Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Zinc-Catalyzed Chemoselective Alkylation of α-Keto Amides with 2-Alkylazaarenes

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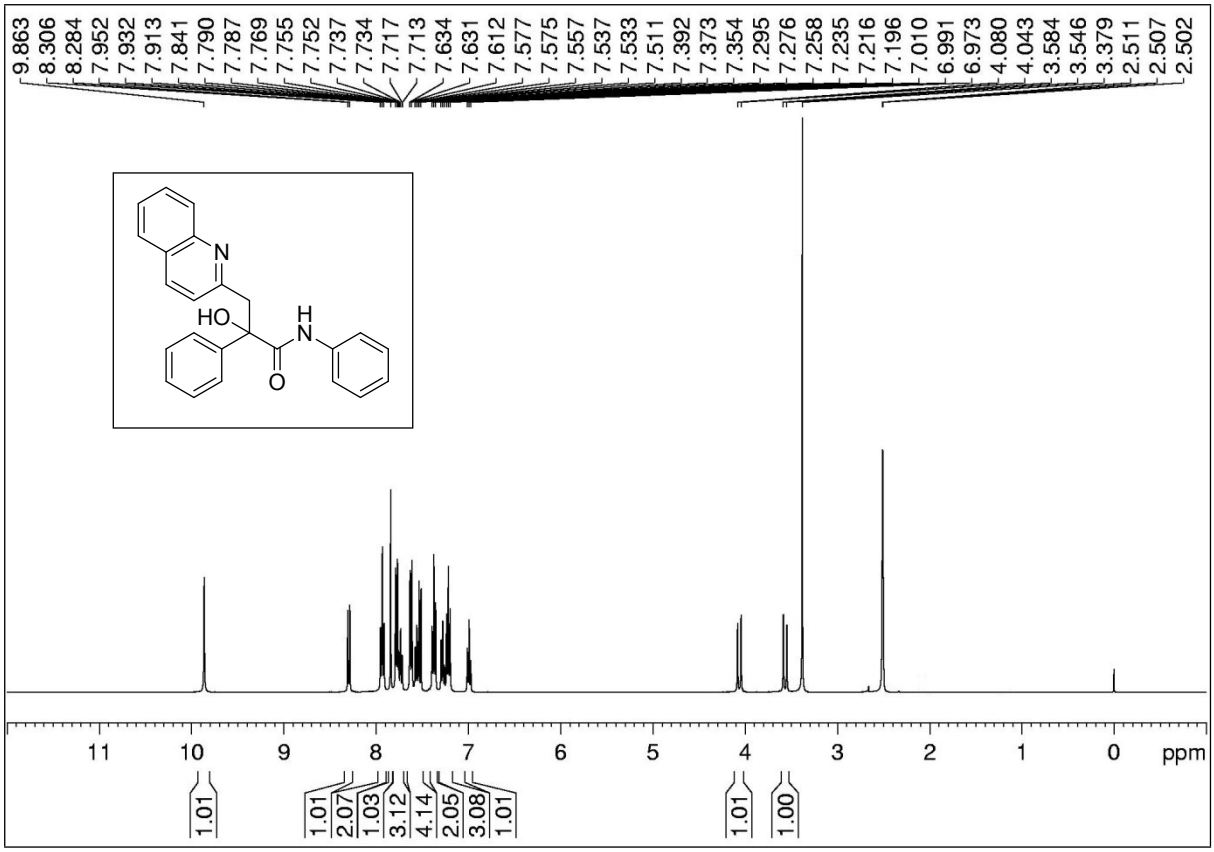
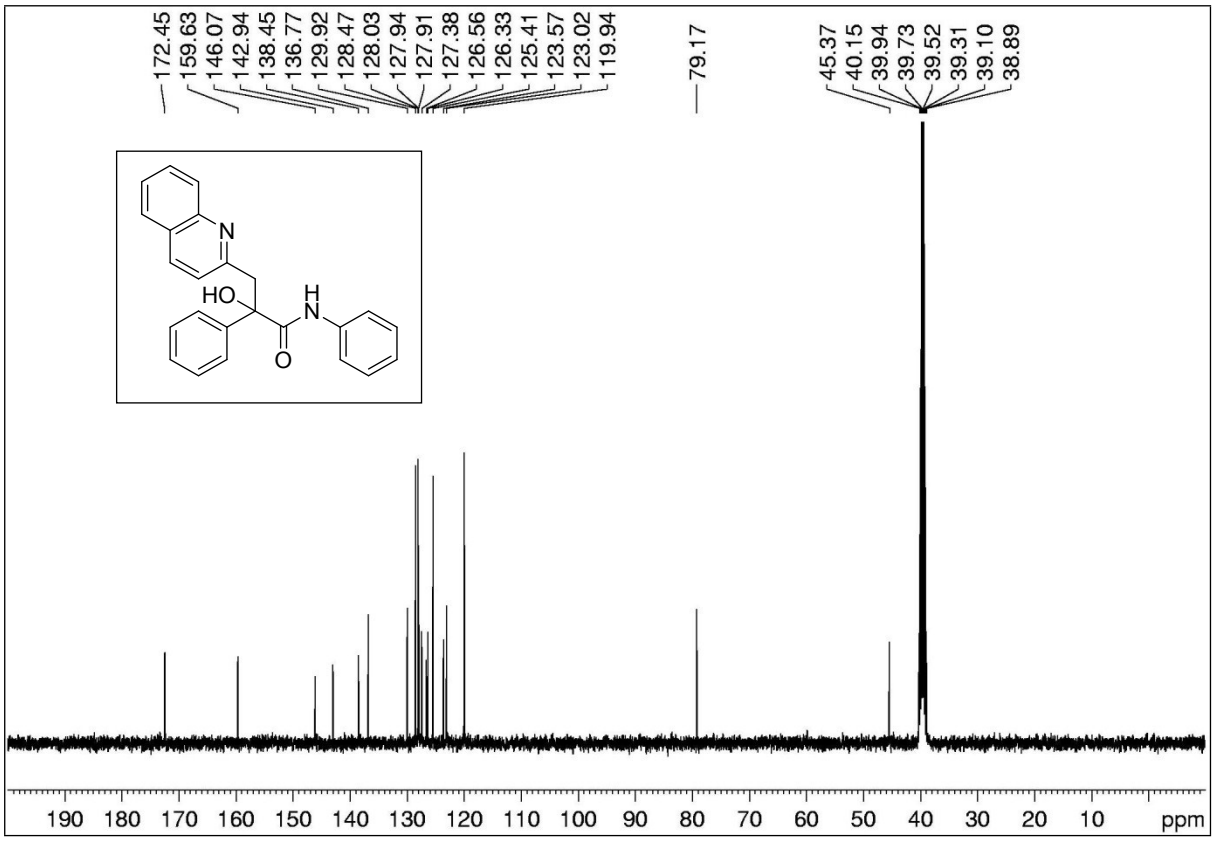
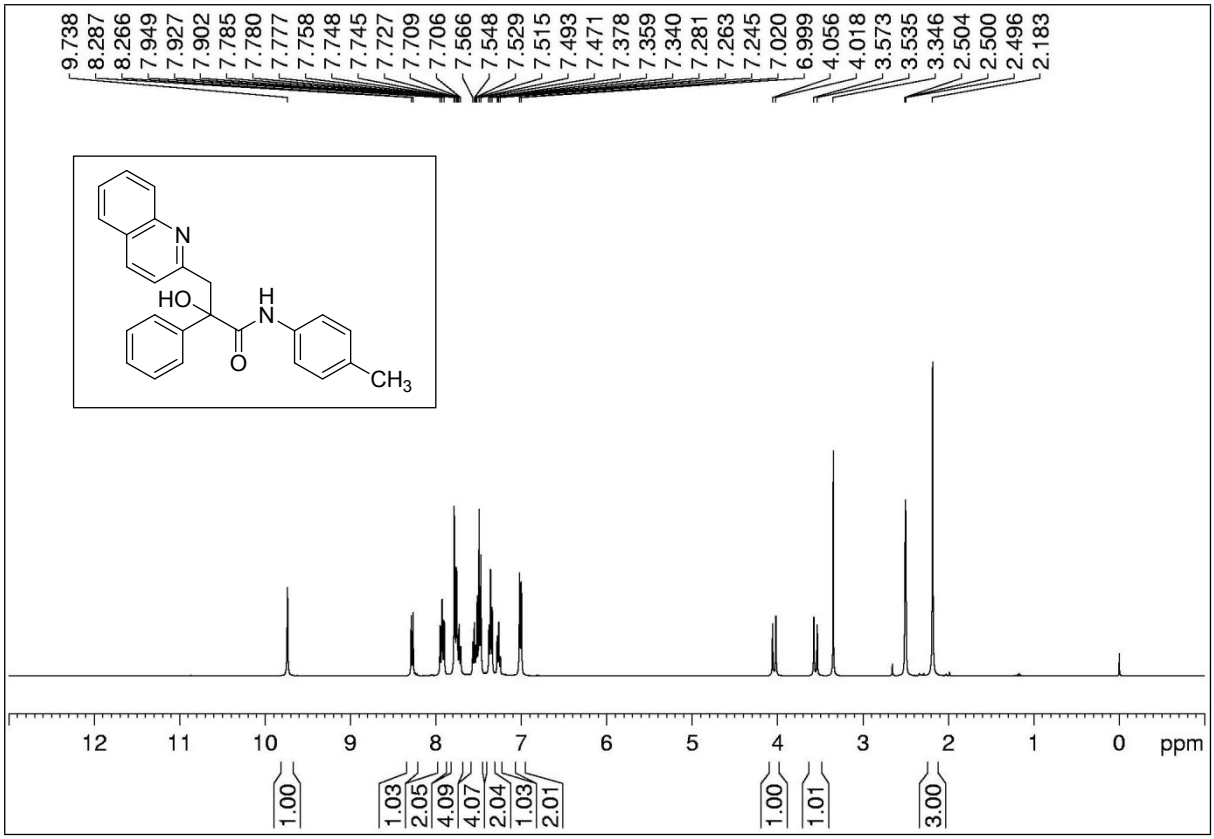
Copies of ^{1}H and ^{13}C spectra for all compounds



400 MHz ^{1}H-NMR spectra of **3a** in DMSO-d_6



100 MHz ^{1}H-NMR spectra of **3a** in DMSO-d_6



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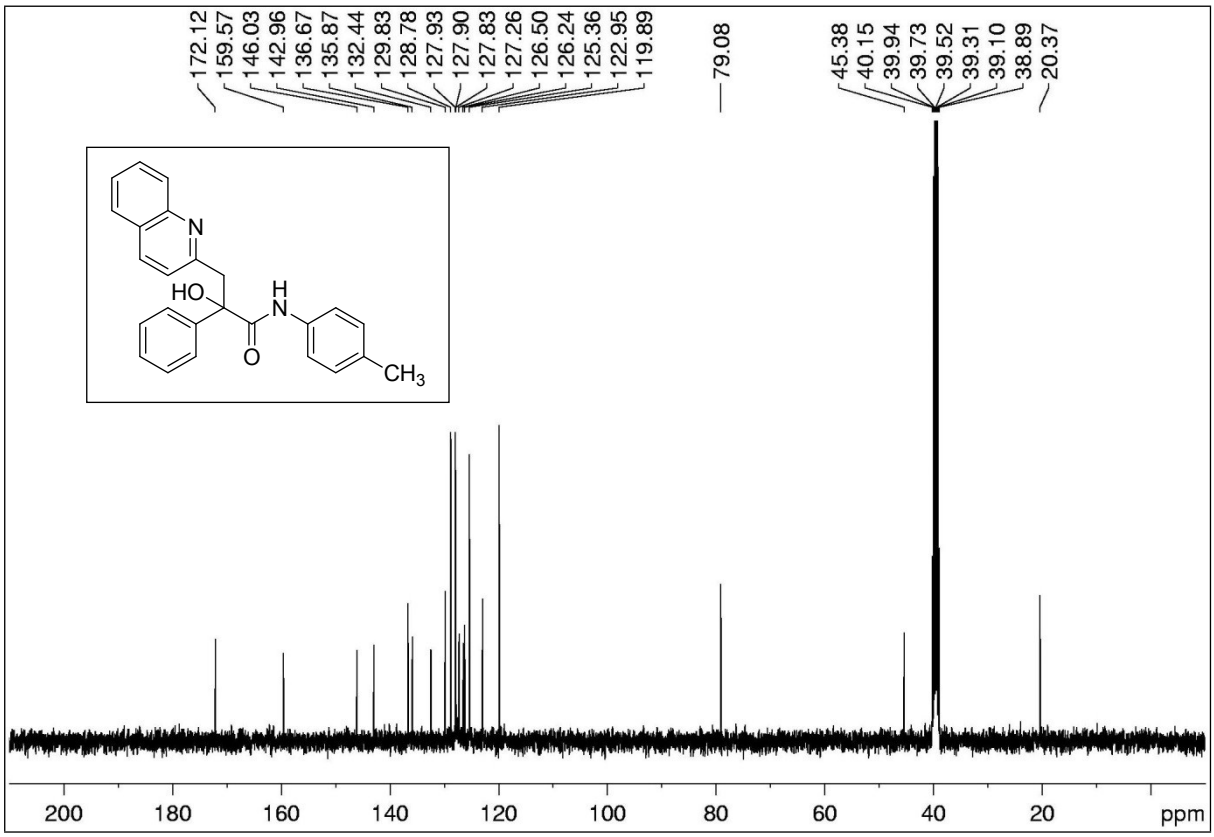

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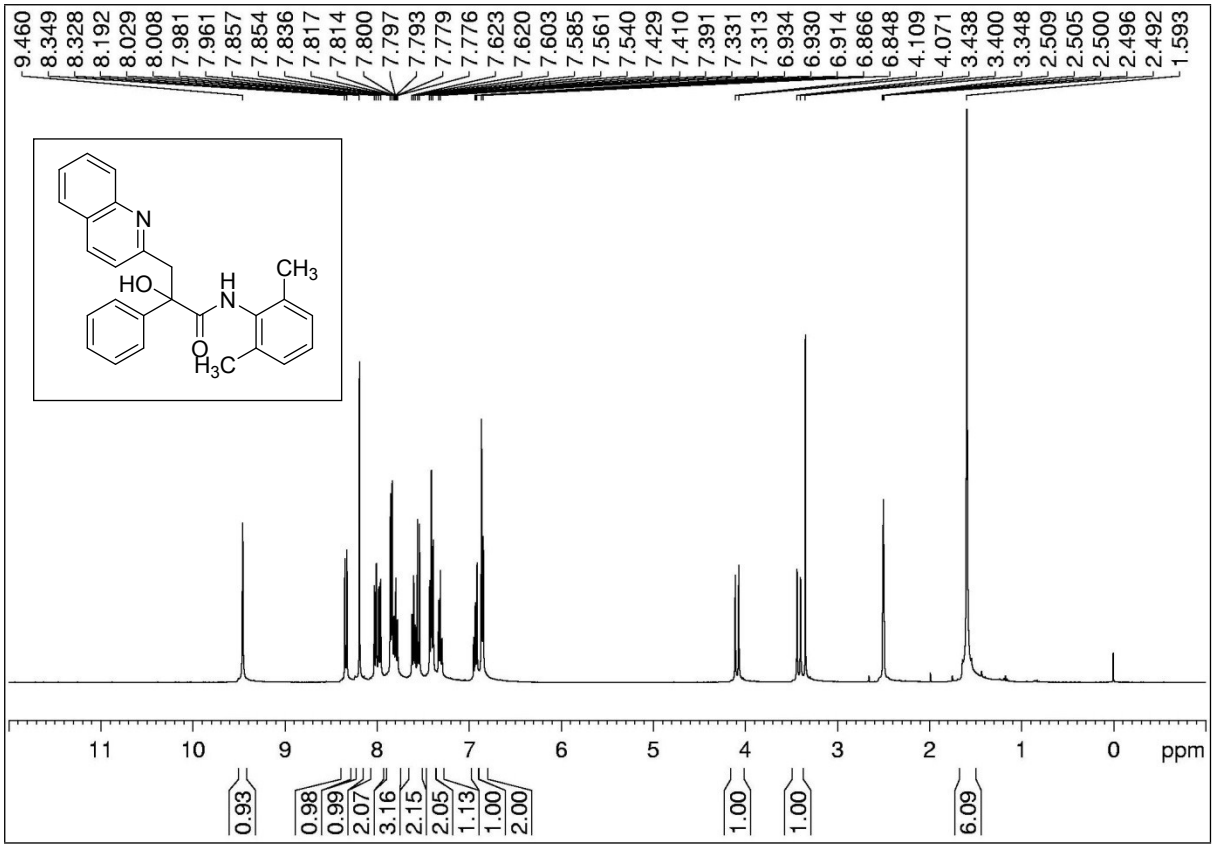

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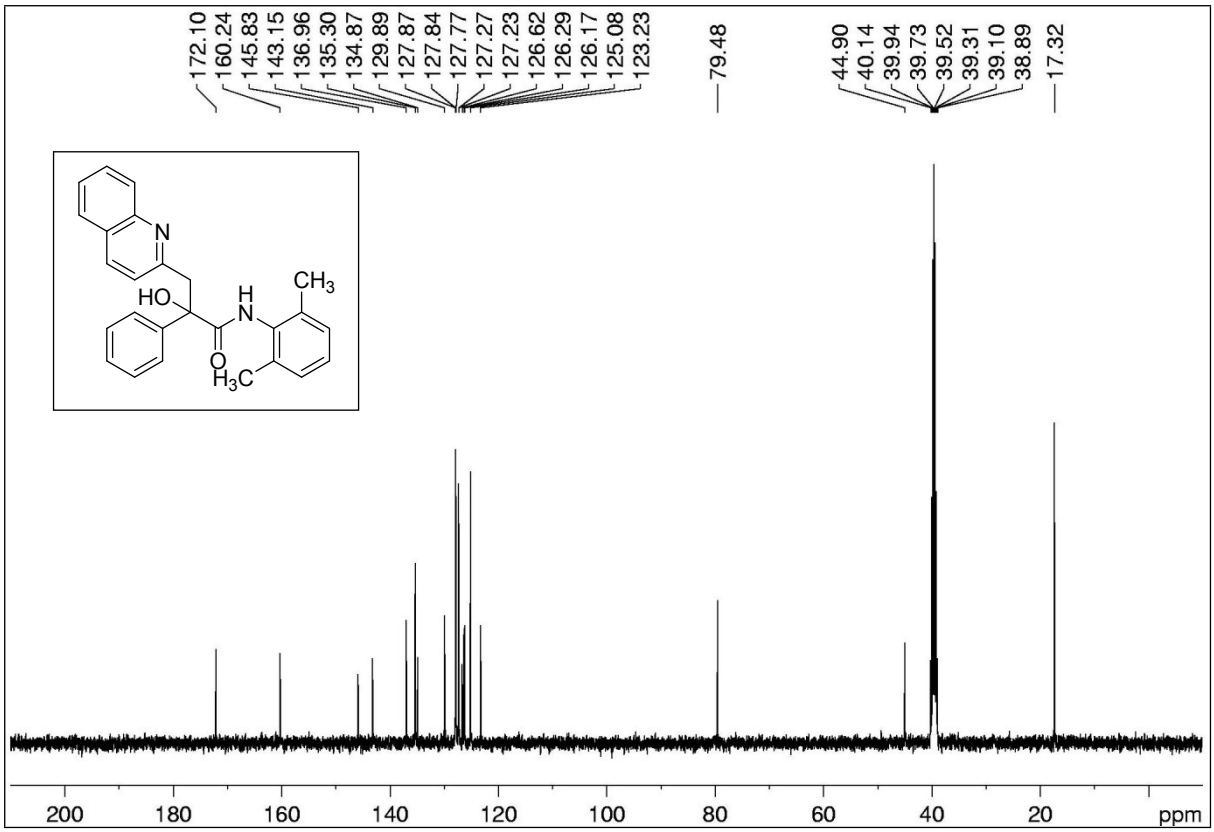

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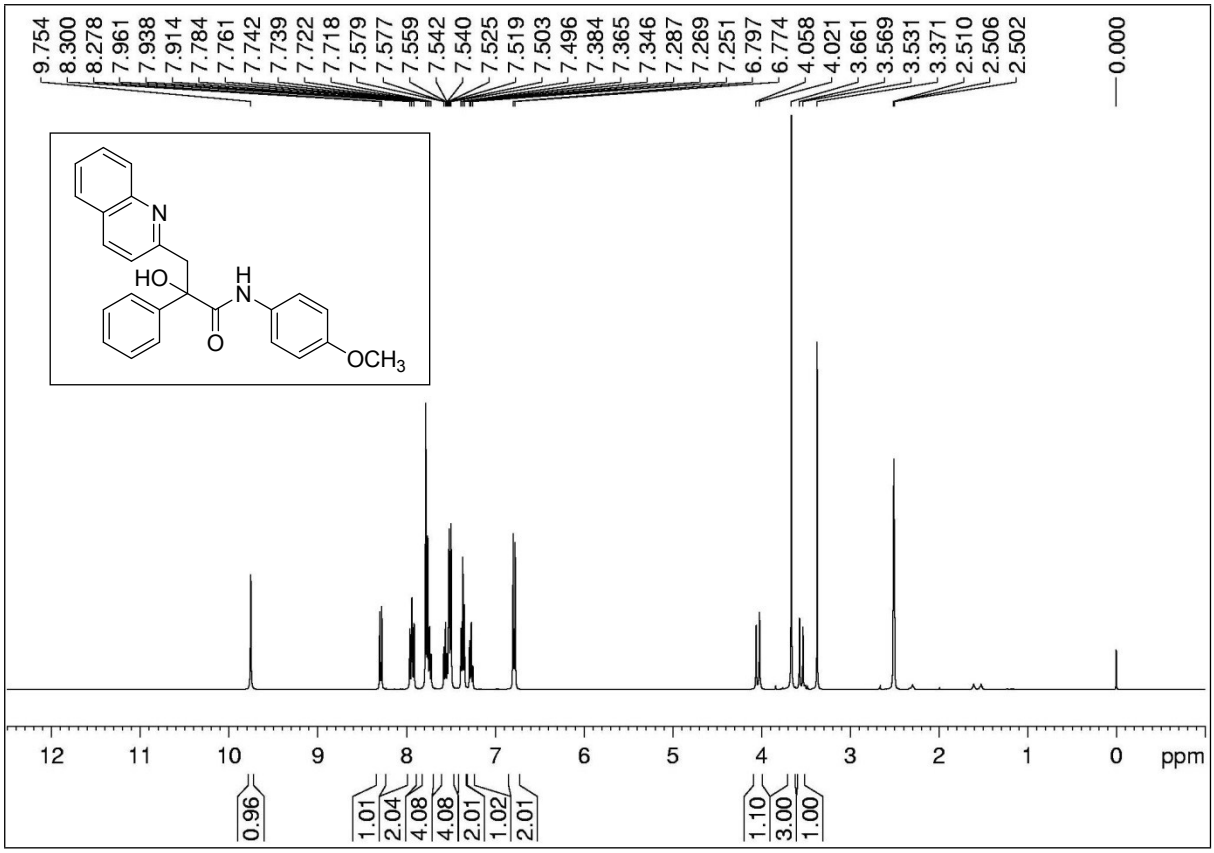

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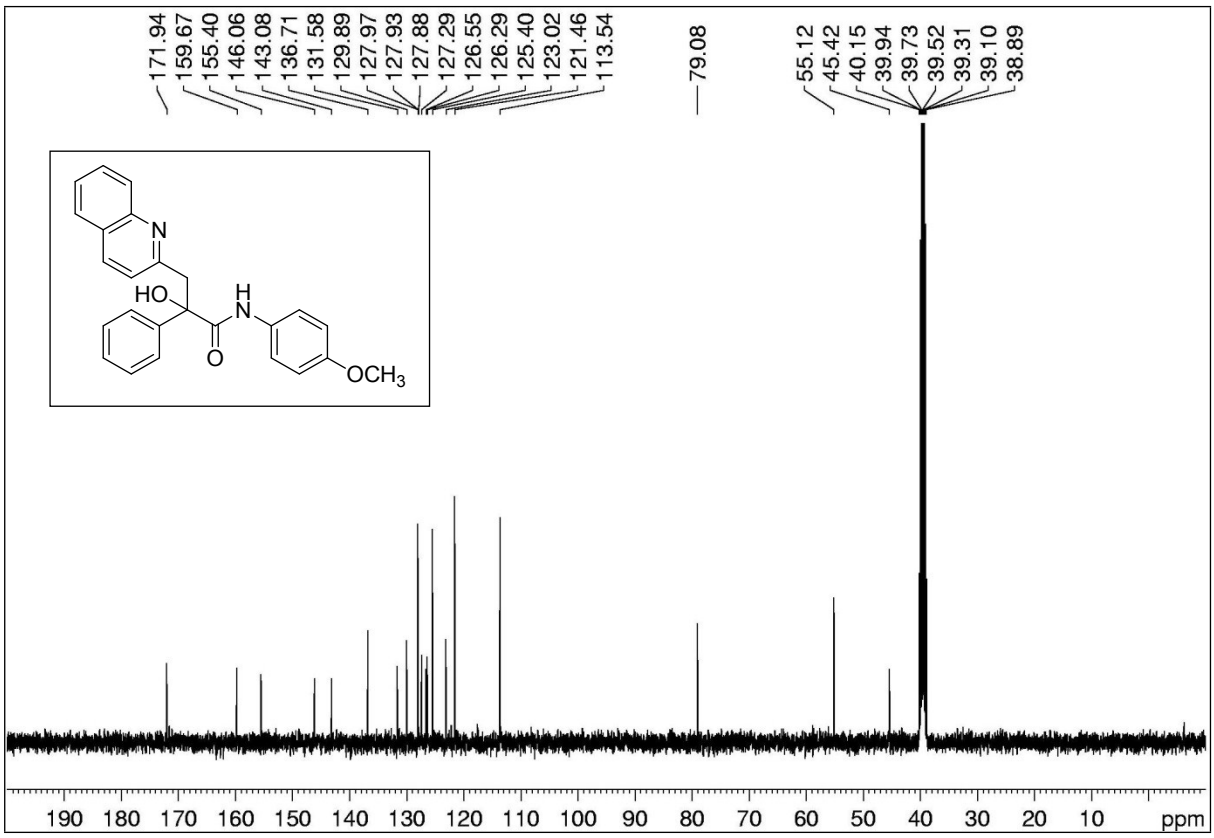

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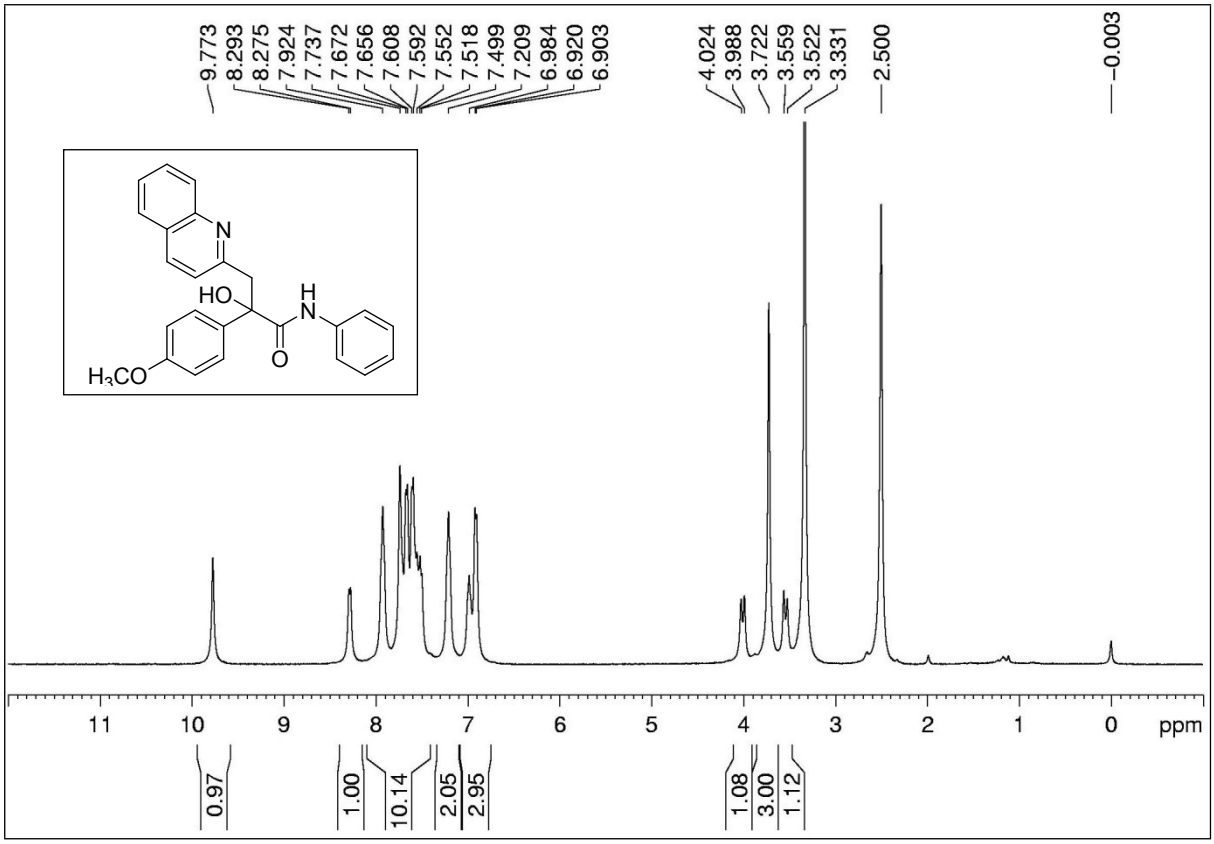

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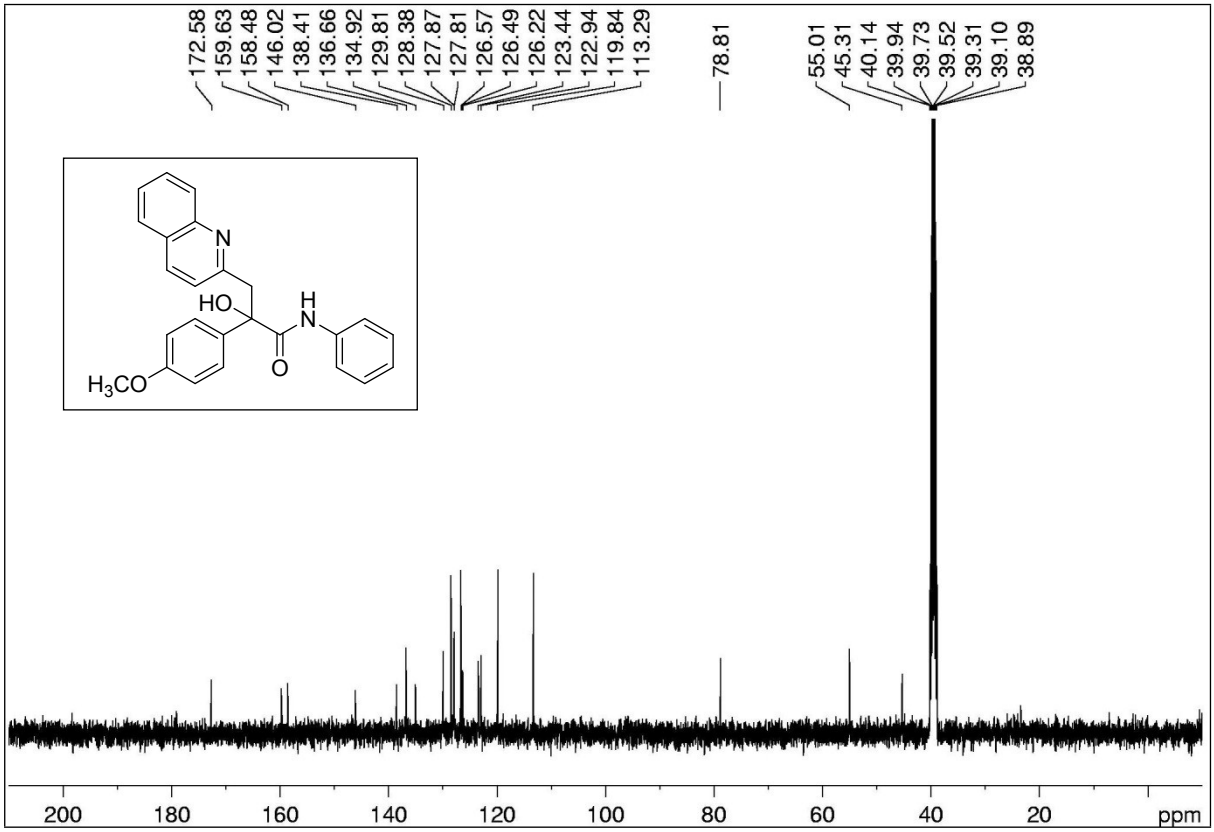

