

**A Rh(III)-Catalyzed Cascade C–H Functionalization/Cyclization
Reaction of Salicylaldehydes with Diazomalonates for the Synthesis
of 4-Hydroxycoumarin Derivatives**

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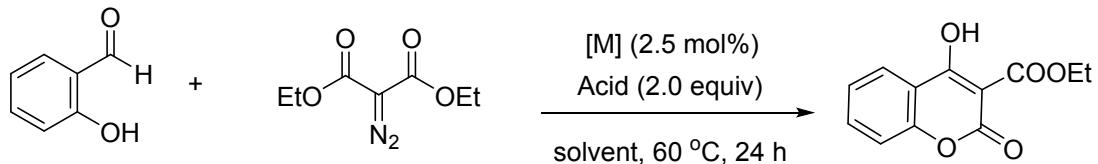
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Electronic Supplementary Information

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1. Optimization of the Reaction Conditions

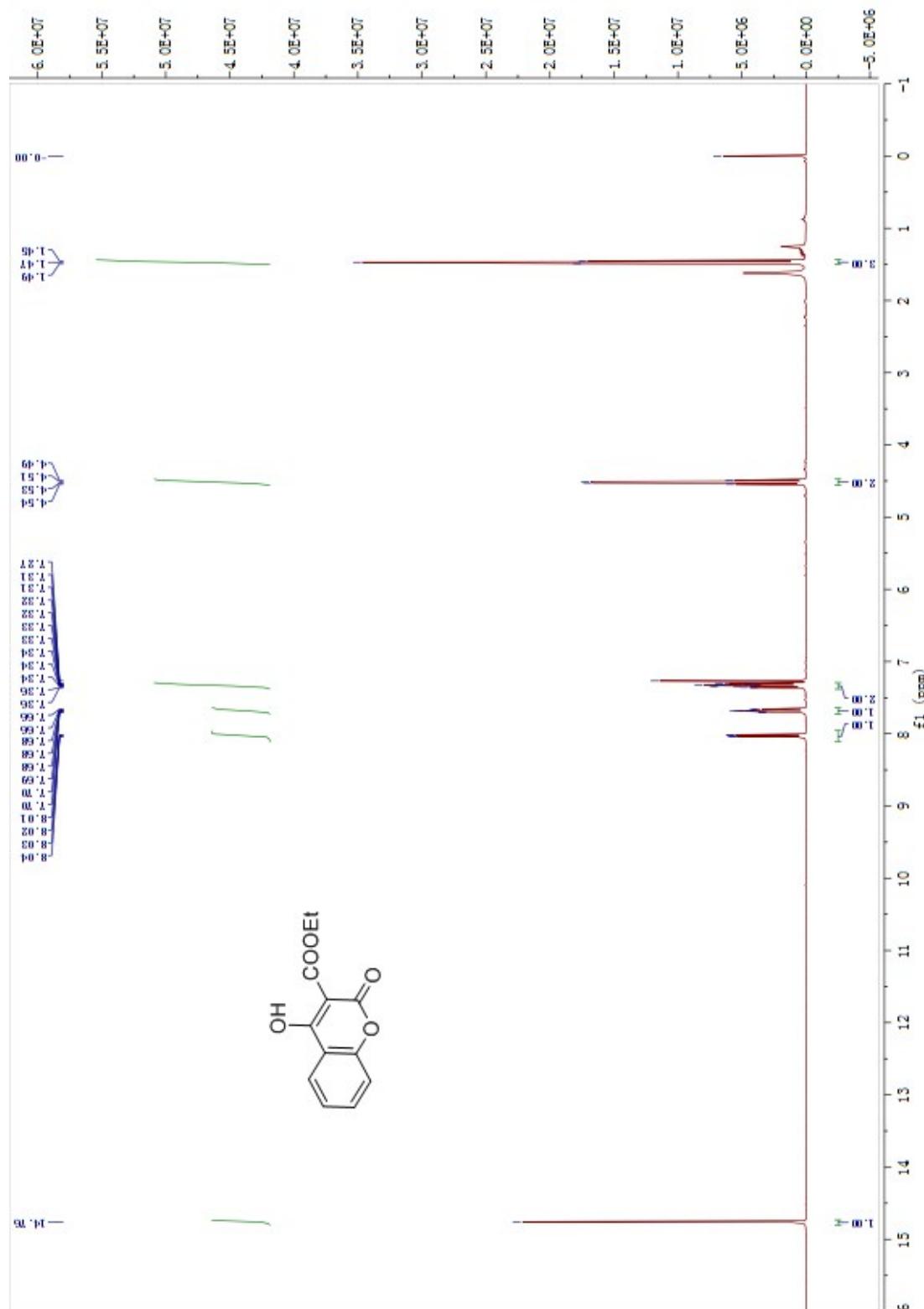


Entry	[M]	Acid	Solvent	Yield (%) ^b
1	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DCE	43
2	$[\text{Cp}^*\text{Rh}(\text{MeCN})_2](\text{SbF}_6)_2$	AcOH	DCE	0
3	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	AcOH	DCE	0
4	$[\text{Cp}^*\text{RhCl}_2]_2/\text{AgSbF}_6^c$	AcOH	DCE	24
5	$[\text{Rh}(\text{COD})_2\text{Cl}]_2$	AcOH	DCE	0
6	$\text{RhCl}(\text{PPh})_3$	AcOH	DCE	0
7	$[\text{Cp}^*\text{IrCl}_2]_2$	AcOH	DCE	0
8	$[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$	AcOH	DCE	0
9	$\text{Pd}(\text{OAc})_2$	AcOH	DCE	0
10	PdCl_2	AcOH	DCE	0
11	$[\text{Cp}^*\text{RhCl}_2]_2$	HCOOH	DCE	0
12	$[\text{Cp}^*\text{RhCl}_2]_2$	PivOH	DCE	40
13	$[\text{Cp}^*\text{RhCl}_2]_2$	TFA	DCE	0
14	$[\text{Cp}^*\text{RhCl}_2]_2$	<i>p</i> -TsOH	DCE	0
15	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	dioxane	0
16	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	EtOH	0
17	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	MeCN	0
18	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DMF	0
19	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	toluene	30
20	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	THF	0
21 ^d	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DCE	21
22 ^e	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DCE	79
23 ^f	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DCE	55
24 ^g	$[\text{Cp}^*\text{RhCl}_2]_2$	AcOH	DCE	trace

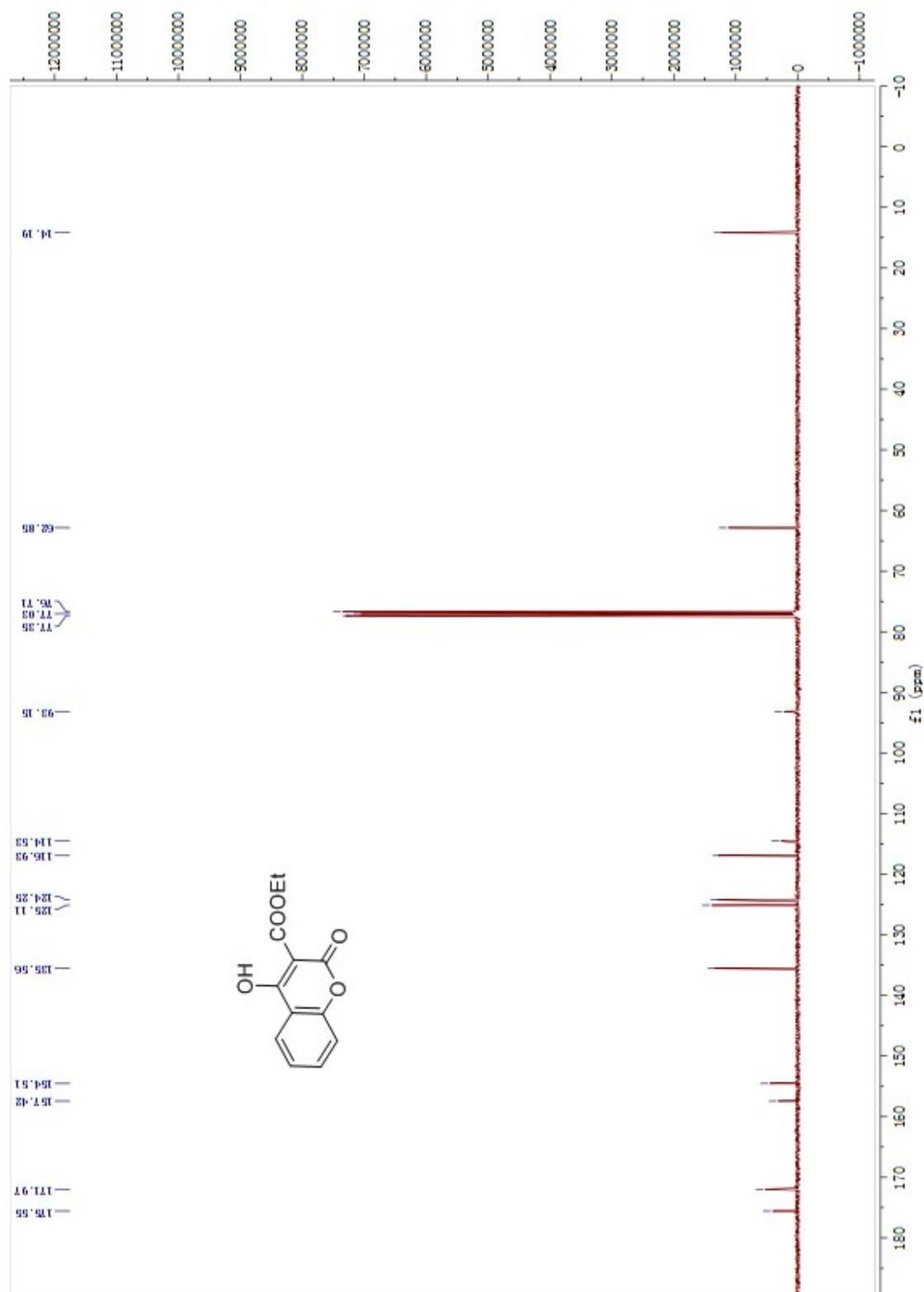
^aReaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), [M] (2.5 mol%), acid (2.0 equiv), solvent (2.0 mL), 60 °C, for 24 h. ^bIsolated yields. ^c AgSbF_6 (5.0 mol%). ^d50 °C. ^e70 °C. ^f80 °C. ^g40 °C.

2. ^1H NMR and ^{13}C NMR Spectra of 4-Hydroxycoumarin Derivatives 3

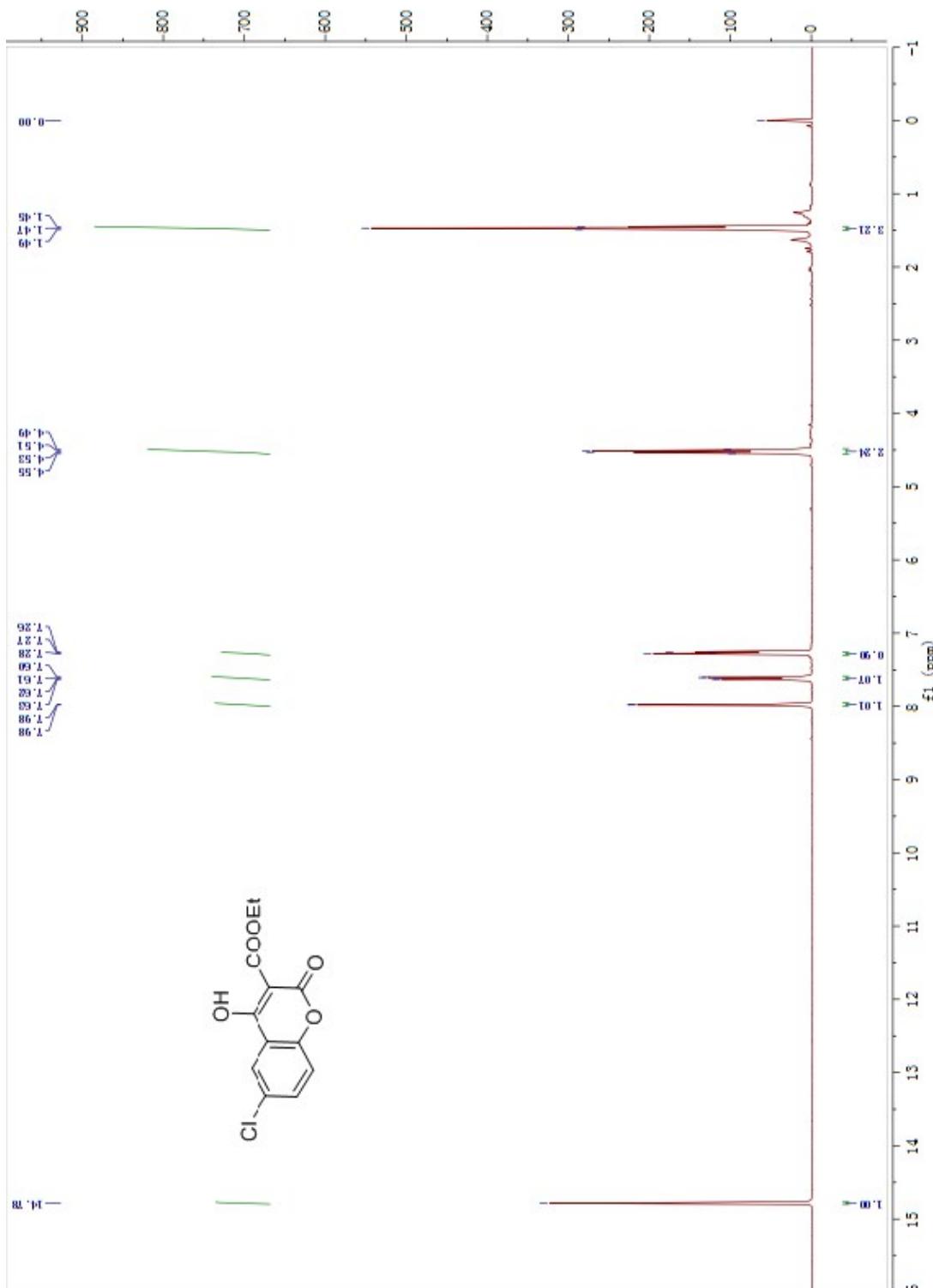
^1H NMR Spectrum of Ethyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3aa**



