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Graphical Abstract

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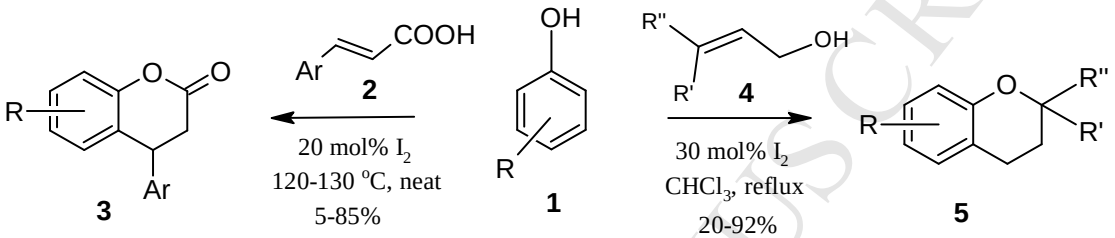

Molecular Iodine Catalyst Promoted Synthesis of Chromans and 4-Aryl-3,4-dihydrobenzopyran-2-ones *via* [3+3] Cyclocoupling

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Key words: Chroman, 3,4-Dihydrobenzopyran-2-one, Iodine, Cyclocoupling, Solvent-free, Phenol, Allylic alcohol, Cinnamic acid

Abstract: Molecular iodine as an inexpensive catalyst is described in the construction of 2-substituted or 2,2-disubstituted chromans and 4-aryl-3,4-dihydrobenzopyran-2-ones *via* [3+3] cyclocoupling. For the synthesis of chromans, phenols and allylic alcohols were refluxed in chloroform in presence of 20 mol% I_2 while [3+3] cyclocoupling of phenols and cinnamic acids proceeded to give 4-aryl-3,4-dihydrobenzopyran-2-ones using 30 mol% I_2. Later reaction occurs *via* a tandem hydroarylation–esterification process at 120-130 ^{0}C under solvent free conditions. Chromans were obtained in 20-92% yields and substituted 4-aryl-3,4-dihydrobenzopyran-2-ones were obtained in 5-85% yields.

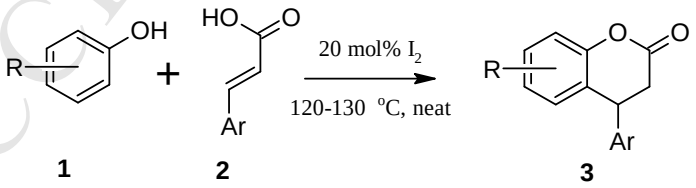
1. Introduction: Molecular iodine is a mild Lewis acid used in plethora of functional group transformations in organic synthesis either as a catalyst or in stoichiometric amount and many reviews have documented its applications.[1] A large number of heterocycles such as benzofurans, furans, benzothiophenes, thiophenes, benzopyrans, benzoselenophenes, selenophenes, α-pyrones, isocoumarins, isoxazoles, chromones, β-lactams, 2,3-dihydropyrroles, pyrroles, furopyridines, furanones, and isochromenes have been prepared by iodine-mediated domino or one-pot multicomponent reactions. Iodine has gained considerable attention as it is readily available, non-toxic, cheap, easy to handle and, hence has become a preferred alternative for toxic and expensive acid catalysts. Also it has high tolerance to air as well as moisture and can be easily removed from reaction systems by washing with reducing agents.

Continuing our interest[2] in catalytic usage of iodine for the synthesis of heterocycles, we in a preliminary communication reported the synthesis of 4-aryl-3,4-dihydrobenzopyran-2-ones *via* the [3+3] cyclocoupling of phenols with cinnamic acids (Scheme 1).[2b] Herein we disclose full account of our work in exploring iodine as catalyst for the synthesis of chromans and 4-

aryl-3,4-dihydrobenzopyran-2-ones. 3,4-Dihydrobenzopyran-2-ones or dihydrocoumarins are well known for fragrance in cosmetics,[3] food flavouring[4] and perfumery industries.[5] 4-Aryl-3,4-dihydrocoumarins are naturally occurring compounds[6] exhibiting some interesting biological activities such as aldose reductase inhibition,[7] antiherpetic,[8] protein kinases[9] and are important synthetic intermediates for pharmaceutical compounds. Many methods are reported for the synthesis of dihydrocoumarins.[10]

Dihydrobenzopyran (chroman) ring system constitutes the basic unit in number of naturally occurring biologically active scaffolds.[11] It prevalently appears in important bioactive compounds such as vitamin E or α-tocopherol,[12] flavonoids,[13] etc. Many chroman derivatives are used as antioxidants for fats and oils[14] and some exhibit weak estrogenic activity.[15] Owing to this property they have attracted the attention of several chemists in recent years and are important drug targets. Most of the reported routes couple phenols and dienes by homogenous or heterogenous acids as catalyst[16] which is an atom economical way of constructing these heterocycles. Cyclocoupling of phenol derivatives with other unsaturated compounds like allylic alcohols,[17] allylic halides[18] have also appeared. Direct aromatic carbon-oxygen bond formation reactions leading to chromans are also well known.[19] Recently devised environmentally sound catalytic systems include annulations of phenols with 1,3-dienes using AgOTf under mild reaction conditions,[16m] recyclable $Sc(OTf)_3$/ionic liquid[16n] and $Cu(OTf)_2$-bipy,[16o] cyclocoupling of phenols with allylic alcohols using Mo/*o*-chloranil,[17d] CuAl-SBA-15,[17e] PPh_3AuNTf_2,[17f] and allyl prenyl ethers using $Mo(CO)_6$.[19e] Conventional methods make use of either hazardous or costly catalysts which prompted us to devise the chroman synthesis using an environmentally benign inexpensive iodine catalyst.

2. Results and discussion:

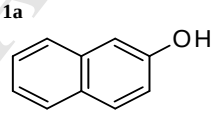
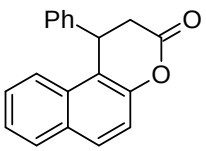
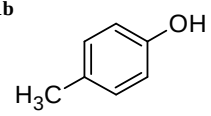
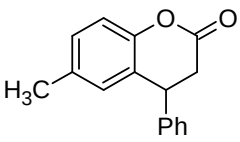


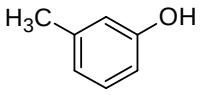
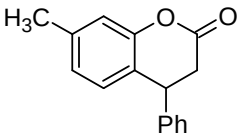
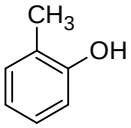
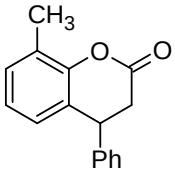
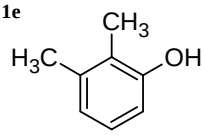
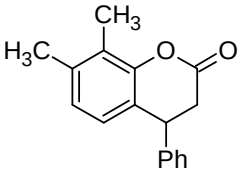
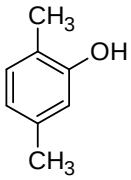
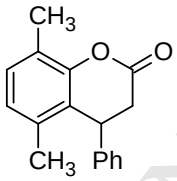
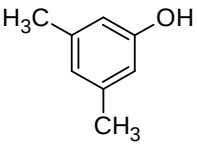
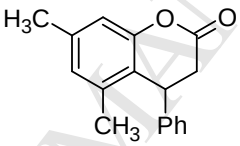
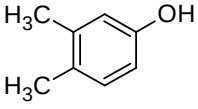
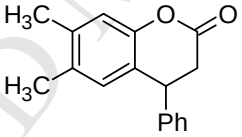
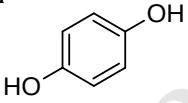
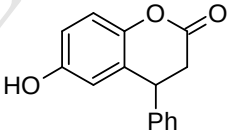
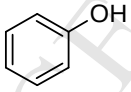
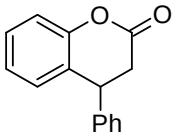
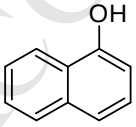
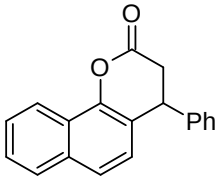
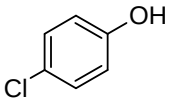
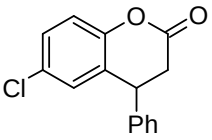
Scheme 1. Reaction of phenol with cinnamic acid.

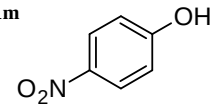
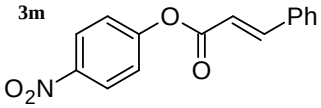
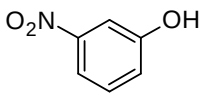
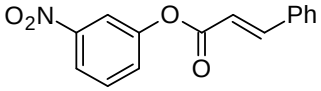
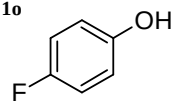
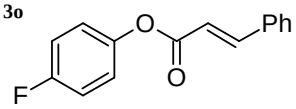
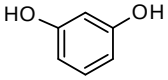
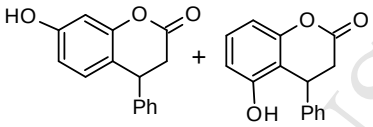
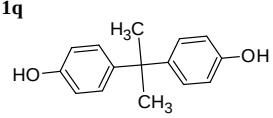
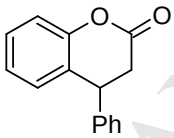
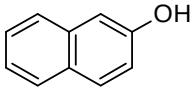
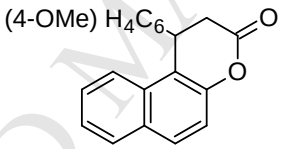
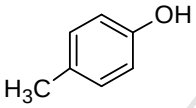
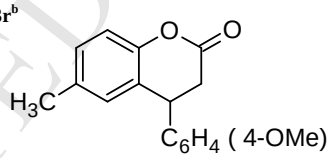
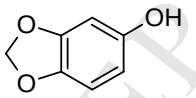
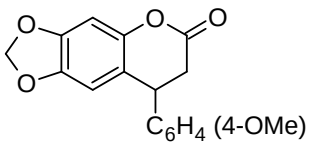
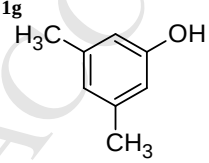
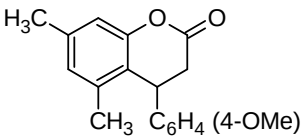
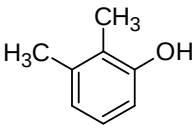
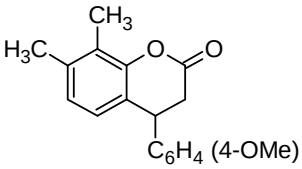
Our work commenced with the synthesis of 4-aryl-3,4-dihydrobenzopyran-2-ones (Scheme 1). Initial studies were done using β-naphthol and cinnamic acid. Solvent studies proved xylene to be the best solvent in refluxing condition to give maximum yield of 70% after 5 h. Under solvent-free condition at 120-130 ^{0}C maximum yield of 80% was isolated after 1 h.

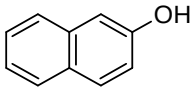
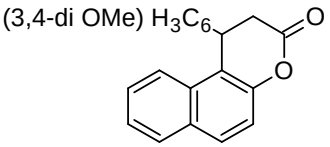
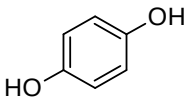
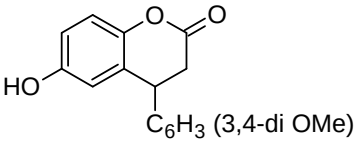
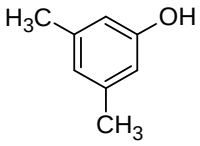
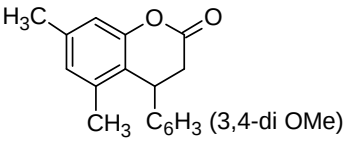
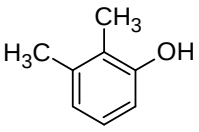
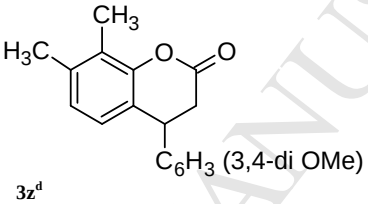
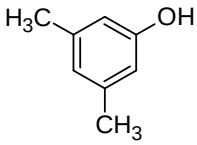
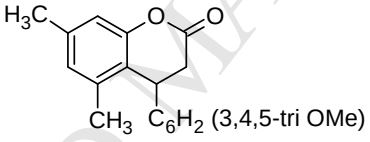
Hence further studies were done for solvent-free condition only. Iodine concentration was also optimized wherein 20 mol% was found to be optimum to give maximum yield of the product and without iodine no product was observed even after heating for 24 h. Generality of this reaction was proved by synthesizing the following derivatives (Table 1). Several electron rich phenols with substituted methyl group were rapidly converted into dihydrocoumarins in good yields (**3b**-**3h**). Quinol rapidly converted to give product (**3i**) in good yield. Parent phenol gave 60% yield of product (**3j**) in 4 hours while α- naphthol gave product (**3k**) in 65% yield. Also, electron deficient p-chlorophenol gave the product (**3l**) in good yield (70%). However phenols with strong electron withdrawing nitro groups at *para* and *meta* positions resulted in formation of the corresponding nitro phenyl cinnamates (**3m** and **3n**) instead of expected dihydrocoumarins after 24 hours in low yields. Similarly *p*-fluorophenol resulted in the formation of ester (**3o**) in 50% yield. Resorcinol gave a mixture of two regioisomeric dihydrocoumarins (**3p**) in 5:1 ratio. Bisphenol A gave a complex mixture from which 5% of product dihydrocoumarin (**3j**) was separated. The formation of dihydrocoumarin could be explained by the concomitant dearylation. The reaction was also performed with substituted cinnamic acids resulting in a series of dihydrocoumarins (**3q**-**3z**). 4-methoxy cinnamic acid smoothly reacted with various phenols to give dihydrocoumarins (**3q**-**3u**) in good yields. Similarly 3,4-dimethoxy cinnamic acid underwent cyclization to form desired products (**3v**-**3y**) in good yields whereas 3,4,5-trimethoxy cinnamic acid on reaction with 3,5-dimethyl phenol gave the corresponding dihydrocoumarin (**3z**) in 63% yield. The reaction of acrylic acid with m-cresol failed to give the corresponding dihydrocoumarin. The formation of dihydrocoumarins could be accounted *via* esterification followed by hydroarylation pathway.

Table 1. Various 4-aryl-3,4-dihydrobenzopyran-2-one derivatives **3a-l, p-z** and substituted phenyl cinnamates **3m-o** produced under optimized reaction conditions

Entry	Substituted Phenol	Product	Time (h)	Yield(%)[a]
1	**1a** 	**3a** 	1	80
2	**1b** 	**3b** 	1	83

3	**1c** 	**3c** 	1.5	78
4	**1d** 	**3d** 	3	60
5	**1e** 	**3e** 	4	83
6	**1f** 	**3f** 	5	65
7	**1g** 	**3g** 	2	85
8	**1h** 	**3h** 	2	85
9	**1i** 	**3i** 	2	77
10	**1j** 	**3j** 	4	60
11	**1k** 	**3k** 	4	65
12	**1l** 	**3l** 	3	70

13	**1m** 	**3m** 		24	20
14	**1n** 	**3n** 		24	30
15	**1o** 	**3o** 		24	50
16	**1p** 	**3pa:3pb (~5:1)** 		5	70
17	**1q** 	**3j** 		10	5
18	**1a** 	**3q**[b] 		4	85
19	**1b** 	**3r**[b] 		1.5	78
20	**1r** 	**3s**[b] 		4	68
21	**1g** 	**3t**[b] 		3	82
22	**1e** 	**3u**[b] 		1	83

23	**1a** 	**3v**[c] 	1.45	80
24	**1i** 	**3w**[c] 	4	72
25	**1g** 	**3x**[c] 	2	77
26	**1e** 	**3y**[c] 	2	60
27	**1g** 	**3z**[d] 	2.3	63

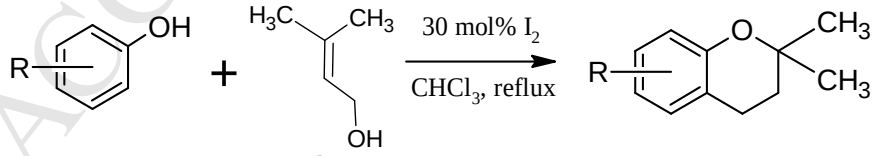
[a] Isolated % yield after column chromatography.

[b] In this case 4-methoxy cinnamic acid was used.

[c] In this case 3,4-dimethoxy cinnamic acid was used.

[d] In this case 3,4,5-trimethoxy cinnamic acid was used.

We then conceived that the Lewis acidity of iodine can be put to use for the synthesis of chromans (Scheme 2).



Scheme 2. Reaction of substituted phenols with prenyl alcohol.

At the outset we examined the effect of iodine catalyst (30 mol%) on cyclization of β-naphthol (**1a**) and prenyl alcohol (**4a**) as substrates at room temperature in chloroform. After prolonged stirring some formation of product chroman **5a** was observed. To reduce the time,

the reaction was refluxed wherein product formation was observed within 1 hour. Next we examined the stoichiometry of substrates. It was observed that when phenol was used in excess (4 equivalents) optimum yield of 92% was observed after 4 hours (Table 2, entry 4). Use of excess of prenyl alcohol led to a complex mixture.

Table 2. Optimization of stoichiometry of starting materials **1a** and **4a**

Entry	**1a**	**4a**	Time (h)	% yield[a,b]
1	1	1	4	78
2	2	1	4	80
3	3	1	4	88
4	4	1	4	92
5	5	1	4	85

[a] Isolated yields based on substrate **4a**

[b] Trace amount of **5a'** (figure 1) was formed

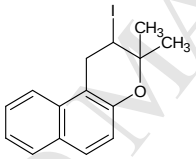


Figure 1. Structure of **5a'**.

Optimization of iodine concentration was studied by varying the amount of iodine (Table 3). No product formation was observed in the absence of iodine (entry 1). When 10 mol% iodine was used, the formation of **5a** was seen and the product yield was found to increase with increase in catalyst loading and with reduction in time. 30 Mol % of iodine in refluxing chloroform was found to be the optimum concentration (entry 4). Further increase in iodine concentration resulted in decreased product yield (entry 5). When the reaction was carried out with stoichiometric amount of iodine at room temperature with 1:1 ratio of **1a**:**4a** the formation of mixture of 3,3-dimethyl-2,3-dihydro-1*H*-benzo[*f*]chromene (**5a**) and 2-iodo-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*f*]chromene (**5a'**) in ~1.2:1 ratio was observed.

Table 3. Optimization of iodine concentration in refluxing chloroform

Entry	Iodine (mol %)	Time (h)	% yield[a]
1	0	24	0

2	10	24	85
3	20	24	89
4	30	4	92
5	40	2	79
6	100[b]	1.3	58, 31[c]

[a] Isolated yields of **5a** based on substrate **4a**

[b] Reaction carried out at room temperature

[c] % yield of **5a'**

Effect of solvents was studied by carrying out this reaction in different solvents (Table 4). Formation of product was seen in almost all solvents. Refluxing in protic solvents like ethanol and methanol found to require longer time. Better results were obtained in chlorinated solvents like chloroform and dichloromethane with less duration of time, of which chloroform was giving maximum yield. Other solvents like toluene, tetrahydrofuran, 1,4-dioxane, 1,2-dichloroethane and acetonitrile resulted in moderate yields.