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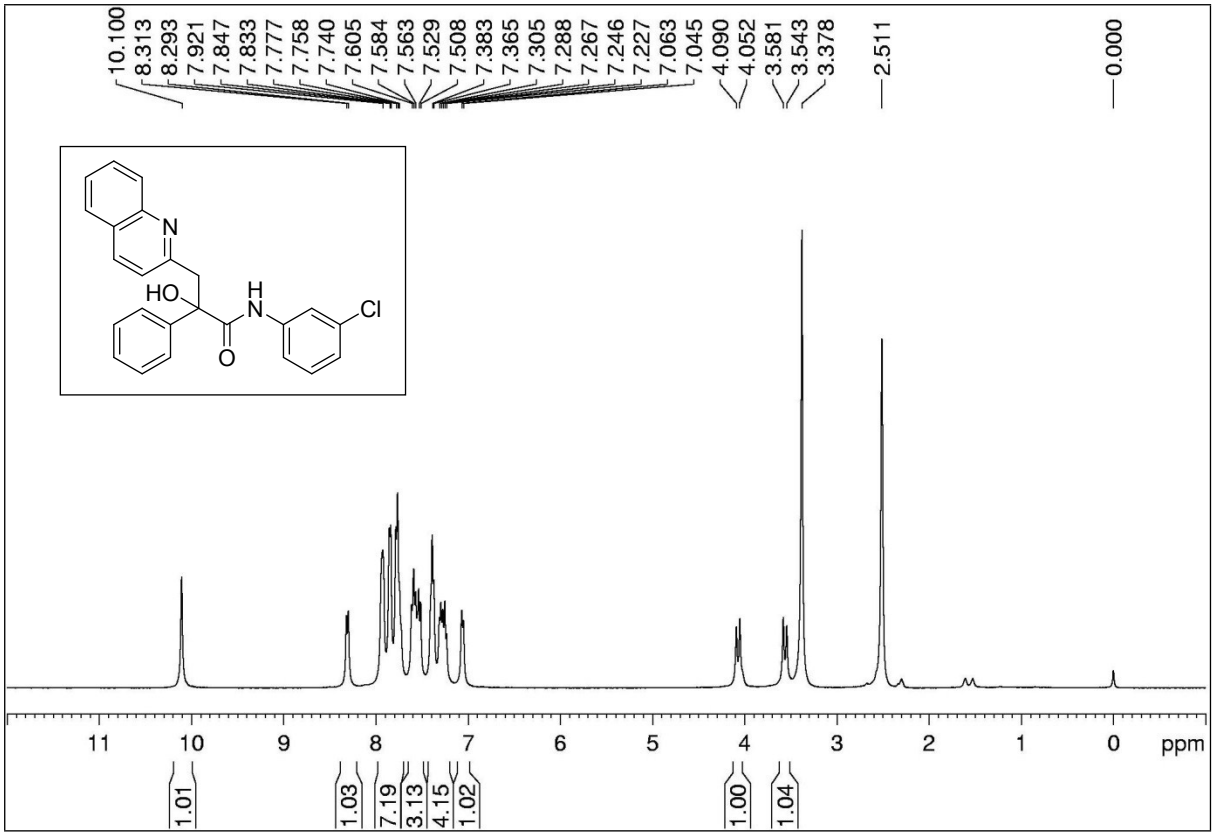

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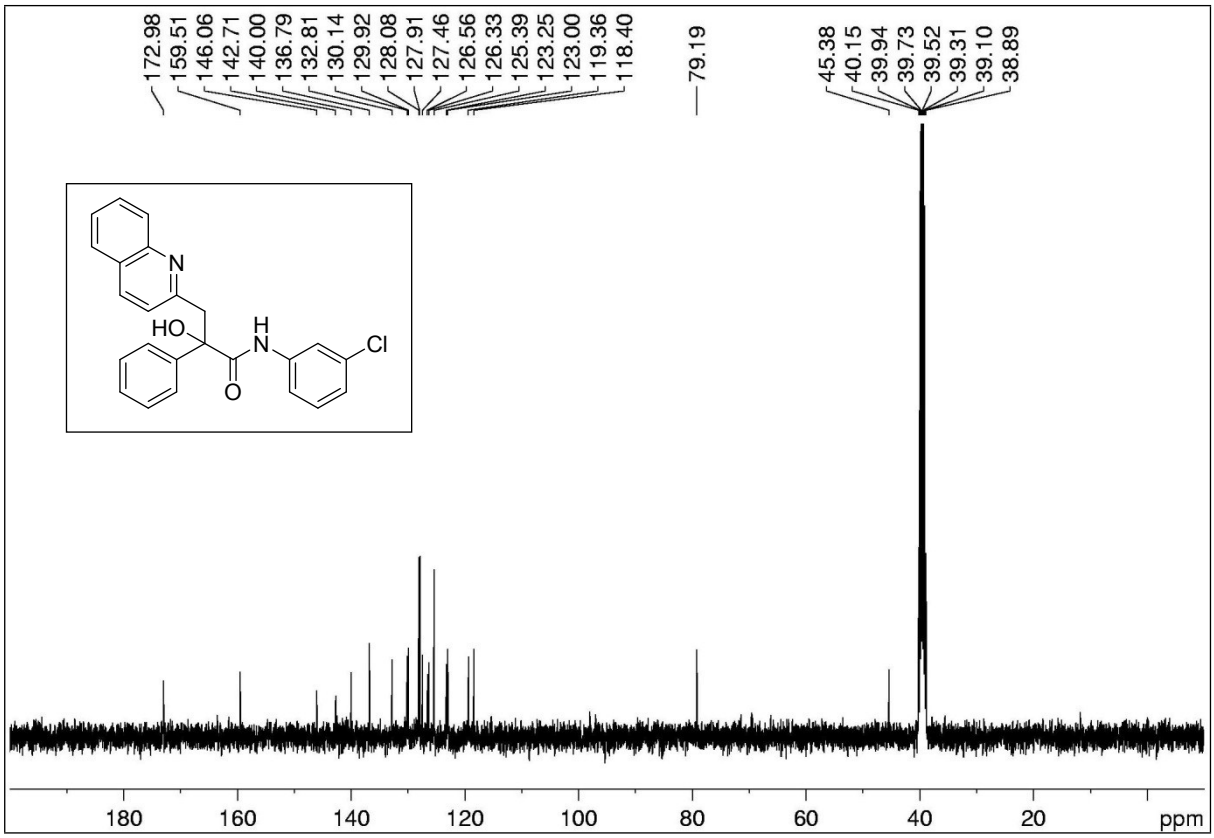

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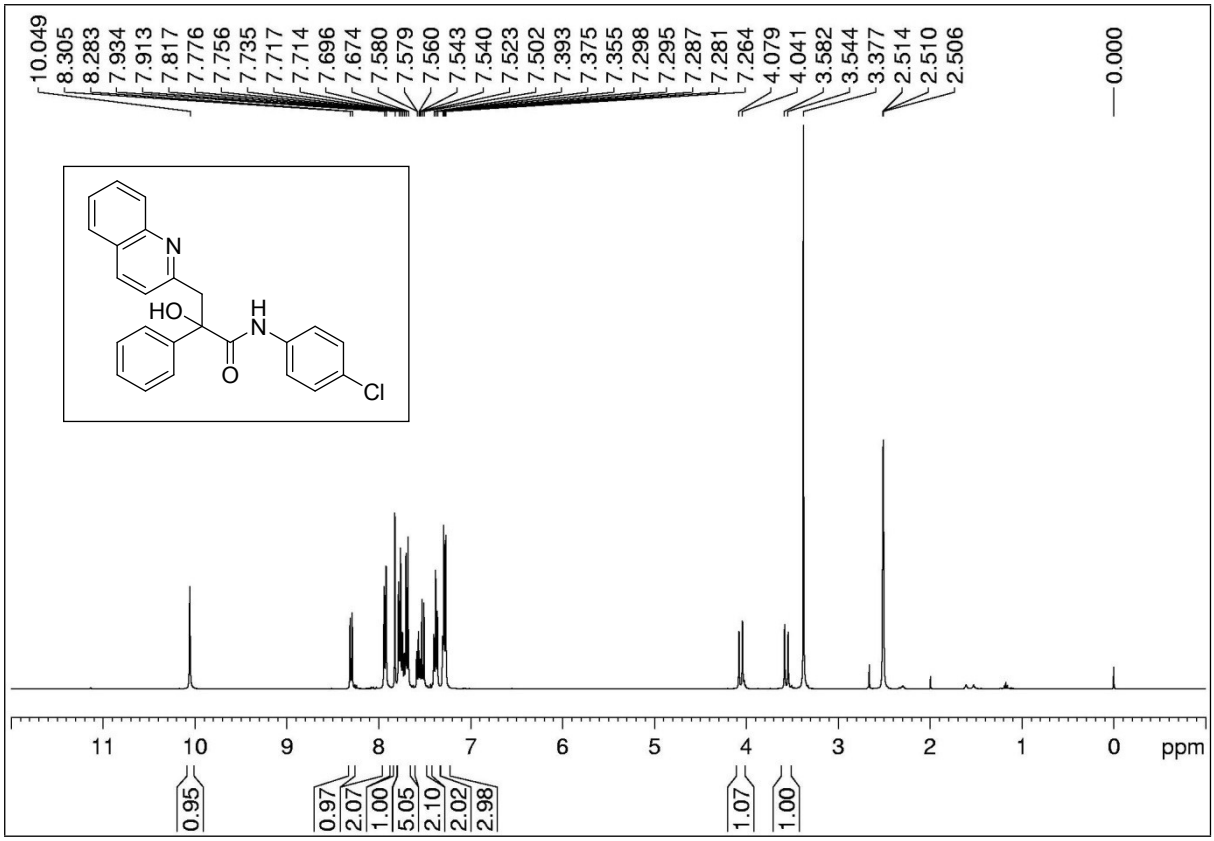

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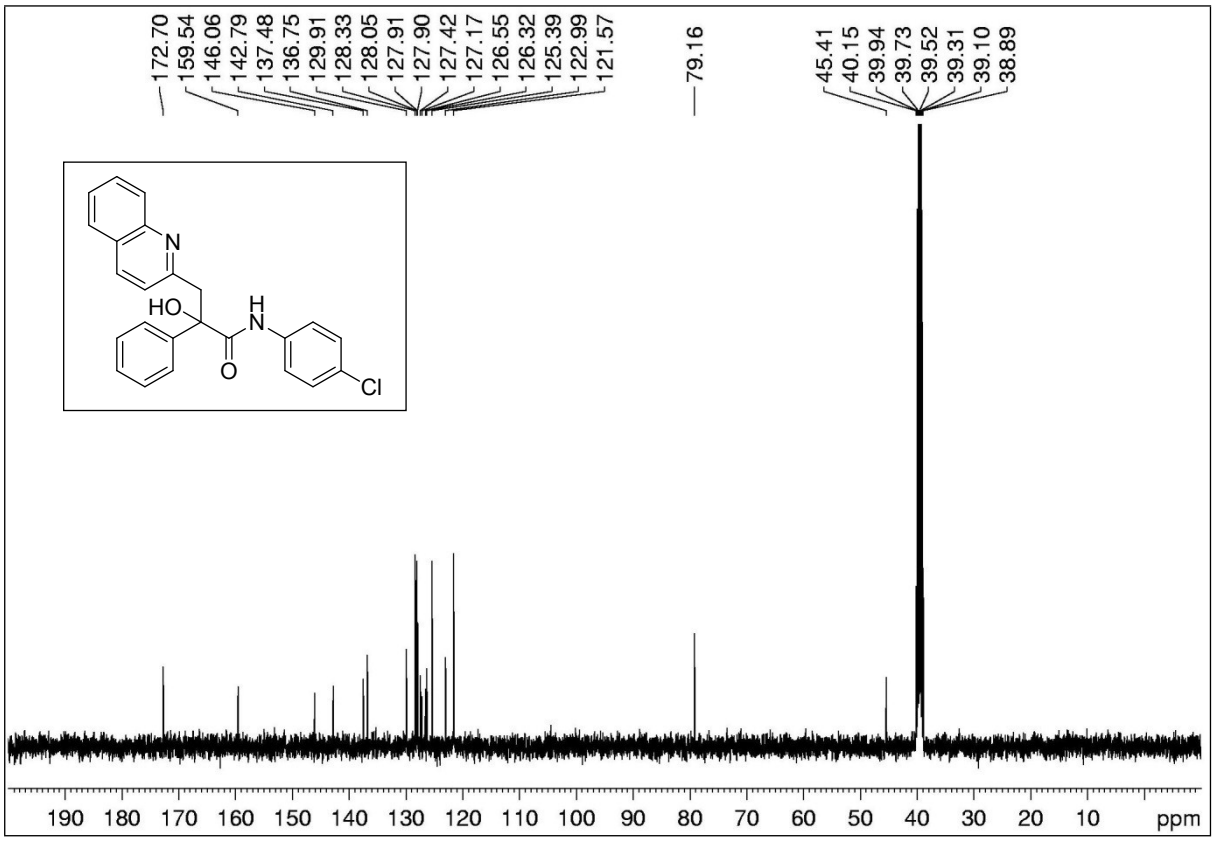

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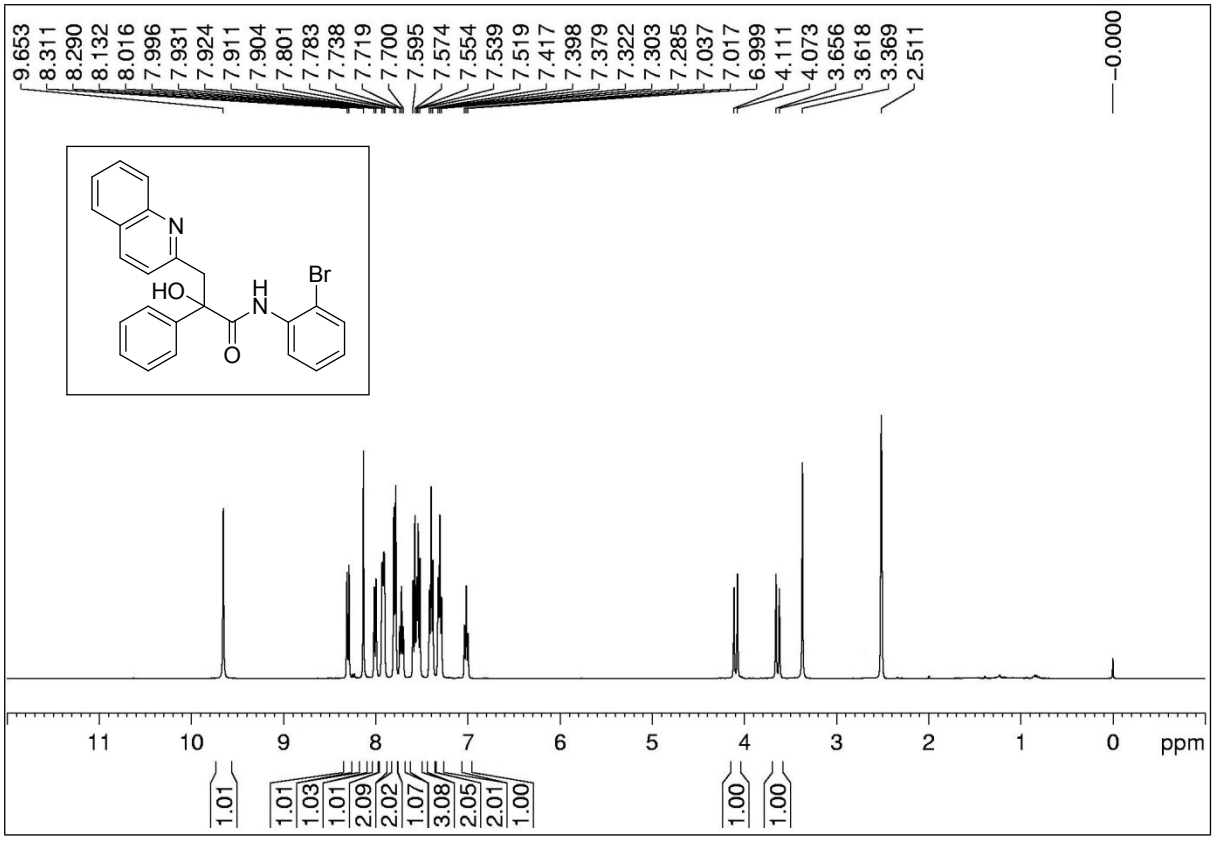

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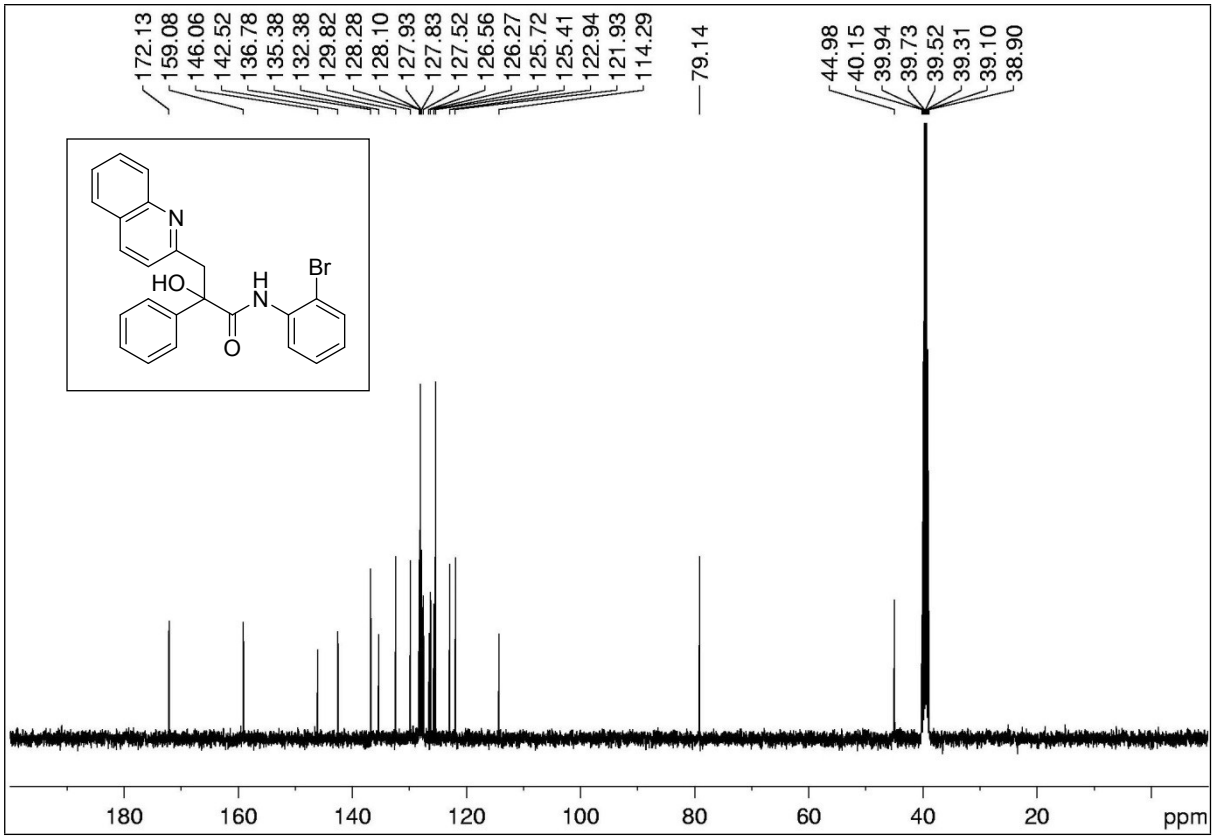

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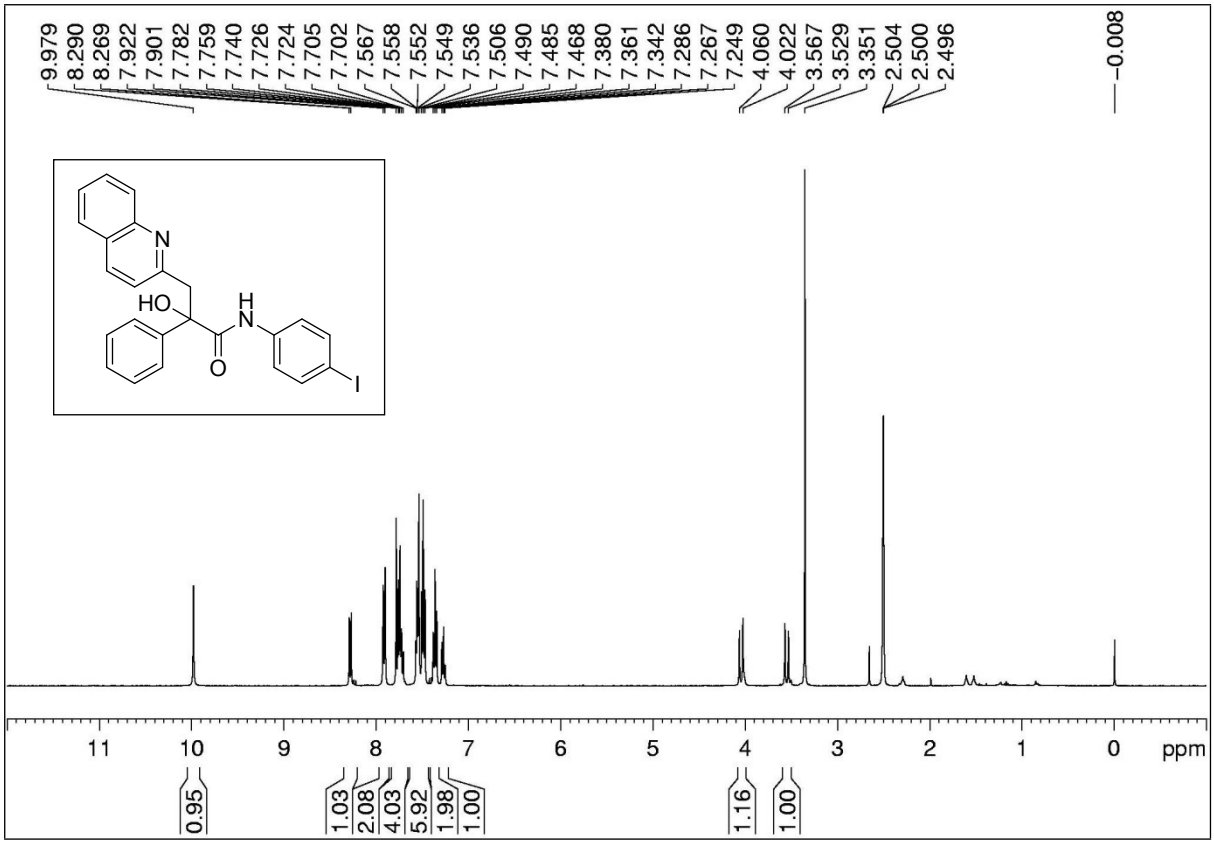

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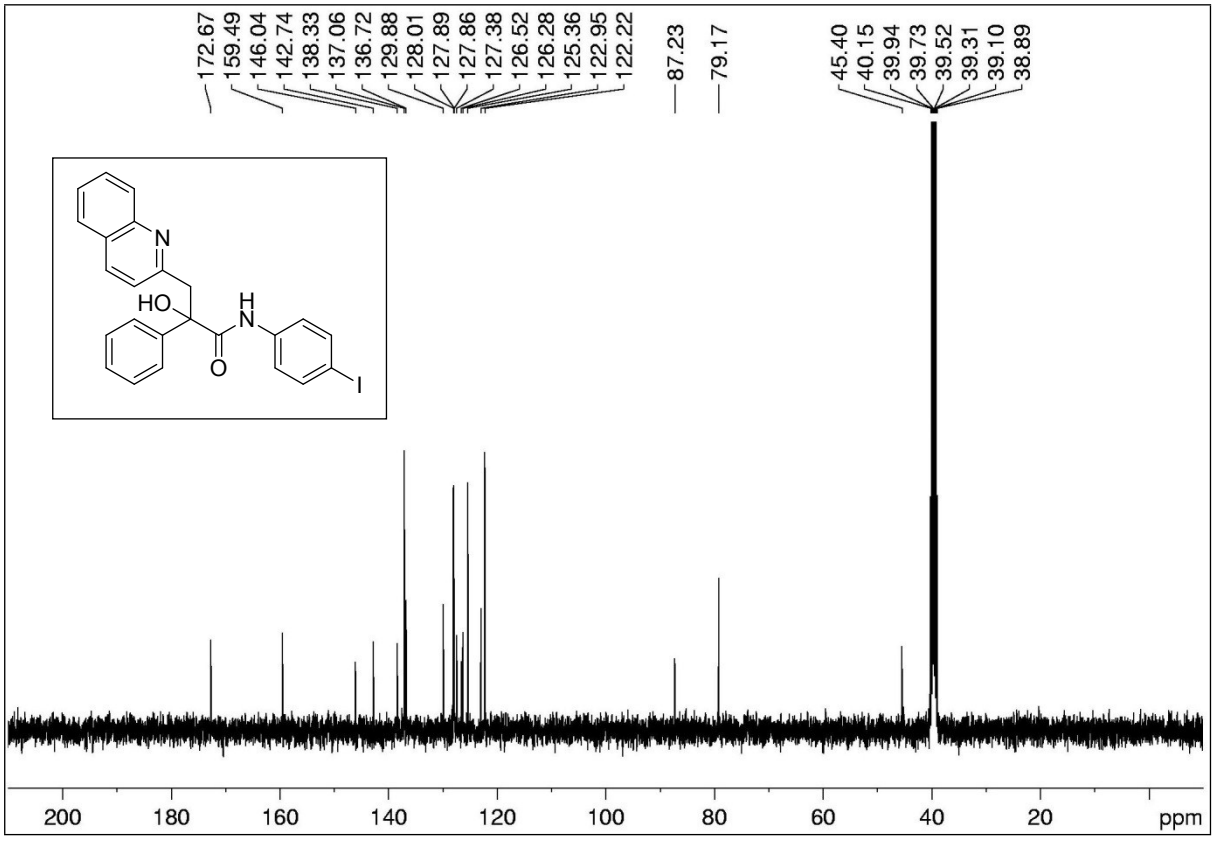

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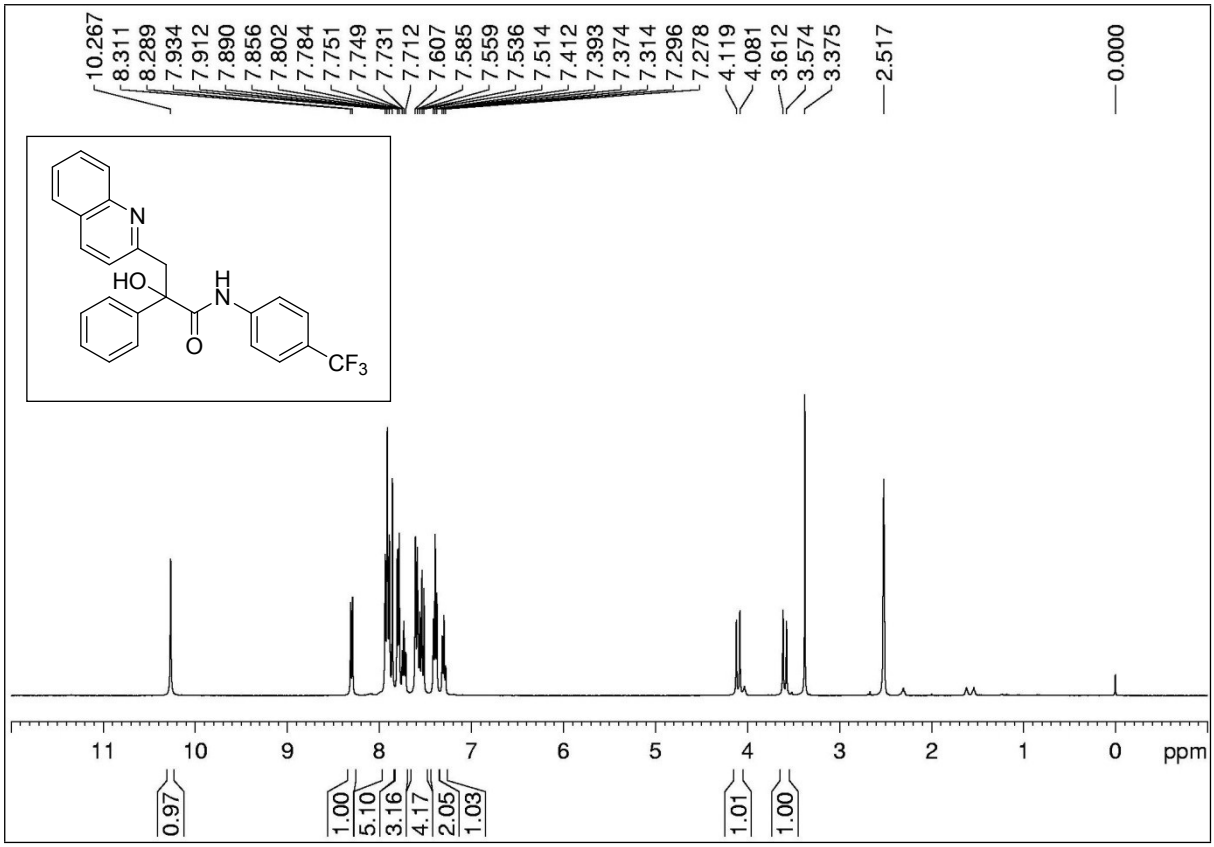

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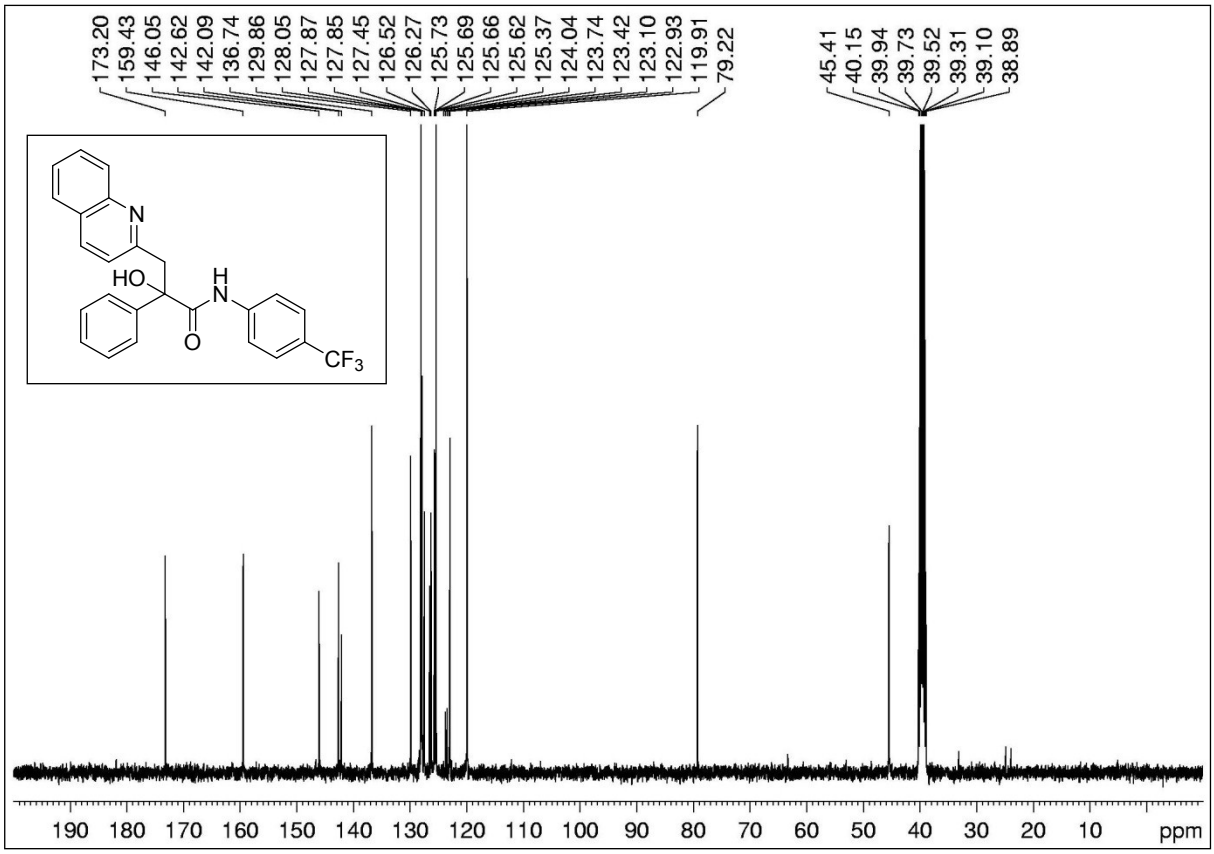

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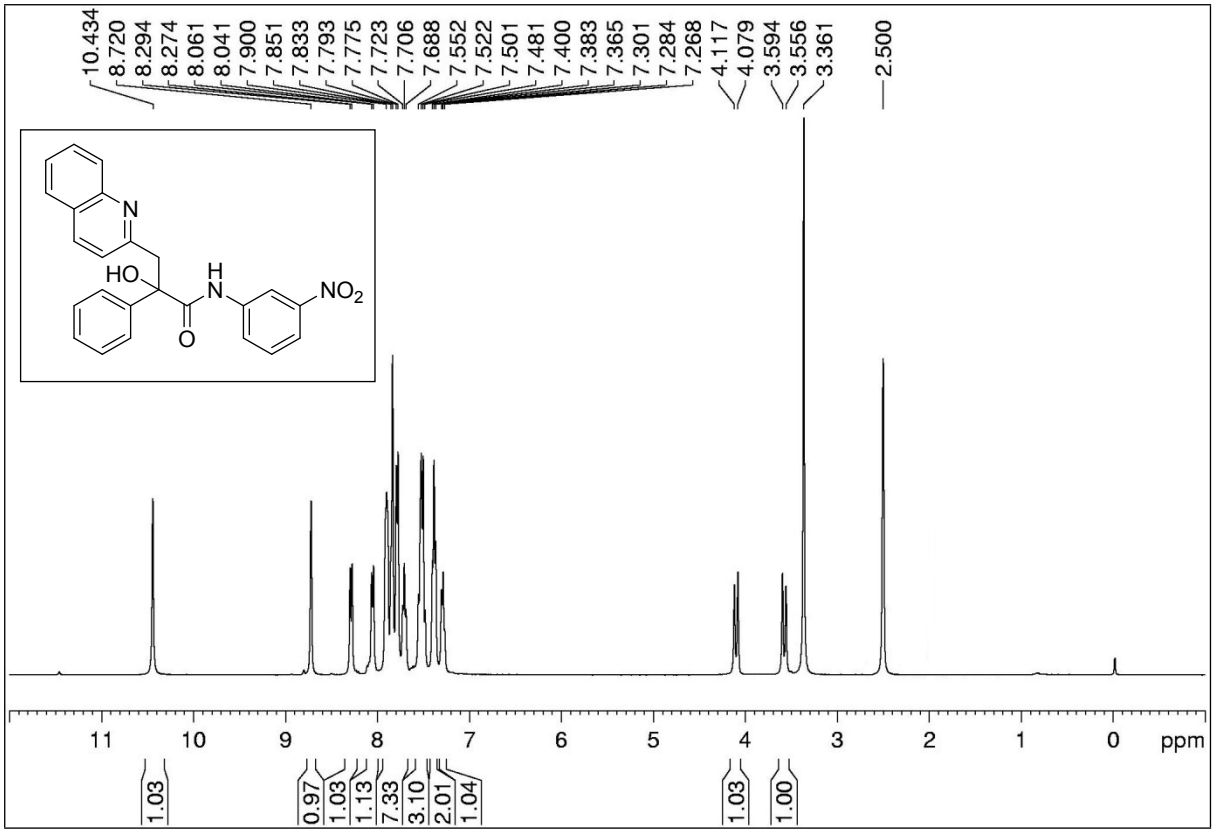