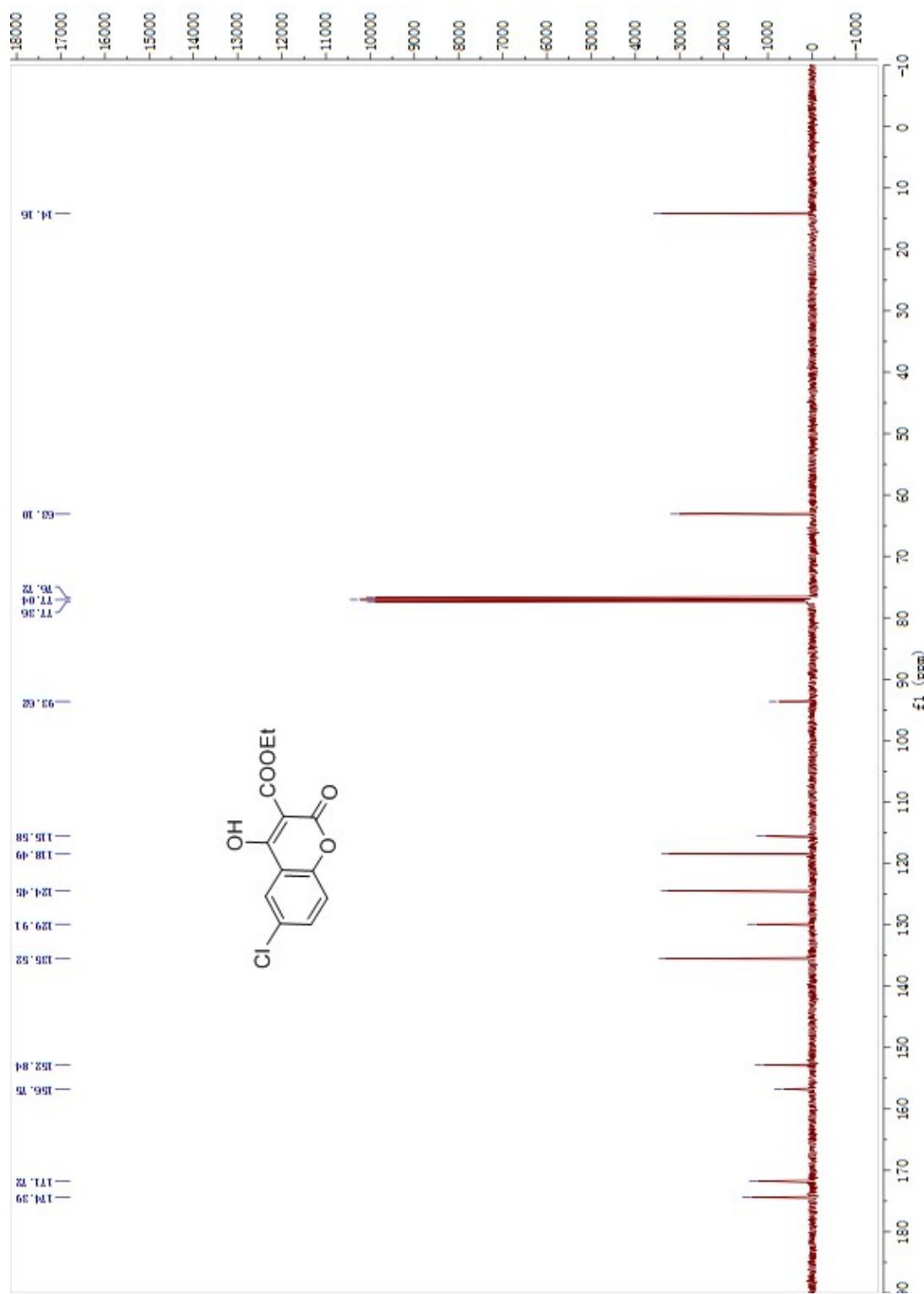
¹³C NMR Spectrum of Ethyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate
3aa



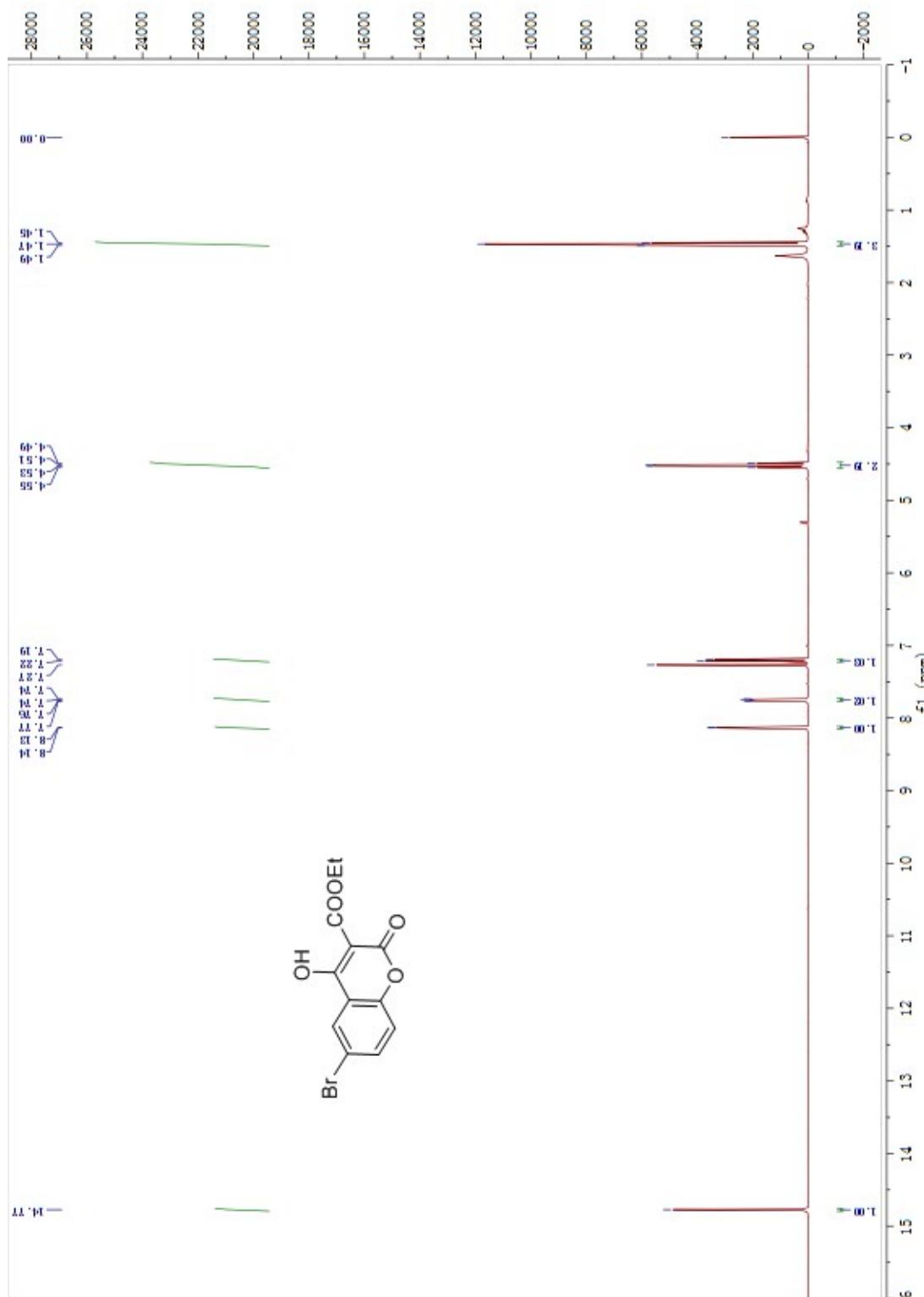
¹H NMR Spectrum of Ethyl 6-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ba**



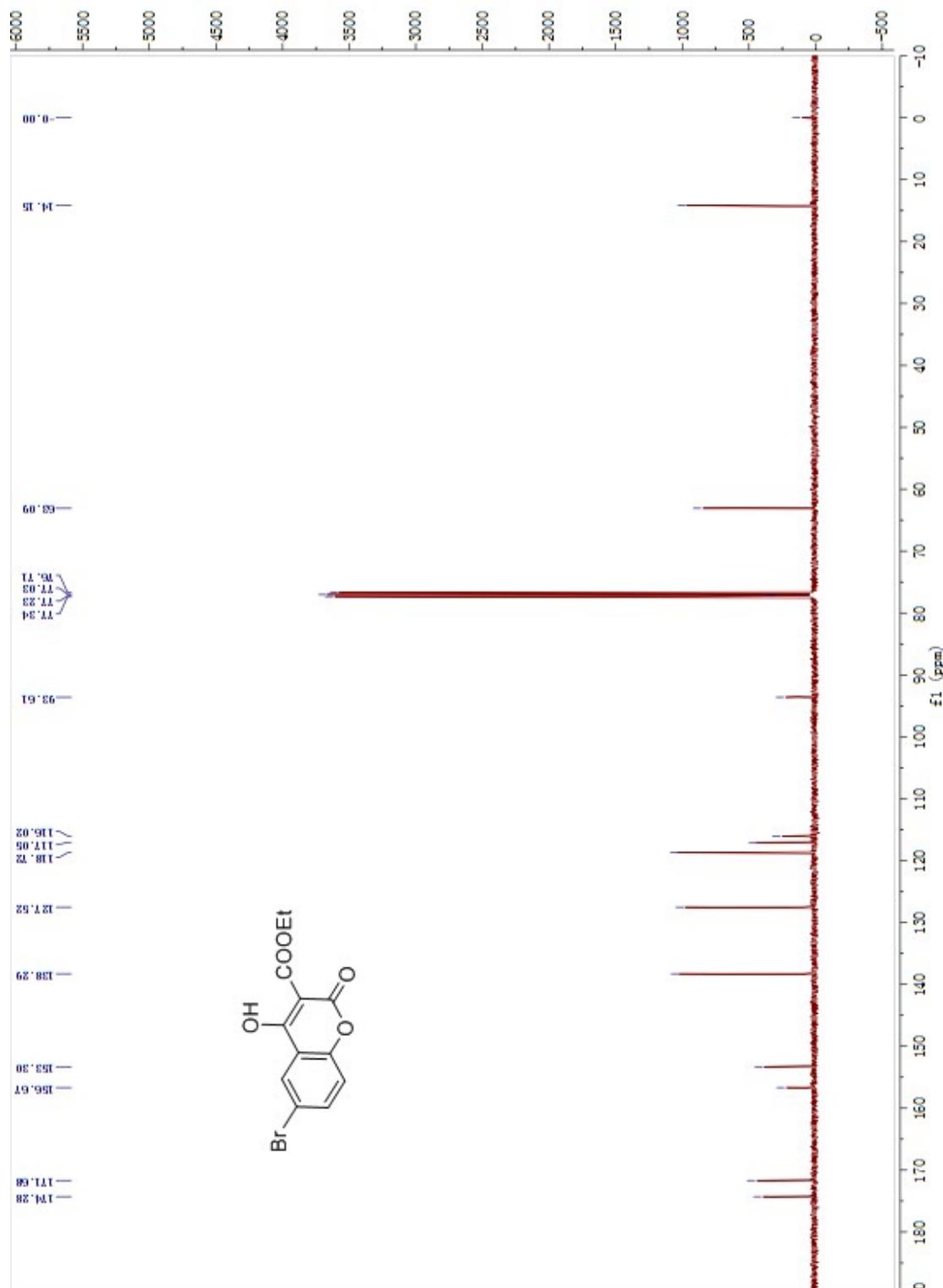
^{13}C NMR Spectrum of Ethyl 6-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ba**



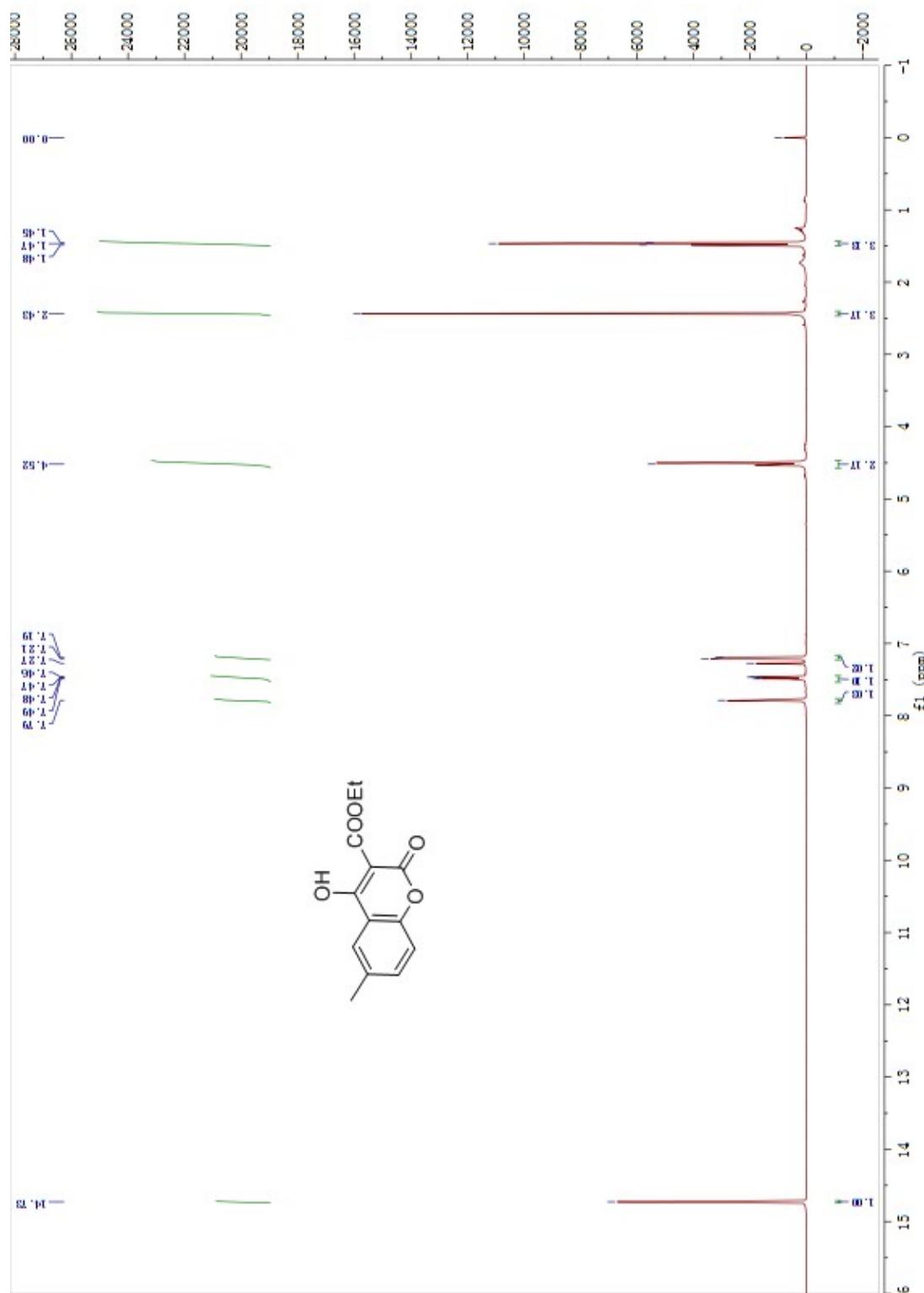
¹H NMR Spectrum of Ethyl 6-Bromo-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ca**



