

**Synthesis of Amino Benzoic Acid Derivatives via Chemoselective Carbene  
Insertion into the -NH Bond Catalyzed by Cu(I) Complex**

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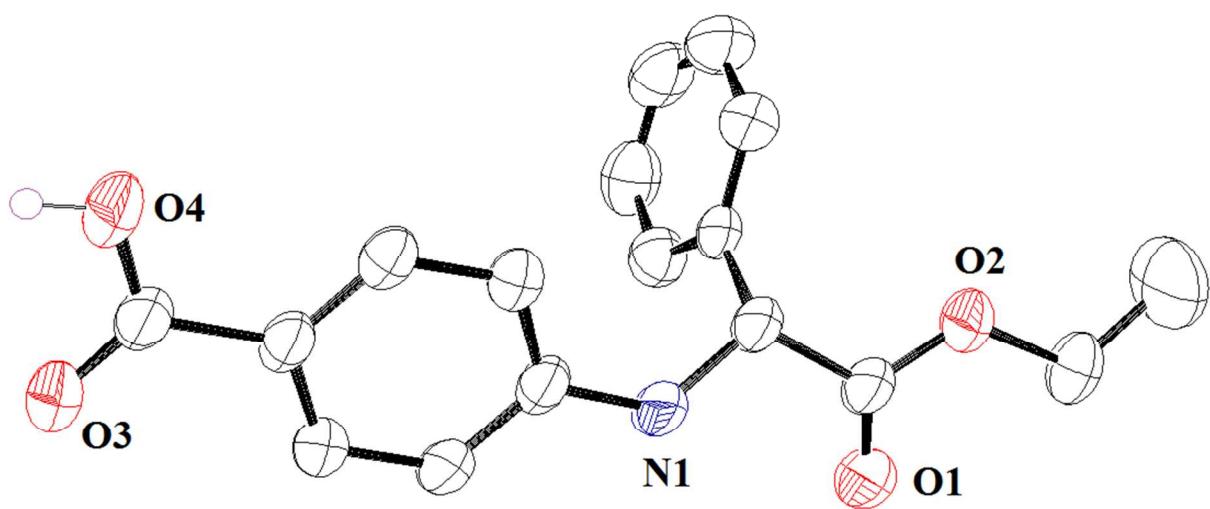
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**Supporting Information**

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**Figure S1.** Molecular structure of 4-((2-ethoxy-2-oxo-1-phenylethyl)amino)benzoic acid (**5b**), thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity (except COOH hydrogen).

## Crystallographic information

Empirical formula	C <sub>17</sub> H <sub>17</sub> NO <sub>4</sub>
Formula weight	299.32
Temperature/K	298K
Crystal system	triclinic
Space group	<i>P</i> 1̄
<i>a</i> /Å	7.9587(6)
<i>b</i> /Å	9.9490(9)
<i>c</i> /Å	10.9208(10)
$\alpha/^\circ$	112.261(8)
$\beta/^\circ$	103.489(7)
$\gamma/^\circ$	90.299(7)
Volume/Å <sup>3</sup>	773.98(12)
<i>Z</i>	2
$\rho_{\text{calc}} \text{g/cm}^3$	1.284
$\mu/\text{mm}^{-1}$	0.092
F(000)	316.0
Crystal size/mm <sup>3</sup>	0.4 × 0.3 × 0.25
Reflections collected	6130
Independent reflections	3513
Parameters	205
Goodness-of-fit on F <sup>2</sup>	1.085
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0643
Final R indexes [all data]	wR <sub>2</sub> = 0.1807
CCDC no.	1447841

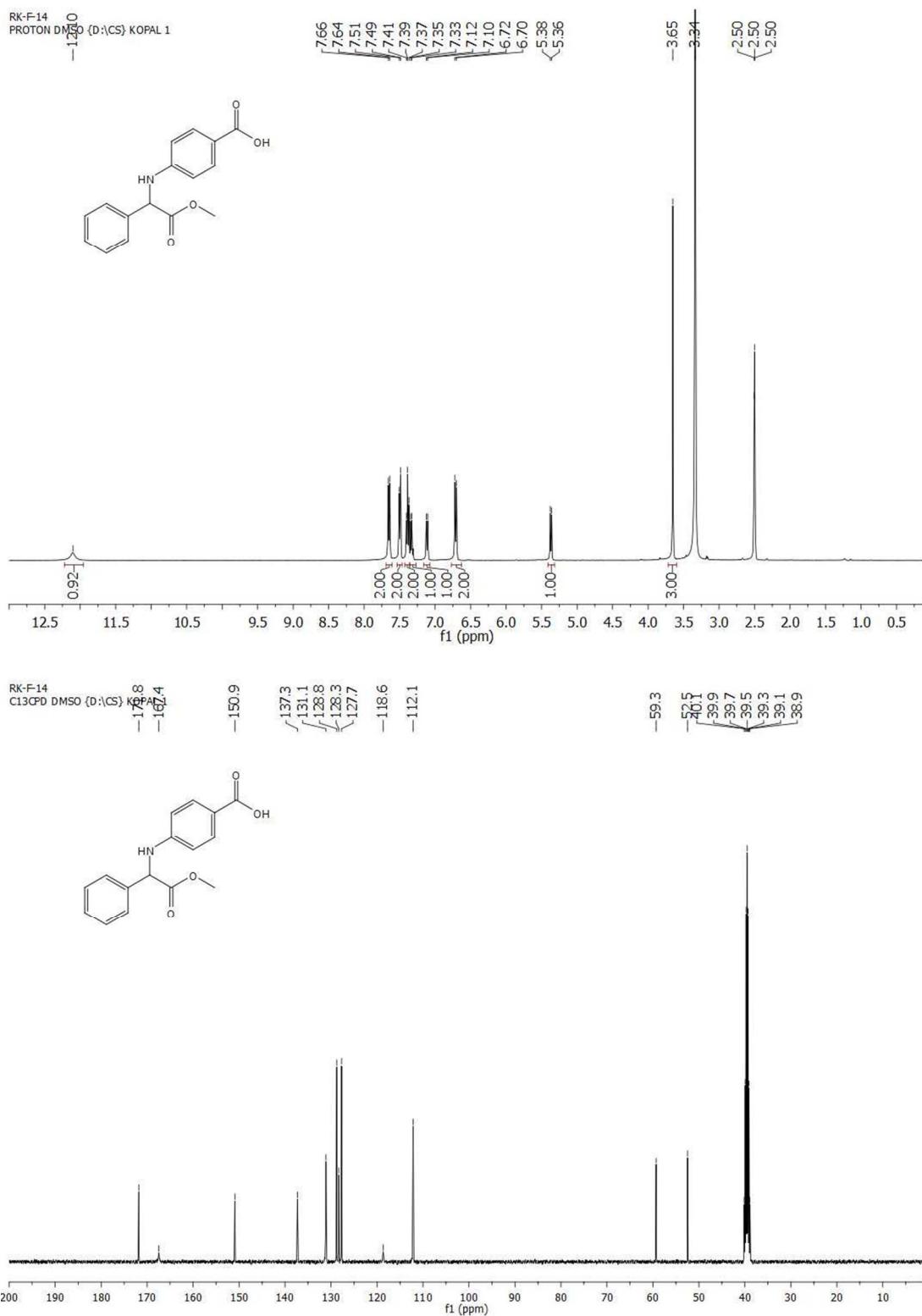
## X-ray Data Collection and Refinement

X-ray crystallographic diffraction data for compound **5b** were collected at 100 K on a SuperNova, Dual, Cu at zero, Eos diffractometer. All calculations were performed using SHELXS-97 and SHELXL-97 respectively using Olex 2-1.1 software package.<sup>1</sup> The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F2). All non-hydrogen atoms were refined anisotropically. Figures are drawn from X-seed version 2.0.<sup>2</sup> CCDC files 1415534 contain supplementary crystallographic data for the compound **5b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

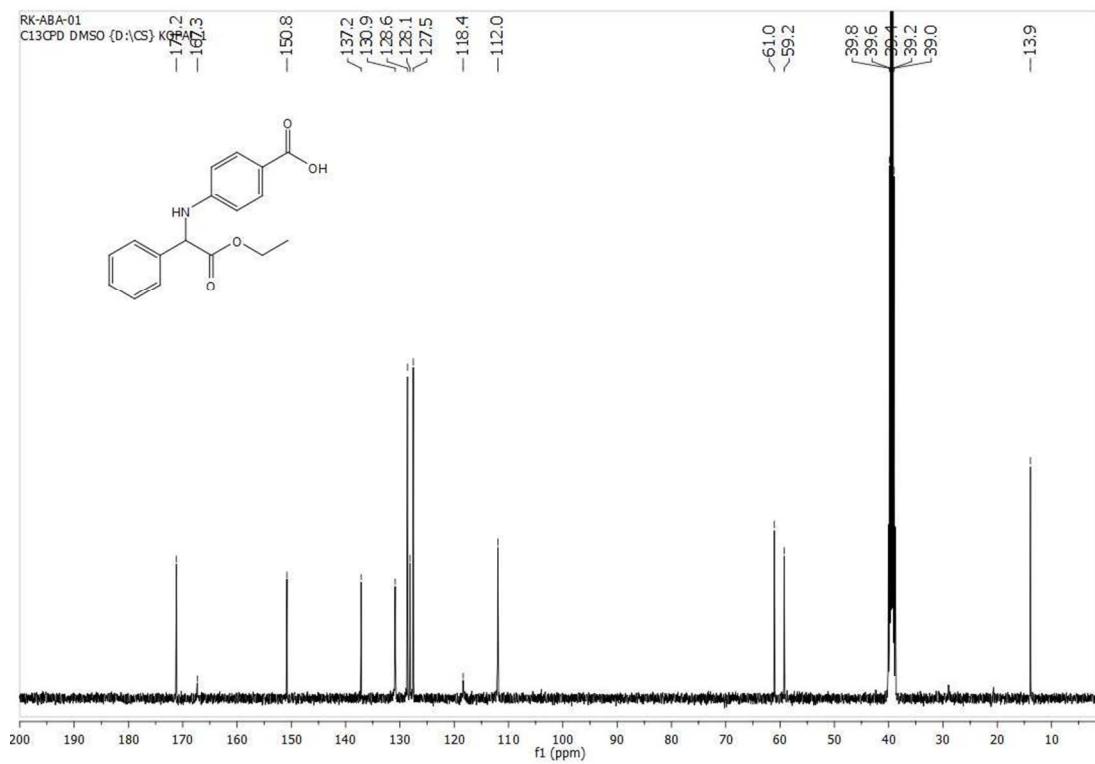
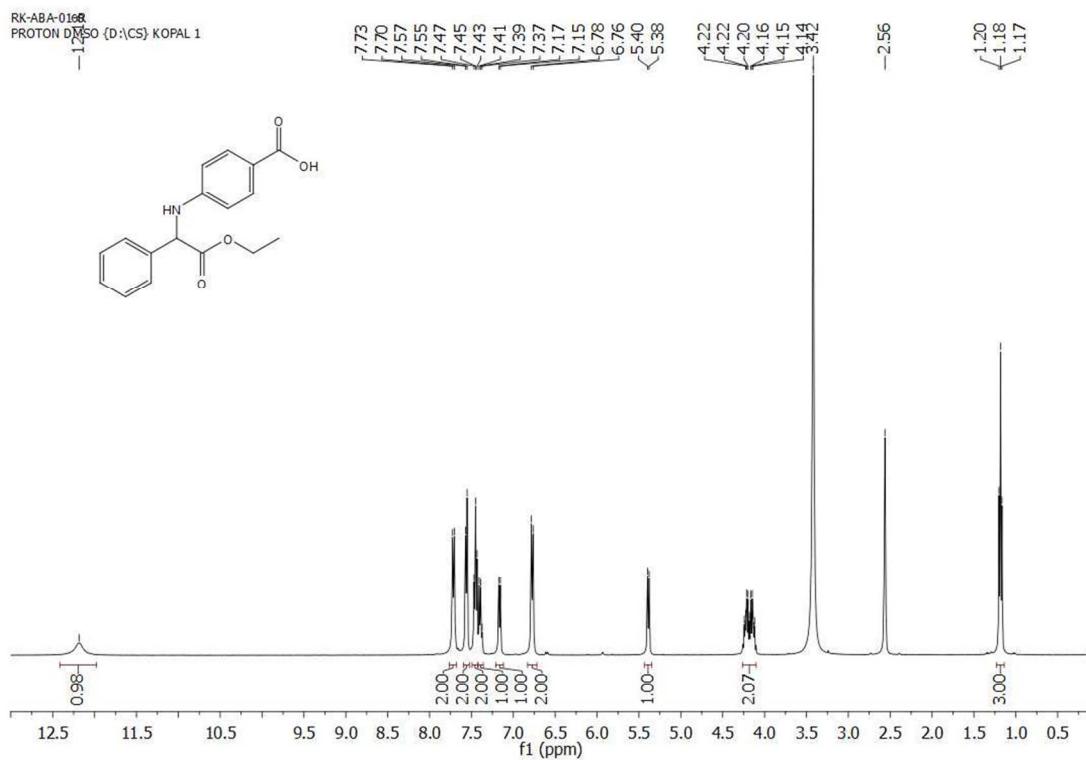
## References

1. Sheldrick, G. M. *SHELX 97, Program for Crystal Structure Determination*, University of Göttingen, Göttingen, Germany, **1997**.
2. Barbour, L. J. *X-Seed, Graphical Interface to SHELX-97 and POV-Ray*, University of Missouri; Columbia: Columbia, MO, **1999**.