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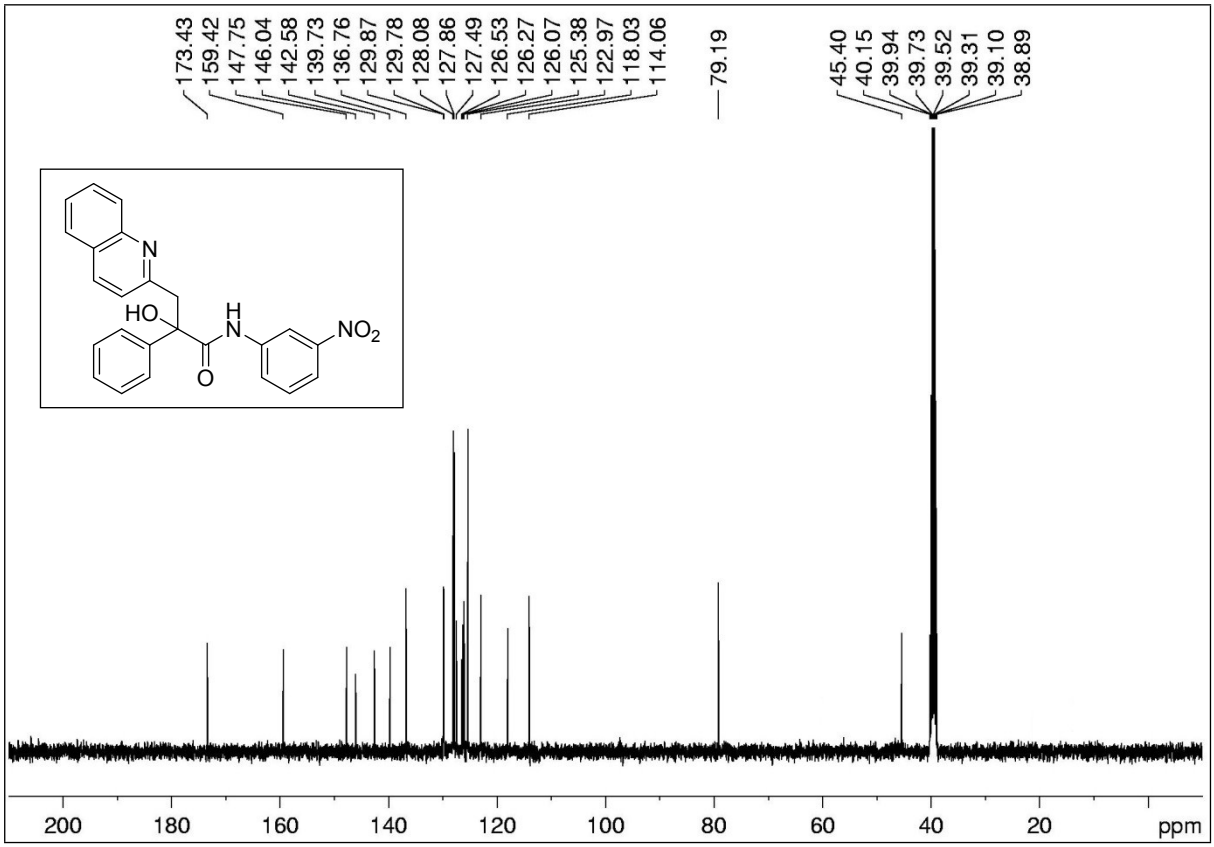
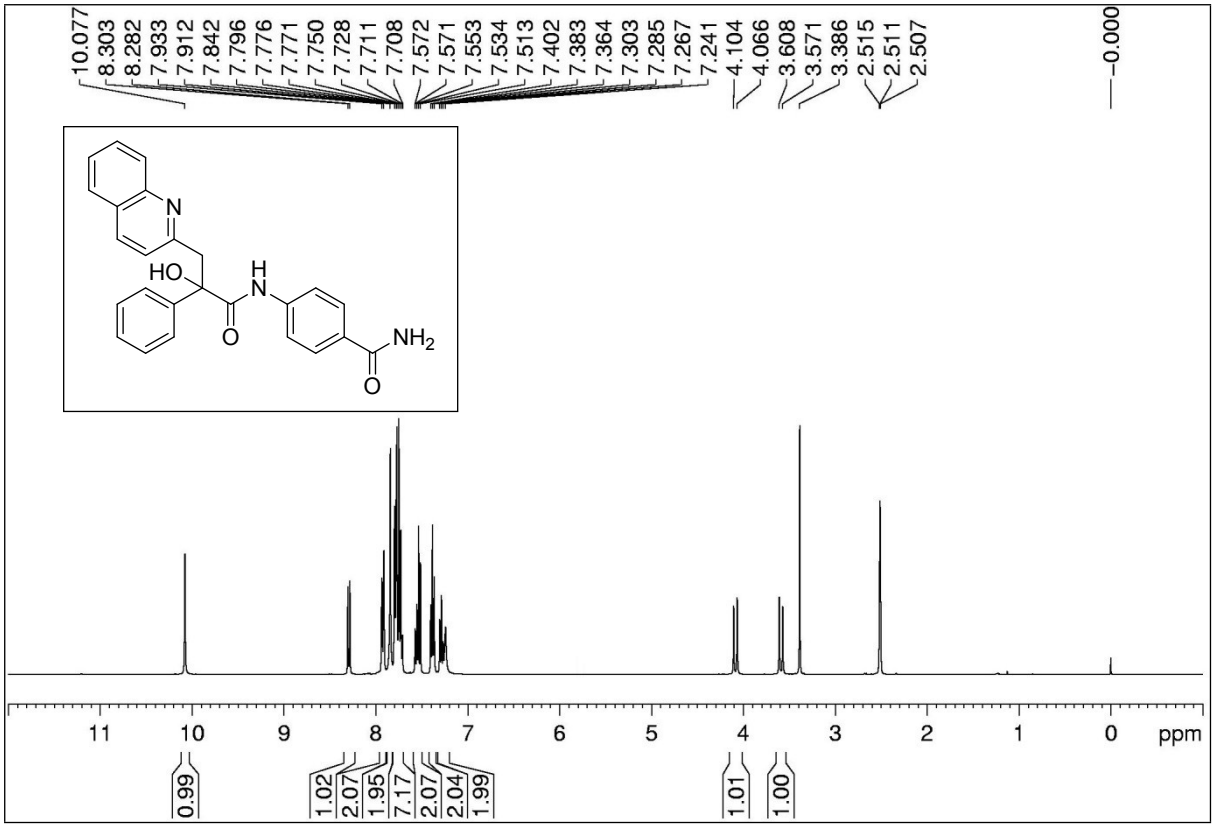


100 MHz ^{1}H-NMR spectra of **3k** in DMSO-d_6



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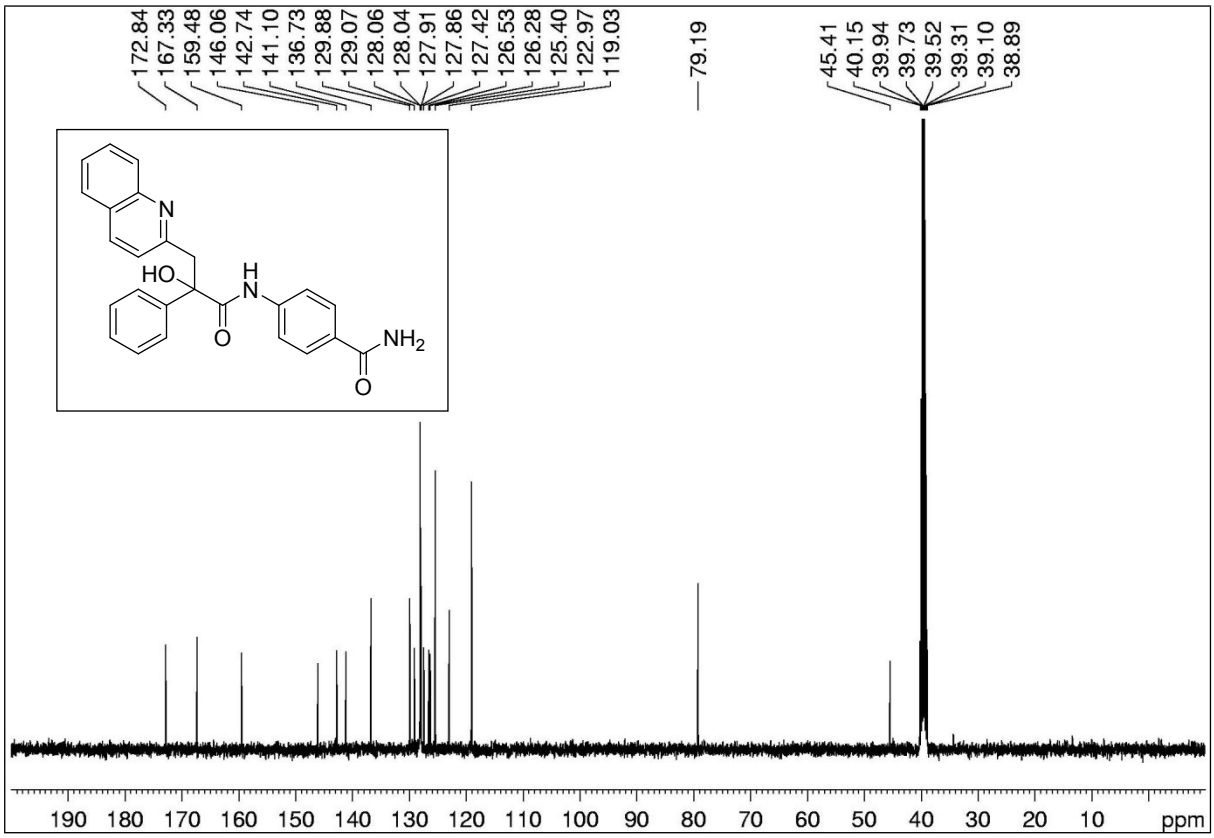
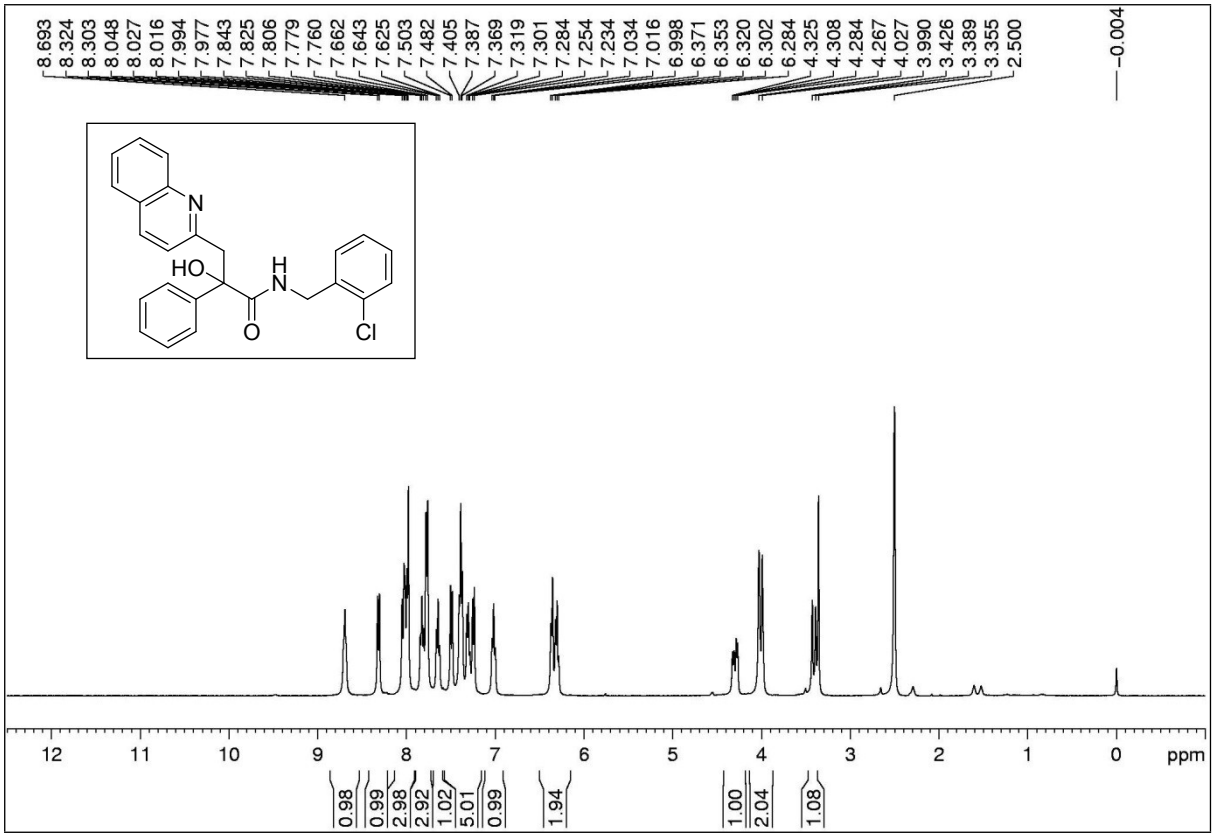


100 MHz ^{1}H-NMR spectra of **3l** in DMSO-d_6



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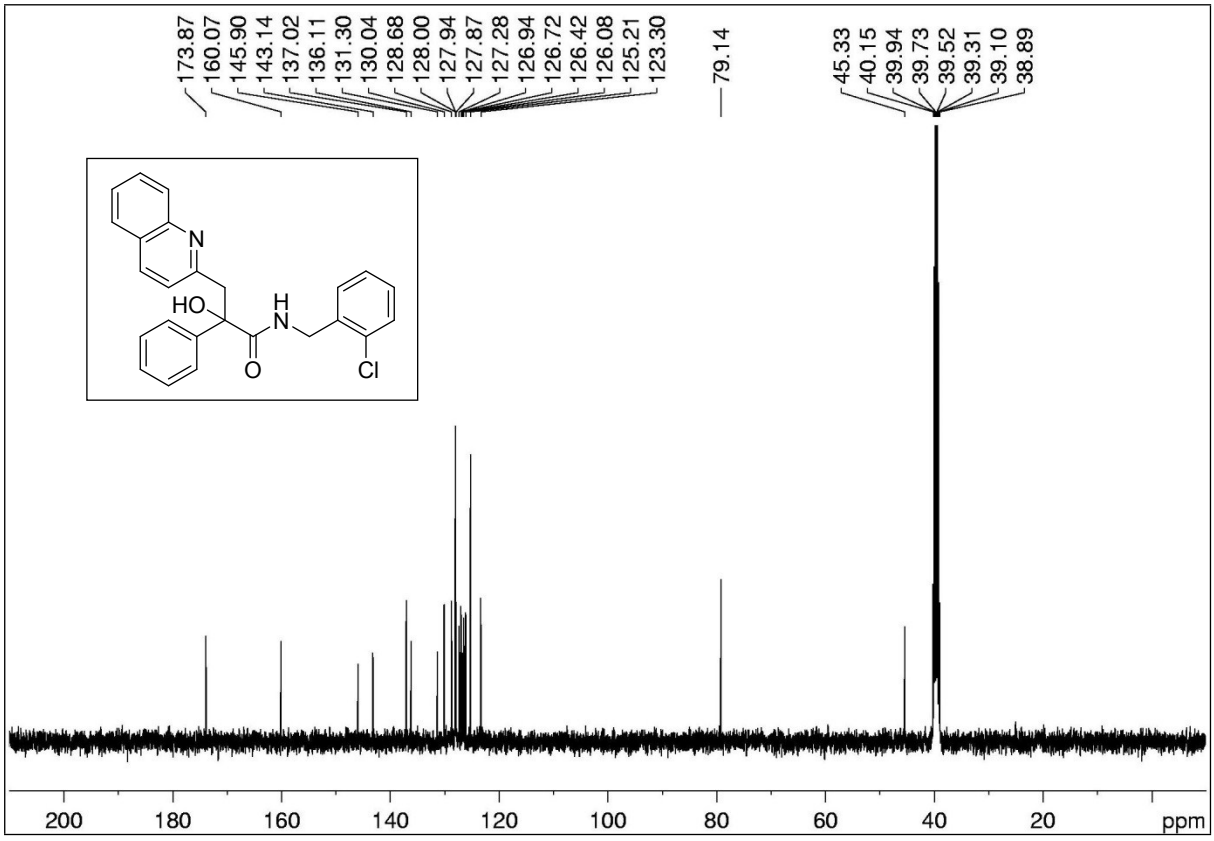
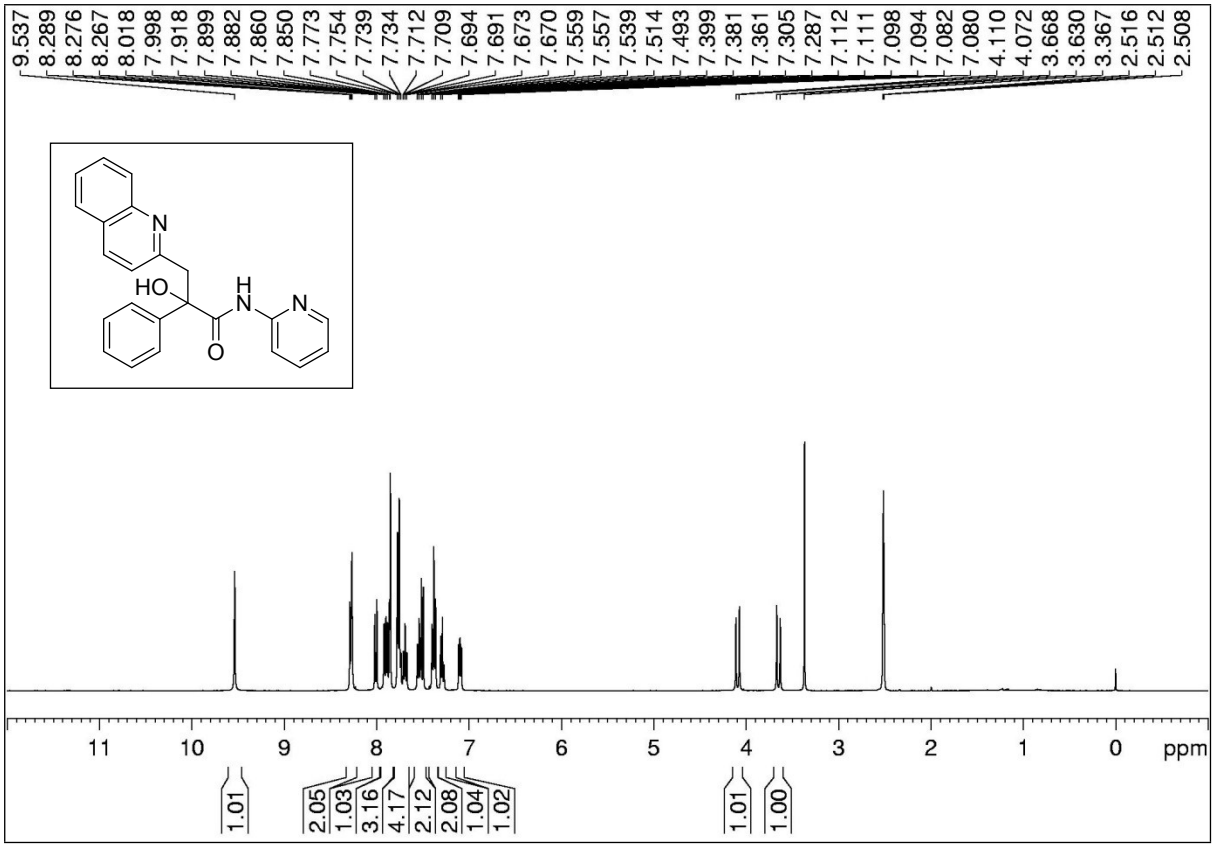


100 MHz ^{1}H-NMR spectra of **3m** in DMSO-d_6



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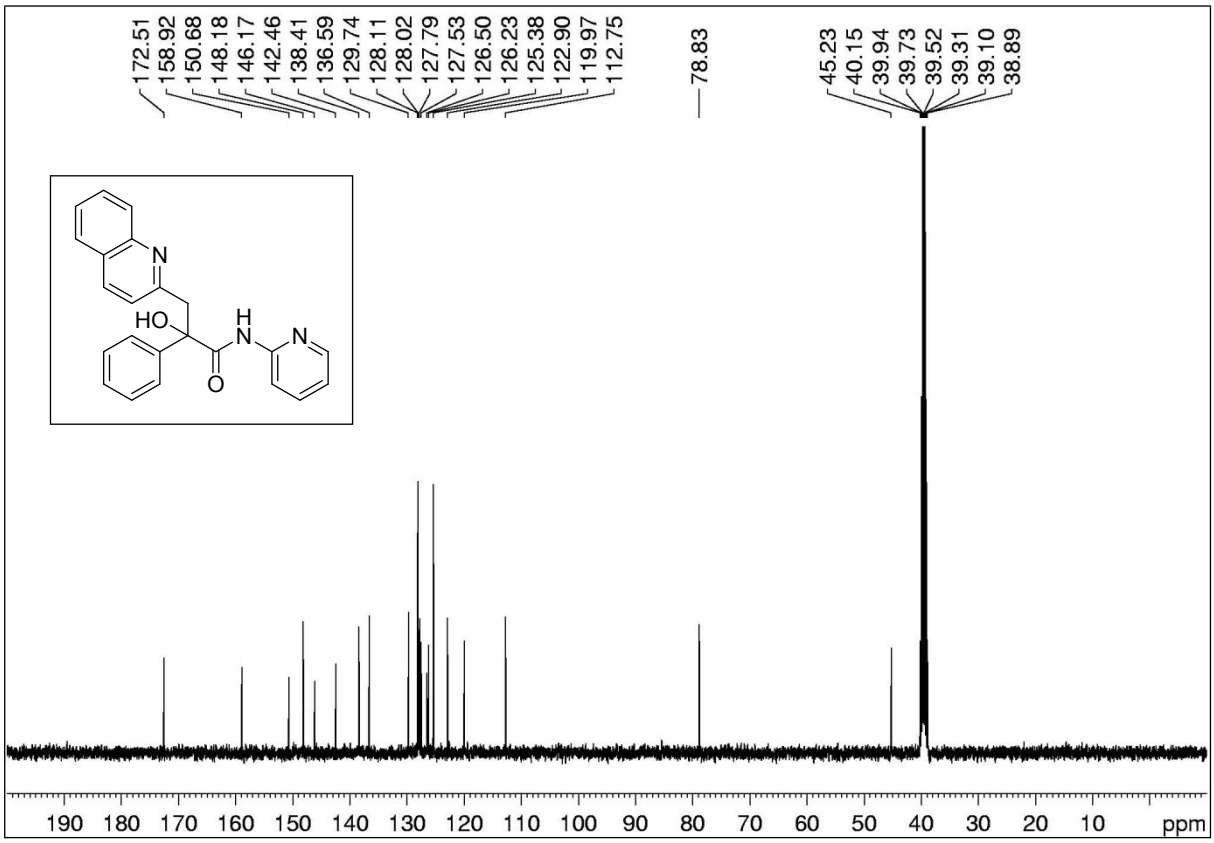
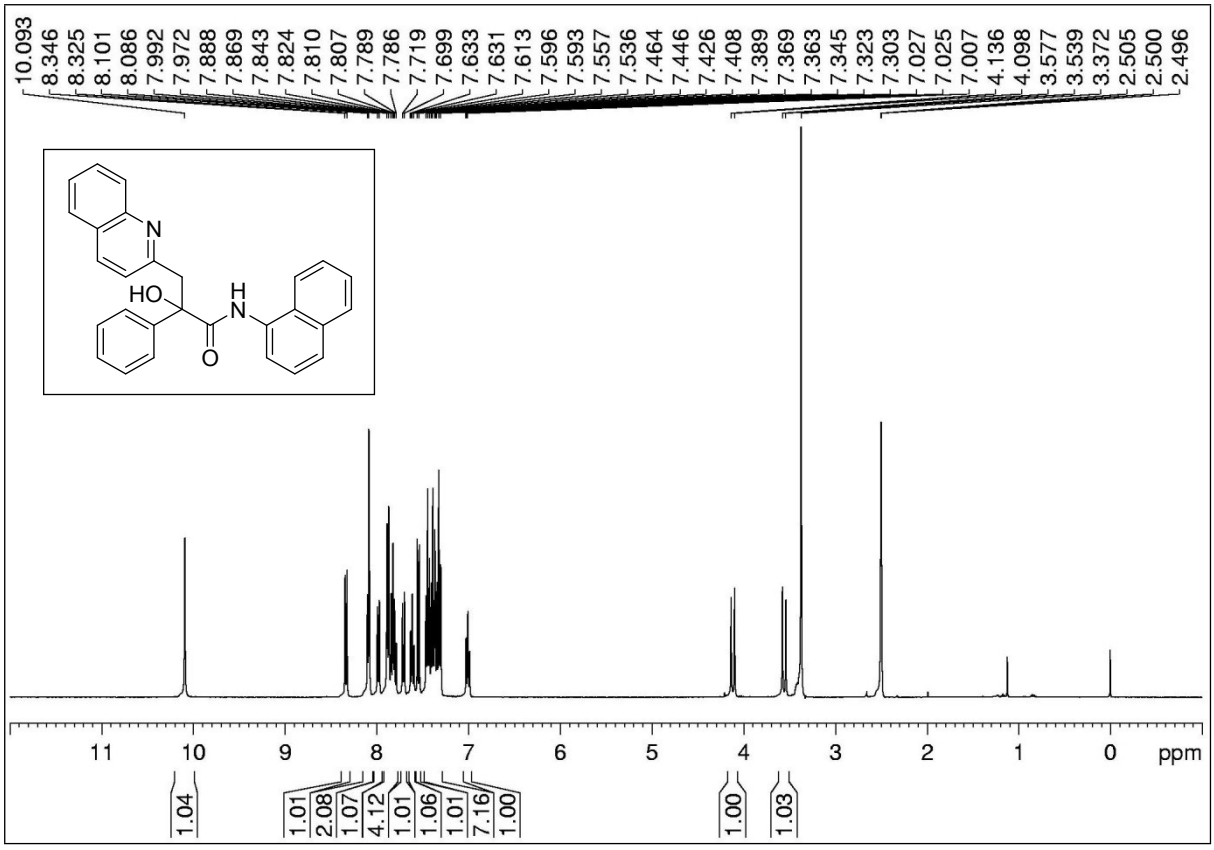


100 MHz ^{1}H-NMR spectra of **3n** in DMSO-d_6



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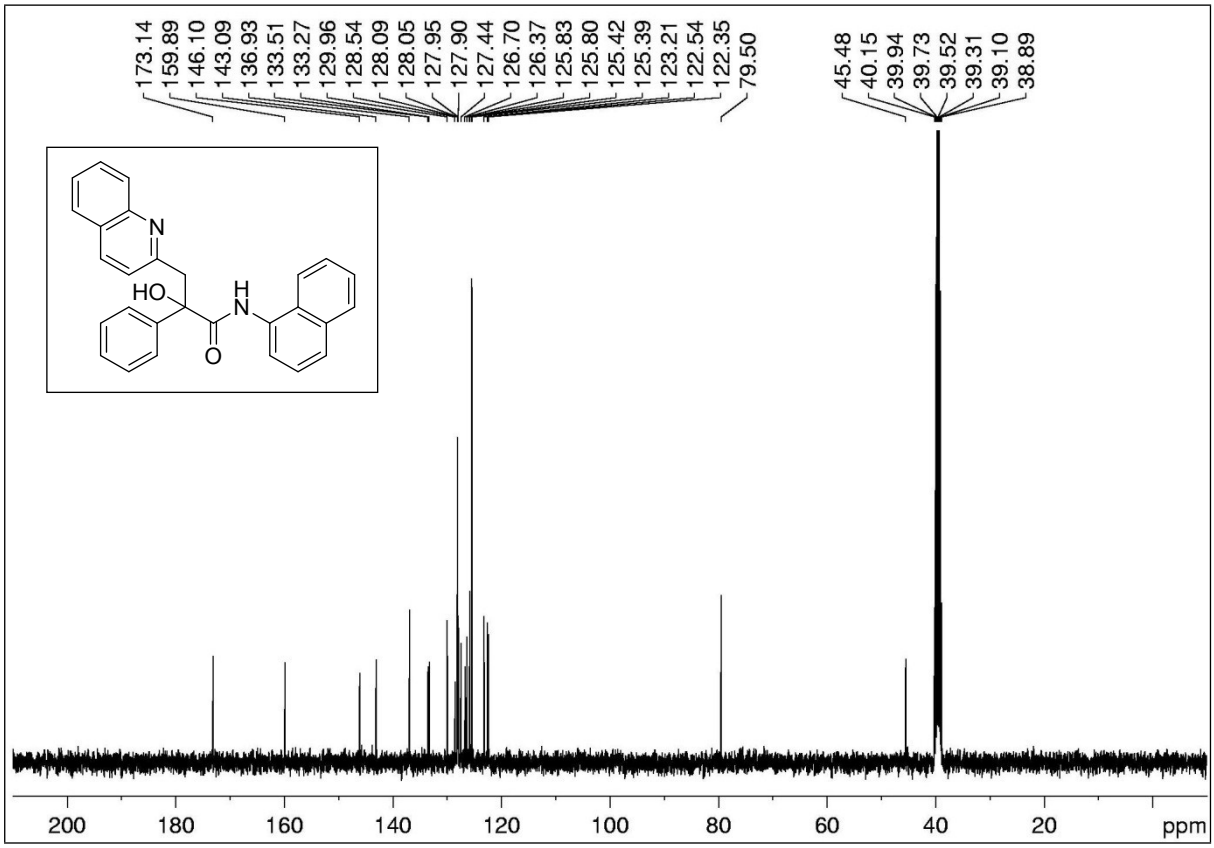
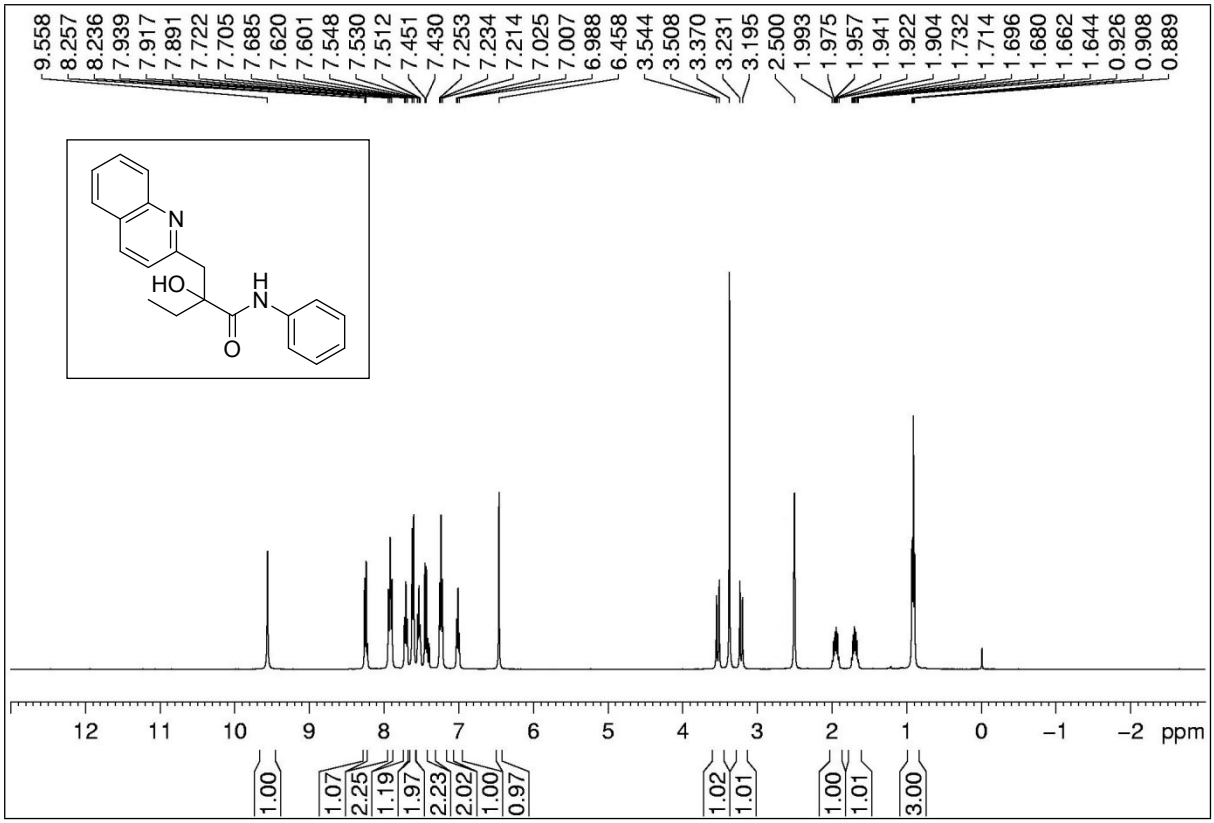


