Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Tunable mono- and di-methylation of amines with methanol over bimetallic CuCo nanoparticle catalysts

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Preparation of γ-Al_2O_3. γ-Al_2O_3 was synthesized from industrial grade boehmite following the literature reports.[1] γ-Al_2O_3 was obtained by calcination of industrial grade boehmite at 700 °C. Typically, 5g boehmite was placed in the muffle furnace and heated from room temperature to 700 °C in 2 h, and remained at this temperature for 3 h. The final sample was cooled to room temperature and used directly.

Experiments for the calculation of initial formation rate of aldehyde. Typically, 10Cu-5Co/Al_2O_3 or 10Cu-5Co/MgAl-LDO (150 mg), and methanol (12 mL) were charged into a stainless steel high pressure reactor. The reactor was sealed and purged with N_2. Then, the reactor was heated to 170 °C and kept for 30 min. After the reactor cooling down to room temperature, octylamine (5 mmol) was added to the reactor and stirred for a period of time at room temperature until the concentration of octylamine remained unchanged monitored by GC. Finally, the reaction mixture was sampled and subjected to product analysis. Subsequently, the reaction conditions were changed to 170 °C, 10 bar H_2 or 190 °C, 10 bar H_2 for further experiments over 10Cu-5Co/MgAl-LDO.

$$k_{\mathrm{HCHO}} = \frac{C(initial) - C(final)}{T}$$

k_{HCHO} = initial formation rate of aldehyde rate (mmol L^{-1} h^{-1}); T= reaction time (h); *c*(initial) = the concentration of octylamine before the reaction; *c*(final) = the concentration of octylamine after the reaction.

Acid-base toxicity test. Typically, aniline (1.0 mmol), 10Cu-5Co/Al_2O_3 (150 mg), methanol (12 mL) and pyridine (2 mmol) or acetic acid (3 mmol) were charged into the reactor with a magnetic stirrer.[2] The reactor was then sealed and purged with N_2 three times to remove air. The reaction was stirred at room temperature for 30 min. Then, the reactor was heated to 170 °C and kept for 4

h. After cooling to room temperature, the reaction mixture was sampled and subjected to product analysis. Subsequently, the reaction conditions were changed to 190 ^{o}C, 10 bar H_2 for further experiments over 10Cu-5Co/MgAl-LDO.

Kinetic isotopic test. The tests were performed in a stainless steel high pressure reactor. Typically, aniline (1.0 mmol), 10Cu-5Co/Al_2O_3 (150 mg), and CH_3OH or CD_3OD (12 mL) were charged into the reactor with a magnetic stirrer. The reactor was then sealed and purged with N_2 three times to remove air. The reactor was heated to 170 °C and kept at this temperature for a period of time (30 min, 40 min or 50 min) at a stirring speed of 750 rpm. At the end of the reaction, the reactor was cooled to room temperature, and the reaction mixture was sampled and subjected to product analysis. The KIE (k_{CH}/k_{CD}) value estimated from the zero-order rate constants (the slope of the lines).[3-4]

Adsorption test. Typically, standard substrate solutions (aniline, *N*-methylaniline or *N, N*-dimethylaniline) in methanol (conc. 0.015 M) were firstly prepared. Then, 100 mg catalyst was added to 5 mL of the above solution and stirred for 4 h at room temperature for adsorption. After the adsorption was finished, the catalyst was precipitated and the supernatant was sampled for GC analysis to calculate the final concentration.[1] The adsorption capacitary was calculated by the following equation:

$$\text{Adsorption rate (\%)}= \frac{C(initial) - C(final)}{C(intial)} \times 100\%$$

c(initial) = the substrate concentration before the reaction; *c*(final) = the substrate concentration after the reaction.

Table S1. Optimization of the reaction conditions.[a]

No.	Catalyst	Time	T	Gas	Con	Yield (%)	
		(h)	(°C)	(bar)	(%)	2a	3a
1	15Co/Al_2O_3	4	150	N_2(1)	13	0	0
2	3Cu-12Co/Al_2O_3	4	150	N_2(1)	39	5	0
3	5Cu-10Co/Al_2O_3	4	150	N_2(1)	80	55	6
4	10Cu-5Co/Al_2O_3	4	150	N_2(1)	93	62	19
5	12Cu-3Co/Al_2O_3	4	150	N_2(1)	100	20	71
6	15Cu/Al_2O_3	4	150	N_2(1)	45	21	6
7	10Cu-5Co/Al_2O_3	4	160	N_2(1)	100	4	90
8	10Cu-5Co/Al_2O_3	4	170	N_2(1)	100	0	99
9	10Cu-5Co/Al_2O_3	4	170	N_2(5)	100	0	96
10	10Cu-5Co/Al_2O_3	4	170	N_2(20)	100	0	96
11	10Cu-5Co/Al_2O_3	4	170	H_2(10)	44	28	2
12	10Cu-5Co/MgAl-LDO	4	170	H_2(10)	40	38	0
13	10Cu-5Co/MgAl-LDO	4	200	H_2(10)	100	35	60
14	10Cu-5Co/MgAl-LDO	8	180	H_2(10)	92	84	7
15	10Cu-5Co/MgAl-LDO	4	170	H_2(20)	28	16	0

[a] Conditions: aniline 1 mmol, catalyst 150 mg, MeOH 12 mL. Conversions and yields were determined by GC with triple runs.

Table S2. The surface acid-base density of as-prepared catalysts.

Catalyst	Acidity (mmol/m^2)				Alkalinity (mmol/m^2)		
	weak	medium	strong	total	weak	strong	total
10Cu-5Co/Al_2O_3	9.0×10^{-4}	3.6×10^{-3}	5.8×10^{-3}	1.0×10^{-2}	5.5×10^{-4}	1.4×10^{-4}	6.9×10^{-4}
10Cu-5Co/MgAl-LDO	1.5×10^{-3}	7.1×10^{-4}	3.7×10^{-3}	6.0×10^{-3}	2.6×10^{-3}	6.2×10^{-4}	3.2×10^{-3}

Table S3. Textural properties of recycled catalysts.

Catalyst	S_{BET} (m^2/g)	Vp (cm^3/g)	Dp (nm)
10Cu-5Co/Al_2O_3 (recycled)	125.4	0.23	7.1
10Cu-10Co/MgAl-LDO (recycled)	92.1	0.18	7.8

Table S4. Electronic energies of related compounds**.**

Compounds	Electronic energies (eV)
$PhNH_2$	-88.30052964
PhNHMe	-104.6069296
MgAl-LDO	-285.9064841
Al_2O_3	-439.3610101
$PhNH_2$@MgAl-LDO	-375.9240512
PhNHMe@MgAl-LDO	-392.0936996
$PhNH_2$@Al_2O_3	-530.0400385
PhNHMe@Al_2O_3	-546.3109038
$PhNH_2$@Cu-Co/MgAl-LDO	-410.2376662
PhNHMe@Cu-Co/Mgl-LDO	-426.7285833
$PhNH_2$@Cu-Co/Al_2O_3	-554.9086402
PhNHMe@Cu-Co/Al_2O_3	-571.2926564
Cu-Co/MgAl-LDO	-320.9291656
Cu-Co/Al_2O_3	-465.2718354

Table S5. Recent progress in *N*-methylation of amines and methanol.

Substrate	Catalyst	Condition	Base	Yield (%)	Productivity[a]	Ref.
Amines (1mmol)	NHC-Ir (2.6mg)	2 mL methanol, 130 °C, 12-84 h	1 equiv. *t*-BuOK	53-98% (*N*-monomethylamines)	0.0317	[5]
Amines (0.5mmol)	0.3wt% Ir/ZnO (0.64g)	5 mL methanol, 150 °C, 2-24 h, 5 bar N_2	/	29-99% (*N,N*-dimethylamines)	0.0002[b]	[6]
	0.3wt% Ir/ZnO (0.16)	1-6 mL mesitylene, 0.5-5 mL methanol, 150 °C, 2-24 h, 5 bar N_2	/	49-83% (*N*-monomethylamines)	0.0002	[6]
Nitroaromatics or amines (1g)	4wt% Ir@YSMCNs (0.05g)	15 mL methanol, 170 °C, 24-72 h	2 equiv. *t*-BuOK	56-98% (*N*-monomethylamines)	0.0004	[7]
Amines (1mmol)	5wt% Pd/C (42.6mg)	3 mL methanol 150 °C, 12-16 h	2 equiv. CH_3ONa	58-99% (*N*-monomethylamines)	0.0027	[8]
Aliphatic amines (1mmol)	5wt% Pt/C (39mg)	30 mmol methanol, catalyst, 150 °C, 36-48 h	1 mmol NaOH	76-96% (*N,N*-dimethylamines)	0.0007[b]	[9]
Nitroaromatics or amines (1mmol)		30 mmol methanol, 130-140 °C, 15-36 h, 40 bar H_2	1 mmol NaOH	74-98% (*N*-monomethylamines)	0.0016	[9]
Amines (1mmol)	3wt% Pd@sPS-NMe_2 (36mg)	3 mL methanol, 150-170 °C, 2-16 h, 40 bar H_2	2 mmol CH_3ONa	56-98% (*N*-monomethylamines)	0.0029	[10]
Nitrobenzene (2mL)	Raney Ni® (7.5 g)	60mL methanol, 170 °C, 5 h, 30 bar N_2	/	98% (*N,N*-dimethylaniline)	0.0005[b]	[11]
Nitroaromatics or amines (1mmol)	10wt% Cu-5wt%Co/Al_2O_3 (150 mg)	12 mL methanol, 140-190 °C, 4-12 h, 1 bar N_2	/	59-99% (*N,N*-dimethylamines)	0.0029[b]	This work
	10wt% Cu-5wt%Co/MgAl-LDO (150 mg)	12 mL methanol, 150-190 °C, 4-12 h, 10 bar H_2	/	56-99% (*N*-monomethylamines)	0.0028	

[a] Productivity= (mmol of *N*-monomethylamines)•(mg catalyst)$^{-1}$•h^{-1}

[b] Productivity= (mmol of *N*-dimethylamines)•(mg catalyst)$^{-1}$•h^{-1}

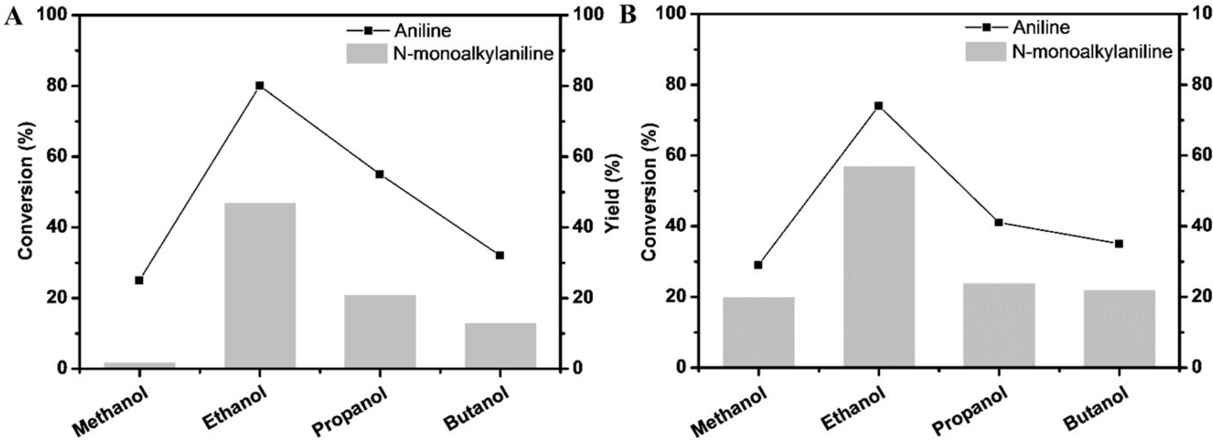


Figure S1. The activities of different alcohols in *N*-alkylation reaction. Conditions: **A** aniline 1 mmol, 10Cu-5Co/Al_2O_3 150 mg, alcohols 12 mL, stop the reaction after 30 min heating up to 160 ^oC, 1 bar N_2. **B** aniline 1 mmol, 10Cu-5Co/ MgAl-LDO 150 mg, alcohols 12 mL, 170 ^oC, 2 h, 10 bar H_2.

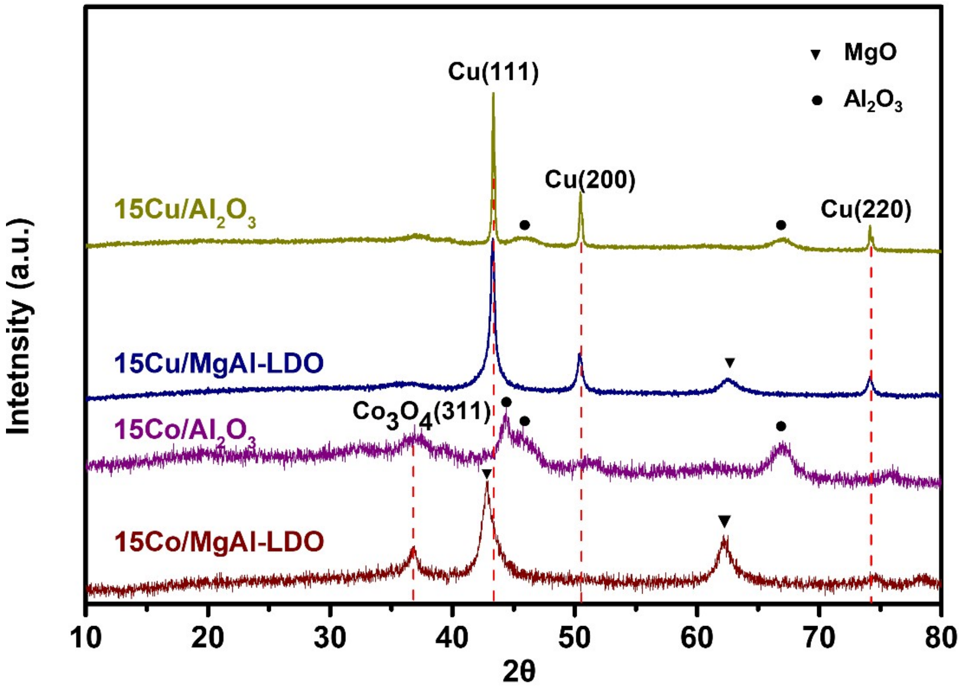


Figure S2. XRD characterization of monometallic catalysts.

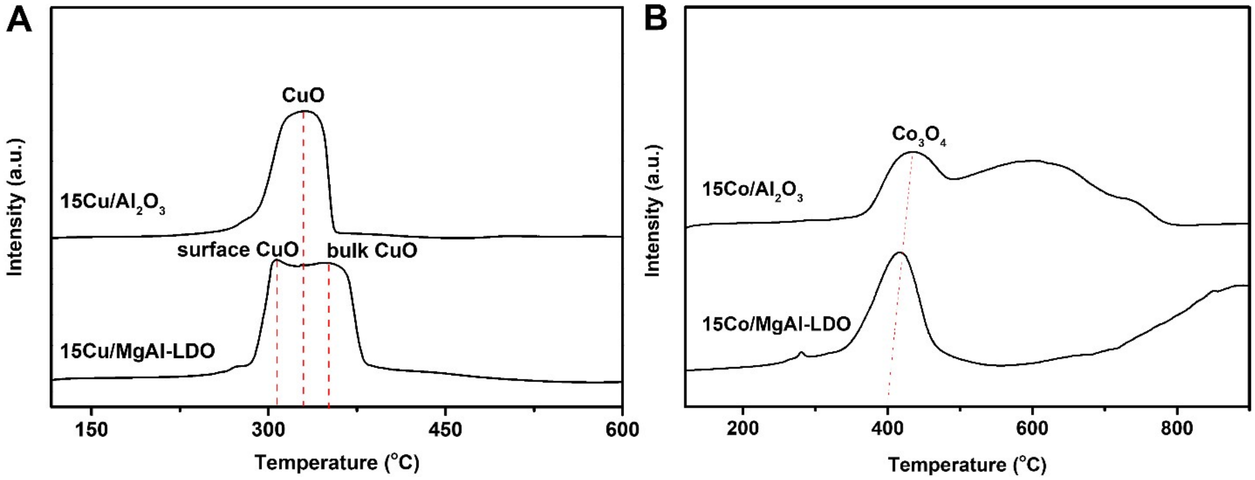


Figure S3. A H_2-TPR characterization of monometallic Cu catalysts. **B** H_2-TPR characterization of monometallic Co catalysts.

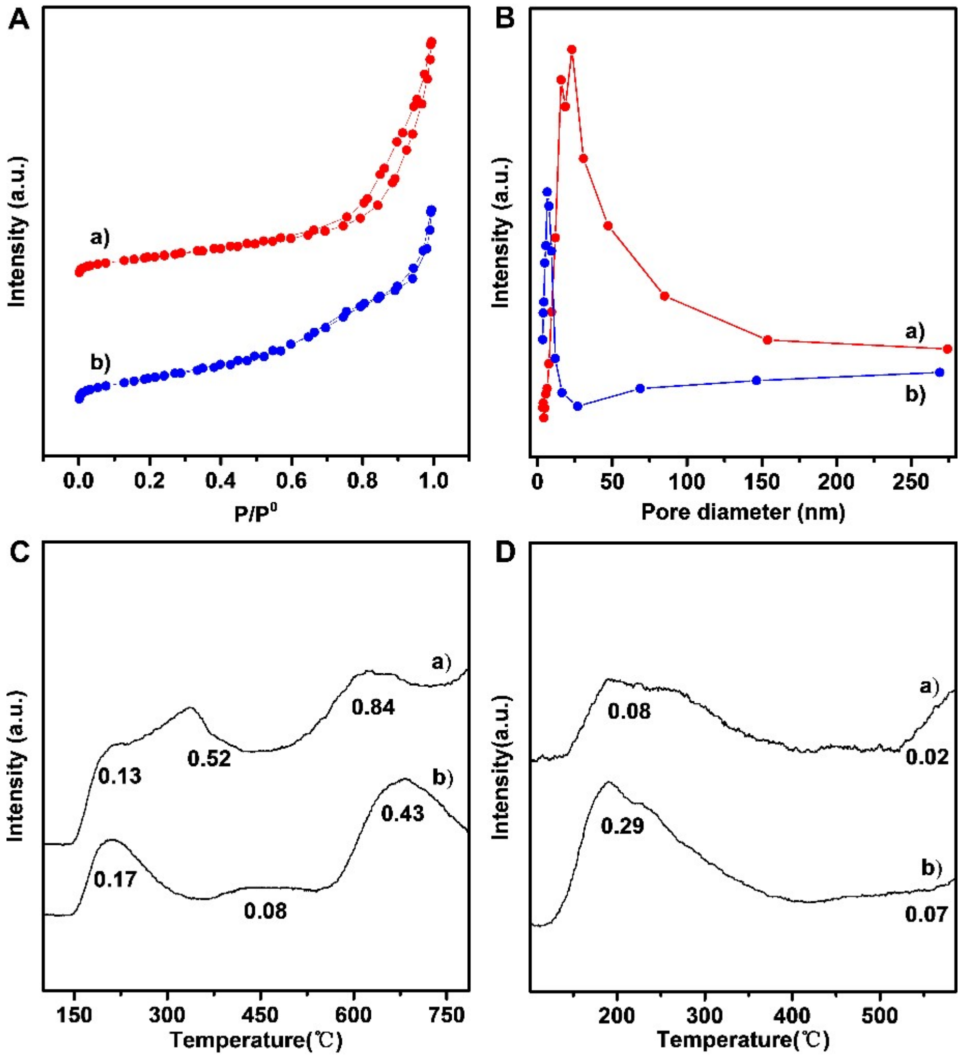


Figure S4. **A** N_2 adsorption-desorption isotherms. **B** Pore size distribution. **C** NH_3-TPD characterization. **D** CO_2-TPD characterization. **a)** 10Cu-5Co/Al_2O_3. **b)** 10Cu-5Co/MgAl-LDO.

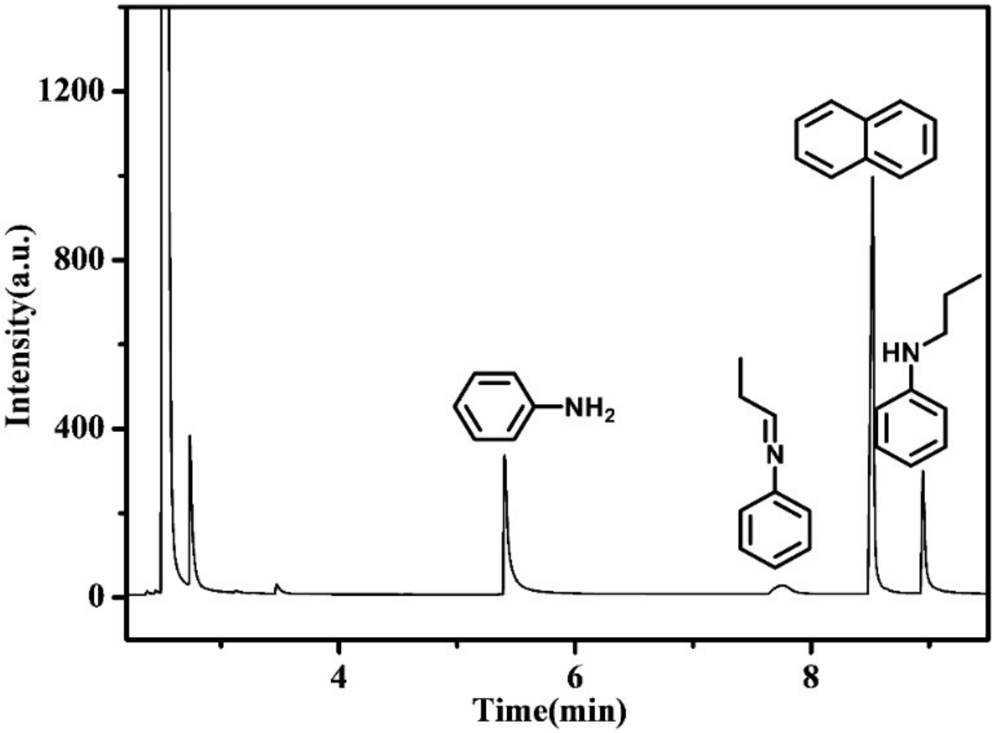
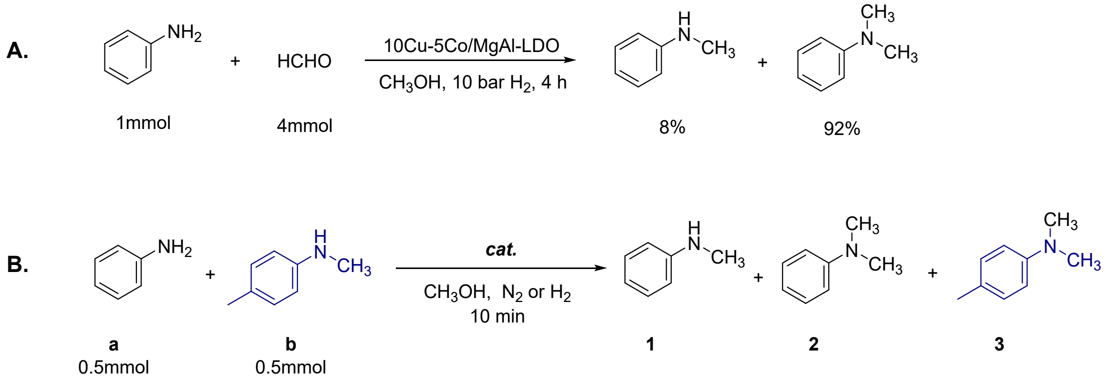


Figure S5. GC result for the reaction of aniline and propanol. Conditions: aniline 1 mmol, 10Cu-5Co/Al_2O_3 150 mg, propanol 12 mL, 1 bar N_2, stop the reaction after 30 min heating up to 170 °C.



cat.	t (min)	Conversion/%		Yield/%		
		a	b	**1**	**2**	**3**
10Cu-5Co/Al_2O_3	10	91	12	85	3	5
	20	100	41	78	15	35
10Cu-5Co/MgAl-LDO	10	46	10	41	1	8
	20	53	11	50	1	10

Figure S6. Control experiments. Conditions: catalyst 150 mg, methanol 12 mL.

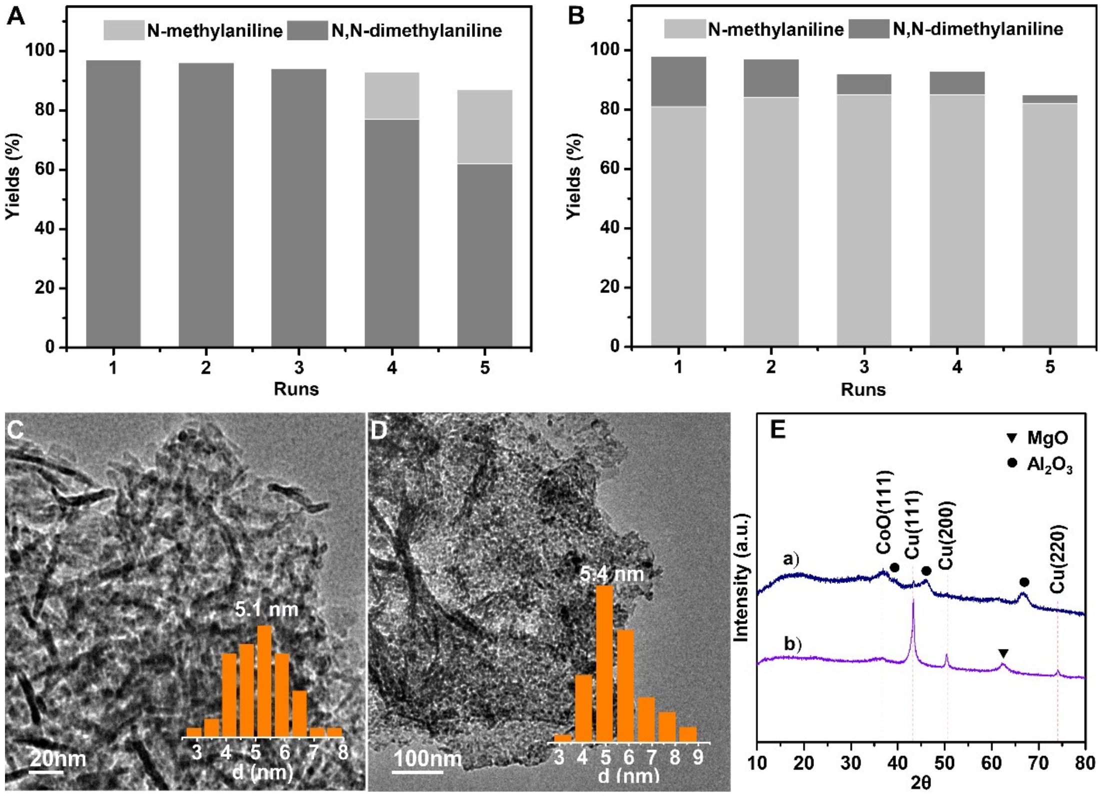


Figure S7. Catalyst recycling test and characterization of the recycled catalysts. A 5-run test of 10Cu-5Co/Al_2O_3. Reaction conditions: aniline 1 mmol, 10Cu-5Co/Al_2O_3 150 mg, MeOH 12 mL, 170 °C, 4 h, 1 bar N_2. **B** 5-run test of 10Cu-5Co/MgAl-LDO. Reaction conditions: aniline 1 mmol, 10Cu-5Co/MgAl-LDO 150 mg, MeOH 12 mL, 190 °C, 4 h, 10 bar H_2. TEM images of recycled **C** 10Cu-5Co/Al_2O_3 and **D** 10Cu-5Co/MgAl-LDO. **E** XRD characterization of recycled catalysts. **a)** 10Cu-5Co/Al_2O_3. **b)** 10Cu-5Co/MgAl-LDO.

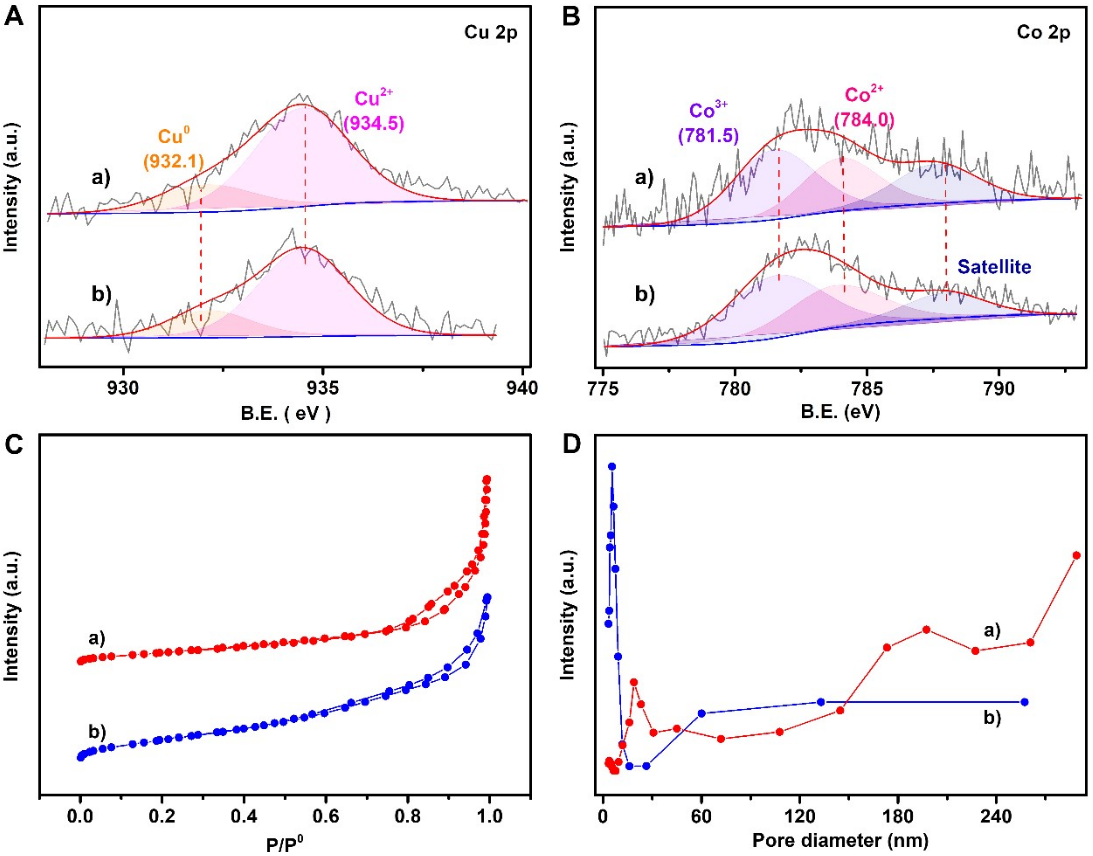


Figure S8. Characterization of the recycled catalysts. XPS spectra of **A** Cu 2p and **B** Co 2p. **C** N_2 adsorption-desorption isotherms. **D** Pore size distribution. **a)** recycled 10Cu-5Co/Al_2O_3. **b)** recycled 10Cu-5Co/MgAl-LDO.

