Supporting Information

Photoredox Cobalt-Catalyzed Hydroaminomethylation of Alkynes with Aminals

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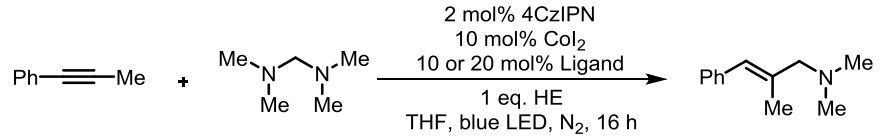
I. General Information

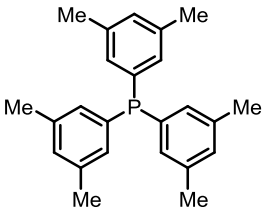
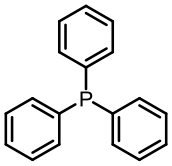
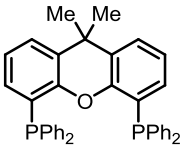
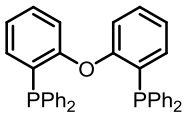
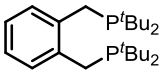
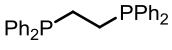
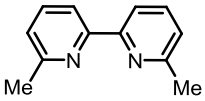
All of the reactions were carried out in oven-dried Schlenk tube and under nitrogen atmosphere if otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 30-60 ^{o}C). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. NMR spectra were recorded on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and $CDCl_3$ as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of $CDCl_3$ (δ 7.26). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); m (multiplet); br (broad). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.00). The photoreactors used in this research were bought from GeAoChem (Blue LEDs, light intensity = 42 mw/cm^2, 5 W for every light bulb; every Schlenk tube was irradiated by 1 light bulbs from the side). All alkynes and diaminomethanes were commercially available or synthesized by known methods. These materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, or other commercial suppliers and used as received unless otherwise noted.

II. Optimization of the Reaction Conditions

Table S1. The Effect of the Ligand for Hydroaminomethylation of Alkyne 1 with Aminal 2[a]



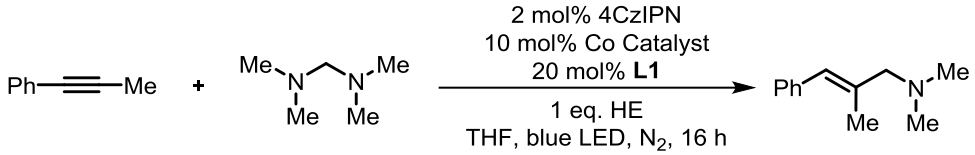
1 **2** **3**, >19:1 rr, >19:1 *E/Z*

			
P(*3,5*-xylyl)$_3$ (**L1**) 36% (25%)[b]	PPh_3 trace	XantPhos 14%	DPEPhos N.R.
			
DTBPMB trace	DPPP trace	DPPE trace	18%

[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), 4CzIPN (2 mol%), CoI_2 (10 mol%), ligand (20 mol% for monodentate ligand, 10 mol% for bidentate ligand), HE (1.0 eq.), THF (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E/Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]Isolated yield in the parenthesis.

Discussion: Various ligands have been investigated. The results is shown here. Most of the ligands do not work or just produce a trace amount of the desired product **3**. The reaction's optimal ligand is tri(3,5-dimethylphenyl)phosphine (**L1**).

Table S2. The Effect of Cobalt Catalyst[a]

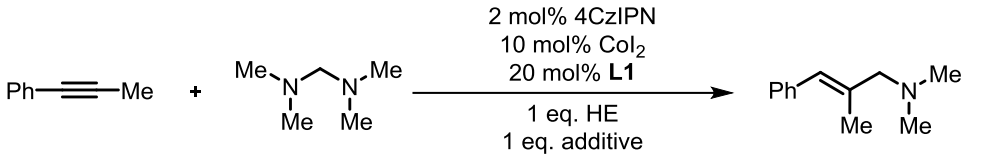


1 **2** **3**, >19:1 rr, >19:1 *E/Z*

Entry	Co catalyst	Yield (%)	Entry	Co catalyst	Yield (%)
1	**CoI_2**	**36 (25)**[b]	7	$Co(NO_3)_2{\cdot}6H_2O$	N.R.
2	$CoBr_2$	25	8	$Co(OTf)_2$	trace
3	$CoCl_2$	18	9	$Co(CO_3)_2$	N.R.
4	CoF_2	trace	10	$Co_3(PO_4)_2$	N.R.
5	$Co(acac)_2$	N.R.	11	$CoI_2{\cdot}MeCN$	10
6	$Co(OAc)_2$	N.R.	12	No Co Catalyst	N.R.

[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), 4CzIPN (2 mol%), Co catalyst (10 mol%), **L1** (20 mol%), HE (1.0 eq.), THF (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E/Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]Isolated yield in the parenthesis.

Table S3. The Effect of Additive[a]



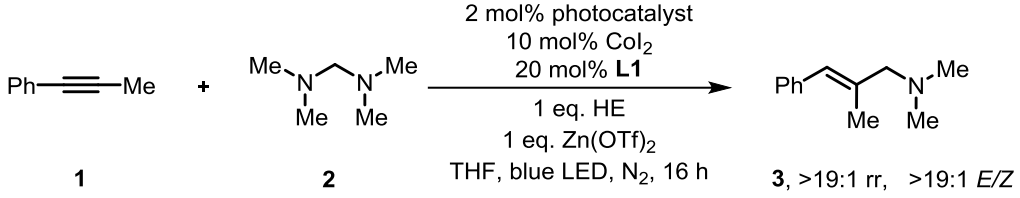
1 **2** **3**, >19:1 rr, >19:1 *E/Z*

Entry	Additive	Yield (%)	Entry	Additive	Yield(%)
1	none	36	12	ZnI_2	64
2	$NaBF_4$	26	**13**	**$Zn(OTf)_2$**	**68**
3	KBARF[b]	26	14	$Zn(OTf)_2$[e]	50
4	NaBARF[c]	24	15	$Zn(CN)_2$	15
5	$KBPhF_3$	16	16	$Zn(OAc)_2$	20
6	$NaHCO_3$	20	17	Zinc pivalate	10
7	CsF	10	18	Zinc propionate	15
8	LiCl	15	19	$Mg(OTf)_2$	32
9	LiOTf	18[d]	20	$Cu(OTf)_2$[f]	N.R.
10	$ZnCl_2$	54	21	$Sc(OTf)_2$	10
11	$ZnBr_2$	60	22	TFA	56

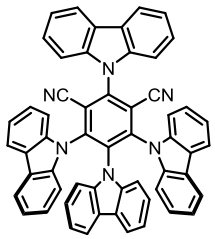
[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), 4CzIPN (2 mol%), CoI_2 (10 mol%), **L1** (20 mol%), HE (1.0 eq.), additive (1 eq.), THF (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E*/*Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]NaBARF: Sodium

tetrakis(pentafluorophenyl)borate. [c]KBARF: Potassium tetrakis(perfluorophenyl)borate. [d]The *E*/*Z* of **3** is 1.3:1. [e]With $Zn(OTf)_2$ (0.5 eq.). [f]Or With $Fe(OTf)_3$.

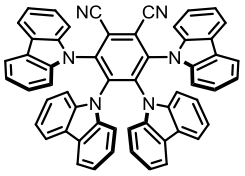
Table S4. The Effect of Photocatalyst[a]



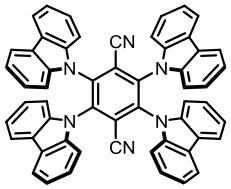
1 **2** **3**, >19:1 rr, >19:1 *E/Z*



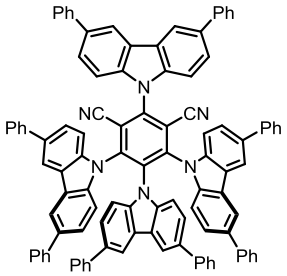
4CzIPN
68%



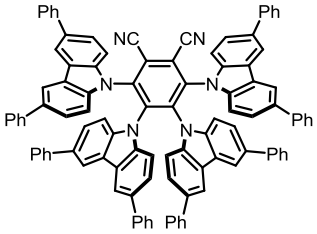
4CzPN
28%



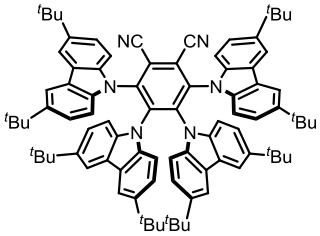
4CzTPN
10%



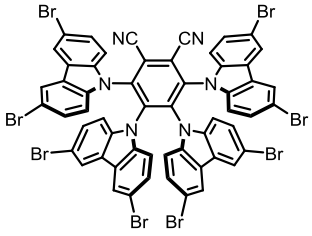
4CzIPN-Ph
60%



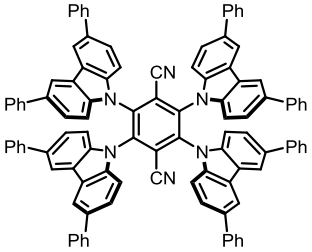
4CzPN-Ph
trace



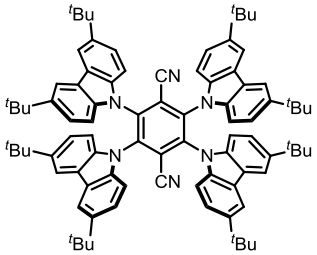
4CzPN-^{t}Bu
trace



4CzPN-Br
trace



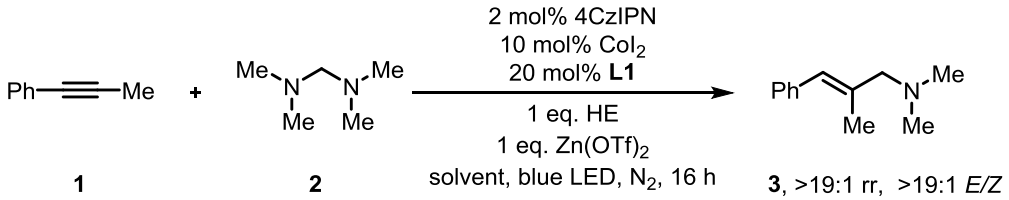
4CzTPN-Ph
32%



4CzTPN-^{t}Bu
50%

[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), photocatalyst (2 mol%), CoI_2 (10 mol%), **L1** (20 mol%), HE (1.0 eq.), $Zn(OTf)_2$ (1 eq.), THF (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E*/*Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard.

Table S5. The Effect of Solvent[a]

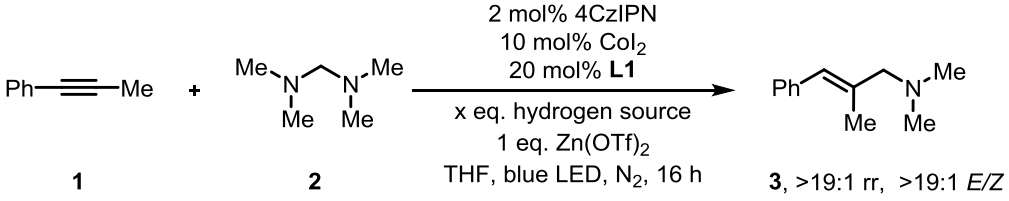


1 **2** **3**, >19:1 rr, >19:1 *E/Z*

Entry	Solvent	Yield (%)
1	**THF**	**68**
2	1,4-dioxane	66
3	MeCN	10
4	DME	68
5	DCE	46
6	2-MeTHF	60

[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), 4CzIPN (2 mol%), CoI_2 (10 mol%), **L1** (20 mol%), HE (1 eq.), $Zn(OTf)_2$ (1 eq.), solvent (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E/Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard.

Table S6. The Effect of Hydrogen Source[a]

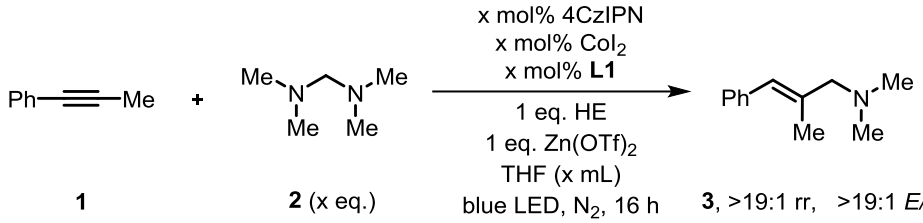


1 **2** **3**, >19:1 rr, >19:1 *E/Z*

Entry	Hydrogen Source (x eq.)	Yield (%)
1	**HE (1)**	**68**
2	H_2O (3)	0
3	MeOH (3)	34
4	MeOH[b]	32
5	EtOH[b]	14
6	MeOH[c]	18

[a]Reaction conditions: **1** (0.2 mmol), **2** (2 eq.), 4CzIPN (2 mol%), CoI_2 (10 mol%), **L1** (20 mol%), hydrogen source (x eq.), $Zn(OTf)_2$ (1 eq.), THF (2 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E*/*Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]As solvent. [c]With THF as mixed solvent (v:v=1:1).

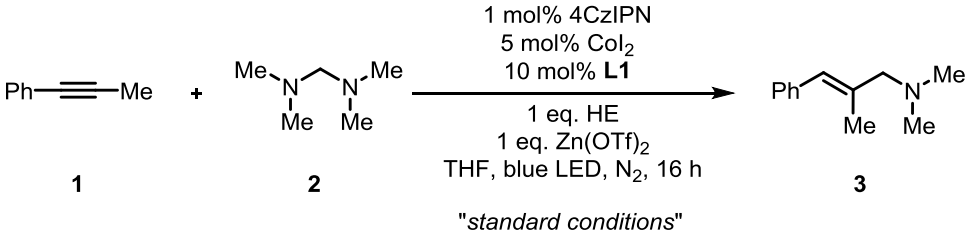
Table S7. The Effect of the Amount of 2, Photocatalyst, CoI_2, L1 and Solvent[a]



Entry	**2** (x eq.)	4CzIPN (x mol%)	CoI_2 (x mol%)	**L1** (x mol%)	THF (x mL)	Yield (%)[b]
1	2	2	10	20	2	68
2	2.5	2	10	20	2	86
3	2.5	1	5	10	2	82
4	**2.5**	**1**	**5**	**10**	**1**	**97 (85)**[b]

[a]Reaction conditions: **1** (0.2 mmol), **2** (x eq.), 4CzIPN (x mol%), CoI_2 (x mol%), **L1** (x mol%), HE (1 eq.), $Zn(OTf)_2$ (1 eq.), THF (x mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E/Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]Isolated yield in the parenthesis.

Table S8. Control Experiments[a]



Entry	Changes from "*standard conditions*"	Yield (%)	rr	*E*/*Z*
1	**none**	**97 (85)**[b]	**>19:1**	**>19:1**
2	without CoI_2	N.R.	-	-
3	without **L1**	16	>19:1	>19:1
4	without 4CzIPN	N.R.	-	-
5	without light	N.R.	-	-
6	without HE	32	>19:1	>19:1

[a]Standard conditions: **1** (0.2 mmol), **2** (2.5 eq.), 4CzIPN (1 mol%), CoI_2 (5 mol%), **L1** (10 mol%), HE (1.0 eq.), $Zn(OTf)_2$ (1.0 eq.), THF (1 mL), 5 W blue LED, r.t., 16 h. Yield, rr and *E/Z* of **3** was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b]Isolated yield in the parenthesis.

III. Investigated Substrates of Alkynes and Aminals

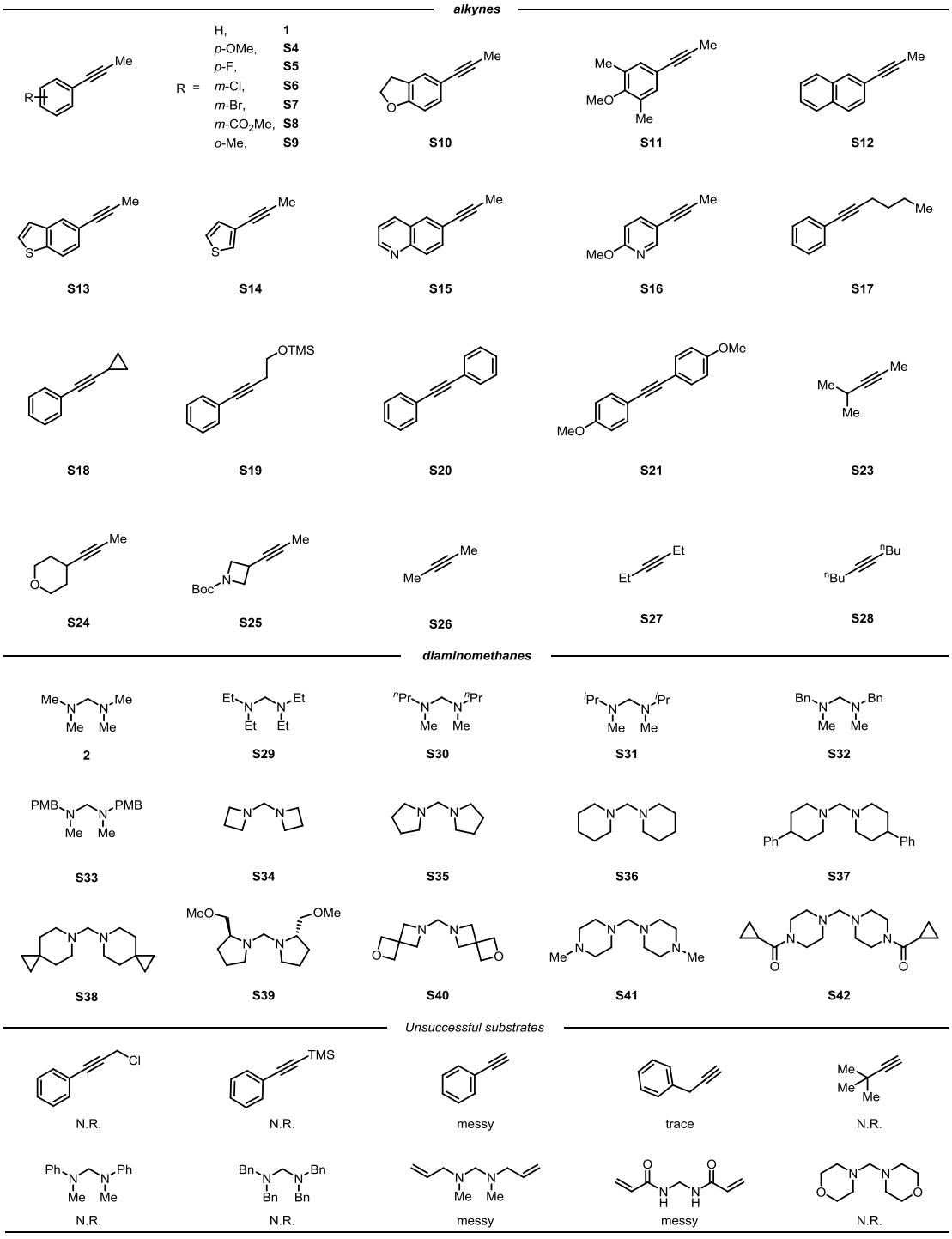
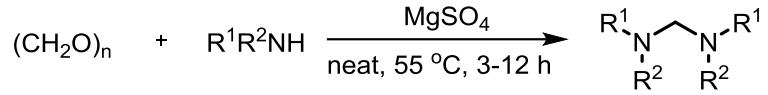


Figure S1. Investigated Substrates in the Photoredox Cobalt-catalyzed Hydroaminomethylation of Alkynes with Aminals.

IV. Preparation of Starting Materials

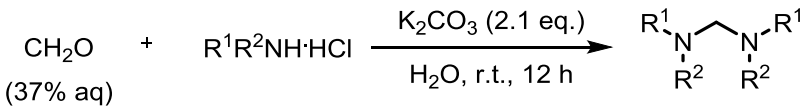
Known alkyne **S4-5**[1]**, S6**[2]**, S7**[3]**, S8-13**[1]**, S15**[1]**, S18-S19**[1], **S14**[4]**, S16**[4] and aminal **S30**[5], **S31**[6], **S32**[7], **S35**[8], **S36**[8], **S41**[8] were prepared according to the reported methods. The other substrates are commercially available and used as received from vendors.

General method A for the synthesis of aminals

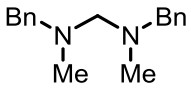


To a round-bottom flask charged with paraformaldehyde (5.0 mmol, 150.0 mg) and $MgSO_4$ (0.4 mmol, 50 mg), free secondary amine (10.0 mmol) was added. The mixture was vigorously stirred for 3–12 h at 55 ℃. The mixture was extracted with dichloromethane (30 mL) and the organic phase was washed with saturated sodium bicarbonate aqueous solution, dried over anhydrous sodium sulfate. After filtration and concentration under reduced pressure, the resulting aminal was obtained in sufficient purity for further use.

General method B for the synthesis of aminals



To a round-bottom flask was added the corresponding amine hydrochloride (10.0 mmol), K_2CO_3 (21.0 mmol, 2.9 g) and water (5 mL). The mixture was stirred at room temperature for 0.5 h. Then, the mixture was cooled to 0 ℃. Aqueous solution of formaldehyde (37% aq., 405.4 mg, 5.0 mmol) was added dropwise and the resulting biphasic mixture was stirred vigorously at room temperature for 12 h. The mixture was extracted with dichloromethane (30 mL) and the organic phase was washed with saturated sodium bicarbonate aqueous solution, dried over anhydrous sodium sulfate. After filtration and concentration under reduced pressure, the resulting title compound in sufficient purity for further use.



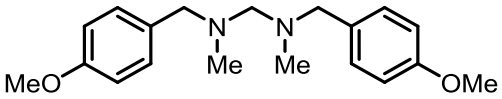
***N,N′*-Dibenzyl-*N,N′*-dimethylmethanediamine (S32)**

According to the general method A, **S32** was synthesized from *N*-methyl-1-phenylmethanamine (10 mmol, 1.21 g) for 12 h. The title compound was isolated as a colorless oil (391.2 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 8H), 7.24 – 7.19 (m, 2H), 3.62 (s, 4H), 3.03 (s, 2H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 129.0, 128.3, 126.8, 79.9, 59.6, 40.6.

HRMS (ESI) calculated for $C_{17}H_{22}N_2Na$ $(M+Na)^+$ 277.1675, found 277.1677.



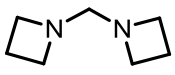
***N,N′*-Bis(4-methoxybenzyl)-*N,N′*-dimethylmethanediamine (S33)**

According to the general method A, **S33** was synthesized from 1-(4-methoxyphenyl)-*N*-methylmethanamine (10 mmol, 1.51 g) for 12 h. The title compound was isolated as a colorless oil (1.35 g, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) 7.23 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 6H), 3.55 (s, 4H), 2.99 (s, 2H), 2.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 131.7, 130.1, 113.6, 79.5, 58.9, 55.4, 40.5.

HRMS (ESI) calculated for $C_{19}H_{26}N_2O_2Na$ $(M+Na)^+$ 337.1886, found 337.1881.



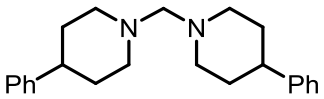
Di(azetidin-1-yl)methane (S34)

According to the general method B, **S34** was synthesized from azetidine hydrochloride (10 mmol, 930 mg). The title compound was isolated as a colorless oil (410.0 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (t, *J* = 7.2 Hz, 8H), 3.03 (s, 2H), 2.08 (p, *J* = 7.2 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 53.7, 17.8.

HRMS (ESI) calculated for $C_7H_{14}N_2Na$ $(M+Na)^+$ 149.1049, found 149.1055.



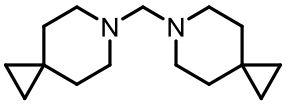
Bis(4-phenylpiperidin-1-yl)methane (S37)

According to the general method A, **S37** was synthesized from 4-phenylpiperidine (10 mmol, 1.61 g) for 12 h. The title compound was isolated as a white solid (1.47 g, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.26 – 7.23 (m, 4H), 7.21 – 7.17 (m, 2H), 3.18 – 3.13 (m, 4H), 3.00 (s, 2H), 2.55 – 2.47 (m, 2H), 2.09 (td, *J* = 11.6, 2.8 Hz, 4H), 1.86 – 1.72 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 128.5, 127.0, 126.2, 82.1, 53.0, 43.4, 33.7.

HRMS (ESI) calculated for $C_{23}H_{30}N_2Na$ $(M+Na)^+$ 357.2301, found 357.2301.



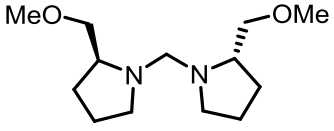
Di(6-azaspiro[2.5]octan-6-yl)methane (S38)

According to the general method A, **S38** was synthesized from 6-azaspiro[2.5]octane (10 mmol, 1.11 g) for 3 h. The title compound was isolated as a colorless oil (1.47 g, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (s, 2H), 2.51 (t, *J* = 11.2 Hz, 8H), 1.37 (t, *J* = 11.2 Hz, 8H), 0.25 (s, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 82.2, 51.9, 35.3, 18.1, 11.6.

HRMS (ESI) calculated for $C_{15}H_{26}N_2Na$ $(M+H)^+$ 235.2169, found 235.2163.



Bis((*S*)-2-(methoxymethyl)pyrrolidin-1-yl)methane (S39)

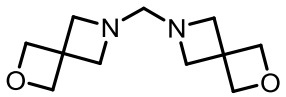
According to the general method A, **S39** was synthesized from (*S*)-2-(methoxymethyl)-pyrrolidine (10 mmol, 1.15 g) for 12 h. The title compound

was isolated as a colorless oil (1.93 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (s, 2H), 3.44 – 3.39 (m, 2H), 3.35 (s, 6H), 3.26 – 3.21 (m, 2H), 3.19 – 3.13 (m, 2H), 2.78 – 2.71 (m, 2H), 2.41 – 2.34 (m, 2H), 1.94 – 1.84 (m, 2H), 1.76 – 1.68 (m, 4H), 1.65 – 1.56 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 76.8, 76.2, 61.0, 59.1, 54.4, 28.9, 23.5.

HRMS (ESI) calculated for $C_{13}H_{27}N_2O_2$ $(M+H)^+$ 243.2067, found 243.2062.



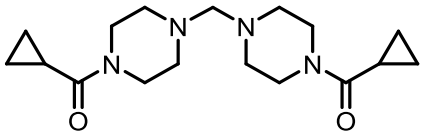
Di(2-oxa-6-azaspiro[3.3]heptan-6-yl)methane (S40)

According to the general method B, **S40** was synthesized from 2-oxa-6-azaspiro[3.3]heptane hydrochloride (10 mmol, 1.35g). The title compound was isolated as a colorless oil (787.5 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 8H), 3.35 (s, 8H), 2.97 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 81.8, 81.5, 62.5, 39.5.

HRMS (ESI) calculated for $C_{11}H_{18}N_2O_2Na$ $(M+Na)^+$ 233.1260, found 233.1267.



(Methylenebis(piperazine-4,1-diyl))bis(cyclopropylmethanone) (S42)

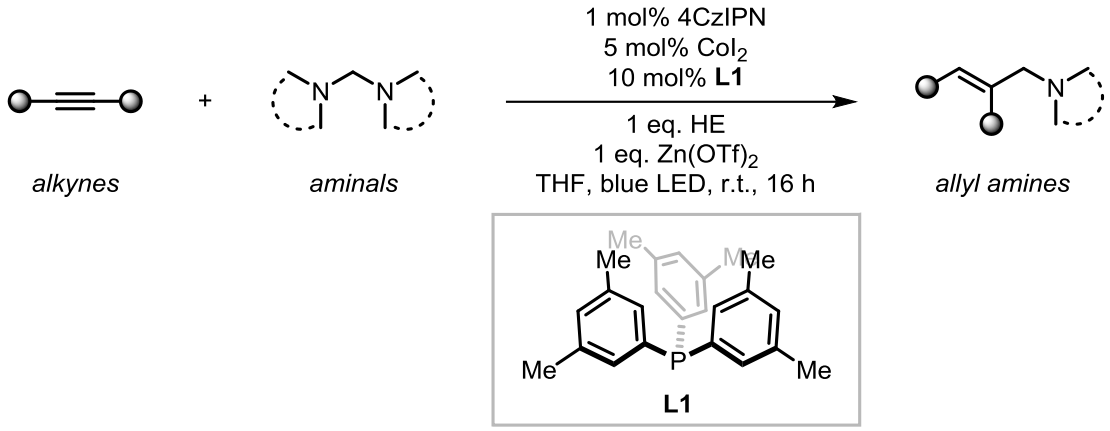
According to the general method A, **S42** was synthesized from cyclopropyl(piperazin-1-yl)methanone (10 mmol, 1.54 g) for 12 h. The title compound was isolated as a white solid (1.25 g, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 – 3.62 (m, 8H), 2.95 (s, 2H), 2.55 – 2.47 (m, 8H), 1.77 – 1.70 (m, 2H), 1.00 – 0.95 (m, 4H), 0.78 – 0.73 (m, 4H).

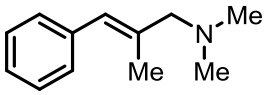
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 80.7, 51.9, 51.3, 45.6, 42.2, 11.1, 7.4.

HRMS (ESI) calculated for $C_{17}H_{28}N_4O_2Na$ $(M+Na)^+$ 343.2104, found 343.2101.

V. General Procedure and Characterization Data



General procedure for photoredox cobalt-catalyzed hydroaminomethylation of alkynes with aminals: In a nitrogen-filled glovebox, a 25 mL Schlenk tube was charged with 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl) phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.2 mmol, 50.6 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), dry THF(1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, alkyne (0.2 mmol) and aminal (0.5 mmol) was sequentially added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, CH_2Cl_2 / MeOH) to afford the desired product.

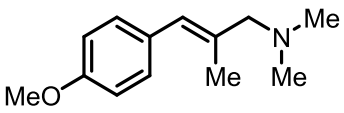


(*E*)-*N*,*N*,2-Trimethyl-3-phenylprop-2-en-1-amine (3)

3 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (29.8 mg, 85% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.32 – 7.27 (m, 3H), 6.70 (s, 1H), 3.76 (s, 2H), 2.93 (s, 6H), 2.05 (d, *J* = 1.2 Hz, 3H). Spectral data are identical to those in the reported literature.[9]



(*E*)-3-(4-Methoxyphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (4)

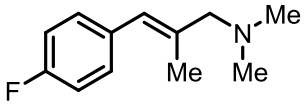
4 was synthesized from 1-methoxy-4-(prop-1-yn-1-yl)benzene (0.2 mmol, 29.2 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (34.5 mg, 84% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.35 (s, 1H), 3.81 (s, 3H), 2.96 (s, 2H), 2.26 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 134.5, 130.6, 130.2, 127.5, 113.7, 69.8, 55.4, 45.4, 16.9.

HRMS (ESI) calculated for $C_{13}H_{20}NO$ $(M+H)^+$ 206.1539, found 206.1549.



(*E*)-3-(4-Fluorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (5)

5 was synthesized from 1-fluoro-4-(prop-1-yn-1-yl)benzene (0.2 mmol, 26.8 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (26.0 mg, 67% yield).

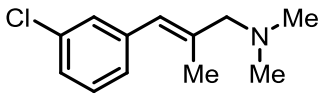
R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.04 – 6.98 (m, 2H), 6.36 (s, 1H), 2.93 (s, 2H), 2.24 (s, 6H), 1.88 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -78.27 (s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, *J* = 244.0 Hz), 135.6, 133.2 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 8.0 Hz), 125.5, 114.1 (d, *J* = 21.0 Hz), 68.6, 44.5, 15.8.

HRMS (ESI) calculated for $C_{12}H_{16}NFK$ $(M+K)^+$ 232.0898, found 232.0899.



(*E*)-3-(3-Chlorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (6)

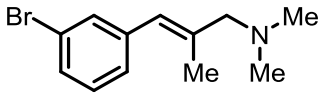
6 was synthesized from 1-chloro-3-(prop-1-yn-1-yl)benzene (0.2 mmol, 30.0 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (31.0 mg, 74% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.19 – 7.14 (m, 2H), 6.35 (s, 1H), 2.93 (s, 2H), 2.24 (s, 6H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 138.3, 134.1, 129.4, 128.9, 127.2, 126.4, 126.2, 69.4, 45.6, 16.9.

HRMS (ESI) calculated for $C_{12}H_{16}NClNa$ $(M+Na)^+$ 232.0863, found 232.0871.



(*E*)-3-(3-Bromophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (7)

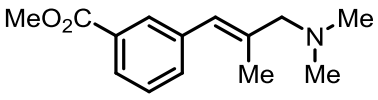
7 was synthesized from 1-bromo-3-(prop-1-yn-1-yl)benzene (0.2 mmol, 38.8 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (30.4 mg, 60% yield).

R_f (CH_2Cl_2 / MeOH = 20/1 = 2/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.35 – 7.33 (m, 1H), 7.20 – 7.18 (m, 2H), 6.34 (s, 1H), 2.93 (s, 2H), 2.23 (s, 6H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 138.3, 131.9, 129.7, 129.3, 127.6, 126.0, 122.3, 69.4, 45.6, 16.9.

HRMS (ESI) calculated for $C_{12}H_{17}NBr$ $(M+H)^+$ 254.0539, found 254.0538.



Methyl (*E*)-3-(3-(dimethylamino)-2-methylprop-1-en-1-yl)benzoate (8)

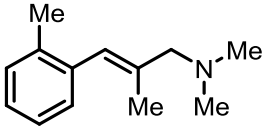
8 was synthesized from methyl 3-(prop-1-yn-1-yl)benzoate (0.2 mmol, 34.8 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (36.8 mg, 79% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 (dd, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 3.92 (s, 3H), 2.95 (s, 2H), 2.25 (s, 6H), 1.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 138.4, 138.0, 133.4, 130.1, 130.1, 128.3, 127.5, 126.5, 69.5, 52.3, 45.6, 16.8.

HRMS (ESI) calculated for $C_{14}H_{20}NO_2$ $(M+H)^+$ 234.1489, found 234.1497.



(*E*)-*N*,*N*,2-Trimethyl-3-(o-tolyl)prop-2-en-1-amine (9)

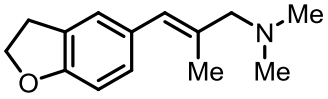
9 was synthesized from 1-methyl-2-(prop-1-yn-1-yl)benzene (0.2 mmol, 26.0 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (22.0 mg, 58% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 4H), 6.39 (s, 1H), 2.97 (s, 2H), 2.26 (s, 6H), 2.24 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.3, 134.9, 130.2, 129.0, 128.2, 128.1, 125.8, 67.0, 43.4, 20.0, 16.3.

HRMS (ESI) calculated for $C_{13}H_{19}NNa$ $(M+Na)^+$ 212.1410, found 212.1401.



(*E*)-3-(2,3-Dihydrobenzofuran-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (10)

10 was synthesized from 5-(prop-1-yn-1-yl)-2,3-dihydrobenzofuran (0.2 mmol, 31.6mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (34.0 mg, 78% yield).

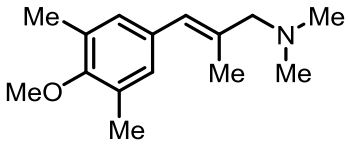
R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.33 (s, 1H), 4.57 (t, *J* = 8.4 Hz, 2H), 3.20 (t, *J* = 8.8 Hz, 2H), 2.92 (s, 2H),

2.23 (s, 6H), 1.90 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 134.5, 130.7, 129.0, 127.5, 126.9, 125.5, 109.0, 71.4, 69.9, 45.5, 29.9, 16.9.

HRMS (ESI) calculated for $C_{14}H_{20}NO$ $(M+H)^+$ 218.1539, found 218.1549.



(*E*)-3-(4-Methoxy-3,5-dimethylphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (11)

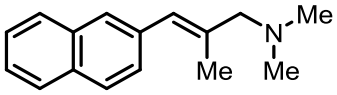
11 was synthesized from 2-methoxy-1,3-dimethyl-5-(prop-1-yn-1-yl)benzene (0.2 mmol, 34.8 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (40.1 mg, 86% yield).

R$_f$ (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.30 (s, 1H), 3.72 (s, 3H), 2.94 (s, 2H), 2.28 (s, 6H), 2.25 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 133.6, 130.5, 129.5, 127.6, 69.8, 59.9, 45.4, 16.9, 16.3.

HRMS (ESI) calculated for $C_{15}H_{23}NOK$ $(M+K)^+$ 272.1411, found 272.1414.



(*E*)-*N*,*N*,2-Trimethyl-3-(naphthalen-2-yl)prop-2-en-1-amine (12)

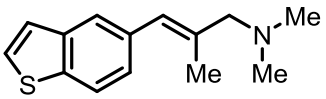
12 was synthesized from 2-(prop-1-yn-1-yl)naphthalene (0.2 mmol, 33.2 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (38.7 mg, 86% yield).

R$_f$ (CH_2Cl_2 / MeOH = 20/1 = 2/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.77 (m, 3H), 7.72 (s, 1H), 7.48 – 7.41 (m, 3H), 6.56 (s, 1H), 2.99 (s, 2H), 2.27 (s, 6H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.6, 133.5, 132.1, 128.0, 127.7, 127.6, 127.6, 127.6, 127.6, 126.1, 125.7, 69.8, 45.6, 17.0.

HRMS (ESI) calculated for $C_{16}H_{20}N$ $(M+H)^+$ 226.1590, found 226.1591.



(*E*)-3-(Benzo[b]thiophen-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (13)

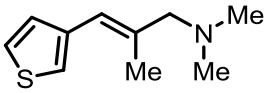
13 was synthesized from 5-(prop-1-yn-1-yl)benzo[*b*]thiophene (0.2 mmol, 34.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (35.6 mg, 77% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (s, 1H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 7.28 – 7.26 (m, 1H), 6.53 (s, 1H), 2.98 (s, 2H), 2.26 (s, 6H), 1.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.8, 136.5, 134.4, 127.6, 126.7, 125.8, 124.0, 123.7, 122.1, 69.7, 45.6, 17.0.

HRMS (ESI) calculated for $C_{14}H_{18}NS$ $(M+H)^+$ 232.1154, found 232.1149.



(*E*)-*N*,*N*,2-Trimethyl-3-(thiophen-3-yl)prop-2-en-1-amine (14)

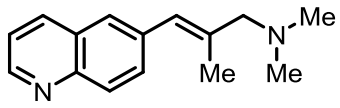
14 was synthesized from 3-(prop-1-yn-1-yl)thiophene (0.2 mmol, 24.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (25.4 mg, 70% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 5.6, 2.4 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 1H), 7.13 (d, *J* = 5.2 Hz, 1H), 6.63 (s, 1H), 3.66 (s, 2H), 2.83 (s, 6H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 129.9, 128.5, 126.4, 125.9, 125.2, 67.9, 43.4, 17.2.

HRMS (ESI) calculated for $C_{10}H_{16}NS$ $(M+H)^+$ 182.0998, found 182.0996.



(*E*)-*N*,*N*,2-Trimethyl-3-(quinolin-6-yl)prop-2-en-1-amine (15)

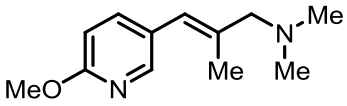
15 was synthesized from 6-(prop-1-yn-1-yl)quinoline (0.2 mmol, 33.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (34.0 mg, 75% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.69 (s, 1H), 7.65 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38 (dd, *J* = 8.2, 4.4 Hz, 1H), 6.58 (s, 1H), 3.02 (s, 2H), 2.29 (s, 6H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.2, 138.1, 136.4, 136.0, 131.2, 129.1, 128.3, 127.2, 126.9, 121.4, 69.5, 45.5, 17.0.

HRMS (ESI) calculated for $C_{15}H_{19}N_2$ $(M+H)^+$ 227.1543, found 227.1551.



(*E*)-3-(6-Methoxypyridin-3-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (16)

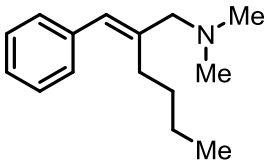
16 was synthesized from 2-methoxy-5-(prop-1-yn-1-yl)pyridine (0.2 mmol, 29.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (32.2 mg, 78% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz 1H), 6.29 (s, 1H), 3.94 (s, 3H), 2.95 (s, 2H), 2.25 (s, 6H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 147.0, 139.1, 136.9, 127.0, 123.7, 110.3, 69.5, 53.6, 45.5, 16.9.

HRMS (ESI) calculated for $C_{12}H_{19}N_2O$ $(M+H)^+$ 207.1492, found 207.1500.



(*E*)-2-Benzylidene-*N*,*N*-dimethylhexan-1-amine (17)

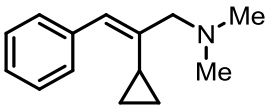
17 was synthesized from hex-1-yn-1-ylbenzene (0.2 mmol, 31.6 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (36.9 mg, 85% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 6.41 (s, 1H), 2.93 (s, 2H), 2.31 – 2.26 (m, 2H), 2.24 (s, 6H), 1.51 – 1.41 (m, 2H), 1.37 – 1.26 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.2, 128.8, 128.2, 127.5, 126.3, 66.8, 45.7, 30.6, 29.4, 23.0, 14.1.

HRMS (ESI) calculated for $C_{15}H_{24}N$ $(M+H)^+$ 218.1903, found 218.1894.



(*E*)-2-Cyclopropyl-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (18)

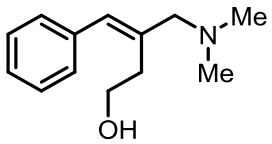
18 was synthesized from (cyclopropylethynyl)benzene (0.2 mmol, 28.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (32.1 mg, 80% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.20 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.46 (s, 1H), 2.77 (s, 2H), 2.23 (s, 6H), 1.75 – 1.82 (m, 1H), 0.74 – 0.68 (m, 2H), 0.62 – 0.66 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.0, 129.3, 128.0, 126.3, 65.2, 45.6, 13.4, 6.8.

HRMS (ESI) calculated for $C_{14}H_{20}N$ $(M+H)^+$ 202.1590, found 202.1595.



(*E*)-3-((Dimethylamino)methyl)-4-phenylbut-3-en-1-ol (19)

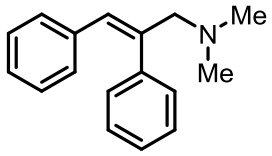
19 was synthesized from trimethyl((4-phenylbut-3-yn-1-yl)oxy)silane (0.2 mmol, 43.6 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. Automatic deprotection of TMS group occurred during purification by flash column chromatography. The title compound was isolated as a colorless oil (38.0 mg, 92% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.24 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.46 (s, 1H), 3.72 (t, *J* = 4.8 Hz, 2H), 2.99 (s, 2H), 2.55 (t, *J* = 4.8 Hz, 2H), 2.32 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.2, 132.2, 129.0, 128.4, 127.0, 68.9, 62.3, 44.6, 35.9.

HRMS (ESI) calculated for $C_{13}H_{20}NO$ $(M+H)^+$ 206.1539, found 206.1533.



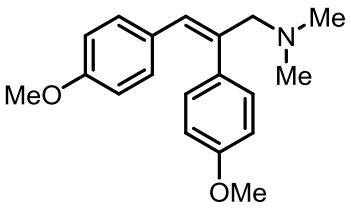
(*E*)-*N*,*N*-Dimethyl-2,3-diphenylprop-2-en-1-amine (20)

20 was synthesized from 1,2-diphenylethyne (0.2 mmol, 35.6 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (47.5 mg, 89% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 3H), 7.23 – 7.21 (m, 2H), 7.11 – 7.08 (m, 3H), 6.98 – 6.96 (m, 2H), 6.60 (s, 1H), 3.27 (s, 2H), 2.28 (d, *J* = 2.4 Hz, 6H).

HRMS (ESI) calculated for $C_{17}H_{19}N$ $(M+H)^+$ 238.1590, found 238.1598. Spectral data are identical to those in the reported literature.[10]



(*E*)-2,3-Bis(4-methoxyphenyl)-*N*,*N*-dimethylprop-2-en-1-amine (21)

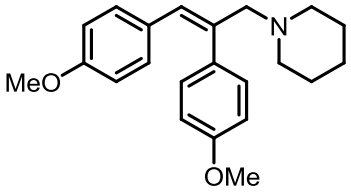
21 was synthesized from 1,2-bis(4-methoxyphenyl)ethyne (0.2 mmol, 47.6 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (47.5 mg, 80% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 6.49 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.24 (s, 2H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.3, 137.2, 132.8, 130.5, 129.9, 129.9, 128.4, 114.2, 113.5, 68.9, 55.3, 55.3, 45.5.

HRMS (ESI) calculated for $C_{19}H_{24}NO_2$ $(M+H)^+$ 298.1802, found 298.1811.



(*E*)-1-(2,3-Bis(4-methoxyphenyl)allyl)piperidine (22)

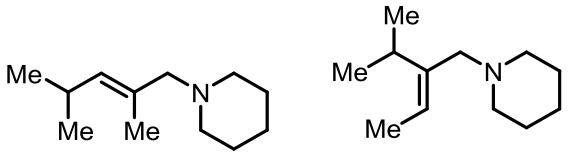
22 was synthesized from 1,2-bis(4-methoxyphenyl)ethyne (0.2 mmol, 47.6 mg) and aminal **S34** (0.5 mmol, 91.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (58.0 mg, 86% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.48 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.20 (s, 2H), 2.44 (brs, 4H), 1.59 – 1.54 (m, 4H), 1.47 – 1.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.3, 132.4, 129.5, 129.1, 129.0, 113.1, 112.5, 66.9, 54.3, 54.3, 53.6, 25.0, 23.5.

HRMS (ESI) calculated for $C_{22}H_{28}NO_2$ $(M+H)^+$ 338.2115, found 338.2120.



23 **23'**

(*E*)-1-(2,4-Dimethylpent-2-en-1-yl)piperidine (23)

23 was synthesized from 4-methylpent-2-yne (0.2 mmol, 16.4 mg) and aminal **S34** (0.5 mmol, 91.0 mg) according to the general procedure, the regioselectivity is 7:1, which was detected by crude ^{1}H NMR. The title compound was isolated as a colorless oil (18.5 mg, 51% yield).

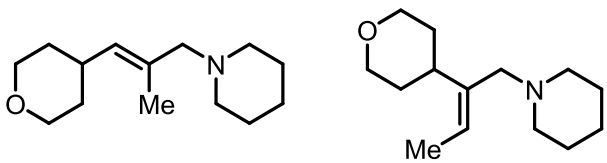
R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR of **23** (400 MHz, $CDCl_3$) 5.46 (d, *J* = 9.6 Hz, 1H), 3.54 (s, 2H), 2.91 – 2.54 (m, 5H), 2.00 – 1.90 (m, 6H), 1.84 (d, *J* = 1.6 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 6H).

^{1}H NMR of **23'** (400 MHz, $CDCl_3$) δ 5.83 (q, *J* = 7.2 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 7.2 Hz, 6H).

^{13}C NMR of **23** (100 MHz, $CDCl_3$) δ 146.1, 122.0, 66.0, 53.4, 27.6, 22.6, 22.4, 22.0, 20.5, 15.3.

HRMS (ESI) calculated for $C_{12}H_{24}N$ $(M+H)^+$ 182.1903, found 182.1893.



24 **24'**

(*E*)-1-(2-Methyl-3-(tetrahydro-2H-pyran-4-yl)allyl)piperidine (24)

24 was synthesized from 4-(prop-1-yn-1-yl)tetrahydro-2H-pyran (0.2 mmol, 24.8 mg) and aminal **S34** (0.5 mmol, 91.0 mg) according to the general procedure, the regioselectivity is 7:1, which was detected by crude ^{1}H NMR. The title compound

was isolated as a colorless oil (28.5 mg, 64% yield).

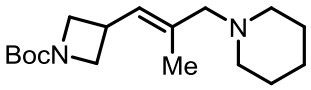
R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR of 24 (400 MHz, $CDCl_3$) δ 5.21 (d, *J* = 8.8 Hz, 1H), 3.97 – 3.92(m, 2H), 3.44 (td, *J* = 11.6, 2.4 Hz, 2H), 2.98 (s, 2H), 2.53 – 2.43 (m, 5H), 1.73 (d, *J* = 1.2 Hz, 3H), 1.70 – 1.64 (m, 4H), 1.55 – 1.38 (m, 6H).

^{1}H NMR of 24' (400 MHz, $CDCl_3$) δ 4.40 (q, *J* = 7.2 Hz, 1H).

^{13}C NMR of **24** (100 MHz, $CDCl_3$) δ 133.9, 129.2, 66.8, 66.6, 53.4, 33.3, 31.7, 24.2, 23.0, 14.5.

HRMS (ESI) calculated for $C_{14}H_{26}NO$ $(M+H)^+$ 224.2009, found 224.2015.



***tert*-Butyl**

(*E*)-3-(2-methyl-3-(piperidin-1-yl)prop-1-en-1-yl)azetidine-1-carboxylate (25)

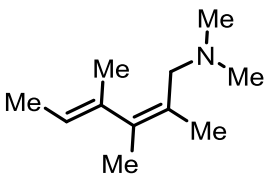
25 was synthesized from *tert*-butyl 3-(prop-1-yn-1-yl)azetidine-1-carboxylate (0.2 mmol, 39.0 mg) and aminal **S34** (0.5 mmol, 91.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (31.8 mg, 54% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, *J* = 8.4 Hz, 1H), 4.15 (dd, *J* = 8.4, 8.4 Hz, 2H), 3.68 (dd, *J* = 5.6, 6.0 Hz, 2H), 3.47 – 3.41 (m, 1H), 3.40 (s, 2H), 2.90 (brs, 4H), 1.91 – 1.85 (m, 4H), 1.76 (d, *J* = 0.8 Hz, 3H), 1.63 – 1.59 (m, 2H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 135.5, 128.6, 79.4, 67.7, 54.7, 28.6, 27.2, 26.1, 24.7, 15.7.

HRMS (ESI) calculated for $C_{17}H_{31}N_2O_2$ $(M+H)^+$ 295.2380, found 295.2388.



(2*Z*,4*E*)-*N*,*N*,2,3,4-Pentamethylhexa-2,4-dien-1-amine (26)

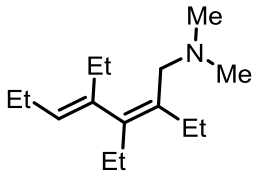
26 was synthesized from 2-butyne (0.2 mmol, 10.8 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (10.9 mg, 65% yield). The stereochemistry of *Z*,*E*-**26** was confirmed by NOE analysis.

R_f (CH_2Cl_2 / MeOH = 20/1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (q, *J* = 6.4 Hz, 1H), 3.72 (s, 2H), 2.79 (s, 6H), 1.84 (s, 3H), 1.80 (s, 3H), 1.67 (s, 3H), 1.66 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 136.7, 123.3, 117.7, 62.0, 43.3, 19.0, 15.9, 15.7, 13.6.

HRMS (ESI) calculated for $C_{11}H_{21}NNa$ $(M+Na)^+$ 190.1566, found 190.1569.



(2*Z*,4*E*)-2,3,4-Triethyl-*N*,*N*-dimethylhepta-2,4-dien-1-amine (27)

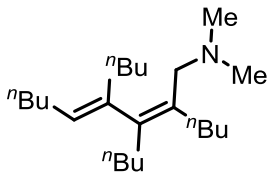
27 was synthesized from 3-hexyne (0.2 mmol, 16.4 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (12.0 mg, 54% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (t, *J* = 7.2 Hz, 1H), 3.31 (s, 2H), 2.44 (s, 6H), 2.21 (q, *J* = 7.6 Hz, 2H), 2.15 – 2.06 (m, 6H), 1.04 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.89 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 139.1, 131.6, 125.5, 59.4, 43.6, 24.1, 23.1, 21.1, 21.1, 14.6, 13.3, 13.0, 12.9.

HRMS (ESI) calculated for $C_{15}H_{29}NNa$ $(M+Na)^+$ 246.2192, found 246.2195.



(2*Z*,4*E*)-2,3,4-Tributyl-*N*,*N*-dimethylnona-2,4-dien-1-amine (28)

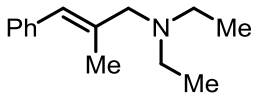
28 was synthesized from 5-decyne (0.2 mmol, 27.6 mg) and aminal **2** (0.5 mmol, 51.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (19.1 mg, 57% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (t, *J* = 7.2 Hz, 1H), 2.92 (s, 2H), 2.17 – 2.11(m, 2H), 2.14 (s, 6H), 2.08 – 2.01(m, 6H), 1.39 – 1.22 (m, 16H), 0.92 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 139.4, 132.3, 128.5, 60.6, 45.6, 32.3, 31.2, 30.9, 30.8, 30.5, 30.2, 28.6, 27.6, 23.4, 23.1, 23.0, 22.7, 14.4, 14.2, 14.2.

HRMS (ESI) calculated for $C_{23}H_{45}NNa$ $(M+Na)^+$ 358.3444, found 358.3446.

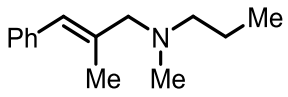


(*E*)-*N*,*N*-Diethyl-2-methyl-3-phenylprop-2-en-1-amine (29)

29 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S29** (0.5 mmol, 79.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (33.0 mg, 81% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.48 (s, 1H), 3.19 (s, 2H), 2.67 (q, *J* = 7.2 Hz, 4H), 1.95 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 6H). Spectral data are identical to those in the reported literature.[11]



(*E*)-*N*,2-Dimethyl-3-phenyl-*N*-propylprop-2-en-1-amine (30)

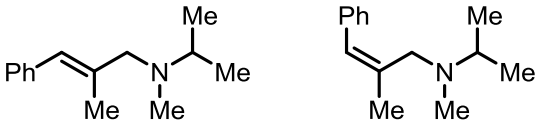
30 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S30** (0.5 mmol, 79.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (30.5 mg, 75% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.44 (s, 1H), 3.07 (s, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 1.94 (s, 3H), 1.57 (tq, *J* = 7.6, 15.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.1, 129.0, 128.2, 127.2, 126.3, 67.7, 59.7, 42.5, 20.7, 16.9, 12.1.

HRMS (ESI) calculated for $C_{14}H_{21}NNa$ $(M+Na)^+$ 226.1566, found 226.1572.



E *Z*

(*E*)-*N*-Isopropyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (31)

31 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S31** (0.5 mmol, 79.0 mg) according to the general procedure. The ratio of *E/Z* is 5:1, which was determined by crude ^{1}H NMR. The title compound was isolated as a colorless oil (35.0 mg, 86% yield).

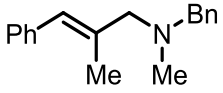
R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR of *E* (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.23 – 7.19 (m, 1H), 6.46 (s, 1H), 3.12 (s, 2H), 3.00 (sept, *J* = 6.4 Hz, 1H), 2.26 (s, 3H), 1.95 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 6H).

^{1}H NMR of *Z* (400 MHz, $CDCl_3$) 6.41 (s, 1H).

^{13}C NMR of *E* (100 MHz, $CDCl_3$) δ 138.4, 137.5, 129.0, 128.2, 126.8, 126.2, 62.7, 52.9, 36.9, 17.8, 16.7.

HRMS (ESI) calculated for $C_{14}H_{21}NNa$ $(M+Na)^+$ 226.1566, found 226.1574.



(*E*)-*N*-Benzyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine(32)

32 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S32** (0.5 mmol, 127.0 mg) according to the general procedure. The title compound was isolated

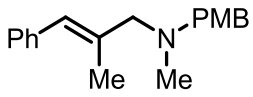
as a colorless oil (36.1 mg, 72% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 7H), 7.27 – 7.24 (m, 2H), 7.23 – 7.28 (m, 1H), 6.47 (s, 1H), 3.51 (s, 2H), 3.04 (s, 2H), 2.19 (s, 3H), 1.94 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.2, 137.1, 129.0, 128.3, 128.2, 127.4, 127.0, 126.3, 67.3, 62.0, 42.4, 16.8.

HRMS (ESI) calculated for $C_{18}H_{22}N$ $(M+H)^+$ 252.1747, found 252.1742.



(*E*)-*N*-(4-Methoxybenzyl)-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (33)

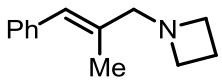
33 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S33** (0.5 mmol, 170.5 mg) according to the general procedure. The title compound was isolated as a colorless oil (40.0 mg, 71% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.4.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 6H), 7.21 – 7.17 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.45 (s, 1H), 3.79 (s, 3H), 3.45 (s, 2H), 3.01 (s, 2H), 2.17 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 138.2, 137.1, 131.7, 130.2, 129.0, 128.2, 127.4, 126.3, 113.7, 67.1, 61.4, 55.4, 42.3, 16.8.

HRMS (ESI) calculated for $C_{19}H_{24}NO$ $(M+H)^+$ 282.1582, found 282.1588.



(*E*)-1-(2-Methyl-3-phenylallyl)azetidine (34)

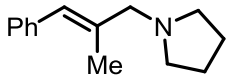
34 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S34** (0.5 mmol, 63.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (29.2 mg, 78% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.27 – 7.19 (m, 3H), 6.44 (s, 1H), 3.42 (td, *J* = 7.2, 1.6 Hz, 4H), 3.23 (s, 2H), 2.21 (p, *J* = 7.2 Hz, 2H), 1.88 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 133.9, 129.0, 128.2, 128.0, 126.6, 68.0, 55.2, 17.5, 17.0.

HRMS (ESI) calculated for $C_{13}H_{18}N$ $(M+H)^+$ 188.1434, found 188.1439.

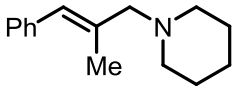


(*E*)-1-(2-Methyl-3-phenylallyl)pyrrolidine (35)

35 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S35** (0.5 mmol, 77.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (34.2 mg, 85% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.27 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.49 (s, 1H), 3.28 (s, 2H), 2.73 – 2.70 (m, 4H), 1.97 (s, 3H), 1.91 – 1.87 (m, 4H). Spectral data are identical to those in the reported literature.[12]

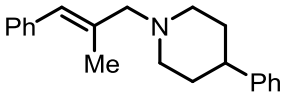


(*E*)-1-(2-Methyl-3-phenylallyl)piperidine (36)

36 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S36** (0.5 mmol, 91.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (38.7 mg, 90% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 6.41 (s, 1H), 2.96 (s, 2H), 2.37 – 2.31 (m, 4H), 1.90 (s, 3H), 1.61 – 1.56 (m, 4H), 1.47 – 1.41(m, 2H). Spectral data are identical to those in the reported literature.[11]



(*E*)-1-(2-Methyl-3-phenylallyl)-4-phenylpiperidine (37)

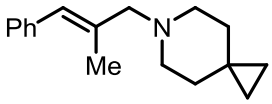
37 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S37** (0.5 mmol, 167.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (39.6 mg, 68% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 6H), 7.25 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 6.45 (s, 1H), 3.05 – 3.01 (m, 4H), 2.55 – 2.47 (m, 1H), 2.04 (td, *J* = 10.8, 4.0 Hz, 2H), 1.94 (d, *J* = 1.2 Hz, 3H), 1.84 – 1.78 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 138.2, 136.5, 129.0, 128.5, 128.2, 127.3, 127.1, 126.3, 126.2, 68.5, 54.6, 43.0, 33.7, 17.1.

HRMS (ESI) calculated for $C_{21}H_{26}N$ $(M+H)^+$ 292.2060, found 292.2062.



