Supporting Information For

A Cascade Reaction of Cinnamyl Azides with Acrylates Directly Generates Tetrahydro-Pyrrolo-Pyrazole Heterocycles

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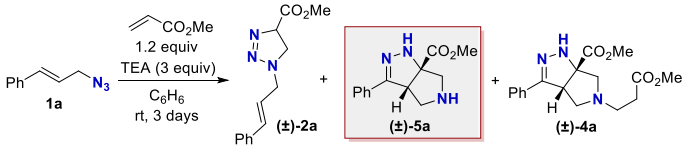
Reaction Optimization

Procedure for screening reaction concentration (Table S1) - A stock solution of azide **1b** (150 mg, 0.942 mmol) and naphthalene (29.9 mg, 0.234 mmol, internal standard) was prepared in C_6H_6 (1.3 mL). Individual 4 mL vials were charged with 0.25 mL portions of this solution and diluted with C_6H_6 (0, 0.25, 0.75, and 1.75 mL) to the appropriate concentration. Methyl acrylate (20 µL) and TEA (80 µL) were added and the vials were sealed under air and heated to 70 °C. After 65 h, the reactions were concentrated under reduced pressure and analyzed by ^{1}H NMR. All other screens were performed via an analogues procedure varying the specified conditions.

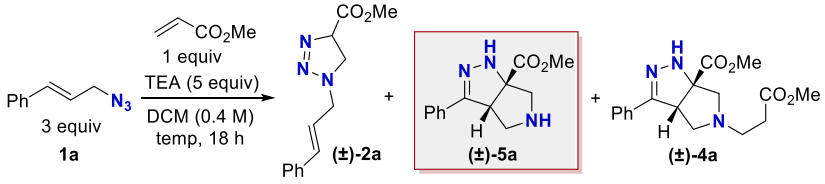
Table S1. Concentration screen.



entry	concentration (M)	1a (%)[a]	5a (%)[a]	4a (%)[a]
1	0.8	8	16	30
2	0.4	4	29	32
3	0.2	10	49	20
4	0.1	22	50	7

[a]Conversion and yield were determined by ^{1}H NMR.

Table S2. Temperature screen.

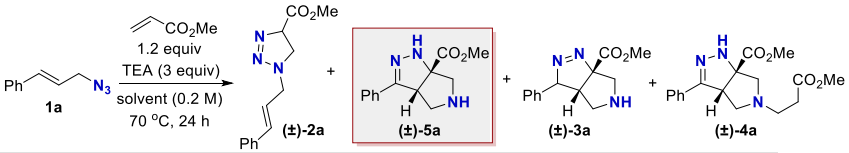


entry	temperature (°C)	**5a** (%)[a]
1	rt	5
2	40	6
3	50	15
4	60	24
5	70	47
6	80	55

[a]Conversion and yield were determined by ^{1}H NMR.

Procedure for screening solvents (Table S3) - Individual 4 mL vials were charged with cinnamyl azide (24.2-27.4 mg, 0.152-0.172 mmol, 1 equiv) and naphthalene (10.5-11.8 mg, 82.0-92.2 µmol). Each respective solvent (0.8 mL, 0.2 M) was added followed by methyl acrylate (17 uL, 0.19 mmol, 1.2 equiv) and TEA (66 uL, 0.47 mmol, 3 equiv). The reactions were sealed under air and heated to 70 °C. After 24 h, the reactions were concentrated under reduced pressure and analyzed by ^{1}H NMR.

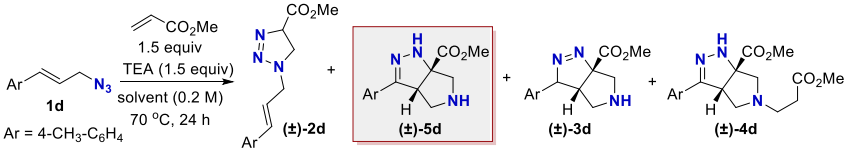
Table S3. Solvent Screen.



Entry	Solvent	1a (%)[a]	5a (%)[a]	3a (%)[a]	4a (%)[a]
1	MeOH	3	3	0	38
2	DMSO	-	21	0	34
3	EtOAc	37	37	6	6
4	Acetone	29	38	2	13
5	DME	34	38	7	8
6	Dioxane	34	41	12	10
7	MTBE	48	31	7	5
8	DCE	27	21	0	-
9	THF	24	37	4	7
10	C_6H_6	19	45	0	9
11	PhMe	40	50	7	8
12	$C_6H_4Cl_2$	29	45	1	12

[a]Conversion and yield were determined by ^{1}H NMR.

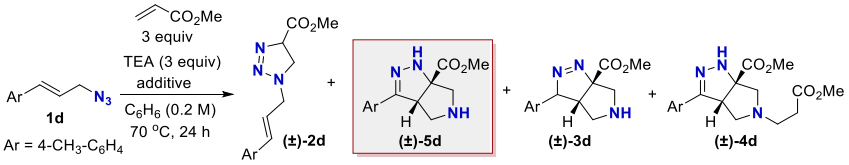
Table S4. Non-polar solvent screen.



entry	solvent	1d (%)[a]	5d (%)[a]	3d (%)[a]	4d (%)[a]
1	Hexanes	18	56	1	10
2	Pentanes	24	52	0	25
3	Petroleum ether	26	53	0	22

[a]Conversion and yield were determined by ^{1}H NMR.

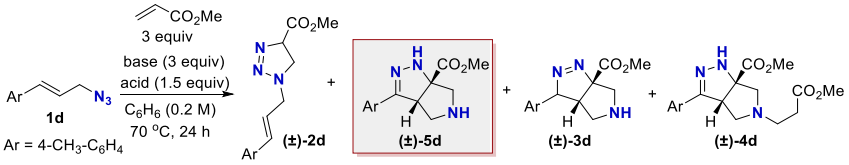
Table S5. Acid additive screen.



entry	additive	**1d** (%)[a]	**5d** (%)[a]	**3d** (%)[a]	**4d** (%)[a]
1	None	1	46	17	9
2	TFA (1.5 eq)	1	21	3	29
3	TFA (2.5 eq)	1	20	2	32
4	AcOH (1.5 eq)	6	9	0	56
5	AcOH (2.5 eq)	4	3	0	67

[a]Conversion and yield were determined by ^{1}H NMR.

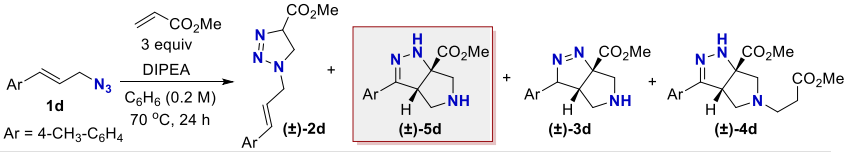
Table S6. Base and buffer additive screen.



entry	base	acid	**5d** (%)[a]	**3d** (%)[a]	**4d** (%)[a]
1	TEA	-	35	4	14
2	DIPEA	-	13	67	0
3	pyridine	-	14	67	0
4	DMAP	-	36	0	25
5	N-methylaniline	-	10	62	0
6	TEA	HCl	37	4	14
7	DIPEA	HCl	22	0	36
8	DMAP	HCl	32	0	27

[a]Conversion and yield were determined by ^{1}H NMR.

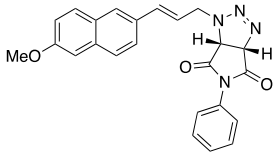
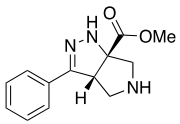
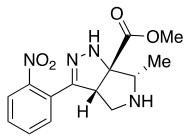
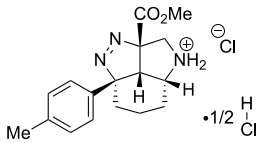
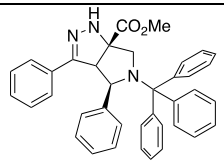
Table S7. Equivalents of DIPEA screen.



entry	DIPEA (equiv)	**2d** (%)[a]	**5d** (%)[a]	**3d** (%)[a]	**4d** (%)[a]
1	3.0	0	22	58	6
2	1.5	0	17	65	3
3	1.0	0	17	65	3
4	0.5	0	41	23	0
5	0	41	0	42	0

[a]Conversion and yield were determined by ^{1}H NMR.

Table S8 X-ray Data

	2hh	5a	5bb	5v·HCl	S1
structure					
CCDC number	1978783	1978781	1978782	1980239	1986830
formula	$C_{24}H_{20}N_4O_3$	$C_{13}H_{15}N_3O_2$	$C_{14}H_{16}N_4O_4$	$C_{17}H_{22}ClN_3O_2 \cdot 1/2$ HCl	$C_{38}H_{33}N_3O_2$
formula weight	412.1535	245.1164	304.1172	353.1285	563.2573
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	C_2
a (Å)	29.875(10)	6.0964(2)	7.1080(4)	14.0598(19)	17.0760(16)
b (Å)	5.607(2)	10.1676(3)	10.7667(6)	15.723(2)	9.7625(10)
c (Å)	12.349(4)	19.2632(7)	18.9286(9)	32.139(4)	18.847(3)
α (˚)	90	90	90	90	90
β (˚)	101.081(13)	90	91.471(2)	91.764(5)	110.108(3)
γ (˚)	90	90	90	90	90
V (Å^3)	2030.1(12)	1194.04(7)	1448.12(13)	7101.3(17)	2950.4(6)
Z	4	4	4	4	4
D_{calcd} (g/cm^3)	1.349	1.364	1.396	1.325	1.269
temperature (K)	100	100	125	125	126
θ_{min}	2.78	2.91	2.18	2.67	2.30
θ_{max}	30.40	30.41	30.52	27.60	26.07
number of reflections	6181	3562	4439	9879	7390
*R*1	0.0573	0.0384	0.0395	0.0403	0.0543
*wR*2	0.1475	0.1073	0.1503	0.1145	0.1518
sample preparation	slow evaporation with DCM	slow diffusion using DCM/hexanes	slow diffusion using DCM/hexanes	slow diffusion using HCl in dioxane/toluene	slow diffusion using DCM/hexanes

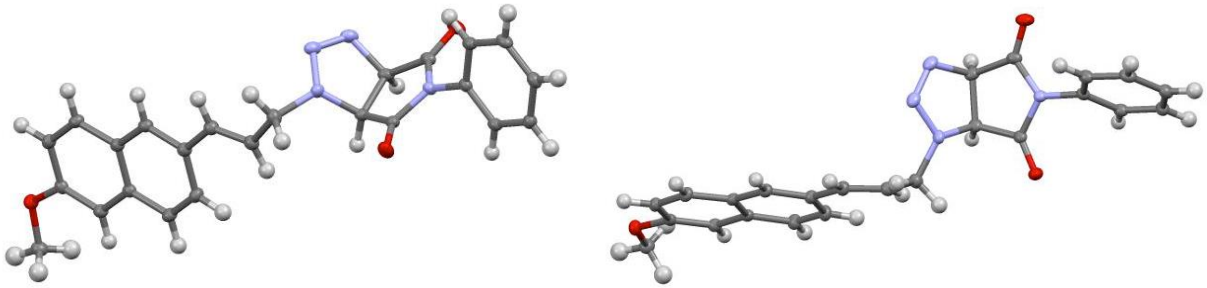


Figure S1. ORTEP drawing of compound **2hh** showing thermal ellipsoids at the 50% probability level

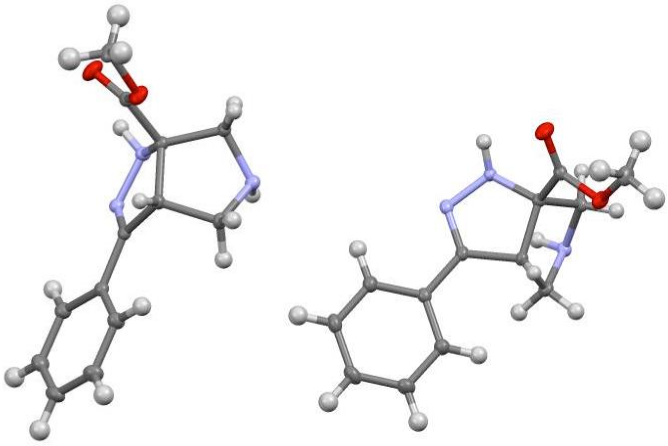


Figure S2. ORTEP drawing of compound **5a** showing thermal ellipsoids at the 50% probability level

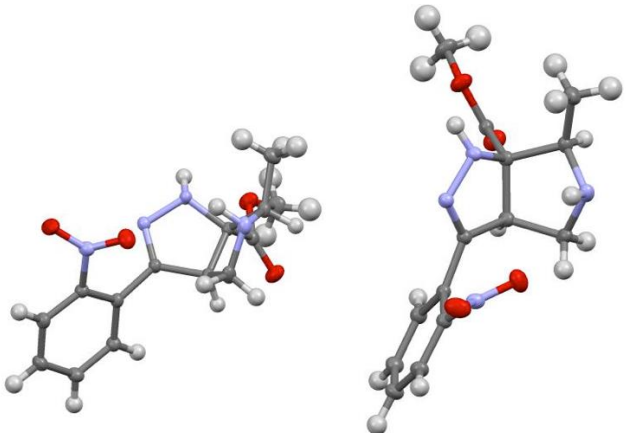


Figure S3. ORTEP drawing of compound **5bb** showing thermal ellipsoids at the 50% probability level

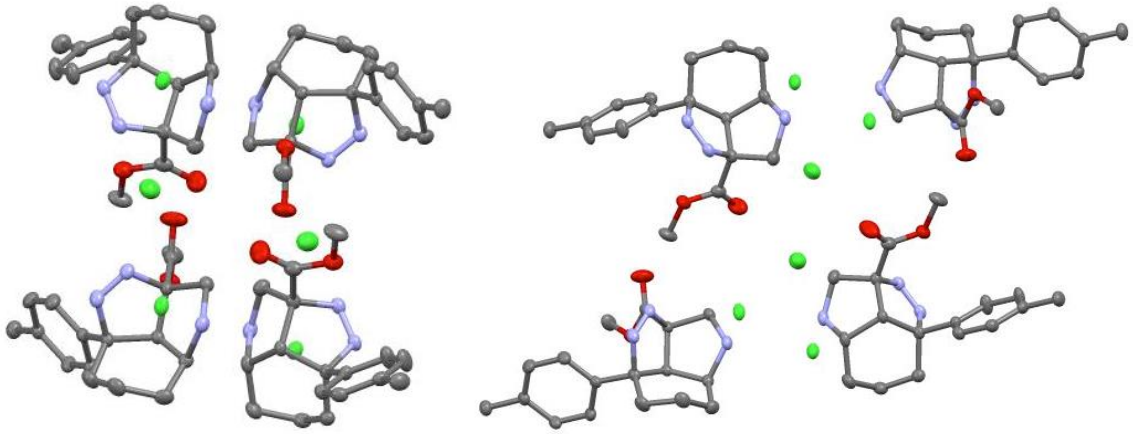


Figure S4. ORTEP drawing of compound **5v·HCl** showing thermal ellipsoids at the 50% probability level (omit hydrogens for clarity)

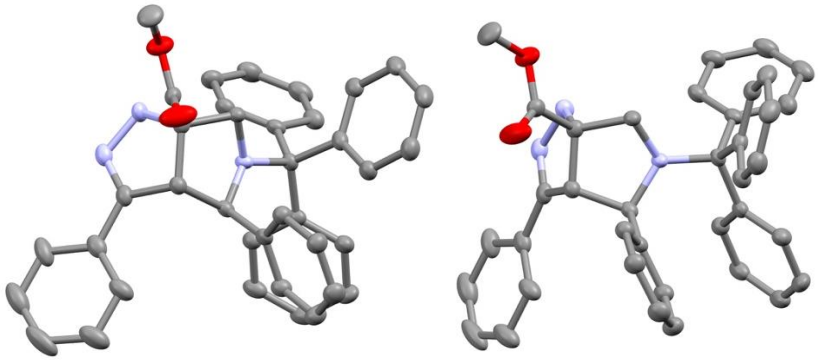


Figure S5. ORTEP drawing of compound **S1** showing thermal ellipsoids at the 50% probability level

HPLC data

General: Enantiomeric ratios were determined using a Shimadzu HPLC with a PDA detector and a RegisPack 5 Micron column or Regis Reflect column (C-Amylose A; 3µ, 250 mm x 4.6 mm). The purification of enantioenriched azide **1v** was adapted from a known method using a semi-preparative chiral HPLC.[1] The absolute configuration of enantioenriched azide **1v** was assigned arbitrarily. Each enantioenriched azide **1v** was converted to the corresponding bicyclic amine **5v**. The yield and er were determined individually and the average value were reported as duplicate trials. Each sample was injected in duplicate. For each sample, the racemic retention time standard was run before and after the sample (4 total injections per sample).

HPLC Images

Compound **1v**: RegisPack 5 Micron, hexane : ^{i}PrOH = 98.8: 0.2 at 1.5 mL/min, T = 40 °C, λ = 249 nm: t_{ent1} = 5.4 min, t_{ent2} = 6.4 min

Figure S6. HPLC trace

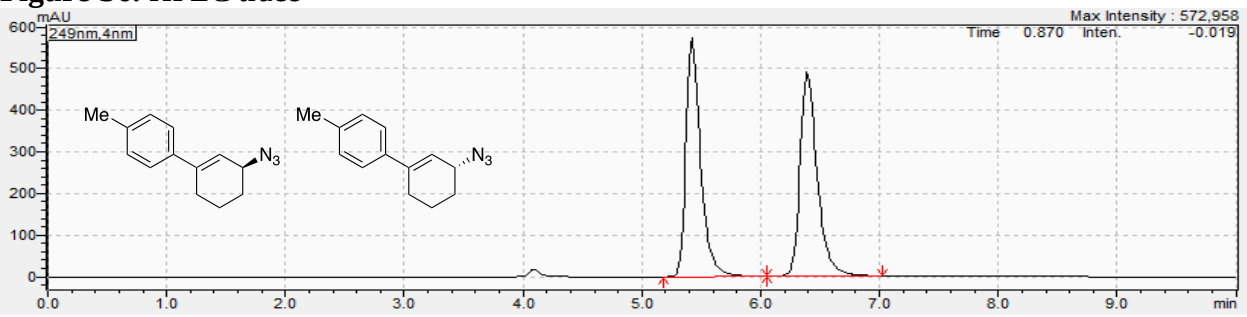


Table S9. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	5.4	4931906	50.0
2	6.4	4939090	50.0
Total		9870996	100.0

Figure S7. HPLC trace

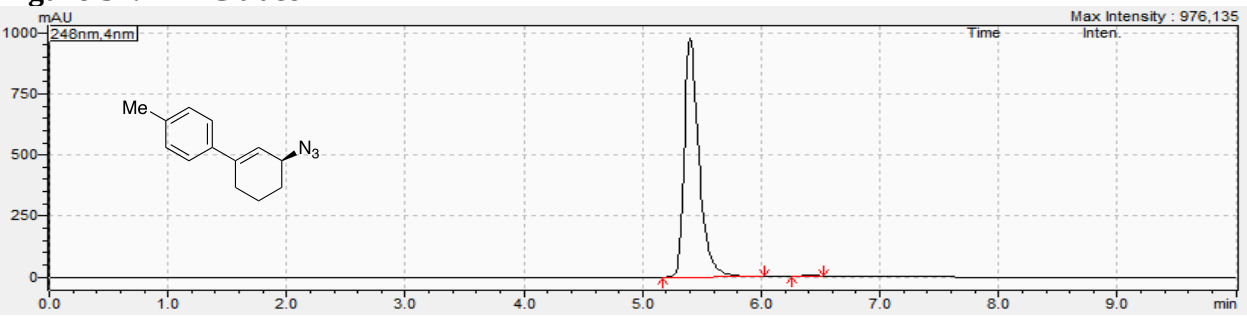


Table S10. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	5.4	8421249	99.5
2	6.4	43427	0.5
Total		8464676	100.0

Figure S8. HPLC trace

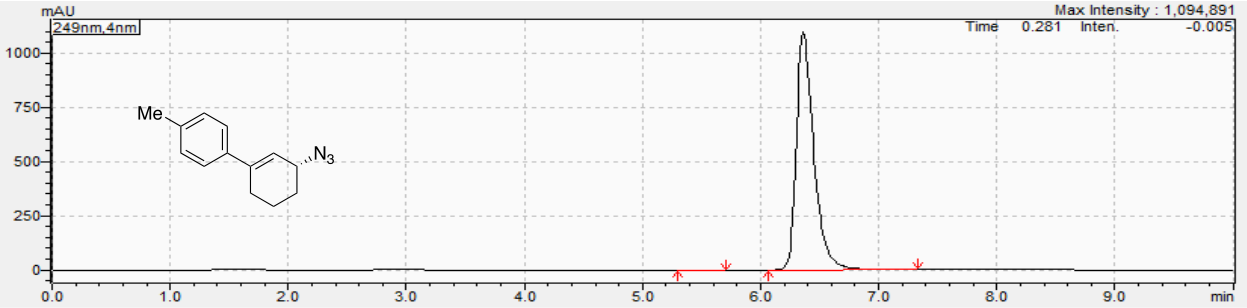


Table S11. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	5.4	4844	0.0
2	6.4	11253374	100.0
Total		11258217	100.0

Compound **5v**: Reflect, C-Amylose A, hexane : ^{i}PrOH = 85: 15 at 1.0 mL/min, T = 40 °C, λ = 215 nm: t_{ent1} = 10.6 min, t_{ent2} = 12.7 min

Figure S9. HPLC trace

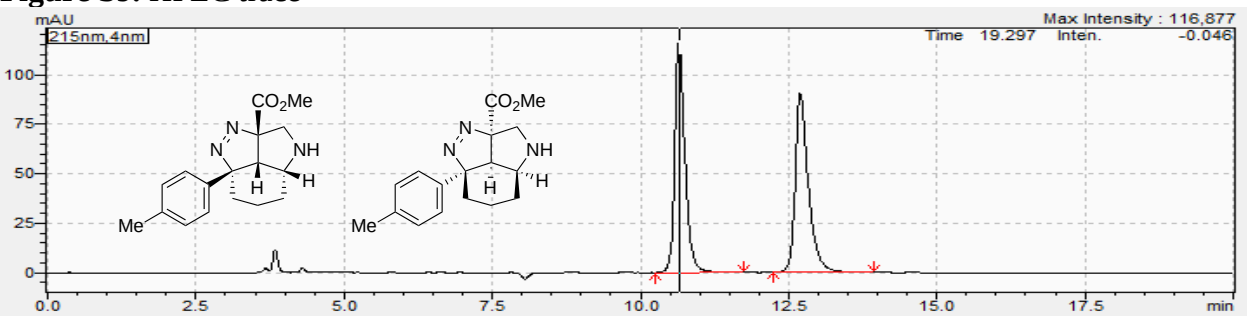


Table S12. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	10.6	1410043	50.1
2	12.7	1402667	49.9
Total		2812709	100.0

Figure S10. HPLC trace

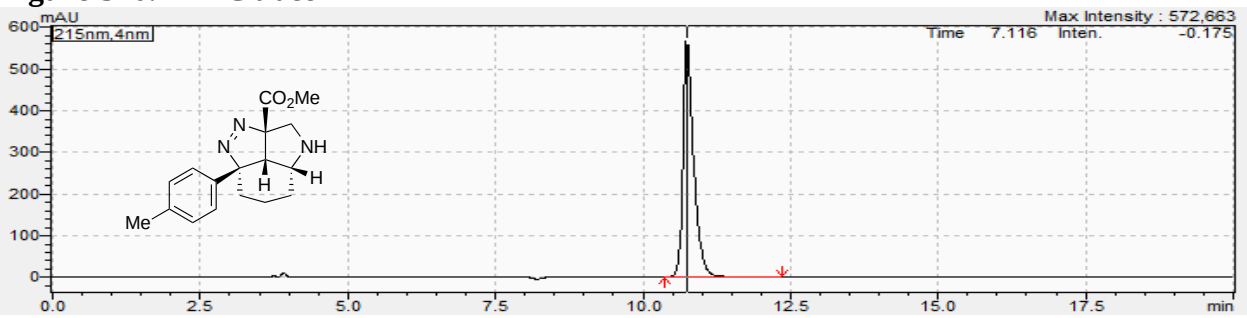


Table S13. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	10.7	7234990	100
Total		7234990	100

Figure S11. HPLC trace

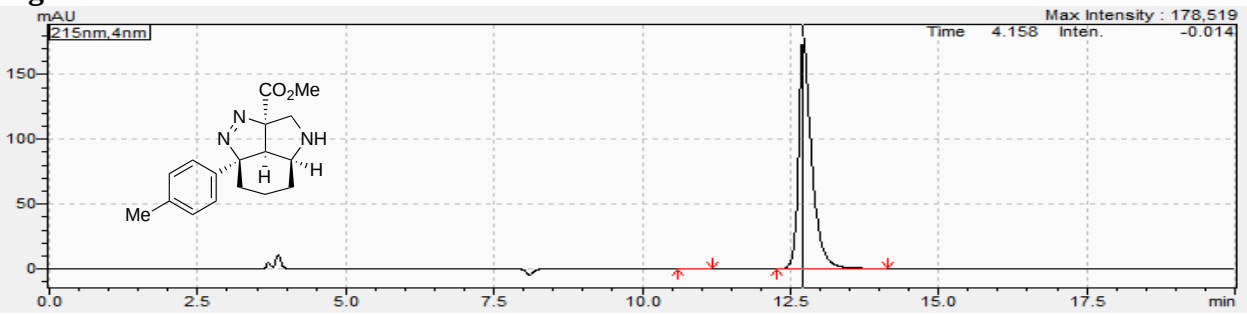


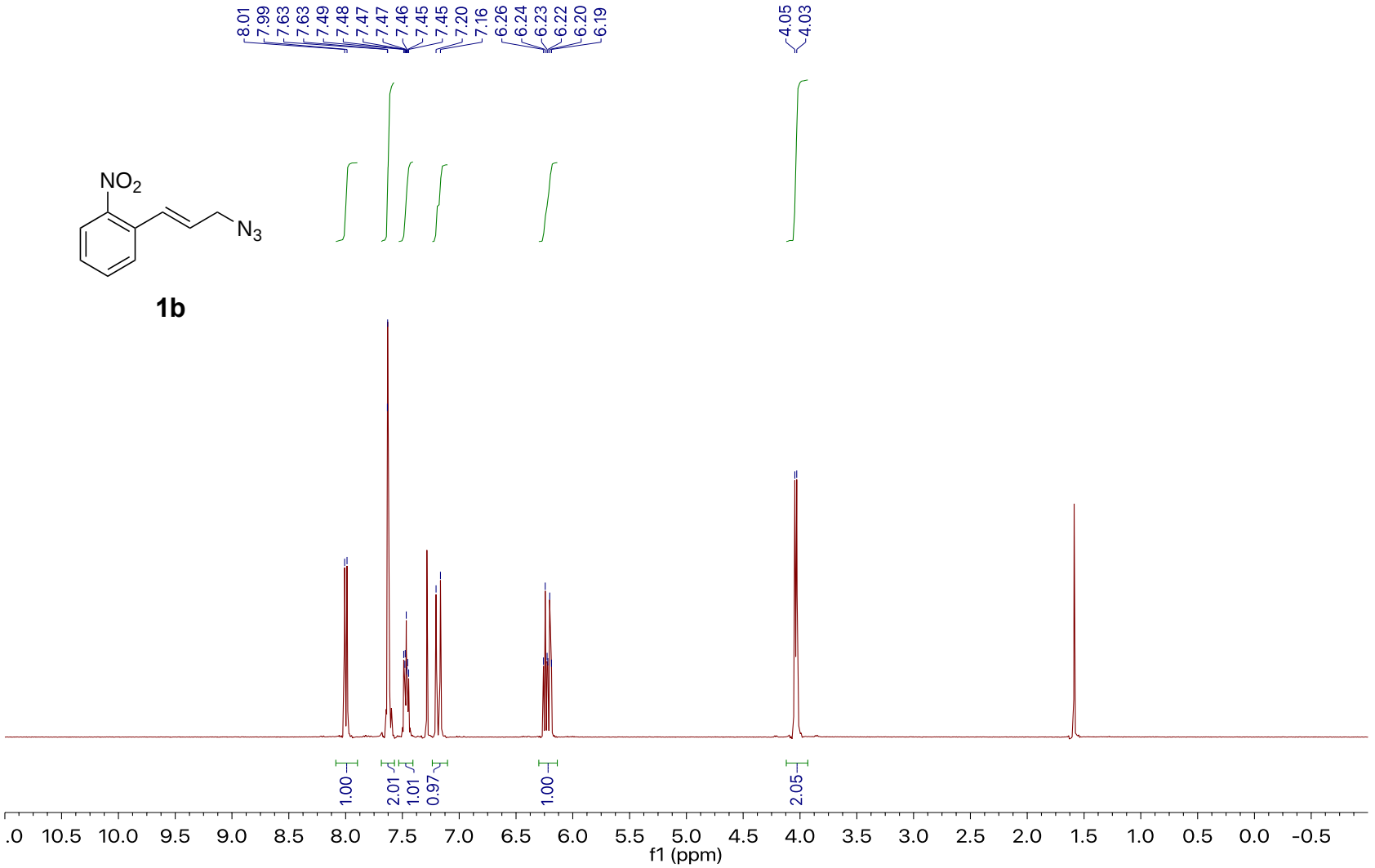
Table S14. Tabulated Areas

Peak#	Ret. Time	Area	Area%
1	10.9	6973	0.3
2	12.8	2757567	99.7
Total		2764540	100.0

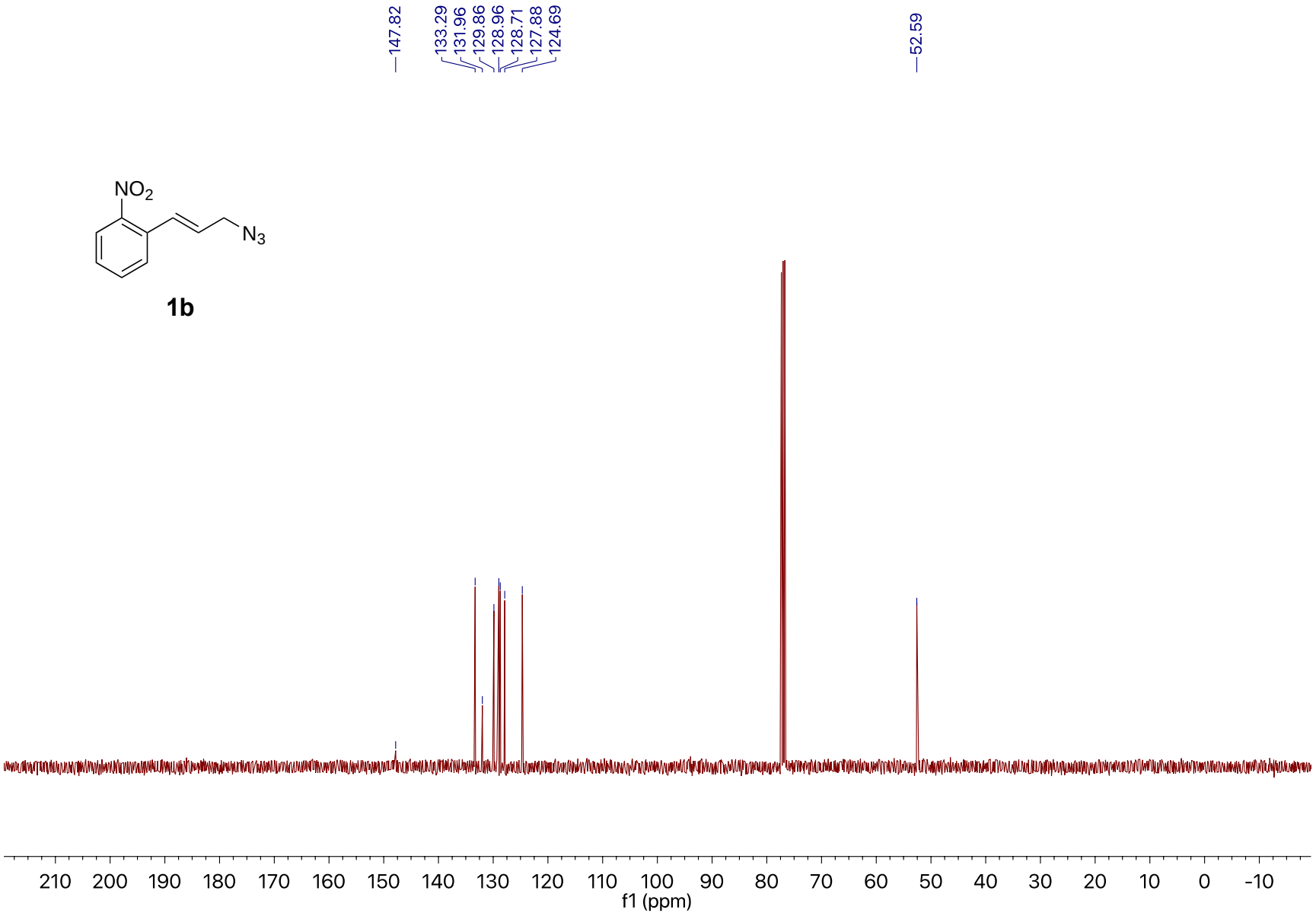
References

(1) Ott, A. A.; Packard, M. H.; Ortuño, M. A.; Johnson, A.; Suding, V. P.; Cramer, C. J.; Topczewski, J. J. Evidence for a Sigmatropic and an Ionic Pathway in the Winstein Rearrangement. *J. Org. Chem.* **2018**, *83*, 8214–8224.

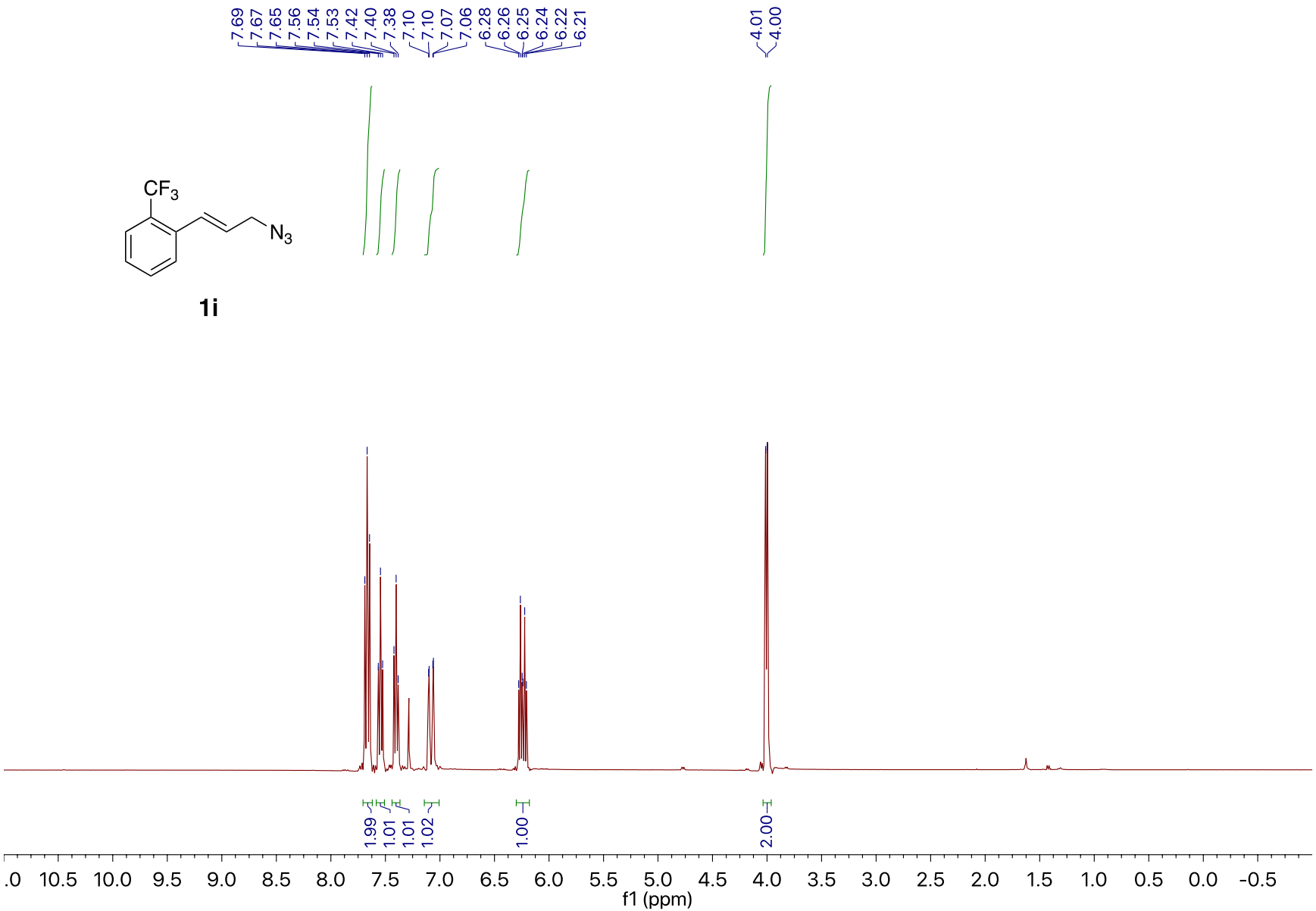
NMR Spectra Images



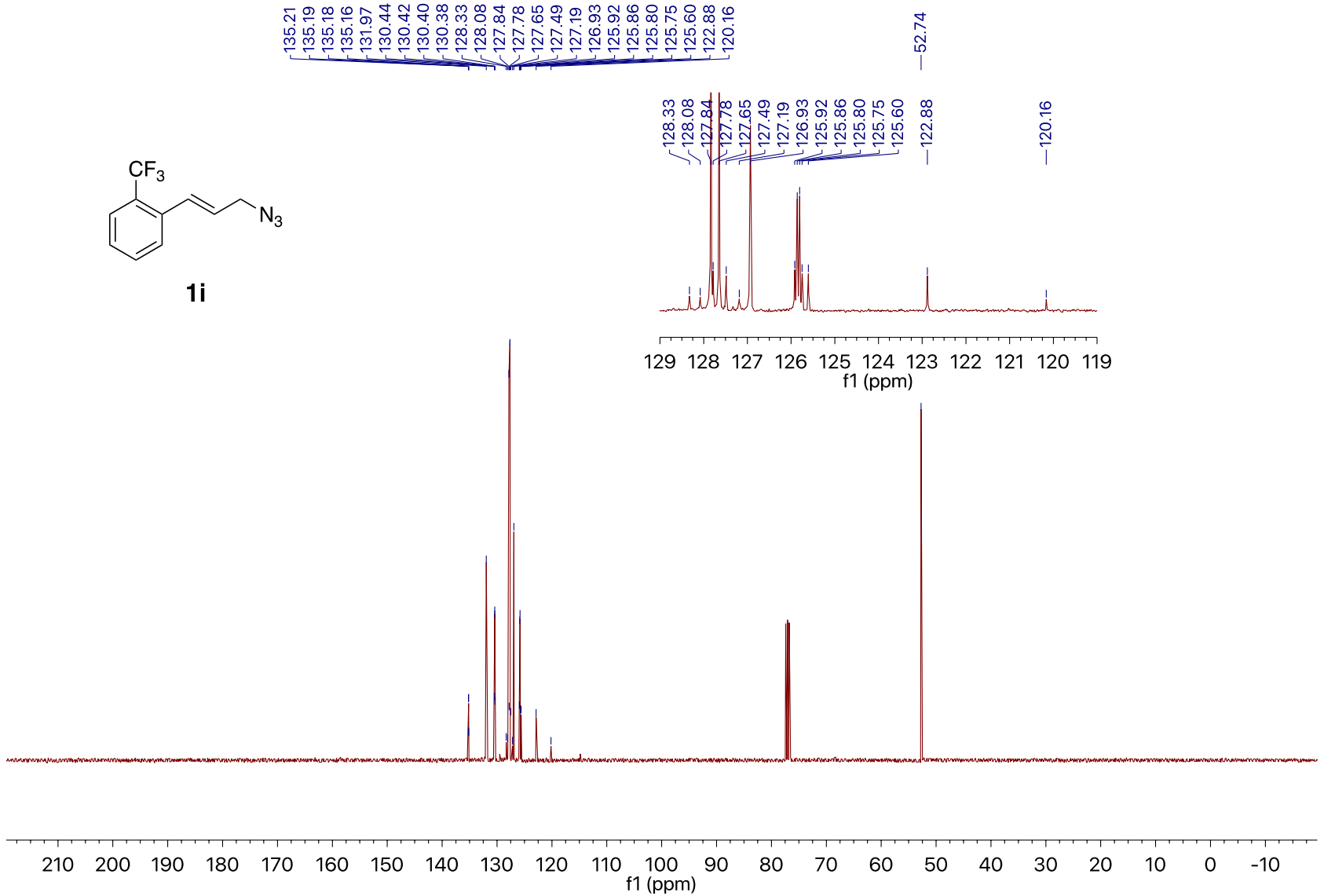
Compound **1b**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



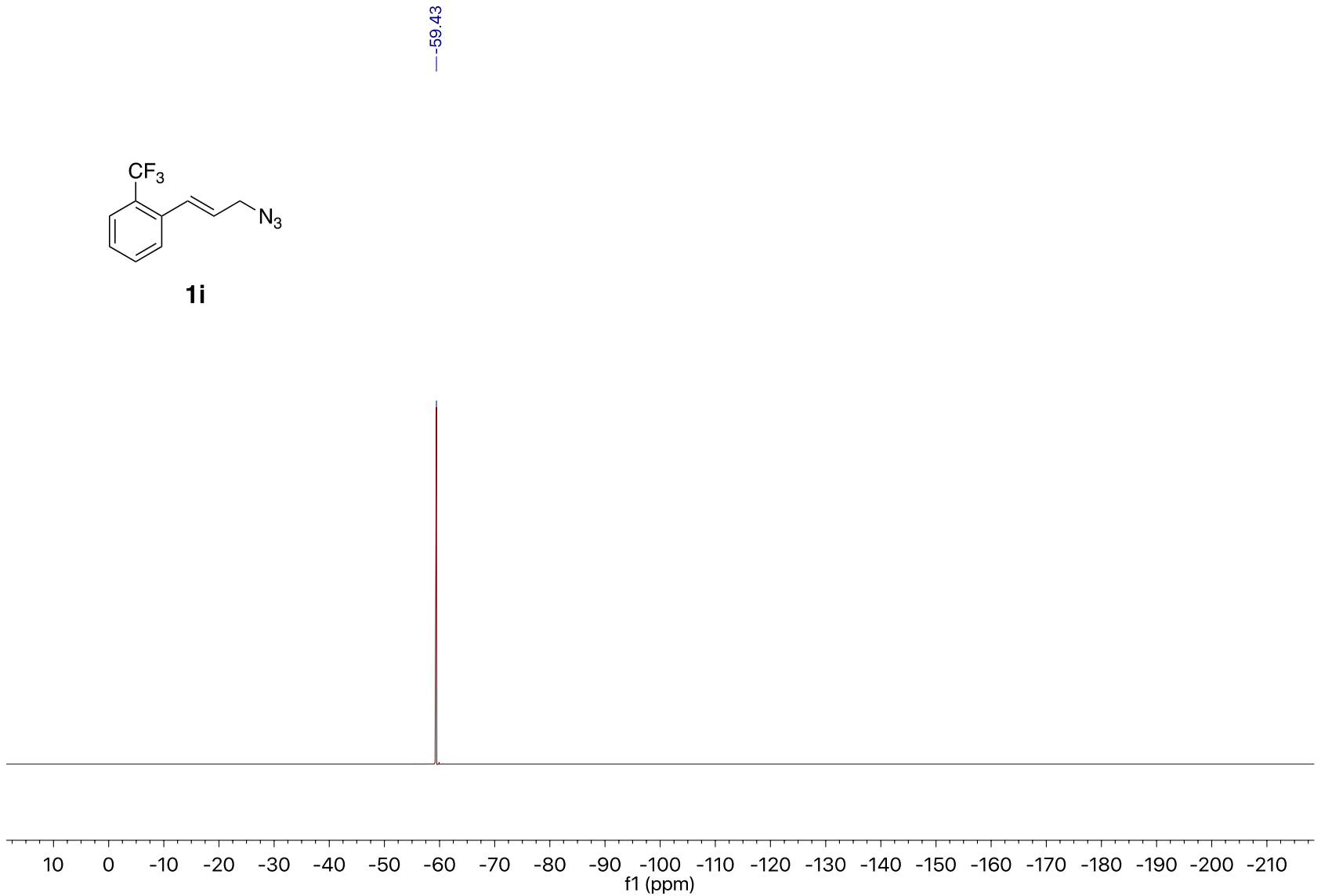
Compound **1b**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



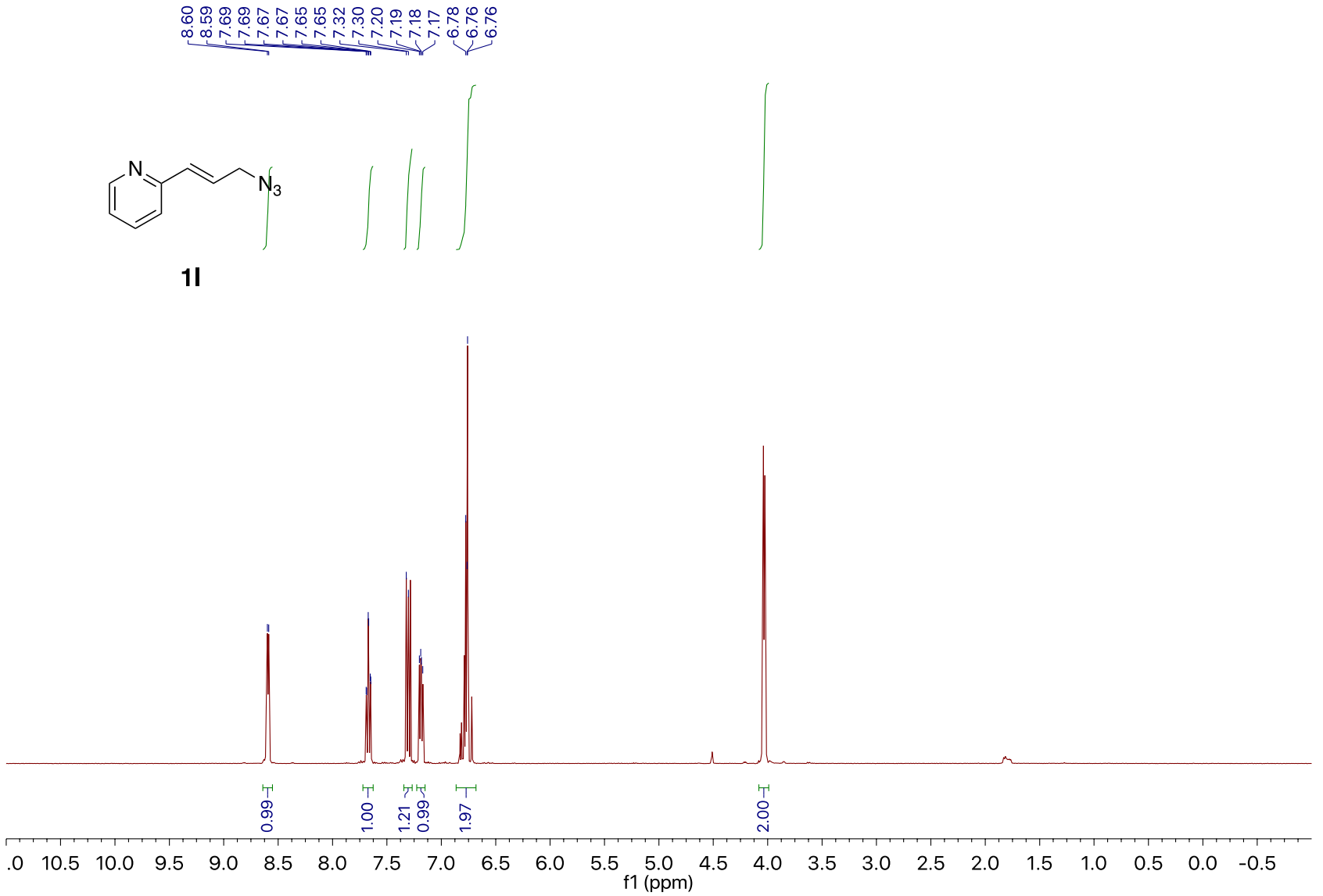
Compound **1i**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



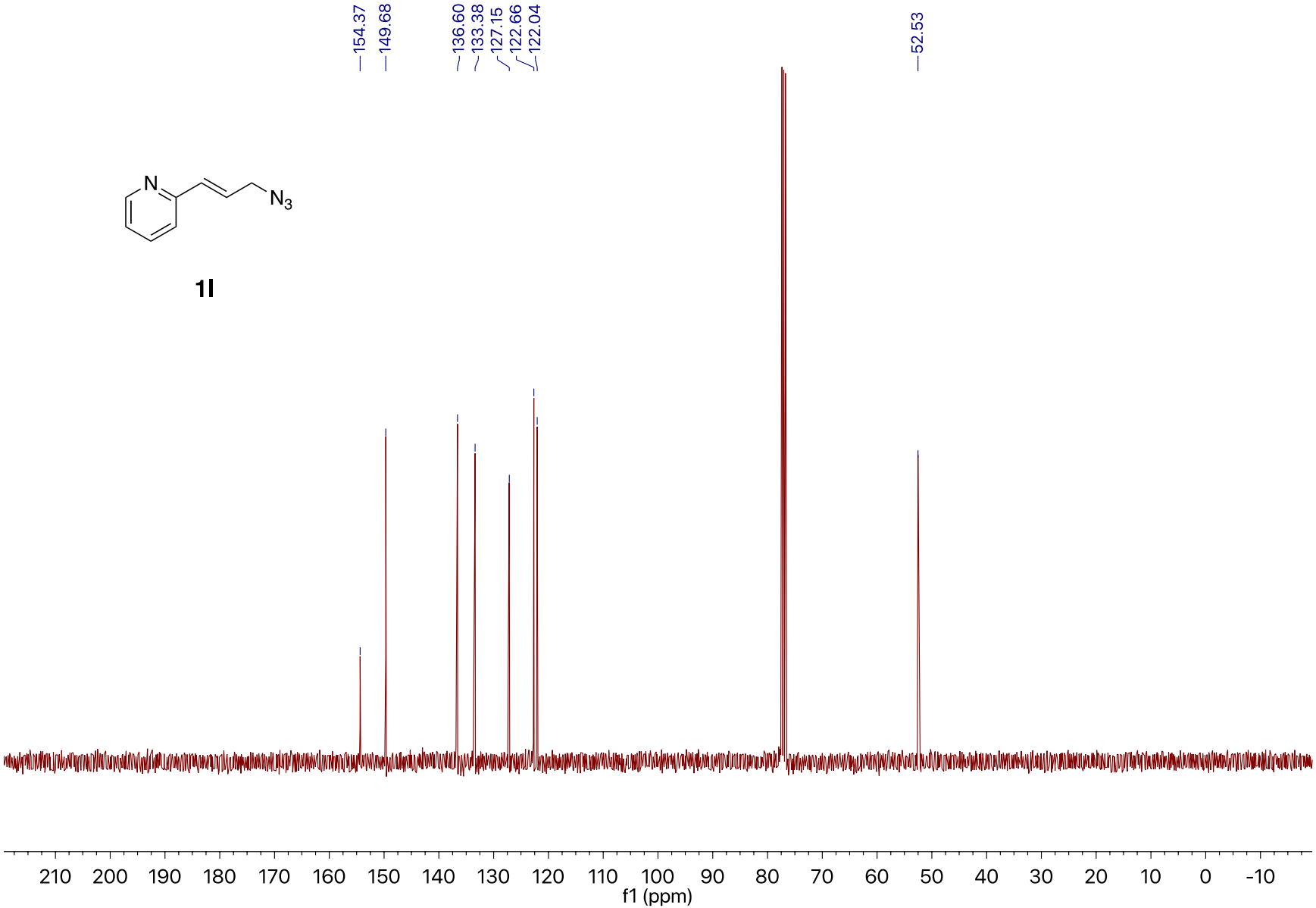
Compound **1i**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



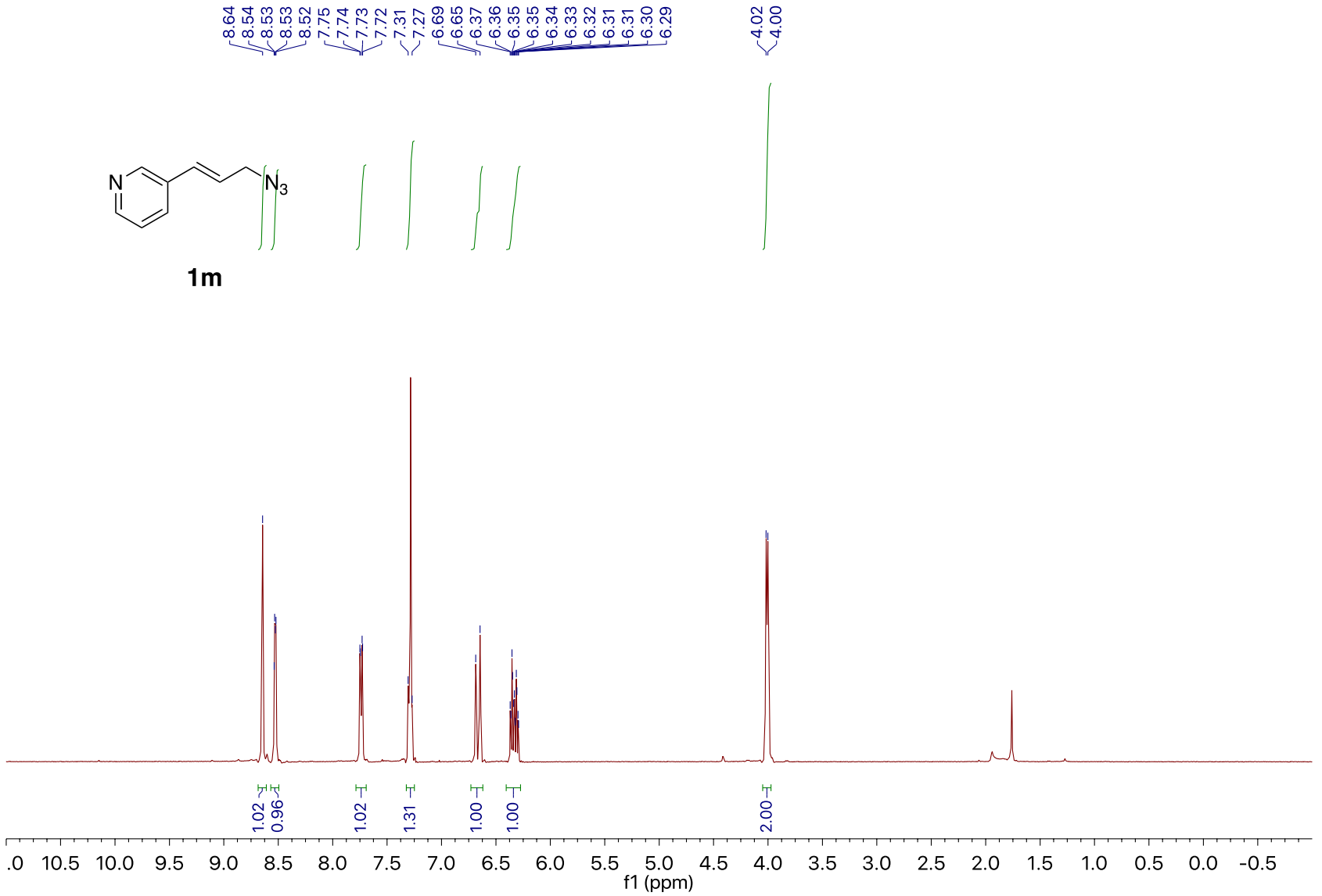
Compound **1i**. 101 MHz ^{19}F NMR spectrum in $CDCl_3$



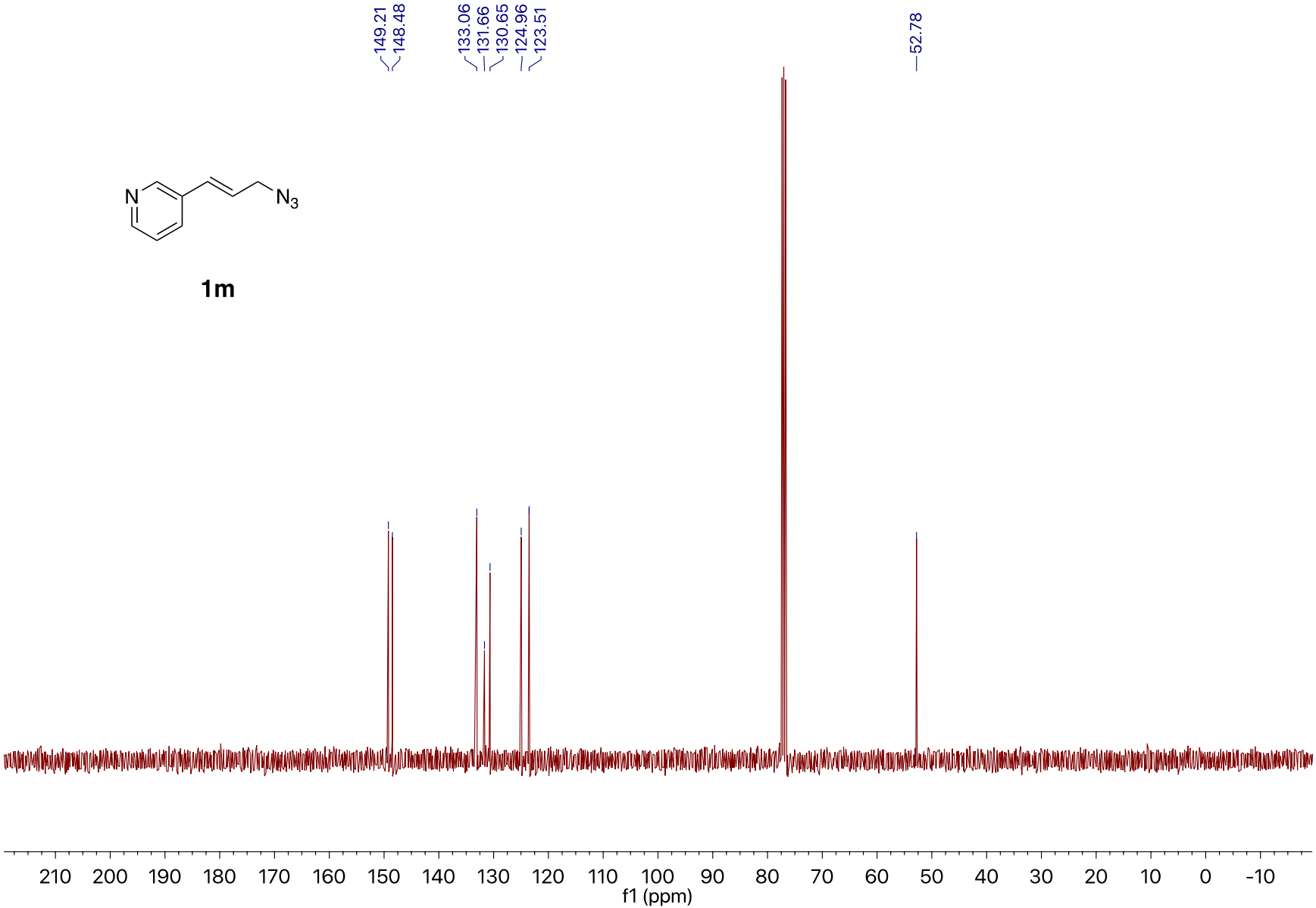
Compound **1l**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