100 MHz ^{1}H-NMR spectra of **3o** in DMSO-d_6



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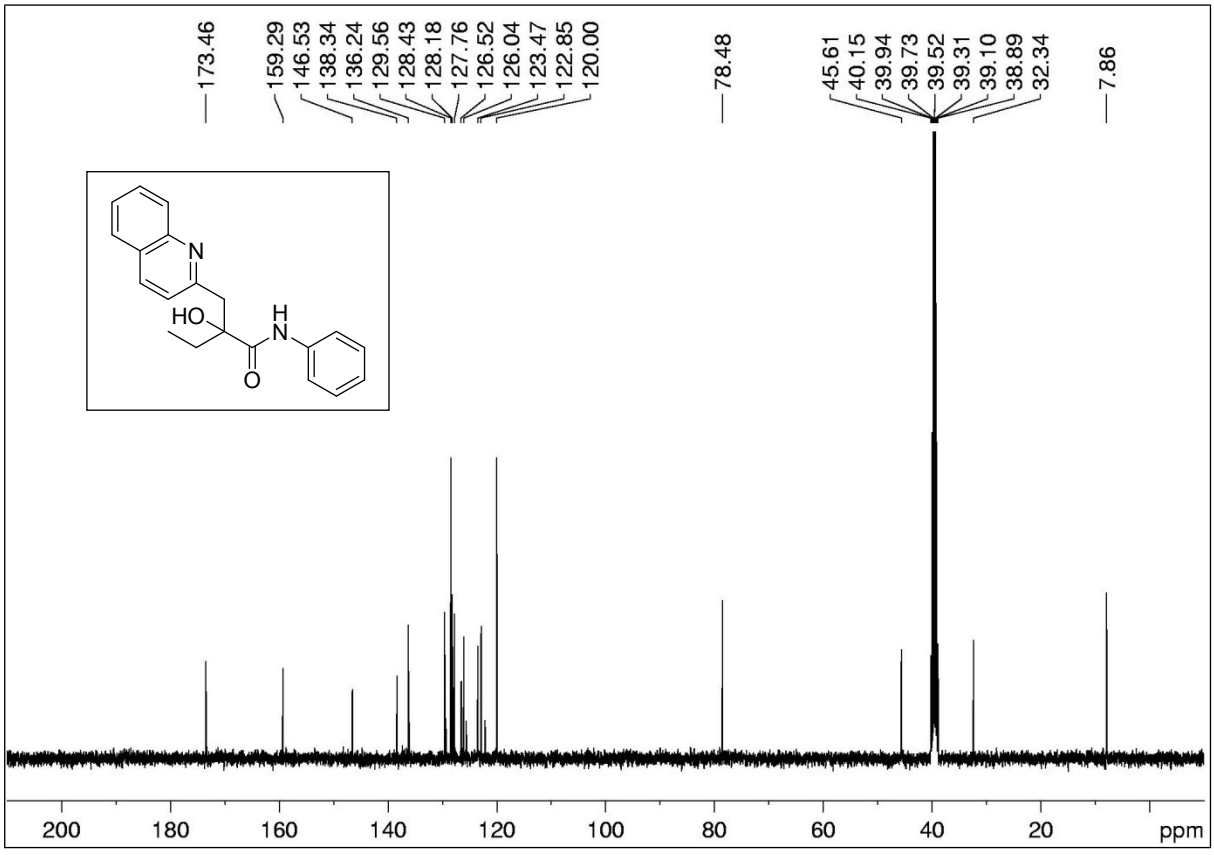
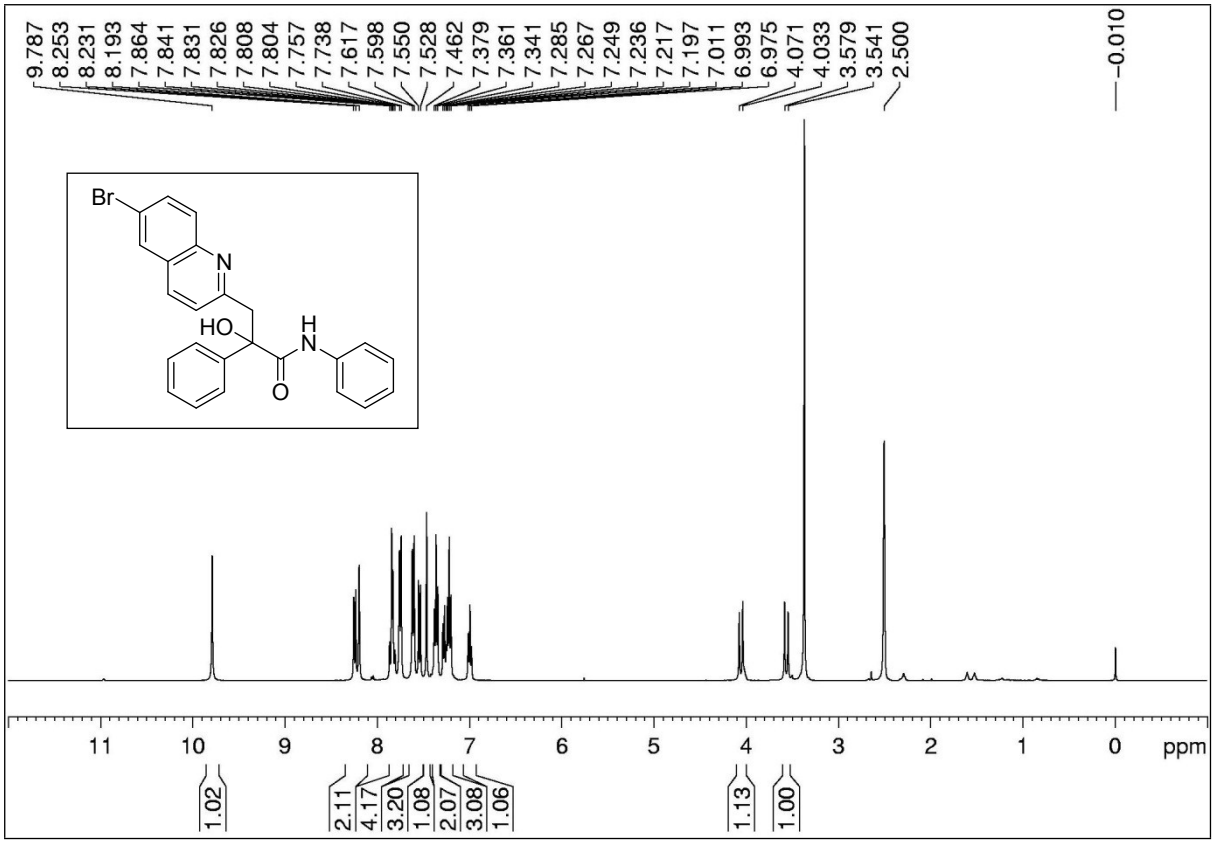


100 MHz ^{1}H-NMR spectra of **3s** in DMSO-d_6



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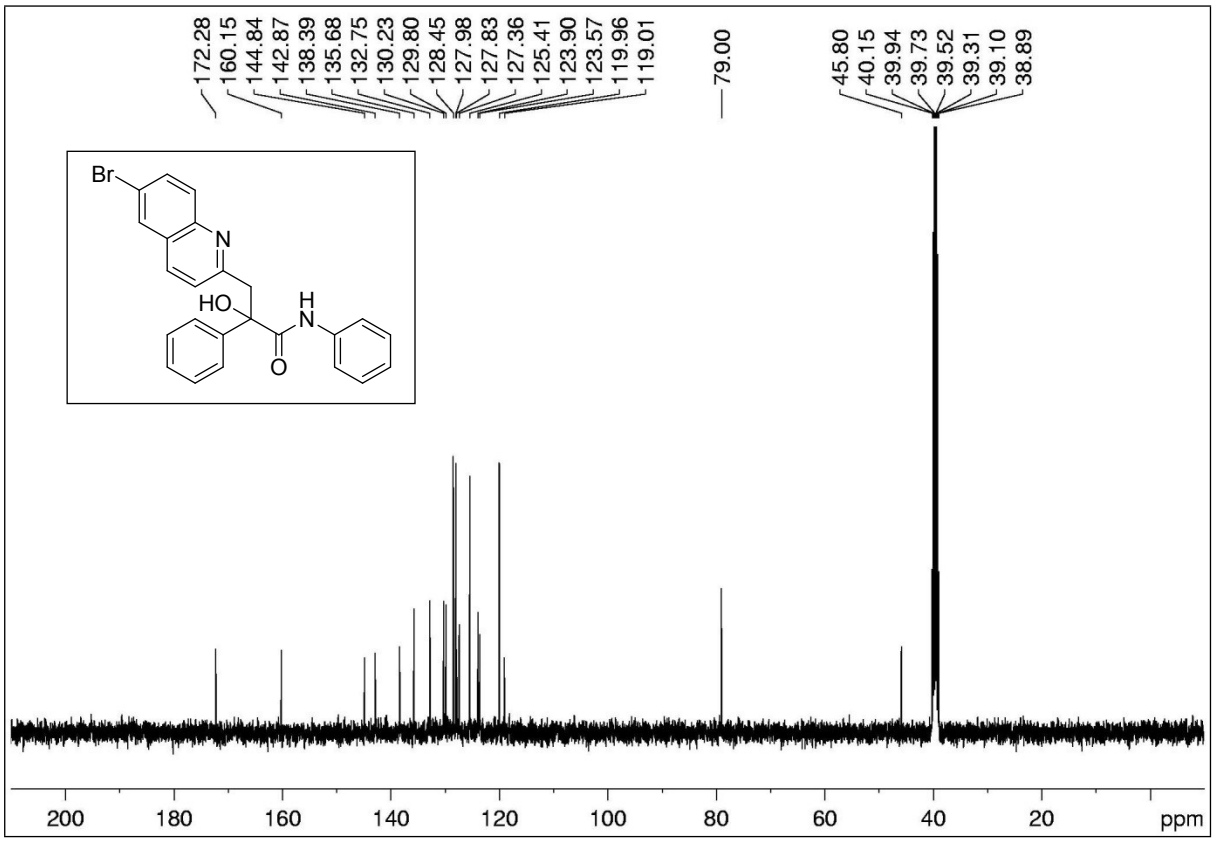
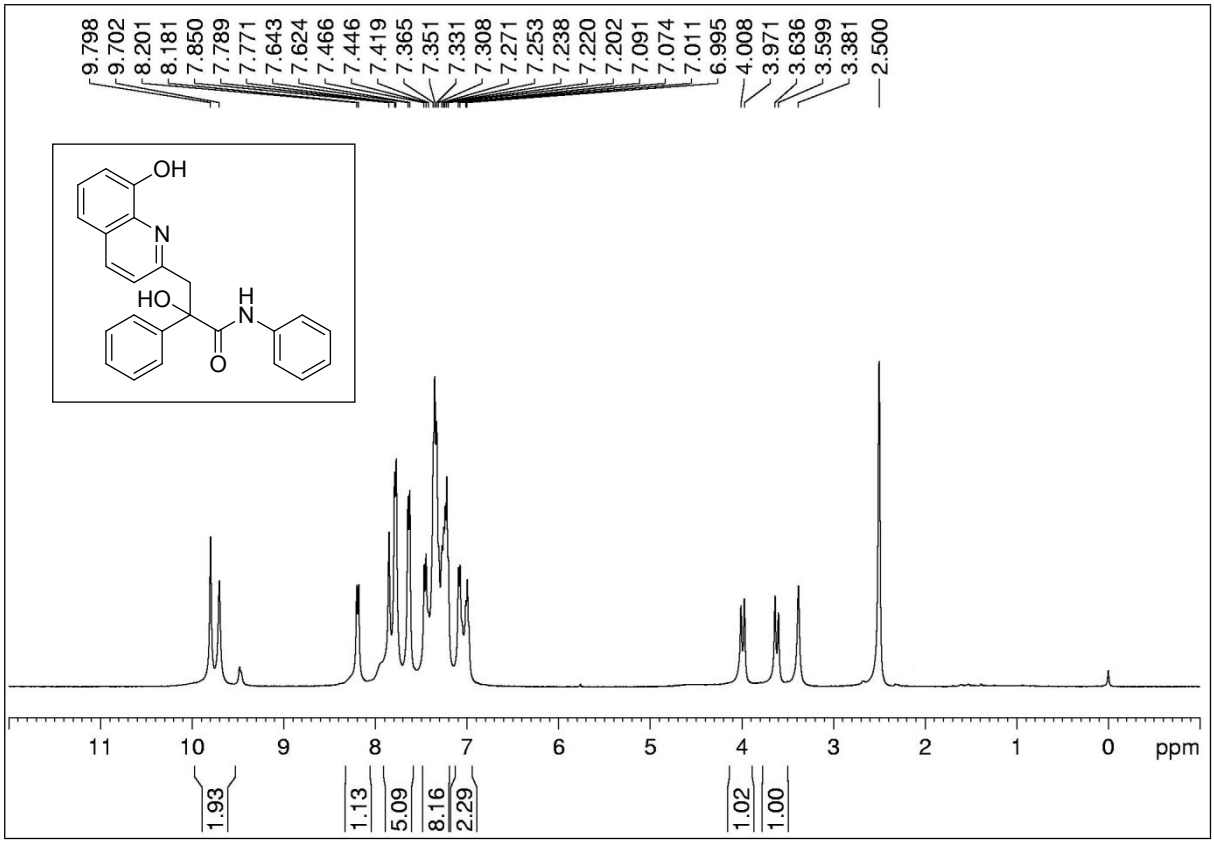


100 MHz ^{1}H-NMR spectra of **5a** in DMSO-d_6



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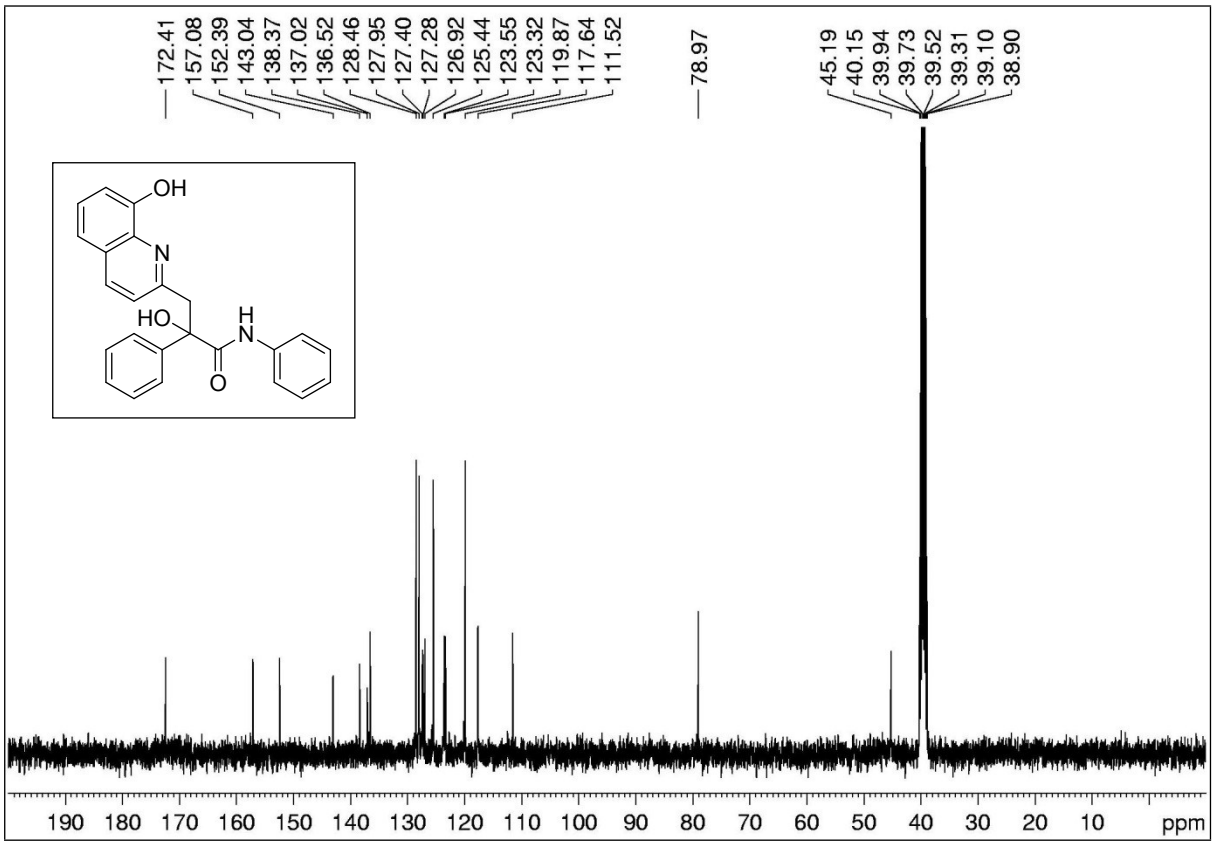
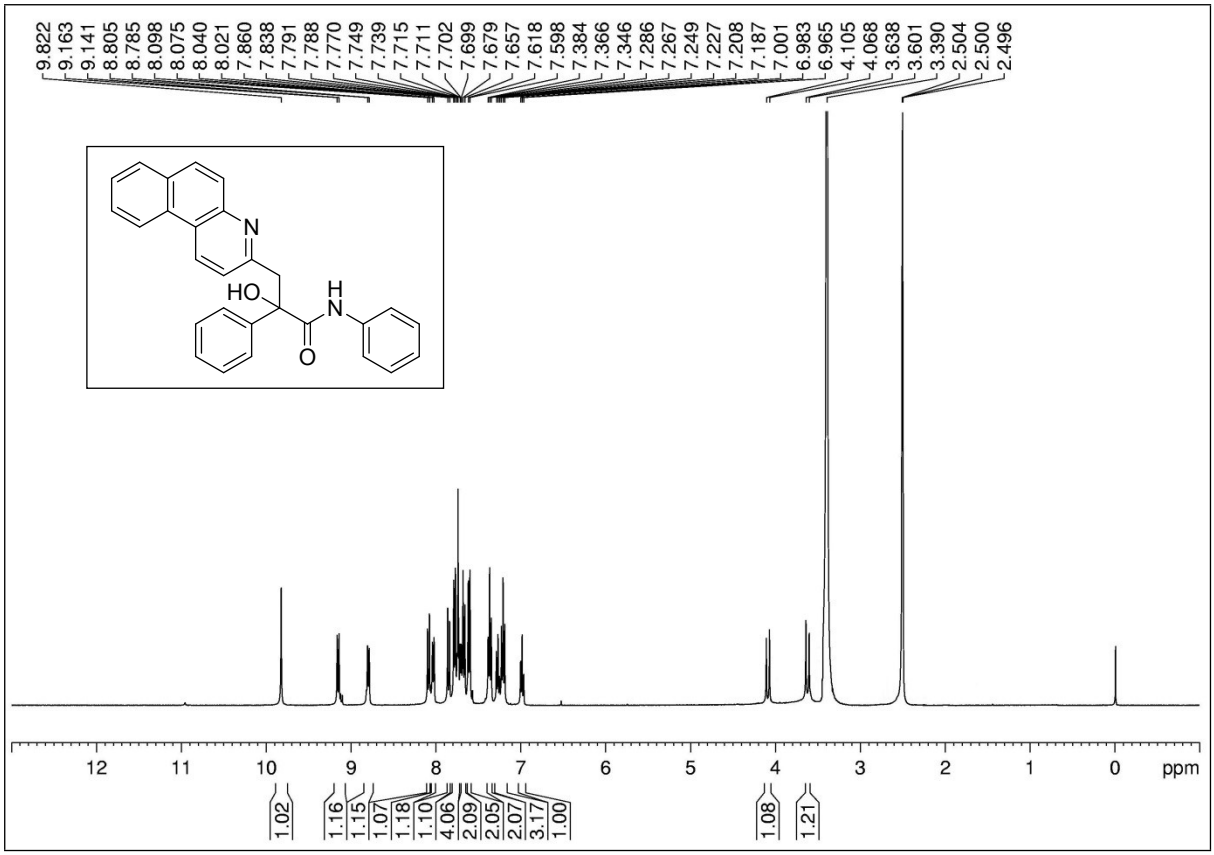


100 MHz ^{1}H-NMR spectra of **5b** in DMSO-d_6



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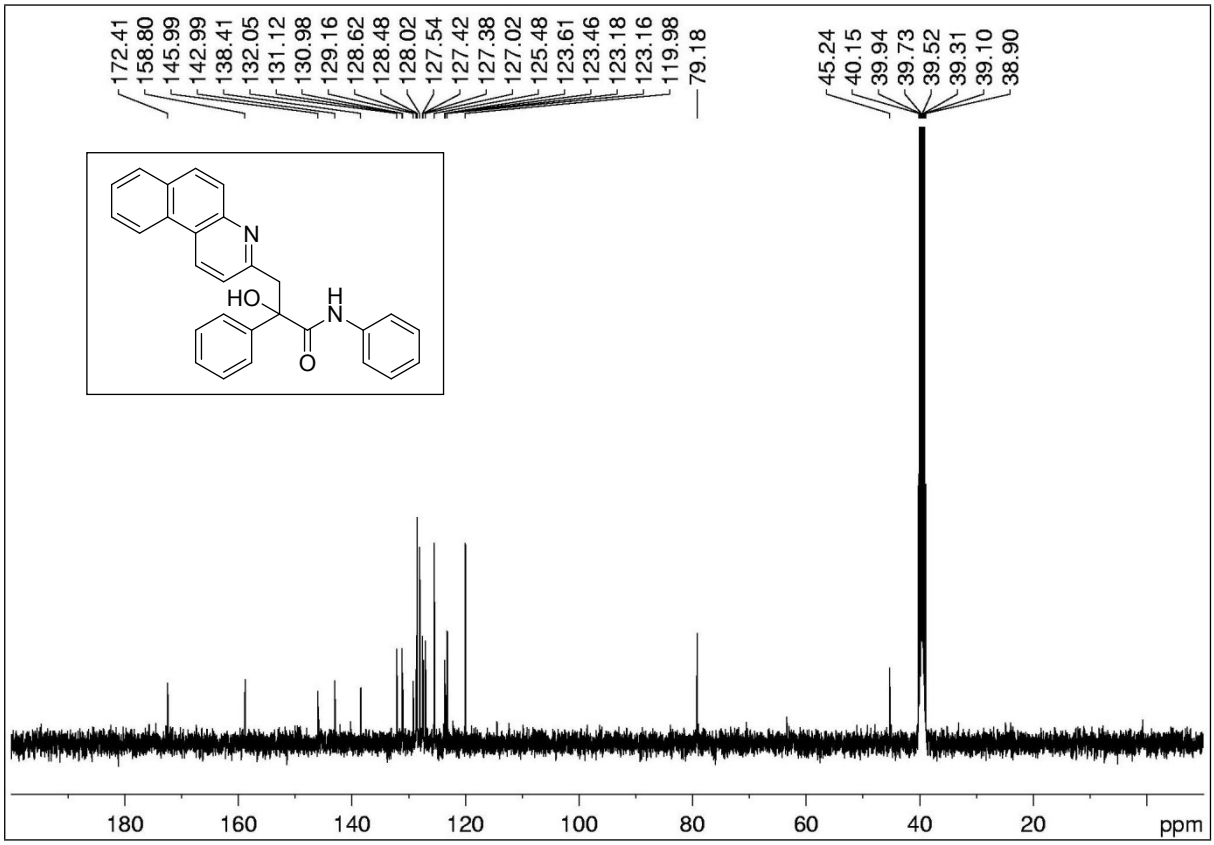
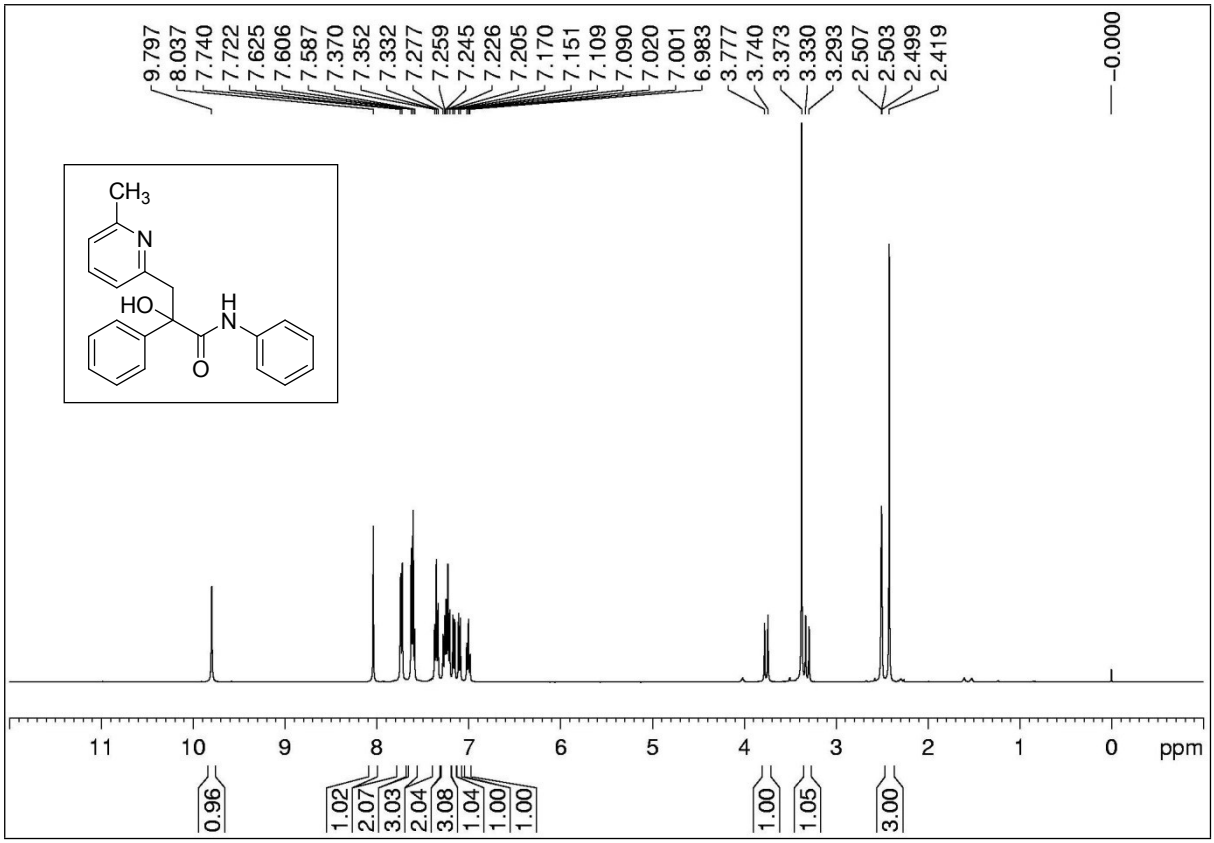


100 MHz ^{1}H-NMR spectra of **5c** in DMSO-d_6



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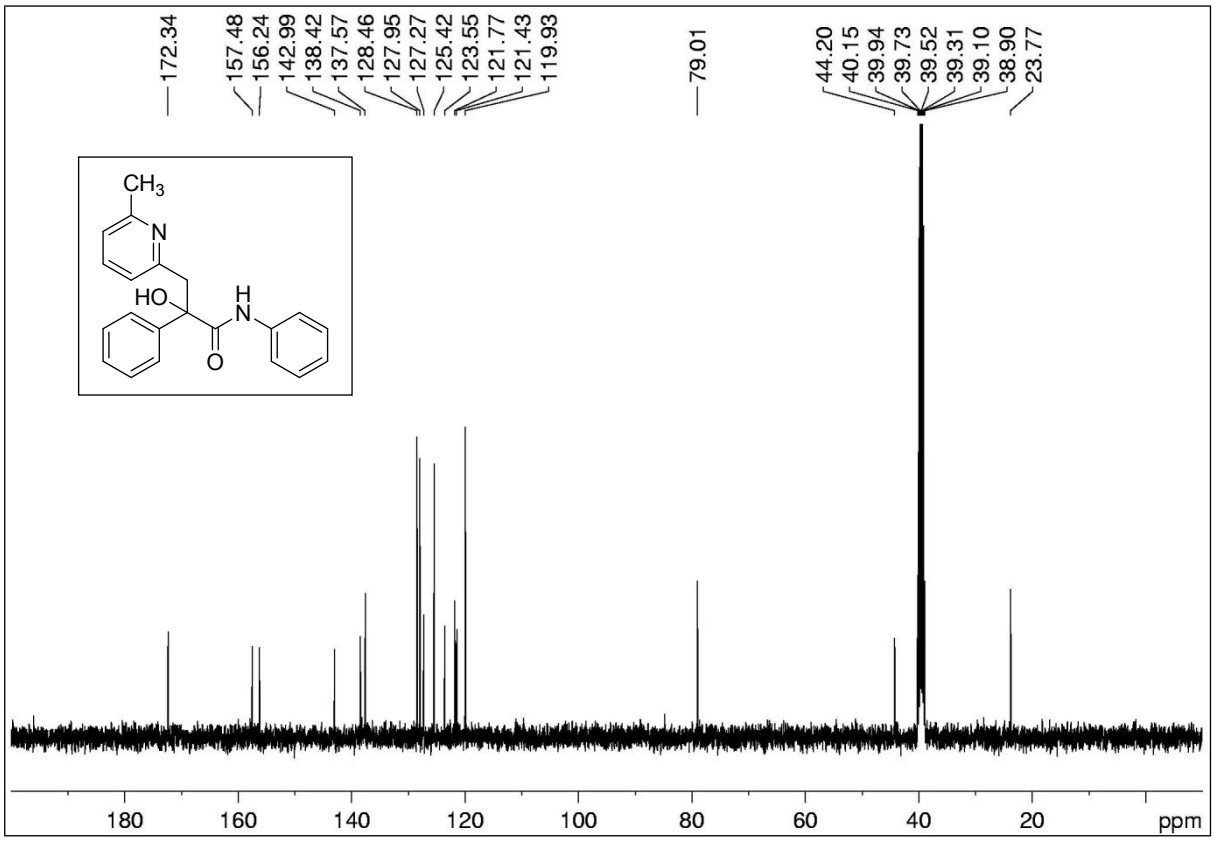

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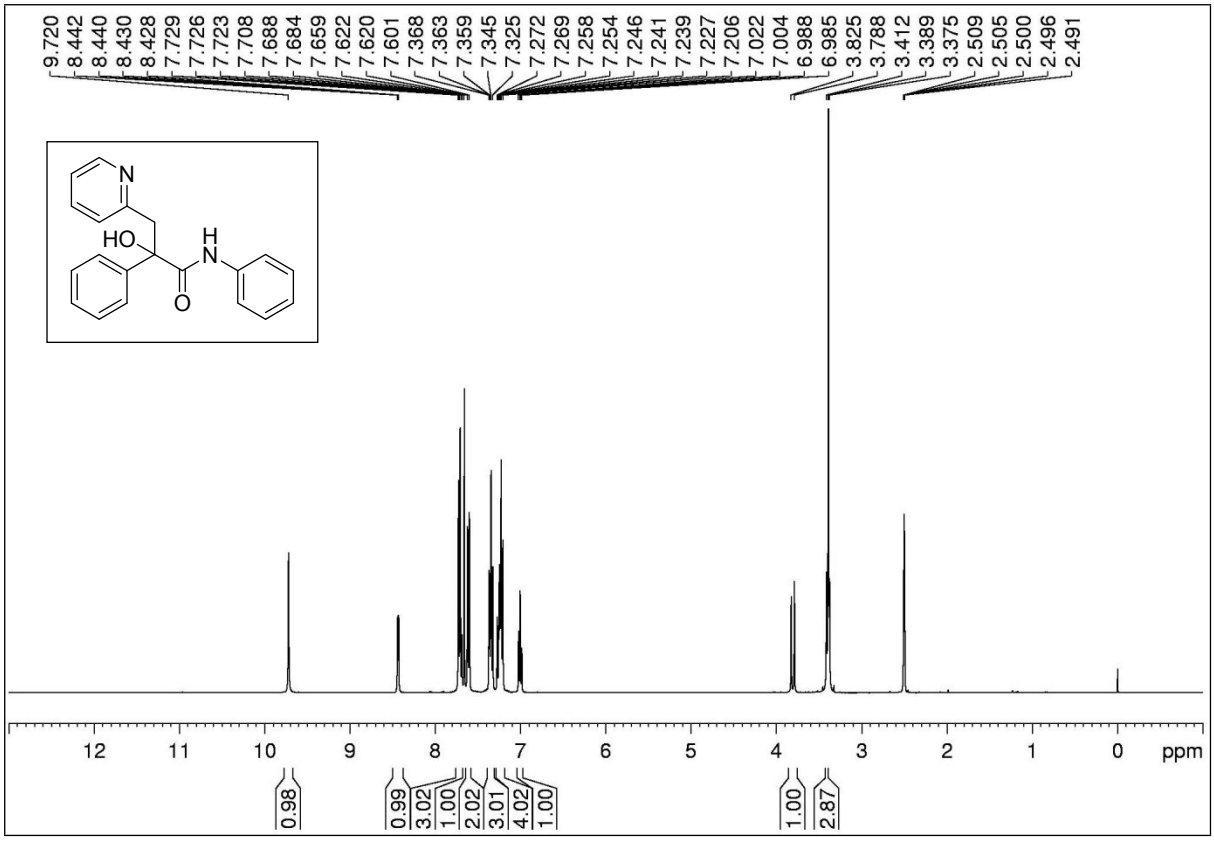