Table 4. Solvent screening

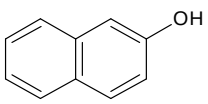
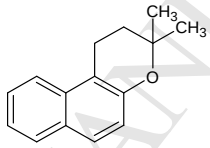
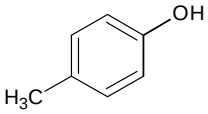
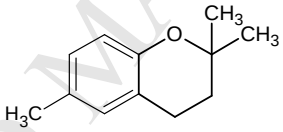
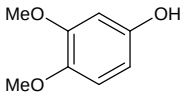
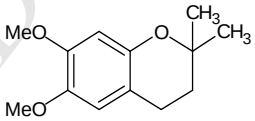
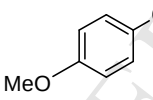
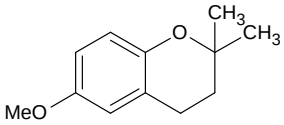
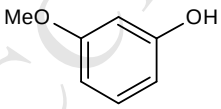
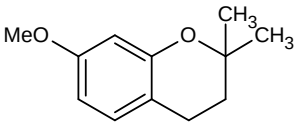
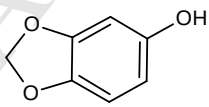
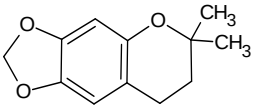
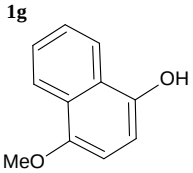
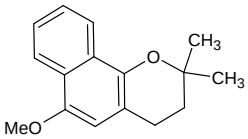
Entry	Solvent	Time (h)	% yield[a]
1	Methanol	24	50
2	Ethanol	24	45
3	Chloroform	4	92
4	Dichloromethane	4	90
5	Toluene	24	30
6	Tetrahydrofuran	7	65
7	1,4-Dioxane	7	60
8	1,2-Dichloroethane	5	68
9	Acetonitrile	24	25

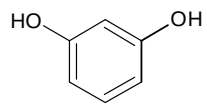
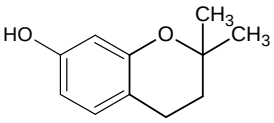
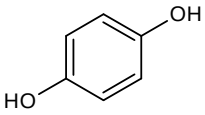
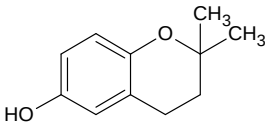
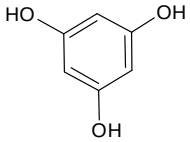
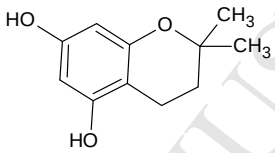
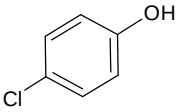
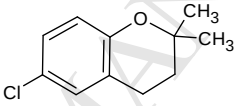
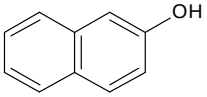
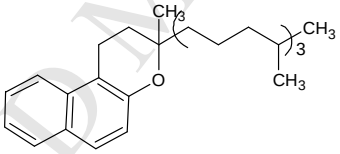
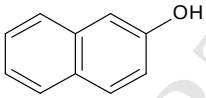
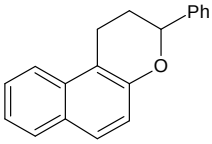
[a] Isolated yields based on substrate **4a**

Inorder to explore the generality of this reaction, various phenols were subjected to the optimum reaction condition (Table 5). The reaction of ß-naphthol with **4a** and 2-methylbut-3-en-2-ol **4b** gave chroman (**5a)** in 92% and 87% yields respectively. Electron rich phenols were converted to respective chromans (**5b**-**5e)** in good to moderate yields. Similarly 3,4-methylenedioxyphenol underwent cyclization readily to afford chroman (**5f**). Naturally

occurring dihydrolapachenole (**5g)** isolated from *Tabebuia chrysantha*[20] was synthesised from 4-methoxynaphthol in good yield. Dihydroxy compounds like resorcinol and quinol which are insoluble in chloroform, when refluxed in methanol afforded respective chromans (**5h)** and (**5i)** in moderate yields. Resorcinol resulted exclusively in one isomer (**5h)**. Similarly phloroglucinol in refluxing methanol afforded chroman (**5j)** in 56% yield. p-Chlorophenol was converted to corresponding chroman (**5k)** in low yield. The slow reaction and low yield is attributed to the electron withdrawing effect of chloro group. Also, we examined the reaction of ß-naphthol with phytol **4c** and cinnamyl alcohol **4d** to afford desired chromans (**5l)** and (**5m)** respectively in good yields.

Table 5. Various chroman derivatives **5a-m** produced under optimized reaction conditions

Entry	Substituted Phenol	Product	Time (h)	Yield(%)[a]
1	**1a** 	**5a** 	4	92, 87[b]
2	**1b** 	**5b** 	4	48
3	**1c** 	**5c** 	2	77
4	**1d** 	**5d** 	4	58
5	**1e** 	**5e** 	4	45
6	**1f** 	**5f** 	4	58
7	**1g** 	**5g** 	2	60

8	**1h** 	**5h** 		4	46*
9	**1i** 	**5i** 		4	33*
10	**1j** 	**5j** 		4	56*
11	**1l** 	**5k** 		24	20
12	**1a** 	**5l** 		4	76[c]
13	**1a** 	**5m** 		4	60[d]

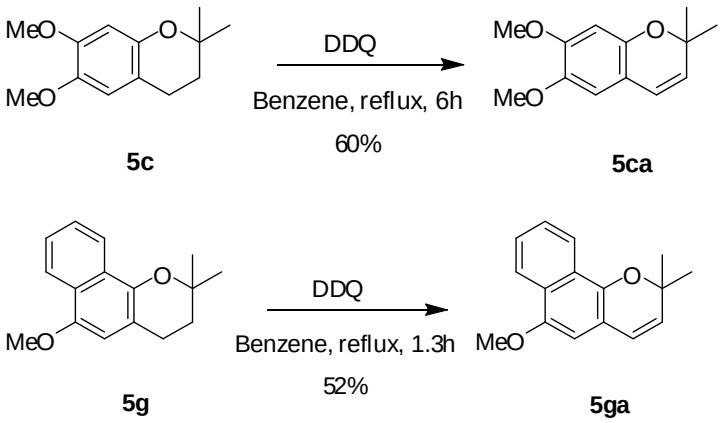
[a] Isolated % yield after column chromatography based on unsaturated alcohol substrate

[b] 2-methylbut-3-en-2-ol **4b**, [c]phytol **4c**, [d]cinnamyl alcohol **4d** were used

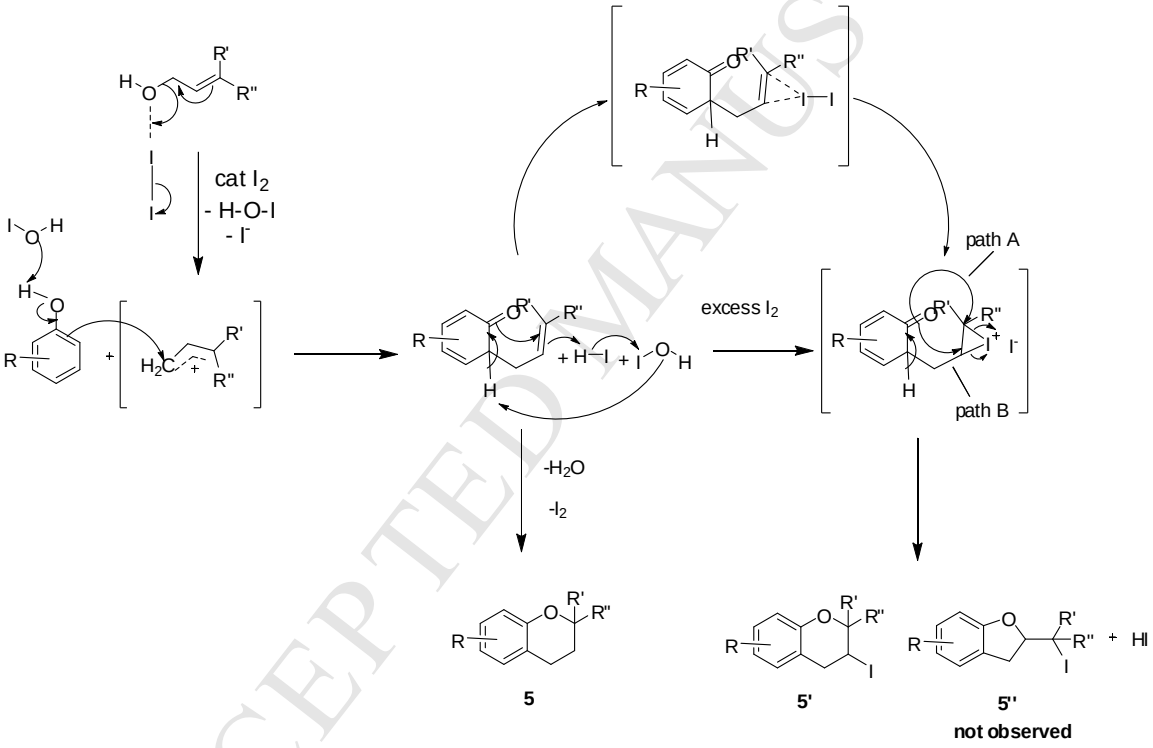
* Reaction carried out in methanol

Unreacted and excess phenols were recovered.

As a further application to our work, synthesis of naturally occurring precocene II **5ca** and lapachenole **5ga** was performed (Scheme 3). **5ca** is an insect growth regulator, genotoxic and produces hepatic centrolobular necrosis in rats[21] whereas **5ga** has been used as a fluorescent photoaffinity label[22] as well as shown to have cancer chemopreventive activity.[23] Chroman **5c** was refluxed in benzene with DDQ for 6 hours to give **5ca** in 60% yield.[24] Similarly chroman **5g** on refluxing for 1.3 h in benzene delivered **5ga** in 52% yield.



Scheme 3. Synthesis of precocene II **5ca** and lapachenole **5ga**.



Scheme 4. Proposed mechanism for the formation of chromans

The proposed mechanistic pathway for the formation of chroman is shown in scheme 4. Loss of alcoholic OH group takes place by coordination of iodine making it a better leaving group facilitated by allylic double bond. Intermolecular electrophillic attack by the phenolic arene ring on less hindered carbon atom of thus formed carbocation followed by intramolecular oxygen attack on more substituted carbon atom of double bond and subsequent aromatization delivered chroman. On the other hand if the double bond coordinates with iodine to form

iodinium ion prior to the intramolecular oxygen attack, oxygen attack can take place either by path A or path B to give **5'** or **5''** respectively. But the obtained product **5a'** indicates the attack at more substituted carbon atom which is favoured when excess of iodine is used.

3. Conclusion

In summary, we have demonstrated utility of molecular iodine as mild Lewis acid for the synthesis of important oxygen heterocycles 4-aryl-3,4-dihydrocoumarins and chromans *via* cyclocoupling. The usefulness of the method is demonstrated by synthesis of naturally occurring chroman dihydrolapachenole **5g**. Further these chromans can be used for the synthesis of chromenes by conventional dehydrogenation which is demonstrated by synthesis of precocene II **5ca** and lapachenole **5ga**.

4. Experimental

4.1. General remarks. All the dihydrocoumarins, chromans and chromenes formed were characterized by spectral analysis (IR; ^{1}H NMR; ^{13}C NMR) and comparison of their melting points with the literature reports. Commercial reagents were used without further purification except p-methoxyphenol and m-methoxyphenol which were prepared using standard procedure from respective dihydroxy compounds. Solvents were distilled prior to use. Column chromatography was performed on 60-120 mesh silica gel. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVANCE 400 instrument in $CDCl_3$ as solvent and TMS as an internal standard. Infrared Spectra (IR) were recorded in a Shimadzu FTIR instrument. Elemental analyses were carried out using Elementar Variomicro Cube CHNS Analyser. High resolution mass spectrum (HRMS) was recorded on a Micro Mass ESQTOF Mass spectrometer at IISc, Bangalore. Melting points are uncorrected. Coupling constants are reported in Hz.

4.2. General procedures

(I) General procedure for the synthesis of dihydrocoumarins.

Iodine (0.13 mmol) was added into a mixture of phenol (0.69 mmol) and cinnamic acid (0.69 mmol) under an air atmosphere and the mixture was neat heated at 120-130 °C for a period of time (1-4 hours). Following completion of the reaction as monitored by TLC, the reaction mixture was cooled, diluted with ethyl acetate, washed with aqueous sodium thiosulphate solution and dried over sodium sulphate. The solvent was removed under vacuum to provide

the crude products. Further purification was done by column chromatography on silica gel with hexanes/ethyl acetate (4:1) as an eluent.

(II) General procedure for the synthesis of chromans.

In a 50 mL round bottom flask, prenyl alcohol (1.16 mmol) was mixed with chloroform (10 mL). To it, substituted phenol (4.0 equivalence) and iodine (0.3 equivalence) were added at room temperature. This reaction mixture was subjected to reflux with stirring for 4 hours. It was then cooled to room temperature. Chloroform was directly washed with saturated solution of sodium thiosulphate followed by dilute sodium hydroxide solution. Finally chloroform layer was washed with water, dried over sodium sulphate and concentrated to furnish the crude product. This was then purified using 60-120 mesh silica gel column chromatography (hexanes-ethyl acetate) to give chroman.

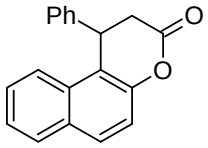
(III) General procedure for the synthesis of chromenes.

To 3,4-dimethoxychroman (0.45 mmol) in a 50 mL round bottom flask, was added DDQ (0.45 mmol) and was subjected to reflux in benzene (10 mL). After completion of reaction, benzene was removed by distillation and crude reaction mixture thus obtained was purified by column chromatography (hexanes-ethyl acetate) to furnish chromene.

4.3. Experimental Procedures and Characterization:

Various 4-aryl-3,4-dihydrobenzopyran-2-one derivatives and substituted phenyl cinnamates:

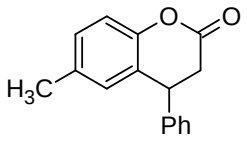
5,6-Benzo-4-phenyl-3,4-dihydrobenzopyran-2-one (**3a**)[25]



A colourless solid (78% yield); mp 115-117 °C; Lit[25] 115-116 °C; IR (KBr): ν_{max} = 1778, 1764 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.16-3.27 (m, 2 H), 4.98 (d, *J* = 6.0 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 2 H), 7.25-7.31 (m, 3 H), 7.38 (d, *J* = 9.2 Hz, 1 H), 7.48-7.52 (m, 2 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.5 (CH_2),

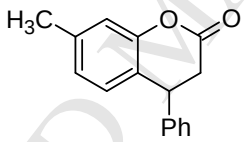
37.7 (CH), 117.6 (CH), 117.7 (Cq), 123.1 (CH), 125.3 (CH), 126.9 (2 X CH), 127.5 (CH), 127.6 (CH), 128.8 (CH), 129.3 (2 X CH), 129.9 (CH), 131.0 (Cq), 131.1 (Cq), 140.6 (Cq), 149.8 (Cq), 167.2 (Cq).

6-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3b**)[26]



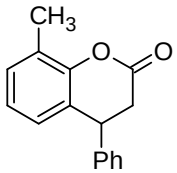
A colourless solid (83% yield); mp 80-83 °C; Lit[26] 83 °C; IR (KBr) 1757 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 3 H), 2.99-3.11 (m, 2 H), 4.32 (t, *J* = 6.8 Hz, 1 H), 6.81 (s, 1 H), 7.05 (d, *J* = 8.0 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.18 (d, *J* = 7.2 Hz, 2 H), 7.29-7.40 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.8 (CH_3), 37.2 (CH_2), 40.7 (CH), 116.9 (CH), 125.3 (Cq), 127.6 (2 X CH), 127.6 (CH), 128.7 (CH), 129.2 (2 X CH), 129.3 (CH), 134.4 (Cq), 140.5 (Cq), 149.7 (Cq), 167.9 (Cq).

7-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3c**)[27]



A colourless solid (78% yield); mp 124 °C; Lit[27] 124 °C; IR (KBr): ν_{max} =1778, 1764 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.38 (s, 3 H), 2.99-3.11 (m, 2 H), 4.33 (t, *J* = 6.8 Hz, 1 H), 6.89 (q, *J* = 8.0 Hz, 2 H), 6.97 (s, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.28-7.32 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1 (CH_3), 37.2 (CH_2), 40.4 (CH), 117.5 (CH), 122.7 (Cq), 125.5 (CH), 127.6 (2 X CH), 127.6 (CH), 128.1 (CH), 129.1 (2 X CH), 139.2 (Cq), 140.6 (Cq), 151.6 (Cq), 167.9 (Cq).

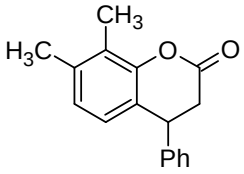
8-Methyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3d**)[28]



A colourless solid (60% yield); mp 106-108 °C; Lit[28] 108 °C; IR (KBr): ν_{max} = 1764 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.36 (s, 3 H), 2.99-3.10 (m, 2 H), 4.32 (t, *J* = 6.8 Hz, 1 H), 6.81 (d, *J* = 7.6 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 3 H), 7.26-7.33 (m, 3 H);

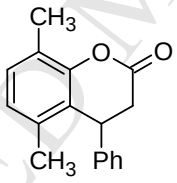
^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.9 (CH_3), 36.9 (CH_2), 40.8 (CH), 124.2 (CH), 125.6 (Cq), 125.9 (CH), 126.5 (Cq), 127.6 (2 X CH), 127.6 (CH), 129.1 (2 X CH), 130.3 (CH), 140.5 (Cq), 150.0 (Cq), 167.9 (Cq).

7,8-Dimethyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3e**)



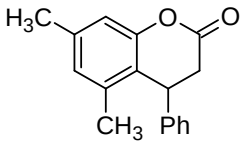
A colourless solid (83% yield); mp 119-120 °C; IR (KBr): ν_{max} = 1768 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.27 (s, 3 H), 2.29 (s, 3 H), 3.00-3.03 (m, 2 H), 4.29 (t, *J* = 6.8 Hz, 1 H), 6.70 (d, *J* = 7.6 Hz, 1 H), 6.88 (d, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 2 H), 7.25-7.35 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.9 (CH_3), 19.9 (CH_3), 37.0 (CH_2), 40.7 (CH), 123.1 (Cq), 124.9 (CH), 125.6 (CH), 127.5 (2 X CH), 127.6 (CH), 129.1 (2 X CH), 137.8 (Cq), 140.7 (Cq), 149.8 (Cq), 168.2 (Cq), 168.2 (Cq).

5,8-Dimethyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3f**)[28]



A colourless solid (65% yield); mp 78-80 °C; Lit[28] 78 °C IR (KBr): ν_{max} = 1764 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3 H), 2.34 (s, 3 H), 3.02-3.04 (m, 2 H), 4.38-4.40 (dd, *J* = 5.6, 3.6 Hz, 1 H), 6.89 (d, *J* = 7.6 Hz, 1 H), 7.03 (d, *J* = 6.8 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.21-7.28 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.8 (CH_3), 18.6 (CH_3), 37.6 (CH_2), 38.3 (CH), 123.0 (Cq), 124.1 (Cq), 125.9 (CH), 127.0 (2 X CH), 127.4 (CH), 129.1 (2 X CH), 130.1 (CH), 134.1 (Cq), 140.1 (Cq), 150.4 (Cq), 167.5 (Cq).

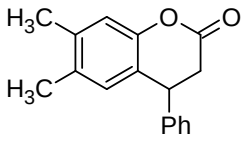
5,7-Dimethyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3g**)[26]



A colourless solid (85% yield); mp 130-132 °C; Lit[26] 134 °C; IR (KBr): ν_{max} = 1753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.16 (s, 3 H), 2.37 (s, 3 H), 3.01-3.11 (m, 2 H), 4.39 (d, *J* = 6.0

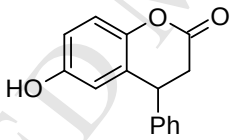
Hz, 1 H), 6.86 (d, *J* = 5.6 Hz, 2 H), 7.06 (d, *J* = 7.6 Hz, 2 H), 7.22-7.31 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.7 (CH_3), 21.1 (CH_3), 37.8 (CH_2), 38.0 (CH), 115.5 (CH), 120.1 (Cq), 126.9 (2 X CH), 127.4 (CH), 127.4 (CH), 129.1 (2 X CH), 136.6 (Cq), 138.8 (Cq), 140.4 (Cq), 152.1 (Cq), 167.6 (Cq).

6,7-Dimethyl-4-phenyl-3,4-dihydrobenzopyran-2-one (**3h**)[28]



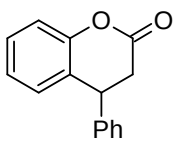
A pale yellow solid (85% yield); mp 110-113 ºC; Lit[28]111 ºC; IR (KBr): ν_{max} = 1759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.17 (s, 3 H), 2.27 (s, 3 H), 2.97-3.09 (m, 2 H), 4.29 (t, *J* = 6.8 Hz, 1 H), 6.75 (s, 1 H), 6.94 (s, 1 H), 7.17 (d, *J* = 7.2 Hz, 2 H), 7.31 (d, *J* = 7.2 Hz, 1 H), 7.35-7.38 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.1 (CH_3), 19.6 (CH_3), 37.4 (CH_2), 40.5 (CH), 117.9 (CH), 122.5 (Cq), 127.5 (2 X CH), 127.5 (CH), 129.0 (CH), 129.1 (2 X CH), 133.0 (Cq), 137.5 (Cq), 140.9 (Cq), 149.7 (Cq), 168.1 (Cq).