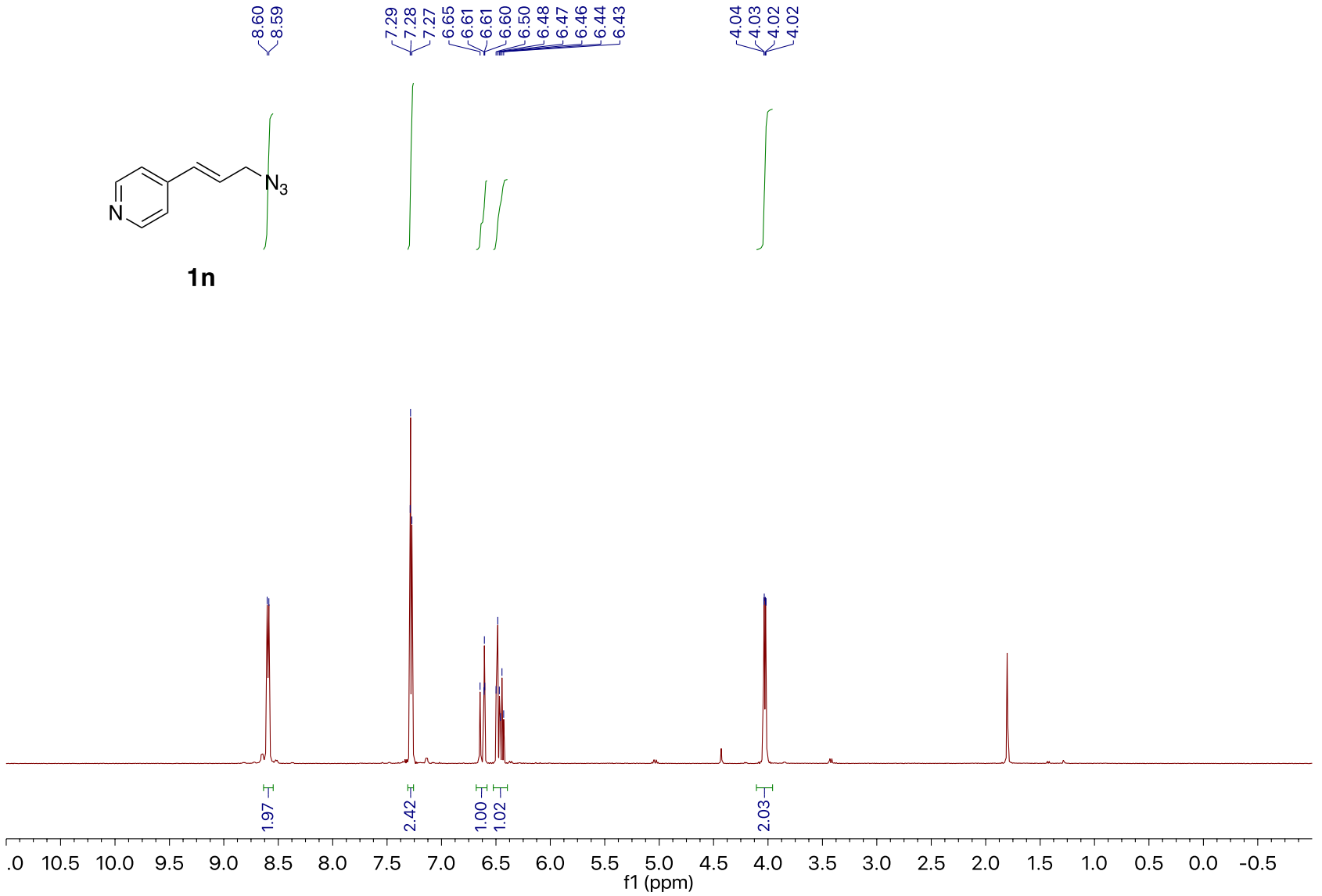
Compound **1l**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



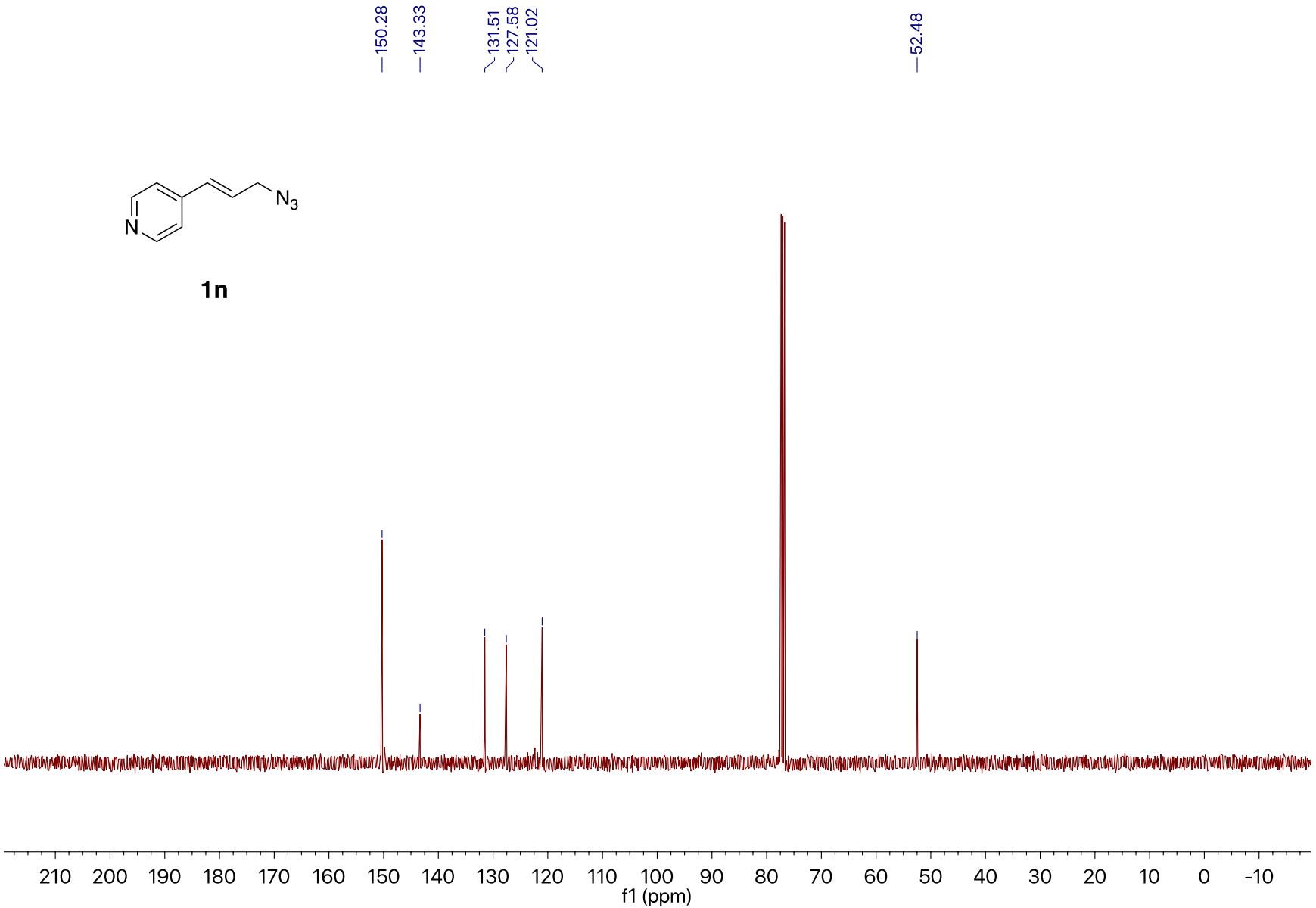
Compound **1m**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



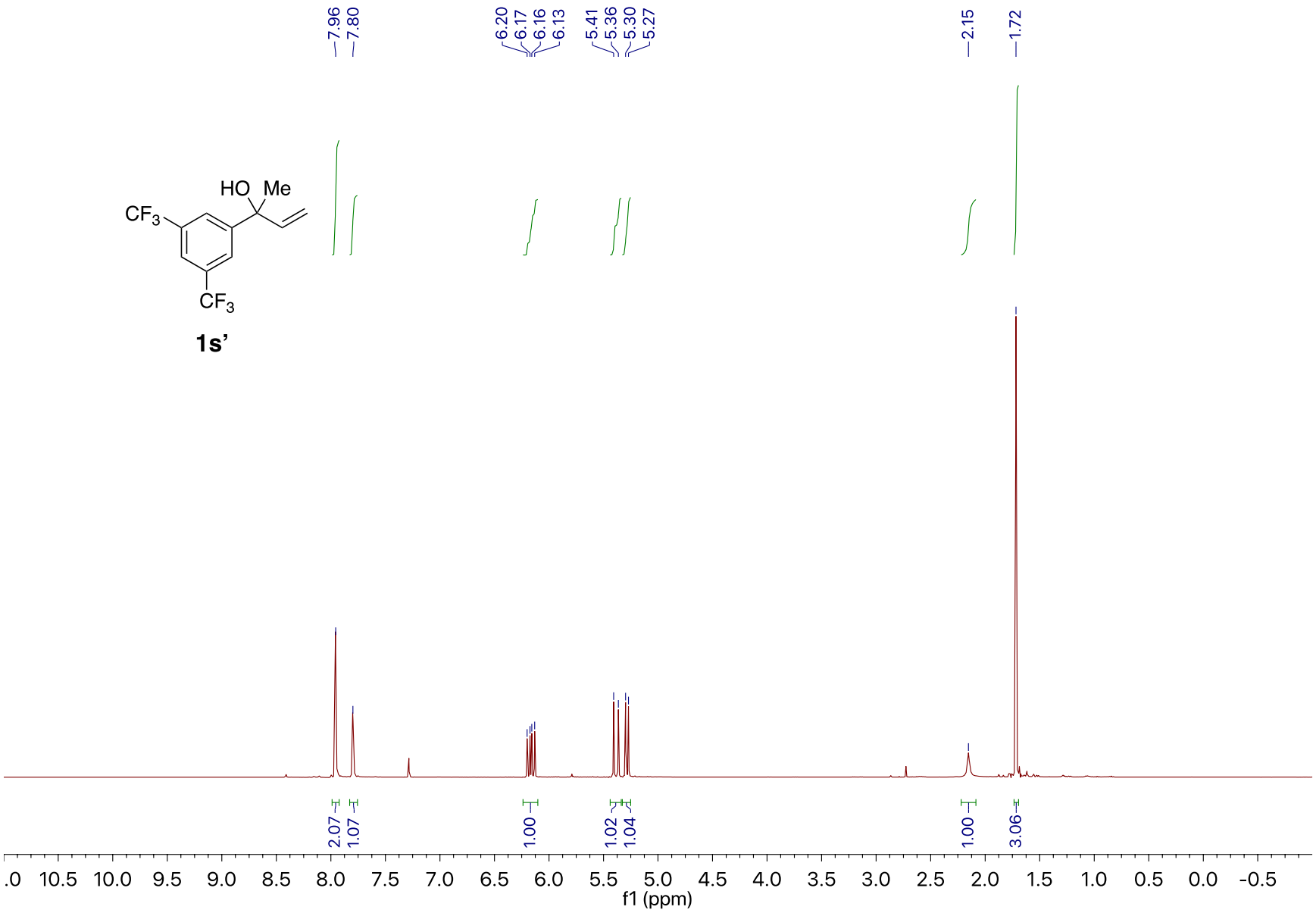
Compound **1m**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



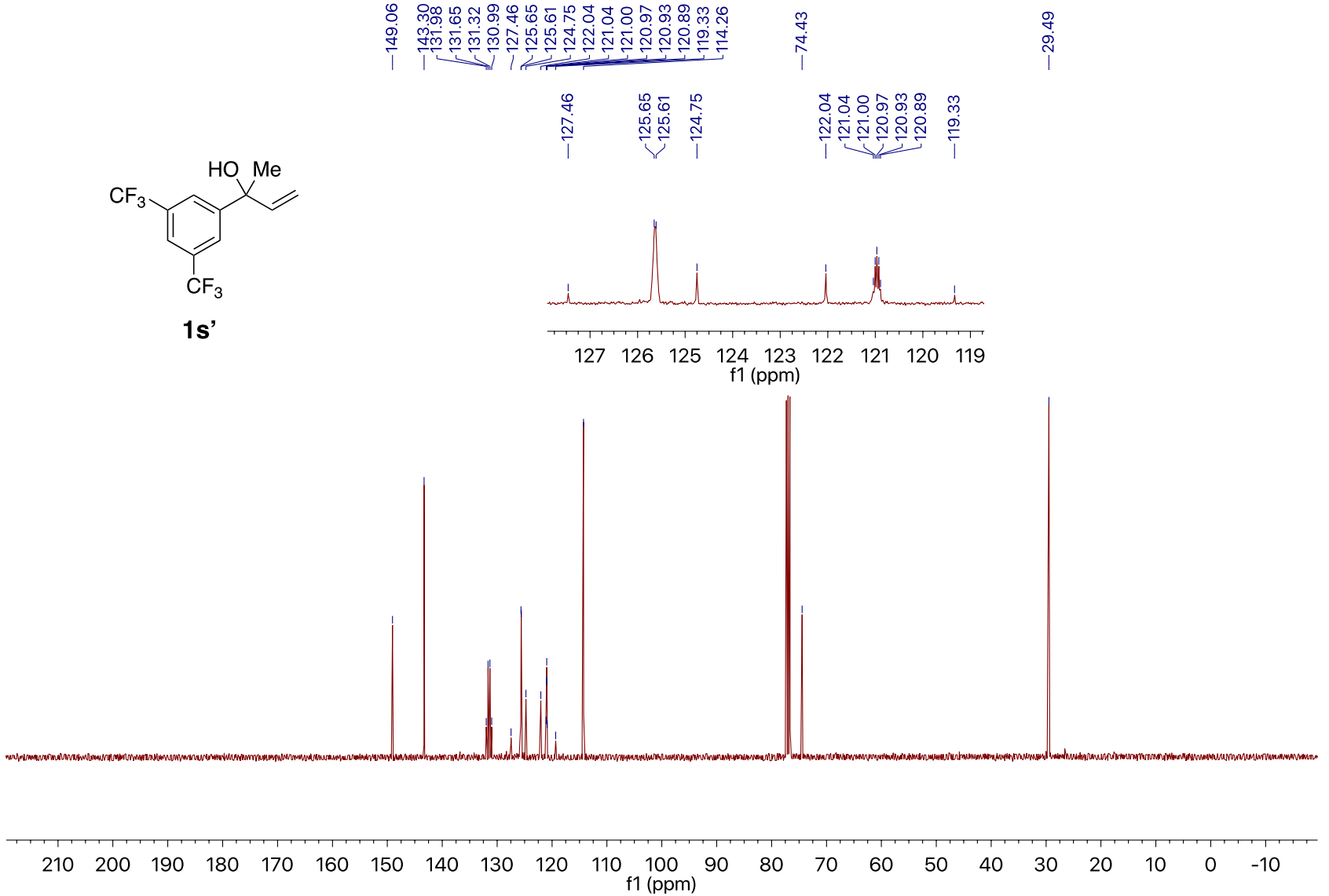
Compound **1n**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



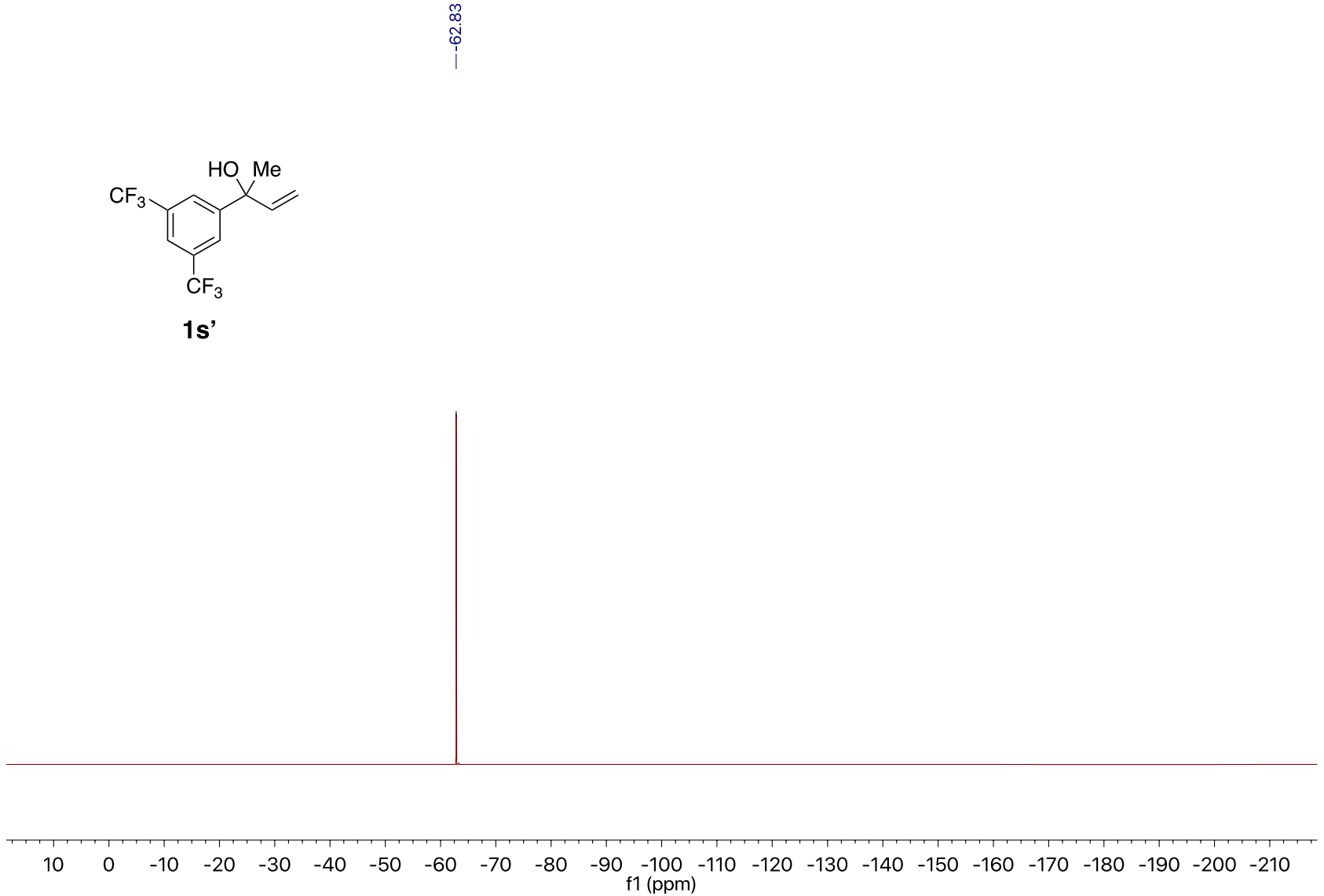
Compound **1n**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



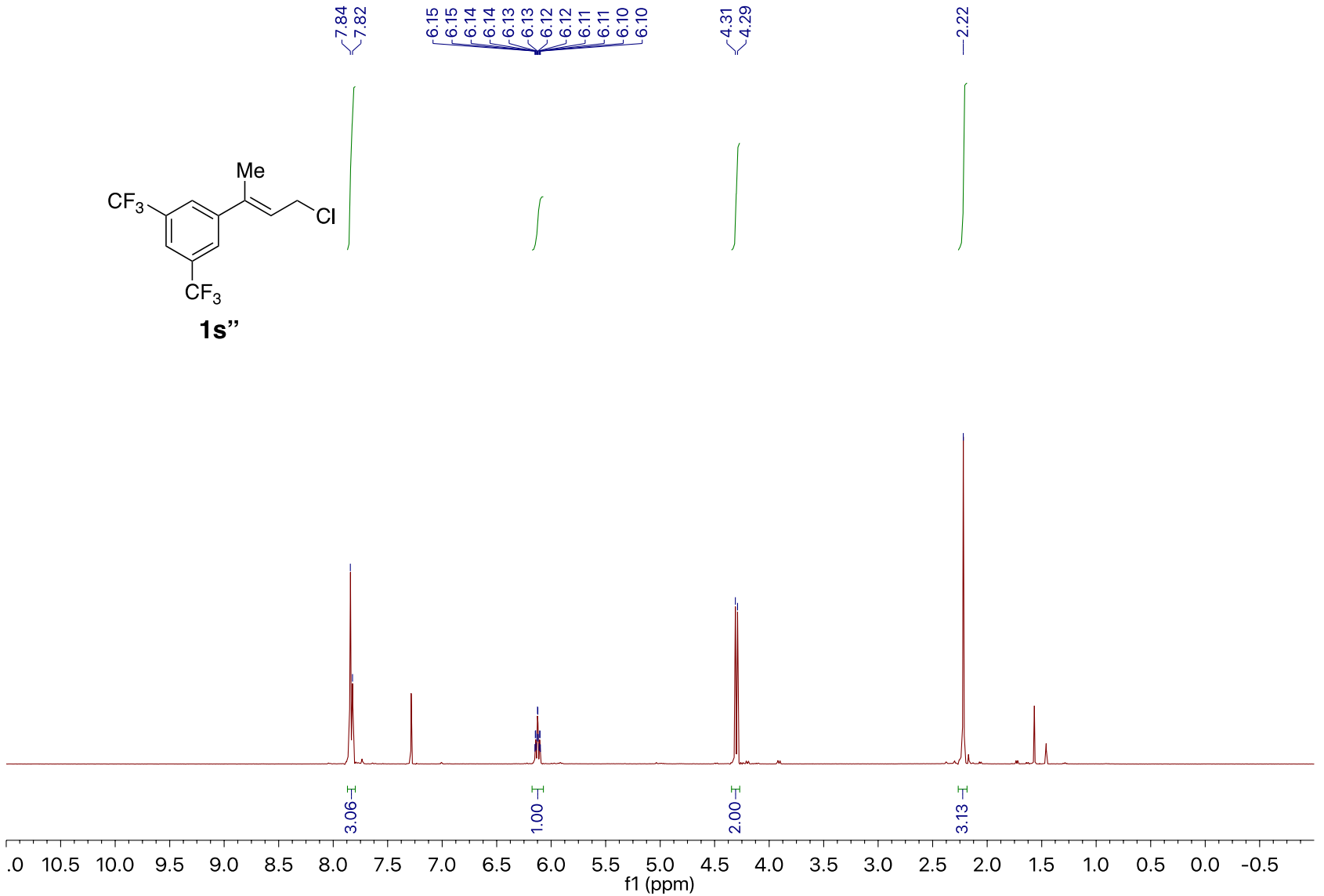
Compound **1s'**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



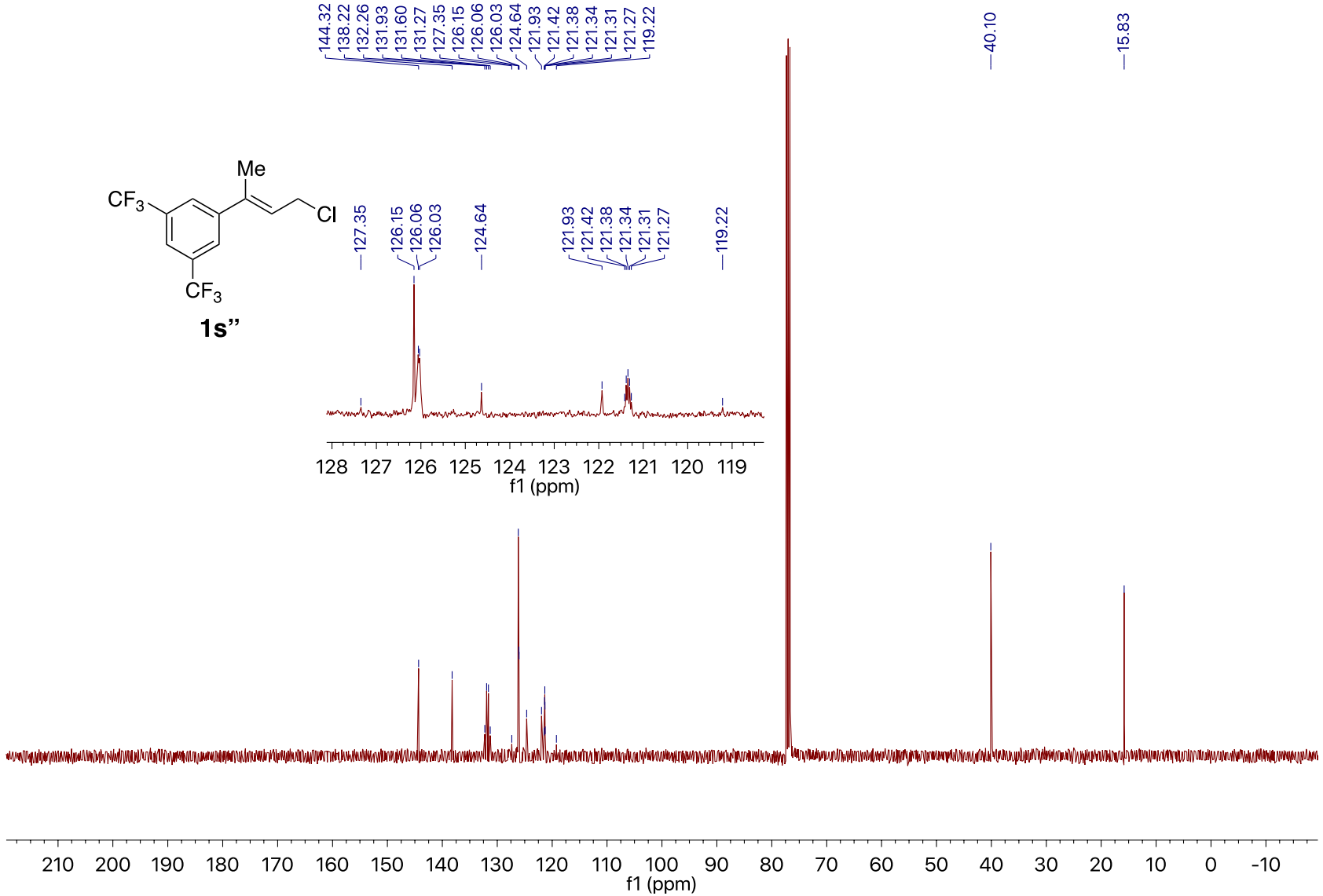
Compound **1s'**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



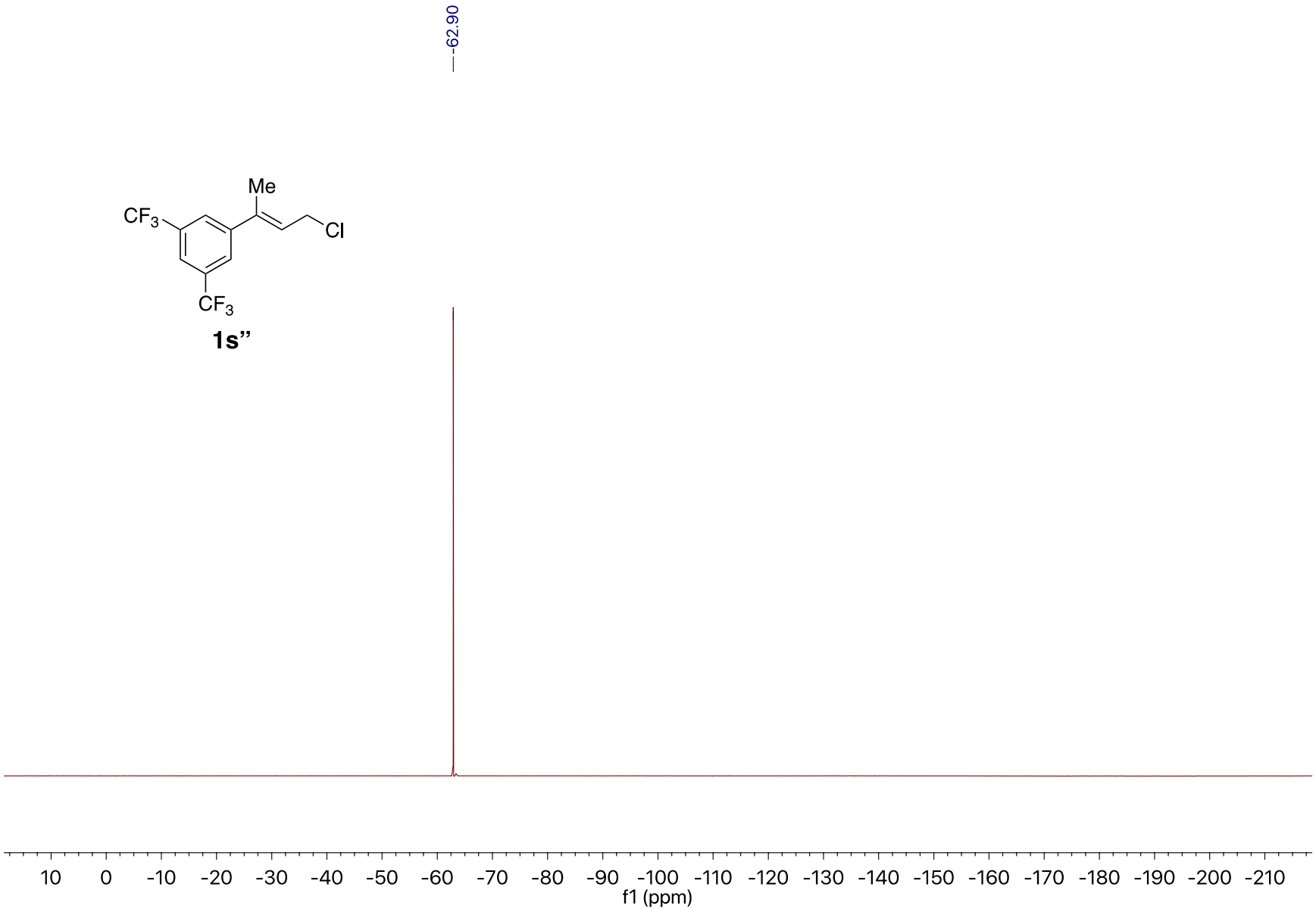
Compound **1s'**. 376 MHz ^{19}F NMR spectrum in $CDCl_3$



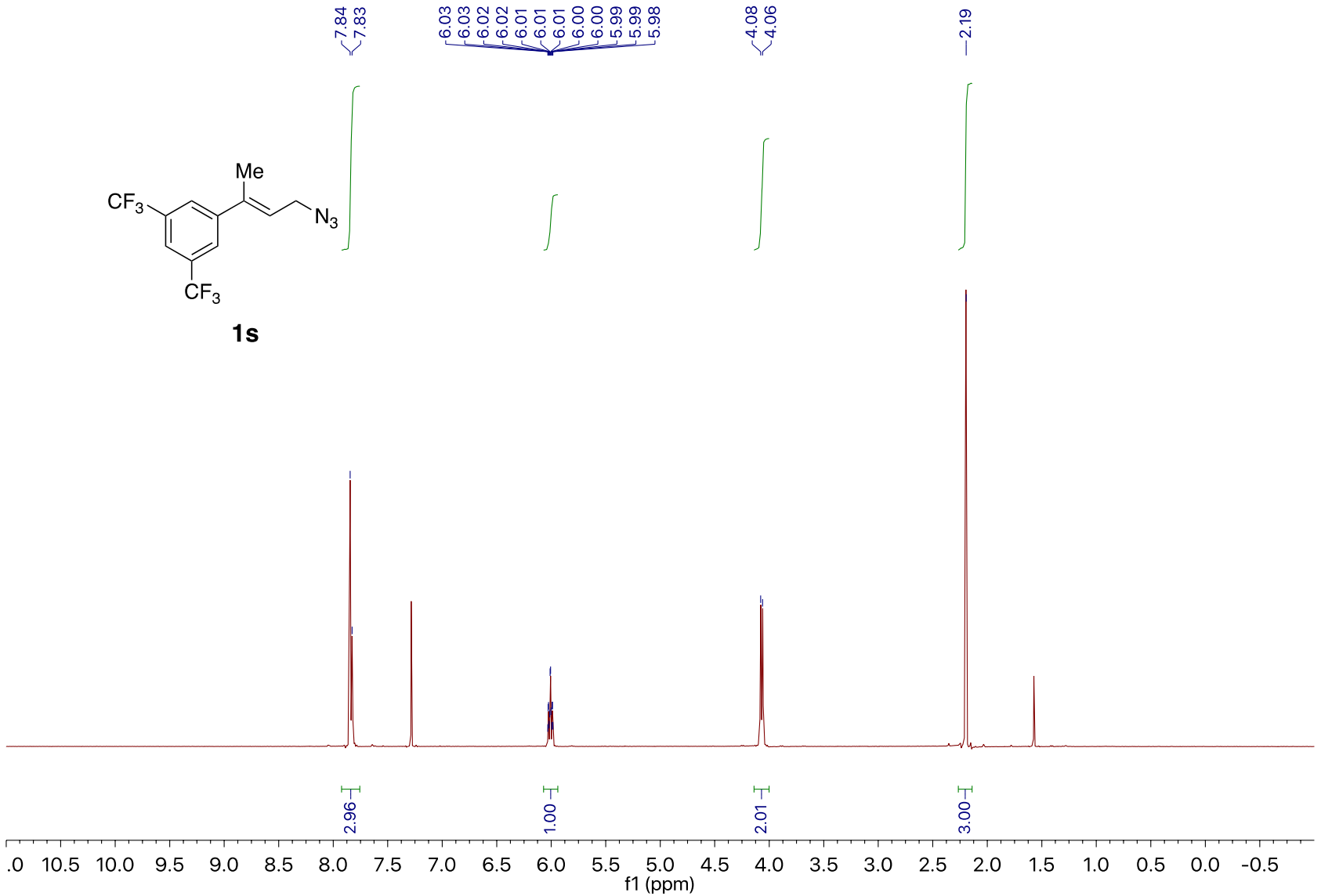
Compound **1s''**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



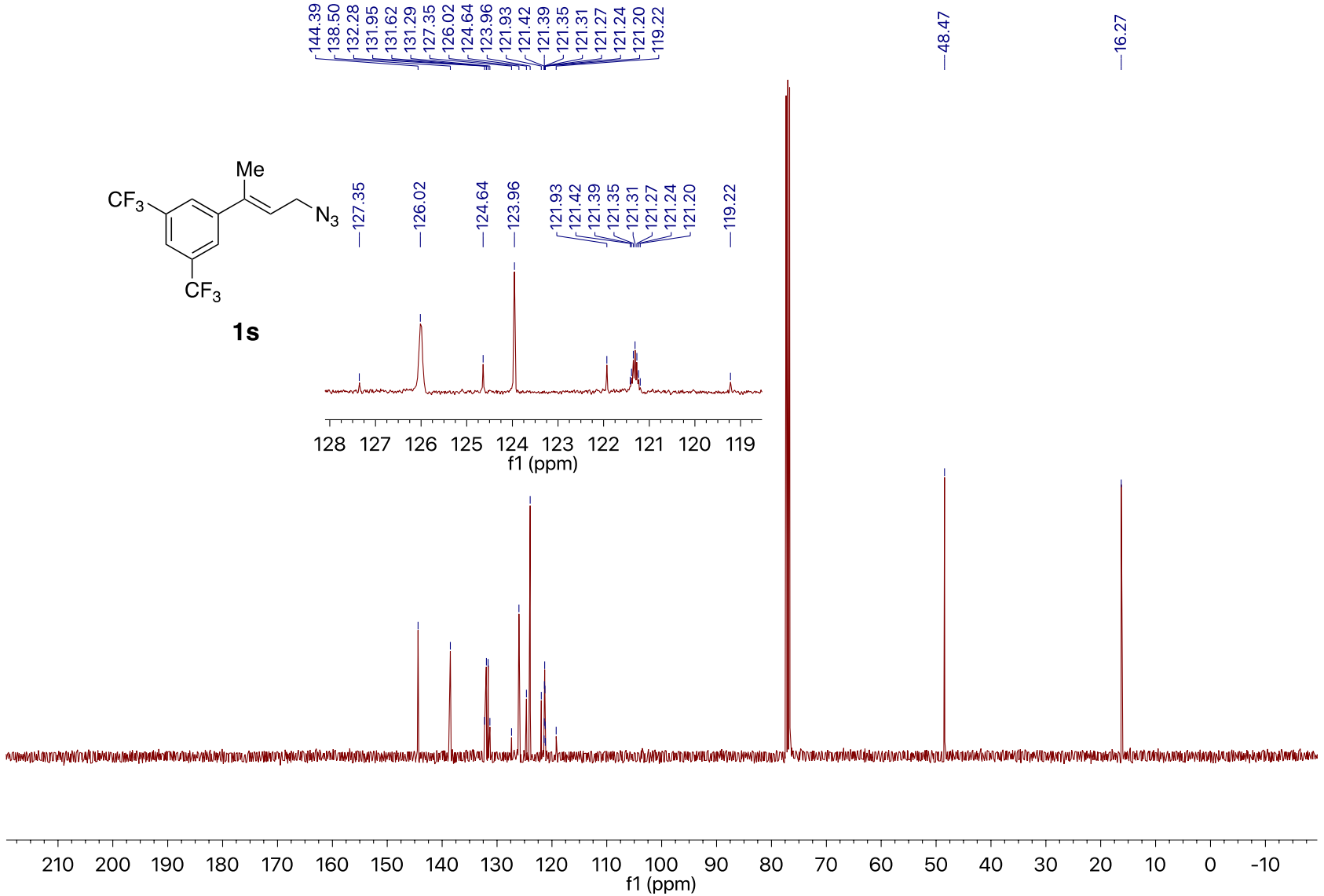
Compound **1s''**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



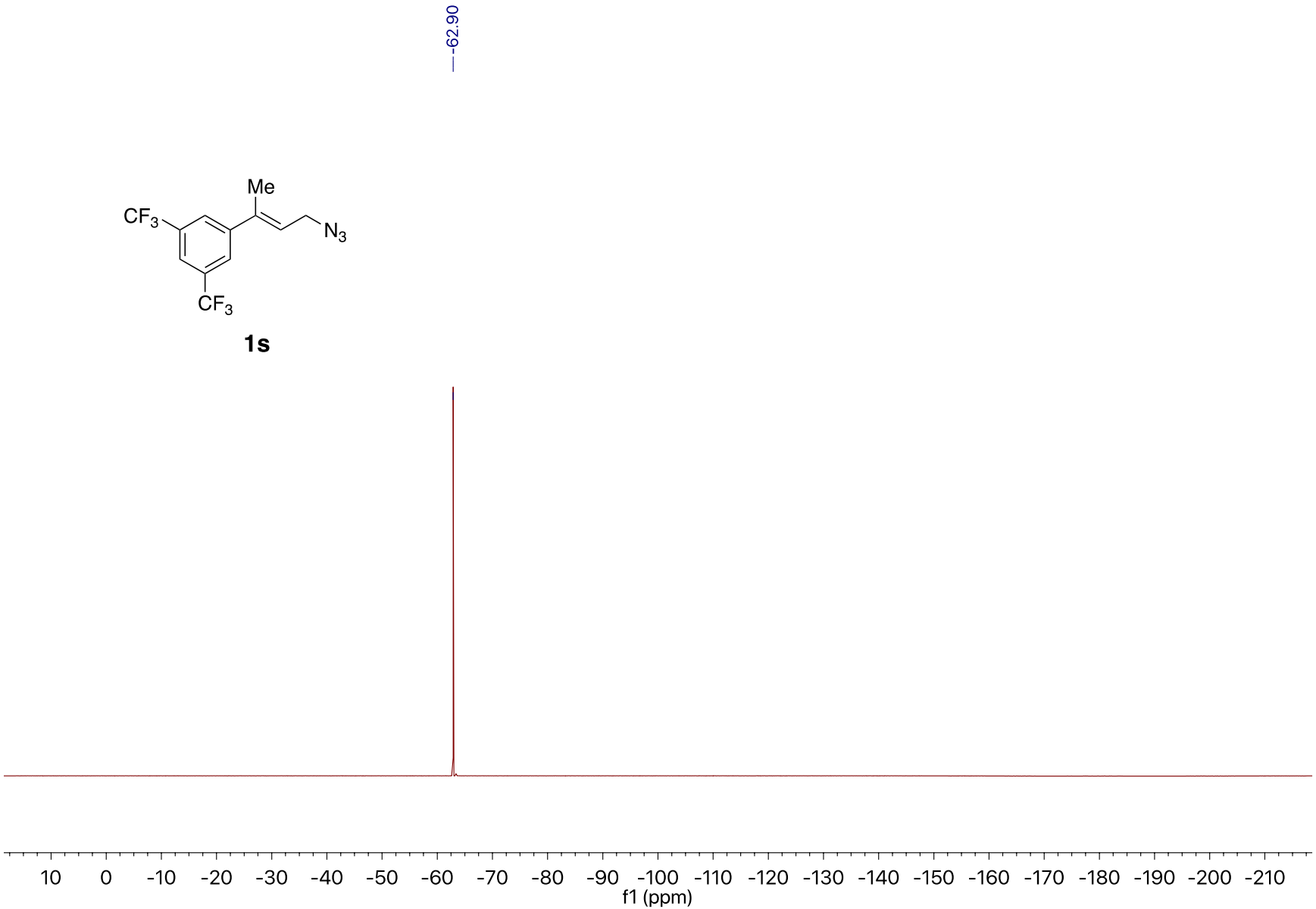
Compound **1s''**. 376 MHz ^{19}F NMR spectrum in $CDCl_3$



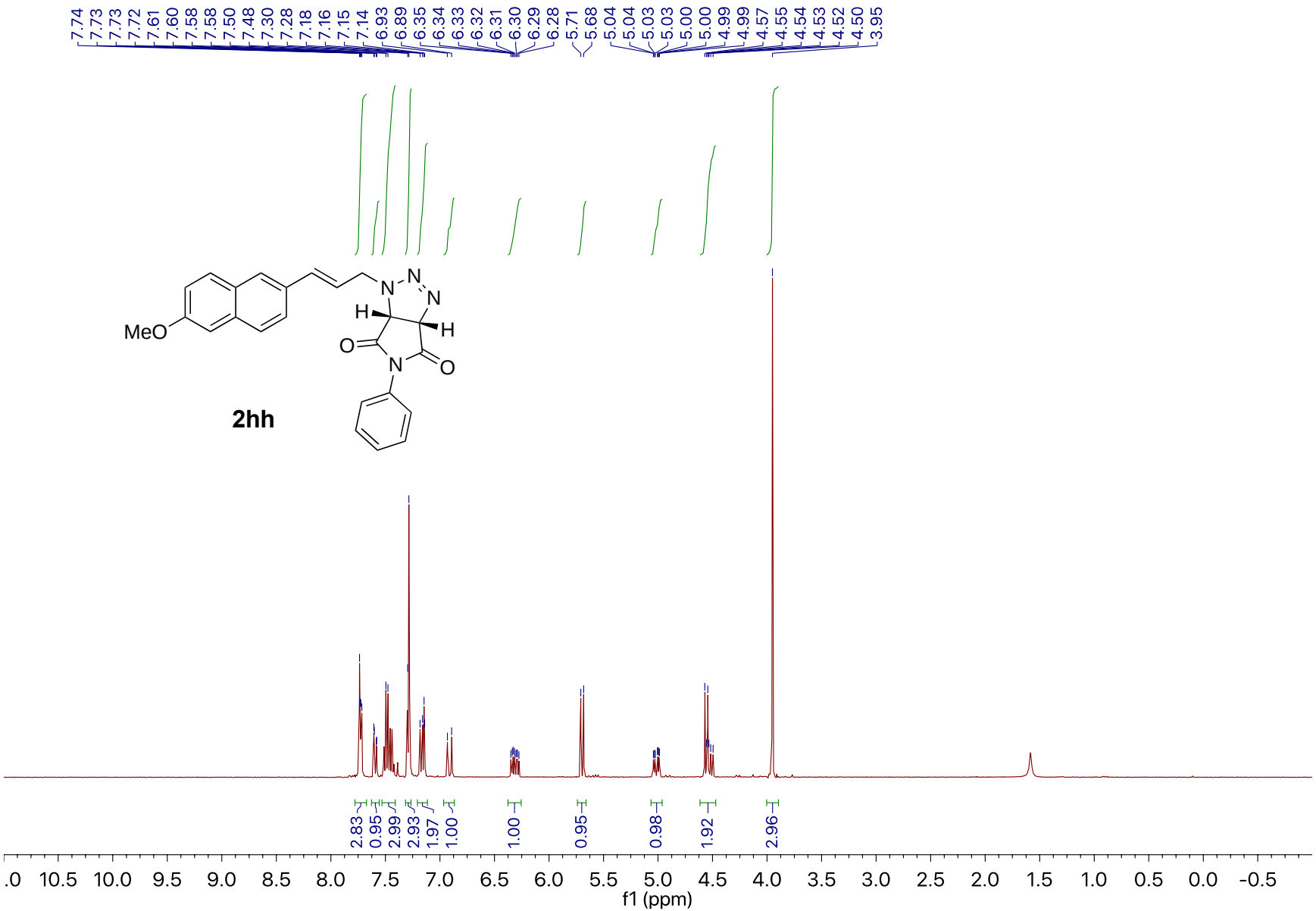
Compound **1s**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



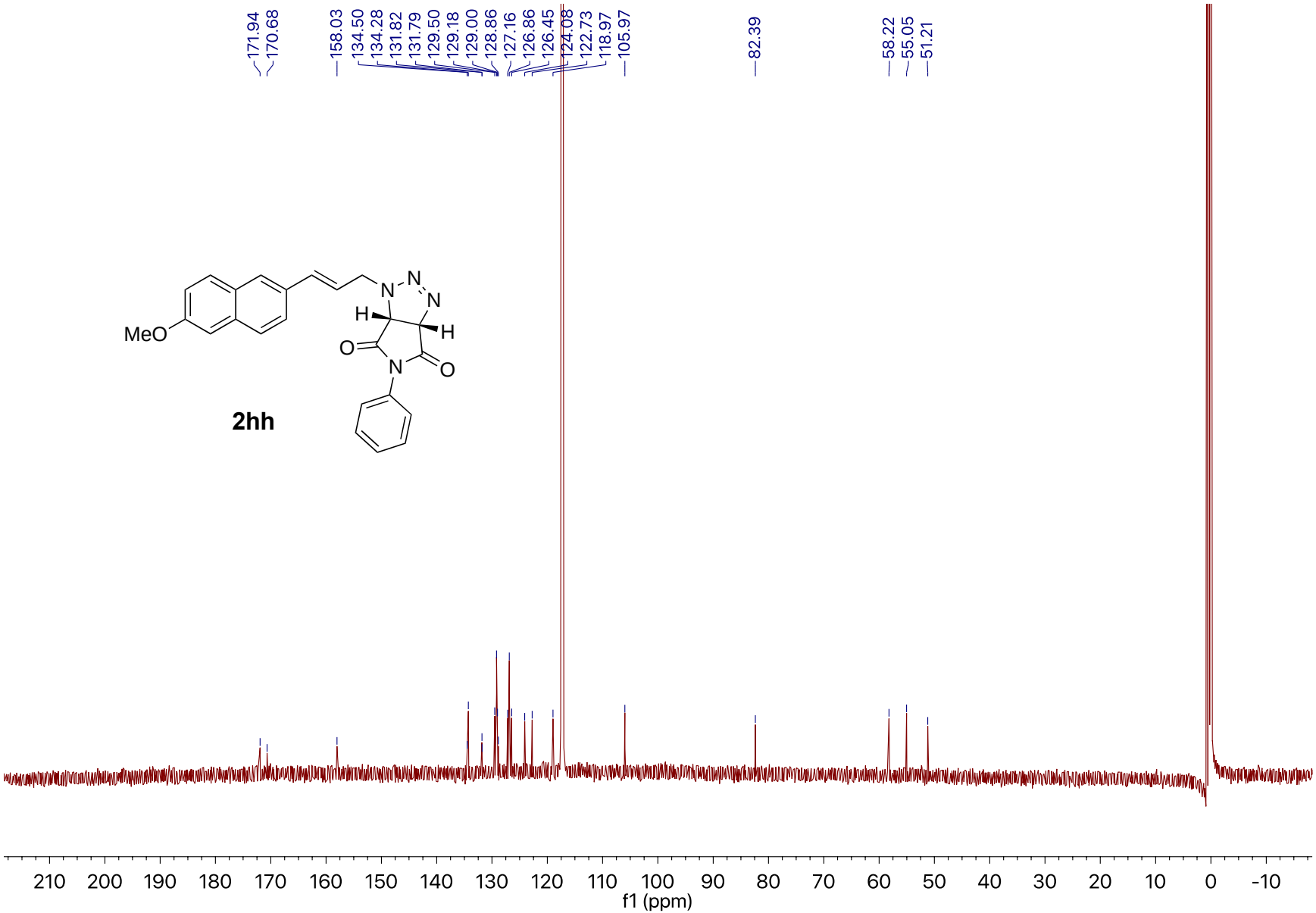
Compound **1s**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



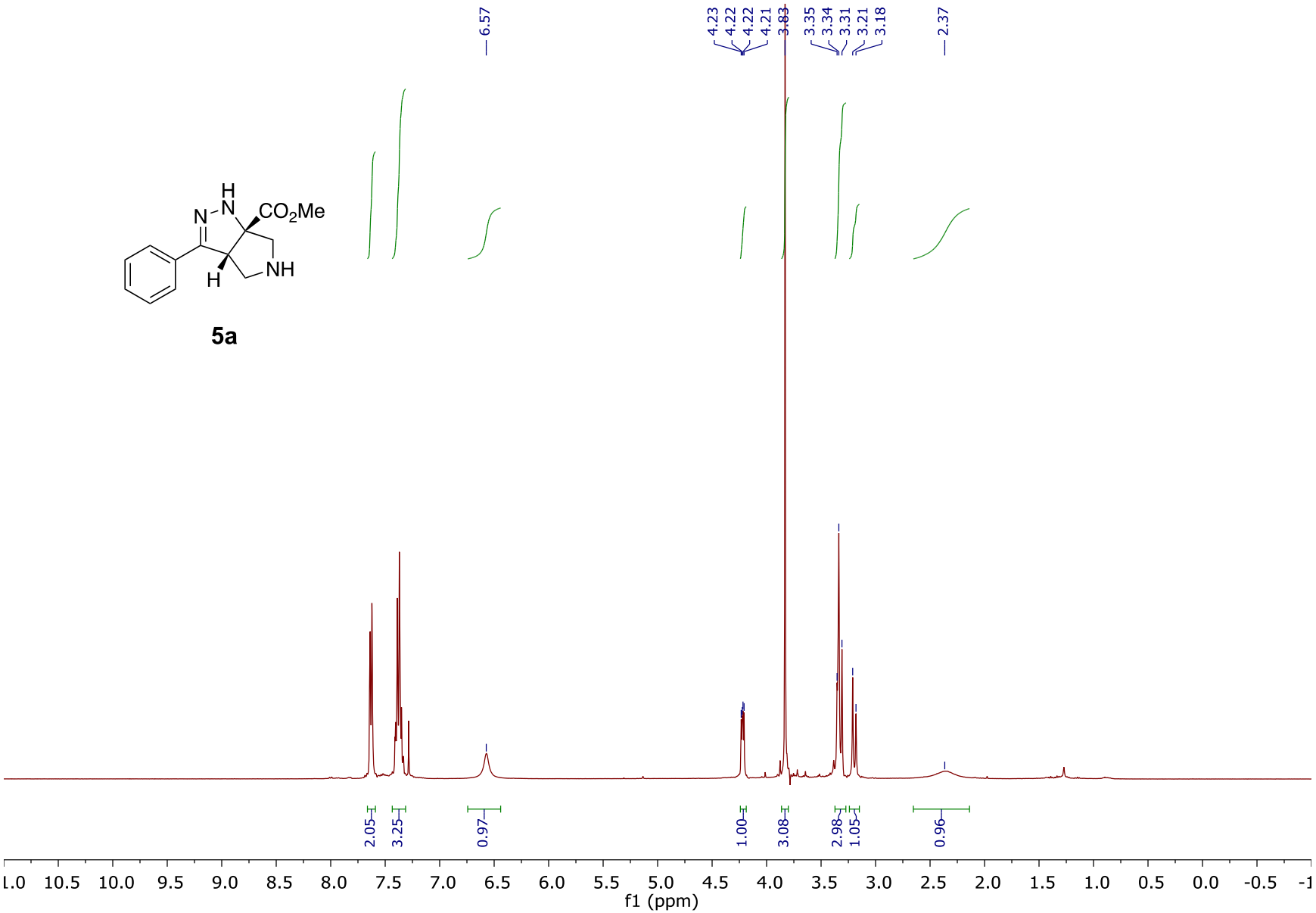
Compound **1s**. 376 MHz ^{19}F NMR spectrum in $CDCl_3$



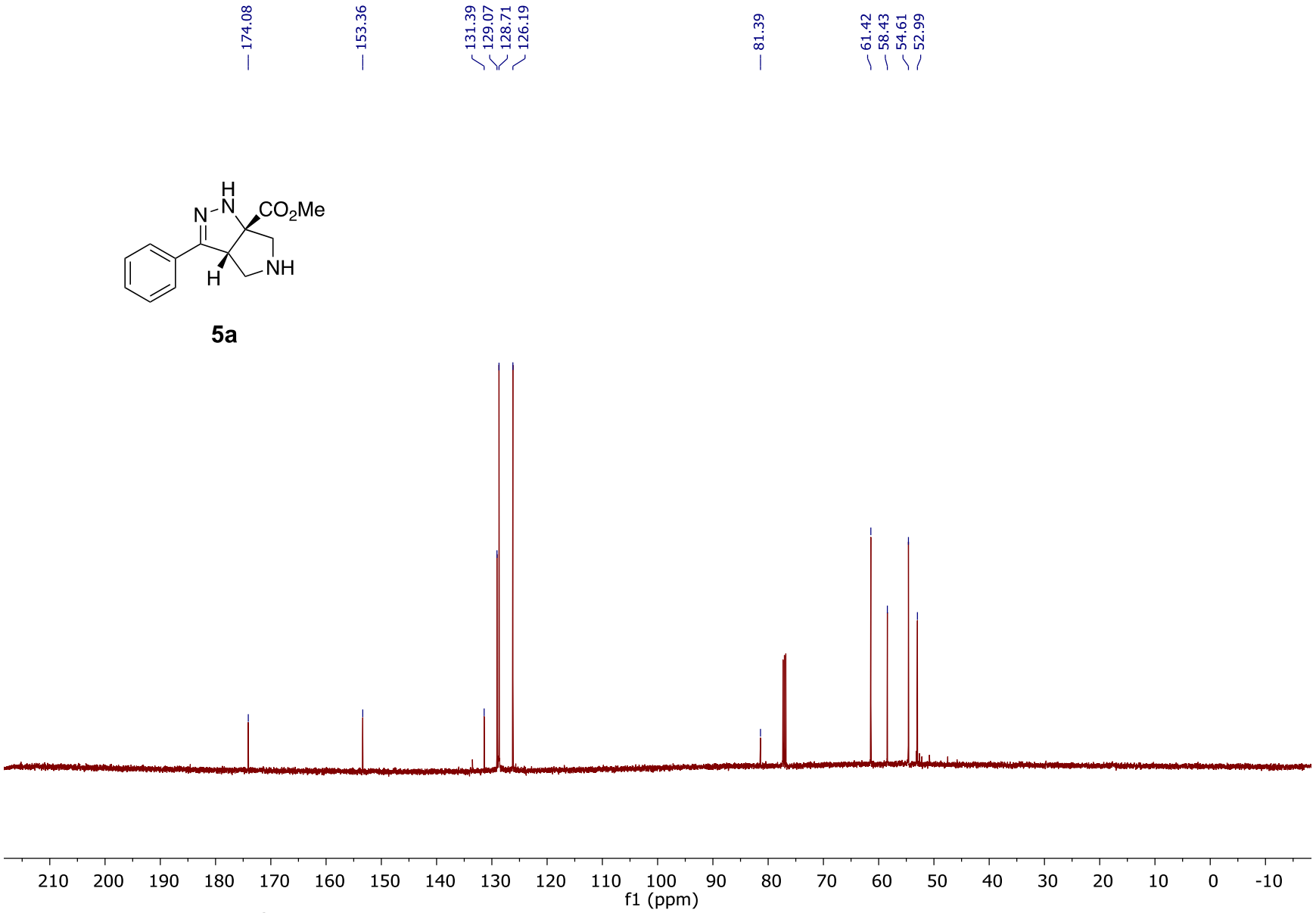
Compound **2hh**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



