SUPPORTING INFORMATION

A Core Switching Strategy to Pyrrolo[2,3-*b*]quinolines and Diazocino[1,2-*a*]indolinones

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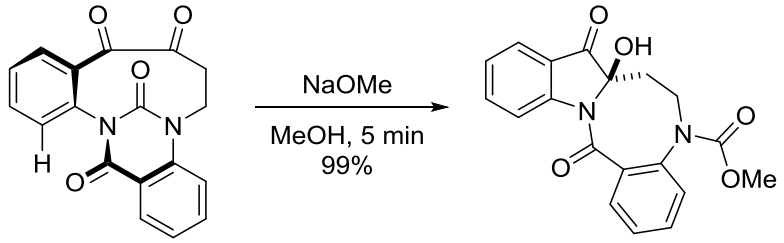
Scheme S1 Chiral memory experiment with enantio-enriched *M*-atropisomer of **1a**[S1] with NaOMe lead to **±2a**



***M*-1a** (91% *ee*)[S1] **2a** (0% ee)

Table S1 Nucleophile screen of the scope of the transformation of **1a** to examples of **2**

Nucleophile	Expected m/z			Observed *m/z*
	$[M+H]^+$	$[M+Na]^+$	$[M-H]^-$	
sodium methoxide	353.3	375.3	351.3	351.3[a]
n-butylamine	394.4	416.4	392.4	392.4[a]
1,4-diaminobutane	409.4	431.4	407.4	407.4[a]
acetylethylenediamine	423.4	445.4	421.4	421.4[a]
Benzylamine	428.4	450.4	426.4	426.4[a]
Aniline[d]	414.4	436.4	412.4	394.0[*,d]
morpholine	408.4	430.4	406.4	406.4[a]
(1*S*,2*S*)-2-benzyloxycyclopentylamine[d]	512.6	534.6	510.6	492.0[*,d]
N-methylhydrazine	367.4	389.4	365.4	365.4[a]
benzyl carbazate	487.5	509.5	485.5	485.5[a]
sodium azide	364.3	386.3	362.3	362.3[a]
glycine *t*-butyl ester. HCl[d]	452.5	474.5	450.5	466.0[*,d]
propan-2-ol[c]	381.4	403.4	379.4	319.0[c]
propargyl alcohol[c]	377.4	399.4	375.4	319.0[c]
methyllithium.LiBr complex	337.3	359.3	335.3	335.3[a]
allyl magnesium bromide	363.4	385.4	361.4	361.4[a]
ethynyl magnesium chloride	347.3	369.3	345.3	345.3[a]
methyl magnesium bromide	337.3	359.3	335.3	335.3[a]
trimethylsilyl cyanide[c]	348.3	370.3	346.3	319.0[c]
triphenylmethanethiol	597.7	619.7	595.7	595.7[a]
Ethylthioglycolate[d]	427.4	449.4	425.4	439.0[*,d]
Benzylmercaptan	445.5	467.5	443.5	445.5[b]

Details: Using a Radleys® Greenhouse parallel synthesiser, to 18 stirred solutions of **1a** (20 mg) in dry THF (5mL) were added 1.1 equivalents of the relevant nucleophile at room temperature for 16 hours. In a separate study, the four reactions using Grignard reactions were carried out at -78 °C and then allowed to warm to 0 °C after 3 hours. LCMS analysis (ES^+/ES^-) of the crude reaction mixtures revealed that 14 / 22 reaction mixtures contained a new product with a *m/z* from either the ES^- ([a] in table) or ES^+ ([b] in table) spectra coupled with the UV_{254nm} trace;

c no reaction was observed and observed m/z consistent with the presence of starting material **1a**; [d] structure of product not determined.

Table S2 Optimisation of the sodium methoxide-induced rearrangement of **1a** to **2a**

Entry	NaOMe (eq.)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	1	MeOH	25	10	95
2	2	MeOH	25	10	99
3	10	MeOH	25	10	95
4	2	THF	25	960	45

Details: Variation of reaction conditions and the resulting isolated yields for the methoxide induced azepinoindole rearrangement of **1a** to give **2a**.

Table S3 Optimisation of the butylamine-induced rearrangement of **1a** to **2i**

entry	eq. *n*BuNH$_2$	time (min)	percentage conversion
1	1	10	40
2	1	60	80
3	1	180	95 (74[a])
4	1	960	[b]
5	2	180	70 (51[a])
6	4	180	[b]
7	10	180	[b]

Details: Percentage conversion as estimated by ^{1}H NMR spectra of the transformation of **1a** to **2i**. [a]Isolated yield (after flash column chromatography); [b]Substantial degradation was observed.

Table S4 ^{1}H and ^{13}C NMR based assignment of **4** (Derived from 2D ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC NMR experiments).

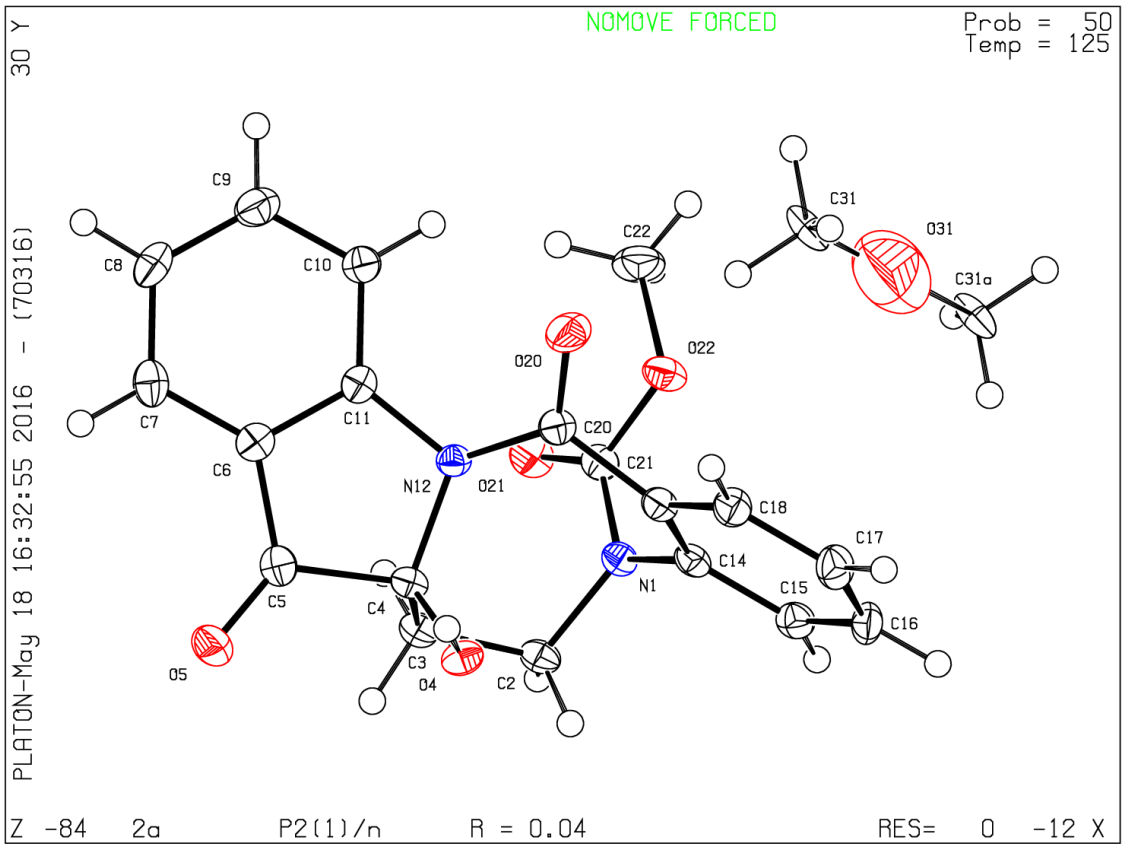
Proton Assignment	δ ^{1}H (ppm)	Multiplicity	Integration	*J* value (Hz)	Carbon Assignment	δ ^{13}C (ppm)
C2-$\underline{H}_2$	4.19	t	2H	7.5	C2	49.8
C3-$\underline{H}_2$	3.36	t	2H	7.4	C3	25.3
					C3a	119.6
C4-O$\underline{H}$	8.55	br s	1H	-	C4	153.1
					C5	178.3
					C5a	126.5
C6-$\underline{H}$	8.42	d	1H	2.6	C6	129.1
					C7	129.6
C8-$\underline{H}$	7.41	dd	1H	8.9, 2.6	C8	134.8
C9-$\underline{H}$	7.28	d	1H	8.8	C9	134.7
					C9a	148.6
					C10a	157.8
					C1’	139.1
					C2’	129.6
C3’-$\underline{H}$	7.90	dd	1H	7.7, 1.5	C3’	130.5
C4’-$\underline{H}$	7.37	dd	1H	7.6, 1.2	C4’	126.5
C5’-$\underline{H}$	7.58	ddd	1H	7.7, 7.7, 1.7	C5’	132.5
C6’-$\underline{H}$	7.32	dd	1H	8.0, 1.0	C6’	125.4
					Ar$\underline{C}O_2Et$	167.0
O$\underline{CH}_2CH_3$	3.96	q	2H	7.2	O$\underline{C}H_2CH_3$	61.1
$OCH_2\underline{CH}_3$	1.06	q	3H	7.2	$OCH_2\underline{C}H_3$	14.1

Table S5 Optimisation of the sodium alkoxide-induced rearrangement of **1e** to **3a**

Entry	NaOMe (eq.)	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	2	MeOH	25	16	77
2	2	MeOH	64	16	59
3	10	MeOH	25	16	71

Details: Variation of the reaction conditions for the alkoxide induced pyrrolo[2,3-*b*]quinoline rearrangement **3a** from **1e** and the resulting isolated yields.

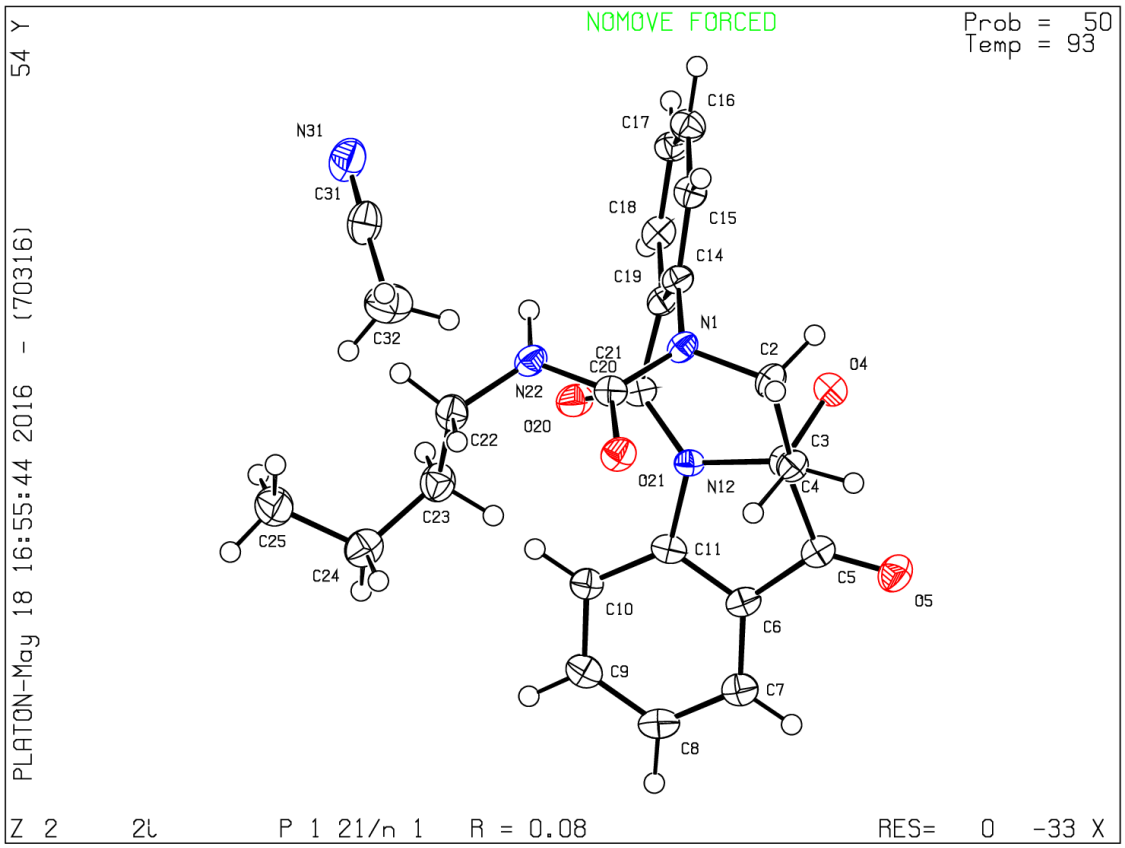
Table S6 Crystal data and structure refinement details for compound **2a**.



Empirical formula	C19.50 H18 N2 O5.50	
Formula weight	368.36	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.7594(12) Å	α= 90°.
	b = 19.459(3) Å	β= 106.142(2)°.
	c = 11.8044(19) Å	γ = 90°.
Volume	1712.1(5) $Å^3$	
Z	4	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	

F(000)	772
Crystal size	.1 x .1 x .01 mm^3
Theta range for data collection	2.08 to 25.49°.
Index ranges	-9<=h<=9, -23<=k<=16, -12<=l<=14
Reflections collected	9839
Independent reflections	3068 [R(int) = 0.0244]
Completeness to theta = 25.49°	96.2 %
Absorption correction	MULTISCAN
Max. and min. transmission	1.00000 and 0.891243
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3068 / 1 / 257
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0971
R indices (all data)	R1 = 0.0552, wR2 = 0.1051
Extinction coefficient	0.0039(9)
Largest diff. peak and hole	0.455 and -0.445 e.$Å^{-3}$

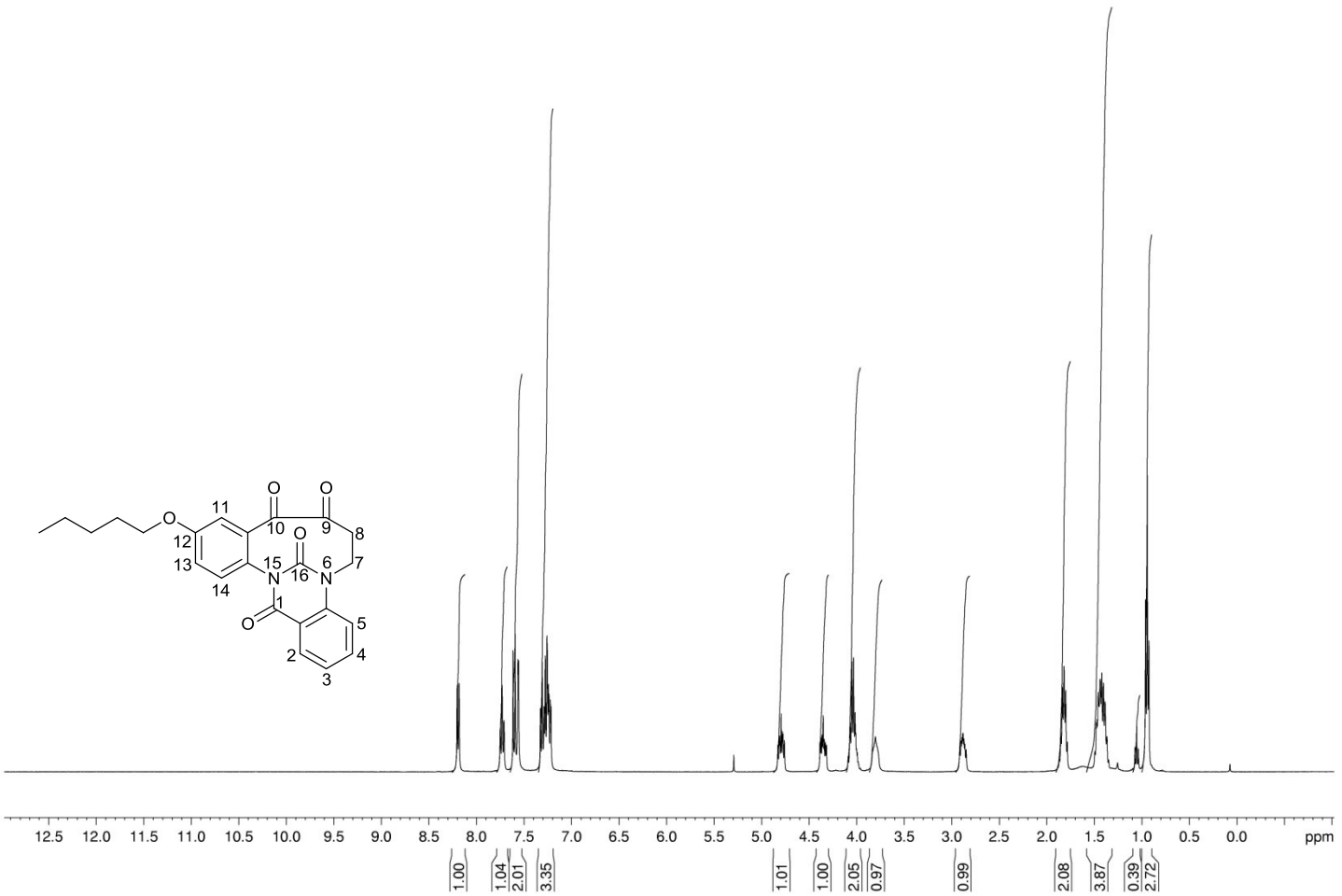
Table S7 Crystal data and structure refinement details for compound **2i**.



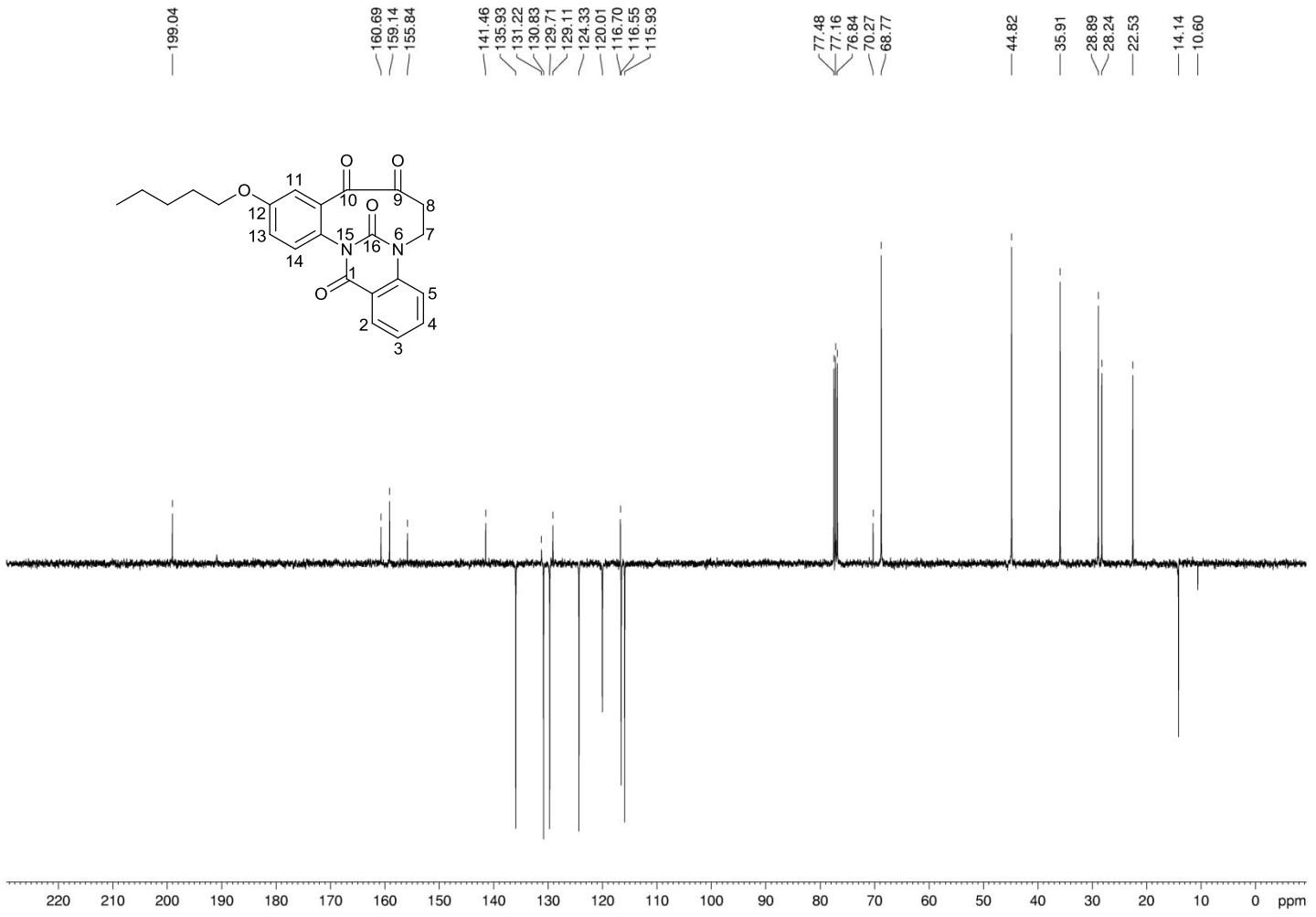
Empirical formula	C24 H26 N4 O4	
Formula weight	434.49	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.8627(13) Å	□= 90°.
	b = 19.295(2) Å	□= 111.323(6)°.
	c = 11.3504(14) Å	□ = 90°.
Volume	2216.1(5) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	

F(000)	920
Crystal size	0.200 x 0.010 x 0.010 mm^3
Theta range for data collection	2.11 to 25.34°.
Index ranges	-13<=h<=12, -16<=k<=23, -12<=l<=13
Reflections collected	15426
Independent reflections	3727 [R(int) = 0.0552]
Completeness to theta = 25.34°	92.0 %
Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.8690
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3727 / 2 / 300
Goodness-of-fit on F^2	1.192
Final R indices [I>2sigma(I)]	R1 = 0.0654, wR2 = 0.1112
R indices (all data)	R1 = 0.0893, wR2 = 0.1211
Extinction coefficient	0.0060(8)
Largest diff. peak and hole	0.234 and -0.224 e.$Å^{-3}$

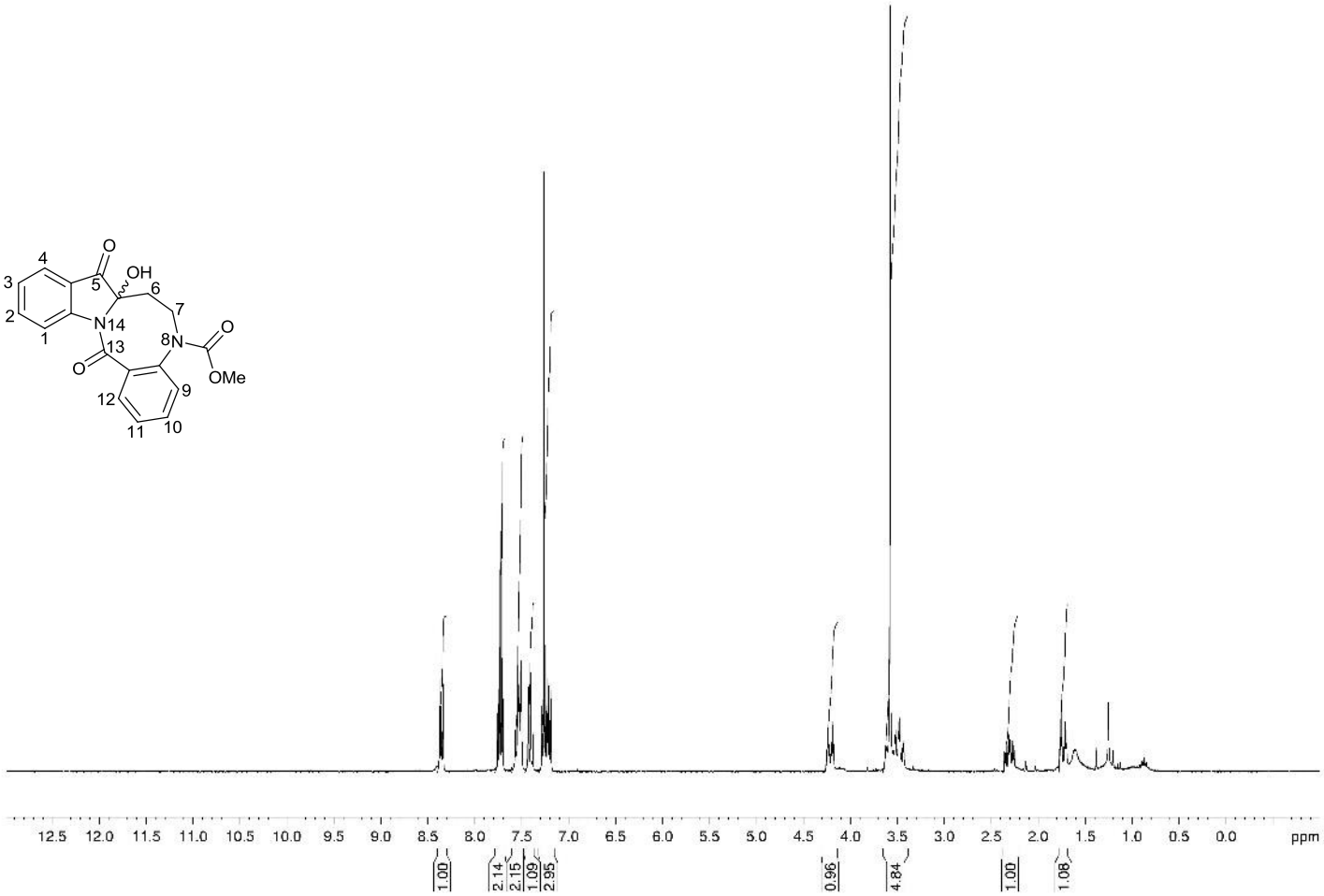
Copies of ^{1}H and ^{13}C NMR spectra: **Compound 1b ^{1}H NMR ($CDCl_3$)**



