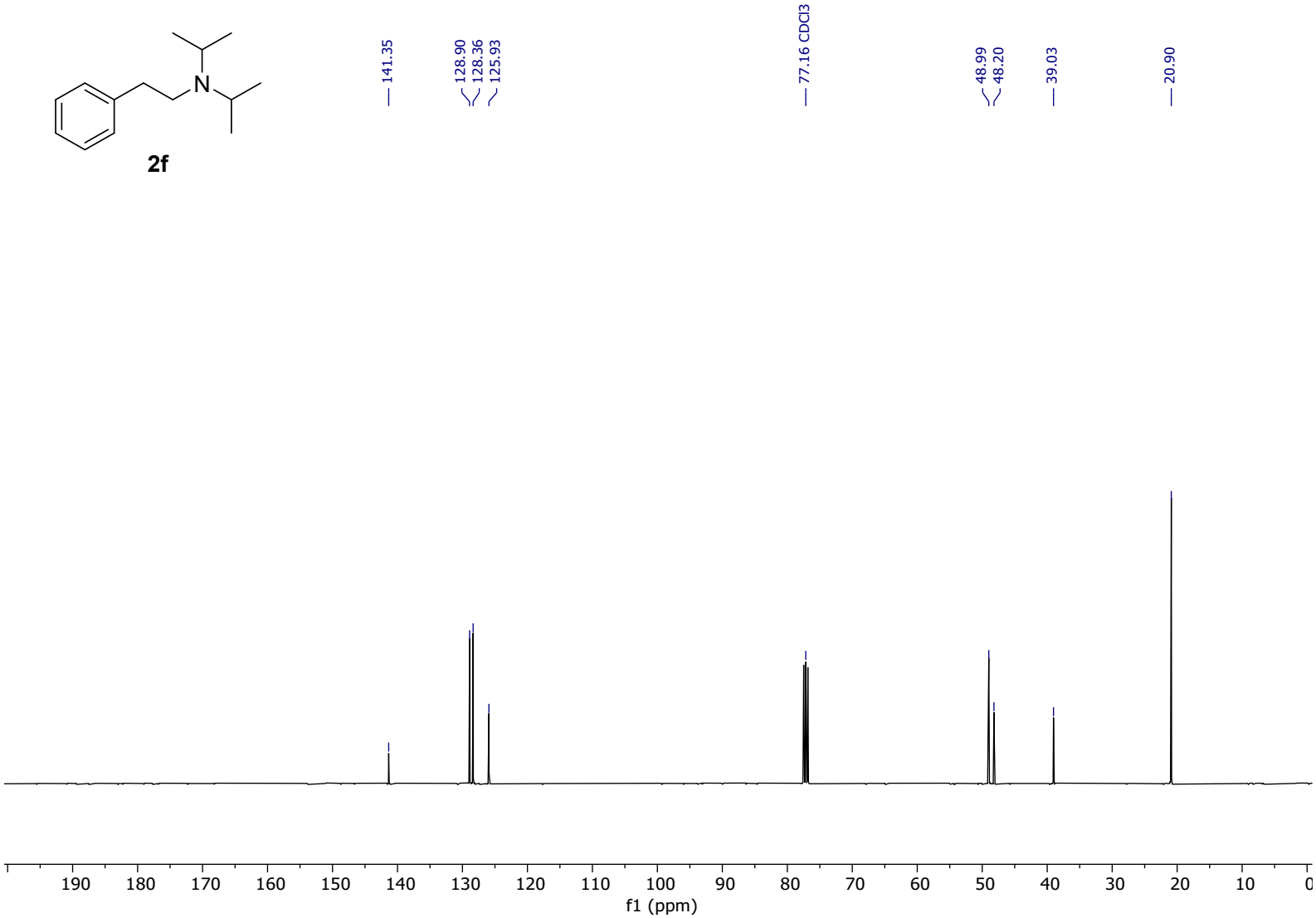

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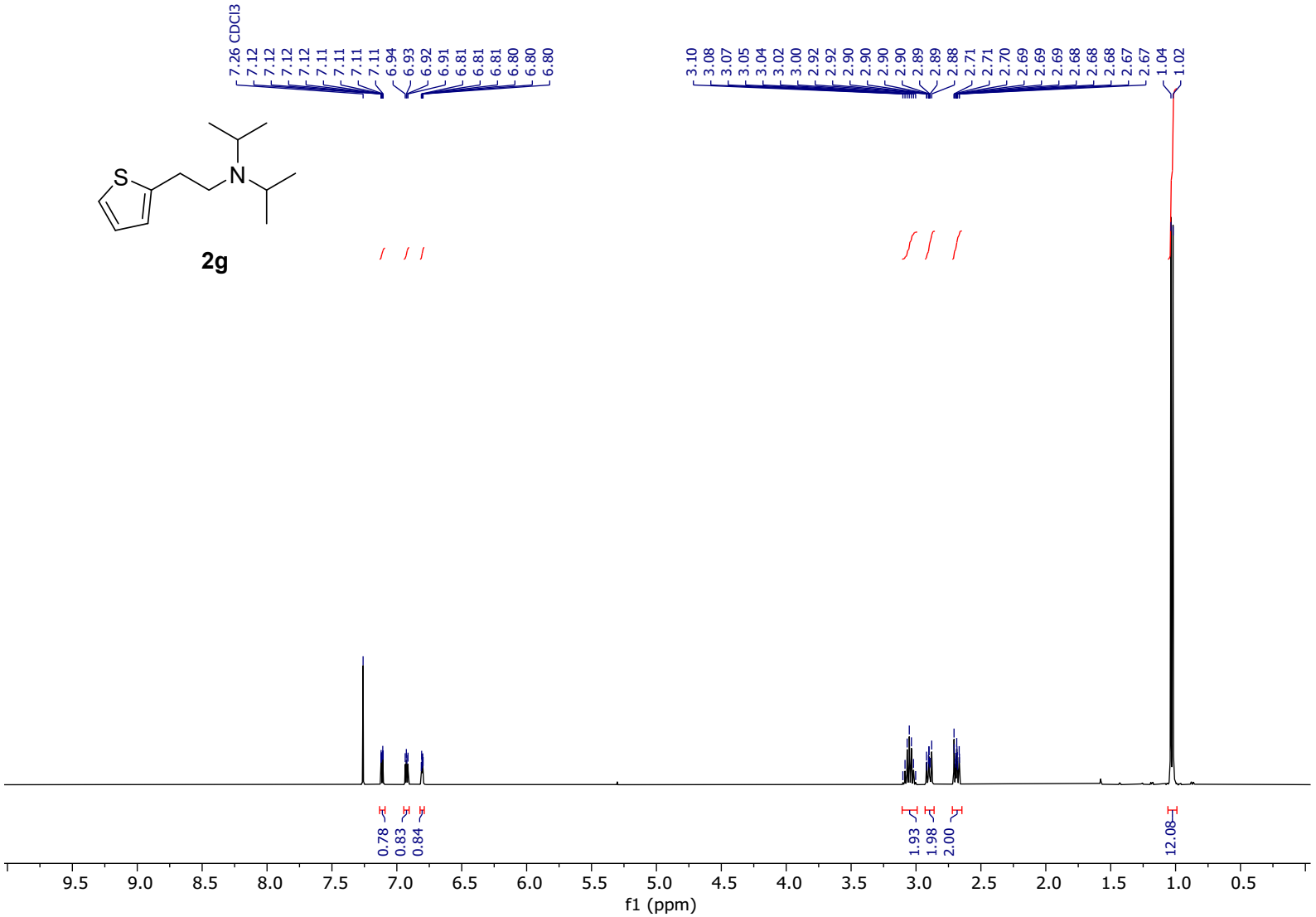
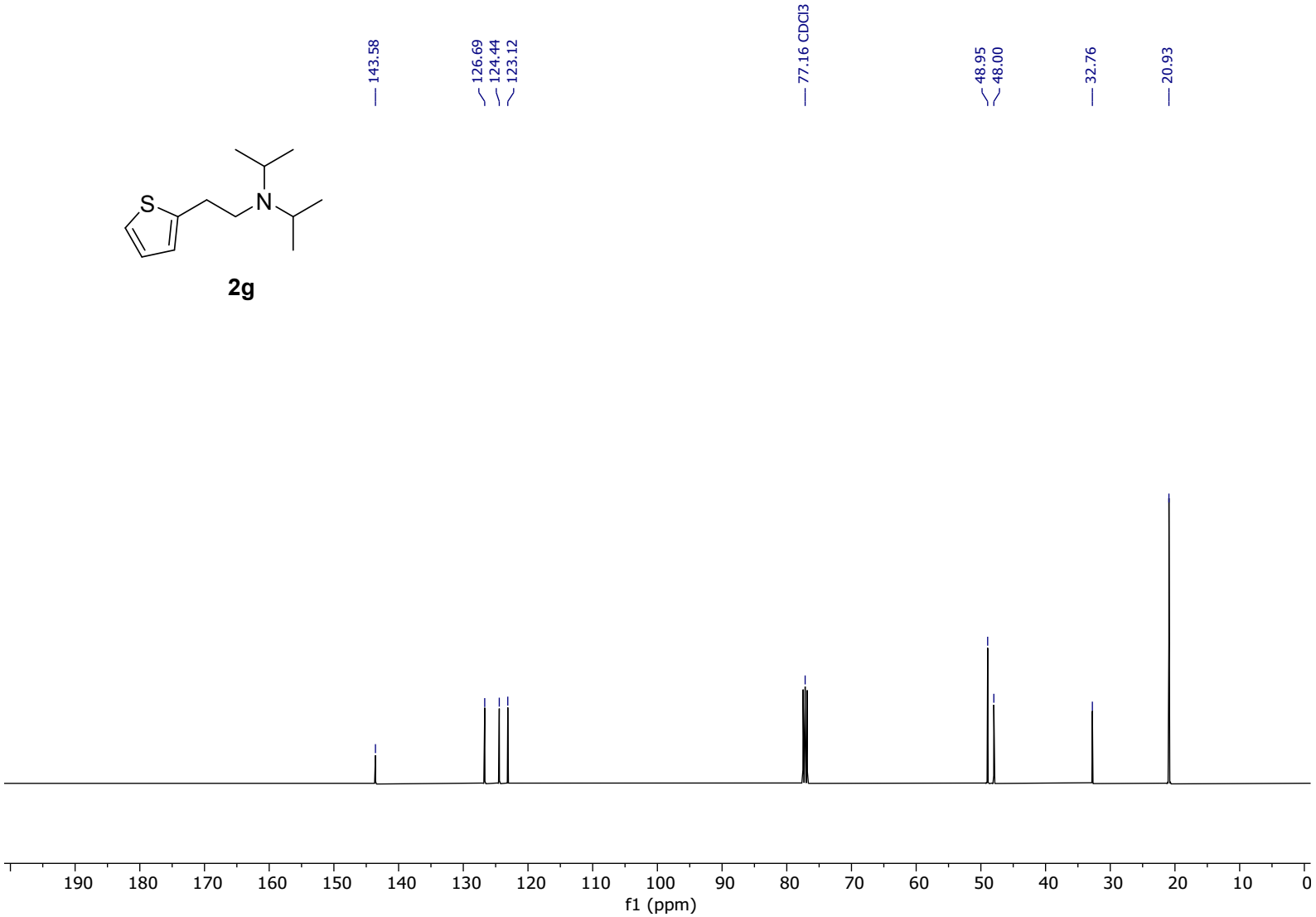


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2g**.



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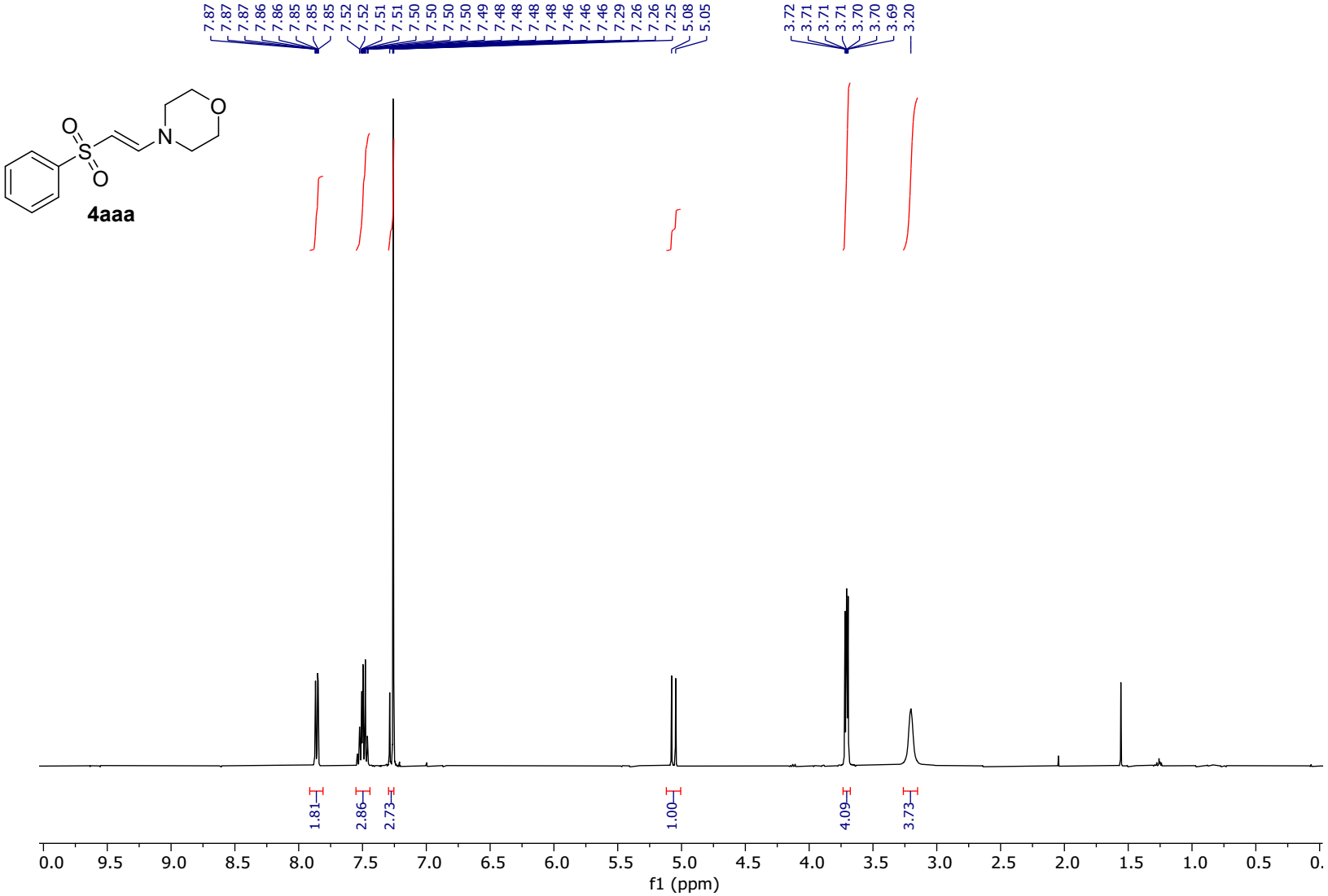
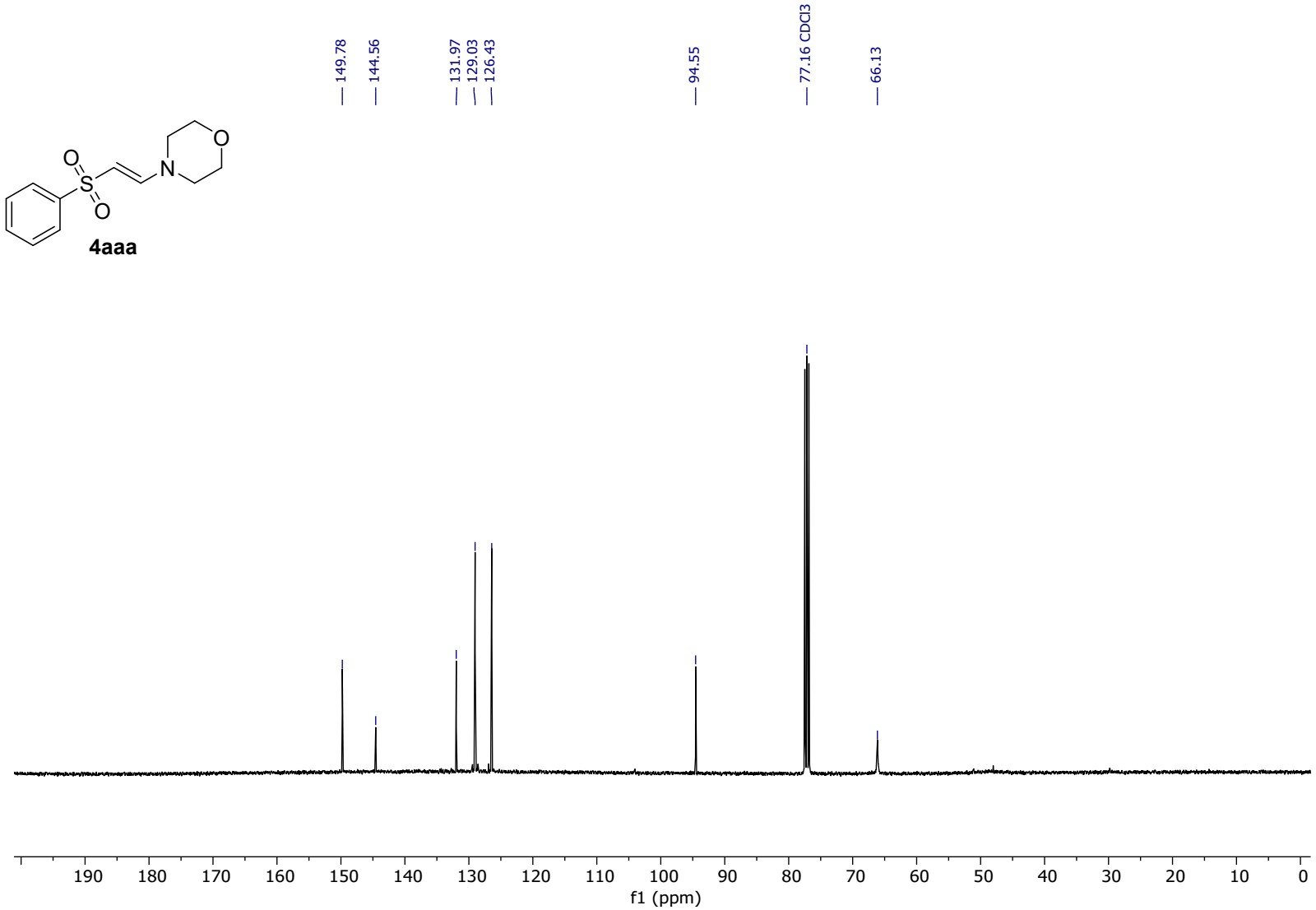
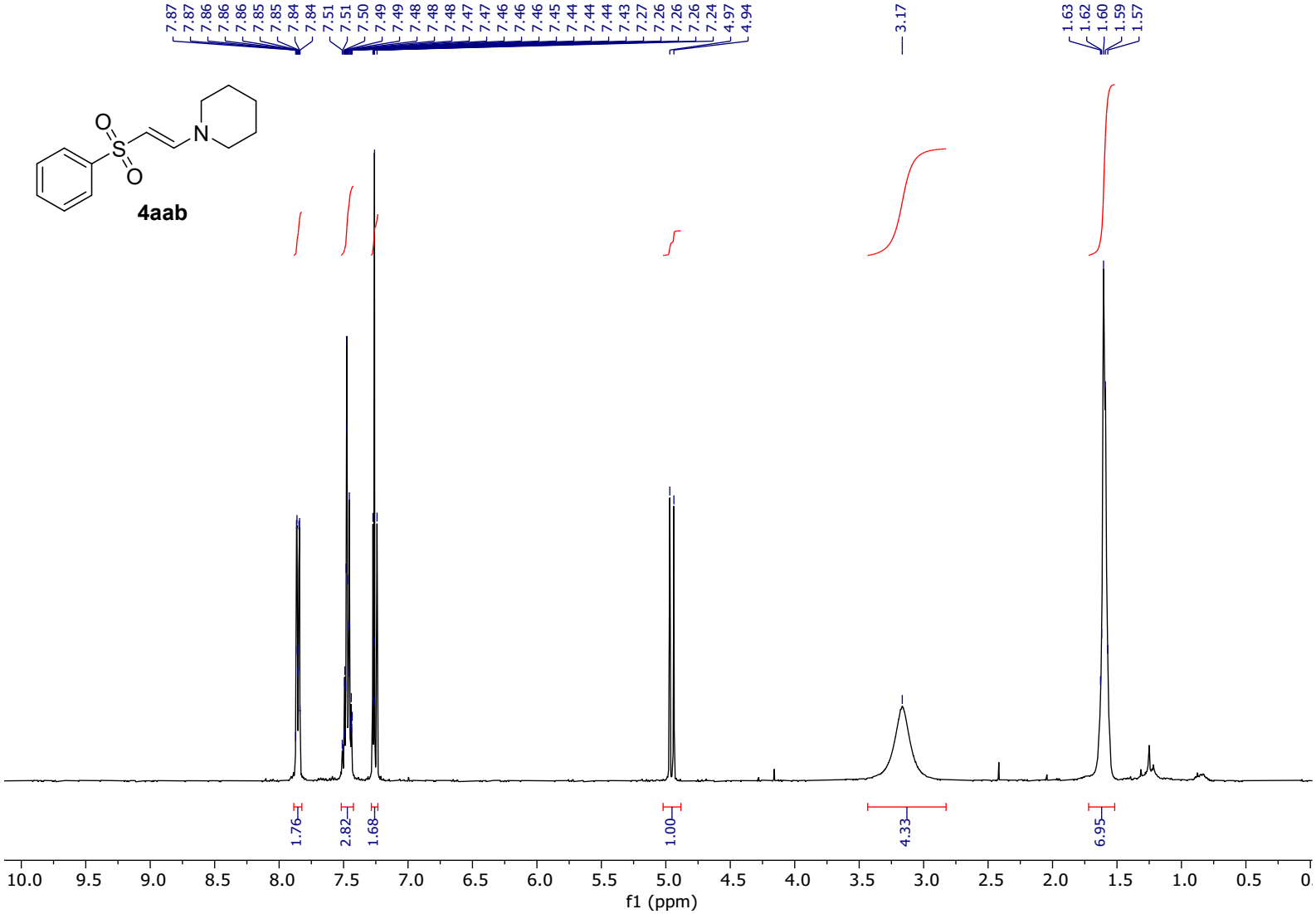


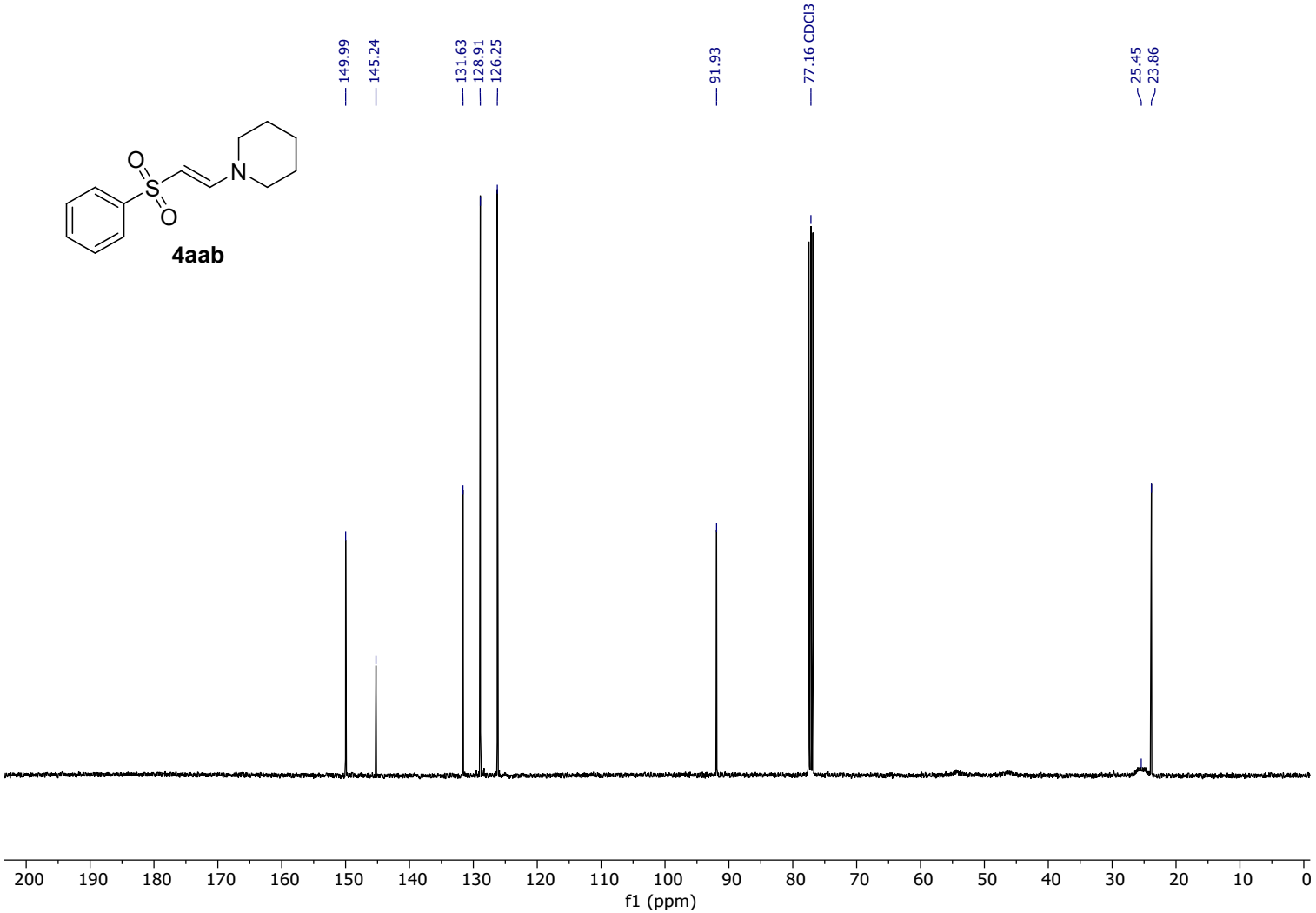
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aaa**.



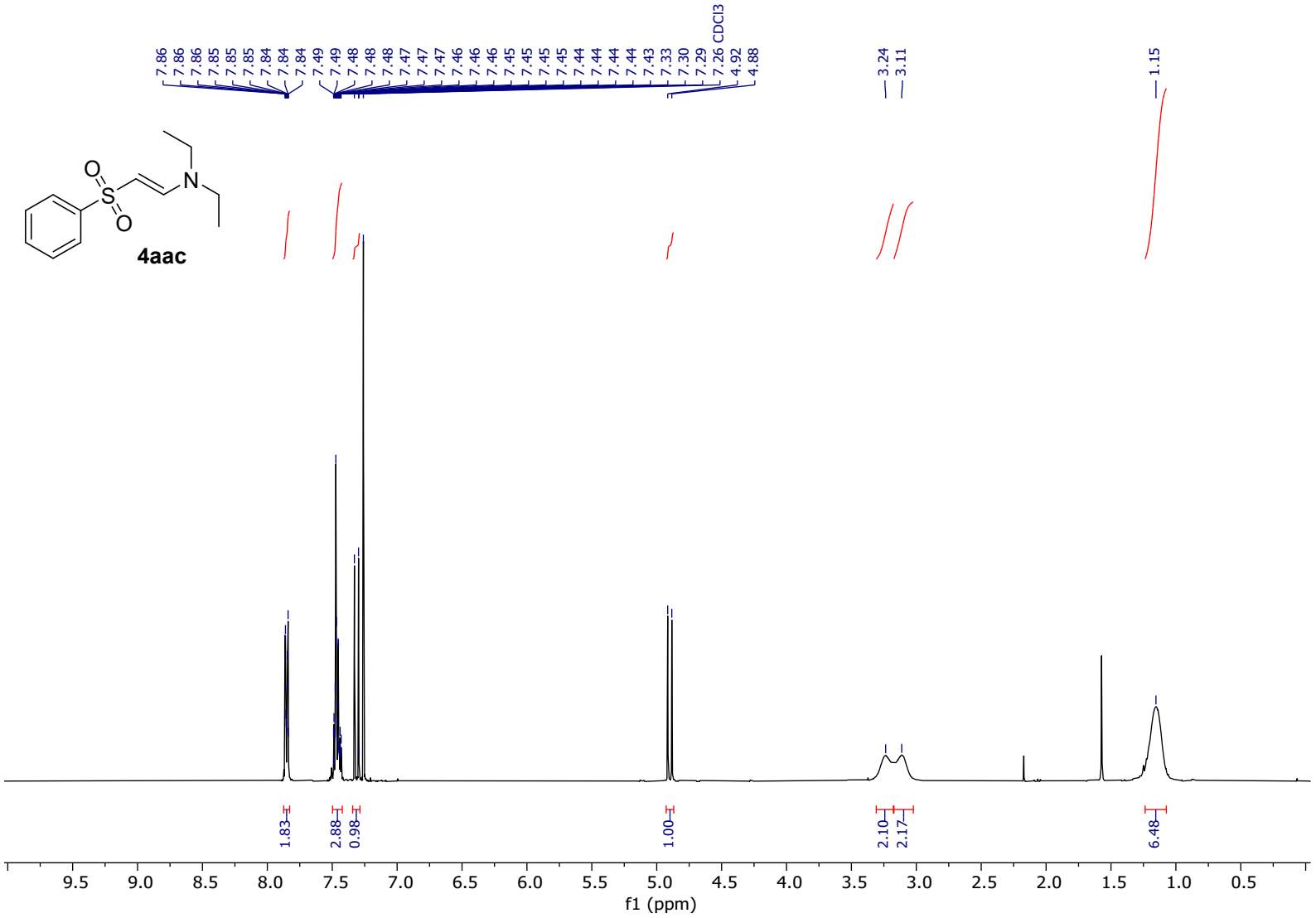
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aaa**.



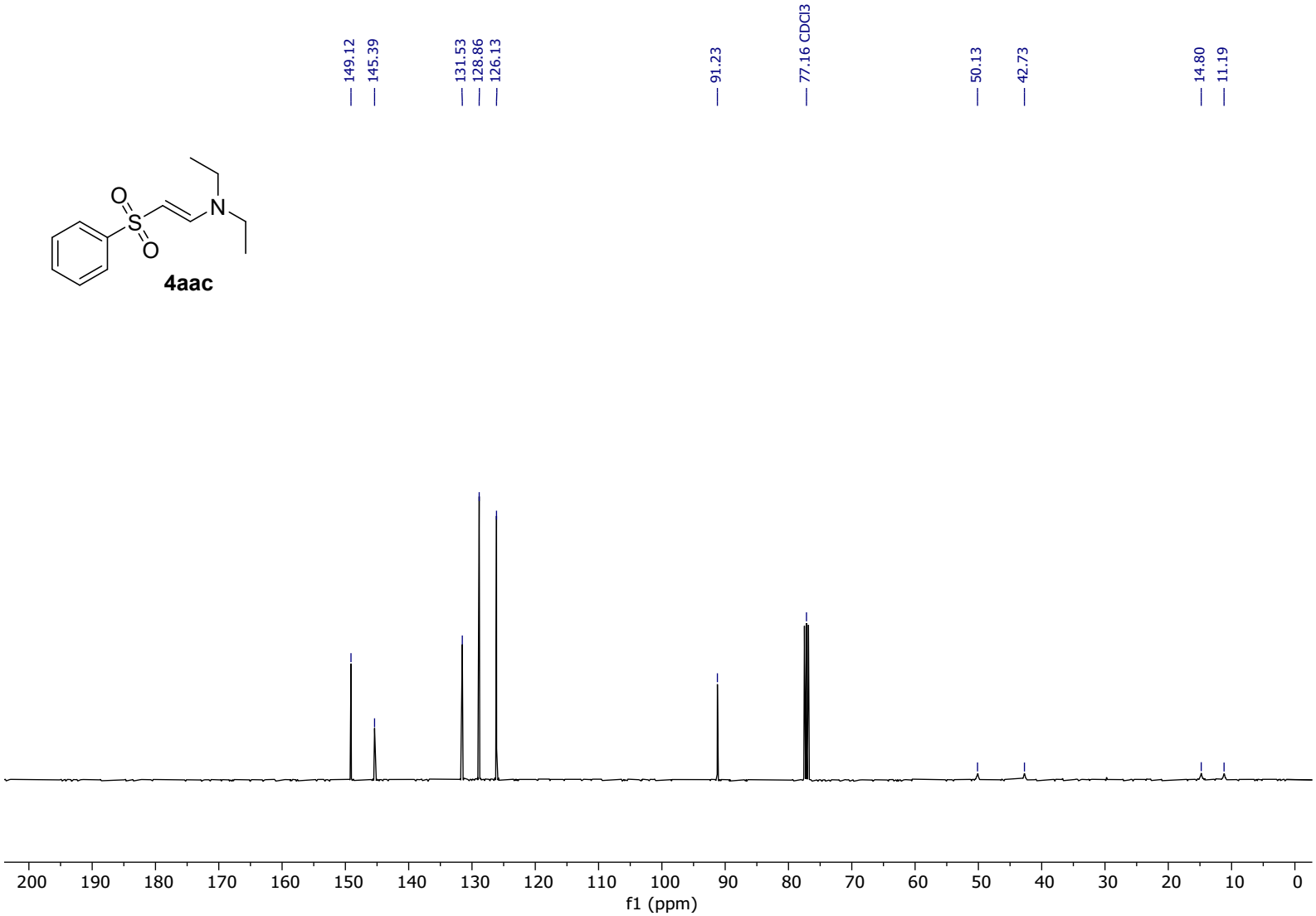
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aab**.



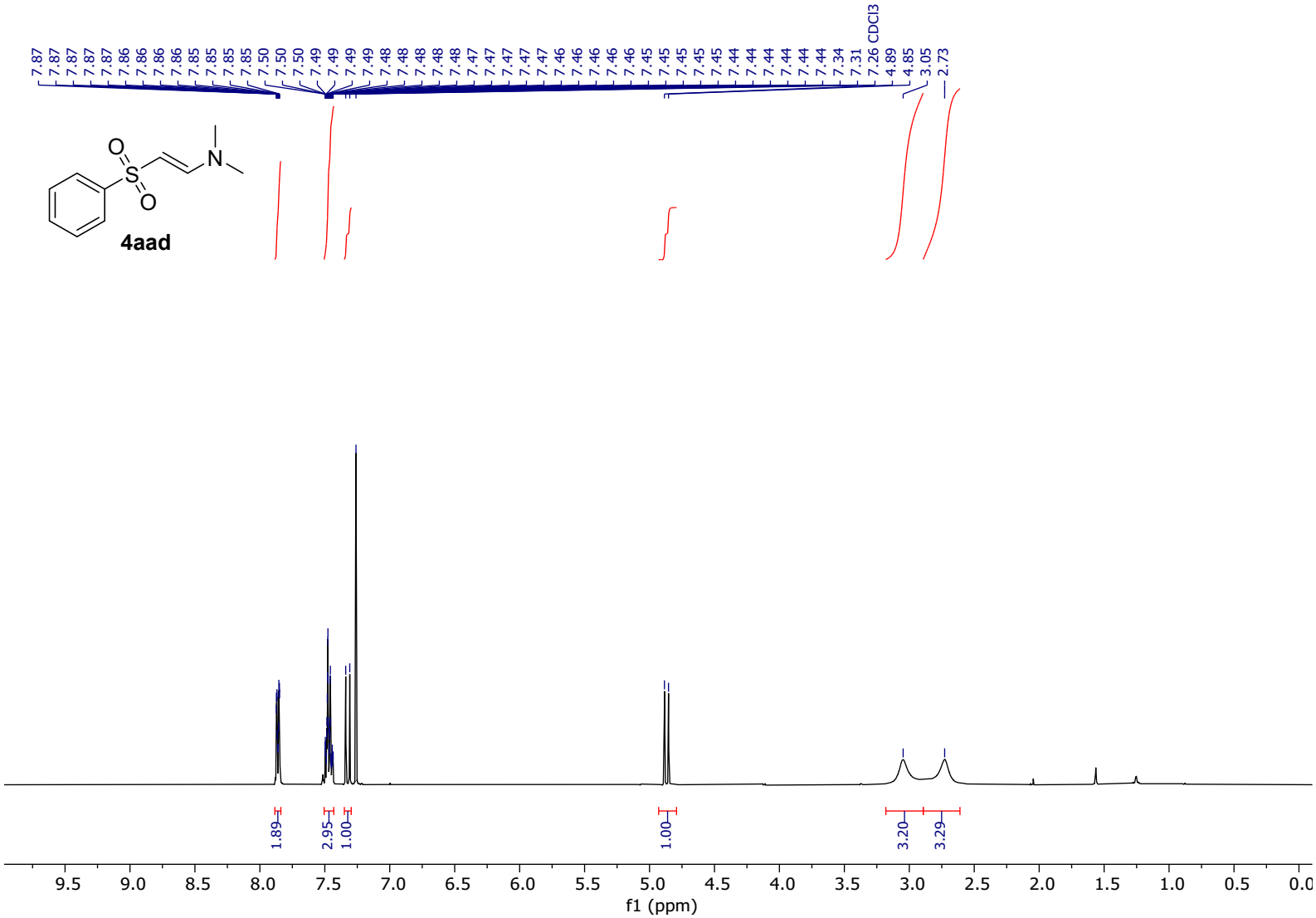
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aab**.