(*E*)-6-(2-Methyl-3-phenylallyl)-6-azaspiro[2.5]octane (38)

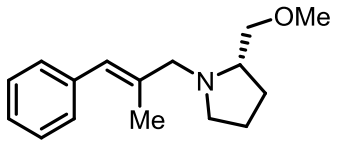
38 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S38** (0.5 mmol, 117.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (37.1 mg, 77% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.21 – 7.17 (m, 1H), 6.43 (s, 1H), 3.03 (s, 2H), 2.45 – 2.42 (m, 4H), 1.92 (d, *J* = 0.8 Hz, 3H), 1.42 – 1.33 (m, 4H), 0.26 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.7, 129.0, 128.2, 127.2, 126.3, 68.4, 53.5, 35.4, 17.8, 17.1, 11.6.

HRMS (ESI) calculated for $C_{17}H_{24}N$ $(M+H)^+$ 242.1903, found 242.1897.



(*S*,*E*)-2-(Methoxymethyl)-1-(2-methyl-3-phenylallyl)pyrrolidine (39)

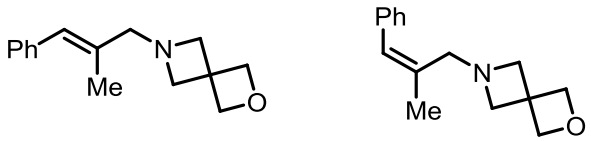
39 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S39** (0.5 mmol, 121.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (24.5 mg, 50% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 6.43 (s, 1H), 3.55 – 3.51 (m, 1H), 3.44 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.36 (s, 3H), 3.28 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.07 – 3.02 (m, 1H), 2.95 – 2.91 (m, 1H), 2.68 – 2.61 (m, 1H), 2.24 – 2.17 (m, 1H), 1.92 (d, *J* = 1.2 Hz, 3H), 1.79 – 1.62 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.9, 129.0, 128.2, 126.3, 126.2, 76.7, 65.4, 63.5, 59.3, 54.9, 28.9, 23.2, 17.1.

HRMS (ESI) calculated for $C_{16}H_{24}NO$ $(M+H)^+$ 246.1852, found 246.1855.



E *Z*

(*E*)-6-(2-Methyl-3-phenylallyl)-2-oxa-6-azaspiro[3.3]heptane (40)

40 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S40** (0.5 mmol, 105.0 mg) according to the general procedure. The ratio of *E*/*Z* is 5:1 was determined by crude ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. The title compound was isolated as a colorless oil (20.2 mg, 44% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.3.

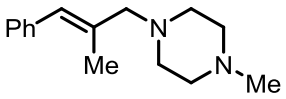
^{1}H NMR of *E* (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.25 – 7.13 (m, 3H), 6.36 (s, 1H), 4.76 (s, 4H), 3.38 (s, 4H), 3.04 (s, 2H), 1.83 (d, *J* = 1.6 Hz, 3H).

^{1}H NMR of *Z* (400 MHz, $CDCl_3$) 6.41 (s, 1H), 4.68 (s, 4H), 3.27 (s, 4H), 3.16 (s, 2H), 1.89 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR of *E* (100 MHz, $CDCl_3$) δ 138.0, 135.3, 129.0, 128.2, 126.7, 126.4, 81.6, 68.5, 64.0, 39.3, 17.0.

^{13}C NMR of *Z* (100 MHz, $CDCl_3$) 137.9, 136.1, 129.1, 128.5, 128.1, 81.5, 64.1, 60.1, 39.2, 23.0.

HRMS (ESI) calculated for $C_{15}H_{20}NO$ $(M+H)^+$ 230.1539, found 230.1534.



(*E*)-1-Methyl-4-(2-methyl-3-phenylallyl)piperazine (41)

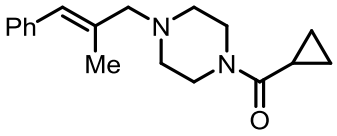
41 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S41** (0.5 mmol, 106.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (23.0 mg, 50% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.27 (d, 2H), 7.22 – 7.18 (m, 1H), 6.43 (s, 1H), 3.01 (s, 2H), 2.46 (brs, 8H), 2.30 (s, 3H), 1.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 136.0, 129.0, 128.2, 127.6, 126.5, 68.0, 55.4, 53.3, 46.2, 17.0.

HRMS (ESI) calculated for $C_{15}H_{23}N_2$ $(M+H)^+$ 231.1856, found 231.1861.



(*E*)-Cyclopropyl(4-(2-methyl-3-phenylallyl)piperazin-1-yl)methanone (42)

42 was synthesized from 1-phenylpropyne (0.2 mmol, 23.2 mg) and aminal **S42** (0.5 mmol, 160.0 mg) according to the general procedure. The title compound was isolated as a colorless oil (36.9 mg, 65% yield).

R_f (CH_2Cl_2 / MeOH = 20/1): 0.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 6.43 (s, 1H), 3.72 – 3.64 (m, 4H), 3.03 (d, *J* = 0.8 Hz, 2H), 2.47 – 2.42 (m,

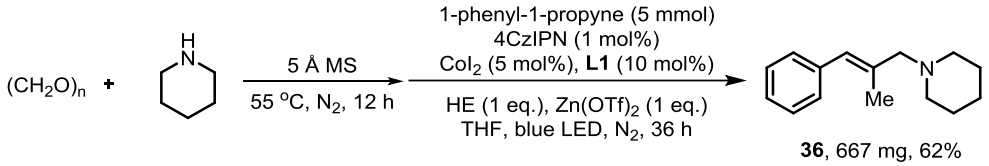
4H), 1.92 (d, *J* = 1.6 Hz, 3H), 1.77 – 1.70 (m, 1H), 1.00 – 0.97 (m, 2H), 0.78 – 0.73 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 137.9, 135.5, 129.0, 128.3, 128.0, 126.5, 67.9, 53.5, 53.0, 45.7, 42.4, 21.5, 16.9, 11.1, 7.5.

HRMS (ESI) calculated for $C_{18}H_{25}N_2O$ $(M+H)^+$ 285.1961, found 285.1958.

VI. Synthetic Applications

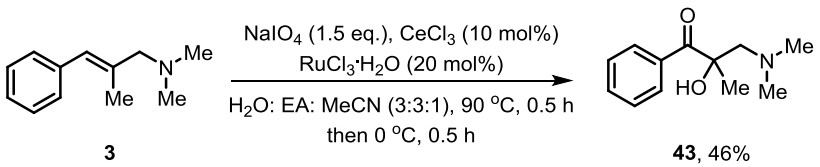
1. Gram scale reaction



36, 667 mg, 62%

To an oven-dried 100 mL Schlenk tube containing a stirrer bar was added paraformaldehyde (16 mmol, 480.0 mg), piperidine (32 mmol, 2.7 g), and 5 Å MS (2.3 g) in neat under nitrogen atmosphere. The Schlenk tube was stirred at 55 ℃ for 12 h. The Schlenk tube was cooled to room temperature and taken into the glovebox. Then, to the Schlenk tube was added 4CzIPN (0.05 mmol, 39.4 mg), CoI_2 (0.25 mmol, 78.2 mg), tri(3,5-dimethylphenyl)phosphine **(L1**, 0.5 mmol, 173.0 mg), Hantzsch ester (HE, 5 mmol, 1.3 g), $Zn(OTf)_2$ (5 mol, 1.8 g), 1-phenyl-1-propyne (5 mmol, 580.8 mg) and dry THF(25 mL). The Schlenk tube was taken out from glovebox and stirred at room temperature under irradiation with a 5 W blue LED for 36 h. The mixture was concentrated in vacuo and purified by flash column chromatography (CH_2Cl_2 / MeOH = 40:1 – 20:1) to give the desired product **36** as a colorless oil (667 mg, 62% yield).

2. Selective oxidation of the double bond in allyl amine 3

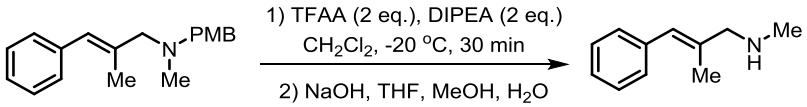


3 **43**, 46%

To an oven-dried 10 mL Schlenk tube containing a stirrer bar was added $NaIO_4$ (0.75

mmol, 160.4 mg), $CeCl_3$ (0.05 mmol, 12.3 mg) in water (1 mL) and heated until a bright yellow suspension was formed. After cooling to 0 ℃, EtOAc (2.5 mL) and MeCN (3 mL) were added and the mixture was stirred for 5 min, $RuCl_3 \cdot H_2O$ (0.1 mmol, 22.5 mg) was added slowly and the mixture was stirred for 5 min. A solution of the allyl amine **3** (0.5 mmol, 87.5 mg) in EtOAc (EA, 0.5 mL) was added and the mixture was stirred until all starting material was consumed. The mixture was washed with saturated Na_2SO_3 solution (10 mL), EtOAc (10 mL), and the organic layer was then collected, dried over anhydrous sodium sulfate, filtered, concentrated under reduced pressure and purified by flash column chromatography (CH_2Cl_2 / MeOH = 20:1) to give **43** (47.6 mg, 46%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 2H), 7.55 – 7.51 (m, 1H), 7.46 – 7.42 (m, 2H), 3.29 (d, *J* = 12.8 Hz, 1H), 2.45 (d, *J* = 12.8 Hz, 1H), 2.24 (s, 6H), 1.50 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.0, 135.8, 132.6, 130.1, 128.6, 128.2, 125.0, 78.2, 67.0, 46.8, 27.1. **HRMS** (ESI) calculated for $C_{14}H_{21}N_2$ $(M+H)^+$ 230.1151, found 230.1160.

3. Selective deprotection of PMB group in allyl amine 33

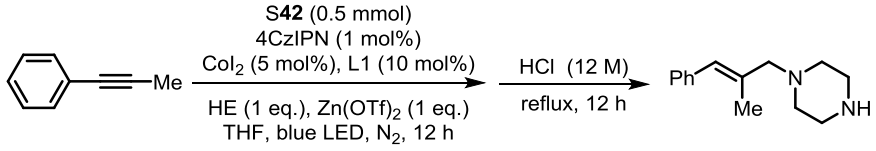


33 **44**, 84%

To a mixture of **33** (0.4 mmol, 112.4 mg) and diisopropylethylamine (0.8 mmol, 103.4 mg) in dichloromethane (4 mL) was added trifluoroacetic anhydride (0.8 mml, 168.0 mg) dropwise over 5 min at －20 ℃. After being stirred at the same temperature for 30 min, the reaction mixture was concentrated under the reduced pressure. The crude product was filtered through short-pad silica gel, eluted with ethyl acetate / hexanes = 1 / 15. The filtration was concentrated under reduced pressure. To a solution of the product in THF (3 mL), H_2O (1 mL) and MeOH (1 mL) was added NaOH (0.8 mmol, 32 mg). After being stirred at room temperature for 1 h, a saturated aqueous solution of sodium bicarbonate (3 mL) was added. The layers were separated and the aqueous layer was extracted with dichloromethane (15 mL). The organic mixture was then collected, dried over anhydrous sodium sulfate, filtered,

concentrated under reduced pressure and purified by flash column chromatography (CH_2Cl_2 / MeOH = 20:1) to give **44** (54.1 mg, 84% for 2 steps) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.28 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.44 (s, 1H), 3.29 (s, 2H), 2.46 (s, 3H), 1.90 (d, *J* = 1.2 Hz, 3H), 1.62 (s, 1H). Spectral data are identical to those in the reported literature.[11]

4. Synthesis of the intermediate of drug candidate

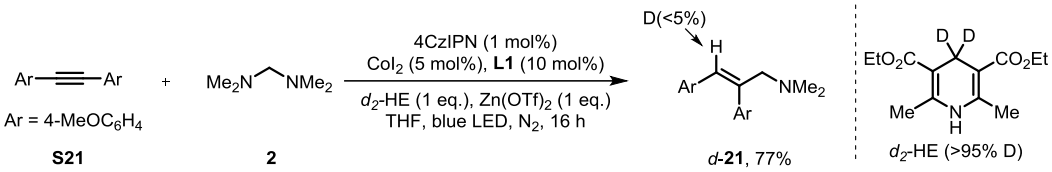


1 **45**, 45%

To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.2 mmol, 50.6 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), **1** (0.2 mmol, 23.2 mg), **S42** (0.5 mmol, 160.0 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. The tube was stirred at room temperature under irradiation with a 5 W blue LED at room temperature for 16 h. Under nitrogen atmosphere, HCl (12 M, 1 mL) was added in the tube and the reaction was stirred at 100 ℃ for 12 h. The tube was cooled to room temperature and extracted with dichloromethane (10 mL)，saturated sodium hydroxide solution (10 mL, PH >10), dried over anhydrous sodium sulfate. After filtration and concentration under reduced pressure, and purified by flash column chromatography (CH_2Cl_2 / MeOH = 15:1) to give the desired product **45** (19.4 mg, 45%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 6.42 (s, 1H), 2.99 (d, *J* = 1.2 Hz, 2H), 2.90 (t, *J* = 4.8 Hz, 4H), 2.40 (brs, 4H), 1.90 (d, *J* = 1.6 Hz, 3H), 1.87 (brs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.2, 135.9, 129.0, 128.2, 127.6, 126.3, 68.7, 54.8, 46.3, 16.9. **HRMS** (ESI) calculated for $C_{14}H_{21}N_2$ $(M+H)^+$ 217.1699, found 217.1704.

VII. Control Experiments and Mechanistic Studies

1. Deuterium labeling experiment with d_2-HE



To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (d_2-HE, >95% D, 0.2 mmol, 51.0 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), alkyne **S21** (0.2 mmol, 47.6 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, aminal **2** (0.5 mmol, 51.0 mg) was added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, CH_2Cl_2 / MeOH) to afford *d*-**21** (45.7 mg, 77%). **^{1}H NMR** of *d*-**21** showed that a trace amount of deuterium was incorporated into the *d*-**21** olefin site.

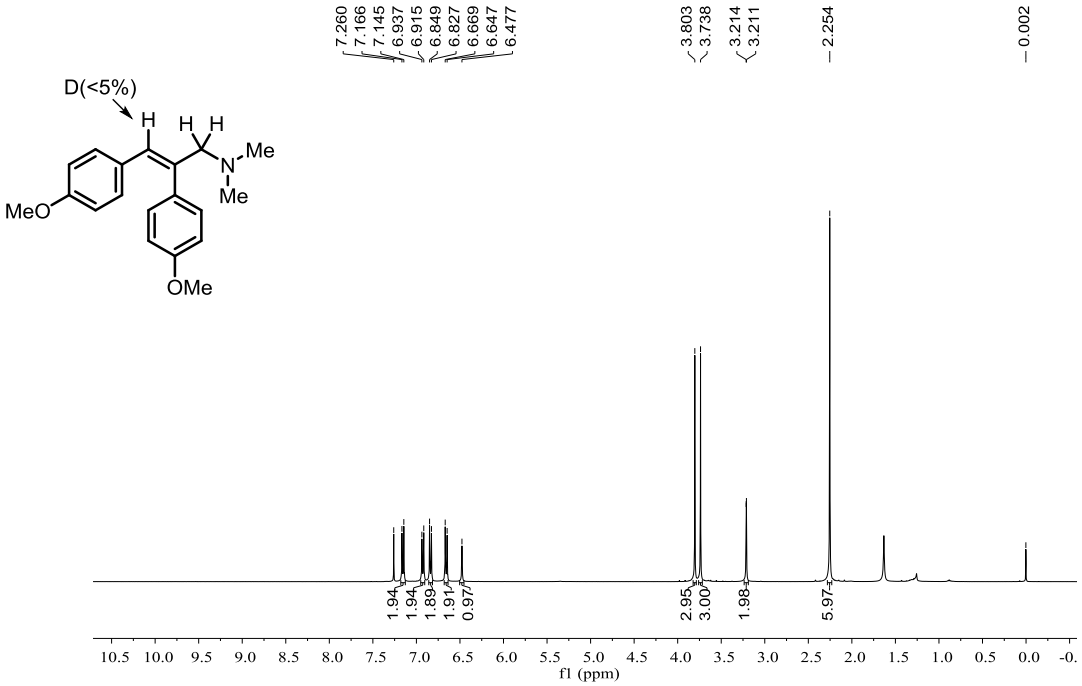
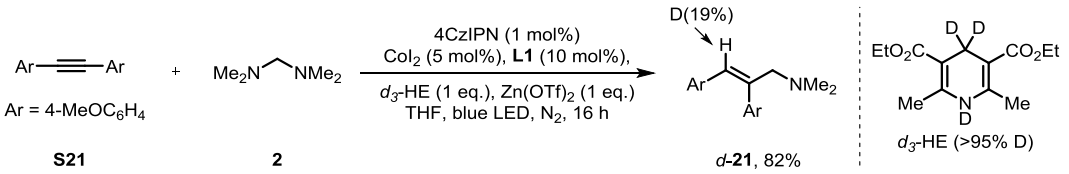


Figure S2. The ^{1}H NMR of *d*-**21** obtained in the control reaction with d_2-HE

2. Deuterium labeling experiment with d_3-HE



To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (d_3-HE, >95% D, 0.2 mmol, 51.0 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), alkyne **S21** (0.2 mmol, 47.6 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, aminal **2** (0.5 mmol, 51.0 mg) was added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED at room temperature for 16 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, CH_2Cl_2 / MeOH) to afford *d*-**21** (48.7 mg, 82%). ^{1}H NMR of *d*-**21** showed that a small amount of deuterium was incorporated into the *d*-**21** olefin site.

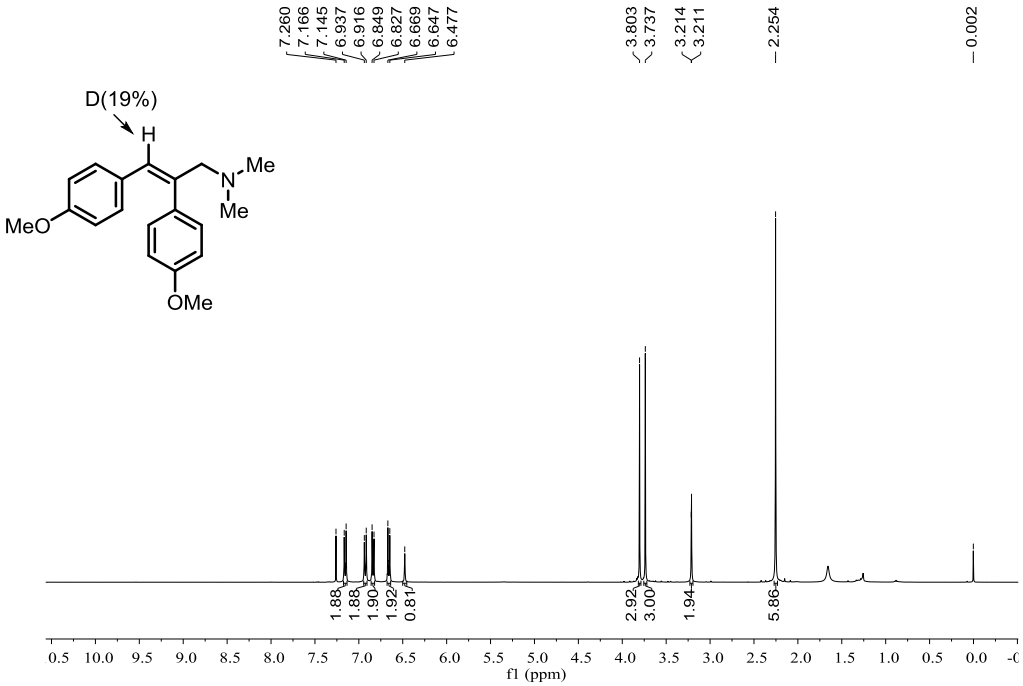
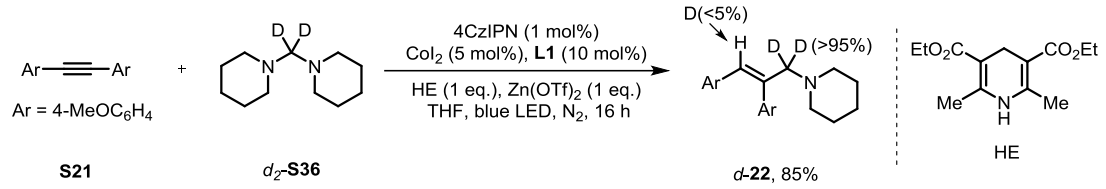


Figure S3. The ^{1}H NMR of *d*-**21** obtained in the control reaction with d_3-HE

3. Deuterium labeling experiment with d_2-S36



To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.2 mmol, 51.0 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), alkyne **S21** (0.2 mmol, 47.6 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, aminal *d*$_2$-**S36** (>99% D, 0.5 mmol, 92.0 mg) was added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, CH_2Cl_2 / MeOH) to afford *d*-**22** (57.6 mg, 85%). ^{1}H NMR of *d*-**22** showed that a small amount of deuterium was incorporated into the ***d*-22** olefin site.

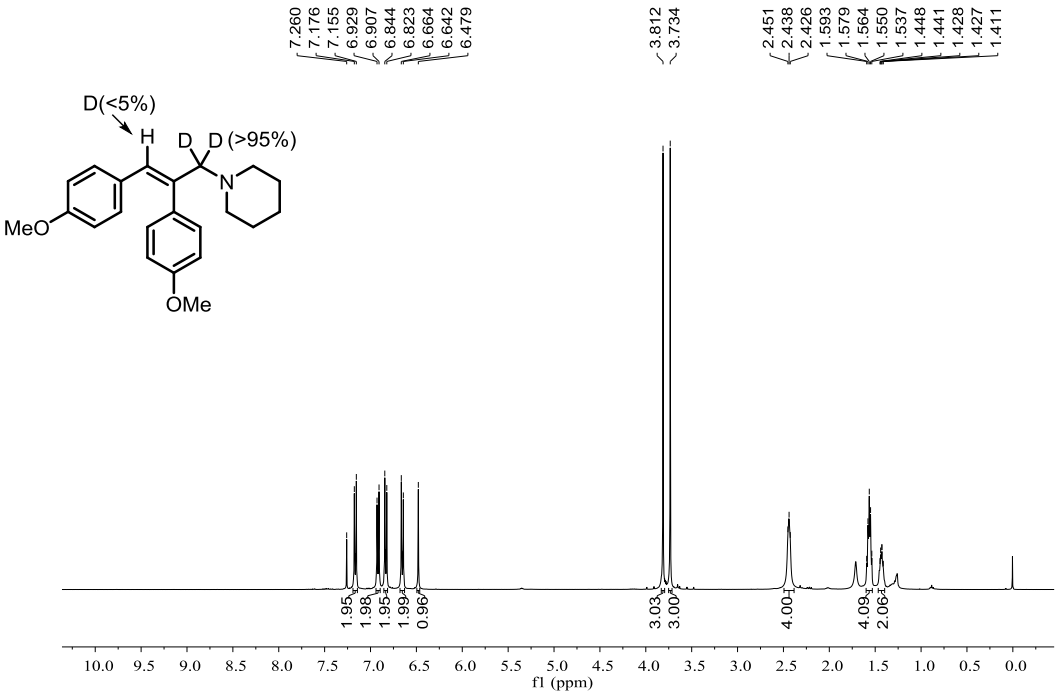
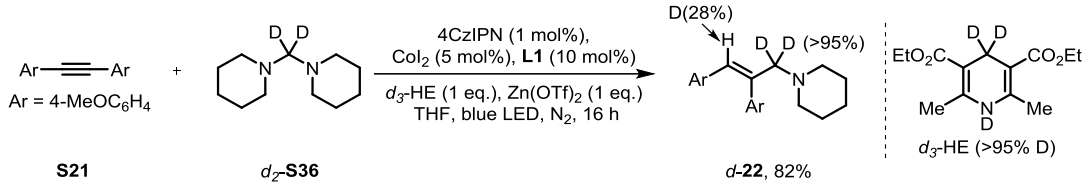


Figure S4. The ^{1}H NMR of *d*-**22** obtained in the control reaction with *d*$_2$-**S36**

4. Deuterium labeling experiment with *d*$_3$-HE and *d*$_2$-S36



To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (d_3-HE, >95% D) (0.2 mmol, 51.0 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), alkyne **S21** (0.2 mmol, 47.6 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, aminal d_2-**S36** (>99% D, 0.5 mmol, 92.0 mg) was sequentially added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (silica gel, CH_2Cl_2 / MeOH) to afford *d*-**22** (55.6 mg, 82%). ^{1}H NMR of *d*-**22** showed that more deuterium was incorporated into the ***d*-22** olefin site compared to previous experiments.

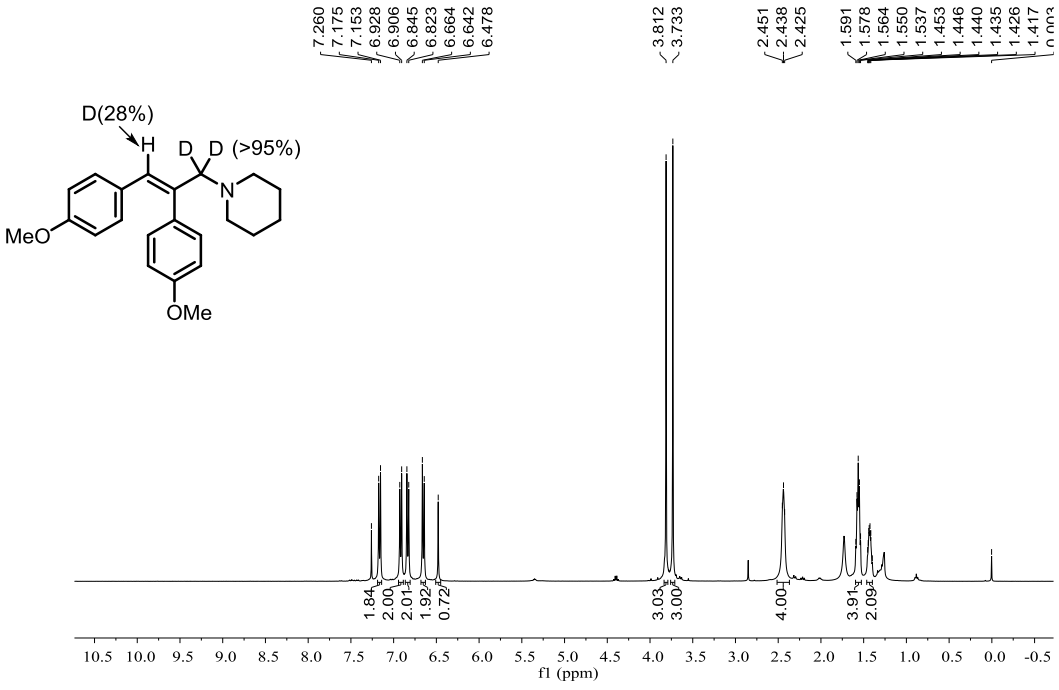
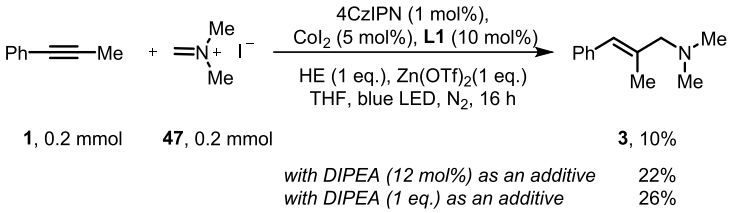


Figure S5. The ^{1}H NMR of *d*-**22** obtained in the control reaction with ***d*$_3$-HE** and d_2-**S36**

5. Control reactions with iminium ion 47

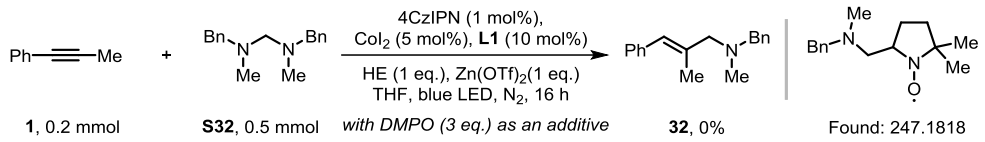


To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.2 mmol, 50.6 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), **47** (0.2 mmol, 36.8 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, alkyne **1** (0.2 mmol, 23.2 mg) was sequentially added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. The reaction was detected **3** (10% yield) by crude ^{1}H NMR. Then, in the above reaction was added DIPEA (12 mol%, 3.1 mg or 1 eq., 25.9 mg). After the reaction, we detected **3** (22% yield or 26% yield) by crude ^{1}H NMR.

6. Crossover experiment with both 47 and S32

To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.4 mmol, 101.2 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), **47** (0.25 mmol, 46.2 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, alkyne **1** (0.2 mmol, 23.2 mg), aminal **S32** (0.25 mmol, 63.5 mg) was sequentially added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. After the reaction, we detected **3** (20% yield) and **32** (44% yield) by crude ^{1}H NMR.

7. Radical inhibiting experiment



To an oven-dried 25 mL Schlenk tube containing a stirrer bar was added 4CzIPN (0.002 mmol, 1.6 mg), CoI_2 (0.01 mmol, 3.1 mg), tri(3,5-dimethylphenyl)phosphine (**L1**, 0.02 mmol, 6.9 mg), Hantzsch ester (HE, 0.2 mmol, 50.6 mg), $Zn(OTf)_2$ (0.2 mol, 72.7 mg), DMPO (0.6 mmol, 67.8 mg) and dry THF (1 mL). Then, the Schlenk tube was removed from glovebox. Under nitrogen atmosphere, alkyne **1** (0.2 mmol, 23.2 mg), aminal **S32** (0.5 mmol, 127.0 mg) was sequentially added into the tube. The tube was stirred at room temperature under irradiation with a 5 W blue LED for 16 h. After the reaction, we didn't detected **32** by TLC or GCMS. However, we detected the α–amino radical addition product with DMPO by HRMS (Cacl. 247.1810; found: 247.1818).

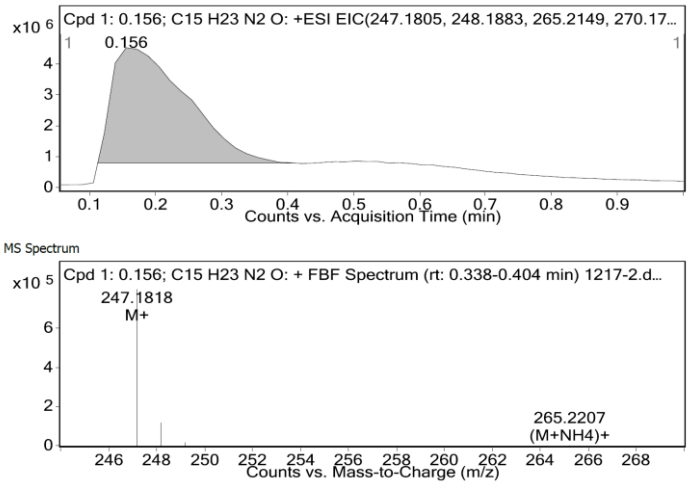


Figure S6. The proposed radical adducts

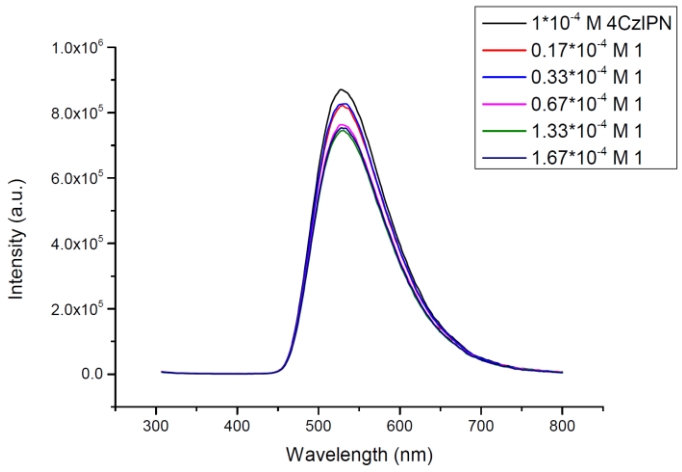
8. Stern-Volmer Fluorescence Quenching Experiments

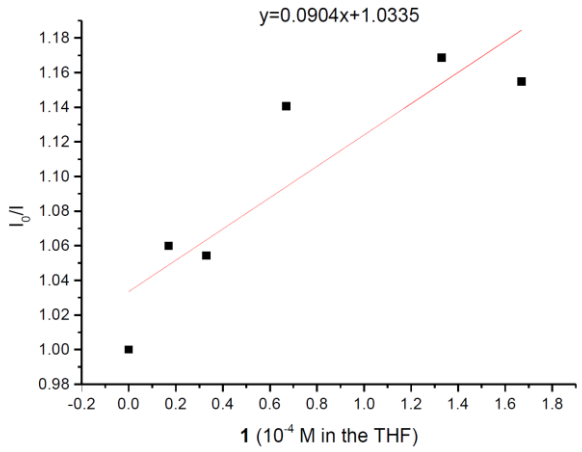
Fluorescence spectra were collected on Lengguang Tech.F97 Pro Fluorescence Spectrophotometer. All 4CzIPN solutions were excitedat 287 nm and the emission intensity was collected at 519 nm. In the glove box, photocatalyst 4CzIPN (7.9 mg, 0.01 mmol) was dissolvedin THF (100 mL) to set the concentration is $1*10^{-4}$ M. 1-Phenyl-1-propyne **1** (0.1 mmol, 11.6 mg) was dissolved in THF (25 mL) to set the

concentration is 4*10^{-3} M. *N*,*N*,*N'*,*N'*-tetramethylmethanediamine (20.4 mg, 0.2 mmol) was dissolved in THF (100 mL) to set the concentration is 2*10^{-3} M. CoI_2 (15.6 mg, 0.05 mmol) and tri(3,5-dimethylphenyl)phosphine (**L1**, 34.7 mg, 0.1 mmol) was dissolved in THF (25 mL) to set the concentration is 2*10^{-3}M. In the glove box, a screw-top quartz cuvette was charged with 3 mL 4CzIPNsolution (1*10^{-4}M). 0 μL,50.0 μL, 75.0 μL,100.0 μL, 200.0 μL, 250.0 μL of 1-phenyl-1-propyne; 0 μL,25.0 μL,50.0 μL, 100.0 μL, 200.0 μL, 250.0 μL of *N*,*N*,*N'*,*N'*-tetramethylmethanediamine; 0 μL, 25.0 μL,50.0 μL, 100.0 μL, 200.0 μL, 250.0 μL of CoI_2/**L1** was added to cuvetteand uniformly stirred. The emission spectra of the samples werecollected, respectively. Follow this method and makechanges to the amount to obtain the Stern–Volmer relationship in turn.

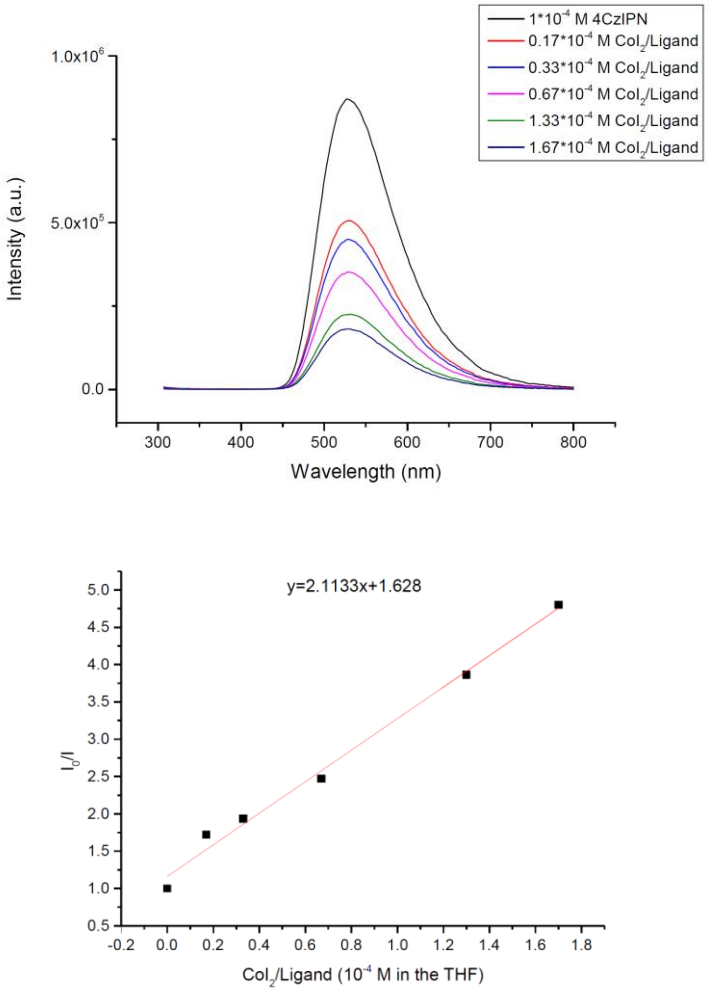
According to previous report of our group, 4CzIPN was not quenched by 1-phenyl-1-propyne, but it was quenched by Hantzsch ester (HE) in THF.[4]

(a) 4CzIPN quenched by 1-phenyl-1-propyne **(1)** in THF.



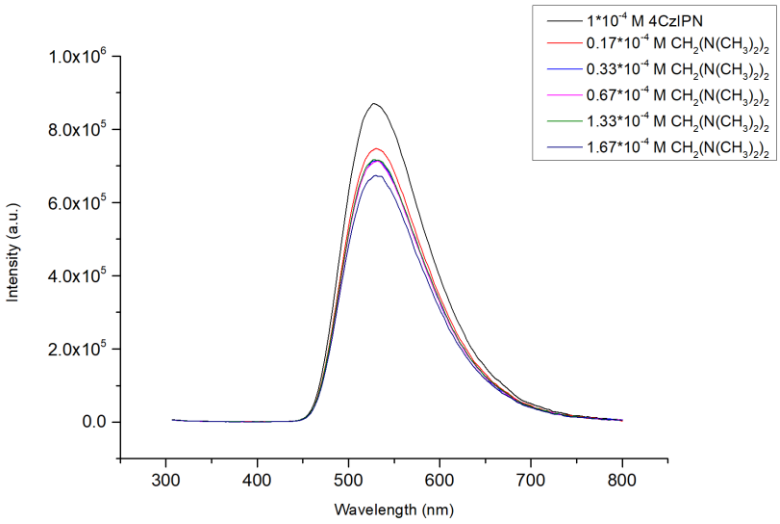


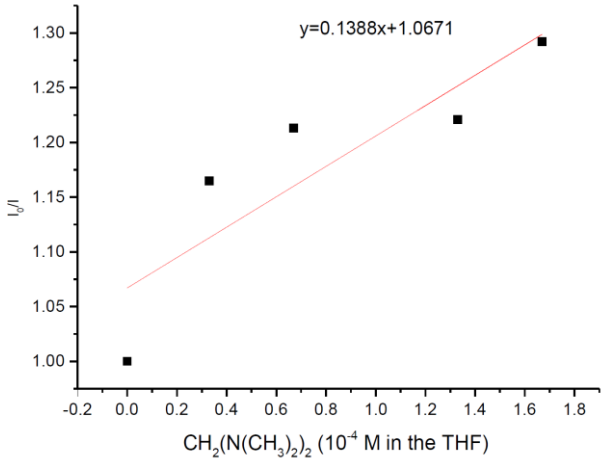
(b) 4CzIPN quenched by CoI_2/**L1** in THF.



The emission intensity of the catalyst 4CzIPN solution strongly affeceted by the gragual increase of the amount of CoI_2/**L1**

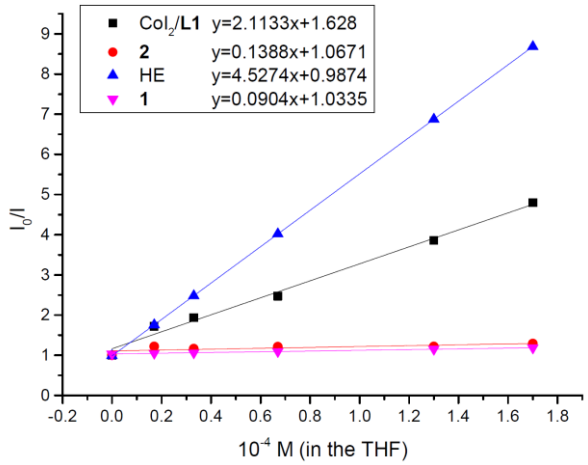
(c) 4CzIPN quenched by *N*,*N*,*N*',*N*'-tetramethylmethanediamine (**2**) in THF.





The emission intensity of the catalyst 4CzIPN solution slightly affected by the gradual increase of the amount of *N*,*N*,*N'*,*N'*-tetramethylmethanediamine.

(d) Stern−Volmer luminescence quenching (SV) study.



The emission intensity of the catalyst 4CzIPN solution was mainly affected by the gradual increase of the amount of CoI_2/**L1** and HE.

VIII. References

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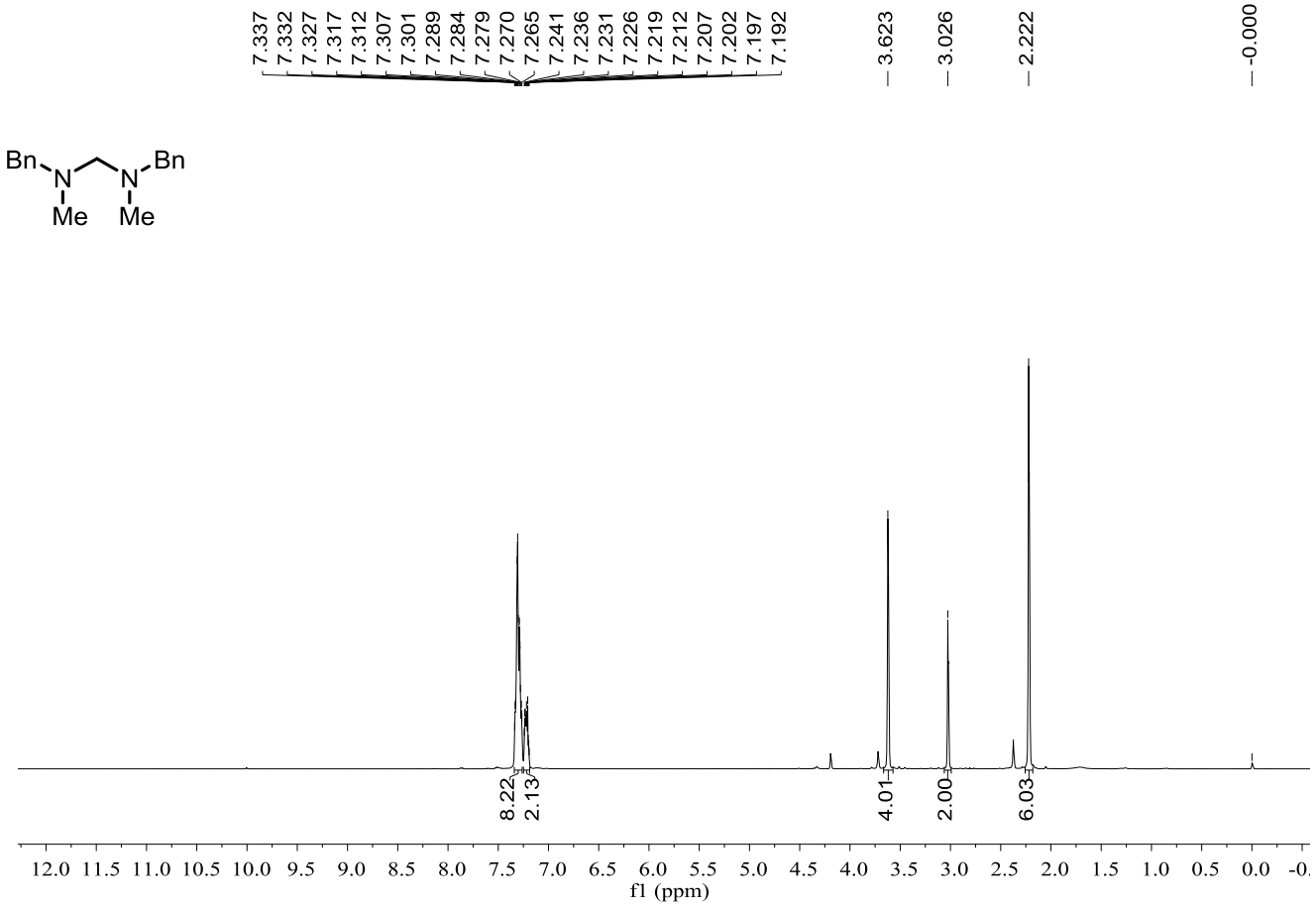
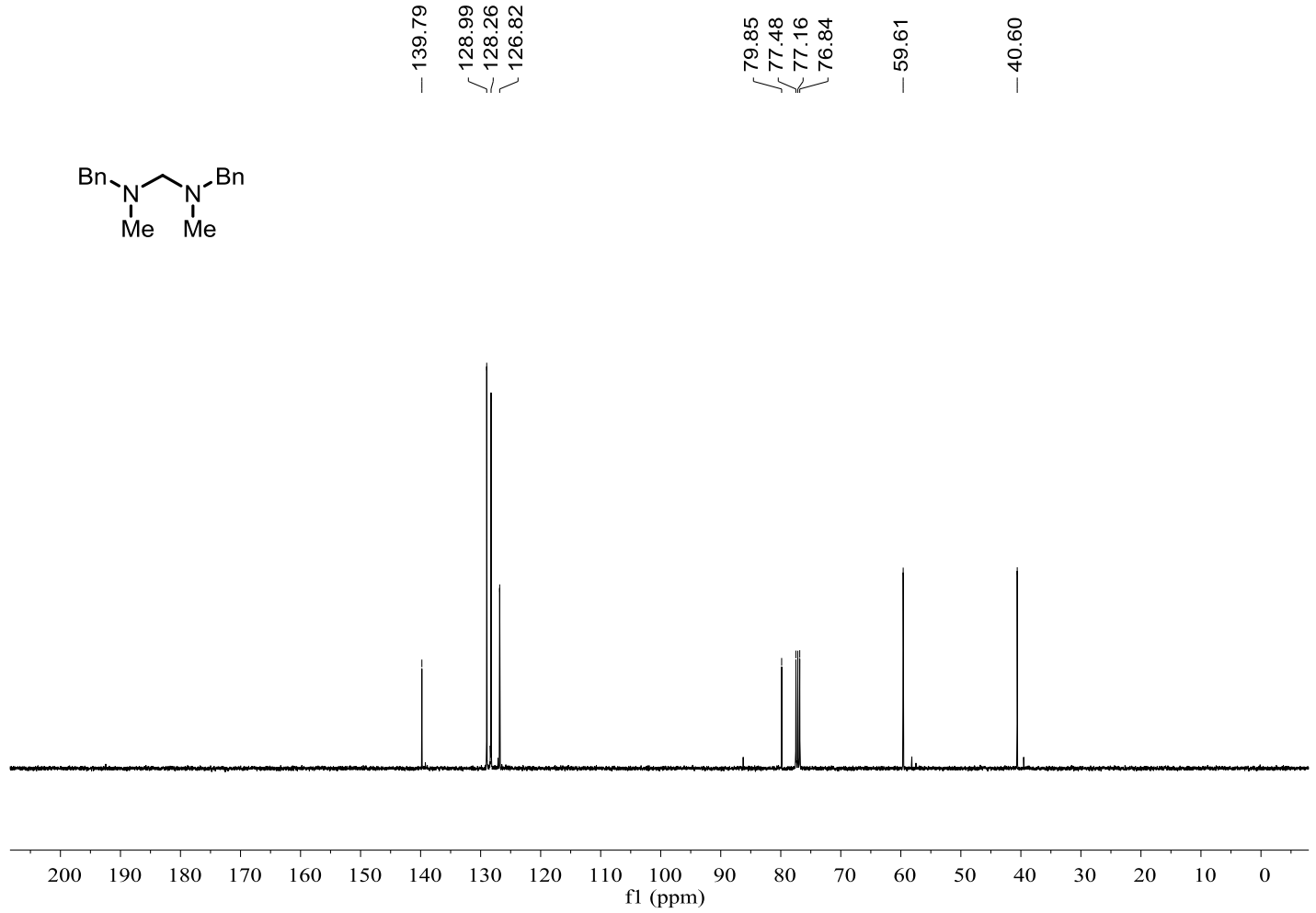
IX. NMR Spectra

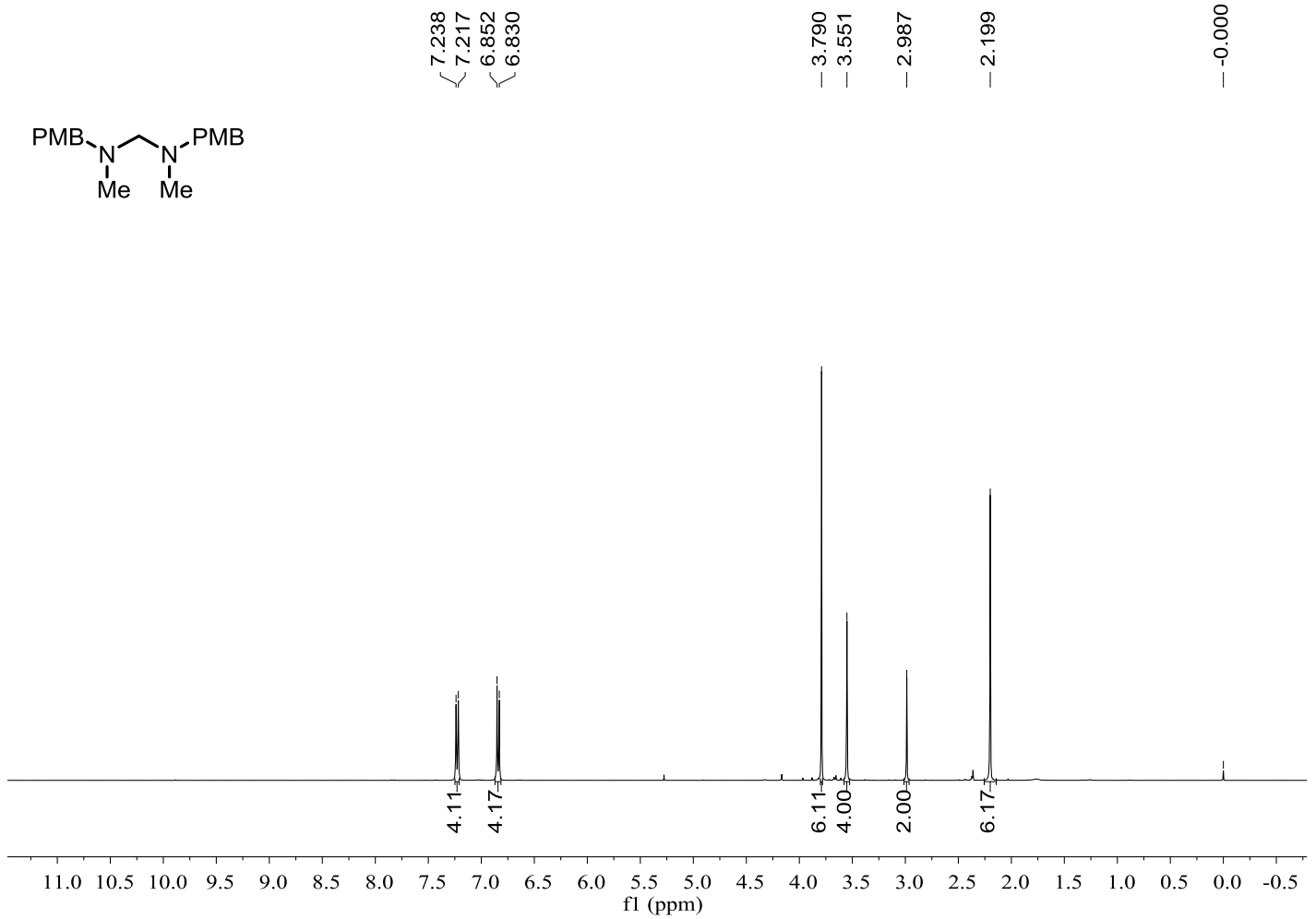
^{1}H NMR spectrum (400 M, $CDCl_3$) of *N,N'*-Dibenzyl-*N,N'*-dimethylmethanediamine (S32)



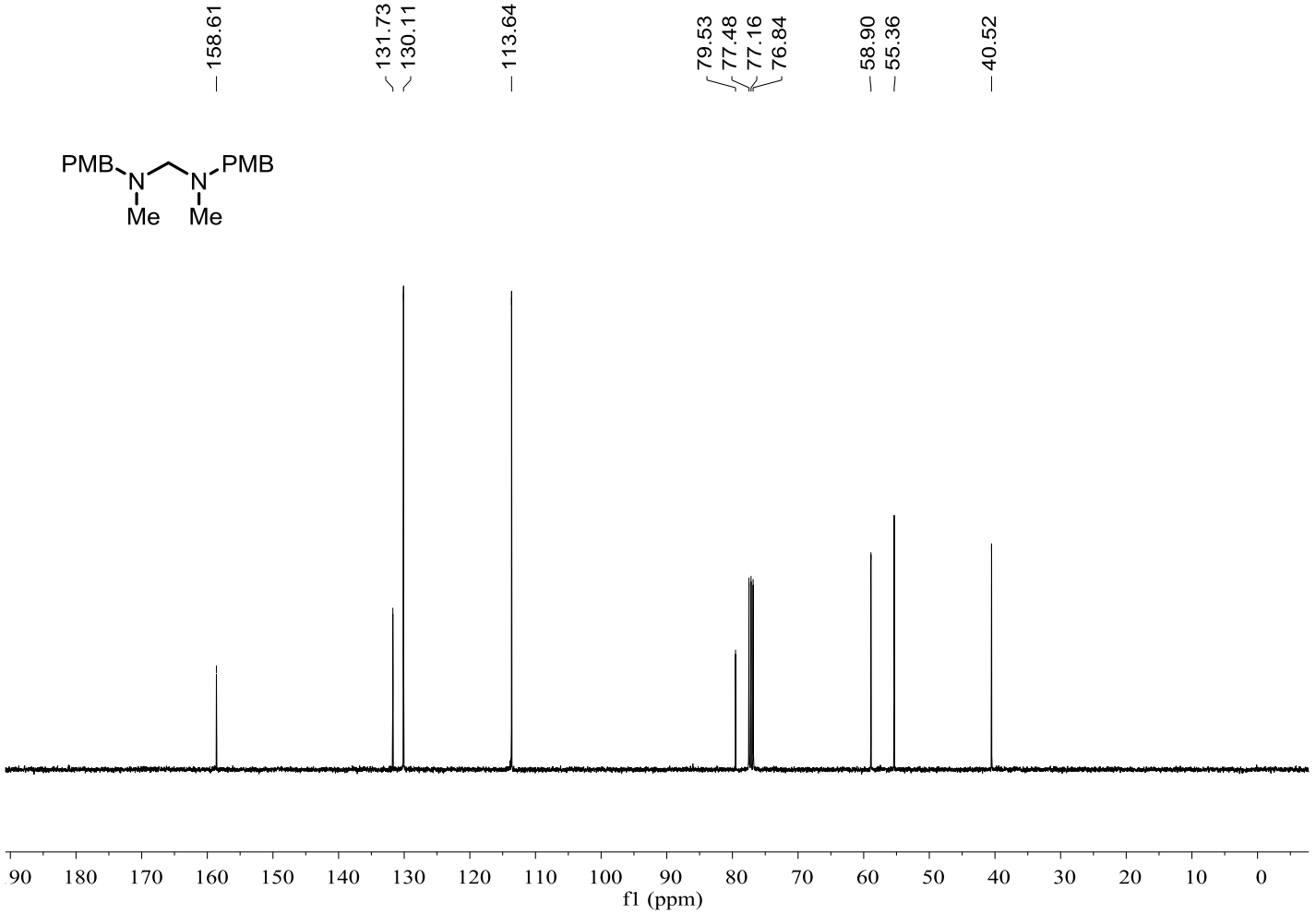
^{13}C NMR spectrum (100 M, $CDCl_3$) of *N,N′*-Dibenzyl-*N,N′*-dimethylmethanediamine (S32)



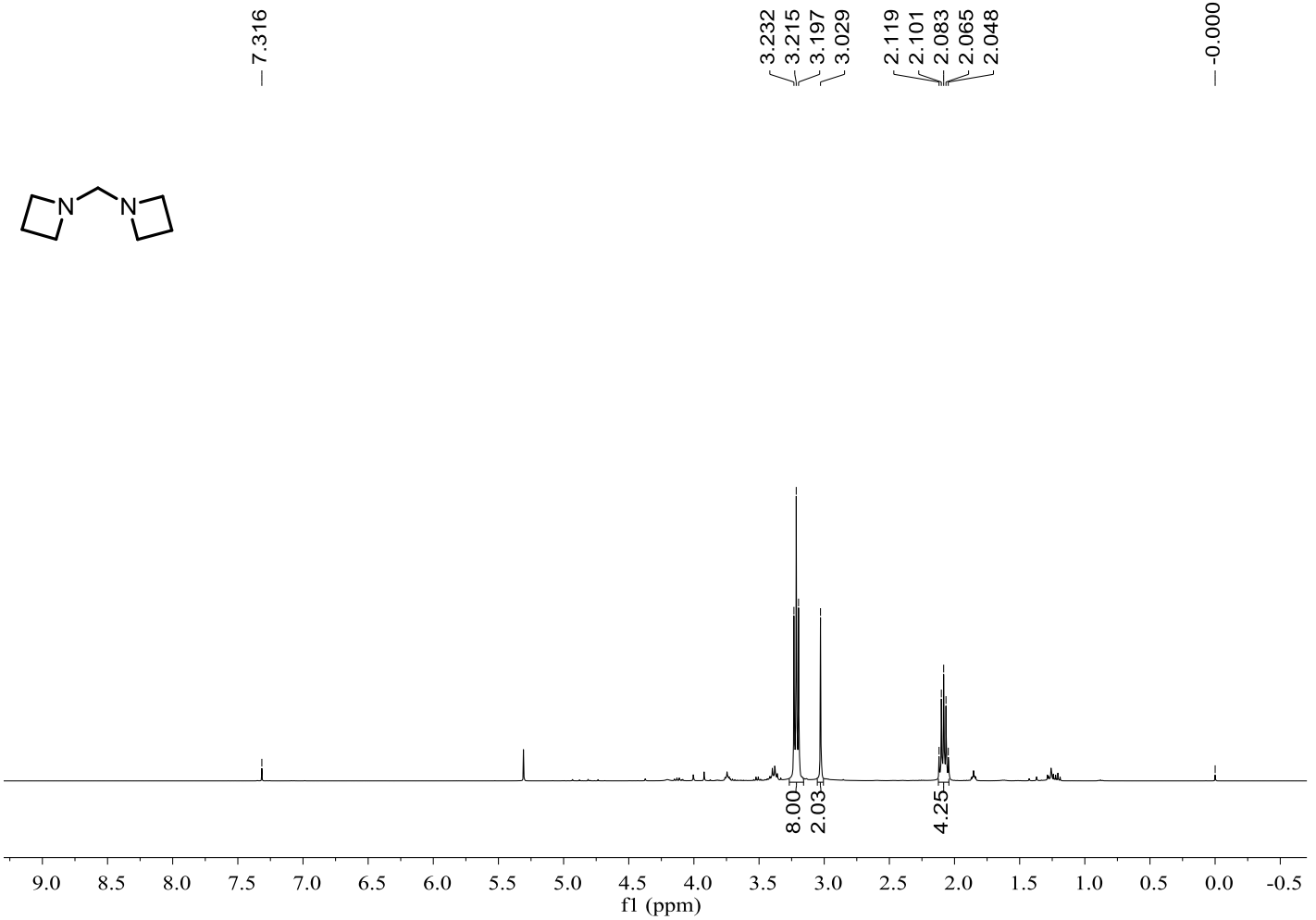
^{1}H NMR spectrum (400 M, $CDCl_3$) of *N,N′*-Bis(4-methoxybenzyl)-*N,N′*-dimethylmethanediamine (S33)