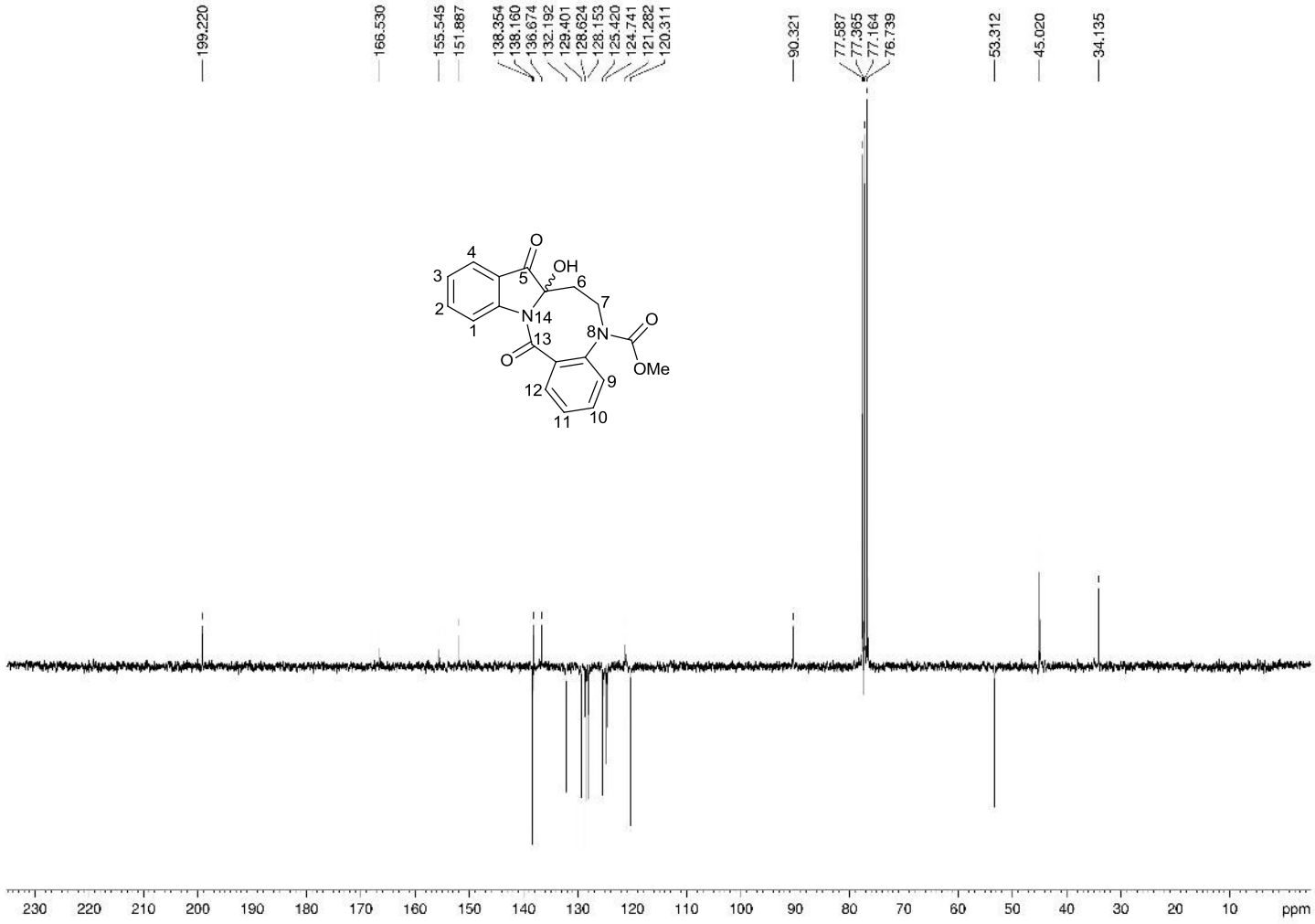
Compound 1b ^{13}C NMR ($CDCl_3$)



Compound 2a ^{1}H NMR ($CDCl_3$)



Compound 2a ^{13}C NMR ($CDCl_3$)



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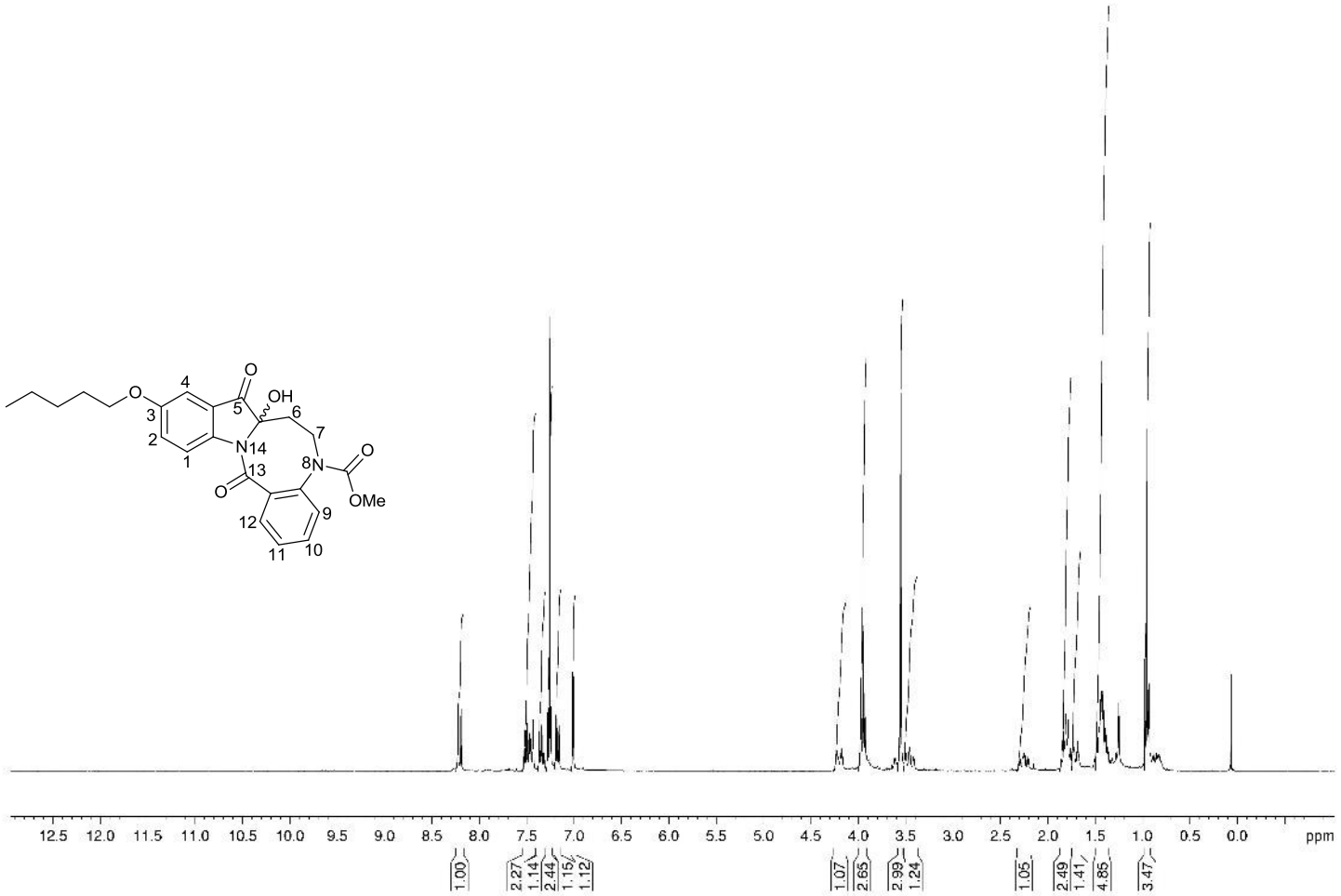

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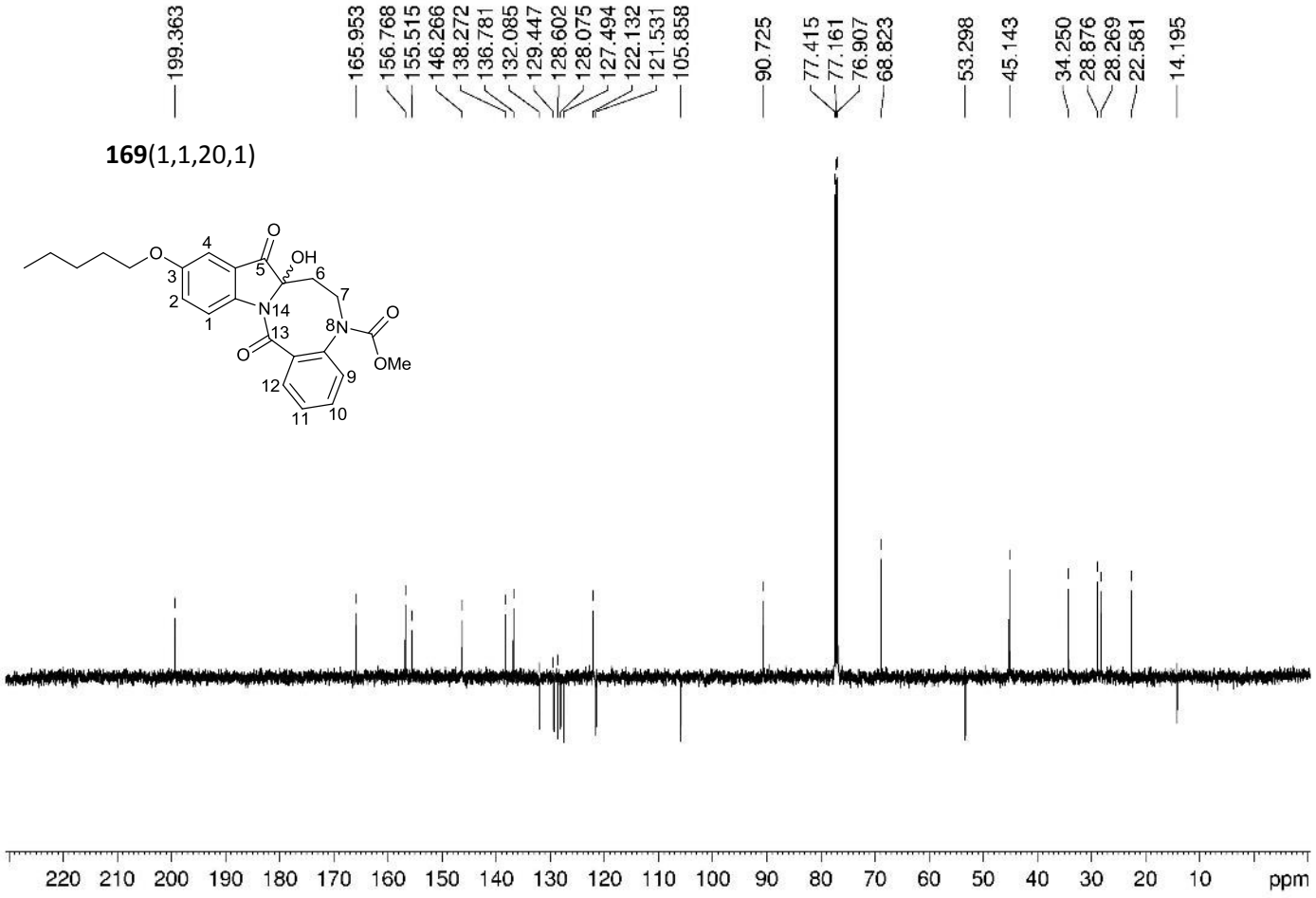
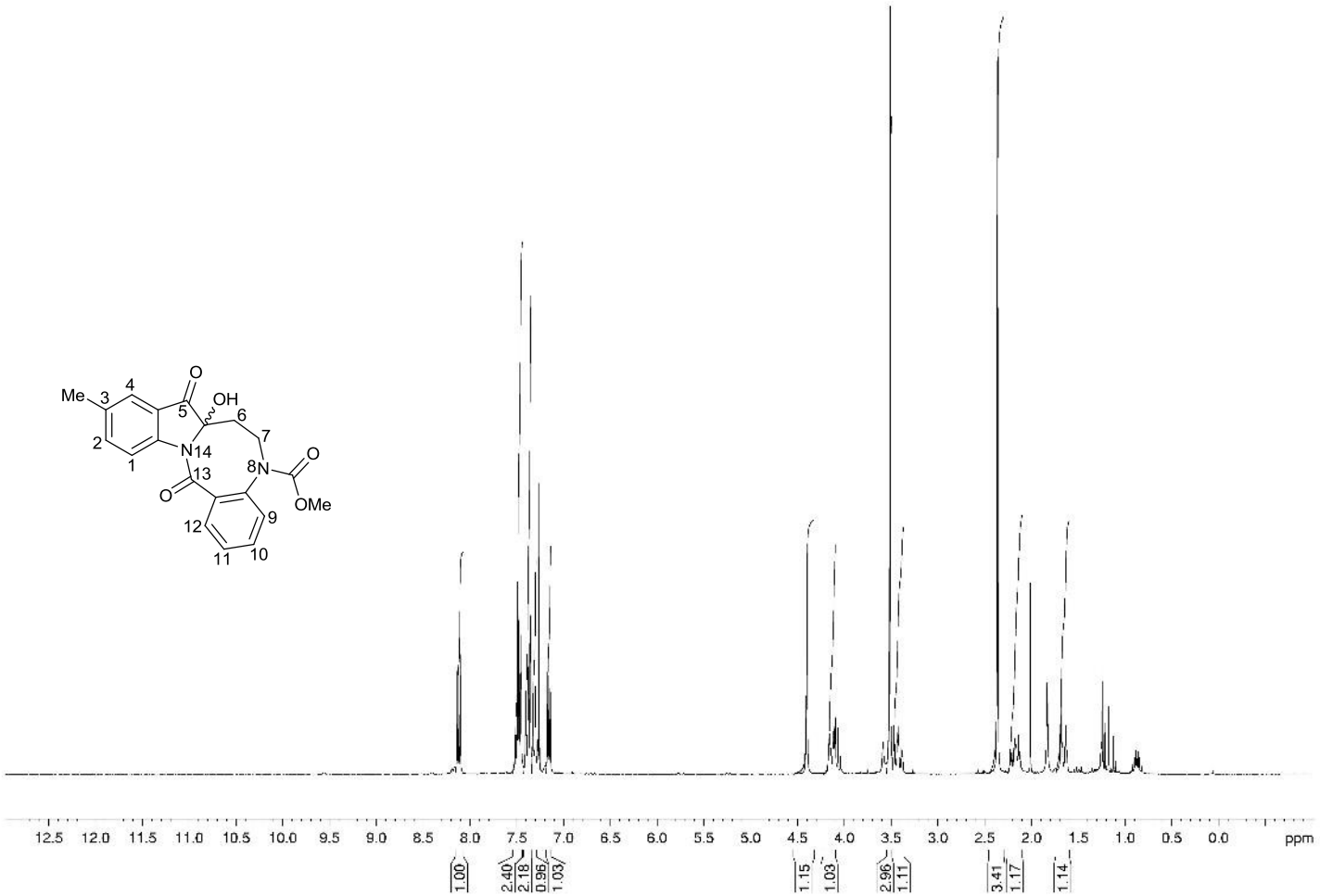


Compound 2c ^{1}H NMR ($CDCl_3$)



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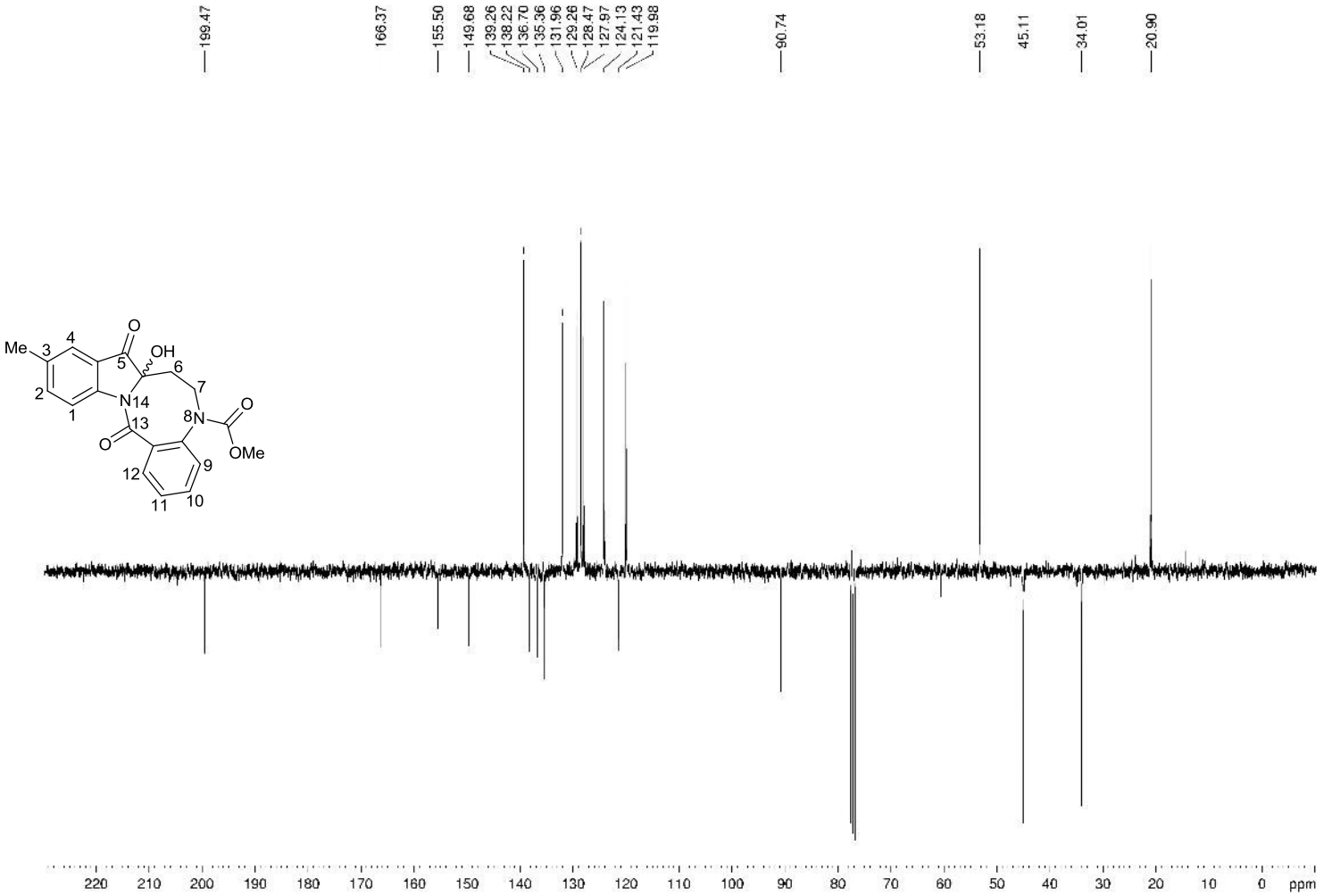

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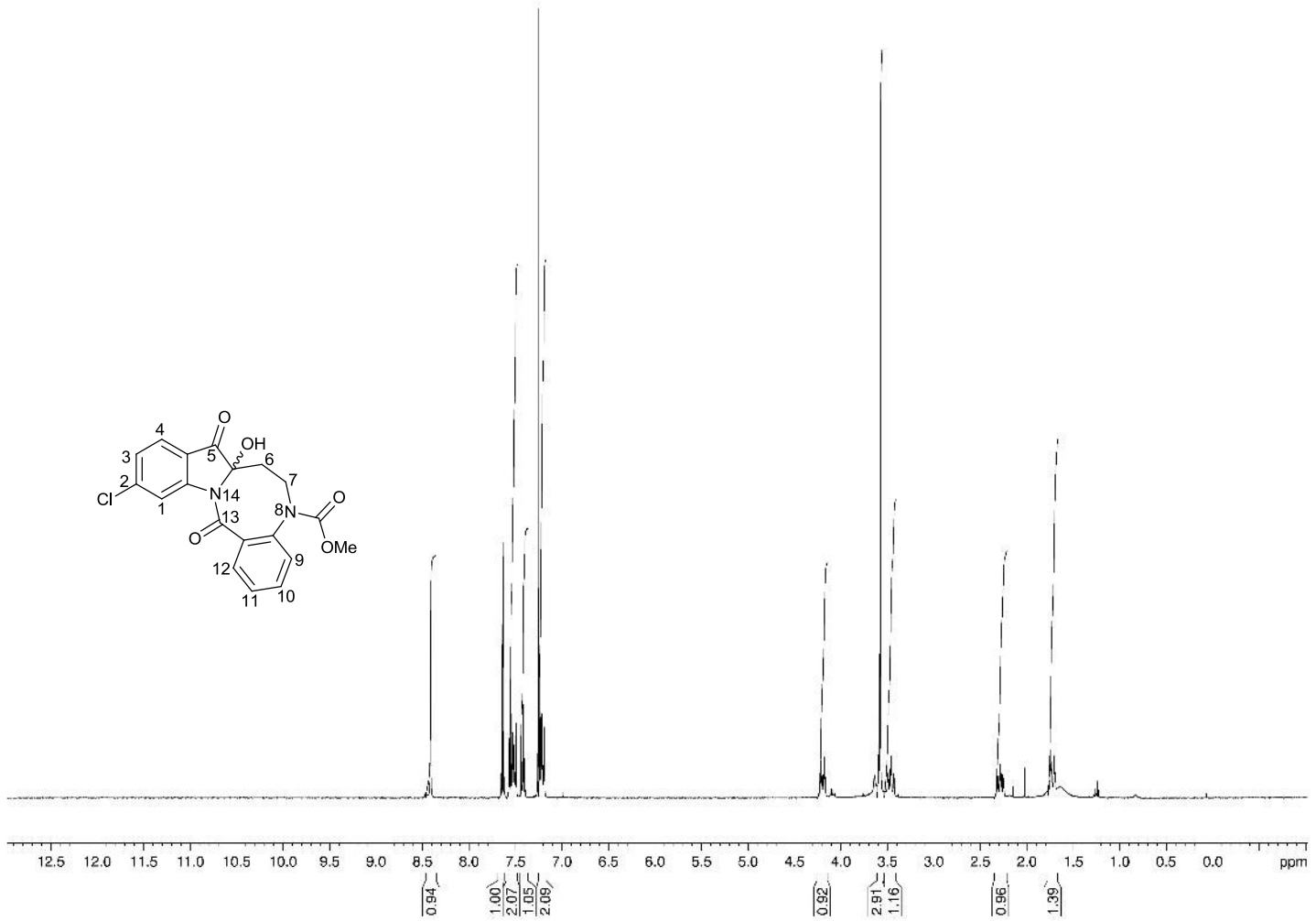

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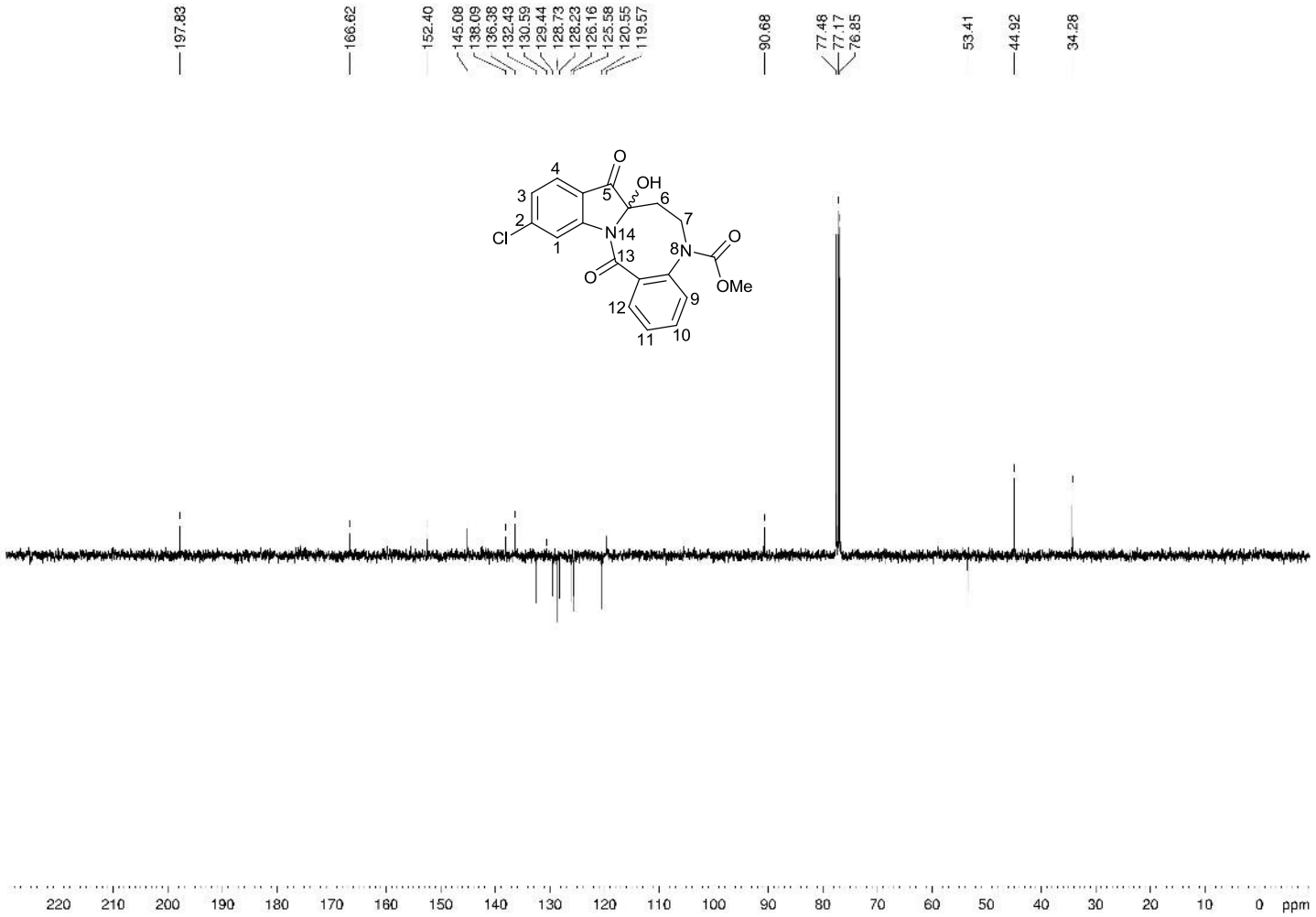