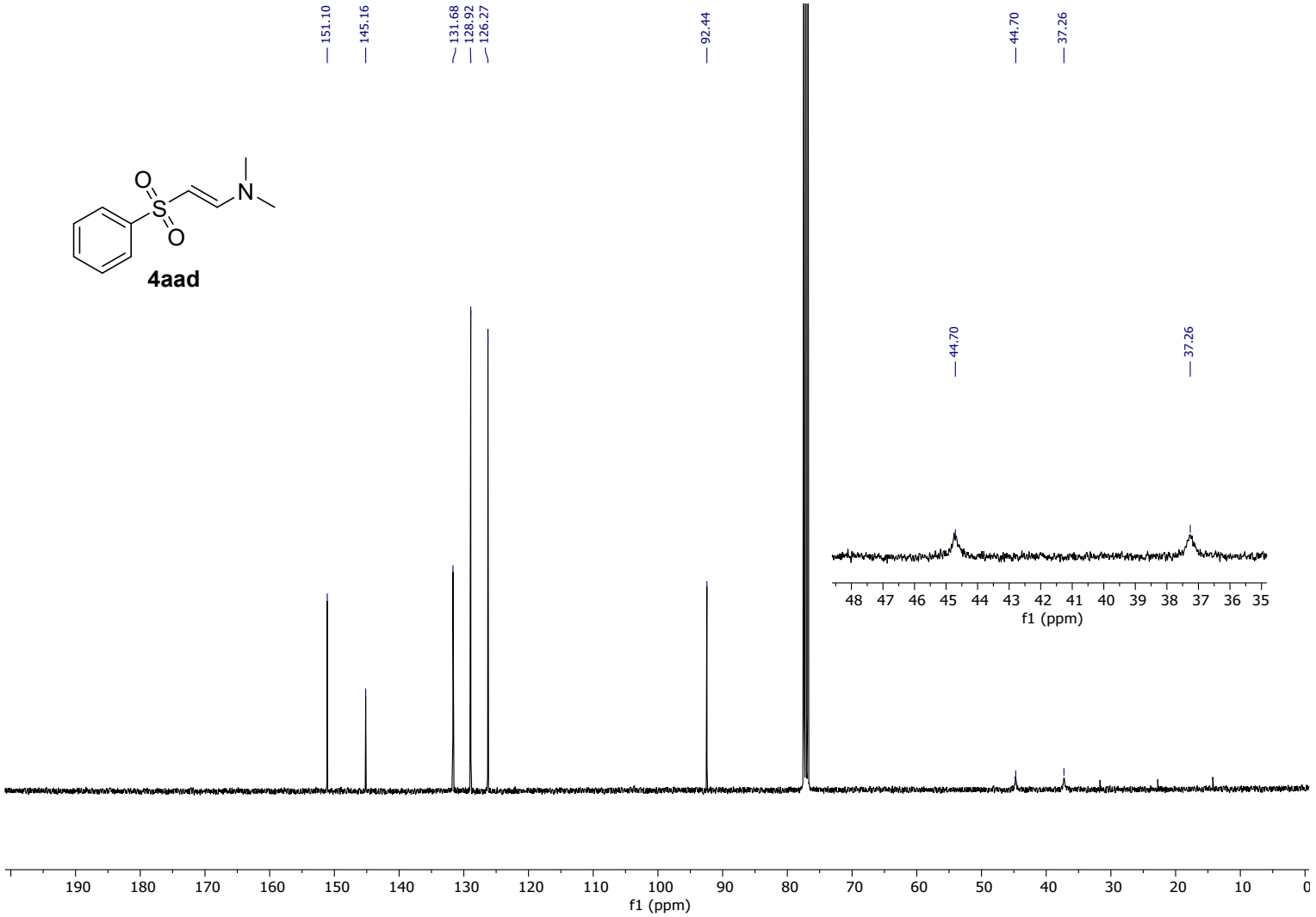
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aac**.



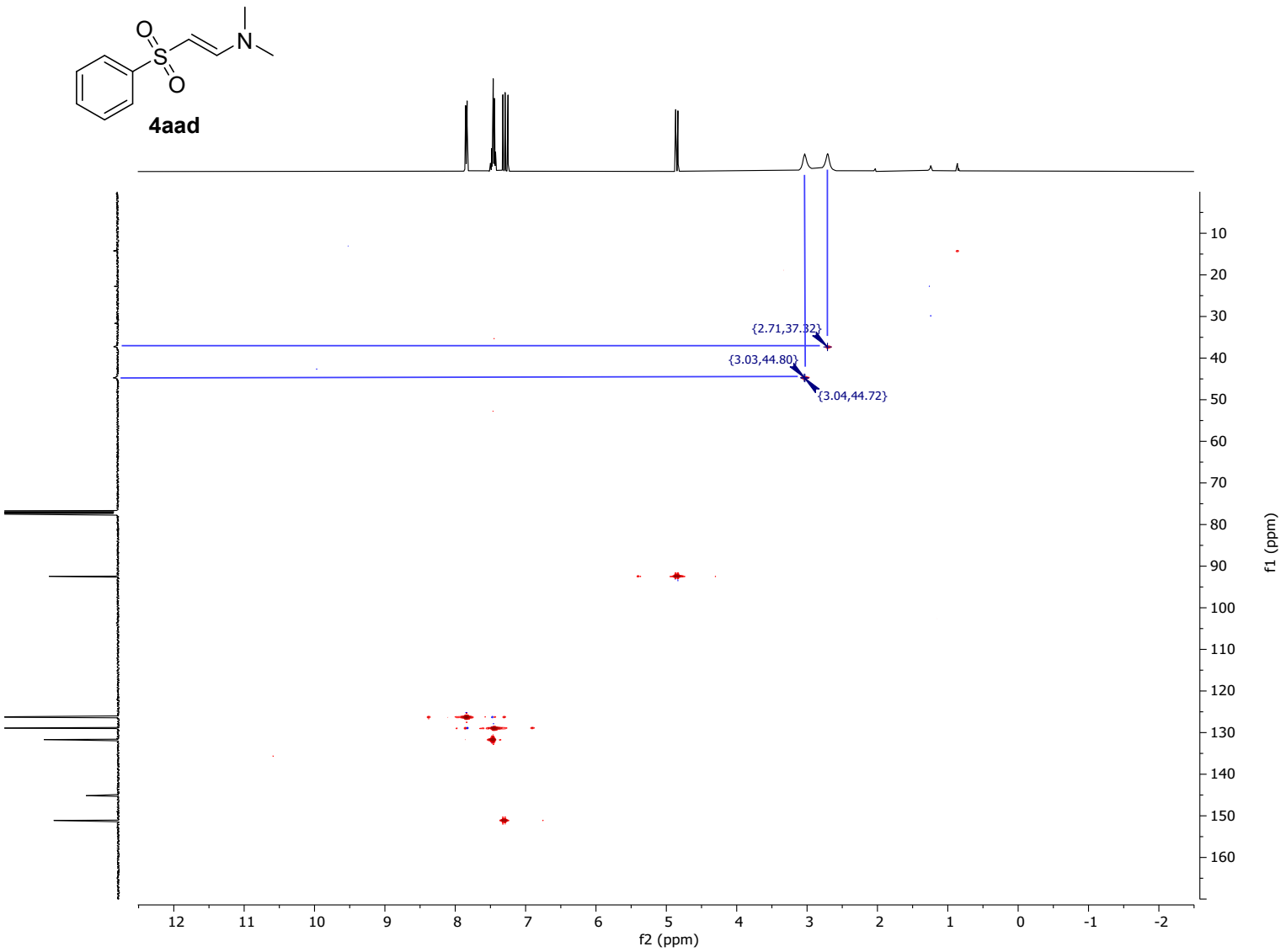
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aac**.



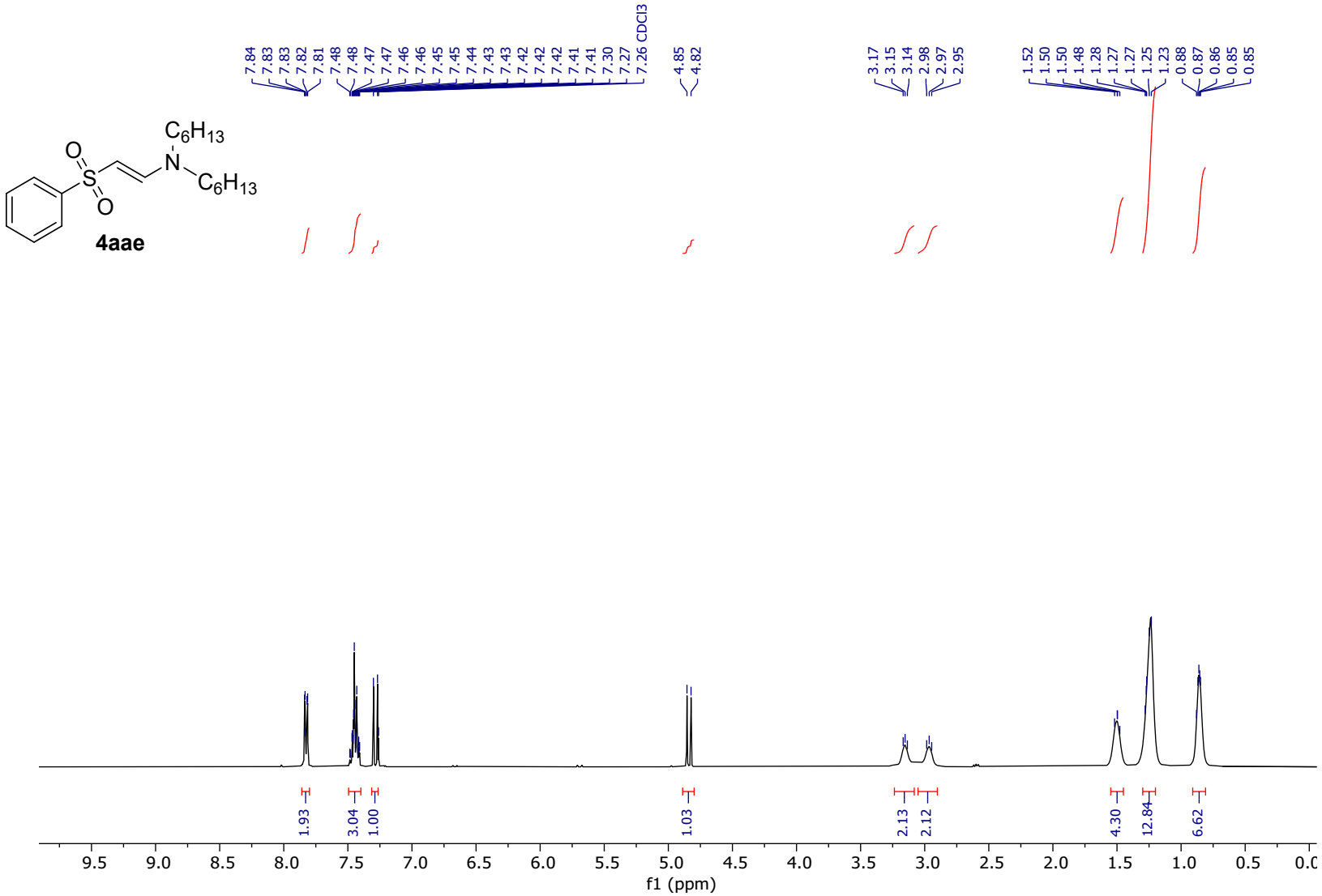
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aad**.



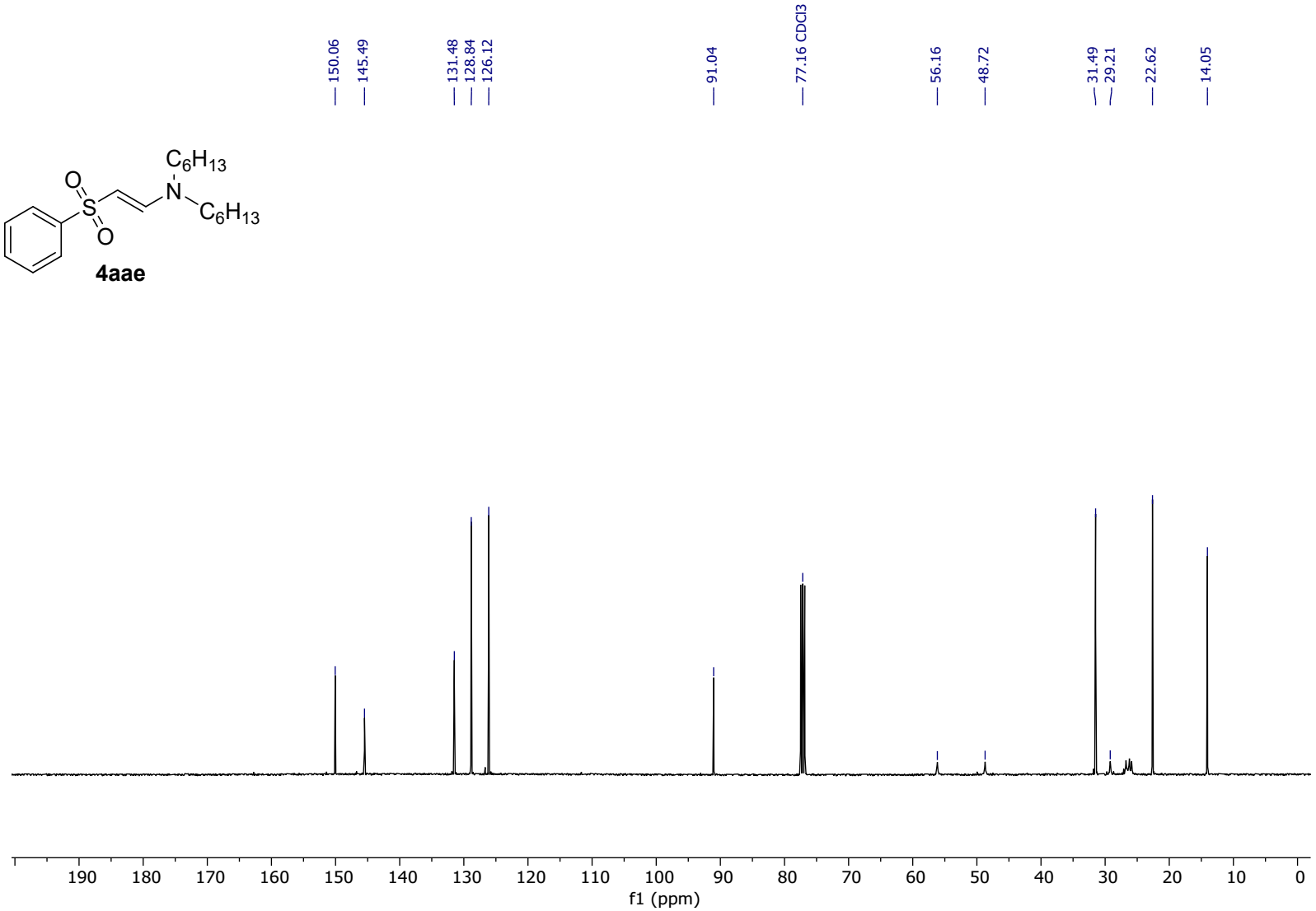
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aad**.



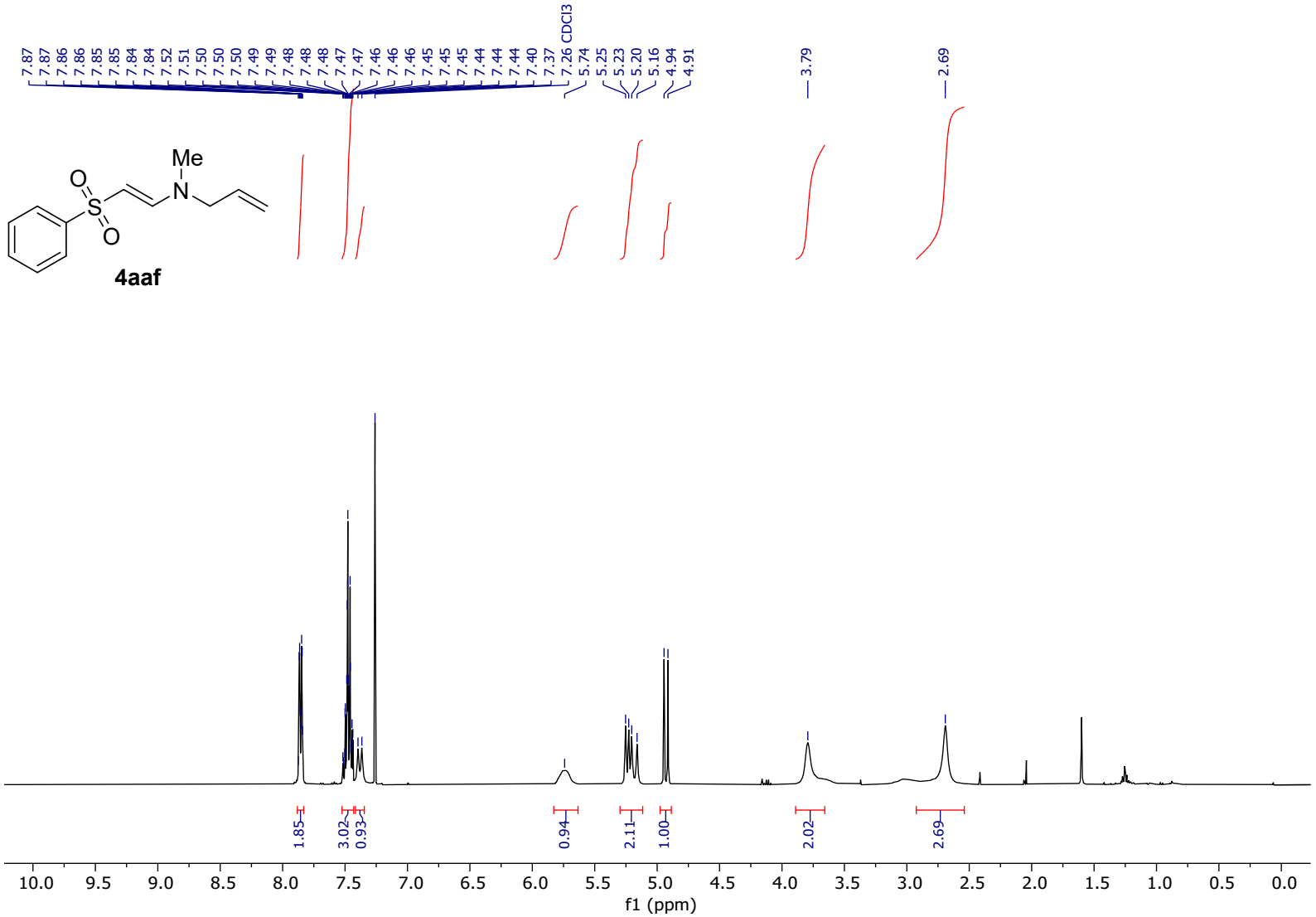
HSQC spectrum of compound **4aad**.



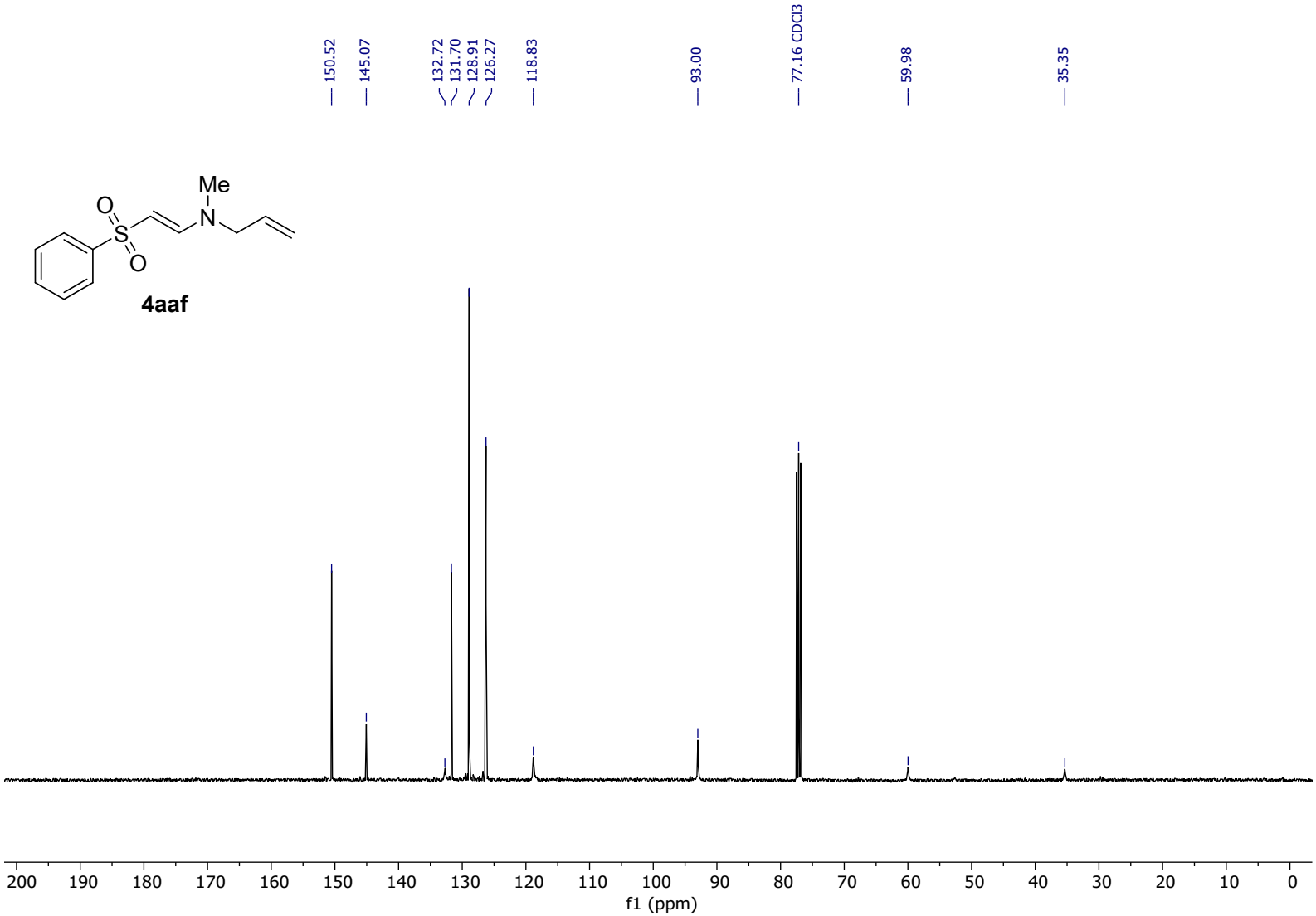
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aae**.



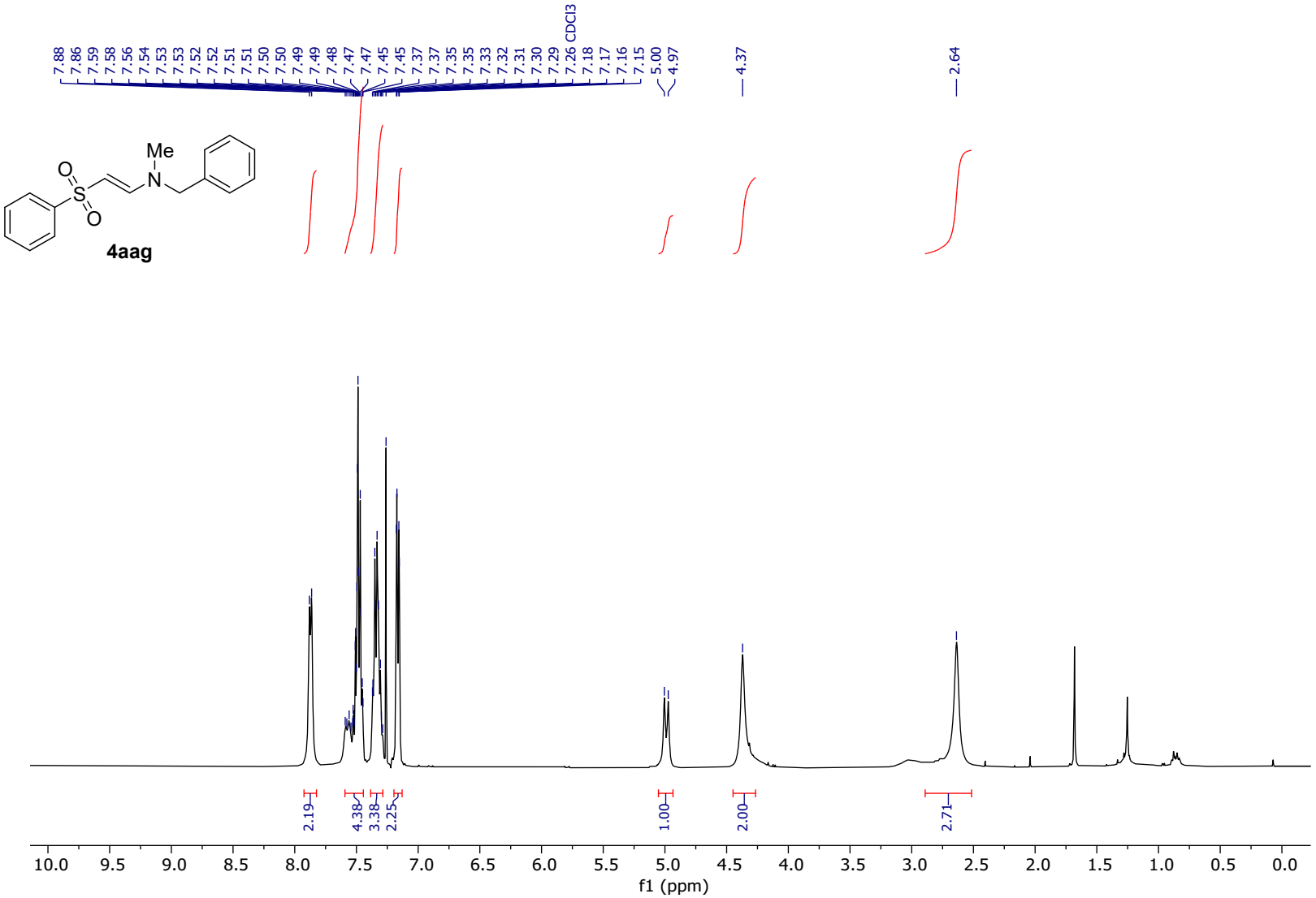
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aae**.



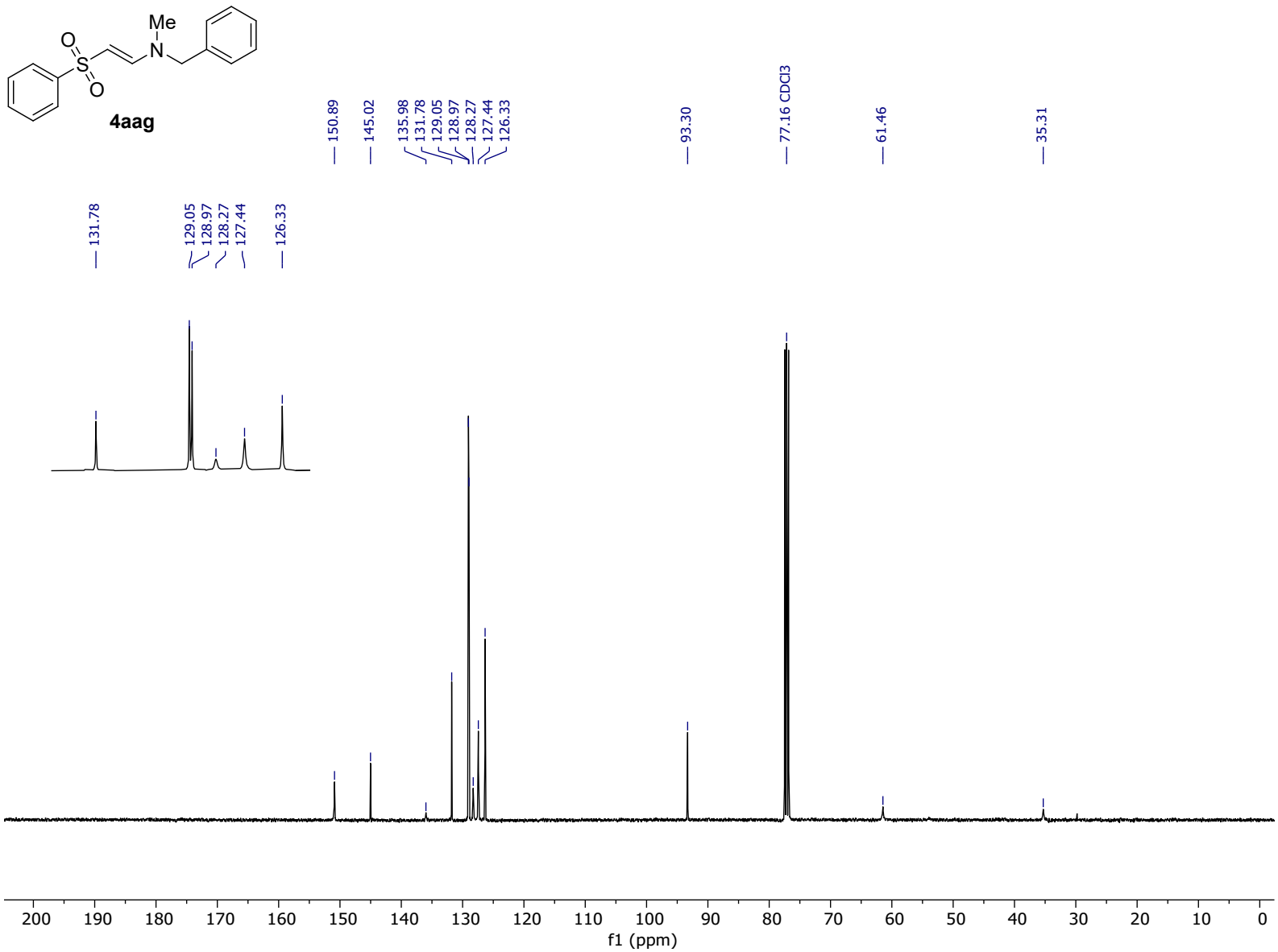
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aaf**.



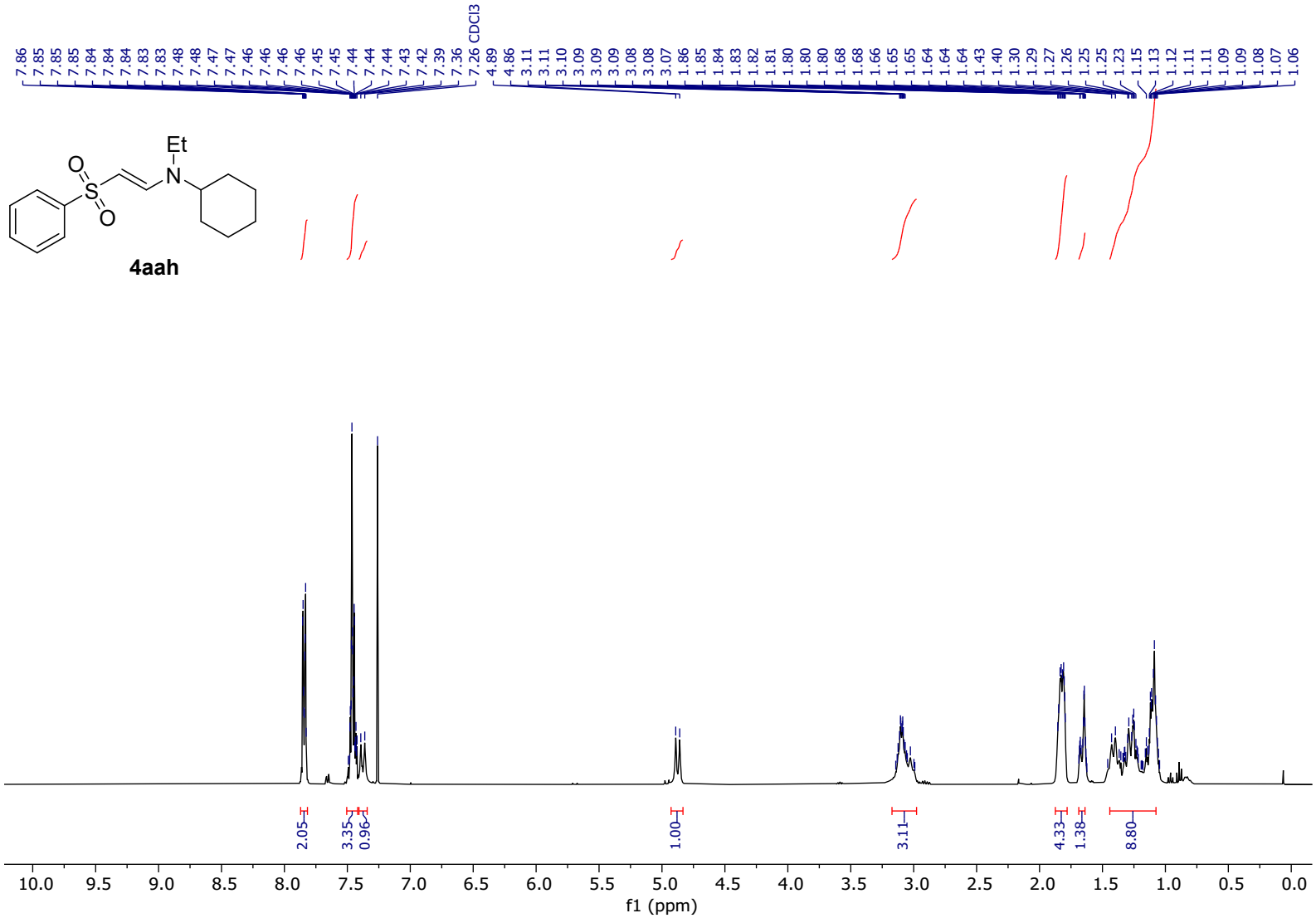
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aaf**.



