

Supporting Information

Temperature-Controlled Thiation of α -Cyano- β -Alkynyl Carbon-yl Derivatives for De Novo Synthesis of 2-Aminothiophenes and Thieno[2,3-*c*]isothiazoles

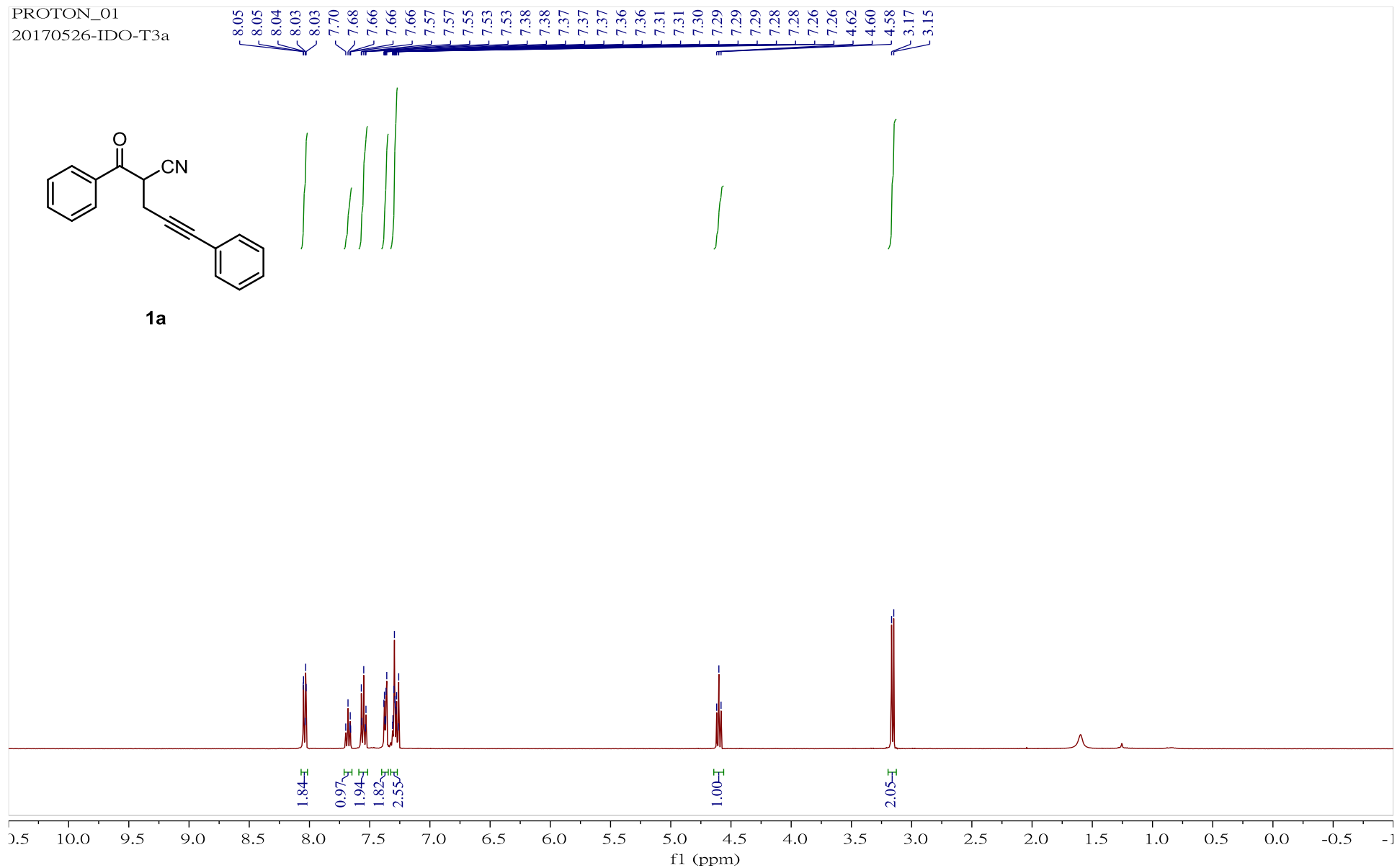
Tzu-Ting Kao[†], Bo-Kai Peng[‡], Min-Chieh Liang[‡], Chia-Jui Lee[†], I-Chia Chen[§], Kak-Shan Shia^{*†} and Yen-Ku Wu^{*‡}

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[‡] *Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan*

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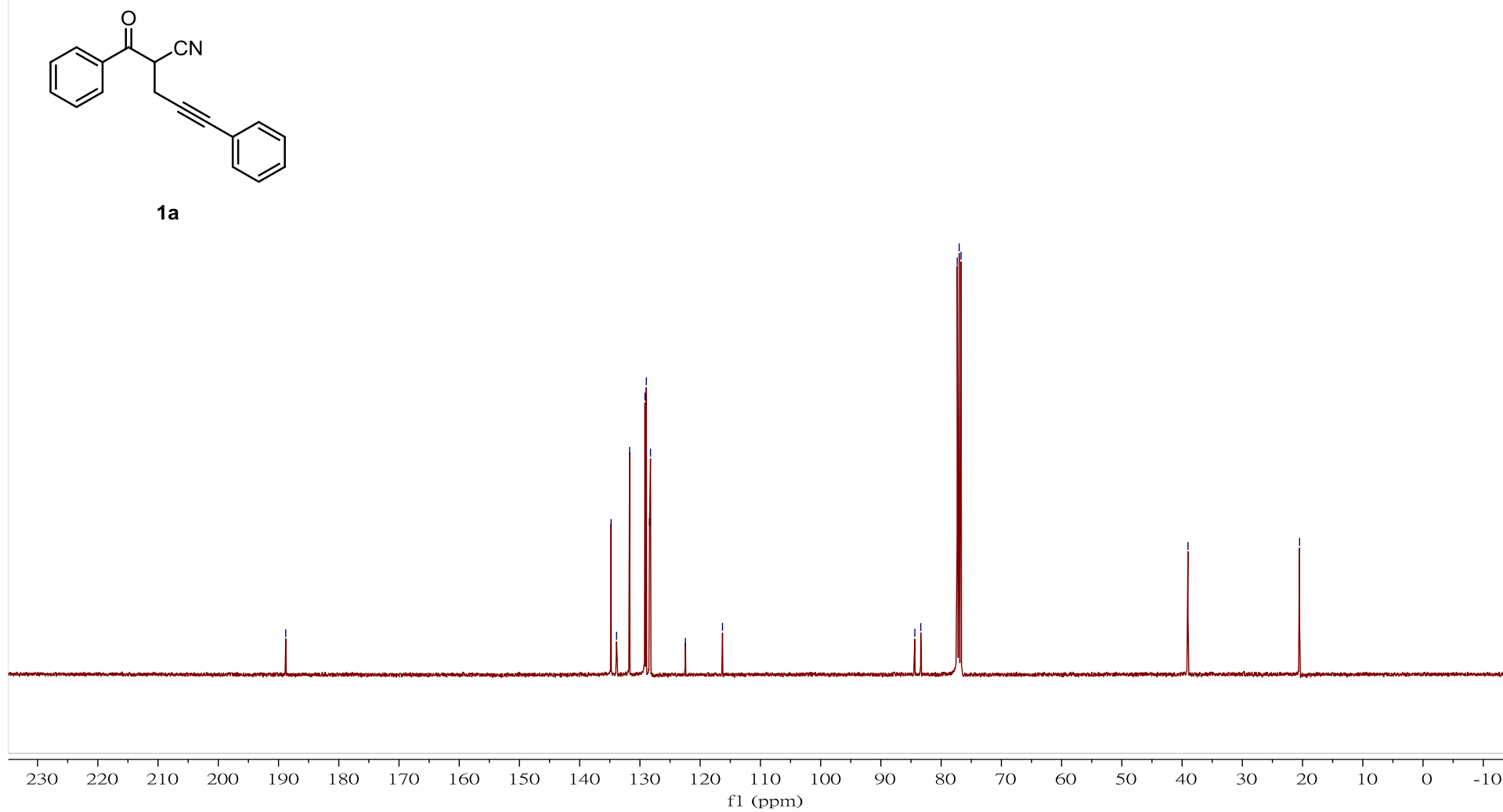
PROTON_01
20170526-IDO-T3a



¹H NMR (400 MHz) spectrum of compound **1a** in CDCl₃

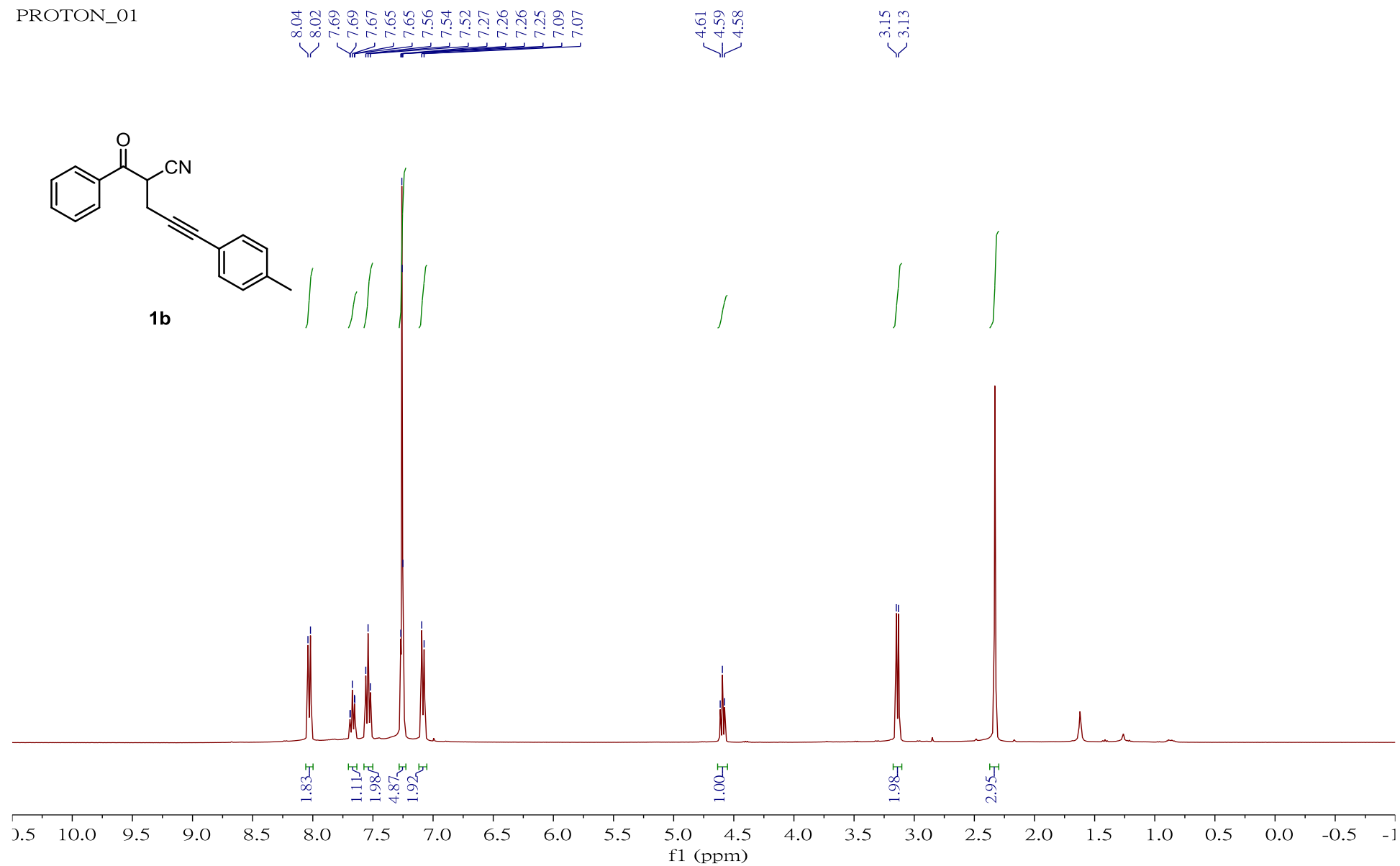
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20170526-IDO-T3a-13C

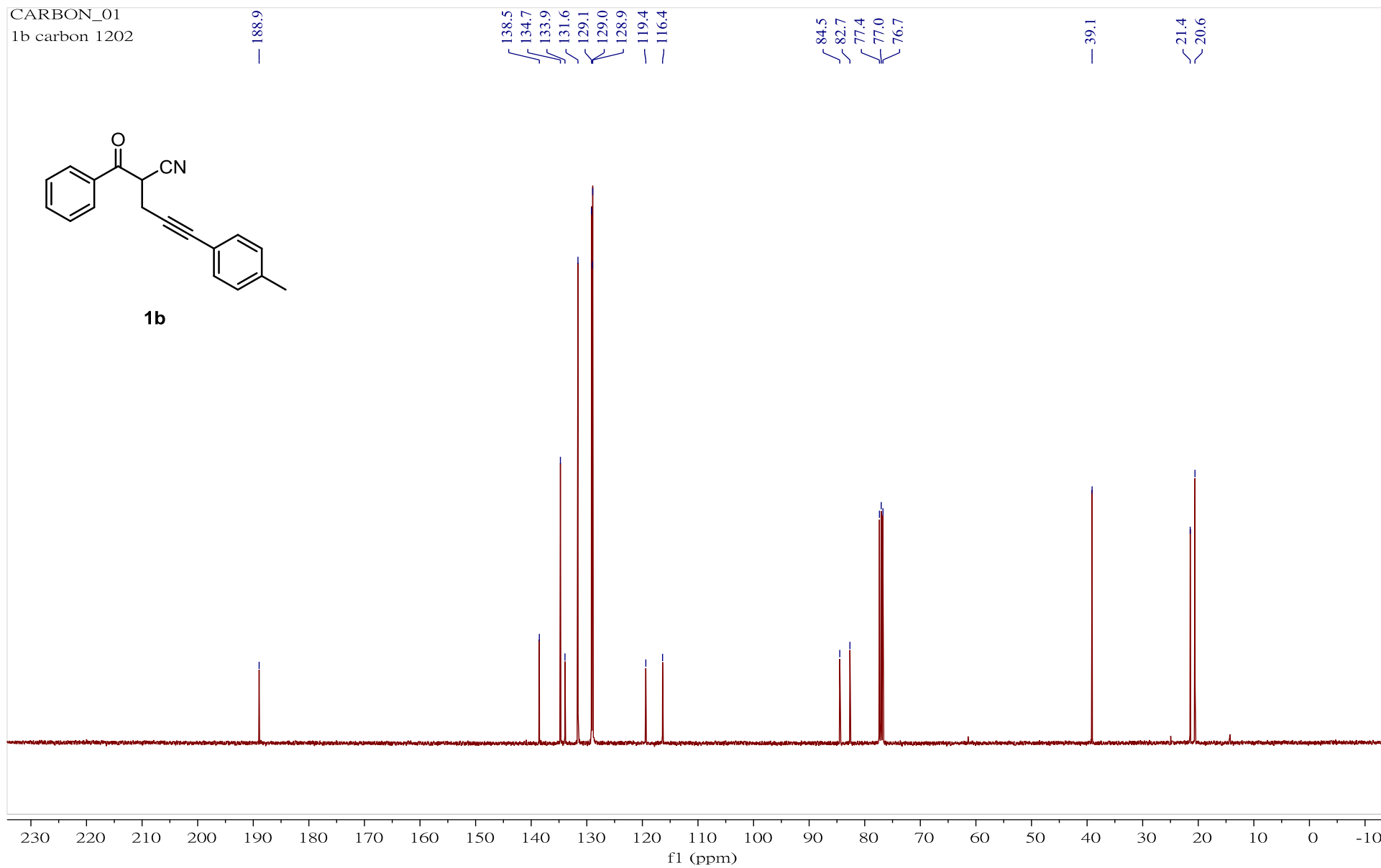


^{13}C NMR (100 MHz) spectrum of compound **1a** in CDCl_3

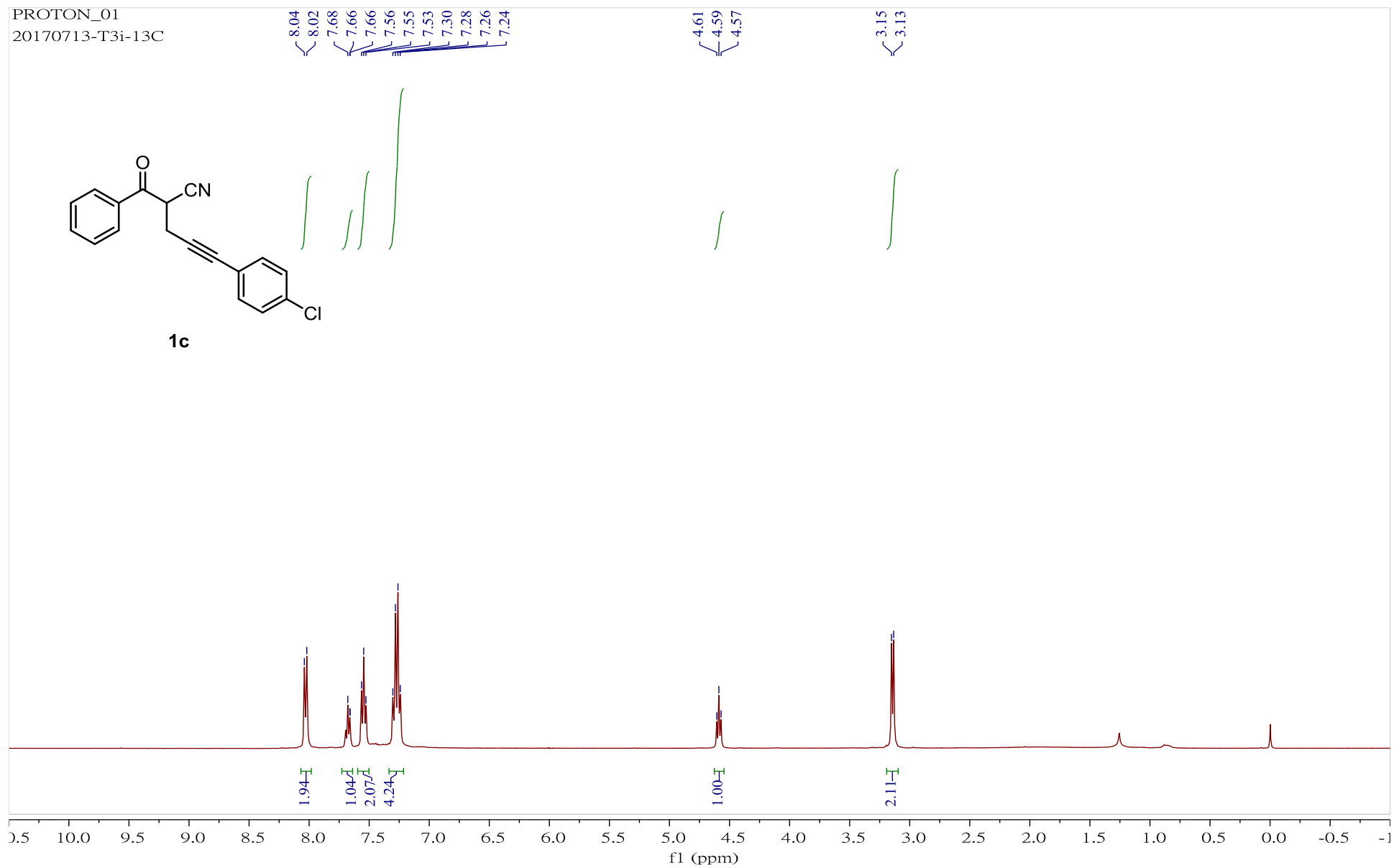
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¹H NMR (400 MHz) spectrum of compound **1b** in CDCl₃

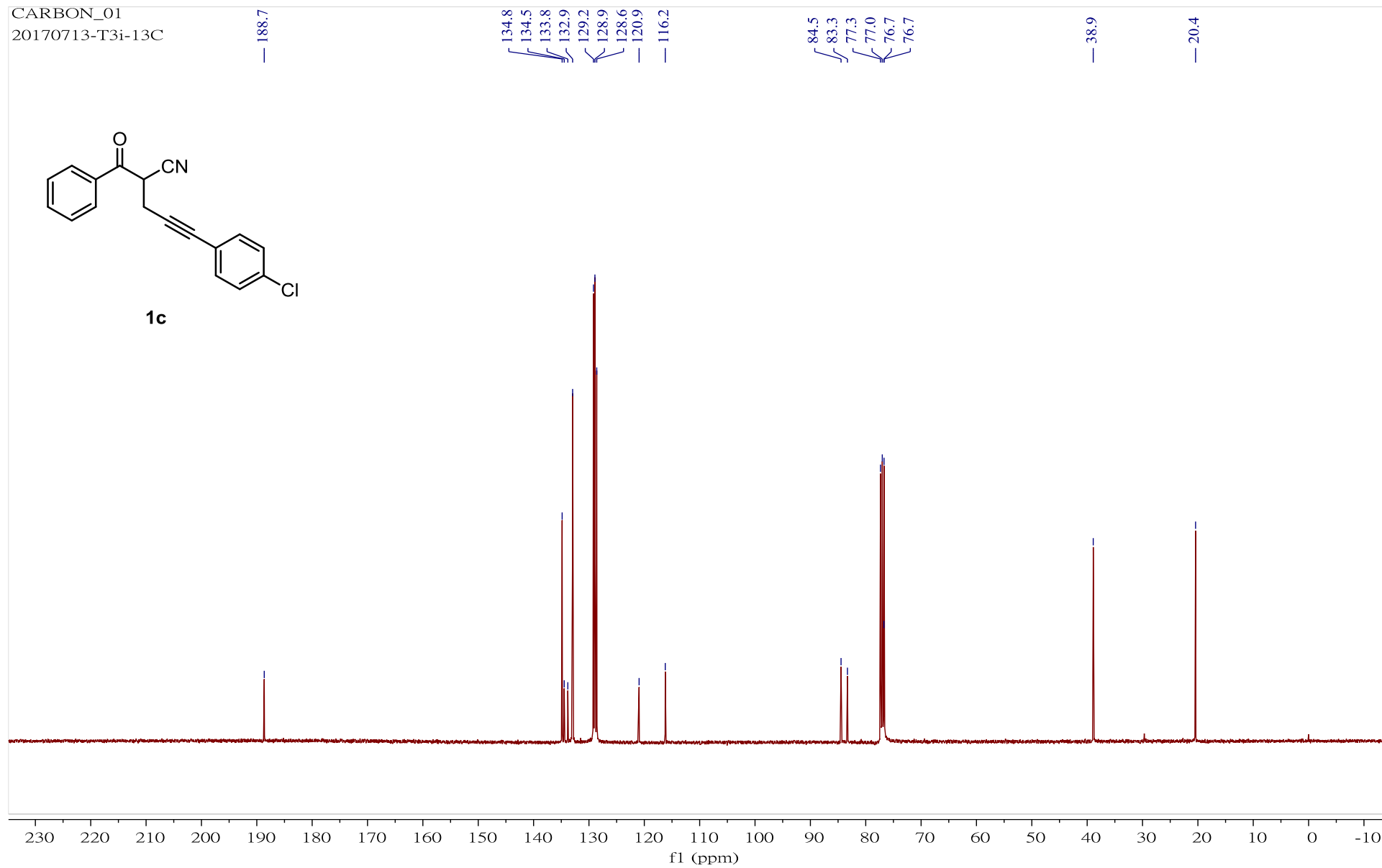


^{13}C NMR (100 MHz) spectrum of compound **1b** in CDCl_3

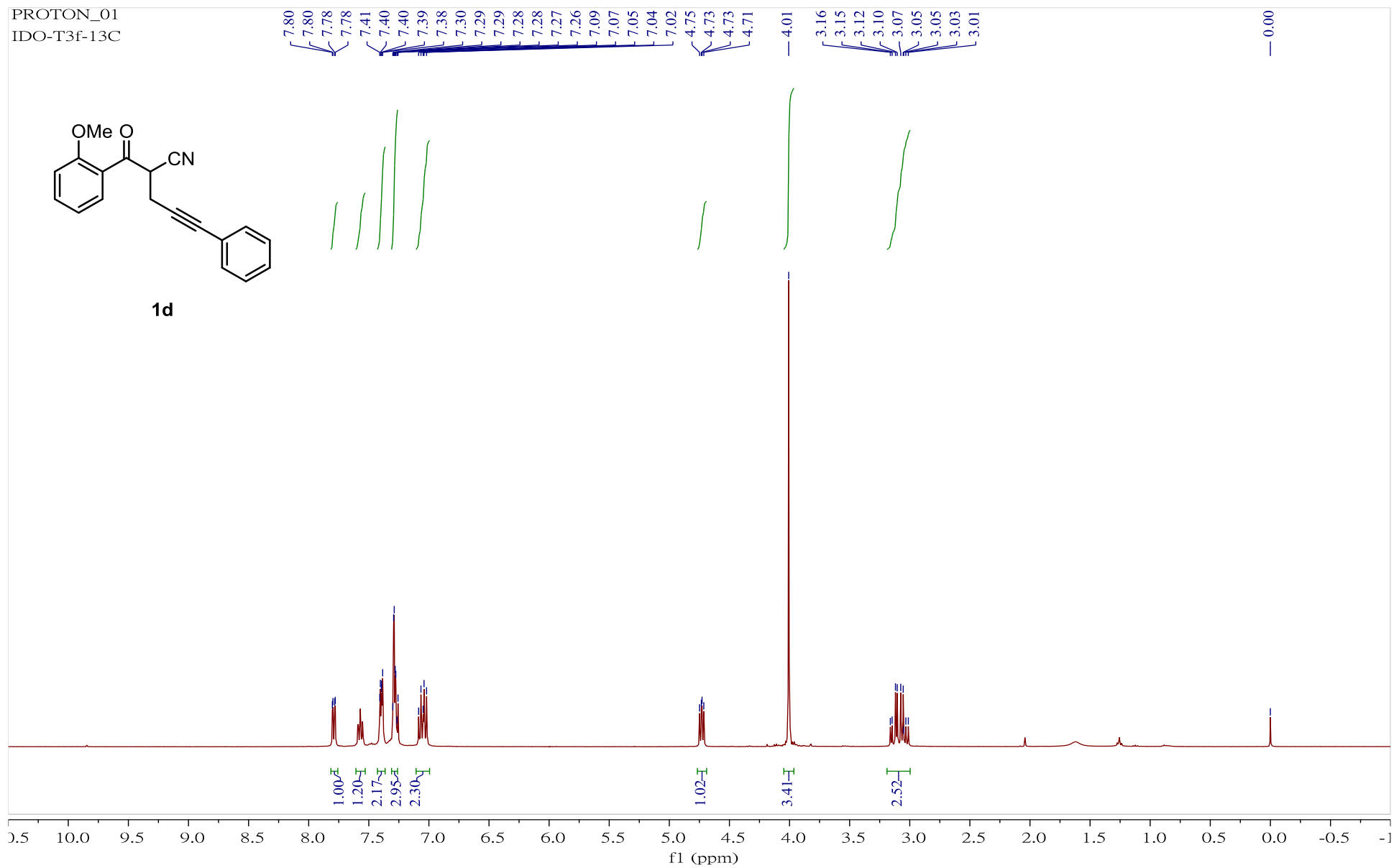


^1H NMR (400 MHz) spectrum of compound **1c** in CDCl_3

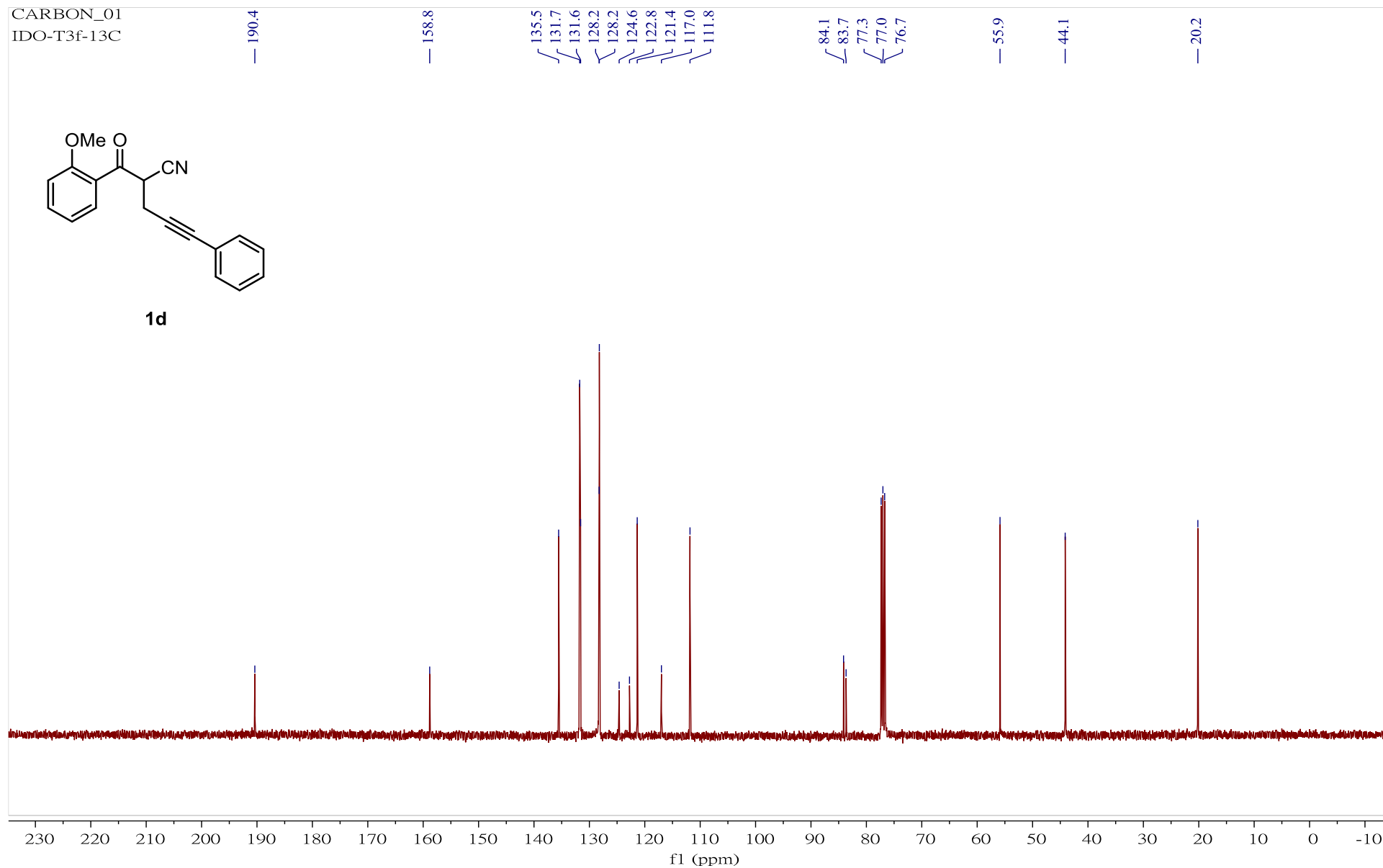
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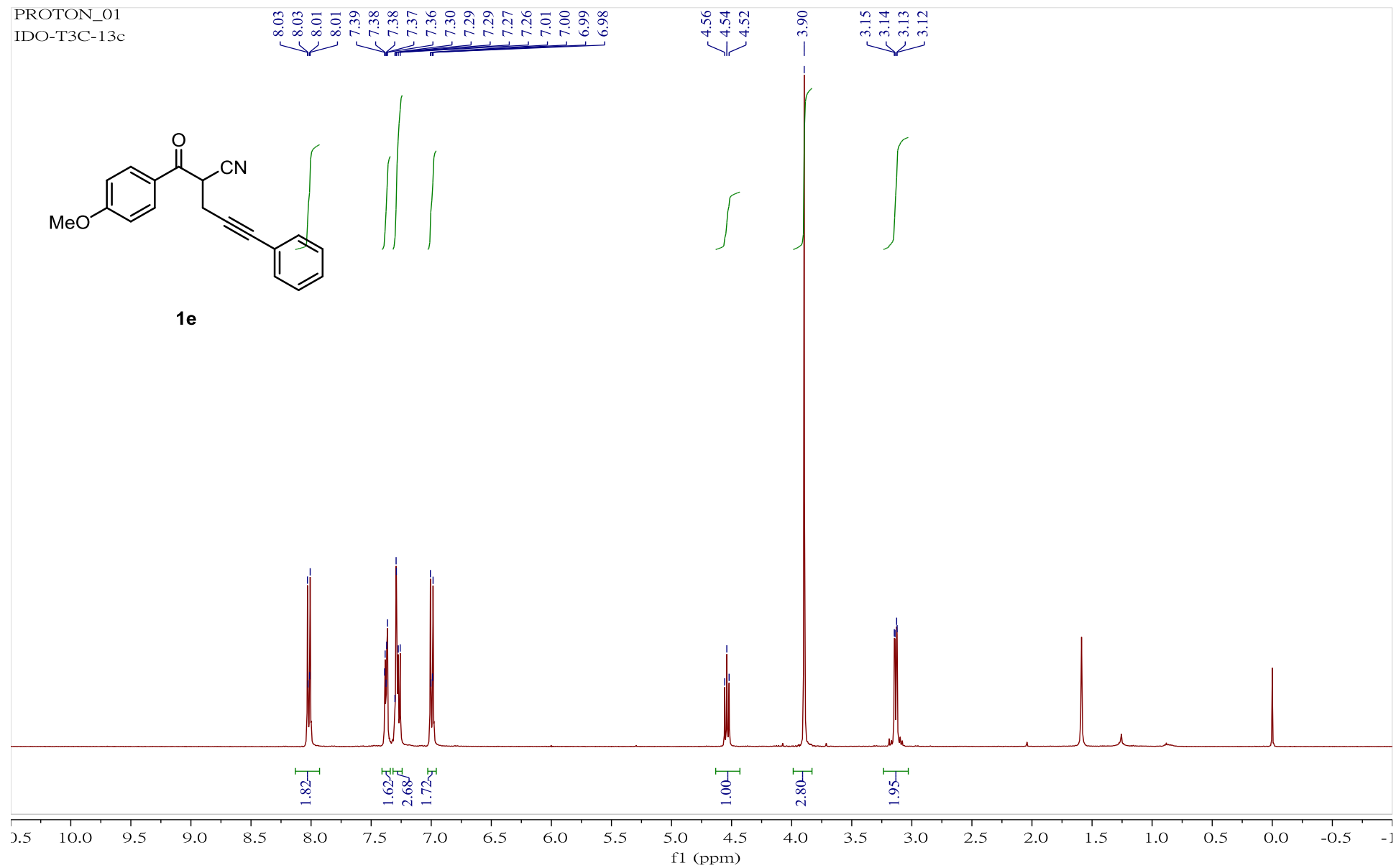
^{13}C NMR (100 MHz) spectrum of compound **1c** in CDCl_3



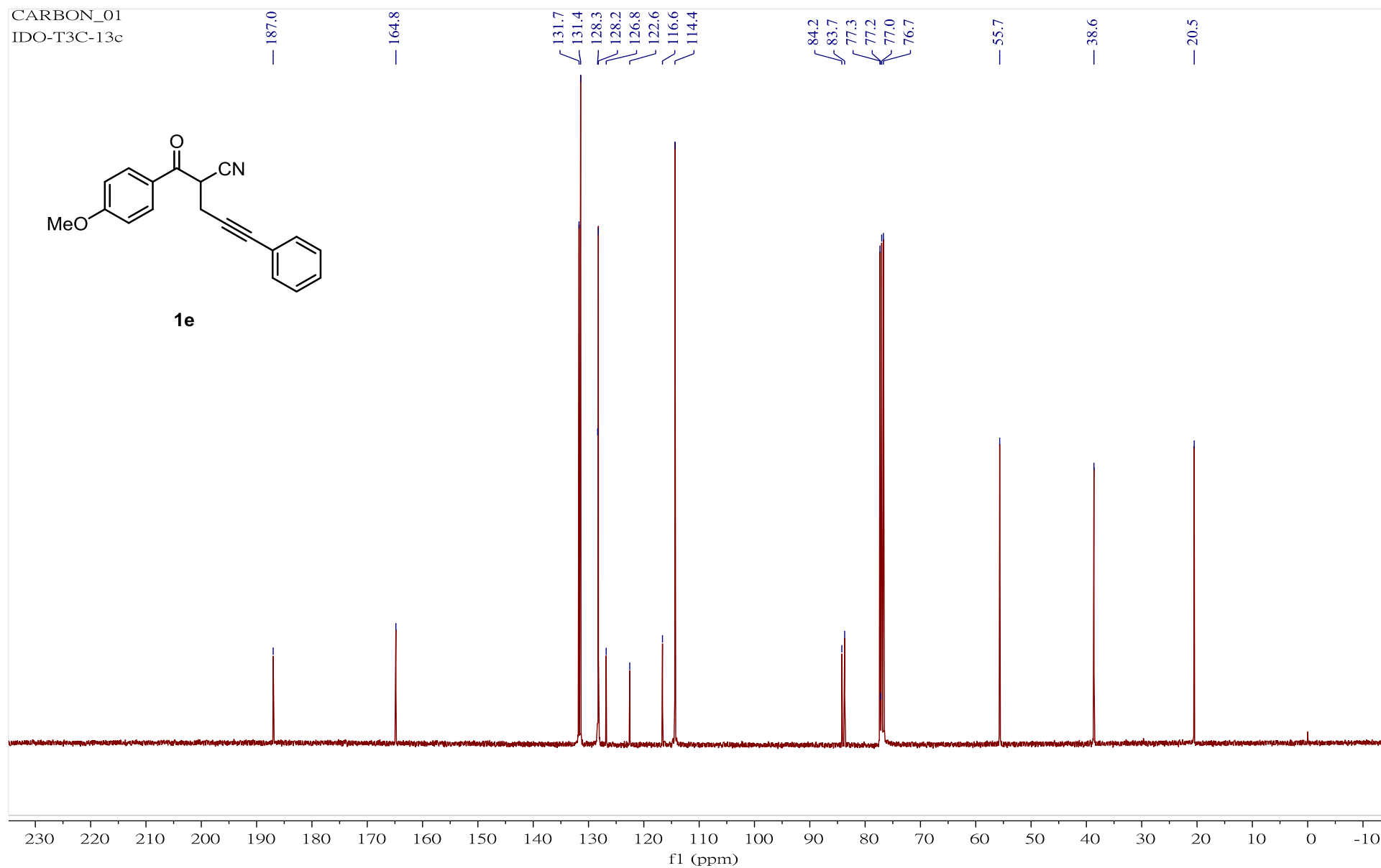
^1H NMR (400 MHz) spectrum of compound **1d** in CDCl_3



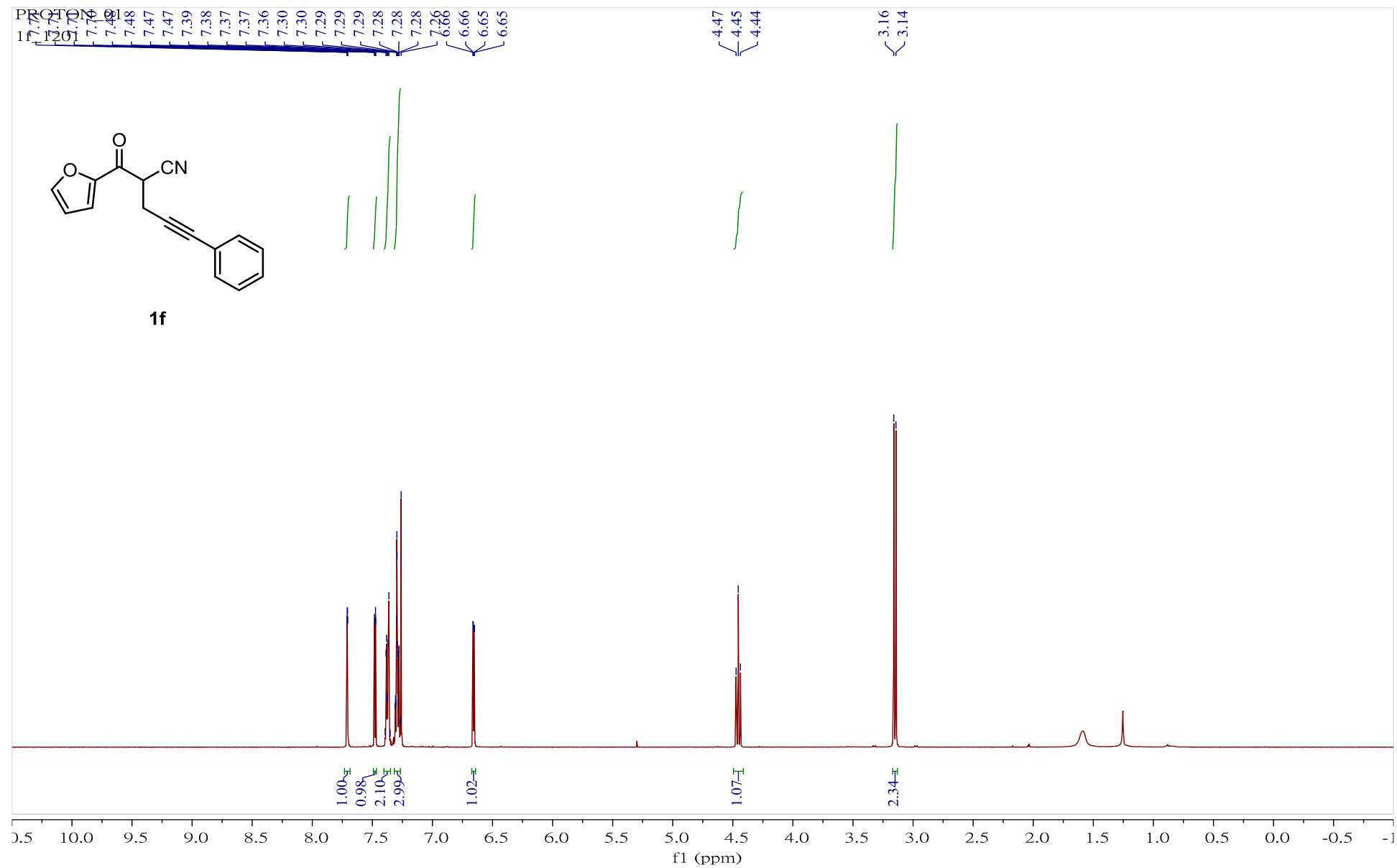
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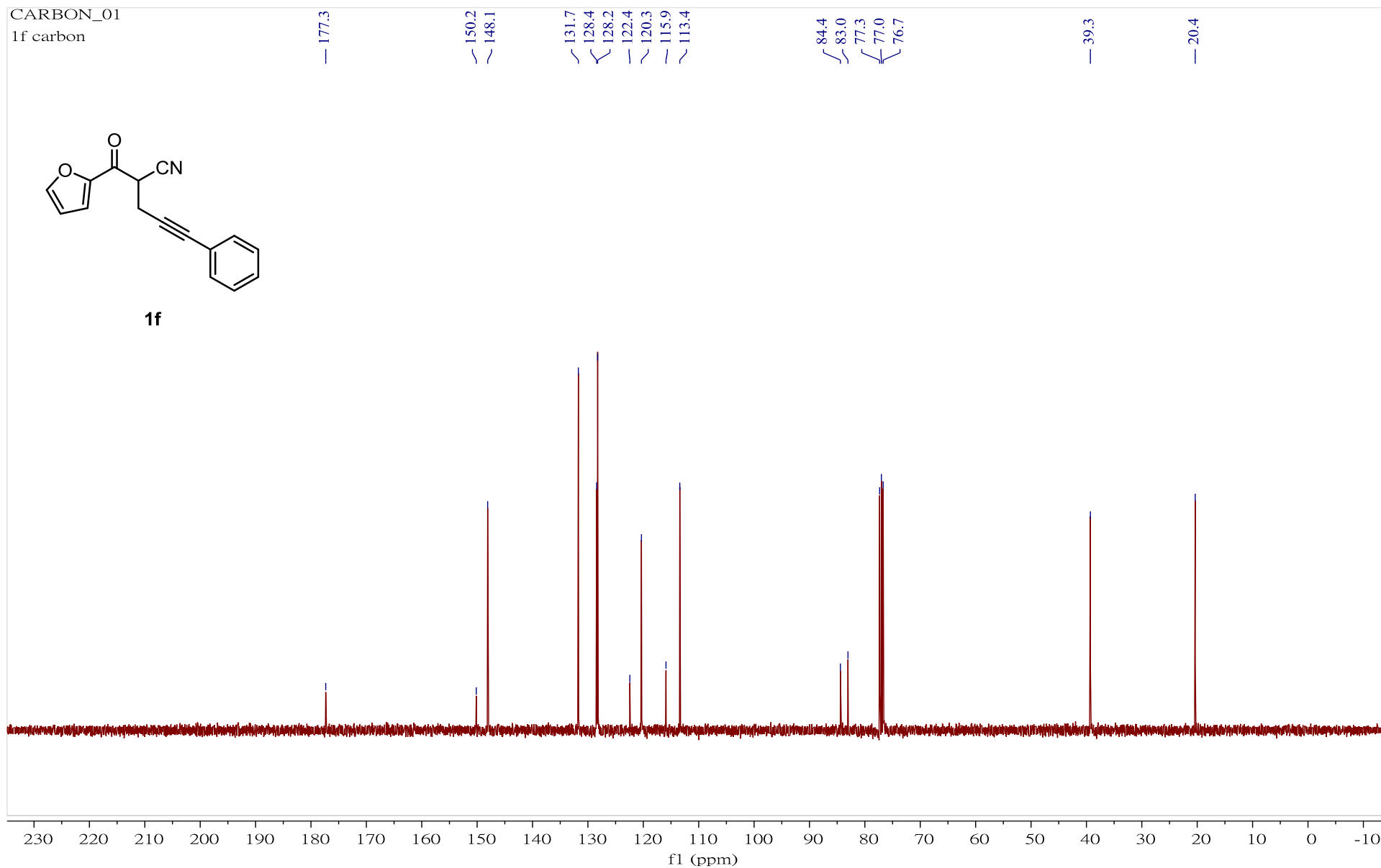
^1H NMR (400 MHz) spectrum of compound **1e** in CDCl_3



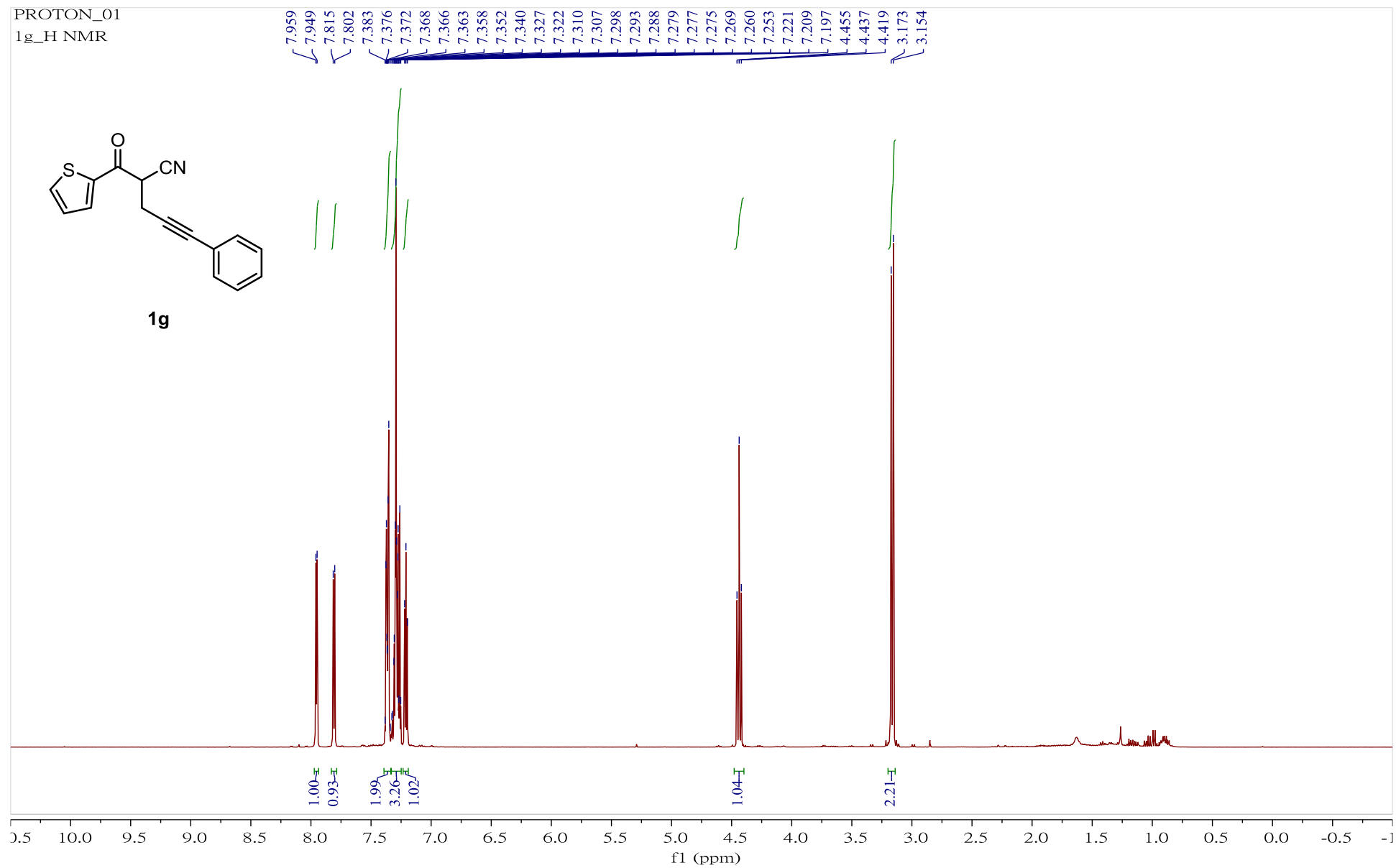
^{13}C NMR (100 MHz) spectrum of compound **1e** in CDCl_3



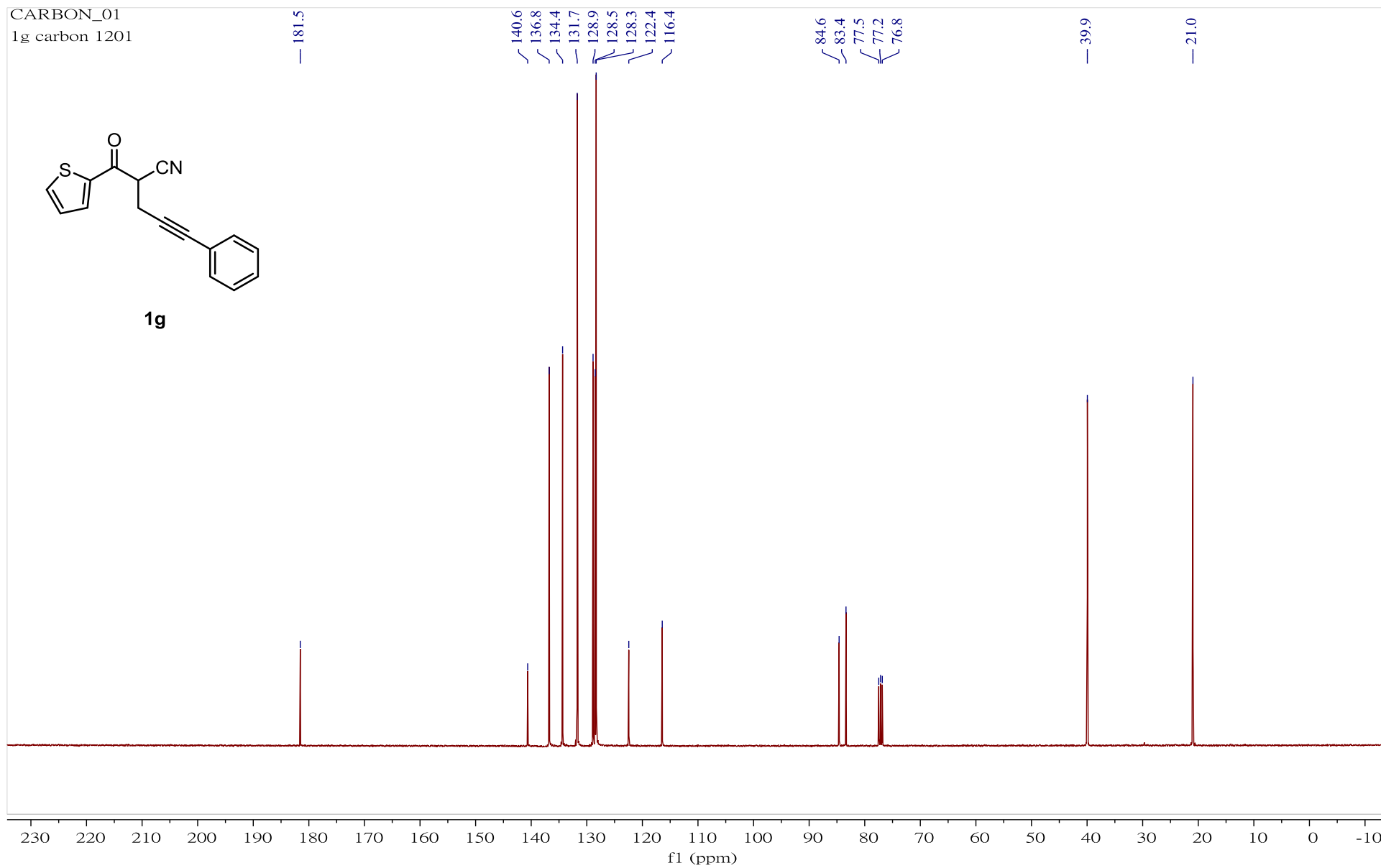
¹H NMR (400 MHz) spectrum of compound **1f** in CDCl₃