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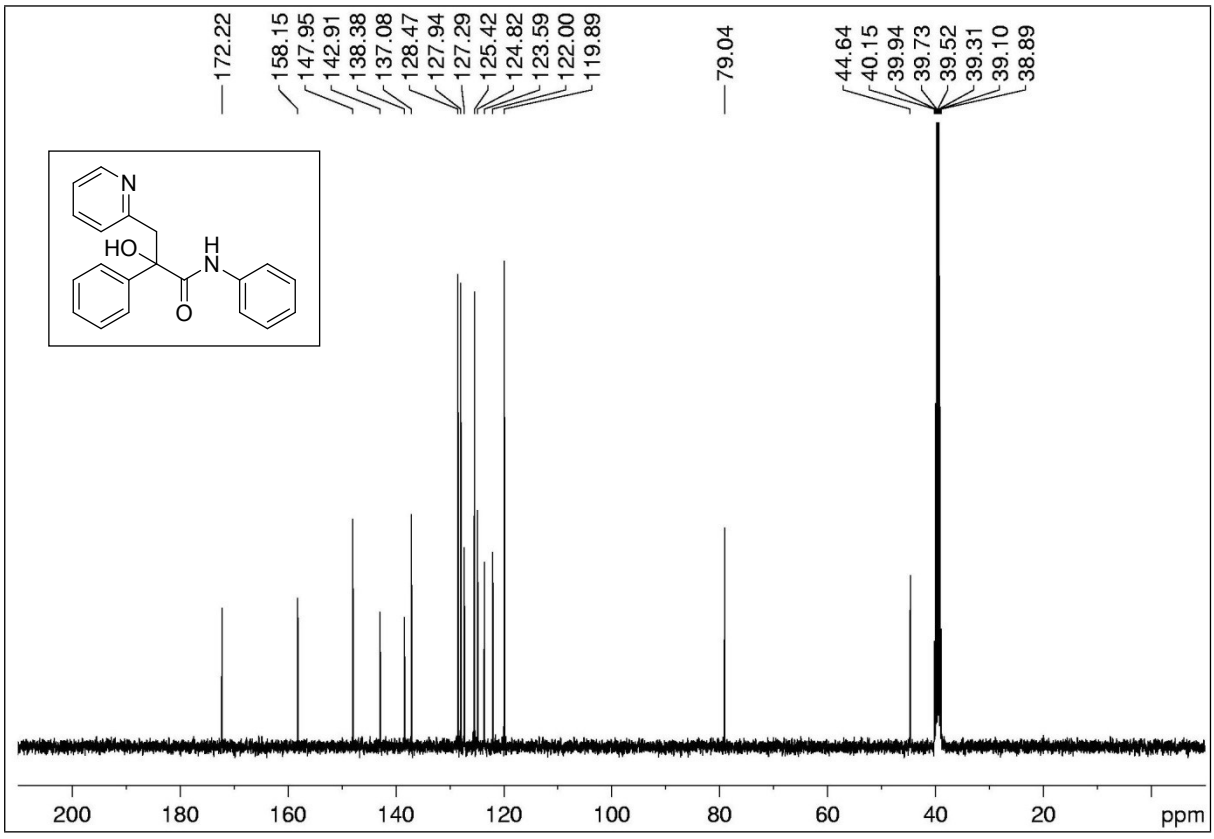
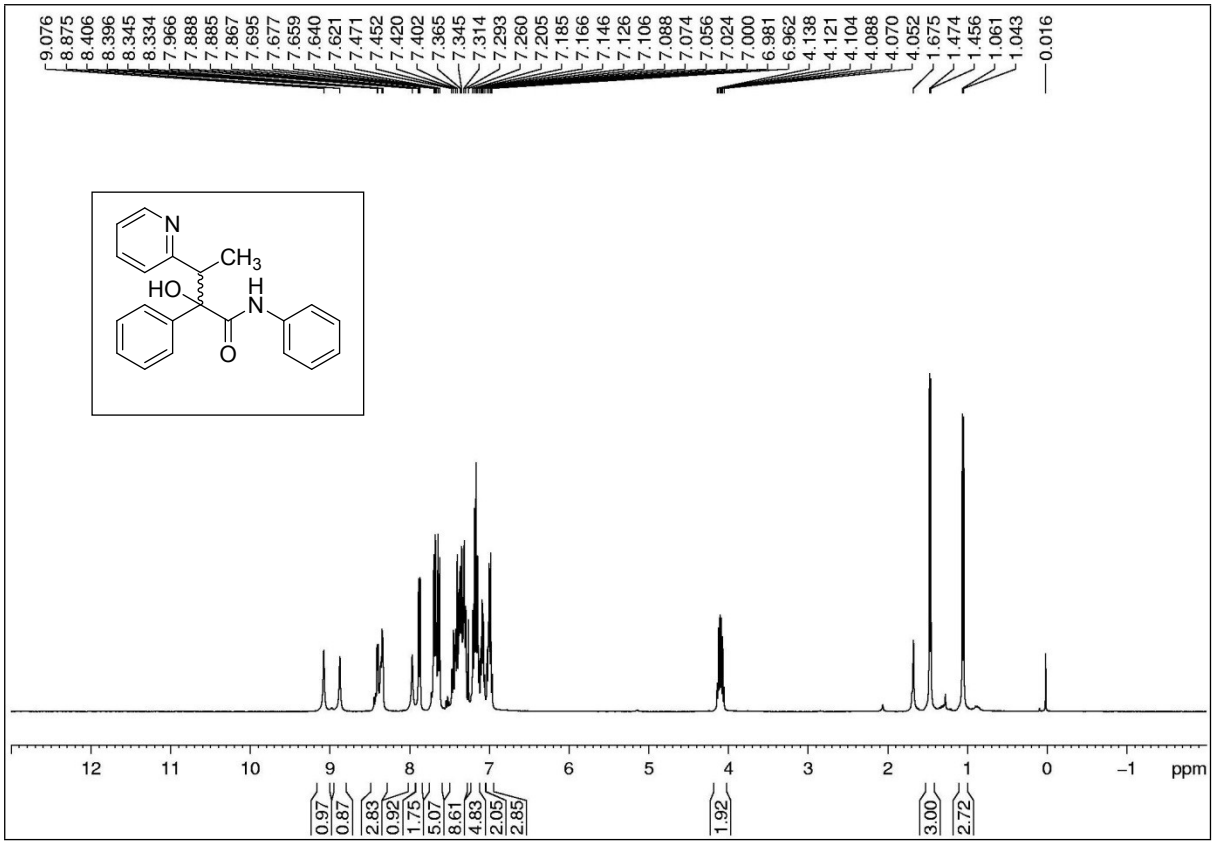
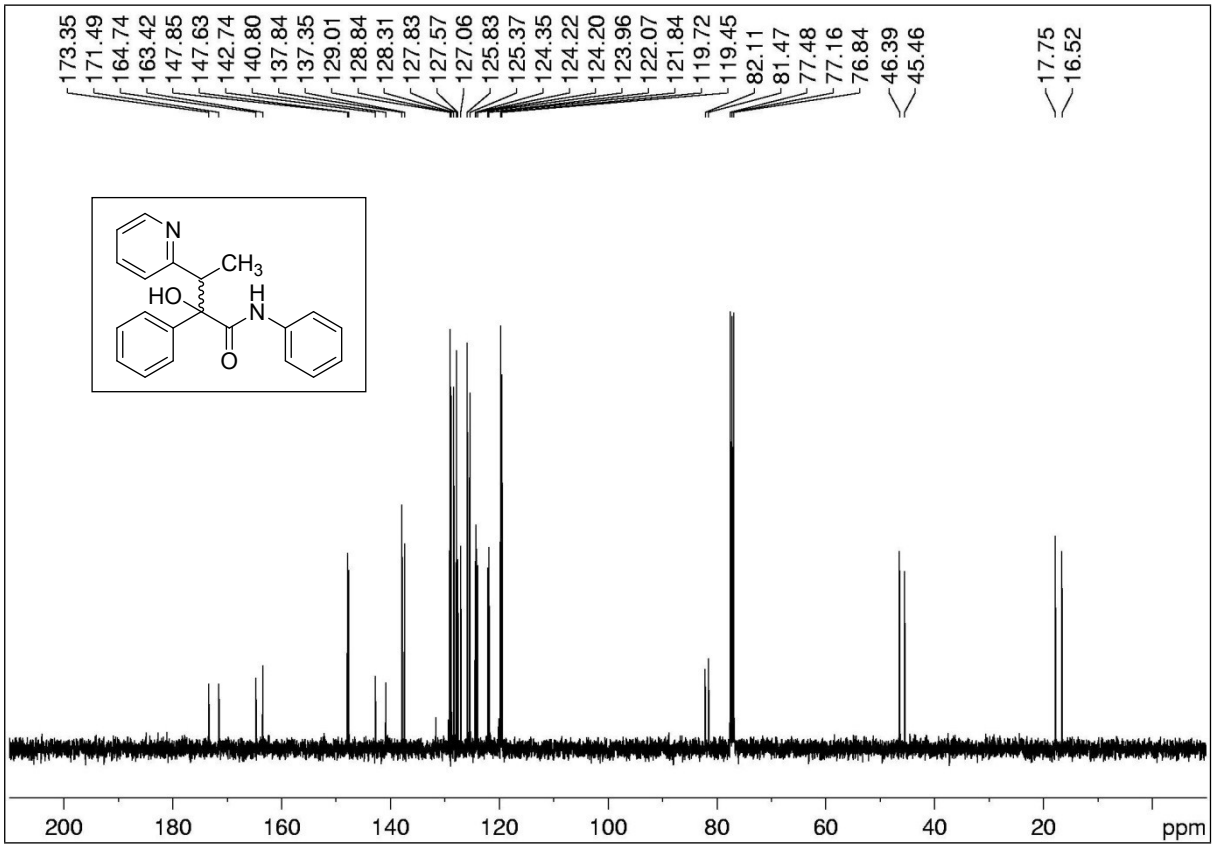


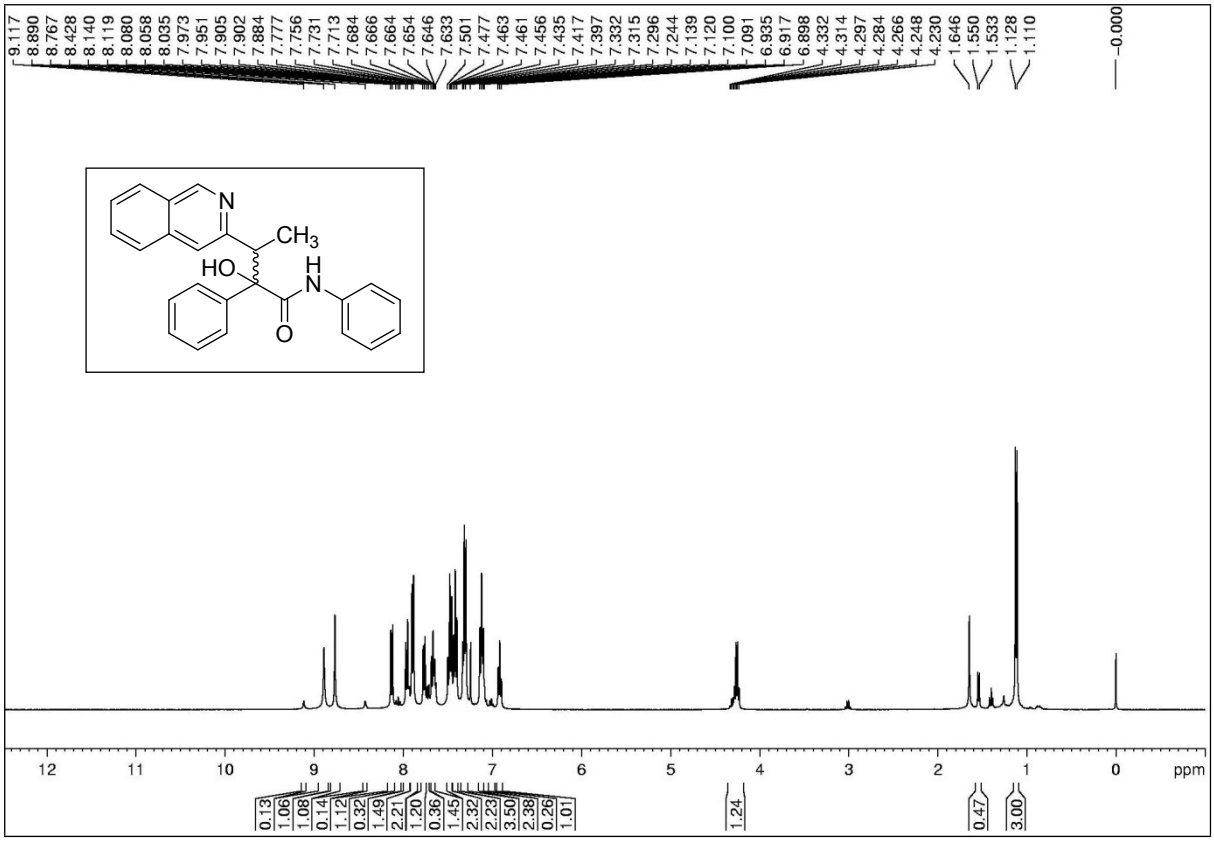
100 MHz ^{1}H-NMR spectra of **5f** in DMSO-d_6



400 MHz ^{1}H-NMR spectra of **5g** in $CDCl_3$



100 MHz ^{1}H-NMR spectra of **5g** in $CDCl_3$



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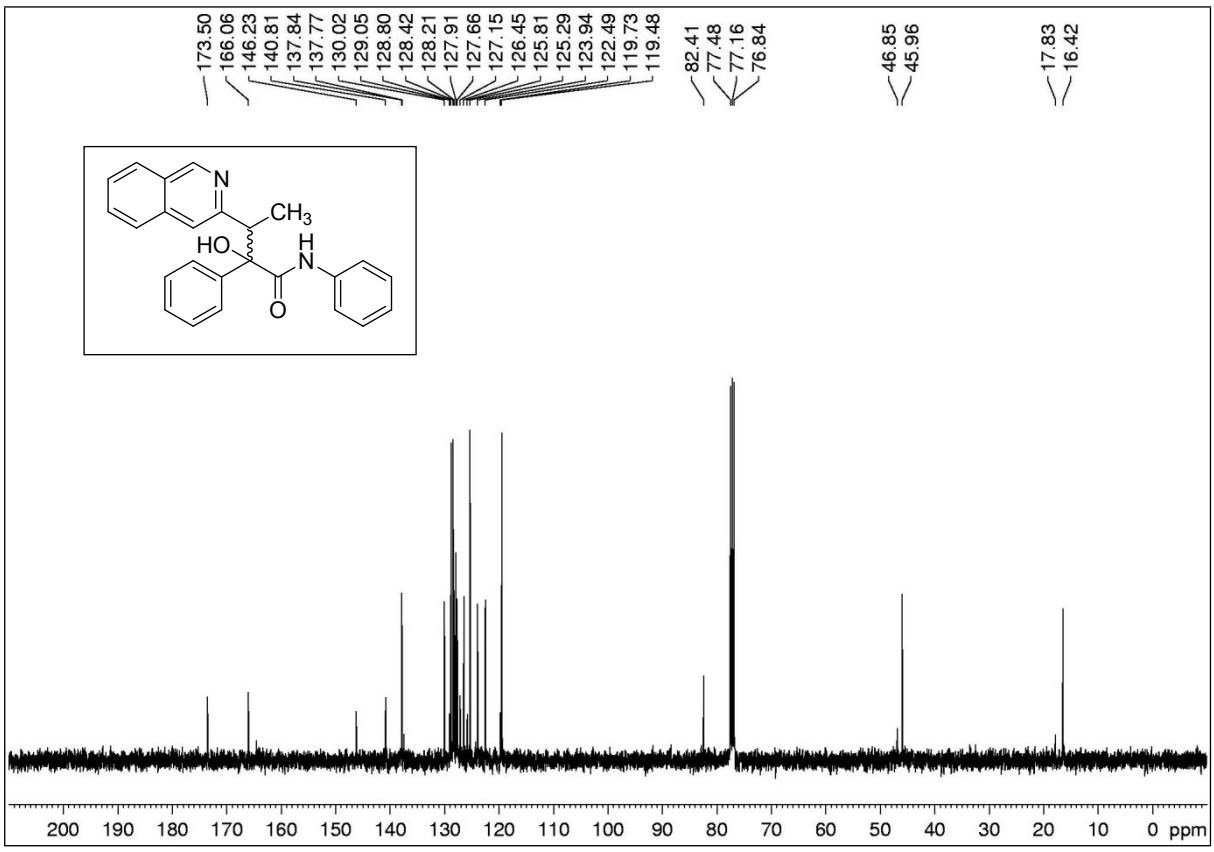

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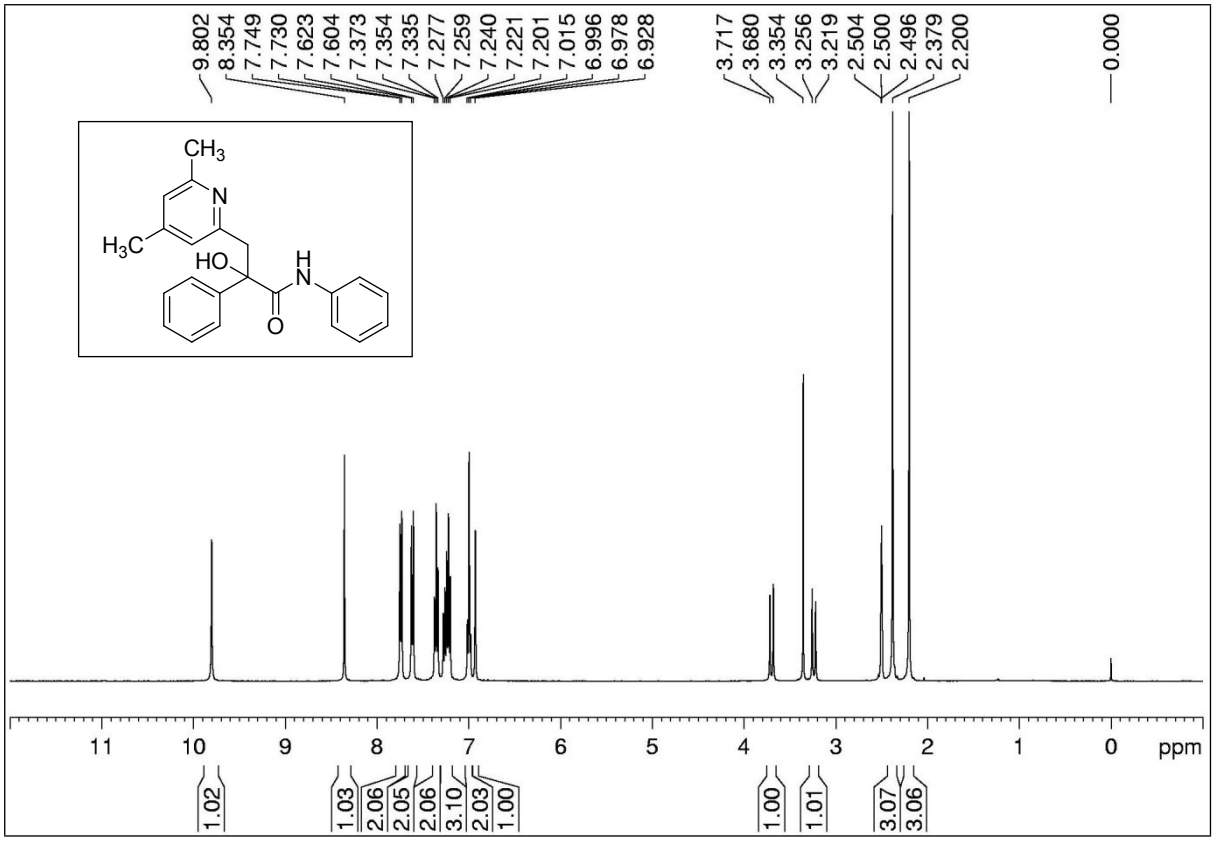

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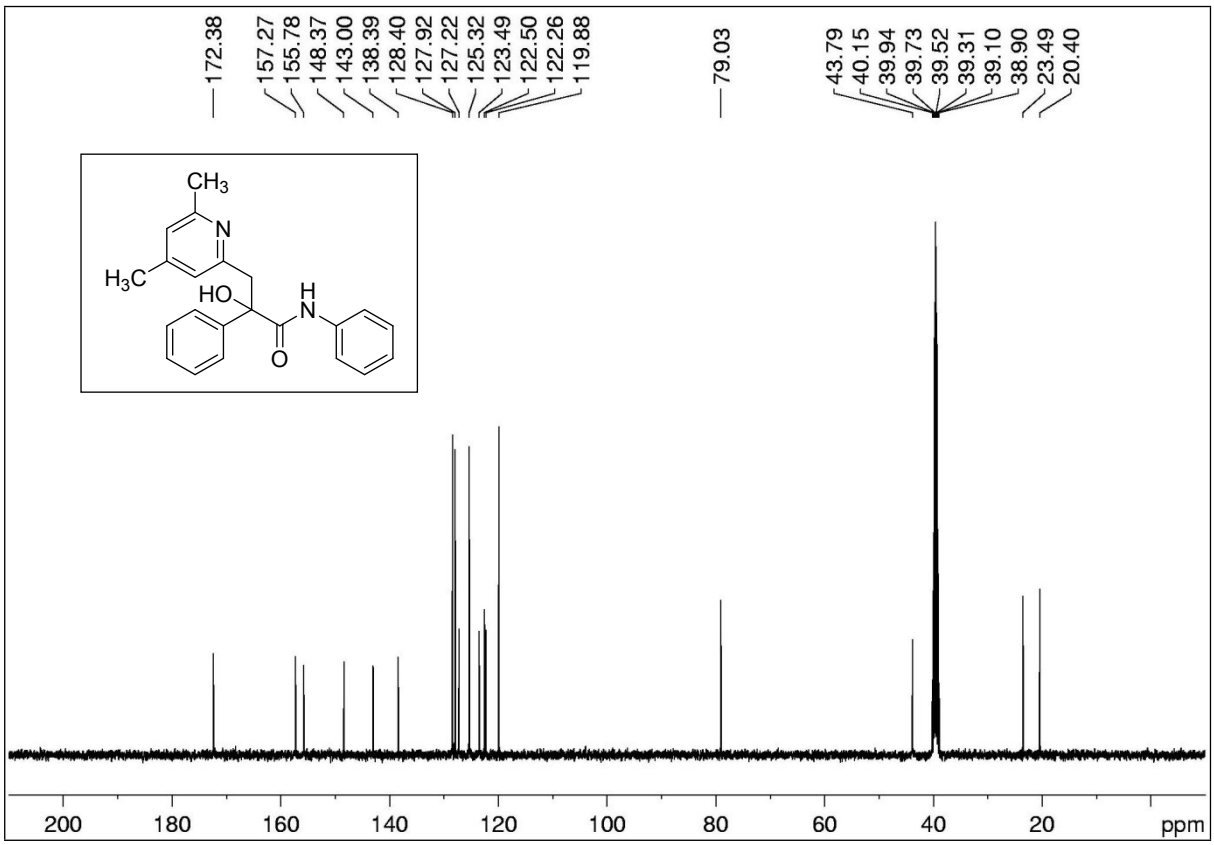

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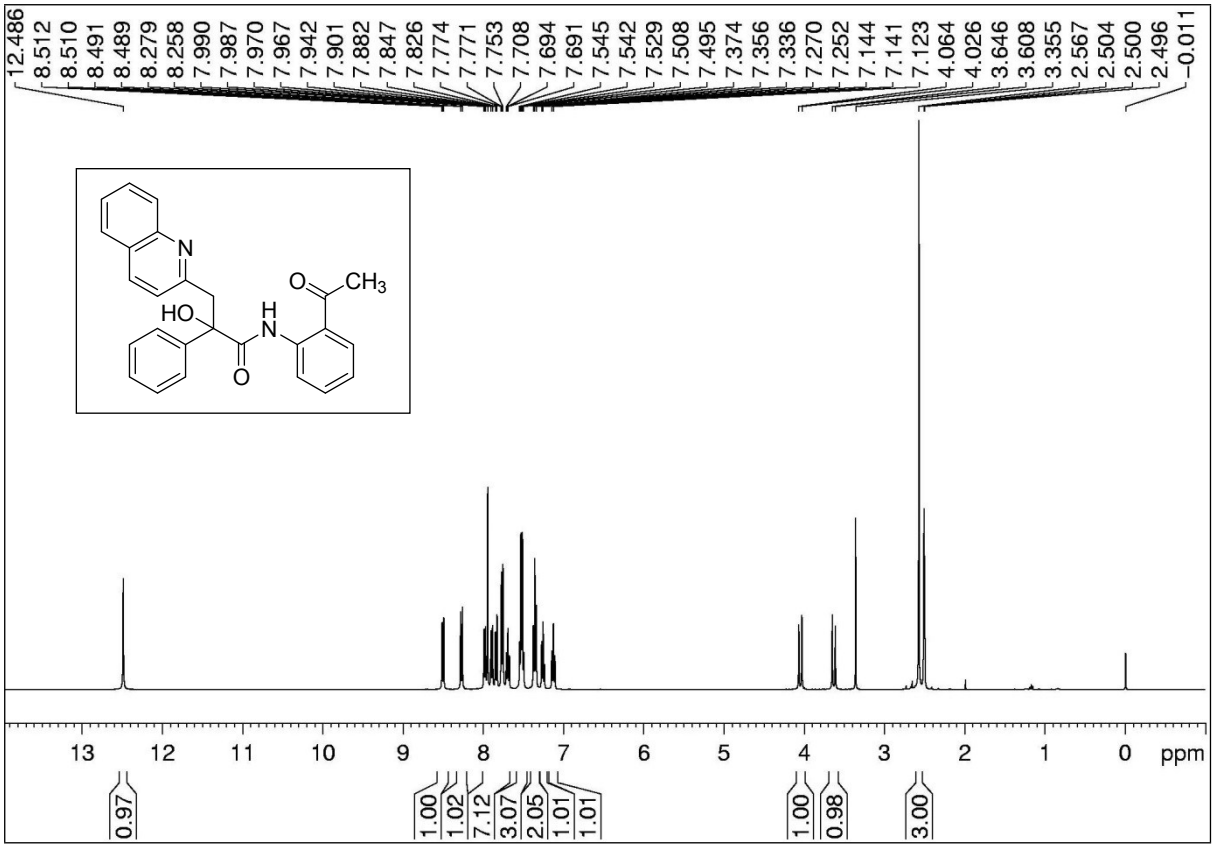

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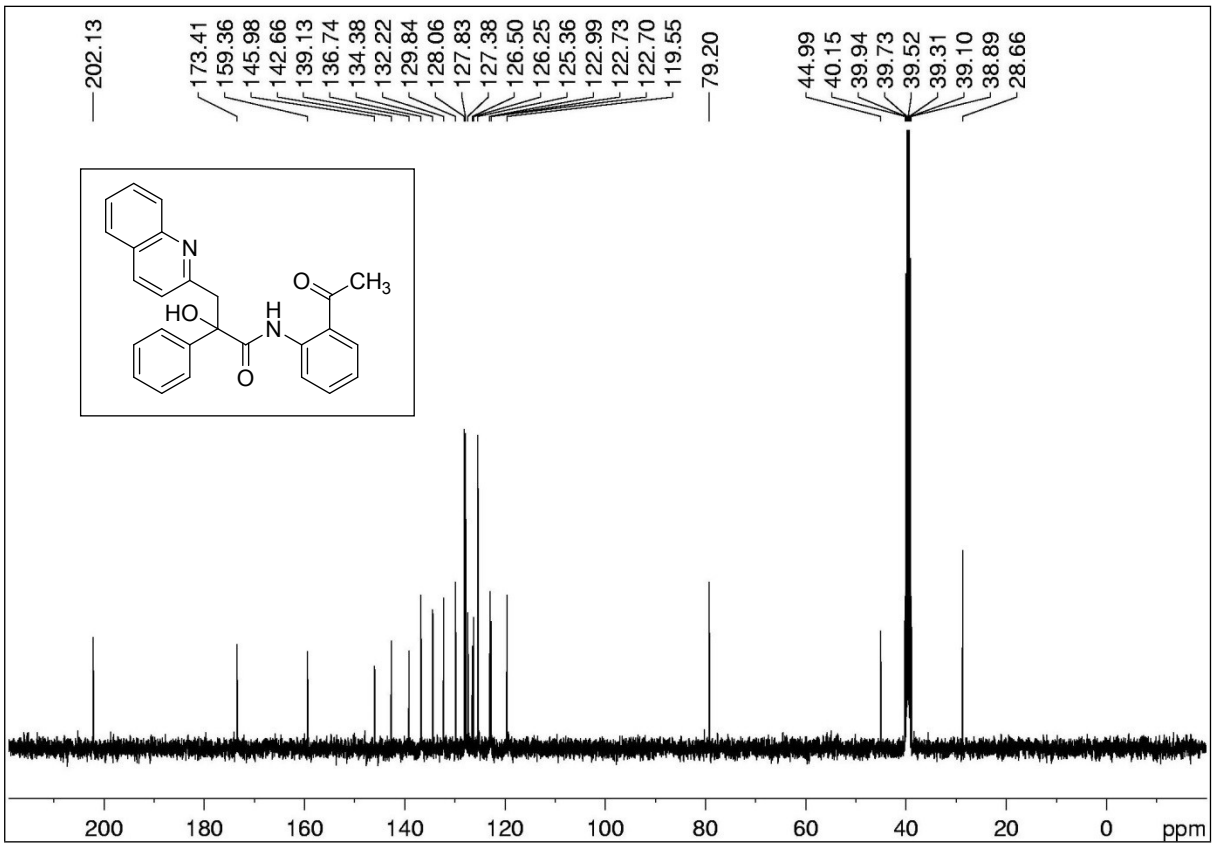
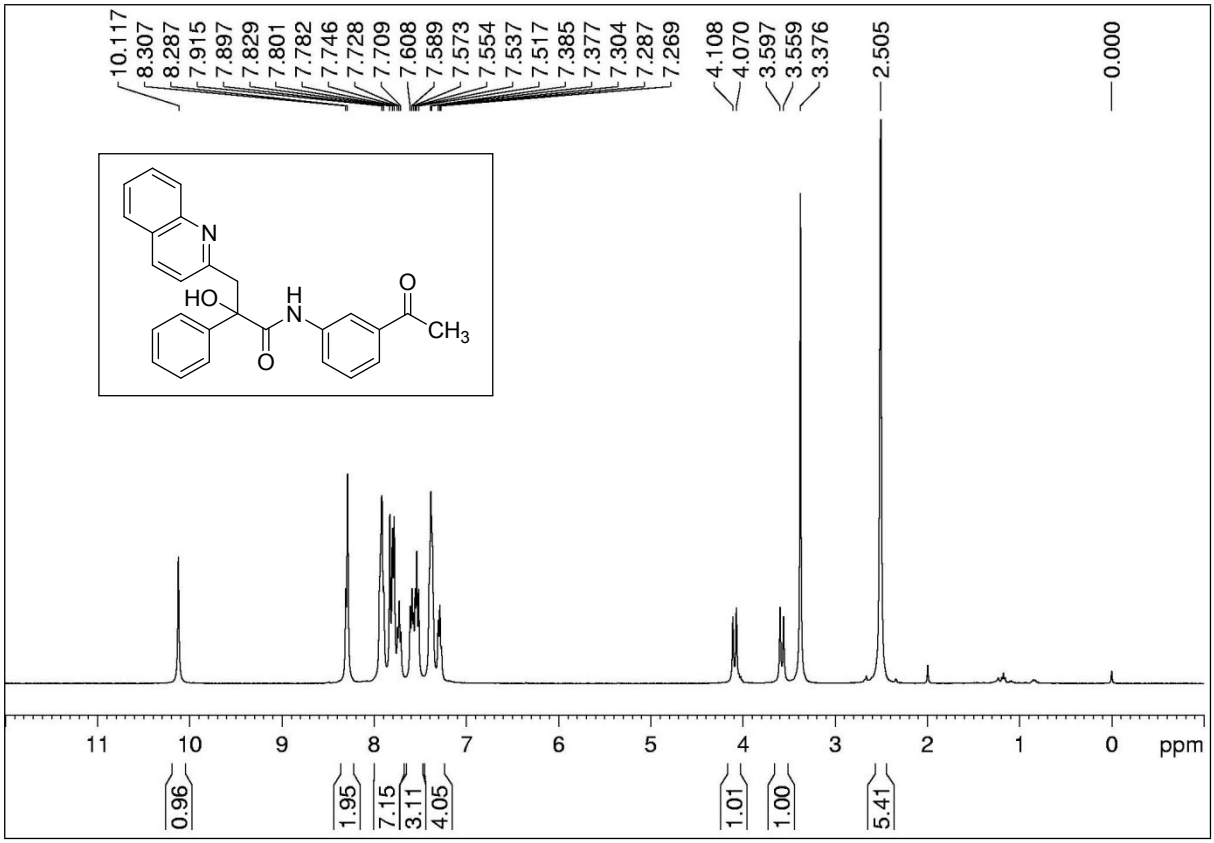