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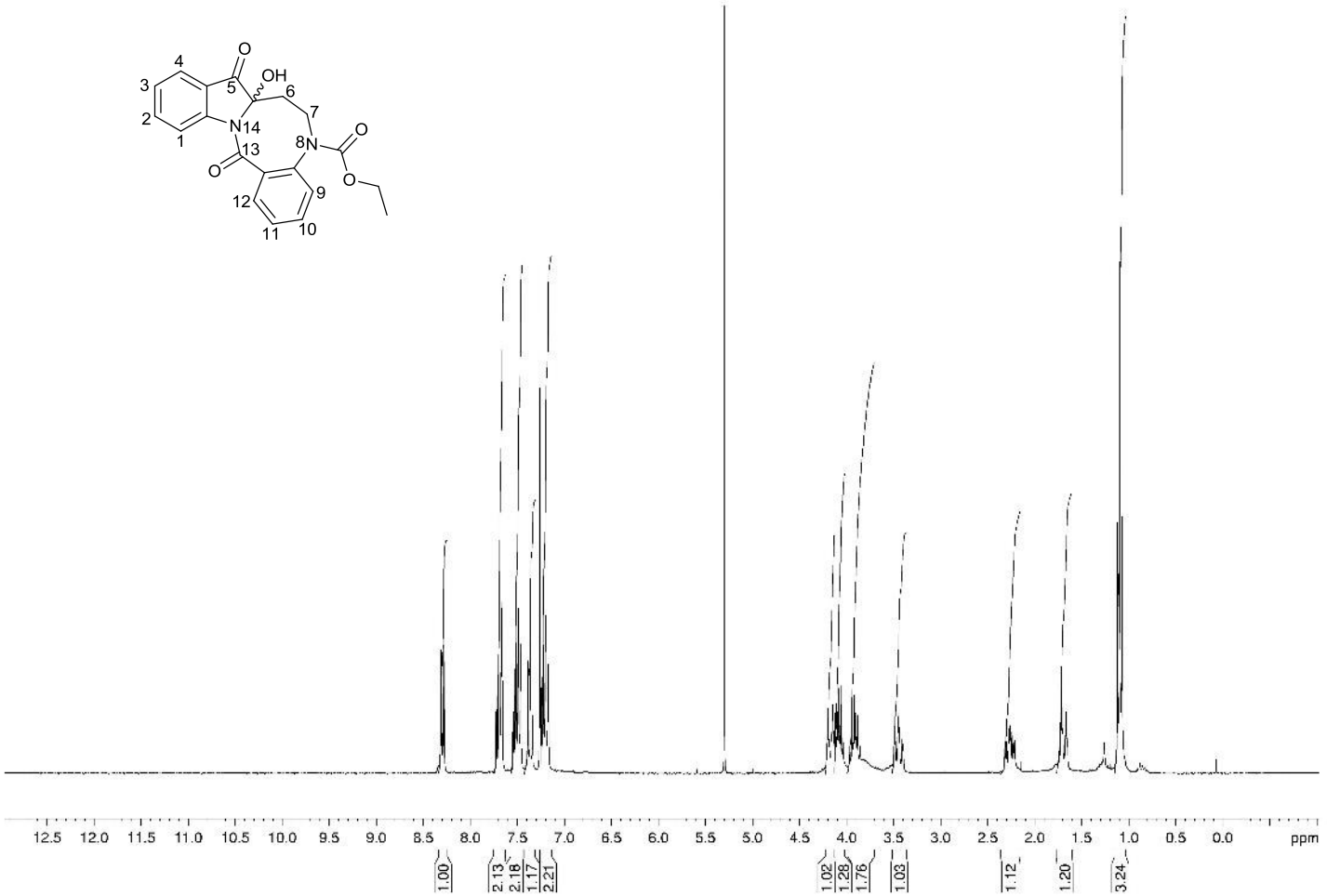

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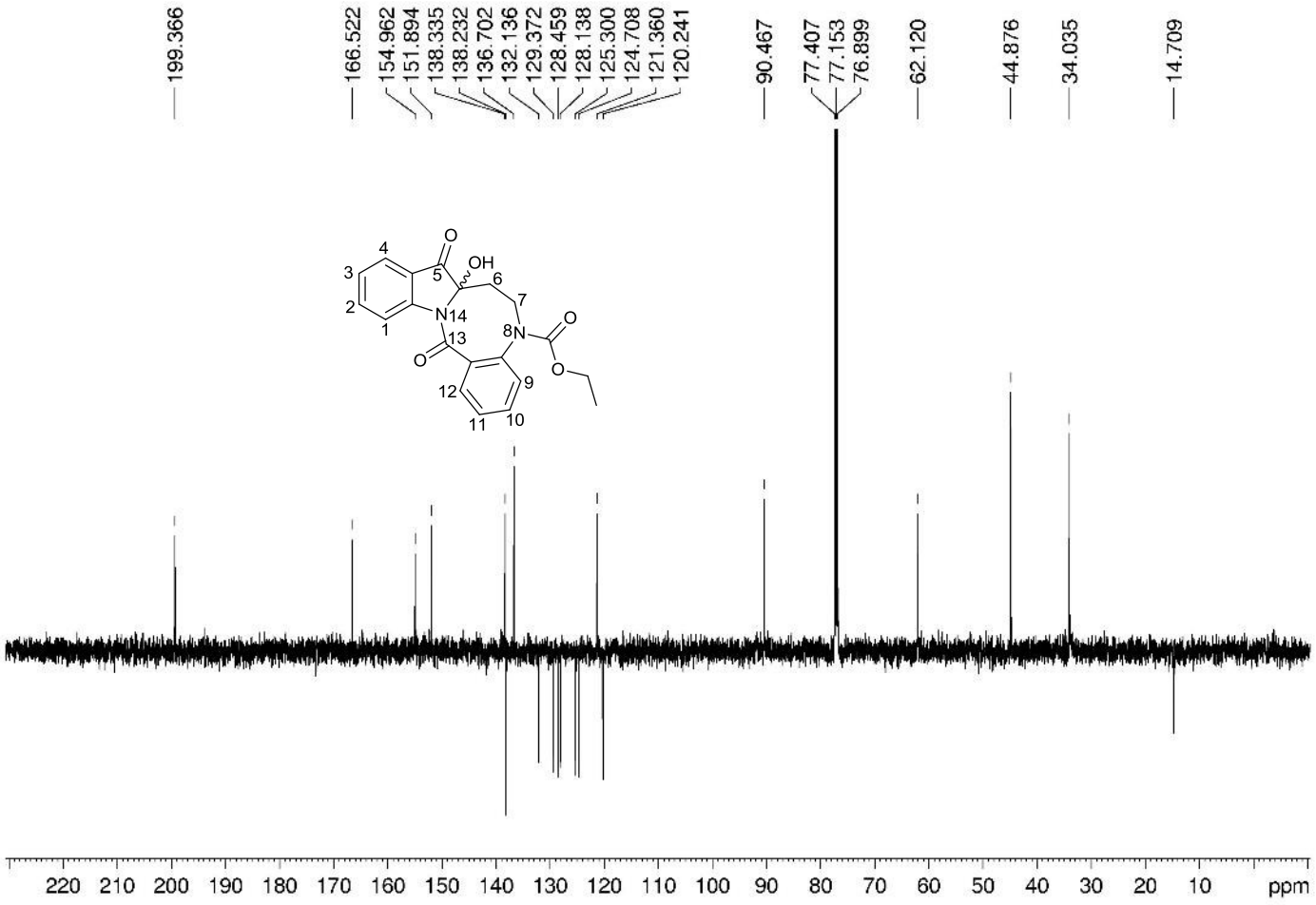

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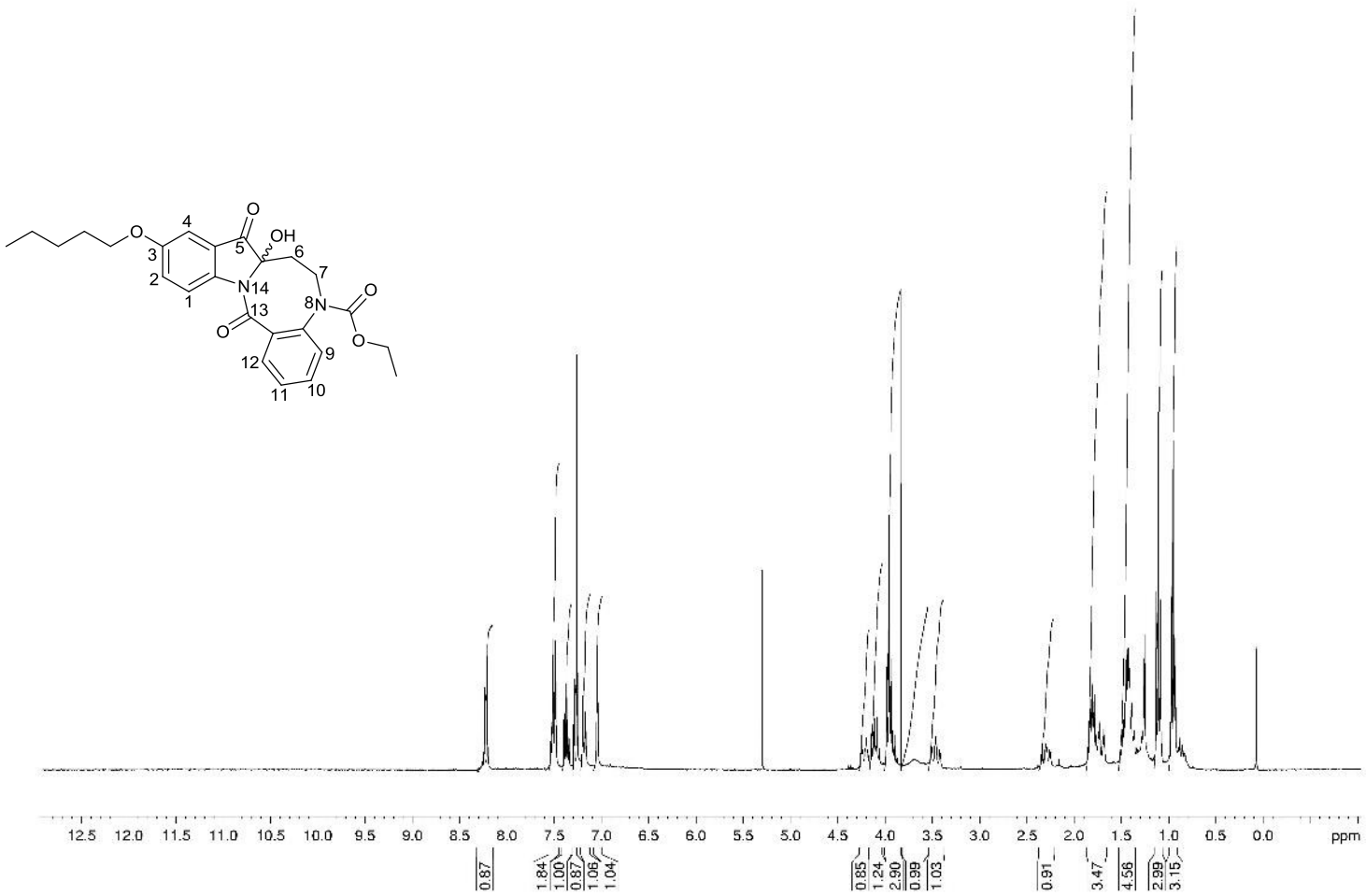

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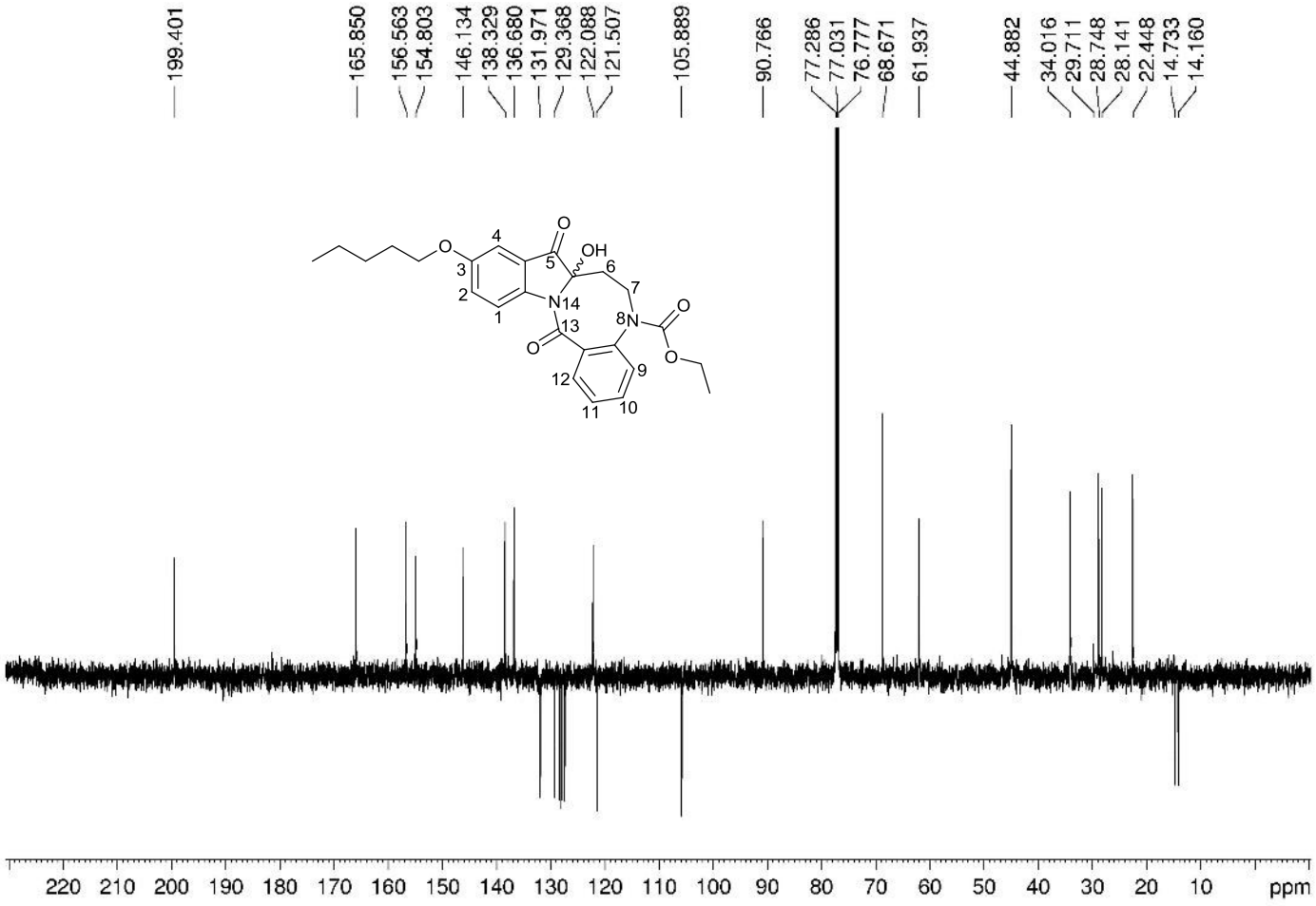
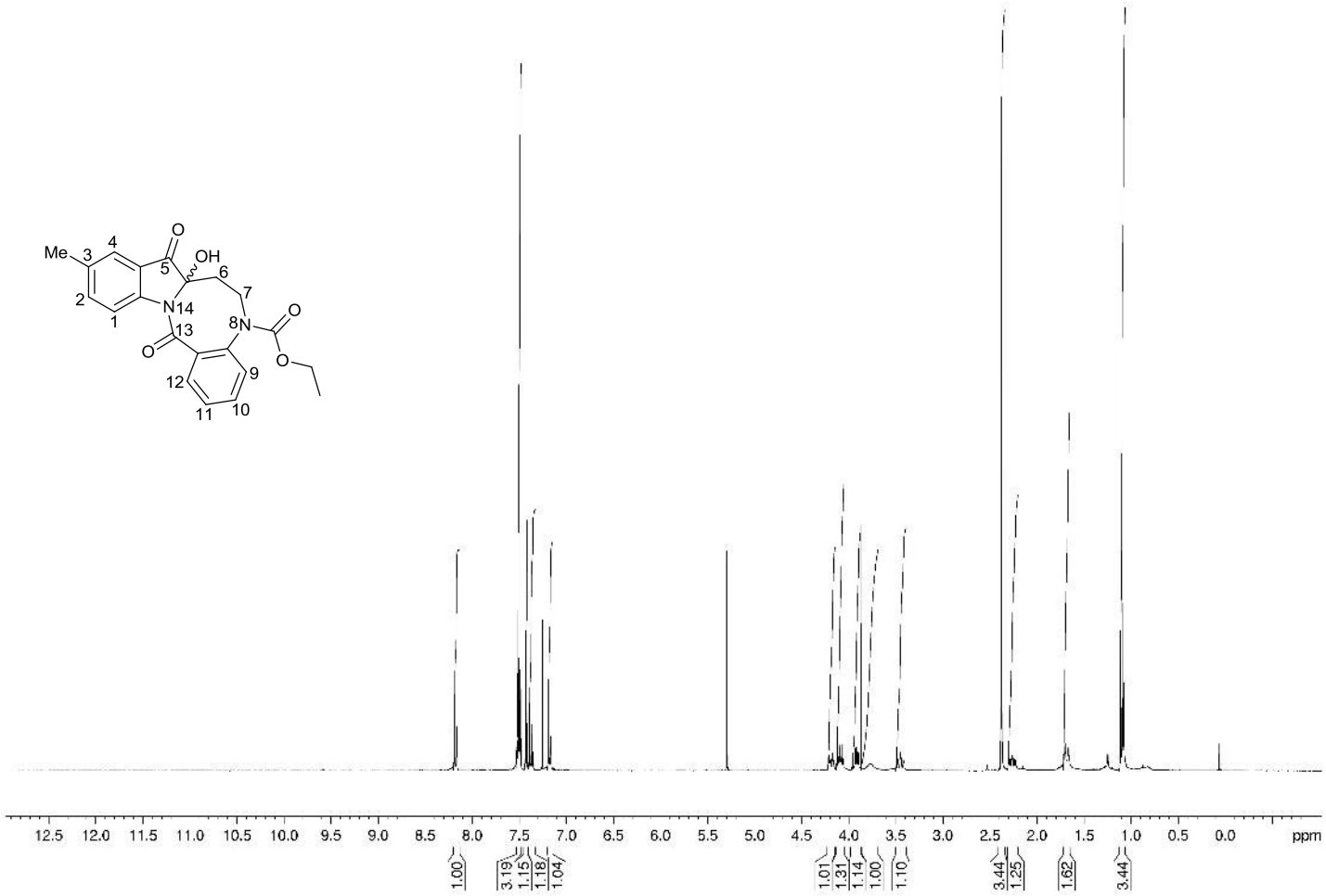


Compound 2g ^{1}H NMR ($CDCl_3$)



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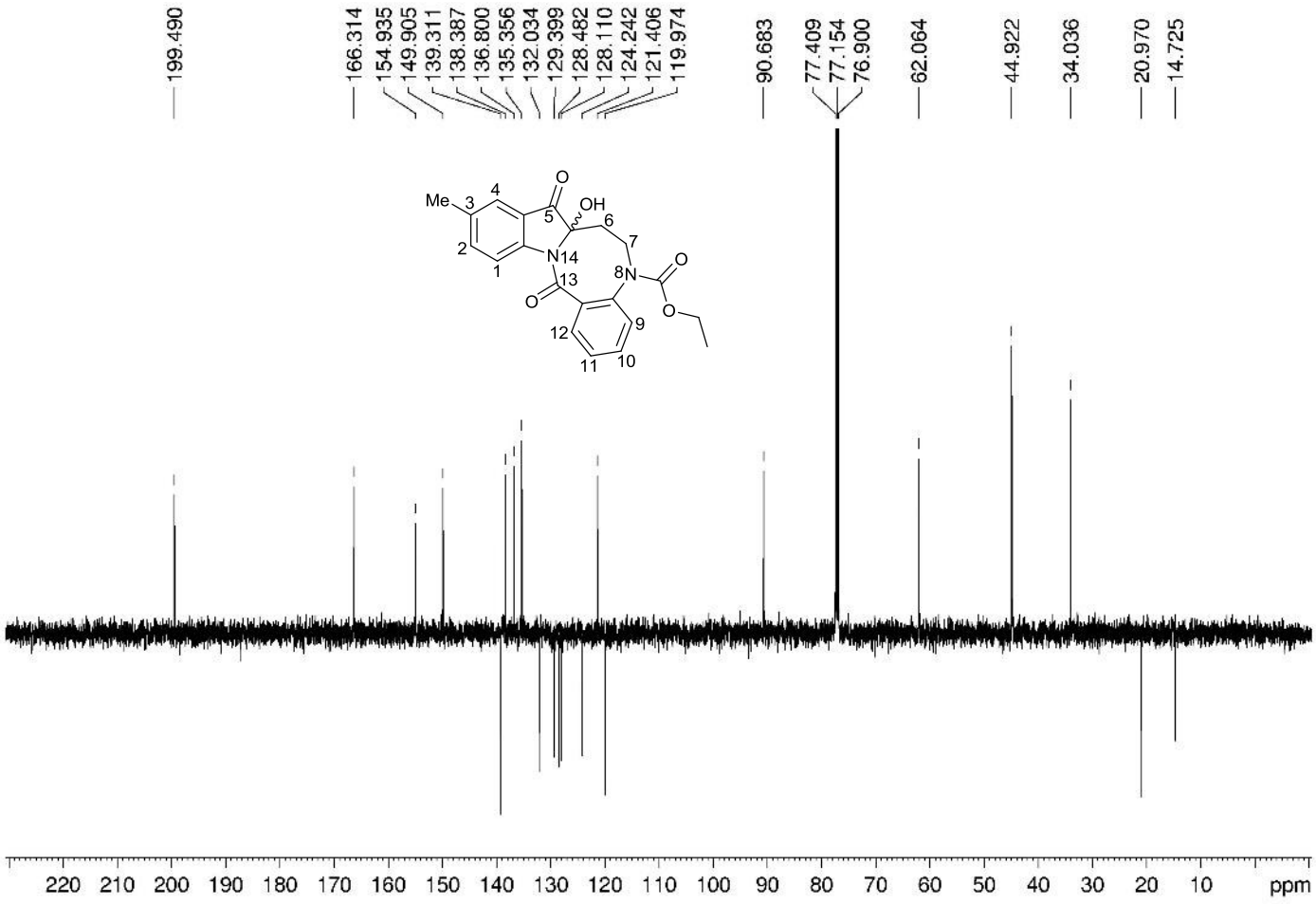

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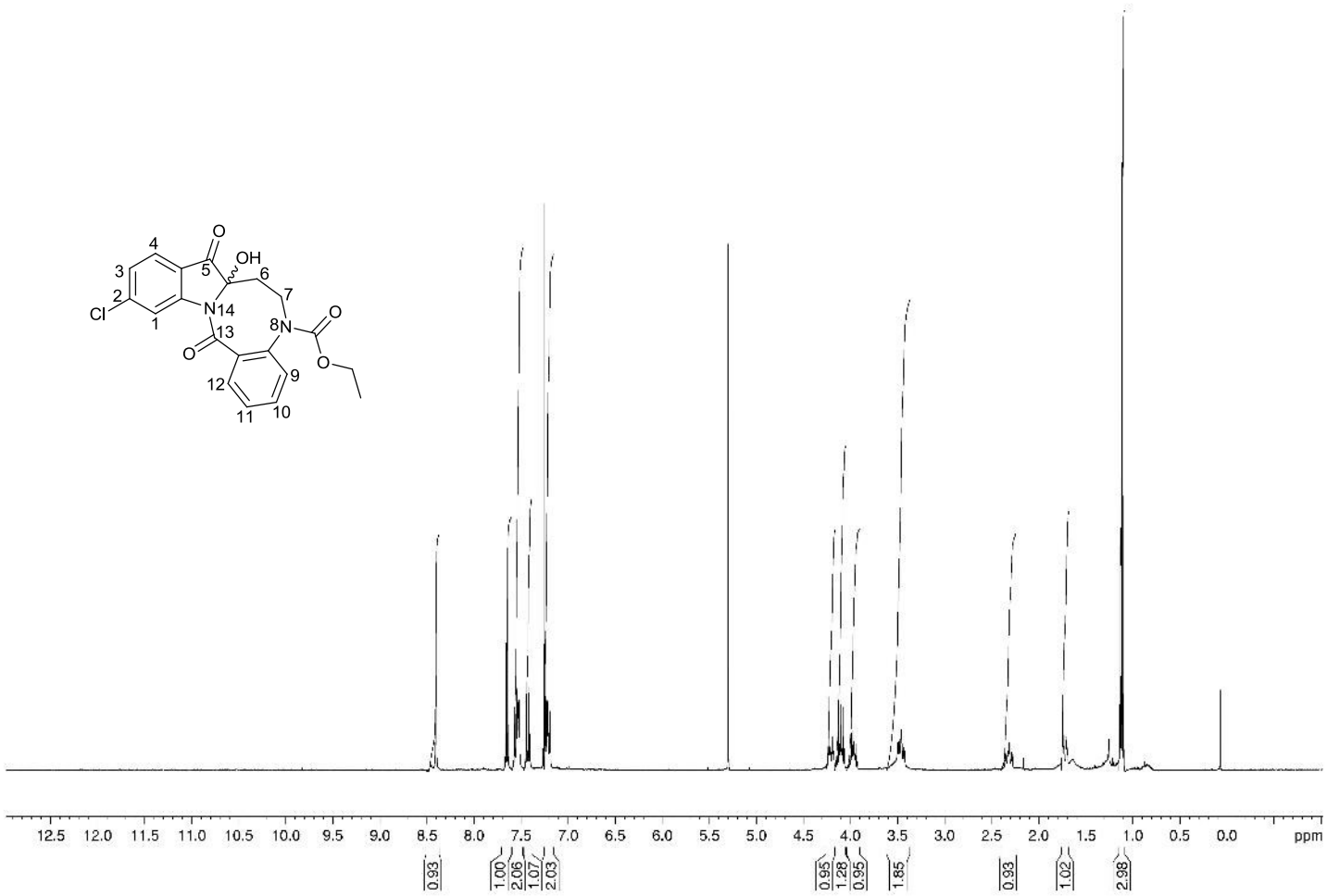

