

**Hydroxyl directed C-arylation: Synthesis of 3-hydroxyflavones and
2-phenyl-3-hydroxy pyran-4-ones under transition-metal free conditions**

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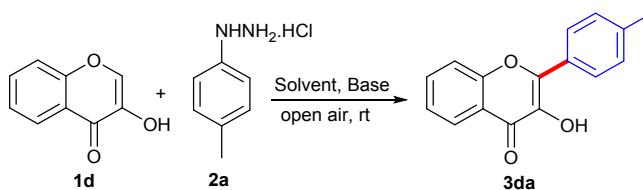
Dr. Homi Bhabha Road, Pune 411 008, India

Supporting Information

Section A:	Table S1: Optimization of Reaction Conditions	S2
Section B:	¹ H, ¹³ C, DEPT, LCMS and HRMS spectra of all the synthesized compounds	S3-S66

Section A:

Table S1. Optimization of Reaction Conditions^a



Entry	Solvent	Base	Oxidant	Time (h)	Yield ^a (%)
1	DMSO	K ₂ CO ₃	Air	12	32
2	DMSO	Cs ₂ CO ₃	Air	10	26
3	MeCN	K ₂ CO ₃	Air	10	54
4	MeCN	Triethyl amine	Air	8	67
5 ^b	MeCN	Diethyl amine	Air	4	71
6 ^c	MeCN	Diethyl amine	Air	4	76
7 ^d	MeCN	Diethyl amine	Air	4	78
8 ^e	MeCN	Diethyl amine	-	52	-
9 ^f	MeCN	-	I ₂	12	-

^a

yield.

^b Reaction conditions: **1d** (0.25 mmol), **2a** (0.30 mmol, 1.2 equiv), base (0.75 mmol, 3.0 equiv), solvent (3 mL).

^c Reaction conditions: **1d** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv.), base (0.75 mmol, 3.0 equiv.), solvent (3 mL).

^d Reaction conditions: **1d** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv.), base (0.875 mmol, 3.5 equiv.), solvent (3 mL).

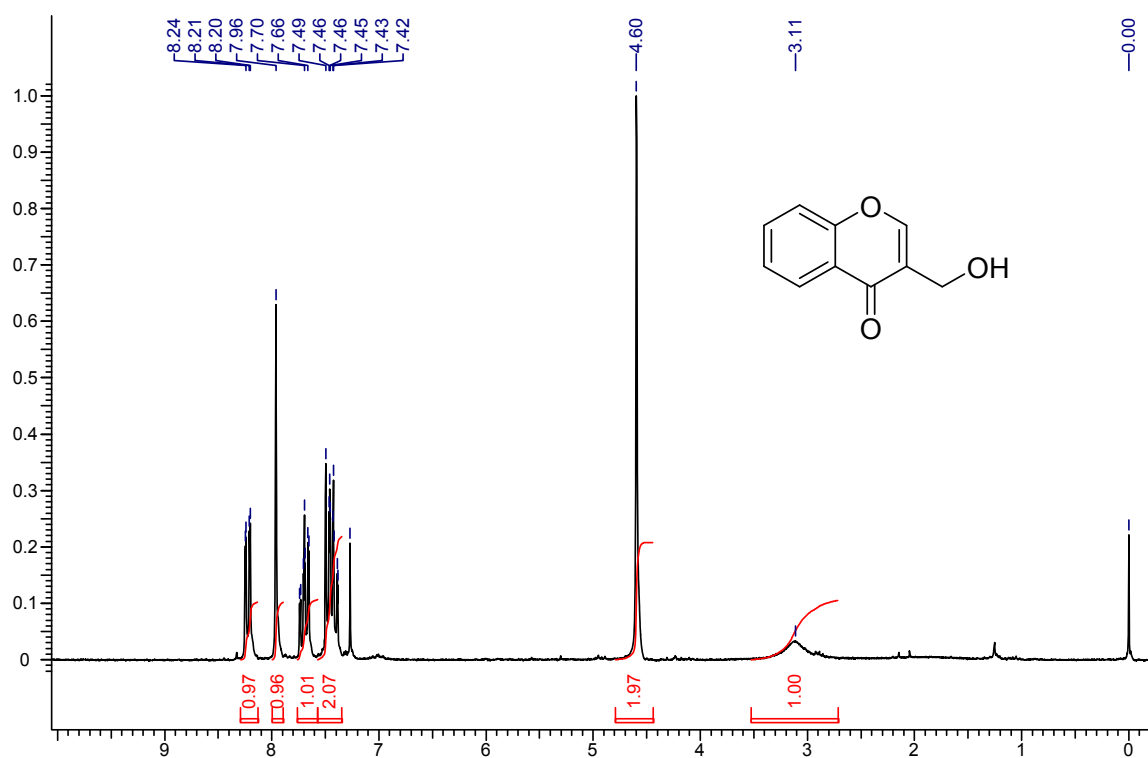
^e Reaction conditions: **1d** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv.), base (0.875 mmol, 3.5 equiv), dry and degassed solvent (3 mL) under argon atmosphere.

^f Reaction conditions: **1d** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv.), base (0.875 mmol, 3.5 equiv.), dry and degassed solvent (3 mL), iodine (0.30 mmol, 1.2 equiv.) under argon atmosphere.

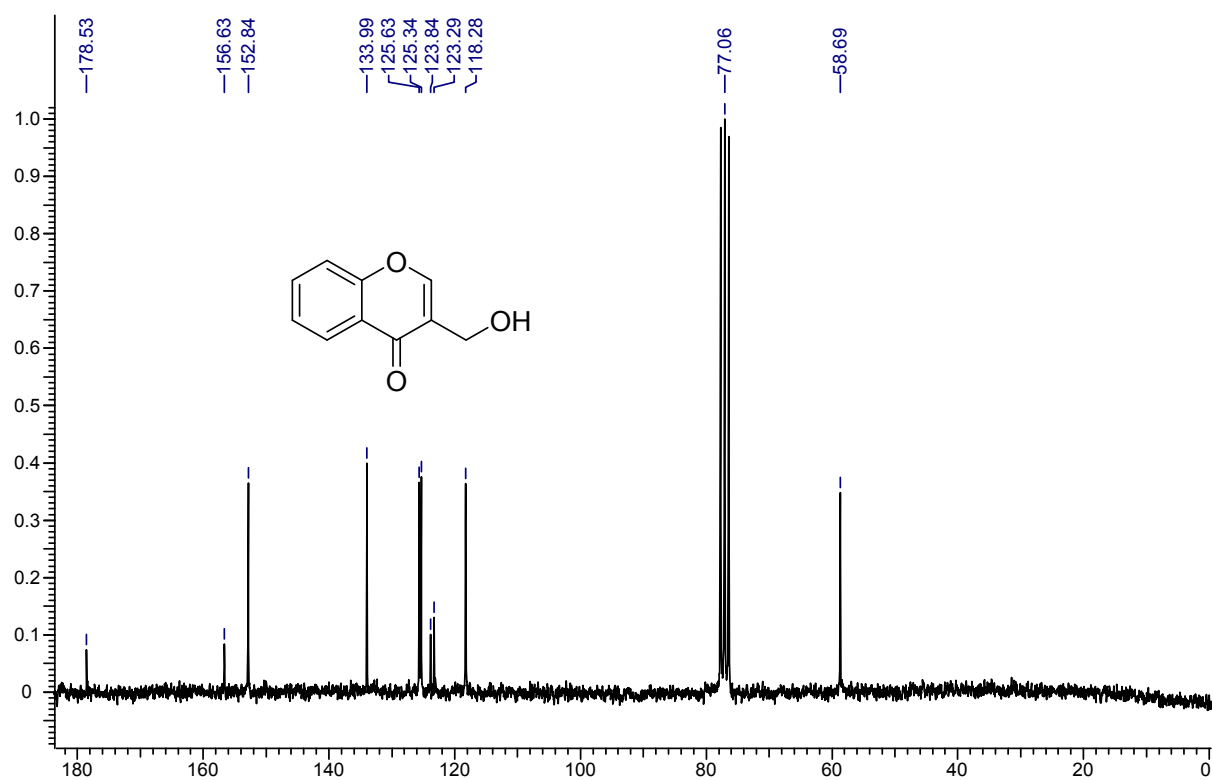
^g Reaction conditions: **1d** (0.25 mmol), **2a** (0.375 mmol, 1.5 equiv), base (0.875 mmol, 3.5 equiv.), dry and degassed solvent (3 mL), K₂S₂O₈ (0.30 mmol, 1.2 equiv.), under argon atmosphere.

Isolated

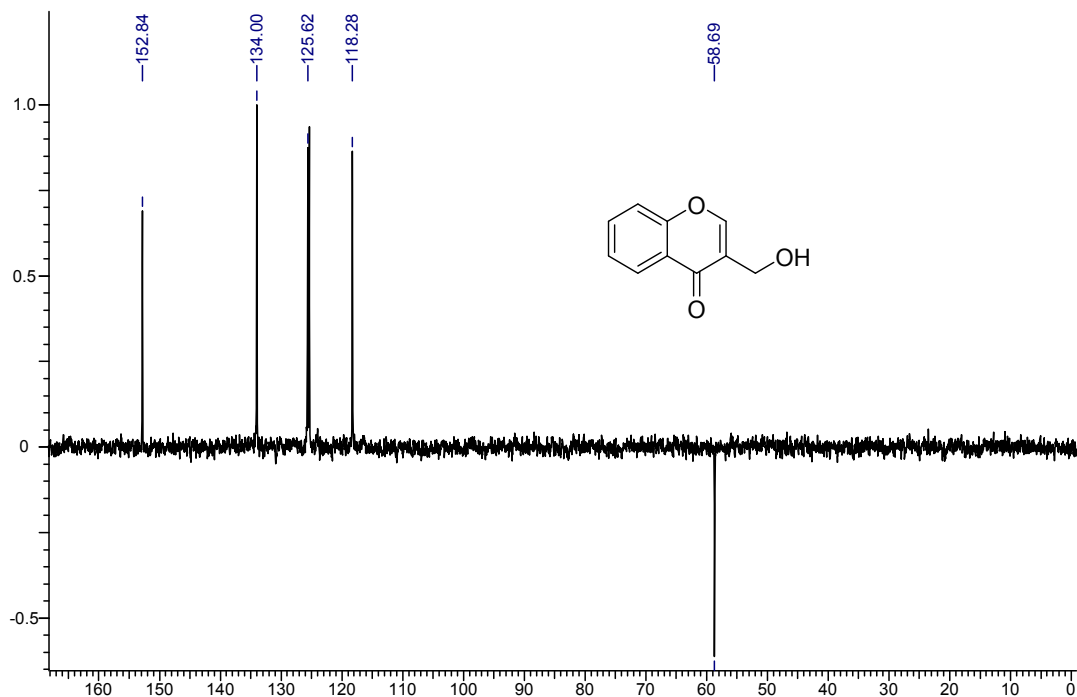
Section B: ^1H , ^{13}C , DEPT, LCMS and HRMS spectra of all the synthesized compounds



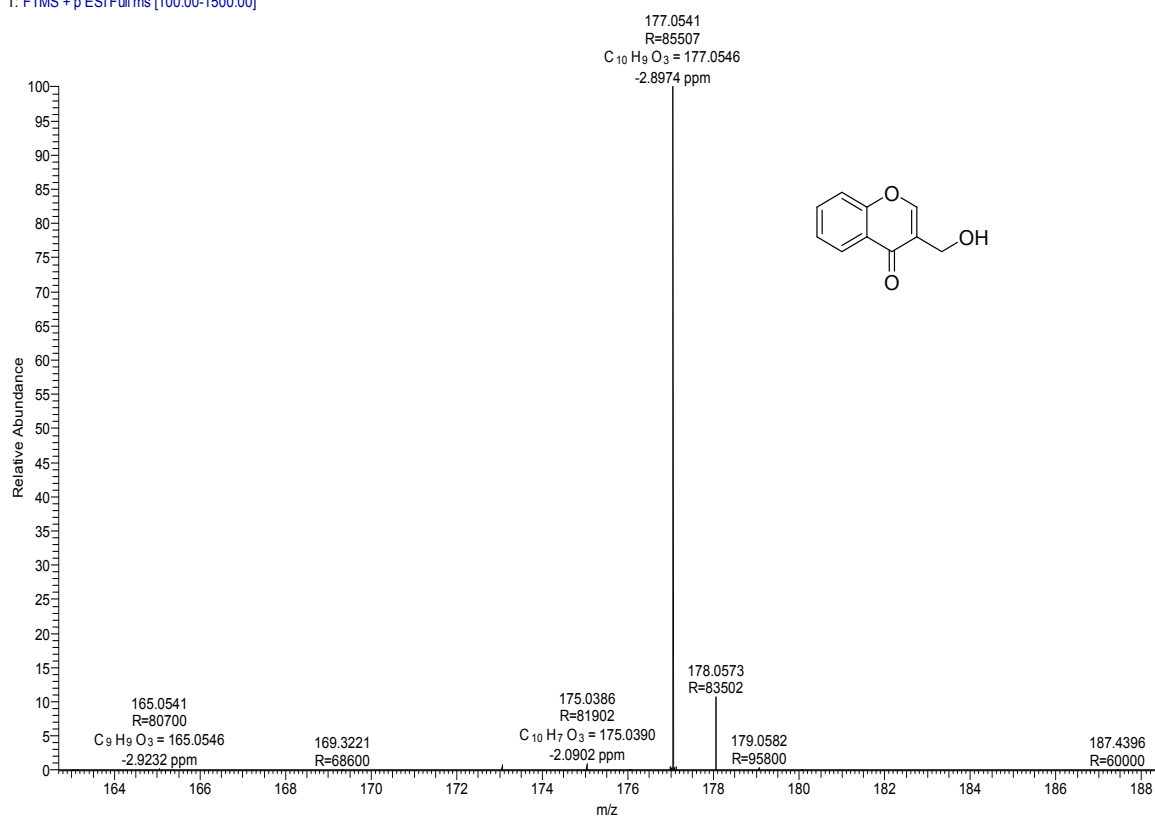
^1H NMR (CDCl₃, 200 MHz) of **1c**

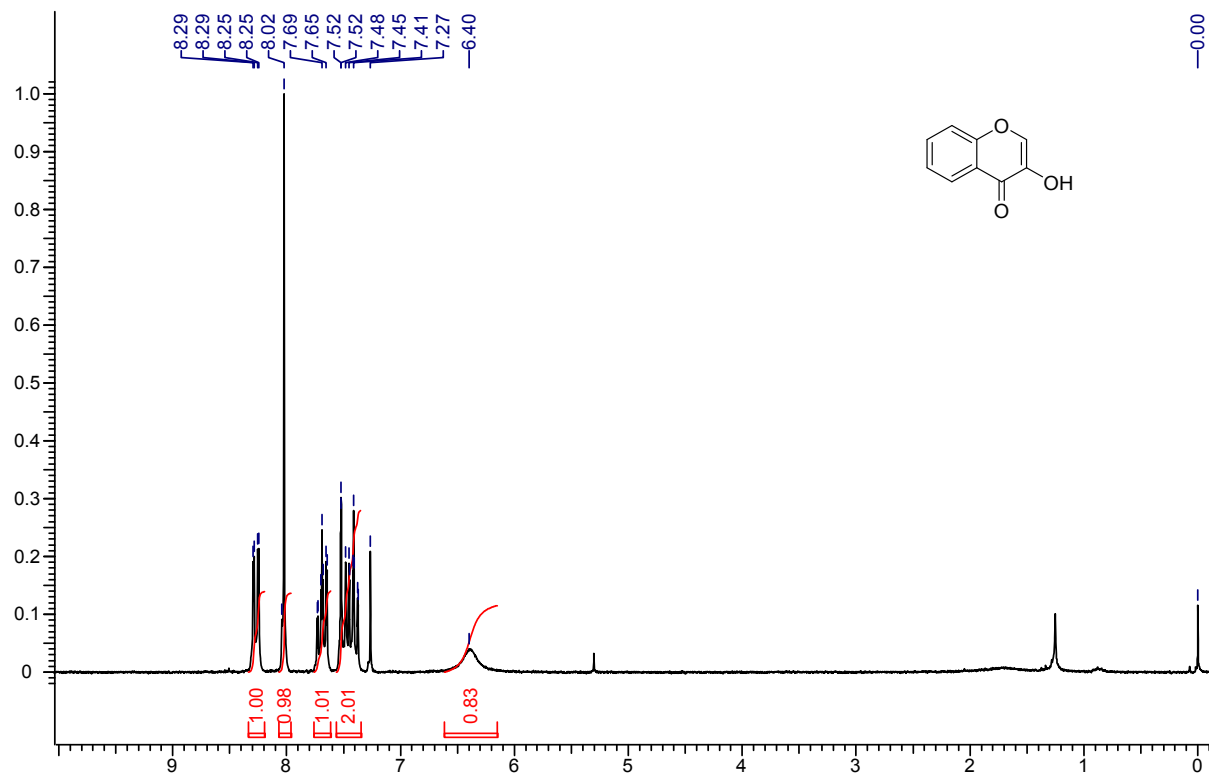


^{13}C NMR (CDCl₃, 50 MHz) of **1c**

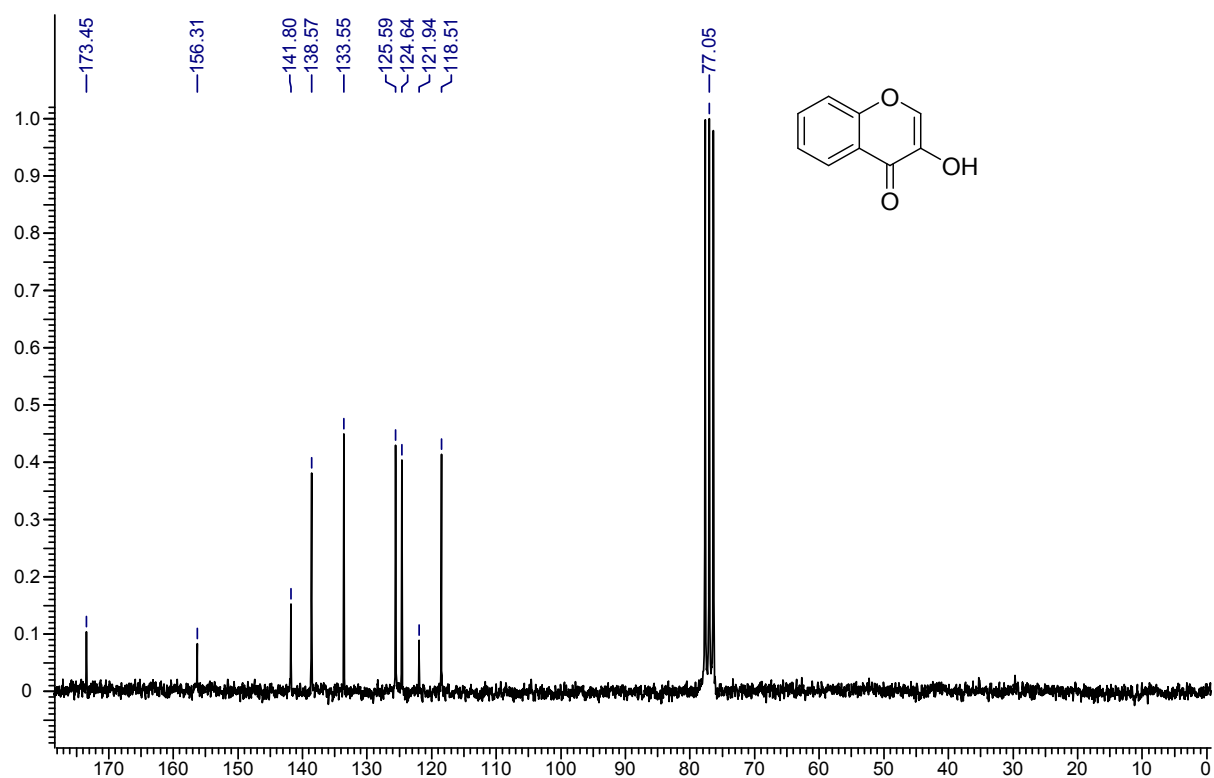


SP-2-71_170113145104 #100 RT: 0.44 AV: 1 NL: 2.60E9
T: FTMS + p ESI Full ms [100.00-1500.00]

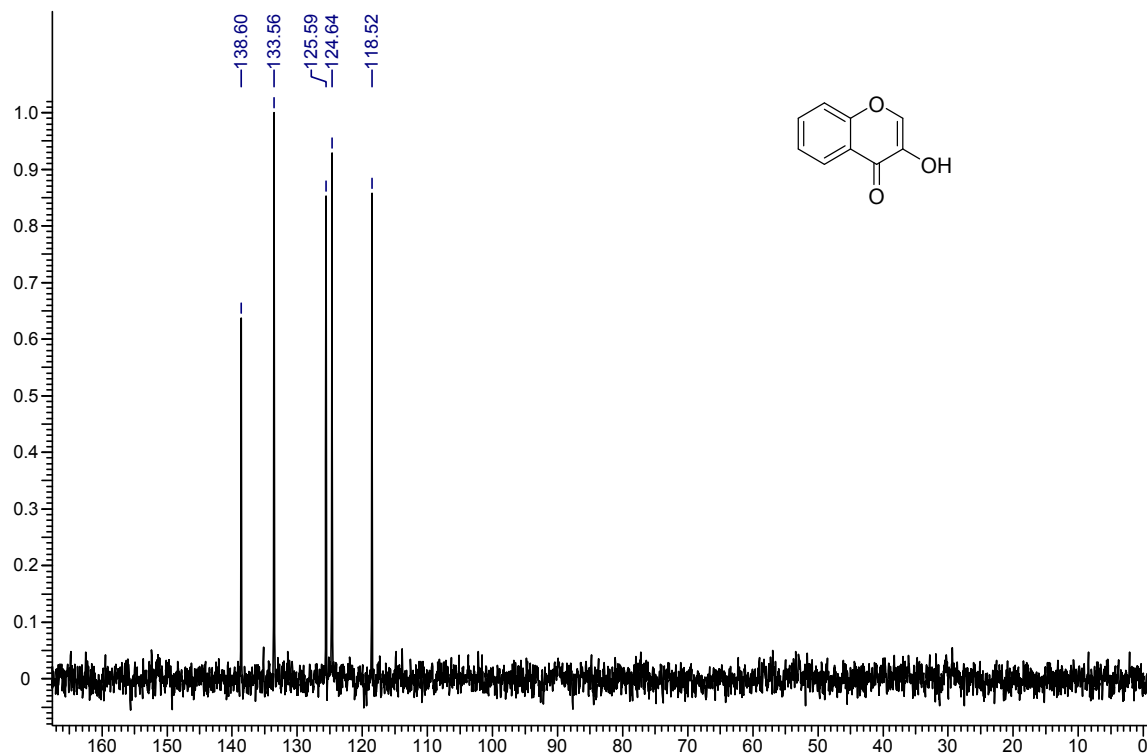




¹H NMR (CDCl₃, 200 MHz) of **1d**

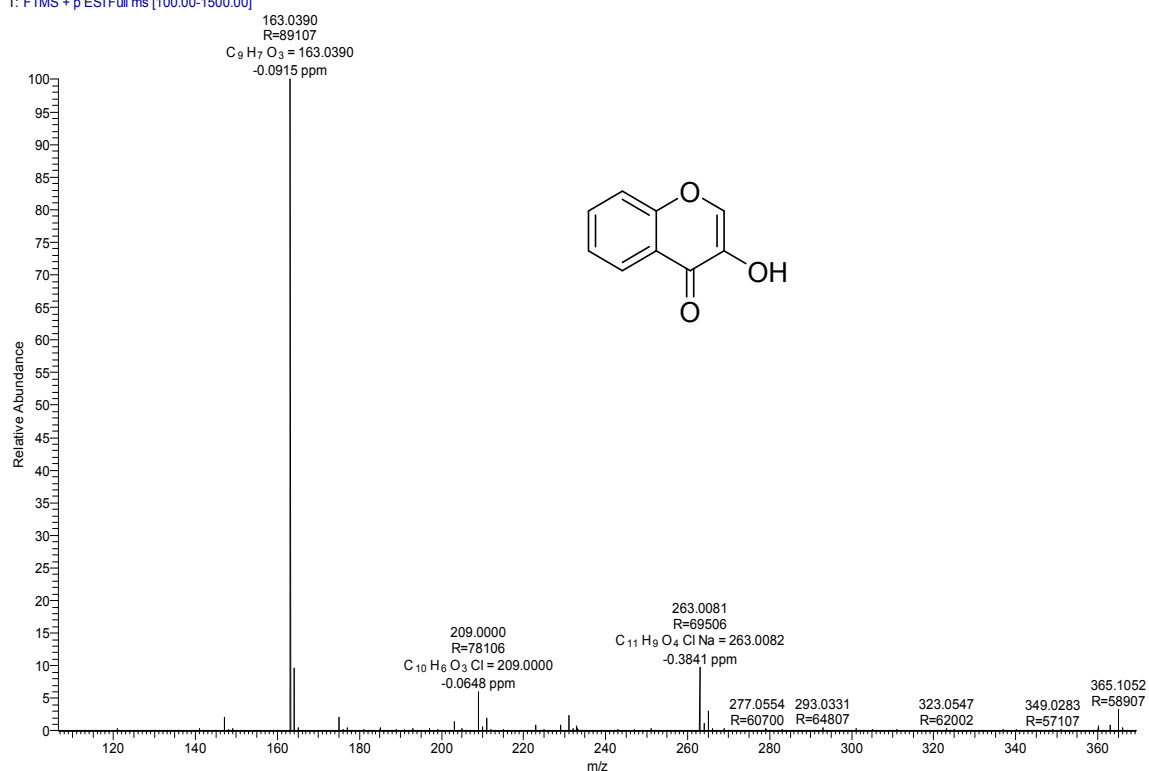


¹³C NMR (CDCl₃, 50 MHz) of **1d**

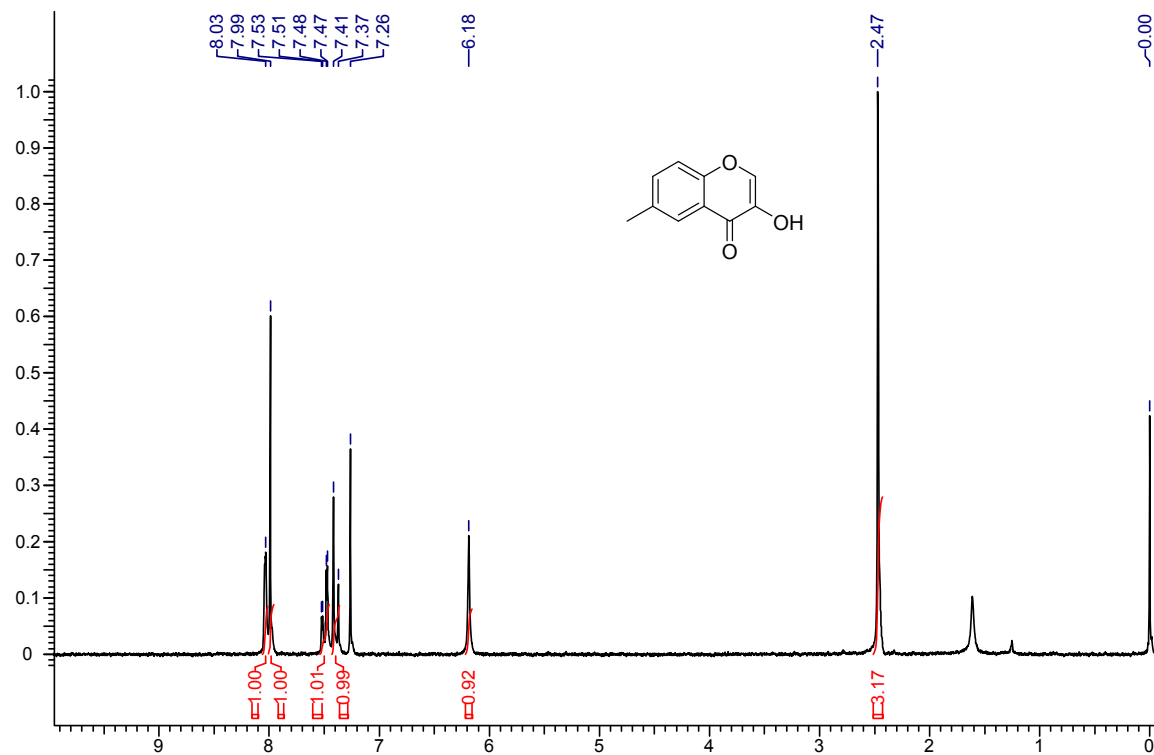


DEPT (CDCl₃, 50 MHz) of 1d

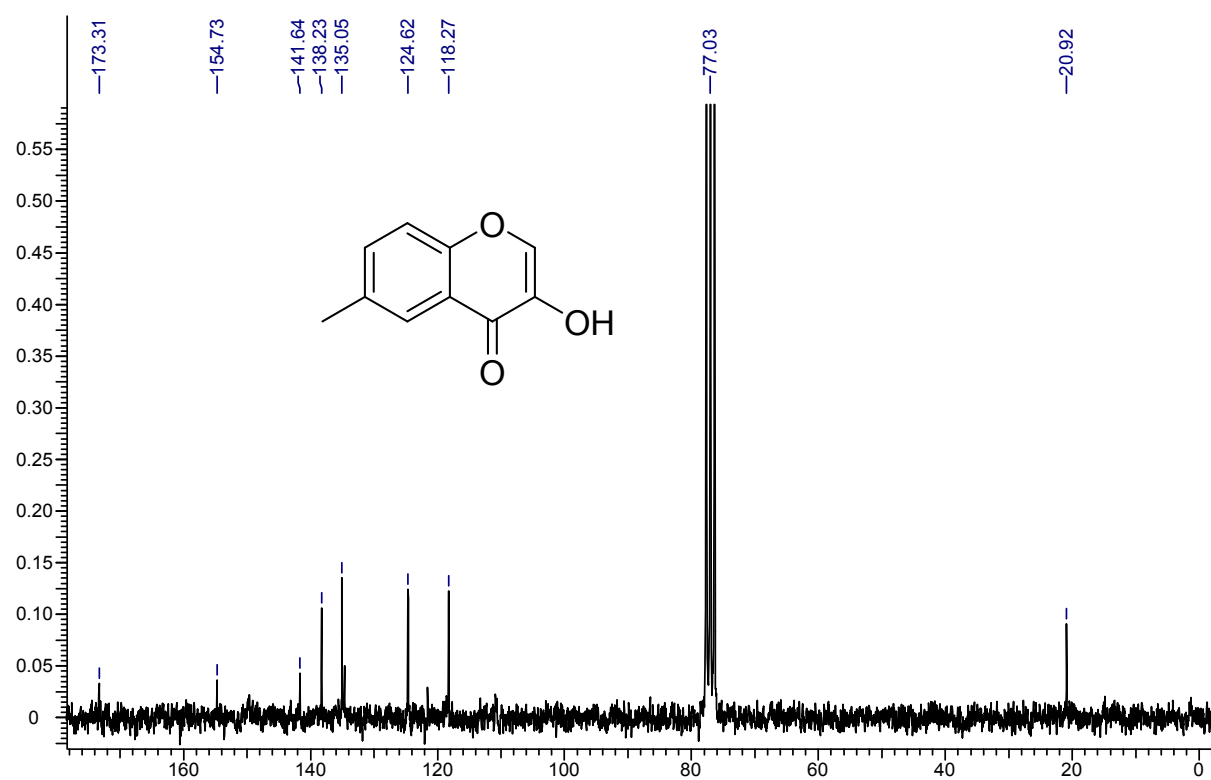
SP-2-42-B #116 RT: 0.52 AV: 1 NL: 2.13E9
T: FTMS + p ESI Full ms [100.00-1500.00]



HRMS of 1d

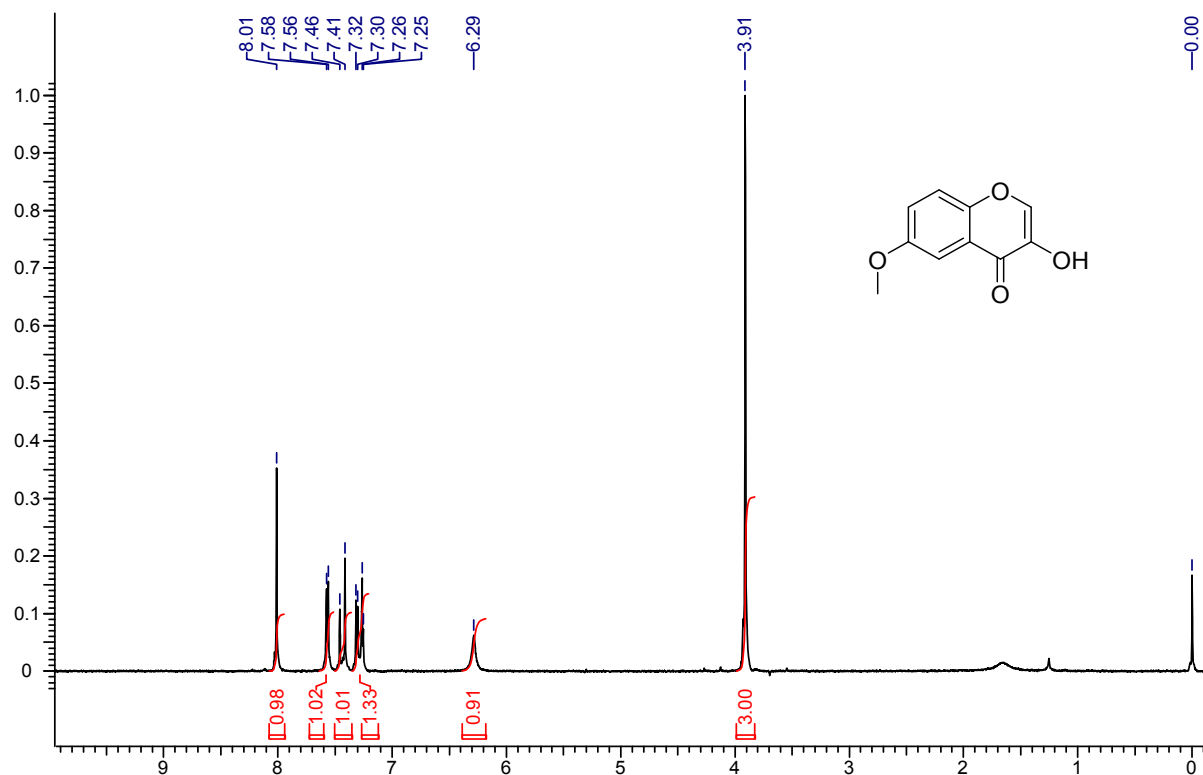
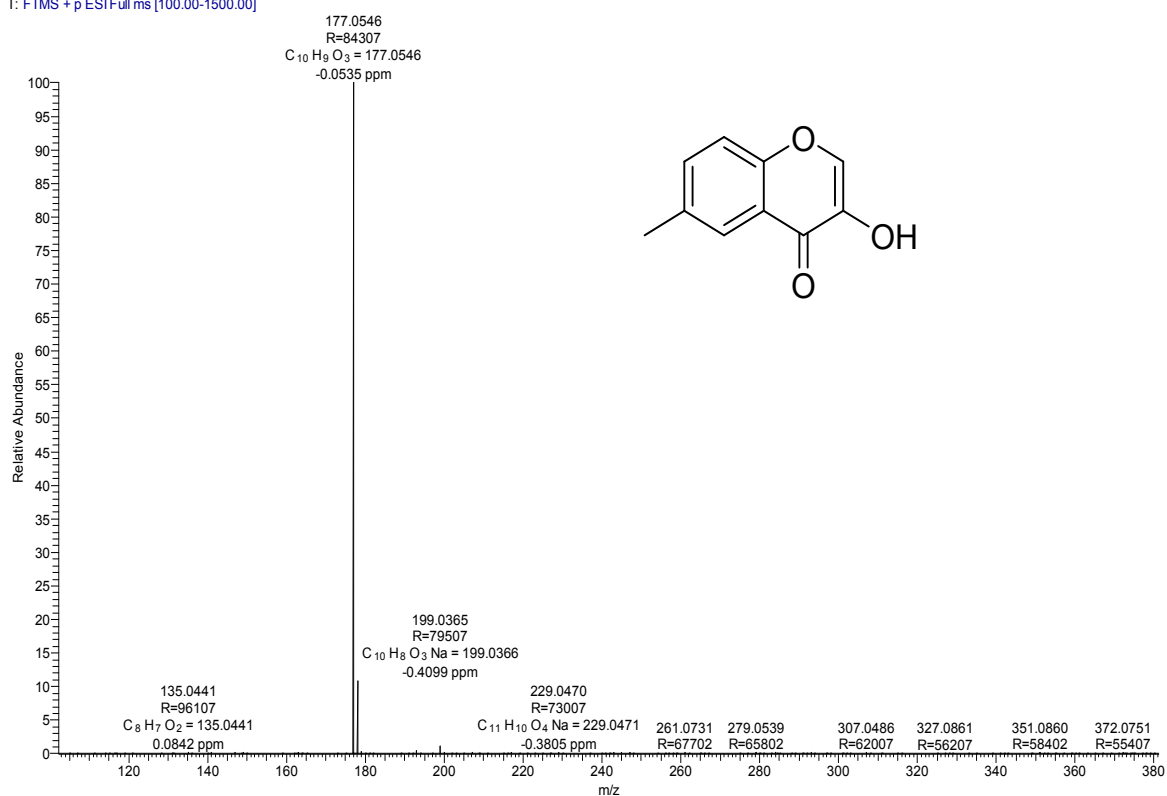


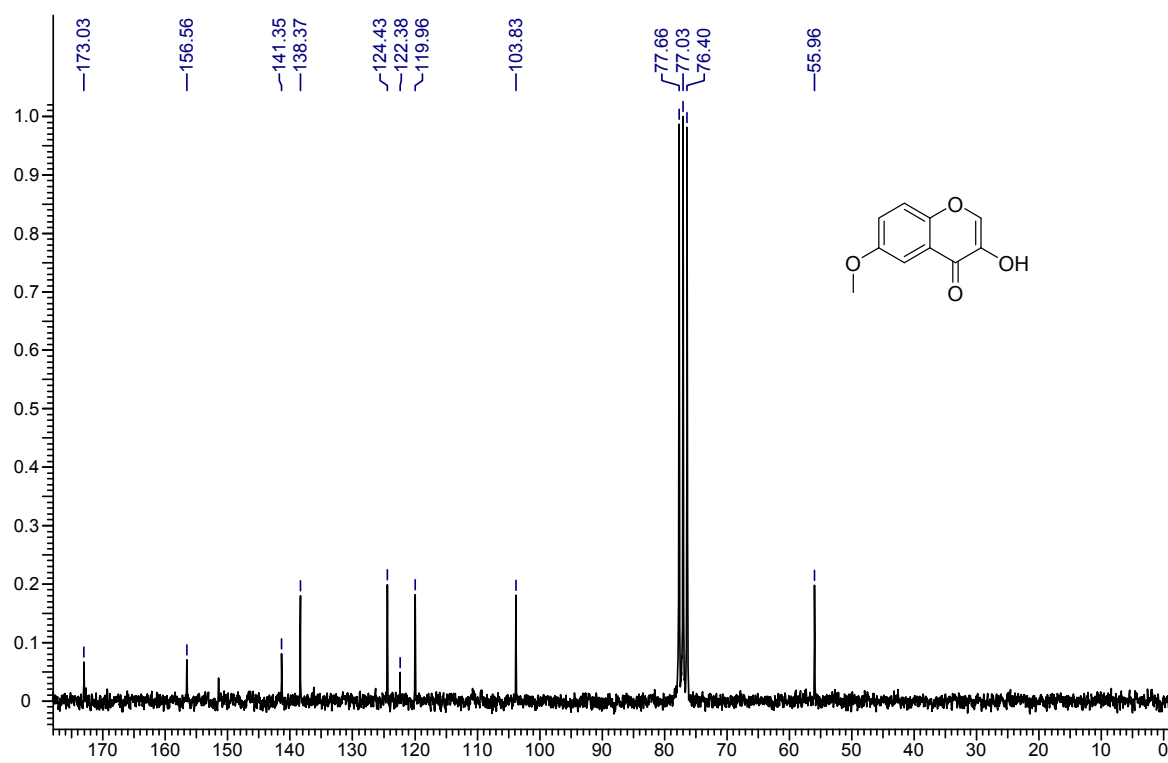
¹H NMR (CDCl₃, 200 MHz) of **1e**



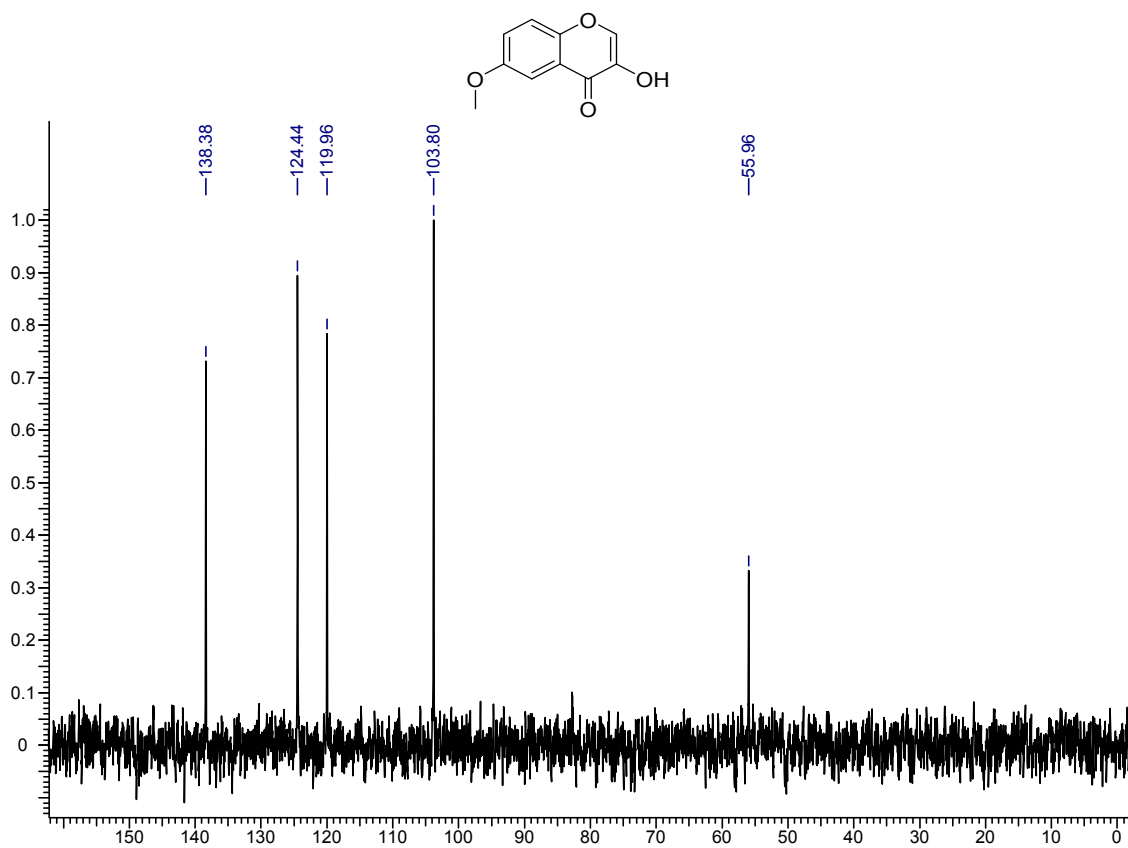
¹³C NMR (CDCl₃, 50 MHz) of **1e**

SP-2-116 #126 RT: 0.56 AV: 1 NL: 2.82E9
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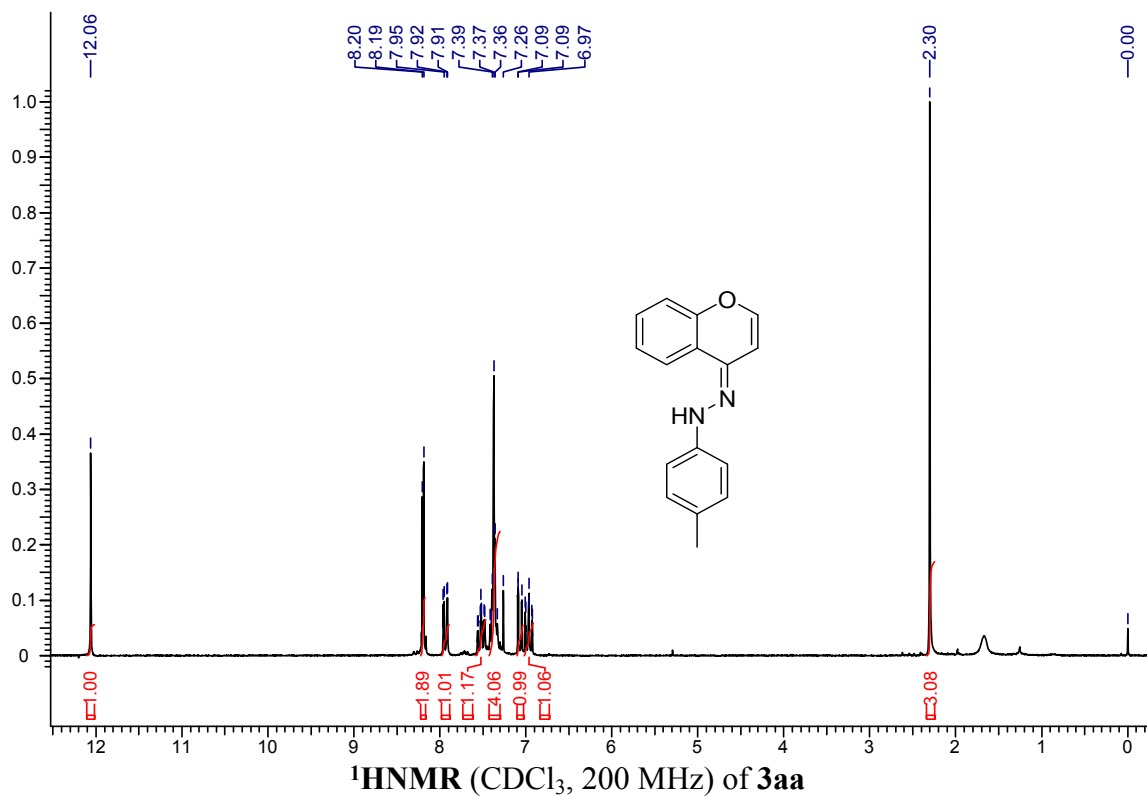
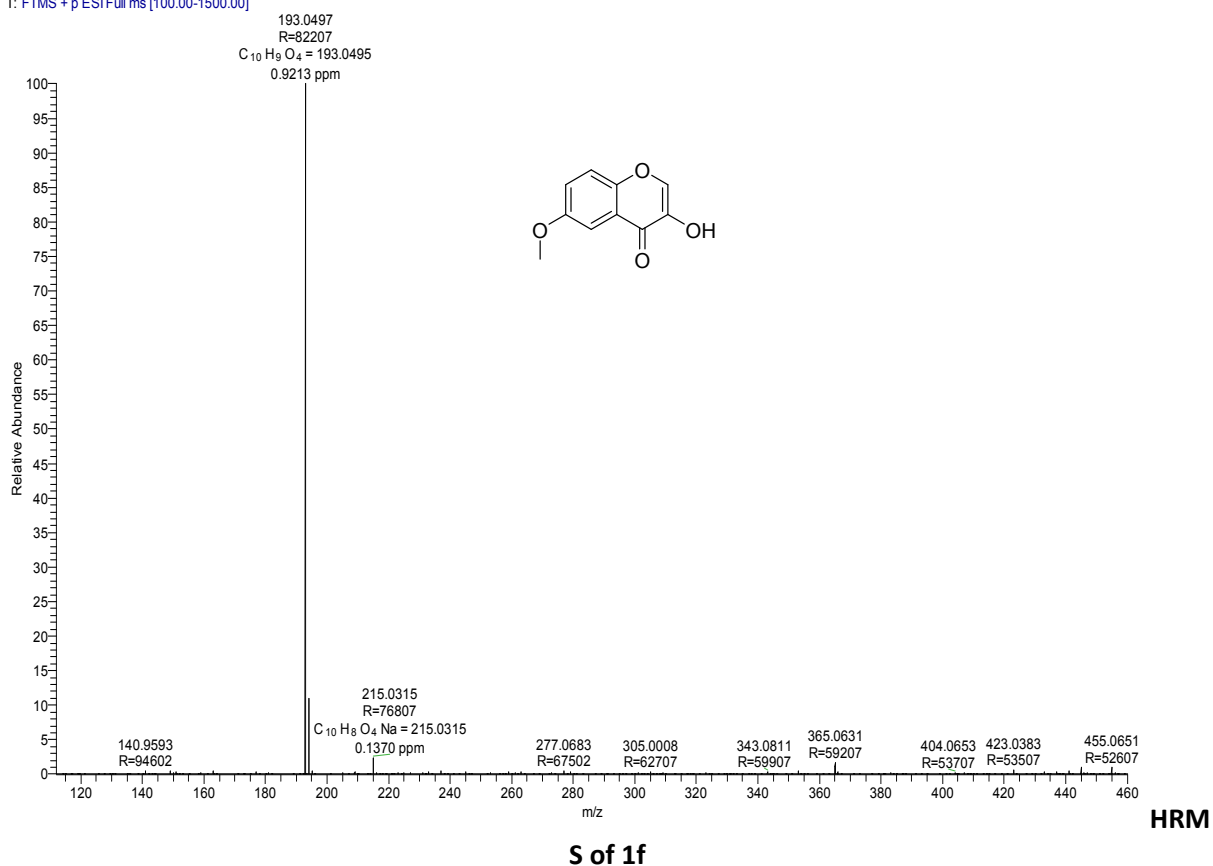