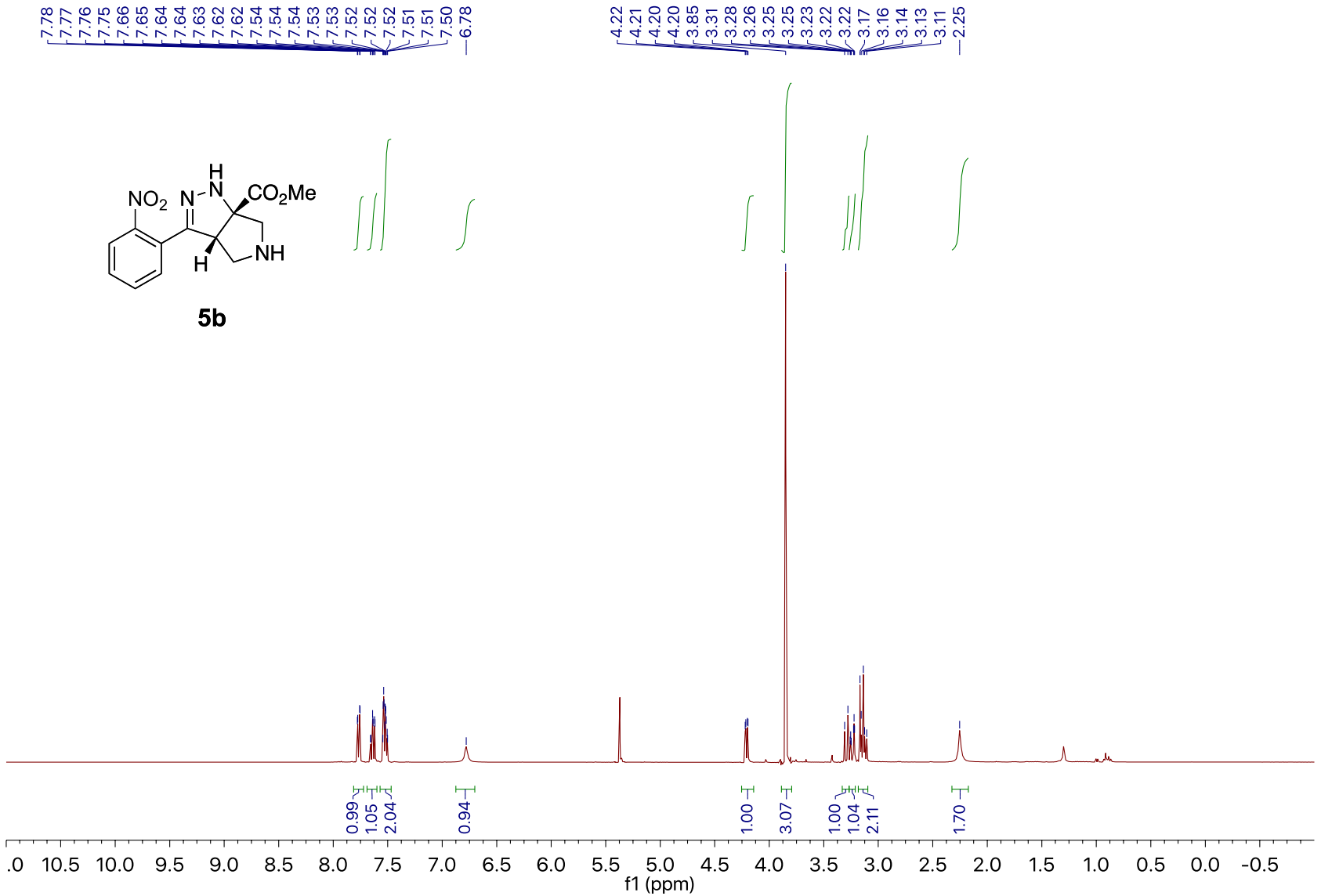
Compound **2hh**. 126 MHz ^{13}C NMR spectrum in CD_3CN



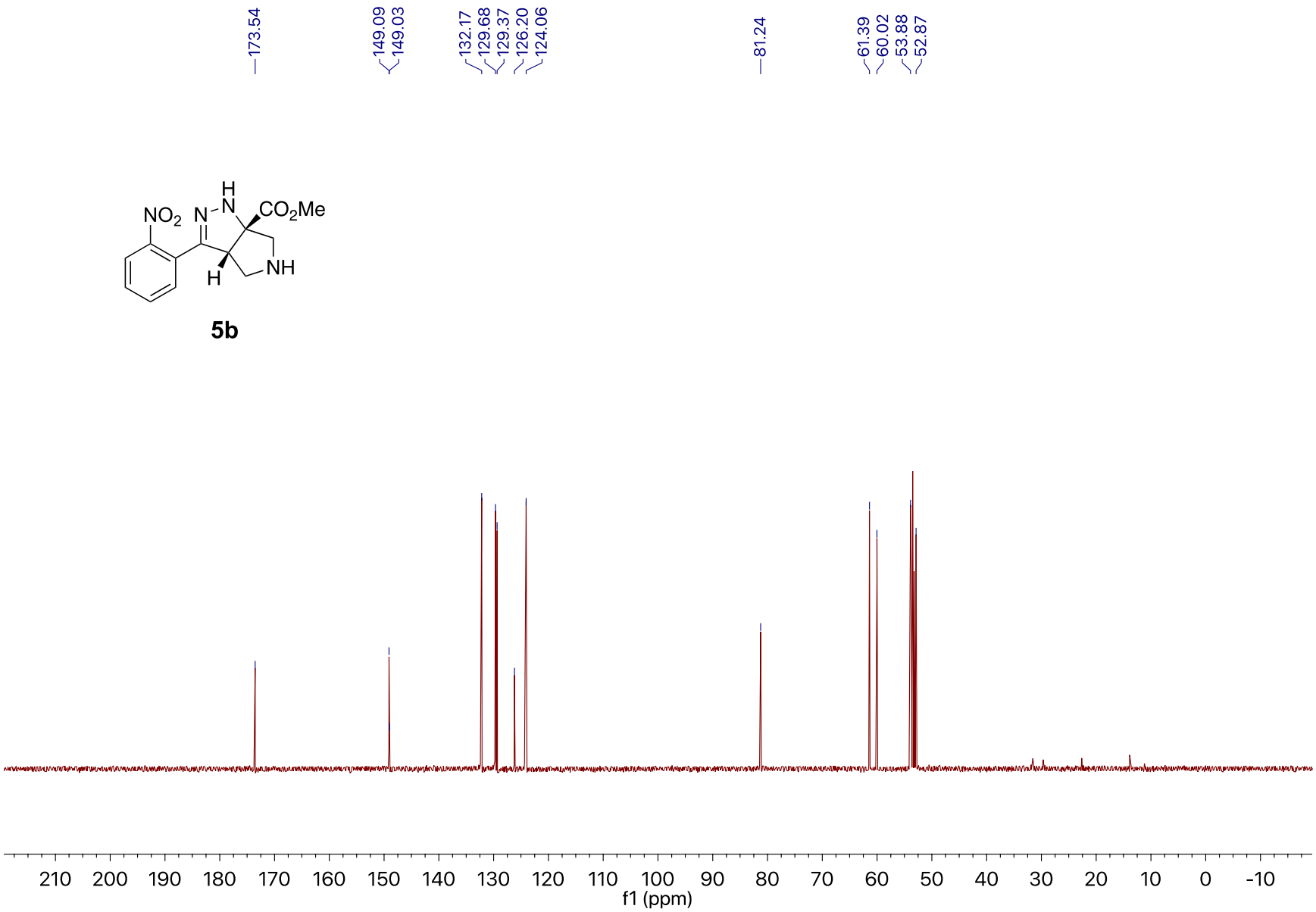
Compound **5a**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



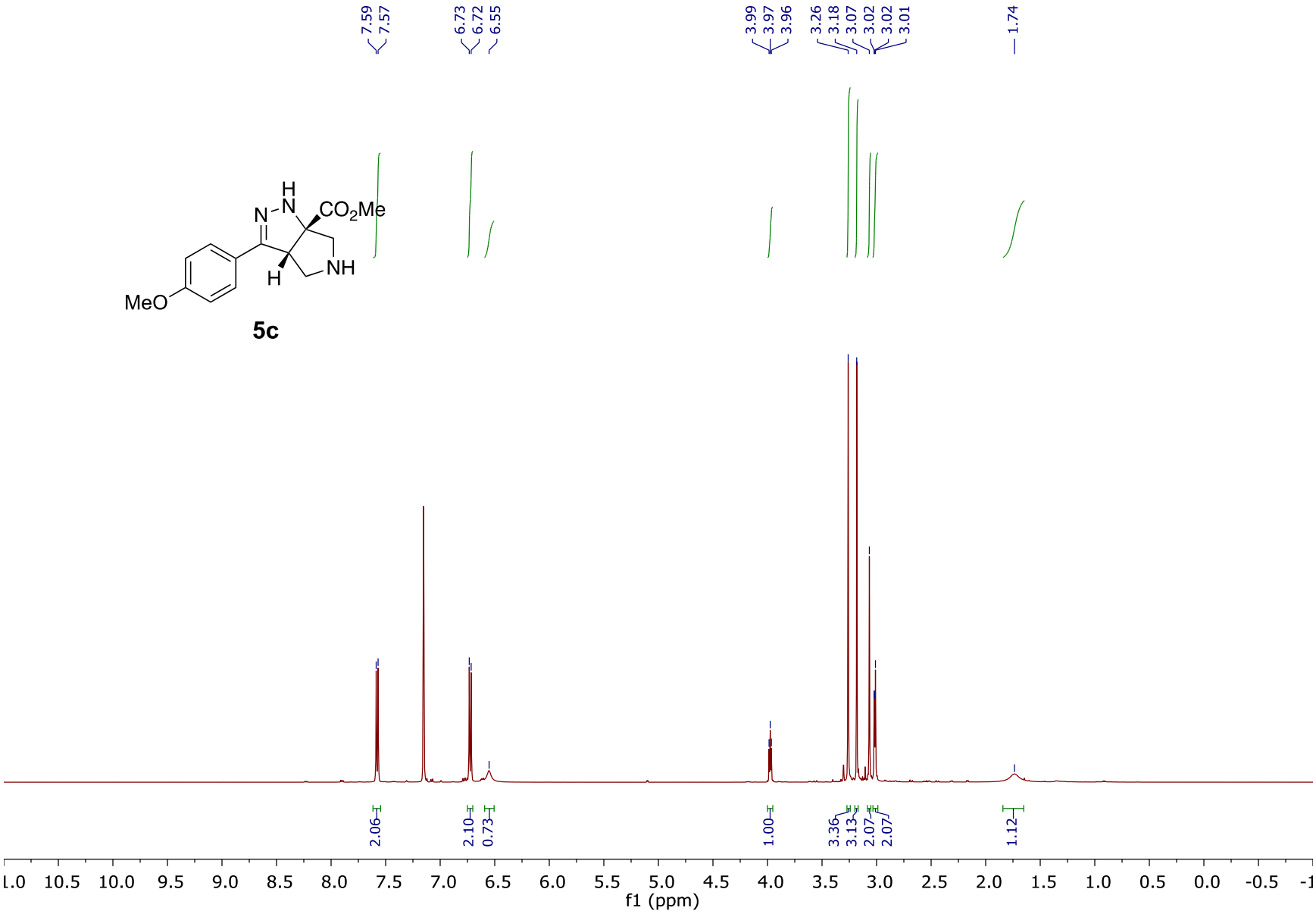
Compound **5a**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



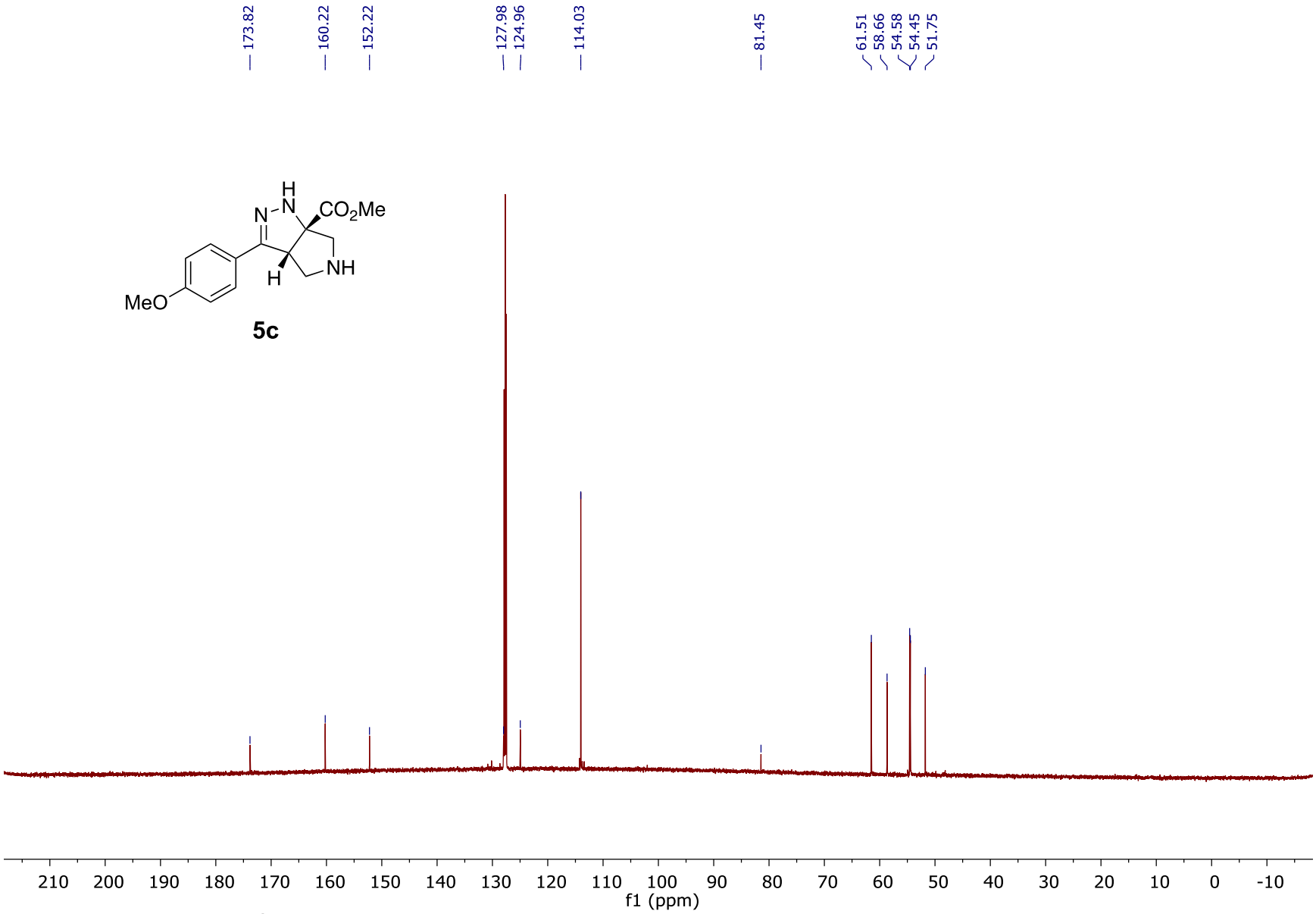
Compound **5b**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



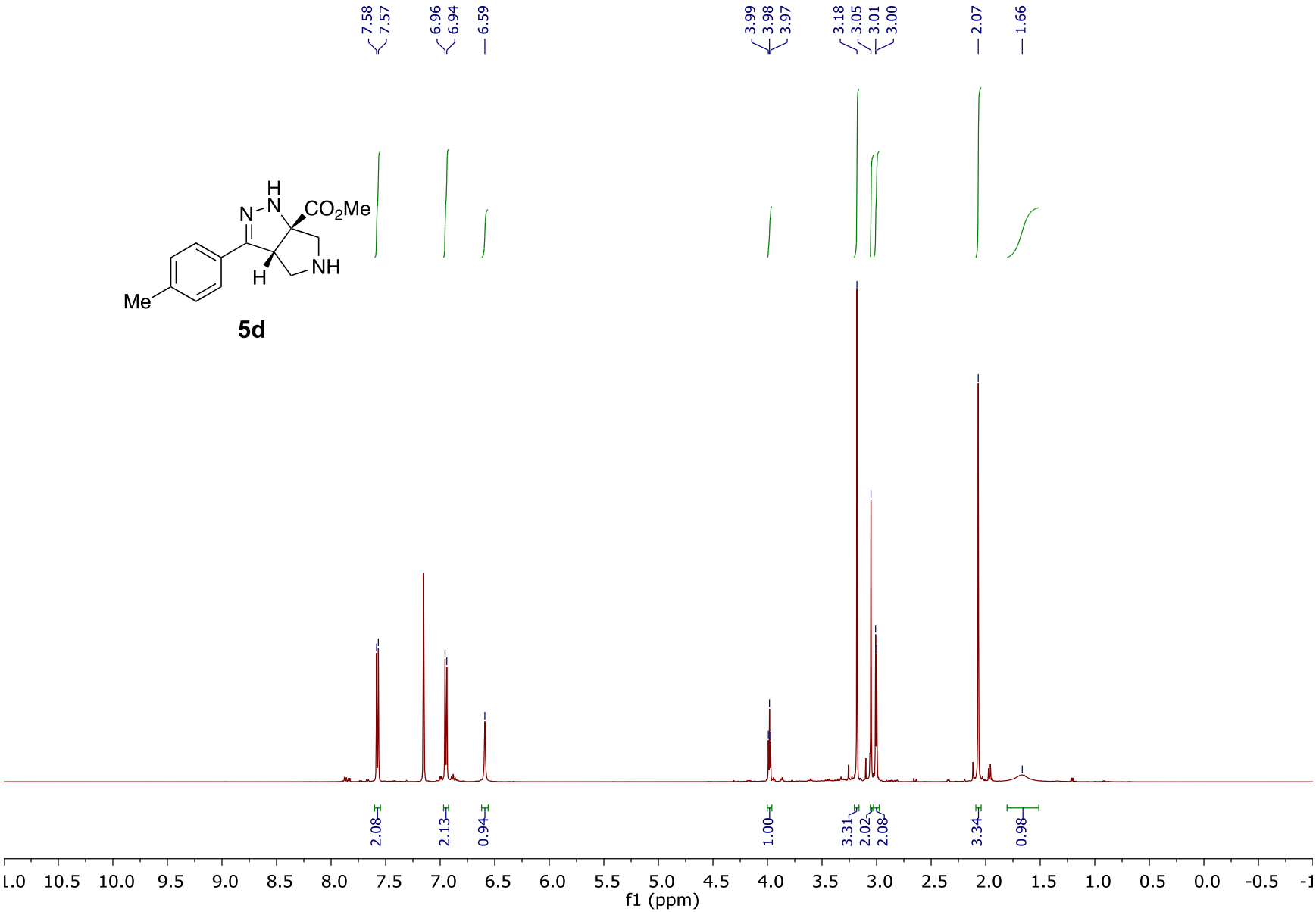
Compound **5b**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



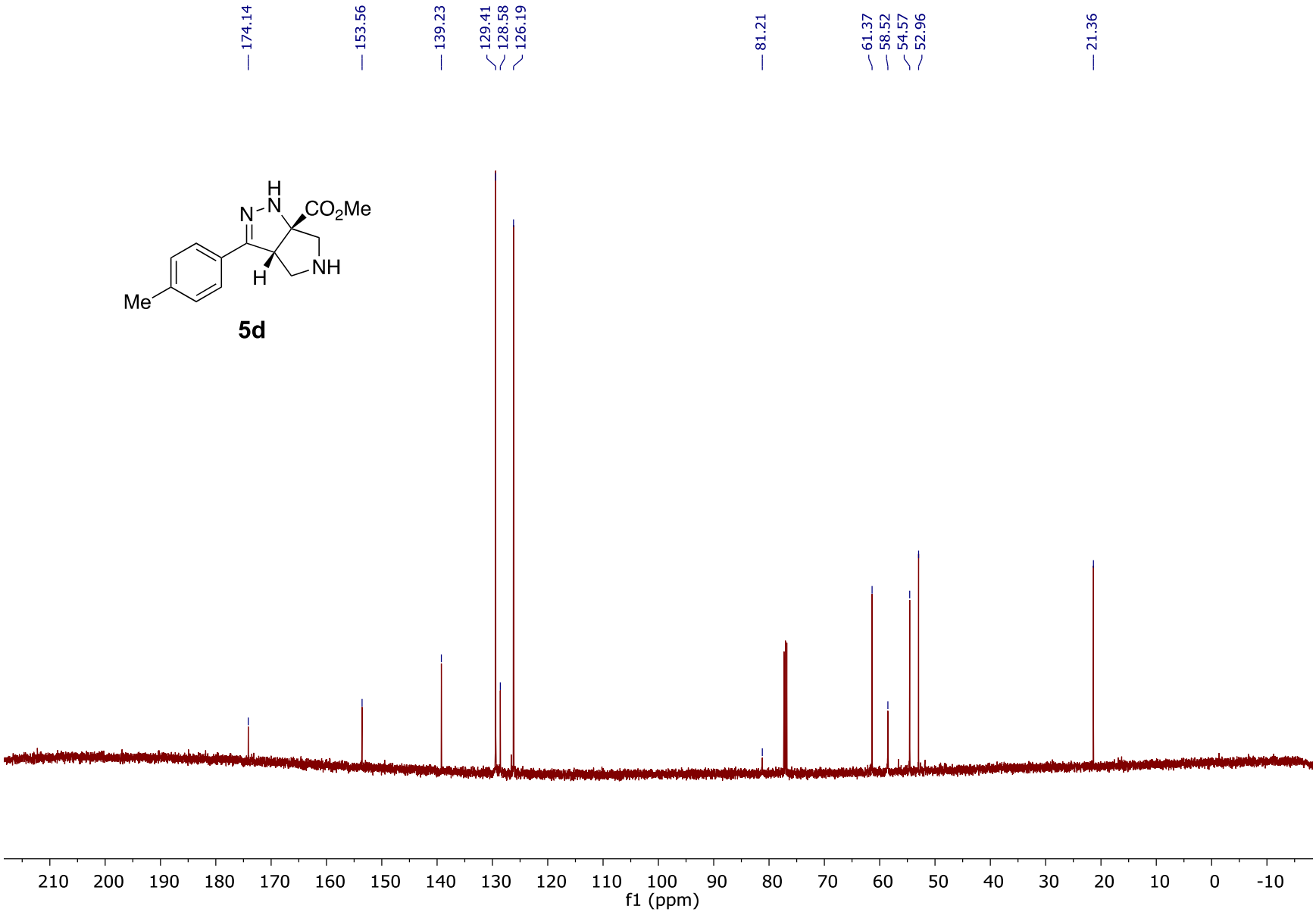
Compound **5c**. 500 MHz ^{1}H NMR spectrum in C_6D_6



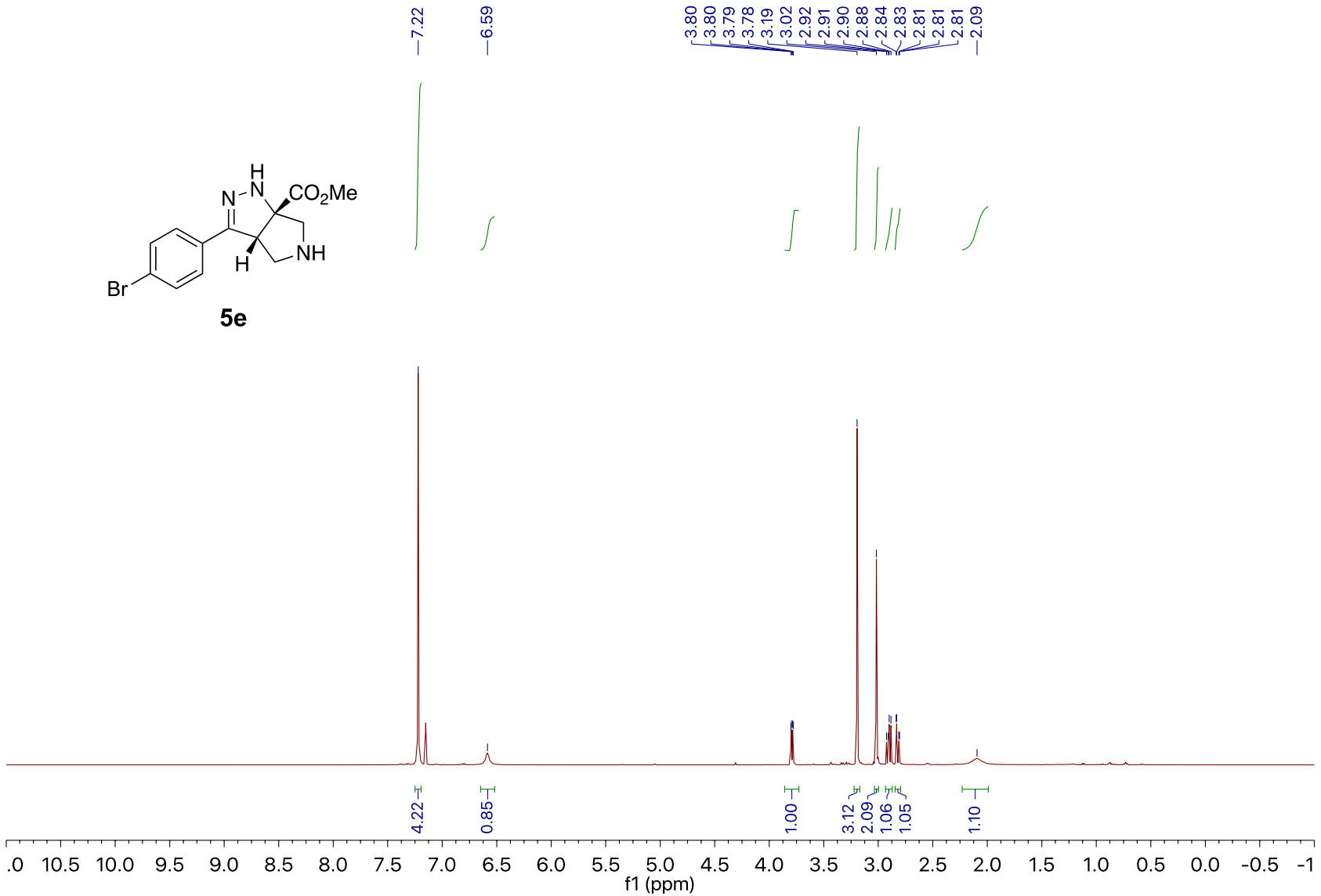
Compound **5c**. 126 MHz ^{13}C NMR spectrum in C_6D_6



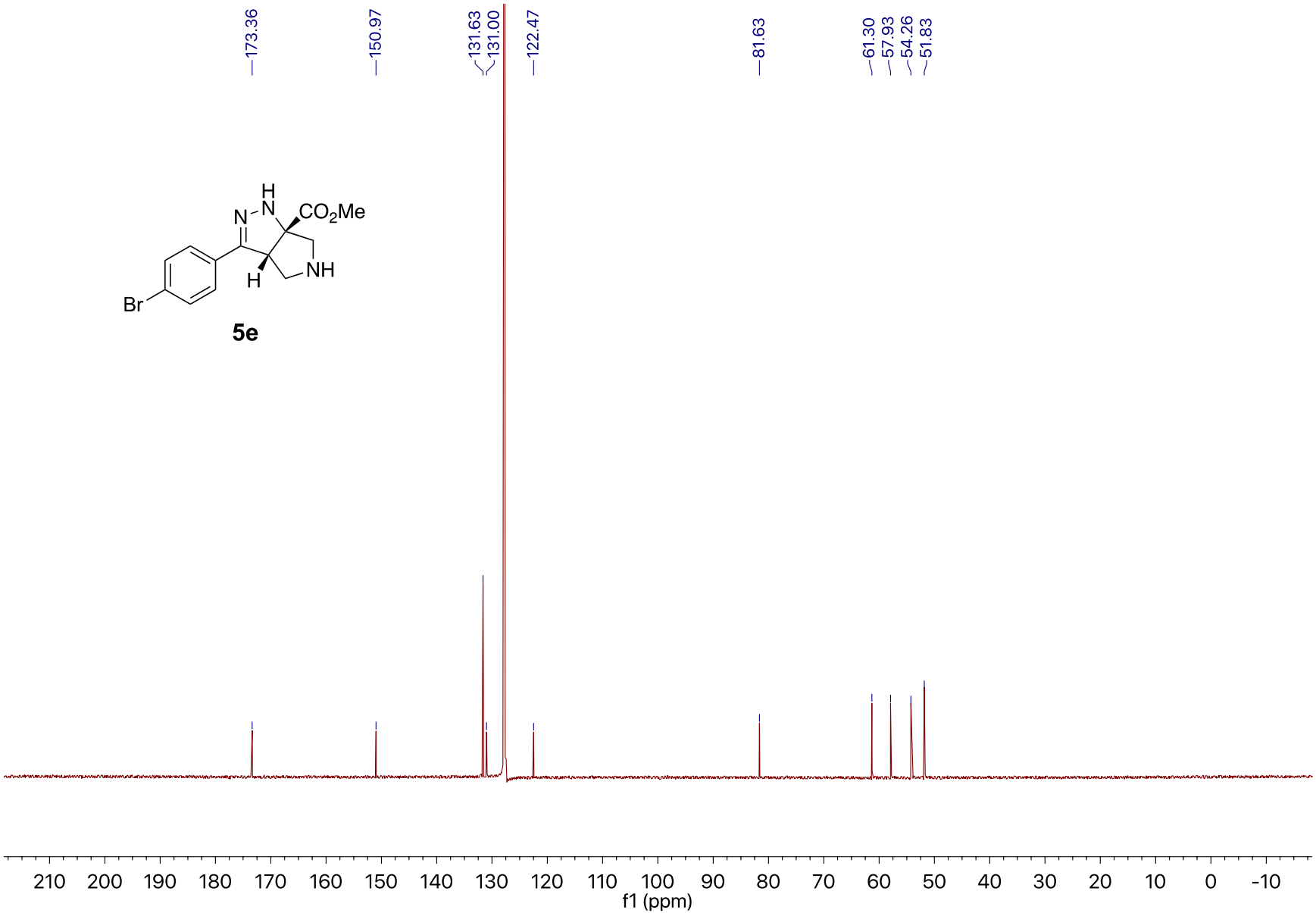
Compound **5d**. 500 MHz ^{1}H NMR spectrum in C_6D_6



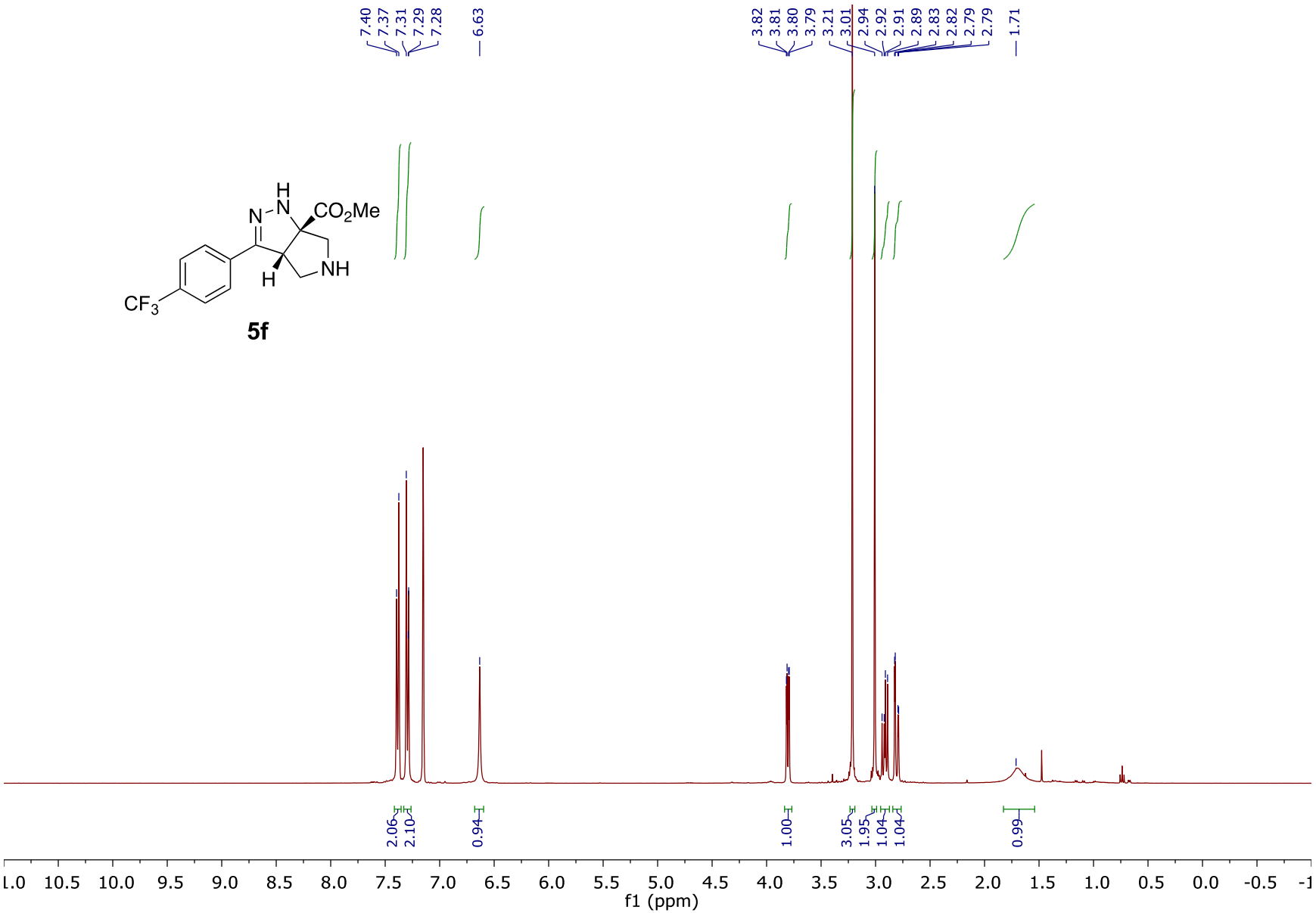
Compound **5d**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



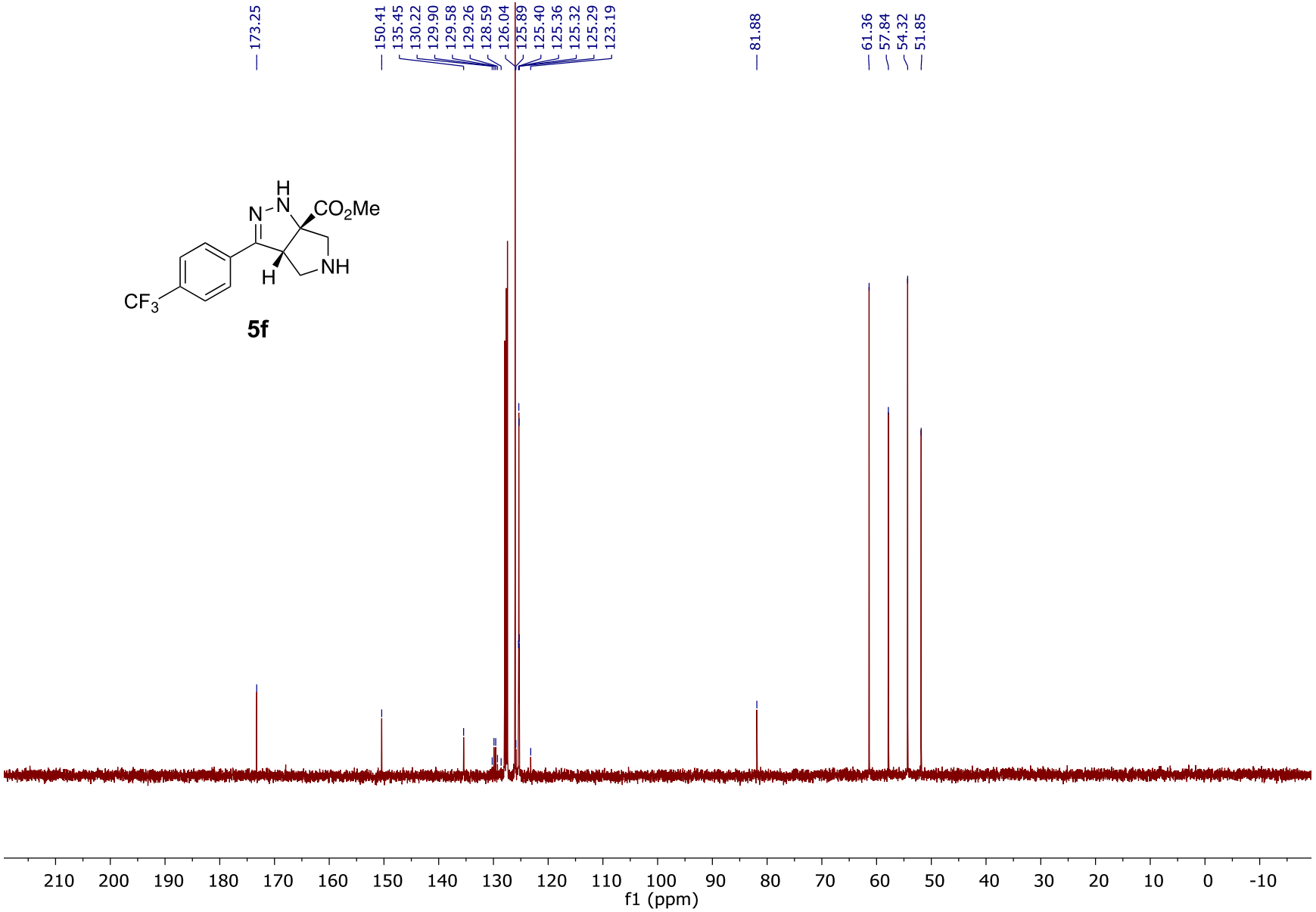
Compound **5e**. 500 MHz ^{1}H NMR spectrum in C_6D_6



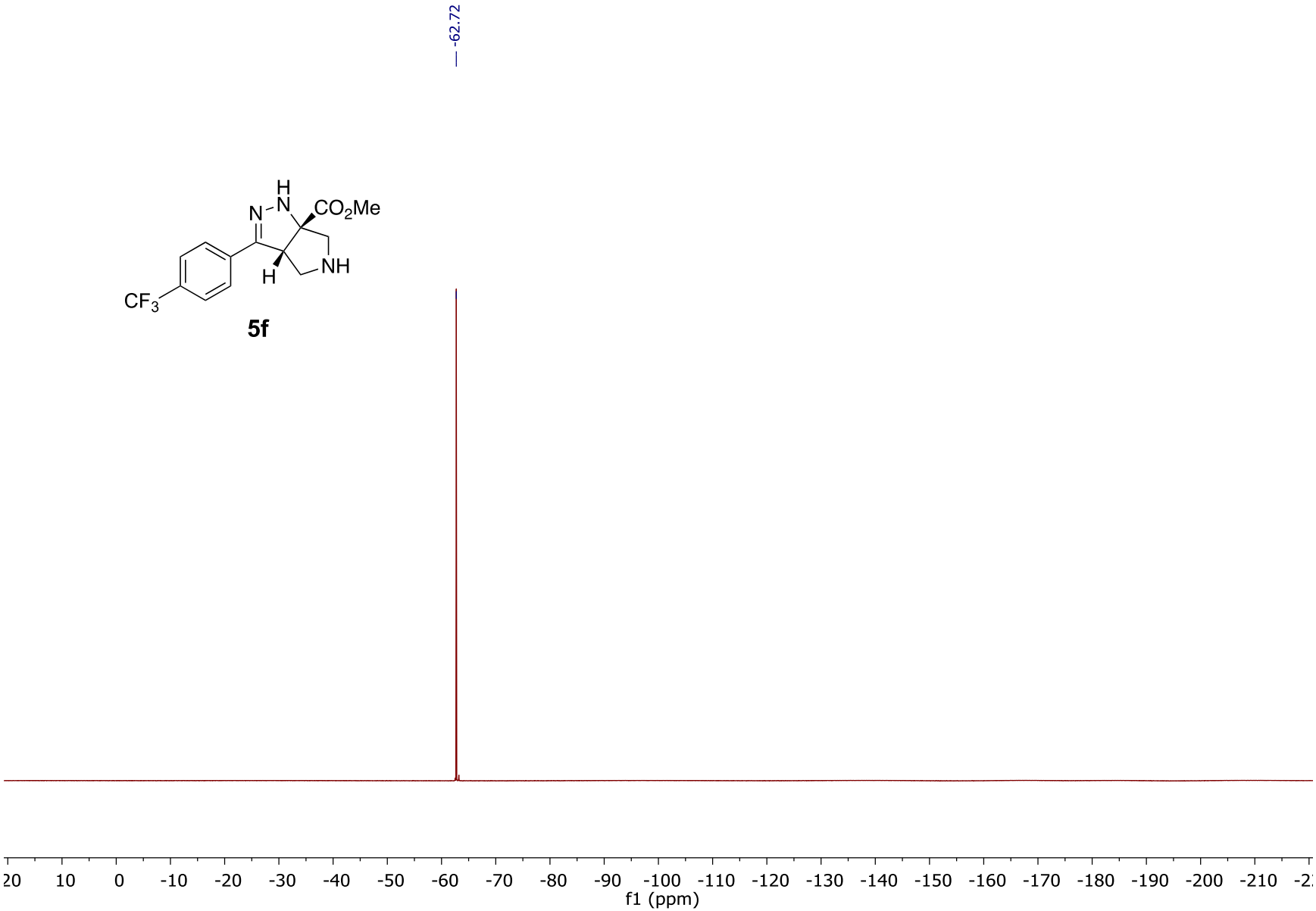
Compound **5e**. 126 MHz ^{13}C NMR spectrum in C_6D_6



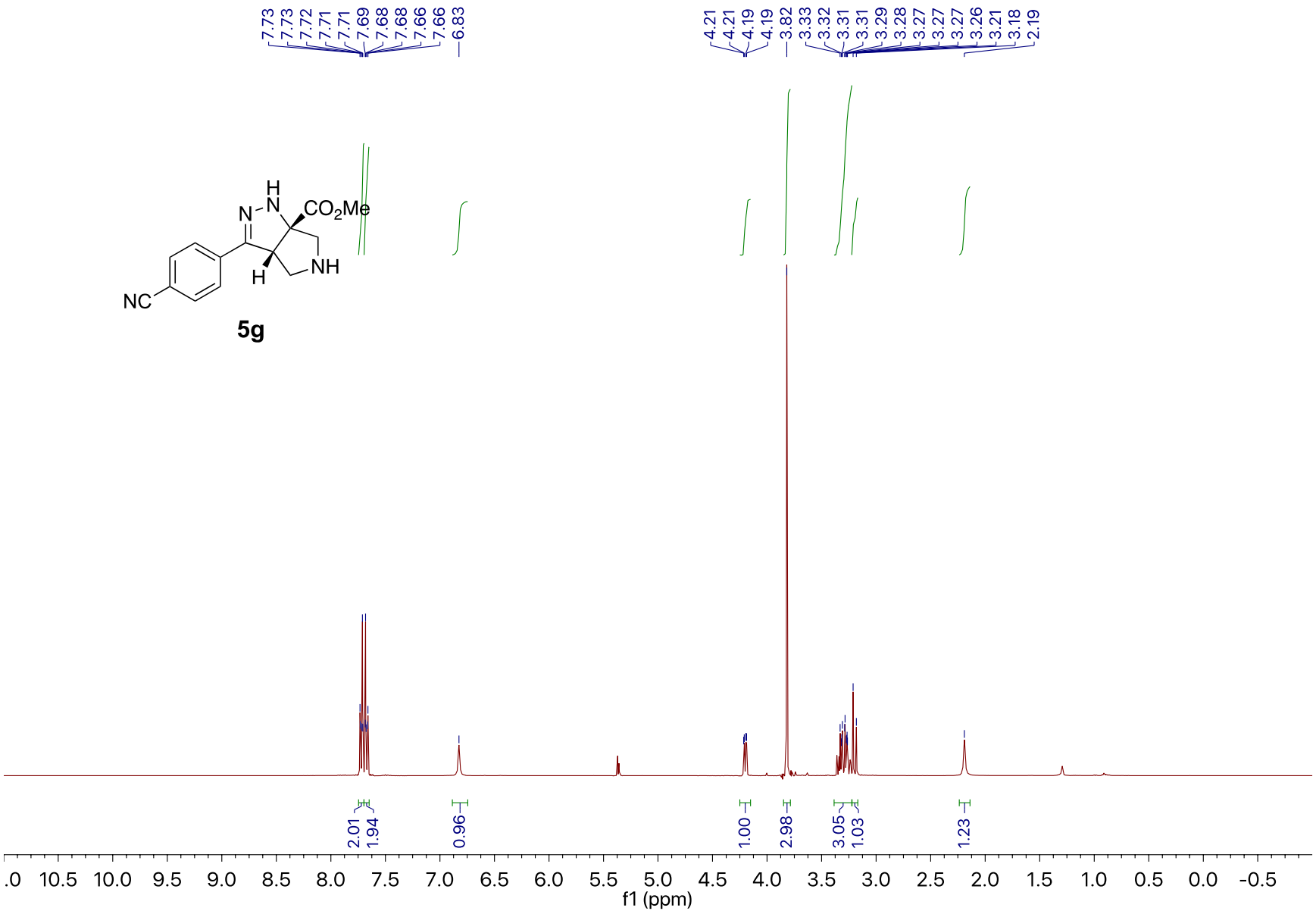
Compound **5f**. 400 MHz ^{1}H NMR spectrum in C_6D_6



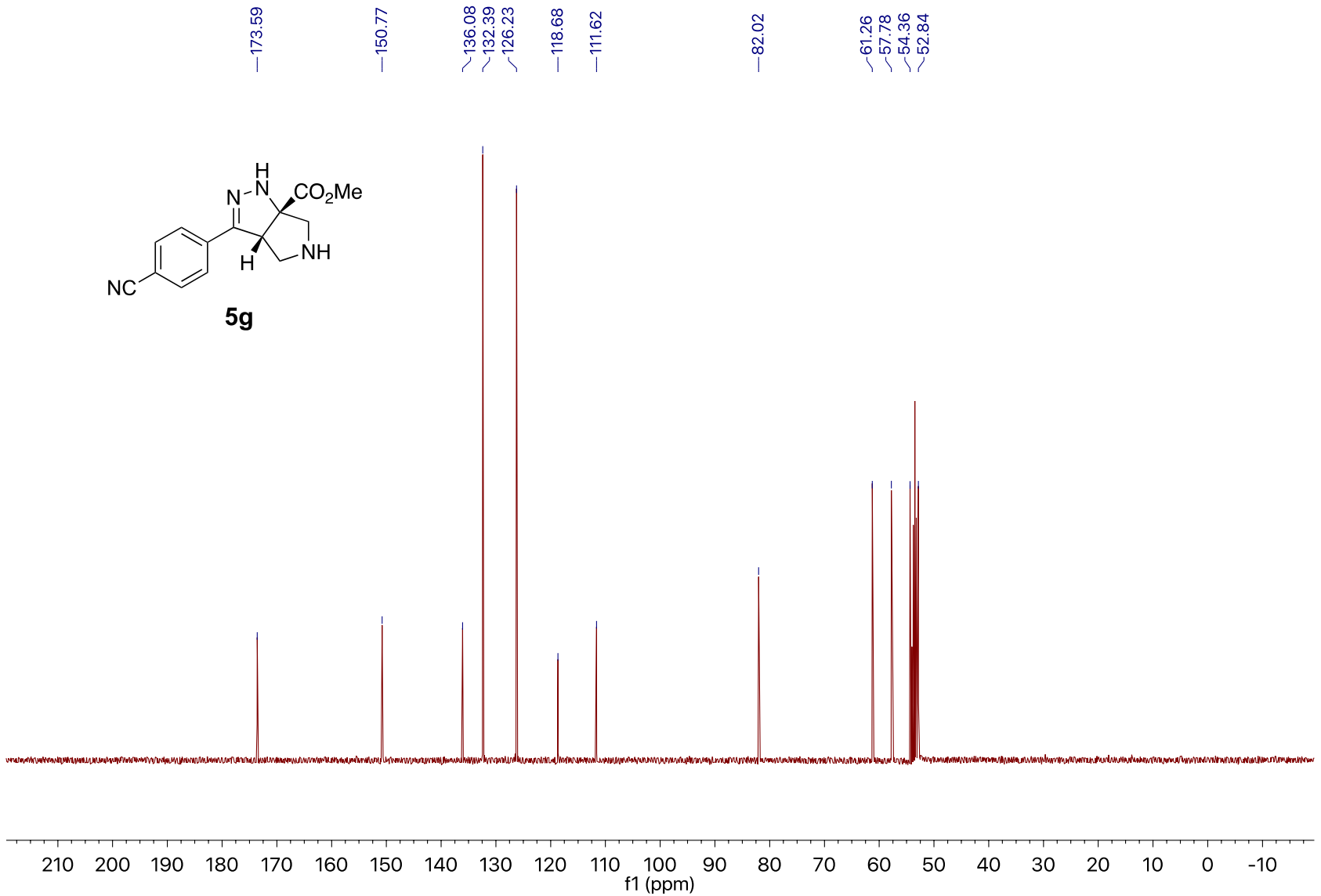
Compound **5f**. 101 MHz ^{13}C NMR spectrum in C_6D_6



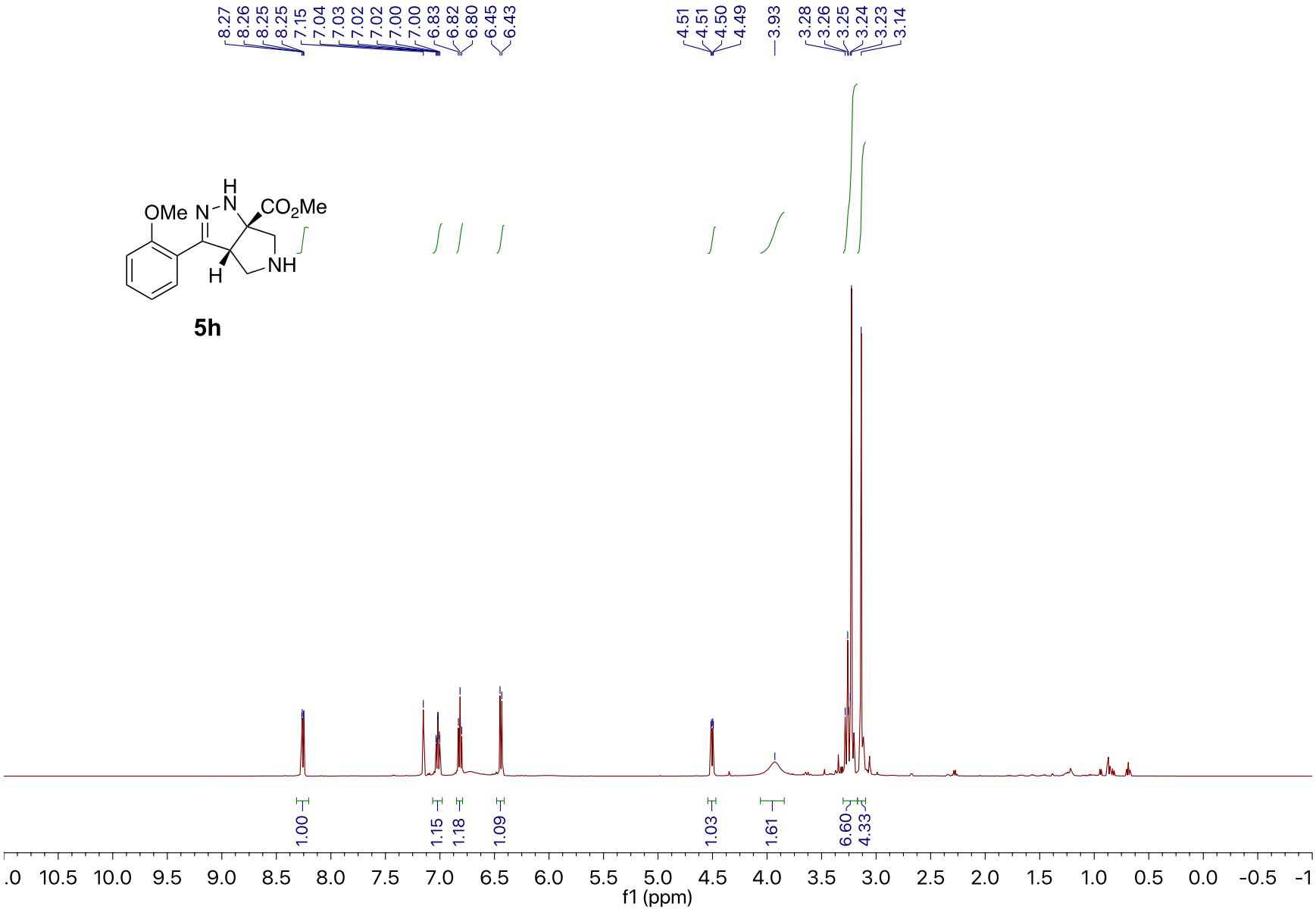
Compound **5f**. 471 MHz ^{19}F NMR spectrum in $CDCl_3$



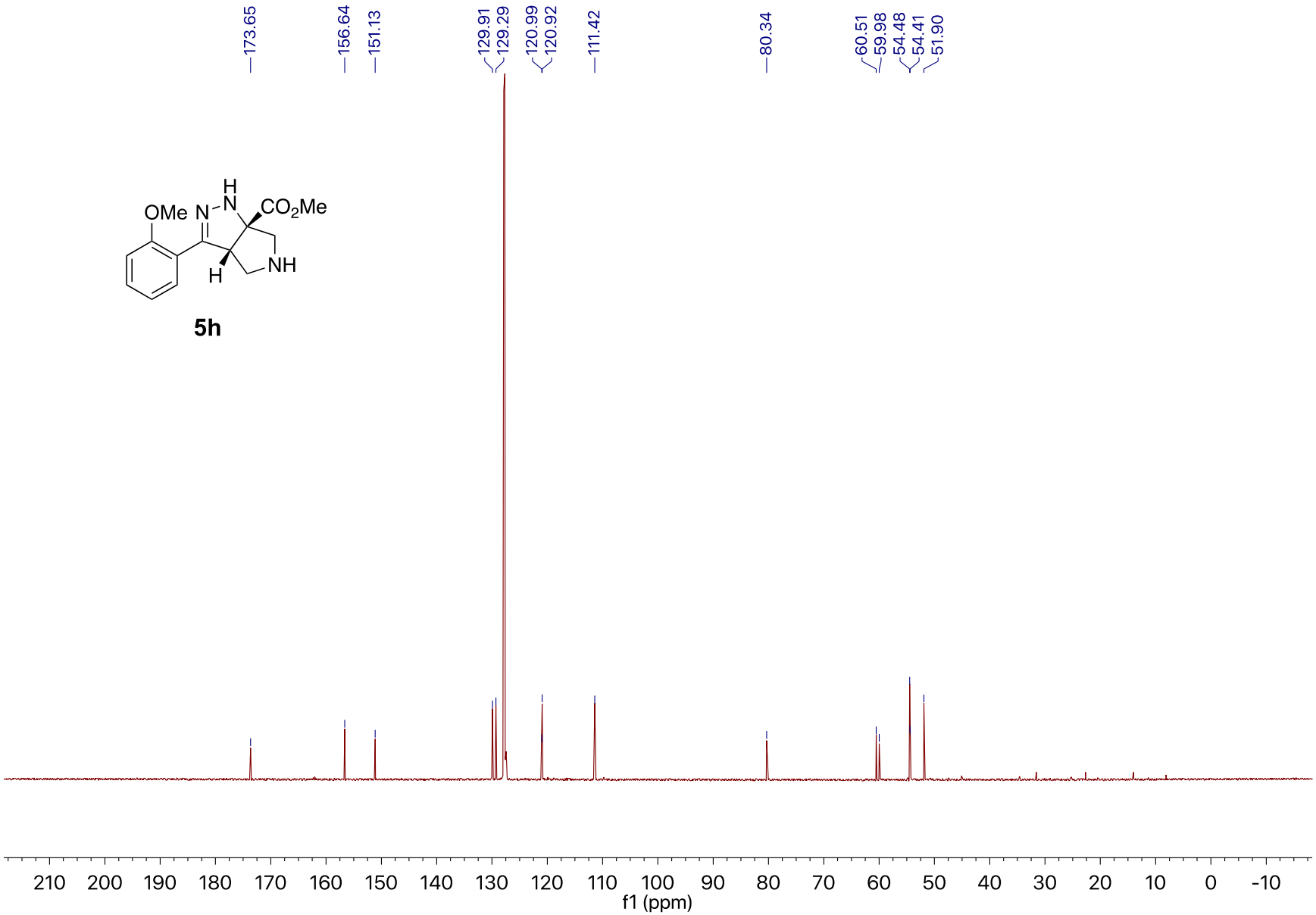
Compound **5g**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



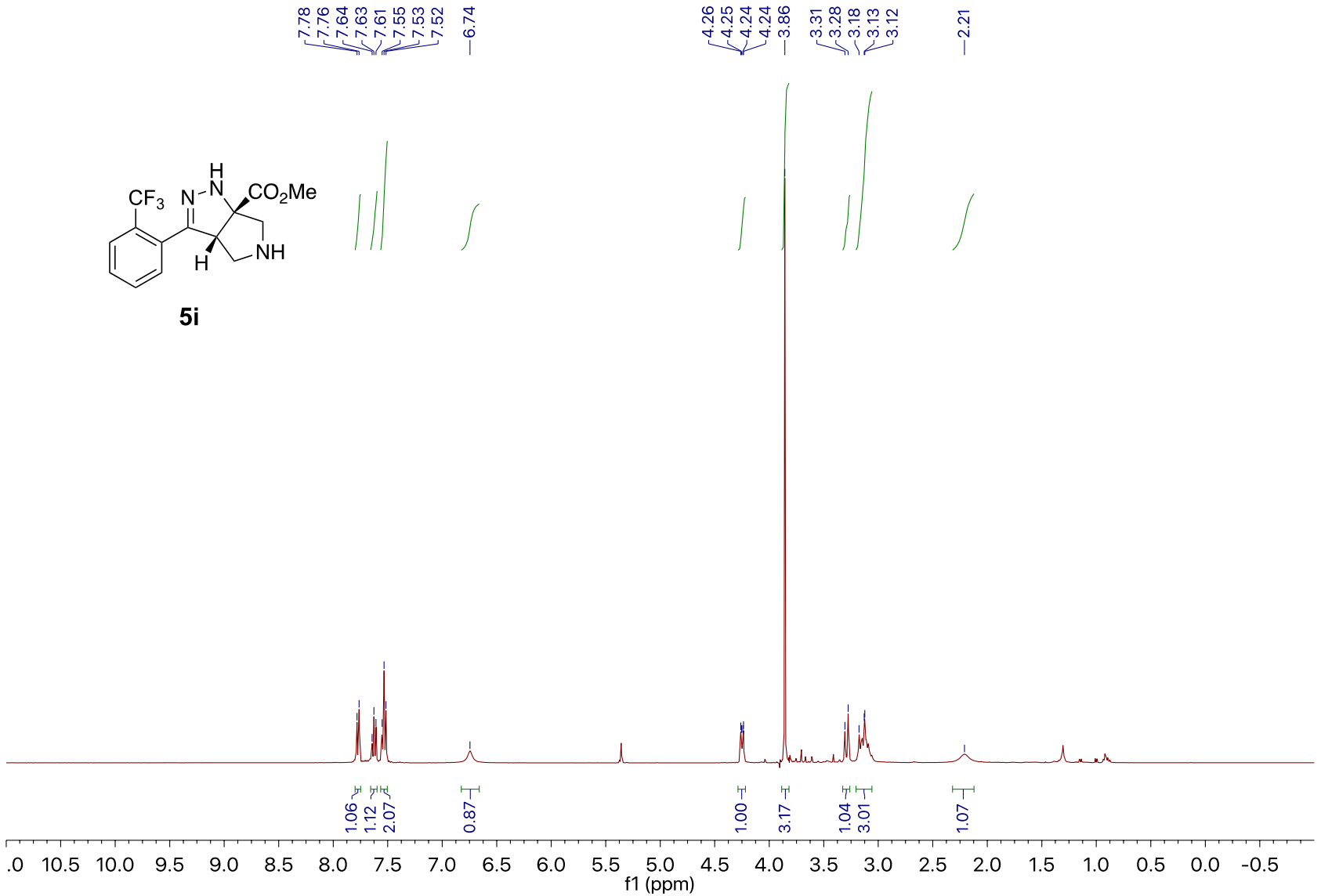
Compound **5g**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



