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Supplementary Information

The Metal-free Aza-Claisen type Ring Expansion from Vinyl Aziridine: An Expeditious Synthesis of Seven Membered *N*-Heterocycles

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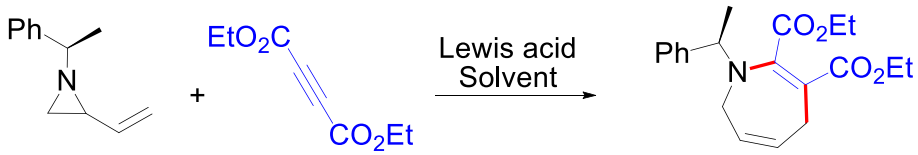
General Information:

All glass wares were washed with detergent, rinsed with acetone and dried in a hot air oven at 120 ℃. The chemicals and reagents were purchased from Aldrich, Alfa Aesar and TCI, were used as received. The solvent and commercial reagents were purified and stored according to literature procedures. All reactions were carried out under an atmosphere of nitrogen and the reagents were added *via* syringe. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, or by immersion in solutions of ninhydrin, phosphomolybdicacid (PMA) followed by heating on a hot plate. Purification of reaction products was carried out by flash chromatography using silica gel (230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded using Bruker AVANCE spectrometer, 400 MHz for ^{1}H and 101MHz for ^{13}C NMR using deuterated solvent using TMS as an internal standard. Chemical shifts were reported relative to TMS (δ = 0.0), for ^{1}H NMR and central line of $CDCl_3$ (δ = 77.2) for ^{13}C NMR respectively. Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Coupling constants are given in Hz. Ambiguous assignments were resolved on the basis of standard one dimensional proton decoupling experiments.

Table S1: Optimization of reaction conditions

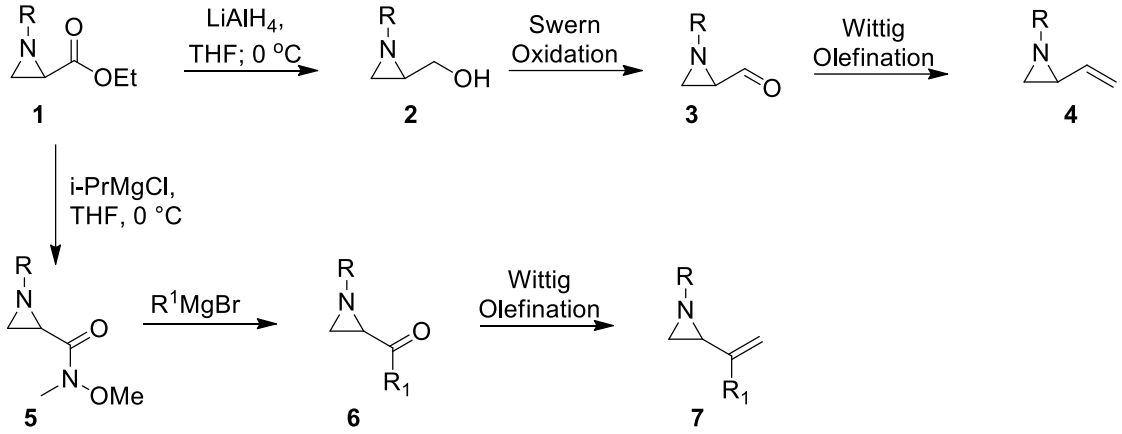


1a **2a** **3a**

Entry	Catalyst	Solvent[a]	Time	Yield (%)[a]
1.	$BF_3{\cdot}OEt_2$	Toluene	12h	62
2.	$BF_3{\cdot}OEt_2$	CH_3CN	8h	66
3.	$BF_3{\cdot}OEt_2$	CH_2Cl_2	6h	72
4.	$BF_3{\cdot}OEt_2$	THF	4h	42
5.	$CeCl_3$	CH_2Cl_2	4h	10
6.	HBF_4	CH_2Cl_2	12h	0
7.	$FeCl_3$	CH_2Cl_2	12h	12
8.	$HSbF_6$	THF	8h	24
9.	None	CH_2Cl_2	48h	0

[a]Reaction Conditions: The reaction mixture containing vinyl aziridine (1a, 1.0 mmol), diethyl acetylene dicarboxylate (2a, 1.5 mmol), Lewis acid (1.2 mmol) in the specified solvent (3.0 mL), were stirred at 25 °C. [b]Isolated yield.

Scheme S1: Preparation of Vinyl Aziridine



R= $C_6H_5CH_2$-, $C_6H_5(CH)Me$; 2,4-$(OMe)_2(C_6H_3)CH_2$-, 4-$(CH_3)_3C(C_6H_4)$-, $CH_3(C_{10}H_{20})CH_2$-, $(CH_3)_2CH$-, $(CH_3)_2CHCH_2$-, $(CH_3)_3C$-, C_6H_{11}-.

The aziridine ester was prepared by our own reported procedure.[1] The aziridine ester was converted to aziridine aldehyde by $LiAlH_4$ reduction followed Swern Oxidation by following of our previous reported protocol. The Wittig Olefination of aziridine aldehyde gave the Vinyl aziridines used as substrate for [5+2] hetero cycloaddition. The aziridine aldehydes with alkyl substituent on Nitrogen was not enough stable for Wittig Olefination. In those case the aziridine ester was converted into its corresponding ketones via preparation of weinerb amide followed by Grignard reaction.[2]

General experimental procedure for Aziridine Aldehyde: To a stirred solution of oxalyl chloride (3.8 mL, 4.5 mmol) in CH_2Cl_2 (30 mL) at −78 °C was added dimethyl sulfoxide (2.40 mL, 9.00 mmol) over 10 min. The resulting mixture was stirred for another 45 min and then a solution of alcohol **2** (3.0 mmol) in CH_2Cl_2 (10.0 mL) was added dropwise. The resulting mixture was stirred for 1 h and added triethylamine (1.4 mL,10.6 mmol). The reaction mixture was stirred for 30 min at −78 °C and then warmed to 0 °C and allowed to stir for 30 min. The reaction mixture was quenched with water (20 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to get crude aldehyde which was used as such for the Wittig reaction without further purification.

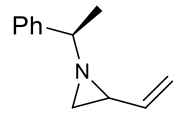
General experimental procedure for Weinerb Amide: To a stirred solution of aziridine ester (1.00 mmol) and N,O-dimethylhydroxylamine hydrochloride (195 mg, 2.00 mmol) in dry THF (15 mL) at −10 °C was slowly added iPrMgCl (2.00 mL, 2.0 M in THF, 4.00 mmol) and the reaction mixture was stirred for 1 h. The reaction mixture was quenched with a solution of NH_4Cl 10% aq. and

extracted with EtOAc (3 × 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, concentrated in vacuum and crude product was purified by a short silica gel column using EtOAc/hexane (7:3) to get desired compound.

General experimental procedure for Ketone: To a stirred solution of Weinerb amide (1.00 mmol) in dry THF was added Grignard reagent (1.10 mmol) at 0 °C and the reaction mixture was allow stirred for 4h. The reaction mixture was quenched with a solution of NH_4Cl 10% aq. and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4, concentrated in vacuum and crude product was purified by silica gel column chromatography by using EtOAc/hexanes (8:2) to get desired compound which was subjected for olefination reaction without further purification.

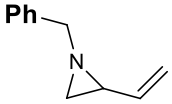
General experimental procedure typical Procedure for Wittig olefination: To a stirred solution of methyltriphenylphosphonium Iodide (808.00 mg, 2.0 mmol) in dry THF (20.00 mL) was added a solution of NaHMDS (1.8 mL, 1M in THF, 1.8 mmol) at 0 °C and the resulting mixture was allowing to stirred at room temperature. After 30 min this solution was cooled to –10 °C and a solution of aldehyde or ketone (1.00 mmol) in THF (5 mL) was added and stirred further for 6h at room temprature. The reaction mixture was quenched with water at 0 °C, and the product was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with water, brine and dried over anhydrous Na_2SO_4. The solvent was removes under reduced pressure and the crude product was purified on a silica gel column using hexanes and ethyl acetate as eluents to give the vinyl aziridine as pure product.

1-((R)-1-phenylethyl)-2-vinylaziridine (1a):



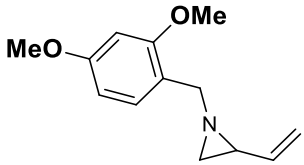
Yellow Liquid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 4H), 7.26 – 7.19 (m, 1H), 5.71 – 5.57 (m, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.21 – 5.04 (m, 1H), 2.49 (q, *J* = 6.5 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.69 (d, *J* = 3.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 1H), 1.44 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 138.5, 128.2, 126.9, 126.7, 115.9, 70.0, 41.7, 34.7, 23.1. HRMS-MALDI (m/z): calcd for $C_{12}H_{15}N$, $[M+H]^+$ 174.1277; found 174.1277.

1-benzyl-2-vinylaziridine (1b):



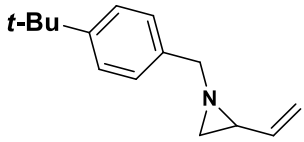
Yellow Liquid, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 5H), 5.63 – 5.55 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 3.50 (d, *J* = 6.1 Hz, 2H), 2.02 (m, 1H), 1.85 (d, *J* = 2.6 Hz, 1H), 1.63 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 138.18, 128.3, 127.8, 126.9, 116.3, 64.4, 41.4, 35.3. HRMS-MALDI (m/z): calcd for $C_{11}H_{13}N$, $[M+H]^+$ 160.1121; found 160.1127.

1-(2,4-dimethoxybenzyl)-2-vinylaziridine (1c):



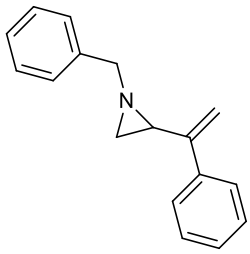
Thick liquid, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 1H), 6.56 – 6.39 (m, 2H), 5.60 (m, 1H), 5.30 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.10 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.79 (d, *J* = 2.4 Hz, 6H), 3.51 (d, *J* = 14.0 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 2.07 – 1.95 (m, 1H), 1.83 (d, *J* = 3.5 Hz, 1H), 1.66 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 157.8, 138.7, 129.5, 119.9, 115.9, 103.8, 98.1, 58.2, 55.2, 41.3, 35.2. HRMS-MALDI (m/z): calcd for $C_{13}H_{17}NO_2$, $[M+H]^+$ 220.1332; found 220.1338.

1-(4-(tert-butyl)benzyl)-2-vinylaziridine (1d):



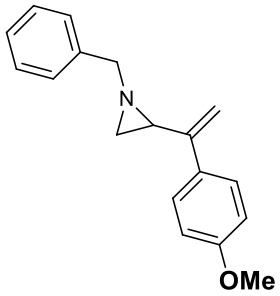
Colorless oil, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (dd, *J* = 8.2, 7.7 Hz, 2H), 5.68 – 5.51 (m, 1H), 5.39 – 5.25 (m, 1H), 5.17 – 5.05 (m, 1H), 3.53 (d, *J* = 13.5 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 2.02 (td, *J* = 7.1, 3.4 Hz, 1H), 1.83 (d, *J* = 3.3 Hz, 1H), 1.62 (d, *J* = 6.5 Hz, 1H), 1.31 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 138.4, 135.95, 127.5, 125.2, 116.1, 64.1, 41.4, 35.3, 34.4, 31.3. HRMS-MALDI (m/z): calcd for $C_{15}H_{21}N$, $[M+H]^+$ 216.1747; found 216.1713.

1-benzyl-2-(1-phenylvinyl)aziridine (1e):



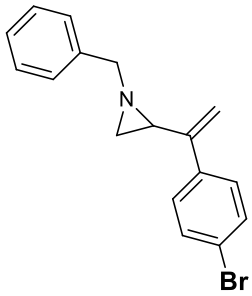
Colorless oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.17 (m, 10H), 5.41 – 5.25 (m, 2H), 3.59 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 2.25 (dd, *J* = 6.4, 3.5 Hz, 1H), 1.90 – 1.78 (m, 1H), 1.67 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 139.6, 138.9, 128.1, 127.8, 127.5, 126.8, 125.8, 112.2, 64.6, 41.4, 36.4. HRMS-MALDI (m/z): calcd for $C_{17}H_{17}N$, $[M+H]^+$ 236.1434; found 236.1436.

1-benzyl-2-(1-(4-methoxyphenyl)vinyl)aziridine (1f):



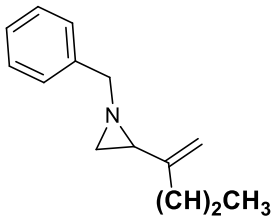
Yellow liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.21 (m, 7H), 6.85 (dd, *J* = 11.6, 5.0 Hz, 2H), 5.31 (t, *J* = 13.2 Hz, 2H), 3.76 (s, 3H), 3.65 (d, *J* = 13.5 Hz, 1H), 3.52 (d, *J* = 13.5 Hz, 1H), 2.29 (s, 1H), 1.89 (s, 1H), 1.72 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 145.0, 139.0, 132.2, 128.2, 127.9, 126.9, 113.5, 110.7, 64.6, 55.0, 41.6, 36.2. HRMS-MALDI (m/z): calcd for $C_{18}H_{19}NO$, $[M+H]^+$ 266.1539; found 266.1536.

1-benzyl-2-(1-(4-bromophenyl)vinyl)aziridine (1g):



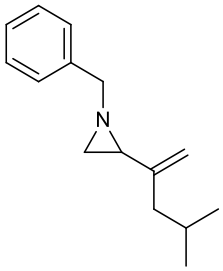
Yellow liquid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.27 – 7.24 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.57 – 6.48 (m, 1H), 5.30 – 5.02 (m, 2H), 3.51 (dd, *J* = 76.3, 13.6 Hz, 2H), 2.18 – 2.02 (m, 1H), 1.82 (d, *J* = 3.4 Hz, 1H), 1.67 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 138.6, 138.4, 133.1, 132.7, 129.5, 128.3, 127.8, 127.1, 116.4, 64.3, 40.8, 35.8. HRMS-MALDI (m/z): calcd for $C_{17}H_{16}BrN$, $[M+H]^+$ 314.0539; found 314.0537.

1-Benzyl-2-(penta-1,3-dien-2-yl)aziridine (1h):



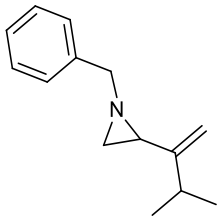
Colorless liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (ddd, *J* = 29.5, 14.5, 7.4 Hz, 5H), 5.00 (d, *J* = 0.9 Hz, 1H), 4.79 (d, *J* = 1.3 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 2.04 – 1.85 (m, 3H), 1.84 (d, *J* = 3.5 Hz, 1H), 1.52 (d, *J* = 6.5 Hz, 1H), 1.49 – 1.35 (m, 2H), 0.87 (dd, *J* = 8.2, 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 139.1, 128.1, 127.8, 126.8, 110.1, 64.7, 42.8, 35.3, 34.8, 20.9, 13.7. HRMS-MALDI (m/z): calcd for $C_{14}H_{17}N$, $[M+H]^+$ 200.1434; found 200.1439.

1-Benzyl-2-(4-methylpent-1-en-2-yl)aziridine (1i):



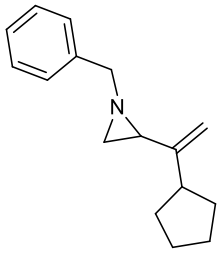
Colorless liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 5H), 5.02 (d, *J* = 0.5 Hz, 1H), 4.76 (d, *J* = 0.9 Hz, 1H), 3.67 (d, *J* = 13.5 Hz, 1H), 3.30 (d, *J* = 13.5 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.86 – 1.77 (m, 2H), 1.71 (dt, *J* = 15.7, 4.3 Hz, 1H), 1.55 (d, *J* = 6.5 Hz, 1H), 0.83 (dd, *J* = 6.5, 4.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 139.2, 128.2, 127.9, 126.8, 111.3, 64.8, 43.6, 42.6, 35.3, 26.4, 22.6, 22.2. HRMS-MALDI (m/z): calcd for $C_{15}H_{21}N$, $[M+H]^+$ 216.1747; found 216.1748.

1-benzyl-2-(3-methylbut-1-en-2-yl)aziridine (1j):



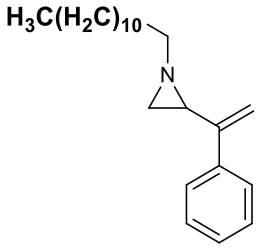
Colorless liquid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 5H), 4.96 (s, 1H), 4.82 – 4.71 (m, 1H), 3.56 (d, *J* = 13.6 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 2.27 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.92 (dd, *J* = 6.5, 3.5 Hz, 1H), 1.77 (dd, *J* = 3.5, 0.7 Hz, 1H), 1.55 (d, *J* = 6.5 Hz, 1H), 1.03 (dd, *J* = 6.9, 1.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 139.1, 128.1, 127.8, 126.8, 107.2, 64.8, 41.5, 35.9, 32.2, 22.0, 21.6. HRMS-MALDI (m/z): calcd for $C_{14}H_{19}N$, $[M+H]^+$ 202.1590; found 202.1594.

1-benzyl-2-(1-cyclopentylvinyl)aziridine (1k):



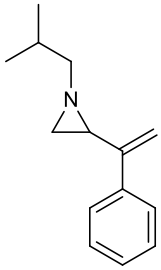
Colorless liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 29.8, 19.8, 7.2 Hz, 5H), 5.01 – 4.91 (m, 1H), 4.81 (s, 1H), 3.59 (d, *J* = 13.5 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 2.48 – 2.32 (m, 1H), 1.94 (dd, *J* = 6.5, 3.5 Hz, 1H), 1.86 – 1.72 (m, 3H), 1.70 – 1.59 (m, 2H), 1.58 – 1.48 (m, 3H), 1.47 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 139.1, 128.1, 127.8, 126.8, 107.5, 64.8, 44.2, 42.0, 35.7, 31.8, 31.4, 24.8. HRMS-MALDI (m/z): calcd for $C_{16}H_{21}N$, $[M+H]^+$ 228.1747; found 228.1744.

1-dodecyl-2-(1-phenylvinyl)aziridine (1l):



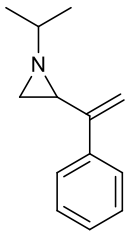
Colorless liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.36 – 7.27 (m, 3H), 5.46 – 5.21 (m, 2H), 2.46 (dt, *J* = 11.5, 7.3 Hz, 1H), 2.30 (dt, *J* = 11.5, 7.0 Hz, 1H), 2.11 (dd, *J* = 6.2, 3.3 Hz, 1H), 1.79 (dd, *J* = 3.4, 0.9 Hz, 1H), 1.70 – 1.51 (m, 3H), 1.45 – 1.20 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 139.9, 128.2, 127.6, 125.9, 112.0, 61.6, 41.5, 36.4, 31.9, 29.87, 29.62, 29.34, 27.4, 22.7, 14.1. MALDI (m/z): calcd for $C_{22}H_{35}N$, $[M+H]^+$ 314.2842; found 314.2844.

1-isobutyl-2-(1-phenylvinyl)aziridine (1m):



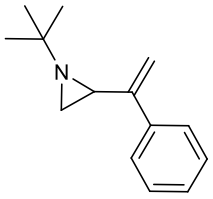
Colorless liquid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.20 (m, 3H), 5.37 (s, 2H), 2.39 (dd, *J* = 11.5, 7.2 Hz, 1H), 2.06 (m, 2H), 1.88 (m, 1H), 1.80 – 1.71 (m, 1H), 1.56 (d, *J* = 6.4 Hz, 1H), 0.99 (dd, *J* = 20.3, 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 139.8, 128.2, 127.5, 125.9, 111.8, 69.5, 41.6, 36.6, 29.2, 20.8. MALDI (m/z): calcd for $C_{14}H_{19}N$, $[M+H]^+$ 202.1590; found 202.1592.

1-isopropyl-2-(1-phenylvinyl)aziridine (1n):



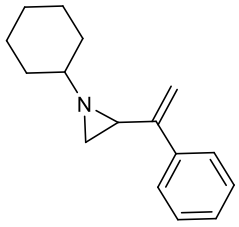
Colorless liquid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.44 (m, 2H), 7.40 – 7.13 (m, 3H), 5.39 (dd, *J* = 3.4, 1.3 Hz, 2H), 2.14 (dd, *J* = 6.6, 3.4 Hz, 1H), 1.74 (d, *J* = 3.4 Hz, 1H), 1.59 (t, *J* = 7.1 Hz, 2H), 1.17 (dd, *J* = 6.3, 1.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.97, 139.8, 128.2, 127.5, 125.9, 112.2, 61.3, 40.8, 35.7, 22.4, 21.8. MALDI (m/z): calcd for $C_{13}H_{17}N$, $[M+H]^+$ 188.1434; found 188.1432.

1-(tert-butyl)-2-(1-phenylvinyl)aziridine (1o):



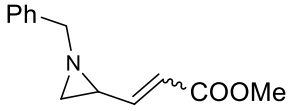
Colorless liquid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.45 (m, 2H), 7.38 – 7.18 (m, 3H), 5.52 – 5.34 (m, 2H), 2.43 (dd, *J* = 6.4, 3.1 Hz, 1H), 1.84 (dd, *J* = 6.5, 0.9 Hz, 1H), 1.53 (d, *J* = 3.2 Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 140.1, 128.2, 127.5, 125.9, 112.2, 52.9, 34.1, 29.4, 26.6. MALDI (m/z): calcd for $C_{14}H_{19}N$, $[M+H]^+$ 202.1590; found 202.1591.

1-cyclohexyl-2-(1-phenylvinyl)aziridine (1p):



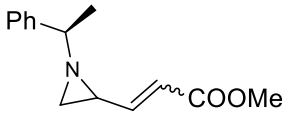
Colorless liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 2H), 7.36 – 7.17 (m, 3H), 5.39 (d, *J* = 2.7 Hz, 2H), 2.23 – 2.07 (m, 1H), 1.91 – 1.70 (m, 5H), 1.60 (dd, *J* = 6.6, 0.9 Hz, 2H), 1.52 – 1.37 (m, 2H), 1.32 – 1.11 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 139.8, 128.1, 127.5, 125.8, 112.2, 69.1, 40.2, 35.0, 32.9, 32.2, 26.1, 24.7. MALDI (m/z): calcd for $C_{16}H_{21}N$, $[M+H]^+$ 228.1747; found 228.1740.

Methyl 3-(1-benzylaziridin-2-yl)acrylate (1q):



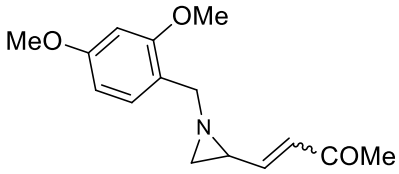
Yellow liquid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 6.70 (m, 0.8H), 6.05 (d, *J* = 15.7 Hz, 0.8H), 5.90 – 5.75 (m, 0.4H), 3.75 – 3.68 (m, 3H), 3.63 – 3.42 (m, 2H), 2.15 – 2.01 (m, 1H), 1.95 – 1.89 (m, 1H), 1.78 (t, *J* = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 150.1, 148.3, 138.4, 138.3, 128.5, 128.2, 127.7, 127.00, 121.3, 120.4, 64.0, 51.3, 51.0, 39.1, 37.1, 36.6, 35.8. MALDI (m/z): calcd for $C_{13}H_{15}NO_2$, $[M+H]^+$ 218.1176; found 218.1171.

Methyl 3-(1-((R)-1-phenylethyl)aziridin-2-yl)acrylate (1r):



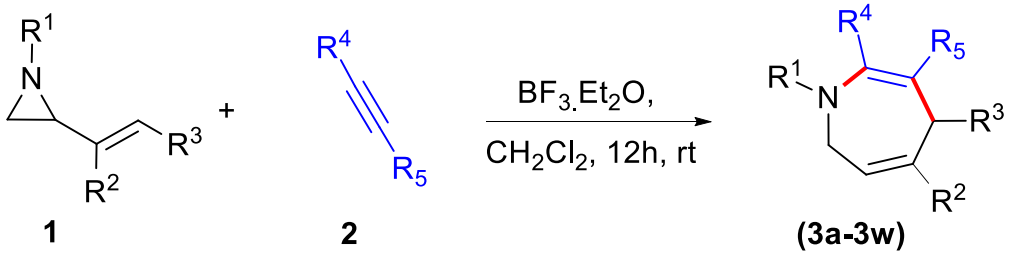
Yellow liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.21 (m, 5H), 6.80 (m, 0.8H), 6.24 – 6.08 (m, 0.8H), 6.02 – 5.78 (m, 0.4H), 3.78 (d, *J* = 12.5 Hz, 3H), 2.60 (q, *J* = 6.5 Hz, 0.5H), 2.60 (q, *J* = 6.5 Hz, 2.5H), 2.22 (m, 1H), 1.79 (d, *J* = 3.1 Hz, 1H), 1.78 (d, *J* = 6.6 Hz, 0.2H), 1.68 (d, *J* = 6.5 Hz, 0.5H), 1.53 – 1.39 (m, 2.5H). MALDI (m/z): calcd for $C_{14}H_{17}NO_2$, $[M+H]^+$ 232.1332; found 232.1331.

4-(1-(2,4-dimethoxybenzyl)aziridin-2-yl)but-3-en-2-one (1w):



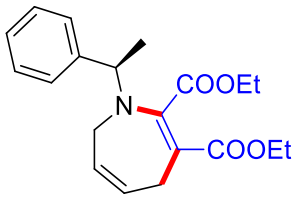
Yellow liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.50 – 6.43 (m, 2H), 3.78 (s, 6H), 3.50 (m, 2H), 2.18 (m, 4H), 1.94 (m, 1H), 1.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 160.0, 157.8, 131.8, 131.2, 129.7, 128.3, 119.0, 103.84, 57.9, 55.1, 39.4, 36.4, 26.3. MALDI (m/z): calcd for $C_{13}H_{15}NO_2$, $[M+H]^+$ 218.1176; found 218.1171. MALDI (m/z): calcd for $C_{15}H_{19}NO_3$, $[M+H]^+$ 262.1438; found 262.1431.

General Experimental procedure for [5+2] cycloaddition towards synthesis of Azepines: In a 25.00 mL two neck round bottom flask fitted with a rubber septum, magnetic bar was charged with molecular sieves powder, (0.300 mg), Vinyl aziridine (1.00 mmol), alkyne (1.5 mmol) and DCM (10.00 mL). The flask was cooled at -10 ℃ and $BF_3.Et_2O$ (1.2 mmol) was added slowly with continuous stirring. The resulting reaction mixture was allowed to warm to room temperature and stirred further for 12hrs, and then quenched with saturated aq. $NaHCO_3$ solution. The reaction mixture was filtered through sintered funnel and the filtrate was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afforded the crude product which was purified by column chromatography on a short column of silica gel.



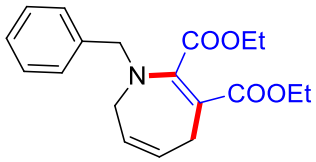
1 **2** **(3a-3w)**

(R)-diethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3a):



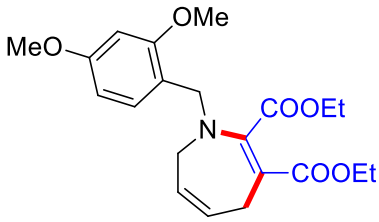
Thick yellow liquid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 4.9, 4.3 Hz, 2H), 7.42 – 7.26 (m, 3H), 5.96 (dt, *J* = 9.5, 6.7 Hz, 1H), 5.54 (m, 1H), 4.59 (q, *J* = 6.8 Hz, 1H), 4.33 (qd, *J* = 7.2, 3.6 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.68 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.53 (dd, *J* = 14.7, 7.1 Hz, 1H), 3.32 (d, *J* = 6.6 Hz, 2H), 1.58 (d, *J* = 6.8 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.0, 152.0, 140.0, 133.1, 128.3, 127.51, 127.50, 127.45, 95.89, 61.5, 60.0, 58.6, 41.7, 24.4, 17.6, 14.3, 13.8. HRMS-MALDI (m/z): calcd for C20H25NO4, $[M+H]^+$ 344.1856; found 344.1853.

Diethyl 1-benzyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3b):



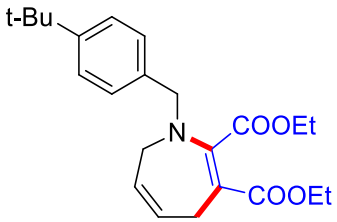
Thick yellow liquid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H), 6.05 (m, 1H), 5.75 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.16 – 4.12 (m, 4H), 3.78 (d, *J* = 6.8 Hz, 2H), 3.32 (dd, *J* = 6.6, 0.7 Hz, 2H), 1.25 (t, *J* = 7.2, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.8, 152.02, 137.11, 133.4, 128.6, 128.1, 127.7, 126.7, 100.1, 61.6, 60.3, 56.9, 47.1, 24.8, 14.3, 13.8. HRMS-MALDI (m/z): calcd for $C_{19}H_{23}NO_4$, $[M+H]^+$ 330.1700; found 330.1704.

Diethyl 1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3c):



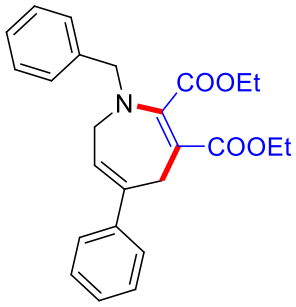
Thick yellow liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 8.4, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 6.01 (dt, *J* = 9.6, 6.6 Hz, 1H), 5.73 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.15 (s, 2H), 4.10 (m, 2H), 3.81 – 3.78 (m, 8H), 3.32 (d, *J* = 6.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.0, 161.0, 158.3, 152.6, 133.2, 130.09, 130.06, 127.0, 117.6, 104.2, 98.3, 61.5, 60.1, 55.3, 50.7, 47.2, 24.7, 14.3, 13.8. HRMS-MALDI (m/z): calcd for $C_{21}H_{27}NO_6$, $[M+H]^+$ 390.1911; found 390.1916.

Diethyl 1-(4-(tert-butyl)benzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3d):



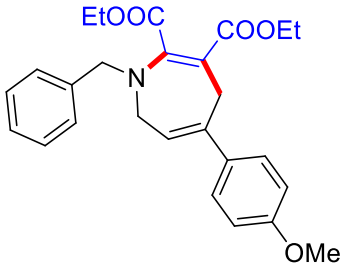
Thick yellow liquid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), 6.04 (dt, *J* = 9.7, 6.6 Hz, 1H), 5.75 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.12 (m, 4H), 3.78 (d, *J* = 6.8 Hz, 2H), 3.33 (d, *J* = 6.6 Hz, 2H), 1.31 (s, 9H), 1.25 (t, *J* = 7.1, 6H superimposed CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.8, 152.1, 150.7, 134.0, 133.4, 127.8, 126.7, 125.5, 99.7, 61.6, 60.2, 56.6, 47.0, 34.5, 32.4, 24.7, 14.4, 13.8. HRMS-MALDI (m/z): calcd for $C_{23}H_{31}NO_4$, $[M+H]^+$ 386.2326; found 386.2326.

Diethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3e):



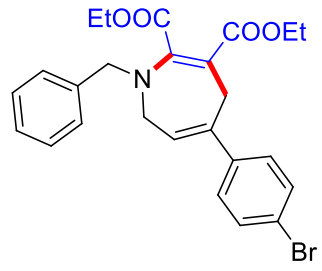
Thick yellow liquid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 9H), 5.99 (t, *J* = 7.4 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.26 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.98 (d, *J* = 7.4 Hz, 2H), 3.87 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 166.7, 151.9, 146.2, 141.0, 137.2, 128.7, 128.4, 128.0, 127.8, 127.5, 125.9, 120.8, 97.5, 61.7, 60.3, 57.3, 47.3, 27.5, 14.4, 13.8. HRMS-MALDI (m/z): calcd for $C_{25}H_{27}NO_4$, $[M+H]^+$ 406.2013; found 406.2013.

Diethyl 1-benzyl-5-(4-methoxyphenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3f):



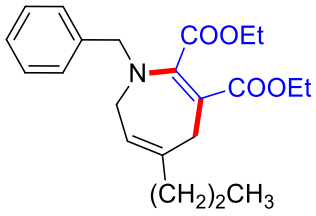
Thick yellow liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 -7.30 (m, 7H), 6.86 (m, 2H), 5.88 (t, *J* = 7.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.20 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 7.4 Hz, 2H), 3.83 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 166.7, 159.2, 151.8, 145.8, 137.2, 133.4, 128.6, 128.0, 127.8, 127.1, 118.76, 113.7, 97.2, 61.6, 60.2, 57.2, 55.3, 47.3, 27.3, 14.4, 13.8. HRMS-MALDI (m/z): calcd for $C_{26}H_{29}NO_5$, $[M+H]^+$ 436.2118; found 436.2116.

Diethyl 1-benzyl-5-(4-bromophenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3g):



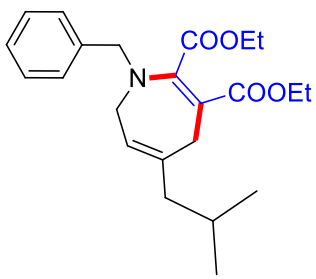
Thick yellow liquid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 9H), 5.93 (t, *J* = 7.4 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.25 (q, *J* = 7.4 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 7.4 Hz, 2H), 3.82 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 166.5, 151.8, 145.1, 139.3, 137.1, 133.4, 128.7, 128.5, 128.0, 127.2, 121.1, 97.2, 61.8, 60.3, 57.4, 47.3, 27.4, 14.4, 13.8. HRMS-MALDI (m/z): calcd for $C_{25}H_{26}BrNO_4$, $[M+H]^+$ 484.1118; found 484.1115.

Diethyl 1-benzyl-5-propyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3h):



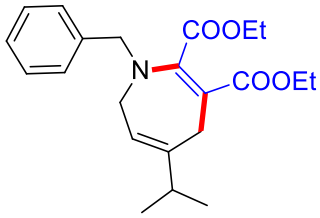
Thick liquid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 5.42 (t, *J* = 7.1 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.17 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 7.1 Hz, 2H), 3.29 (s, 2H), 2.02 (t, *J* = 7.4 Hz, 2H), 1.43 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.28 – 1.20 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.9, 151.7, 148.0, 137.2, 128.5, 128.0, 127.6, 118.8, 97.6, 61.6, 60.1, 56.9, 47.0, 40.2, 28.3, 20.1, 14.4, 13.8, 13.7. HRMS-MALDI (m/z): calcd for $C_{22}H_{29}NO_4$, $[M+H]^+$ 372.2169; found 372.2169.

Diethyl 1-benzyl-5-isobutyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3i):



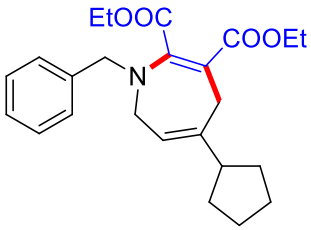
Thick yellow liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 5.43 (t, *J* = 7.1 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.14 (m, 4H), 3.75 (d, *J* = 7.1 Hz, 2H), 3.29 (s, 2H), 1.92 (d, *J* = 6.9 Hz, 2H), 1.79 (m, 1H), 1.26 (t, *J* = 7.1, 6H), 0.87 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.8, 151.7, 147.1, 137.2, 128.5, 128.0, 127.7, 120.1, 97.7, 61.5, 60.1, 56.9, 48.1, 47.0, 28.2, 26.1, 22.5, 14.3, 13.8. HRMS-MALDI (m/z): calcd for $C_{23}H_{31}NO_4$, $[M+H]^+$ 386.2326; found 386.2326.

Diethyl 1-benzyl-5-isopropyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3j):



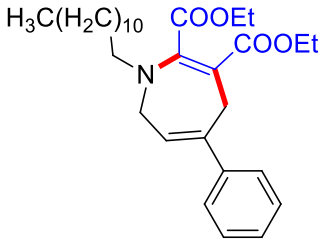
Thick yellow liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.35 (m, 7.0 Hz, 3H), 6.16 (t, *J* = 7.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.15 (q, *J* = 4.17 Hz, 2H), 3.97 (d, *J* = 7.6 Hz, 2H), 3.83 (s, 2H), 3.61 – 3.57 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 166.7, 152.1, 145.6, 141.3, 128.3, 127.4, 126.0, 121.8, 94.0, 61.4, 60.0, 52.5, 40.4, 27.9, 21.4, 14.4, 13.9. HRMS-MALDI (m/z): calcd for $C_{22}H_{29}NO_4$, $[M+H]^+$ 372.2169; found 372.2167.

Diethyl 1-benzyl-5-cyclopentyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3k):



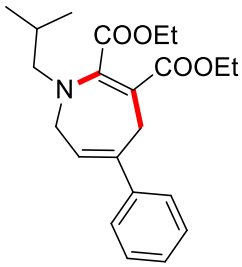
Thick yellow liquid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 5.41 (t, *J* = 7.6, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.19 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 7.2 Hz, 2H), 3.34 (s, 2H), 2.53 – 2.40 (m, 1H), 1.74 (m, 2H), 1.70 – 1.63 (m, 2H), 1.61 – 1.53 (m, 2H), 1.40 – 1.34 (m, 2H), 1.24 (t, 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 166.8, 151.7, 151.3, 137.3, 128.5, 128.0, 127.6, 116.9, 97.8, 61.5, 60.1, 57.1, 47.4, 47.1, 30.8, 26.7, 25.4, 14.3, 13.8. HRMS-MALDI (m/z): calcd for $C_{24}H_{31}NO_4$, $[M+H]^+$ 398.2326; found 398.2321.

Diethyl 1-dodecyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3l):



Thick yellow liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.35 (m, 2H), 7.31 – 7.26 (m, 1H), 6.20 (t, *J* = 7.5 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.12 (d, *J* = 7.5 Hz, 2H), 3.82 (s, 2H), 3.04 – 3.00 (m, 2H), 1.68 – 1.56 (m, 2H), 1.35 – 1.31 (m, 6H), 1.30 – 1.22 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 166.4, 151.9, 146.1, 141.1, 128.3, 127.5, 126.0, 120.4, 95.1, 61.5, 60.0, 55.0, 48.1, 31.9, 29.9, 29.6, 29.3, 27.3, 26.6, 22.6, 14.4, 14.1, 13.8. HRMS-MALDI (m/z): calcd for $C_{30}H_{45}NO_4$, $[M+H]^+$ 484.3421; found 484.3429.

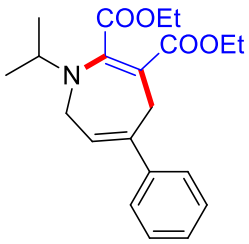
Diethyl 1-isobutyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3m):



Thick yellow liquid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 6.19 (t, *J* = 7.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.06 (d, *J* = 7.4 Hz, 2H), 3.84 (s, 2H), 2.87 (d, *J* = 7.5 Hz, 2H), 1.99 (dt, *J* = 13.7, 7.0 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 166.3, 152.4, 145.8, 141.3, 128.3, 127.5, 126.0, 120.9, 95.3, 61.6, 61.5,

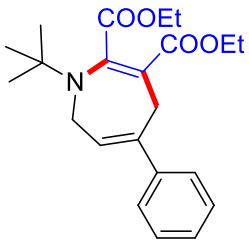
60.1, 48.6, 28.5, 27.8, 19.8, 14.4, 14.0. HRMS-MALDI (m/z): calcd for $C_{22}H_{29}NO_4$, $[M+H]^+$ 372.2169; found 372.2160.

Diethyl 1-isopropyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3n):



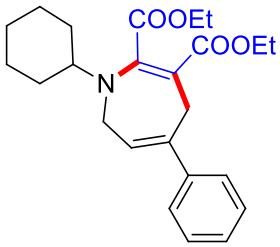
Colorless liquid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.35 (m, 3H), 6.14 (t, *J* = 7.6 Hz, 1H), 4.34 – 4.28 (m, 2H), 4.14 (t, *J* = 7.1 Hz, 2H), 3.97 (d, *J* = 7.6 Hz, 2H), 3.83 (s, 2H), 3.57 – 3.51 (m, 1H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 166.7, 152.1, 145.6, 141.3, 128.3, 127.4, 126.0, 121.8, 94.0, 61.4, 60.0, 52.5, 40.4, 28.9, 21.4, 14.4, 14.0. HRMS-MALDI (m/z): calcd for $C_{21}H_{27}NO_4$, $[M+H]^+$ 358.2013; found 358.2008.

Diethyl 1-(tert-butyl)-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3o):



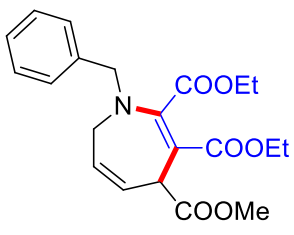
Yellow liquid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.22 (dd, *J* = 7.4, 5.0 Hz, 1H), 5.78 (t, *J* = 4.3 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.92 (dt, *J* = 4.0, 1.9 Hz, 2H), 3.72 (d, *J* = 1.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29 – 1.22 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 143.5, 135.6, 128.2, 126.8, 125.8, 125.6, 61.2, 60.8, 56.1, 47.2, 32.0, 29.0, 14.1, 13.8. HRMS-MALDI (m/z): calcd for $C_{22}H_{29}NO_4$, $[M+H]^+$ 372.2169; found 372.2175.

Diethyl 1-cyclohexyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3p):



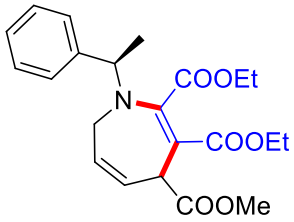
Colorless liquid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.33 (m, 3H), 6.13 (t, *J* = 7.5 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 7.6 Hz, 2H), 3.83 (s, 2H), 3.04 (m, 1H), 1.84 (m, 4H), 1.61 (m, 2H), 1.45 – 1.42 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 – 1.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.6, 152.2, 145.1, 141.5, 128.3, 127.4, 126.0, 122.1, 94.0, 61.3, 60.0, 41.8, 31.9, 28.1, 25.8, 25.3, 14.4, 14.0. HRMS-MALDI (m/z): calcd for $C_{24}H_{31}NO_4$, $[M+H]^+$ 398.2326; found 398.2323.

2,3-Diethyl 4-methyl 1-benzyl-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3q):



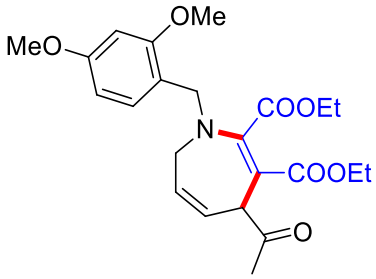
Thick yellow liquid, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 5H), 6.00 (m, 1H), 5.80 (dt, *J* = 9.7, 7.1 Hz, 1H), 4.46 – 4.39 (m, 2H), 4.30 – 4.28 (m, 3H), 4.21 – 4.10 (m, 3H), 3.69 (s, 3H), 3.11 (ddd, *J* = 14.9, 7.1, 1.4 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 167.9, 166.4, 153.0, 136.6, 130.9, 129.5, 128.7, 128.2, 127.6, 96.8, 61.9, 60.4, 56.8, 52.3, 46.1, 43.3, 14.2, 13.8. HRMS-MALDI (m/z): calcd for $C_{21}H_{25}NO_6$, $[M+H]^+$ 388.1755; found 388.1762.

2,3-Diethyl 4-methyl 1-((R)-1-phenylethyl)-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3r):



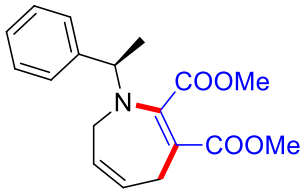
Thick yellow liquid, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 5H), 6.85– 6.55 (m, 0.2H), 6.10 – 5.91 (m, 1.8H), 4.76 – 4.59 (m, 1H), 4.46 (m, 1H), 4.3 (m, 2H), 4.20 – 4.01 (m, 3H), 3.74 (s, 3H), 2.90 (m, 1H), 1.56 (d, *J* = 6.8 Hz, 2H), 1.40 – 1.21 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 168.1, 166.8, 166.7, 165.7, 153.8, 153.0, 143.6, 139.3, 138.8, 130.8, 128.8, 128.5, 128.3, 127.7, 127.4, 124.0, 95.0, 89.3, 61.8, 60.2, 58.7, 53.5, 52.2, 50.8, 43.5, 41.5, 19.4, 14.3, 13.8. HRMS-MALDI (m/z): calcd for $C_{22}H_{27}NO_6$, $[M+H]^+$ 402.1911; found 402.1911.

Diethyl 4-acetyl-1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3s):



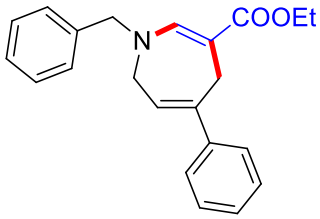
Thick yellow liquid, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 1H), 6.49 – 6.41 (m, 2H), 5.99 (m, 1H), 5.77 (dt, *J* = 9.7, 7.0 Hz, 1H), 4.44 (d, *J* = 9.5 Hz, 1H), 4.29 (m, 3H), 4.26 – 4.19 (m, 1H), 4.11 (m, 3H), 3.80 (s, 3H), 3.10 (m, 1H), 2.20 (s, 3H), 1.29 (m, t, *J* = 7.2 Hz, 3H), 1.20 (m, t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.8, 168.0, 166.4, 160.6, 158.3, 153.8, 130.6, 130.3, 129.9, 117.1, 104.2, 98.2, 96.4, 61.7, 60.3, 55.4, 55.2, 52.1, 50.9, 46.4, 28.1, 14.2, 14.0. HRMS-MALDI (m/z): calcd for $C_{23}H_{29}NO_7$, $[M+H]^+$ 432.2017; found 432.2012.

(R)-Dimethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3t):



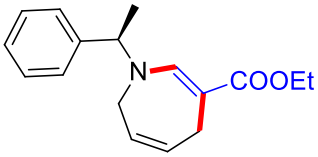
Thick yellow liquid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.97 (dt, *J* = 9.5, 6.7 Hz, 1H), 5.55 – 5.52 (m, 1H), 4.54 (q, *J* = 6.7 Hz, 1H), 3.87 (s, 3H), 3.75 – 3.62 (m, 4H), 3.52 (m, 1H), 3.30 (dd, *J* = 6.7, 0.8 Hz, 2H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 167.5, 152.2, 139.9, 133.3, 128.5, 127.7, 127.57, 127.52, 95.4, 59.0, 52.7, 51.5, 41.7, 24.3, 17.7. HRMS-MALDI (m/z): calcd for $C_{18}H_{21}NO_4$, $[M+H]^+$ 316.1543; found 316.1535.

Ethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-3-carboxylate (3u):



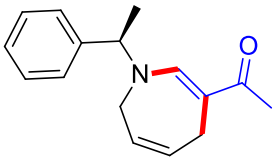
Thick yellow liquid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.48 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.36 – 7.29 (m, 6H), 5.98 (t, *J* = 7.6 Hz, 1H), 4.37 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.93 (d, *J* = 7.6 Hz, 2H), 3.79 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 149.1, 147.5, 141.4, 137.4, 128.8, 128.4, 127.8, 127.3, 126.0, 119.1, 94.5, 62.3, 59.5, 45.6, 25.8, 14.7. HRMS-MALDI (m/z): calcd for $C_{22}H_{23}NO_2$, $[M+H]^+$ 334.1802; found 334.1809.