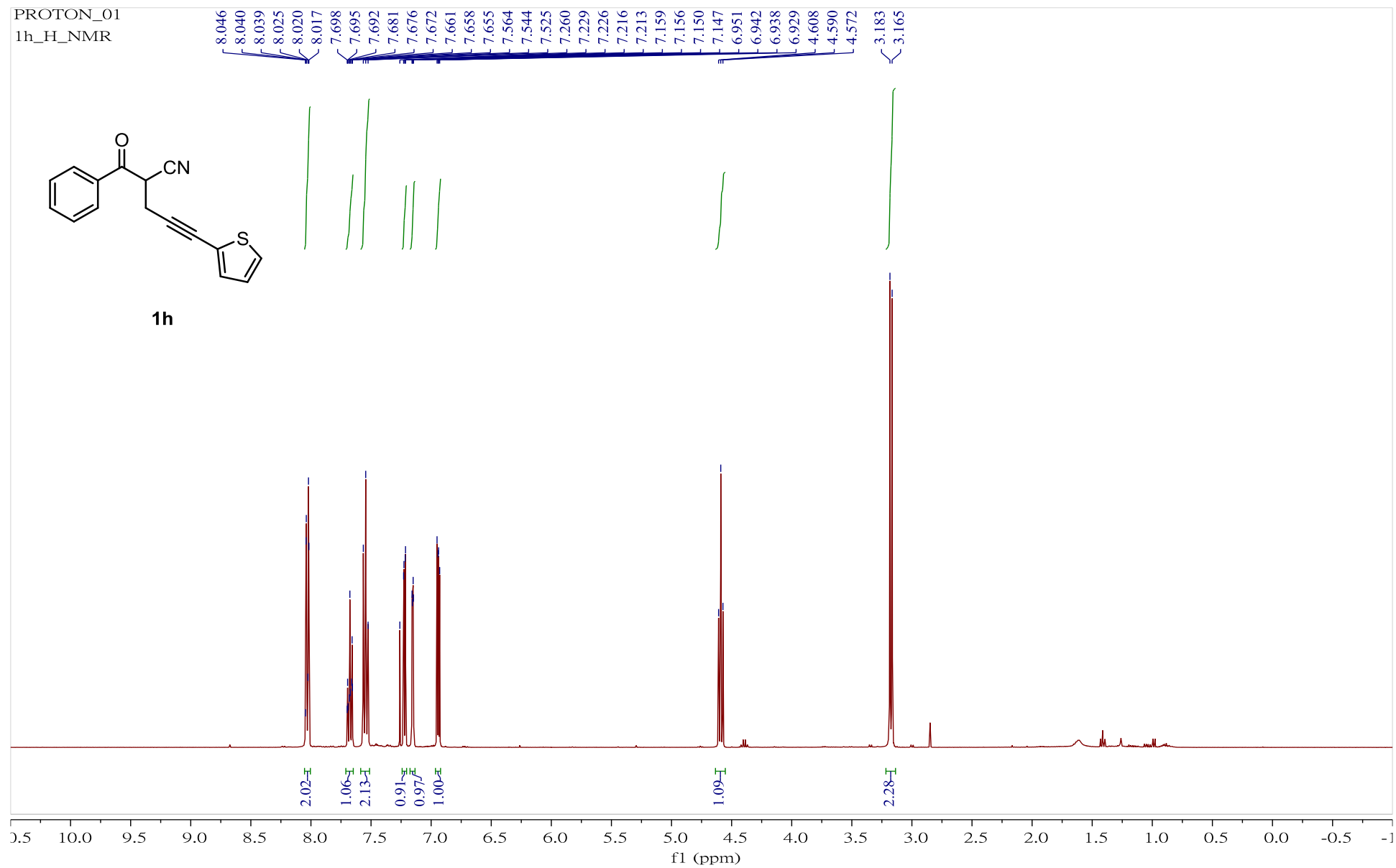
^{13}C NMR (100 MHz) spectrum of compound **1f** in CDCl_3



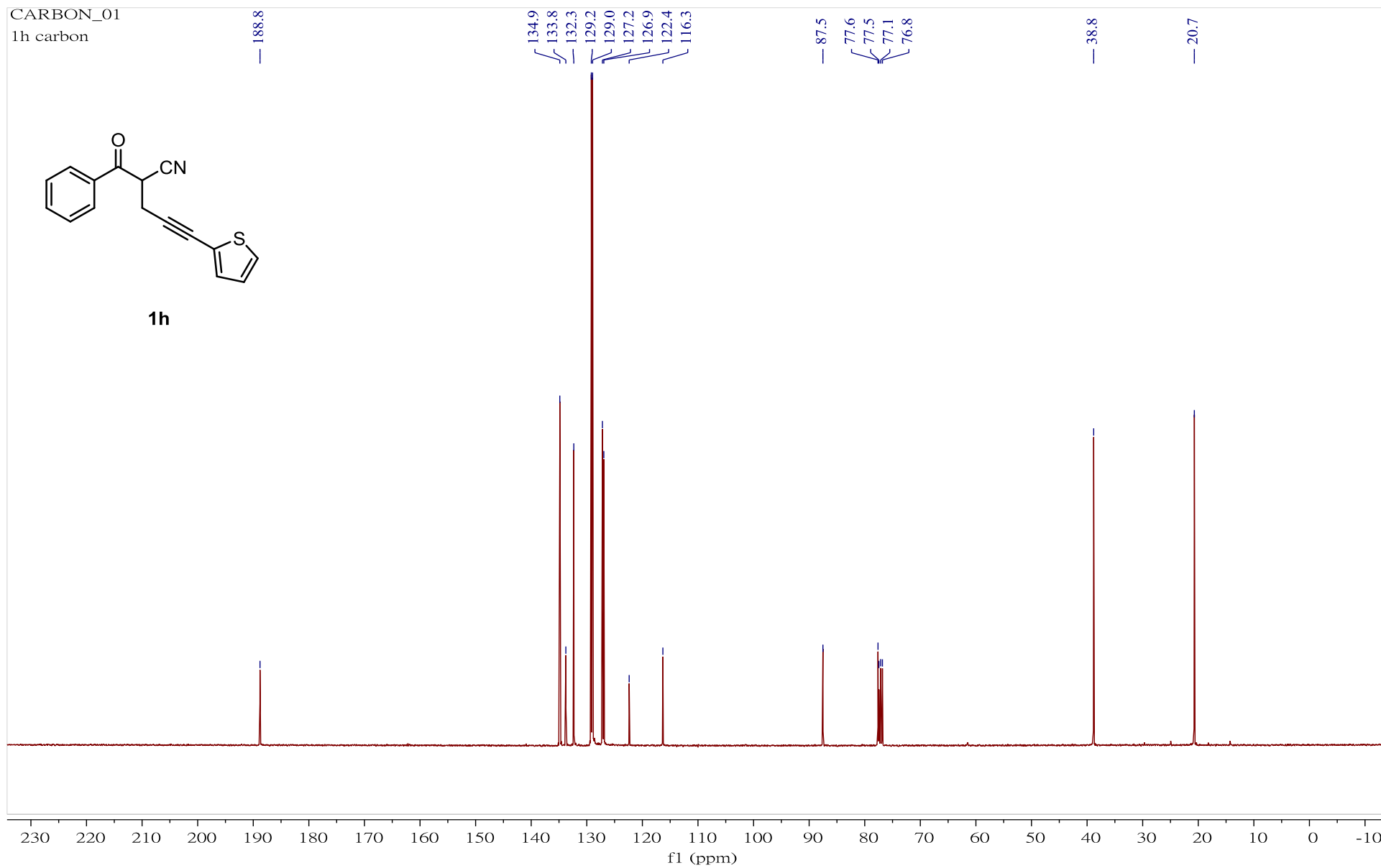
^{13}C NMR (100 MHz) spectrum of compound **1g** in CDCl_3



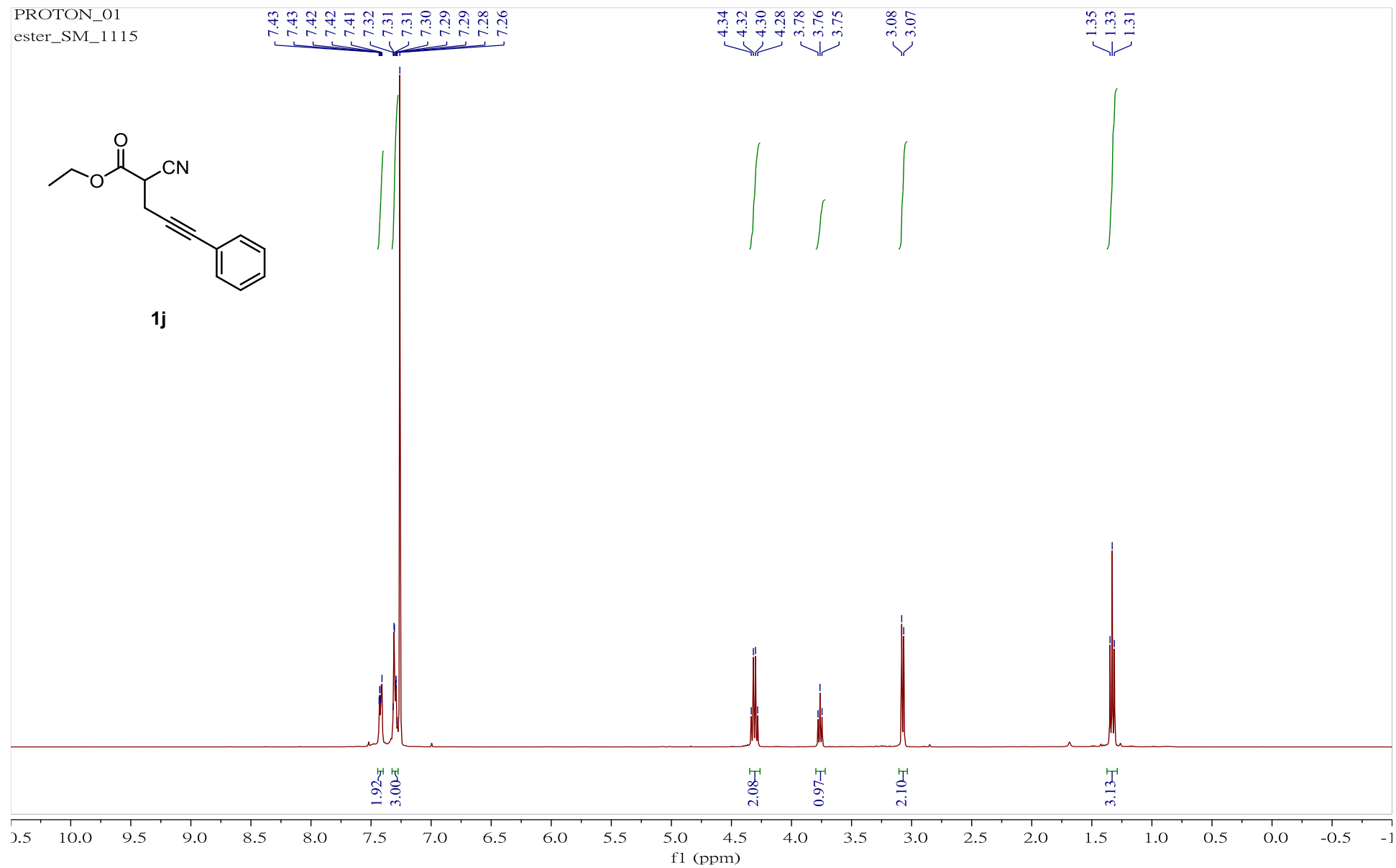
^{13}C NMR (100 MHz) spectrum of compound **1g** in CDCl_3



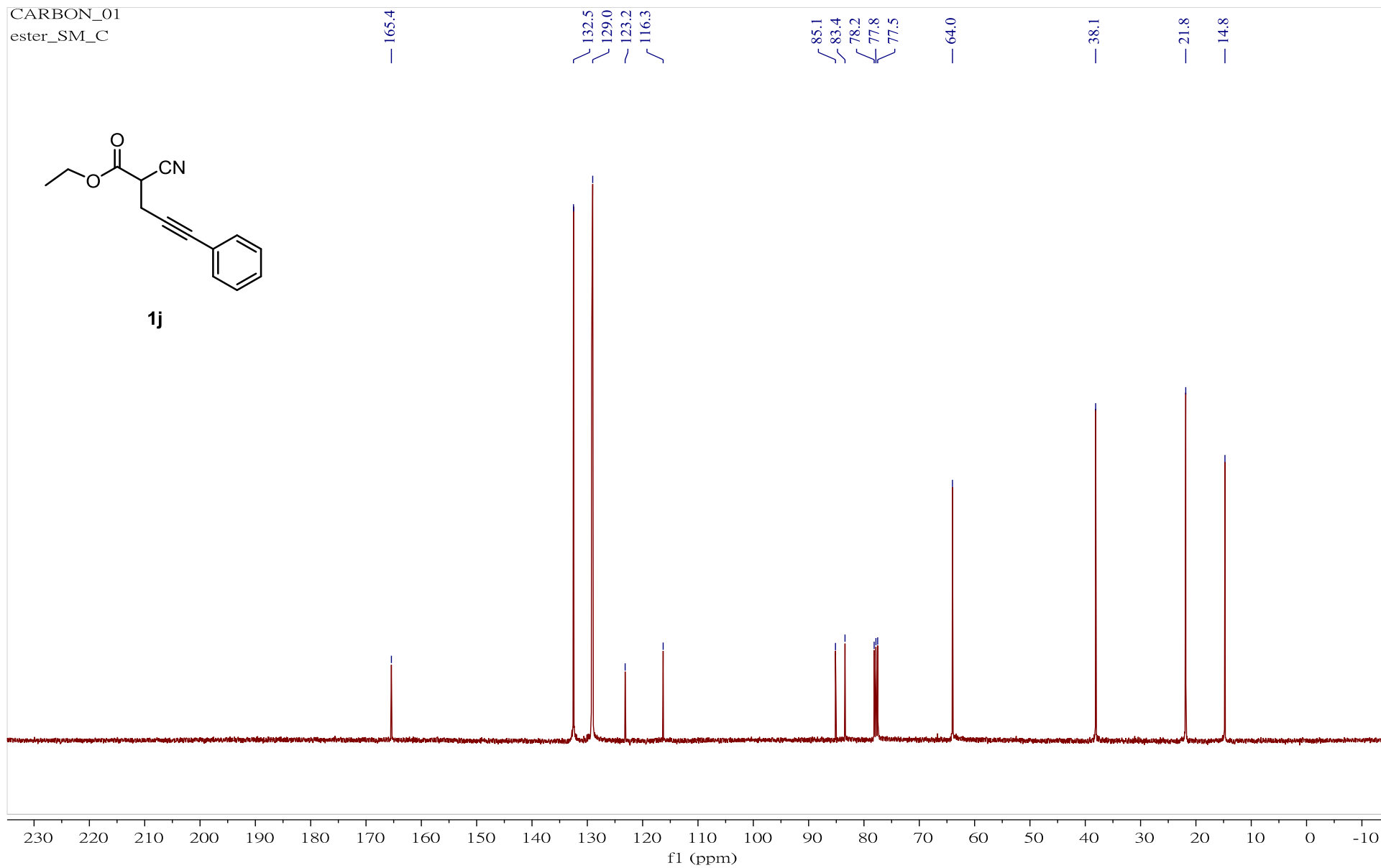
^{13}C NMR (100 MHz) spectrum of compound **1h** in CDCl_3



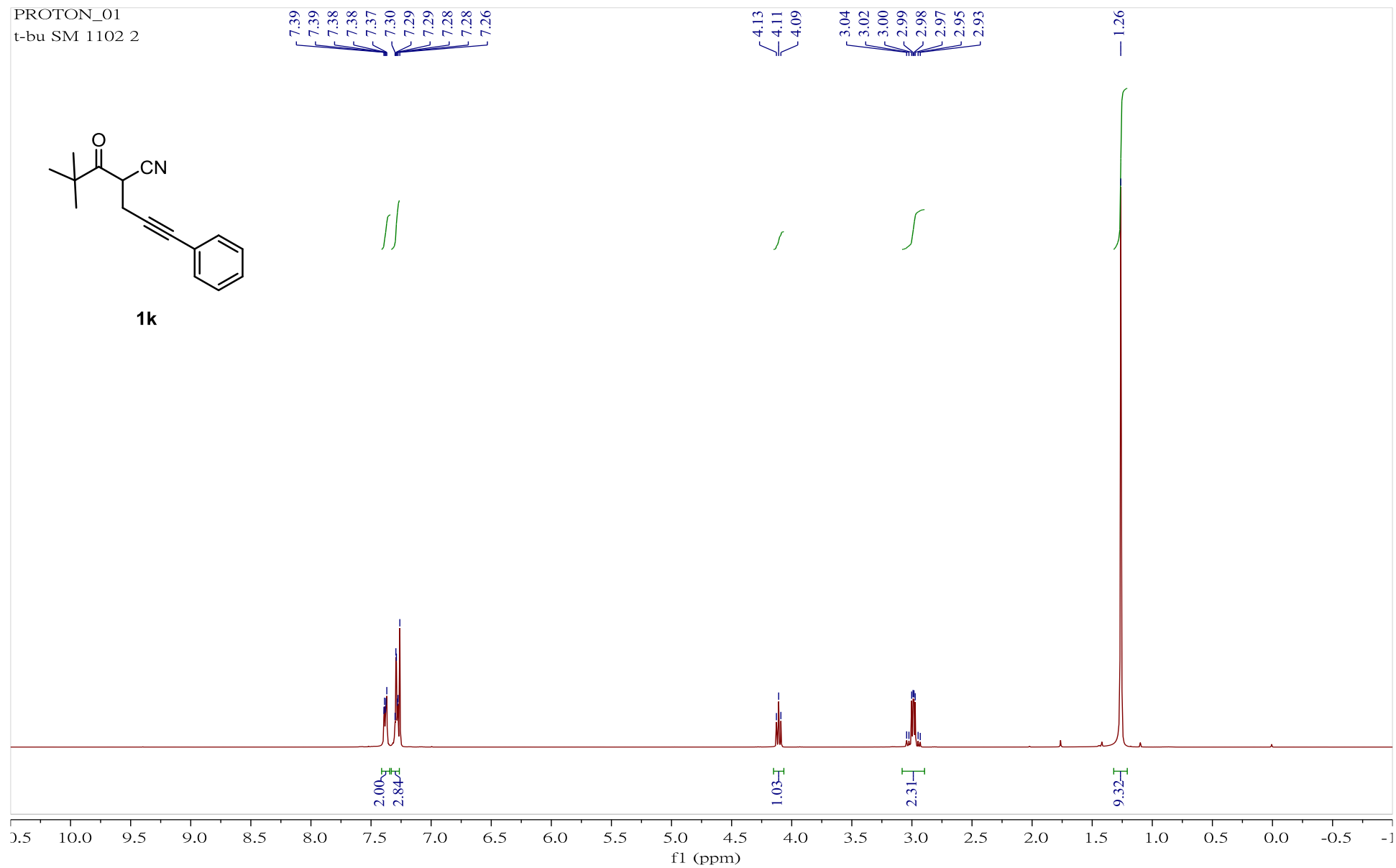
^{13}C NMR (100 MHz) spectrum of compound **1h** in CDCl_3



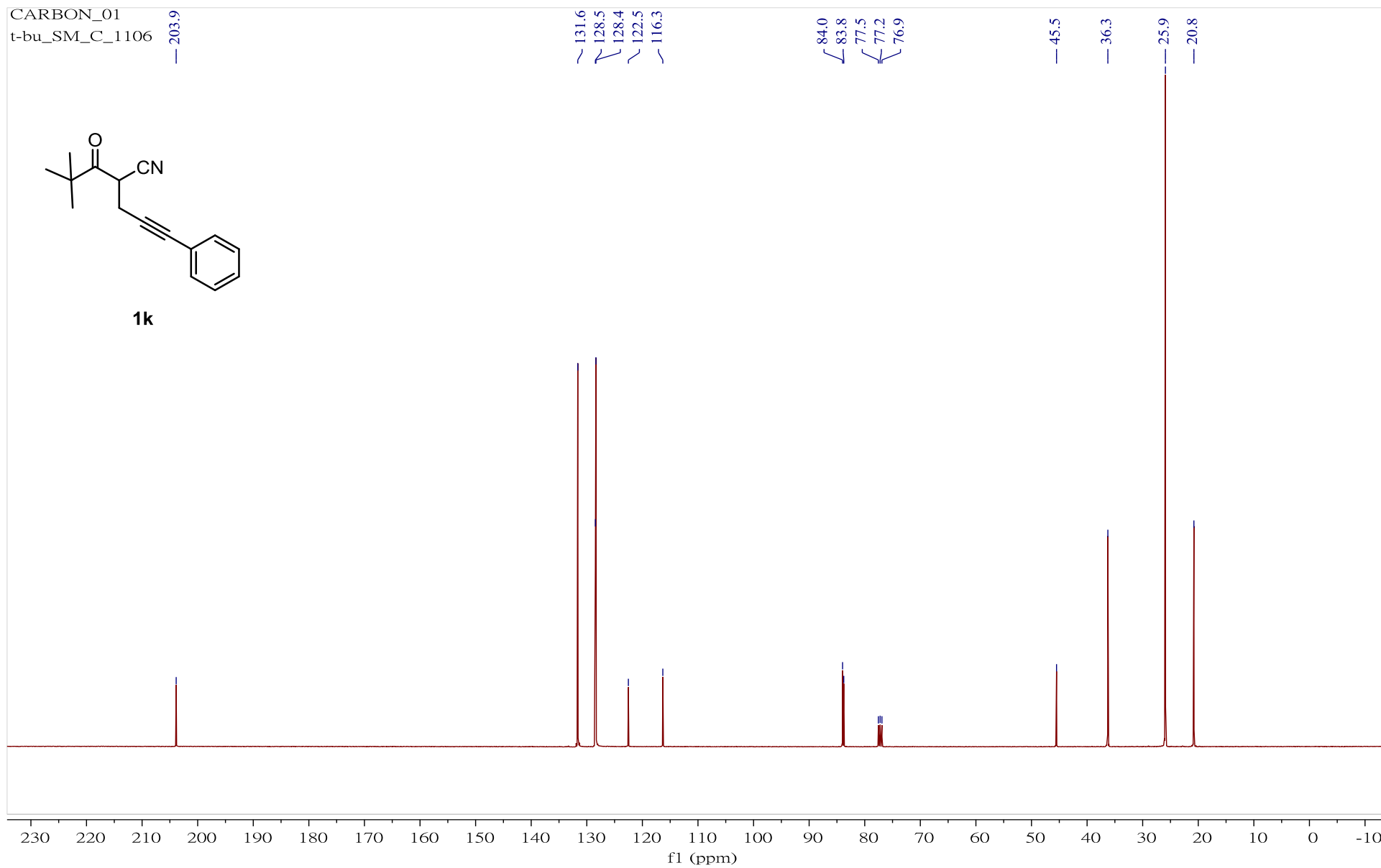
^1H NMR (400 MHz) spectrum of compound **1j** in CDCl_3



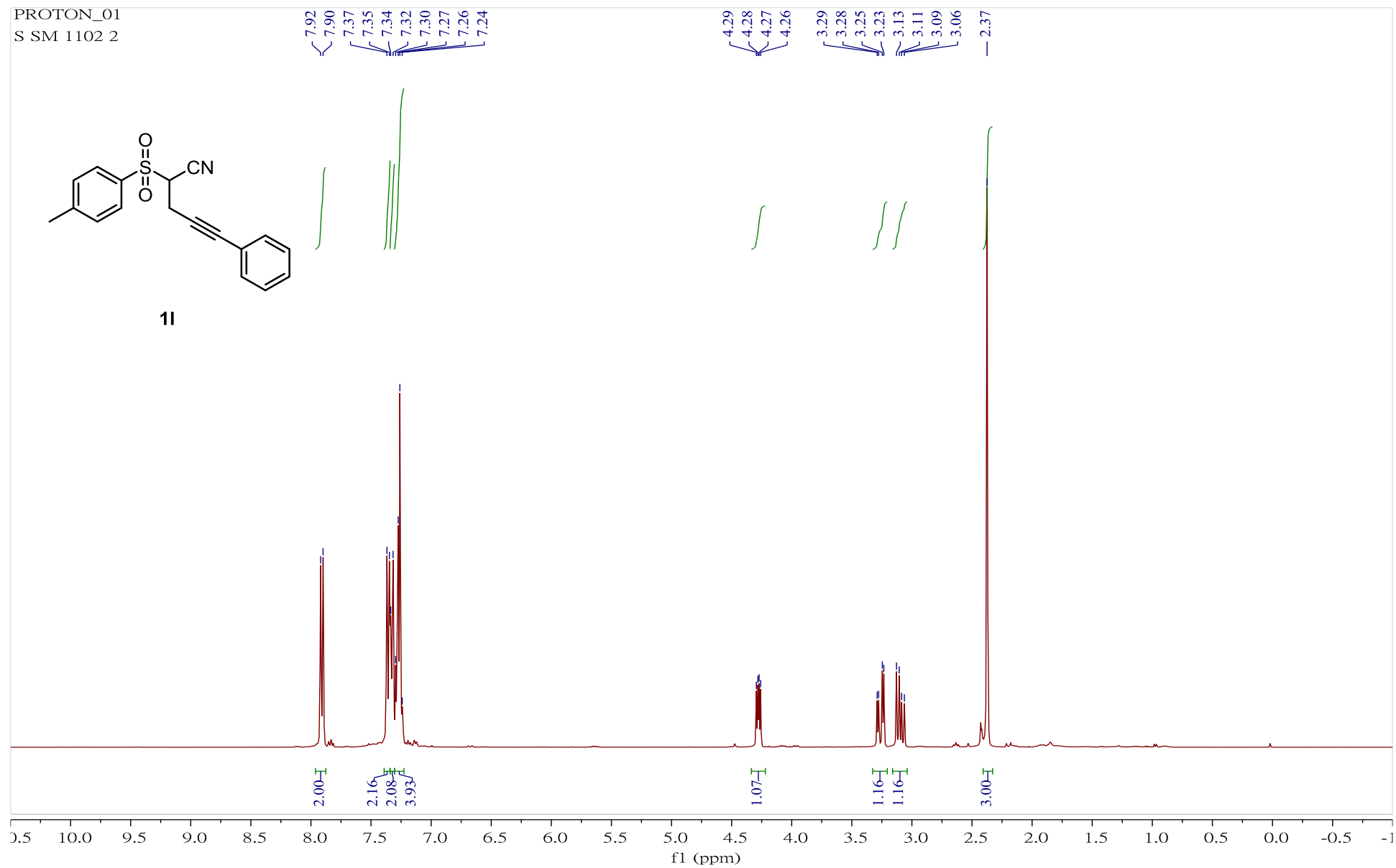
^{13}C NMR (100 MHz) spectrum of compound **1j** in CDCl_3



^1H NMR (400 MHz) spectrum of compound **1k** in CDCl_3

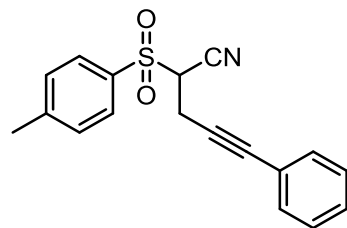


^{13}C NMR (100 MHz) spectrum of compound **1k** in CDCl_3

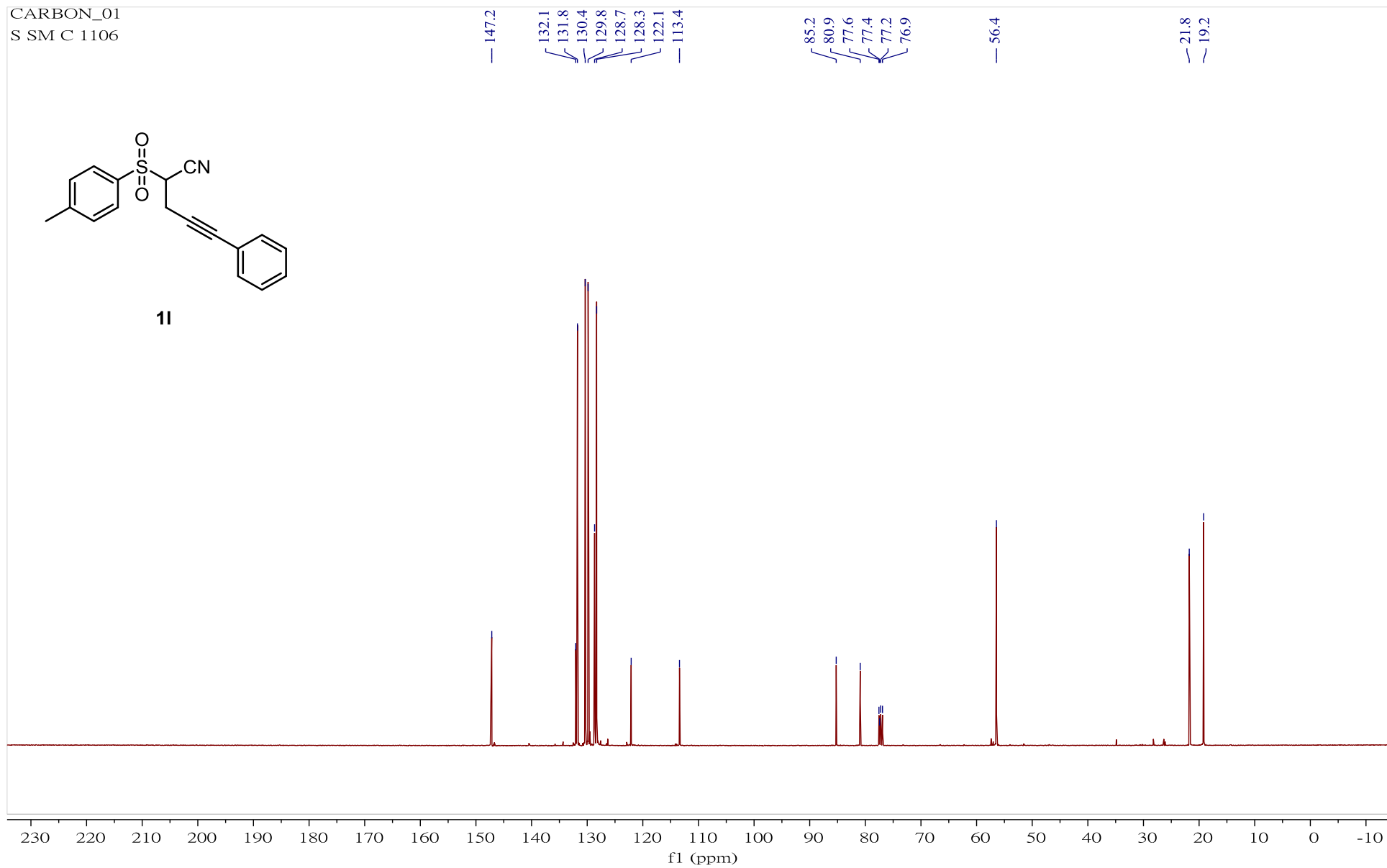


^1H NMR (400 MHz) spectrum of compound **11** in CDCl_3

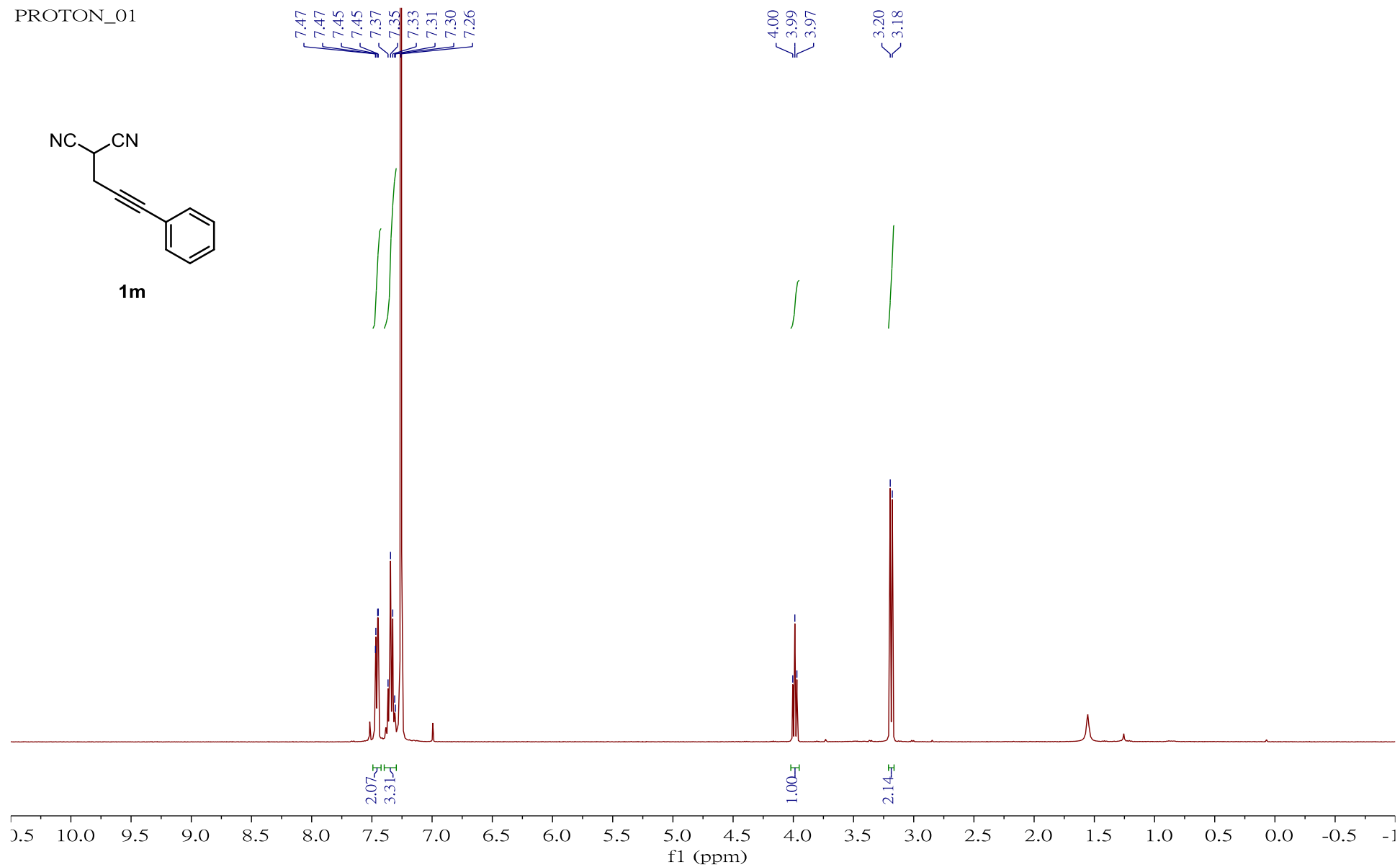
CARBON_01
S SM C 1106



11

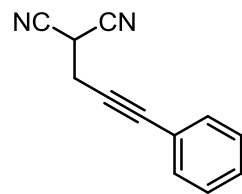


^{13}C NMR (100 MHz) spectrum of compound **11** in CDCl_3

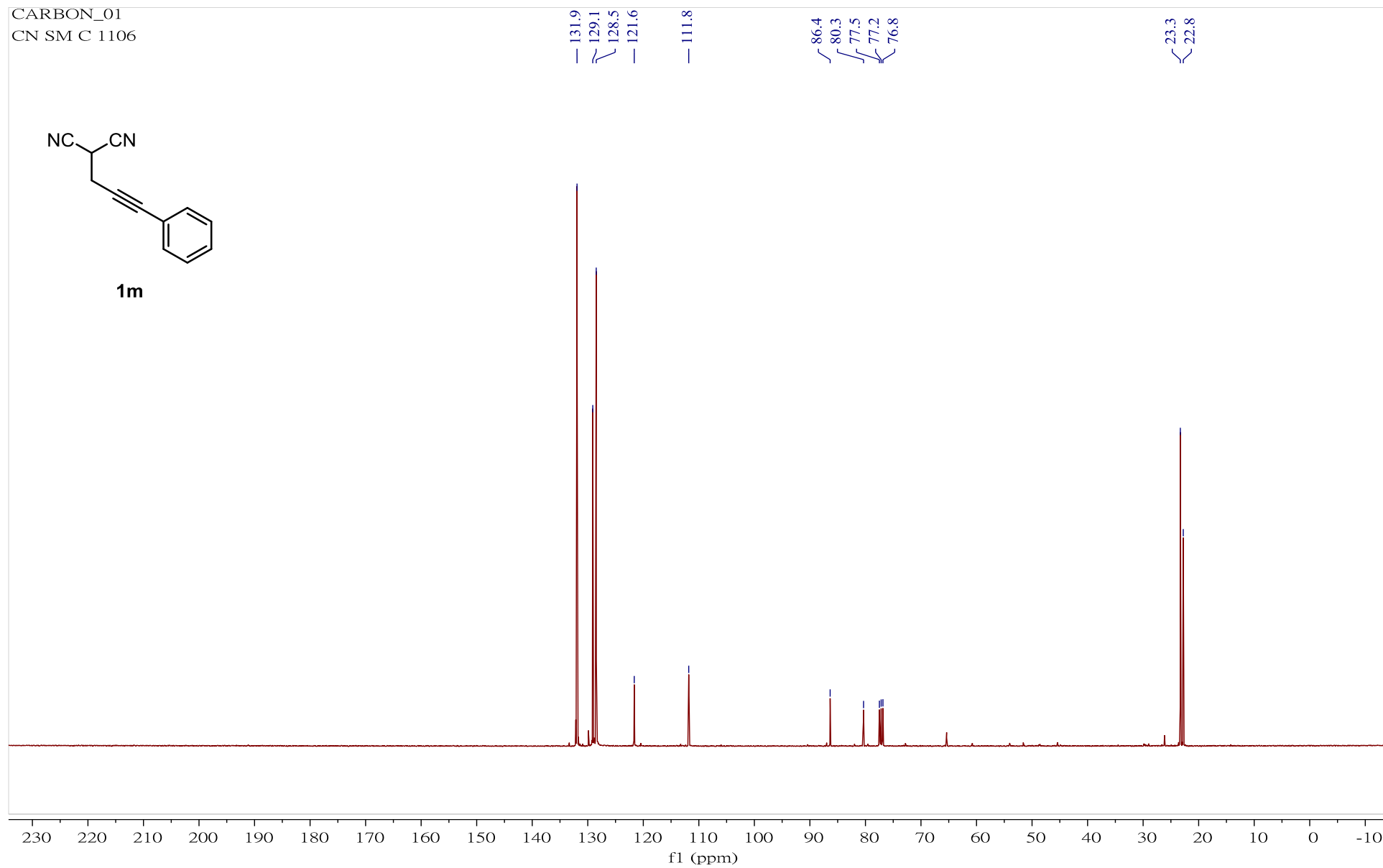


^1H NMR (400 MHz) spectrum of compound **1m** in CDCl_3

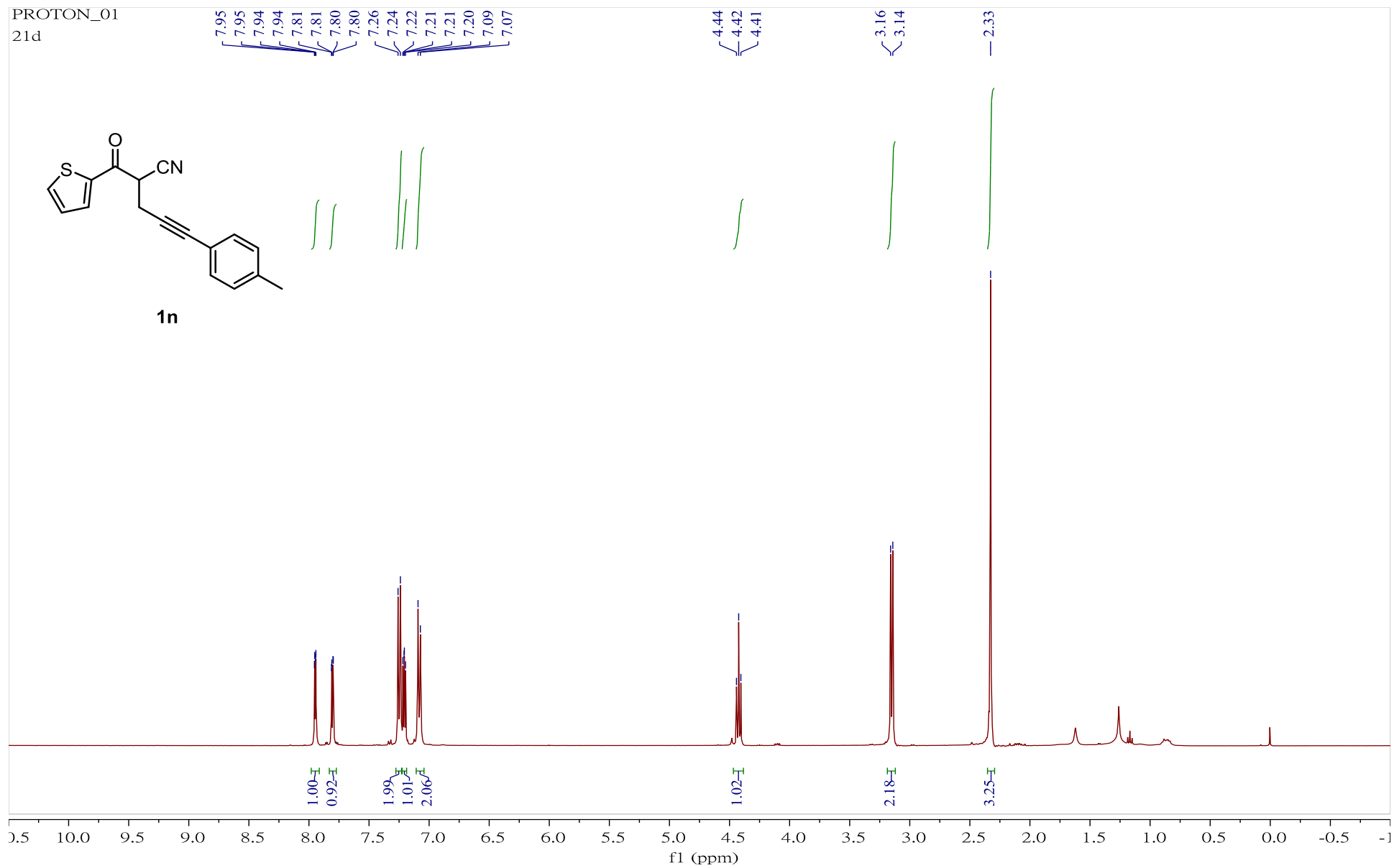
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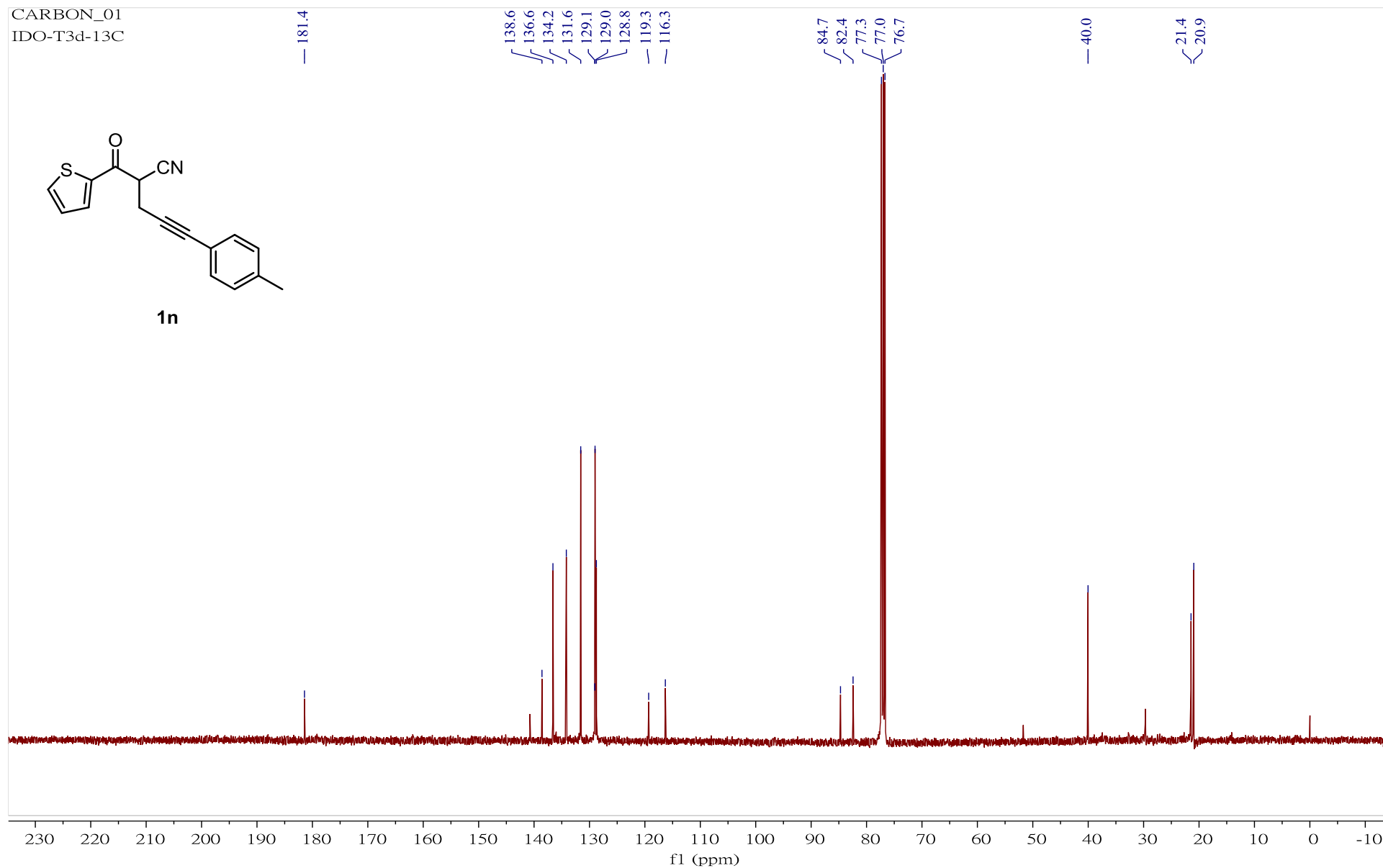
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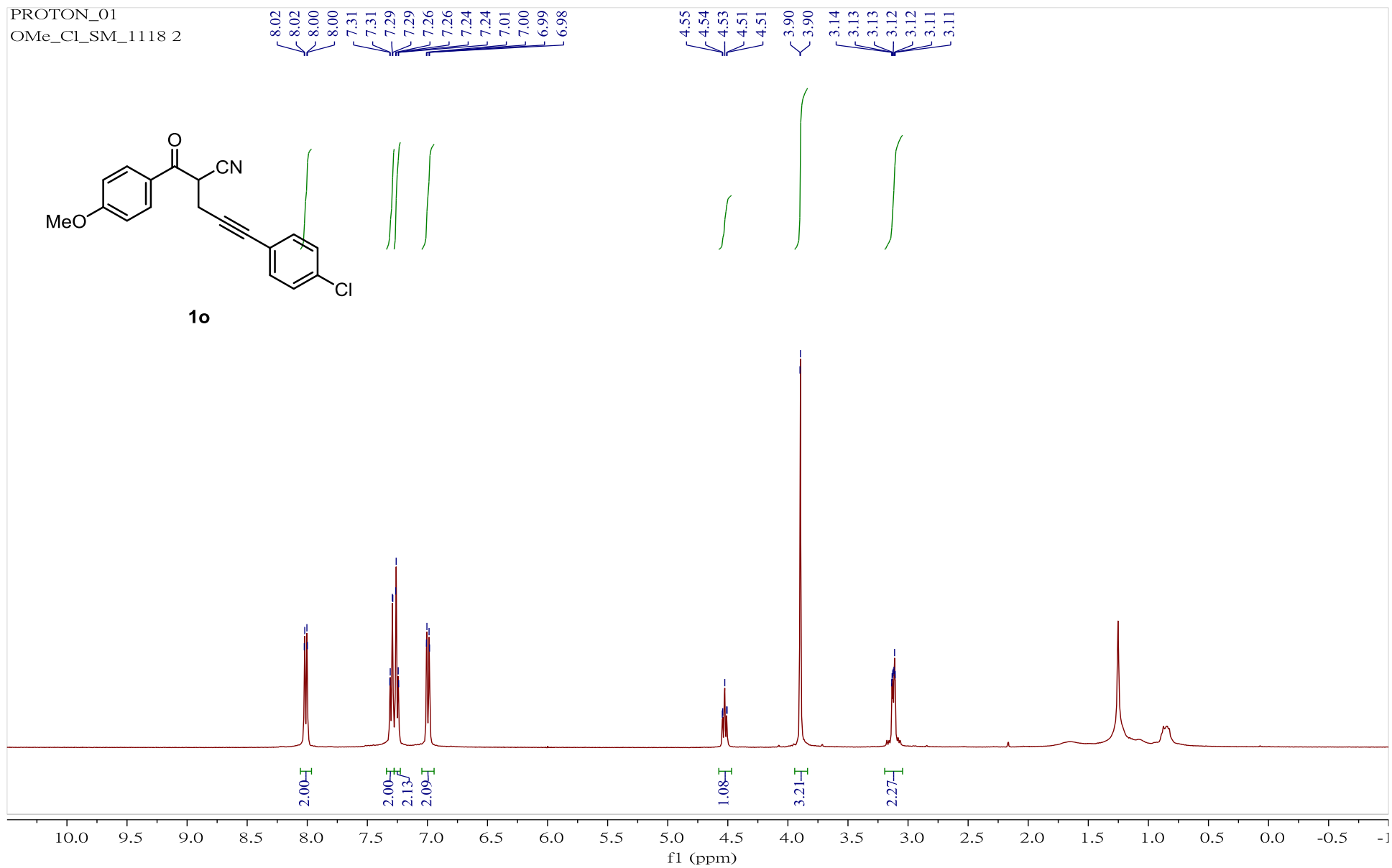
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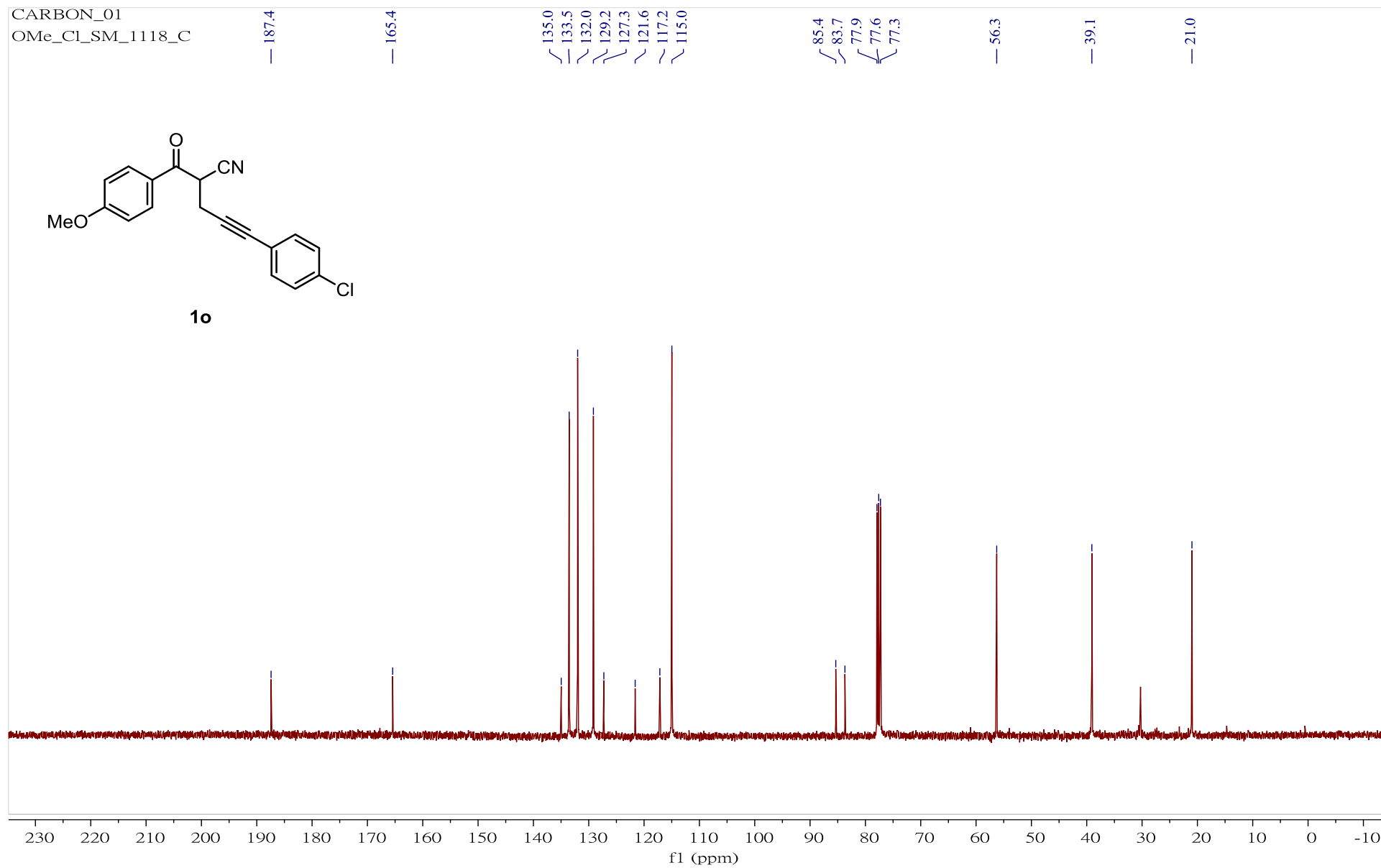
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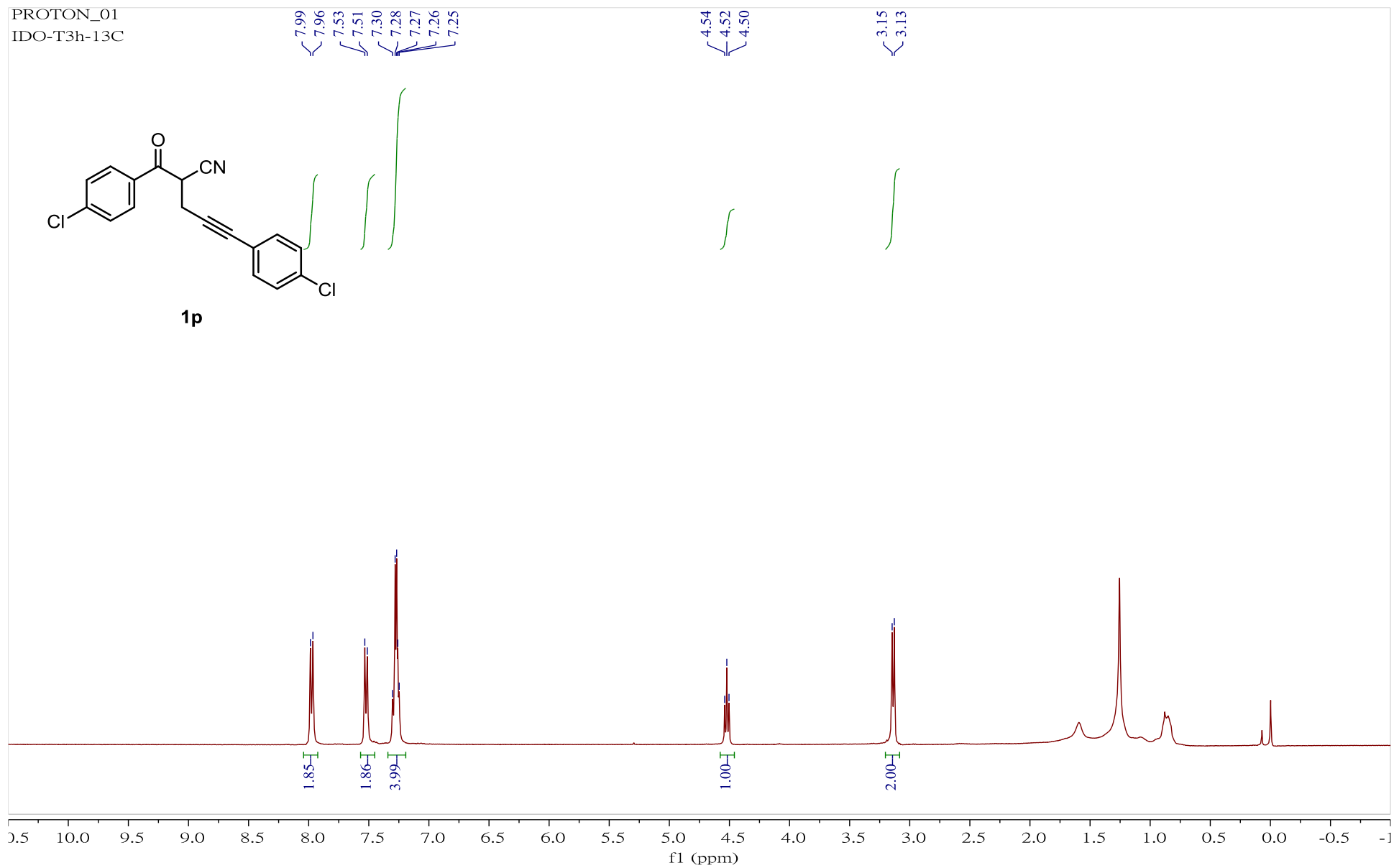
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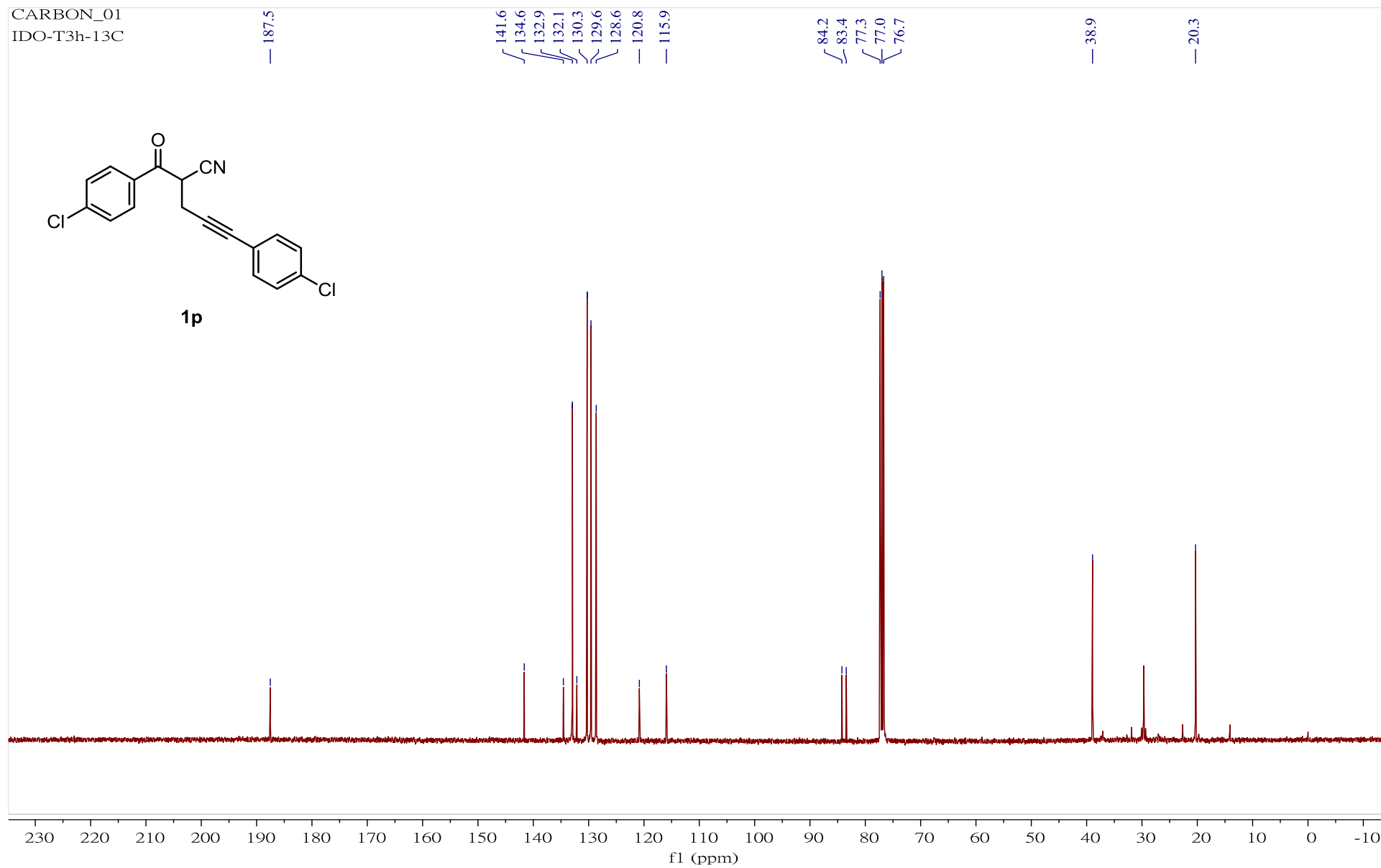
¹H NMR (400 MHz) spectrum of compound **1o** in CDCl₃