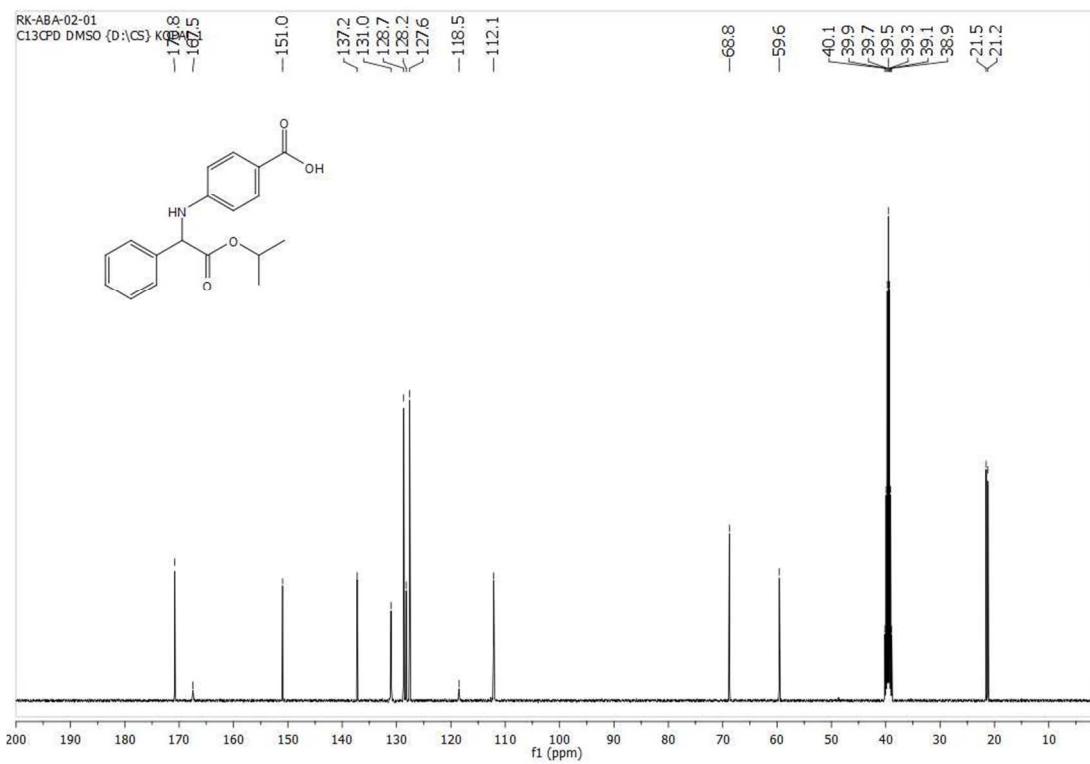
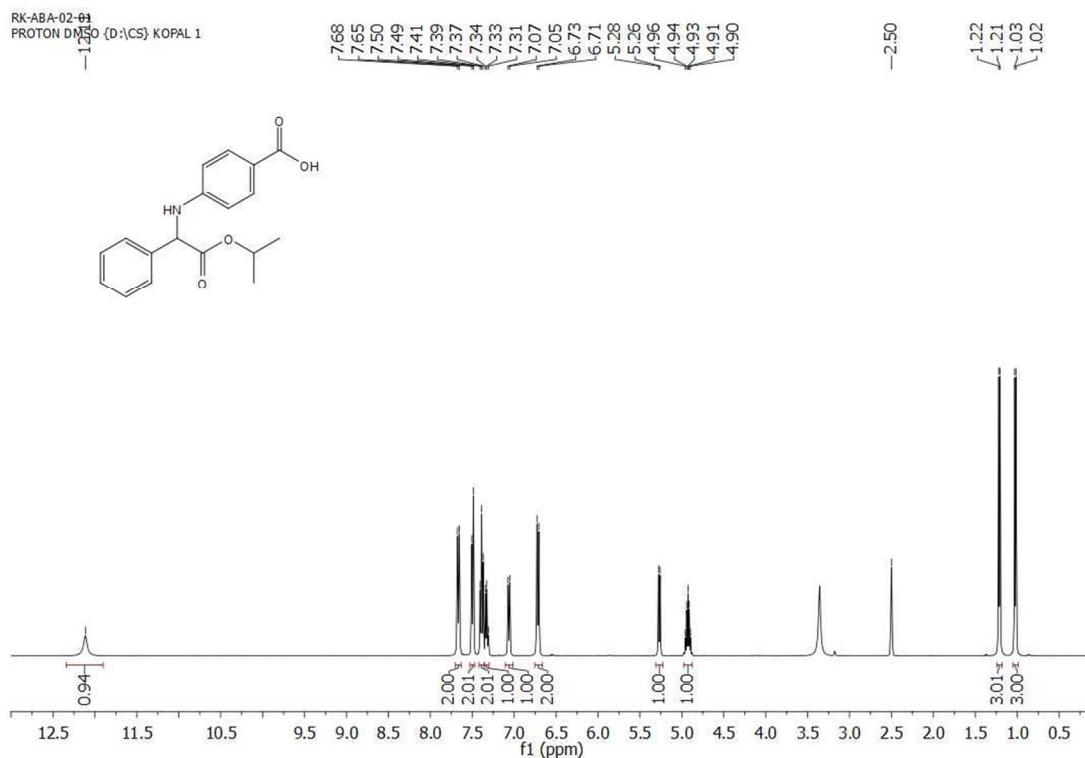
**4-((2-methoxy-2-oxo-1-phenylethyl)amino)benzoic acid (5a):**



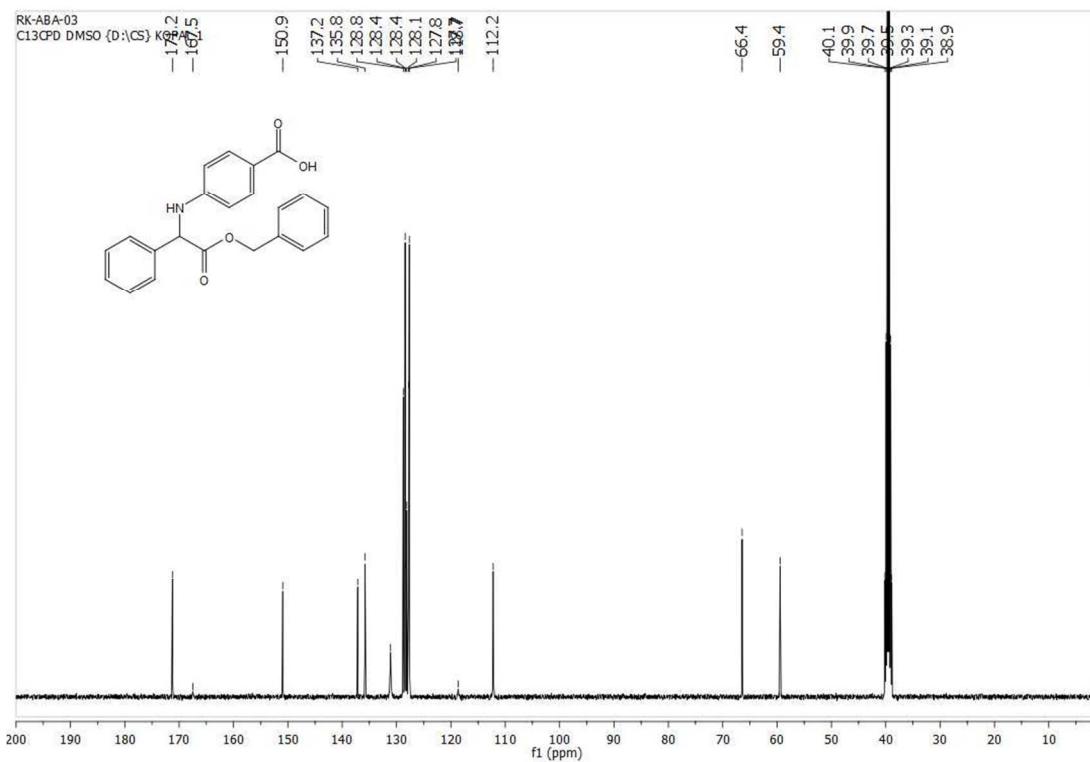
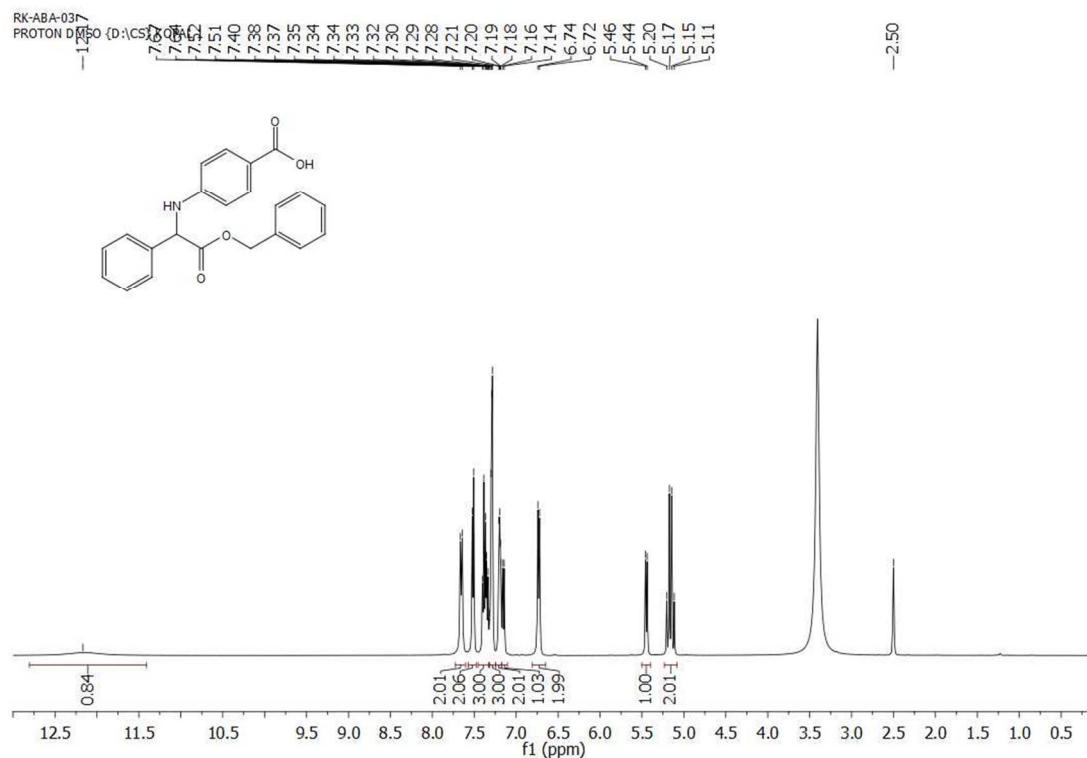
**4-((2-ethoxy-2-oxo-1-phenylethyl)amino)benzoic acid (5b):**



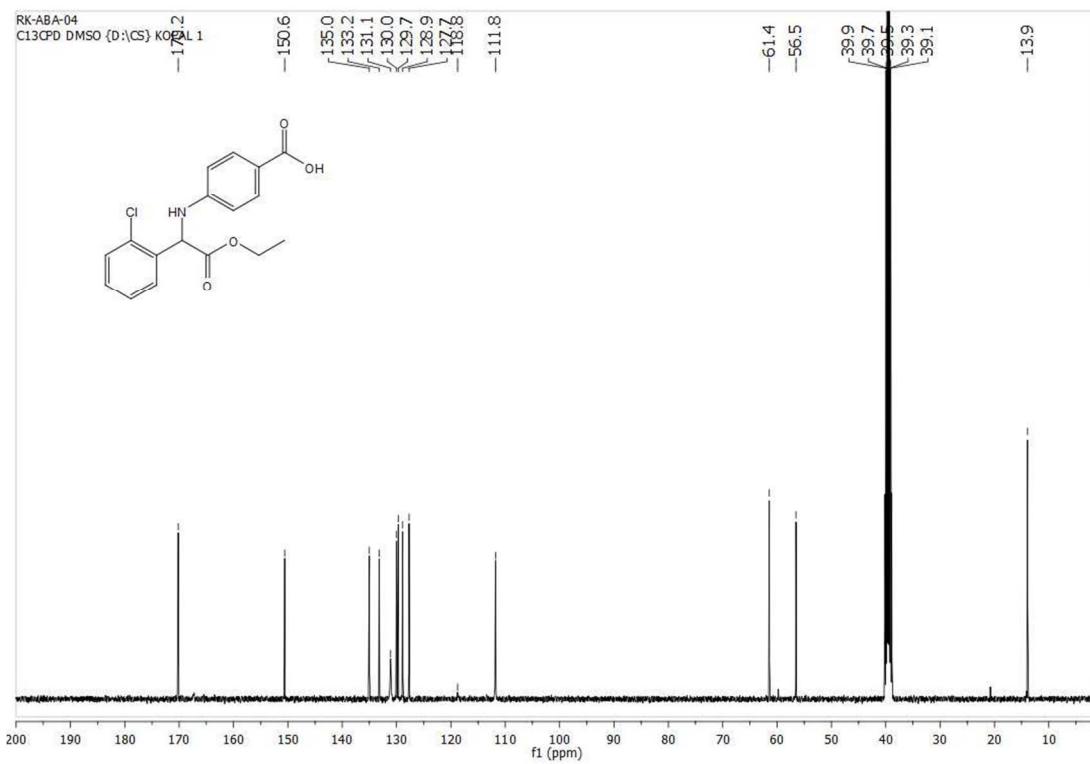
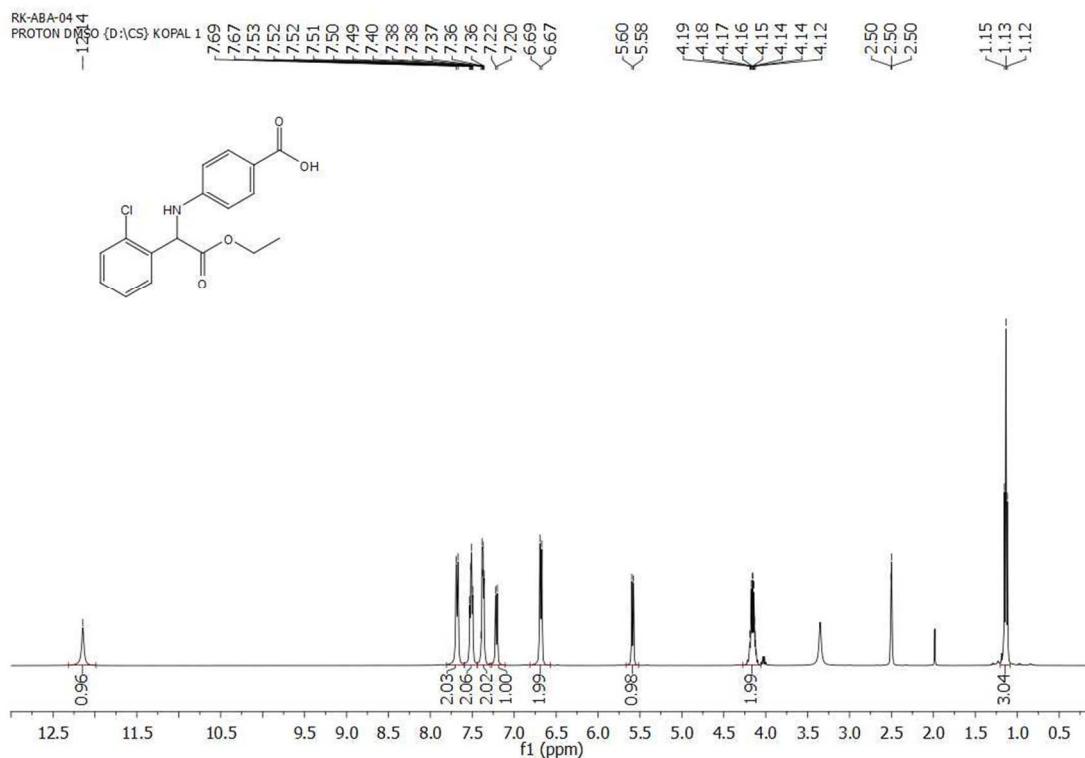
#### 4-((2-isopropoxy-2-oxo-1-phenylethyl)amino)benzoic acid (5c):



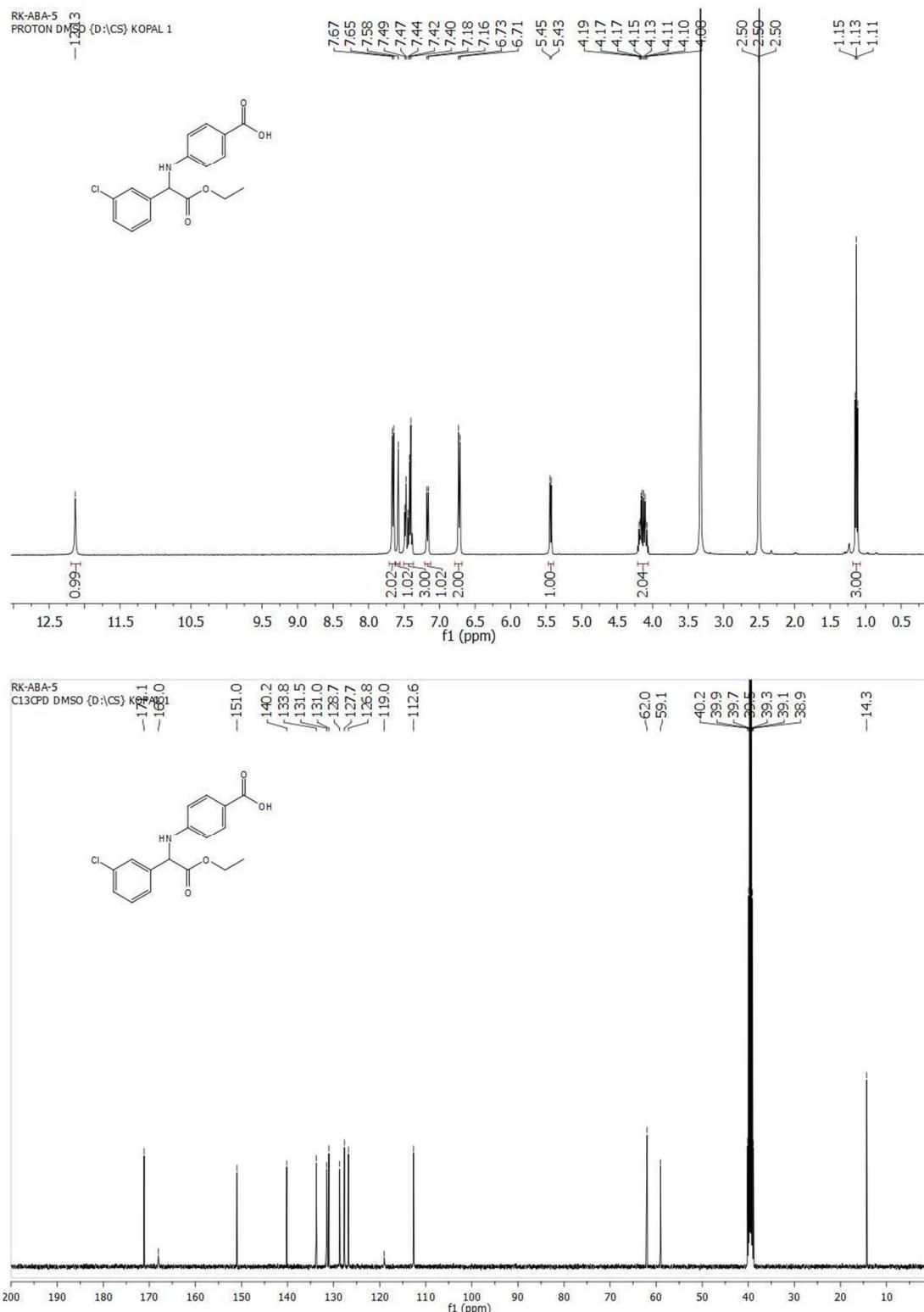
**4-((2-(benzyloxy)-2-oxo-1-phenylethyl)amino)benzoic acid (5d):**