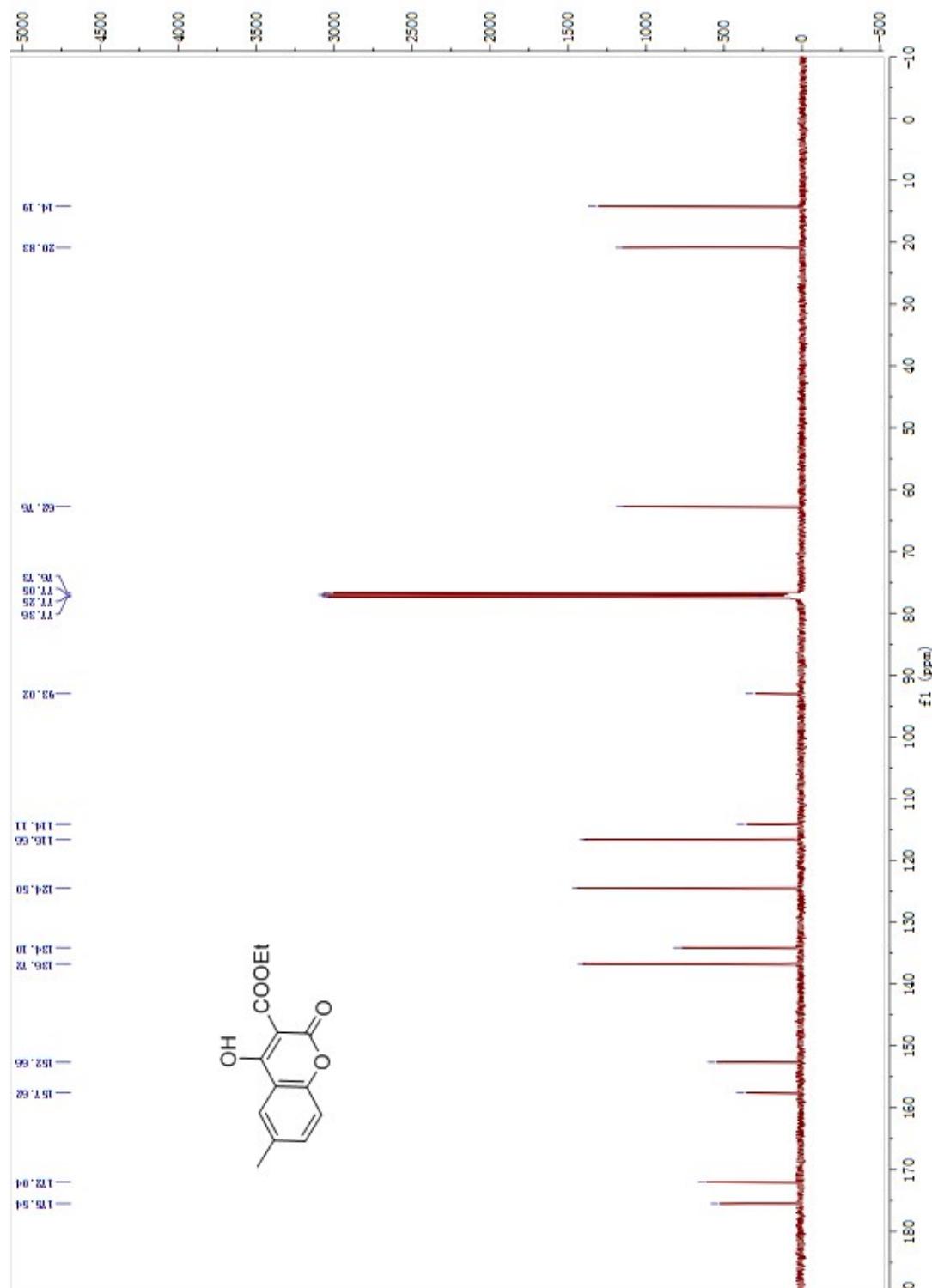
¹³C NMR Spectrum of Ethyl 6-Bromo-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ca**



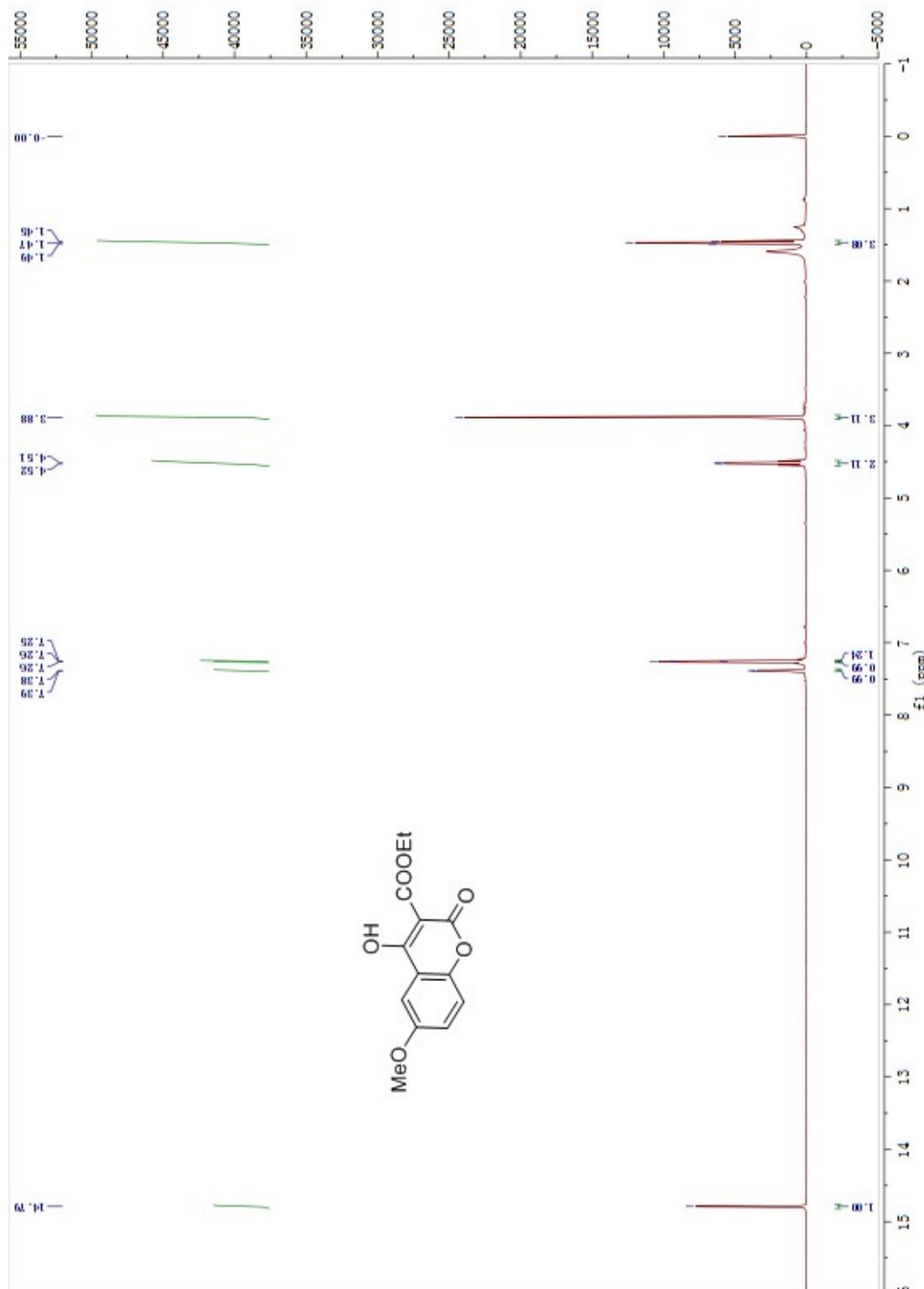
¹H NMR Spectrum of Ethyl 4-Hydroxy-6-methyl-2-oxo-2H-chromene-3-carbo-xylate **3da**



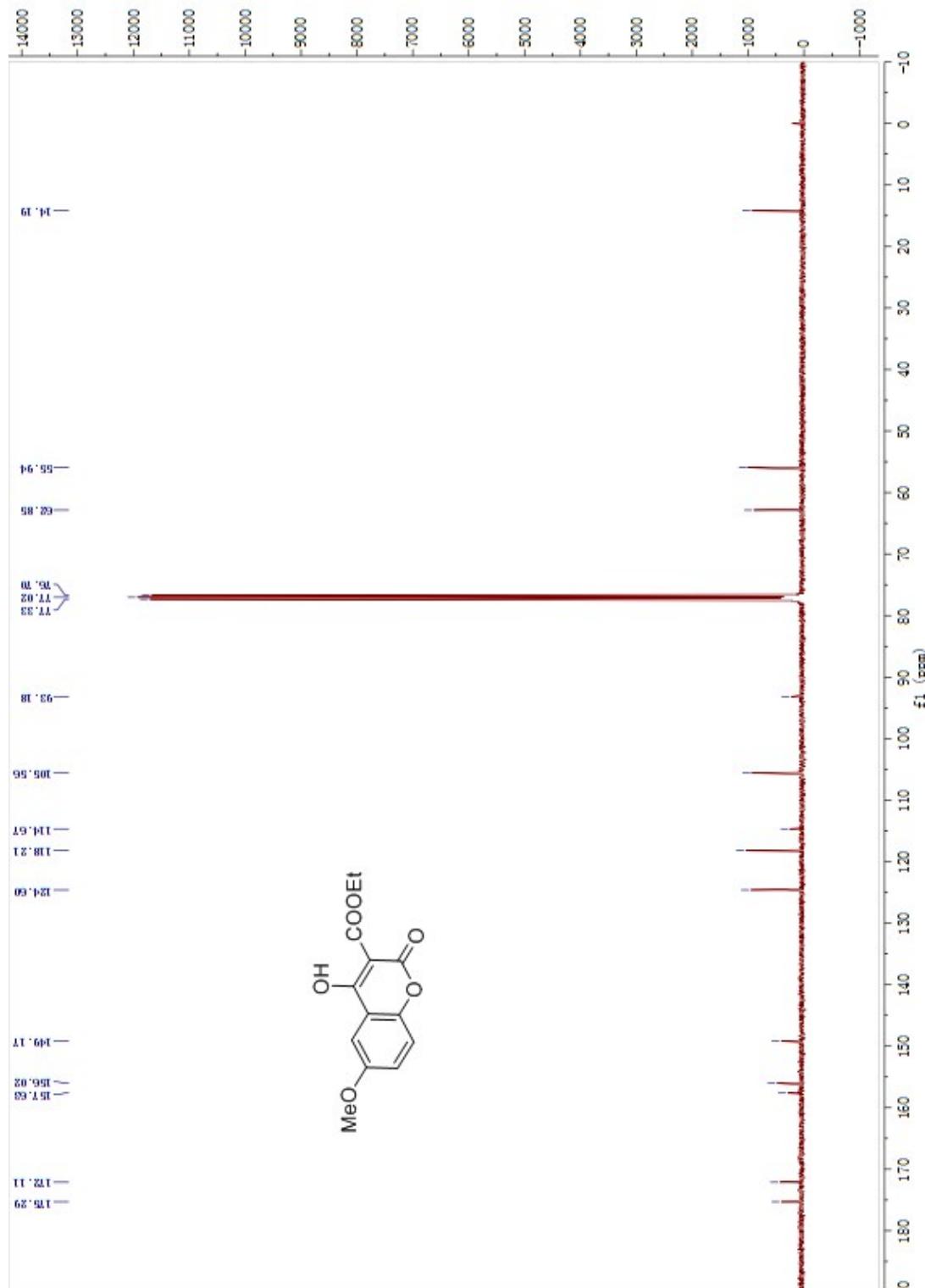
¹³C NMR Spectrum of Ethyl 4-Hydroxy-6-methyl-2-oxo-2H-chromene-3-carbo-xylate **3da**



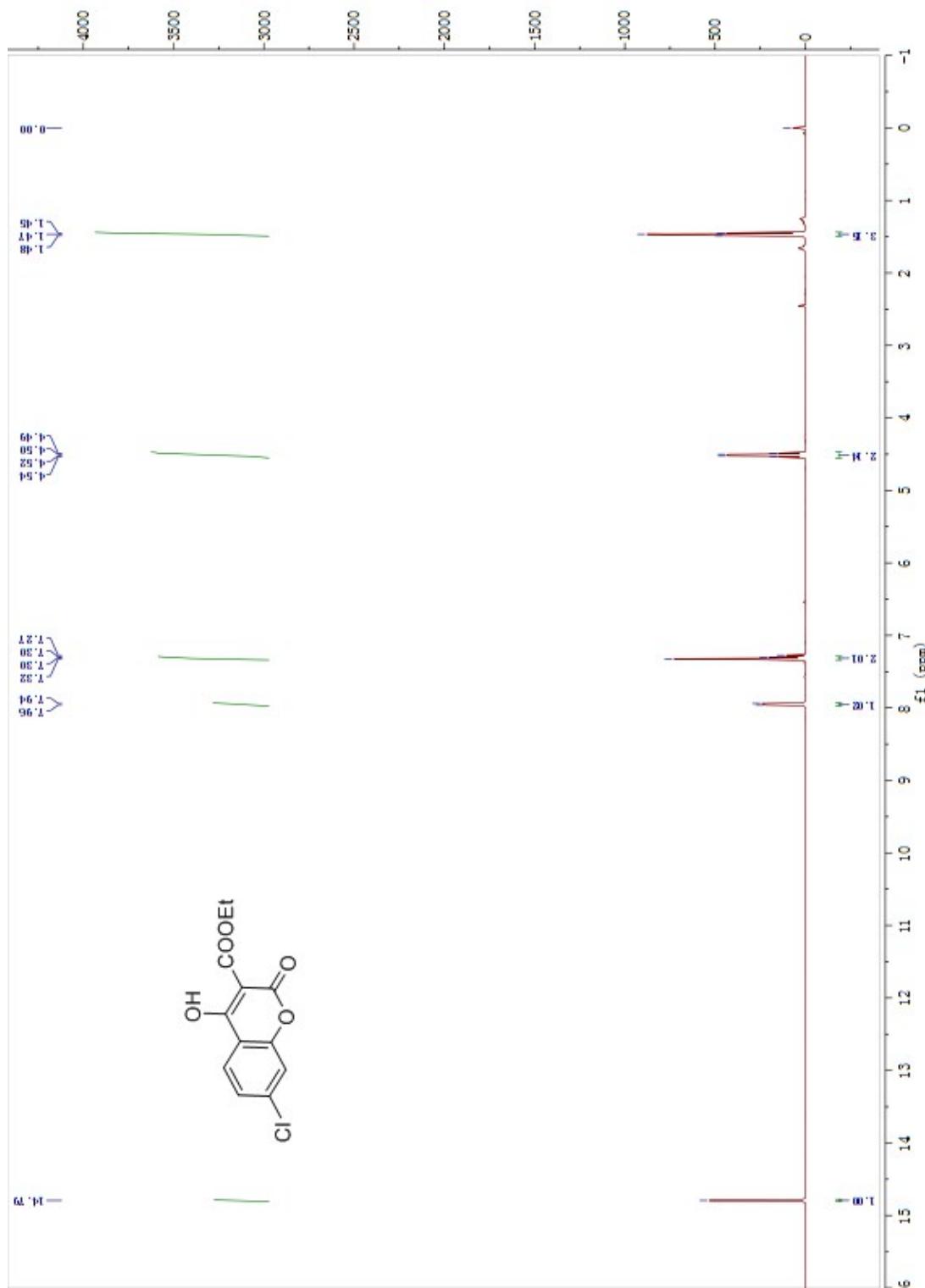
¹H NMR Spectrum of Ethyl 4-Hydroxy-6-methoxy-2-oxo-2H-chromene-3-carboxylate **3ea**