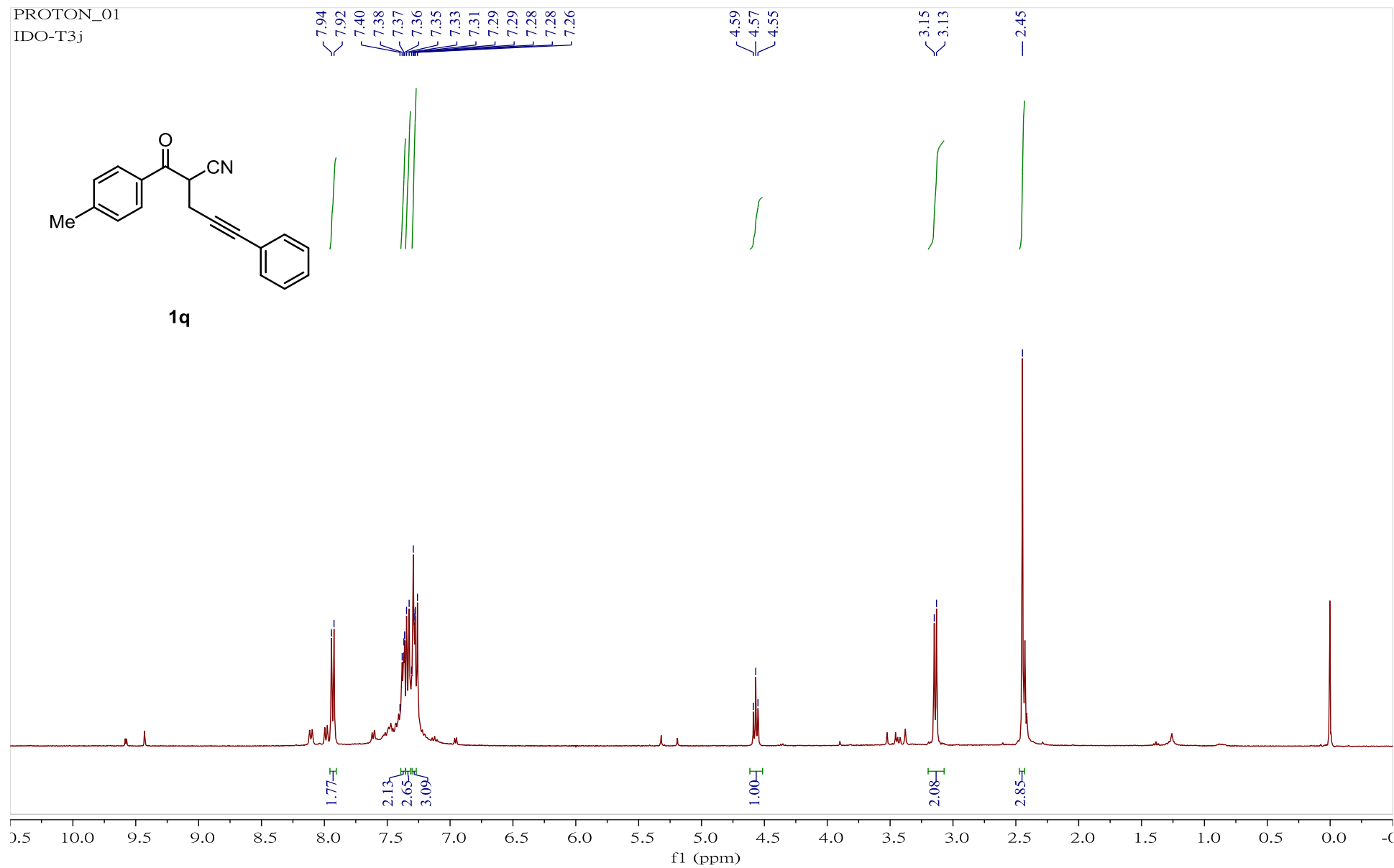
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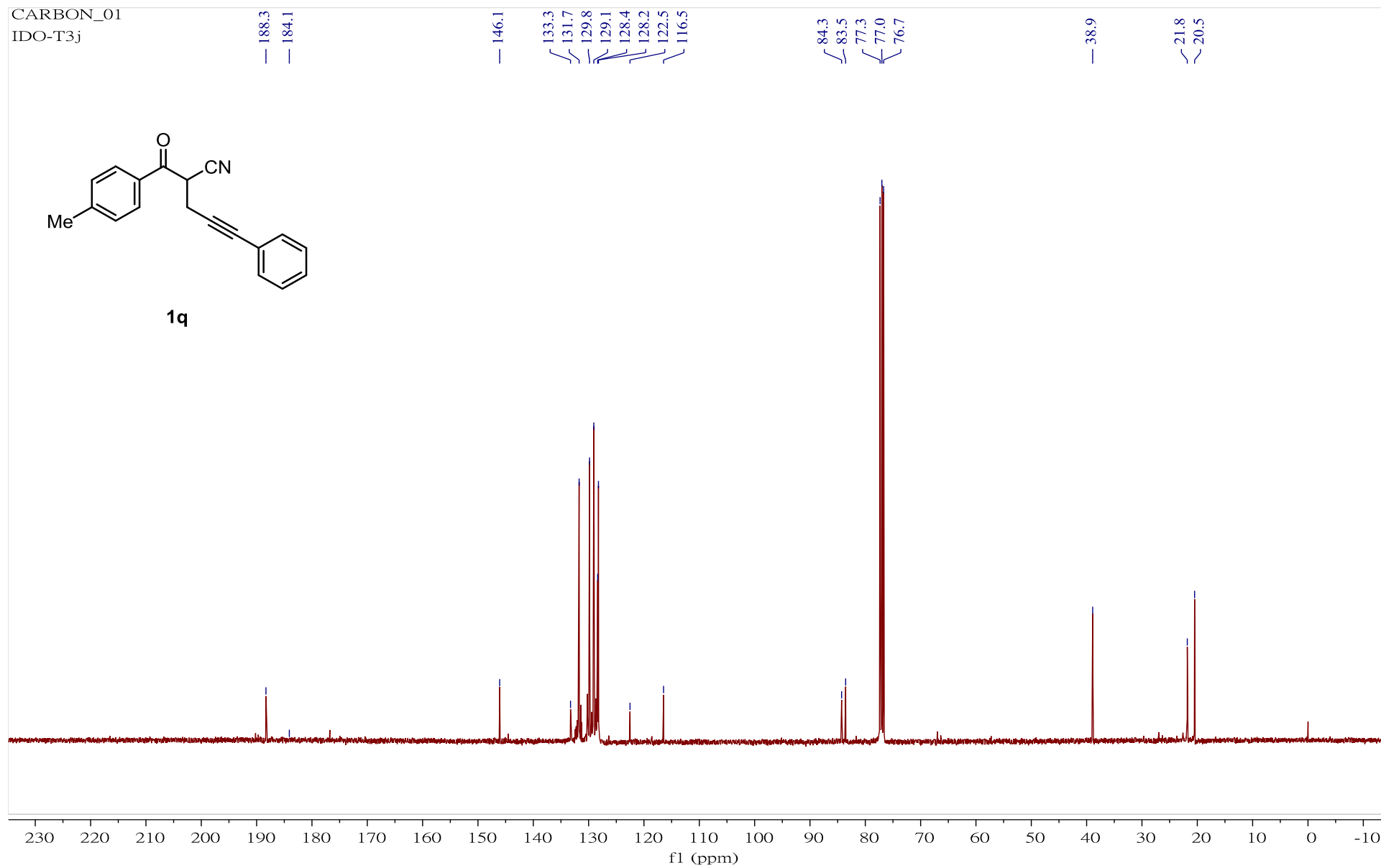
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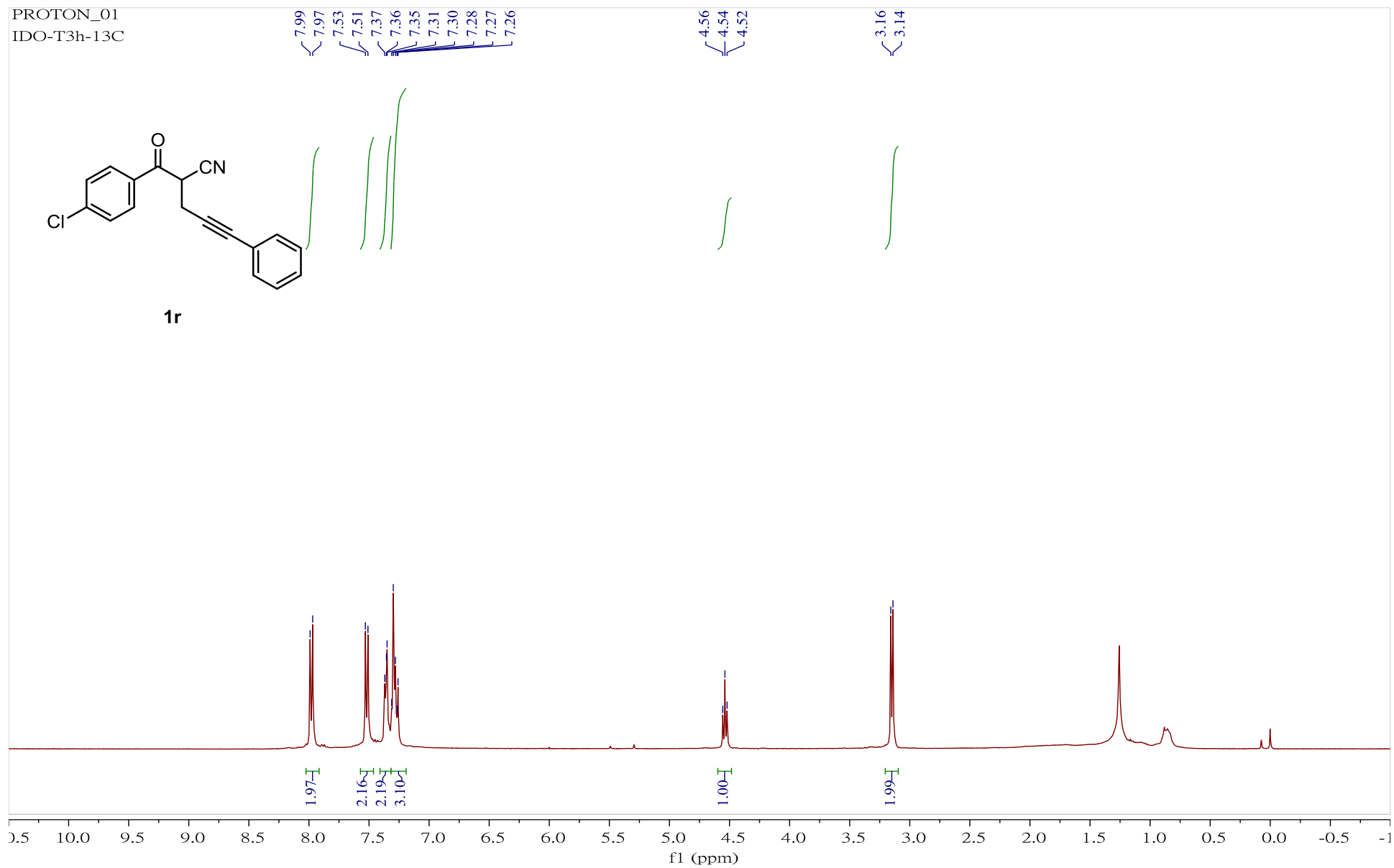
^{13}C NMR (100 MHz) spectrum of compound **1p** in CDCl_3



¹H NMR (400 MHz) spectrum of compound **1q** in CDCl₃

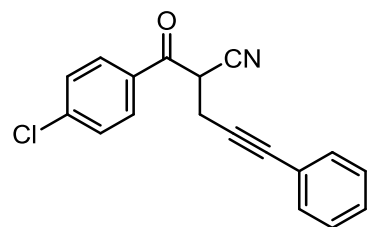


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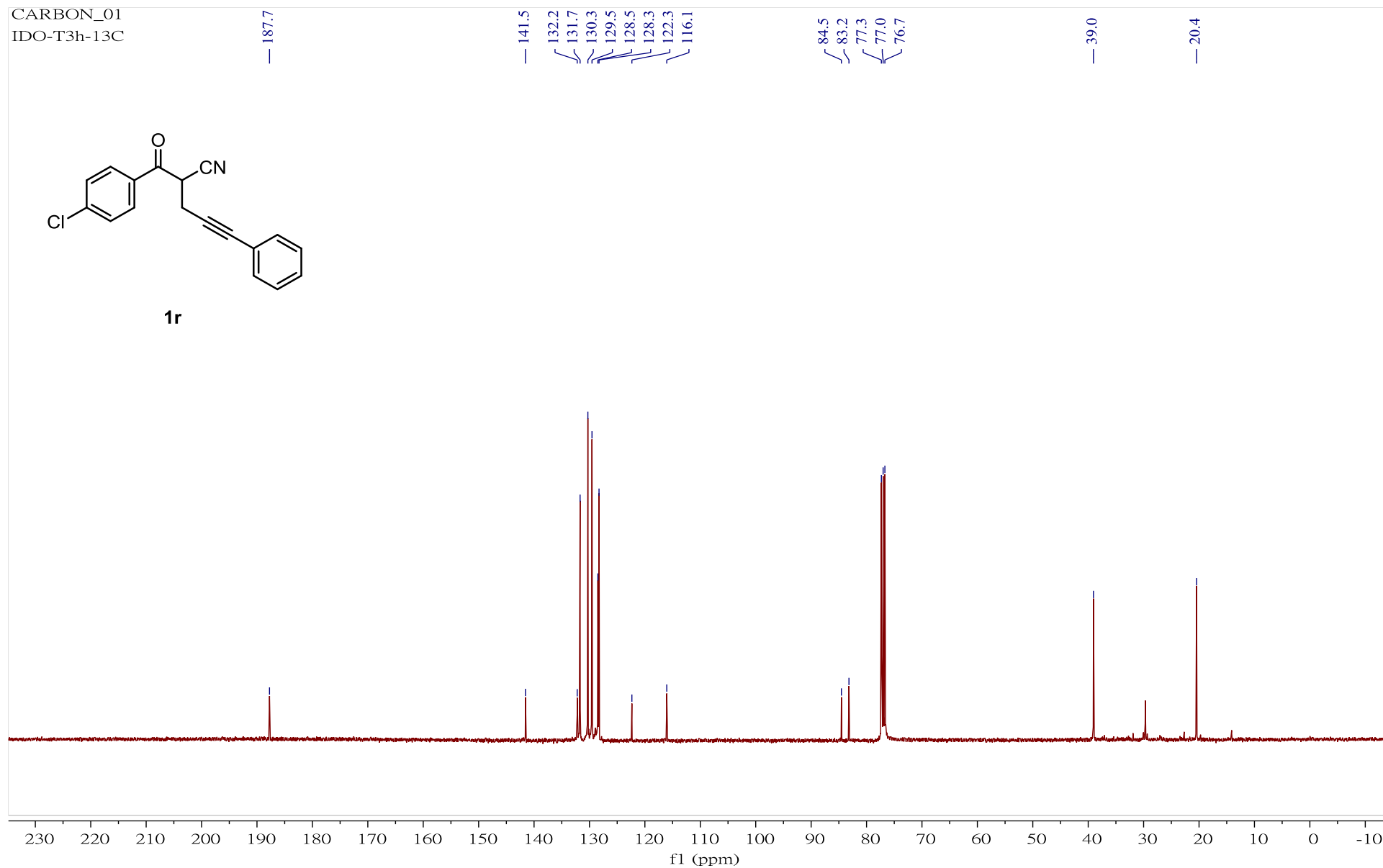


¹H NMR (400 MHz) spectrum of compound **1r** in CDCl₃

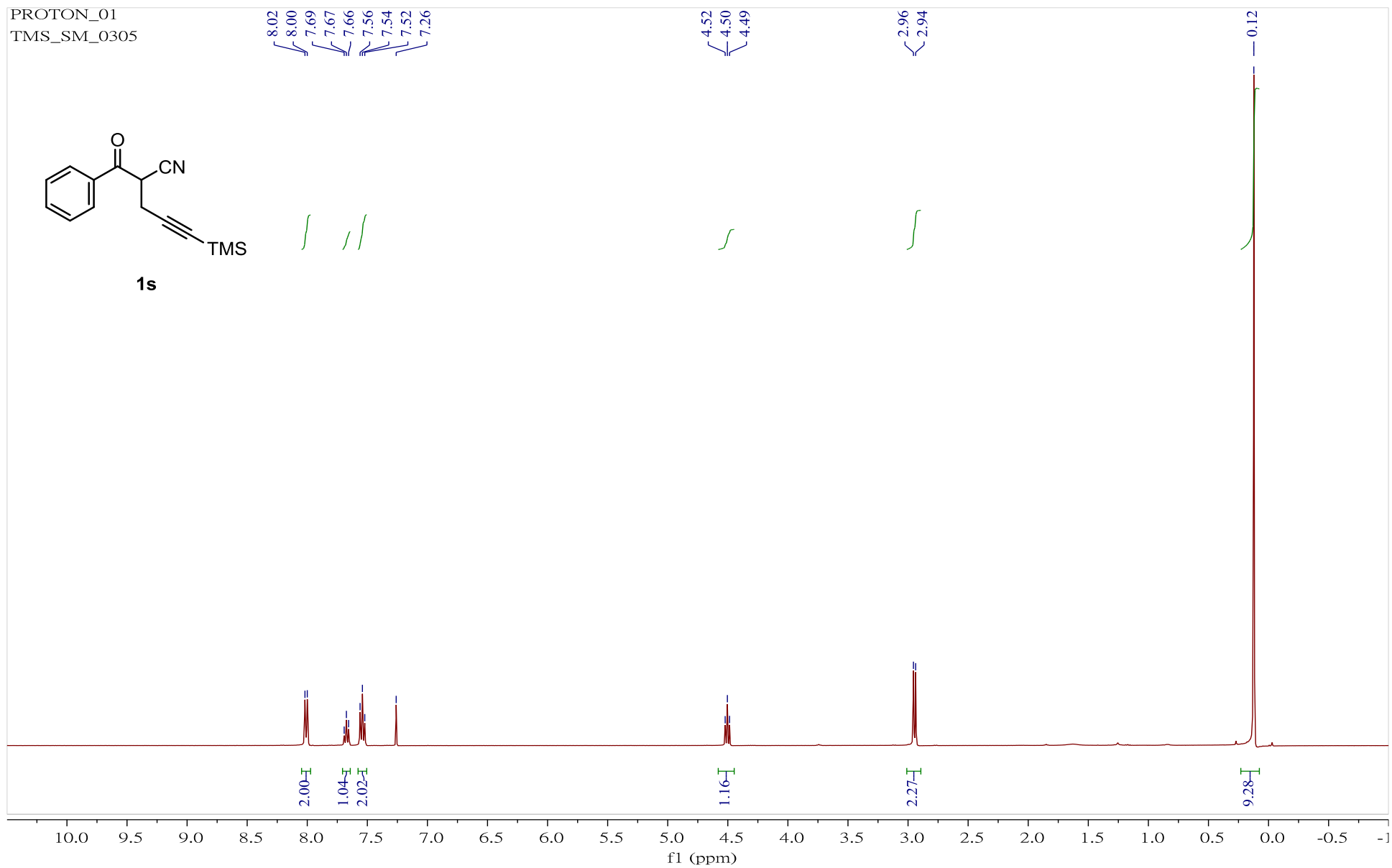
CARBON_01
IDO-T3h-13C



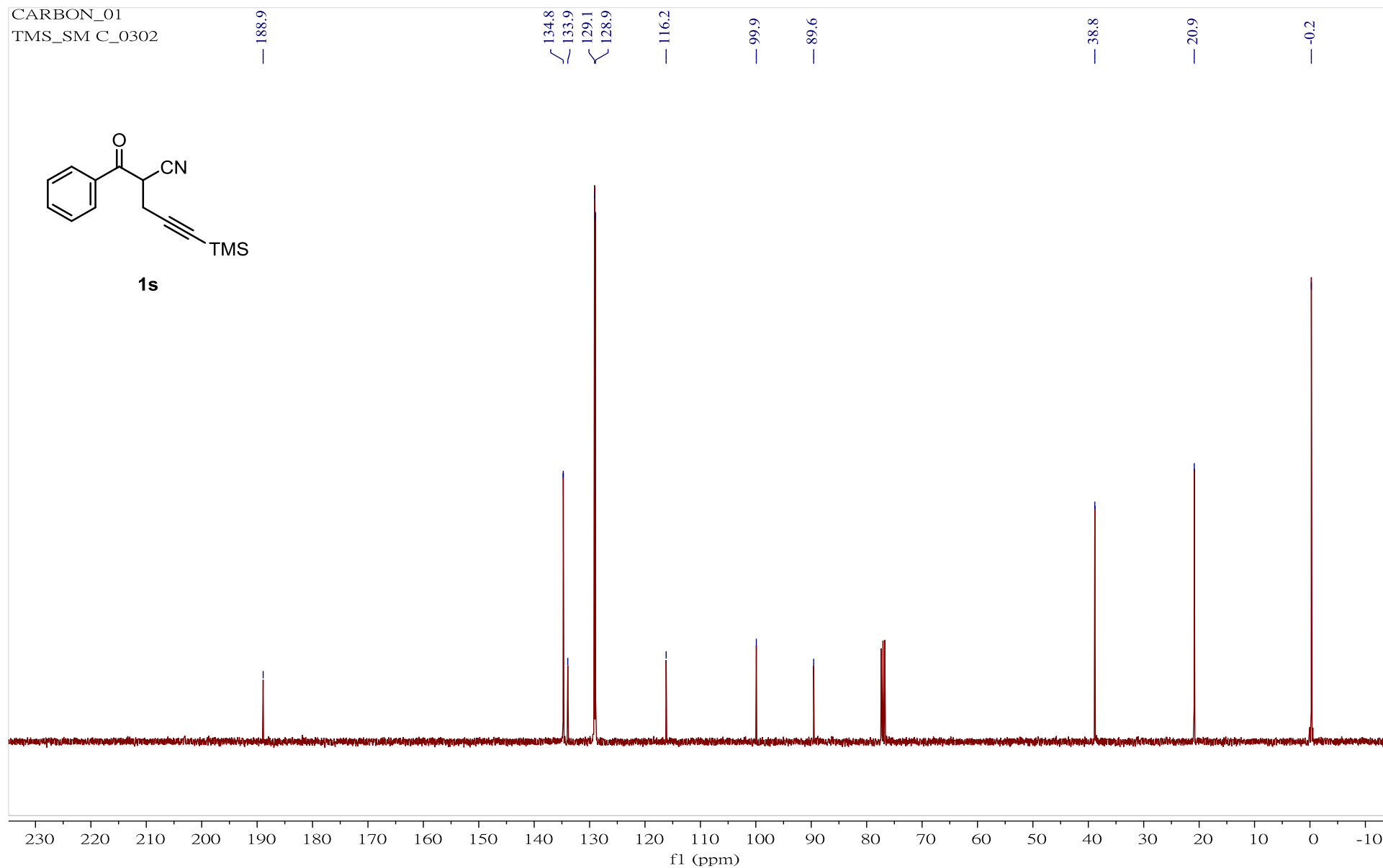
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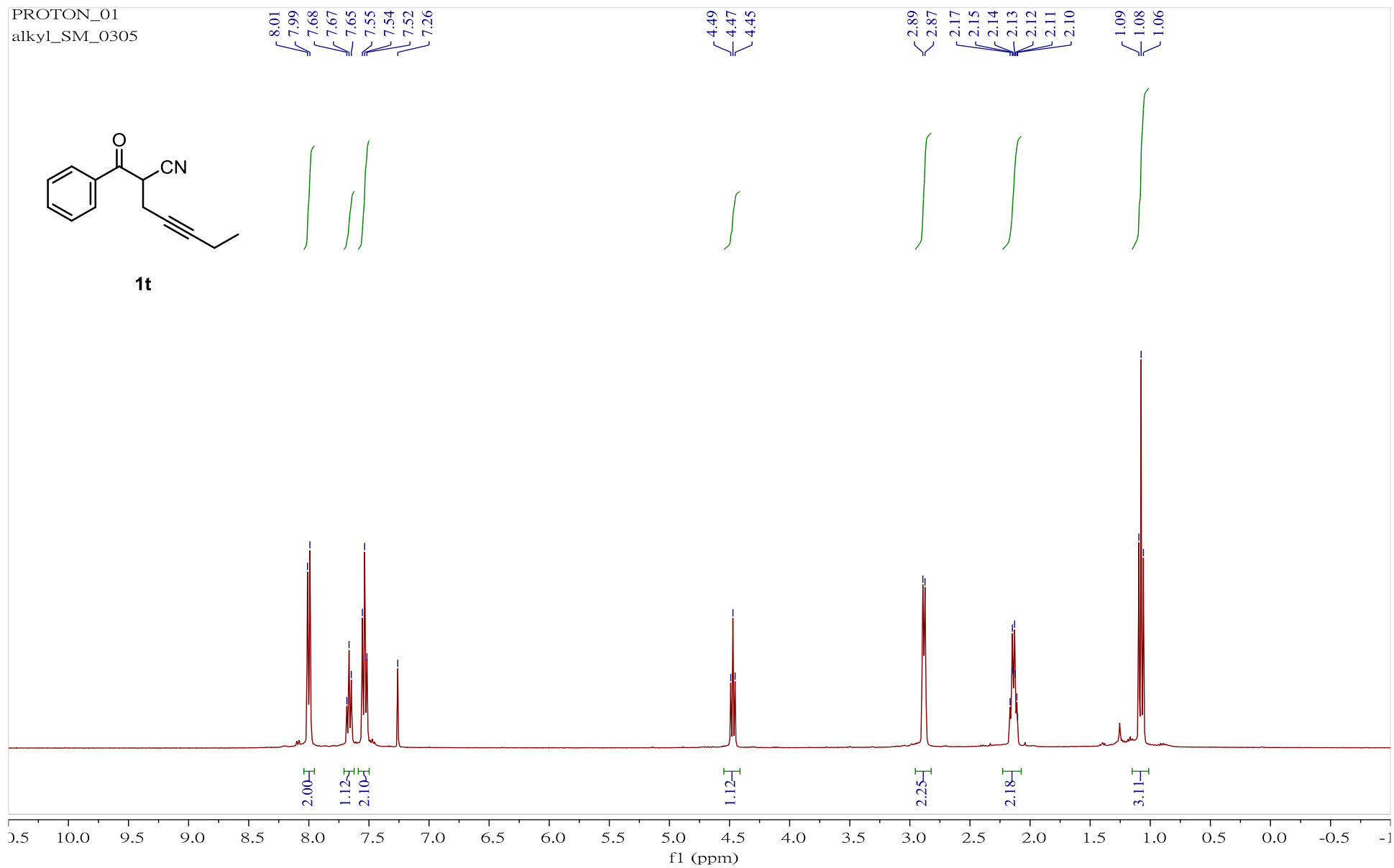
¹³C NMR (100 MHz) spectrum of compound **1r** in CDCl₃



^1H NMR (400 MHz) spectrum of compound **1s** in CDCl_3

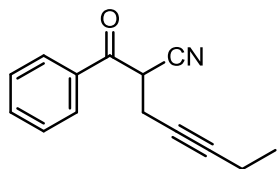


^{13}C NMR (100 MHz) spectrum of compound **1s** in CDCl_3

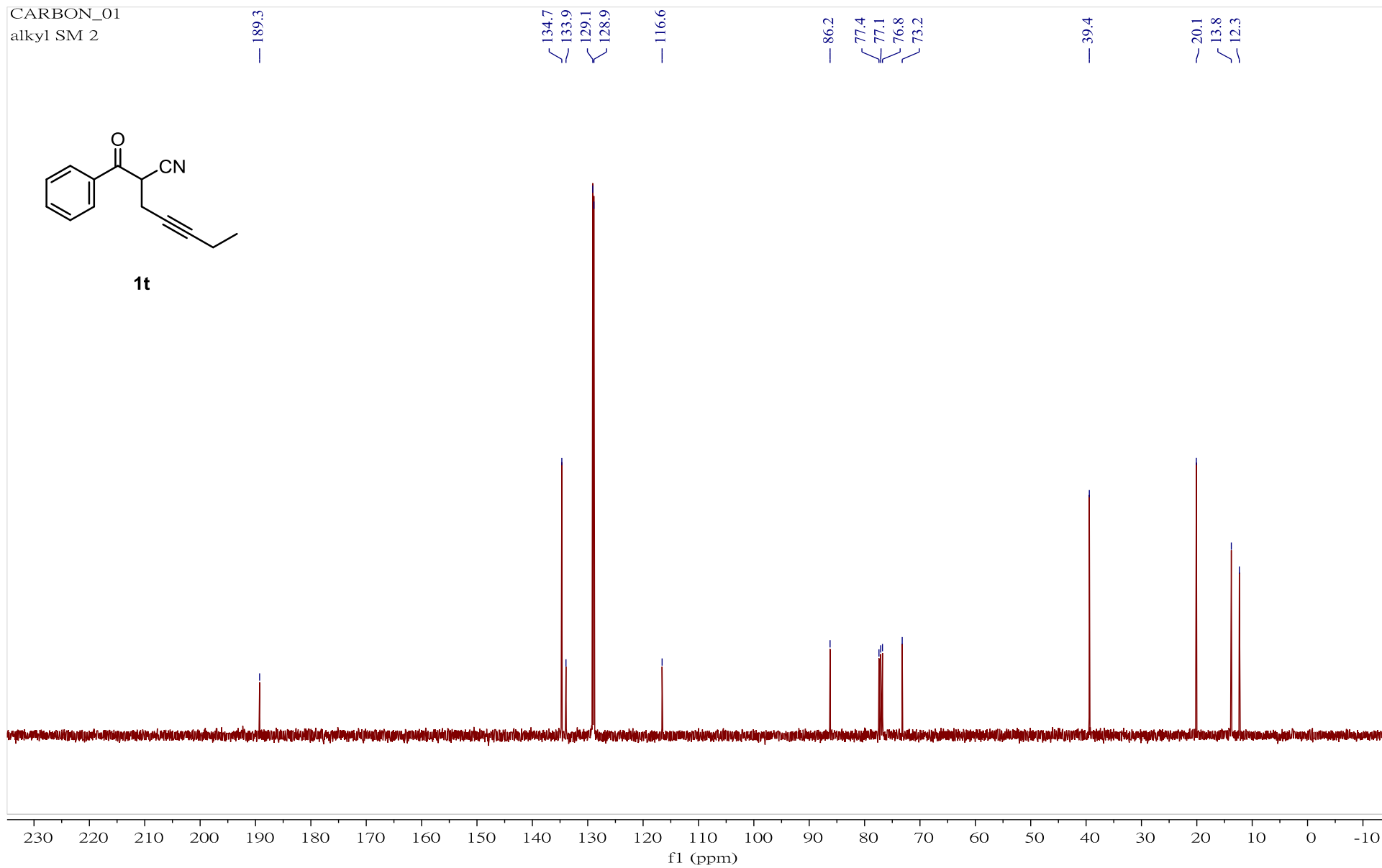


^1H NMR (400 MHz) spectrum of compound **1t** in CDCl_3

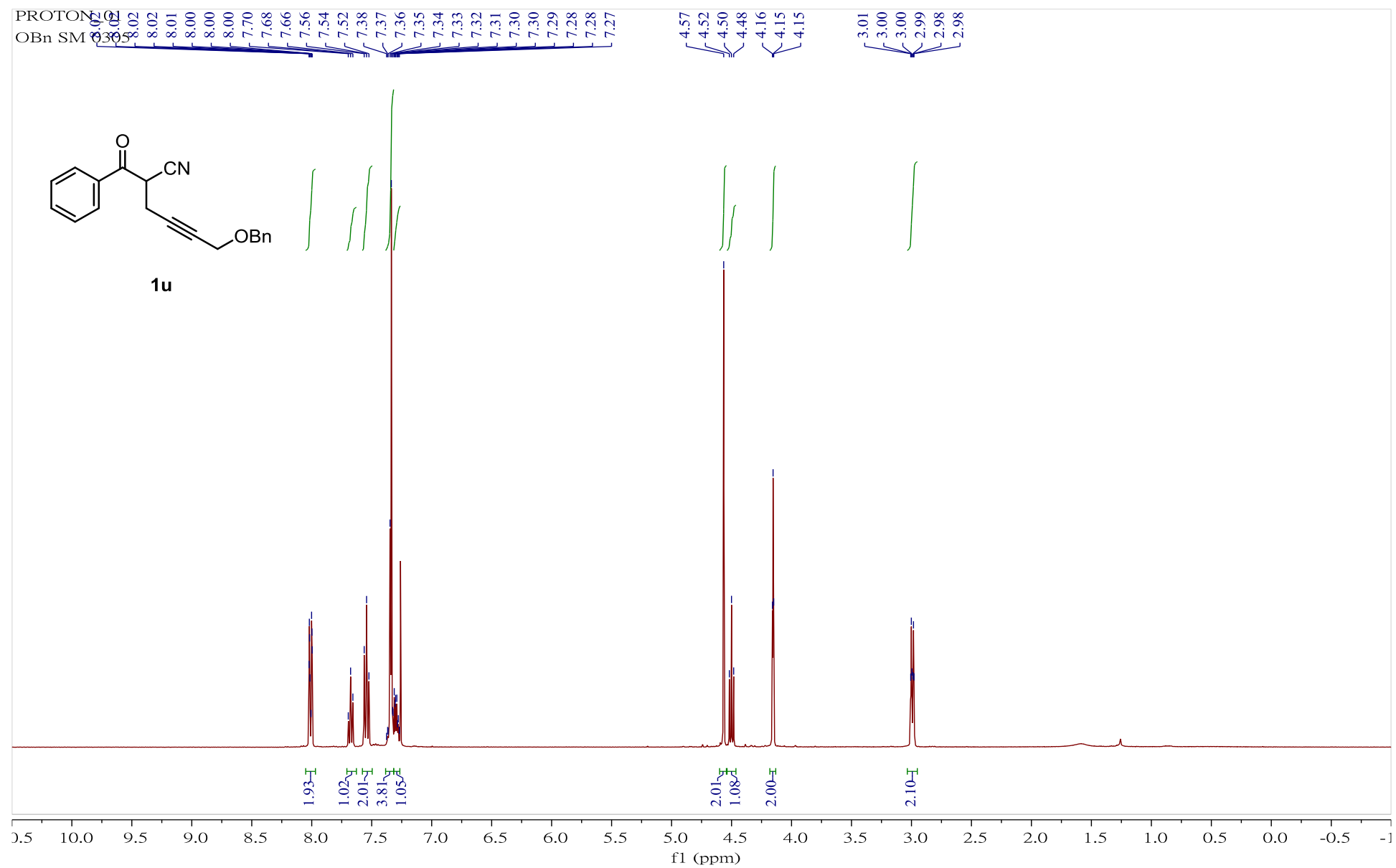
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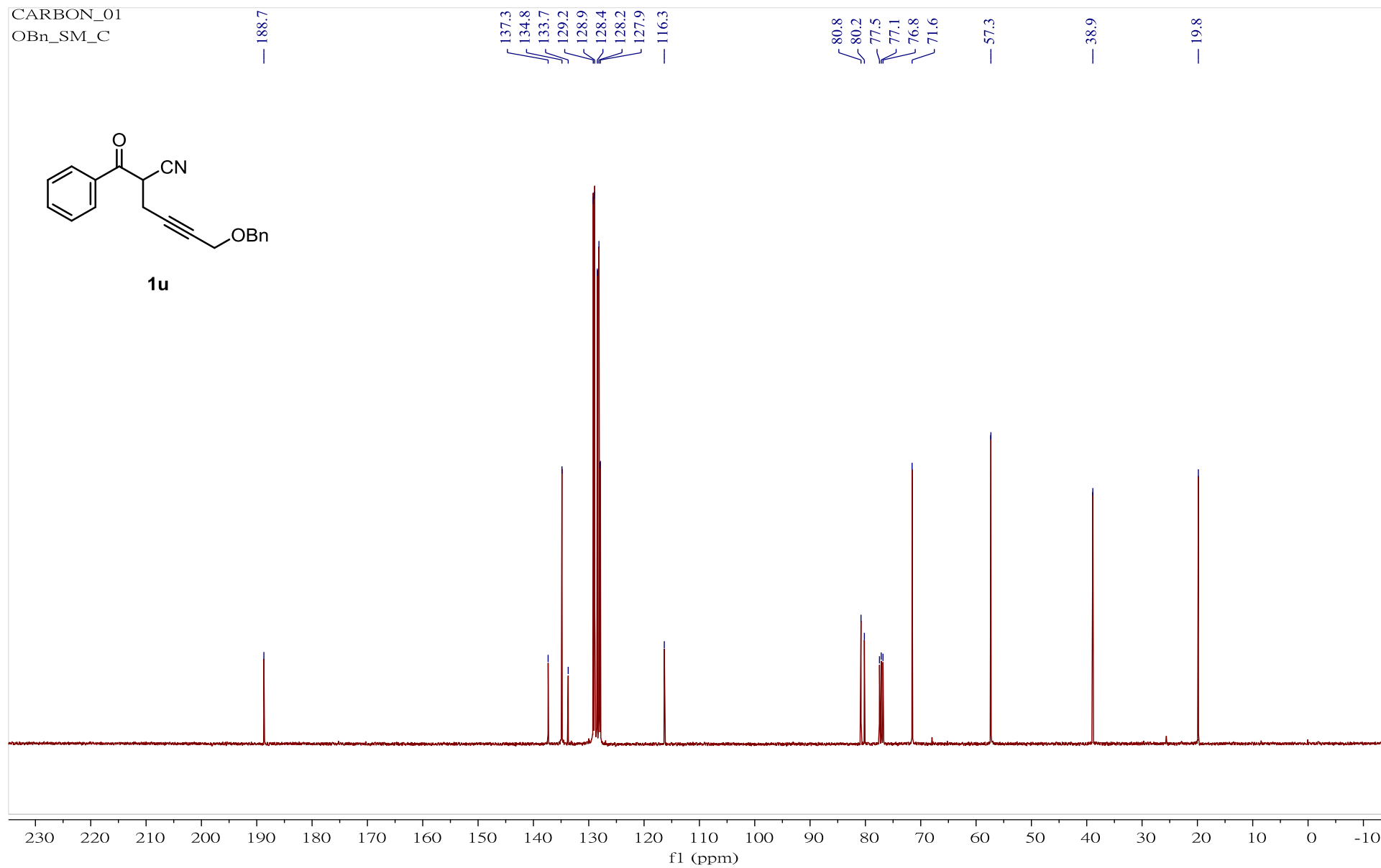
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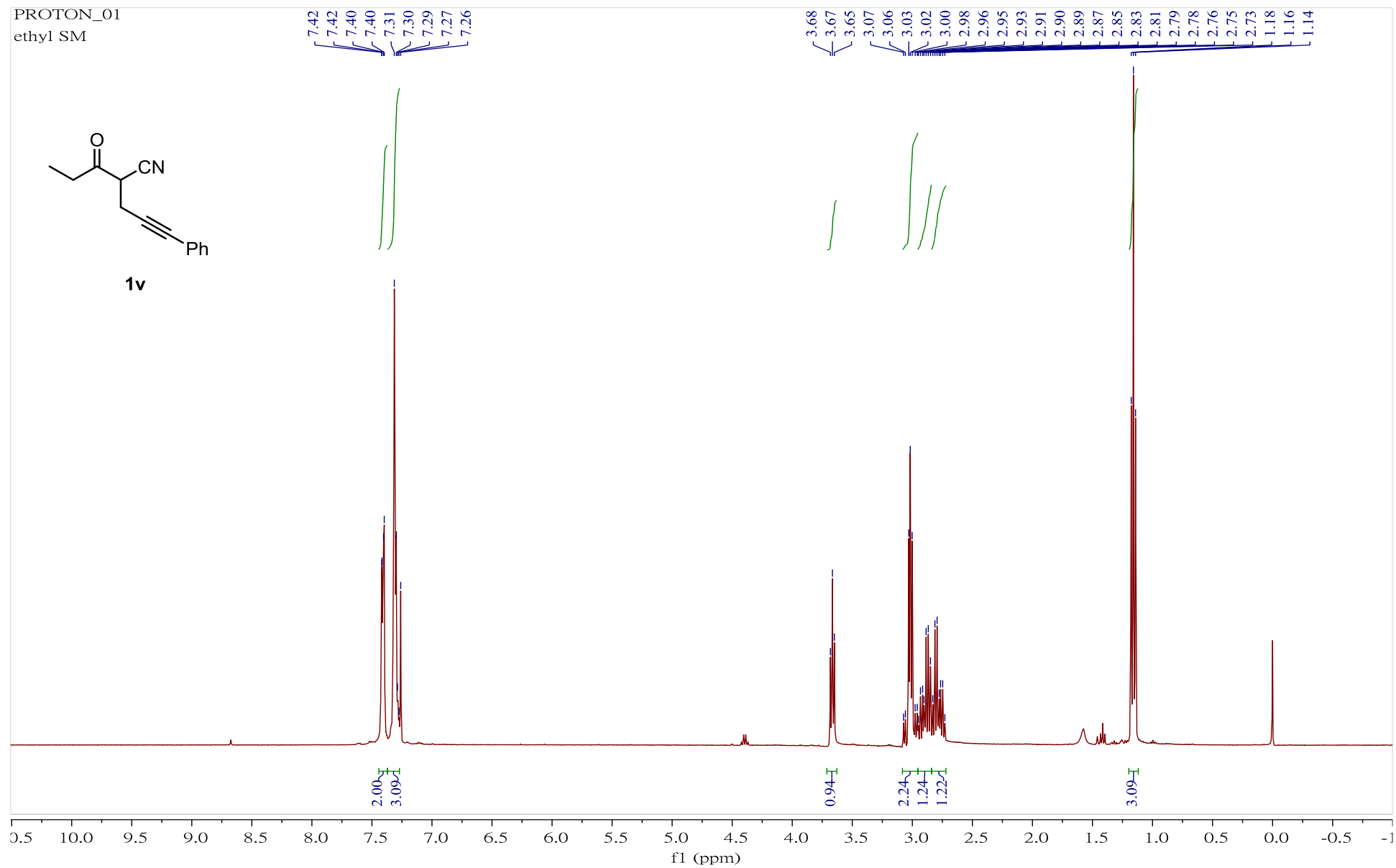
¹³C NMR (100 MHz) spectrum of compound **1t** in CDCl₃



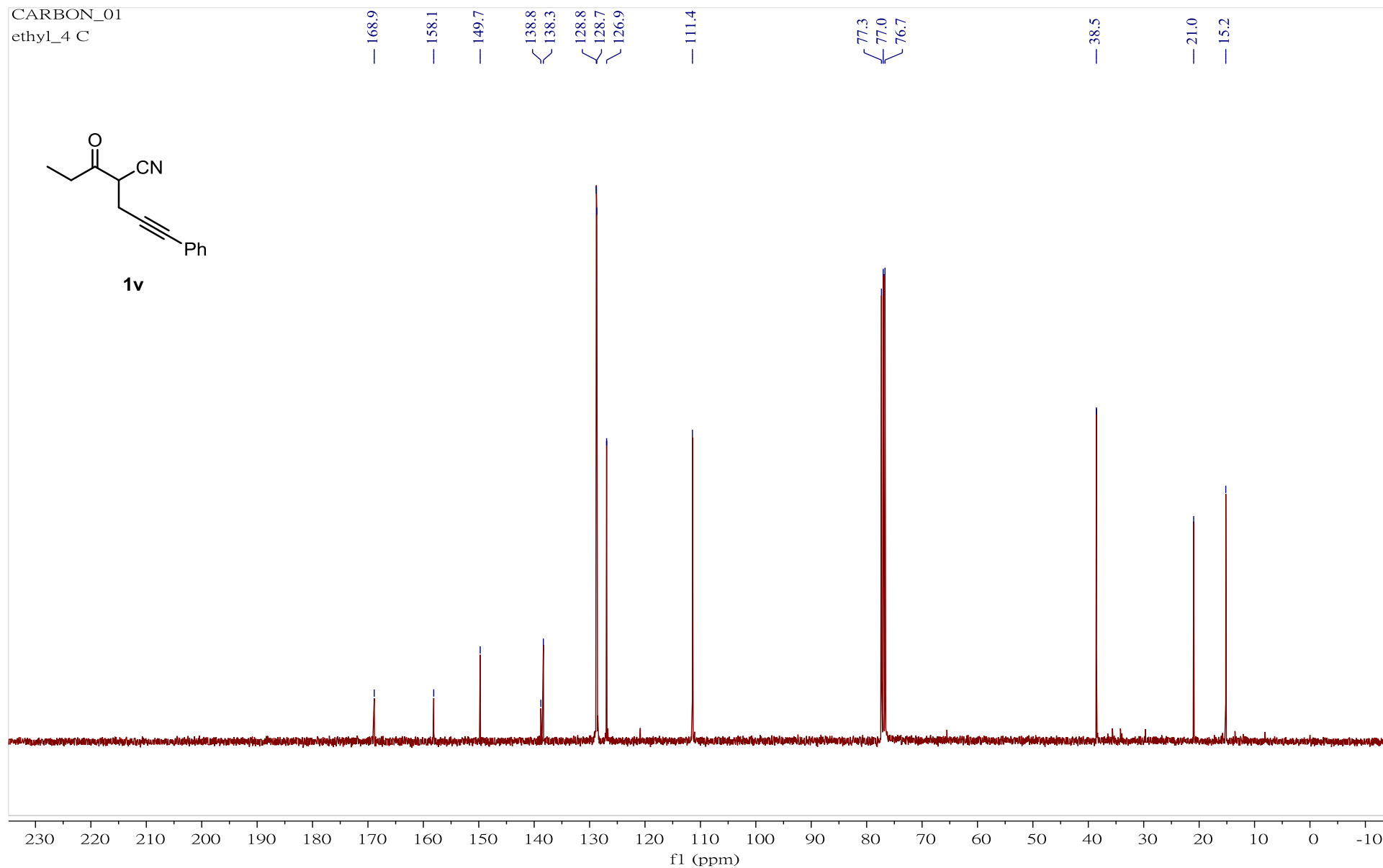
^1H NMR (400 MHz) spectrum of compound **1u** in CDCl_3