(R)-ethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-3-carboxylate (3v):



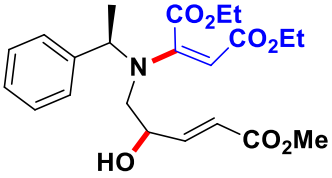
Thick yellow liquid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.38 – 7.29 (m, 5H), 6.11 (dt, *J* = 9.9, 6.8 Hz, 1H), 5.64 (ddd, *J* = 9.8, 8.4, 7.3 Hz, 1H), 4.46 (q, *J* = 6.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.63 (m, 2H), 3.23 (d, *J* = 6.9 Hz, 2H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 147.8, 141.2, 134.8, 128.6, 127.6, 126.8, 125.0, 93.9, 64.8, 59.5, 42.8, 22.8, 18.9, 14.7. HRMS-MALDI (m/z): calcd for $C_{17}H_{21}NO_2$, $[M+H]^+$ 272.1645; found 272.1641.

(R)-1-(1-(1-phenylethyl)-4,7-dihydro-1H-azepin-3-yl)ethanone (3w):



Colorless liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 6H), 6.12 (dt, *J* = 9.7, 6.9 Hz, 1H), 5.66 (dd, *J* = 16.9, 7.3 Hz, 1H), 4.48 (q, *J* = 6.9 Hz, 1H), 3.70 (t, *J* = 7.7 Hz, 2H), 3.29 (d, *J* = 6.9 Hz, 2H), 2.18 (s, 3H), 1.62 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 149.8, 140.5, 135.4, 128.7, 127.8, 126.7, 124.6, 108.3, 65.3, 43.2, 24.2, 21.3, 19.0. HRMS-MALDI (m/z): calcd for $C_{16}H_{19}NO$, $[M+H]^+$ 242.1539; found 242.1536.

Diethyl 2-(((E)-2-hydroxy-5-methoxy-5-oxopent-3-en-1-yl)((R)-1-phenylethyl)amino)maleate (5):



Thick yellow liquid, 10% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 6.80 (dd, *J* = 15.6, 4.7 Hz, 1H), 6.01 (dd, *J* = 15.6, 1.7 Hz, 1H), 4.79 (s, 1H), 4.75 (q, *J* = 5.1 Hz, 3H), 4.40 (m, 3H), 4.10 (td, *J* = 7.1, 2.3 Hz, 2H), 3.71 (s, 3H), 3.00 (m, 2H), 1.58 (d, *J* = 7.0 Hz, 9H), 1.36 (t, *J* = 7.2 Hz, 14H), 1.23 (t, *J* = 7.1 Hz, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 166.4, 166.1, 154.0, 146.8, 139.0, 128.7, 128.1, 127.2, 120.8, 88.2, 67.1, 62.3, 59.4, 58.5, 51.43, 50.5, 16.6, 14.2, 13.7. HRMS-MALDI (m/z): calcd for $C_{22}H_{29}NO_7$, $[M+H]^+$ 420.2017; found 420.2013.

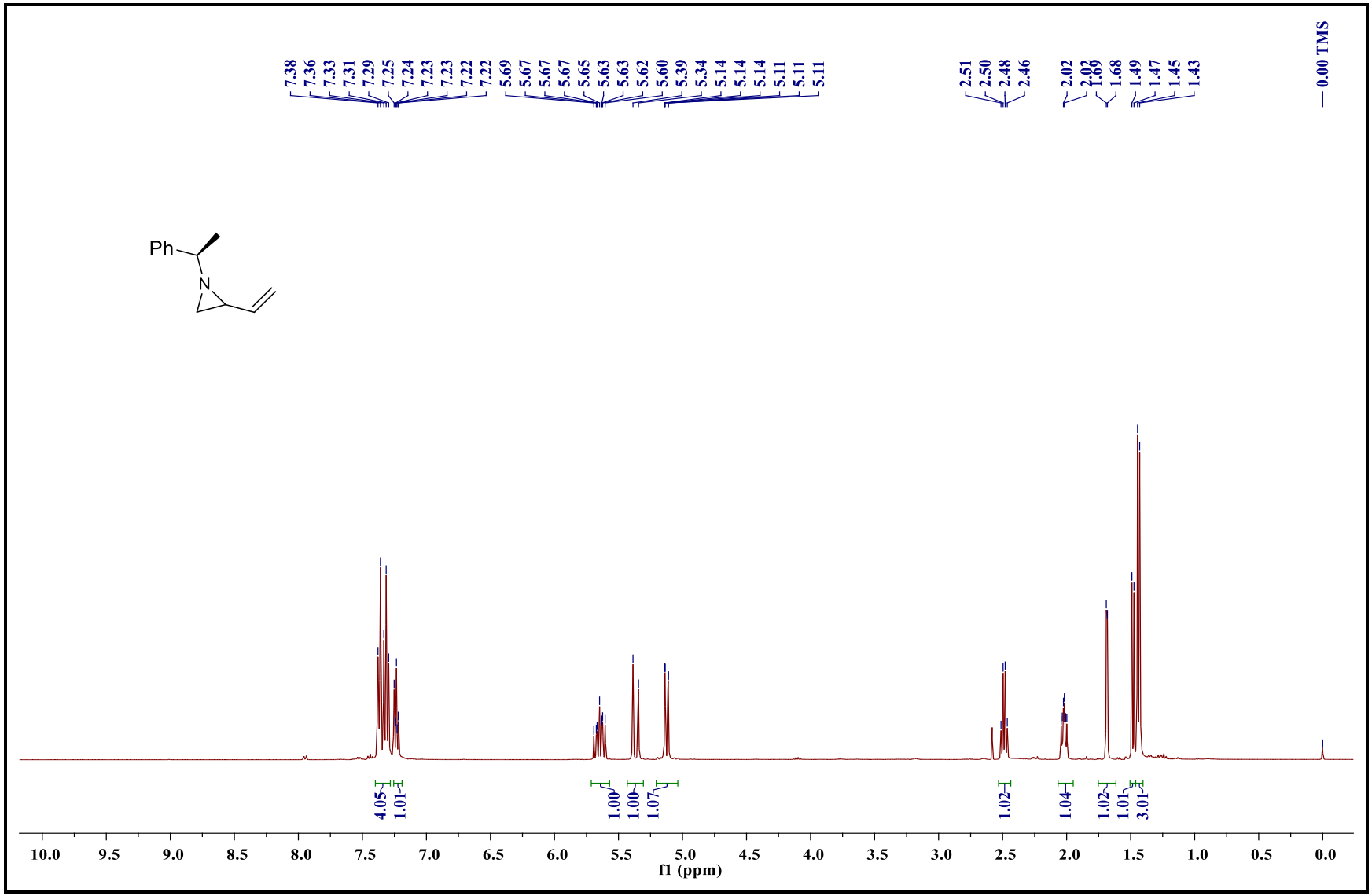
References:

(1) (a) Lee, W. K.; Ha, H.-J. *Aldrichimica Acta* **2003**, *36*, 57; (b) Kim, J. H.; Lee, S. B.; Lee, W. K.; Yoon, D. H.; Ha H. J. *Tetrahedron* **2011**, 67, 3553.

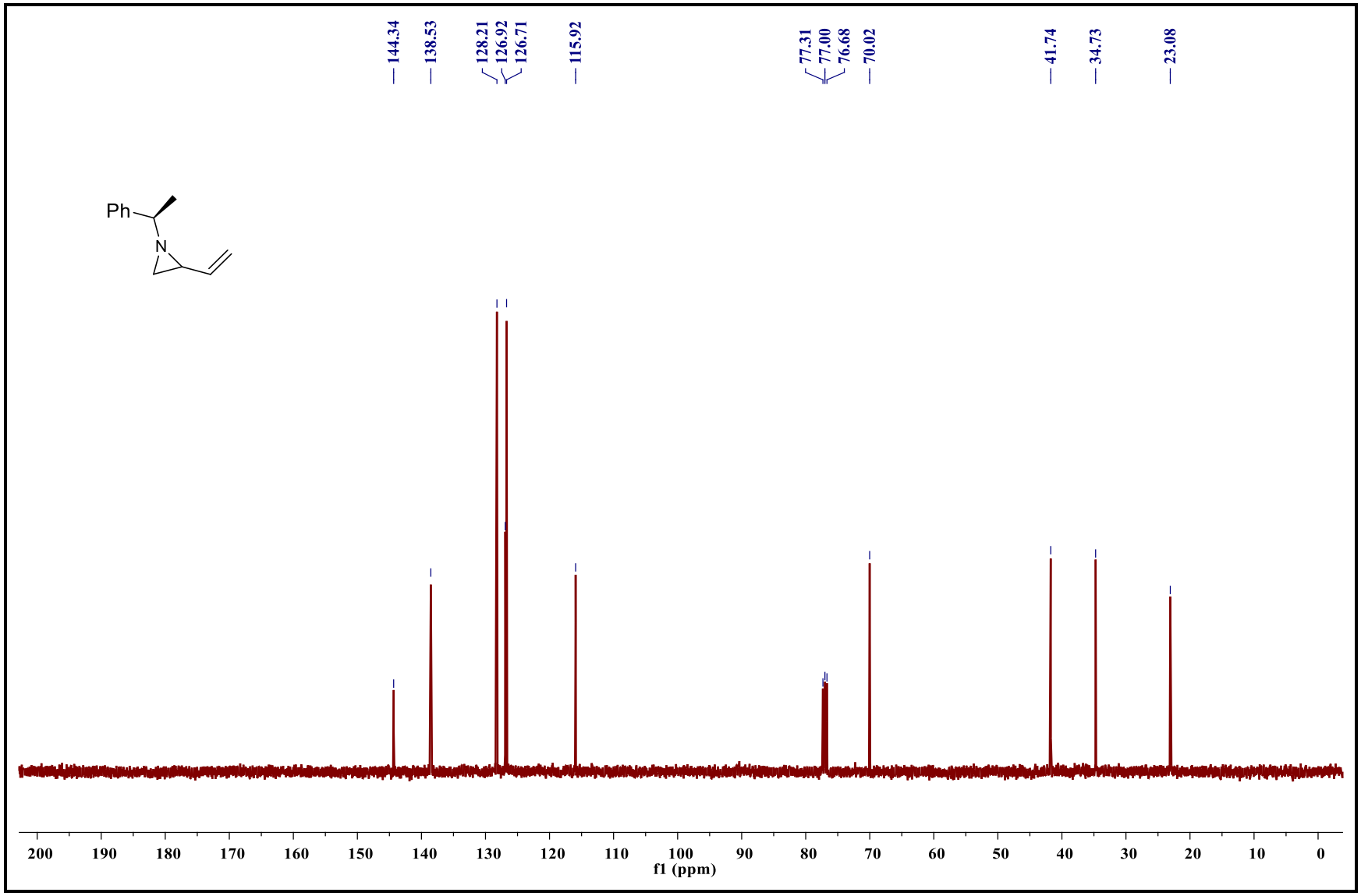
(2) Yadav, N. N.; Choi, J.; Ha, H. J. *Org. Biomol. Chem.*, **2016**, *14*, 6426.

1H and 13C NMR Spectra of Vinyl Aziridines

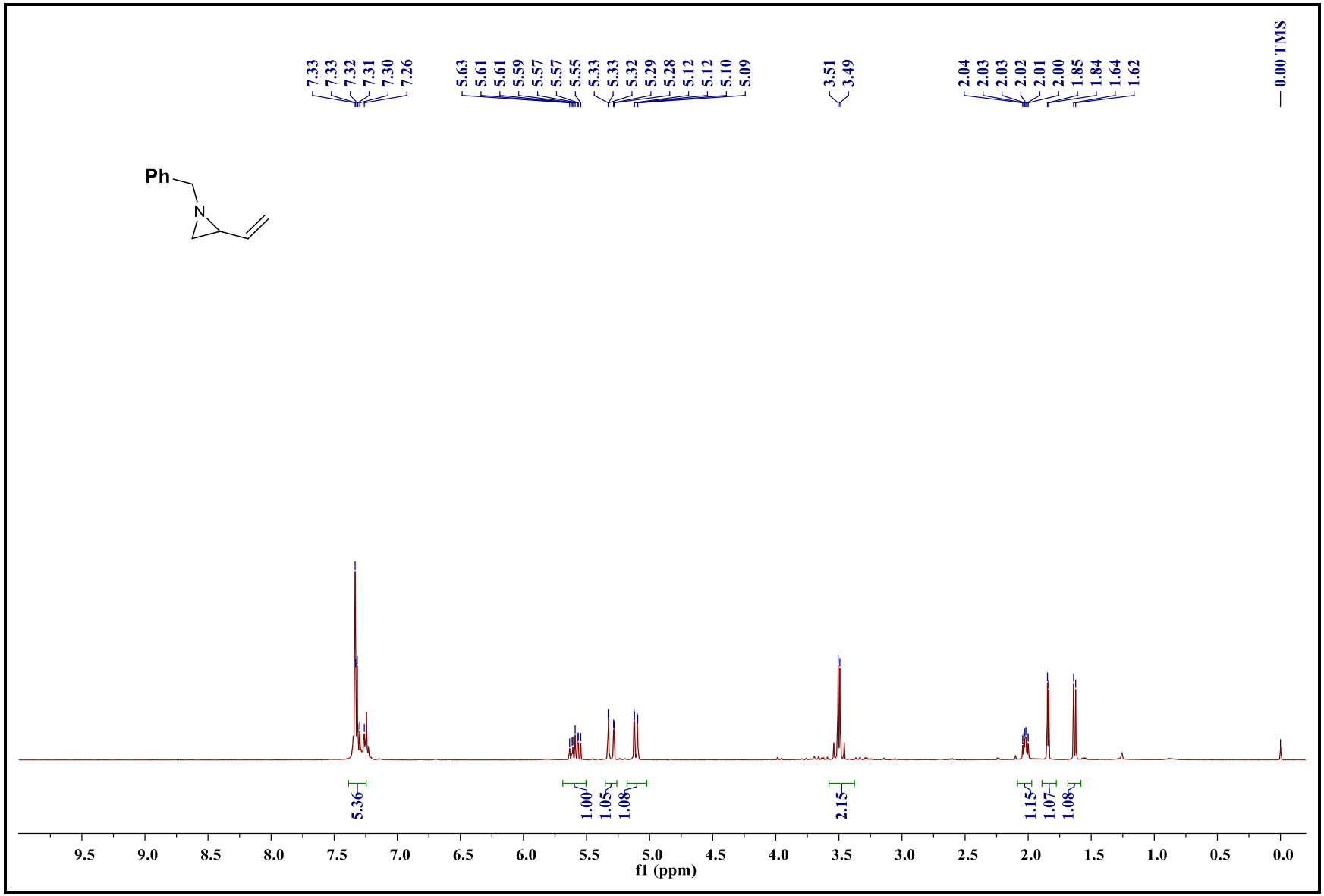
1H NMR Spectrum of 1-((R)-1-phenylethyl)-2-vinylaziridine (1a):



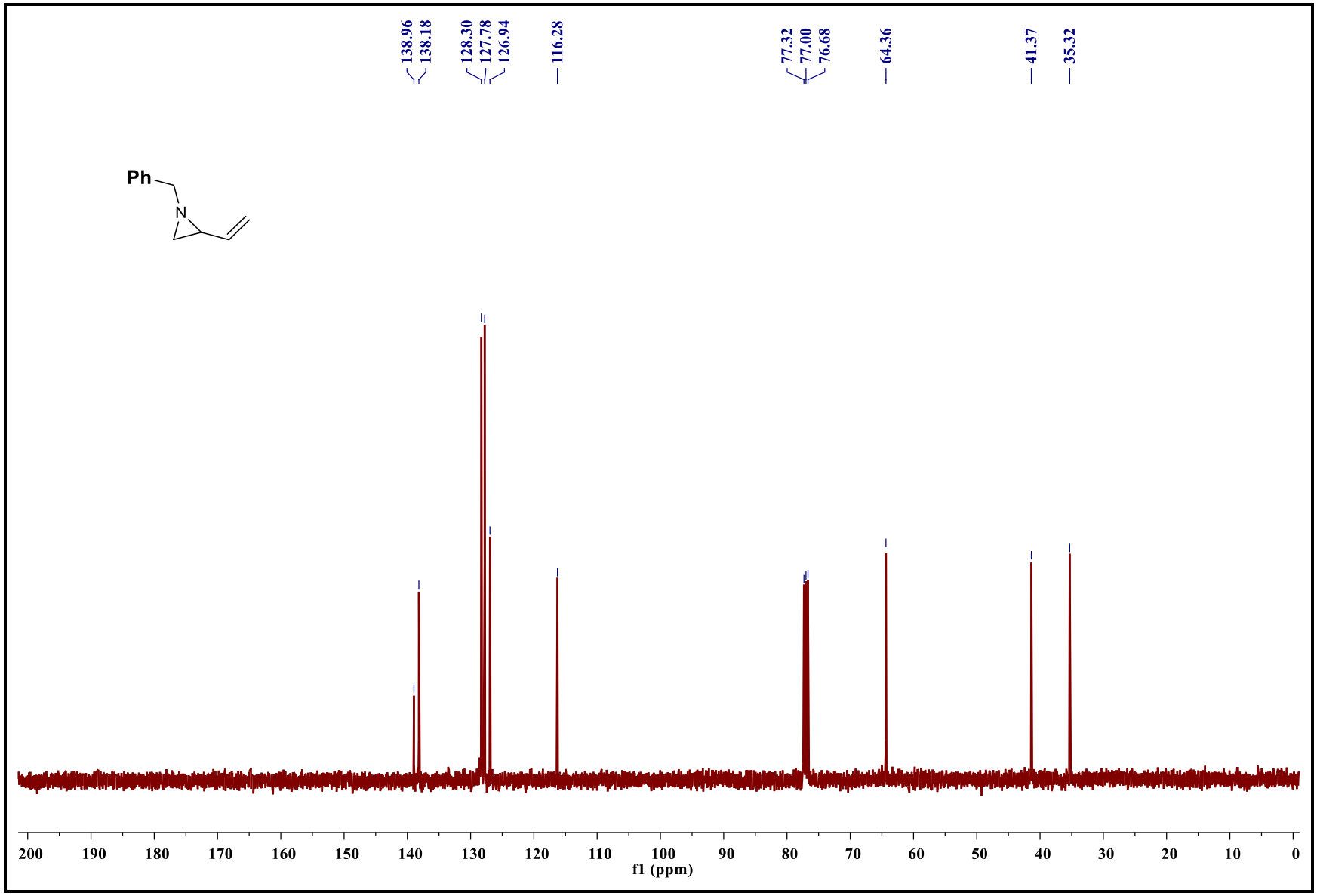
13C NMR spectrum of 1-((R)-1-phenylethyl)-2-vinylaziridine (1a):



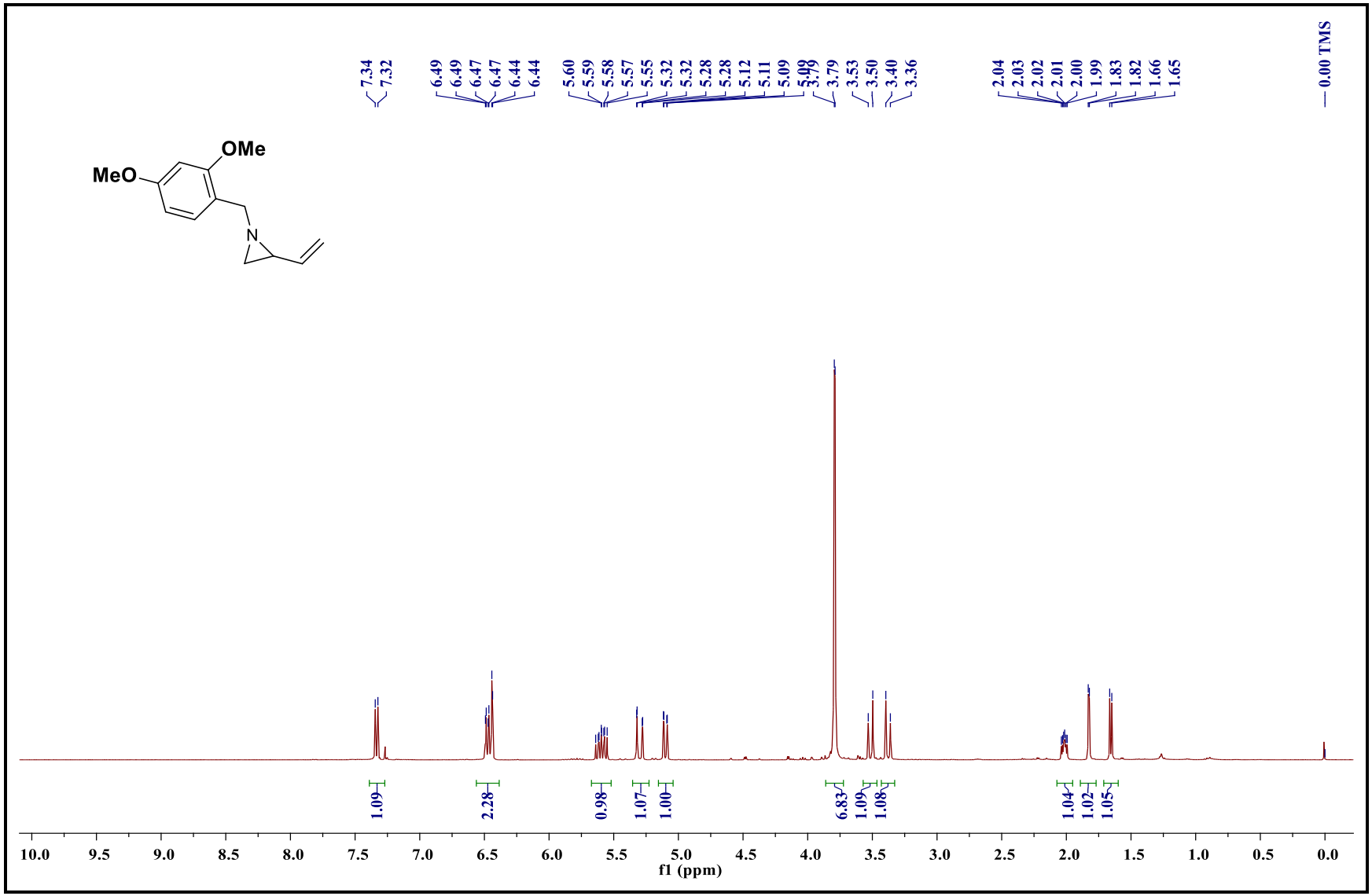
1H NMR spectrum of 1-benzyl-2-vinylaziridine (1b):



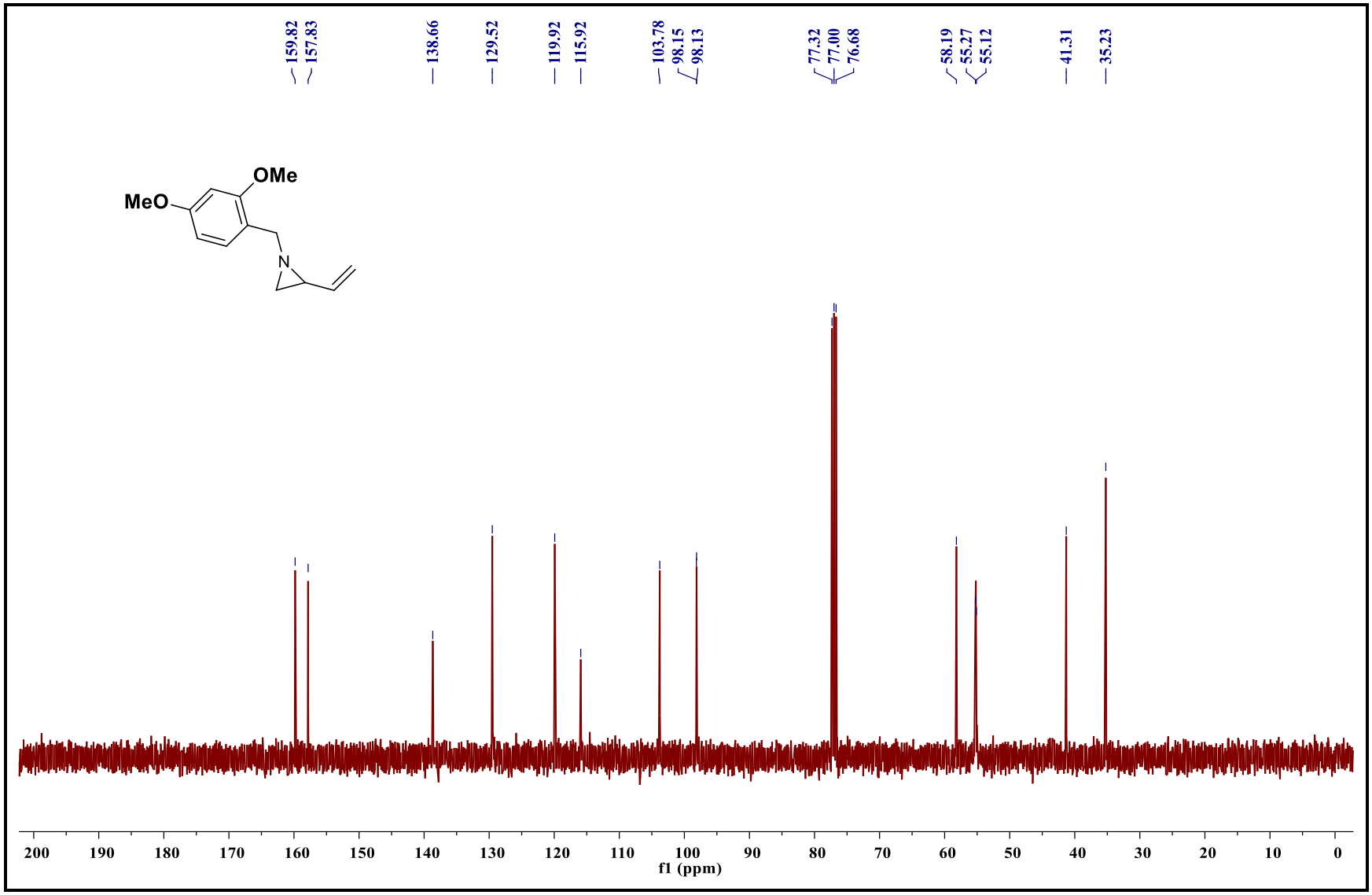
13C NMR spectrum of 1-benzyl-2-vinylaziridine (1b):



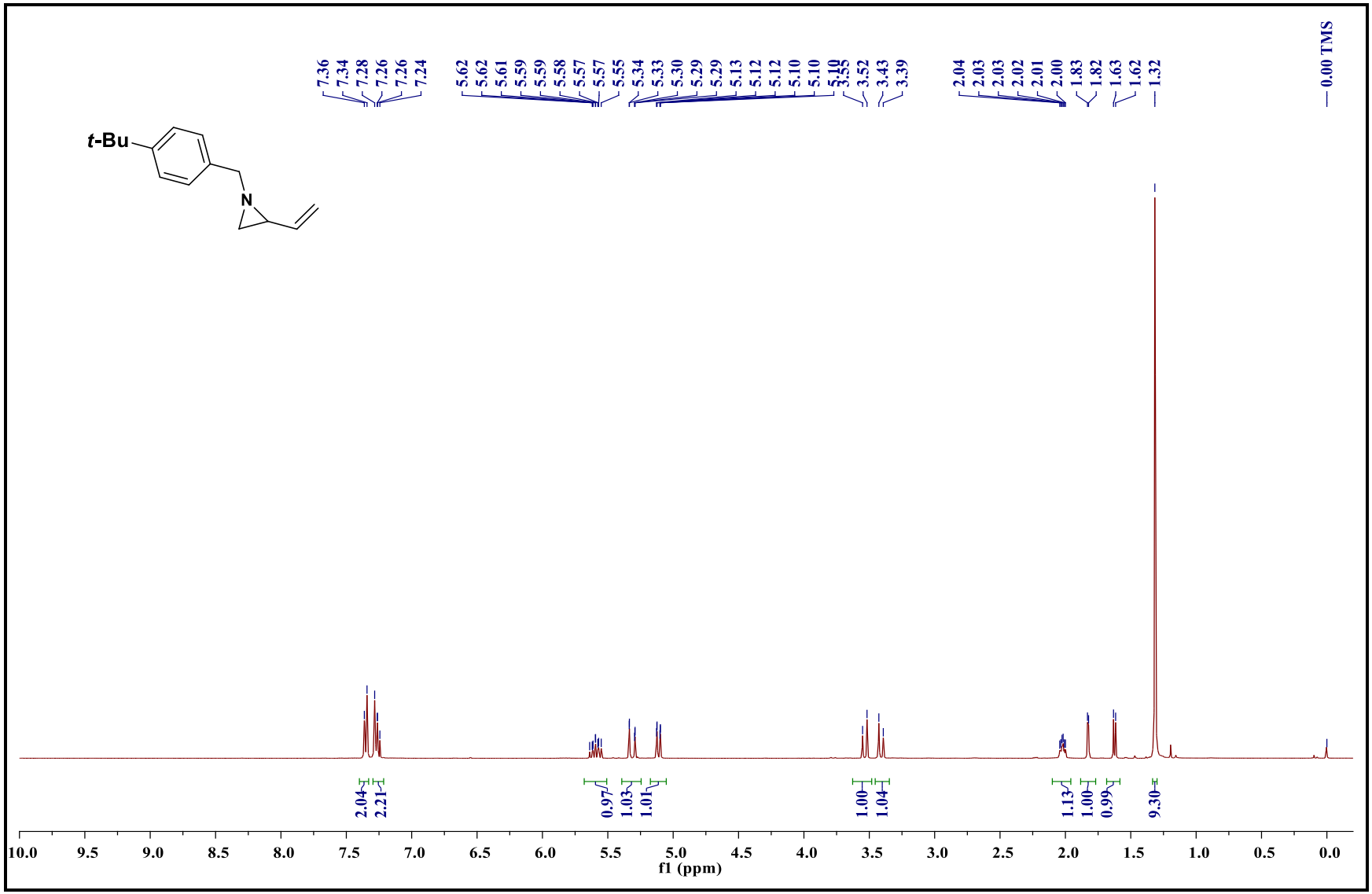
1H NMR spectrum of 1-(2,4-dimethoxybenzyl)-2-vinylaziridine (1c):



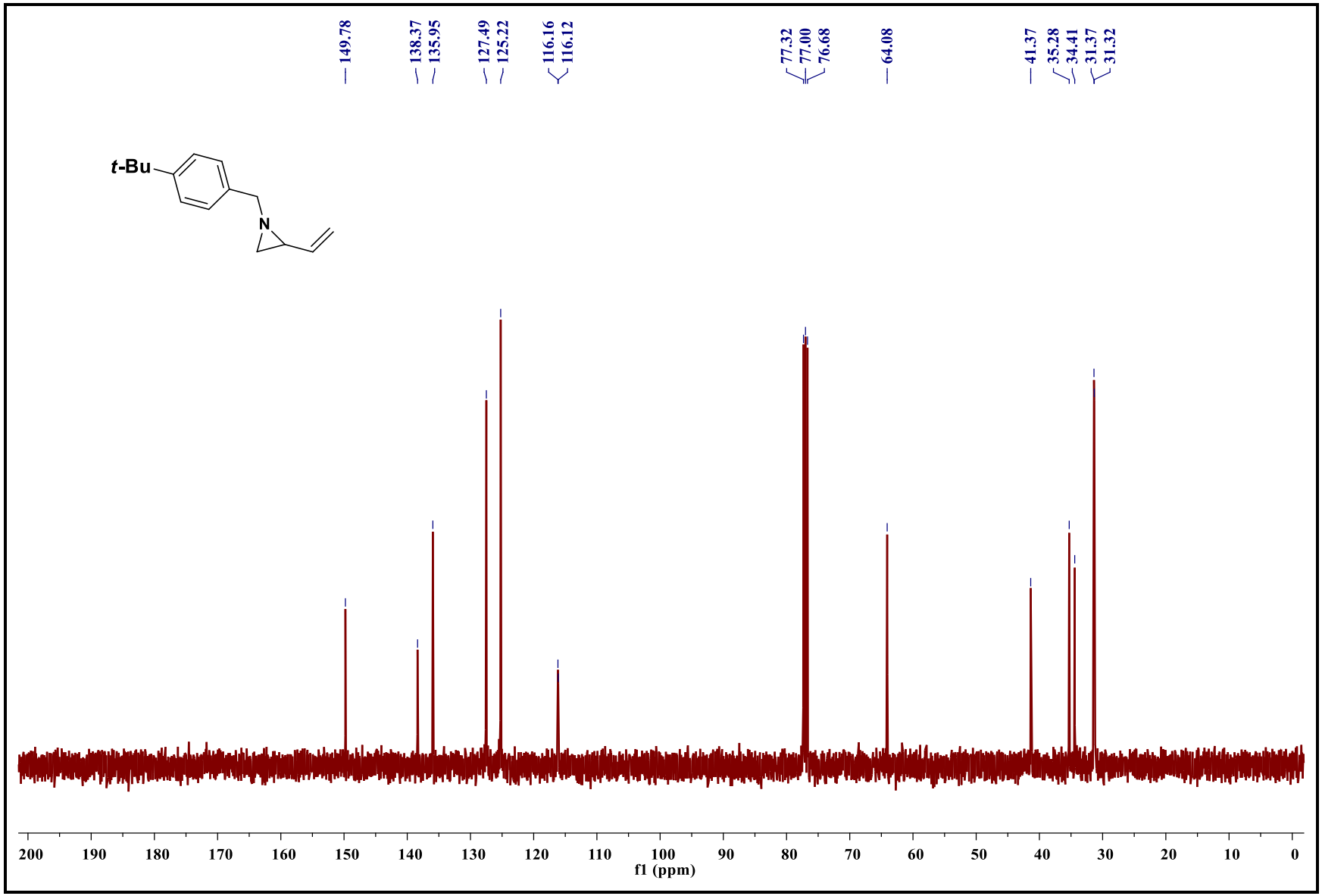
13C NMR spectrum of 1-(2,4-dimethoxybenzyl)-2-vinylaziridine (1c):



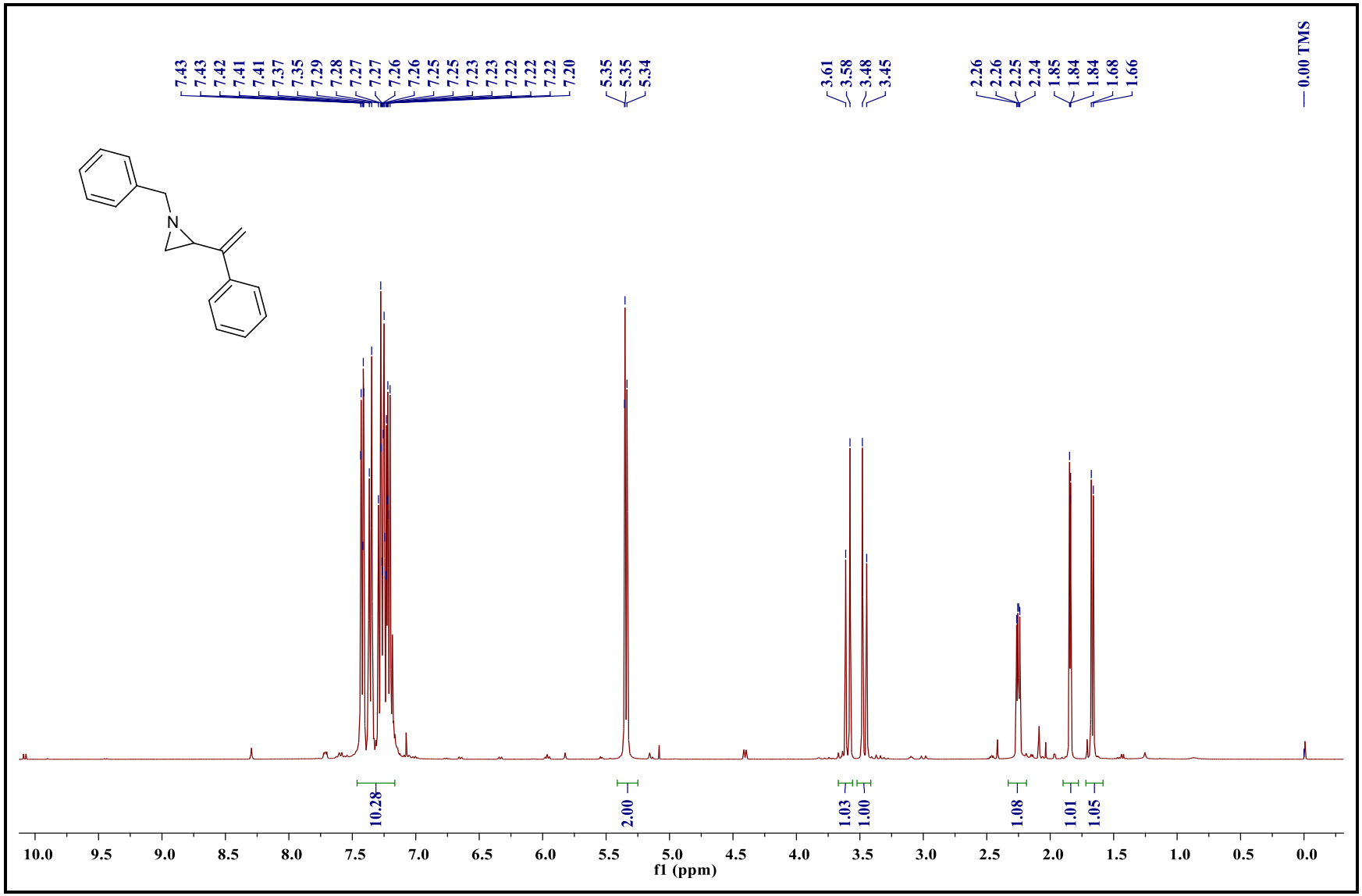
1H NMR spectrum 1-(4-(tert-butyl)benzyl)-2-vinylaziridine (1d):



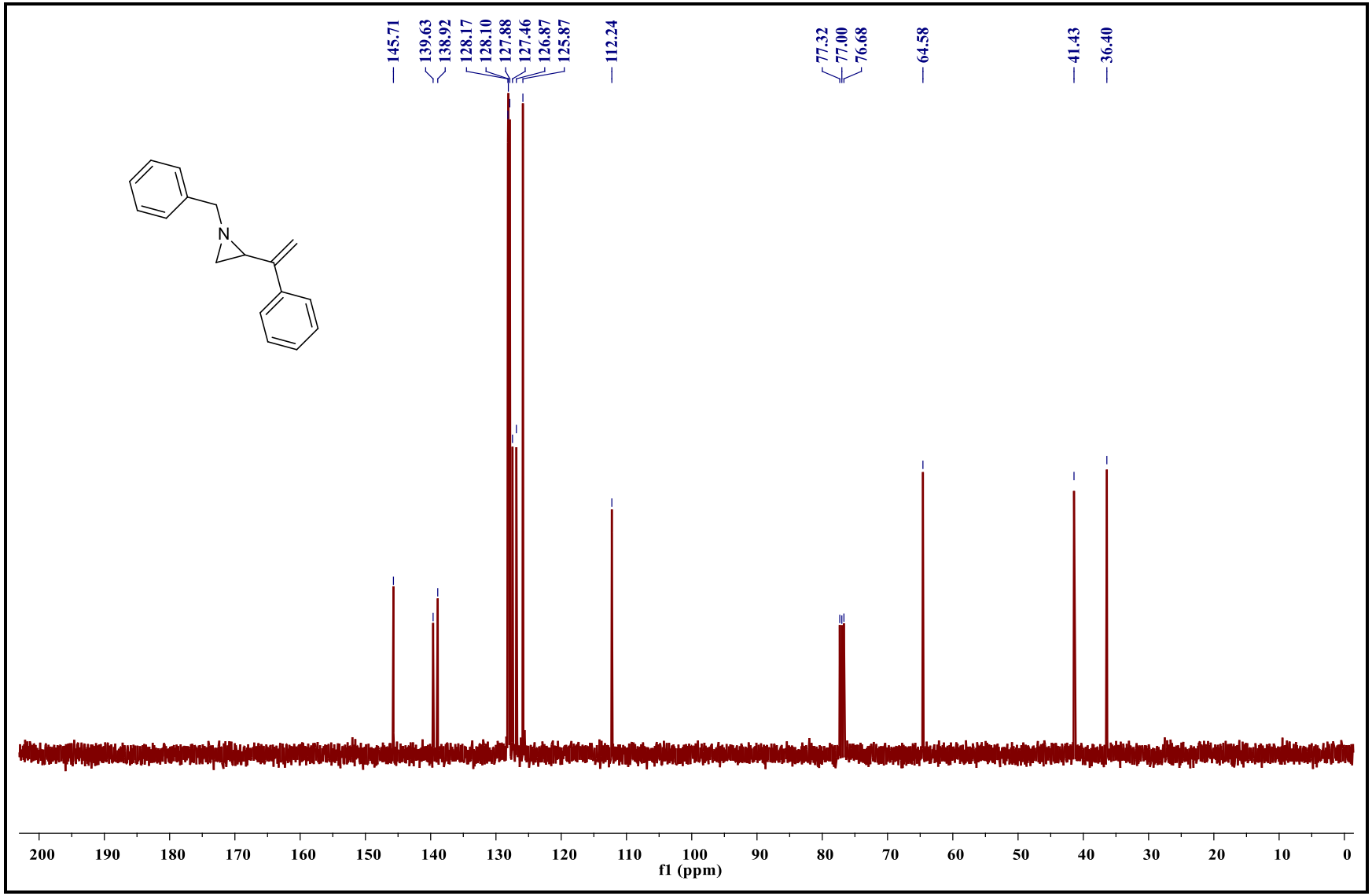
13C NMR spectrum of 1-(4-(tert-butyl)benzyl)-2-vinylaziridine (1d):



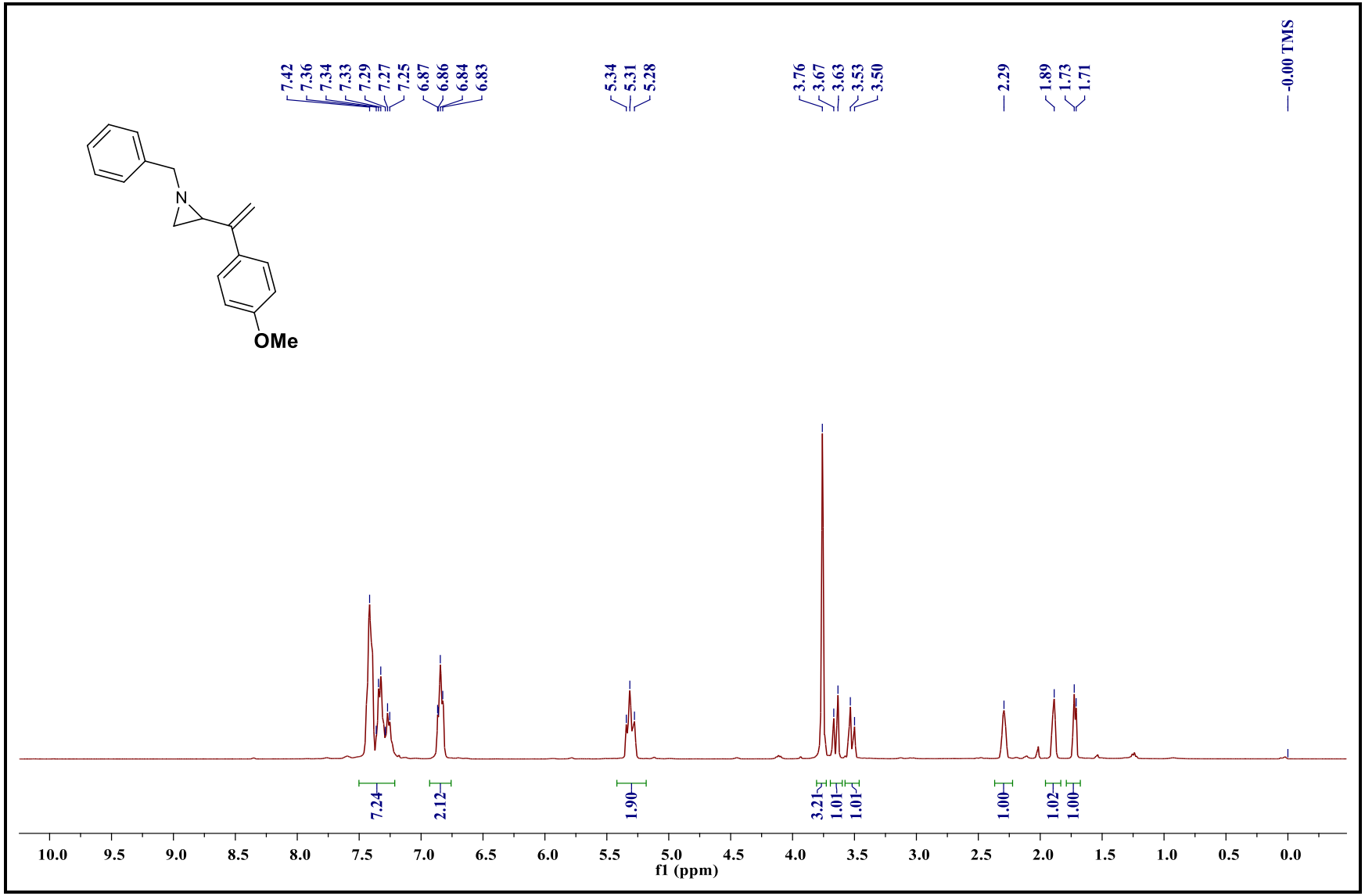
1H NMR spectrum of 1-benzyl-2-(1-phenylvinyl)aziridine (1e):



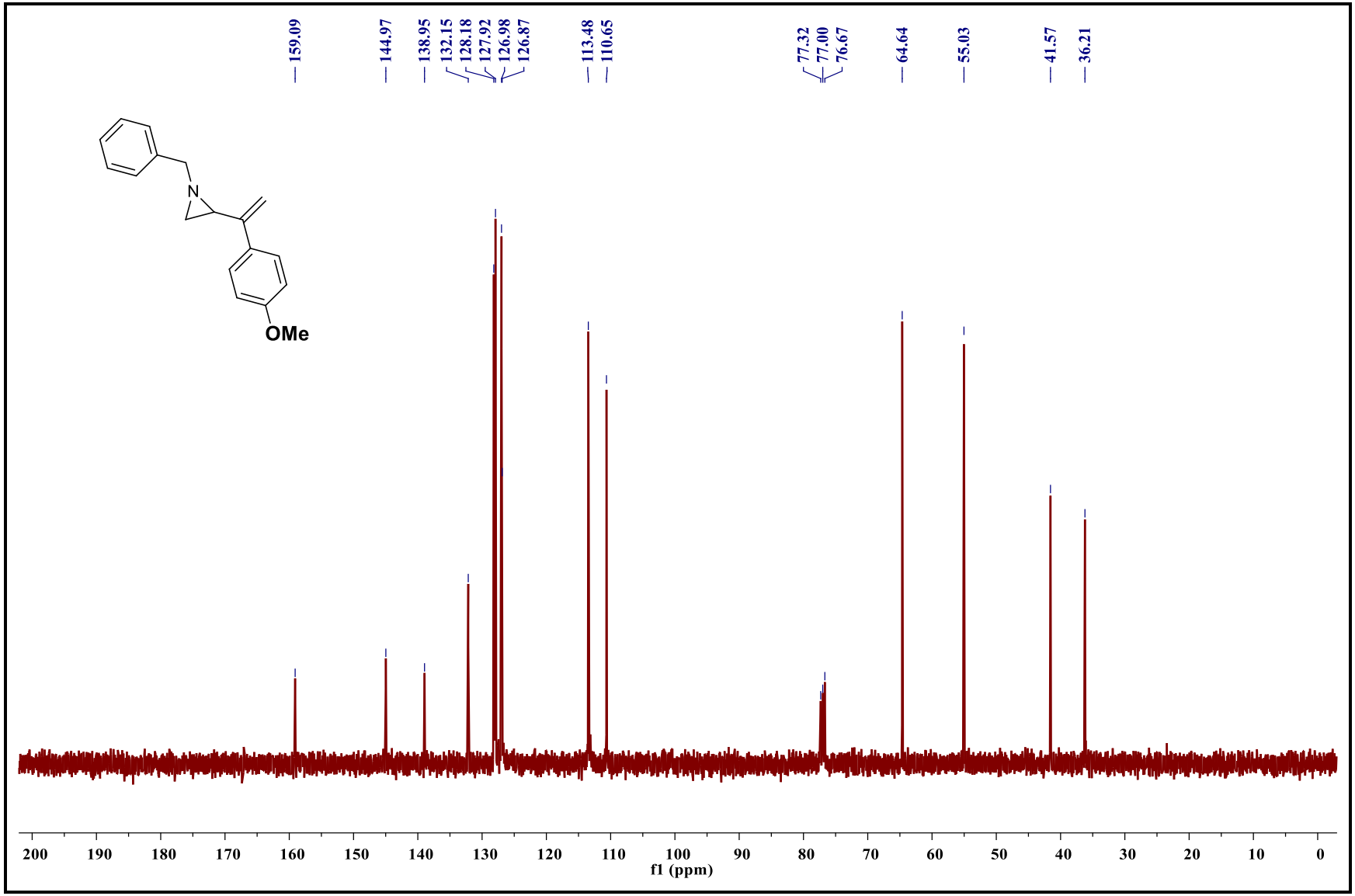
13C NMR spectrum of 1-benzyl-2-(1-phenylvinyl)aziridine (1e):