6-Hydroxy-4-phenyl-3,4-dihydrobenzopyran-2-one (**3i**)[29]



A colourless solid (77% yield); mp 125-130 ºC; Lit[29] 133 ºC; IR (KBr): ν_{max} = 3331 cm^{-1} & 1741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.96-3.08 (m, 2 H), 4.27 (t, *J* = 6.8 Hz, 1 H), 5.55 (bs, 1 H), 6.43 (s, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 7.00 (d, *J* = 8.8 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.29-7.38 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.9 (CH_2), 40.7 (CH), 114.7 (CH), 115.5 (CH), 118.0 (CH), 126.9 (Cq), 127.5 (2 X CH), 127.8 (CH), 129.2 (2 X CH), 139.9 (Cq), 145.4 (Cq), 152.6 (Cq), 168.5 (Cq).

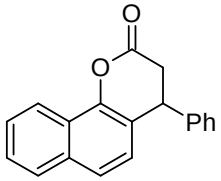
4-Phenyl-3,4-dihydrobenzopyran-2-one (**3j**)[27]



A colourless solid (60% yield from phenol and 5% yield from bisphenol A); mp 78-80 ºC; Lit[27] 78 ºC; IR (KBr): ν_{max} = 1759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.02-3.14 (m, 2 H),

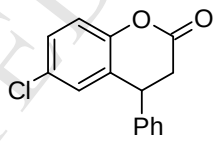
4.37 (t, *J* = 7.2 Hz, 1 H), 7.00 (d, *J* = 7.6 Hz, 1 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 7.15 (s, 1 H), 8.40 (d, *J* = 7.2 Hz, 2 H), 7.32-7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.0 (CH_2), 40.7 (CH), 117.2 (CH), 124.7 (CH), 125.8 (Cq), 127.6 (2 X CH), 127.7 (CH), 128.4 (CH), 128.8 (CH), 129.2 (2 X CH), 140.3 (Cq), 151.7 (Cq), 167.7 (Cq).

7,8-Benzo-4-phenyl-3,4-dihydrobenzopyran-2-one (**3k**)[28]



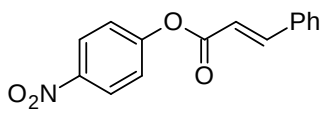
A pale yellow solid (65% yield); mp 112 °C; Lit[28] 112 °C; IR (KBr): ν_{max} = 1762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.14-3.26 (m, 2 H), 4.51 (s, 1 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 6.4 Hz, 2 H), 7.32 (s, 1 H), 7.35 (d, *J* = 6.8 Hz, 2 H), 7.57 (s, 1 H), 7.60 (d, *J* = 10.4 Hz, 2 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 8.33 (d, *J* = 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.3 (CH_2), 41.1 (CH), 119.9 (Cq), 121.4 (CH), 123.7 (Cq), 124.3 (CH), 125.3 (CH), 126.8 (CH), 126.9 (CH), 127.5 (2 X CH), 127.6 (CH), 127.7 (CH), 129.2 (2 X CH), 133.7 (Cq), 140.7 (Cq), 146.8 (Cq), 167.5 (Cq).

6-Chloro-4-phenyl-3,4-dihydrobenzopyran-2-one (**3l**)[30]



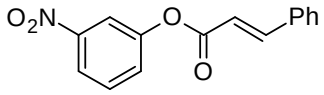
A colourless solid (70% yield); mp 110 °C; Lit[30] 103-104 °C; IR (KBr): ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.00-3.12 (m, 2 H), 4.33 (t, *J* = 6.8 Hz, 1 H), 6.96 (s, 1 H), 7.10 (d, *J* = 8.8 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 2 H), 7.30 (s, 1 H), 7.35-7.40 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.6 (CH_2), 40.6 (CH), 118.5 (CH), 127.5 (2 X CH), 127.6 (Cq), 128.0 (CH), 128.2 (CH), 128.9 (CH), 129.4 (2 X CH), 129.8 (Cq), 139.4 (Cq), 150.2 (Cq), 166.9 (Cq).

4-Nitro-phenyl cinnamate (**3m**)[31]



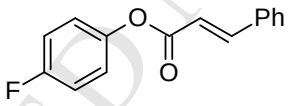
A colourless solid (20% yield); mp 142-144 °C; Lit[31] 142-146 °C; IR(KBr): ν_{max} = 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.56 (d, *J* = 16.0 Hz, 1 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 7.37-7.39 (m, 3 H), 7.53-7.55 (m, 2 H), 7.85 (d, *J* = 16.0 Hz, 1 H), 8.24 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 115.1 (CH), 121.4 (2 X CH), 124.2 (2 X CH), 127.5 (2 X CH), 128.1 (2 X CH), 130.2 (CH), 132.7 (Cq), 144.2 (Cq), 147.0 (CH), 154.6 (Cq), 163.3 (Cq).

3-Nitro-phenyl cinnamate (**3n**)[31]



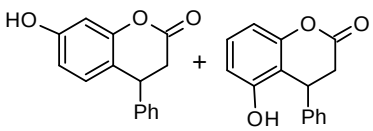
A colourless solid (30% yield); mp 106-108 °C; Lit[31] 108-110 °C; IR(KBr): ν_{max} = 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.64 (d, *J* = 16.0 Hz, 1 H), 7.45-7.47 (m, 3 H), 7.56-7.63 (m, 4 H), 7.92 (d, *J* = 16.0 Hz, 1 H), 8.09 (t, *J* = 2.4 Hz, 1 H), 8.13-8.15 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 115.1 (CH), 116.4 (CH), 119.7 (CH), 126.7 (CH), 127.4 (2 X CH), 128.1 (2 X CH), 129.0 (CH), 130.1 (CH), 132.8 (Cq), 146.9 (CH), 147.8 (Cq), 150.1 (Cq), 163.7 (Cq).

4-Fluoro-phenyl cinnamate (**3o**)[32]



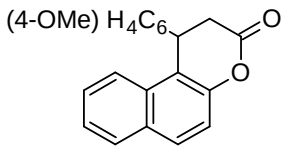
A colourless solid (50% yield); mp 70-75 °C; Lit[32] 73-74.5 °C; IR(KBr): ν_{max} = 1735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.64 (d, *J* = 15.6 Hz, 1 H), 7.12-7.15 (m, 4 H), 7.46 (s, 3 H), 7.61 (s, 2 H), 7.89 (d, *J* = 16.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 115.9 (CH), 116.2 (CH), 116.9 (CH), 123.0 (CH), 123.1 (CH), 128.4 (2 X CH), 129.1 (2 X CH), 130.8 (CH), 134.1 (Cq), 146.9 (CH), 159.0 (Cq), 161.5 (Cq), 165.4 (Cq).

7-Hydroxy-4-phenyl-3,4-dihydro-2*H*-chromen-2-one and 5-hydroxy-4-phenyl-3,4-dihydro-2*H*-chromen-2-one (3pa+3pb)[33]



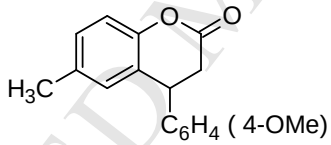
A colourless solid (70% yield); **3pa (3pb)** 5:1; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.99-3.12 (m), 4.30 (4.65) (t), 6.60 (d), 6.71 (s), 6.84 (d), 7.17 (d), 7.29-7.38 (m).

5,6-Benzo-4-(4-methoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3q**)[34]



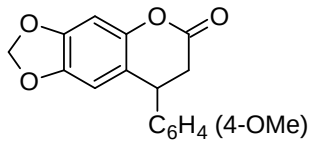
A colorless solid (85% yield); mp 128-130 °C; Lit[34] 130-131 °C; IR (KBr): ν_{max} =1762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.04-3.16 (m, 2 H), 3.66 (s, 3 H), 4.85 (dd, *J* = 6.4, 2 Hz, 1 H), 6.72 (d, *J* = 6.4 Hz, 2 H), 6.97 (d, *J* = 6.4 Hz, 2 H), 7.27 (d, *J* = 9.2 Hz, 1 H), 7.37-7.43 (m, 2 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 9.2 Hz, 2 H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.8 (CH), 37.7 (CH_2), 55.2 (OCH_3), 114.6 (2 X CH), 117.6 (CH), 118.1 (Cq), 123.1 (CH), 125.3 (CH), 127.5 (CH), 128.1 (2 X CH), 128.8 (CH), 129.9 (CH), 131.0 (Cq), 131.1 (Cq), 132.6 (Cq), 149.7 (Cq), 158.9 (Cq), 167.4 (Cq).

6-Methyl-4-(4-methoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3r**)[28]



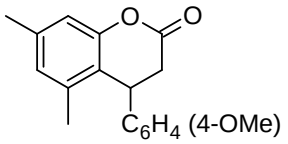
A colourless solid (78% yield); mp 115 °C; Lit[28] 120 °C; IR (KBr): ν_{max} = 1757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.27 (s, 3 H), 2.95-3.07 (m, 2 H), 3.82 (s, 3 H), 4.27 (t, *J* = 6.8 Hz, 1 H), 6.79 (s, 1 H), 6.89 (d, *J* = 7.2 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 7.08-7.11 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.8 (CH_3), 37.3 (CH_2), 39.9 (CH), 55.3 (CH_3), 114.5 (2 X CH), 116.8 (CH), 125.8 (Cq), 128.6 (2 X CH), 128.6 (CH), 129.2 (CH), 132.5 (Cq), 134.3 (Cq), 149.6 (Cq), 158.9 (Cq), 168.1 (Cq).

6,7-Methylenedioxy-4-(4-methoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3s**)[34]



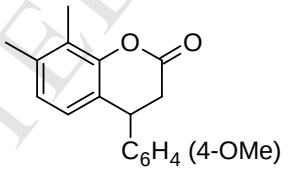
A colorless solid (68% yield); mp 136-138 °C; Lit[34] 136.5-137.5 °C; IR (KBr): ν_{max} = 1753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.83-2.97 (m, 2 H), 3.73 (s, 3 H), 4.11 (dd, *J* = 8.0, 6.0 Hz, 1 H), 5.88 (dd, *J* = 3.2, 1.6 Hz, 2 H), 6.32 (s, 1 H), 6.58 (s, 1 H), 6.79-6.82 (m, 2 H), 6.98-7.01 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.2 (CH_2), 39.9 (CH), 55.3 (OCH_3), 99.1 (CH), 101.7 (CH_2), 107.3 (CH), 114.5 (2 X CH), 118.4 (Cq), 128.6 (2 X CH), 132.4 (Cq), 144.4 (Cq), 146.1 (Cq), 147.5 (Cq), 159.0 (Cq), 167.8 (Cq).

5,7-Dimethyl-4-(4-methoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3t**)[35]



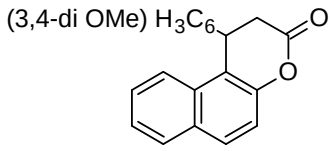
A colorless solid (82% yield); mp 166-168 °C; Lit[35] 166-168 °C; IR (KBr): ν_{max} = 1766 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.08 (s, 3 H), 2.27 (s, 3 H), 2.89-2.99 (m, 2 H), 3.68 (s, 3 H), 4.26 (dd, *J* = 6.0, 2.4 Hz, 1 H), 6.72 (d, *J* = 8.0 Hz, 2 H), 6.76 (d, *J* = 3.2 Hz, 2 H), 6.88 (d, *J* = 8.4, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.7 (CH_3), 21.1 (CH_3), 37.2 (CH), 37.9 (CH_2), 55.3 (OCH_3), 114.4 (2 X CH), 115.4 (CH), 120.5 (Cq), 127.3 (CH), 128.0 (2 X CH), 132.3 (Cq), 136.6 (Cq), 138.7 (Cq), 152.0 (Cq), 158.8 (Cq) 167.8 (Cq).

7,8-Dimethyl-4-(4-methoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3u**)[36]



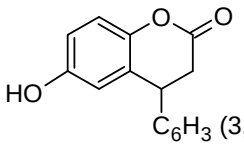
A colorless solid (83% yield); mp 112-114 °C; Lit[36] 114 °C IR (KBr): ν_{max} = 1749 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.19 (s, 3 H), 2.22 (s, 3 H), 2.86-2.97 (m, 2 H), 3.72 (s, 3 H), 4.18 (t, *J* = 6.8 Hz, 1 H), 6.63 (d, *J* = 7.6 Hz, 1 H), 6.78-6.82 (m, 3 H), 6.99 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.9 (CH_3), 19.9 (CH_3), 37.2 (CH_2), 39.9 (CH), 55.3 (OCH_3), 114.4 (2 X CH), 123.5 (Cq), 124.9 (CH), 124.9 (Cq), 125.6 (CH), 128.6 (2 X CH), 132.6 (Cq), 137.7 (Cq), 149.7 (Cq), 158.9 (Cq), 168.4 (Cq).

5,6-Benzo-4-(3,4-dimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3v**)[34]



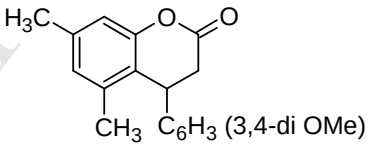
A colorless solid (80% yield); mp 152-154 °C; Lit[34] 156-159 °C; IR (KBr): ν_{max} =1757 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 3.05-3.16 (m, 2 H), 3.72 (s, 6 H), 4.82-4.84 (m, 1 H), 6.50-6.53 (dd, *J* = 2.0 Hz, 1 H), 6.62-6.63 (m, 1 H), 6.65 (s, 1 H), 7.27 (d, *J* = 8.8 Hz, 1 H), 7.35-7.44 (m, 2 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.3 (CH), 37.7 (CH_2), 55.9 (CH_3), 55.9 (CH_3), 110.0 (CH), 111.6 (CH), 117.5 (CH), 117.9 (Cq), 119.1 (CH), 123.1 (CH), 125.3 (CH), 127.5 (CH), 128.8 (CH), 129.9 (CH), 131.0 (Cq), 131.1 (Cq), 133.0 (Cq), 148.4 (Cq), 149.5 (Cq), 149.7 (Cq), 167.4 (Cq).

6-Hydroxy-4-(3,4-dimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3w**)[37]



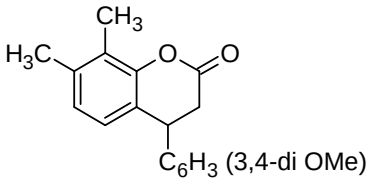
A colorless solid (72% yield); mp 164-166 °C; Lit[37] 168-170 °C; IR (KBr): ν_{max} = 3267, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.87-2.99 (m, 2 H), 3.77 (s, 3 H), 3.80 (s, 3 H), 4.15 (dd, *J* = 8.8, 6.0 Hz, 1 H), 4.86 (bs, 1 H), 6.35 (dd, *J* = 2.8, 0.4 Hz, 1 H), 6.60 (d, *J* = 2.0 Hz, 1 H), 6.64 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.68 (dd, *J* = 8.8, 2.8 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.94 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.0 (CH_2), 40.4 (CH), 55.9 (2 X OCH_3), 110.6 (CH), 111.5 (CH), 114.6 (CH), 115.4 (CH), 117.9 (CH), 119.9 (CH), 127.3 (Cq), 132.4 (Cq), 145.3 (Cq), 148.4 (Cq), 149.3 (Cq), 152.7 (Cq), 168.4 (Cq).

5,7-Dimethyl-4-(3,4-dimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3x**)[38]



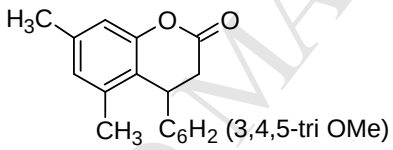
A colorless solid (77% yield); mp 137-139 °C; Lit[38]135 °C; IR (KBr): ν_{max} = 1764 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.07 (s, 3 H), 2.25 (s, 3 H), 2.92-2.94 (m, 2 H), 3.71 (s, 3 H), 3.73 (s, 3 H), 4.22-4.25 (m, 1 H), 6.42-6.45 (dd, *J* = 2.0 Hz, 1 H), 6.52 (d, *J* = 2.0 Hz, 1 H), 6.64 (d, *J* = 8.4 Hz, 1 H), 6.74 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.7 (CH_3), 21.1 (CH_3), 37.6 (CH), 37.9 (CH_2), 55.9 (2 X CH_3), 110.2 (CH), 111.5 (CH), 115.4 (CH), 119.0 (CH), 120.3 (Cq), 127.3 (CH), 132.9 (Cq), 136.6 (Cq), 138.7 (Cq), 148.3 (Cq), 149.3 (Cq), 152.0 (Cq), 167.7 (Cq).

7,8-Dimethyl-4-(3,4-dimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3y**)[38]



A colorless solid (60% yield); mp 98-100 °C; Lit[38] 98-99 °C; IR (KBr): ν_{max} = 1766 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3 H), 2.30 (s, 3 H), 2.98-3.02 (m, 2 H), 3.84 (s, 3 H), 3.87 (s, 3 H), 4.22-4.24 (m, 1 H), 6.68-6.70 (m, 2 H), 6.74 (s, 1 H), 6.82 (m, 1 H), 6.90 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.8 (CH_3), 19.9 (CH_3), 37.1 (CH_2), 40.4 (CH), 55.9 (2 X CH_3), 110.7 (CH), 111.6 (CH), 119.8 (CH), 123.4 (Cq), 124.8 (CH), 124.9 (Cq), 125.5 (CH), 133.1 (Cq), 137.7 (Cq), 148.4 (Cq), 149.4 (Cq), 149.7 (Cq), 168.2 (Cq).

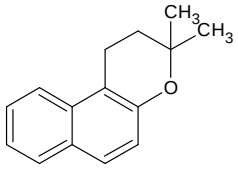
5,7-Dimethyl-4-(3,4,5-trimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3z**)



A mixture of 3.5-dimethyl phenol (0.69 mmol), 3,4,5-trimethoxycinnamic acid (0.69 mmol) and iodine (0.13 mmol) was neat heated at 120-130 °C under an air atmosphere for a period of 2.3 hours. Following completion of the reaction as monitored by TLC, the reaction mixture was cooled, diluted with ethyl acetate, washed with aqueous sodium thiosulphate solution and dried over sodium sulphate. The solvent was removed under vacuum to provide the crude product. Further purification was done by using 60-120 mesh silica gel column chromatography (hexanes/ethyl acetate, 7.5:2.5) as an eluent to give 5,7-dimethyl-4-(3,4,5-trimethoxyphenyl)-3,4-dihydrobenzopyran-2-one (**3z**) (709.0 mg, 63%) as a colourless solid; Rf (hexanes/ethyl acetate, 7:3) 0.47; mp 110-112 °C; IR (KBr): ν_{max} = 1774 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 3 H), 2.27 (s, 3 H), 2.94-2.96 (m, 2 H), 3.68 (s, 6 H), 3.72 (s, 3 H), 4.21-4.23 (m, 1 H), 6.16 (s, 2 H), 6.76 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 18.8 (CH_3), 21.1 (CH_3), 37.9 (CH_2), 38.3 (CH), 56.1 (2 X CH_3), 60.8 (CH_3), 103.9 (2 X CH), 115.4 (CH), 119.9 (Cq), 127.4 (CH), 136.2 (Cq), 136.7 (Cq), 137.2 (Cq), 138.9 (Cq), 152.0 (Cq), 153.6 (2 X Cq), 167.7 (Cq); HRMS: *m/z* calcd for $C_{20}H_{22}O_5Na$ $[M+Na]^+$: 365.1365; found: 365.1362.

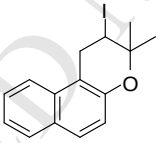
Various chroman derivatives:

3,3-Dimethyl-2,3-dihydro-1*H*-benzo[f]chromene (5a)[17d]



A colourless solid (92% yield from **4a** and 87% yield from **4b**); mp 68-70 °C, Lit[17d] 68-69 °C; IR (KBr): ν_{max} = 2974, 1620, 1597, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.38 (s, 6 H), 1.95 (t, *J* = 6.8 Hz, 2 H), 3.03 (t, *J* = 6.8 Hz, 2 H), 7.02 (d, *J* = 8.8 Hz, 1 H), 7.32 (ddd, *J* = 8.0, 7.6, 0.8 Hz, 1 H), 7.47 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.3 (CH_2), 26.6 (2 X CH_3), 32.7 (CH_2), 74.0 (Cq), 112.4 (Cq), 119.8 (CH), 121.9 (CH), 122.9 (CH), 126.2 (CH), 127.7 (CH), 128.4 (CH), 128.7 (Cq), 133.1 (Cq), 151.3 (Cq).