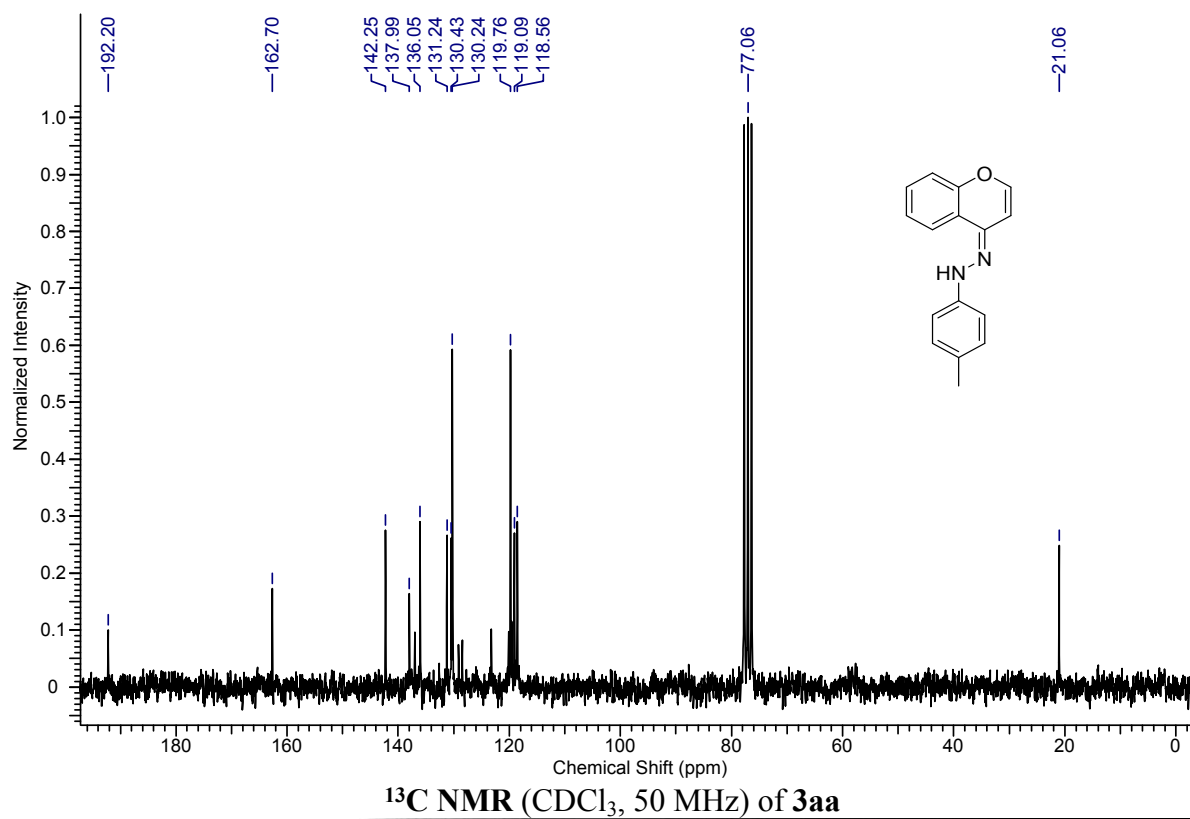
^{13}C NMR (CDCl_3 , 50 MHz) of **1f**



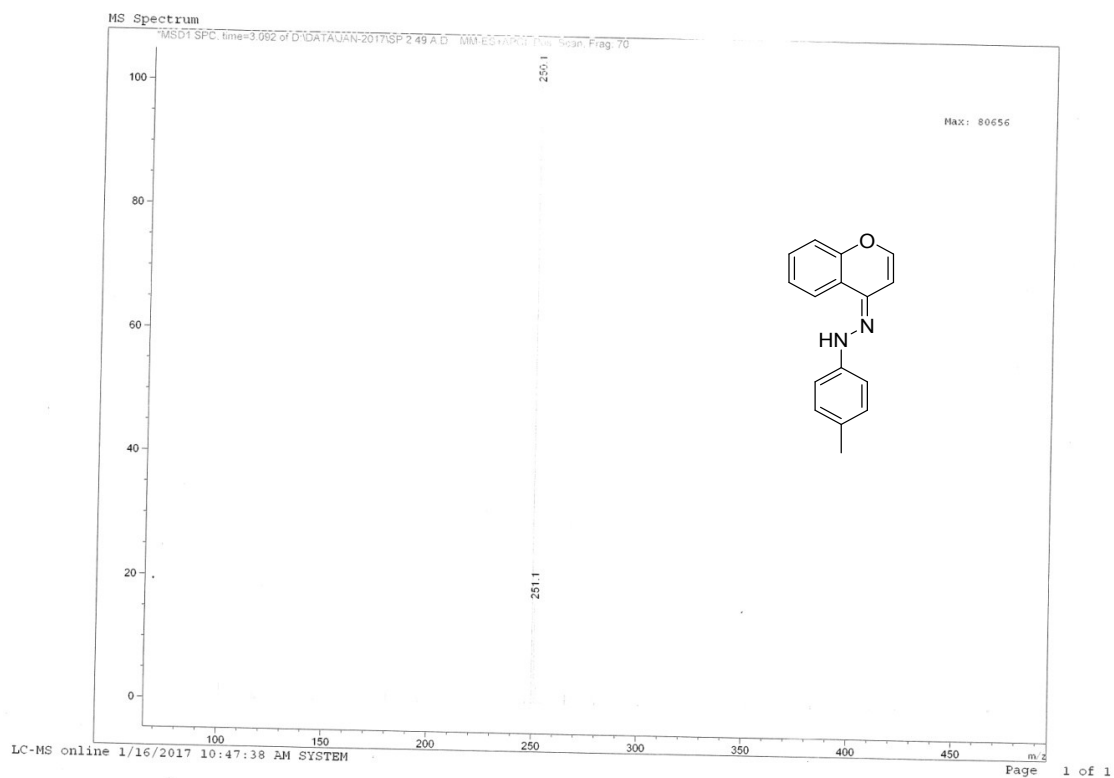
DEPT (CDCl_3 , 50 MHz) of **1f**

SP-2-118 #118 RT: 0.52 AV: 1 NL: 1.79E9
T: FTMS + p ESI Full ms [100.00-1500.00]

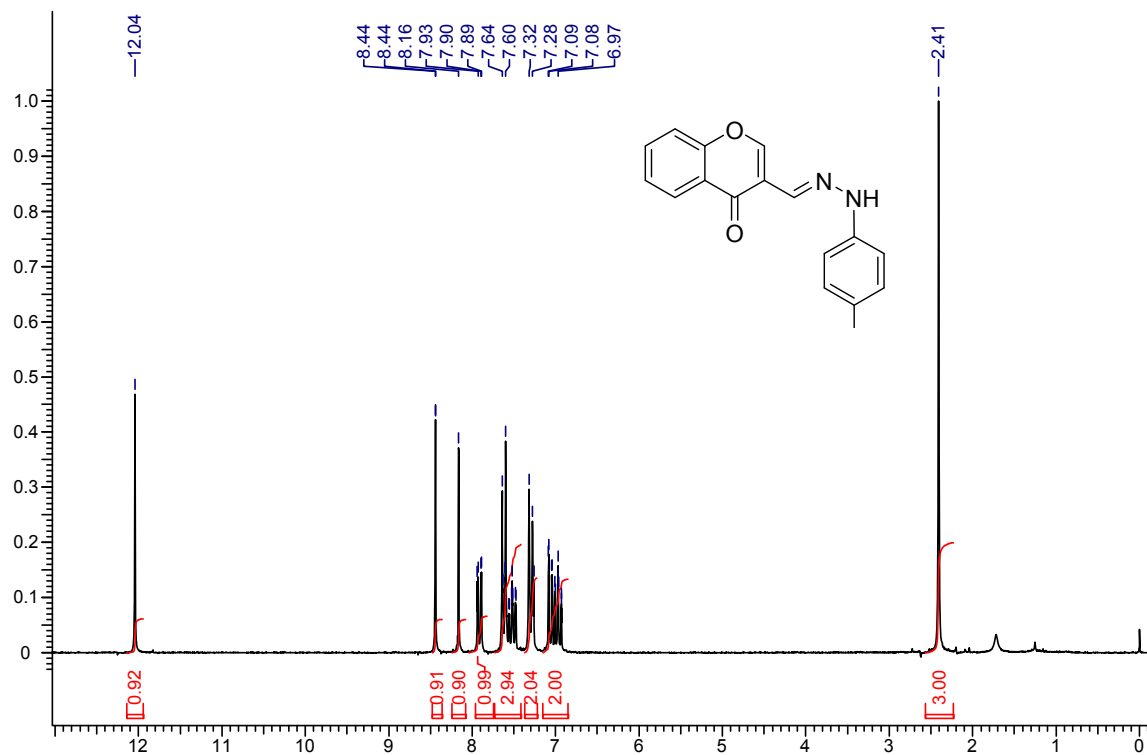




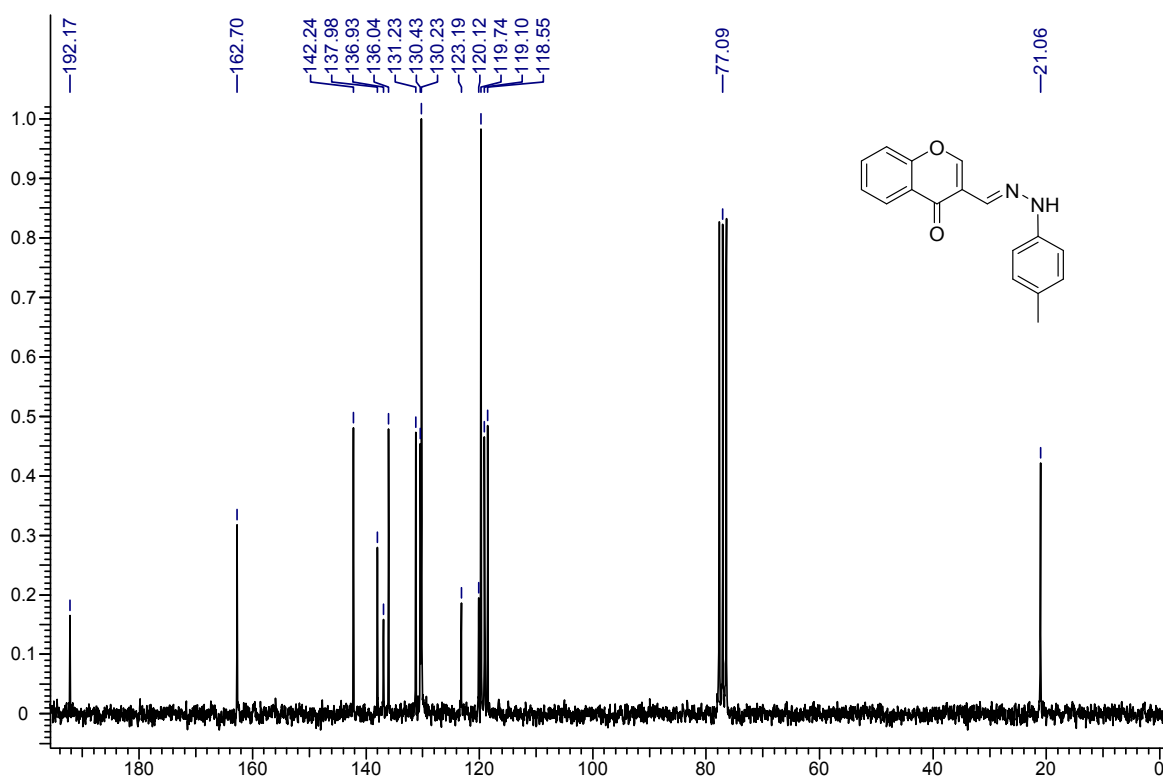
Print of window 80: MS Spectrum



LCMS of 3aa

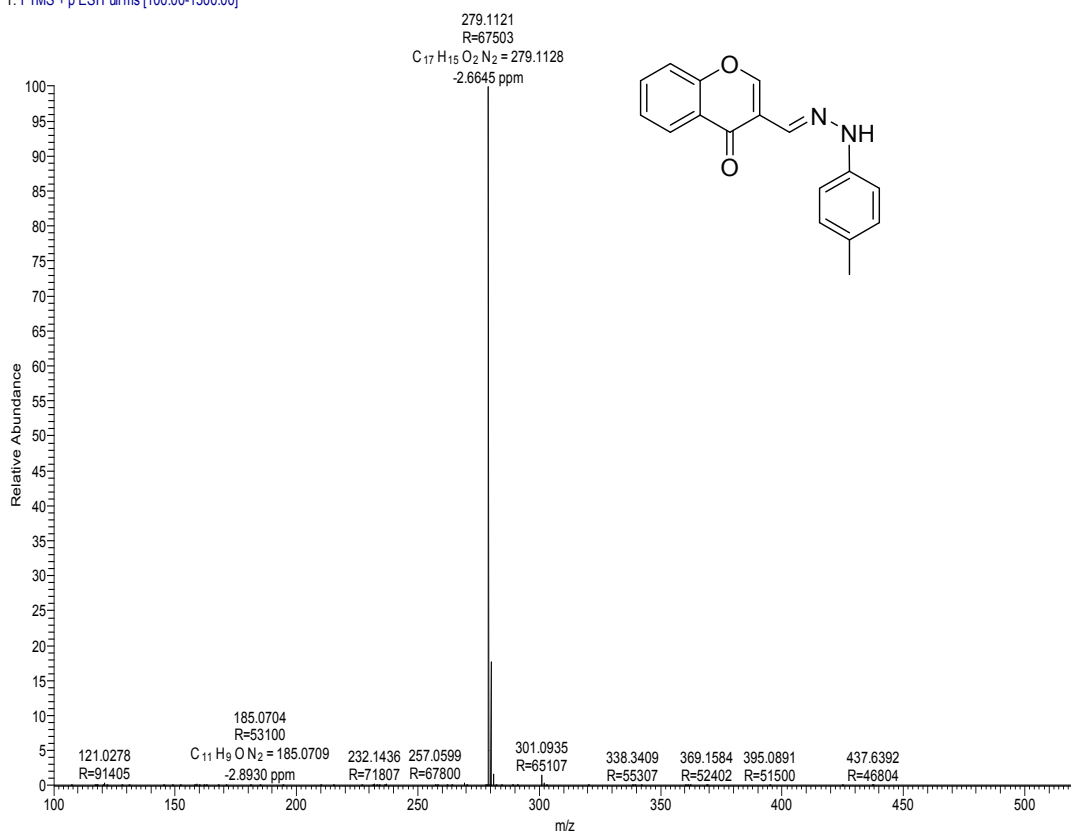


¹H NMR (CDCl₃, 200 MHz) of **3ba**

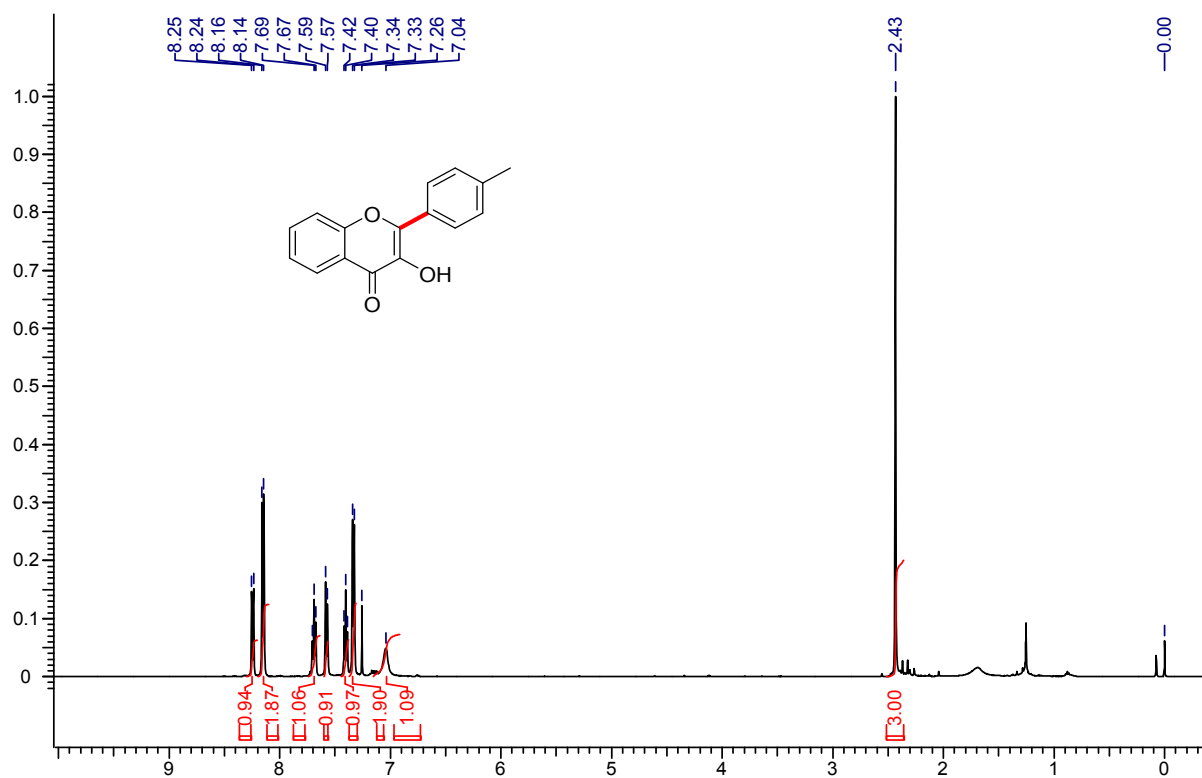


¹³C NMR (CDCl₃, 50 MHz) of **3ba**

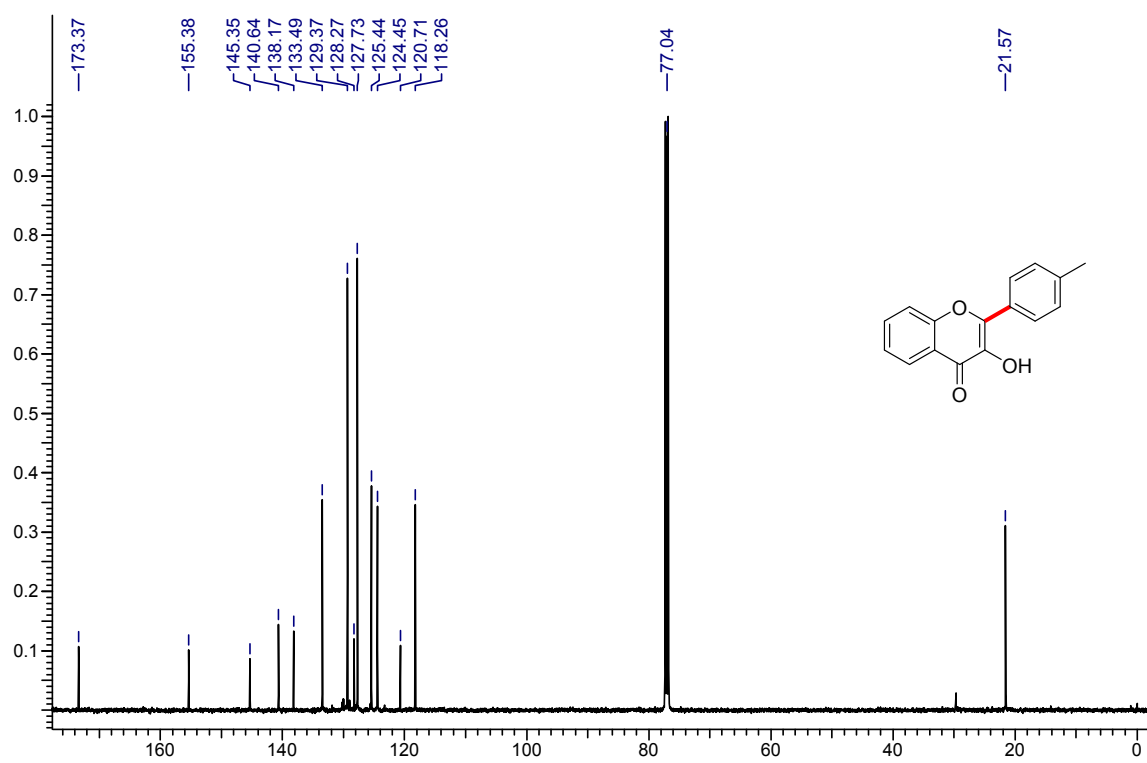
SP-242-HYDRO #134 RT: 0.59 AV: 1 NL: 1.06E10
T: FTMS + p ESI Full ms [100.00-1500.00]



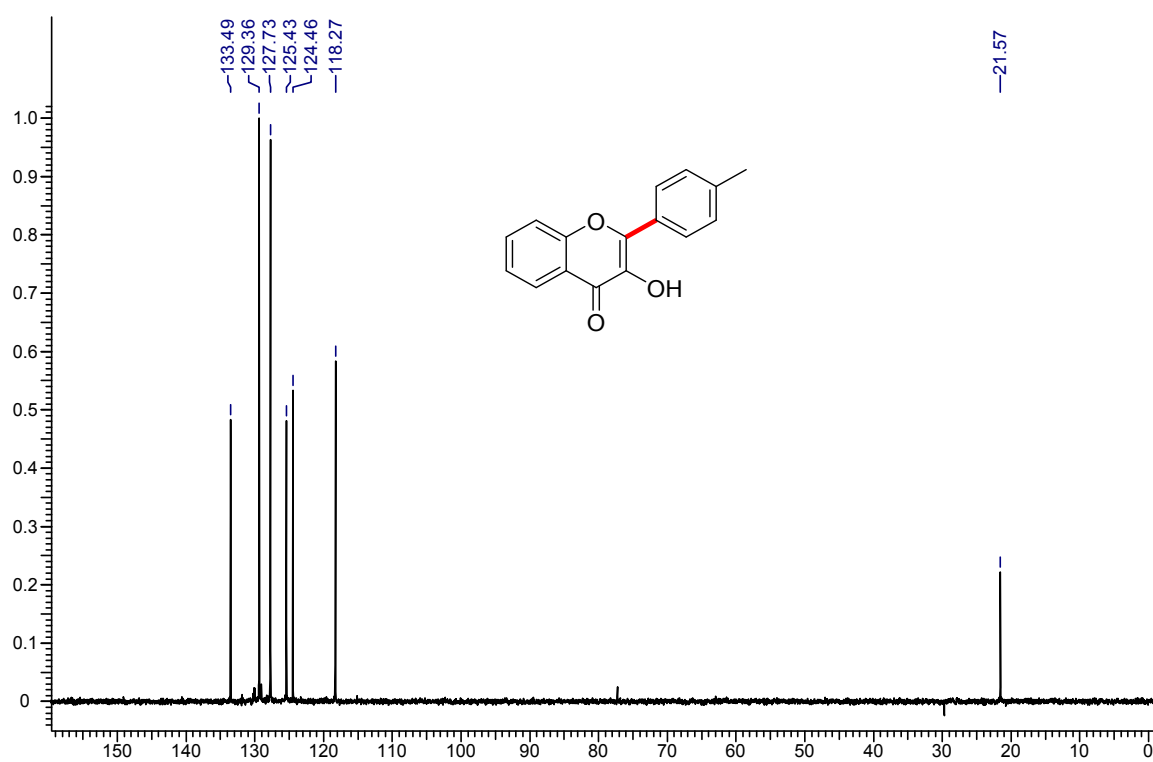
HRMS of 3ba



¹H NMR (CDCl₃, 500 MHz) of 3da

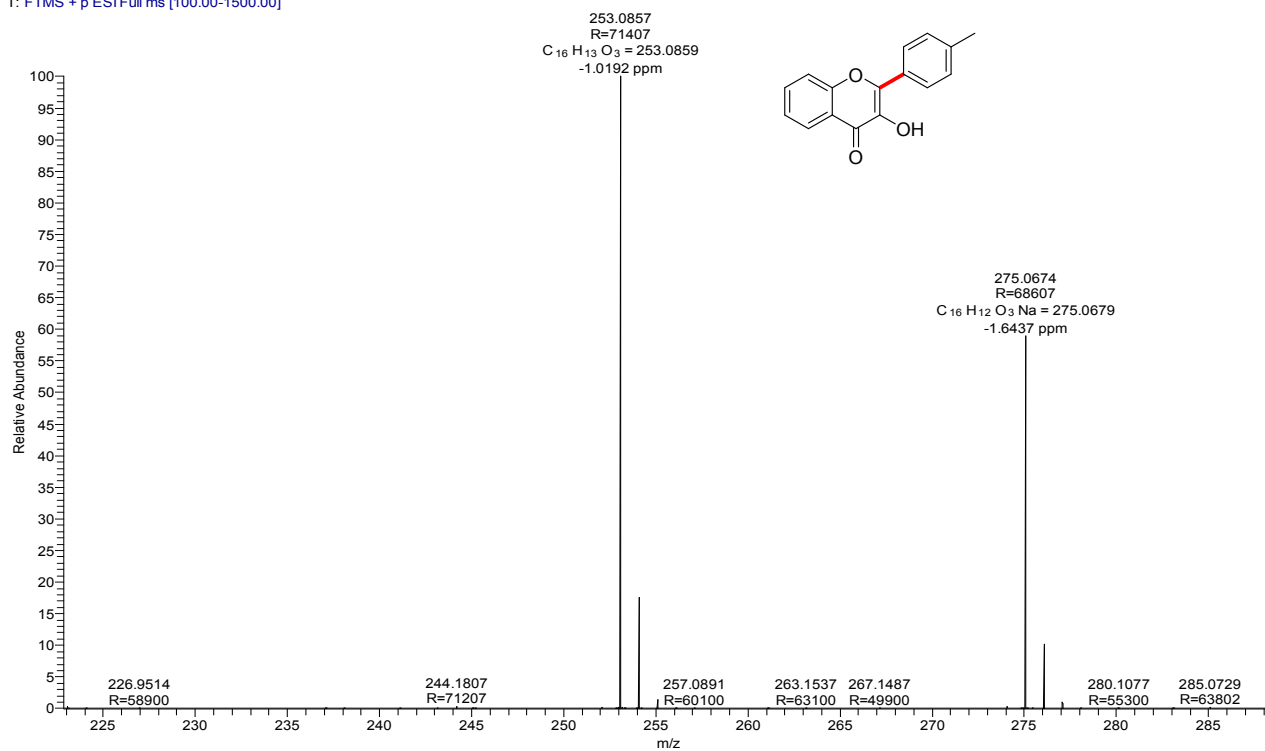


^{13}C NMR (CDCl_3 , 125 MHz) of **3da**

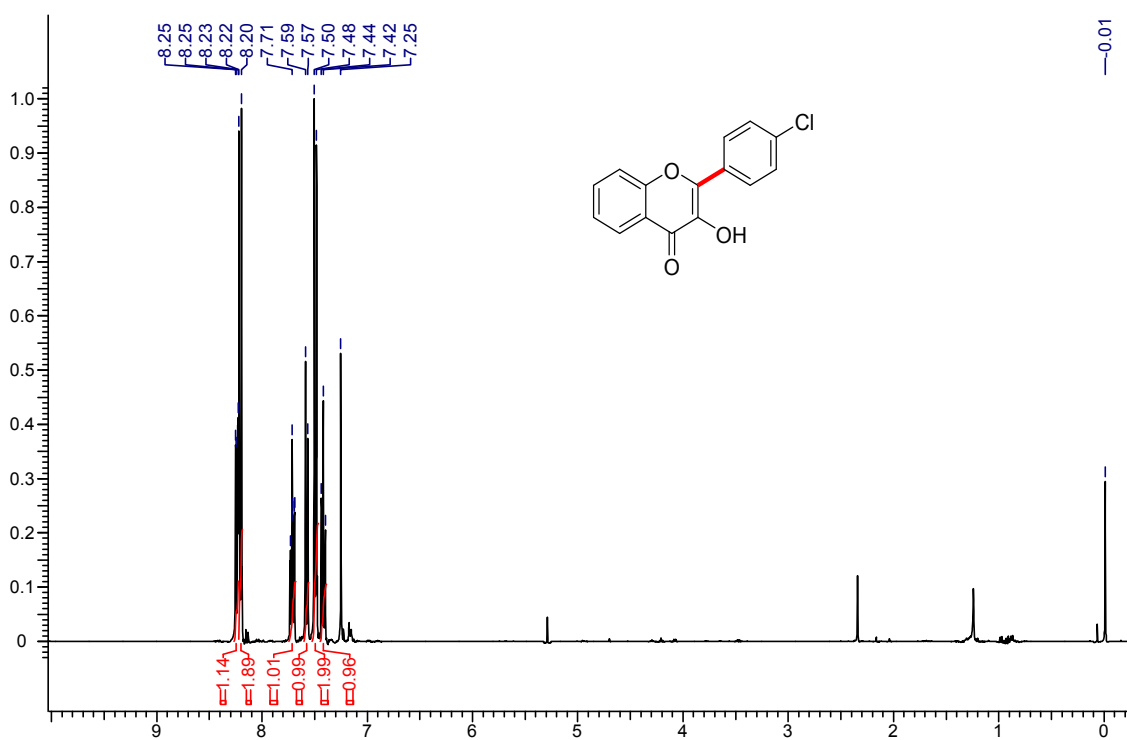


DEPT (CDCl_3 , 125 MHz) of **3da**

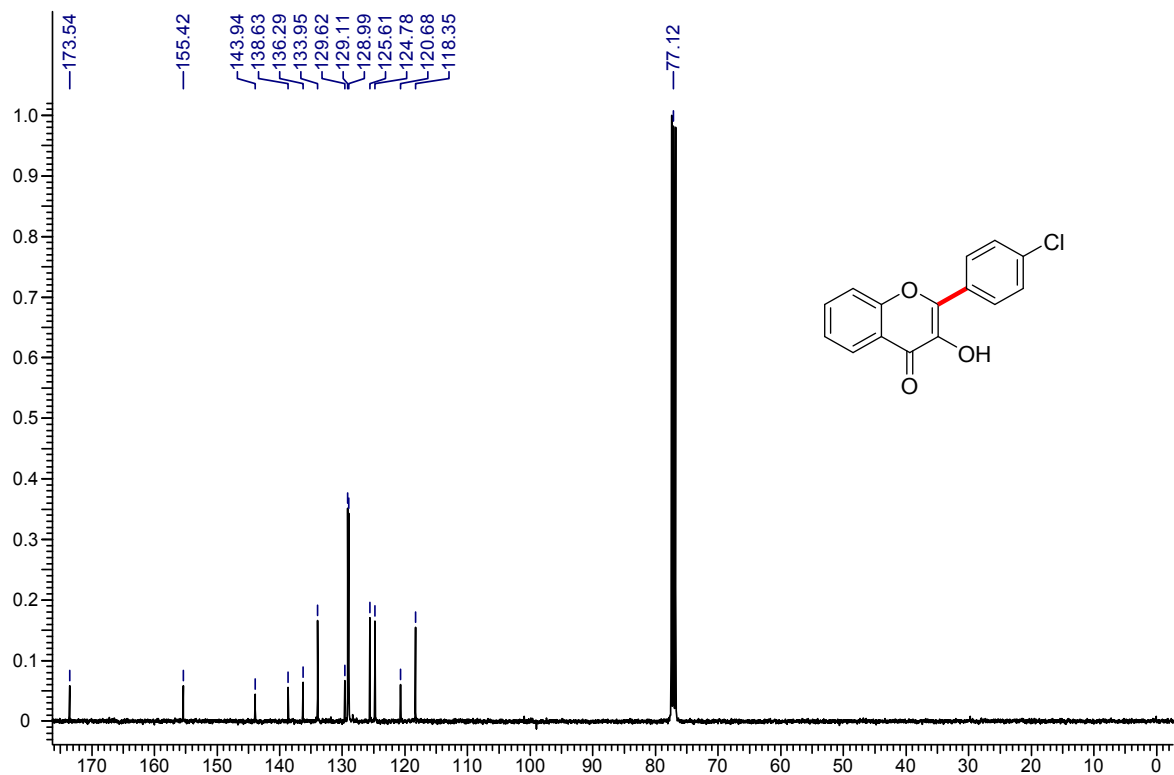
SP-2-44 #144 RT: 0.64 AV: 1 NL: 5.75E9
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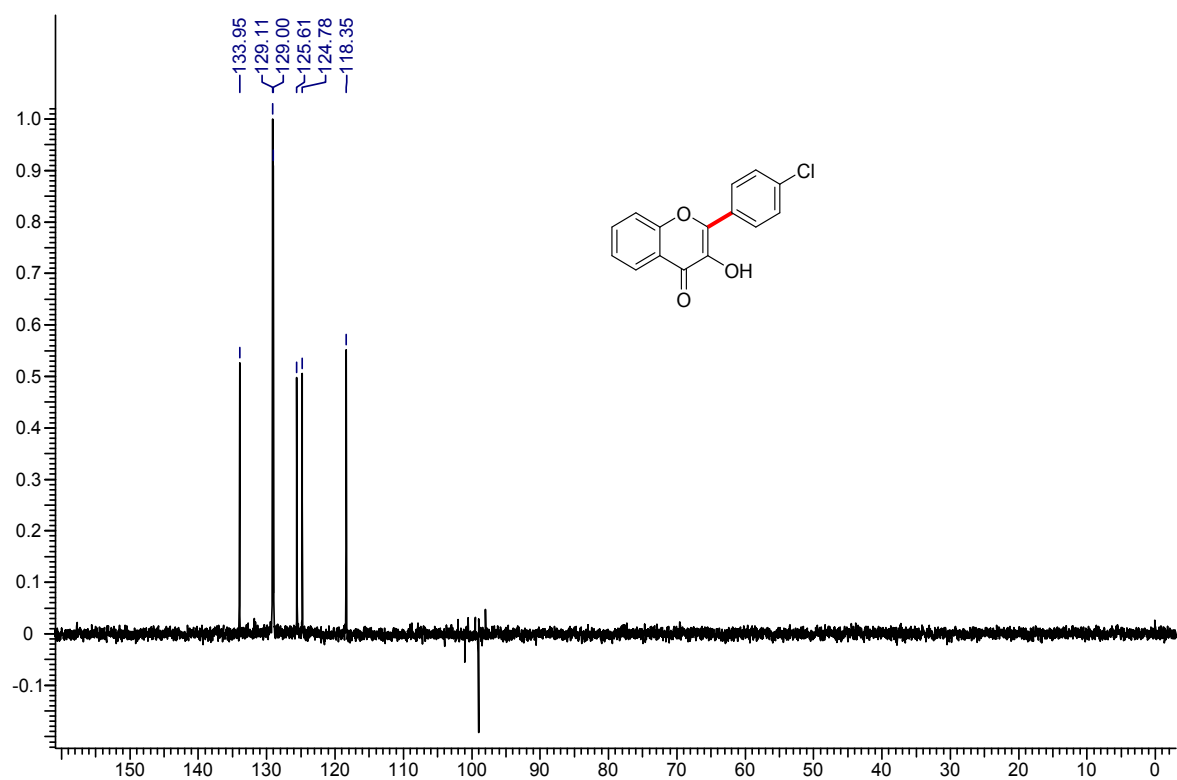
HRMS of 3da



¹H NMR (CDCl₃, 400 MHz) of 3db

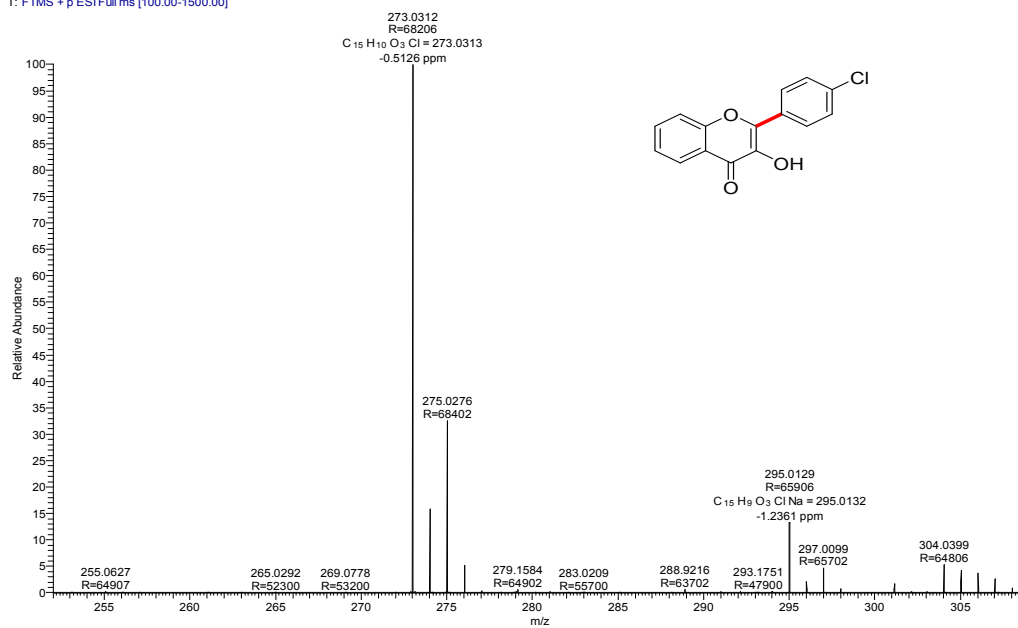


^{13}C NMR (CDCl_3 , 100 MHz) of **3db**

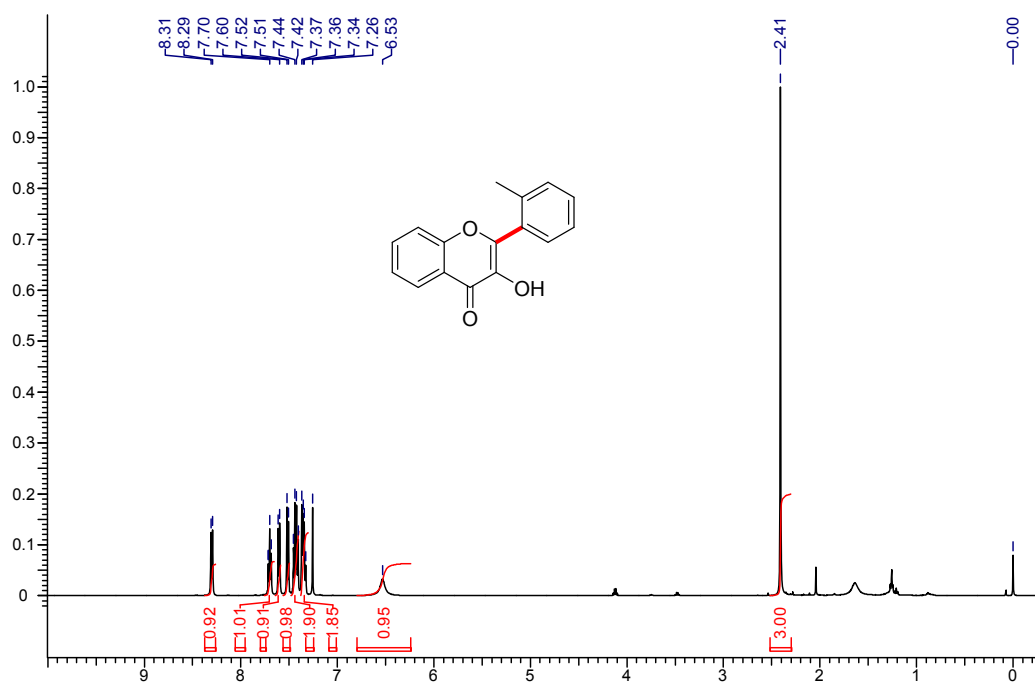


DEPT (CDCl_3 , 100 MHz) of **3db**

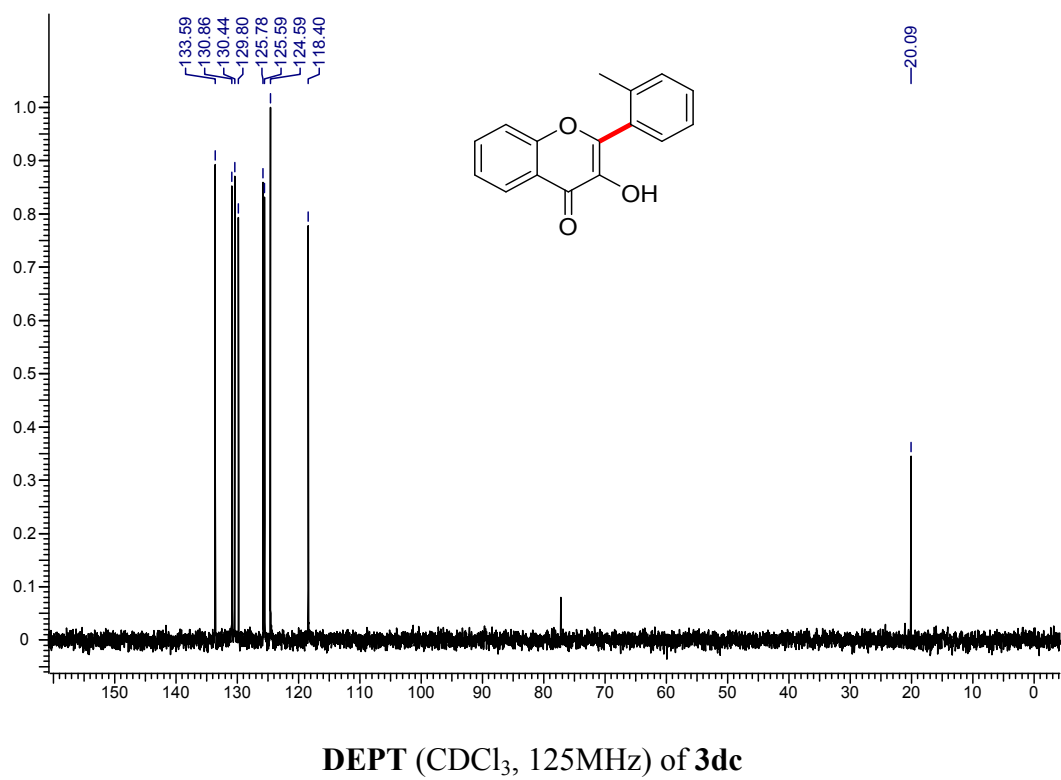
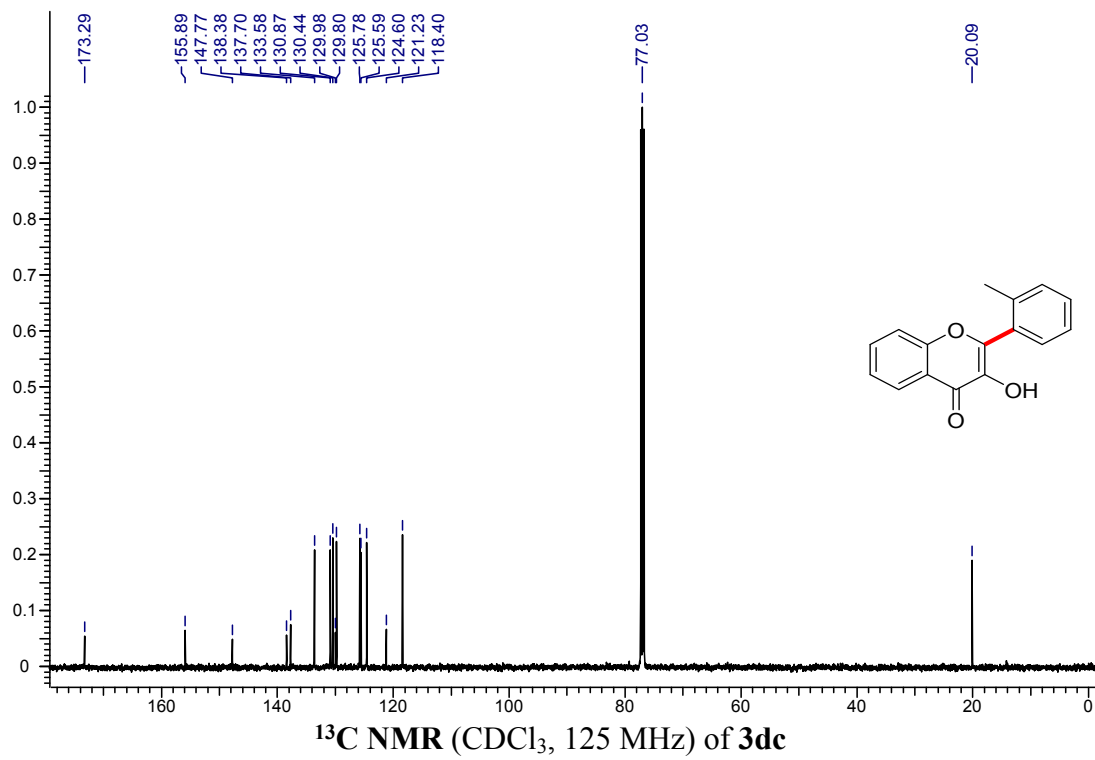
SP-2-43 #154 RT: 0.68 AV: 1 NL: 9.99E8
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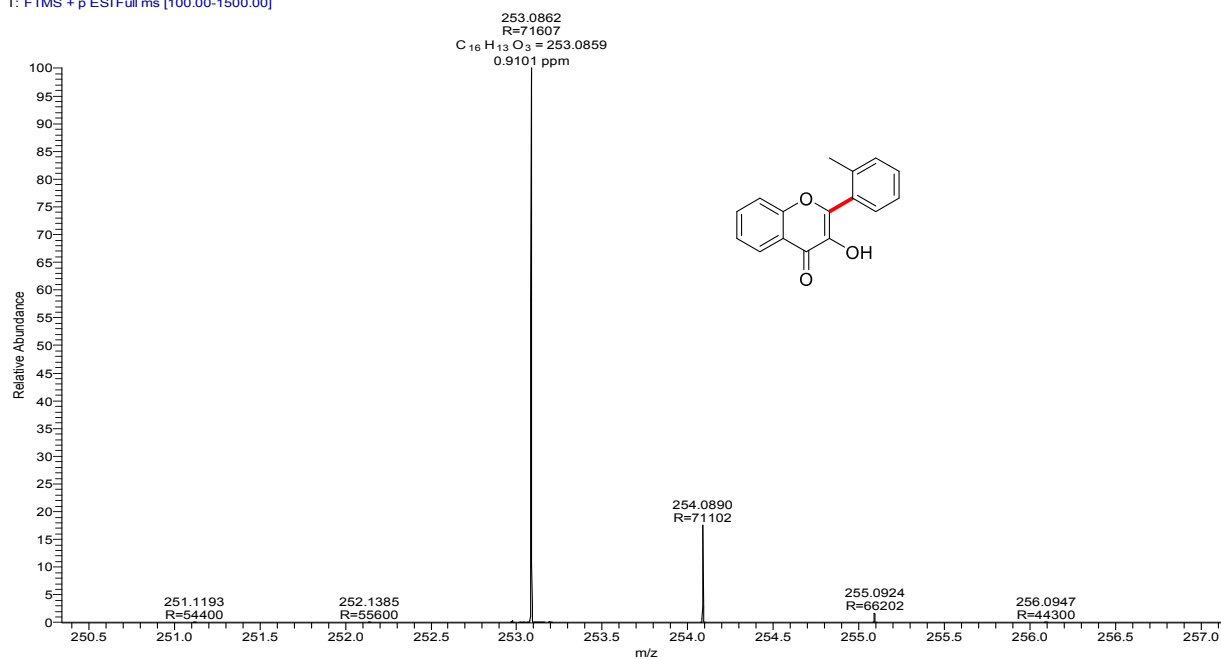
HRMS of 3db