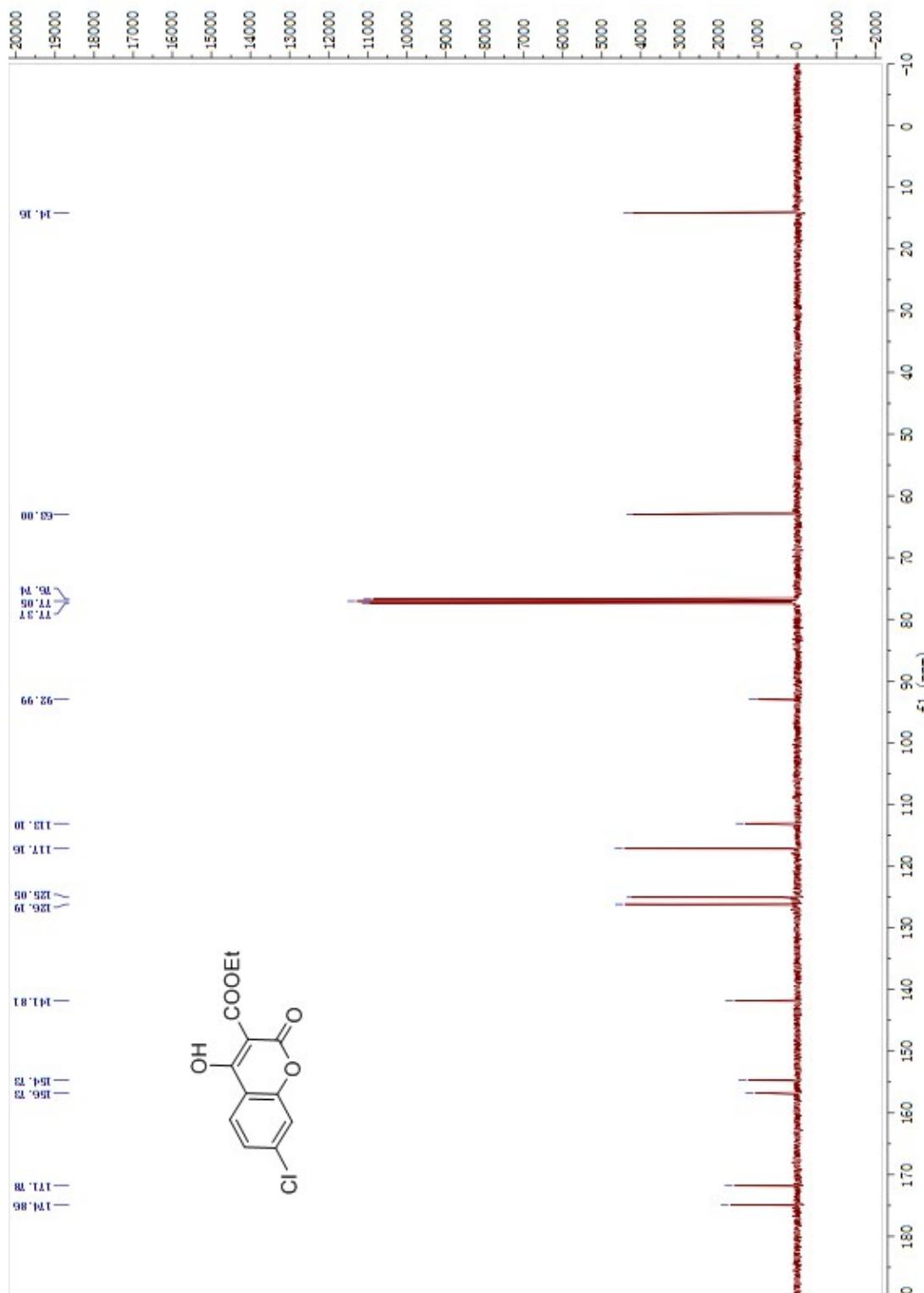
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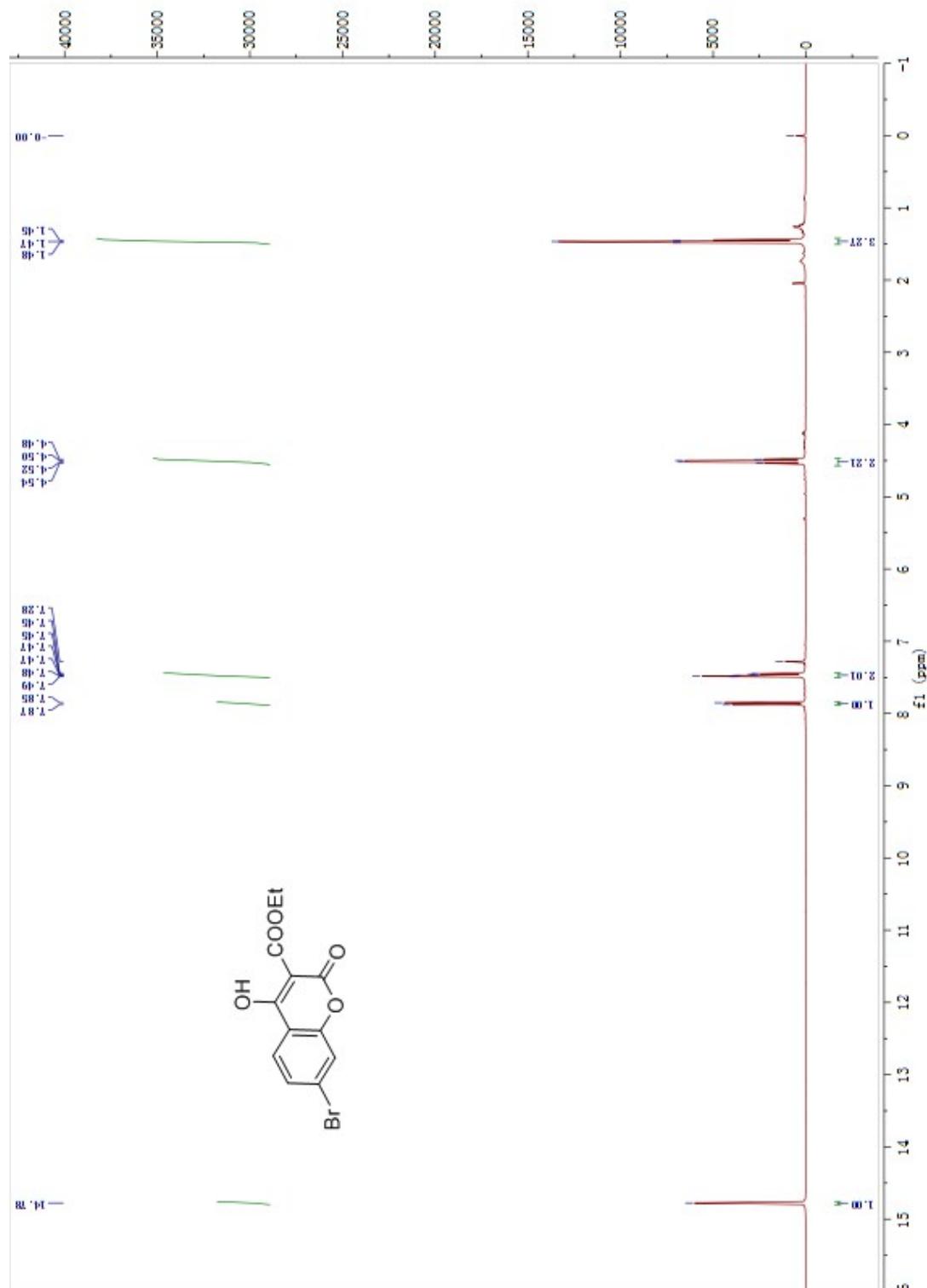
¹H NMR Spectrum of Ethyl 7-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3fa**



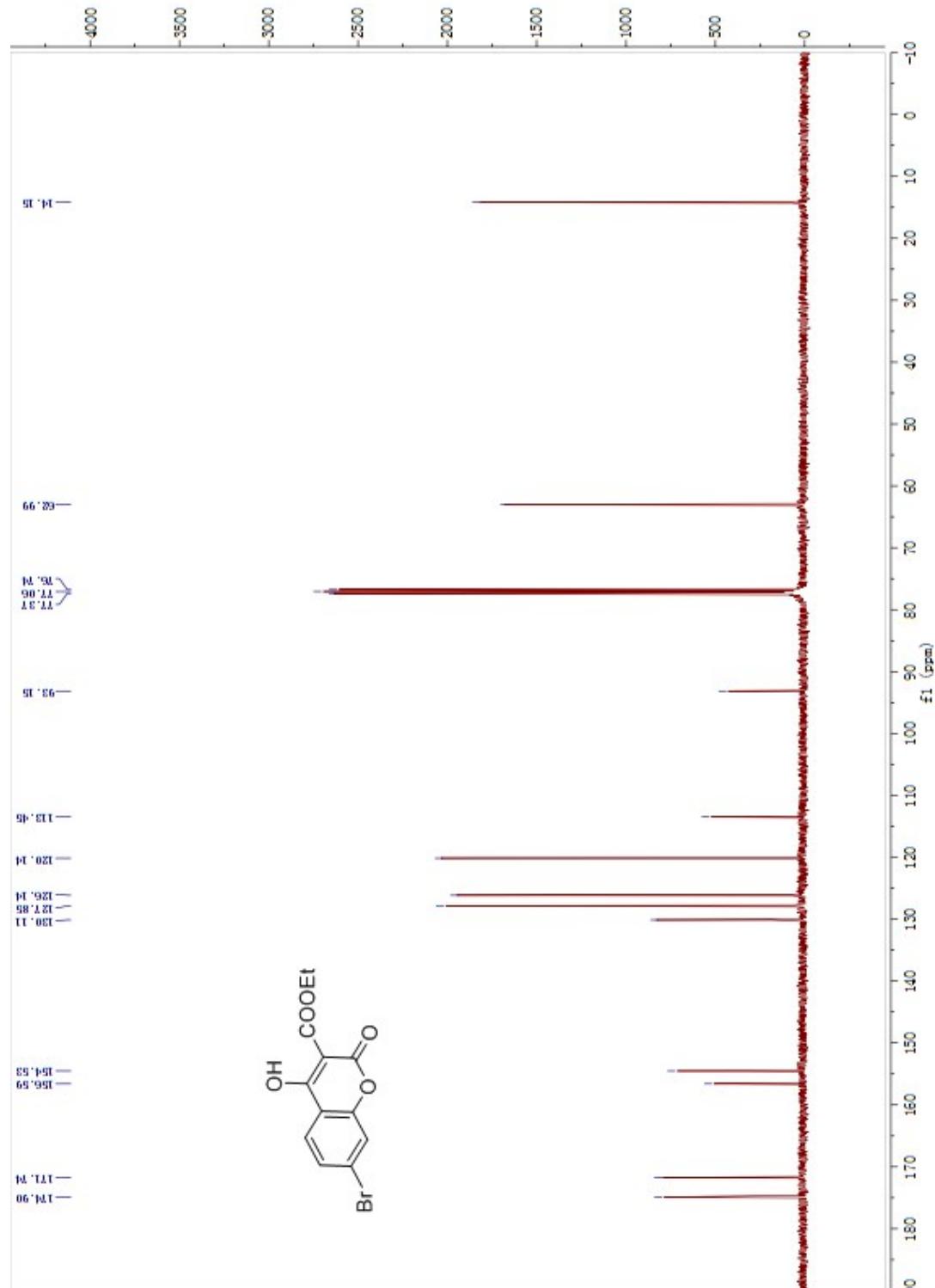
^{13}C NMR Spectrum of Ethyl 7-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3fa**



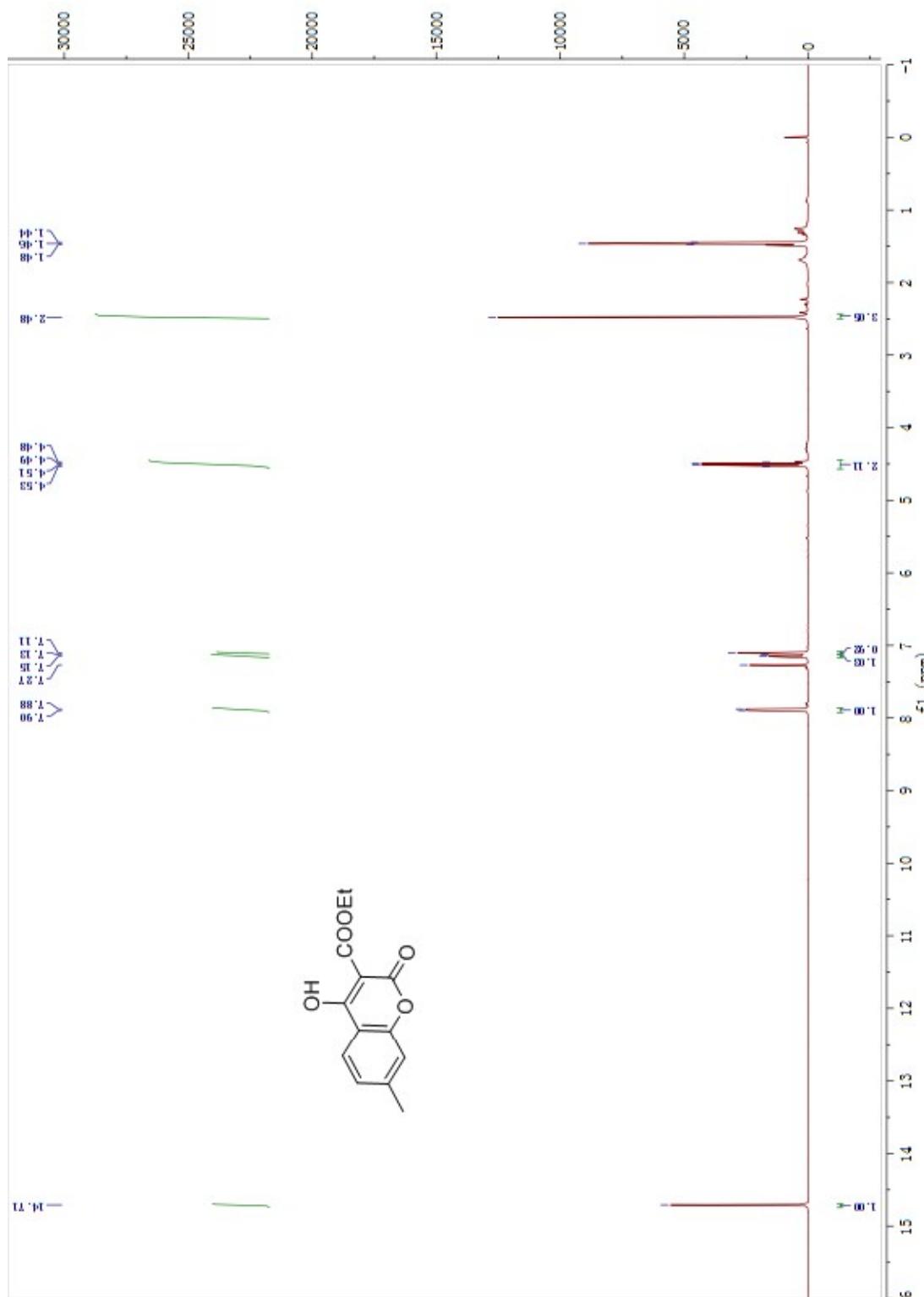
¹H NMR Spectrum of Ethyl 7-Bromo-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ga**