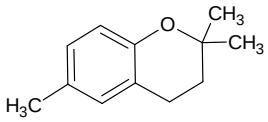
2-Iodo-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*f*]chromene (5a')



A mixture of prenyl alcohol (1.16 mmol), β-naphthol (1.16 mmol) and iodine (1.16 mmol) in chloroform (10 mL) was stirred for 1.3 hours at room temperature. Chloroform was then directly washed with saturated solution of sodium thiosulphate followed by dilute sodium hydroxide solution. Finally chloroform layer was washed with water, dried over sodium sulphate and concentrated to furnish the crude product. This was then purified using 60-120 mesh silica gel column chromatography (hexanes/ethyl acetate, 9.8:0.2) to give 2-iodo-3,3-dimethyl-2,3-dihydro-1*H*-benzo[*f*]chromene (**5a'**) (120.5 mg, 31%) as a colourless solid; Rf (hexanes/ethyl acetate, 9.5:0.5) 0.56; mp 108-110 °C; IR (KBr) 2974, 1622, 1597, 1236 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.45 (s, 3 H), 1.57 (s, 3 H), 3.55-3.75 (m, 2 H), 4.51 (dd, *J* = 9.6, 6.0 Hz, 1 H), 6.96 (d, *J* = 9.2 Hz, 1 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.60 (d, *J* = 9.2 Hz, 1 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (DMSO, 100 MHz) δ 24.3 (CH_3), 26.6 (CH_3), 33.1 (CH_2), 34.3 (CH), 76.1 (Cq), 111.5 (Cq),

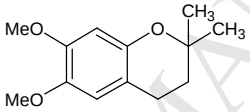
119.0 (CH), 121.9 (CH), 123.4 (CH), 126.6 (CH), 128.2 (2 X CH), 128.5 (Cq), 131.9 (Cq), 149.6 (Cq). Anal. Calcd. For $C_{15}H_{15}IO$: C, 53.3; H, 4.4 %; Found: C, 53.4; H, 4.5 %.

6-Methyl-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5b)[17d]



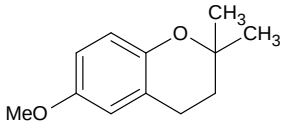
A colourless oil (48% yield); IR (neat): ν_{max} = 2976, 1498, 1261, 1105 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.23 (s, 6 H), 1.69 (t, *J* = 6.8 Hz, 2 H), 2.16 (s, 3 H), 2.64 (t, *J* = 6.8 Hz, 2 H), 6.60 (d, *J* = 8.0 Hz, 1 H), 6.78 (s, 1 H), 6.80 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.4 (CH_3), 21.4 (CH_2), 25.8 (2 X CH_3), 31.8 (CH_2), 72.8 (Cq), 115.9 (CH), 119.5 (Cq), 126.9 (CH), 127.6 (Cq), 128.7 (CH), 150.6 (Cq).

6,7-Dimethoxy-2,2-dimethyl-3,4-dihydro-2*H*-chromene (5c)[39]



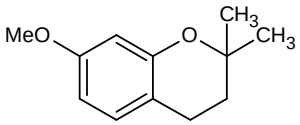
A colourless oil (77% yield); IR (neat): ν_{max} = 2974, 2933, 1620, 1514, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.24 (s, 6 H), 1.70 (t, *J* = 6.8 Hz, 2 H), 2.61 (t, *J* = 6.8 Hz, 2 H), 3.74 (s, 6 H), 6.30 (s, 1 H), 6.48 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.1 (CH_2), 26.7 (2 X CH_3), 32.9 (CH_2), 55.8 (CH_3), 56.4 (CH_3), 73.9 (Cq), 101.2 (CH), 111.2 (Cq), 112.2 (CH), 142.6 (Cq), 147.6 (Cq), 148.3 (Cq).

6-Methoxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5d)[16m]



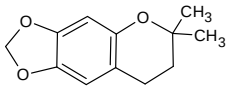
A colourless oil (58% yield); IR (neat): ν_{max} = 2972, 1492, 1247 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.23 (s, 6 H), 1.69 (t, *J* = 6.8 Hz, 2 H), 2.66 (t, *J* = 6.8 Hz, 2 H), 3.65 (s, 3 H), 6.52 (d, *J* = 2.4 Hz, 1 H), 6.60-6.64 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.8 (CH_2), 26.8 (2 X CH_3), 32.8 (CH_2), 55.7 (CH_3), 73.8 (Cq), 113.4 (CH), 113.9 (CH), 117.8 (CH), 121.5 (Cq), 148.0 (Cq), 152.9 (Cq).

7-Methoxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5e)[19d]



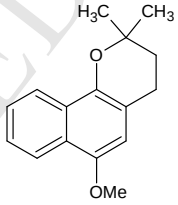
A colourless oil (45% yield); IR (neat): ν_{max} = 2974, 1620, 1504, 1151 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.25 (s, 6 H), 1.71 (t, *J* = 6.8 Hz, 2 H), 2.63 (t, *J* = 6.8 Hz, 2 H), 3.67 (s, 3 H), 6.28 (d, *J* = 2.4 Hz, 1 H), 6.36 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.8 (CH_2), 26.9 (2 X CH_3), 32.9 (CH_2), 55.2 (CH_3), 74.3 (Cq), 101.7 (CH), 106.9 (CH), 112.9 (Cq), 129.9 (CH), 154.7 (Cq), 159.1 (Cq).

6,6-Dimethyl-7,8-dihydro-6*H*-[1,3]dioxolo[4,5-*g*]chromene (5f)[16m]



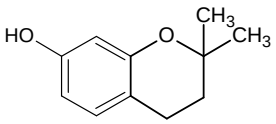
A colourless oil (58% yield); IR (neat): ν_{max} = 2974, 1504, 1479, 1151 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.22 (s, 6 H), 1.67 (t, *J* = 6.8 Hz, 2 H), 2.59 (t, *J* = 6.8 Hz, 2 H), 5.77 (s, 2 H), 6.26 (s, 1 H), 6.42 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.6 (CH_2), 26.6 (2 X CH_3), 32.8 (CH_2), 73.9 (Cq), 98.9 (CH), 100.7 (CH_2), 108.1 (CH), 112.2 (Cq), 140.9 (Cq), 146.4 (Cq), 148.4 (Cq).

6-Methoxy-2,2-dimethyl-3,4-dihydro-2*H*-benzo[*h*]chromene (5g)[17d]



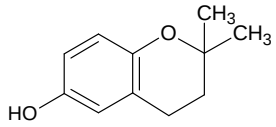
A colourless solid (60% yield); mp 74-75 °C, Lit[17d] 77-78 °C; IR (KBr): ν_{max} = 2974, 1633, 1597, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.30 (s, 6 H), 1.79 (t, *J* = 6.8 Hz, 2 H), 2.73 (t, *J* = 6.8 Hz, 2 H), 3.82 (s, 3 H), 6.38 (s, 1 H), 7.33 (dt, *J* = 7.6, 1.6 Hz, 1 H); 7.37 (dt, *J* = 7.2, 1.6 Hz, 1 H); 8.05 (dd, *J* = 8.4, 1.6 Hz, 1 H); 8.08 (dd, *J* = 8.8, 1.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.4 (CH_2), 26.9 (2 X CH_3), 33.1 (CH_2), 55.8 (CH_3), 73.9 (Cq), 105.4 (CH), 113.4 (Cq), 121.4 (CH), 121.7 (CH), 125.0 (CH), 125.3 (Cq), 125.7 (CH), 126.5 (Cq), 142.5 (Cq), 148.5 (Cq).

7-Hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5h)[16g]



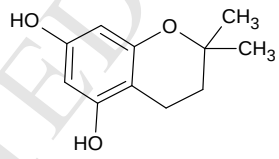
A colourless solid (46% yield); mp 68-70 °C, Lit[16g] 72-73 °C; IR (KBr): ν_{max} = 3383, 2974, 1593, 1149 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.24 (s, 6 H), 1.69 (t, *J* = 6.8 Hz, 2 H), 2.60 (t, *J* = 6.8 Hz, 2 H), 6.22 (s, 1 H), 6.28 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.81 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.7 (CH_2), 25.8 (2 X CH_3), 31.9 (CH_2), 73.5 (Cq), 102.7 (CH), 106.5 (CH), 112.2 (Cq), 129.1 (CH), 153.5 (Cq), 153.8 (Cq).

6-Hydroxy-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5i)[16l]



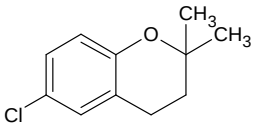
A colourless solid (33% yield); mp 77-78 °C, Lit[16l] 77-78 °C; IR (KBr): ν_{max} = 3379, 2974, 1502, 1195 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.23 (s, 6 H), 1.69 (t, *J* = 6.8 Hz, 2 H), 2.63 (t, *J* = 6.8 Hz, 2 H), 6.48 (d, *J* = 2.8 Hz, 1 H), 6.52 (dd, *J* = 8.8, 2.8 Hz, 1 H), 6.57 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6 (CH_2), 25.7 (2 X CH_3), 31.7 (CH_2), 72.9 (Cq), 113.4 (CH), 114.4 (CH), 116.8 (CH), 120.8 (Cq), 146.8 (Cq), 147.5 (Cq).

2,2-Dimethyl-3,4-dihydro-2*H*-chromene-5,7-diol (5j)[16g,40]



A colourless solid (56% yield); mp 158-160 °C, Lit[16g,40] 163-164 °C; IR (KBr): ν_{max} = 3375, 1600, 1144, 1053 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.13 (s, 6 H), 1.56 (t, *J* = 6.4 Hz, 2 H), 2.39 (t, *J* = 6.4 Hz, 2 H), 5.81 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.4 (CH_2), 26.6 (2 X CH_3), 32.2 (CH_2), 74.4 (Cq), 94.7 (CH), 96.6 (CH), 100.9 (Cq), 154.6 (Cq), 155.0 (Cq), 155.5 (Cq).

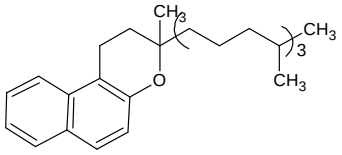
6-Chloro-2,2-dimethyl-3,4-dihydro-2*H*-1-benzopyran (5k)[17d]



A colourless oil (20% yield); IR (neat): ν_{max} = 2976, 1479, 1261, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (s, 6 H), 1.77 (t, *J* = 6.8 Hz, 2 H), 2.73 (t, *J* = 6.8 Hz, 2 H), 6.70

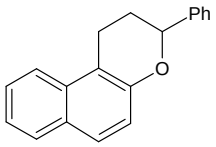
(d, *J* = 9.2 Hz, 1 H), 7.02 (d, *J* = 9.6 Hz, 1 H), 7.03 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.4 (CH_2), 26.8 (2 X CH_3), 32.4 (CH_2), 74.5 (Cq), 118.6 (CH), 122.5 (Cq), 124.2 (Cq), 127.2 (CH), 128.9 (CH), 152.6 (Cq).

3-Methyl-3-(4,8,12-trimethyltridecyl)-2,3-dihydro-1*H*-benzo[*f*]chromene (5l)



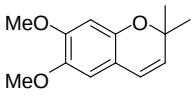
A mixture of phytol (1.16 mmol), β-naphthol (4.65 mmol), and iodine (0.35 mmol) in chloroform (10 mL) was subjected to reflux with stirring for 4 hours. It was then cooled to room temperature. Chloroform was directly washed with saturated solution of sodium thiosulphate followed by dilute sodium hydroxide solution. Finally chloroform layer was washed with water, dried over sodium sulphate and concentrated to furnish the crude product. This was then purified using 60-120 mesh silica gel column chromatography (hexanes/ethyl acetate, 9.8:0.2) to give 3-methyl-3-(4,8,12-trimethyltridecyl)-2,3-dihydro-1*H*-benzo[*f*]chromene (**5l**) (108.7 mg, 76%) as a pale yellow oil; Rf (hexanes/ethyl acetate, 9.5:0.5) 0.50; IR (neat): ν_{max} = 2951, 1625, 1598, 1234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.80-0.87 (m, 12 H), 1.10-1.15 (m, 7 H), 1.24-1.67 (m, 14 H), 1.32 (s, 3 H), 1.89-1.99 (m, 2 H), 2.99 (t, *J* = 6.8 Hz, 2 H) 7.03 (d, *J* = 8.8 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 8.8 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.1 (CH_2), 19.7-19.8 (3 peak tops, CH_3), 21.2 (CH_2), 22.7-22.8 (2 peak tops, CH_3), 23.9 (CH_3), 24.5 (CH_2), 24.8-24.9 (2 peak tops, CH_2), 28.0 (CH), 30.8-30.9 (2 peak tops, CH_2), 32.7-32.8 (4 peak tops, CH), 37.3-37.6 (6 peak tops, CH_2), 39.4-39.6 (3 peak tops, CH_2), 76.1 (Cq), 112.6 (Cq), 119.9 (CH), 121.9 (CH), 122.9 (CH), 126.2 (CH), 127.7 (CH), 128.4 (CH), 128.7 (Cq), 133.1 (Cq), 151.4 (Cq); Anal. Calcd. For $C_{30}H_{46}O$: C, 85.3; H, 10.9 %; Found: C, 85.6; H, 11.1 %; GCMS: *m/z* calcd for $C_{30}H_{46}O$ $[M]^+$: 422.68; found: 422.22.

3-Phenyl-2,3-dihydro-1*H*-benzo[*f*]chromene (5m)[41]



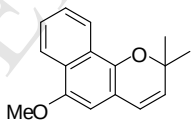
A colourless solid (60% yield); mp 84-86 °C, Lit[41] 86 °C; IR (KBr): ν_{max} = 3062, 2924, 1597, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.11-2.19 (m, 1 H), 2.28-2.33 (m, 1 H), 3.06-3.10 (m, 2 H), 5.04 (dd, *J* = 10.0, 2.0 Hz, 1 H), 7.07 (d, *J* = 8.8 Hz, 1 H), 7.23-7.43 (m, 7 H), 7.56 (d, *J* = 8.8 Hz, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.8 (CH_2), 29.7 (CH_2), 77.5 (CH), 113.6 (Cq), 119.2 (CH), 121.9 (CH), 123.3 (CH), 126.1 (2 X CH), 126.4 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 128.6 (2 X CH), 129.0 (Cq), 133.0 (Cq), 141.6 (Cq), 152.7 (Cq).

6,7-Dimethoxy-2,2-dimethyl-2*H*-chromene (5ca)[42,43]



A colourless solid; (60% yield); mp 46-48 °C; IR (KBr): ν_{max} = 2974, 1500, 1458, 1278, 1195 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.34 (s, 6 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 5.41 (d, *J* = 10.0 Hz, 1 H), 6.17 (d, *J* = 10.0 Hz, 1 H), 6.34 (s, 1 H), 6.46 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.6 (2 X CH_3), 54.9 (OCH_3), 55.5 (OCH_3), 74.9 (Cq), 99.9 (CH), 108.7 (CH), 112.0 (Cq), 120.9 (CH), 127.2 (CH), 142.0 (Cq), 146.2 (Cq), 148.6 (Cq).

6-Methoxy-2,2-dimethyl-2*H*-benzo[*h*]chromene (5ga)[44,45]



A colourless solid (52% yield); mp 63-64 °C; IR (KBr): ν_{max} = 2974, 2933, 1641, 1597, 1276 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.42 (s, 6 H), 3.89 (s, 3 H), 5.58 (d, *J* = 9.6 Hz, 1 H), 6.33 (d, *J* = 9.6 Hz, 1 H), 6.44 (s, 1 H), 7.34-7.42 (m, 2 H), 8.08 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.6 (2 X CH_3), 55.8 (OCH_3), 76.2 (Cq), 102.5 (CH), 114.8 (Cq), 121.7 (CH), 121.8 (CH), 123.0 (CH), 125.5 (CH), 125.9 (CH), 126.0 (Cq), 128.3 (Cq), 129.9 (CH), 141.9 (Cq), 149.3 (Cq).

5. Acknowledgment

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Supporting Information

Molecular iodine catalyst promoted synthesis of chromans and 4-aryl-3,4-dihydrobenzopyran-2-ones *via* [3+3] cyclocoupling

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General Considerations: All the dihydrocoumarins, chromans and chromenes formed were characterized by spectral analysis (IR; ^{1}H NMR; ^{13}C NMR) and comparison of their melting points with the literature reports. Commercial reagents were used without further purification except p-methoxyphenol and m-methoxyphenol which were prepared using standard procedure from respective dihydroxy compounds. Solvents were distilled prior to use. Column chromatography was performed on 60-120 mesh silica gel. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVANCE 400 instrument in $CDCl_3$ as solvent and TMS as an internal standard. Coupling constants are reported in Hz. Infrared Spectra (IR) were recorded in a Shimadzu FTIR instrument. Elemental analyses were carried out using Elementar Variomicro Cube CHNS Analyser. High resolution mass spectrum (HRMS) was recorded on a Micro Mass ESQTOF Mass spectrometer at IISc, Bangalore. Melting points are uncorrected. Coupling constants are reported in Hz.

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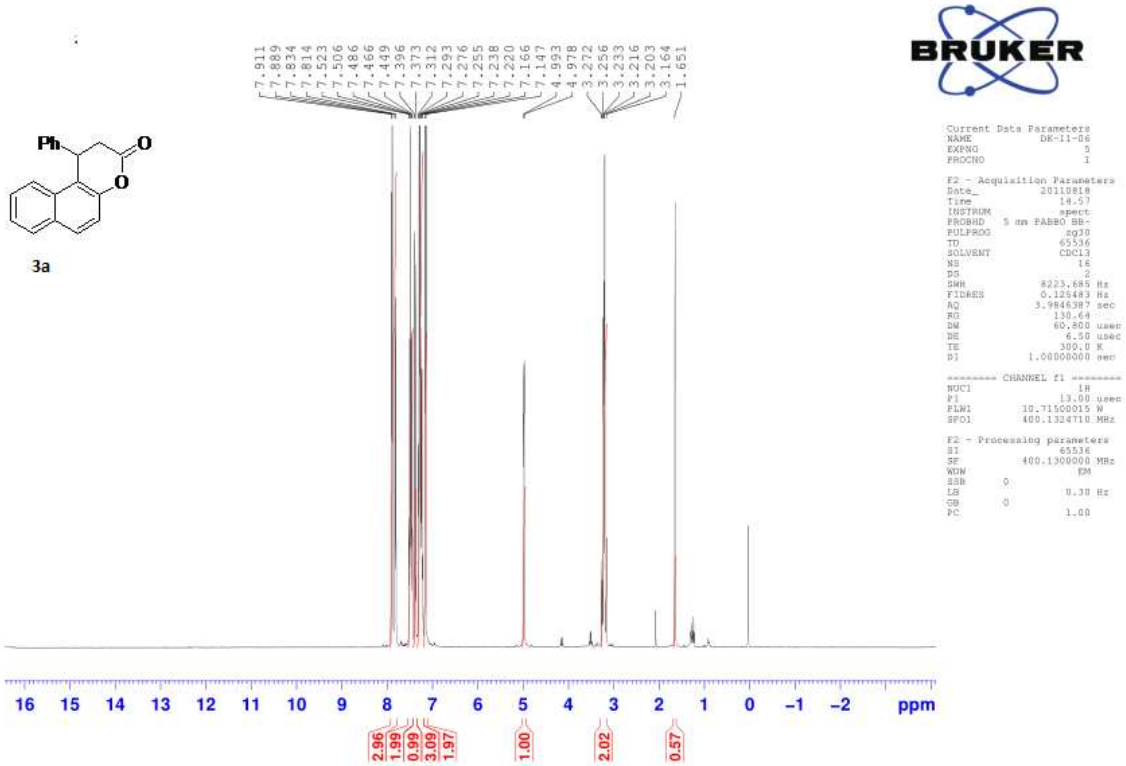