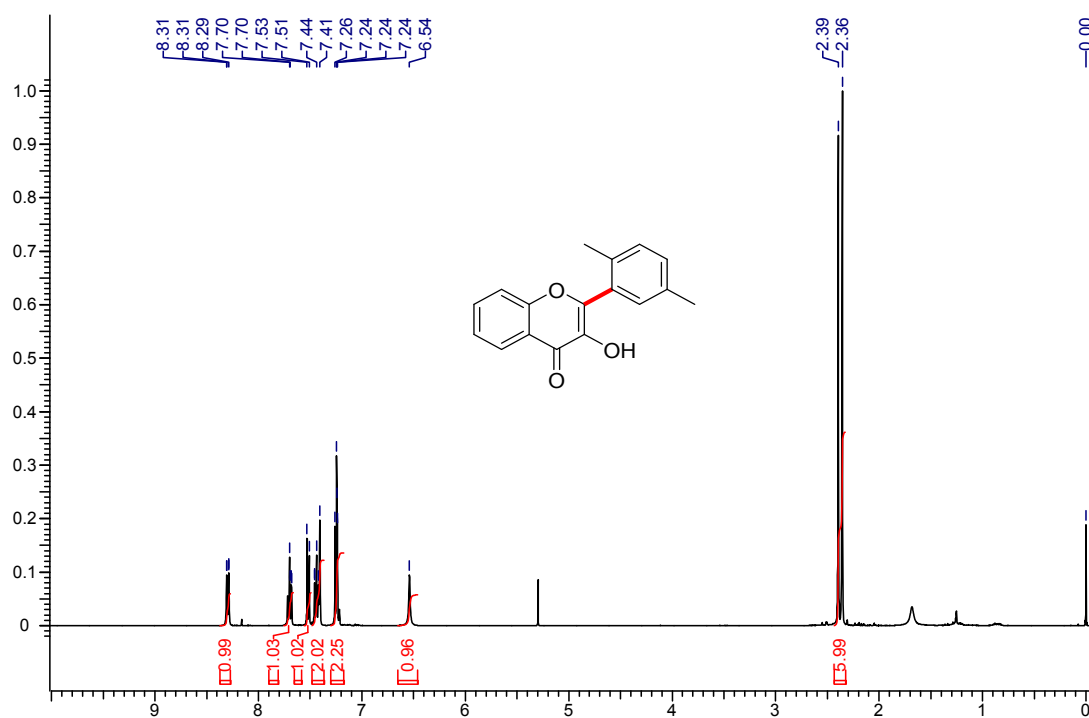
¹H NMR (CDCl₃, 500 MHz) of 3dc



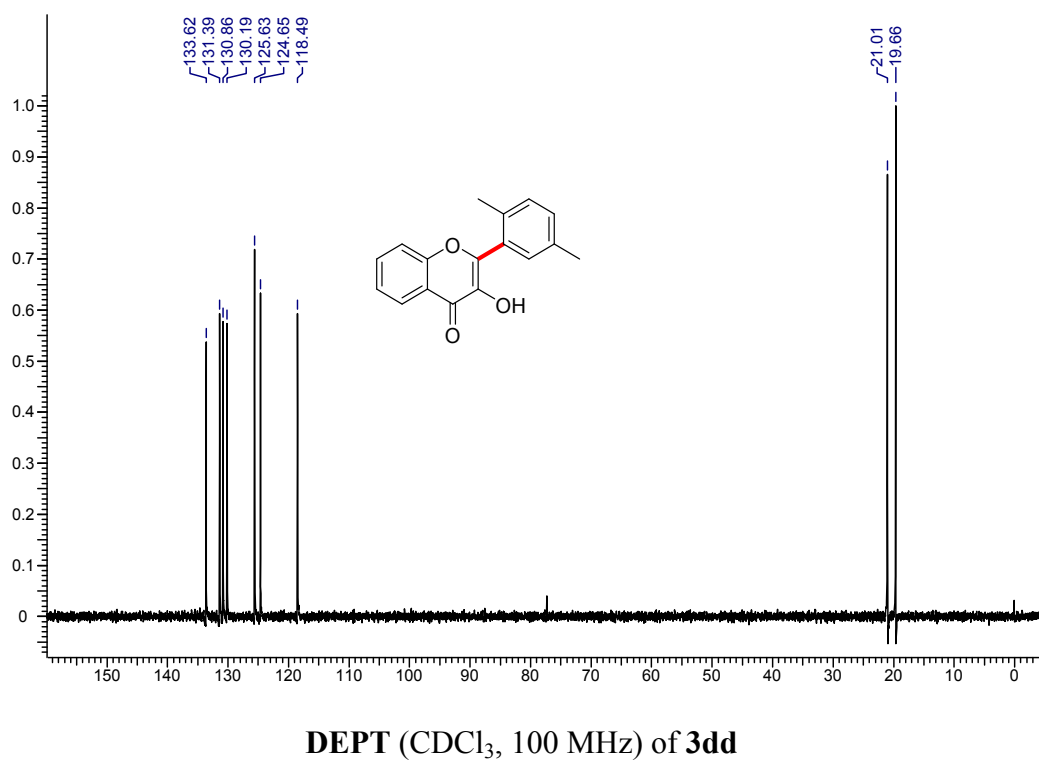
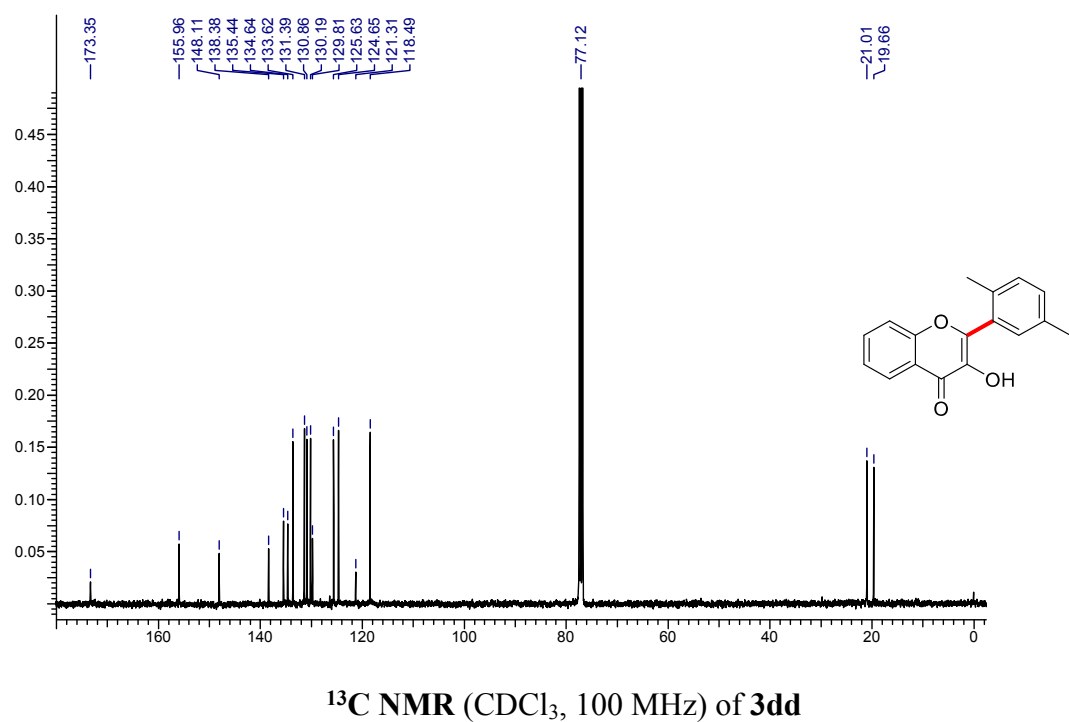
SP-2-48 #121 RT: 0.54 AV: 1 NL: 8.88E8
T: FTMS + p ESI Full ms [100.00-1500.00]



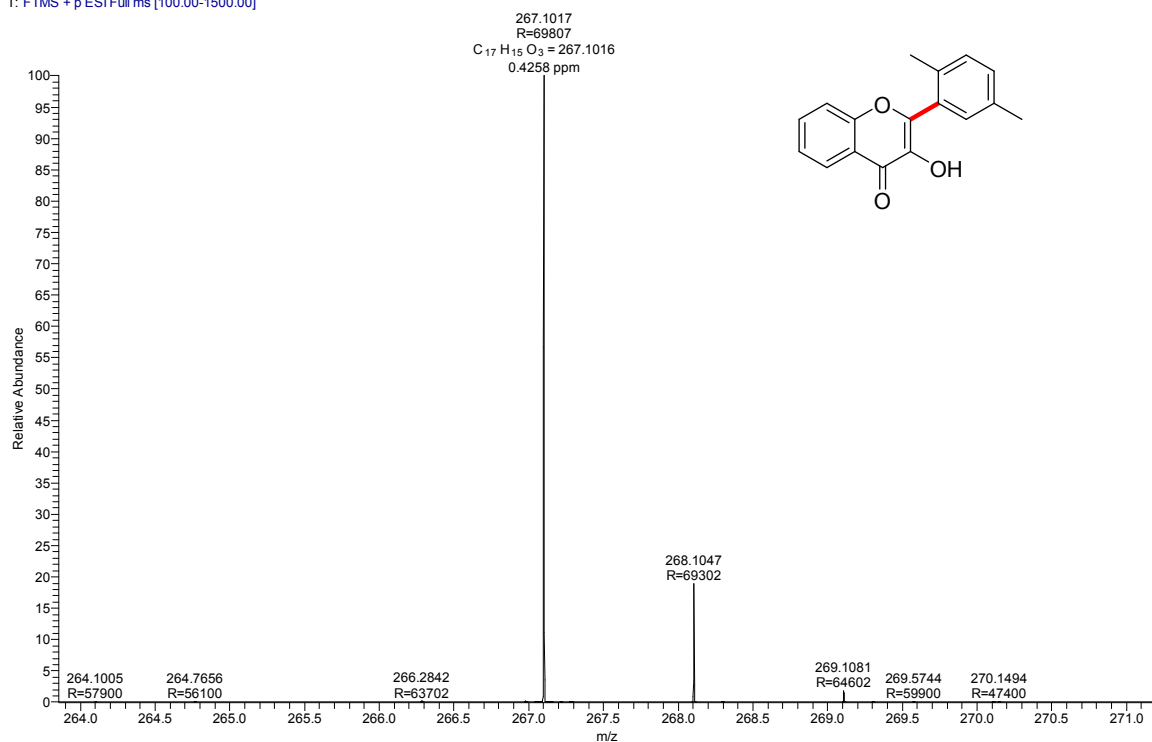
HRMS of 3dc



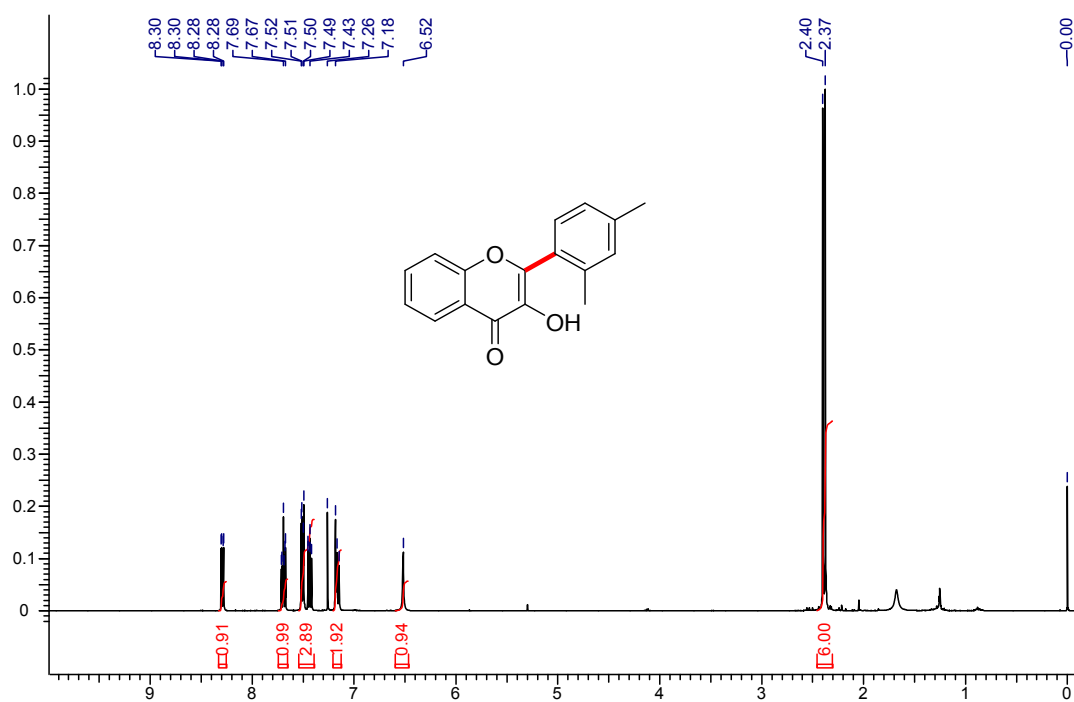
¹H NMR (CDCl₃, 400 MHz) of 3dd



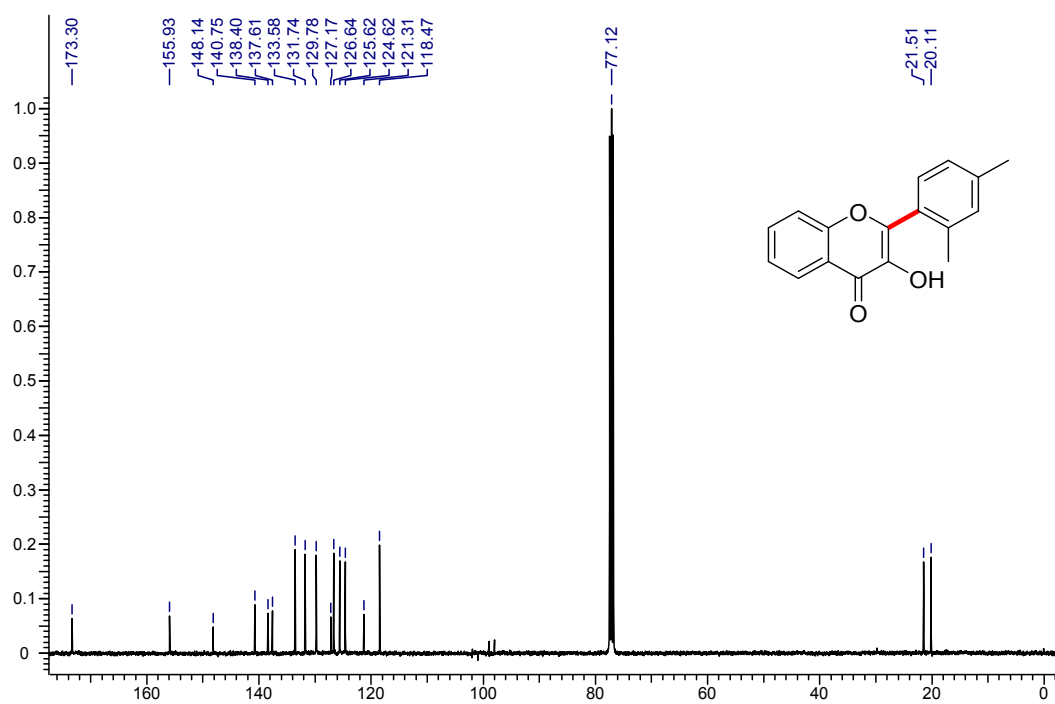
SP-2-50 #132 RT: 0.58 AV: 1 NL: 6.55E8
T: FTMS + p ESI Full ms [100.00-1500.00]



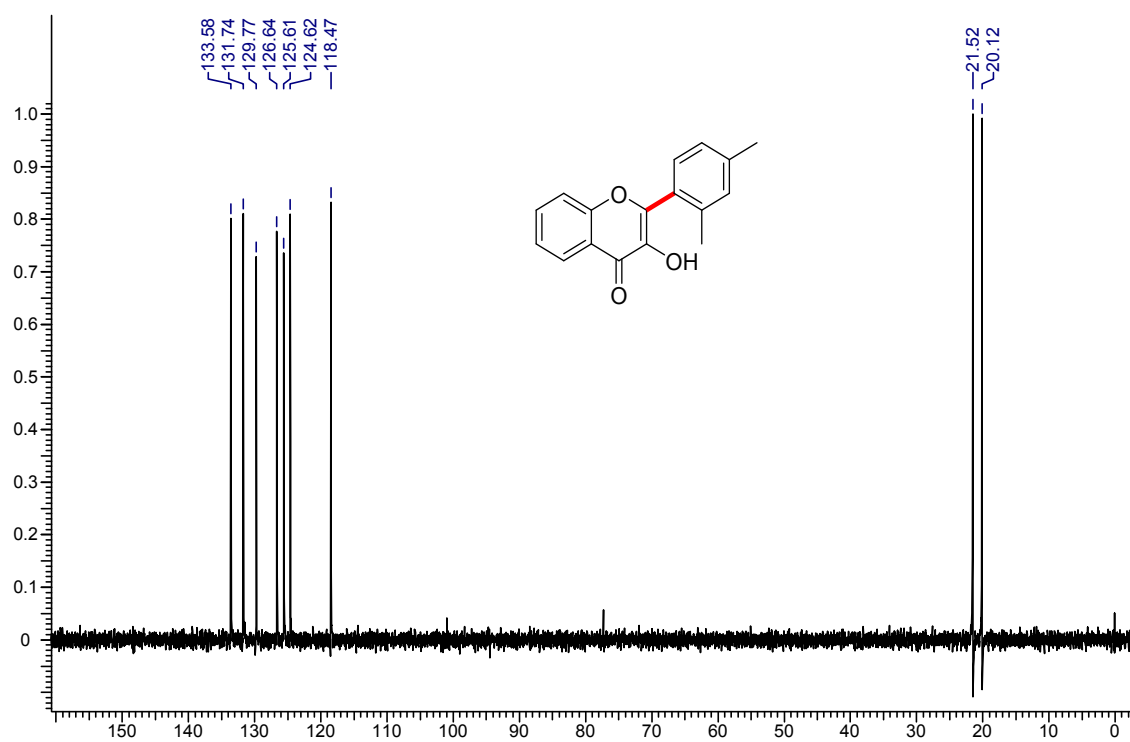
HRMS of 3dd



¹H NMR (CDCl₃, 400 MHz) of 3de

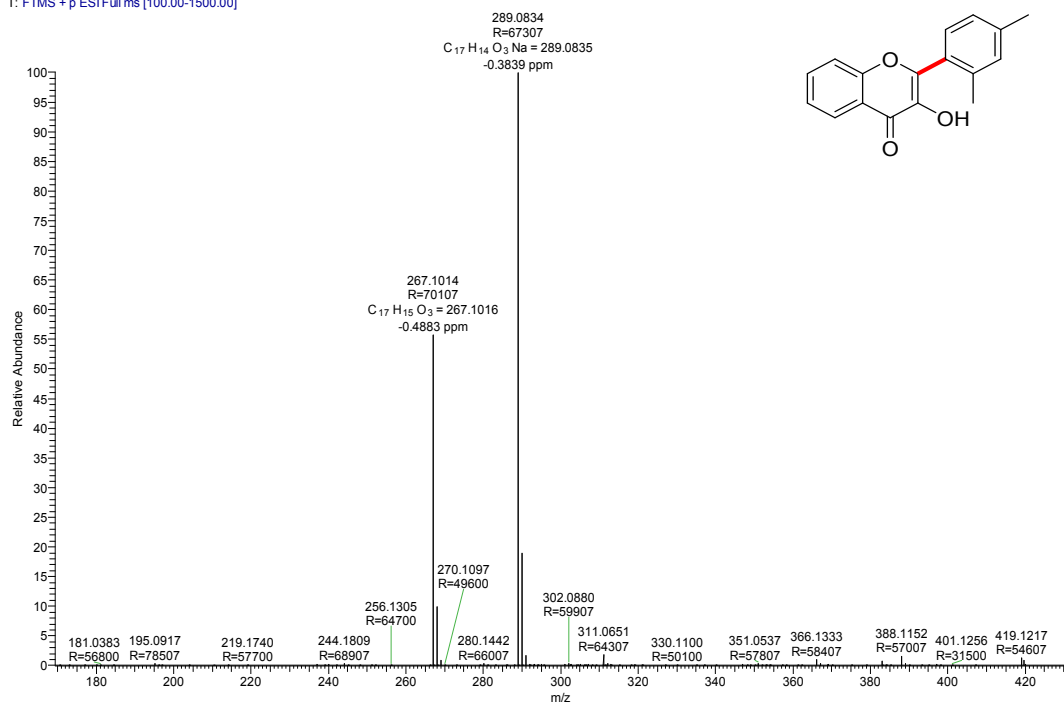


^{13}C NMR (CDCl_3 , 100 MHz) of **3de**

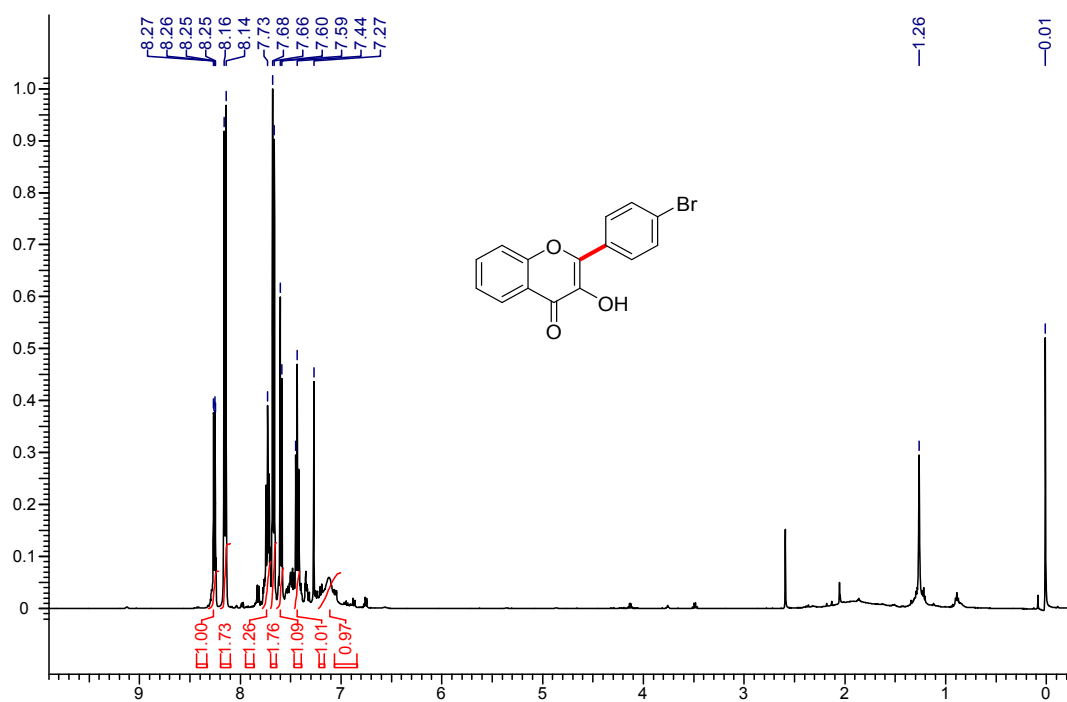


DEPT (CDCl_3 , 100 MHz) of **3de**

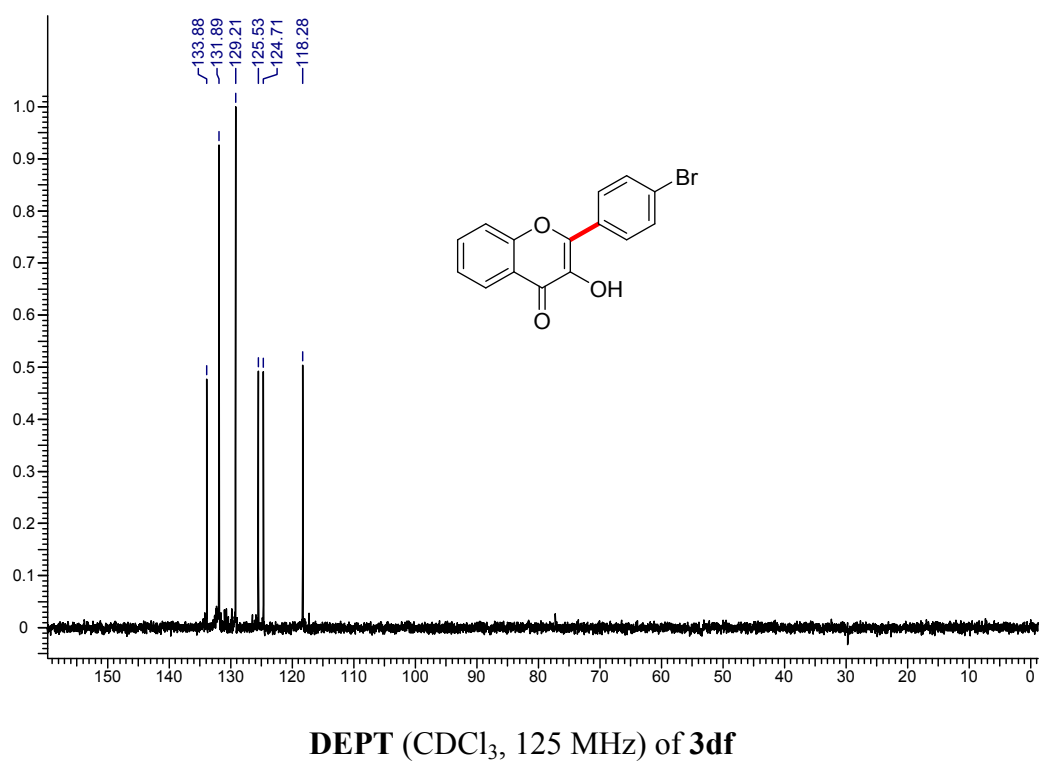
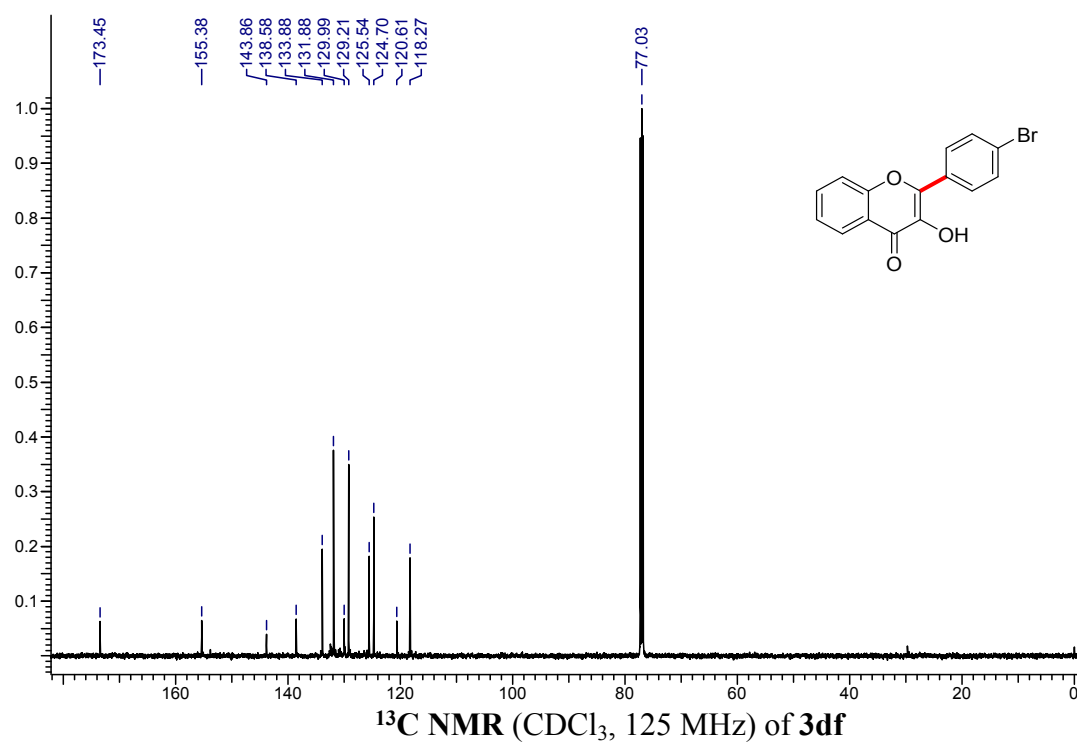
SP-2-51 #132 RT: 0.58 AV: 1 NL: 2.09E9
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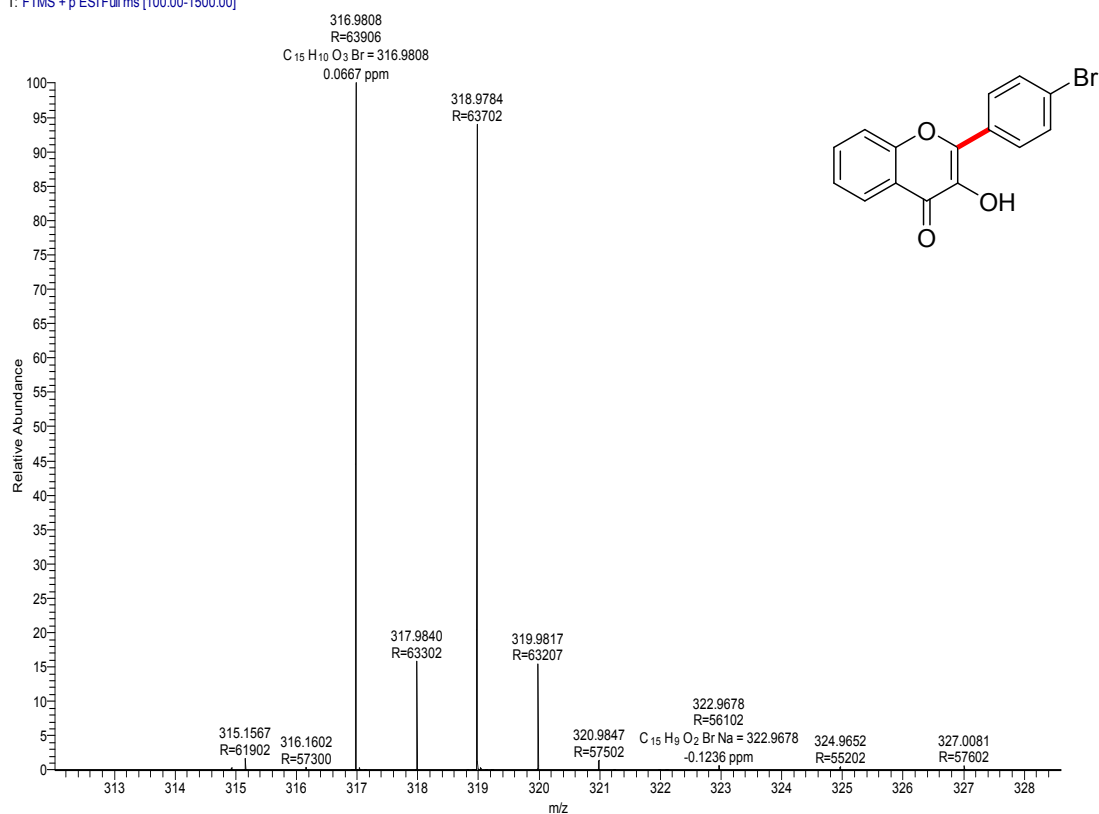
HRMS of 3de



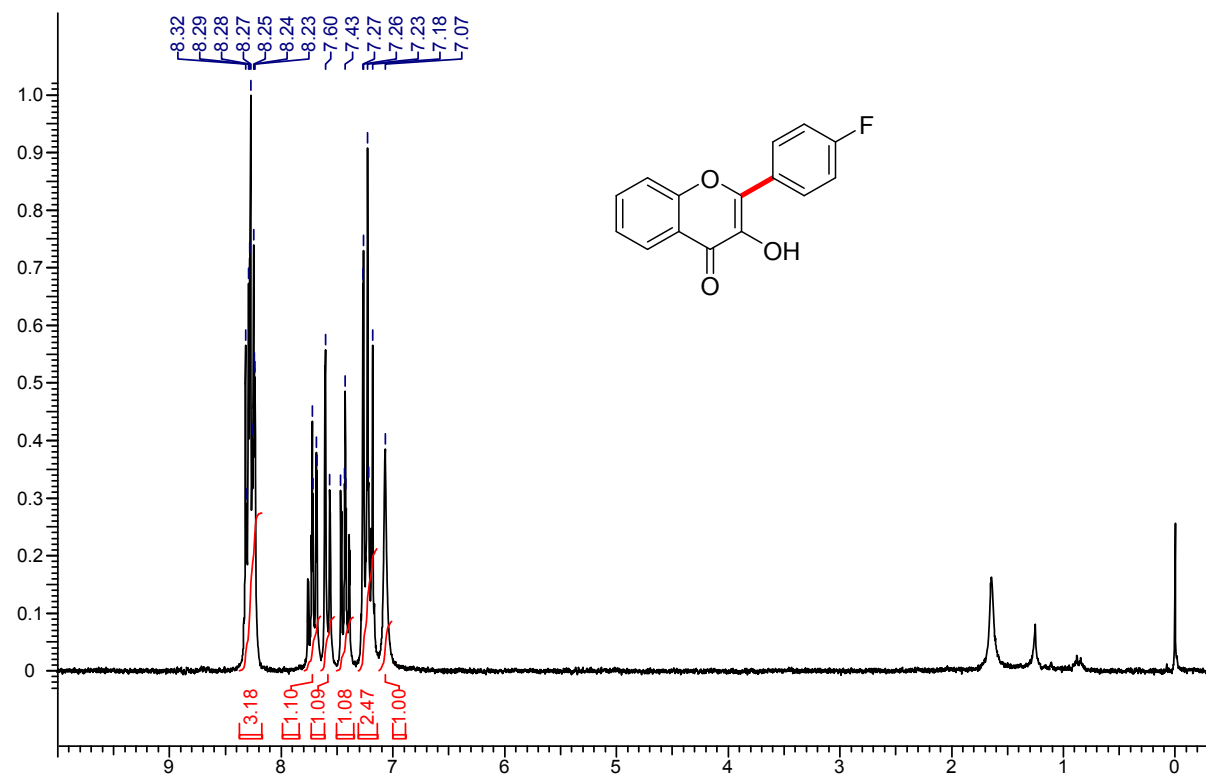
¹H NMR (CDCl₃, 500 MHz) of 3df



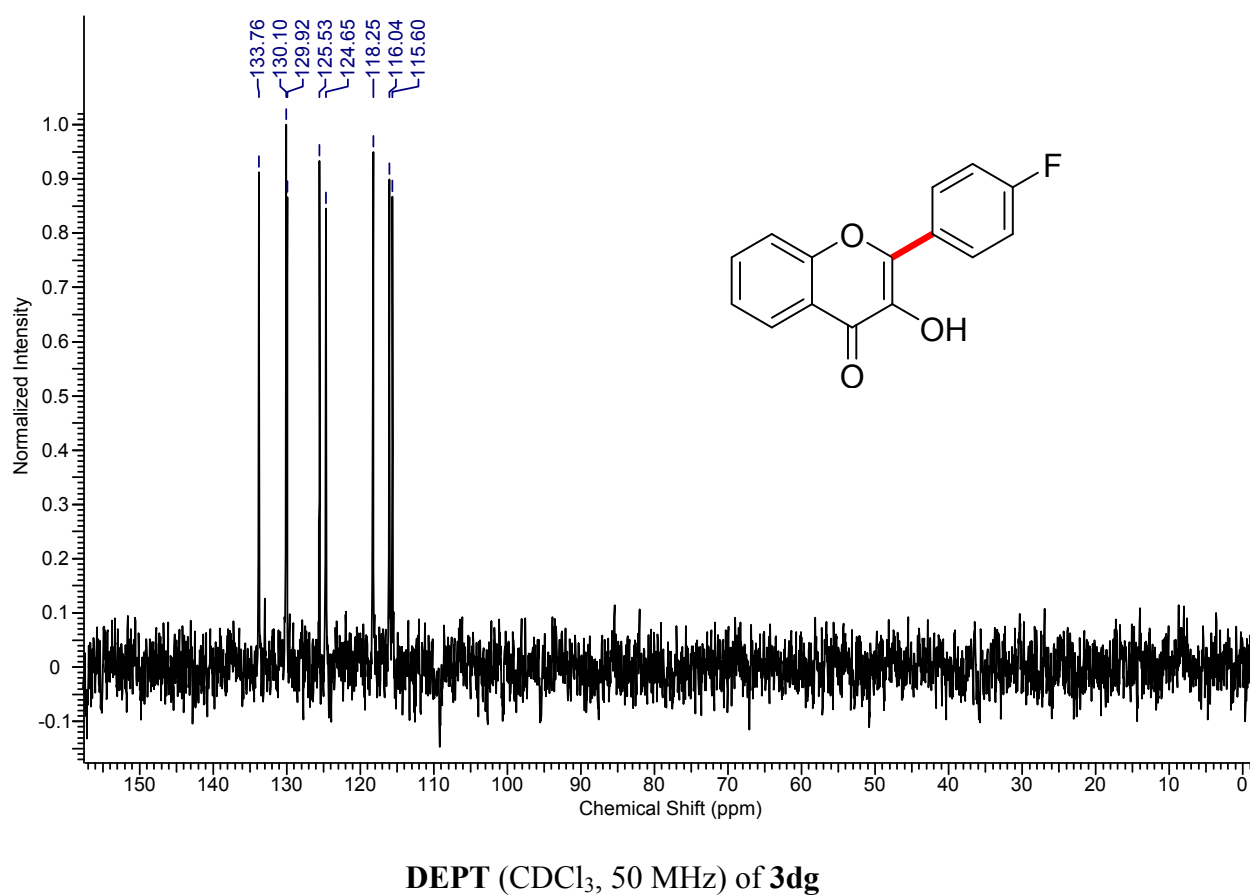
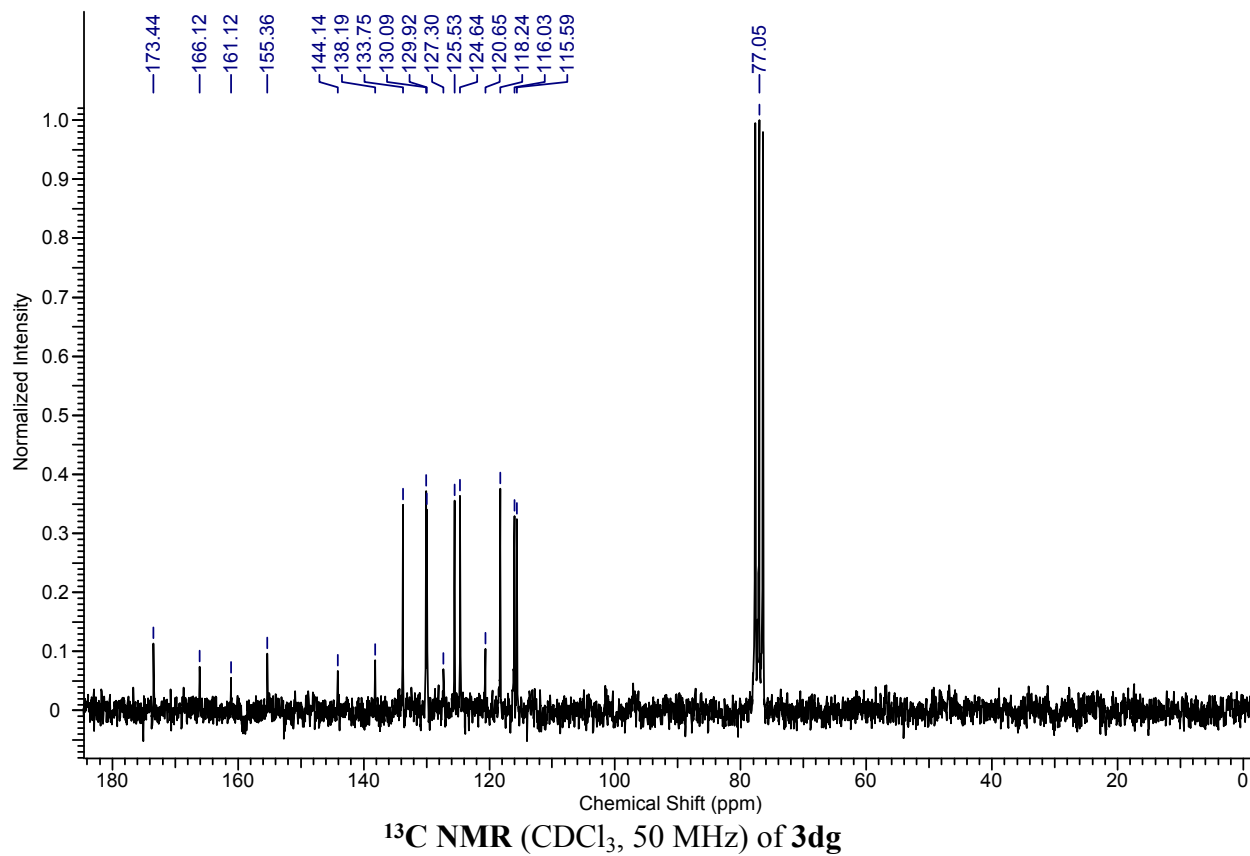
SP-2-52 #161 RT: 0.71 AV: 1 NL: 9.57E7
T: FTMS + p ESIFull.ms [100.00-1500.00]



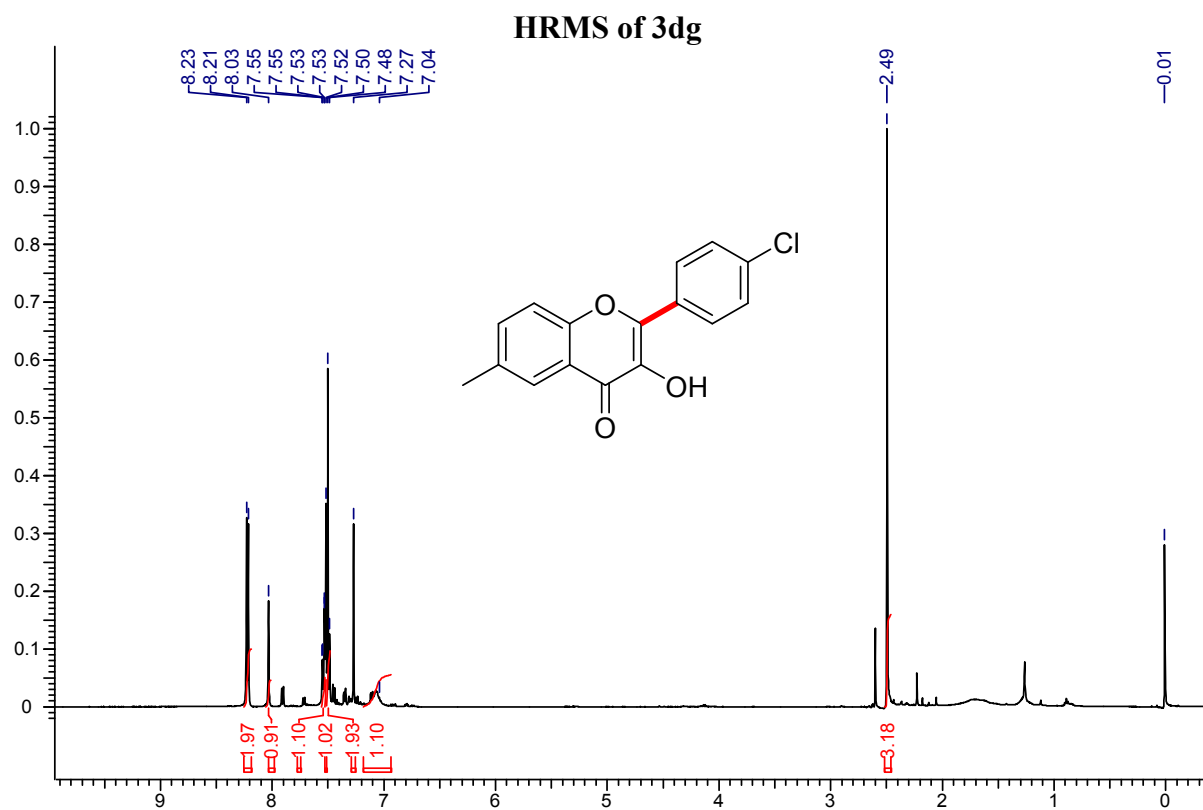
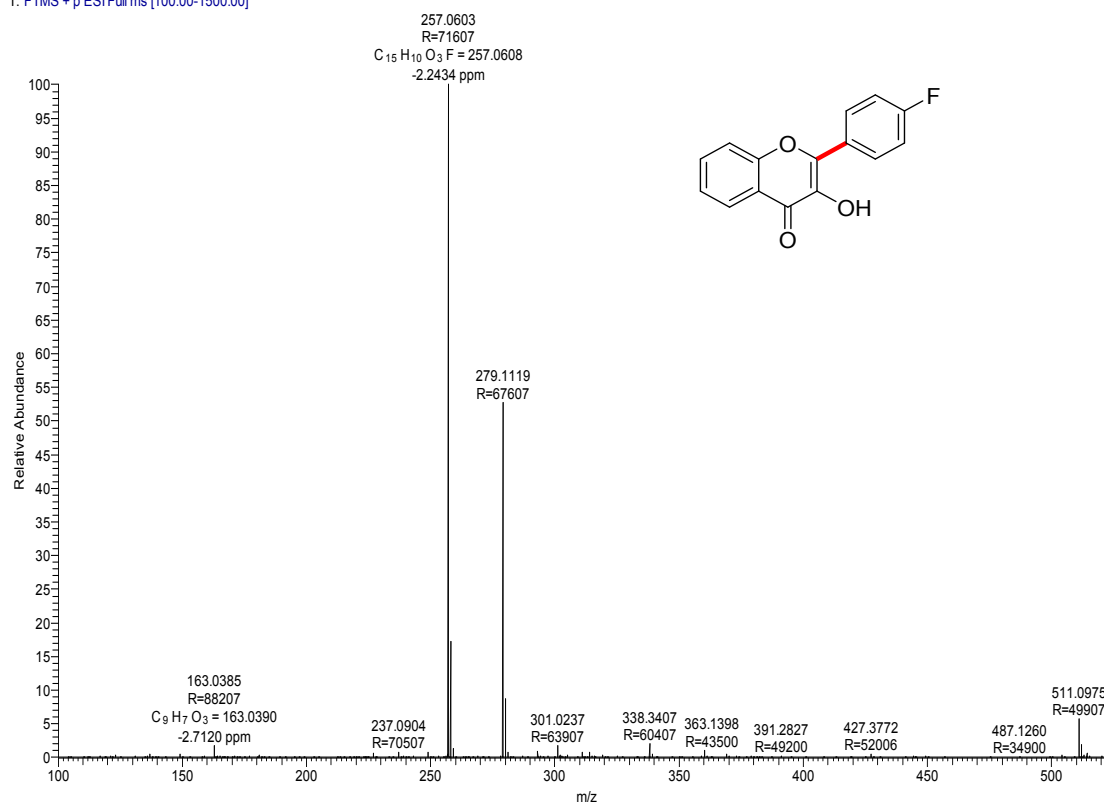
HRMS of 3df