^{13}C NMR (100 MHz) spectrum of compound **1u** in CDCl_3

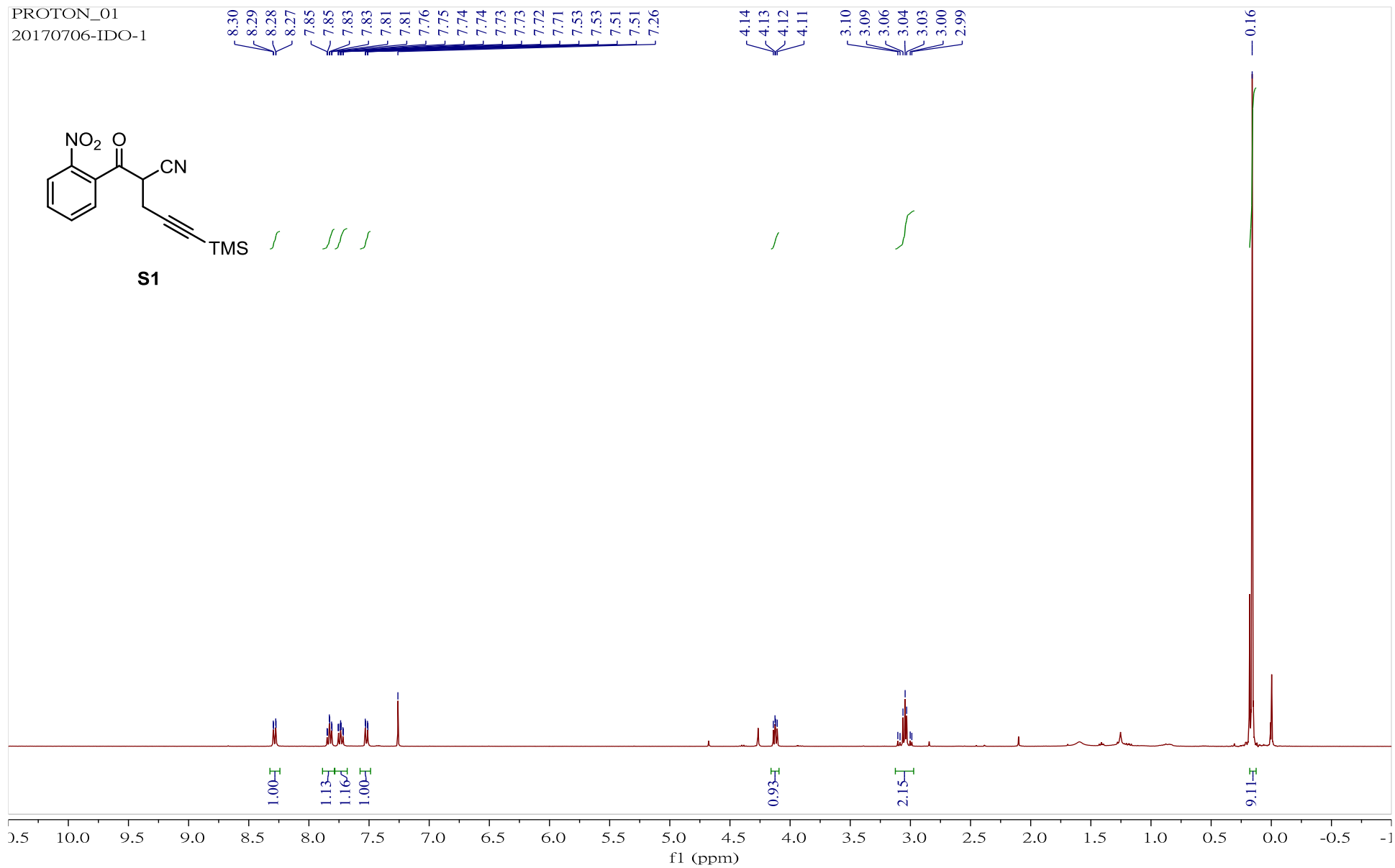


¹H NMR (400 MHz) spectrum of compound **1v** in CDCl₃



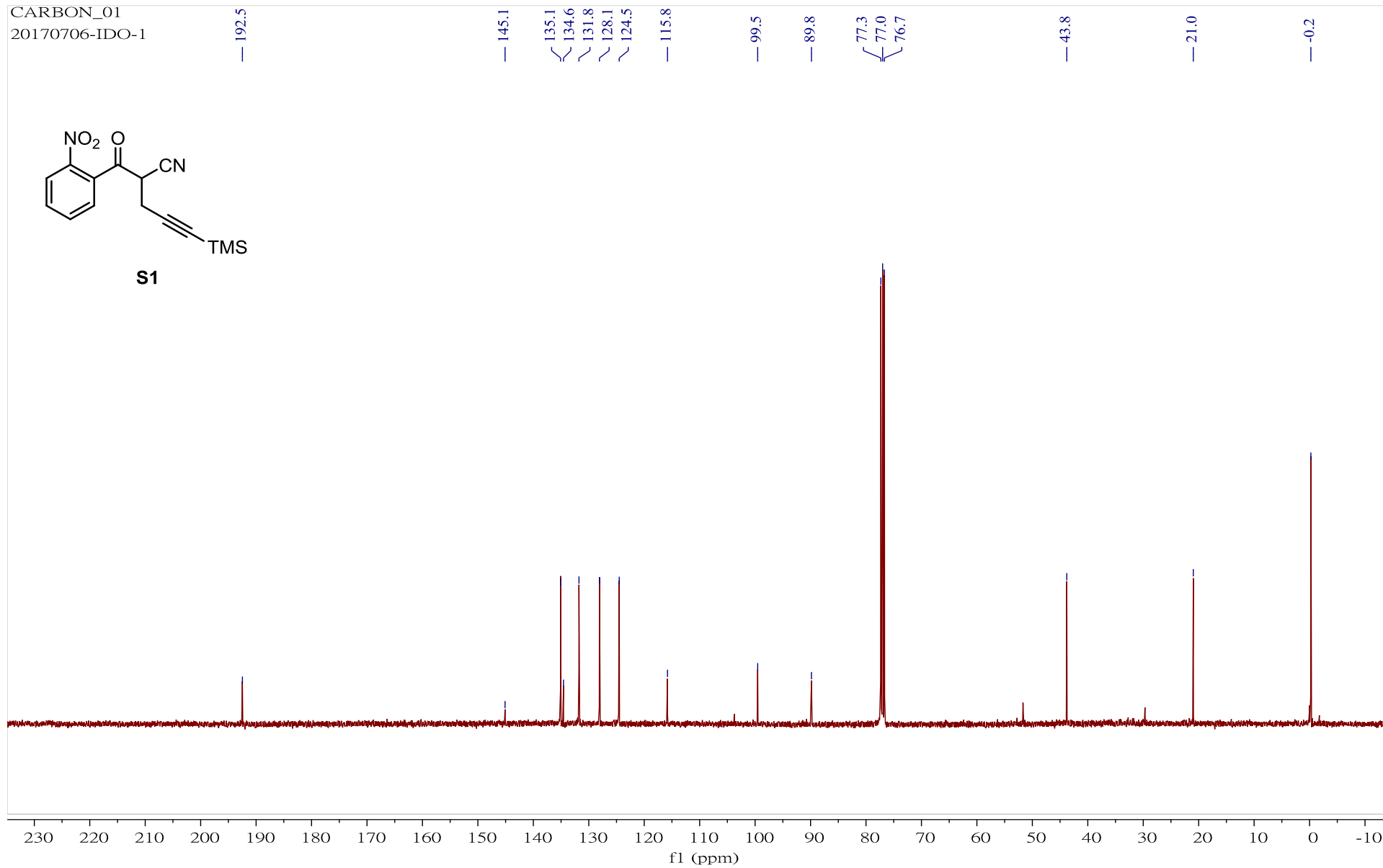
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PROTON_01
20170706-IDO-1



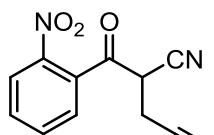
^1H NMR (400 MHz) spectrum of compound **S1** in CDCl_3

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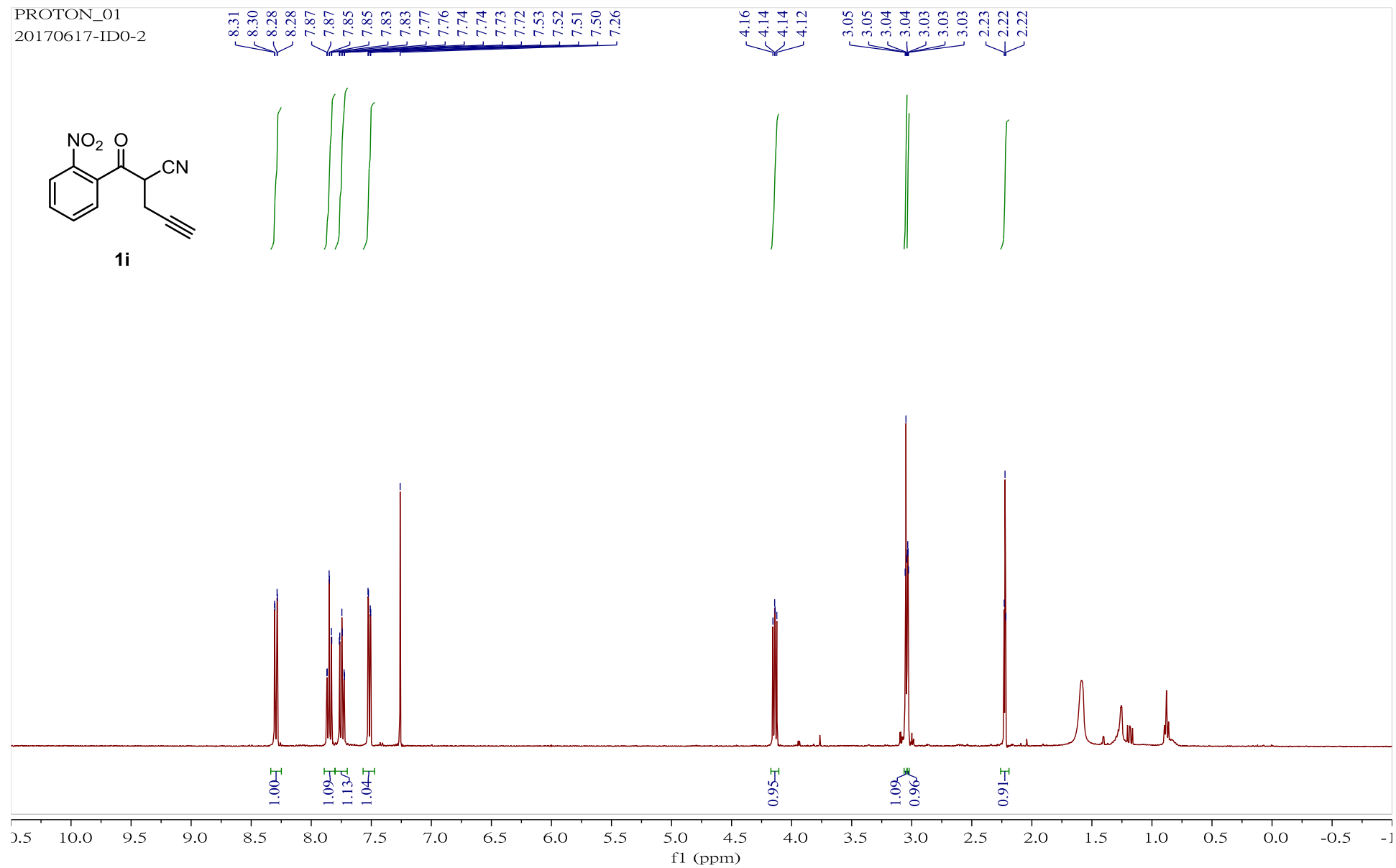


^{13}C NMR (100 MHz) spectrum of compound **S1** in CDCl_3

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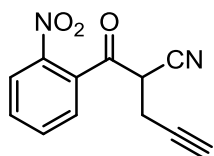


1i

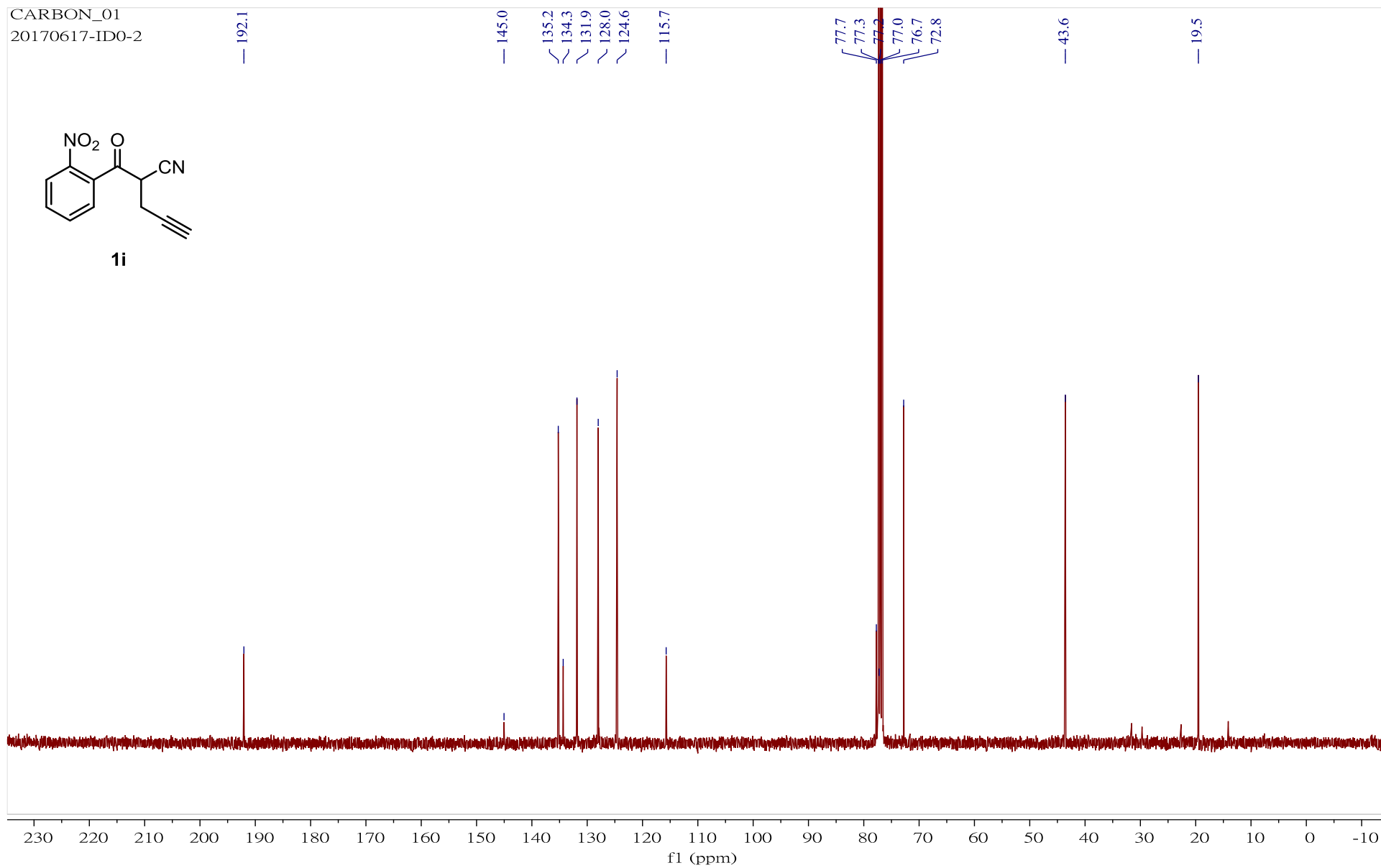


¹H NMR (400 MHz) spectrum of compound **1i** in CDCl₃

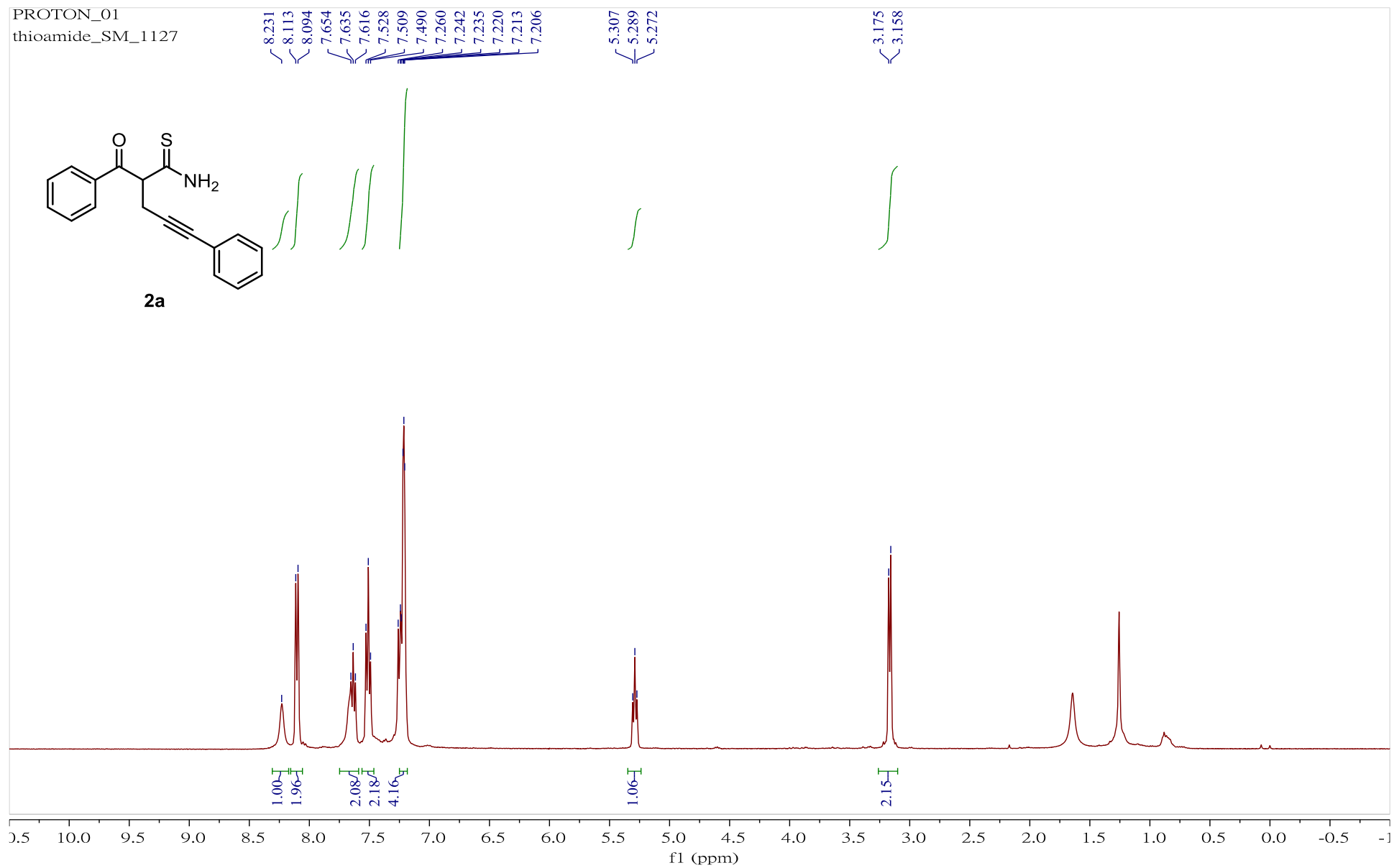
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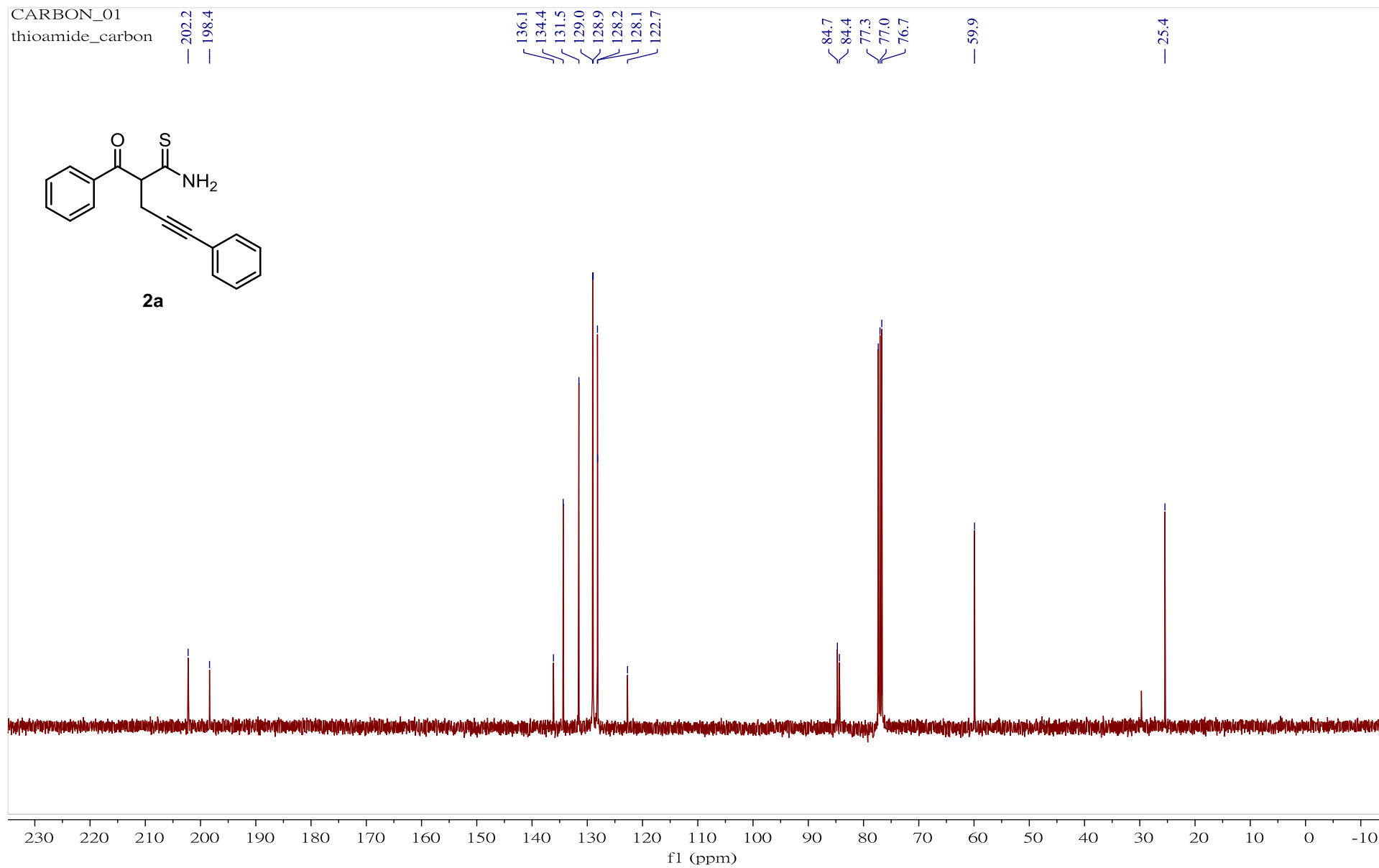
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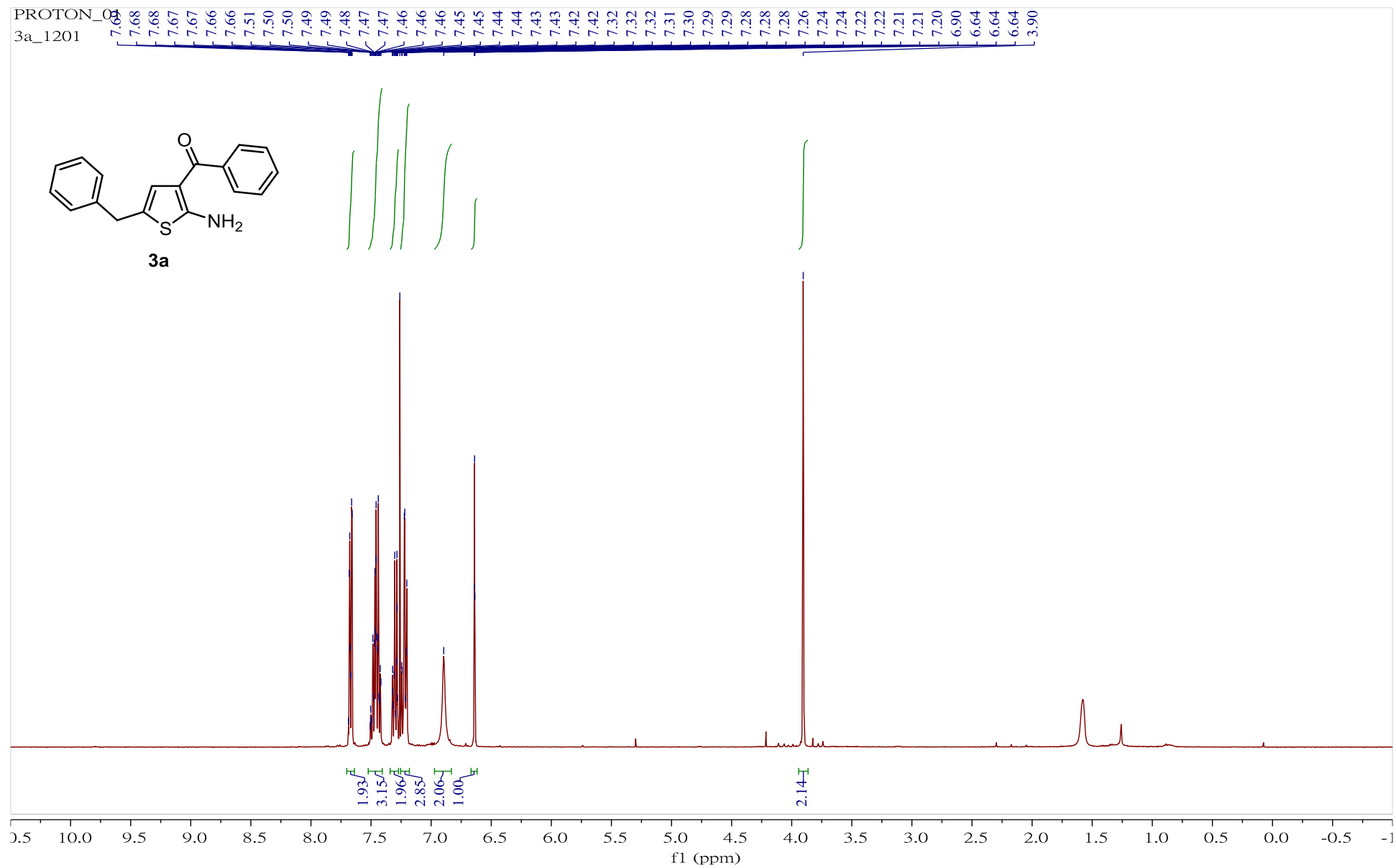
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¹H NMR (400 MHz) spectrum of compound **2a** in CDCl₃

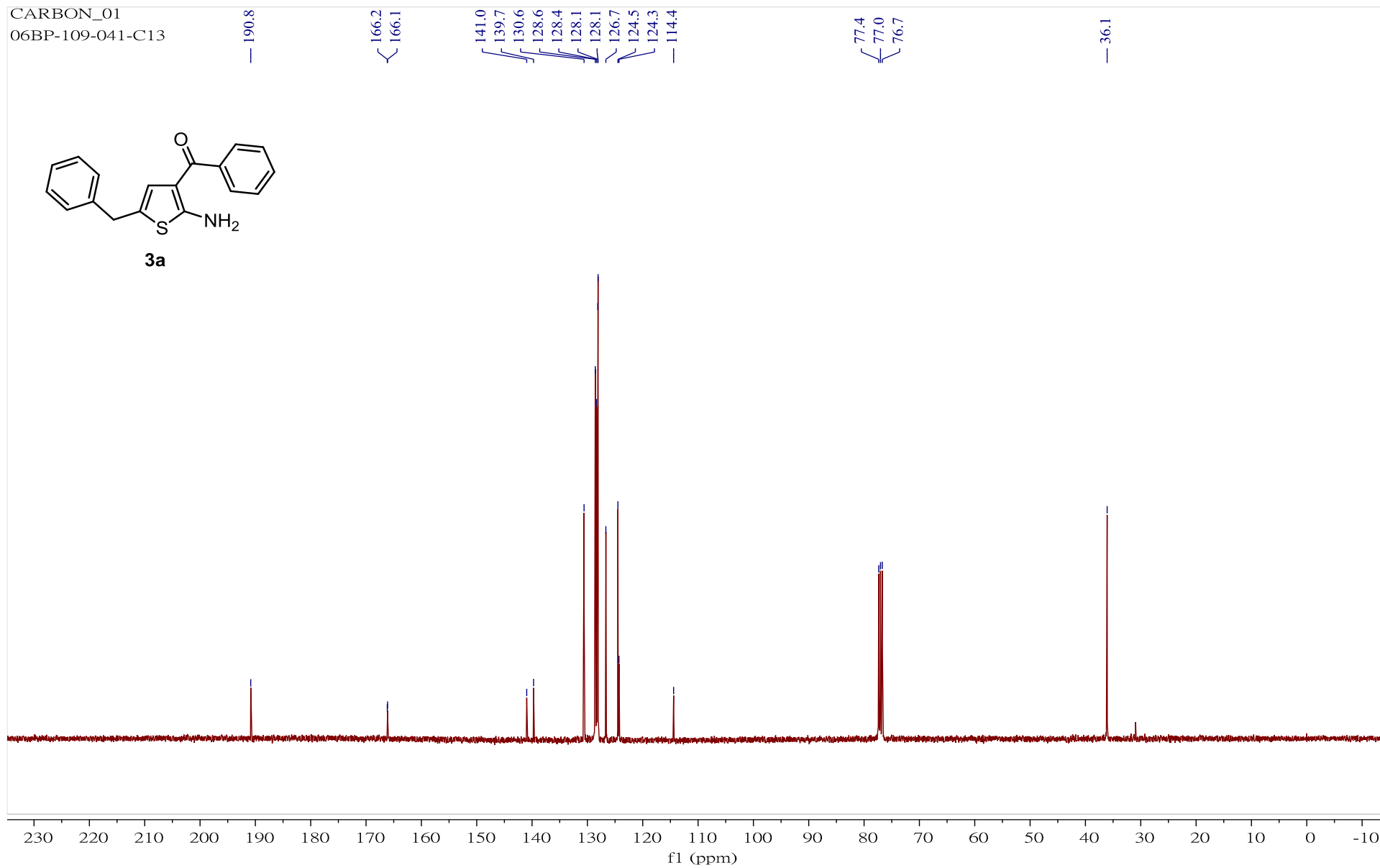


^{13}C NMR (100 MHz) spectrum of compound **2a** in CDCl_3

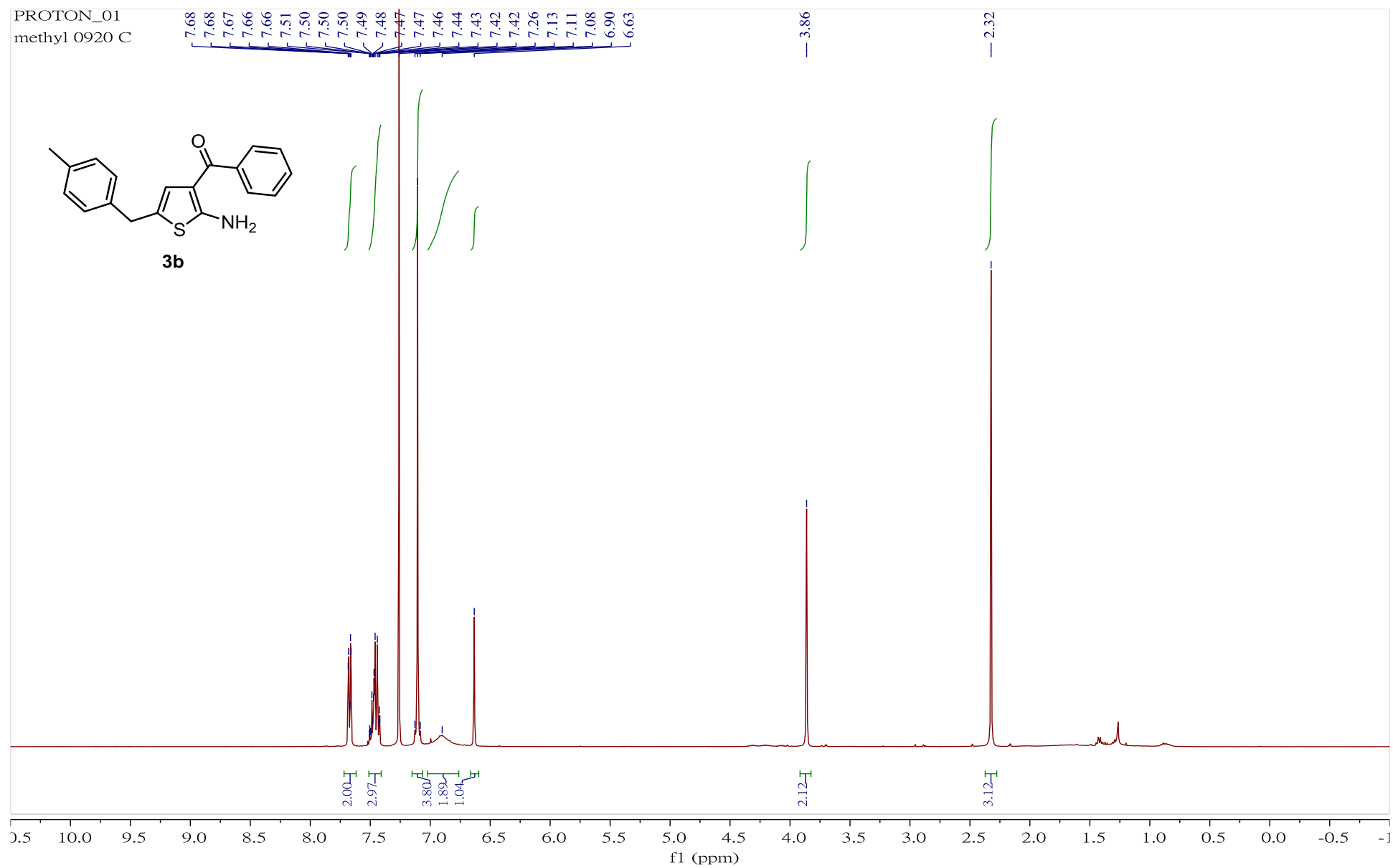


^1H NMR (400 MHz) spectrum of compound **3a** in CDCl_3

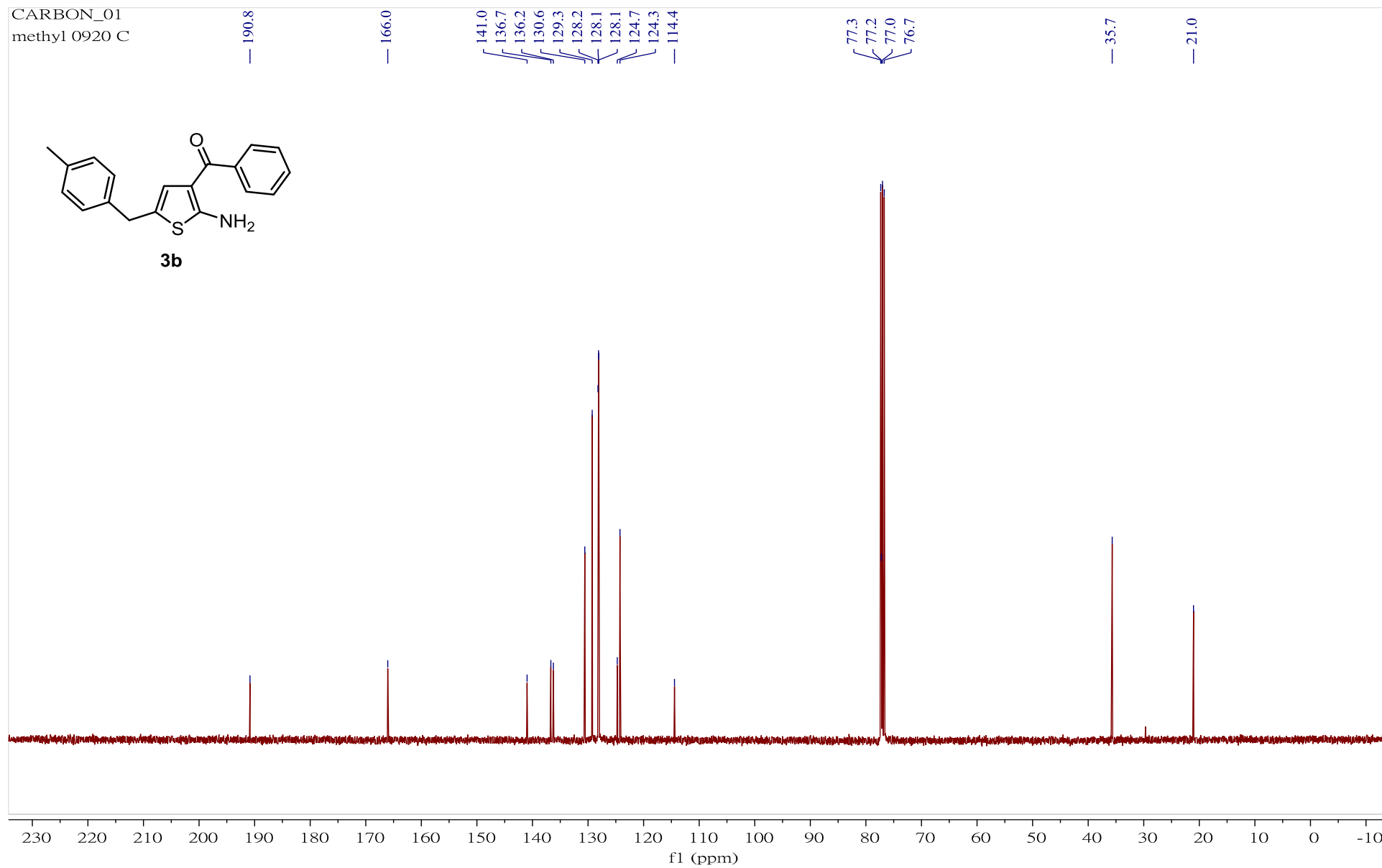
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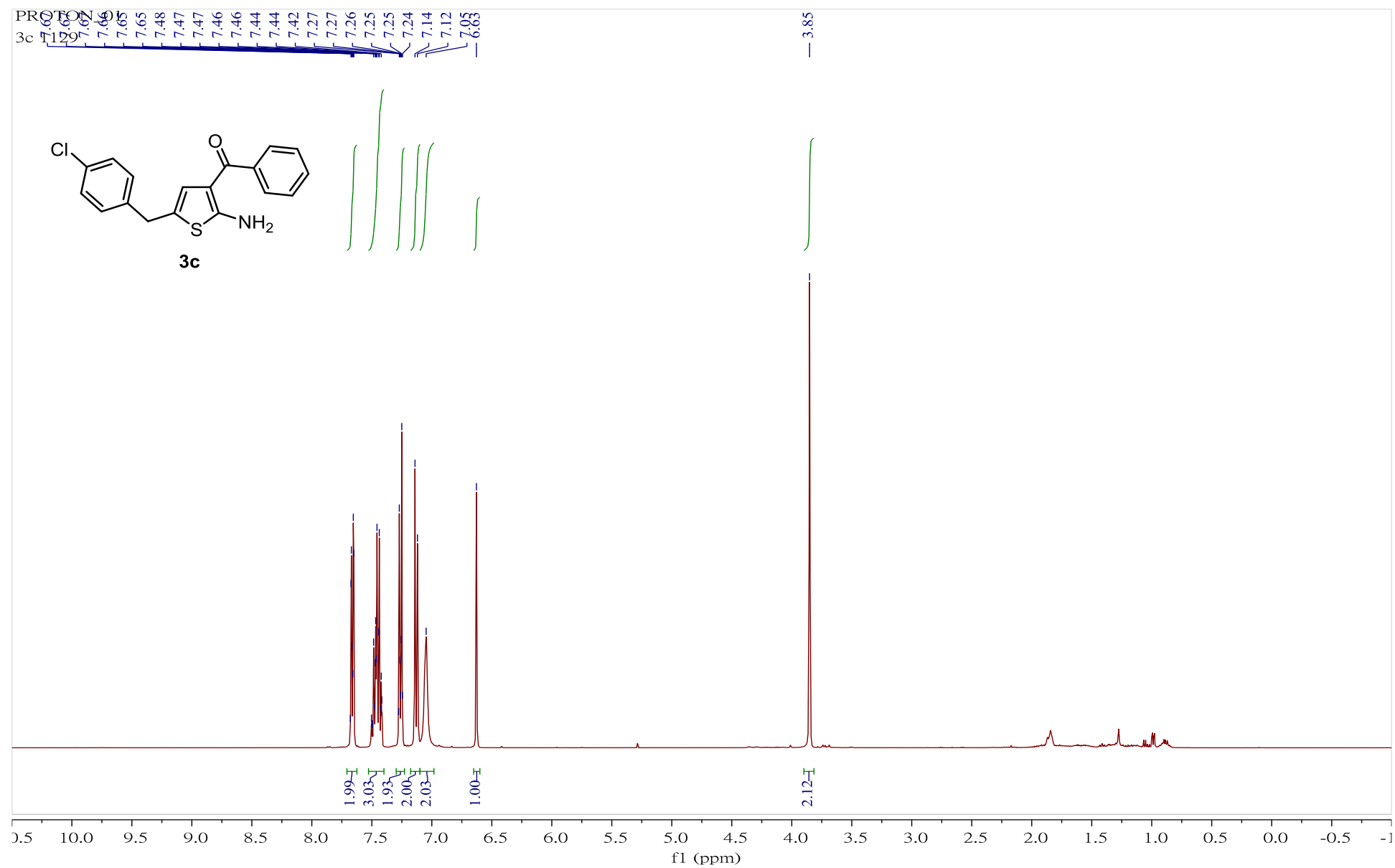
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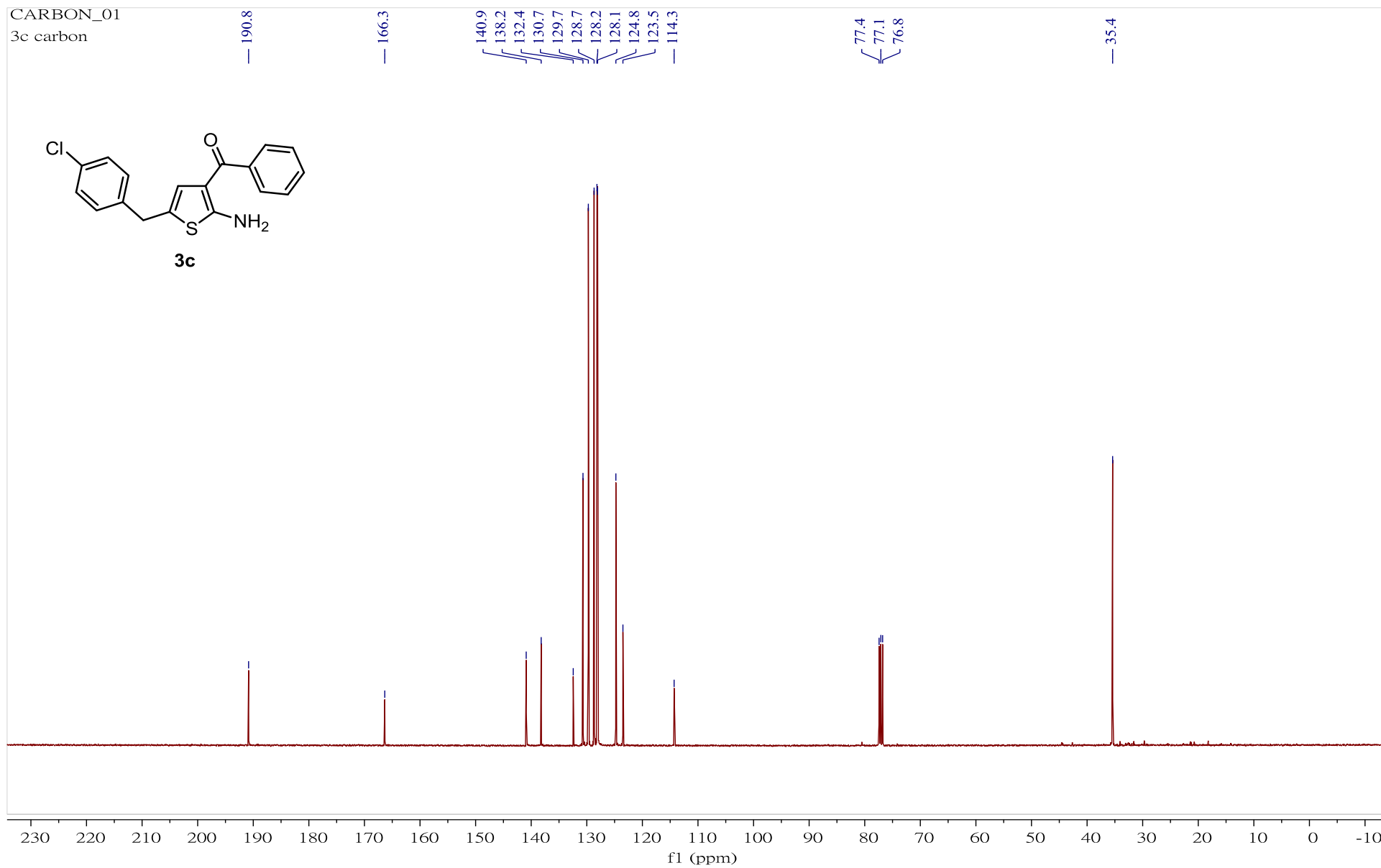
^1H NMR (400 MHz) spectrum of compound **3b** in CDCl_3



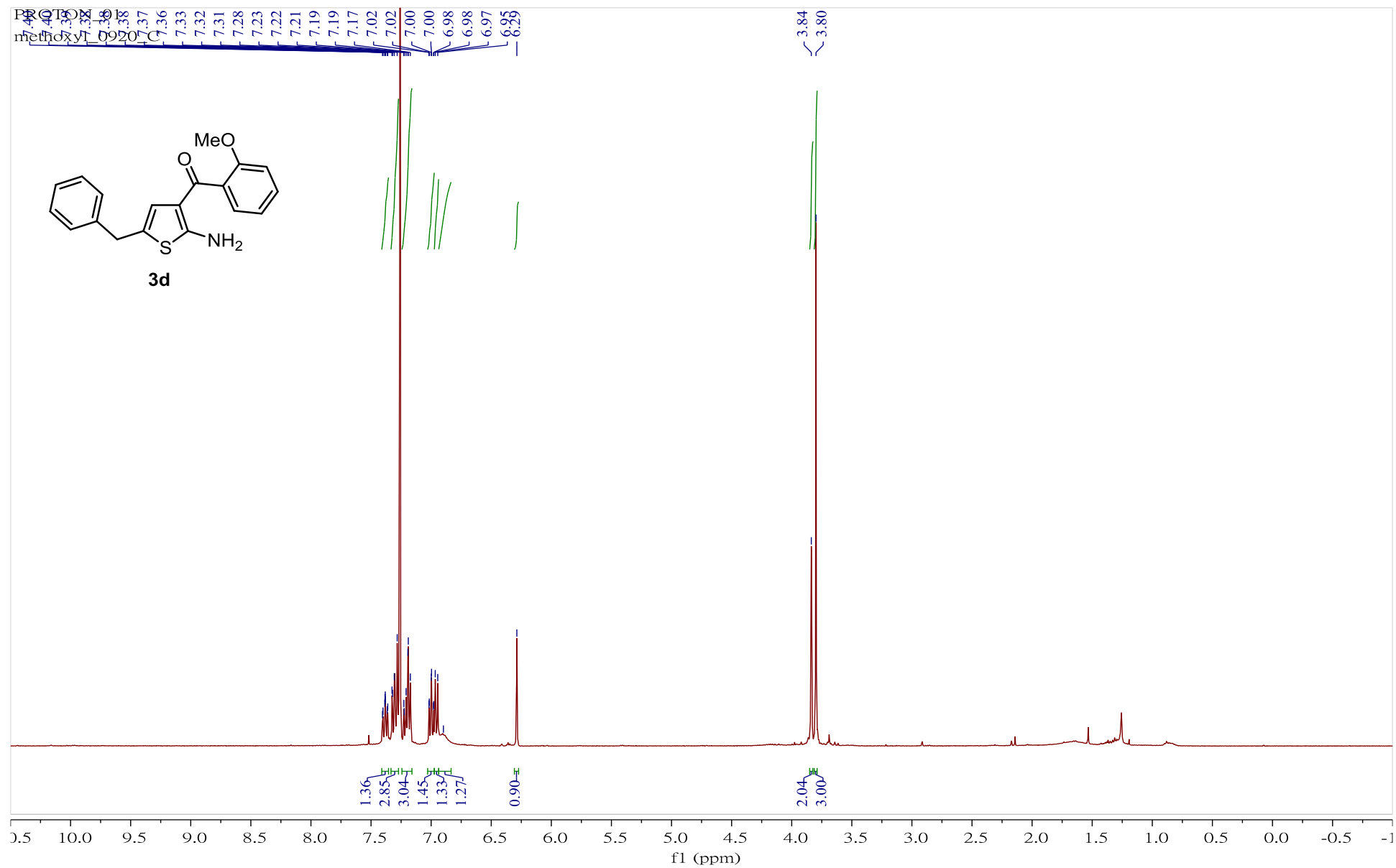
^{13}C NMR (100 MHz) spectrum of compound **3b** in CDCl_3



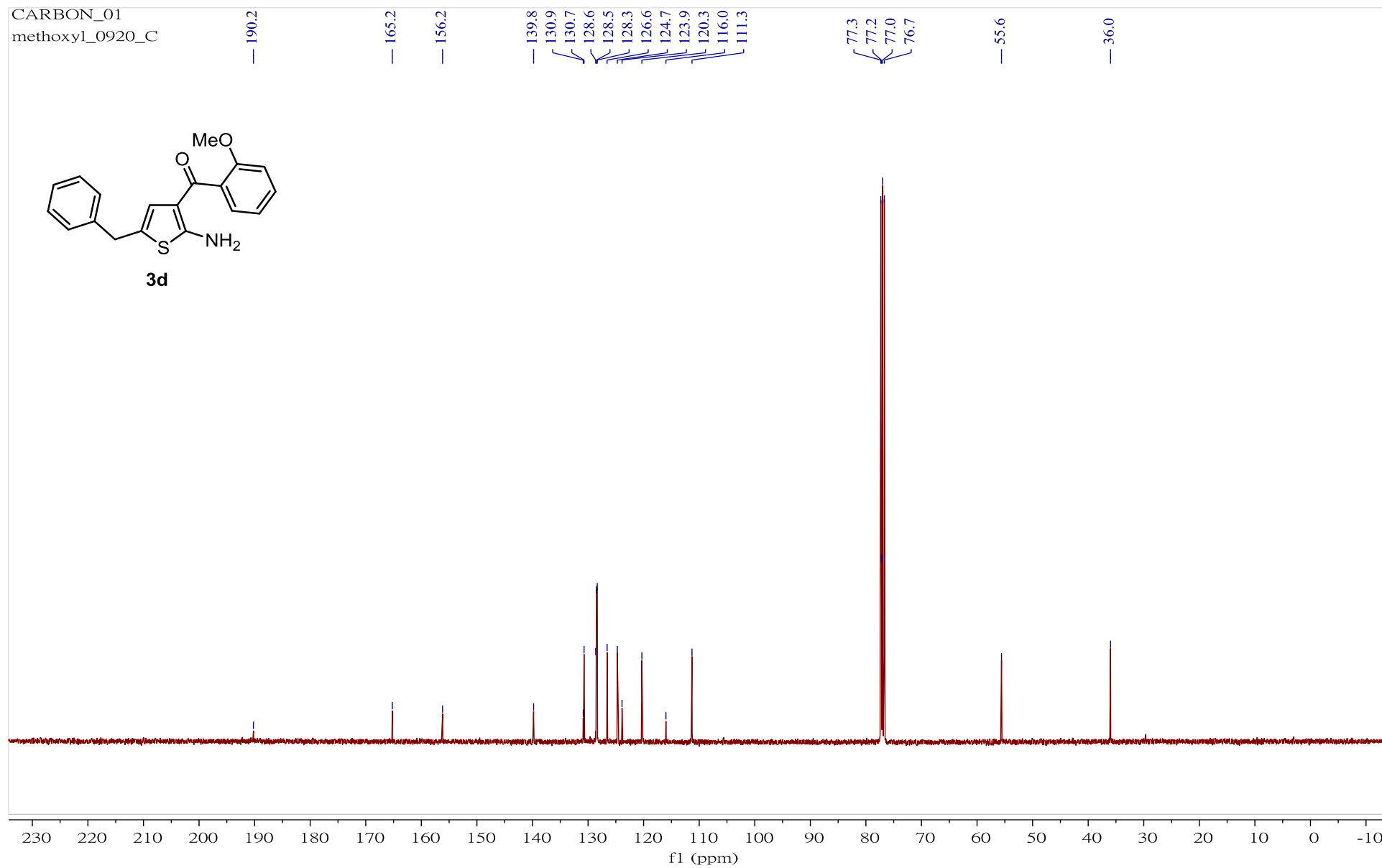
^1H NMR (400 MHz) spectrum of compound **3c** in CDCl_3