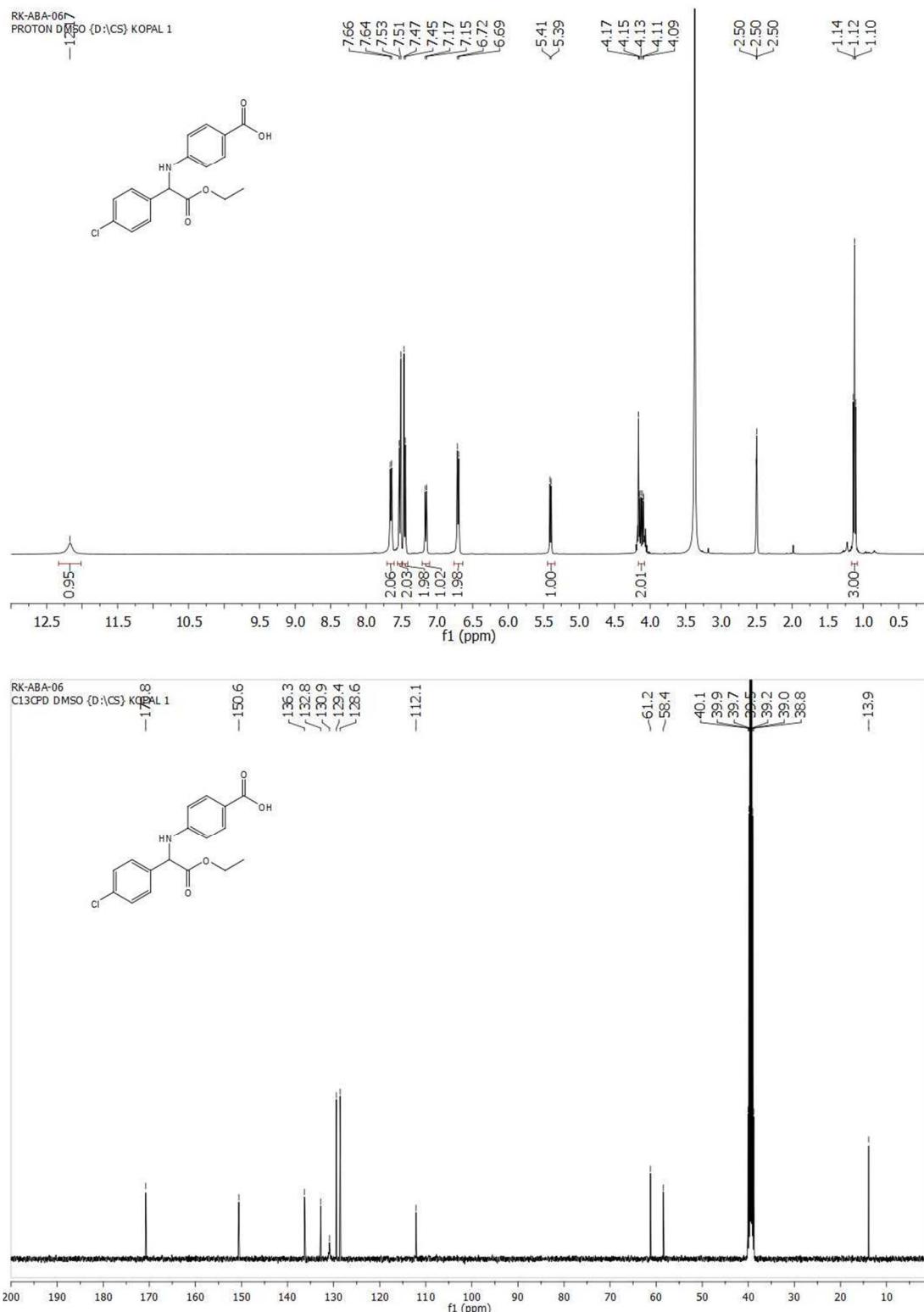
**4-((1-(2-chlorophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (5e):**



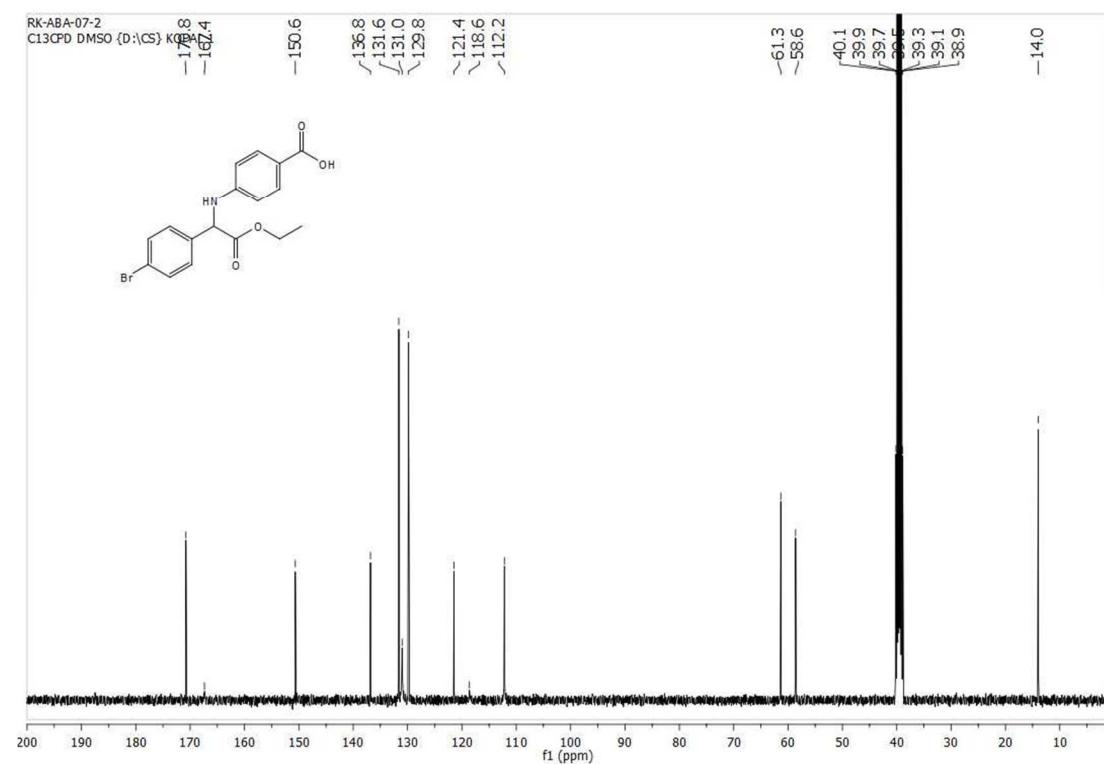
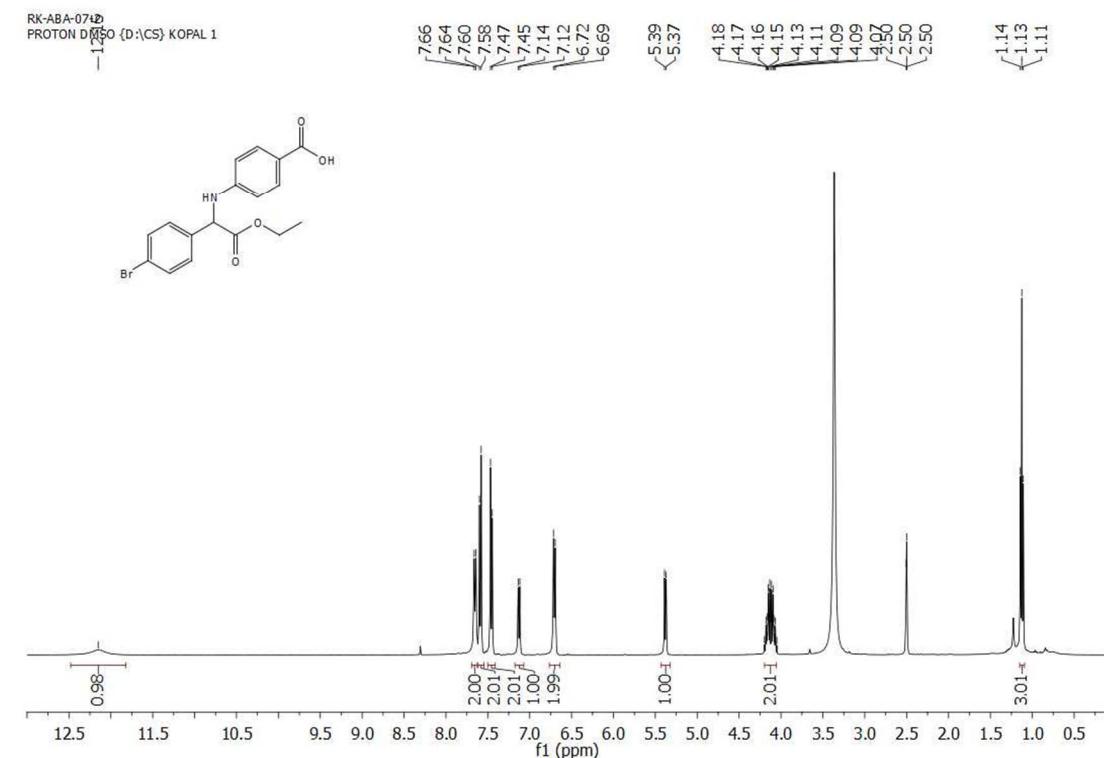
**4-((1-(3-chlorophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (5f):**



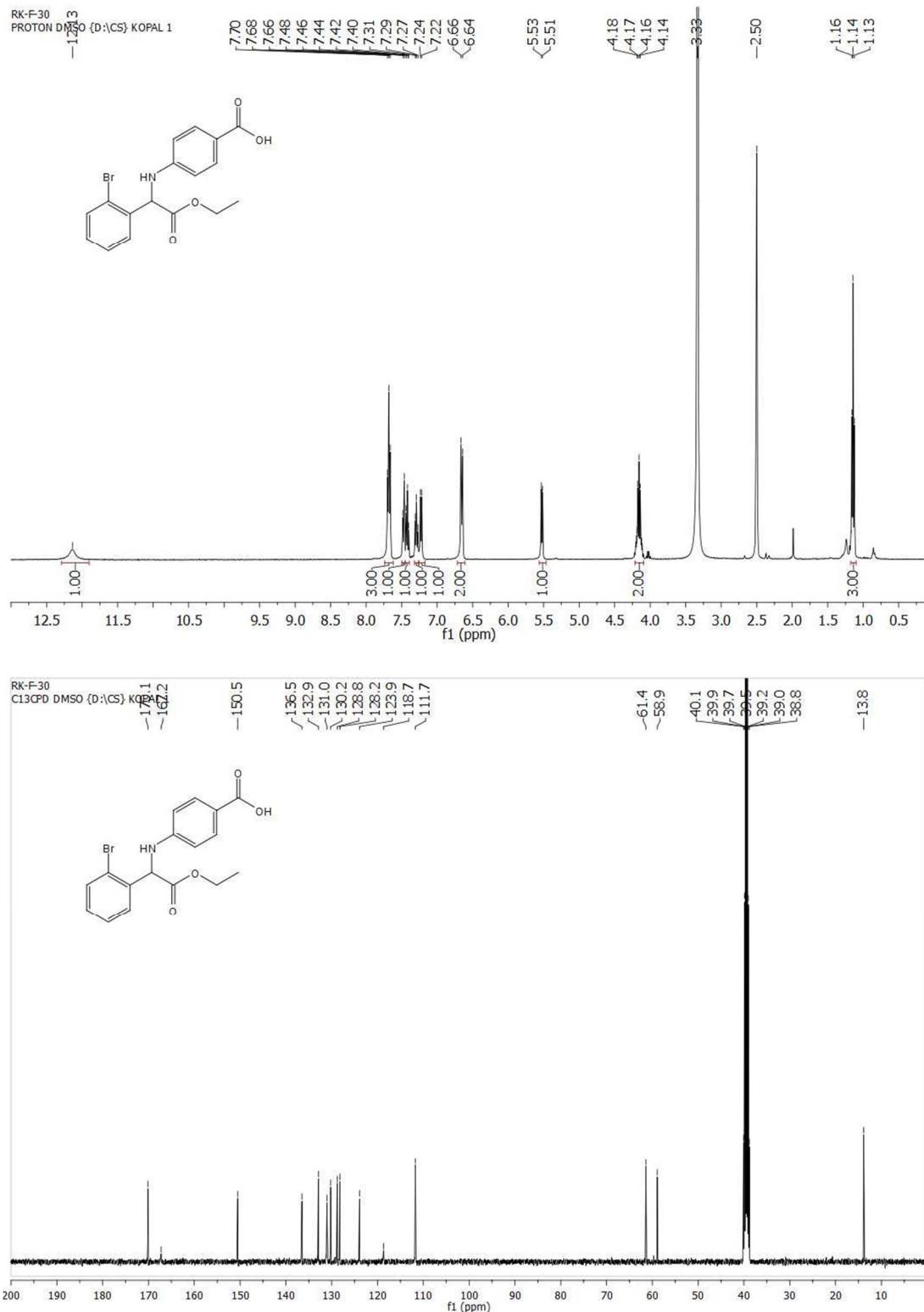
**4-((1-(4-chlorophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (5g):**