100 MHz ^{1}H-NMR spectra of **7a** in DMSO-d_6



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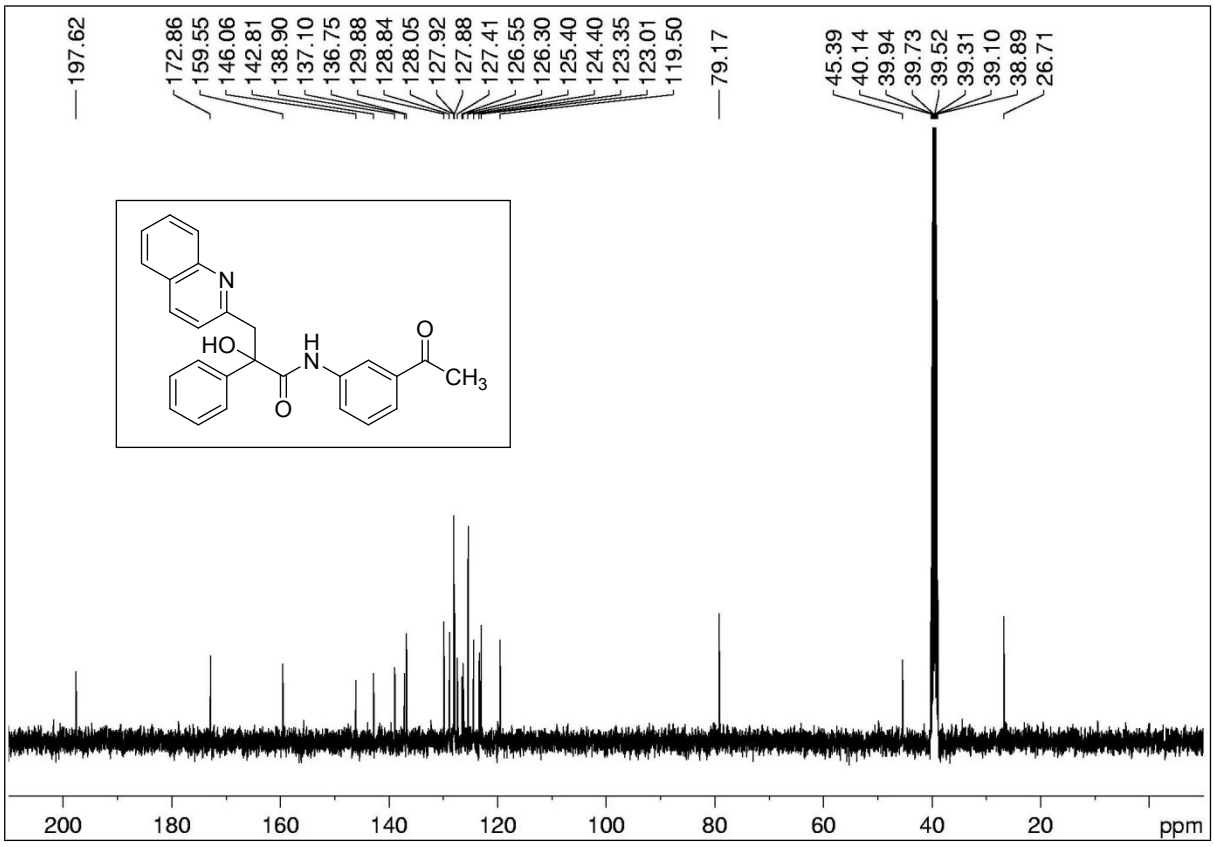
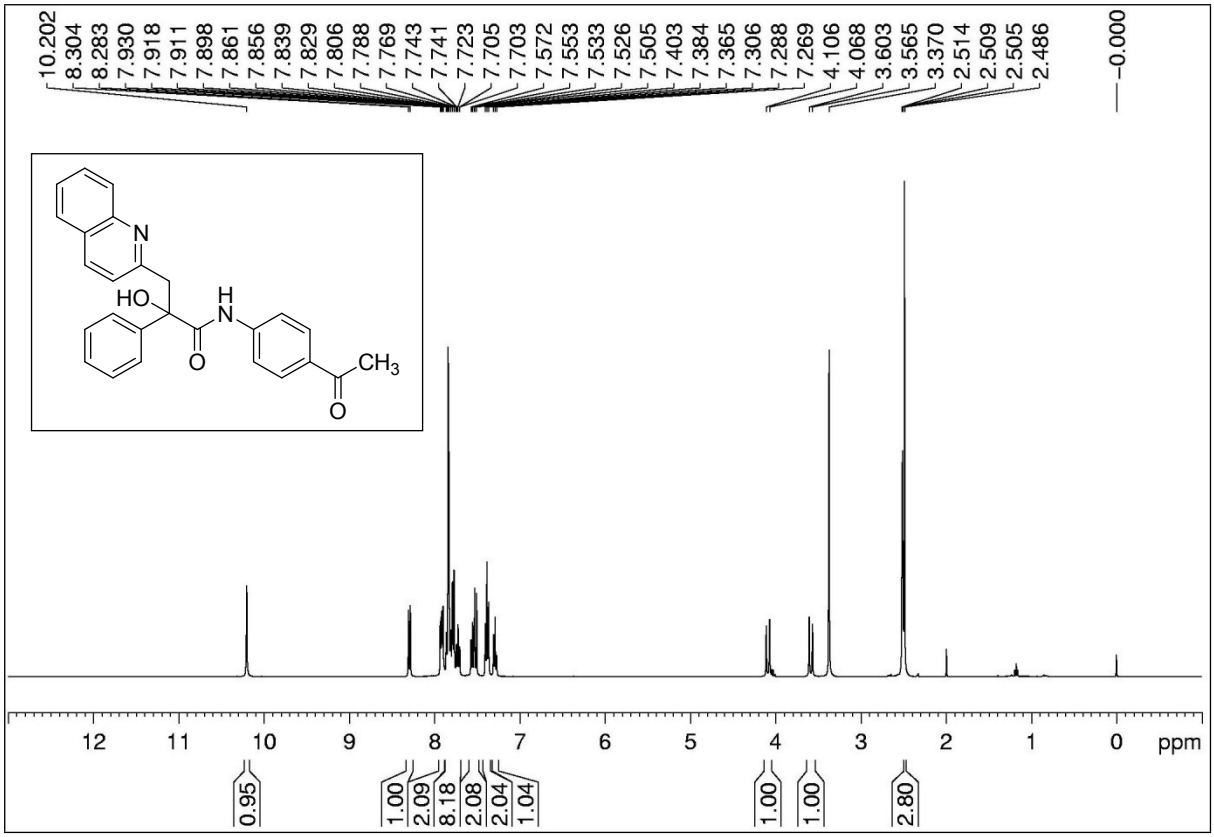
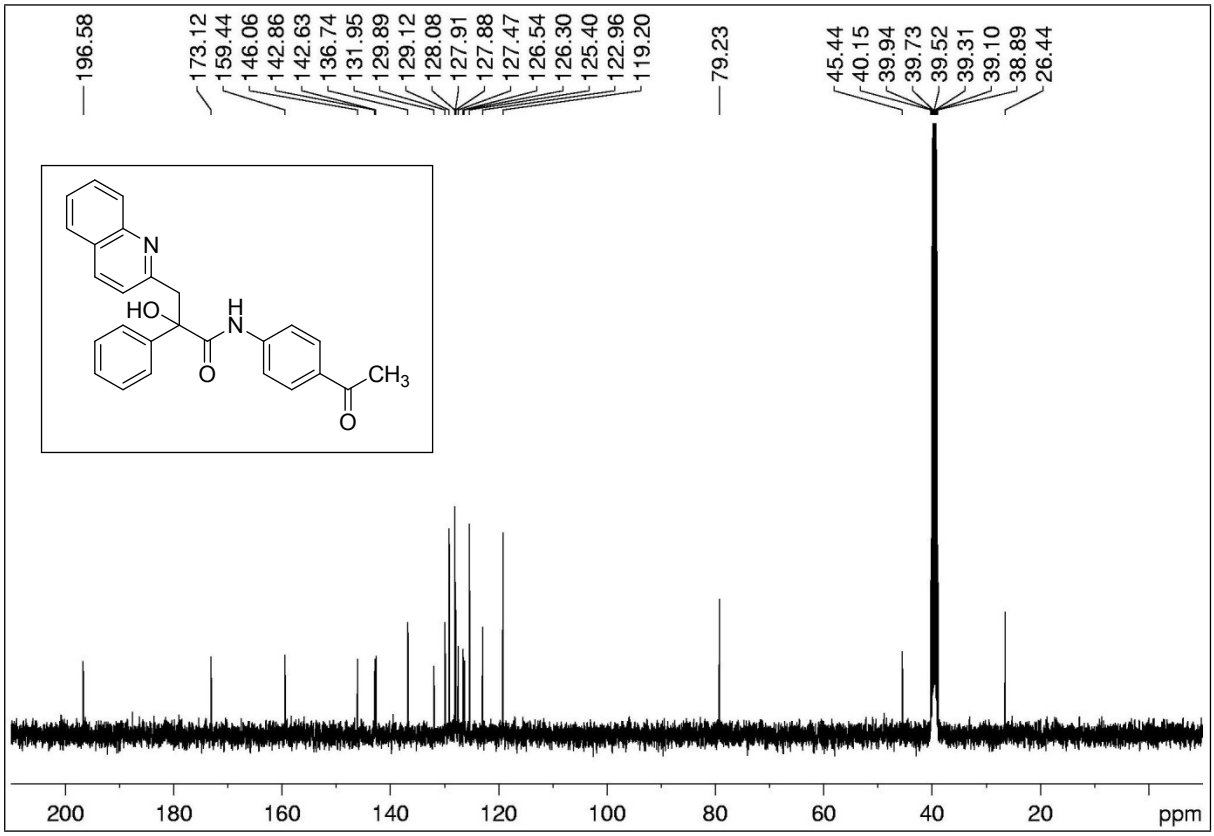


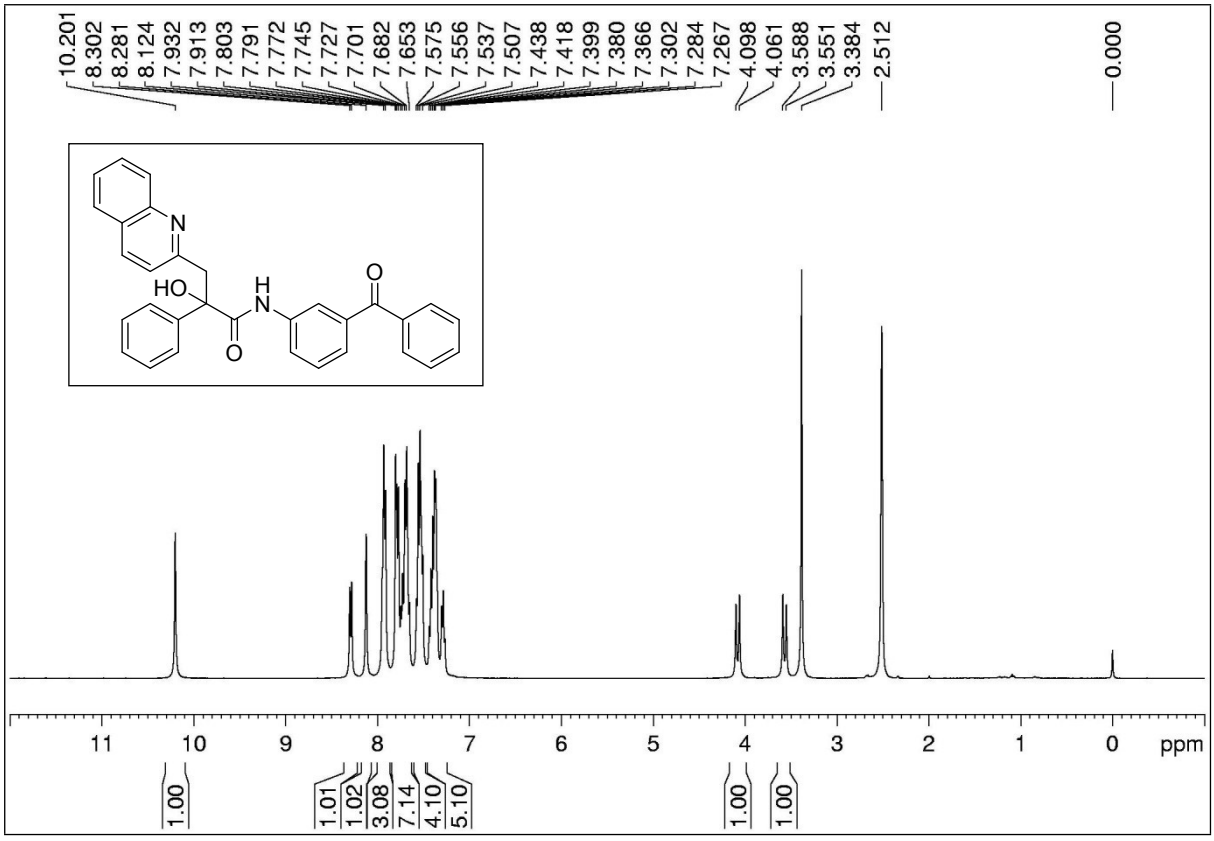
100 MHz ^{1}H-NMR spectra of **7b** in DMSO-d_6



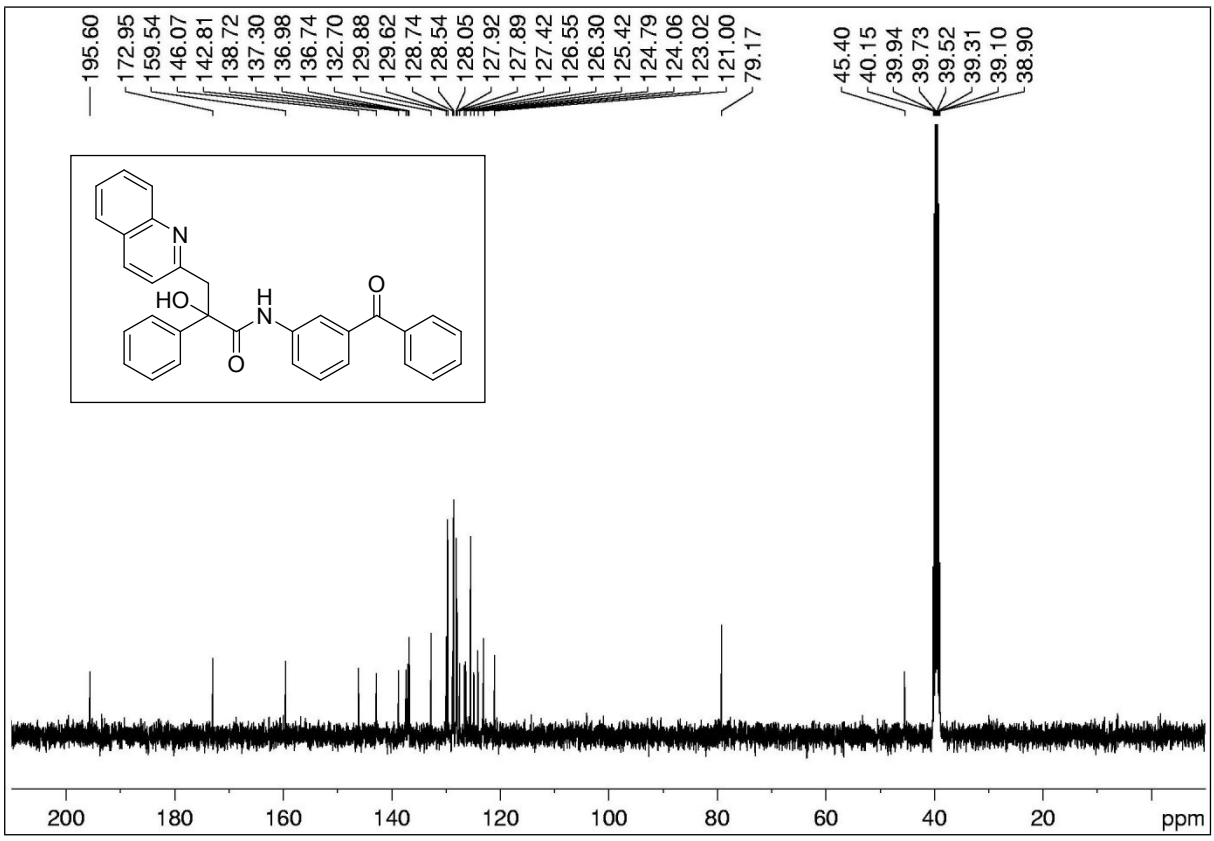
400 MHz ^{1}H-NMR spectra of **7c** in DMSO-d_6



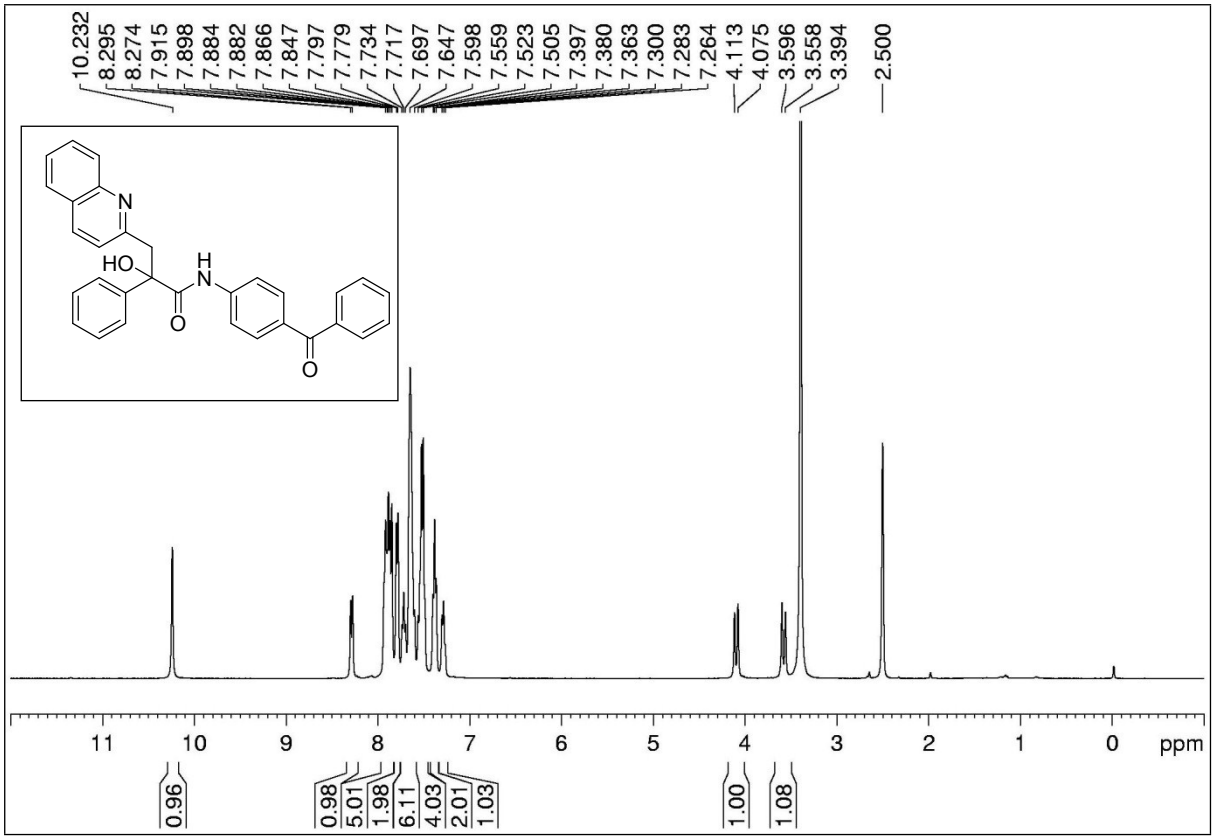
100 MHz ^{1}H-NMR spectra of **7c** in DMSO-d_6



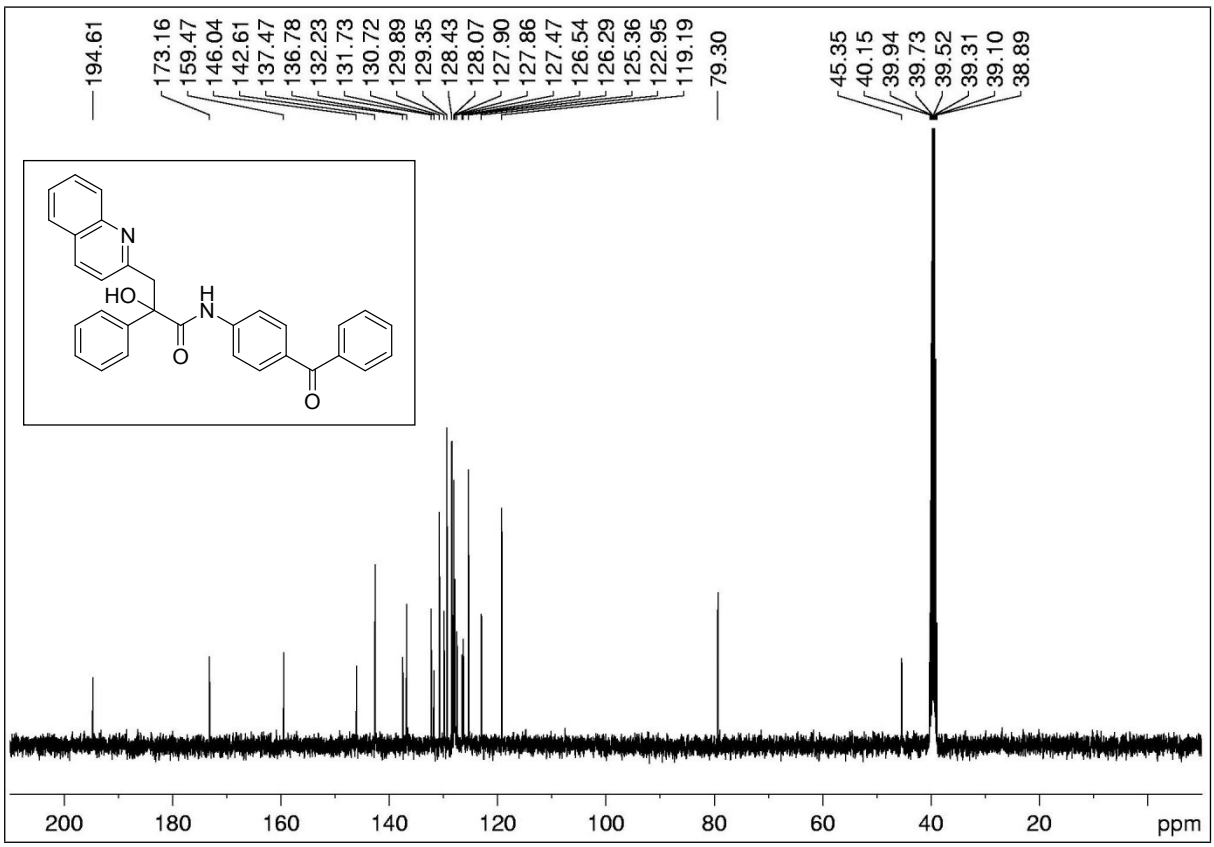
400 MHz ^{1}H-NMR spectra of **7d** in DMSO-d_6



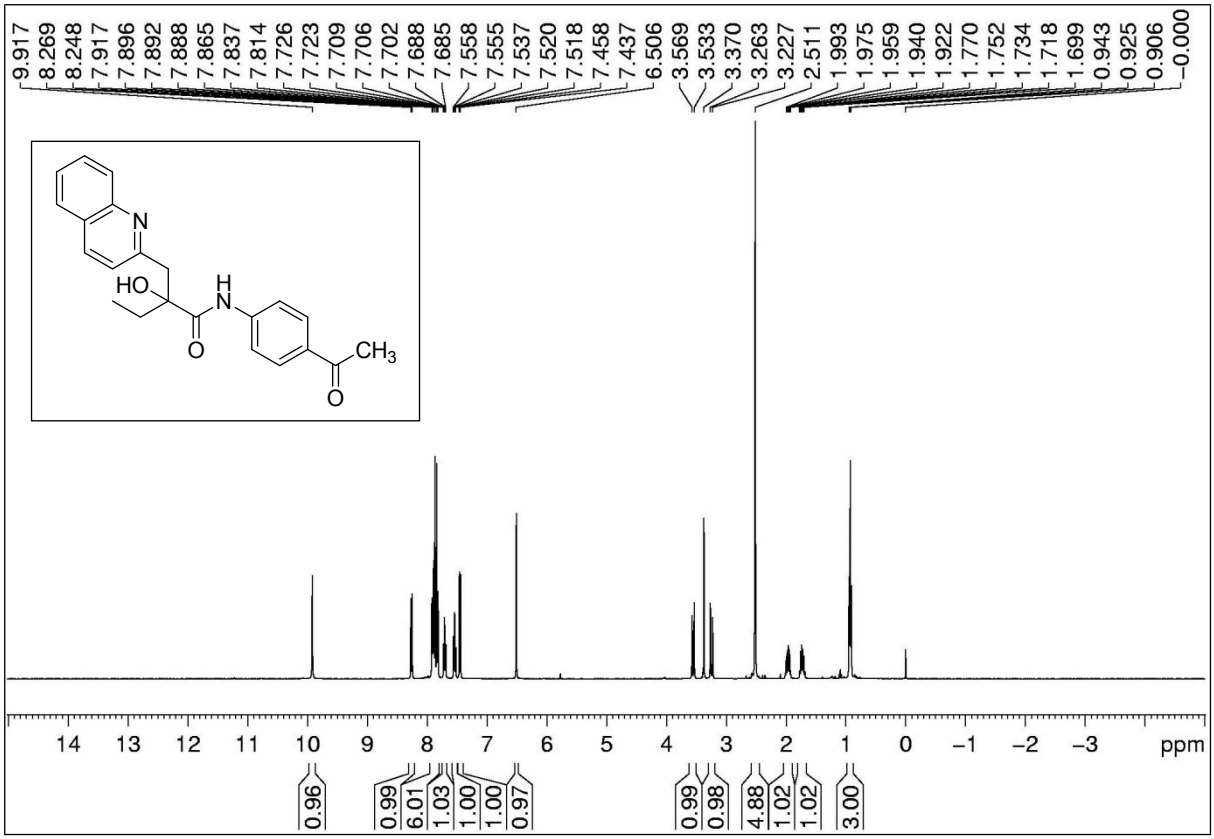
100 MHz ^{1}H-NMR spectra of **7d** in DMSO-d_6



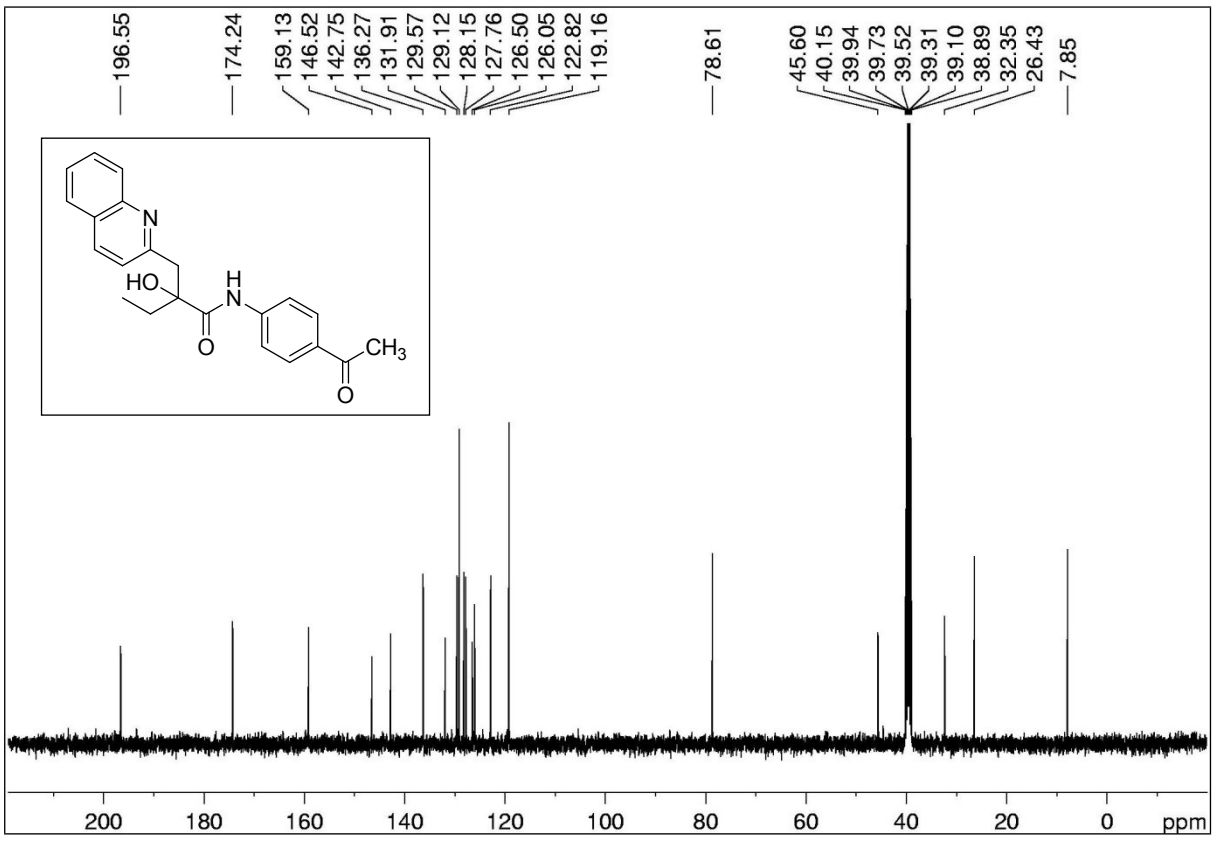
400 MHz ^{1}H-NMR spectra of **7e** in DMSO-d_6



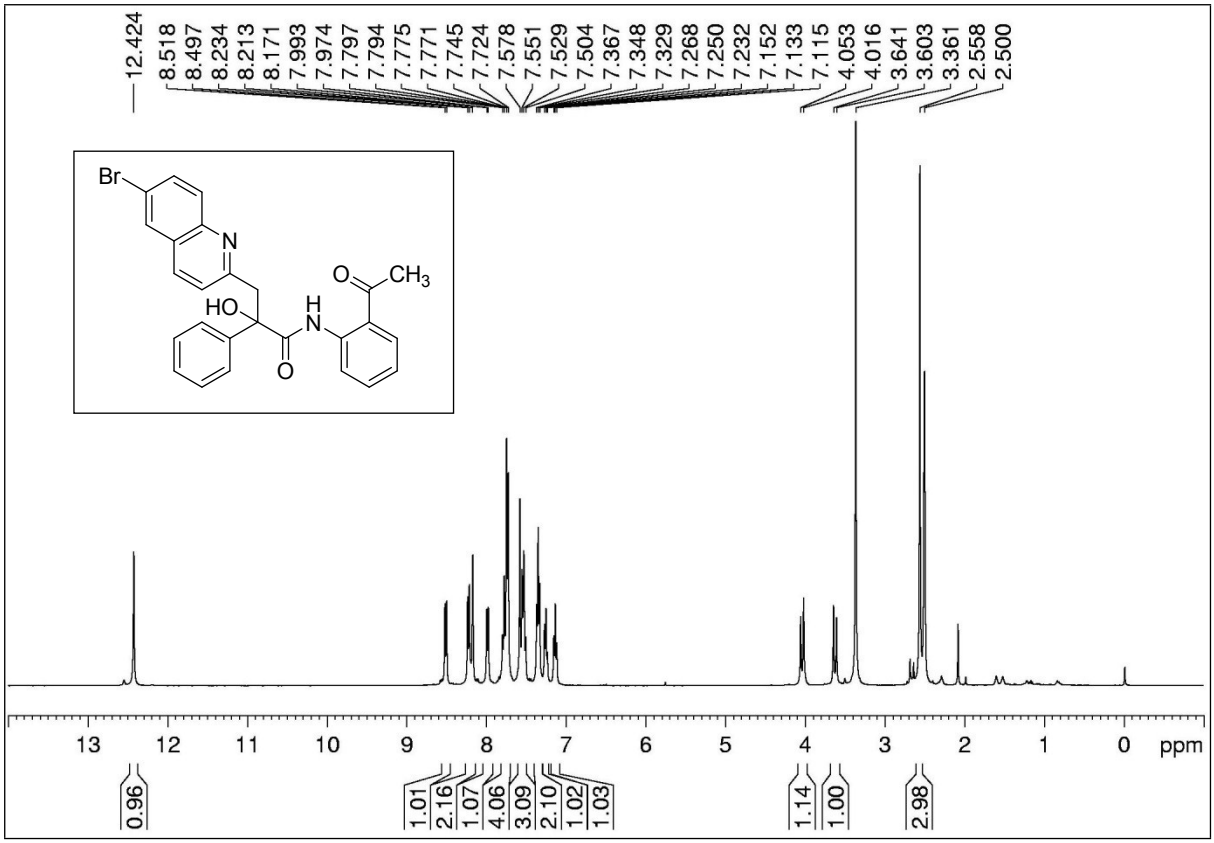
100 MHz ^{1}H-NMR spectra of **7e** in DMSO-d_6



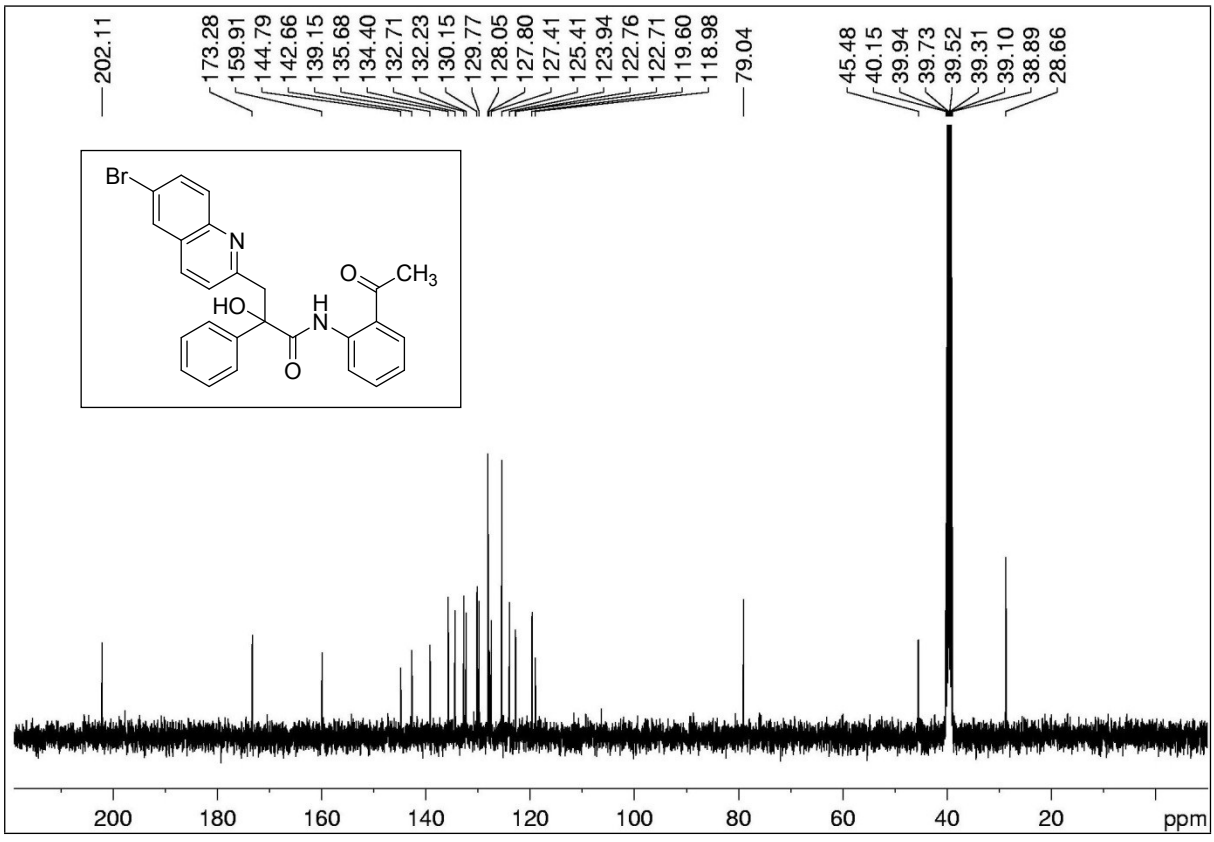
400 MHz ^{1}H-NMR spectra of **7f** in DMSO-d_6