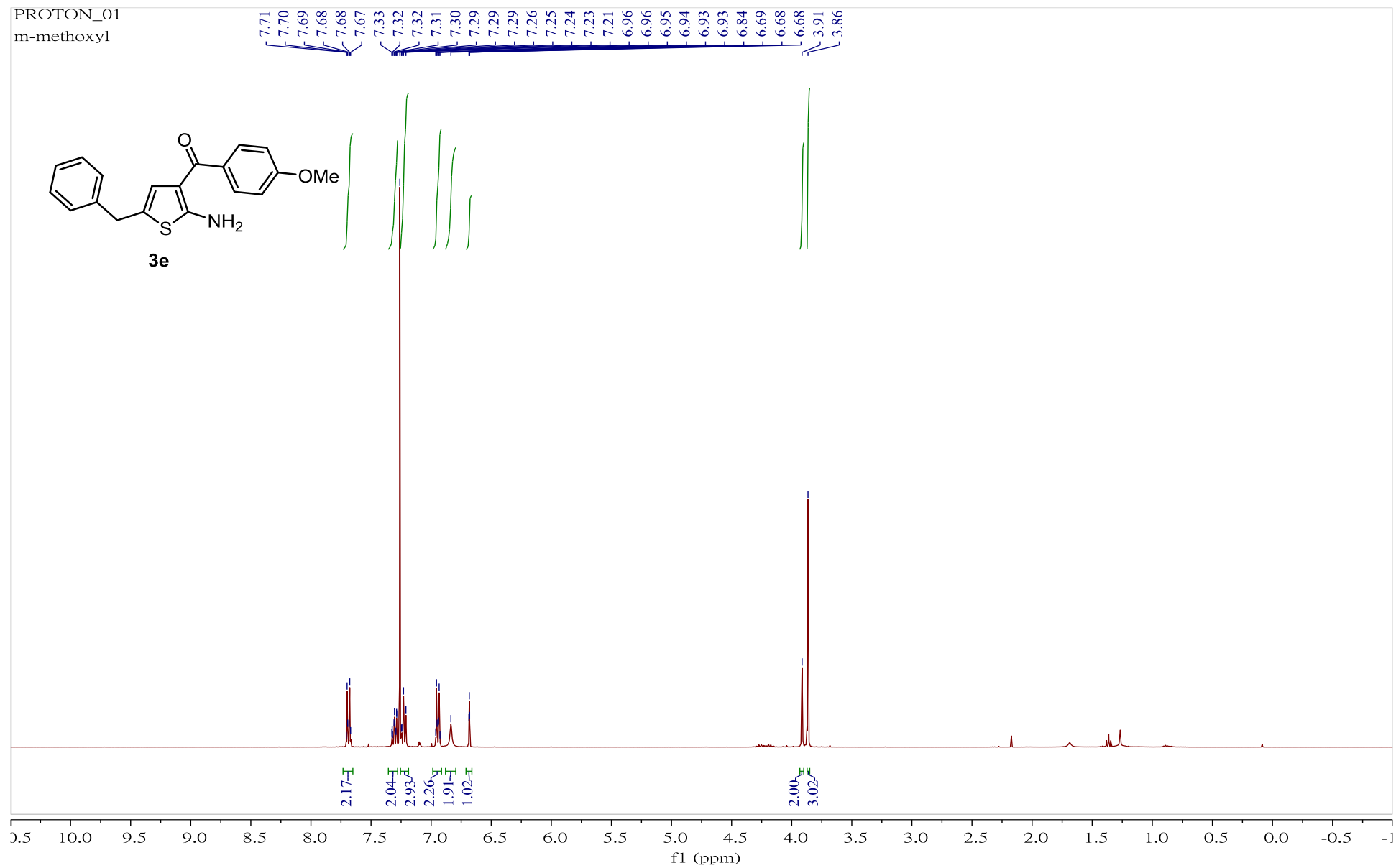
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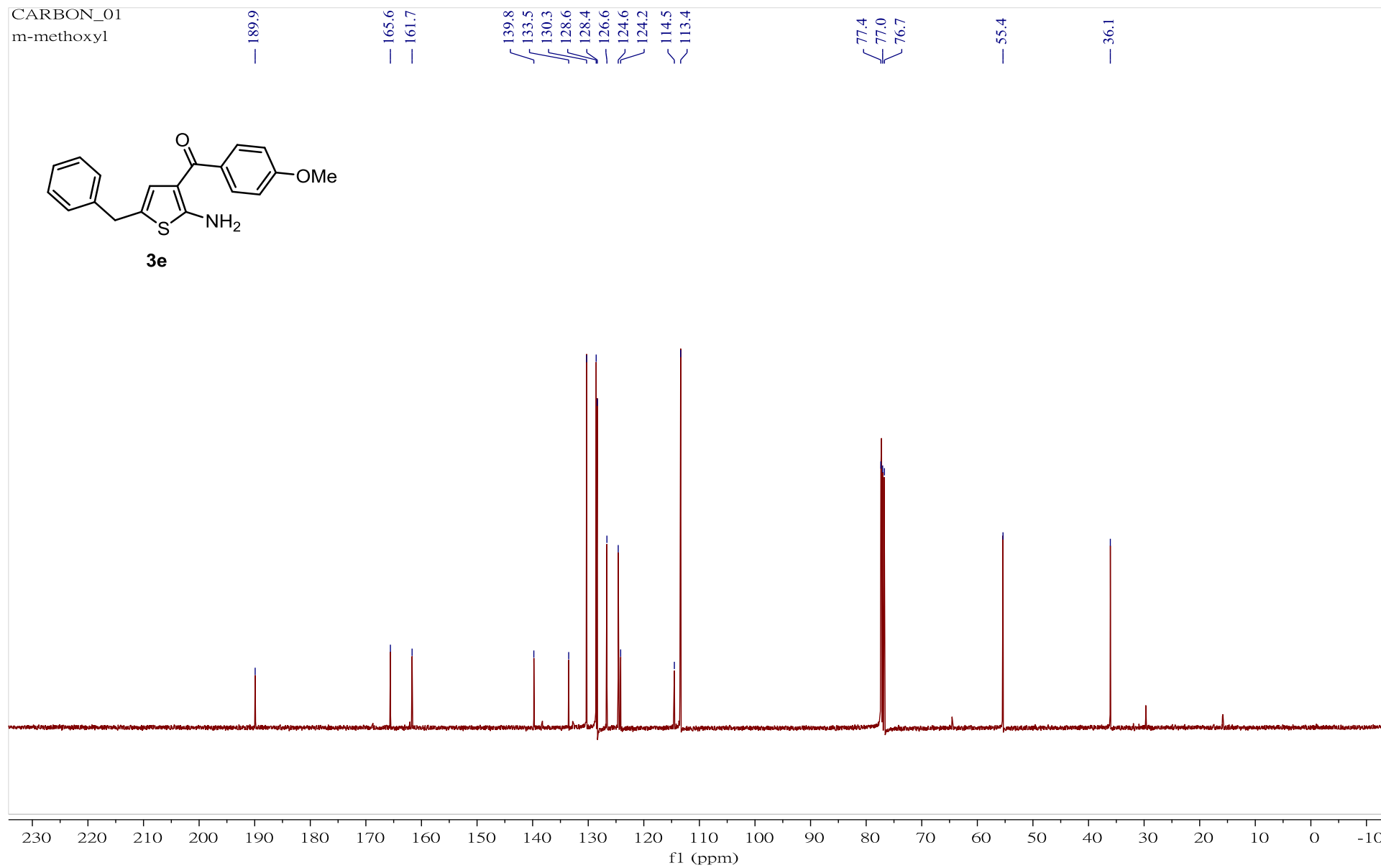
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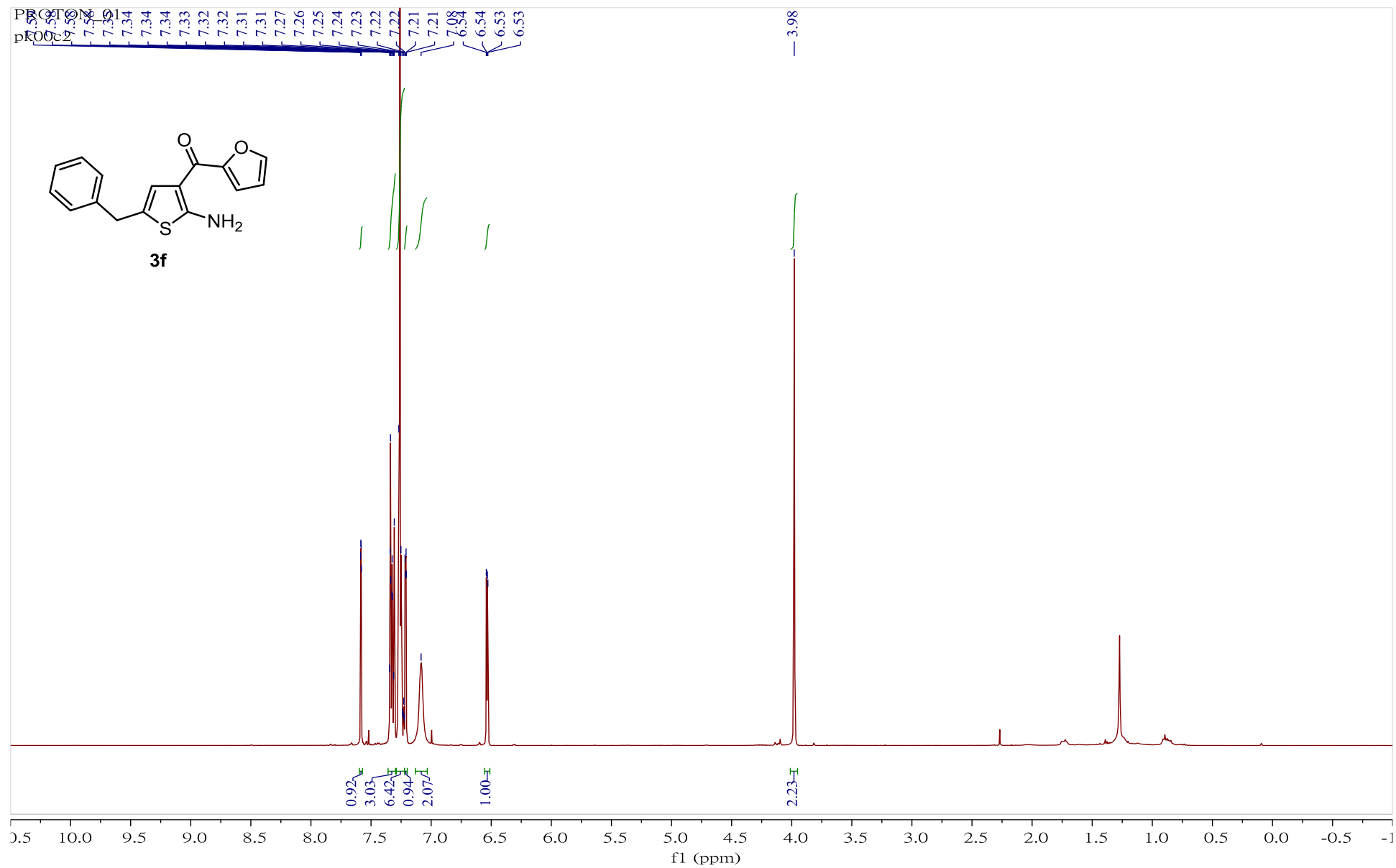
¹³C NMR (100 MHz) spectrum of compound **3d** in CDCl₃



^1H NMR (400 MHz) spectrum of compound **3e** in CDCl_3

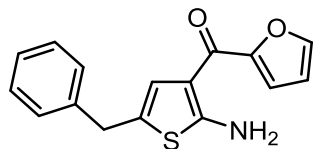


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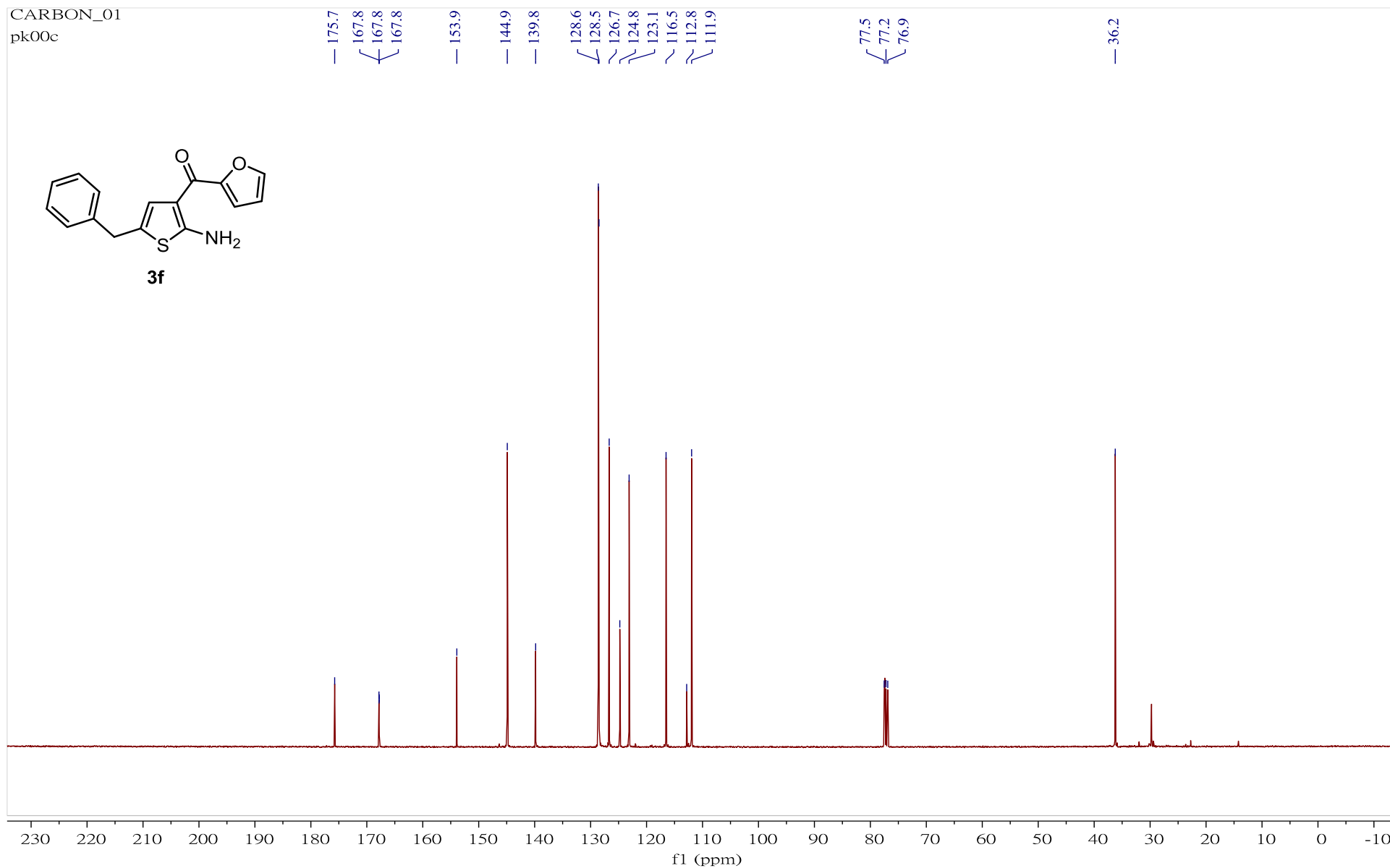


¹H NMR (400 MHz) spectrum of compound **3f** in CDCl₃

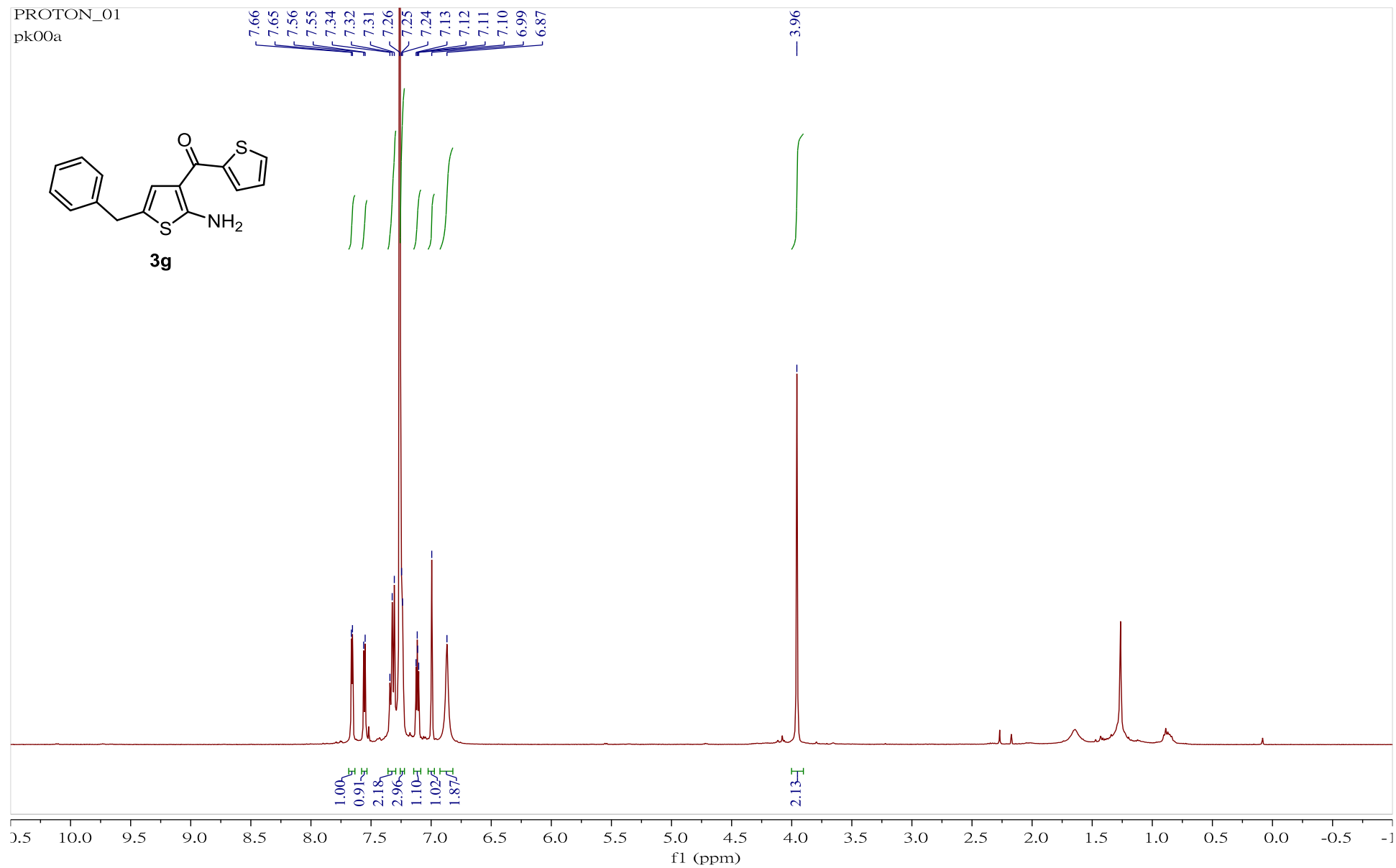
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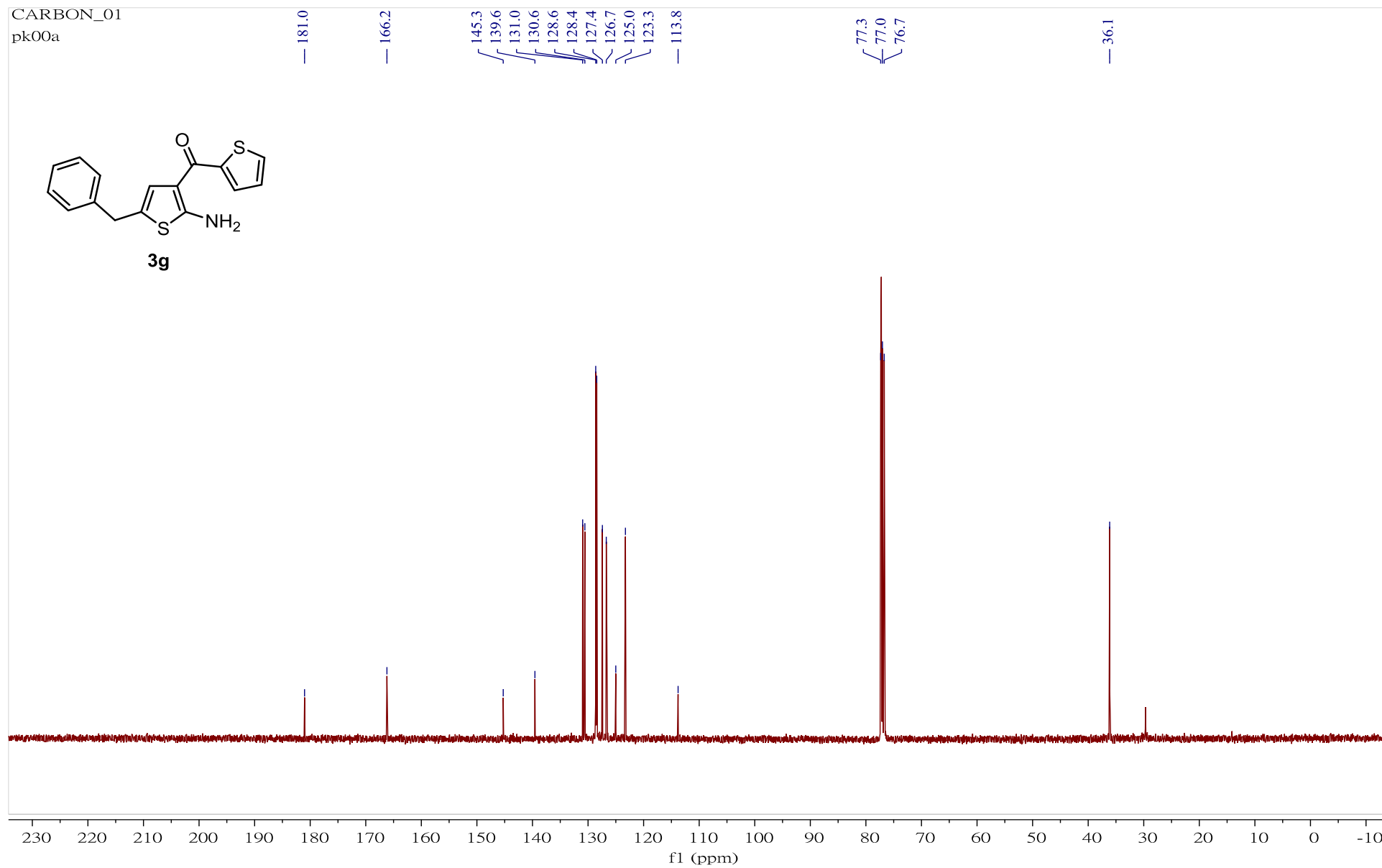
3f



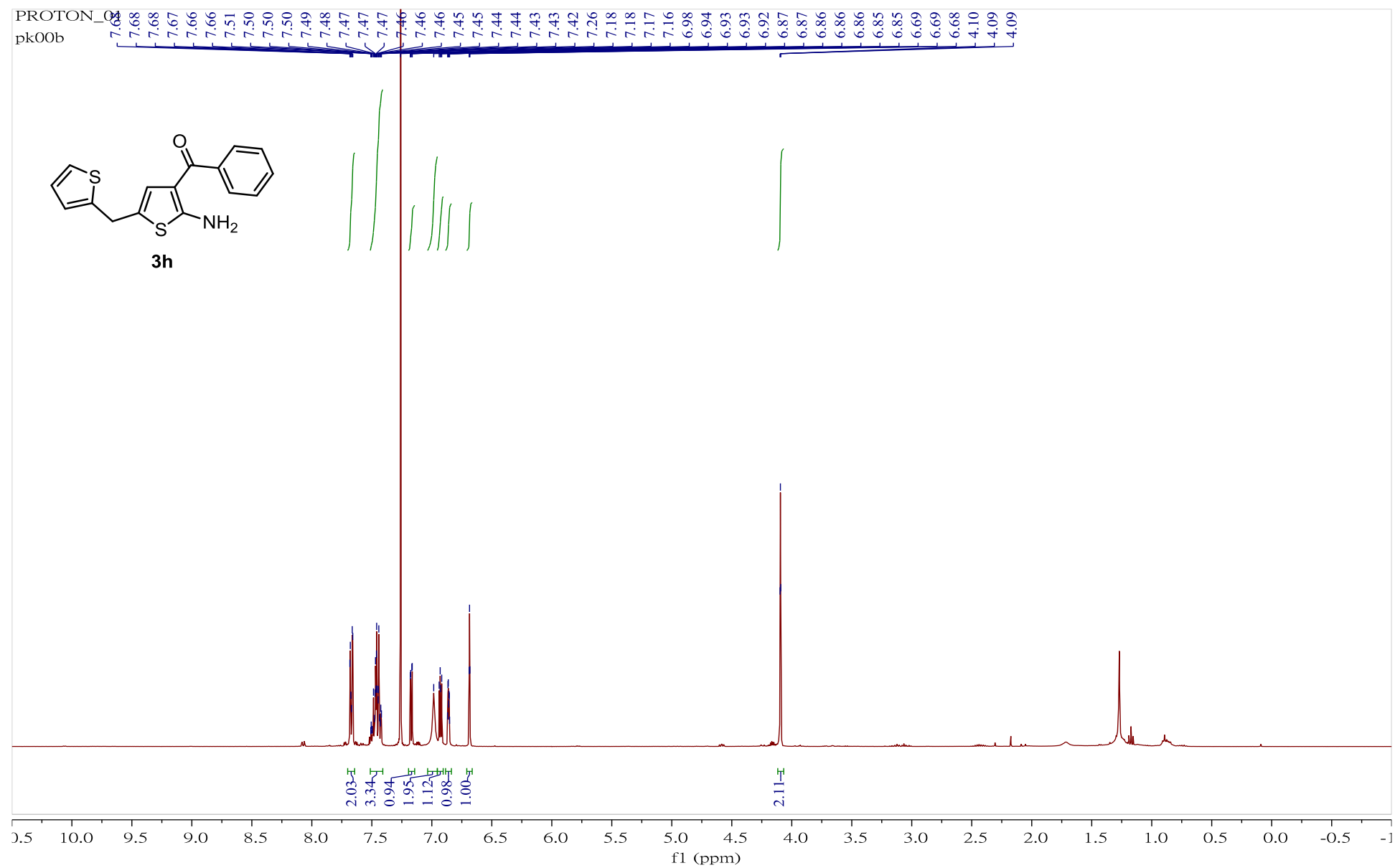
^{13}C NMR (100 MHz) spectrum of compound **3f** in CDCl_3



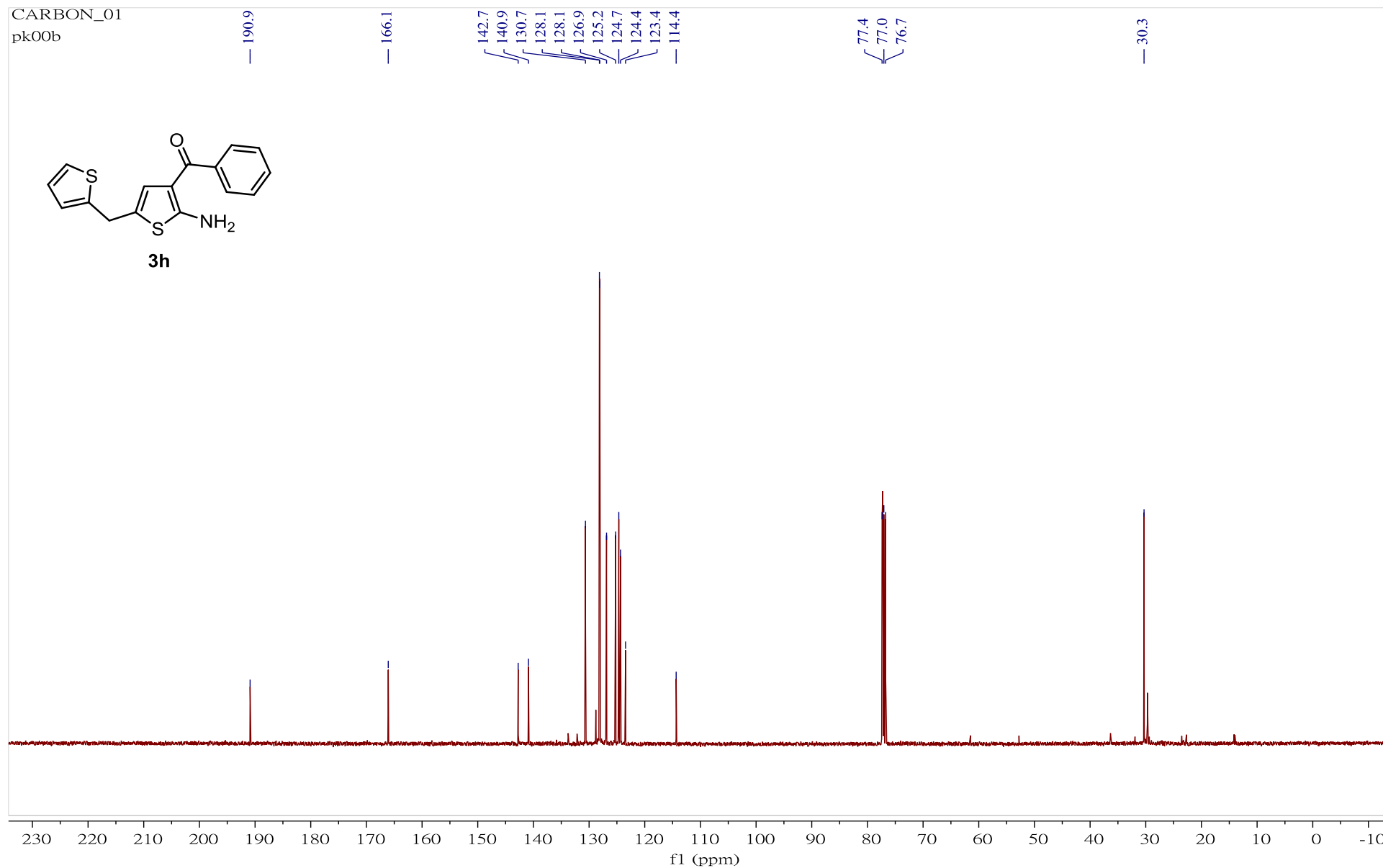
^1H NMR (400 MHz) spectrum of compound **3g** in CDCl_3



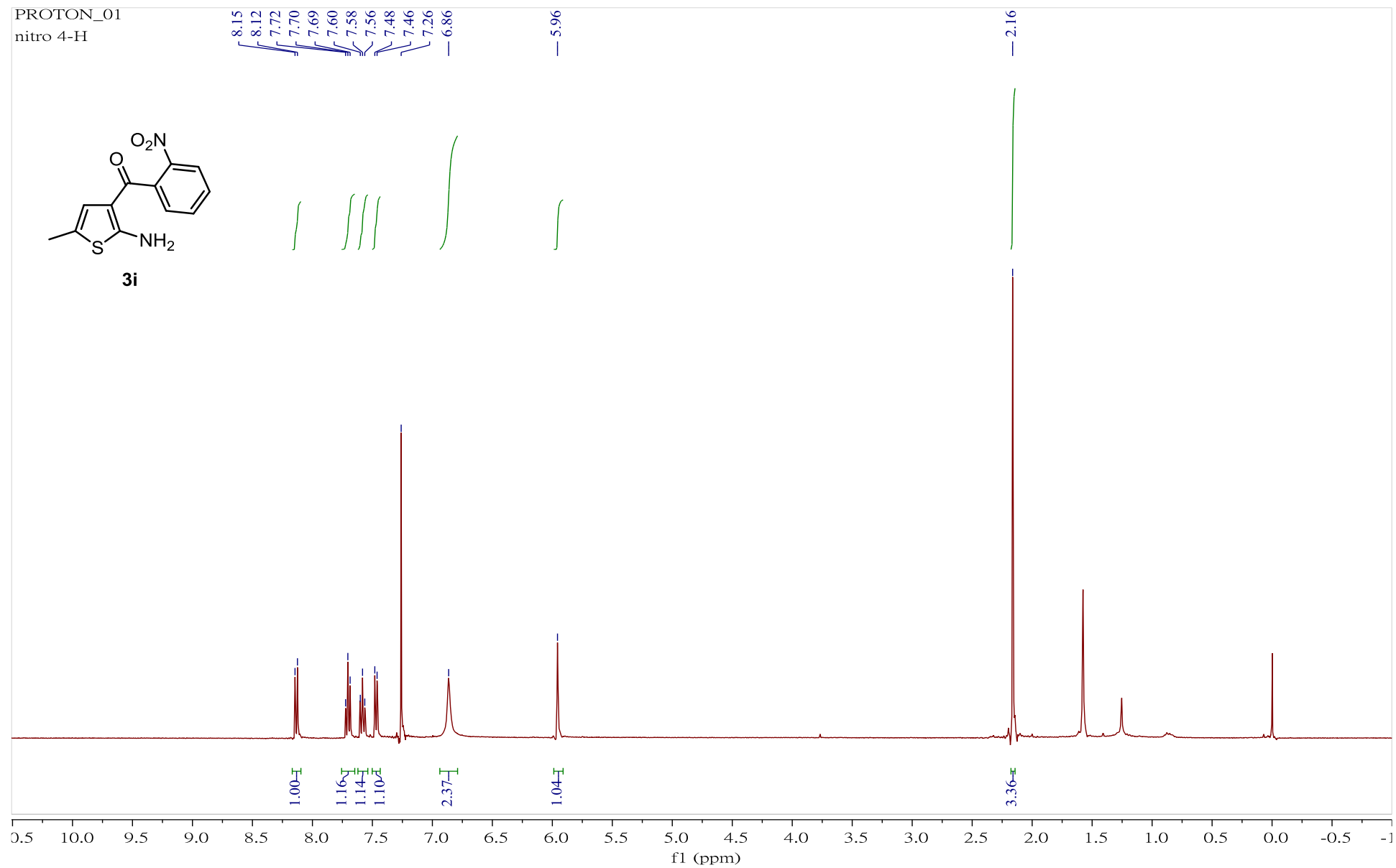
^{13}C NMR (100 MHz) spectrum of compound **3g** in CDCl_3



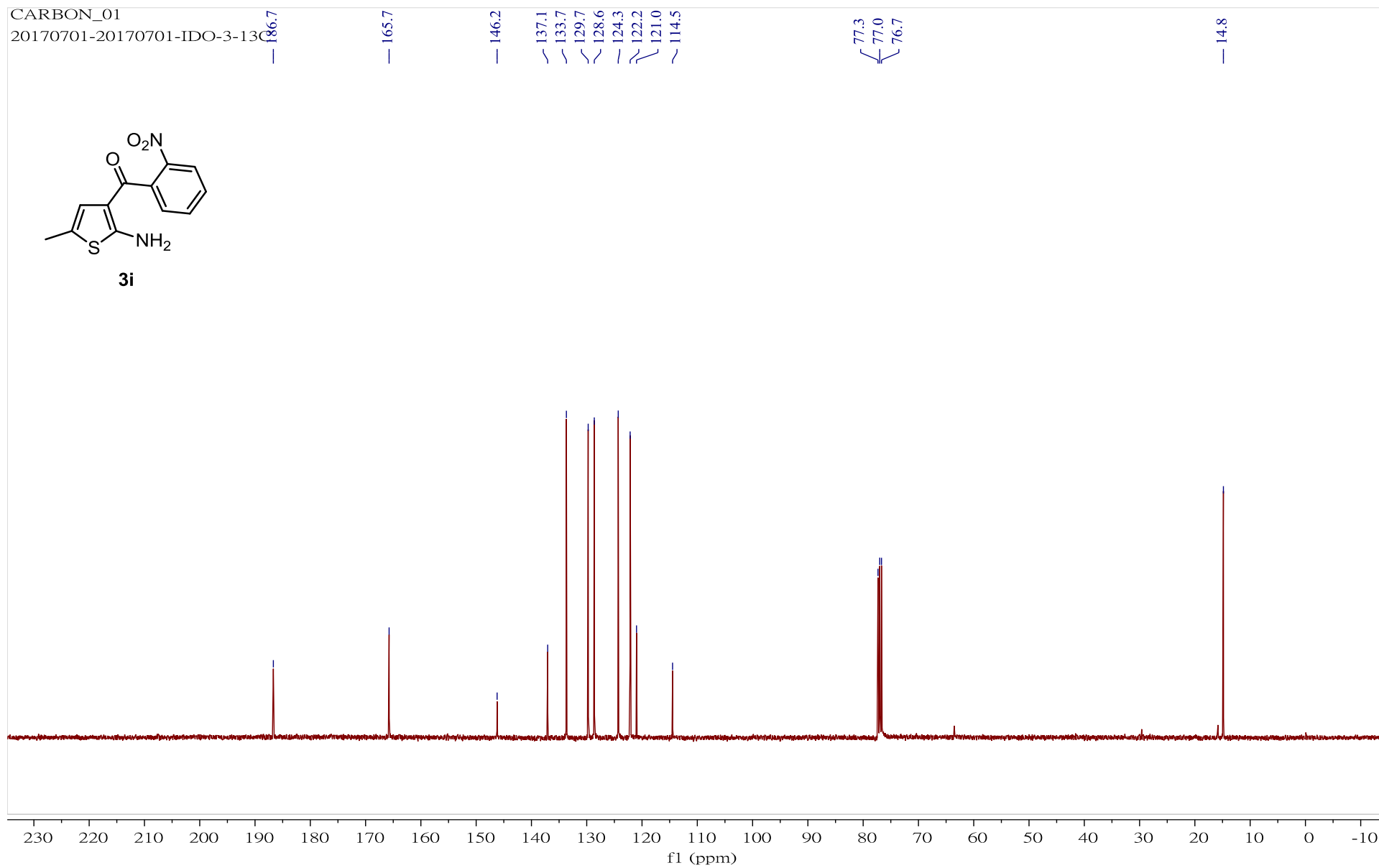
^1H NMR (400 MHz) spectrum of compound **3h** in CDCl_3



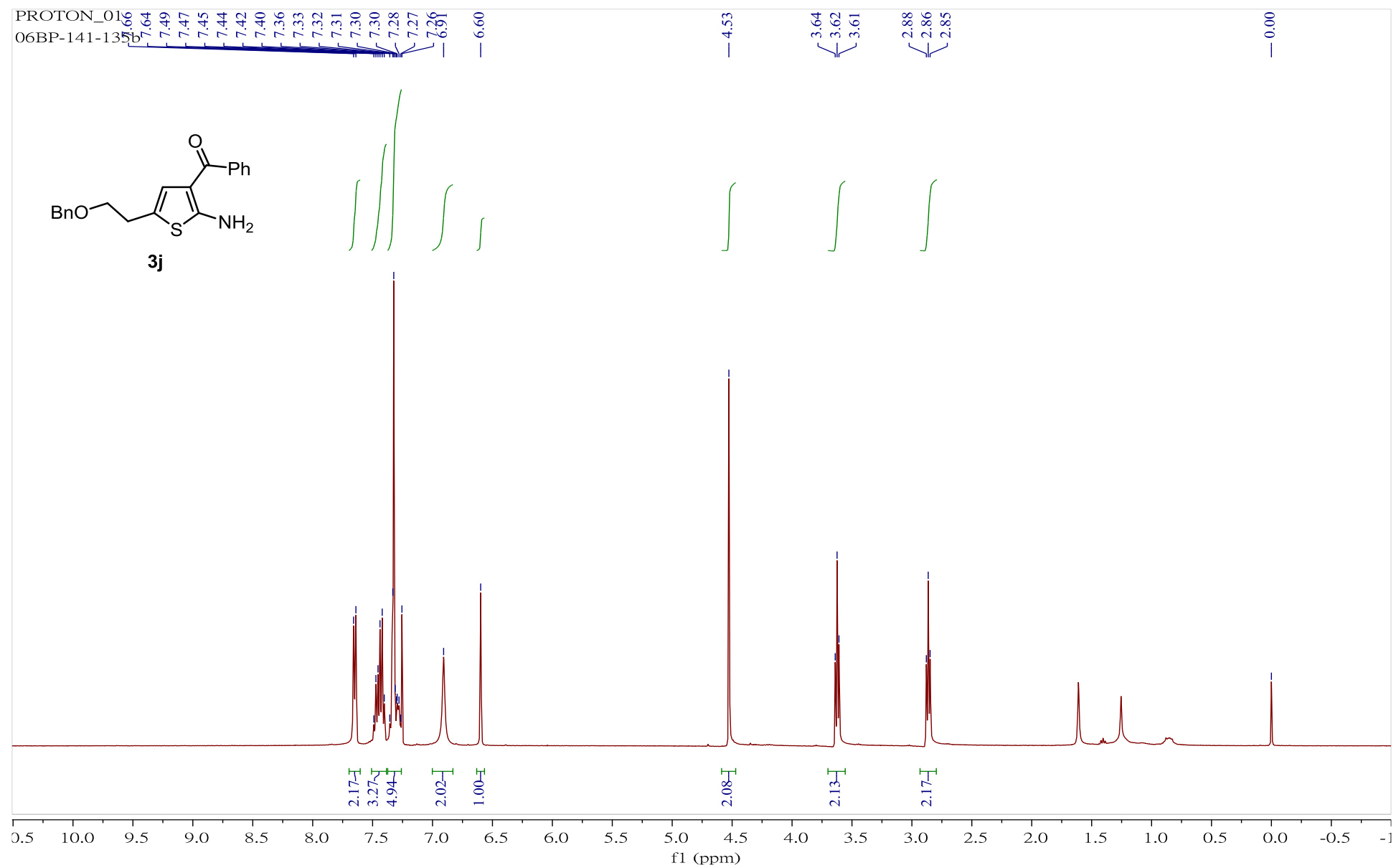
¹³C NMR (100 MHz) spectrum of compound **3h** in CDCl₃



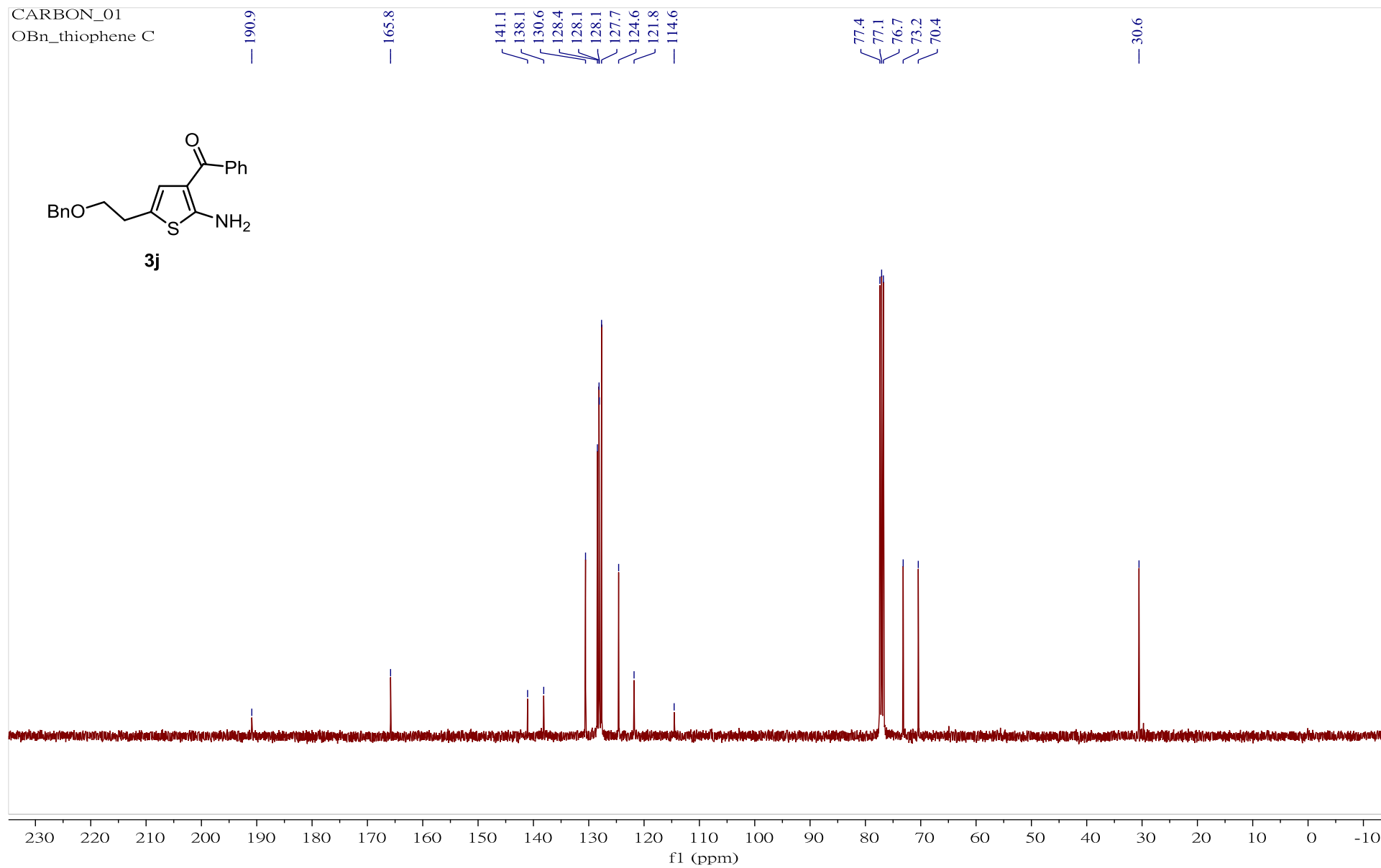
^1H NMR (400 MHz) spectrum of compound **3i** in CDCl_3



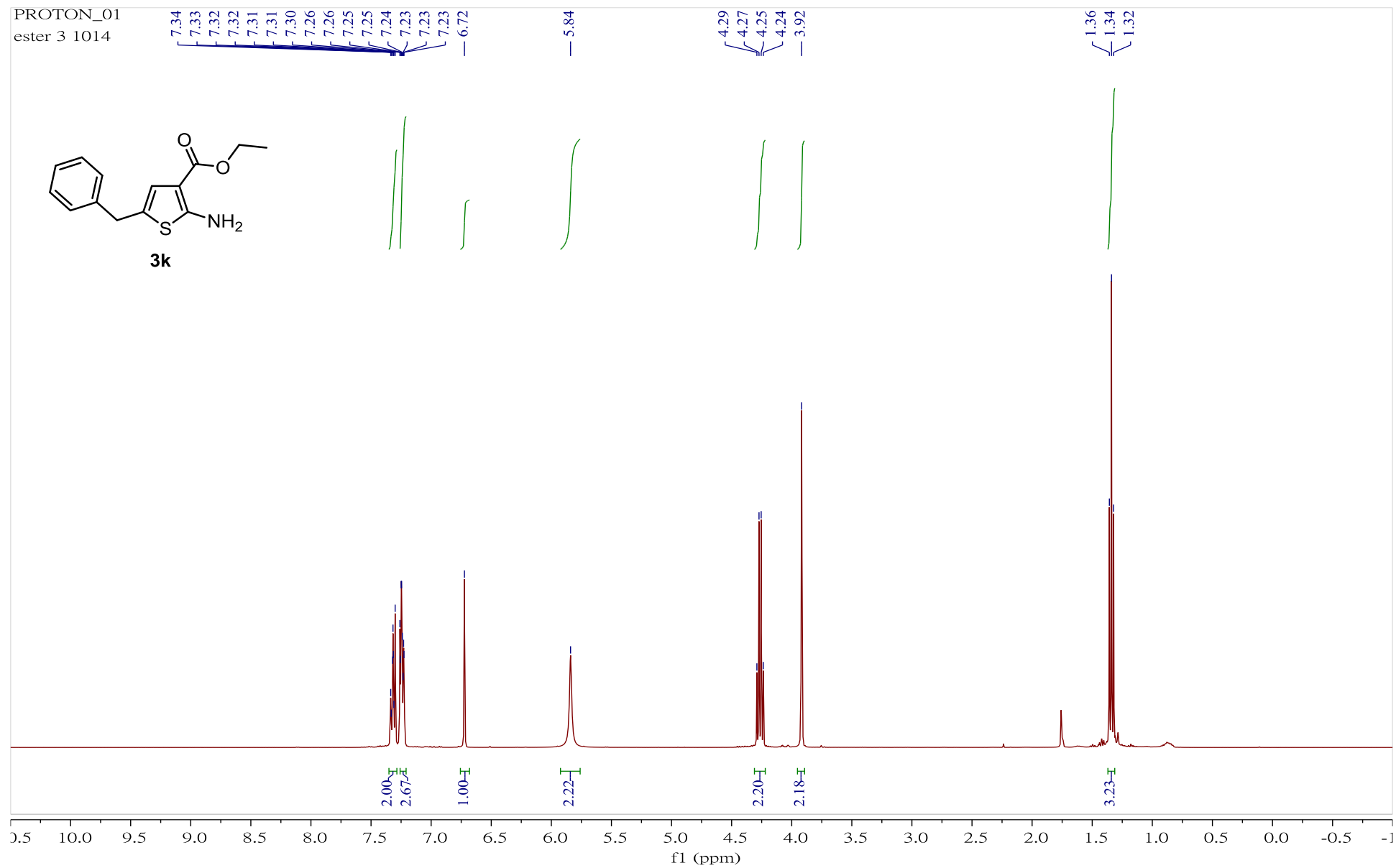
¹³C NMR (100 MHz) spectrum of compound **3i** in CDCl₃



^1H NMR (400 MHz) spectrum of compound **3j** in CDCl_3

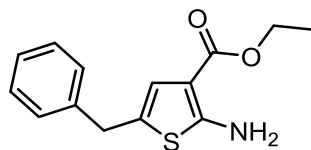


^{13}C NMR (100 MHz) spectrum of compound **3j** in CDCl_3

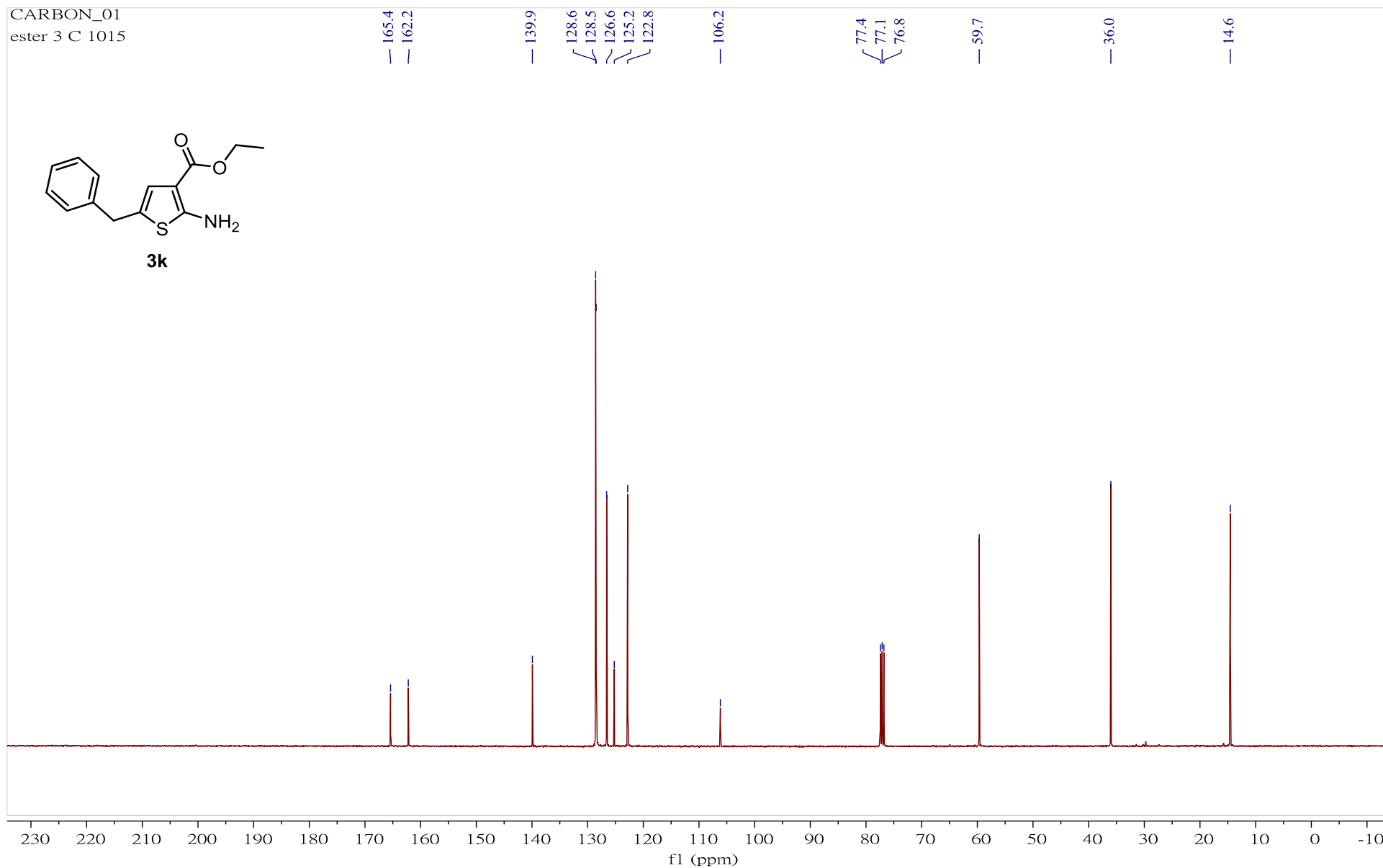


^1H NMR (400 MHz) spectrum of compound **3k** in CDCl_3

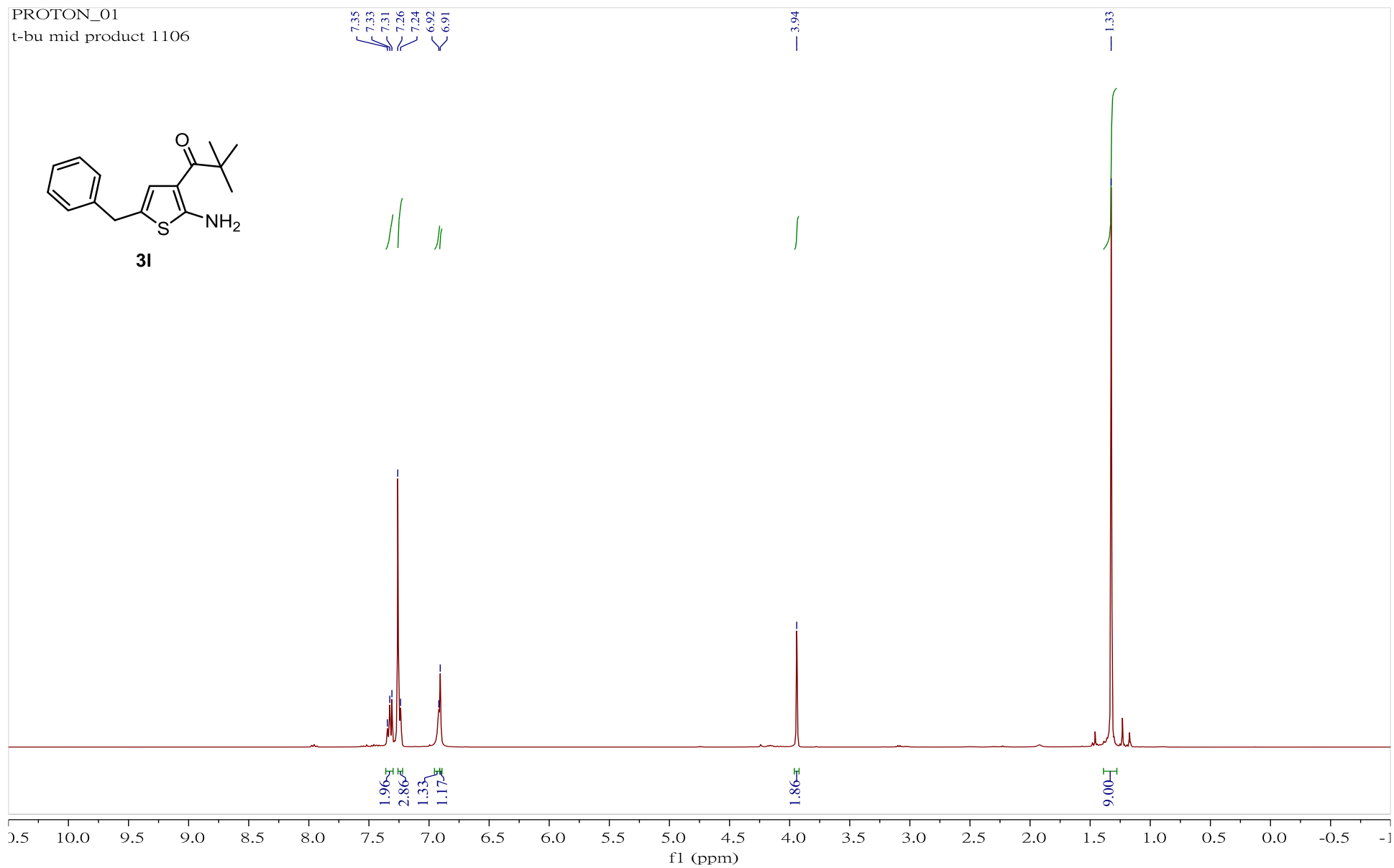
CARBON_01
ester 3 C 1015



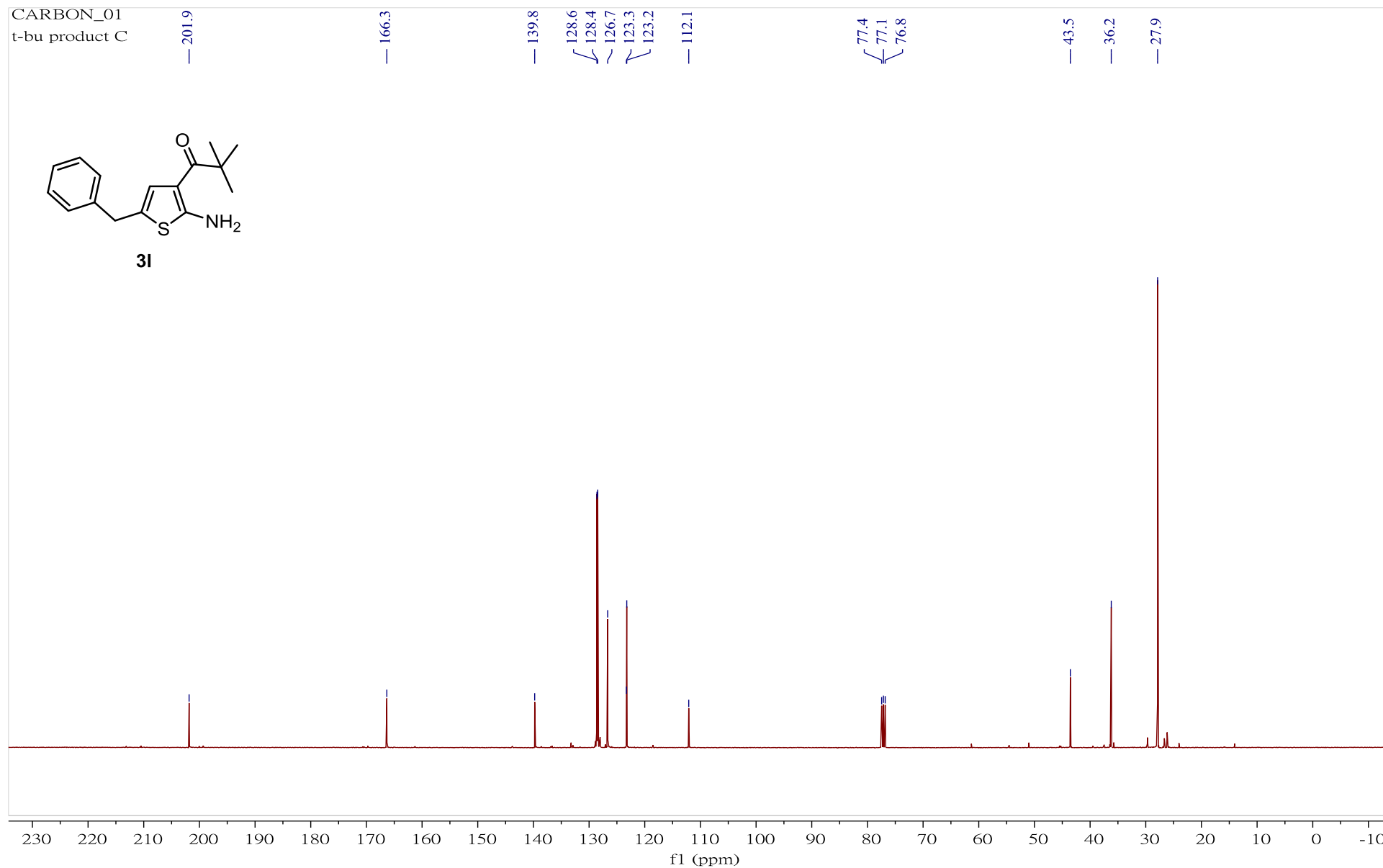
3k



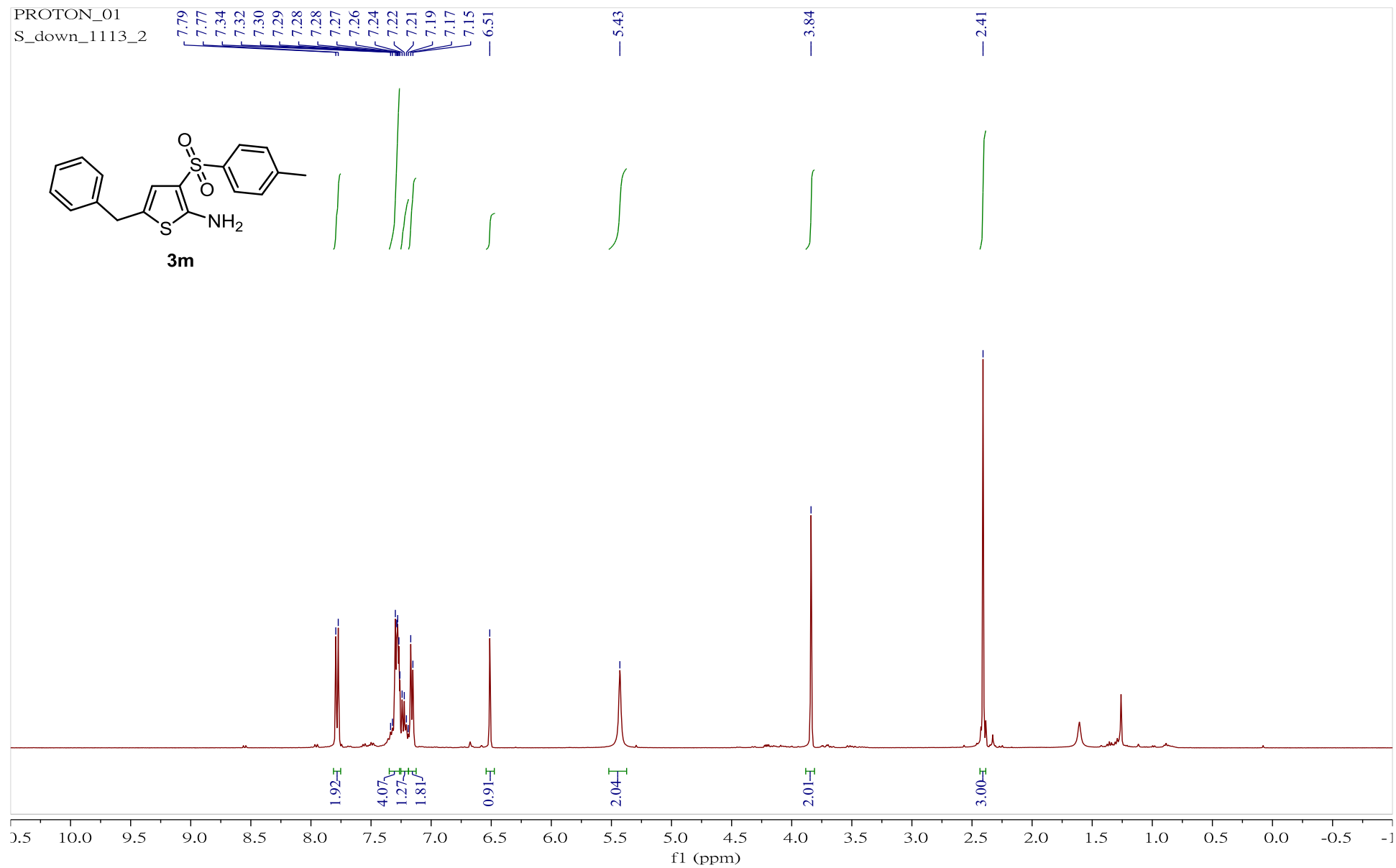
¹³C NMR (100 MHz) spectrum of compound **3k** in CDCl₃