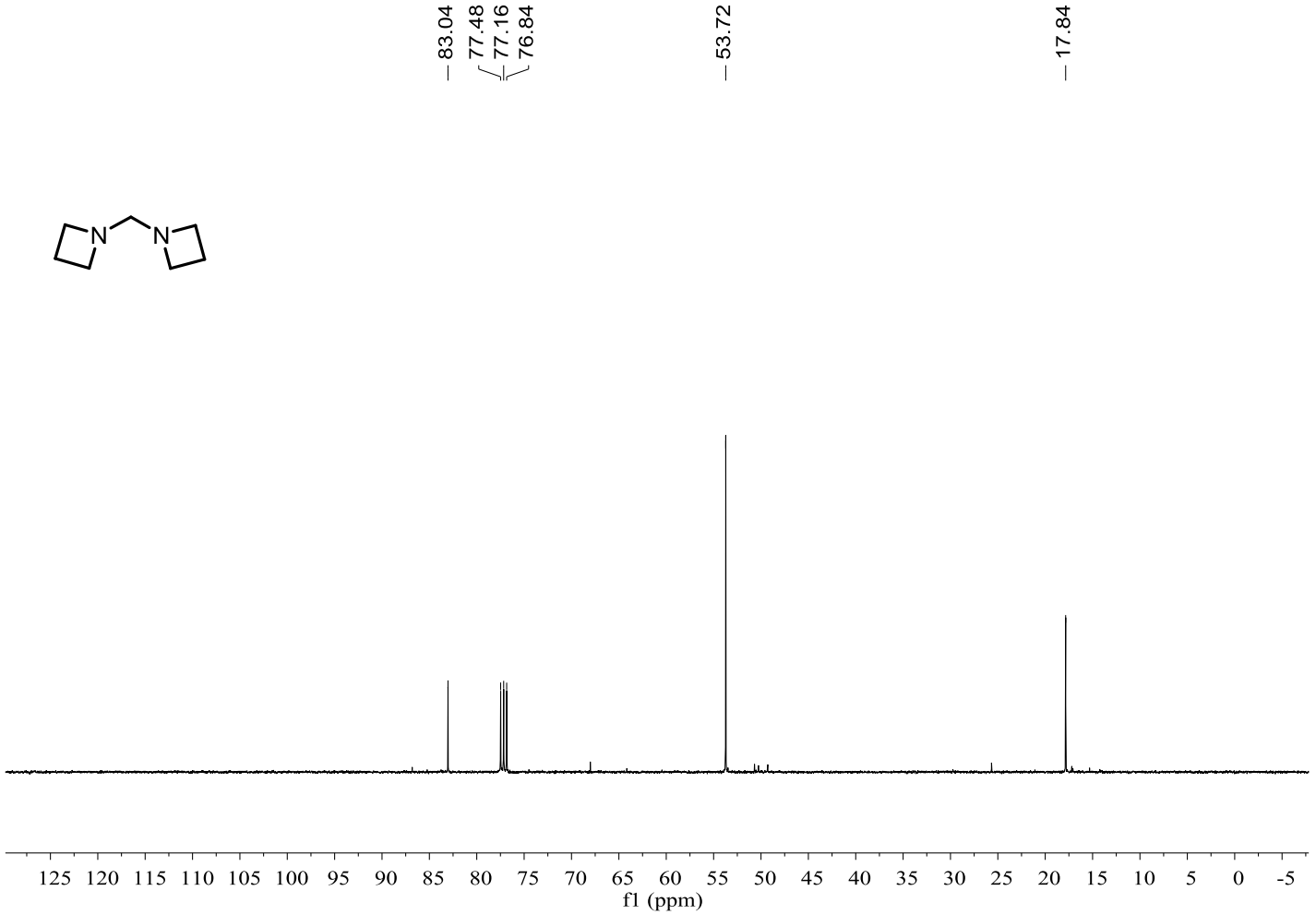
^{13}C NMR spectrum (100 M, $CDCl_3$) of *N,N'*-Bis(4-methoxybenzyl)-*N,N'*-dimethylmethanediamine (S33)



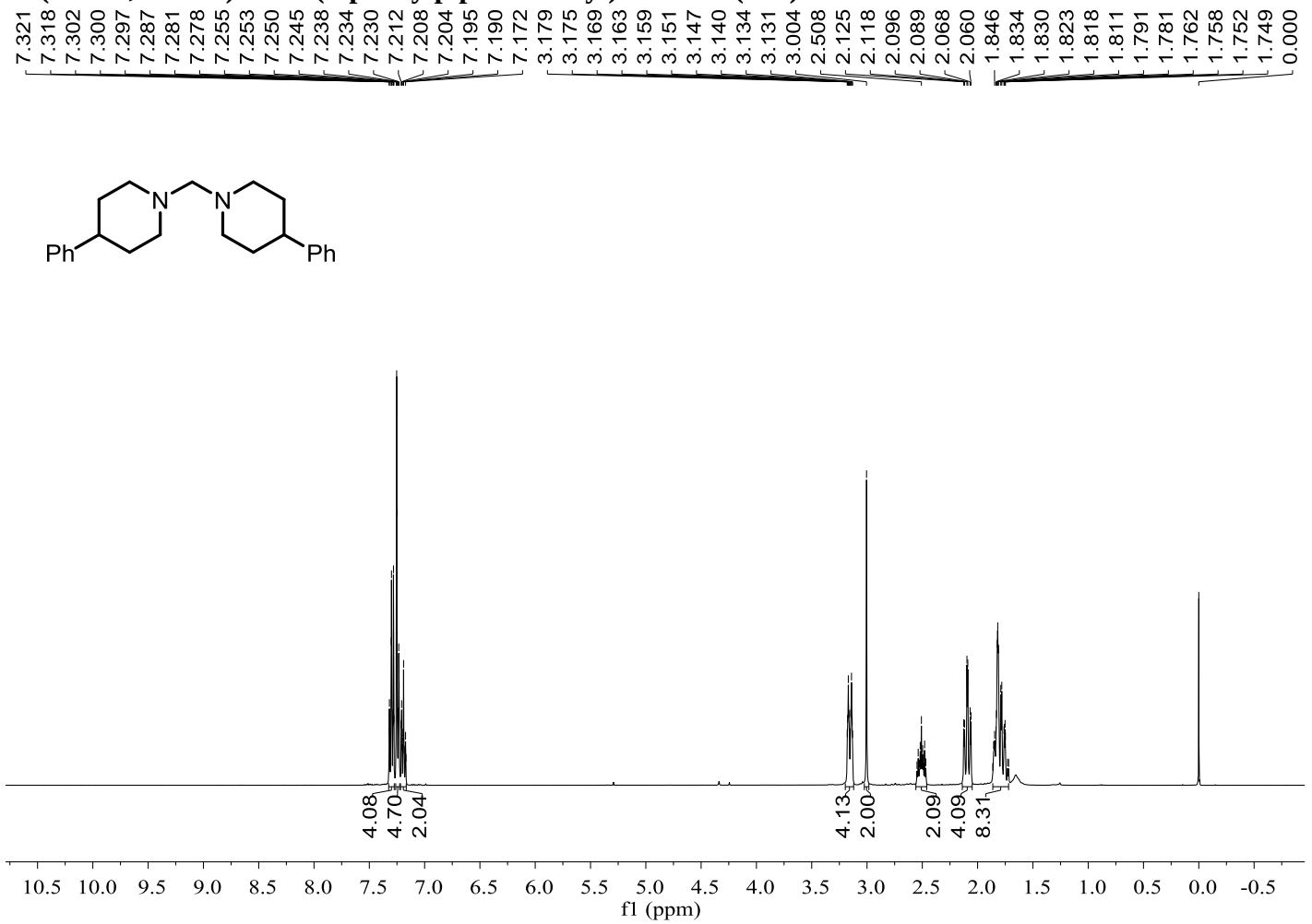
^{1}H NMR spectrum (400 M, $CDCl_3$) of Di(azetidin-1-yl)methane (S34)



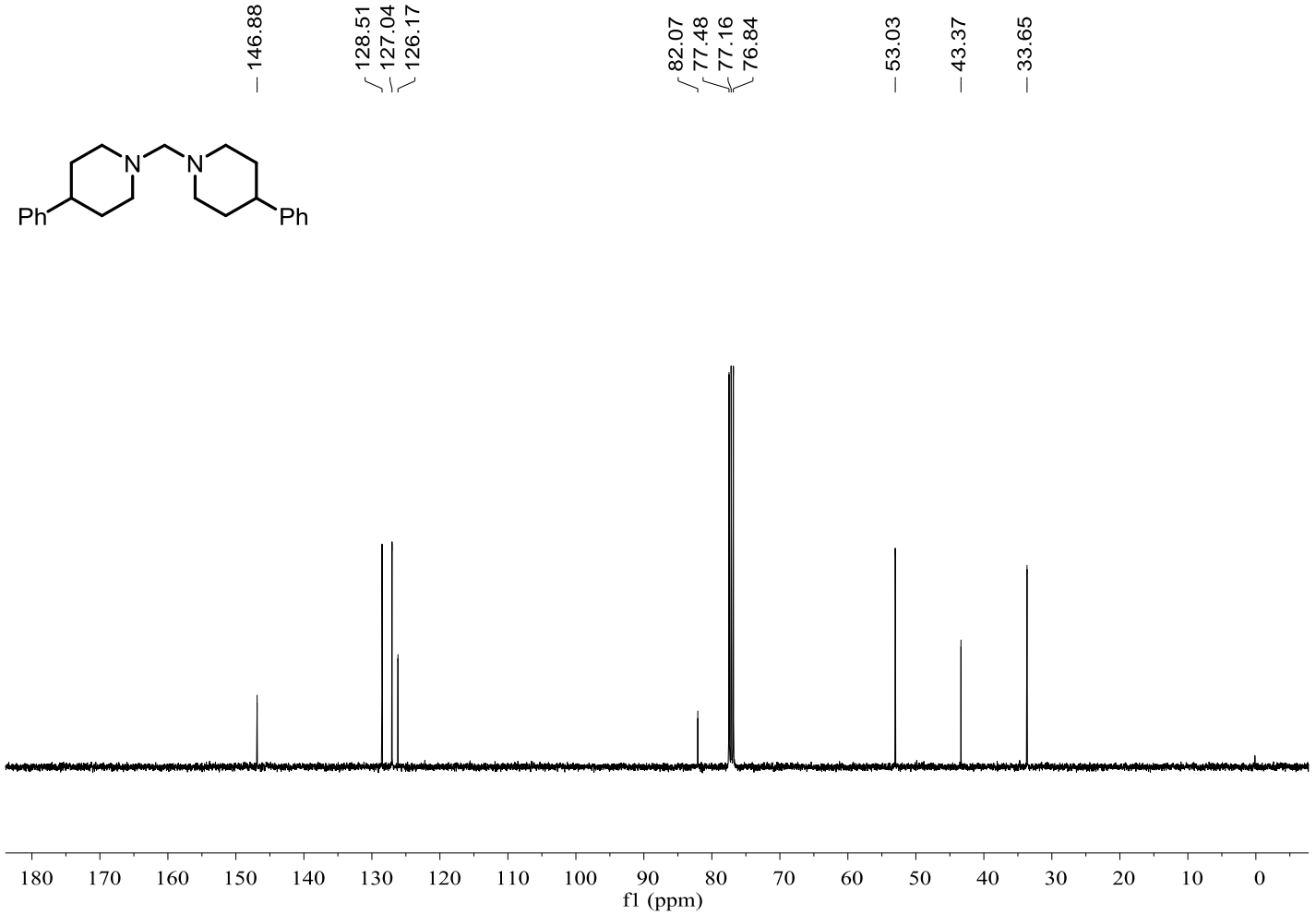
^{13}C NMR spectrum (100 M, $CDCl_3$) of Di(azetidin-1-yl)methane (S34)



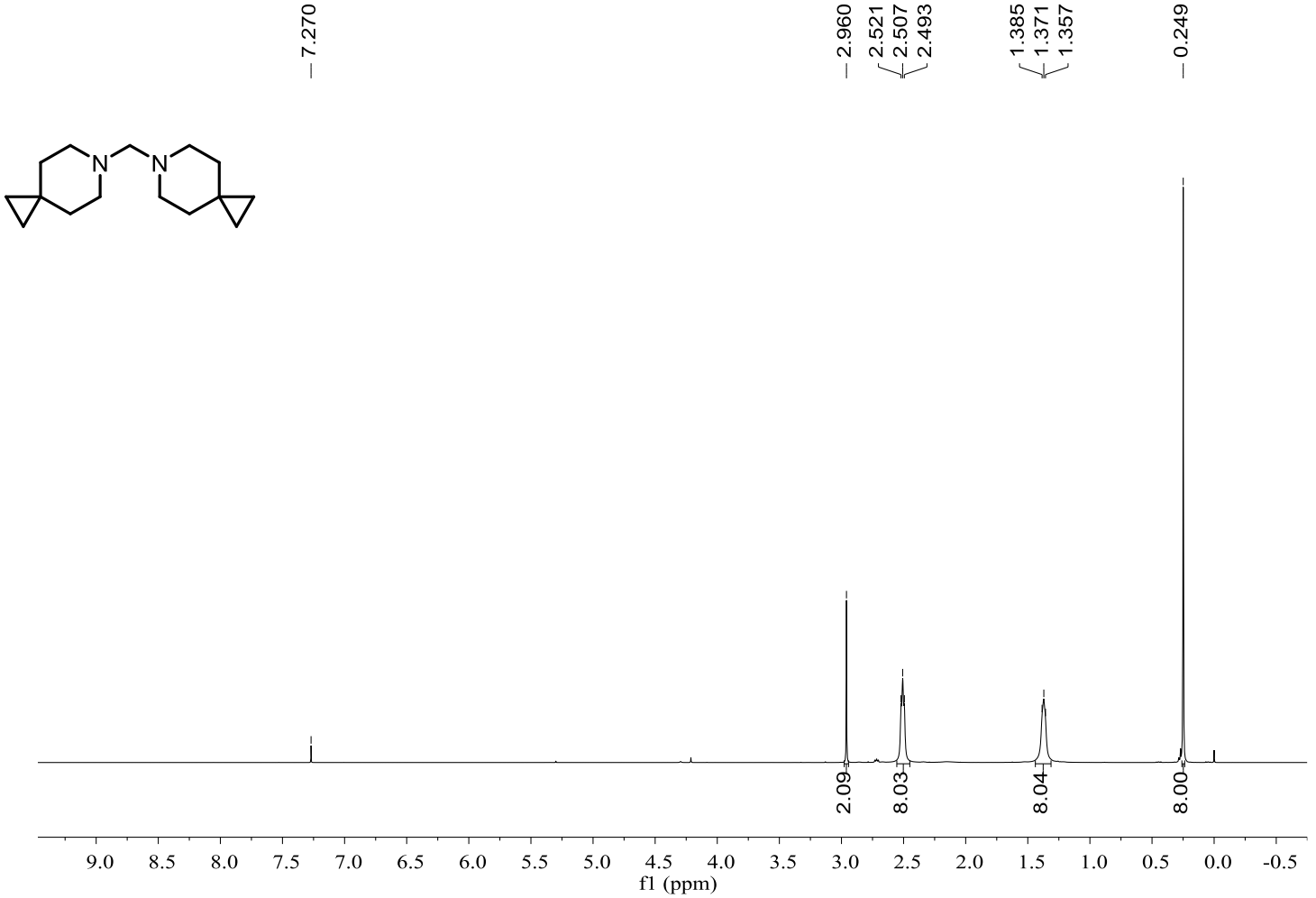
^{1}H NMR spectrum (400 M, $CDCl_3$) of Bis(4-phenylpiperidin-1-yl)methane (S37)



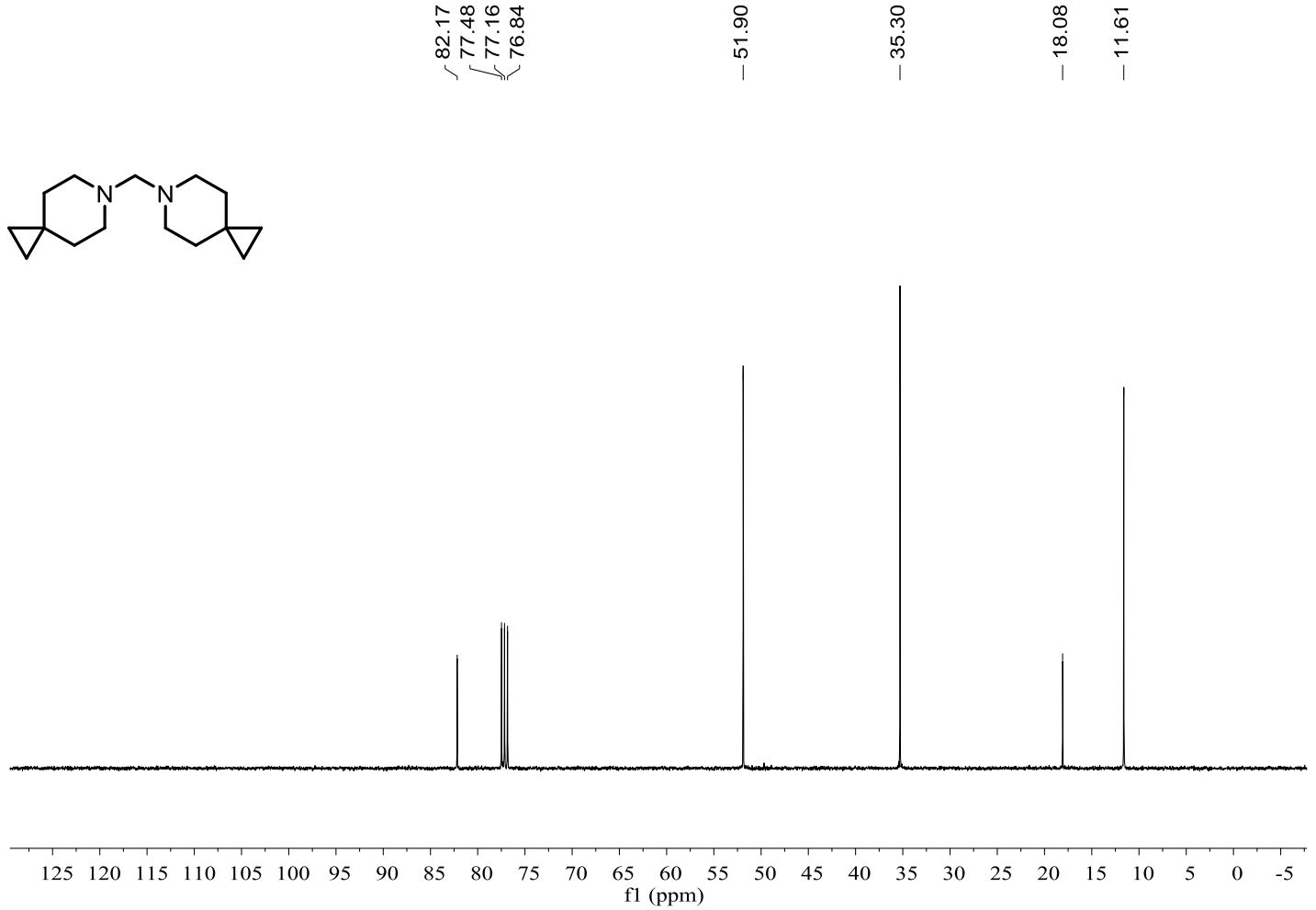
^{13}C NMR spectrum (100 M, $CDCl_3$) of Bis(4-phenylpiperidin-1-yl)methane (S37



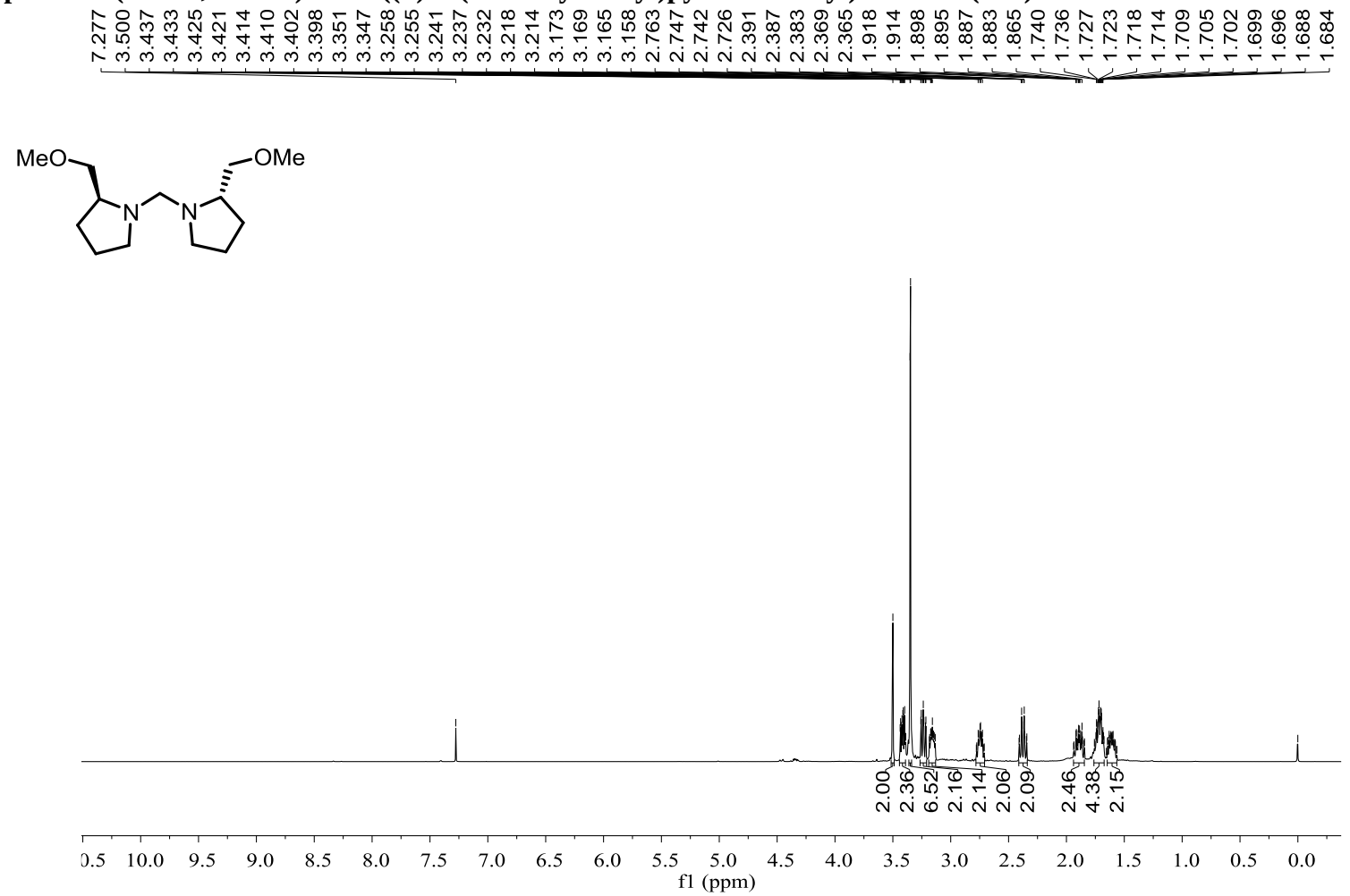
^{1}H NMR spectrum (400 M, $CDCl_3$) of Di(6-azaspiro[2.5]octan-6-yl)methane (S38)



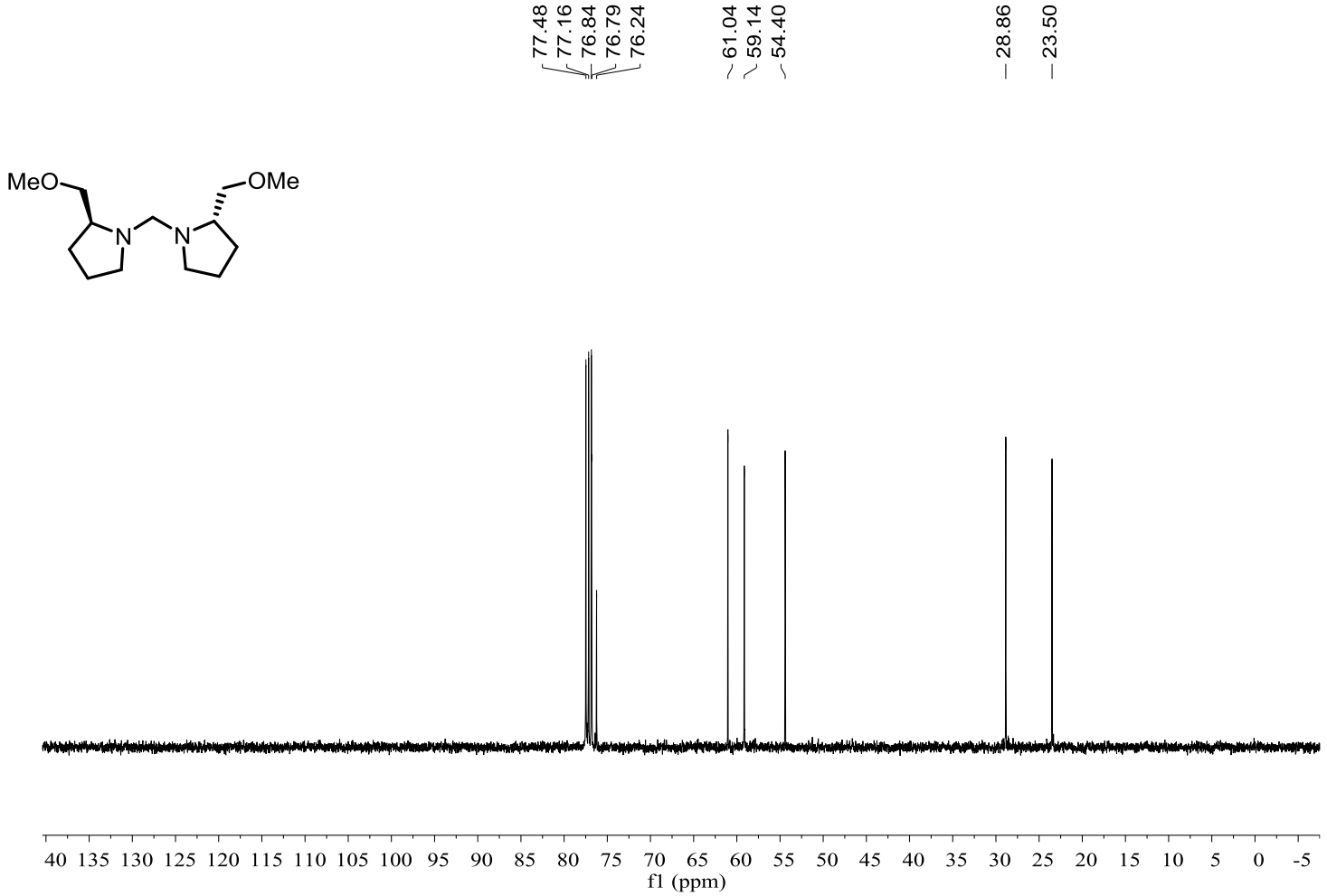
^{13}C NMR spectrum (100 M, $CDCl_3$) of Di(6-azaspiro[2.5]octan-6-yl)methane (S38)



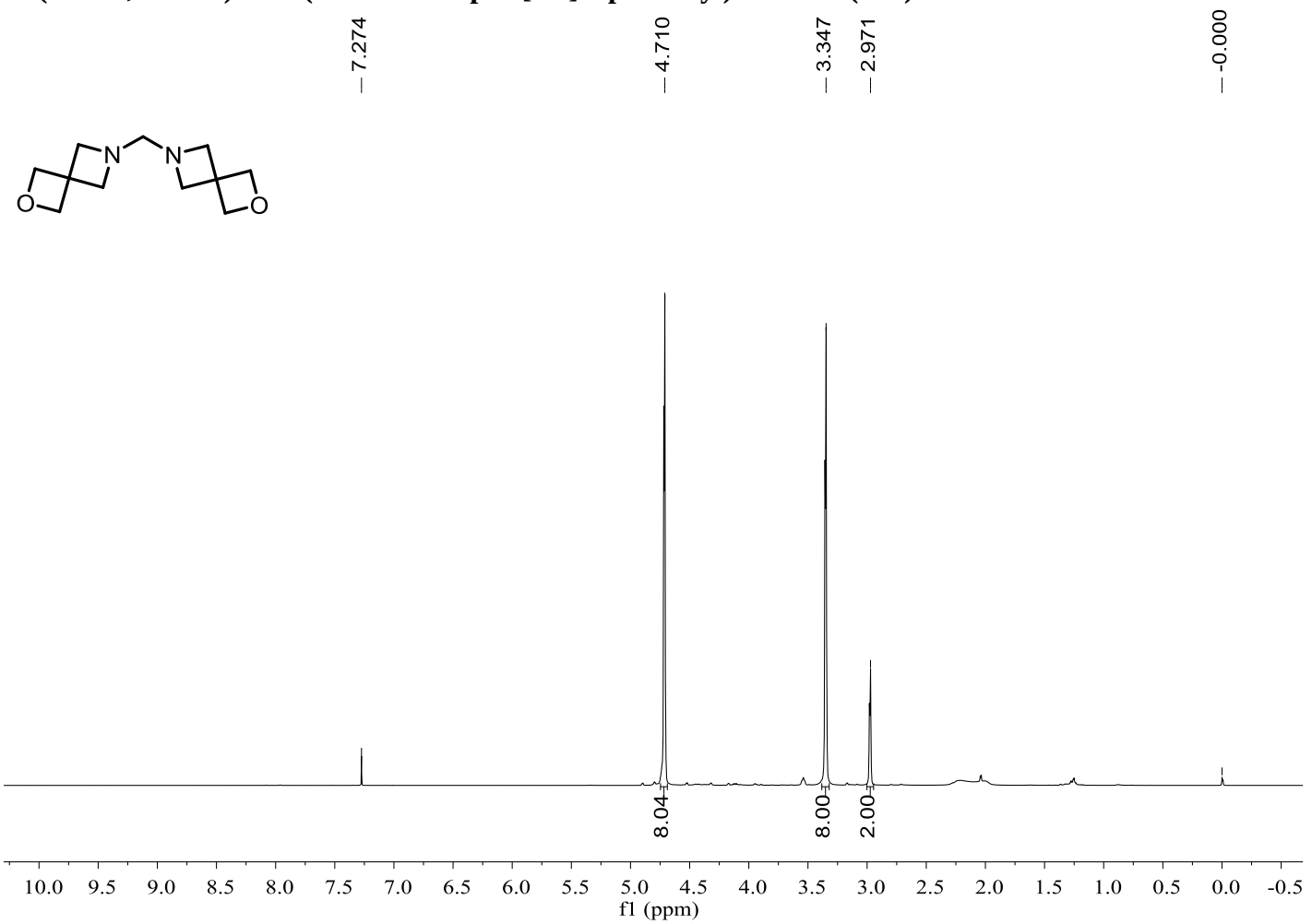
^{1}H NMR spectrum (400 M, $CDCl_3$) of Bis((S)-2-(methoxymethyl)pyrrolidin-1-yl)methane (S39)



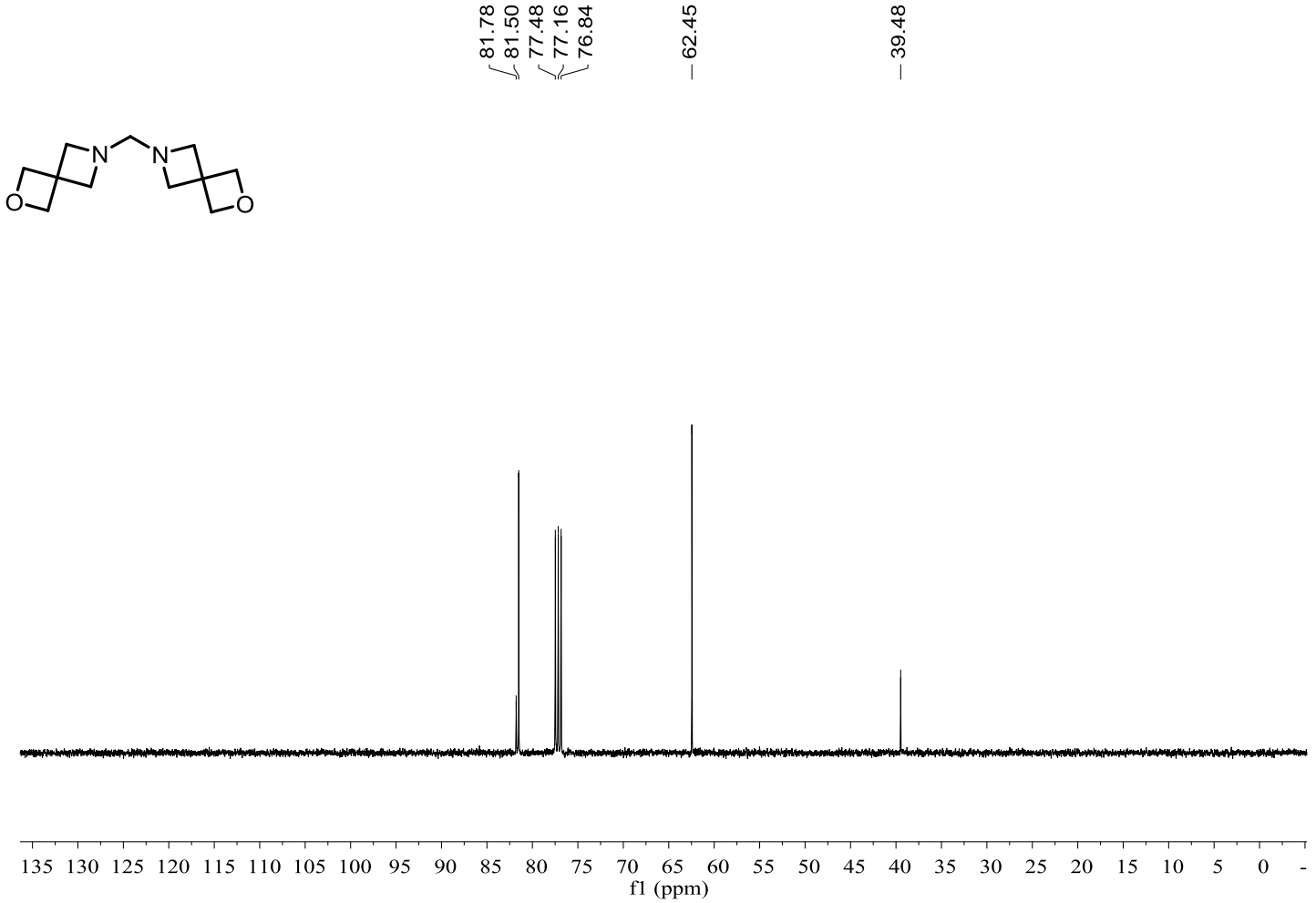
^{13}C NMR spectrum (100 M, $CDCl_3$) of Bis((S)-2-(methoxymethyl)pyrrolidin-1-yl)methane (S39)



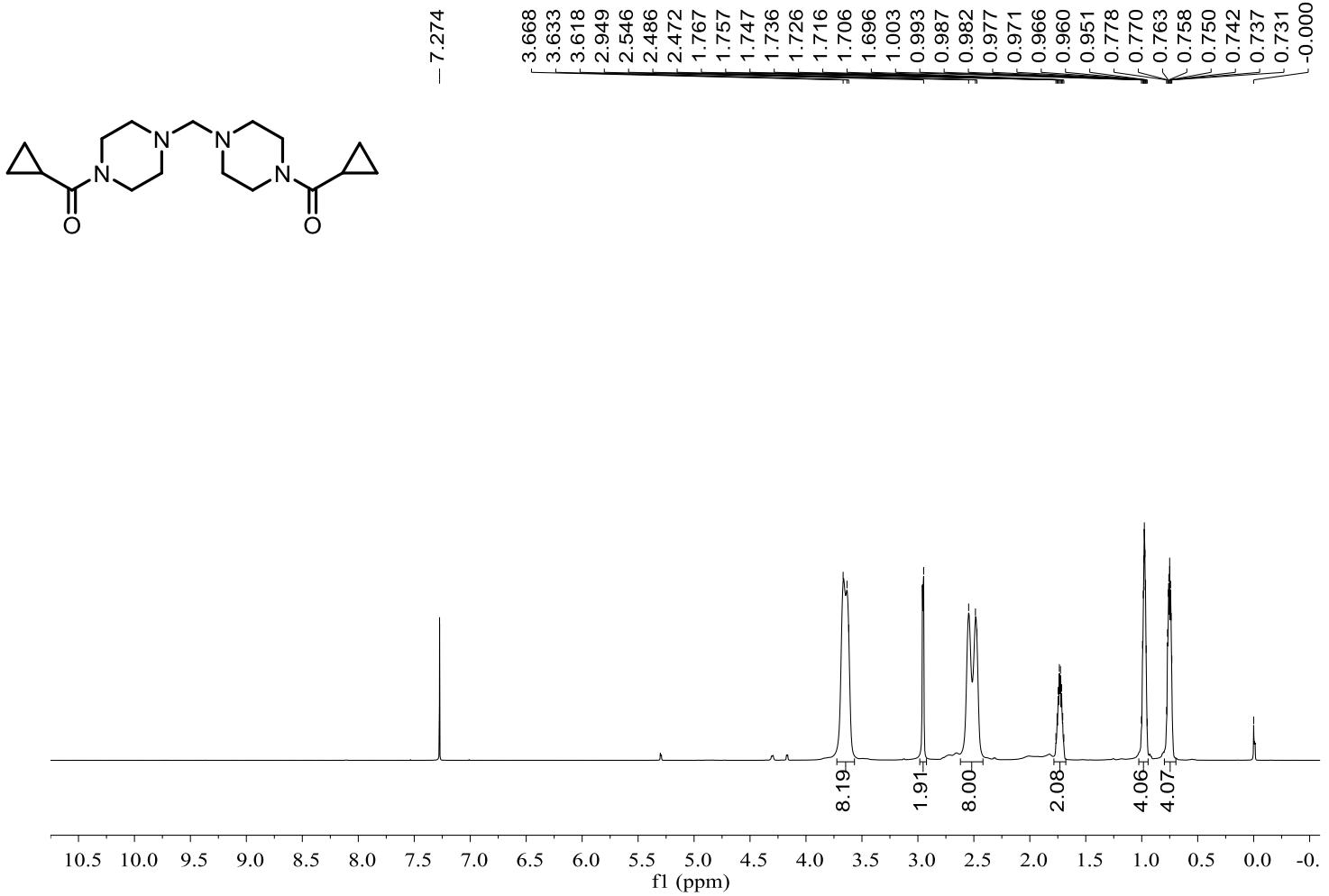
^{1}H NMR spectrum (400 M, $CDCl_3$) of Di(2-oxa-6-azaspiro[3.3]heptan-6-yl)methane (S40)



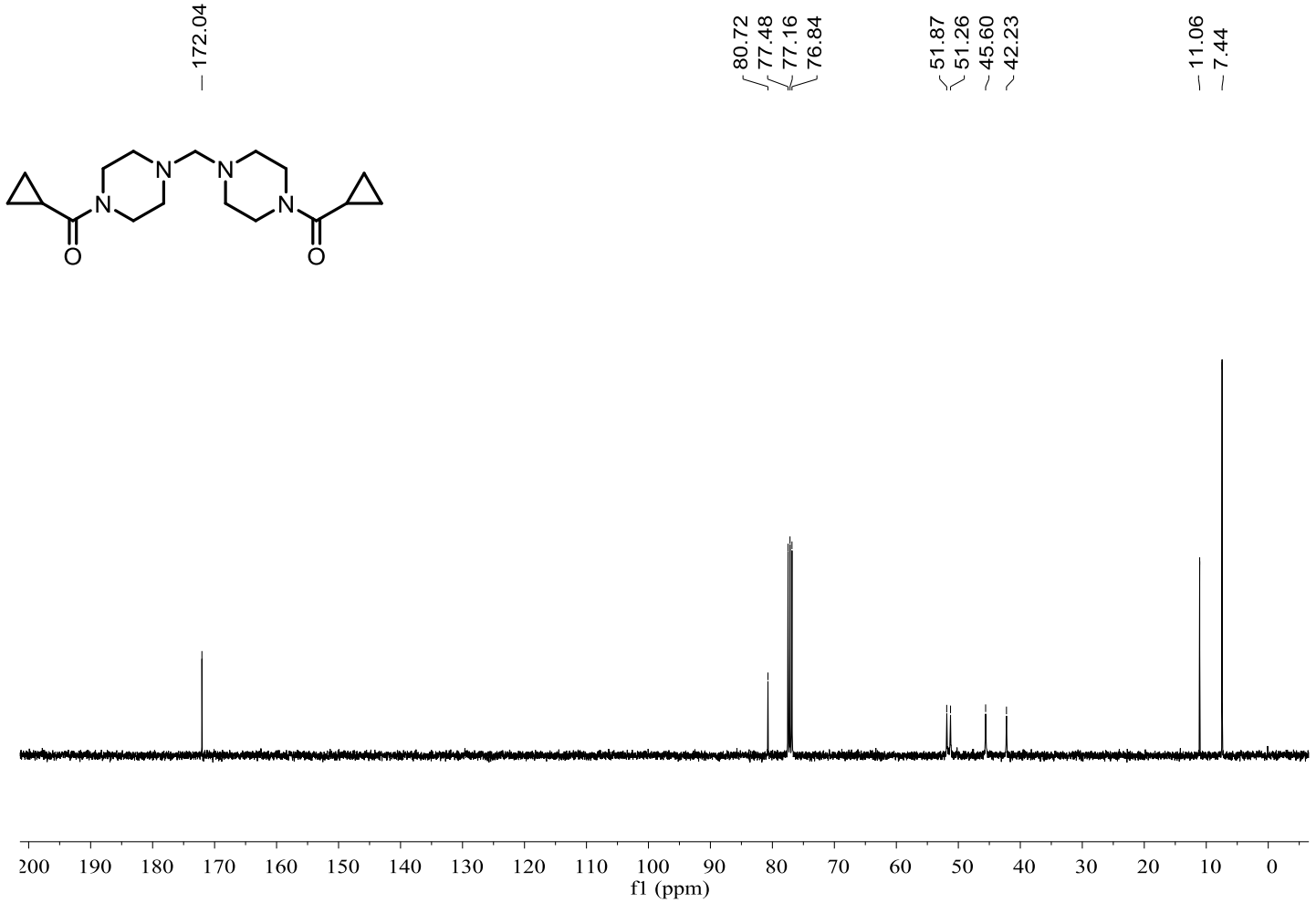
^{13}C NMR spectrum (100 M, $CDCl_3$) of Di(2-oxa-6-azaspiro[3.3]heptan-6-yl)methane (S40)



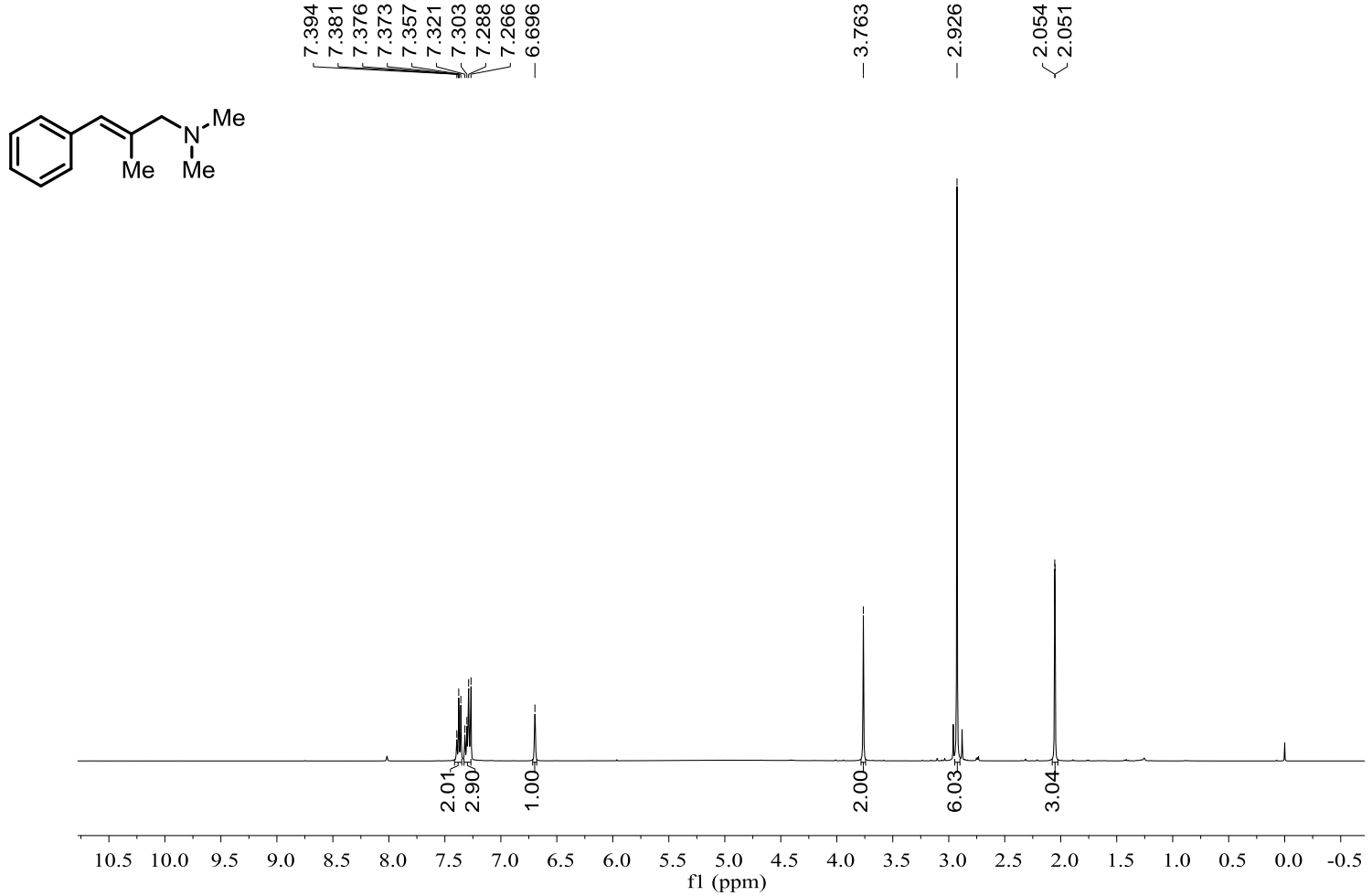
^{1}H NMR spectrum (400 M, $CDCl_3$) of (Methylenebis(piperazine-4,1-diyl))bis(cyclopropylmethanone) (S42)



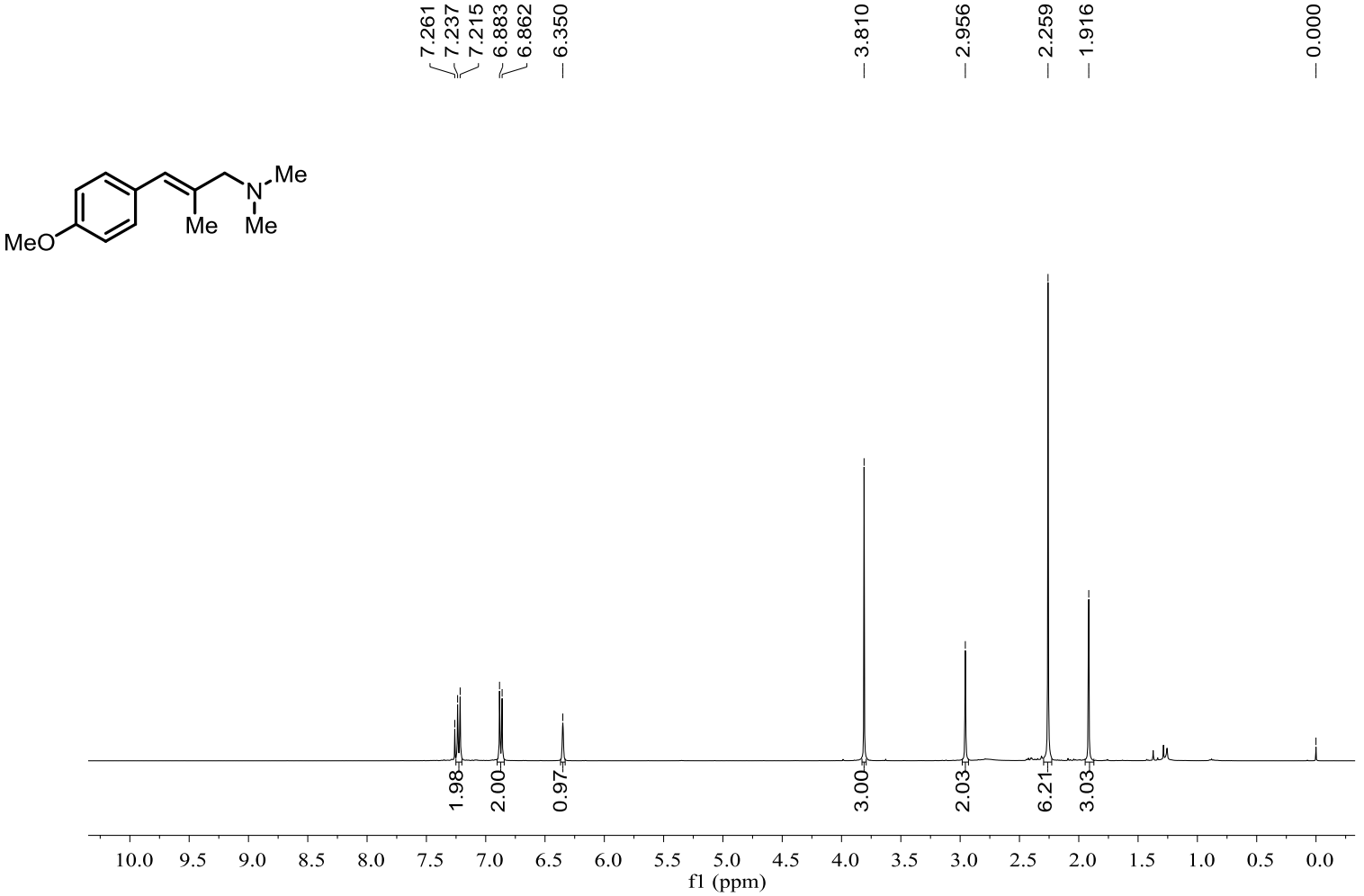
^{13}C NMR spectrum (100 M, $CDCl_3$) of (Methylenebis(piperazine-4,1-diyl))bis(cyclopropylmethanone) (S42)



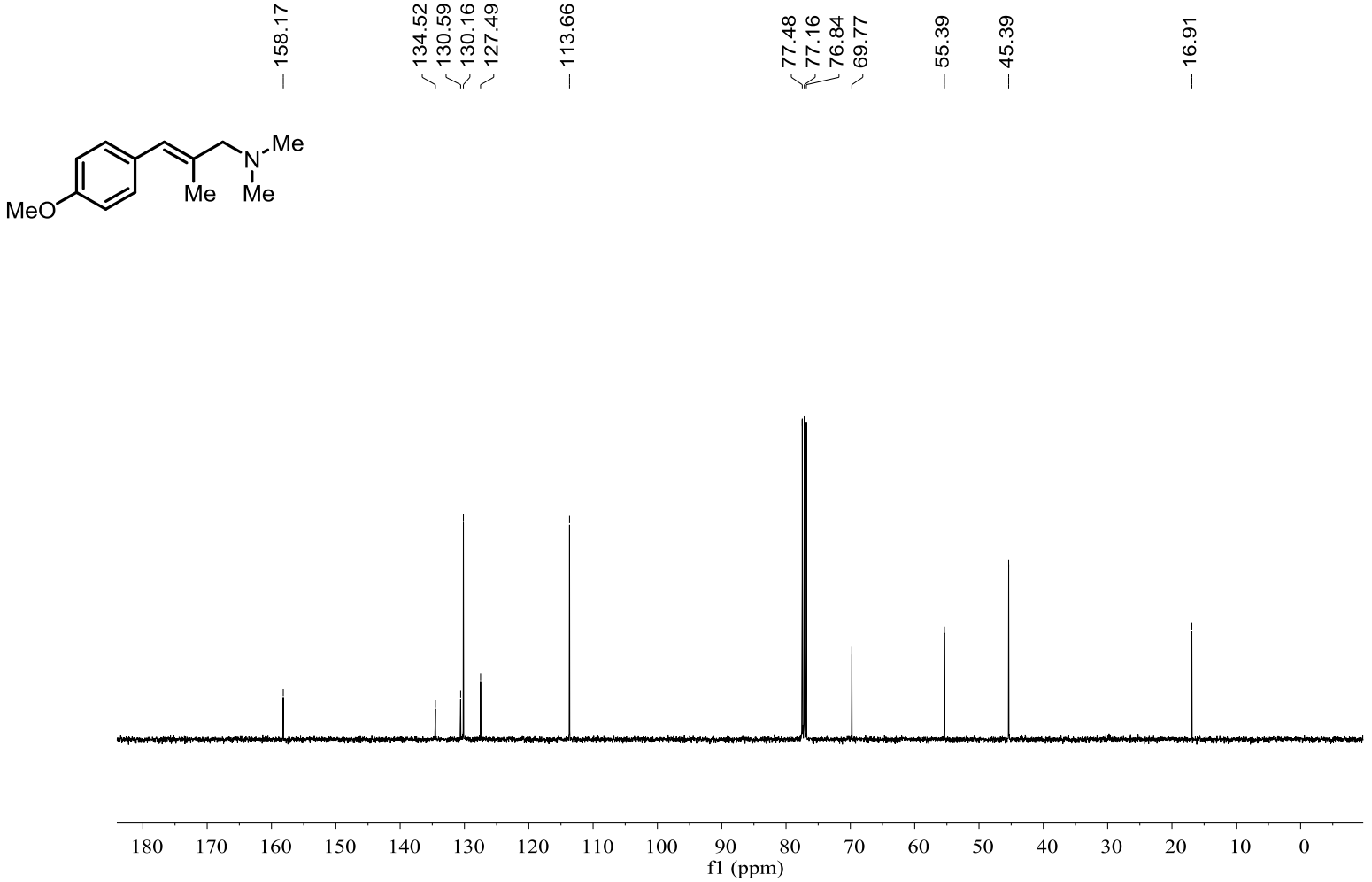
^{1}H NMR spectrum (400 M, $CDCl_3$) of (E)-*N*,*N*,2-Trimethyl-3-phenylprop-2-en-1-amine (3)



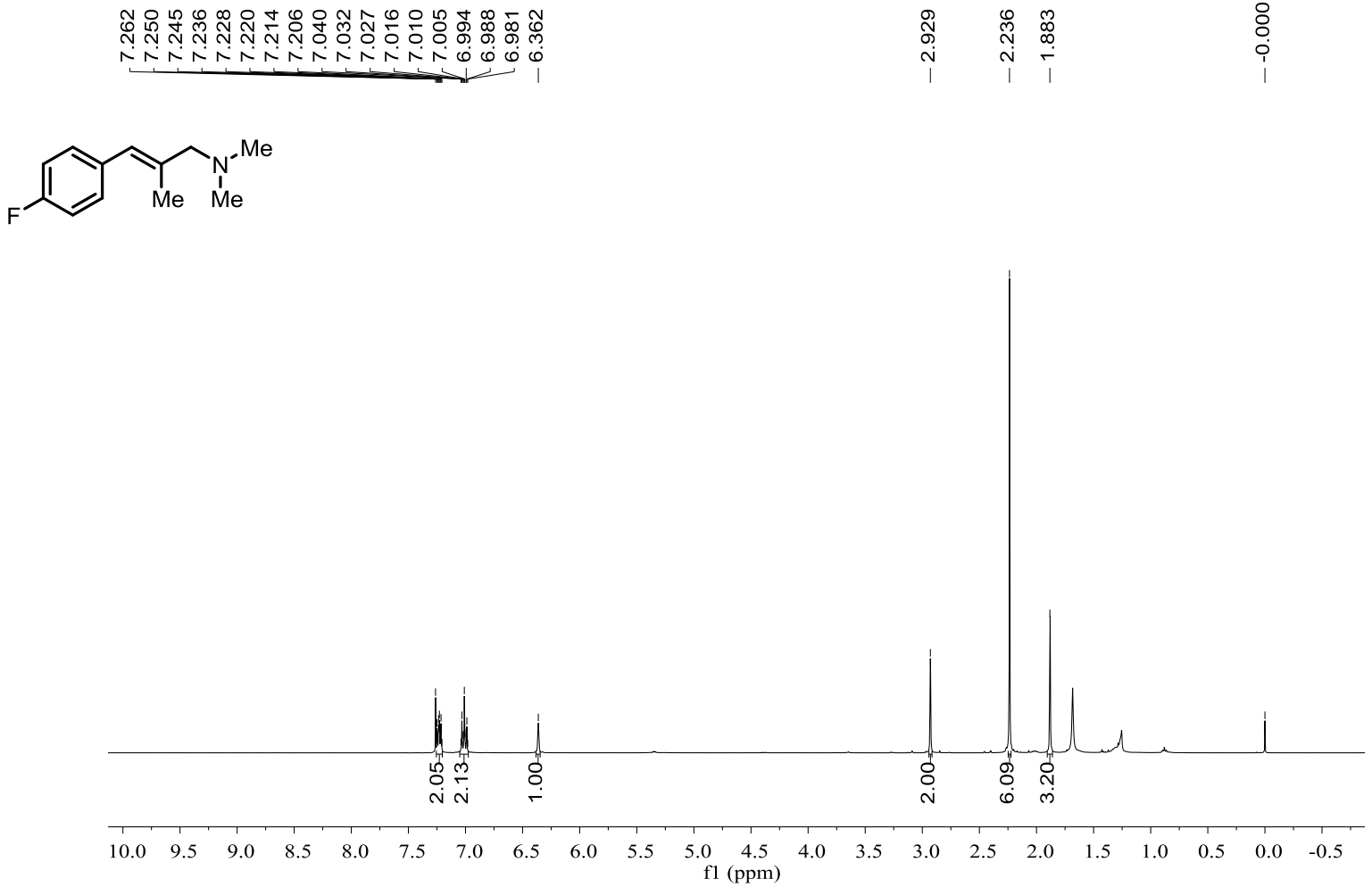
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(4-Methoxyphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (4)