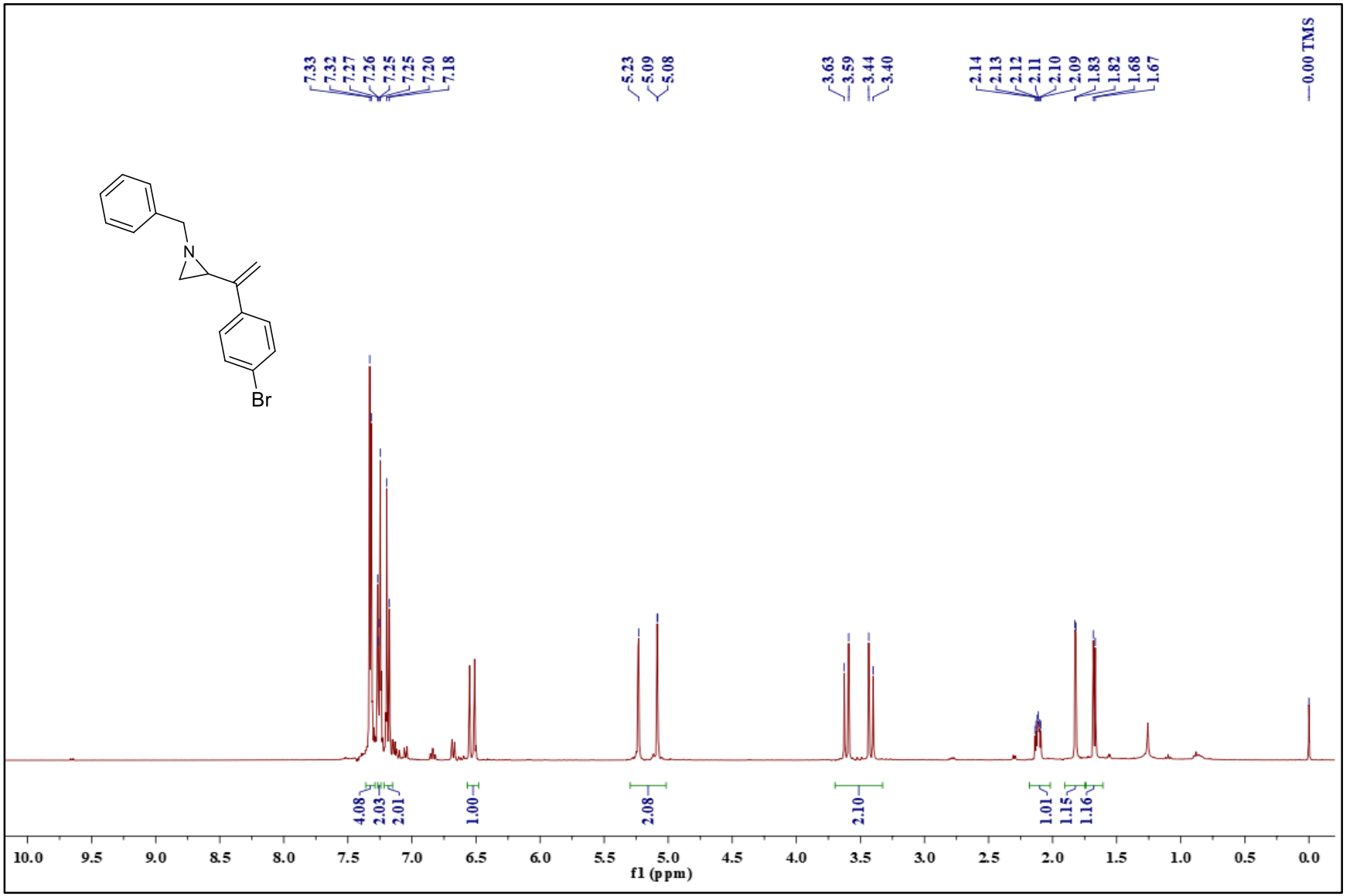
1H NMR spectrum of 1-benzyl-2-(1-(4-methoxyphenyl)vinyl)aziridine (1f):



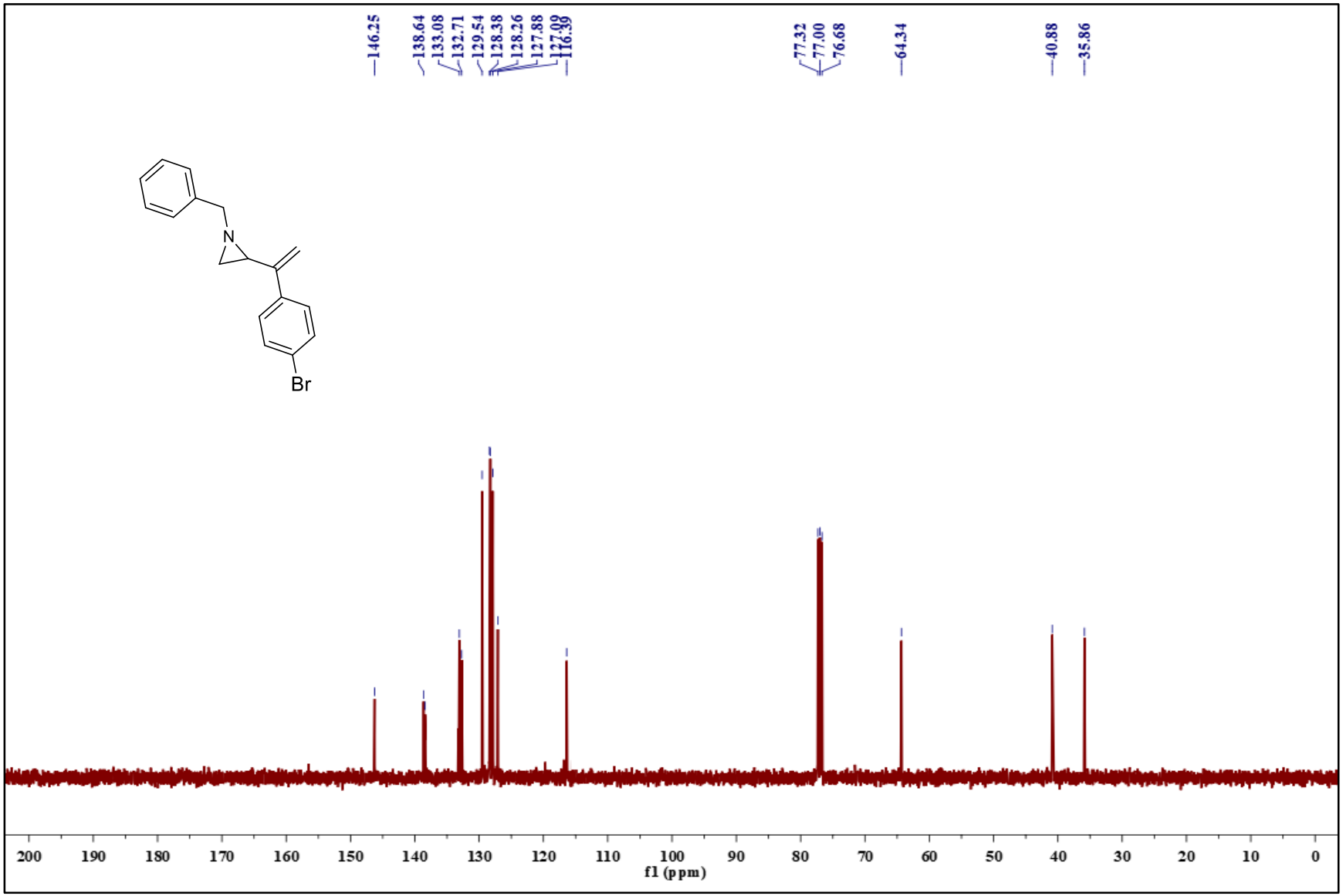
13C NMR spectrum of 1-benzyl-2-(1-(4-methoxyphenyl)vinyl)aziridine (1f):



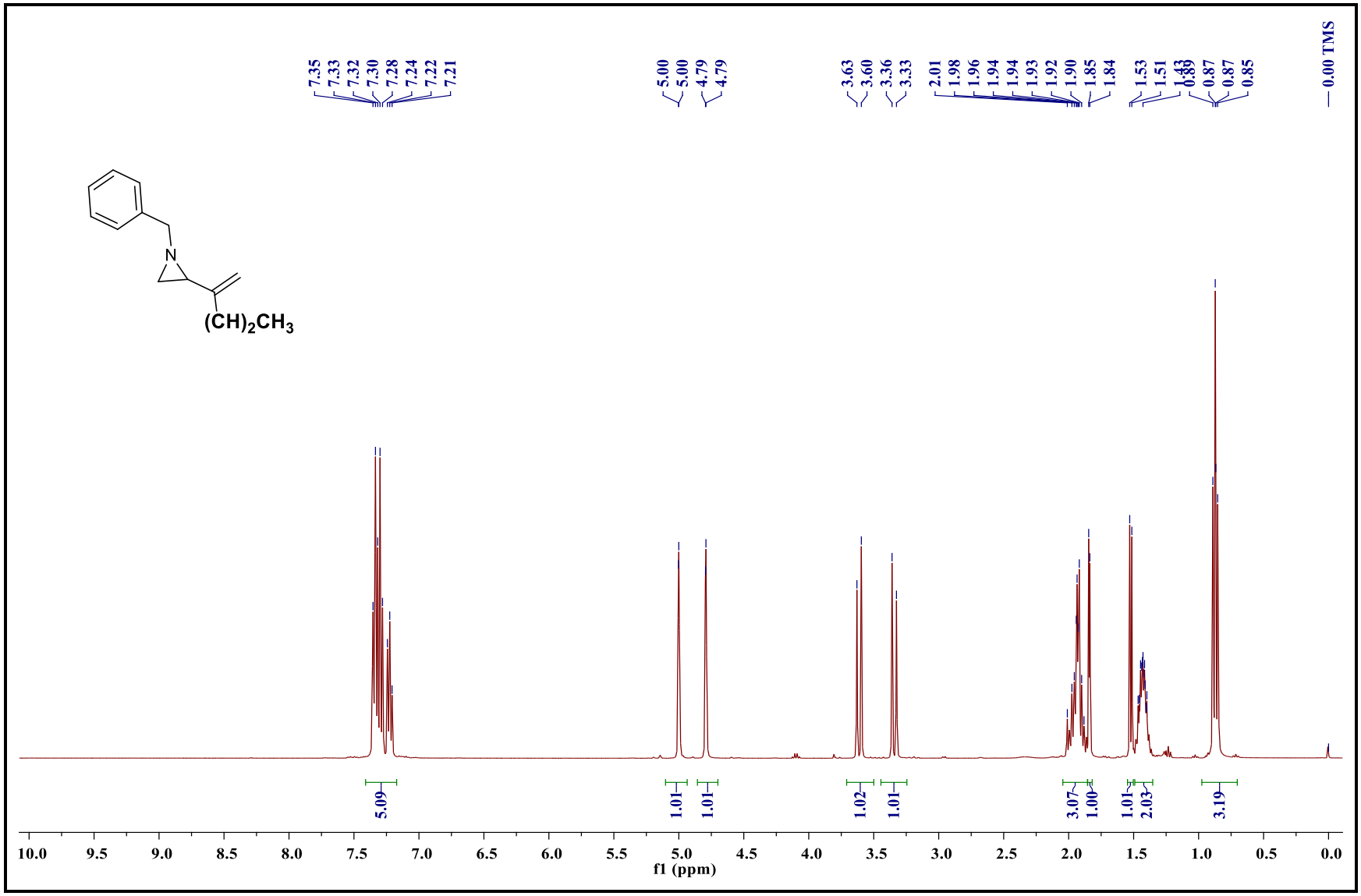
1H NMR spectrum of 1-benzyl-2-(1-(4-bromophenyl)vinyl)aziridine (1g):



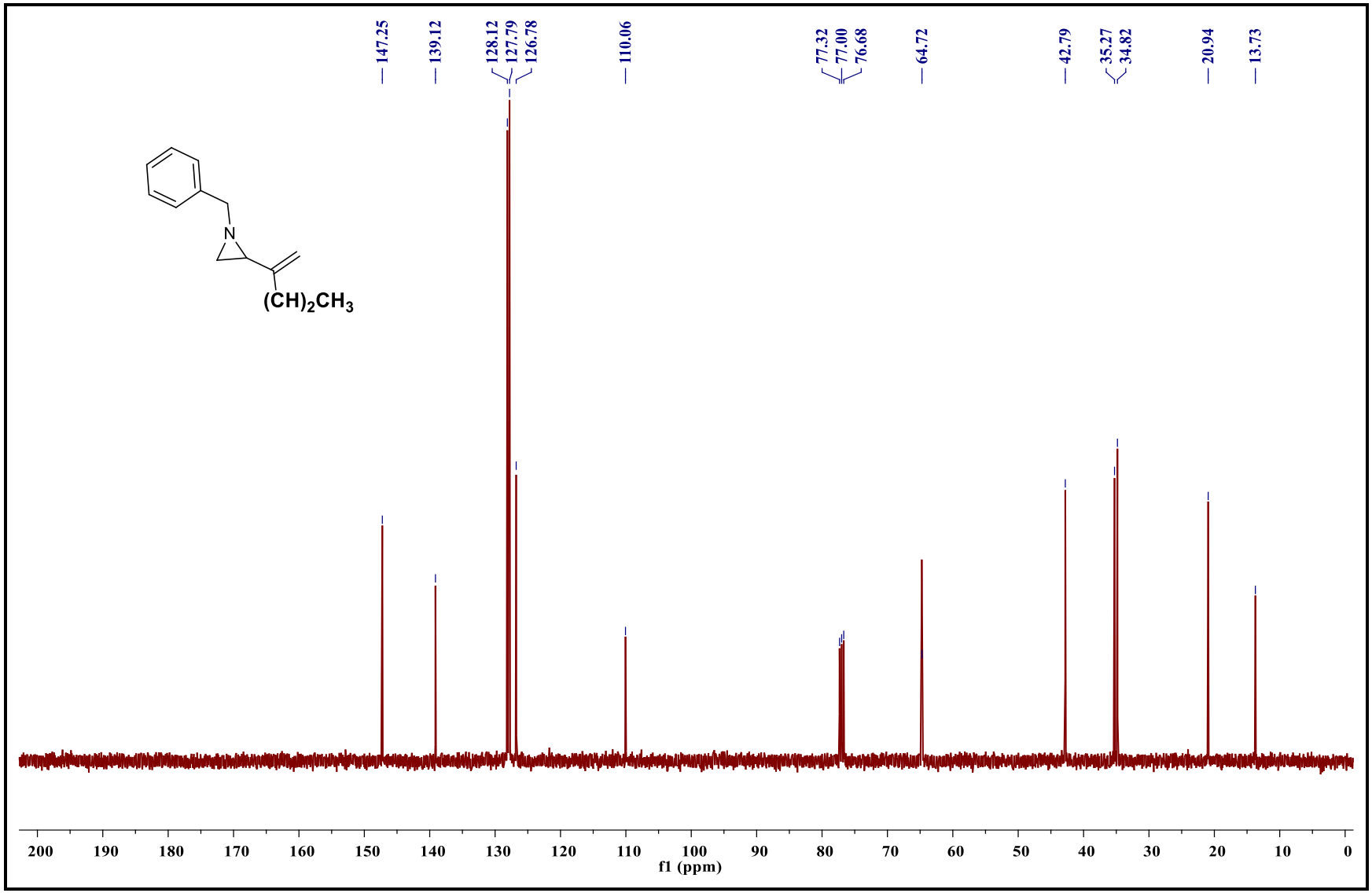
1H NMR spectrum of 1-benzyl-2-(1-(4-bromophenyl)vinyl)aziridine (1g):



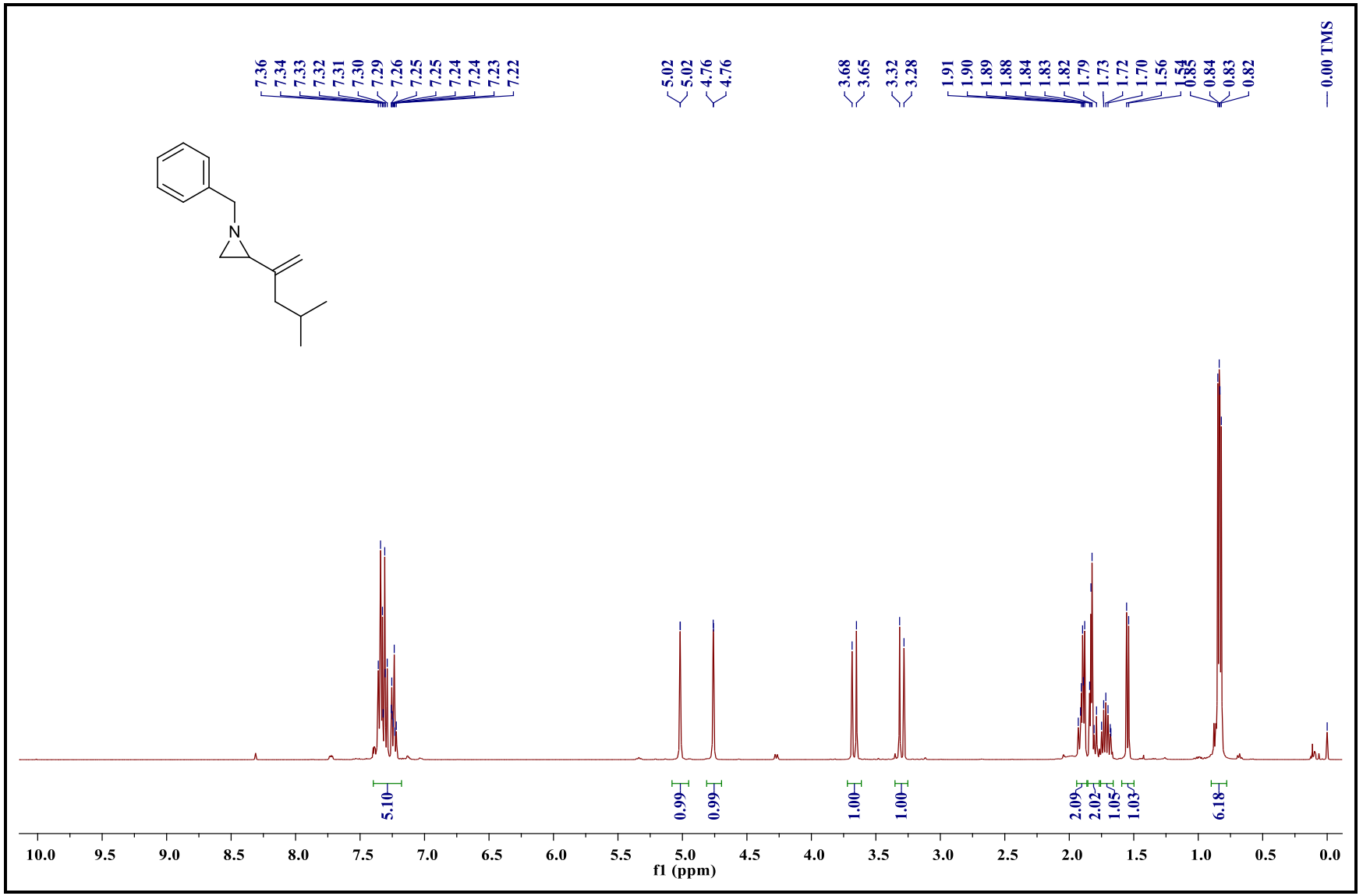
1H NMR spectrum of 1-benzyl-2-(penta-1,3-dien-2-yl)aziridine (1h):



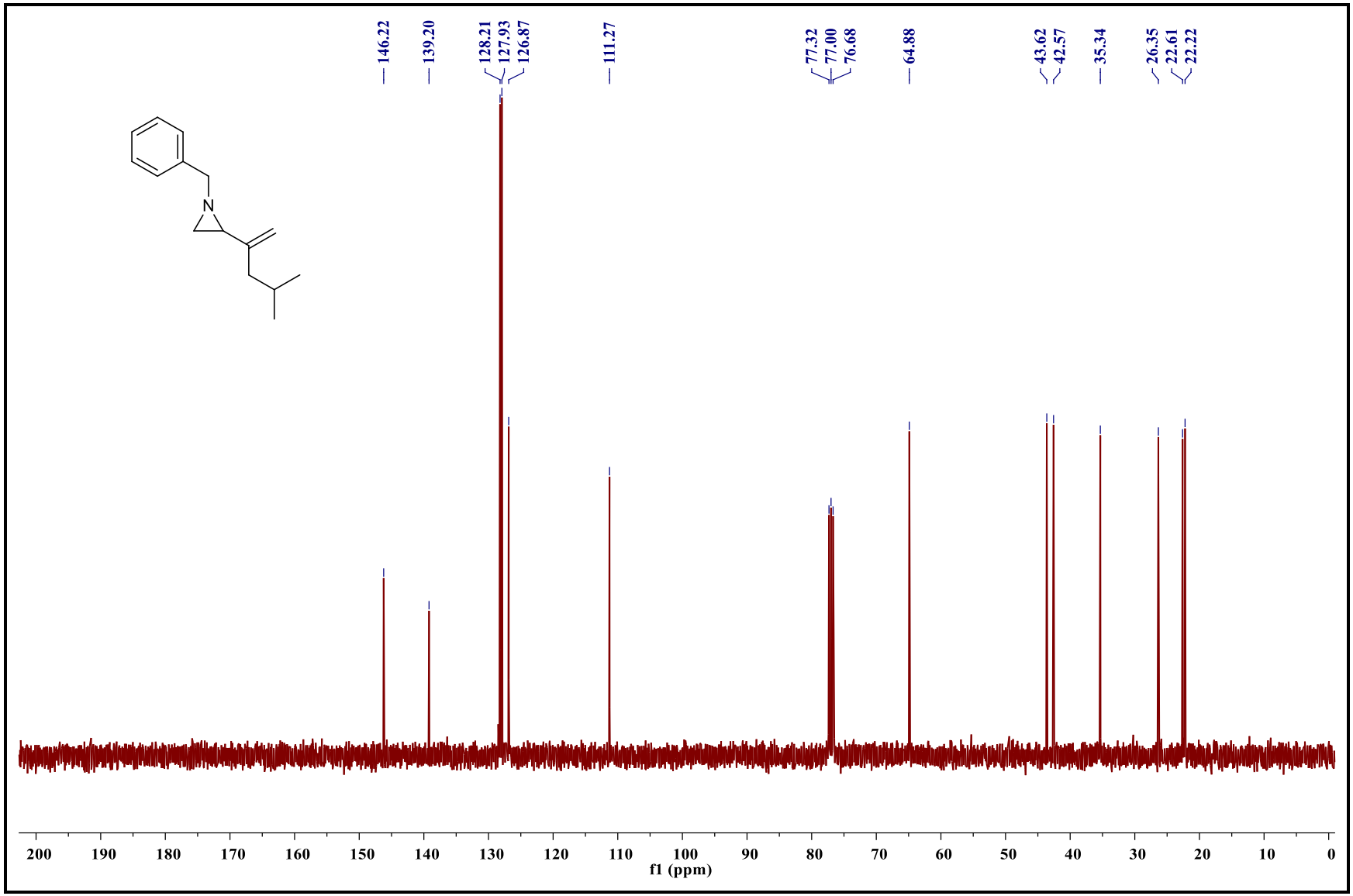
1H NMR spectrum of 1-benzyl-2-(penta-1,3-dien-2-yl)aziridine (1h):



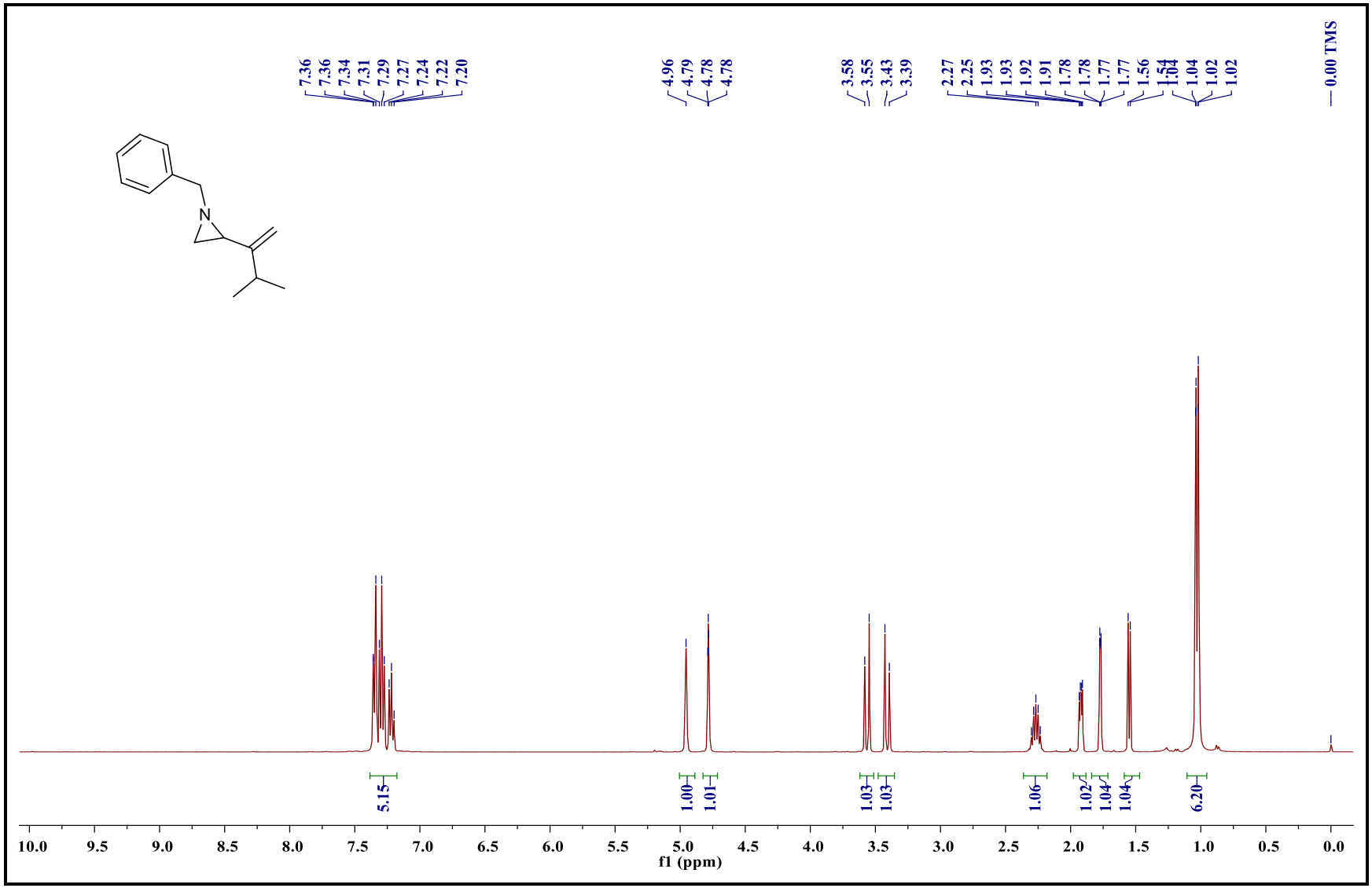
1H NMR spectrum of 1-benzyl-2-(4-methylpent-1-en-2-yl)aziridine (1i):



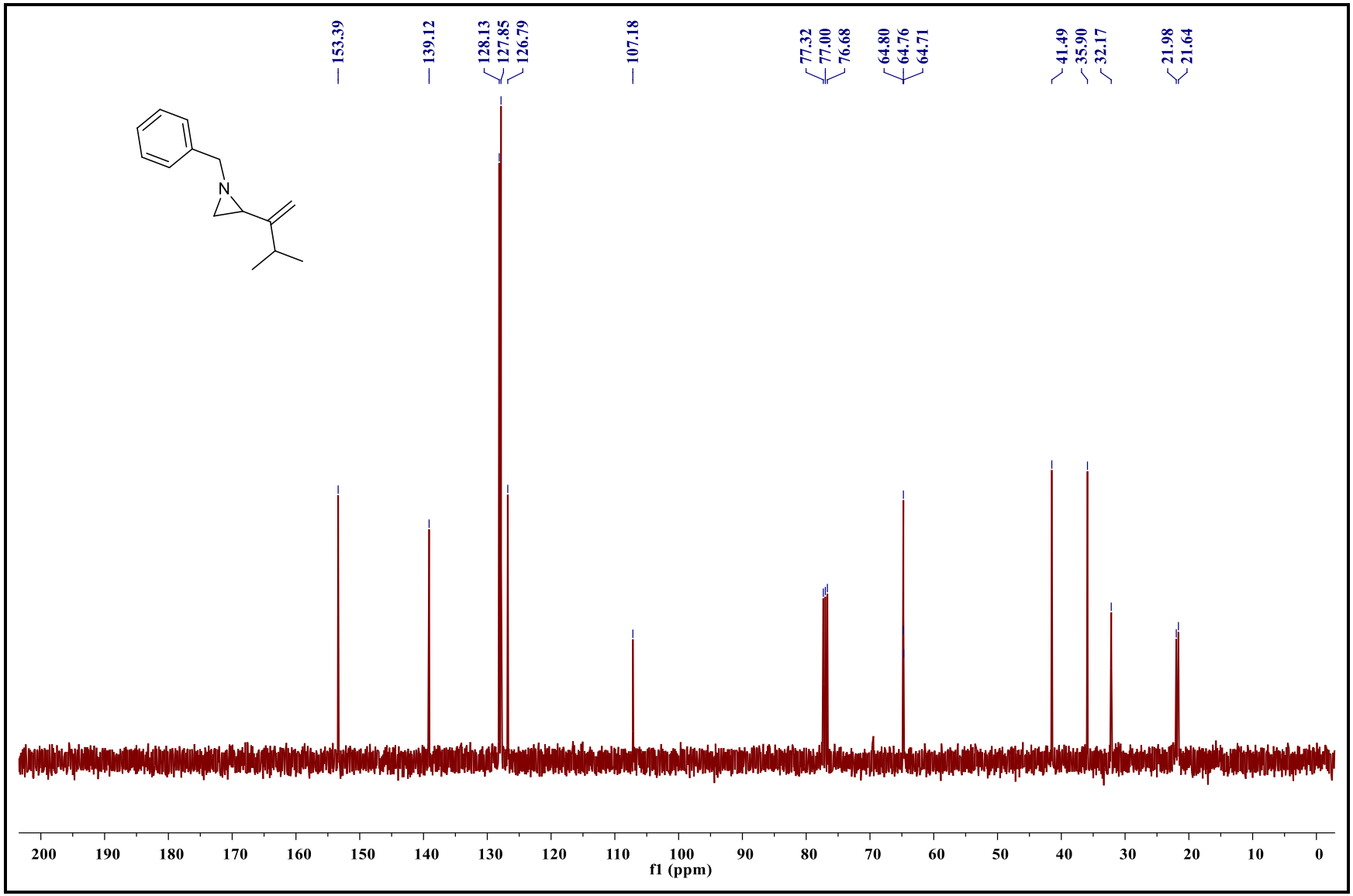
1H NMR spectrum of 1-benzyl-2-(4-methylpent-1-en-2-yl)aziridine (1i):



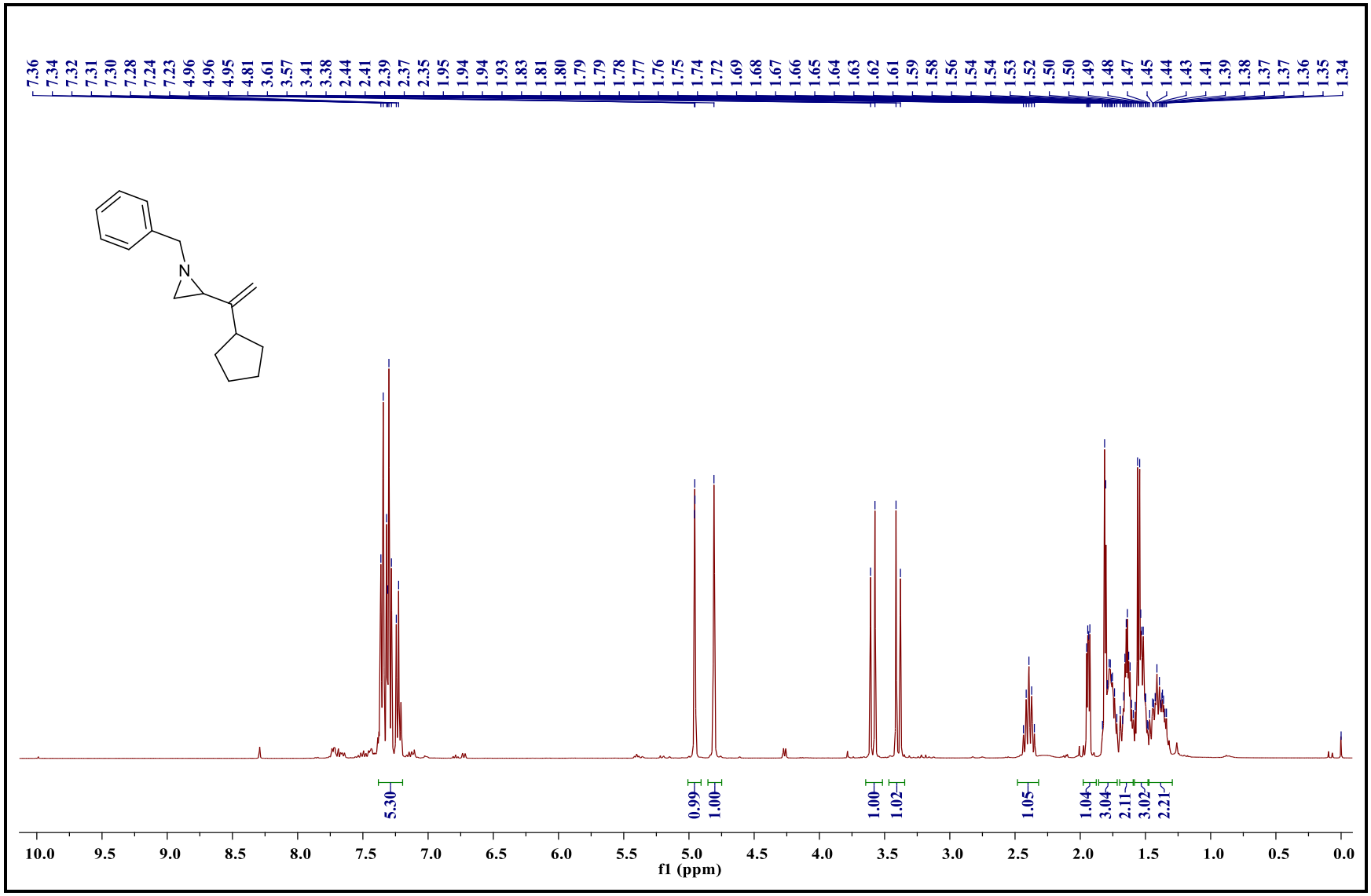
1H NMR spectrum of 1-benzyl-2-(3-methylbut-1-en-2-yl)aziridine (1j):



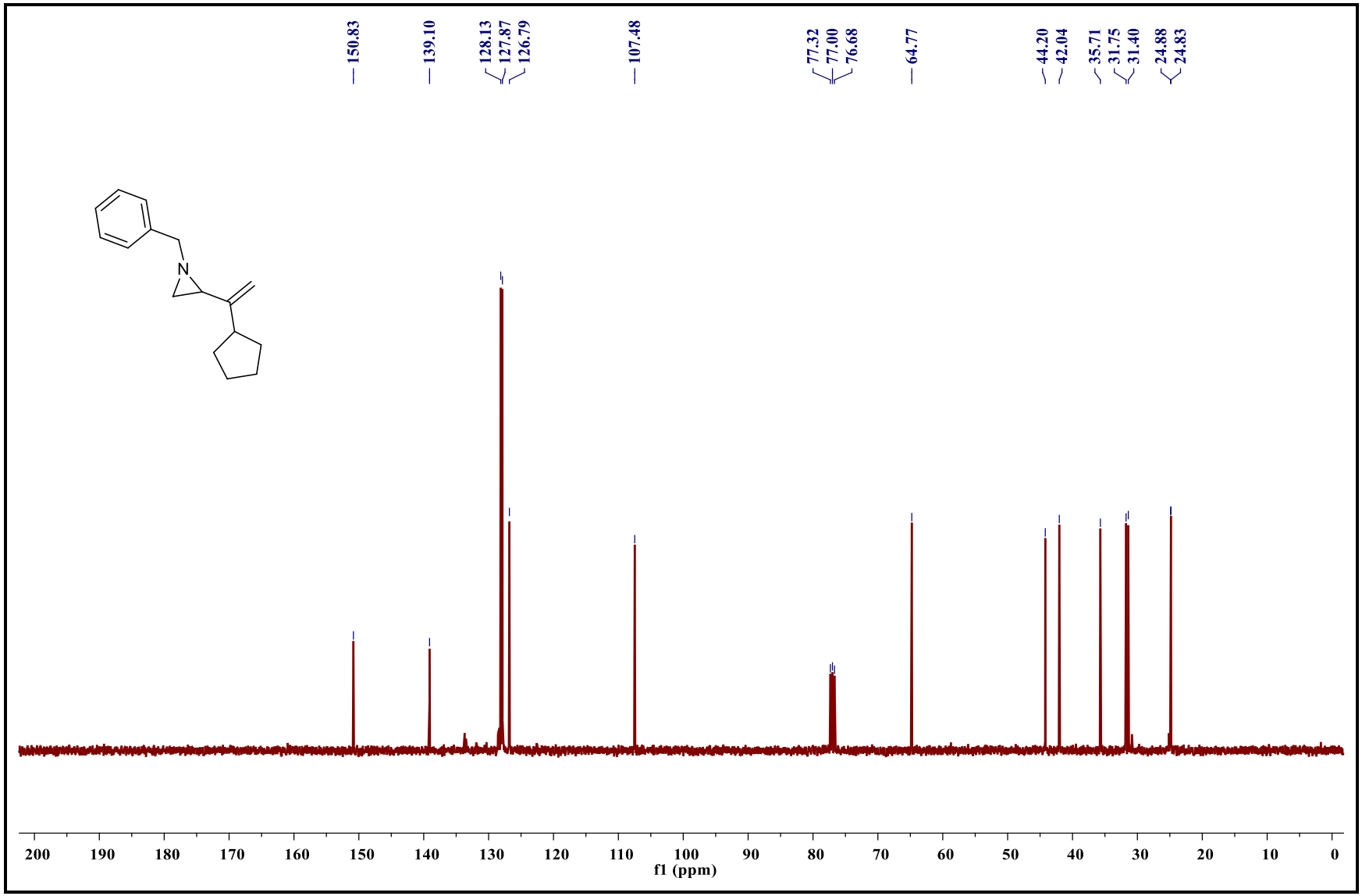
13C NMR spectrum of 1-benzyl-2-(3-methylbut-1-en-2-yl)aziridine (1j):



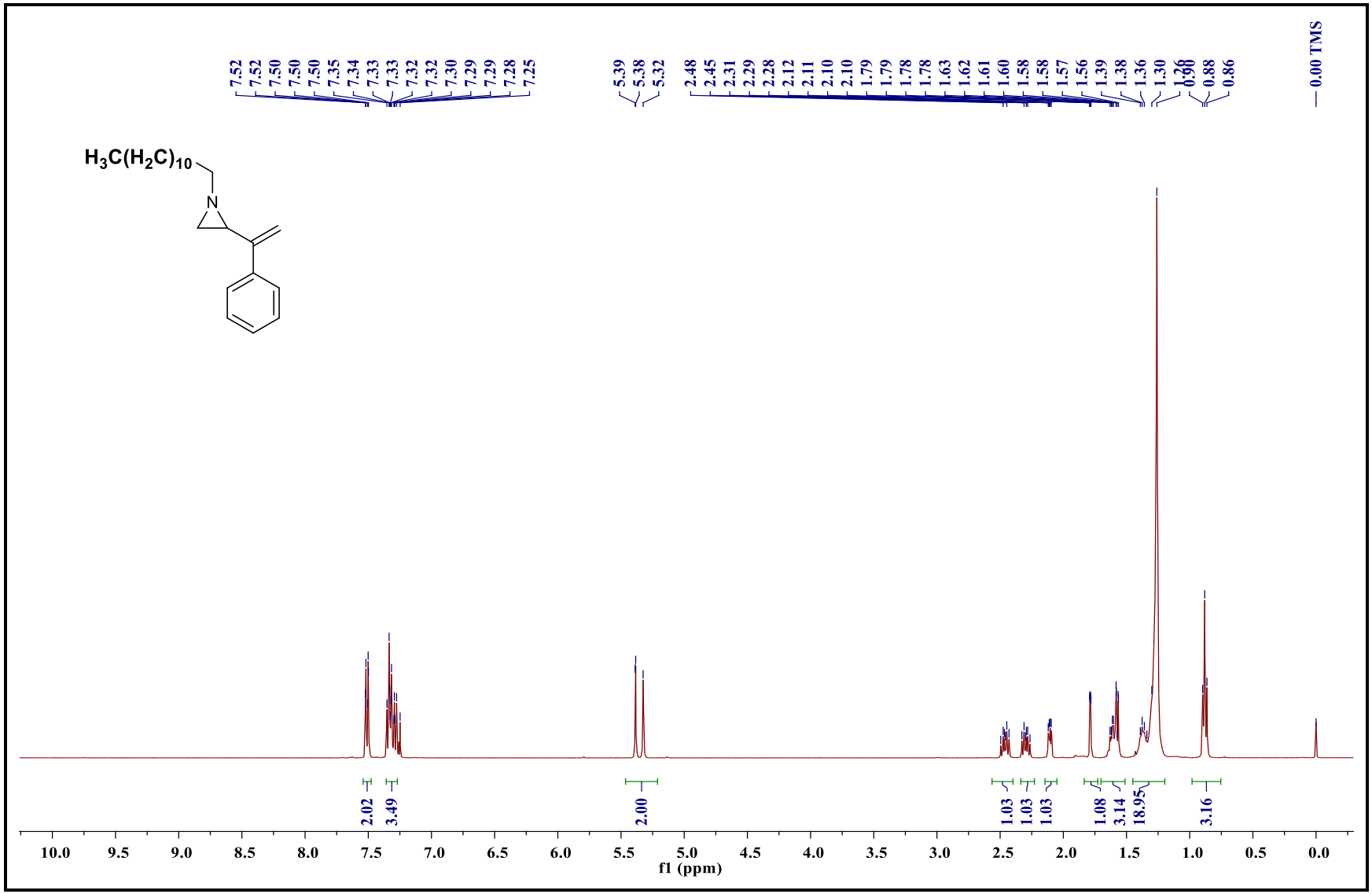
1H NMR spectrum of 1-benzyl-2-(1-cyclopentylvinyl)aziridine (1k):



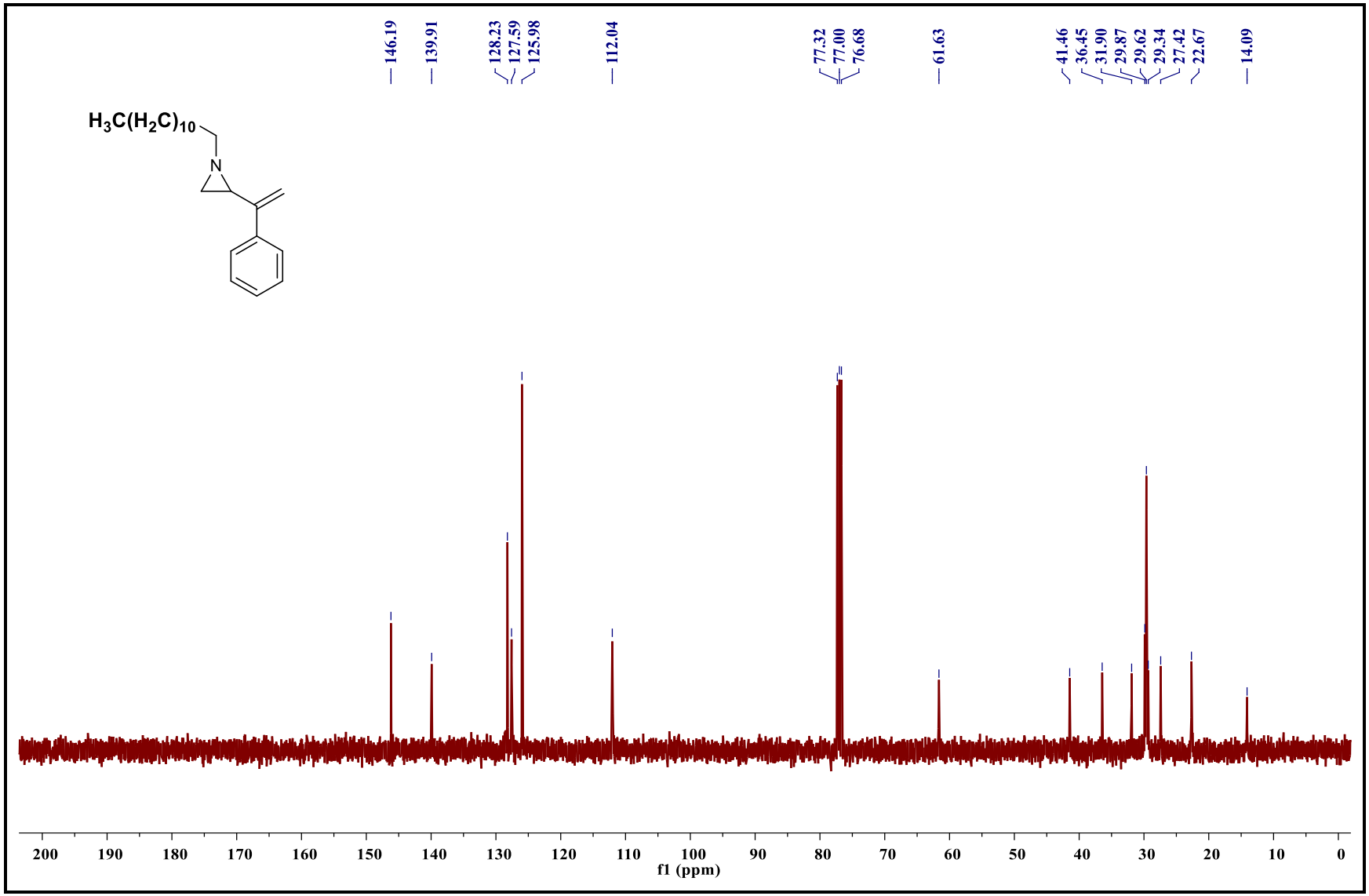
13C NMR spectrum of 1-benzyl-2-(1-cyclopentylvinyl)aziridine (1k):