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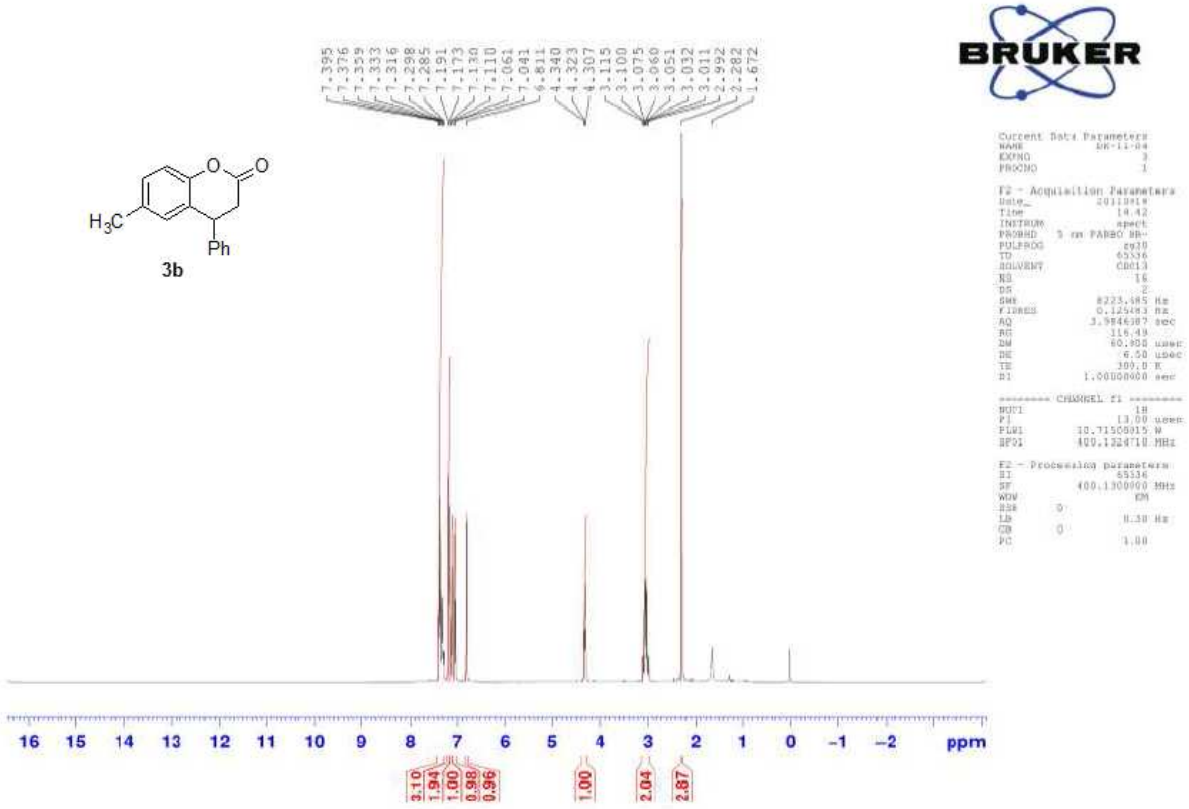

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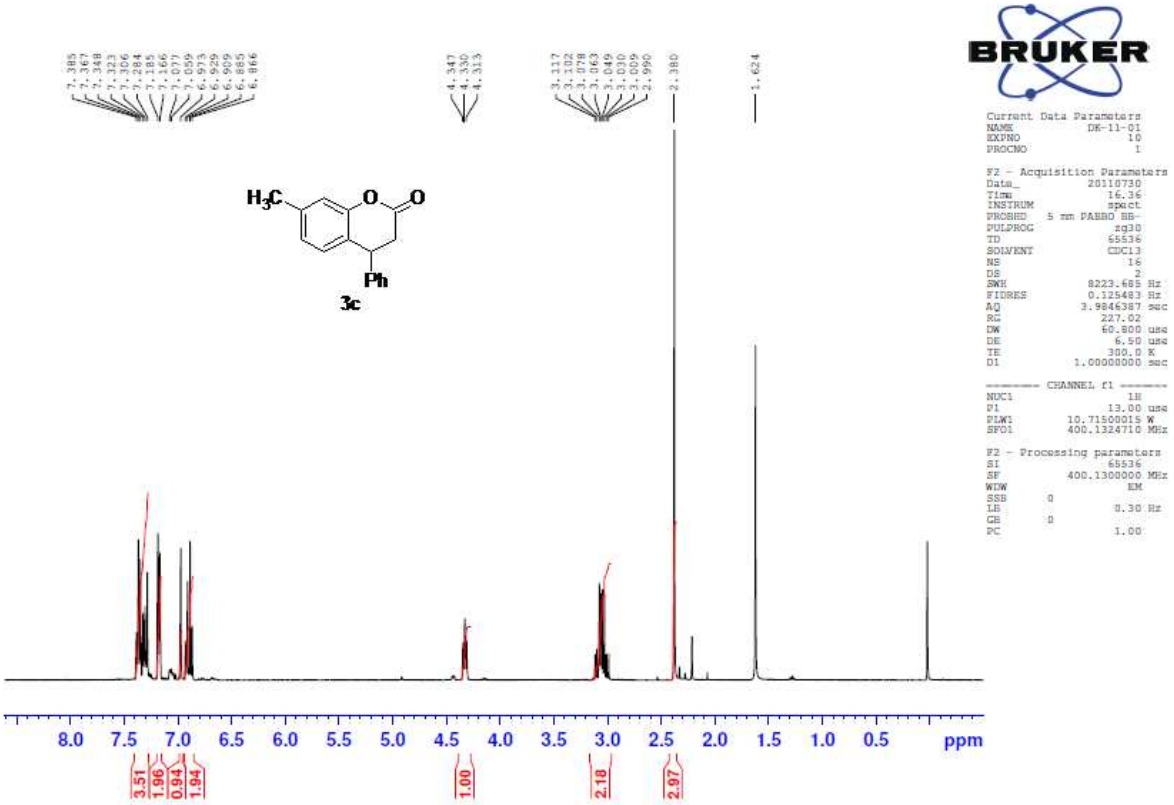

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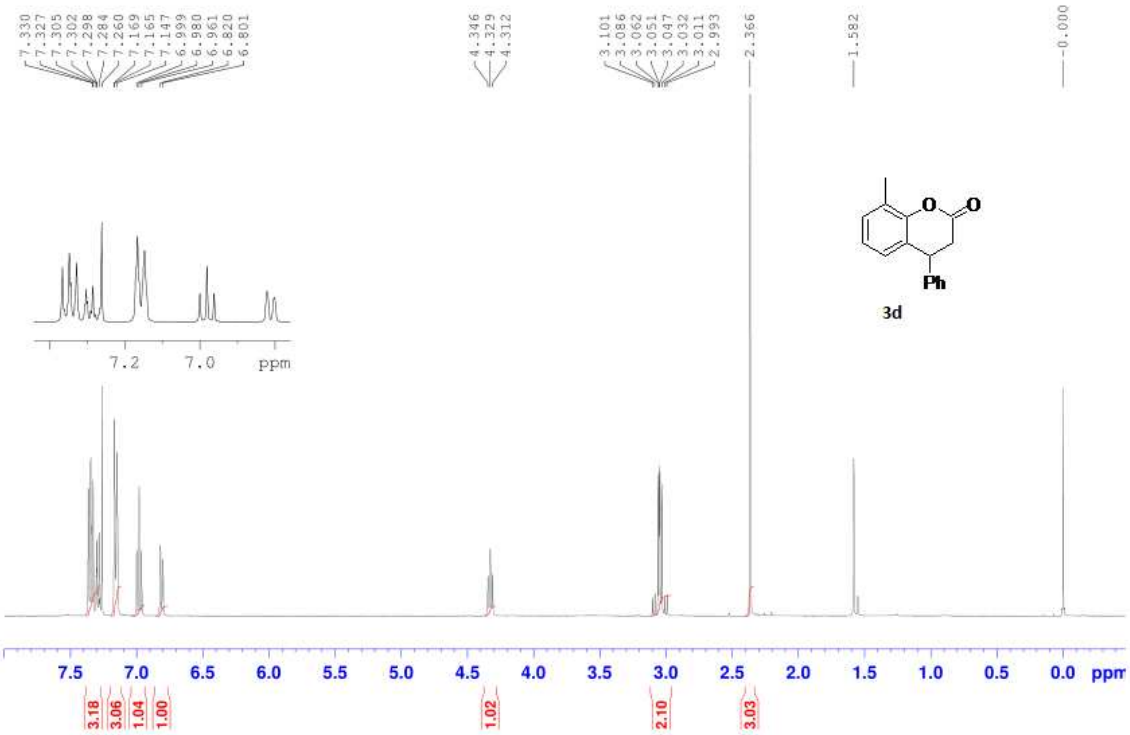

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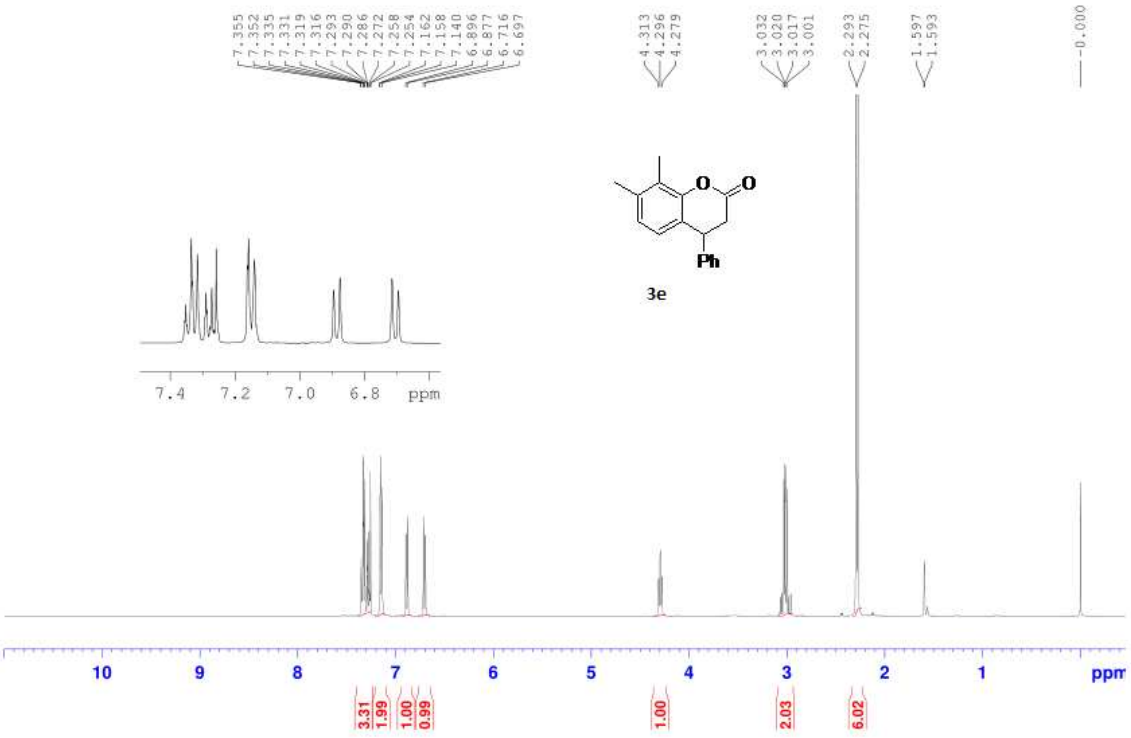

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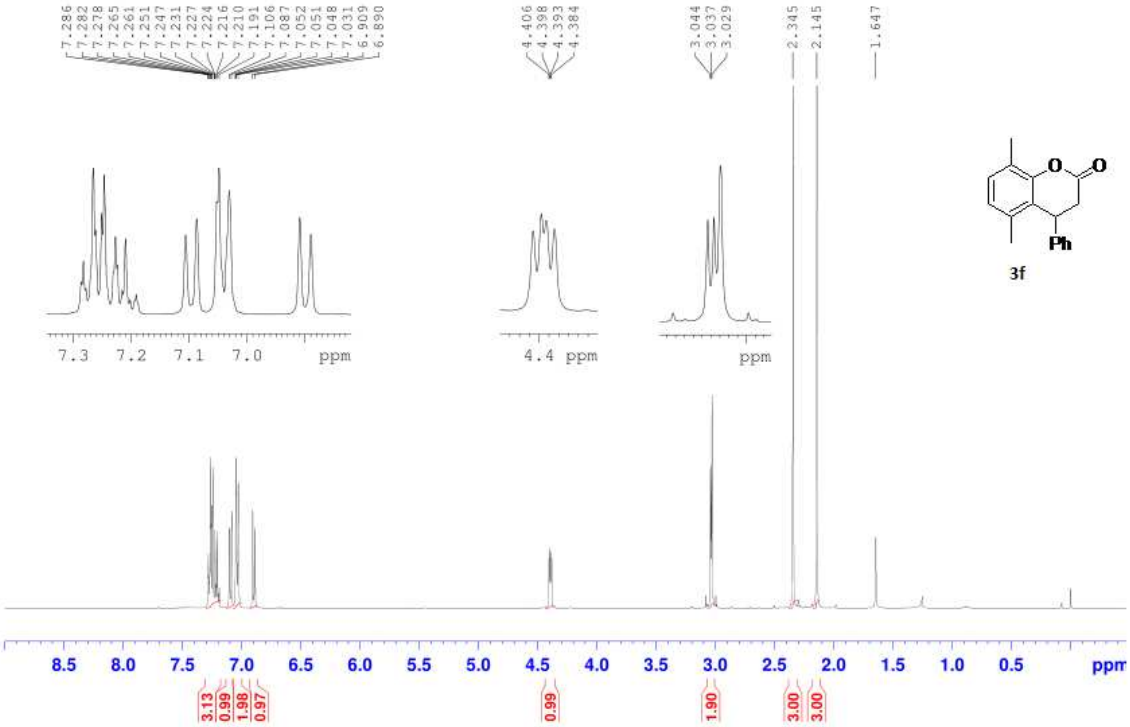
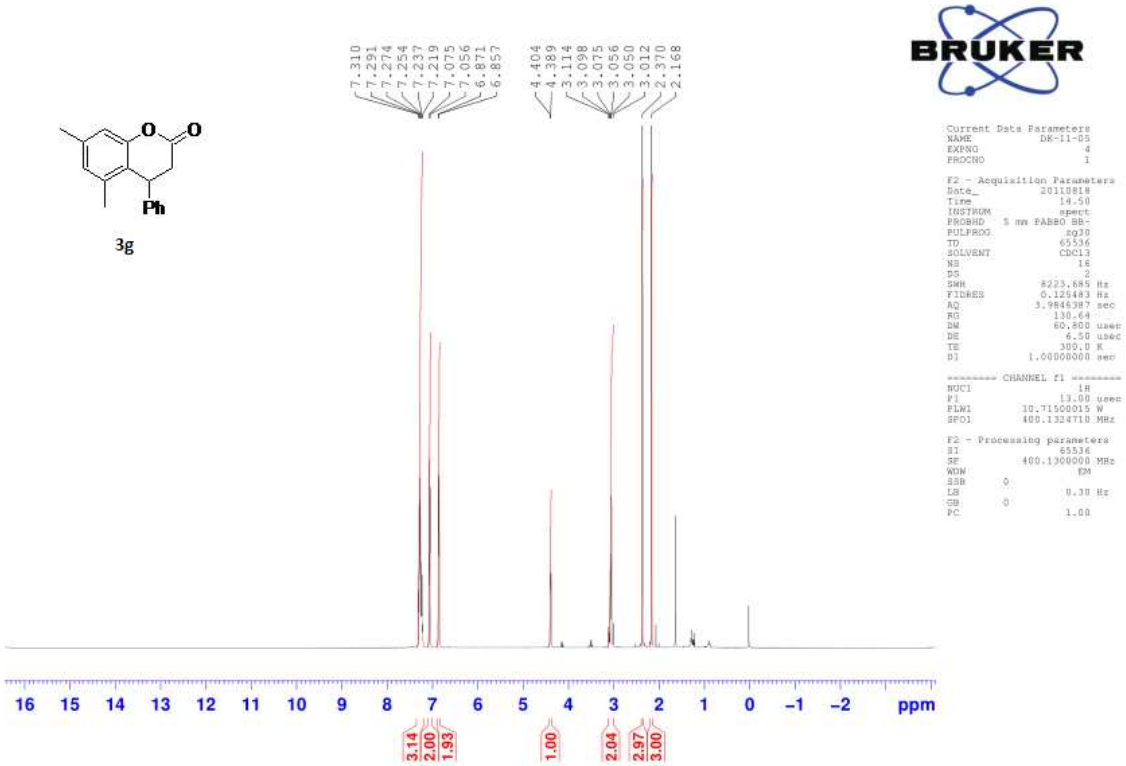
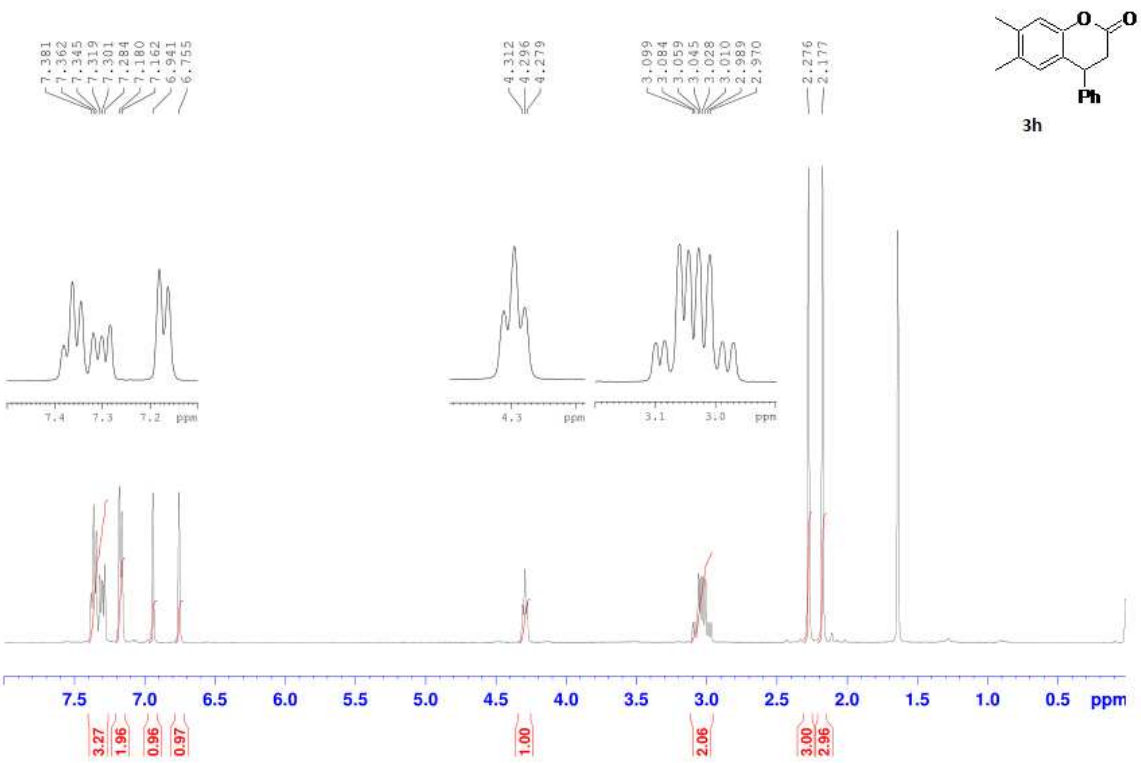


^{1}H NMR of compound 3g



^{1}H NMR of compound 3h



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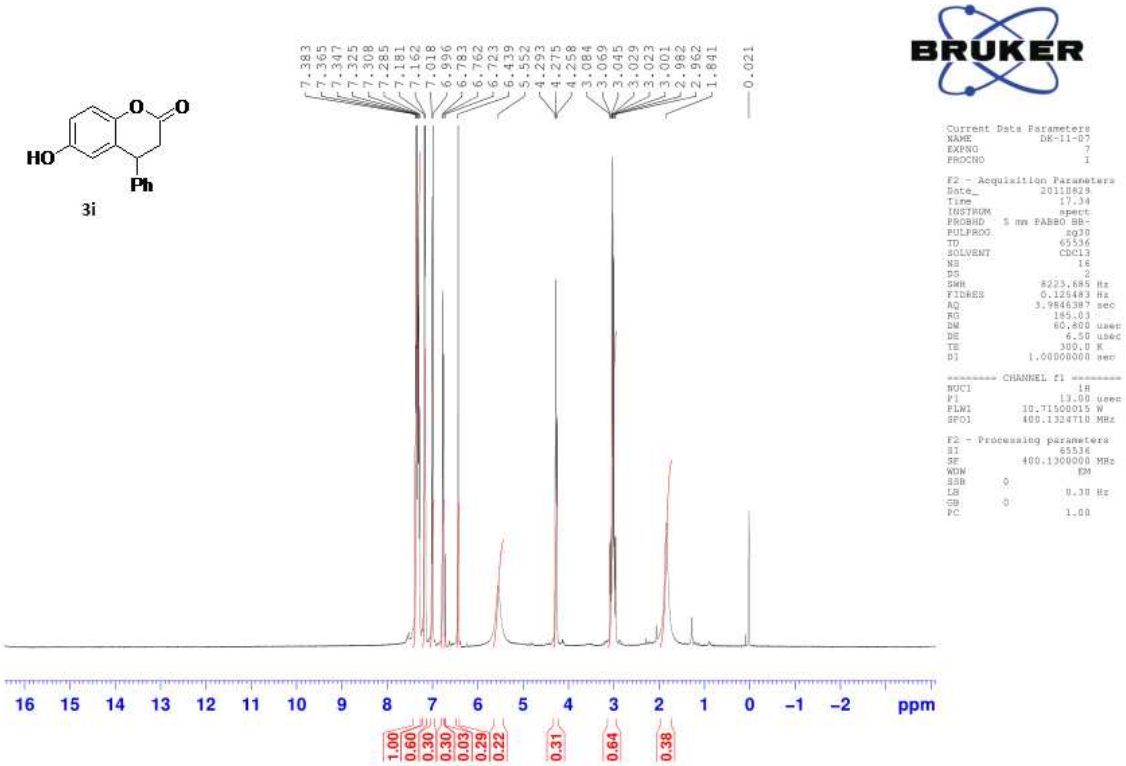