^1H NMR (400 MHz) spectrum of compound **3l** in CDCl_3

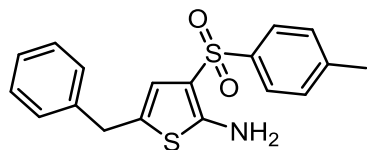


^{13}C NMR (100 MHz) spectrum of compound **3I** in CDCl_3

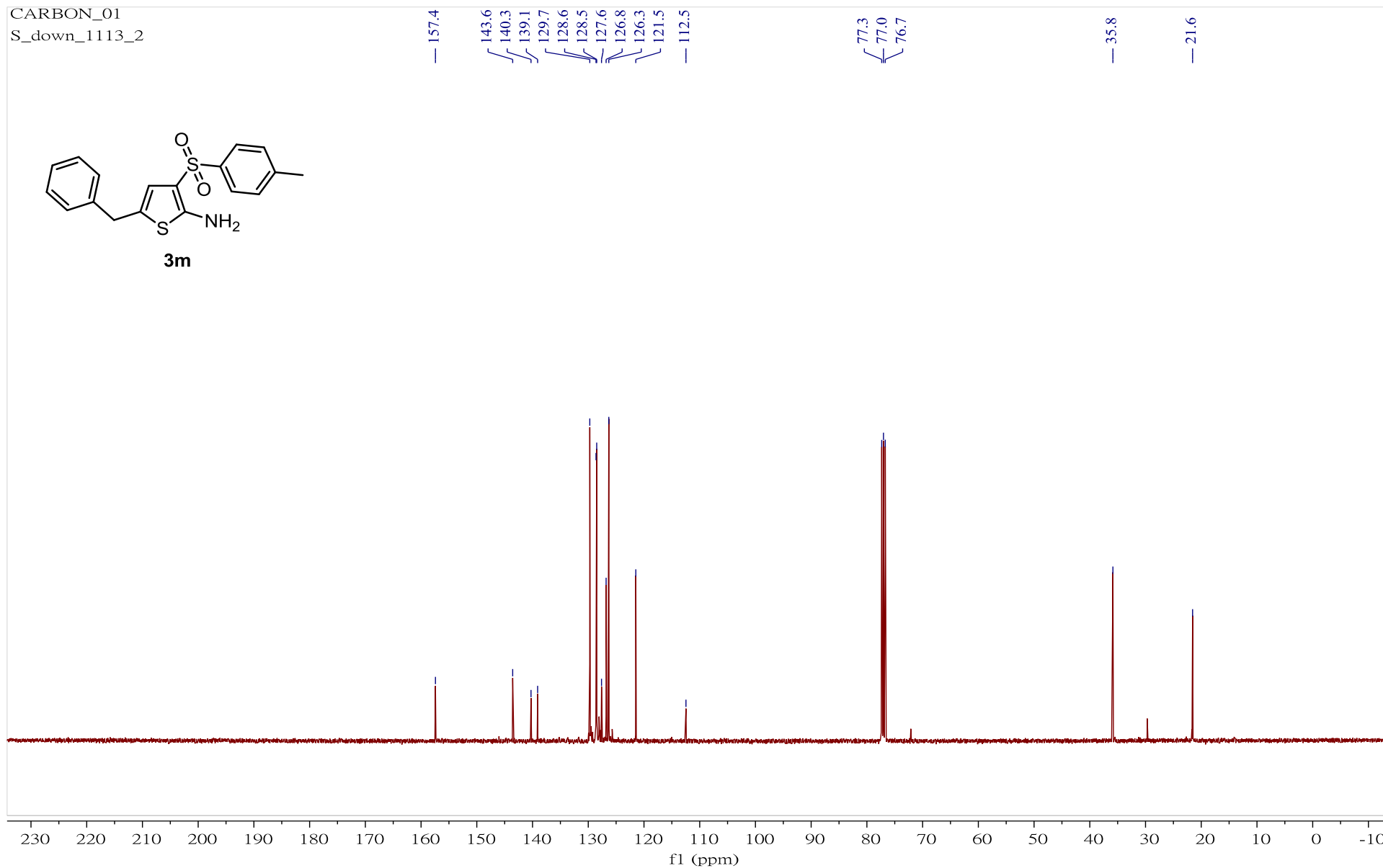


^1H NMR (400 MHz) spectrum of compound **3m** in CDCl_3

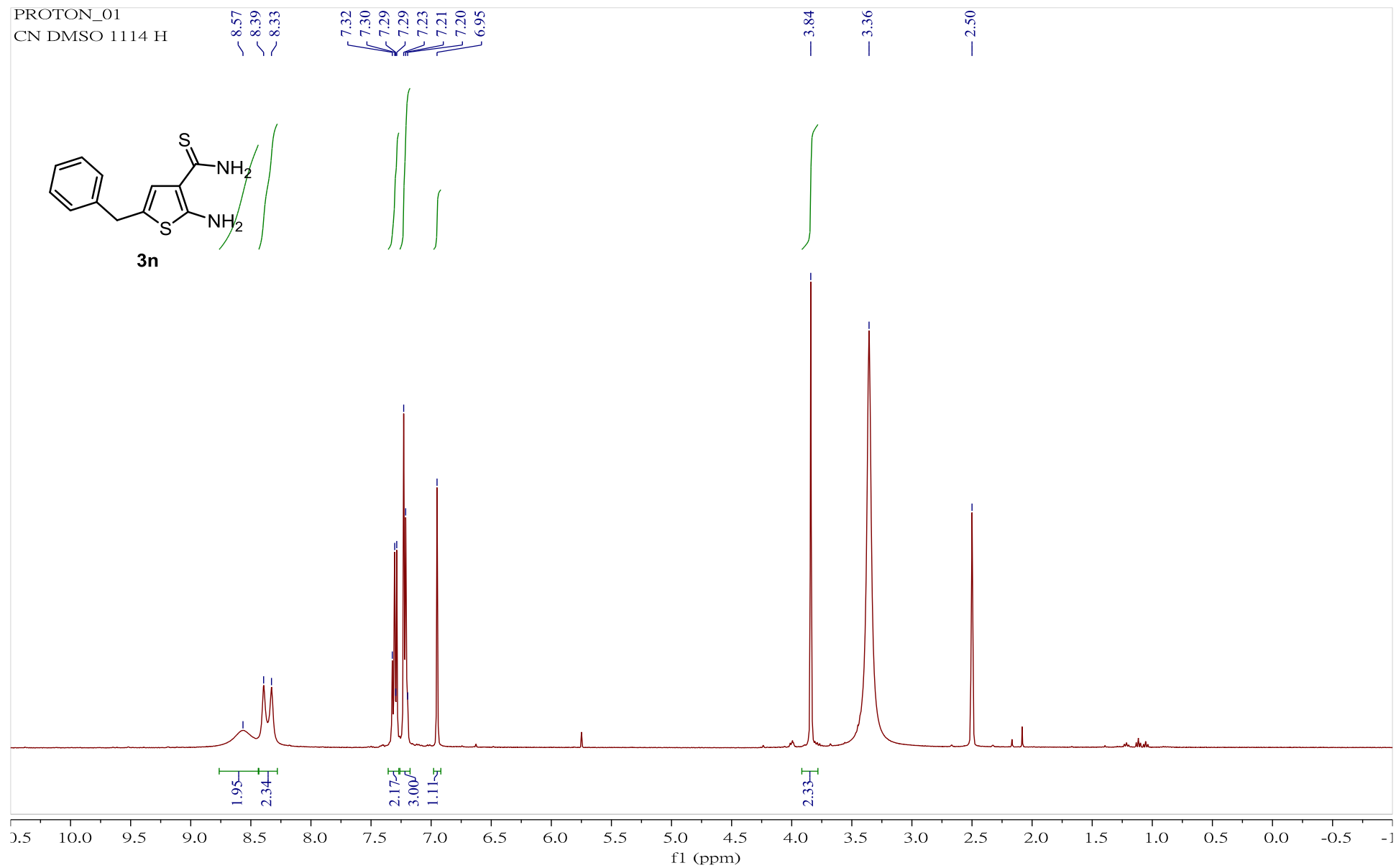
CARBON_01
S_down_1113_2



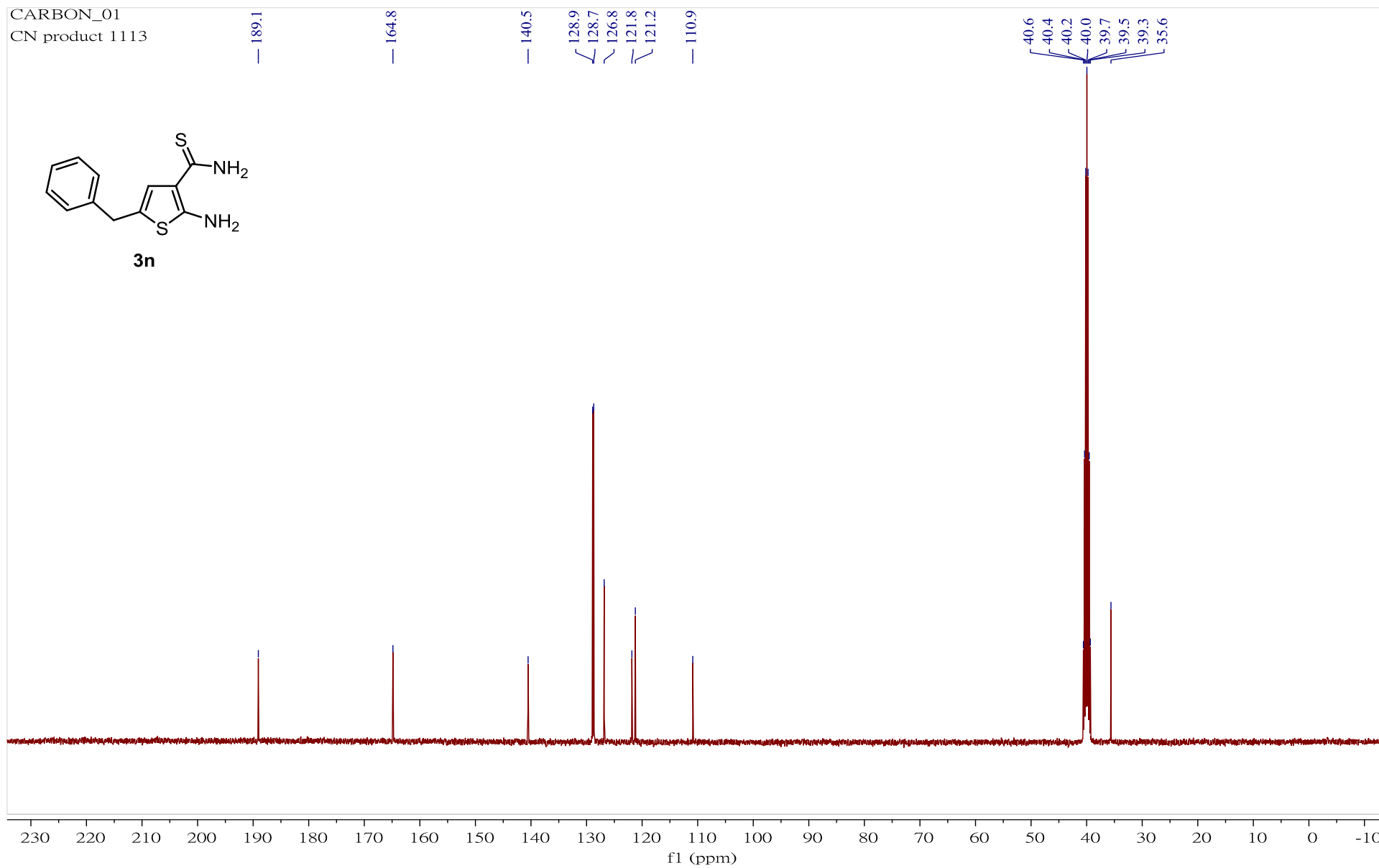
3m



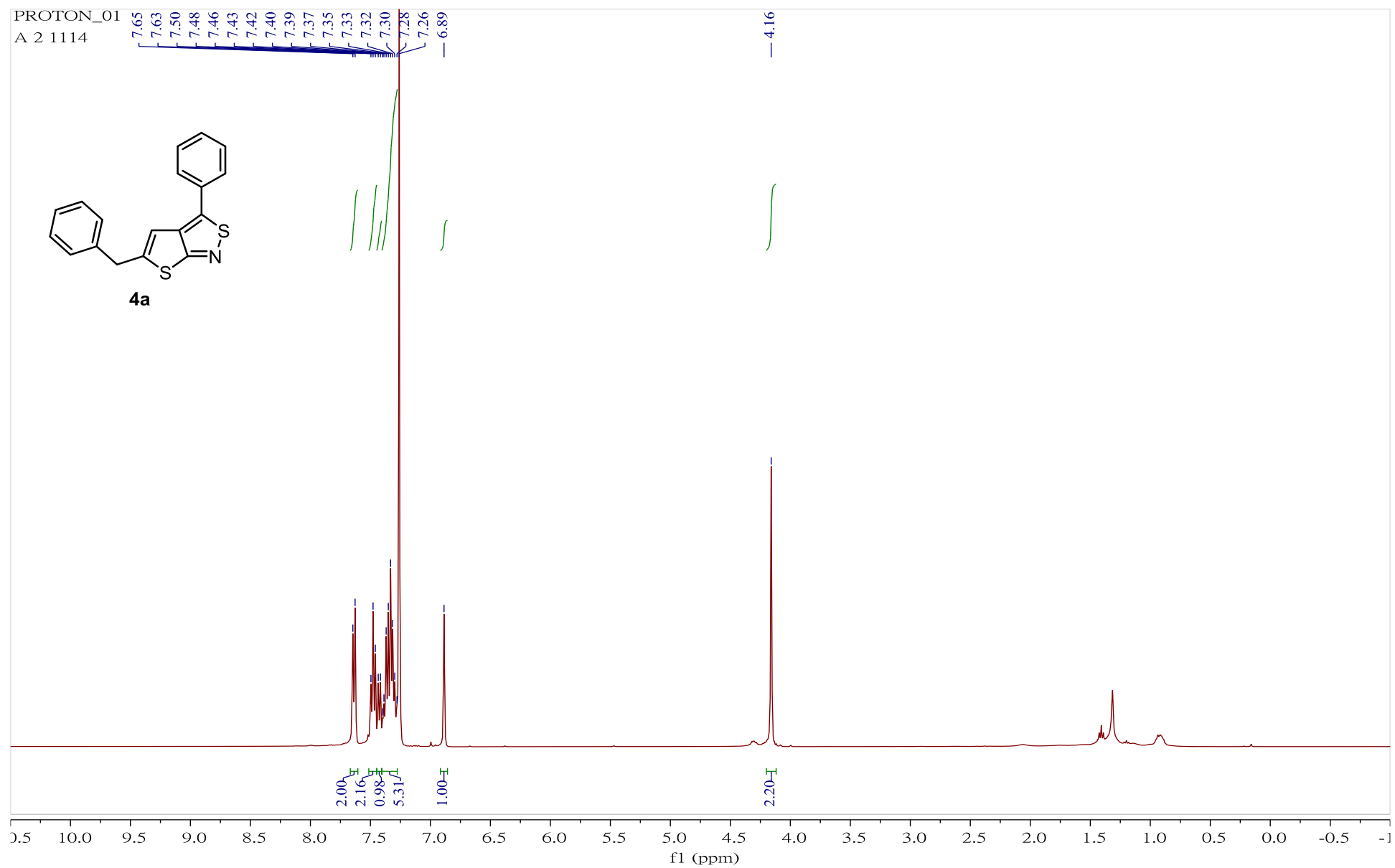
^{13}C NMR (100 MHz) spectrum of compound **3m** in CDCl_3



^1H NMR (400 MHz) spectrum of compound **3n** in DMSO- d_6



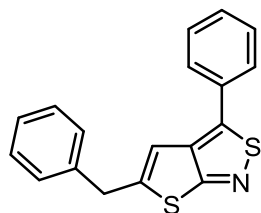
¹³C NMR (100 MHz) spectrum of compound **3n** in DMSO-d₆



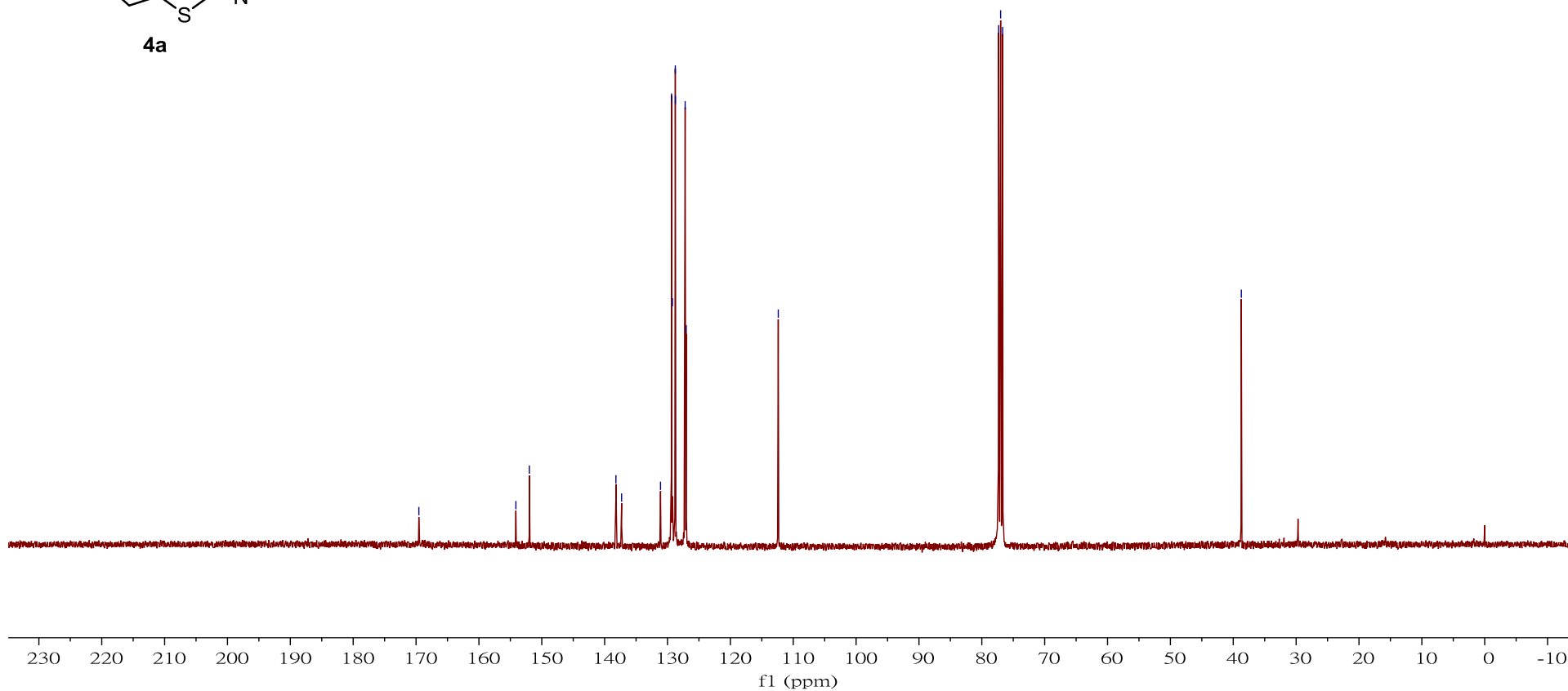
^1H NMR (400 MHz) spectrum of compound **4a** in CDCl_3

CARBON_01
T4a-13C

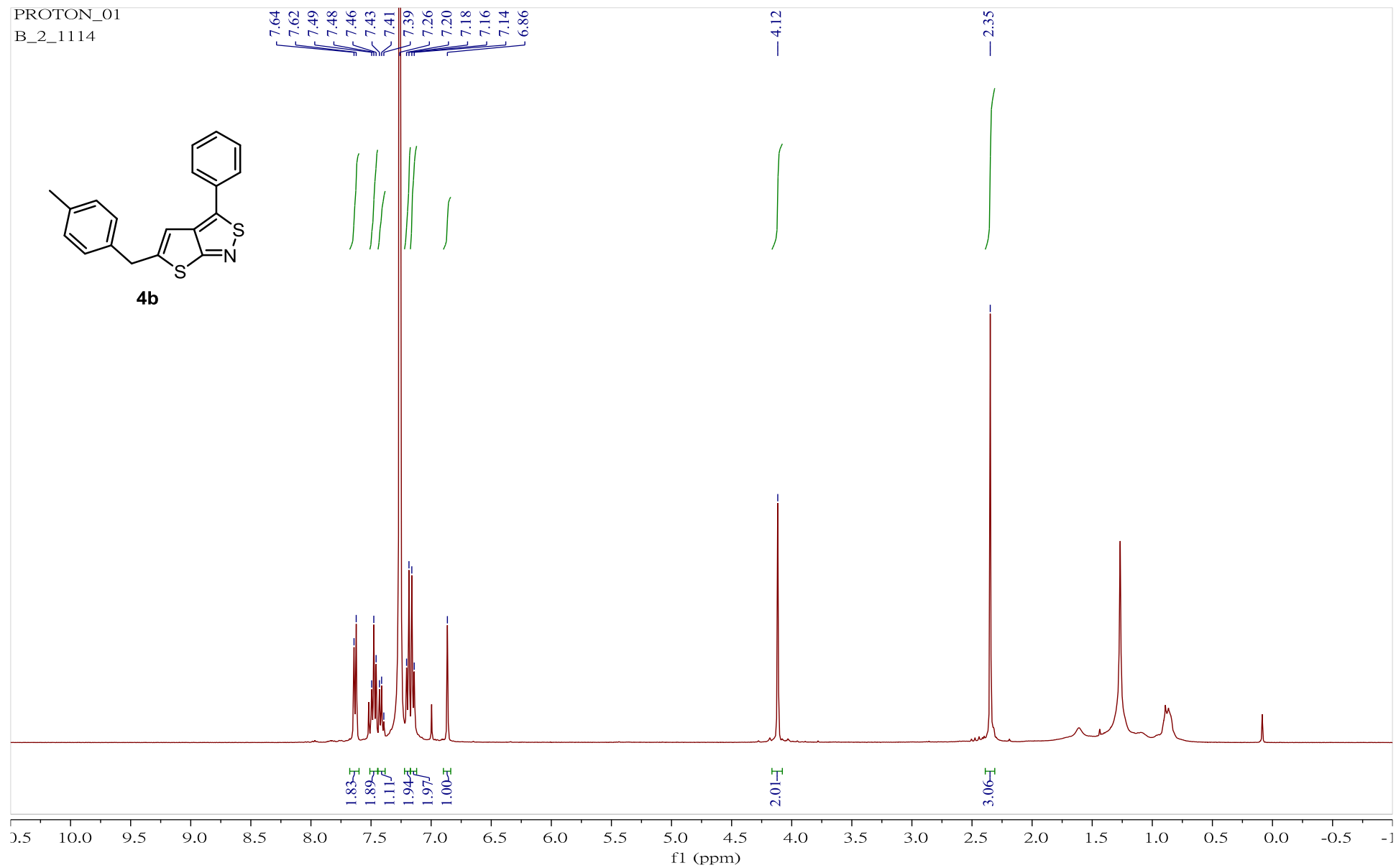
169.6
154.1
152.0
138.2
137.3
131.1
129.4
129.2
128.8
128.7
127.2
127.0
112.4
77.3
77.0
76.7
38.7



4a



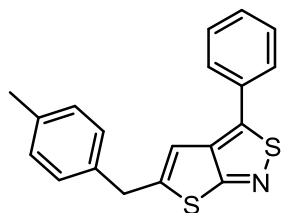
^{13}C NMR (100 MHz) spectrum of compound **4a** in CDCl_3



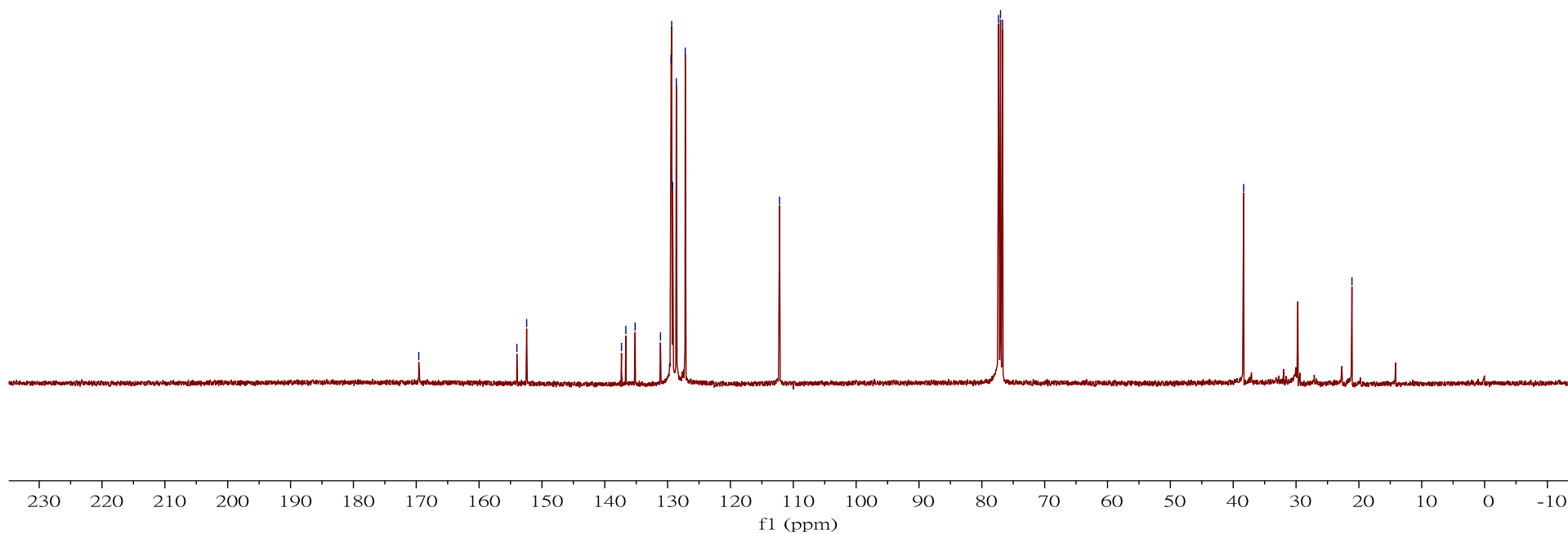
^1H NMR (400 MHz) spectrum of compound **4b** in CDCl_3

CARBON_01
IDO-T4c-13C

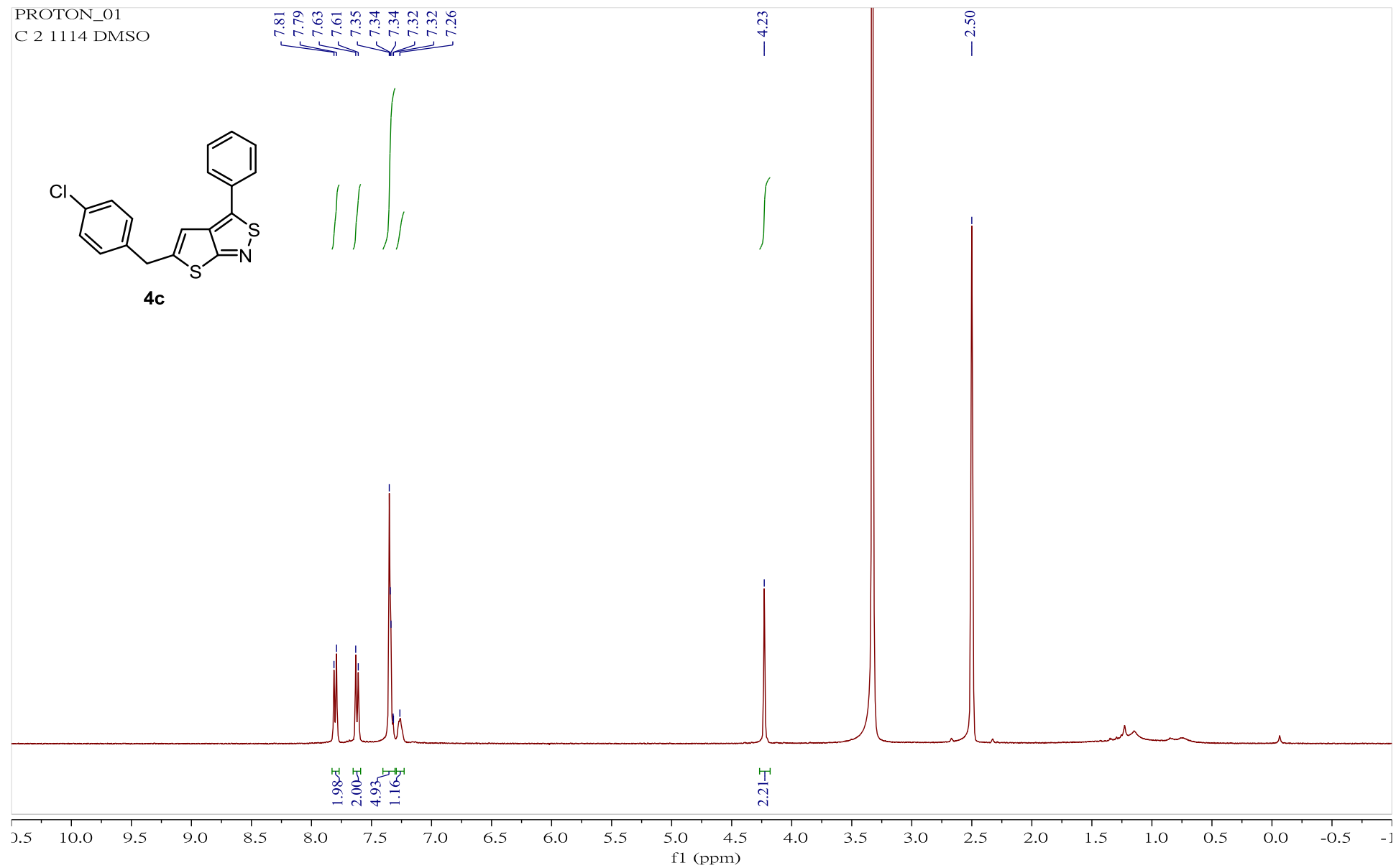
— 169.6
— 154.0
— 152.4
— 137.3
— 136.6
— 135.2
— 131.1
— 129.4
— 129.4
— 129.2
— 128.6
— 127.2
— 112.2
— 77.3
— 77.0
— 76.7
— 38.3
— 21.1



4b

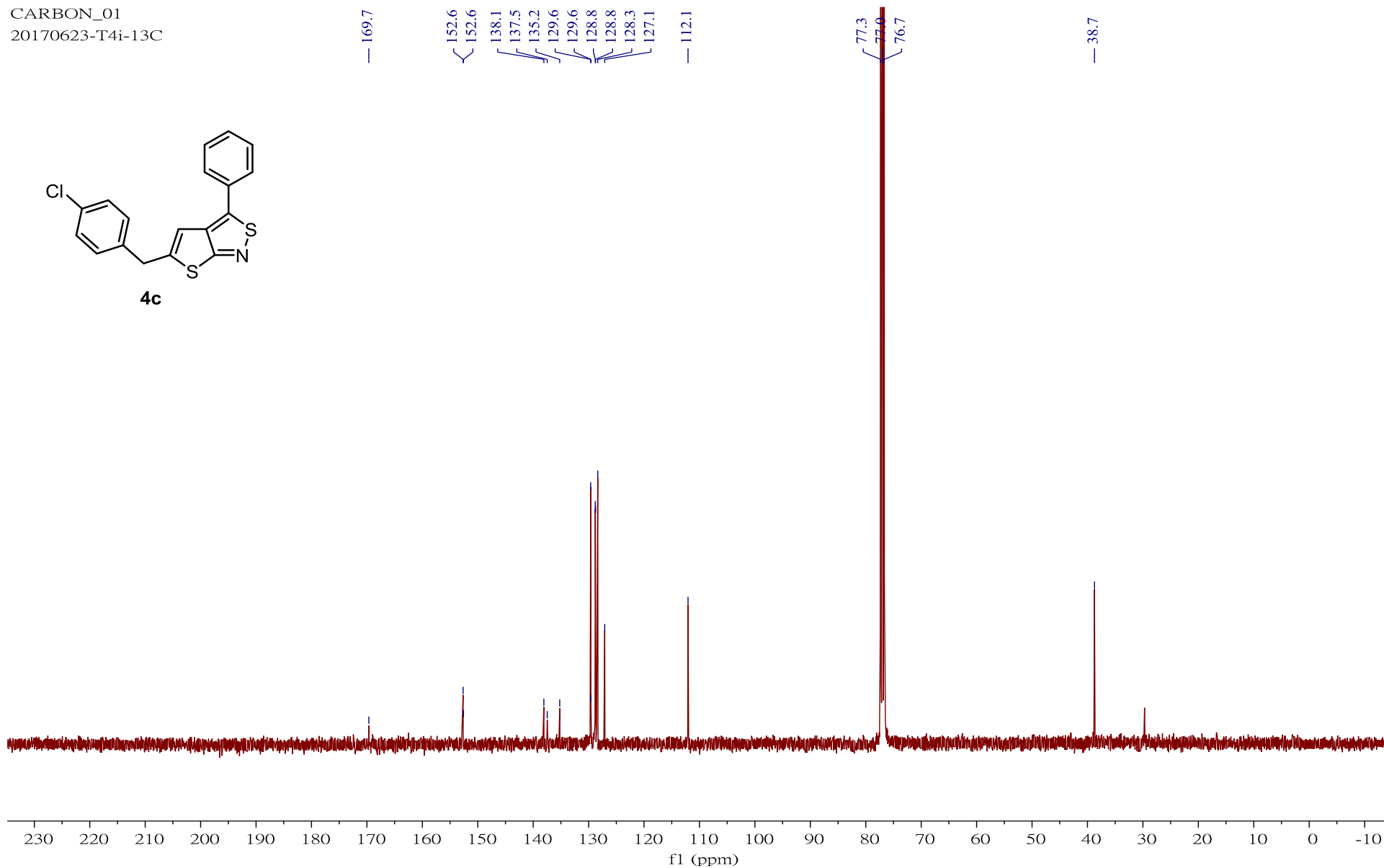
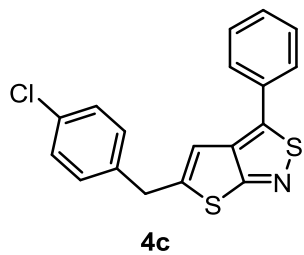


¹³C NMR (100 MHz) spectrum of compound **4b** in CDCl₃



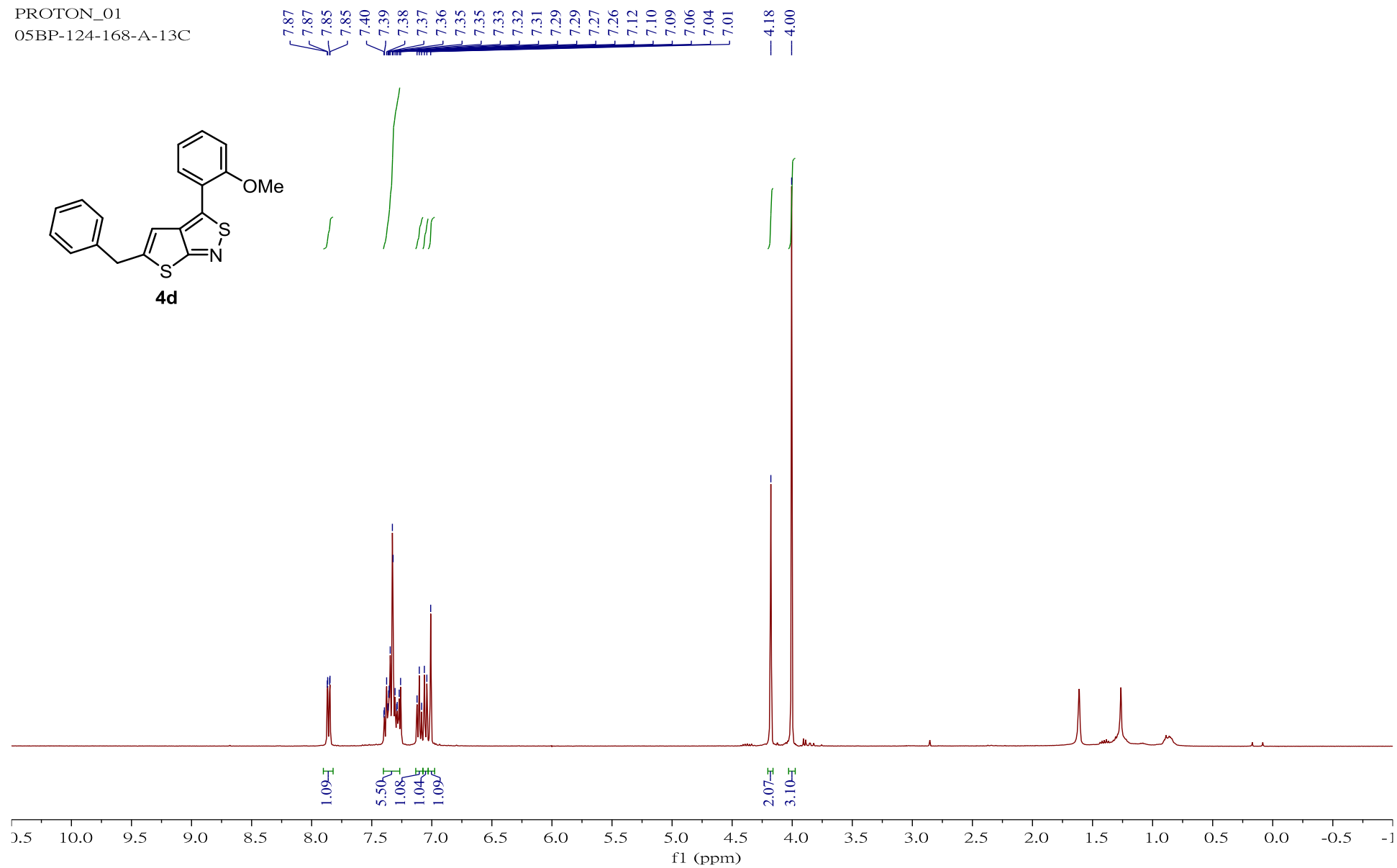
^1H NMR (400 MHz) spectrum of compound **4c** in DMSO- d_6

CARBON_01
20170623-T4i-13C



^{13}C NMR (100 MHz) spectrum of compound **4c** in CDCl_3

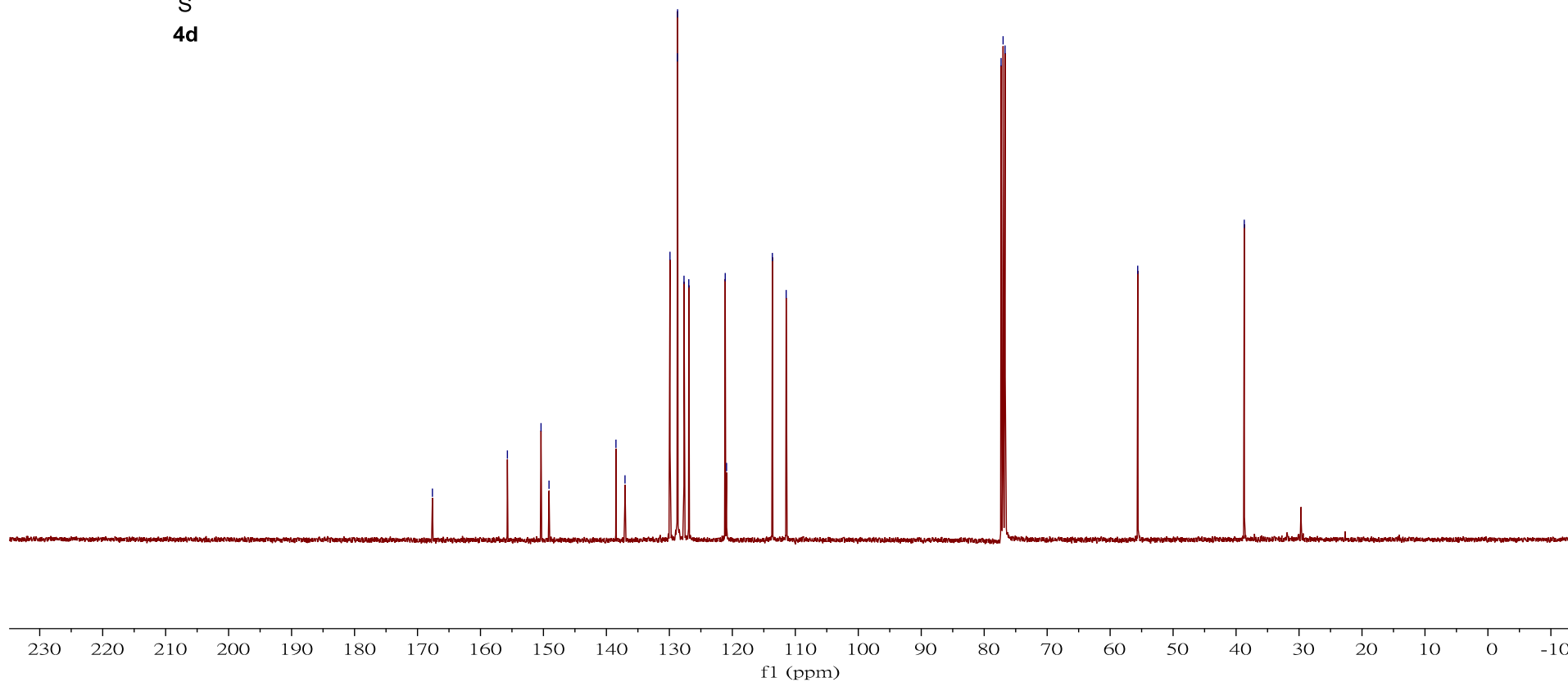
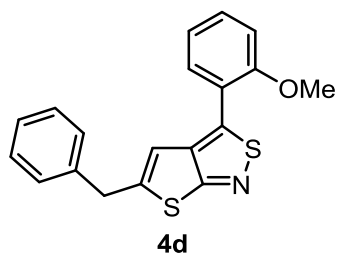
PROTON_01
05BP-124-168-A-13C



¹H NMR (400 MHz) spectrum of compound **4d** in CDCl₃

CARBON_01
05BP-124-168-A-13C

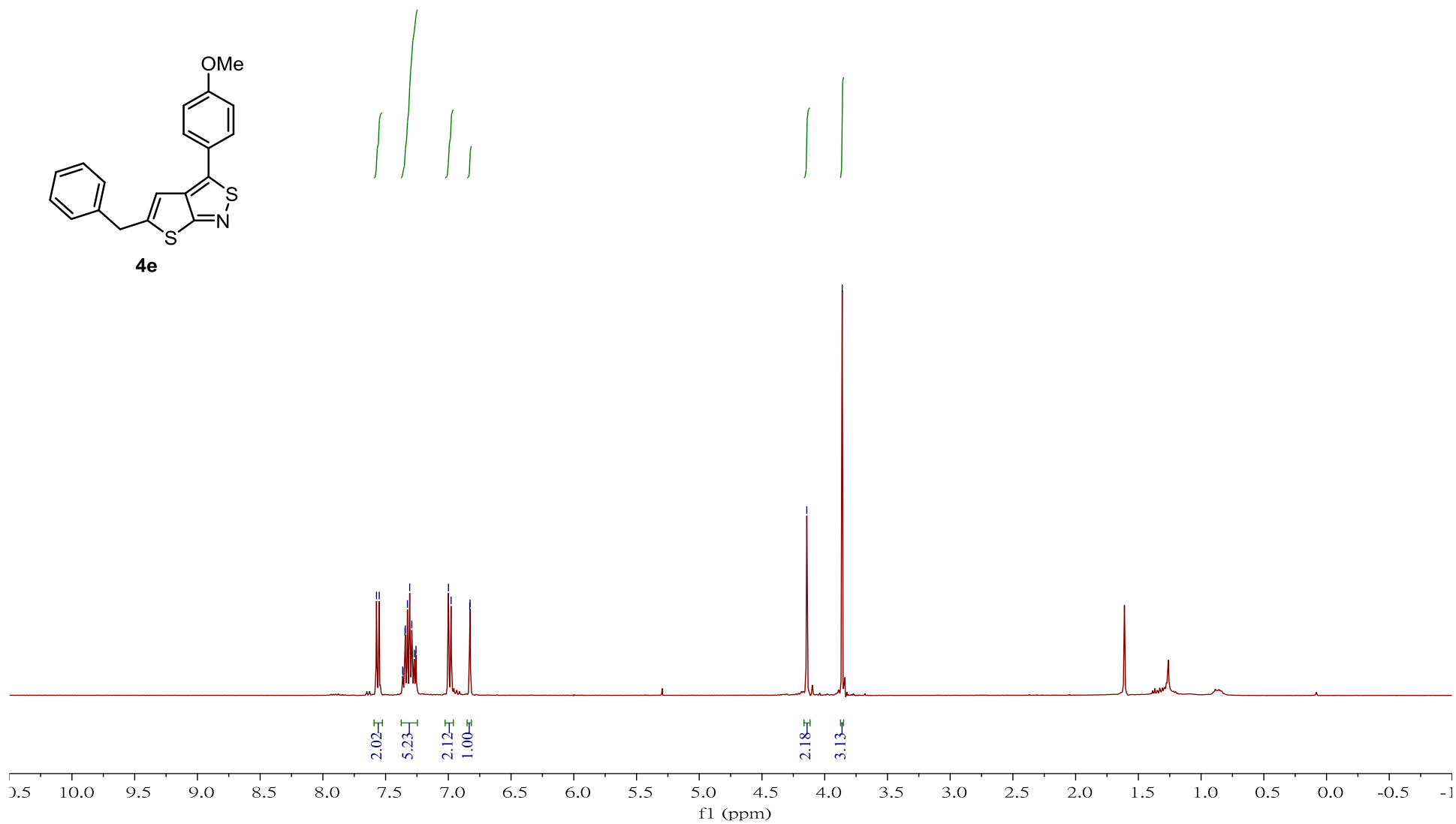
167.6
155.7
150.4
149.1
138.5
137.0
129.9
128.7
128.7
127.7
126.9
121.1
120.9
113.6
111.4
77.3
77.0
76.7
55.6
38.7