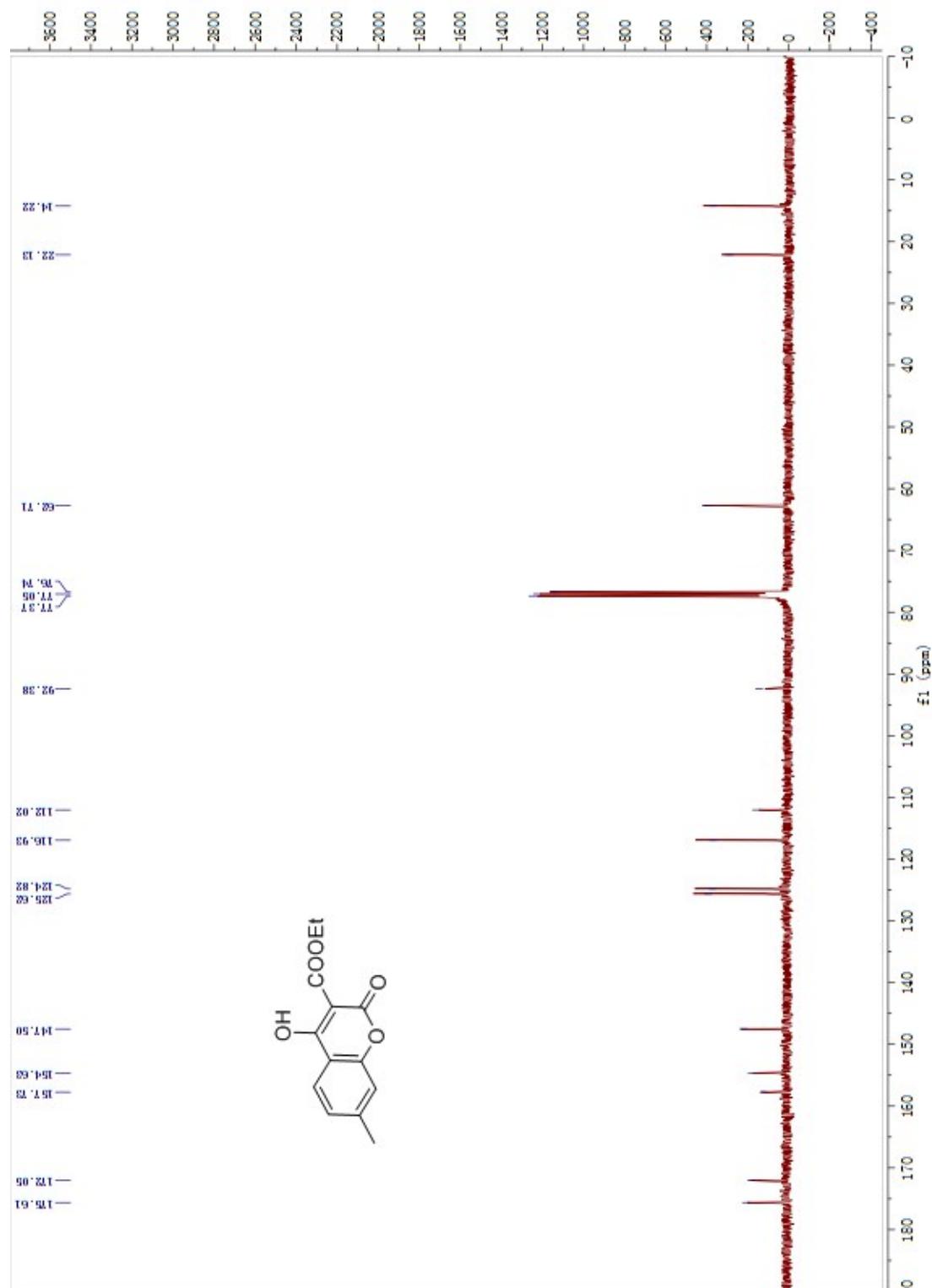
¹³C NMR Spectrum of Ethyl 7-Bromo-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ga**



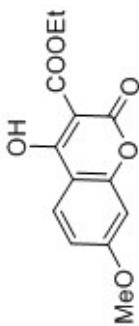
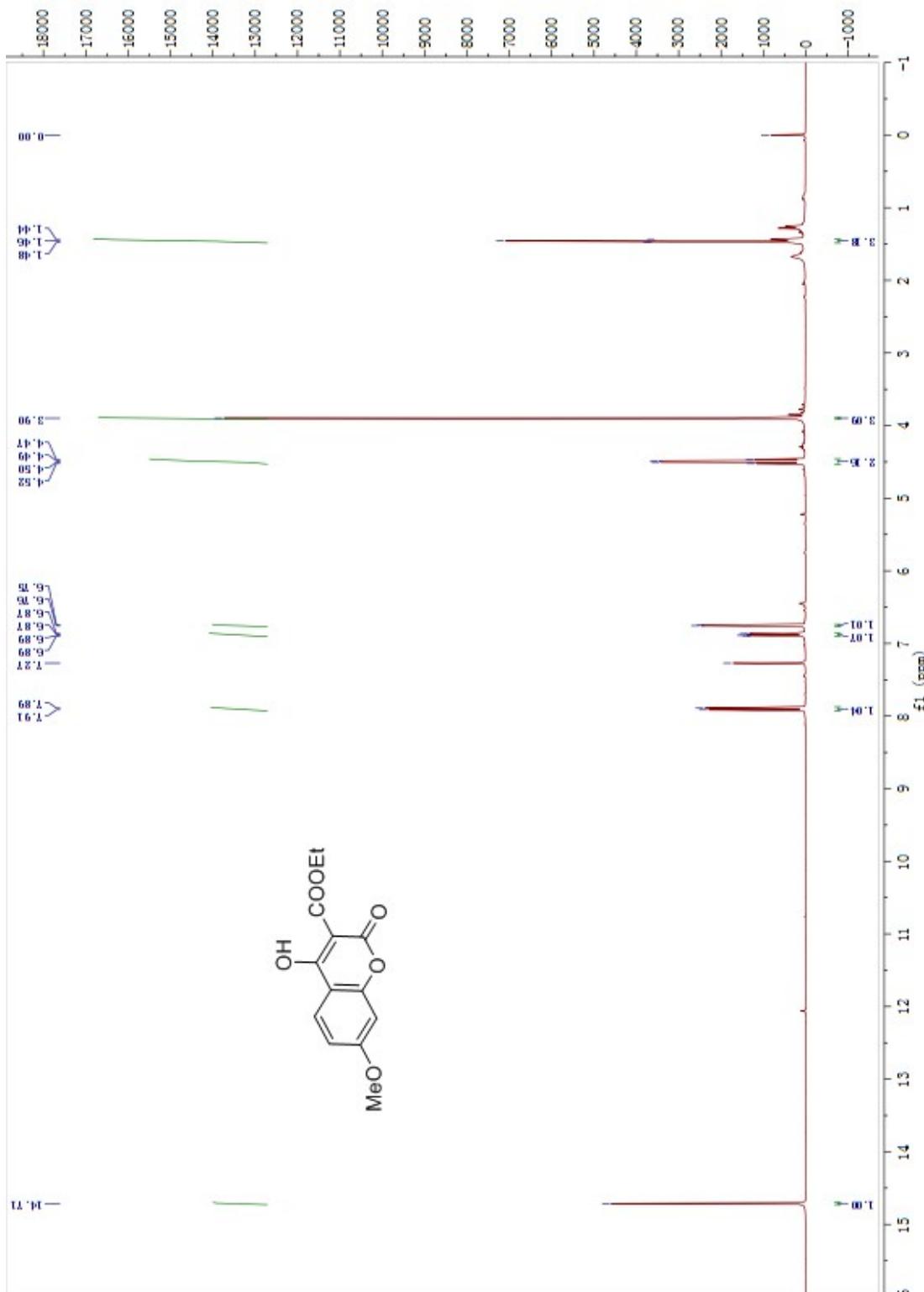
¹H NMR Spectrum of Ethyl 4-Hydroxy-7-methyl-2-oxo-2H-chromene-3-carbo-xylate **3ha**



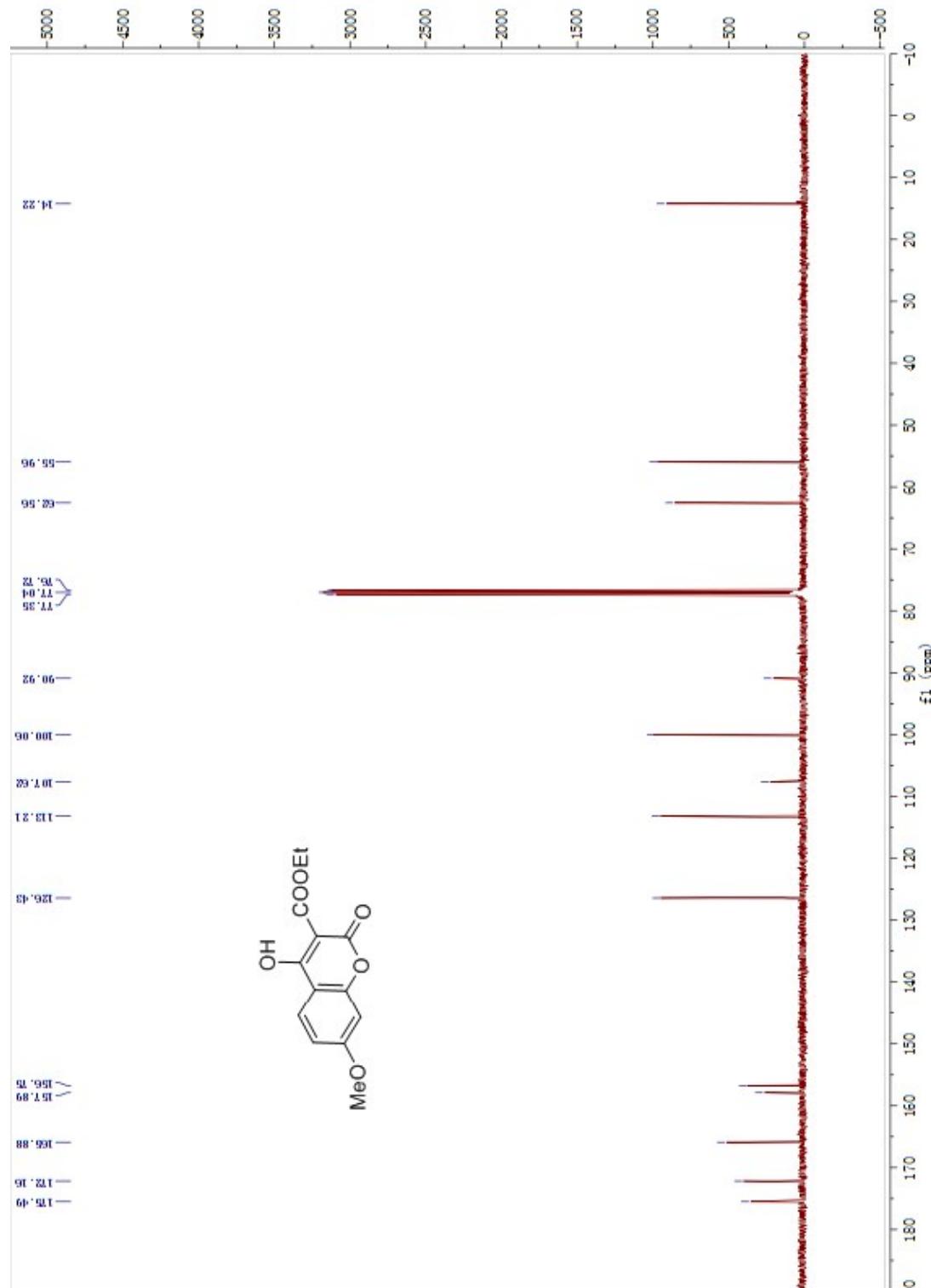
¹³C NMR Spectrum of Ethyl 4-Hydroxy-7-methyl-2-oxo-2H-chromene-3-carbo-xylate **3ha**



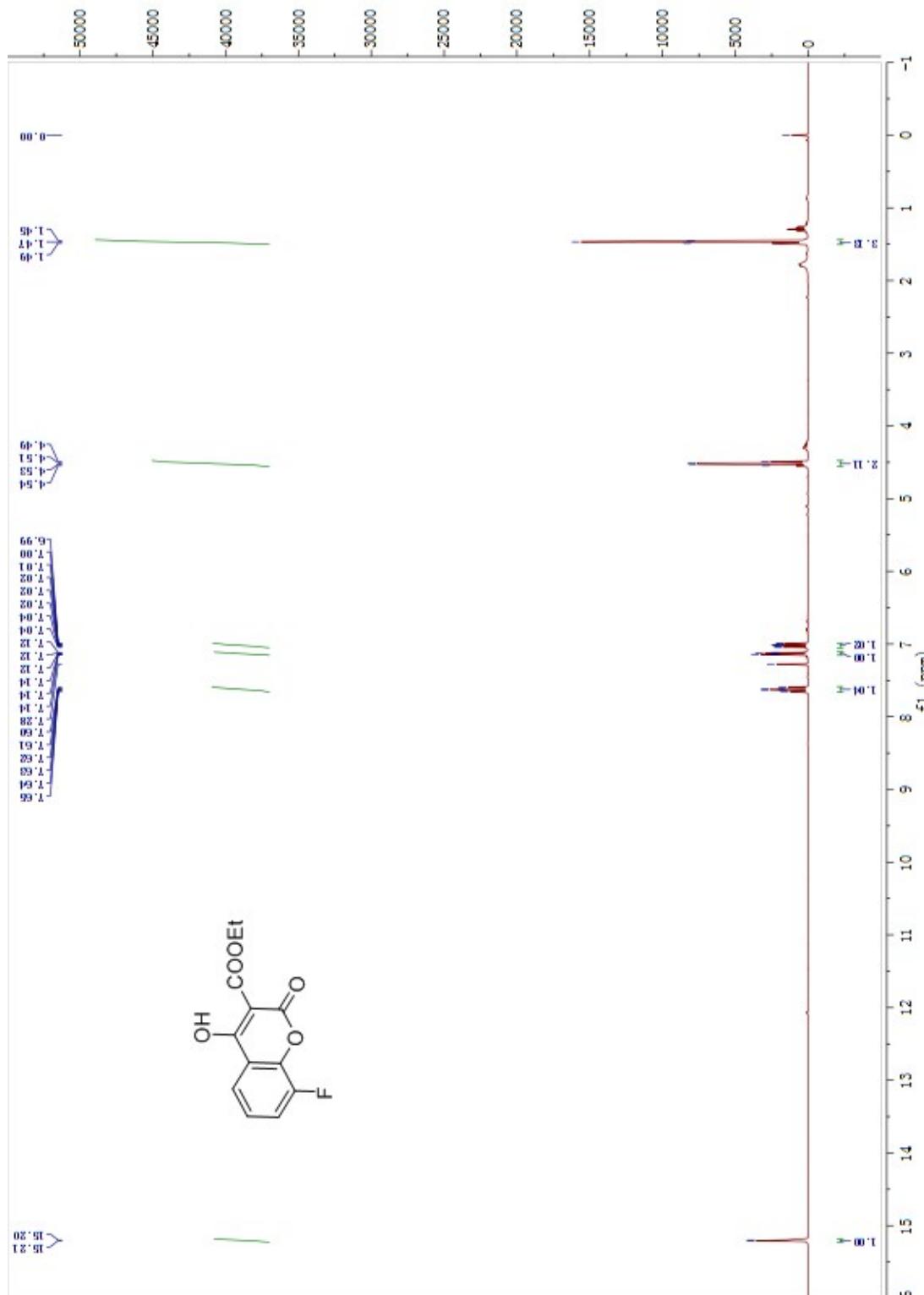
¹H NMR Spectrum of Ethyl 4-Hydroxy-7-methoxy-2-oxo-2H-chromene-3-carboxylate **3ia**