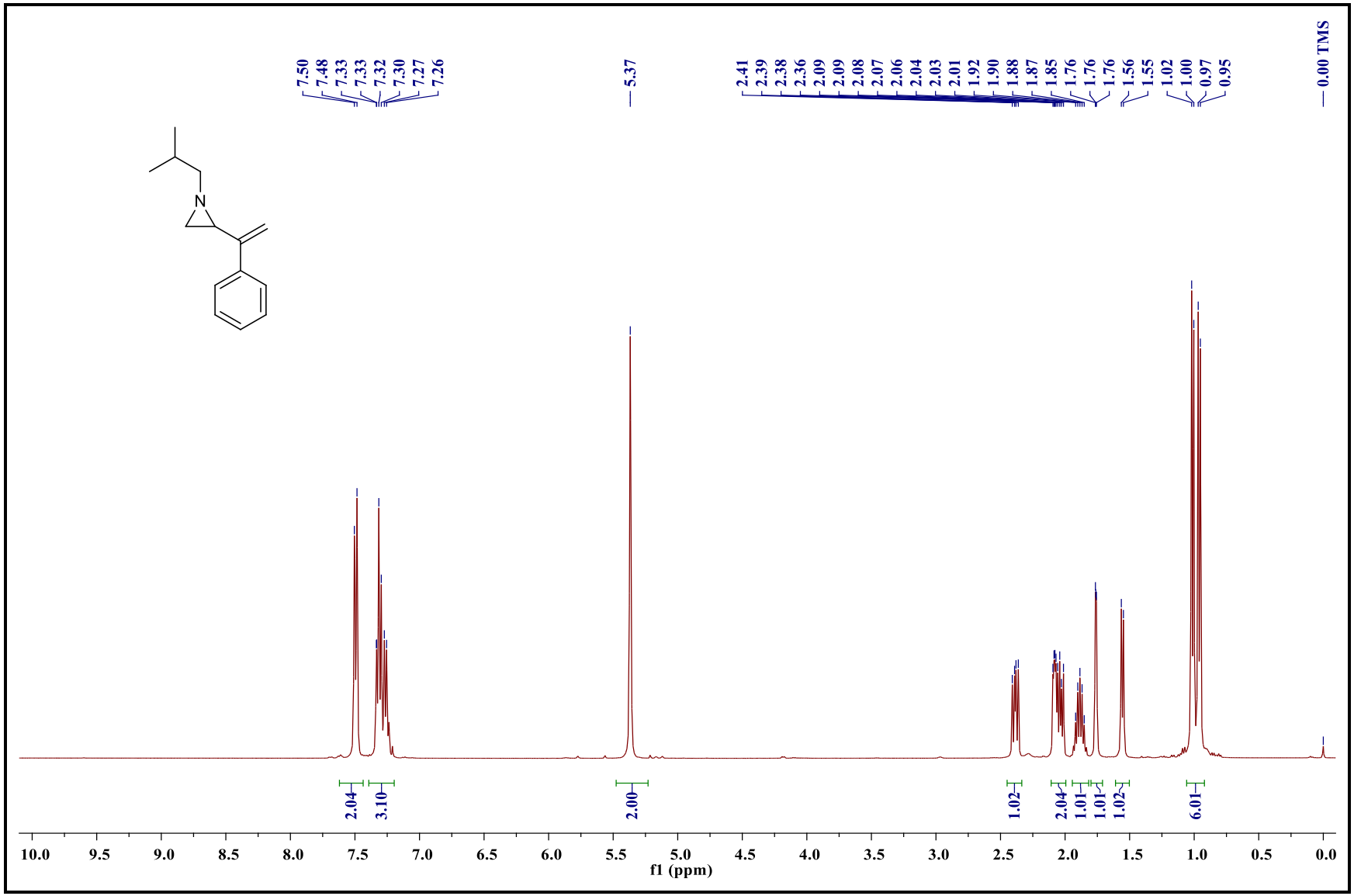
1H NMR spectrum of 1-dodecyl-2-(1-phenylvinyl)aziridine (1l):



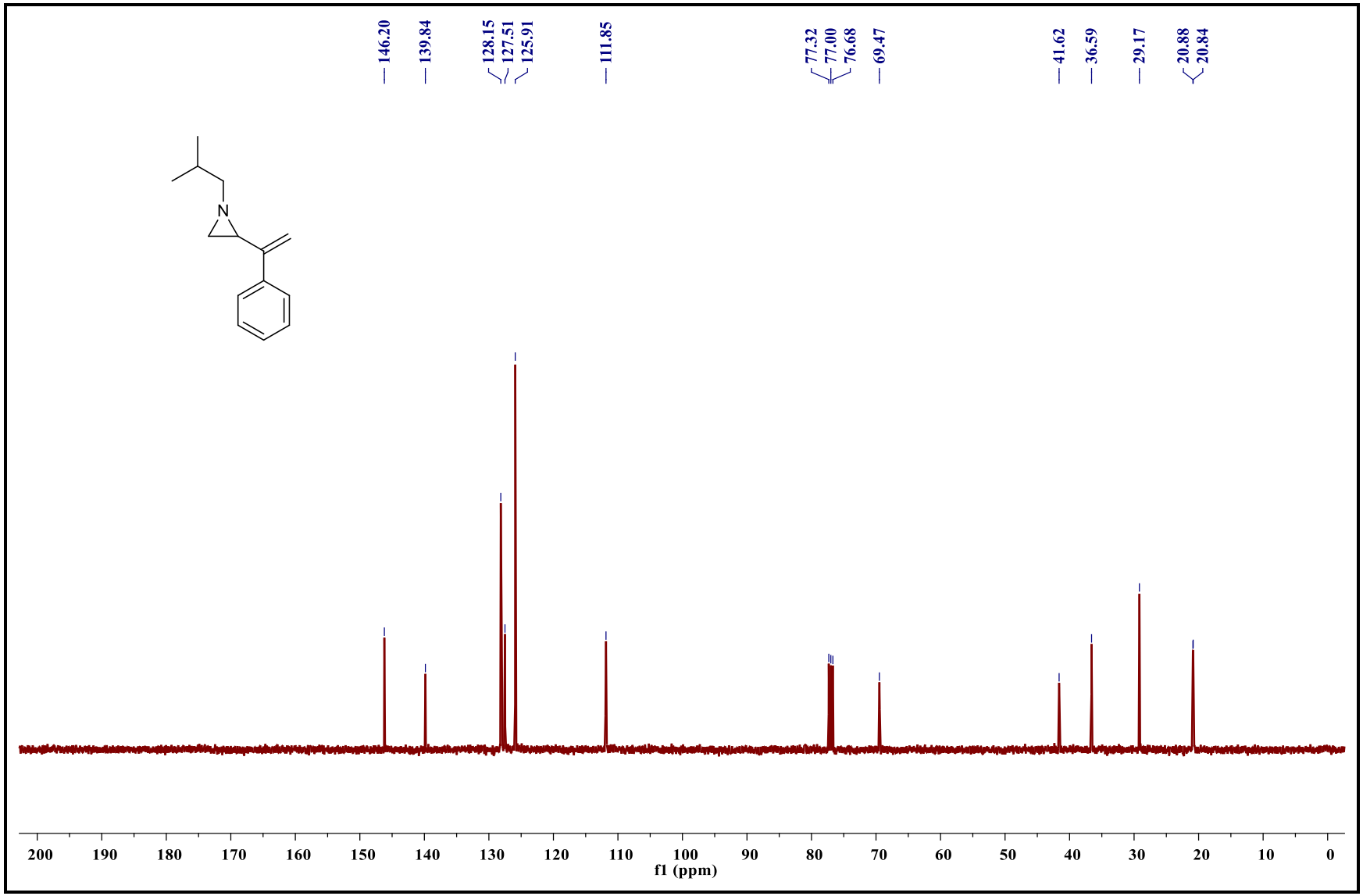
13C NMR spectrum of 1-dodecyl-2-(1-phenylvinyl)aziridine (1l):



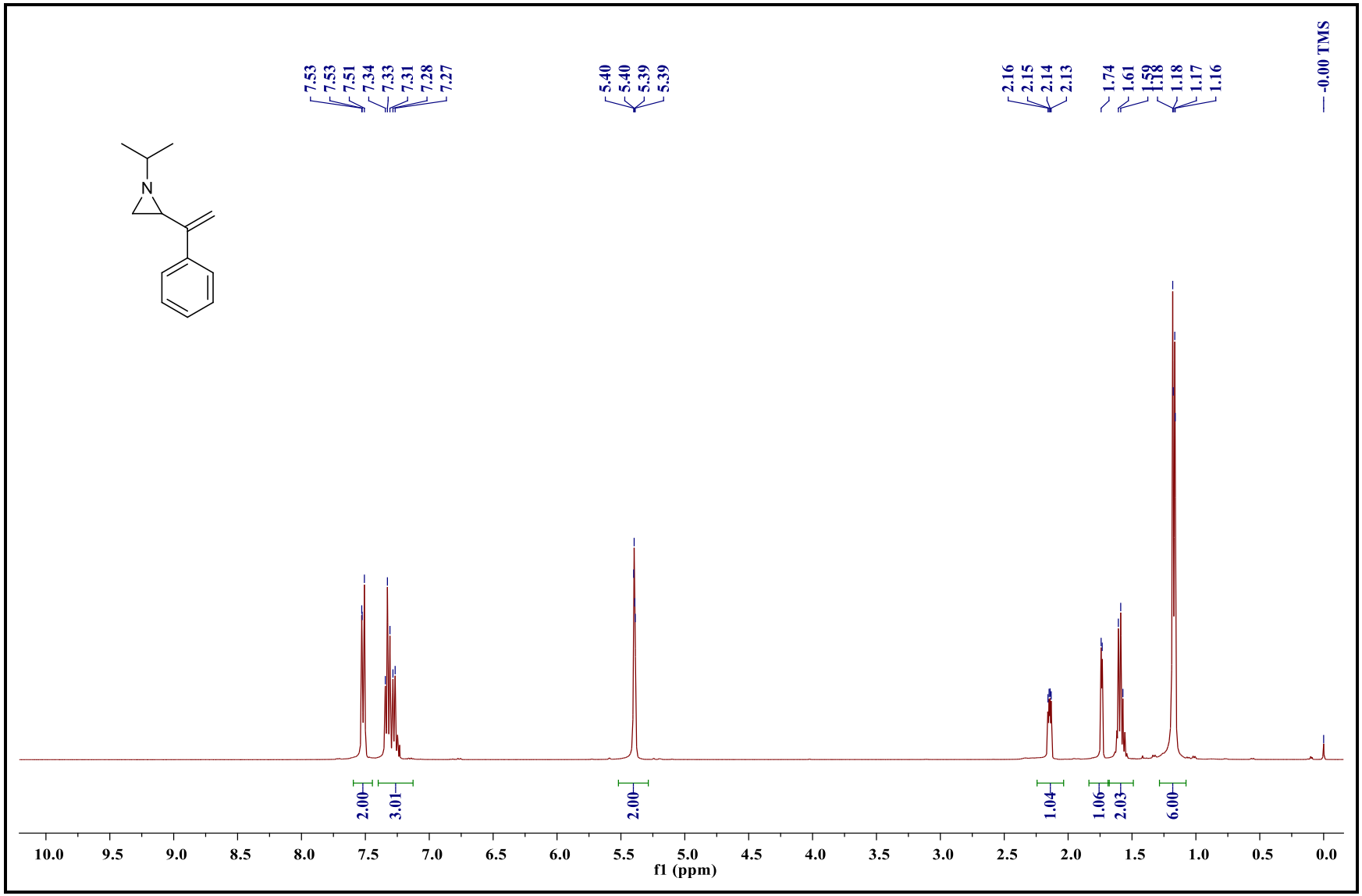
1H NMR spectrum of 1-isobutyl-2-(1-phenylvinyl)aziridine (1m):



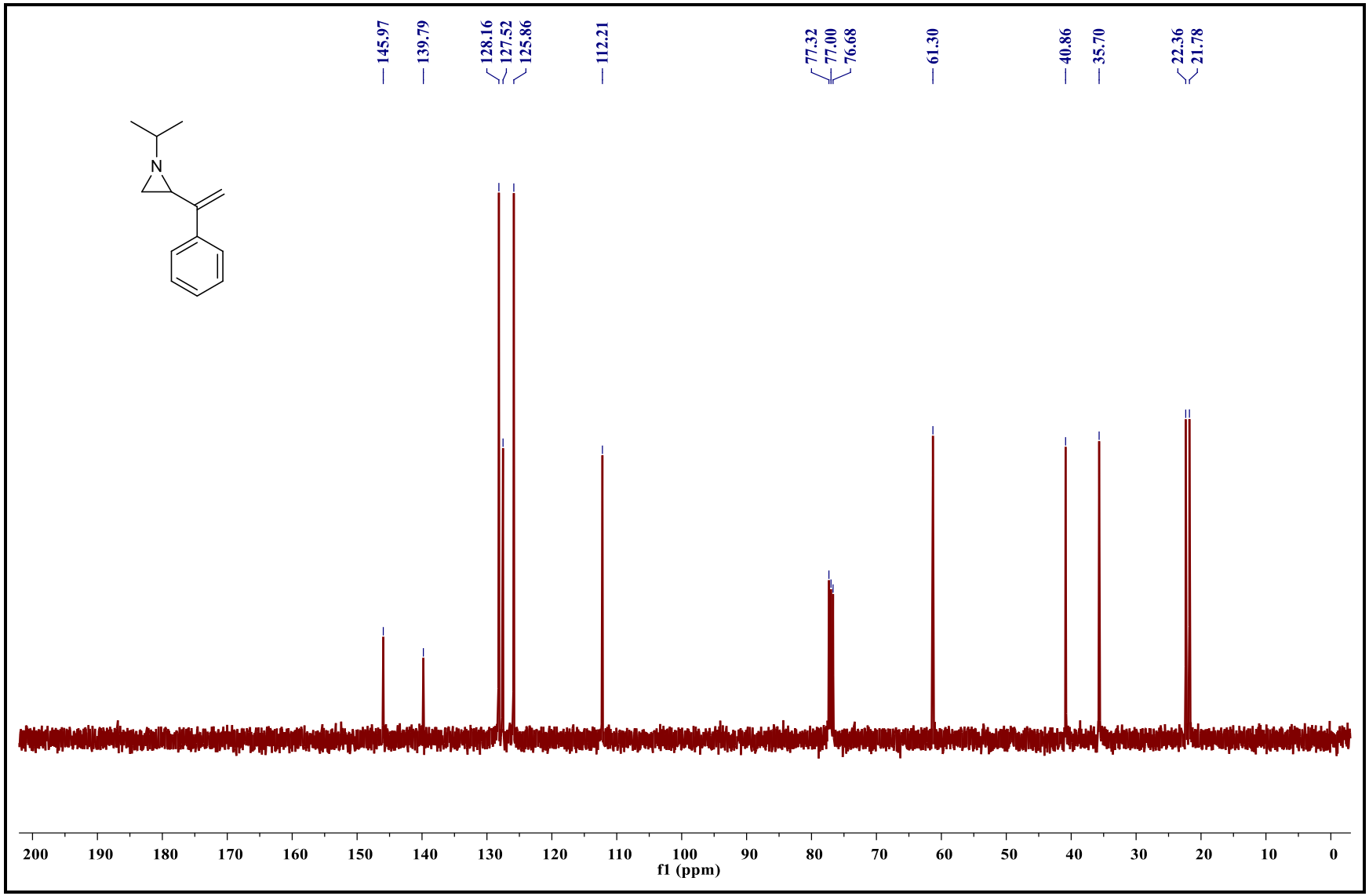
13C NMR spectrum of 1-isobutyl-2-(1-phenylvinyl)aziridine (1m):



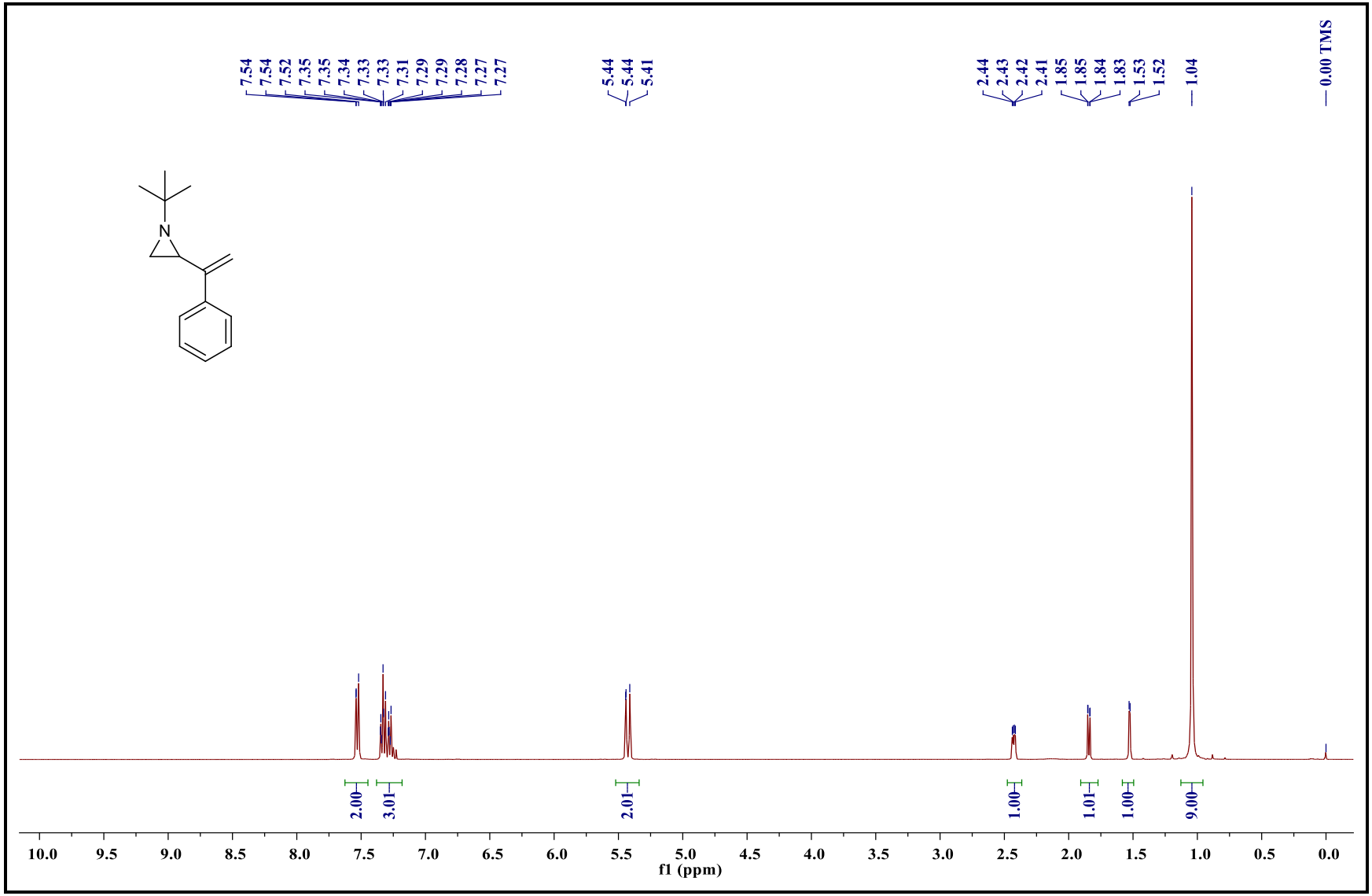
1H NMR spectrum of 1-isopropyl-2-(1-phenylvinyl)aziridine (1n):



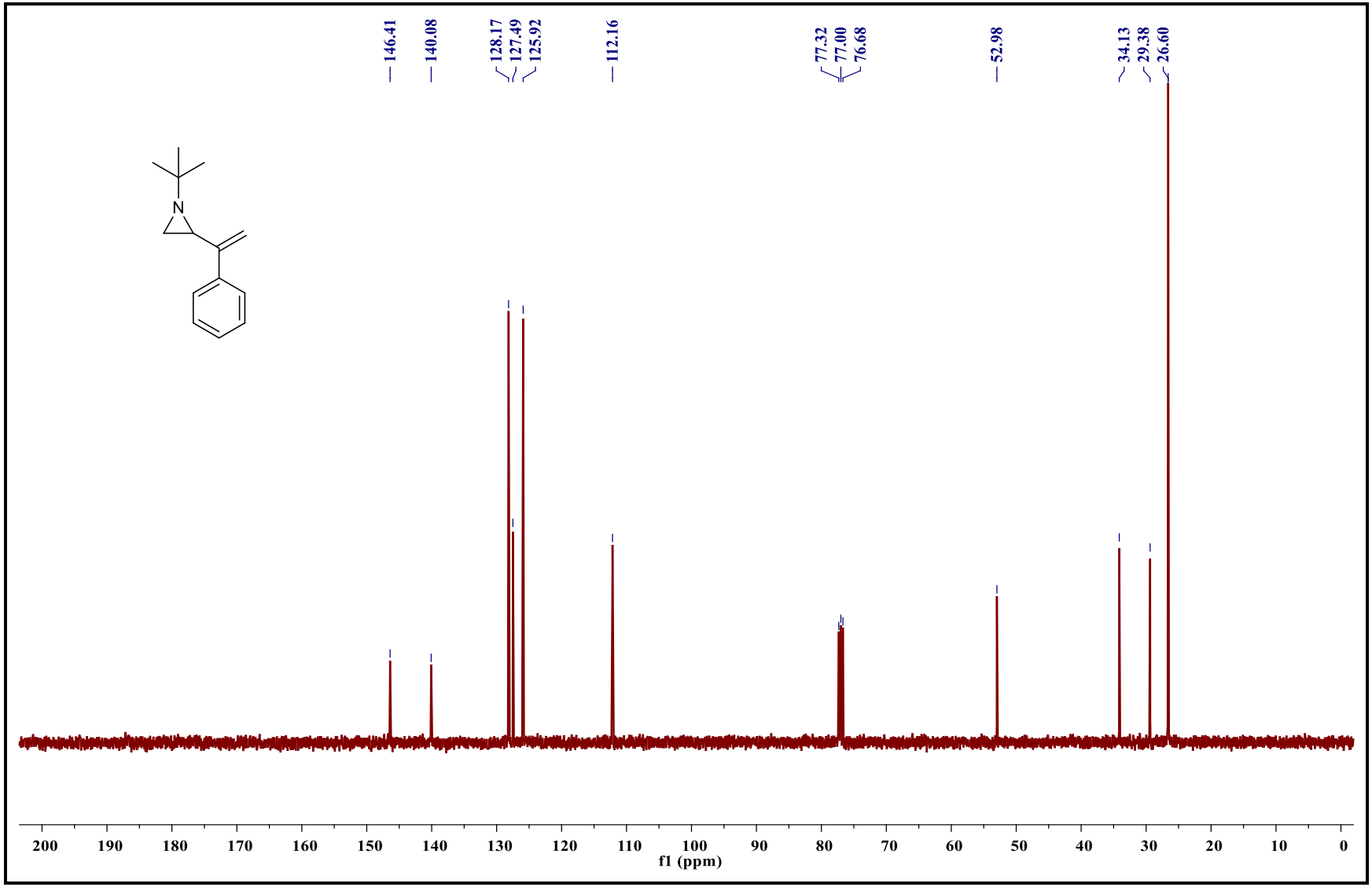
13C NMR spectrum of 1-isopropyl-2-(1-phenylvinyl)aziridine (1n):



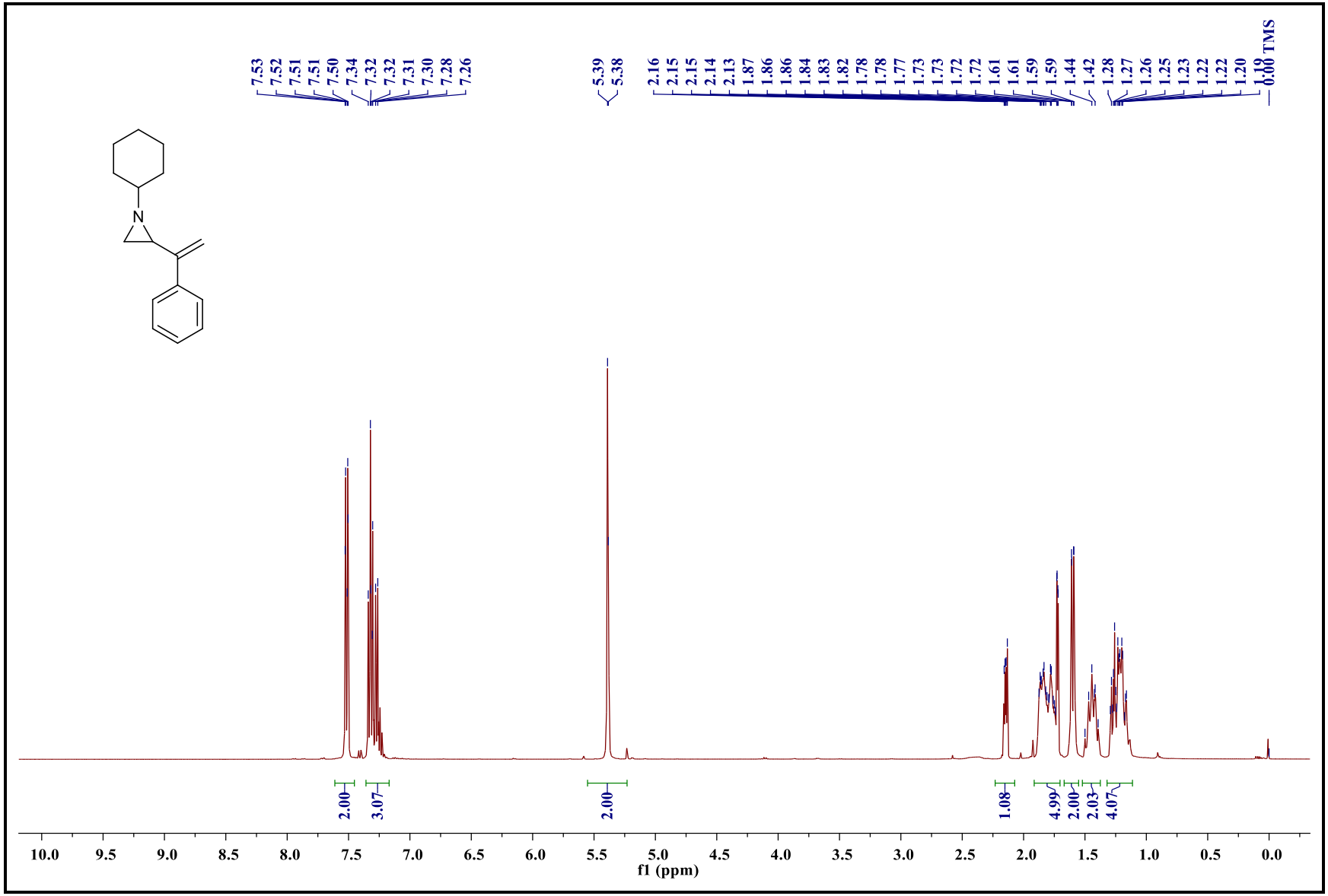
1H NMR spectrum of 1-(tert-butyl)-2-(1-phenylvinyl)aziridine (1o):



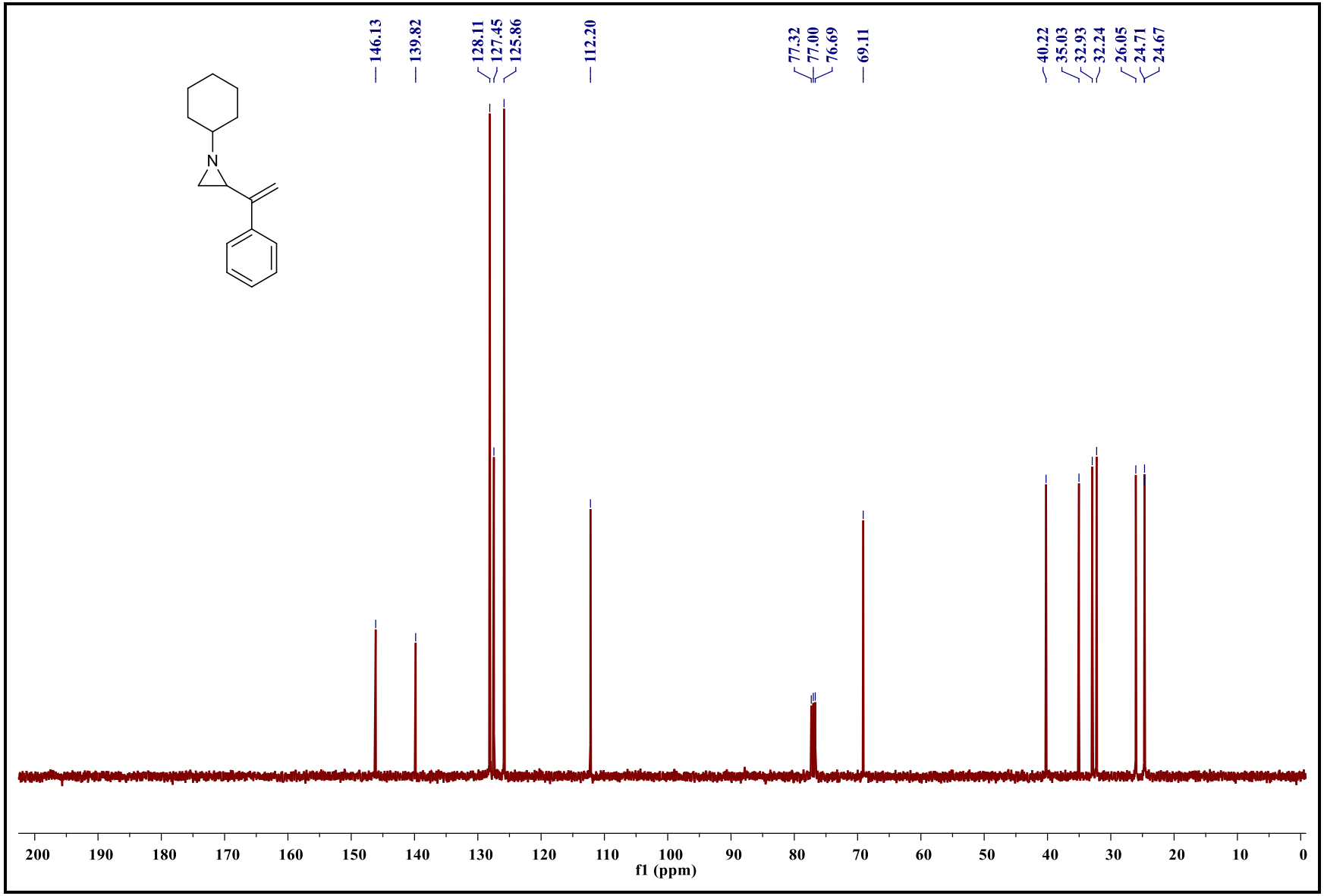
13C NMR spectrum of 1-(tert-butyl)-2-(1-phenylvinyl)aziridine (1o):



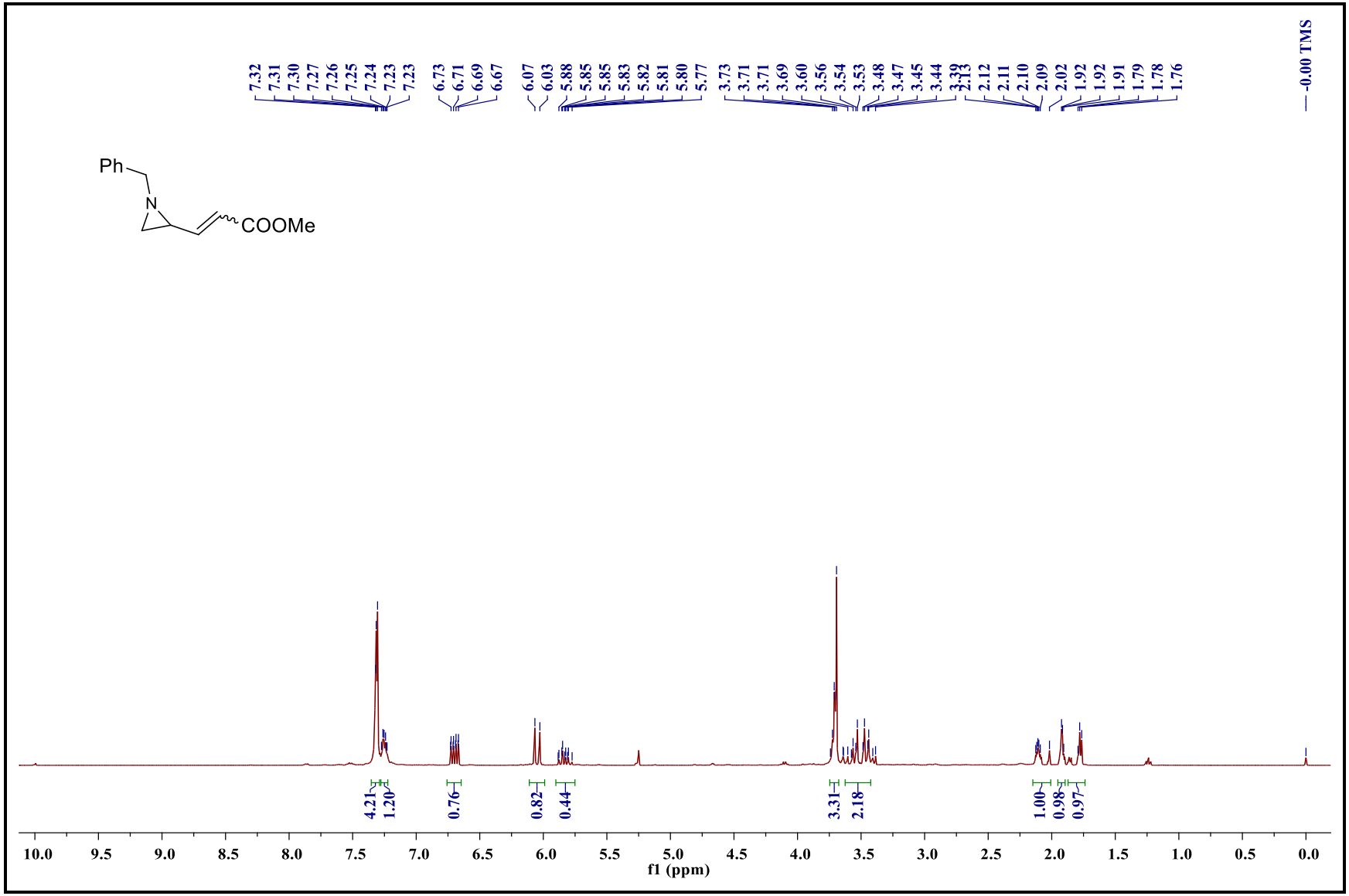
1H NMR spectrum of 1-cyclohexyl-2-(1-phenylvinyl)aziridine (1p):



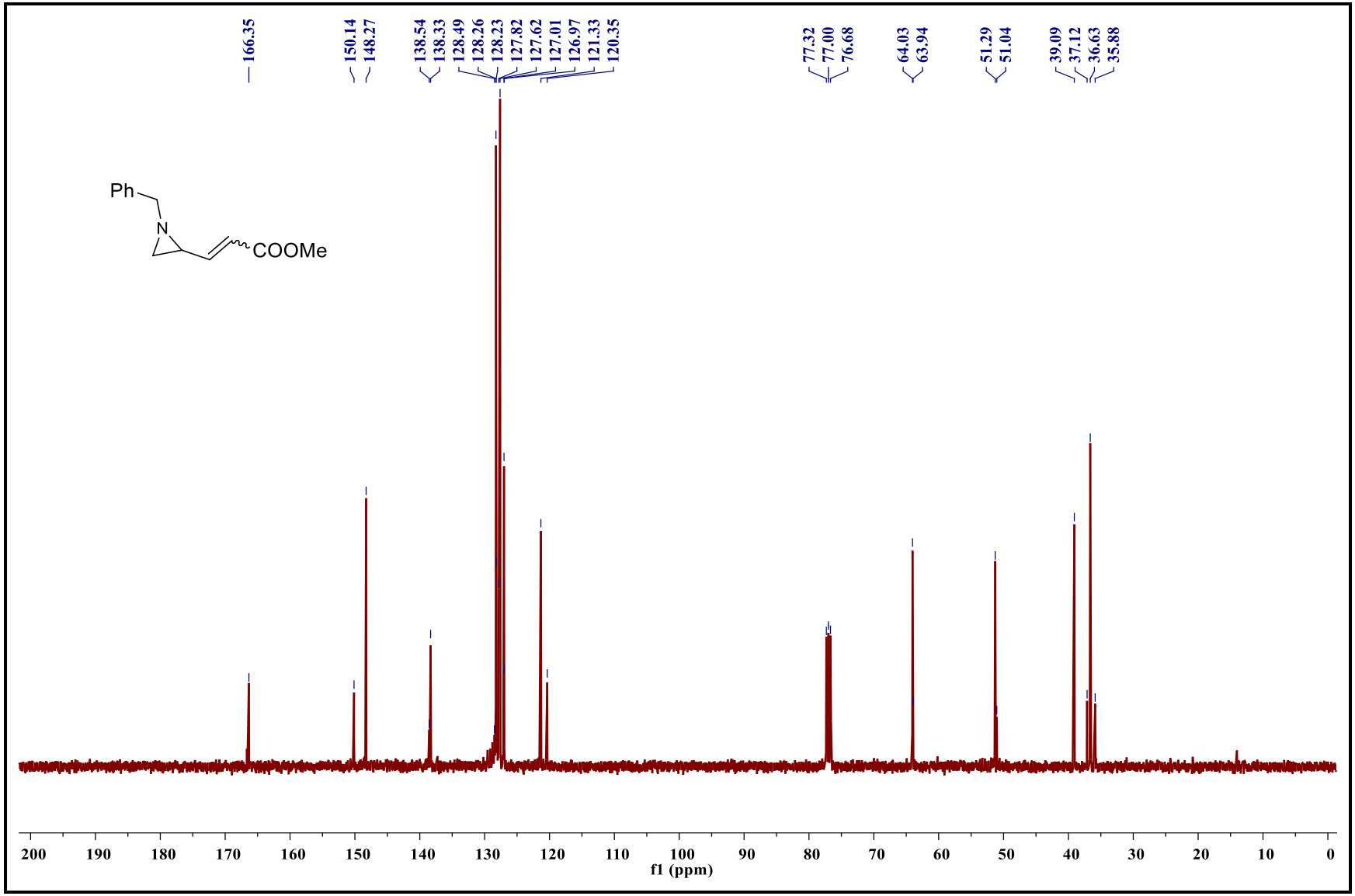
1H NMR spectrum of 1-cyclohexyl-2-(1-phenylvinyl)aziridine (1p):



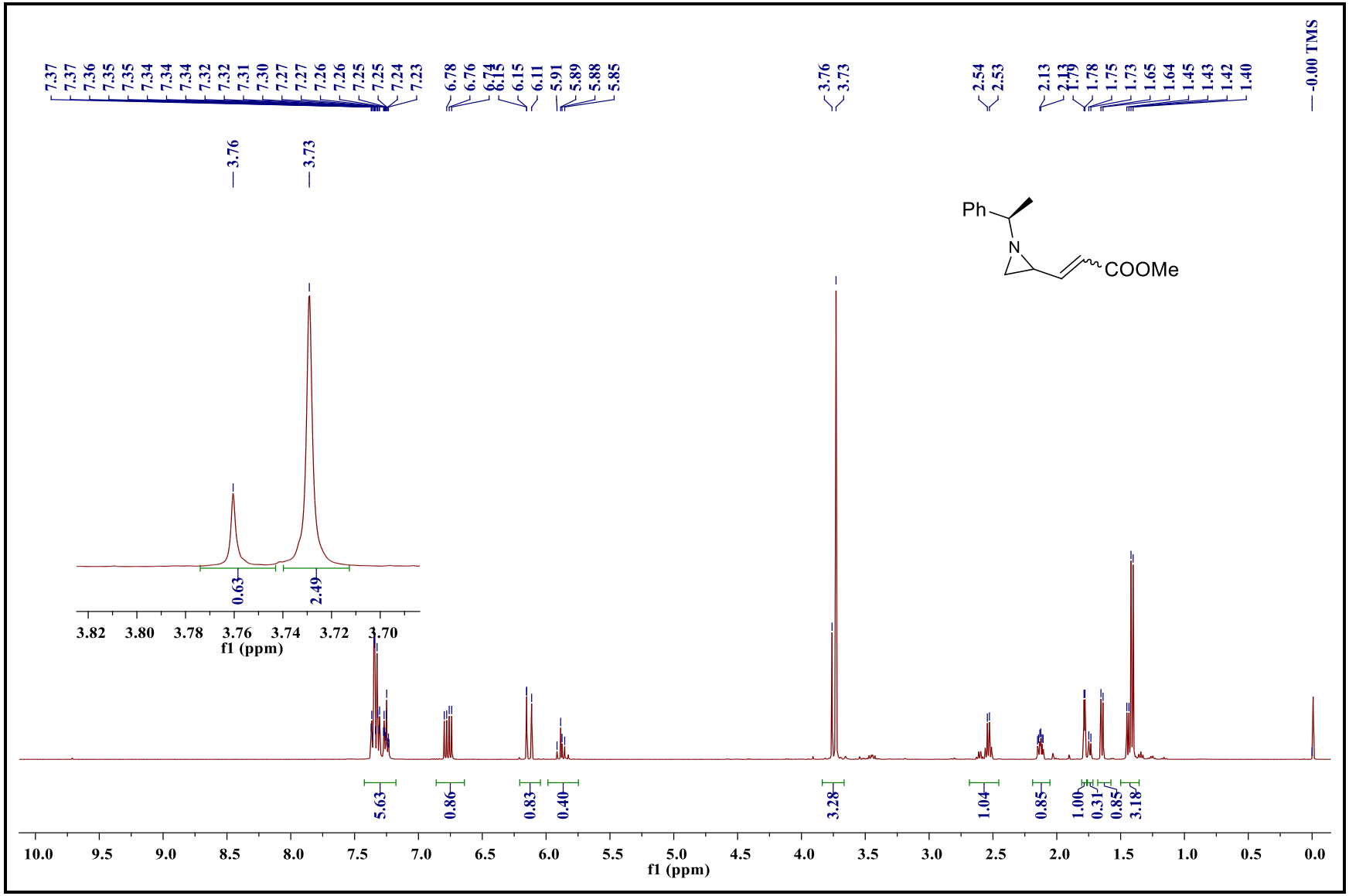
1H NMR spectrum of methyl 3-(1-((R)-1-phenylethyl)aziridin-2-yl)acrylate (E:Z 80:20) (1q):



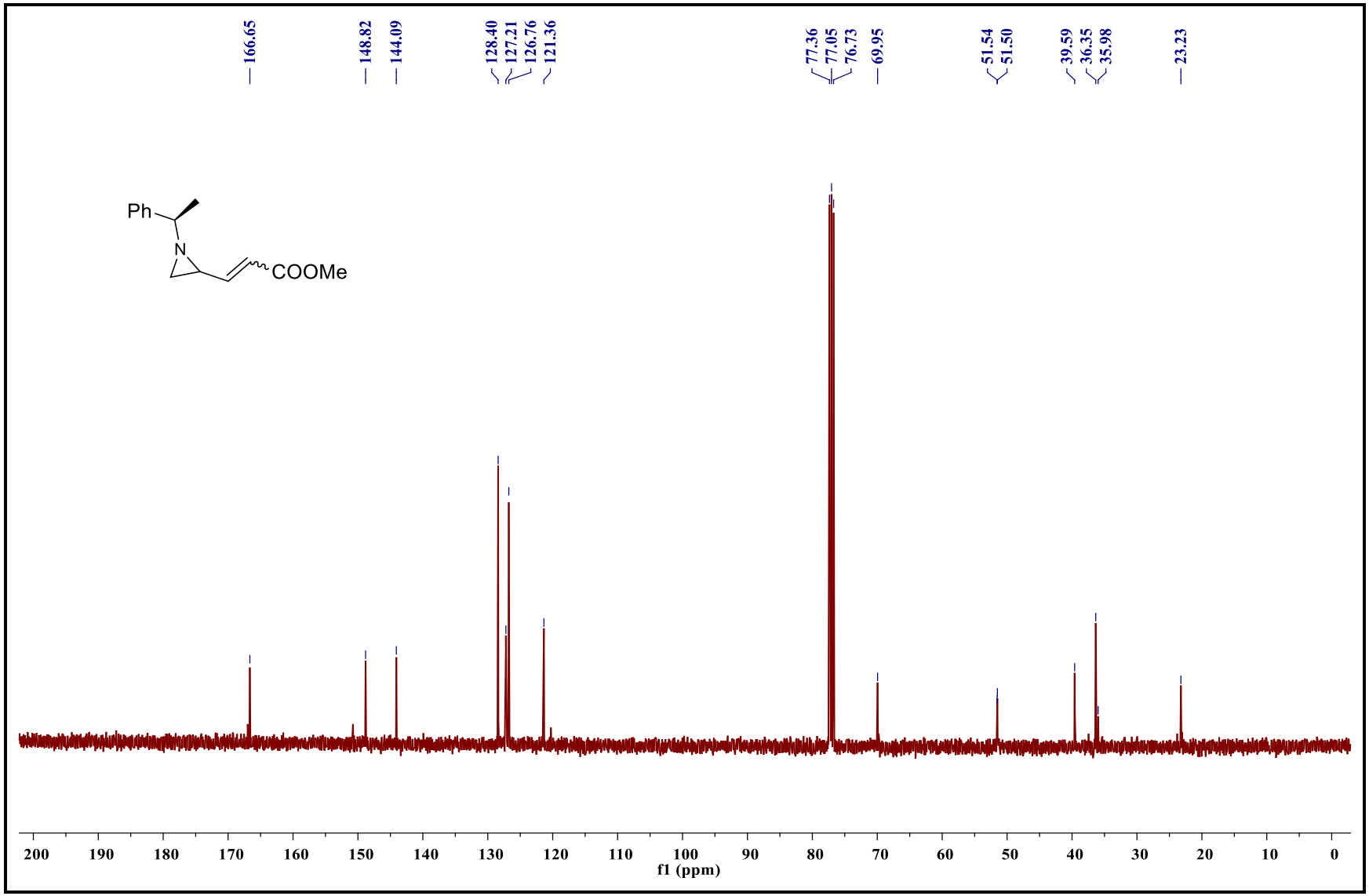
13C NMR spectrum of methyl 3-(1-((R)-1-phenylethyl)aziridin-2-yl)acrylate (E:Z 80:20) (1q):