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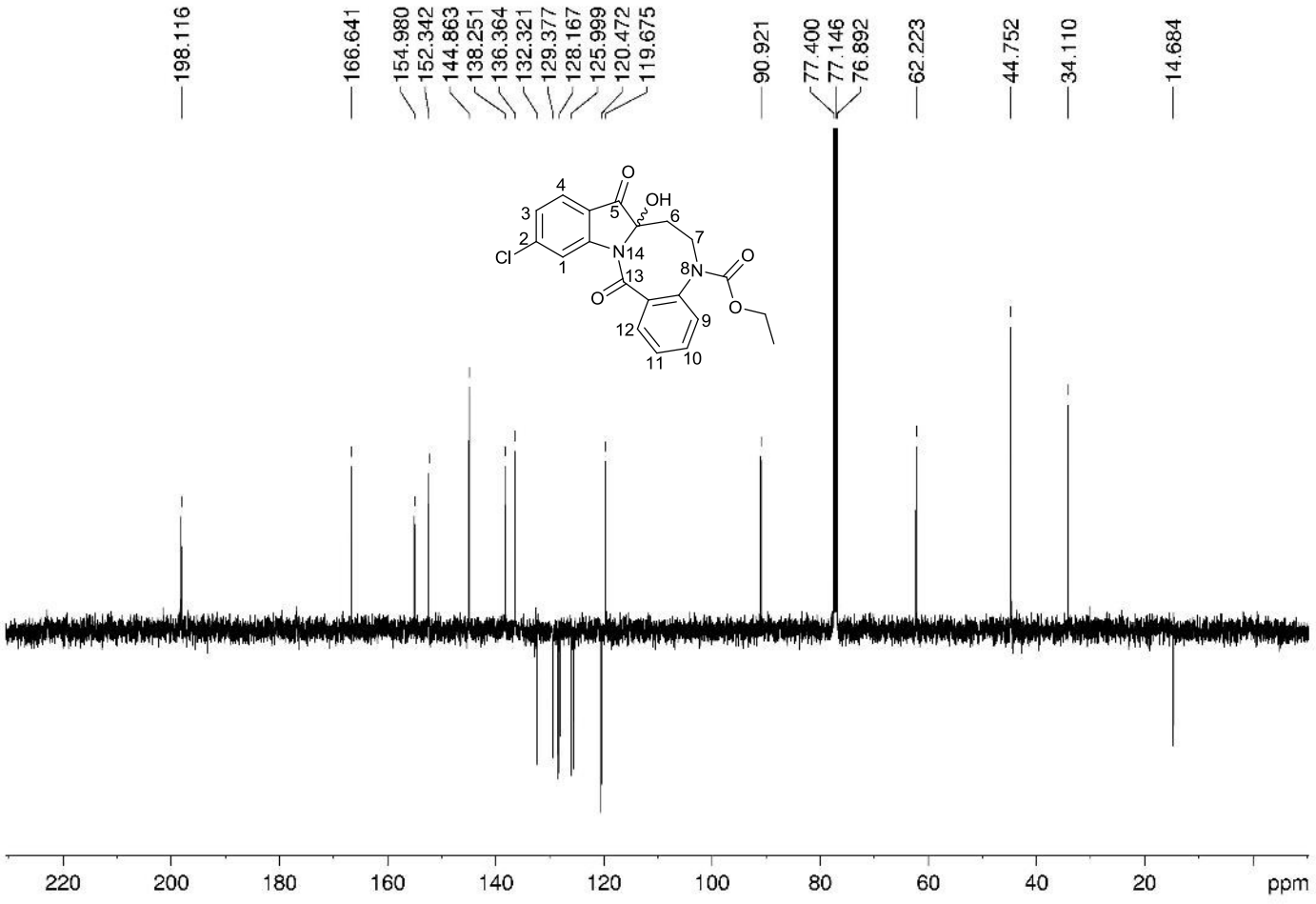

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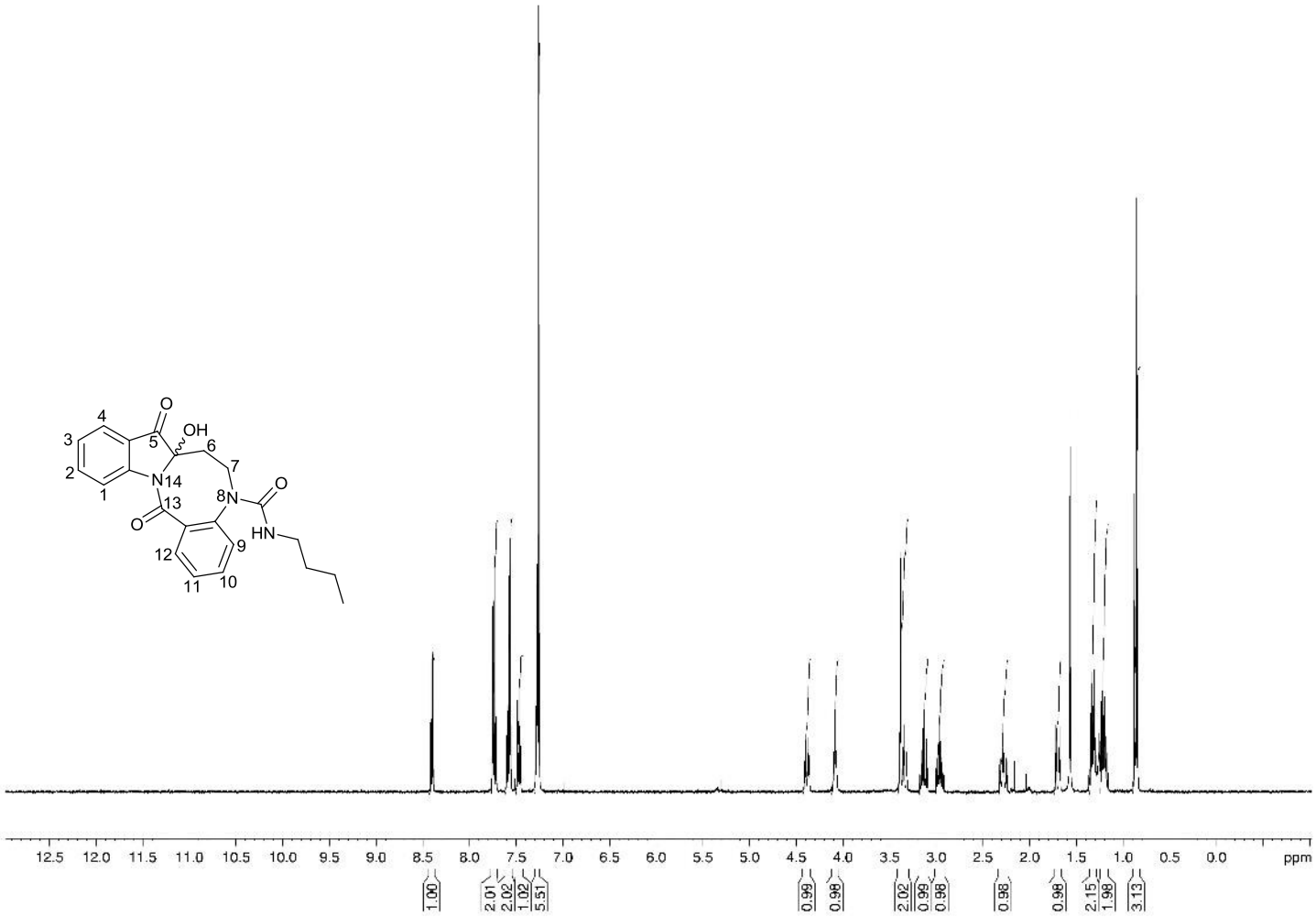

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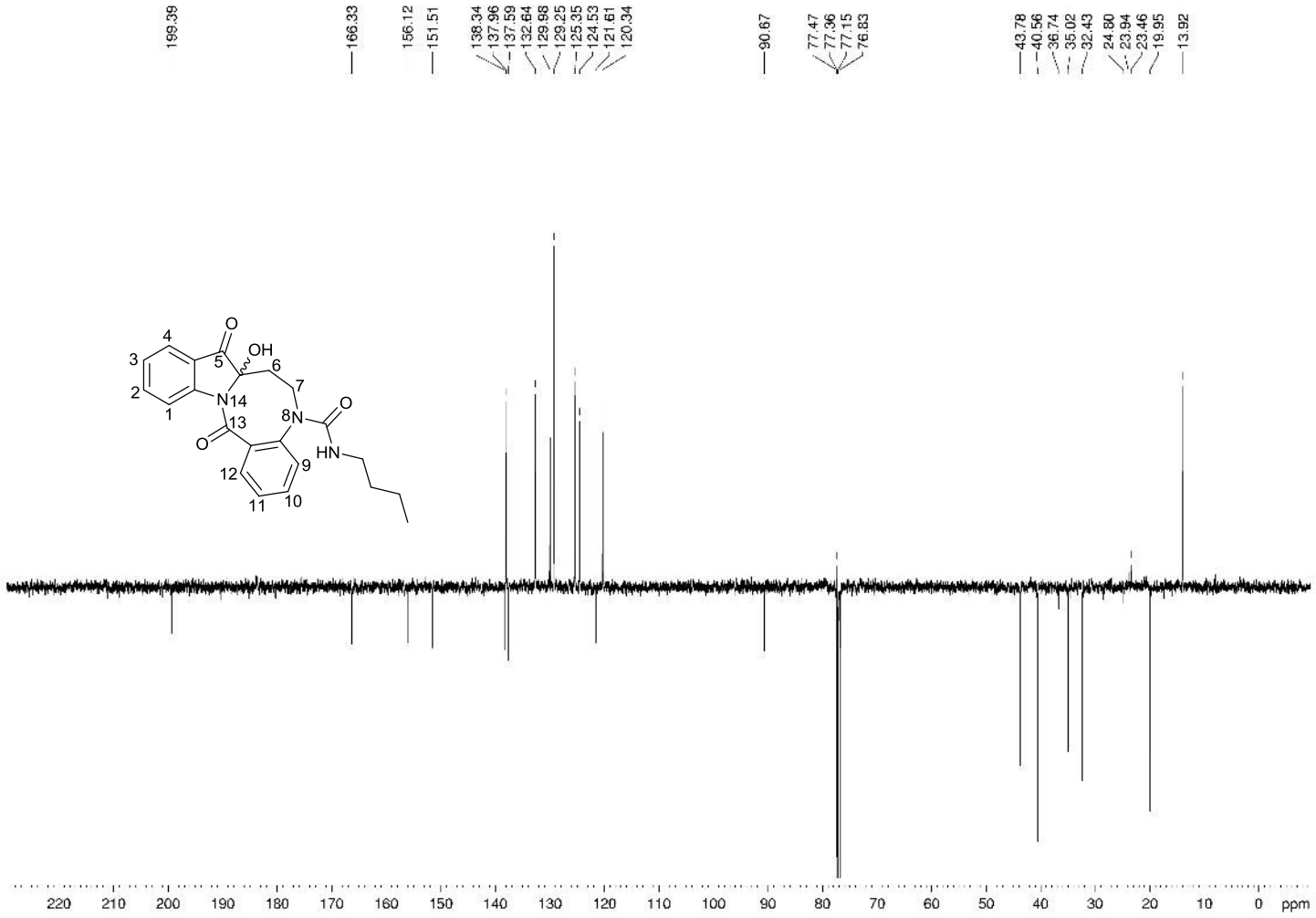

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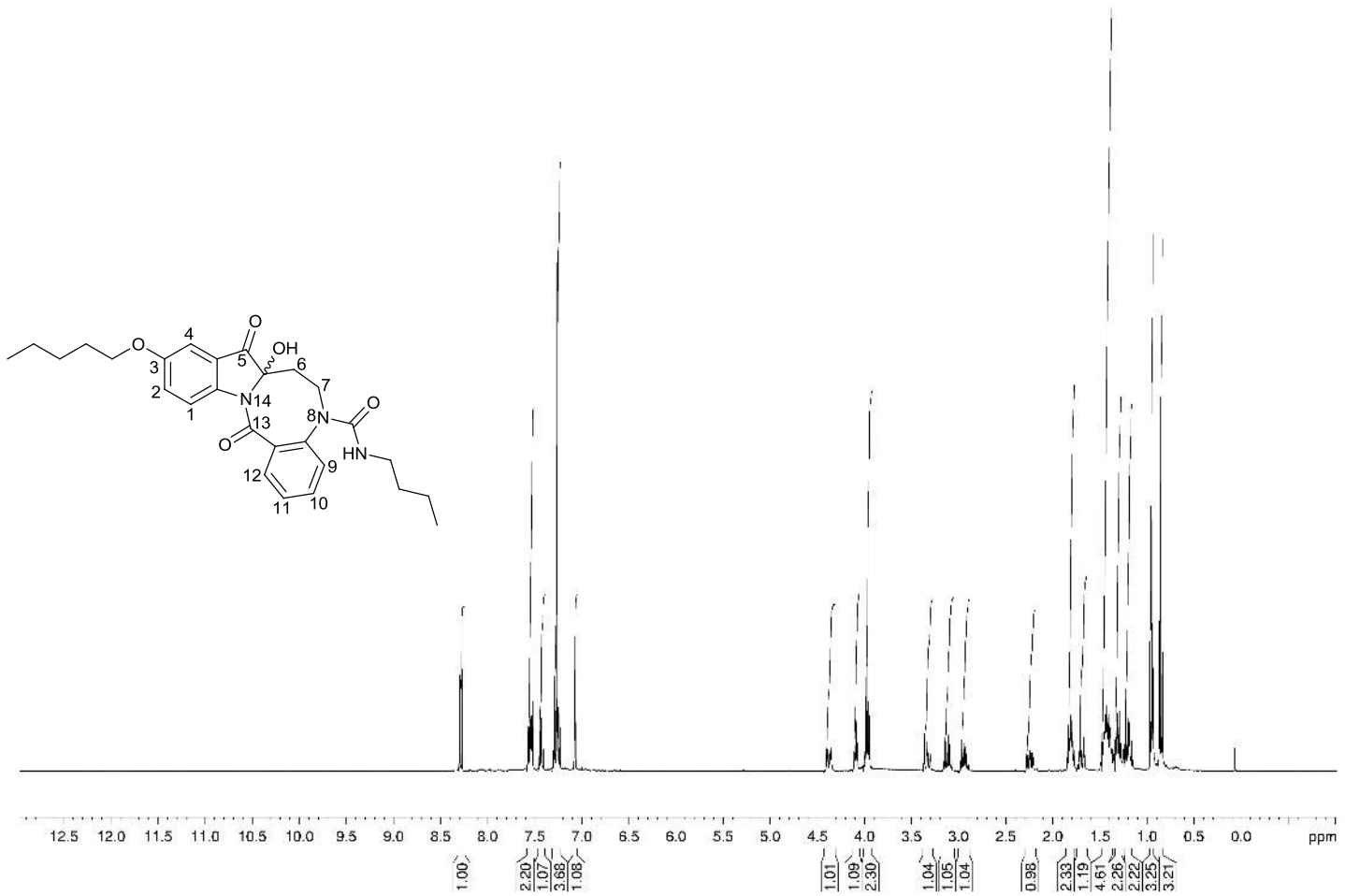

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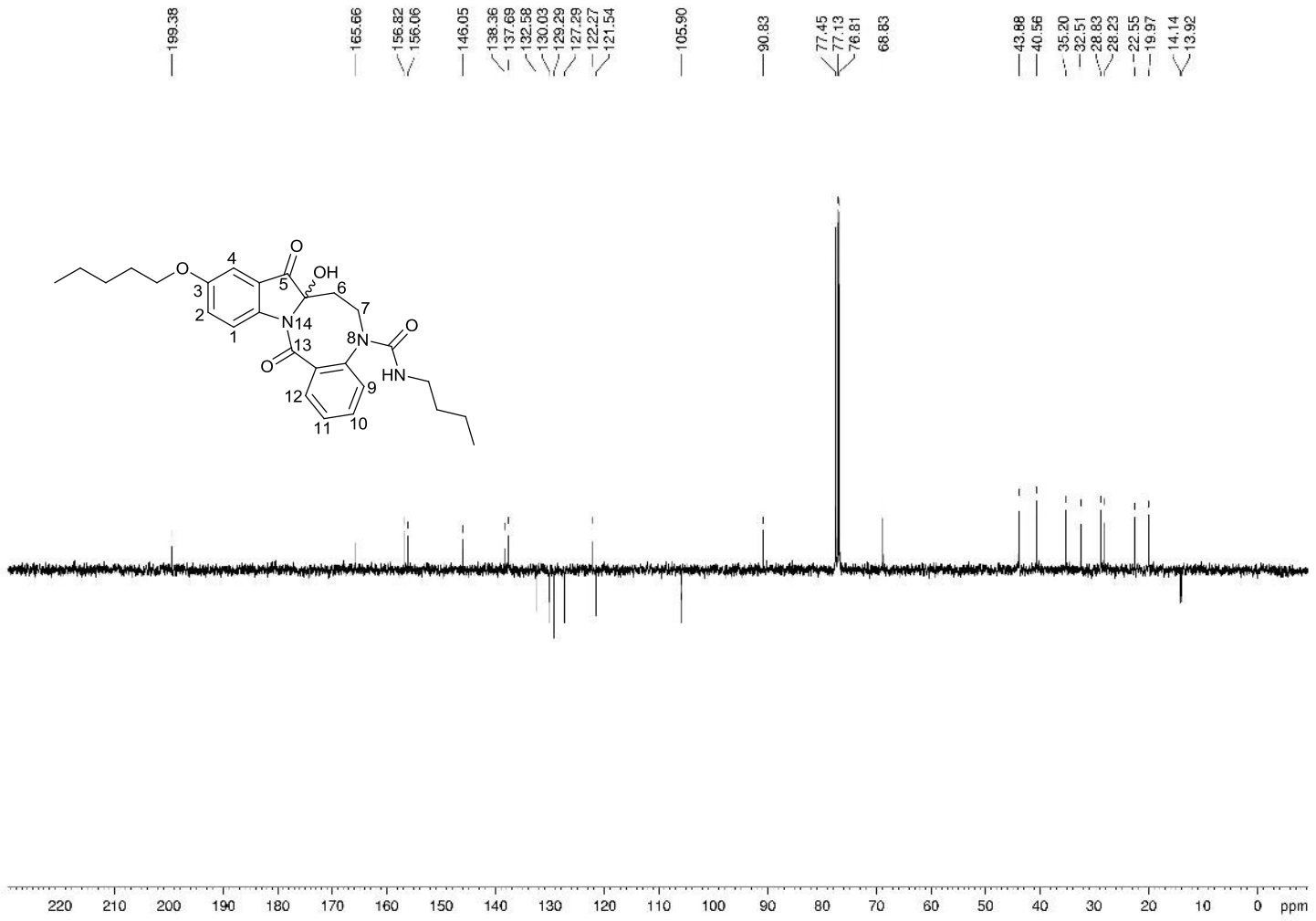
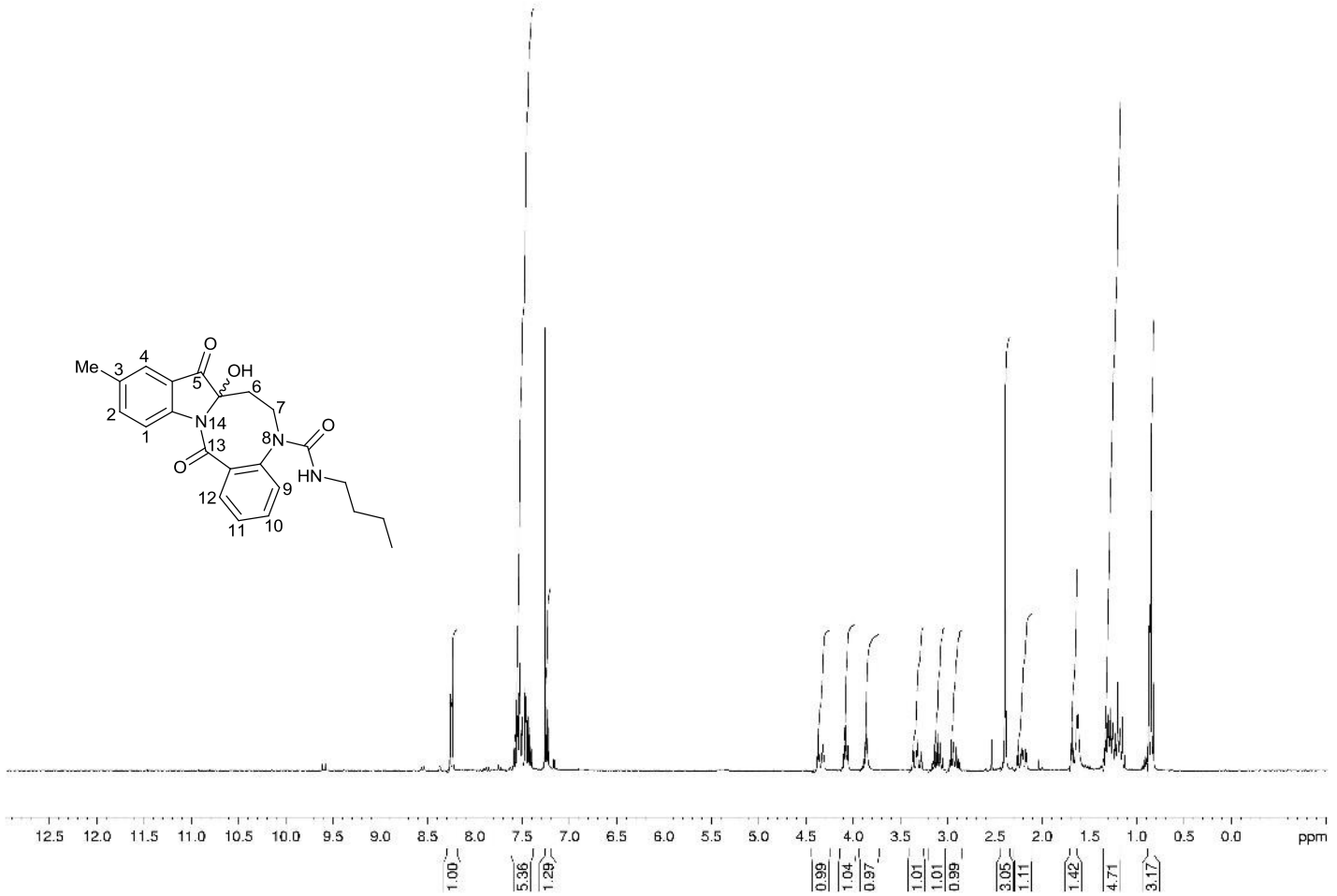
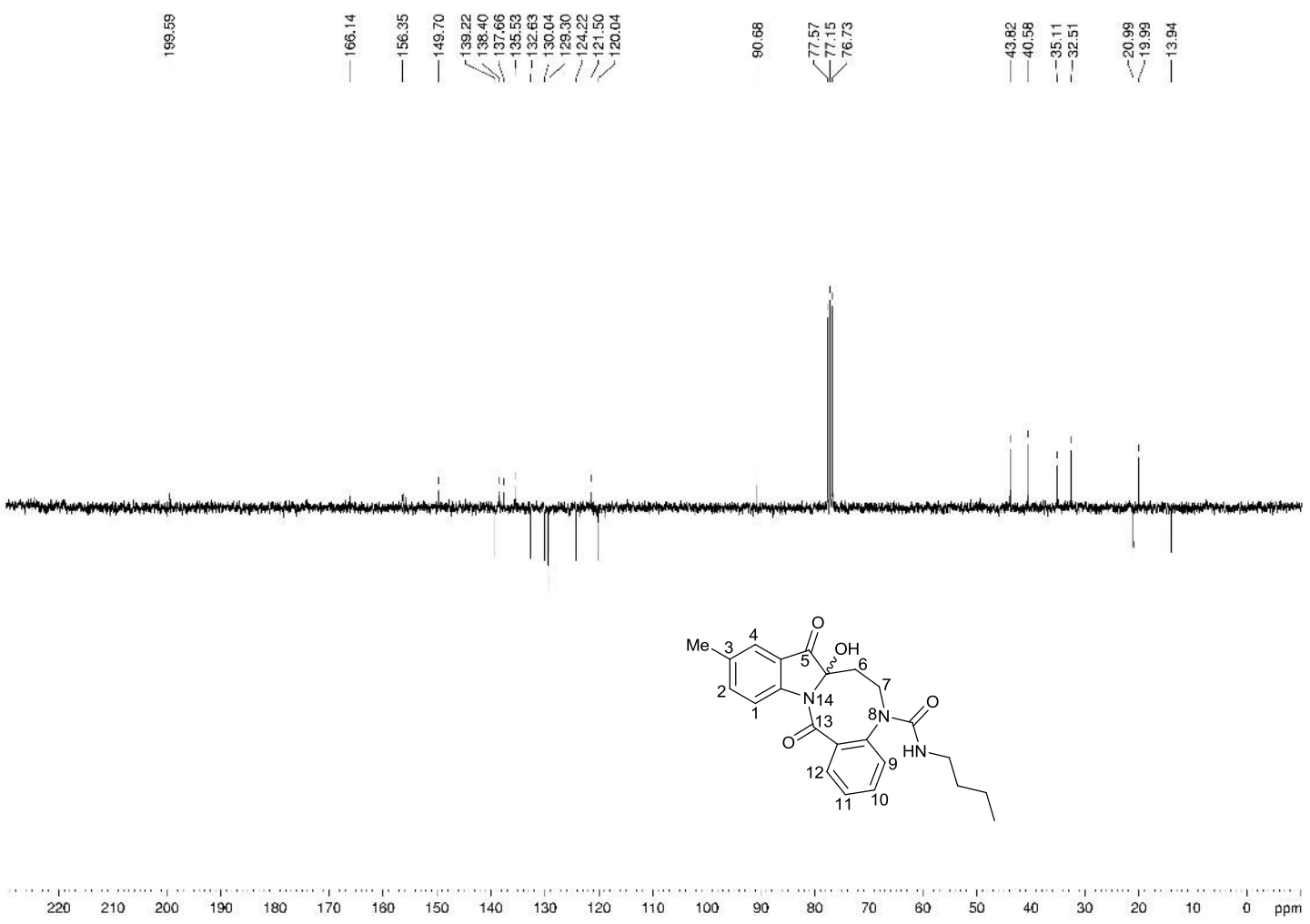