^{13}C NMR (100 MHz) spectrum of compound **4d** in CDCl_3

PROTON_01

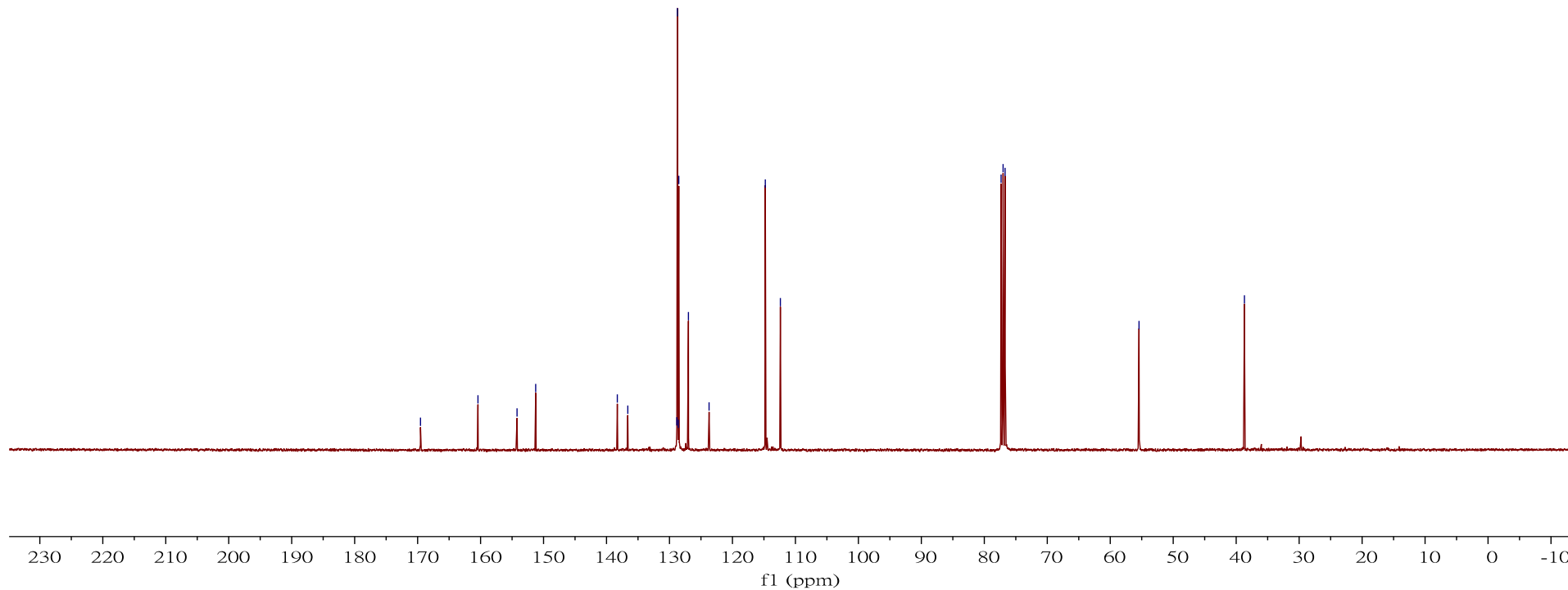
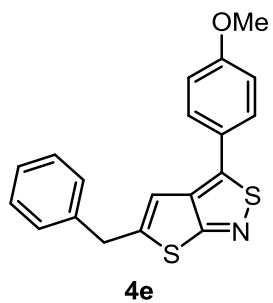
20170620-05BP-124-168-2-13



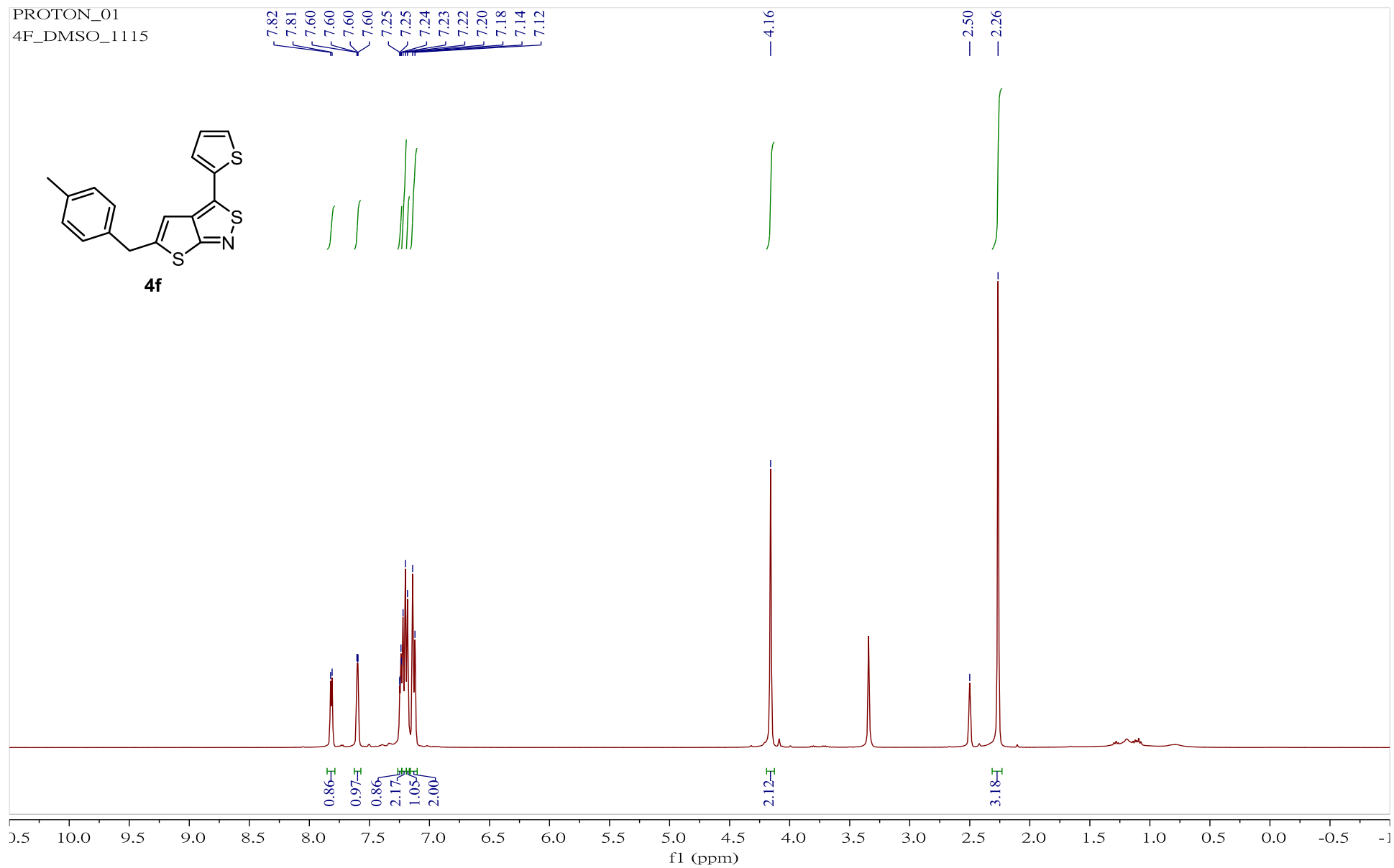
¹H NMR (400 MHz) spectrum of compound **4e** in CDCl₃

CARBON_01
20170620-05BP-124-168-2-13C

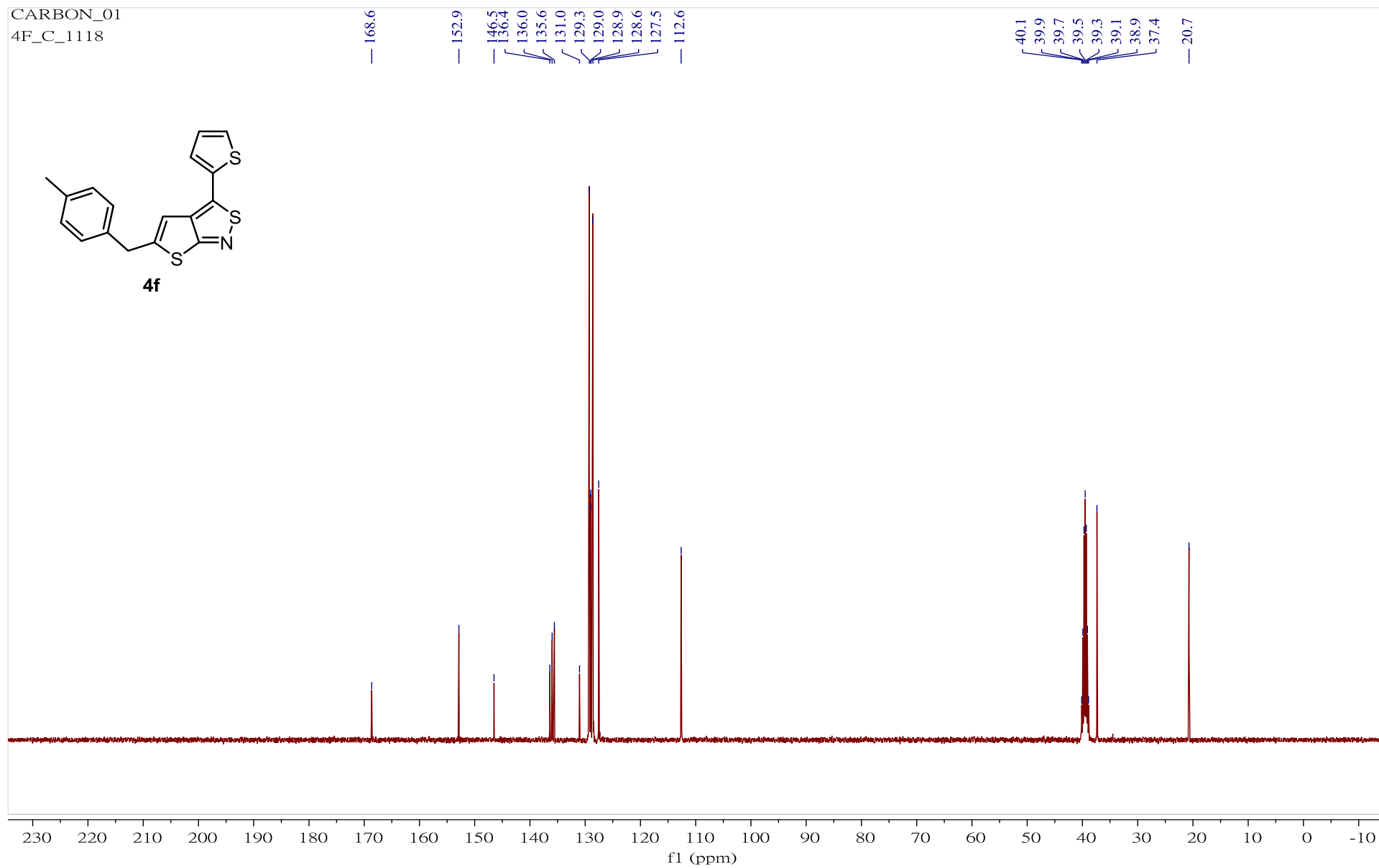
169.5
160.4
154.2
151.2
138.3
136.6
128.8
128.7
128.6
128.5
127.0
123.7
114.8
112.4
77.3
77.0
76.7
55.4
38.7



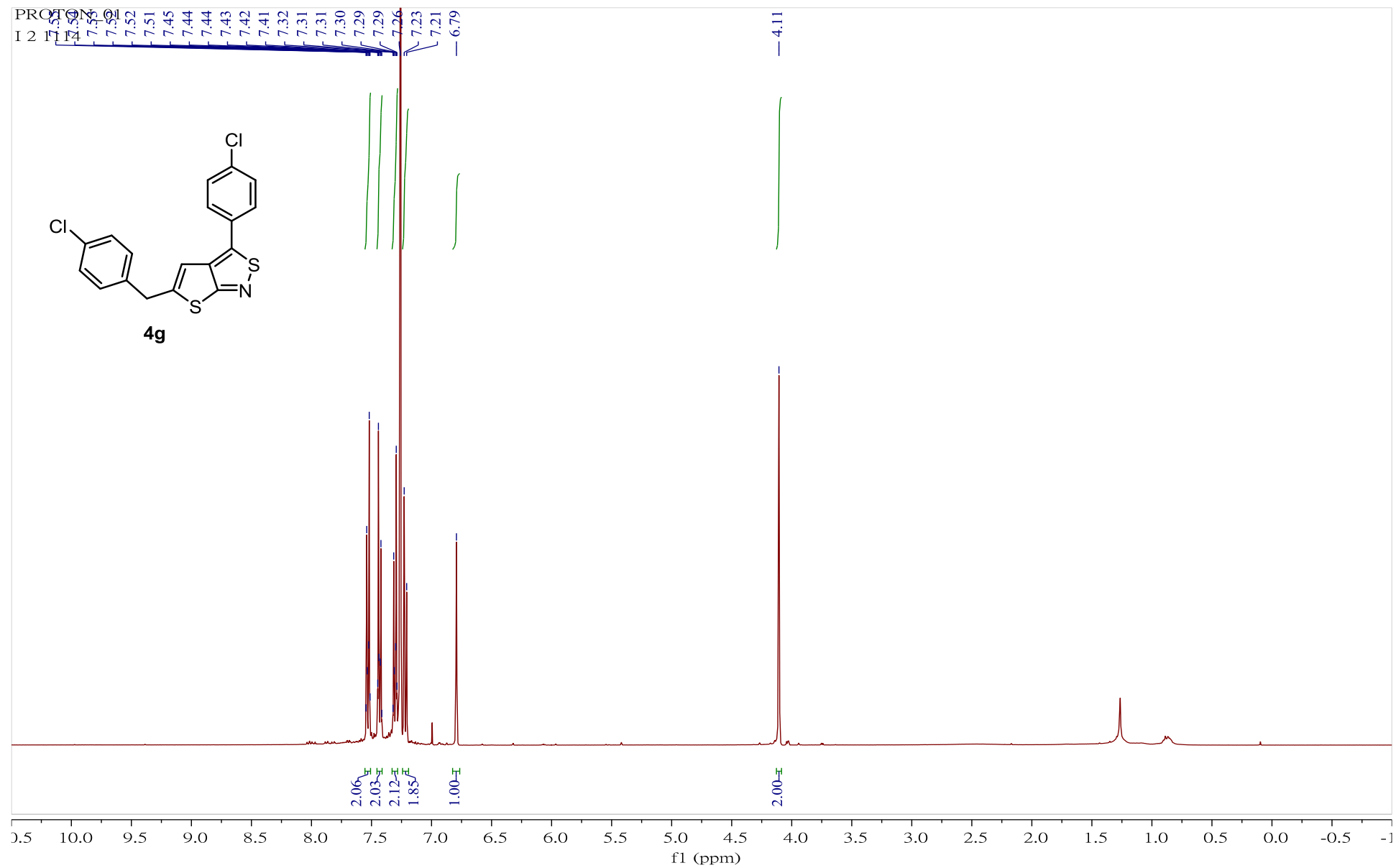
¹³C NMR (100 MHz) spectrum of compound **4e** in CDCl₃



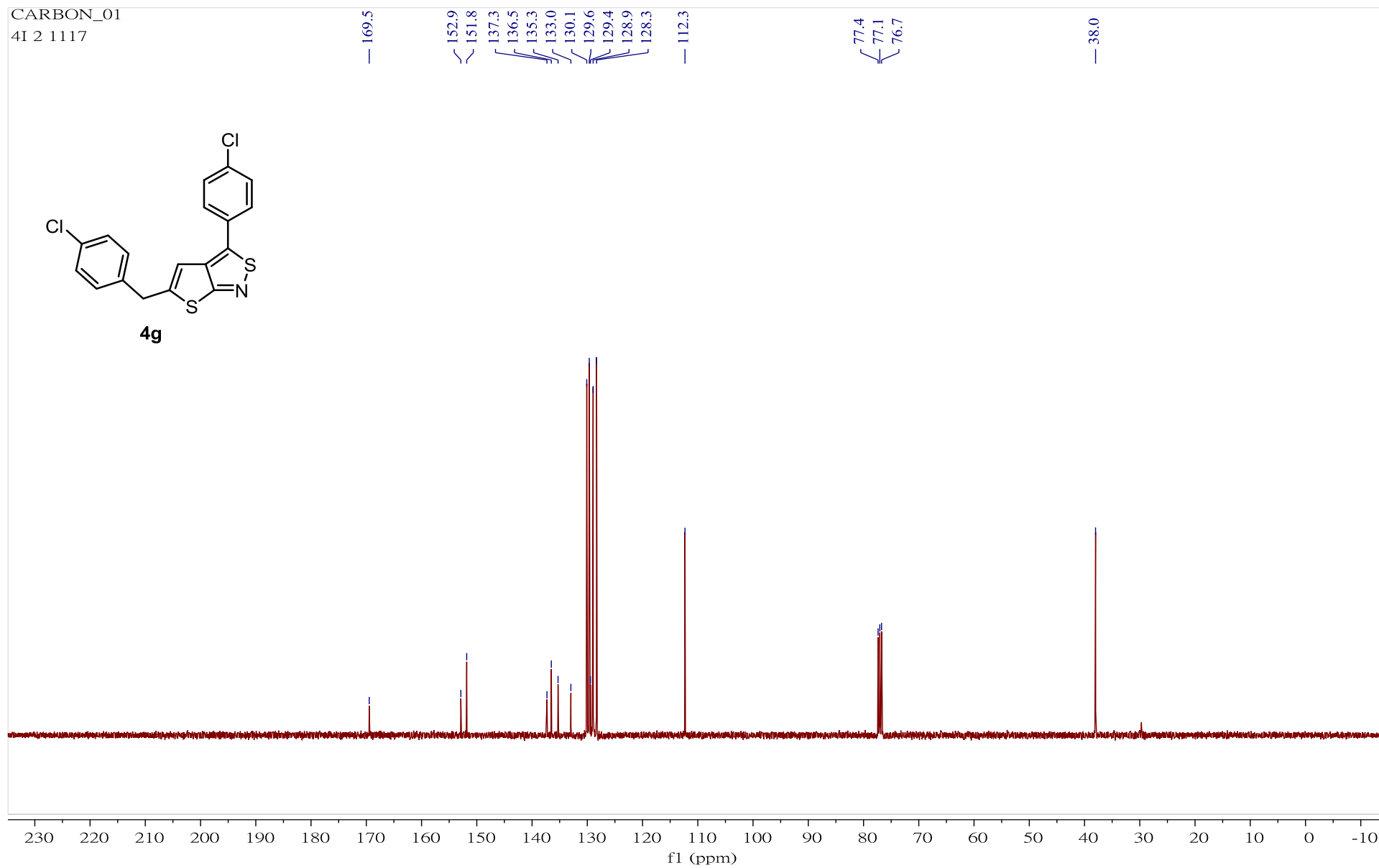
^1H NMR (400 MHz) spectrum of compound **4f** in DMSO- d_6



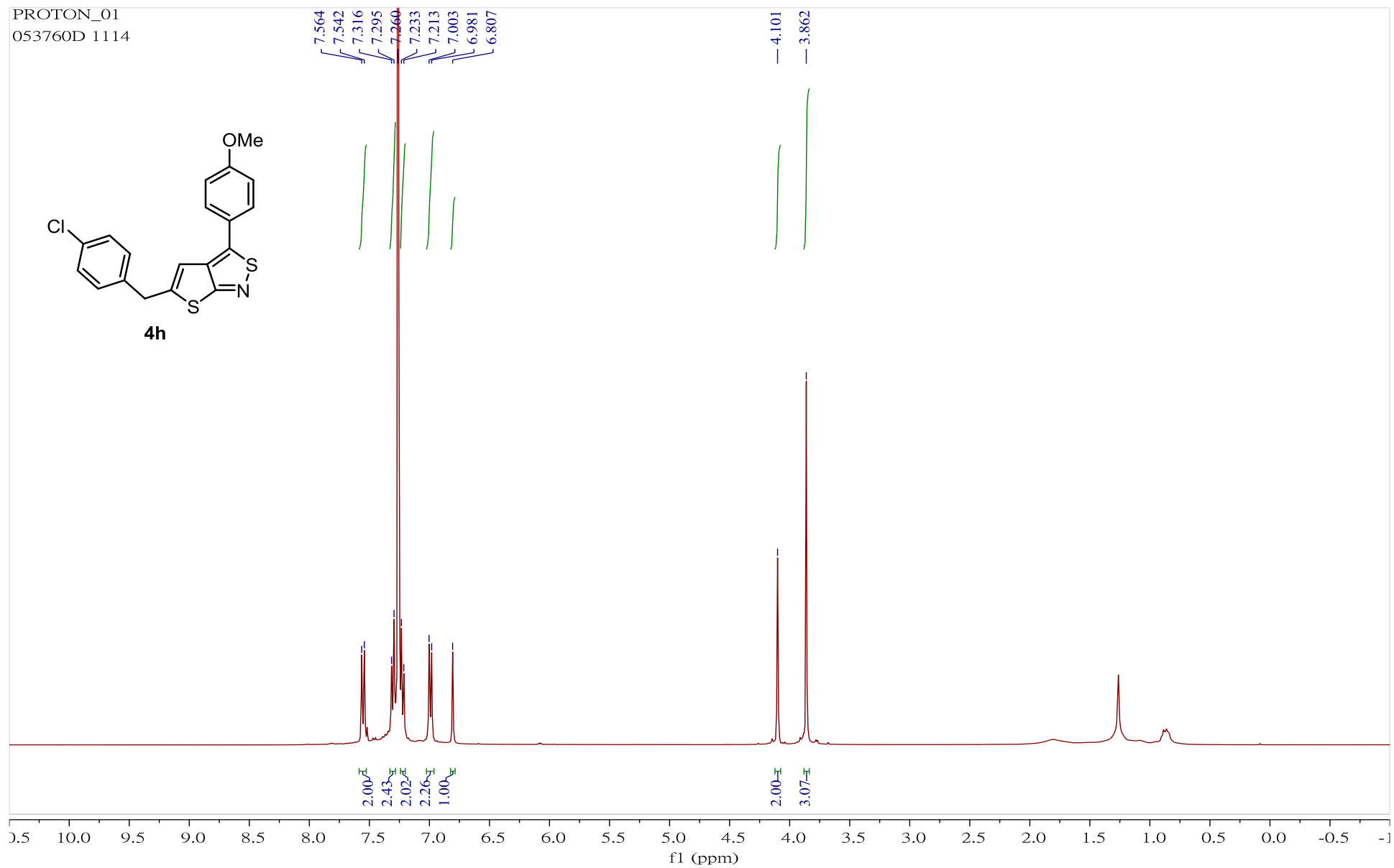
^{13}C NMR (100 MHz) spectrum of compound **4f** in DMSO- d_6



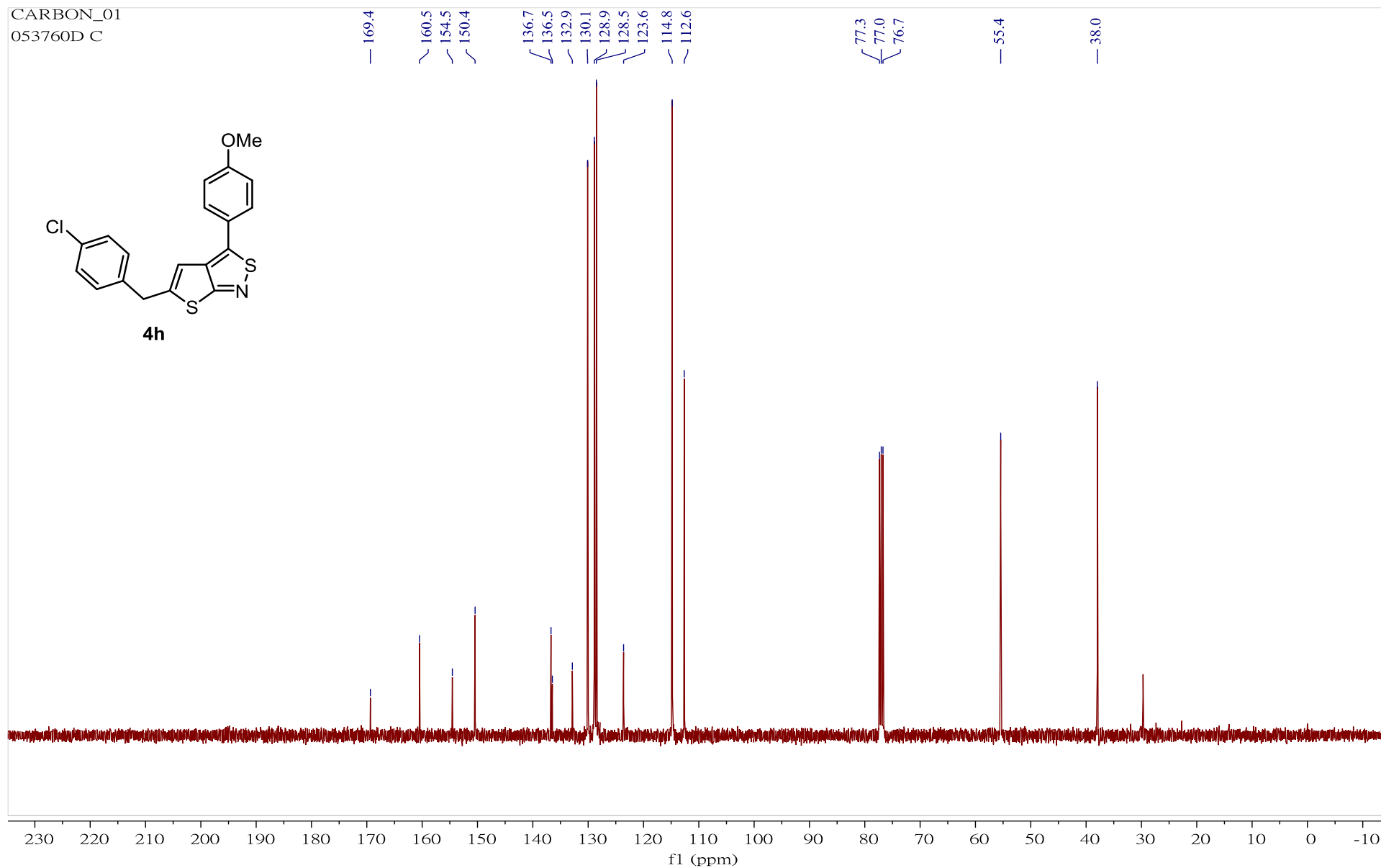
¹H NMR (400 MHz) spectrum of compound **4g** in CDCl₃



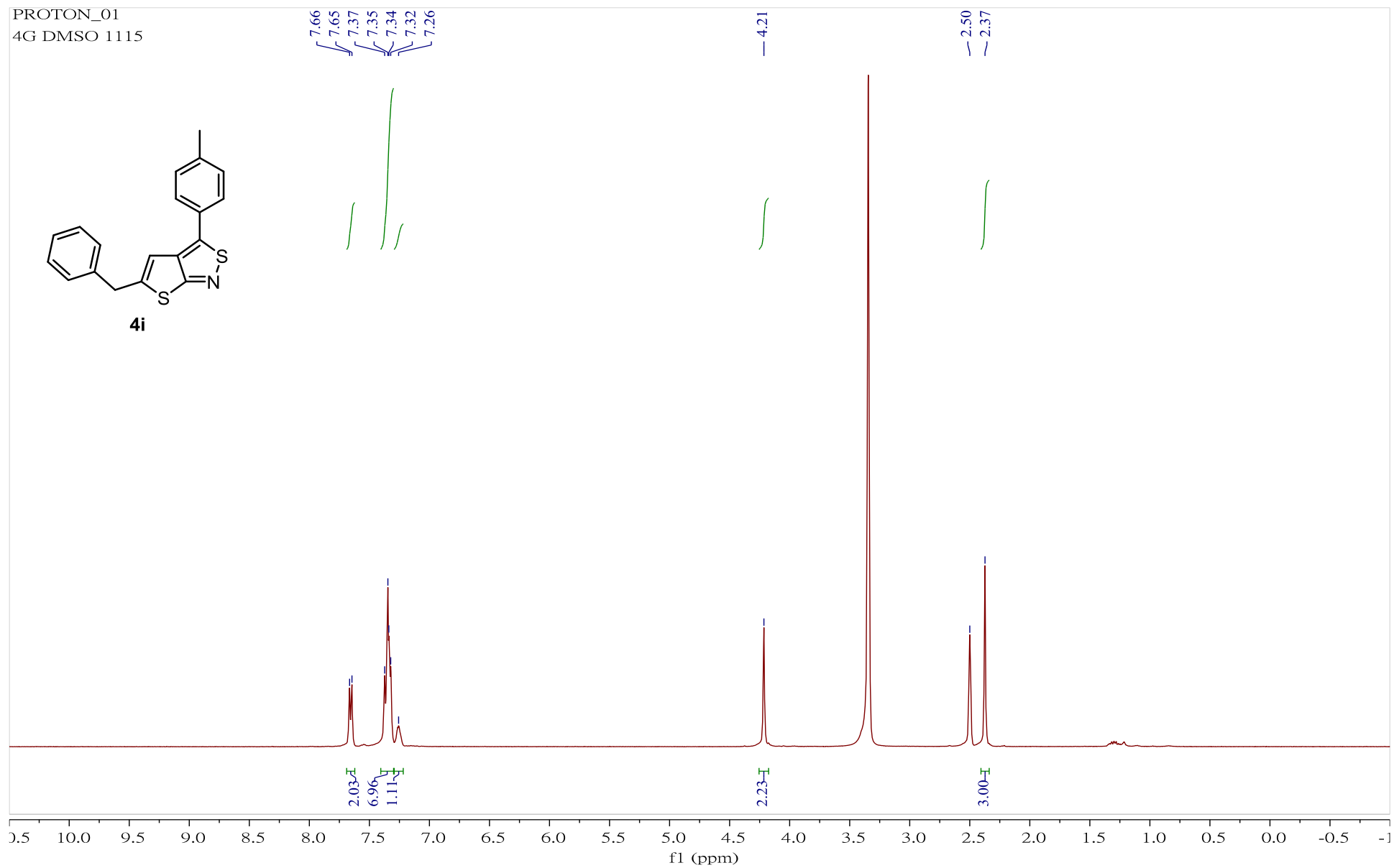
^{13}C NMR (100 MHz) spectrum of compound **4g** in CDCl_3



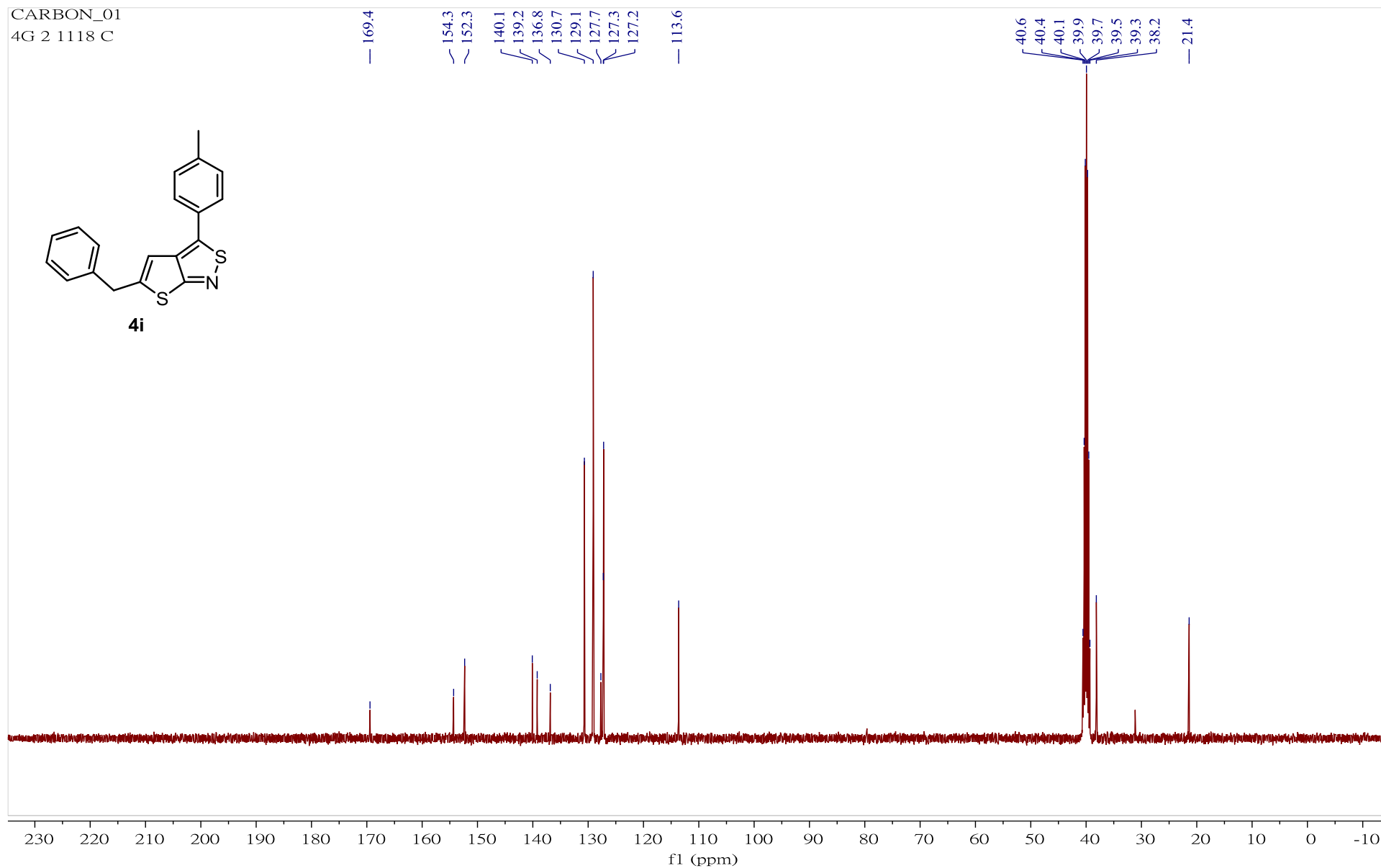
^1H NMR (400 MHz) spectrum of compound **4h** in CDCl_3



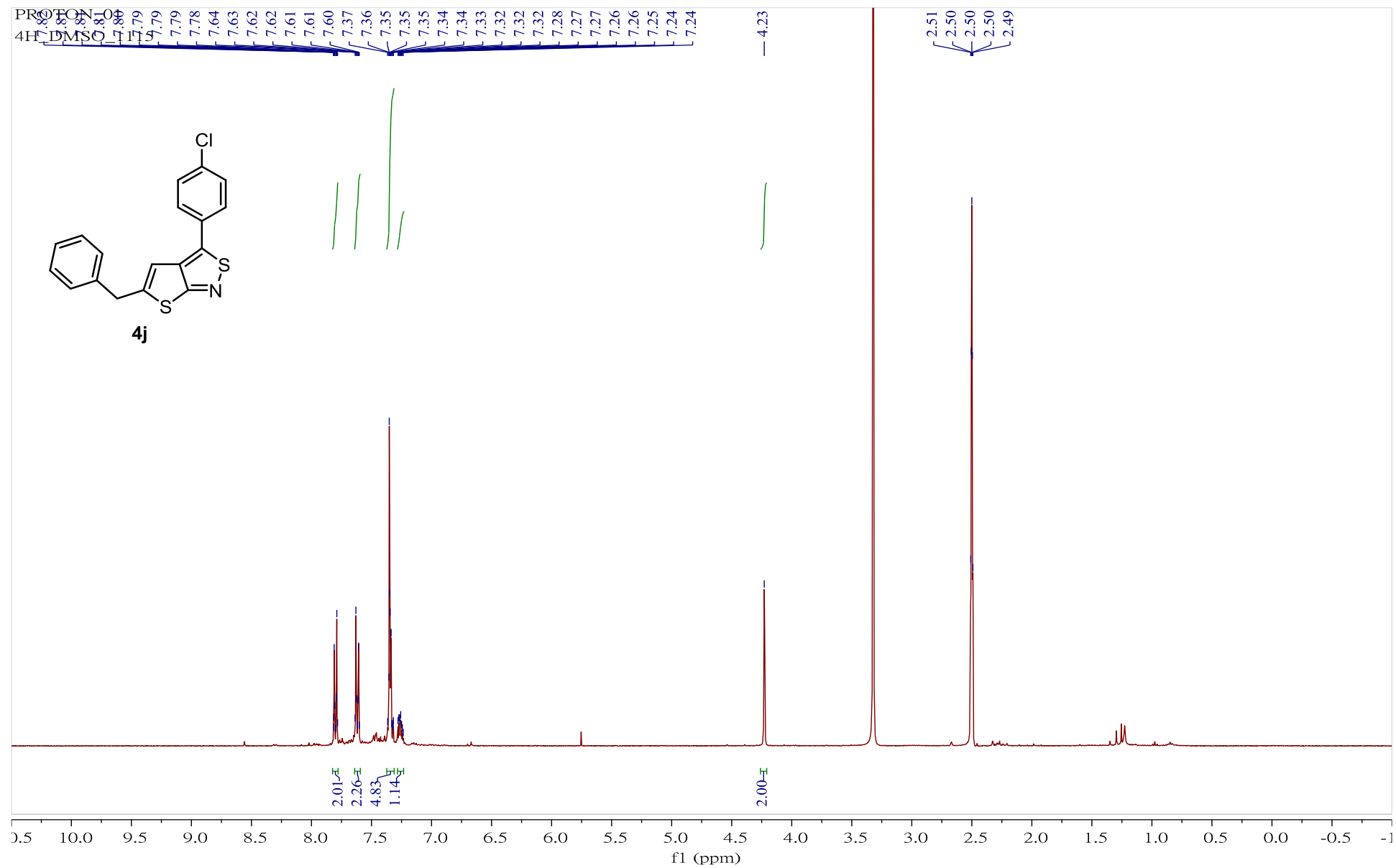
^{13}C NMR (100 MHz) spectrum of compound **4h** in CDCl_3



^1H NMR (400 MHz) spectrum of compound **4i** in DMSO- d_6



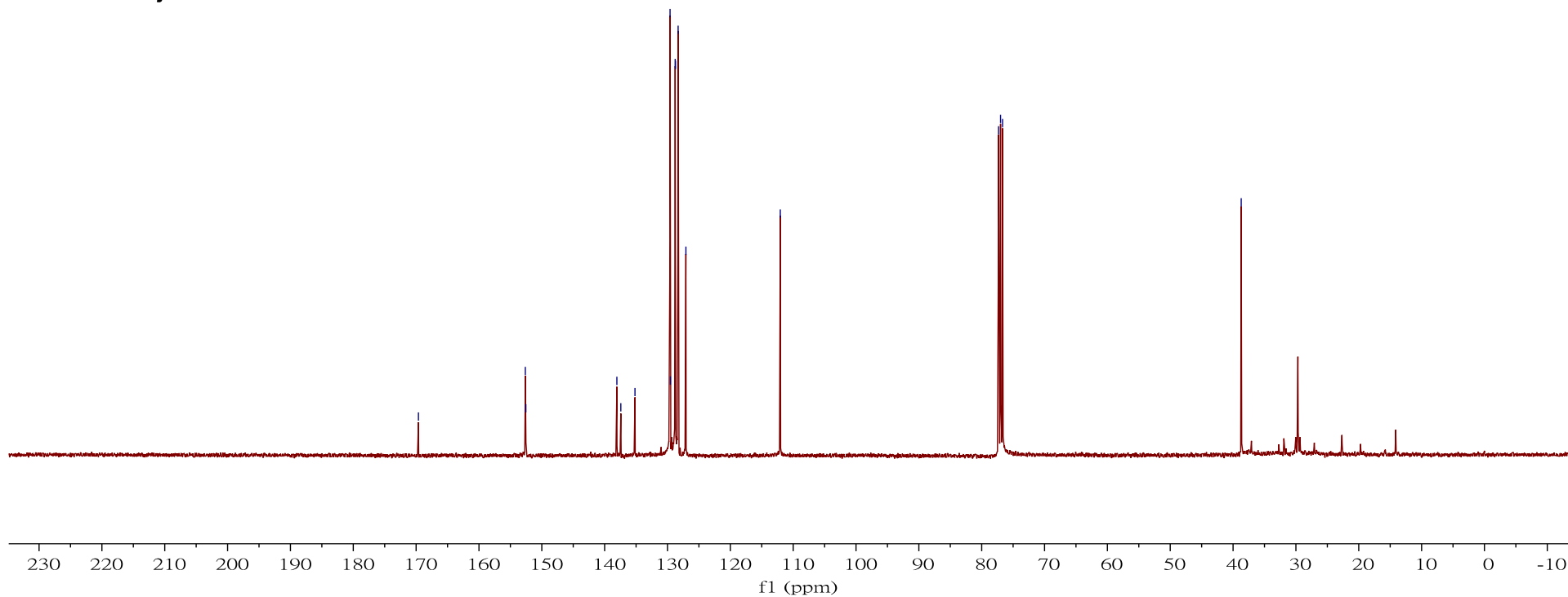
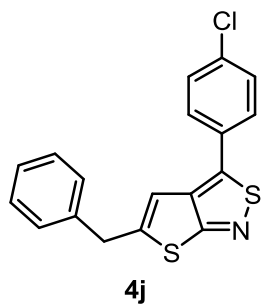
^{13}C NMR (100 MHz) spectrum of compound **4i** in DMSO- d_6



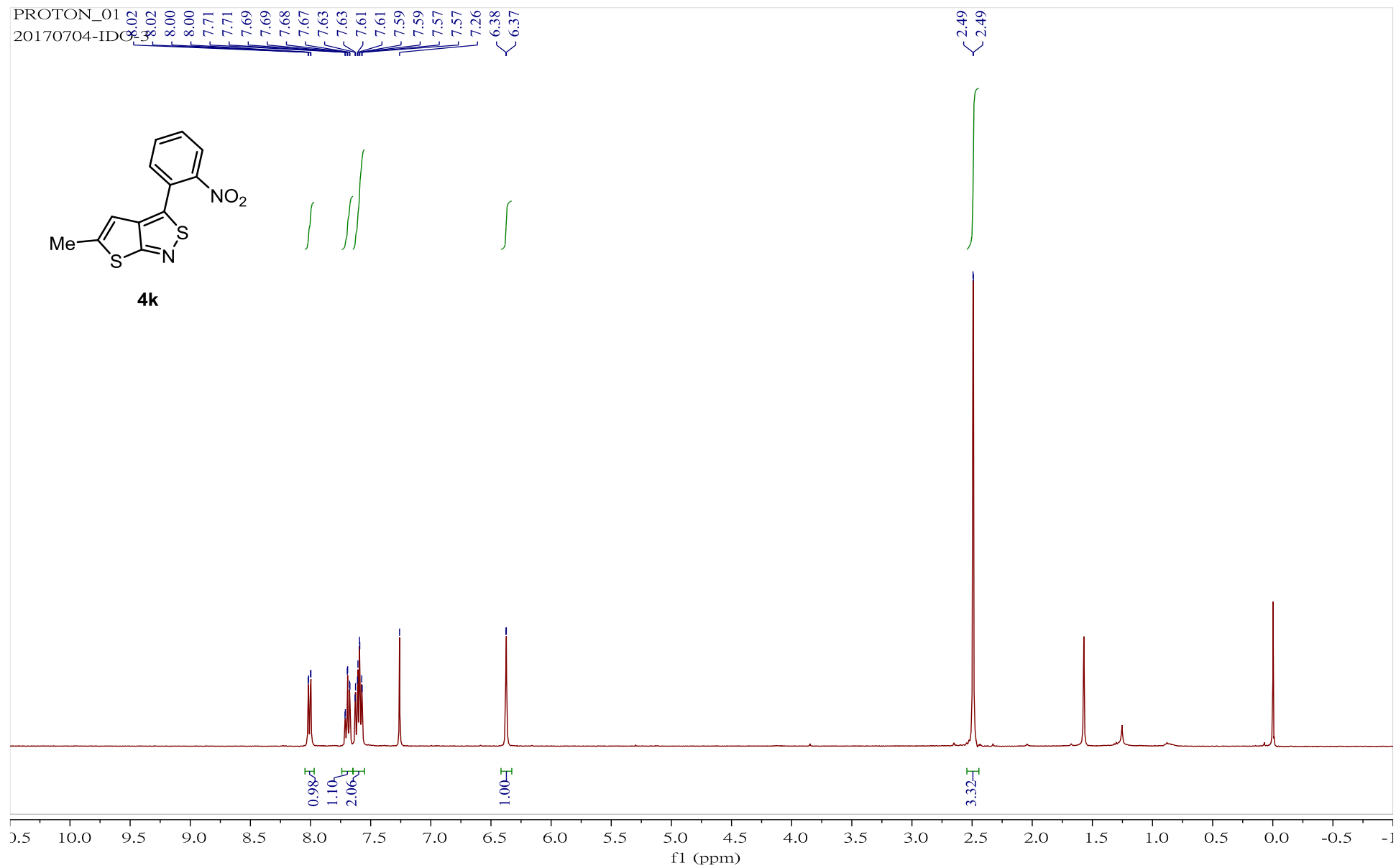
^1H NMR (400 MHz) spectrum of compound **4j** in DMSO- d_6

CARBON_01
20170511-05BP-124-136-13C

— 169.6
152.6
152.5
138.1
137.4
135.2
129.6
129.5
128.8
128.7
128.3
127.1
— 112.0
77.3
77.0
76.7
— 38.7

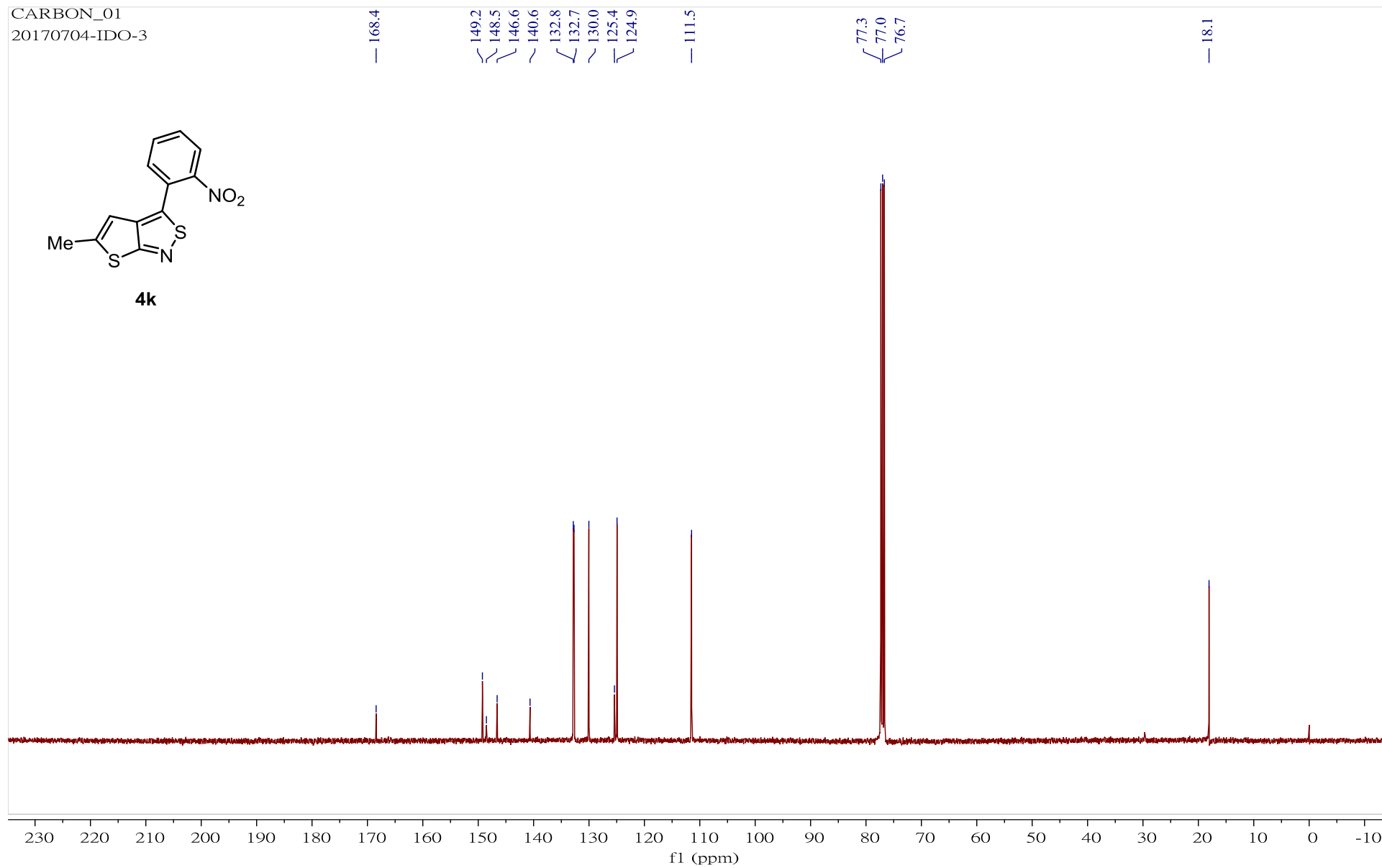


^{13}C NMR (100 MHz) spectrum of compound **4j** in CDCl_3

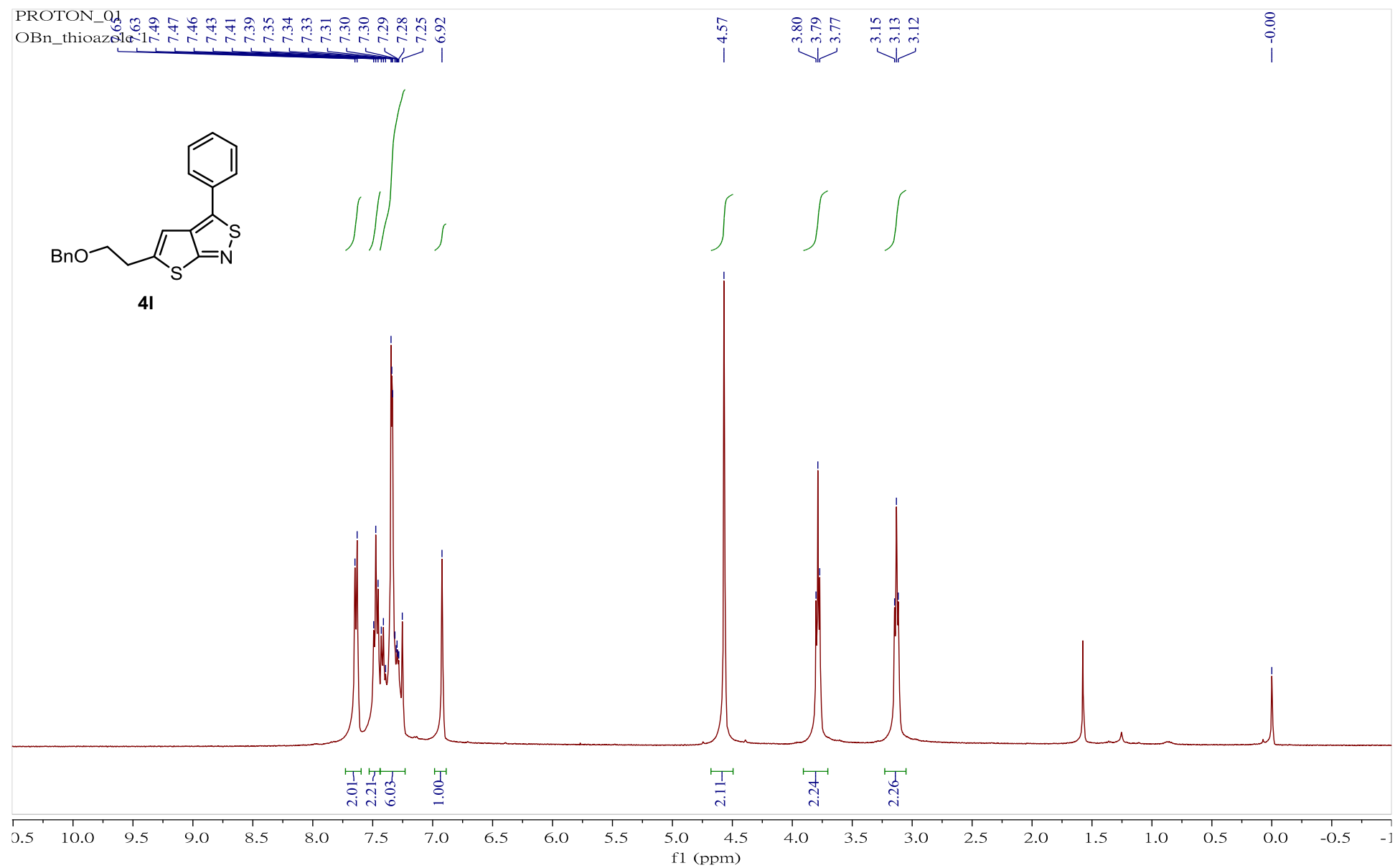


^1H NMR (400 MHz) spectrum of compound **4k** in CDCl_3

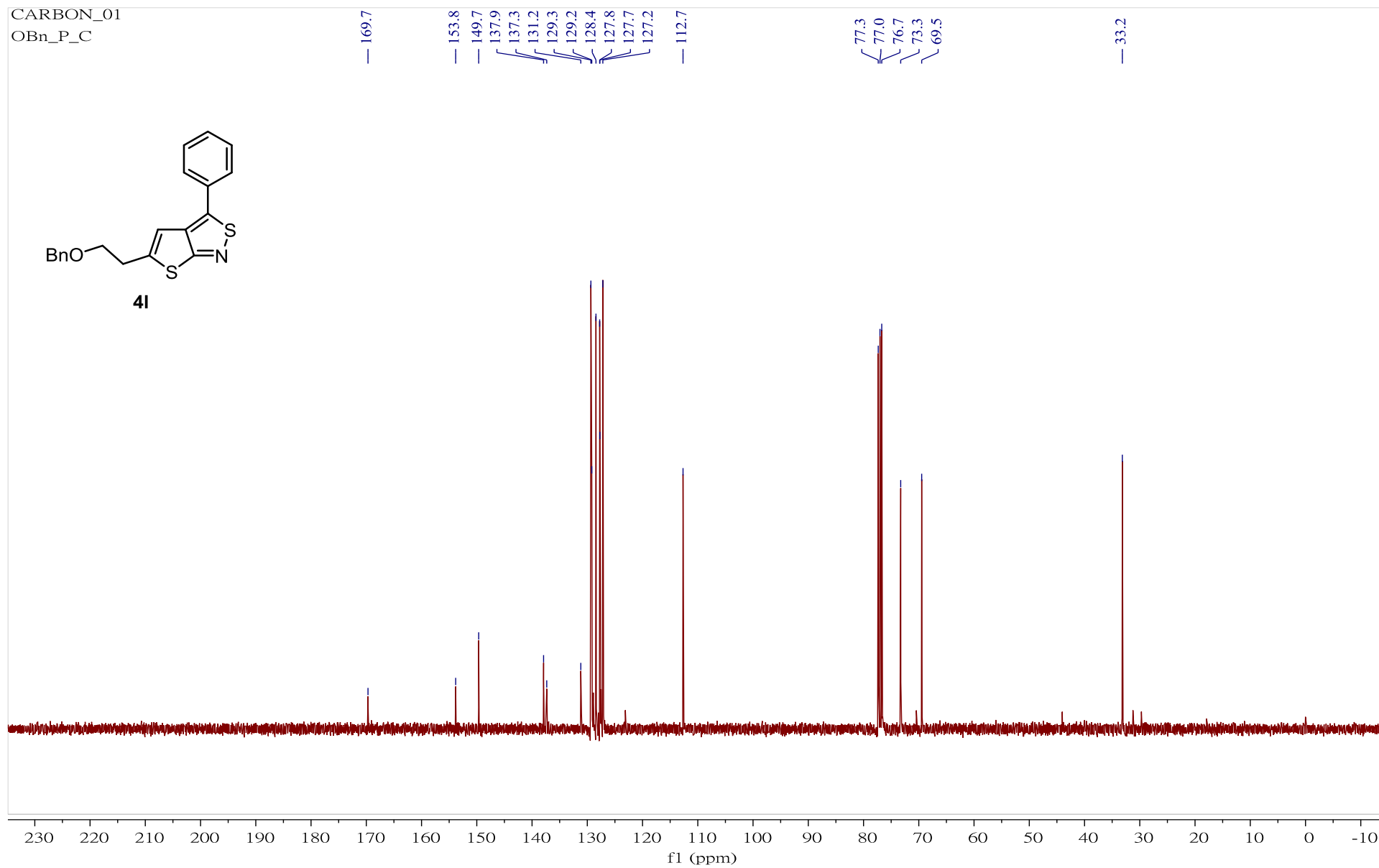
CARBON_01
20170704-IDO-3



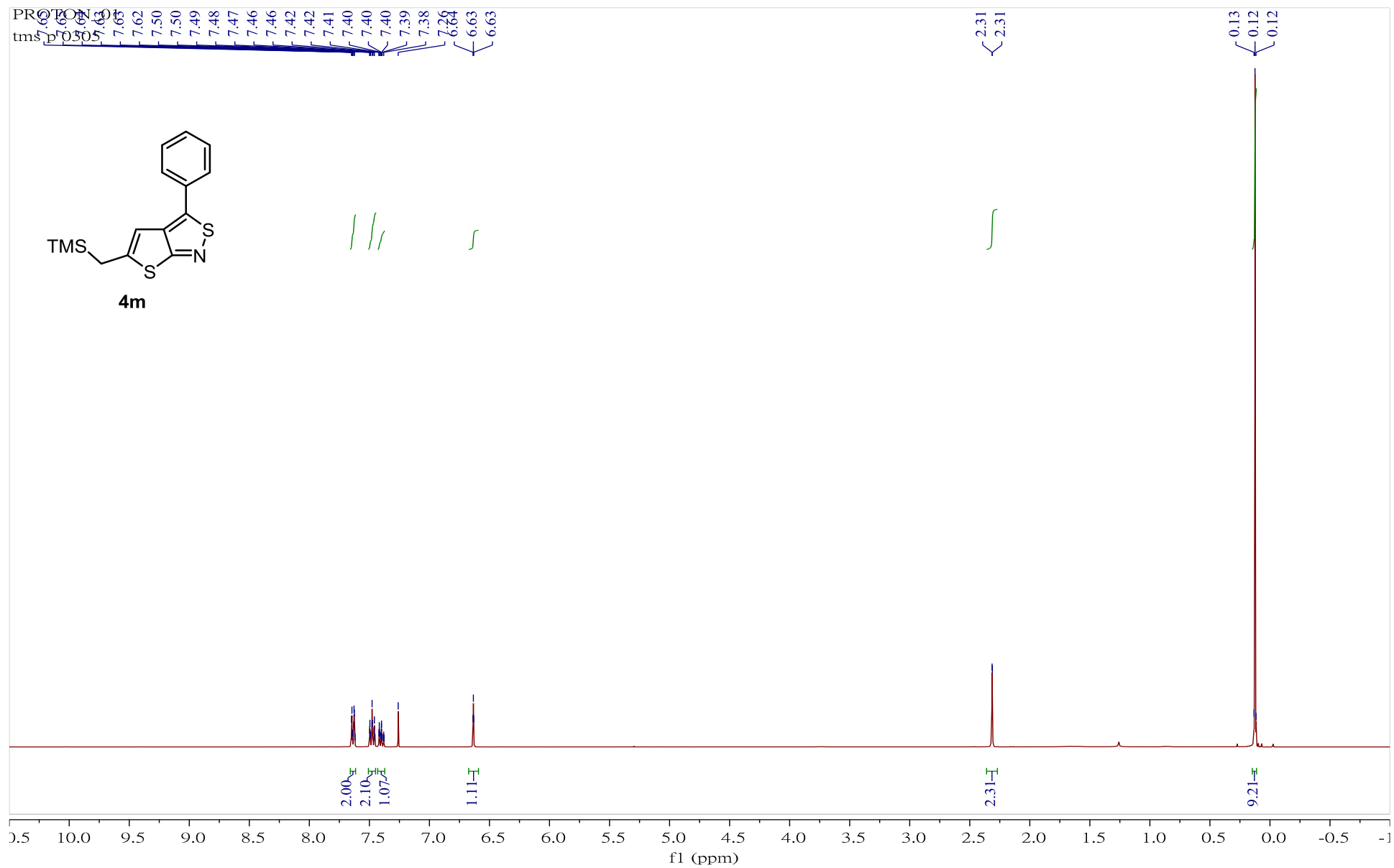
¹³C NMR (100 MHz) spectrum of compound **4k** in CDCl₃