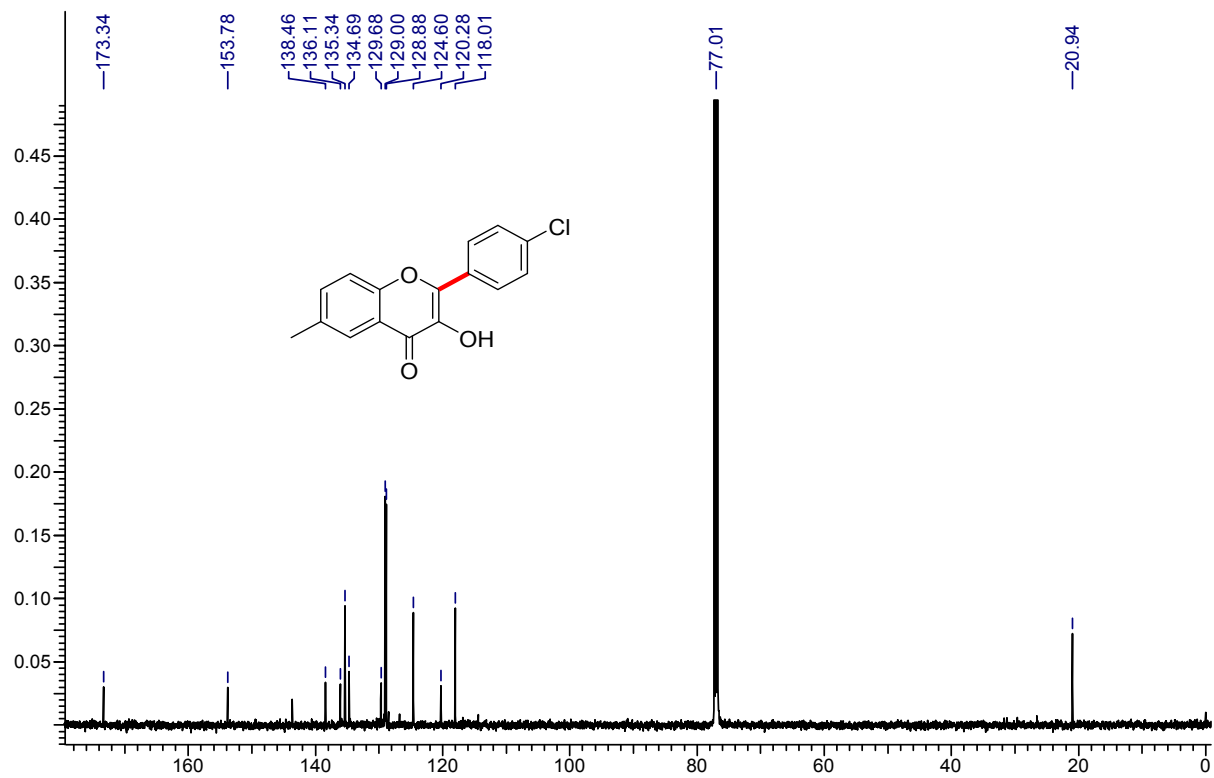


¹H NMR (CDCl₃, 200 MHz) of 3dg

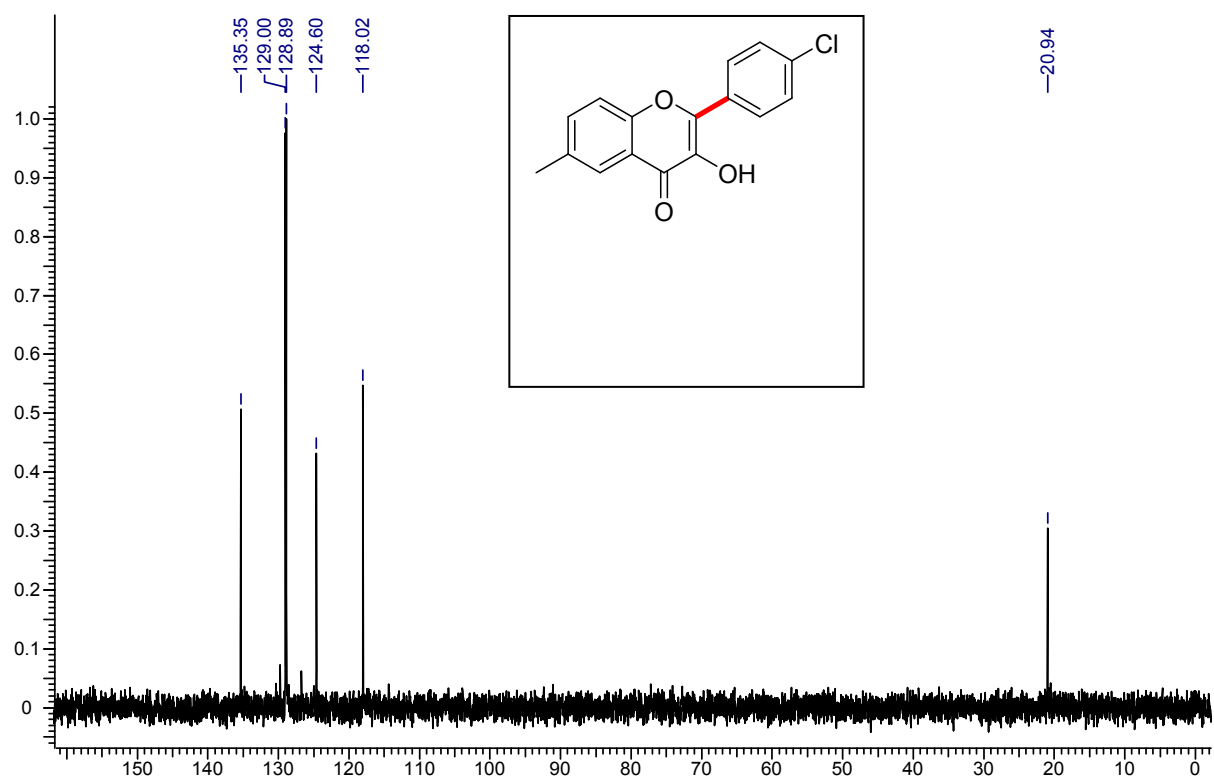


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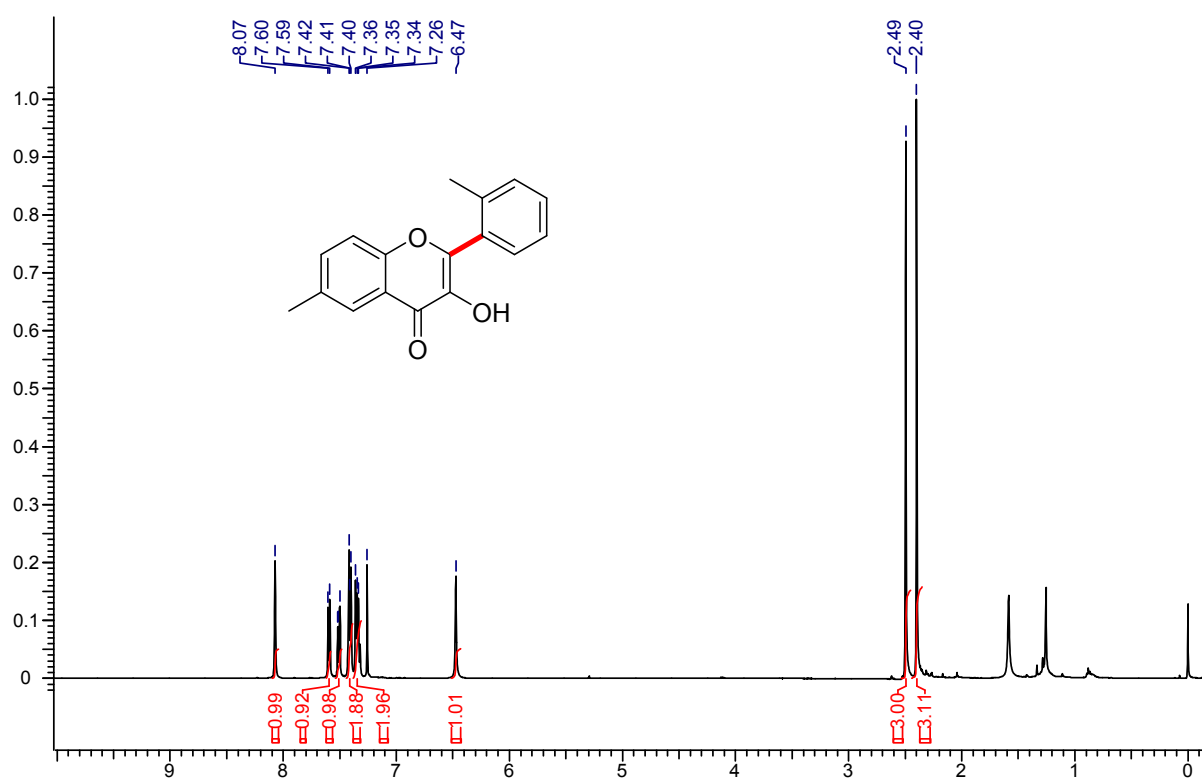
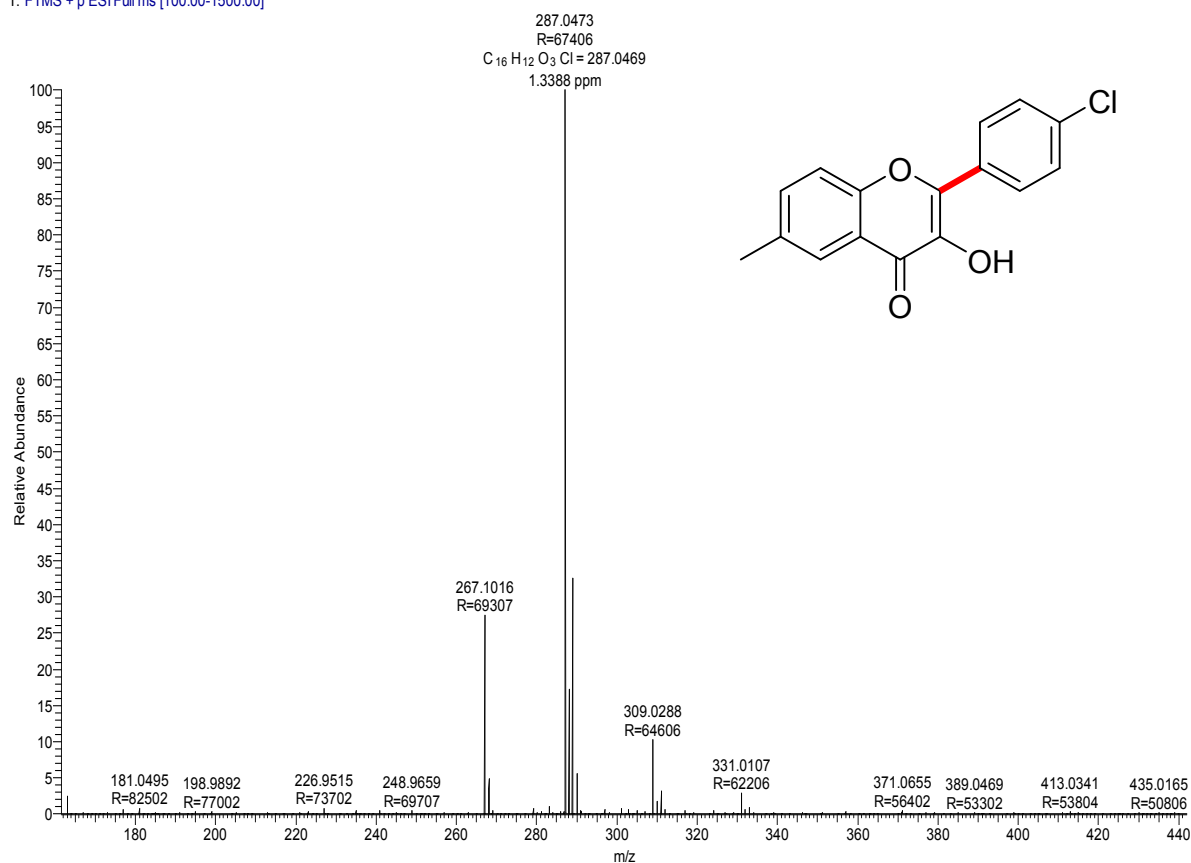


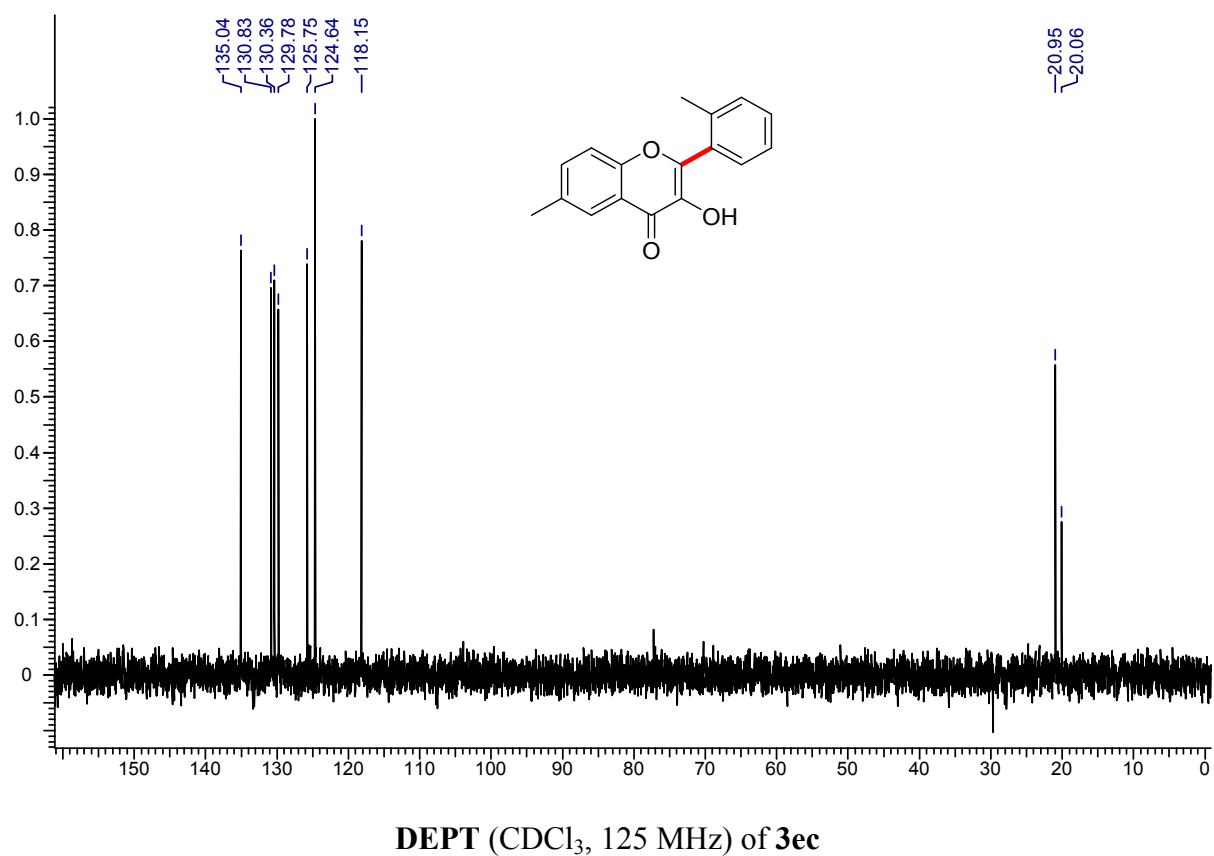
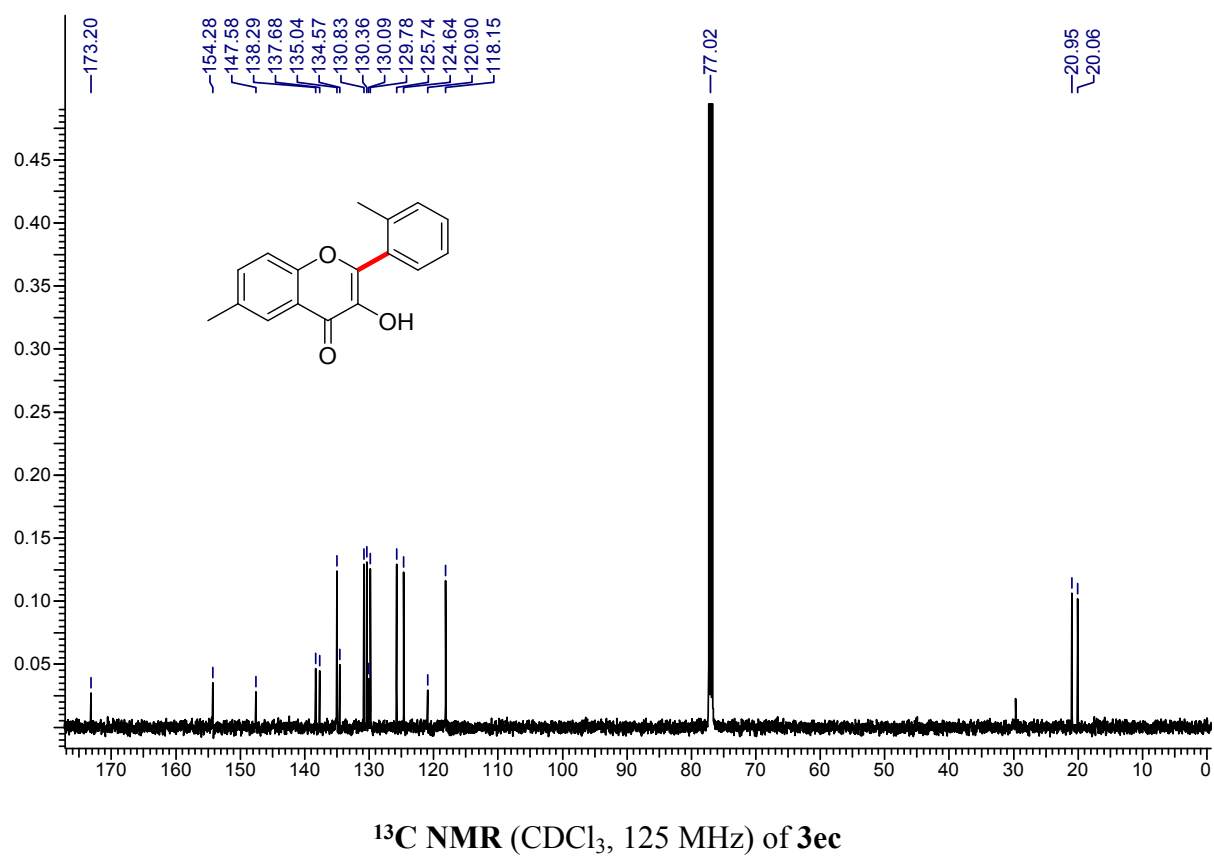
^{13}C NMR (CDCl₃, 125 MHz) of **3eb**



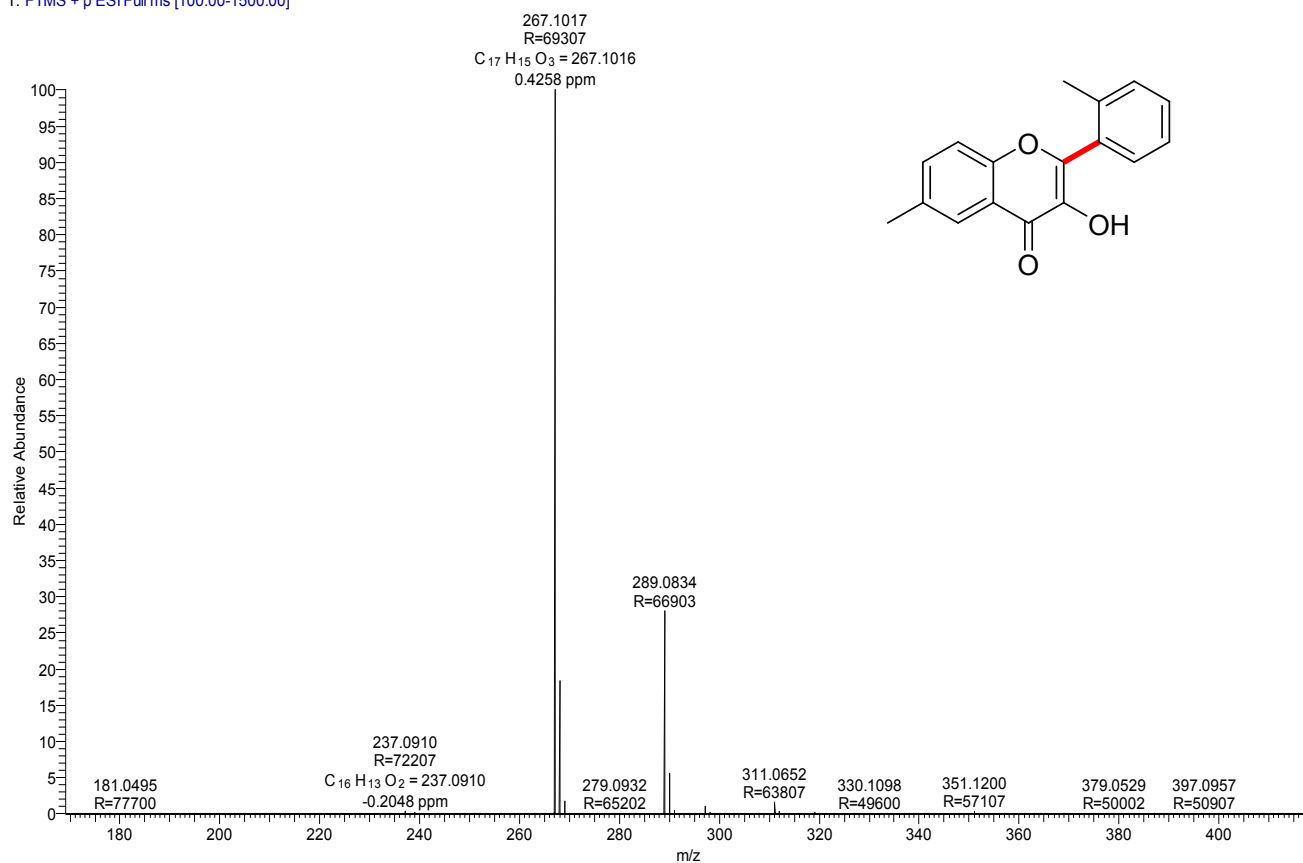
DEPT (CDCl₃, 125 MHz) of **3eb**

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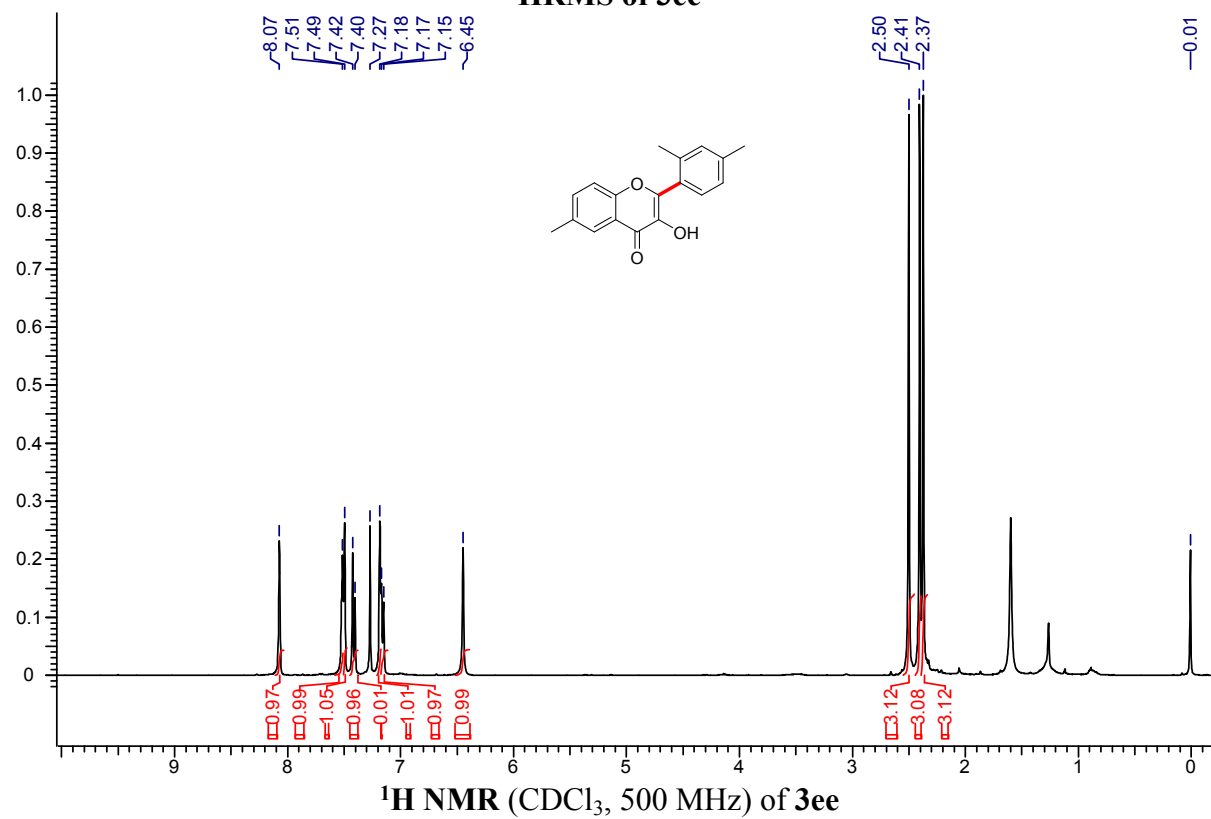


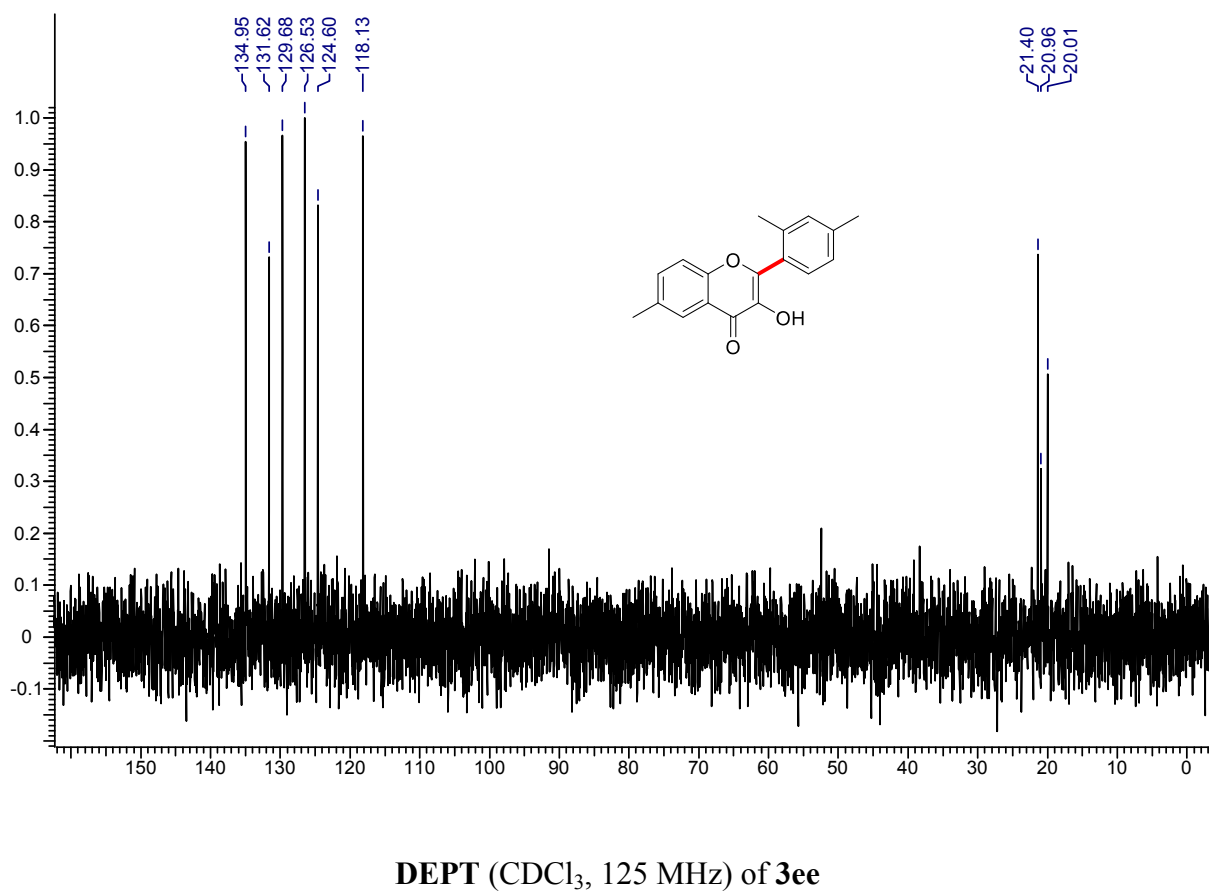
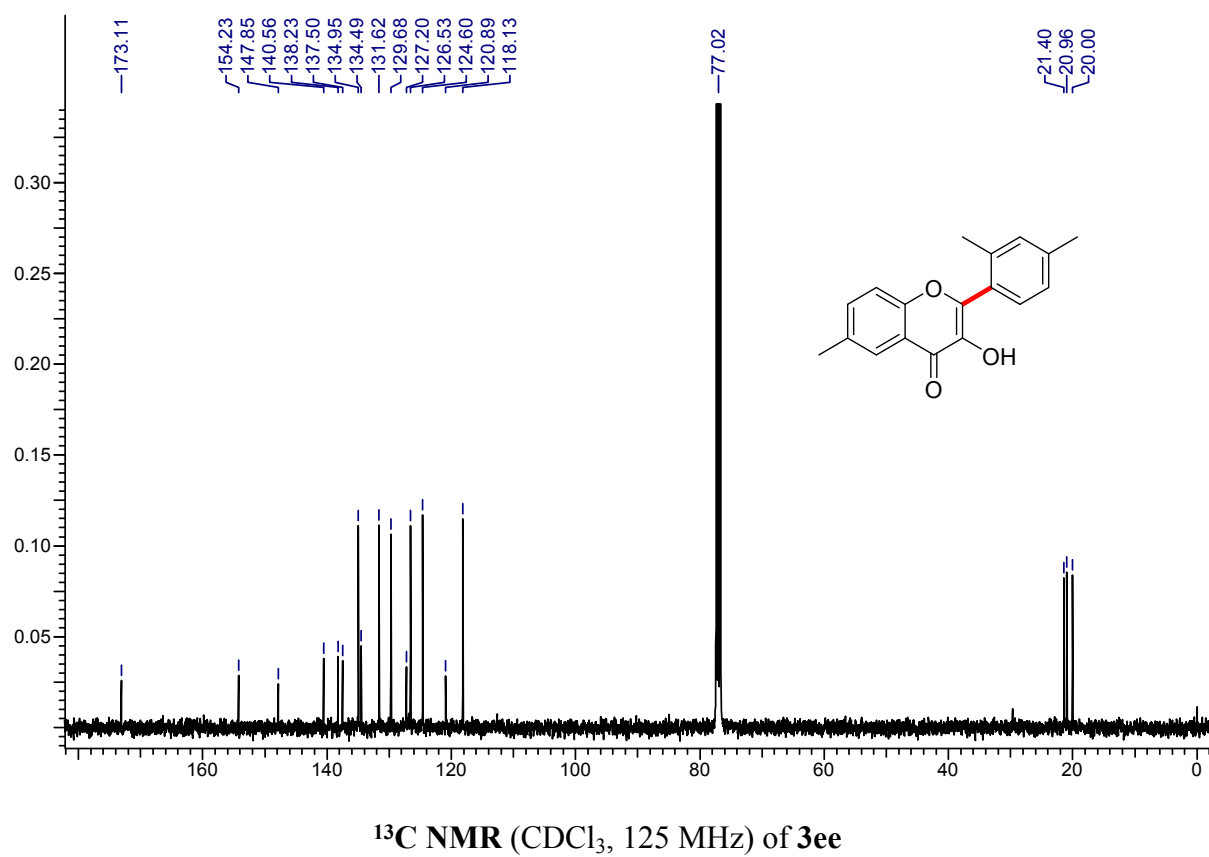


MT-10SP-2-131 #134 RT: 0.60 AV: 1 NL: 4.43E9
T: FTMS + p ESI Full ms [100.00-1500.00]

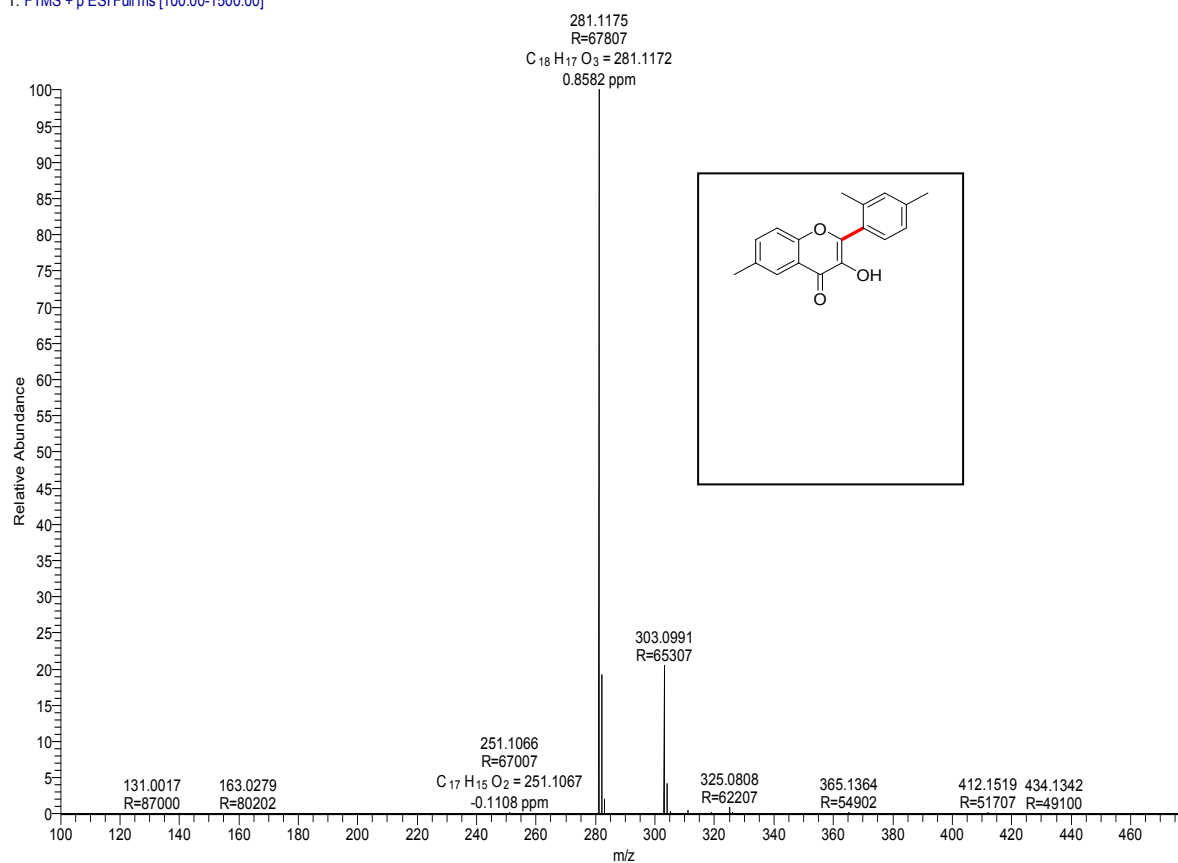


HRMS of 3ec

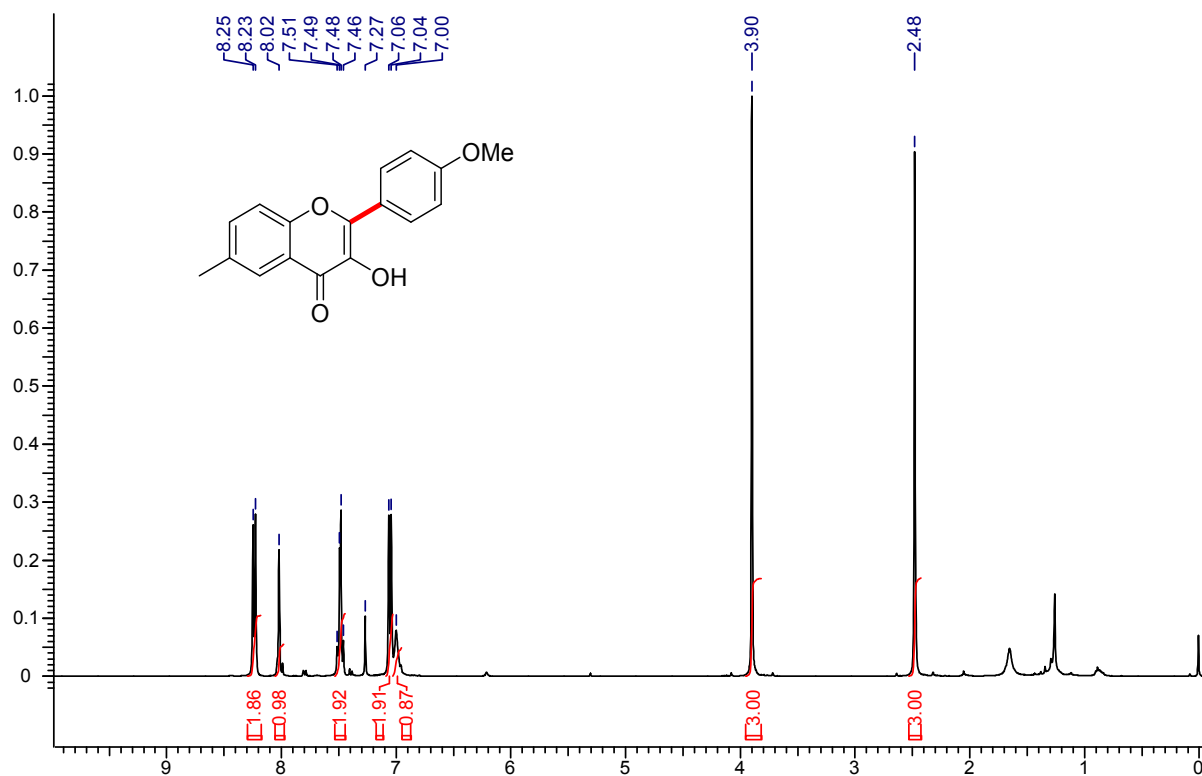




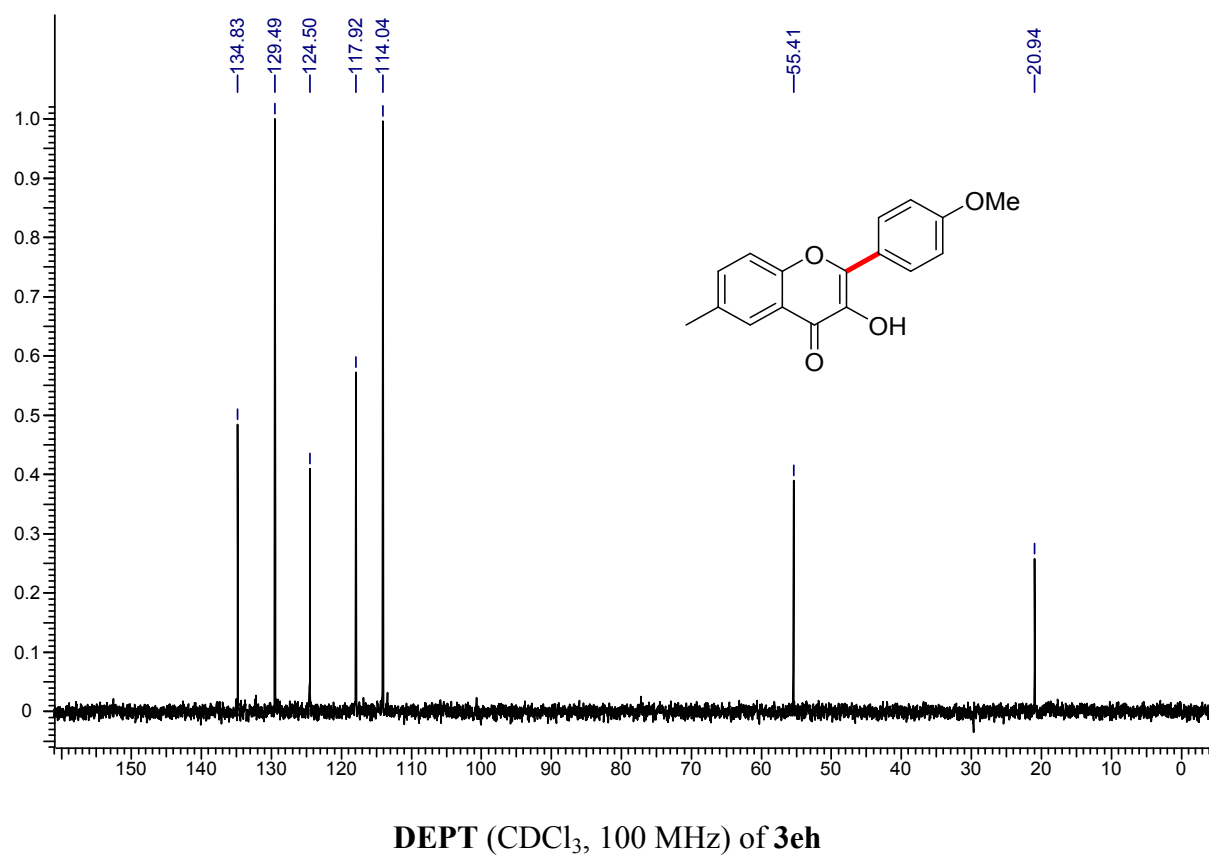
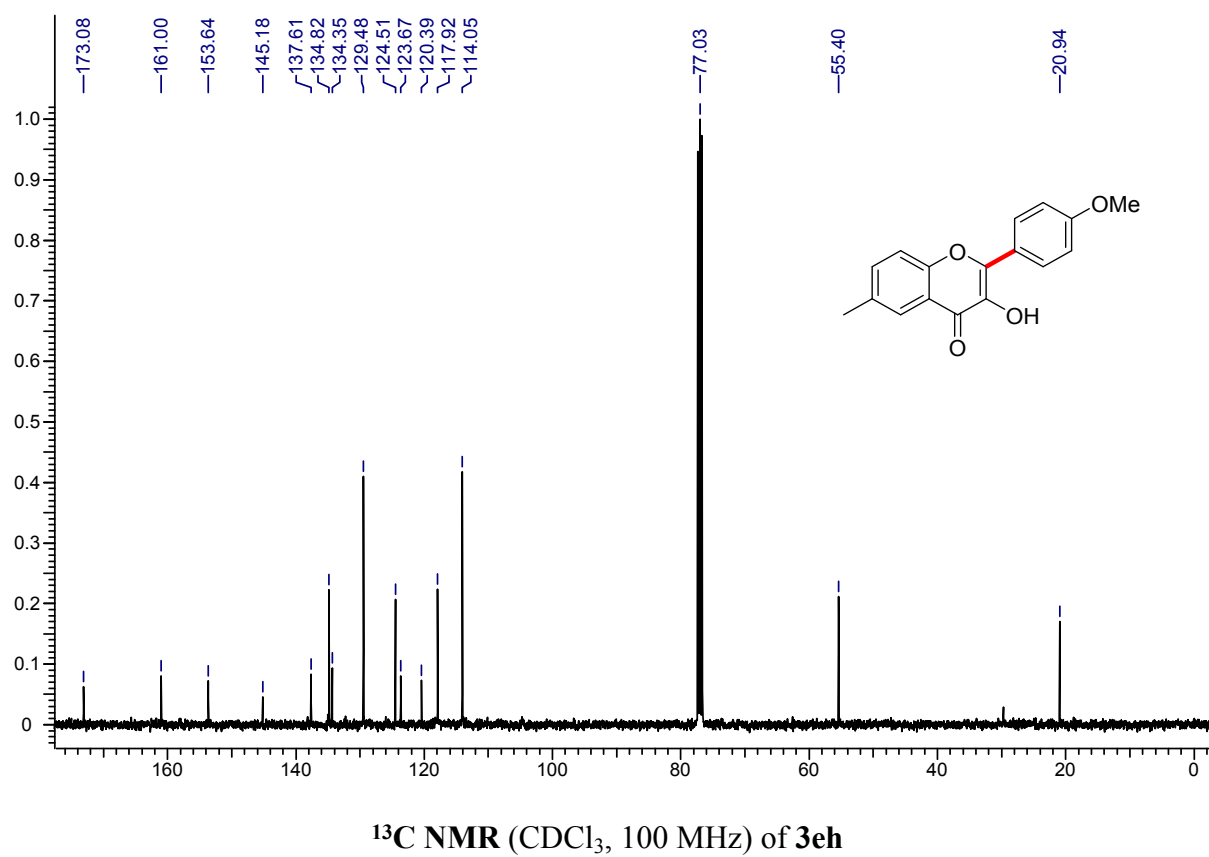
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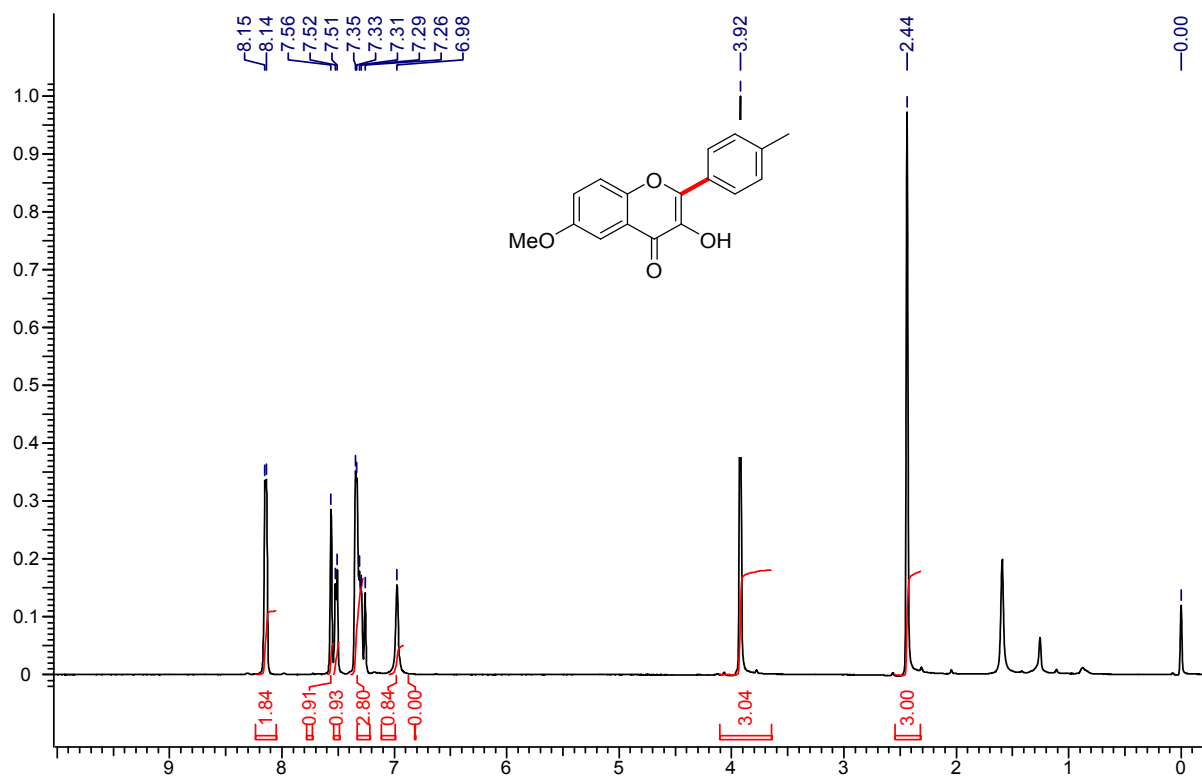
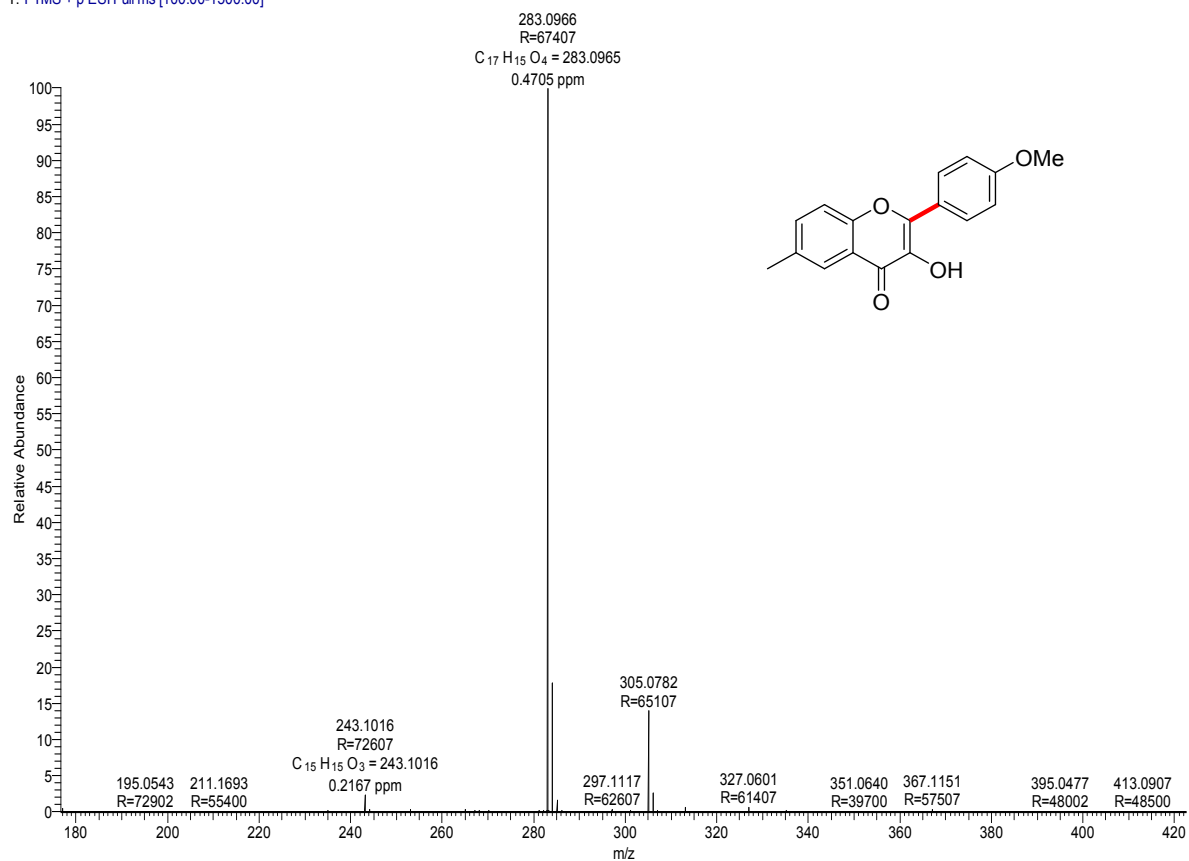
HRMS of 3ee