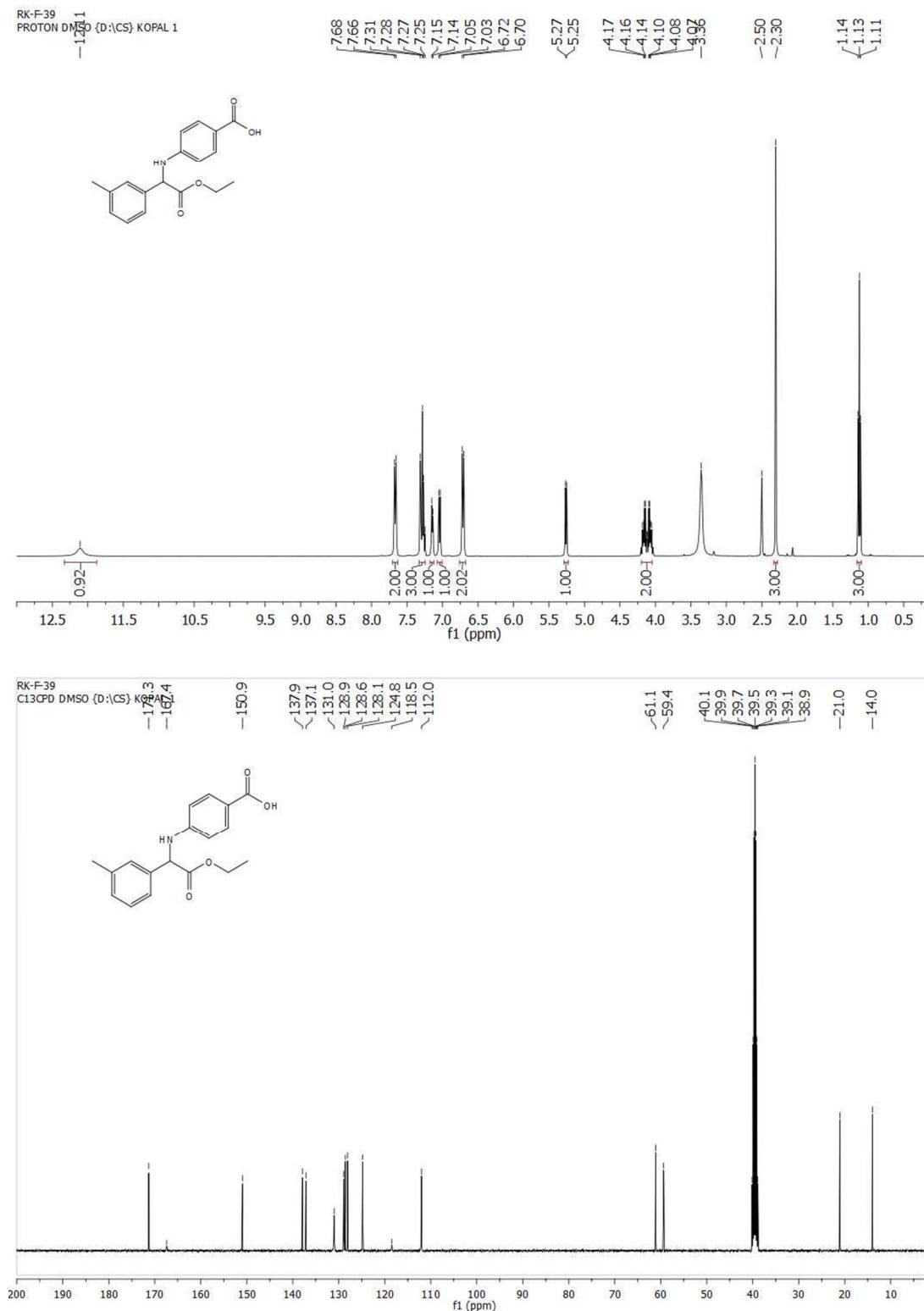
**4-((1-(4-bromophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (5h):**



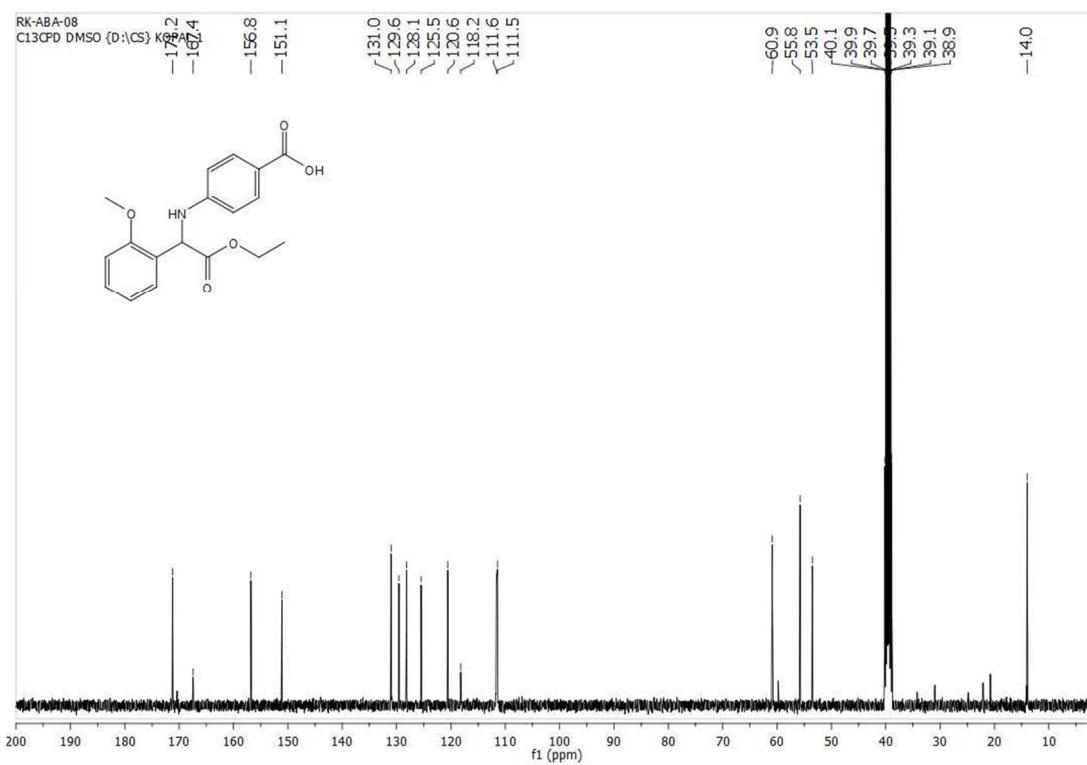
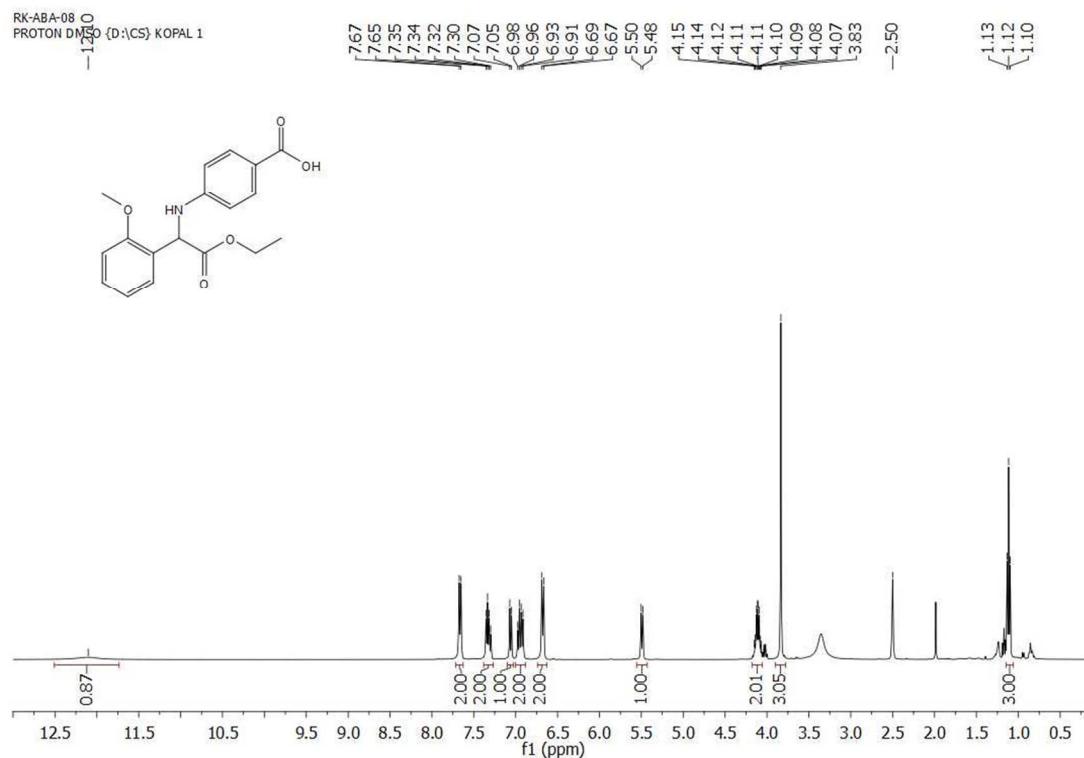
**4-((1-(2-bromophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (5i):**



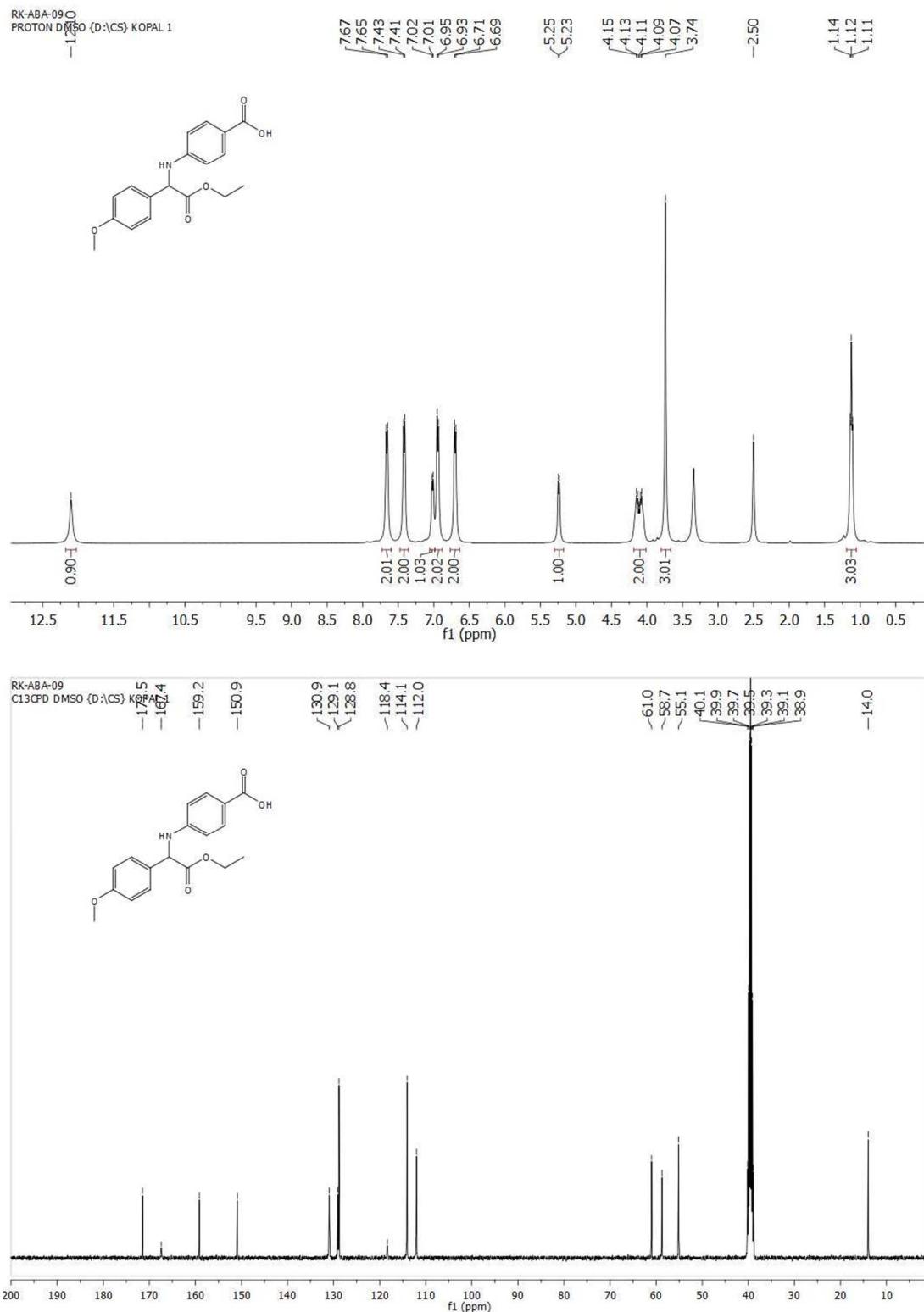
**4-((2-ethoxy-2-oxo-1-(m-tolyl)ethyl)amino)benzoic acid (5j):**



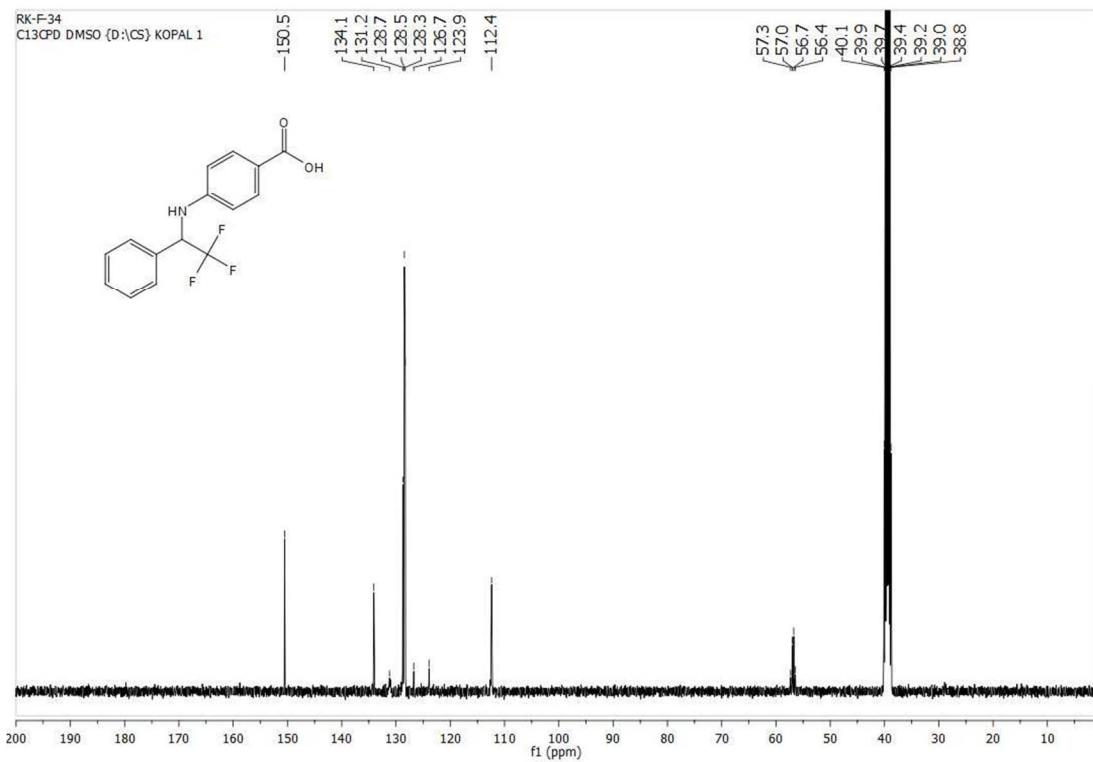
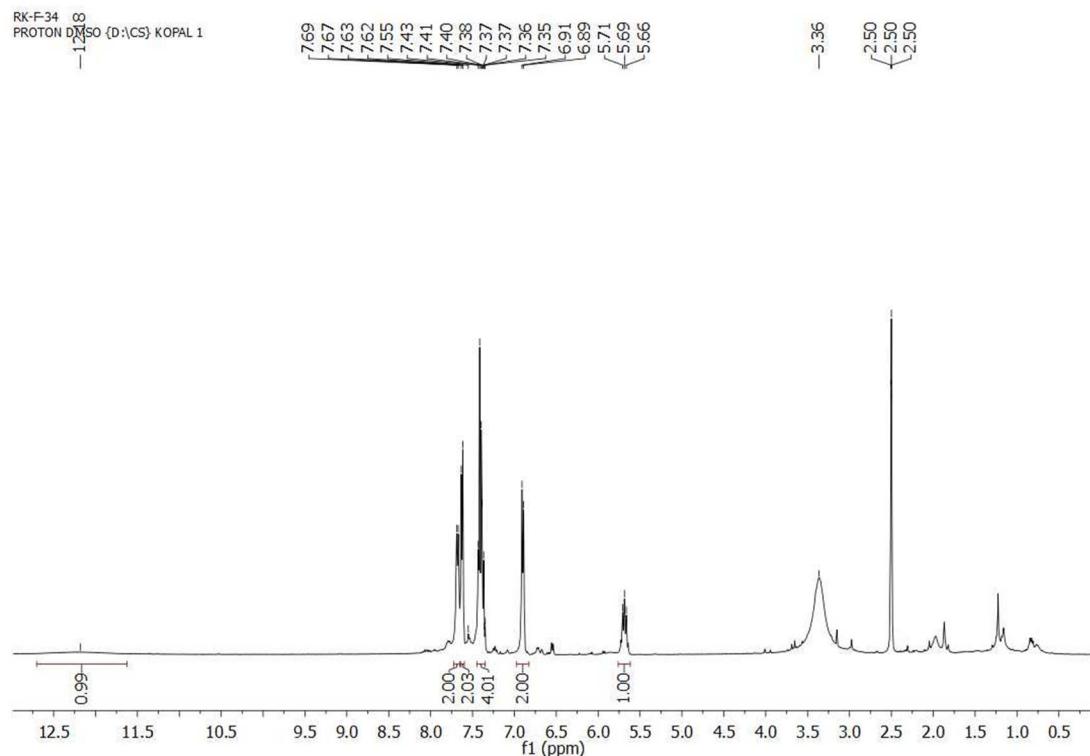
#### 4-((2-ethoxy-1-(2-methoxyphenyl)-2-oxoethyl)amino)benzoic acid (5k):