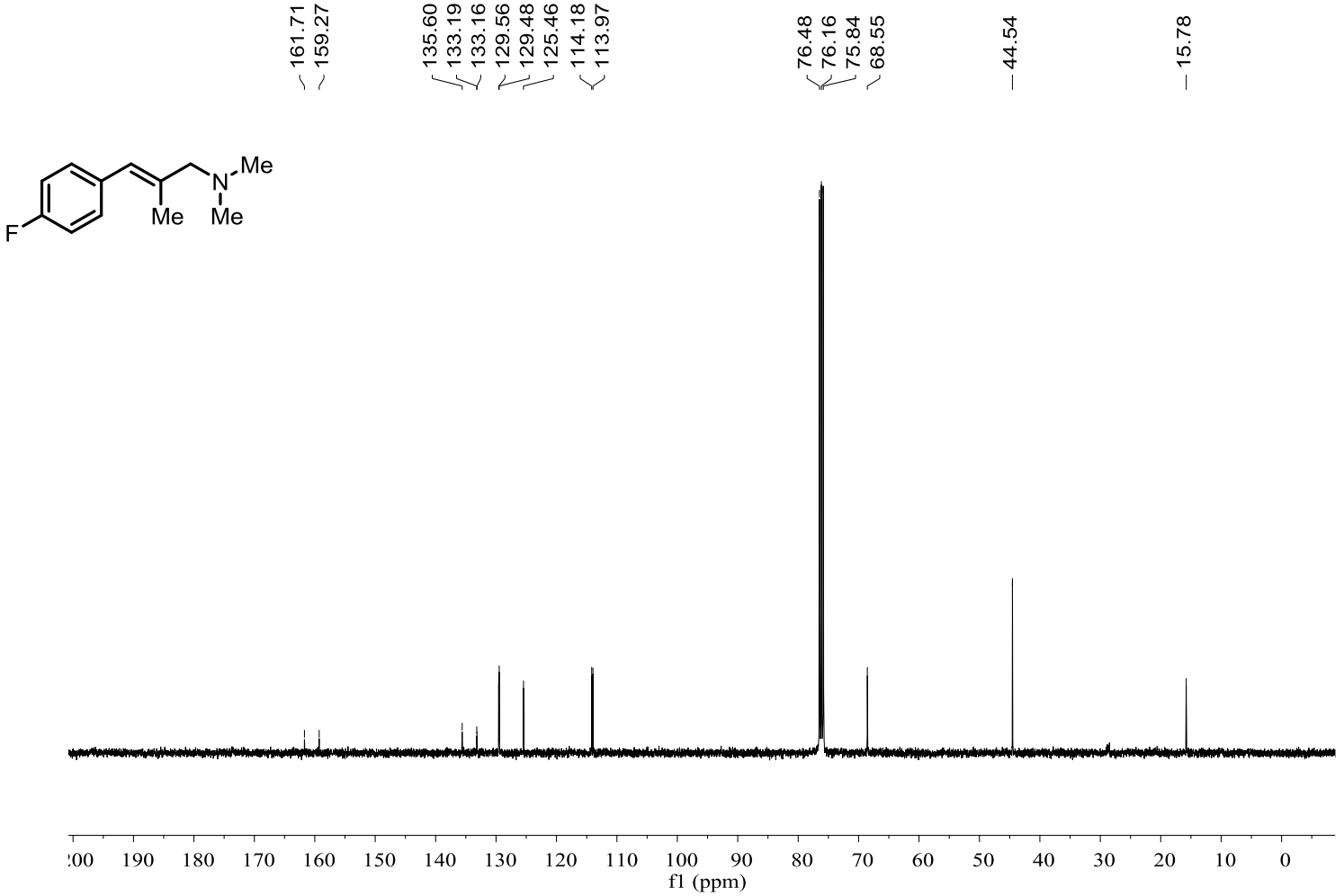
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(4-Methoxyphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (4)



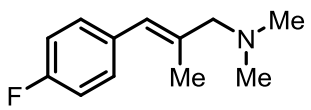
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(4-Fluorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (5)



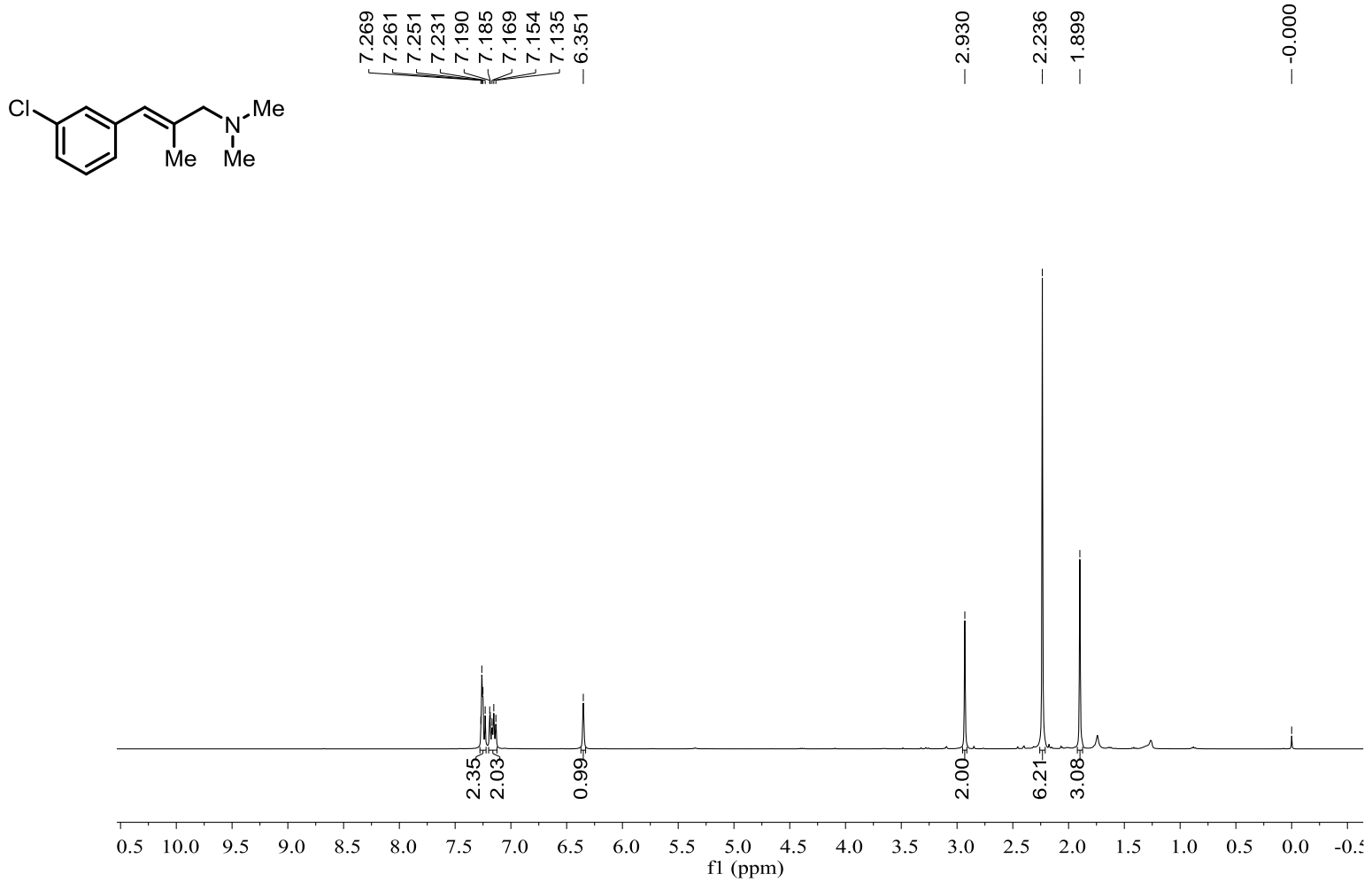
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(4-Fluorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (5)



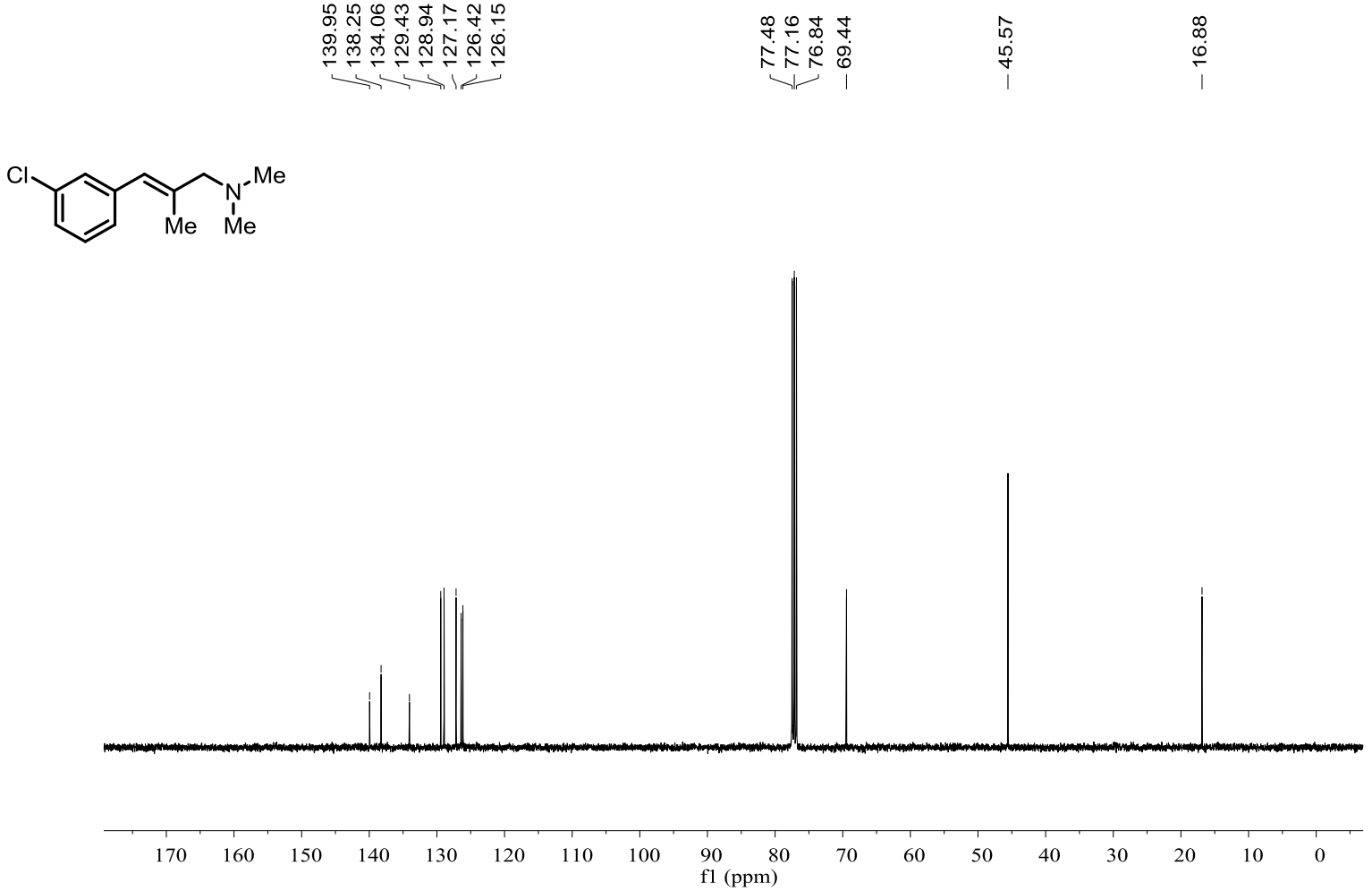
^{19}F NMR spectrum (376 M, $CDCl_3$) of (*E*)-3-(4-Fluorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (5)



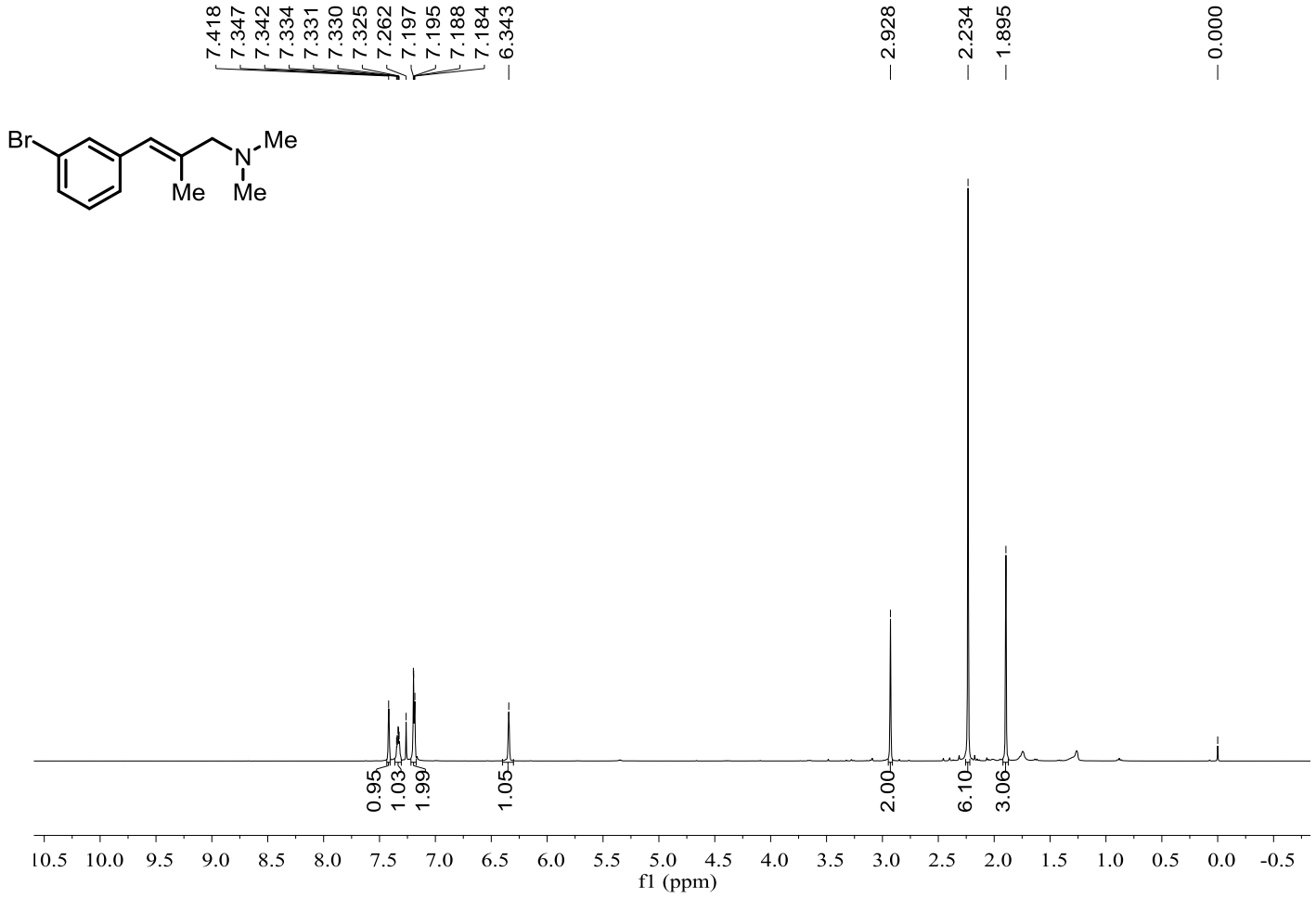
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(3-Chlorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (6)



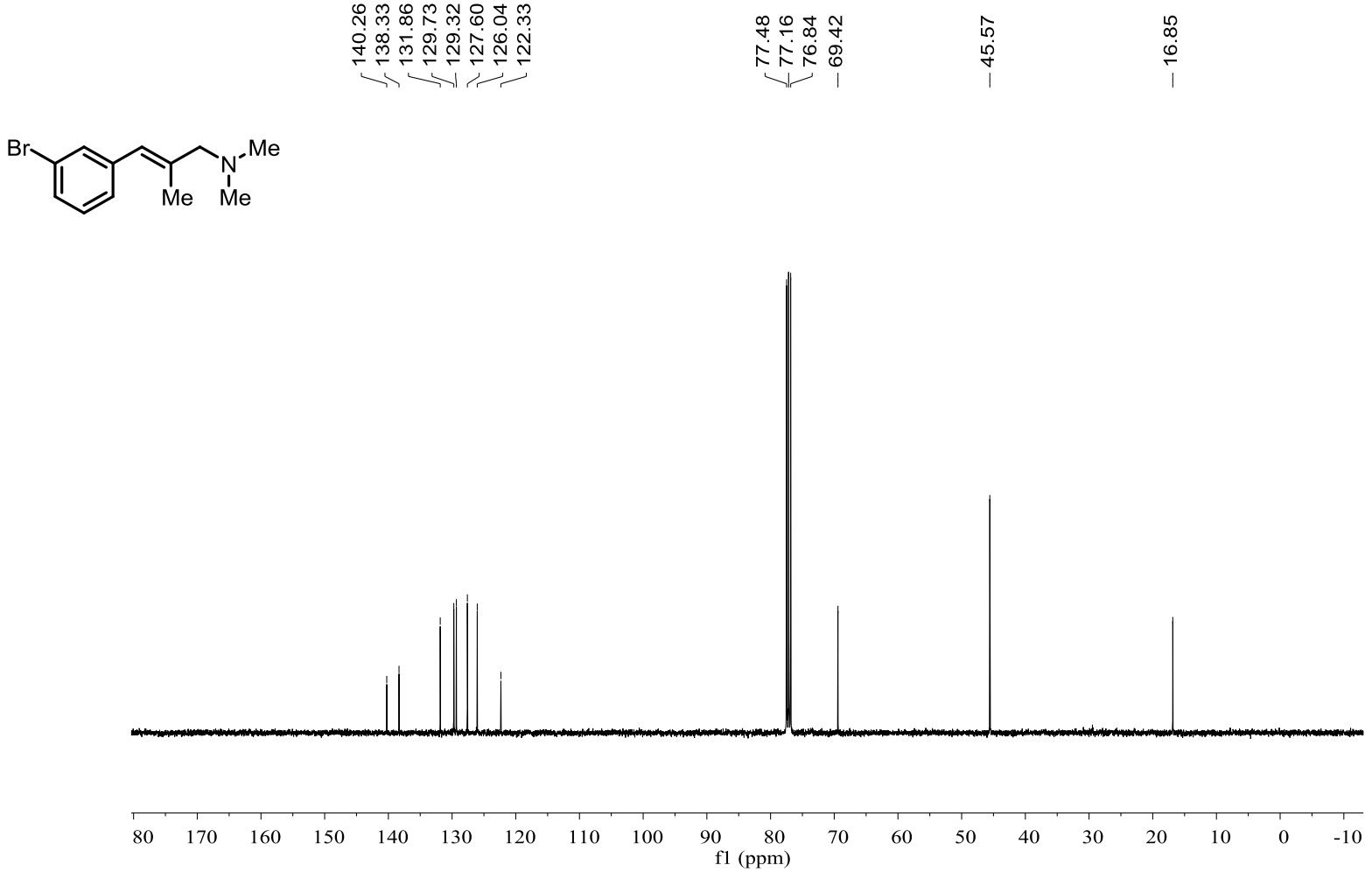
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(3-Chlorophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (6)



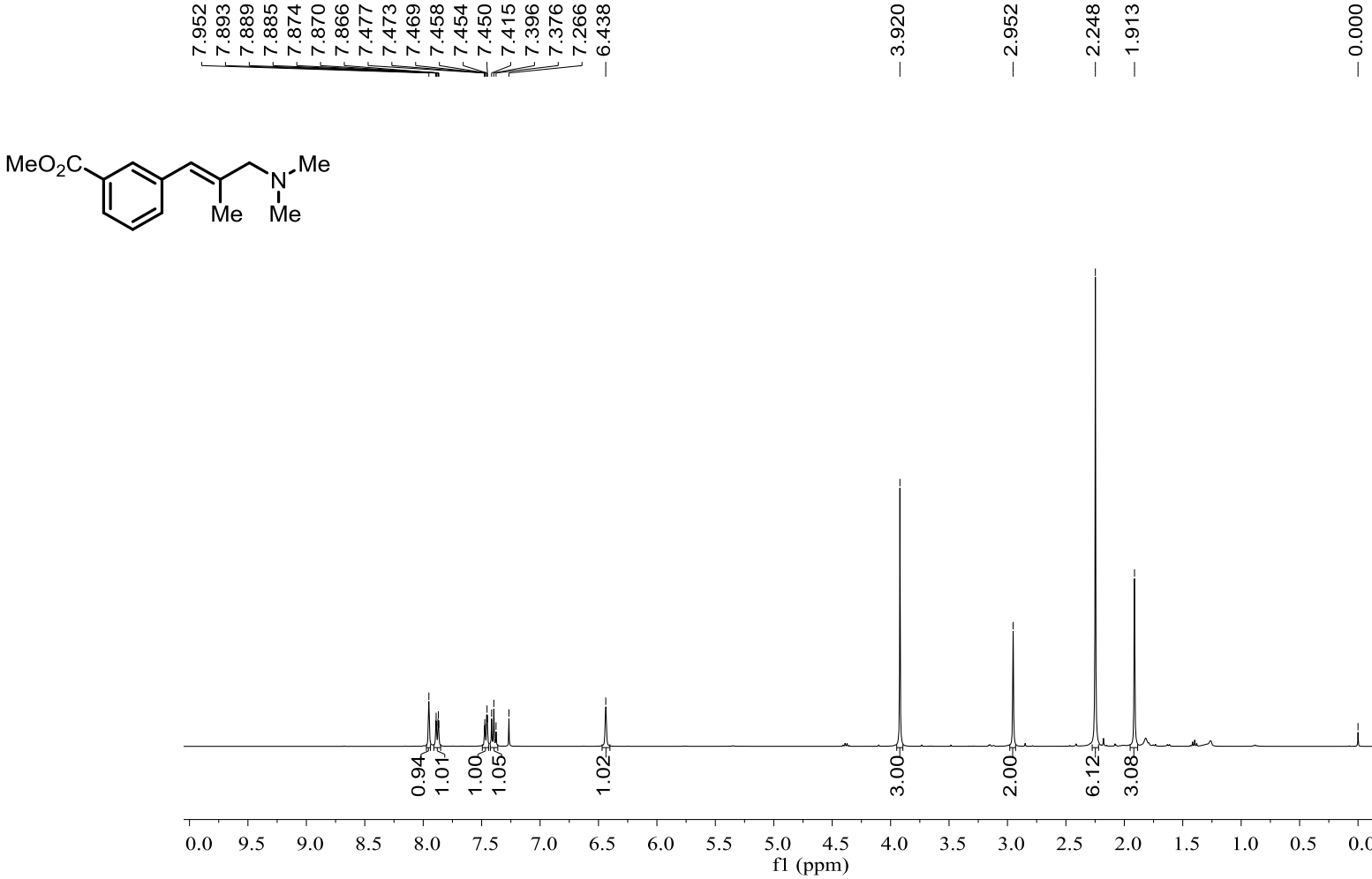
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(3-Bromophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (7)



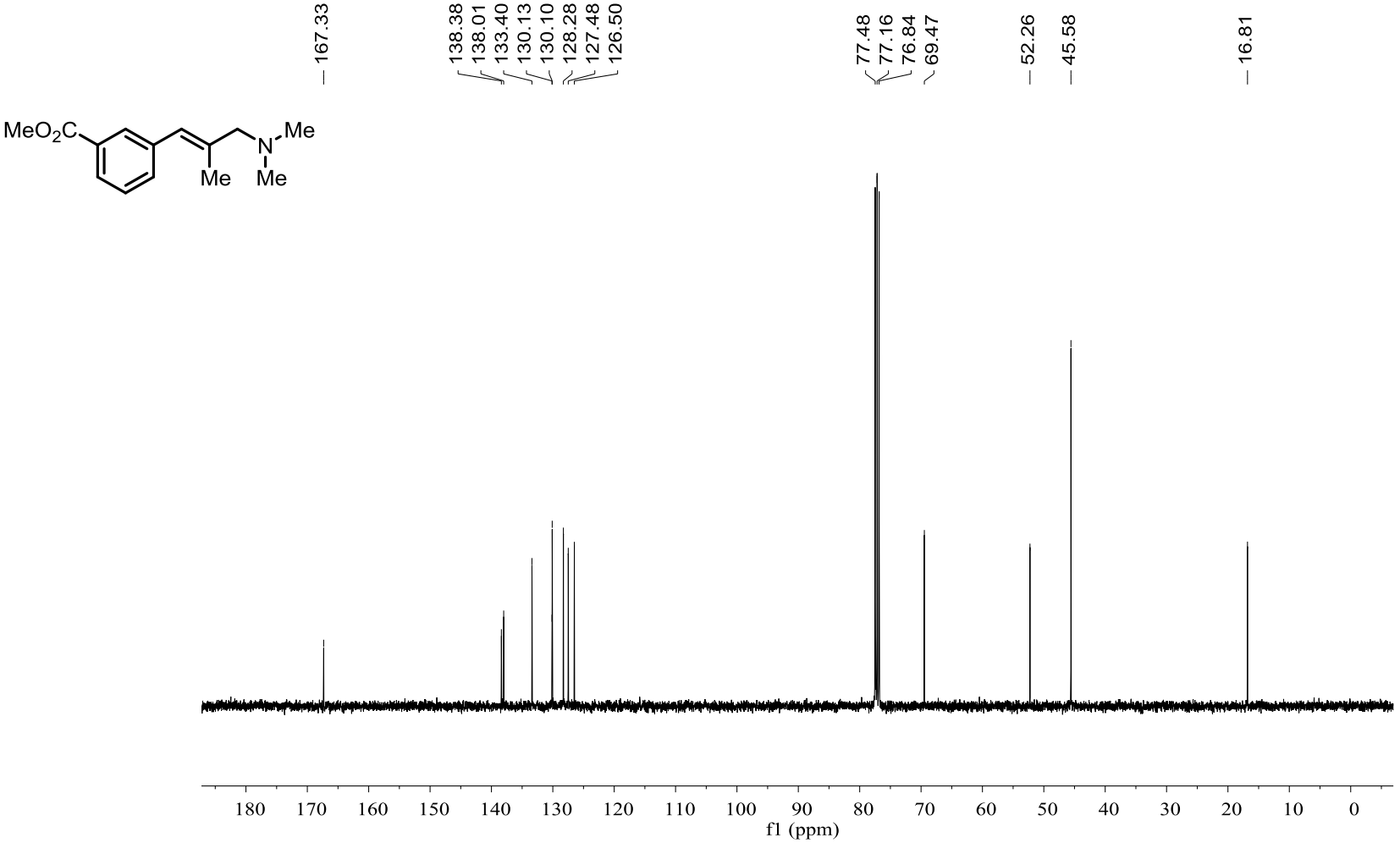
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(3-Bromophenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (7)



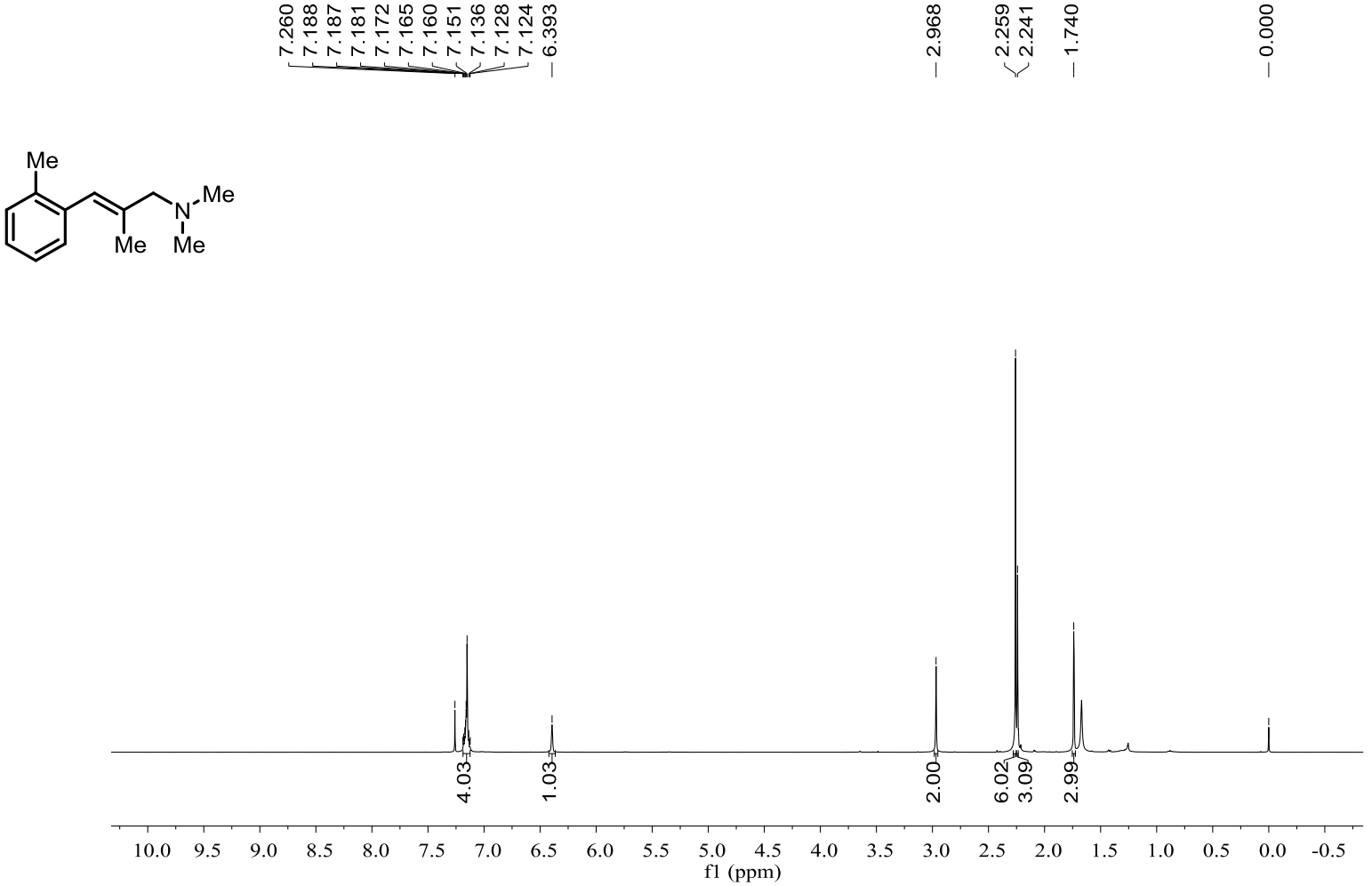
^{1}H NMR spectrum (400 M, $CDCl_3$) of Methyl (*E*)-3-(3-(dimethylamino)-2-methylprop-1-en-1-yl)benzoate (8)



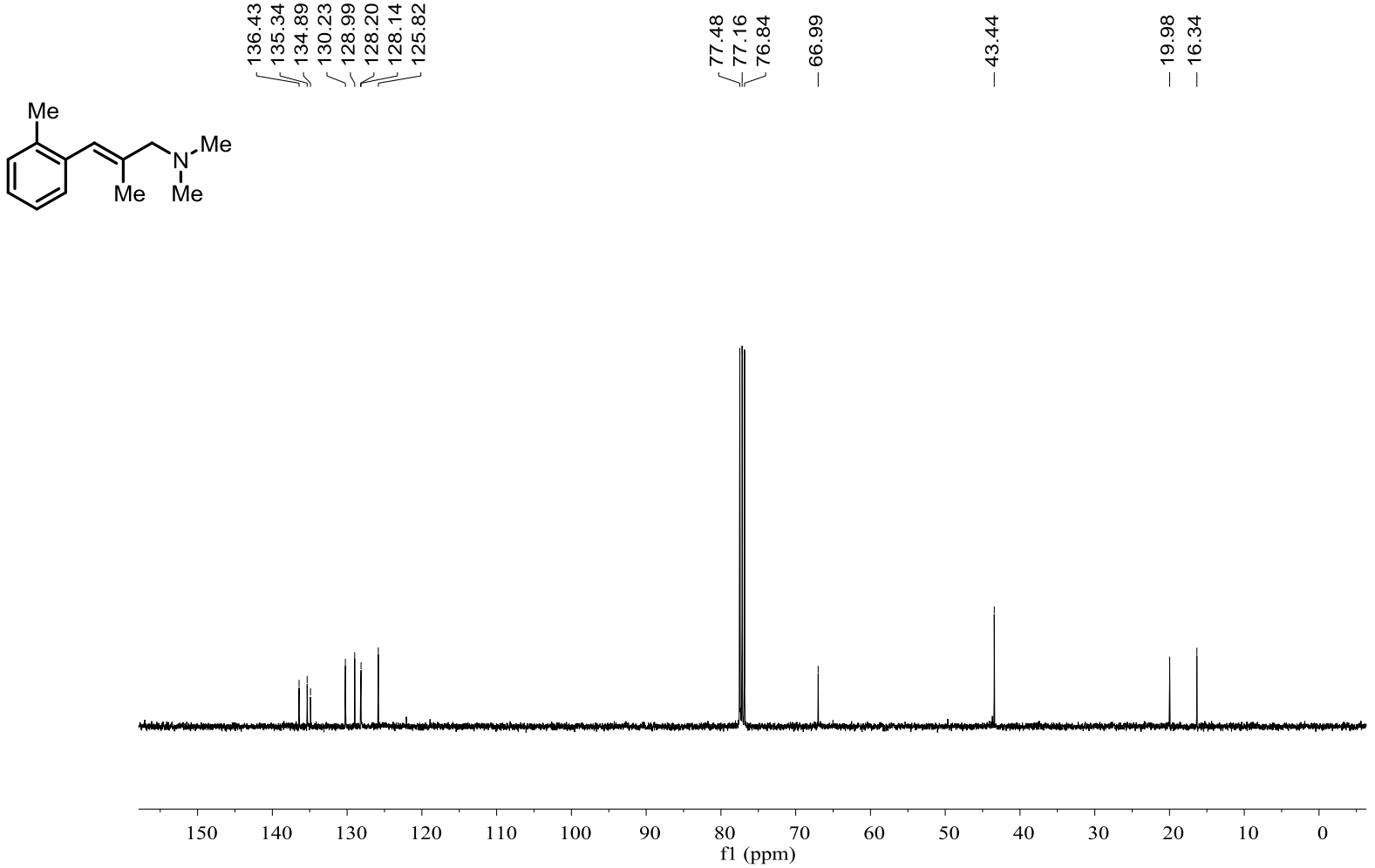
^{13}C NMR spectrum (100 M, $CDCl_3$) of Methyl (*E*)-3-(3-(dimethylamino)-2-methylprop-1-en-1-yl)benzoate (8)



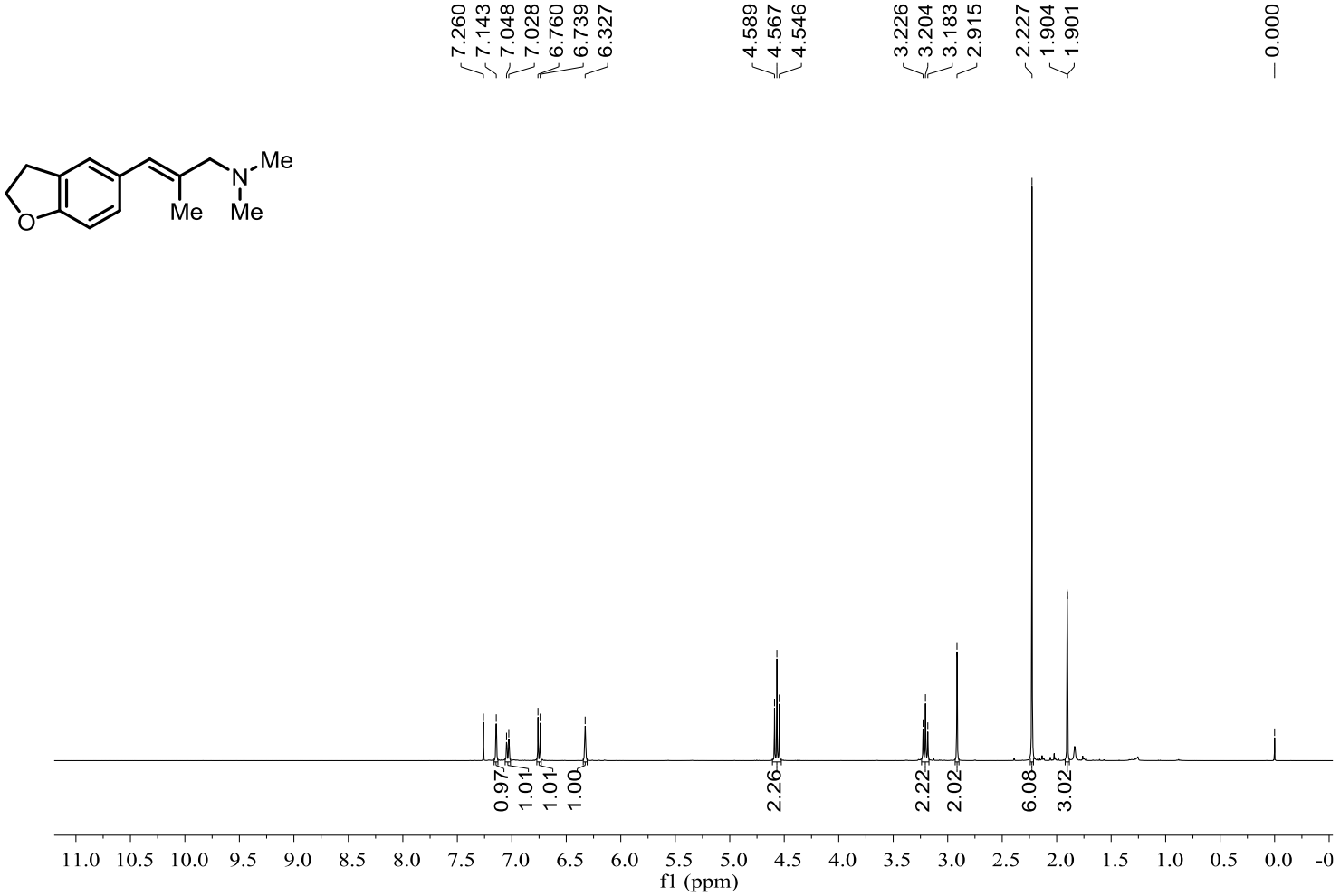
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(o-tolyl)prop-2-en-1-amine (9)



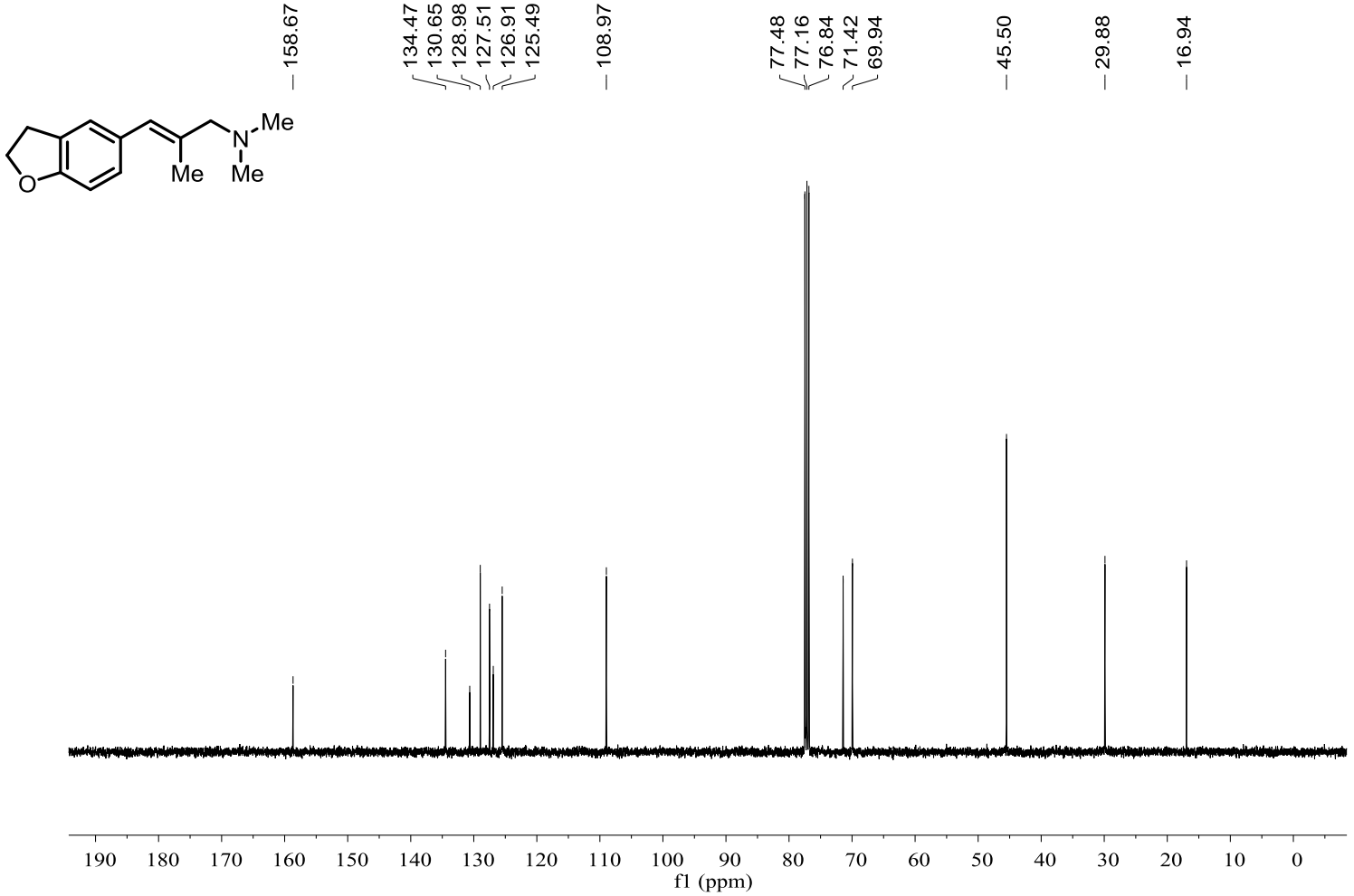
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(o-tolyl)prop-2-en-1-amine (9)



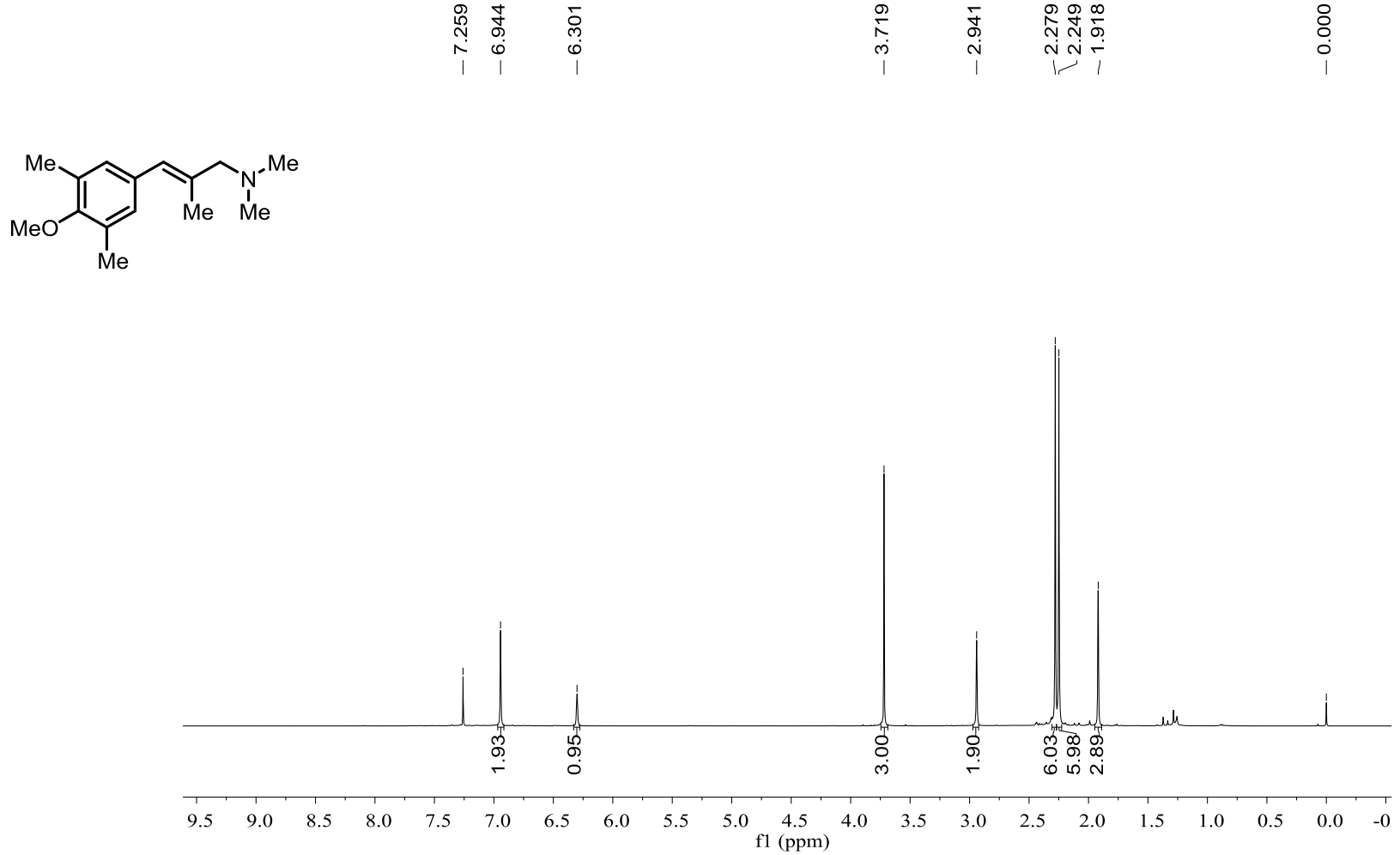
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(2,3-Dihydrobenzofuran-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (10)



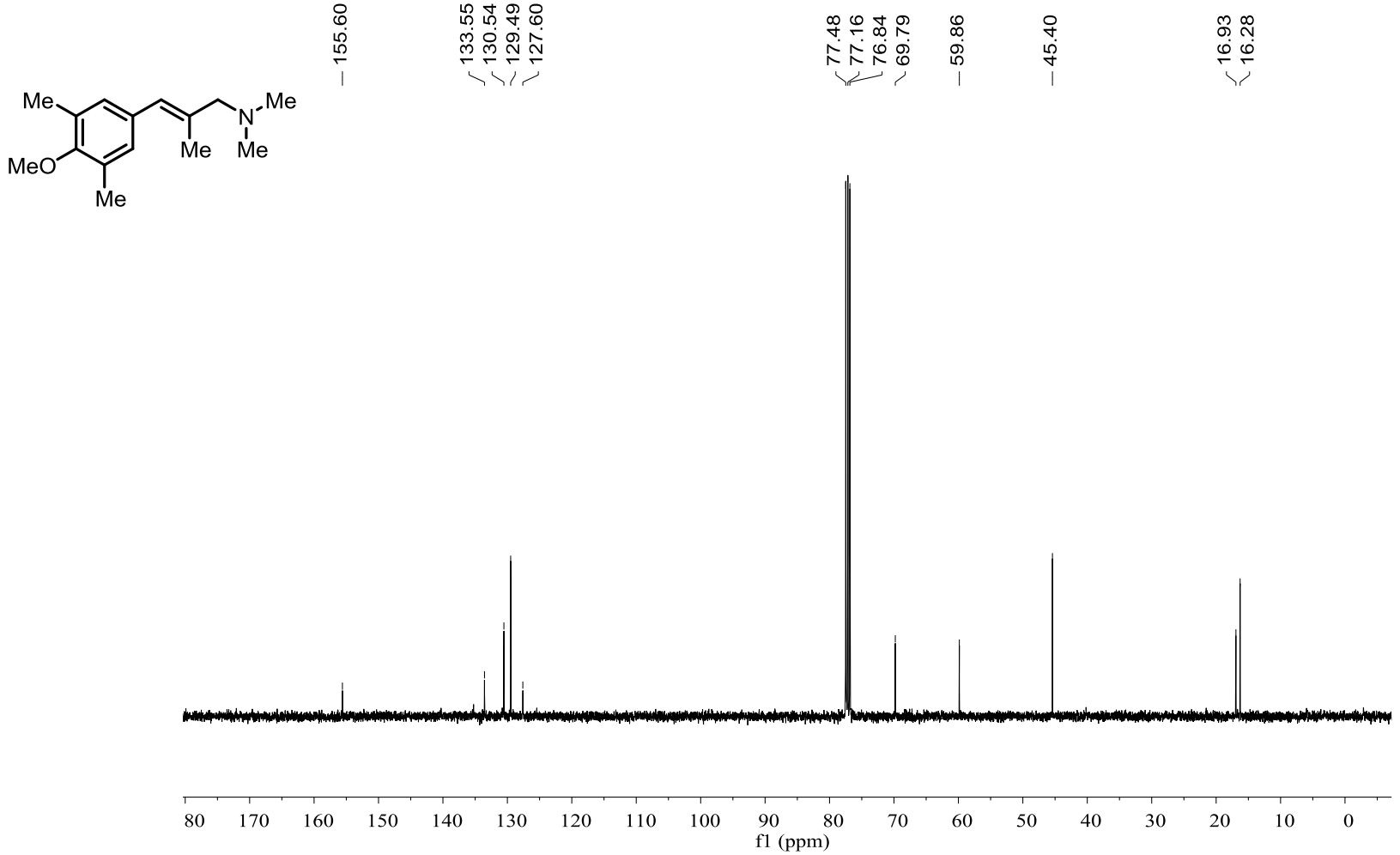
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(2,3-Dihydrobenzofuran-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (10)



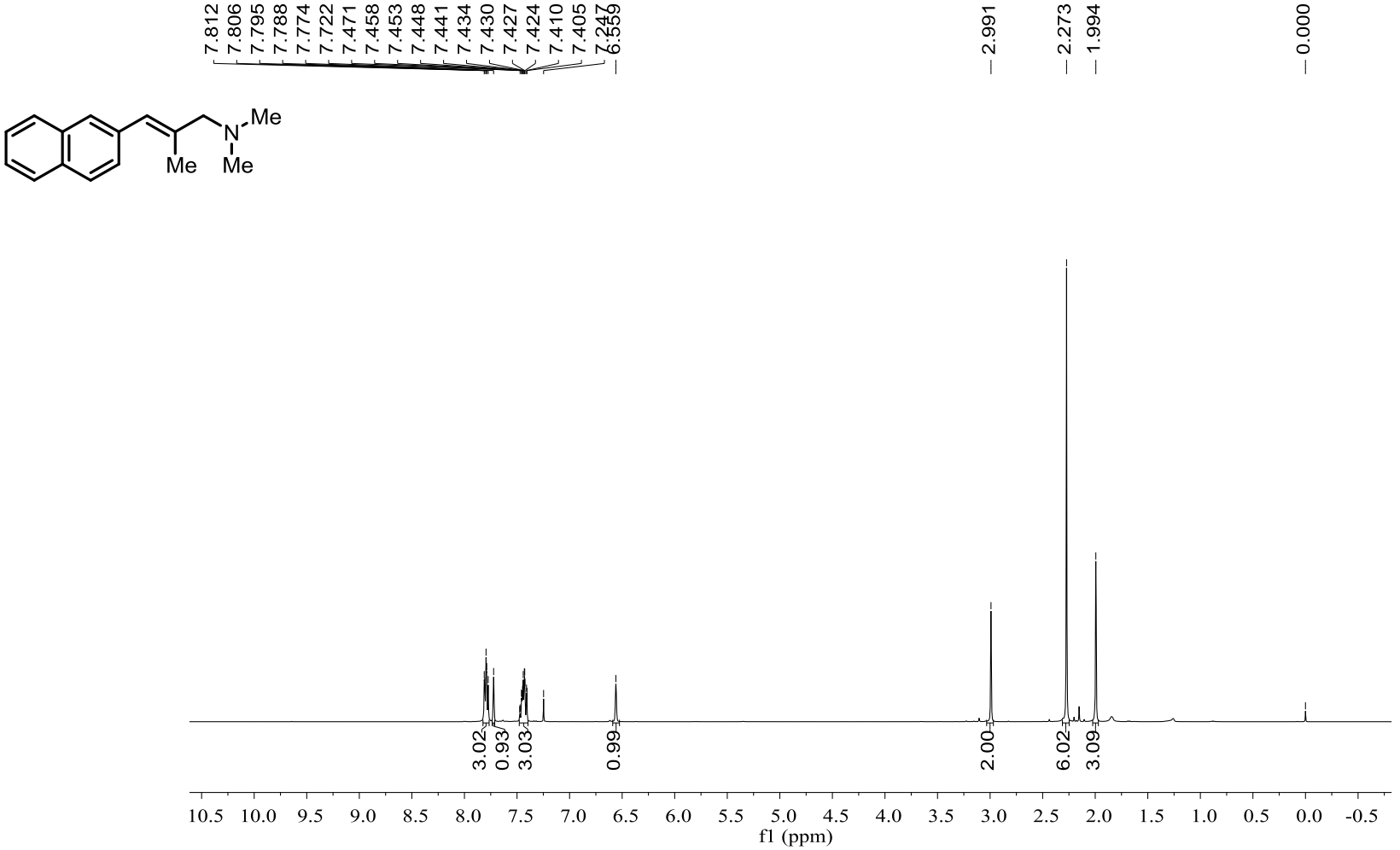
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(4-Methoxy-3,5-dimethylphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (11)



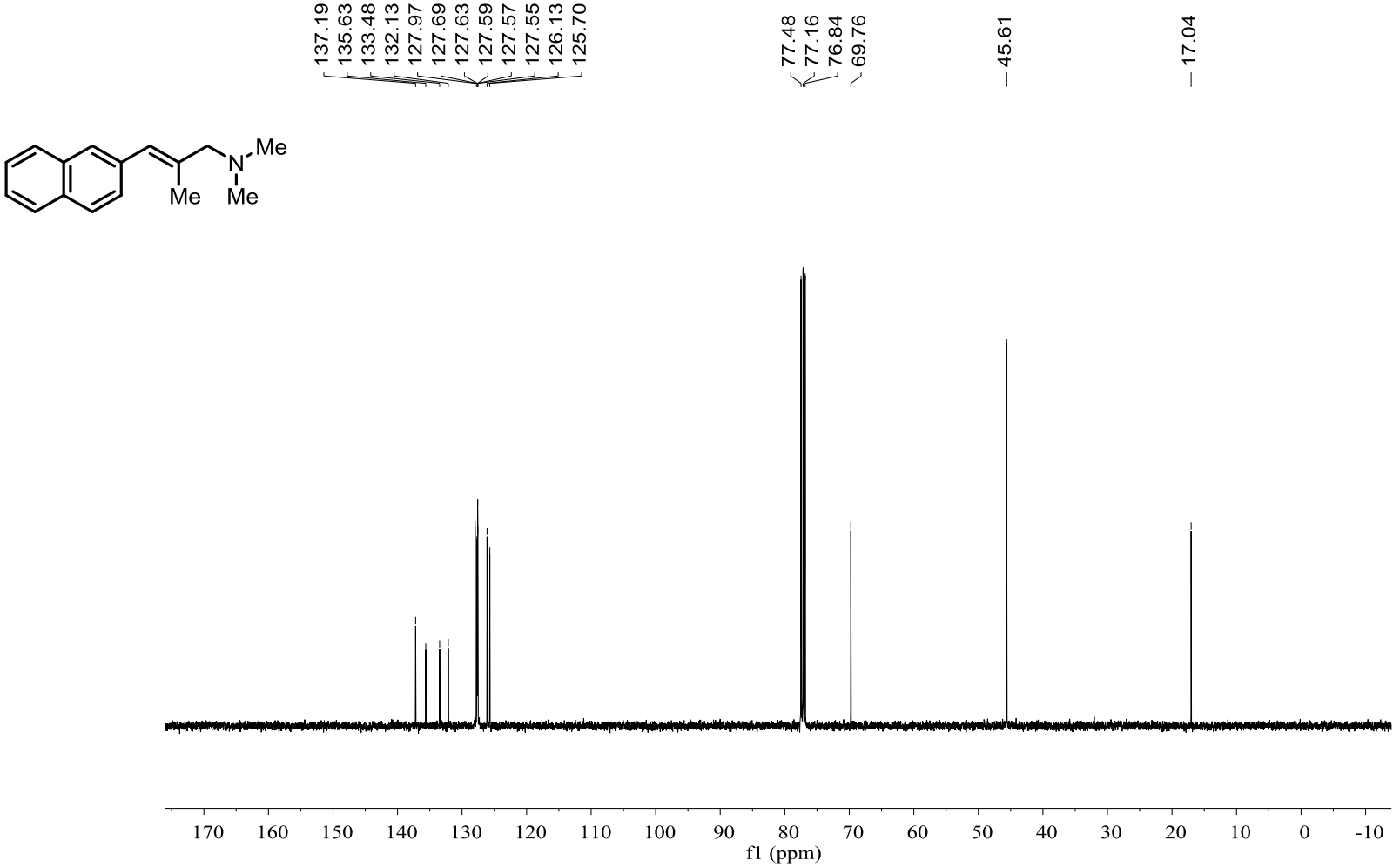
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(4-Methoxy-3,5-dimethylphenyl)-*N*,*N*,2-trimethylprop-2-en-1-amine (11)



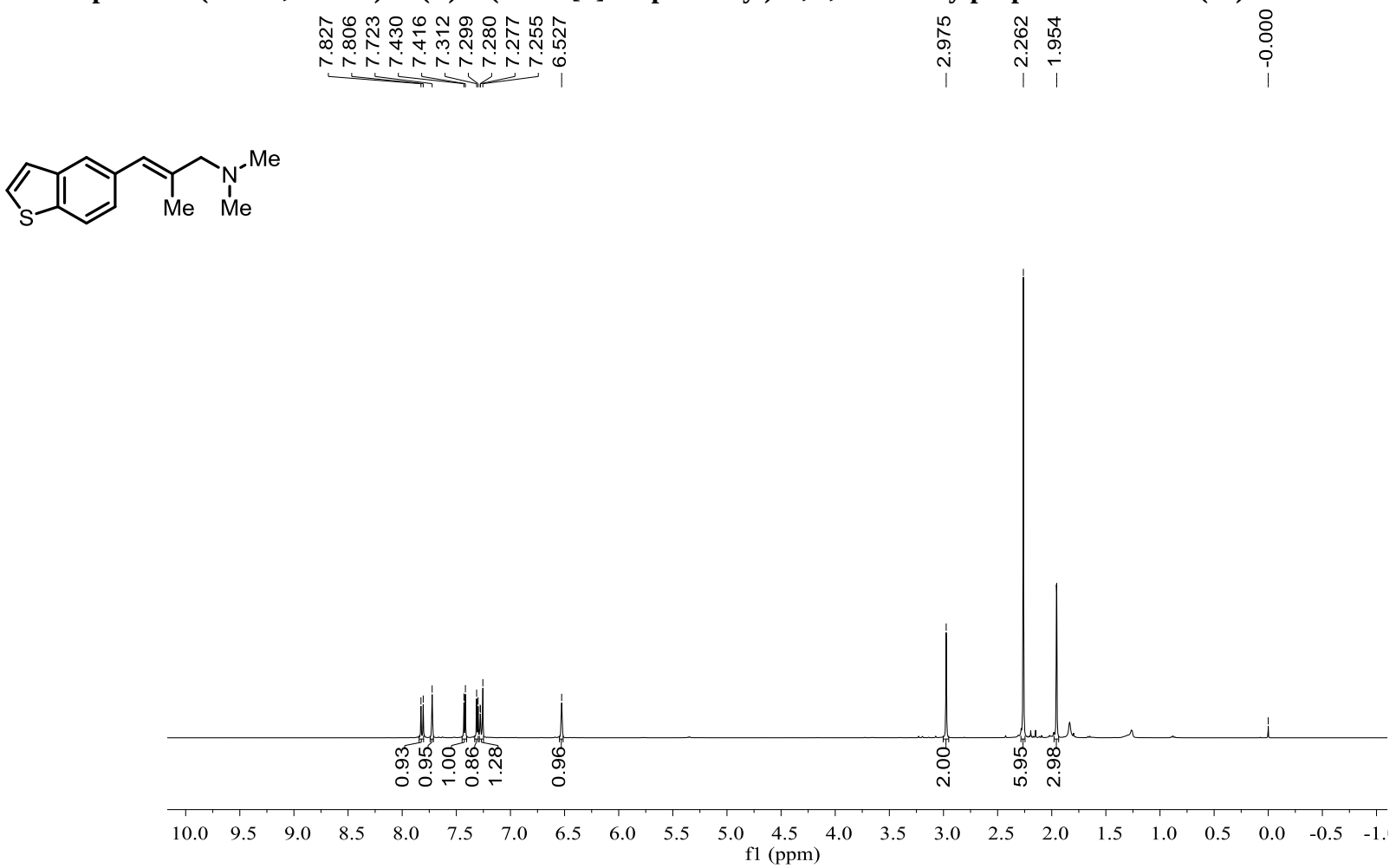
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(naphthalen-2-yl)prop-2-en-1-amine (12)