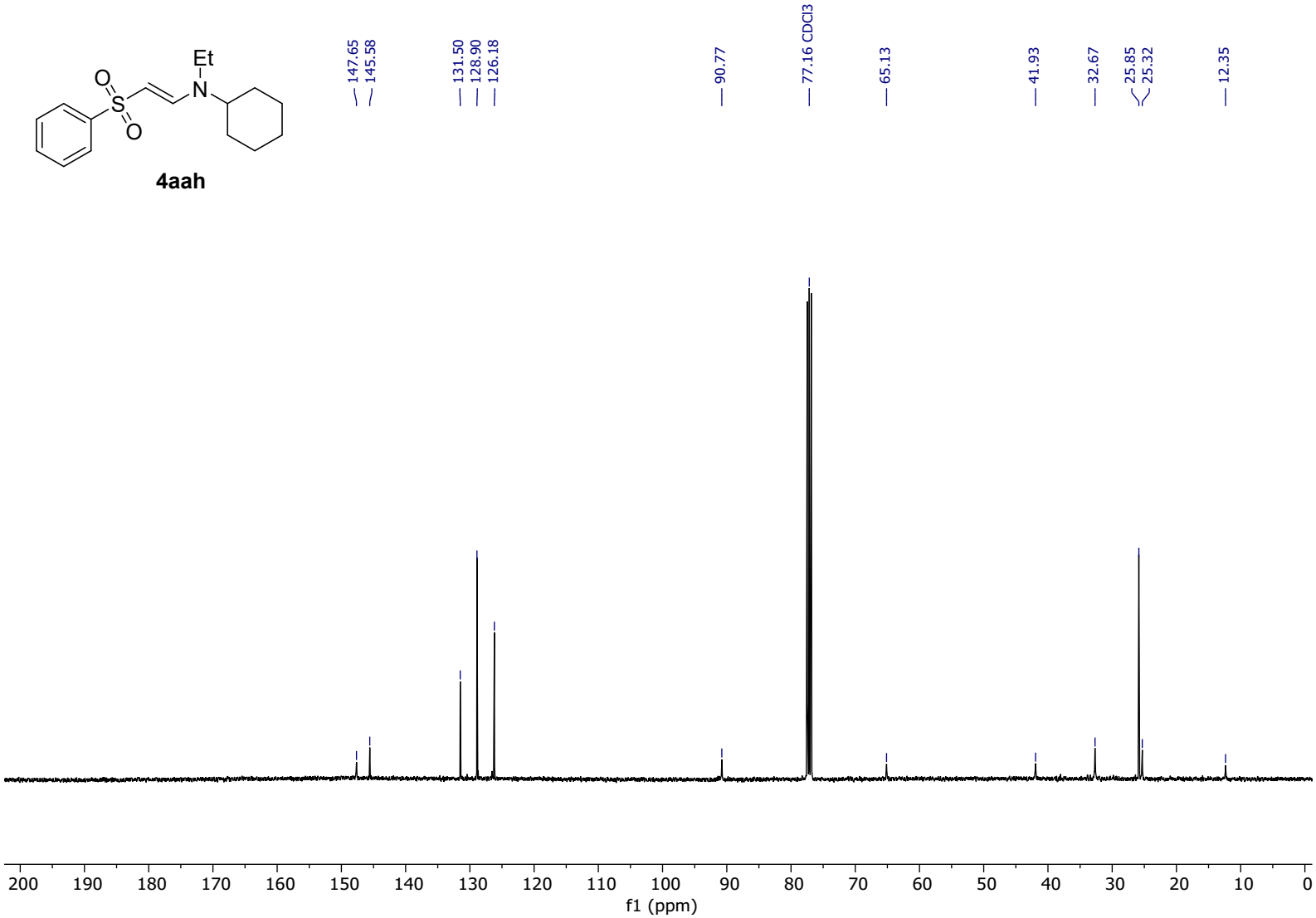
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aag**.



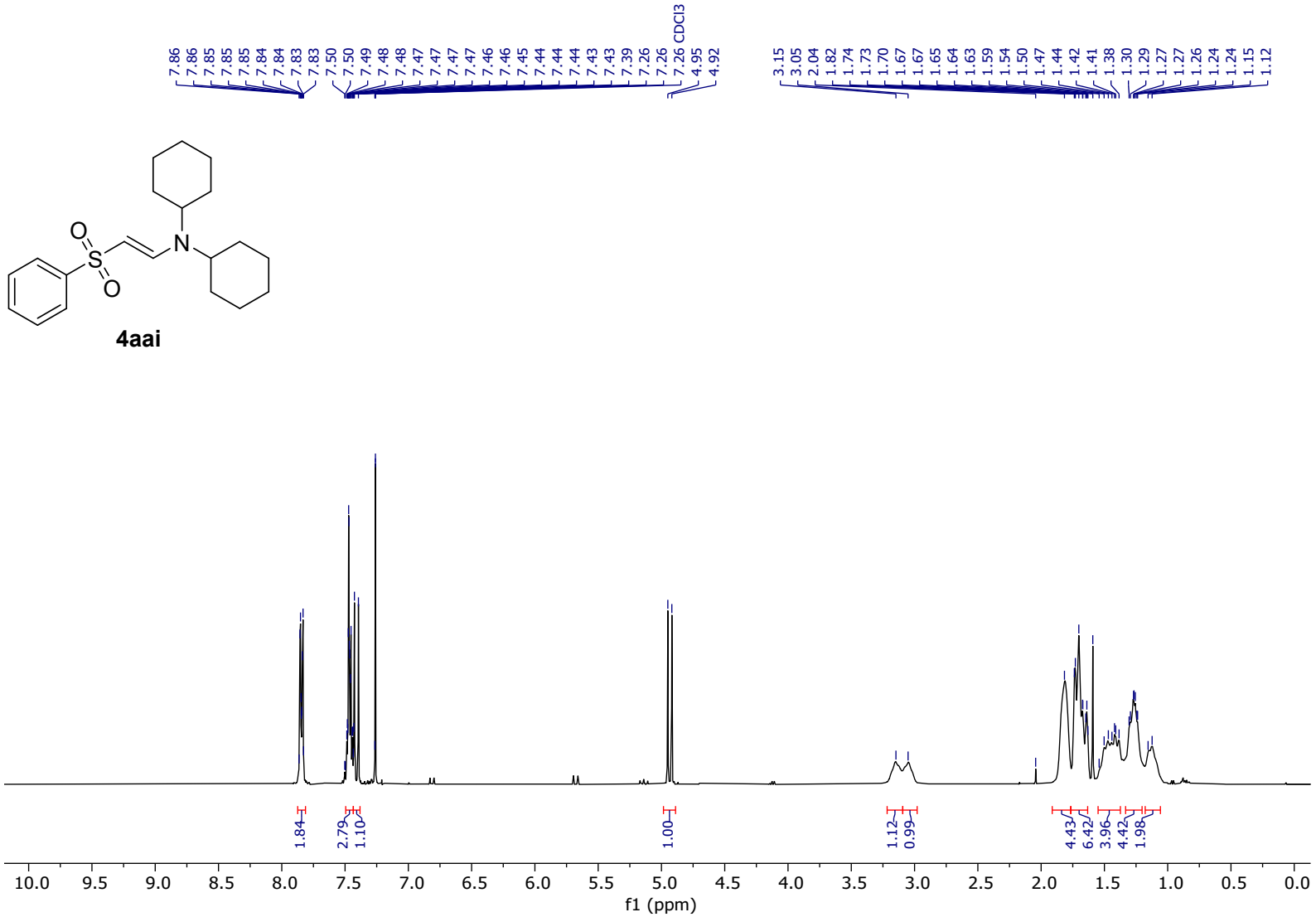
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aag**.



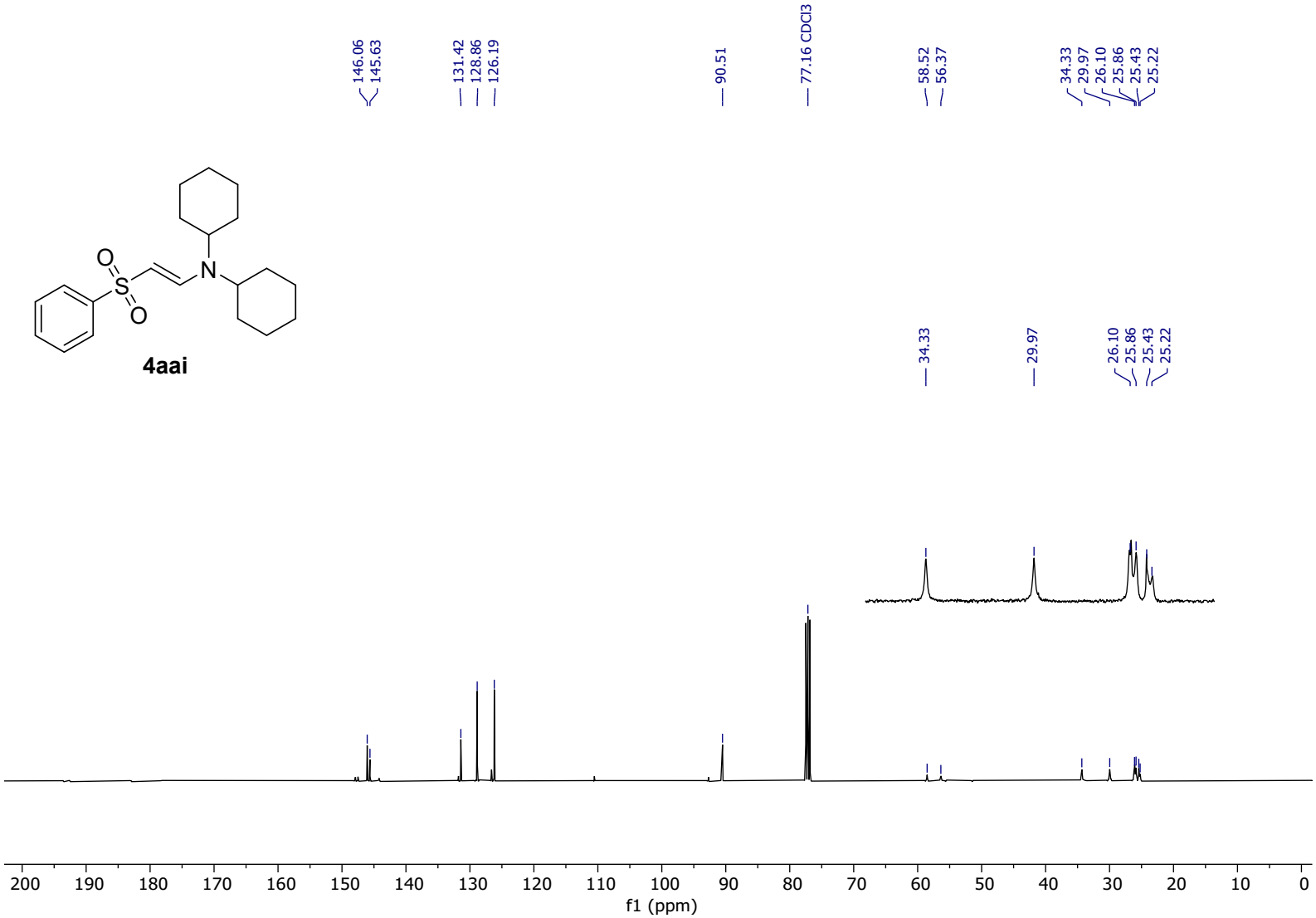
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aah**.



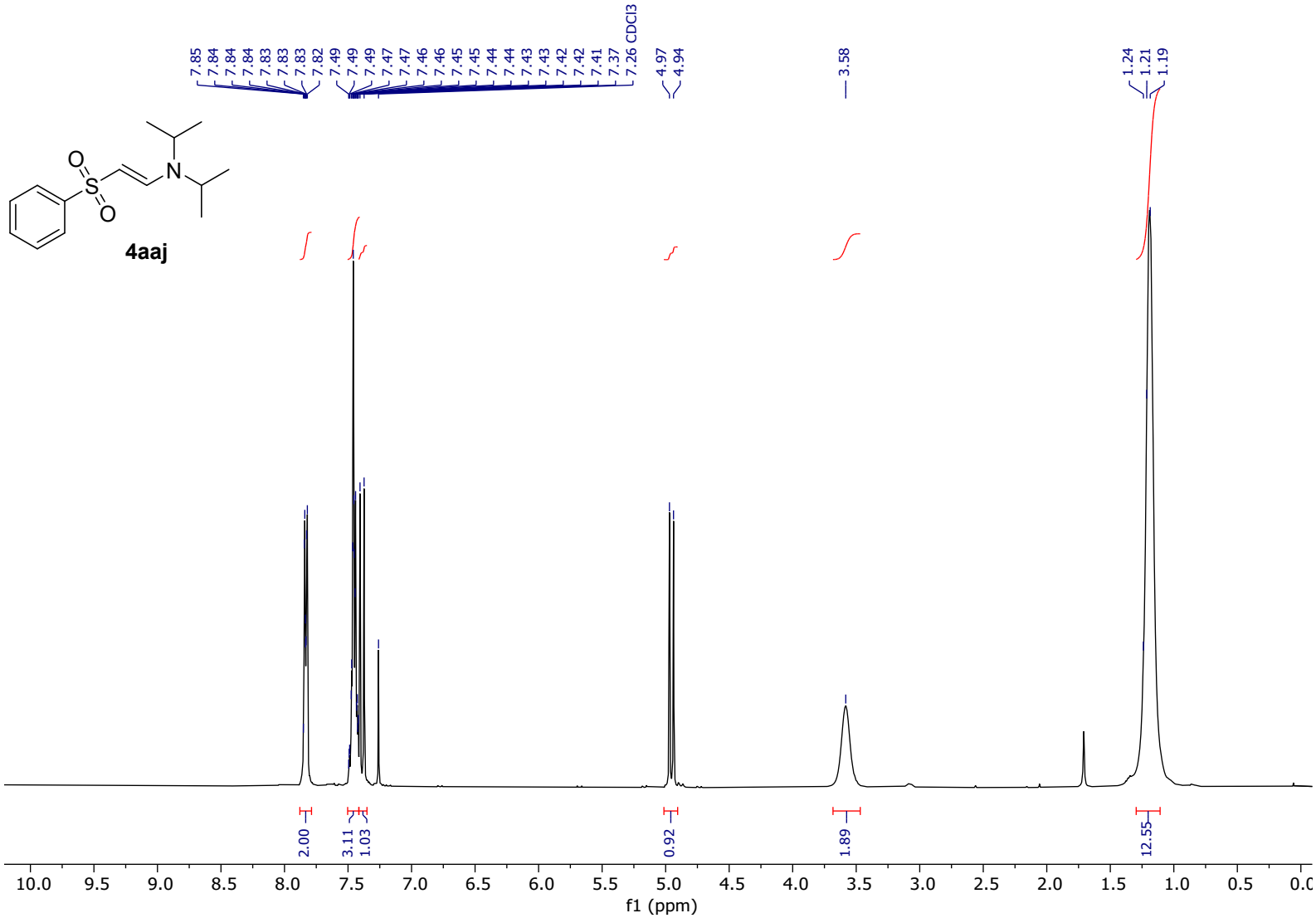
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aah**.



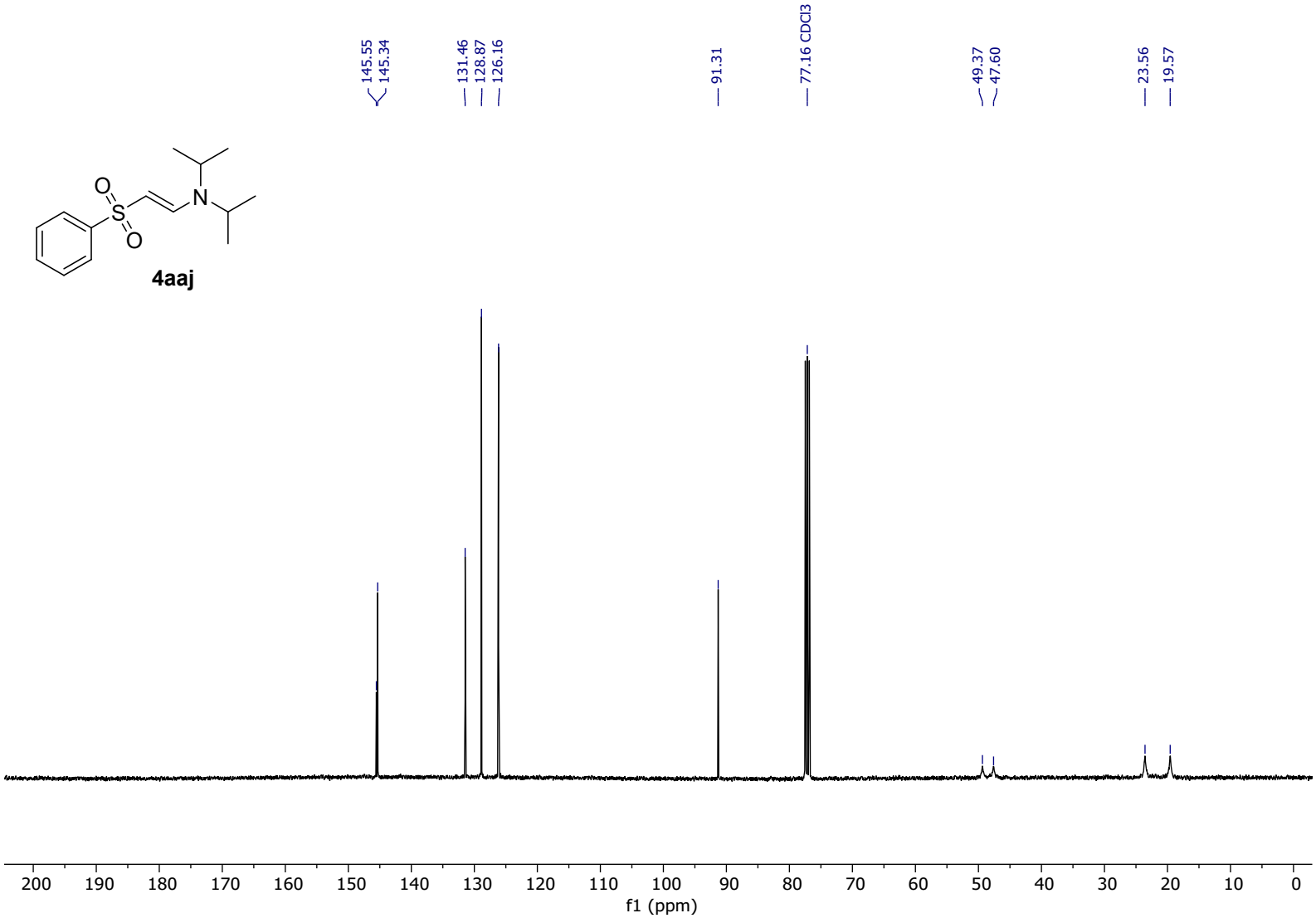
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aai**.



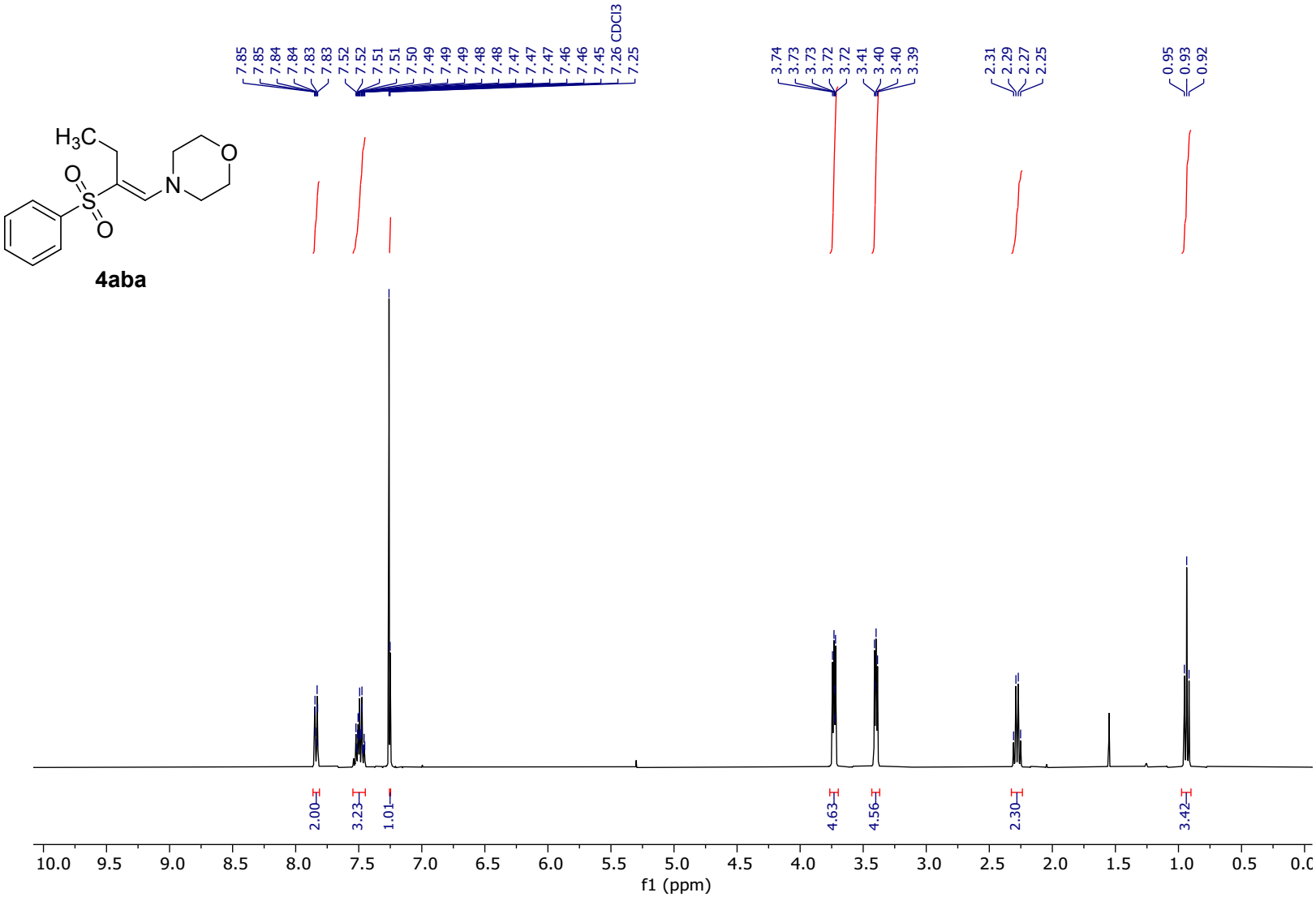
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aai**.



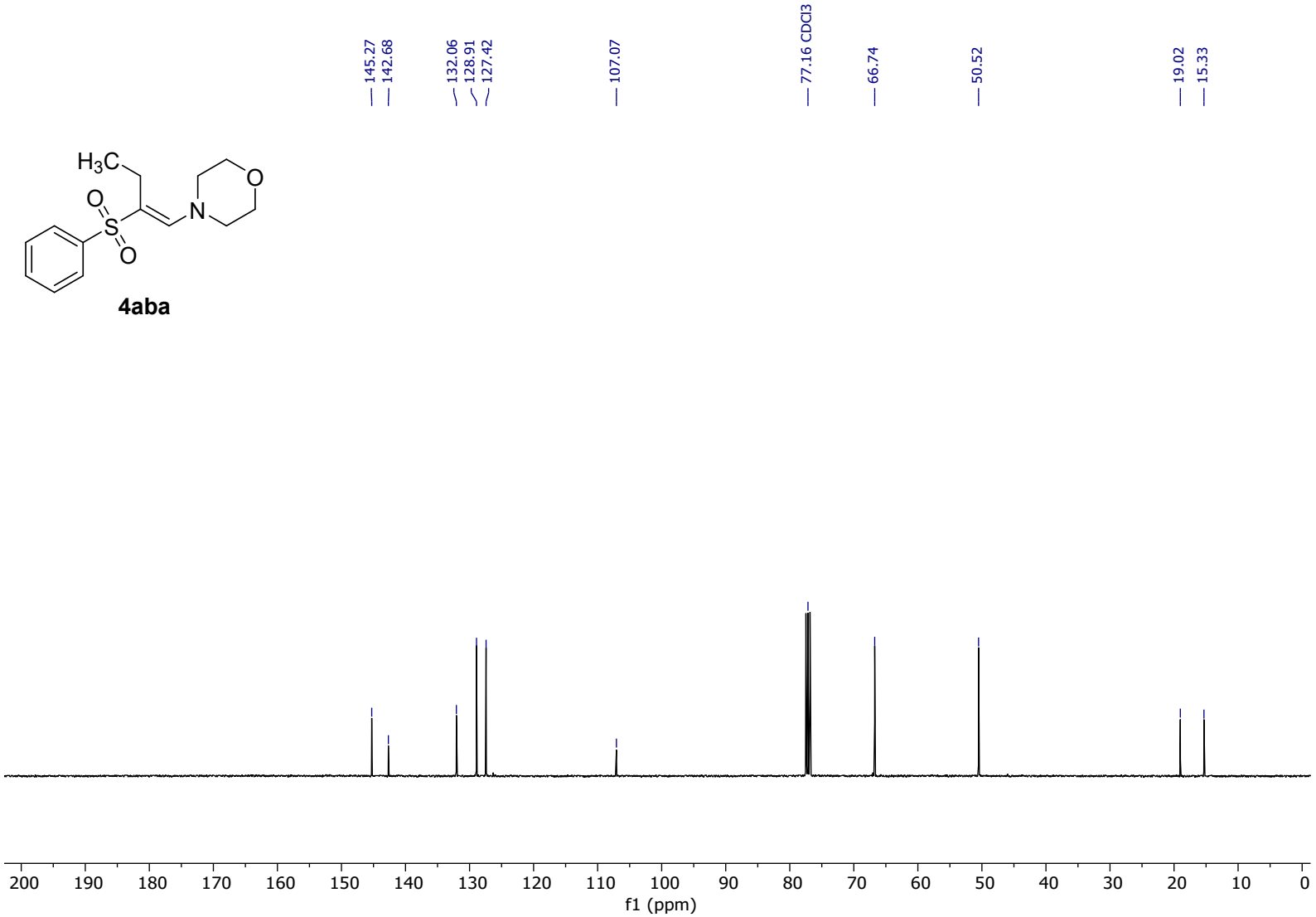
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aaj**.



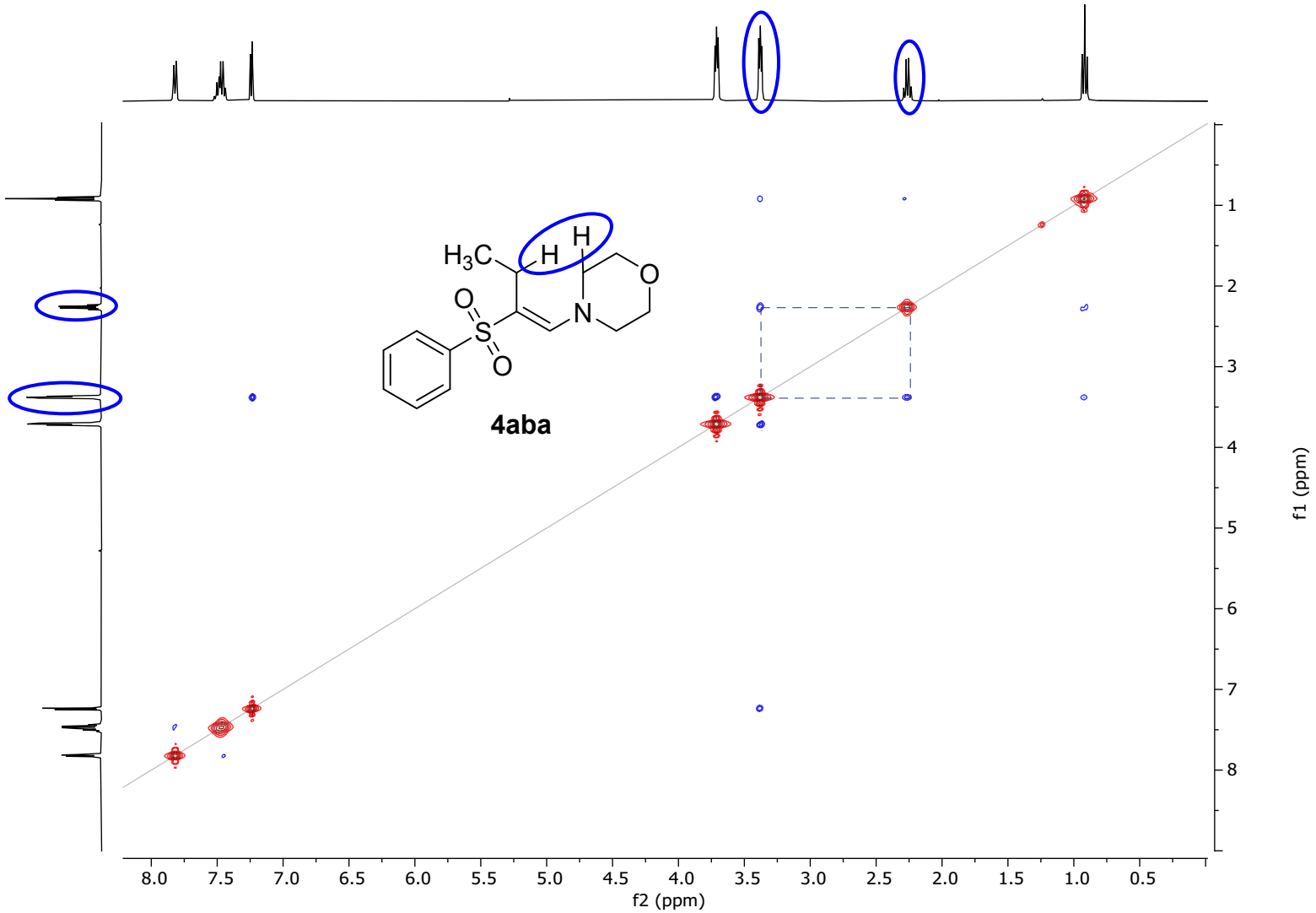
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aaj**.



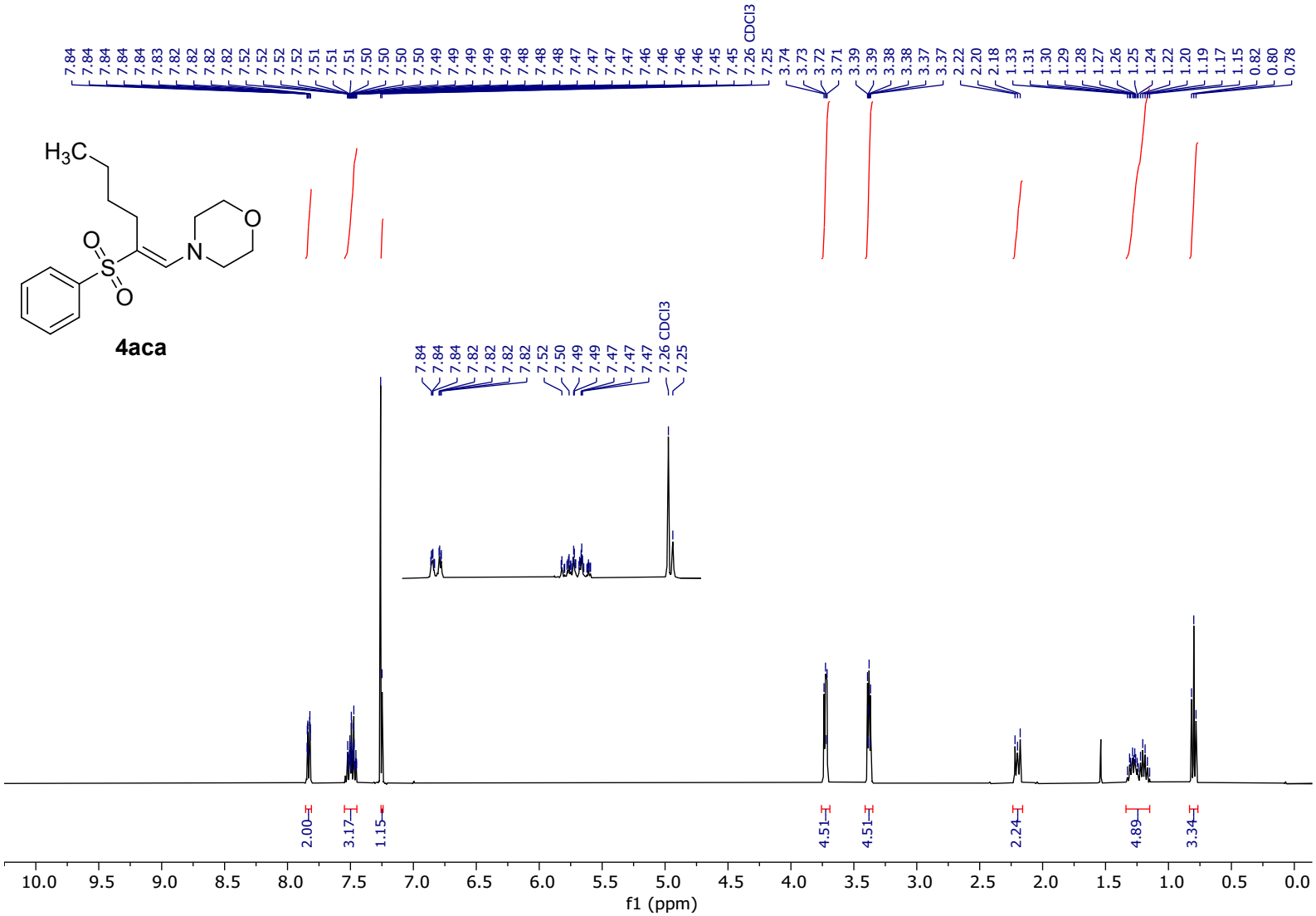
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aba**.



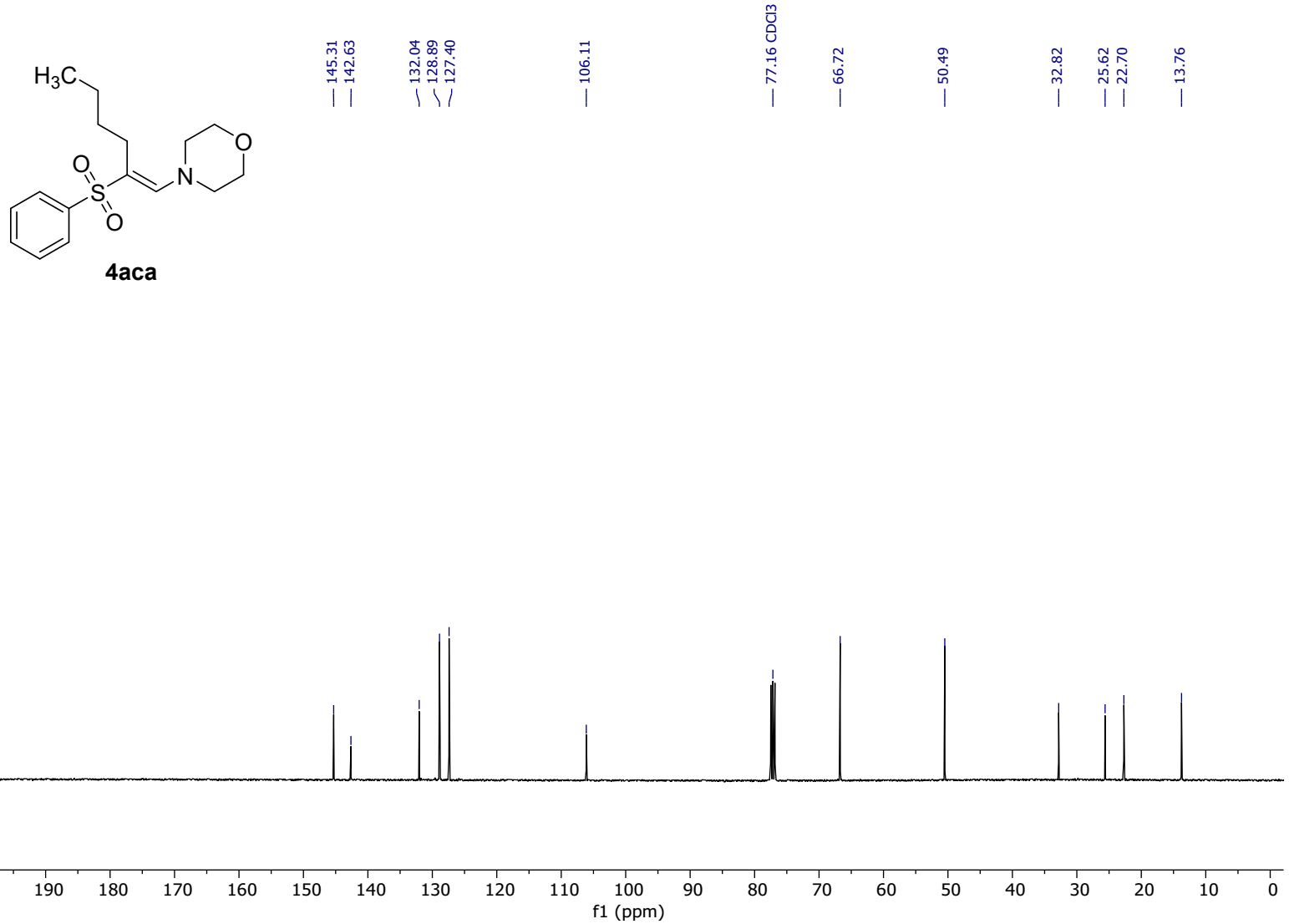
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aba**.