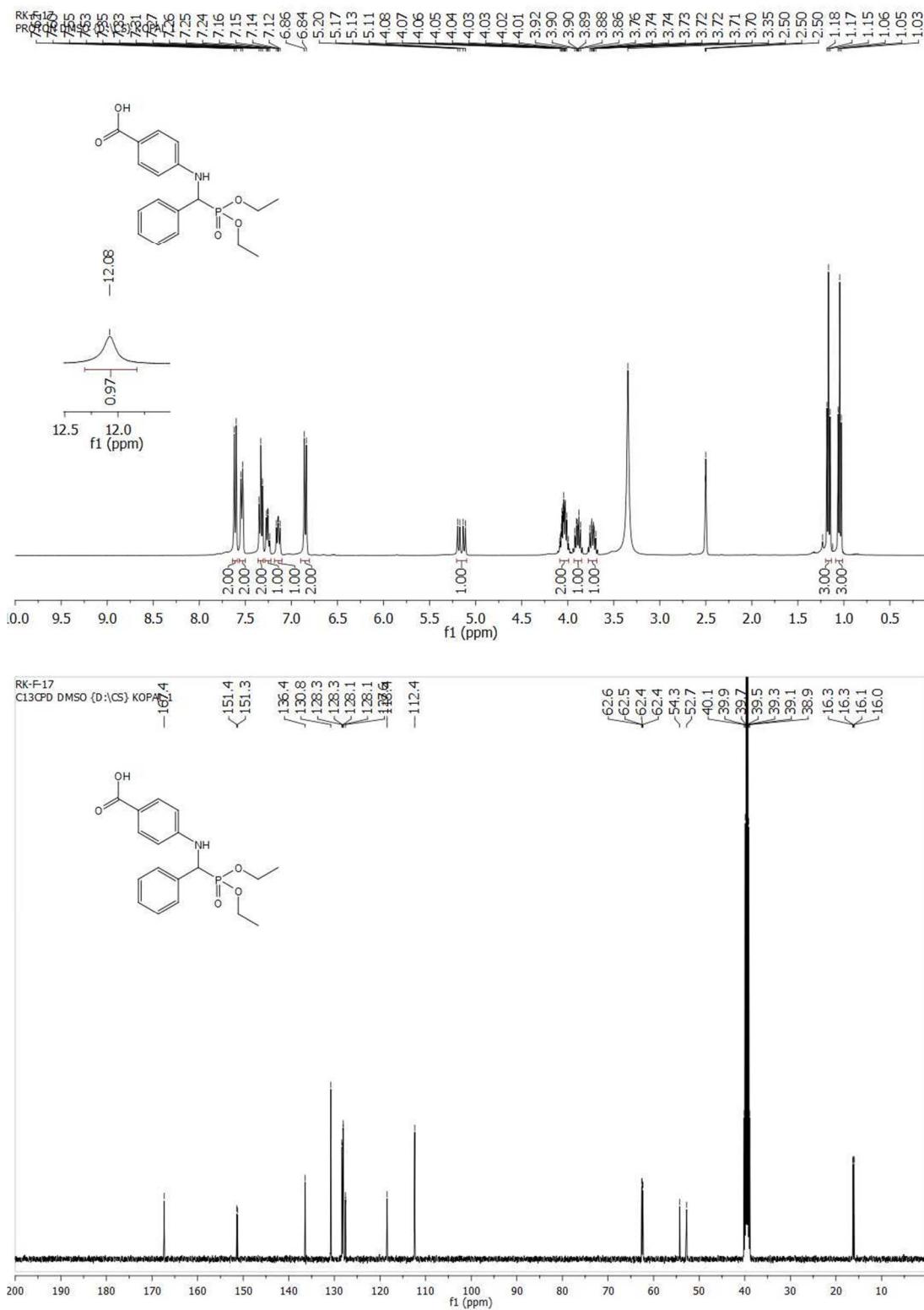
**4-((2-ethoxy-1-(4-methoxyphenyl)-2-oxoethyl)amino)benzoic acid (5l):**



**4-((2,2,2-trifluoro-1-phenylethyl)amino)benzoic acid (7a):**

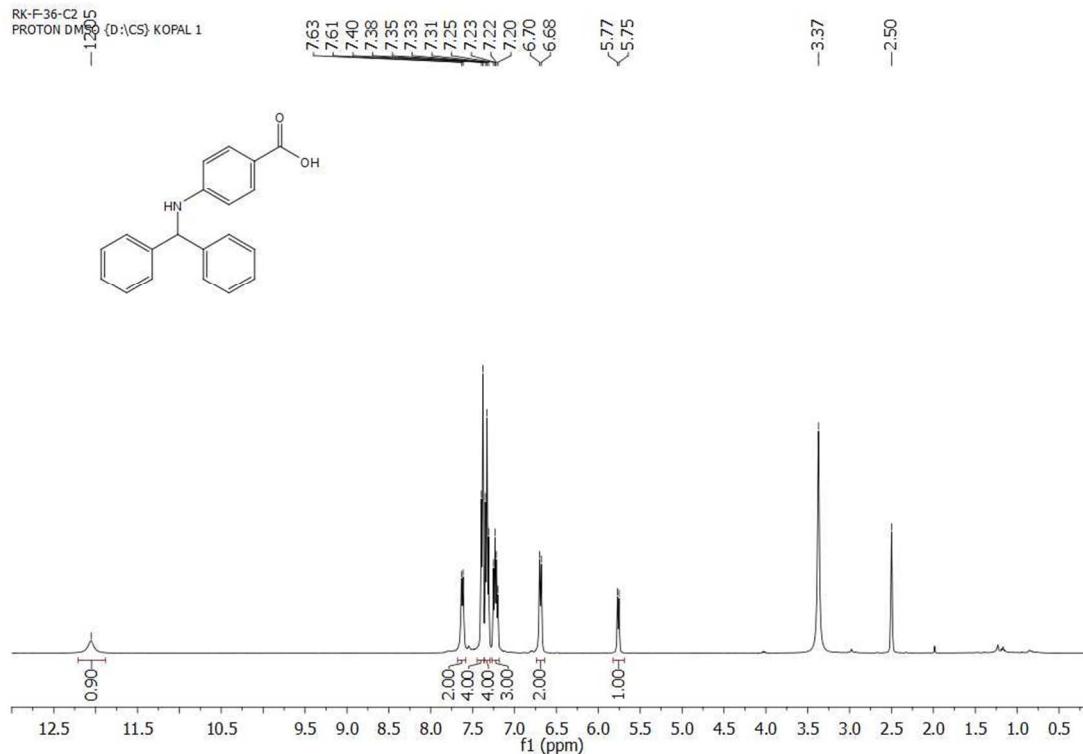


**4-(((diethoxyphosphoryl)(phenyl)methyl)amino)benzoic acid (7b):**

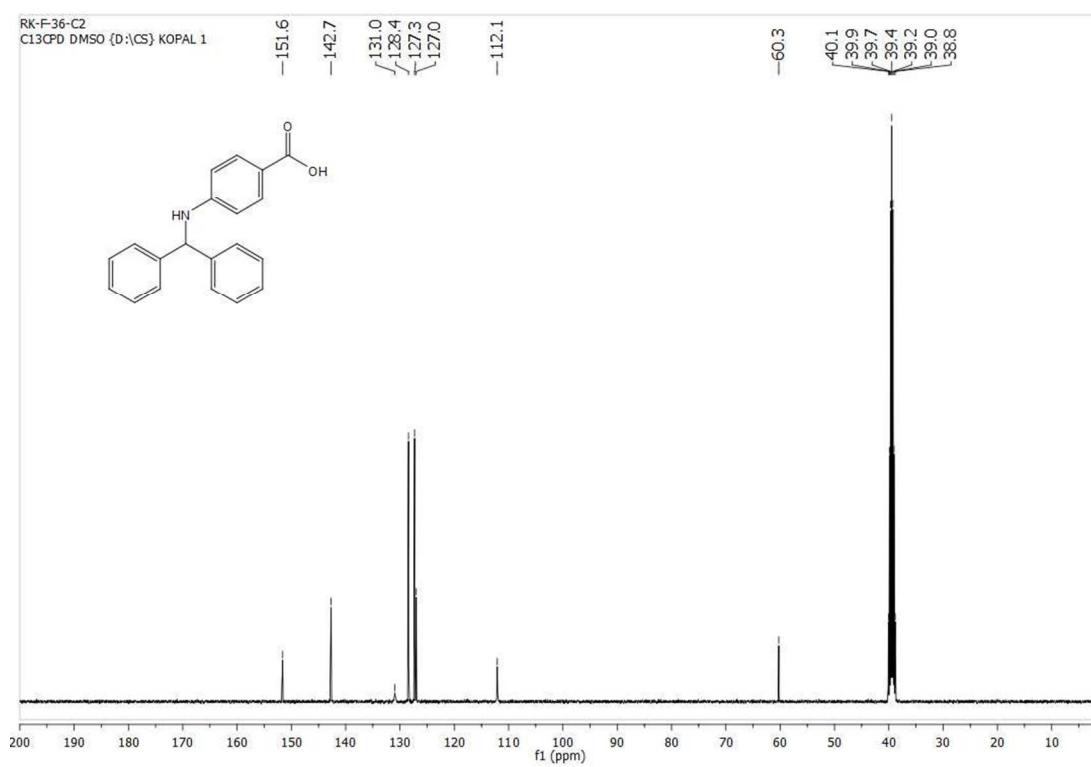


**4-(benzhydrylaminobenzoic acid (7c):**

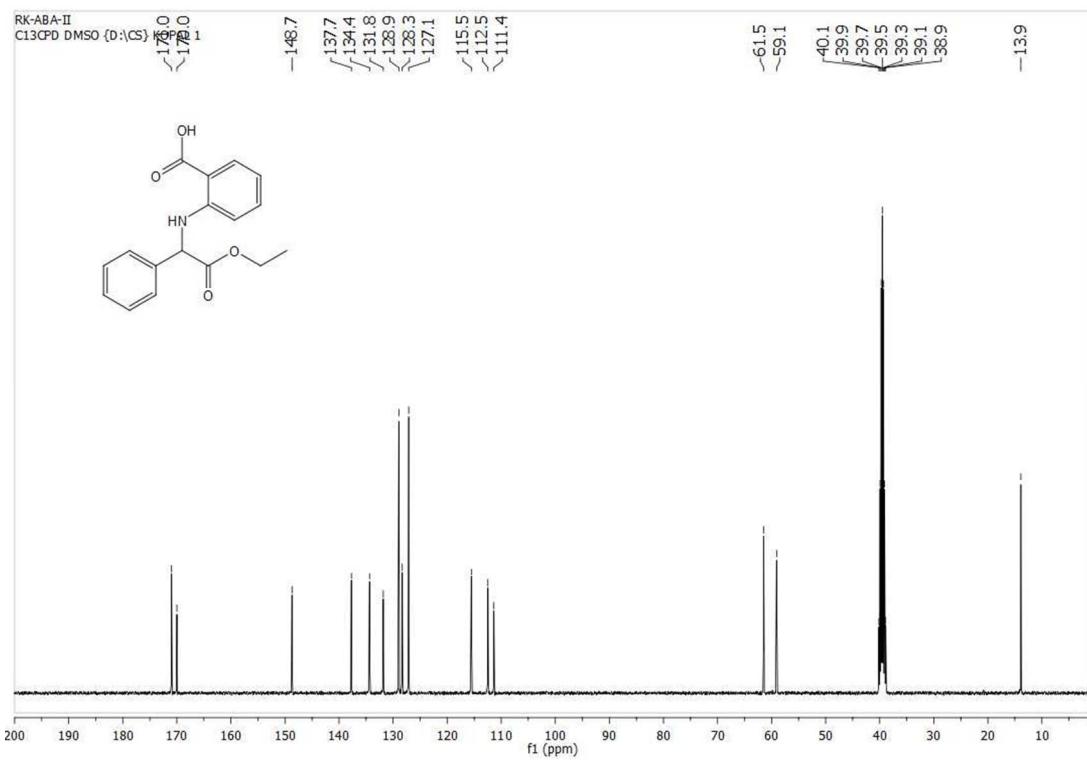
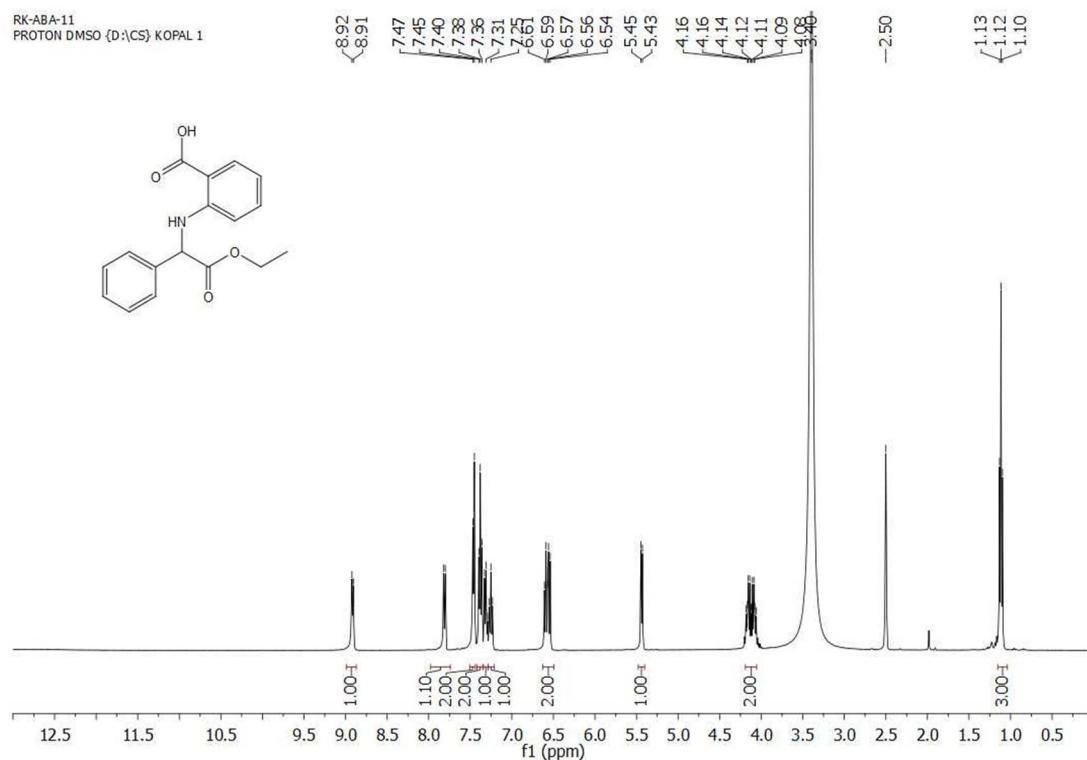
RK-F-36-C2 5  
PROTON DMSO {D:(CS)} KOPAL 1  
-120.5