^1H NMR (400 MHz) spectrum of compound **4I** in DMSO-d_6

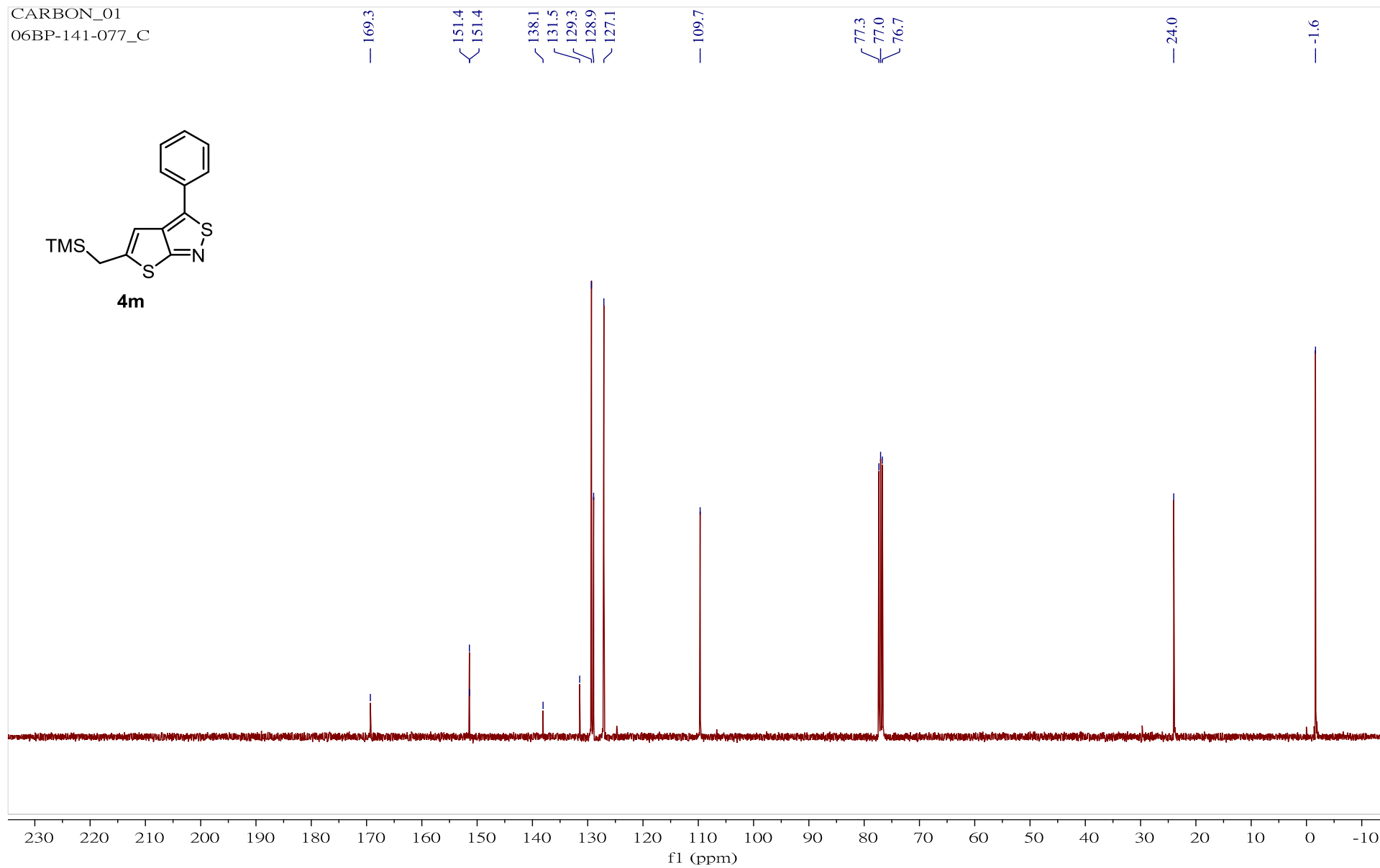
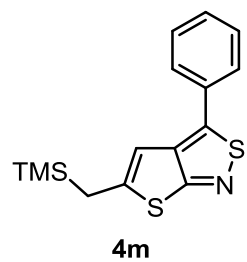


¹³C NMR (100 MHz) spectrum of compound **4I** in DMSO-d₆

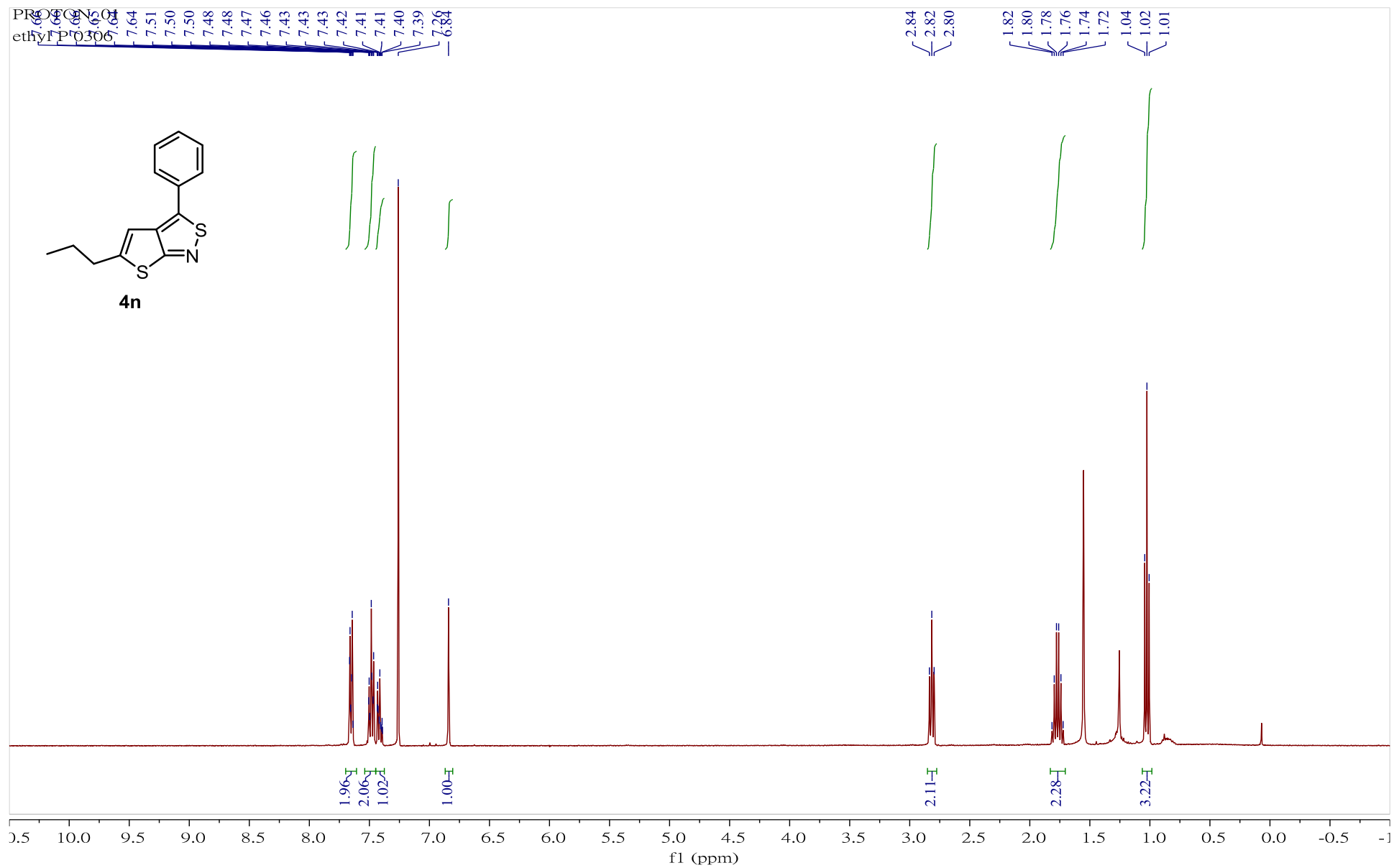


^1H NMR (400 MHz) spectrum of compound **4m** in CDCl_3

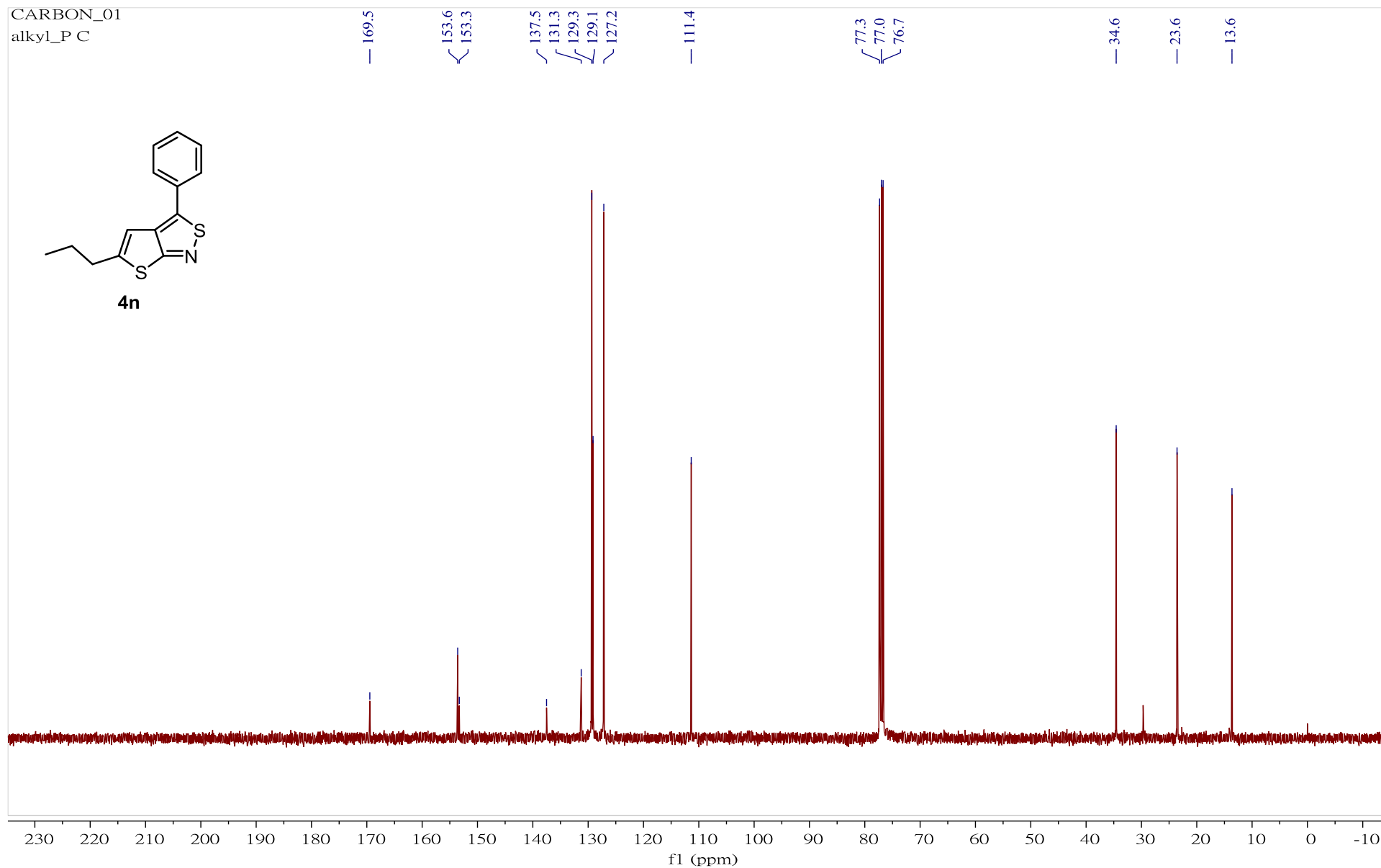
CARBON_01
06BP-141-077_C



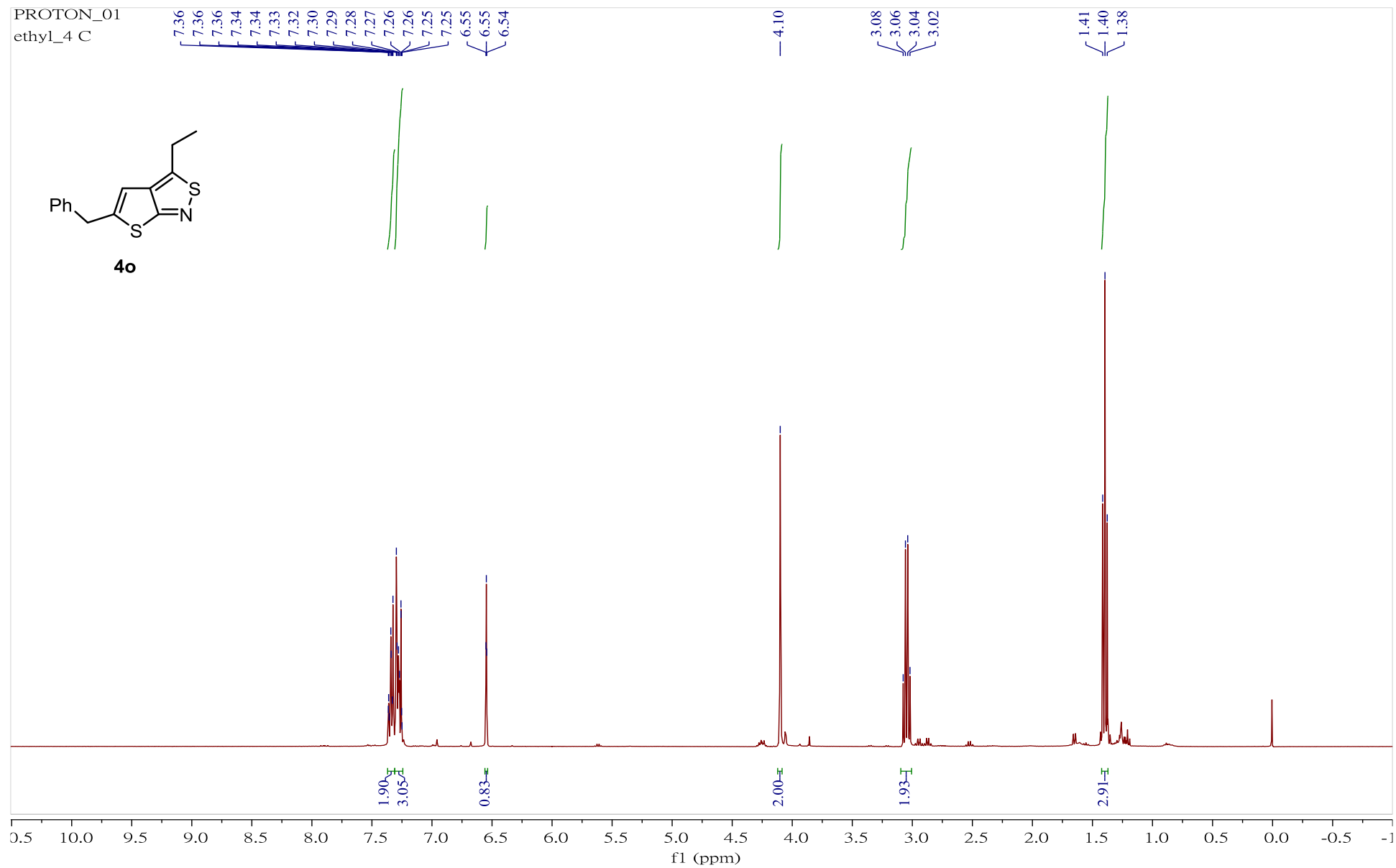
^{13}C NMR (100 MHz) spectrum of compound **4m** in CDCl_3



¹H NMR (400 MHz) spectrum of compound **4n** in CDCl₃

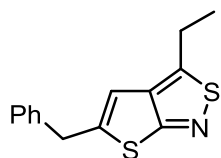


^{13}C NMR (100 MHz) spectrum of compound **4n** in CDCl_3

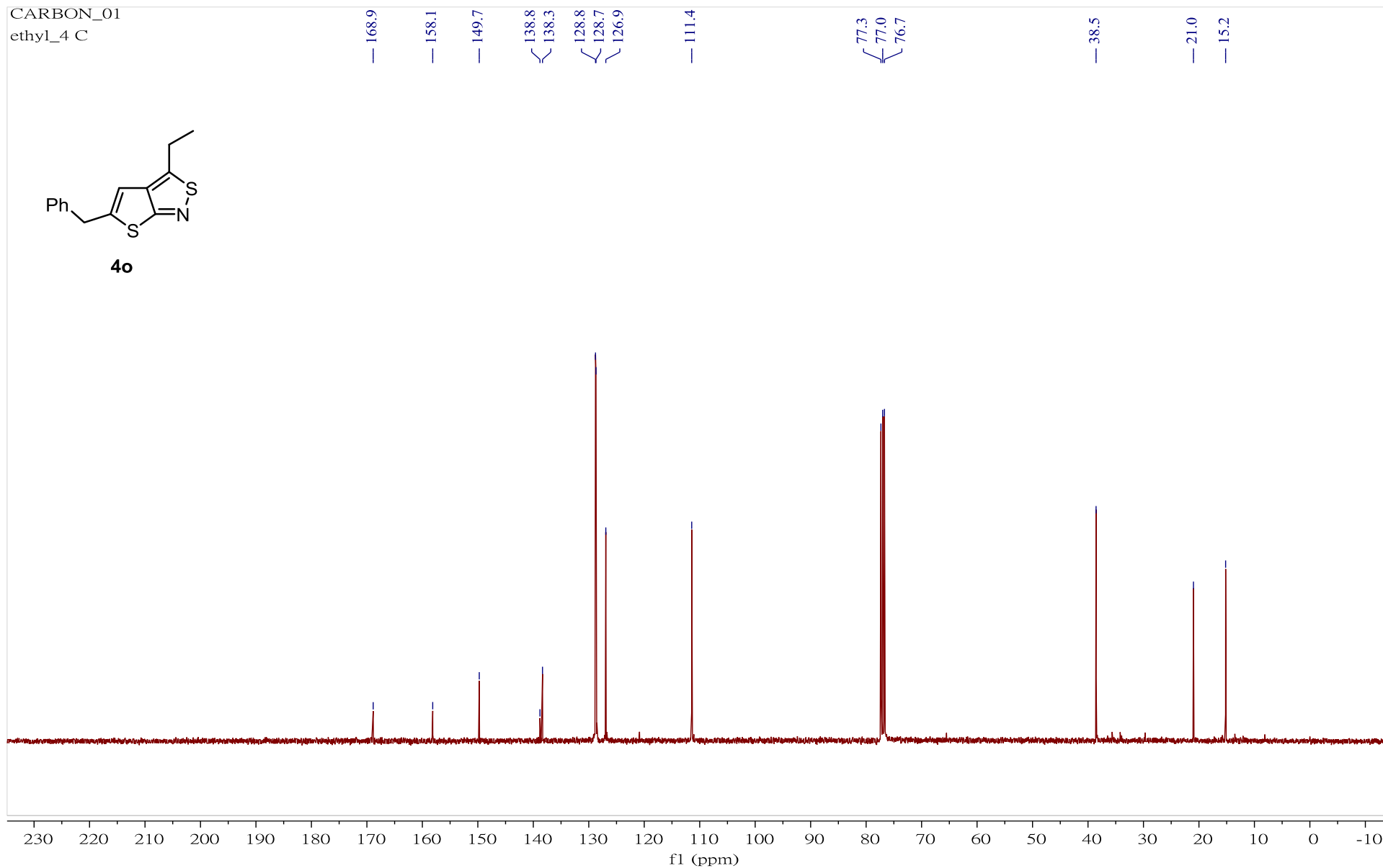


^1H NMR (400 MHz) spectrum of compound **4o** in CDCl_3

CARBON_01
ethyl_4 C

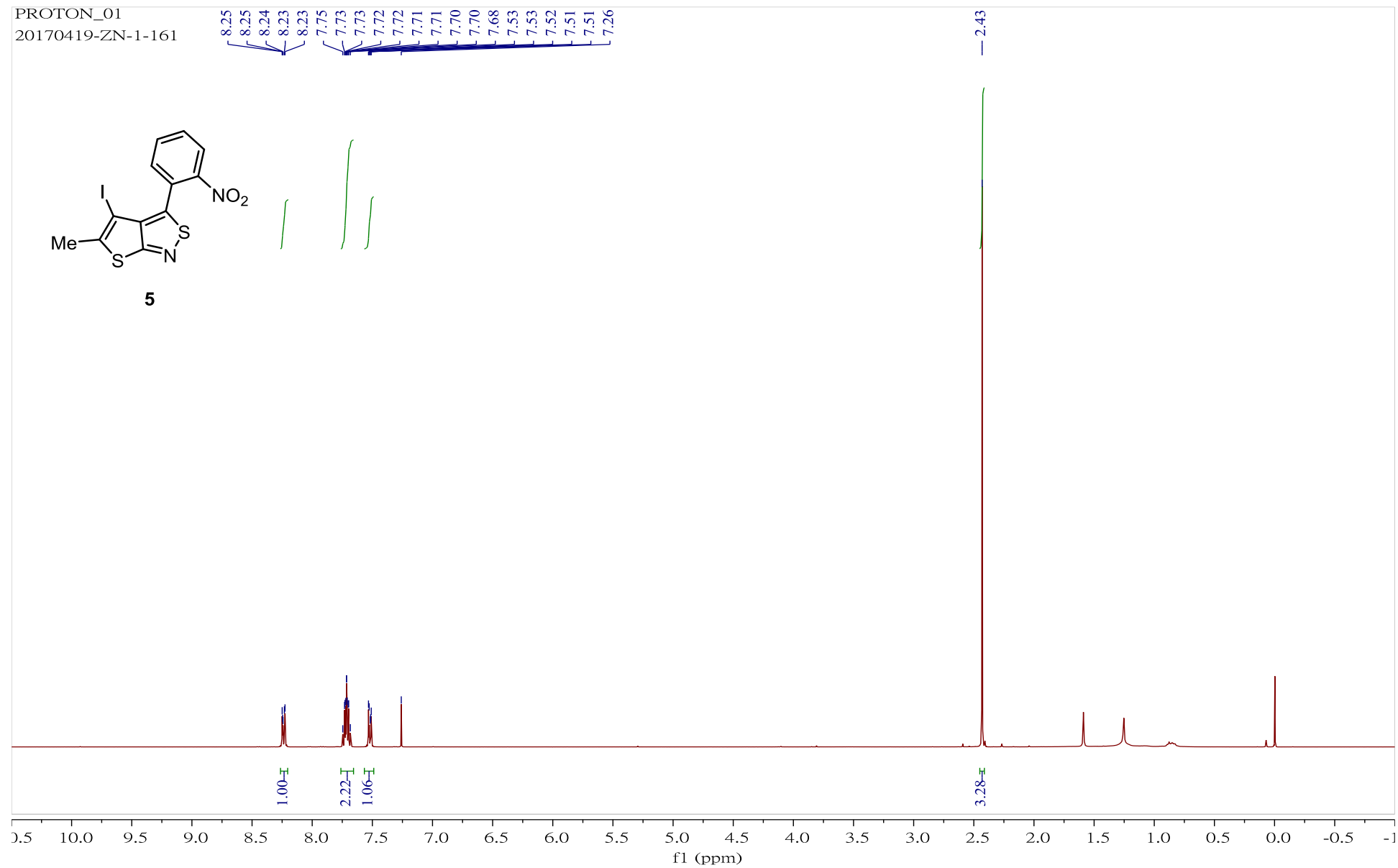


4o



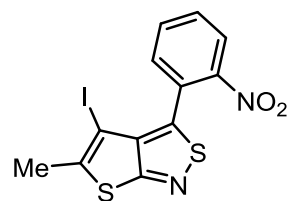
¹³C NMR (100 MHz) spectrum of compound **4o** in CDCl₃

PROTON_01
20170419-ZN-1-161

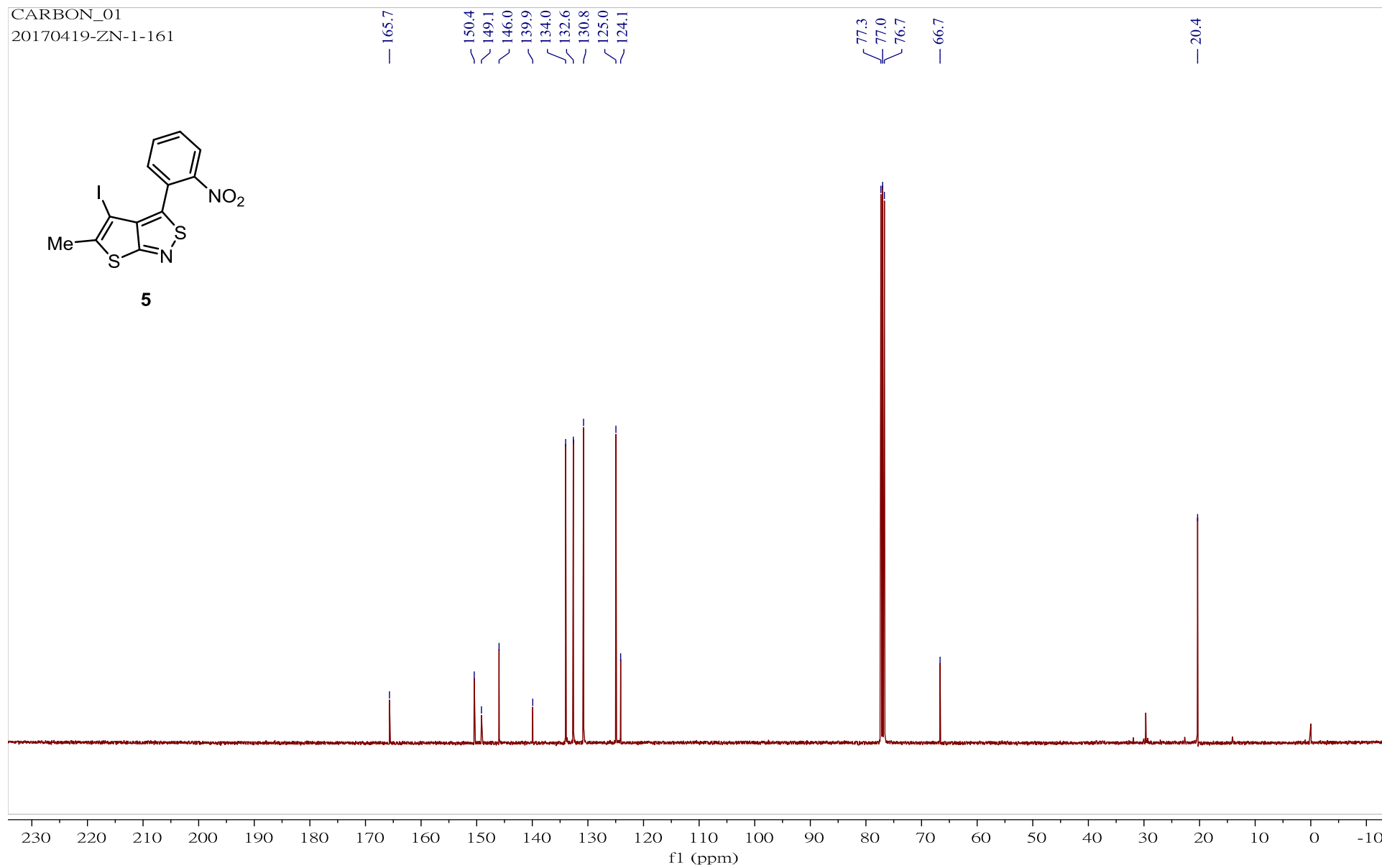


¹H NMR (400 MHz) spectrum of compound **5** in CDCl₃

CARBON_01
20170419-ZN-1-161

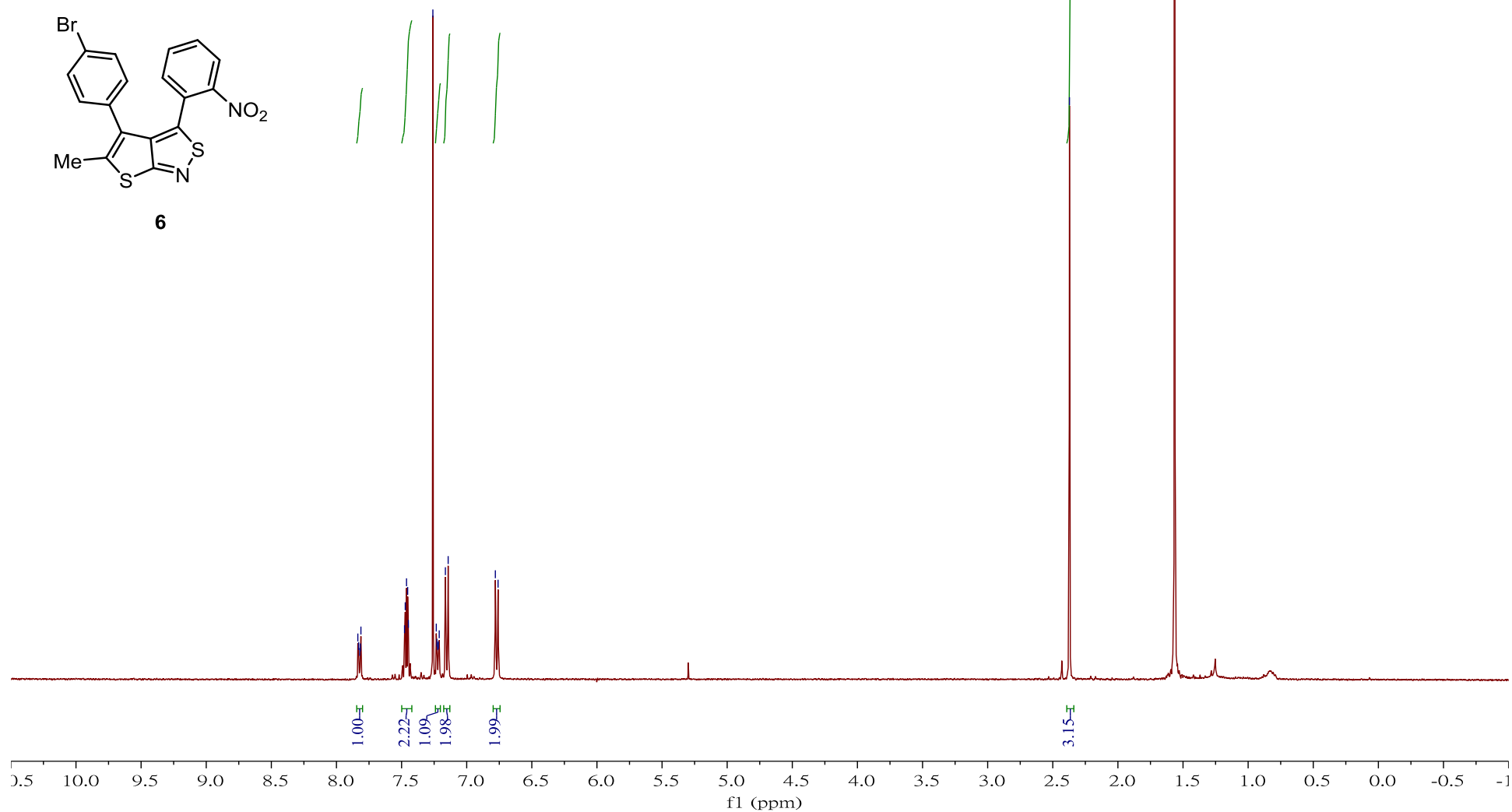
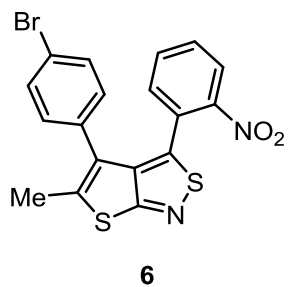


5



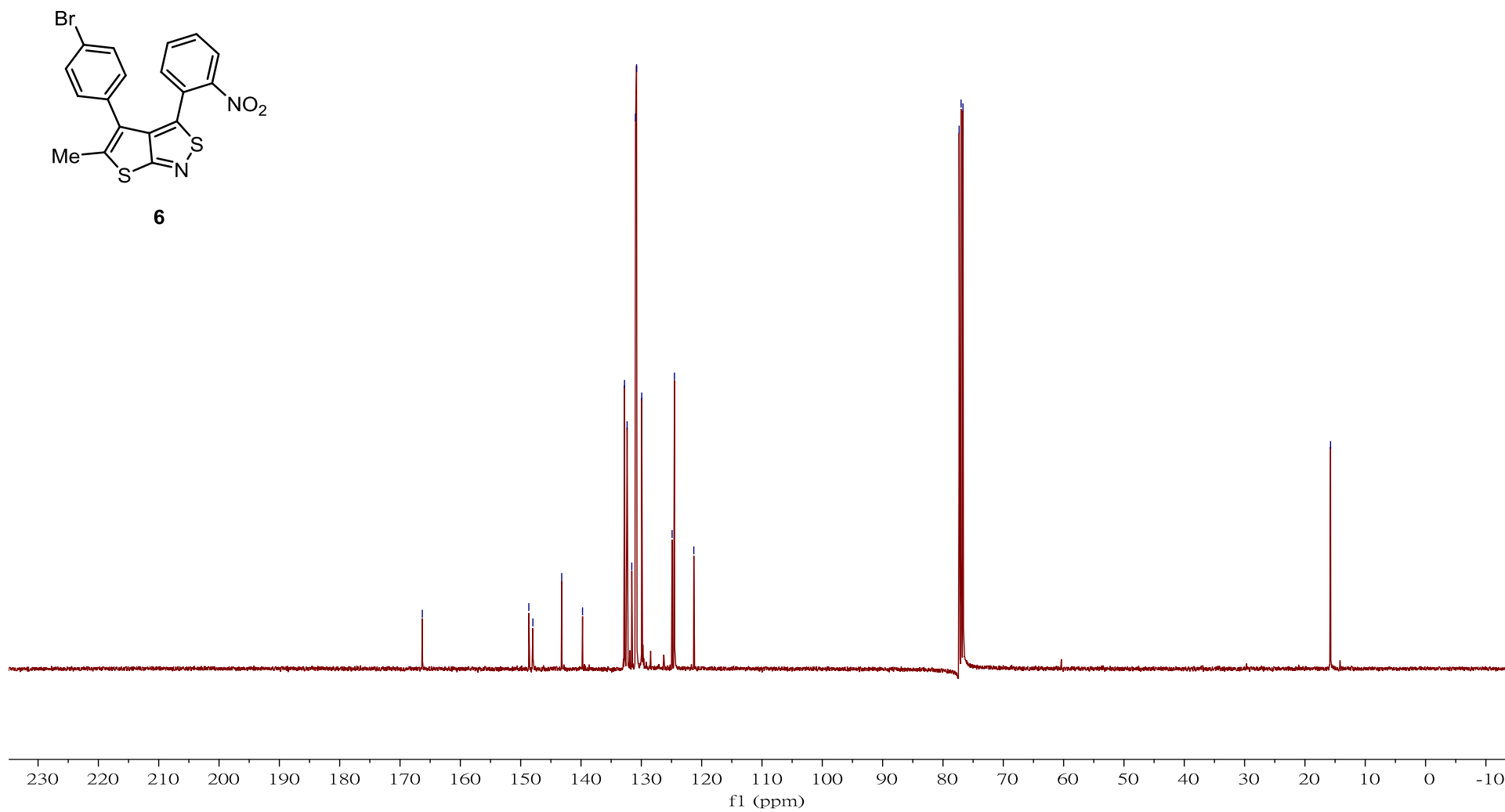
^{13}C NMR (100 MHz) spectrum of compound **5** in CDCl_3

PROTON 1
20170601-0511-124-163



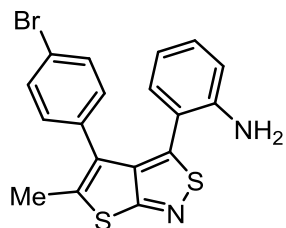
^1H NMR (400 MHz) spectrum of compound **6** in CDCl_3

CARBON_01
20170531-05BP-124-163-13C

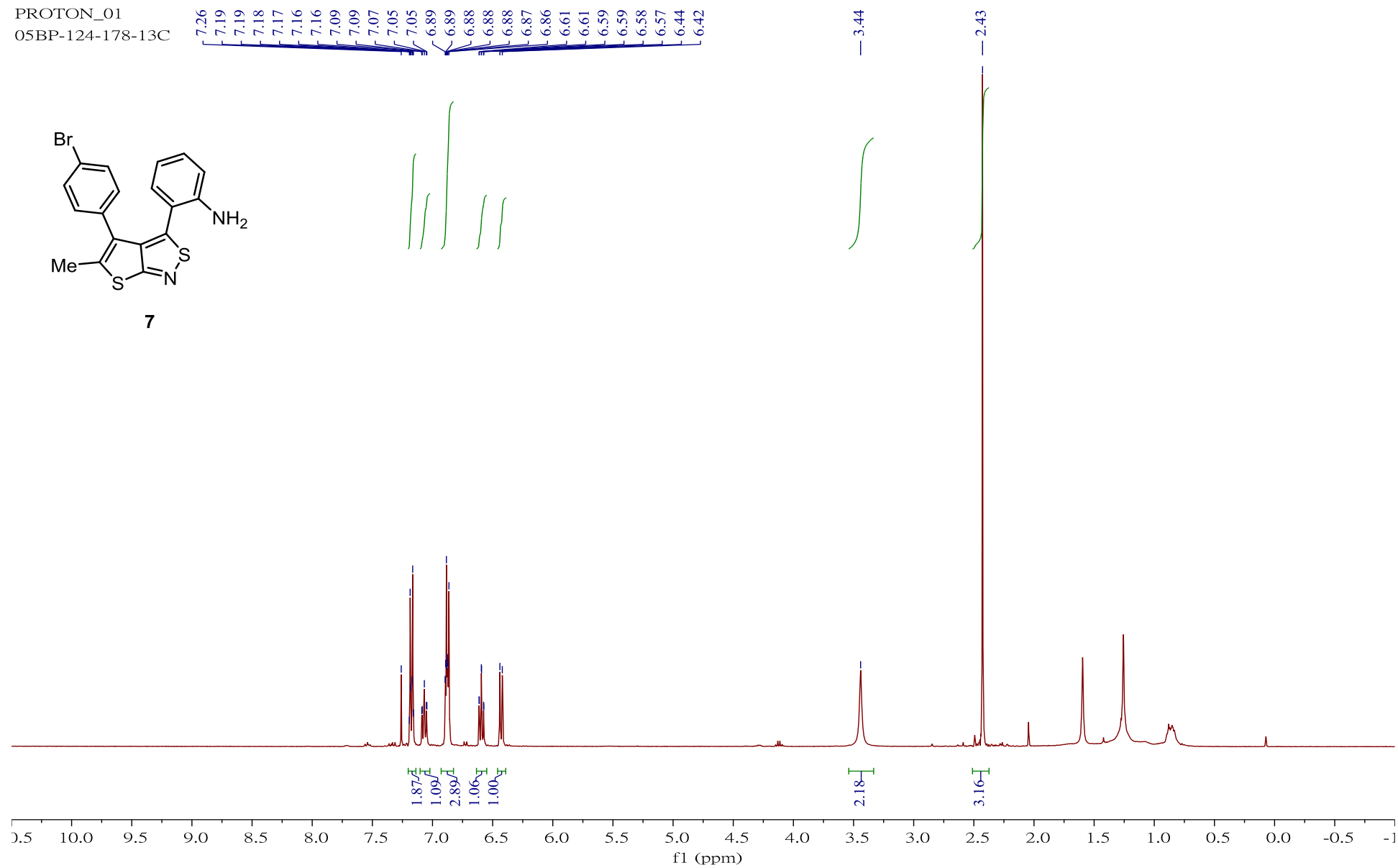


¹³C NMR (100 MHz) spectrum of compound **6** in CDCl₃

PROTON_01
05BP-124-178-13C



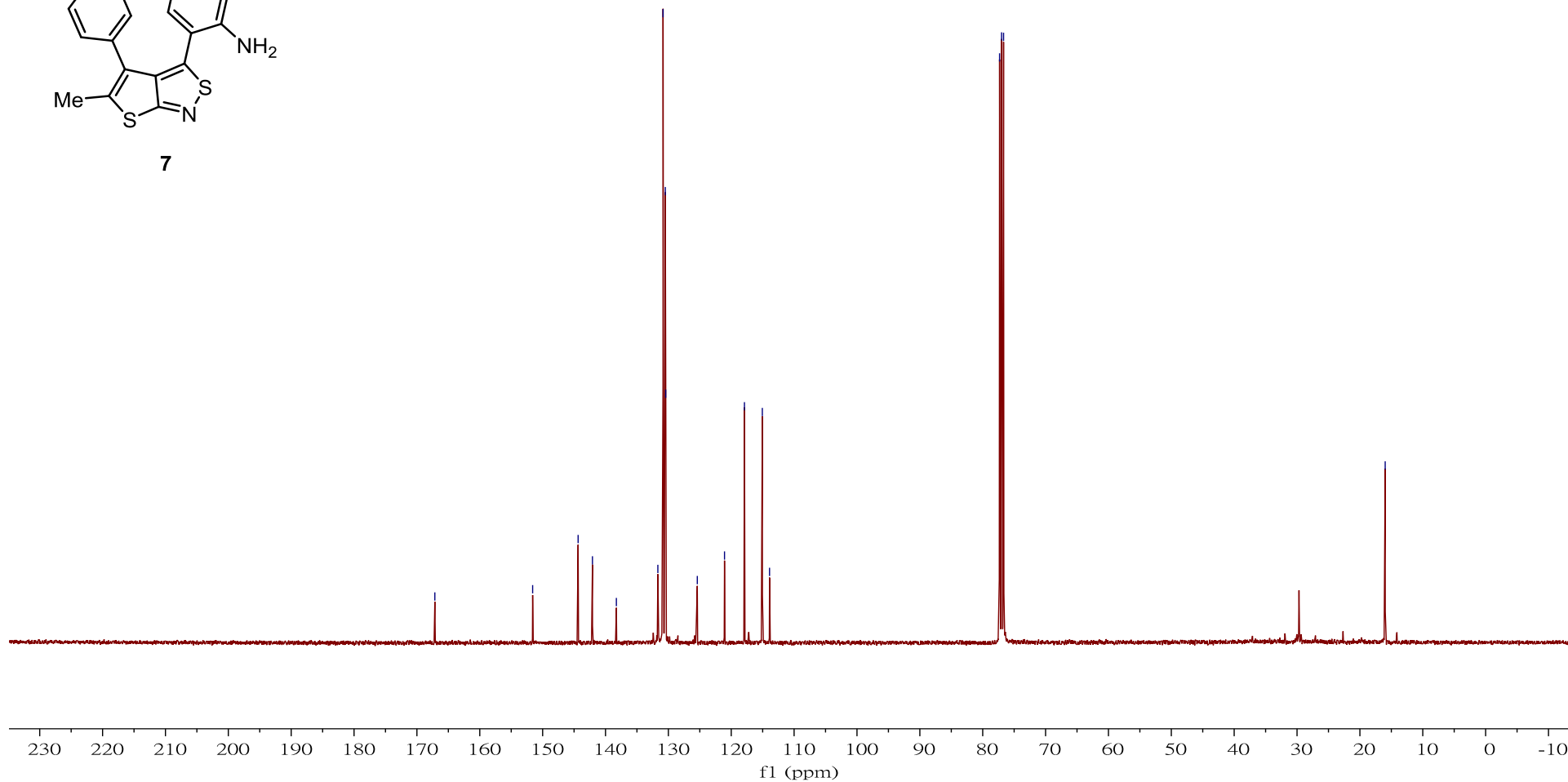
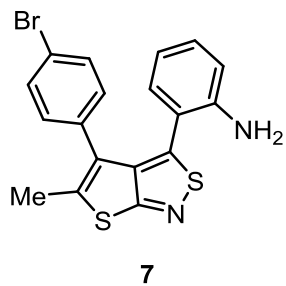
7



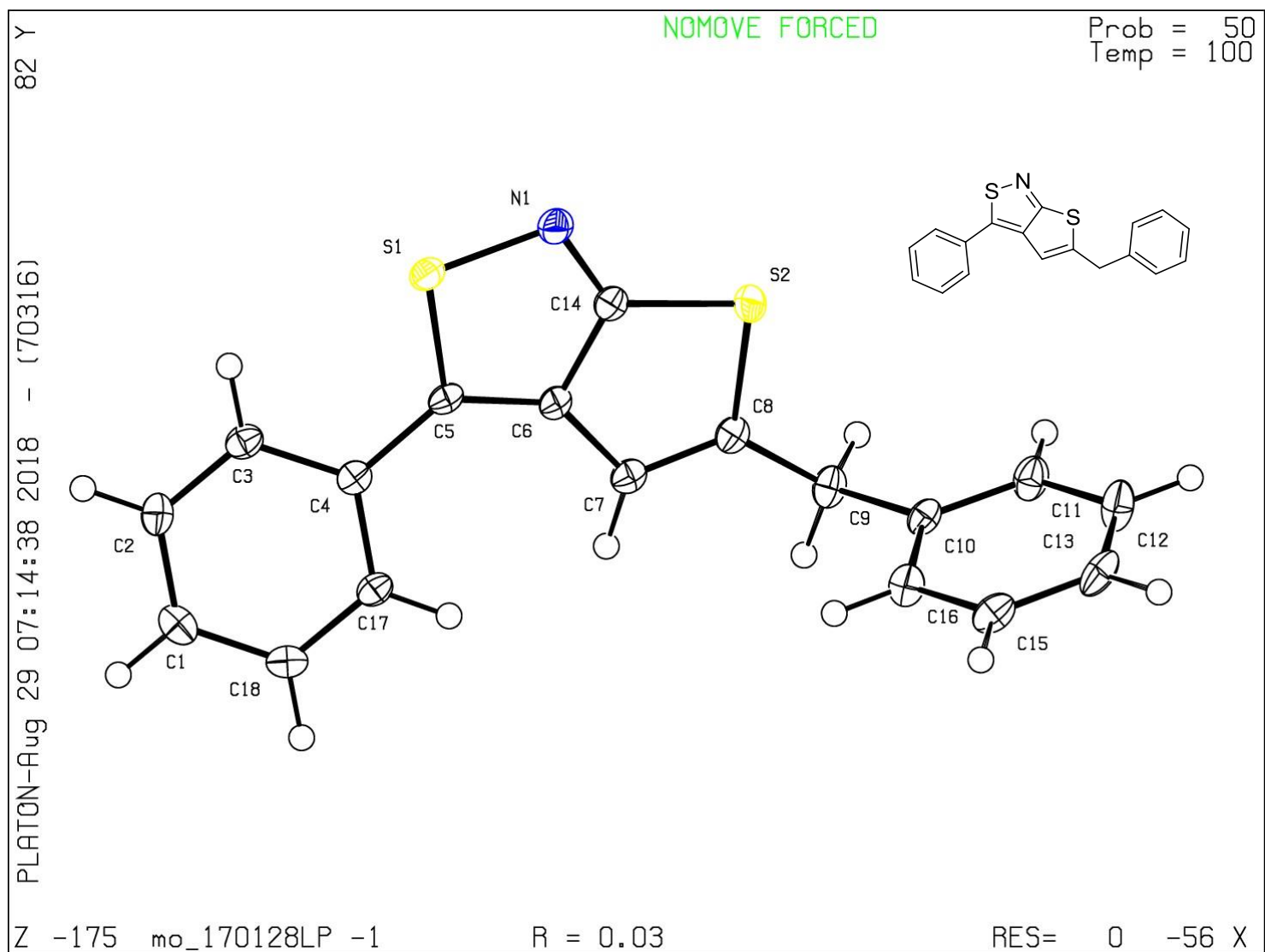
¹H NMR (400 MHz) spectrum of compound 7 in CDCl₃

CARBON_01
05BP-124-178-13C

167.1
151.6
144.4
142.1
138.3
131.7
130.8
130.5
130.4
125.4
121.1
117.9
115.1
113.9
77.3
77.0
76.7
16.0



^{13}C NMR (100 MHz) spectrum of compound **7** in CDCl_3



The ORTEP diagram of **4a** (thermal ellipsoids are shown at 50% probability).

- Sample Preparation: A crystalline solid was obtained via slow evaporation of compound **4a** in CH₂Cl₂: hexane= 1: 4 at room temperature.
- Crystal data and structure refinement for compound **4a** (CCDC: 1532241)

Bond precision: C-C = 0.0021 Å Wavelength=0.71073

Cell: a=8.4886(9) b=8.9588(10) c=10.1158(11)
 alpha=86.119(3) beta=83.374(2) gamma=71.079(3)
 Temperature: 100 K

	Calculated	Reported Volume
	722.48(14)	722.48(14)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C18 H13 N S2	?
Sum formula	C18 H13 N S2	C18 H13 N S2
Mr	307.41	307.41
Dx, g cm ⁻³	1.413	1.413
Z	2	2
Mu (mm ⁻¹)	0.360	0.360
F000	320.0	320.0
F000'	320.59	
h,k,lmax	10,11,12	10,11,12
Nref	2997	2971
Tmin,Tmax	0.907,0.924	0.845,0.948
Tmin'	0.907	

Correction method= # Reported T Limits: Tmin=0.845 Tmax=0.948
 AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 26.475

R(reflections)= 0.0316(2539) wR2(reflections)= 0.0871(2971)

S = 1.053 Npar= 190