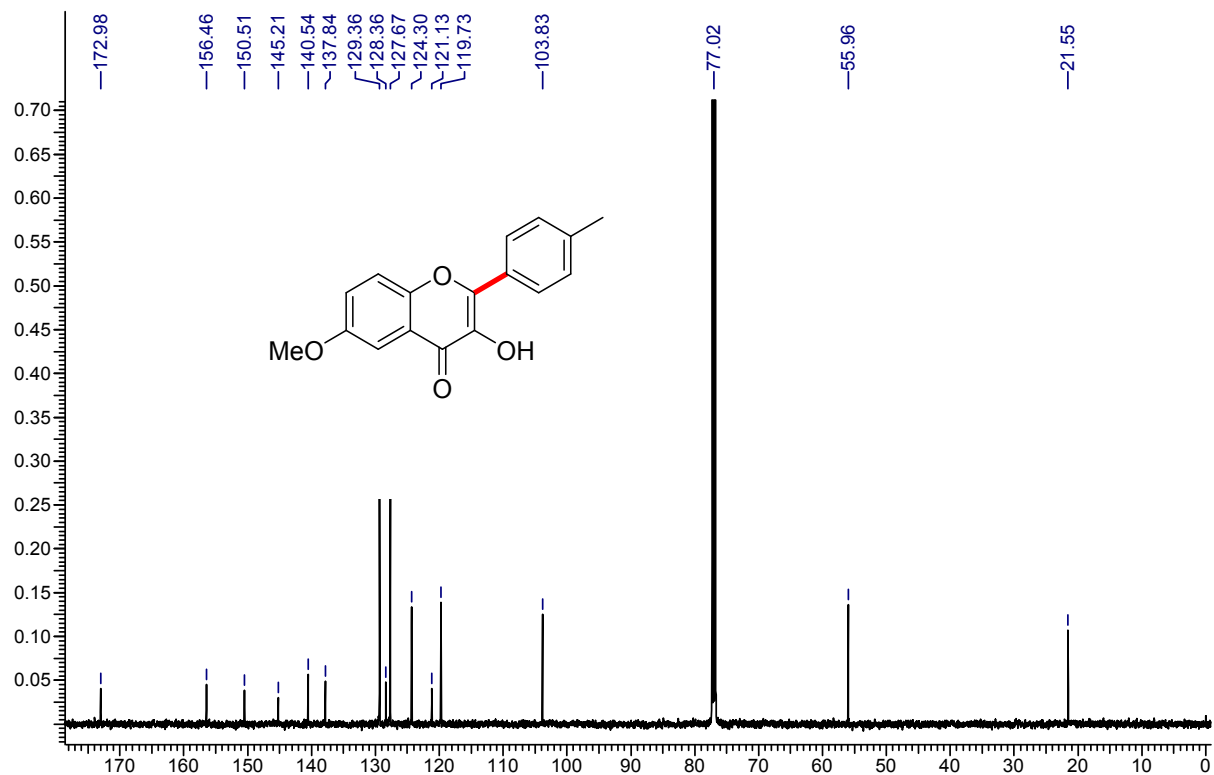


¹H NMR (CDCl₃, 400 MHz) of 3eh

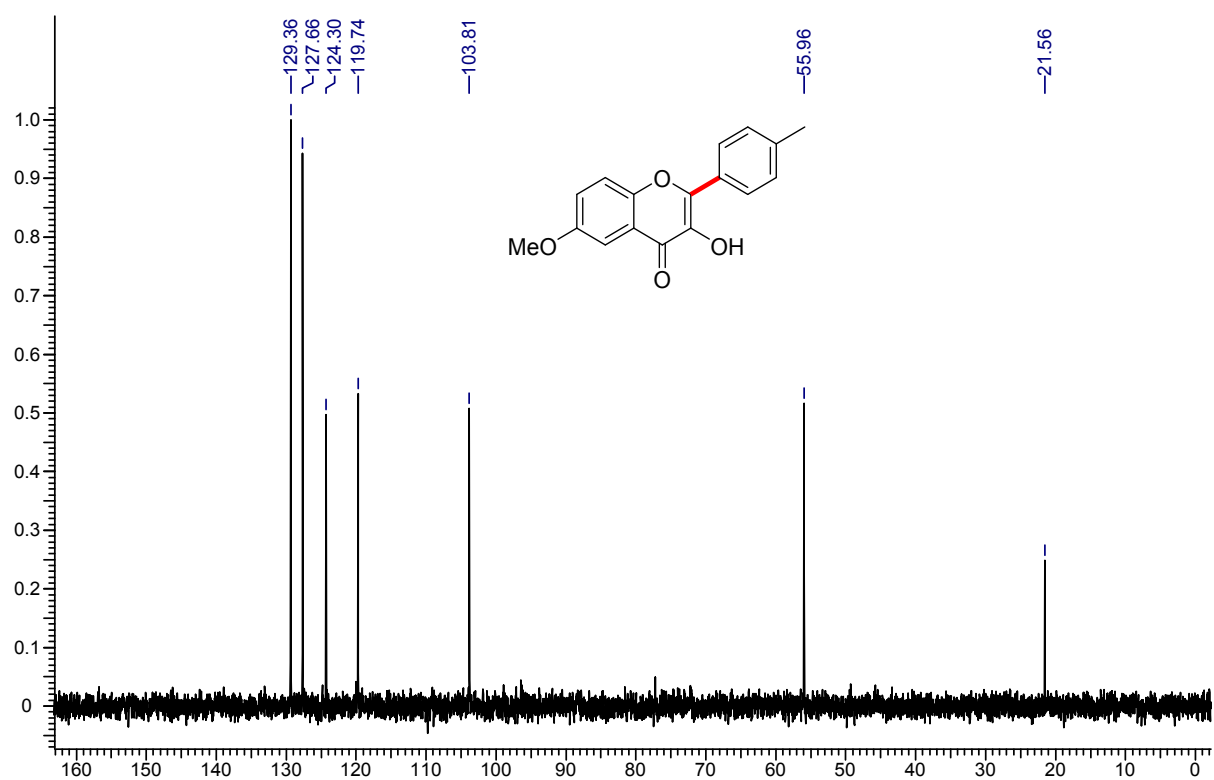


MT-10SP-2-132 #156 RT: 0.69 AV: 1 NL: 2.76E9
T: FTMS + p ESI Full ms [100.00-1500.00]



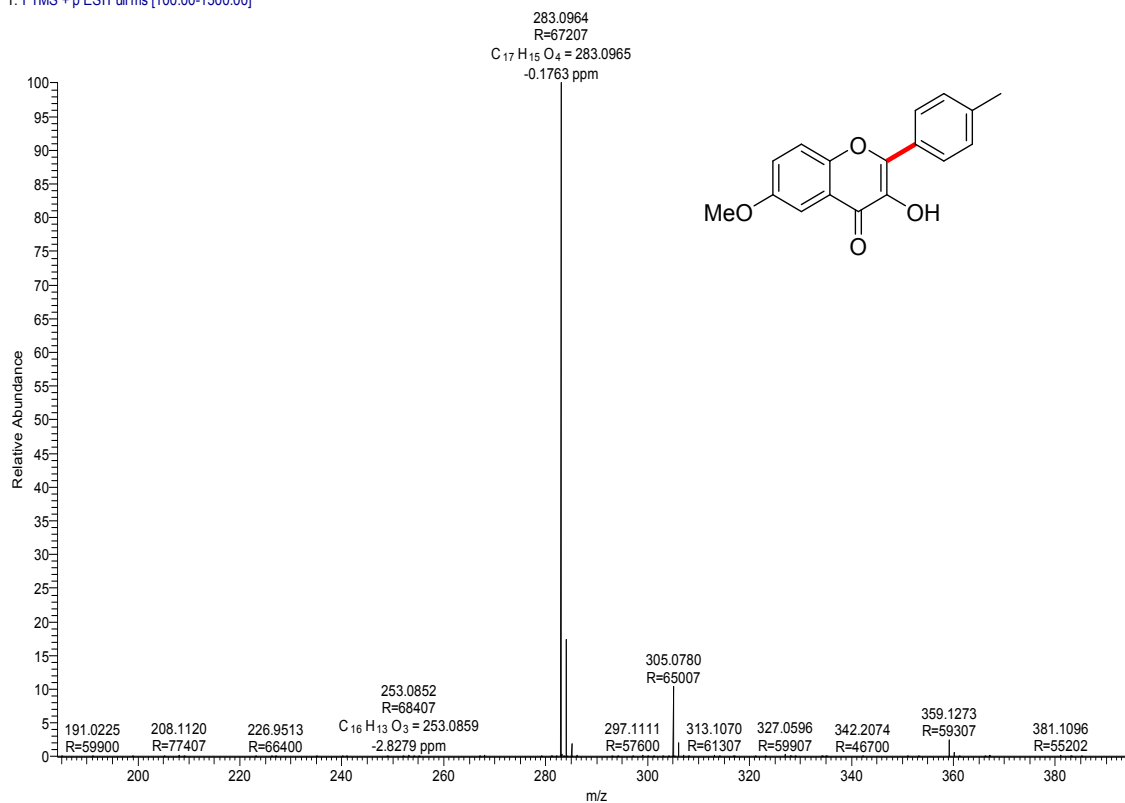


¹³C NMR (CDCl₃, 125 MHz) of **3fa**

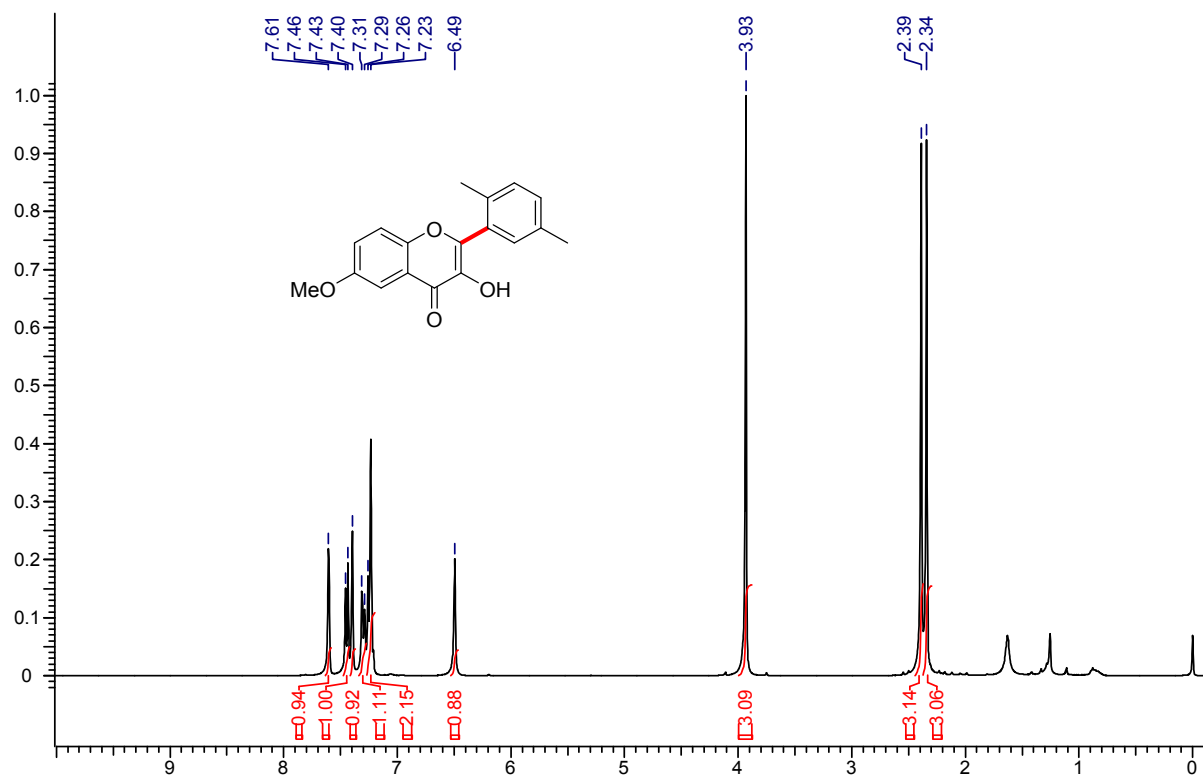


DEPT (CDCl₃, 125 MHz) of **3fa**

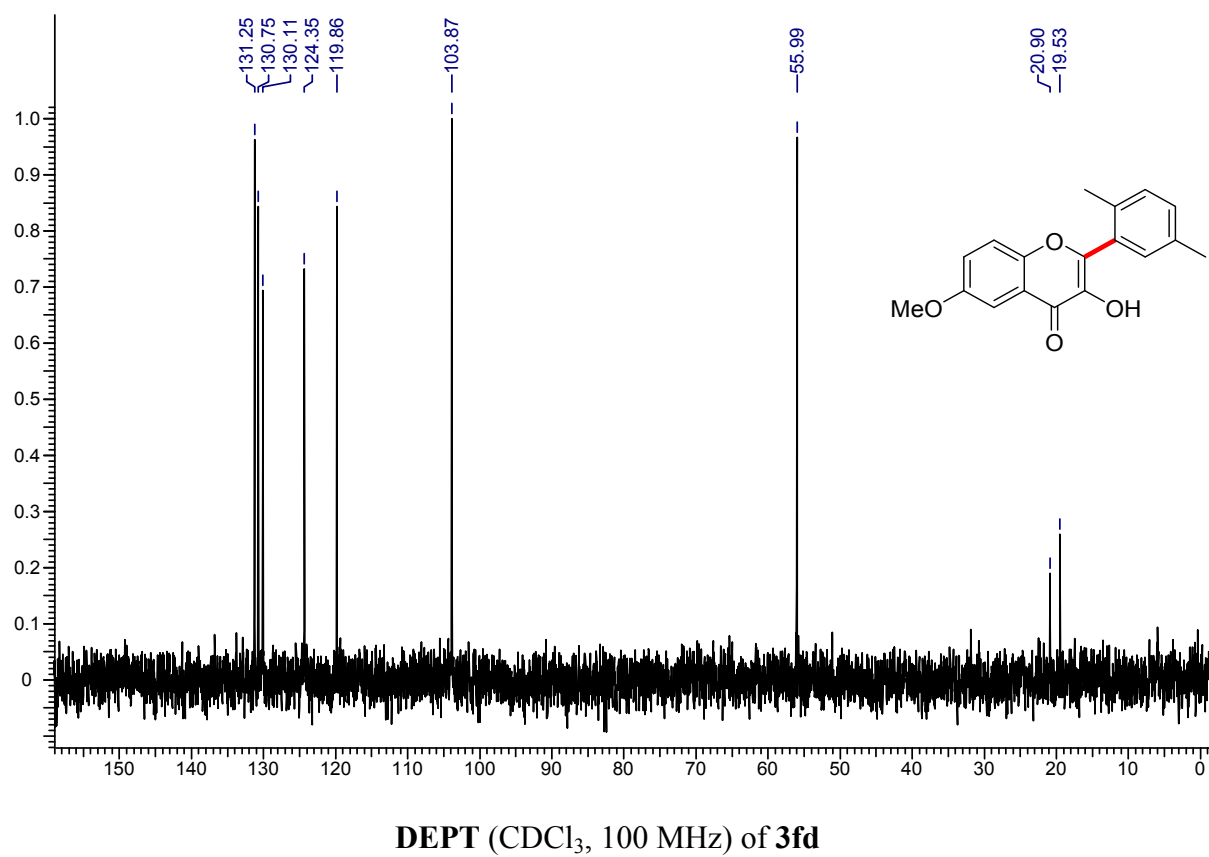
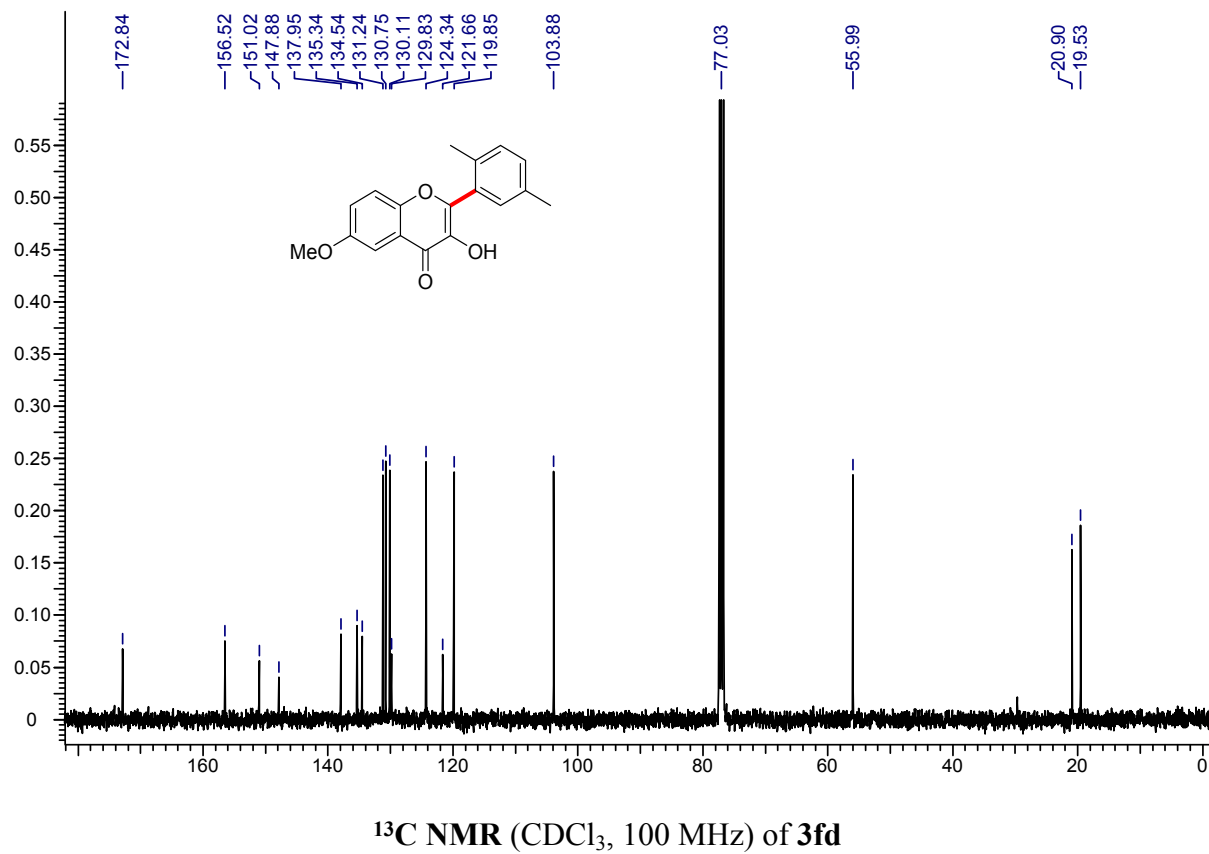
MT-10SP-2-135 #168 RT: 0.75 AV: 1 NL: 6.19E9
T: FTMS + p ESI Full ms [100.00-1500.00]

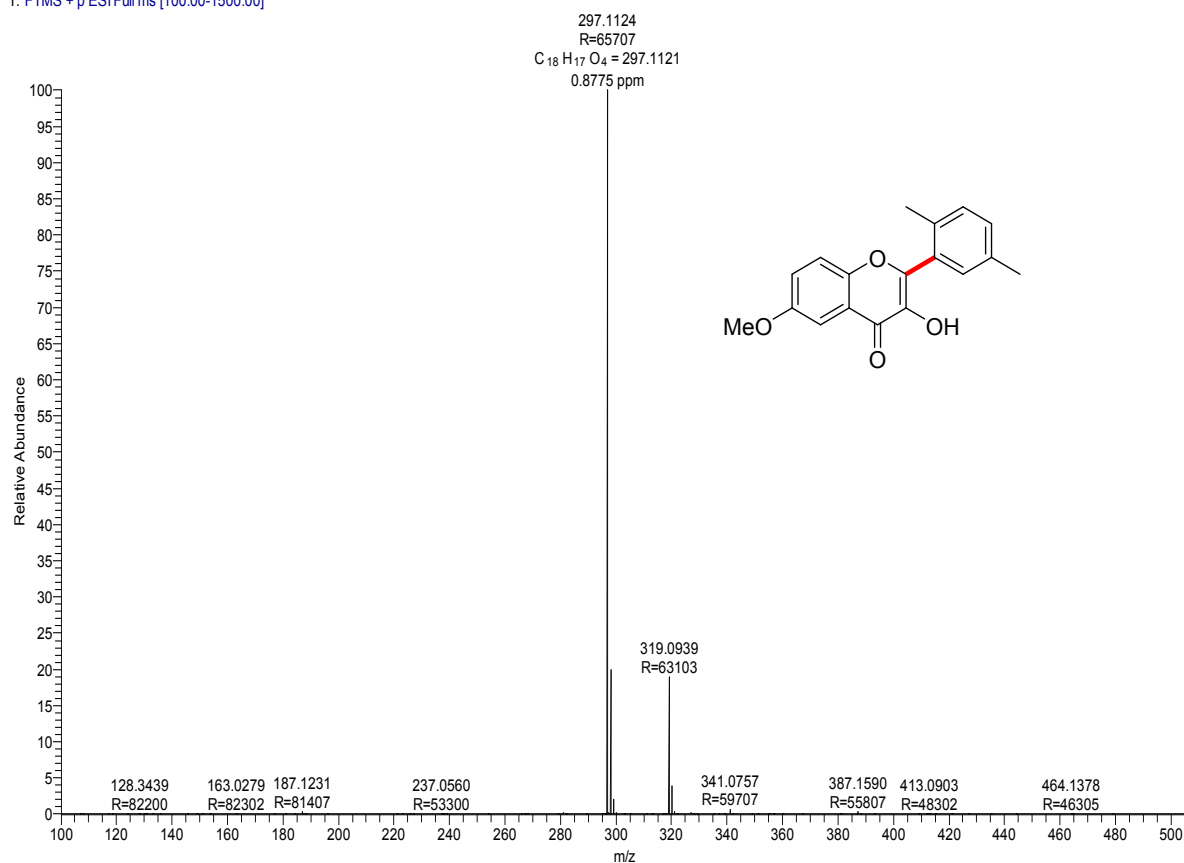


HRMS of 3fa

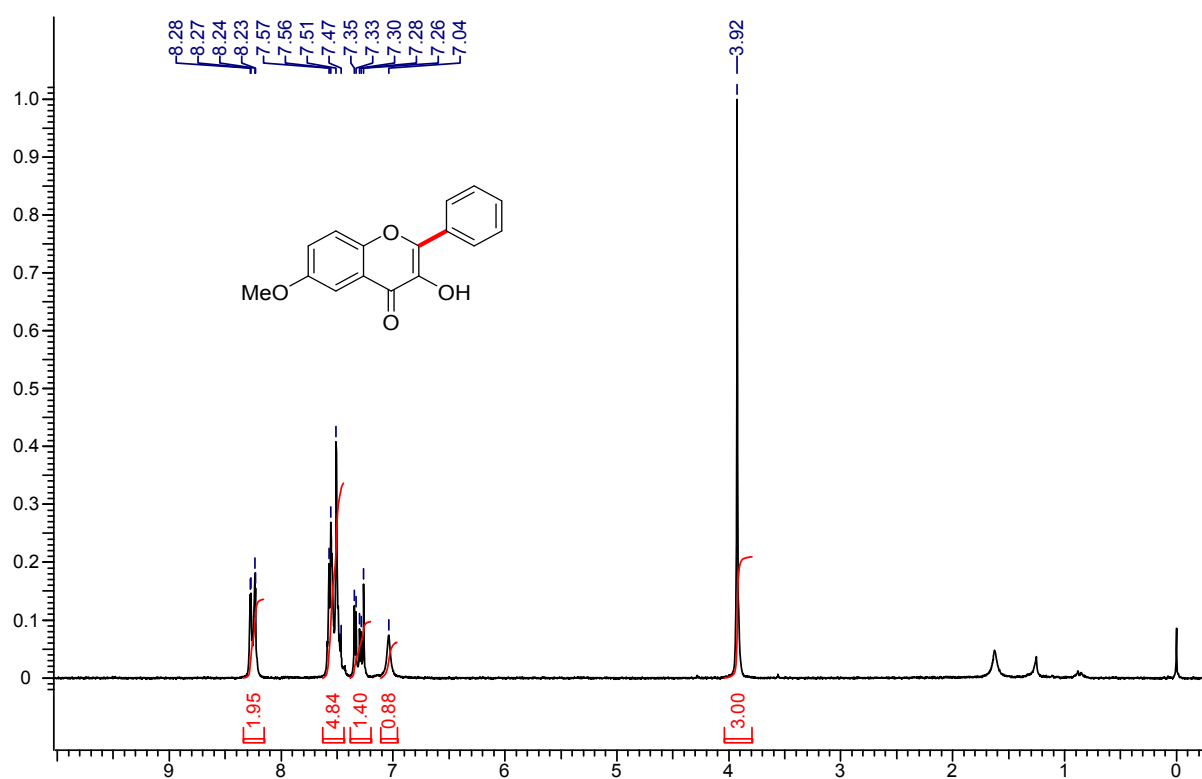


¹H NMR (CDCl₃, 400 MHz) of 3fd

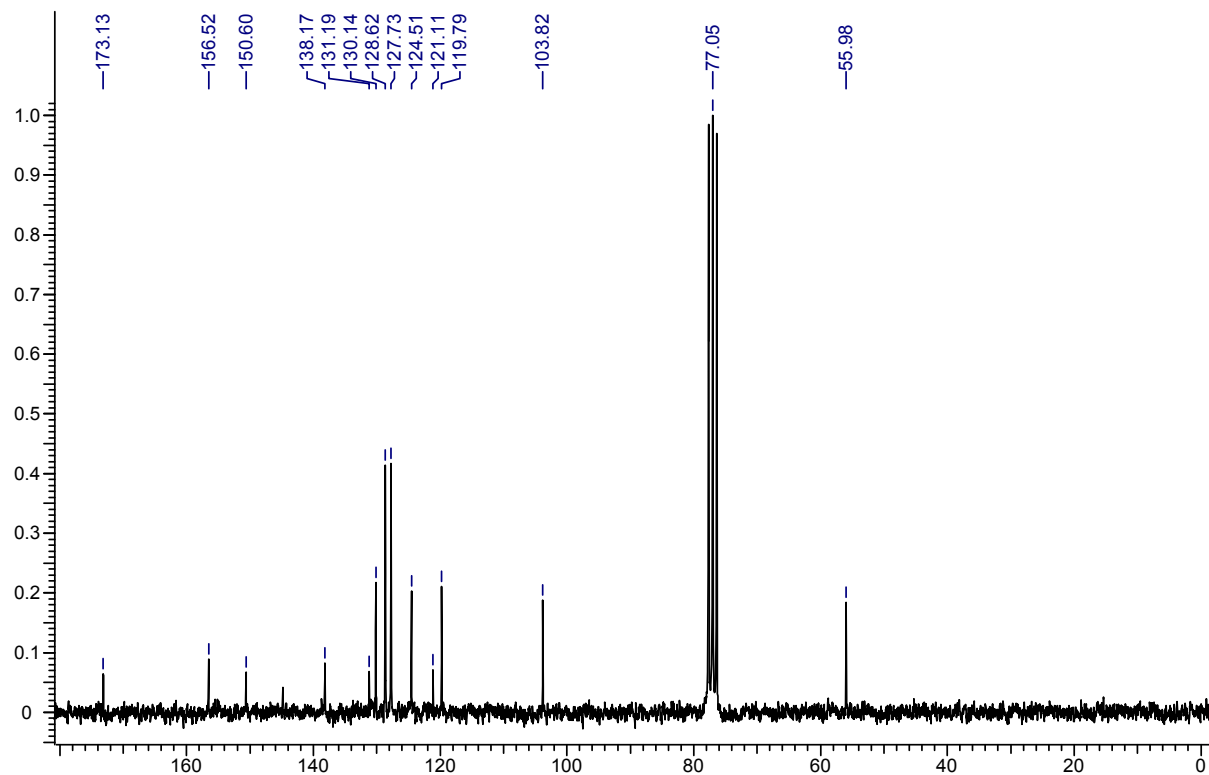




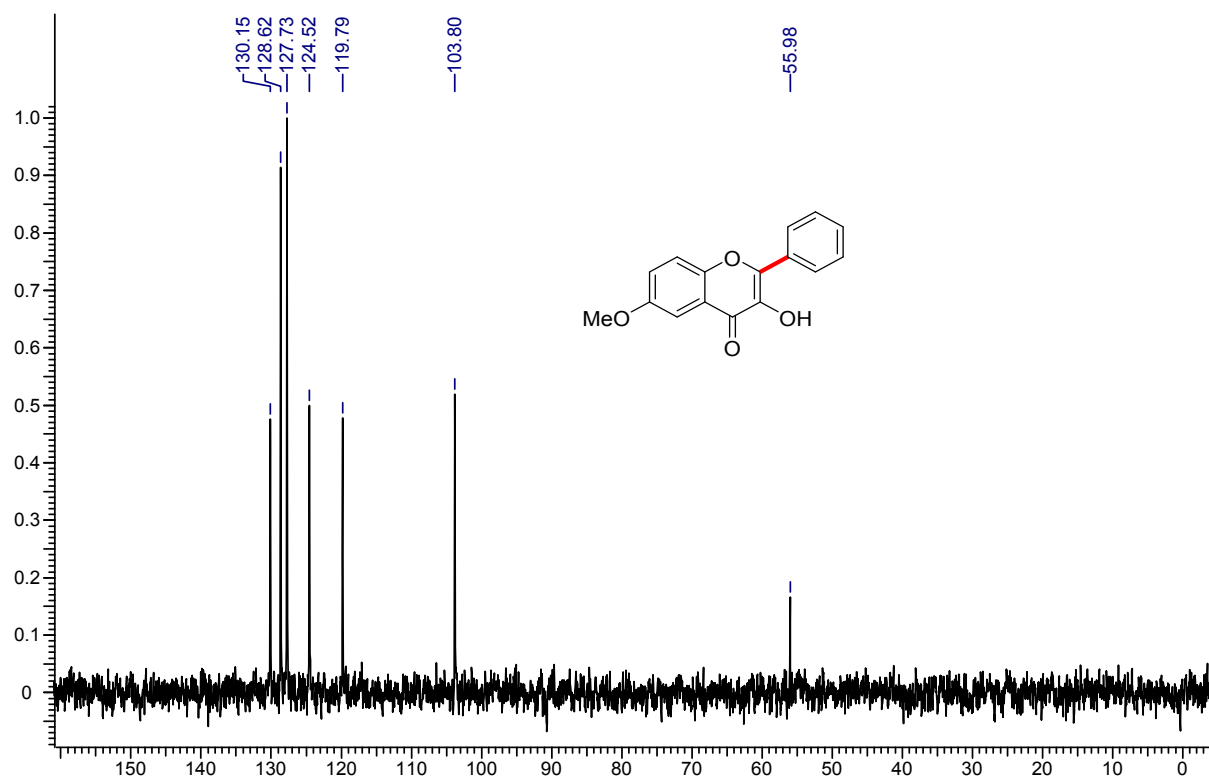
HRMS of 3fd



¹H NMR (CDCl₃, 200 MHz) of 3fi

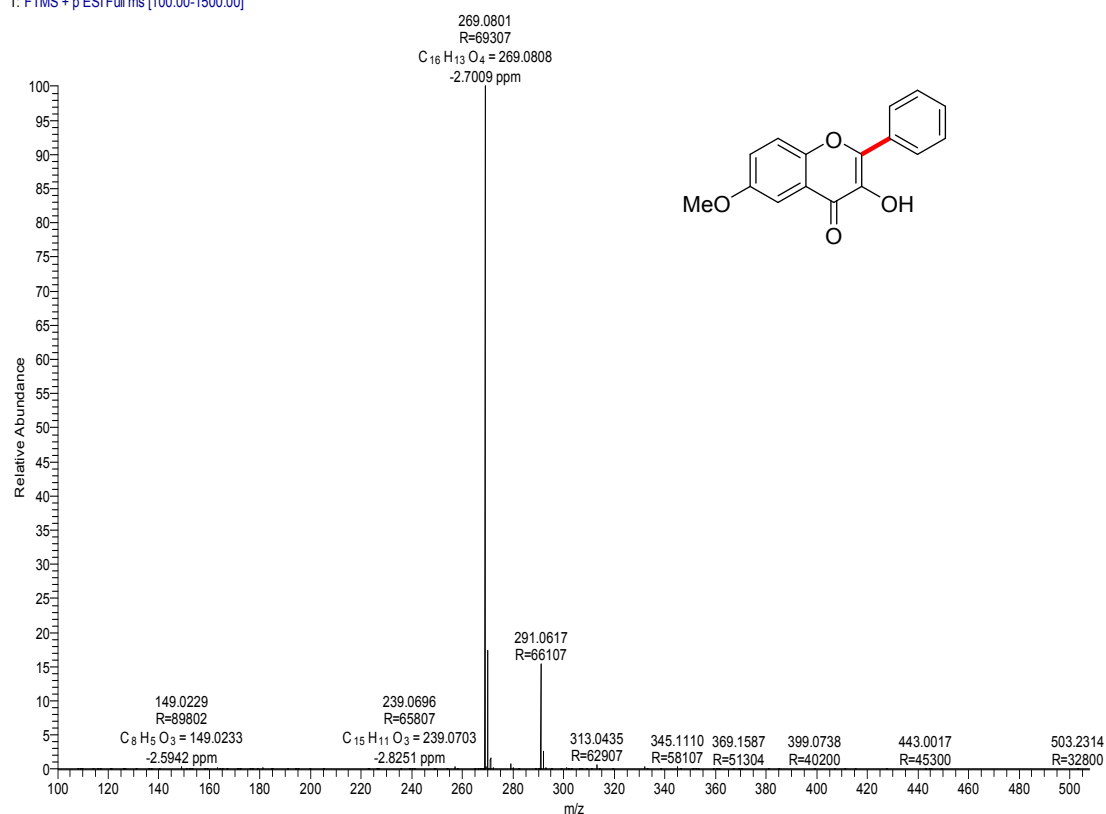


^{13}C NMR (CDCl_3 , 50 MHz) of **3fi**

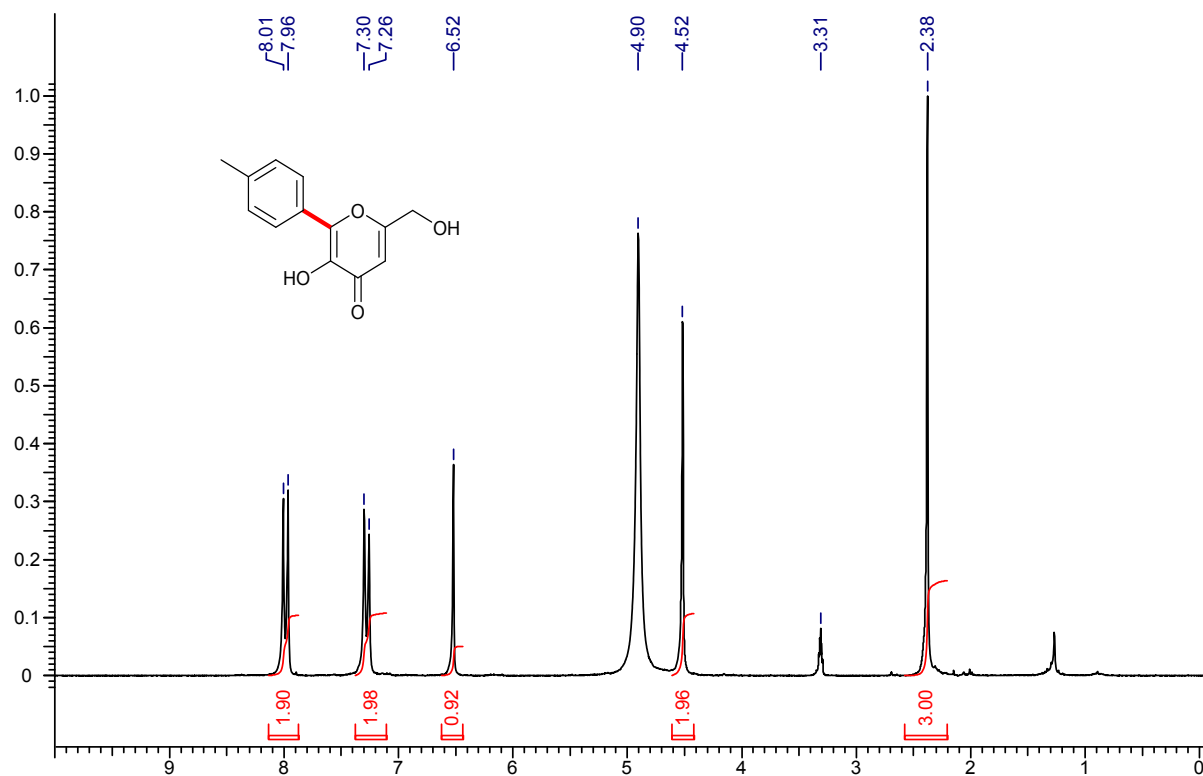


DEPT (CDCl_3 , 50 MHz) of **3fi**

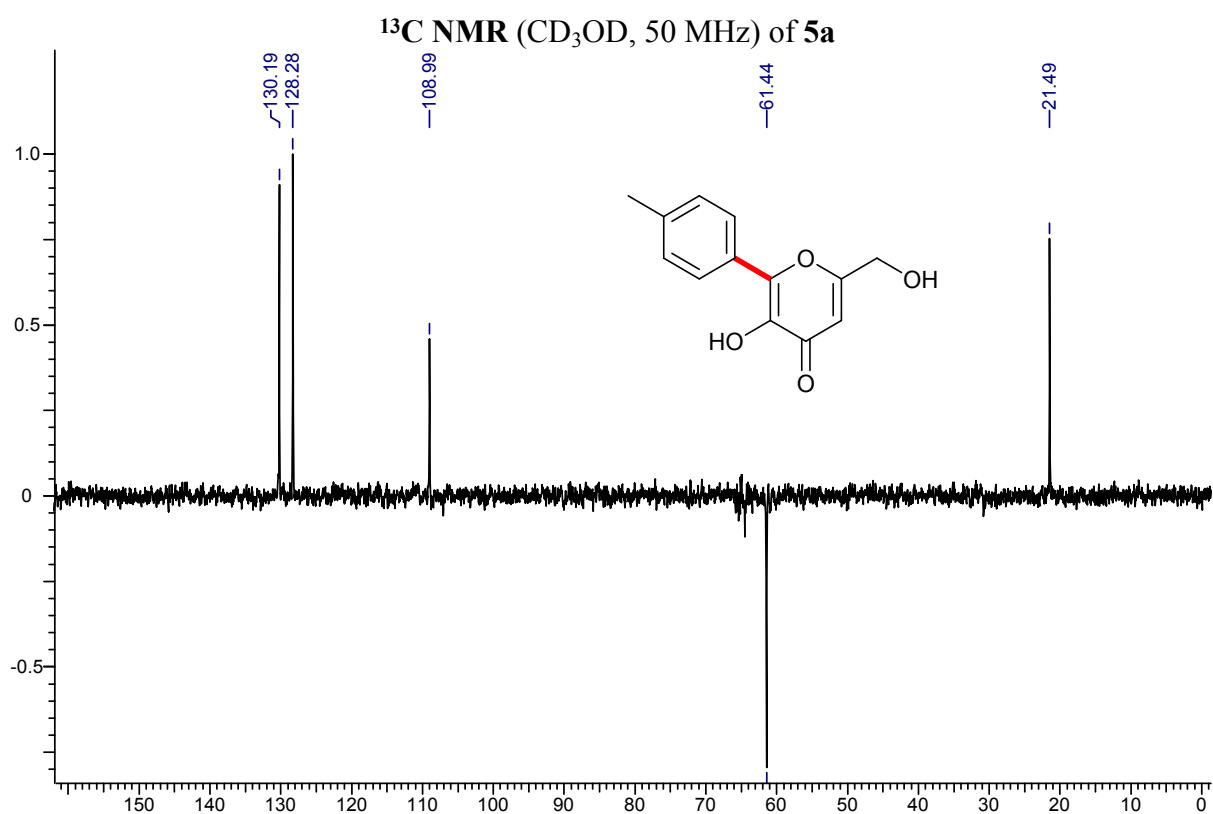
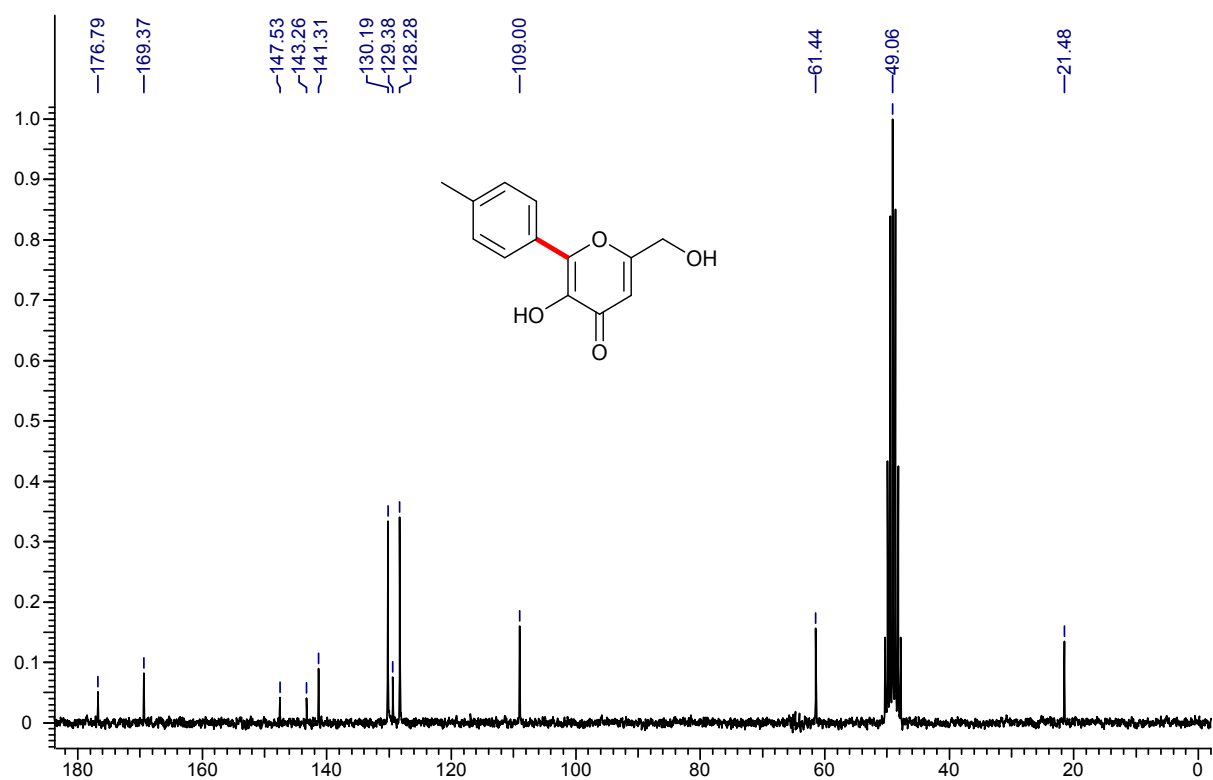
SP-2-138 #136 RT: 0.60 AV: 1 NL: 4.30E9
T: FTMS + p ESI Full ms [100.00-1500.00]