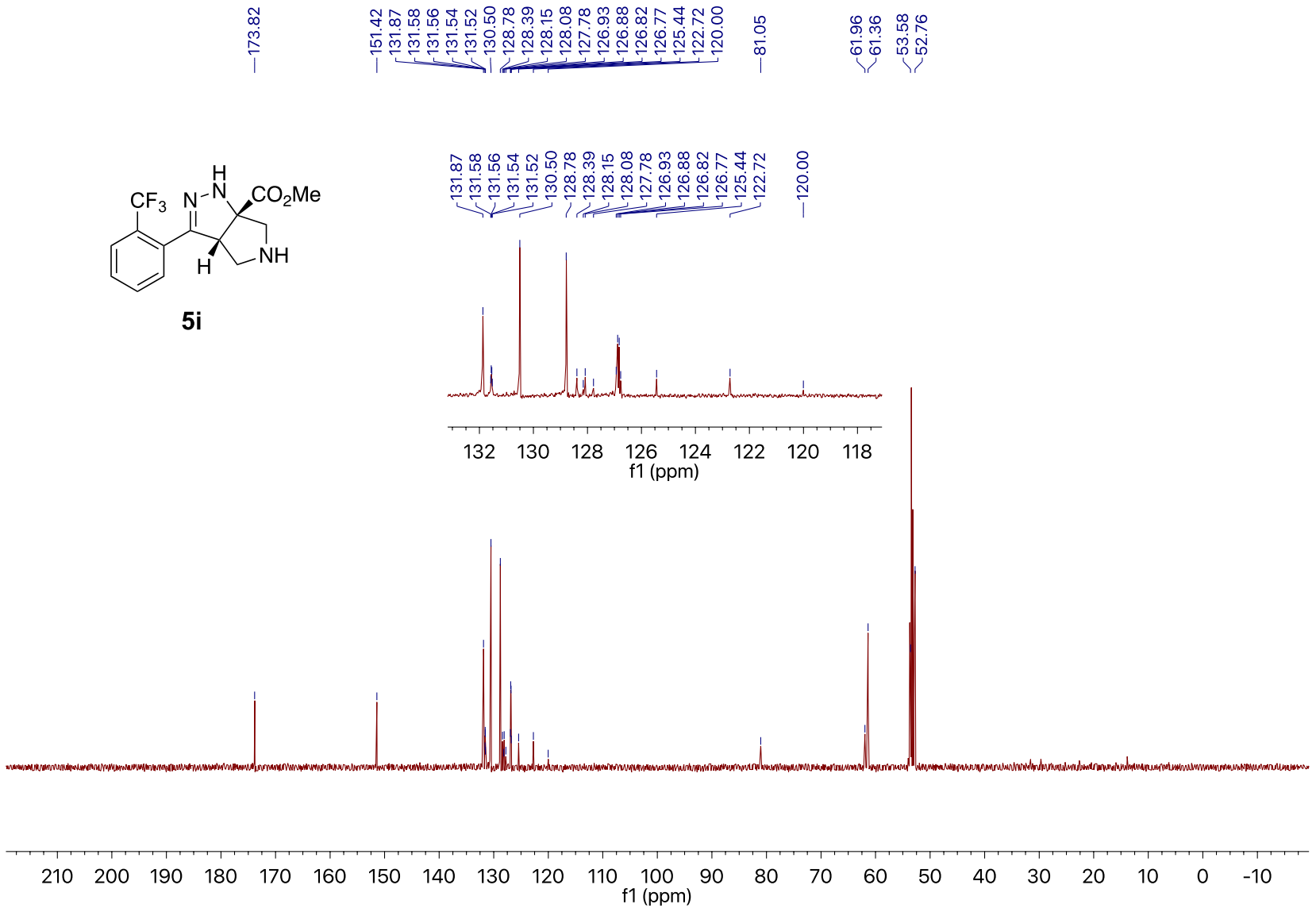
Compound **5h**. 500 MHz ^{1}H NMR spectrum in C_6D_6



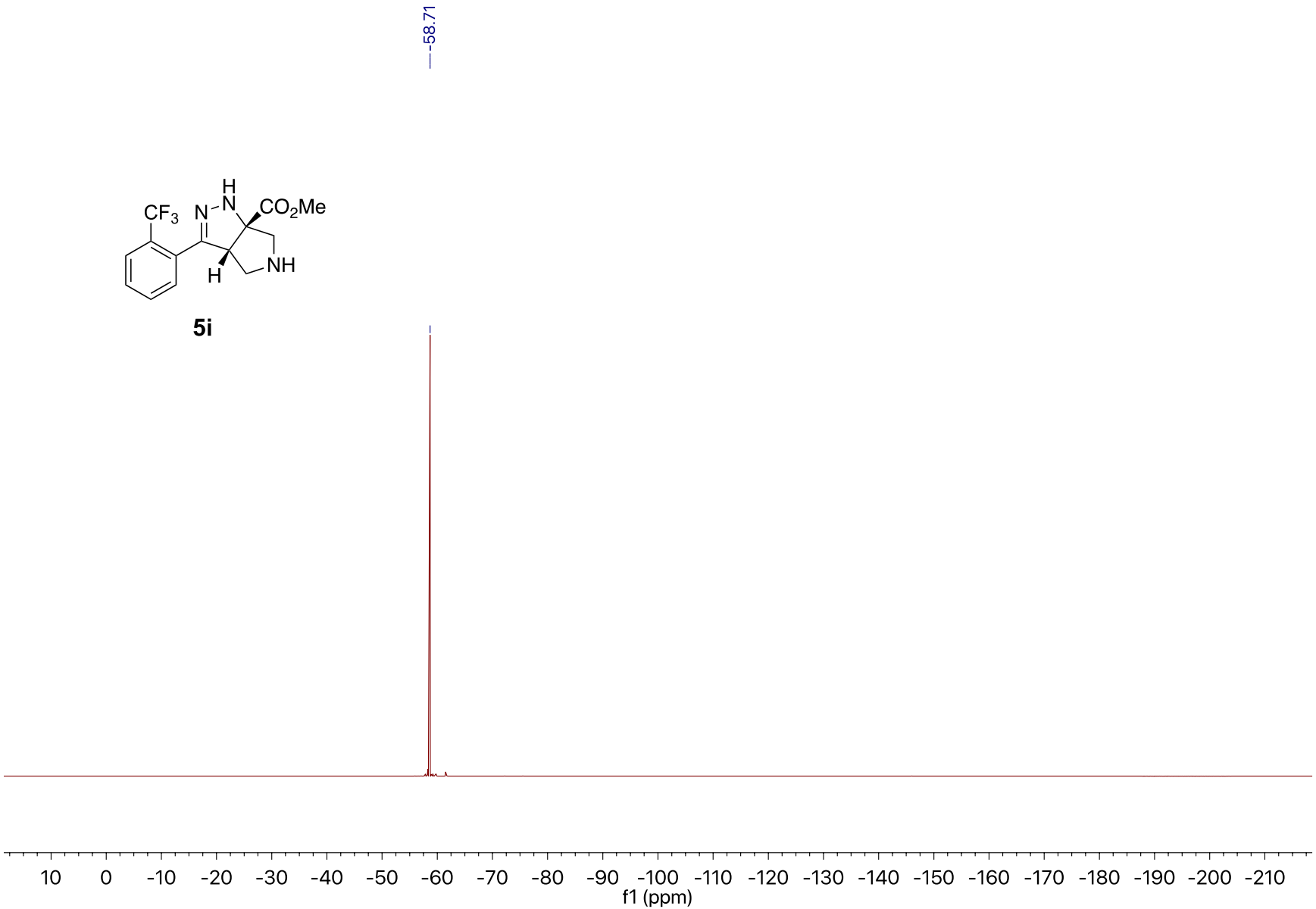
Compound **5h**. 126 MHz ^{13}C NMR spectrum in C_6D_6



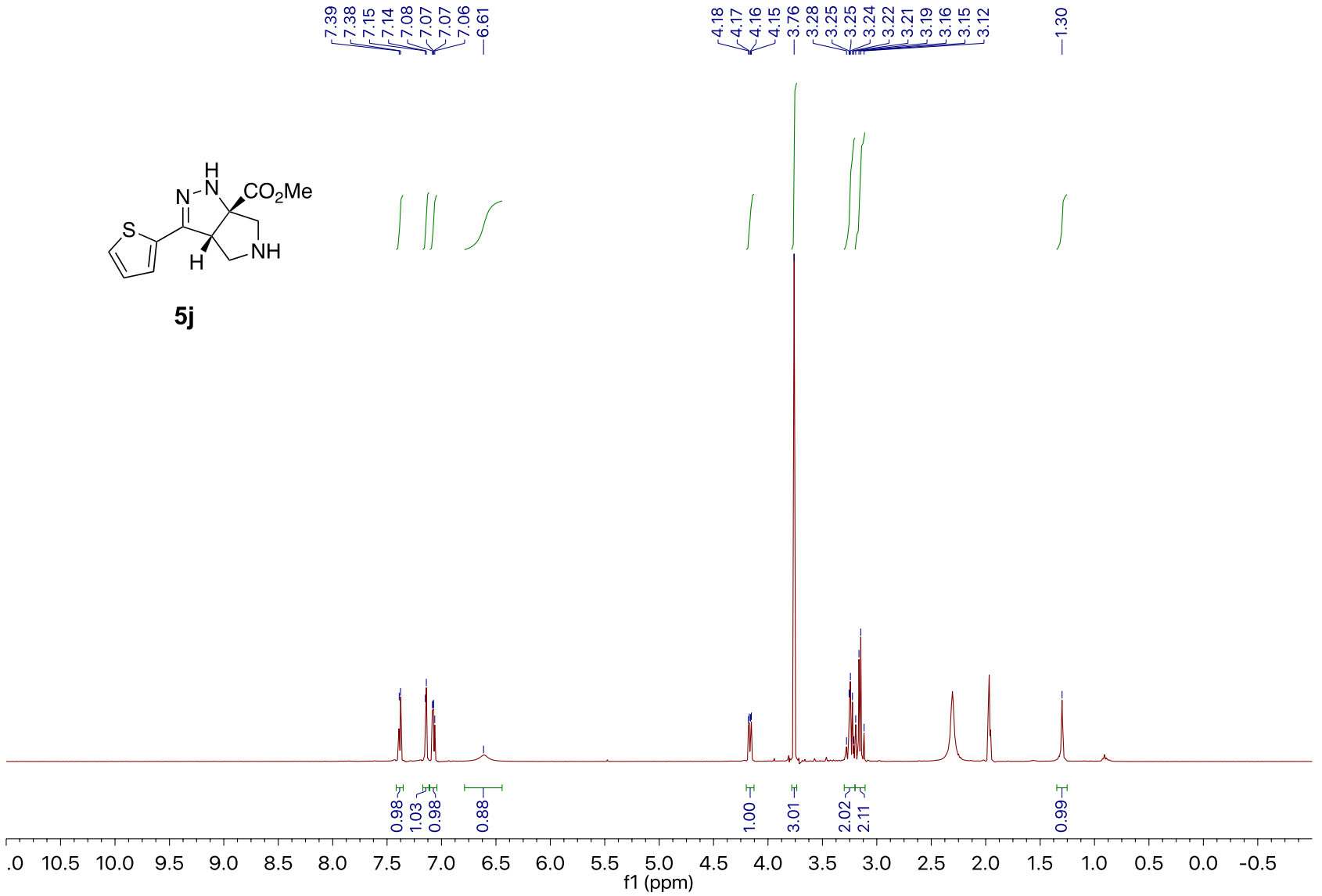
Compound **5i**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



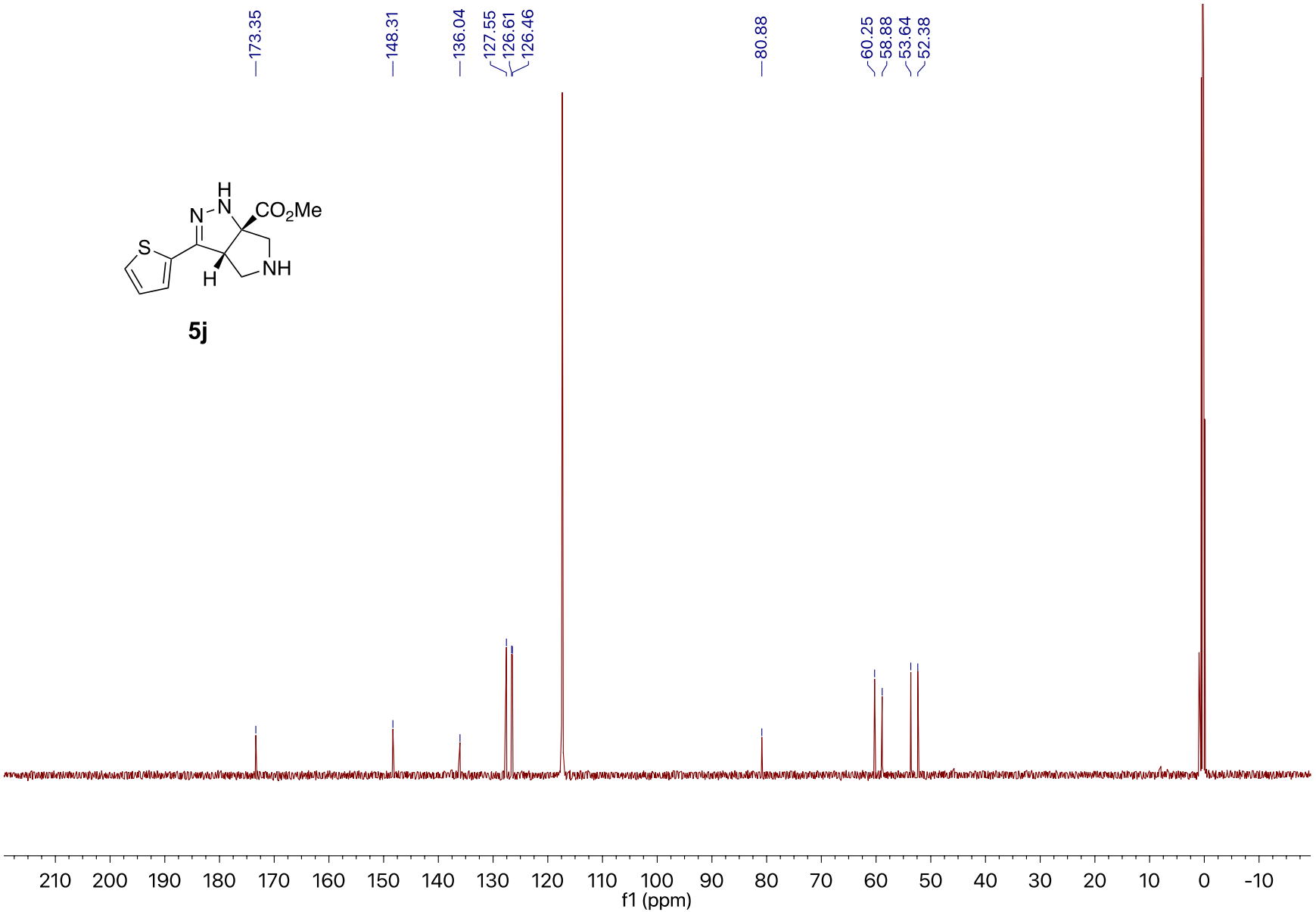
Compound **5i**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



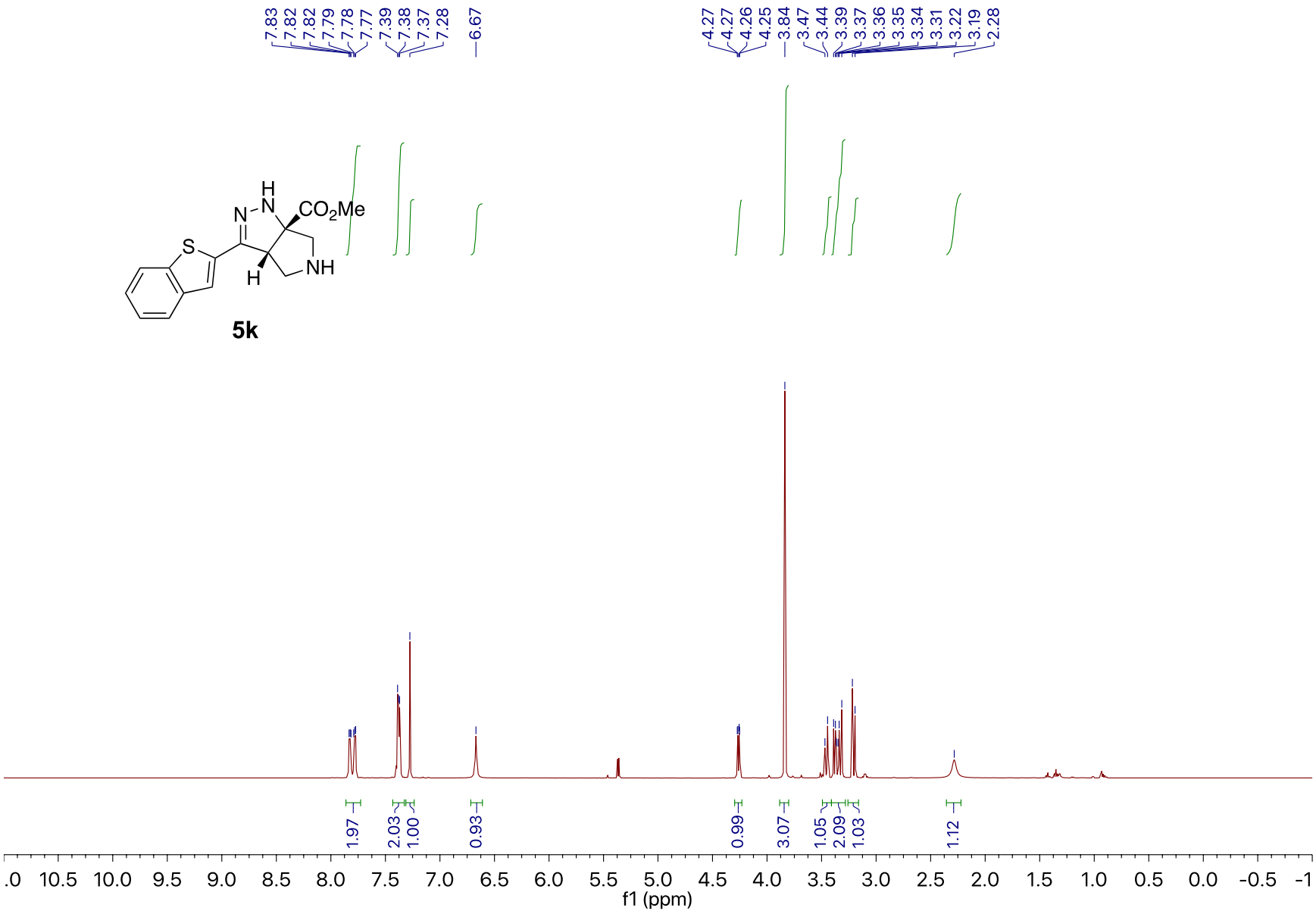
Compound **5i**. 376 MHz ^{19}F NMR spectrum in CD_2Cl_2



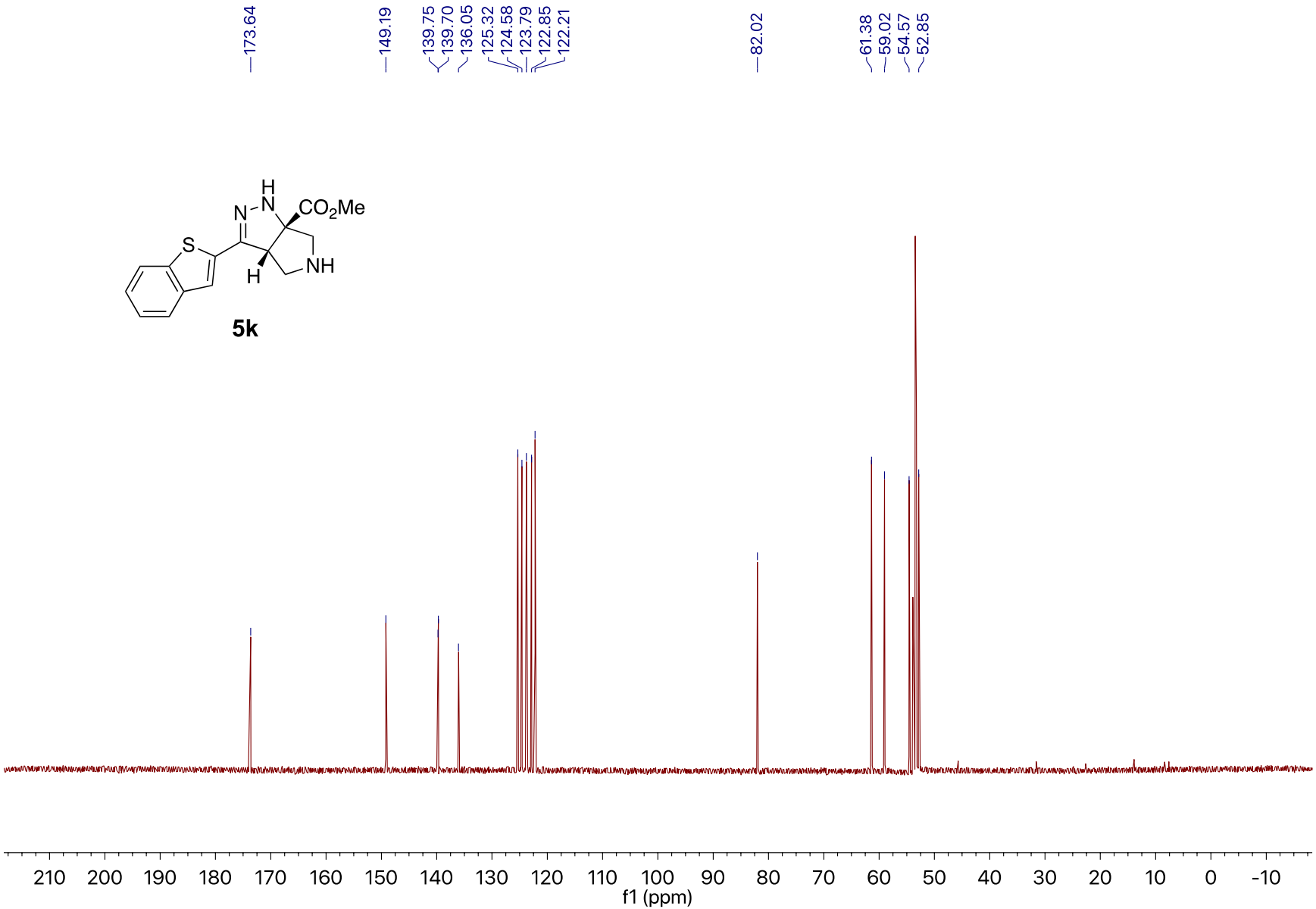
Compound **5j**. 400 MHz ^{1}H NMR spectrum in CD_3CN



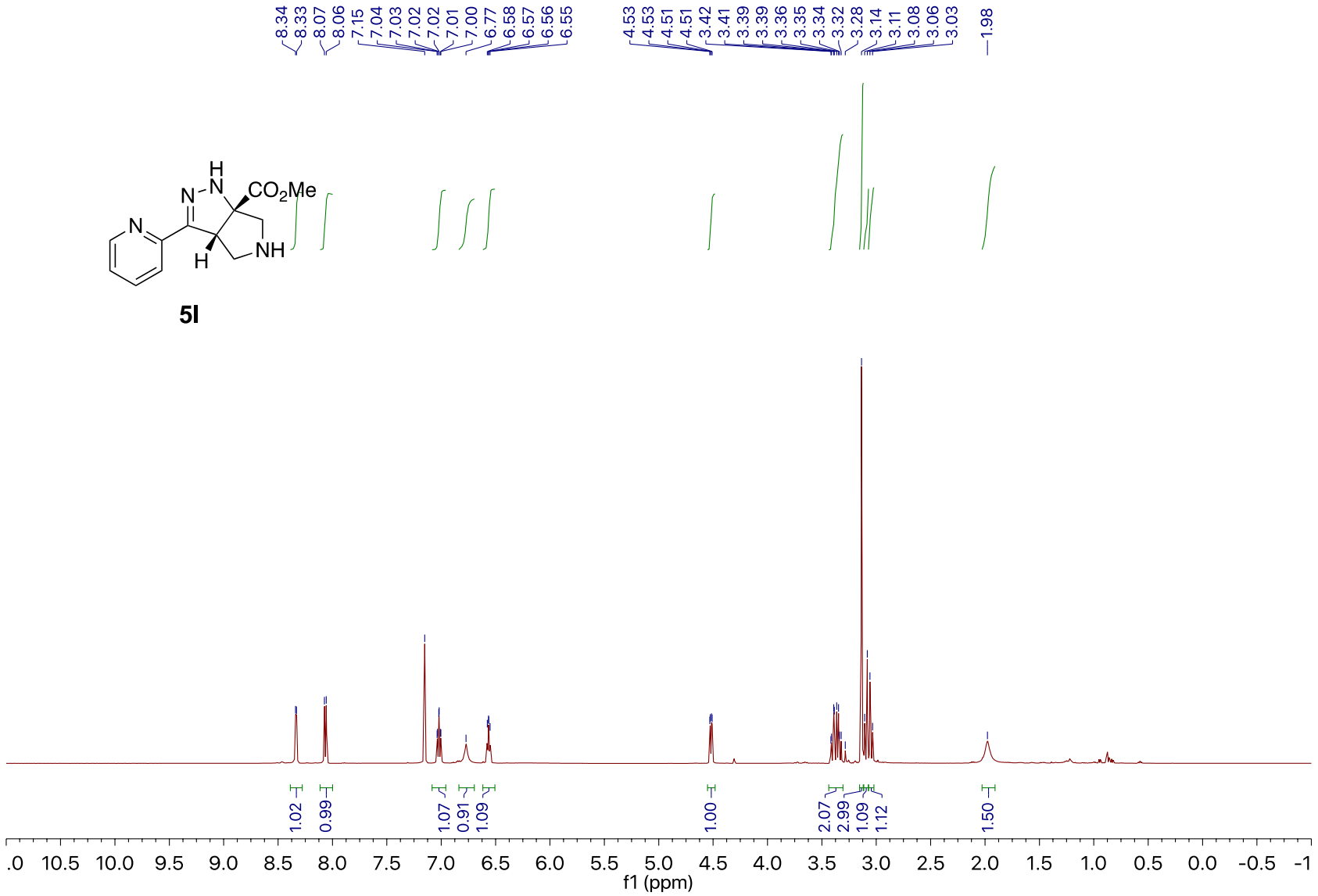
Compound **5j**. 101 MHz ^{13}C NMR spectrum in CD_3CN



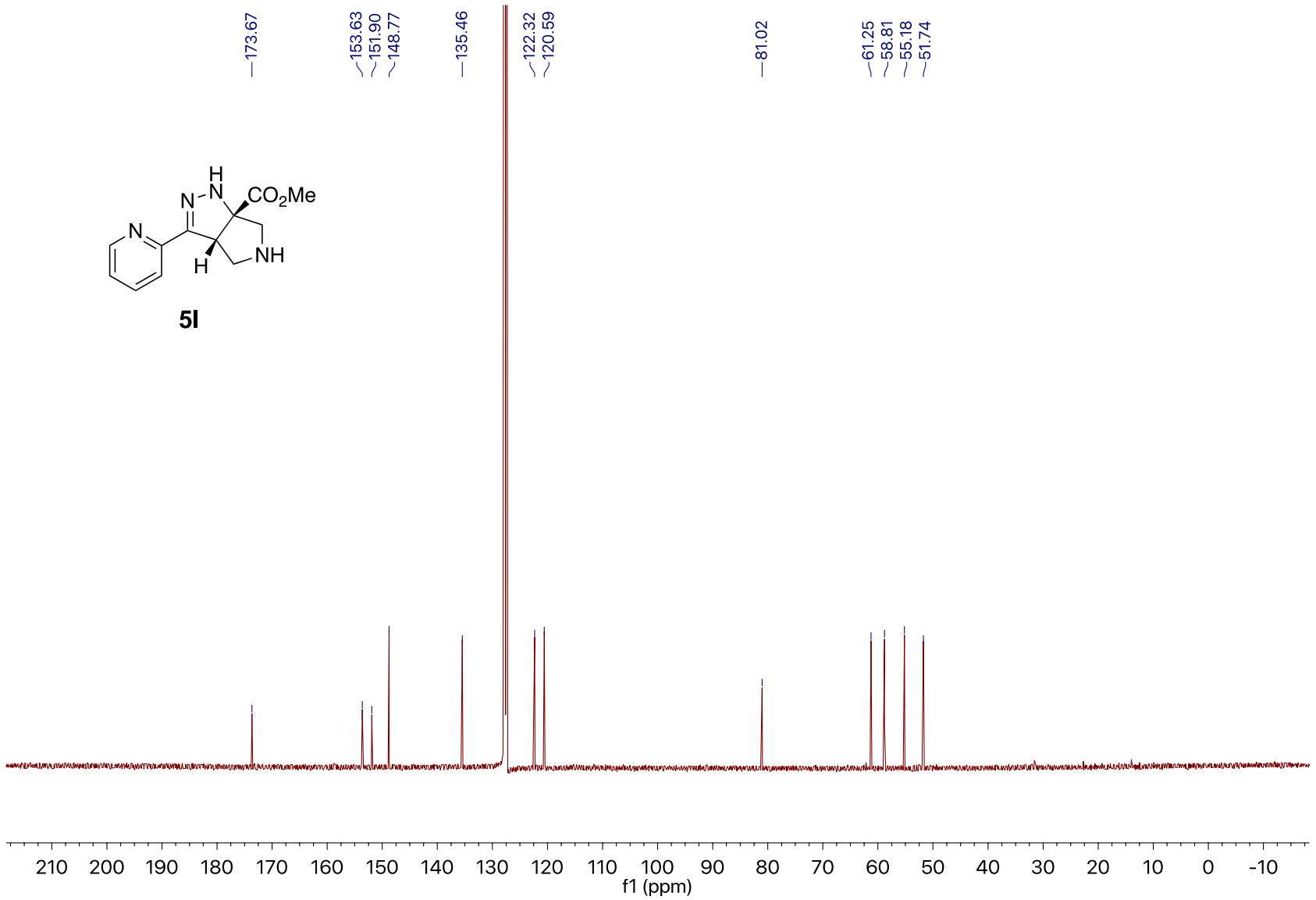
Compound **5k**. 500 MHz ^{1}H NMR spectrum in CD_2Cl_2



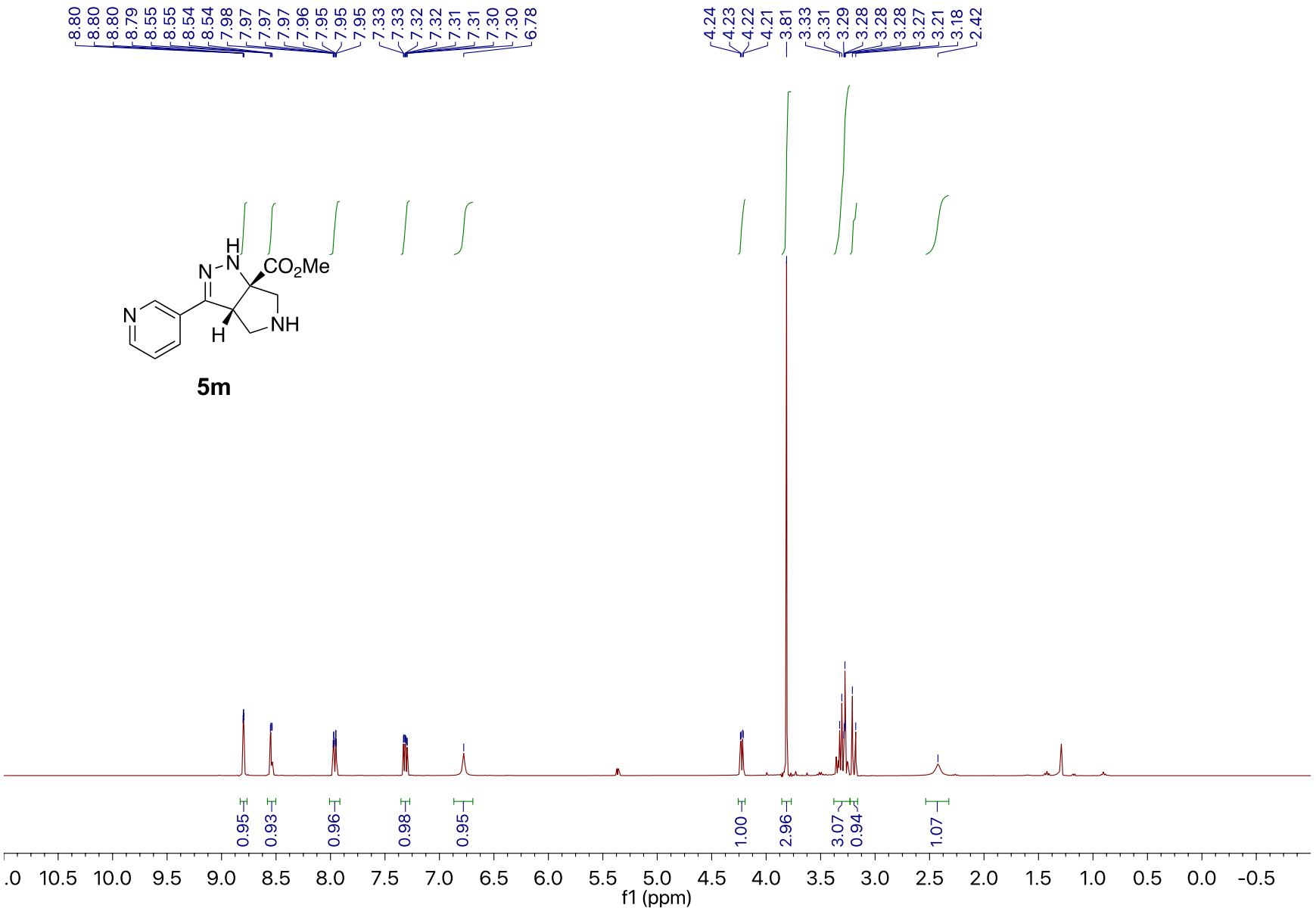
Compound **5k**. 126 MHz ^{13}C NMR spectrum in CD_2Cl_2



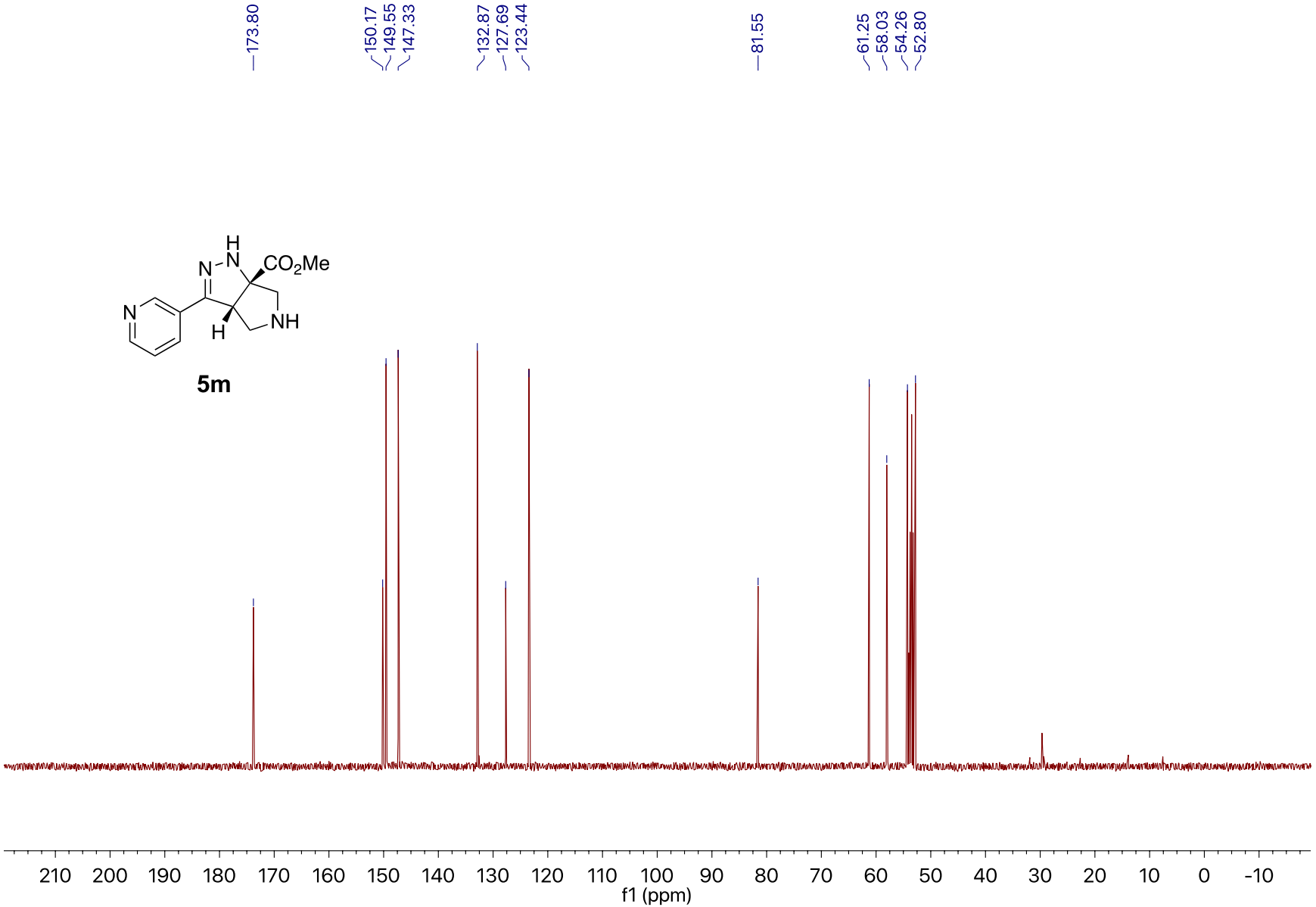
Compound **5l**. 500 MHz ^{1}H NMR spectrum in C_6D_6



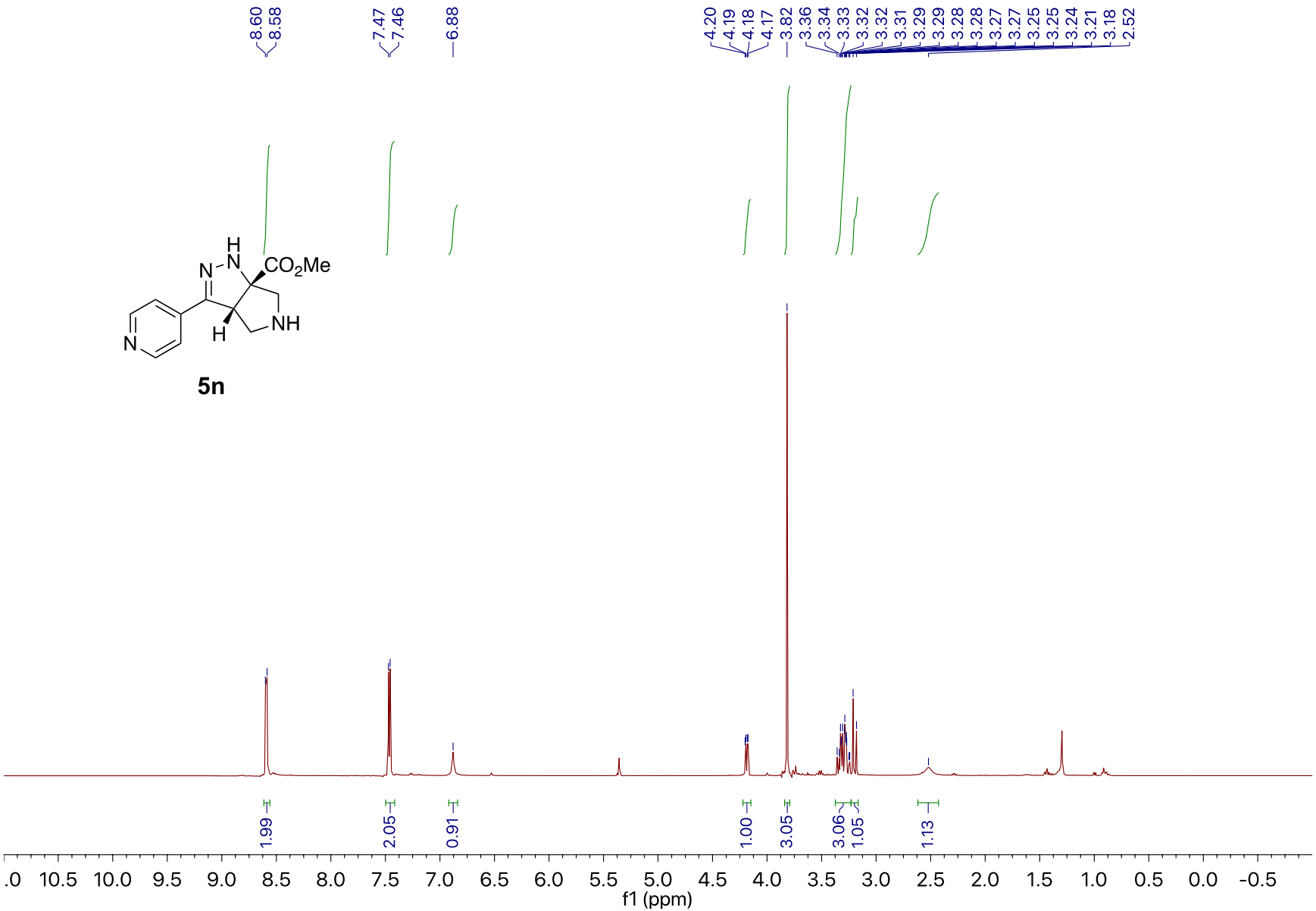
Compound **5l**. 126 MHz ^{13}C NMR spectrum in C_6D_6



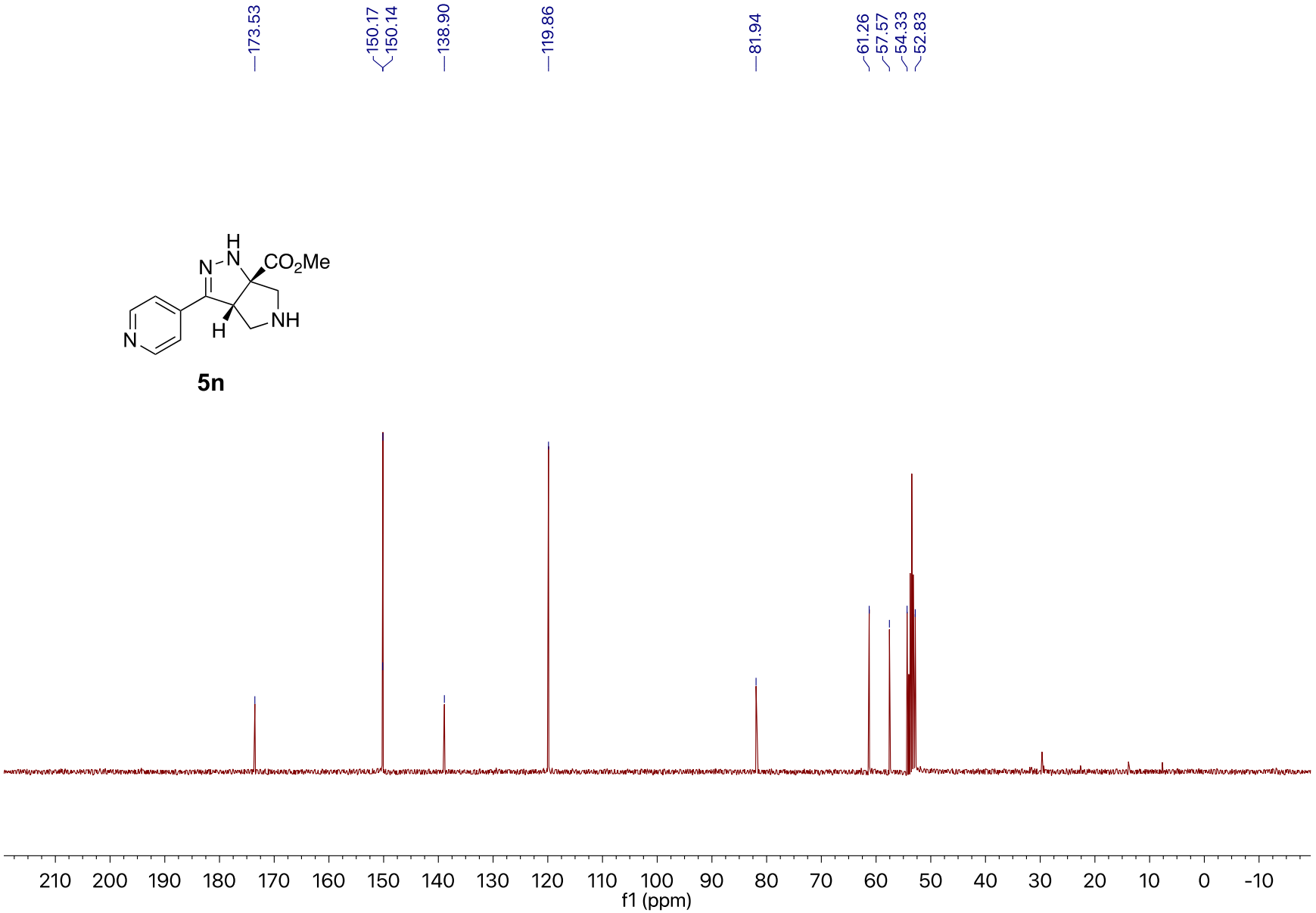
Compound **5m**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



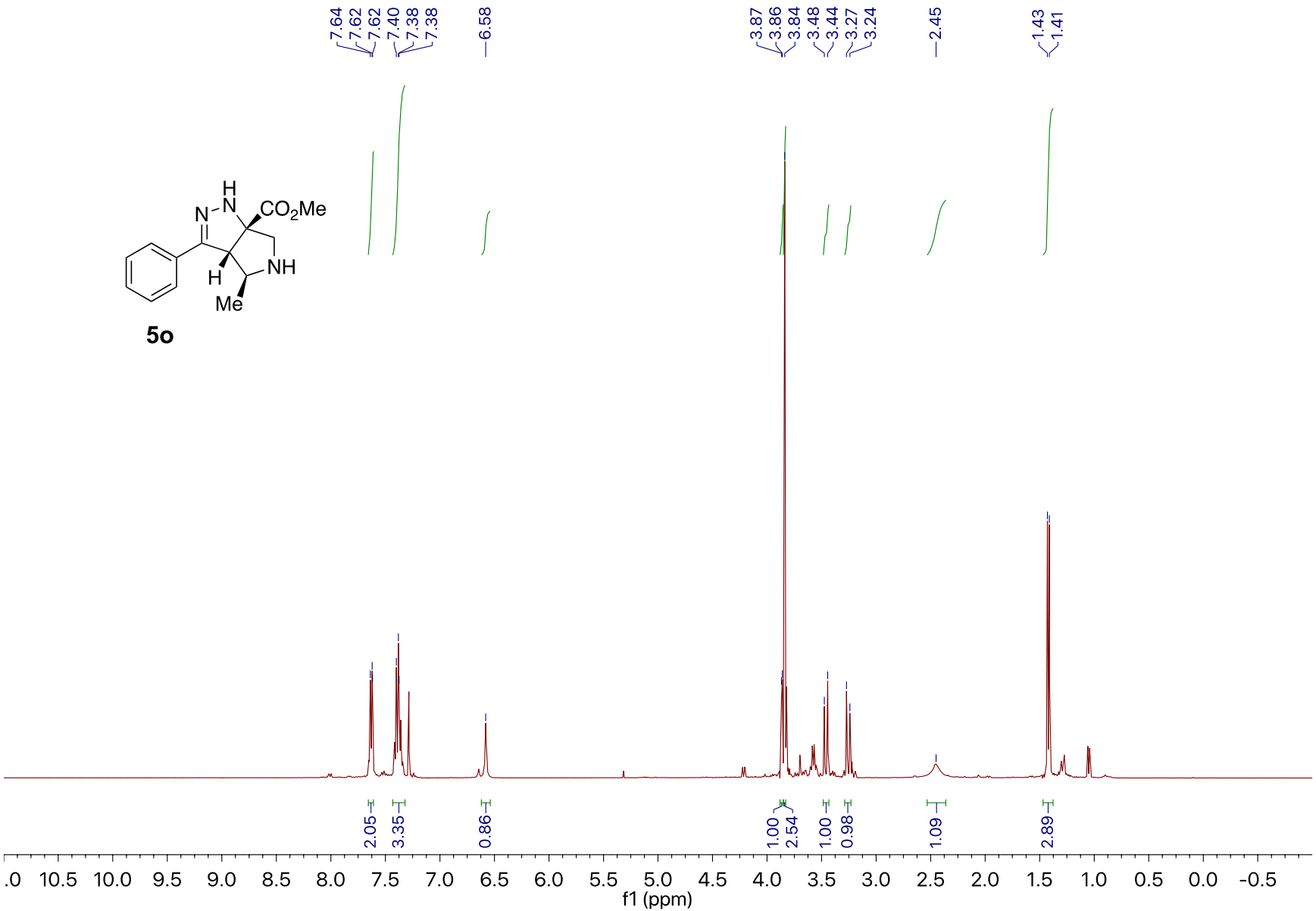
Compound **5m**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



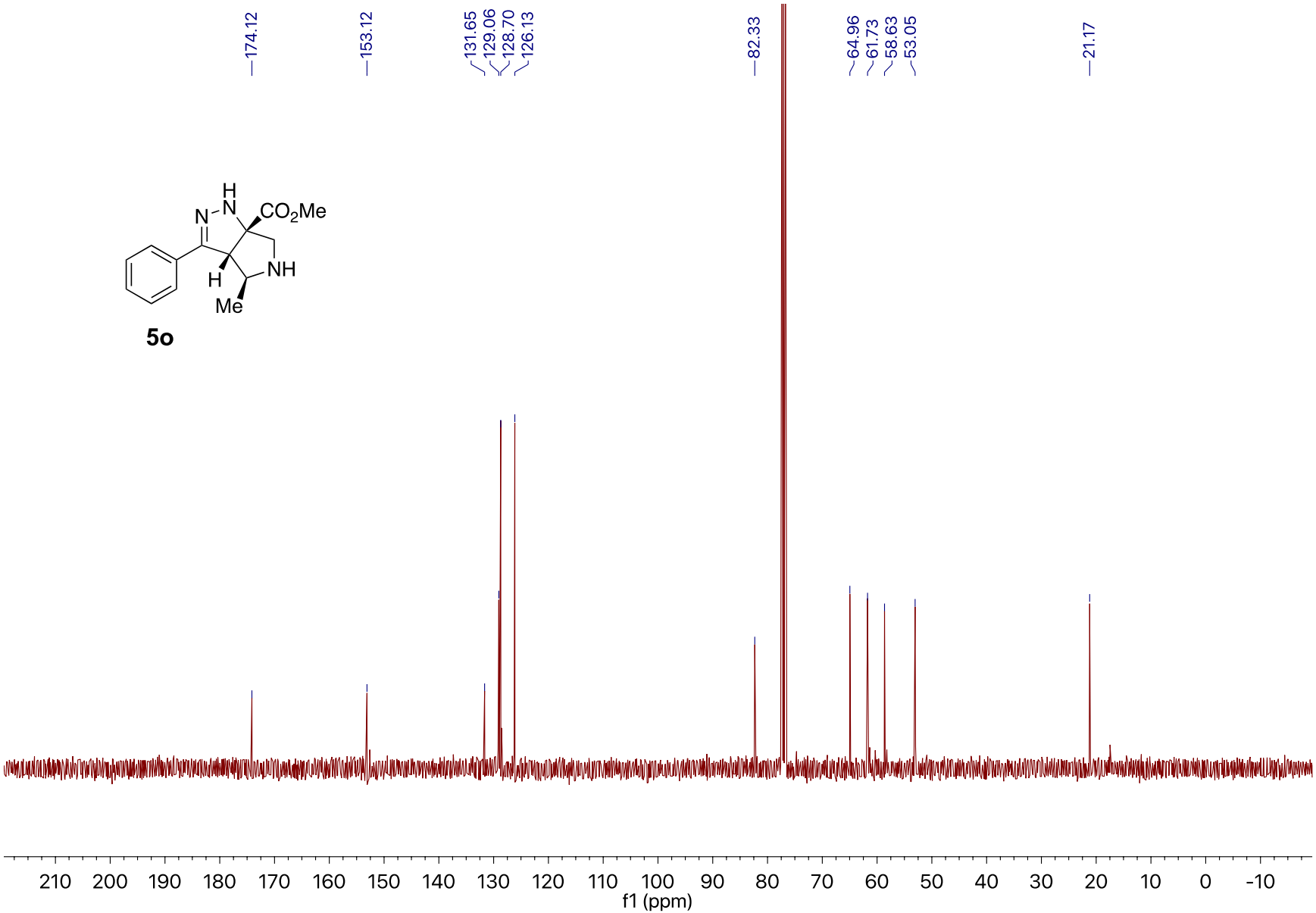
Compound **5n**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



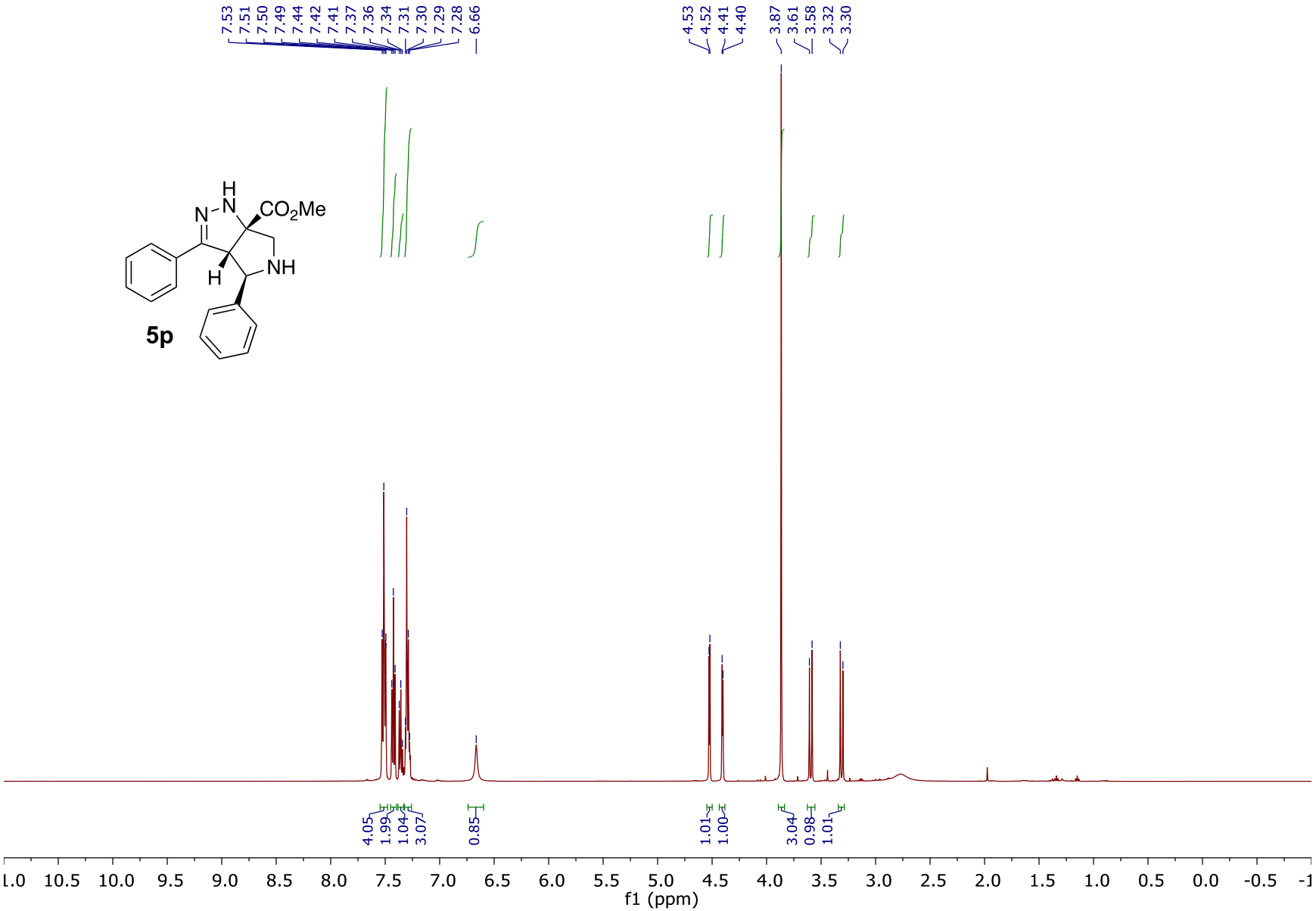
Compound **5n**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