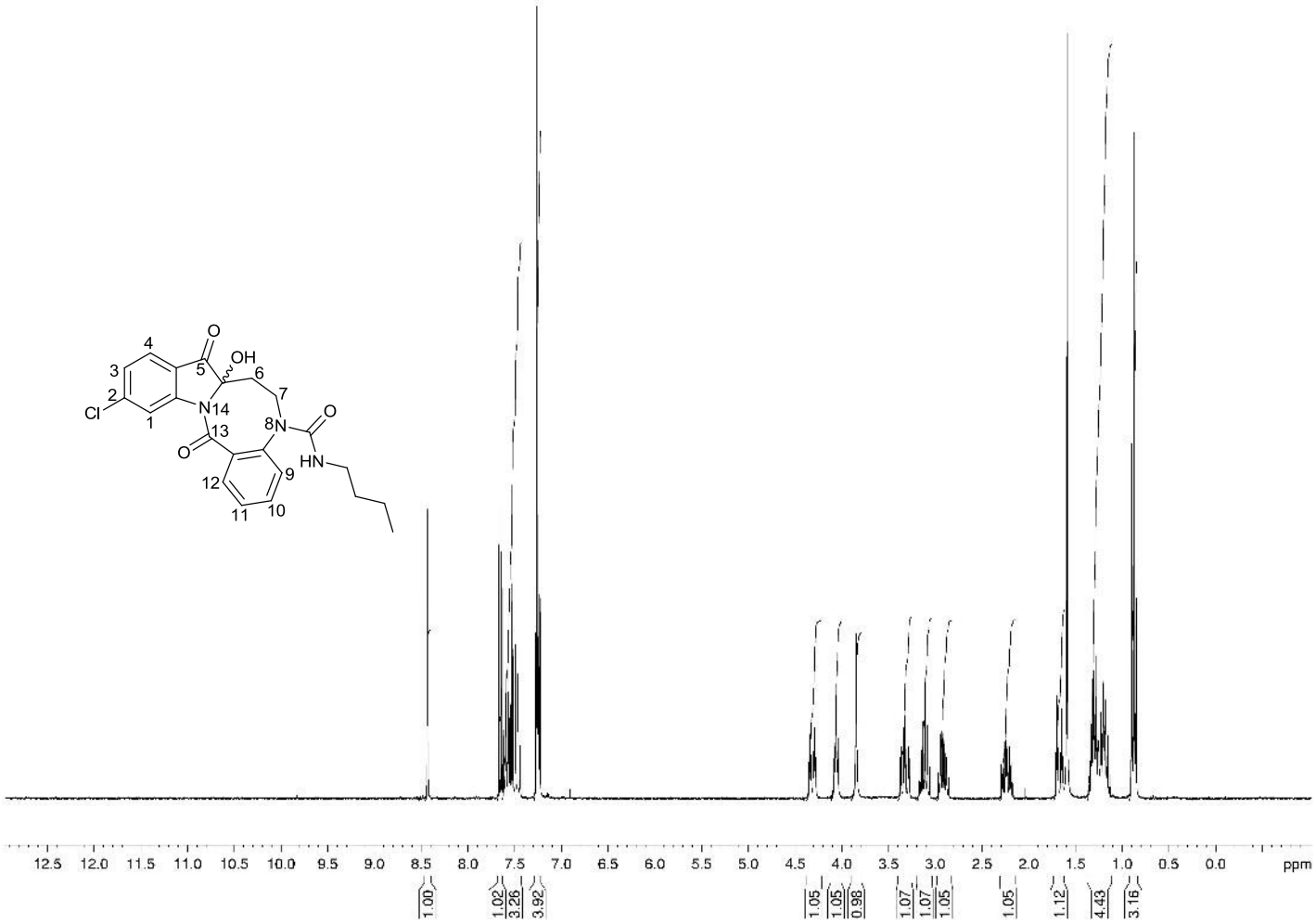
Compound 2k ^{1}H NMR ($CDCl_3$)



Compound 2k ^{13}C NMR ($CDCl_3$)



Compound 2l ^{1}H NMR ($CDCl_3$)



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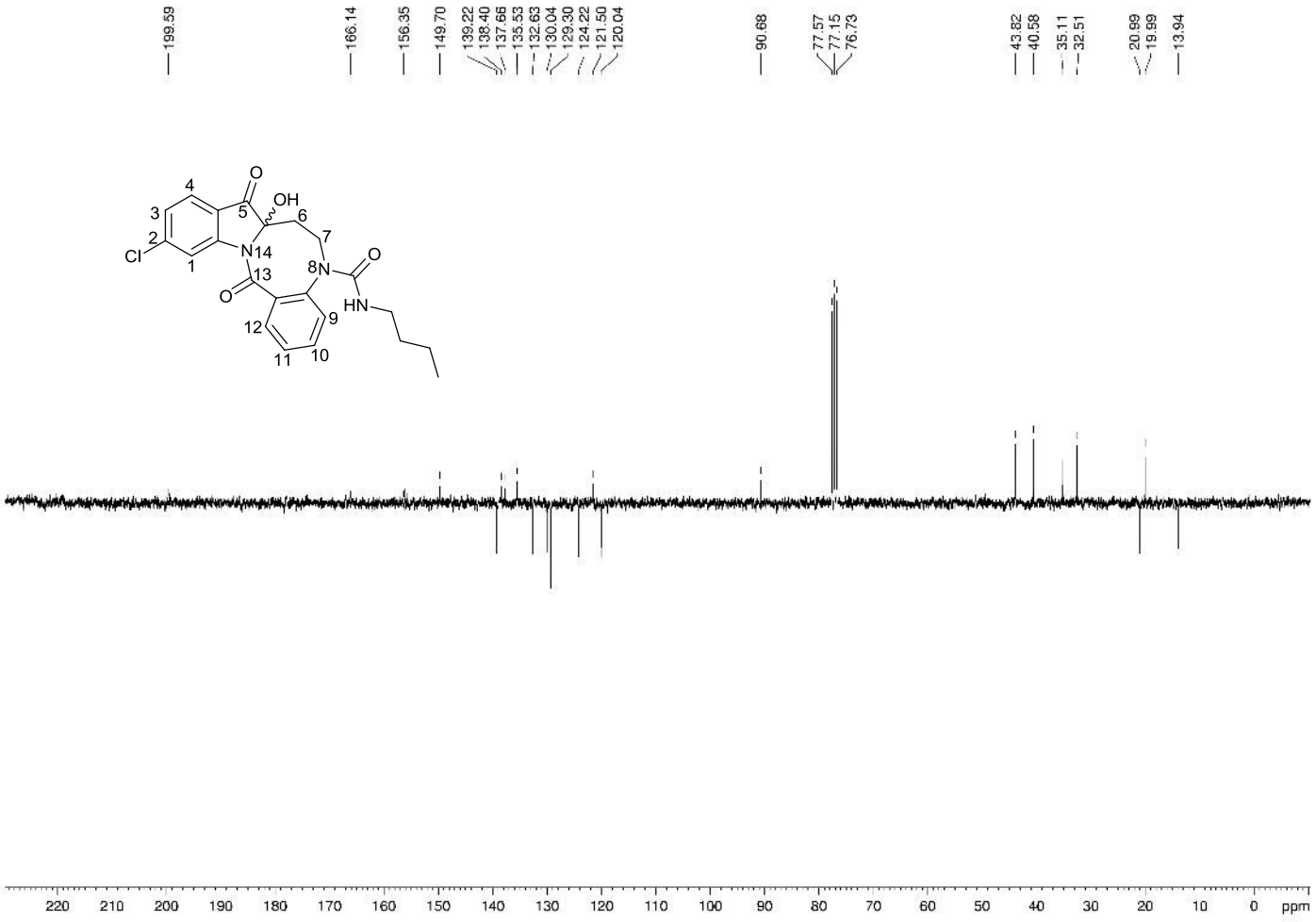
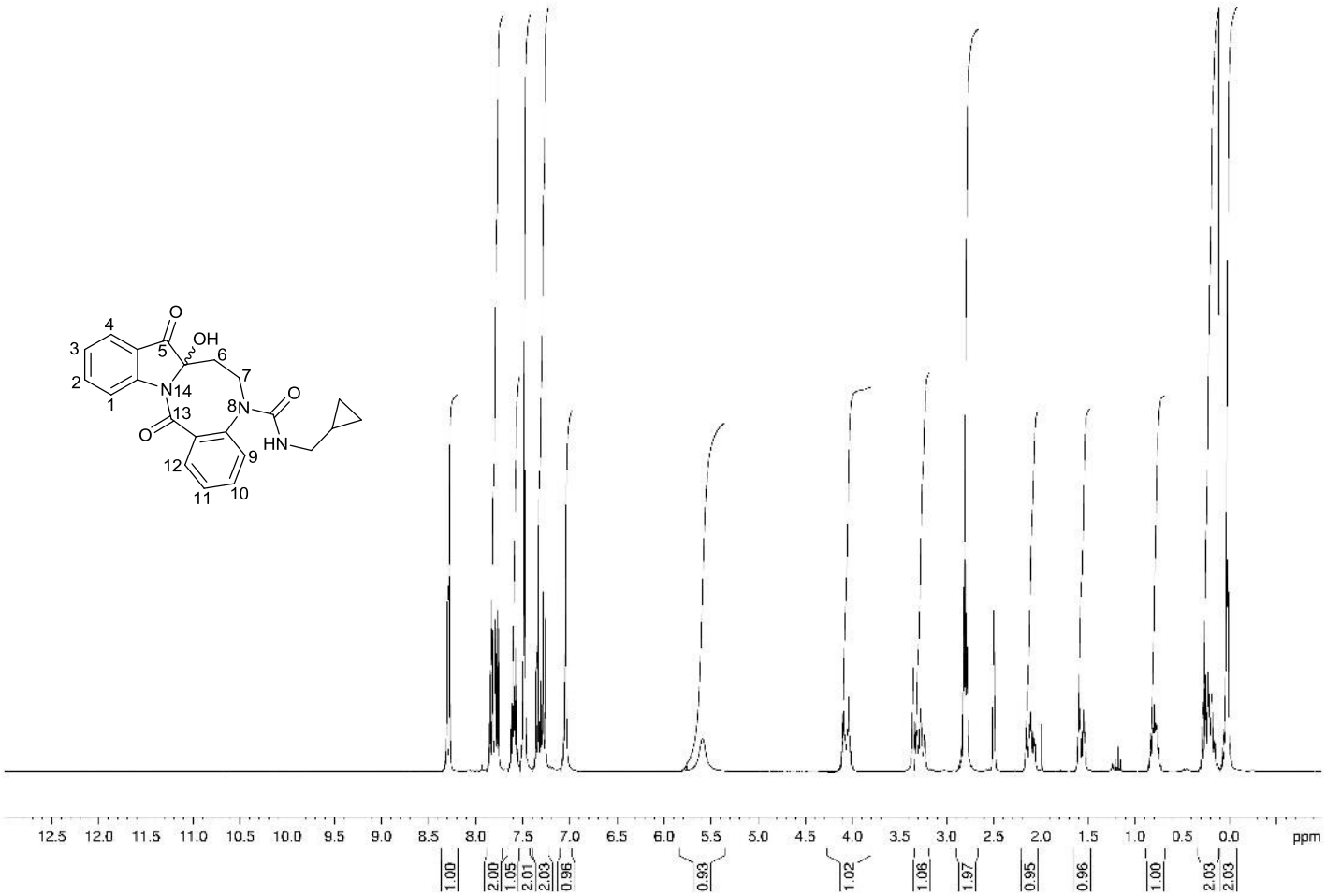


Compound 2m ^{1}H NMR (d_6-DMSO)



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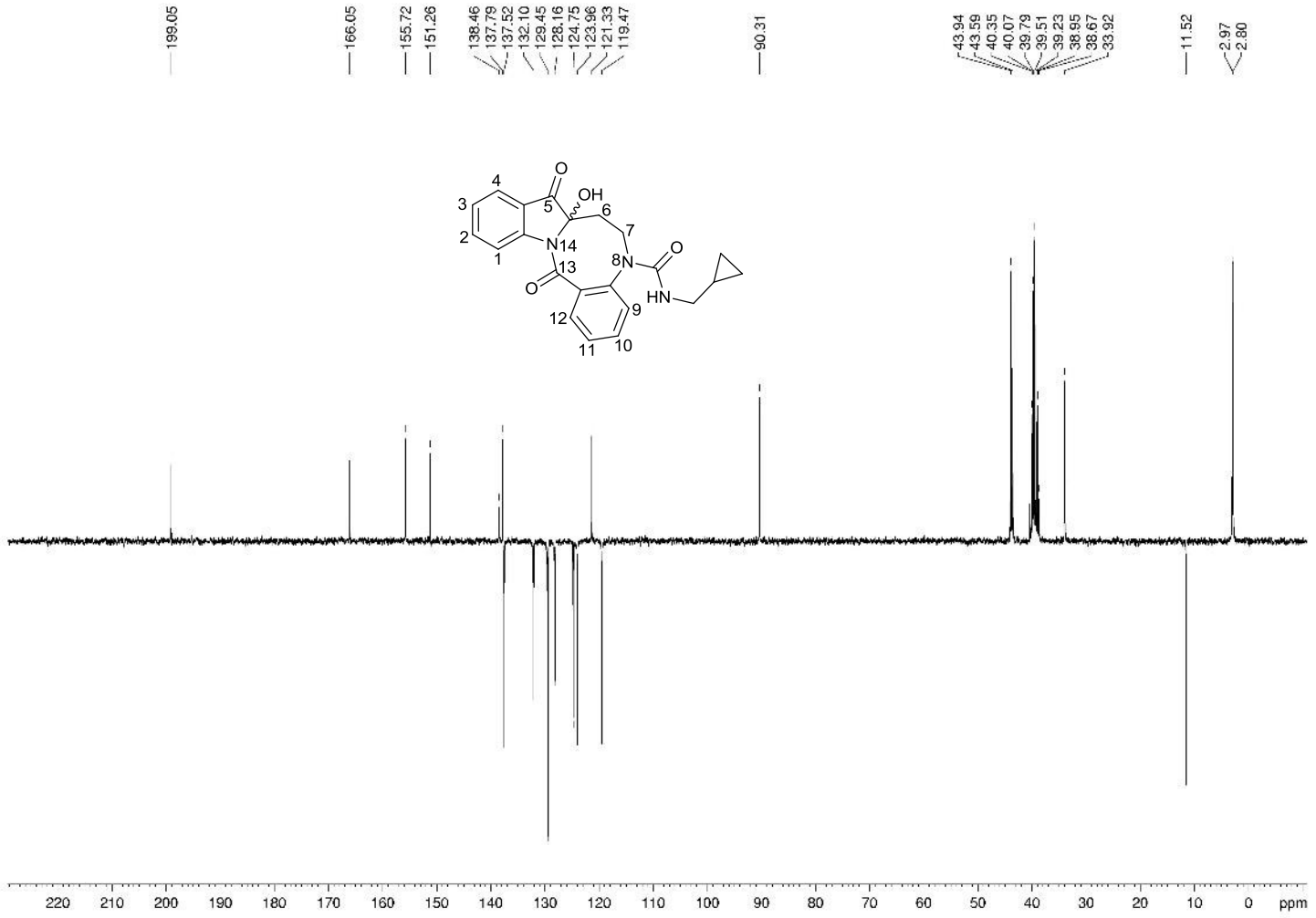
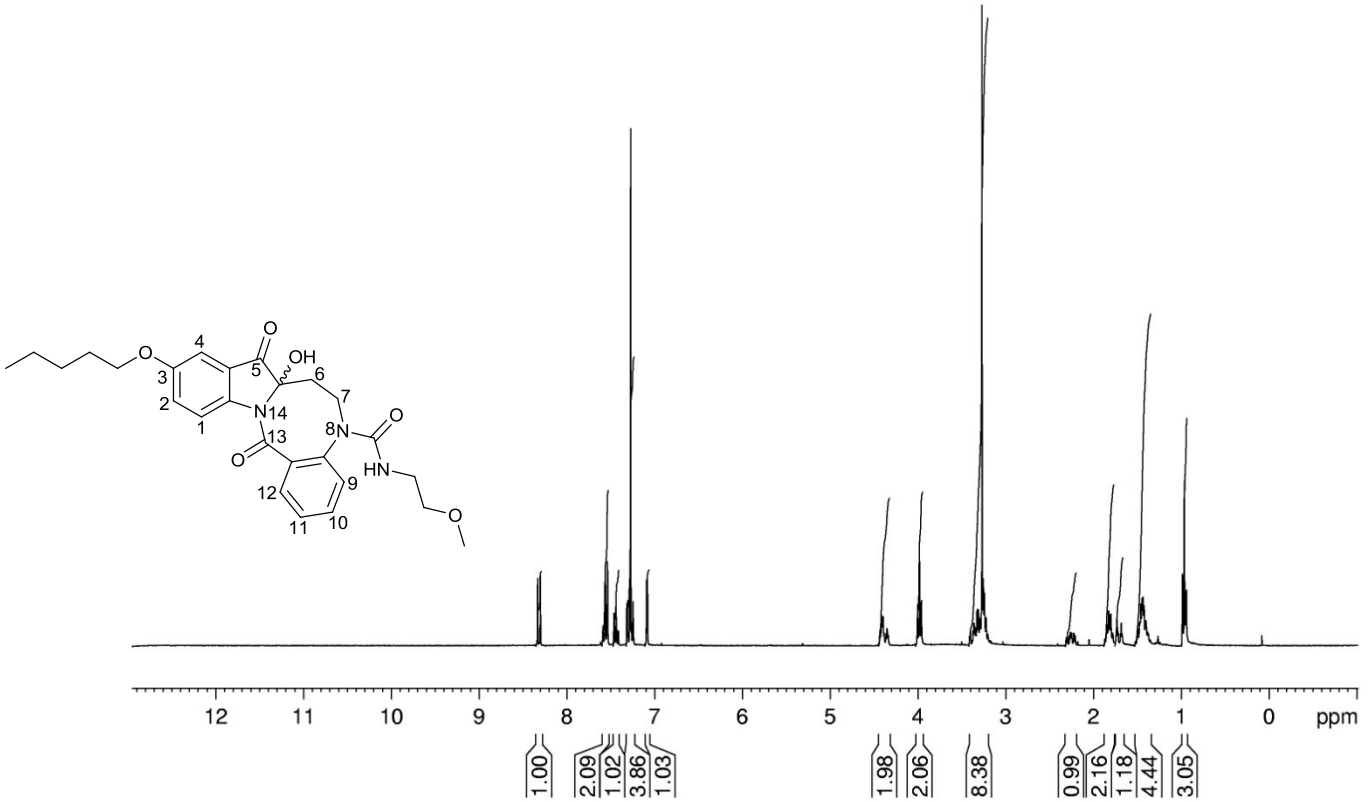
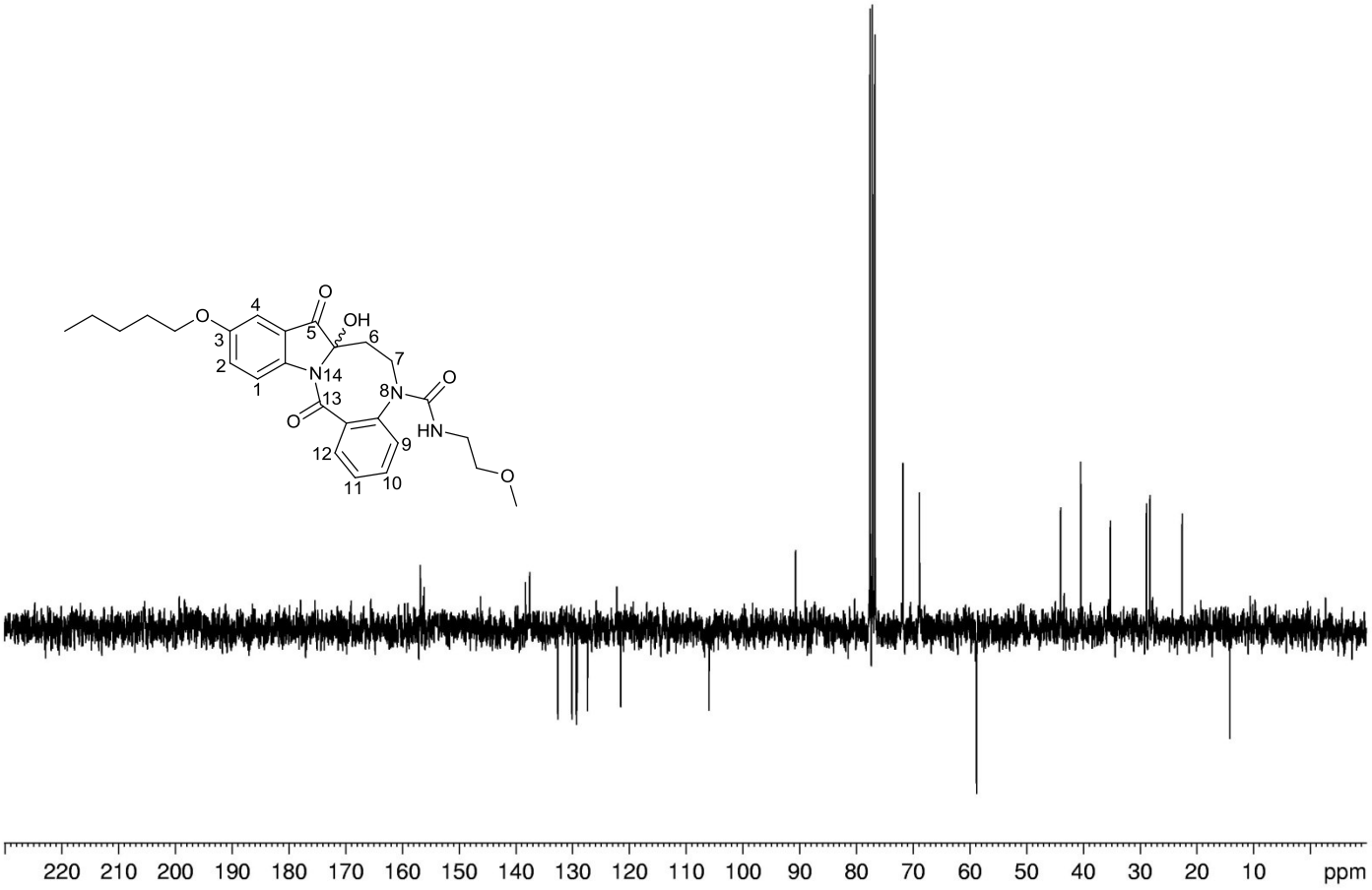


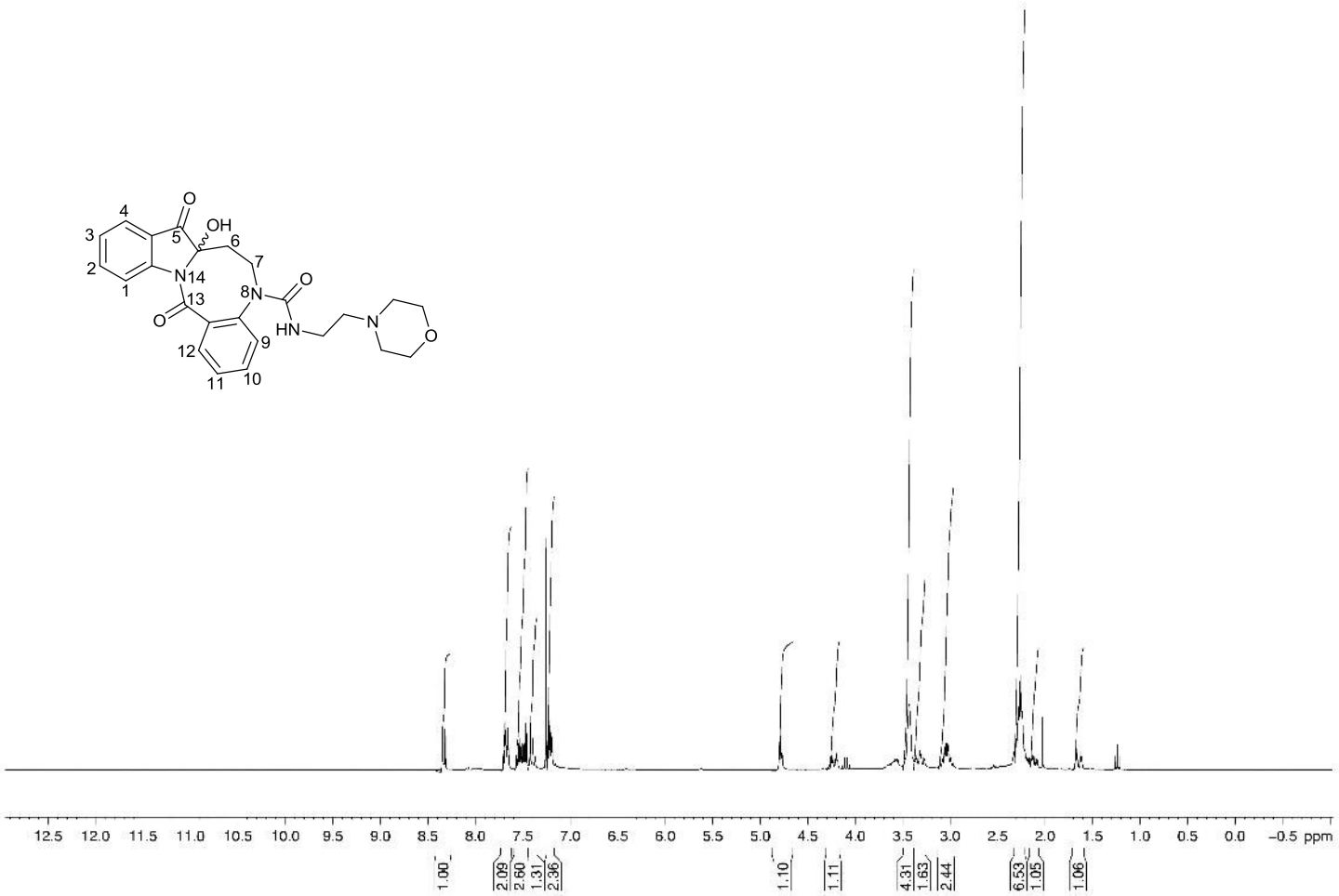
Compound 2n ^{1}H NMR ($CDCl_3$)