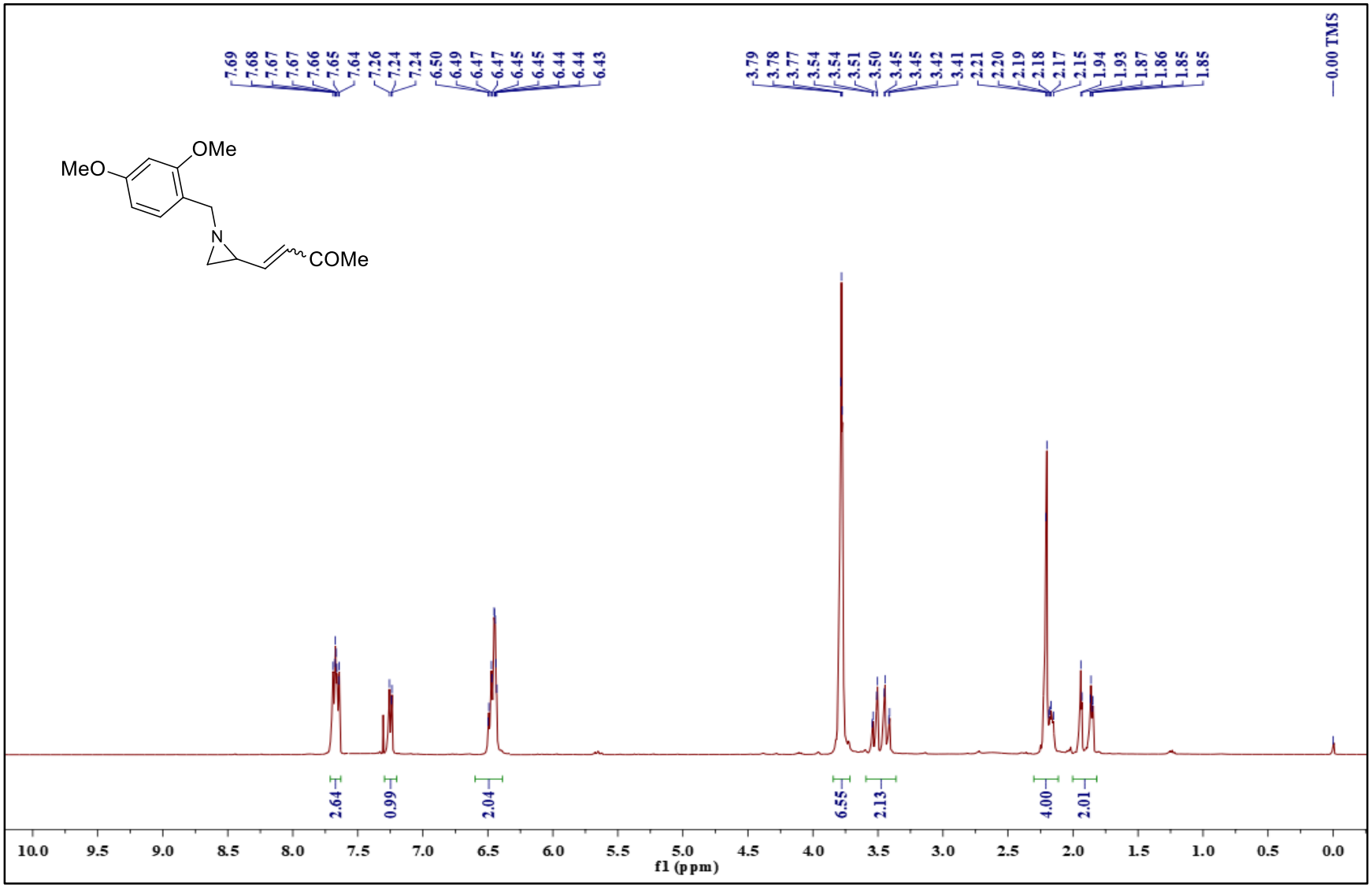
1H NMR spectrum of Ethyl 3-(1-((R)-1-phenylethyl)aziridin-2-yl)acrylate (E:Z 80:20) (1r):



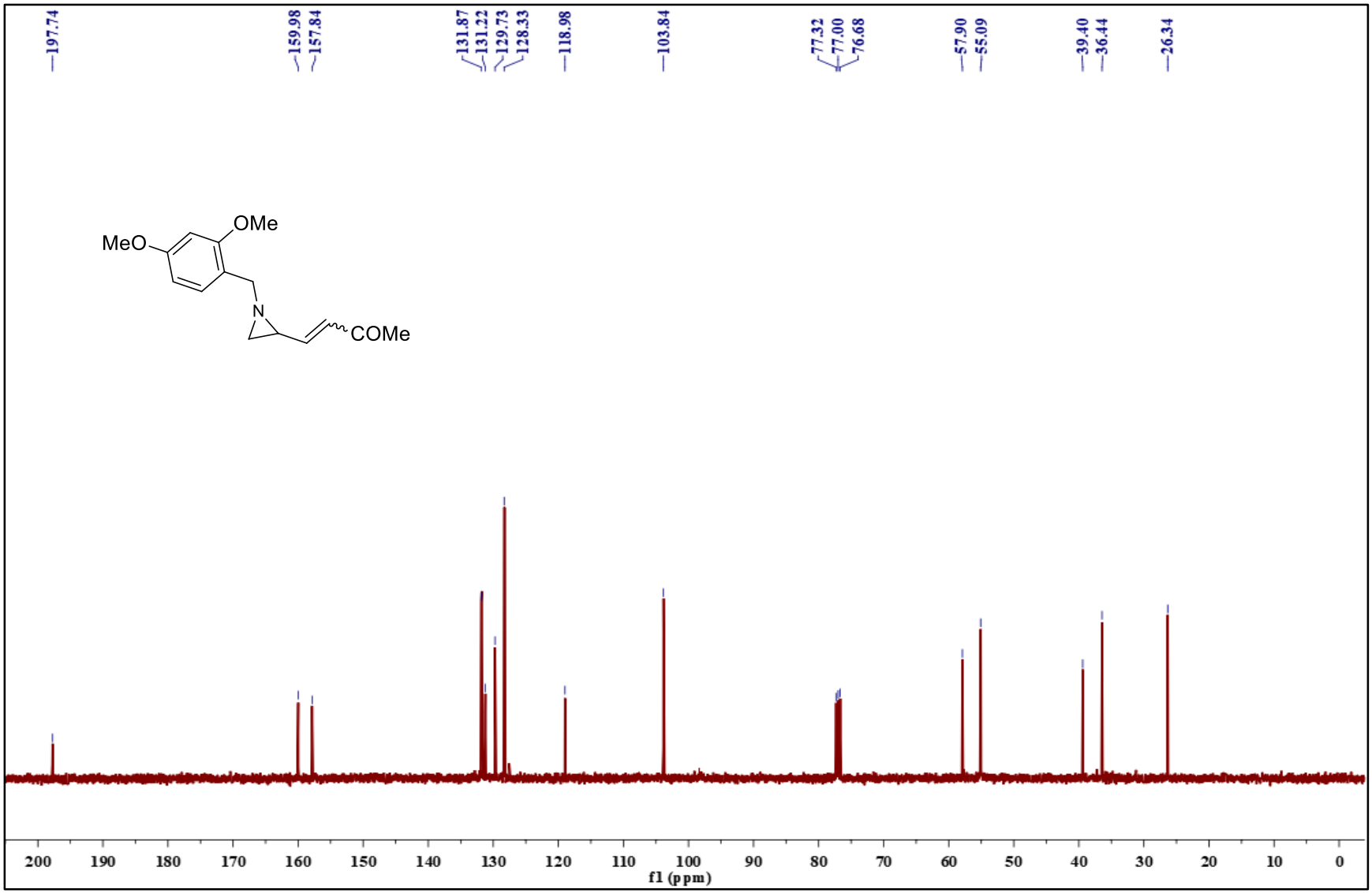
1H NMR spectrum of Ethyl 3-(1-((R)-1-phenylethyl)aziridin-2-yl)acrylate (1r) (E:Z 80:20):



1H NMR spectrum of 4-(1-(2,4-dimethoxybenzyl)aziridin-2-yl)but-3-en-2-one (1w):

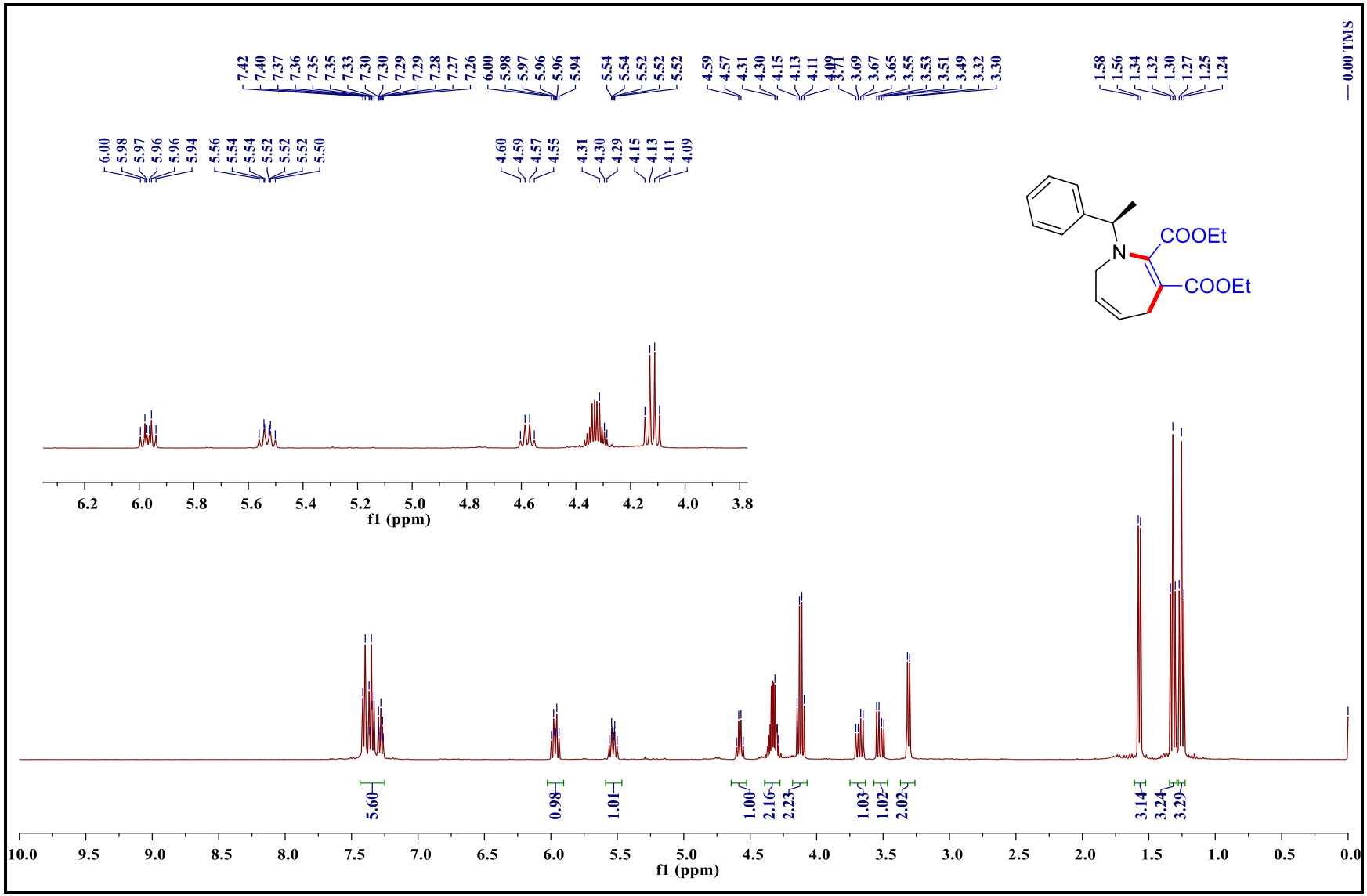


13C NMR spectrum of 4-(1-(2,4-dimethoxybenzyl)aziridin-2-yl)but-3-en-2-one (1w):

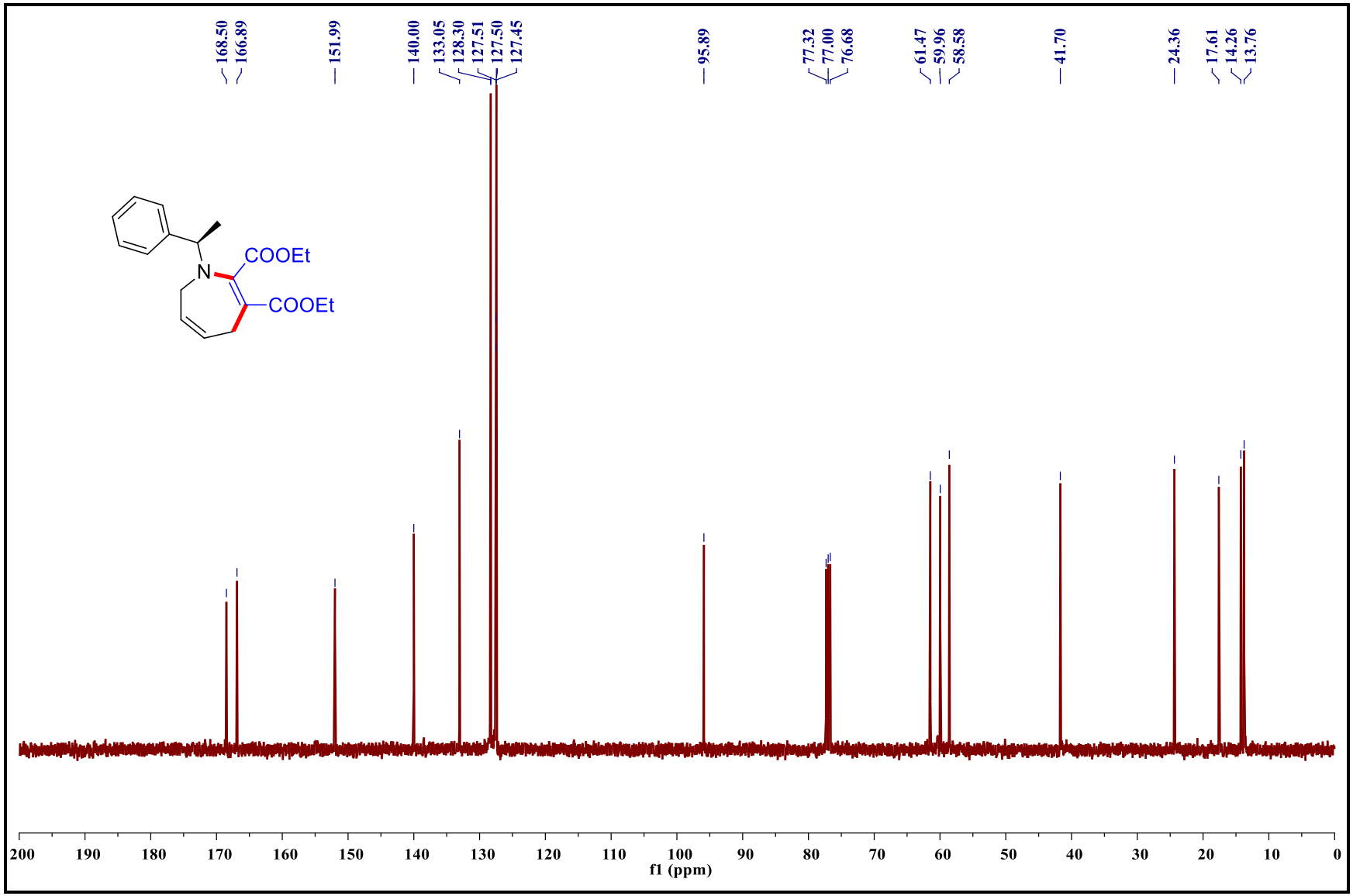


1H and 13C NMR spectra of Azepines

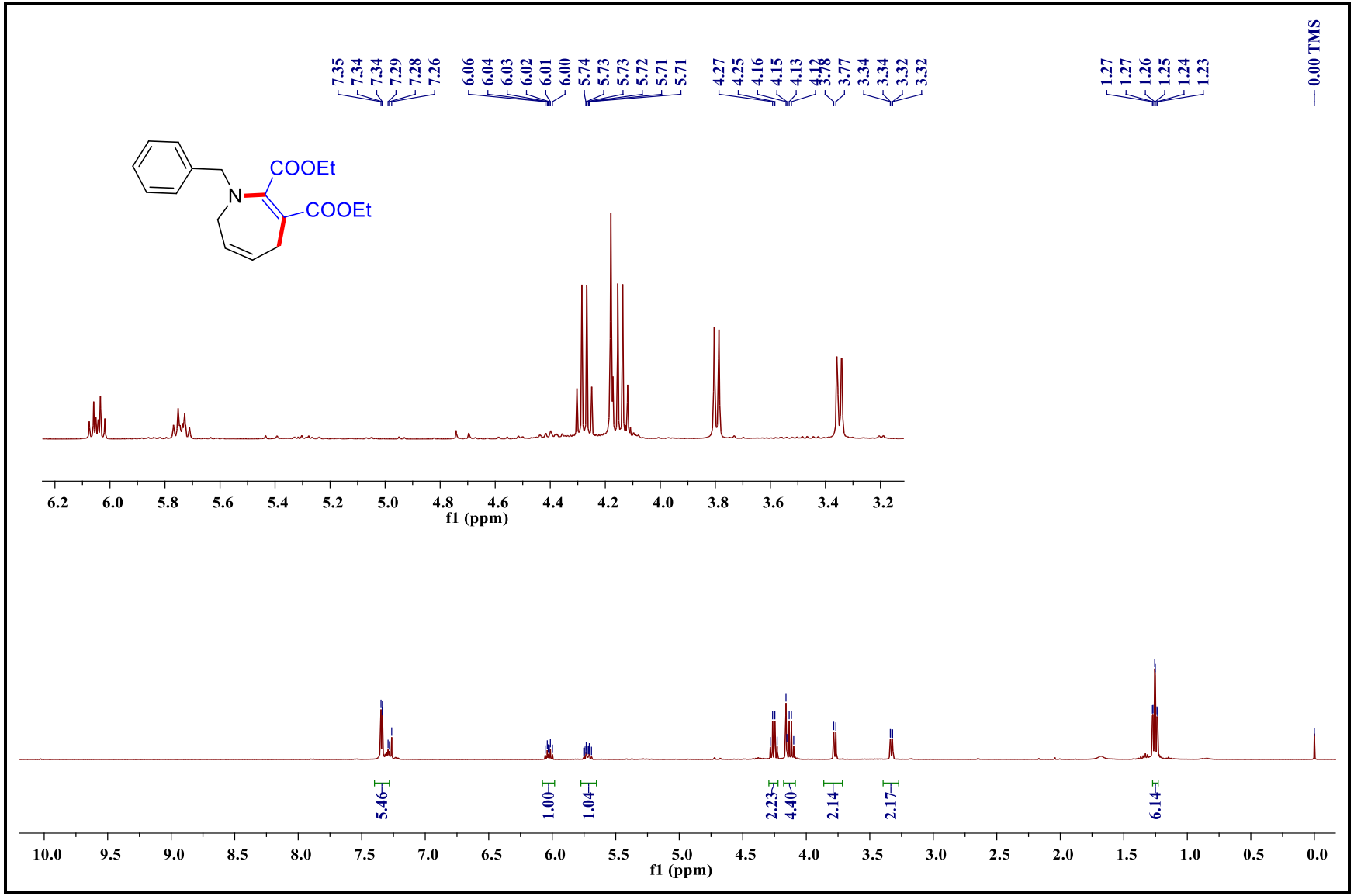
1H NMR spectrum of (R)-diethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3a):



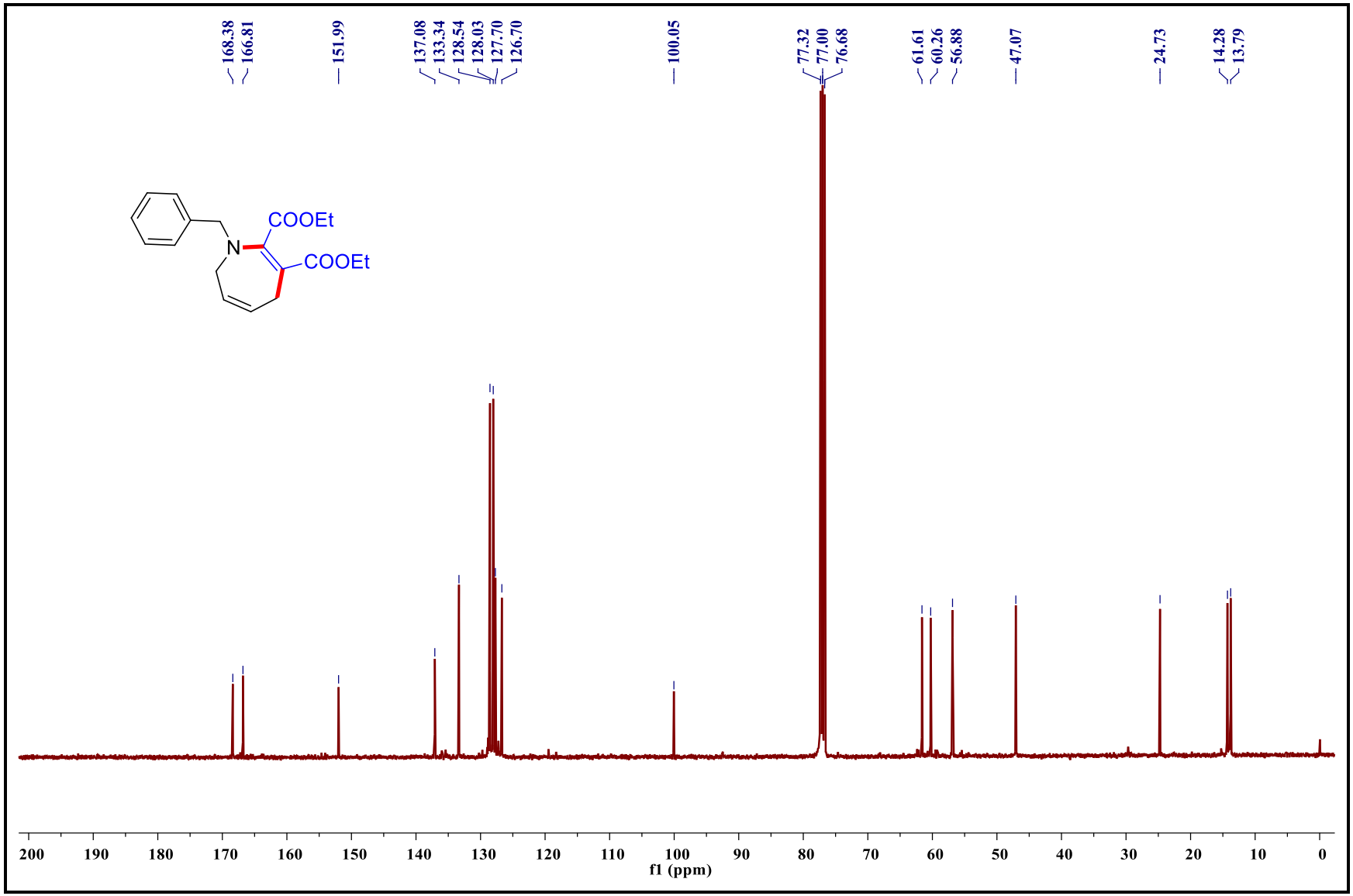
13C NMR spectrum of (R)-diethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3a):



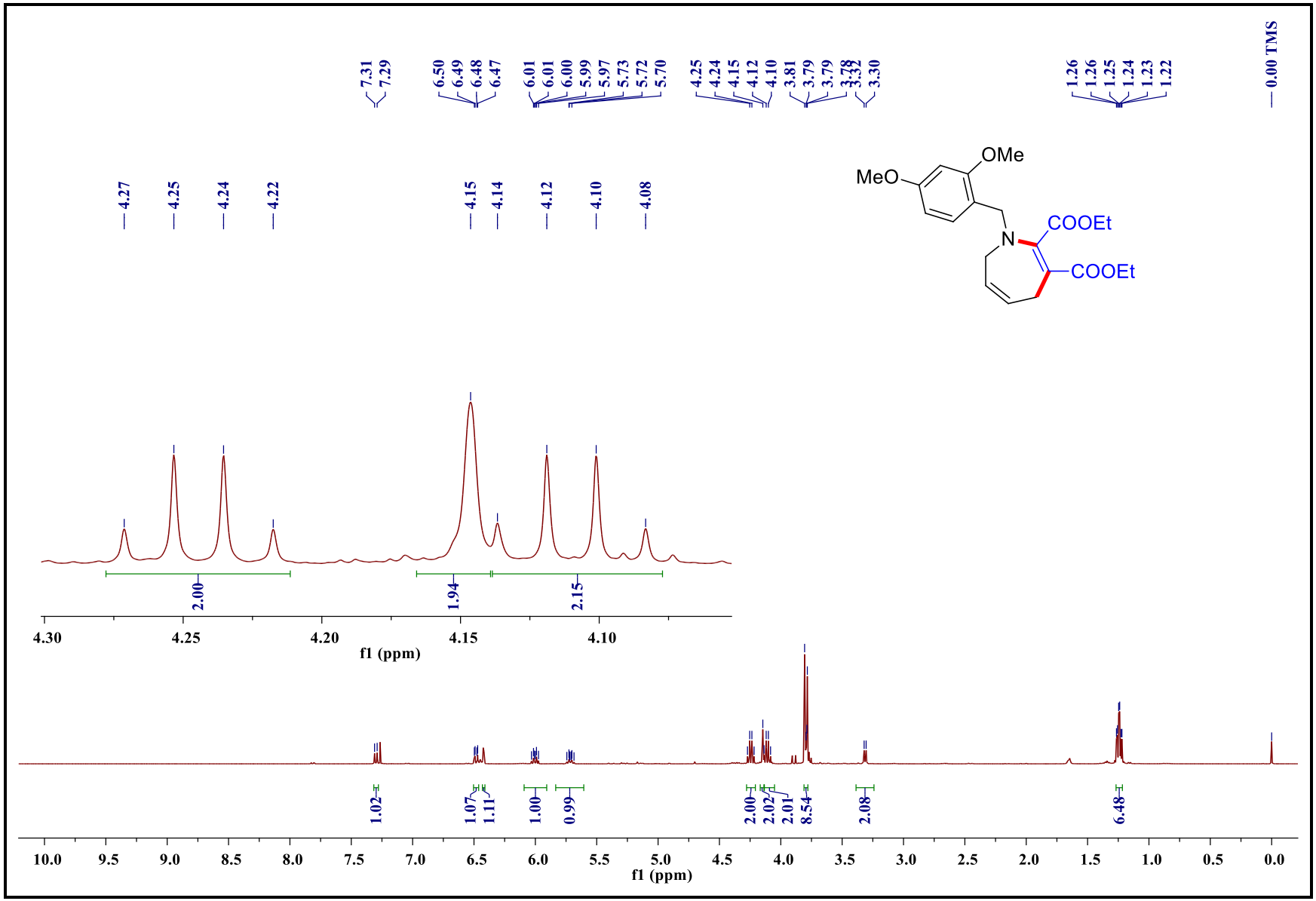
1H NMR spectrum of diethyl 1-benzyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3b):



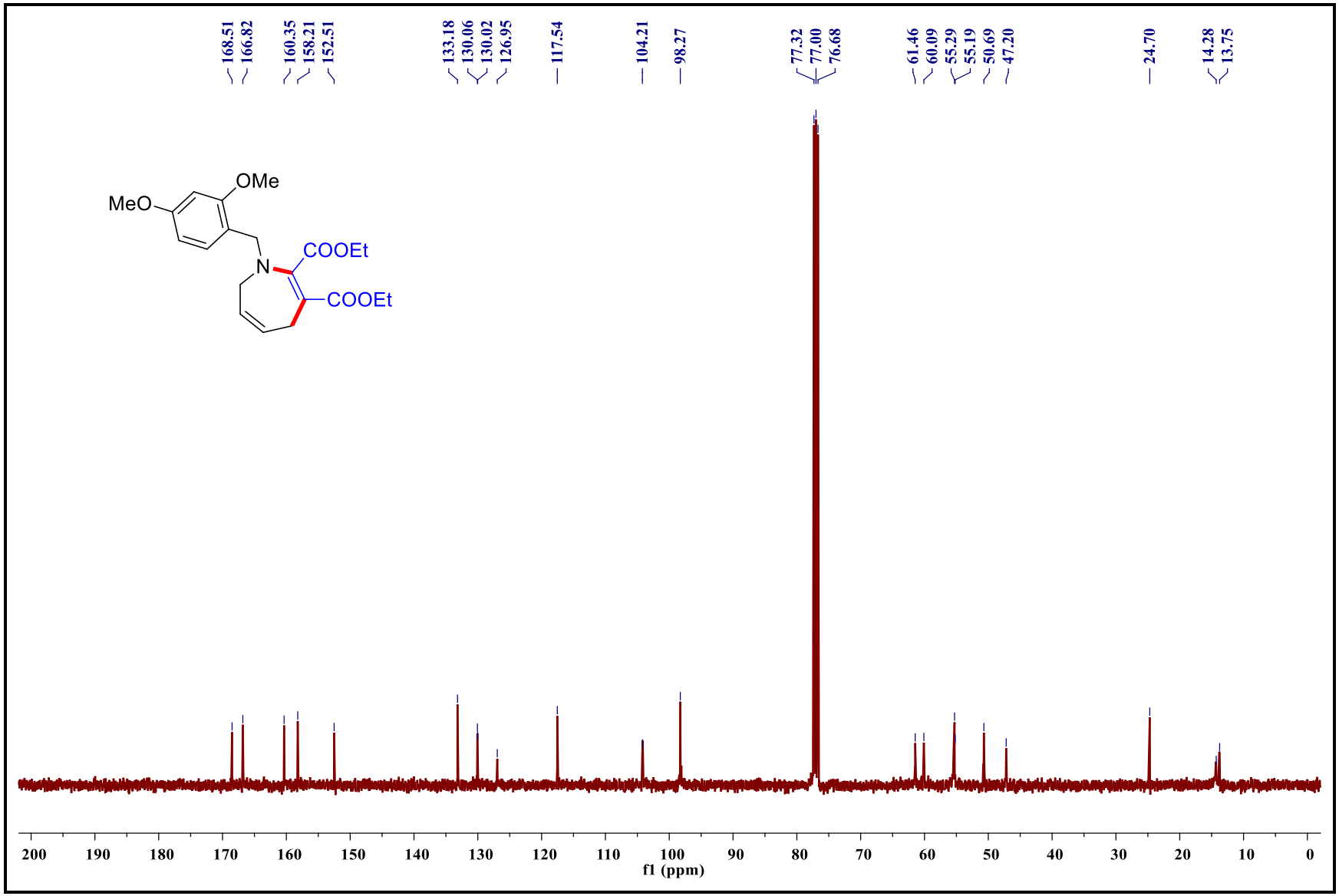
13C NMR spectrum of diethyl 1-benzyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3b):



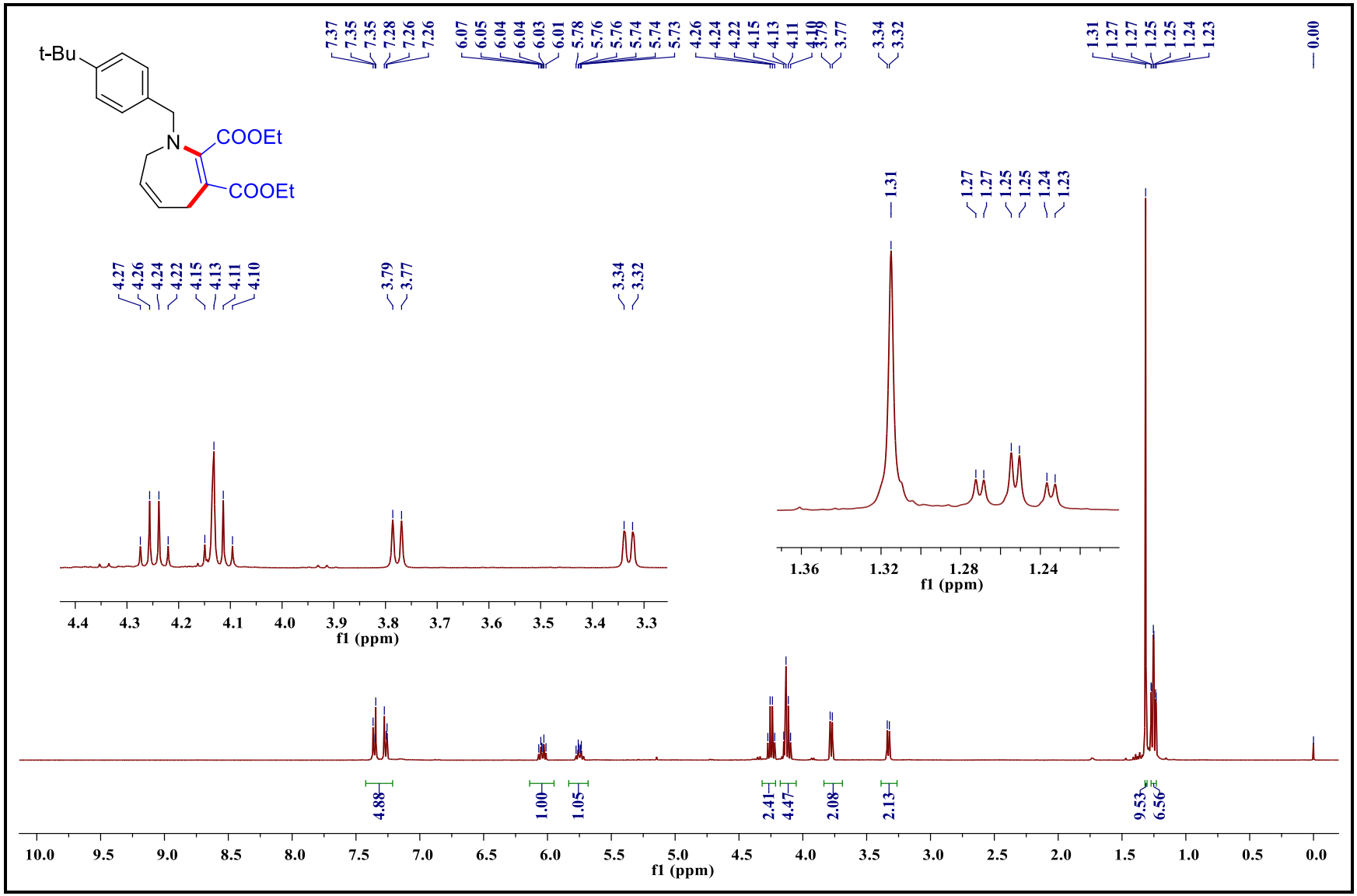
1H NMR spectrum of diethyl 1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3c):



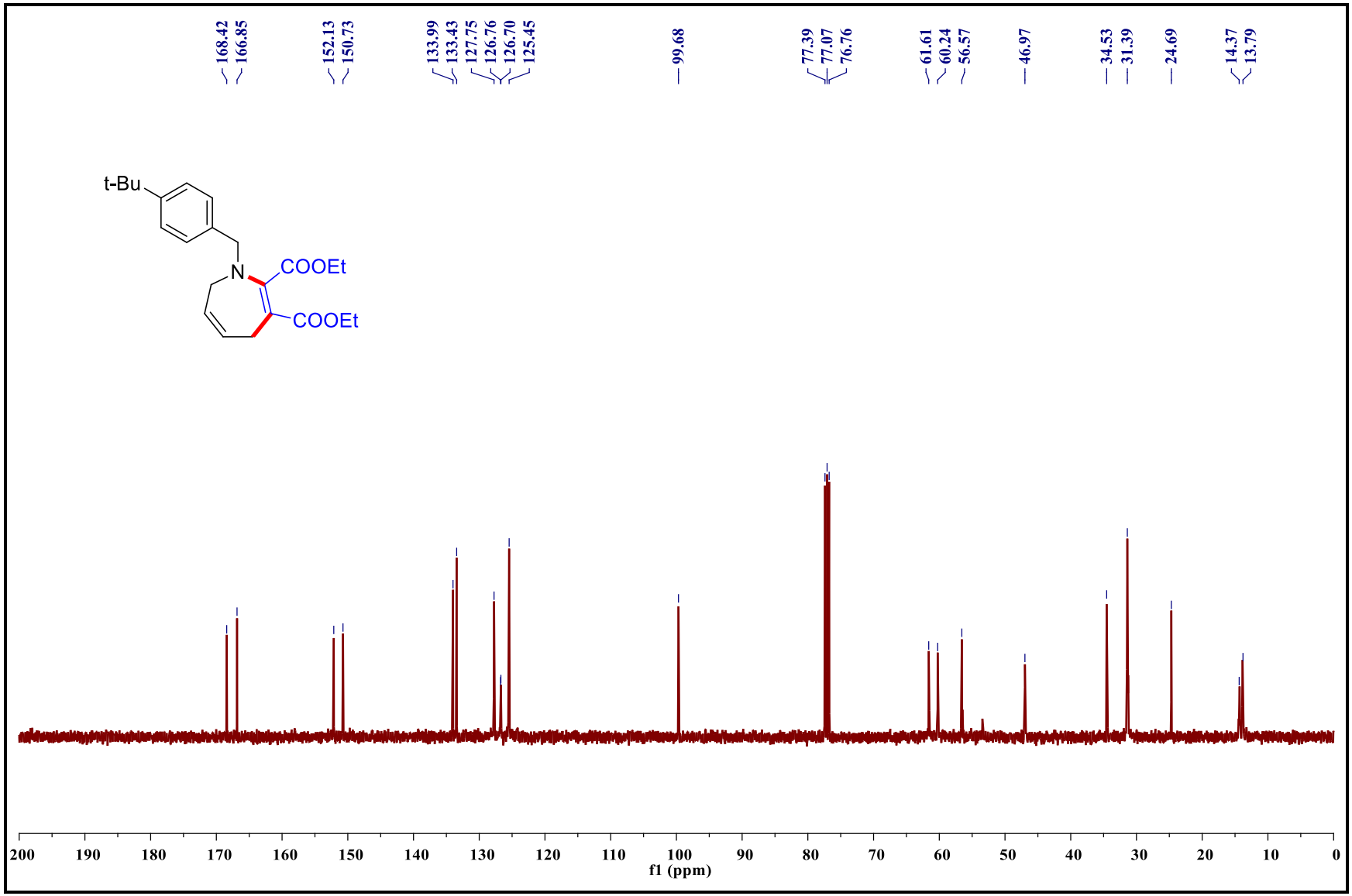
13C NMR spectrum of diethyl 1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3c):



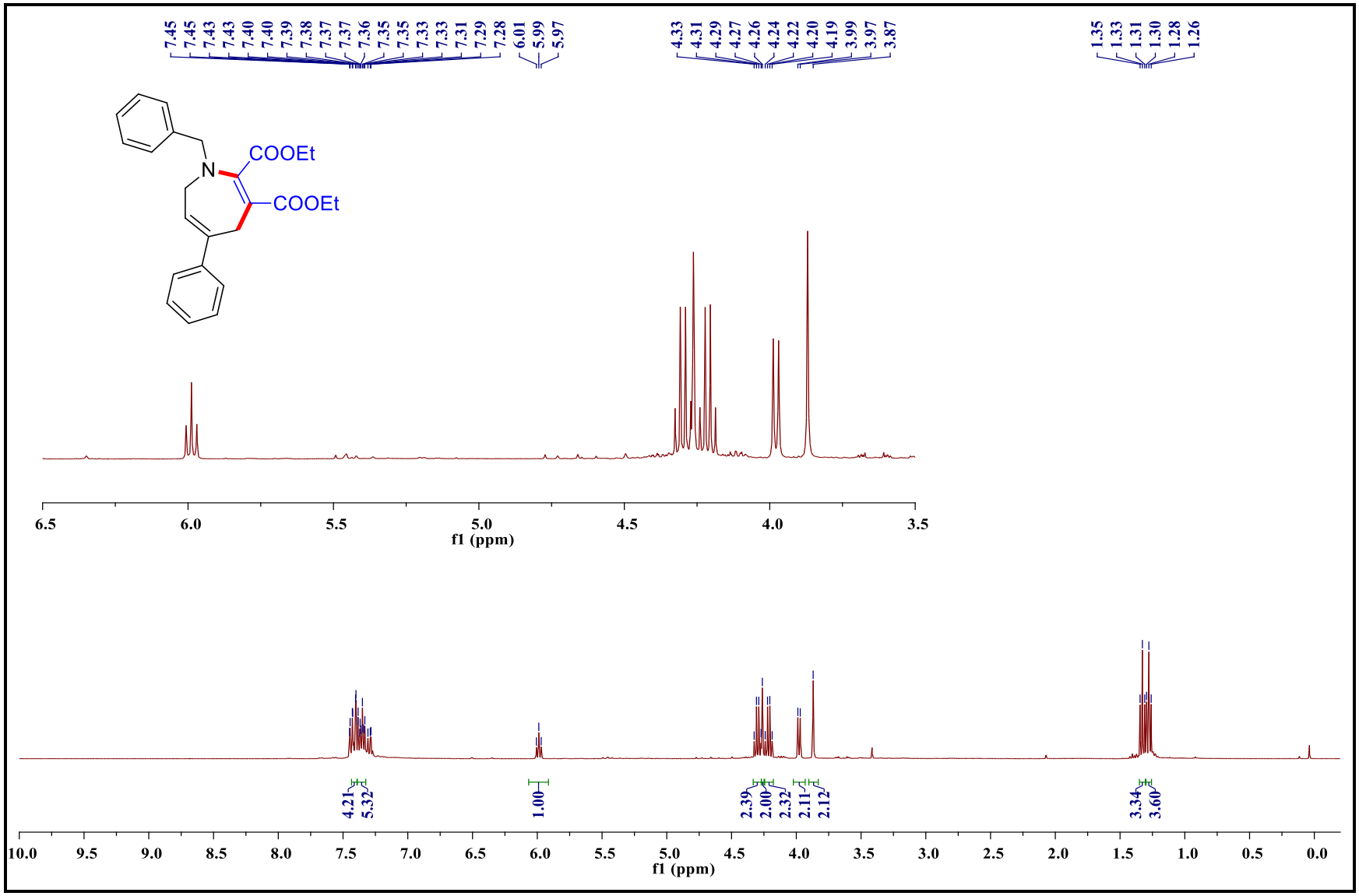
1H NMR spectrum of diethyl 1-(4-(tert-butyl)benzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3d):



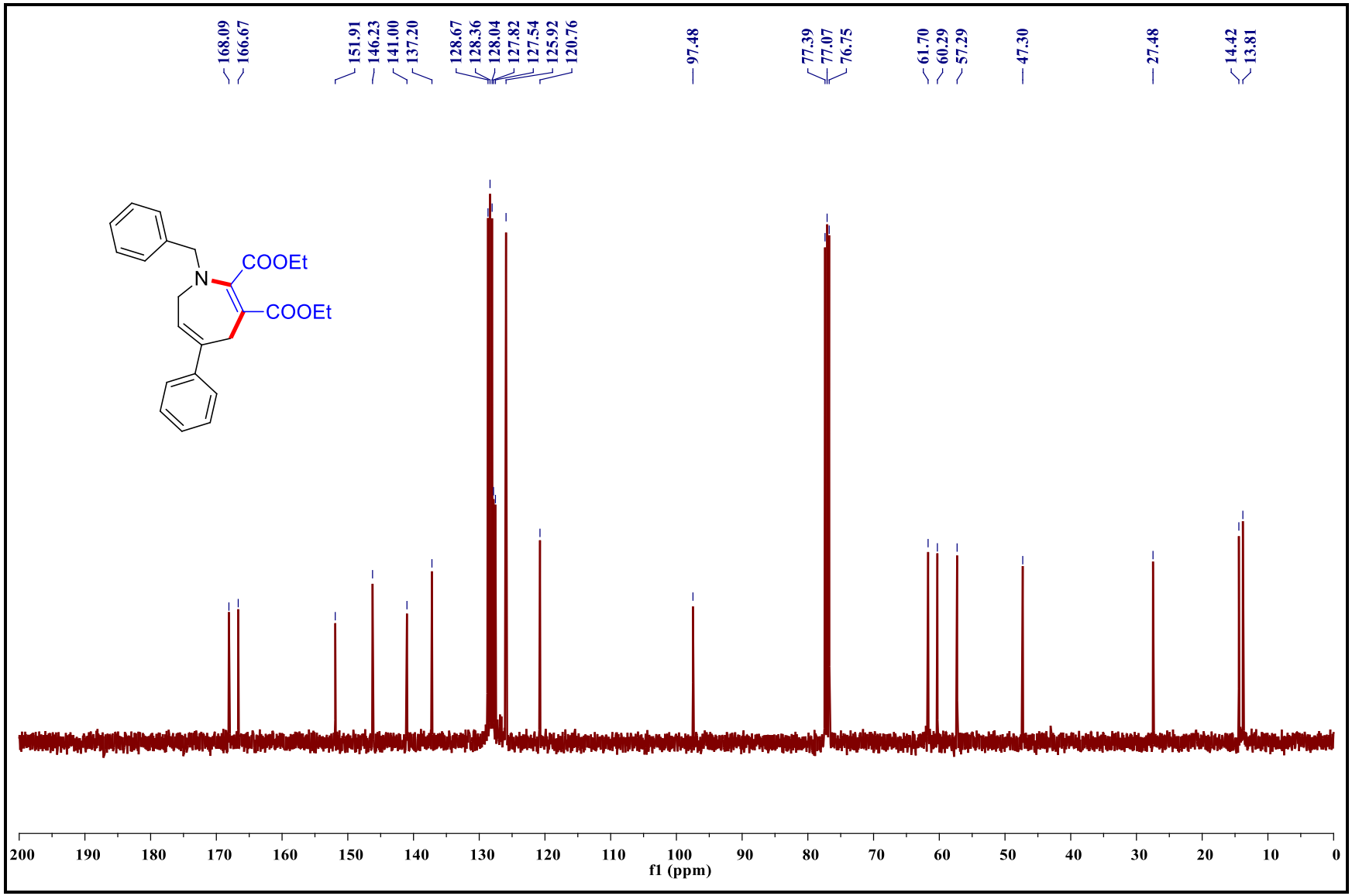
13C NMR spectrum of diethyl 1-(4-(tert-butyl)benzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3d):