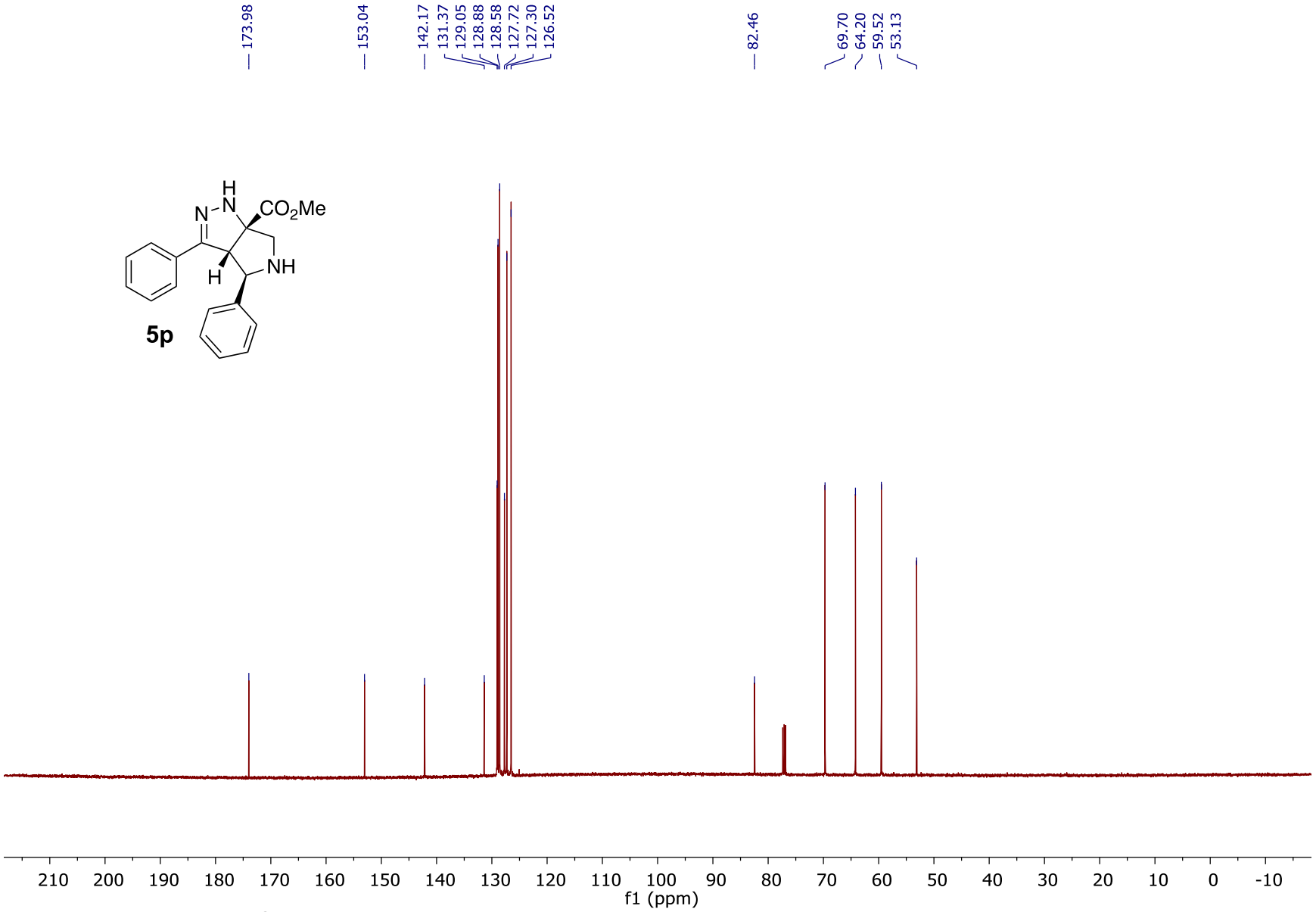
Compound **5o**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



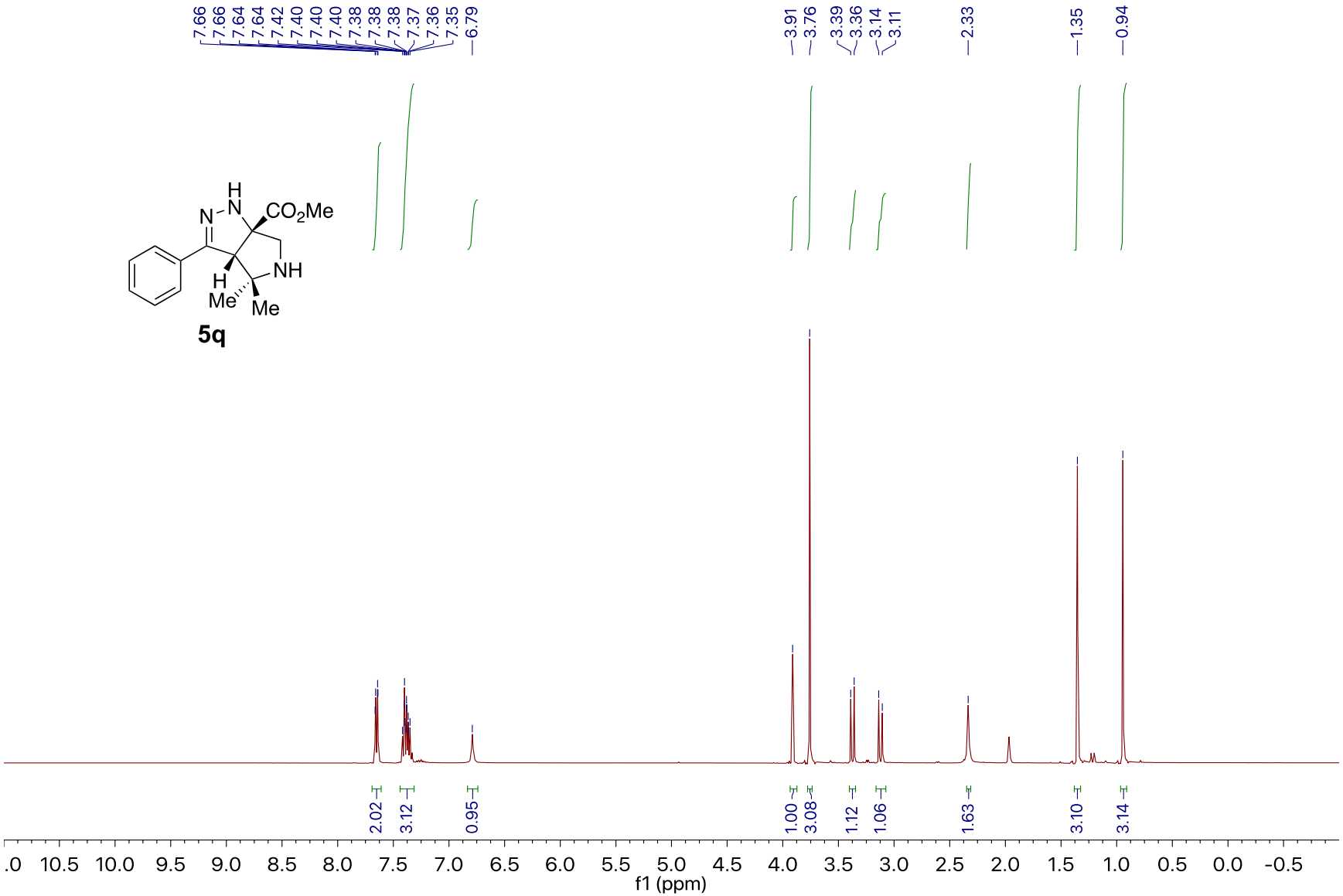
Compound **5o**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



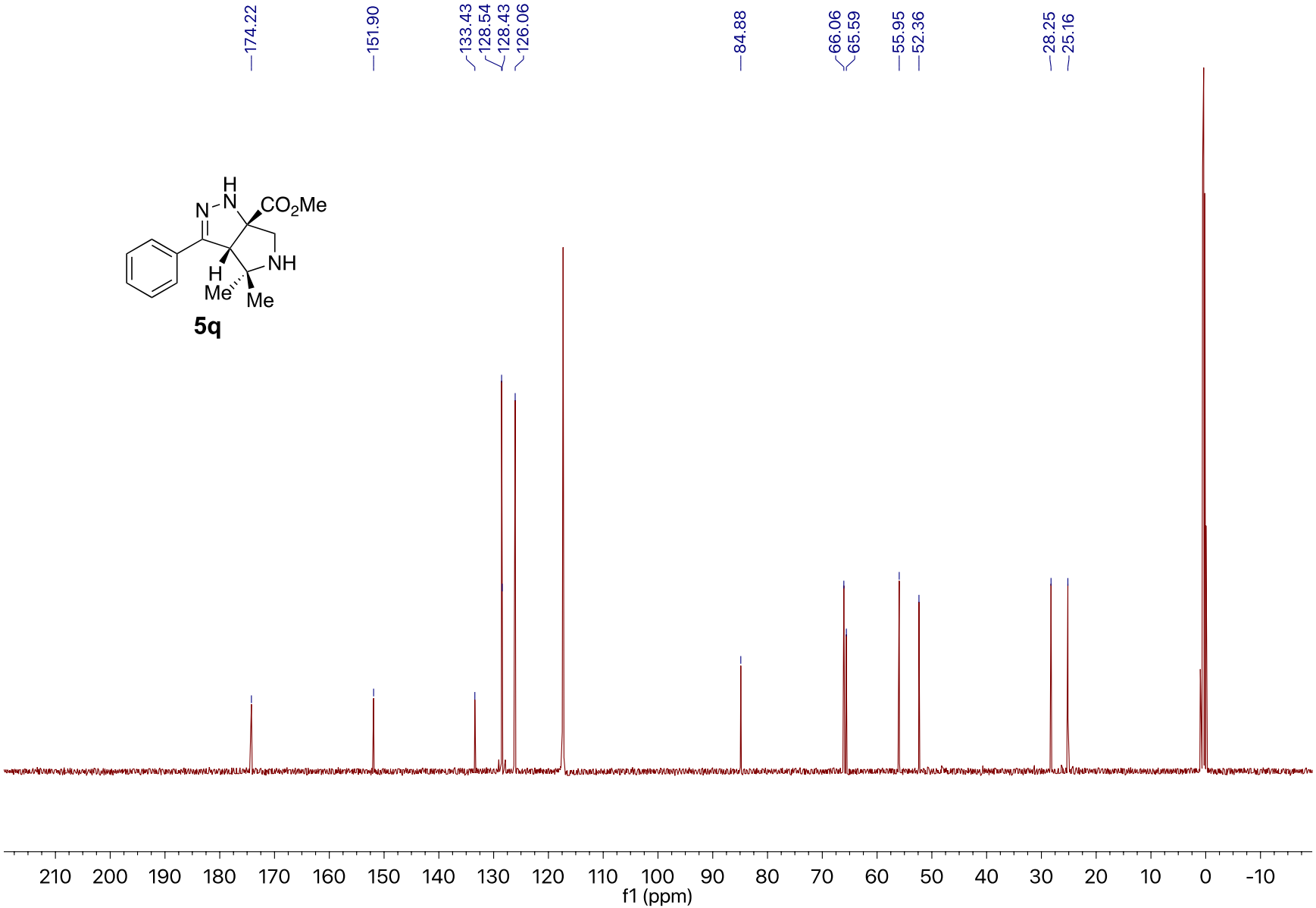
Compound **5p**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



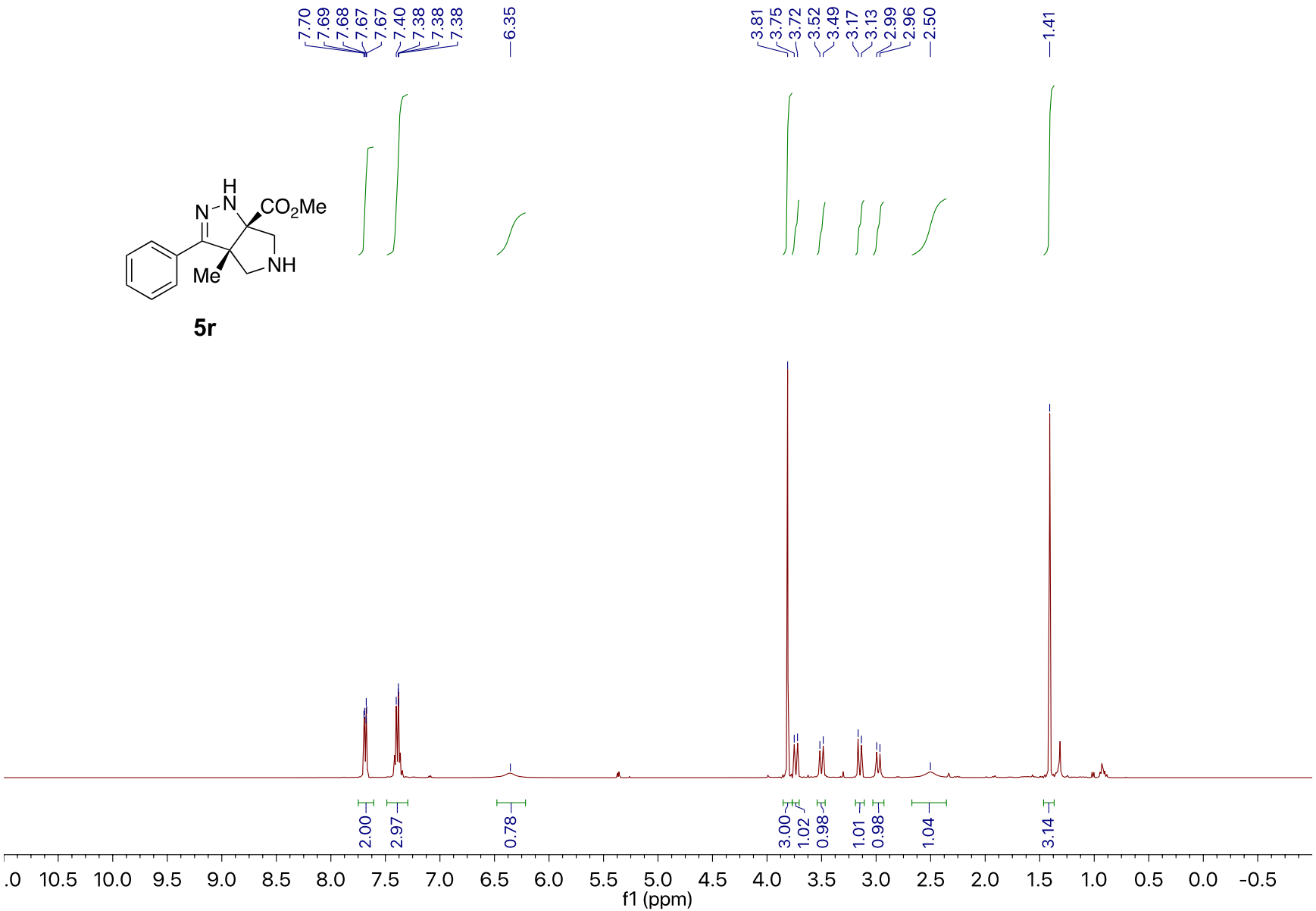
Compound **5p**. 126 MHz ^{13}C NMR spectrum in CDCl



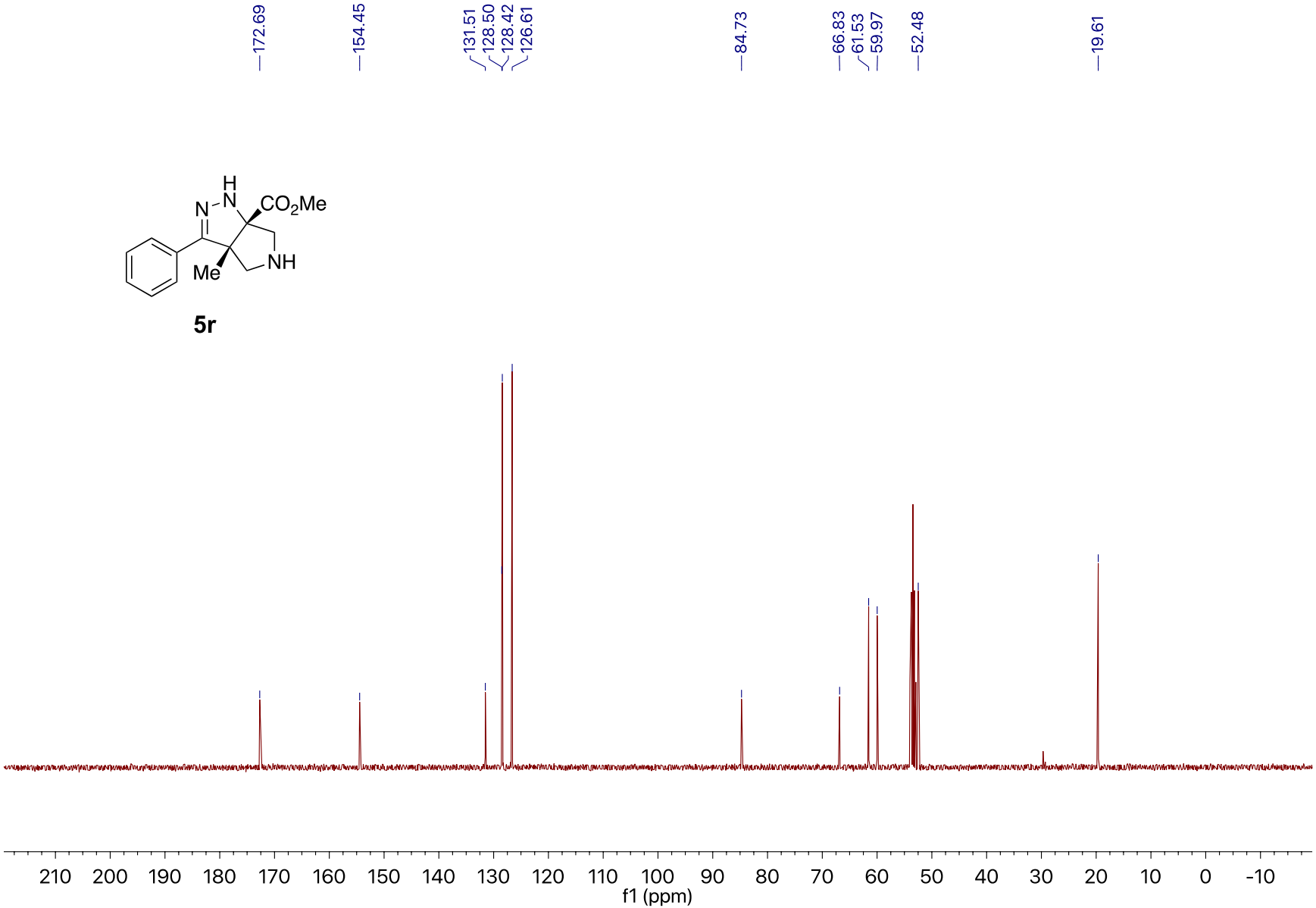
Compound **5q**. 400 MHz ^{1}H NMR spectrum in CD_3CN



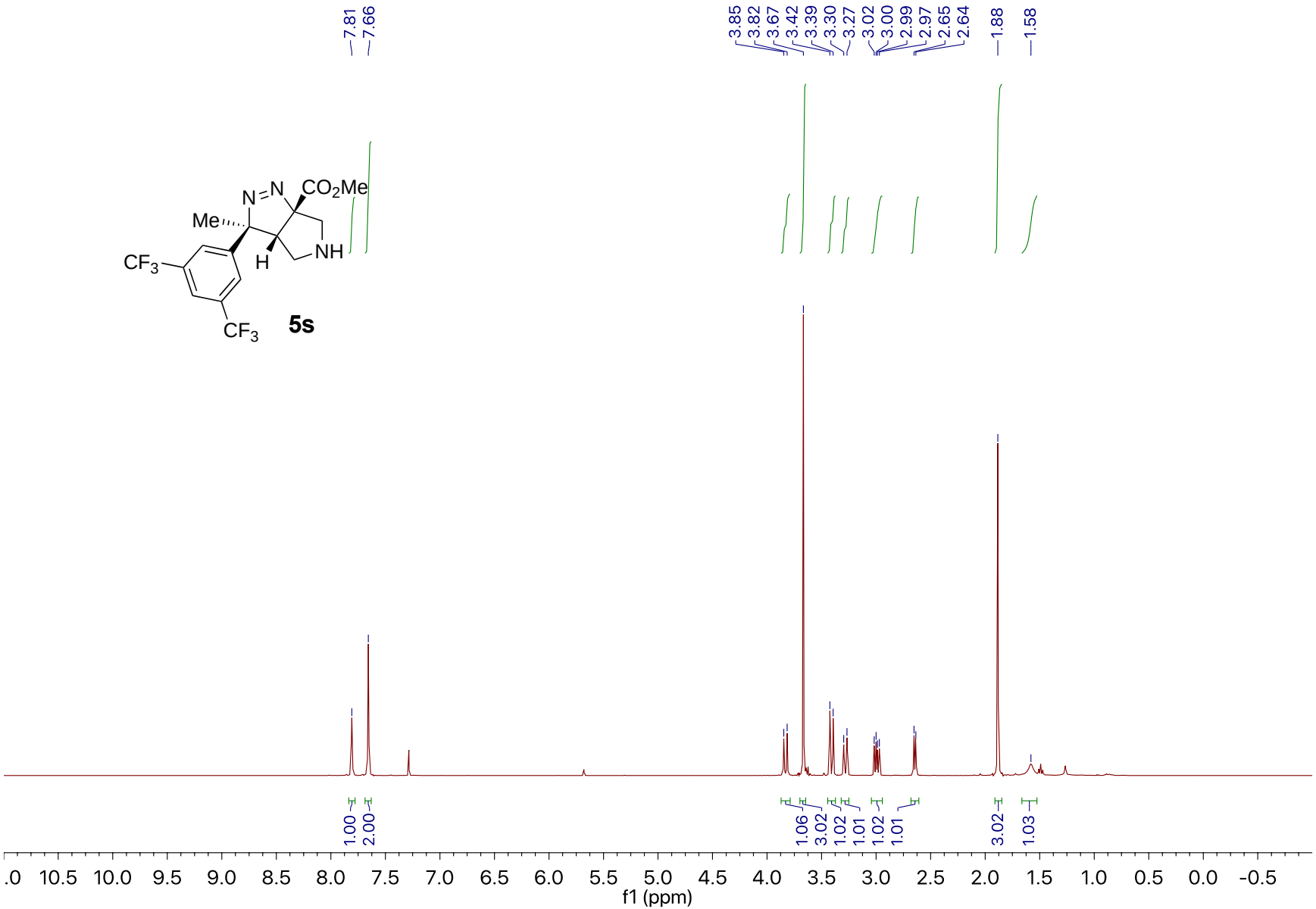
Compound **5q**. 101 MHz ^{13}C NMR spectrum in CD_3CN



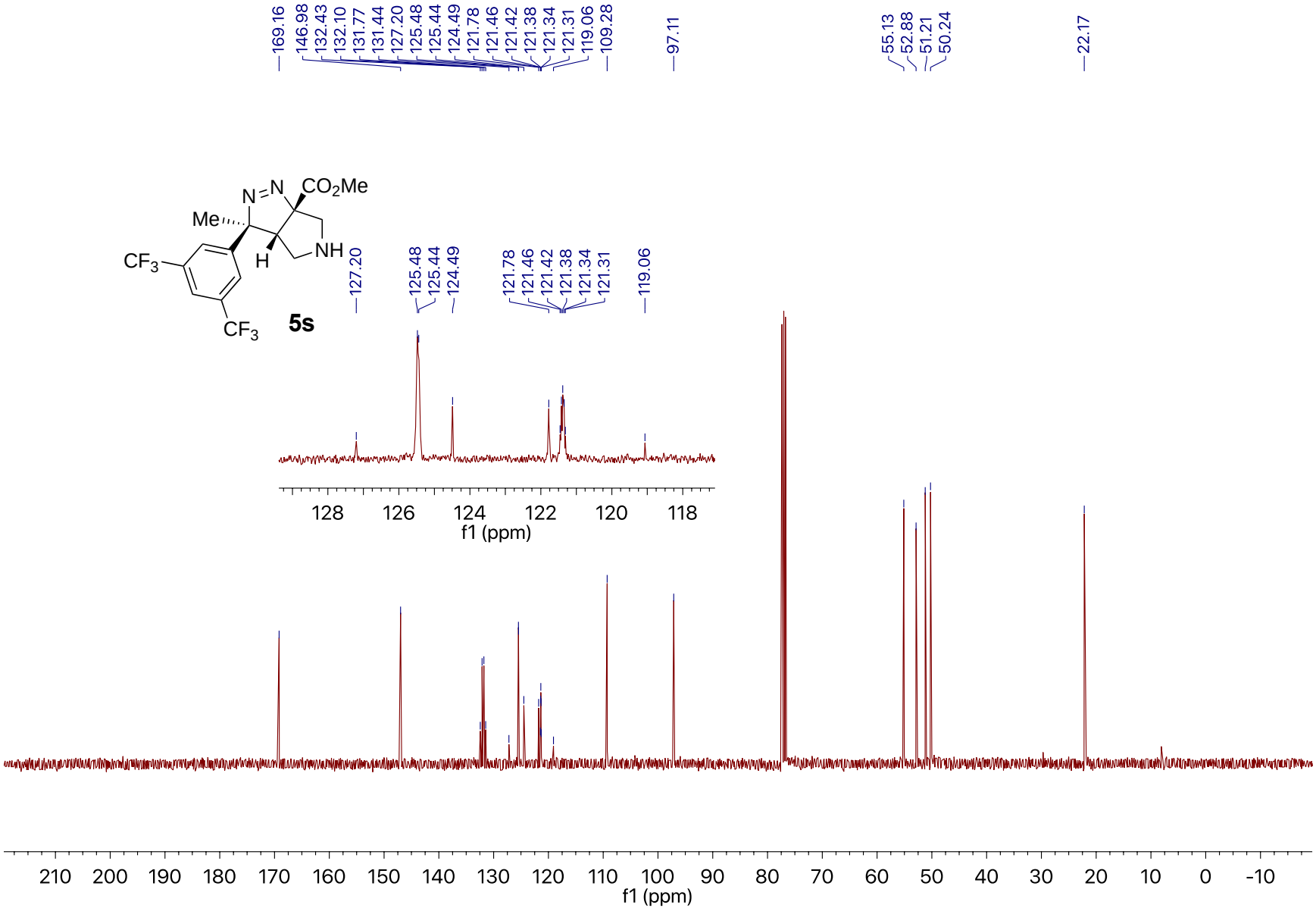
Compound **5r**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



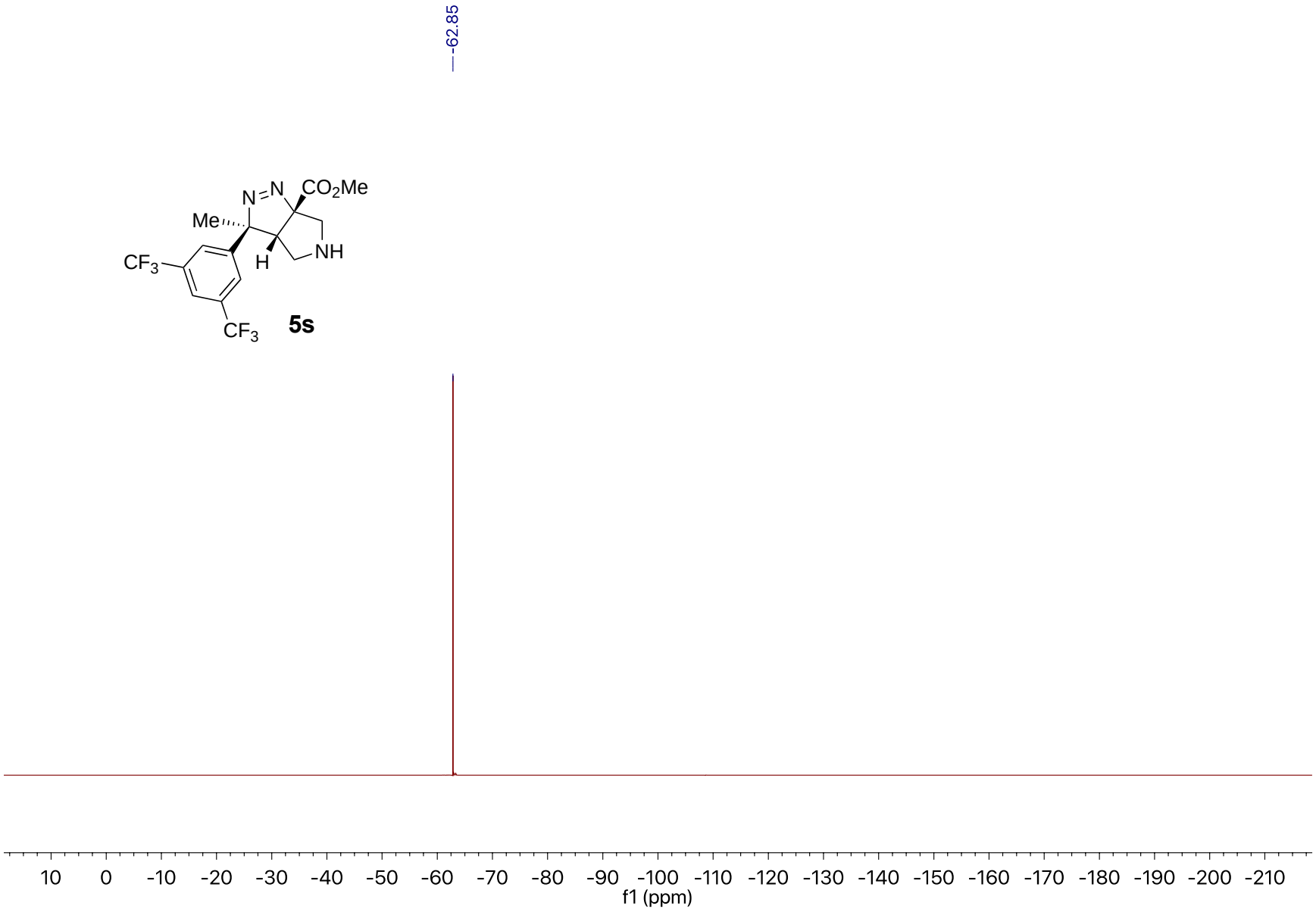
Compound **5r**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



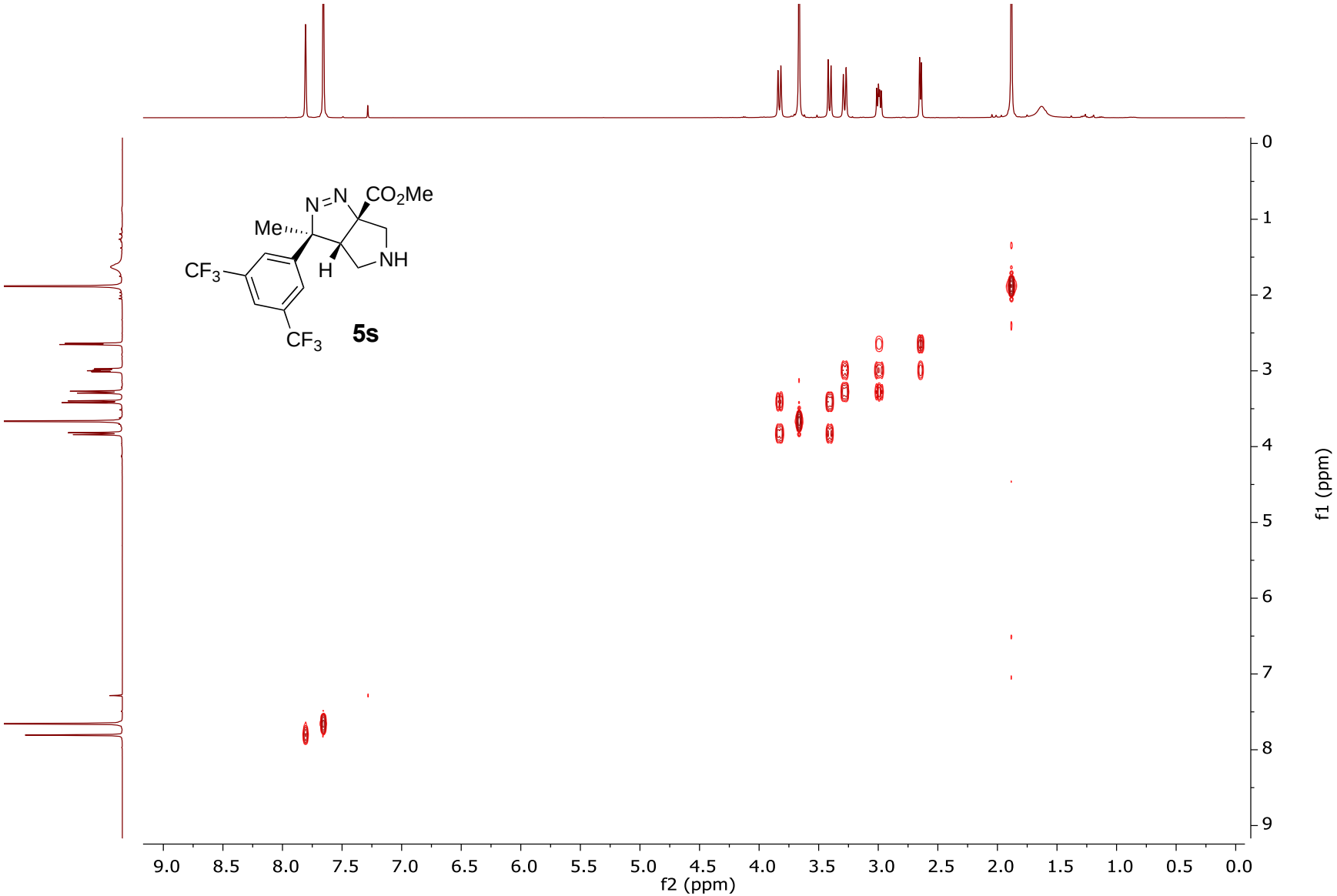
Compound **5s**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



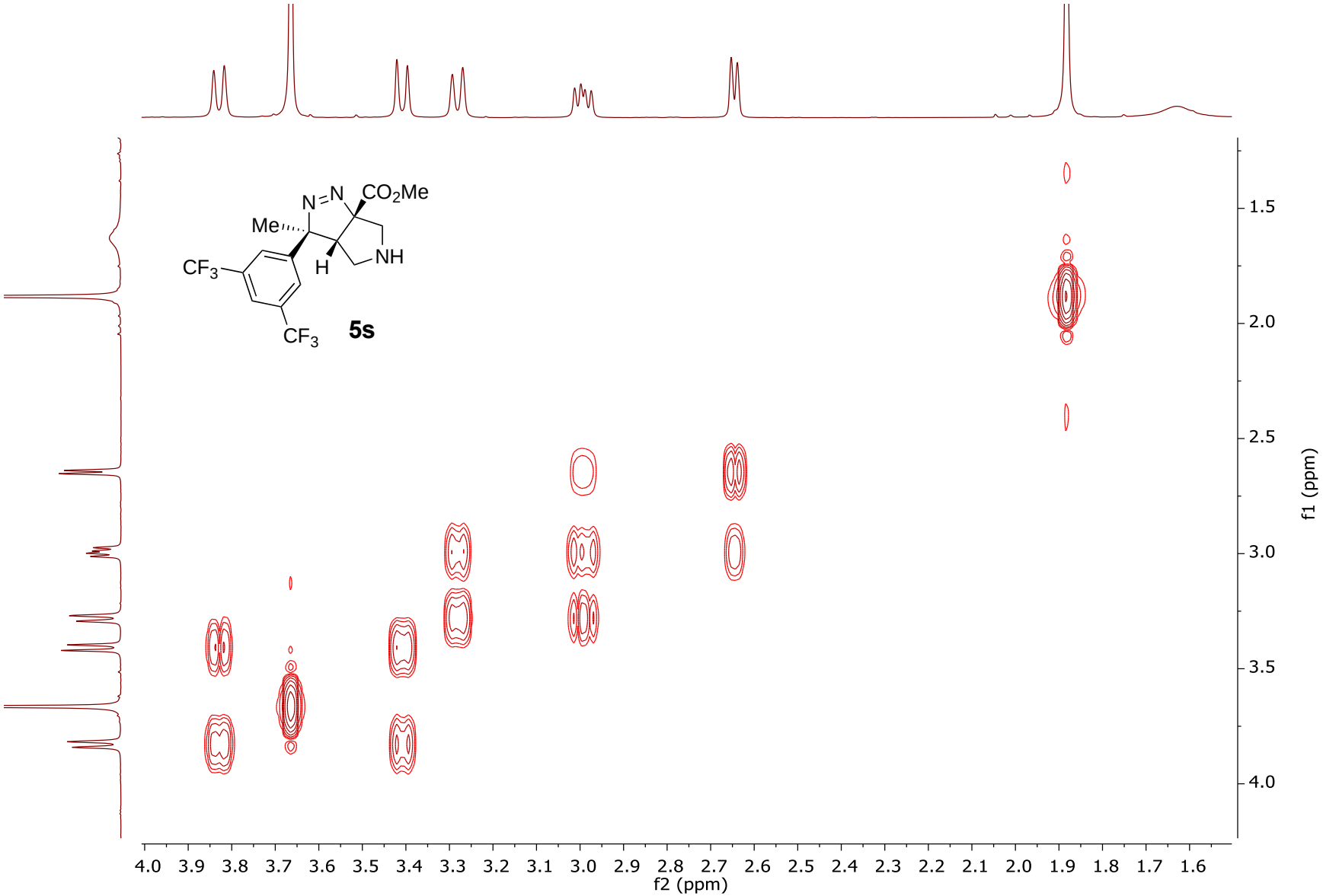
Compound **5s**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



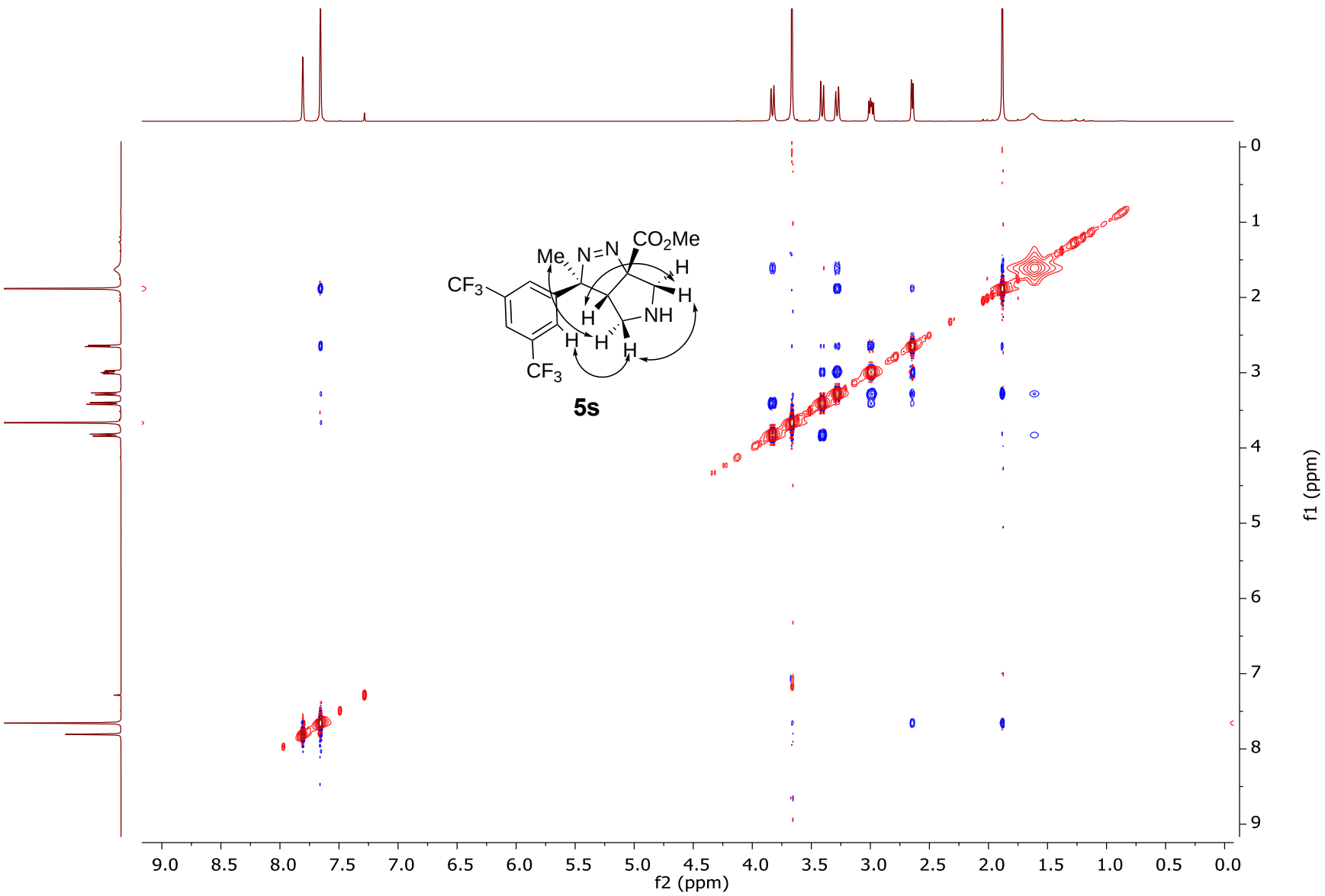
Compound **5s**. 376 MHz ^{19}F NMR spectrum in $CDCl_3$



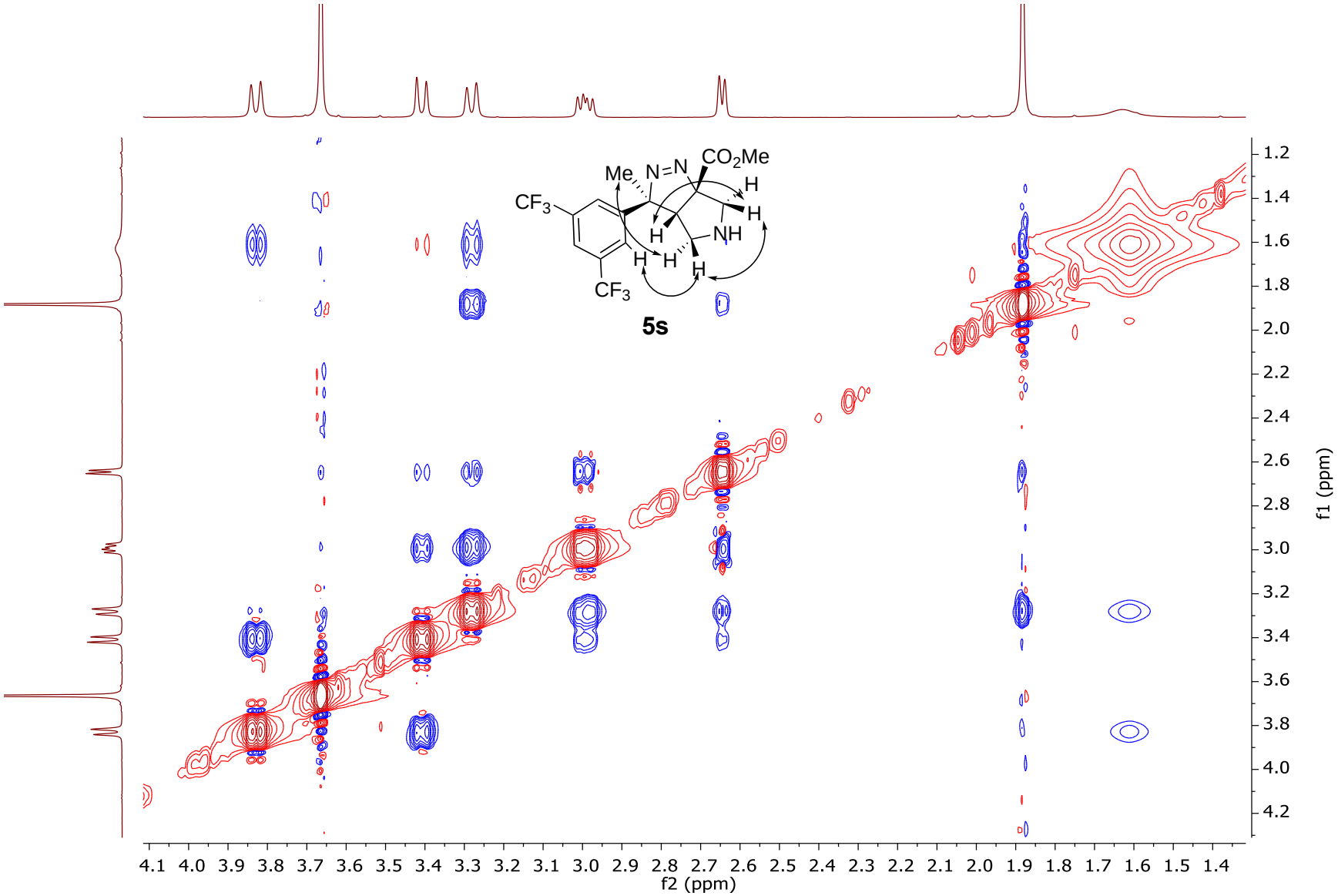
Compound **5s**. COSY NMR spectrum in $CDCl_3$



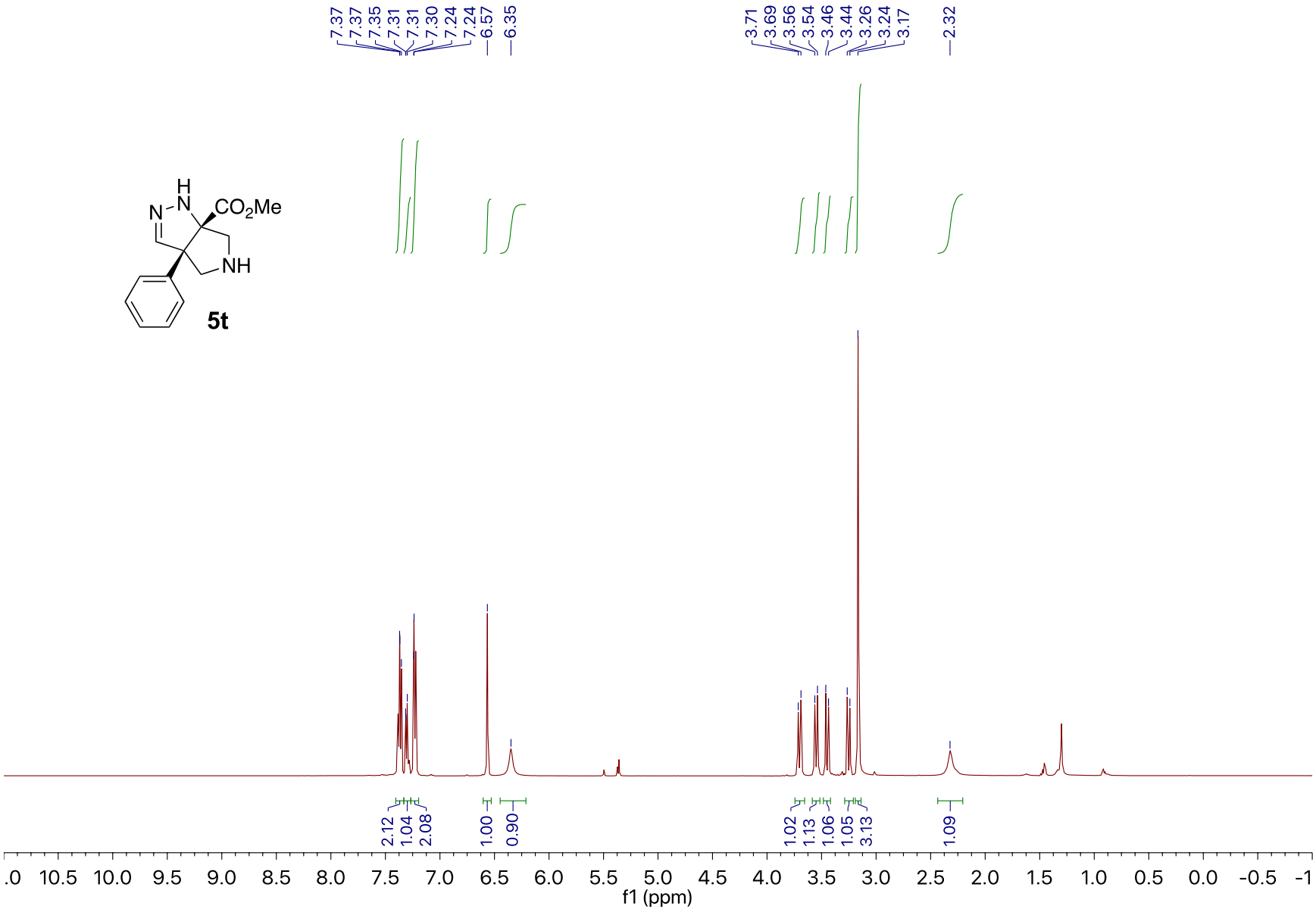
Compound **5s**. COSY NMR spectrum in $CDCl_3$ (expansion)



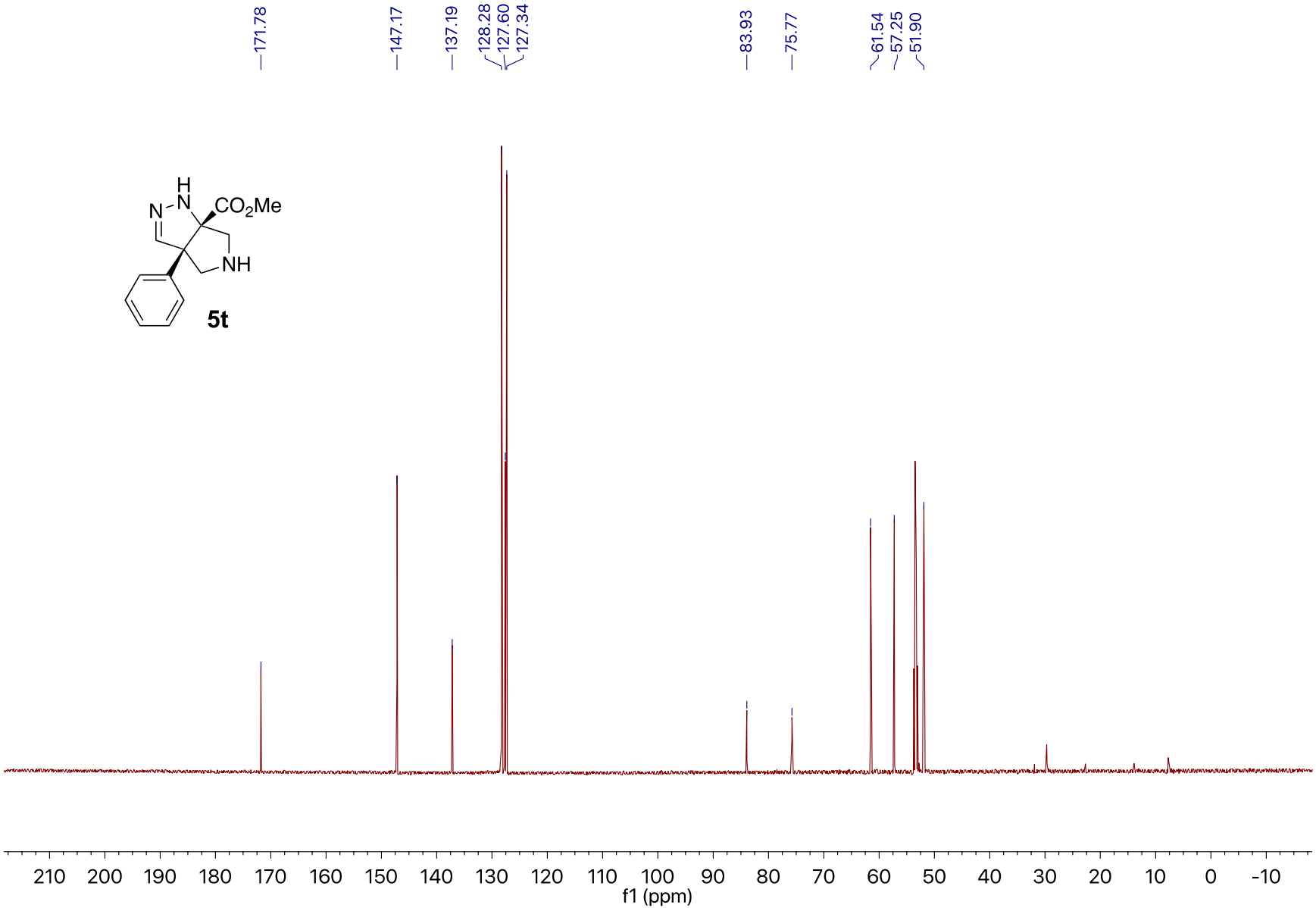
Compound **5s**. NOESY spectrum in $CDCl_3$



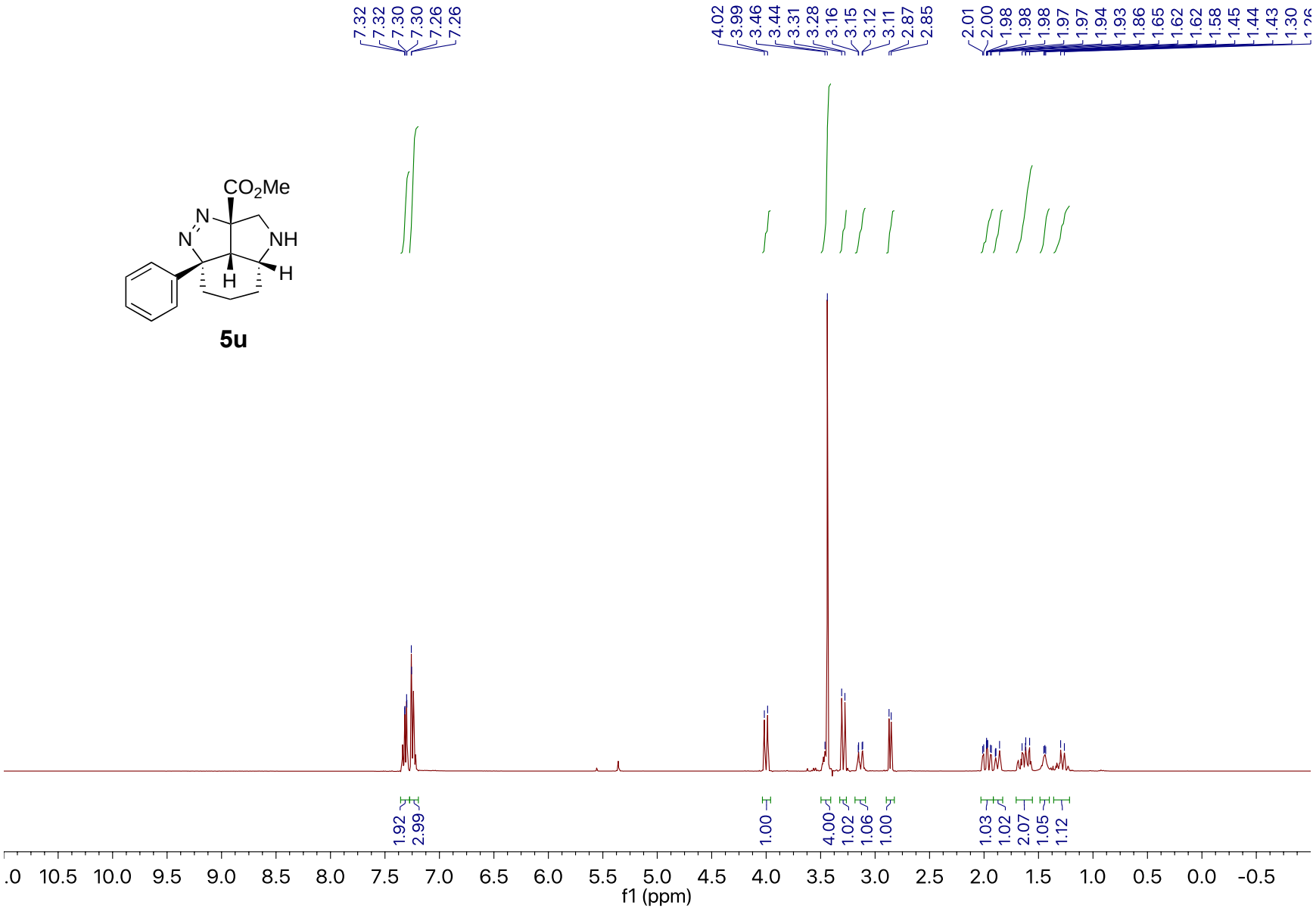
Compound **5s**. NOESY spectrum in $CDCl_3$ (expansion)



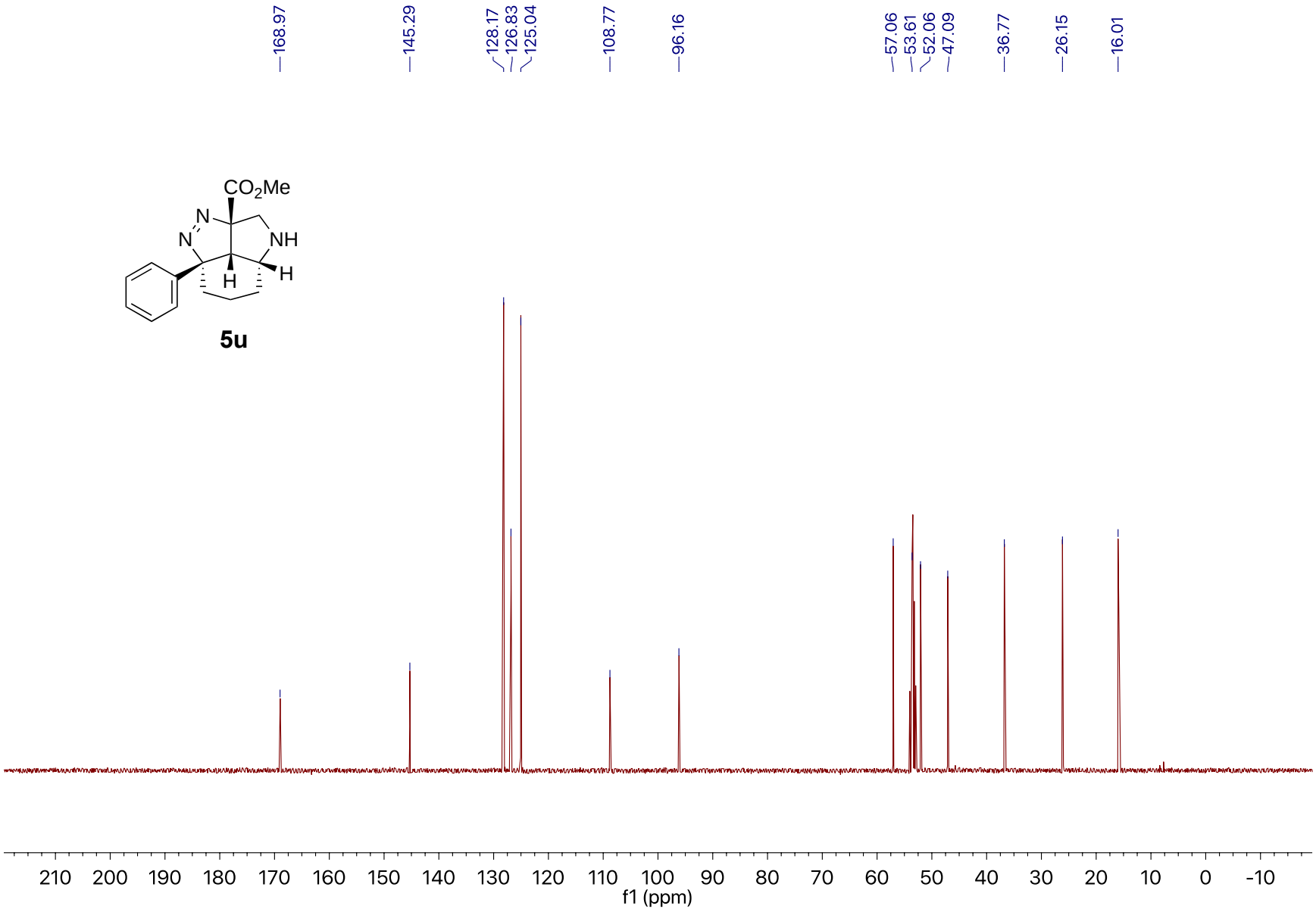
Compound **5t**. 500 MHz ^{1}H NMR spectrum in CD_2Cl_2