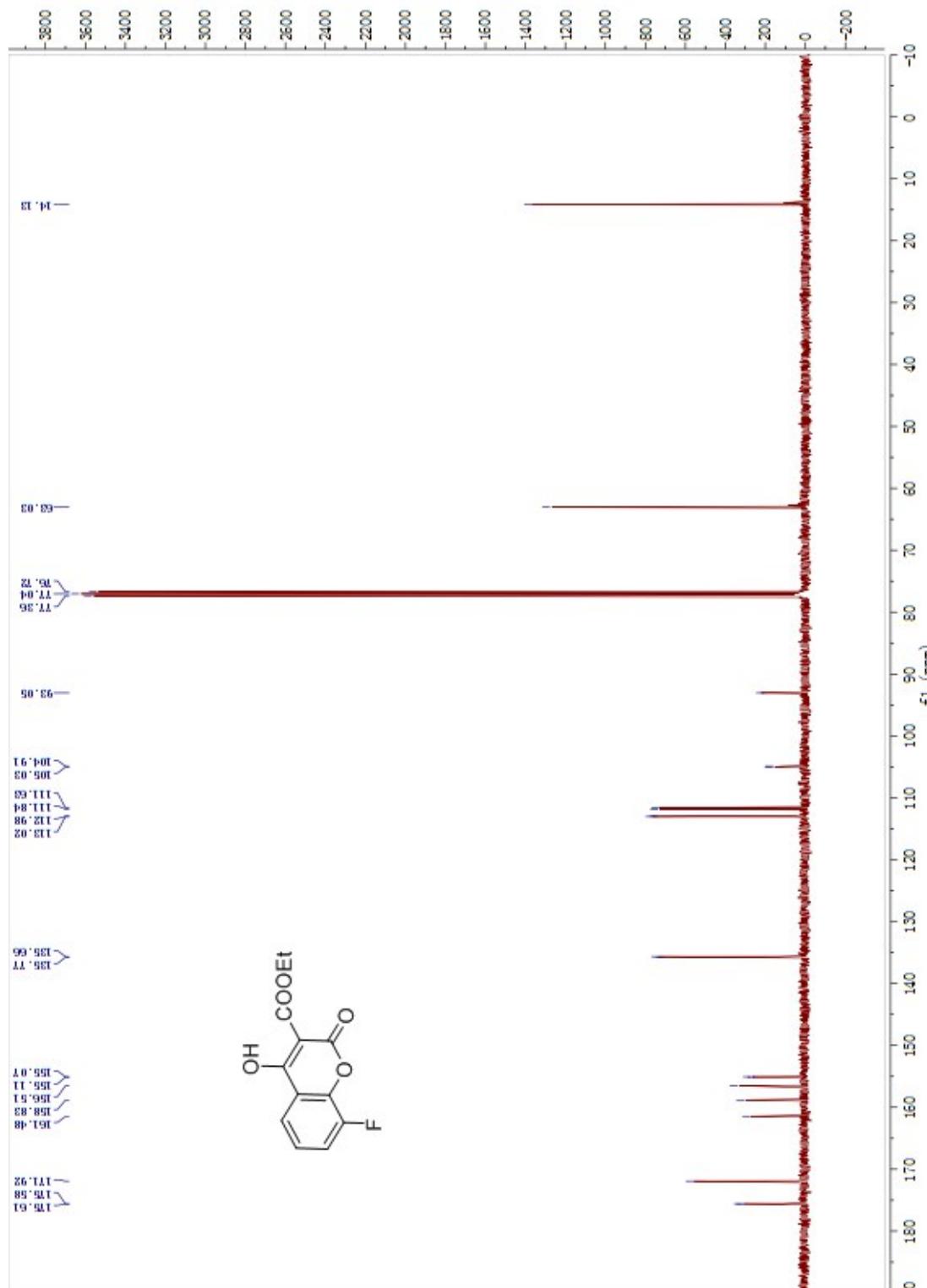
¹³C NMR Spectrum of Ethyl 4-Hydroxy-7-methoxy-2-oxo-2H-chromene-3-carboxylate **3ia**



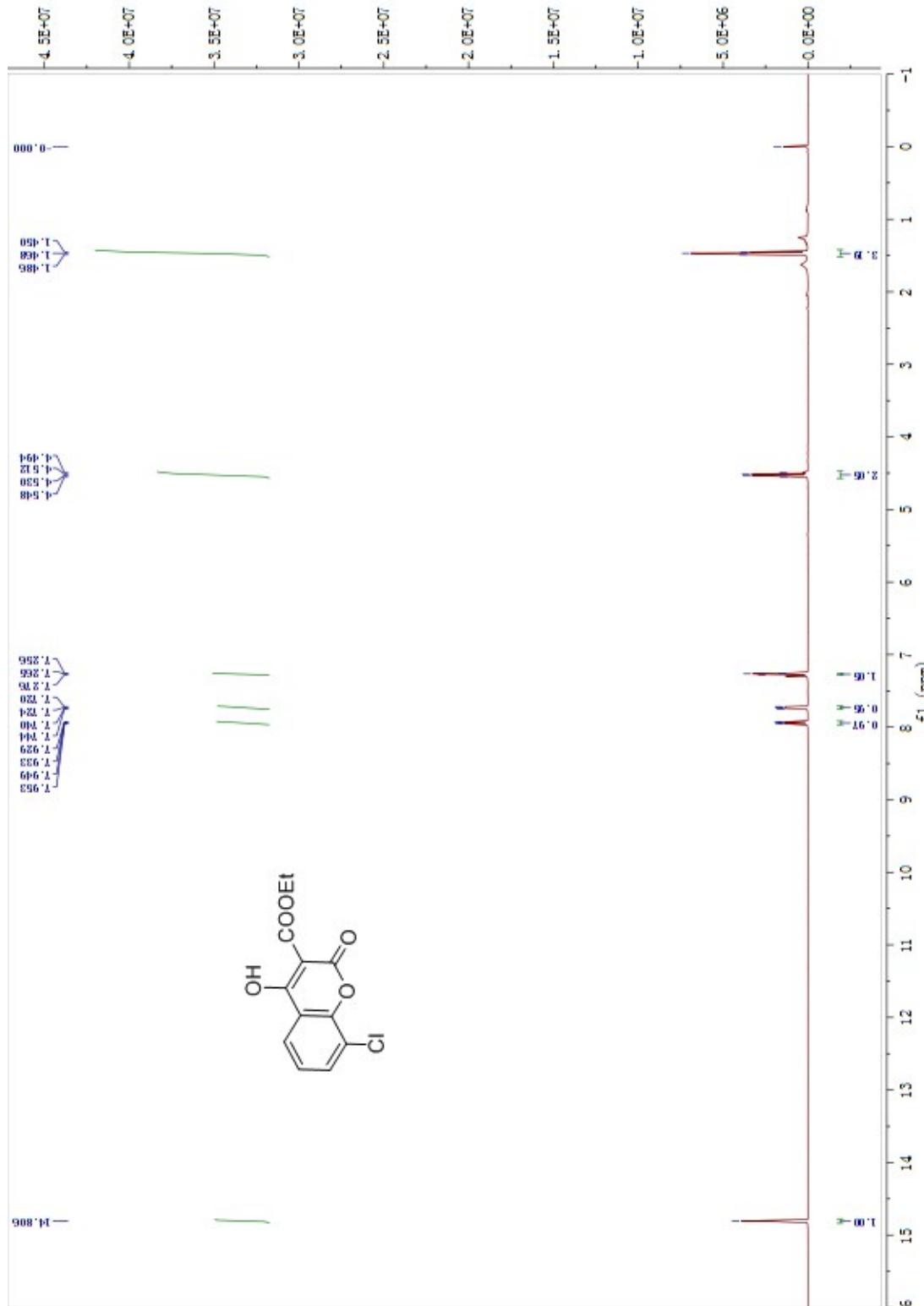
¹H NMR Spectrum of Ethyl 8-Fluoro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-
-xylate **3ja**



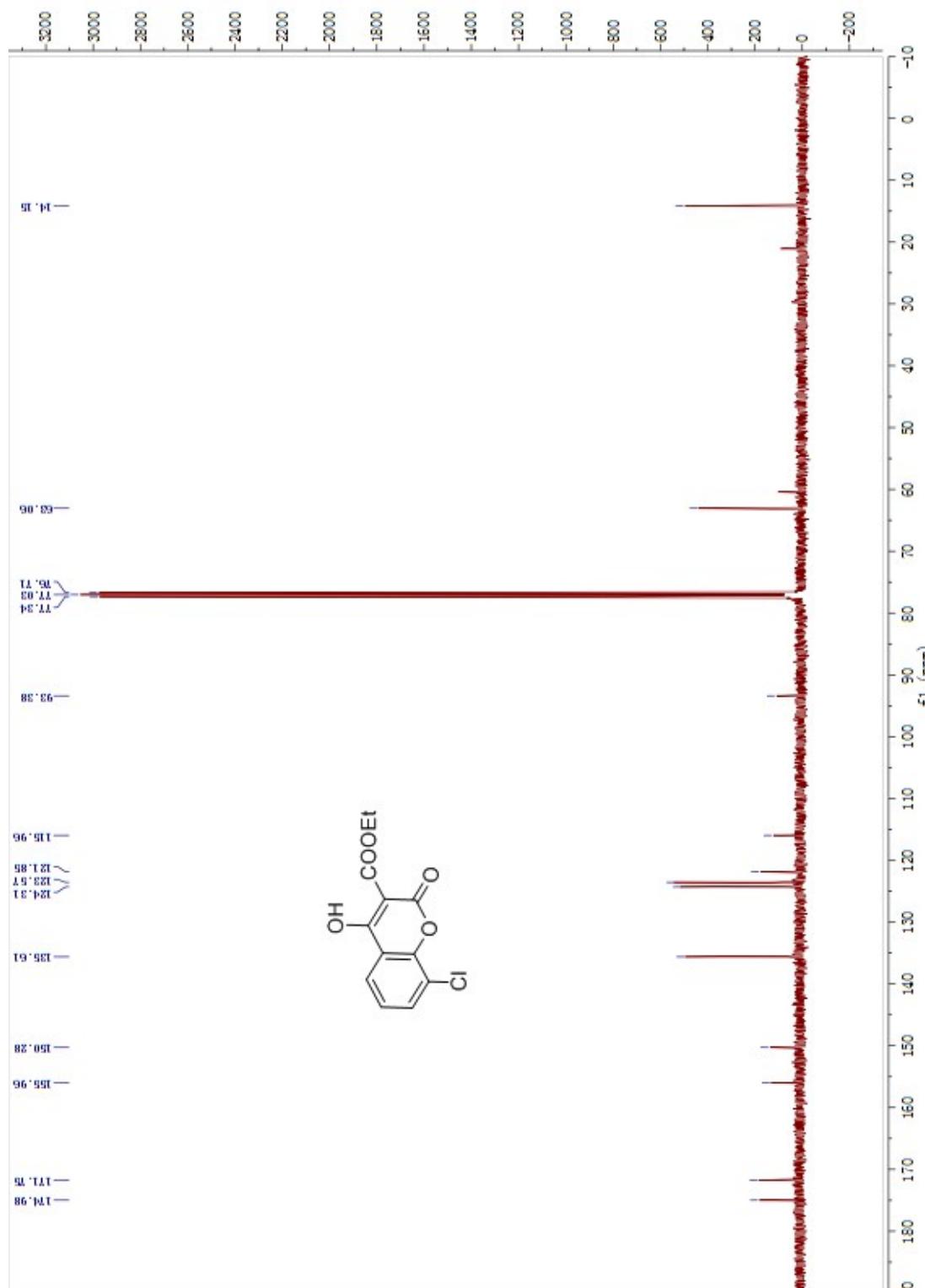
¹³C NMR Spectrum of Ethyl 8-Fluoro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-
-xylate **3ja**



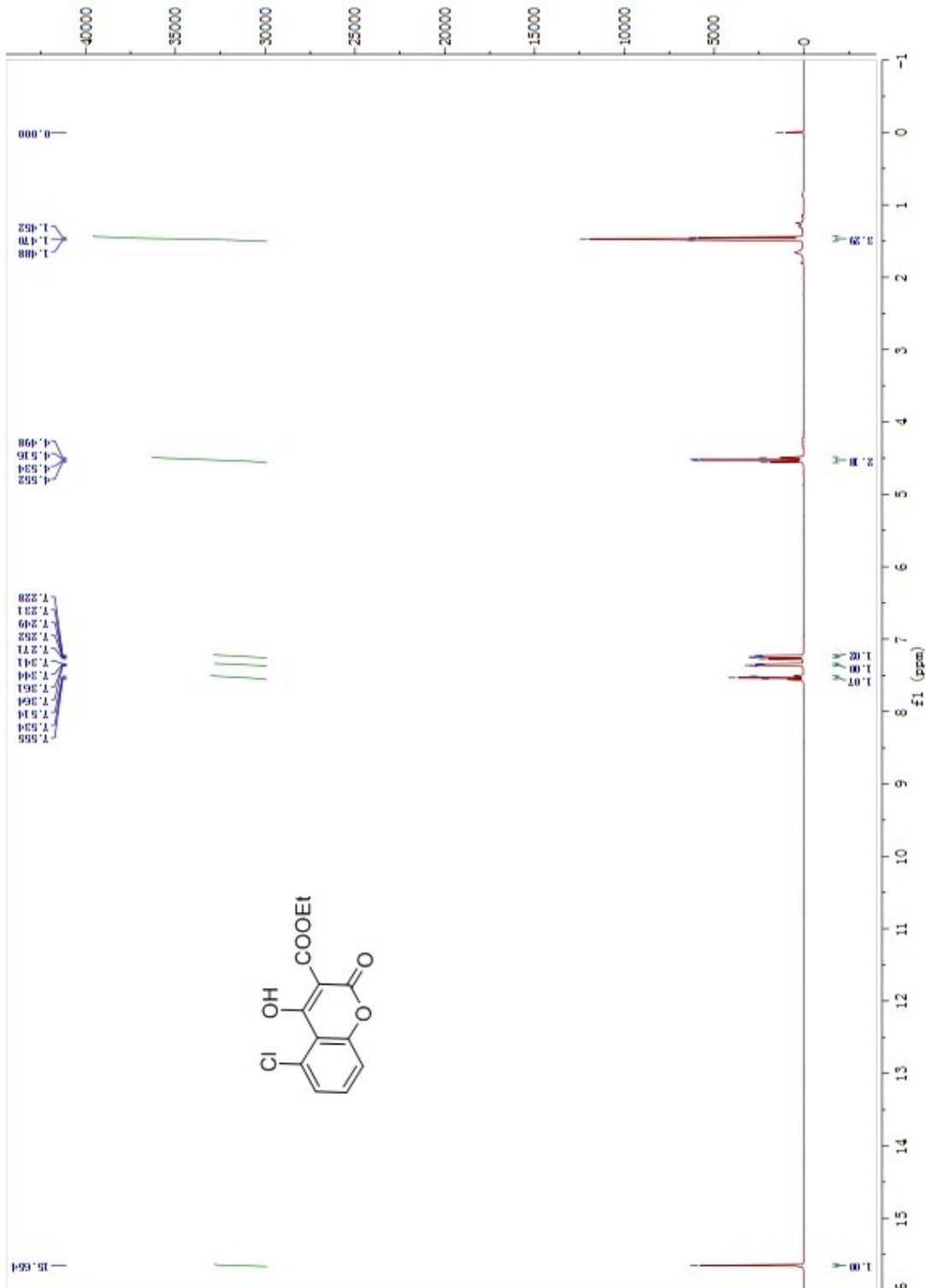
¹H NMR Spectrum of Ethyl 8-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3ka**