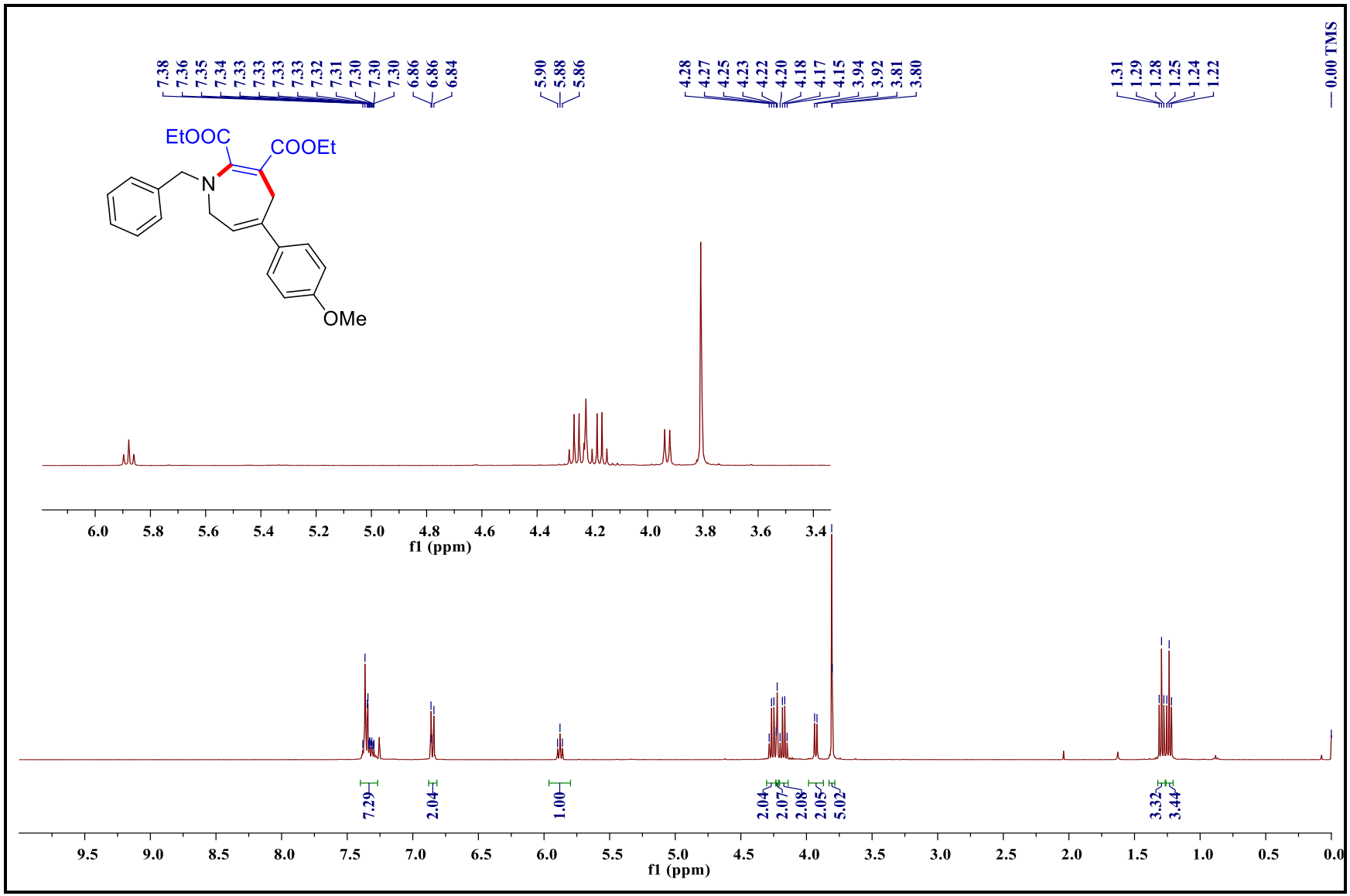
1H NMR spectrum of diethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3e):



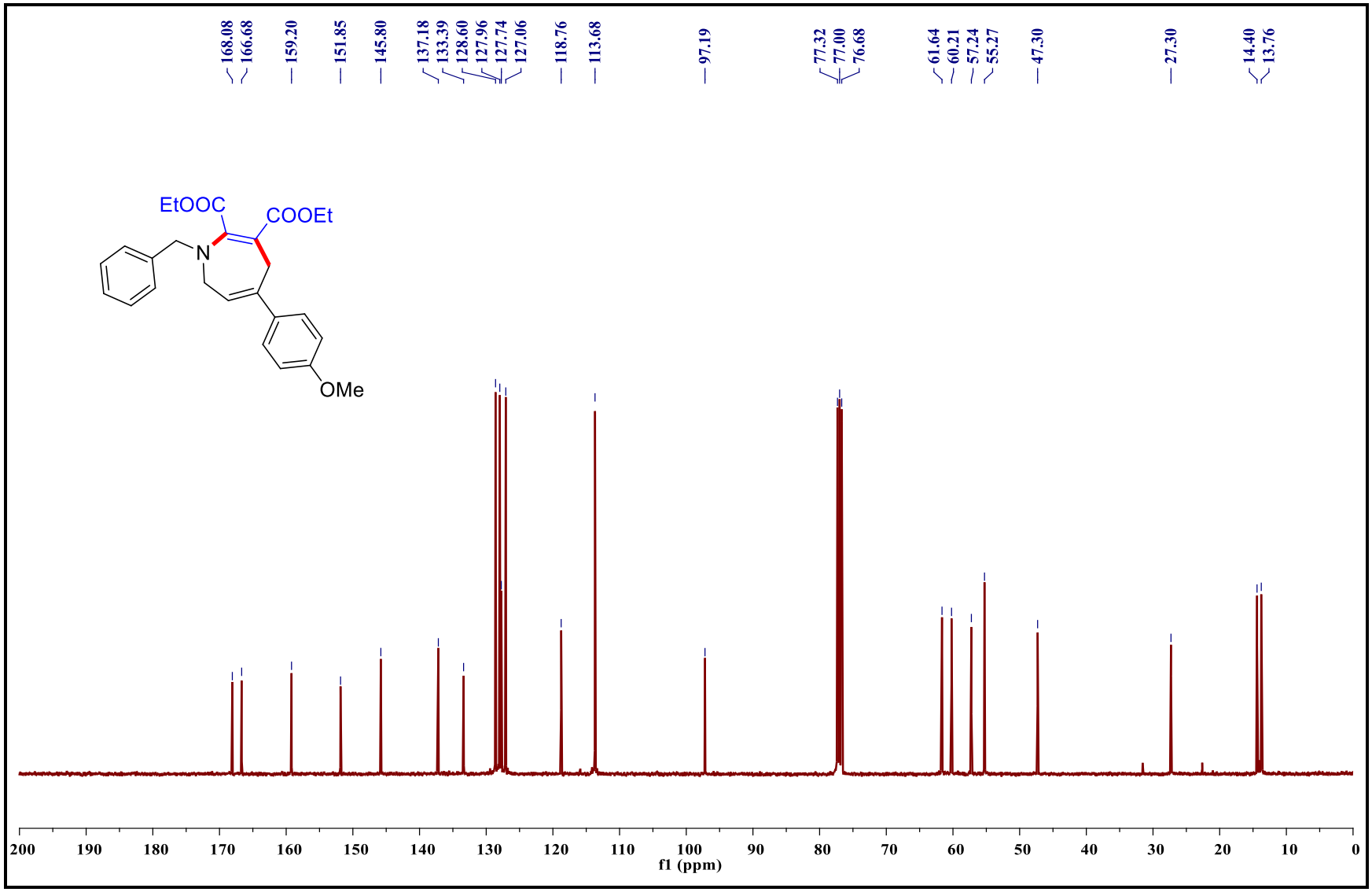
13C NMR spectrum of diethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3e):



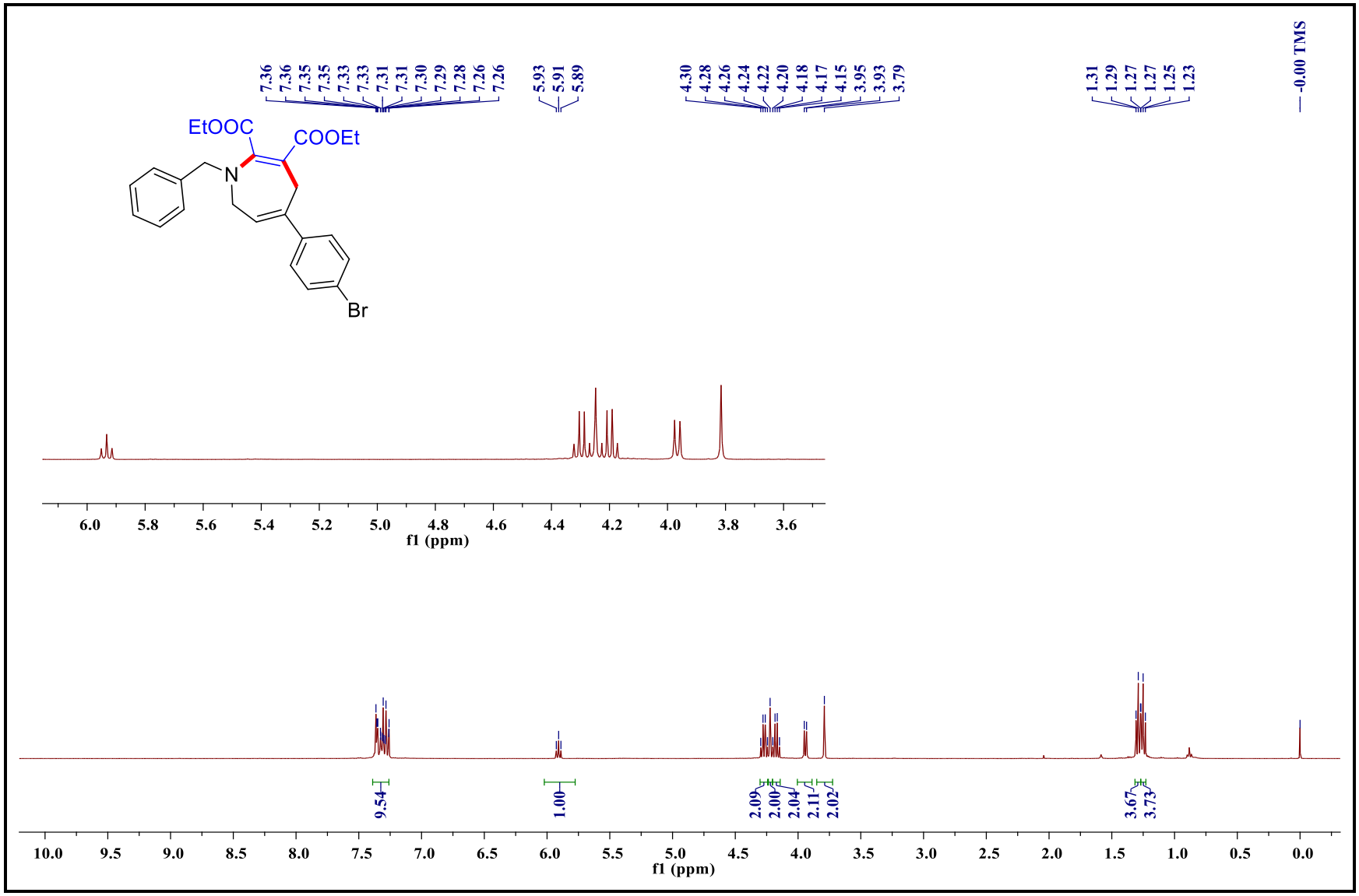
1H NMR spectrum of diethyl 1-benzyl-5-(4-methoxyphenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3f):



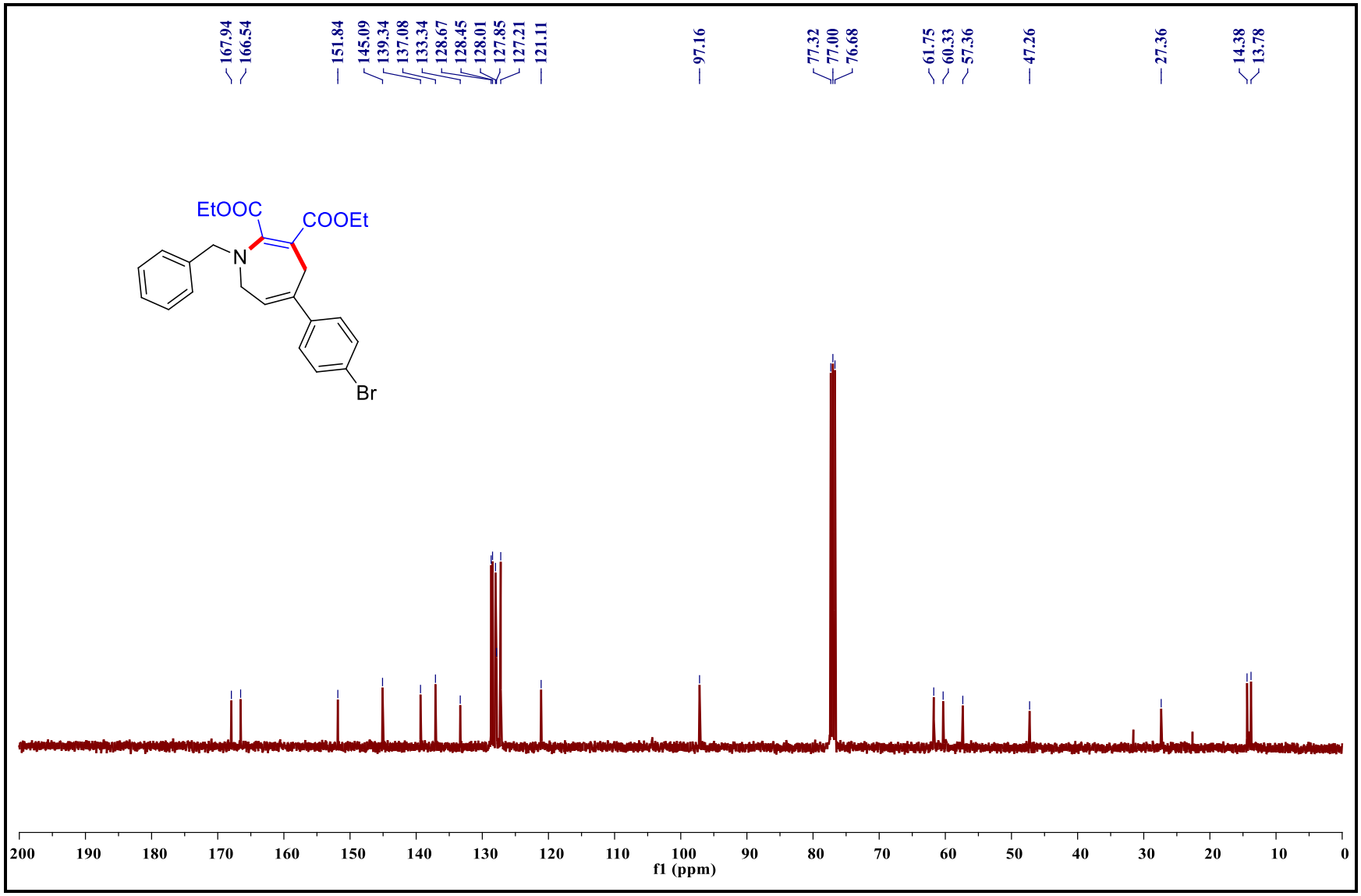
13C NMR spectrum of diethyl 1-benzyl-5-(4-methoxyphenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3f):



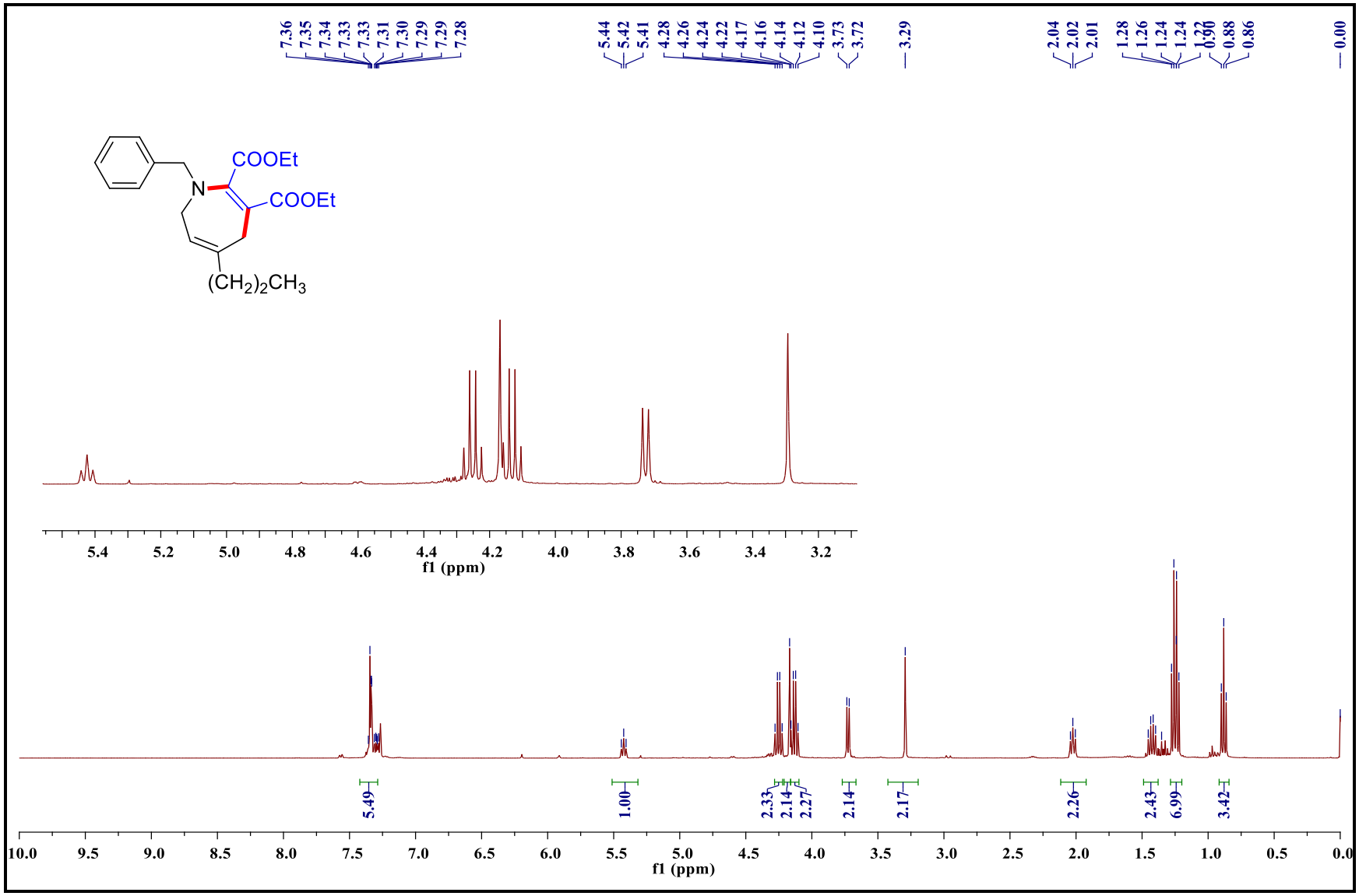
1H NMR diethyl 1-benzyl-5-(4-bromophenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3g):



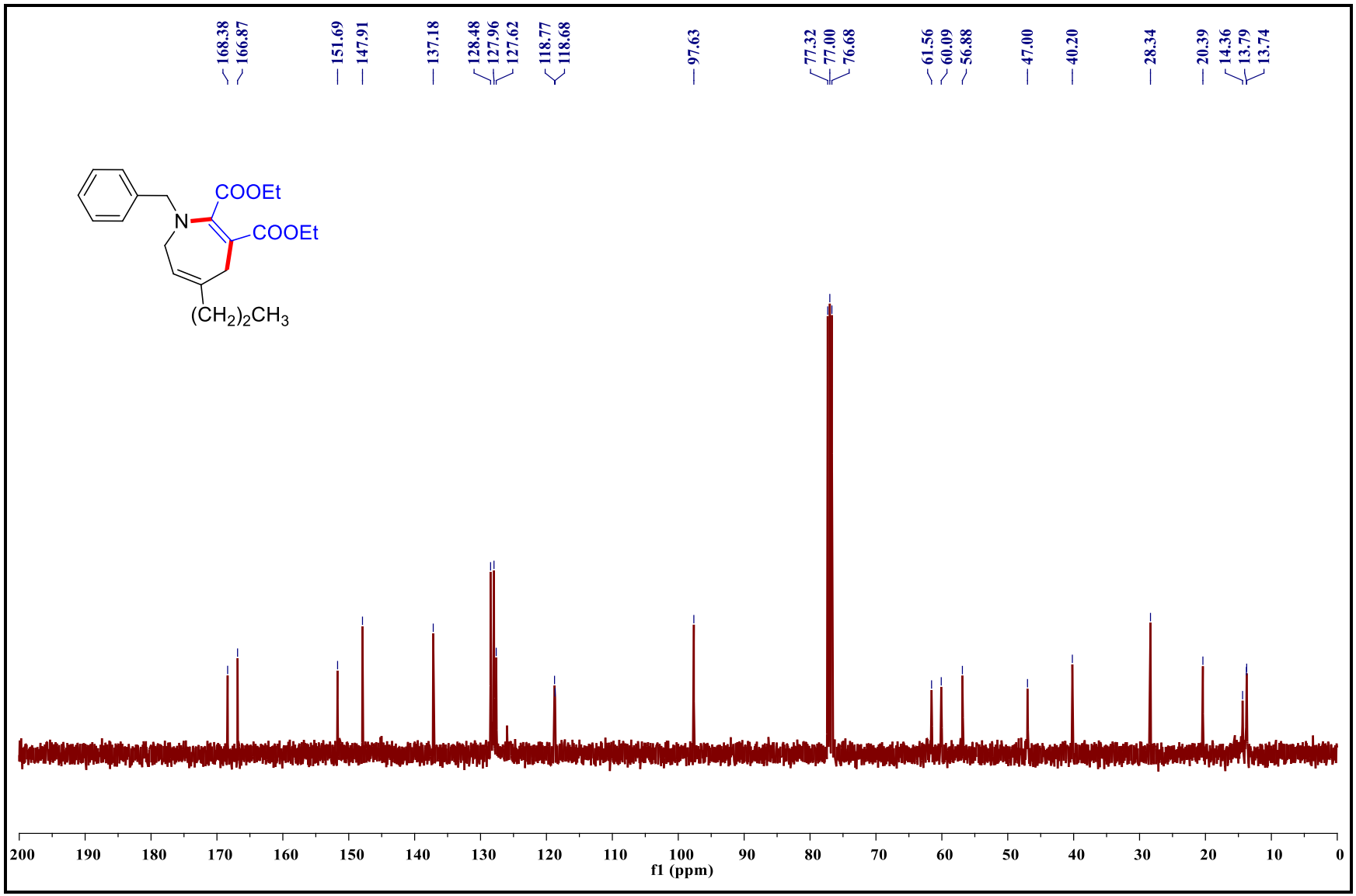
13C NMR spectrum of diethyl 1-benzyl-5-(4-bromophenyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3g):



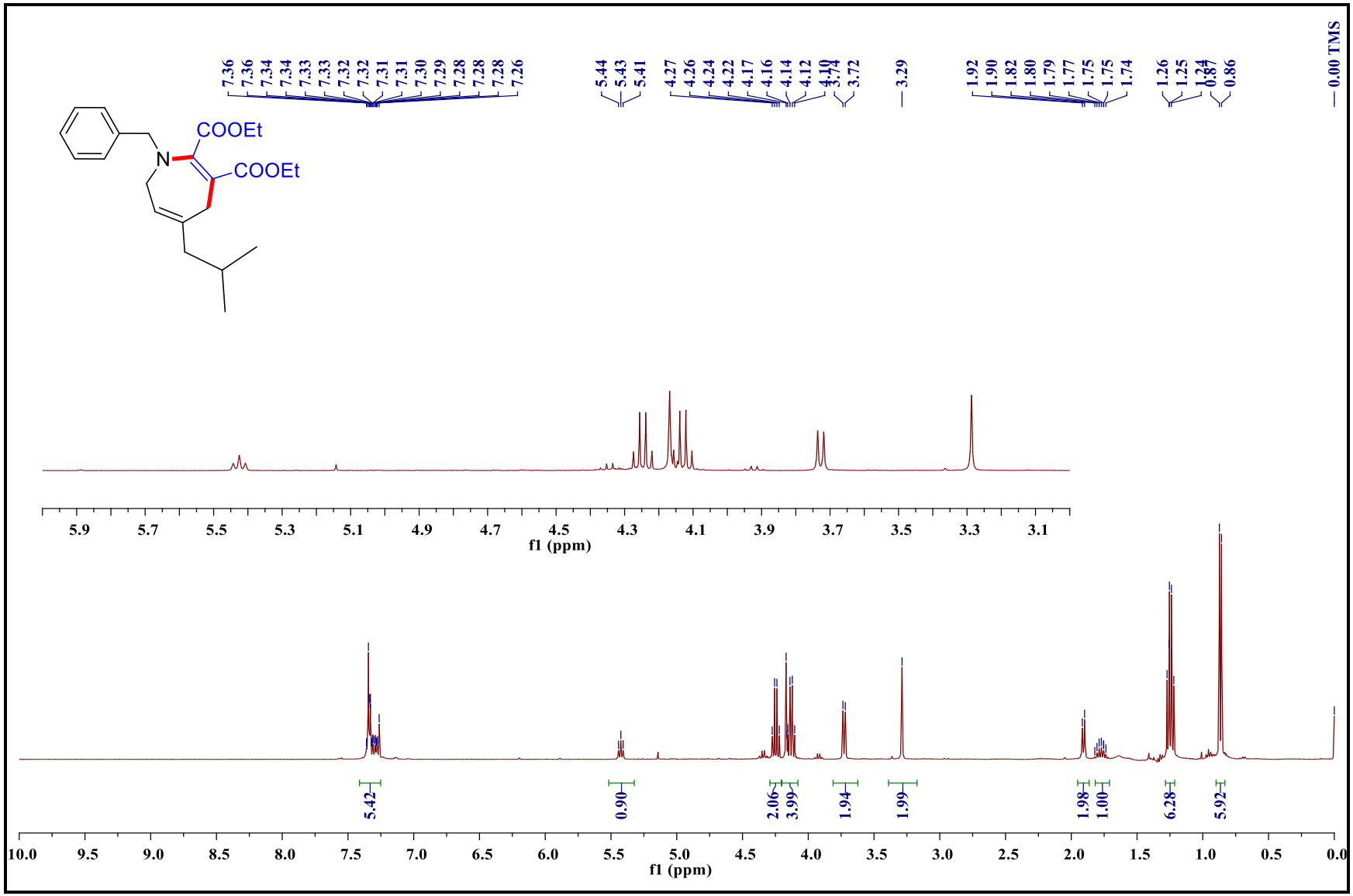
1H NMR spectrum of diethyl 1-benzyl-5-propyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3h):



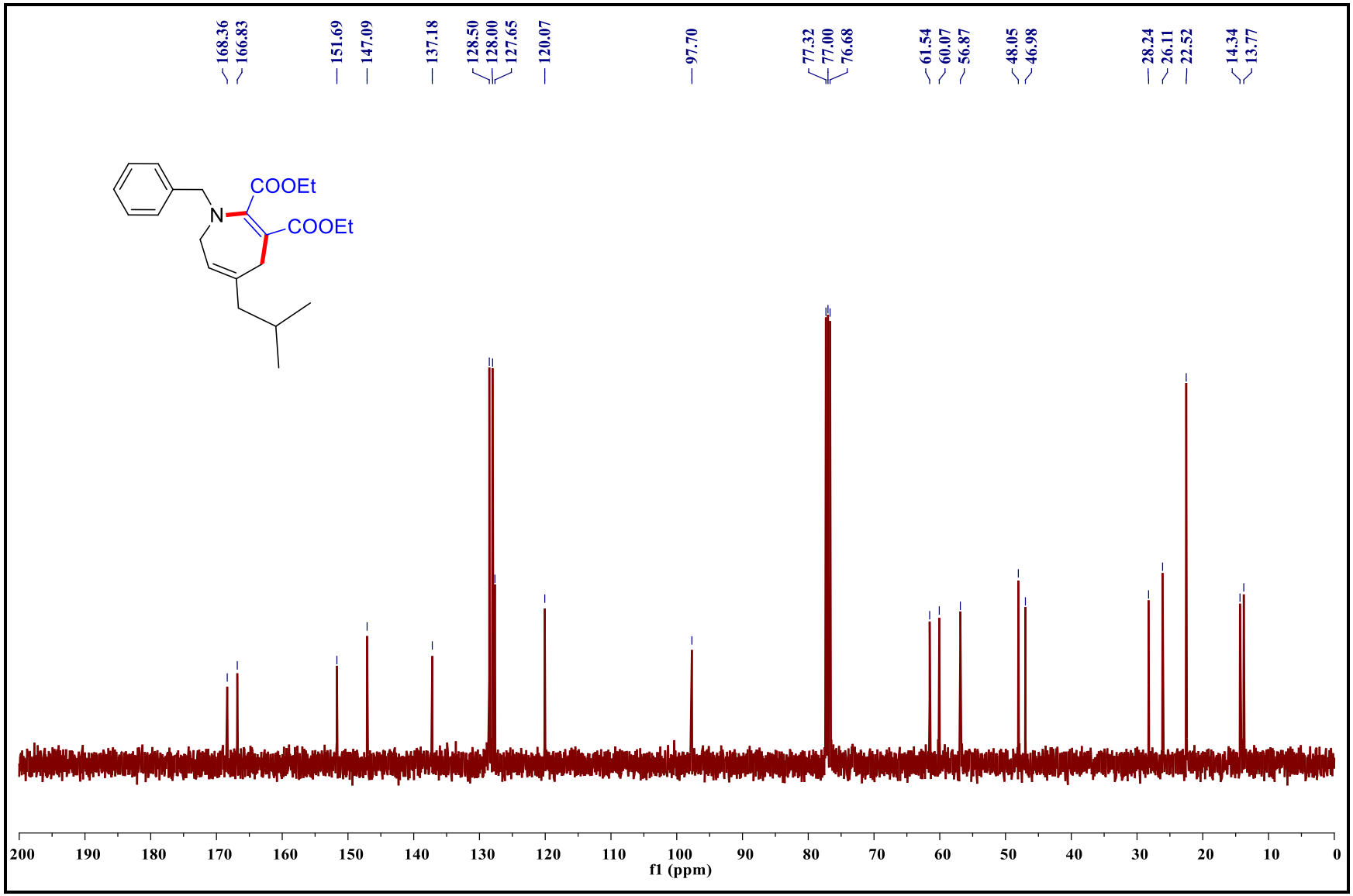
13C NMR spectrum of diethyl 1-benzyl-5-propyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3h):



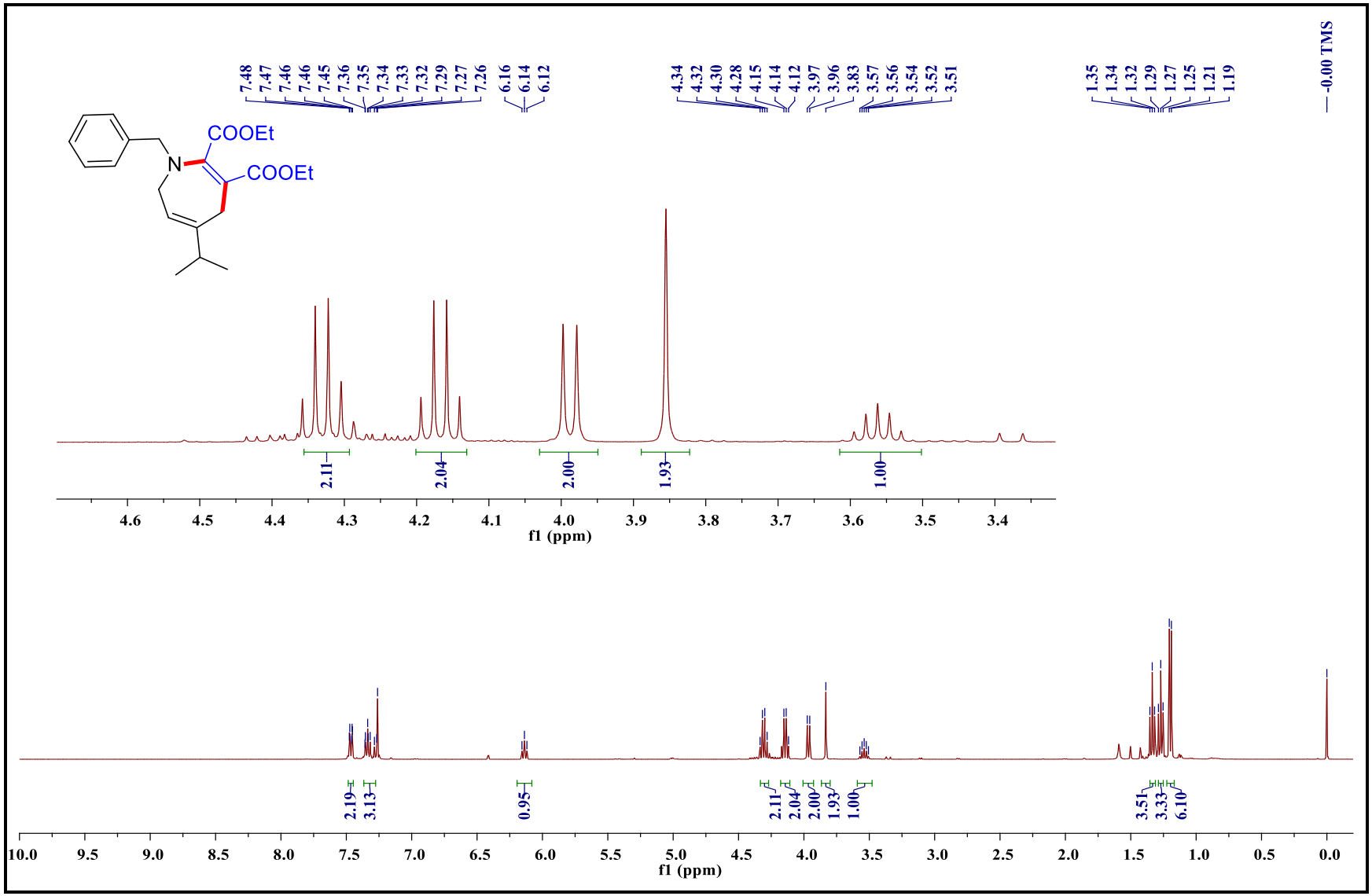
1H NMR spectrum of diethyl 1-benzyl-5-isobutyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3i):



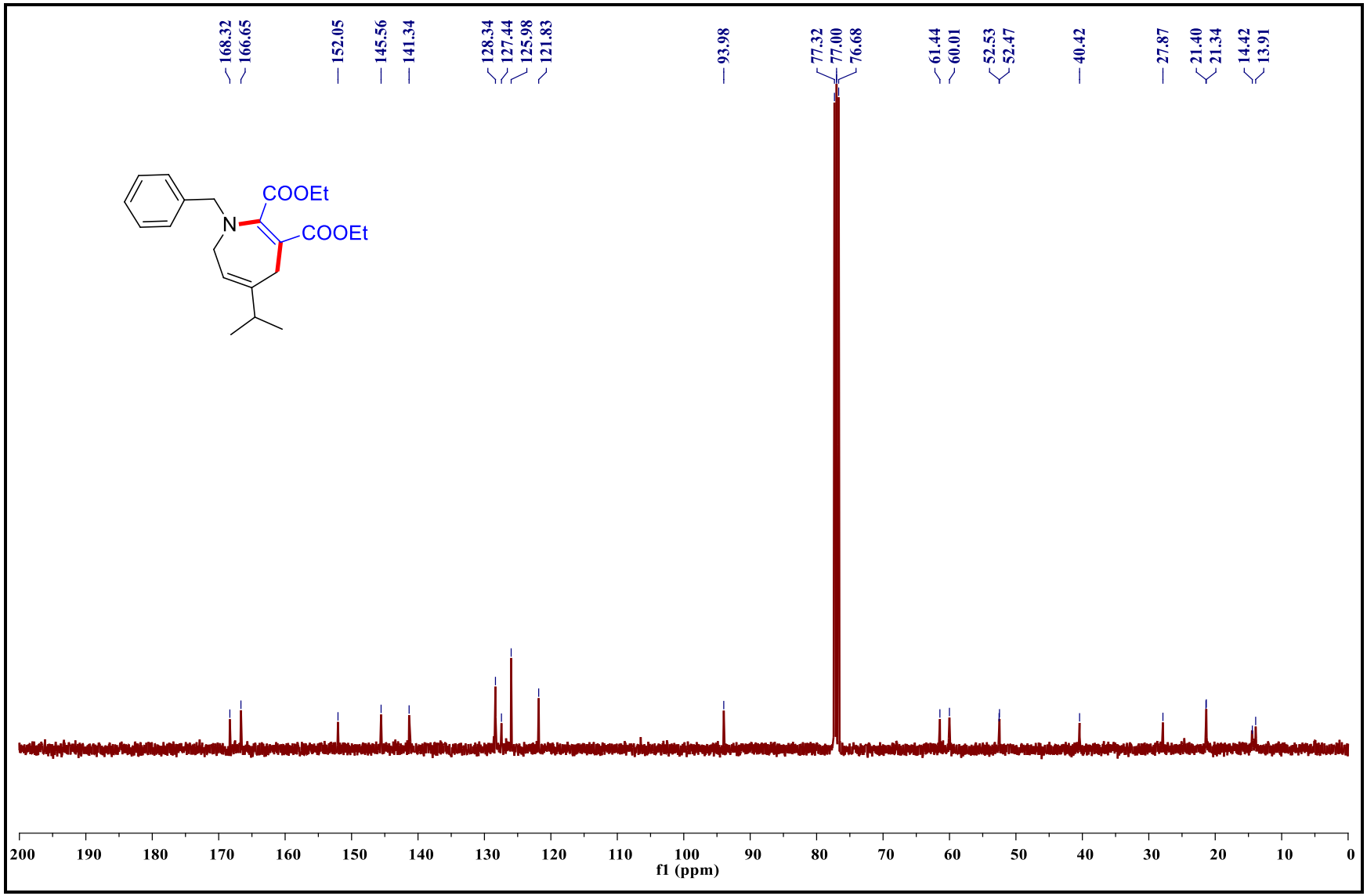
13C NMR spectrum of diethyl 1-benzyl-5-isobutyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3i):



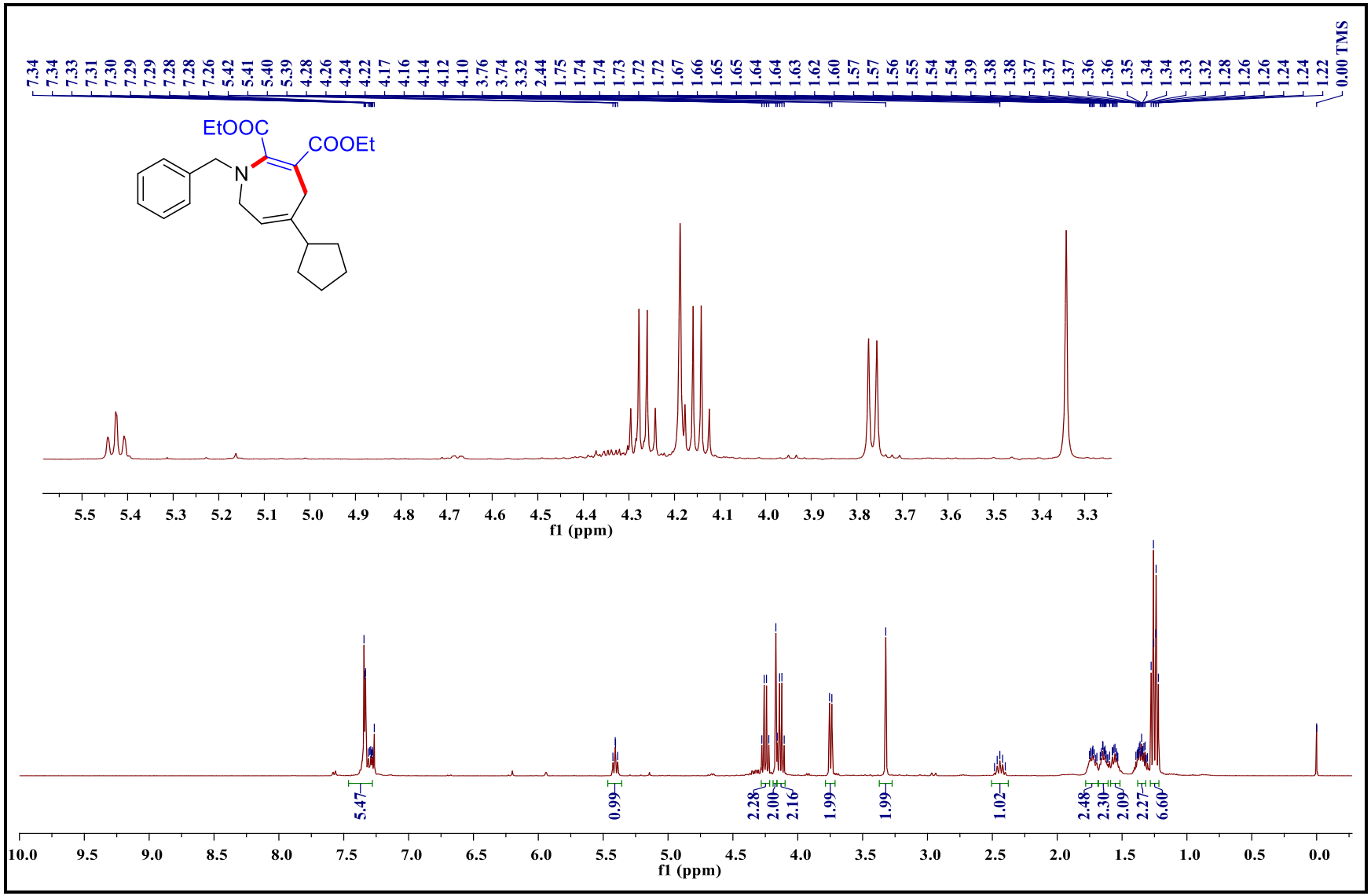
1H NMR spectrum of diethyl 1-benzyl-5-isopropyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3j):



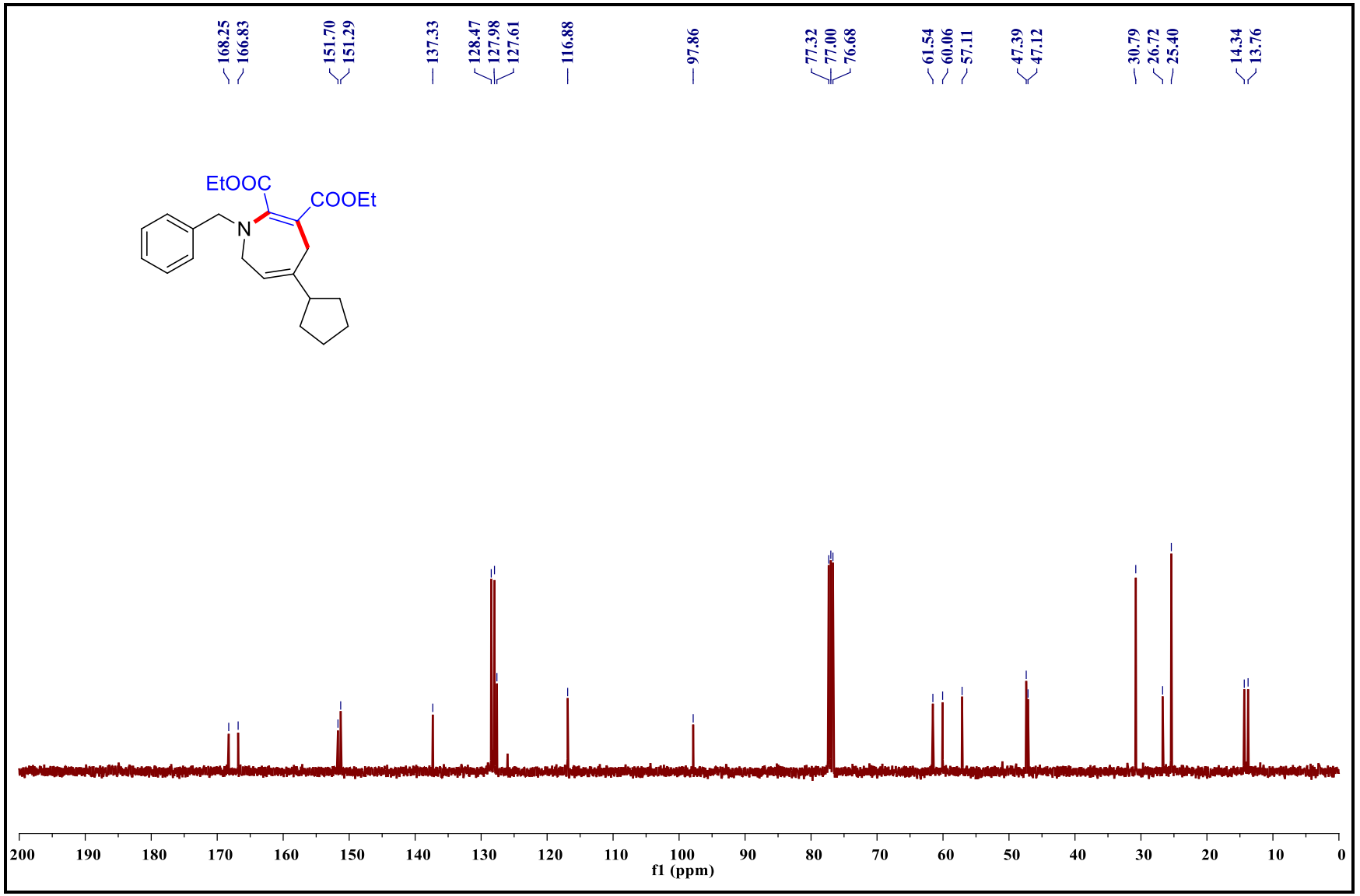
13C NMR of diethyl 1-benzyl-5-isopropyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3j):



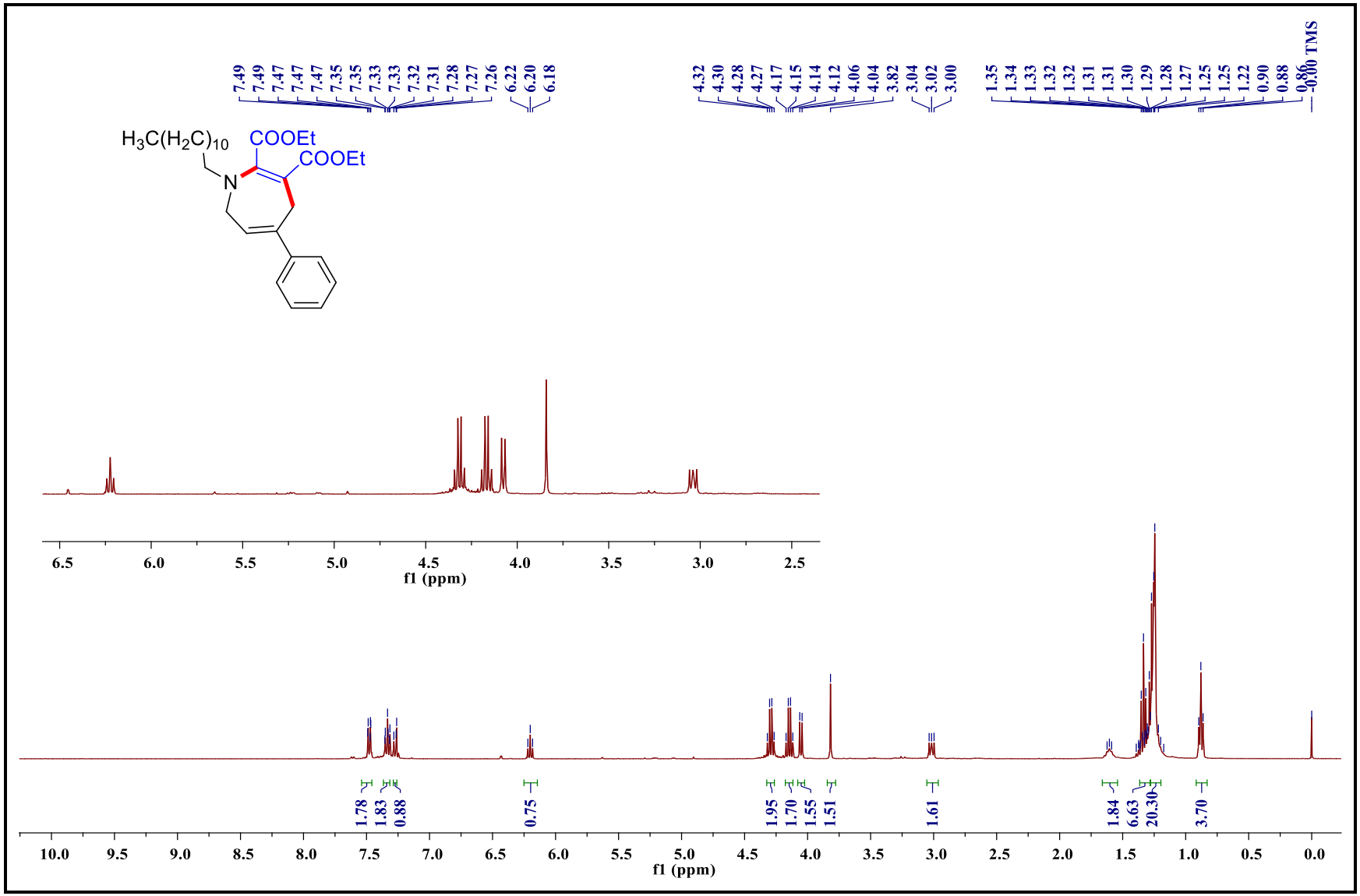
1H NMR of diethyl 1-benzyl-5-cyclopentyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3k):