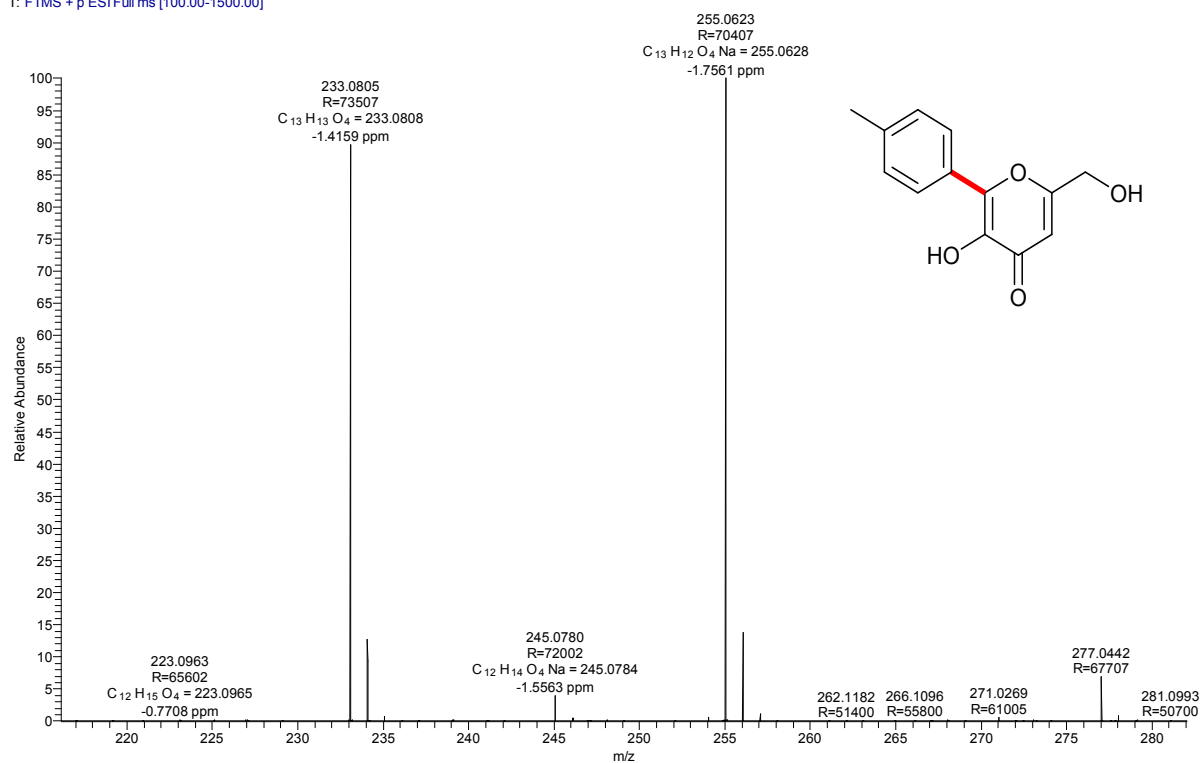
HRMS of 3fi



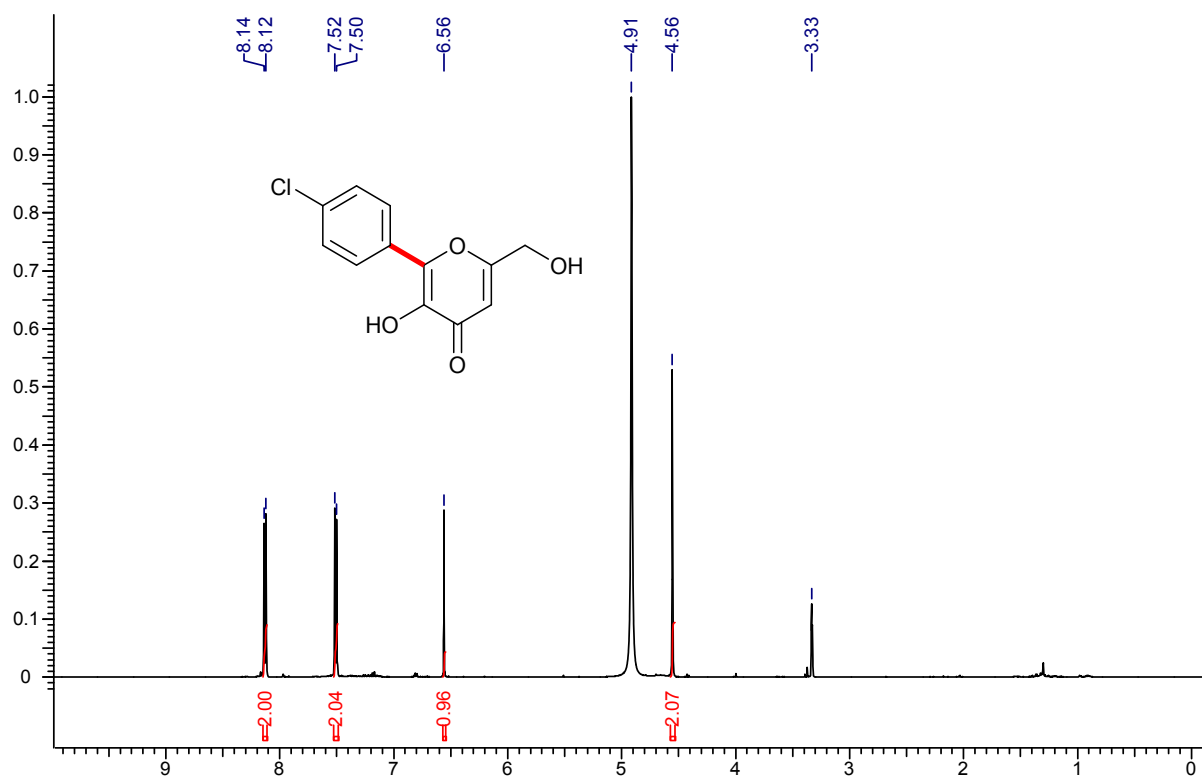
¹H NMR (CD₃OD, 200 MHz) of 5a



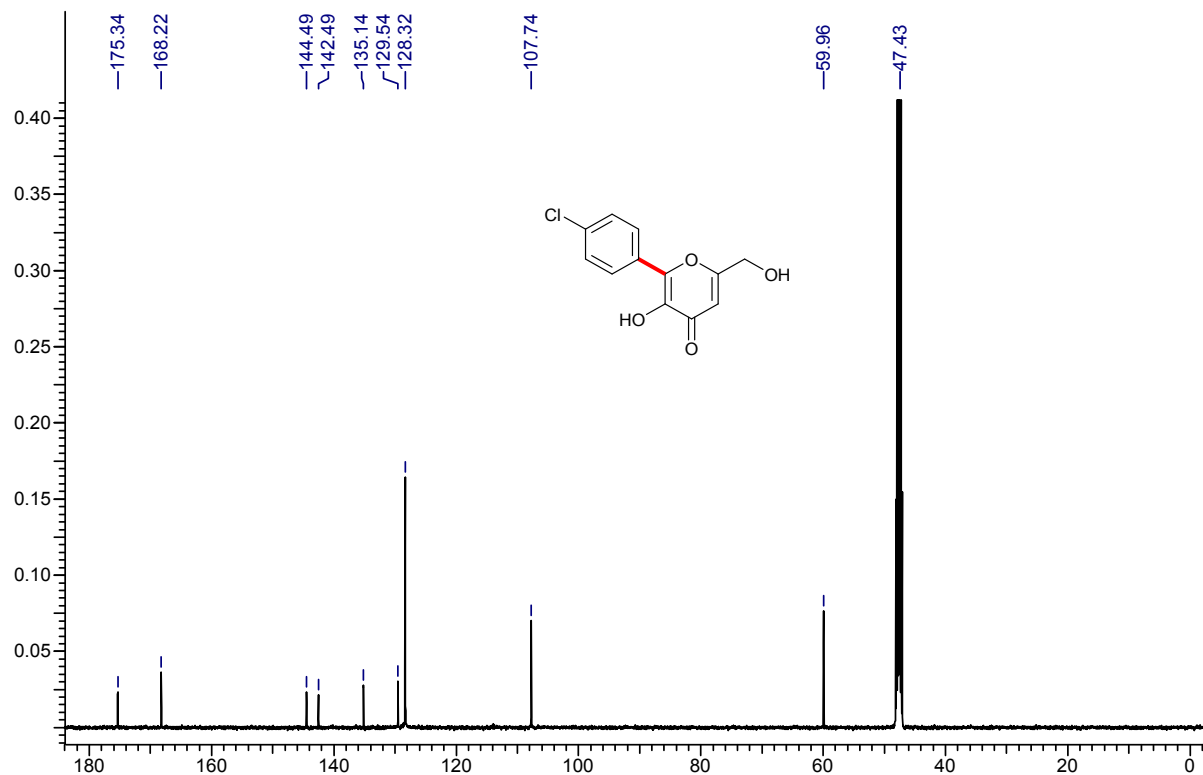
SP-1-113 #104 RT: 0.46 AV: 1 NL: 6.47E8
T: FTMS + p ESI Full ms [100.00-1500.00]



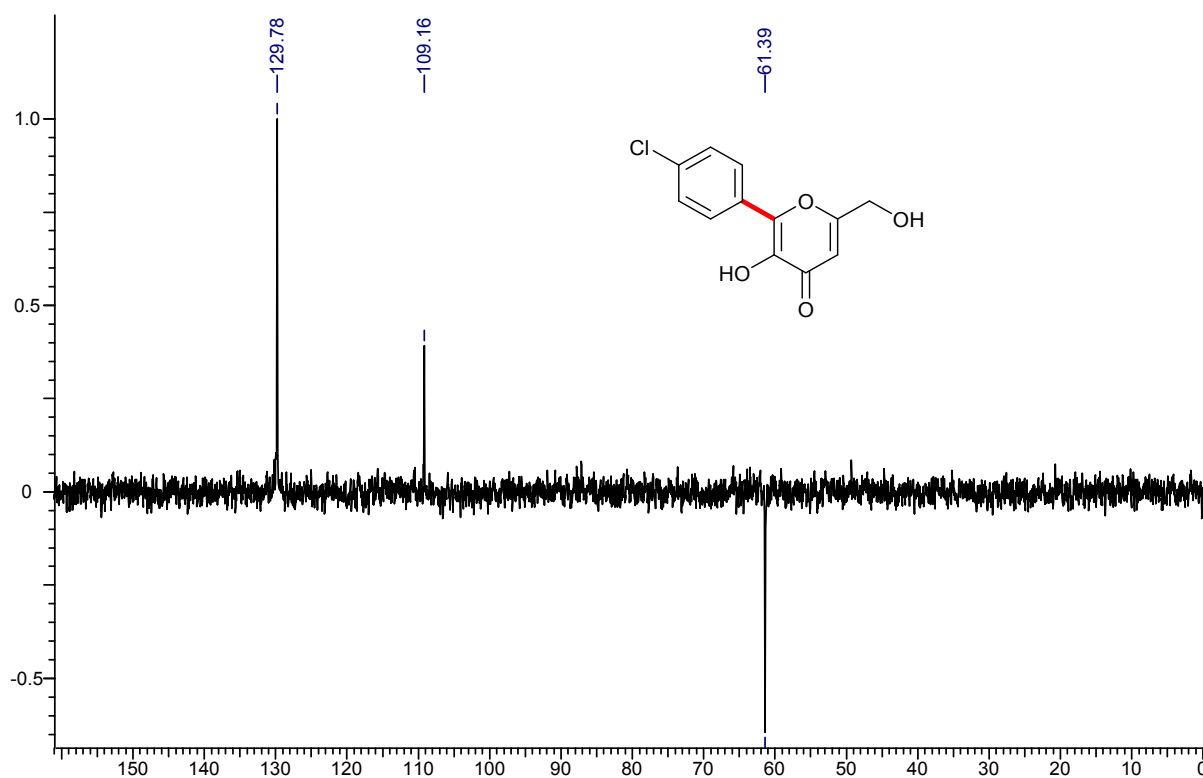
HRMS of **5a**



¹H NMR (CD₃OD, 500 MHz) of **5b**

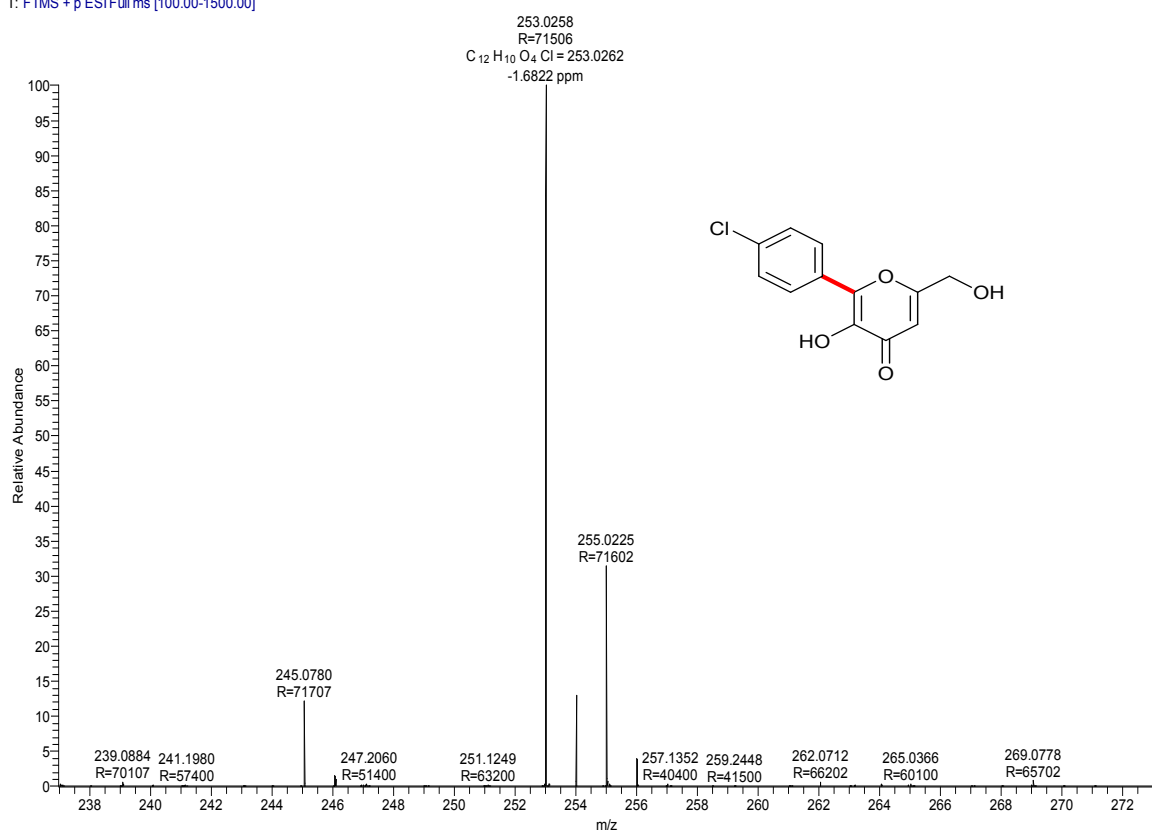


¹³C NMR (CD₃OD, 125 MHz) of **5b**

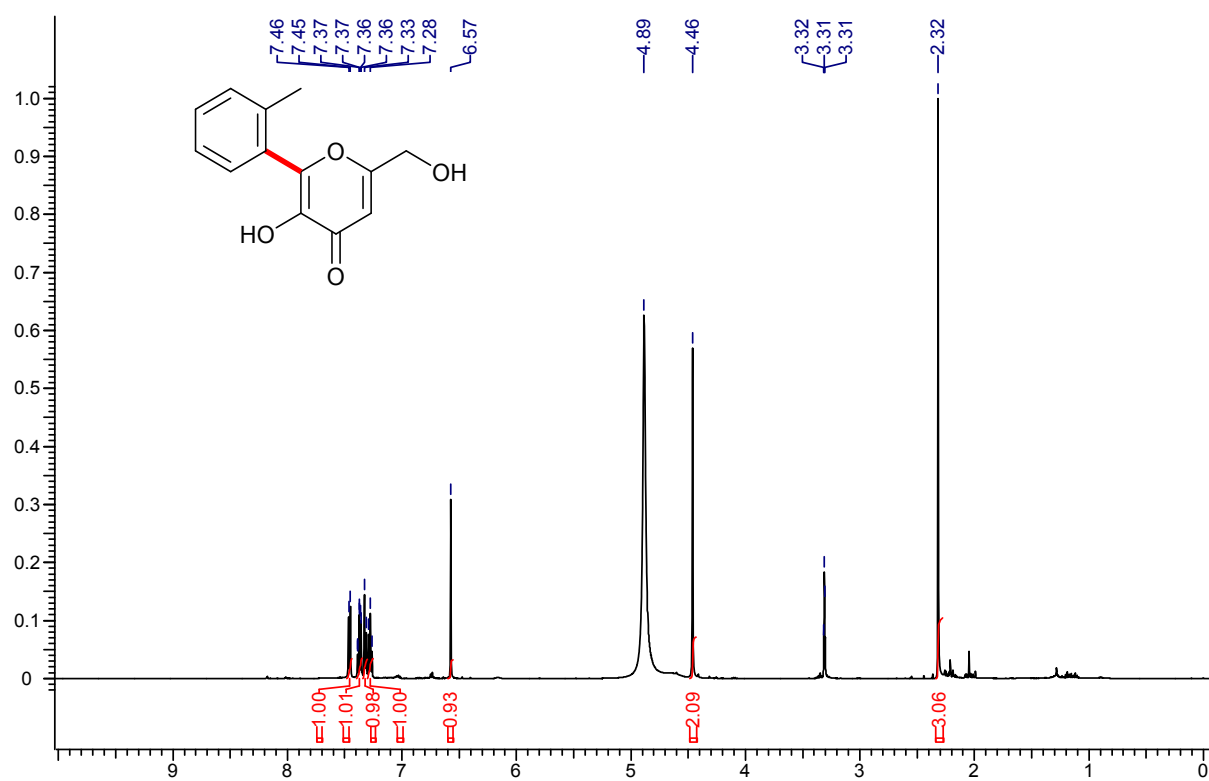


DEPT (CD₃OD, 50 MHz) of **5b**

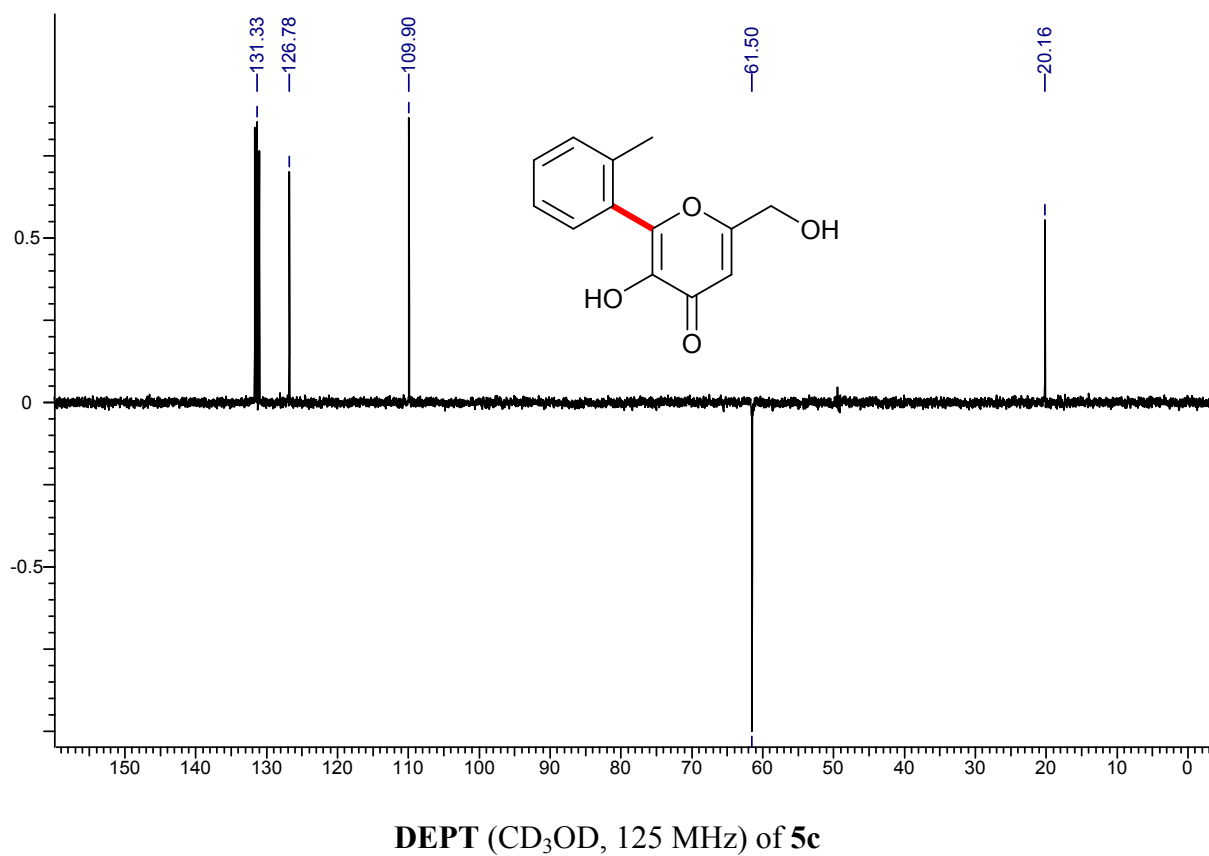
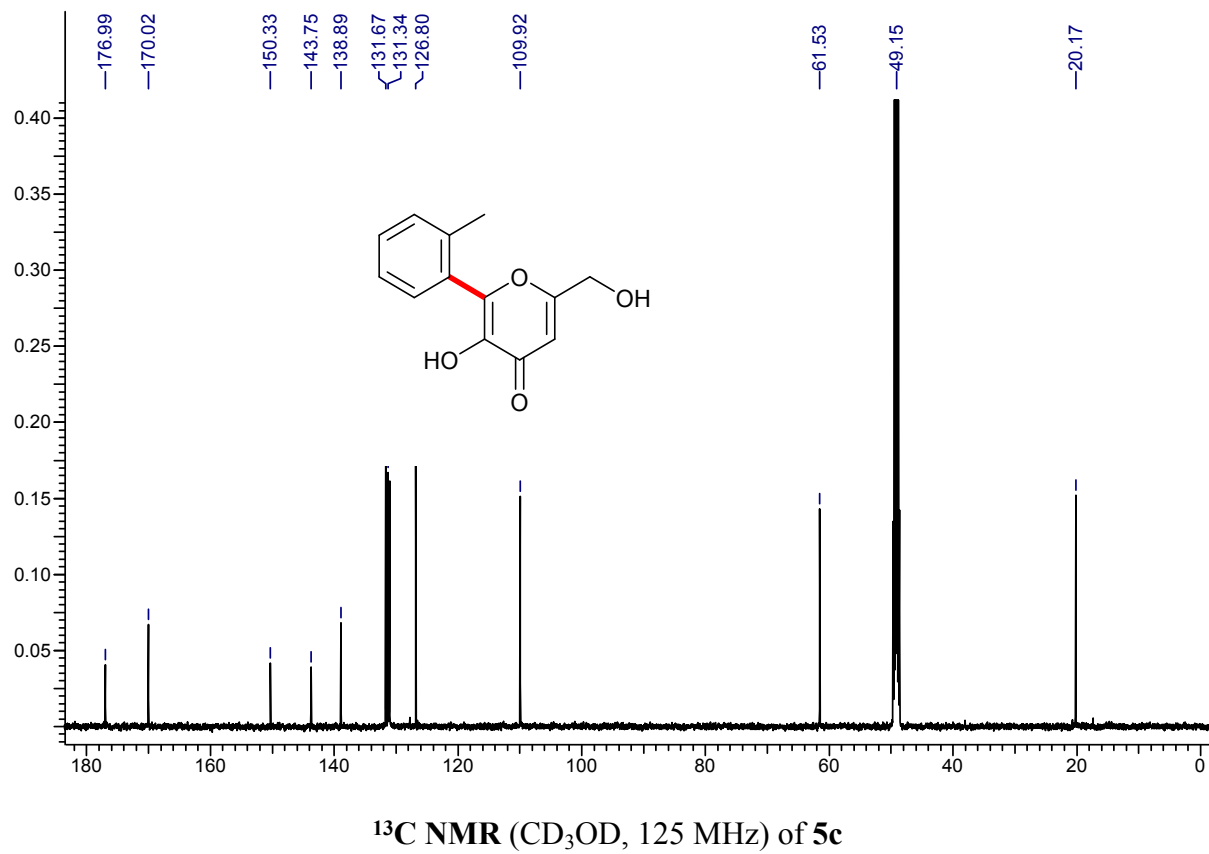
SP-1-93 #107 RT: 0.47 AV: 1 NL: 2.26E8
T: FTMS + p ESI Full ms [100.00-1500.00]

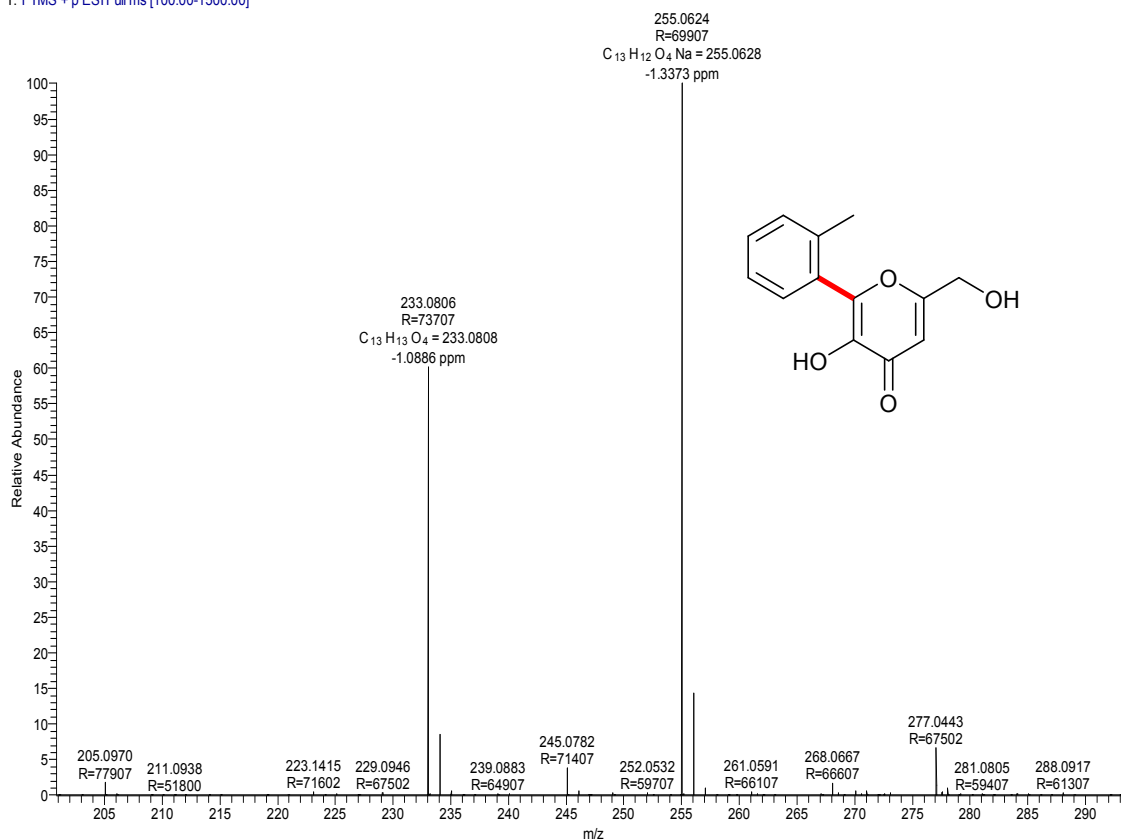


HRMS of 5b

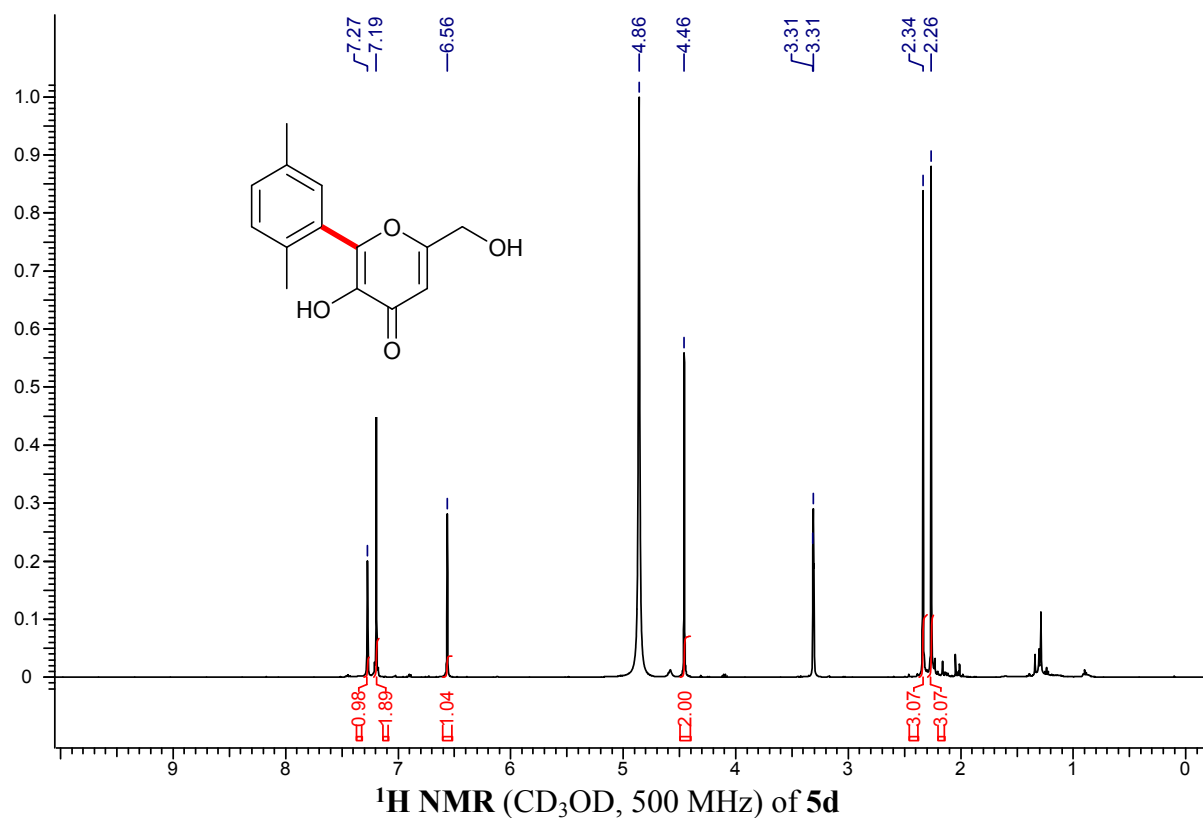


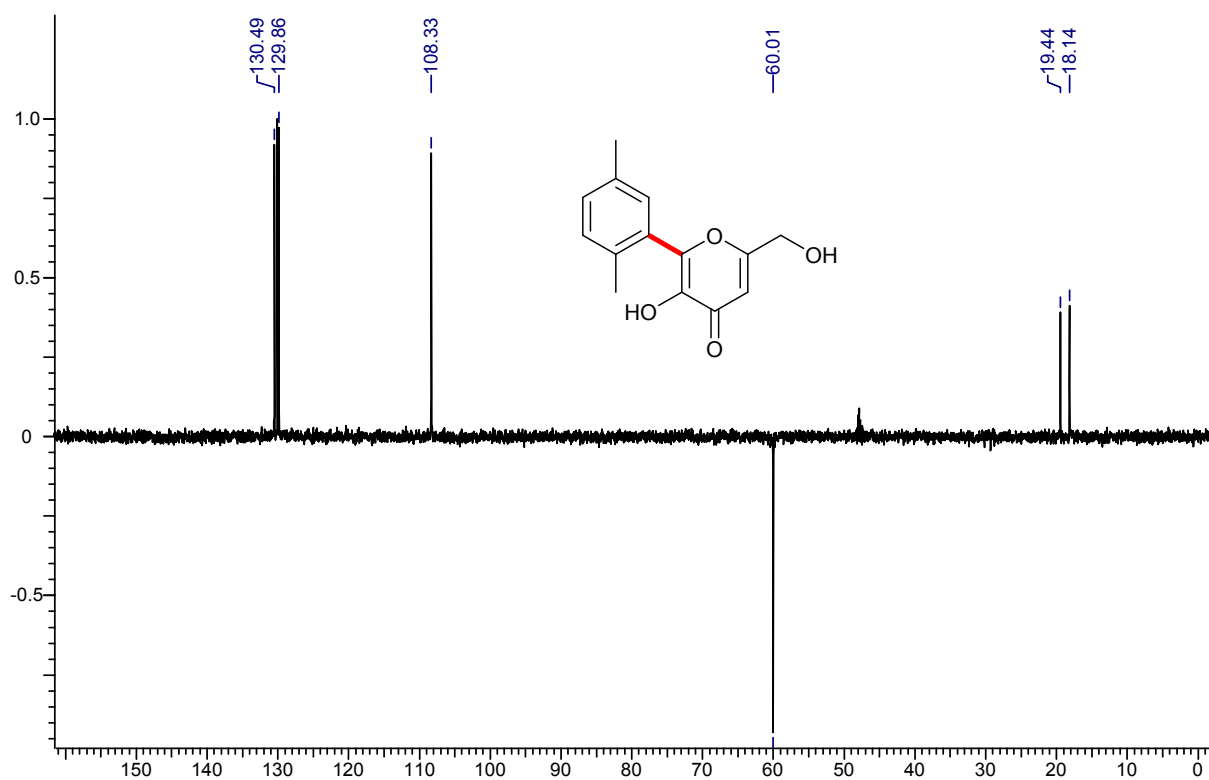
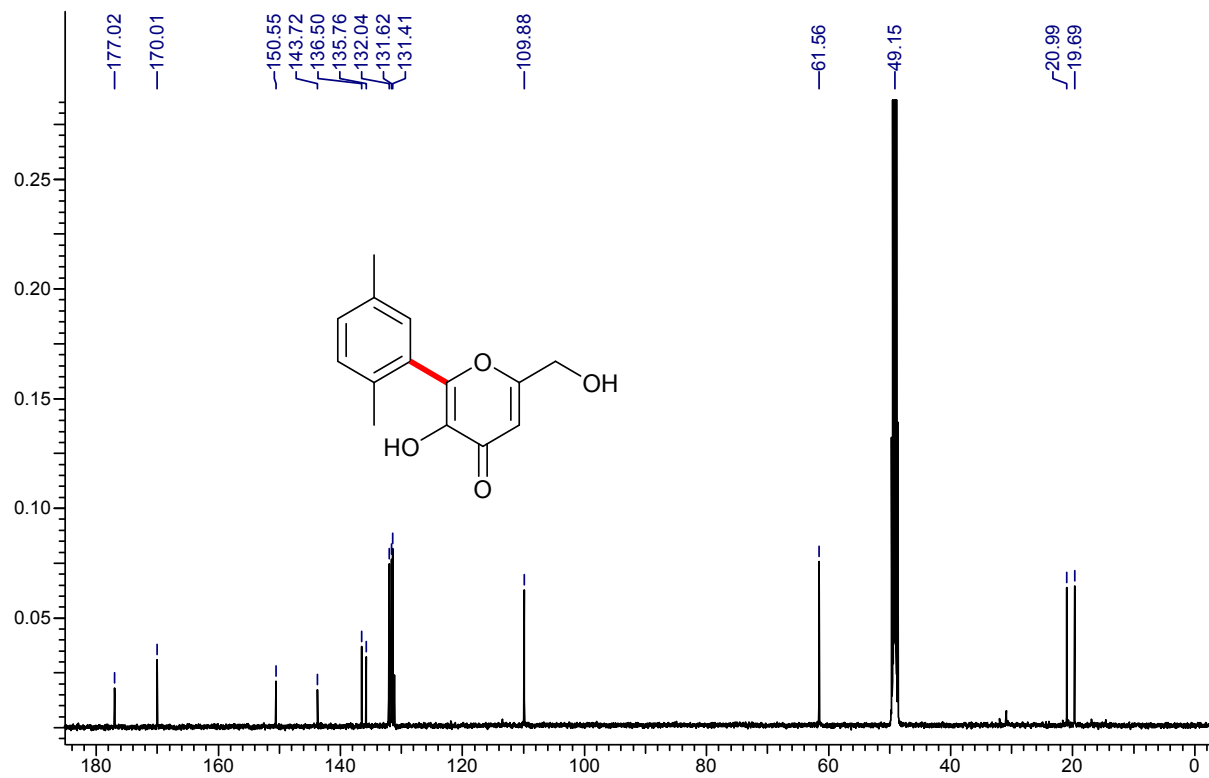
¹H NMR (CD₃OD, 500 MHz) of 5c



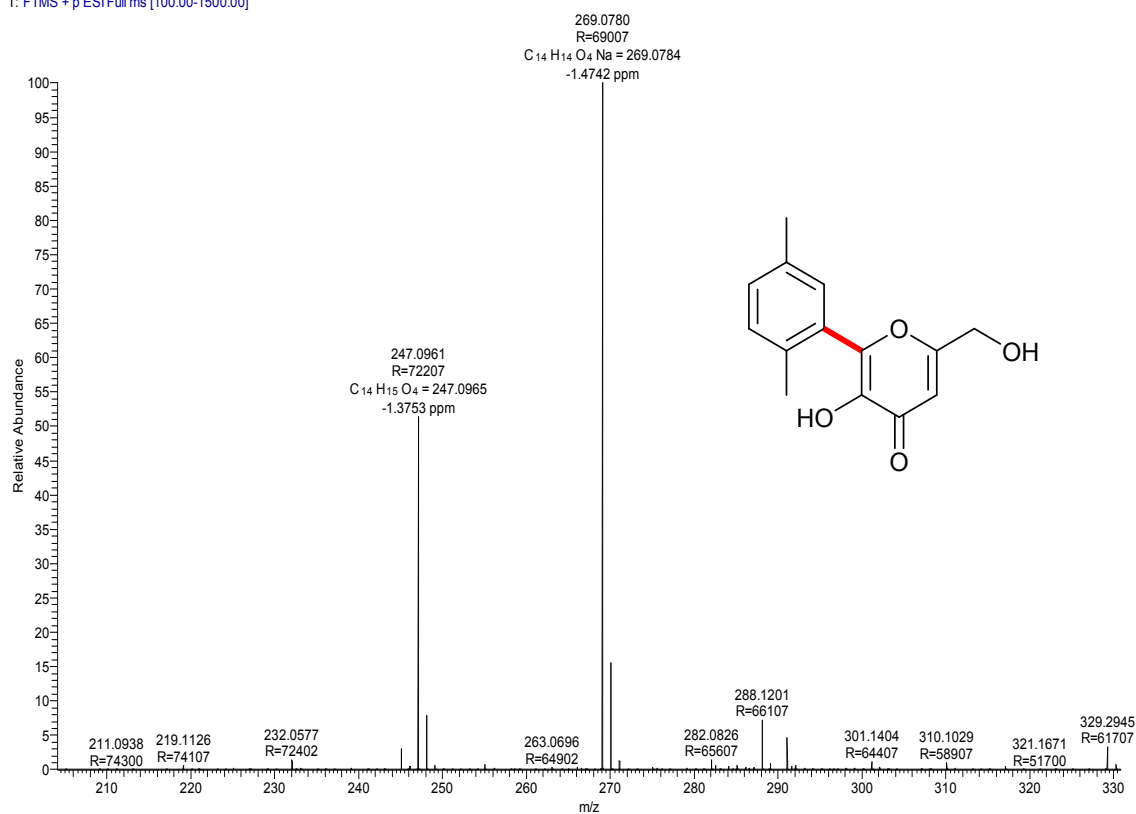


HRMS of 5c

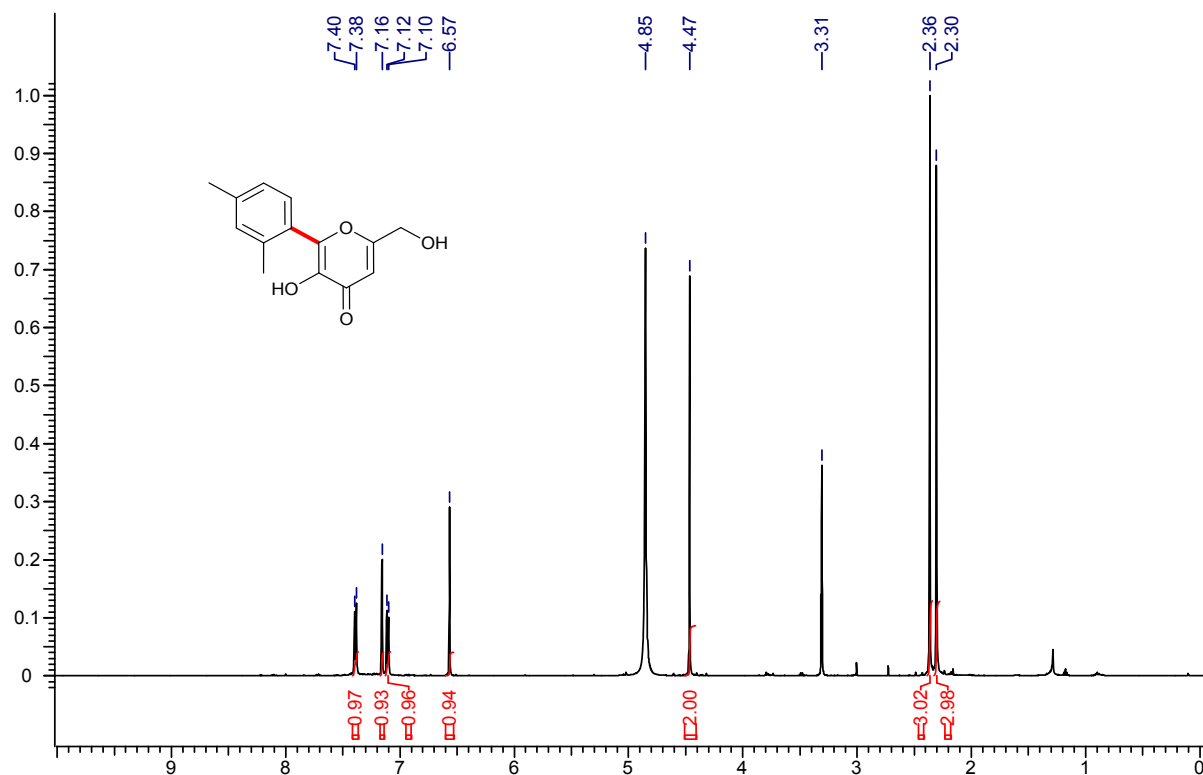




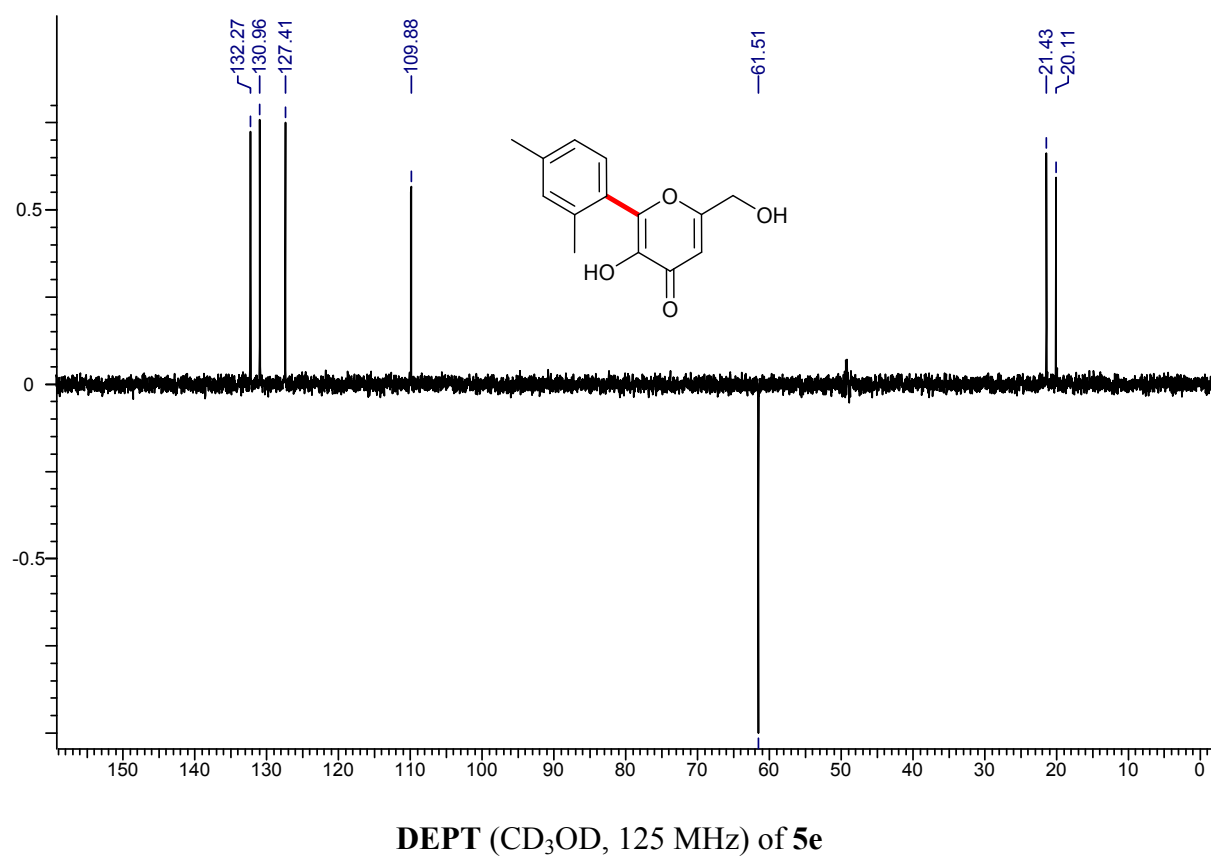
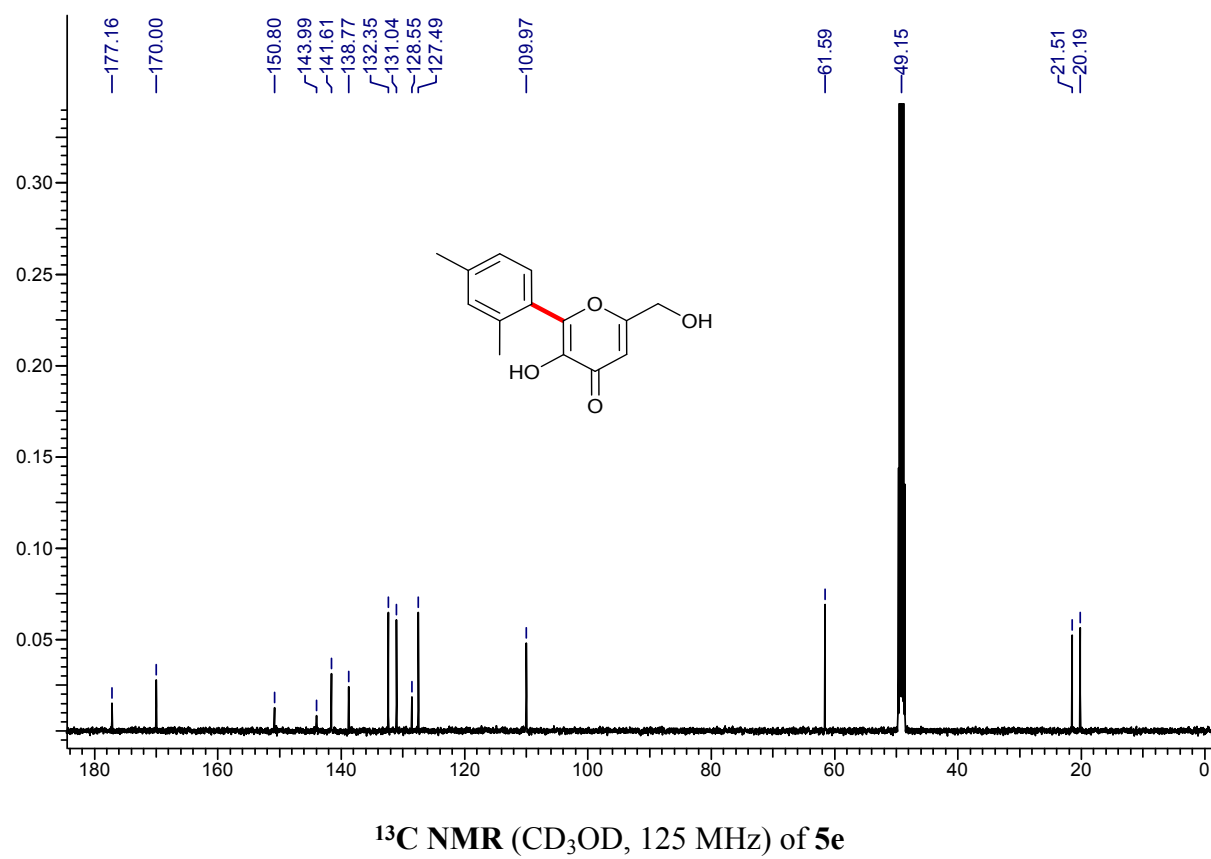
SP-2-14 #102 RT: 0.45 AV: 1 NL: 7.69E8
T: FTMS + p ESI Full ms [100.00-1500.00]