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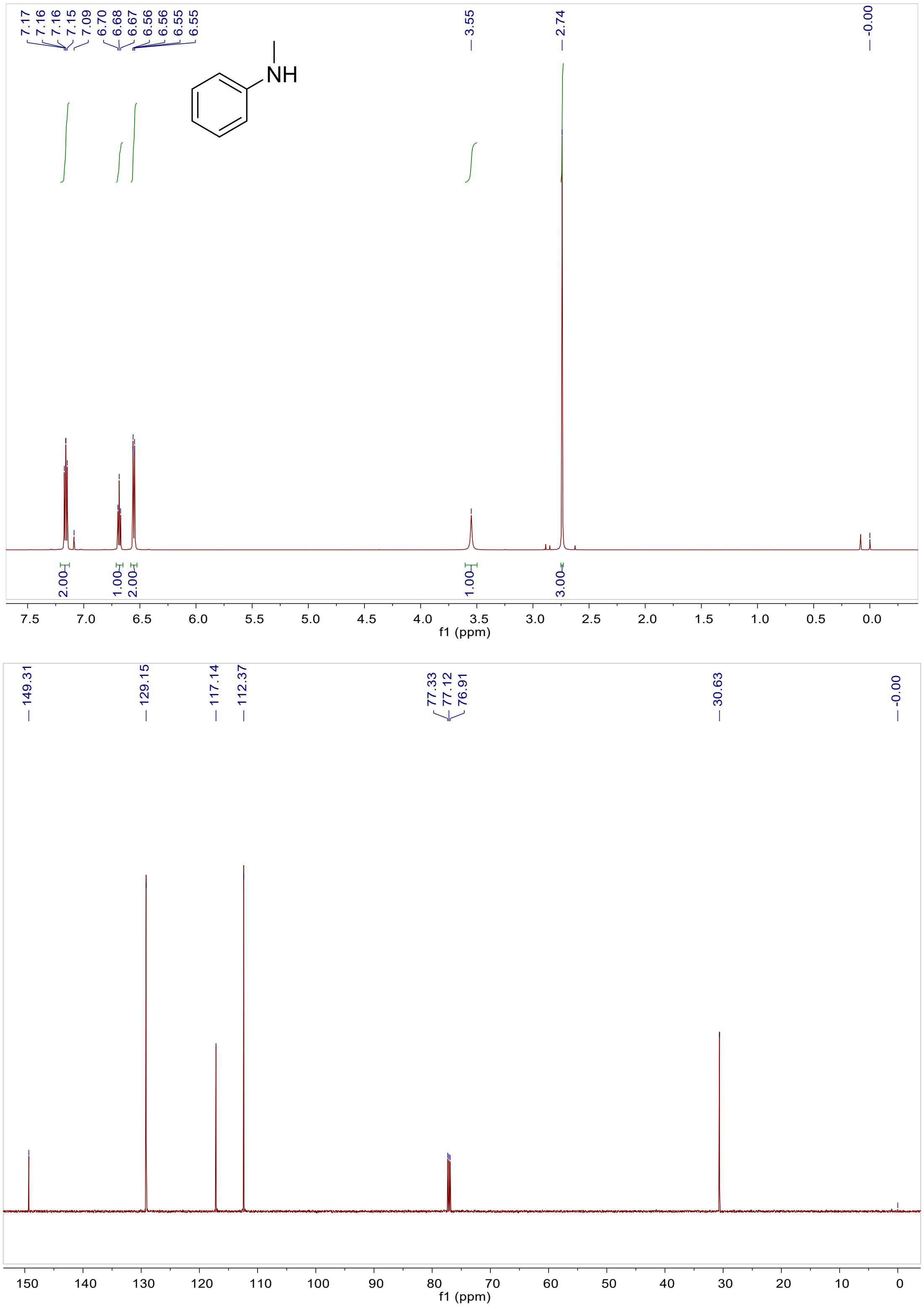
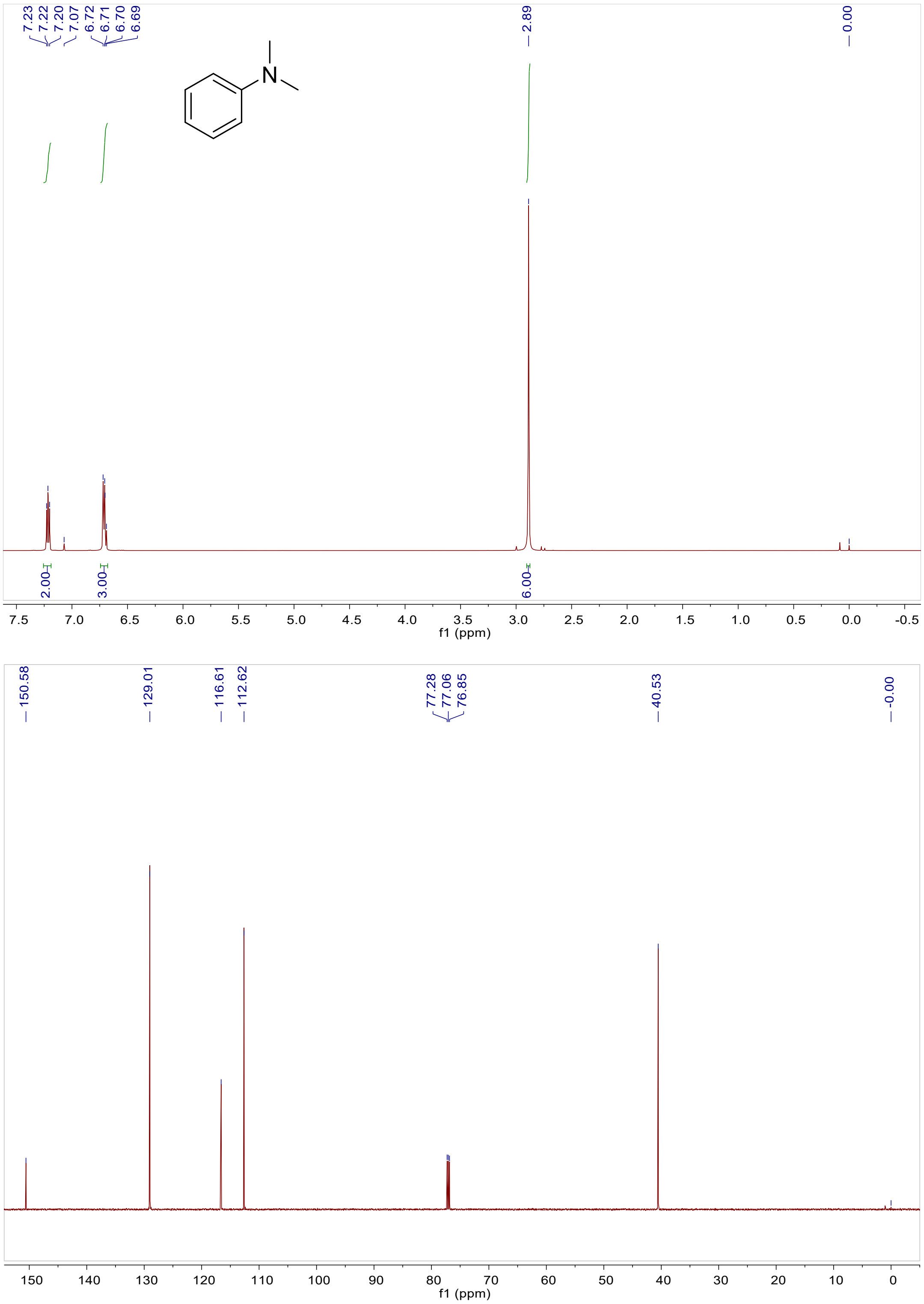
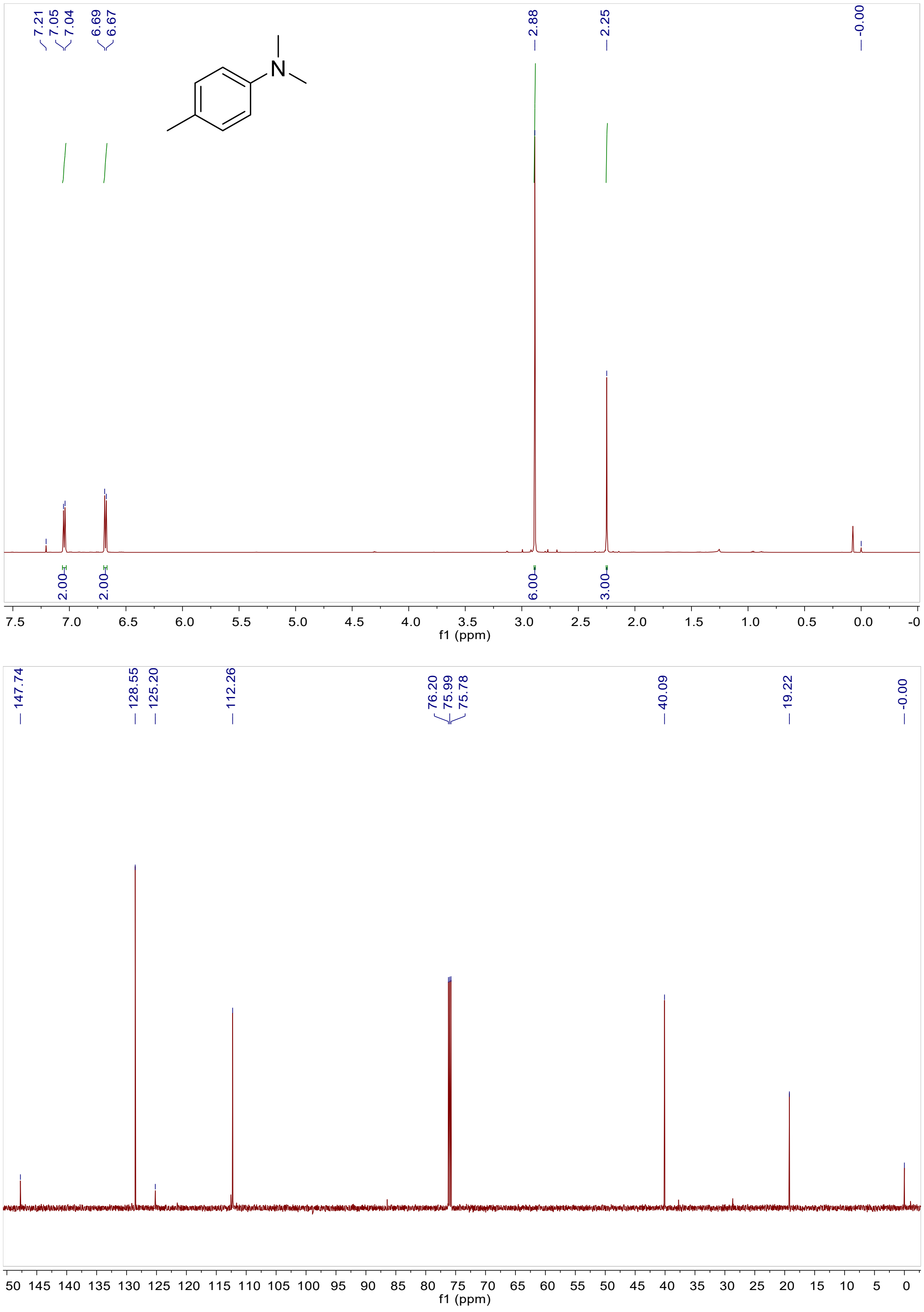
NMR Results



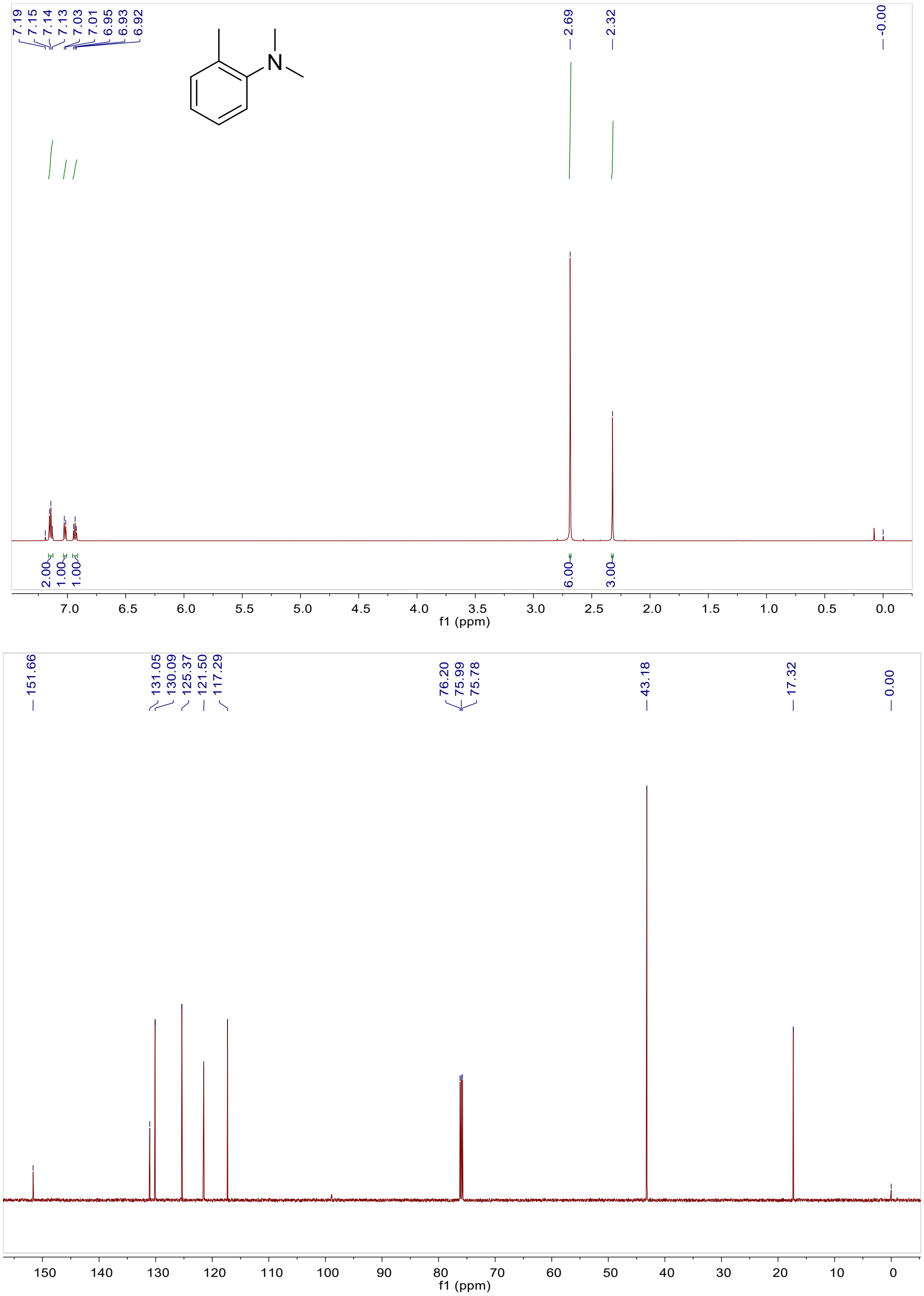
^{1}H-NMR and ^{13}C-NMR of ***N*-methylaniline**.



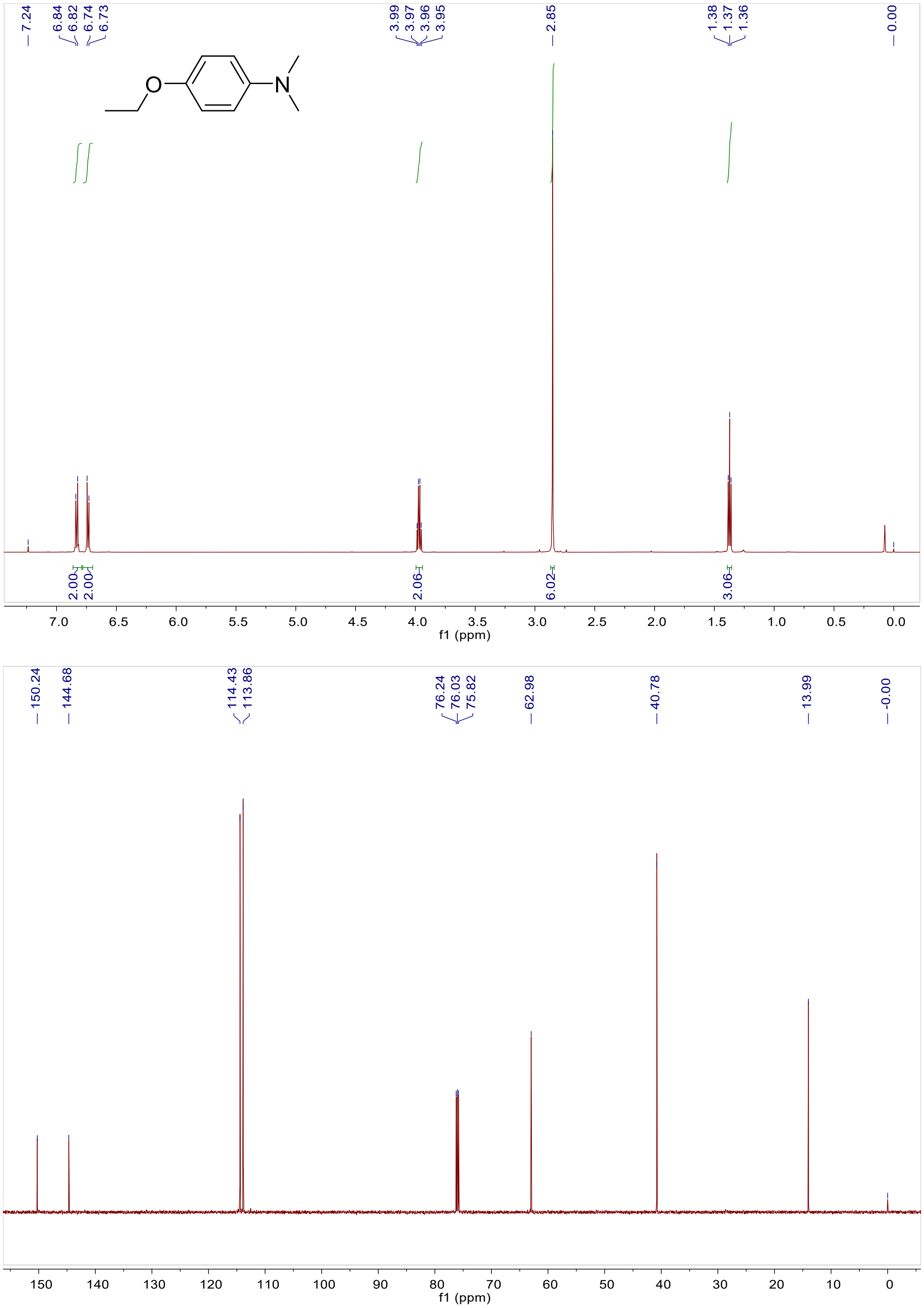
^{1}H-NMR and ^{13}C-NMR of ***N*, *N*-dimethylaniline**.



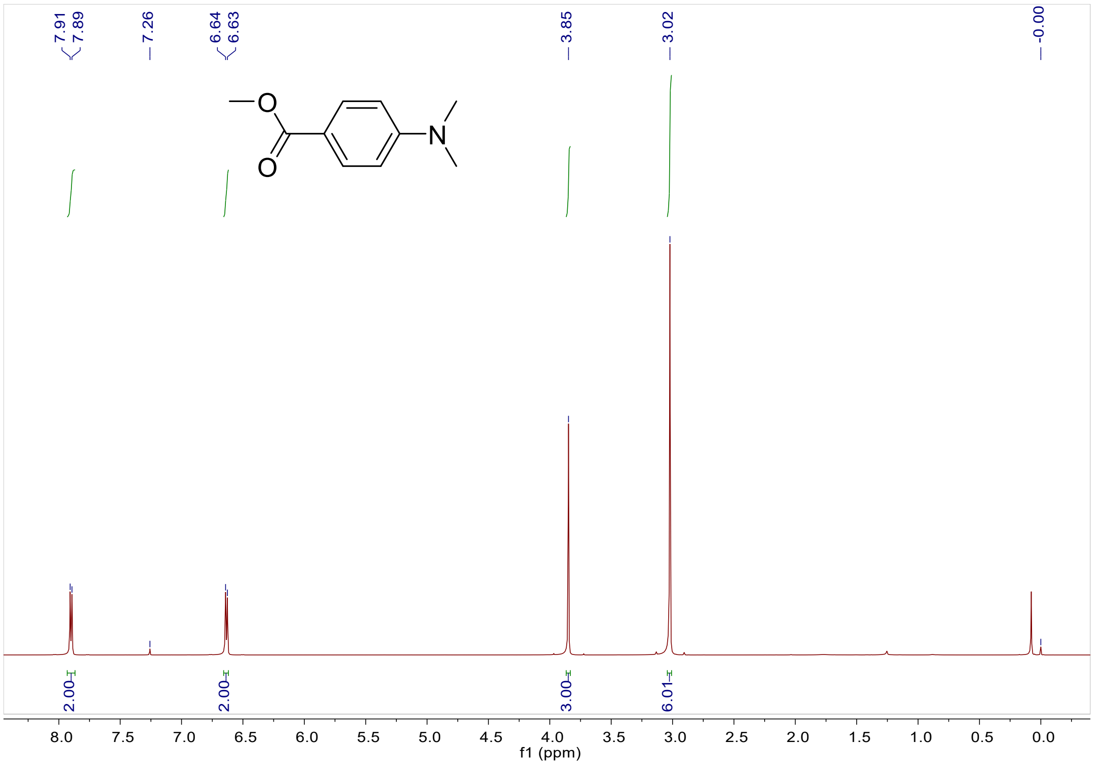
^{1}H-NMR and ^{13}C-NMR of compound **2b**.

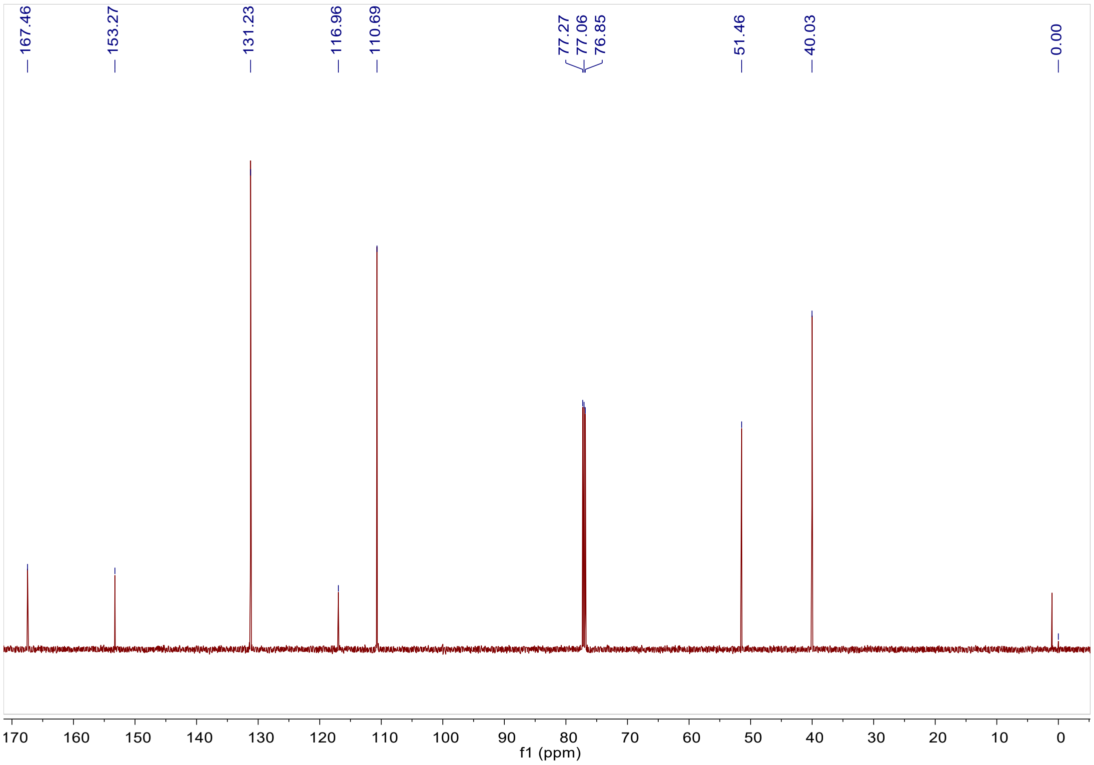


^{1}H-NMR and ^{13}C-NMR of compound **2c**.

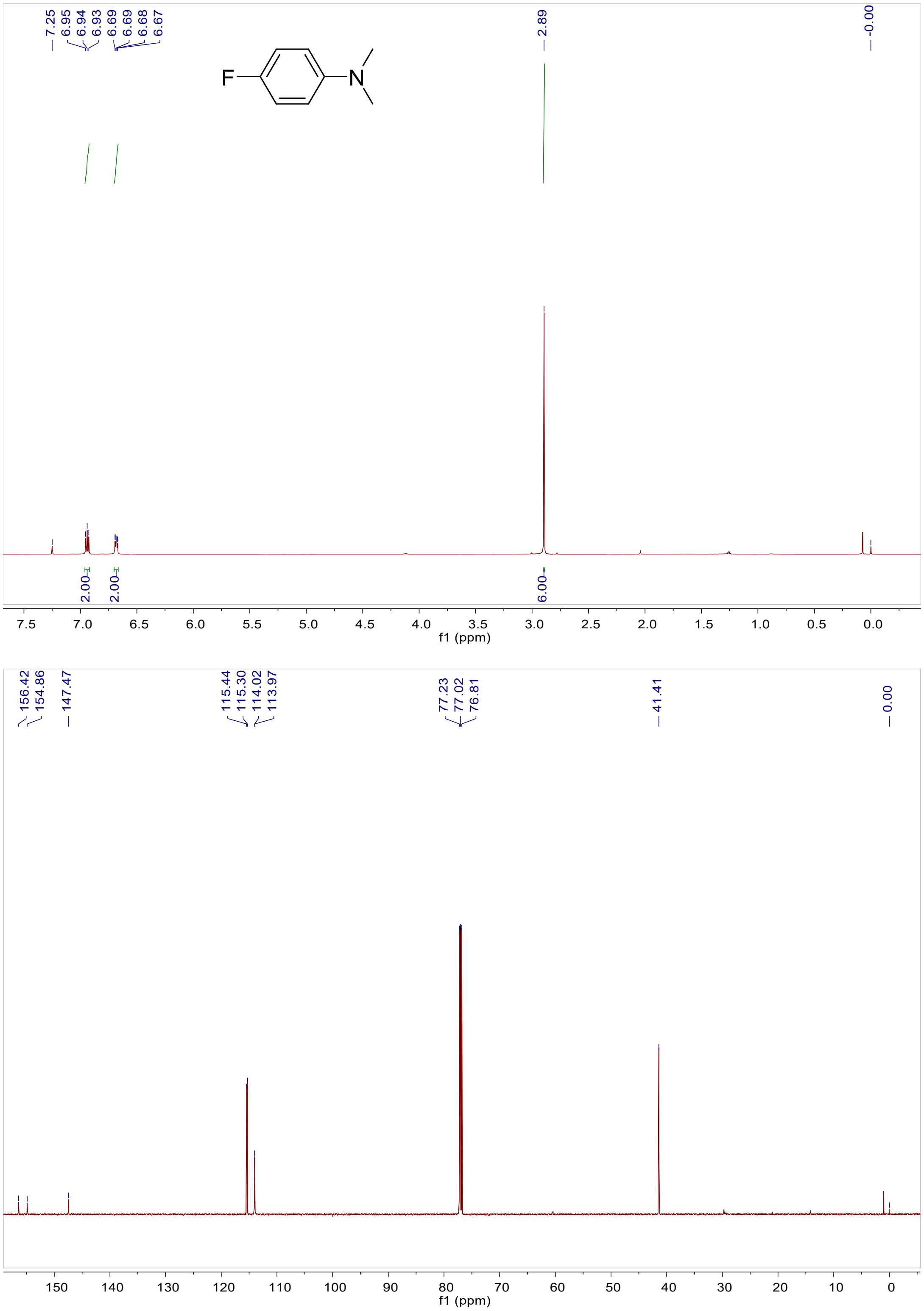


^{1}H-NMR and ^{13}C-NMR of compound **2d**.