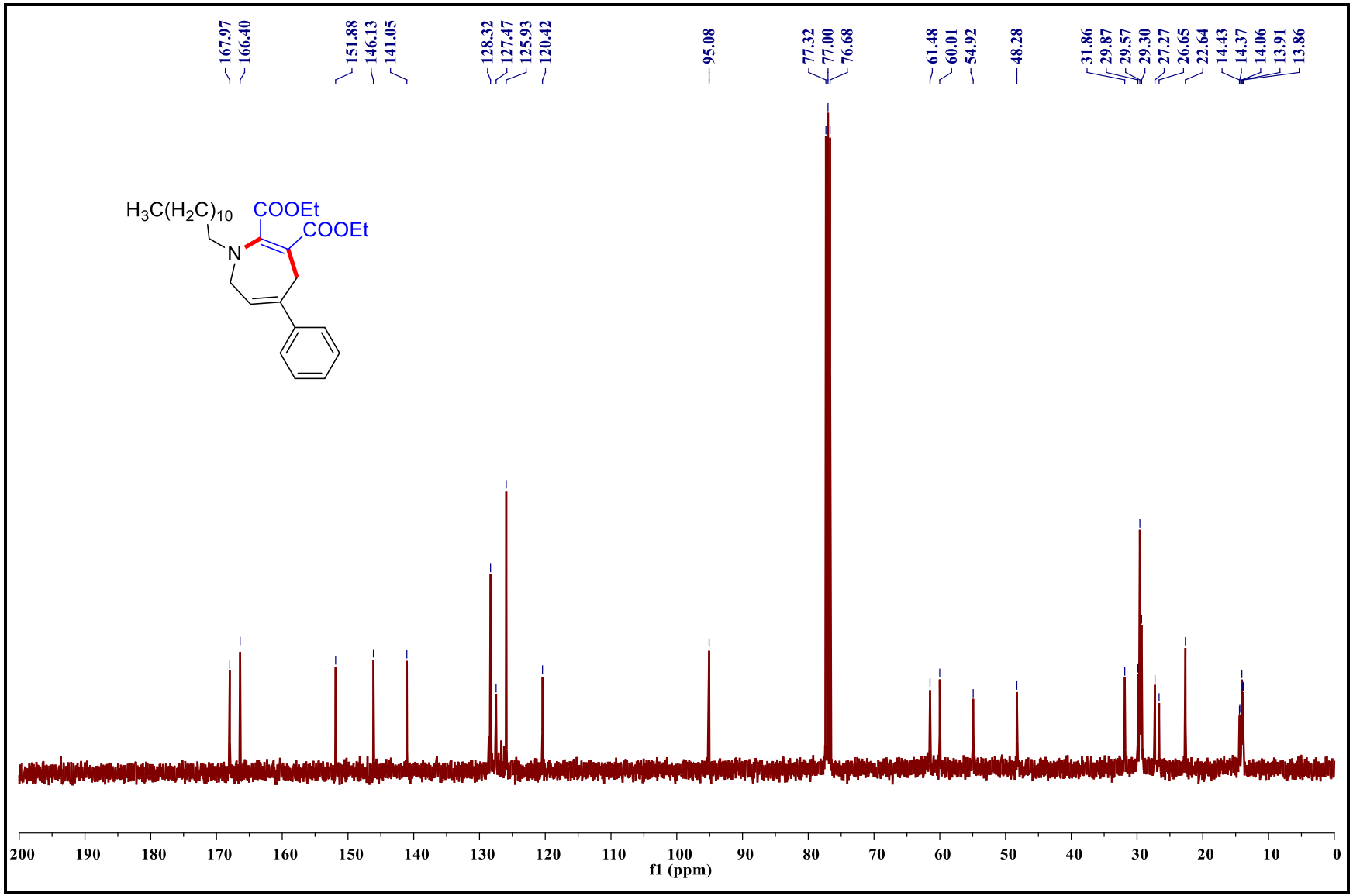
13C NMR of diethyl 1-benzyl-5-cyclopentyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3k):



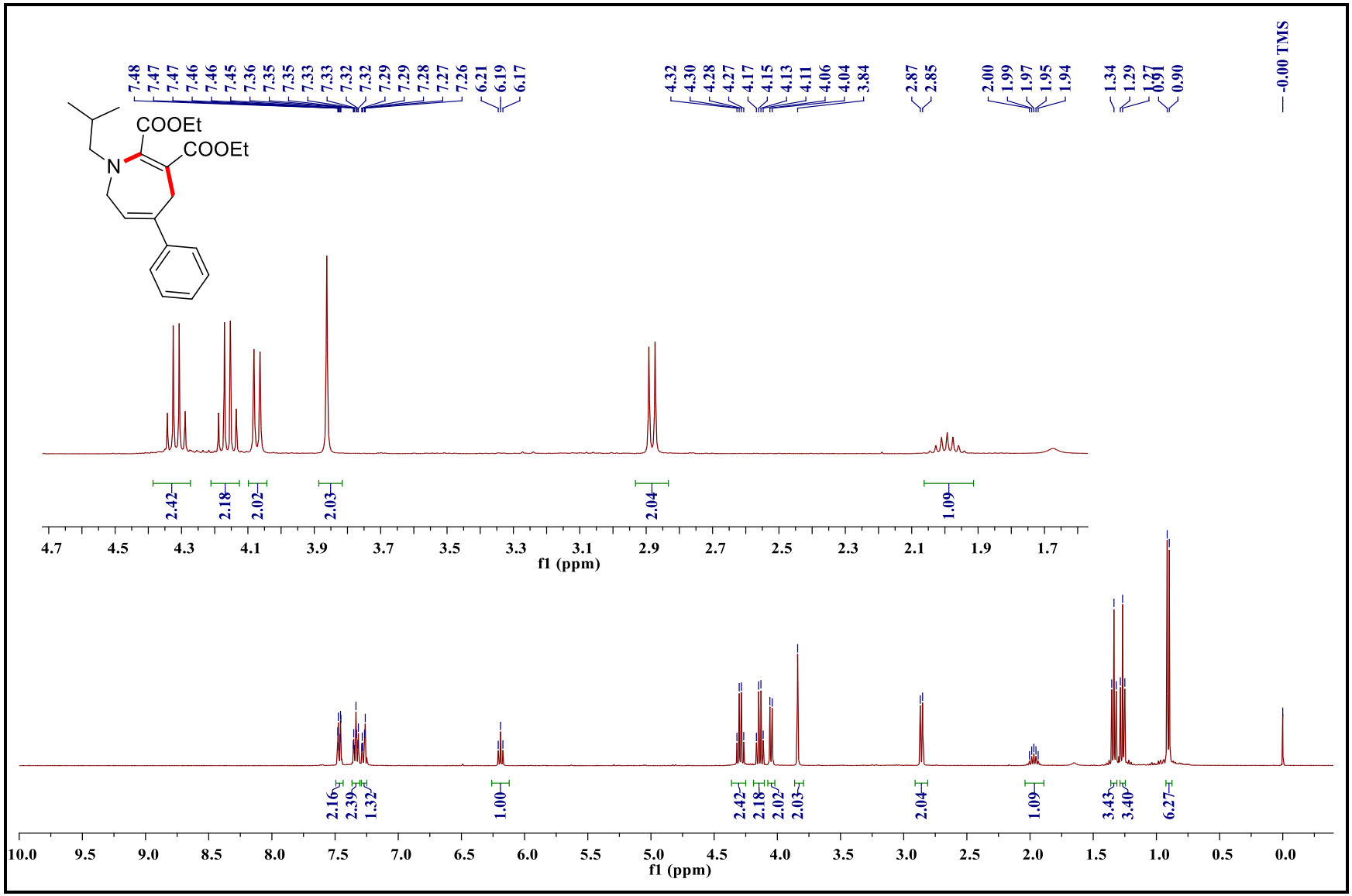
1H NMR spectrum of diethyl 1-dodecyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3l):



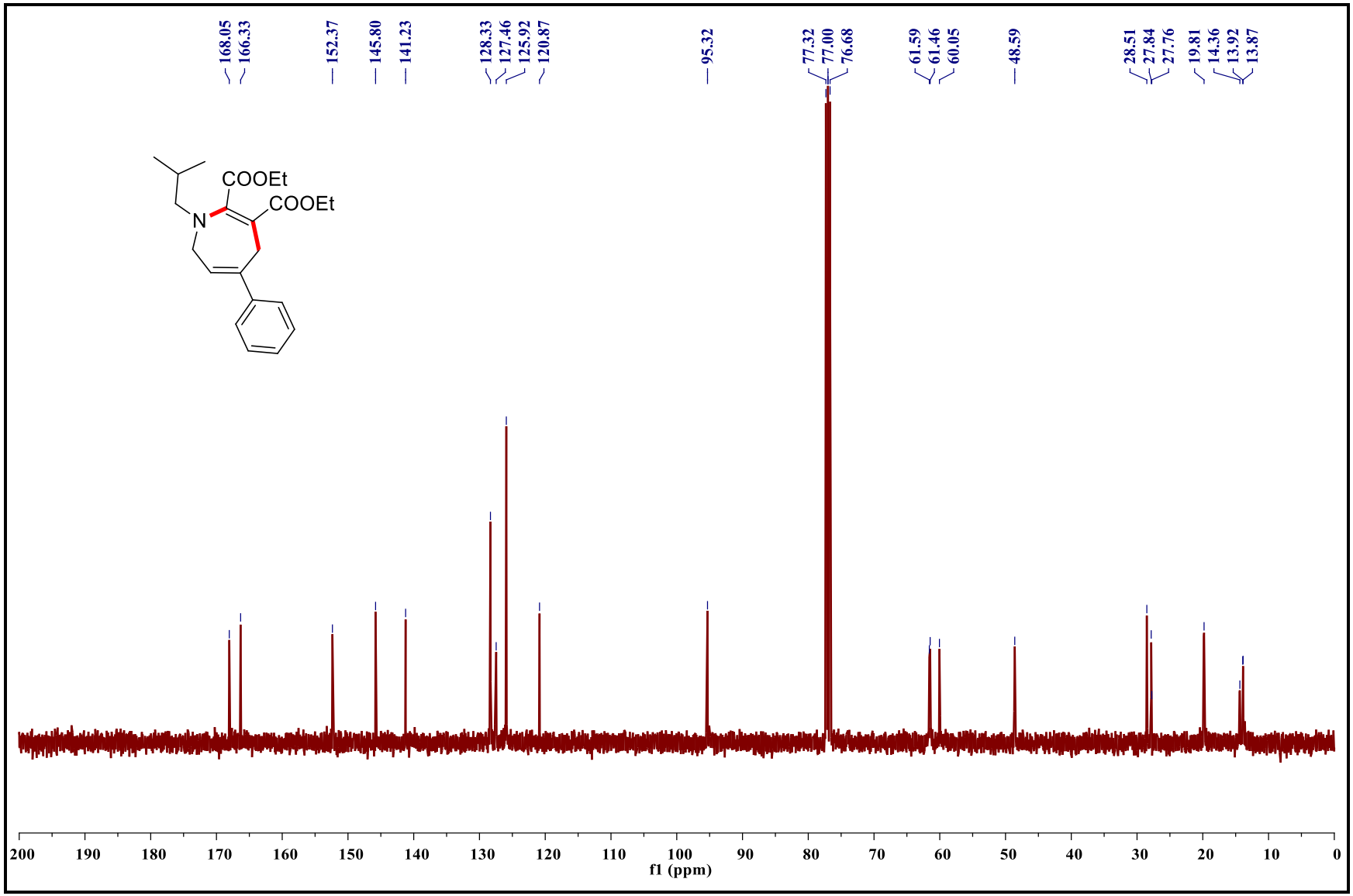
1H NMR spectrum of diethyl 1-dodecyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3l):



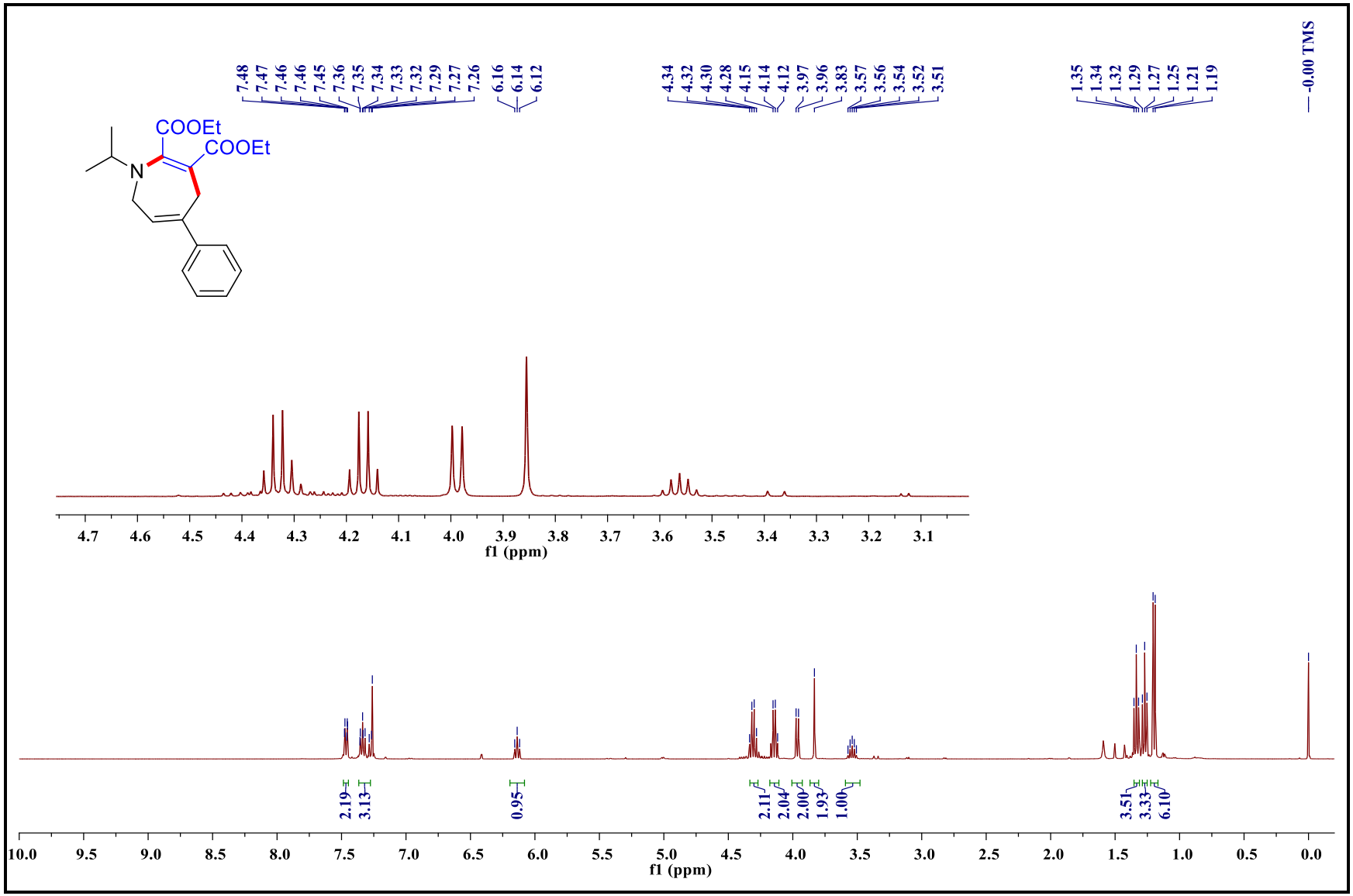
1H NMR spectrum of diethyl 1-isobutyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3m):



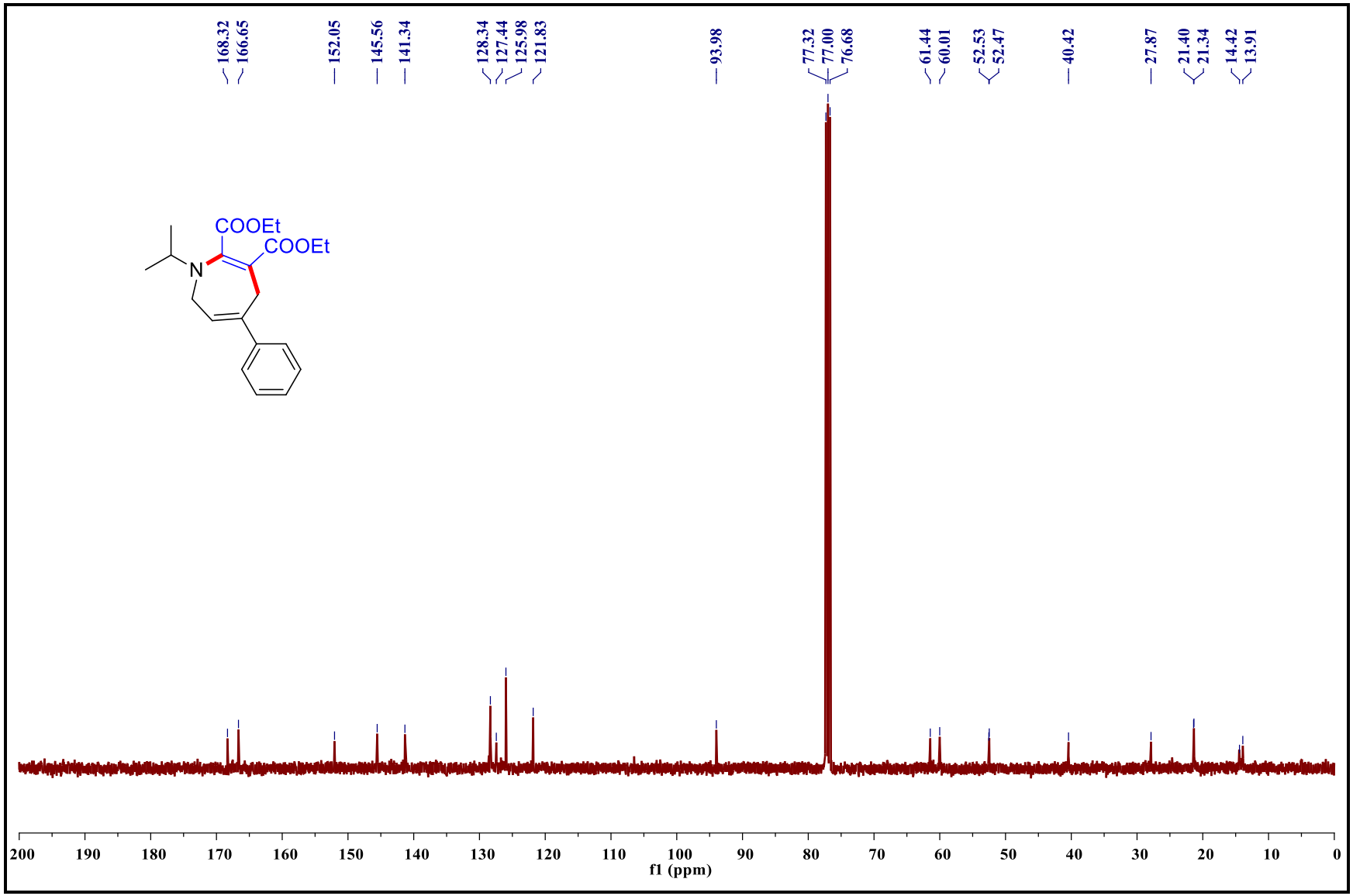
13C NMR spectrum of diethyl 1-isobutyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3m):



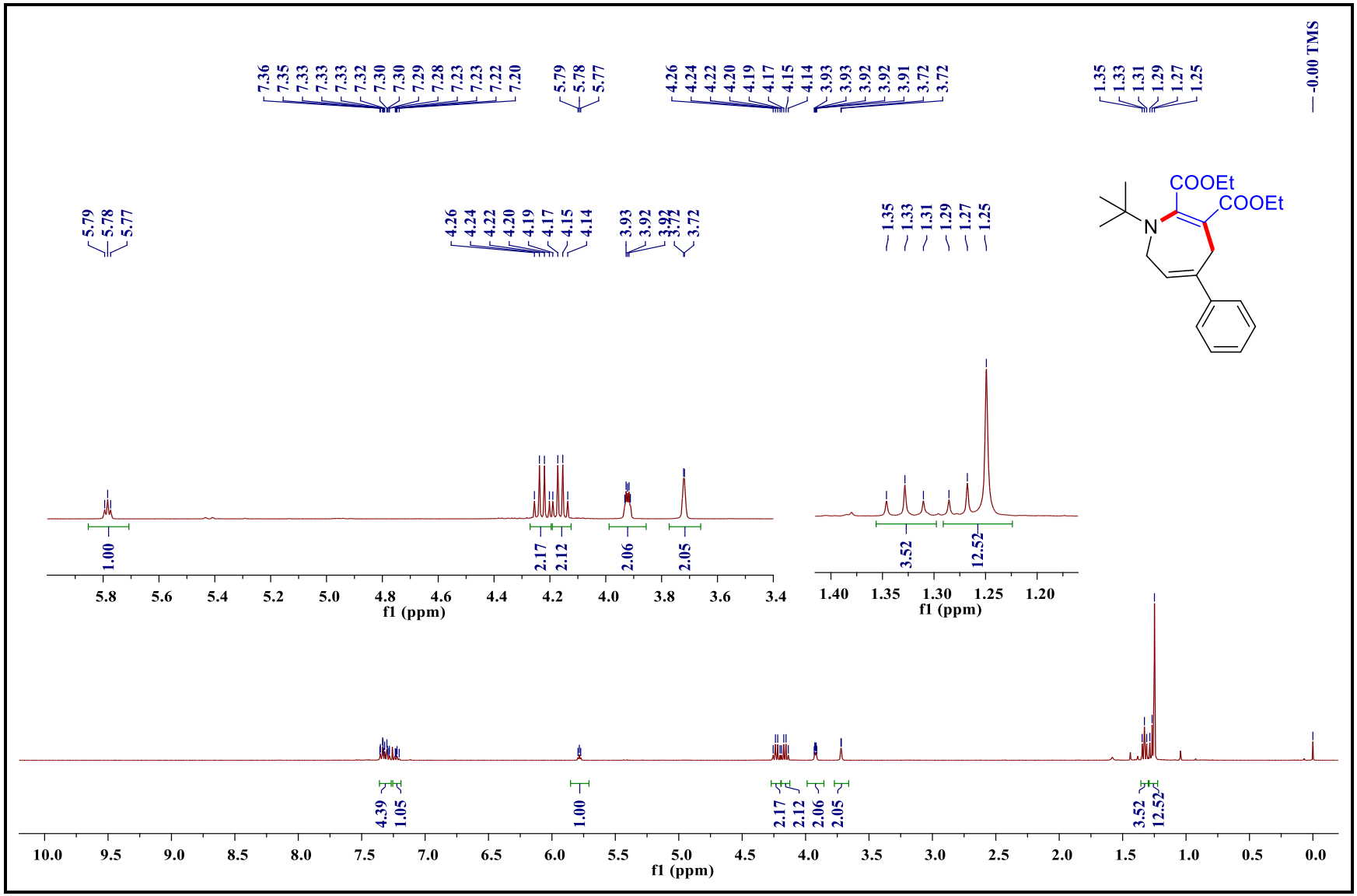
1H NMR spectrum of diethyl 1-isopropyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3n):



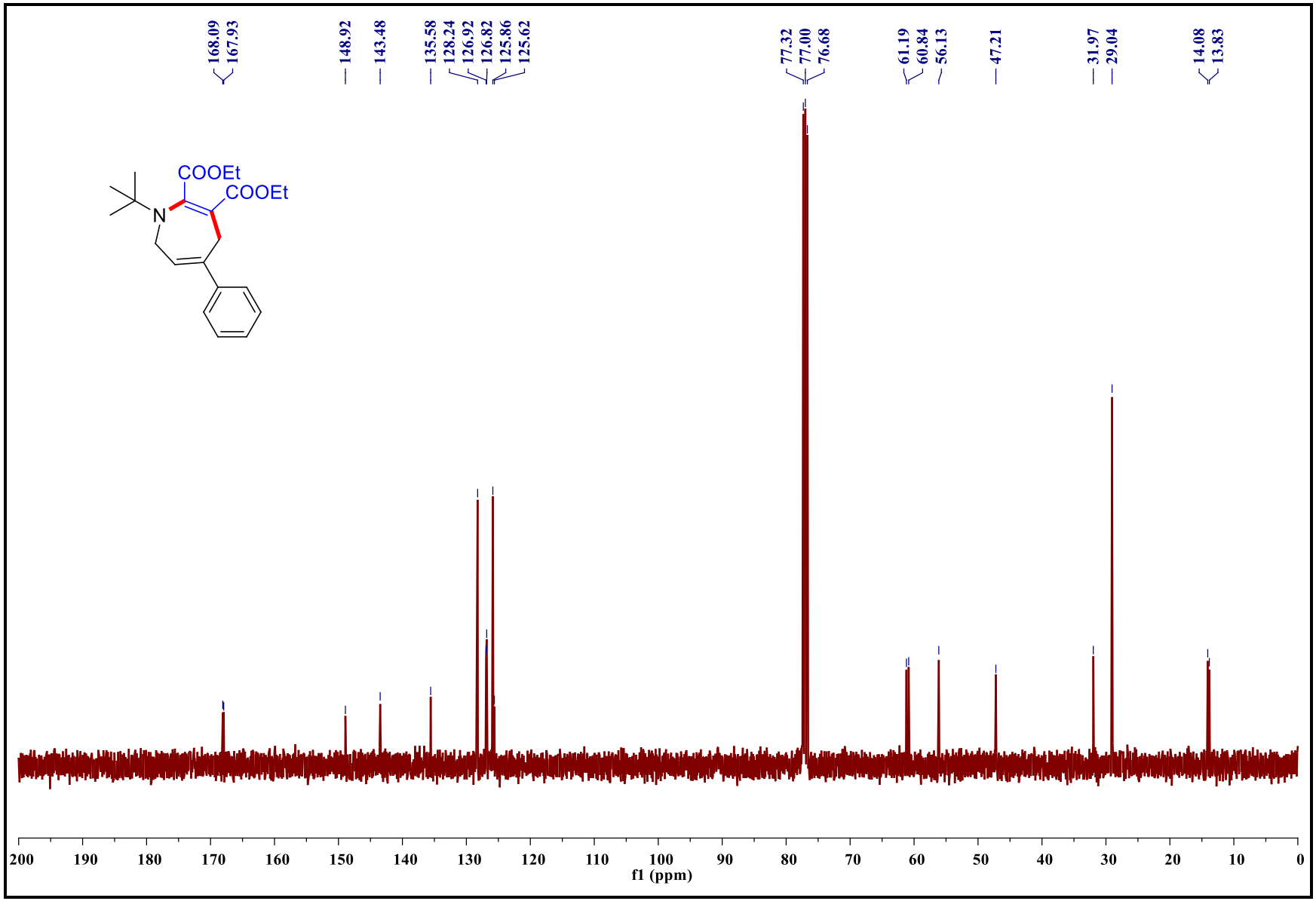
1H NMR spectrum of diethyl 1-isopropyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3n):



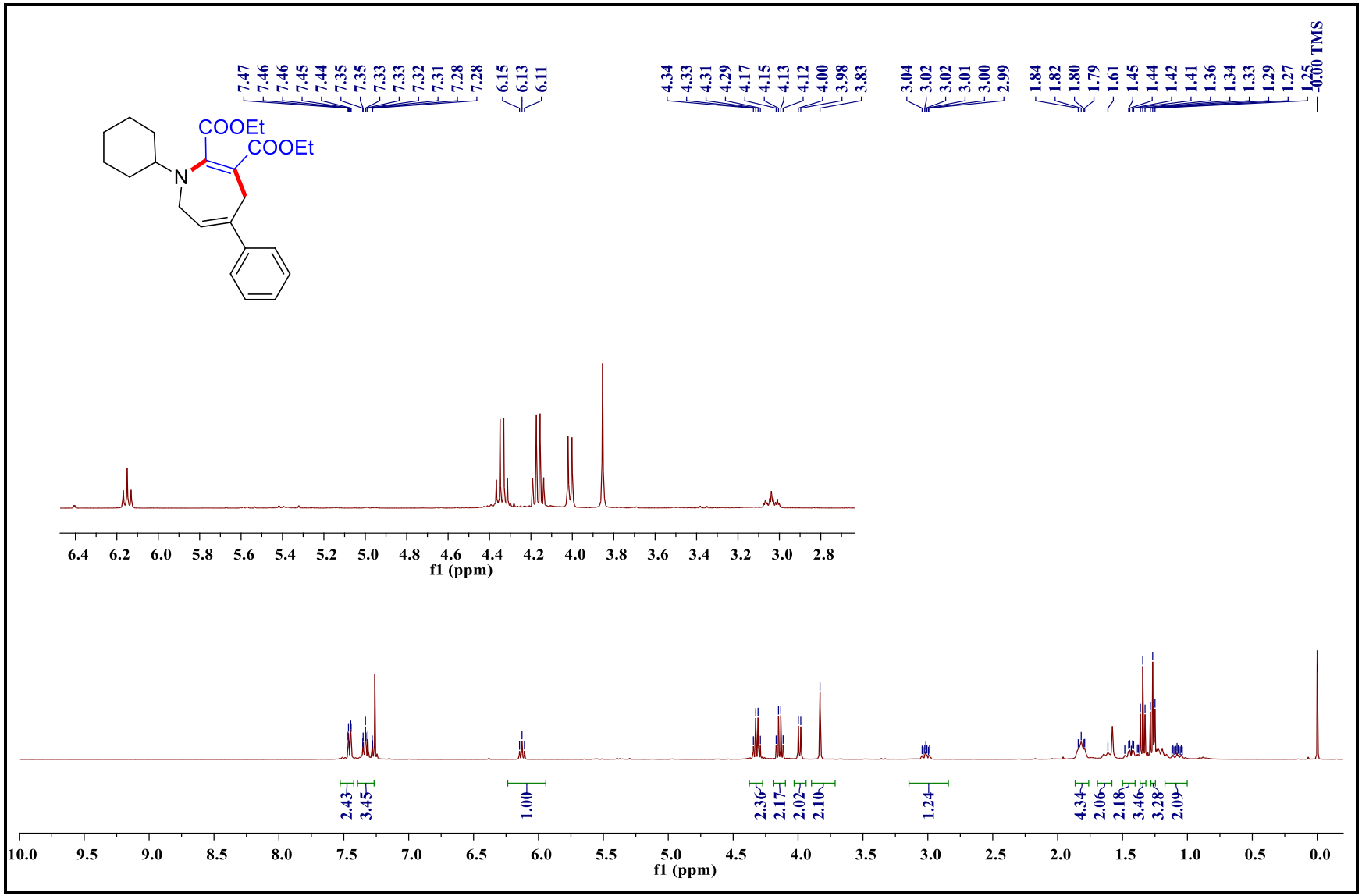
1H NMR spectrum of diethyl 1-(tert-butyl)-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3o):



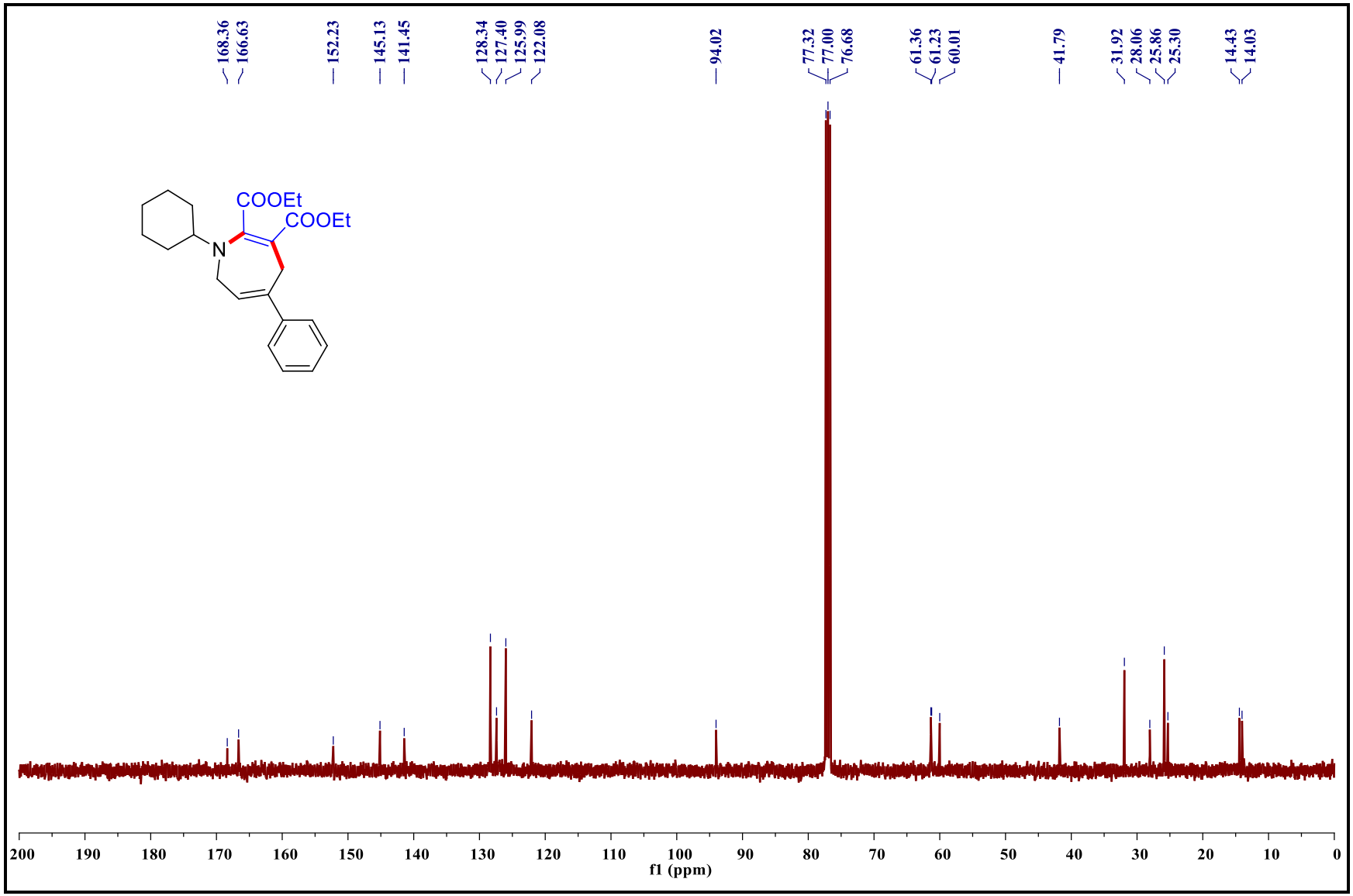
13C NMR spectrum of diethyl 1-(tert-butyl)-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3o):



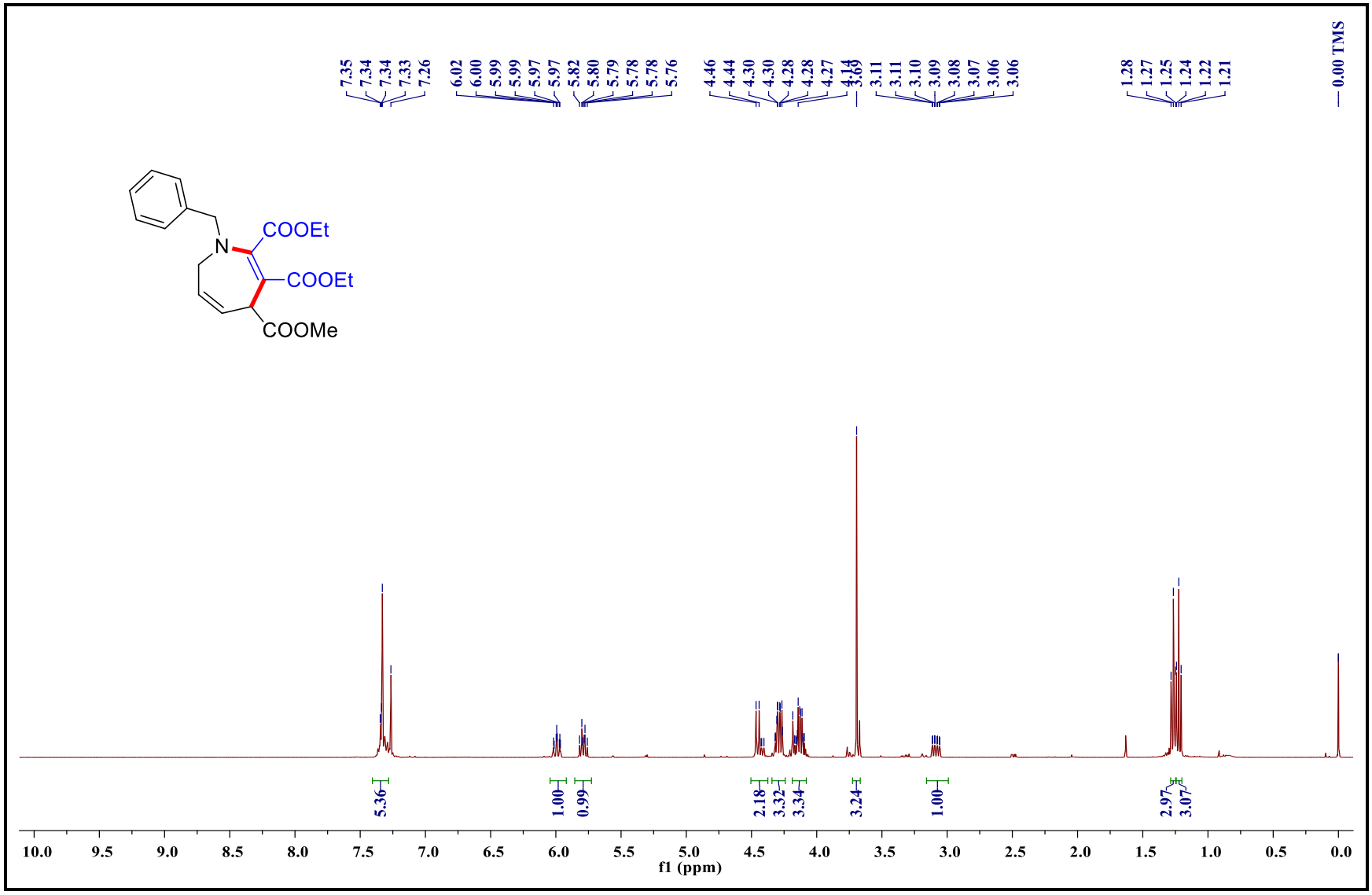
1H NMR spectrum of diethyl 1-cyclohexyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3p):



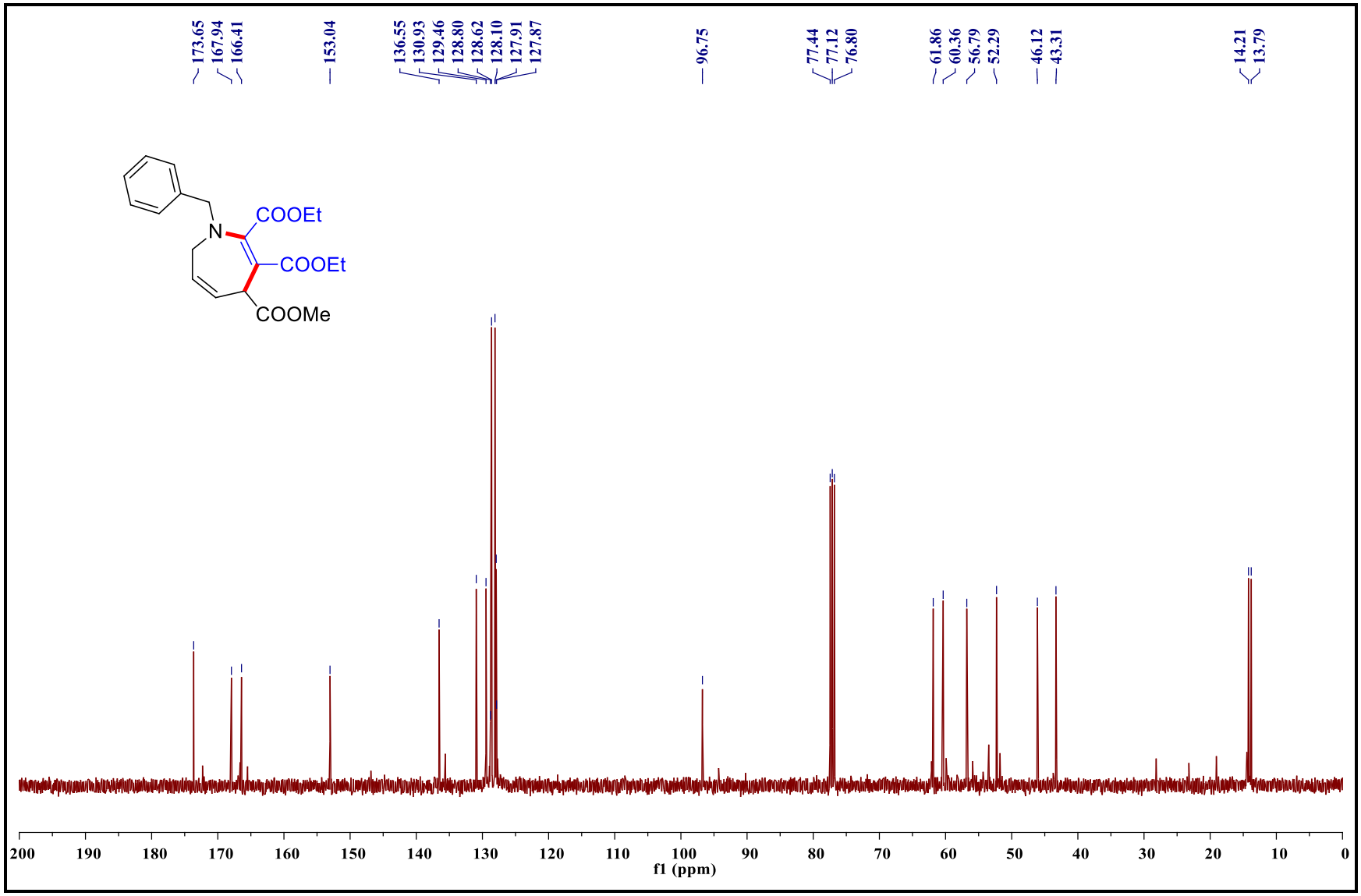
13C NMR spectrum of diethyl 1-cyclohexyl-5-phenyl-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3p):



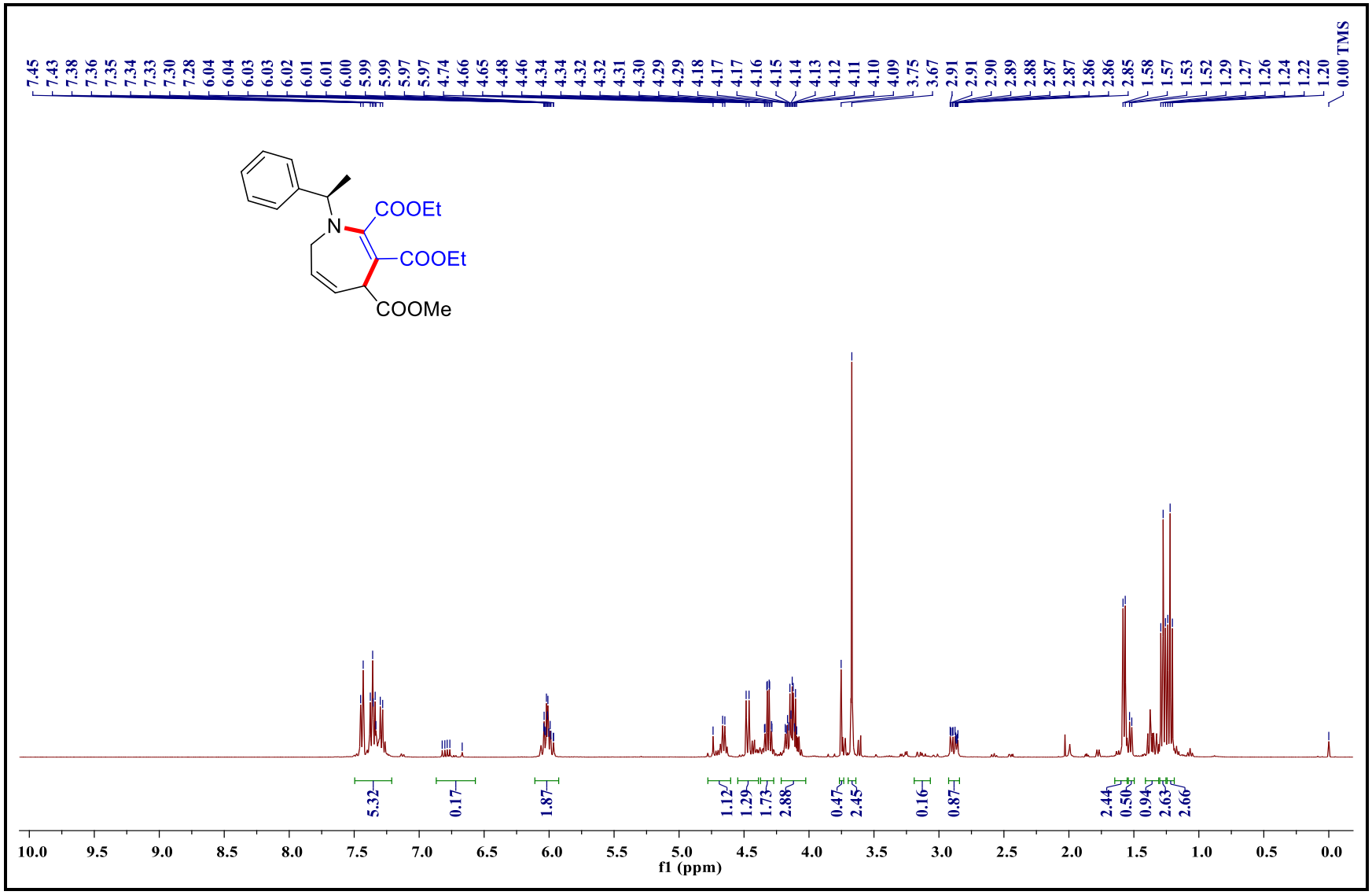
1H NMR spectrum of 2,3-diethyl 4-methyl 1-benzyl-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3q):