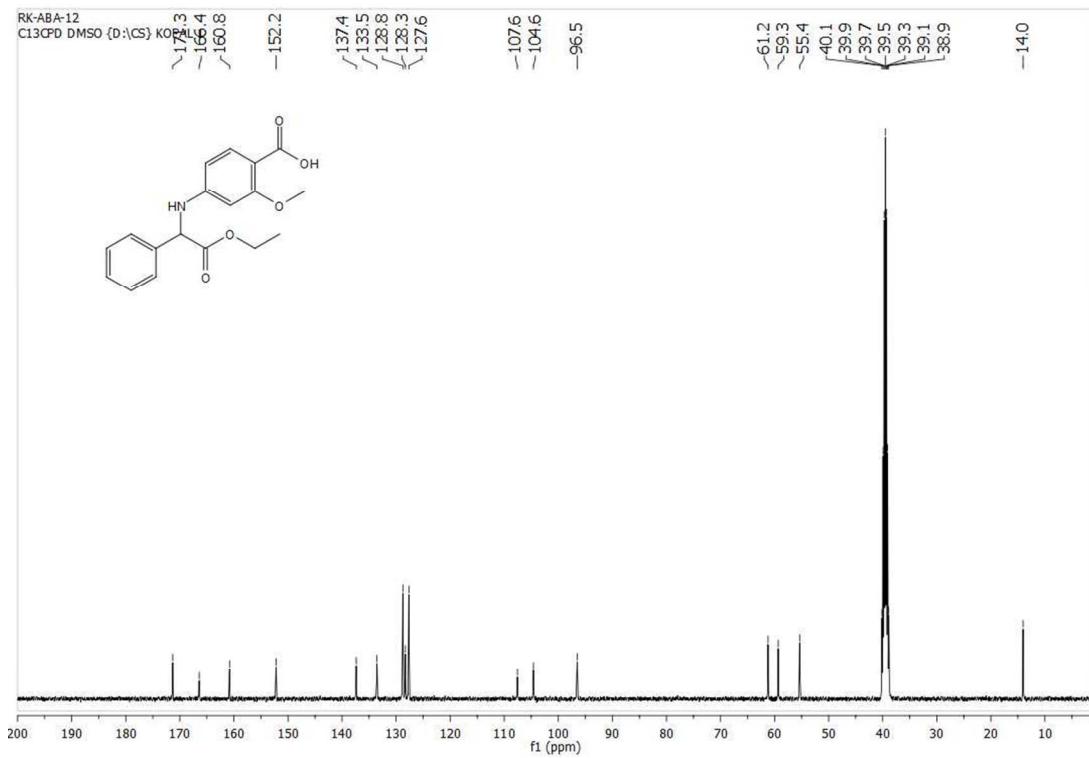
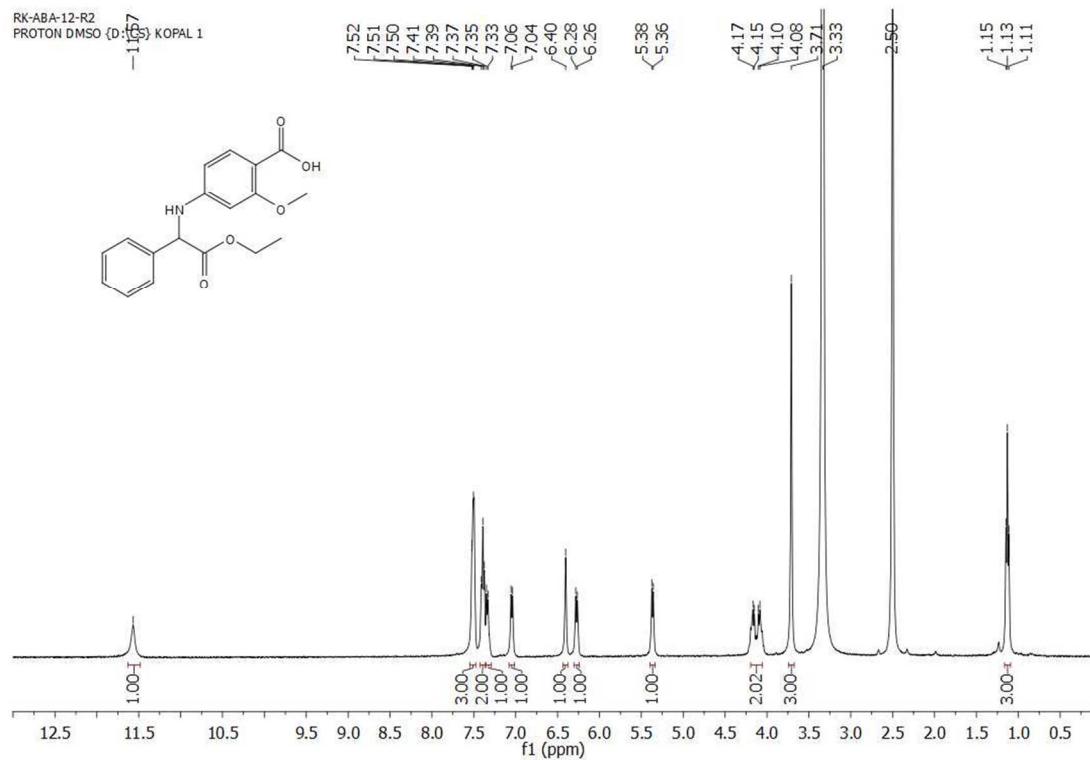
RK-F-36-C2  
C13CPD DMSO {D:(CS)} KOPAL 1



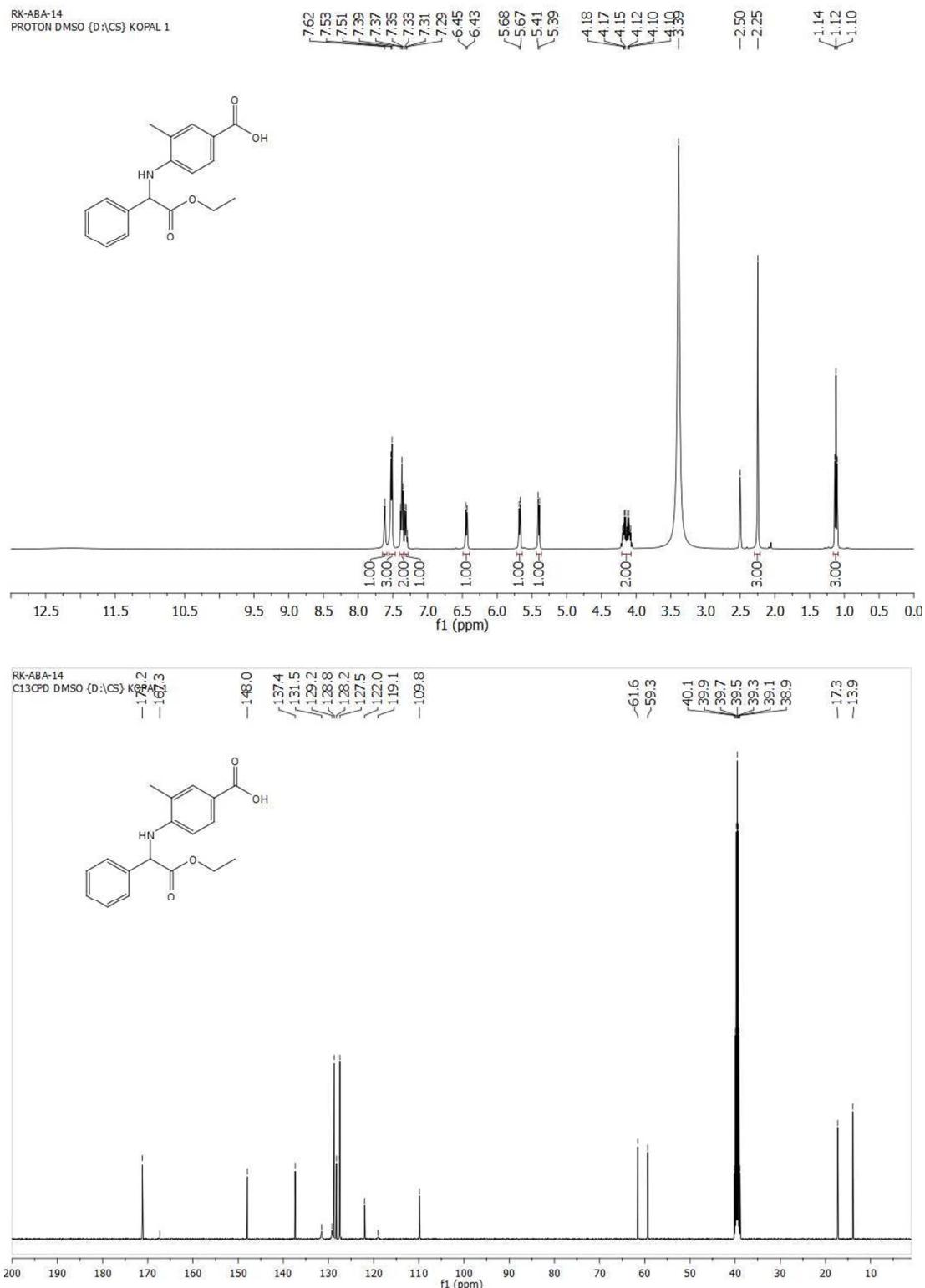
**2-((2-ethoxy-2-oxo-1-phenylethyl)amino)benzoic acid (8a):**



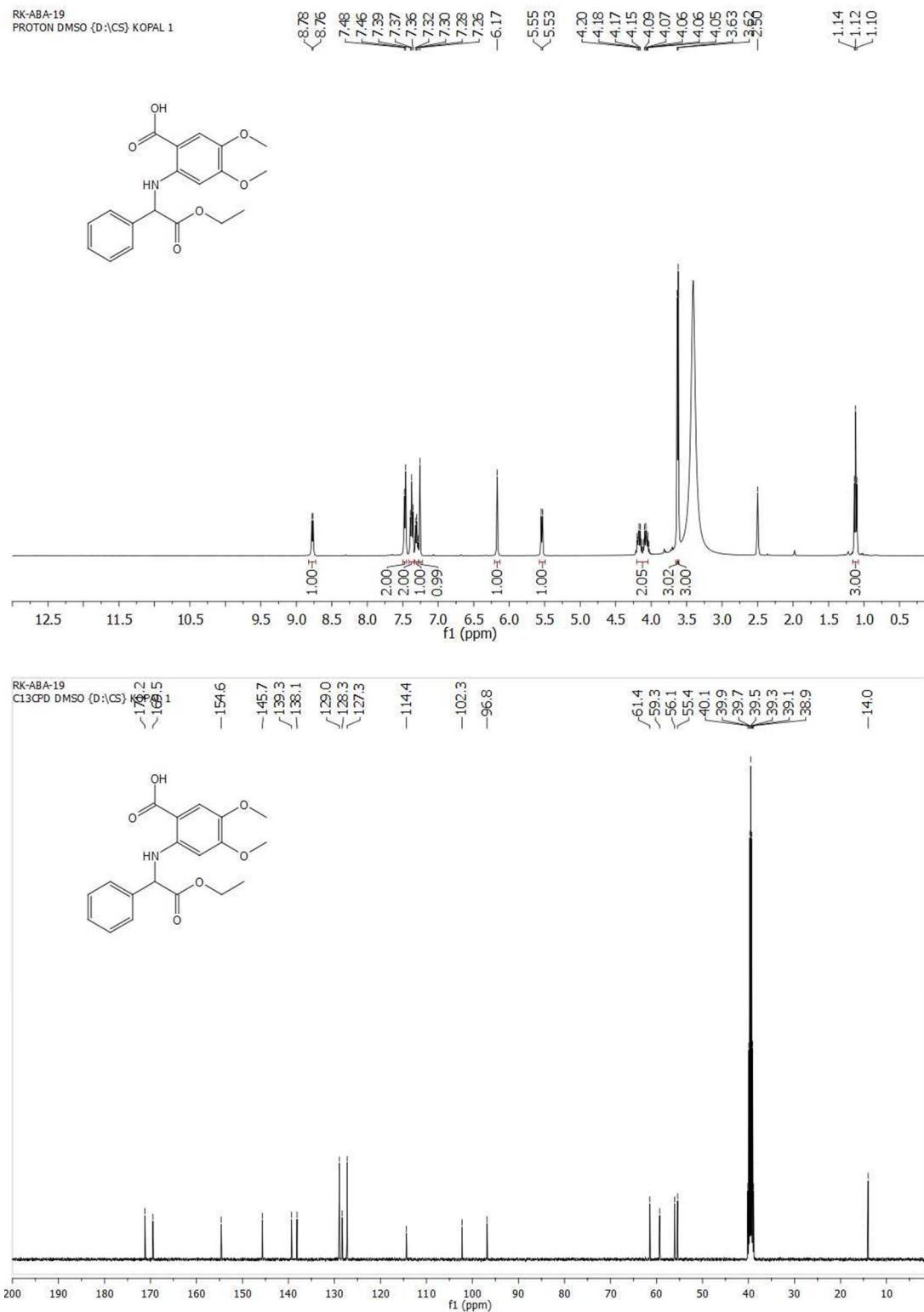
**4-((2-ethoxy-2-oxo-1-phenylethyl)amino)-2-methoxybenzoic acid (8b):**