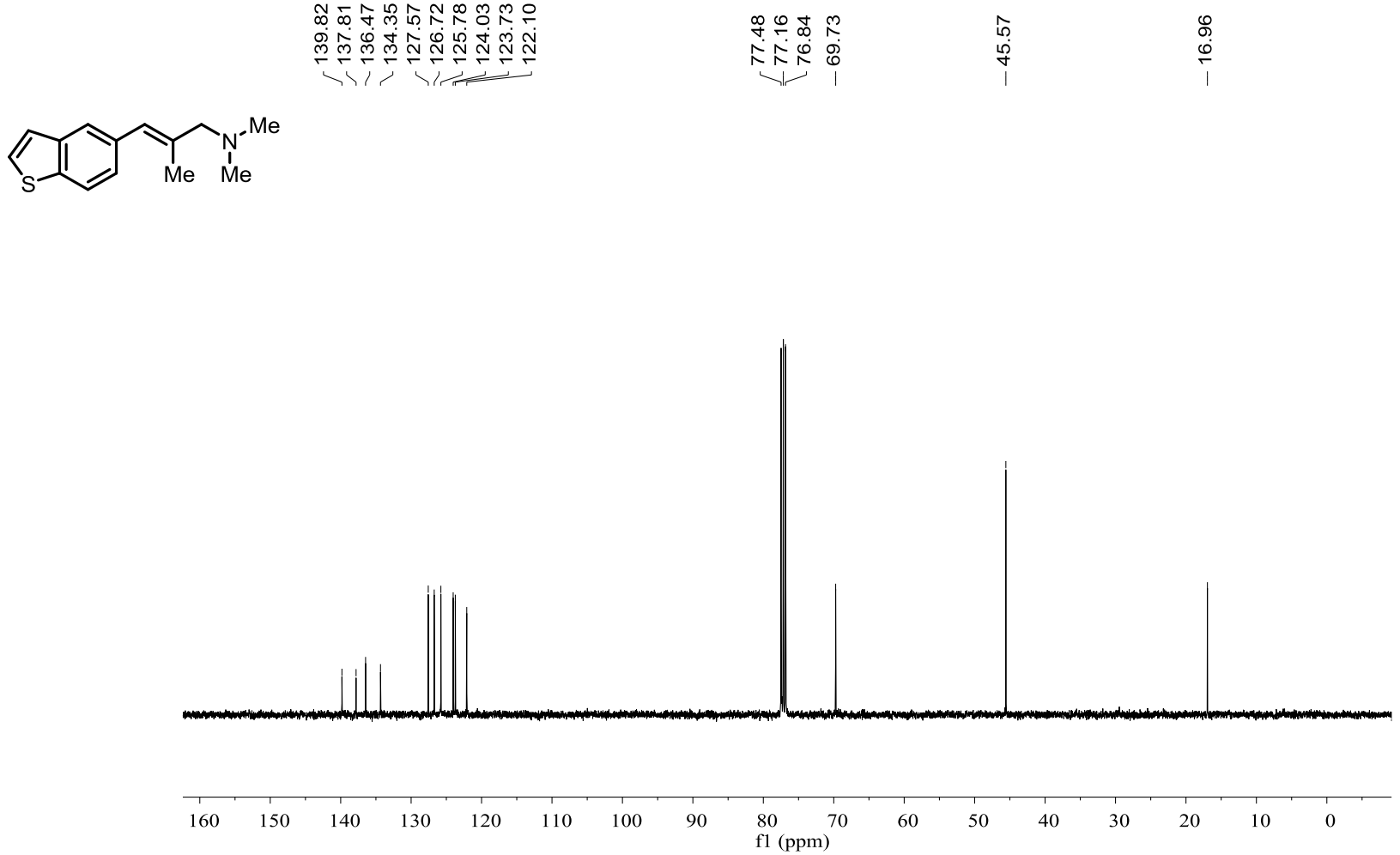
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(naphthalen-2-yl)prop-2-en-1-amine (12)



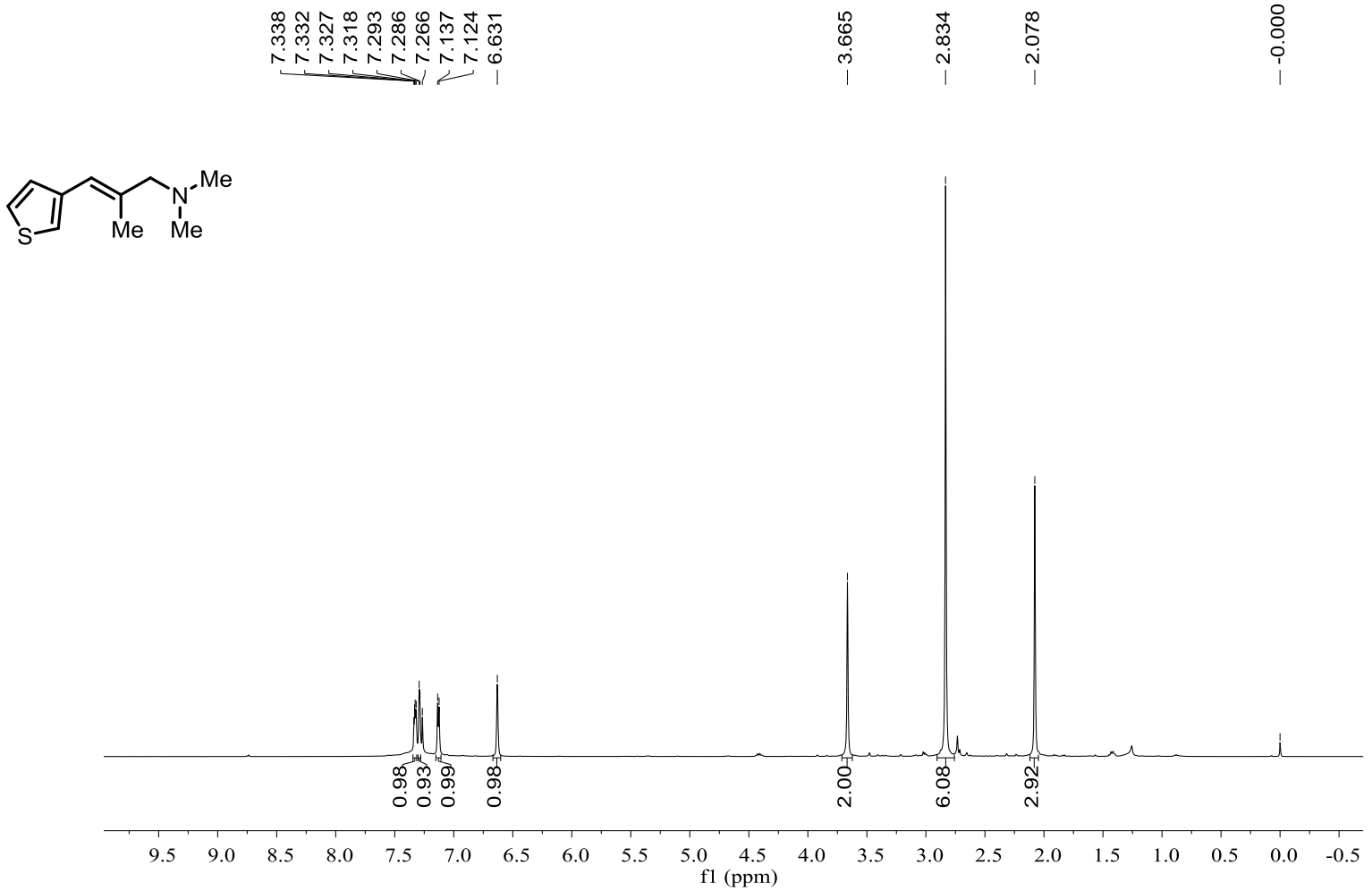
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(Benzo[b]thiophen-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (13)



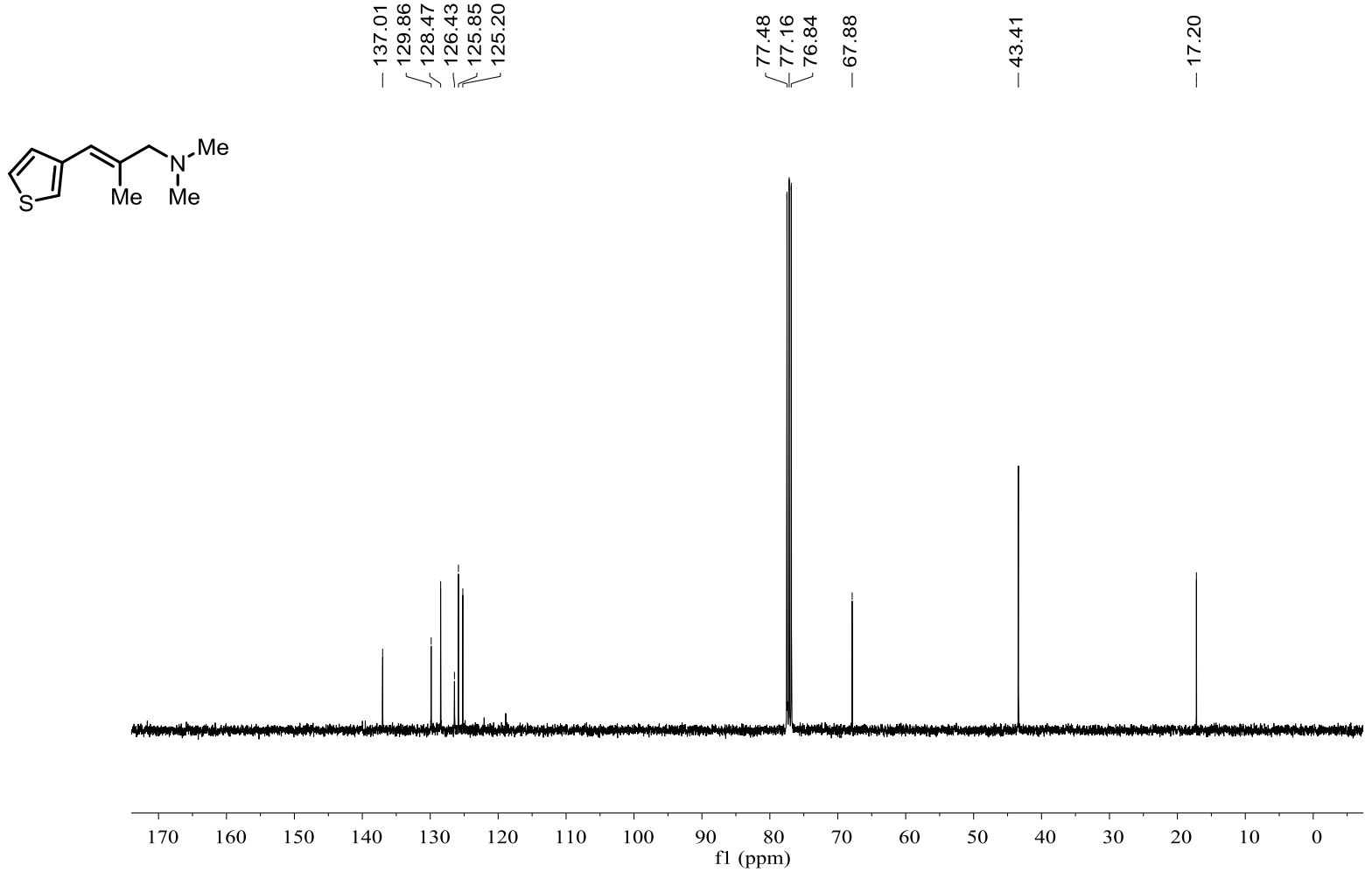
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(Benzo[b]thiophen-5-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (13)



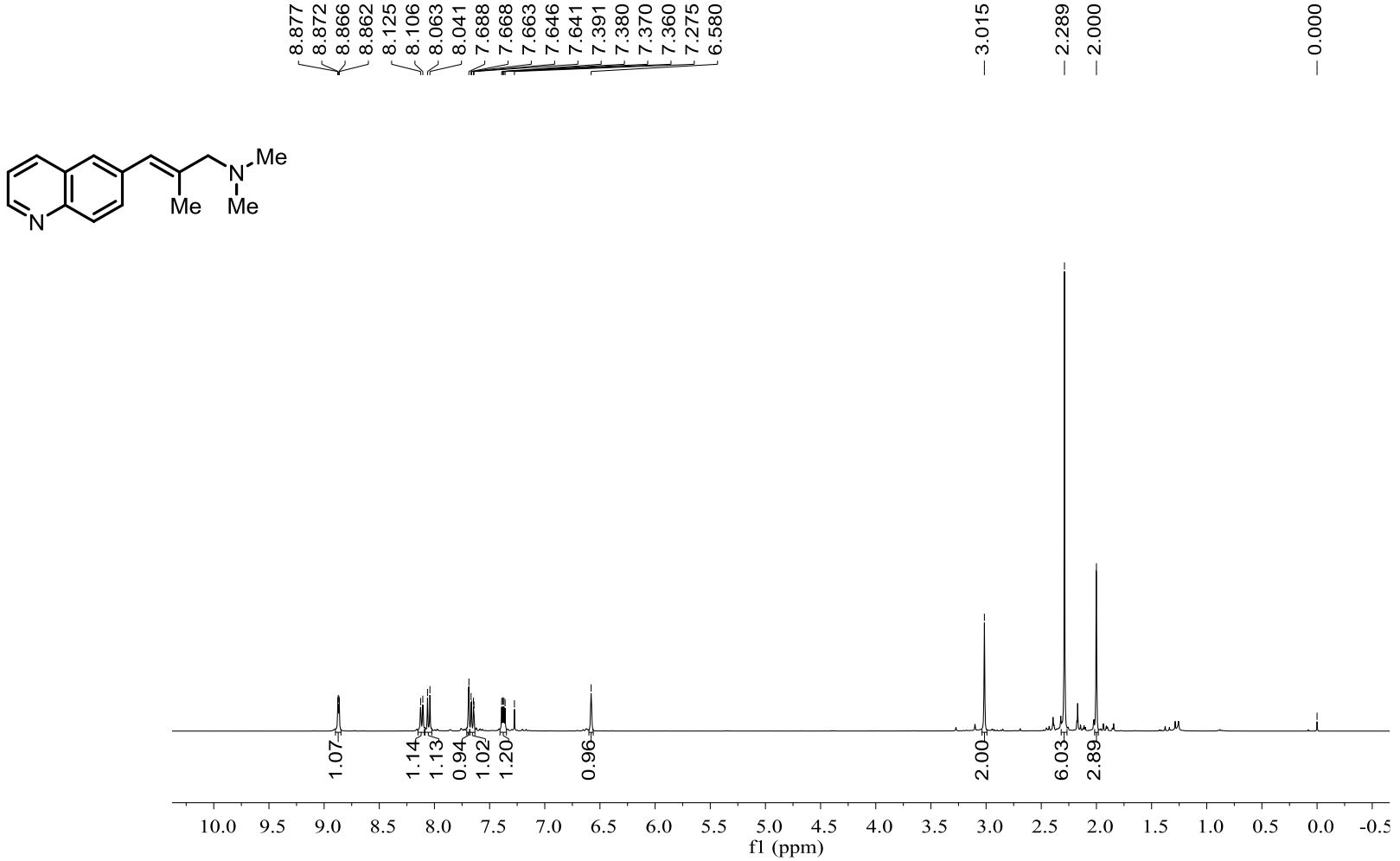
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(thiophen-3-yl)prop-2-en-1-amine (14)



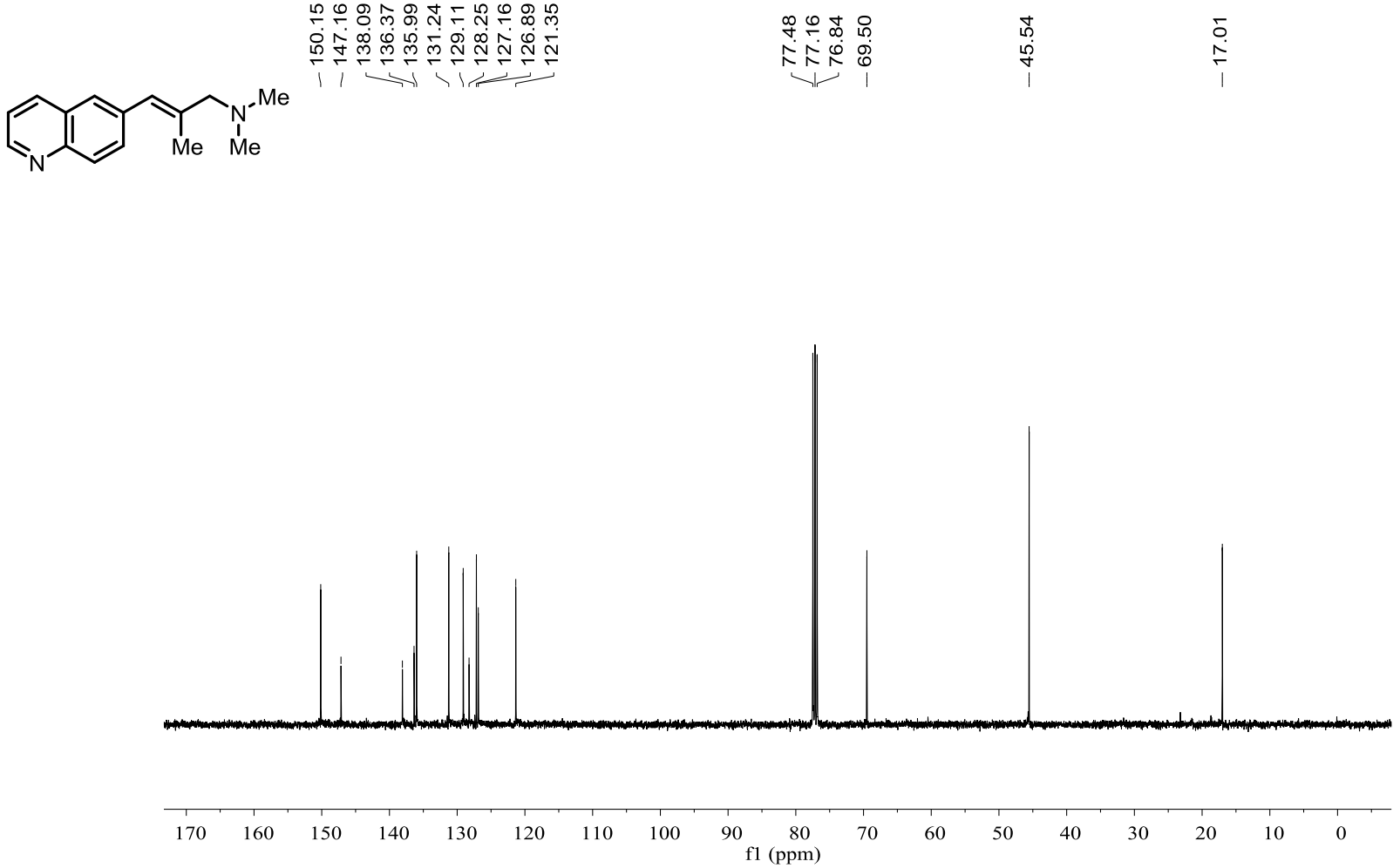
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(thiophen-3-yl)prop-2-en-1-amine (14)



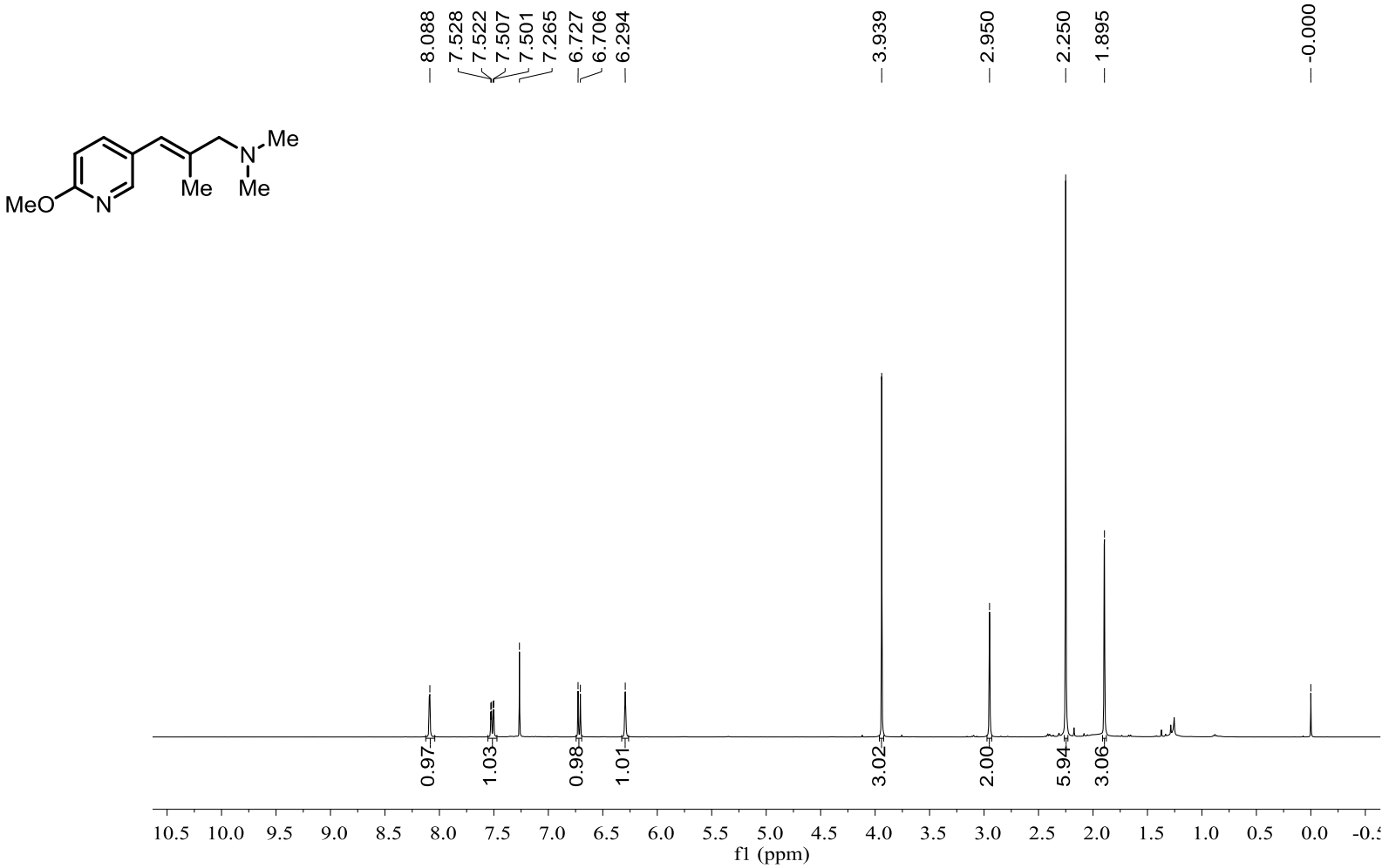
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(quinolin-6-yl)prop-2-en-1-amine (15)



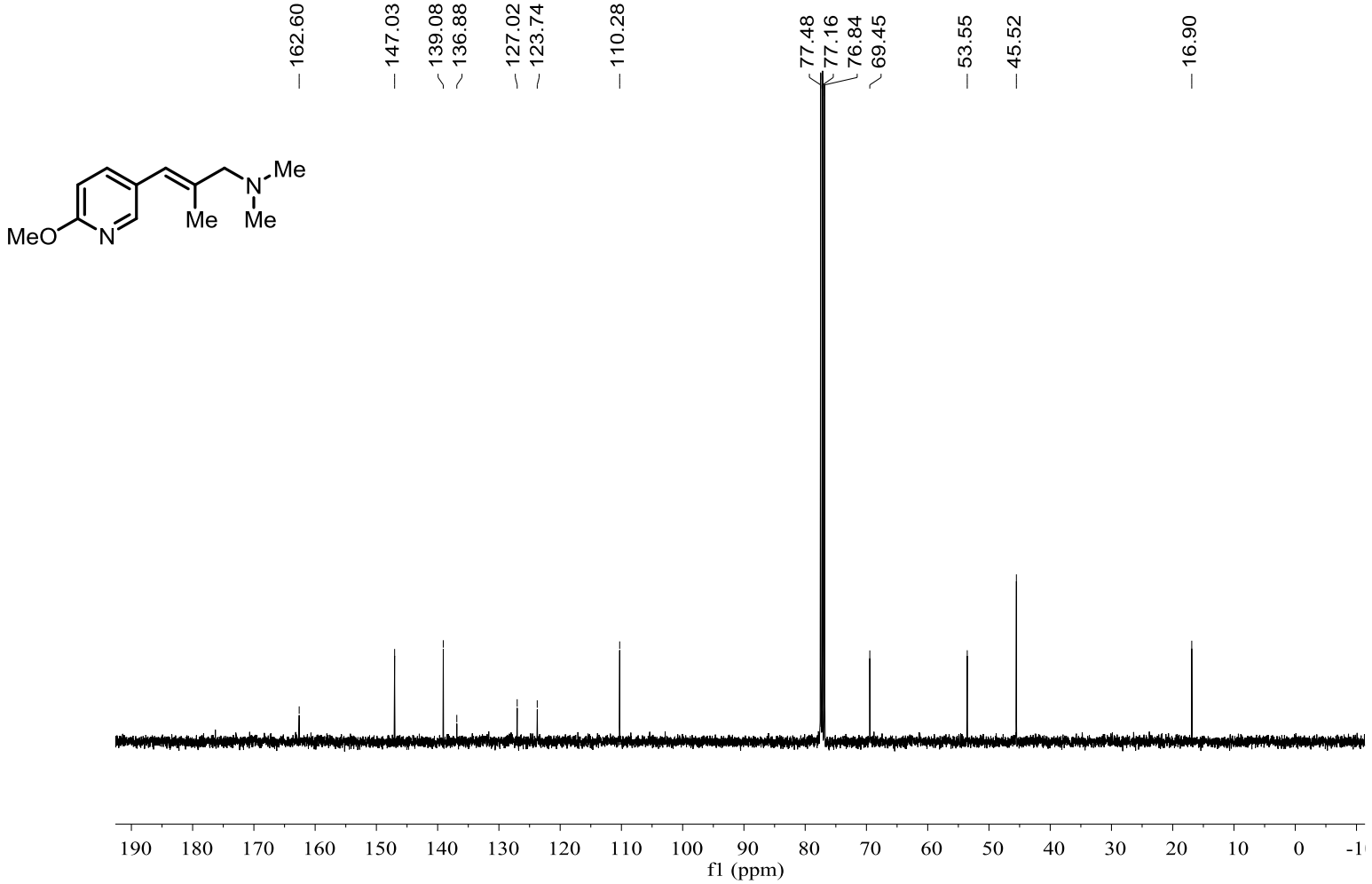
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*,*N*,2-Trimethyl-3-(quinolin-6-yl)prop-2-en-1-amine (15)



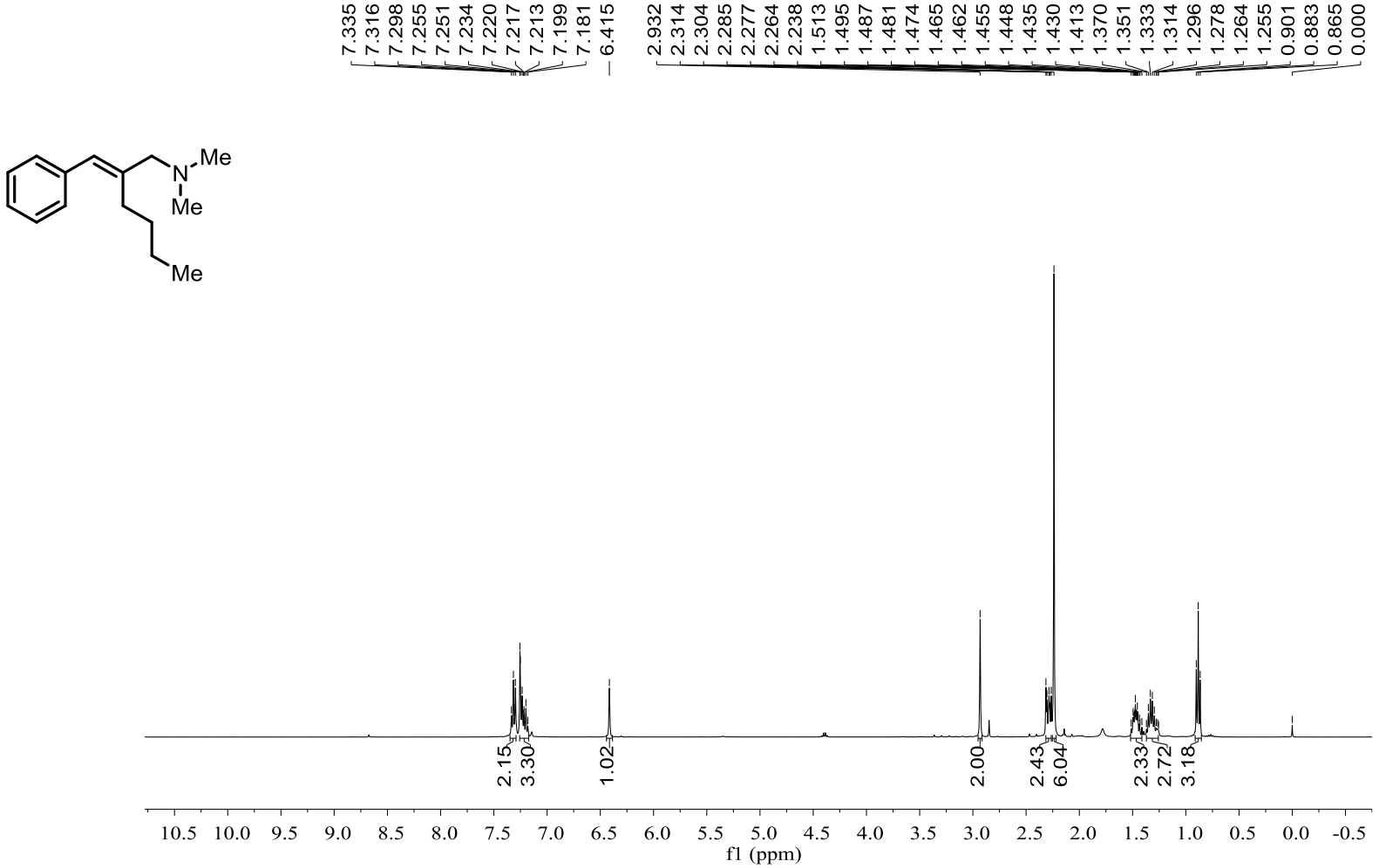
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-(6-Methoxypyridin-3-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (16)



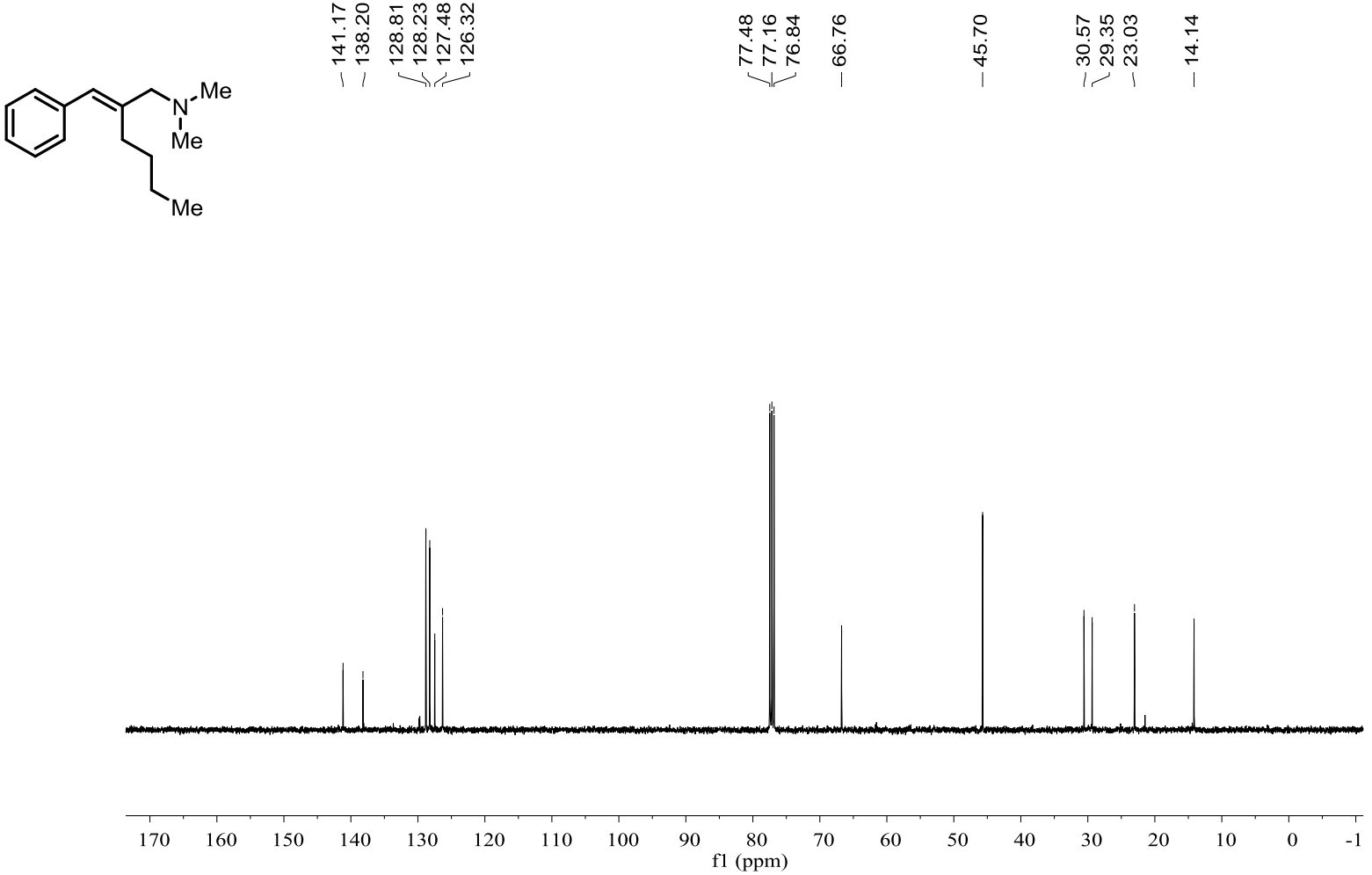
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-(6-Methoxypyridin-3-yl)-*N*,*N*,2-trimethylprop-2-en-1-amine (16)



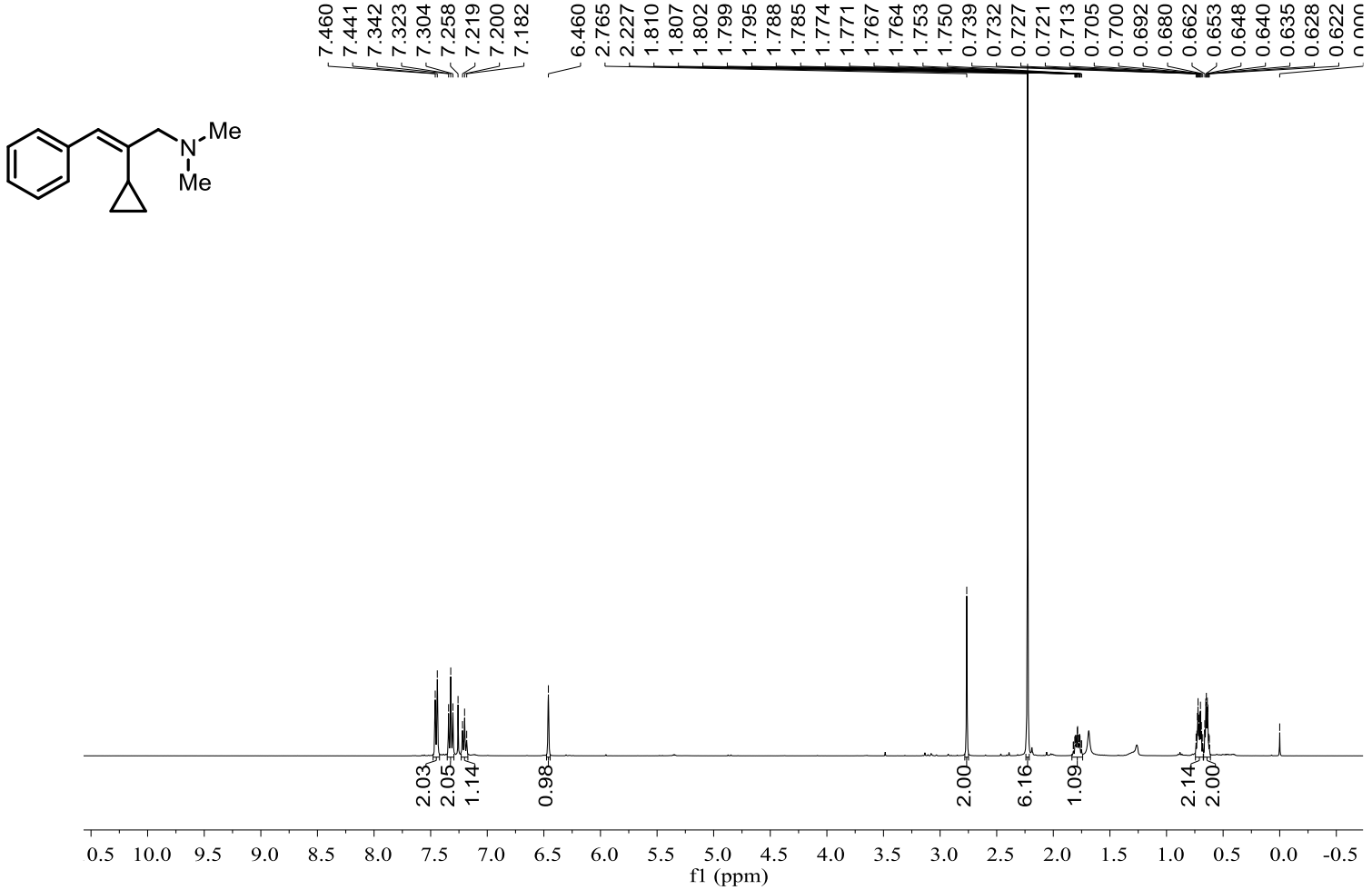
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-2-Benzylidene-*N*,*N*-dimethylhexan-1-amine (17)



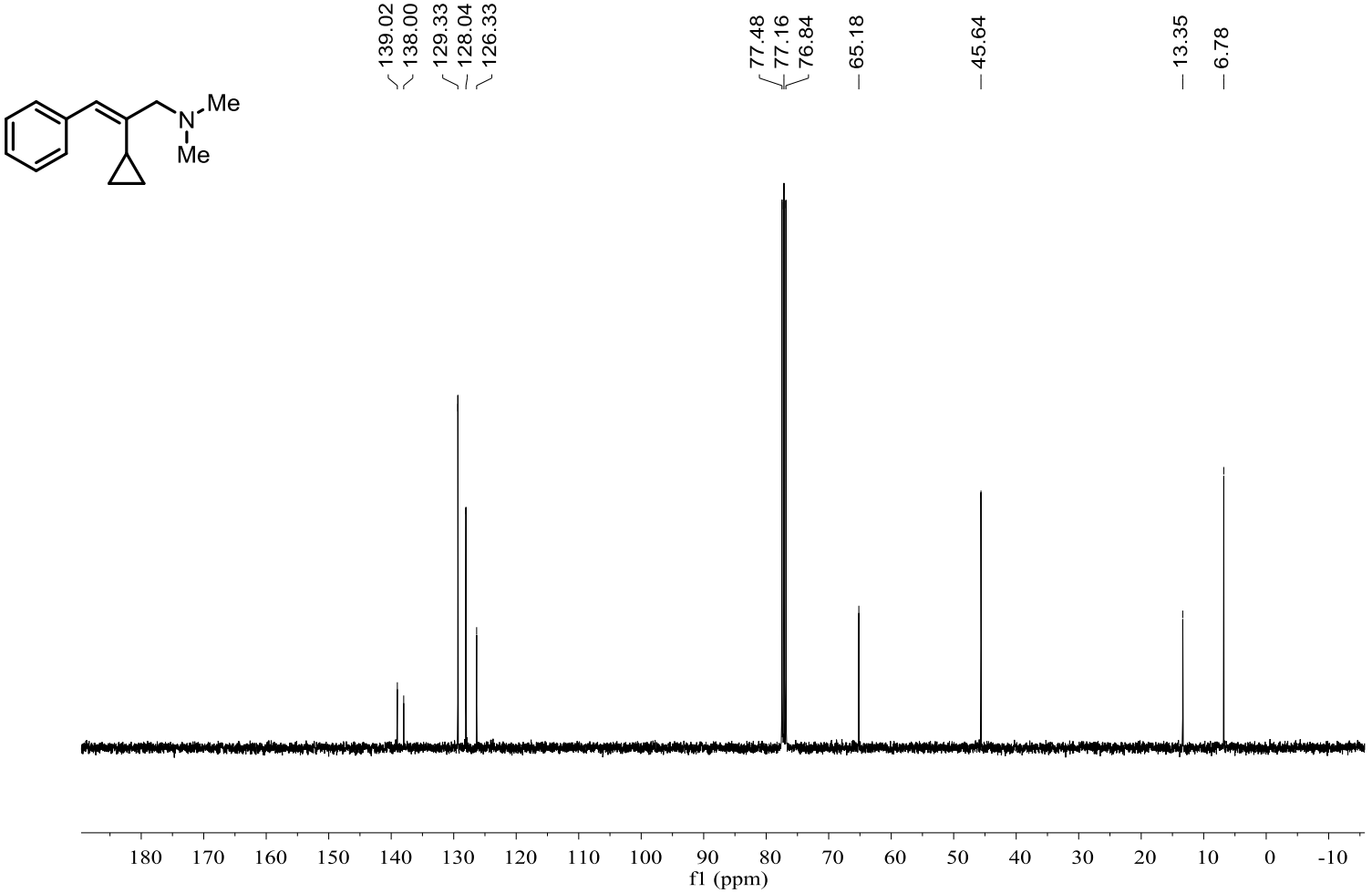
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-2-Benzylidene-*N*,*N*-dimethylhexan-1-amine (17)



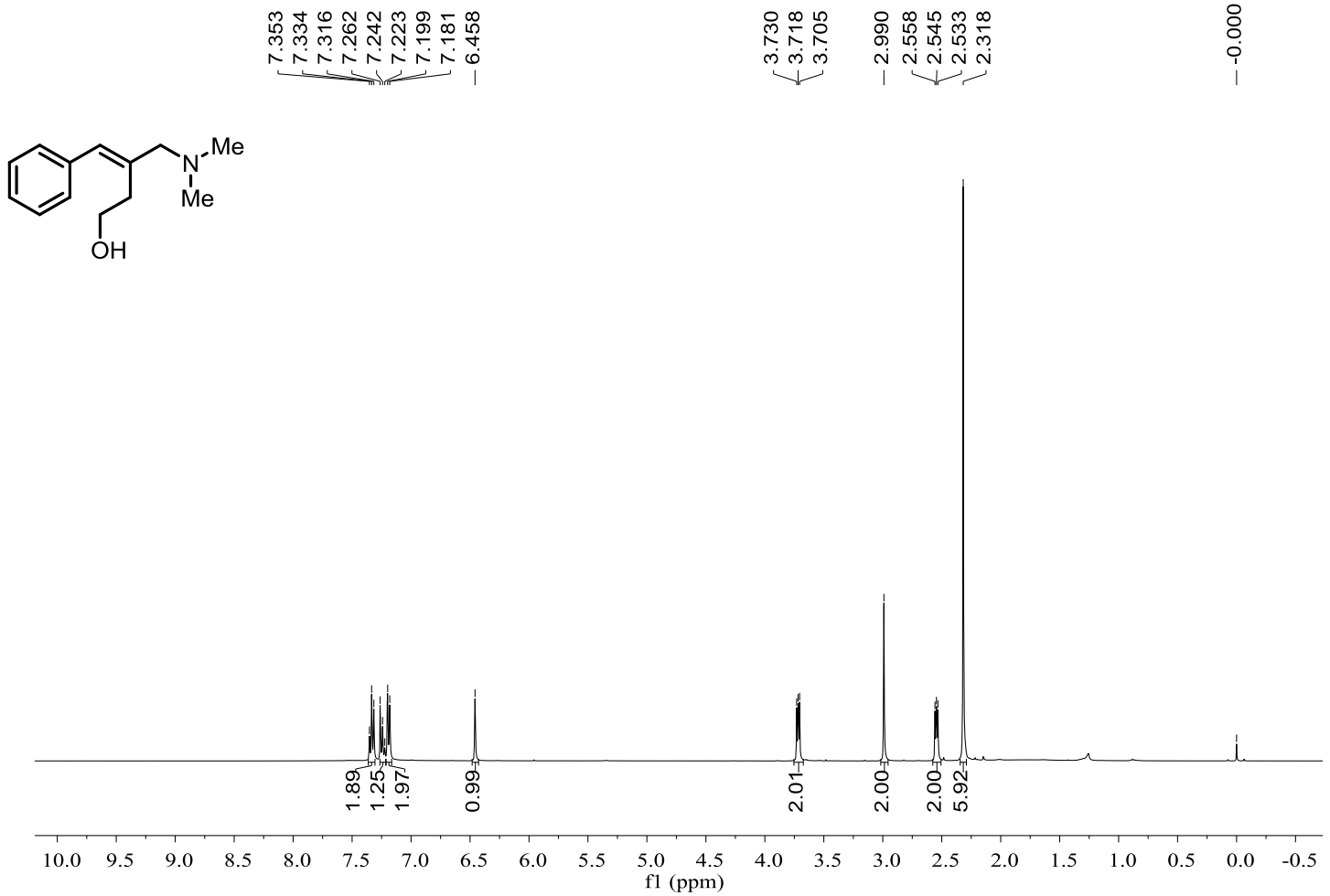
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-2-Cyclopropyl-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (18)



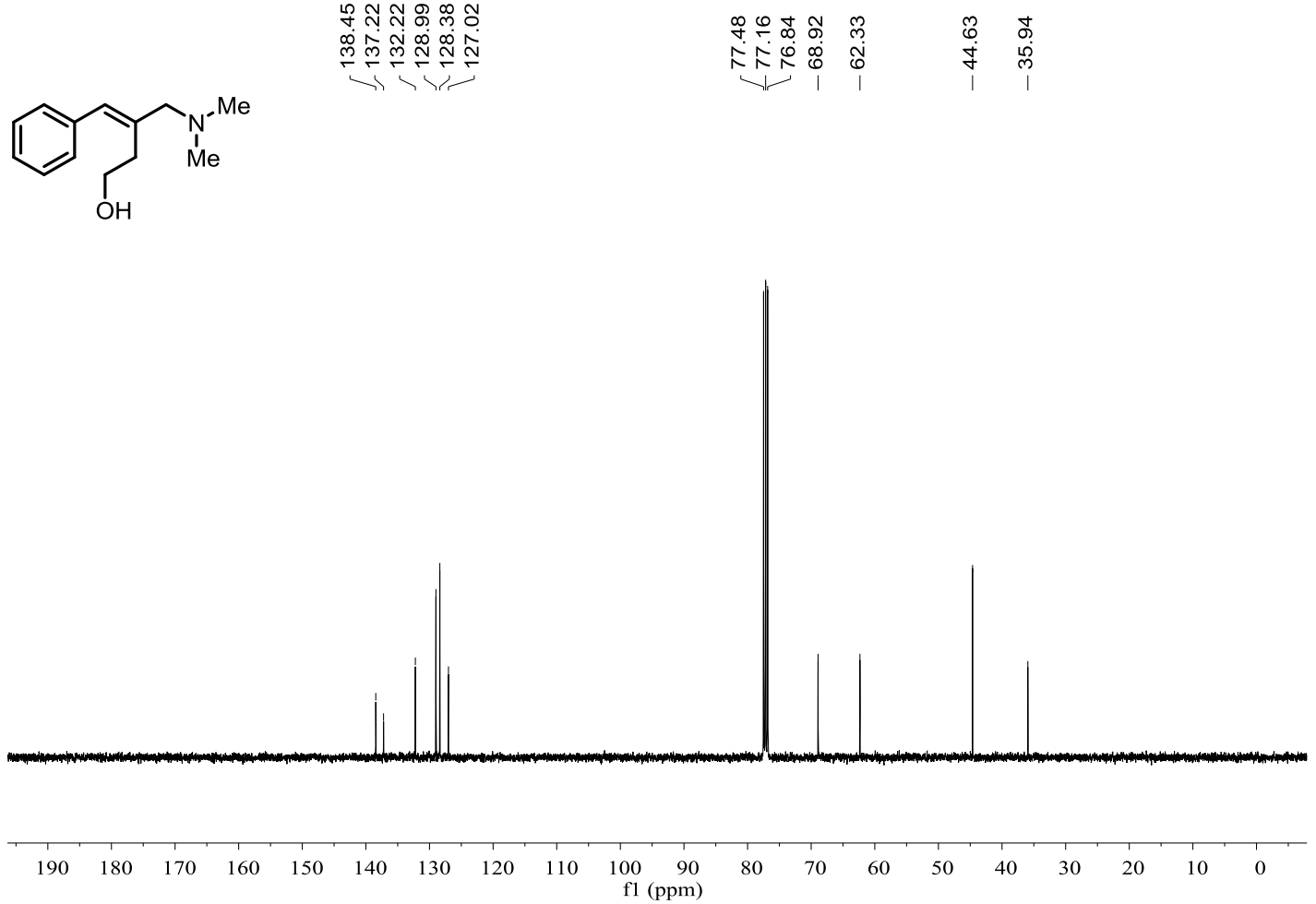
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-2-Cyclopropyl-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (18)



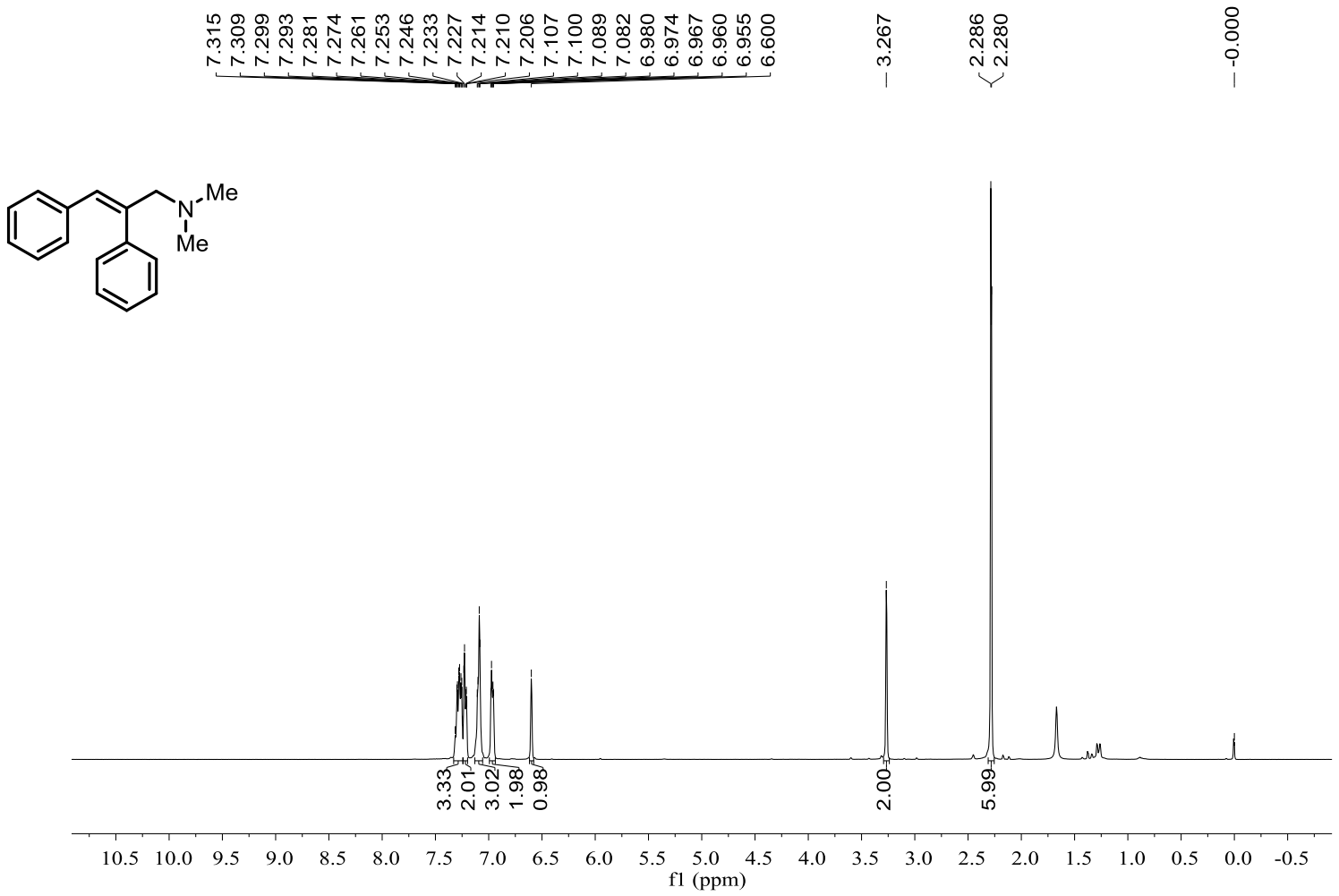
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-3-((Dimethylamino)methyl)-4-phenylbut-3-en-1-ol (19)



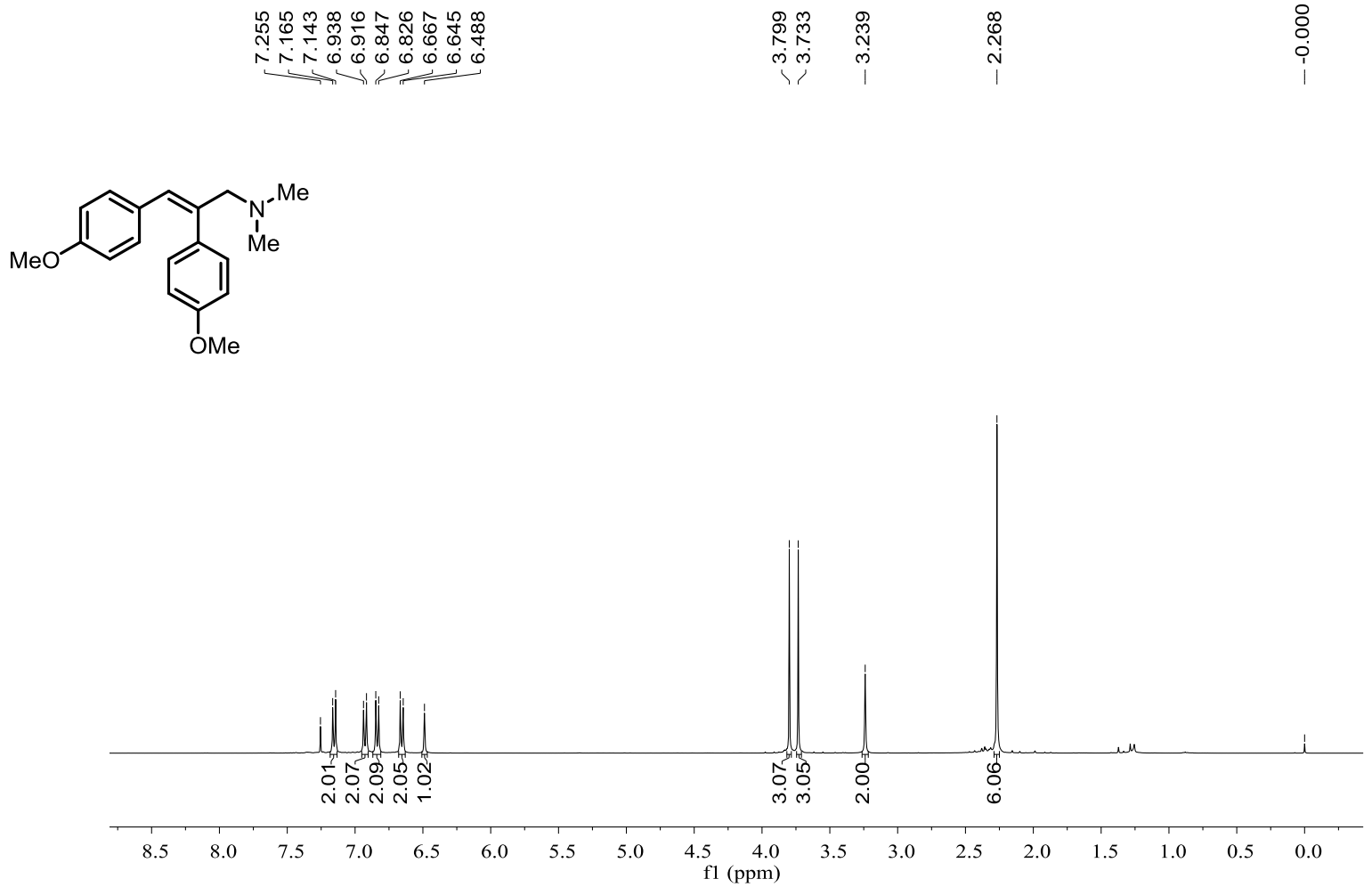
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-3-((Dimethylamino)methyl)-4-phenylbut-3-en-1-ol (19)