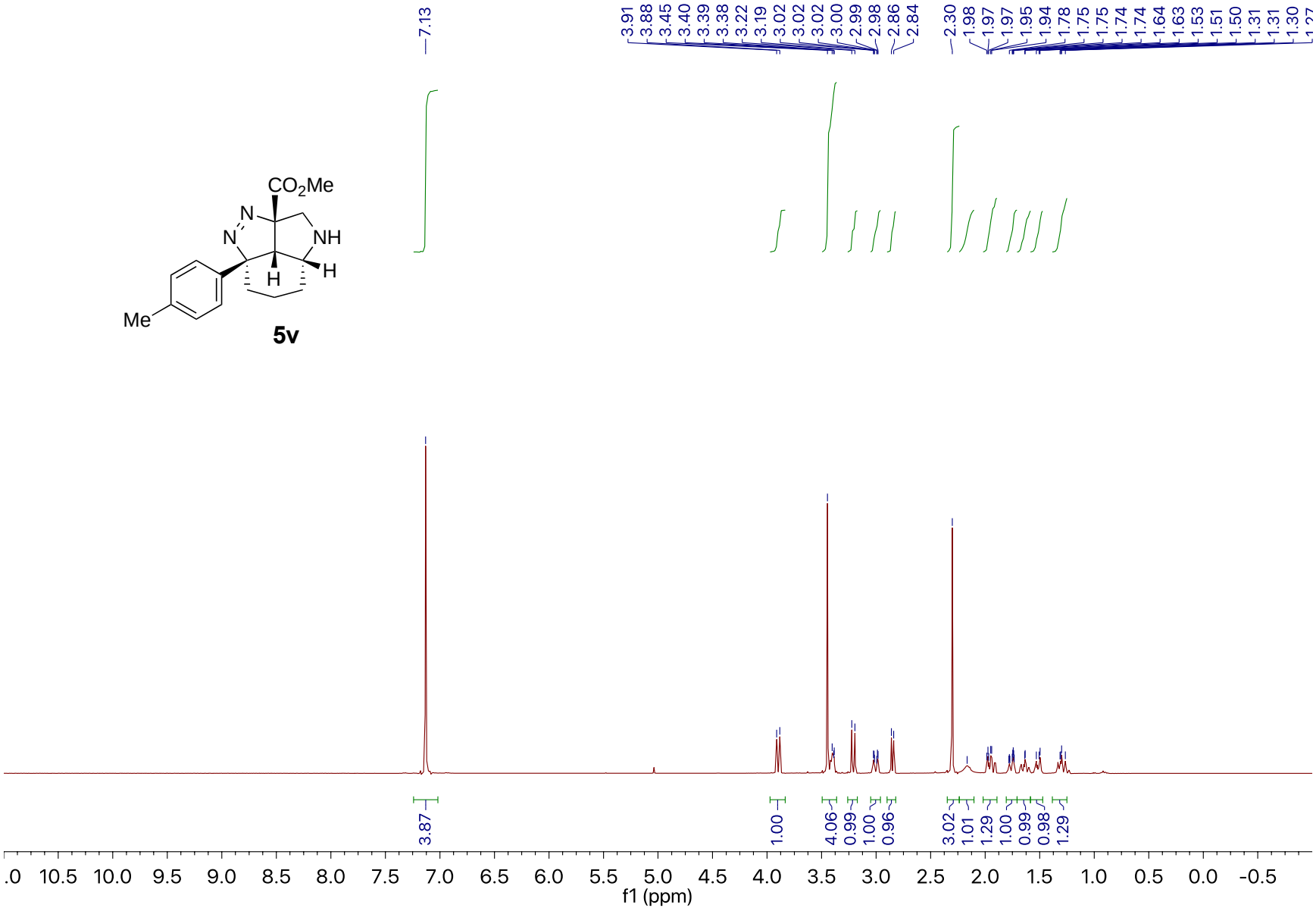
Compound **5t**. 126 MHz ^{13}C NMR spectrum in CD_2Cl_2



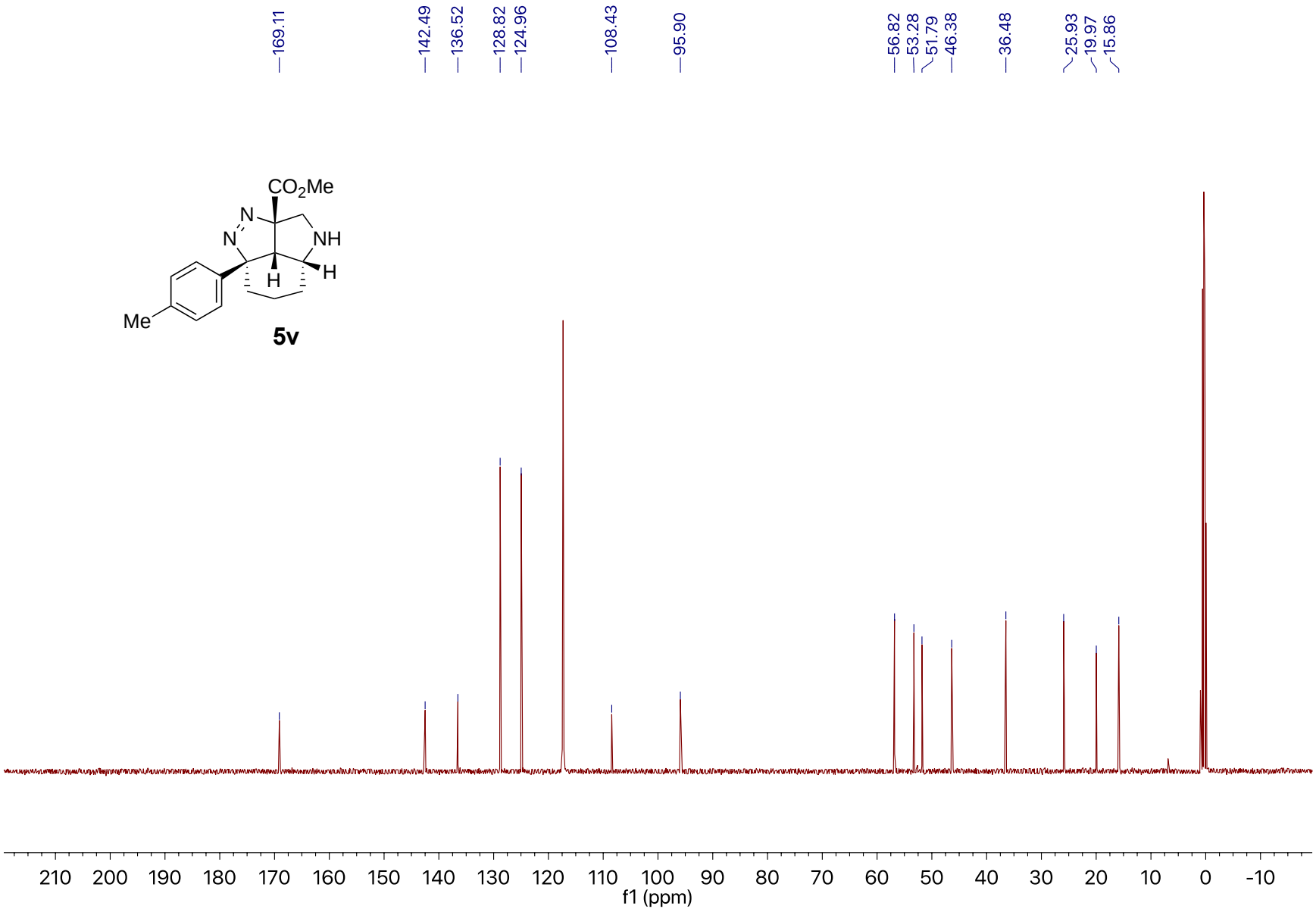
Compound **5u**. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2



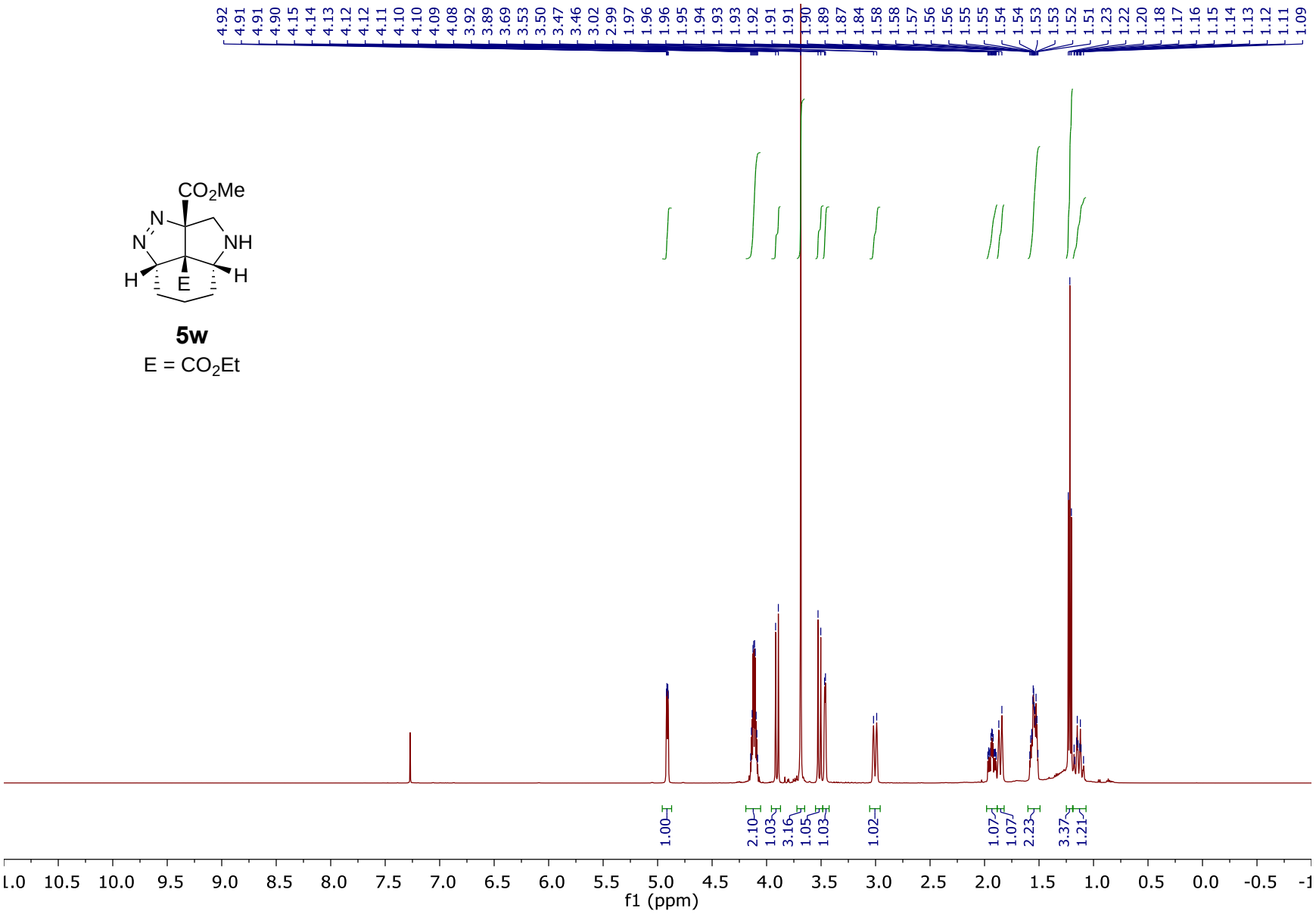
Compound **5u**. 101 MHz ^{13}C NMR spectrum in CD_2Cl_2



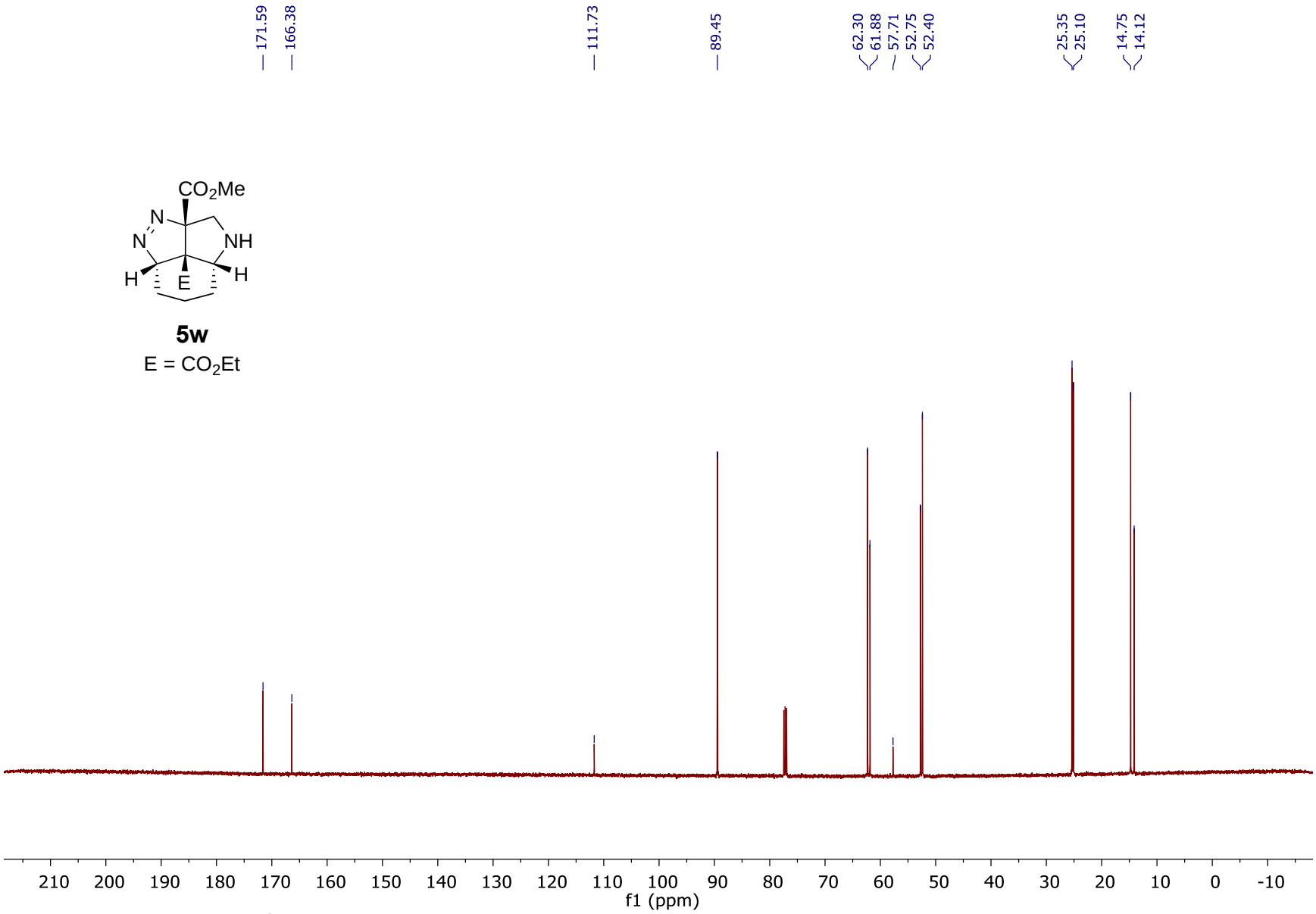
Compound **5v**. 400 MHz ^{1}H NMR spectrum in CD_3CN



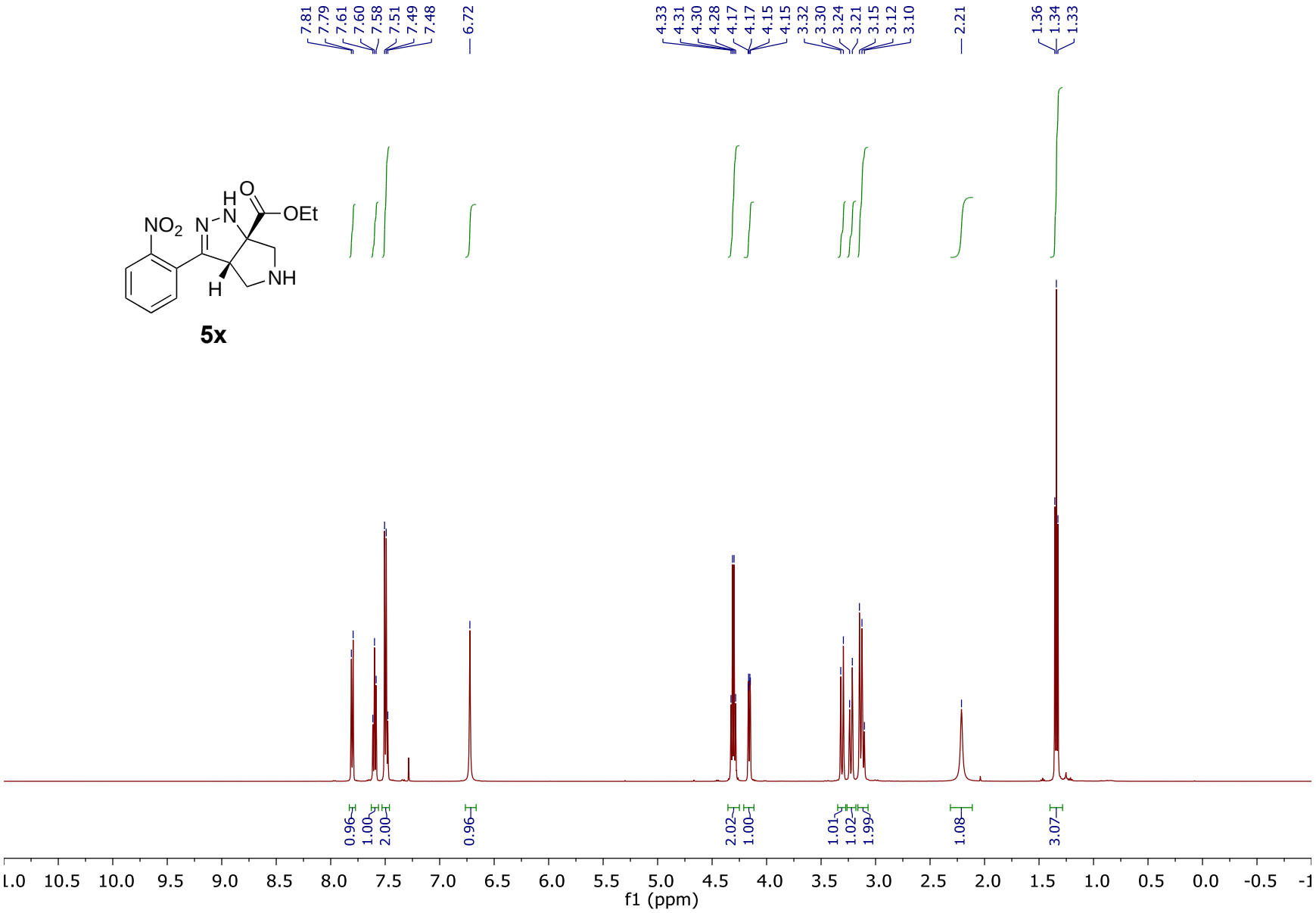
Compound **5v**. 101 MHz ^{13}C NMR spectrum in CD_3CN



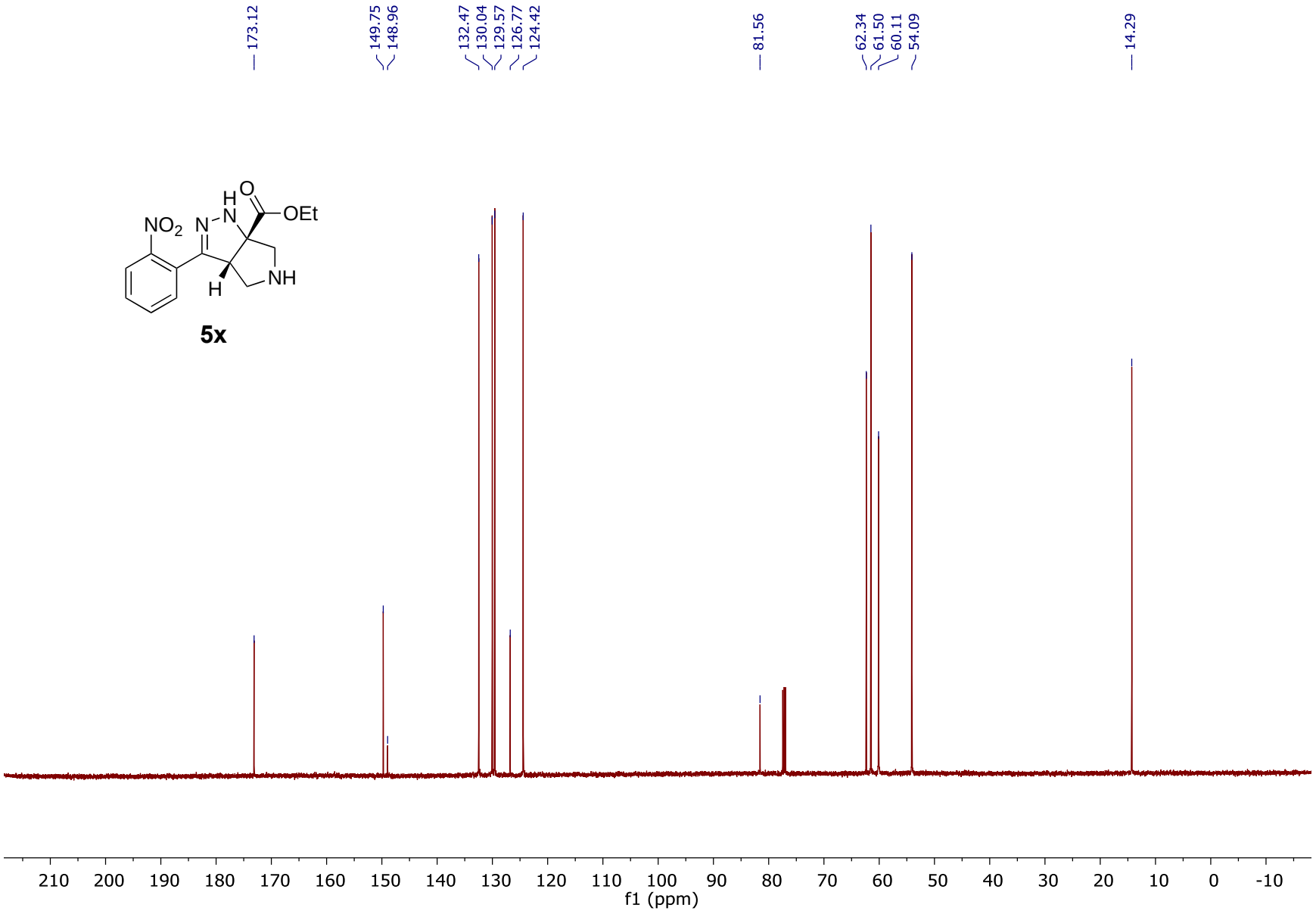
Compound **5w**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



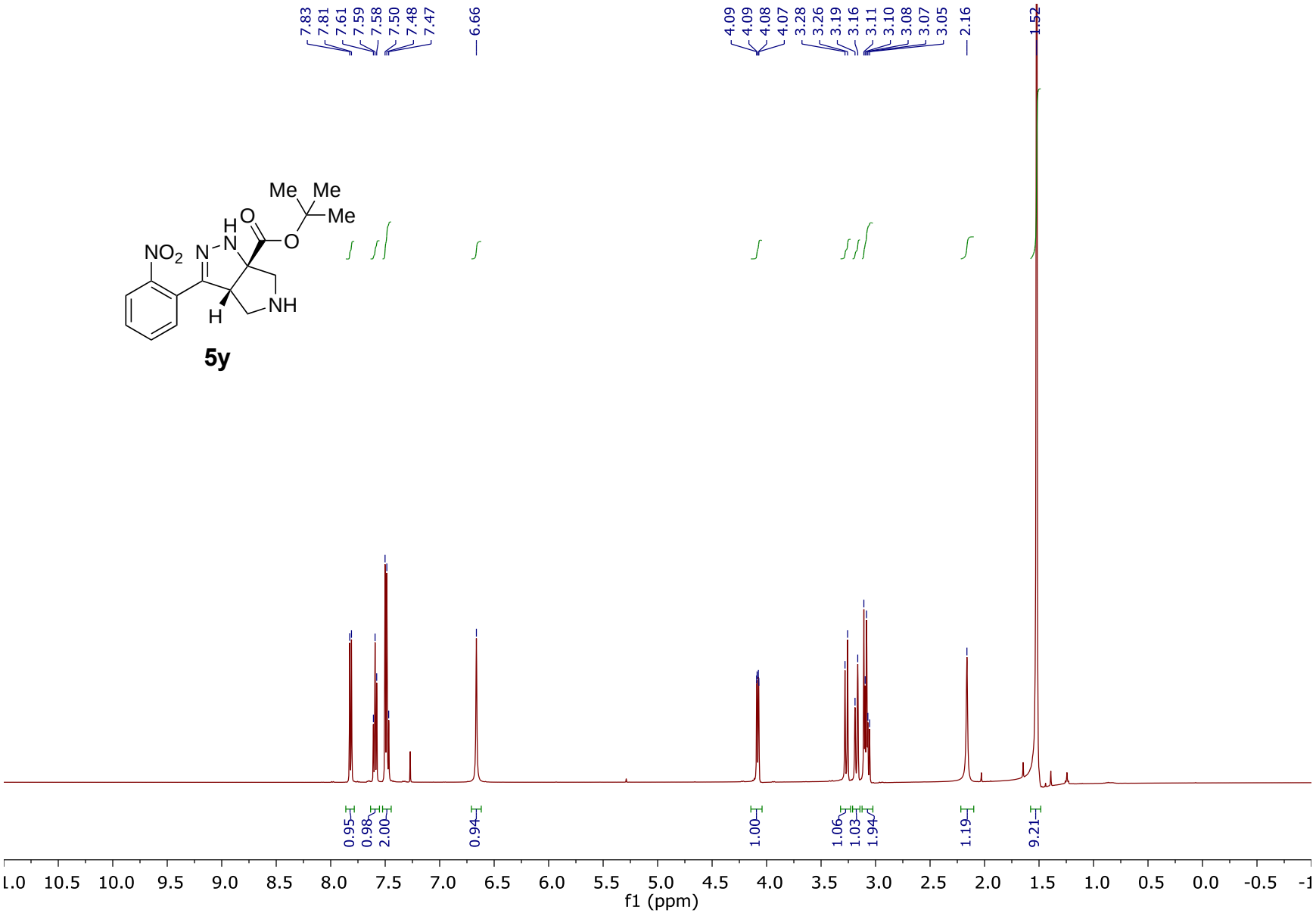
Compound **5w**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



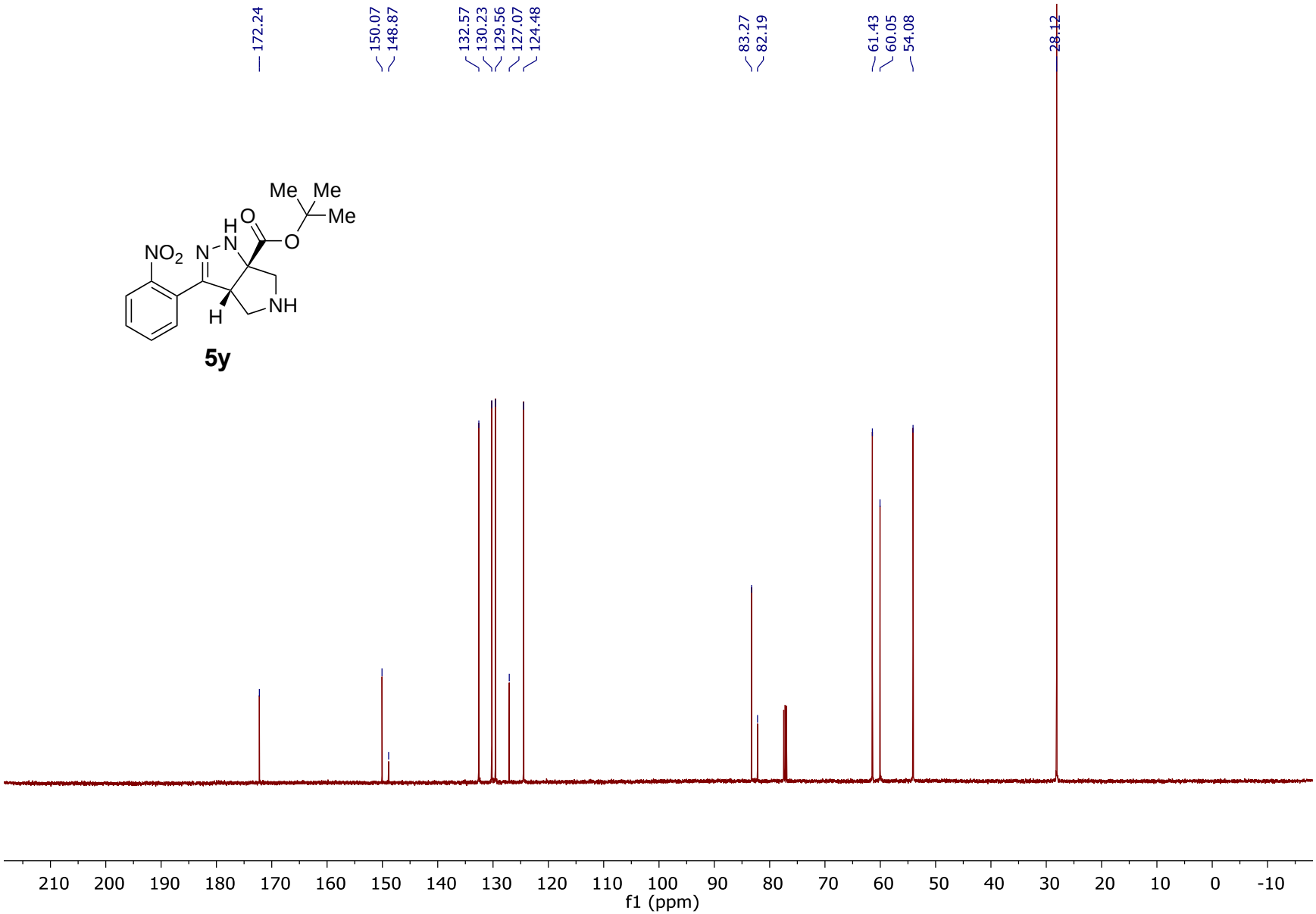
Compound **5x**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



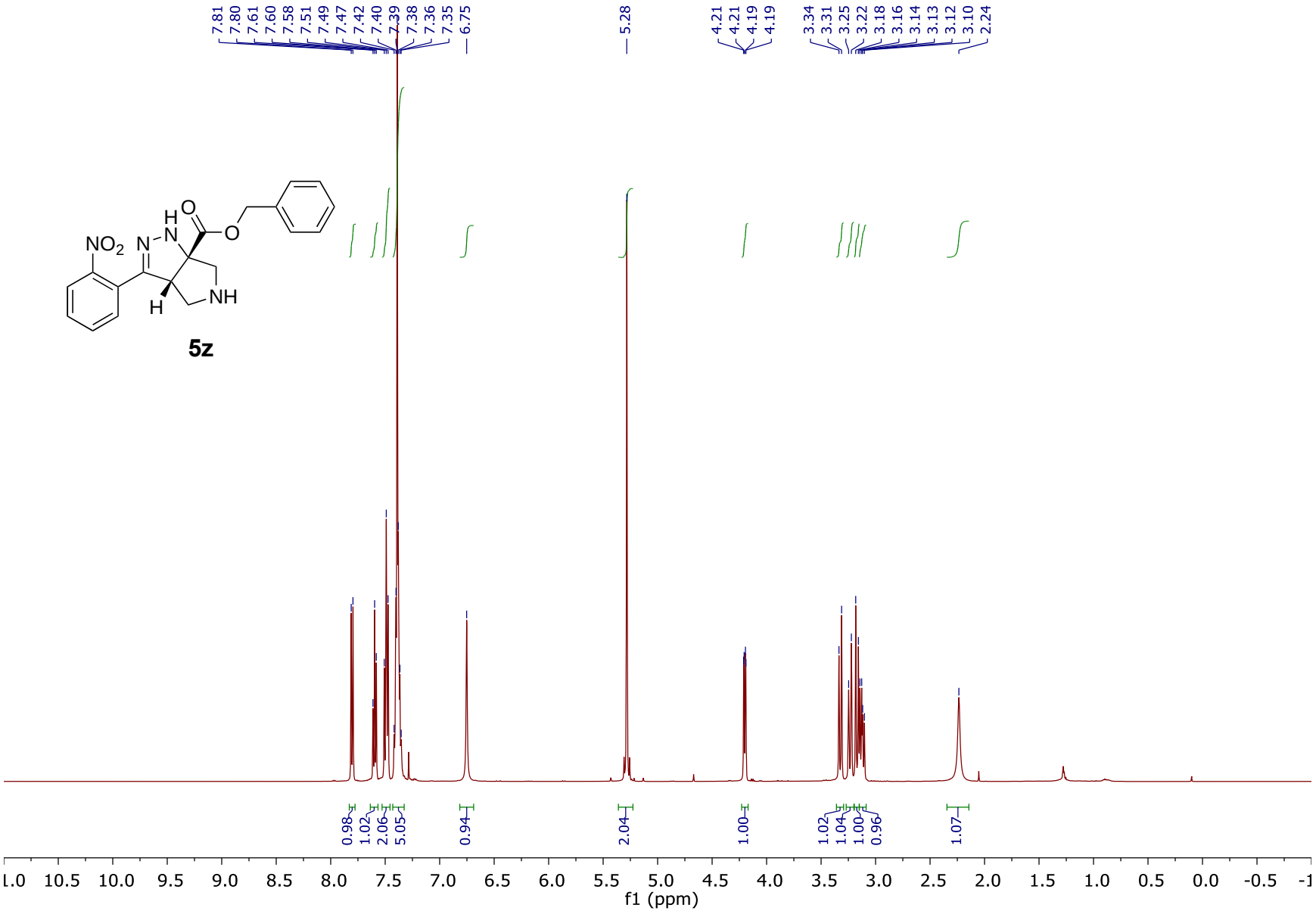
Compound **5x**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



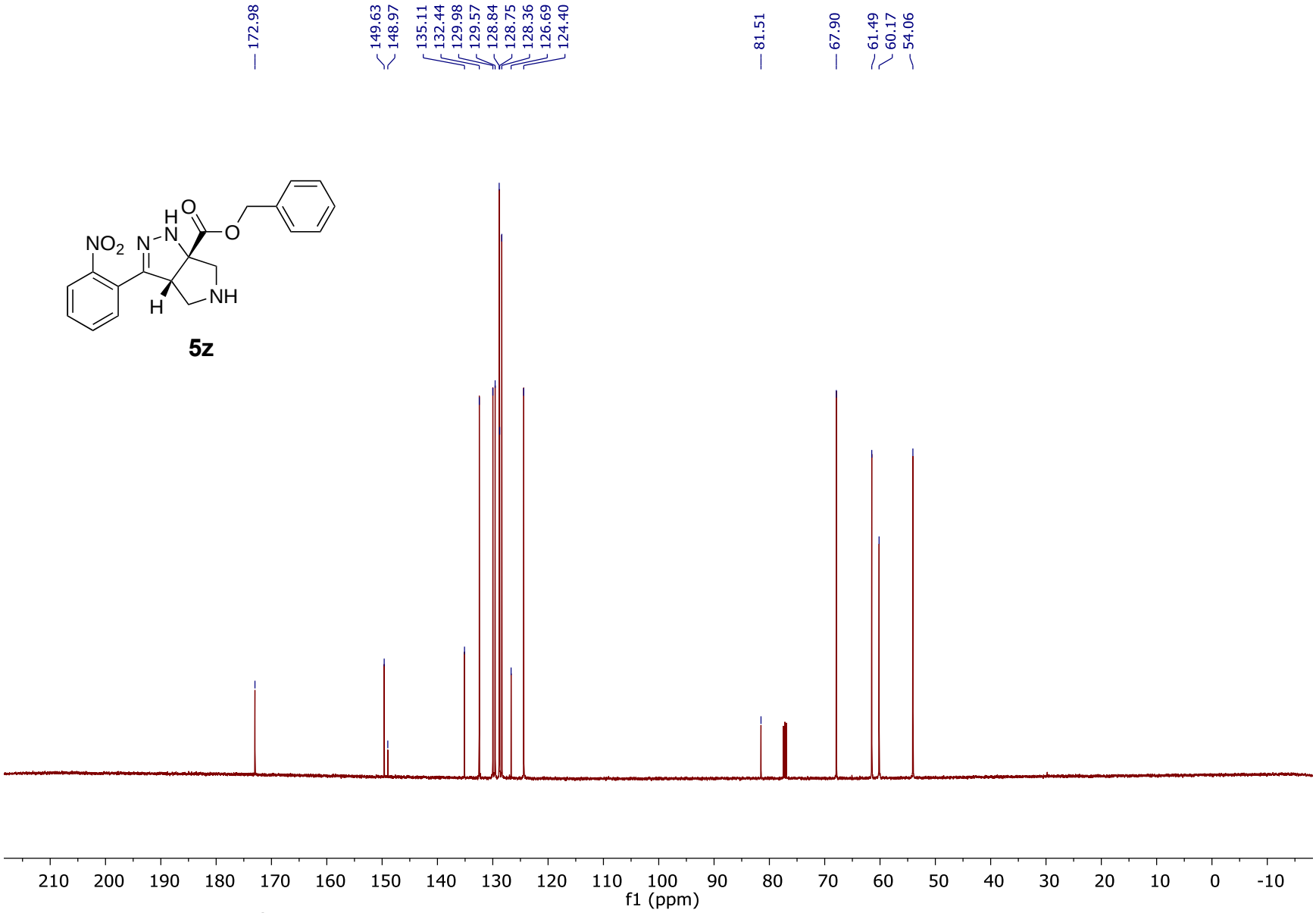
Compound **5y**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



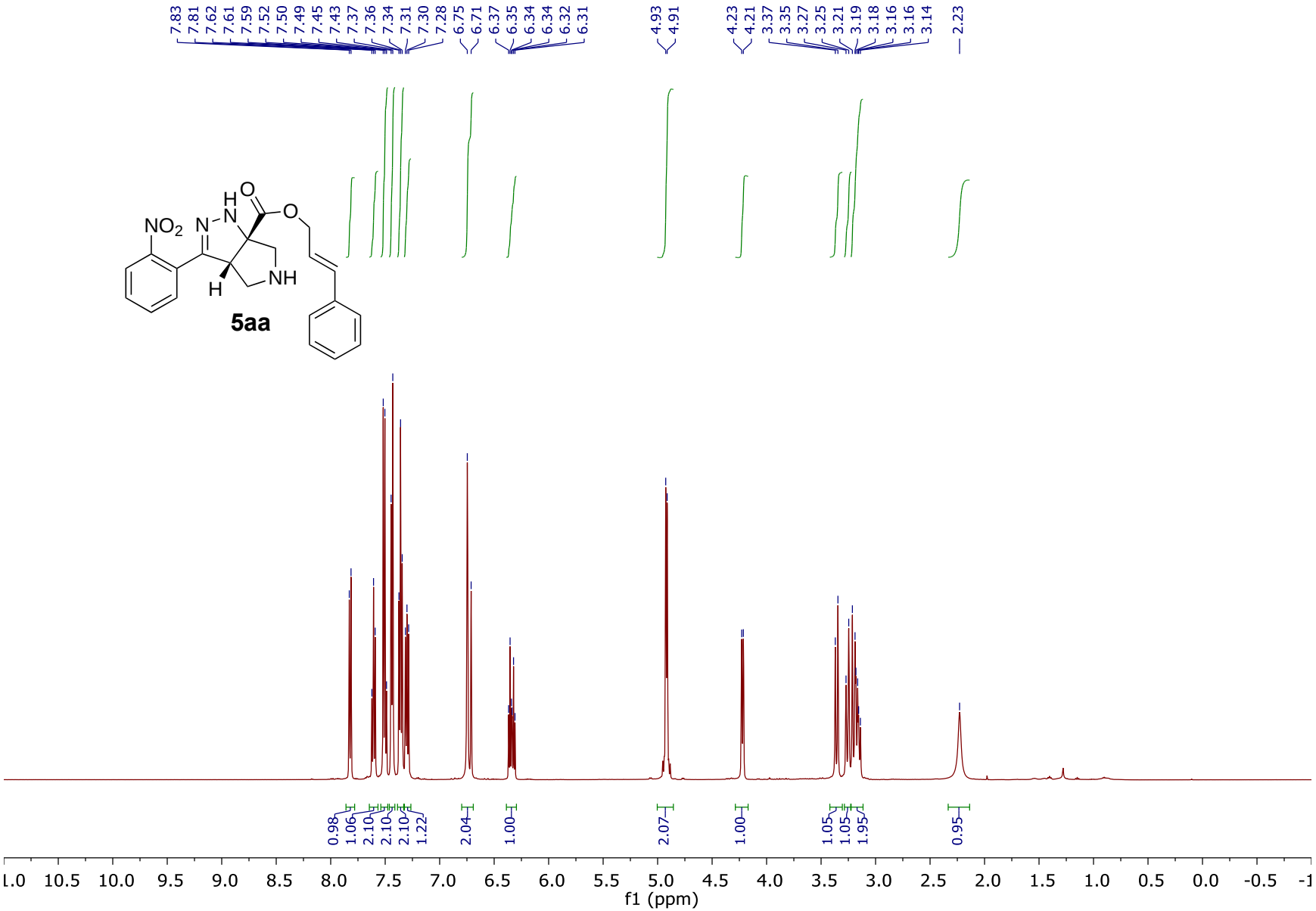
Compound **5y**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



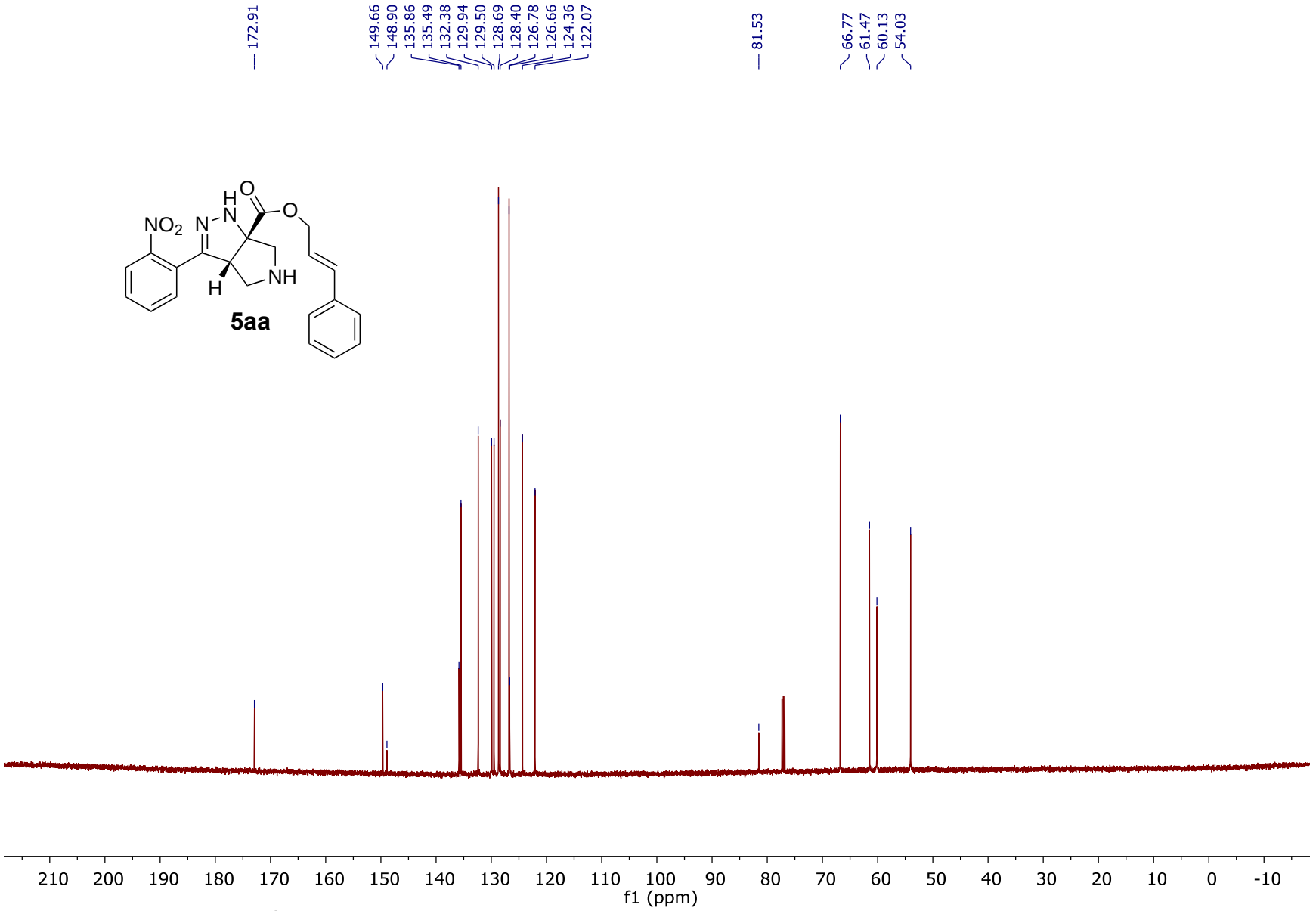
Compound **5z**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



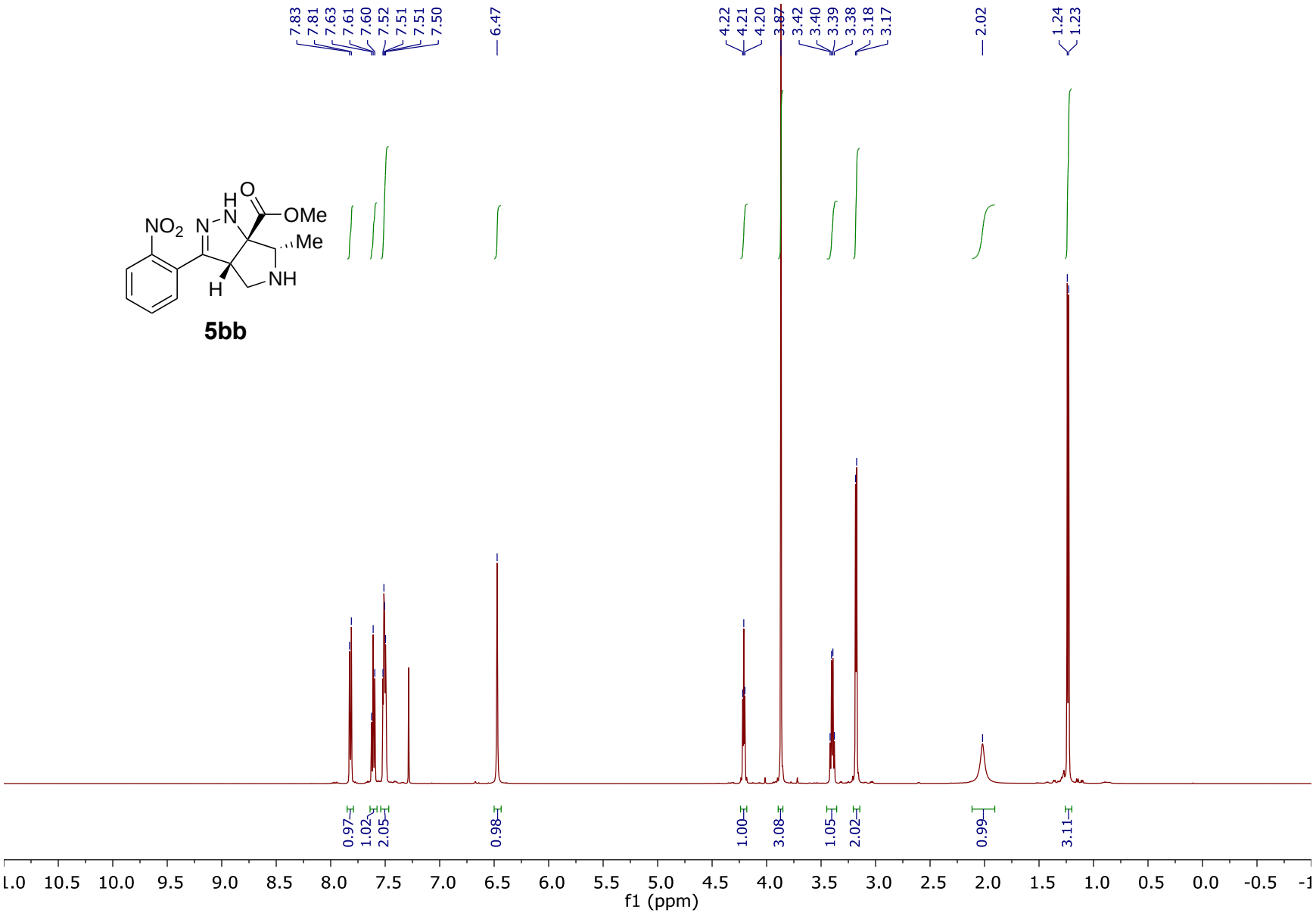
Compound **5z**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



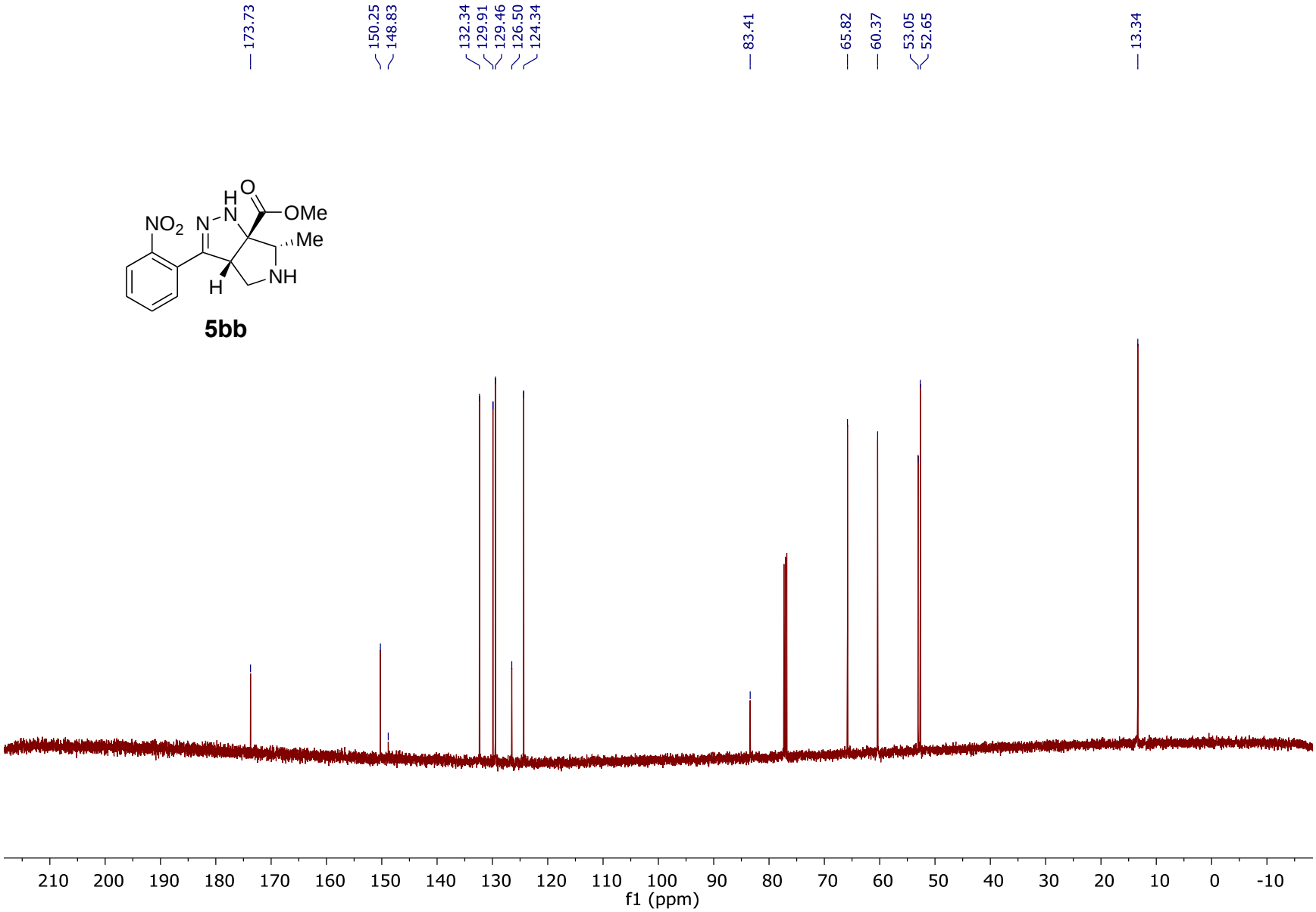
Compound **5aa**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



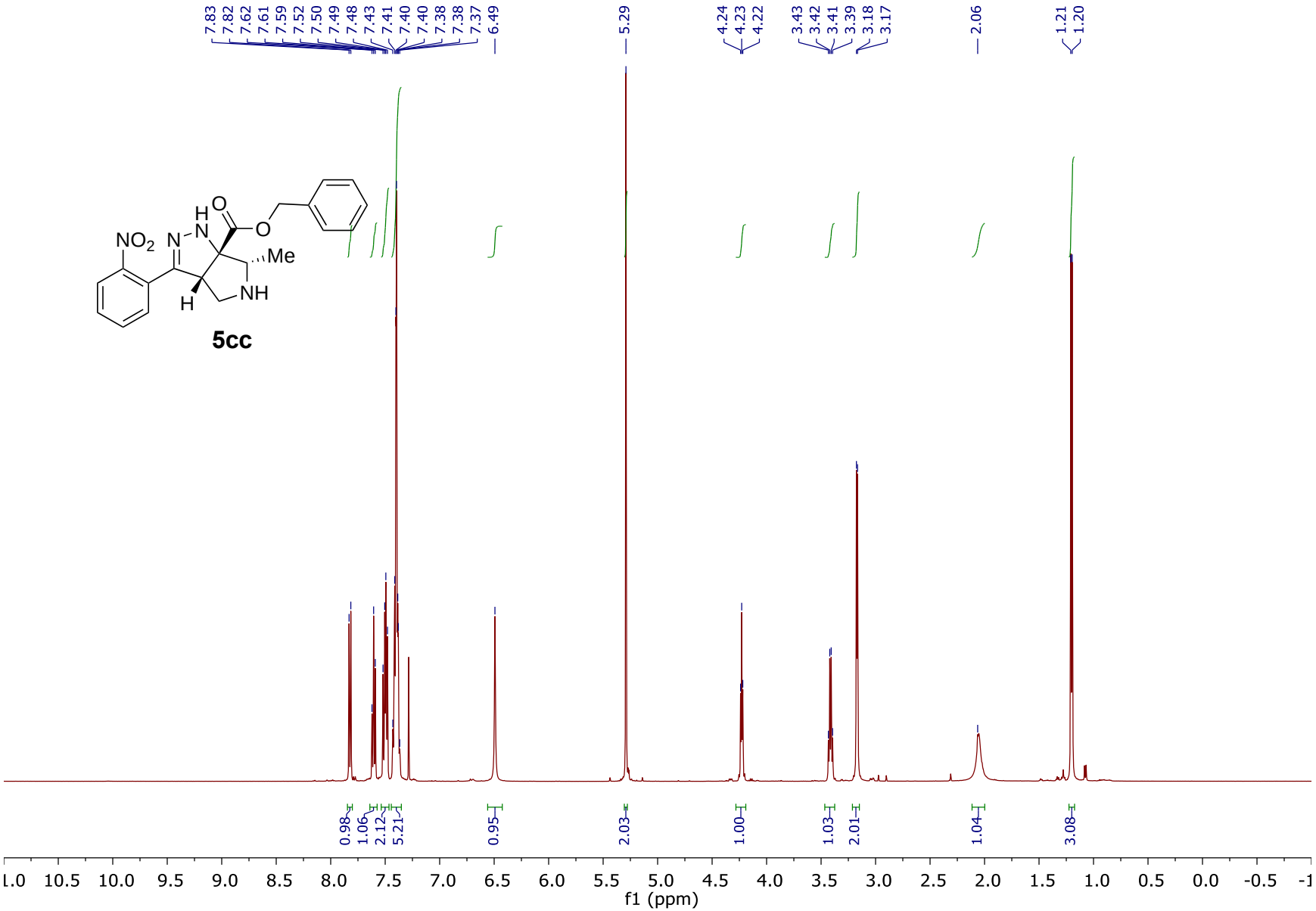
Compound **5aa**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