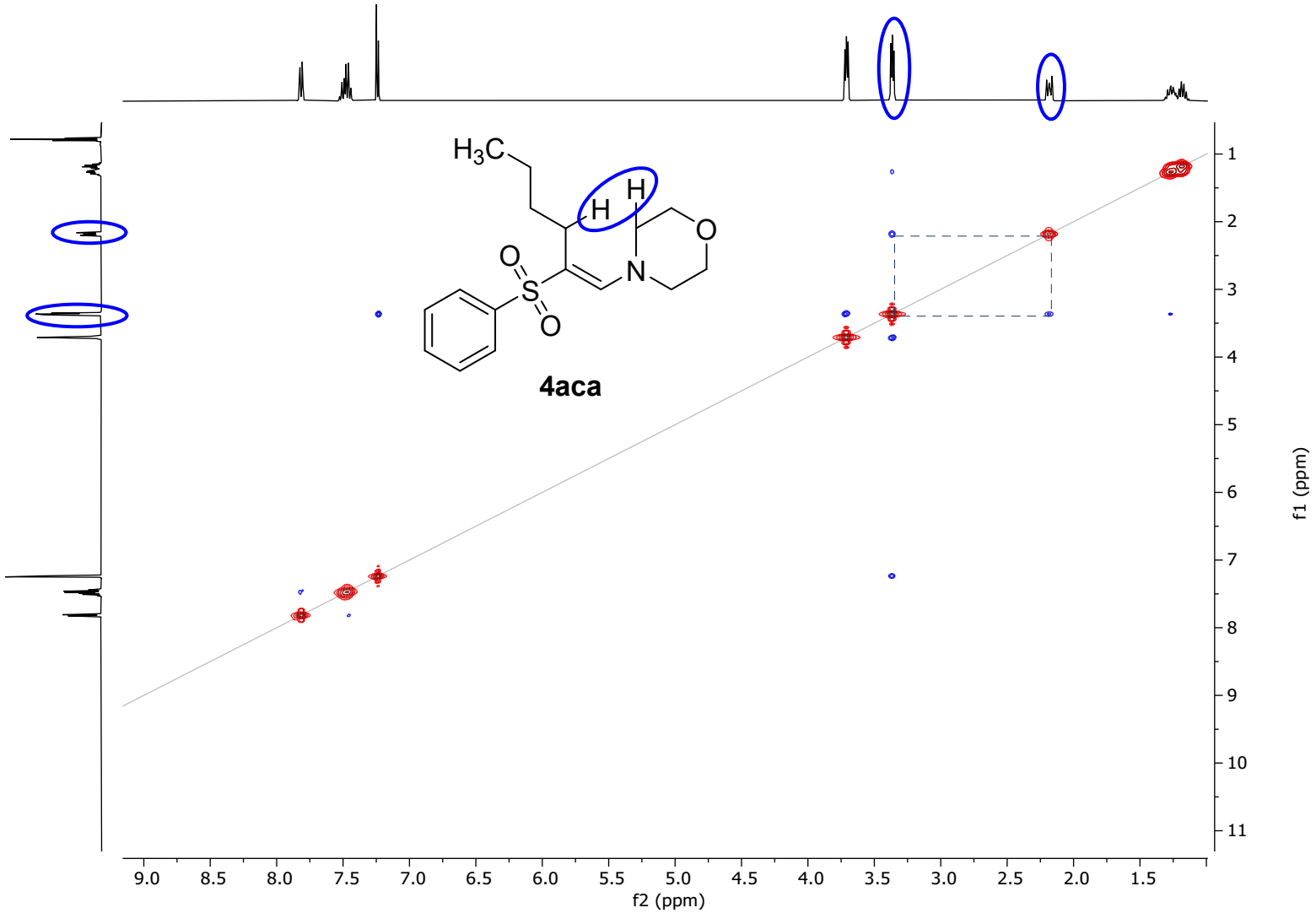
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4aba**.



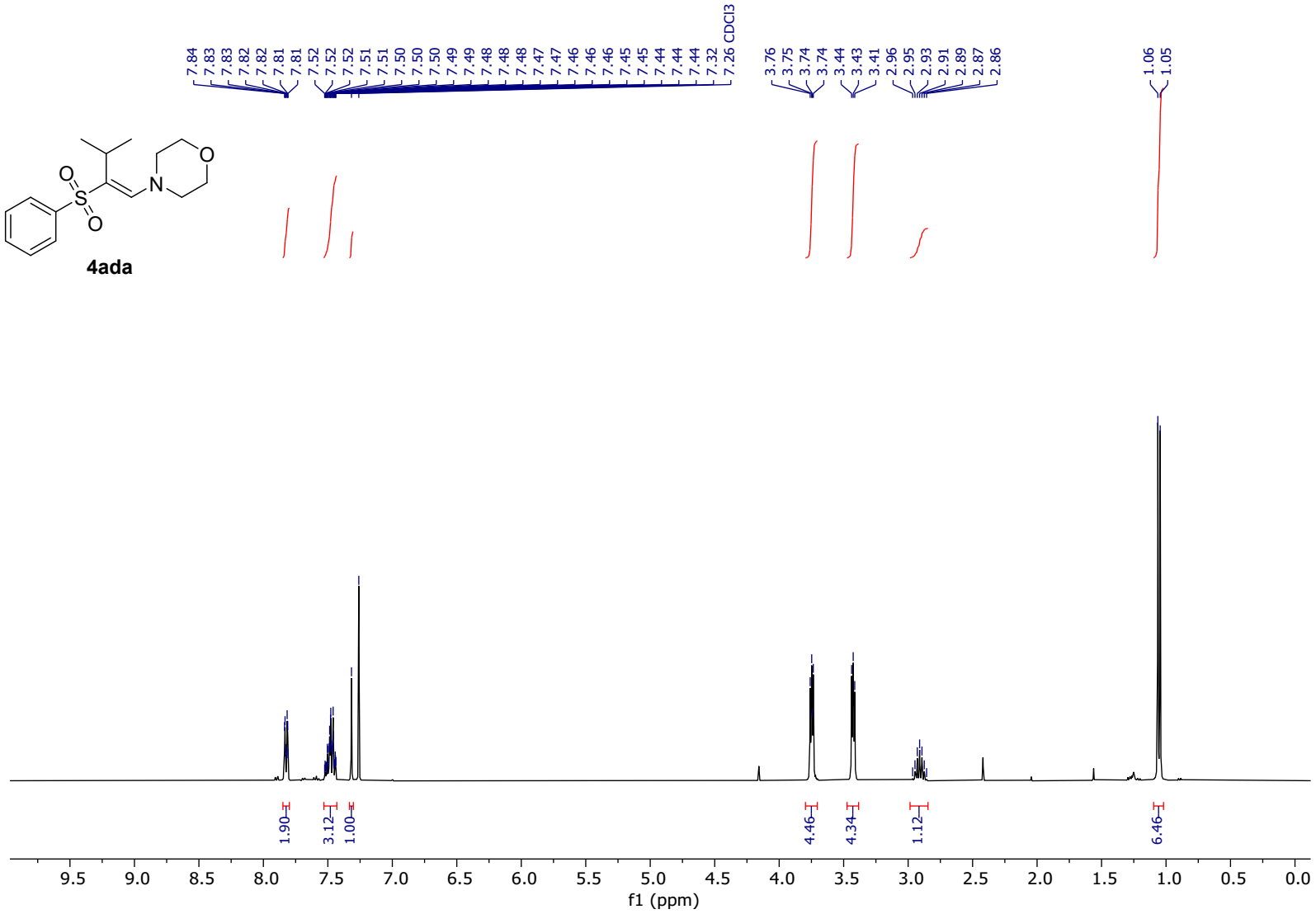
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aca**.



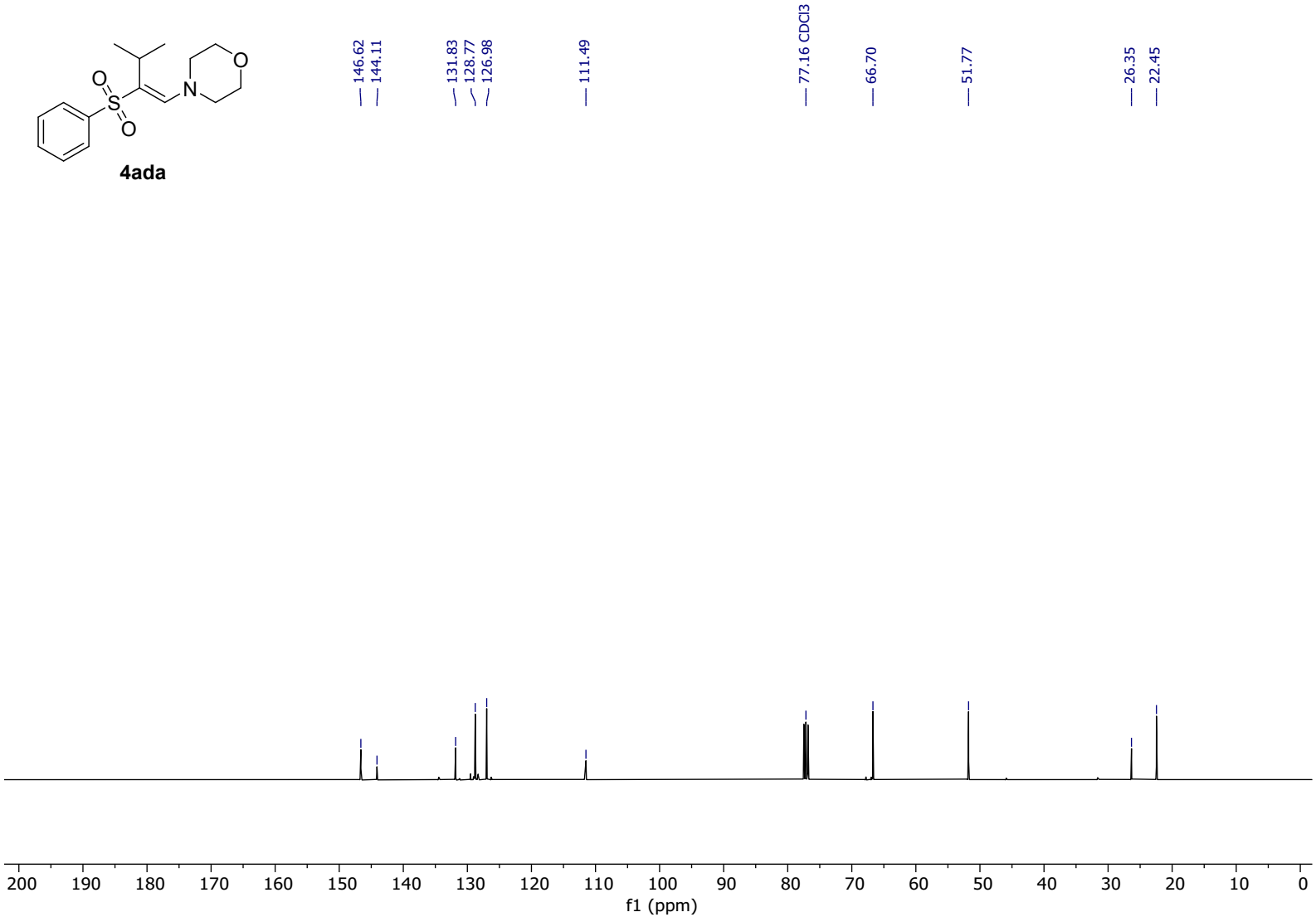
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aca**.



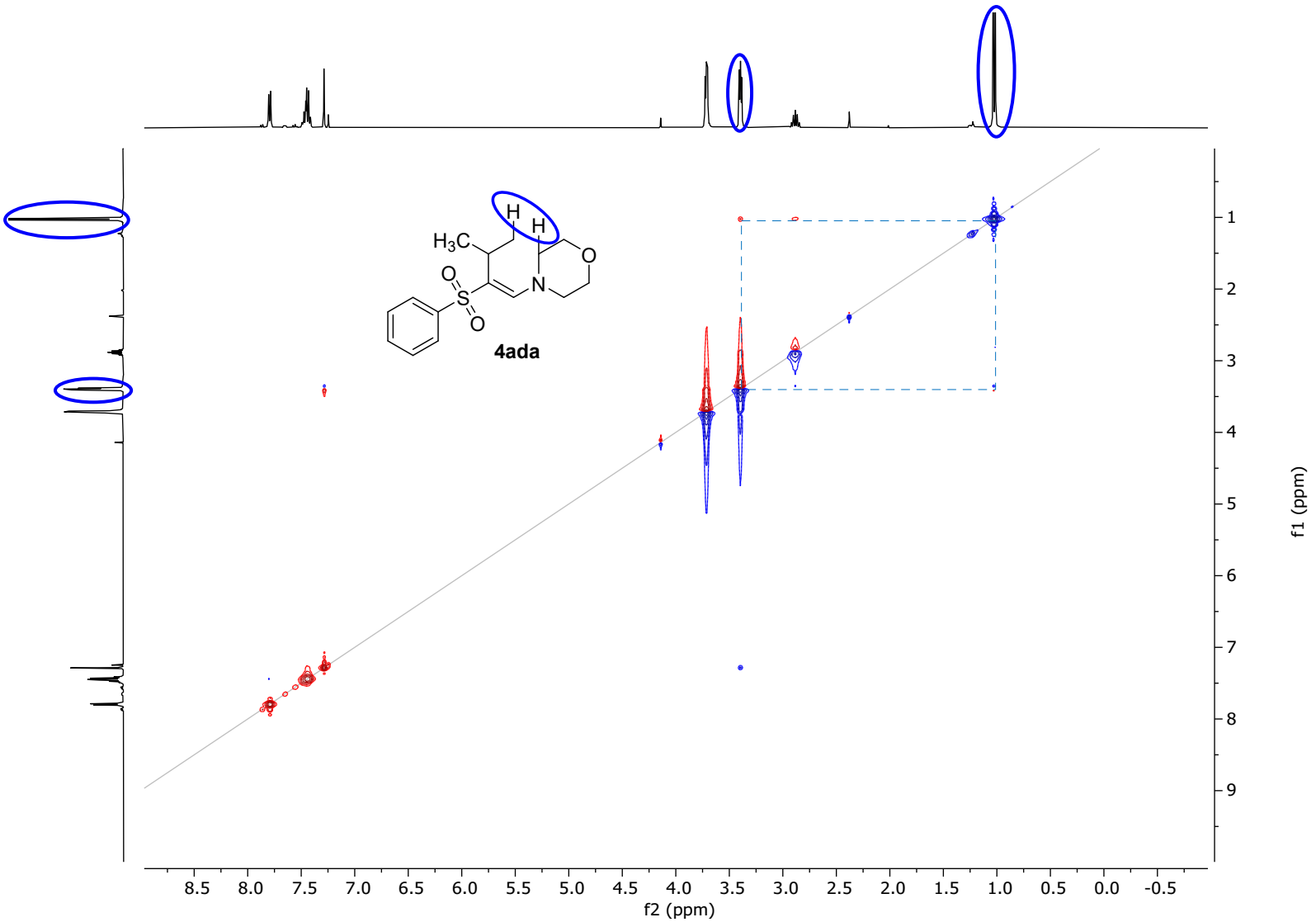
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4aca**.



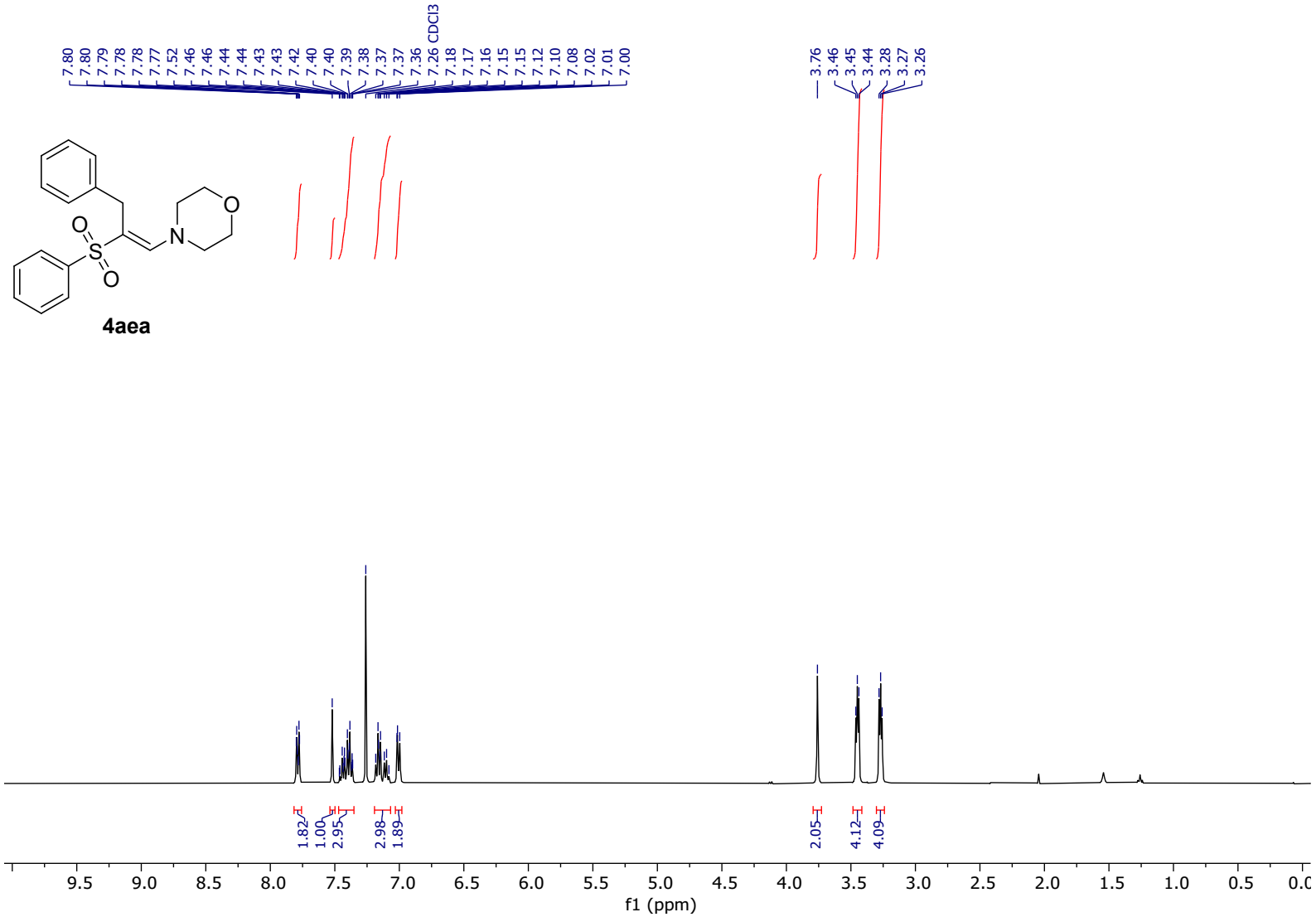
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4ada**.



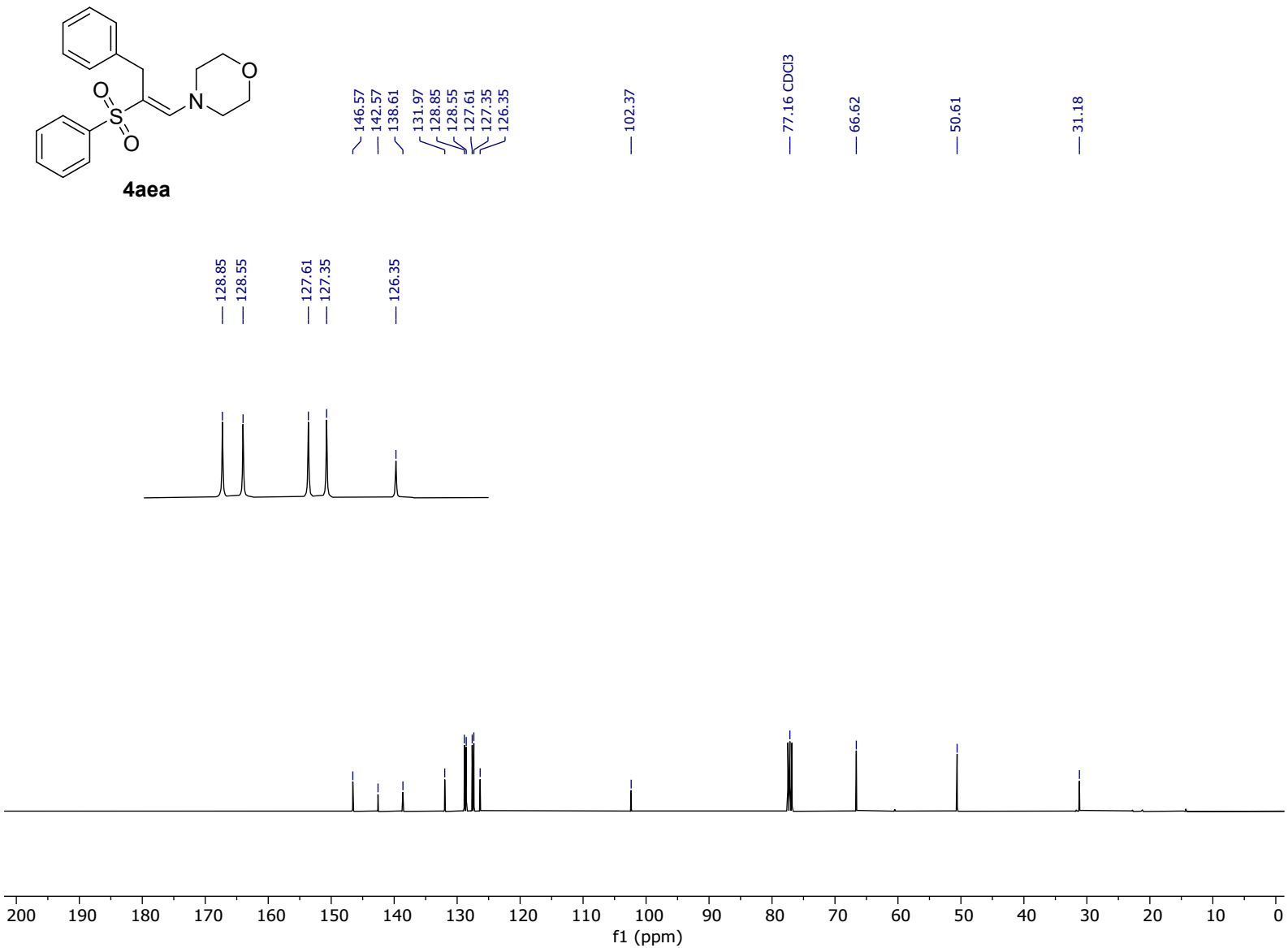
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4ada**.



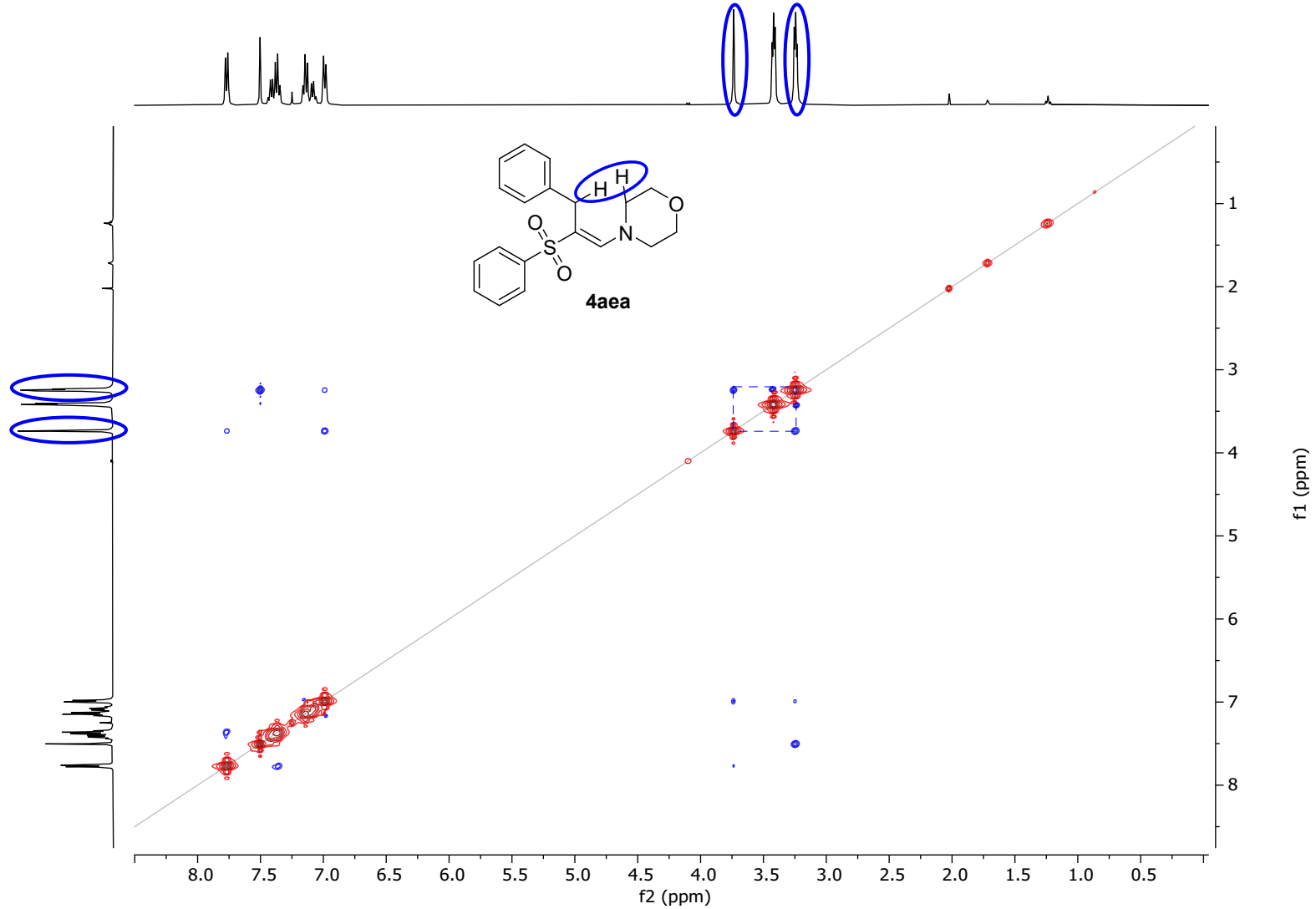
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4ada**.



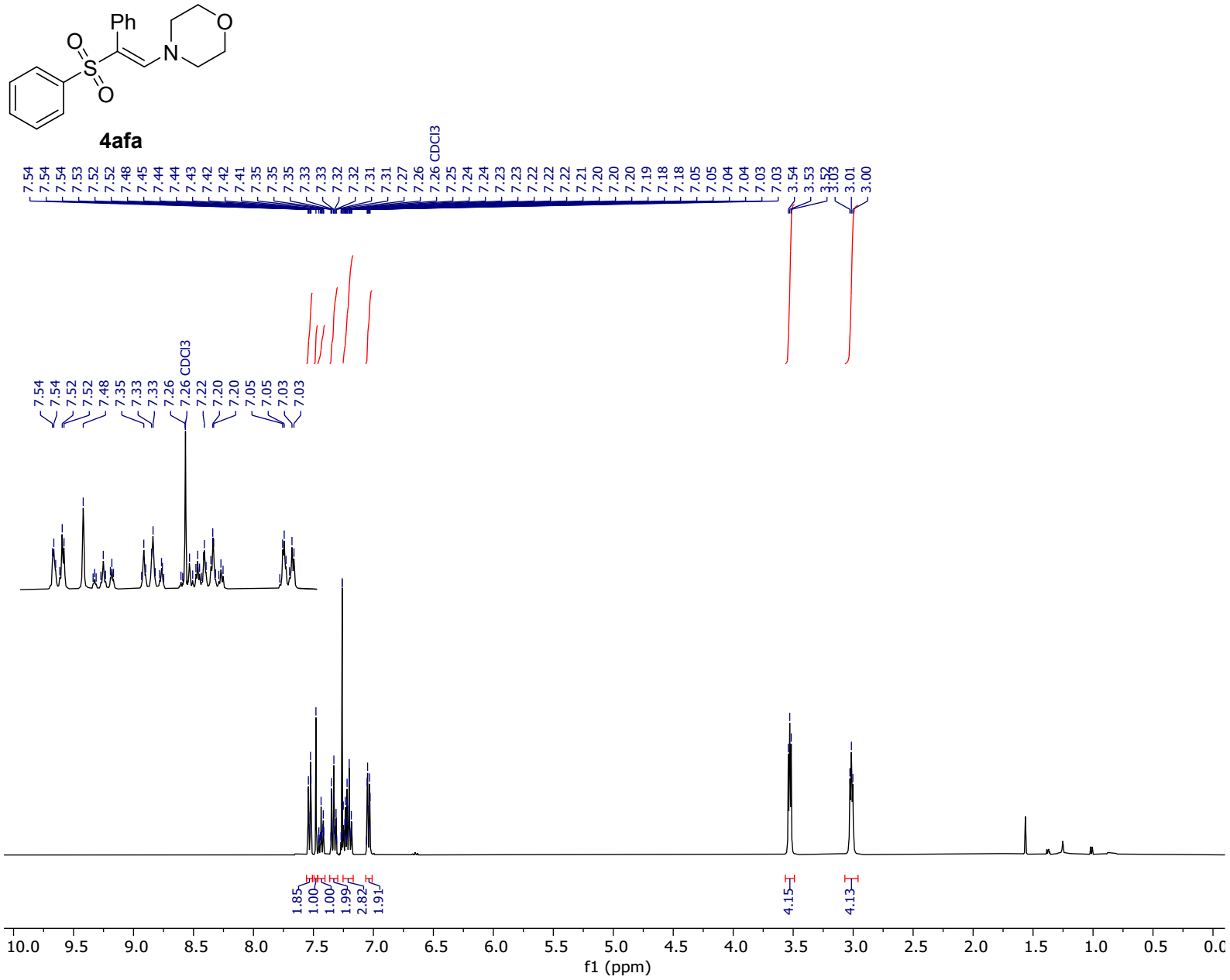
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aea**.



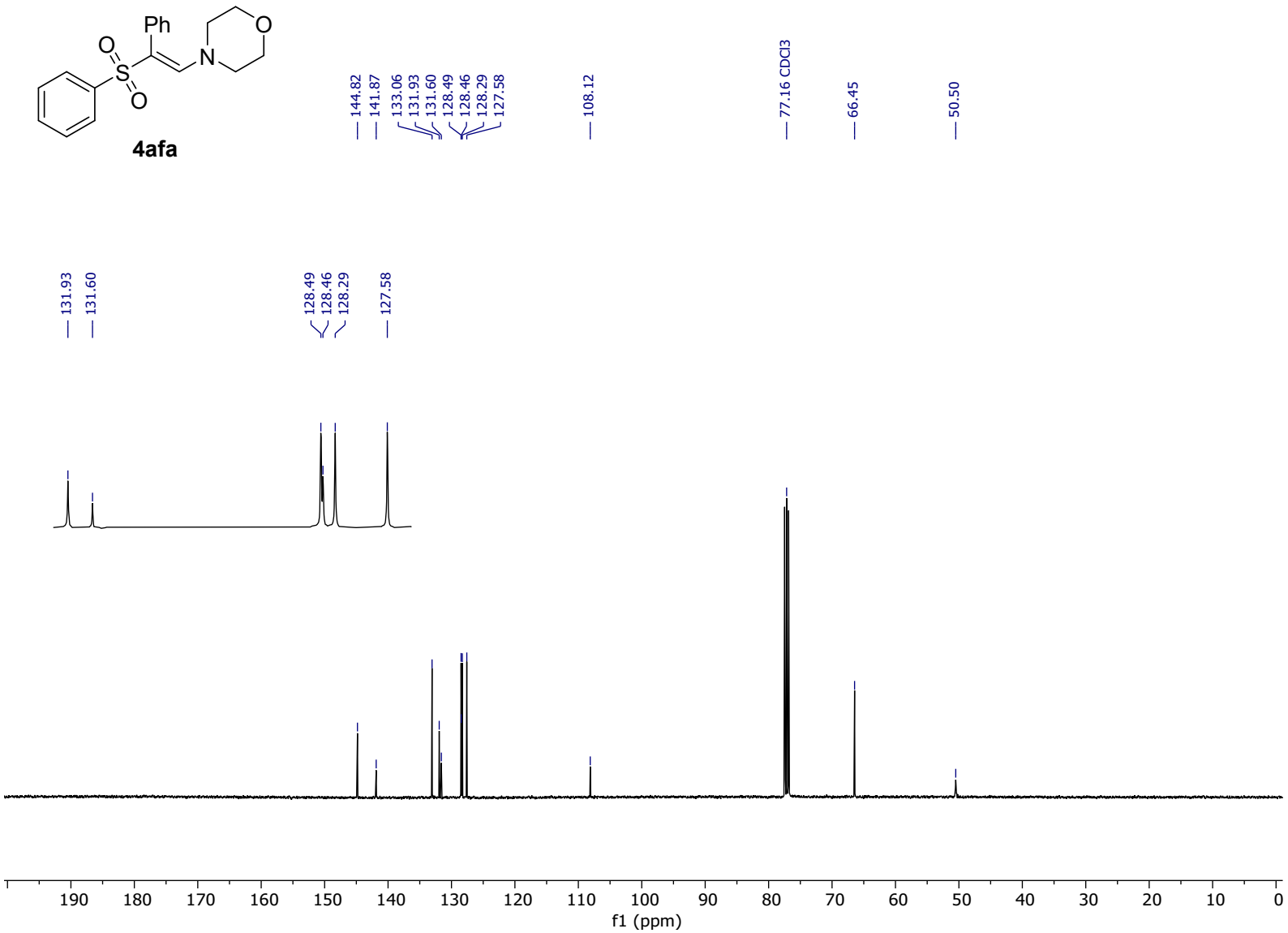
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aea**.