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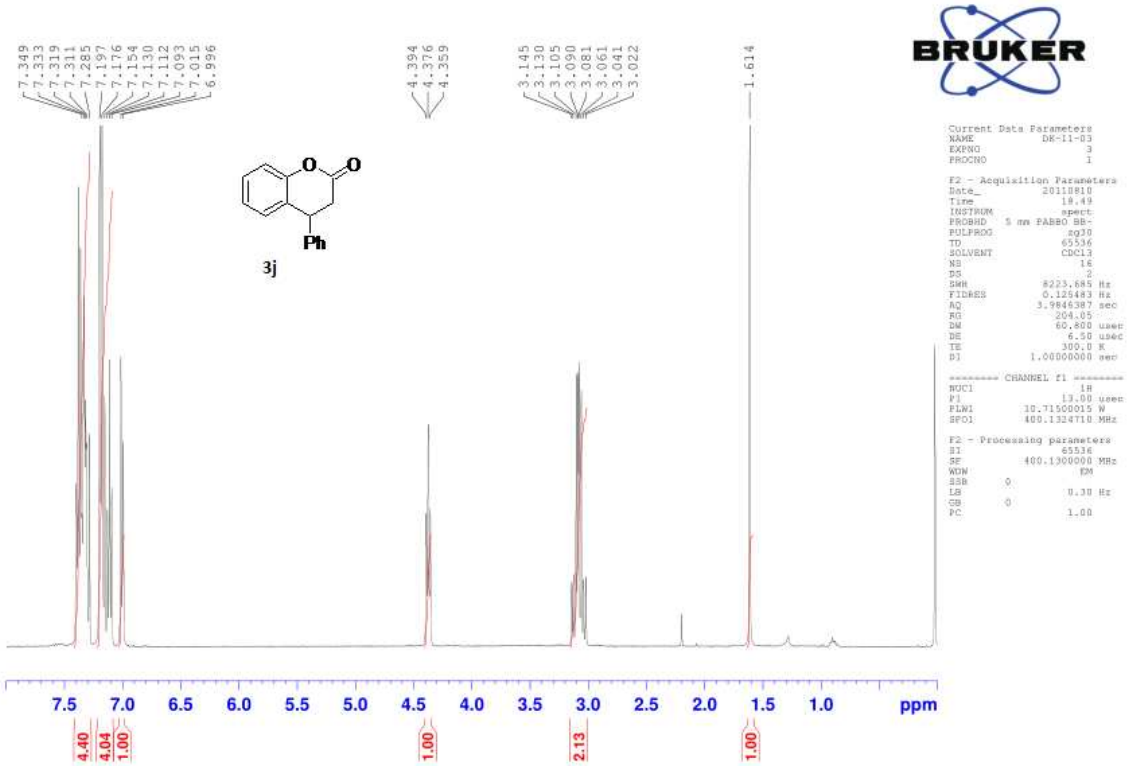

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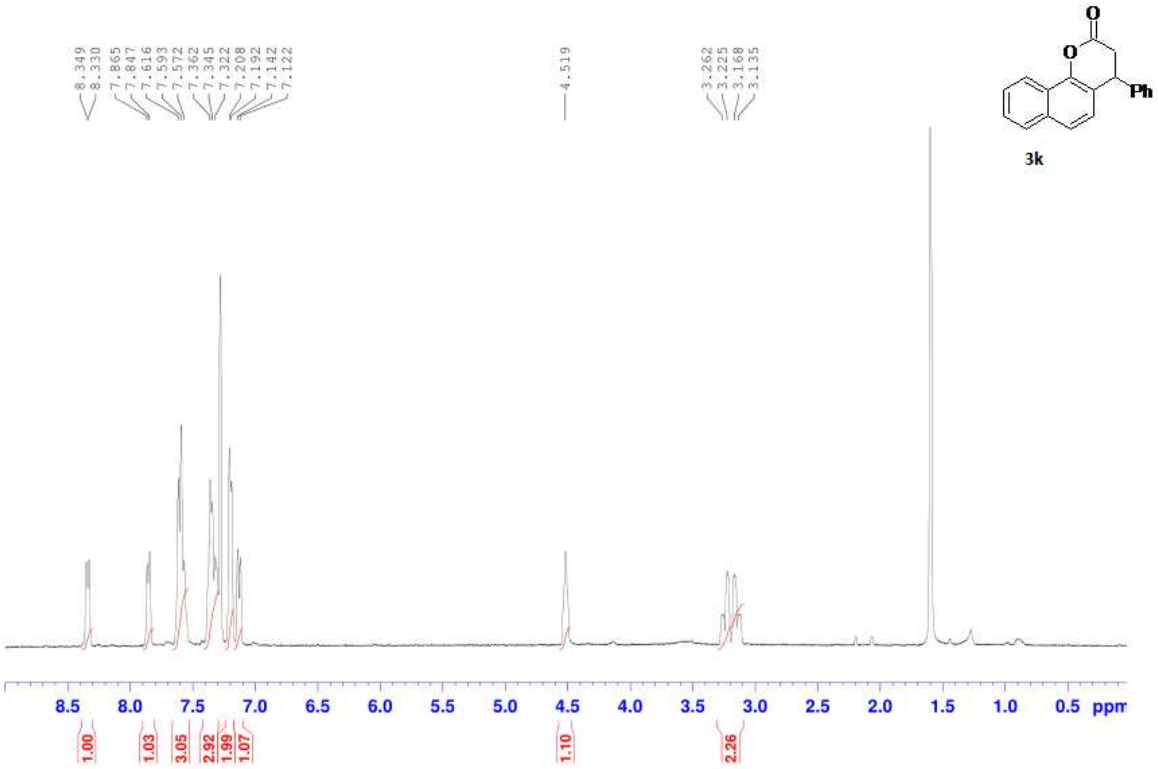

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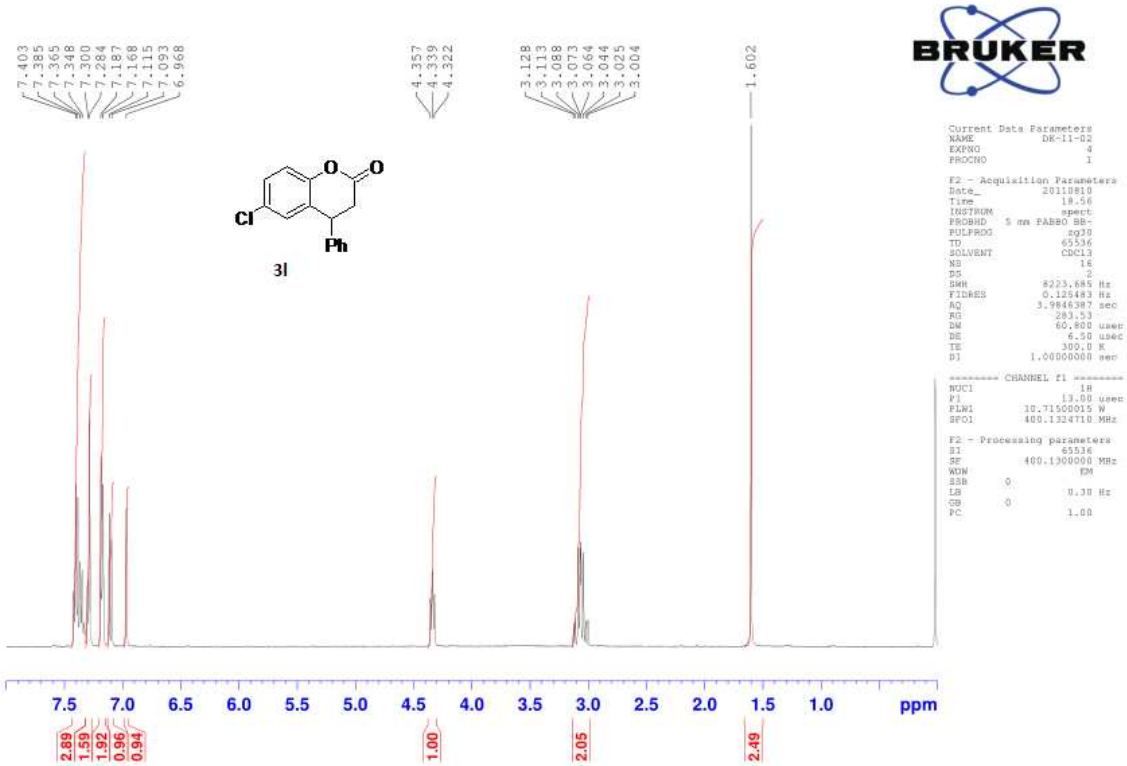

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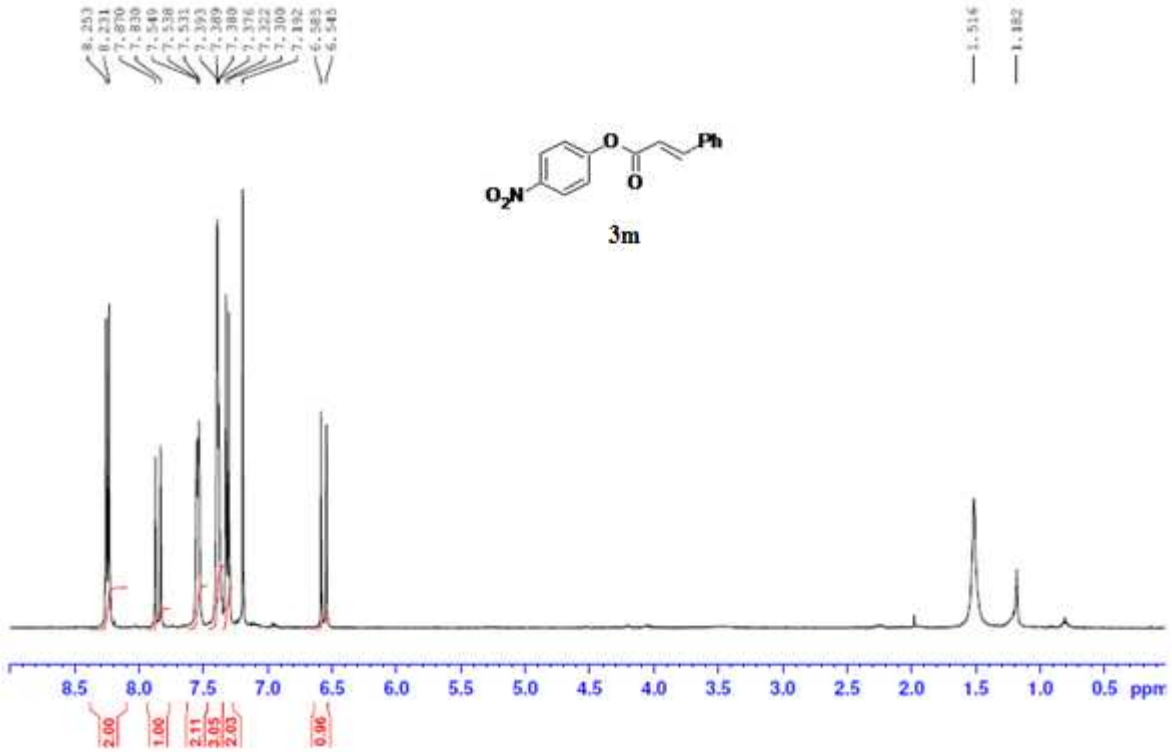

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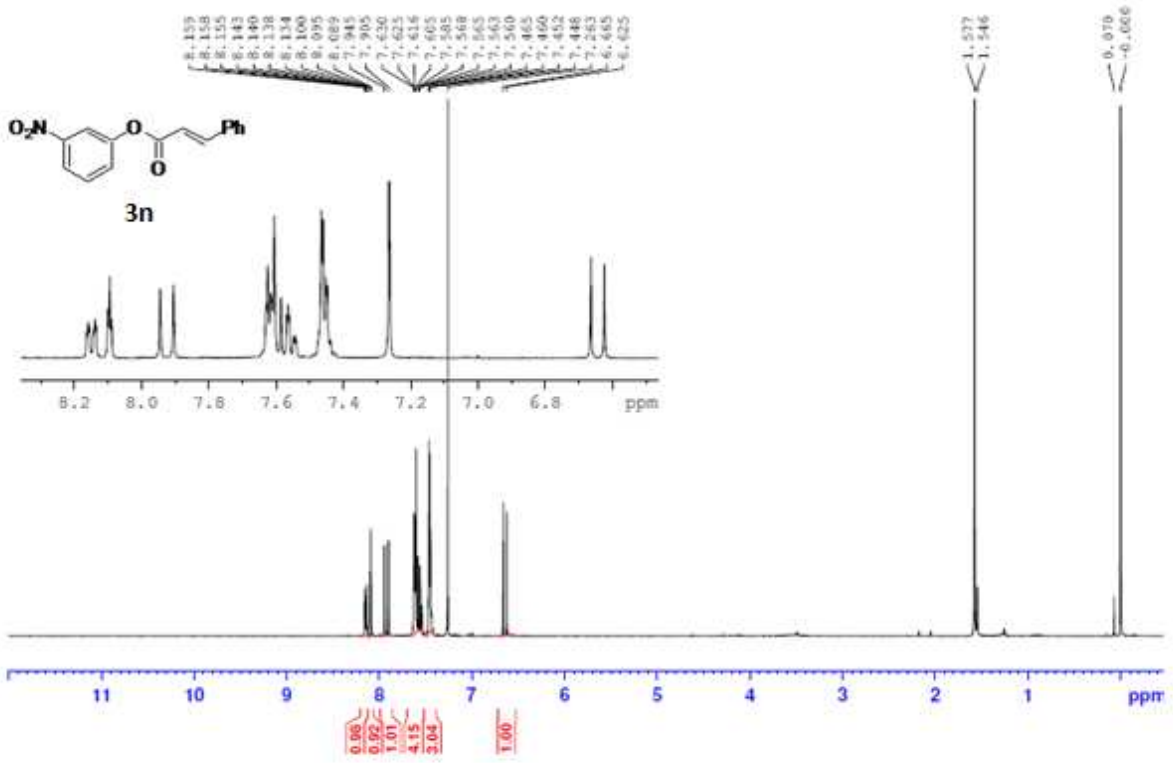

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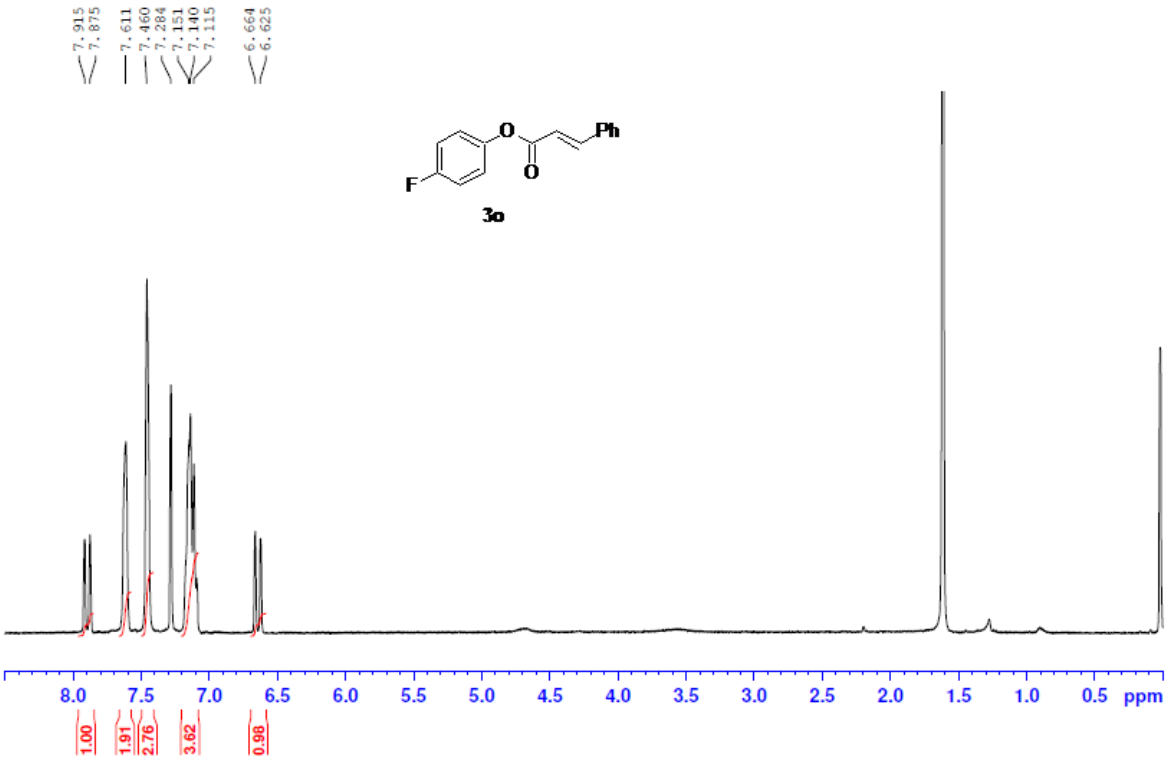

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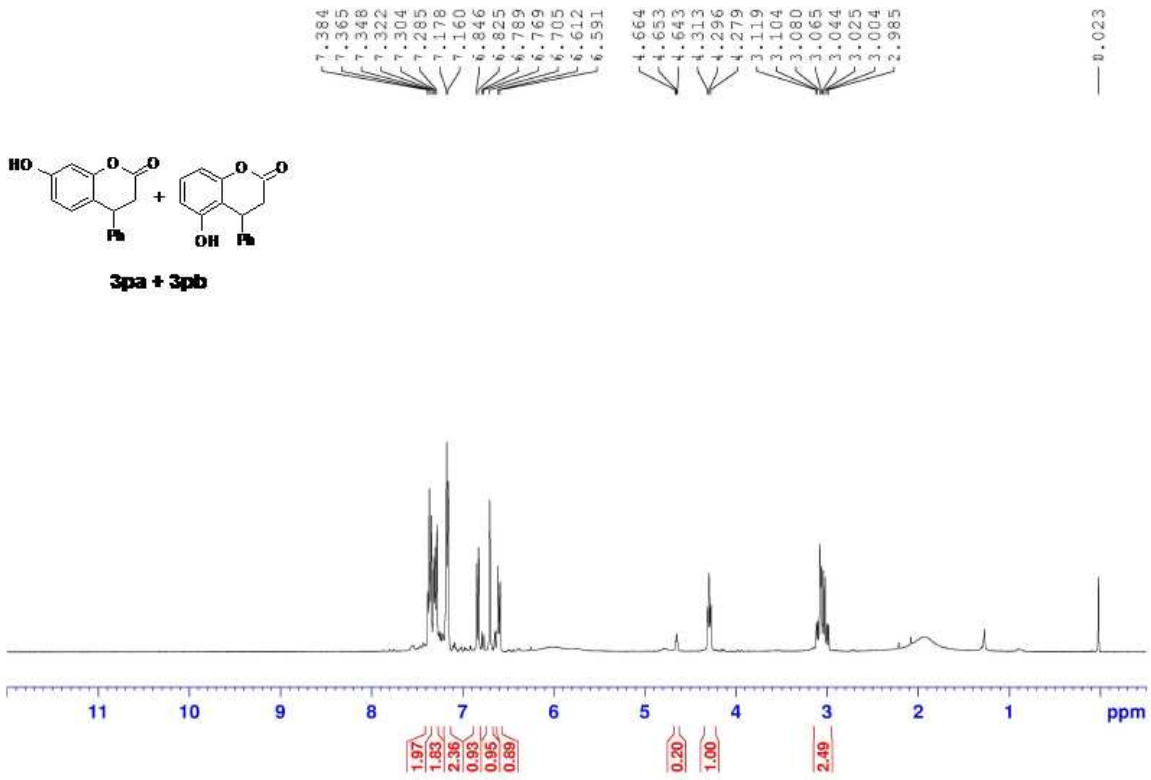