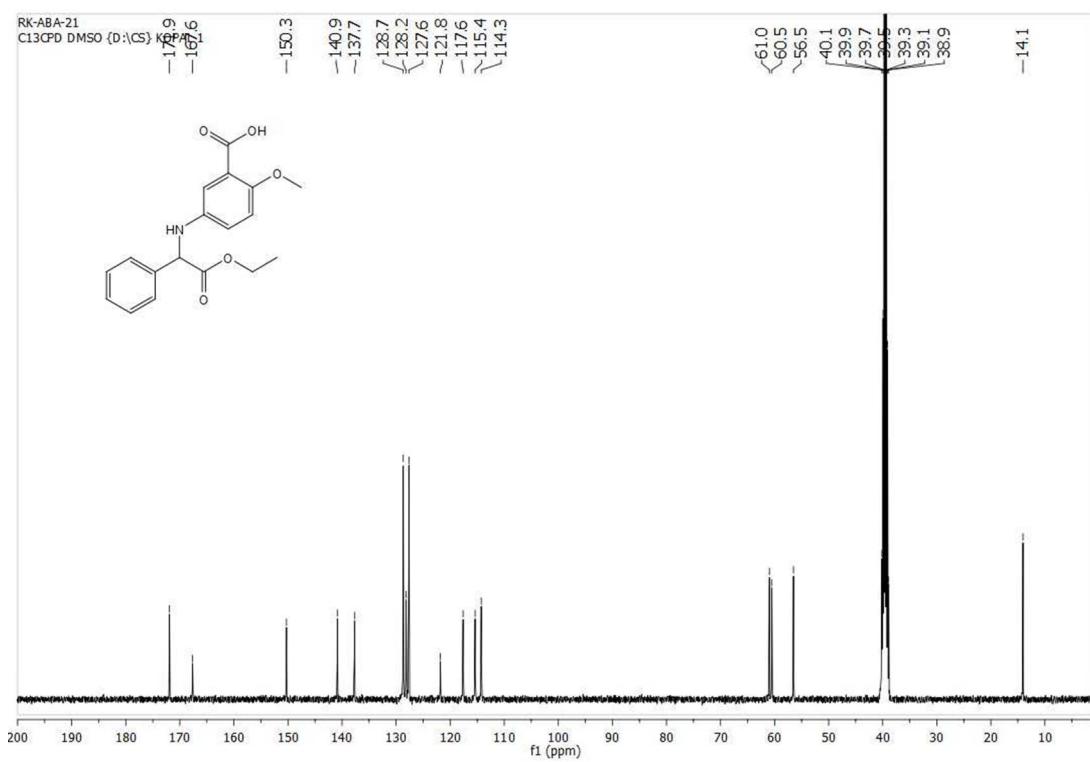
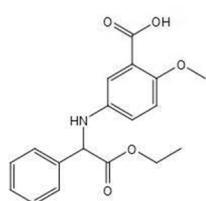
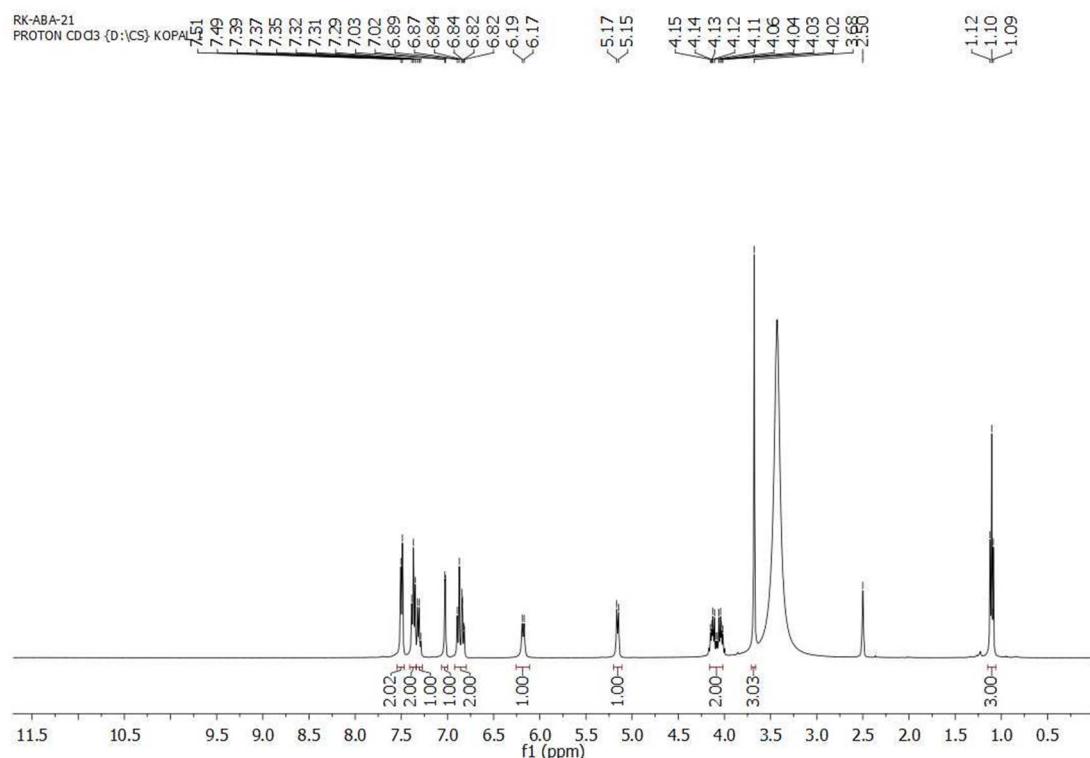
**4-((2-ethoxy-2-oxo-1-phenylethyl)amino)-3-methylbenzoic acid (8c):**



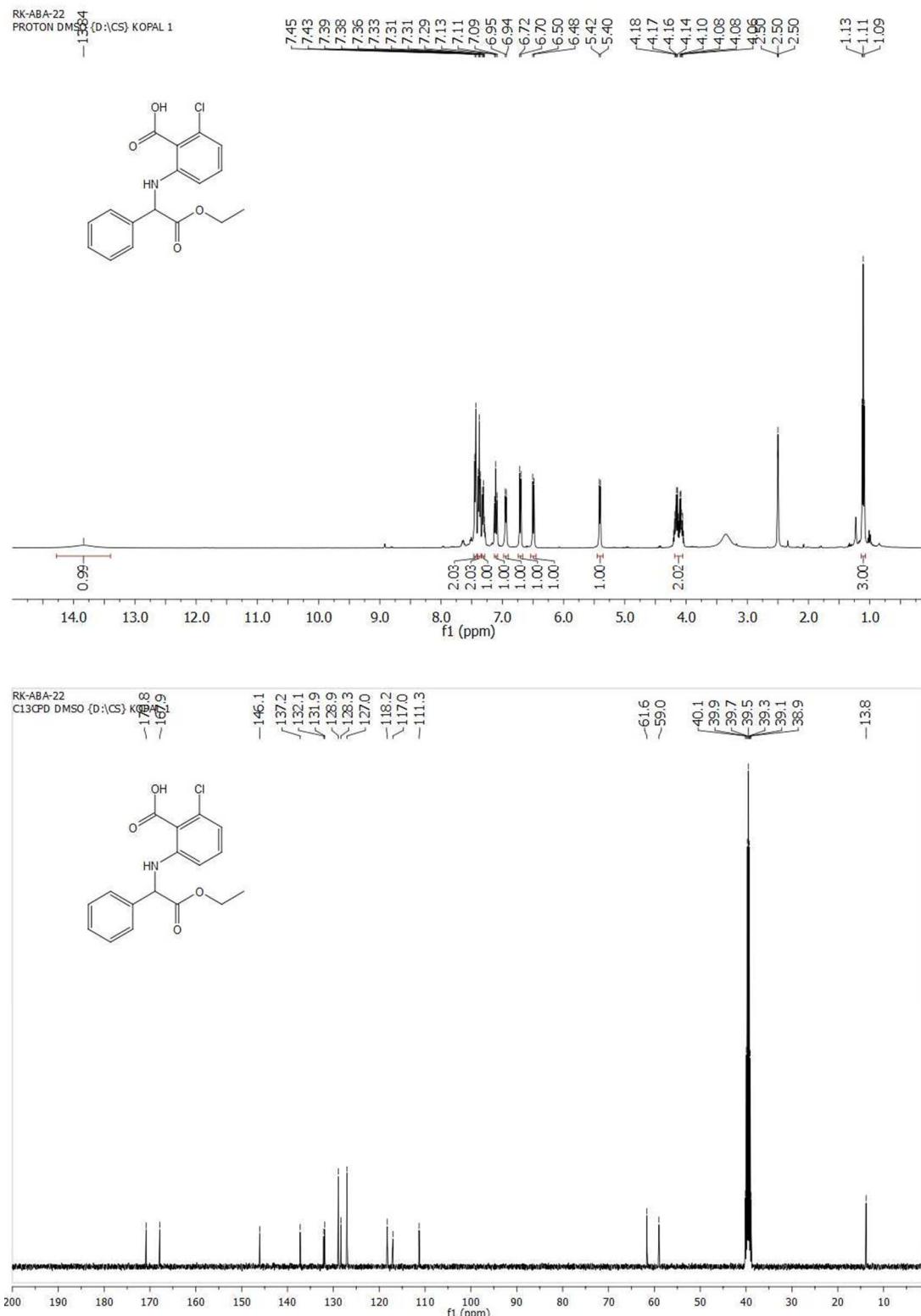
**2-((2-ethoxy-2-oxo-1-phenylethyl)amino)-4,5-dimethoxybenzoic acid (8d):**



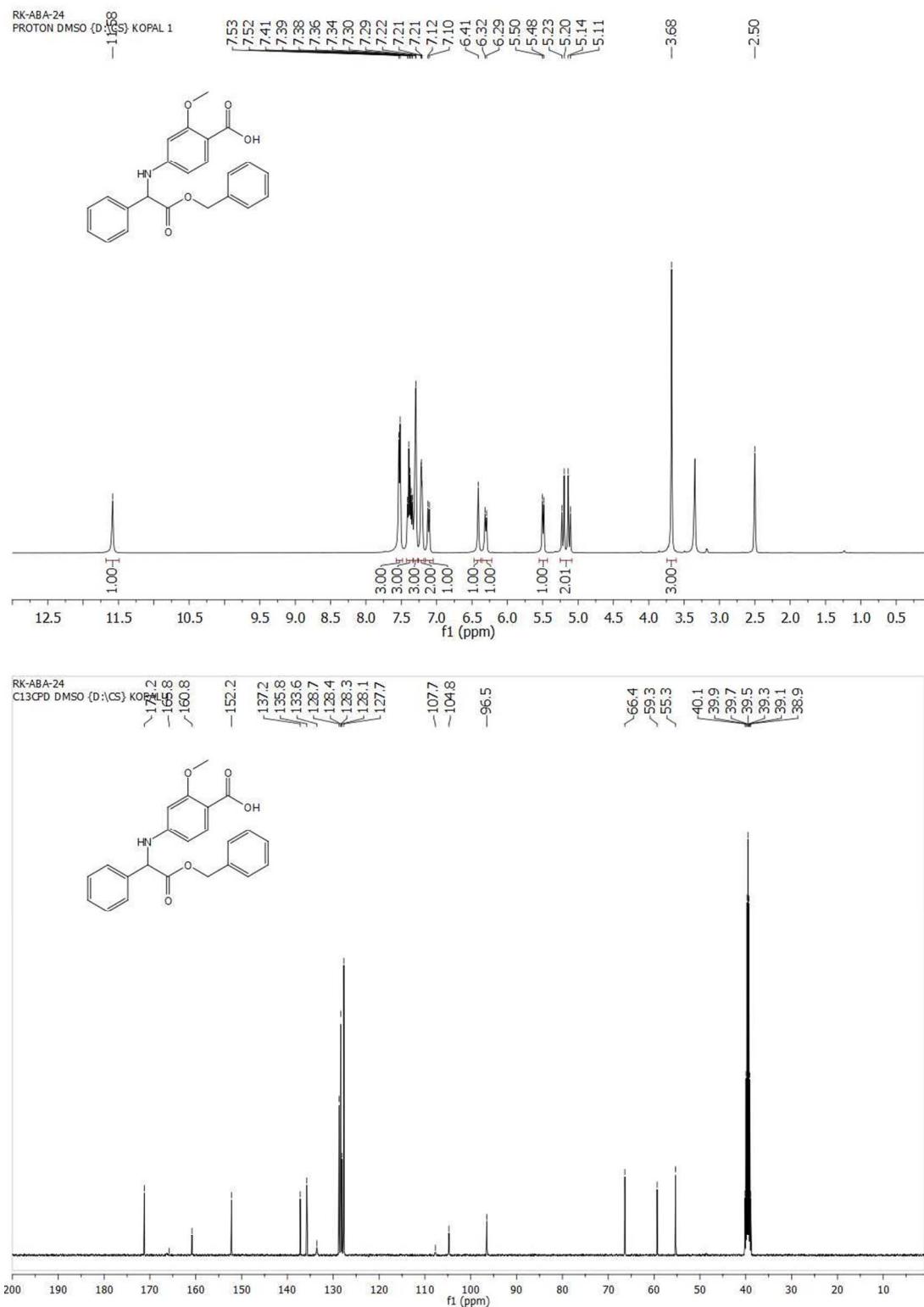
### 5-((2-ethoxy-2-oxo-1-phenylethyl)amino)-2-methoxybenzoic acid (8e):



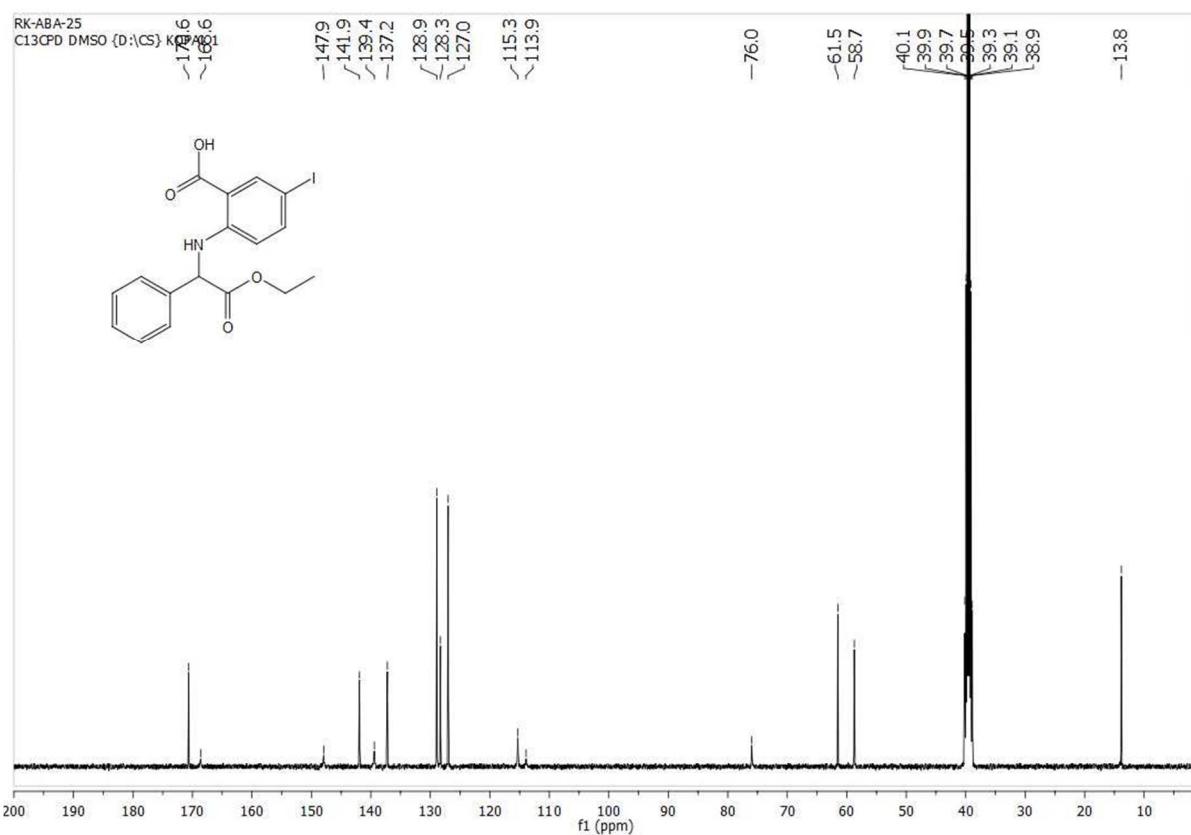
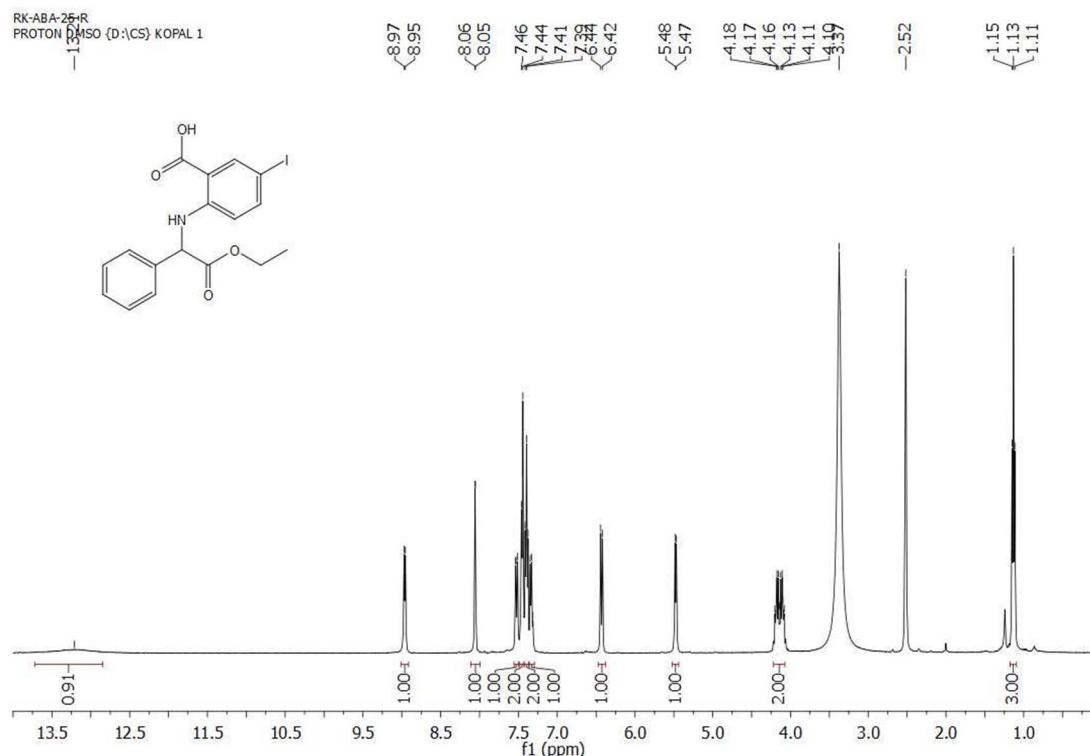
**2-chloro-6-((2-ethoxy-2-oxo-1-phenylethyl)amino)benzoic acid (8f):**