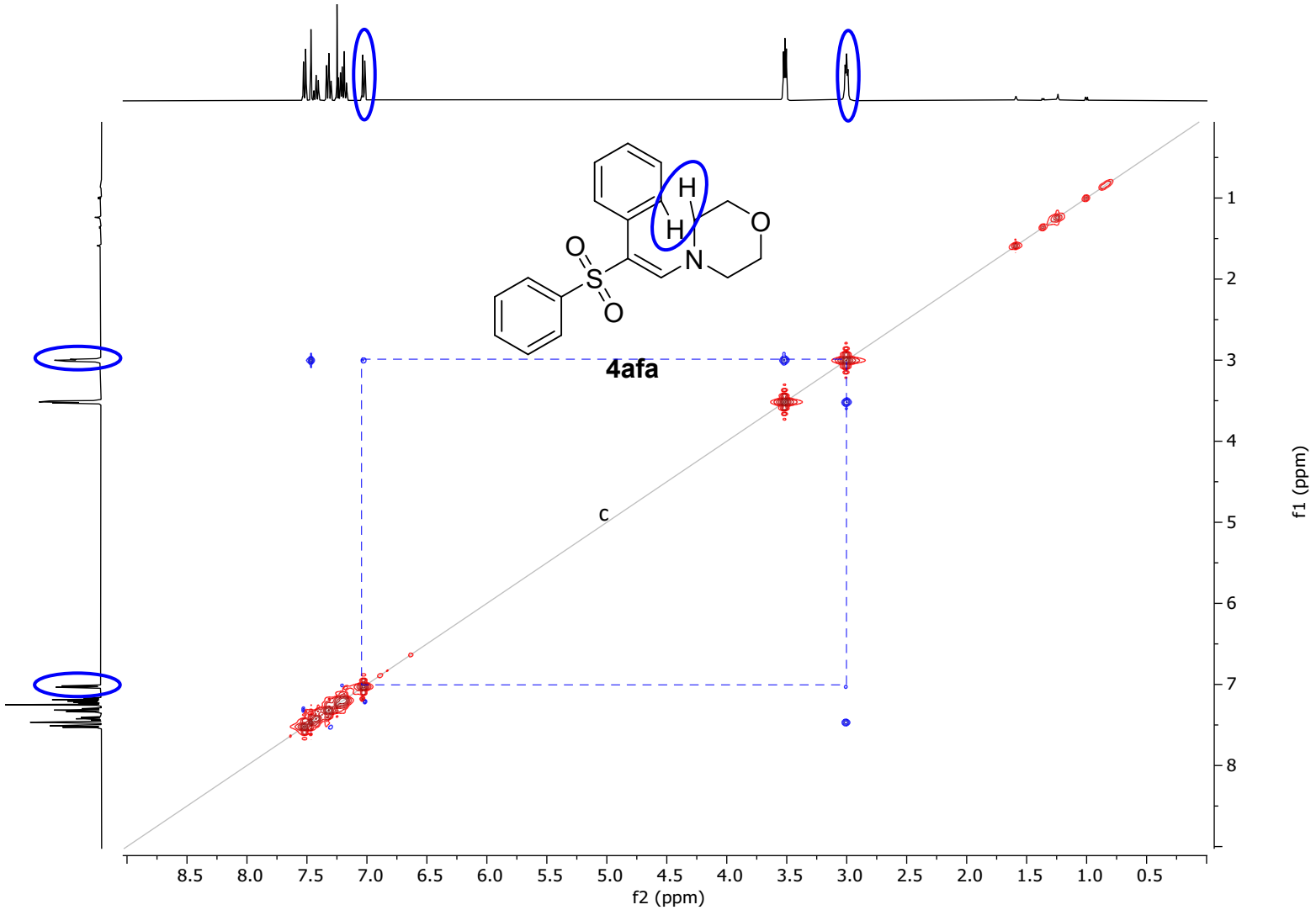
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4aea**.



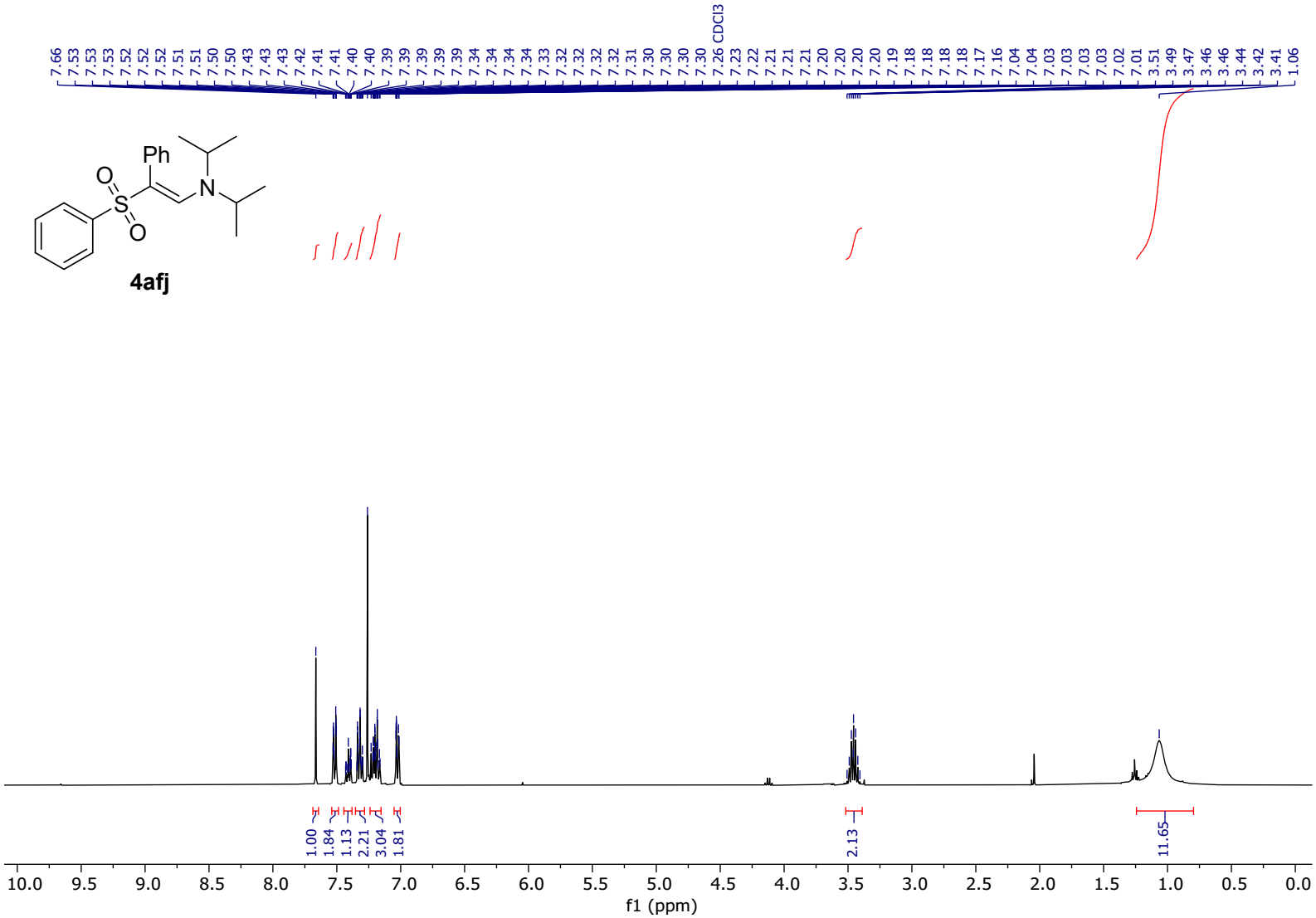
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4afa**.



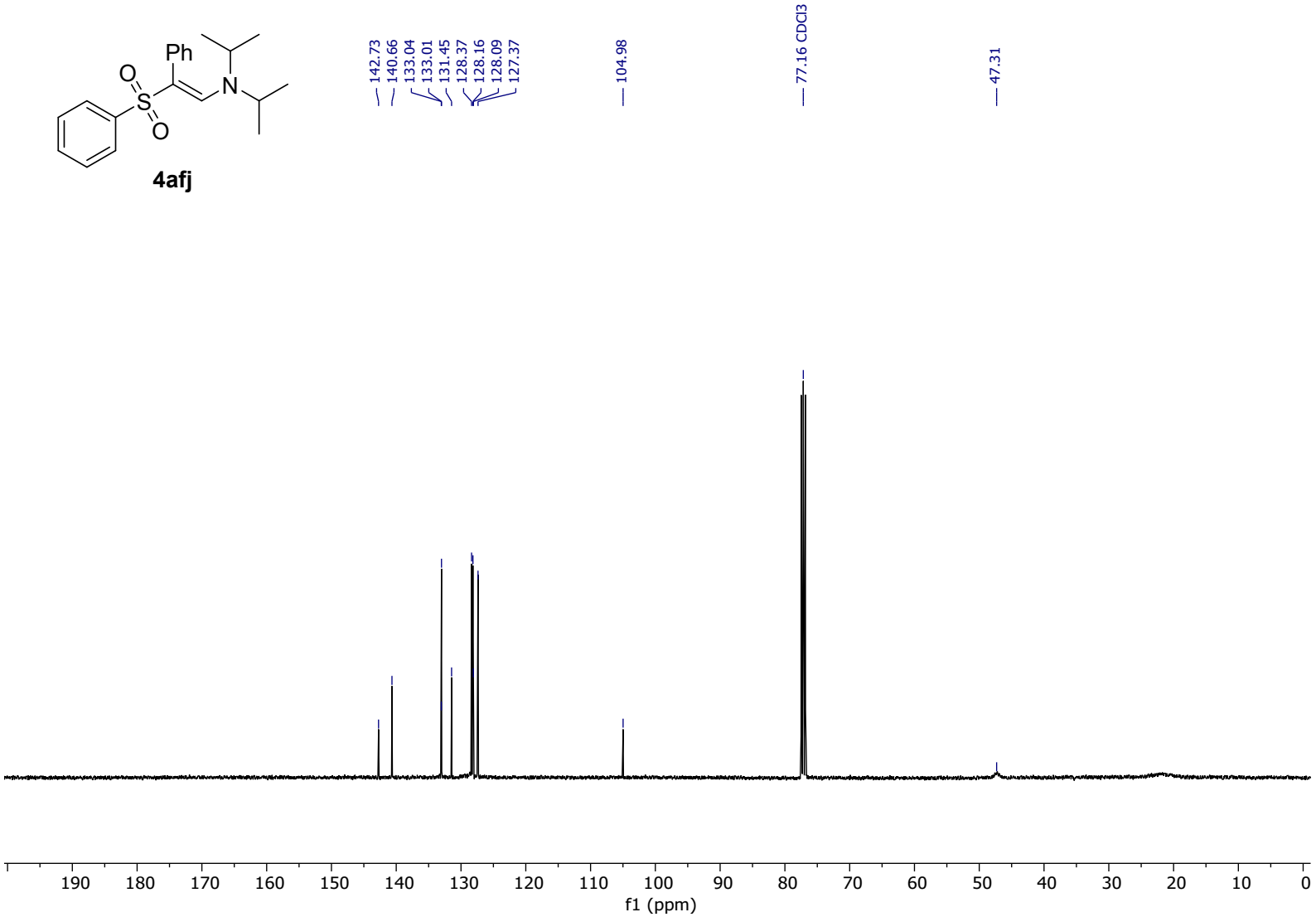
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4afa**.



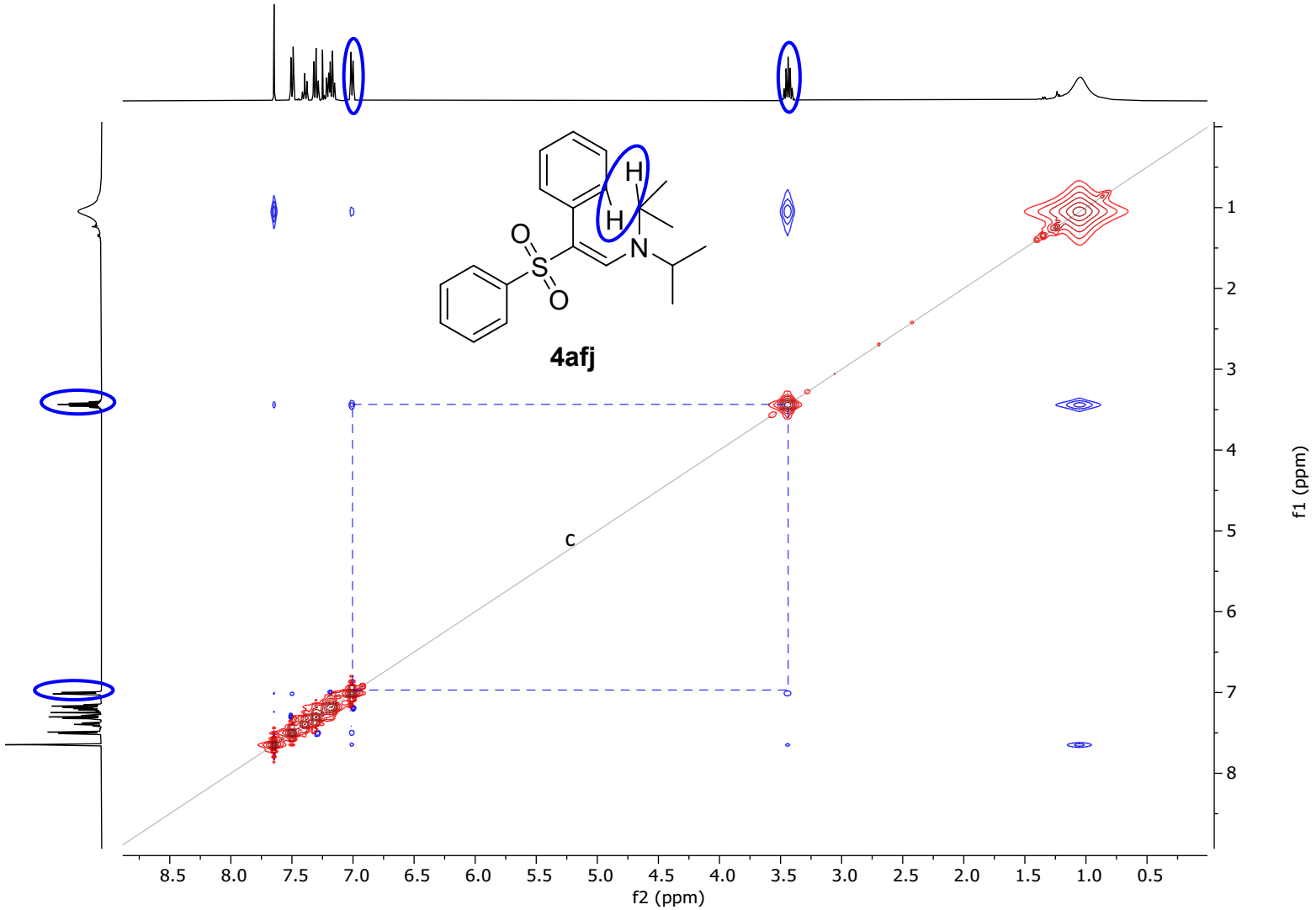
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4afa**.



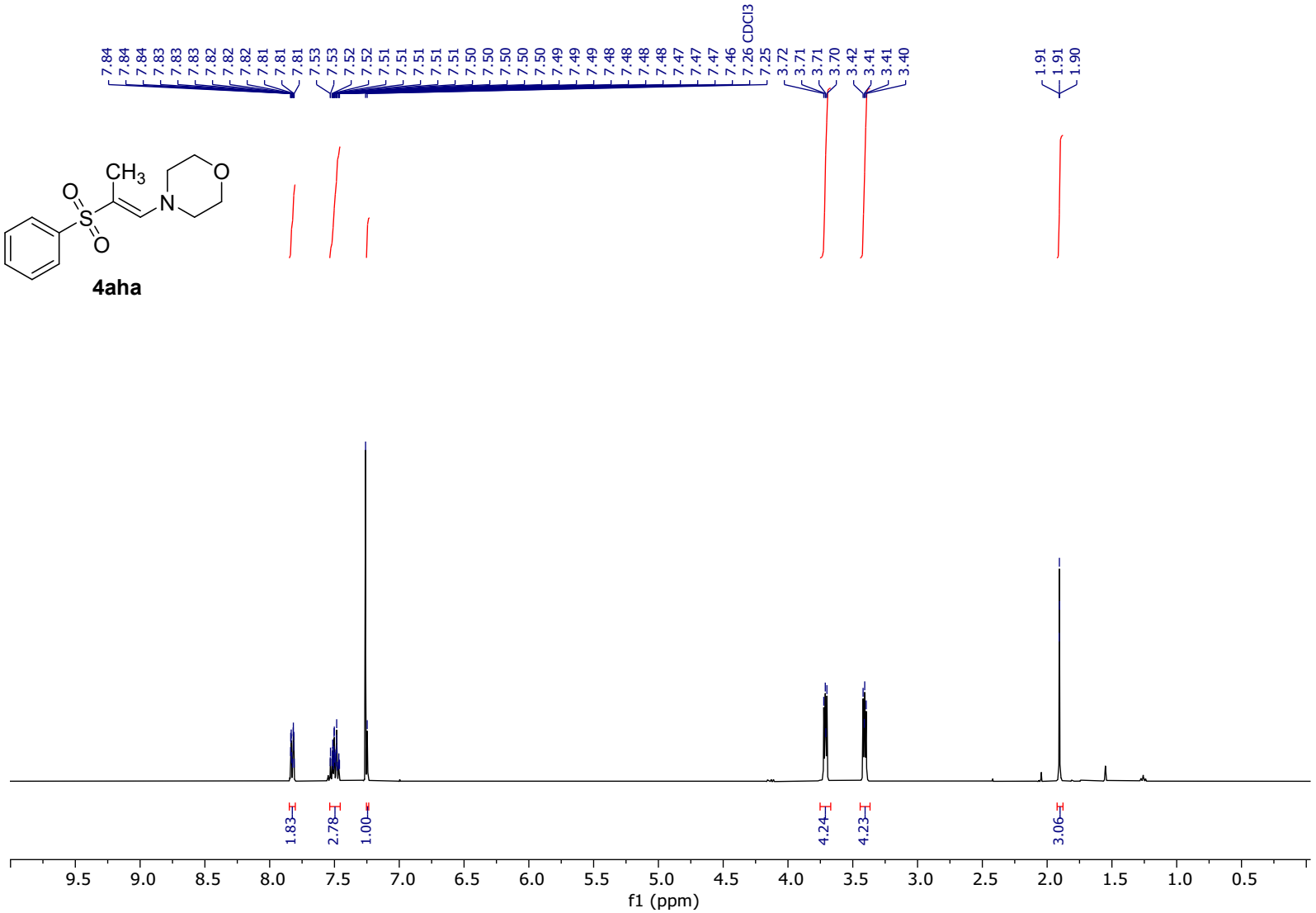
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4afj**.



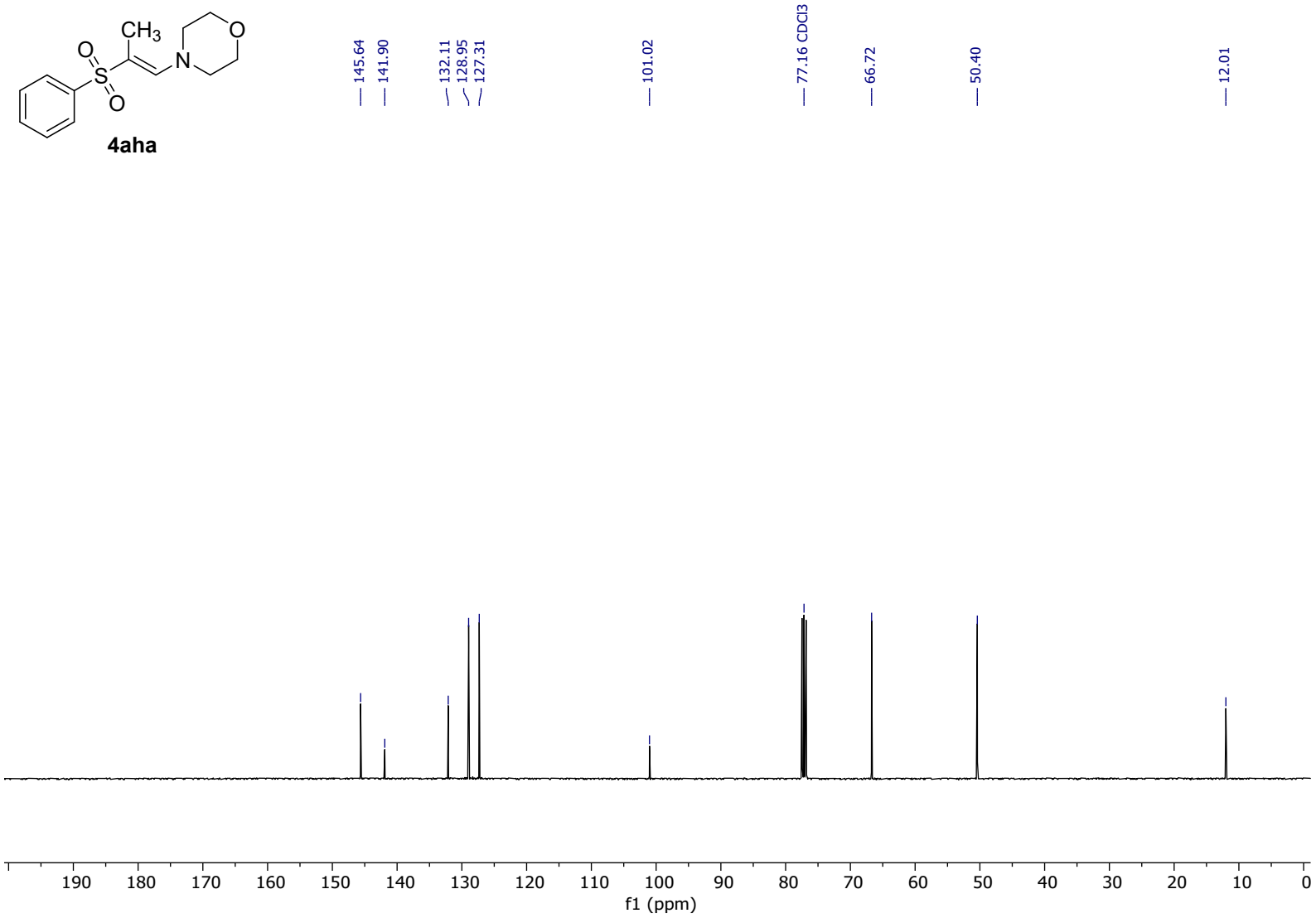
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4afj**.



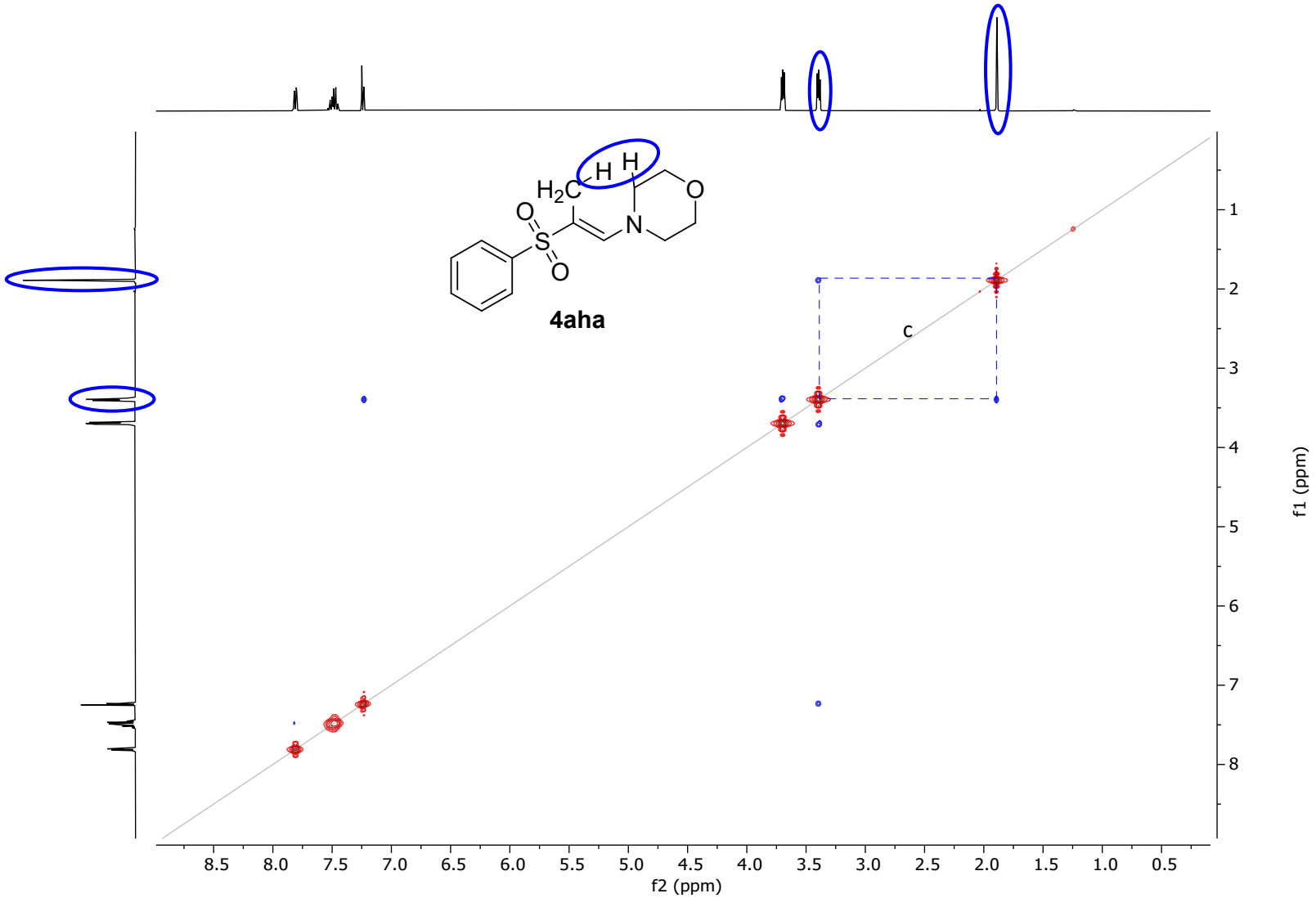
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4afj**.



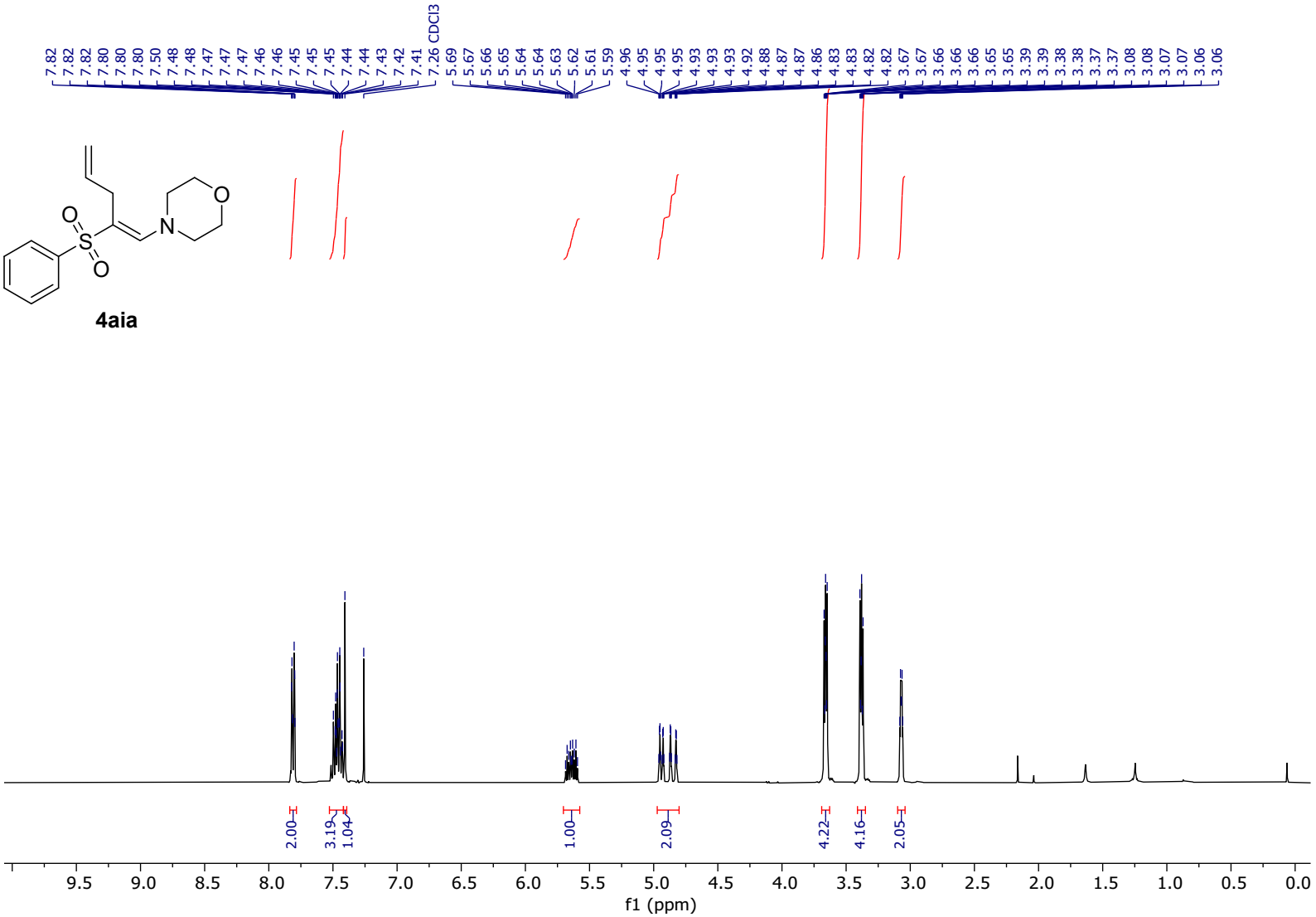
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aha**.



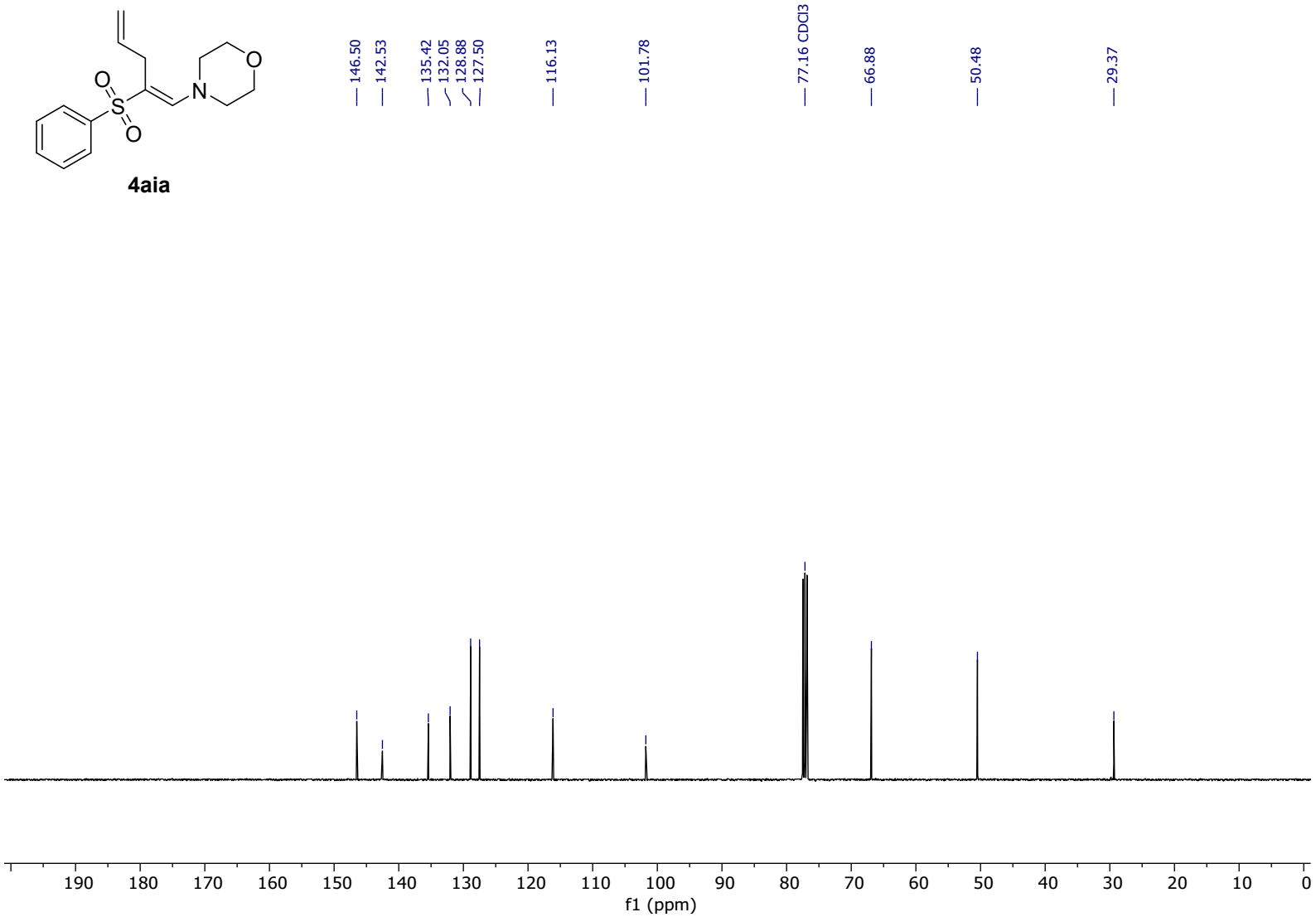
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aha**.



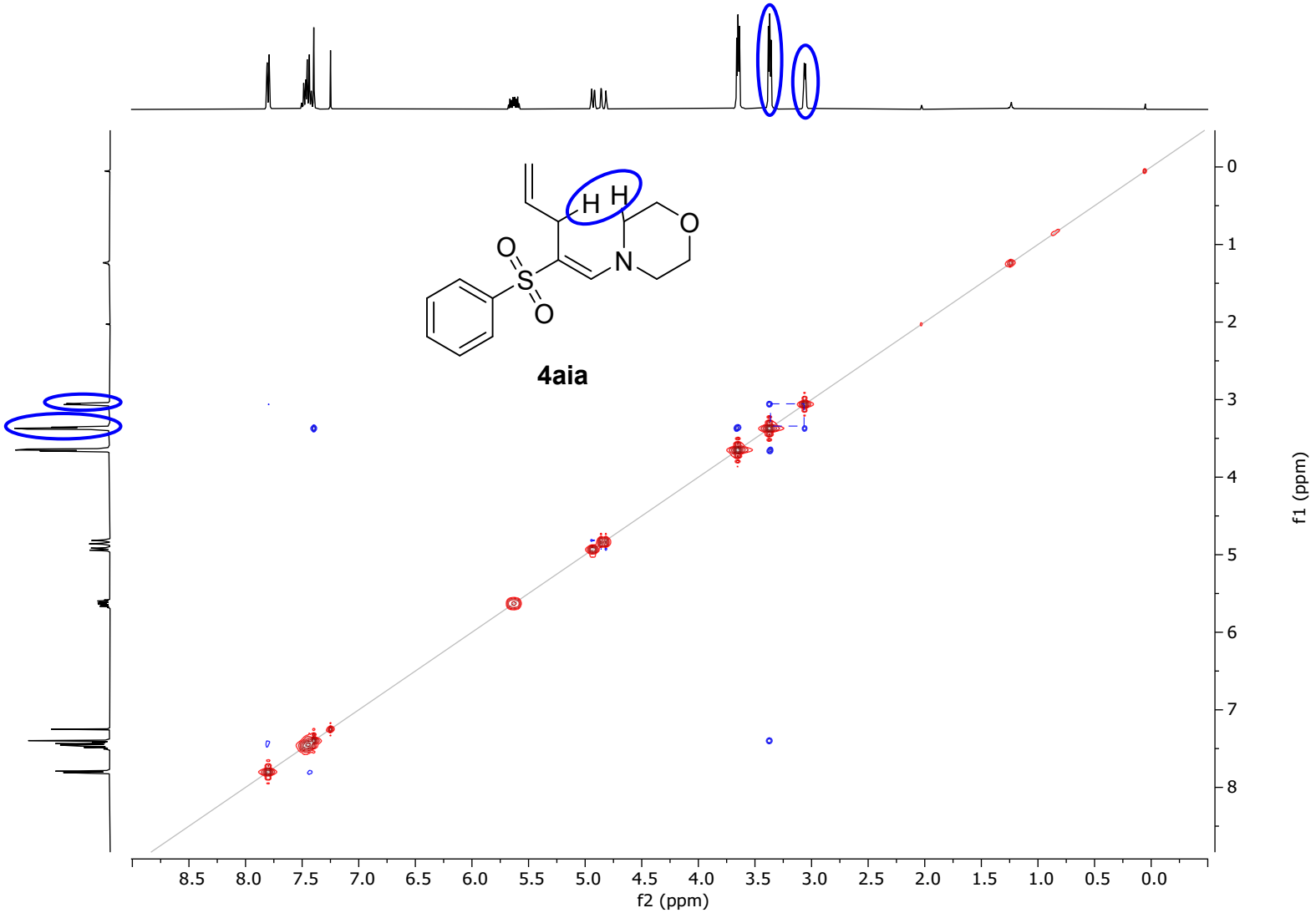
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4aha**.