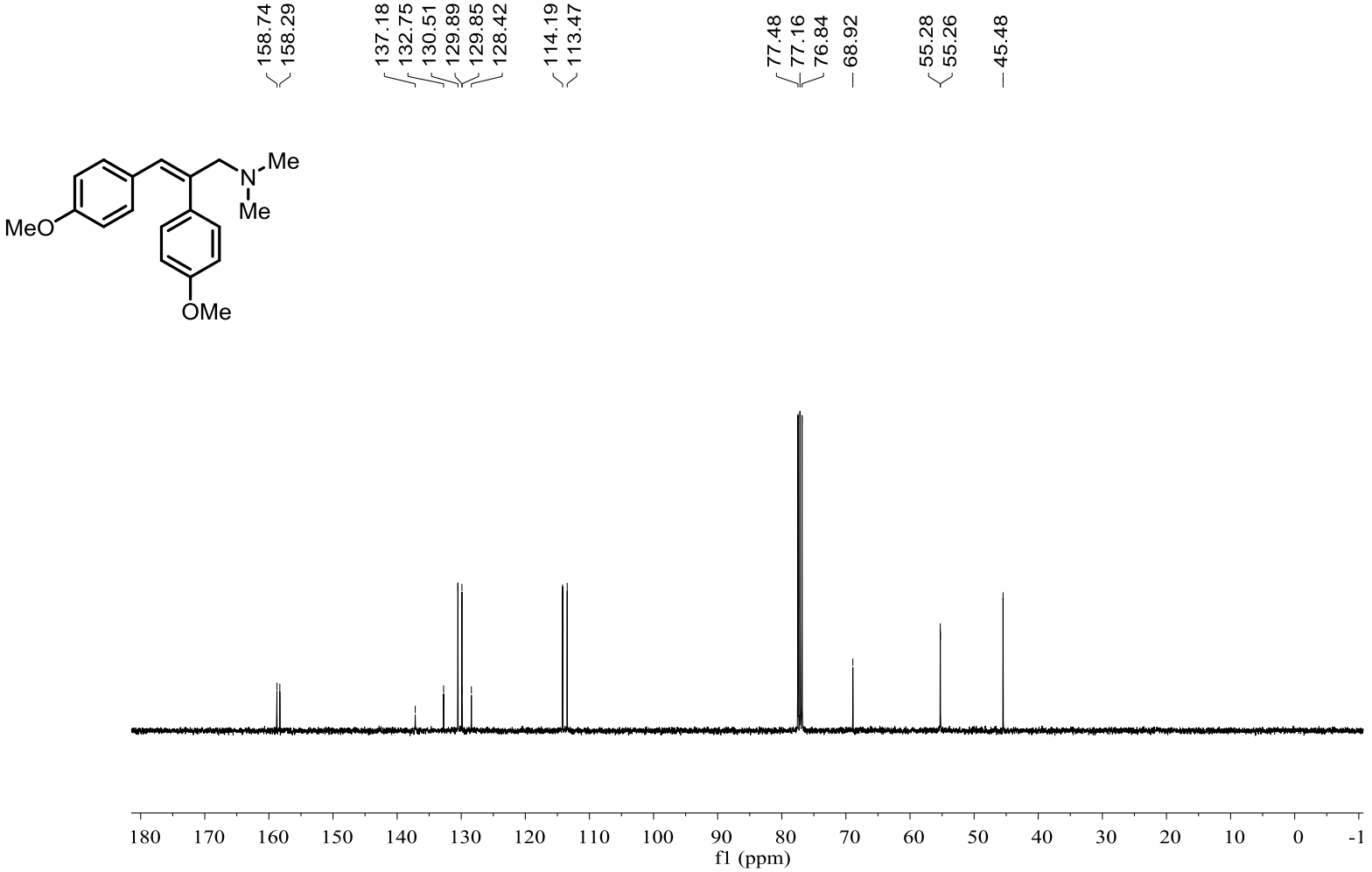
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*-Dimethyl-2,3-diphenylprop-2-en-1-amine (20)



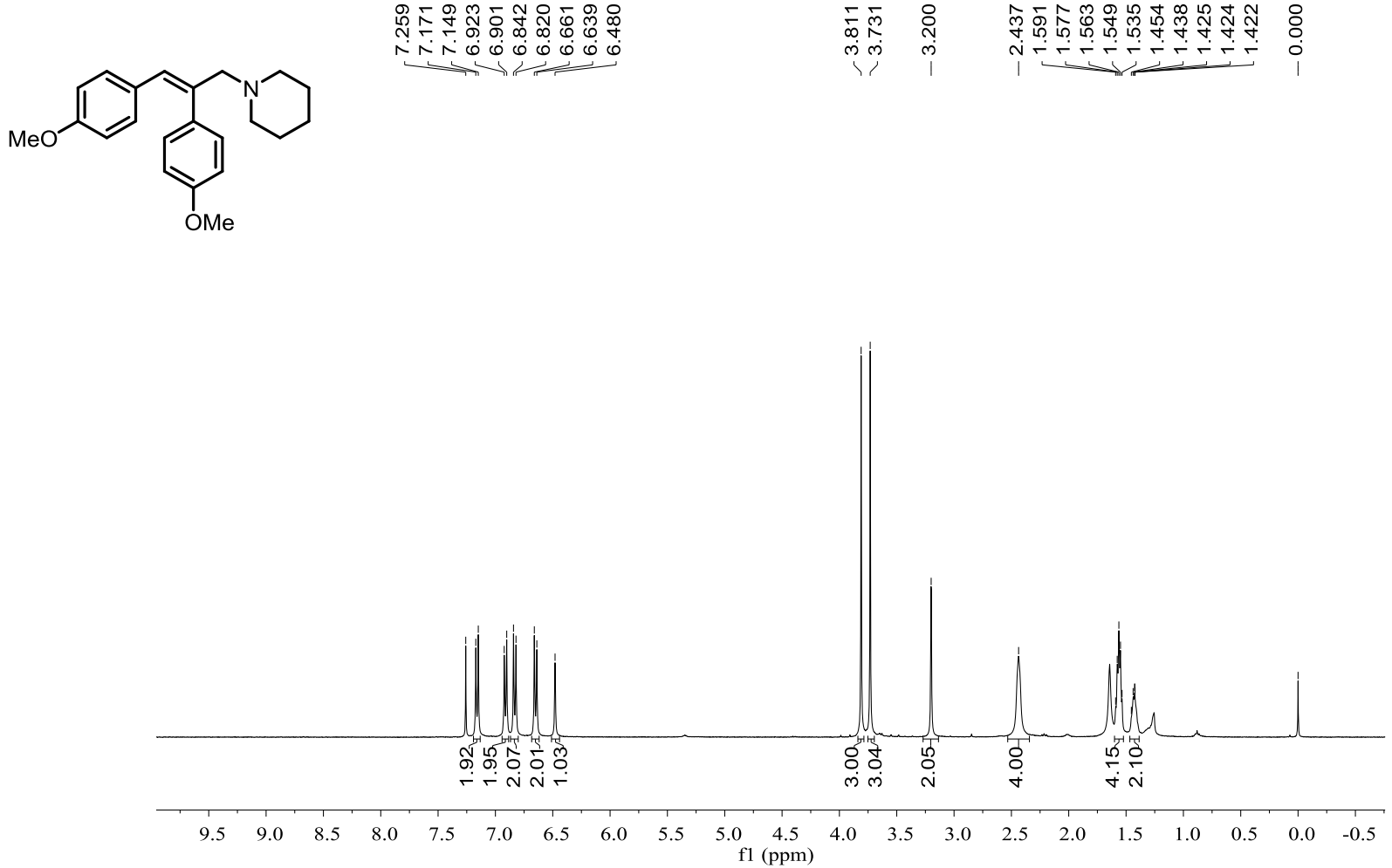
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-2,3-Bis(4-methoxyphenyl)-*N*,*N*-dimethylprop-2-en-1-amine (21)



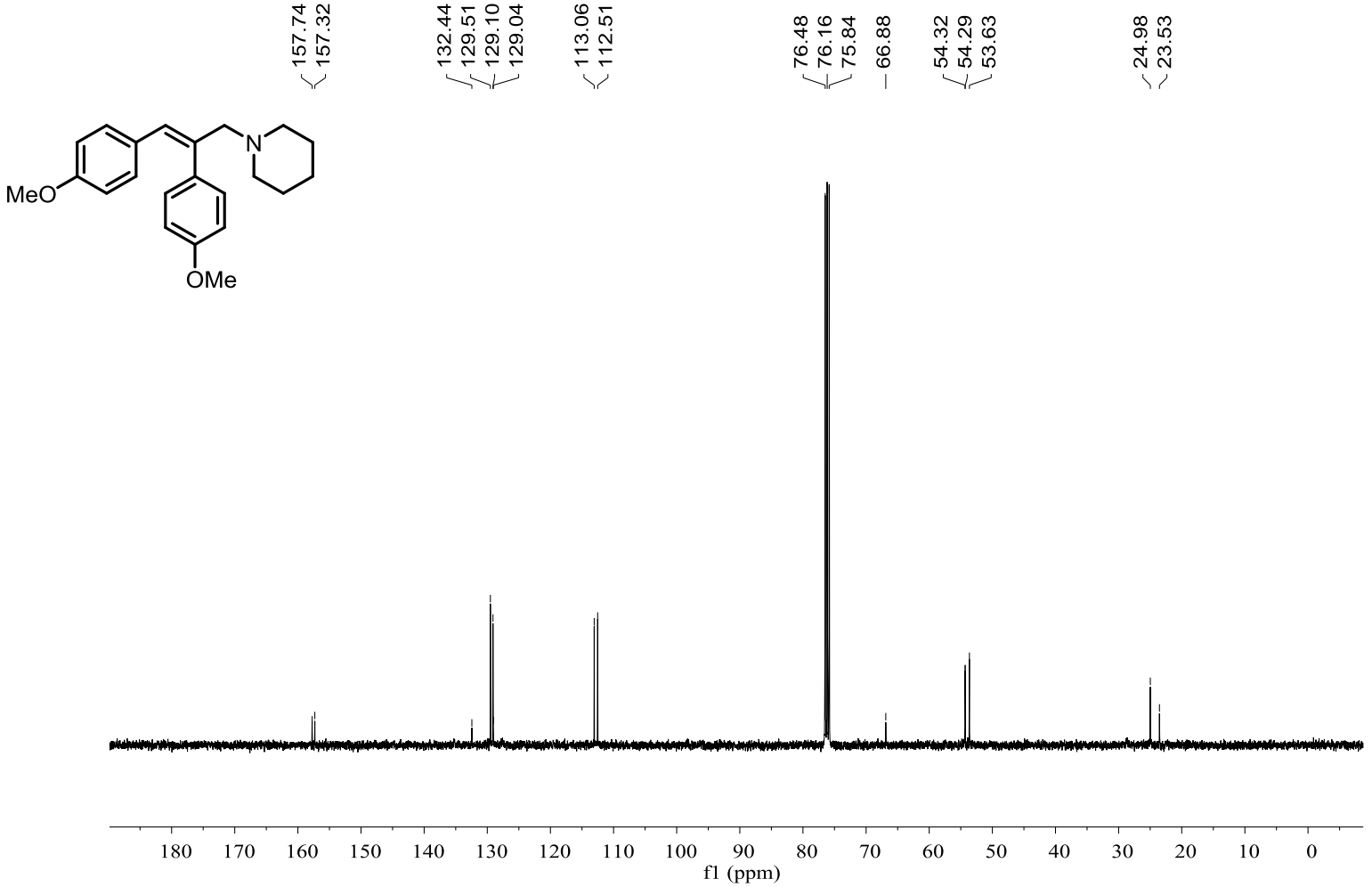
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-2,3-Bis(4-methoxyphenyl)-*N*,*N*-dimethylprop-2-en-1-amine (21)



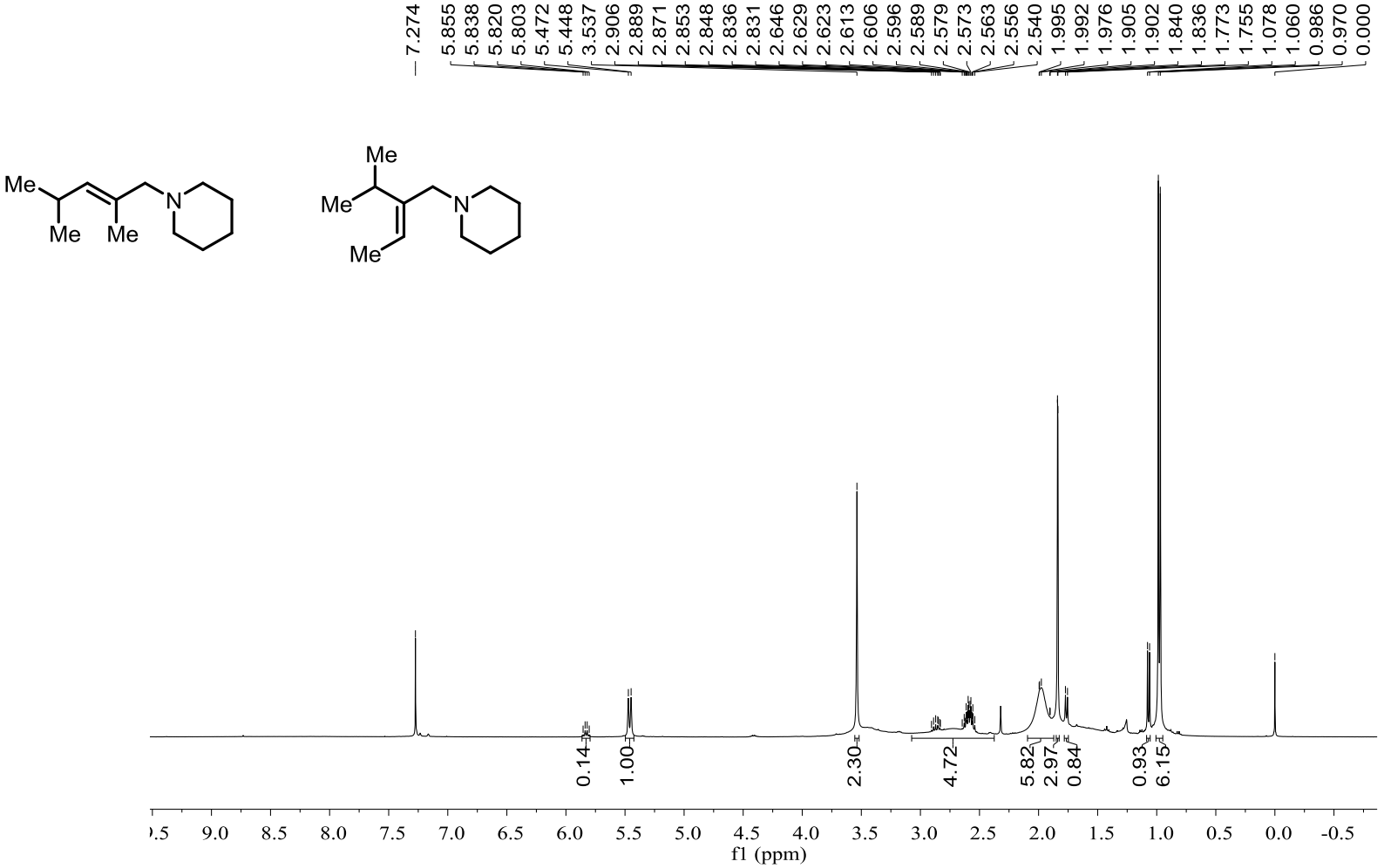
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2,3-Bis(4-methoxyphenyl)allyl)piperidine (22)



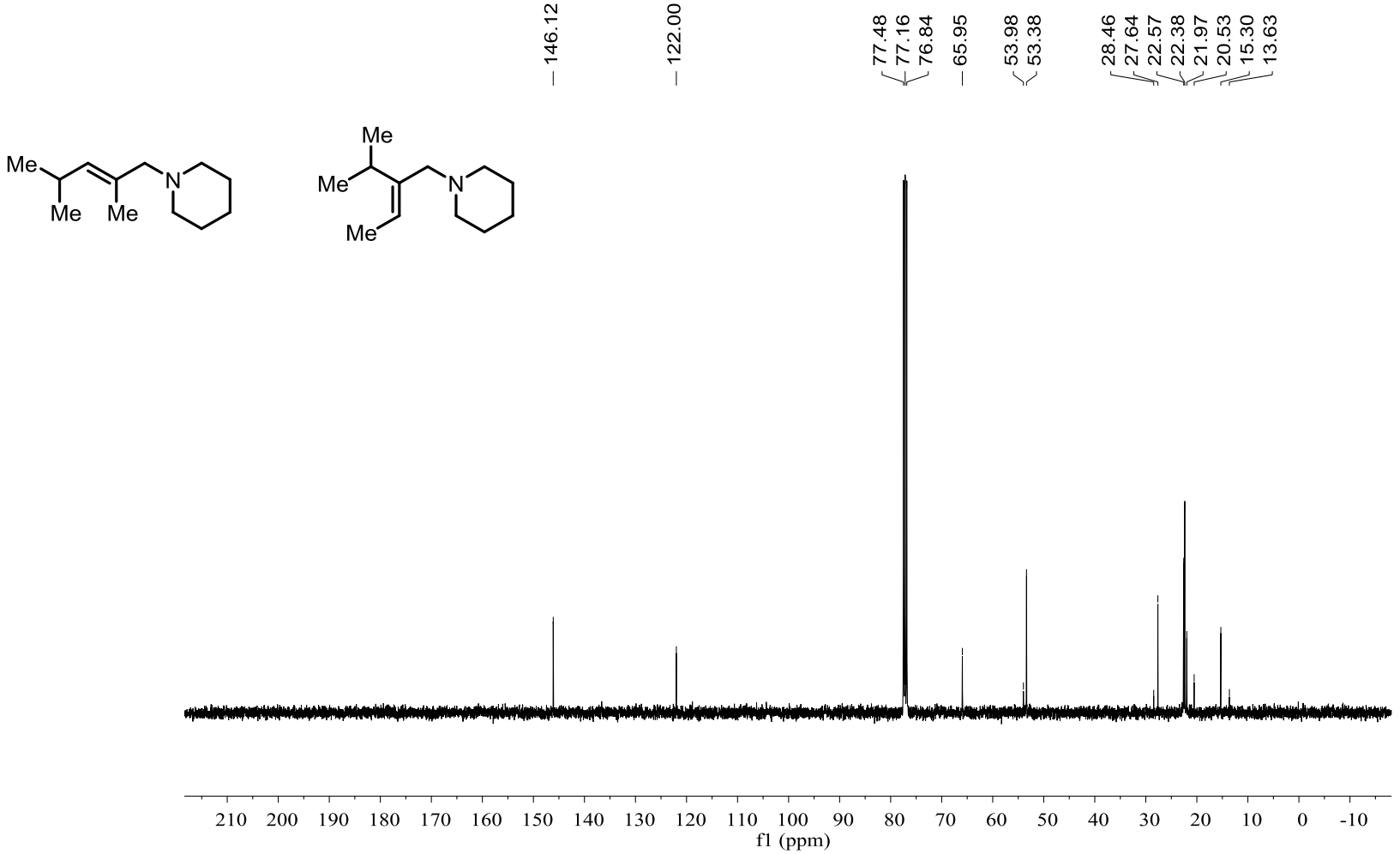
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2,3-Bis(4-methoxyphenyl)allyl)piperidine (22)



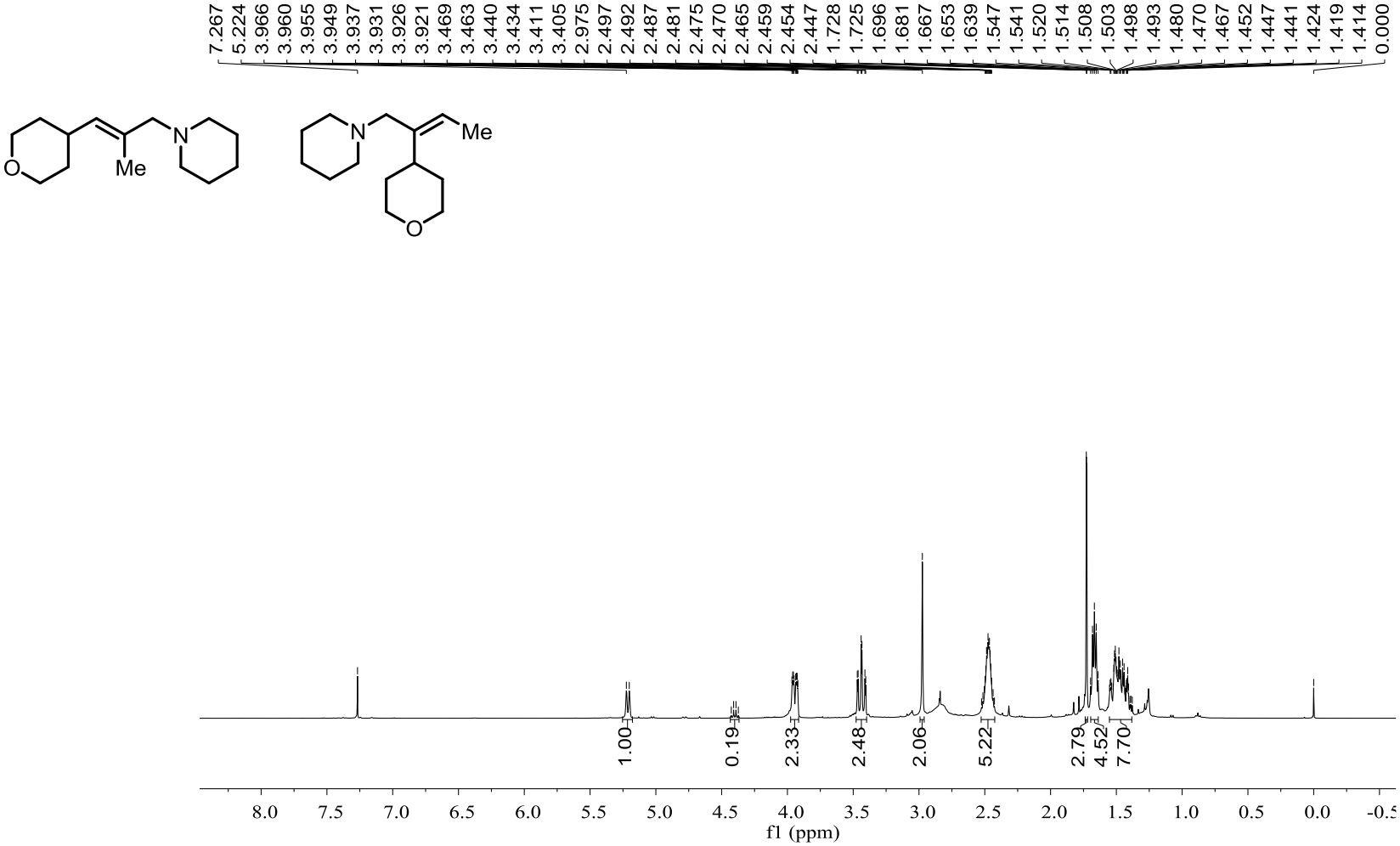
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2,4-Dimethylpent-2-en-1-yl)piperidine (23)



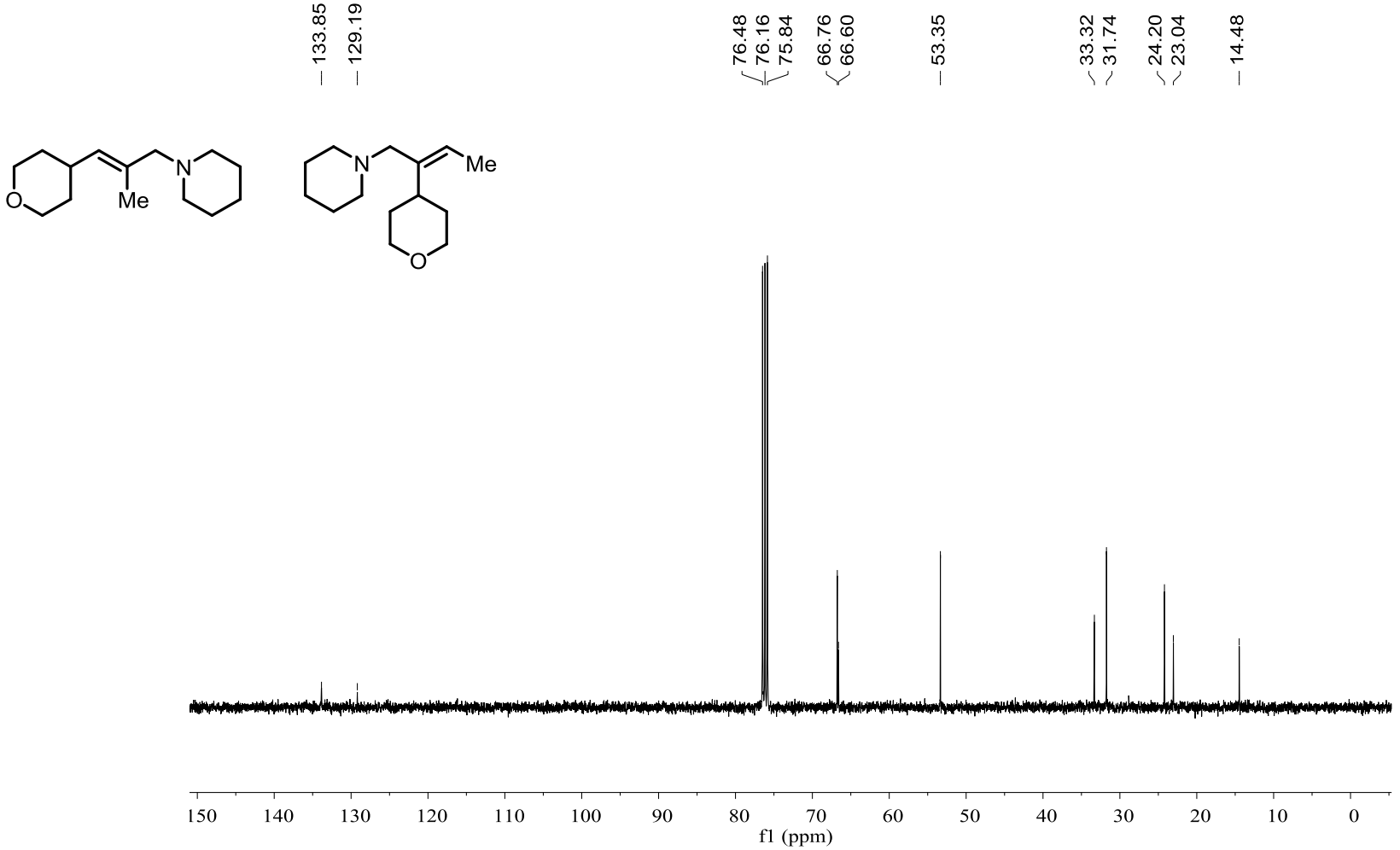
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2,4-Dimethylpent-2-en-1-yl)piperidine (23)



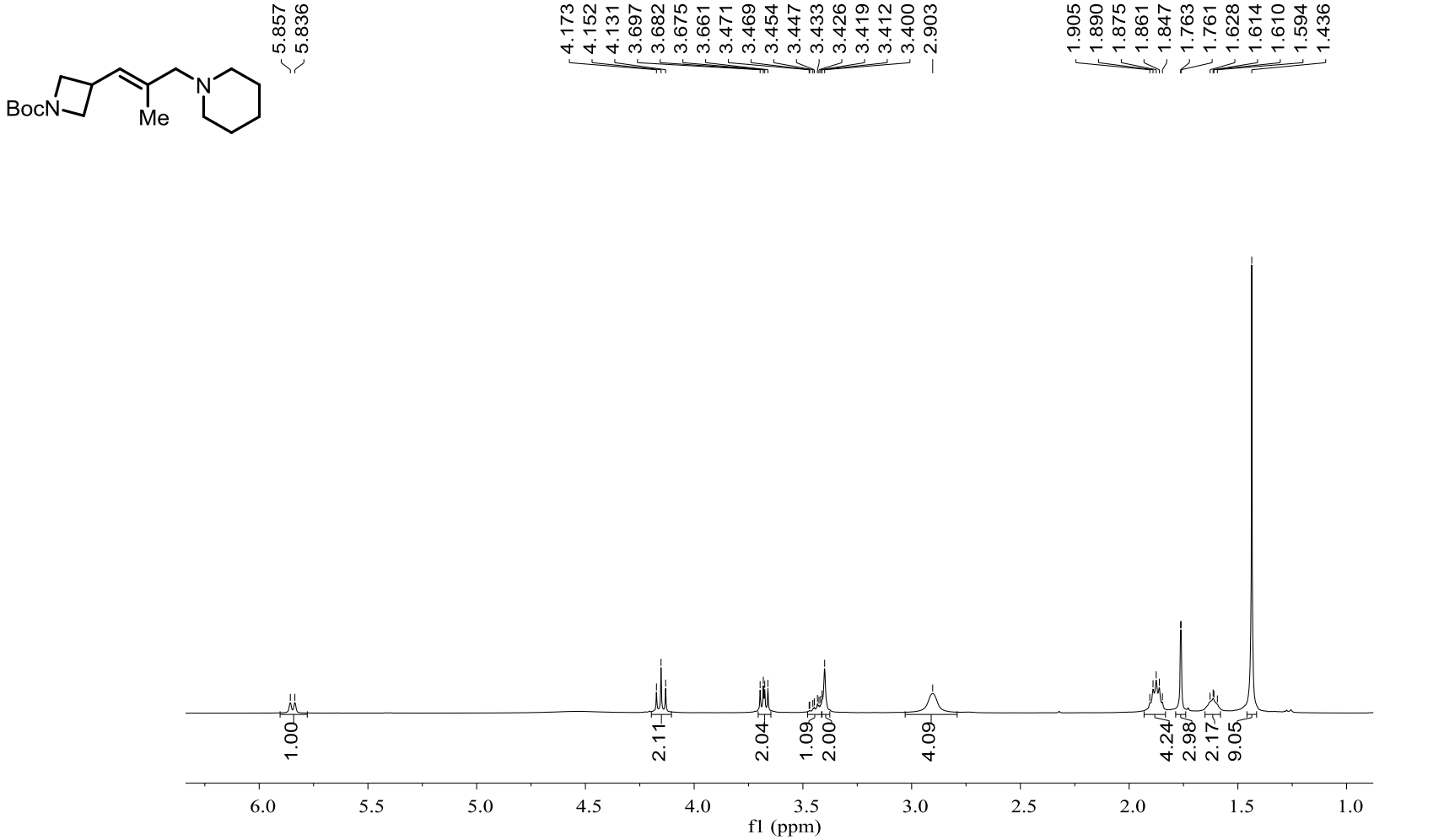
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-(tetrahydro-2H-pyran-4-yl)allyl)piperidine (24)



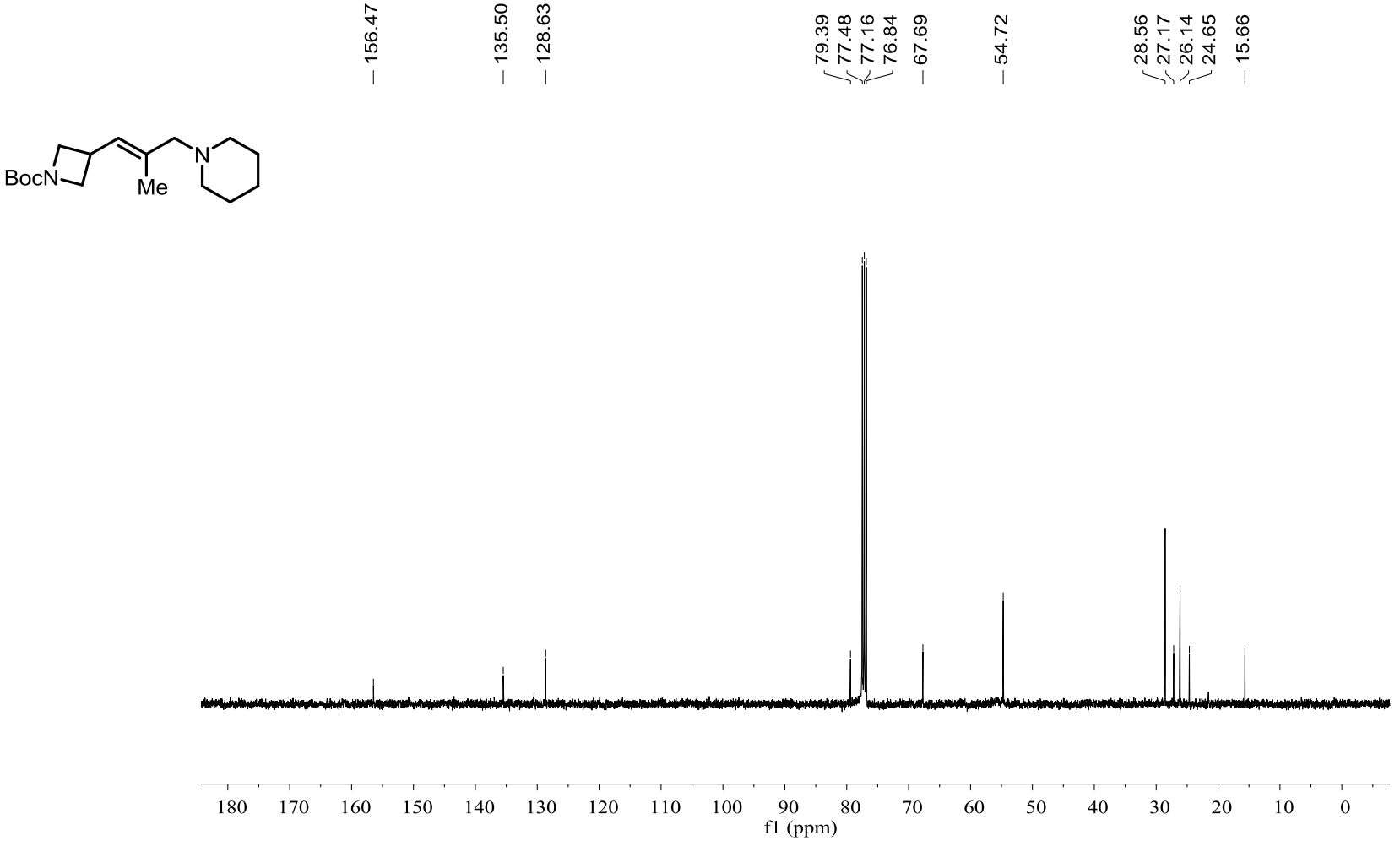
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-(tetrahydro-2H-pyran-4-yl)allyl)piperidine (24)



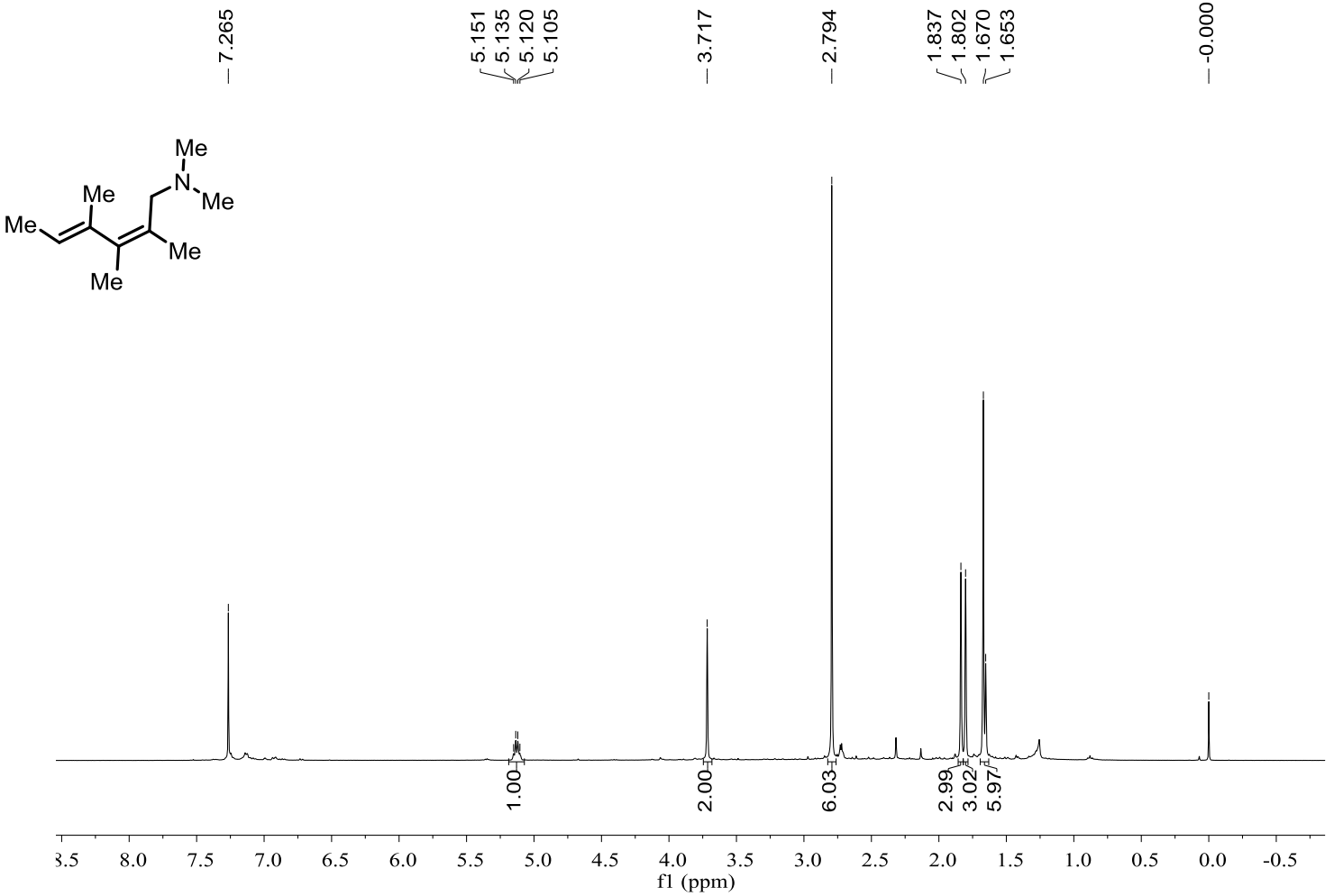
^{1}H NMR spectrum (400 M, $CDCl_3$) of Tert-butyl (*E*)-3-(2-methyl-3-(piperidin-1-yl)prop-1-en-1-yl)azetidine-1-carboxylate (25)



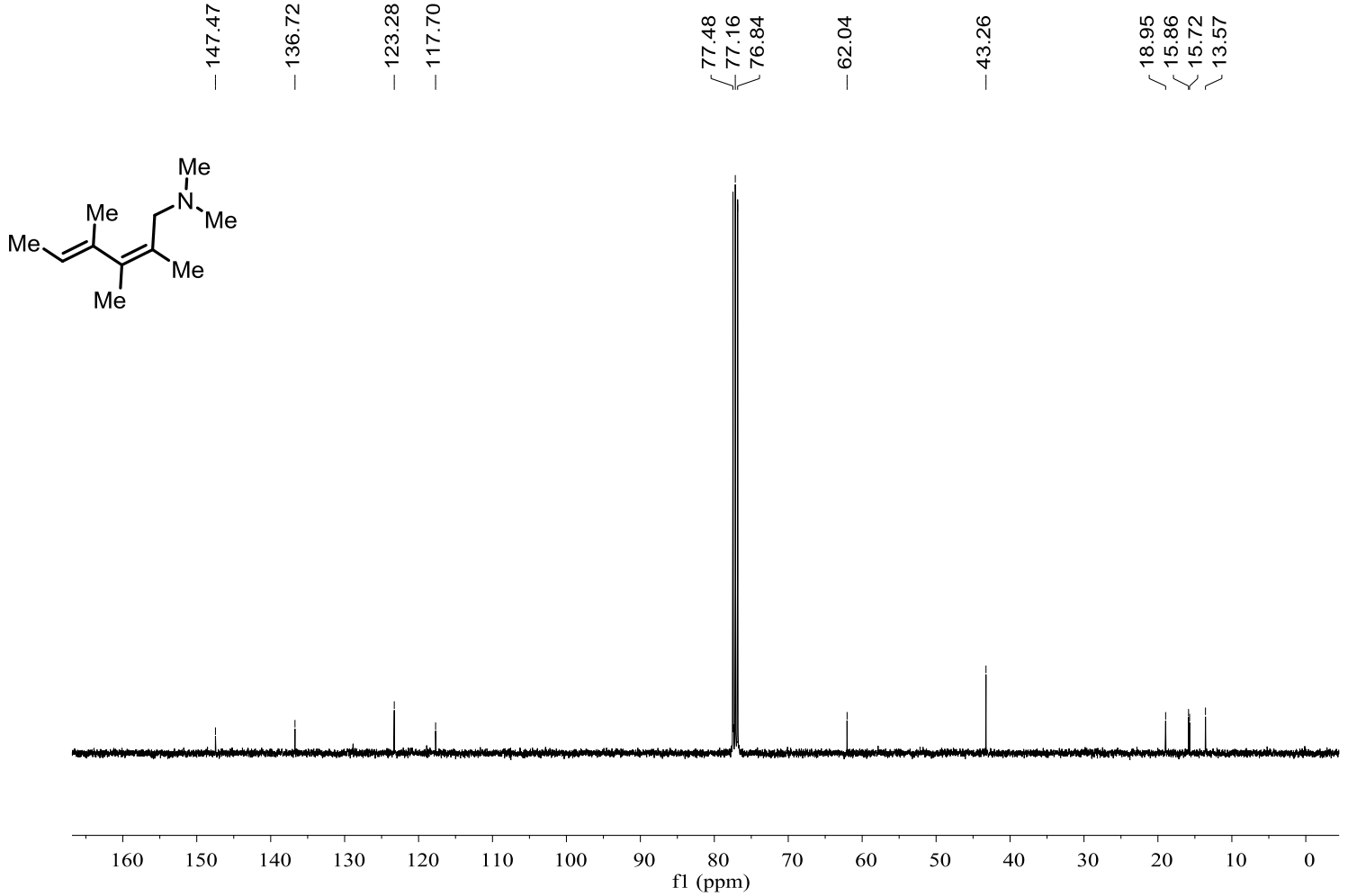
^{13}C NMR spectrum (100 M, $CDCl_3$) of Tert-butyl (*E*)-3-(2-methyl-3-(piperidin-1-yl)prop-1-en-1-yl)azetidine-1-carboxylate (25)



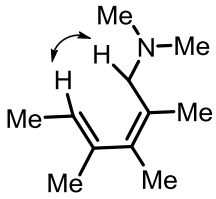
^{1}H NMR spectrum (400 M, $CDCl_3$) of (2*Z*,4*E*)-*N*,*N*,2,3,4-pentamethylhexa-2,4-dien-1-amine (26)

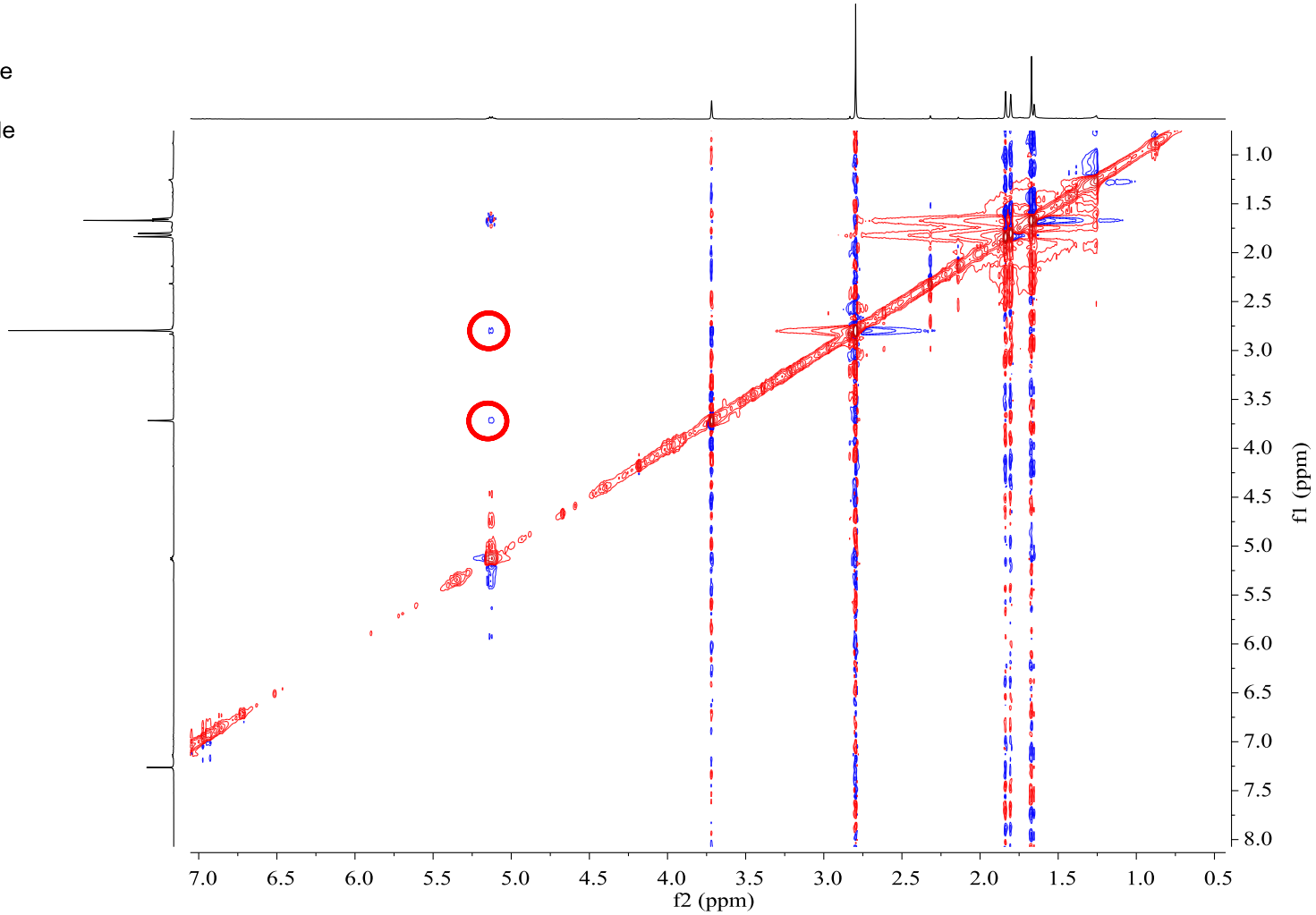


^{13}C NMR spectrum (100 M, $CDCl_3$) of (2*Z*,4*E*)-*N*,*N*,2,3,4-Pentamethylhexa-2,4-dien-1-amine (26)

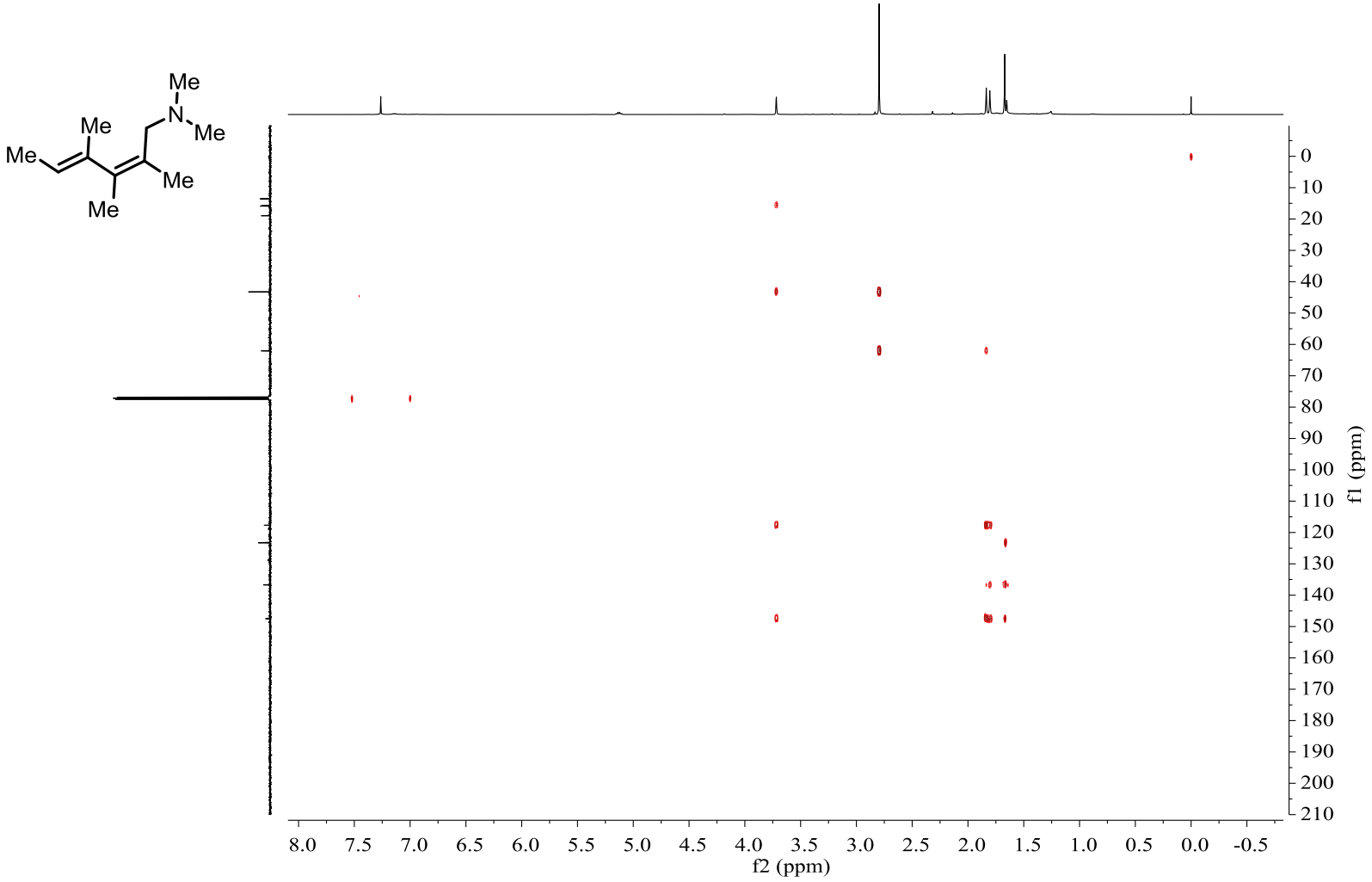


NOE of (2*Z*,4*E*)-*N*,*N*,2,3,4-Pentamethylhexa-2,4-dien-1-amine (26)

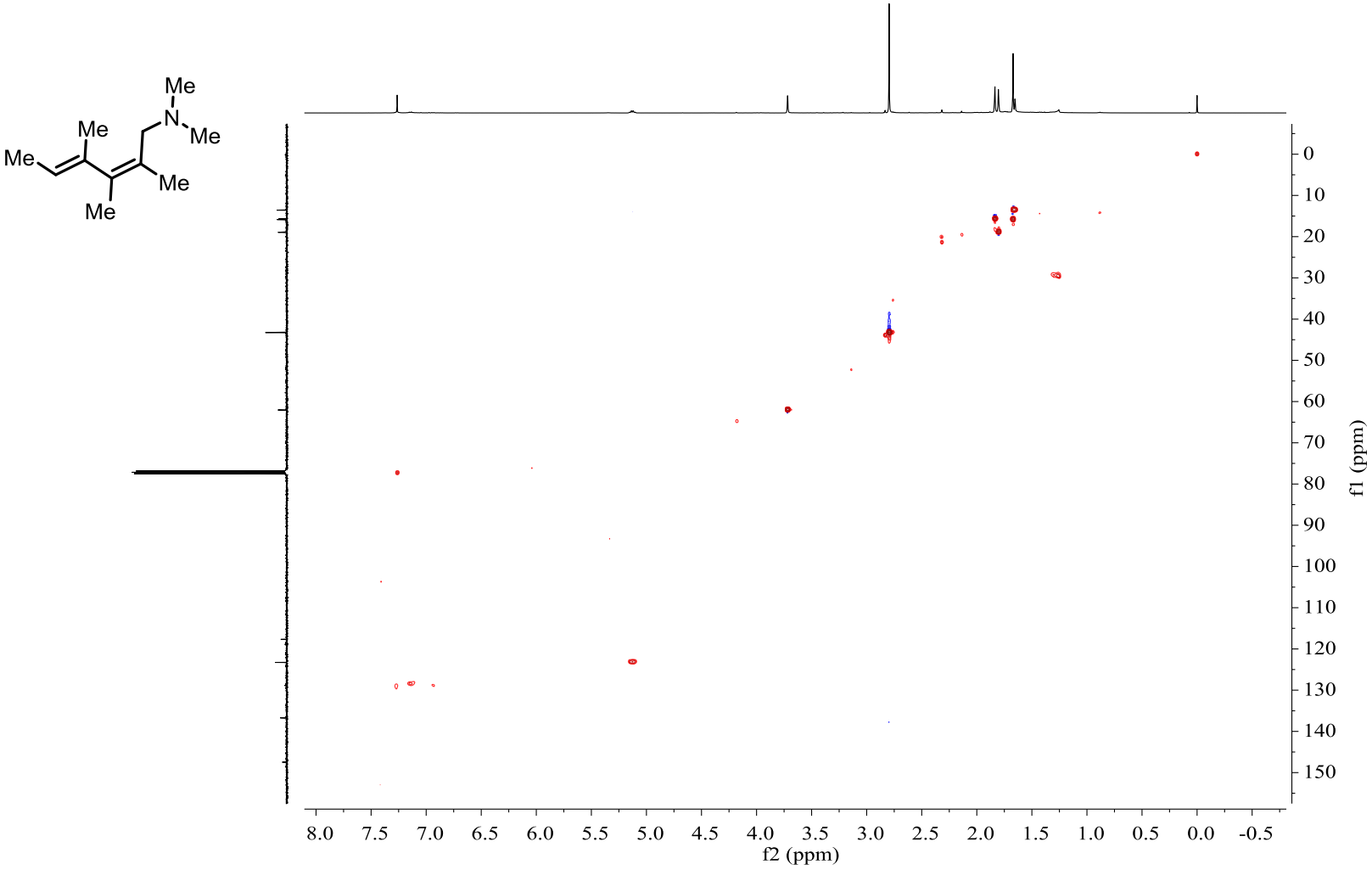




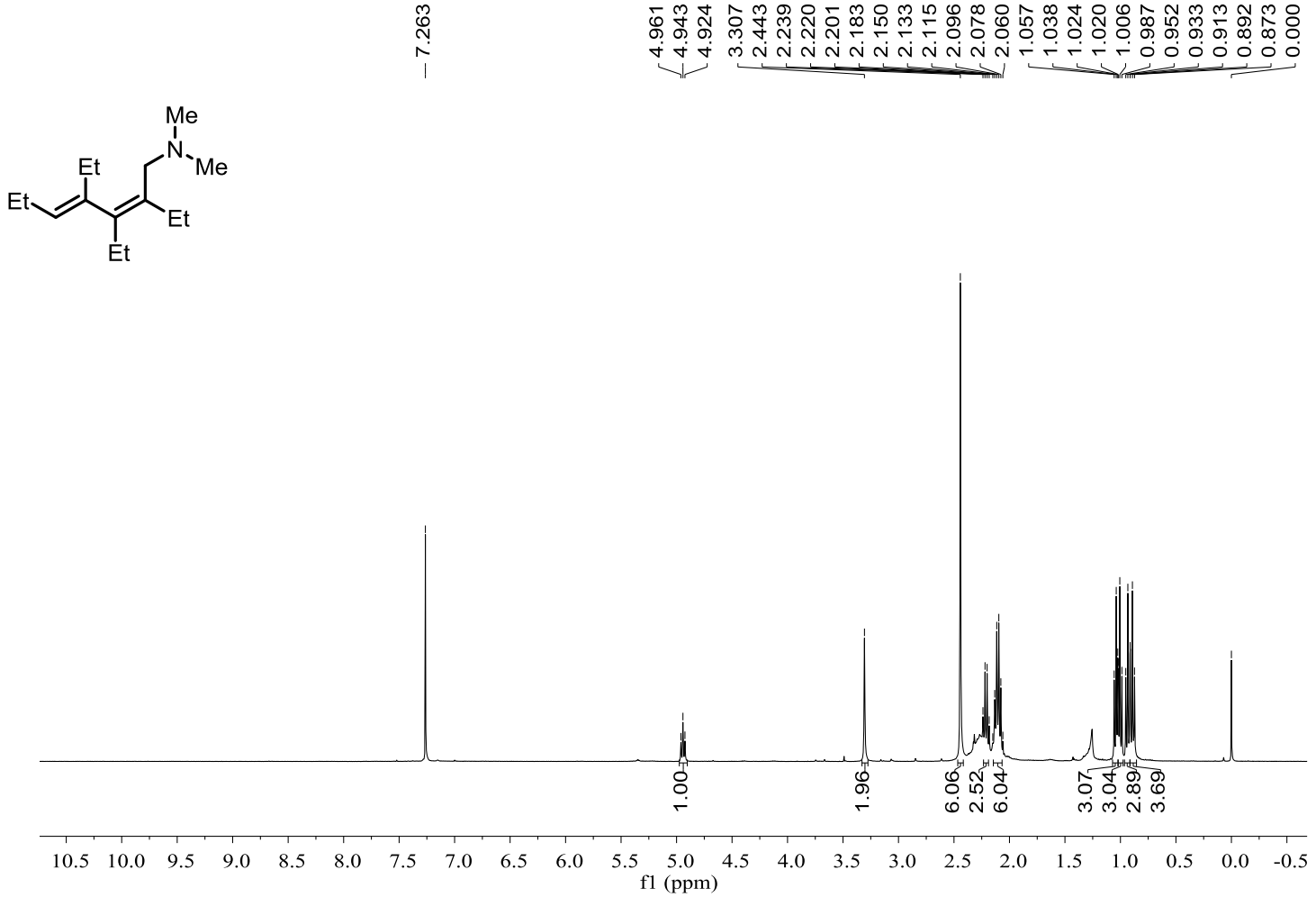
HMBC of (2*Z*,4*E*)-*N*,*N*,2,3,4-Pentamethylhexa-2,4-dien-1-amine (26)



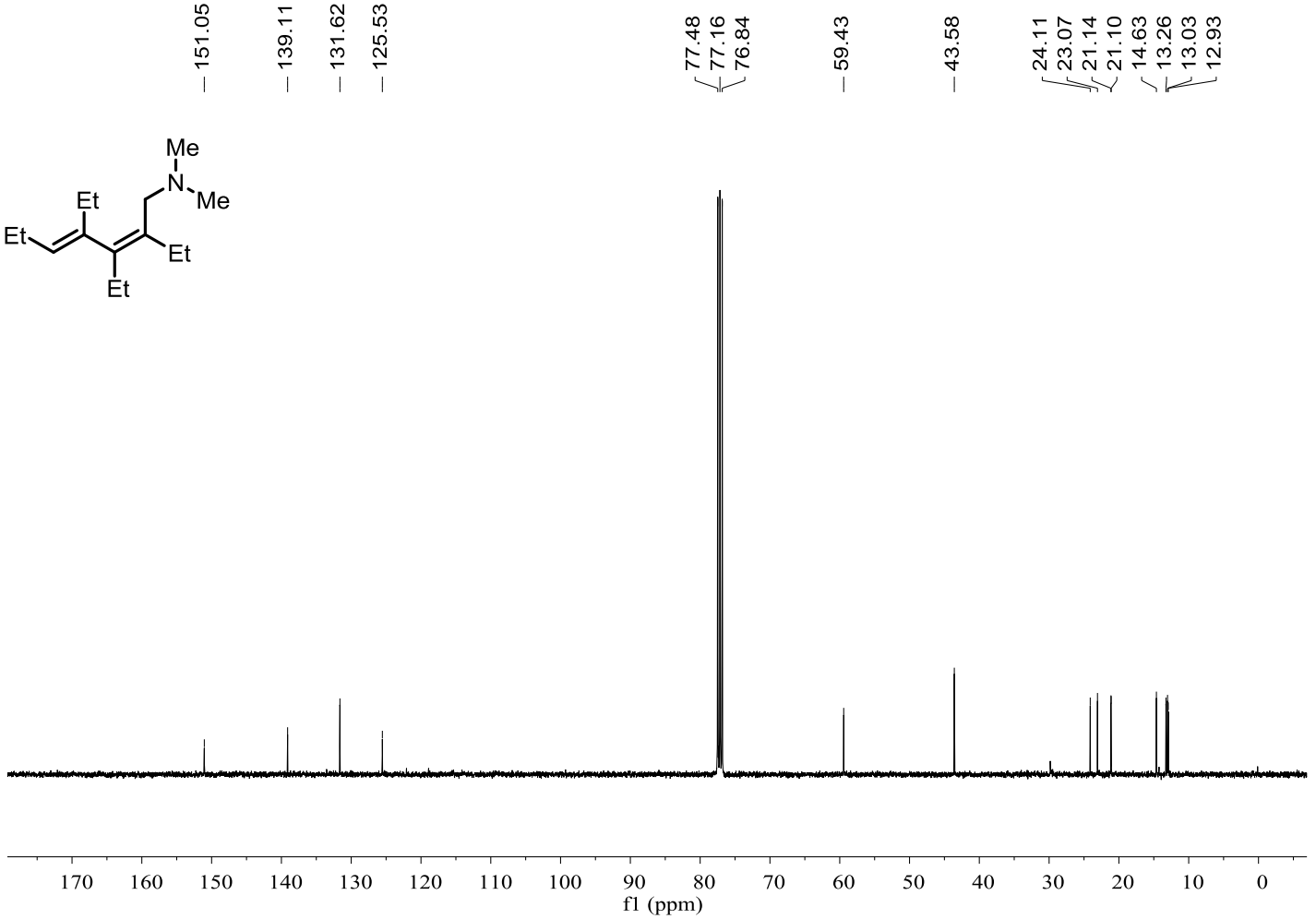
HSQC of (2*Z*,4*E*)-*N*,*N*,2,3,4-Pentamethylhexa-2,4-dien-1-amine (26)