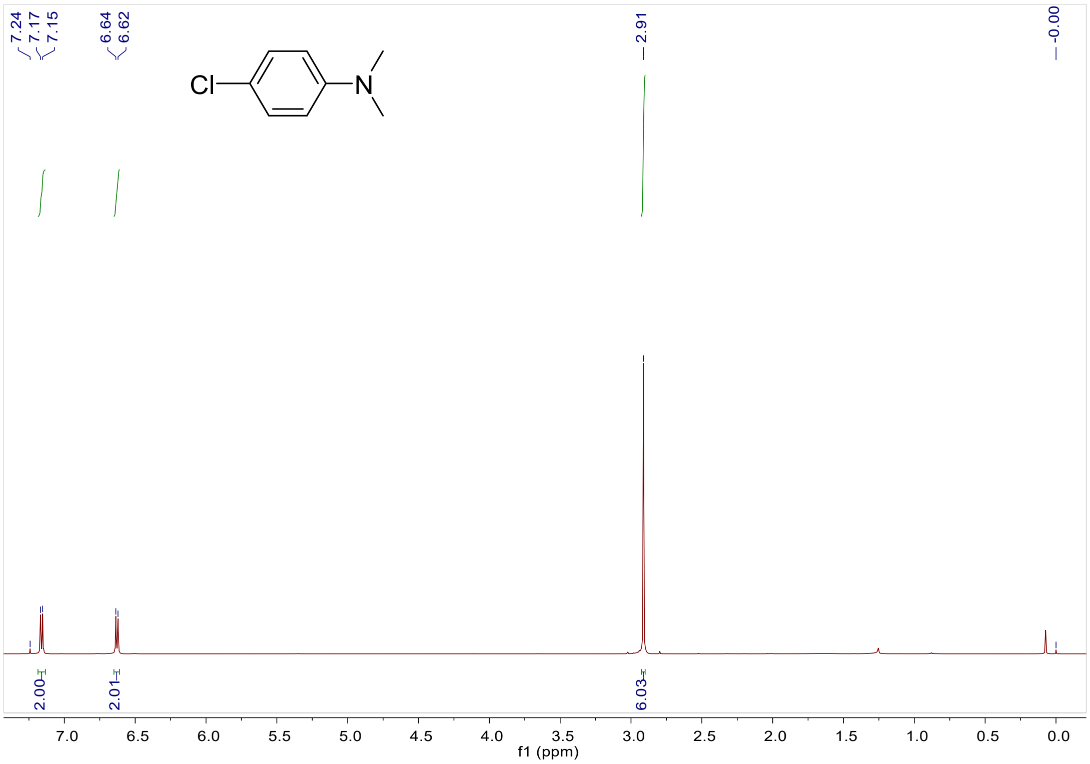


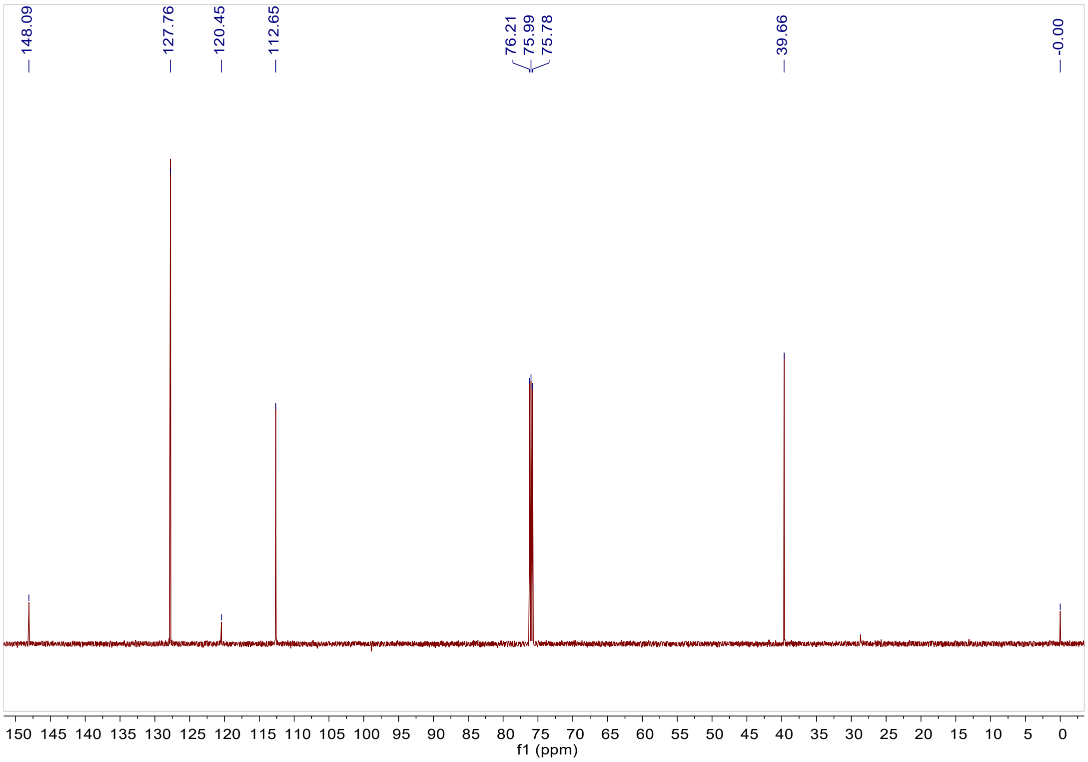


^{1}H-NMR and ^{13}C-NMR of compound **2e**.

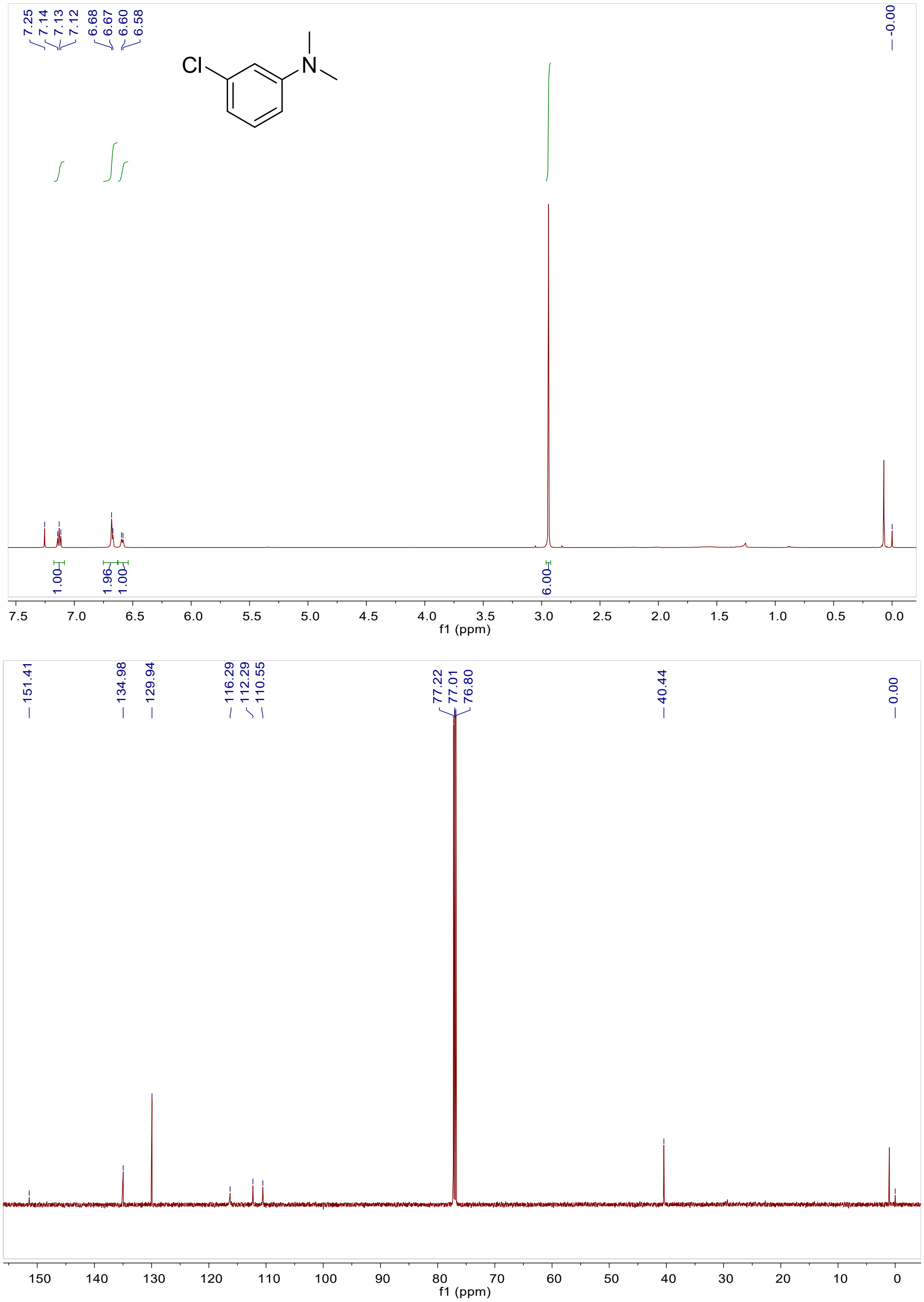


^{1}H-NMR and ^{13}C-NMR of compound **2f**.

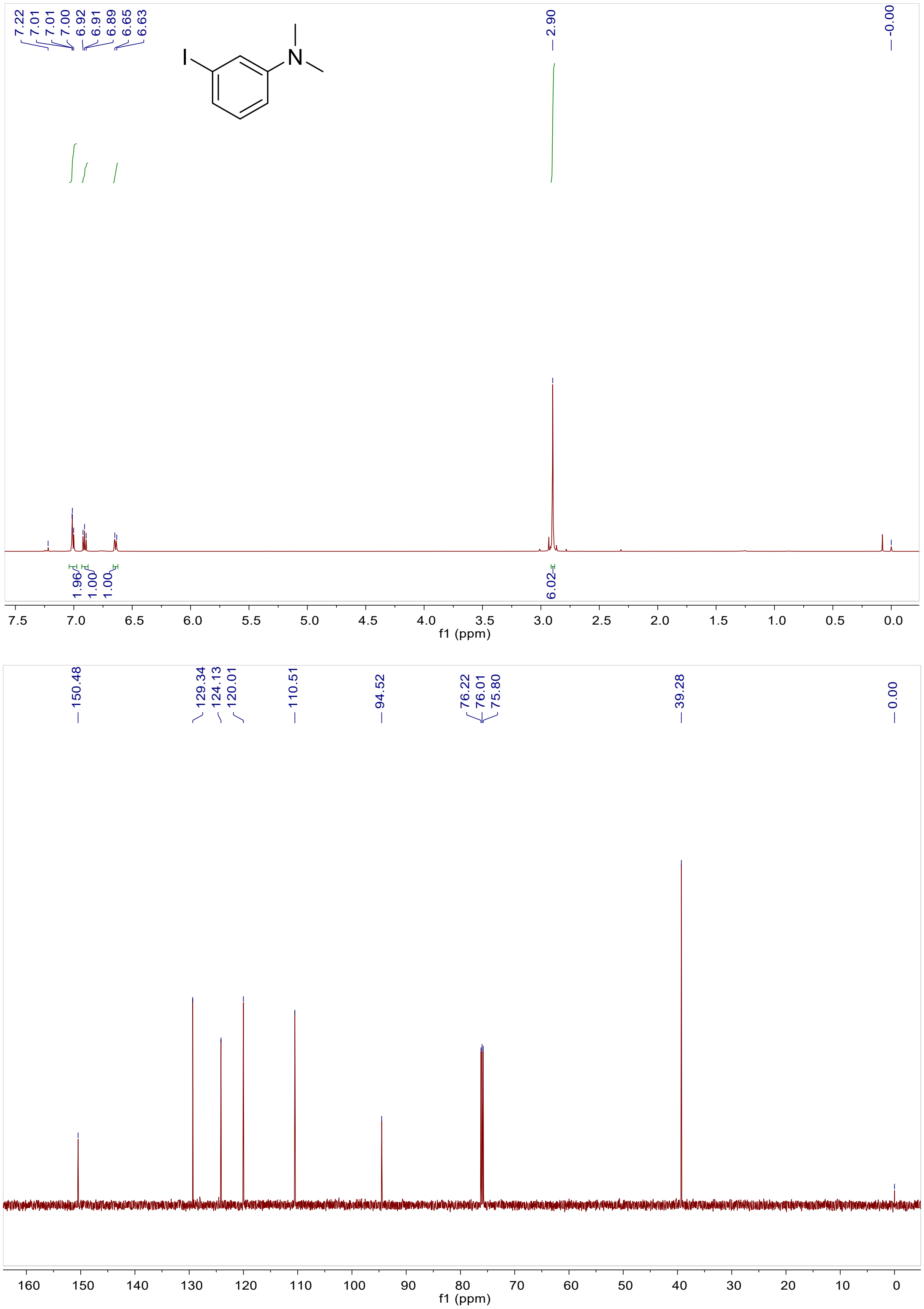




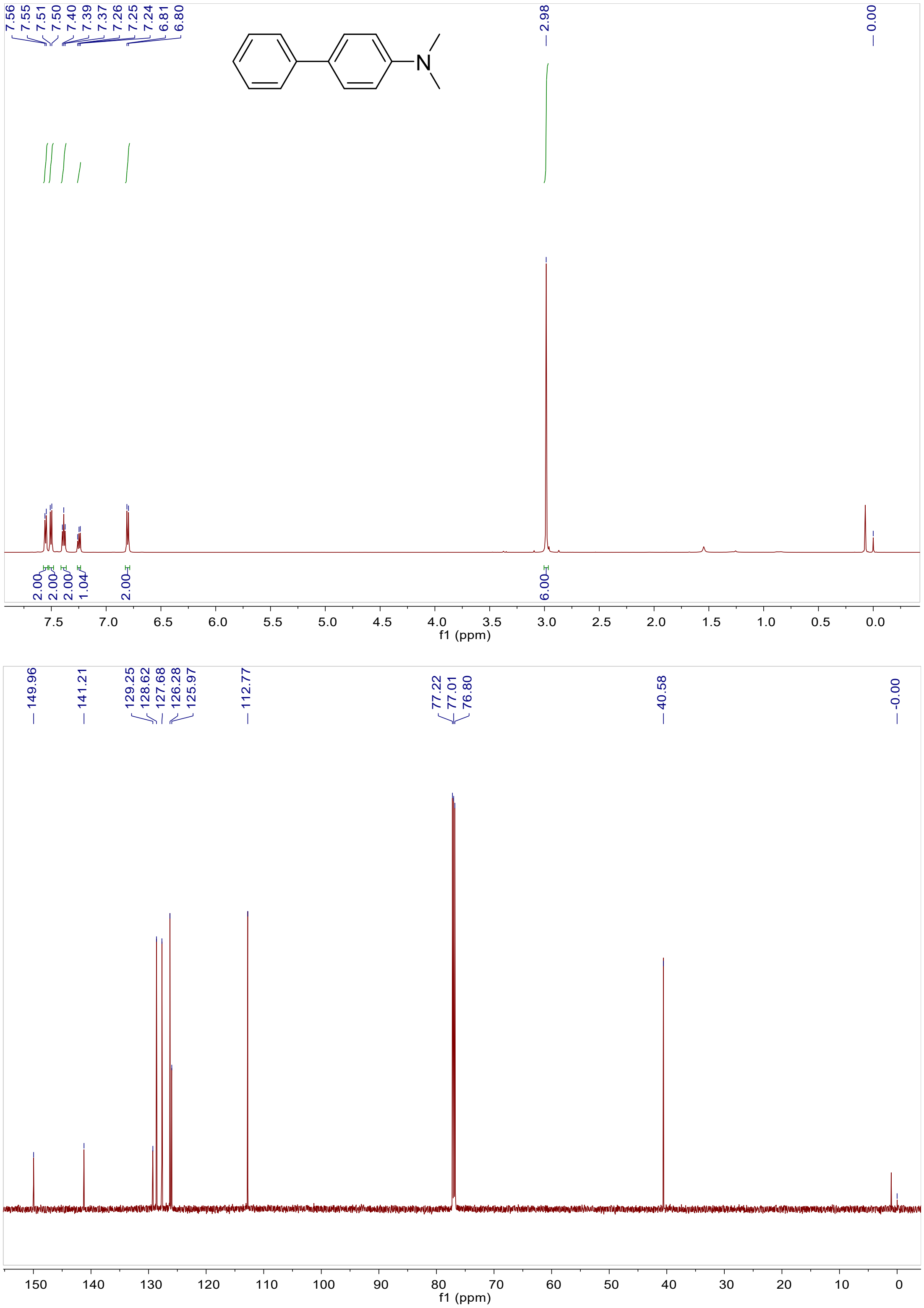
^{1}H-NMR and ^{13}C-NMR of compound **2g**.



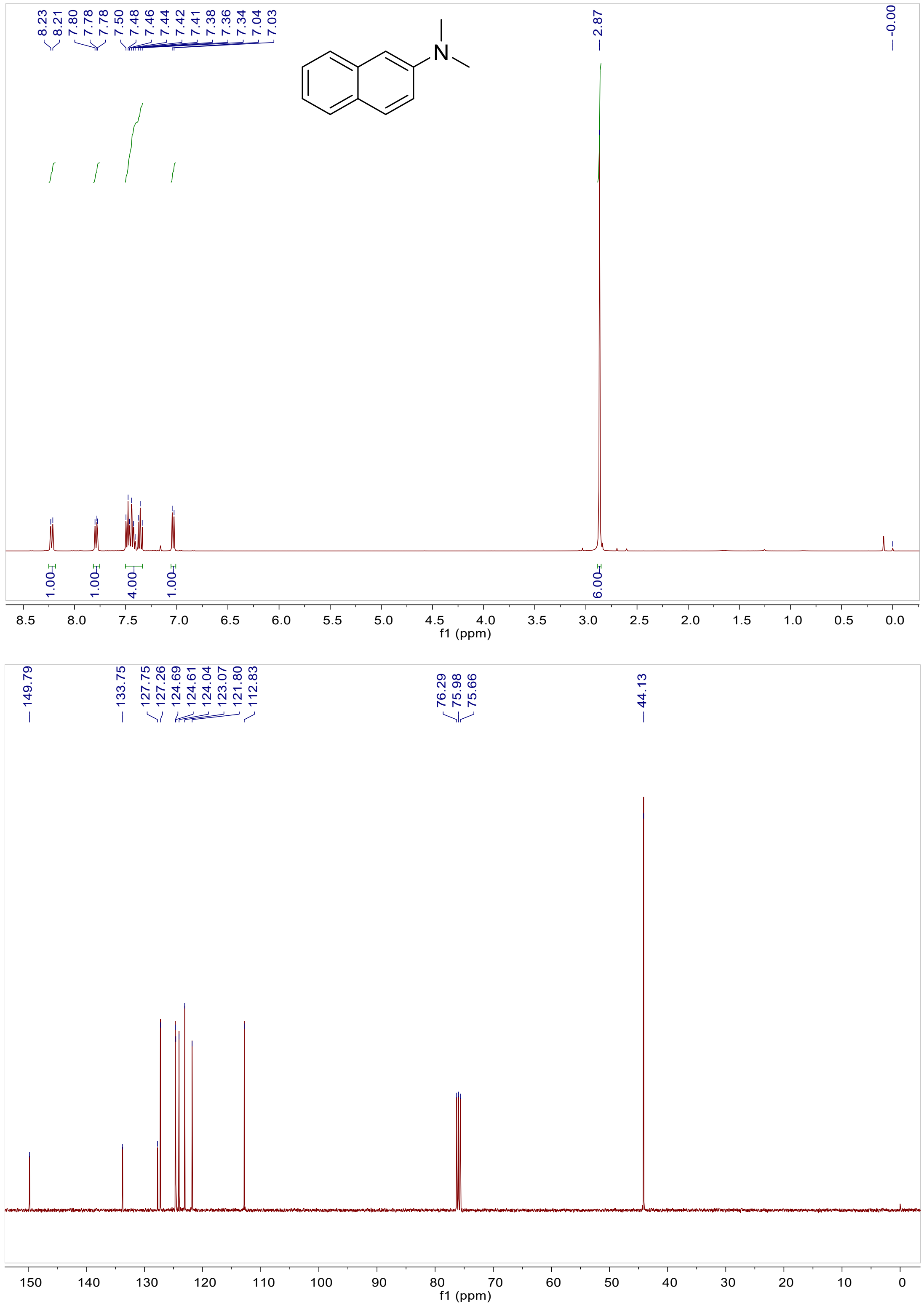
^{1}H-NMR and ^{13}C-NMR of compound **2h**.



^{1}H-NMR and ^{13}C-NMR of compound **2i**.



^{1}H-NMR and ^{13}C-NMR of compound **2j**.



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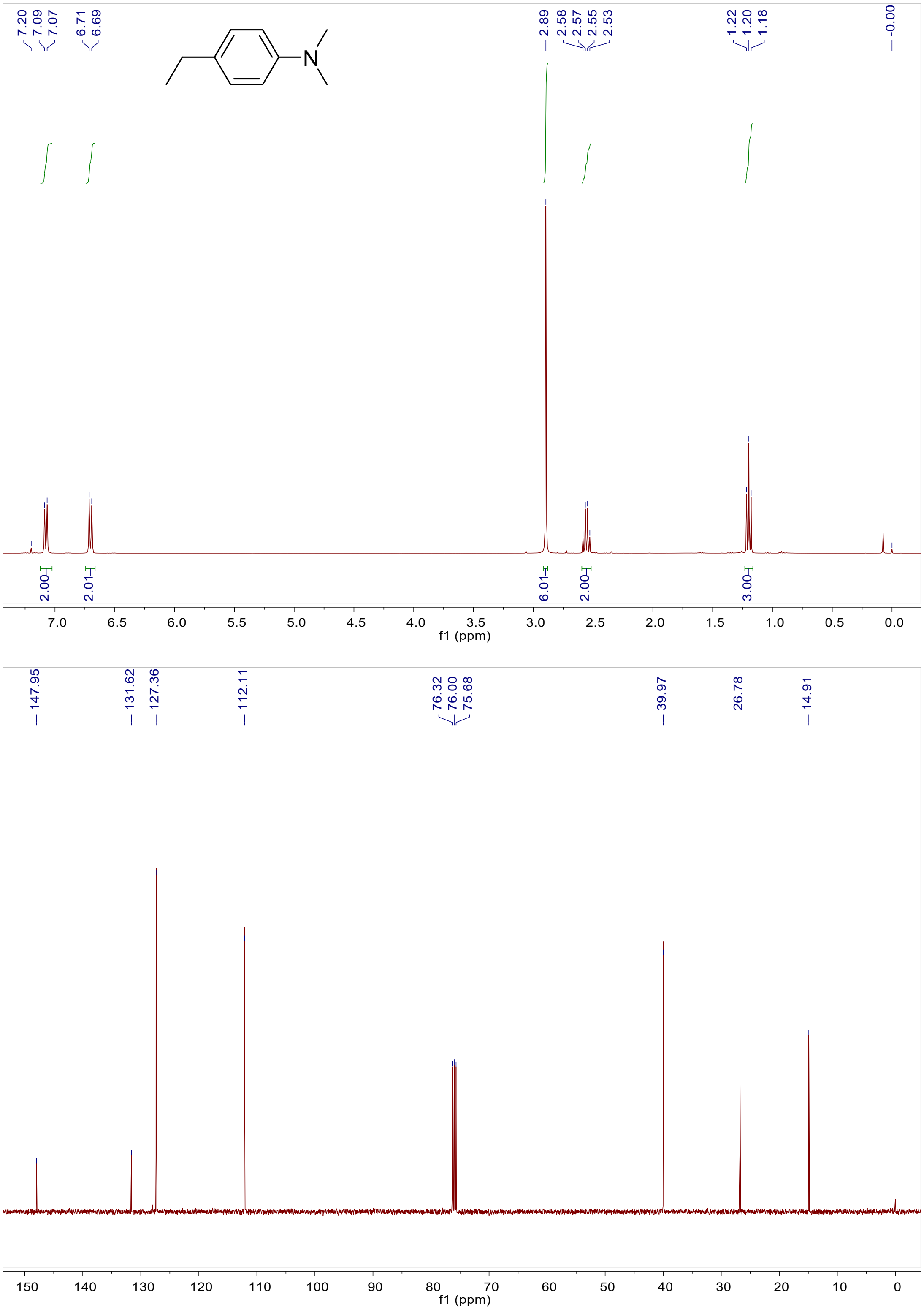

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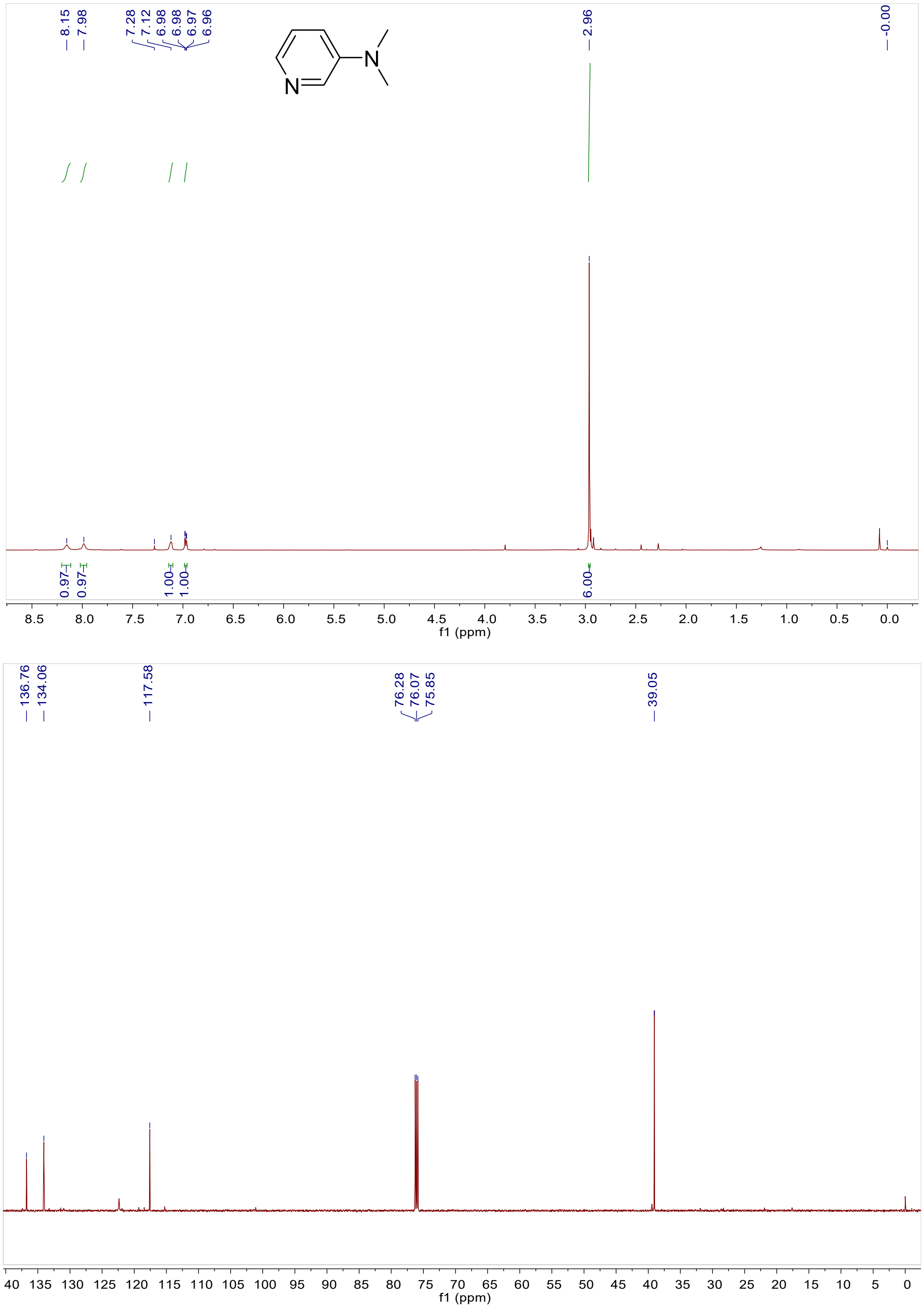
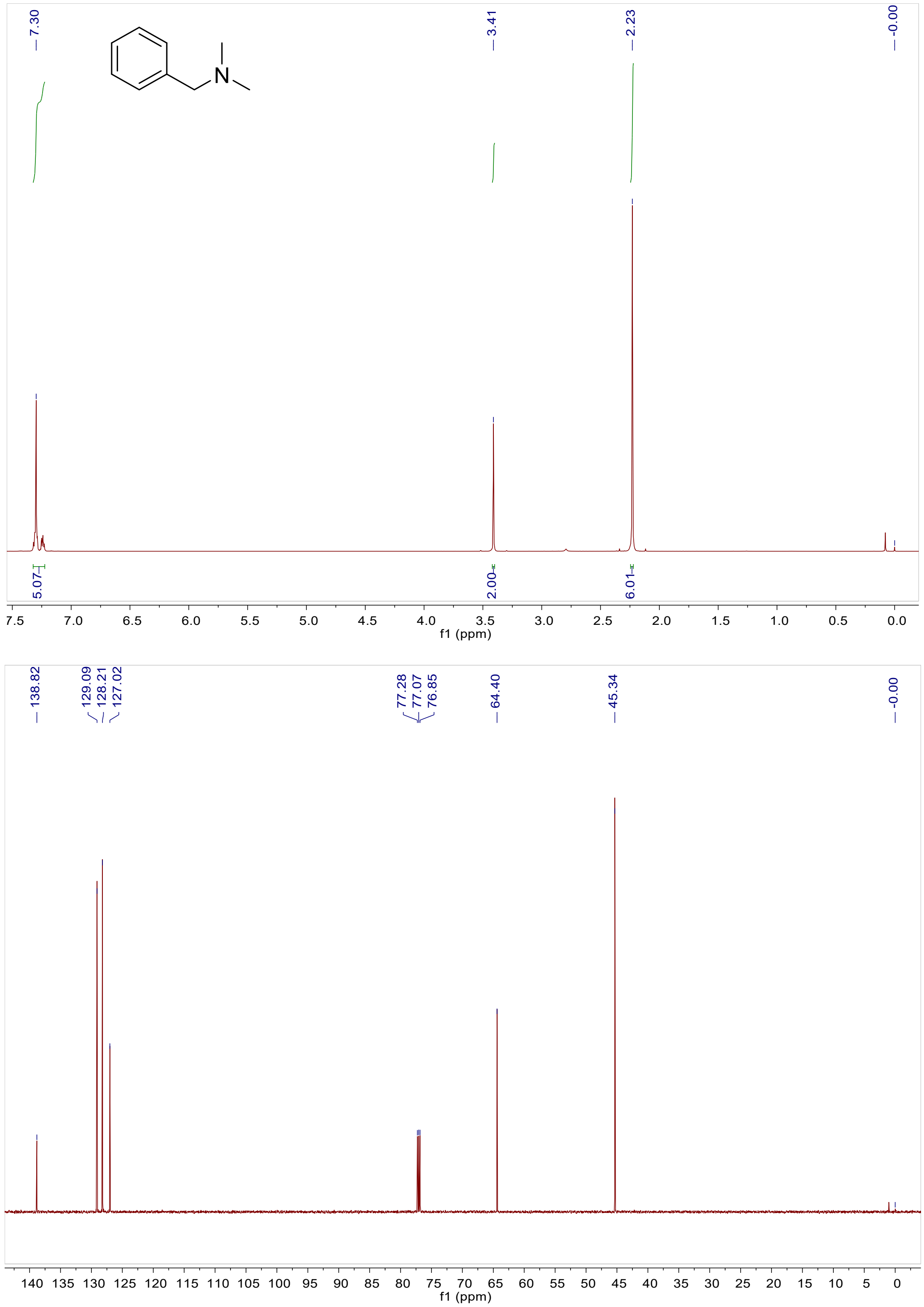
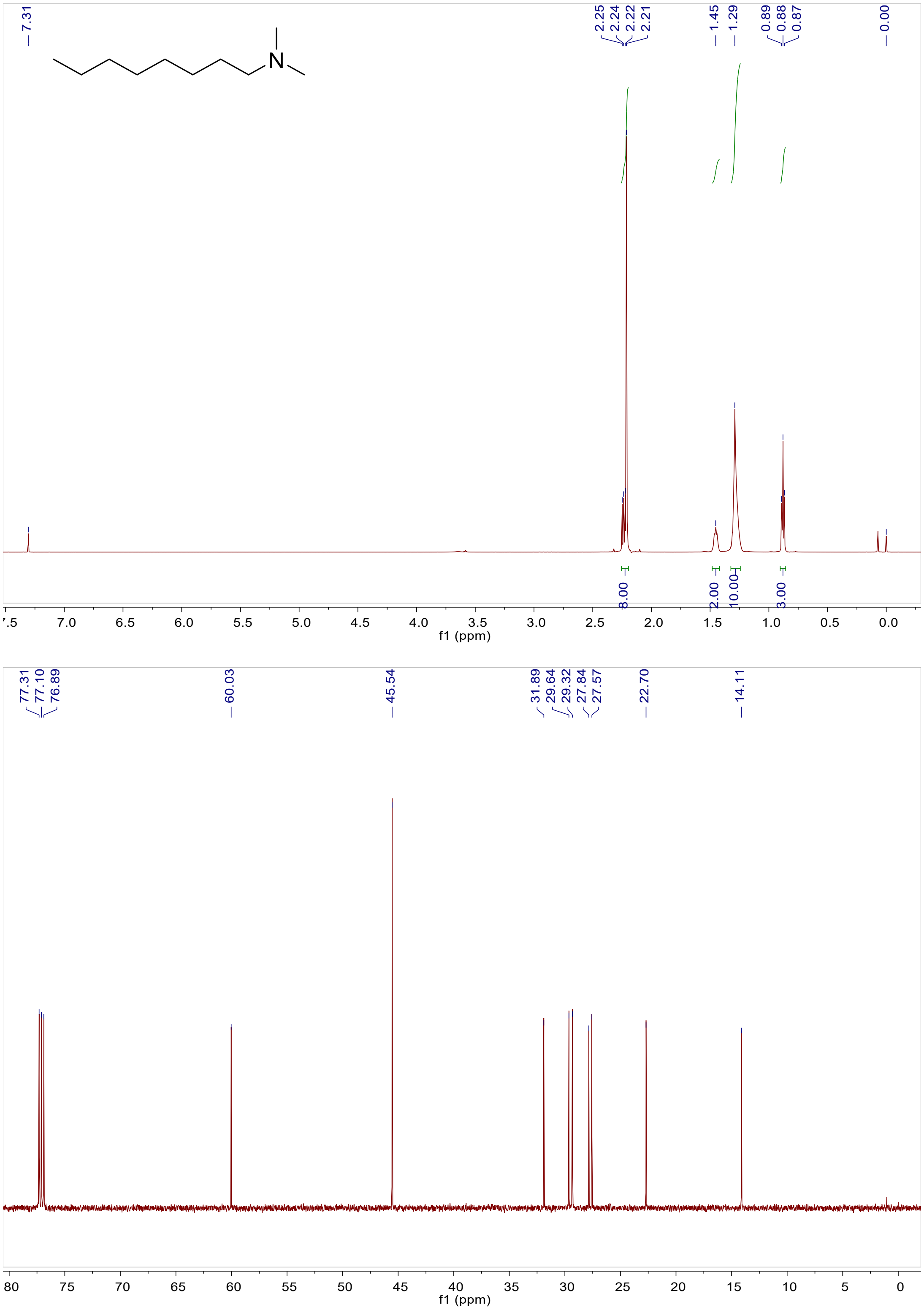