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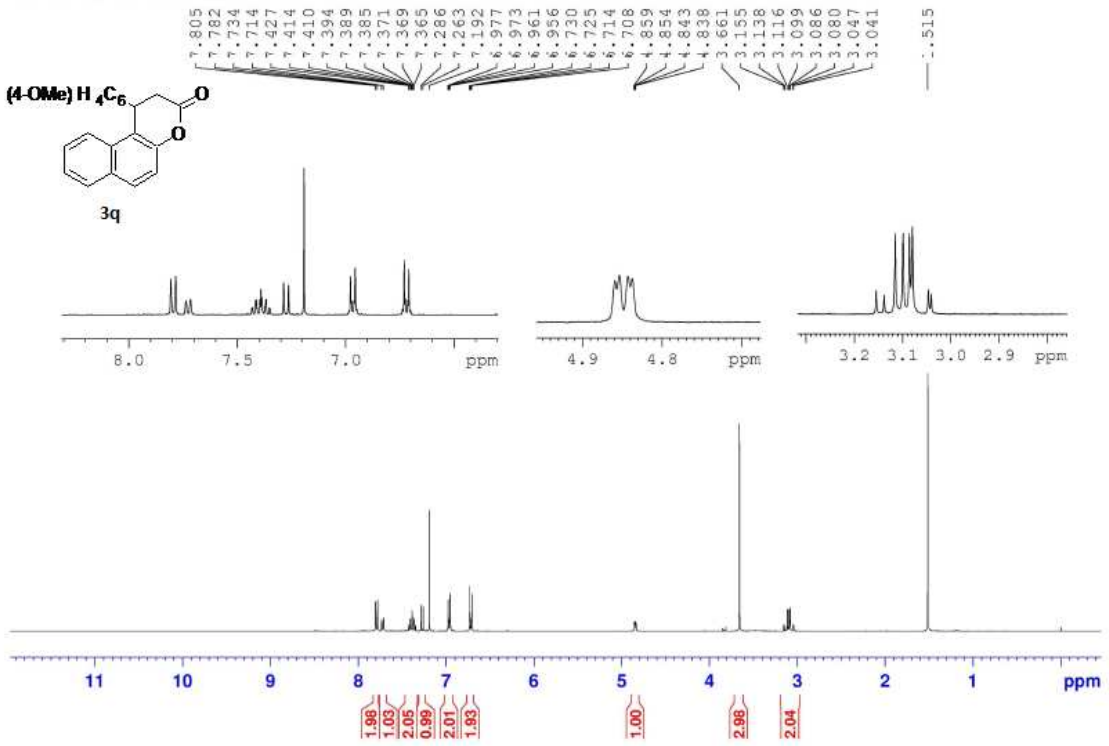

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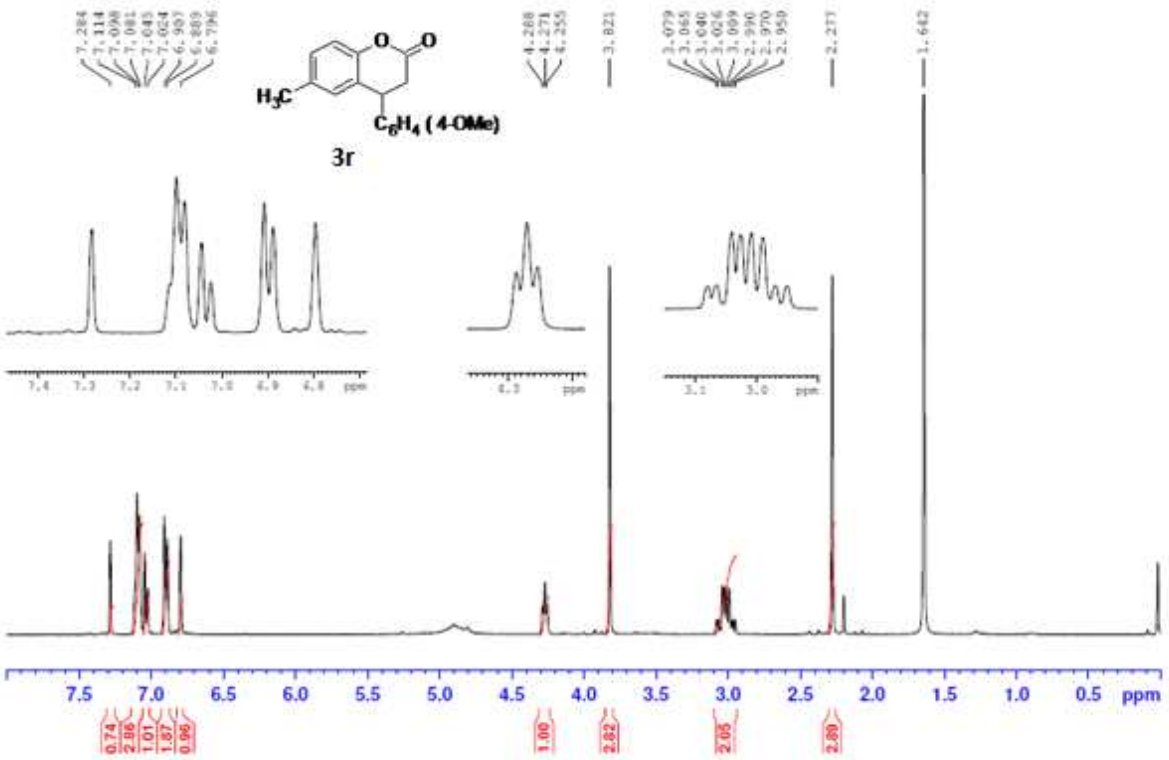
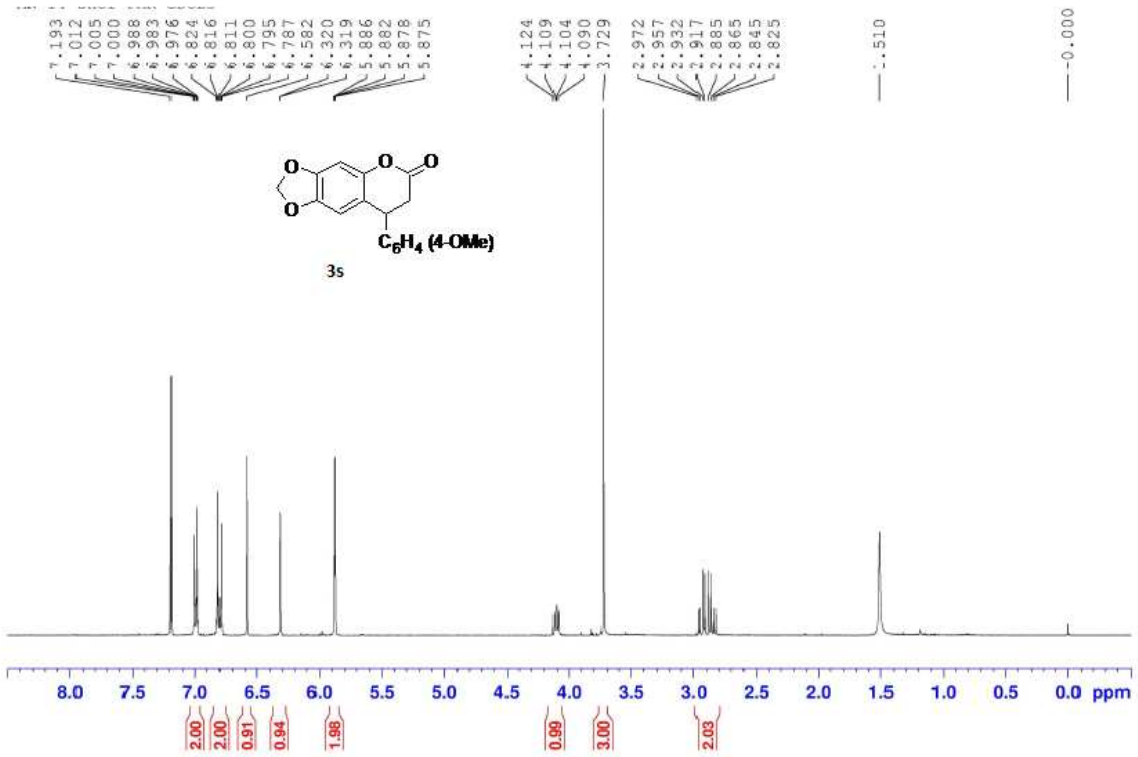


[1]H NMR of compound 3s



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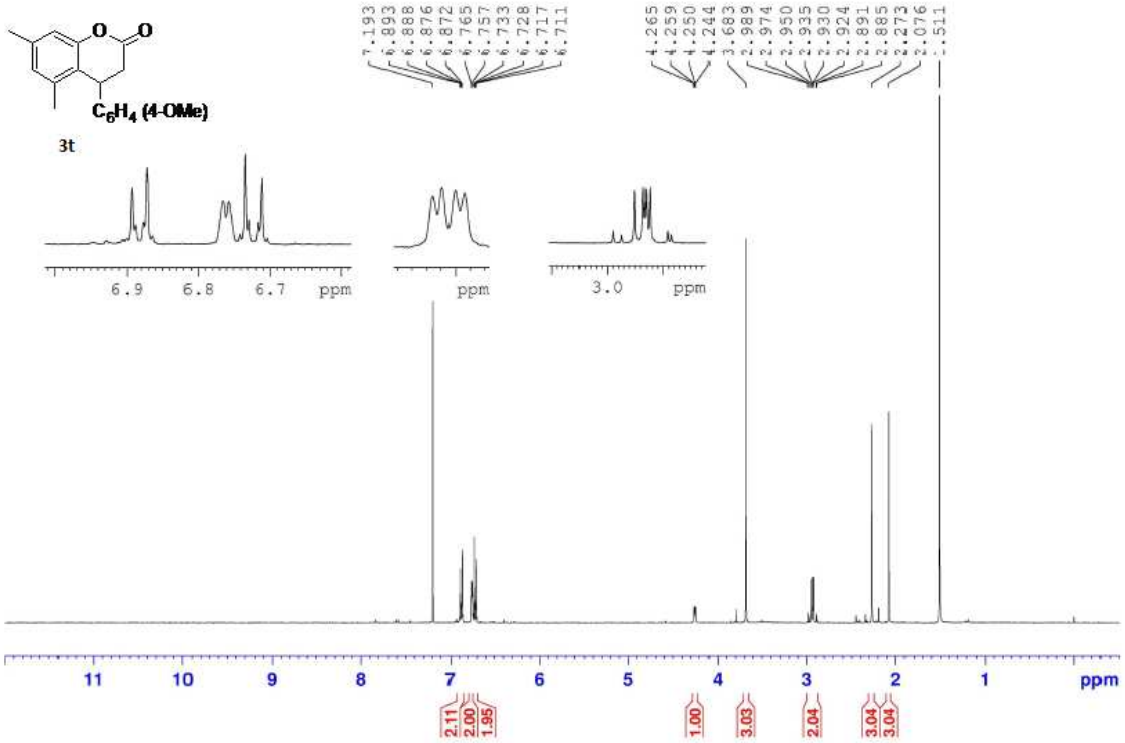

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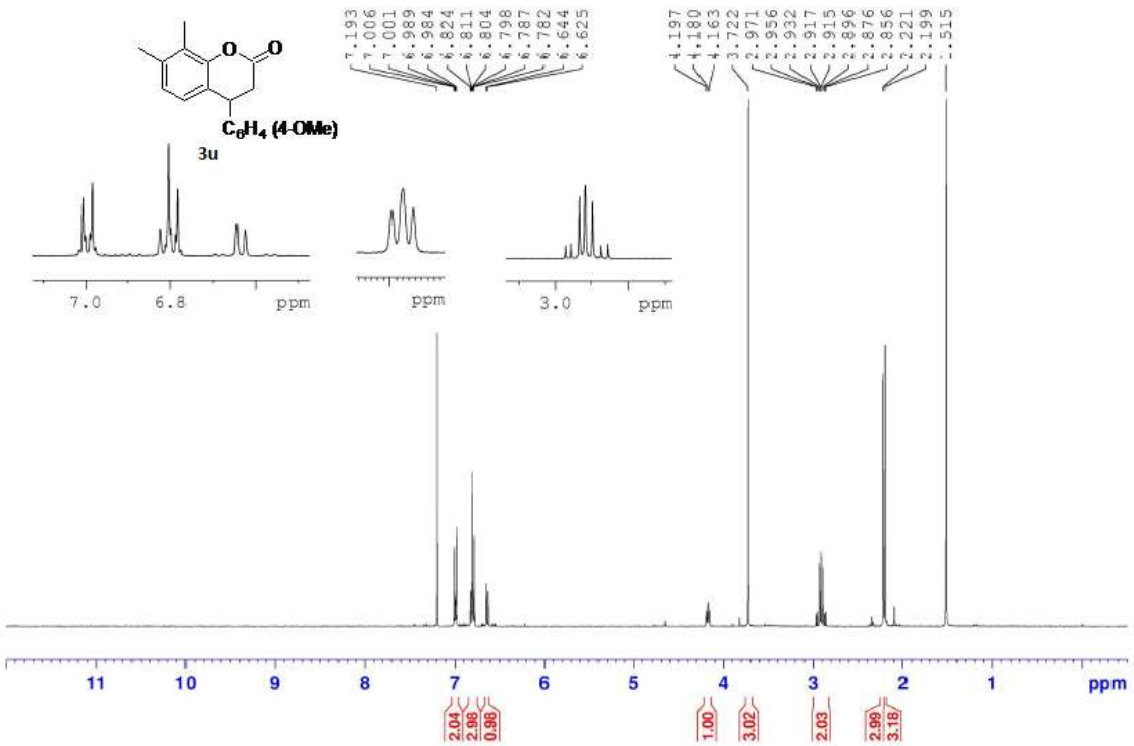
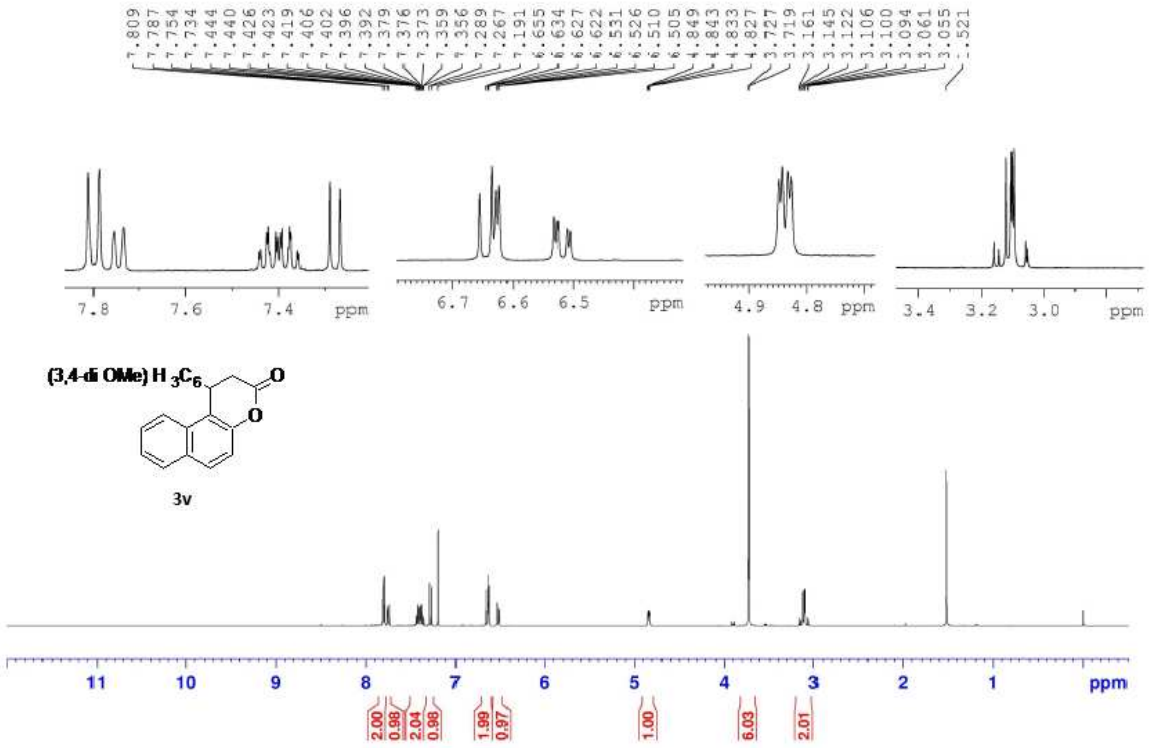
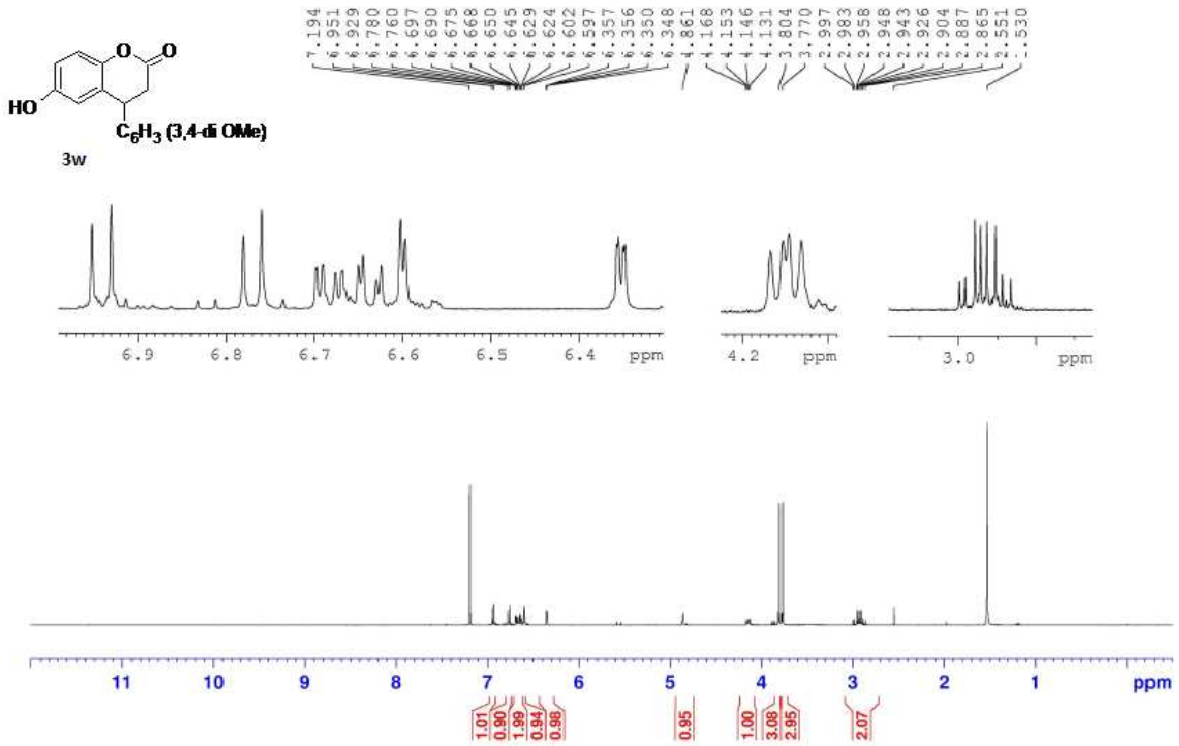