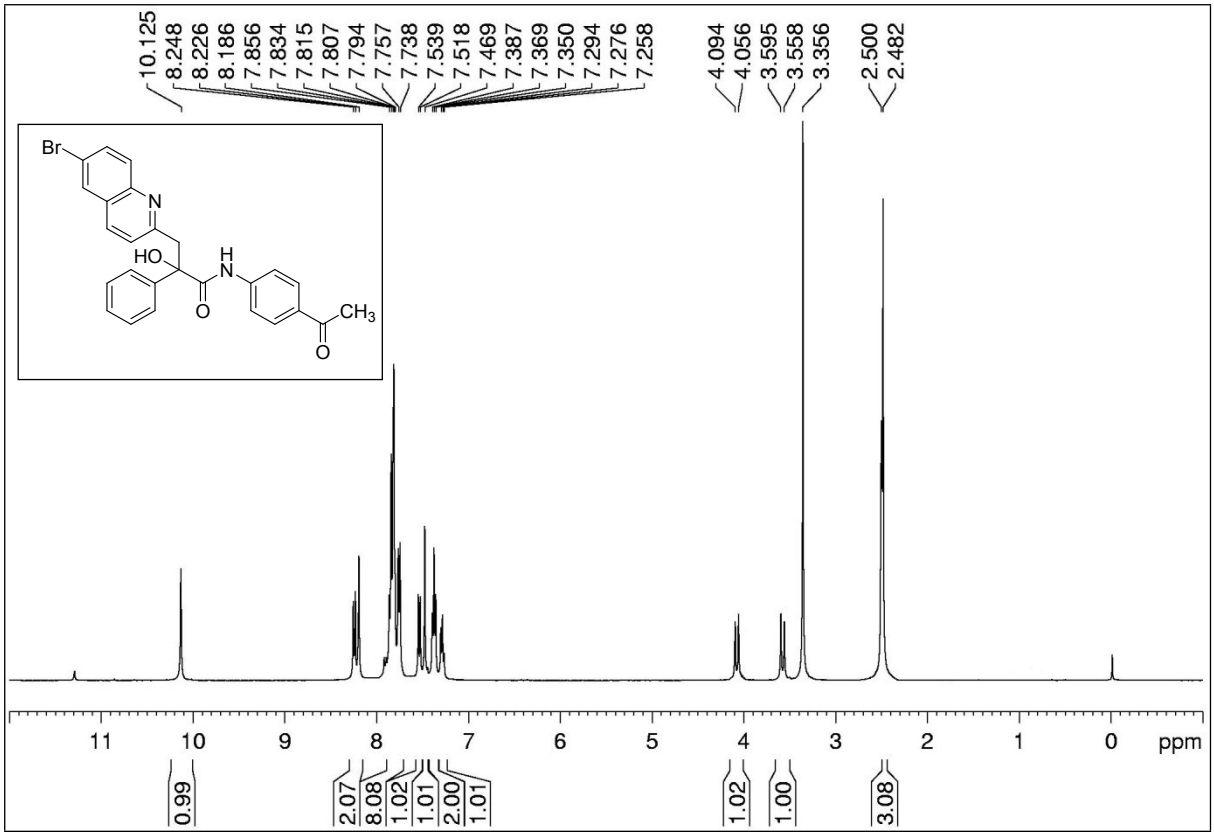
100 MHz ^{1}H-NMR spectra of **7f** in DMSO-d_6



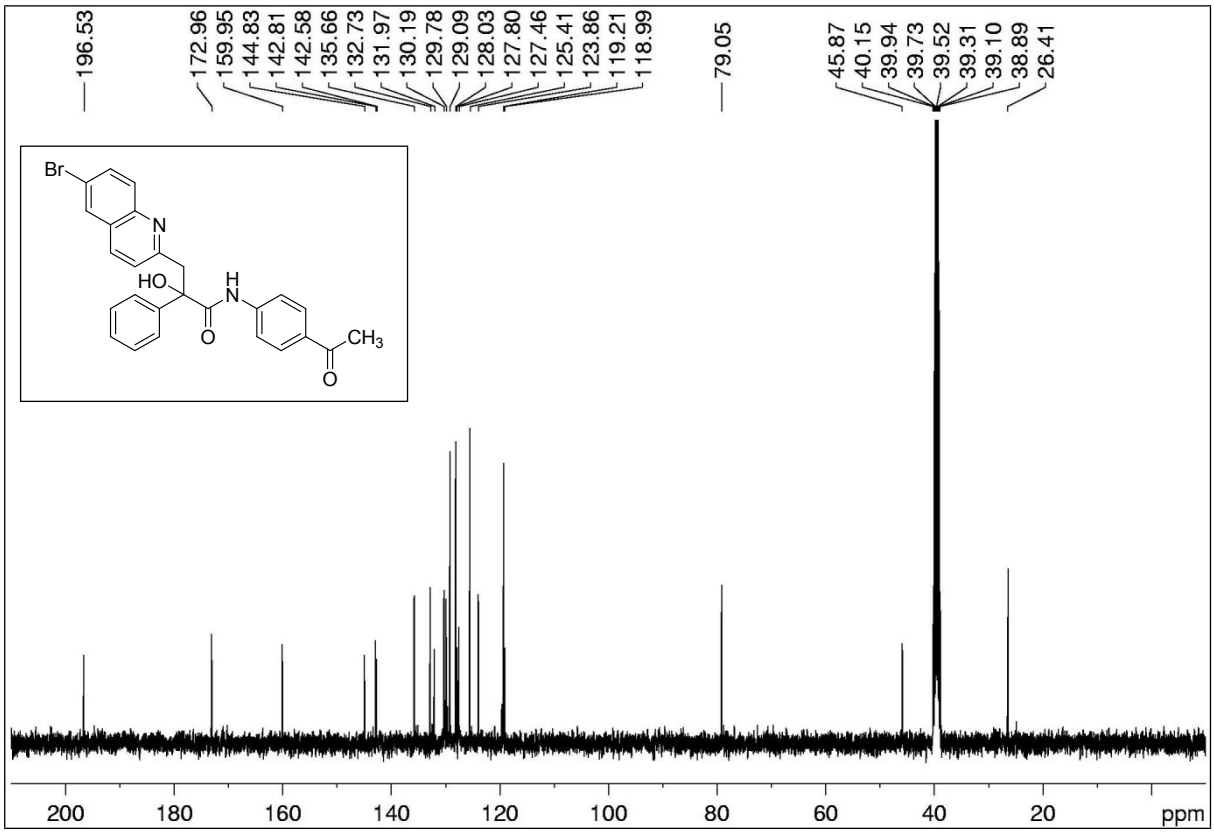
400 MHz ^{1}H-NMR spectra of **7g** in DMSO-d_6



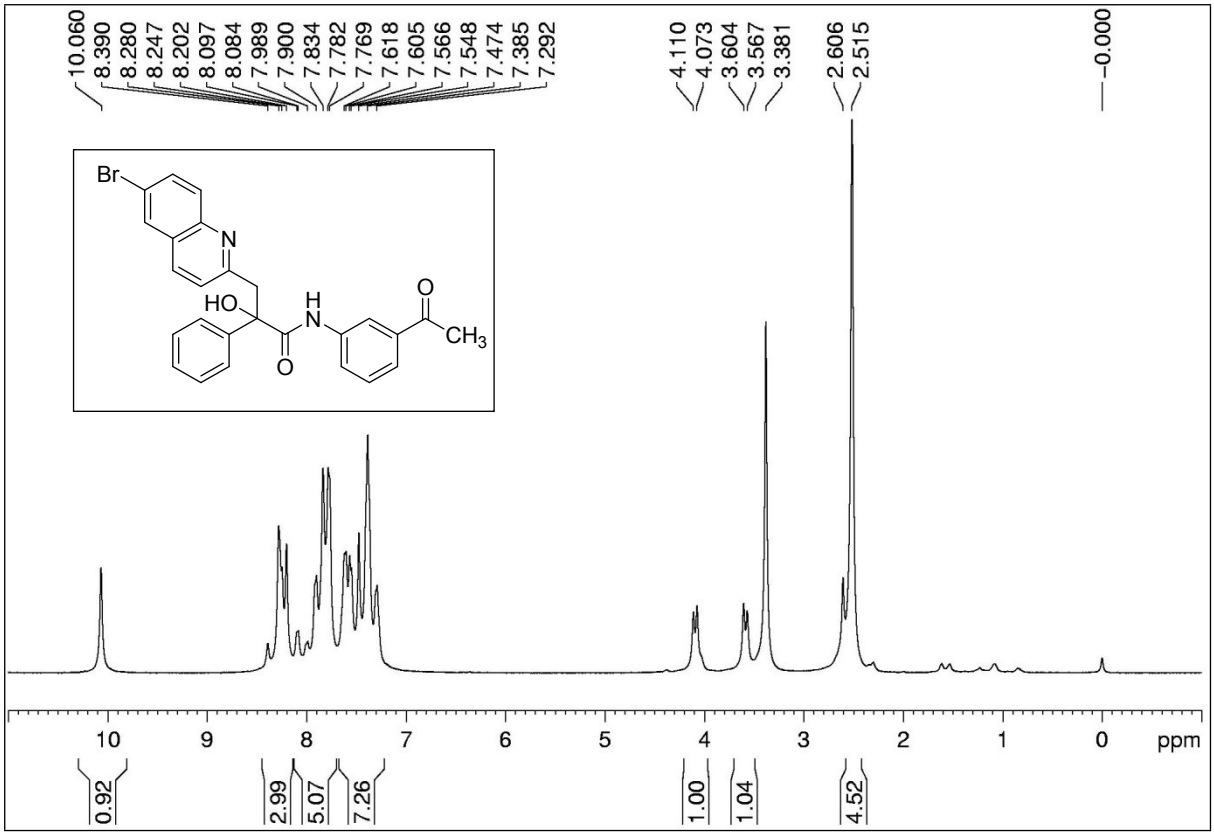
100 MHz ^{1}H-NMR spectra of **7g** in DMSO-d_6



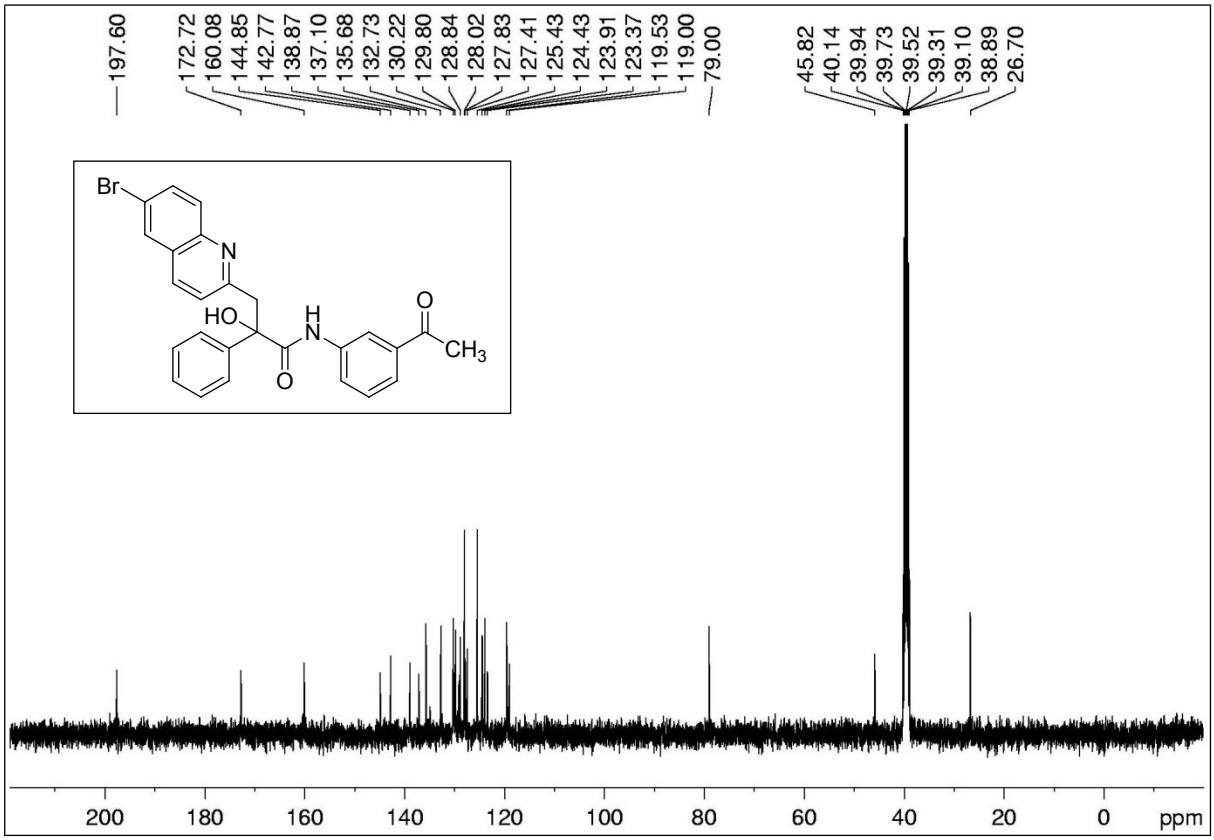
400 MHz ^{1}H-NMR spectra of **7h** in DMSO-d_6



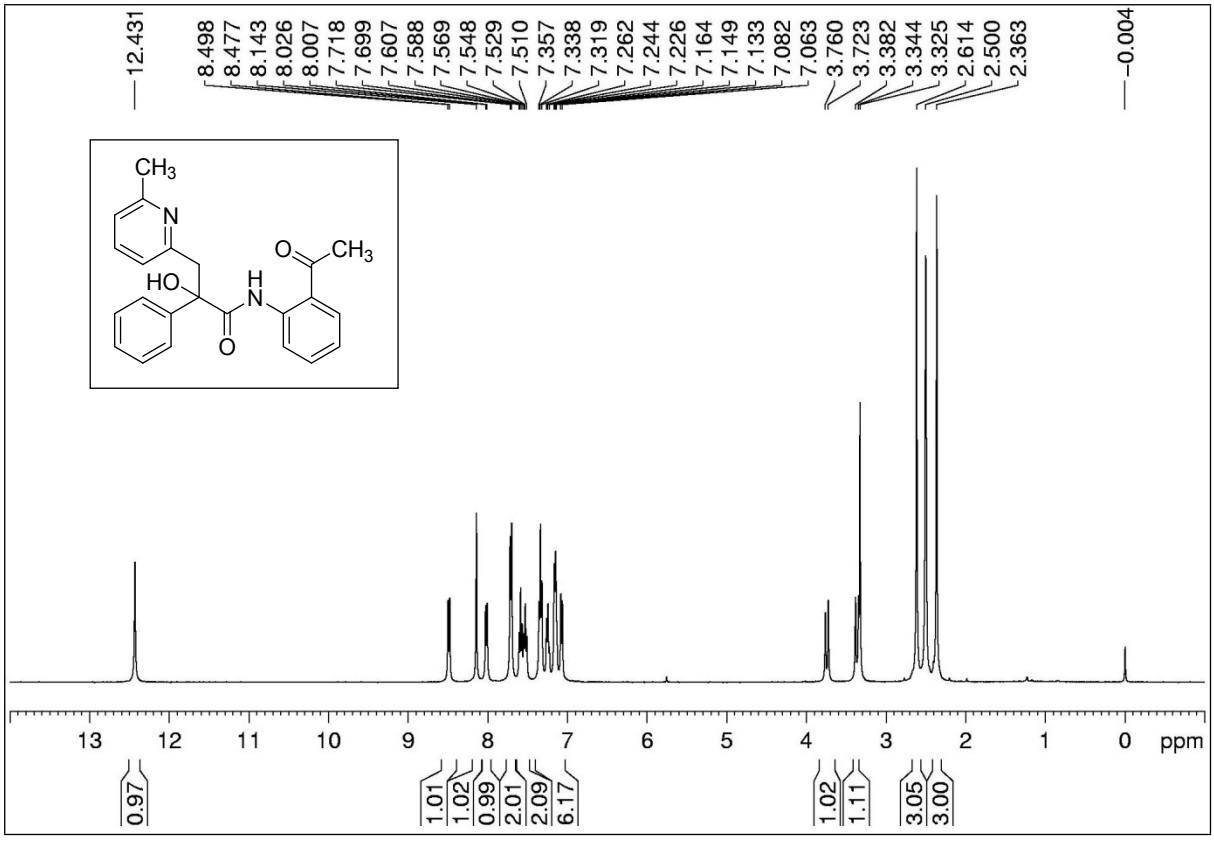
100 MHz ^{1}H-NMR spectra of **7h** in DMSO-d_6



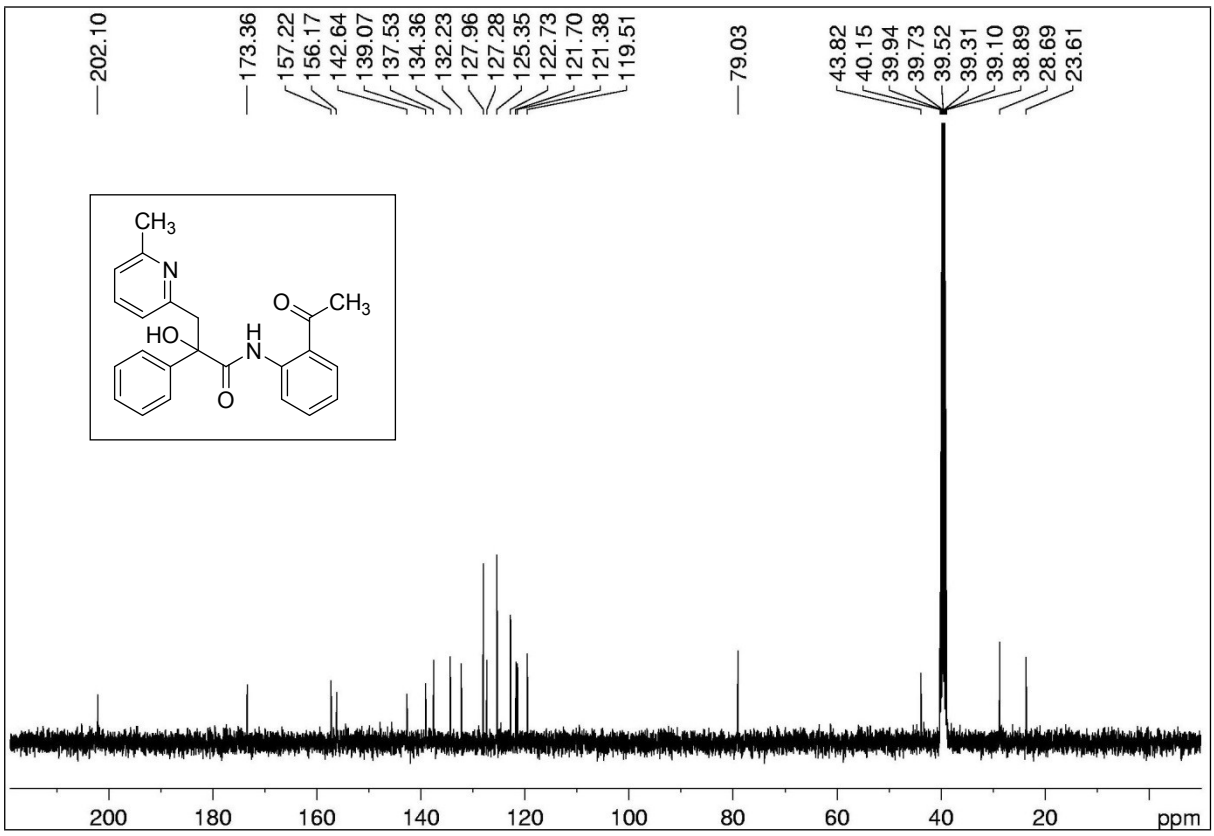
400 MHz ^{1}H-NMR spectra of **7i** in DMSO-d_6



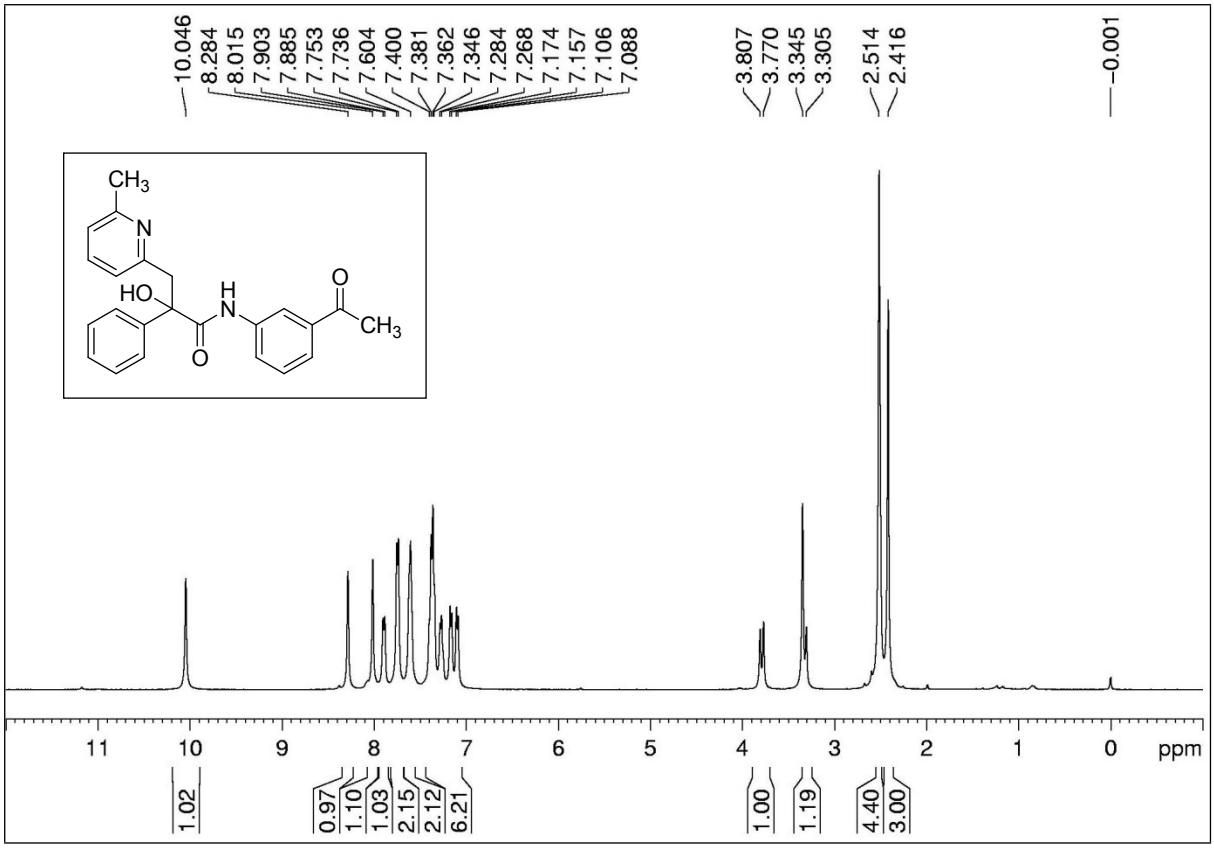
100 MHz ^{1}H-NMR spectra of **7i** in DMSO-d_6



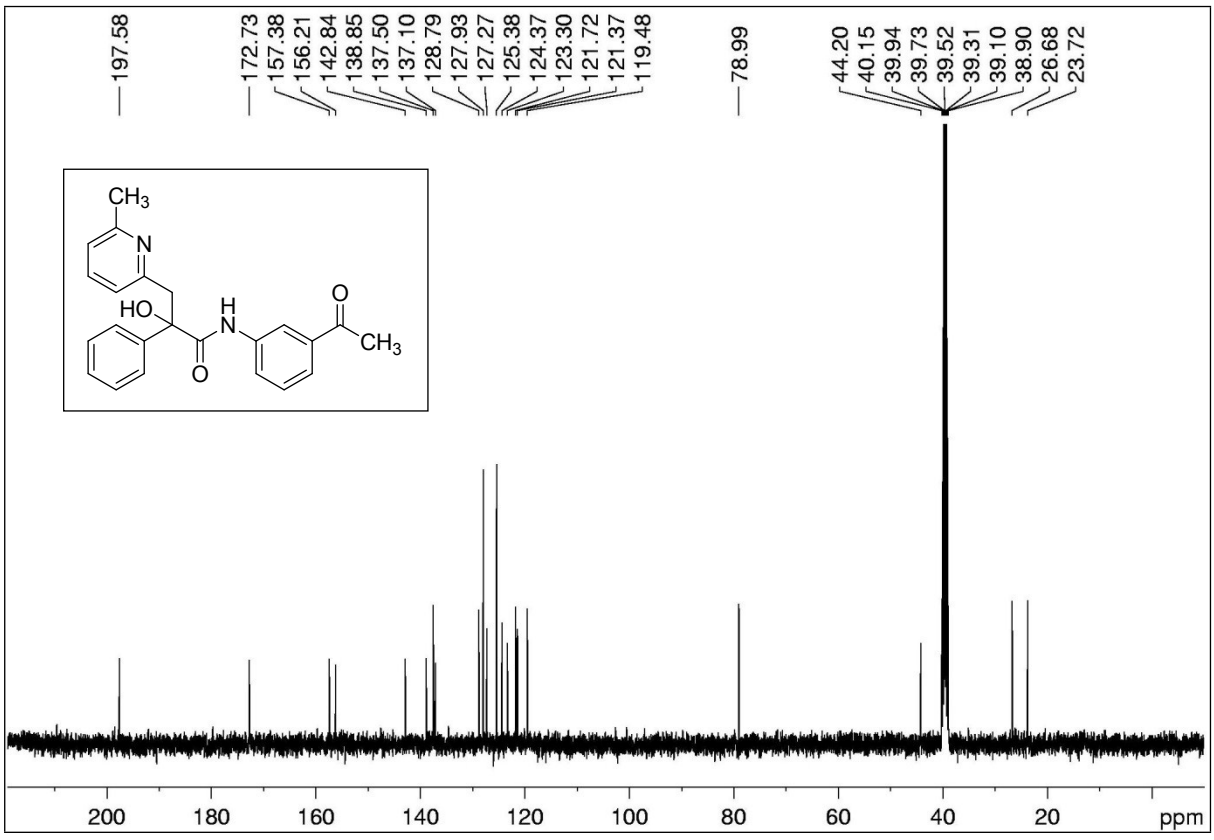
400 MHz ^{1}H-NMR spectra of **7j** in DMSO-d_6



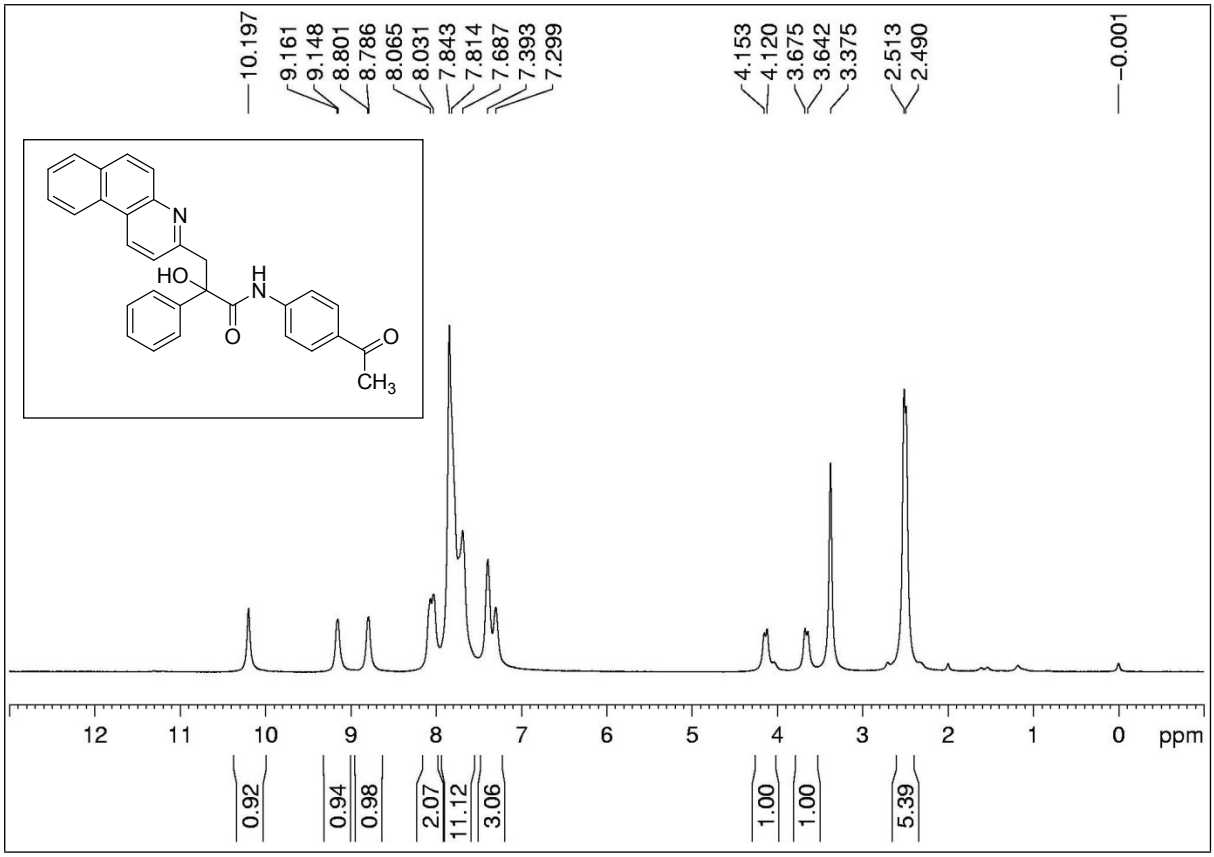
100 MHz ^{1}H-NMR spectra of **7j** in DMSO-d_6



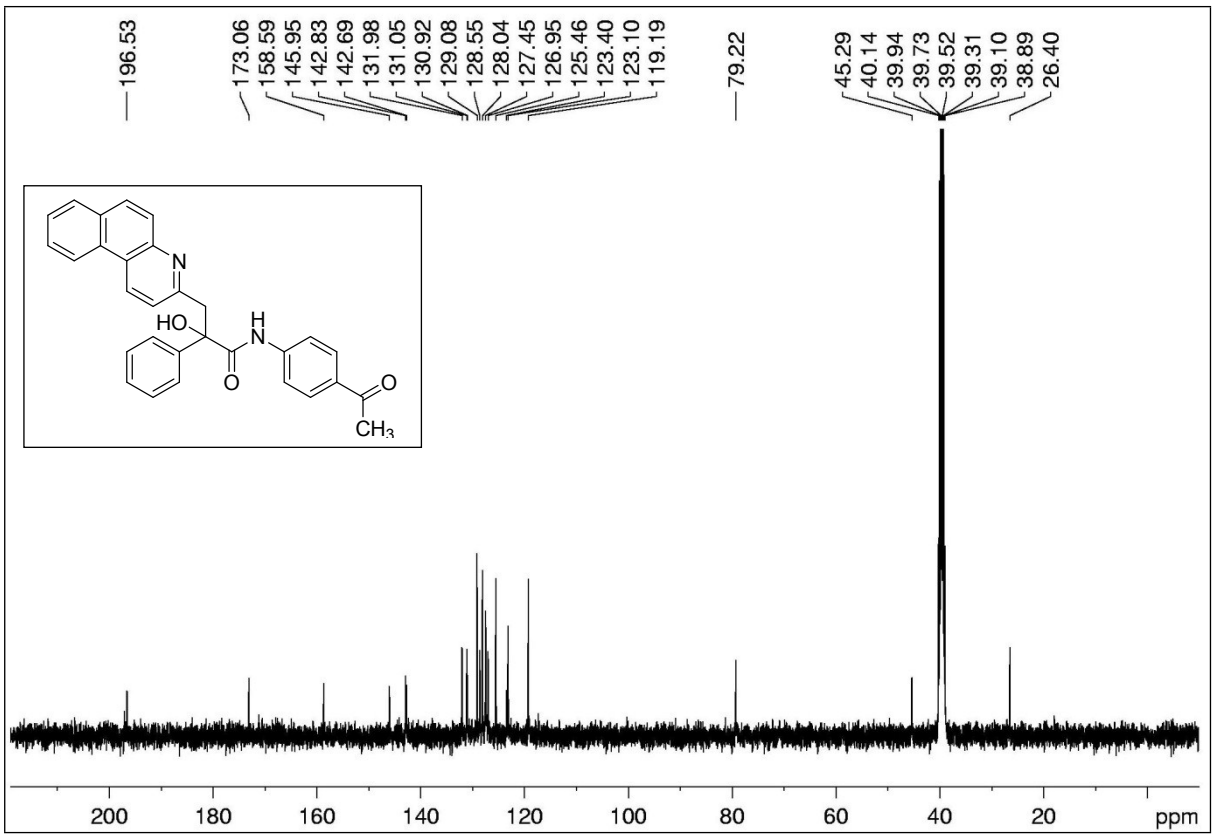
400 MHz ^{1}H-NMR spectra of **7k** in DMSO-d_6