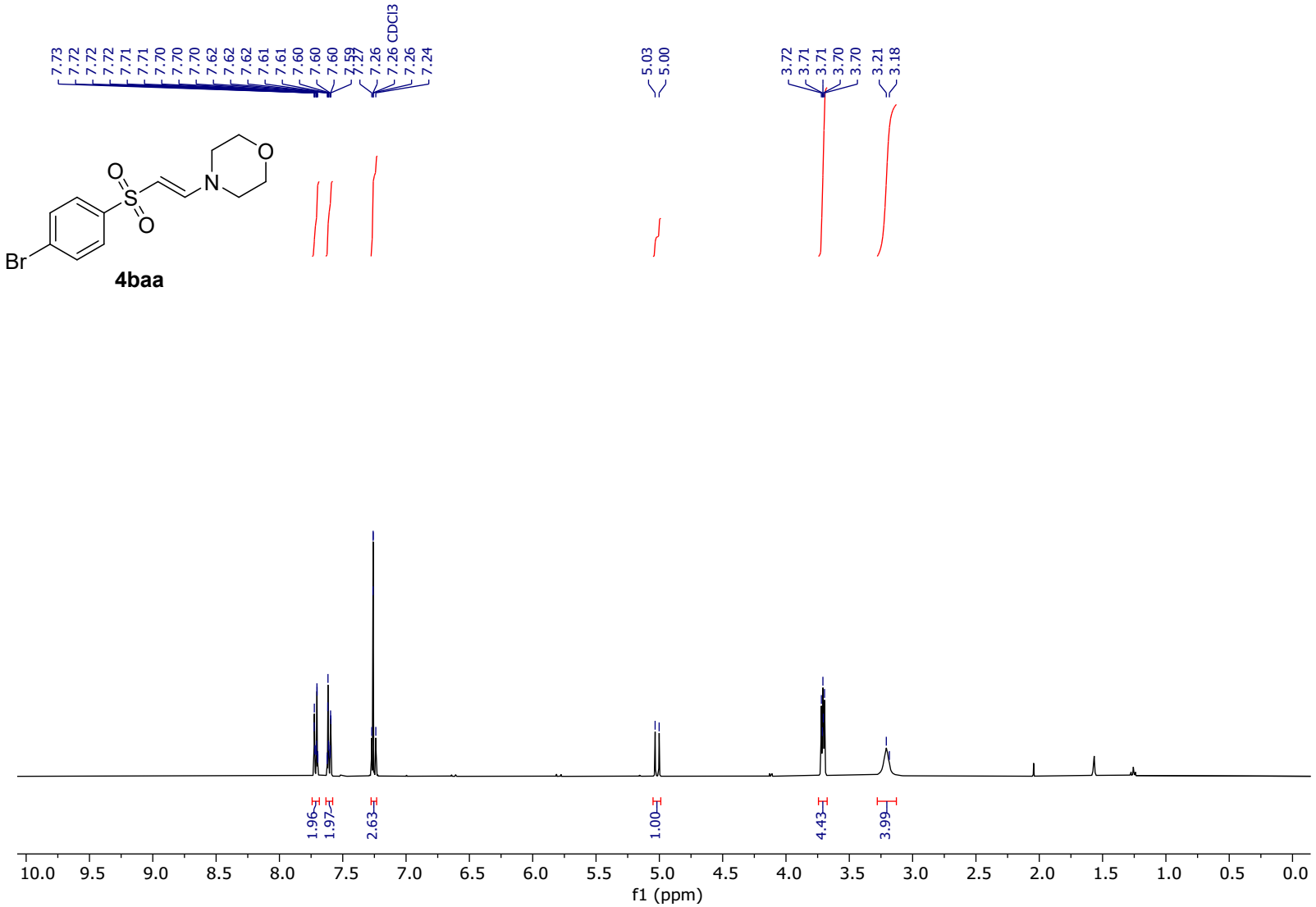
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aia**.



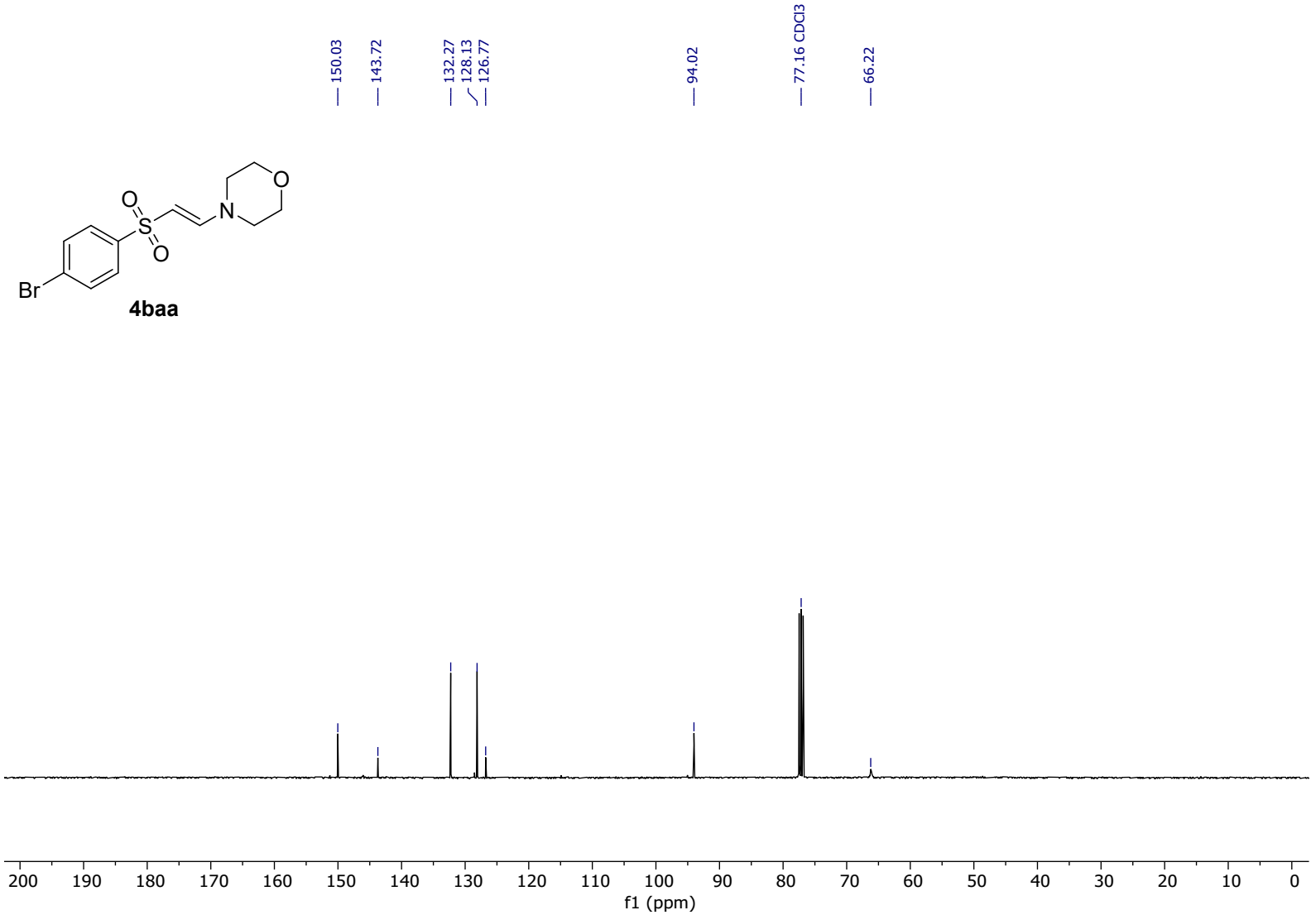
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4aia**.



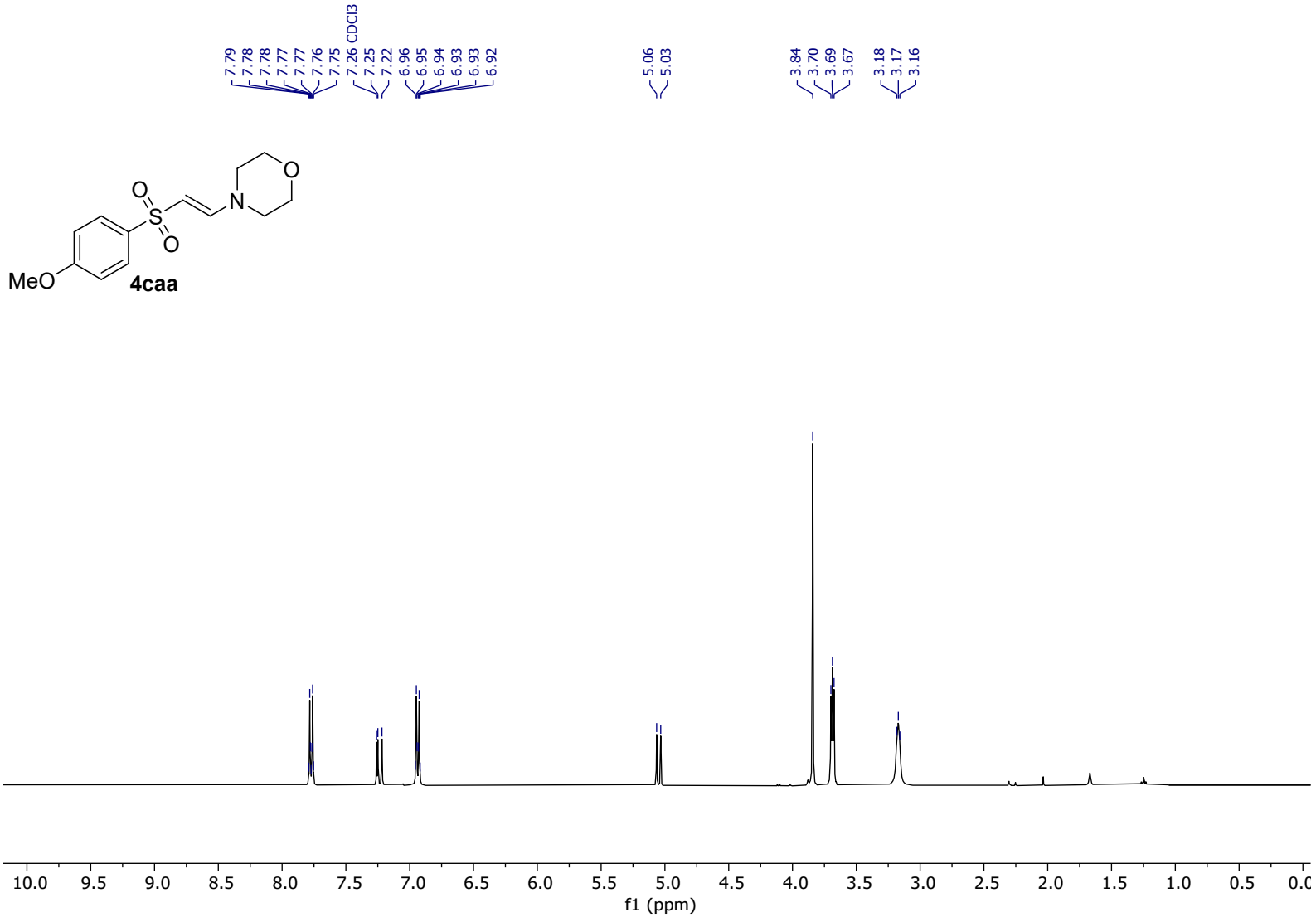
2D ^{1}H–^{1}H NOESY (400 MHz, $CDCl_3$) spectrum of compound **4aia**.



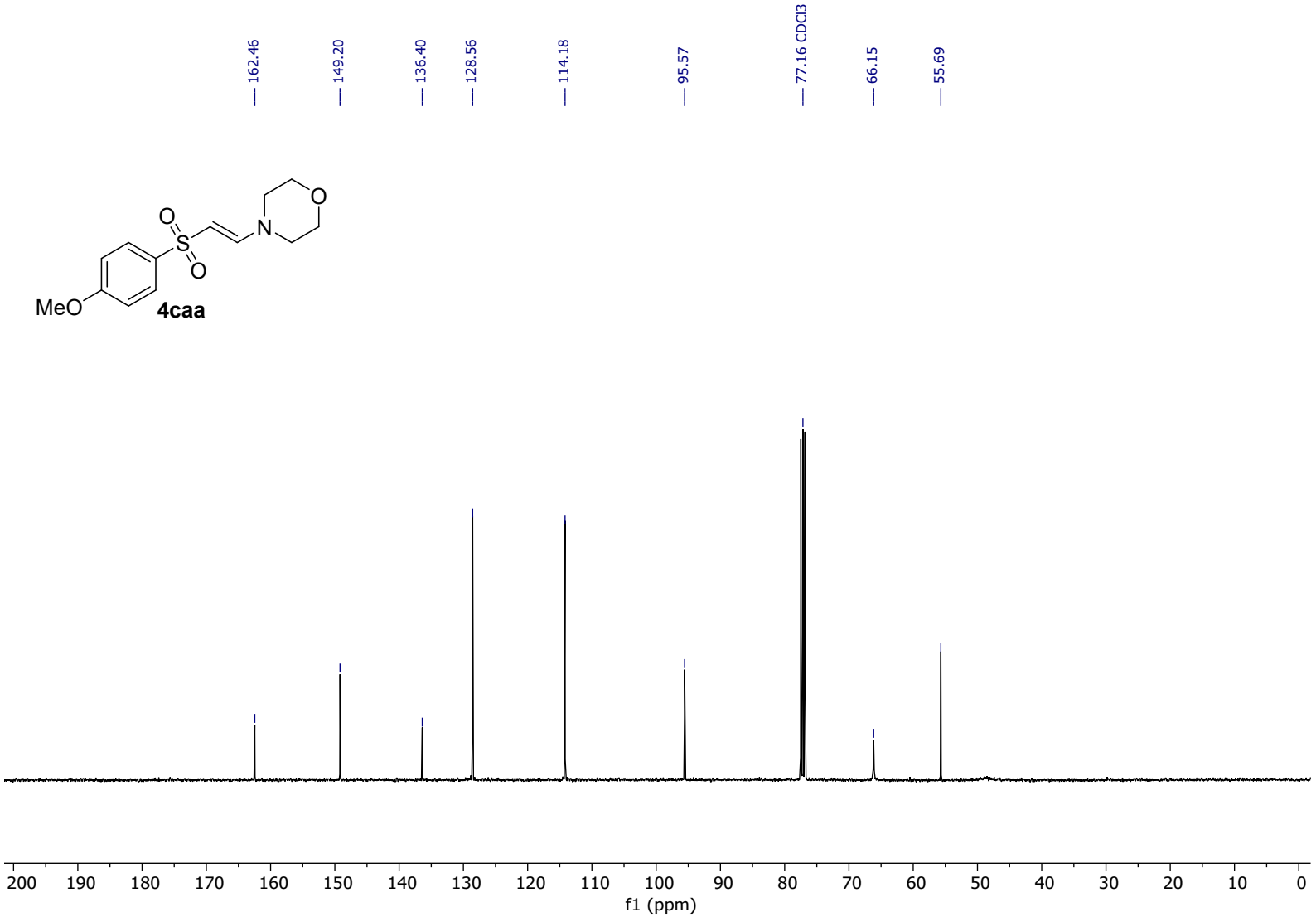
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4baa**.



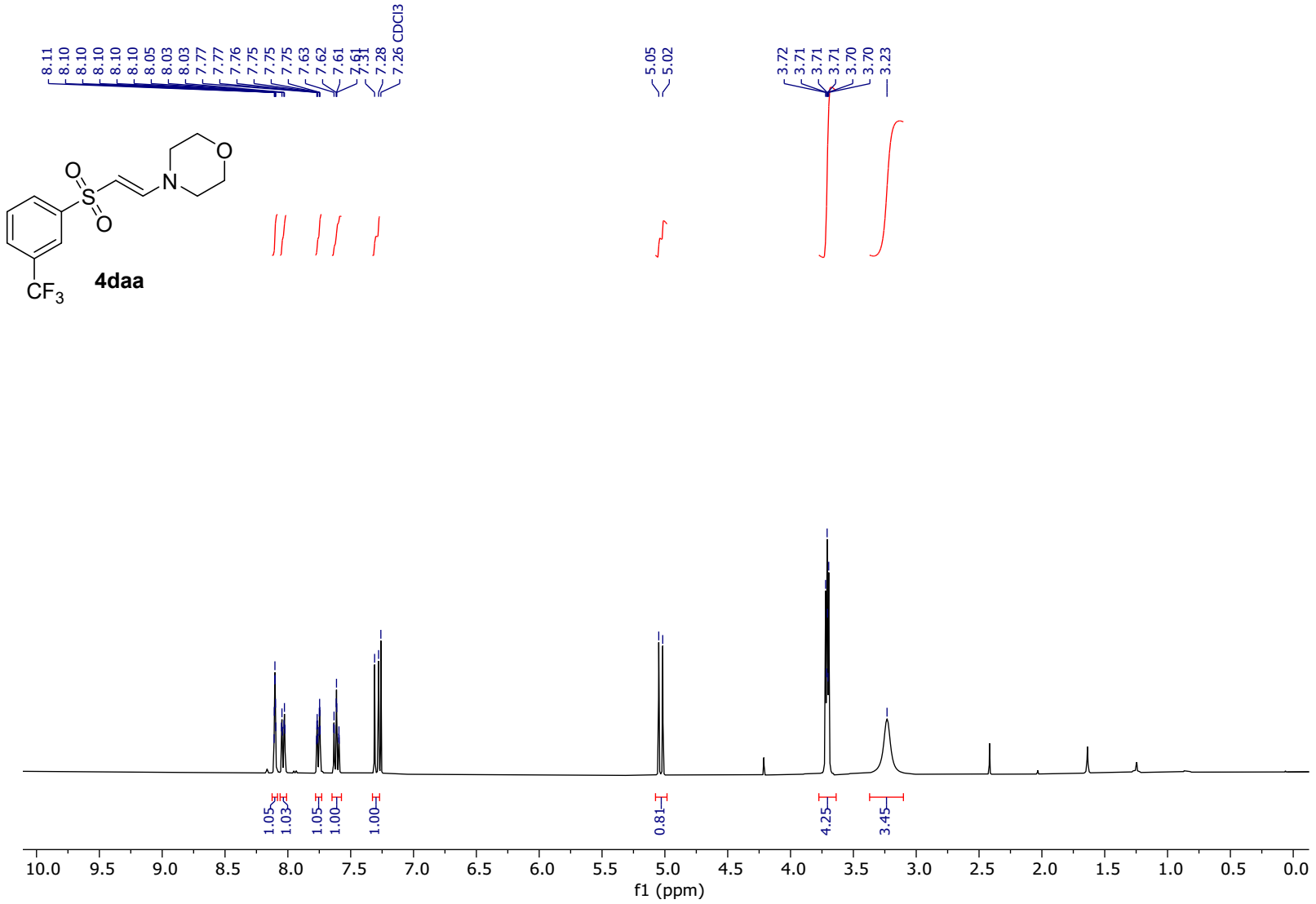
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4baa**.



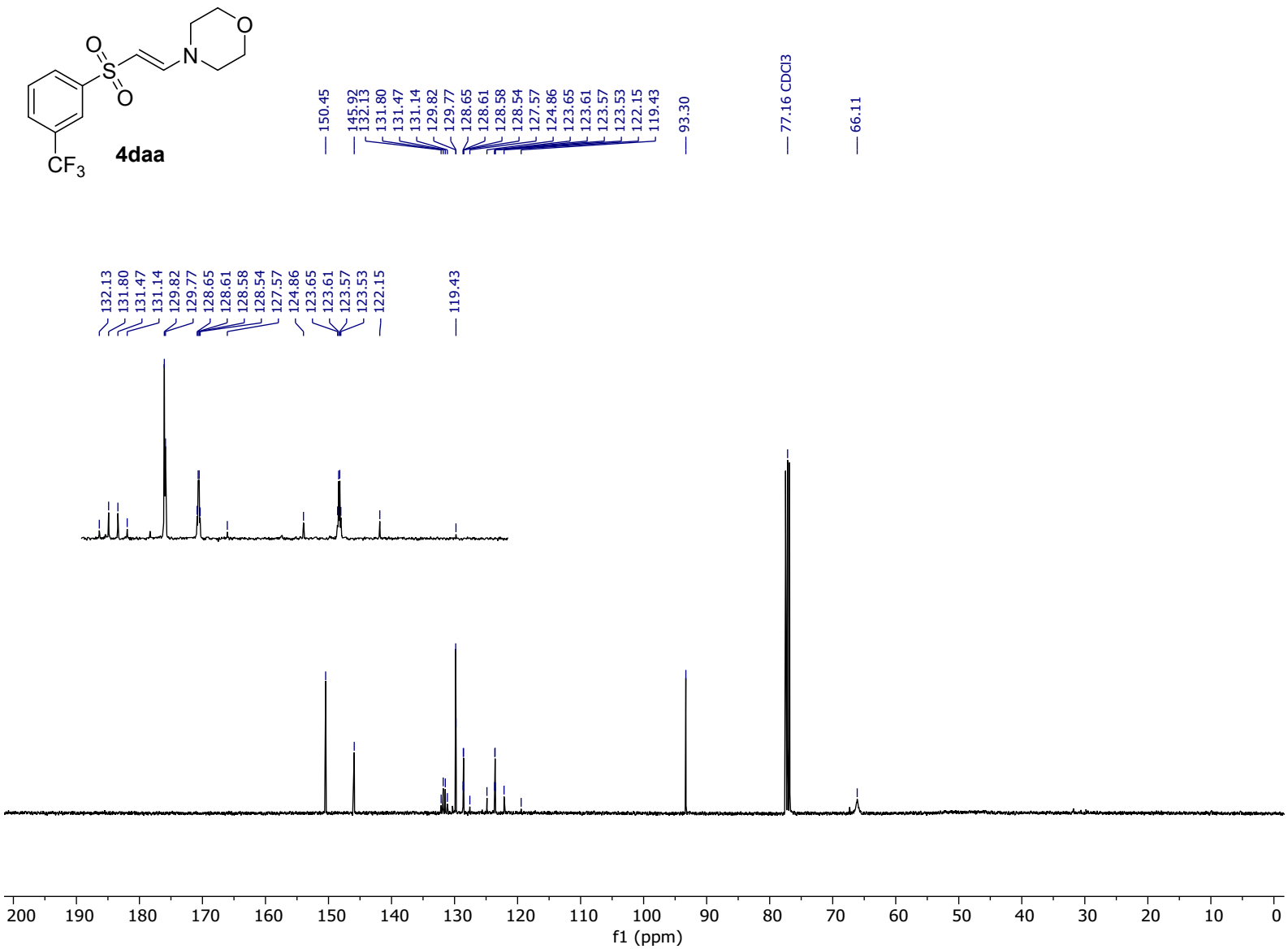
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4caa**.



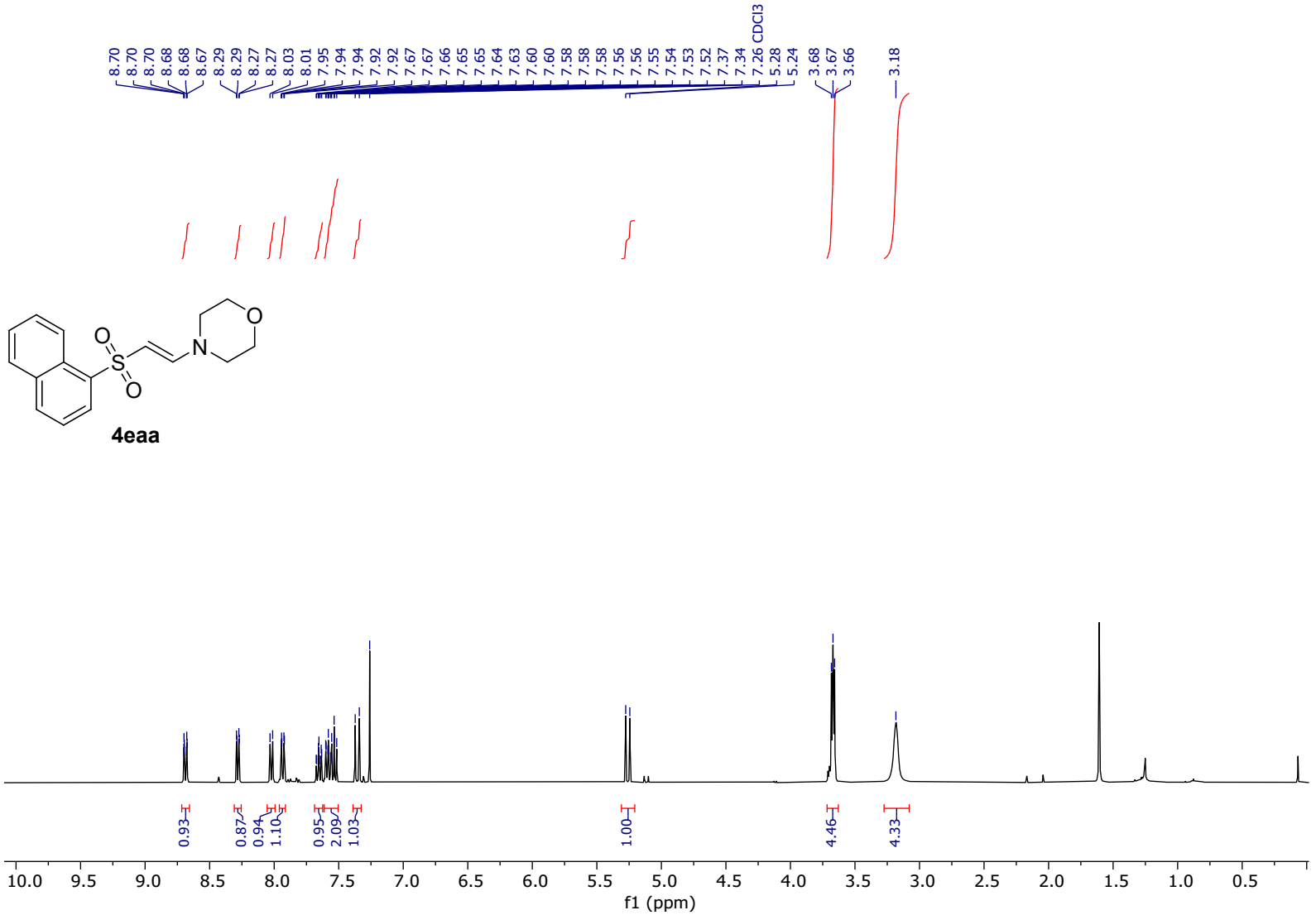
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4caa**.



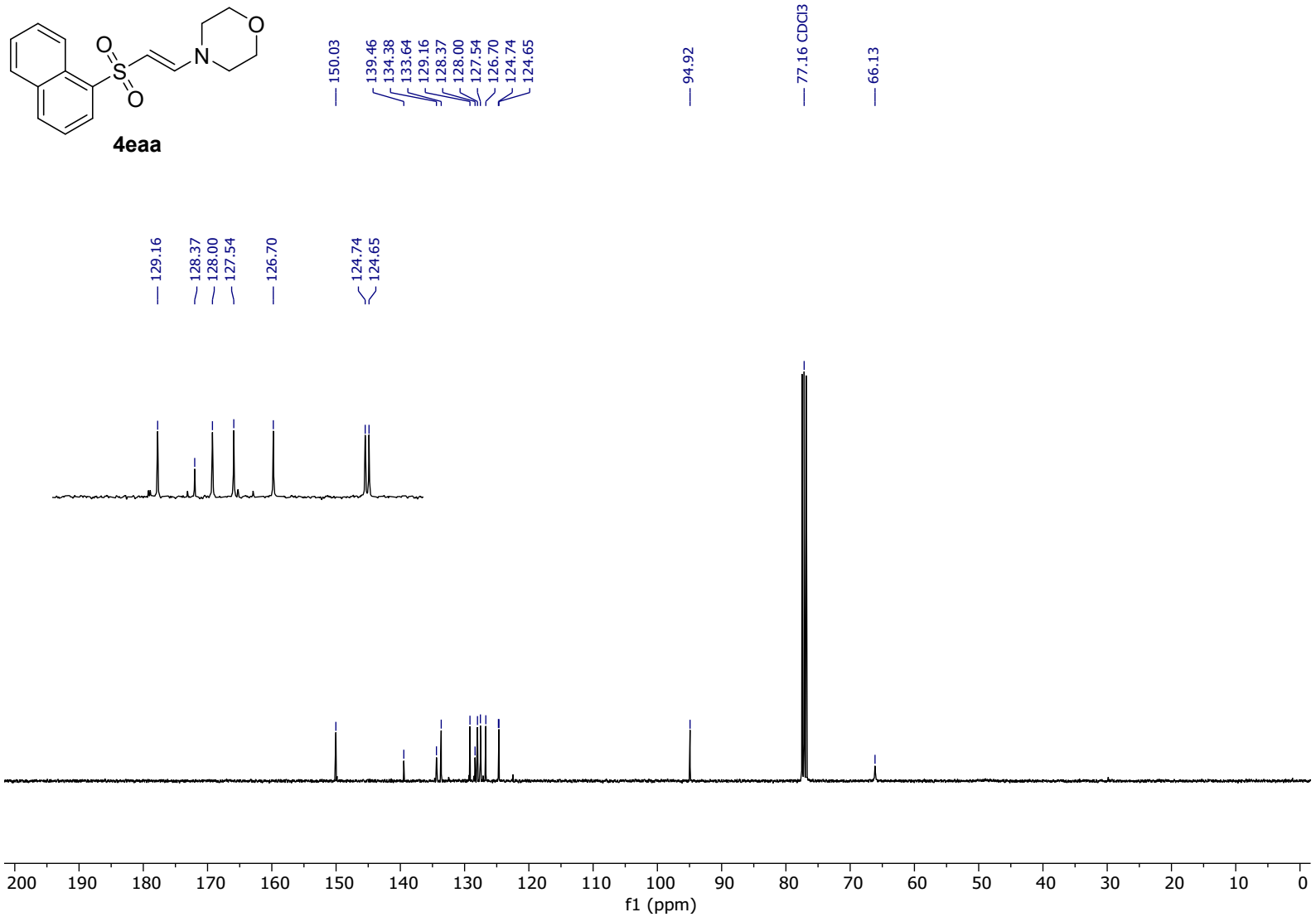
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4daa**.



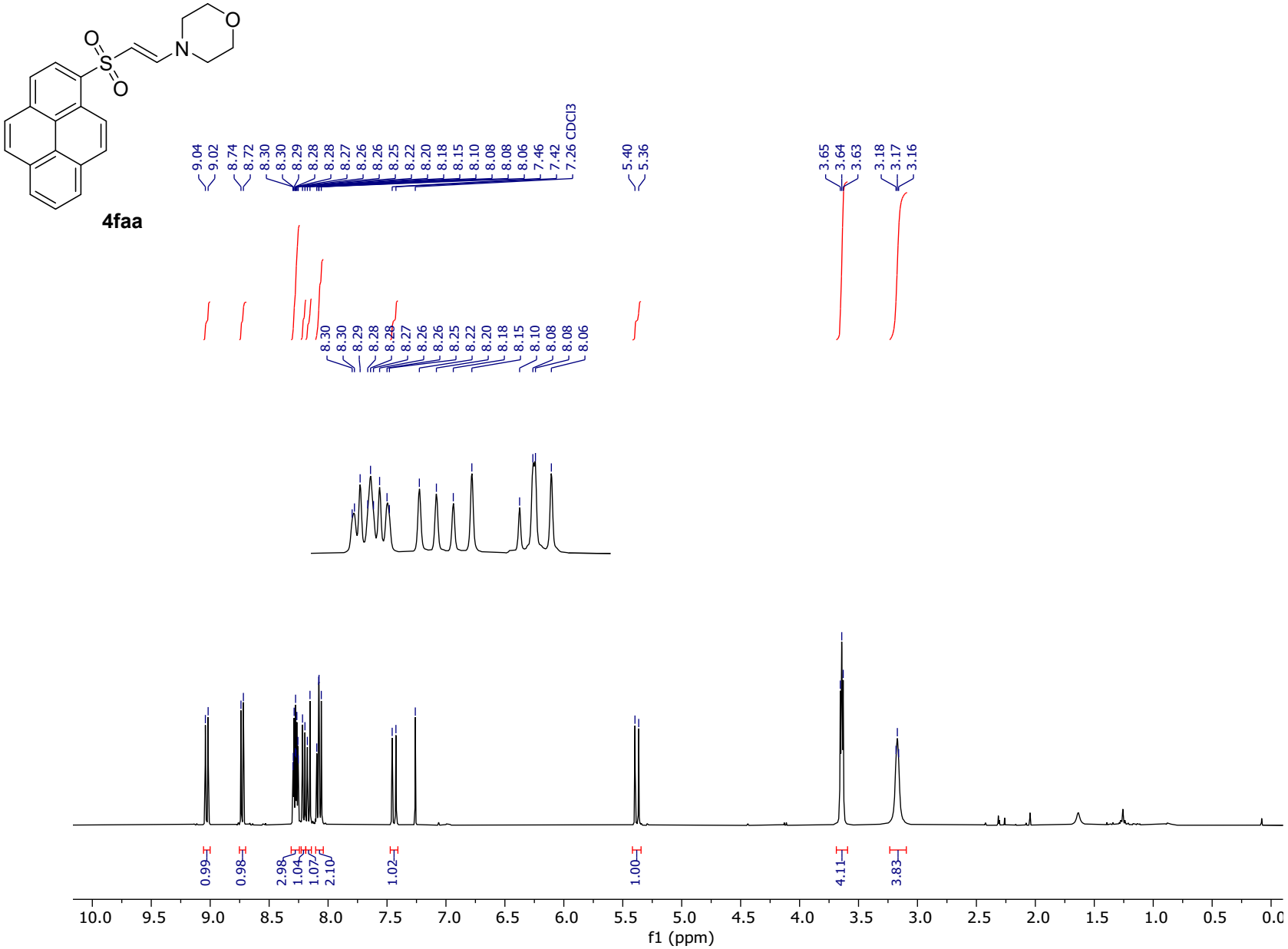
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4daa**.