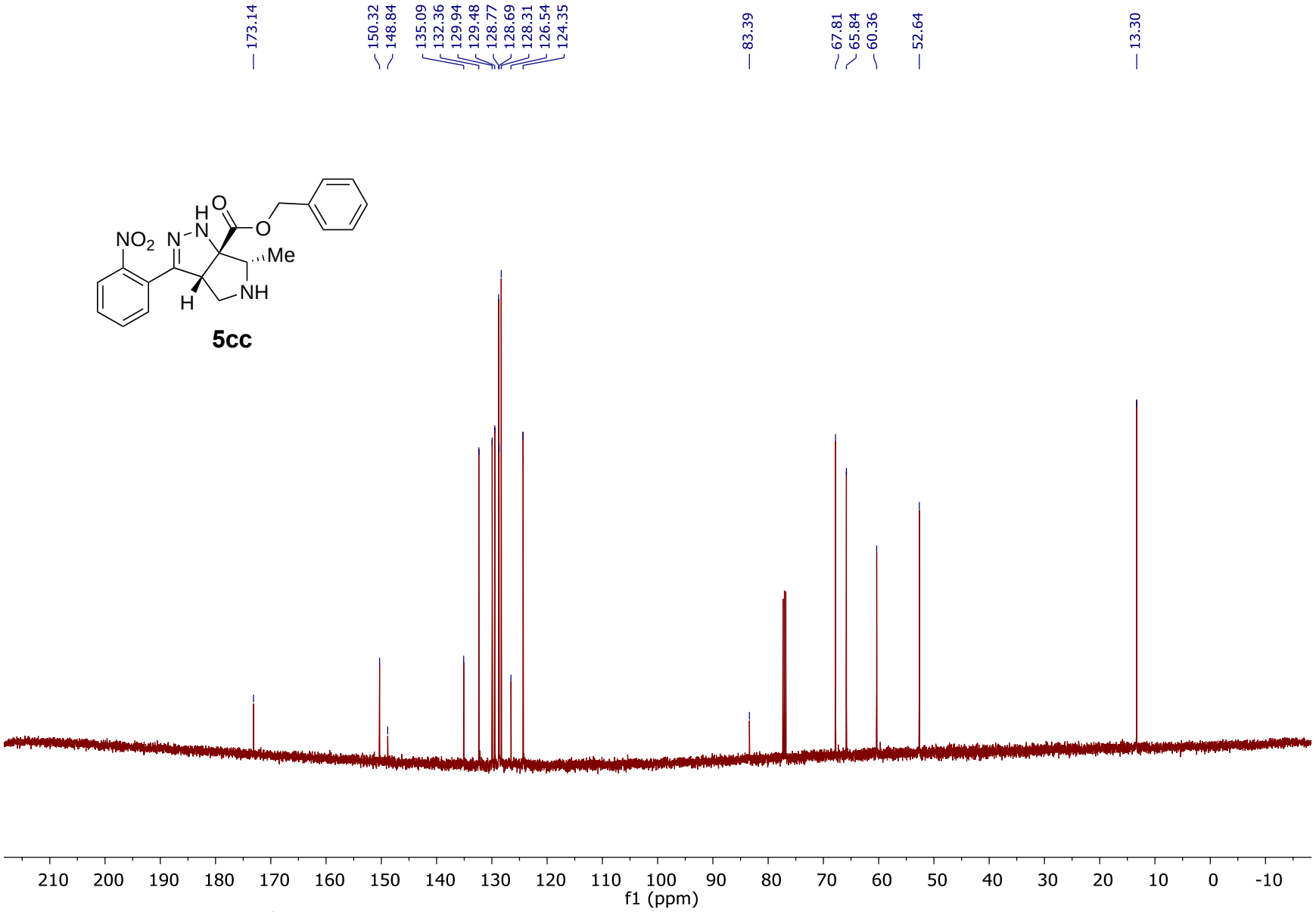
Compound **5bb**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



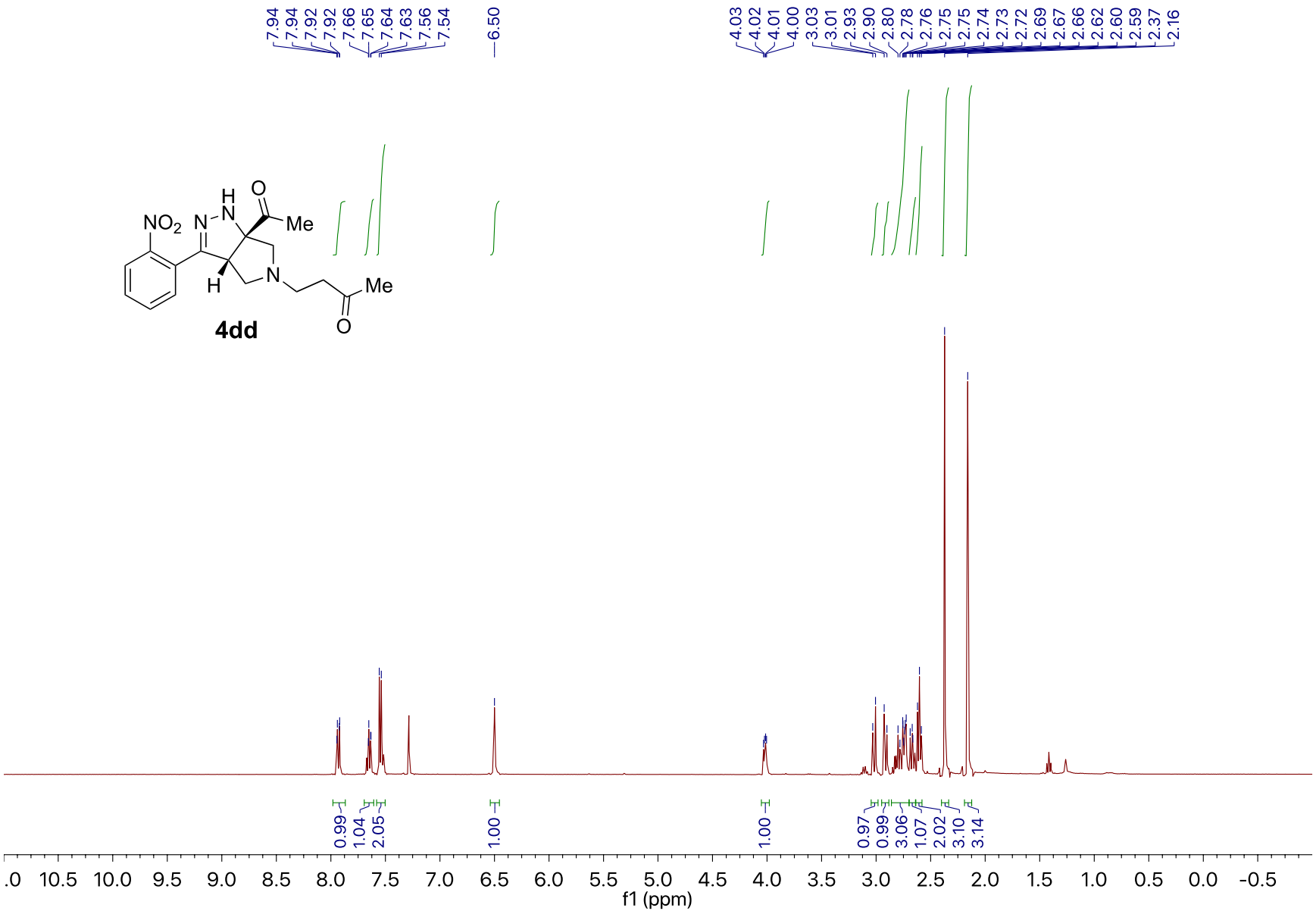
Compound **5bb**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



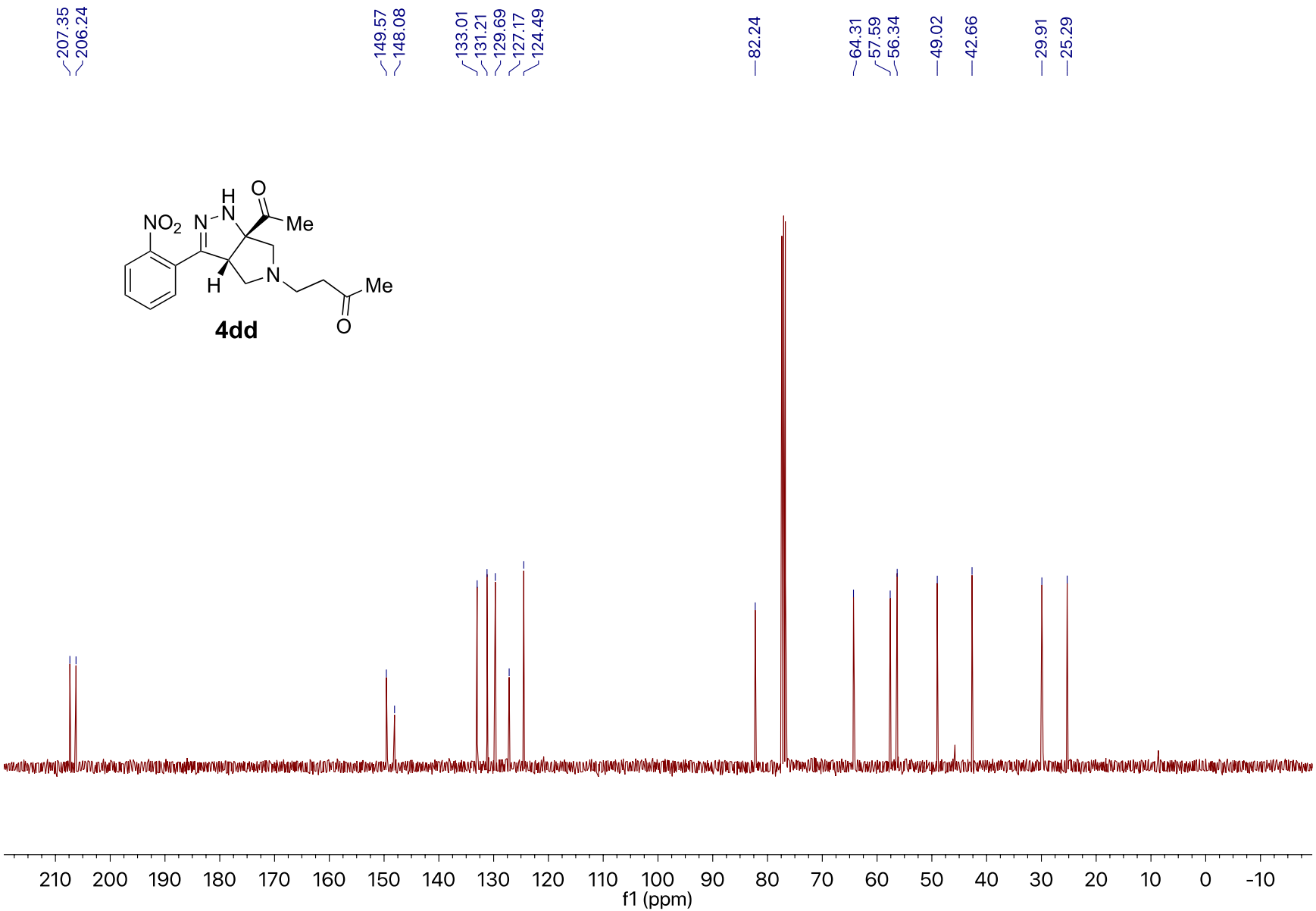
Compound **5cc**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



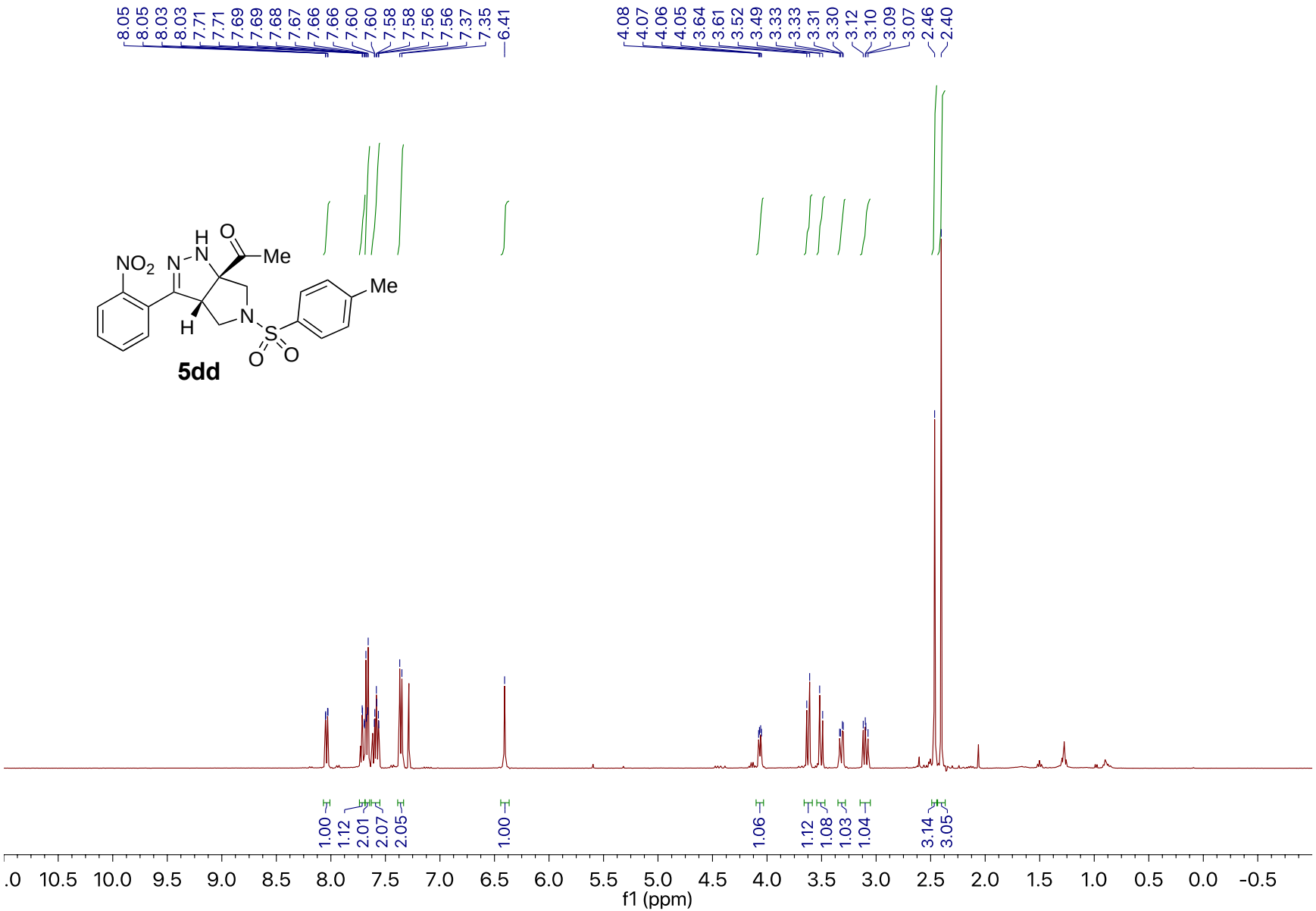
Compound **5cc**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



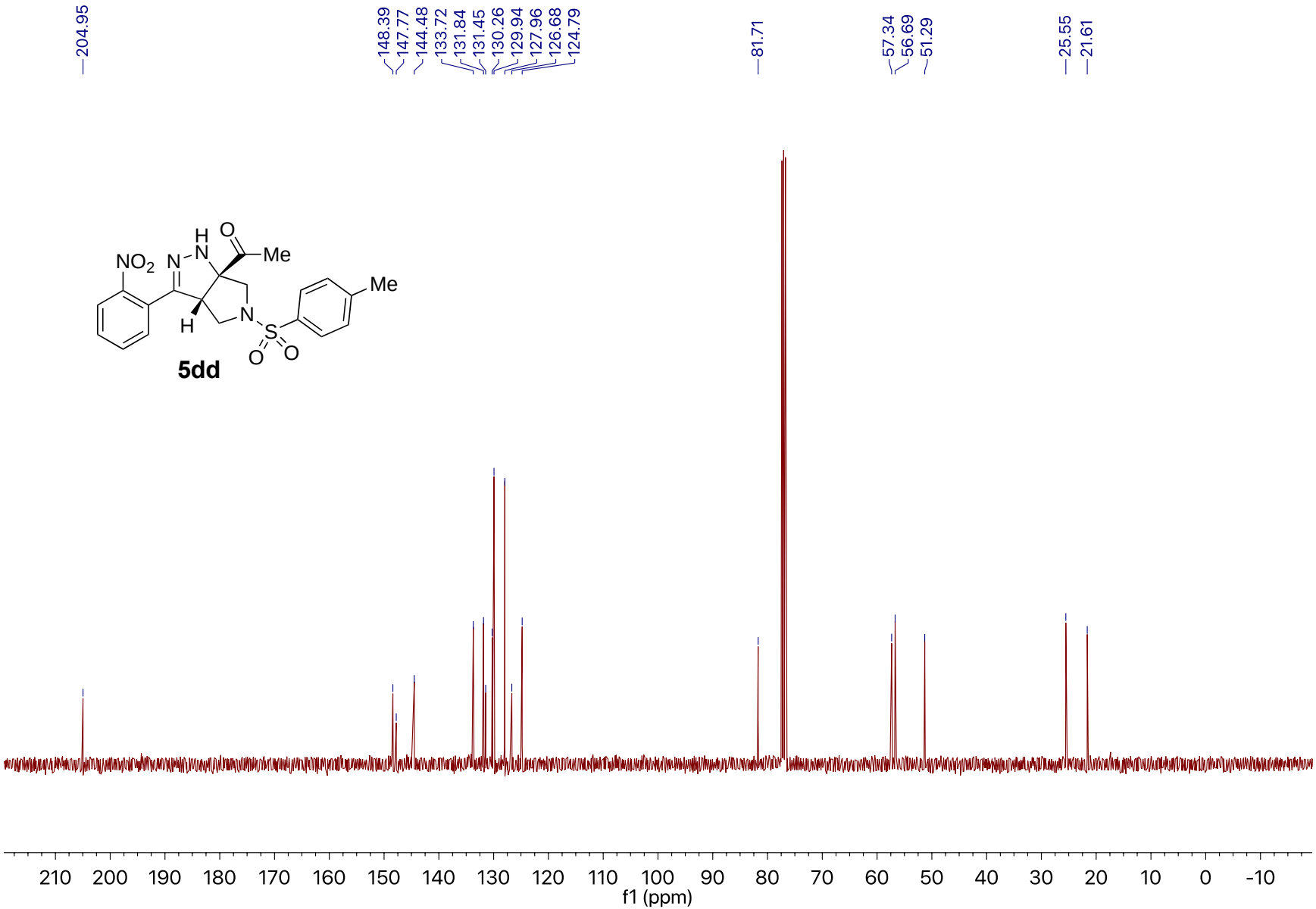
Compound **4dd**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



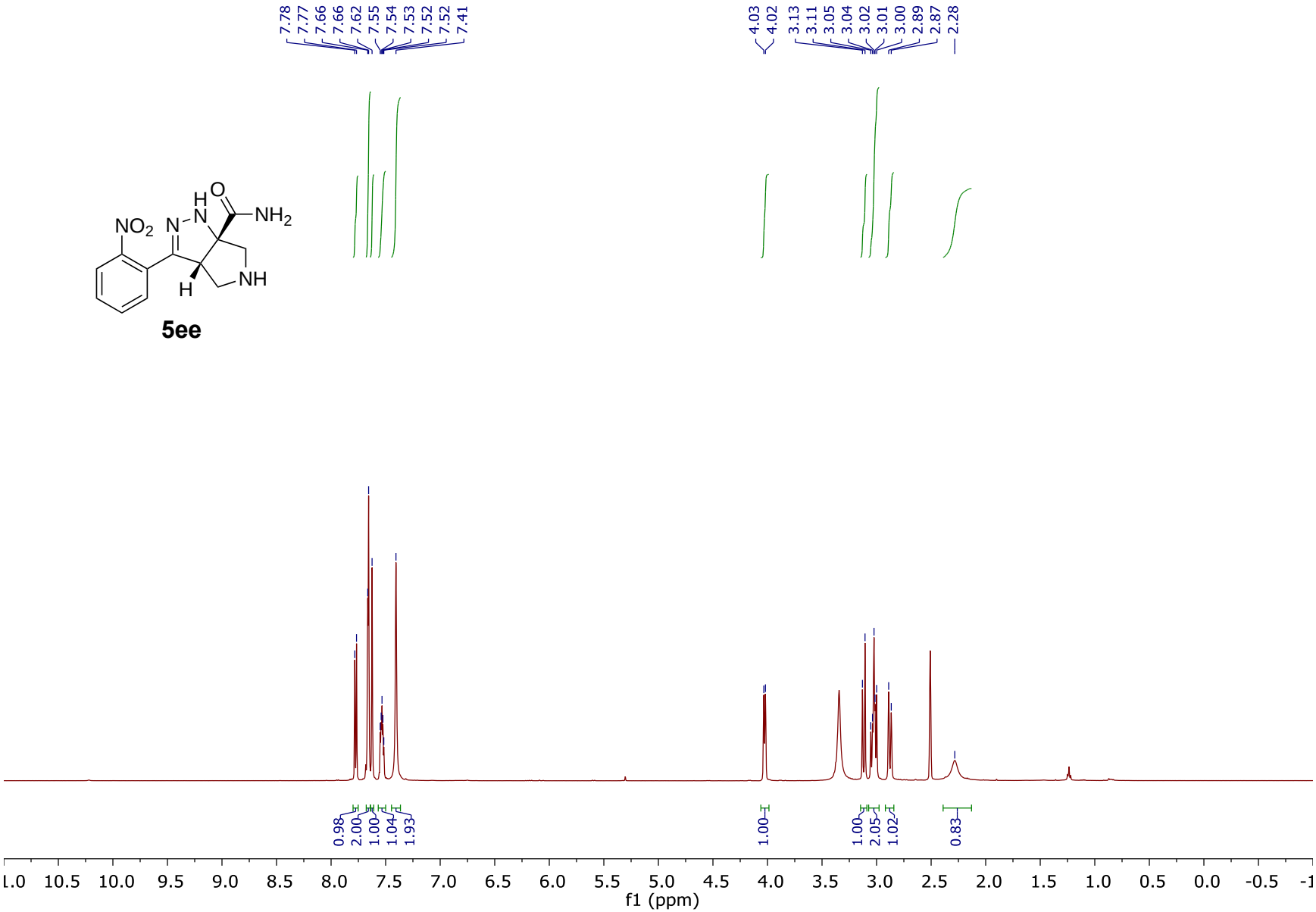
Compound **4dd**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



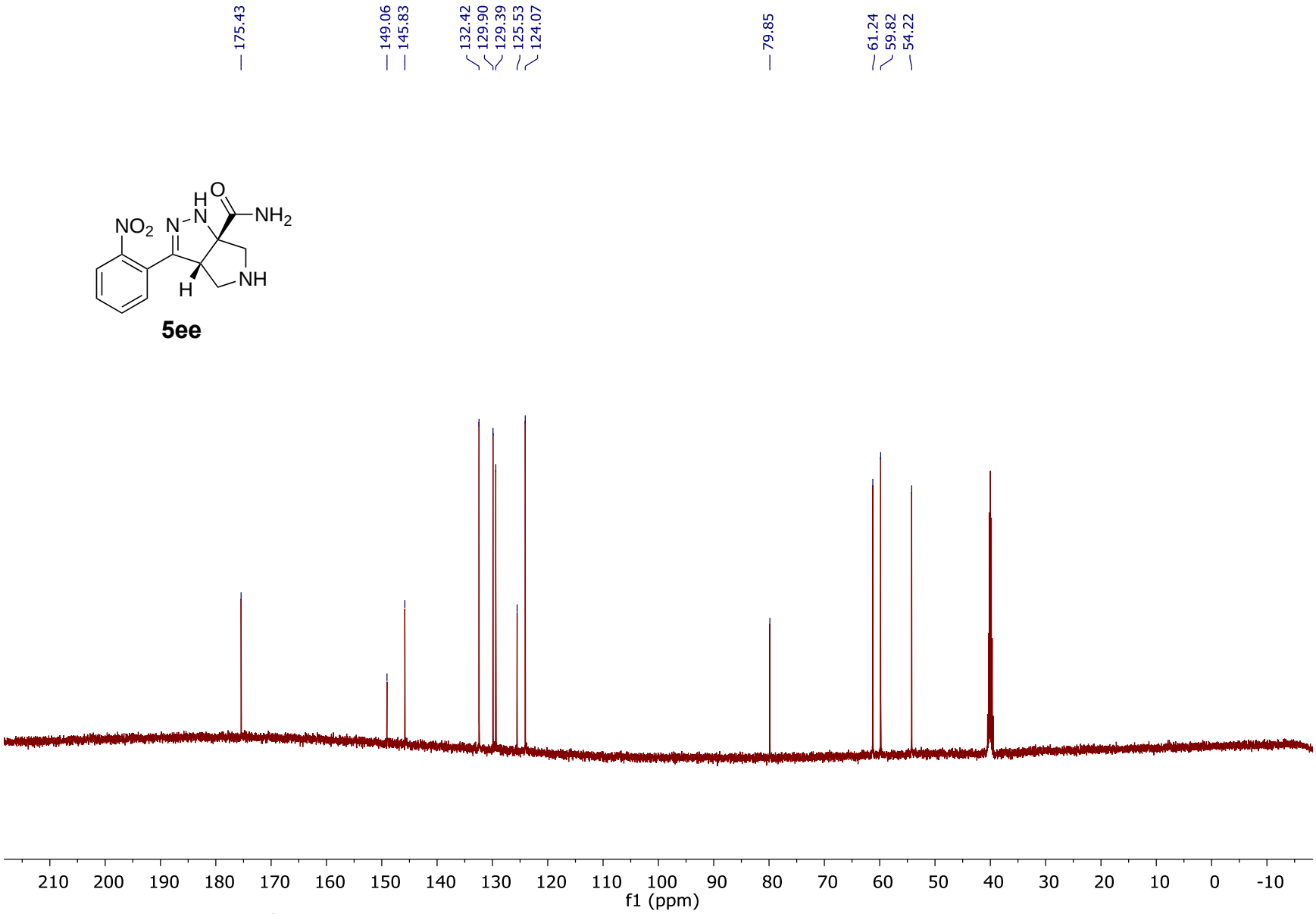
Compound **5dd**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



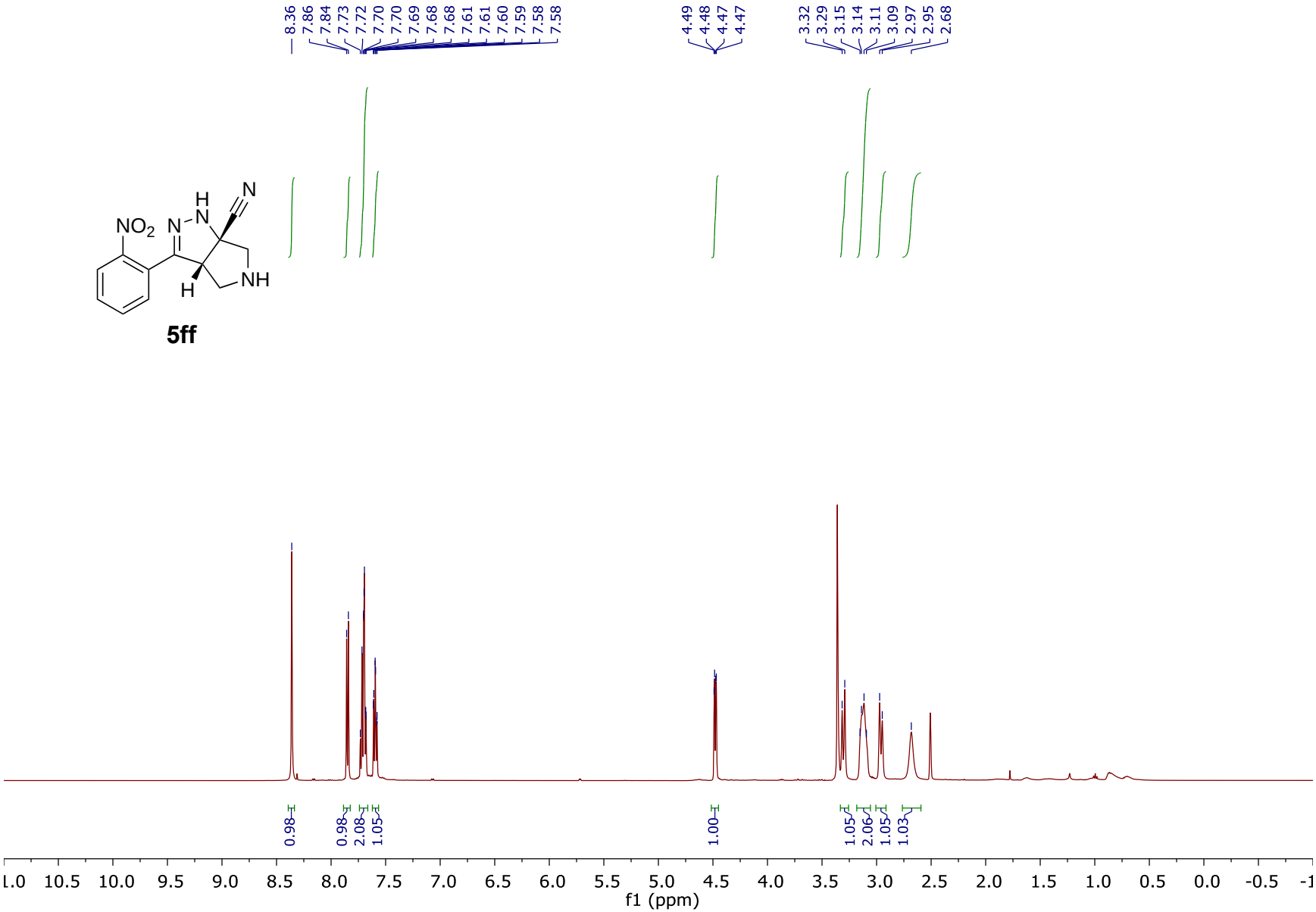
Compound **5dd**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



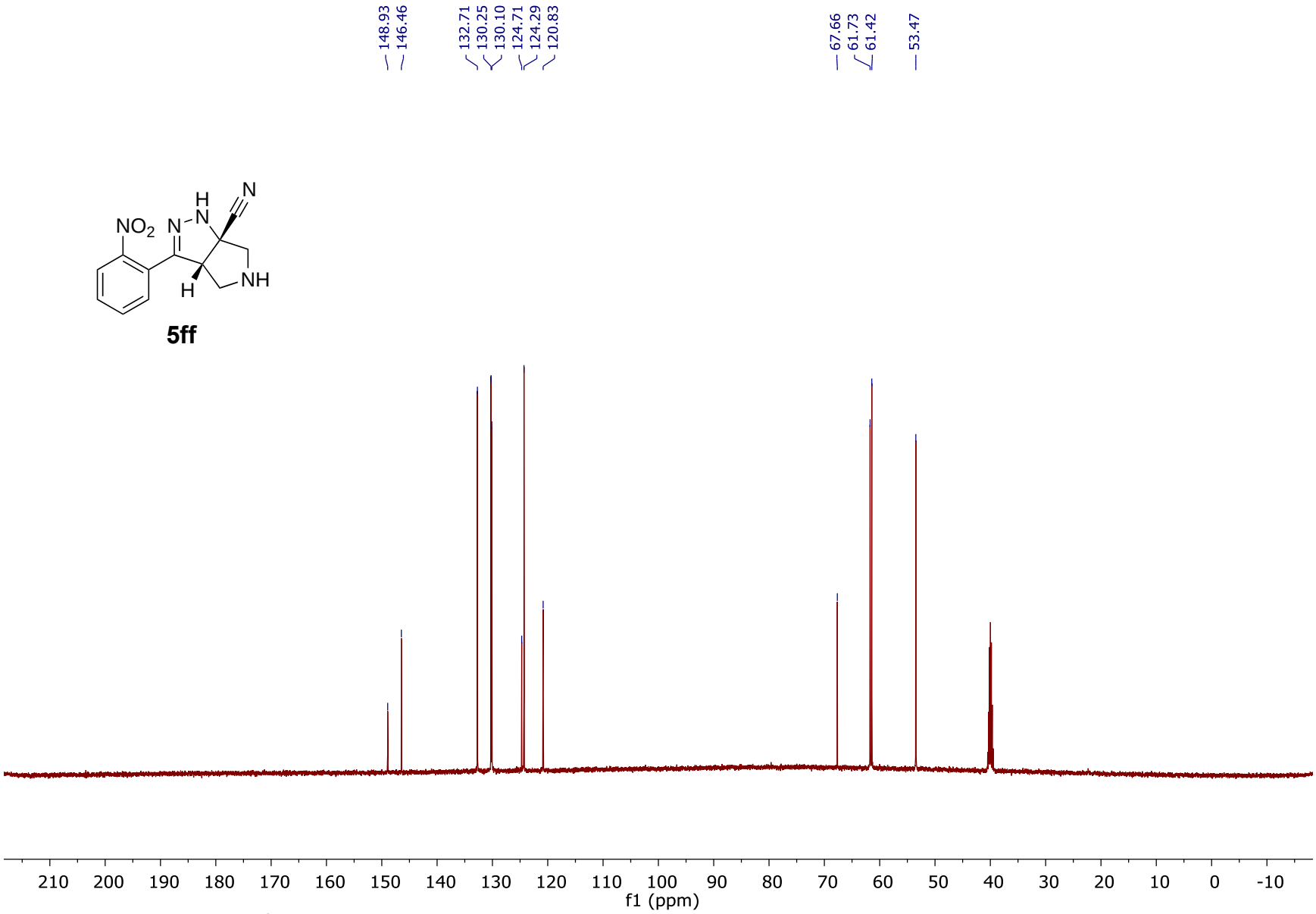
Compound **5ee**. 500 MHz ^{1}H NMR spectrum in DMSO-d_6



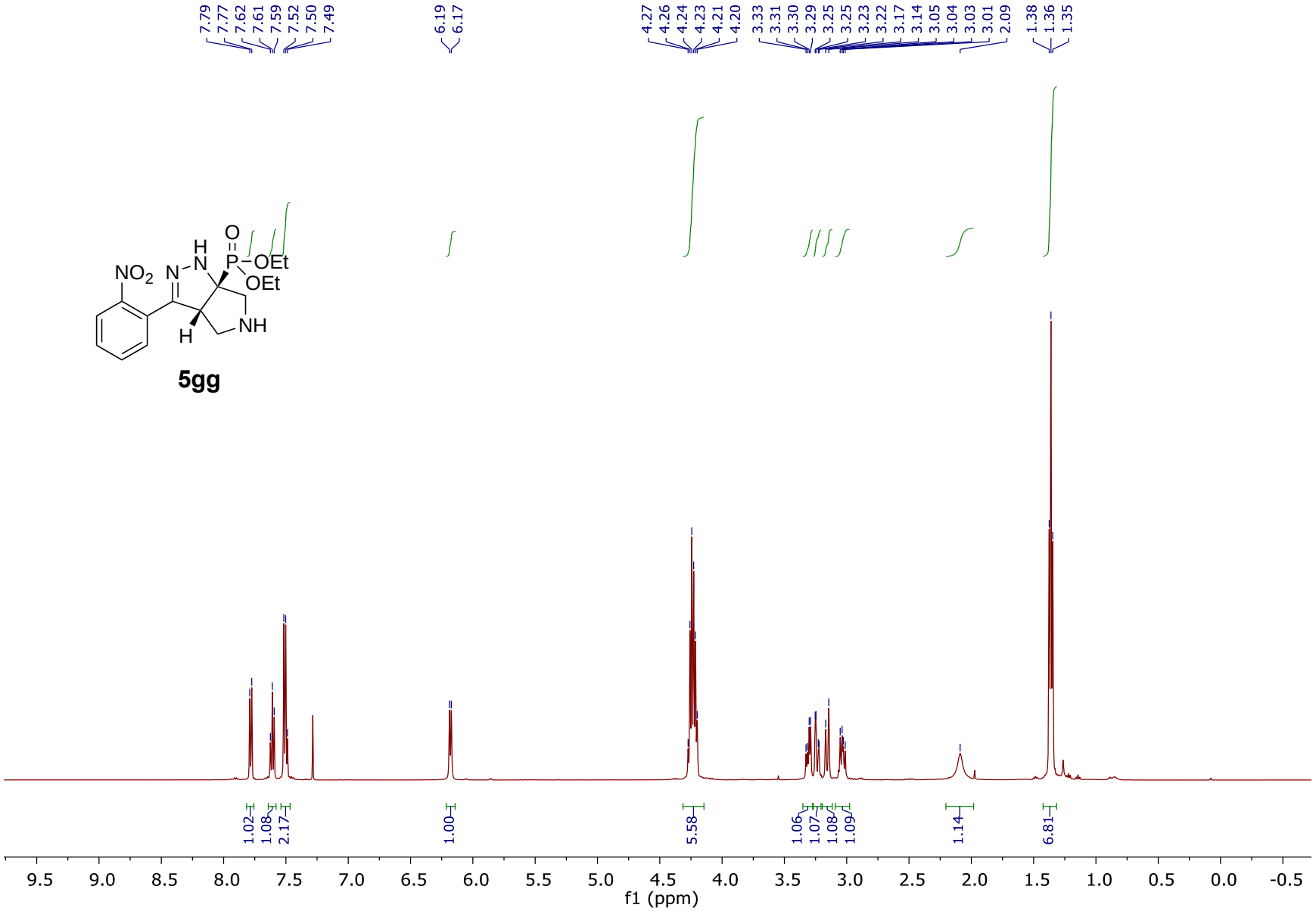
Compound **5ee**. 126 MHz ^{13}C NMR spectrum in DMSO-d_6



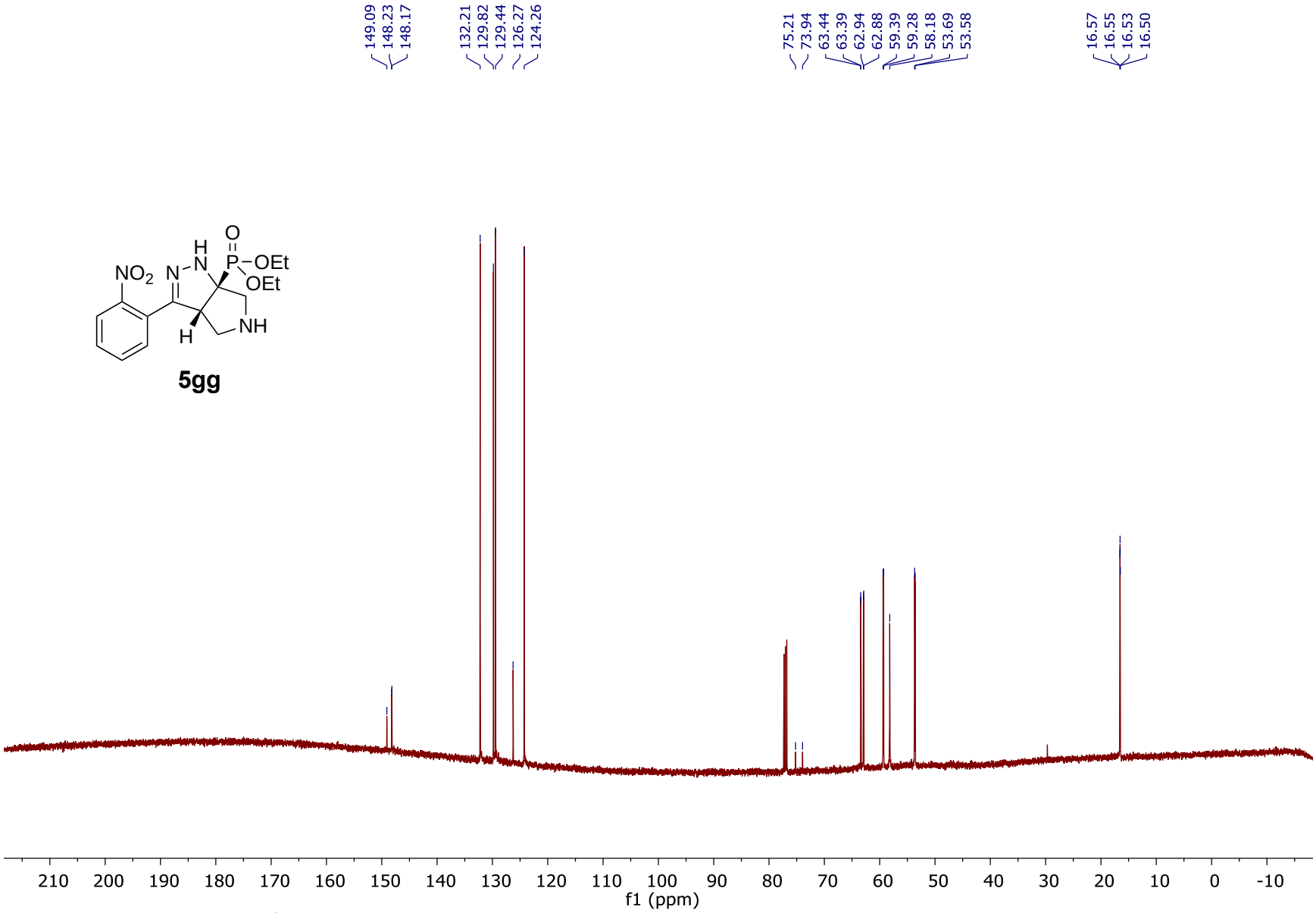
Compound **5ff**. 500 MHz ^{1}H NMR spectrum in DMSO-d_6



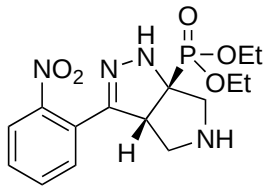
Compound **5ff**. 126 MHz ^{13}C NMR spectrum in DMSO-d_6



Compound **5gg**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$

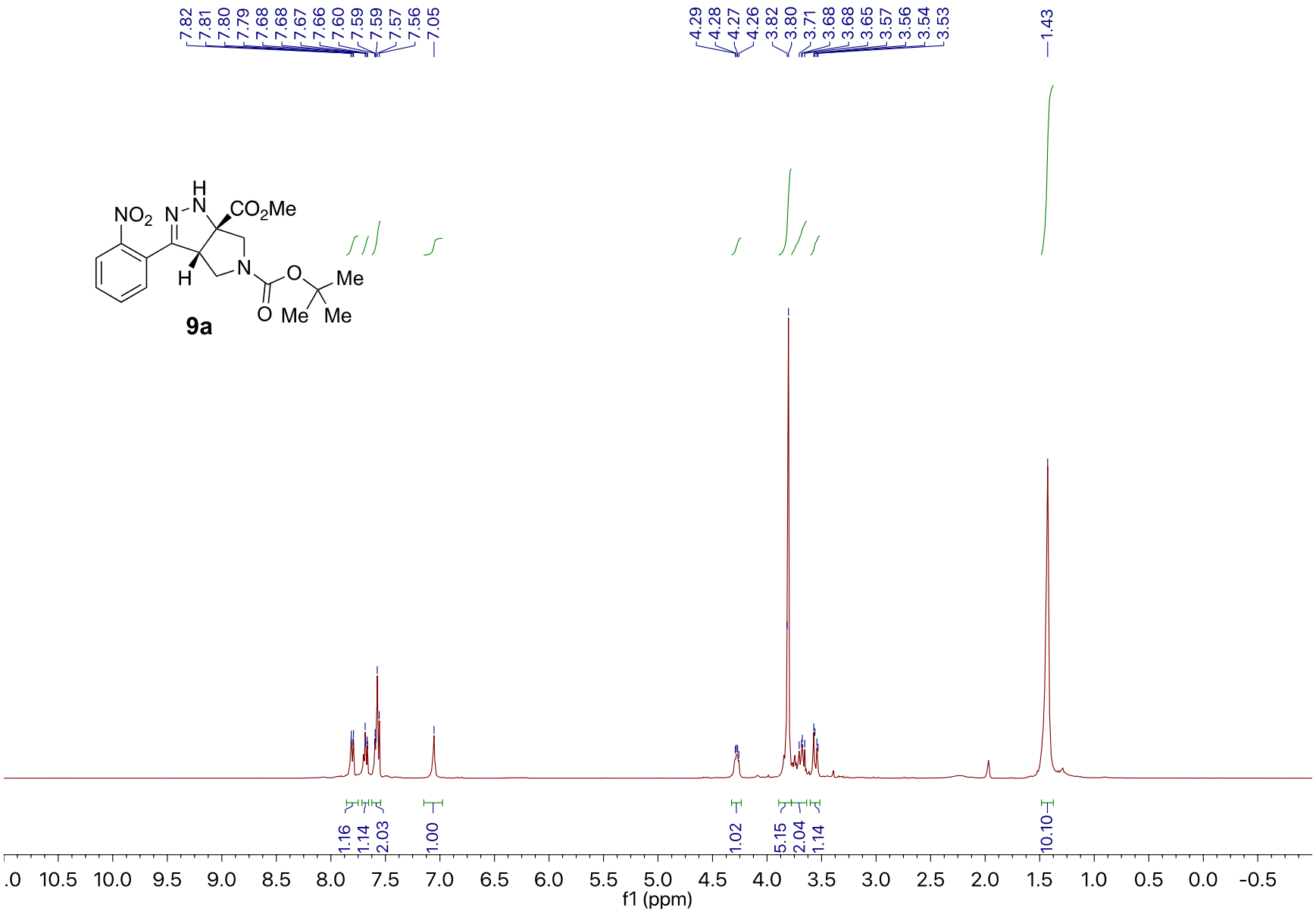


Compound **5gg**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$

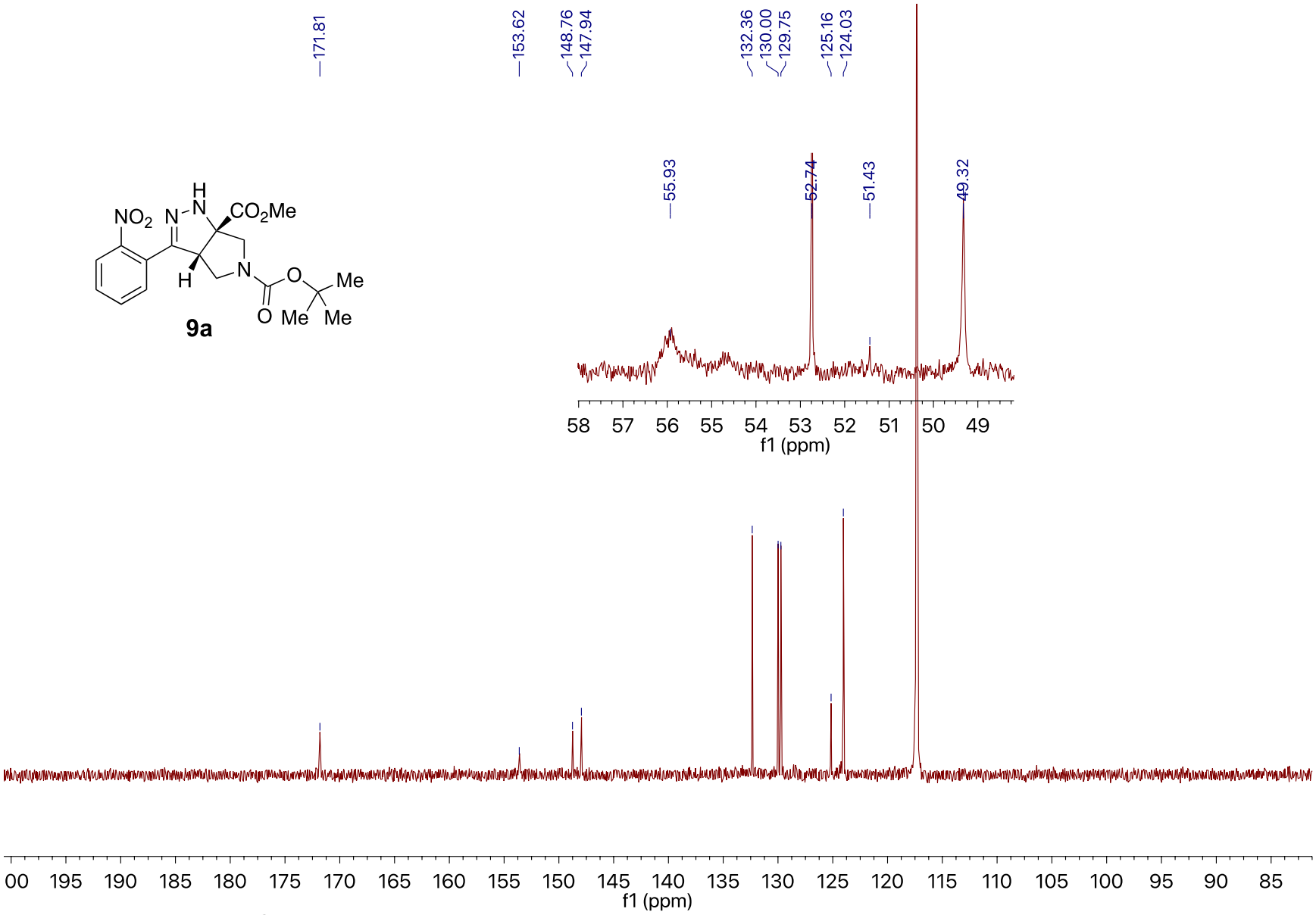


5gg

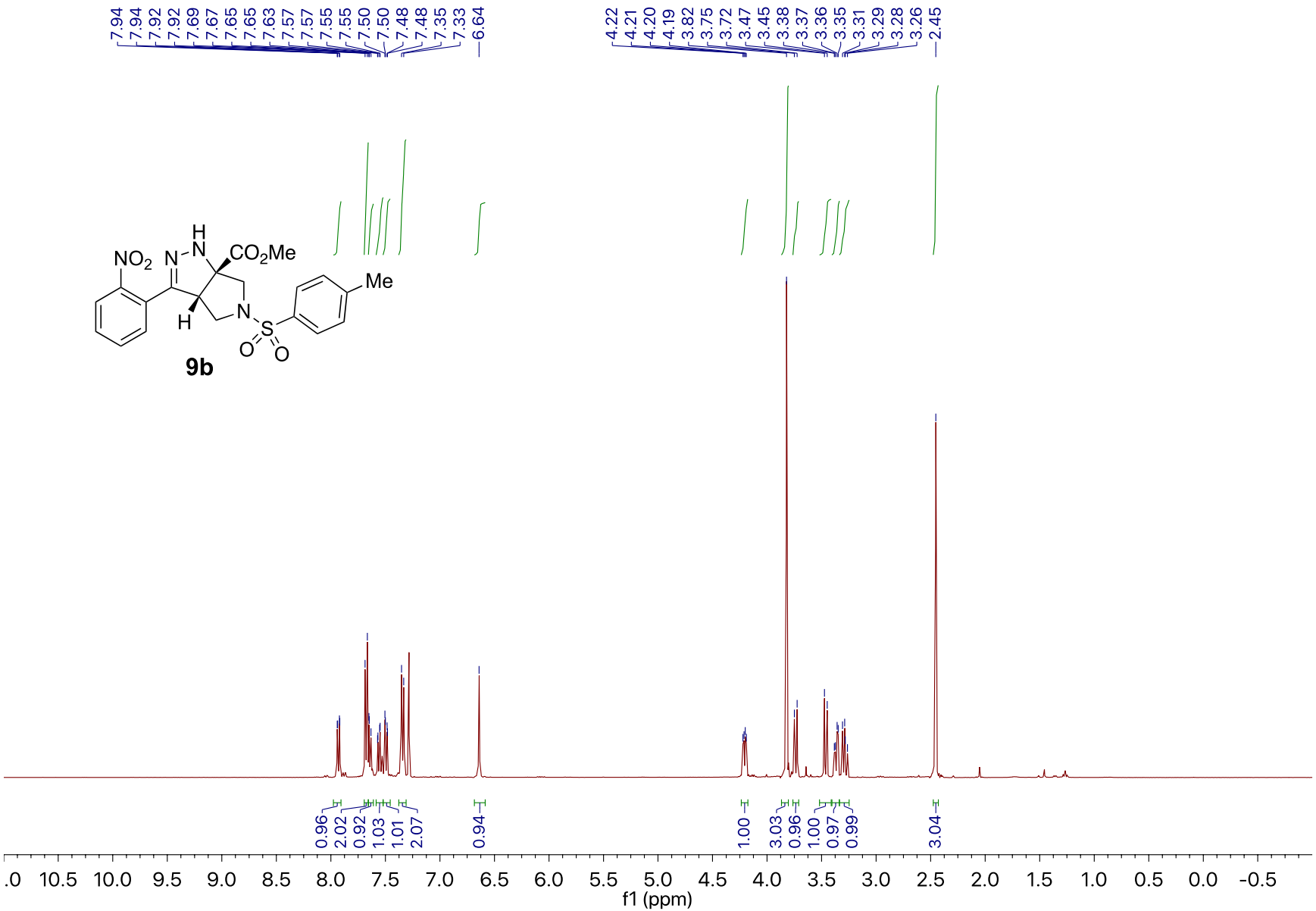
Compound **5gg**. 162 MHz ^{31}P NMR spectrum in $CDCl_3$



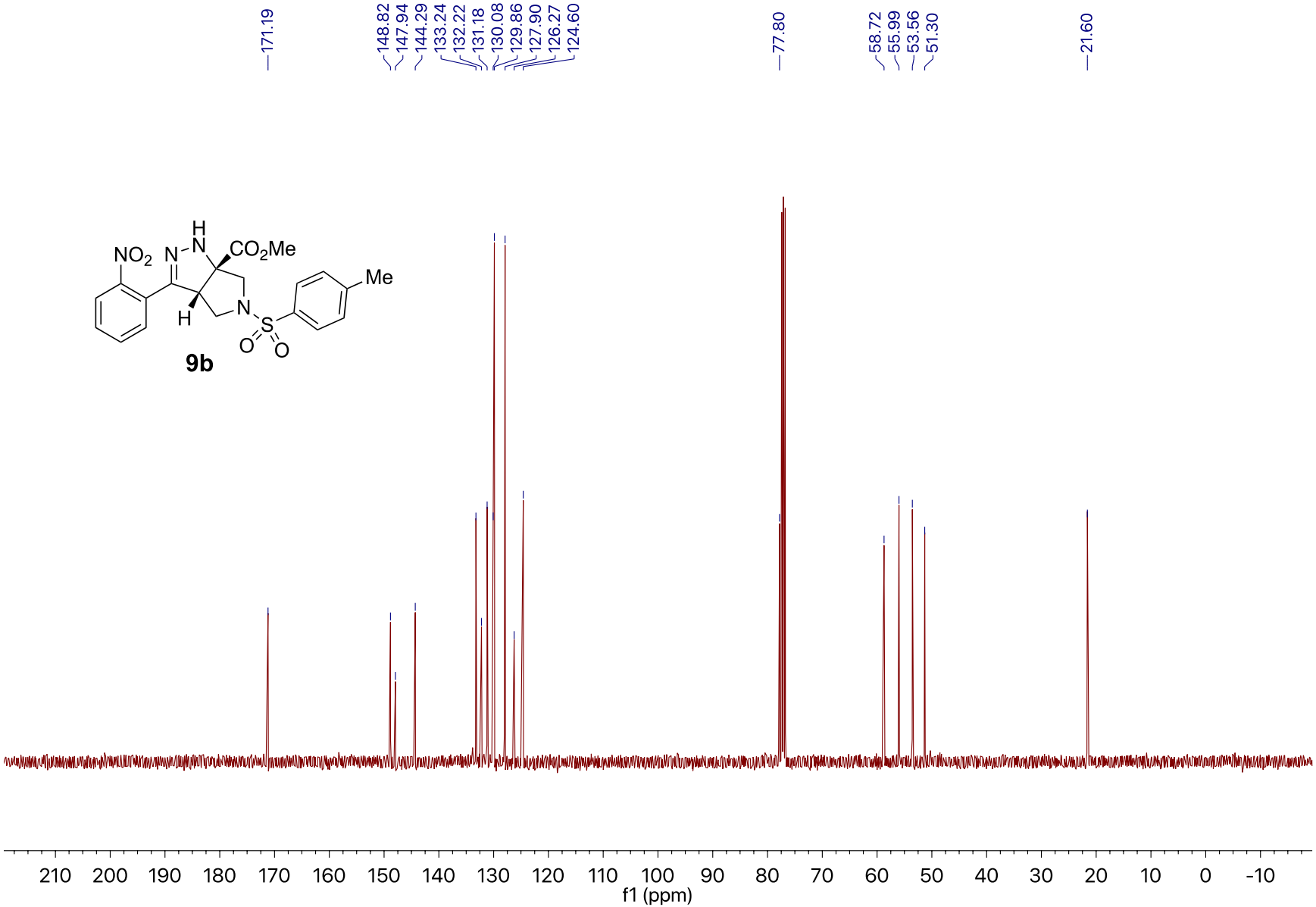
Compound **9a**. 400 MHz ^{1}H NMR spectrum in CD_3CN



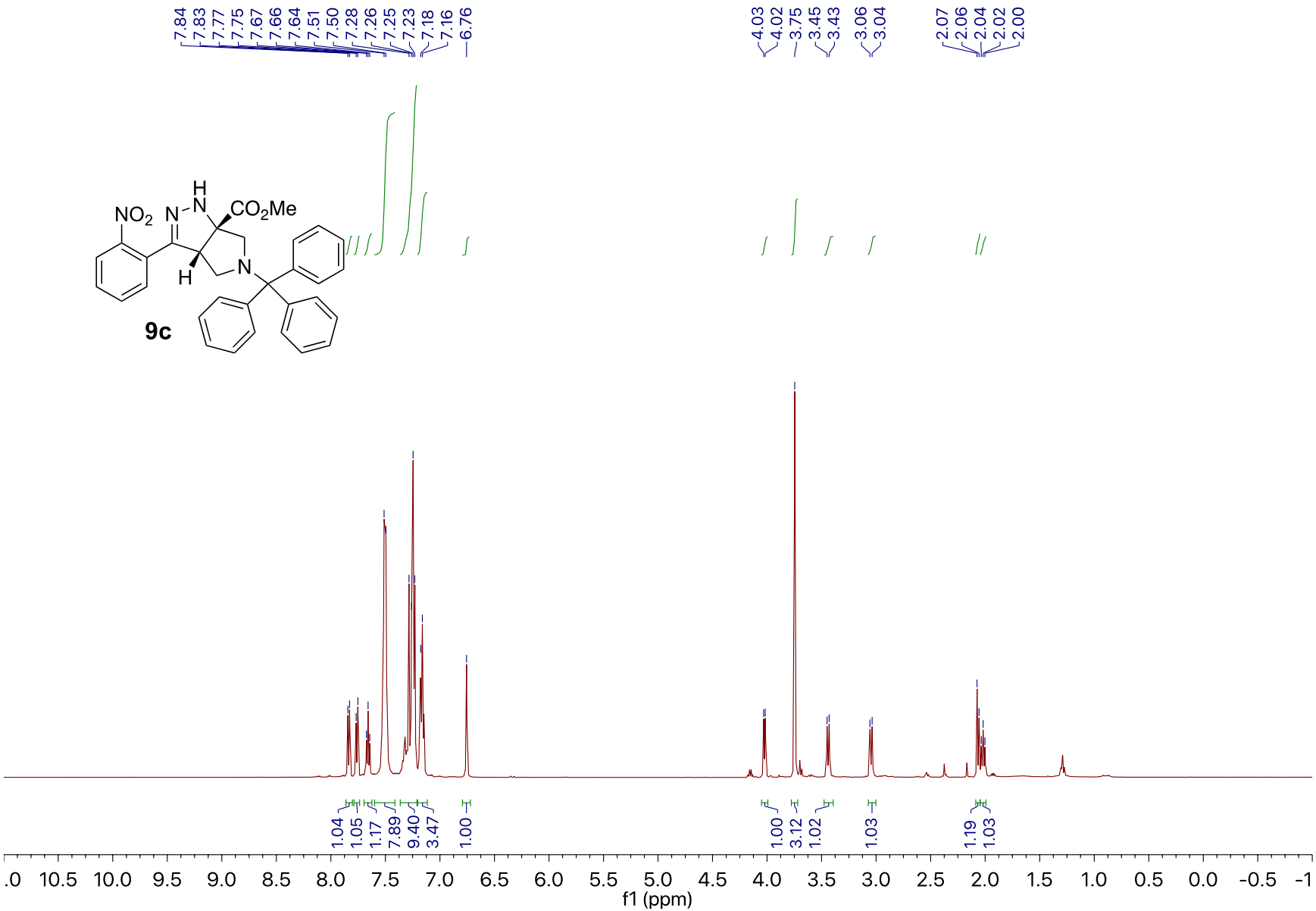
Compound **9a**. 100 MHz ^{13}C NMR spectrum in CD_3CN