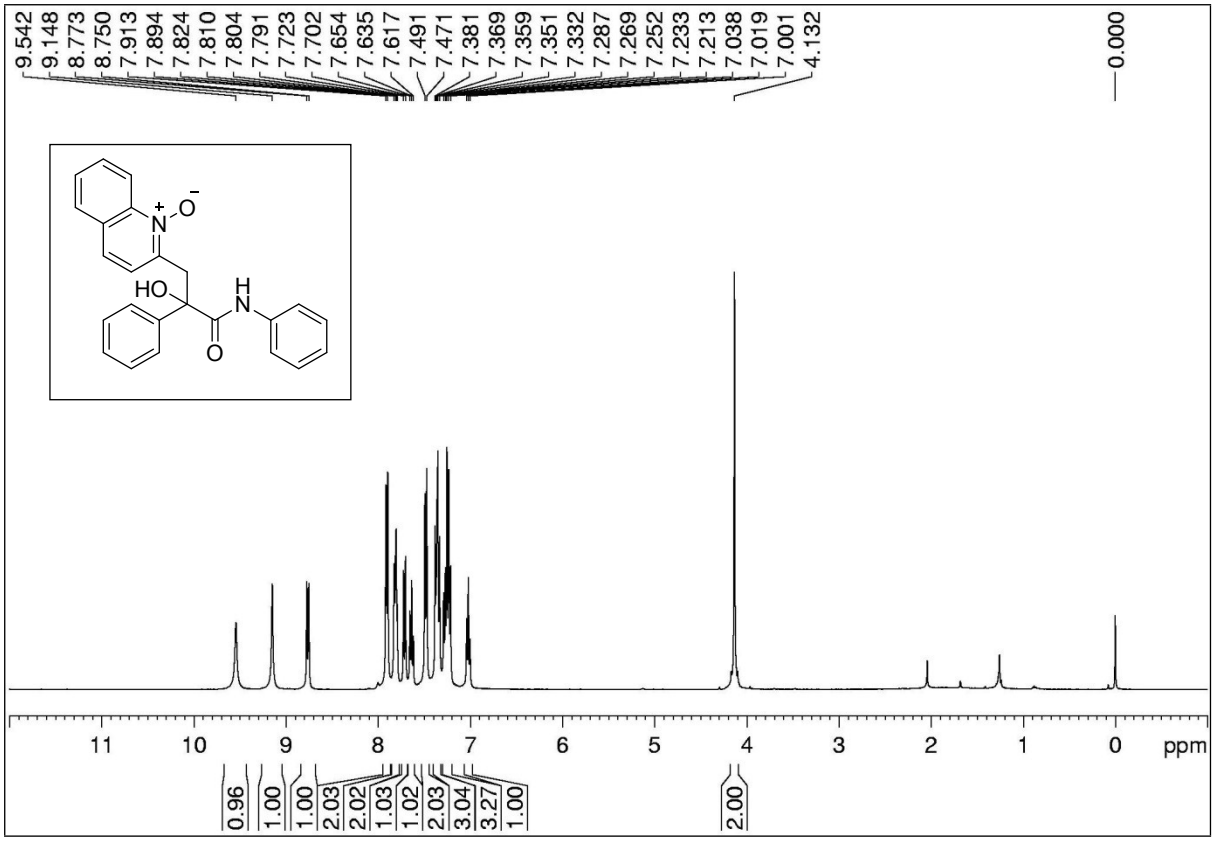
100 MHz ^{1}H-NMR spectra of **7k** in DMSO-d_6



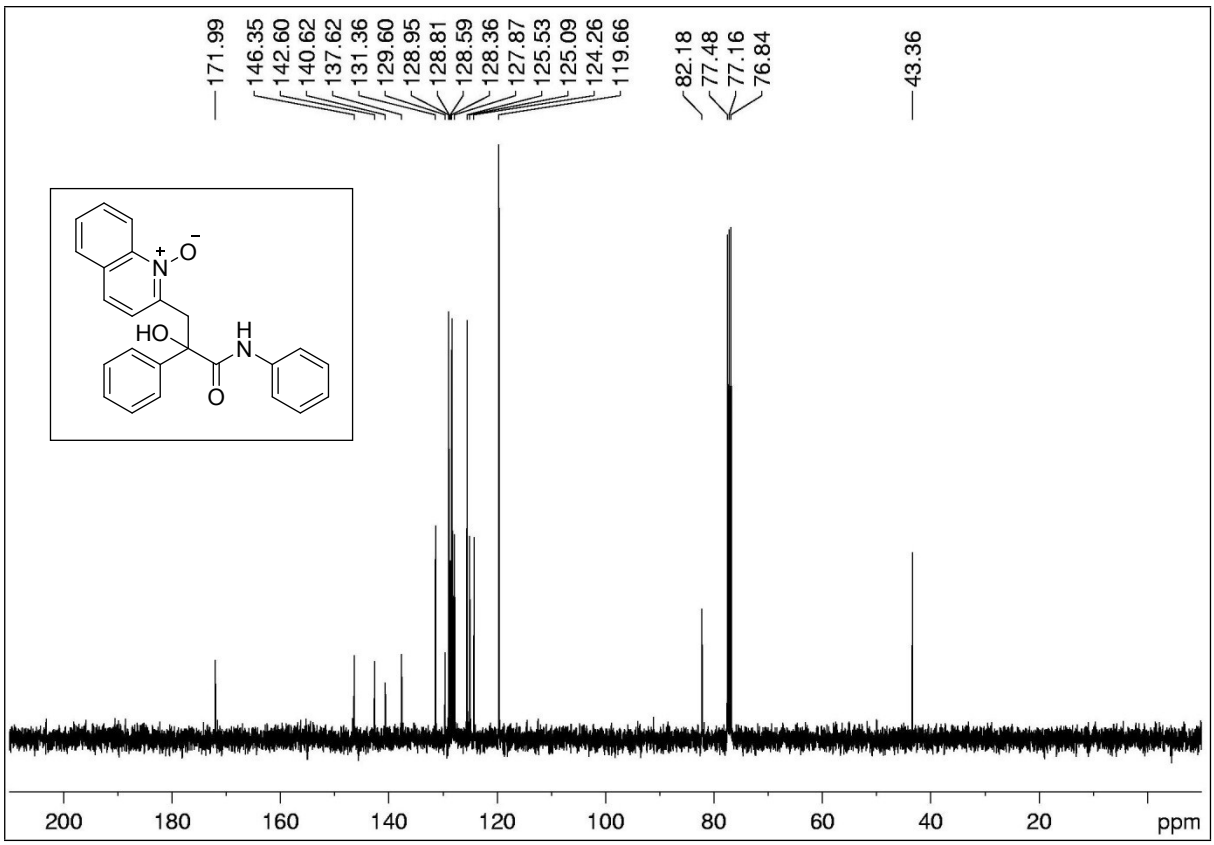
400 MHz ^{1}H-NMR spectra of **7l** in DMSO-d_6



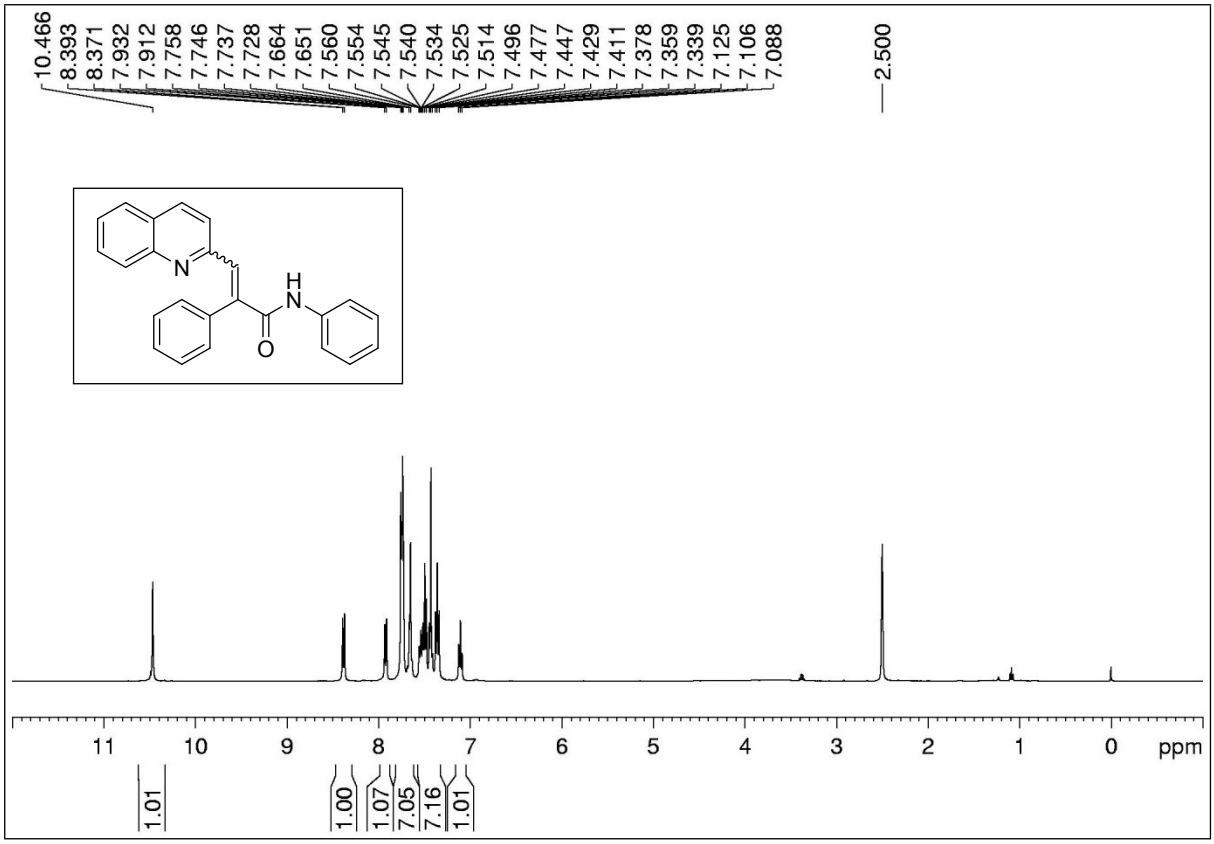
100 MHz ^{1}H-NMR spectra of **7l** in DMSO-d_6



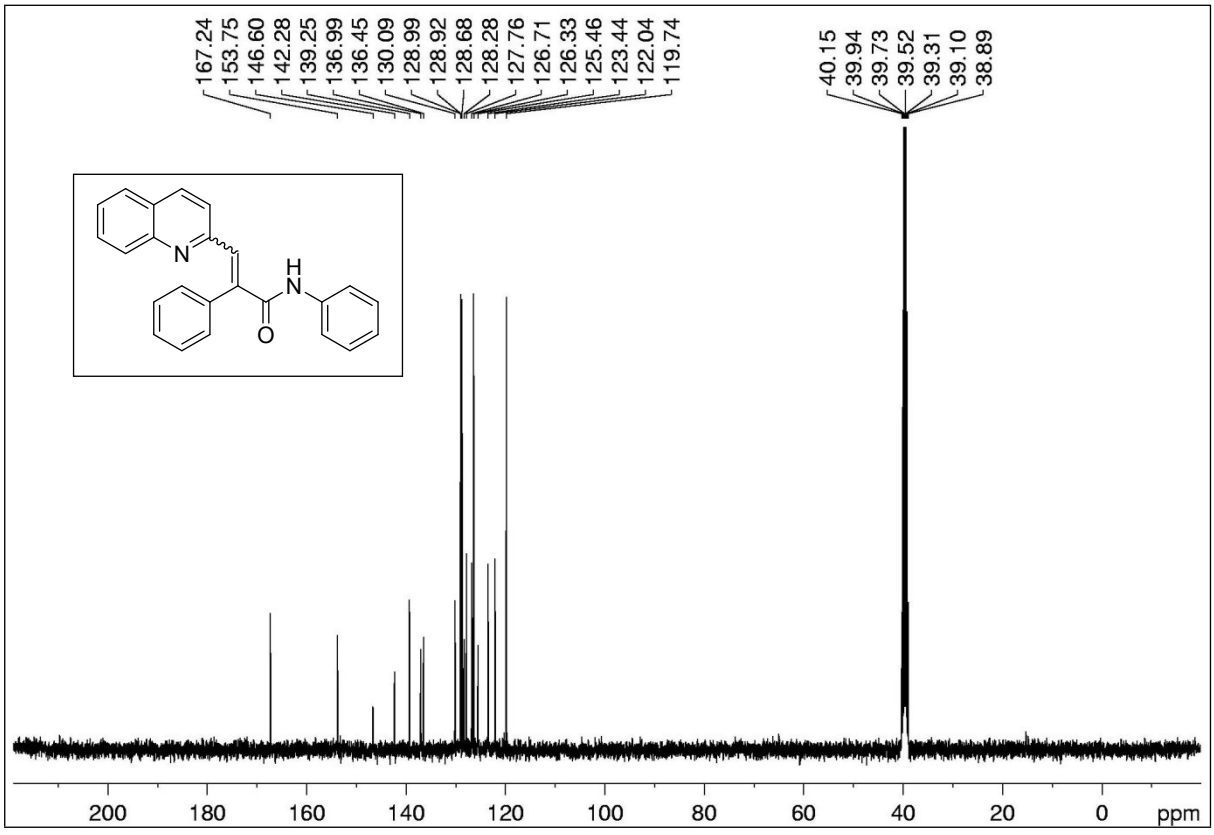
400 MHz ^{1}H-NMR spectra of **8** in $CDCl_3$



100 MHz ^{1}H-NMR spectra of **8** in $CDCl_3$



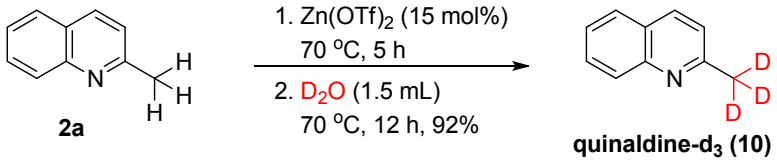
400 MHz ^{1}H-NMR spectra of **9** in DMSO-d_6



100 MHz ^{1}H-NMR spectra of **9** in DMSO-d_6

Mechanistic investigation

Interaction of 2-methylquinoline with $Zn(OTf)_2$ and Deuterium exchange experiments



To an oven dried reaction tube equipped with a magnetic stir bar, $Zn(OTf)_2$ (0.15 mmol), 2-methylquinoline (1.5 mmol) (Figure 1) were sequentially added. The reaction tube was then closed with a glass stopper and placed into a pre-heated oil bath at 70 °C for 5 h. The reaction mass turned red colour. A small amount of sample was drawn from the reaction mixture and analyzed by ^{1}H NMR spectroscopy (Figure 2). Then, D_2O (1.5 mL) was added to the reaction mixture and allowed for stirring at 70 °C for 12 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL), the extracted organic layer was passed through a short pad of silica gel then dried using $MgSO_4$ crystals and concentrated in vacuo. The resulting residue (in 92% isolated yield) was analyzed by ^{1}H NMR spectroscopy from which the formation of quinaldine-d_3 (**10**) was identified (Figure 3) and confirmed by GC-MS (Figure 4).

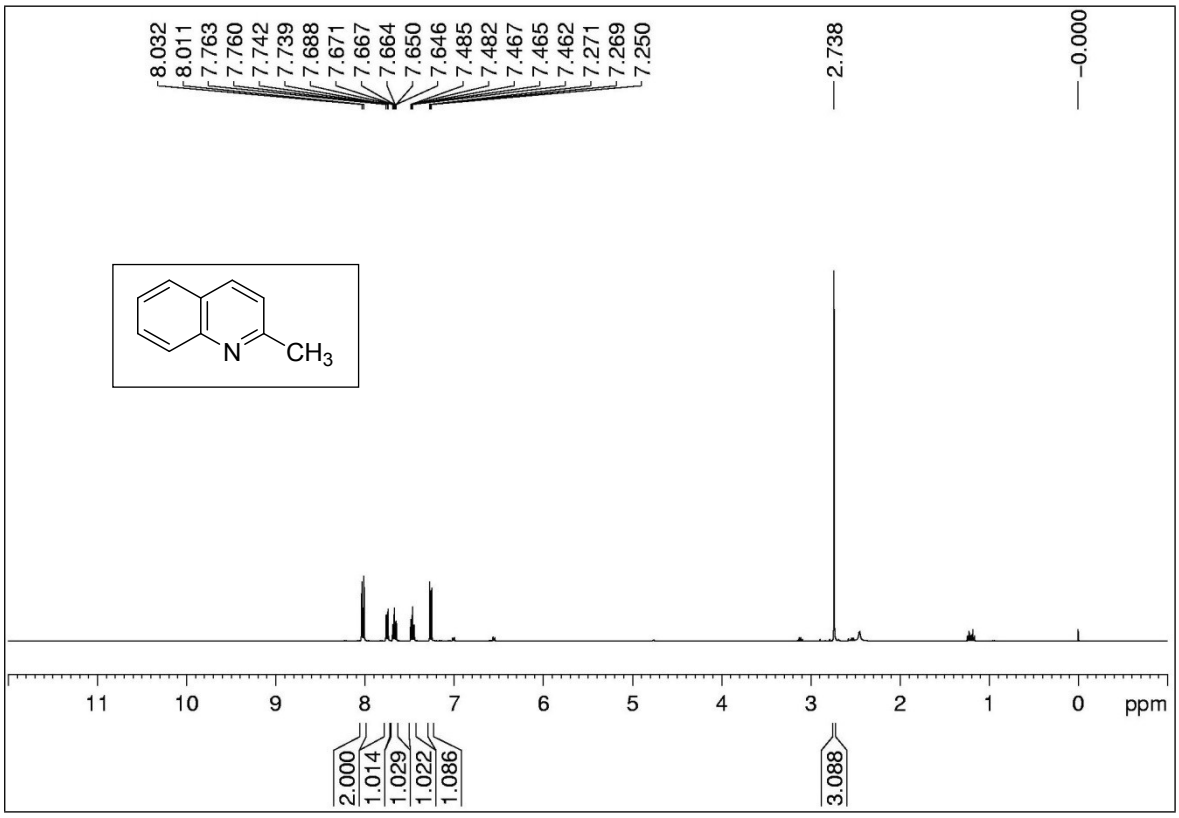


Figure 1. 400 MHz ^{1}H-NMR spectra of 2-methylquinoline **2a** in $CDCl_3$

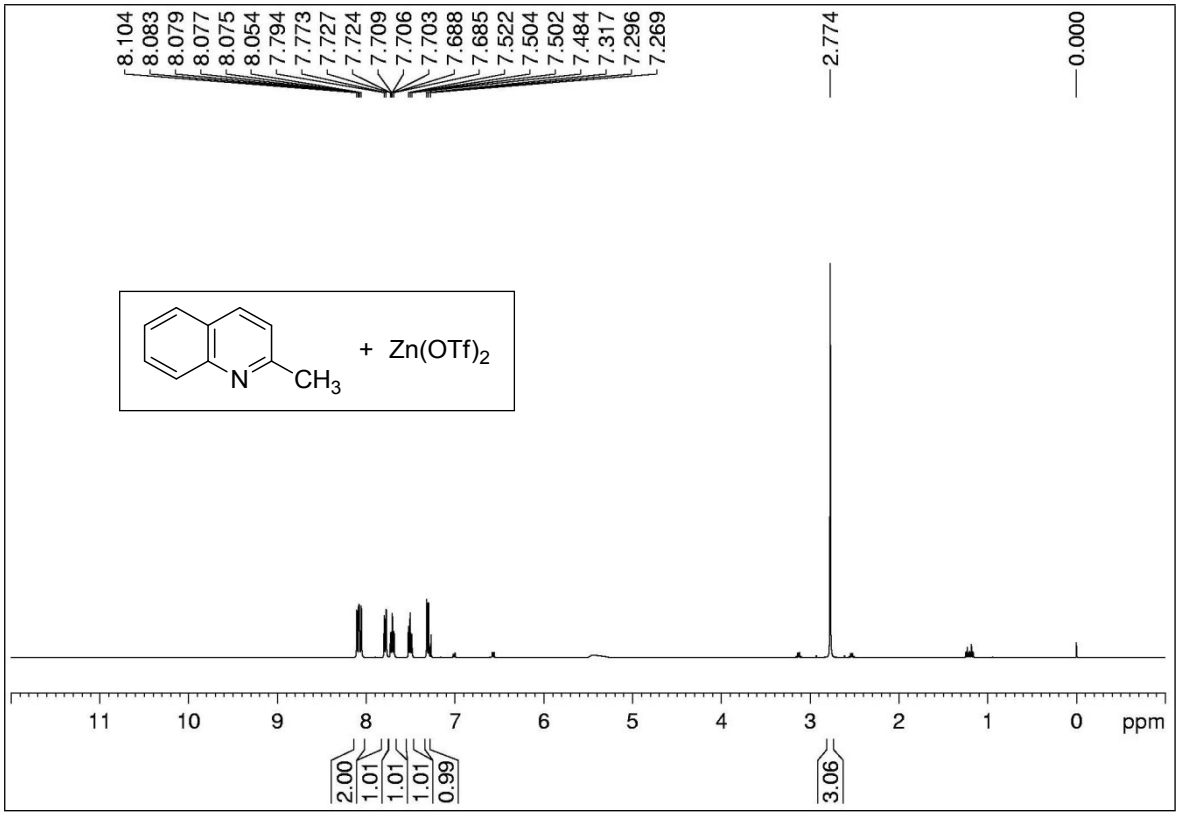


Figure 2. 400 MHz ^{1}H-NMR spectra of 2-methylquinoline **2a** with $Zn(OTf)_2$ in $CDCl_3$

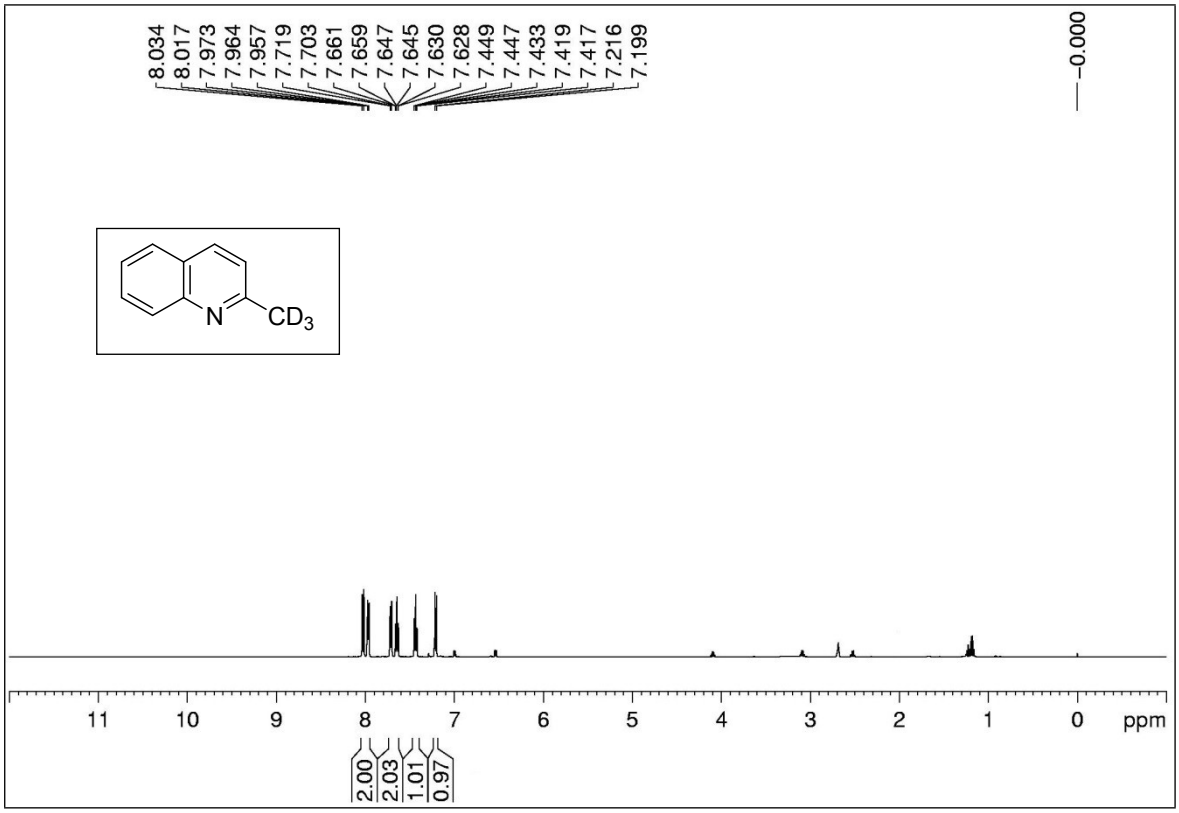


Figure 3. 400 MHz ^{1}H-NMR spectra of quinaldine-d_3 **10** in $CDCl_3$

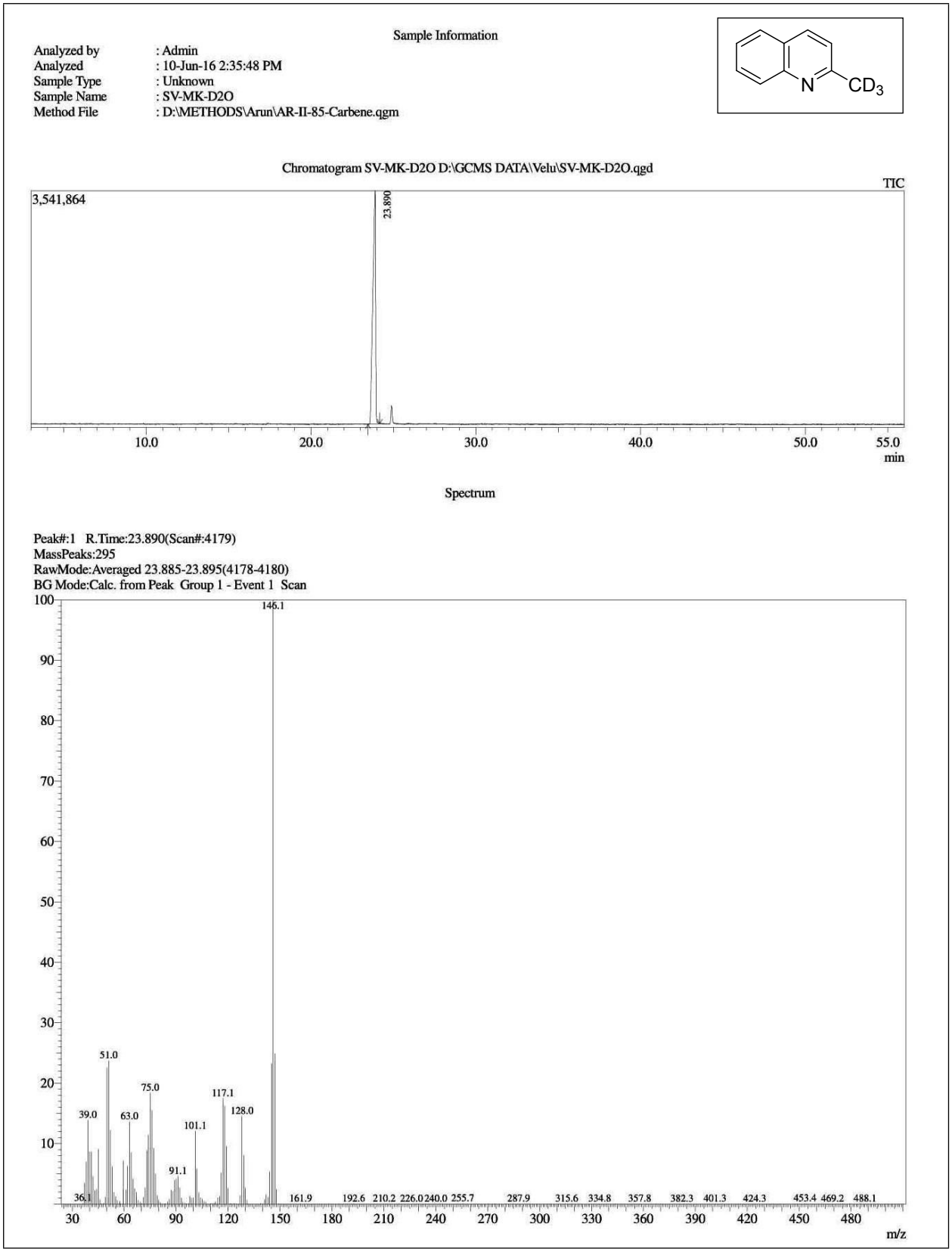


Figure 4. GC-MS spectra of quinaldine-d_3 **10**

Crystallographic experimental section

XRD Data for Compound 3a (CCDC 1503214)

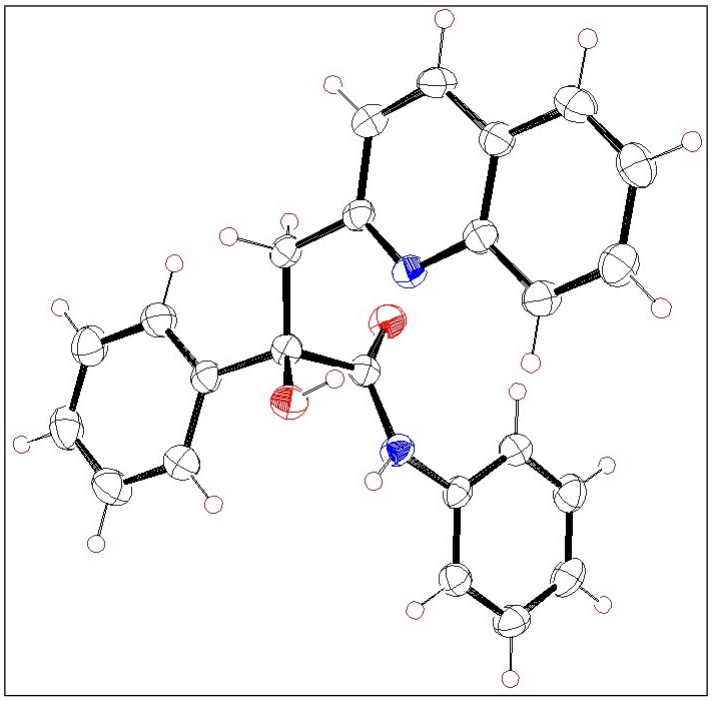


Table 1. Crystal data and structure refinement for **3a** (**CCDC 1503214**)

Empirical formula	C_{24} H_{20} N_2 O_2
Formula weight	368.42
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a=14.7029(5) Å α=90 deg.
	b=5.8234(2) Å β=109.2178(17) deg.
	c=22.2875(7) Å γ=90 deg.
Volume	1801.93(11) A^3
Z, Calculated density	4, 1.358 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	776
Crystal size	0.250 x 0.250 x 0.200 mm
Theta range for data collection	1.467 to 24.999 deg.
Limiting indices	-17<=h<=17, -6<=k<=6, -26<=l<=26
Reflections collected / unique	13725 / 3172 [R(int) = 0.0268]
Completeness to theta = 24.999	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	3172 / 0 / 262
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0872
R indices (all data)	R1 = 0.0547, wR2 = 0.1006
Largest diff. peak and hole	0.175 and -0.153 e.A^-3

XRD Data for Compound 7b (CCDC No. 1503215)

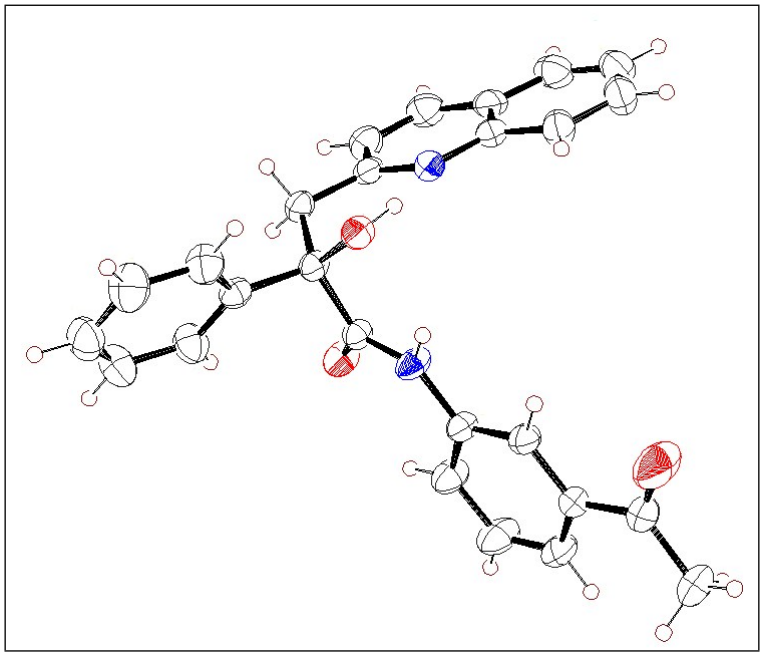


Table 2. Crystal data and structure refinement for **7b** (**CCDC 1503215**)

Empirical formula	$C_{26}H_{22}N_2O_3$
Formula weight	410.45
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a=10.6354(7) Å α=66.546 (3) deg.
	b=10.7608 (7) Å β=66.529 (2) deg.
	c=11.0786(7) Å γ=84.182 (3) deg.
Volume	1064.45(12) A^3
Z, Calculated density	2, 1.281 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	432
Crystal size	0.250 x 0.220 x 0.160 mm

Theta range for data collection	2.068 to 26.950 deg.
Limiting indices	-13<=h<=10, -13<=k<=12, -14<=l<=14
Reflections collected / unique	17160 / 4569 [R(int) = 0.0182]
Completeness to theta = 26.950	98.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4569 / 0 / 289
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1052
R indices (all data)	R1 = 0.0554, wR2 = 0.1160
Largest diff. peak and hole	0.64 and -0.181 e.A^-3