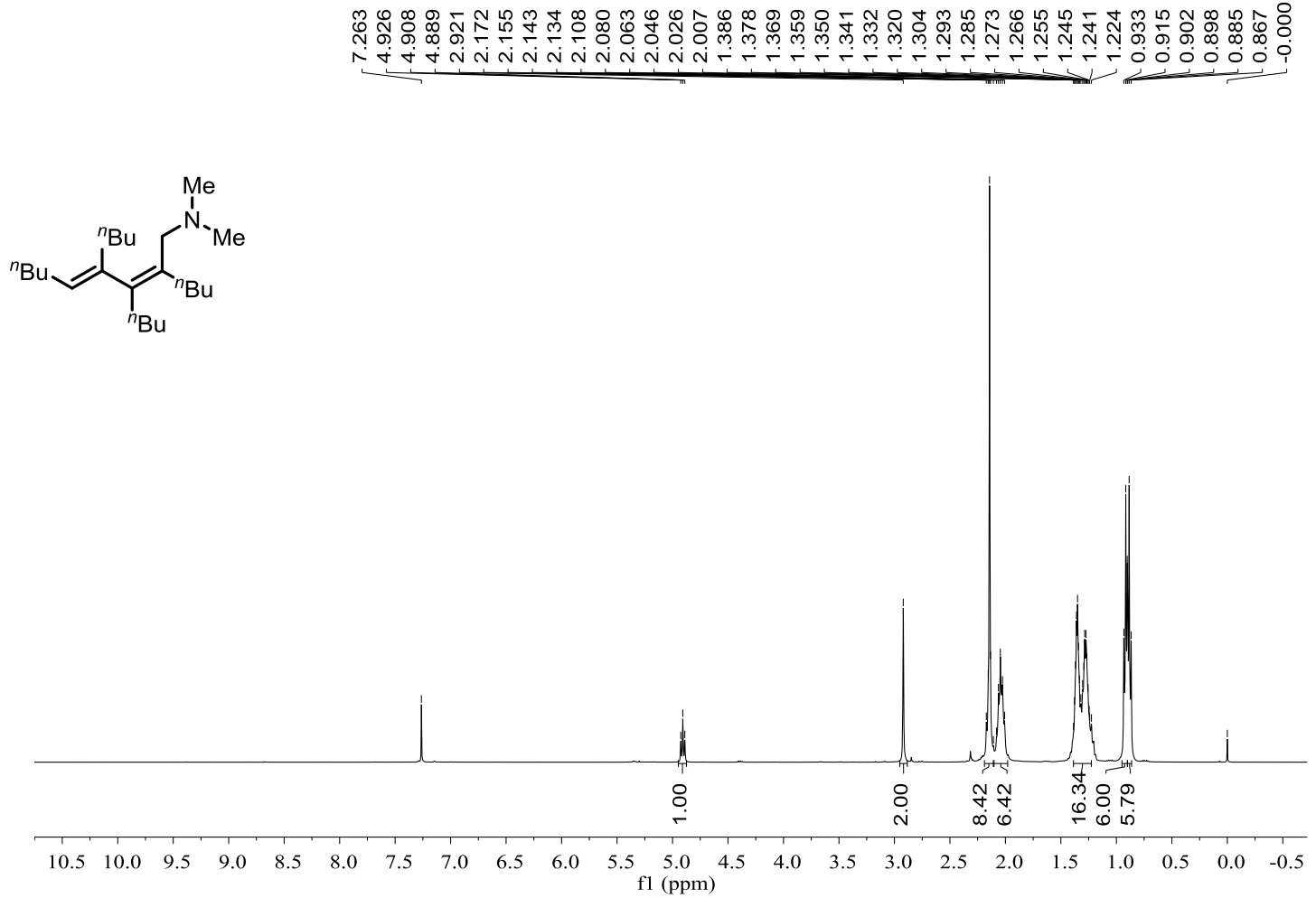
^{1}H NMR spectrum (400 M, $CDCl_3$) of (2*Z*,4*E*)-2,3,4-Triethyl-*N*,*N*-dimethylhepta-2,4-dien-1-amine (27)



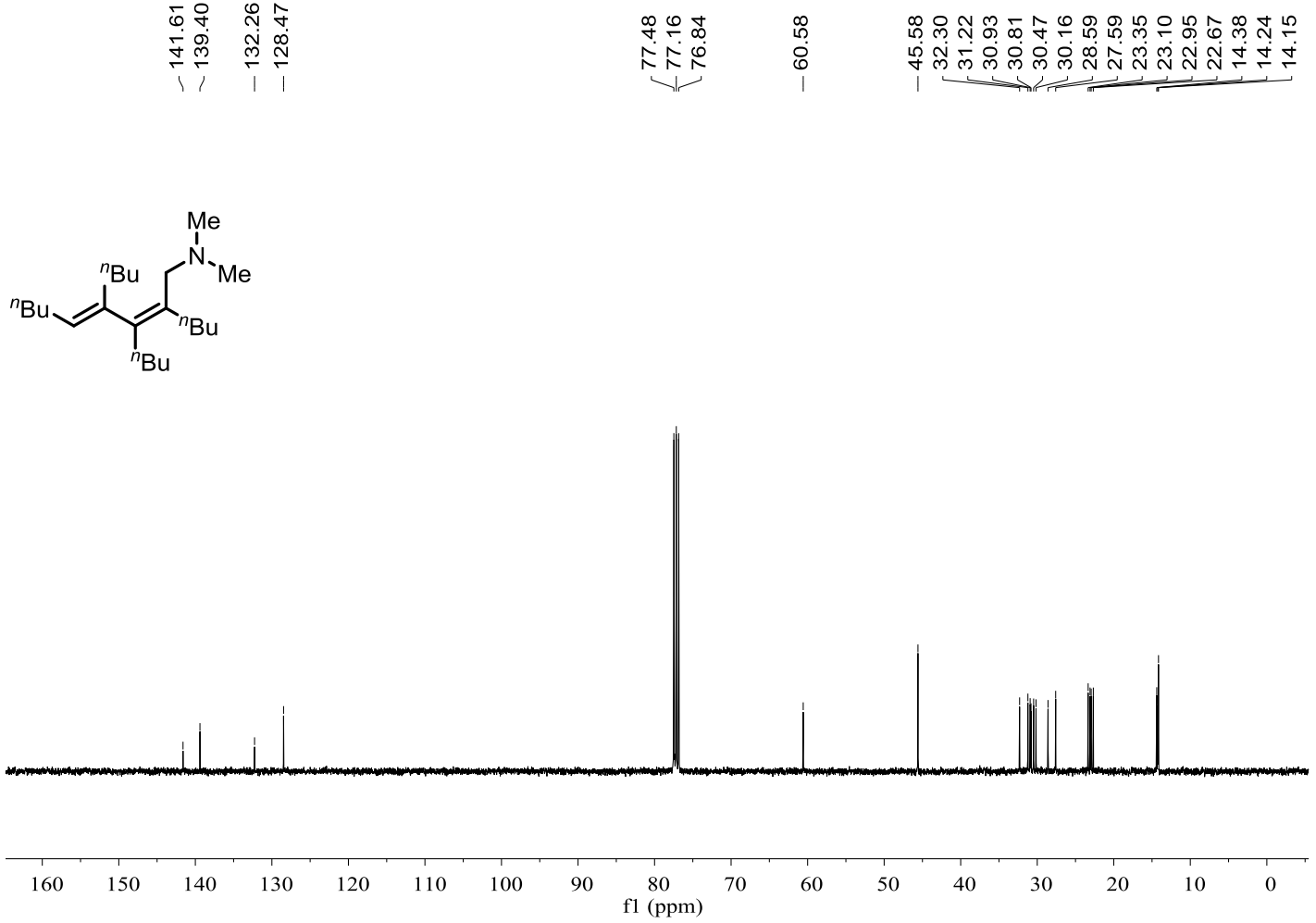
^{13}C NMR spectrum (100 M, $CDCl_3$) of (2*Z*,4*E*)-2,3,4-Triethyl-*N*,*N*-dimethylhepta-2,4-dien-1-amine (27)



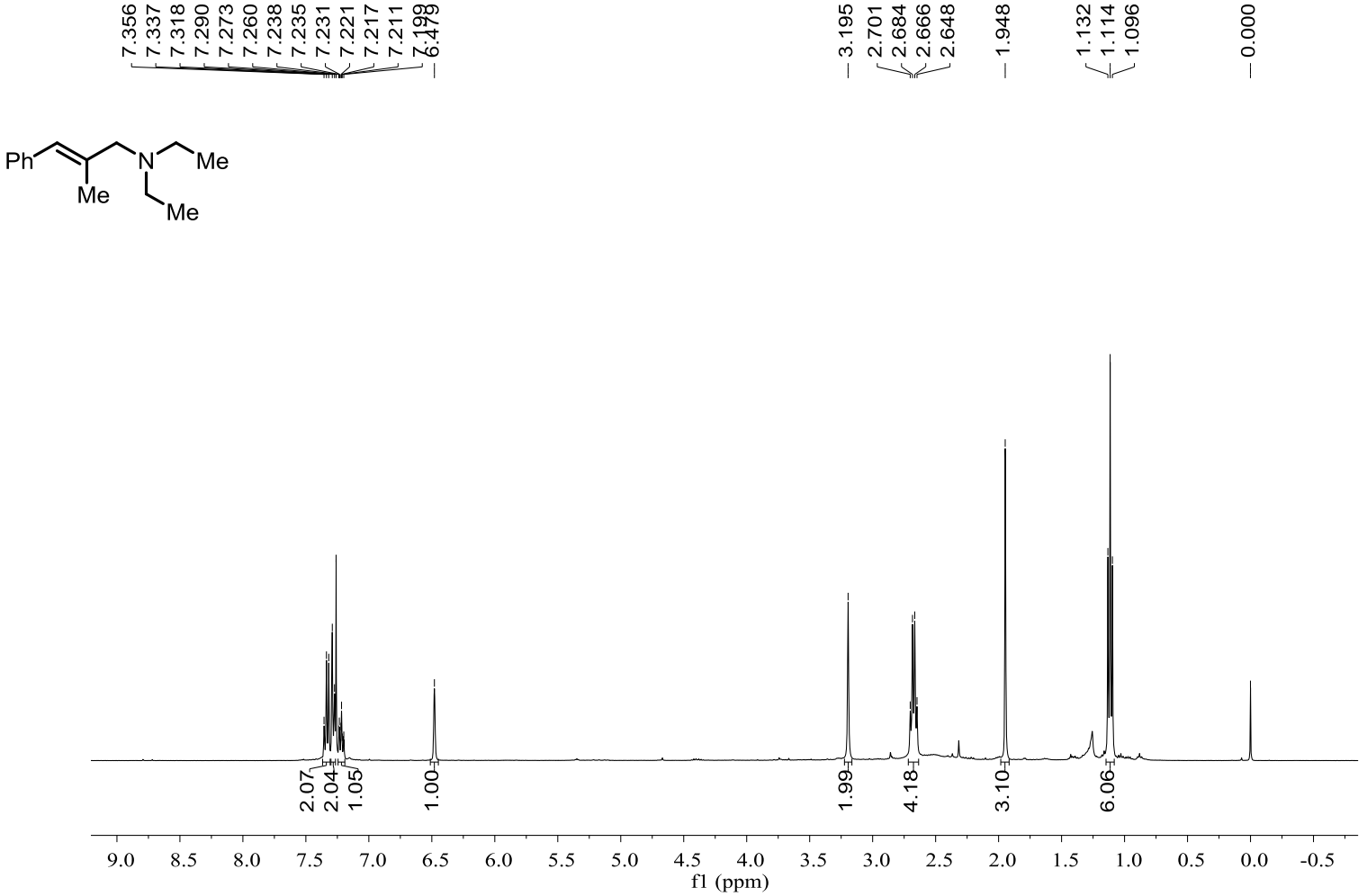
^{1}H NMR spectrum (400 M, $CDCl_3$) of (2*Z*,4*E*)-2,3,4-Tributyl-N,N-dimethylnona-2,4-dien-1-amine (28)



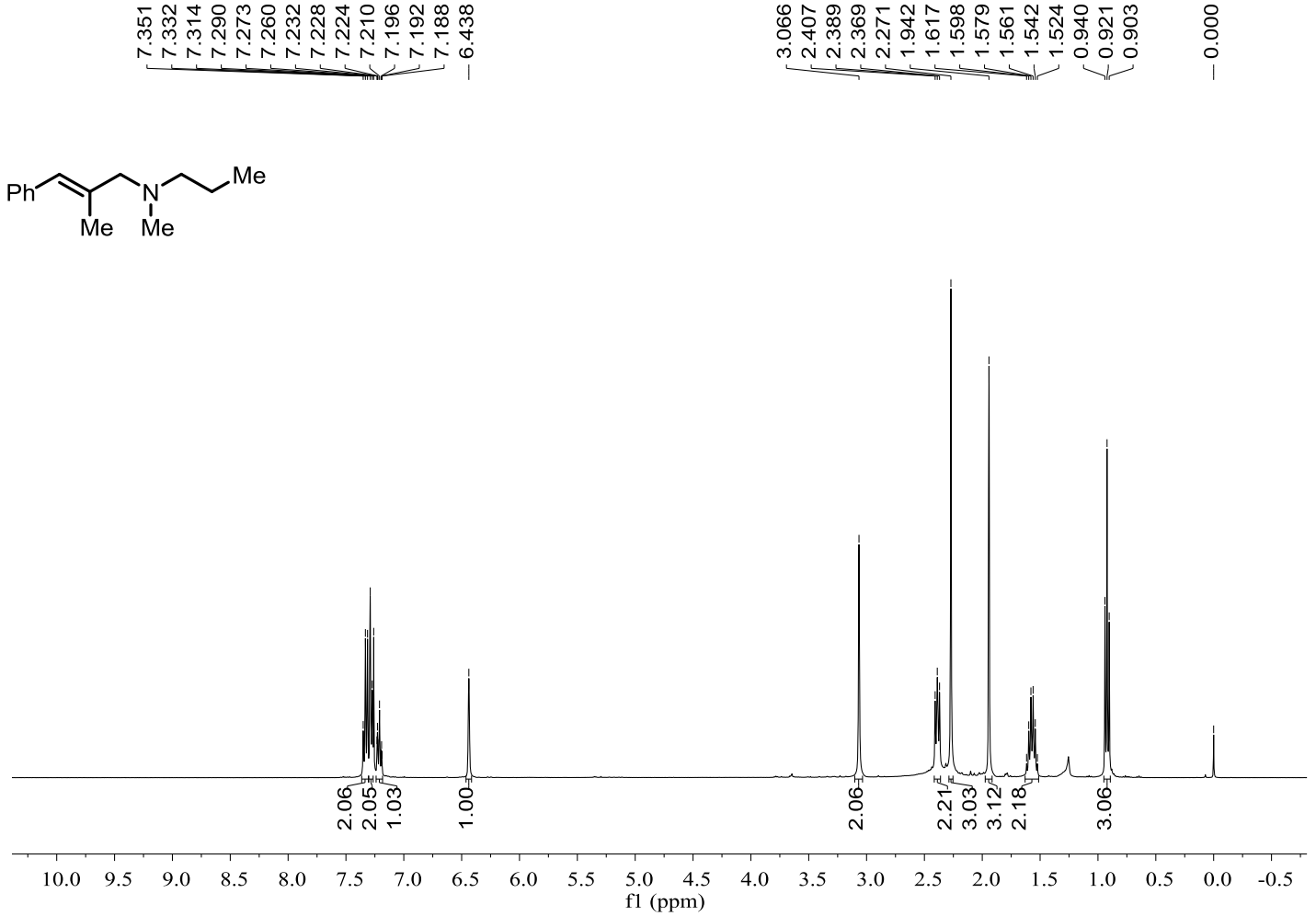
^{13}C NMR spectrum (100 M, $CDCl_3$) of (2*Z*,4*E*)-2,3,4-Tributyl-N,N-dimethylnona-2,4-dien-1-amine (28)



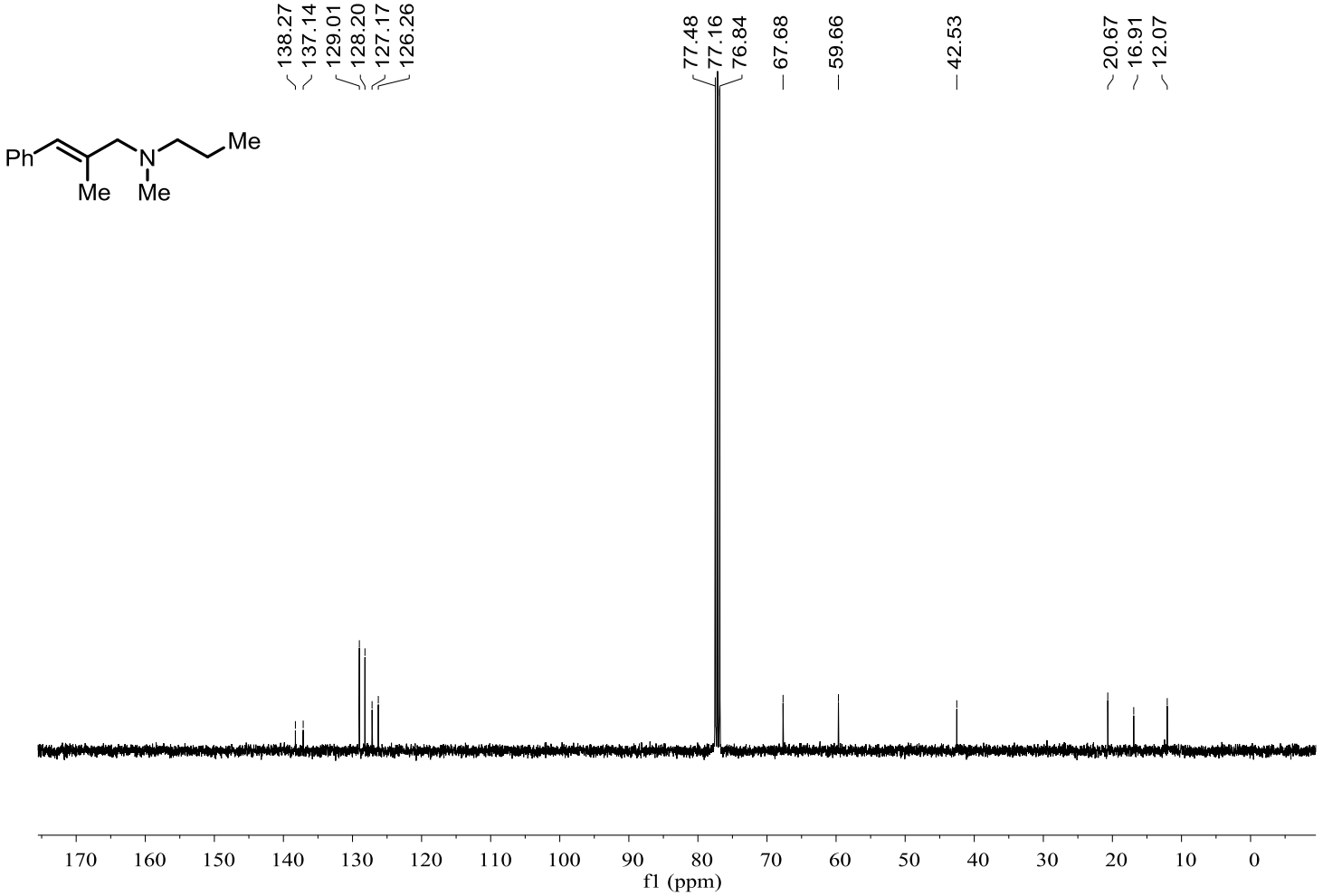
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*N*-Diethyl-2-methyl-3-phenylprop-2-en-1-amine (29)



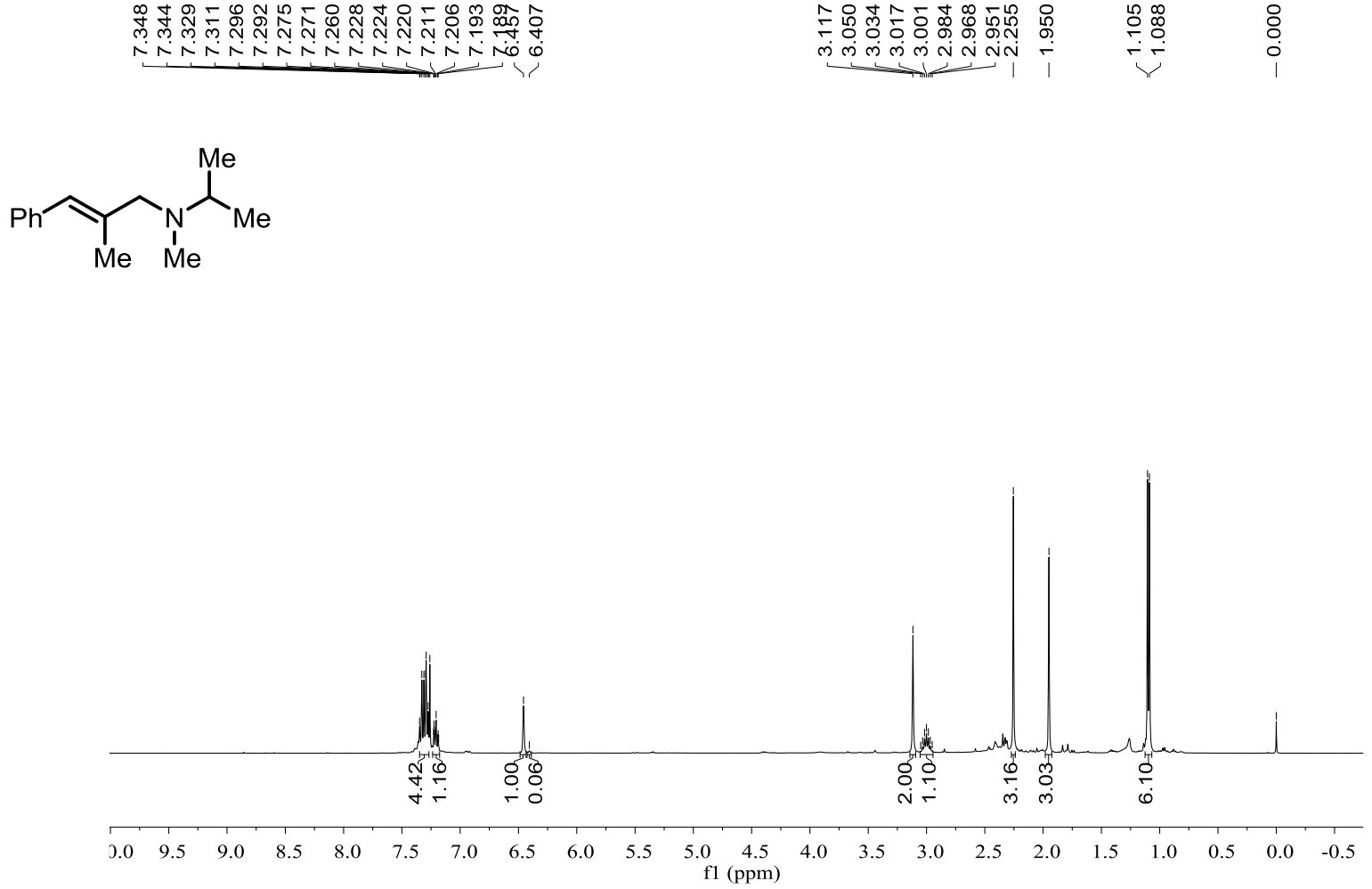
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*2*-Dimethyl-3-phenyl-*N*-propylprop-2-en-1-amine (30)



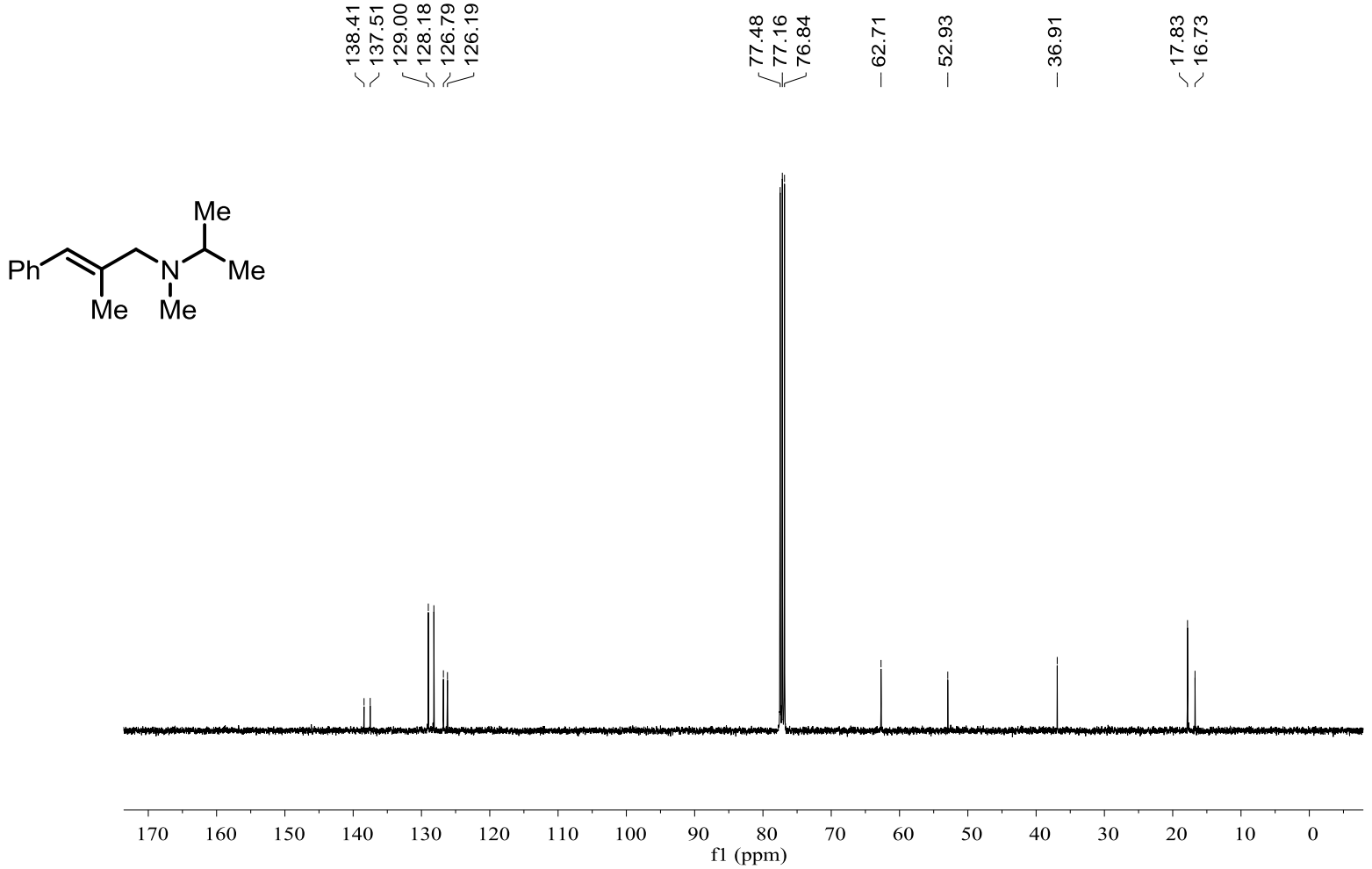
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*,2-Dimethyl-3-phenyl-*N*-propylprop-2-en-1-amine (30)



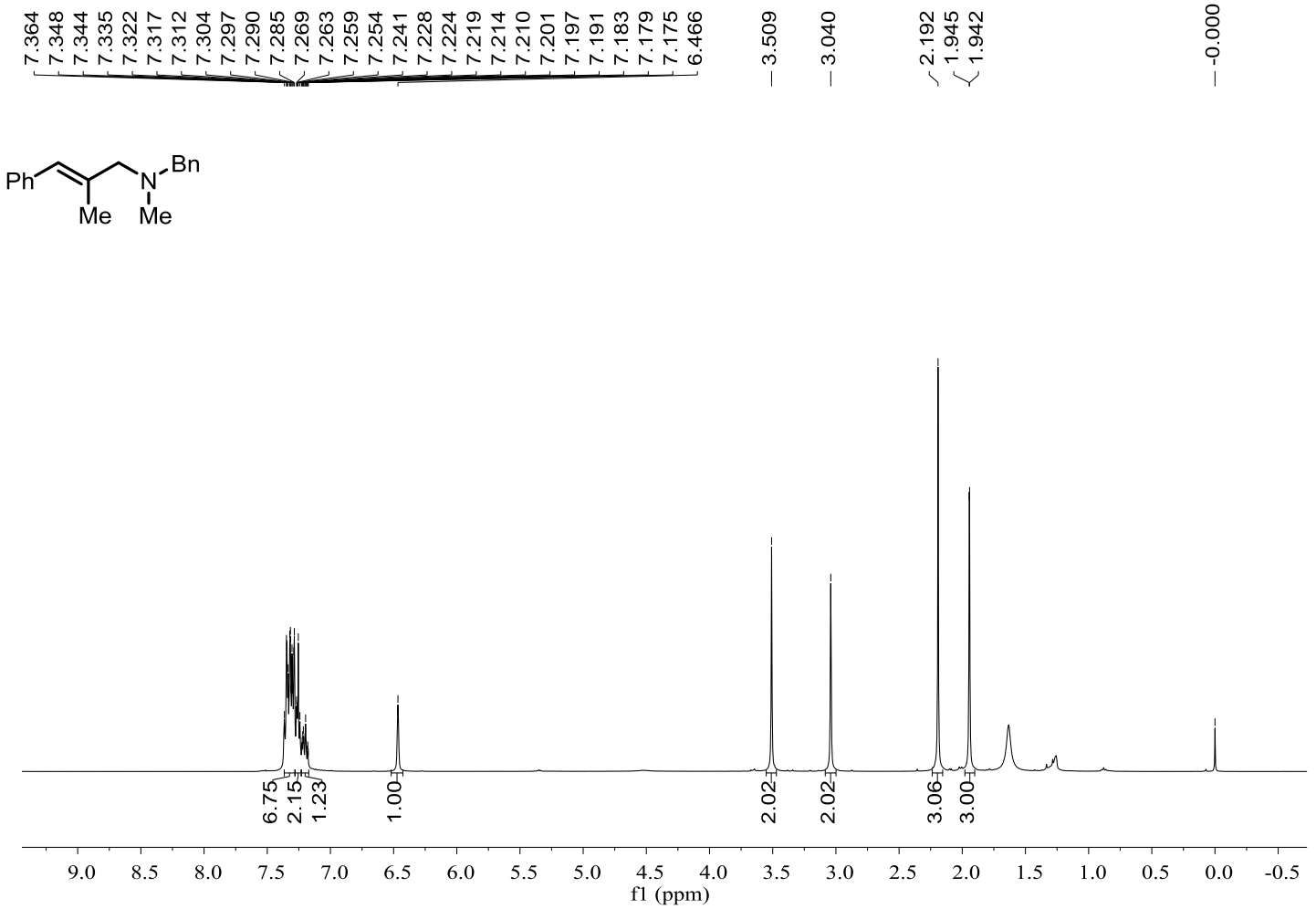
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*-Isopropyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (31)



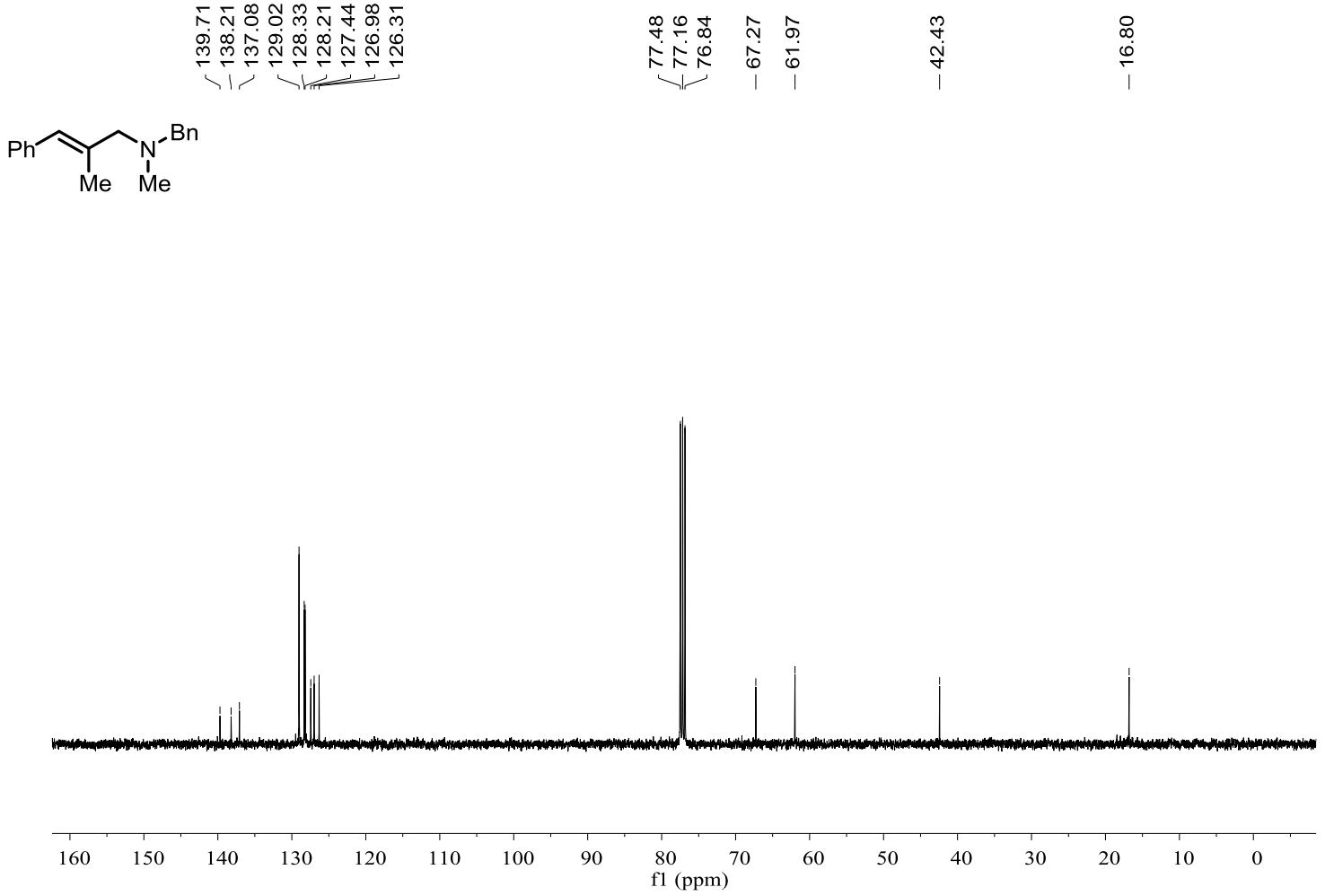
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*-Isopropyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (31)



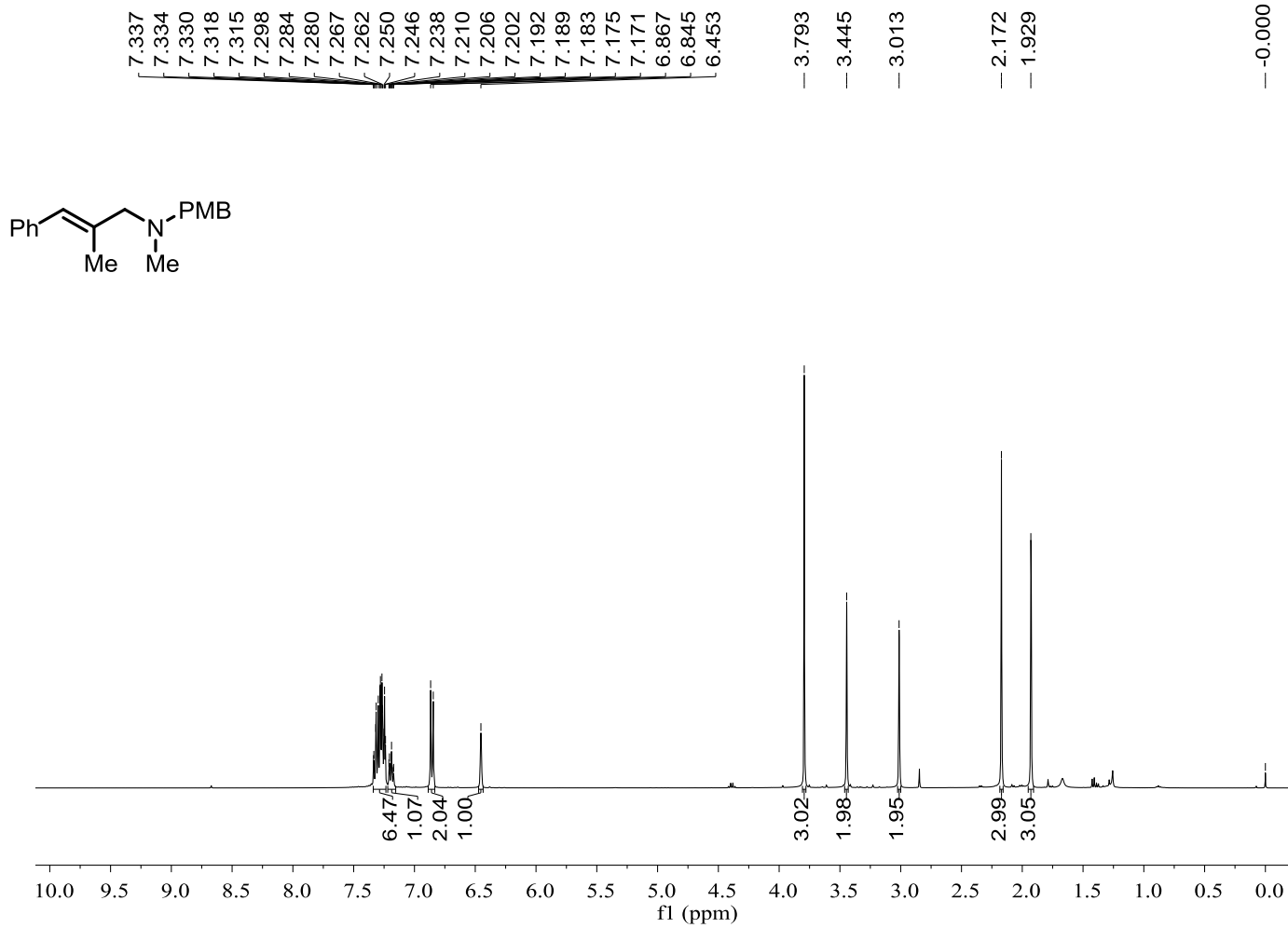
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*-Benzyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (32)



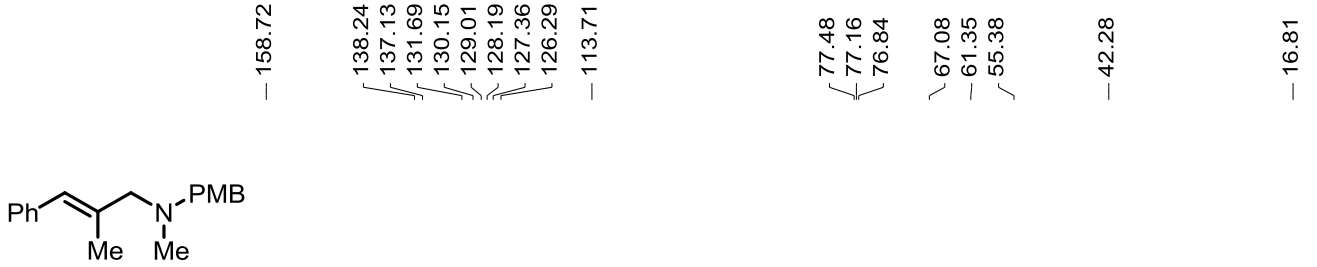
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*-Benzyl-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (32)

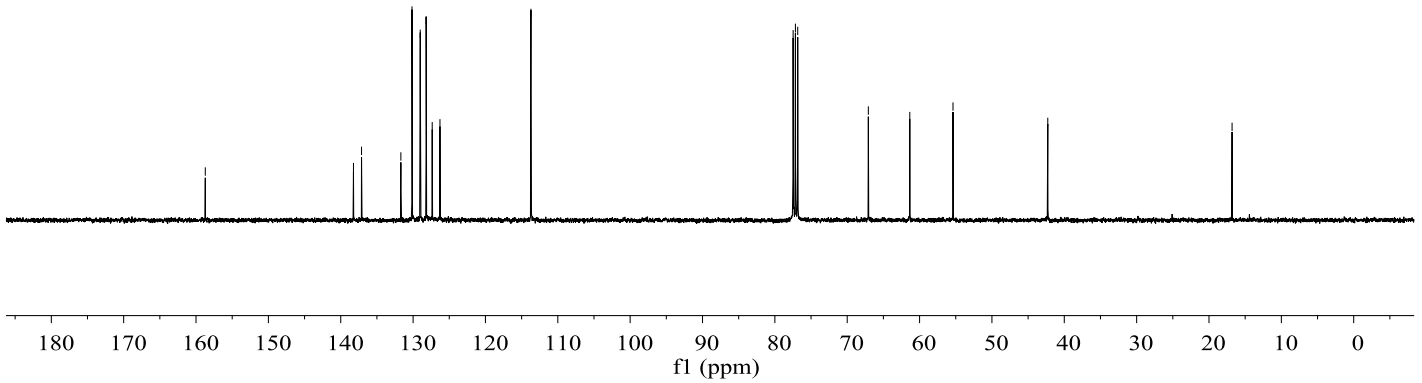


^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*-(4-Methoxybenzyl)-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (33)

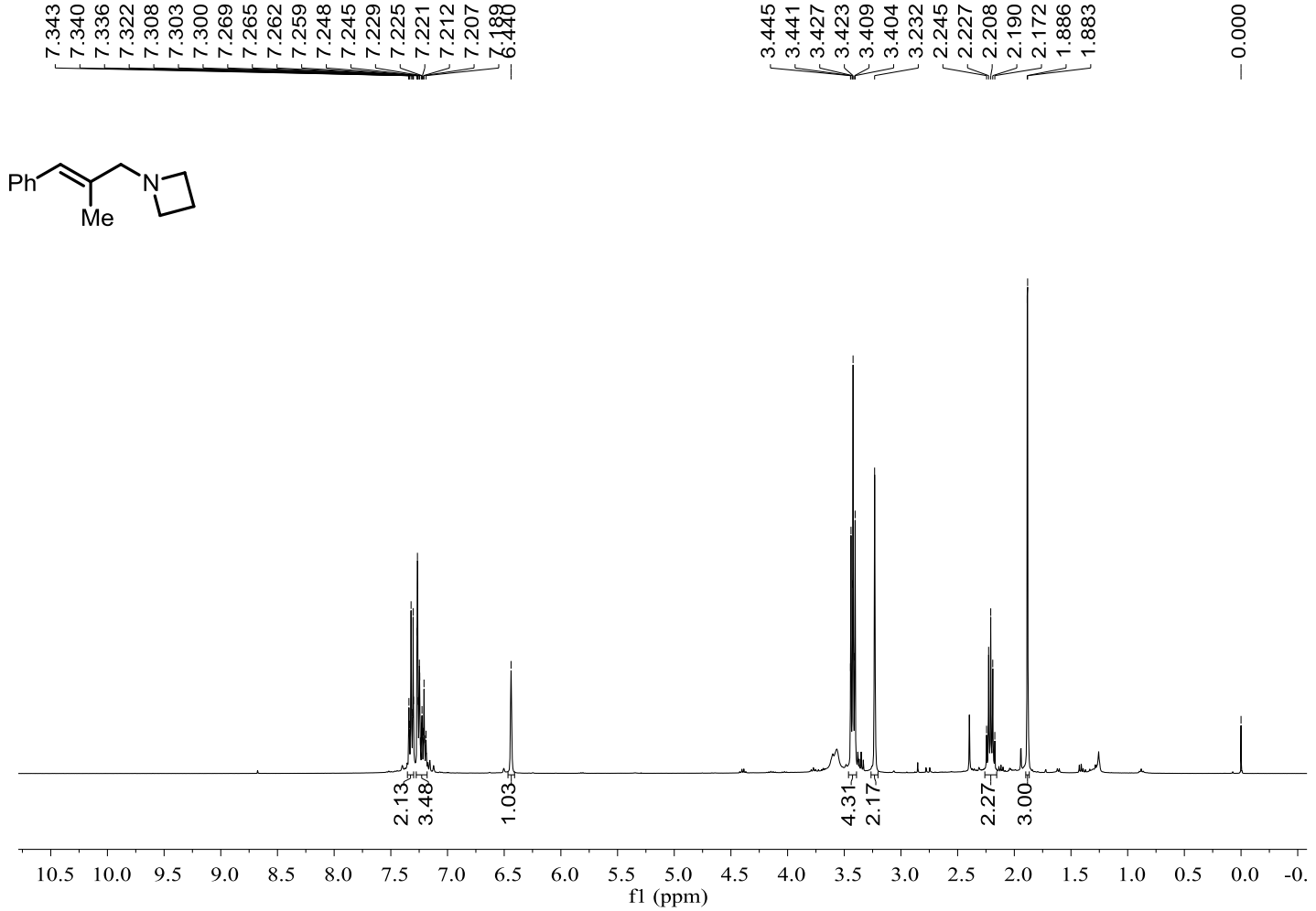


^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-*N*-(4-Methoxybenzyl)-*N*,2-dimethyl-3-phenylprop-2-en-1-amine (33)

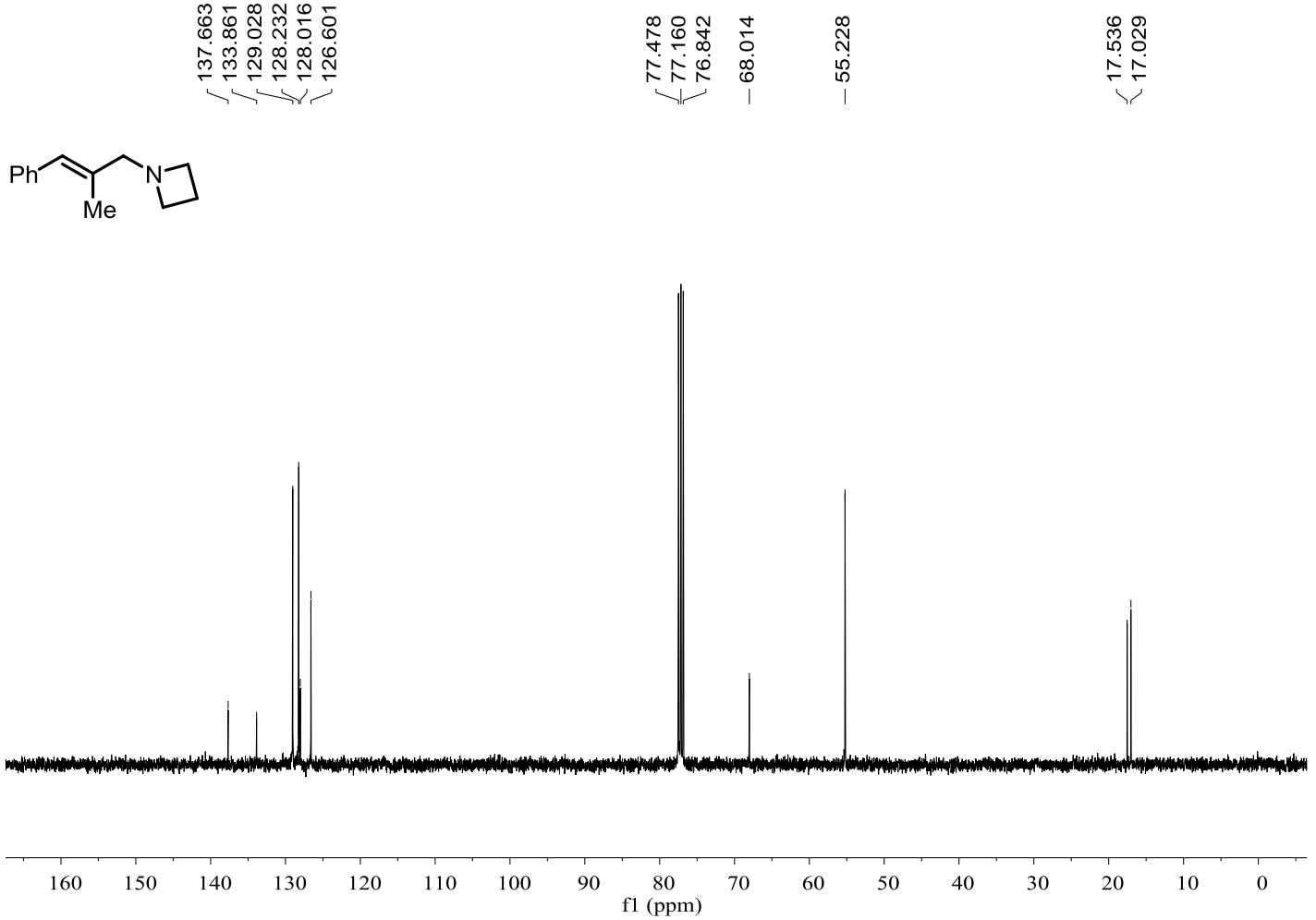




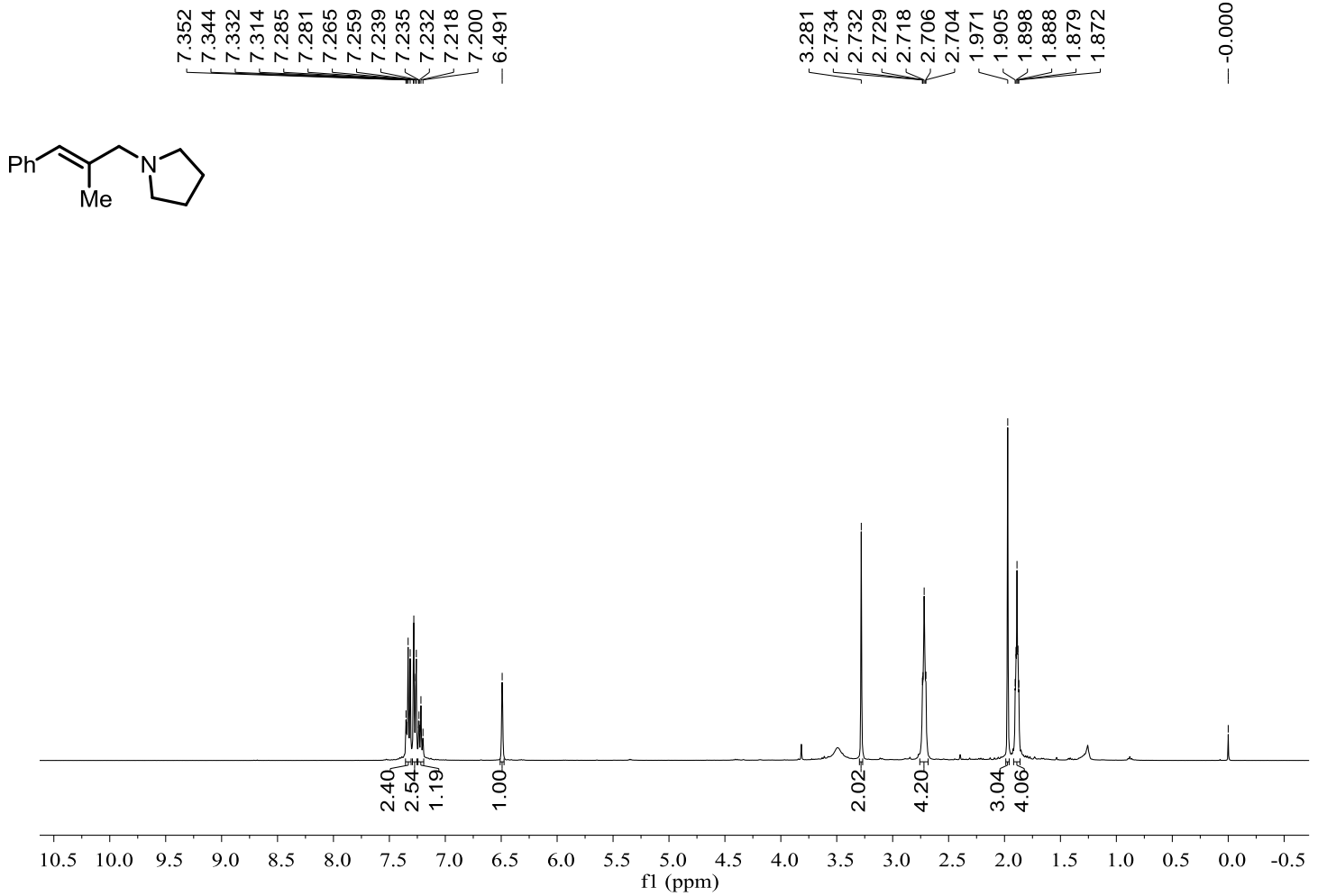
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)azetidine (34)



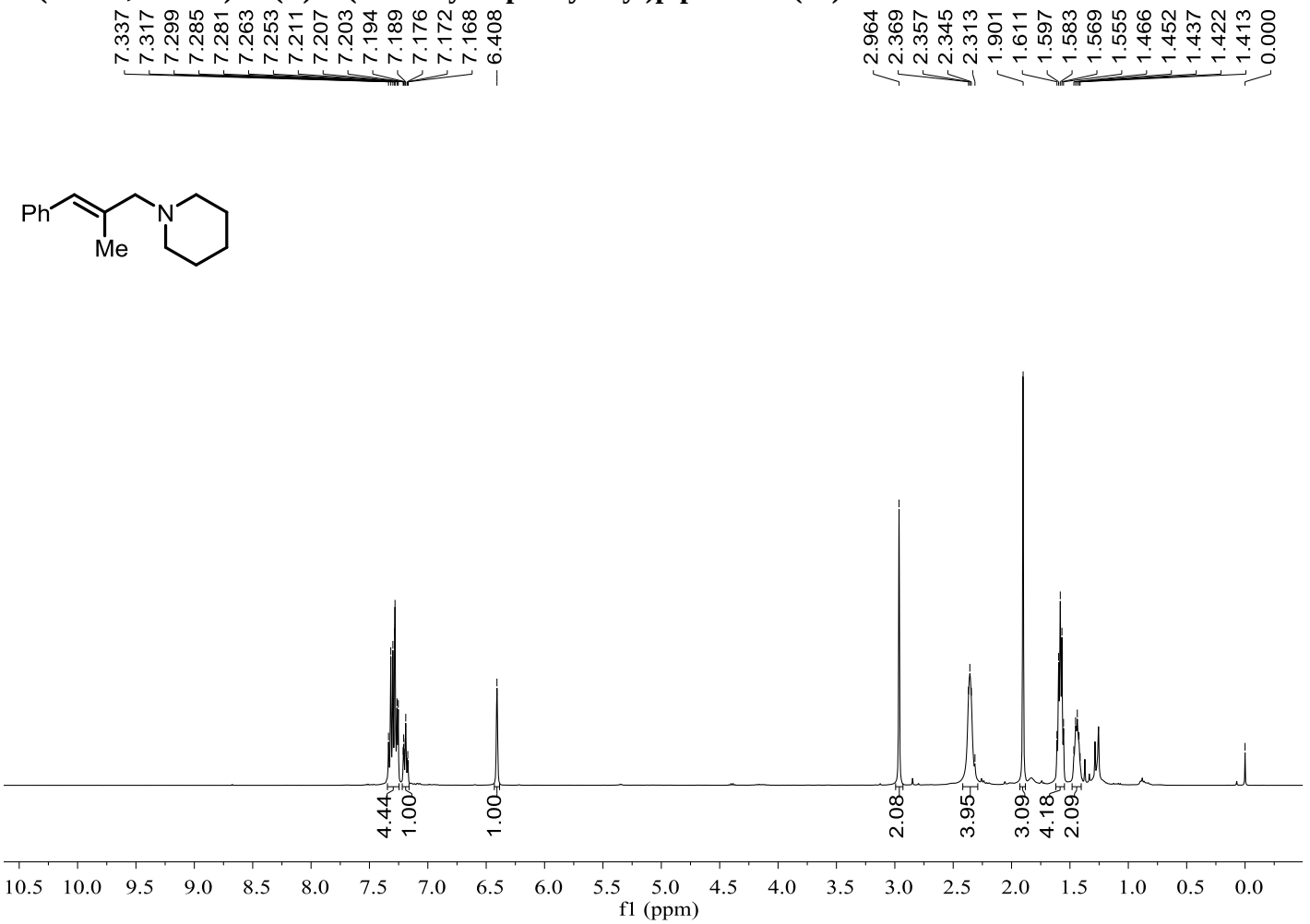
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)azetidine (34)