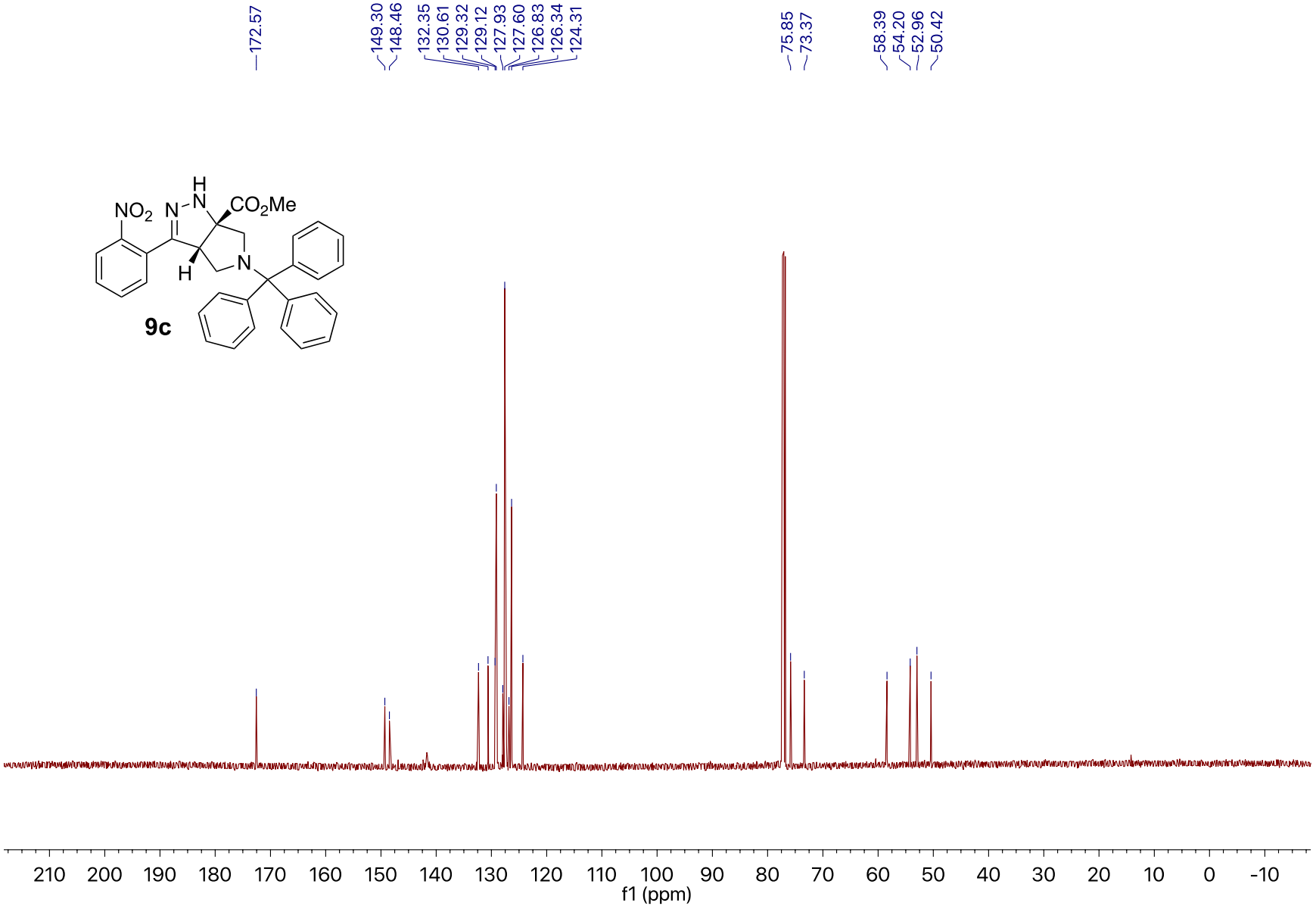
Compound **9b**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



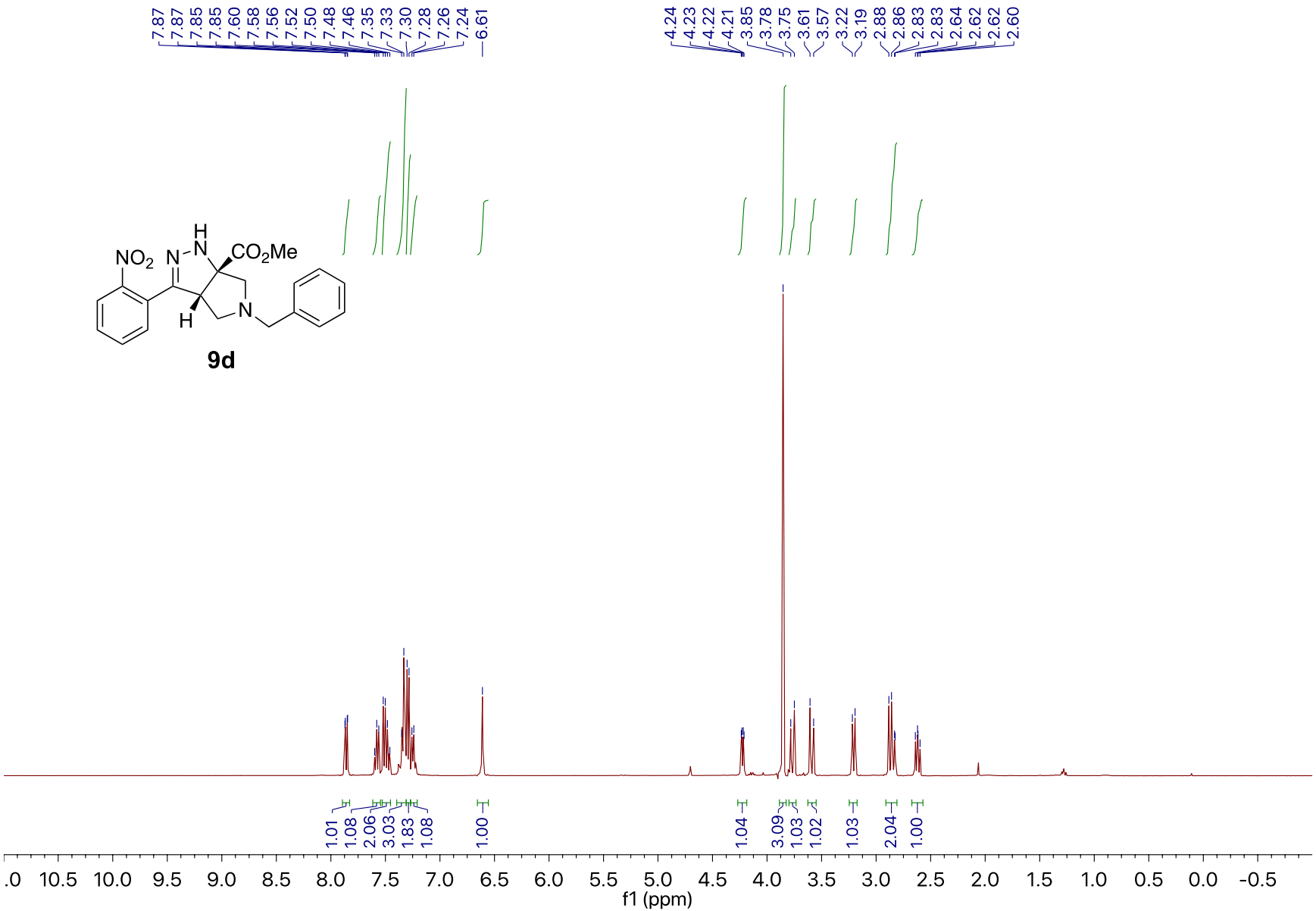
Compound **9b**. 100 MHz ^{13}C NMR spectrum in $CDCl_3$



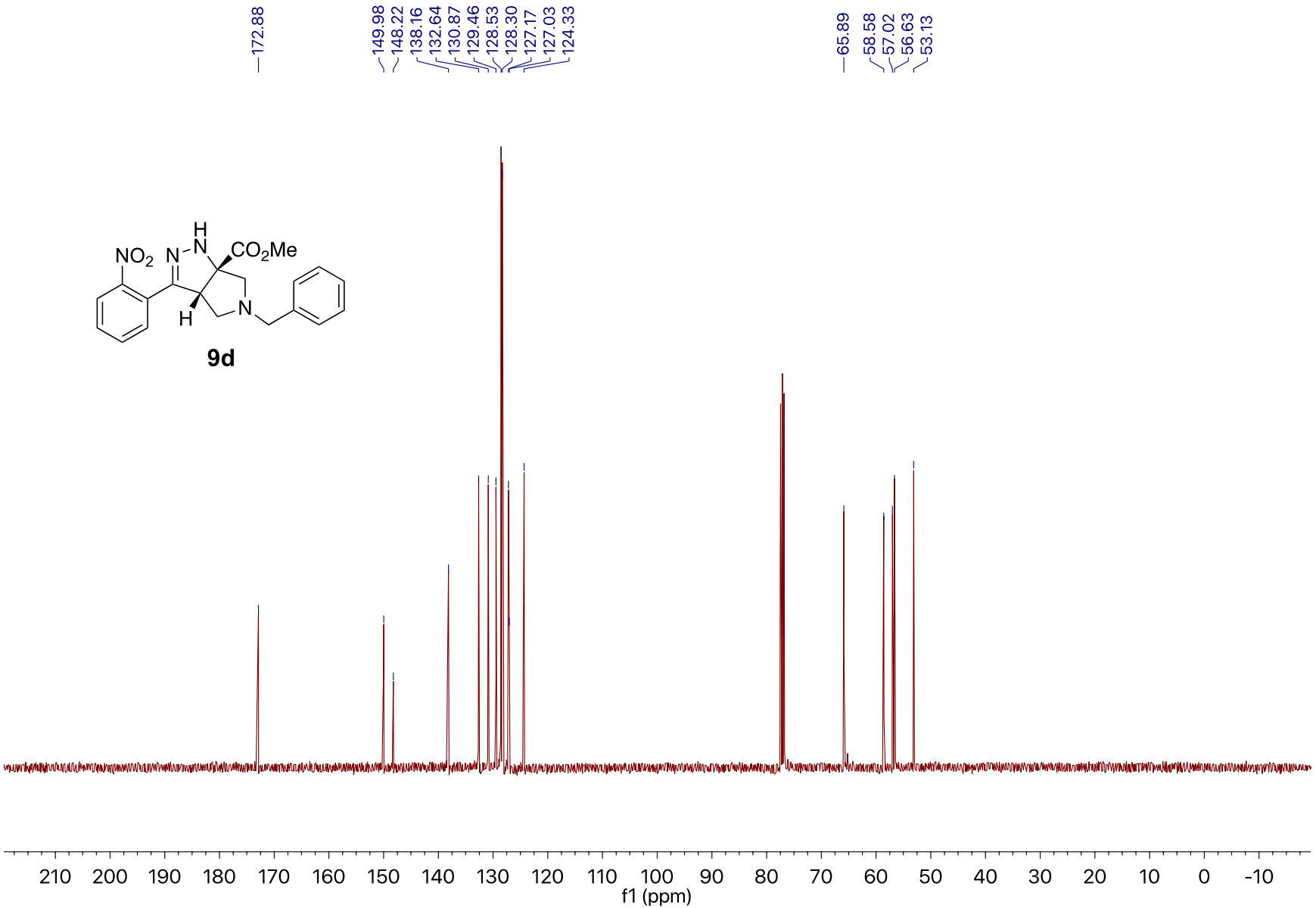
Compound **9c**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



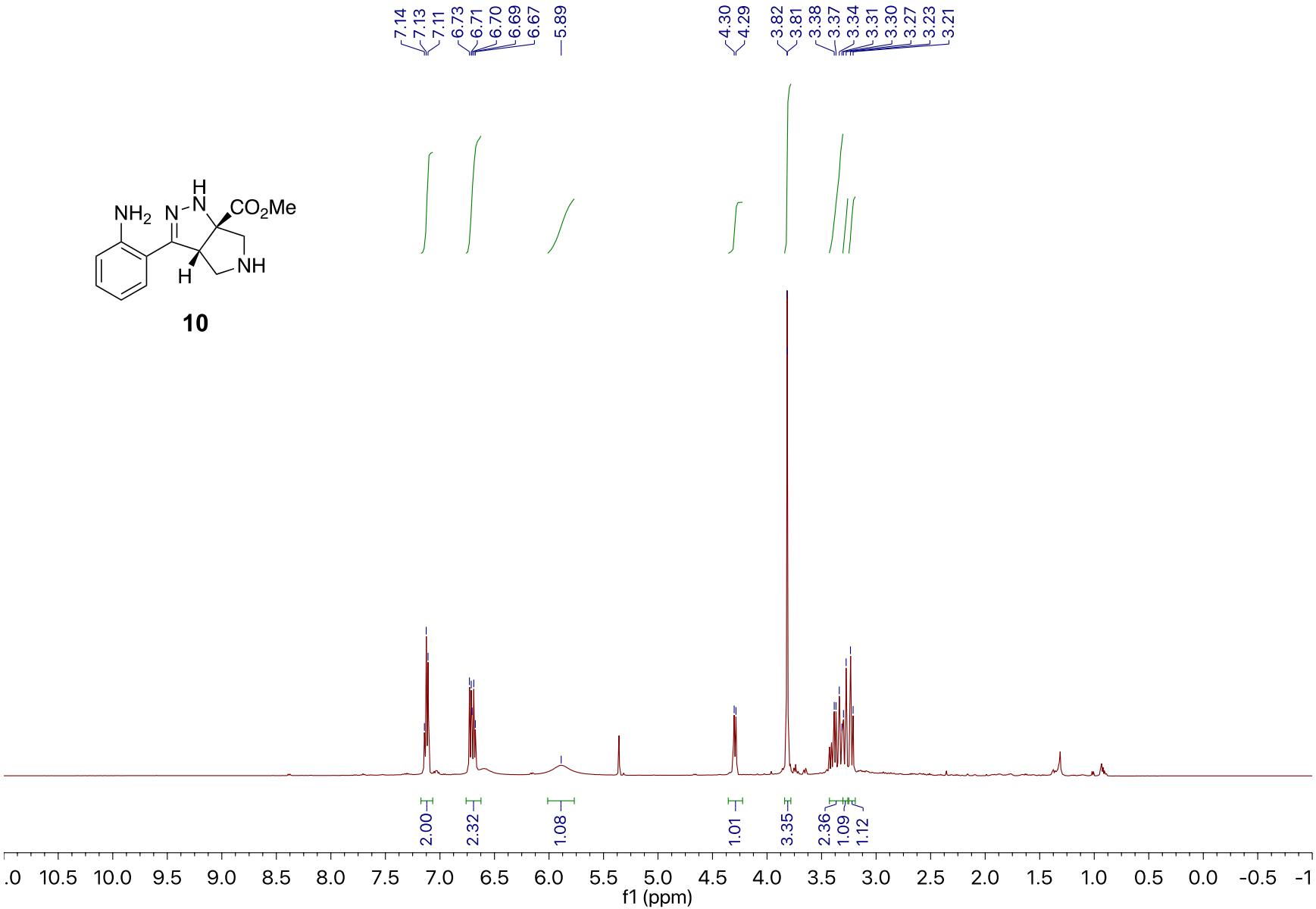
Compound **9c**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$



Compound **9d**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$

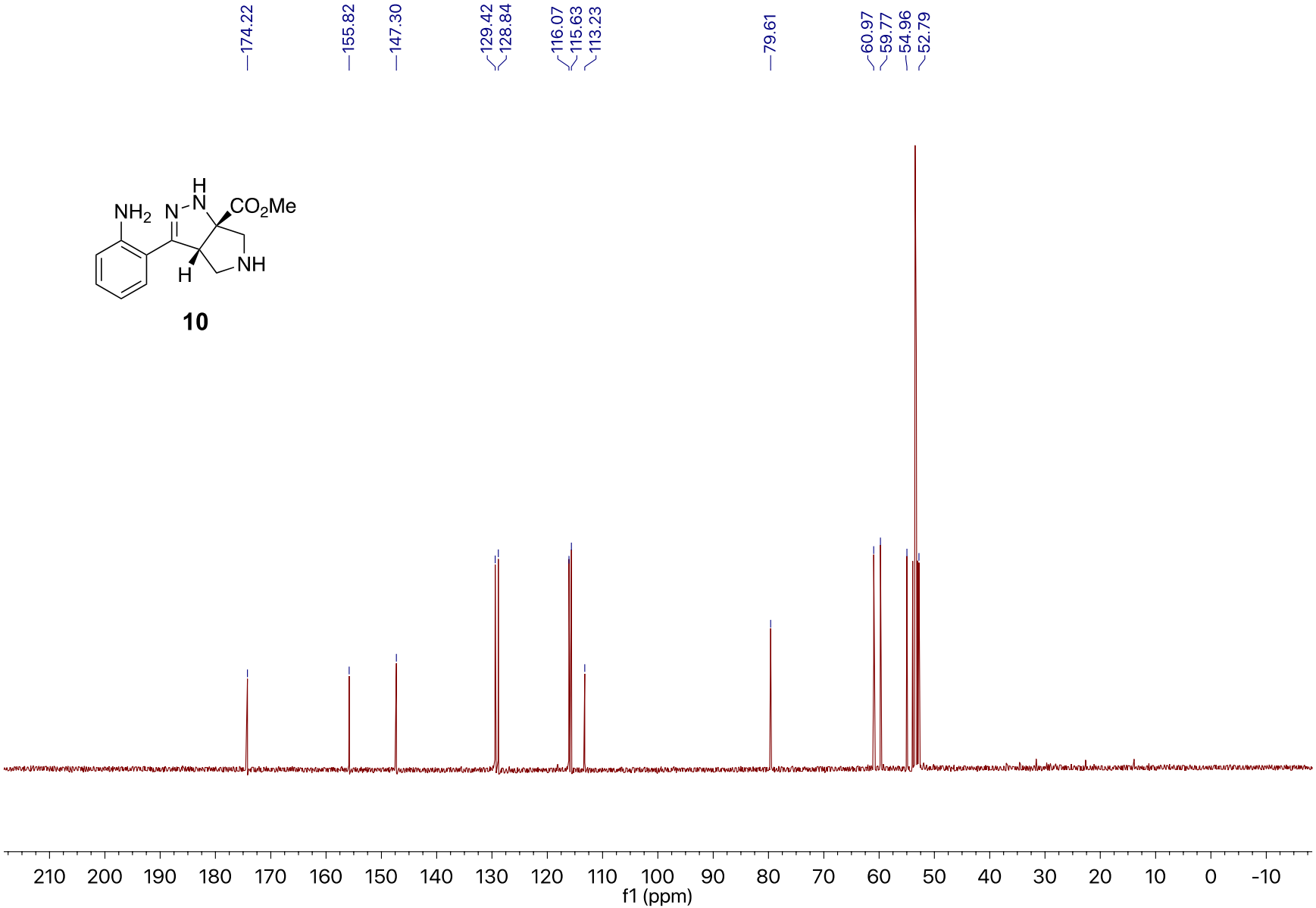


Compound **9d**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$

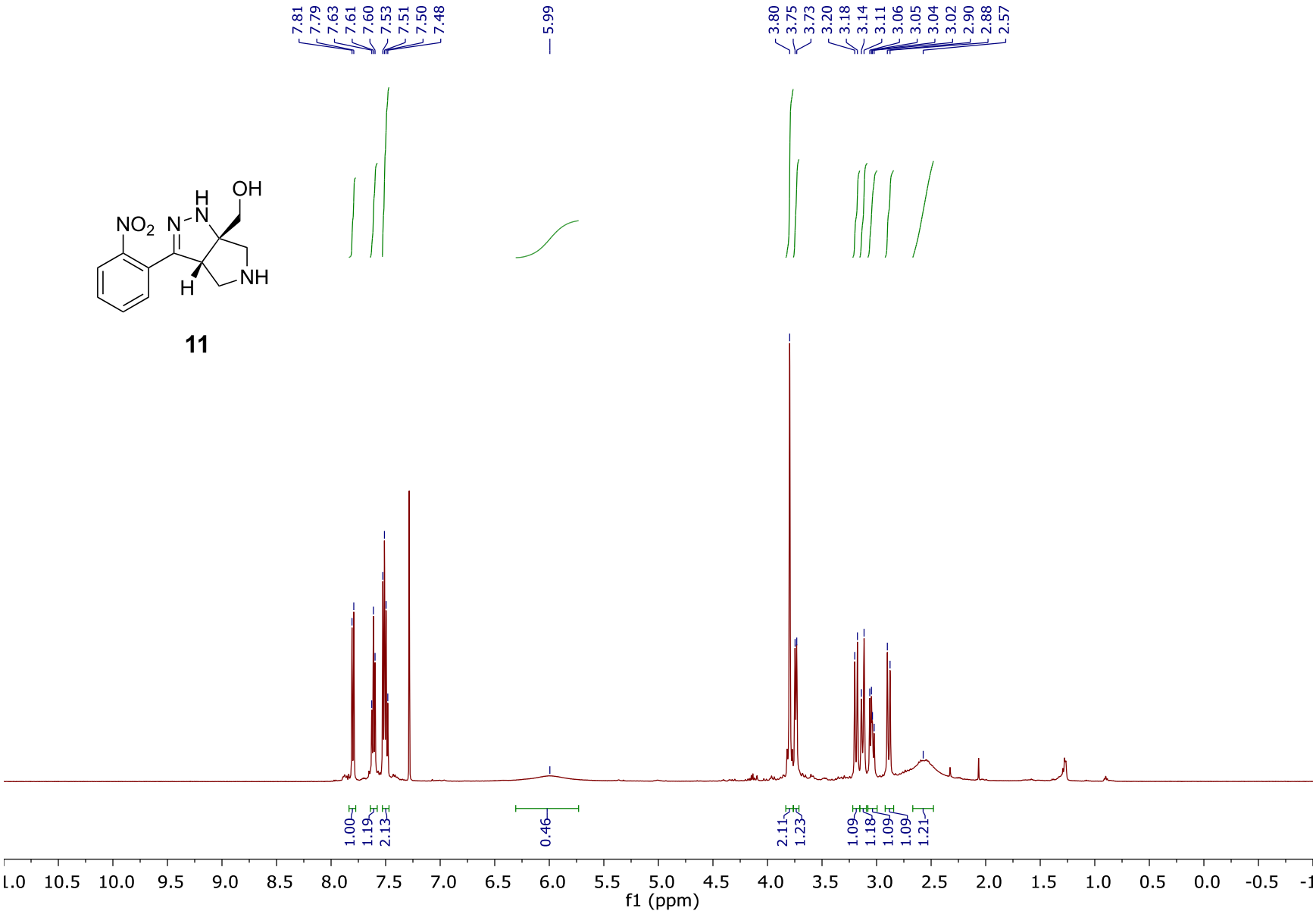


10

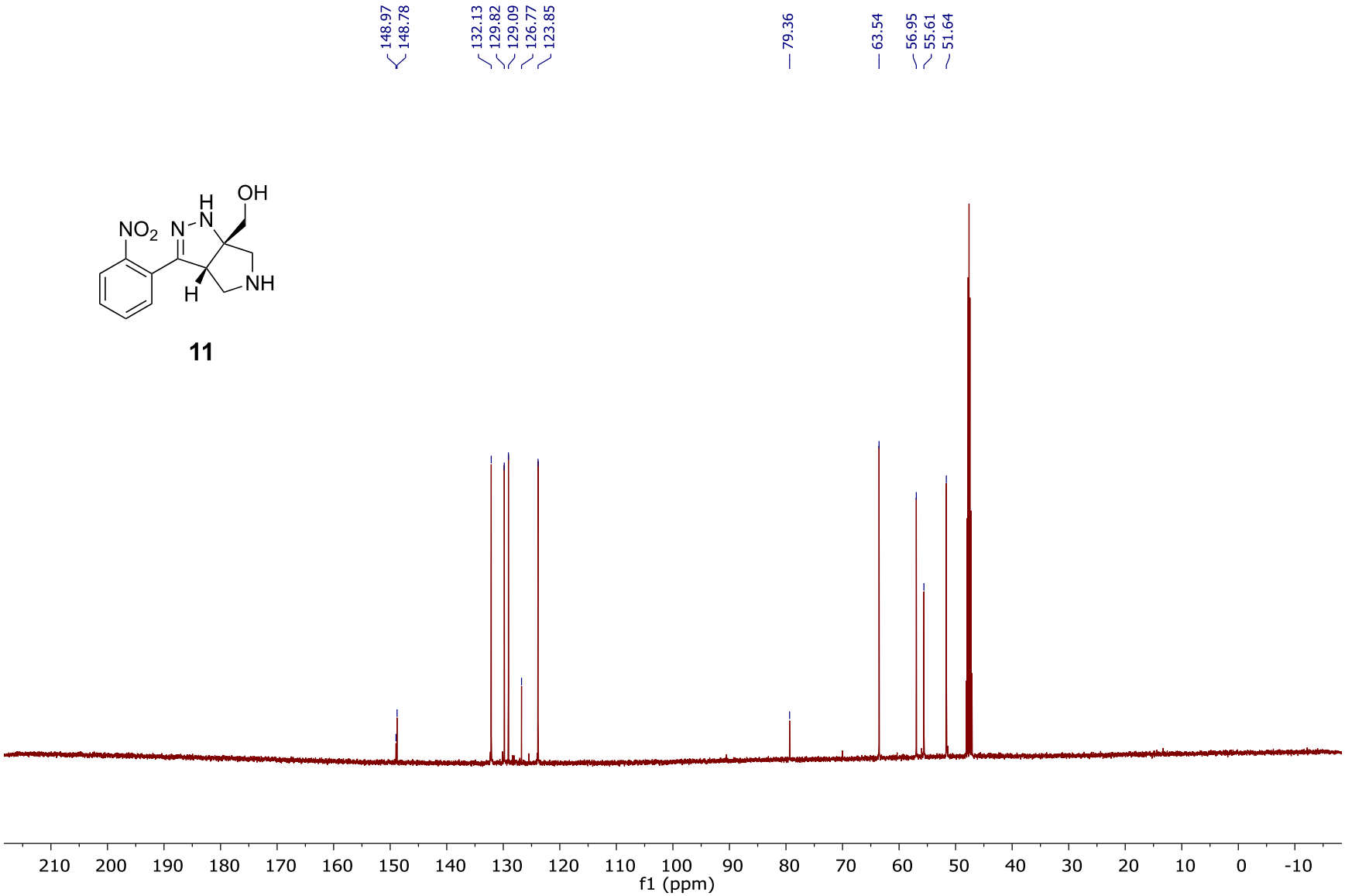
Compound **10**. 500 MHz ^{1}H NMR spectrum in CD_2Cl_2



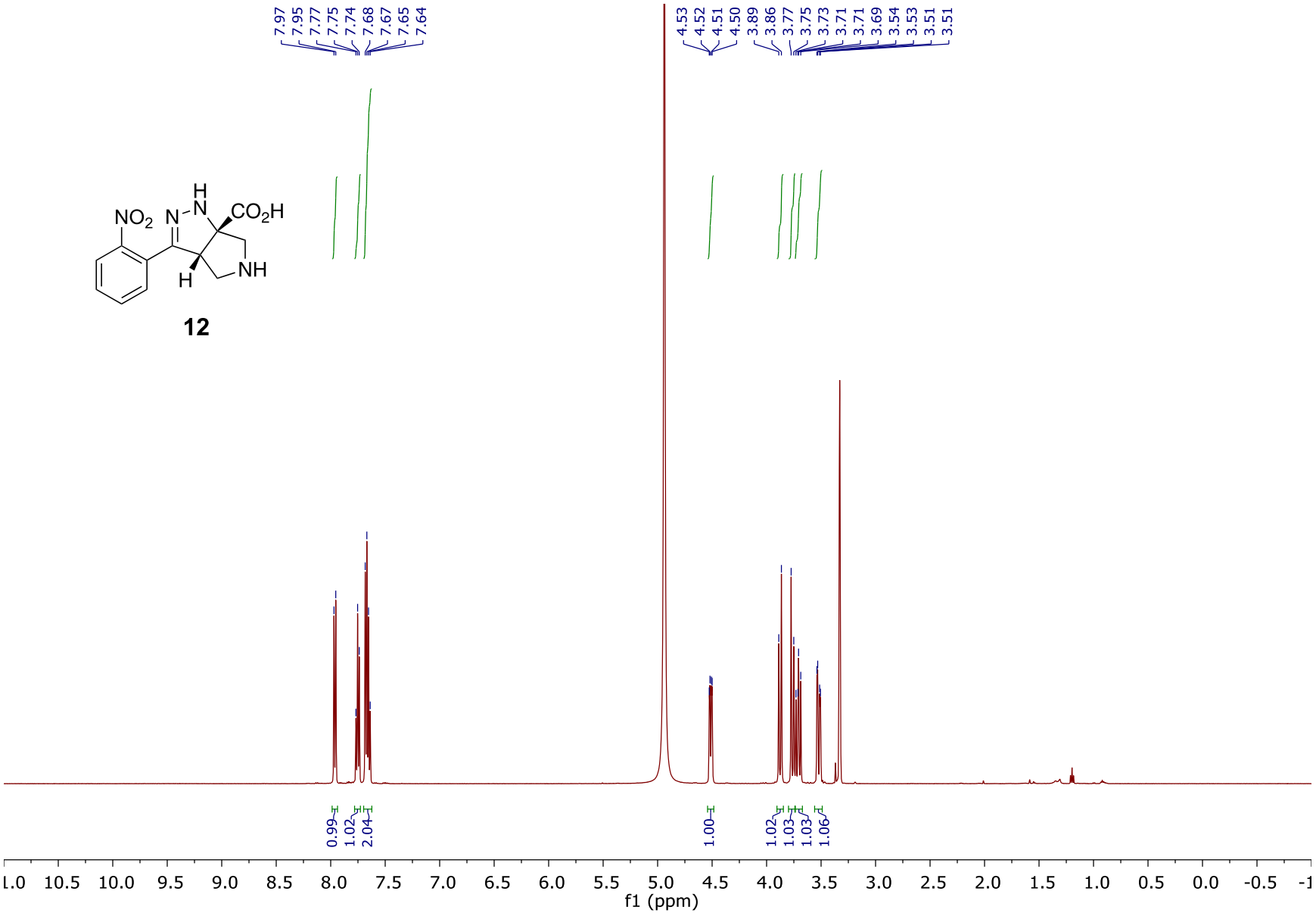
Compound **10**. 126 MHz ^{13}C NMR spectrum in CD_2Cl_2



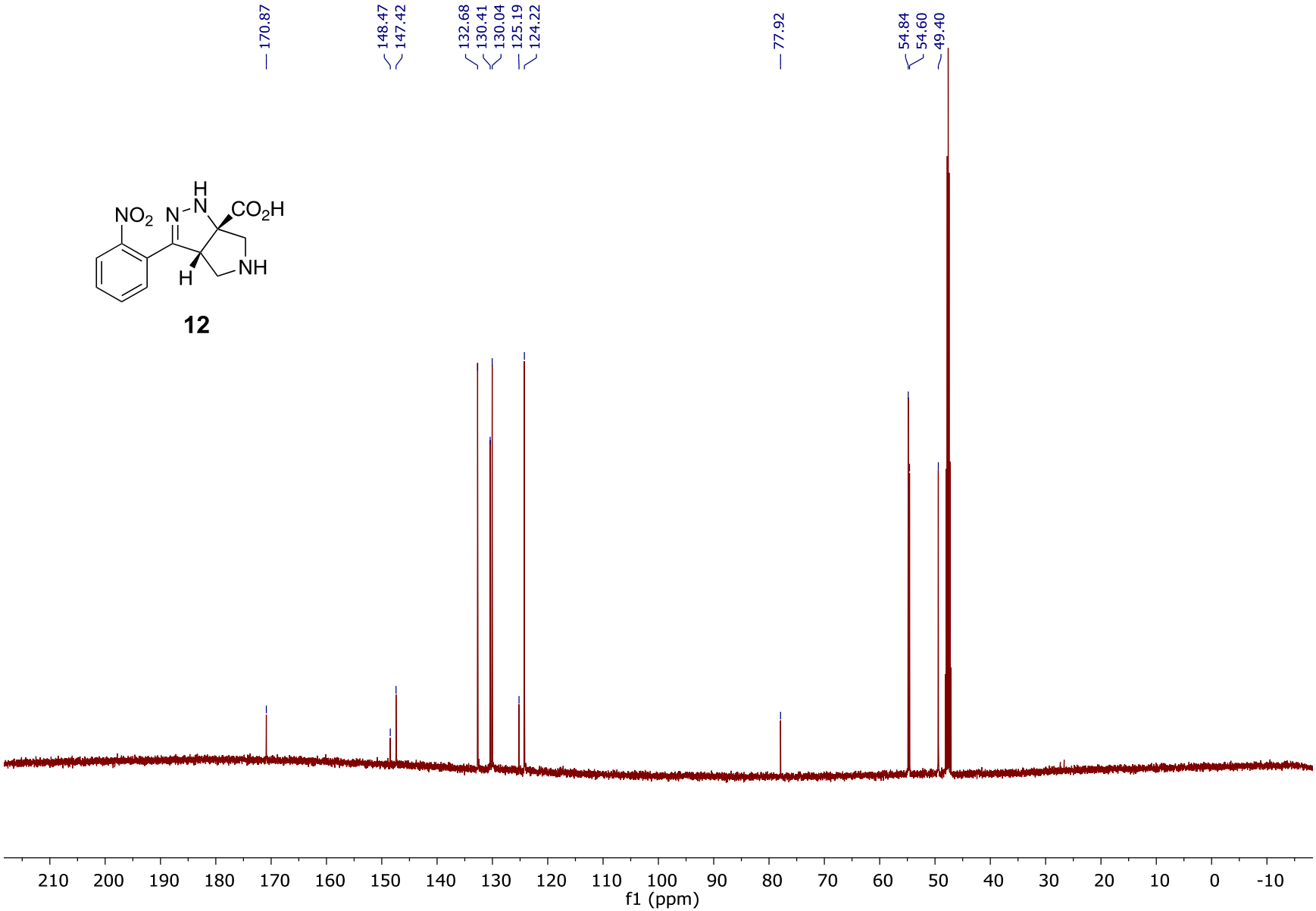
Compound **11**: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



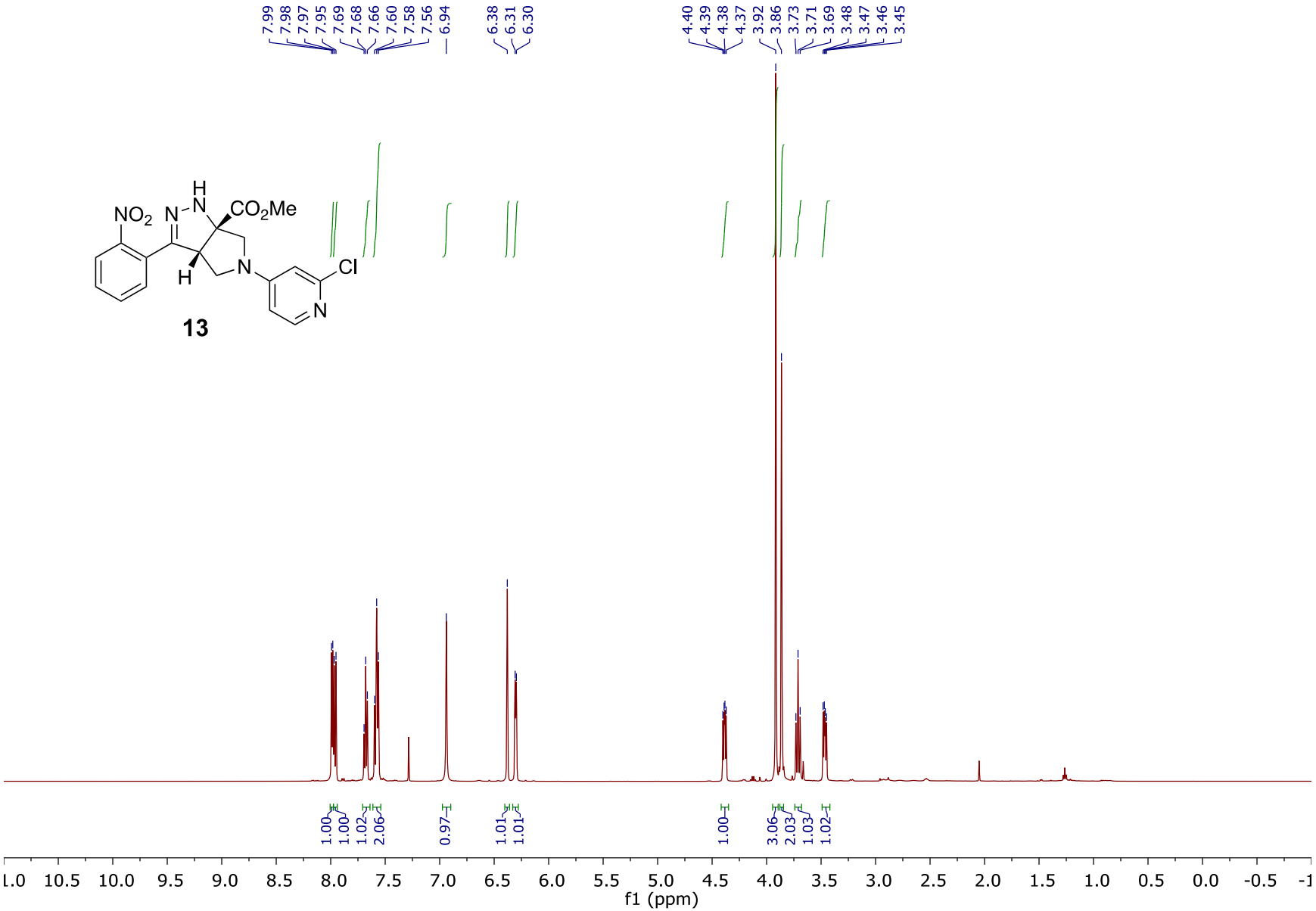
Compound **11**: 126 MHz ^{13}C NMR spectrum in MeOD



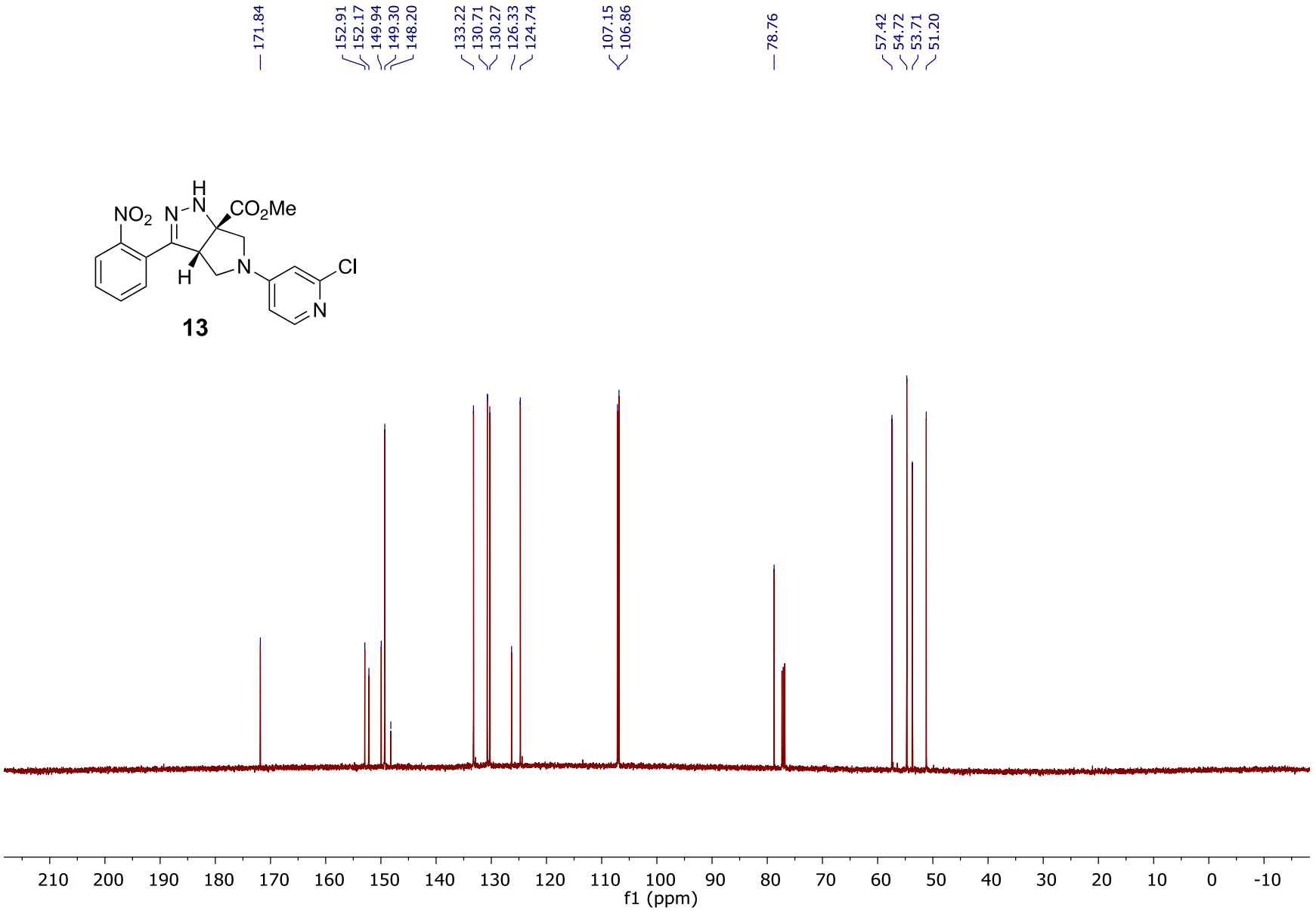
Compound **12**. 500 MHz ^{1}H NMR spectrum in MeOD:TFA (50:1)



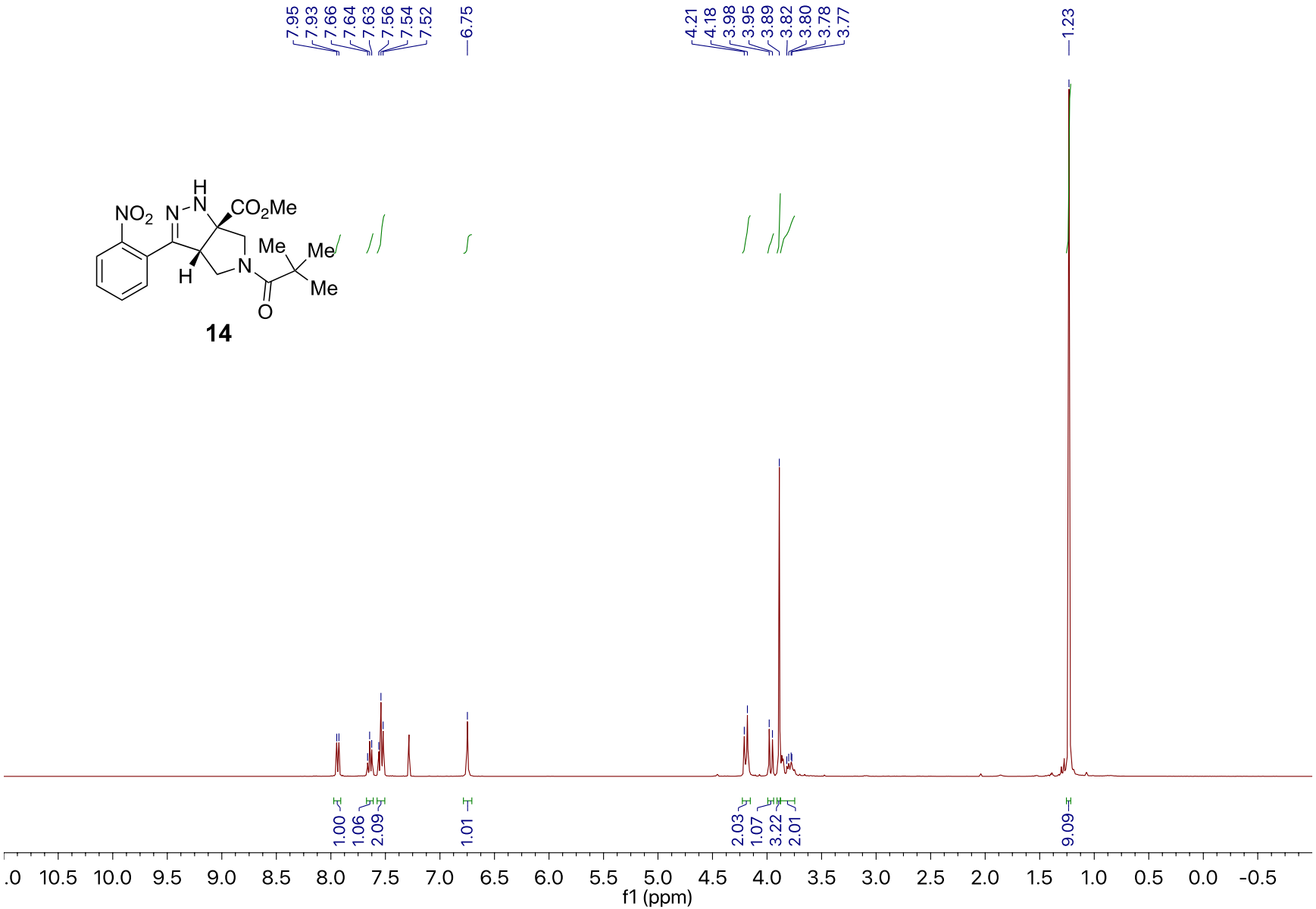
Compound **12**. 126 MHz ^{13}C NMR spectrum in MeOD:TFA (50:1)



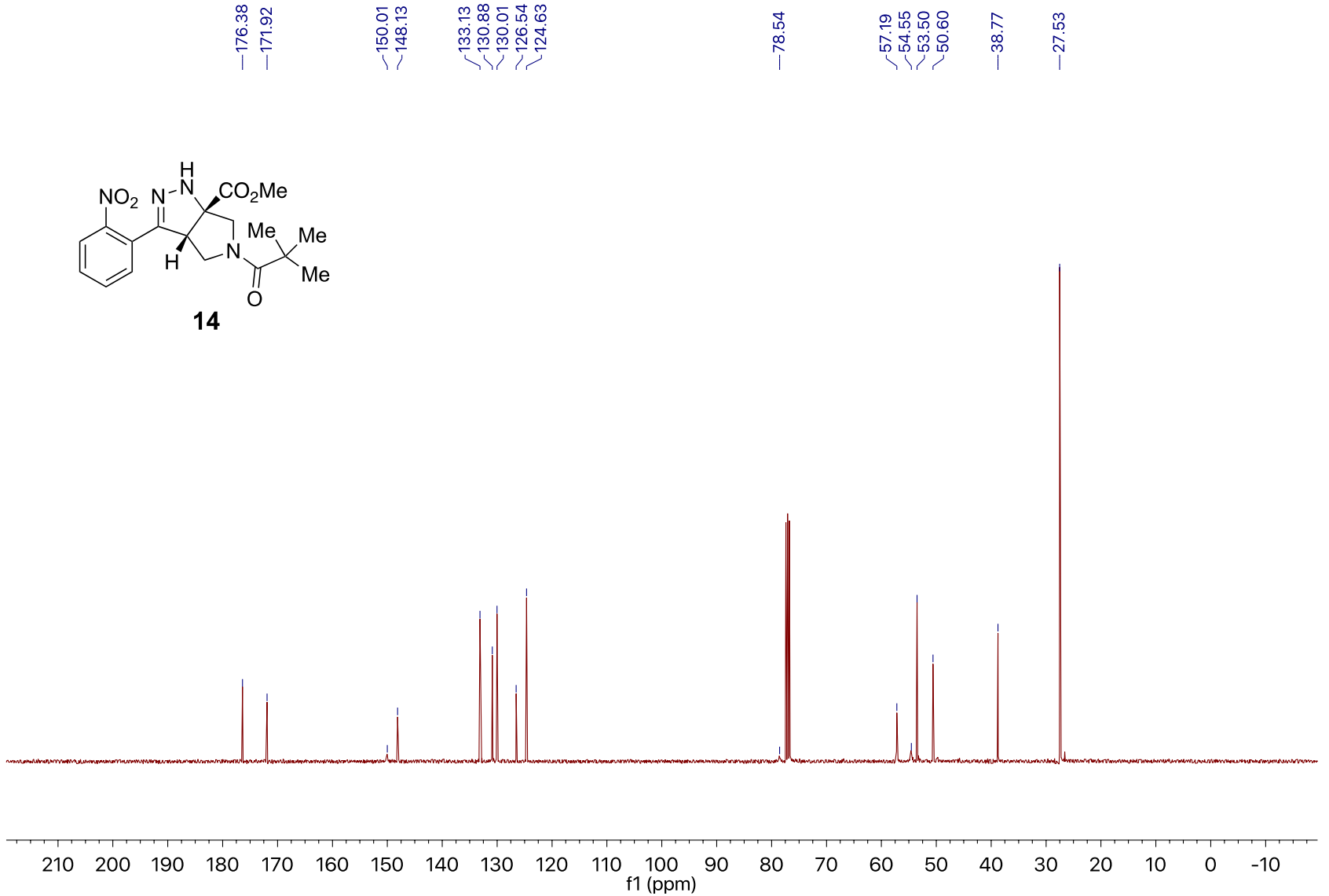
Compound **13**: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



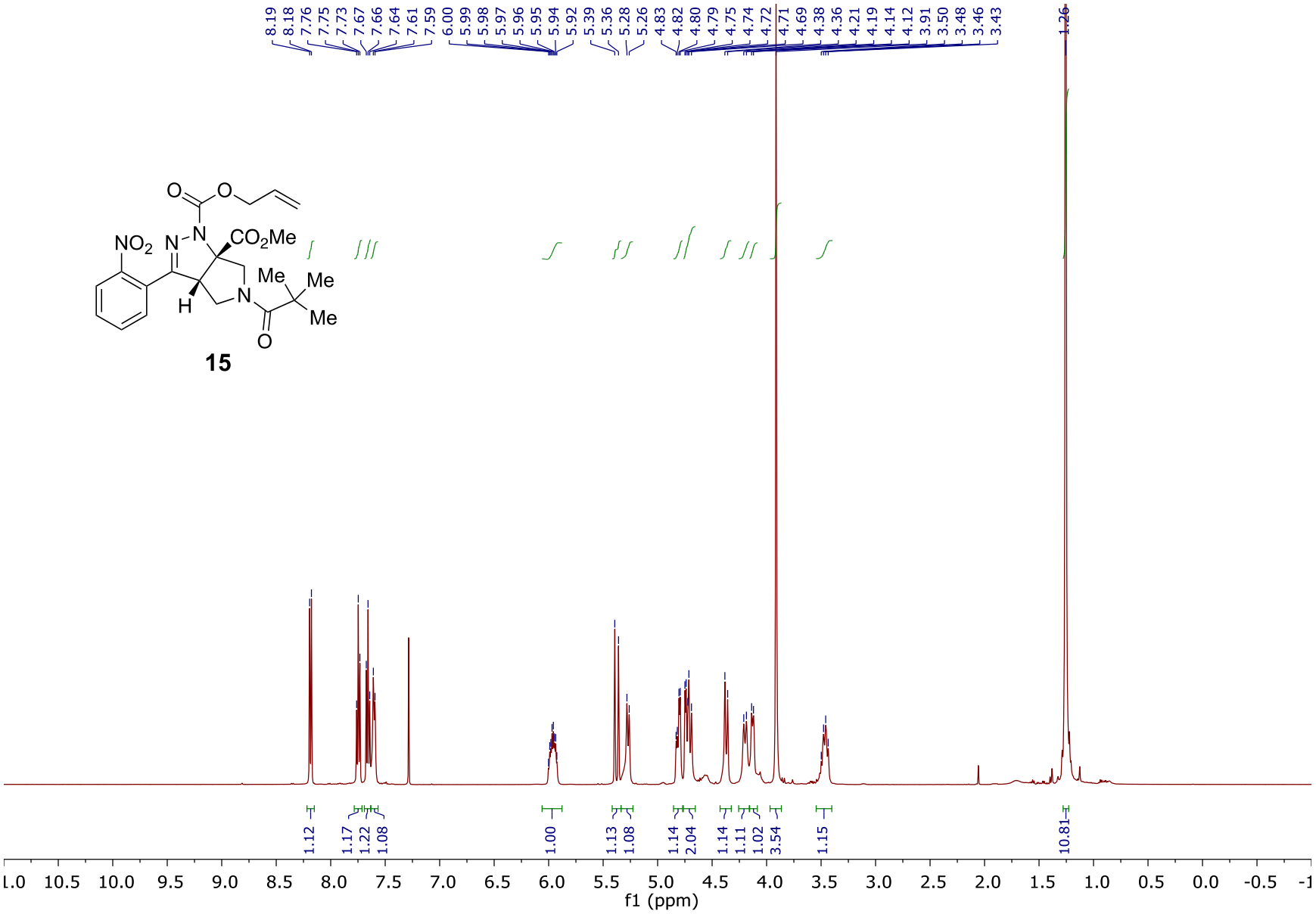
Compound **13**: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



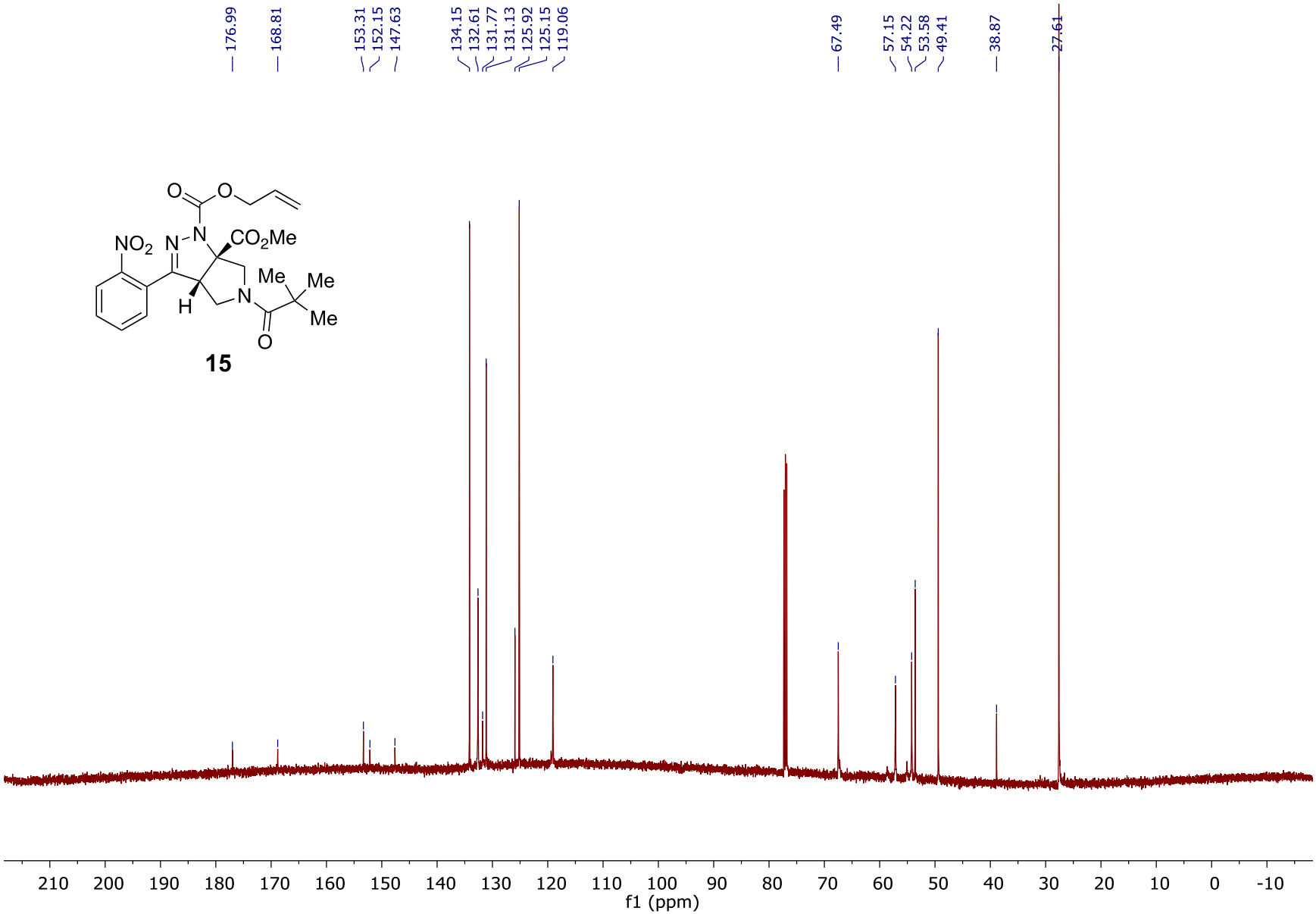
Compound **14**. 400 MHz ^{1}H NMR spectrum in $CDCl_3$



Compound **14**. 101 MHz ^{13}C NMR spectrum in $CDCl_3$



Compound **15**. 500 MHz ^{1}H NMR spectrum in $CDCl_3$



Compound **15**. 126 MHz ^{13}C NMR spectrum in $CDCl_3$