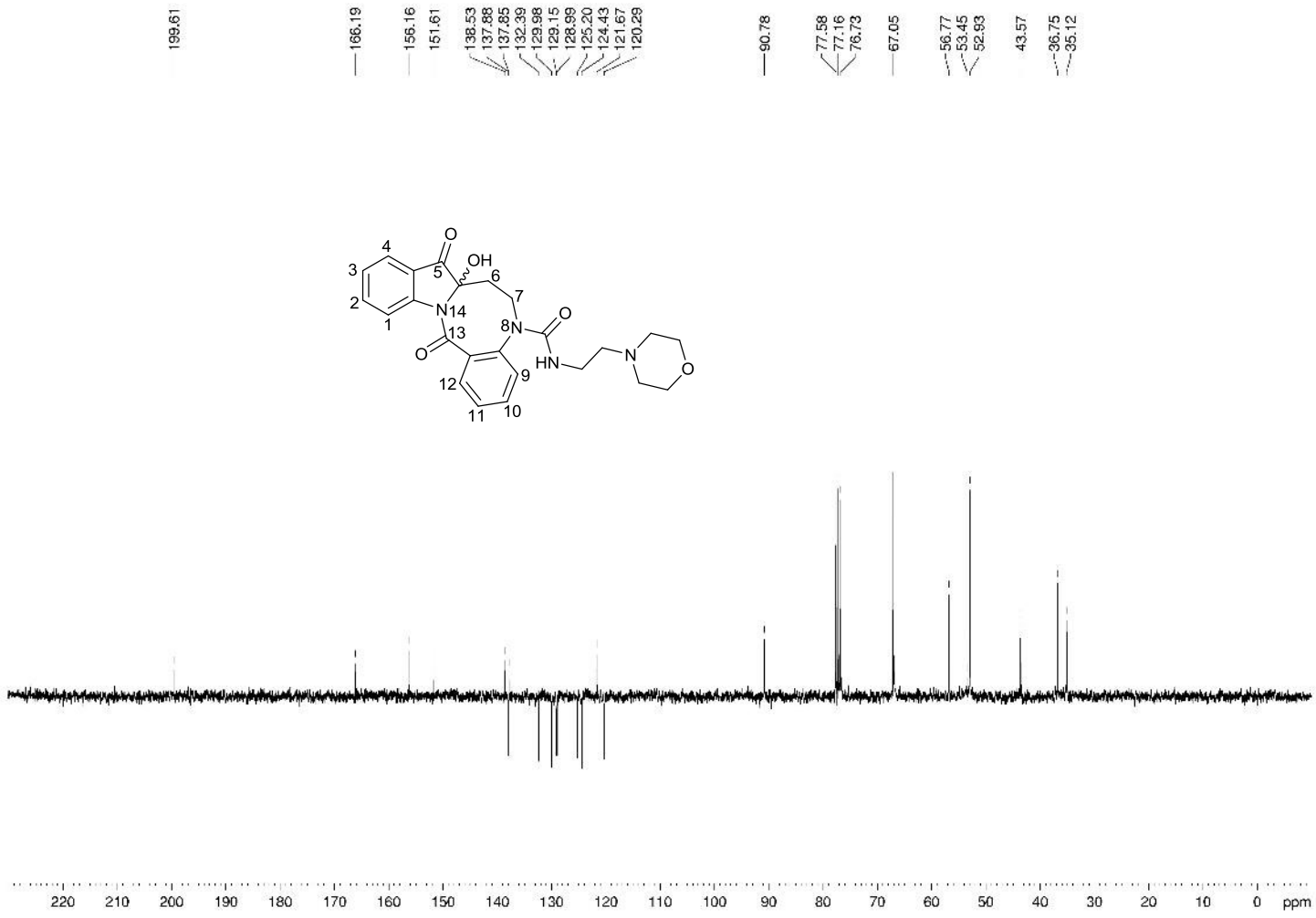
Compound 2n ^{13}C NMR ($CDCl_3$)



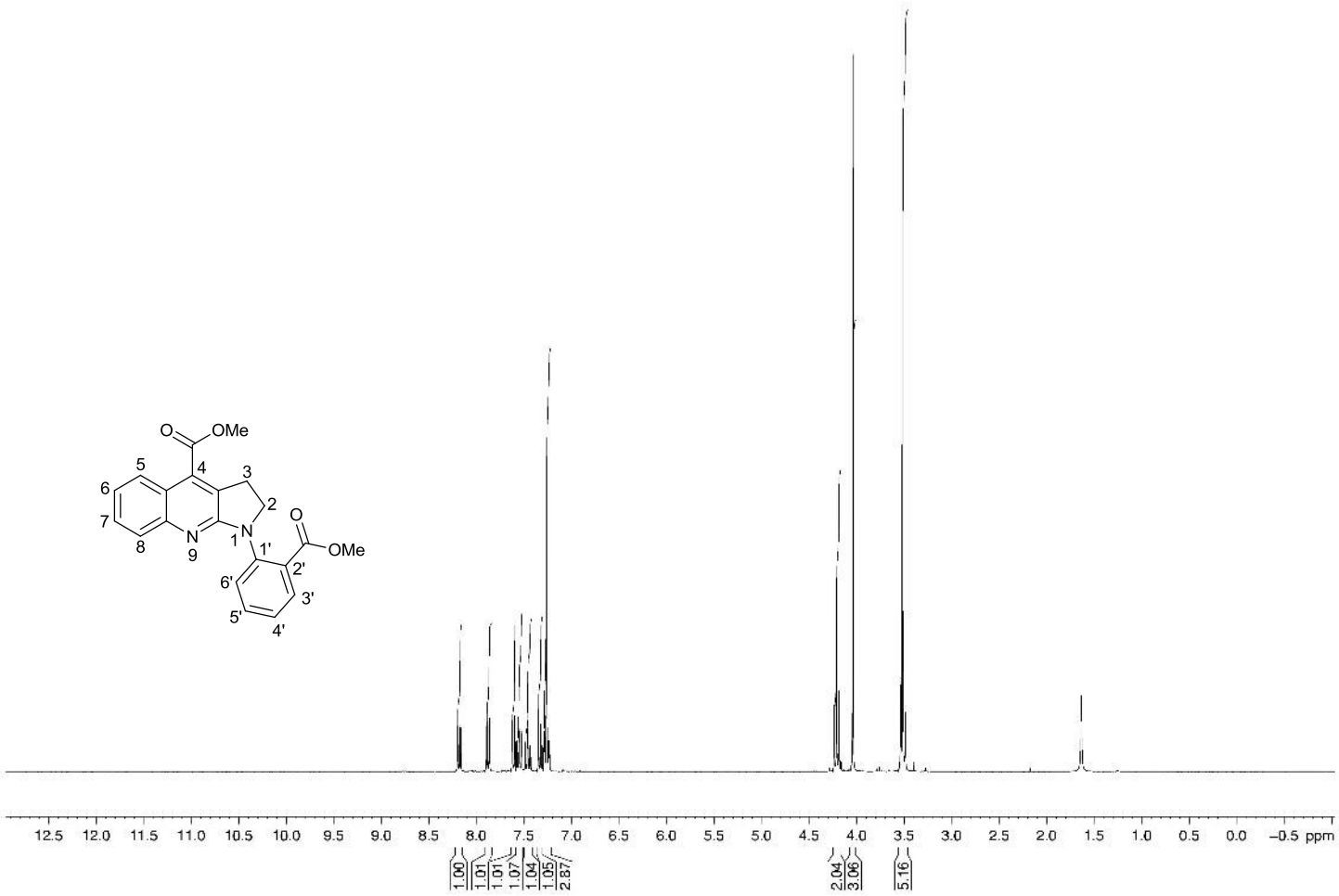
Compound 2o ^{1}H NMR ($CDCl_3$)



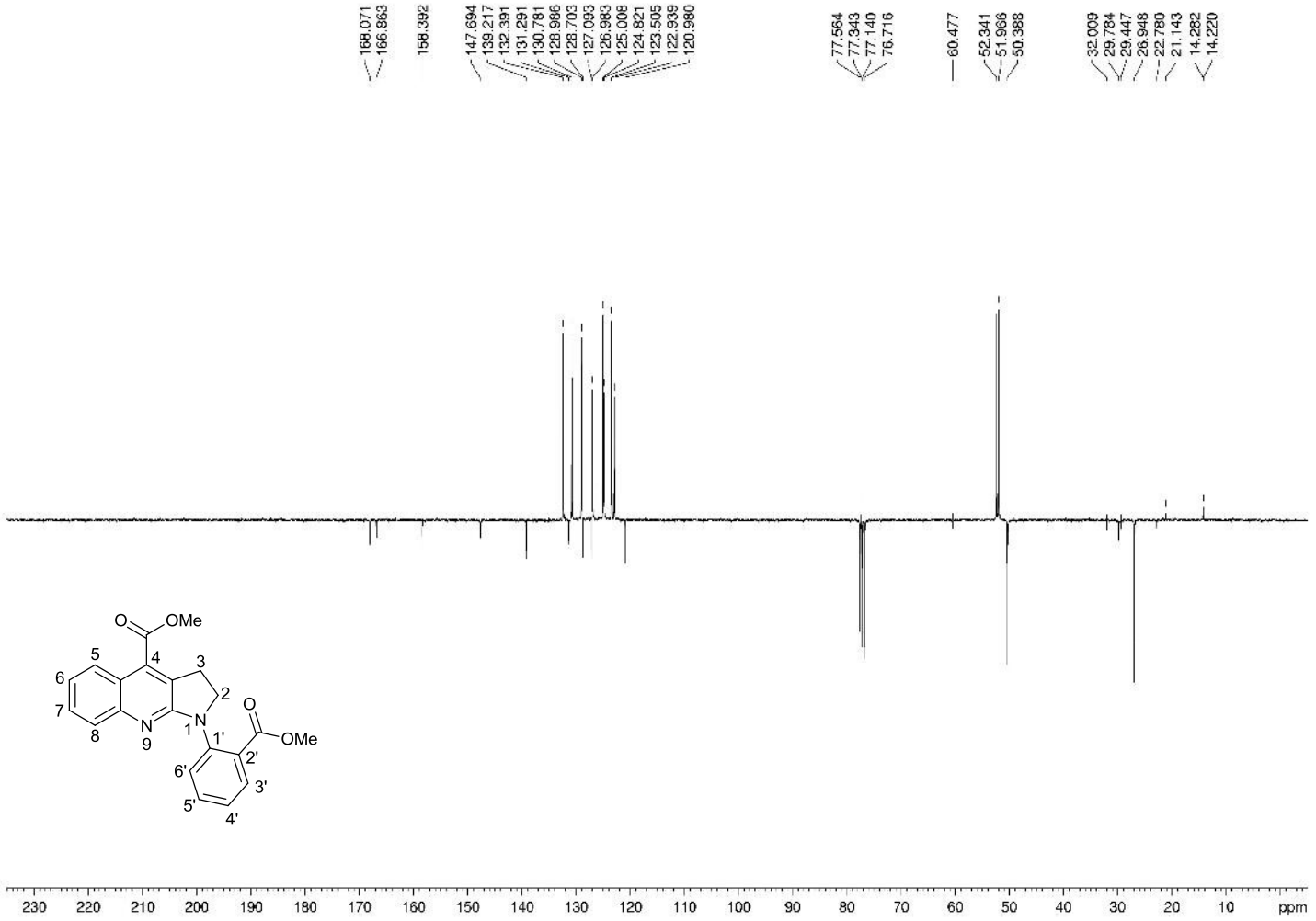
Compound 2o ^{13}C NMR ($CDCl_3$)



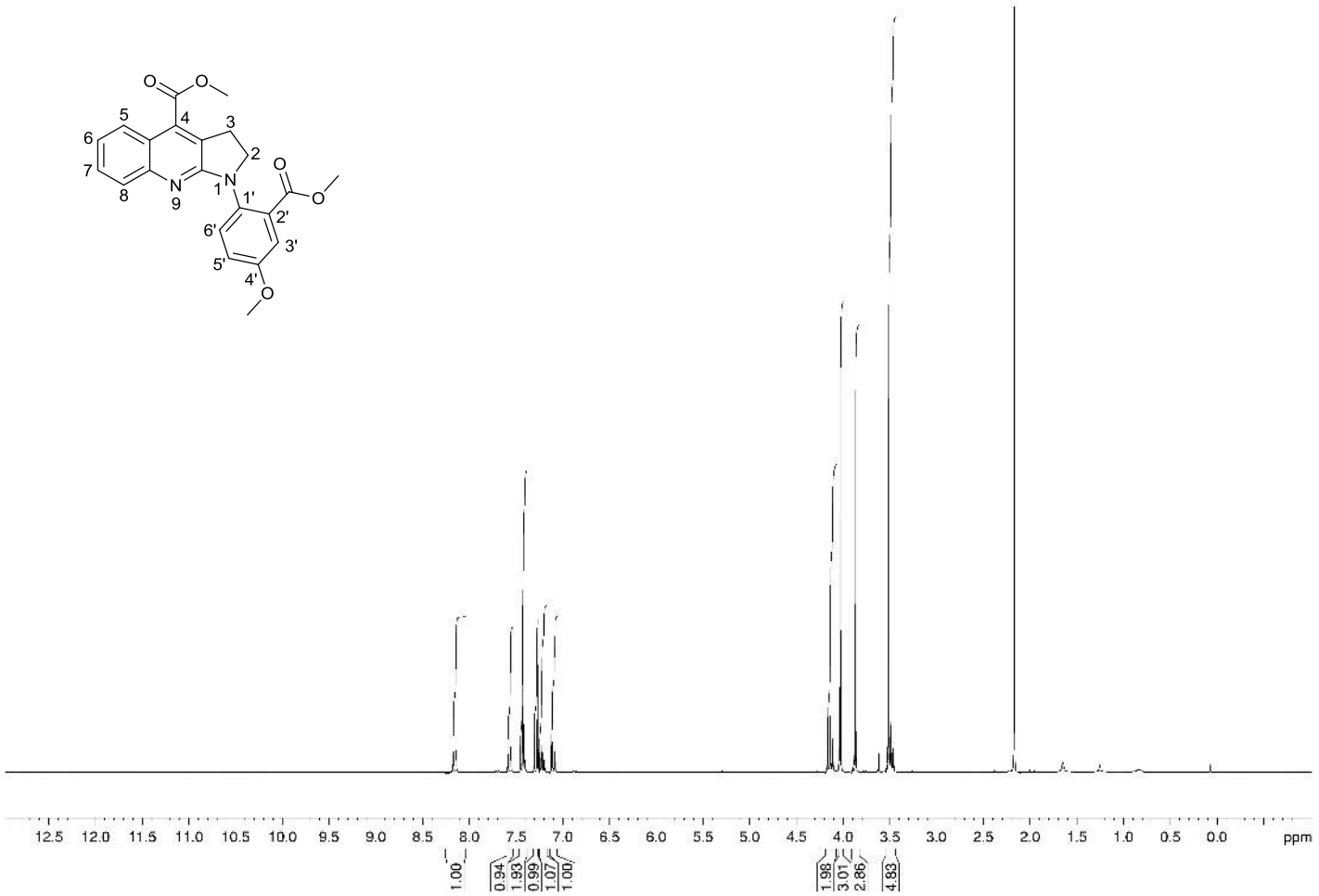
Compound 3a ^{1}H NMR ($CDCl_3$)



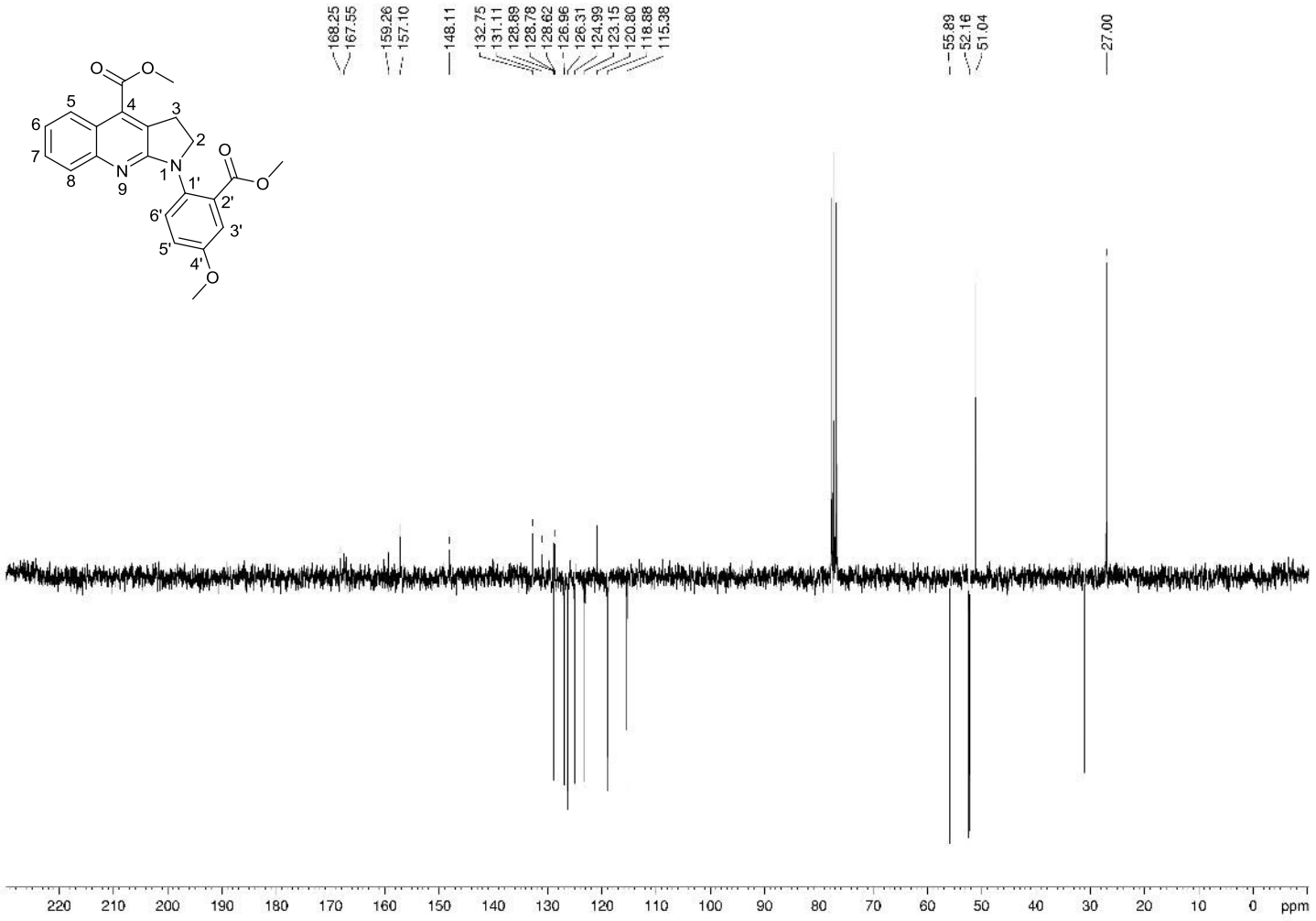
Compound 3a ^{13}C NMR ($CDCl_3$)



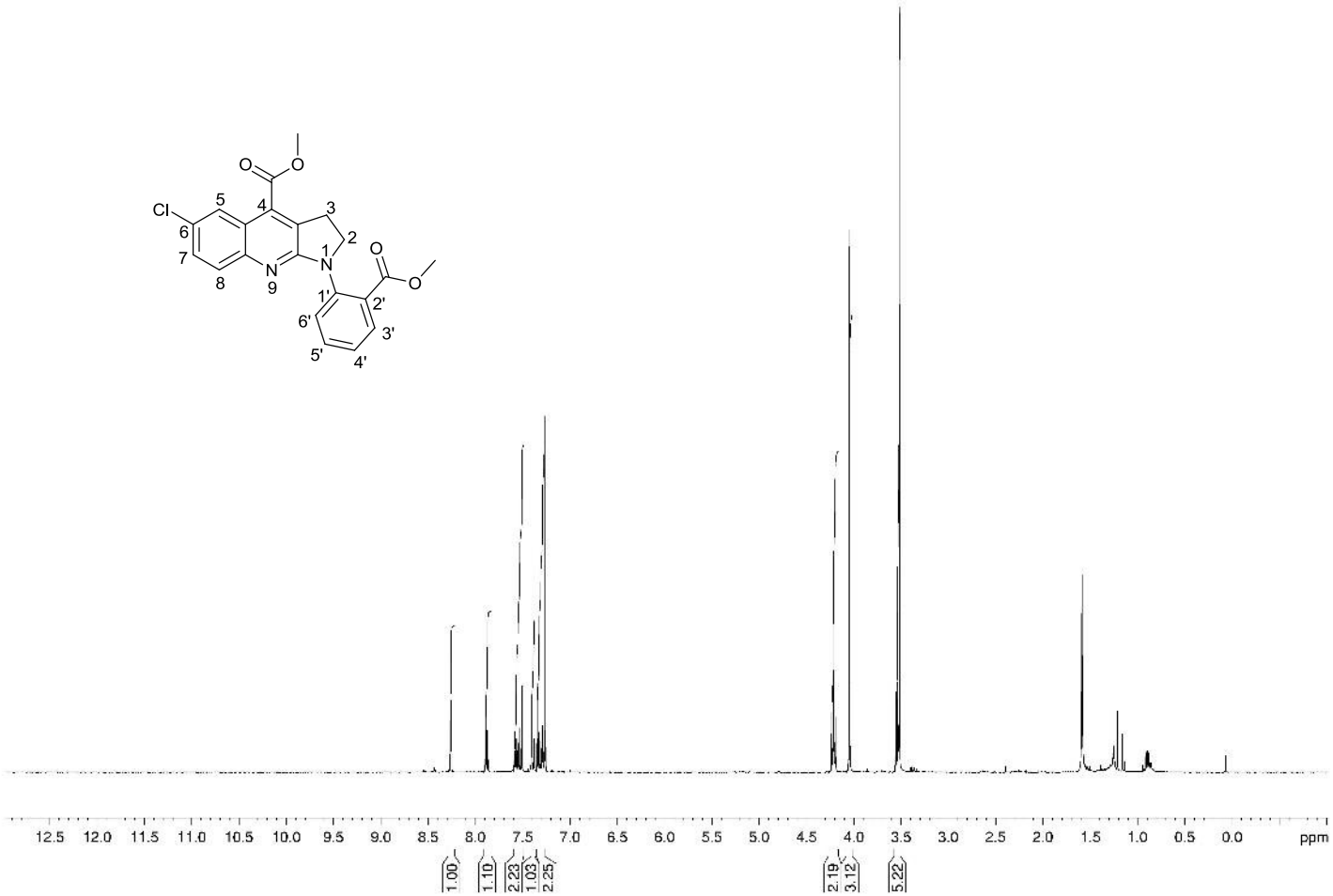
Compound 3b ^{1}H NMR ($CDCl_3$)



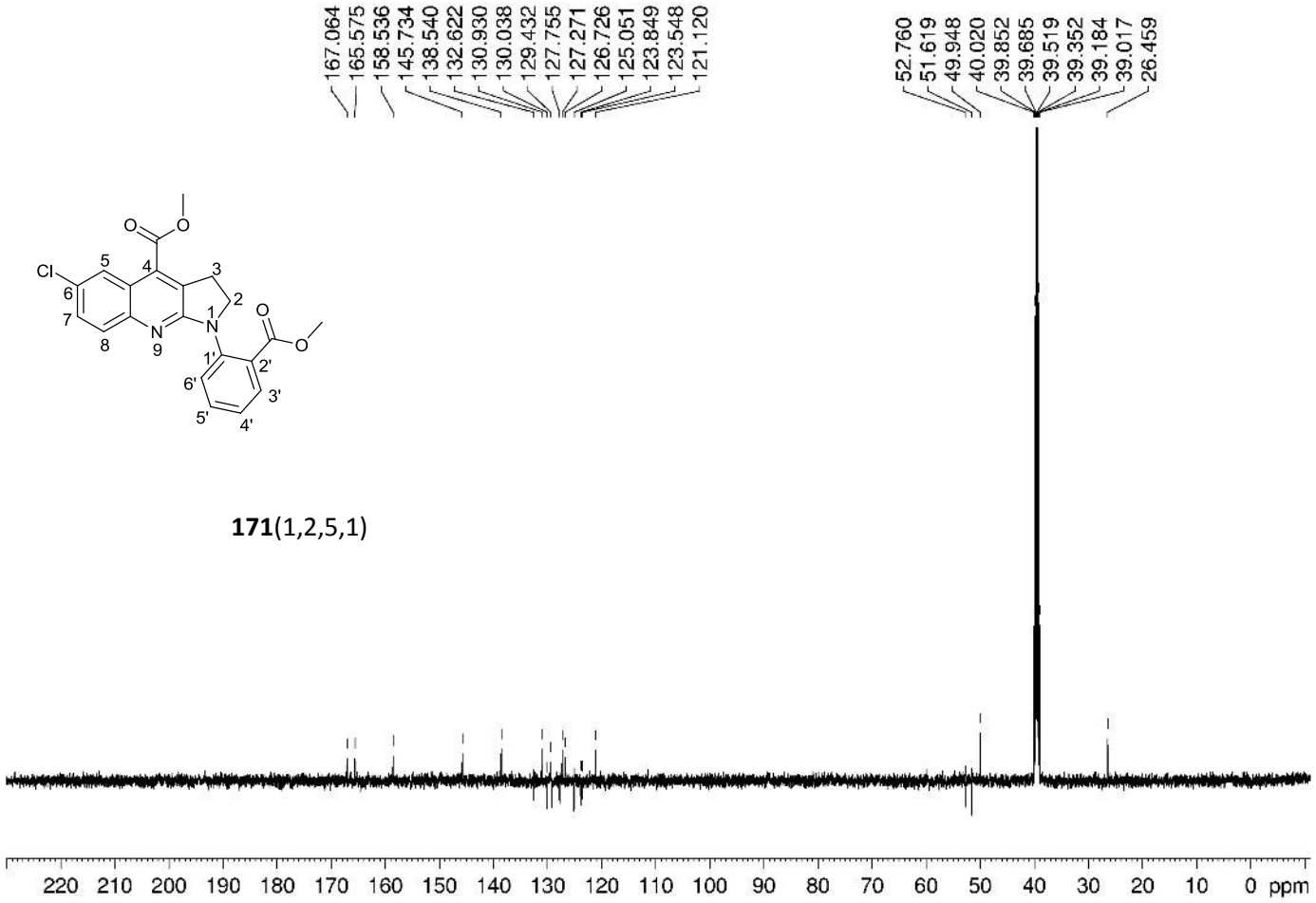
Compound 3b ^{13}C NMR ($CDCl_3$)



Compound 3c ^{1}H NMR ($CDCl_3$)