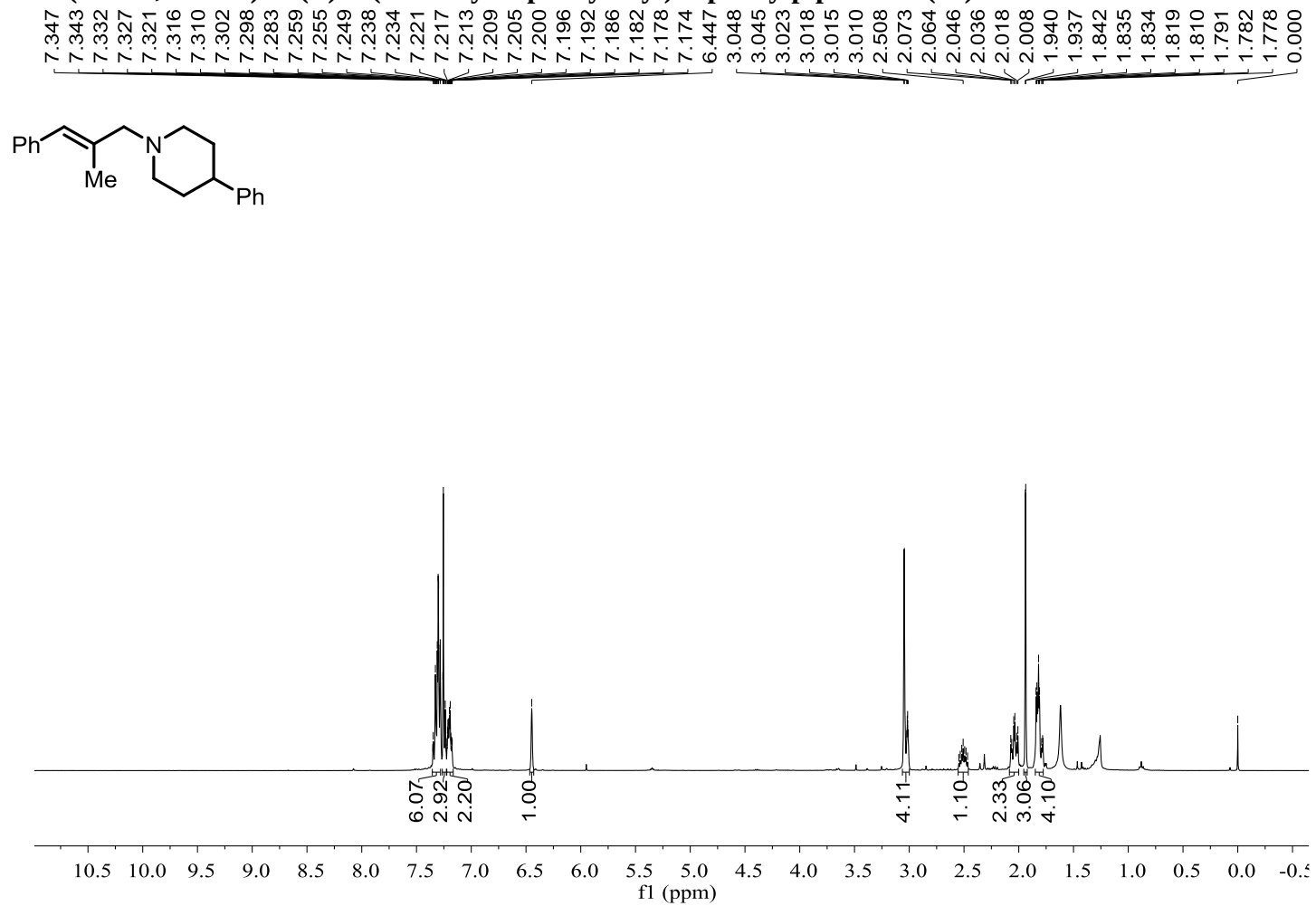
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)pyrrolidine (35)



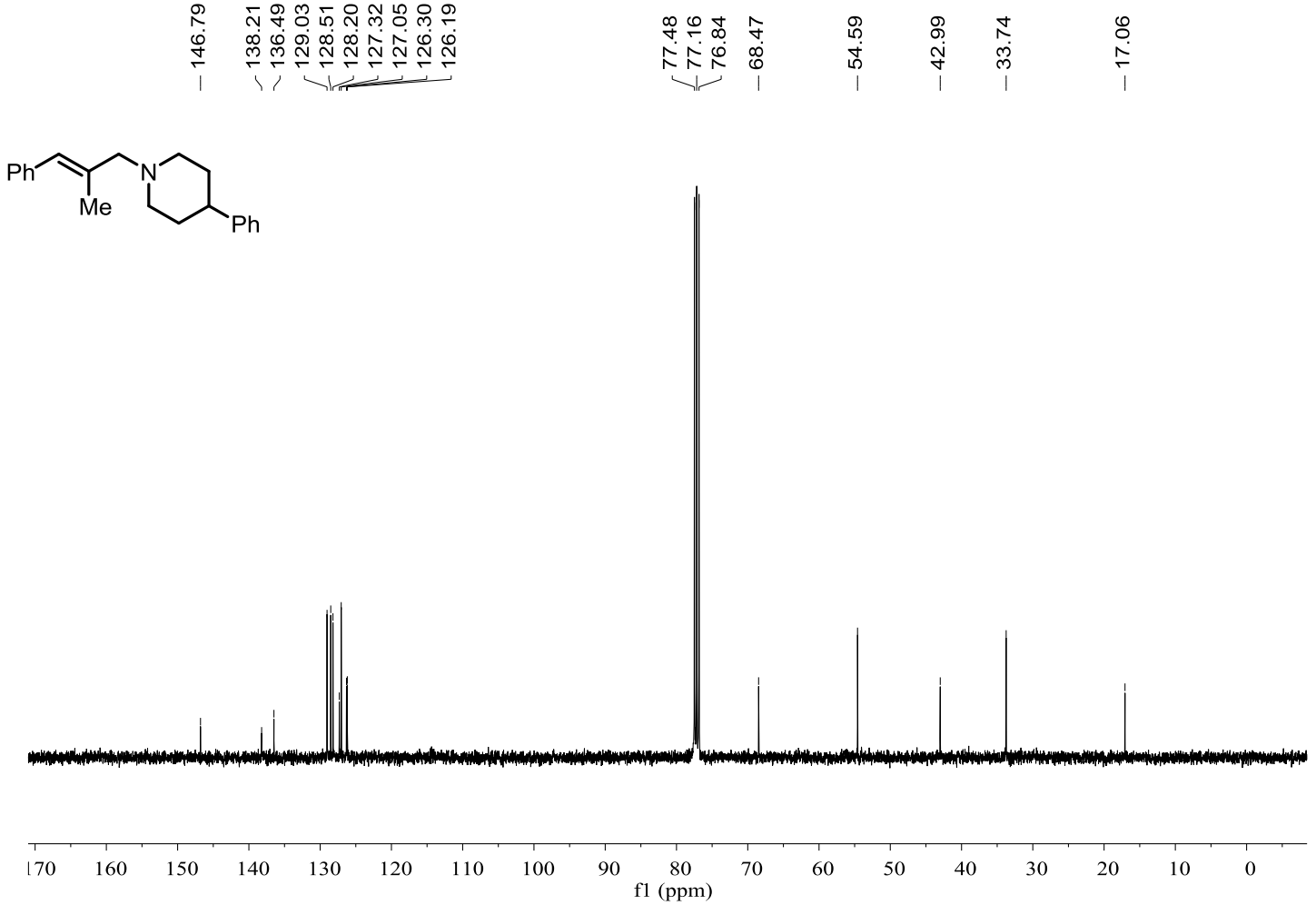
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)piperidine (36)



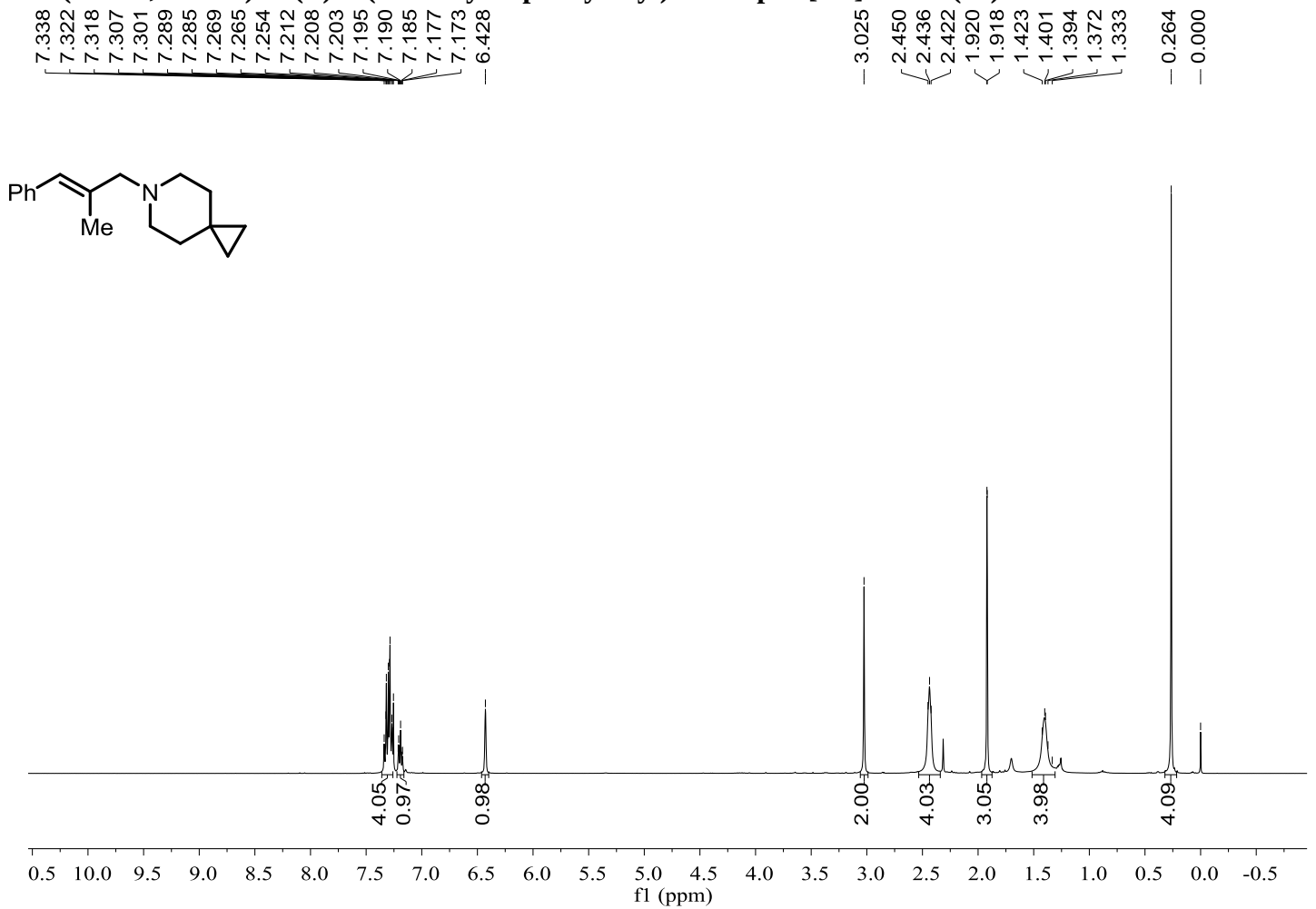
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)-4-phenylpiperidine (37)



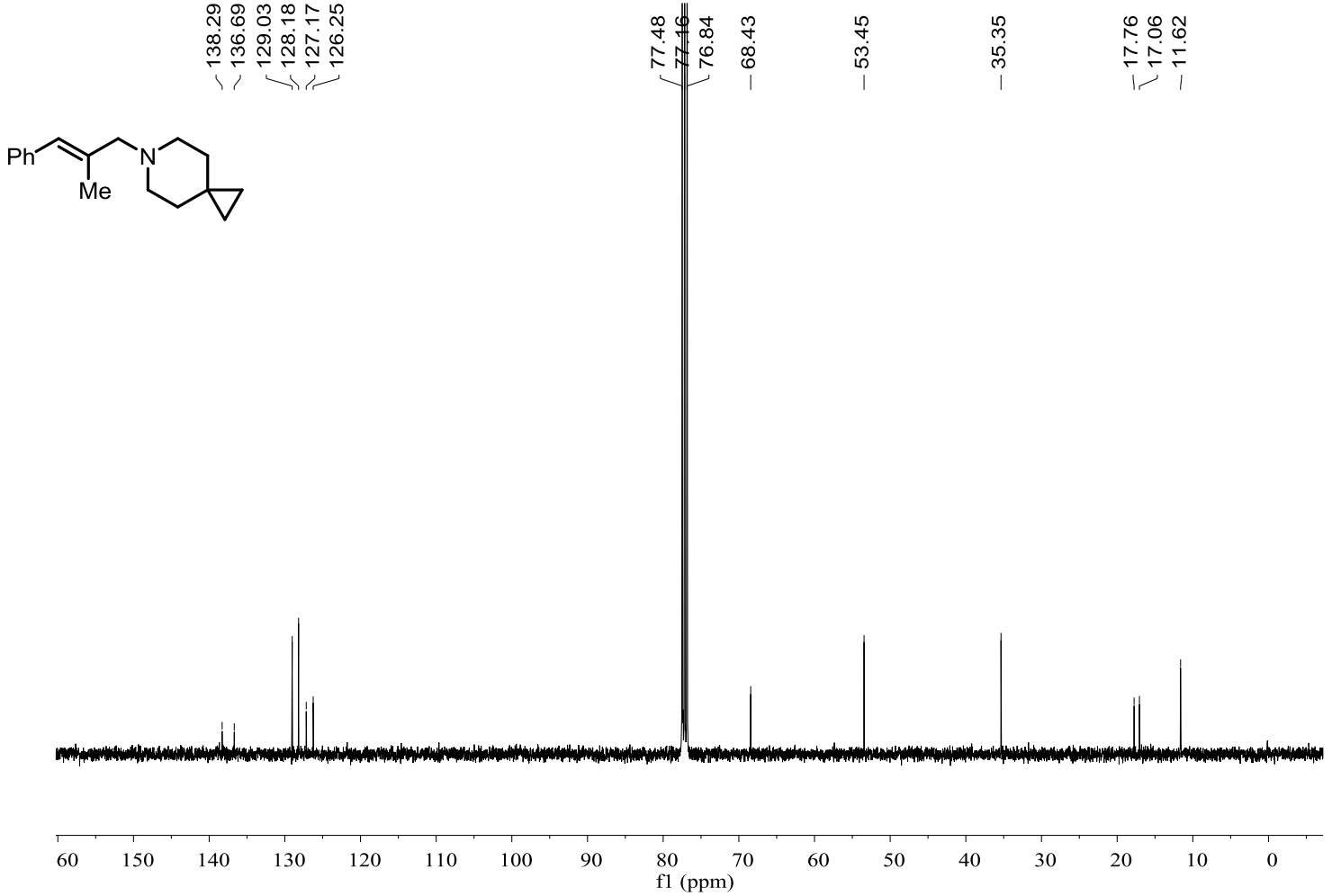
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)-4-phenylpiperidine (37)



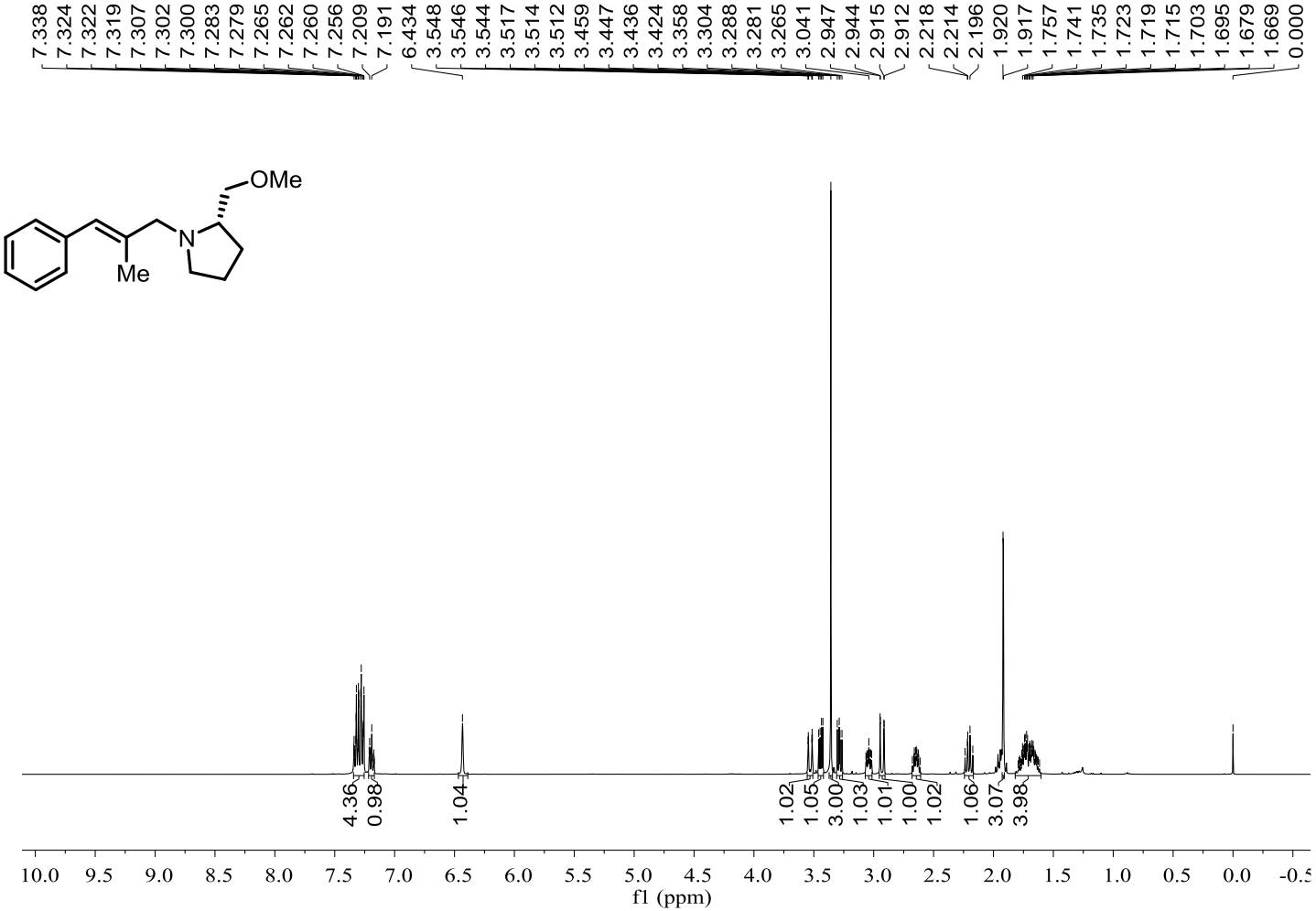
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-6-(2-Methyl-3-phenylallyl)-6-azaspiro[2.5]octane (38)



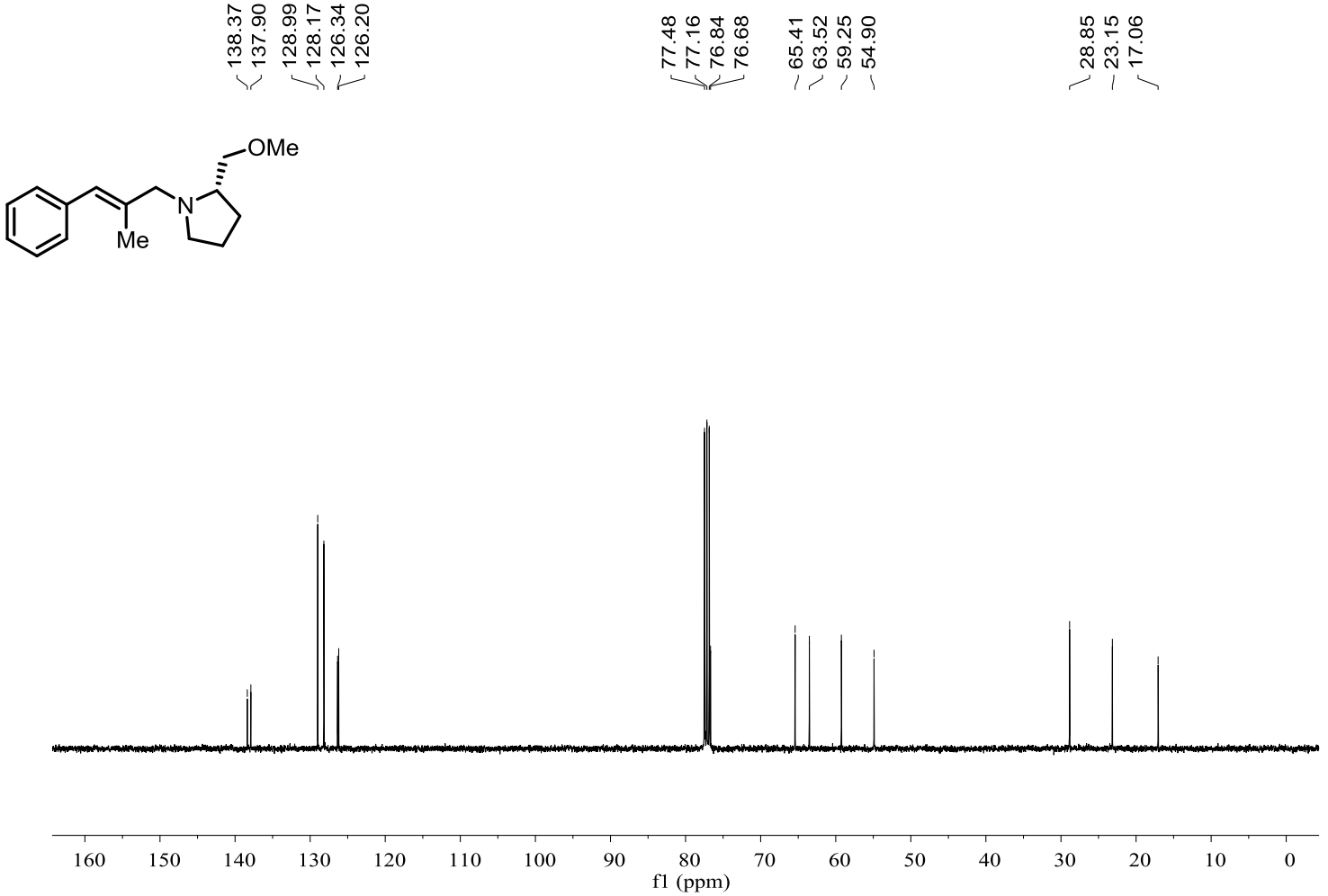
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-6-(2-Methyl-3-phenylallyl)-6-azaspiro[2.5]octane (38)



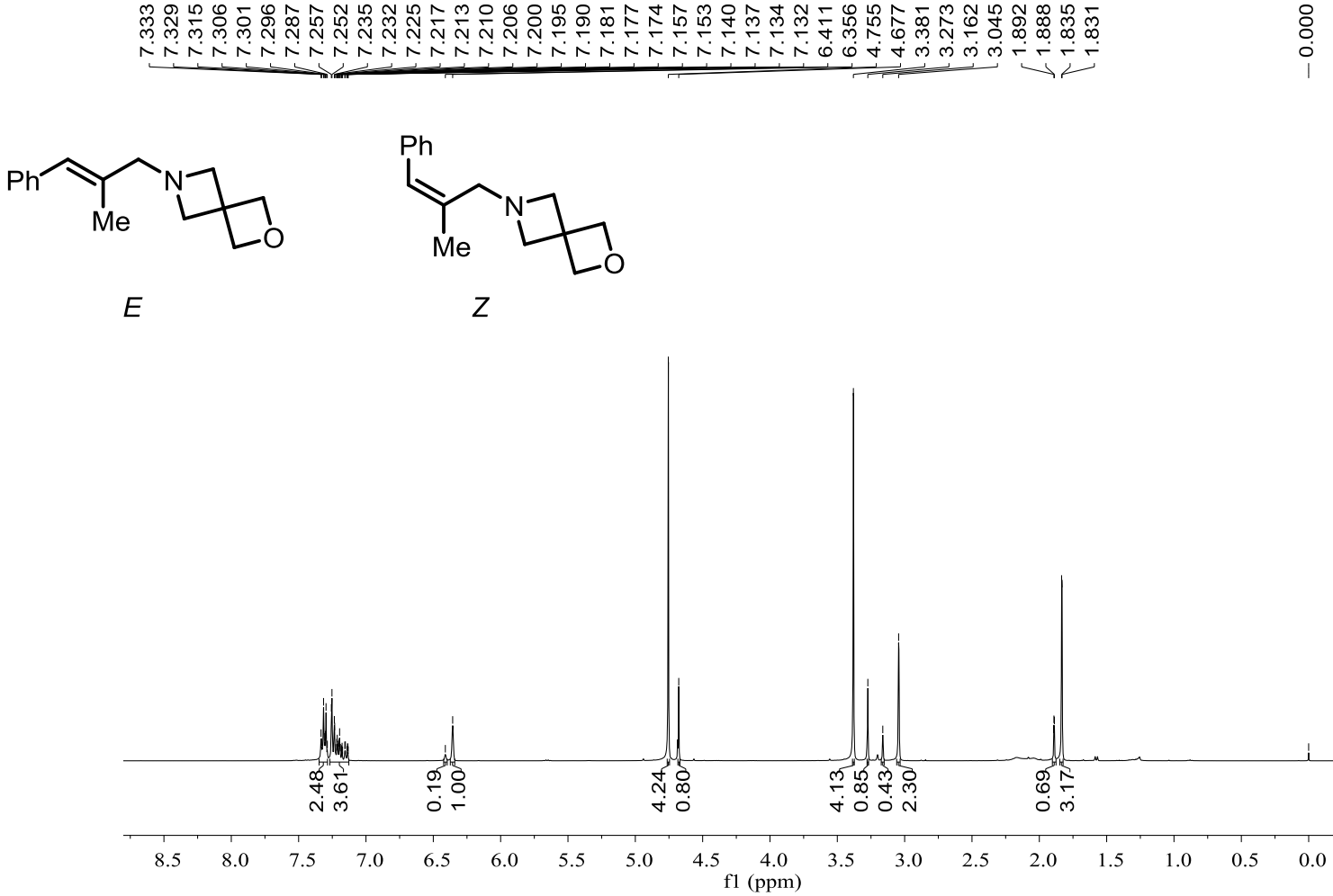
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*S*,*E*)-2-(Methoxymethyl)-1-(2-methyl-3-phenylallyl)pyrrolidine (39)



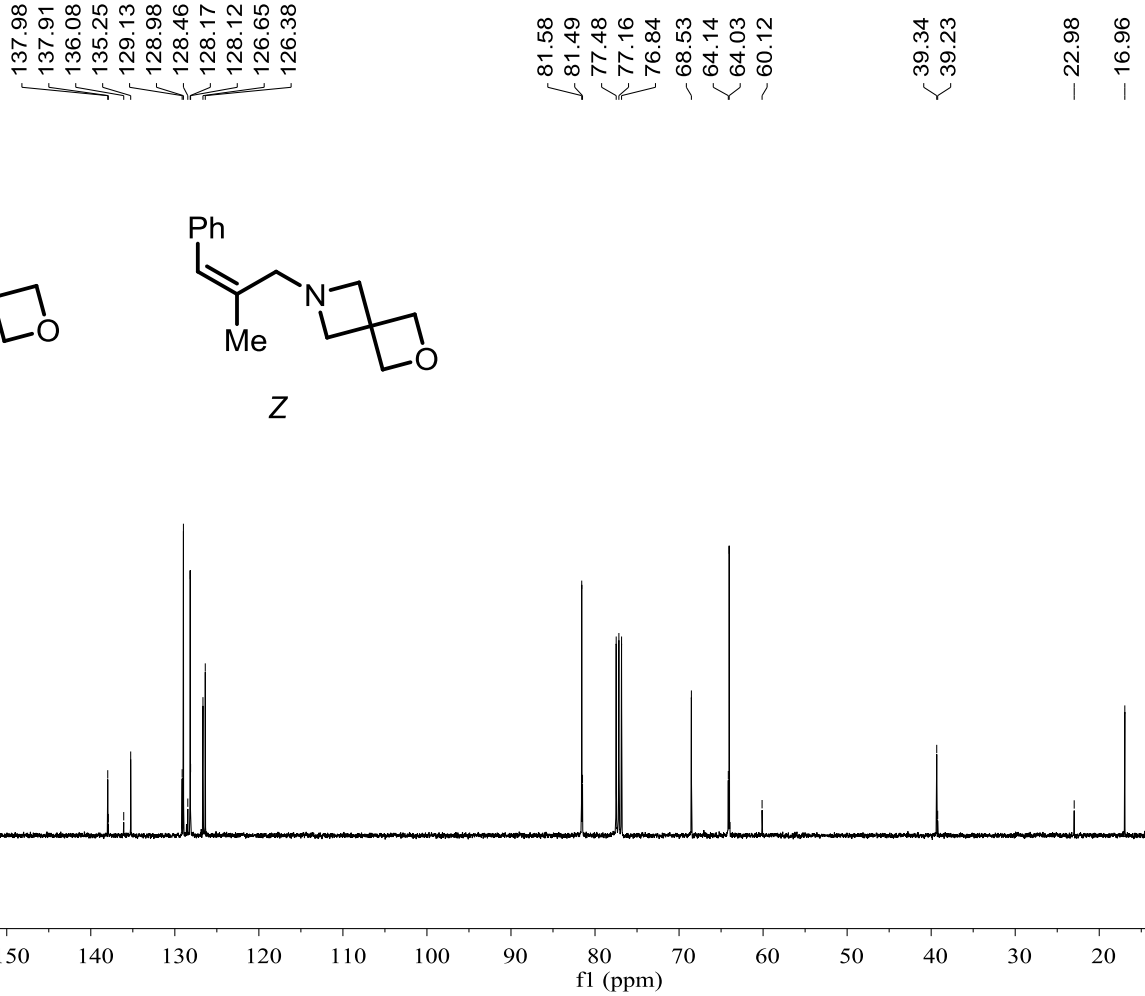
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*S*,*E*)-2-(Methoxymethyl)-1-(2-methyl-3-phenylallyl)pyrrolidine (39)



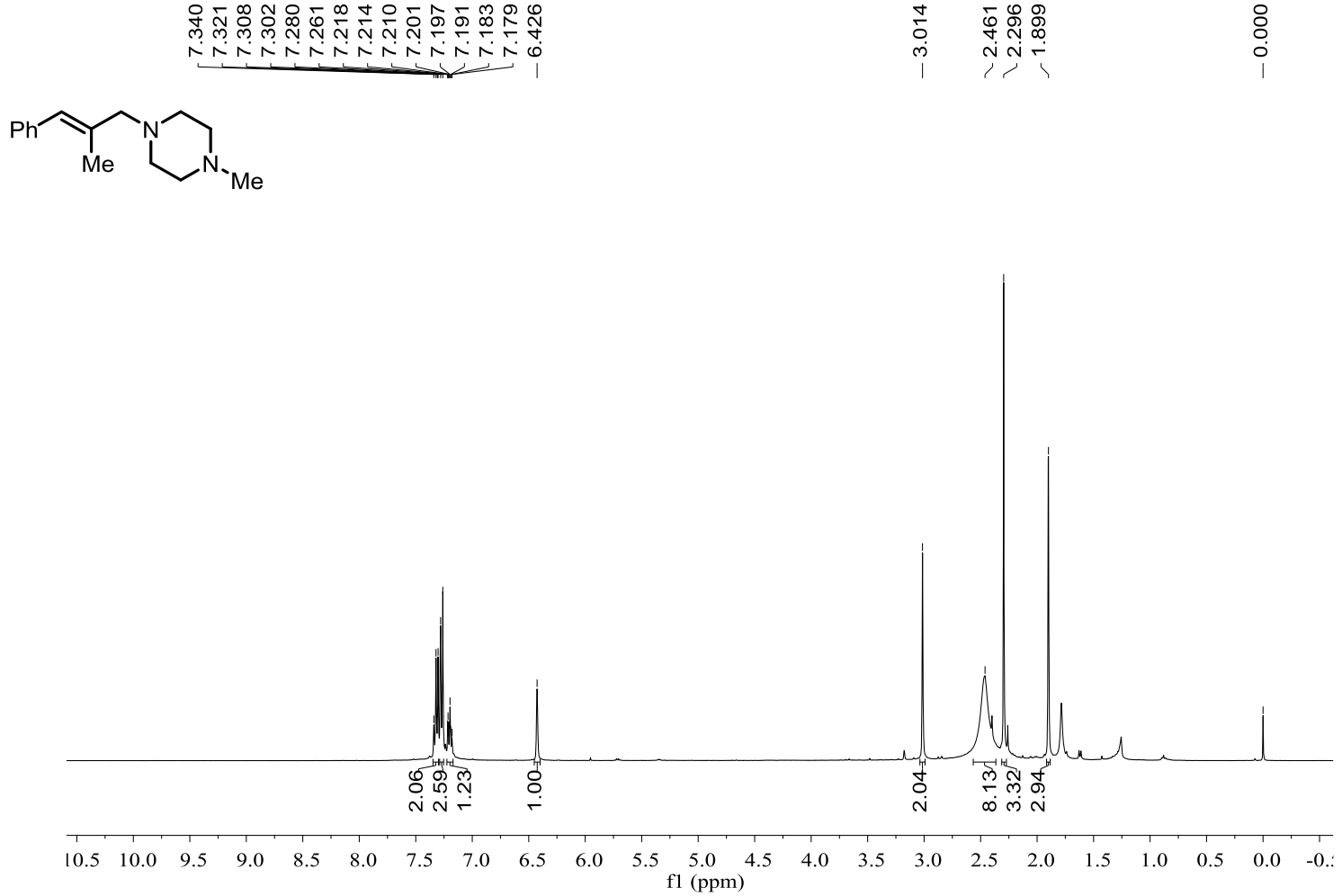
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-6-(2-Methyl-3-phenylallyl)-2-oxa-6-azaspiro[3.3]heptane (40)



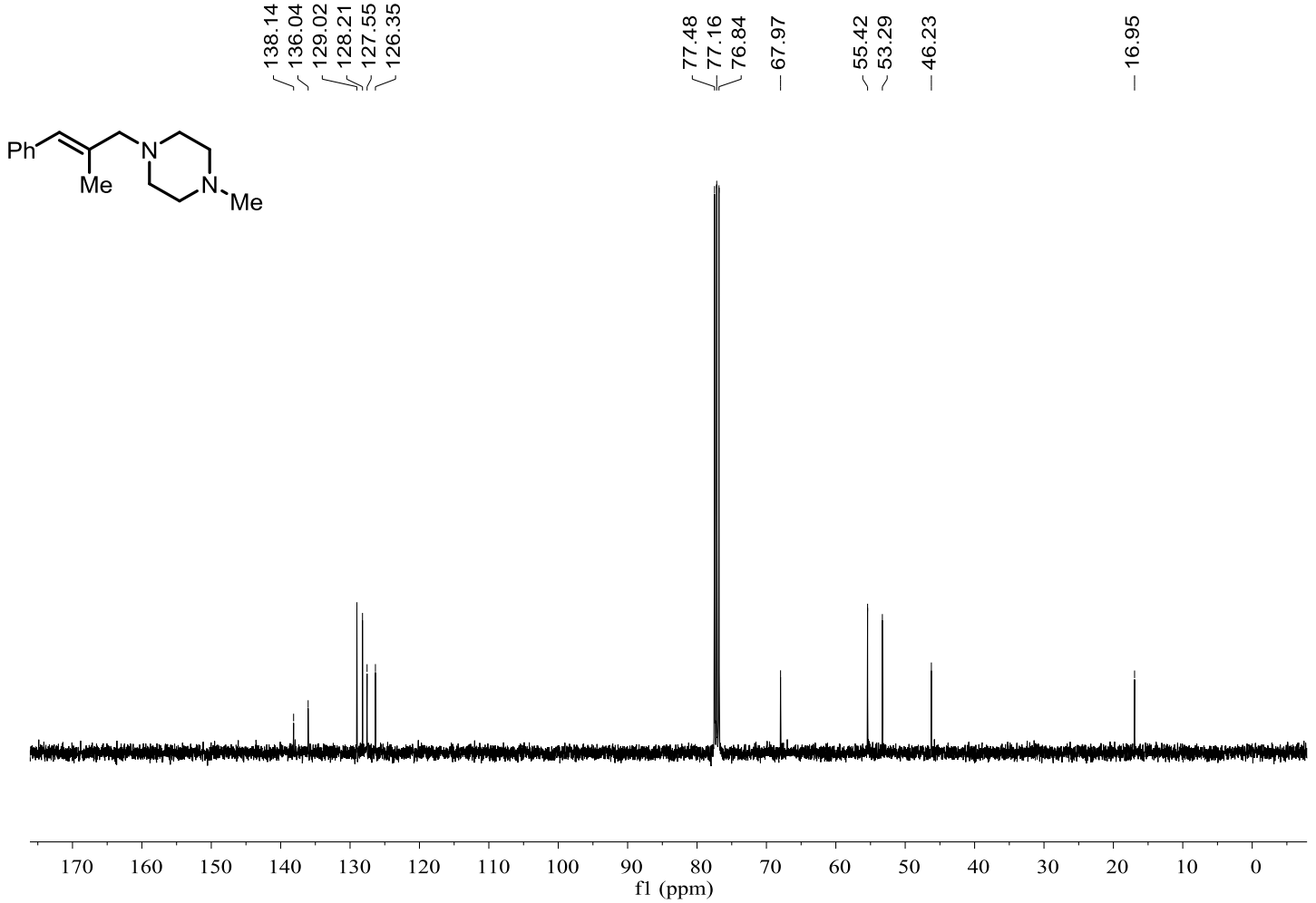
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-6-(2-Methyl-3-phenylallyl)-2-oxa-6-azaspiro[3.3]heptane (40)



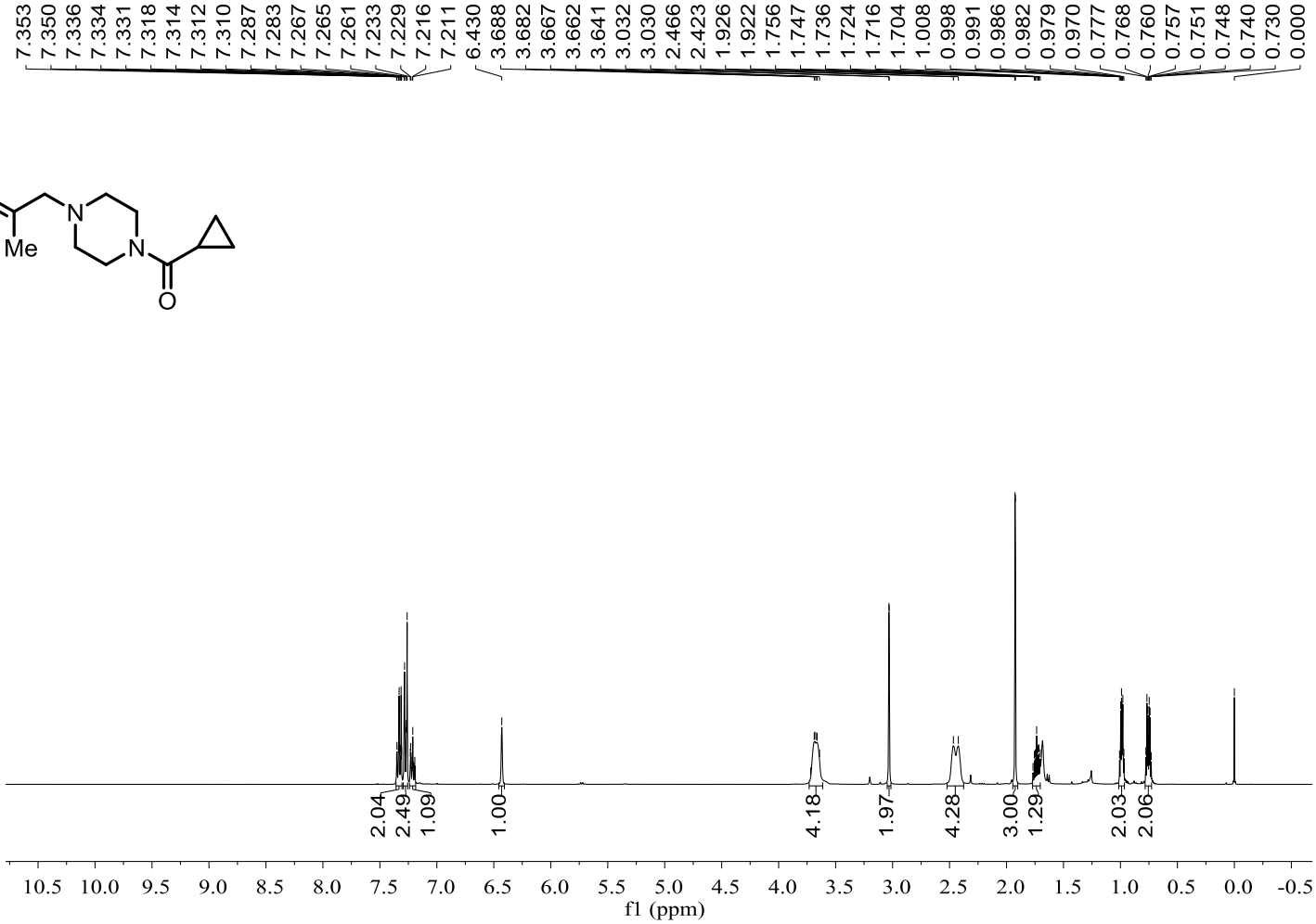
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-Methyl-4-(2-methyl-3-phenylallyl)piperazine (41)



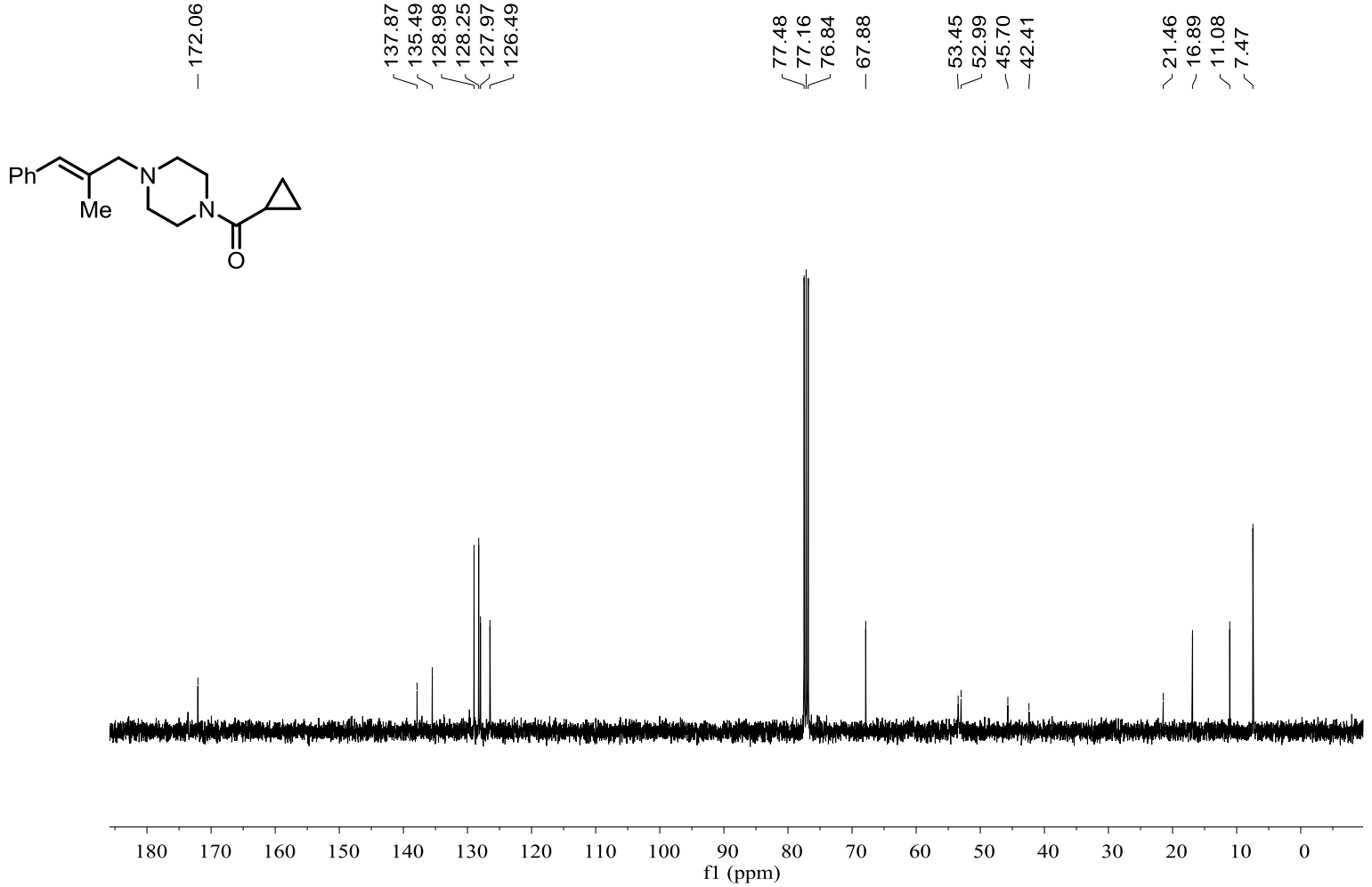
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-Methyl-4-(2-methyl-3-phenylallyl)piperazine (41)



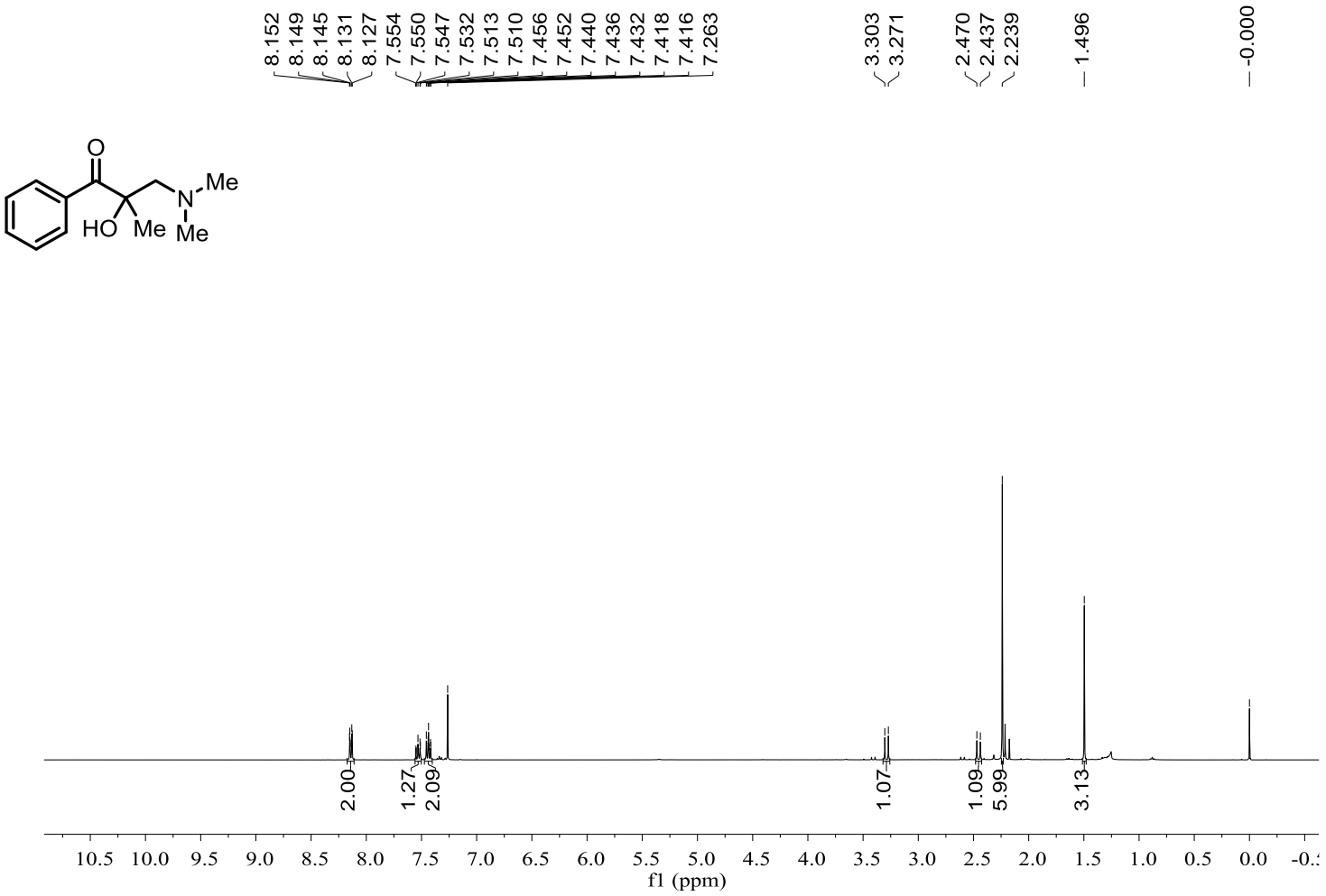
^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-Cyclopropyl(4-(2-methyl-3-phenylallyl)piperazin-1-yl)methanone (42)



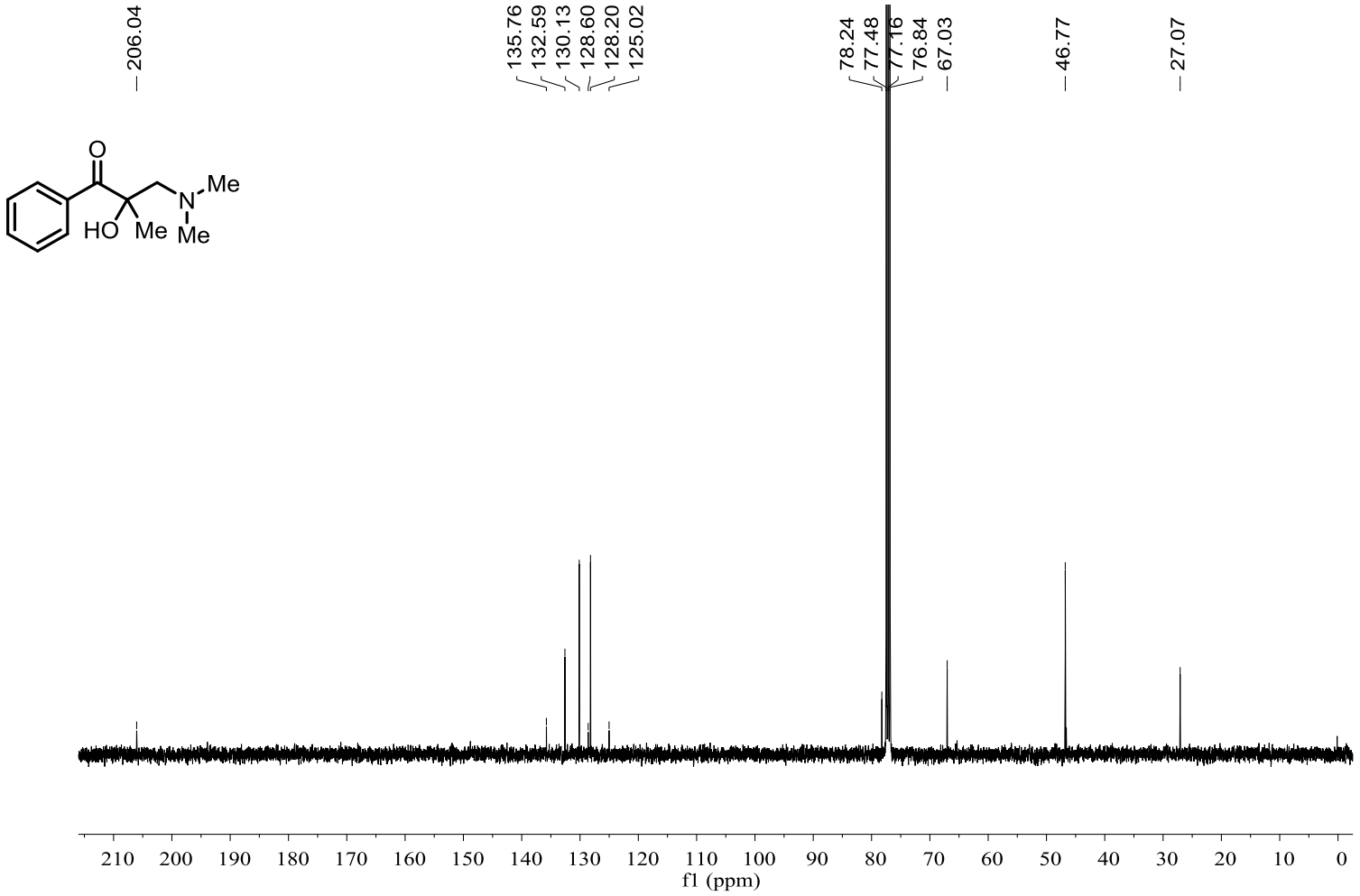
^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-Cyclopropyl(4-(2-methyl-3-phenylallyl)piperazin-1-yl)methanone (42)



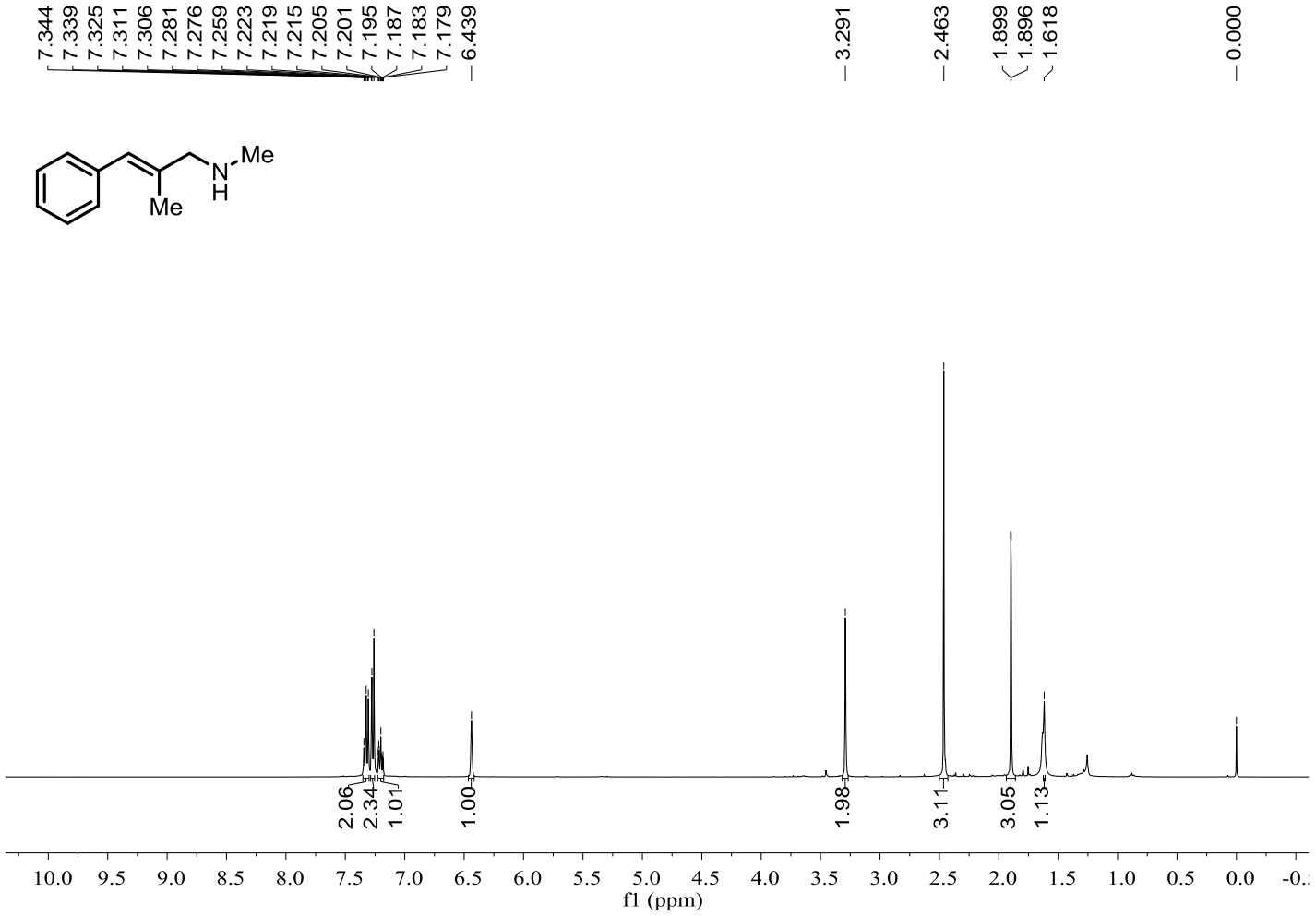
^{1}H NMR spectrum (400 M, $CDCl_3$) of 3-(Dimethylamino)-2-hydroxy-2-methyl-1-phenylpropan-1-one (43)



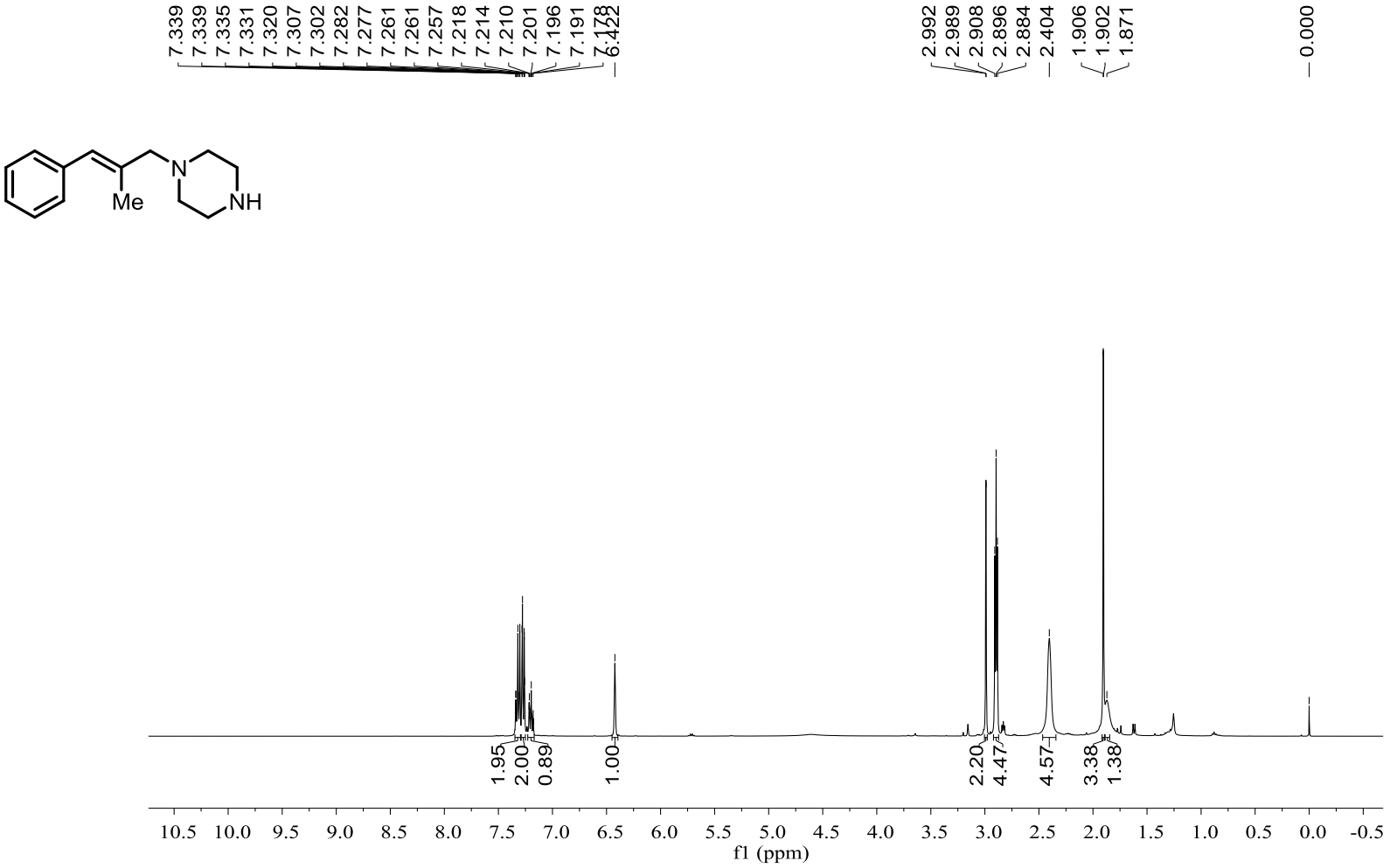
^{13}C NMR spectrum (100 M, $CDCl_3$) of 3-(Dimethylamino)-2-hydroxy-2-methyl-1-phenylpropan-1-one (43)



^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-*N*,*2*-Dimethyl-3-phenylprop-2-en-1-amine (44)



^{1}H NMR spectrum (400 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)piperazine (45)



^{13}C NMR spectrum (100 M, $CDCl_3$) of (*E*)-1-(2-Methyl-3-phenylallyl)piperazine (45)