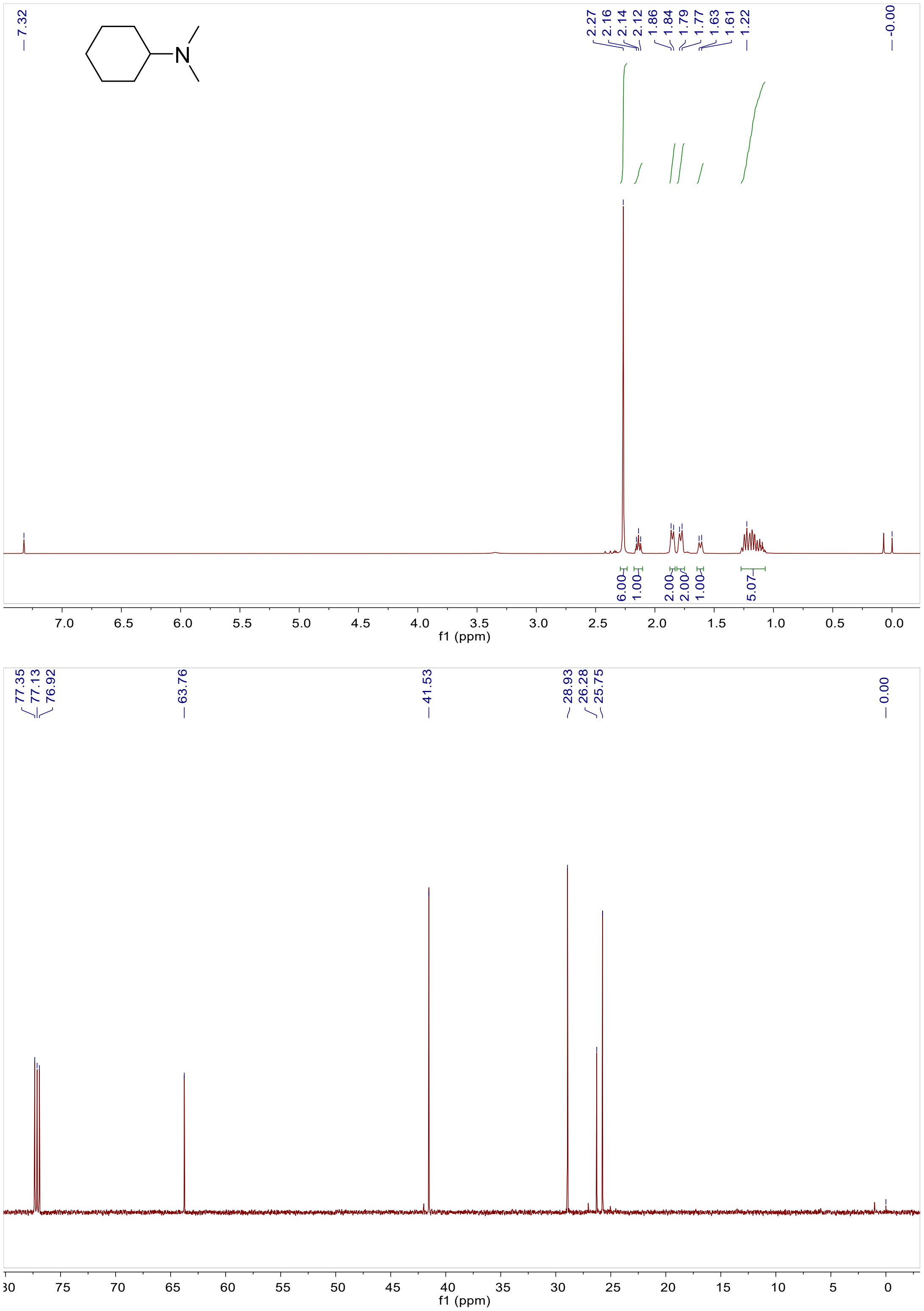
^{1}H-NMR and ^{13}C-NMR of compound **2m**.



^{1}H-NMR and ^{13}C-NMR of compound **2n**.



^{1}H-NMR and ^{13}C-NMR of compound **2o**.



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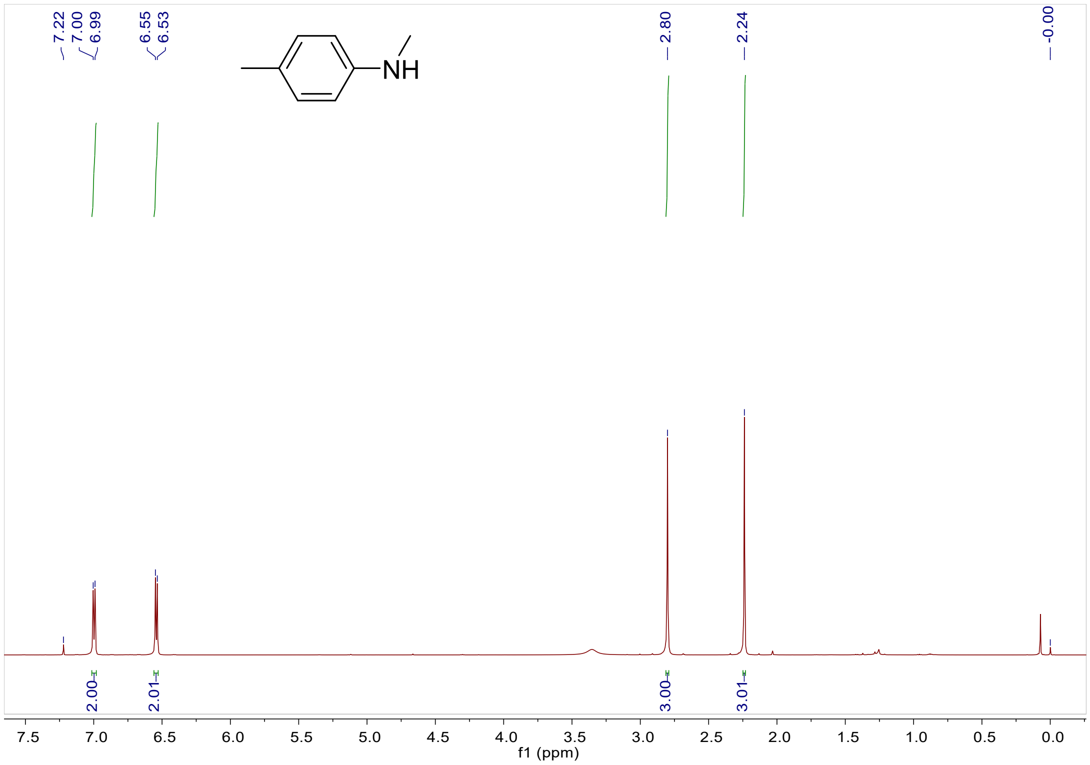
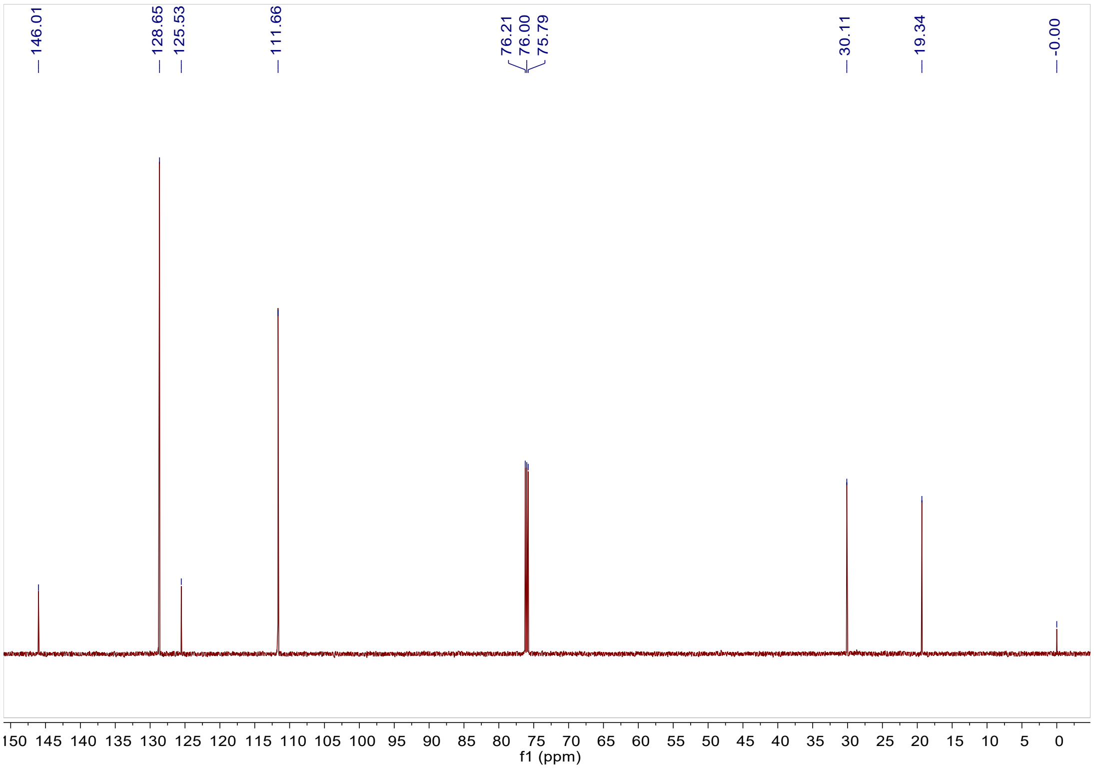
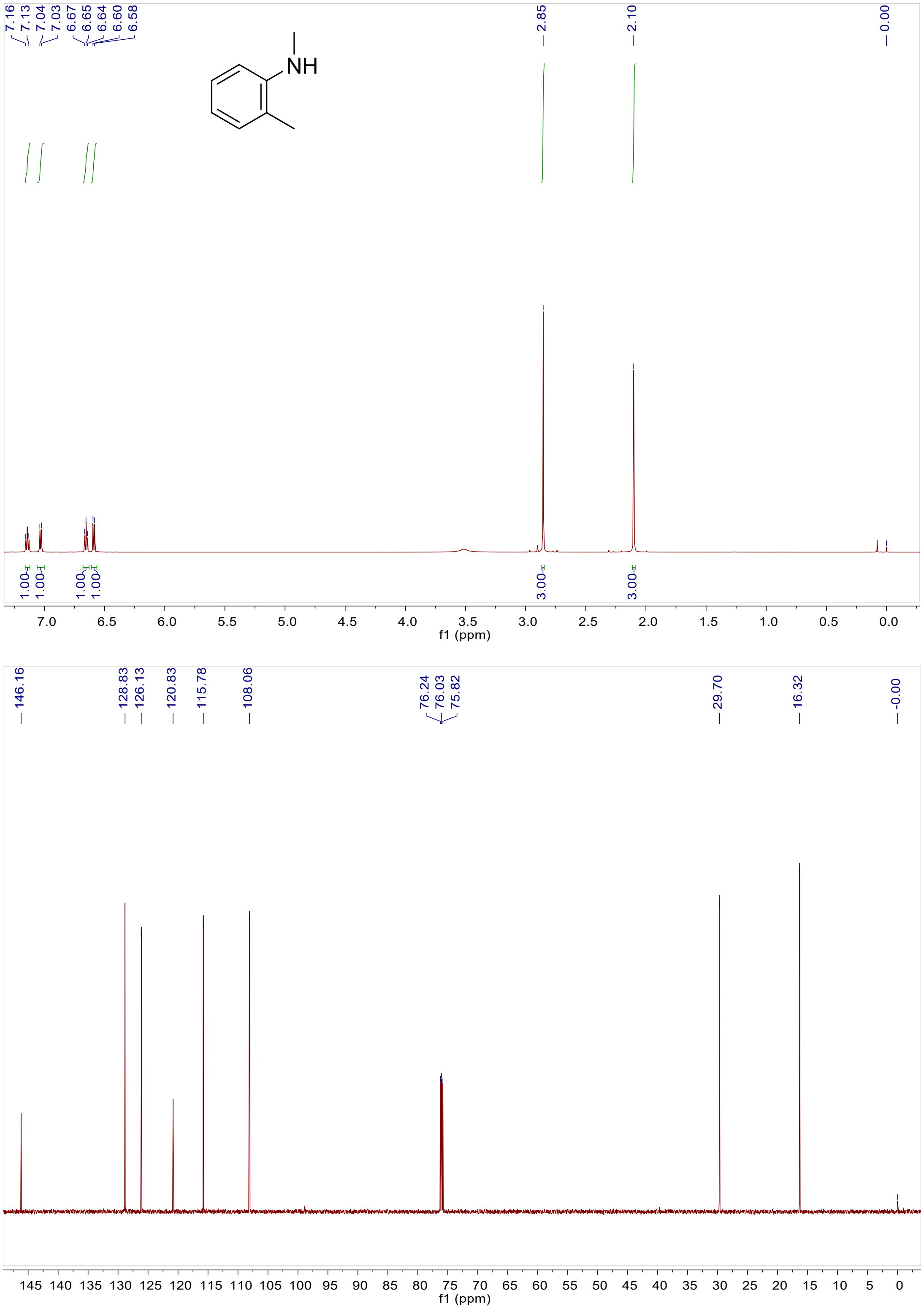
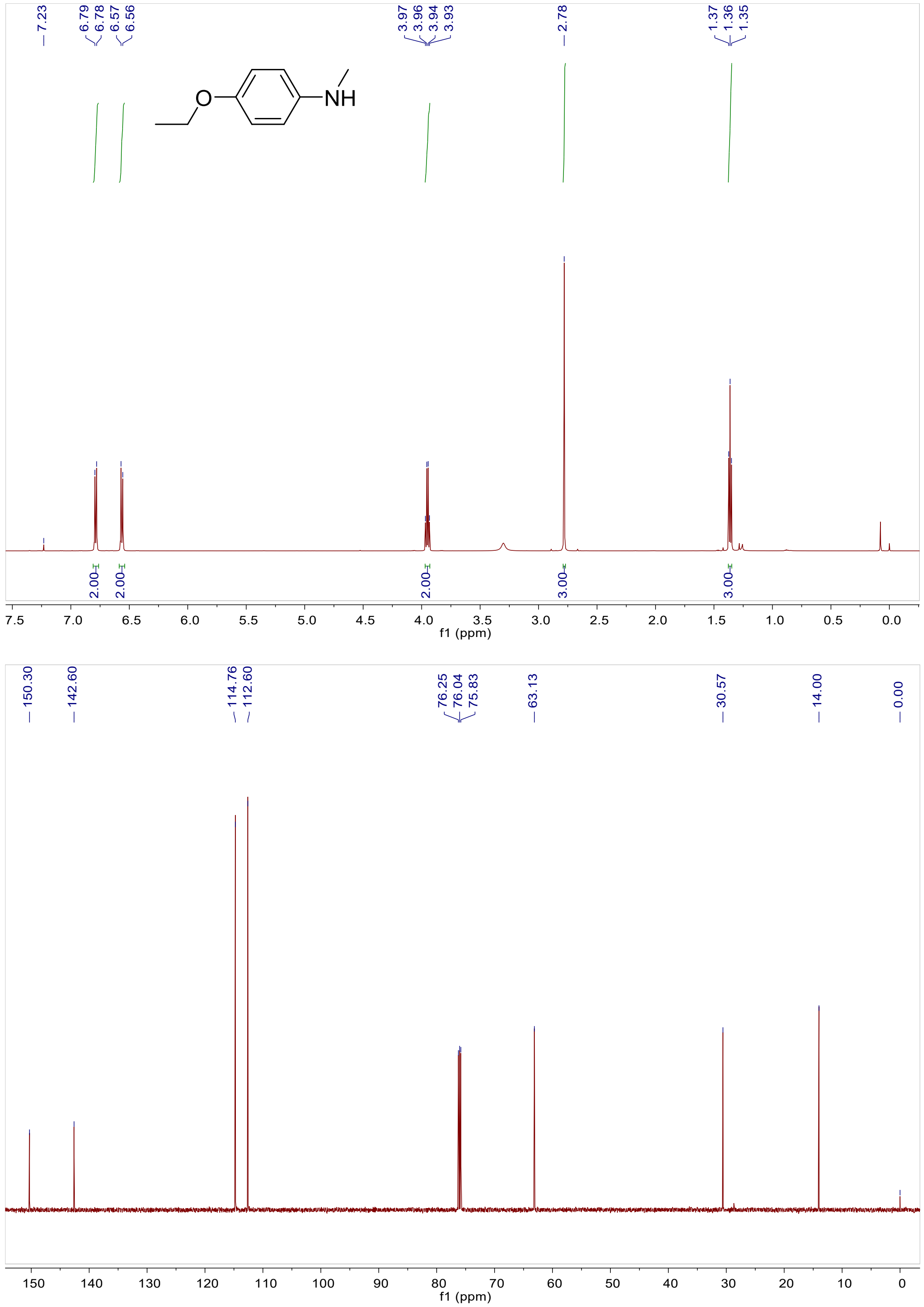




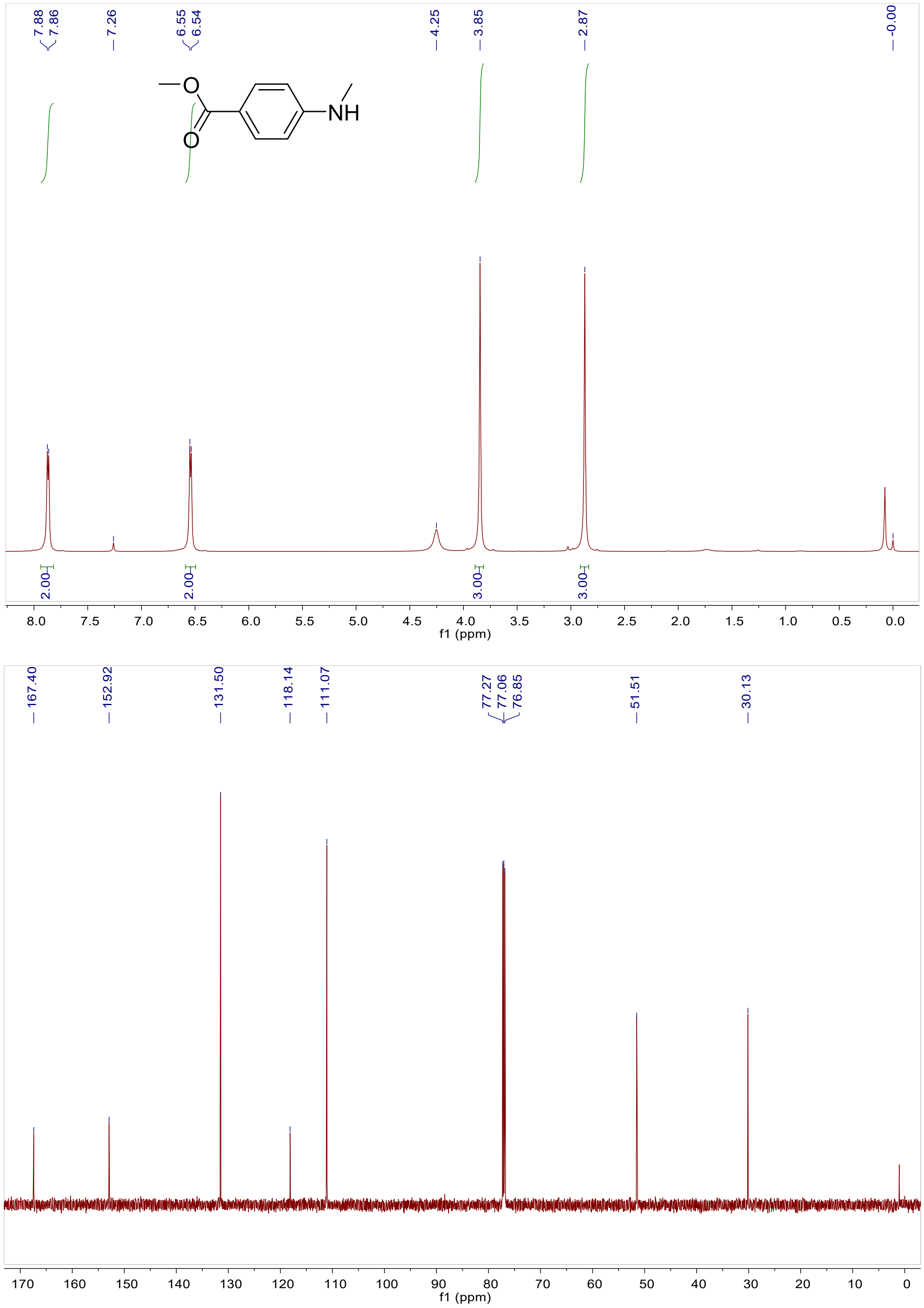
^{1}H-NMR and ^{13}C-NMR of compound **3b**.



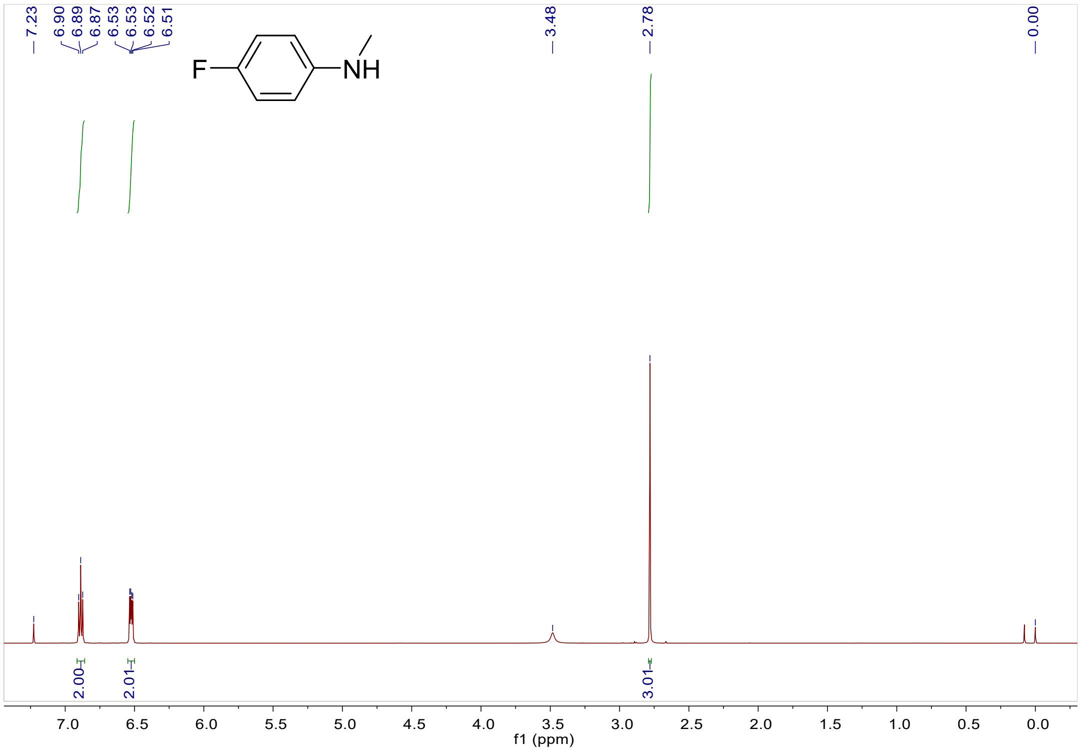
^{1}H-NMR and ^{13}C-NMR of compound **3c**.