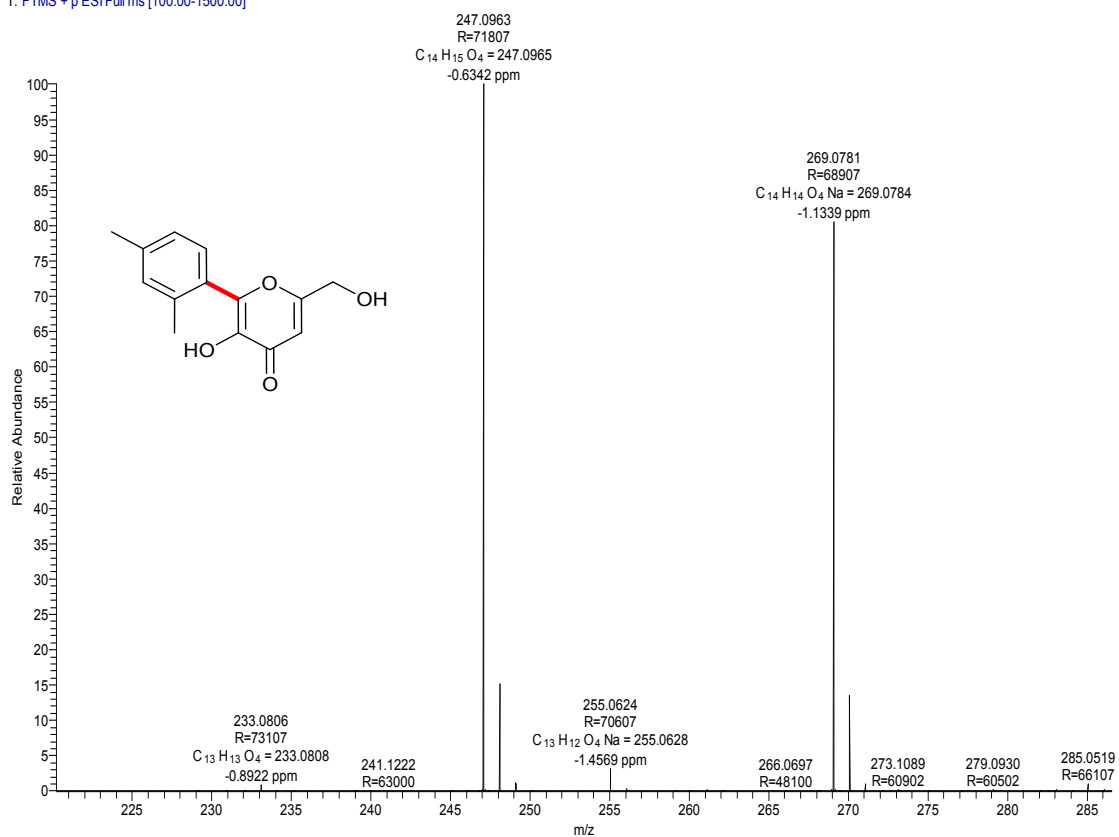
HRMS of 5d



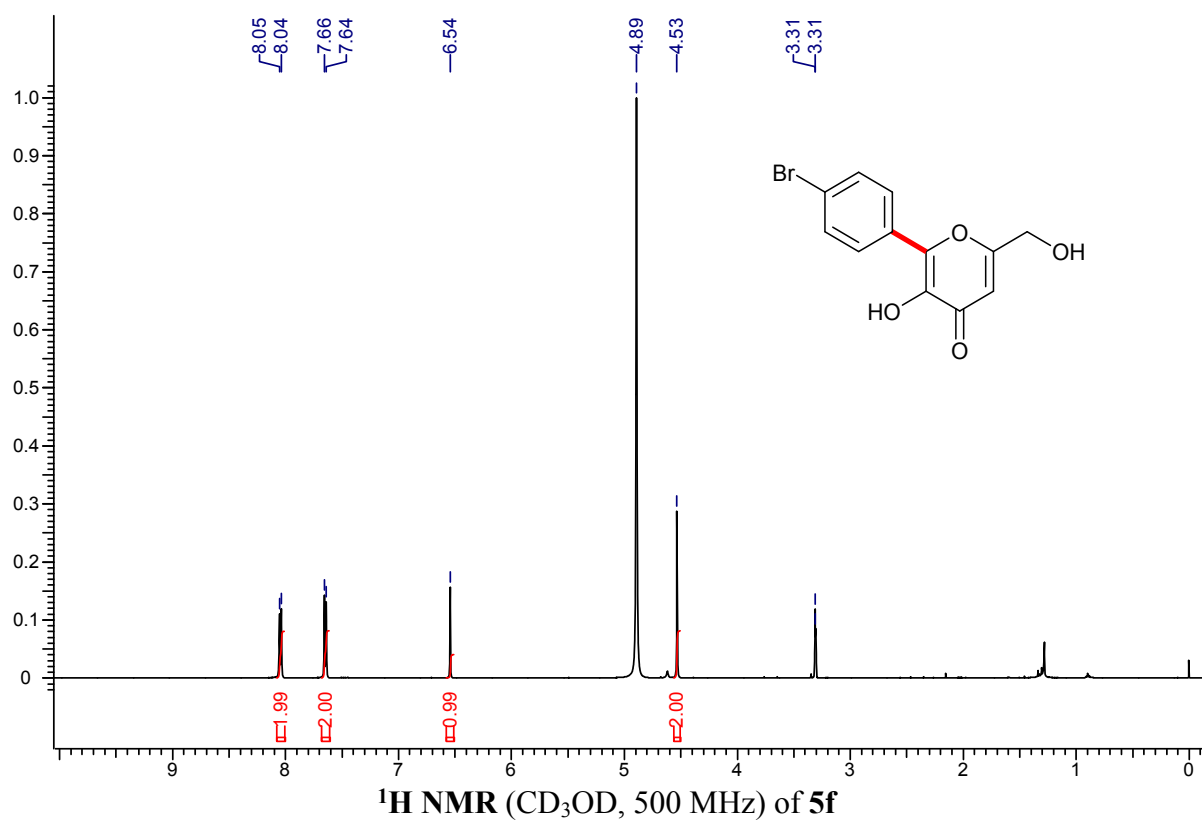
¹H NMR (CD₃OD, 500 MHz) of 5e



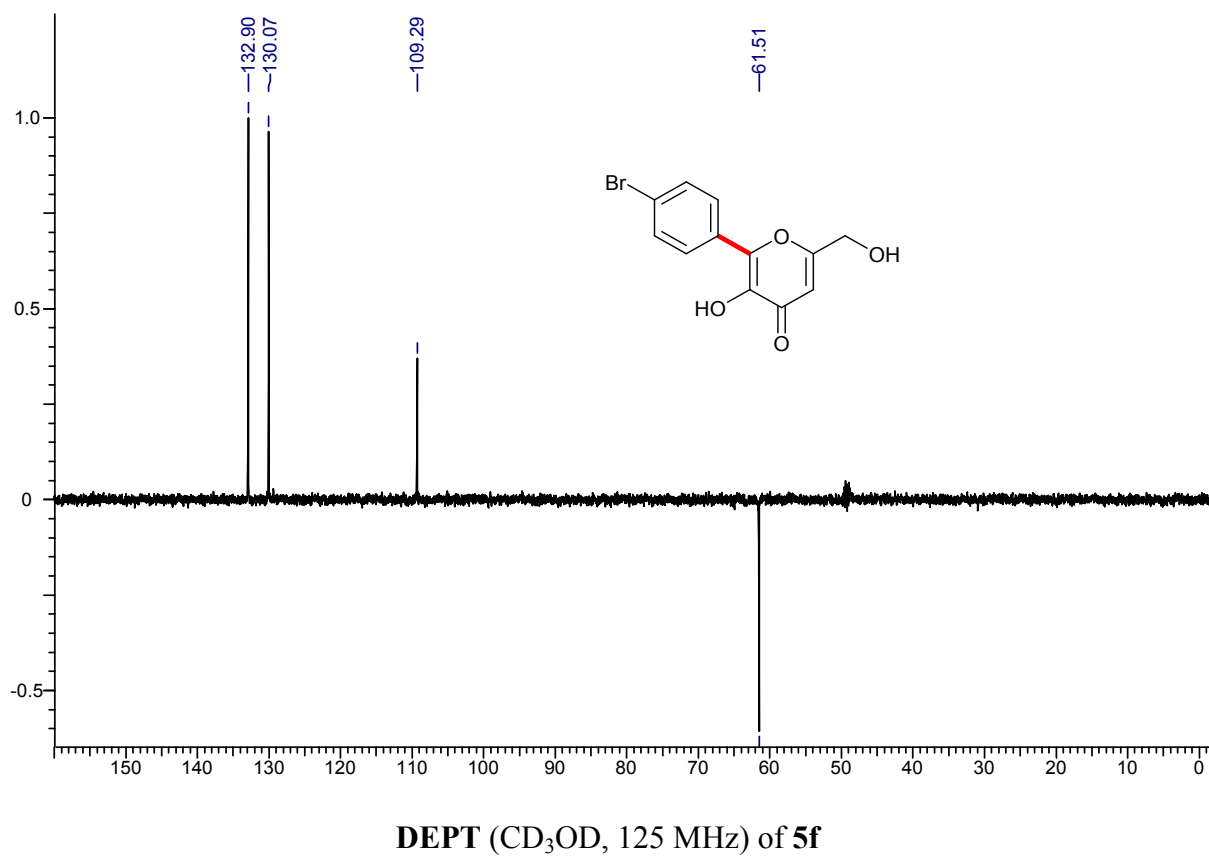
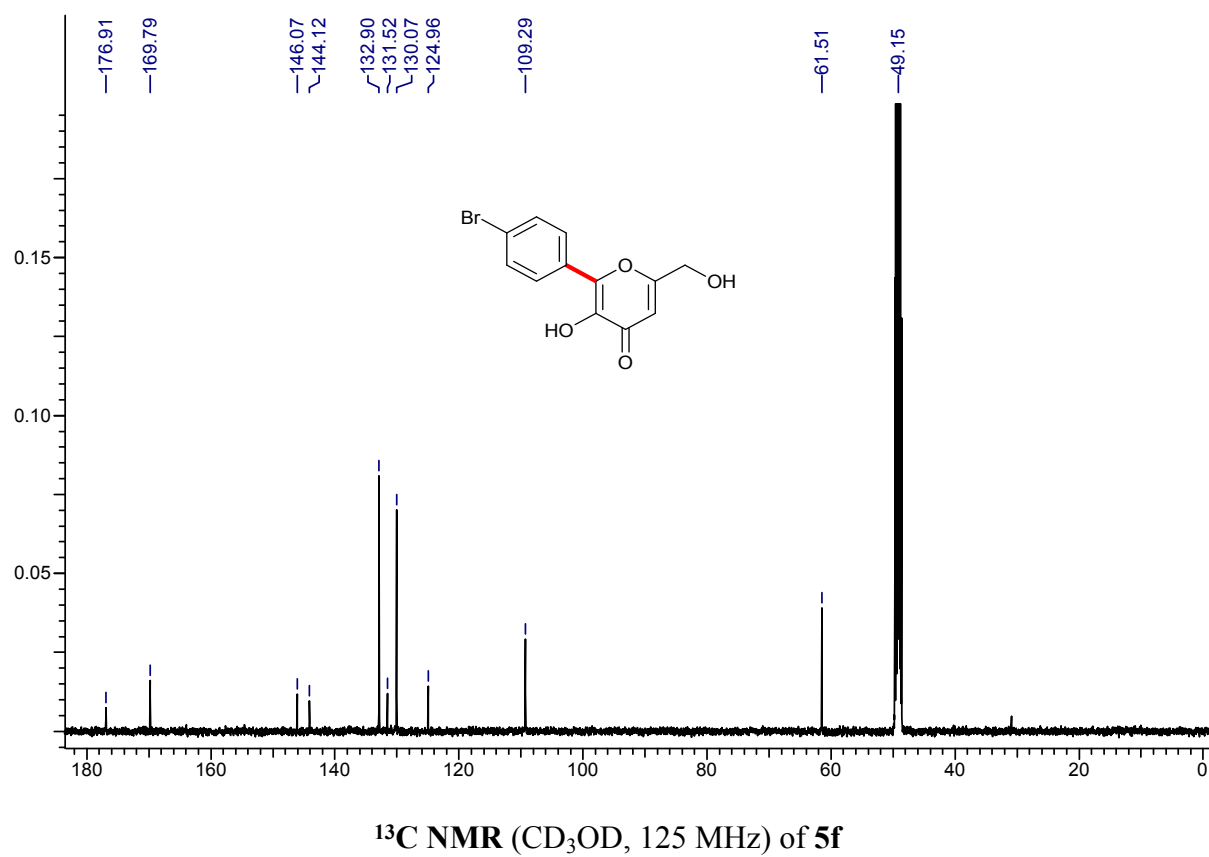
SP-2-15 #106 RT: 0.47 AV: 1 NL: 3.55E9
T: FTMS + p ESI/Full ms [100.00-1500.00]



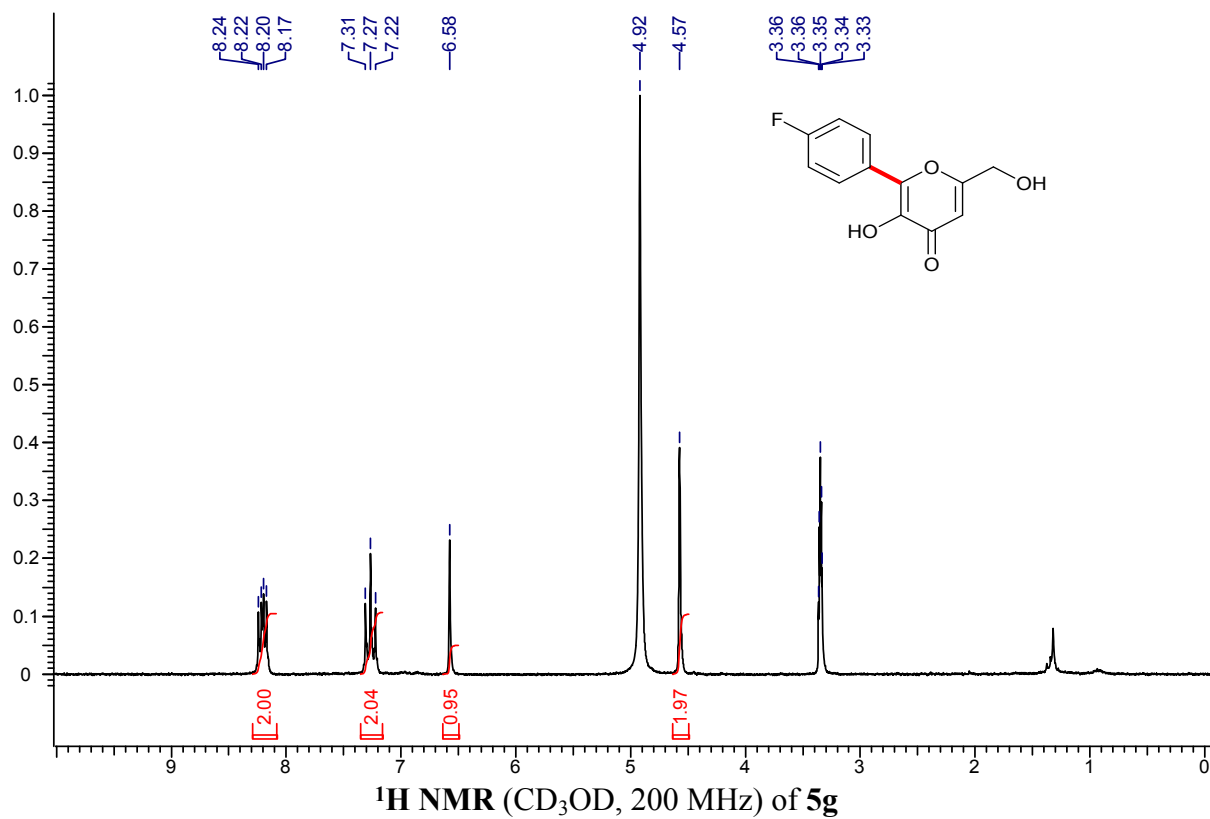
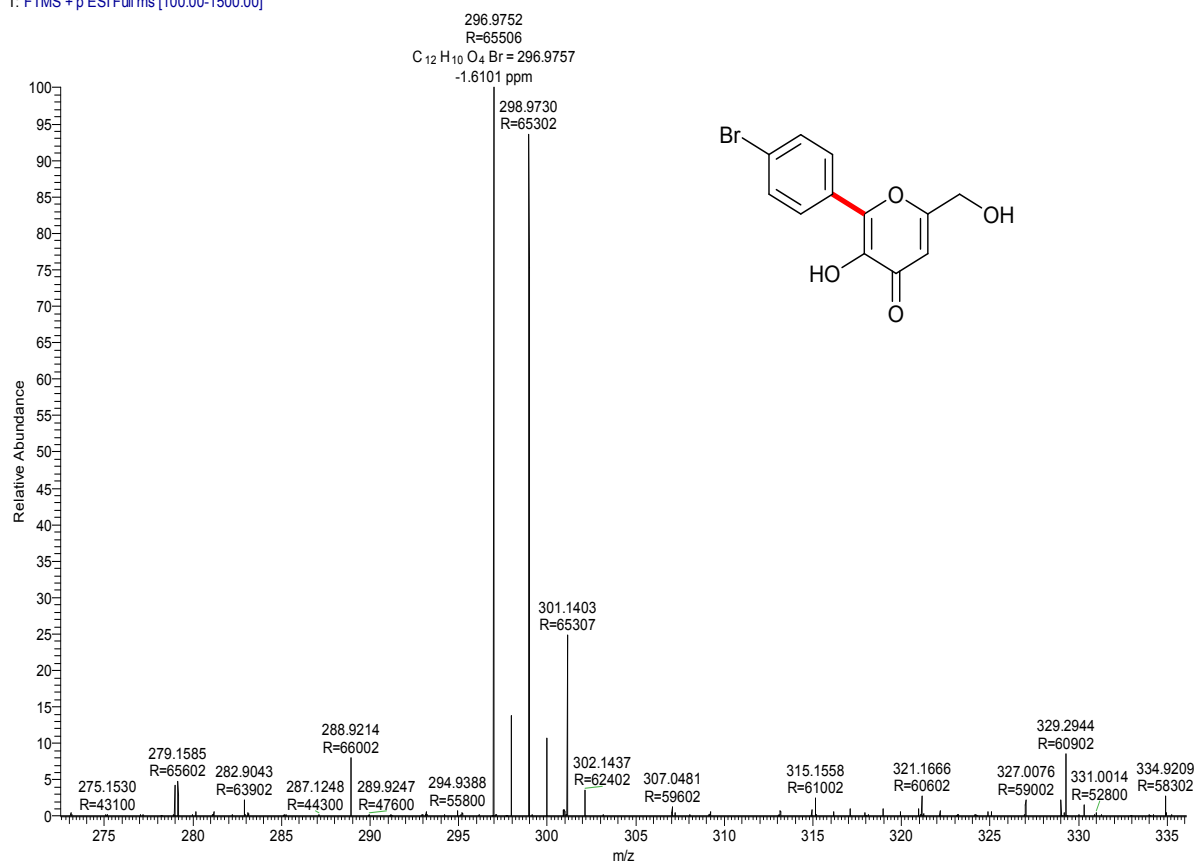
HRMS of 5e

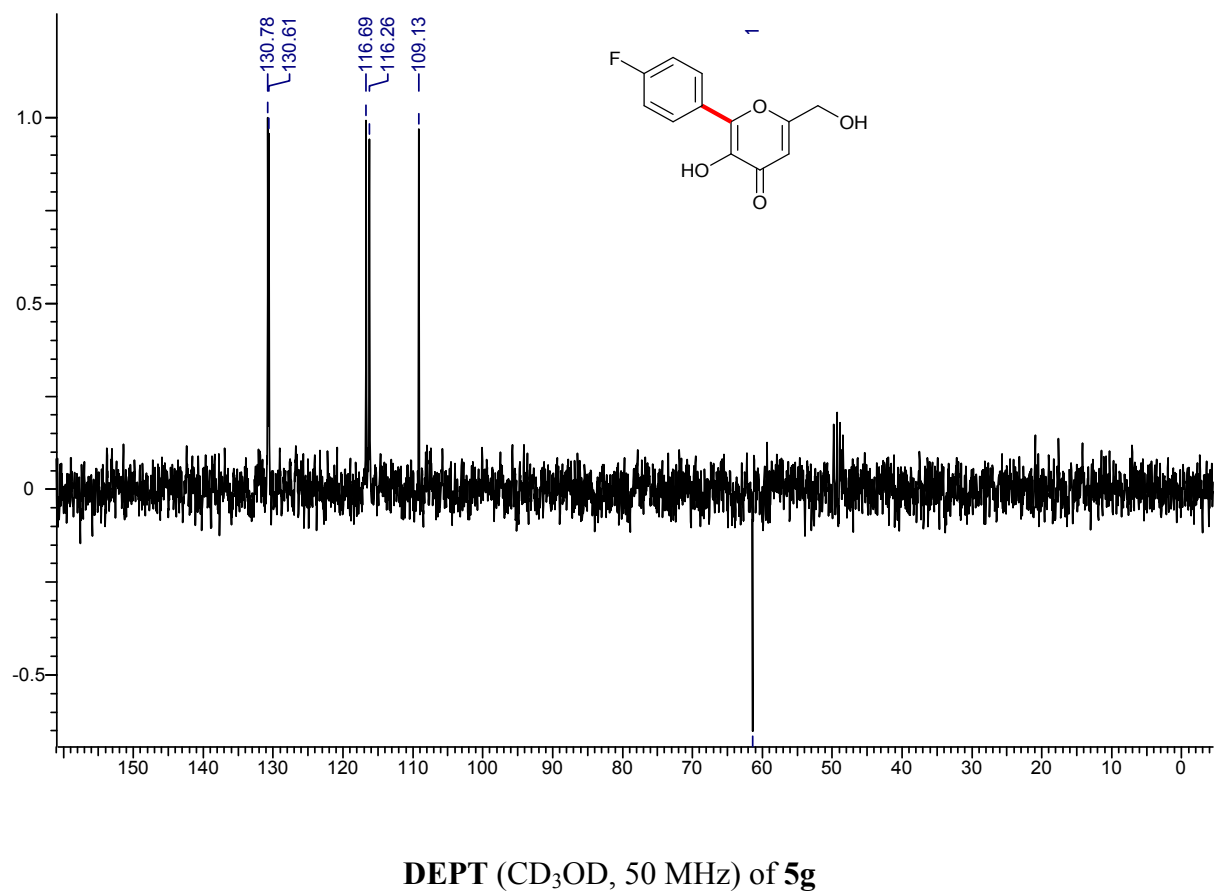
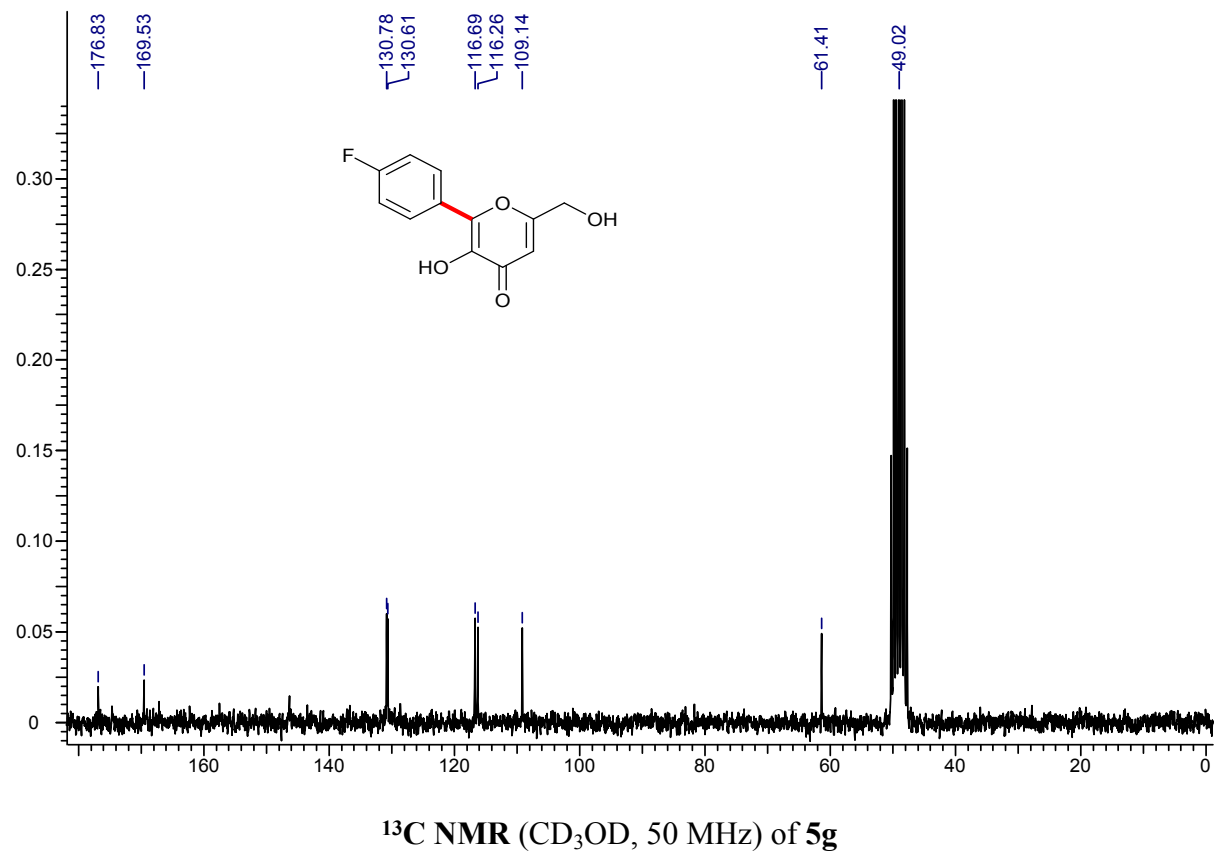


¹H NMR (CD₃OD, 500 MHz) of 5f

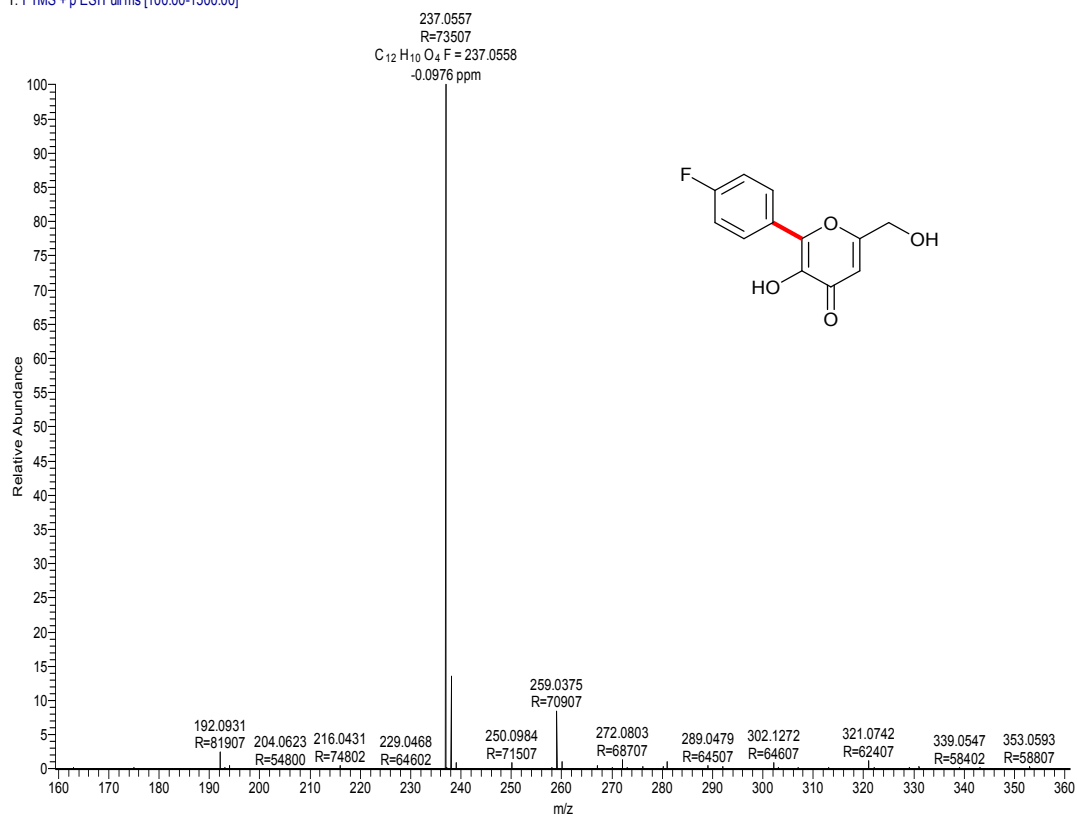


SP-1-134 #112 RT: 0.50 AV: 1 NL: 4.07E7
T: FTMS + p ESI Full ms [100.00-1500.00]

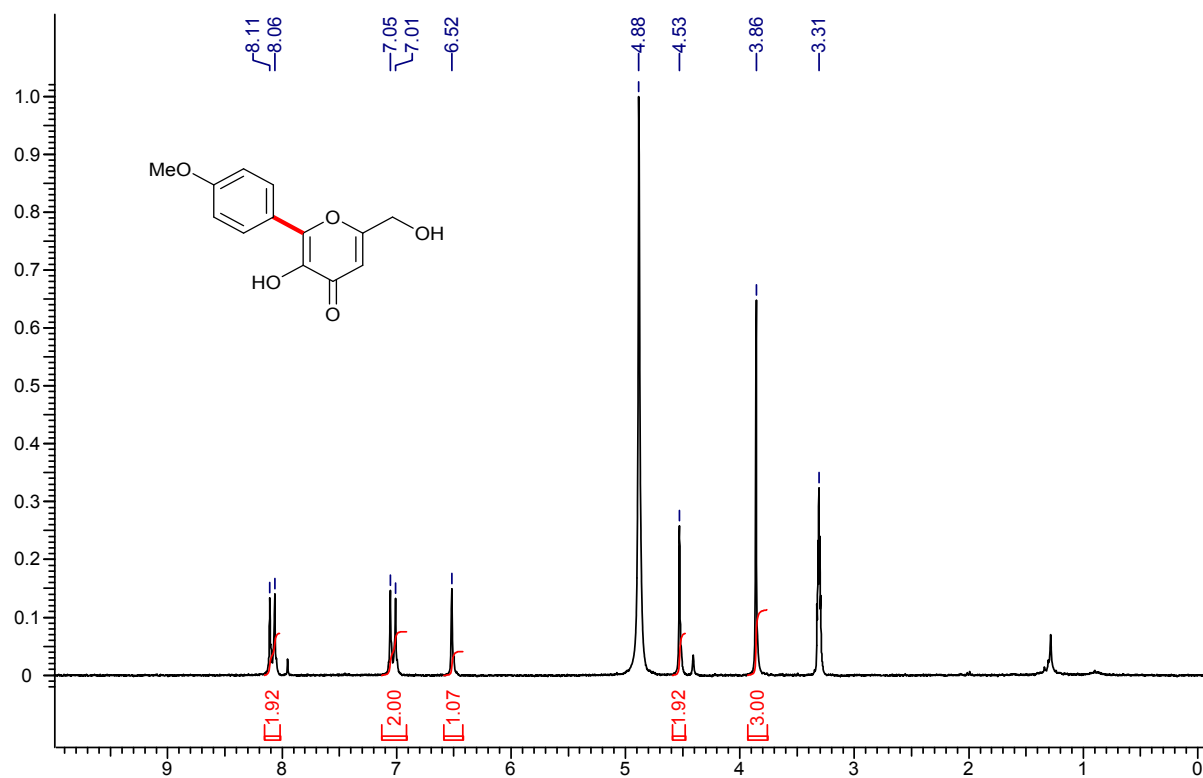




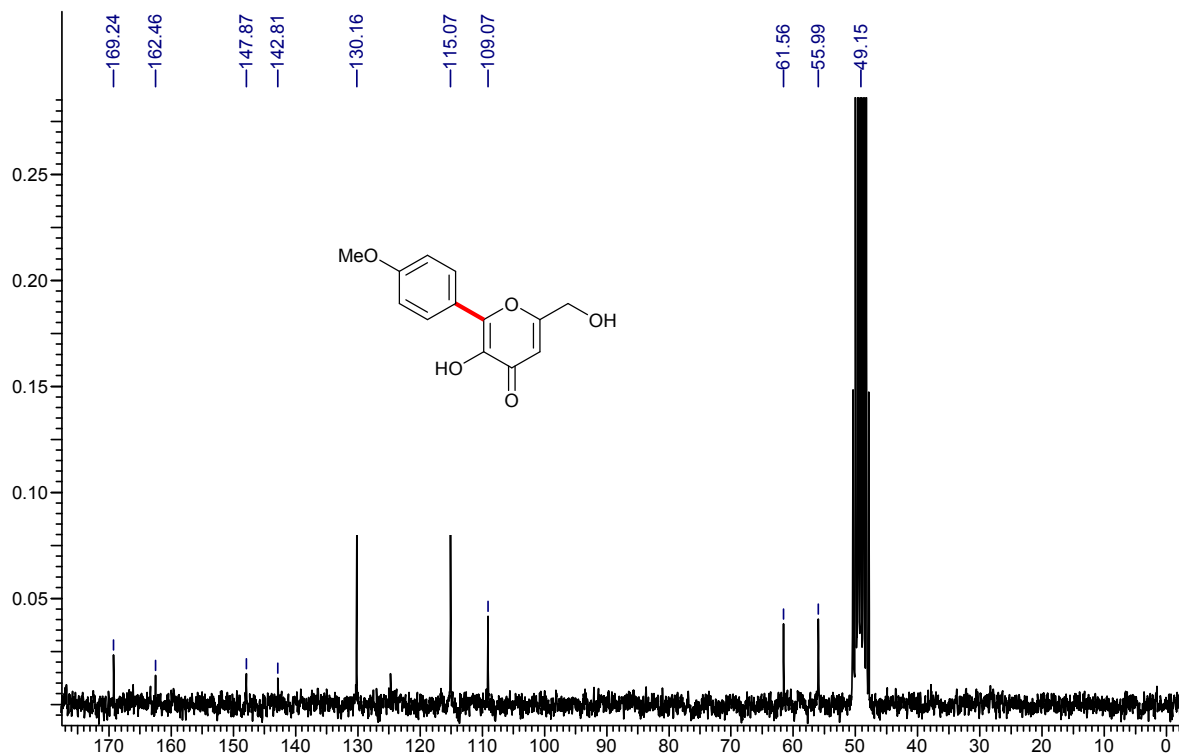
M1-103F-2-123 #10/ R1.0.46 AV. 1 INL. 2/11/19
T: FTMS + p ESI Full ms [100.00-1500.00]



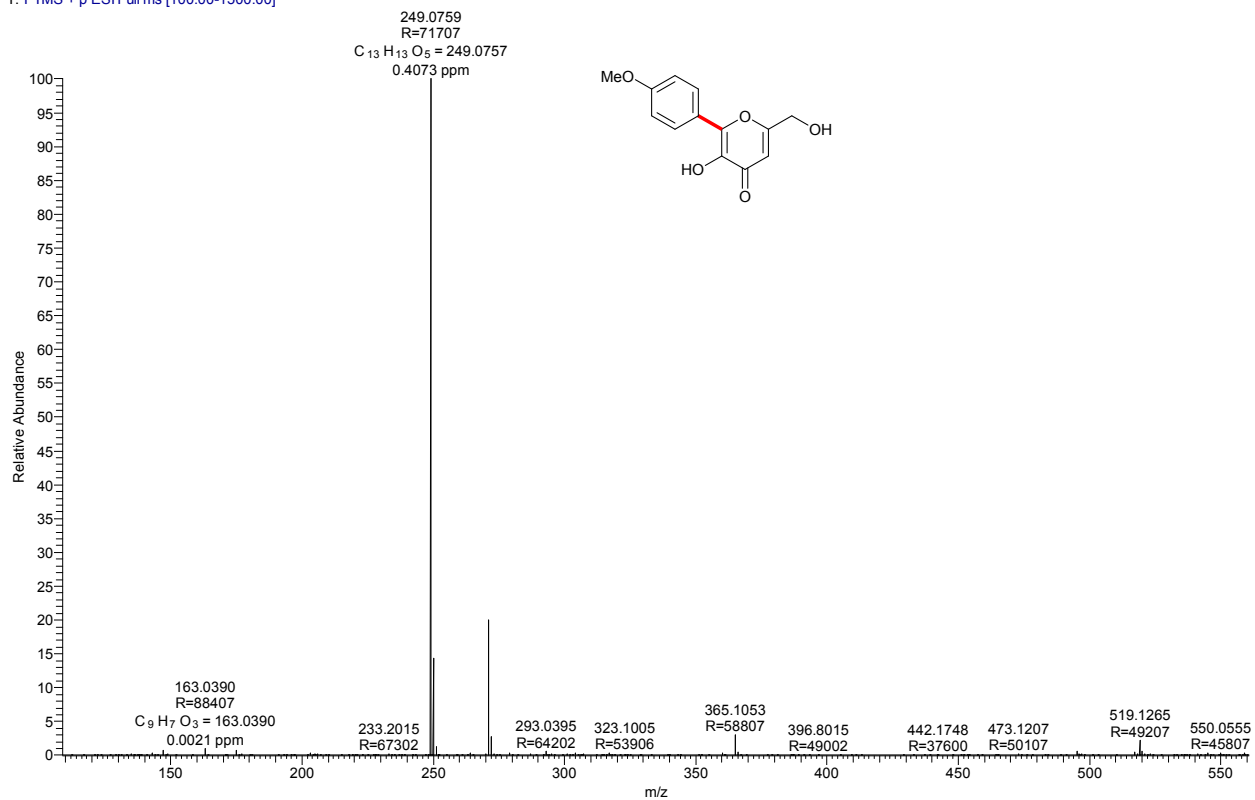
HRMS of 5g

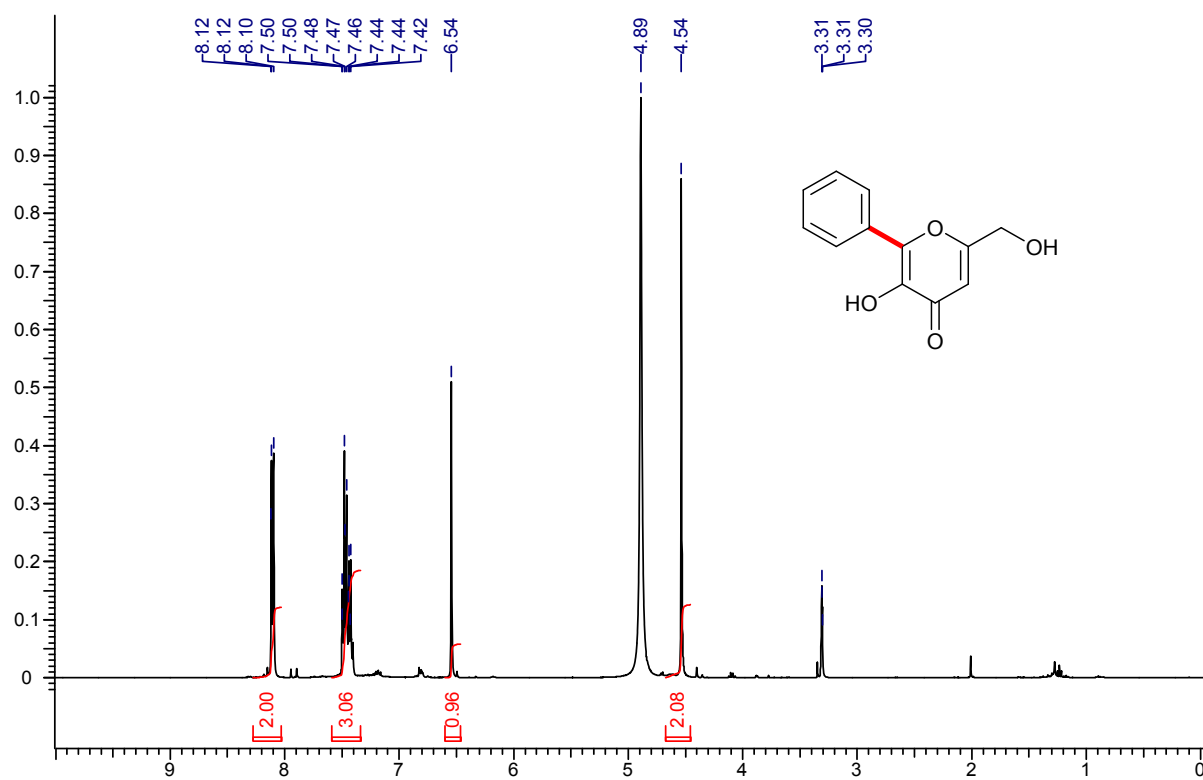


1H NMR (CD_3OD , 200 MHz) of 5h

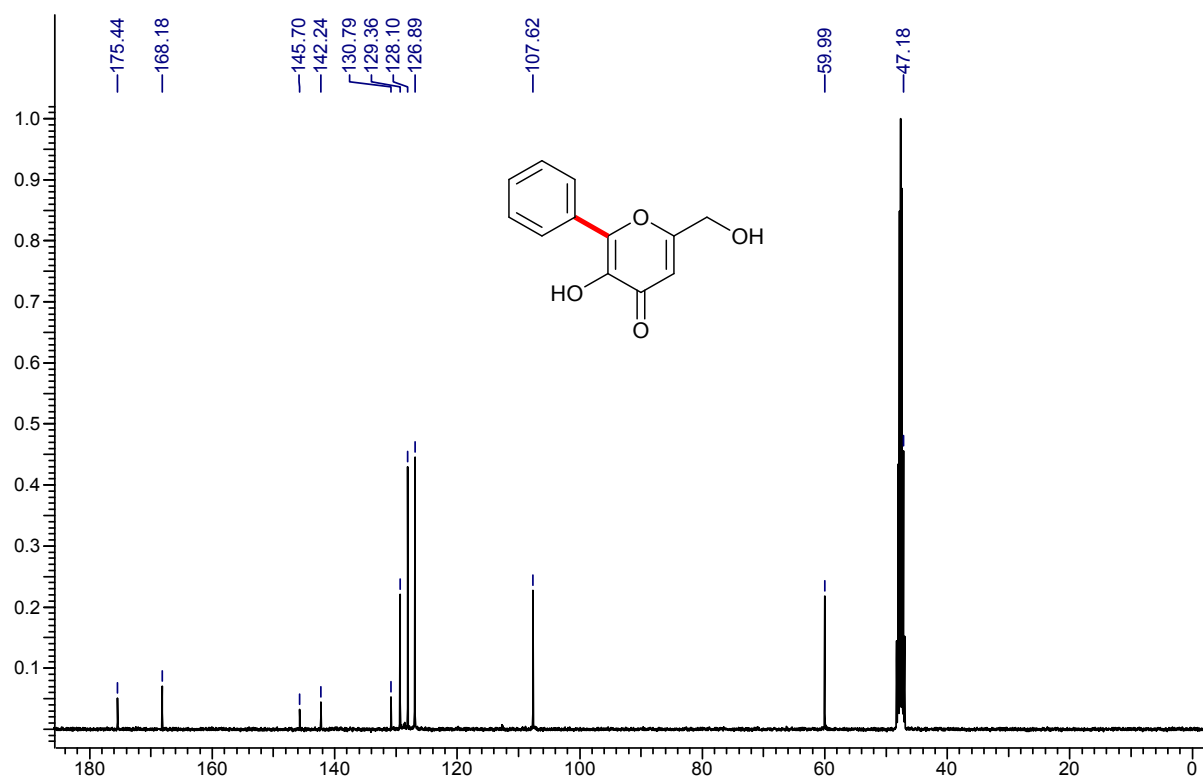


SP-2-124 #111 RT: 0.49 AV: 1 NL: 2.95E9
T: FTMS + p ESI Full ms [100.00-1500.00]