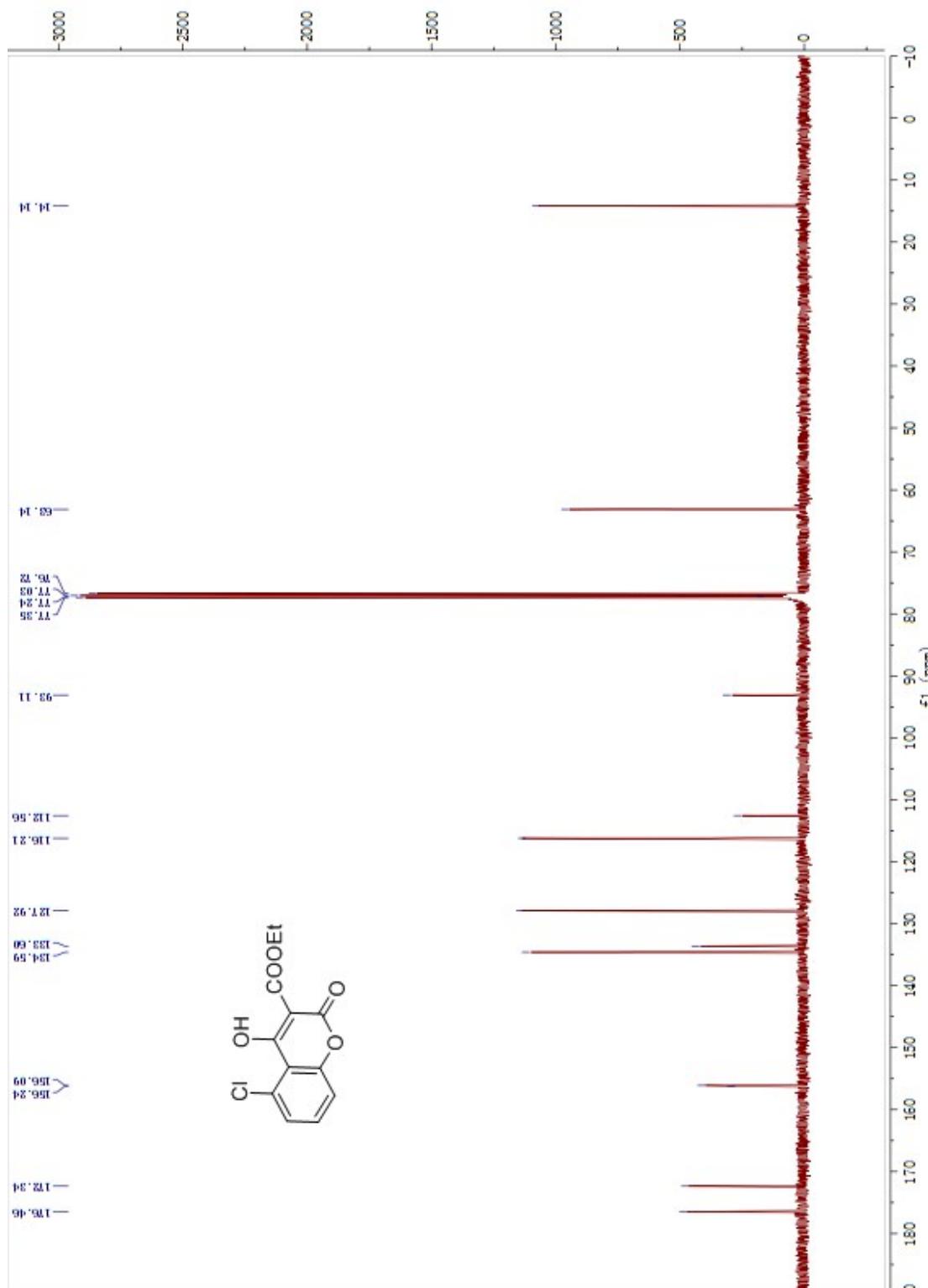
¹³C NMR Spectrum of Ethyl 8-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-
-xylate **3ka**



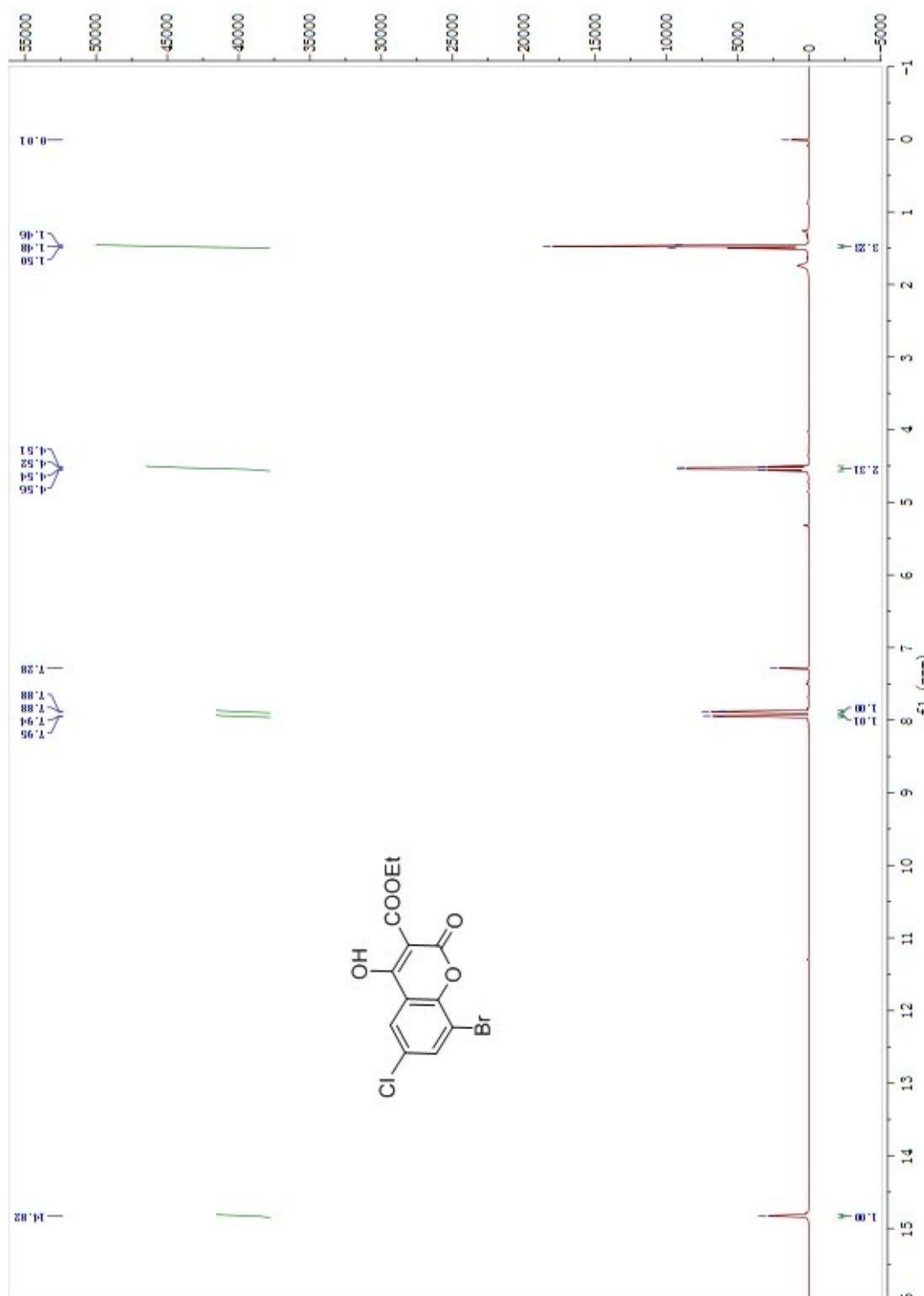
¹H NMR Spectrum of Ethyl 5-chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-
-xylate **3la**



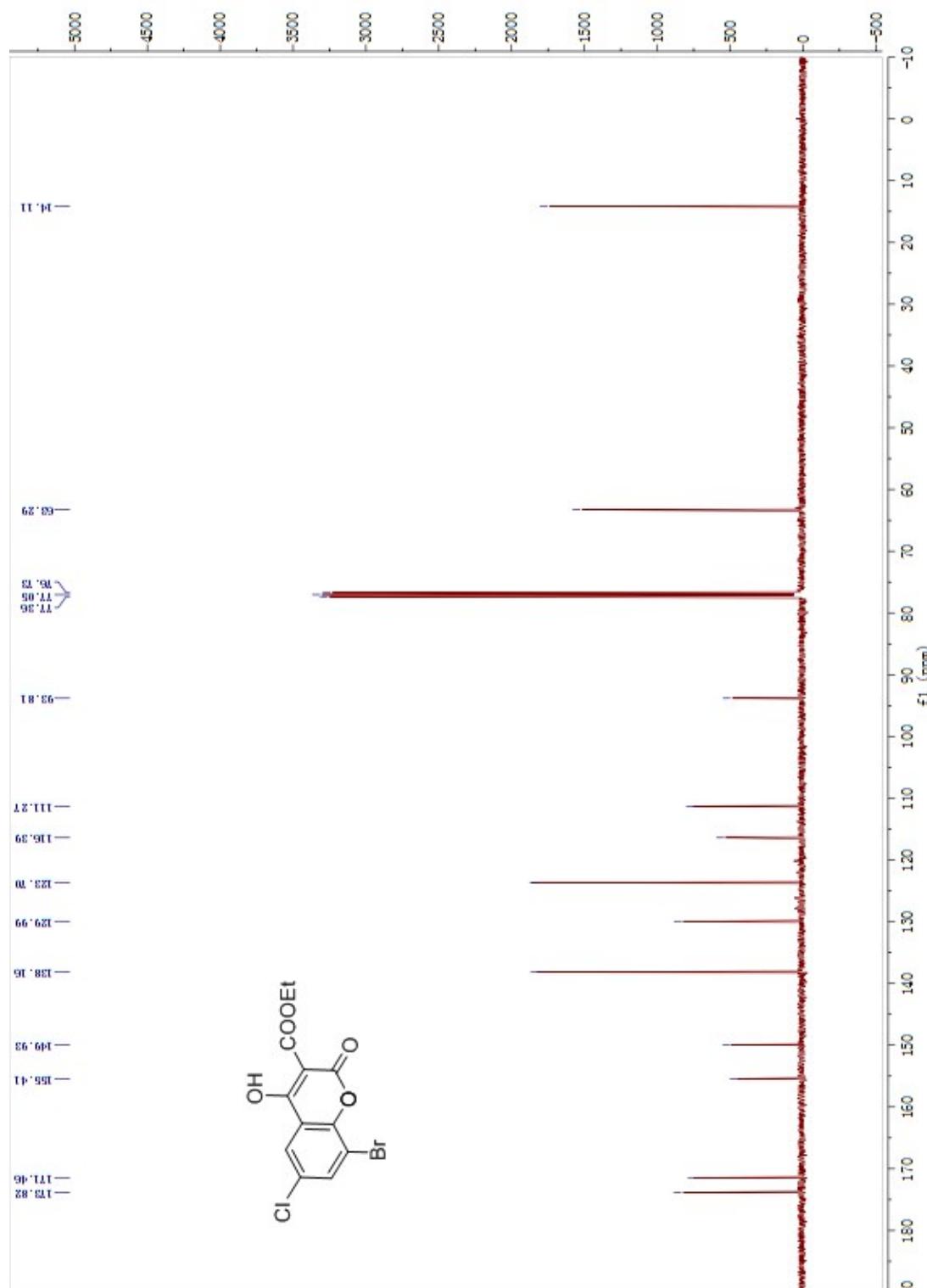
¹³C NMR Spectrum of Ethyl 5-Chloro-4-Hydroxy-2-oxo-2H-chromene-3-carbo-xylate **3la**



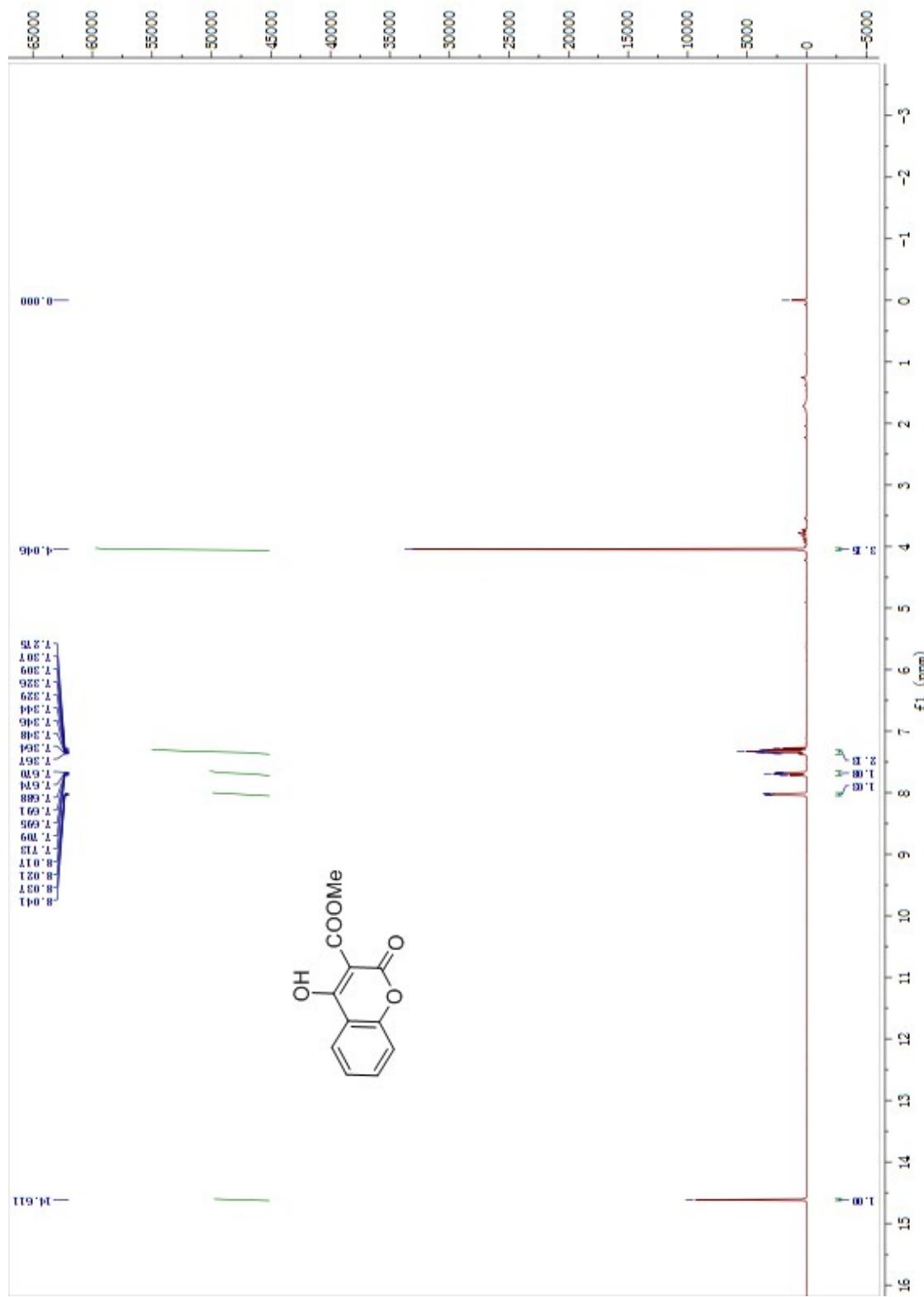
¹H NMR Spectrum of Ethyl 8-Bromo-6-chloro-4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ma**