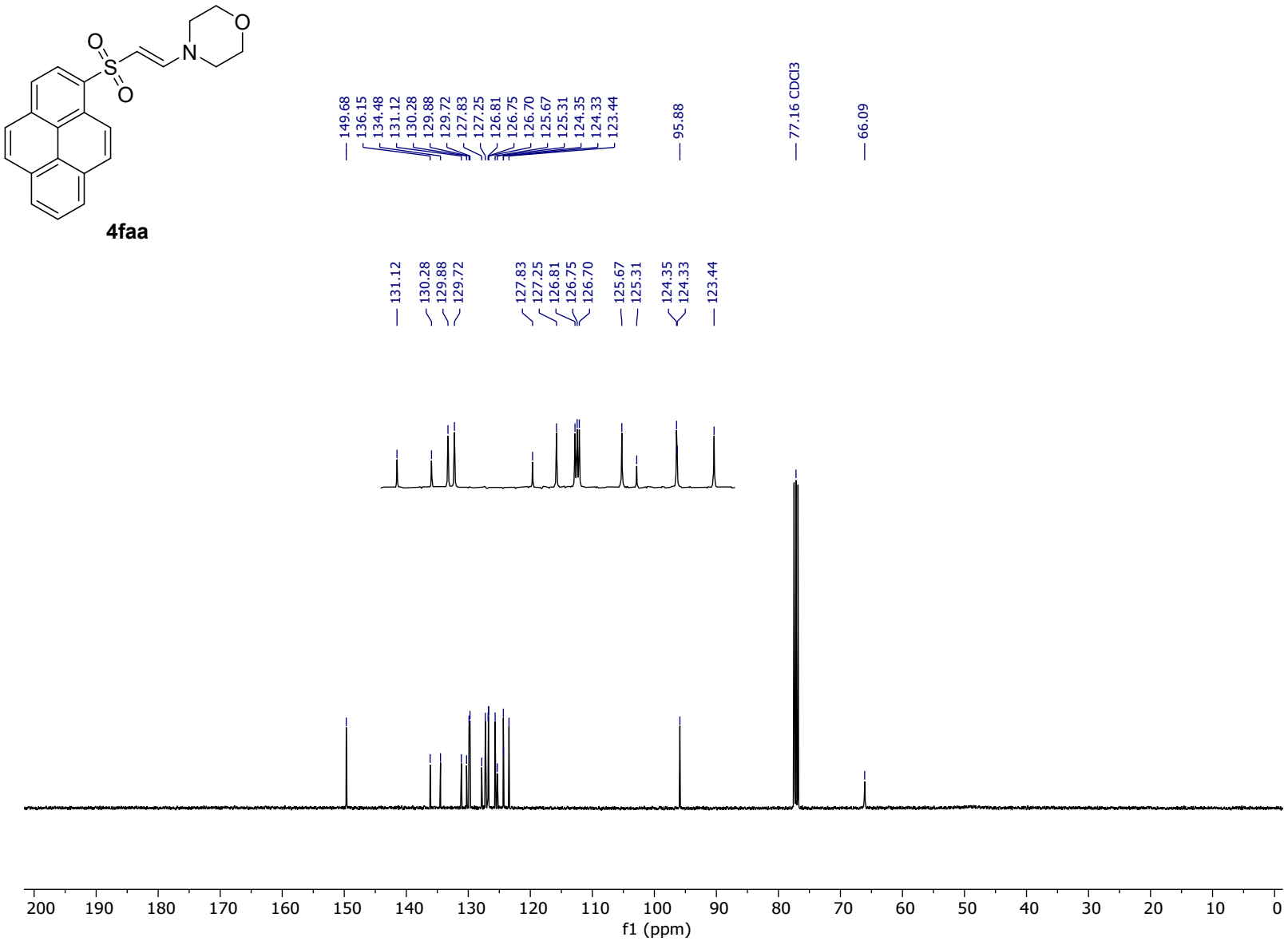
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4eaa**.



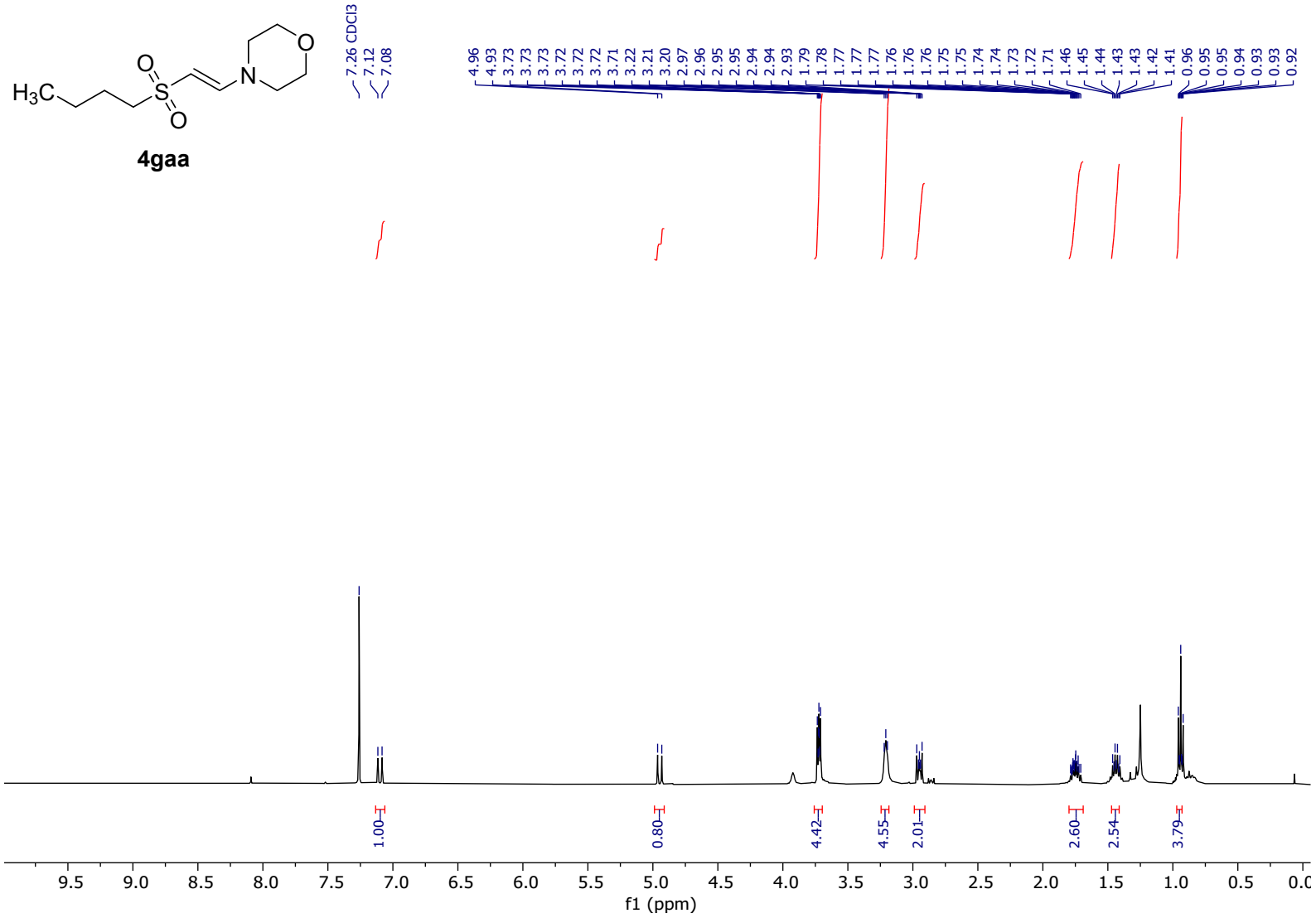
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4eaa**.



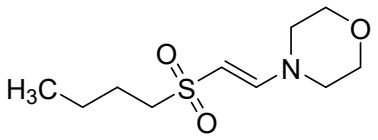
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4faa**.



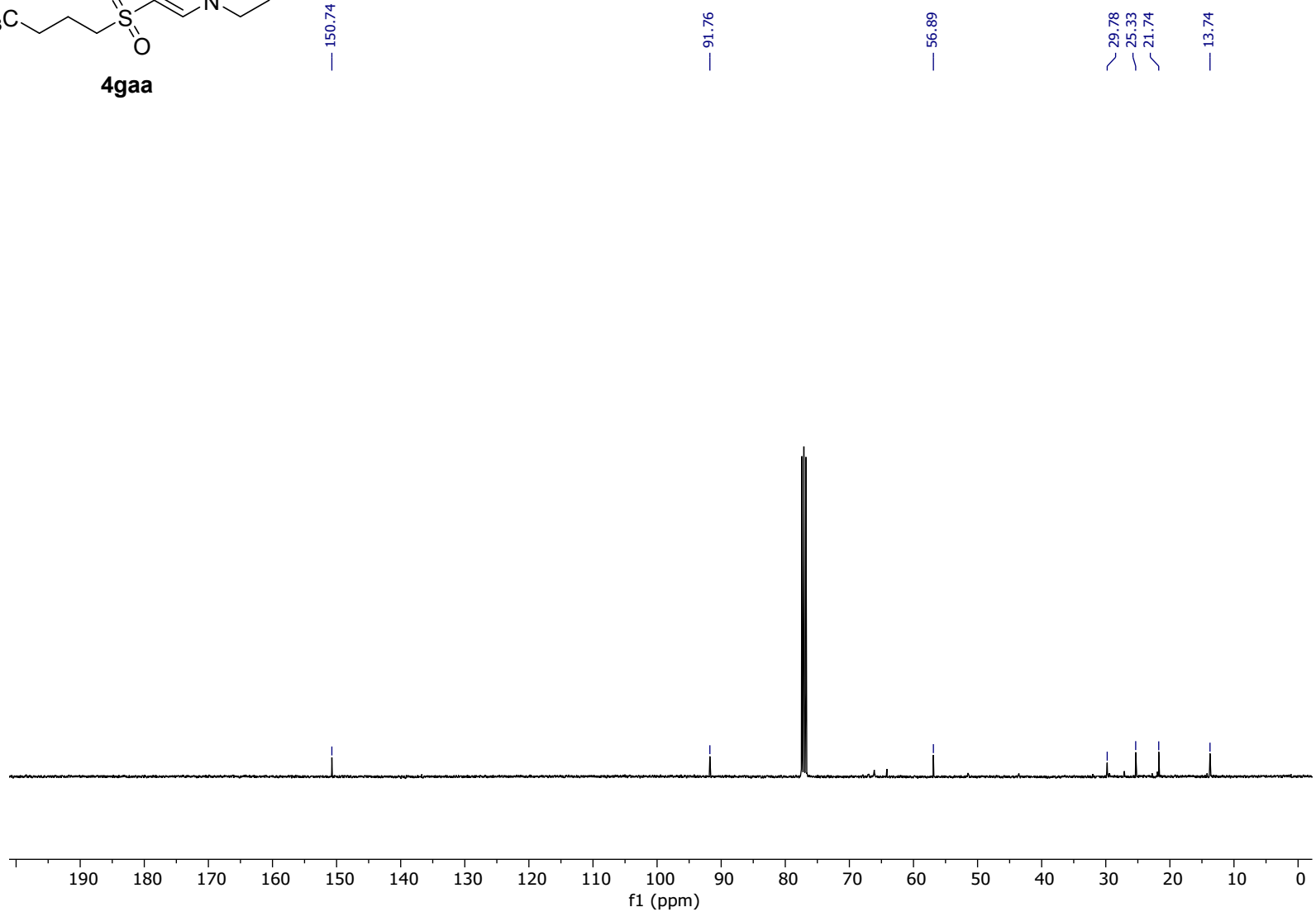
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4faa**.



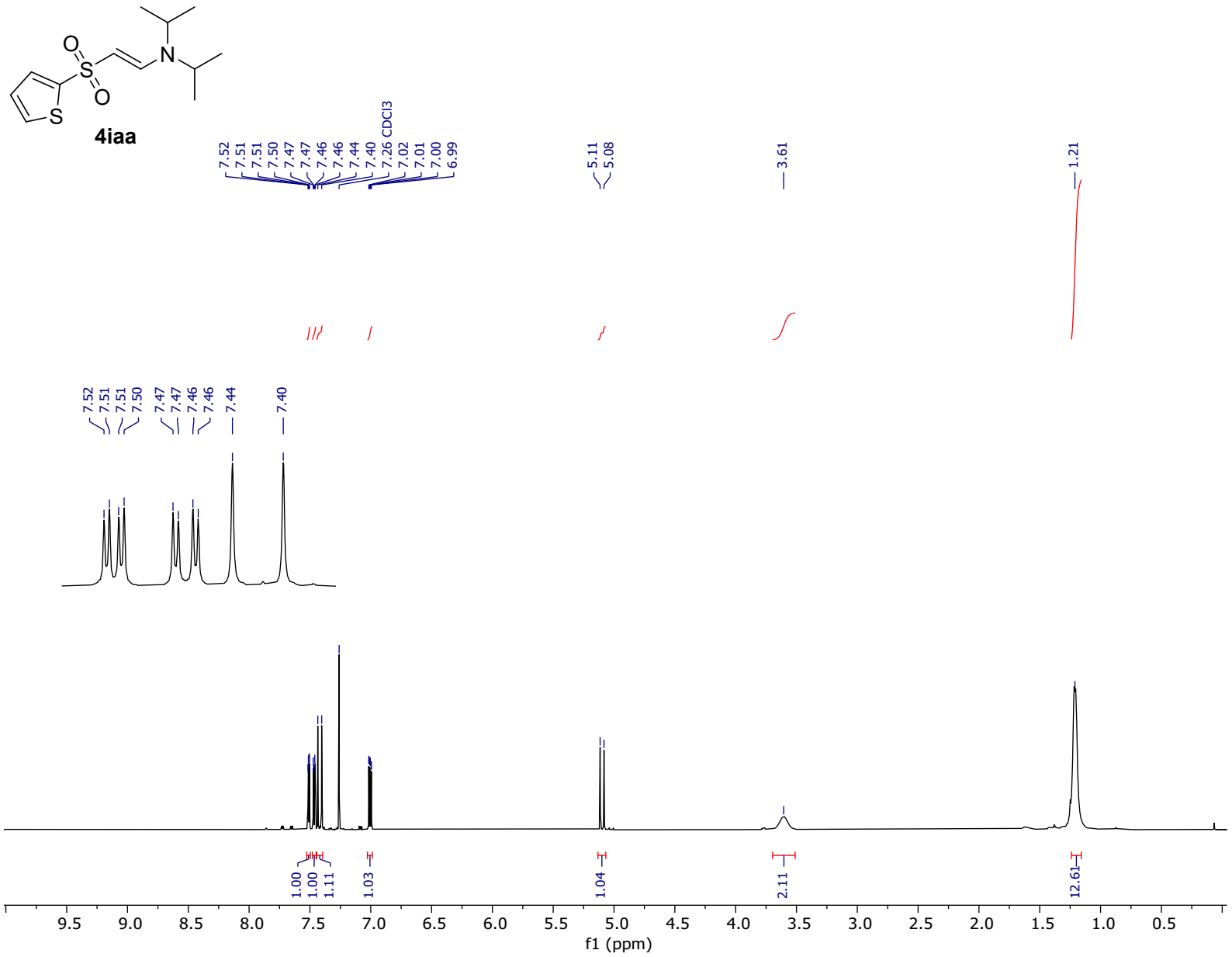
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4gaa**.



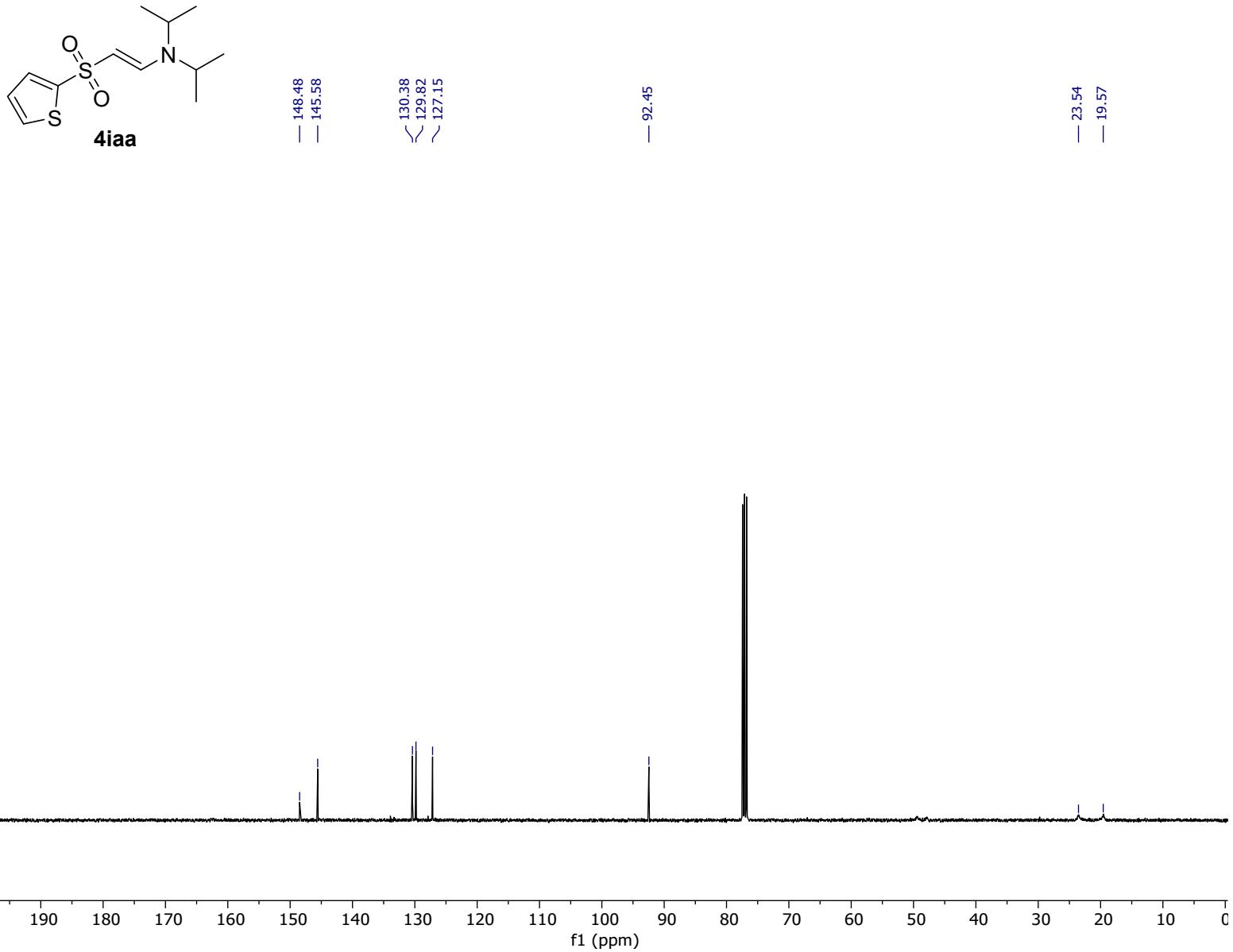
4gaa



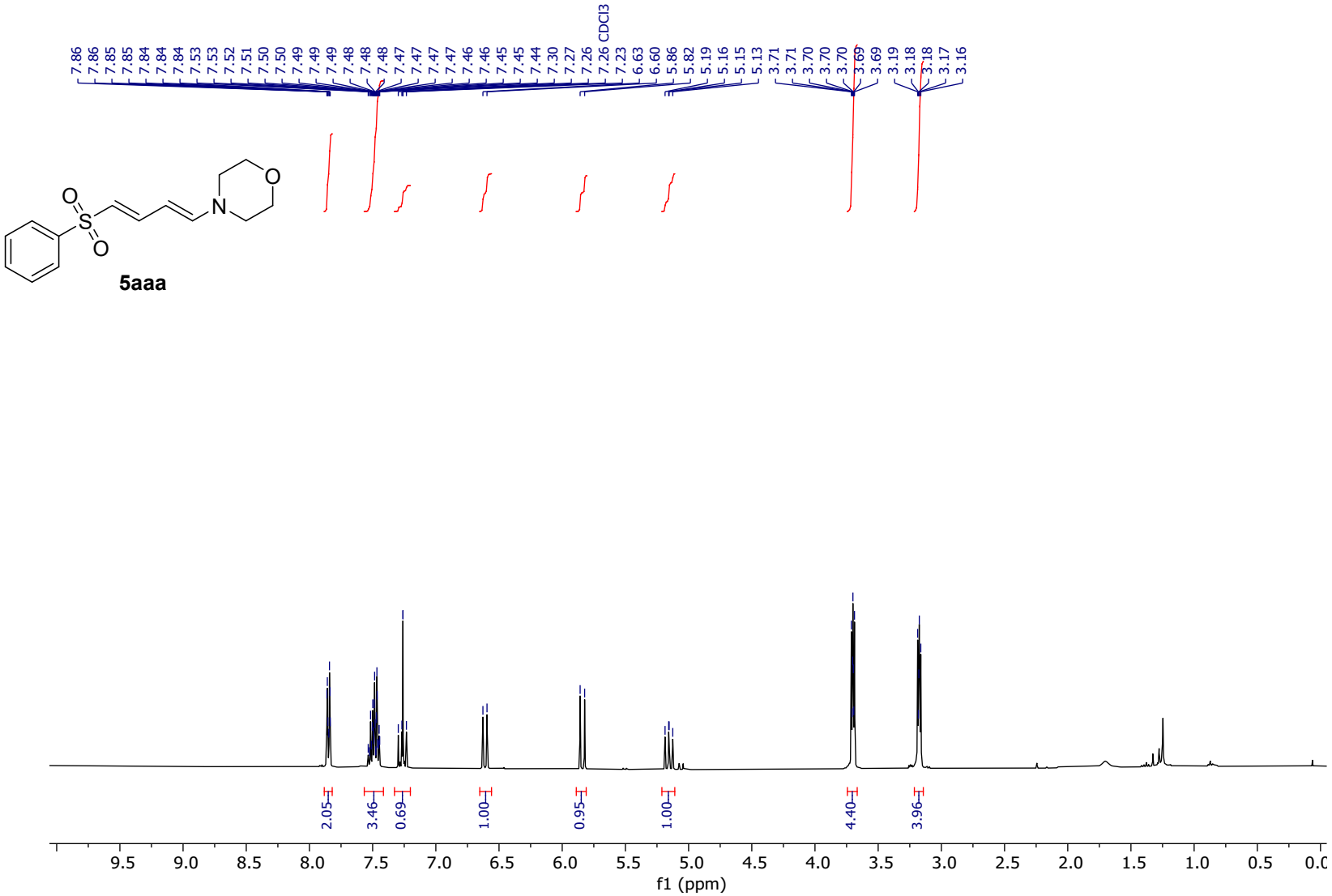
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4gaa**.



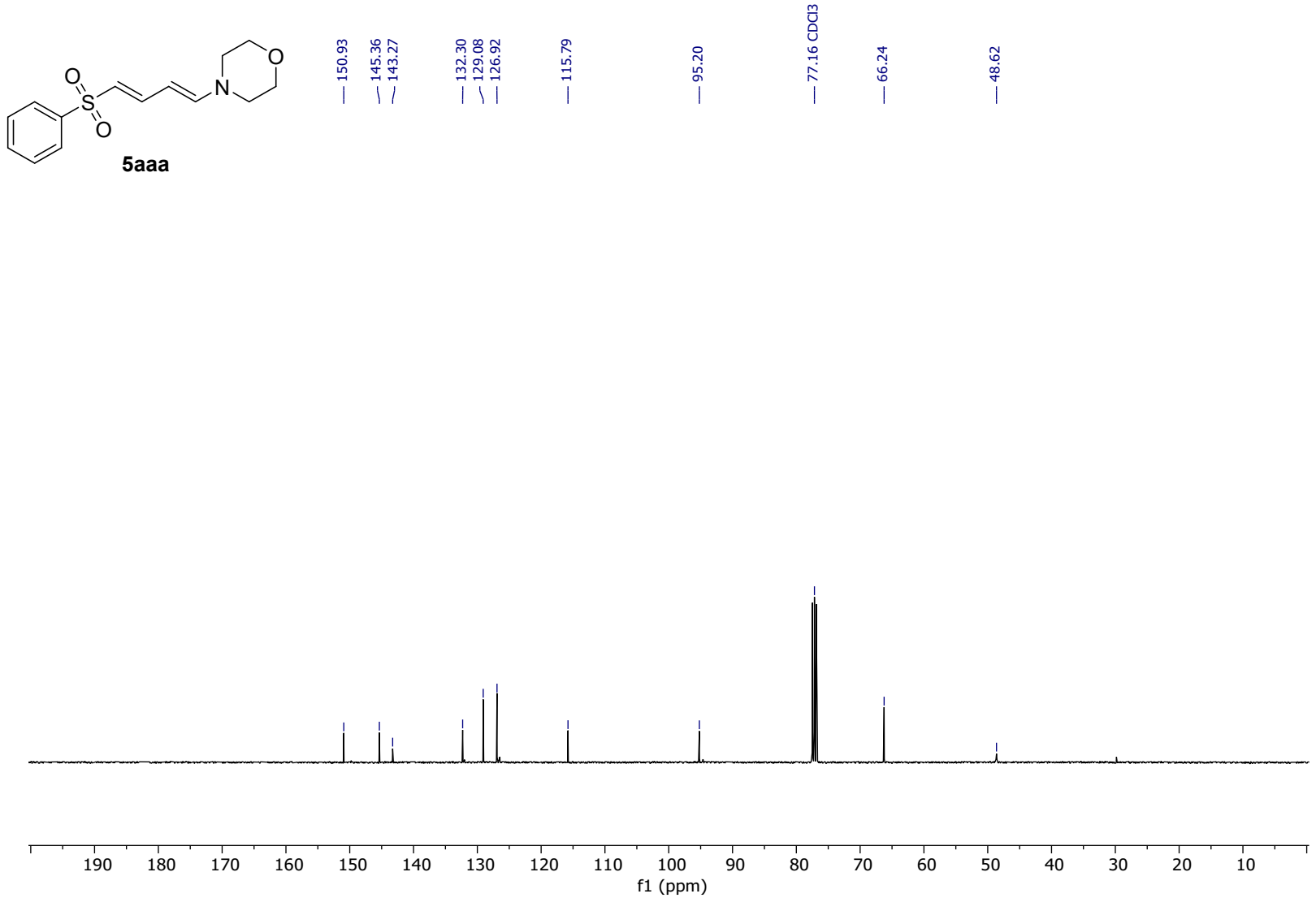
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4iaa**.



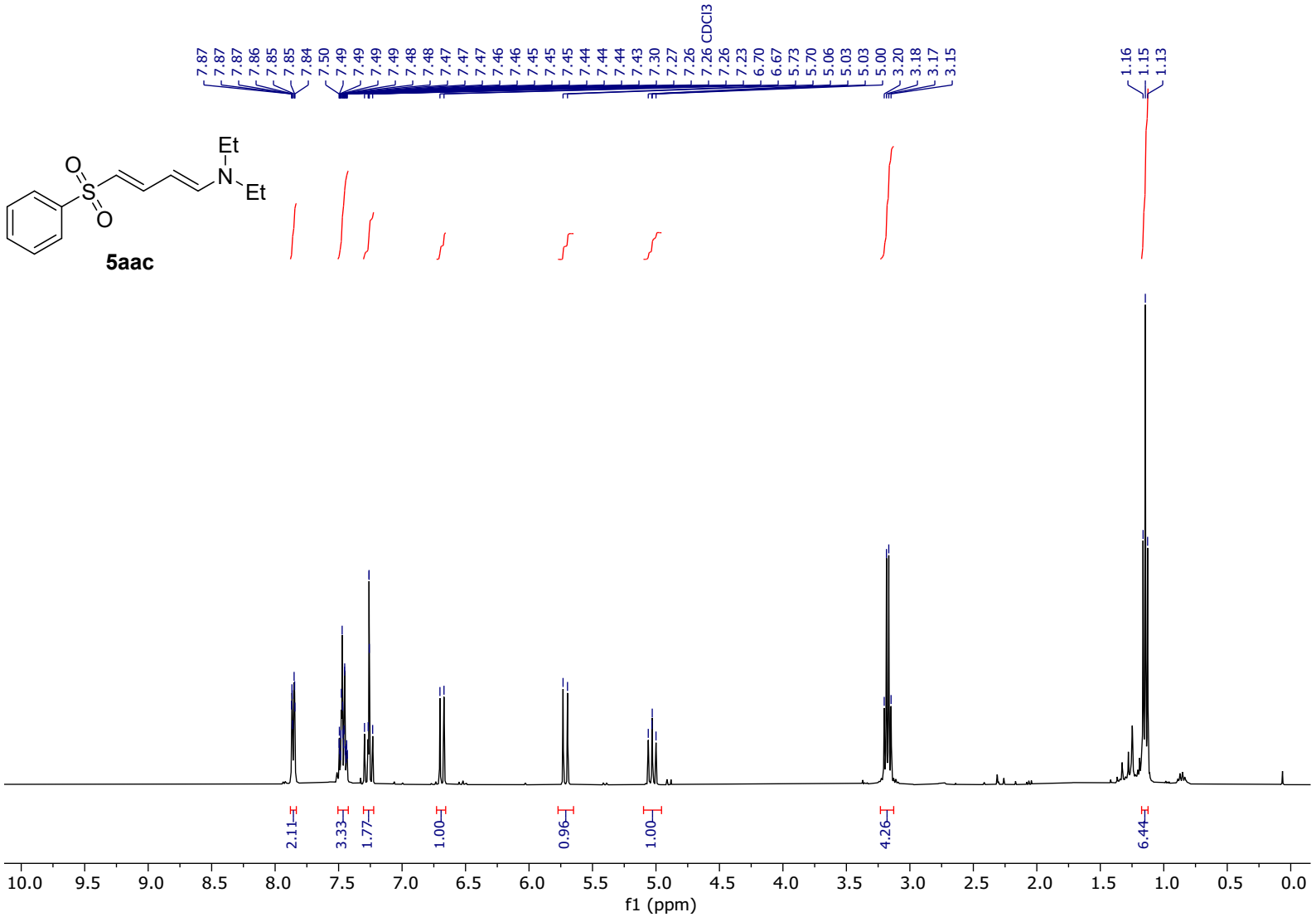
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4iaa**.



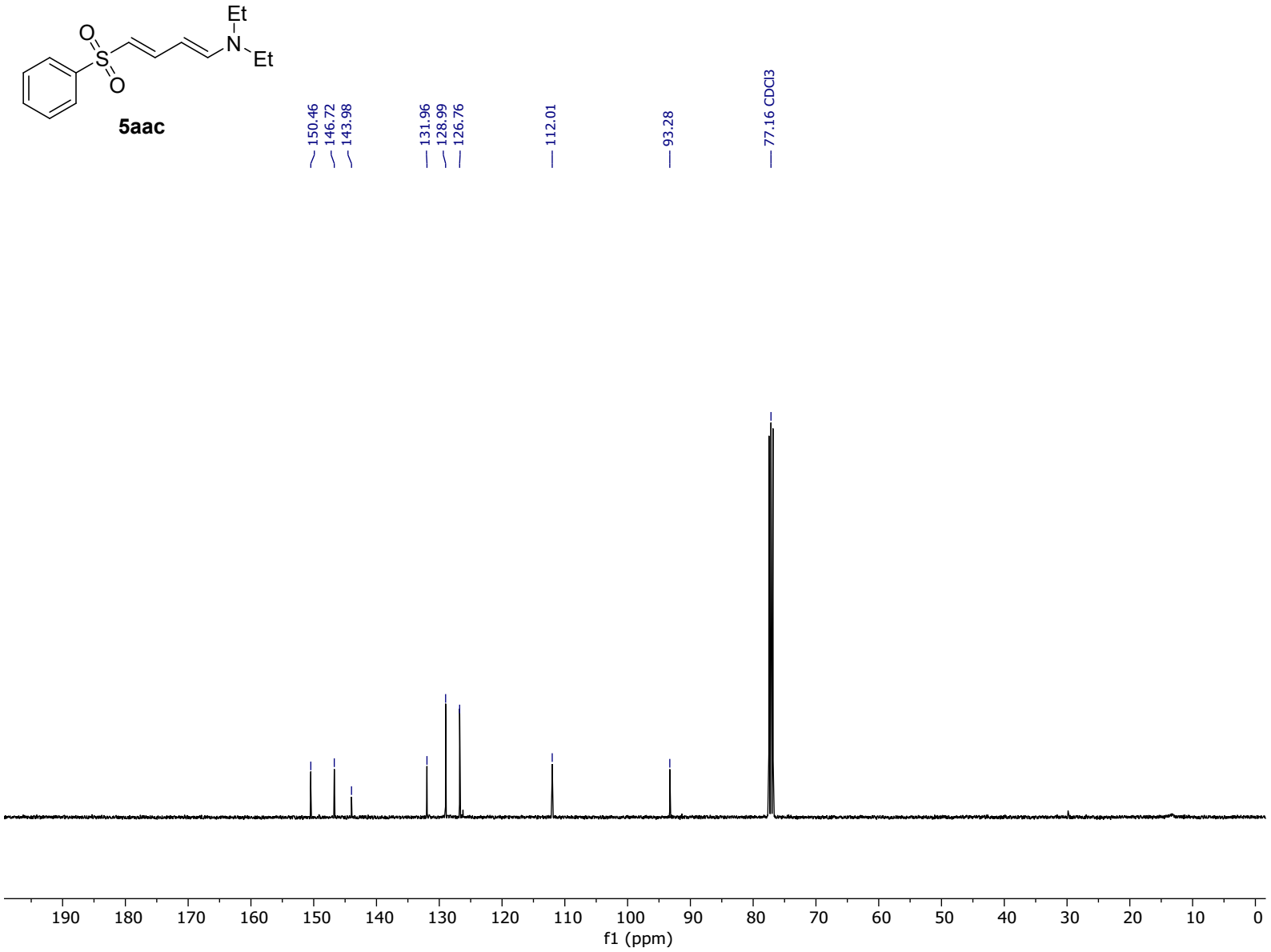
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aaa**.