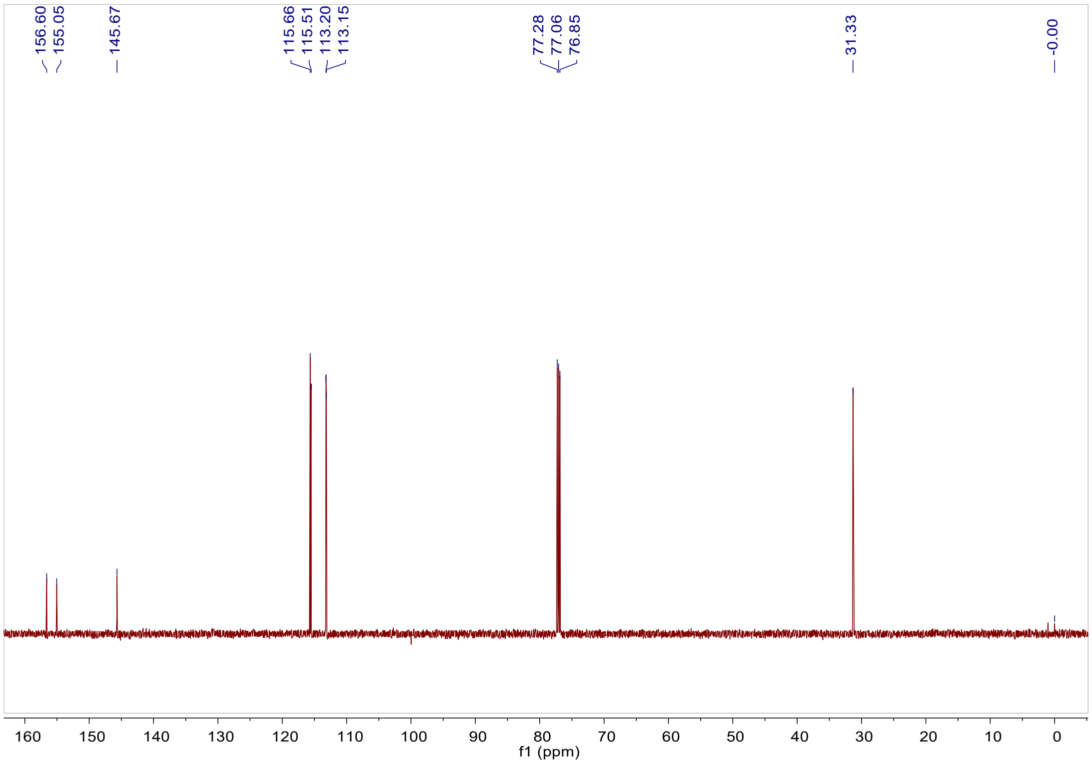


^{1}H-NMR and ^{13}C-NMR of compound **3d**.

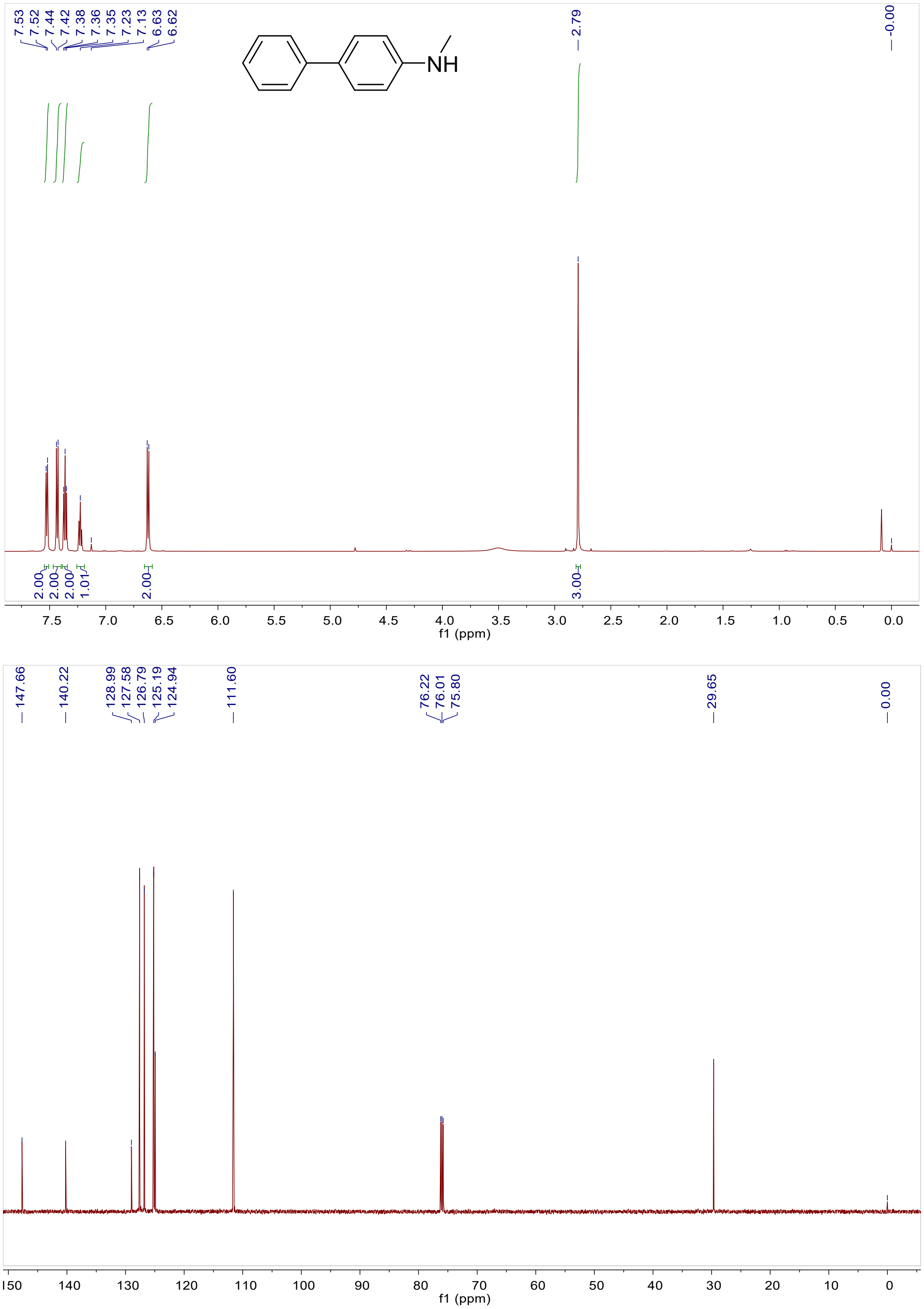


^{1}H-NMR and ^{13}C-NMR of compound **3e**.

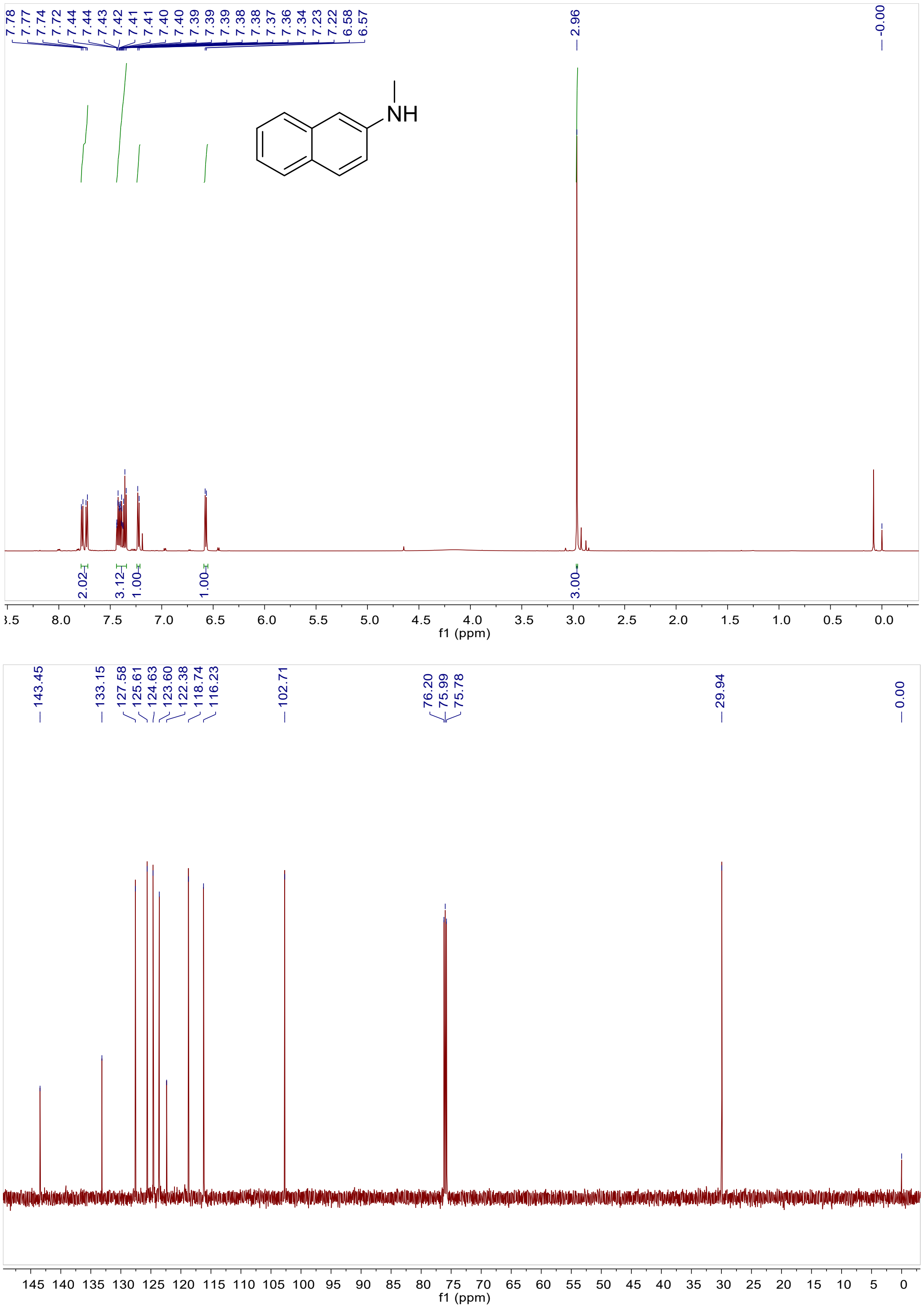




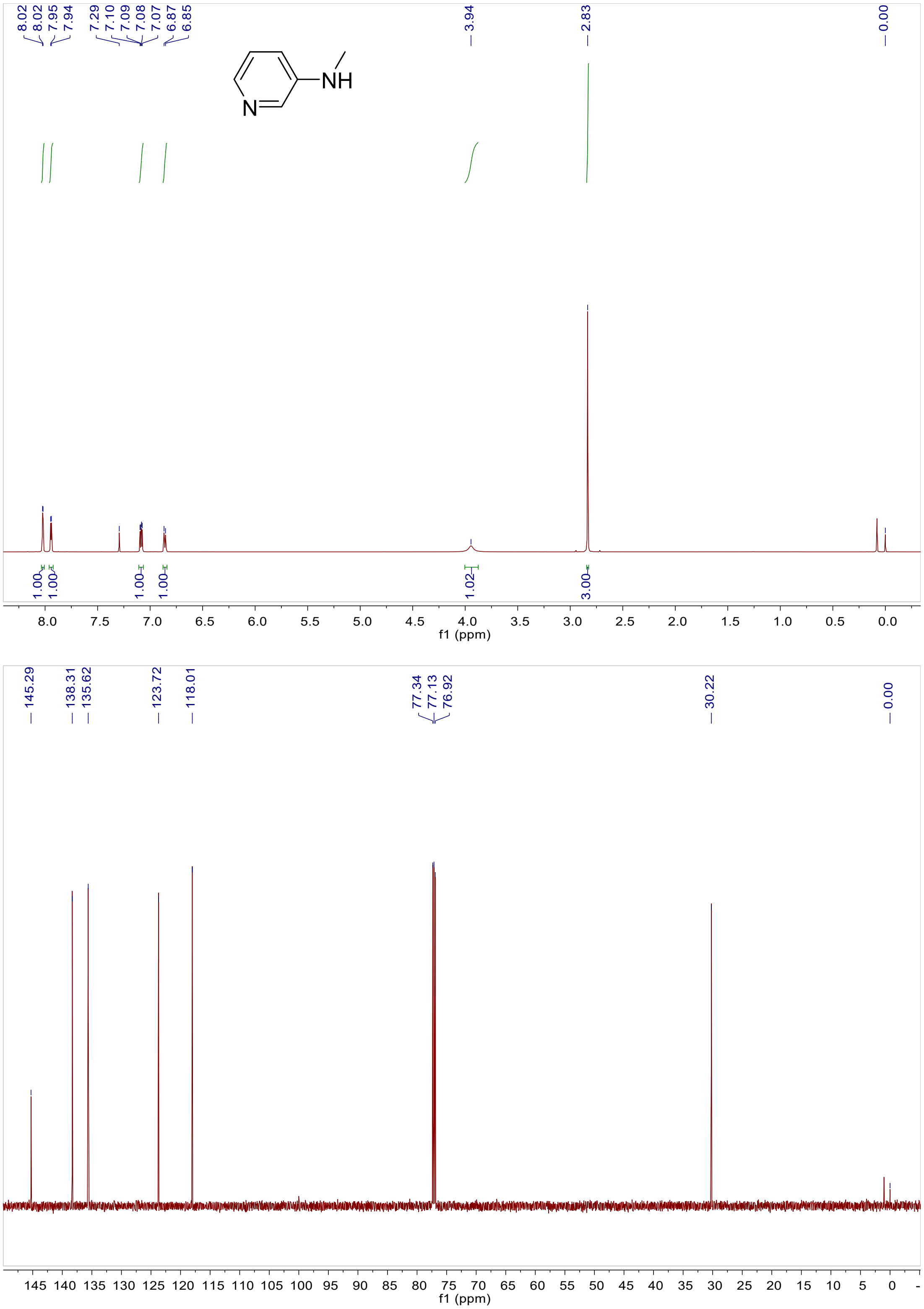
^{1}H-NMR and ^{13}C-NMR of compound **3f**.



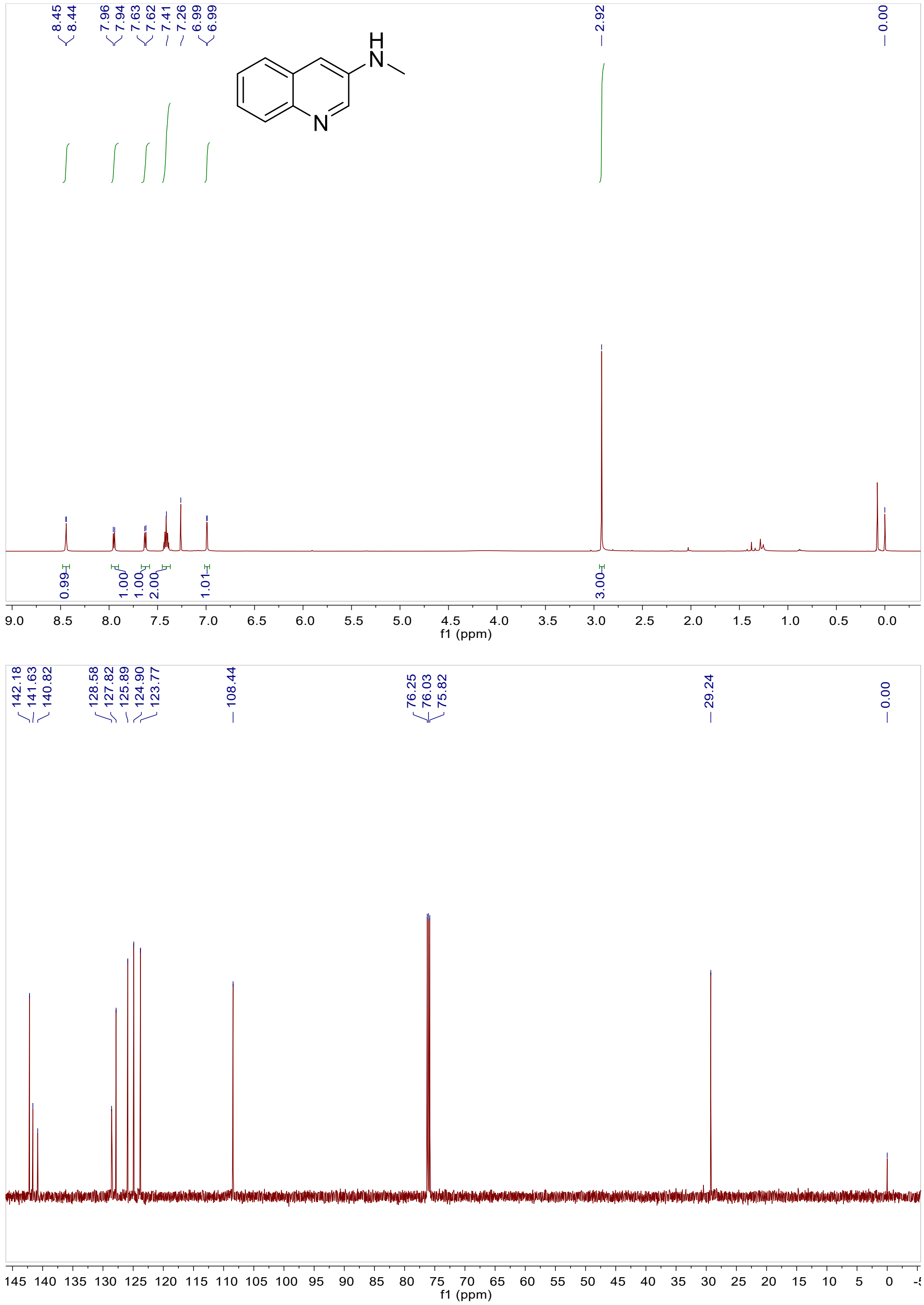
^{1}H-NMR and ^{13}C-NMR of compound **3g**.



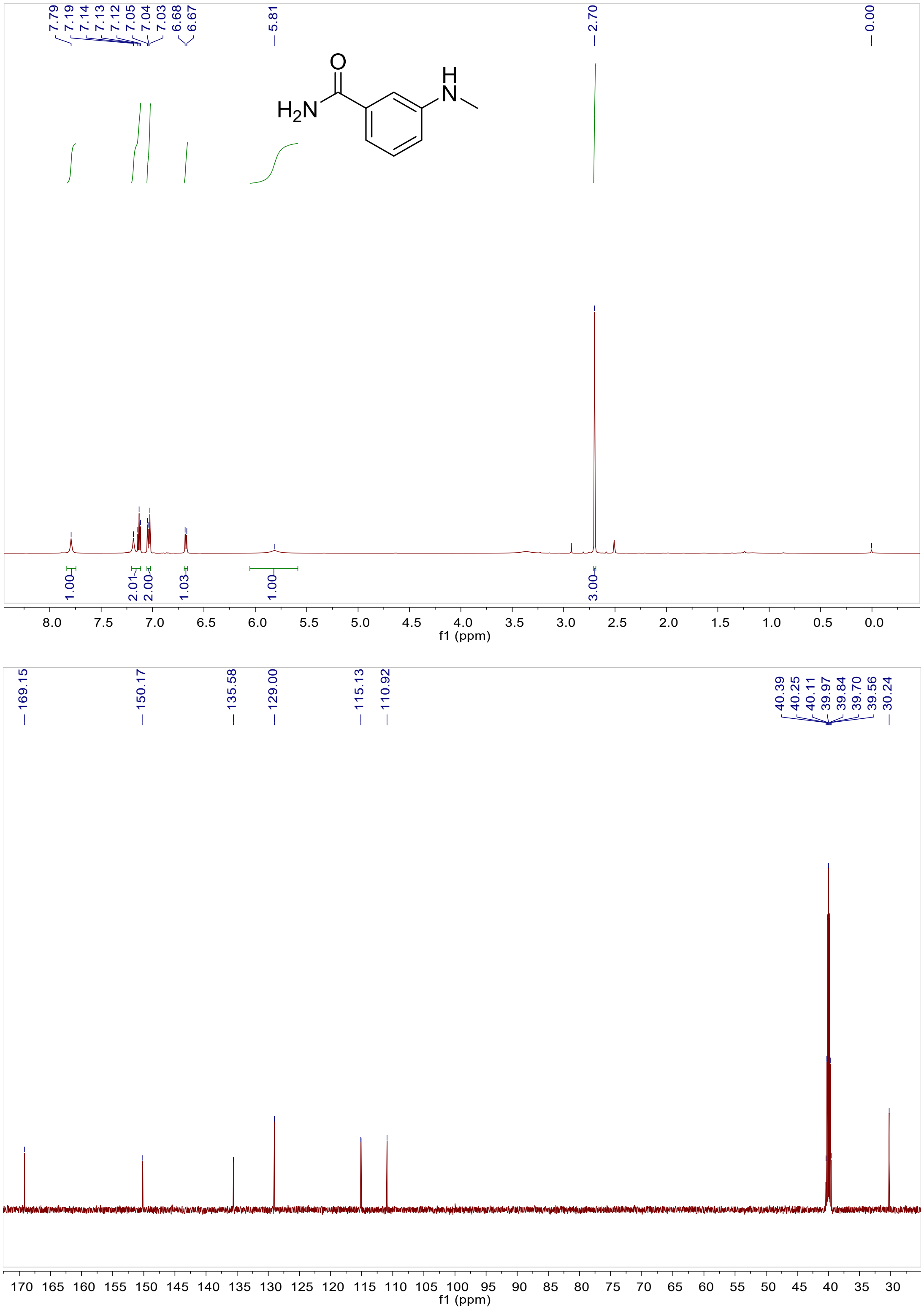
^{1}H-NMR and ^{13}C-NMR of compound **3h**.



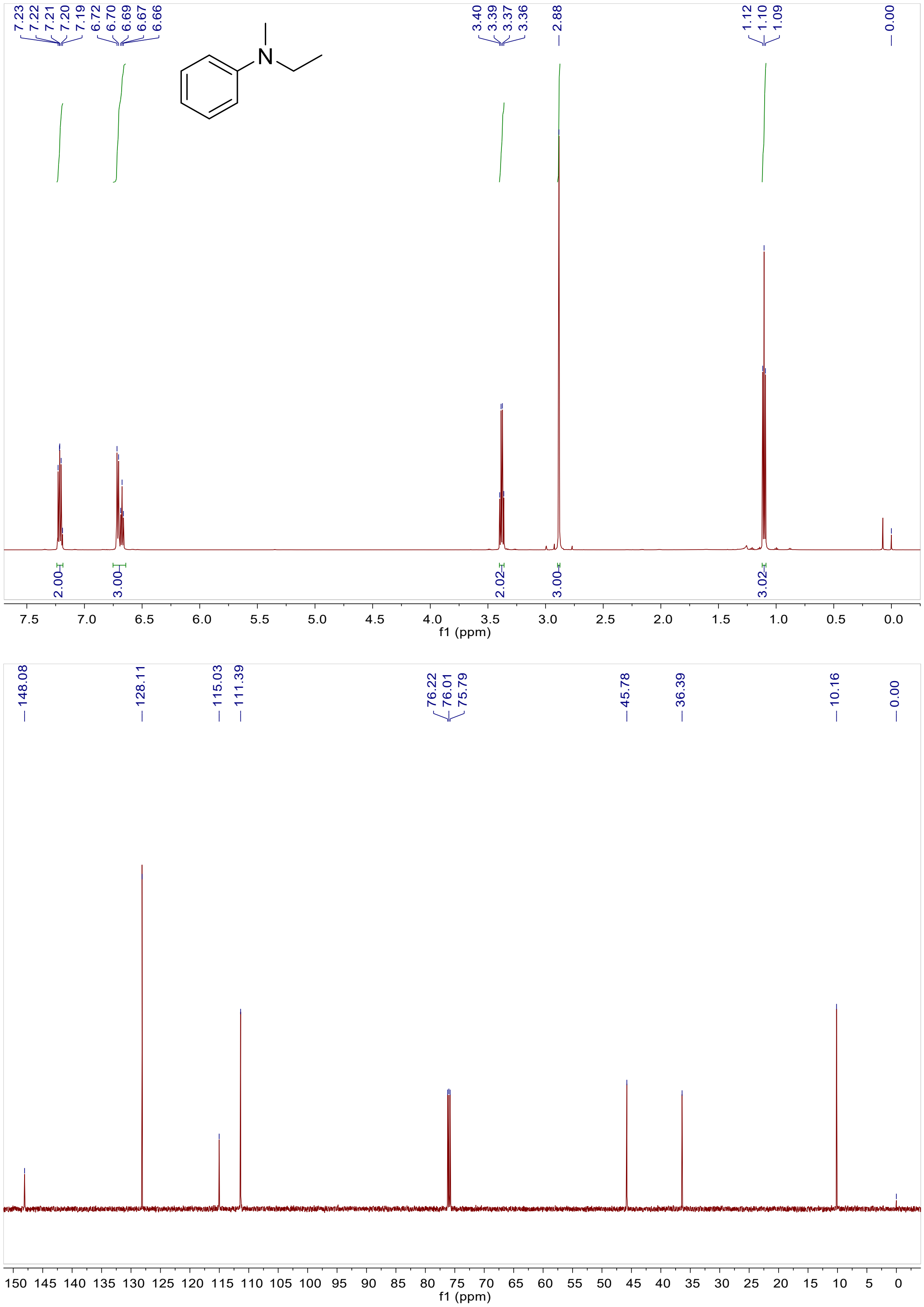
^{1}H-NMR and ^{13}C-NMR of compound **3i**.



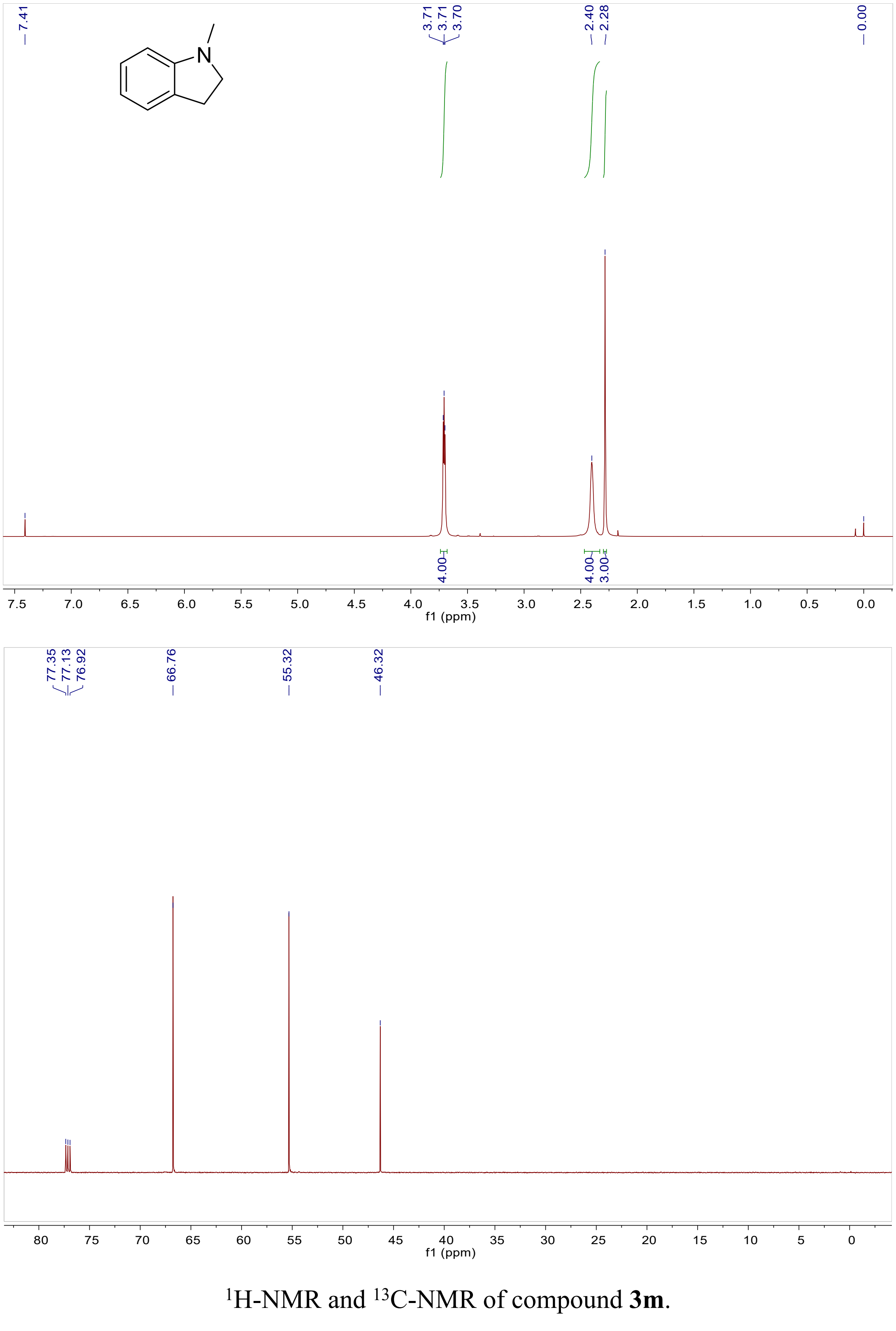
^{1}H-NMR and ^{13}C-NMR of compound **3j**.