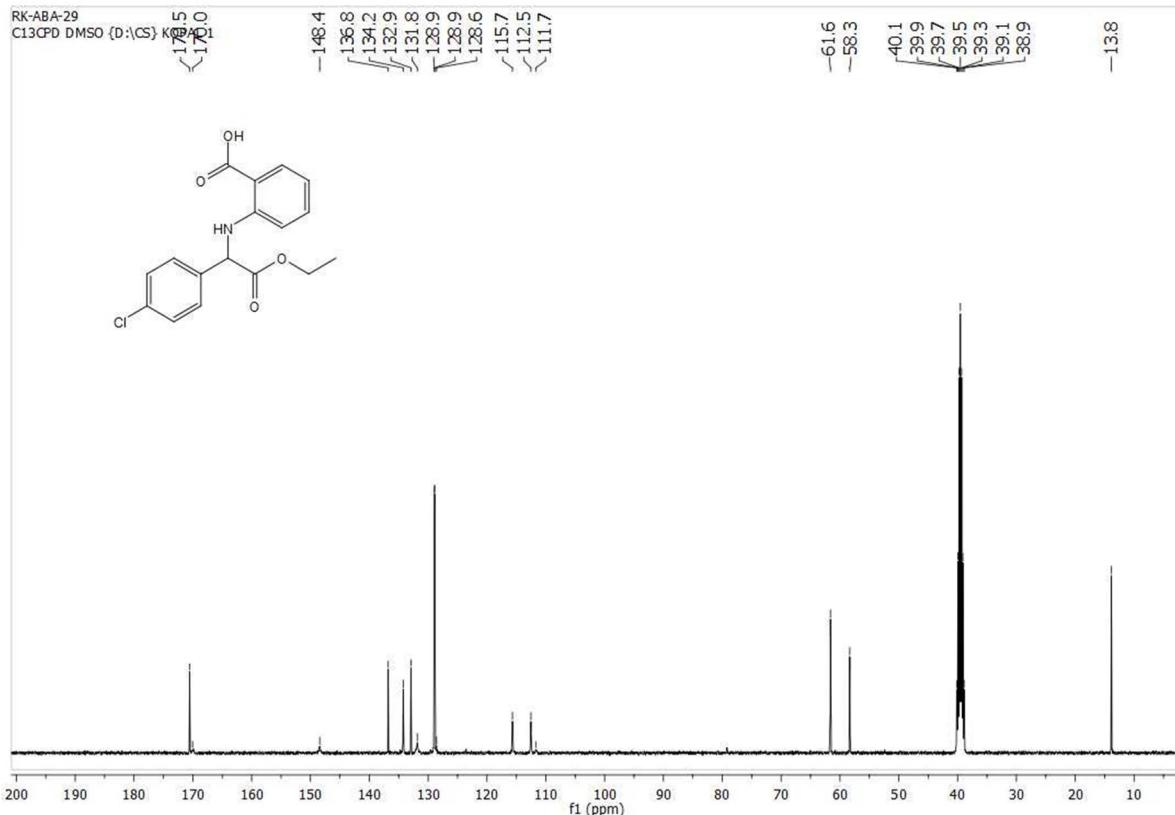
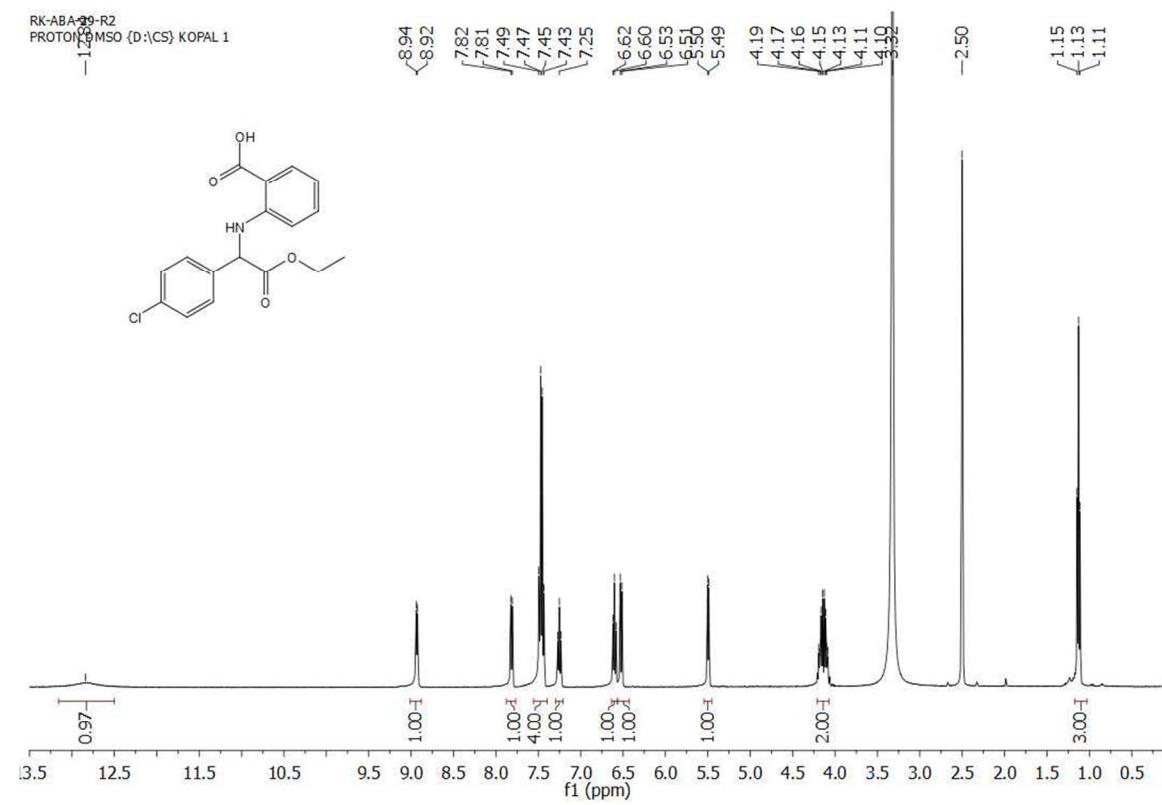
**4-((2-(benzyloxy)-2-oxo-1-phenylethyl)amino)-2-methoxybenzoic acid (8g):**



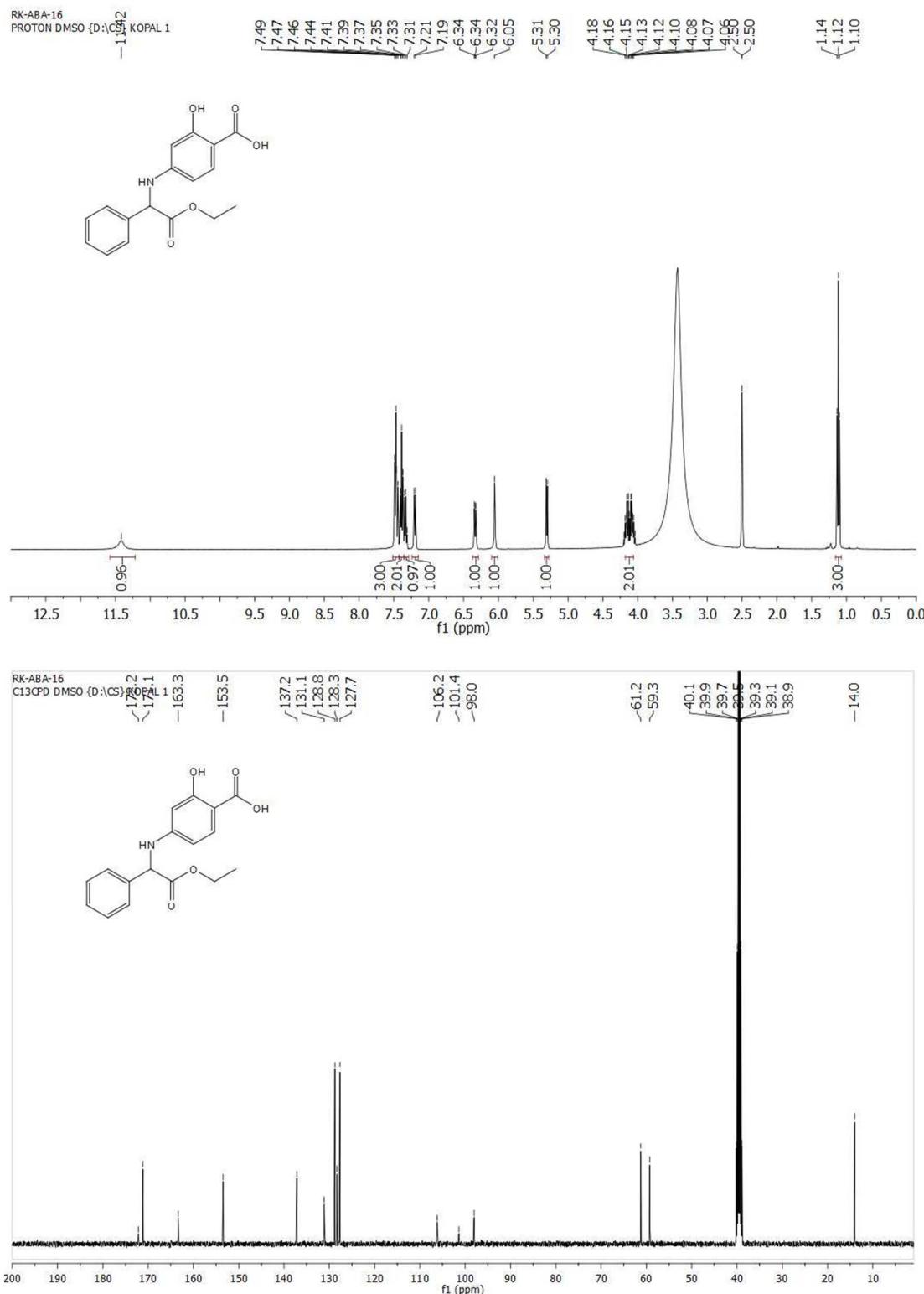
**2-((2-ethoxy-2-oxo-1-phenylethyl)amino)-5-iodobenzoic acid (8h):**



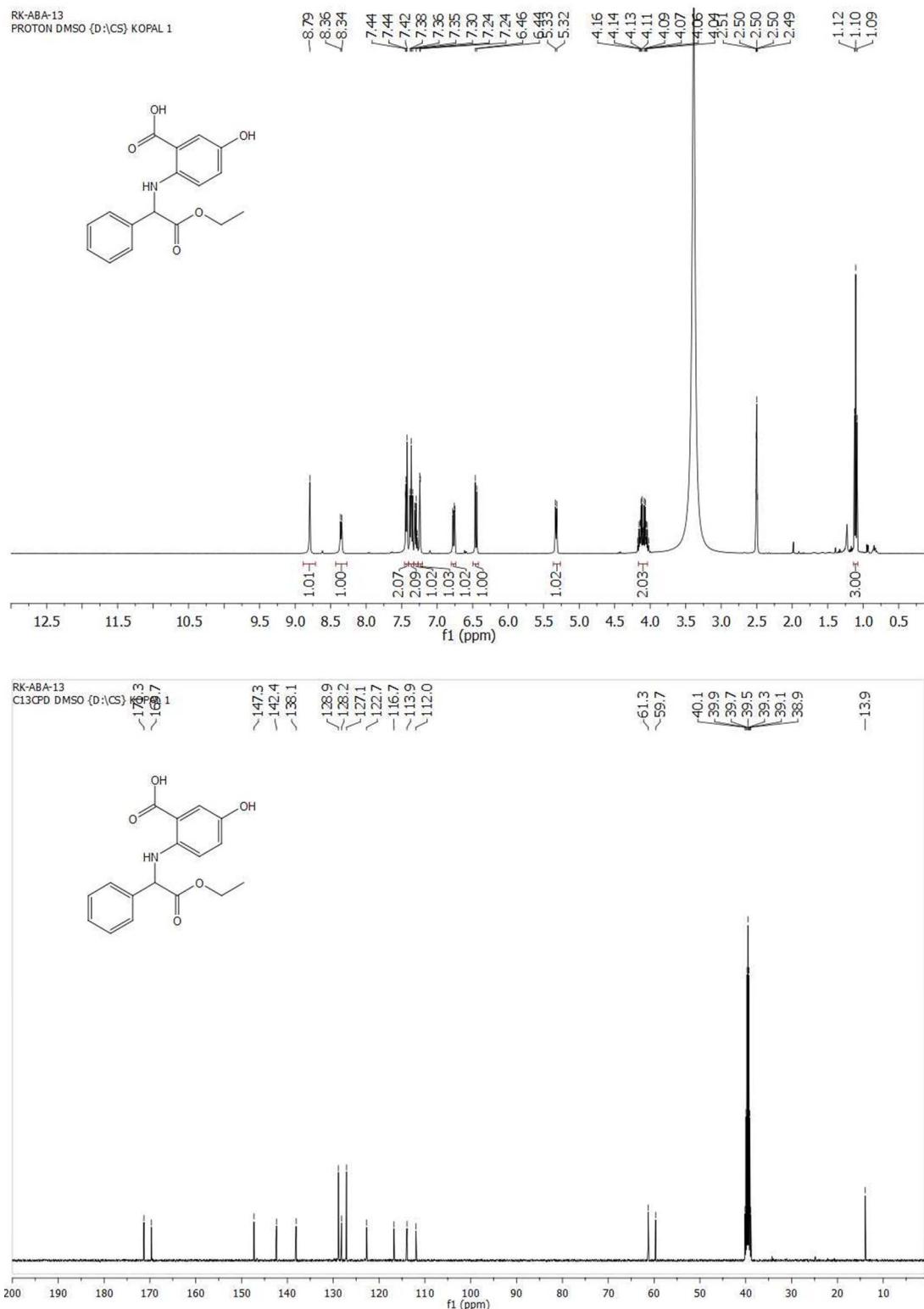
**2-((1-(4-chlorophenyl)-2-ethoxy-2-oxoethyl)amino)benzoic acid (8i):**



**4-((2-ethoxy-2-oxo-1-phenylethyl)amino)-2-hydroxybenzoic acid (9a):**



**2-((2-ethoxy-2-oxo-1-phenylethyl)amino)-5-hydroxybenzoic acid (9b):**



**4-((1-(4-bromophenyl)-2-ethoxy-2-oxoethyl)amino)-2-hydroxybenzoic acid (9c):**