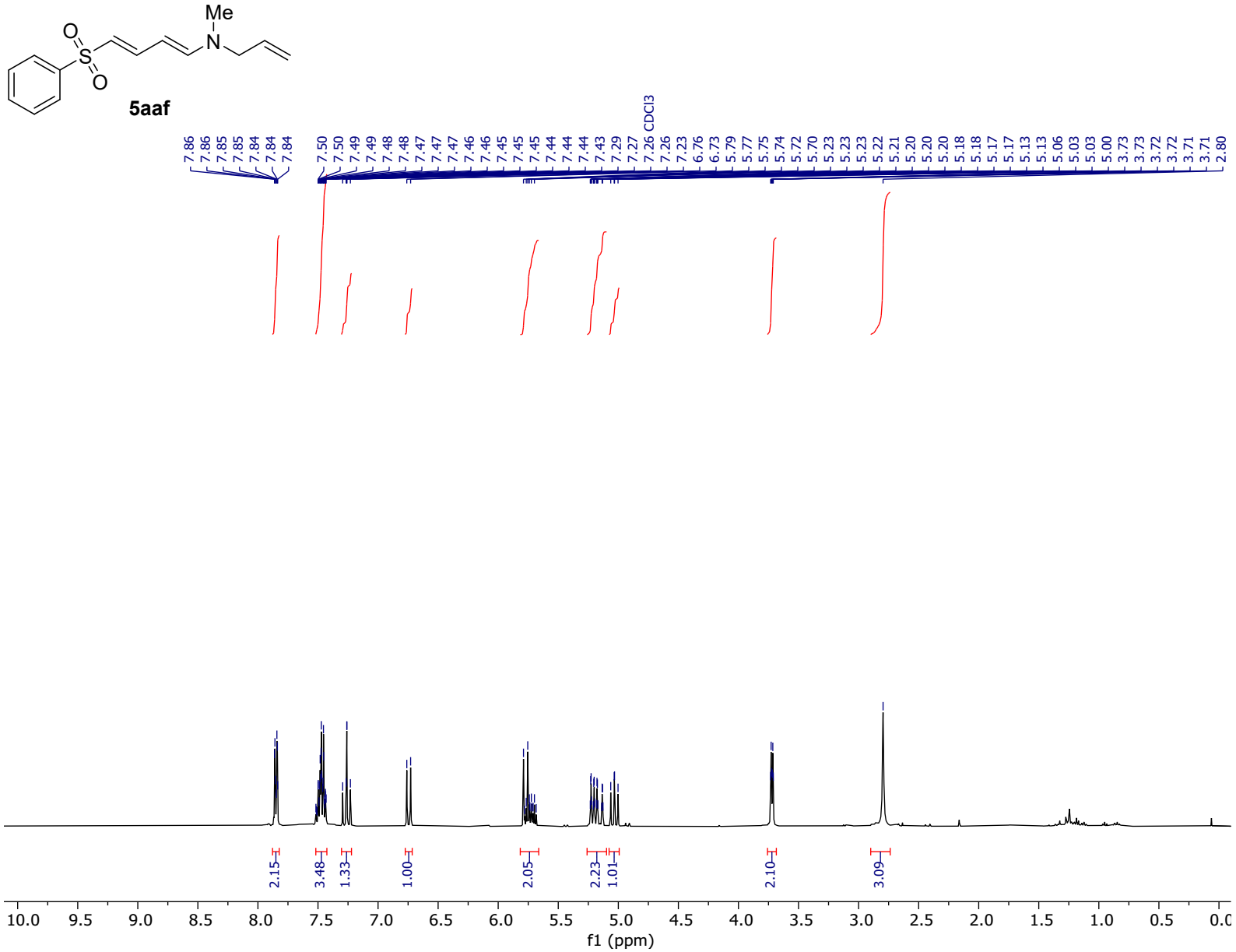
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aaa**.



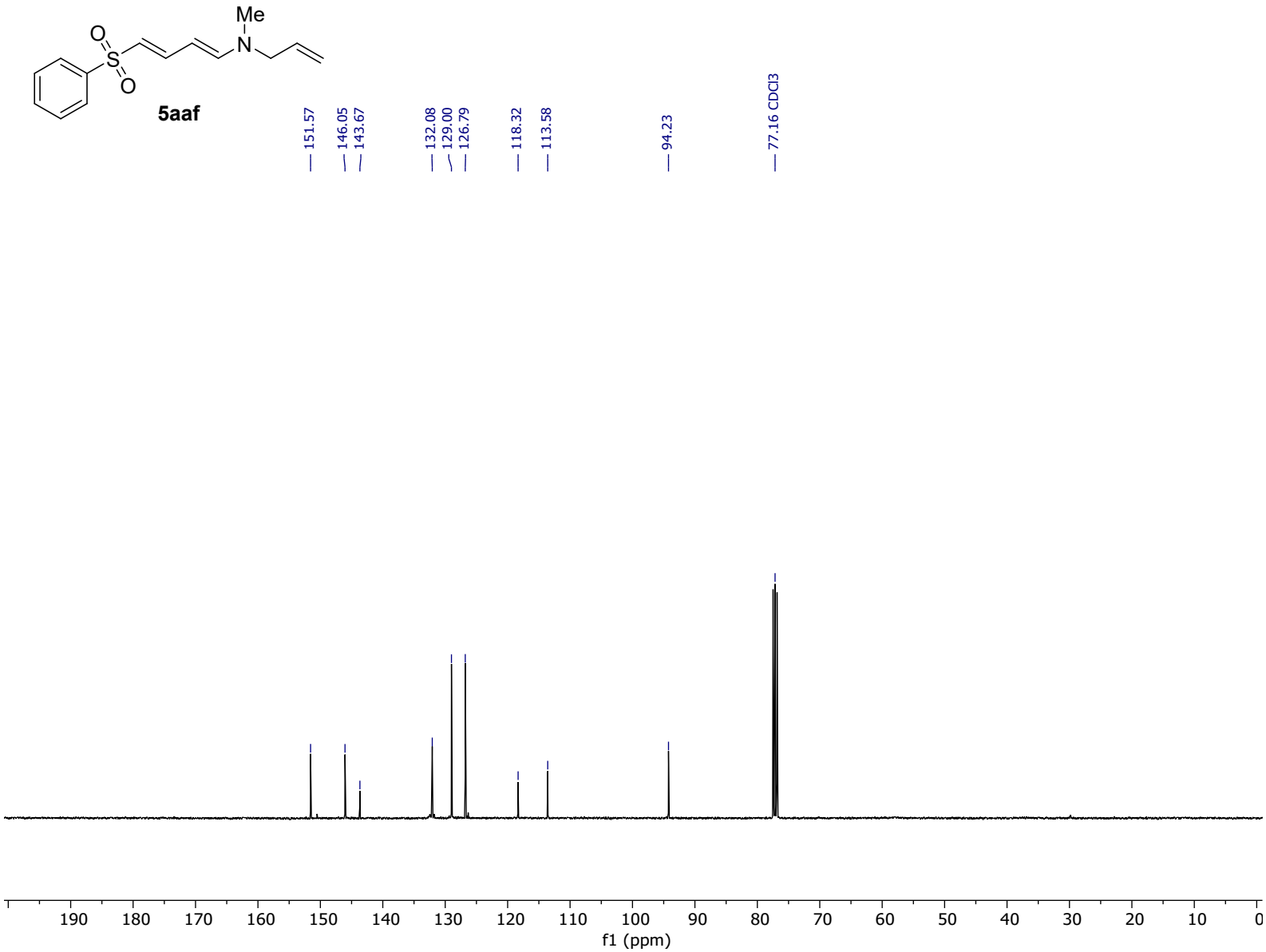
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aac**.



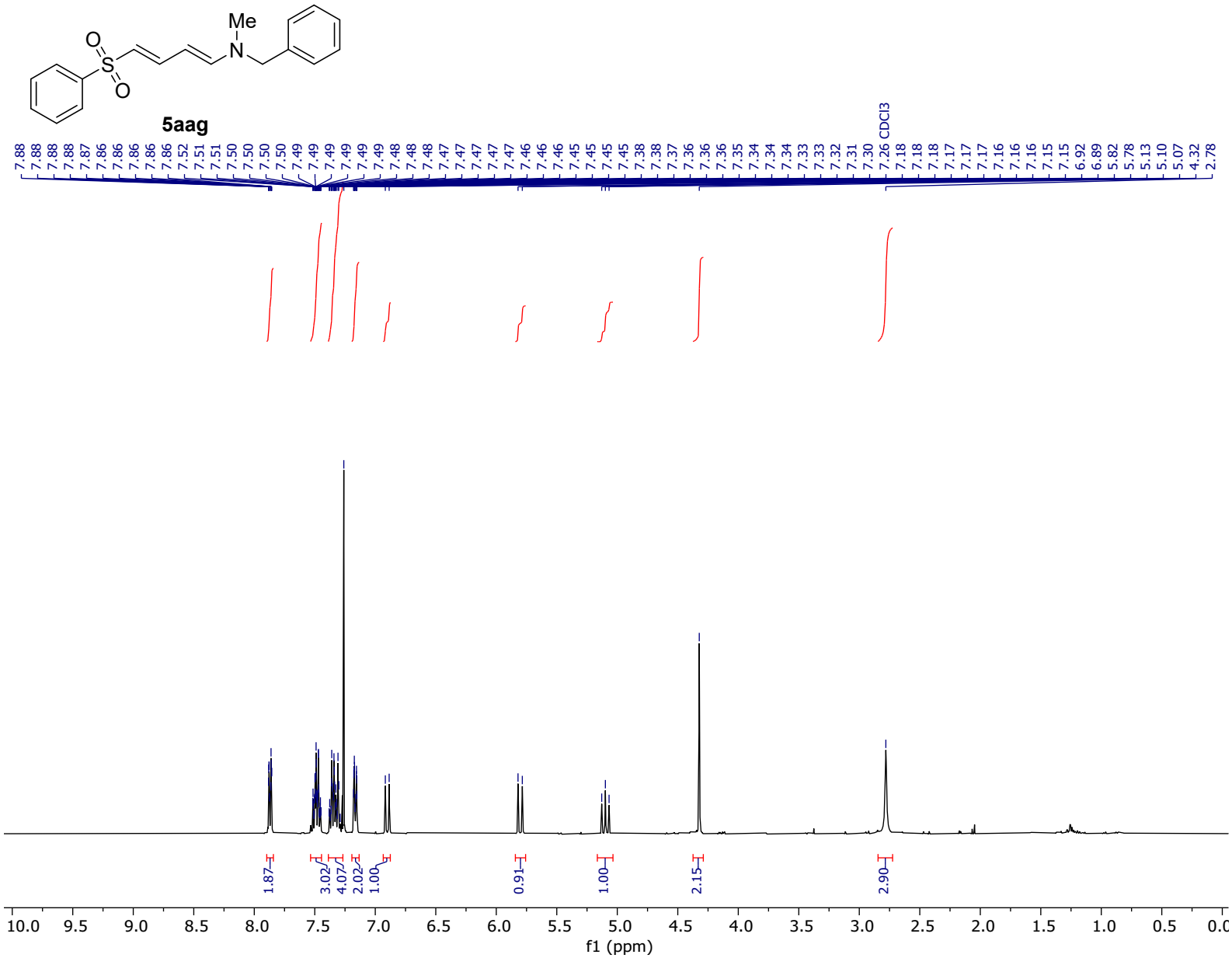
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aac**.



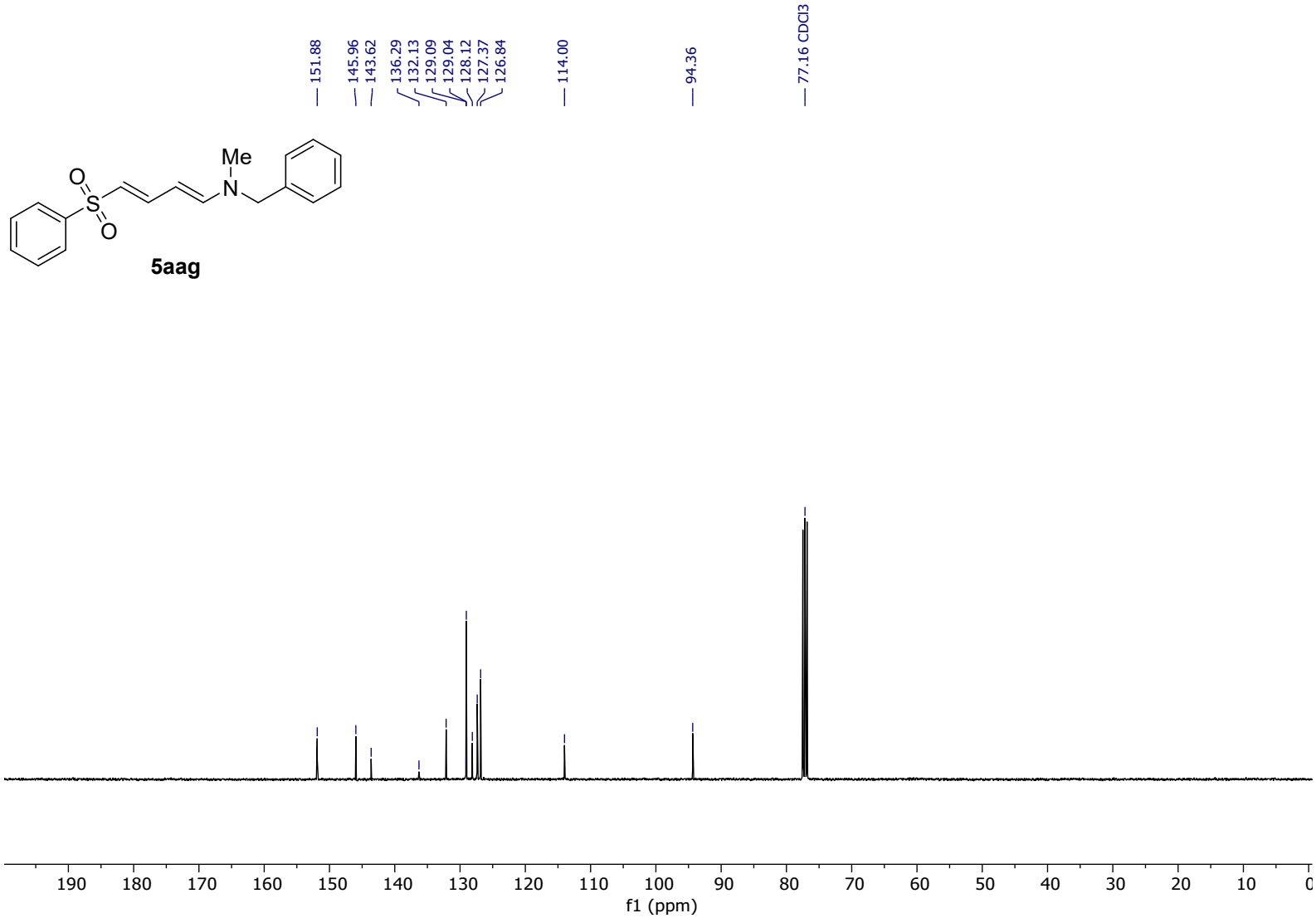
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aaf**.



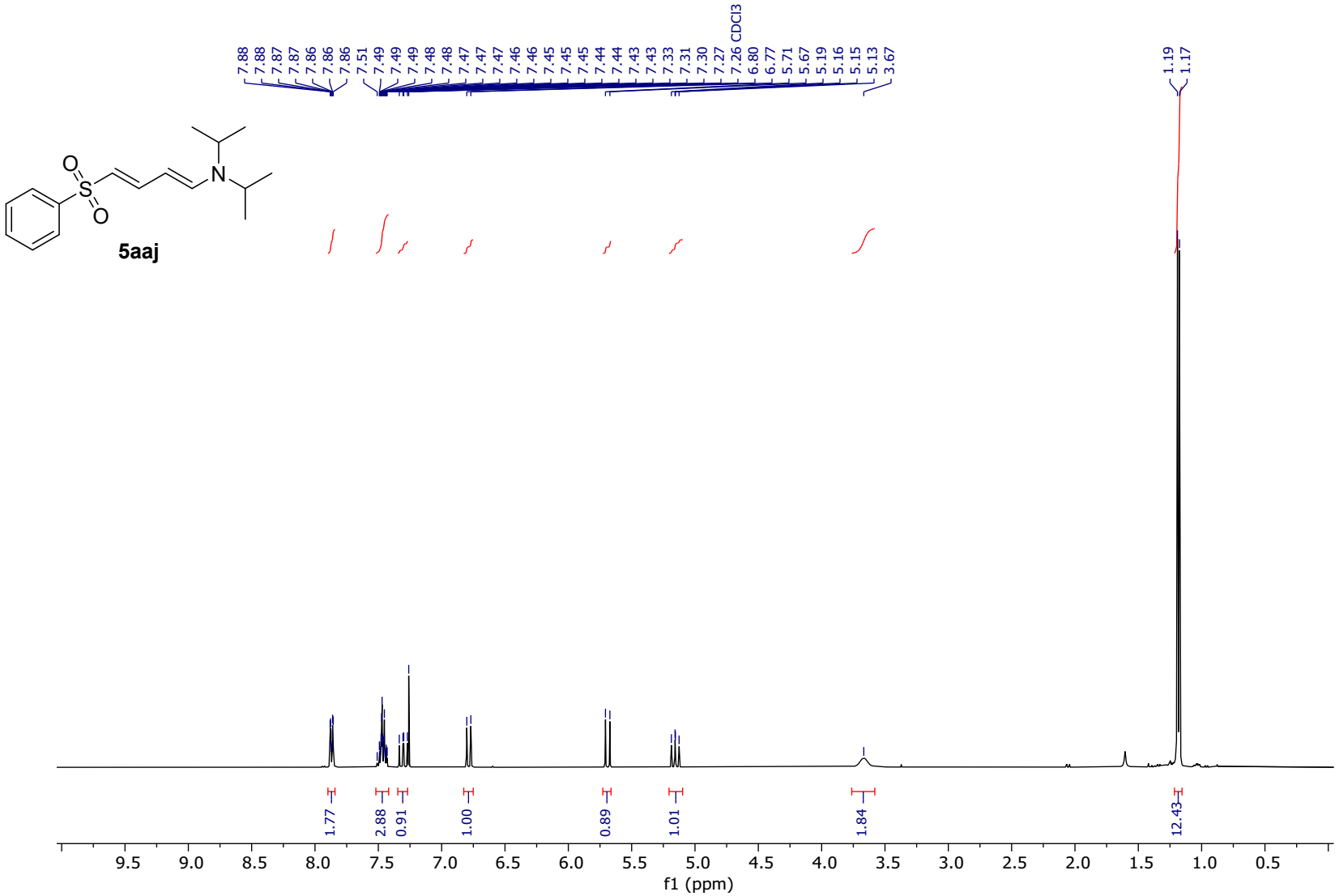
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aaf**.



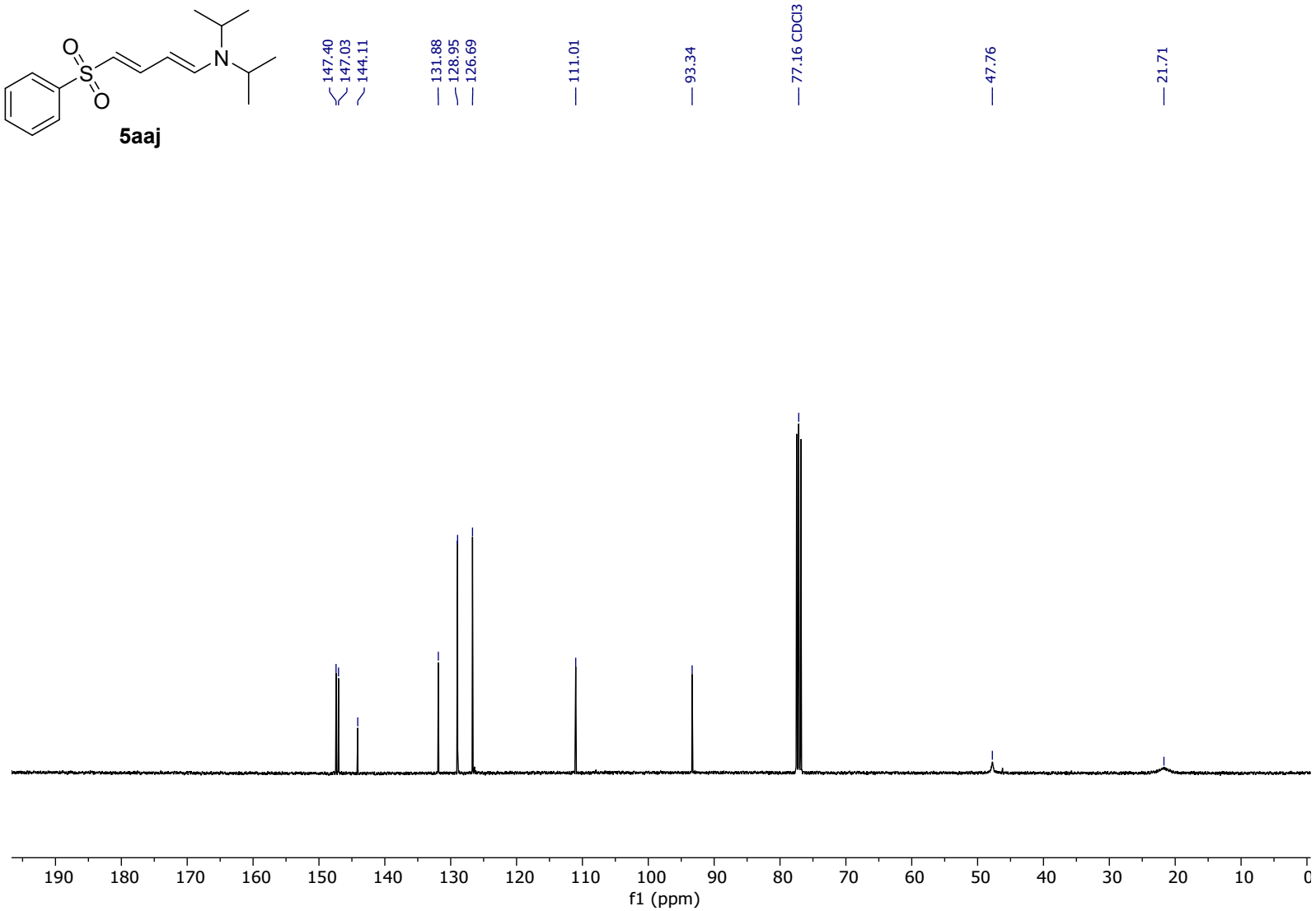
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aag**.



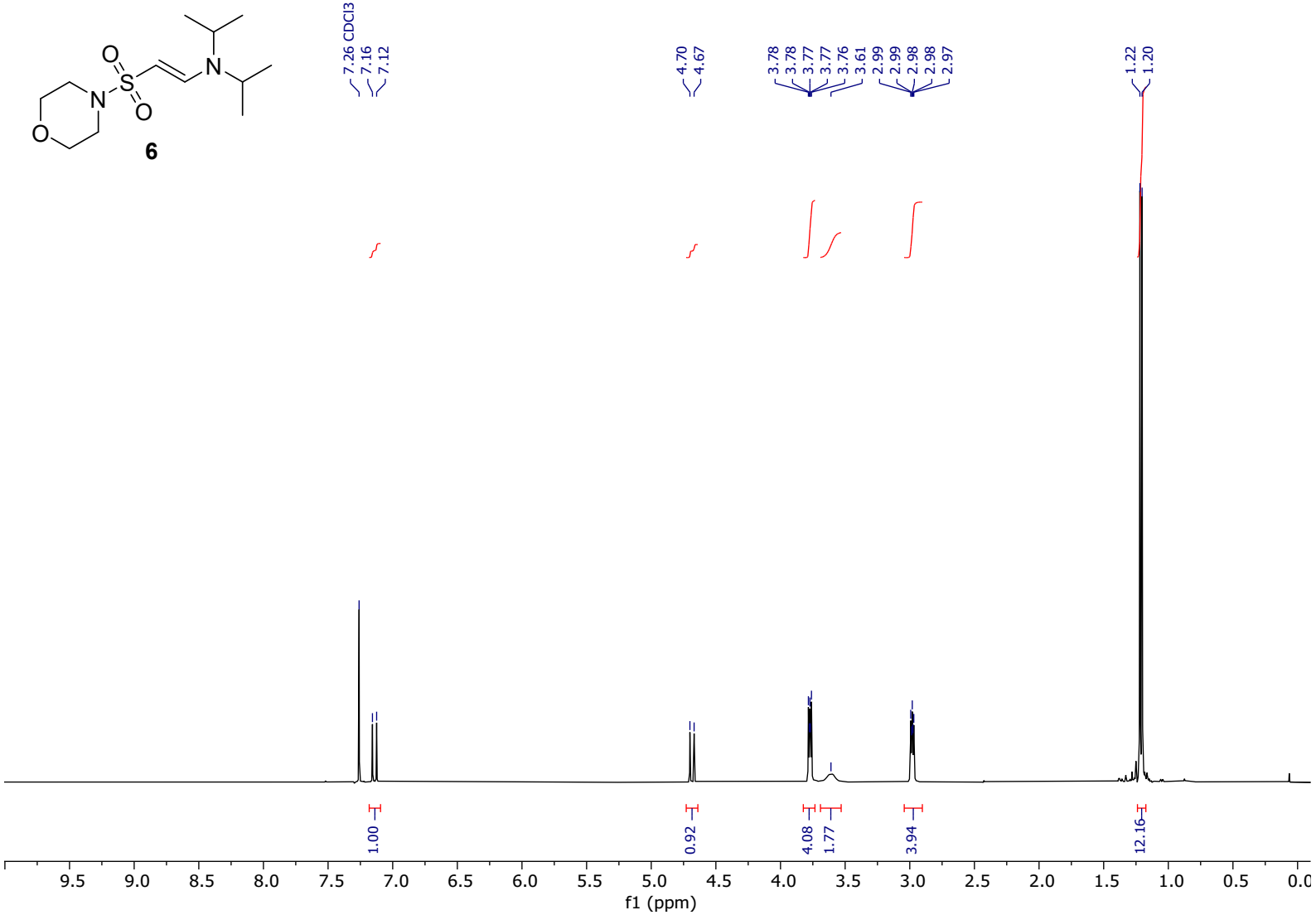
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aag**.



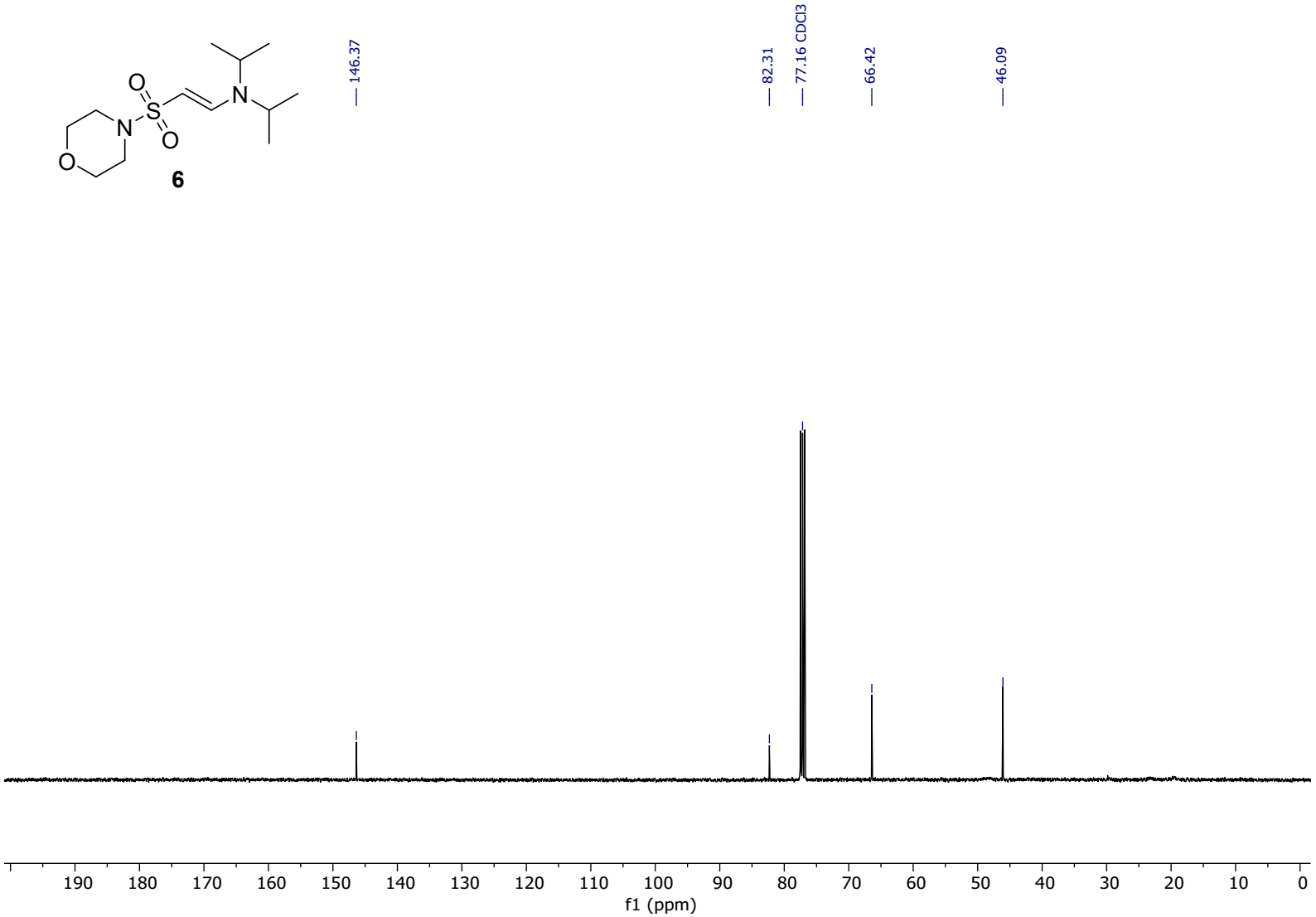
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5aaj**.



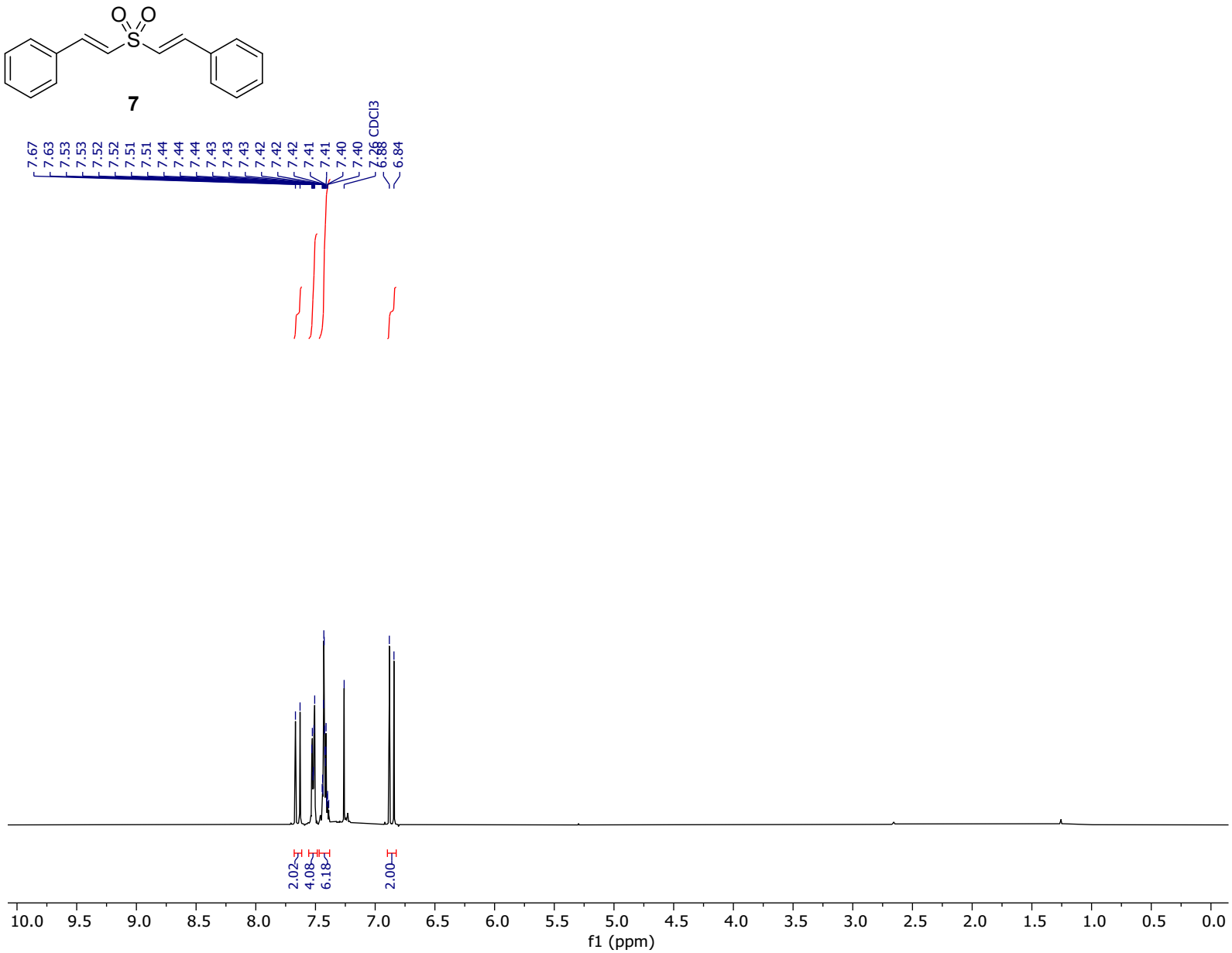
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **5aaj**.



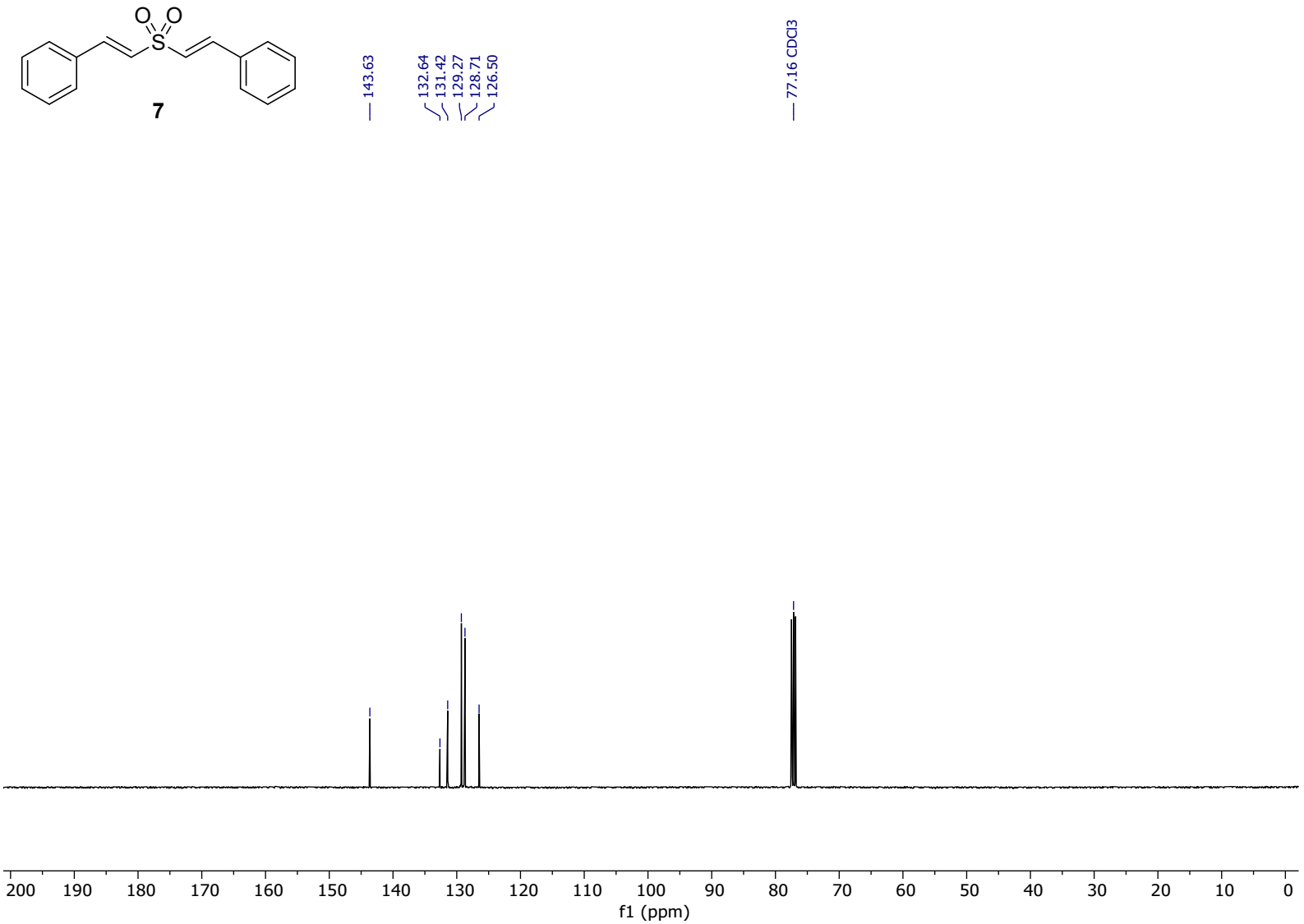
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**.



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **6**.



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



$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **7**.