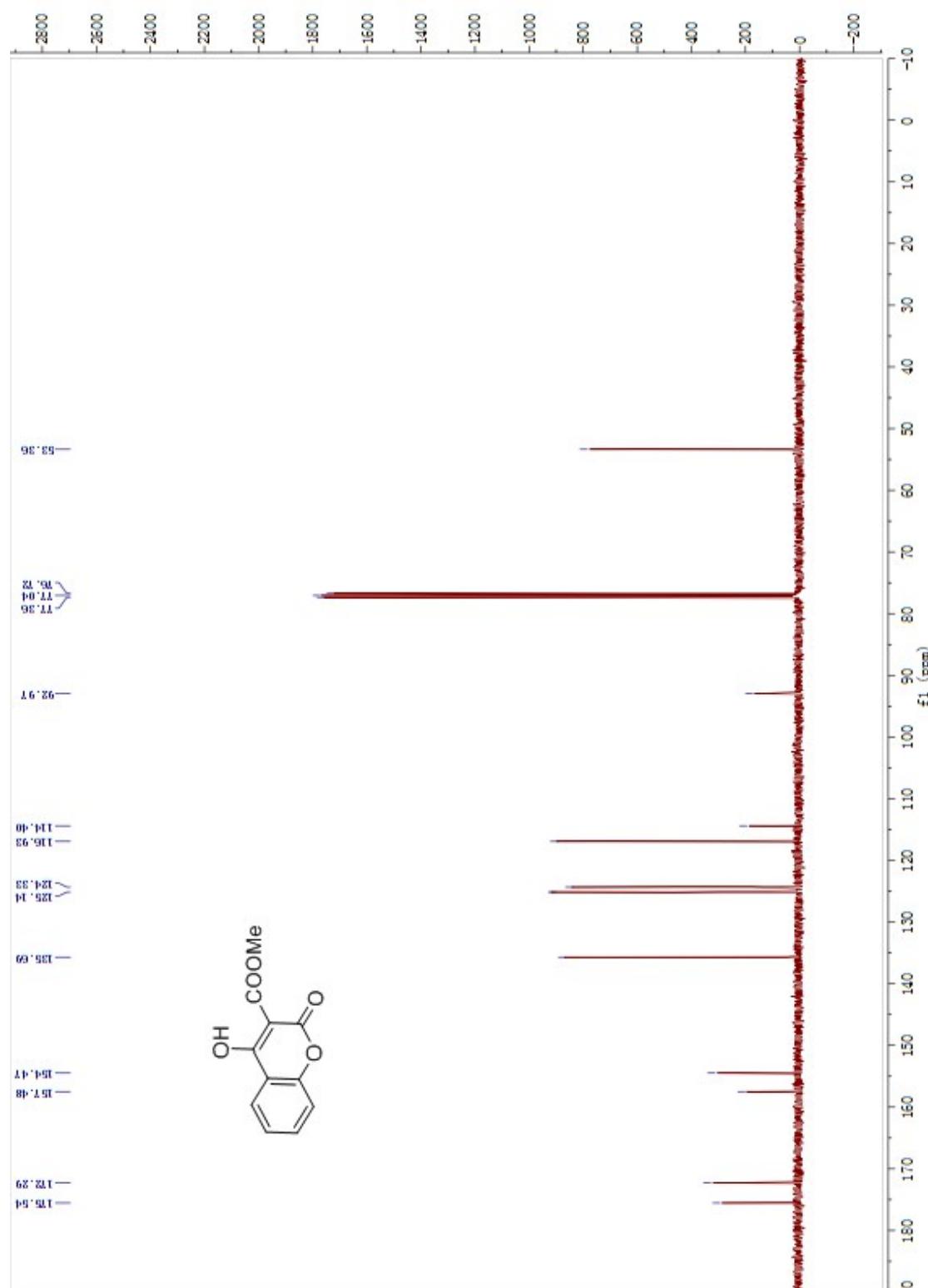
¹³C NMR Spectrum of Ethyl 8-Bromo-6-chloro-4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ma**



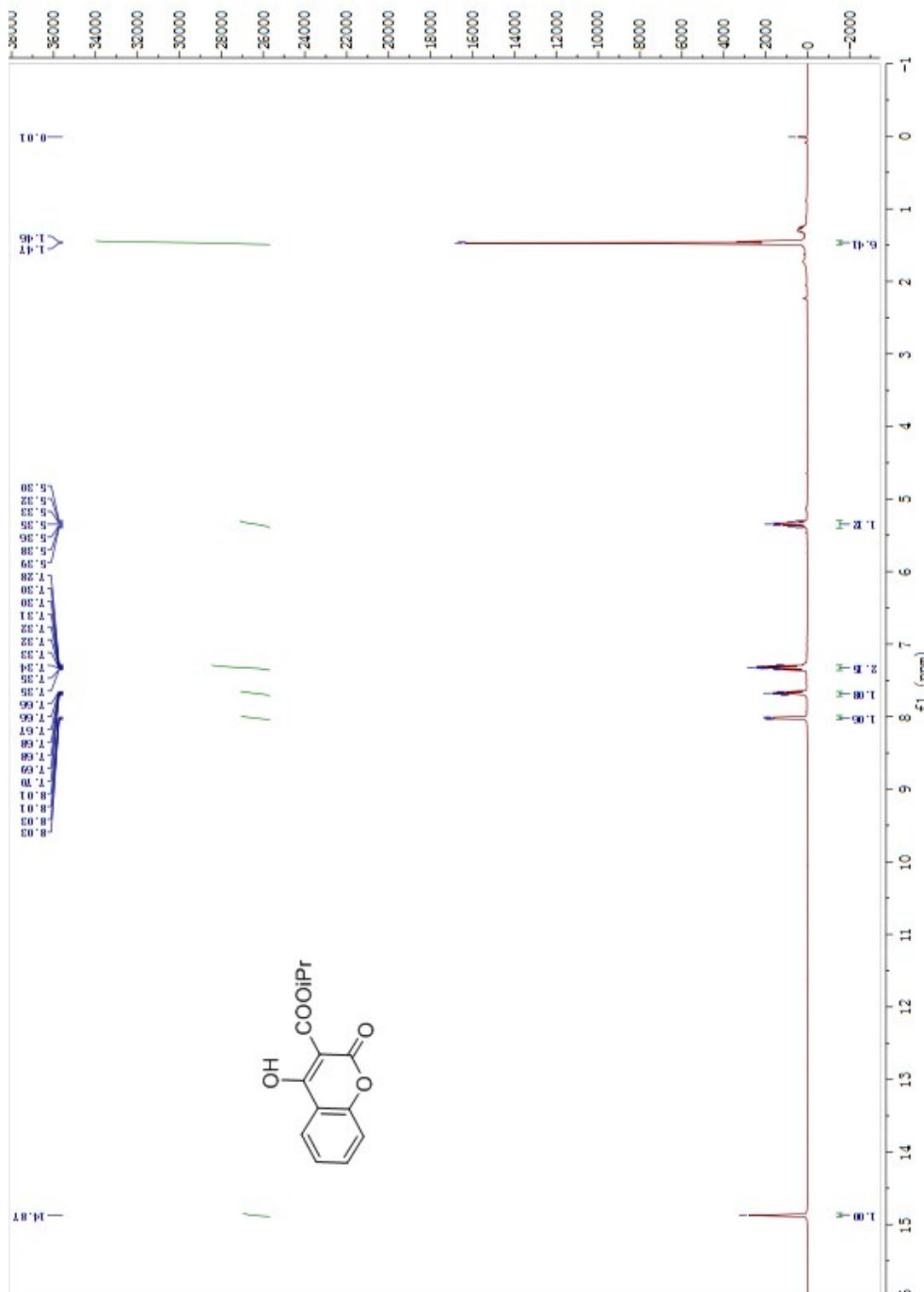
¹H NMR of Methyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ab**



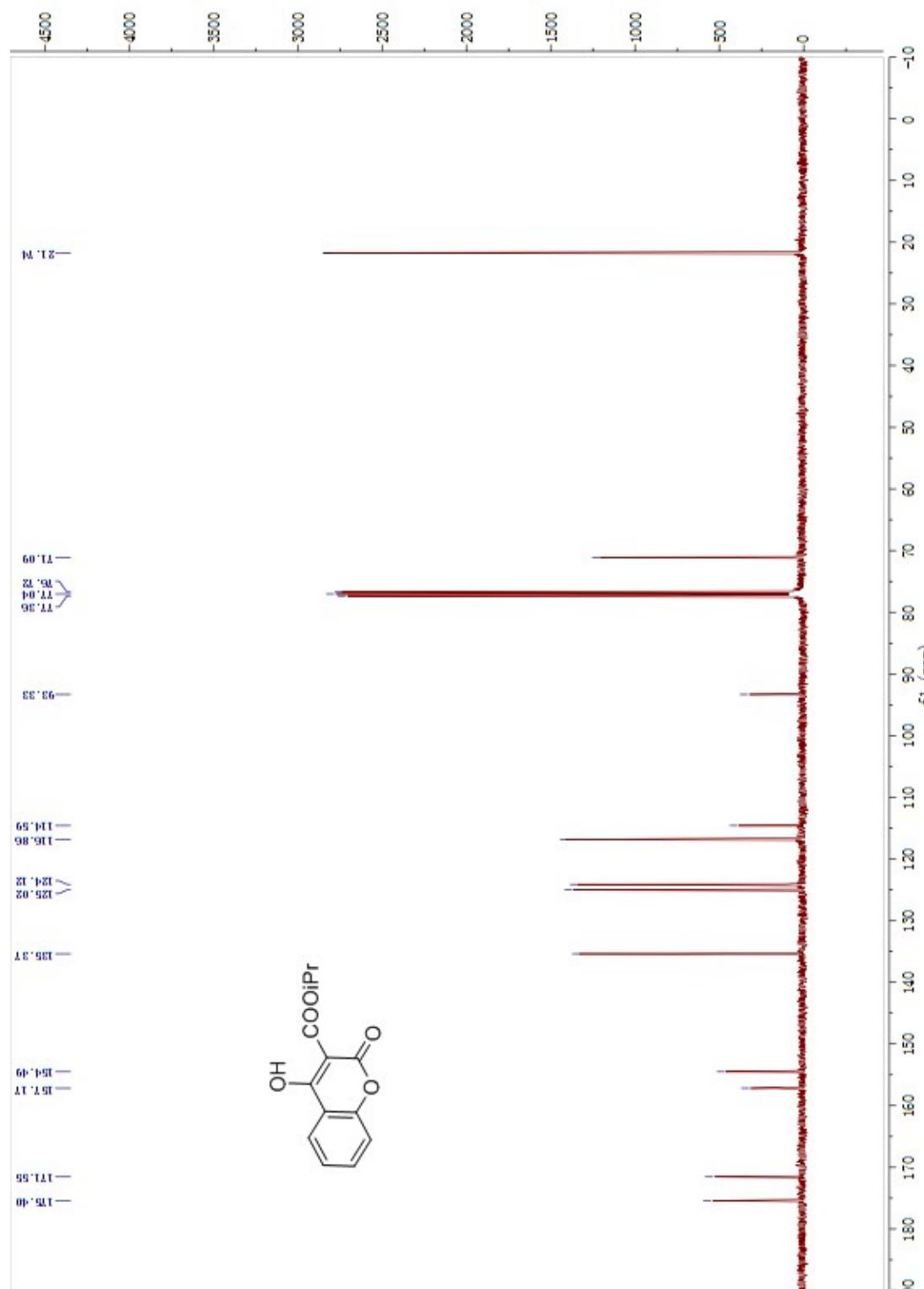
¹³C NMR of Methyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ab**



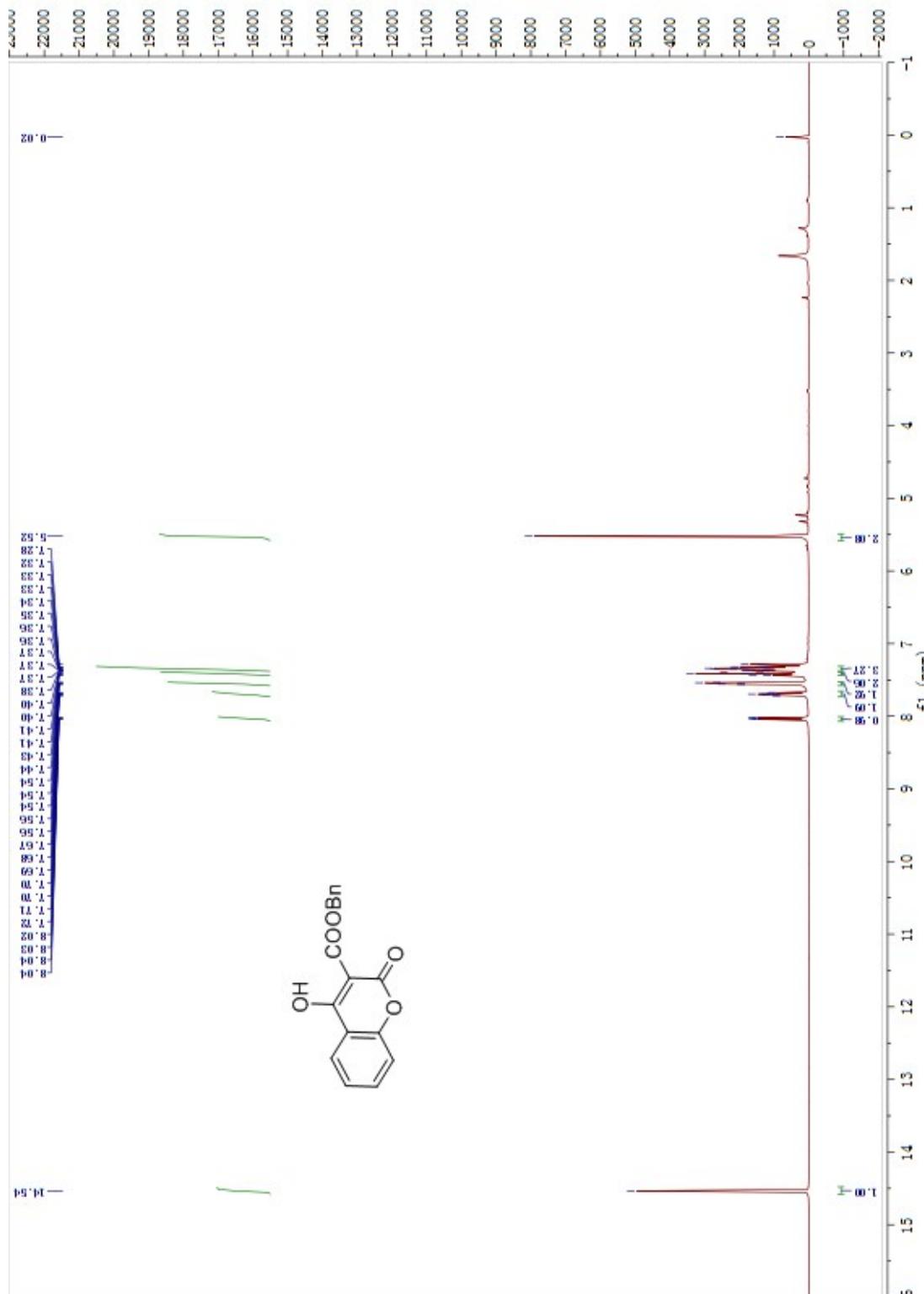
¹H NMR Spectrum of Isopropyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ac**



¹³C NMR Spectrum of Isopropyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate **3ac**



¹H NMR Spectrum of Benzyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate
3ad



¹³C NMR Spectrum of Benzyl 4-Hydroxy-2-oxo-2H-chromene-3-carboxylate
3ad