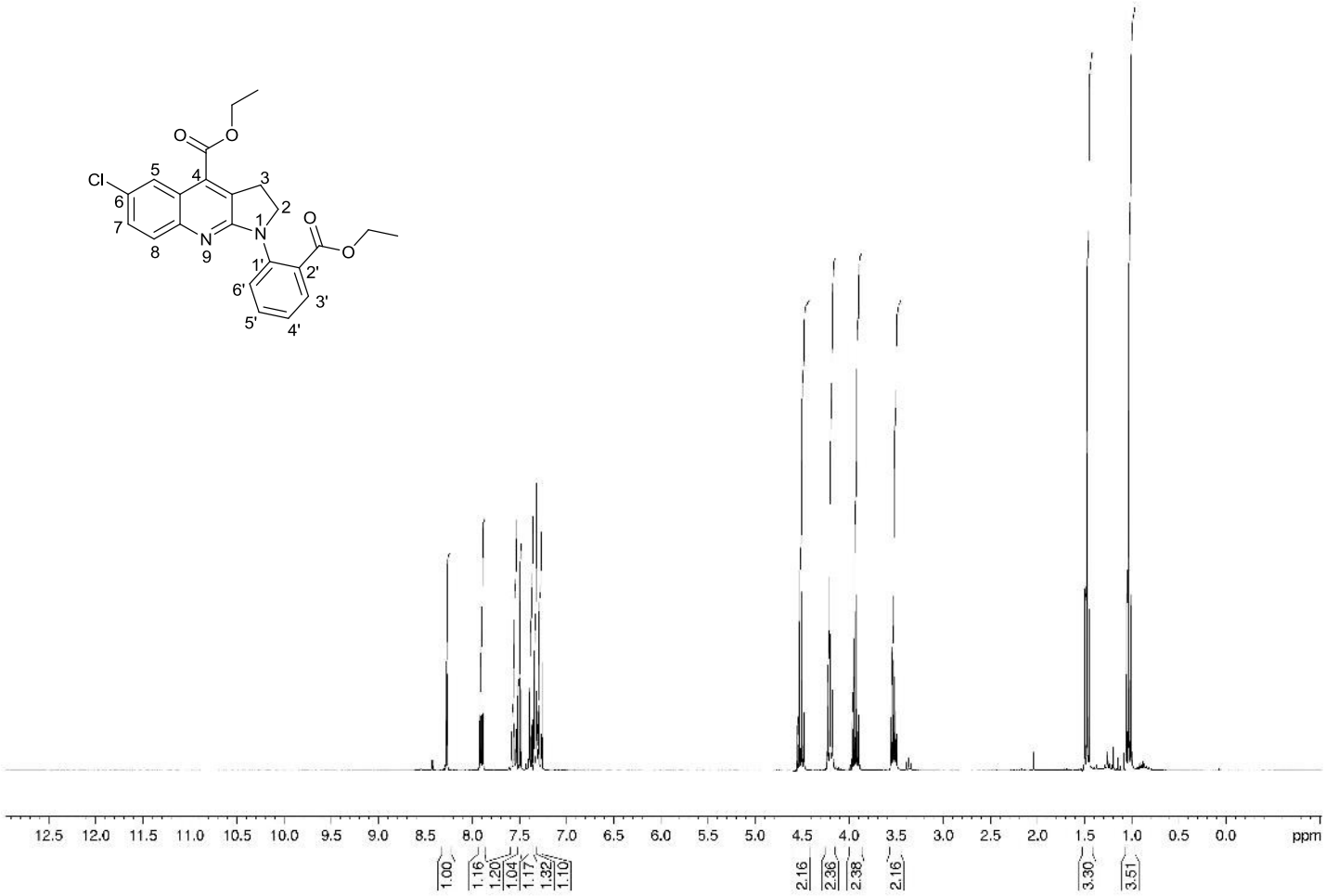


Compound 3c ^{13}C NMR (d_6-DMSO)

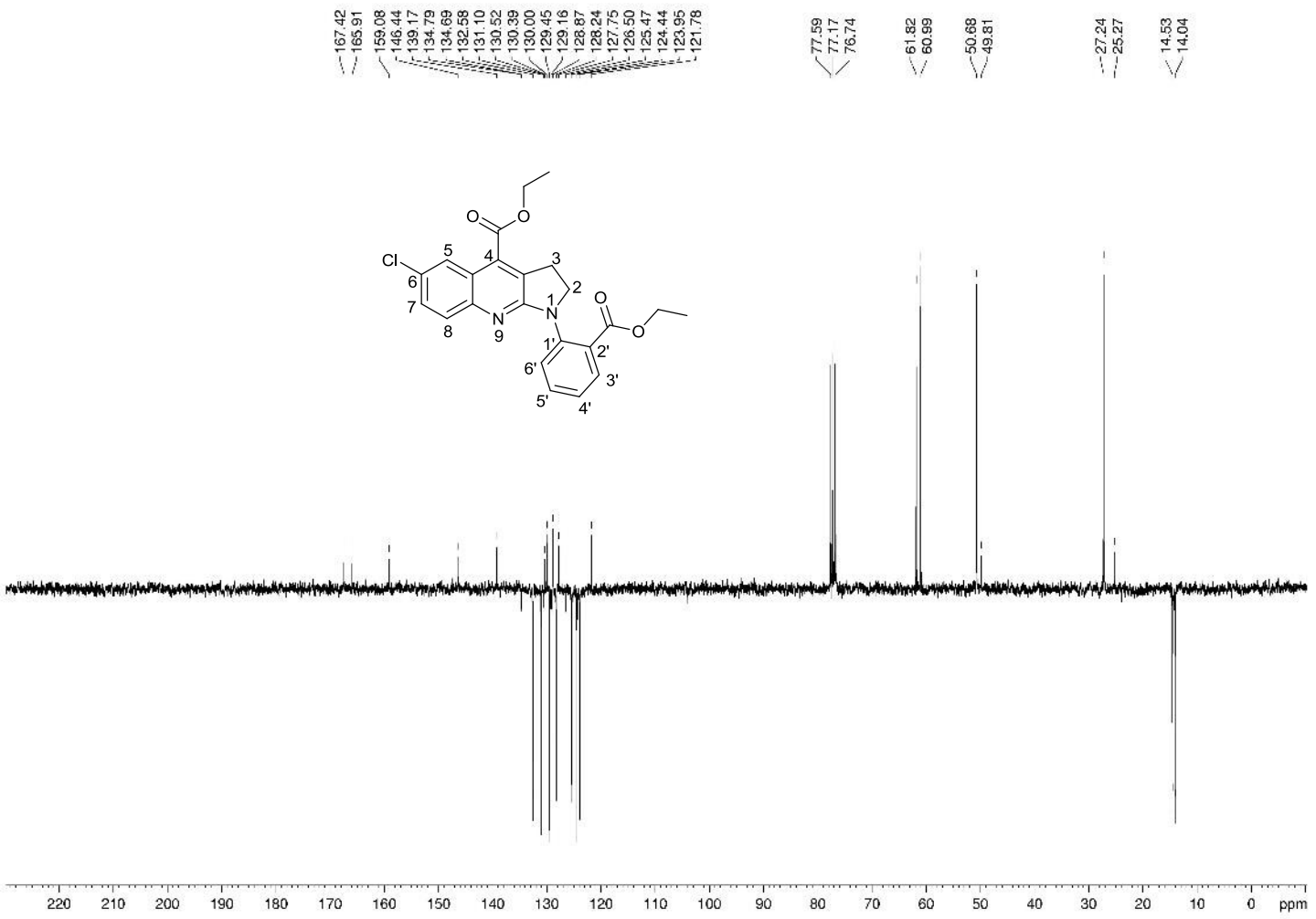


171(1,2,5,1)

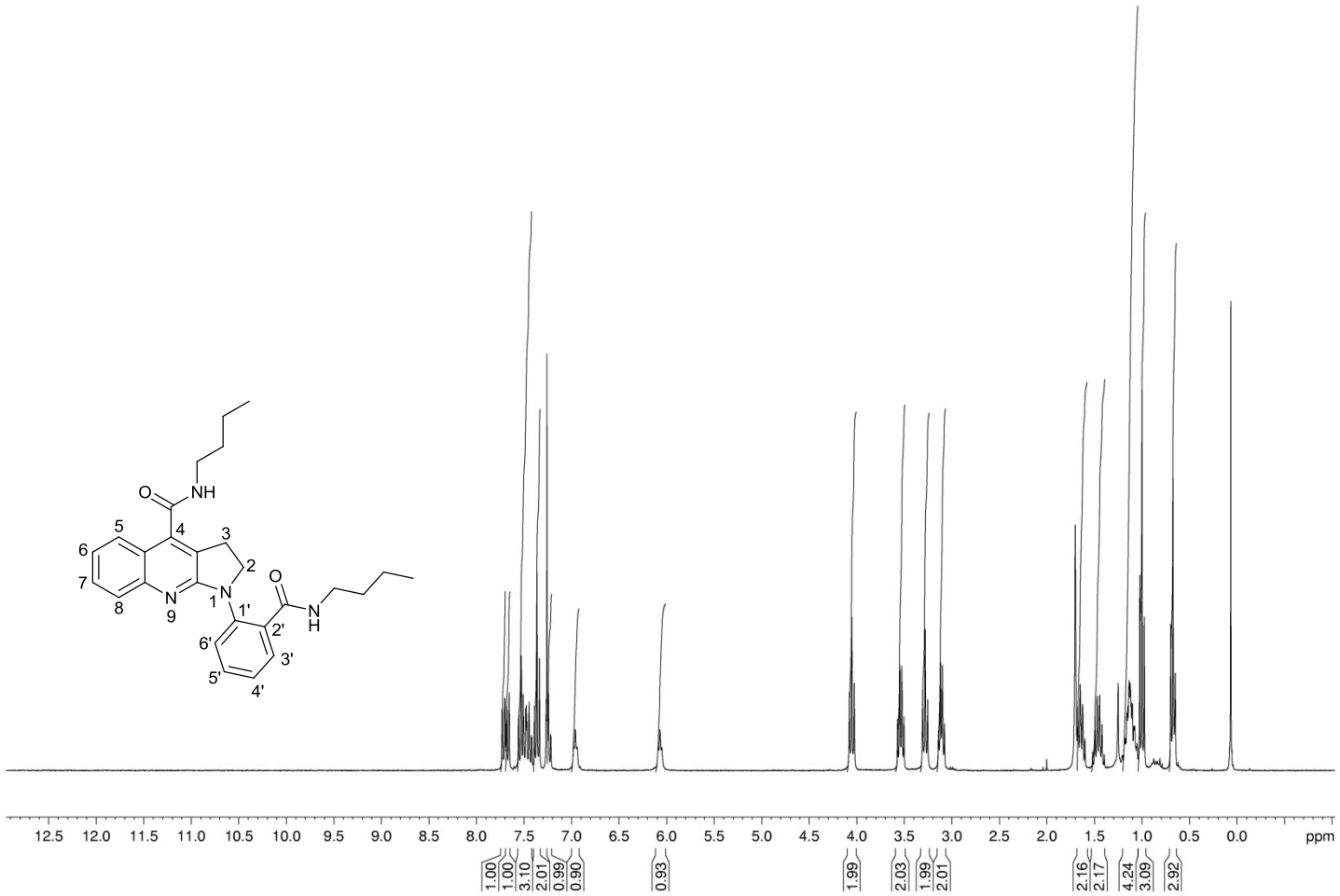
Compound 3d ^{1}H NMR ($CDCl_3$)



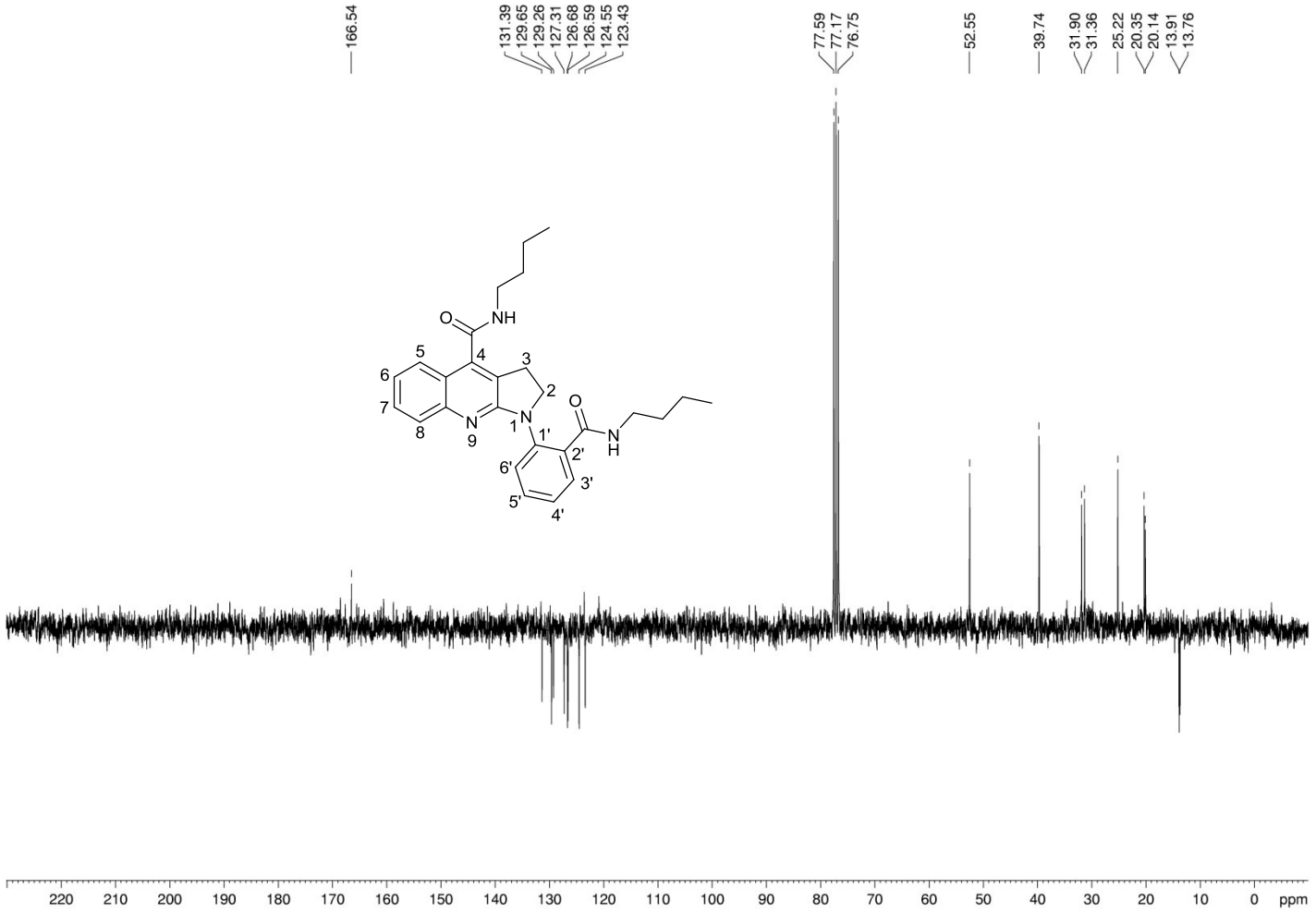
Compound 3d ^{13}C NMR ($CDCl_3$)



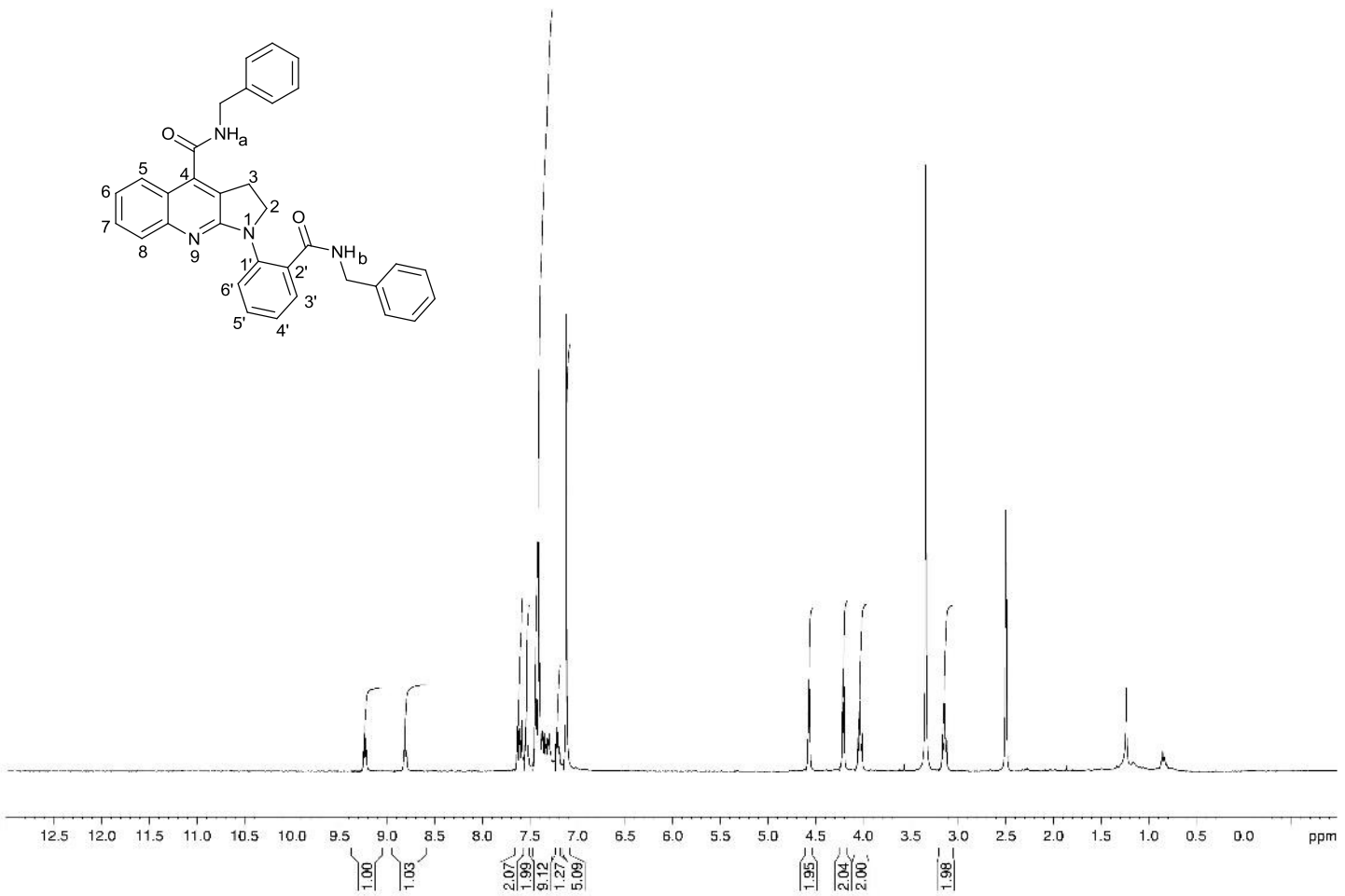
Compound 3e ^{1}H NMR ($CDCl_3$)



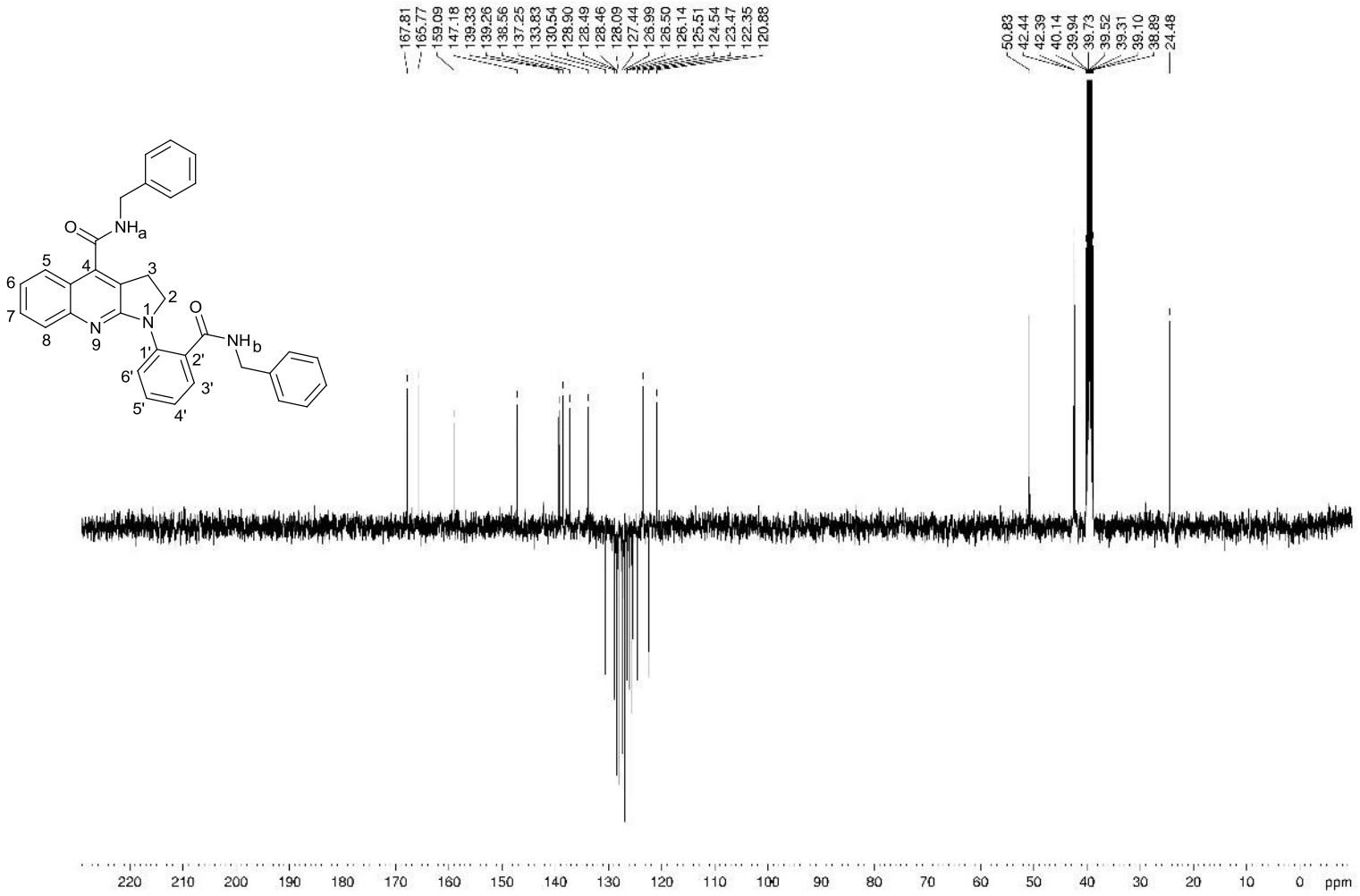
Compound 3e ^{13}C NMR ($CDCl_3$)



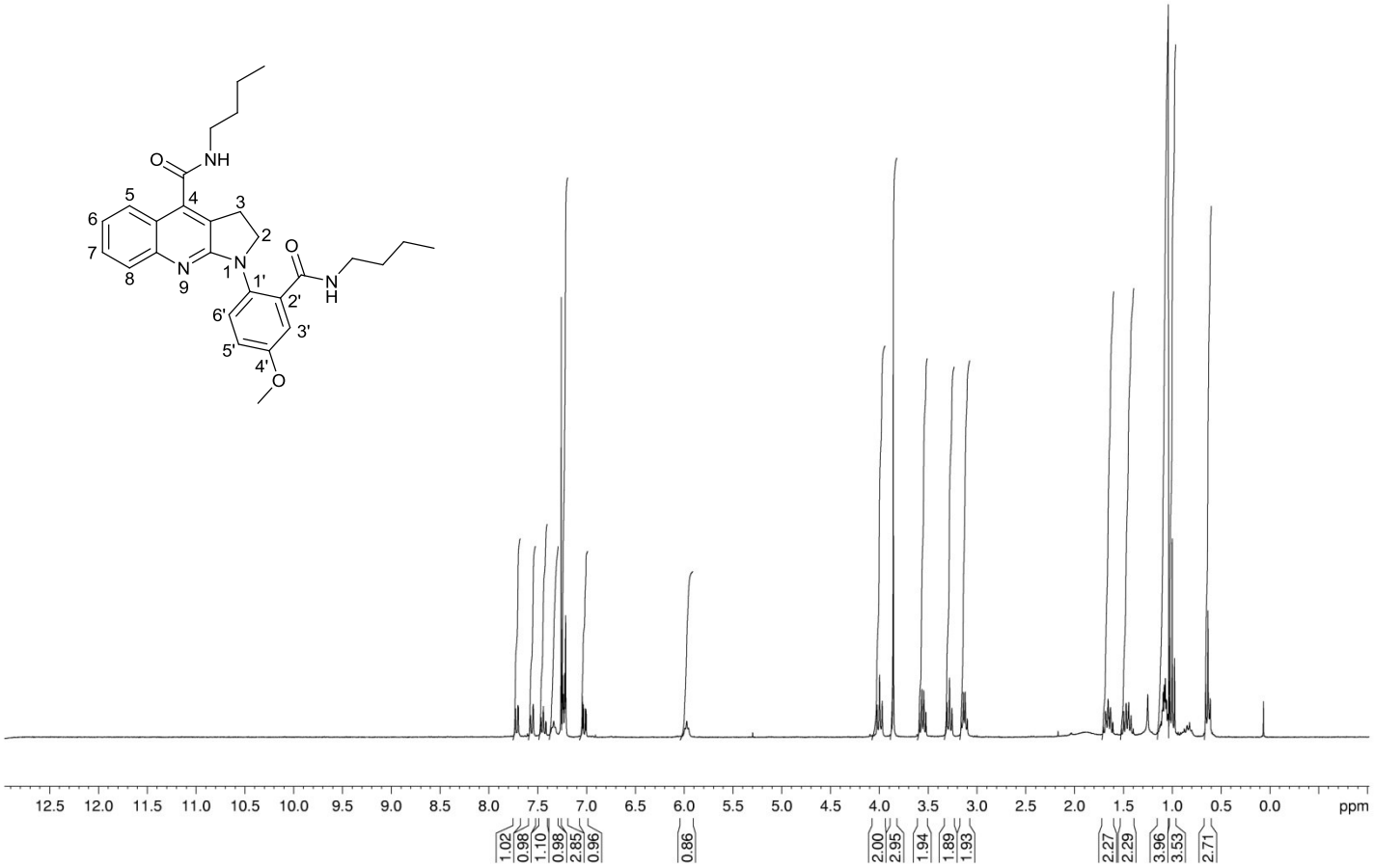
Compound 3f ^{1}H NMR (d_6-DMSO)