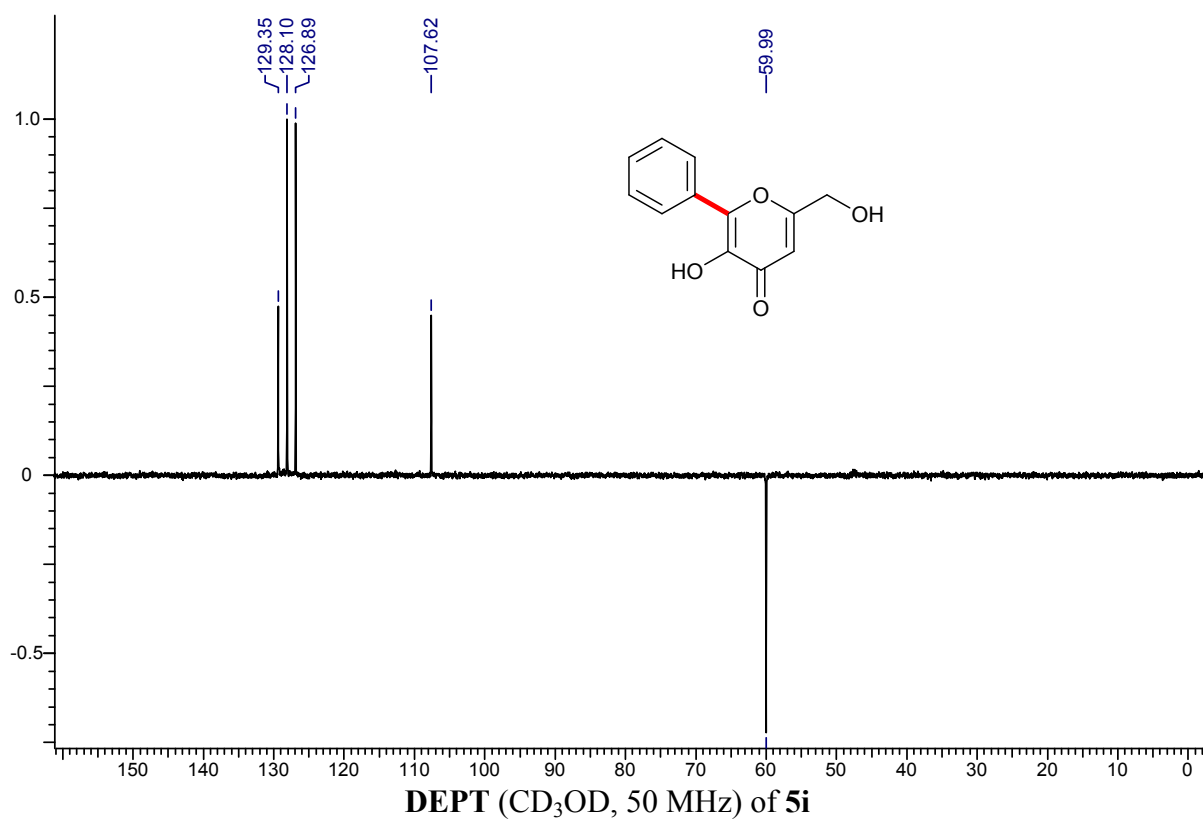




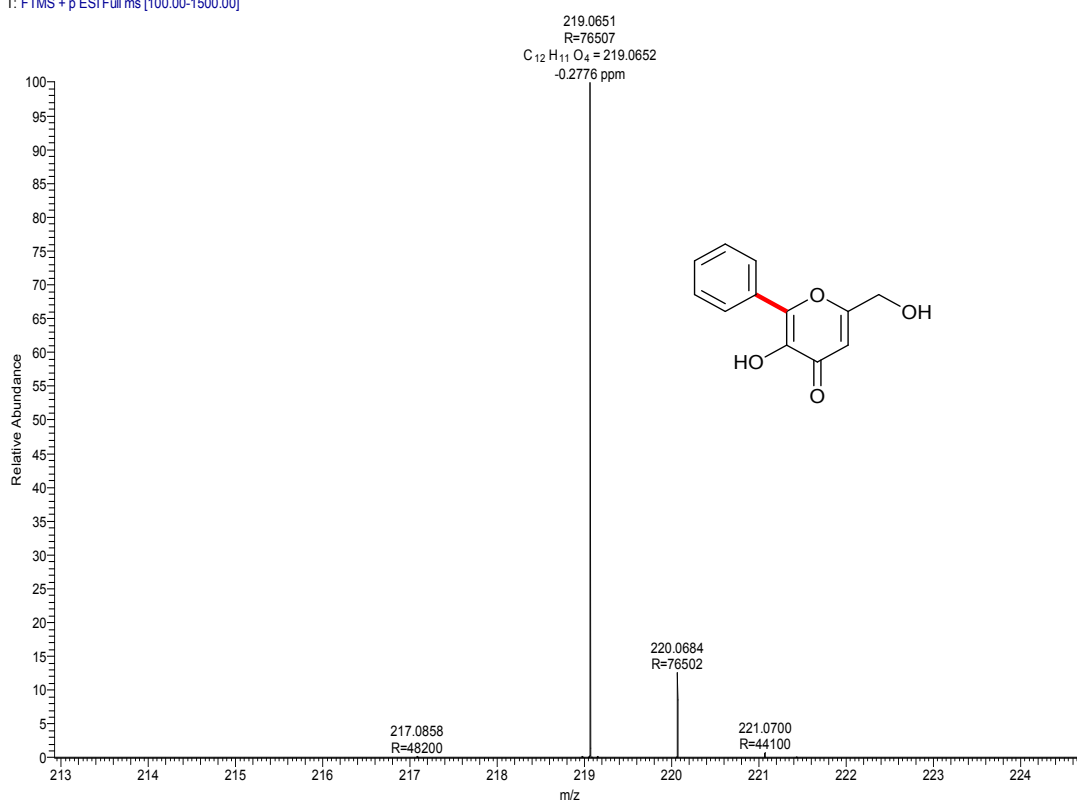
¹H NMR (CD₃OD, 400 MHz) of **5i**

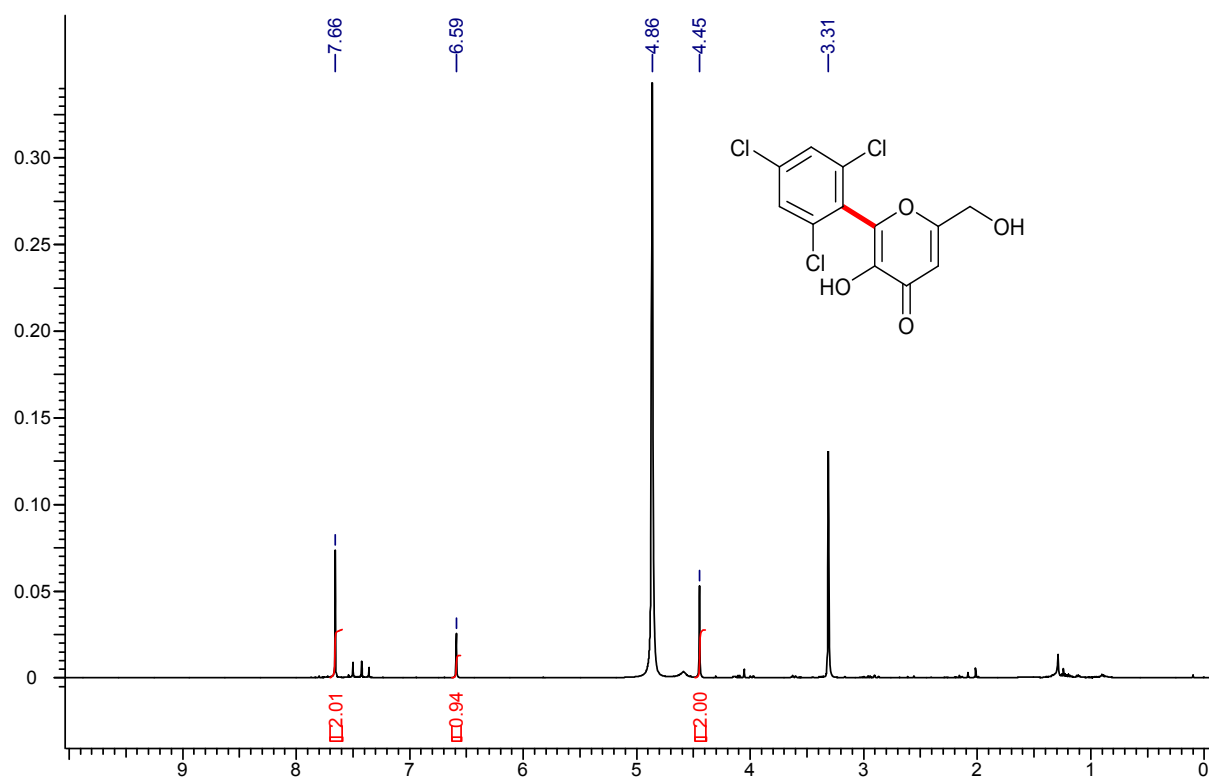


¹³C NMR (CD₃OD, 100 MHz) of **5i**

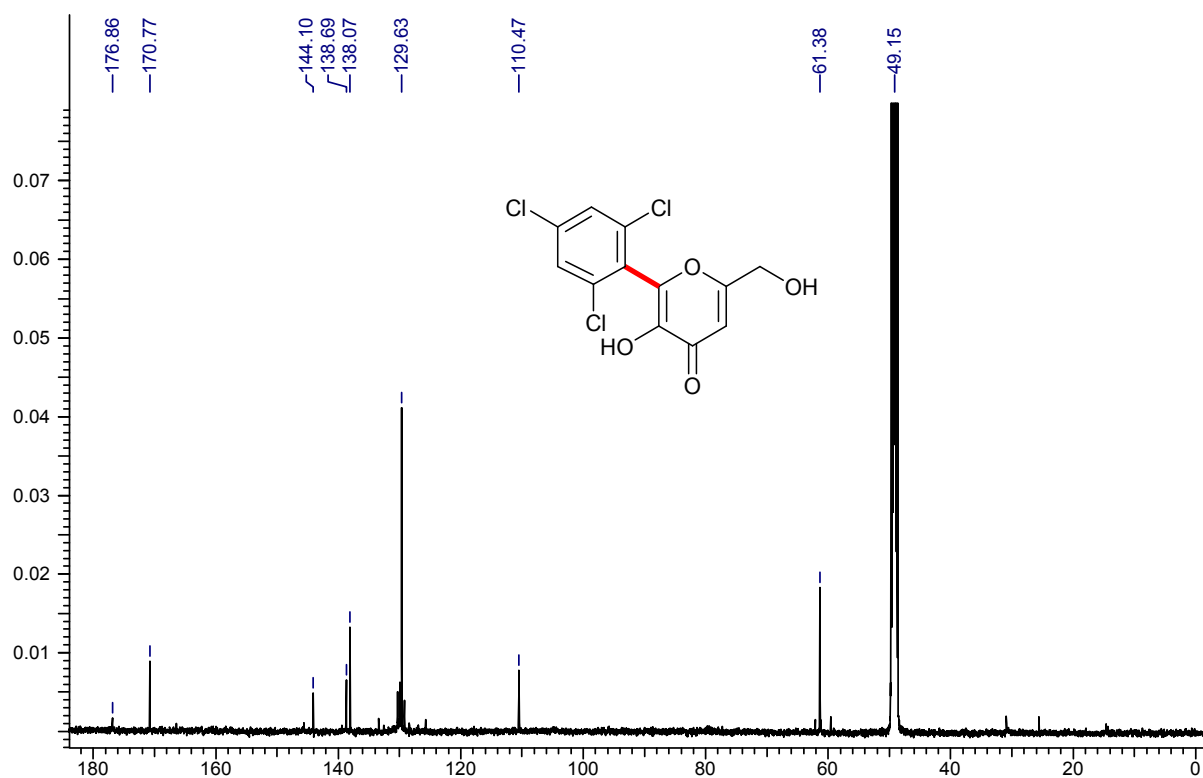


SP-1-88_160620142730 #103 RT: 0.46 AV: 1 NL: 9.83E8
 T: FTMS + p ESI Full ms [100.00-1500.00]

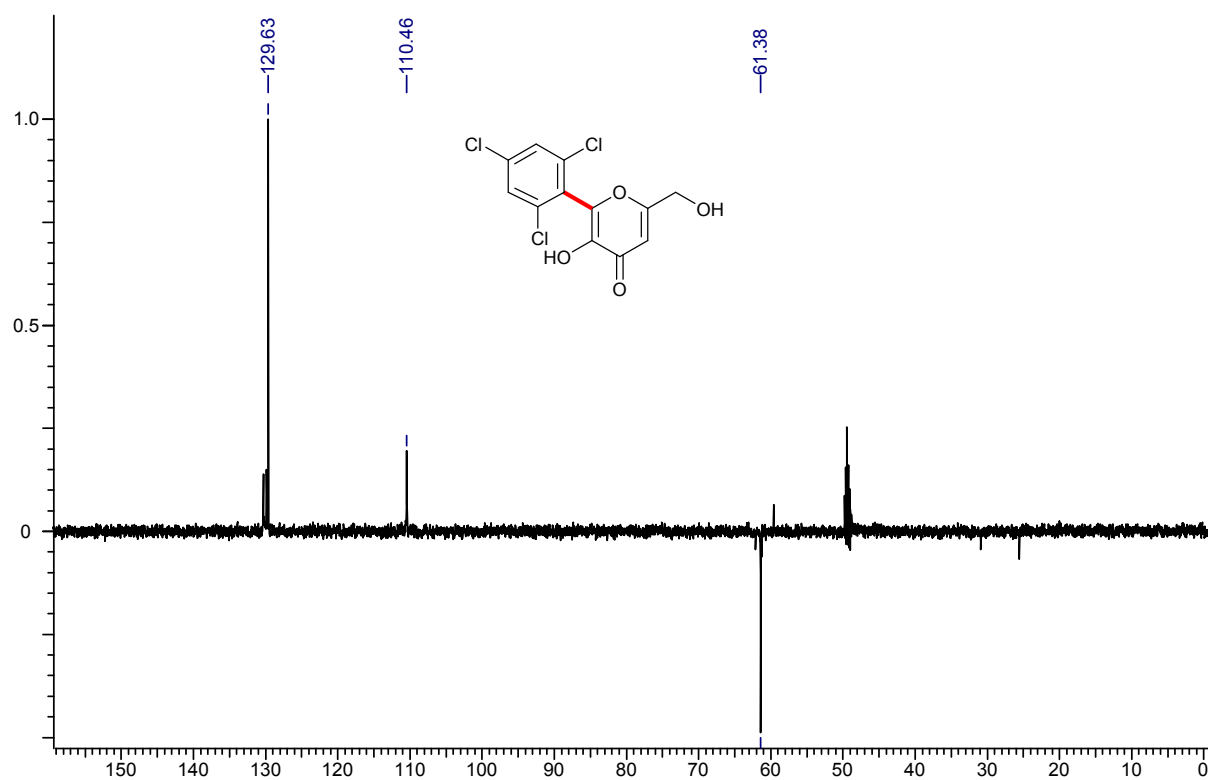




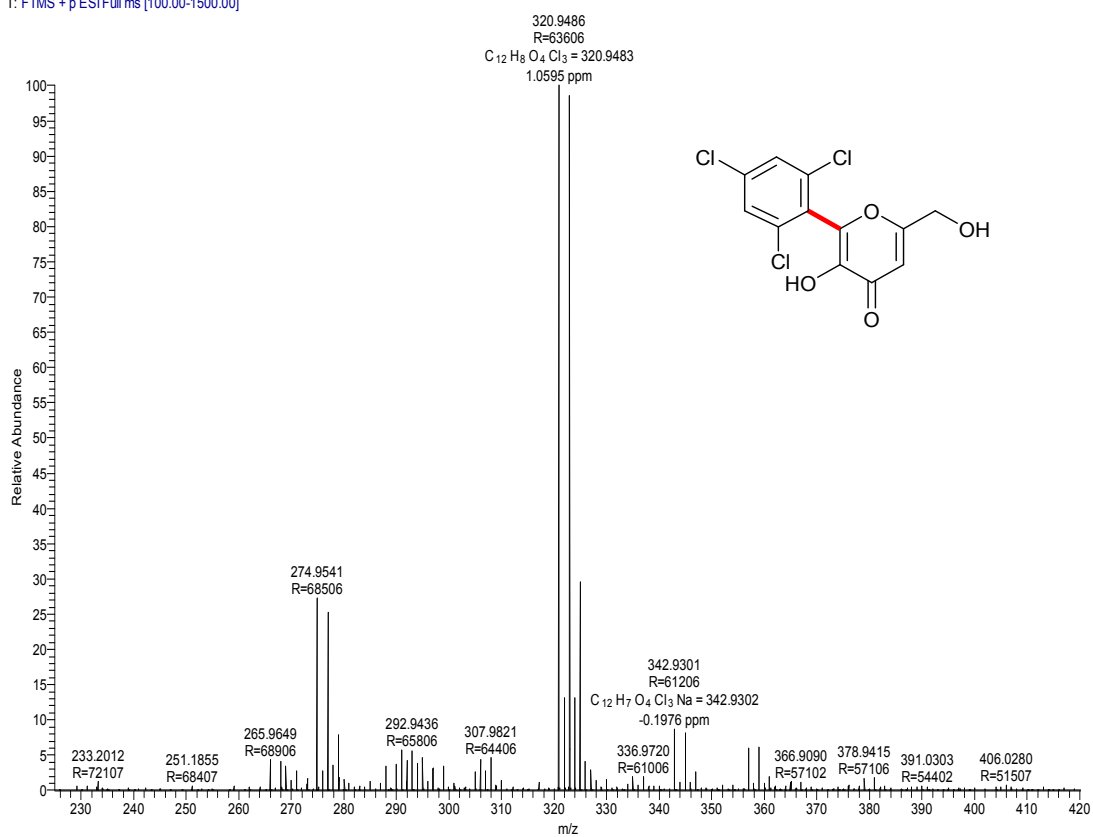
^1H NMR (CD_3OD , 500 MHz) of **5j**

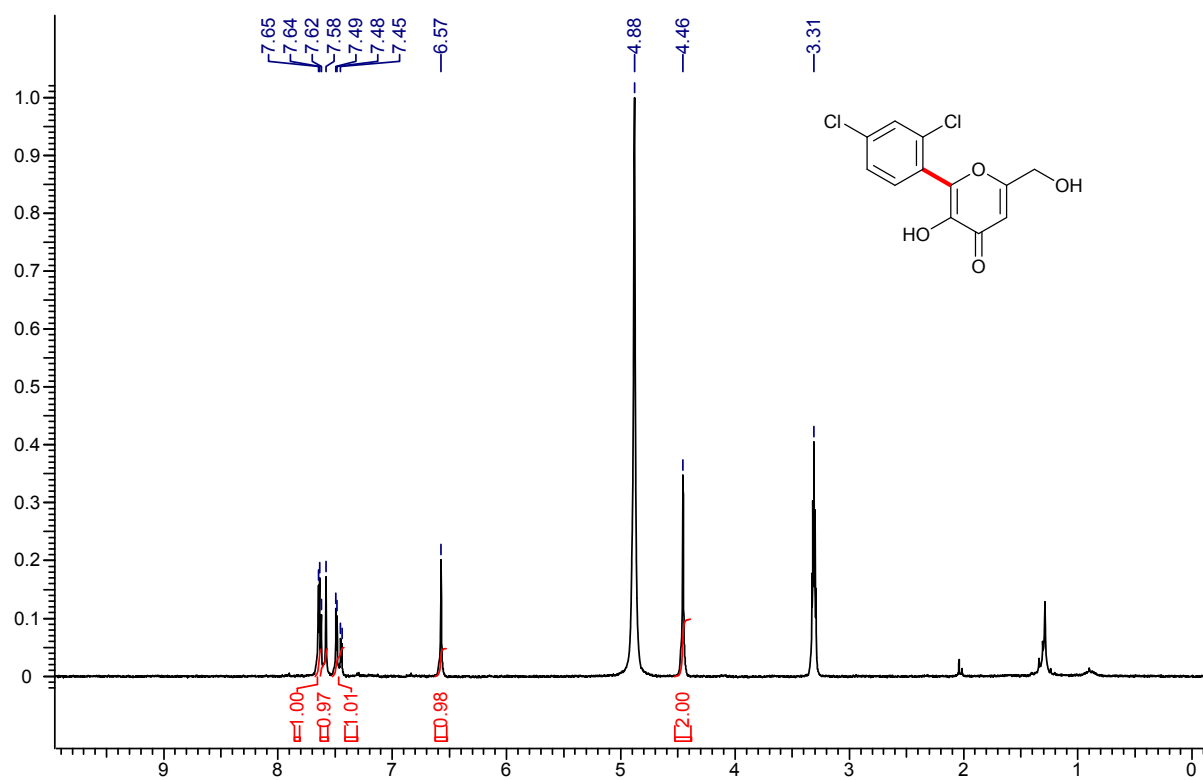


^{13}C NMR (CD_3OD , 125 MHz) of **5j**

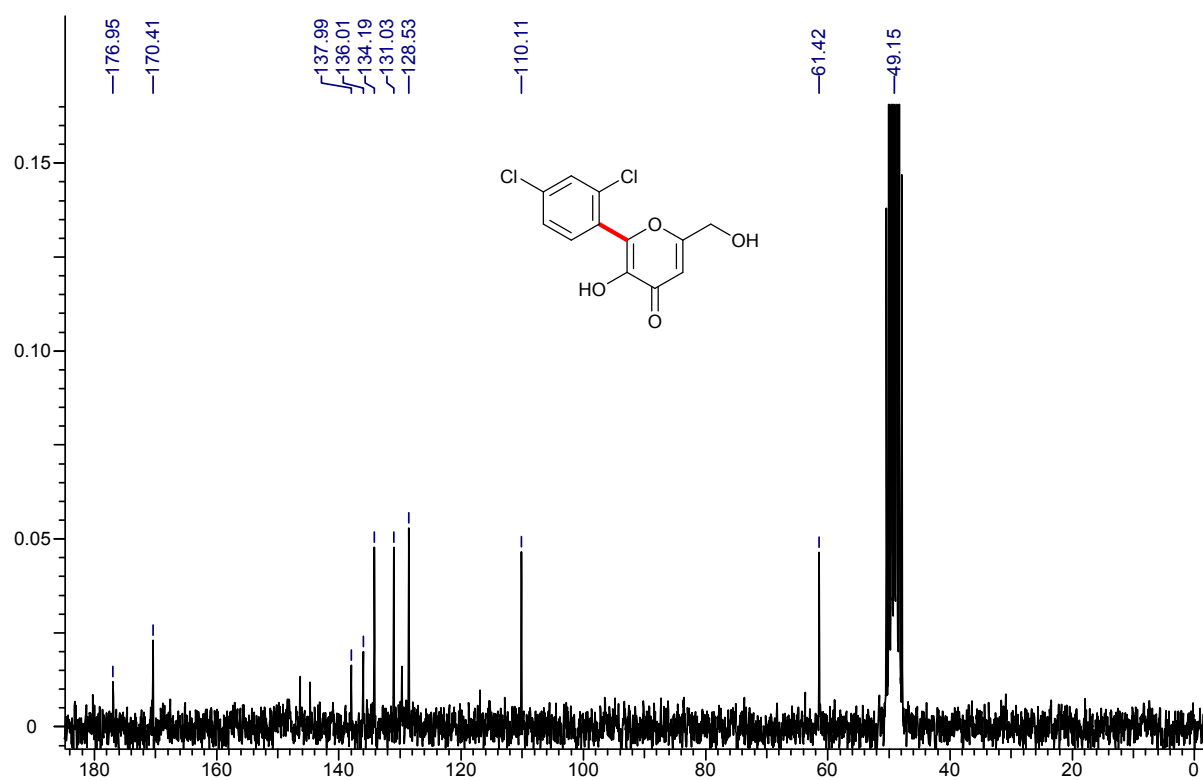


SP-2-108 #120 RT: 0.54 AV: 1 NL: 4.84E8
T: FTMS + p ESI Full ms [100.00-1500.00]

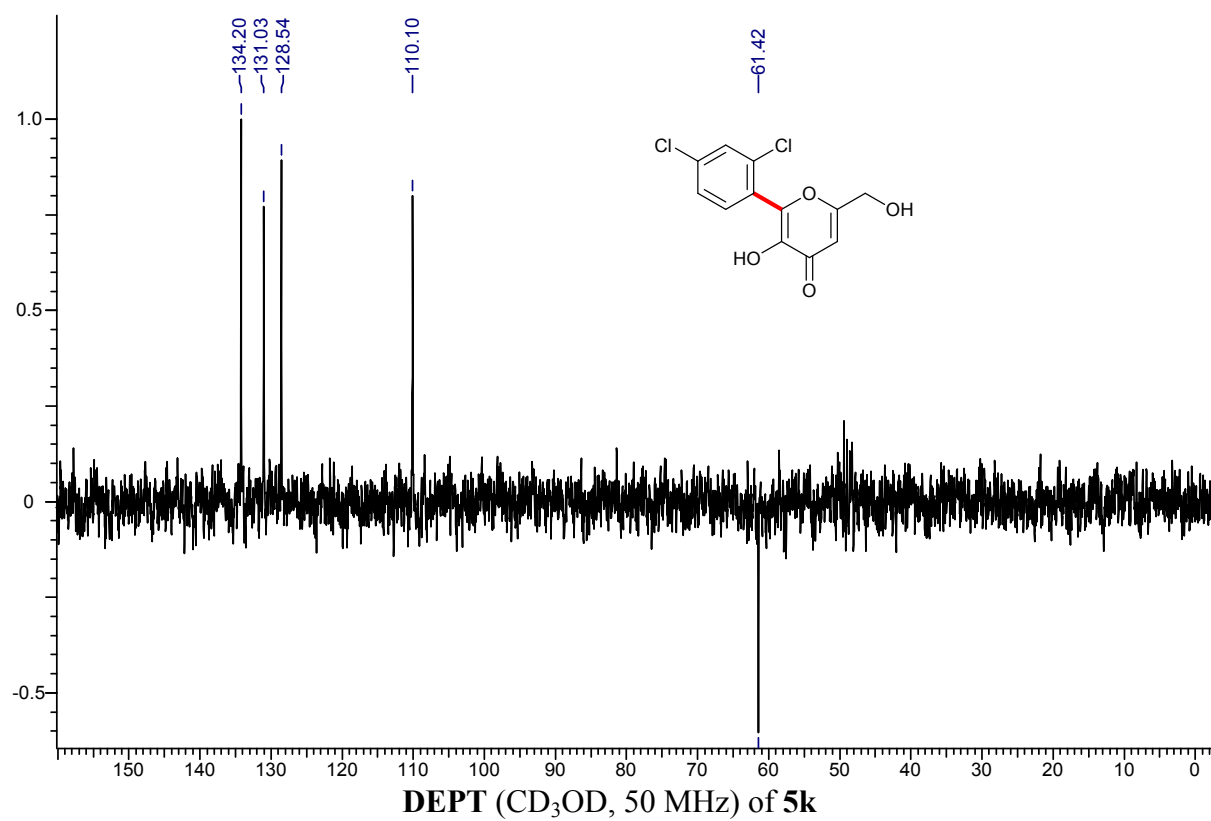




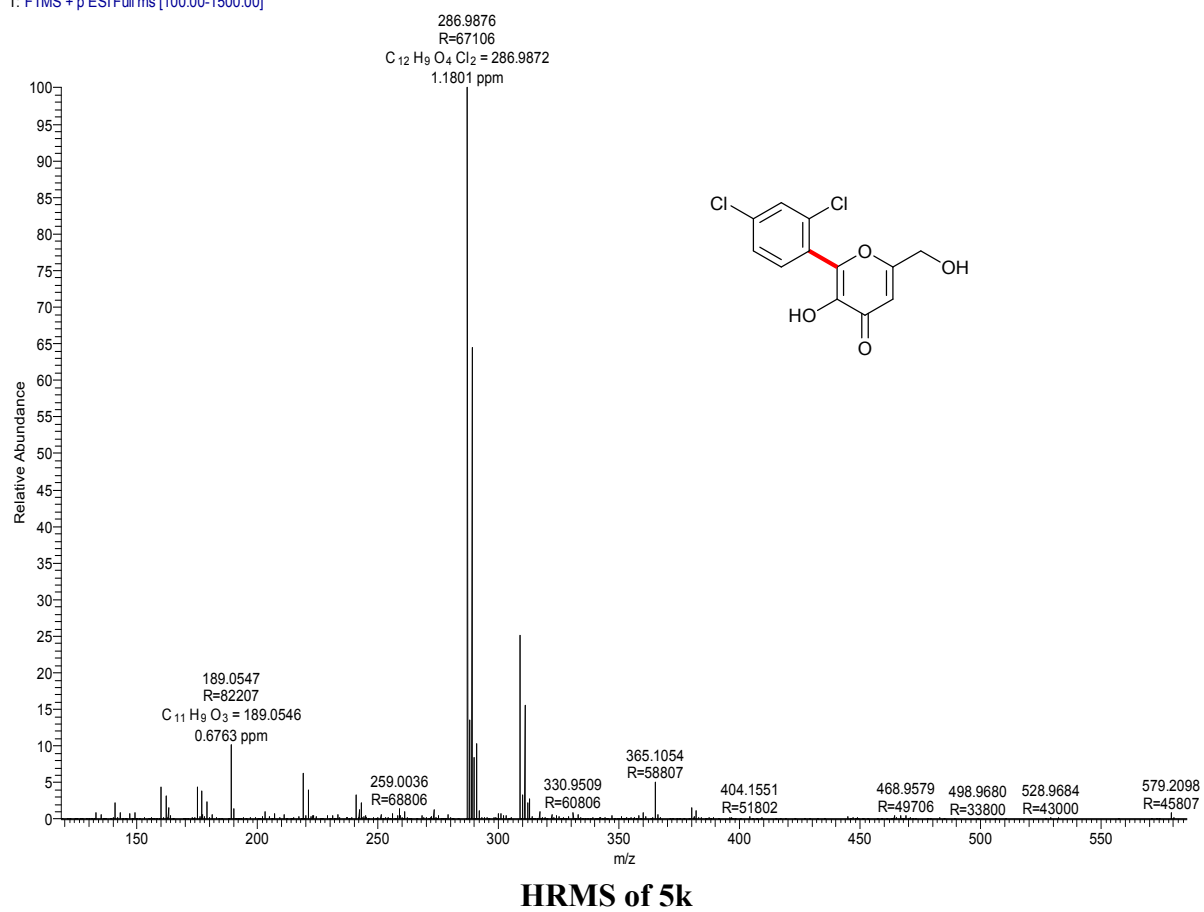
^1H NMR (CD_3OD , 200 MHz) of **5k**

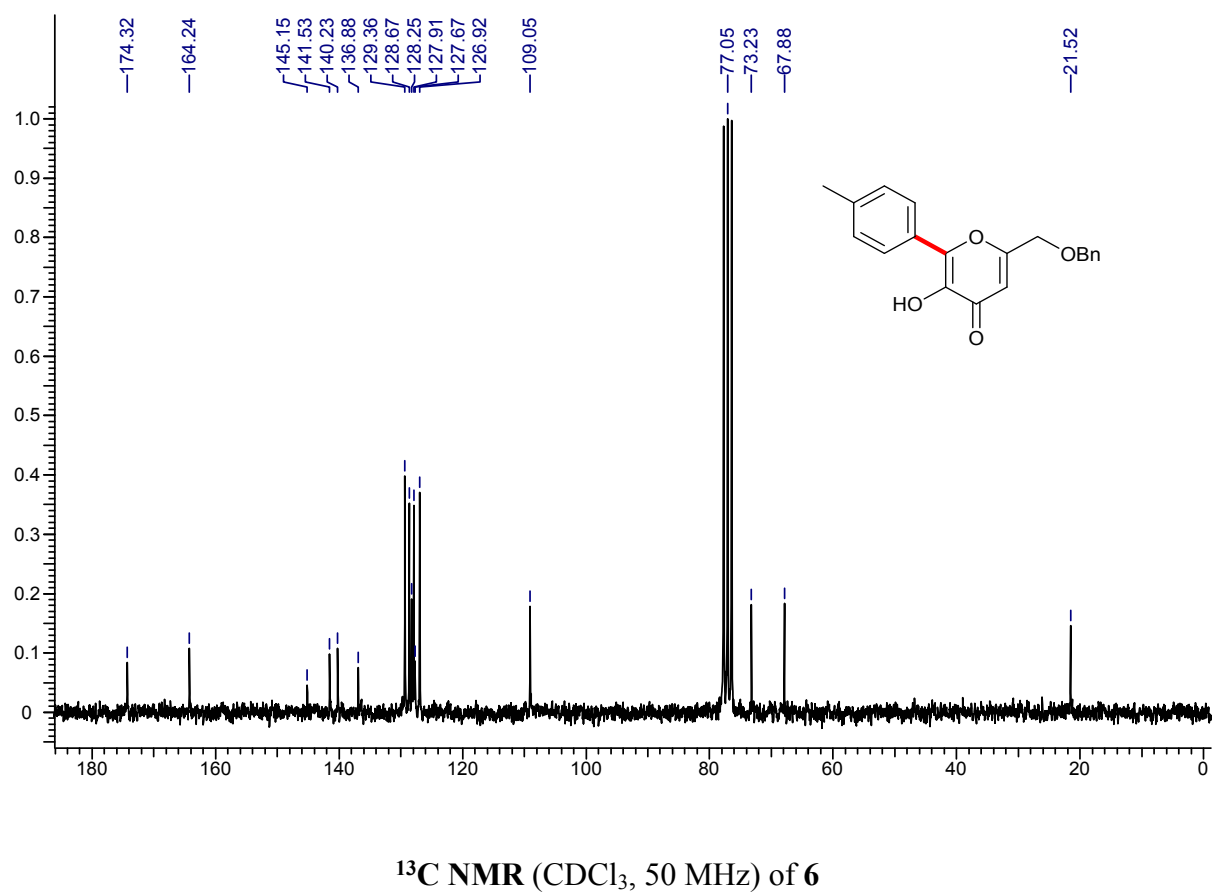
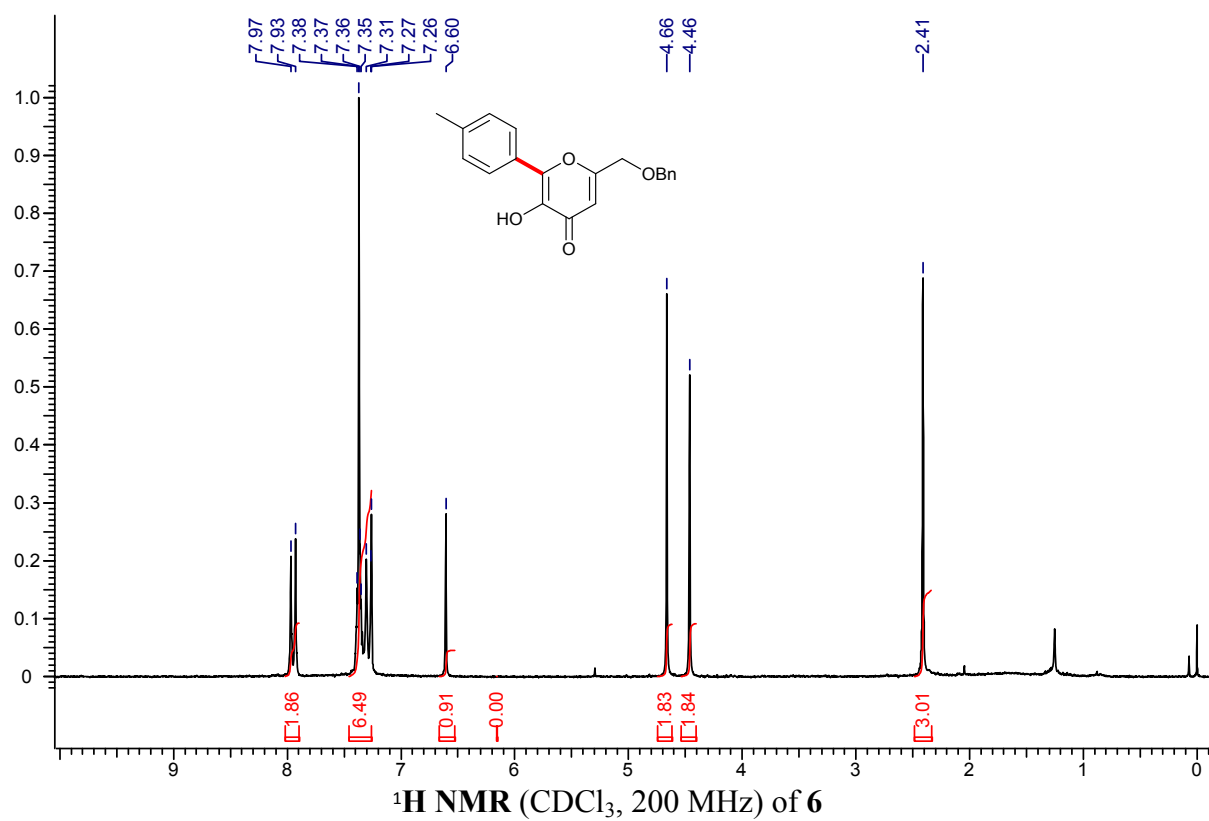


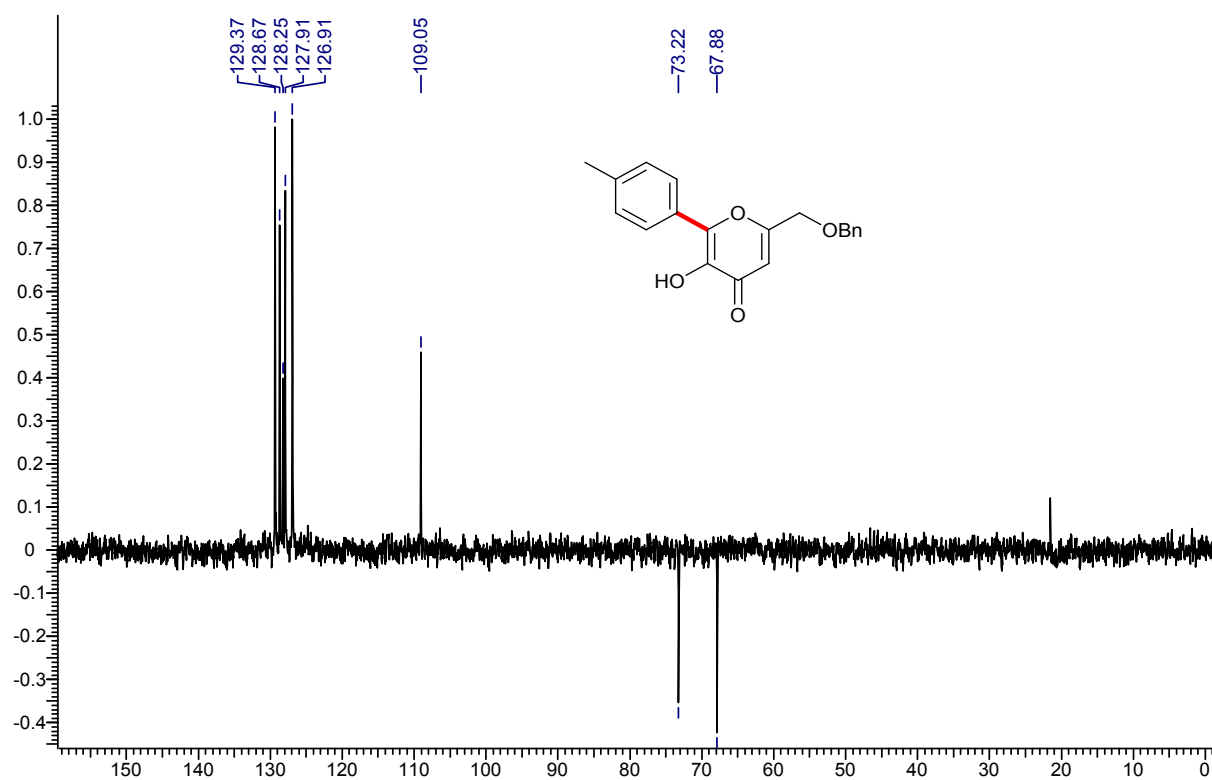
^{13}C NMR (CD_3OD , 50 MHz) of **5k**



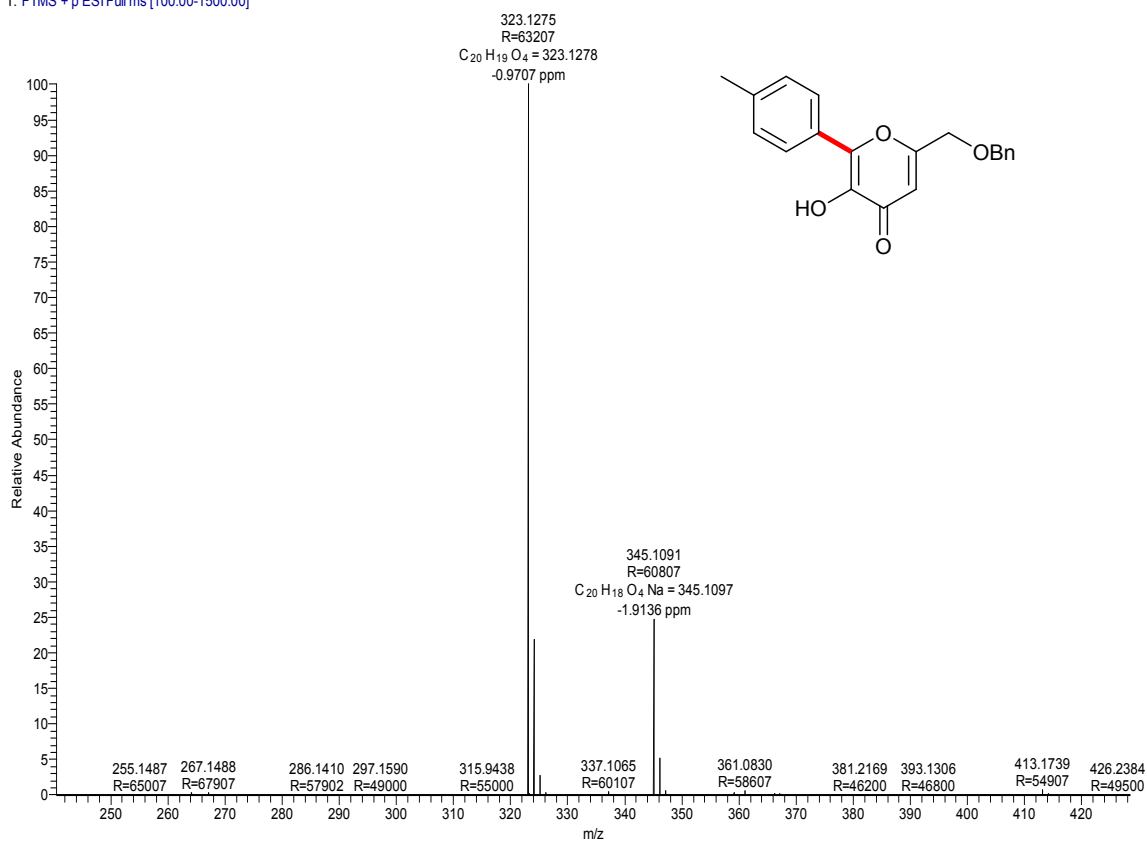
SP-2-122 #118 RT: 0.53 AV: 1 NL: 8.10E8
T: FTMS + p ESI Full ms [100.00-1500.00]

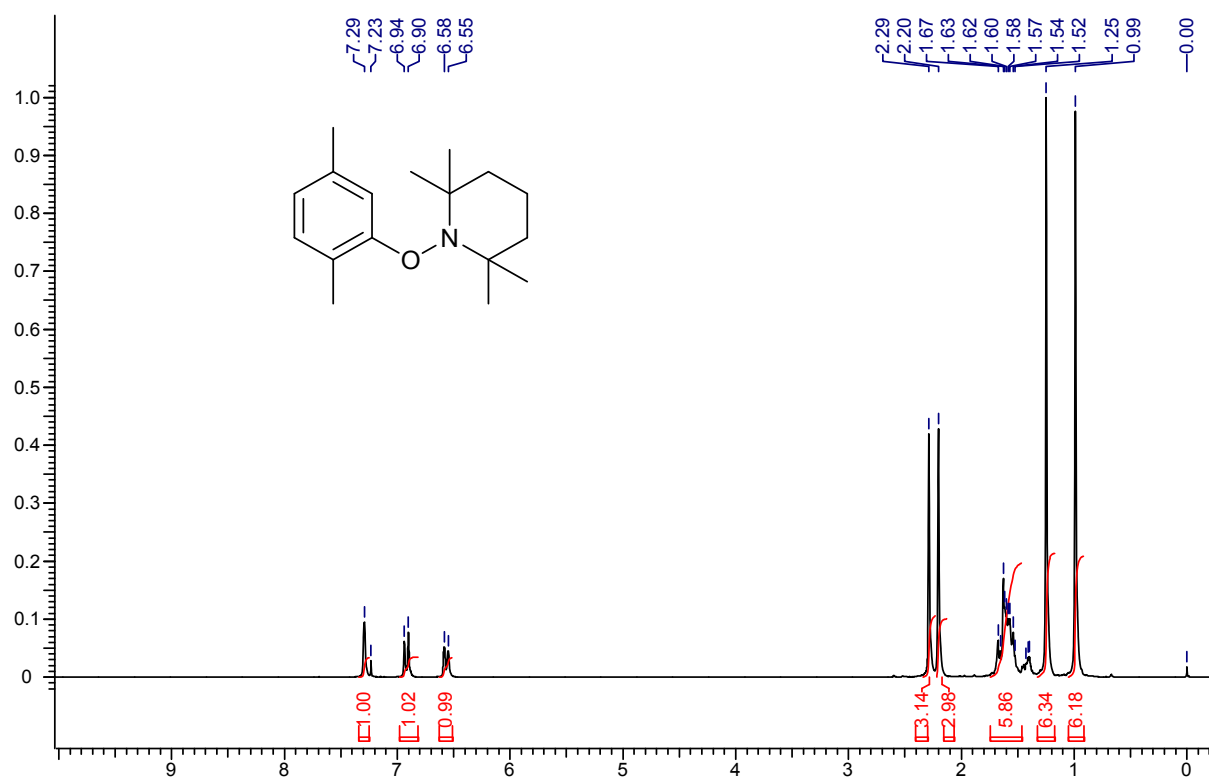




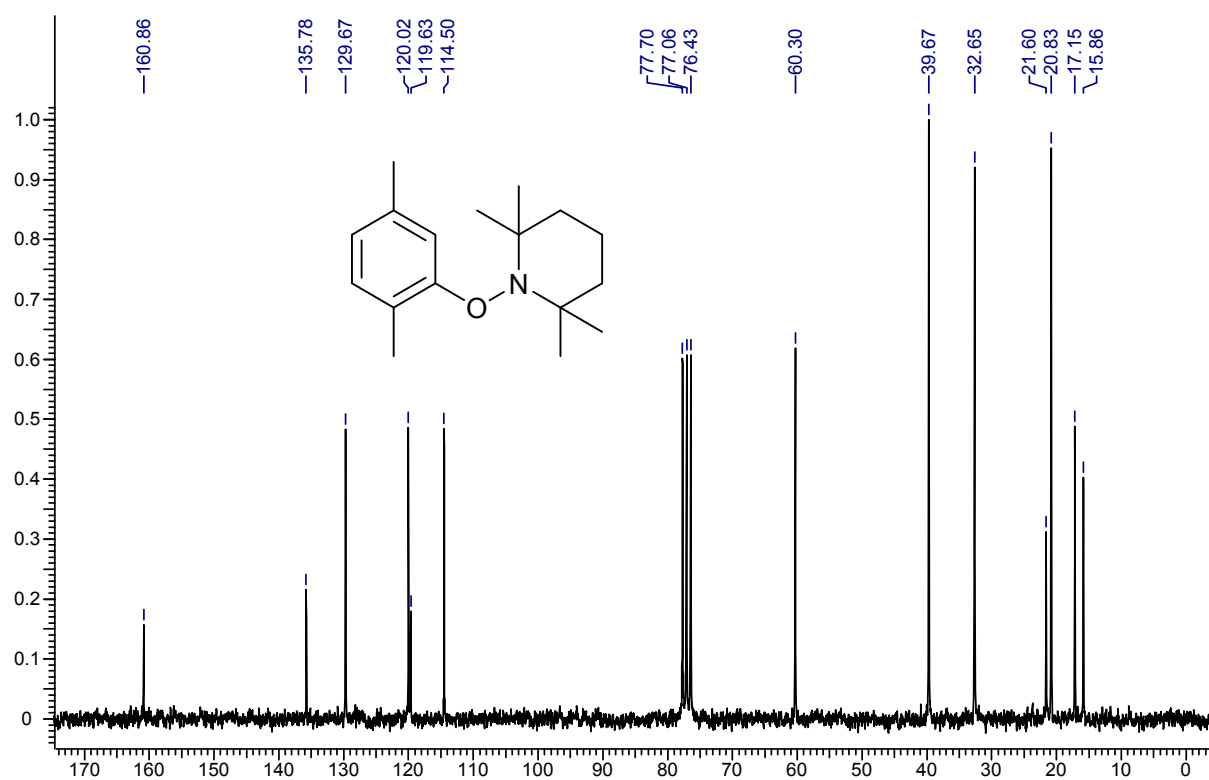


SP-7-37 #136 RT: 0.60 AV: 1 NL: 8.74E9
T: FTMS + p ESI Full ms [100.00-1500.00]

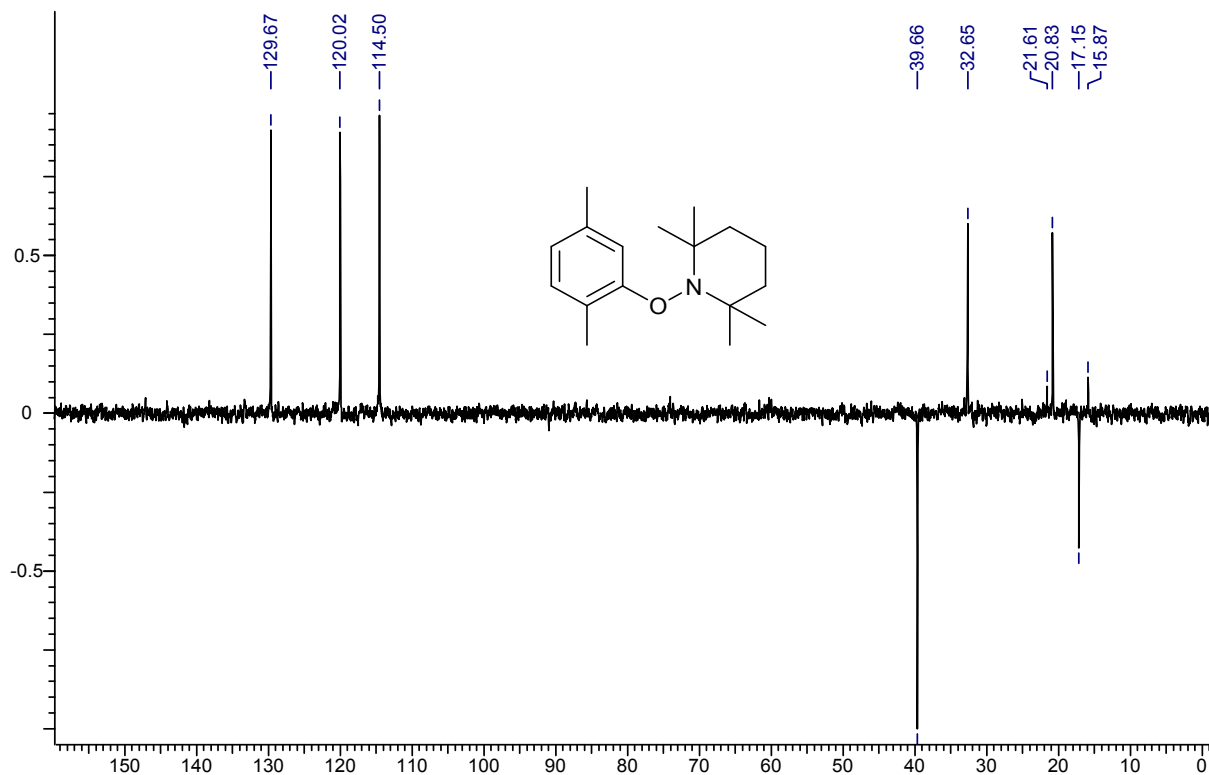




¹H NMR (CDCl₃, 200 MHz) of 7



¹³C NMR (CDCl₃, 50 MHz) of 7



SP-2-96 #291 RT: 1.30 AV: 1 NL: 2.04E9
T: FTMS + p ESI Full ms [100.00-1500.00]