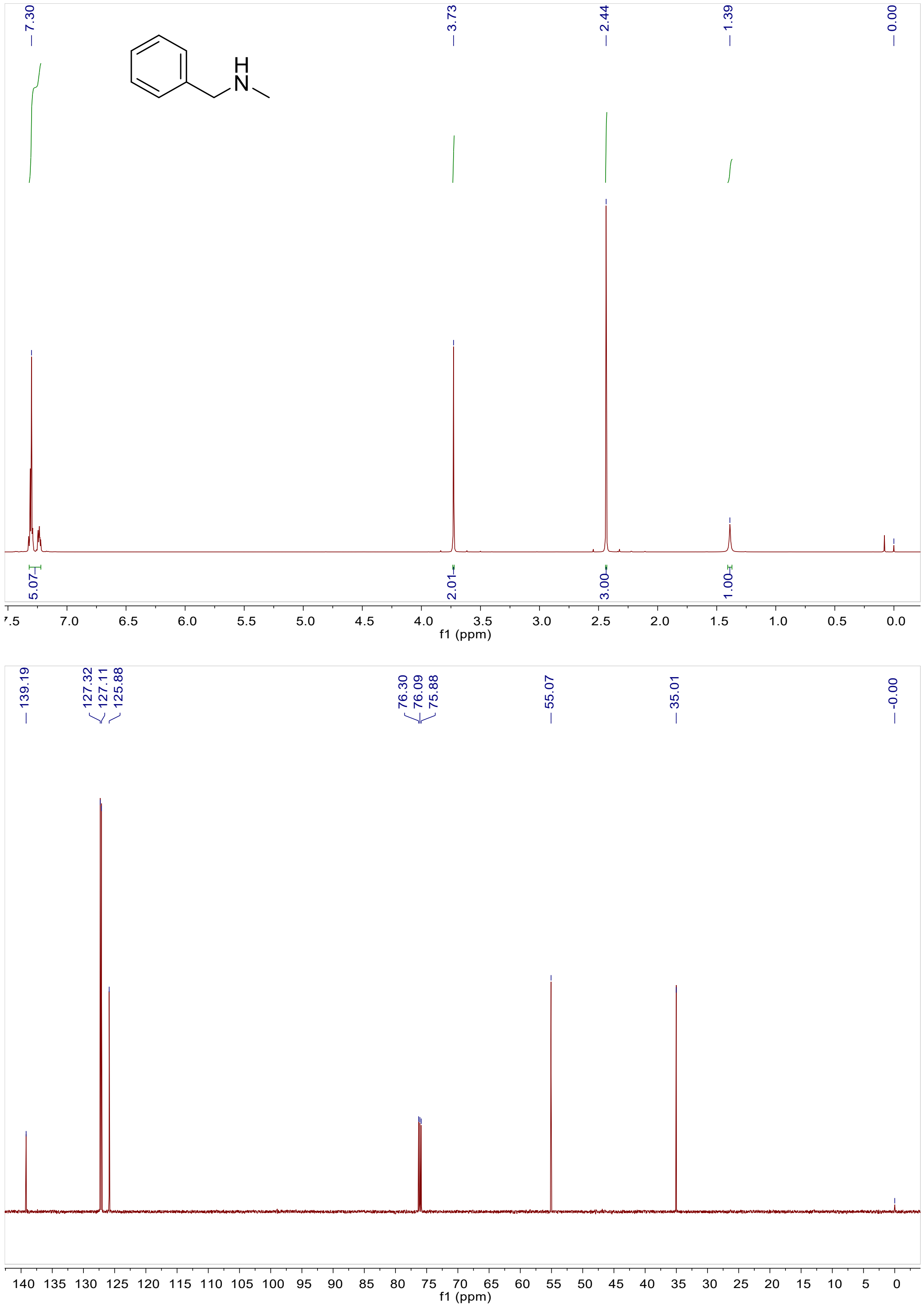
^{1}H-NMR and ^{13}C-NMR of compound **3k**.



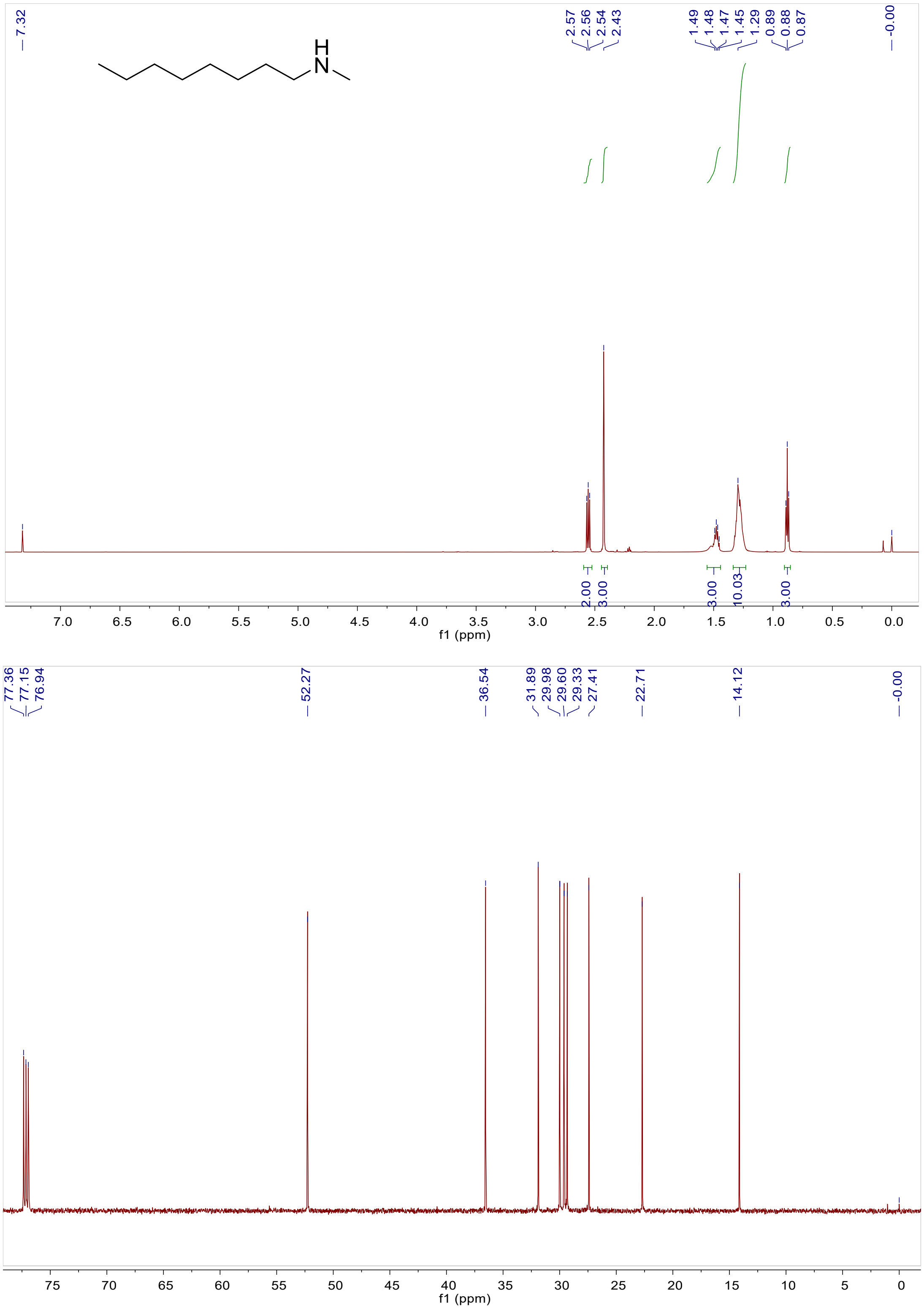
^{1}H-NMR and ^{13}C-NMR of compound **3l**.



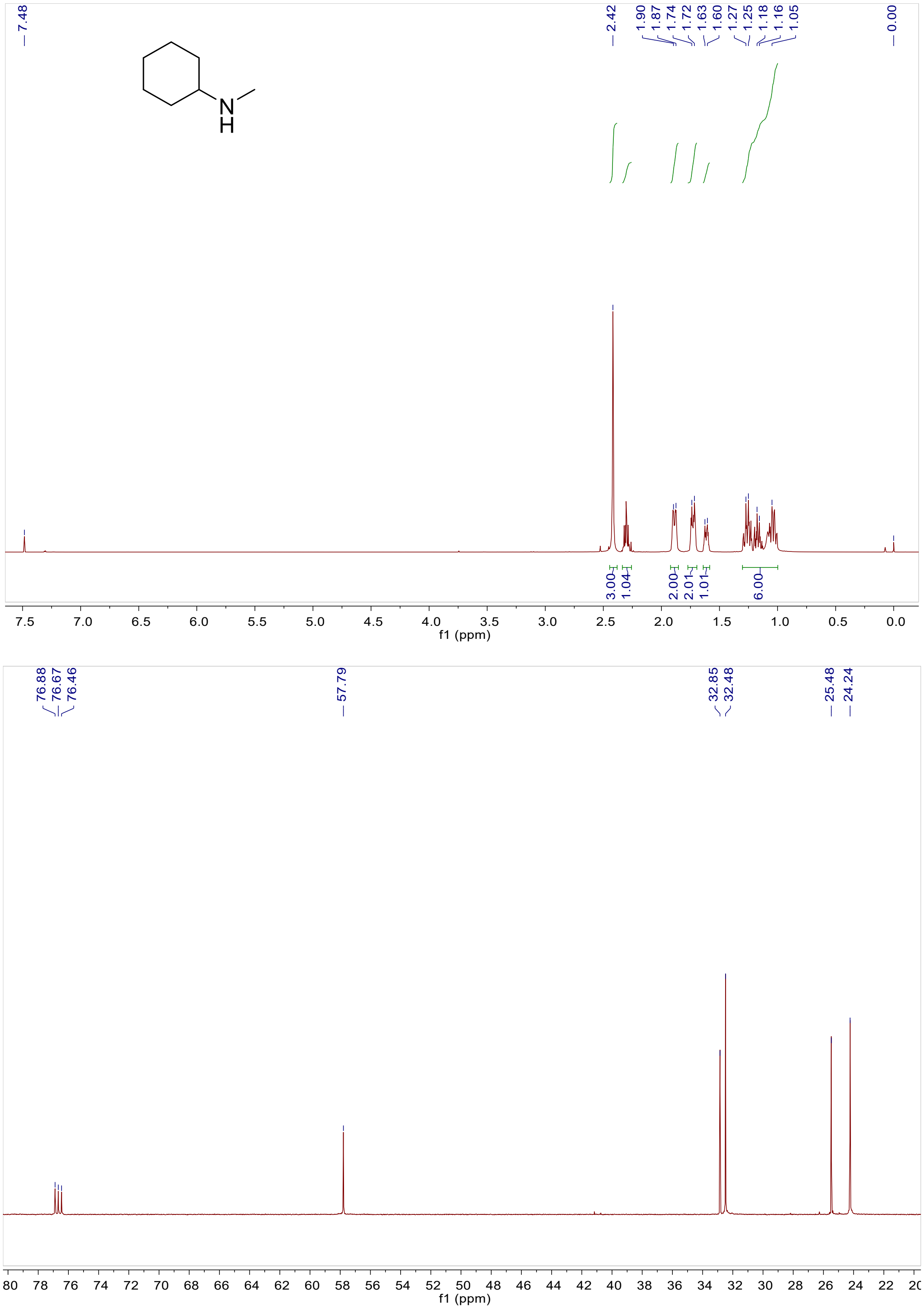
^{1}H-NMR and ^{13}C-NMR of compound **3m**.



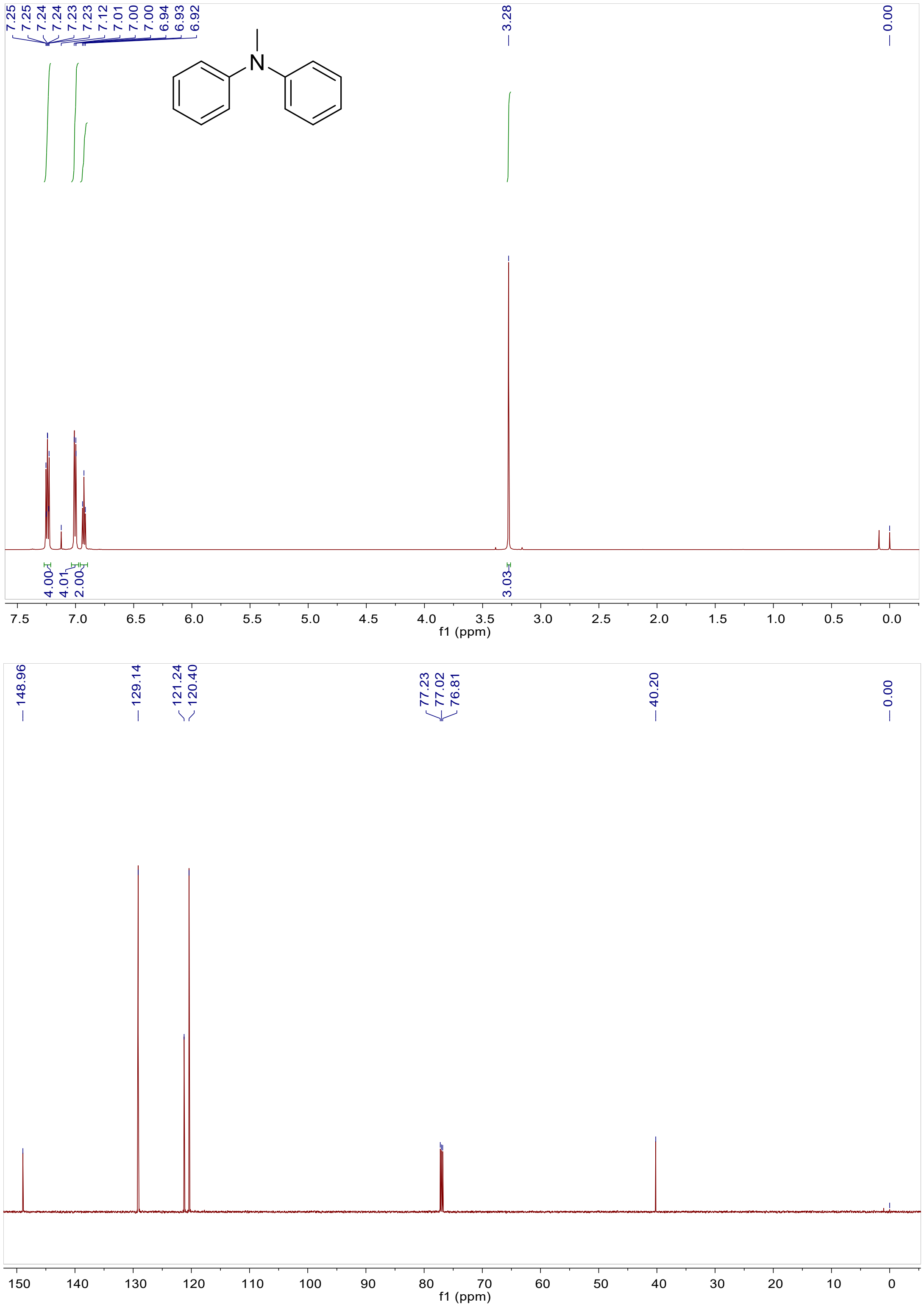
^{1}H-NMR and ^{13}C-NMR of compound **3n**.



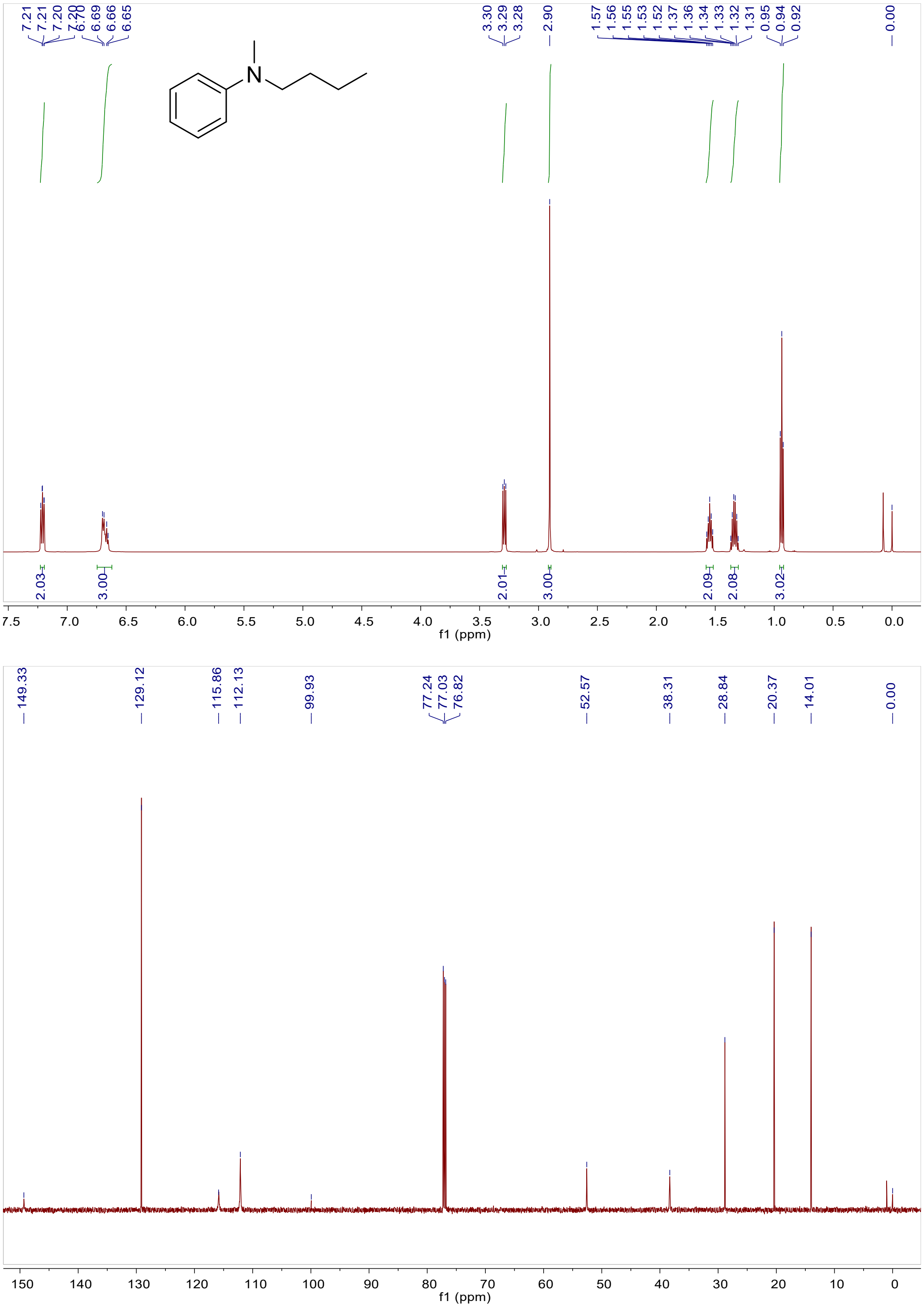
^{1}H-NMR and ^{13}C-NMR of compound **3o**.



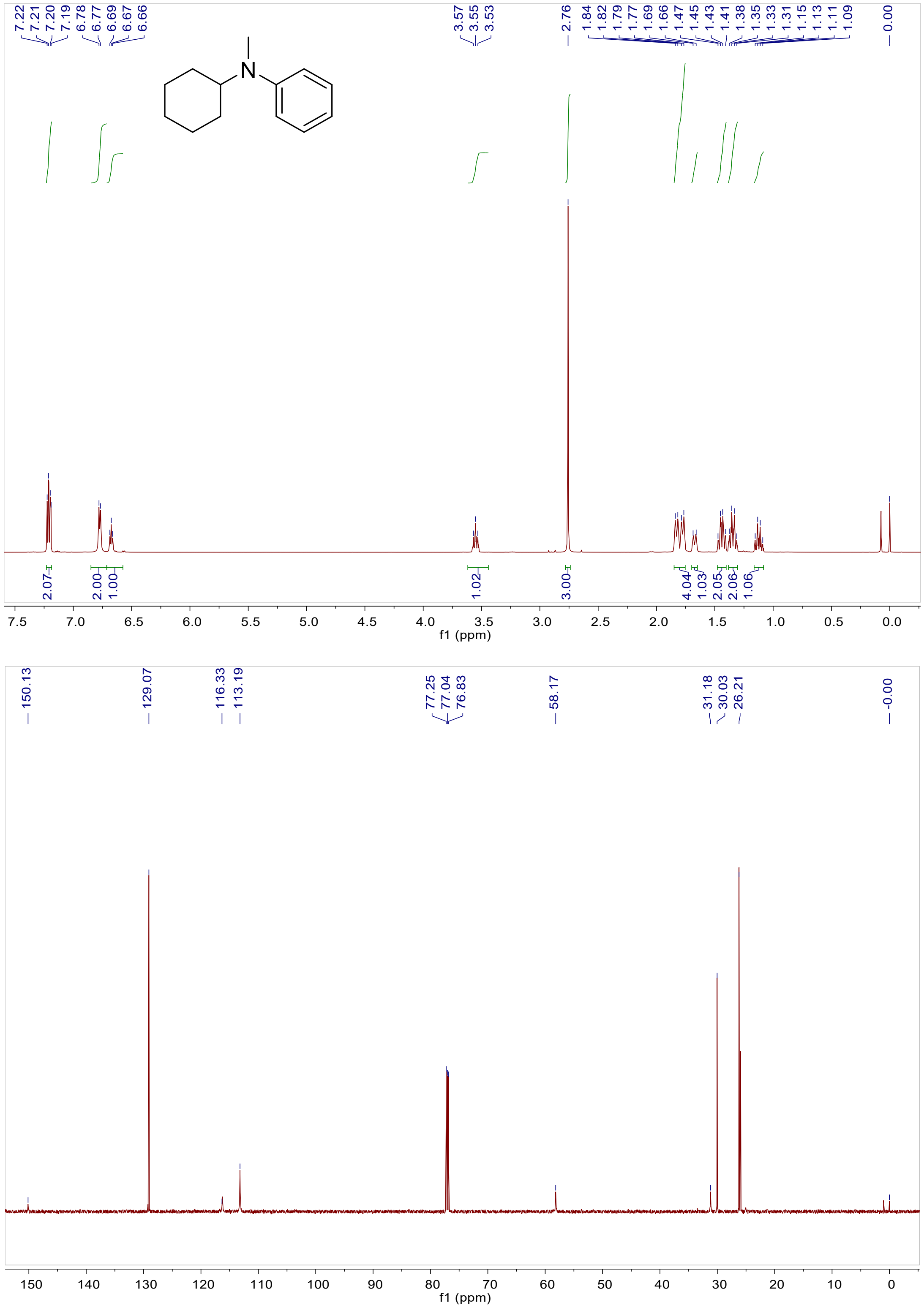
^{1}H-NMR and ^{13}C-NMR of compound **3p**.



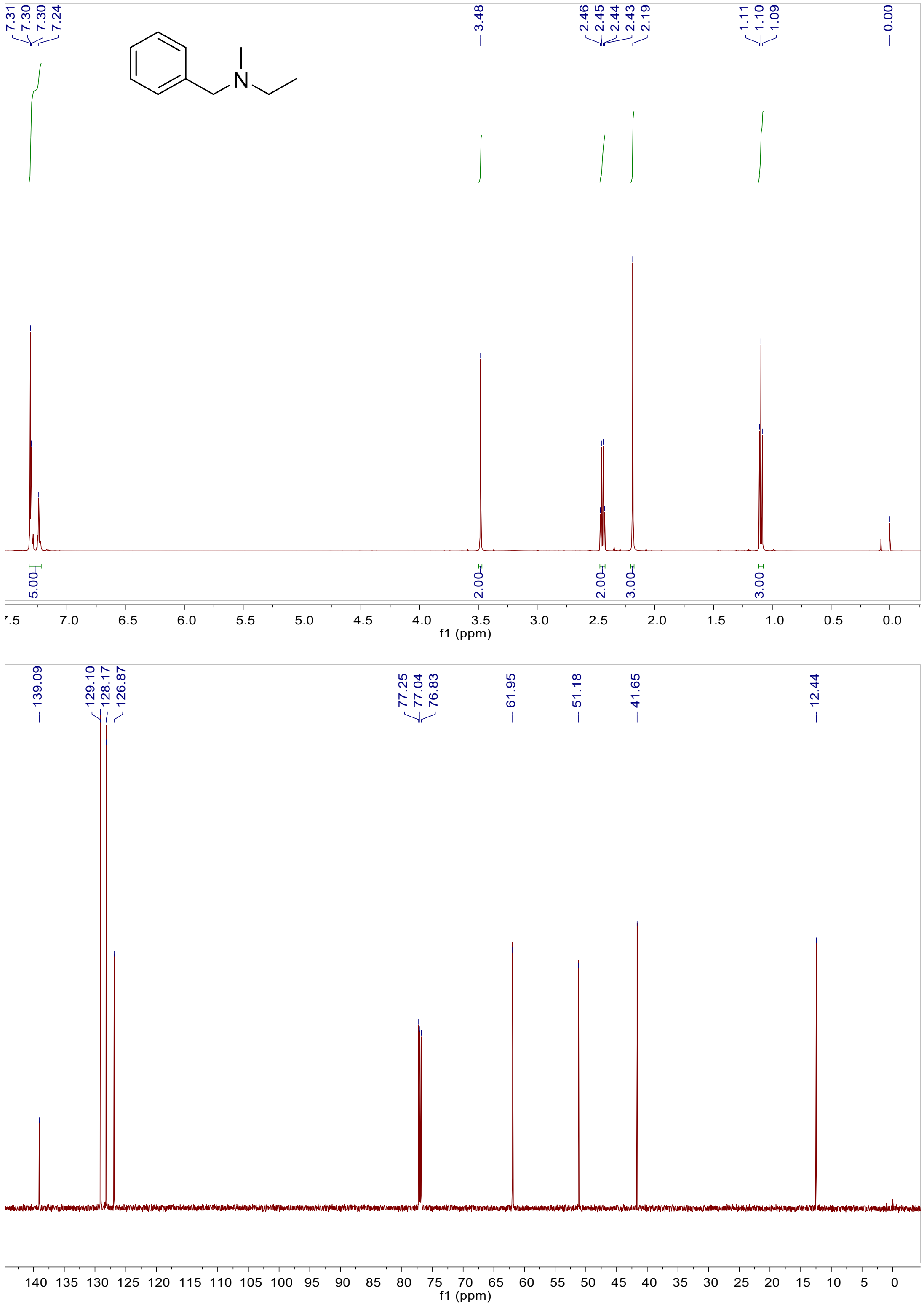
^{1}H-NMR and ^{13}C-NMR of compound **4a**.



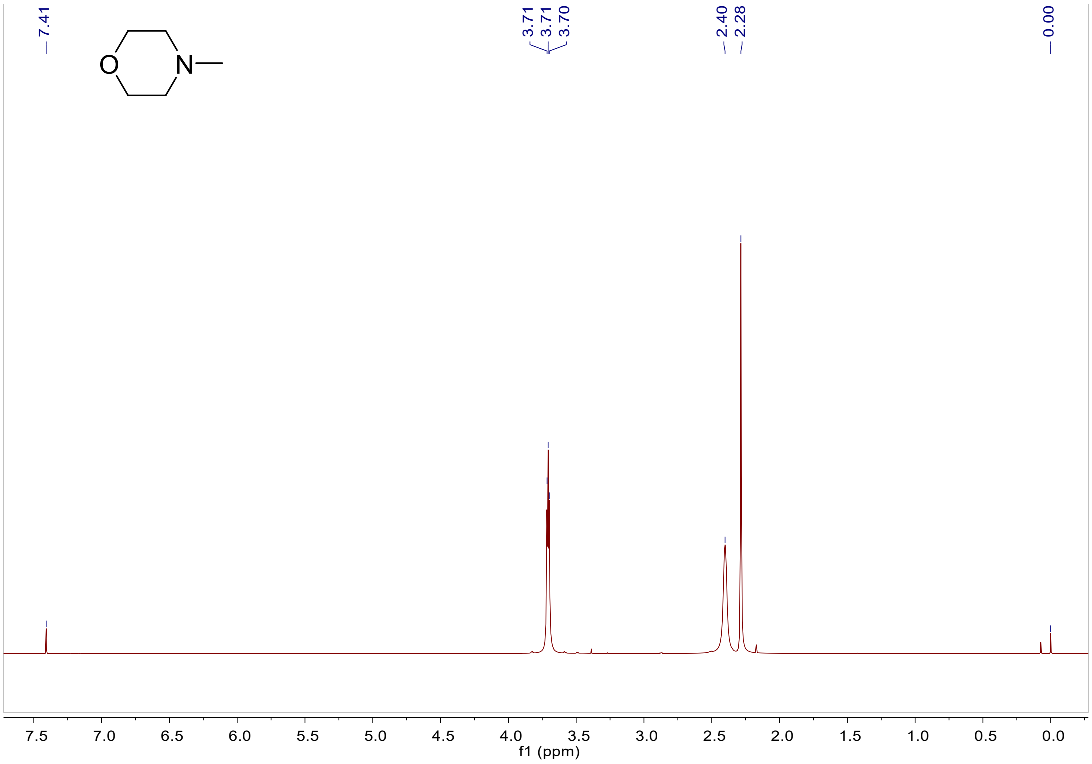
^{1}H-NMR and ^{13}C-NMR of compound **4b**.

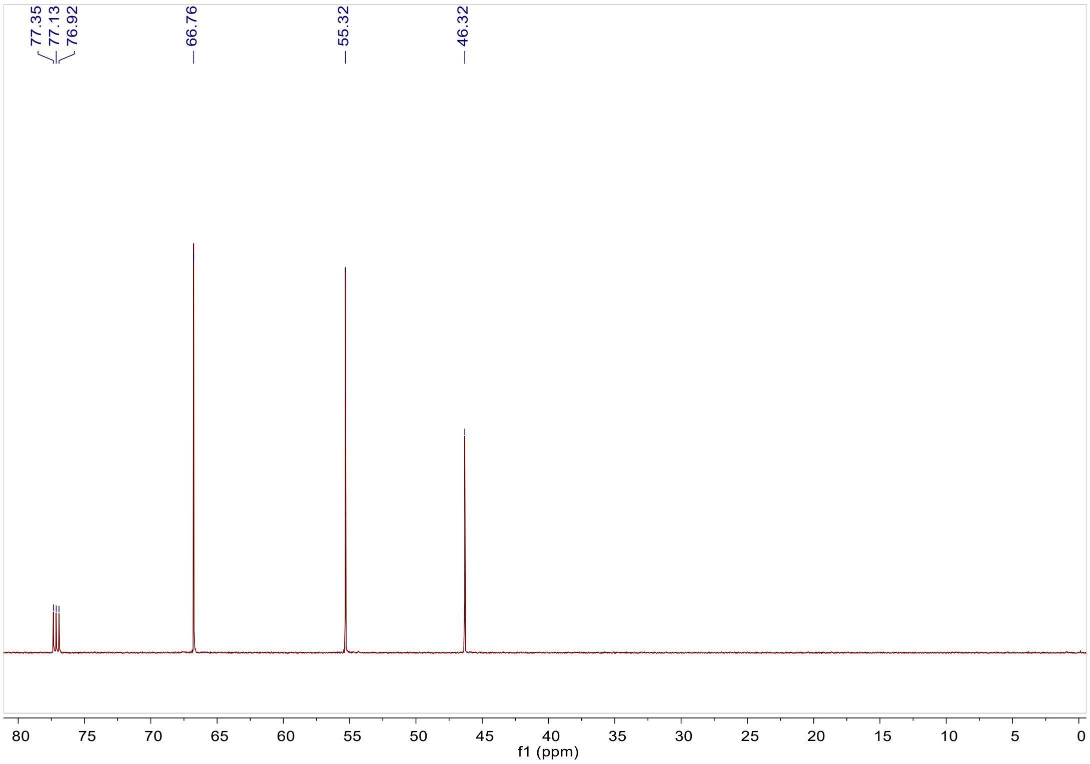


^{1}H-NMR and ^{13}C-NMR of compound **4c**.