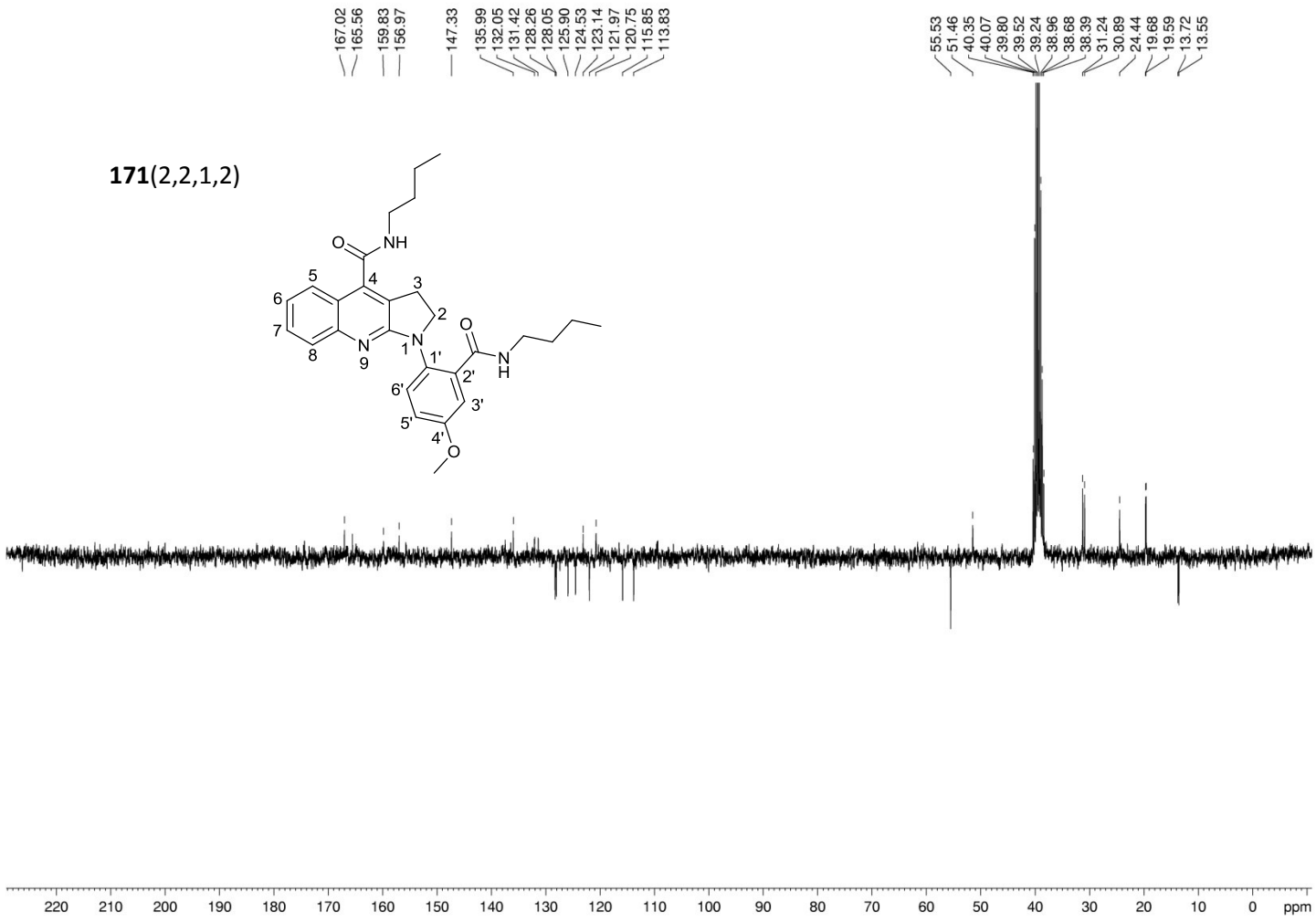
Compound 3f ^{13}C NMR (d_6-DMSO)



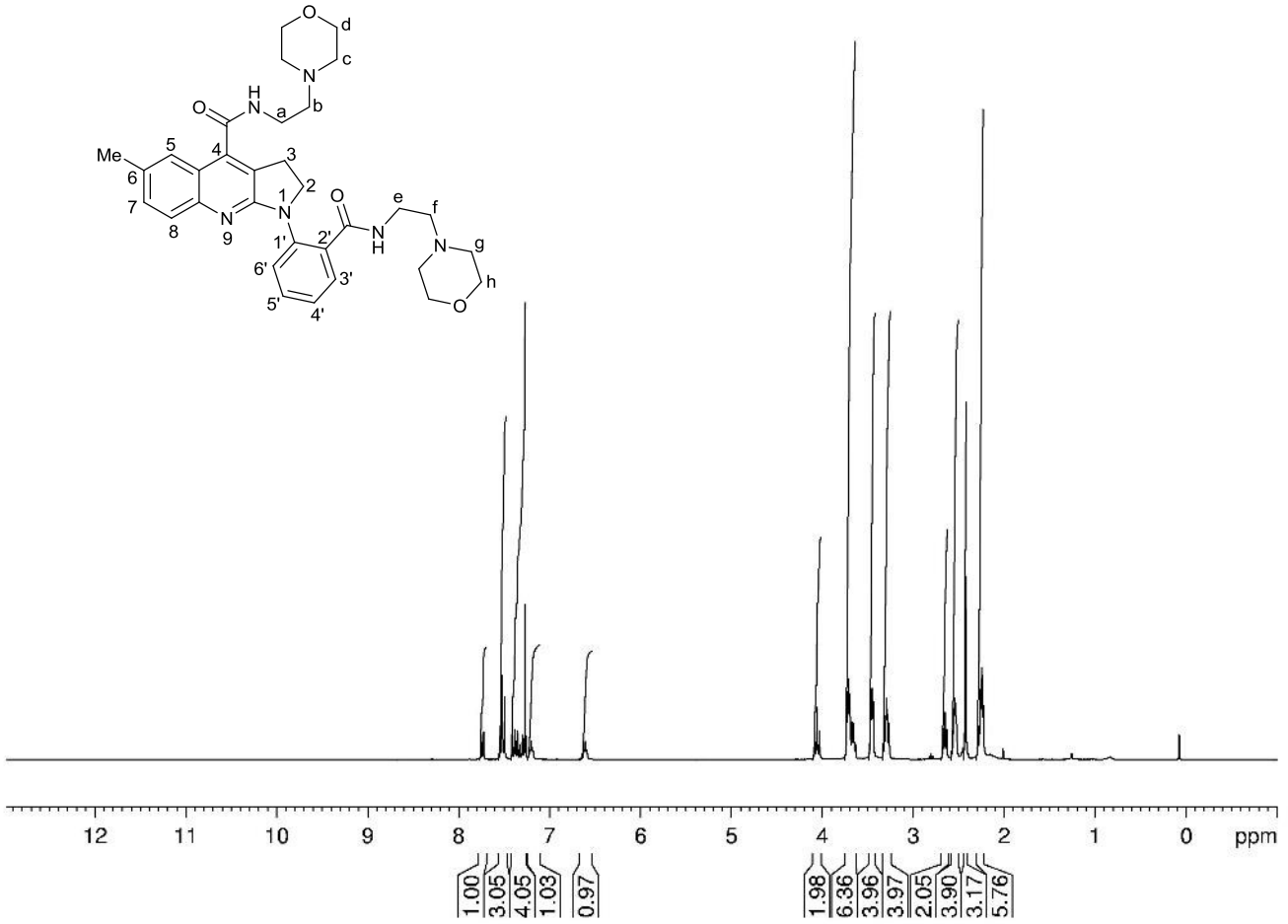
Compound 3g ^{1}H NMR ($CDCl_3$)



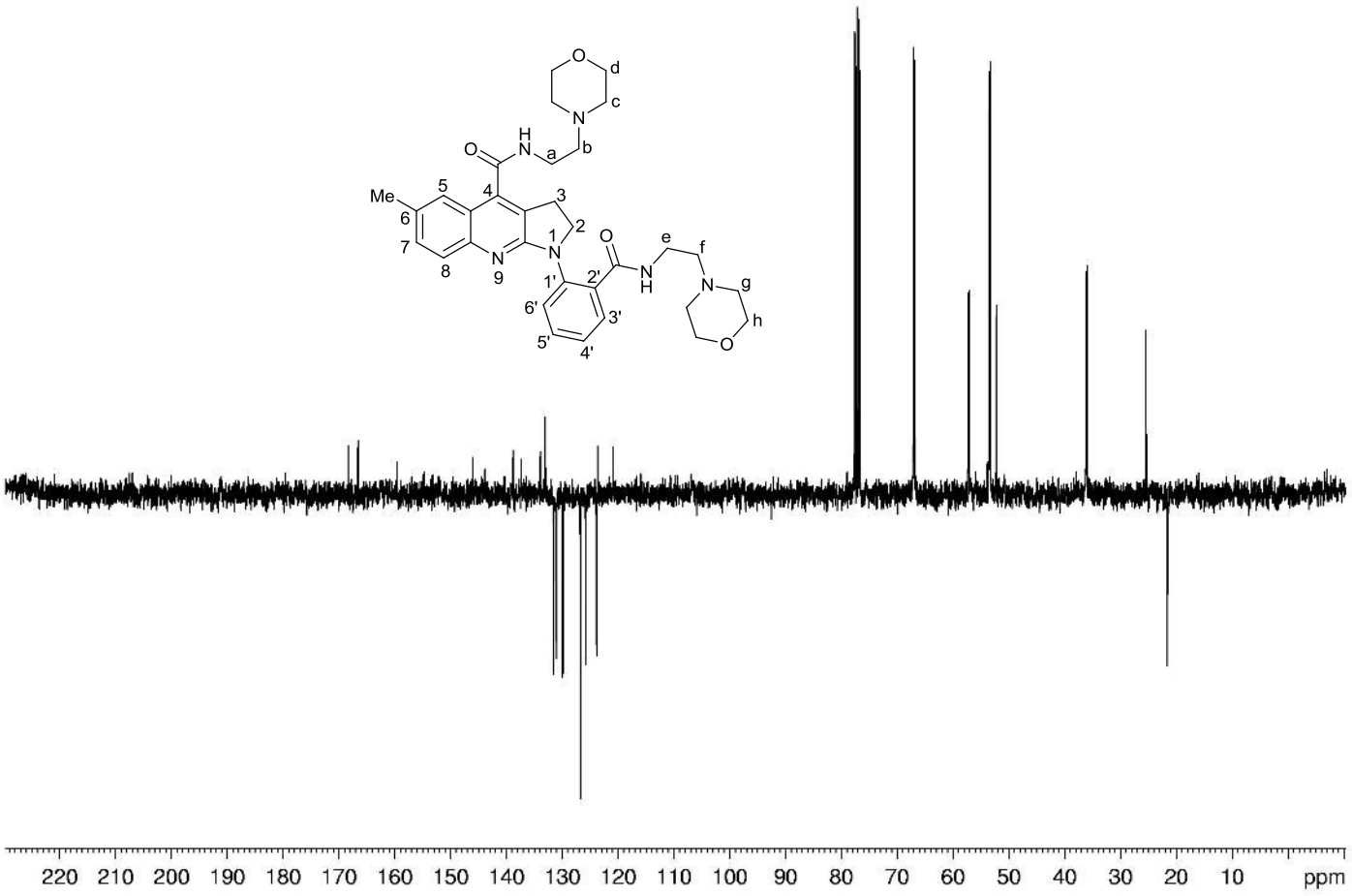
Compound 3g ^{13}C NMR (d_6-DMSO)



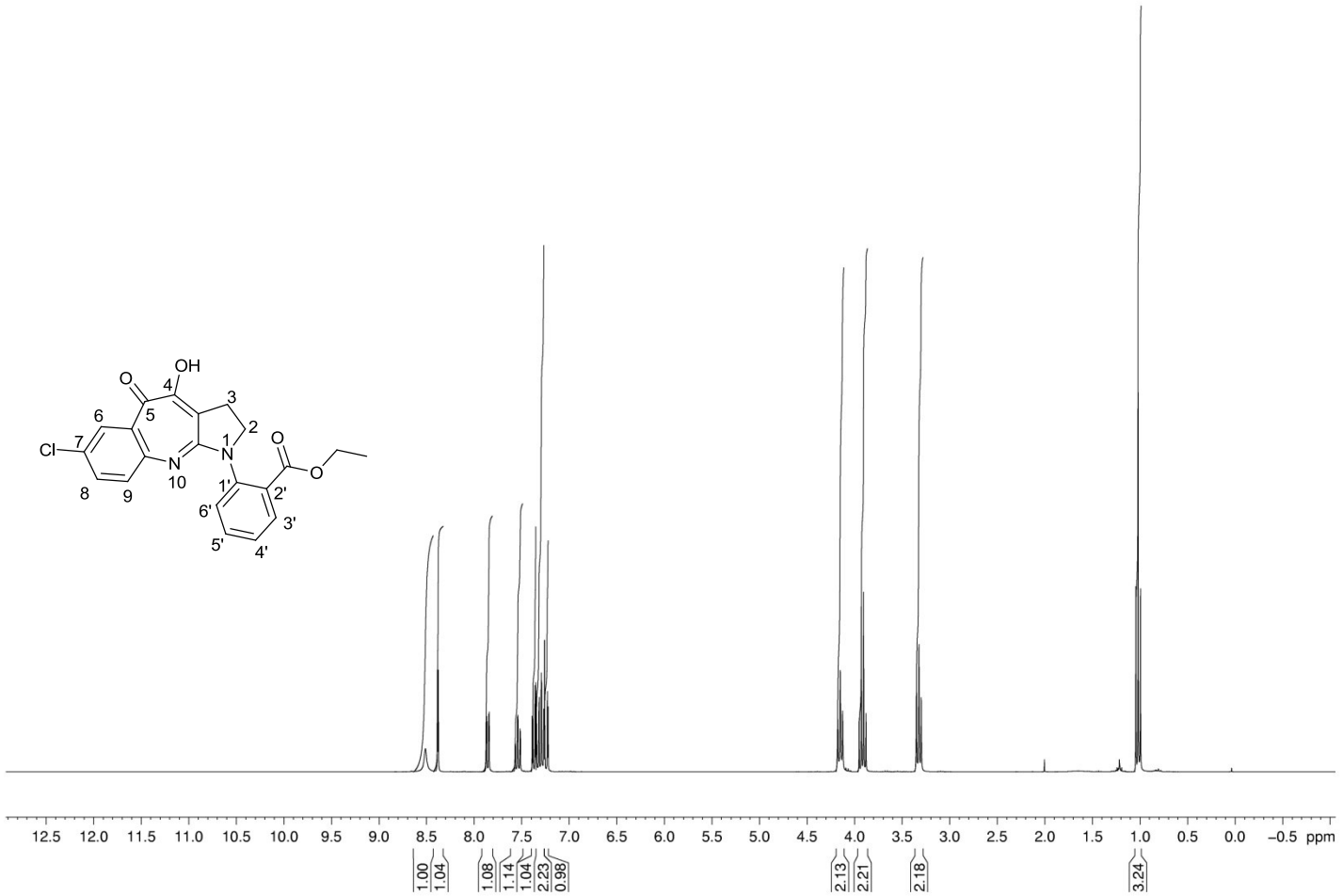
Compound 3h ^{1}H NMR ($CDCl_3$)



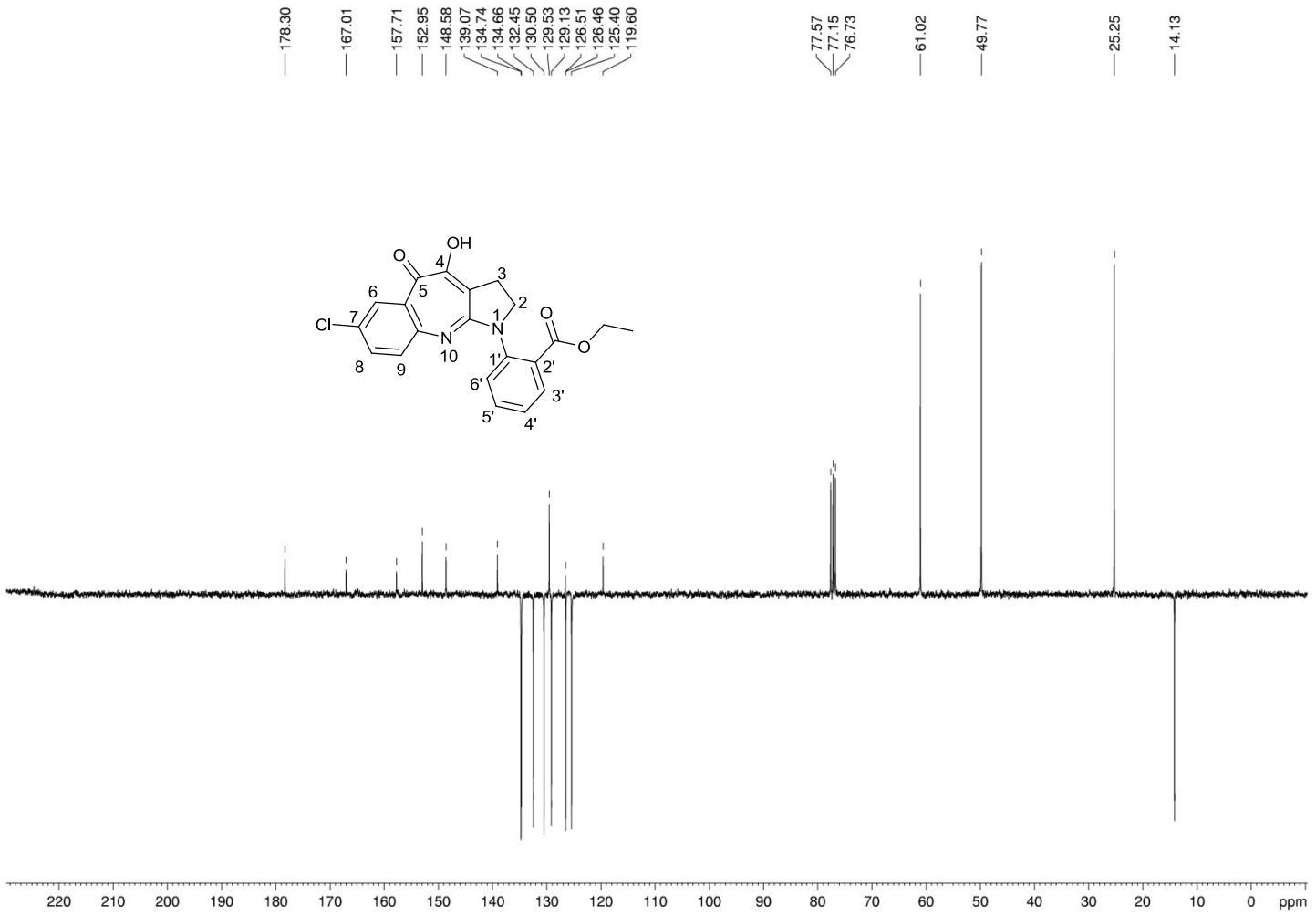
Compound 3h ^{13}C NMR ($CDCl_3$)



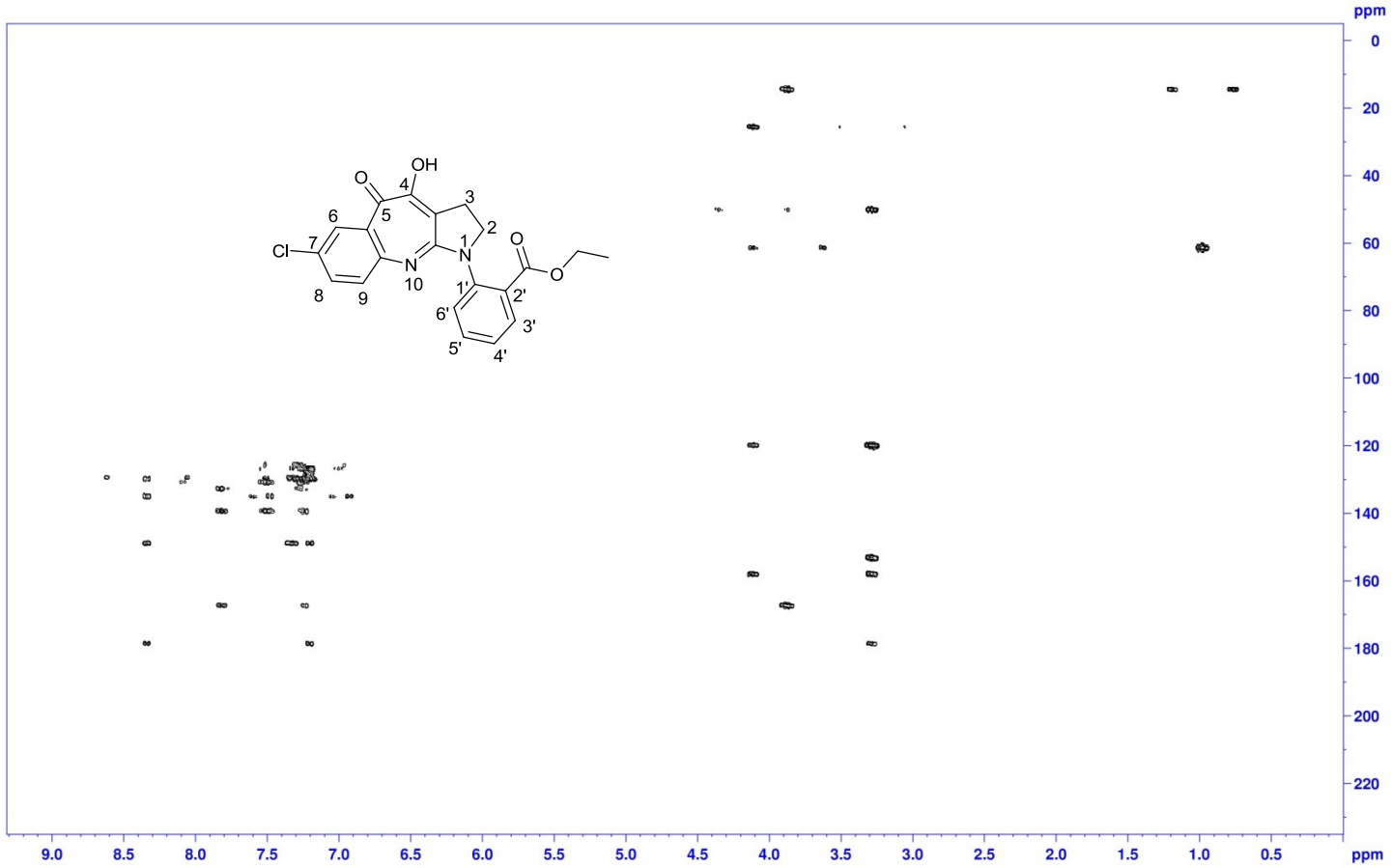
Compound 4 ^{1}H NMR ($CDCl_3$)



Compound 4 ^{13}C NMR ($CDCl_3$)



Compound 4 2D NMR ($CDCl_3$)



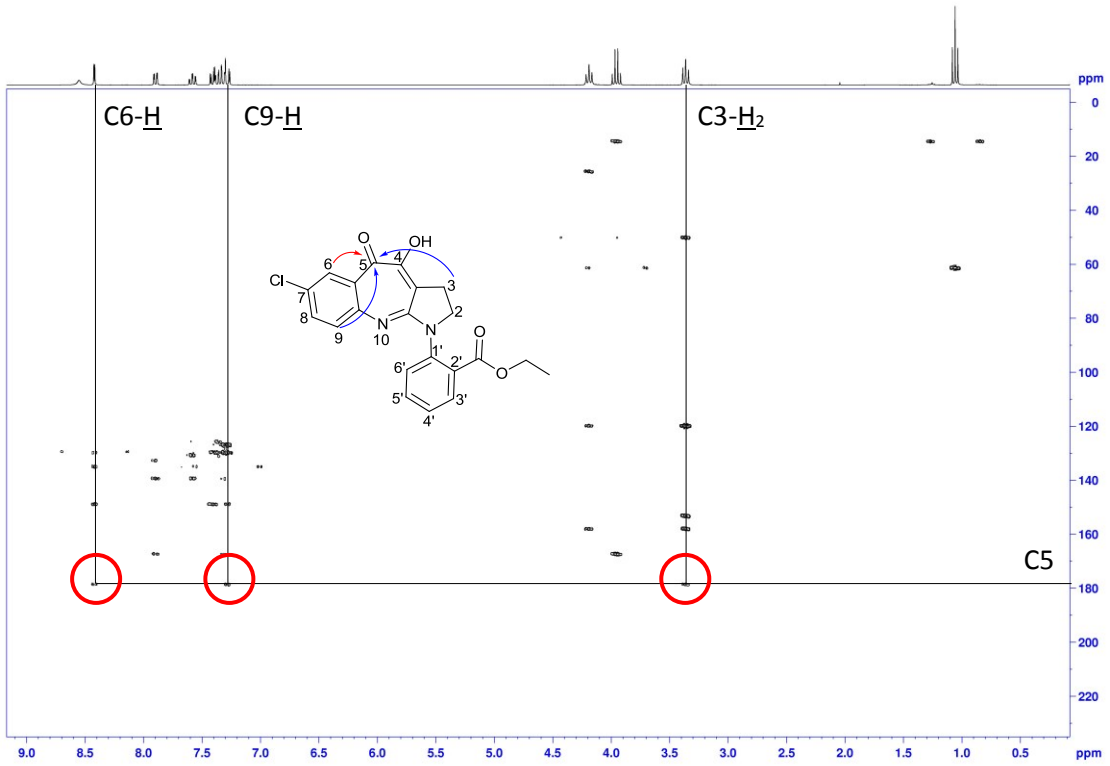


Figure S1: ^{1}H-^{13}C HMBC NMR spectrum of **4** showing selected correlations that were used to determine the structure of ring B.

References

S1 A. M.Jones, G. Liu, M. M. Lorion, S. Patterson, A. M. Z. Slawin, N. J. Westwood, *Chem. Eur. J.,* 2011, **17**, 5714.

S2 J. L. C. Marais, W. Pickl, B. Staskun, *J. Org. Chem.,* 1990, **55**, 1969.