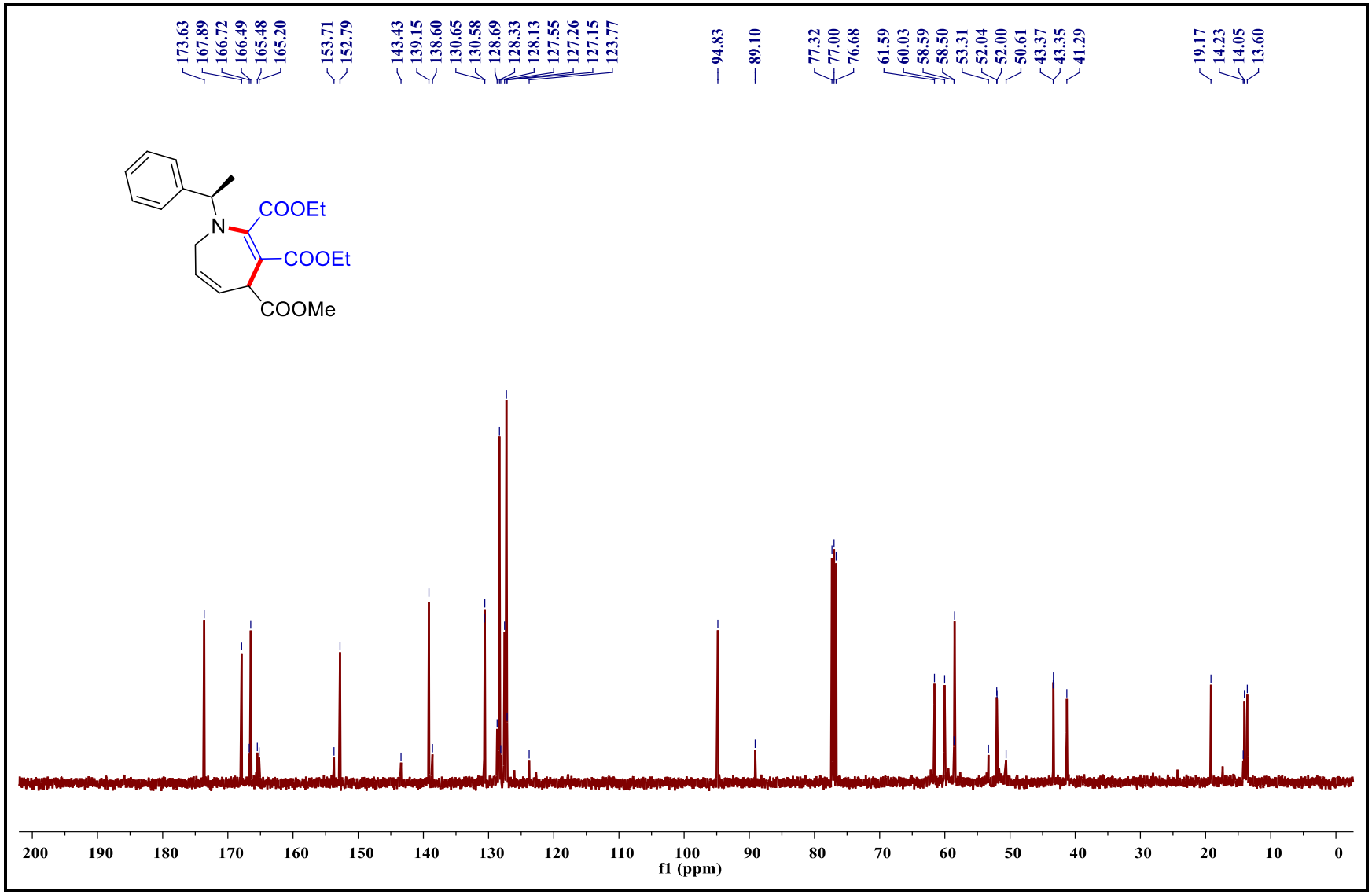
13C NMR spectrum of 2,3-diethyl 4-methyl 1-benzyl-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3q):



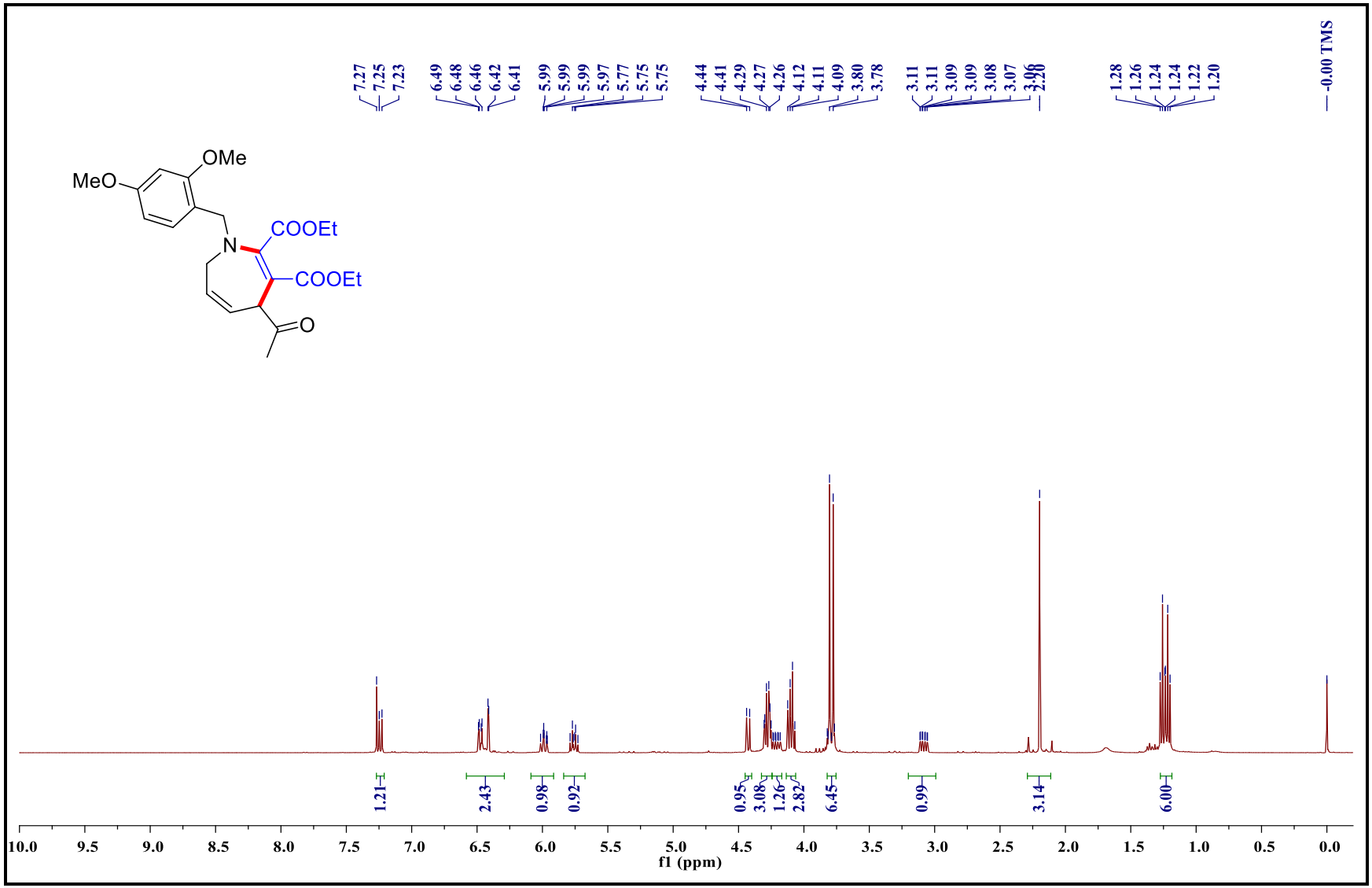
1H NMR spectrum of 2,3-diethyl 4-methyl 1-((R)-1-phenylethyl)-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3r):



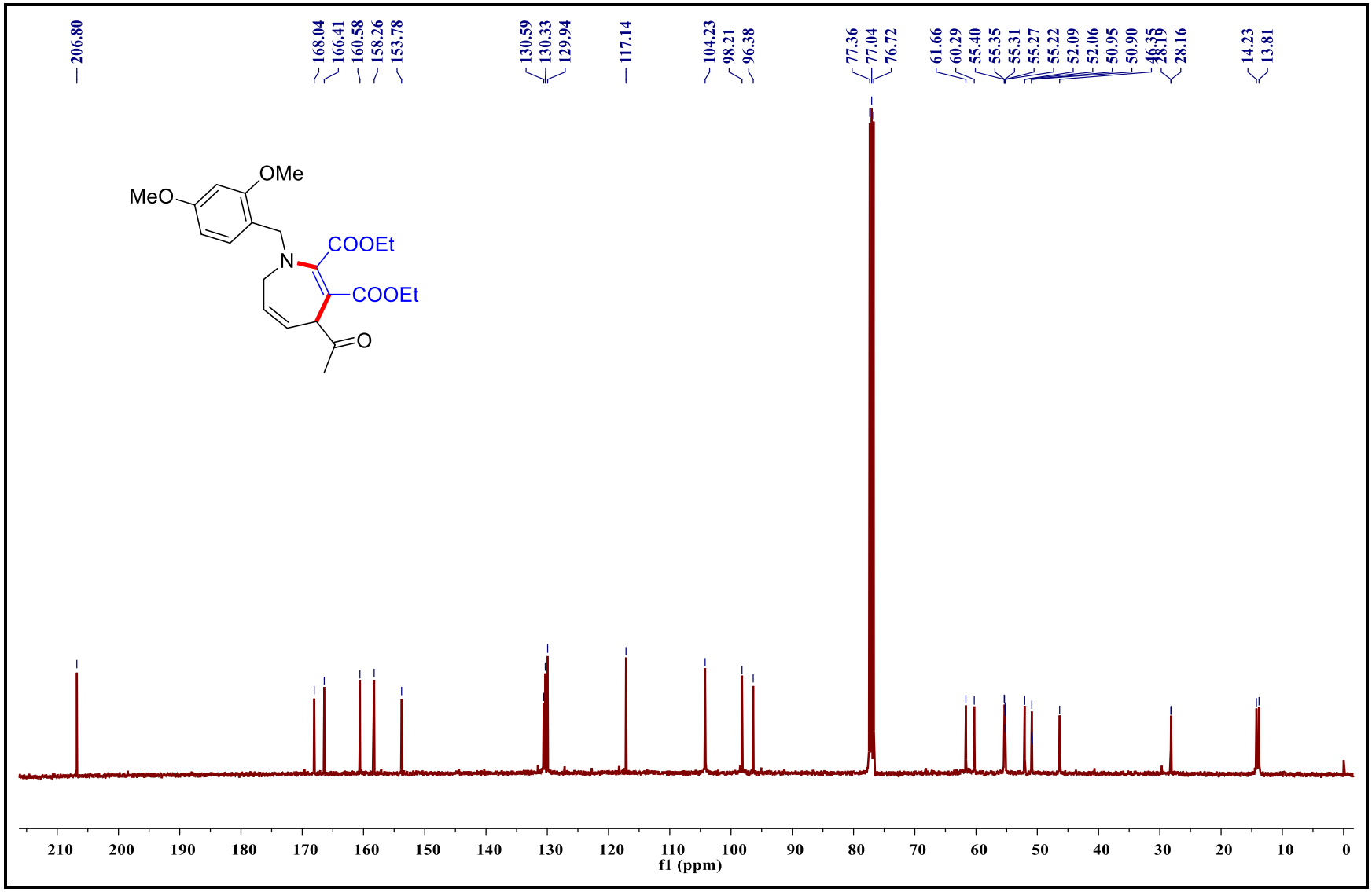
1H NMR spectrum of 2,3-diethyl 4-methyl 1-((R)-1-phenylethyl)-4,7-dihydro-1H-azepine-2,3,4-tricarboxylate (3r):



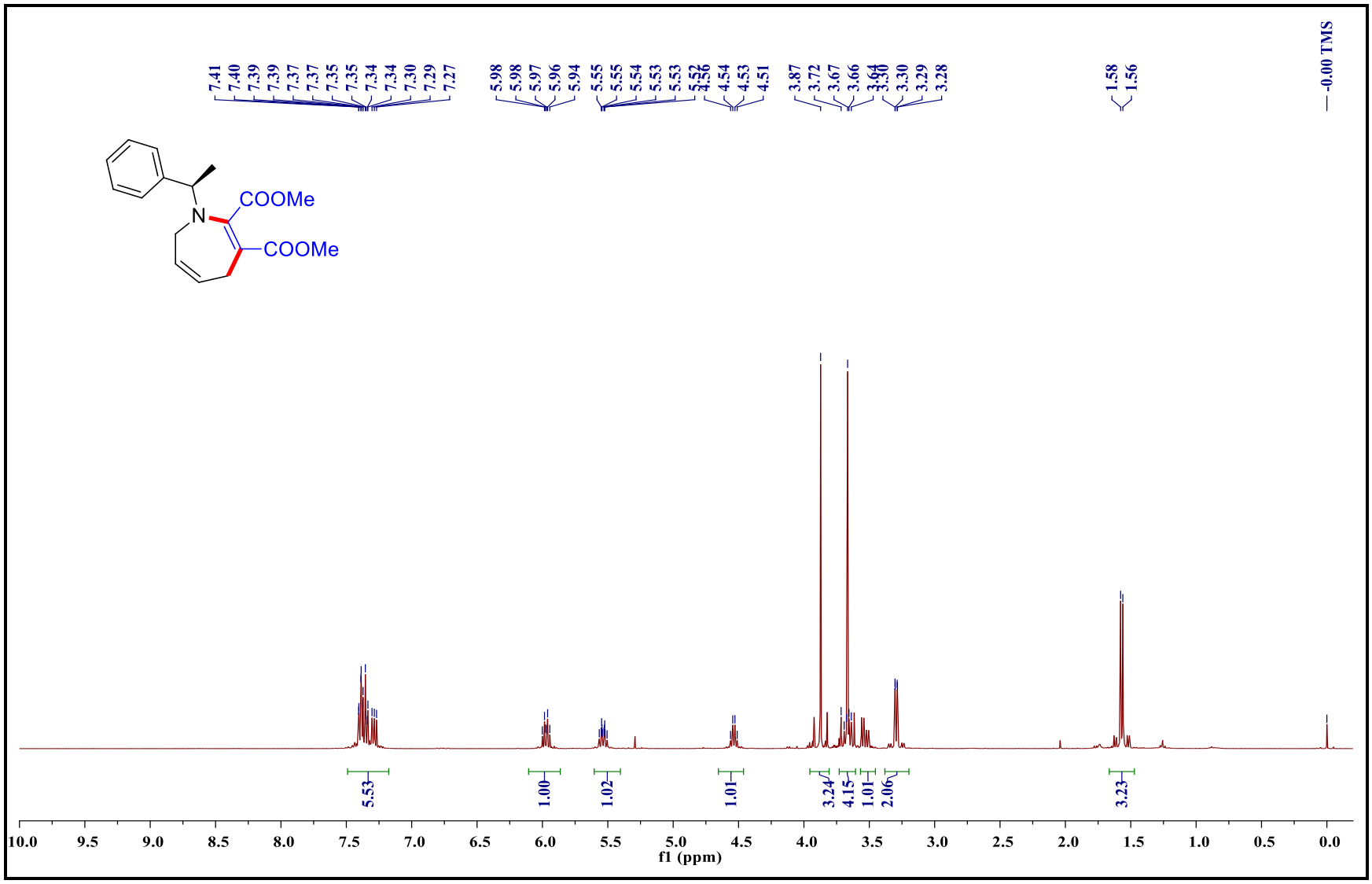
1H NMR spectrum of diethyl 4-acetyl-1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3s):



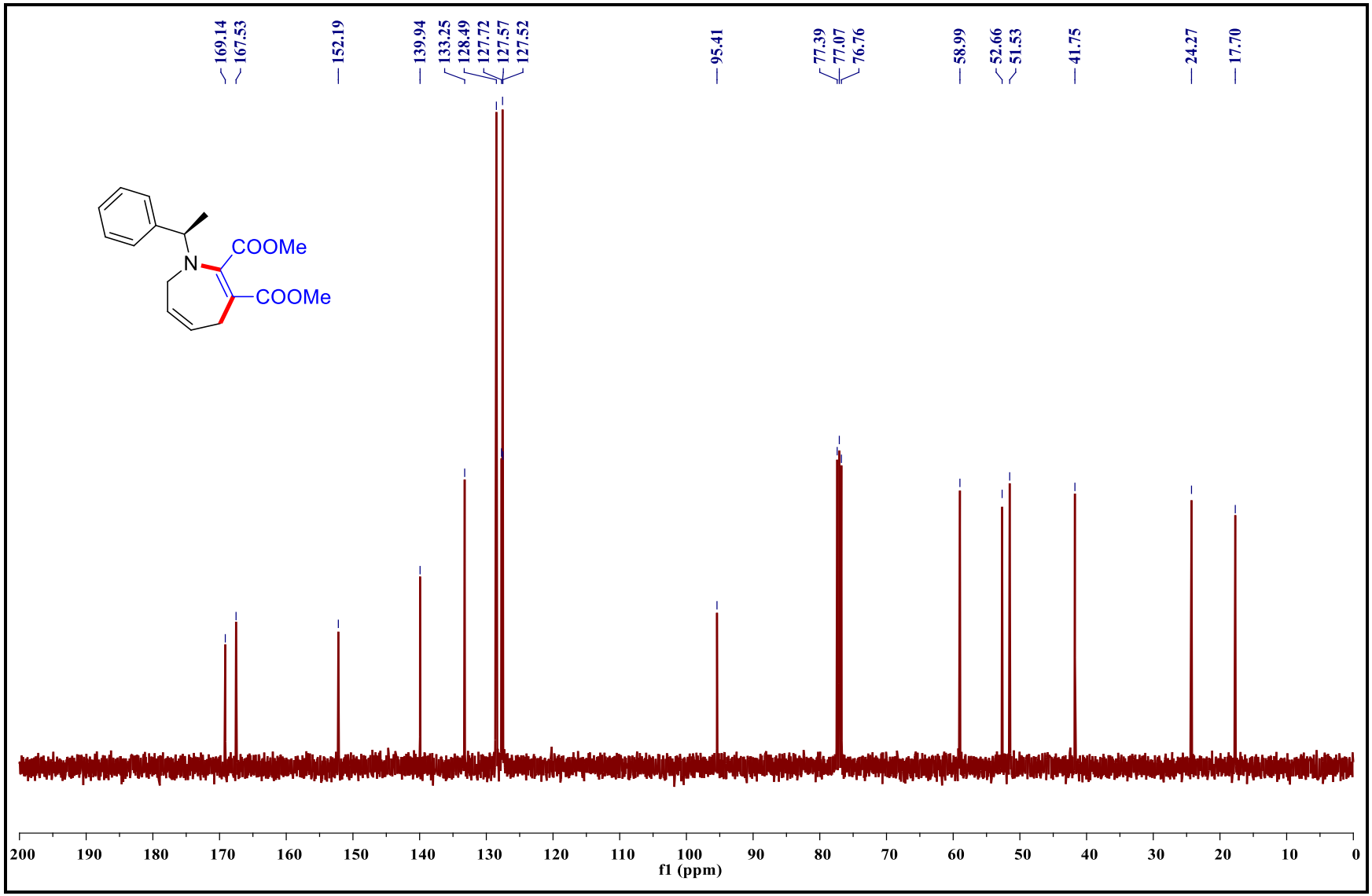
13C NMR spectrum of diethyl 4-acetyl-1-(2,4-dimethoxybenzyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3s):



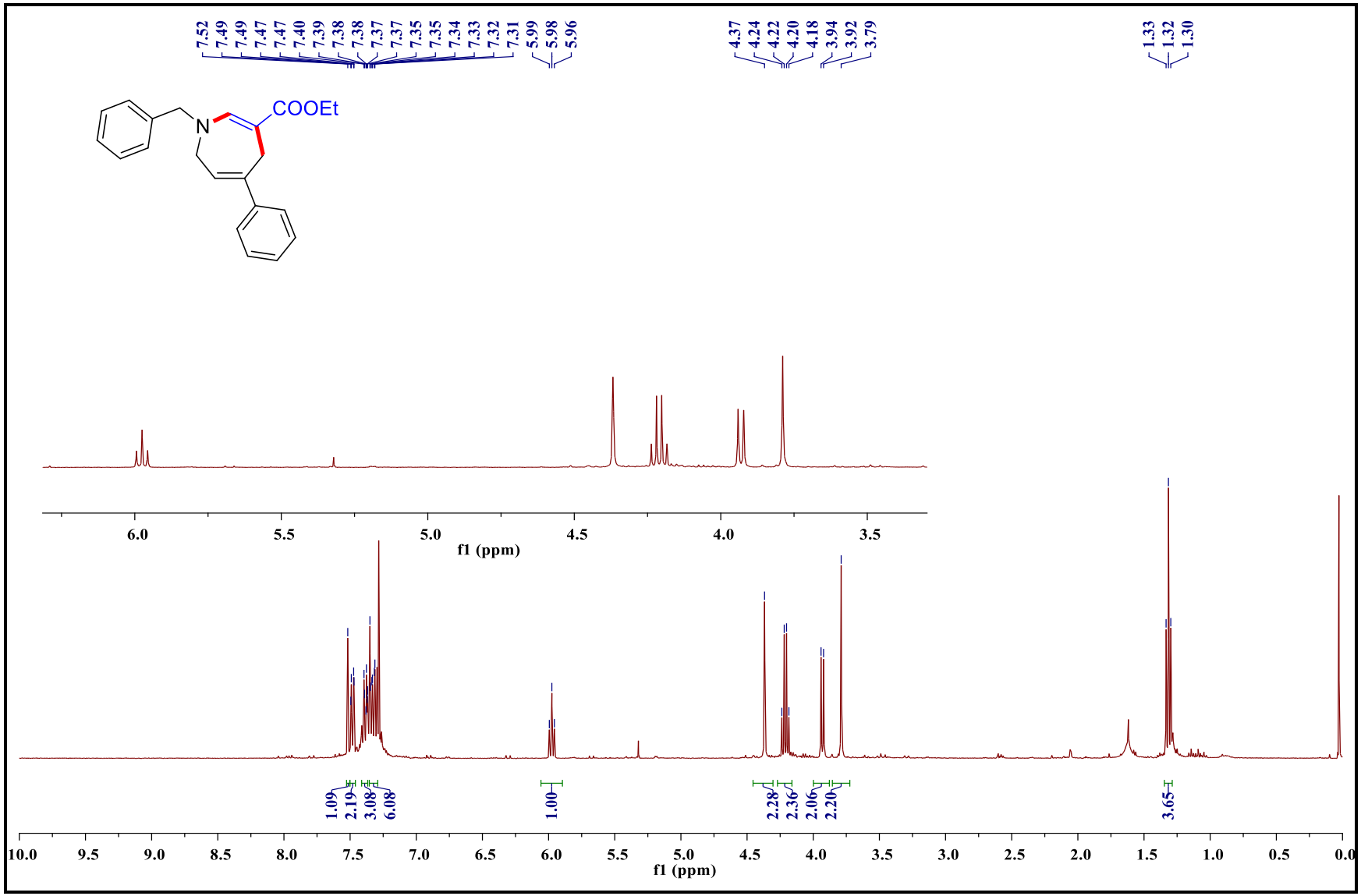
1H NMR spectrum of (R)-dimethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3t):



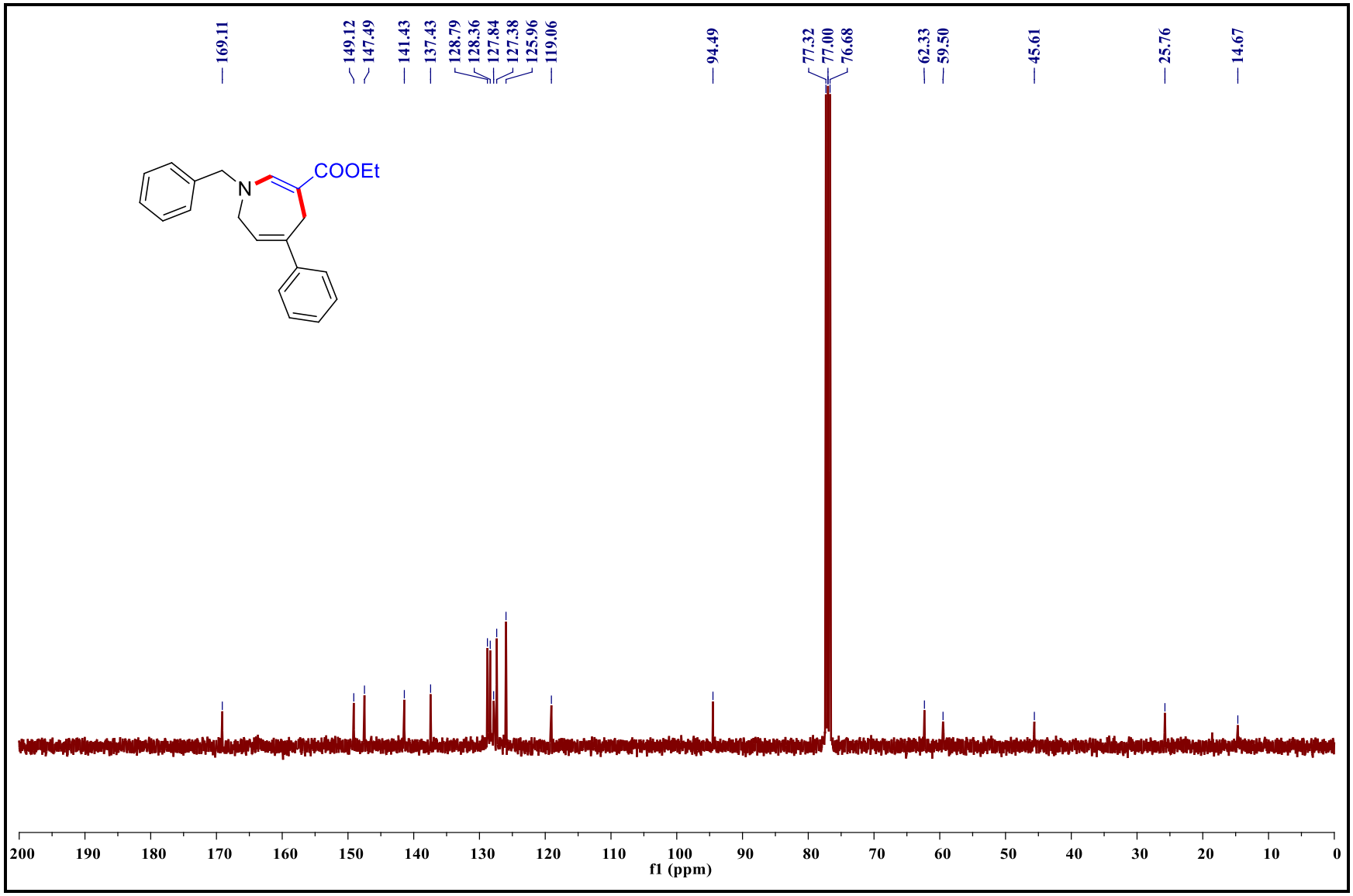
13C NMR spectrum of (R)-dimethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-2,3-dicarboxylate (3t):



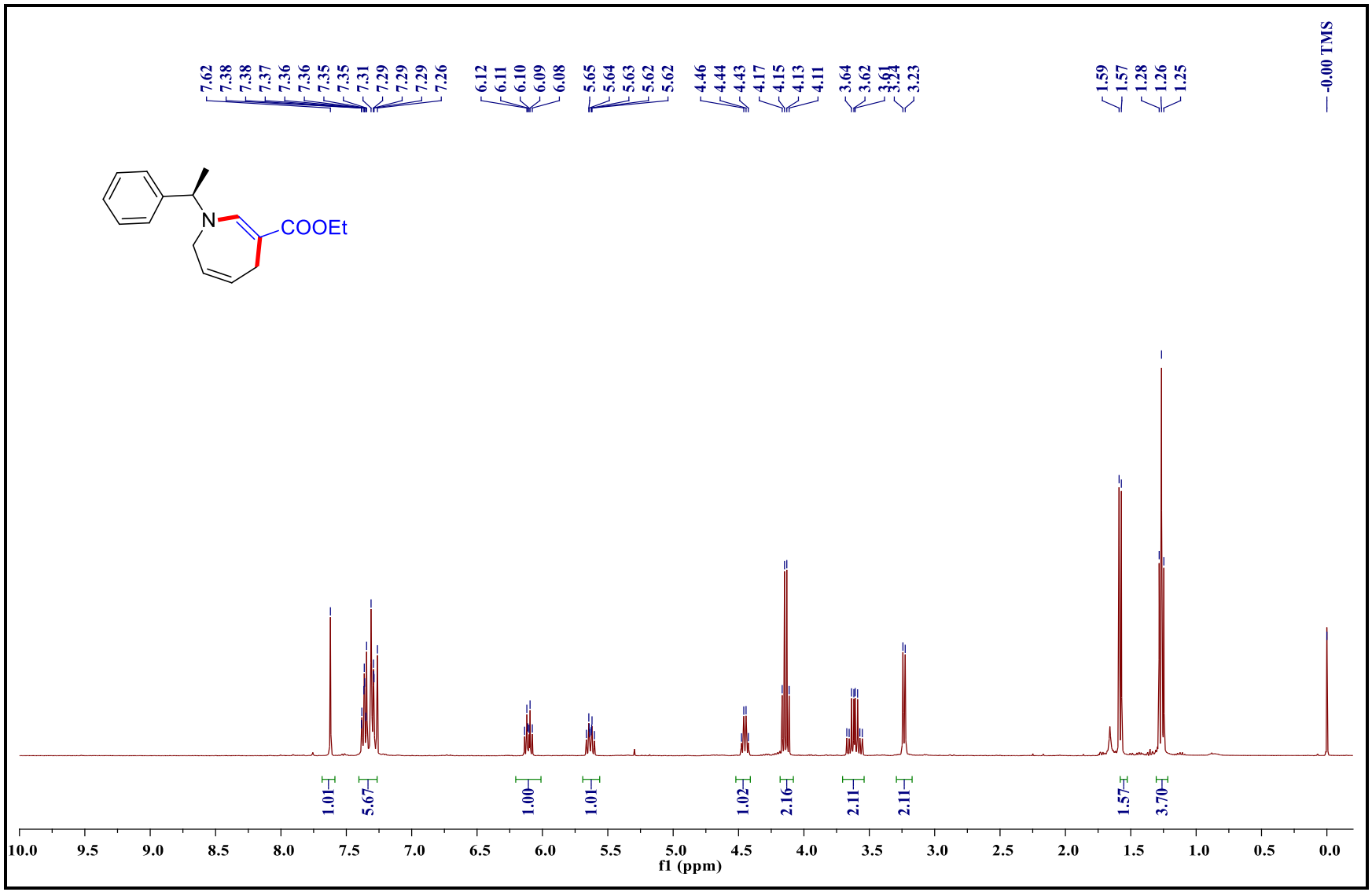
1H NMR spectrum of ethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-3-carboxylate (3u):



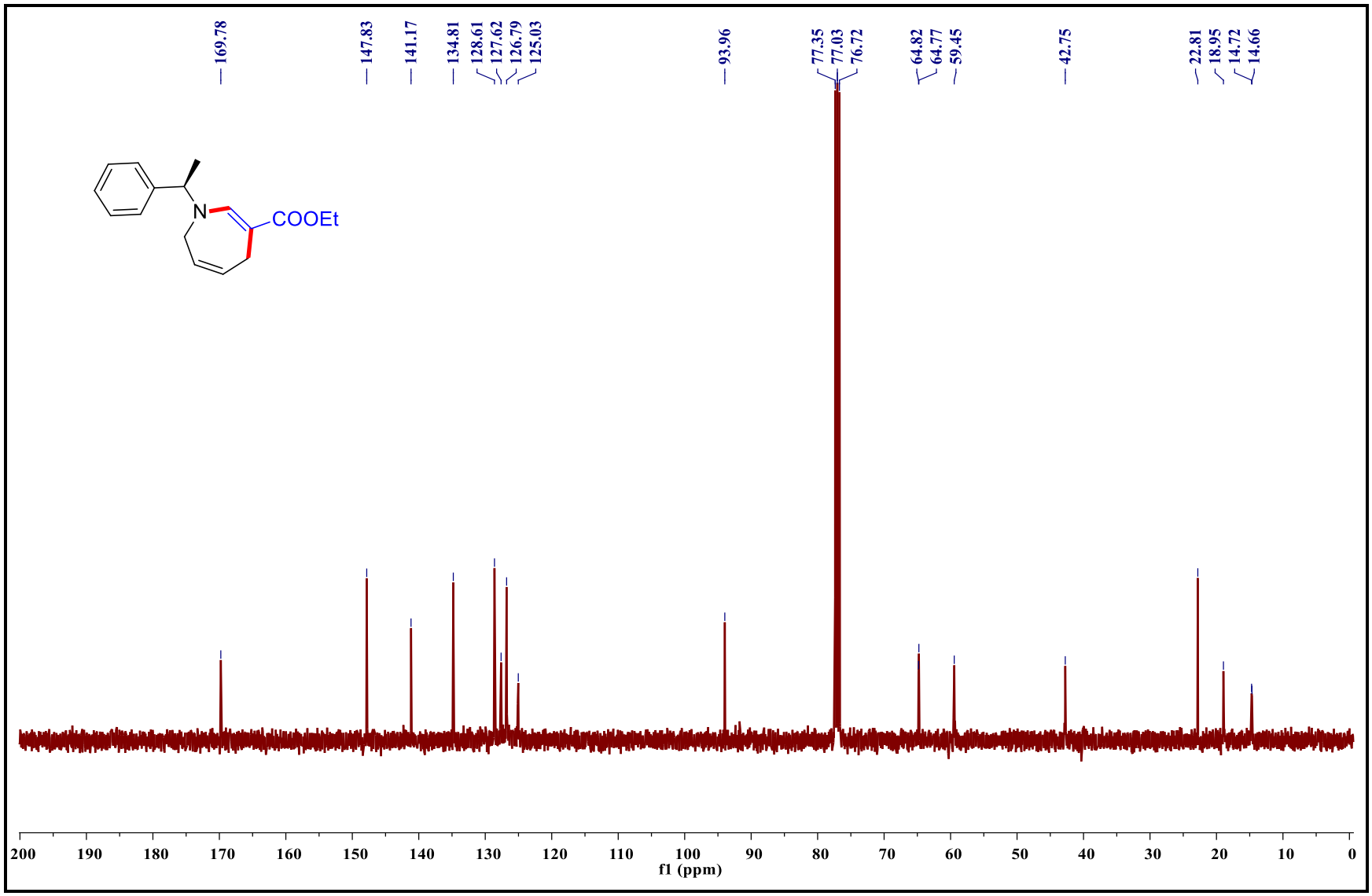
13C NMR spectrum of ethyl 1-benzyl-5-phenyl-4,7-dihydro-1H-azepine-3-carboxylate (3u):



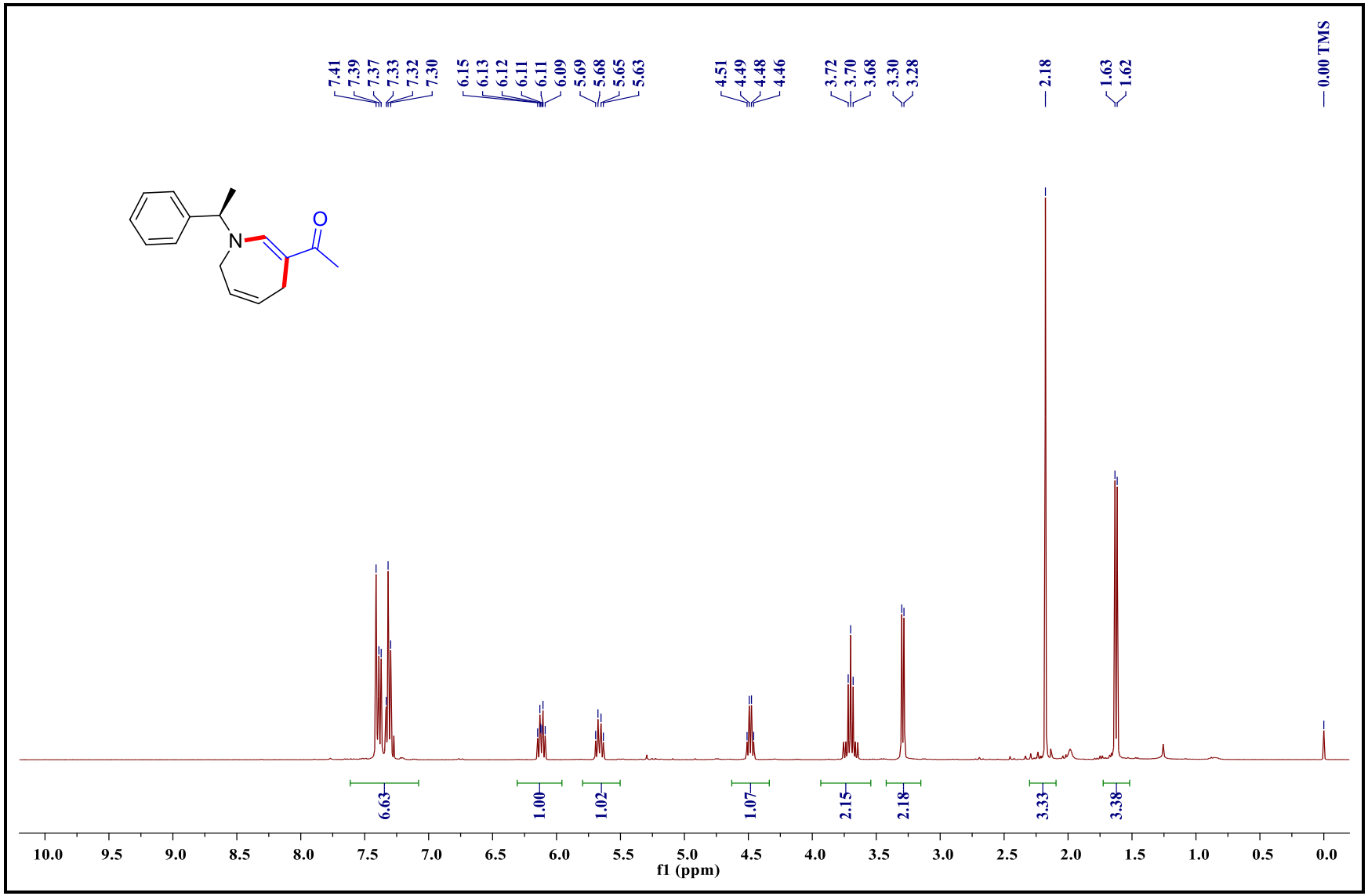
1H NMR spectrum of (R)-ethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-3-carboxylate (3v):



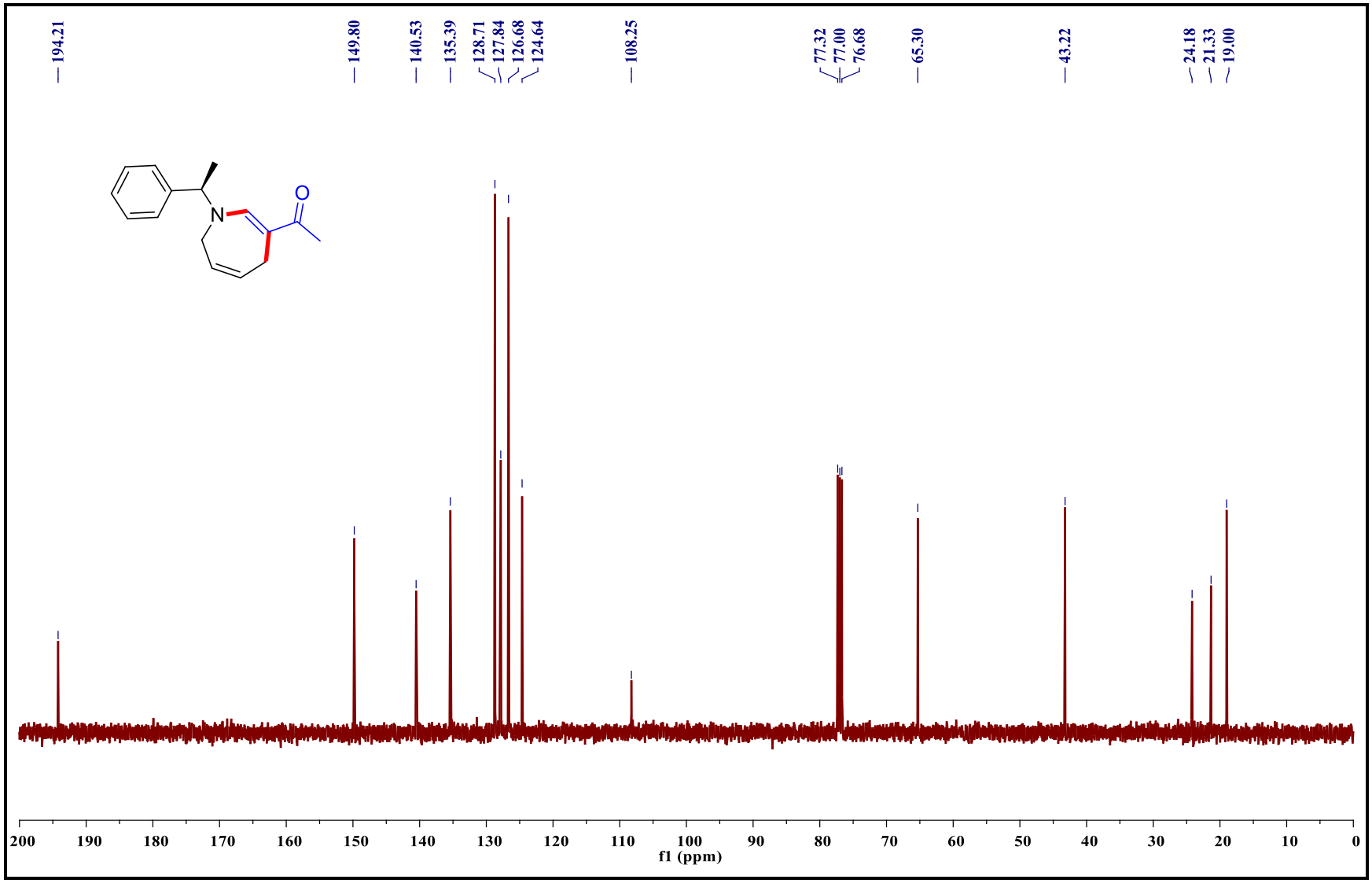
13C NMR spectrum of (R)-ethyl 1-(1-phenylethyl)-4,7-dihydro-1H-azepine-3-carboxylate (3v):



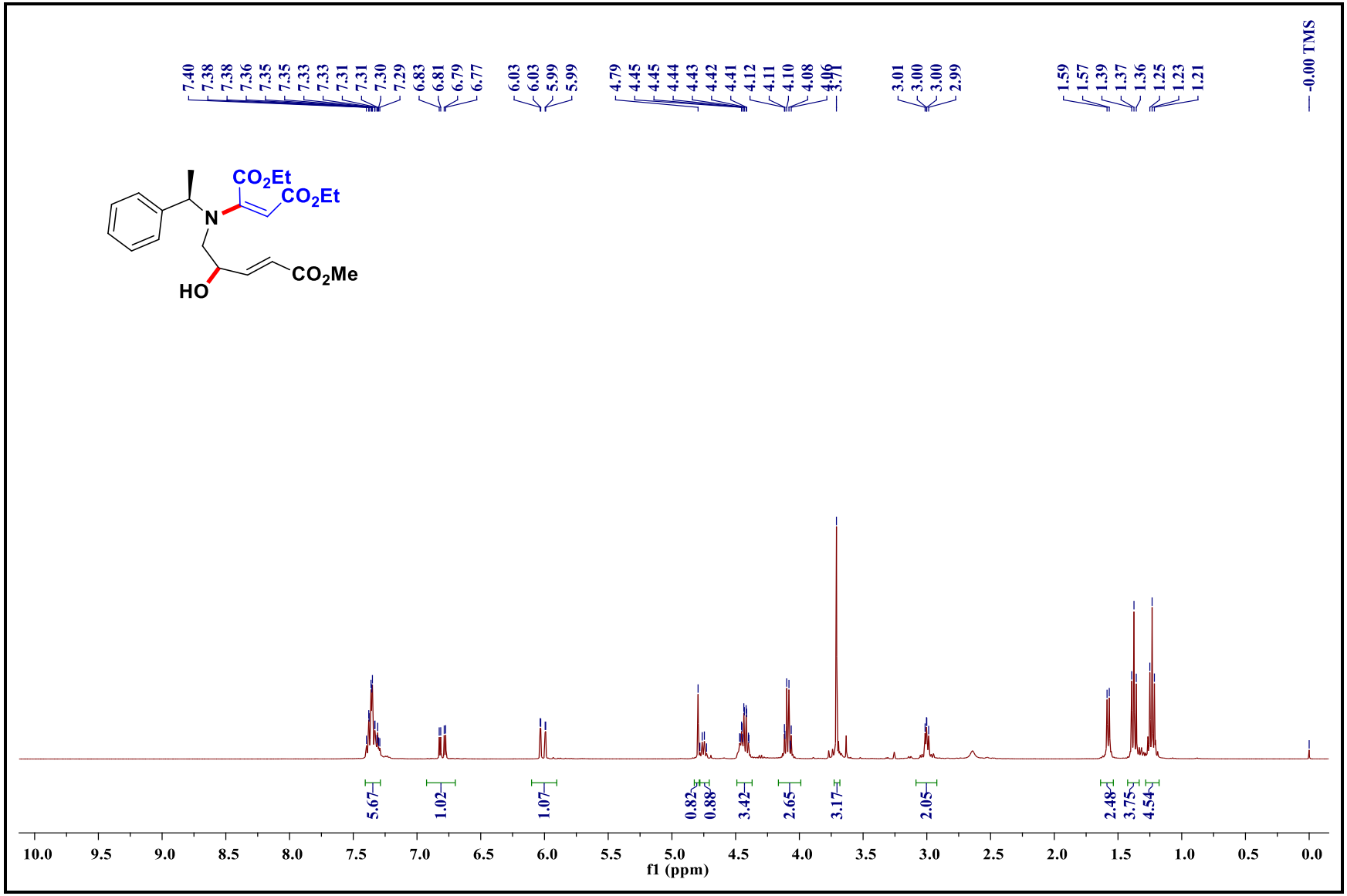
1H NMR spectrum of (R)-1-(1-(1-phenylethyl)-4,7-dihydro-1H-azepin-3-yl)ethanone (3w):



13C NMR spectrum of (R)-1-(1-(1-phenylethyl)-4,7-dihydro-1H-azepin-3-yl)ethanone (3w):



1H NMR Diethyl 2-(((E)-2-hydroxy-5-methoxy-5-oxopent-3-en-1-yl)((R)-1-phenylethyl)amino)maleate (5):



13C NMR Diethyl 2-(((E)-2-hydroxy-5-methoxy-5-oxopent-3-en-1-yl)((R)-1-phenylethyl)amino)maleate (5):