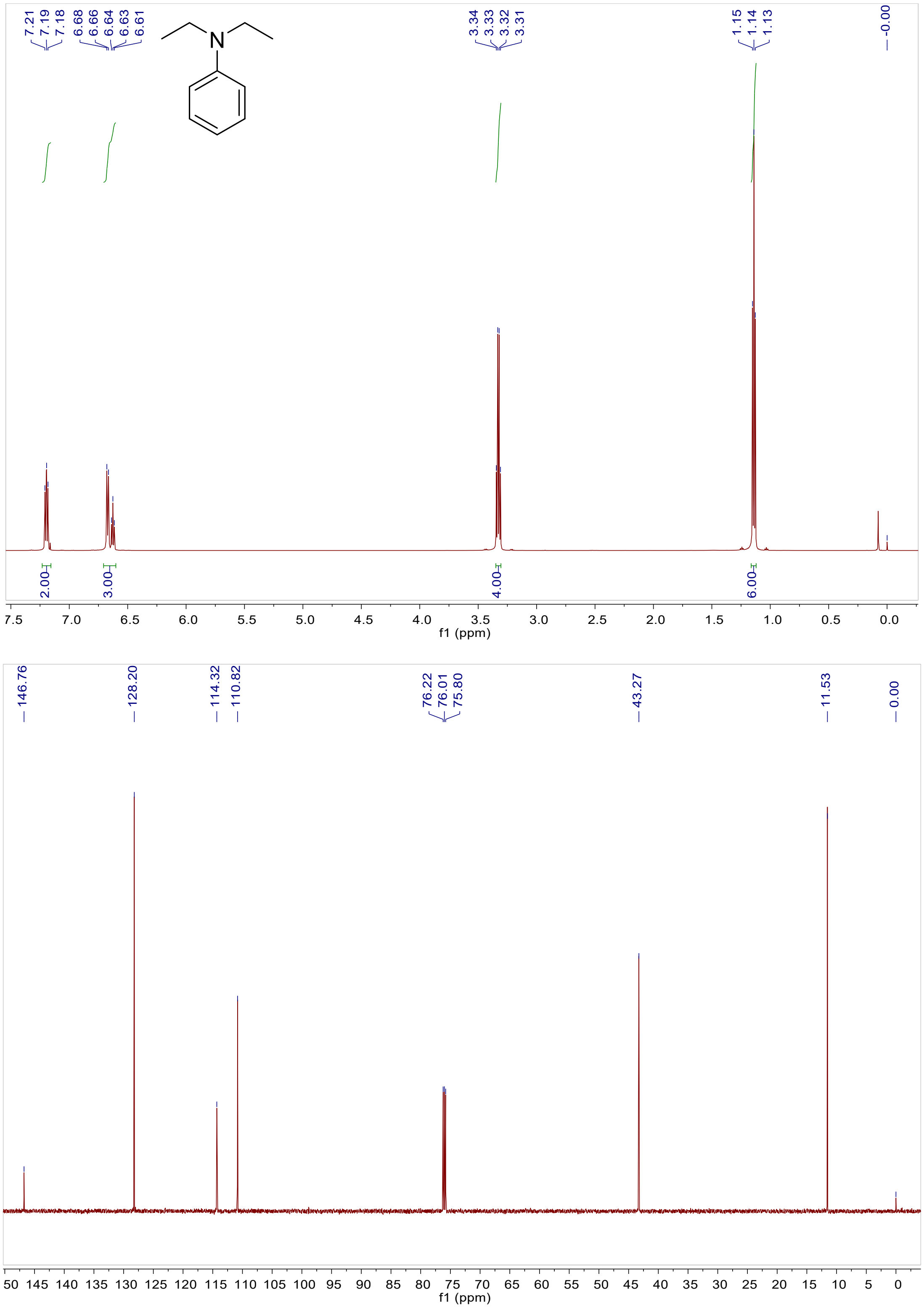


^{1}H-NMR and ^{13}C-NMR of compound **4d**.

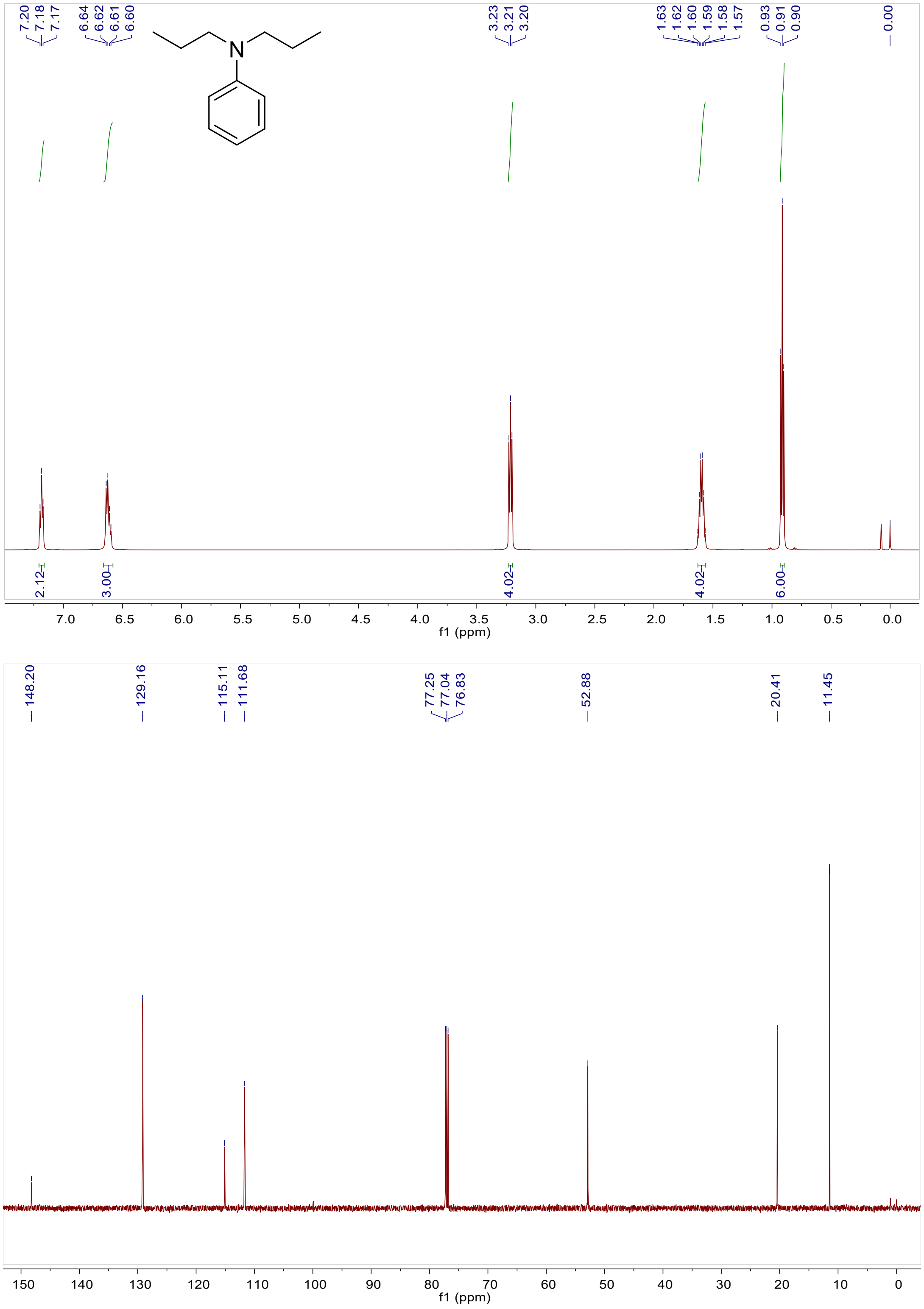




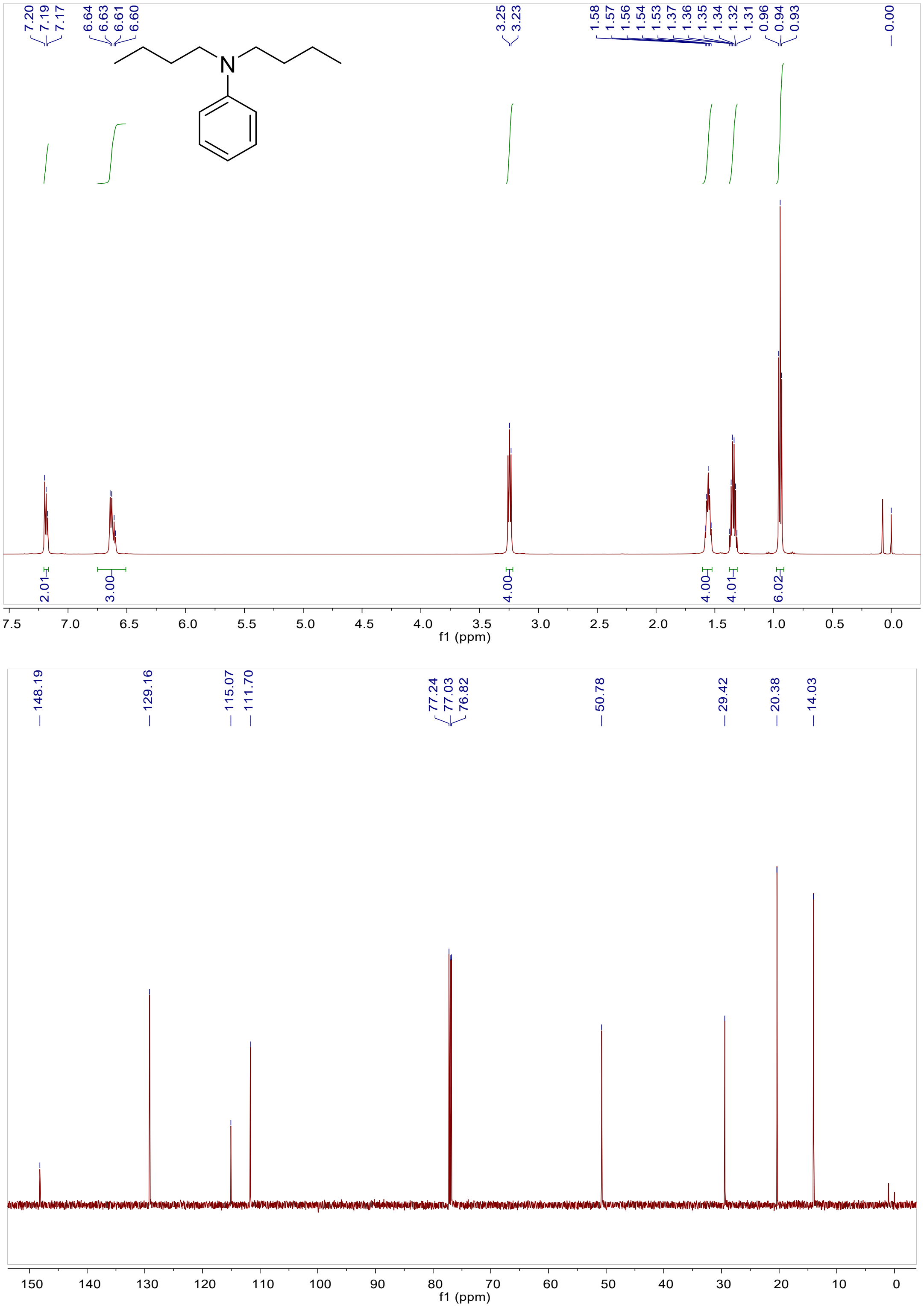
^{1}H-NMR and ^{13}C-NMR of compound **4e**.



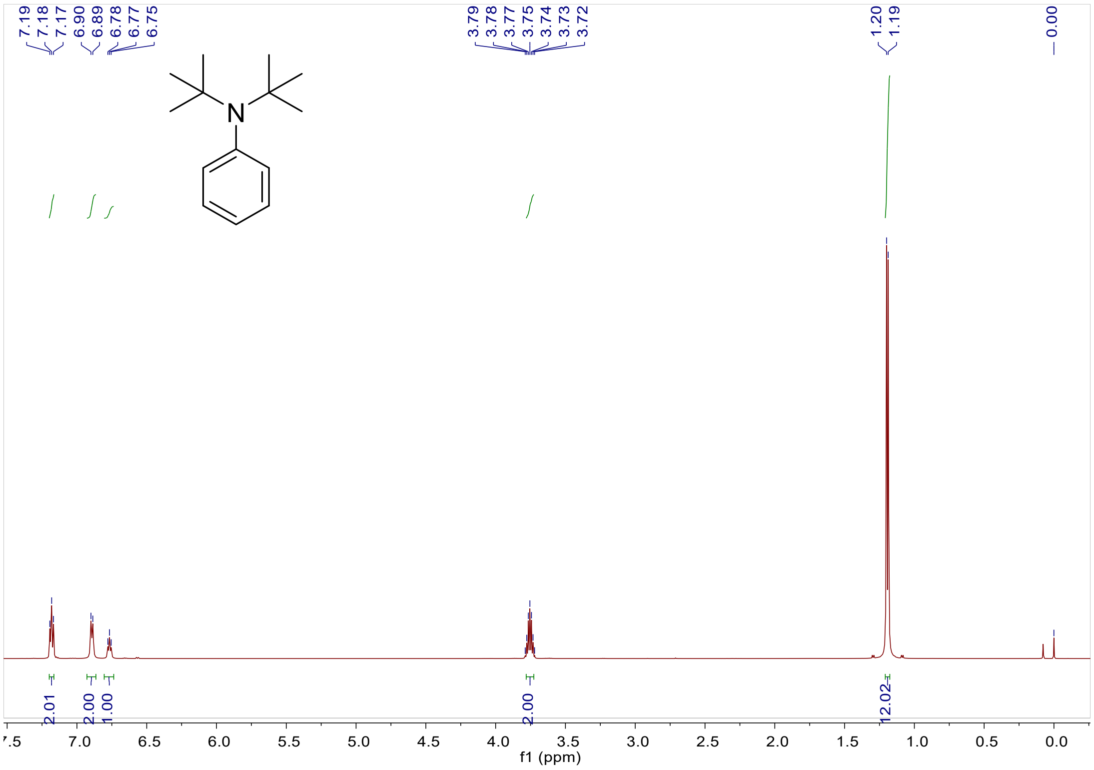
^{1}H-NMR and ^{13}C-NMR of compound **5a**.

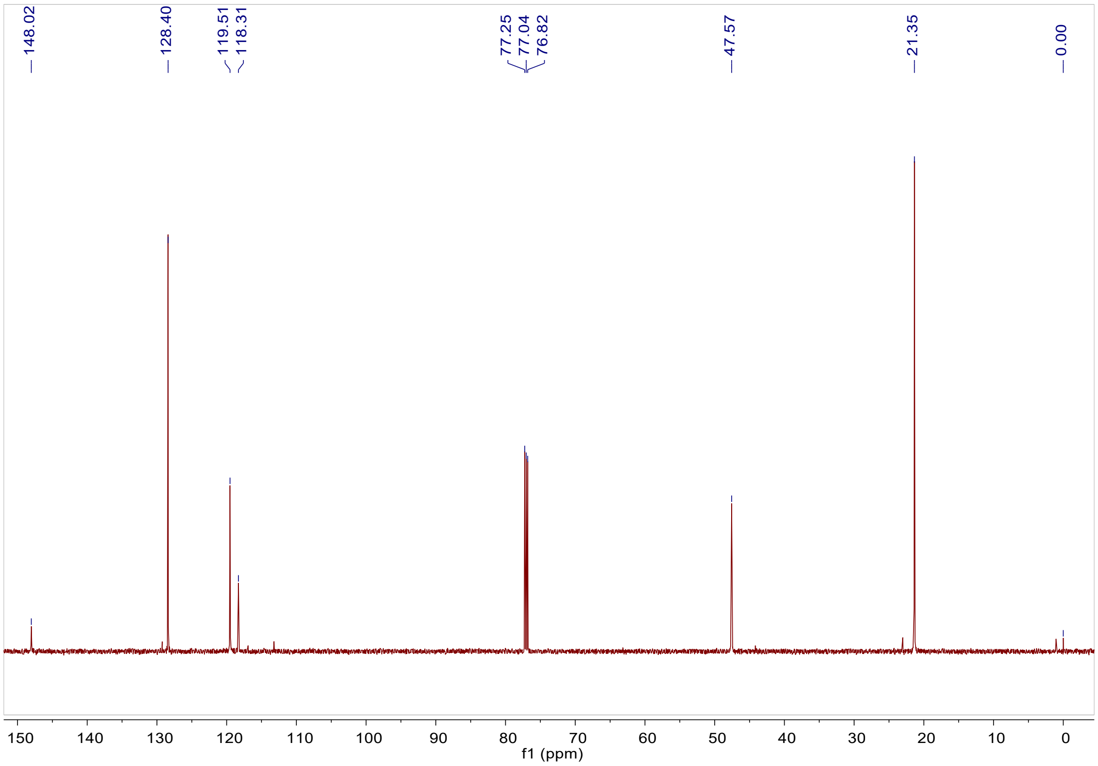


^{1}H-NMR and ^{13}C-NMR of compound **5b**.

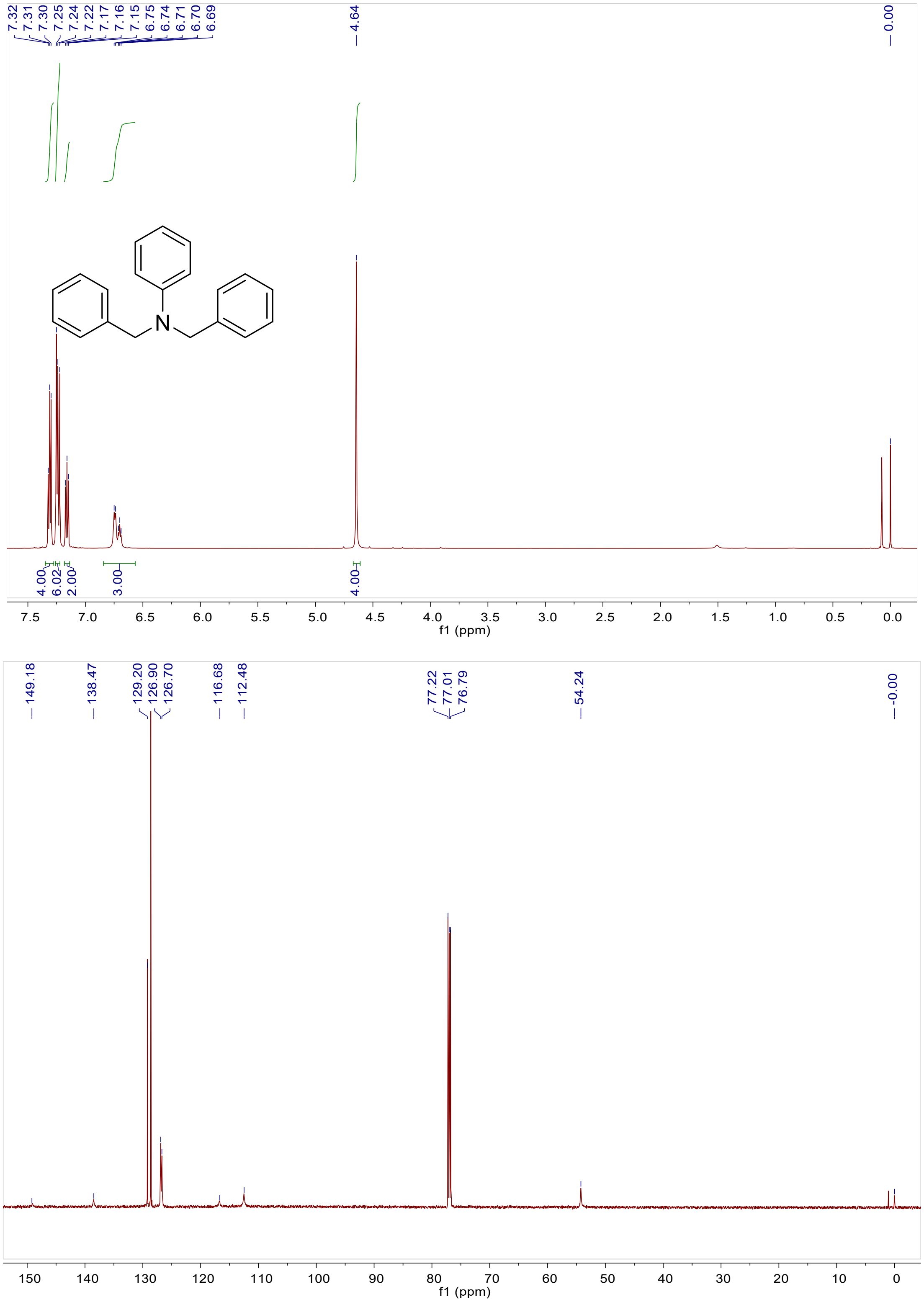


^{1}H-NMR and ^{13}C-NMR of compound **5c**.

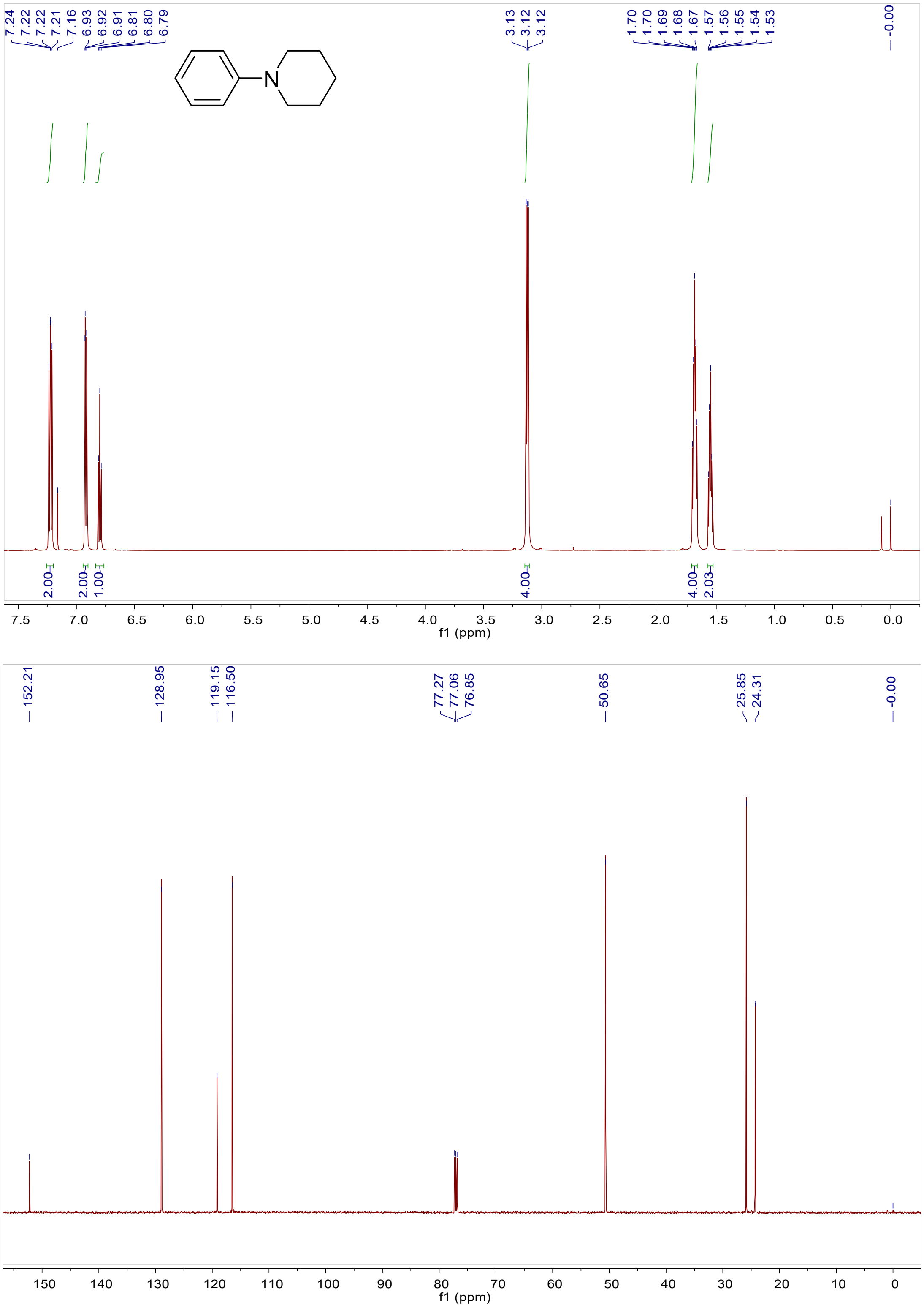




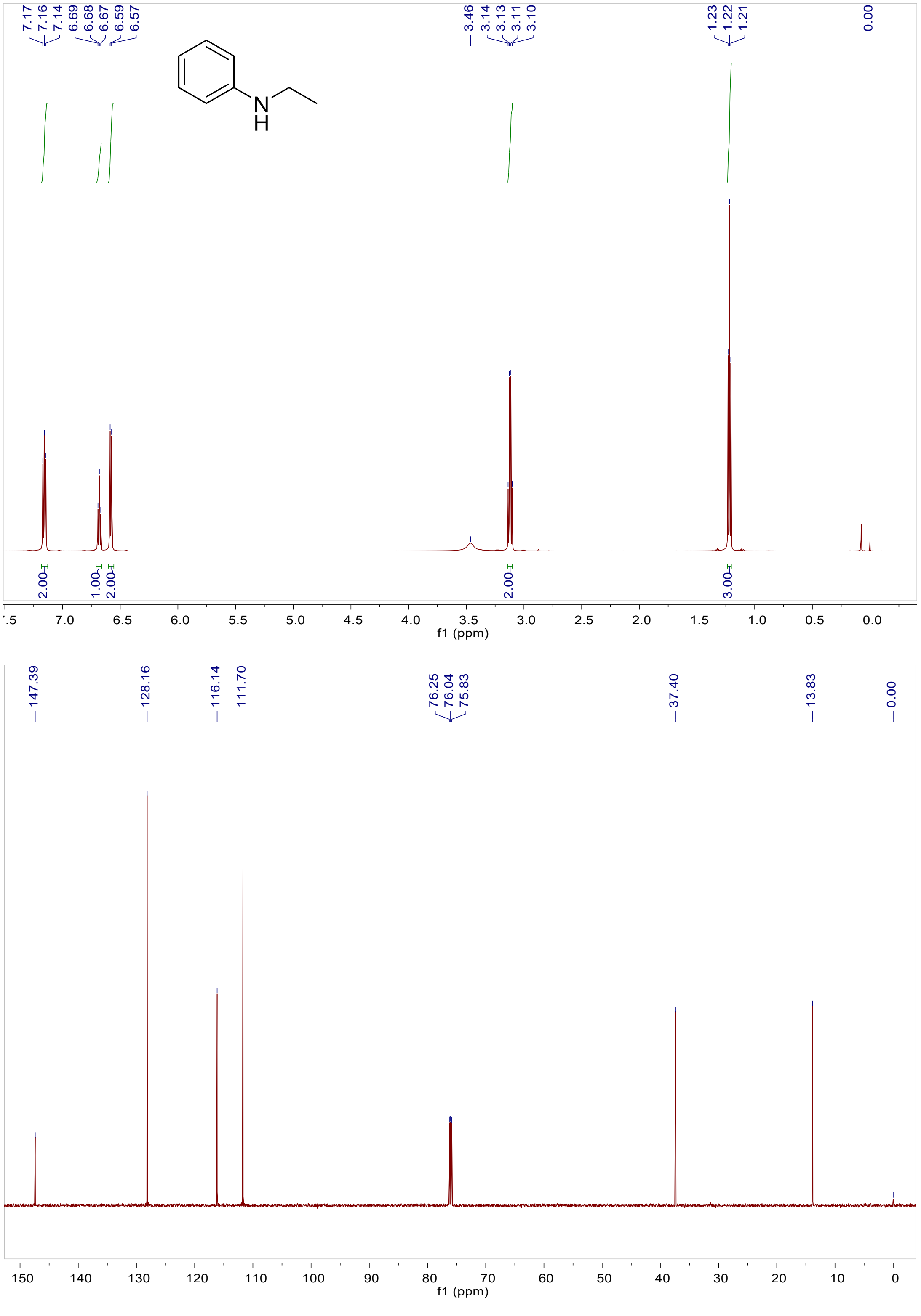
^{1}H-NMR and ^{13}C-NMR of compound **5d**.



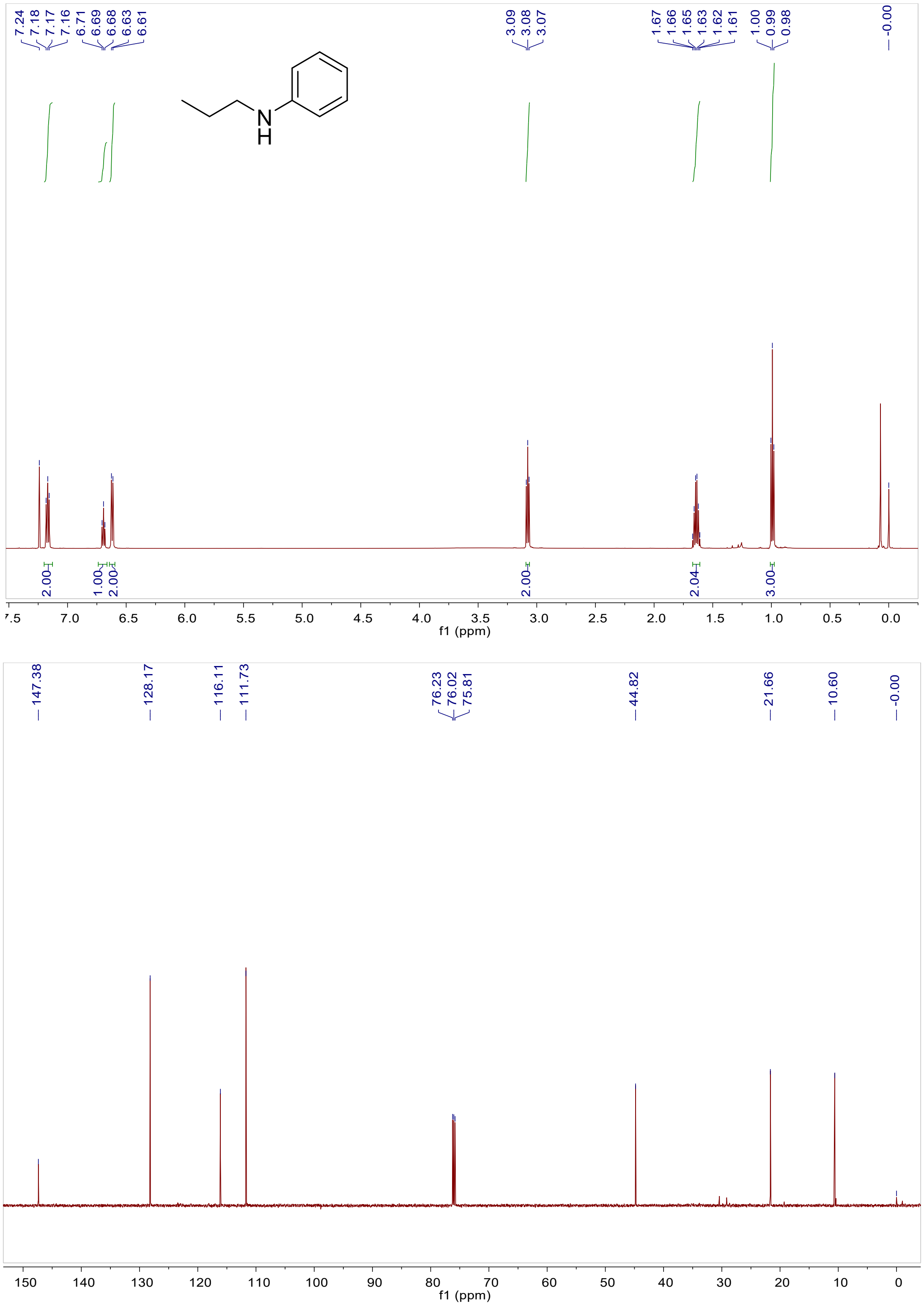
^{1}H-NMR and ^{13}C-NMR of compound **5e**.



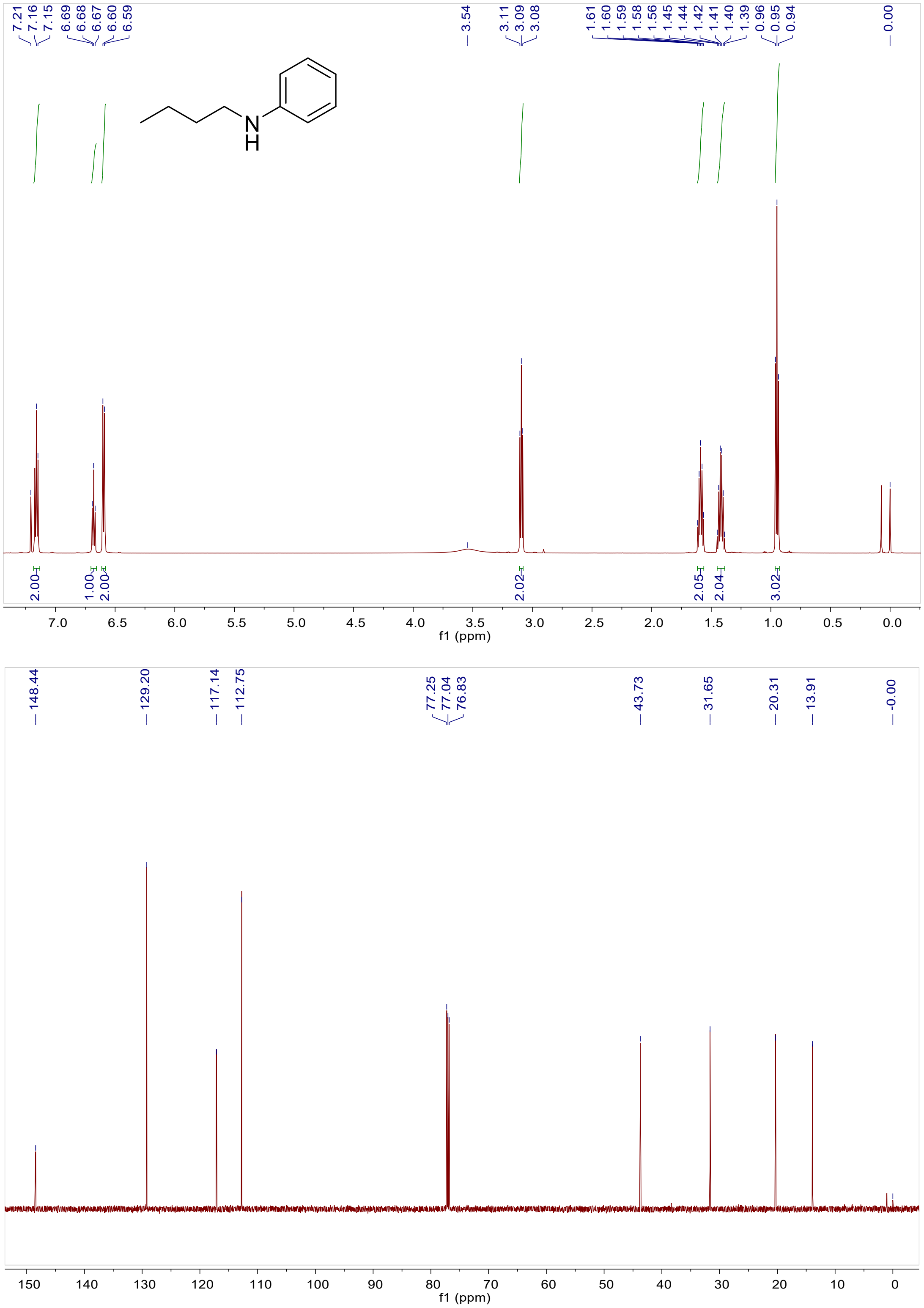
^{1}H-NMR and ^{13}C-NMR of compound **5f**.



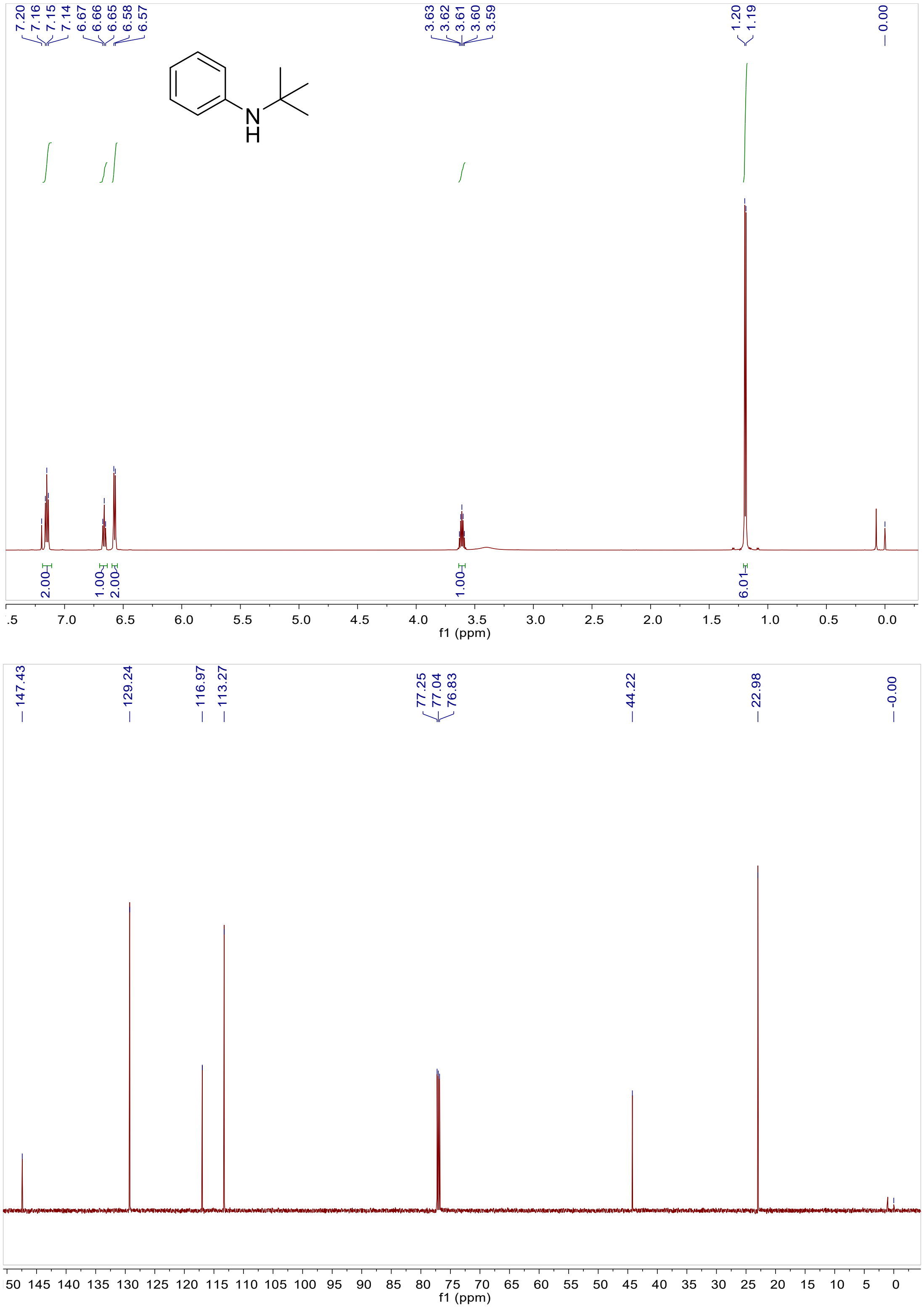
^{1}H-NMR and ^{13}C-NMR of compound **6a**.



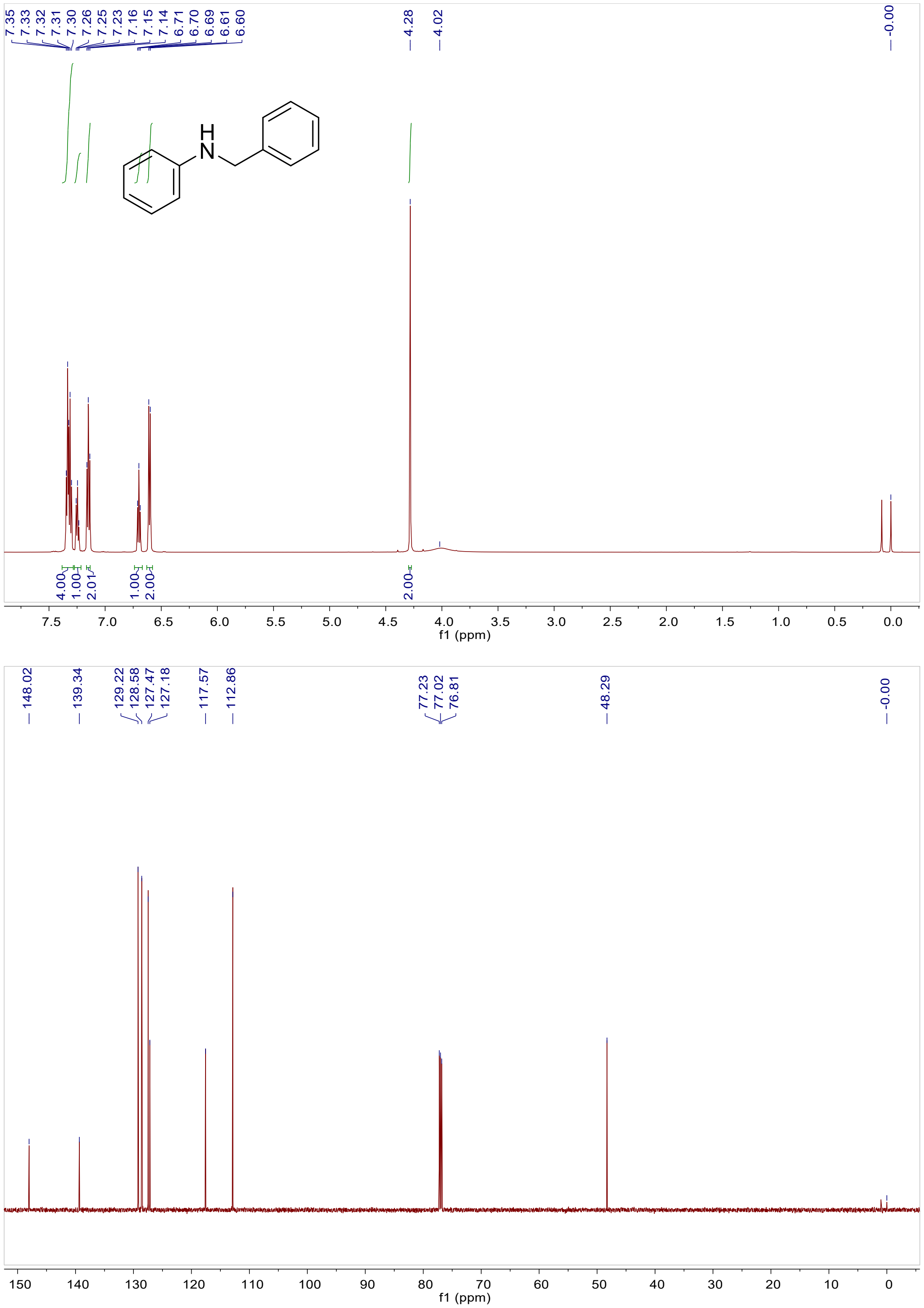
^{1}H-NMR and ^{13}C-NMR of compound **6b**.



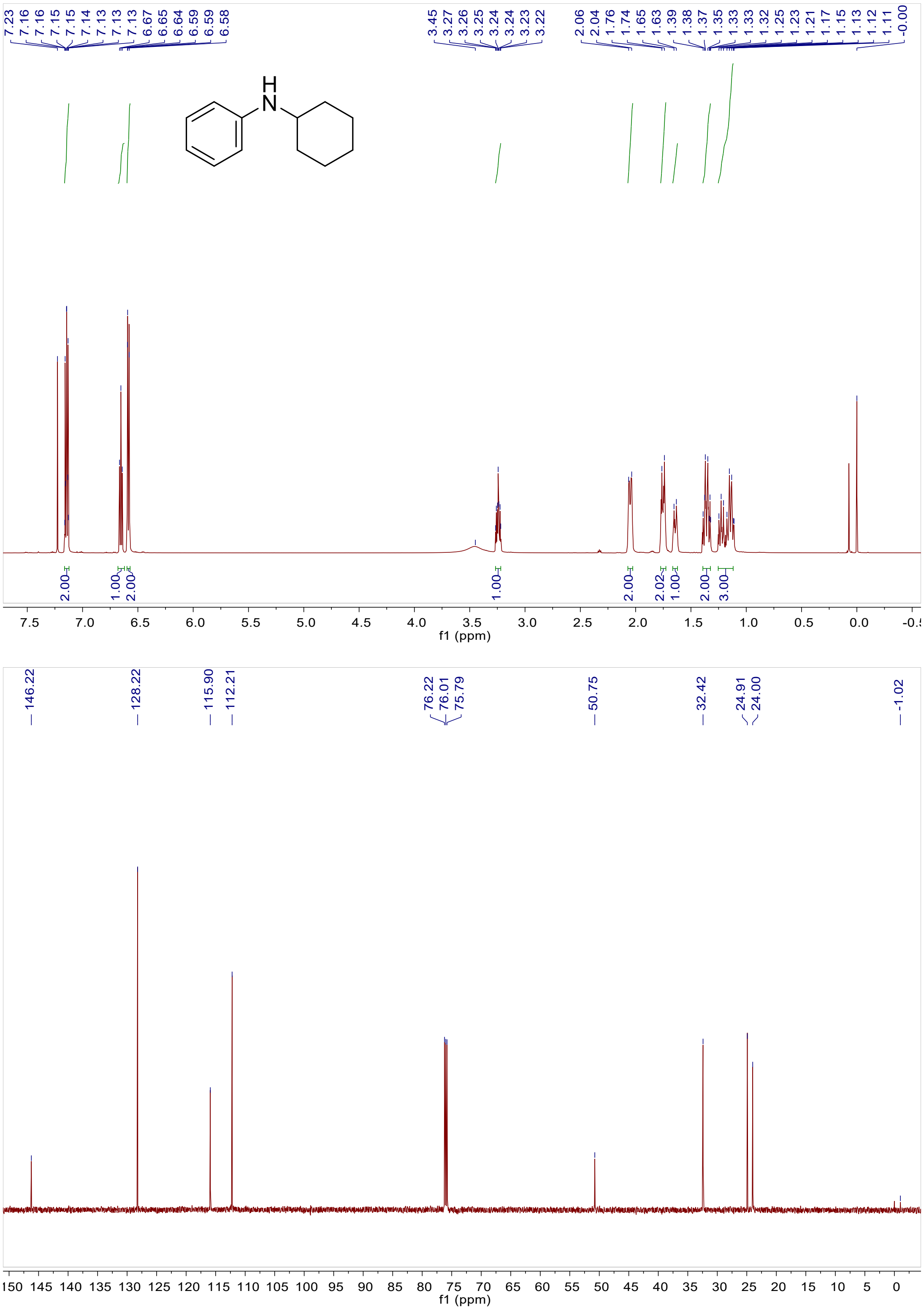
^{1}H-NMR and ^{13}C-NMR of compound **6c**.



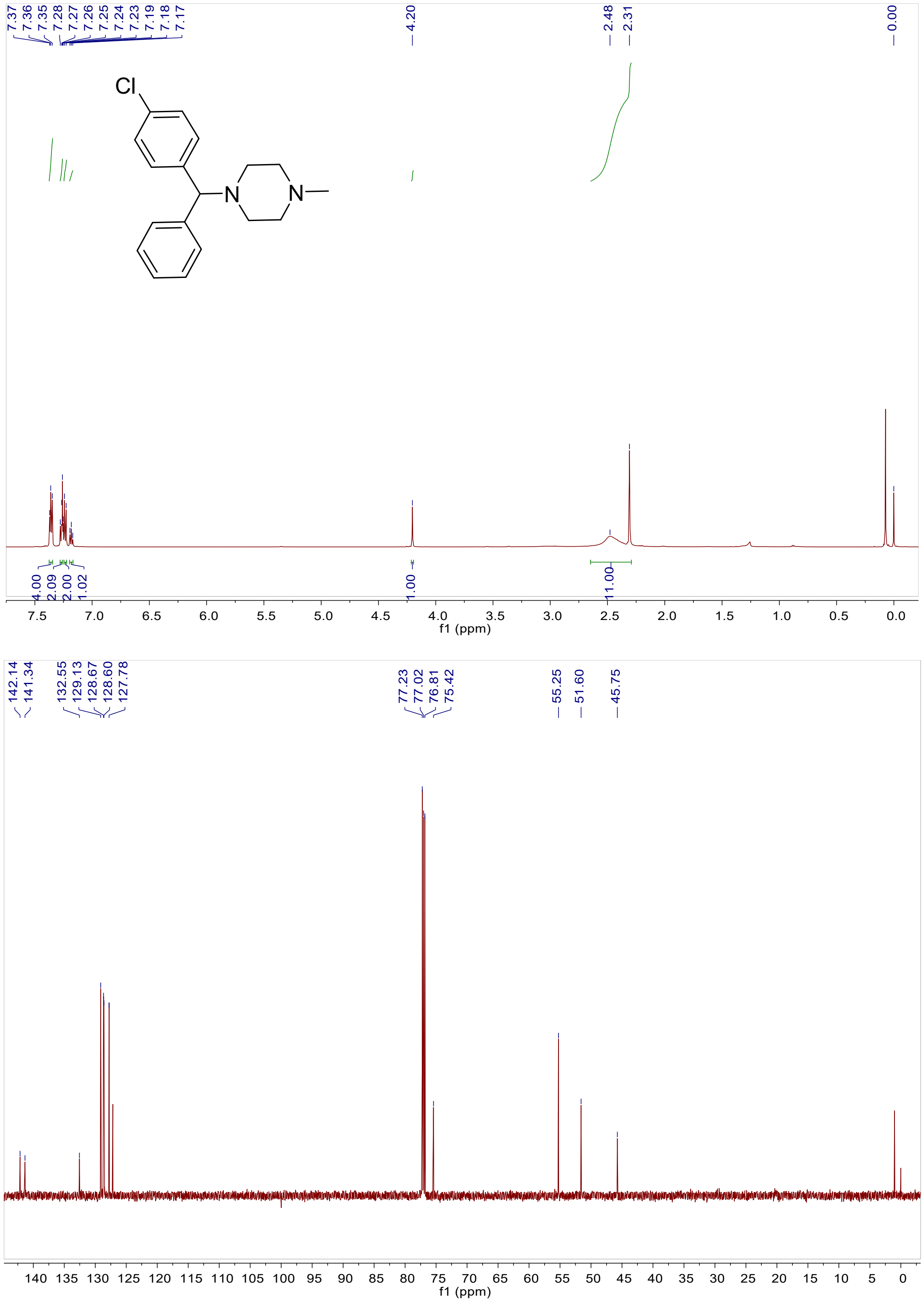
^{1}H-NMR and ^{13}C-NMR of compound **6d**.



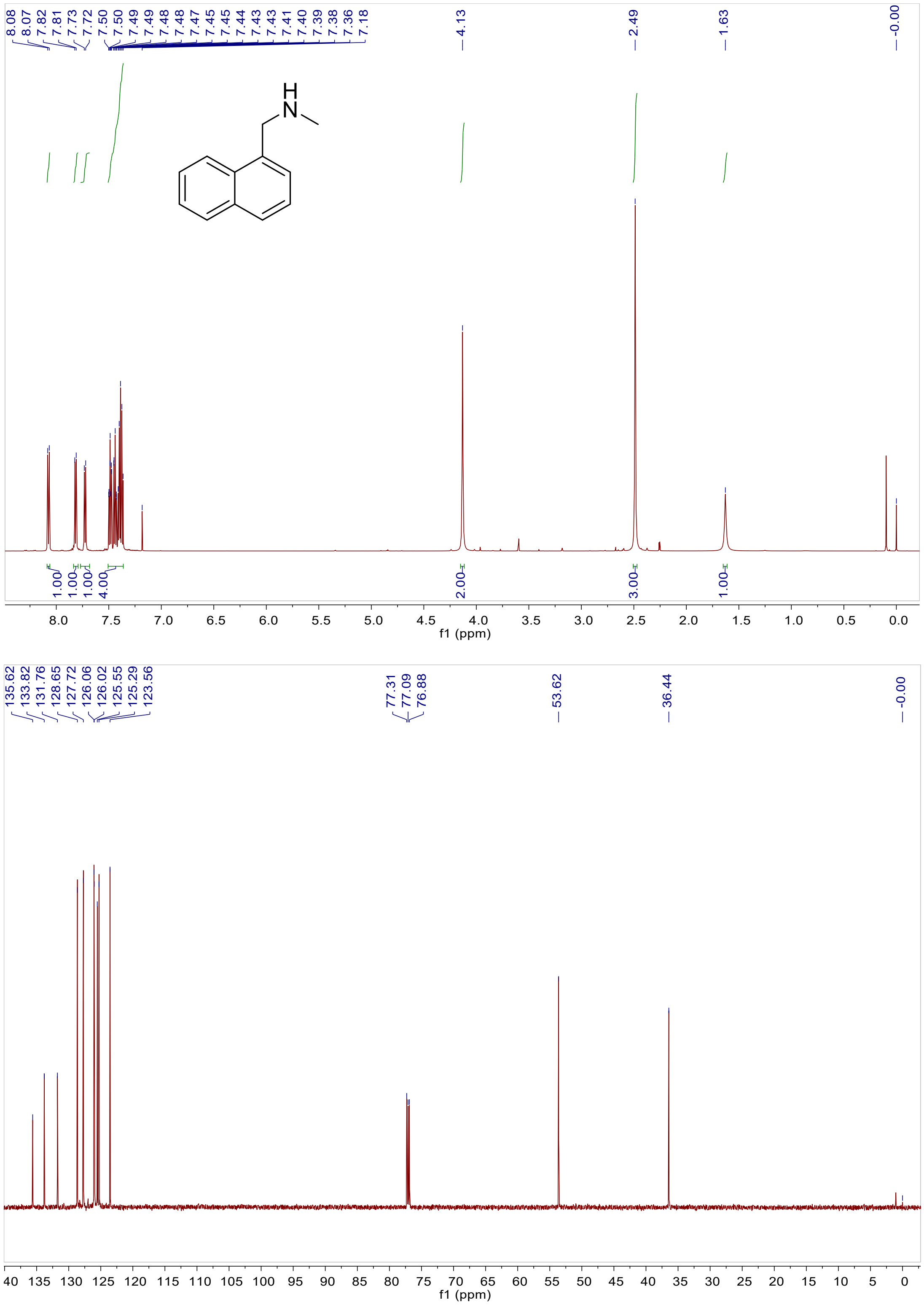
^{1}H-NMR and ^{13}C-NMR of compound **6e**.



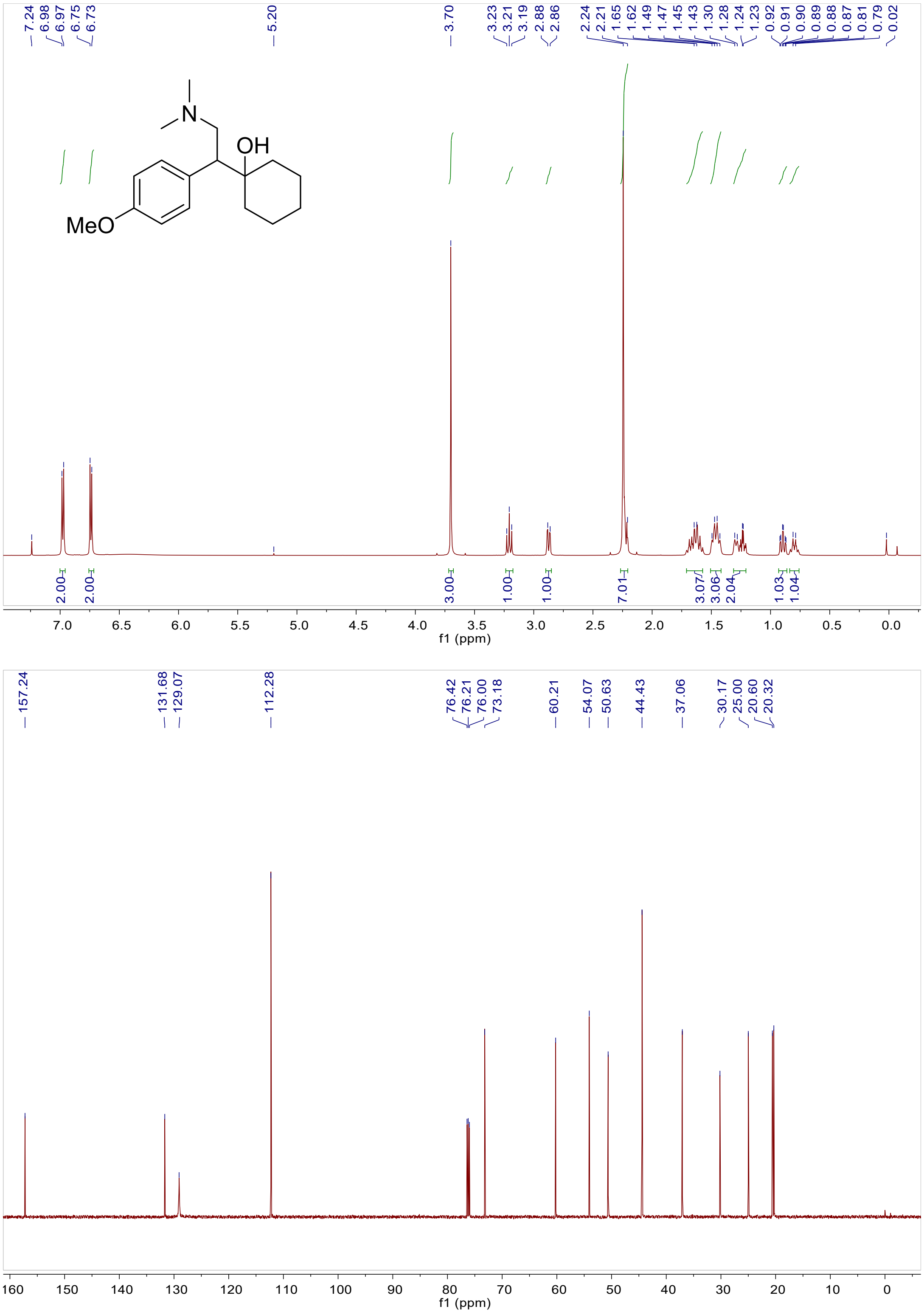
^{1}H-NMR and ^{13}C-NMR of compound **6f.**



^{1}H-NMR and ^{13}C-NMR of **chlorocyclopyridine.**



^{1}H-NMR and ^{13}C-NMR of **AURORA KA-7760.**



^{1}H-NMR and ^{13}C-NMR of **venlafaxine.**