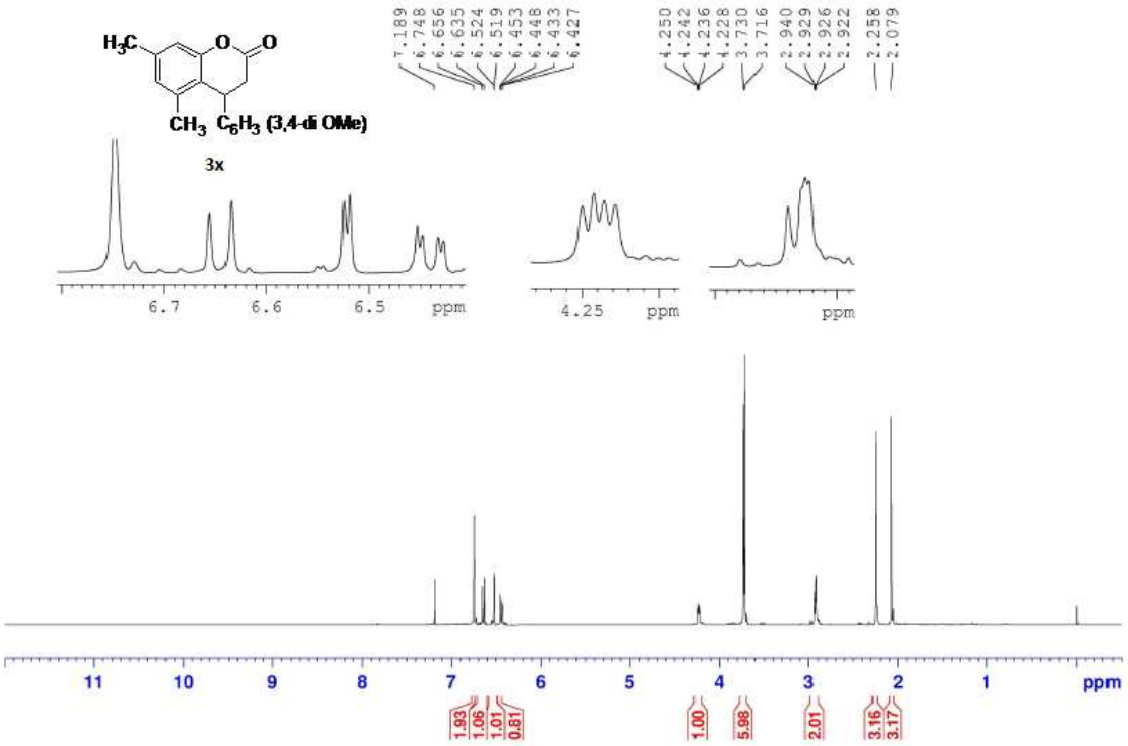
^{1}H NMR of compound 3v



^{1}H NMR of compound 3w



^{1}H NMR of compound 3x



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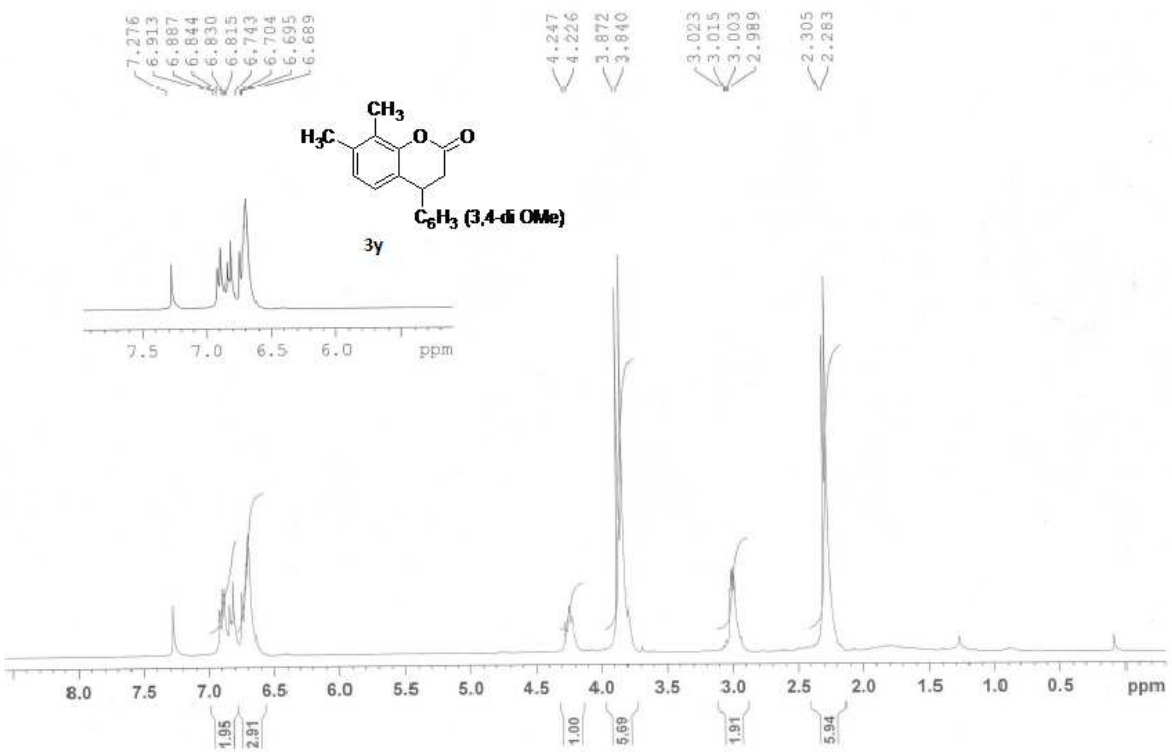

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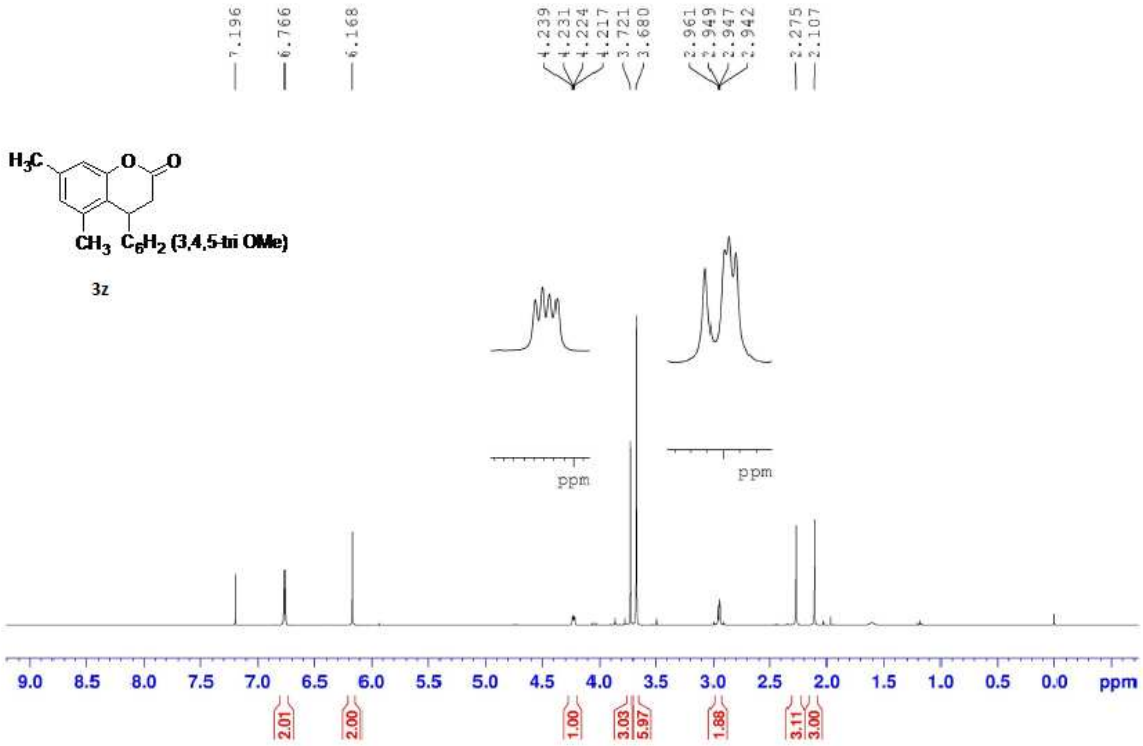
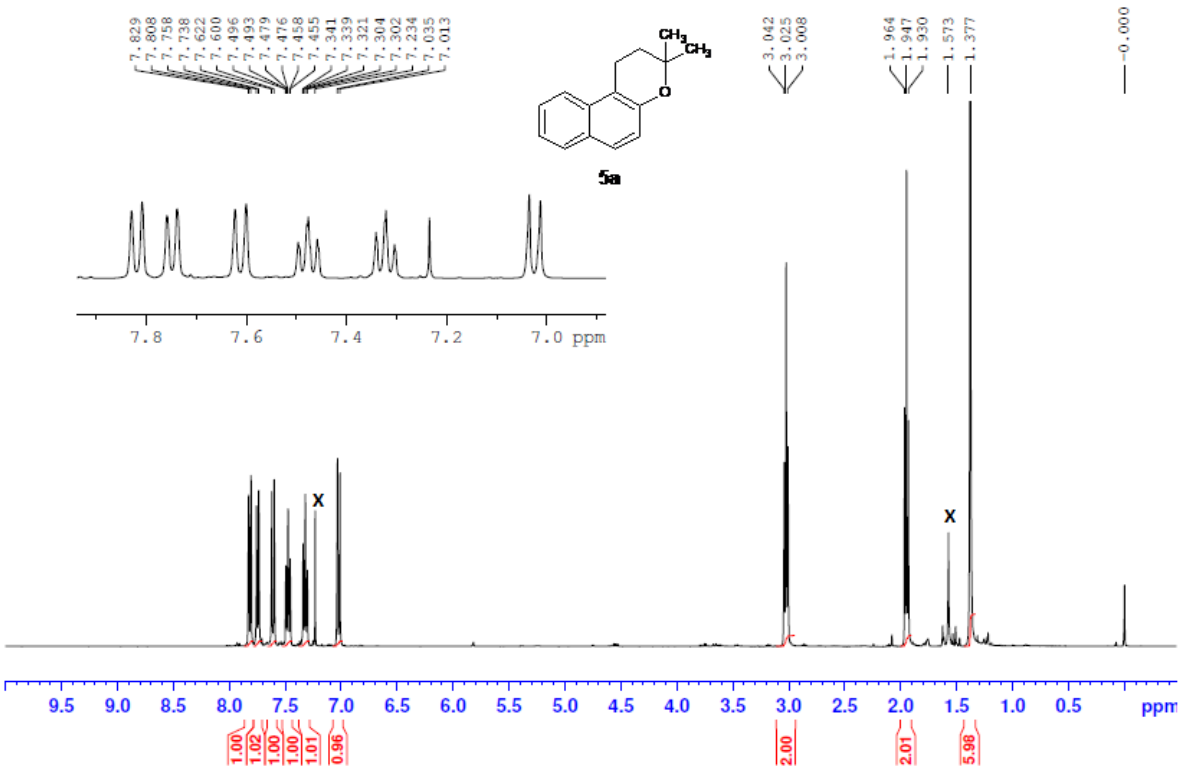
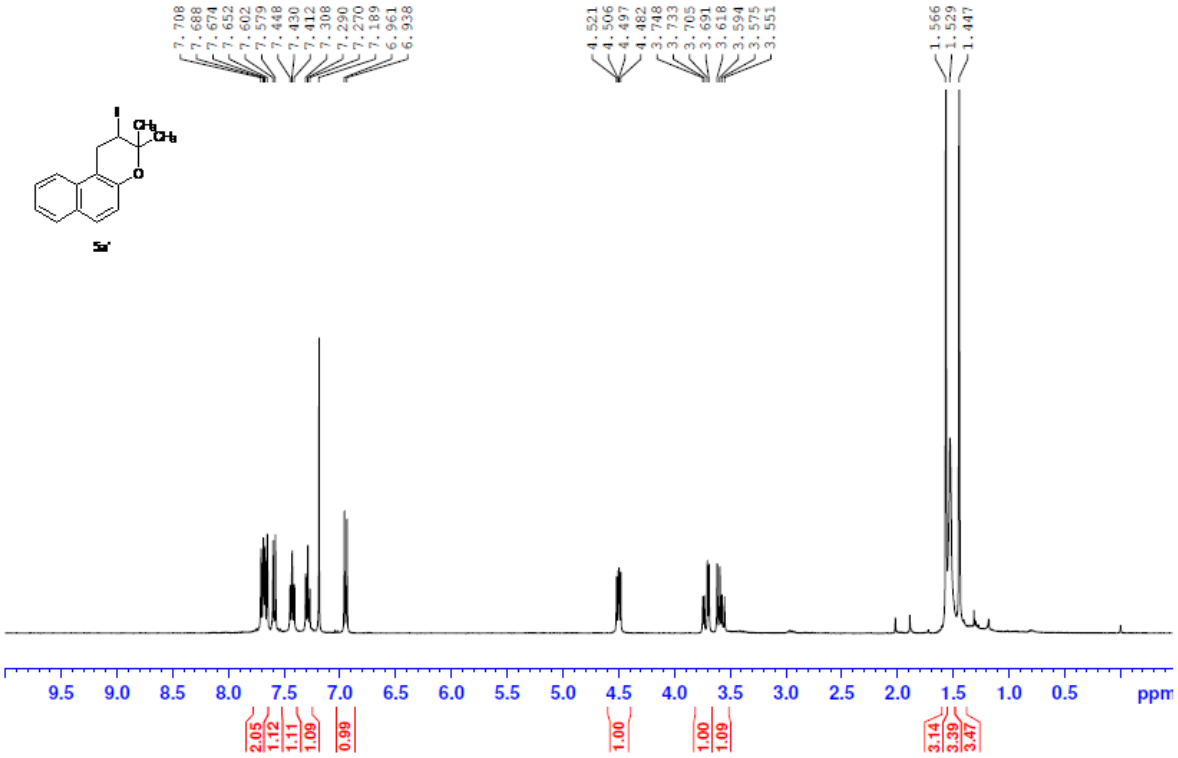


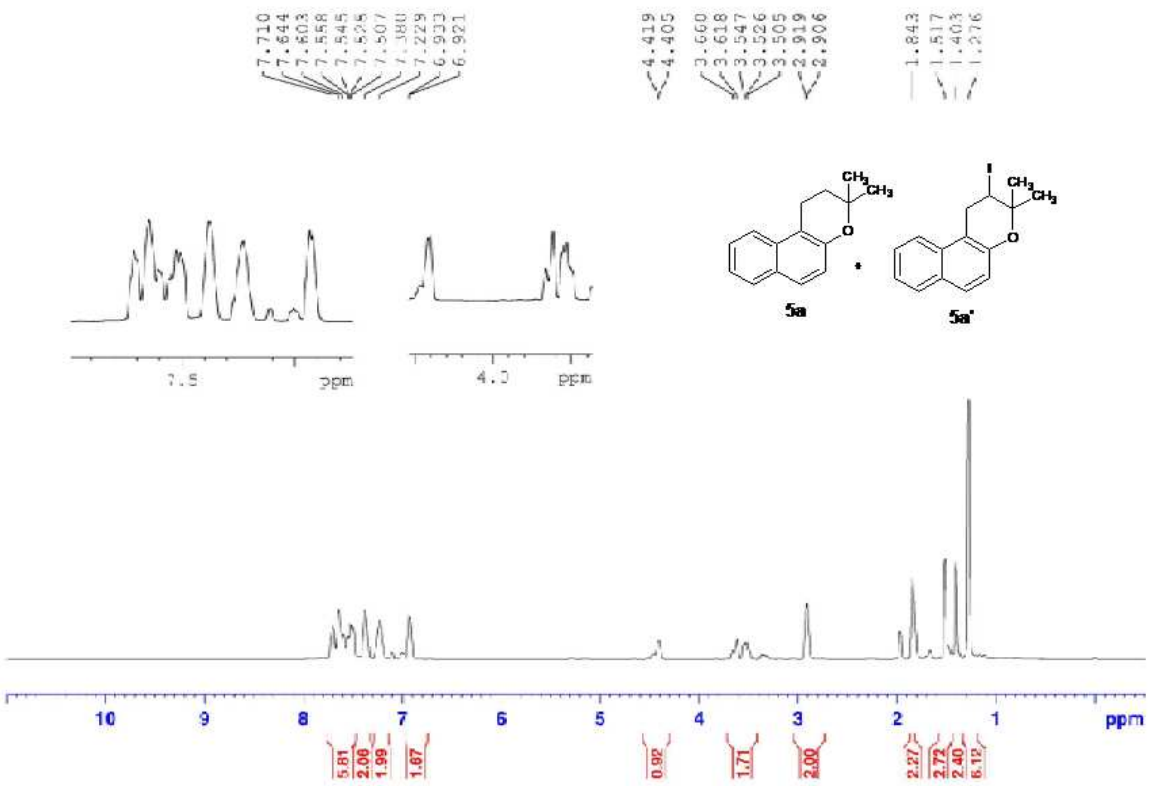
^{1}H NMR of compound 5a



^{1}H NMR of compound 5a'



^{1}H NMR of compound 5a:5a' (~1.2:1)



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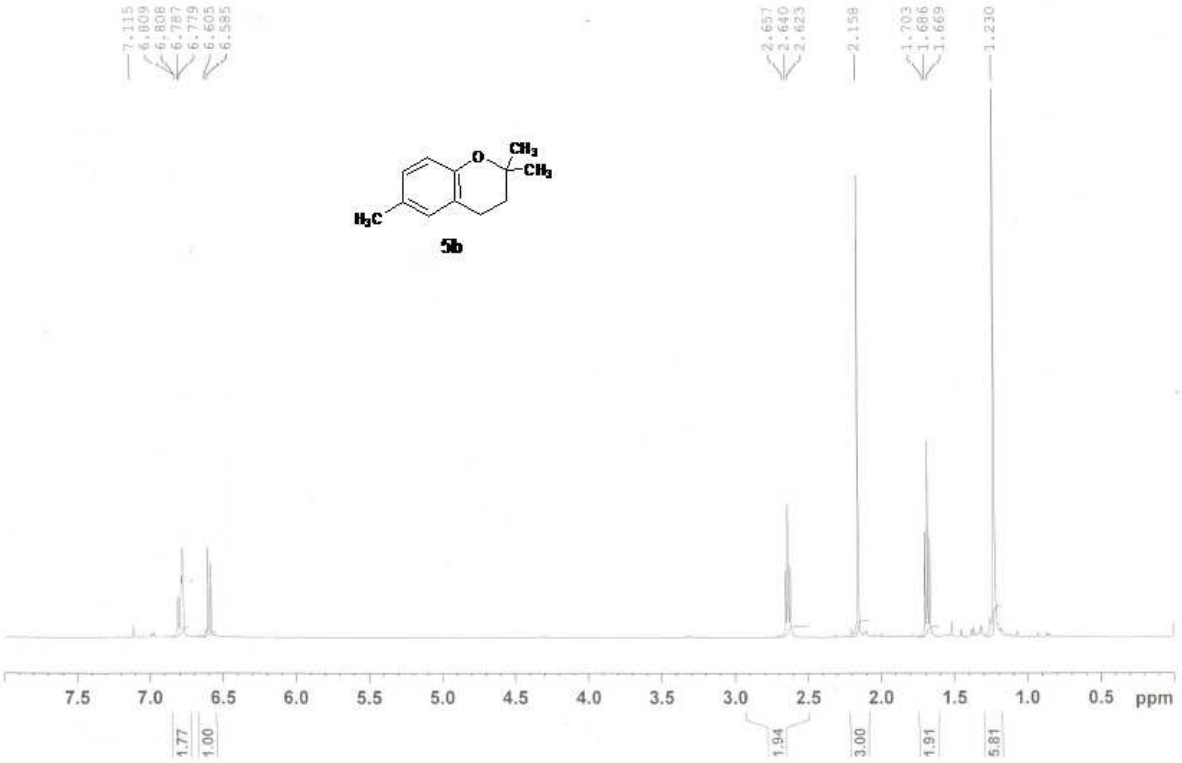

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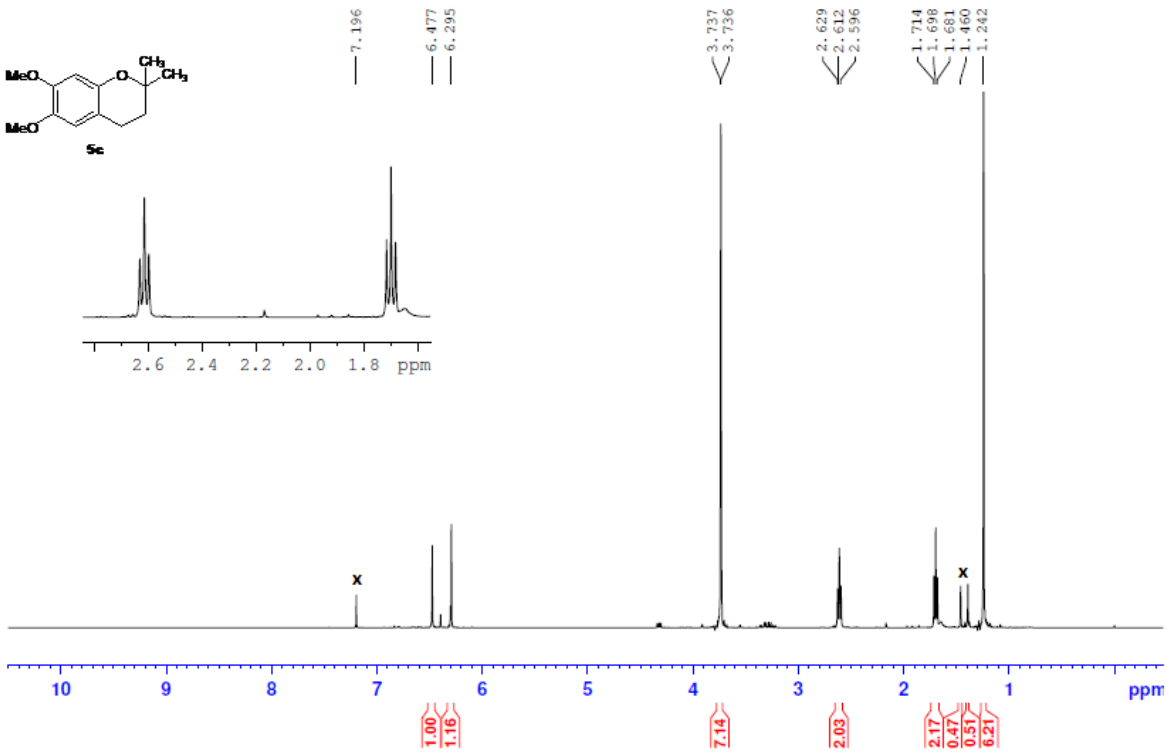

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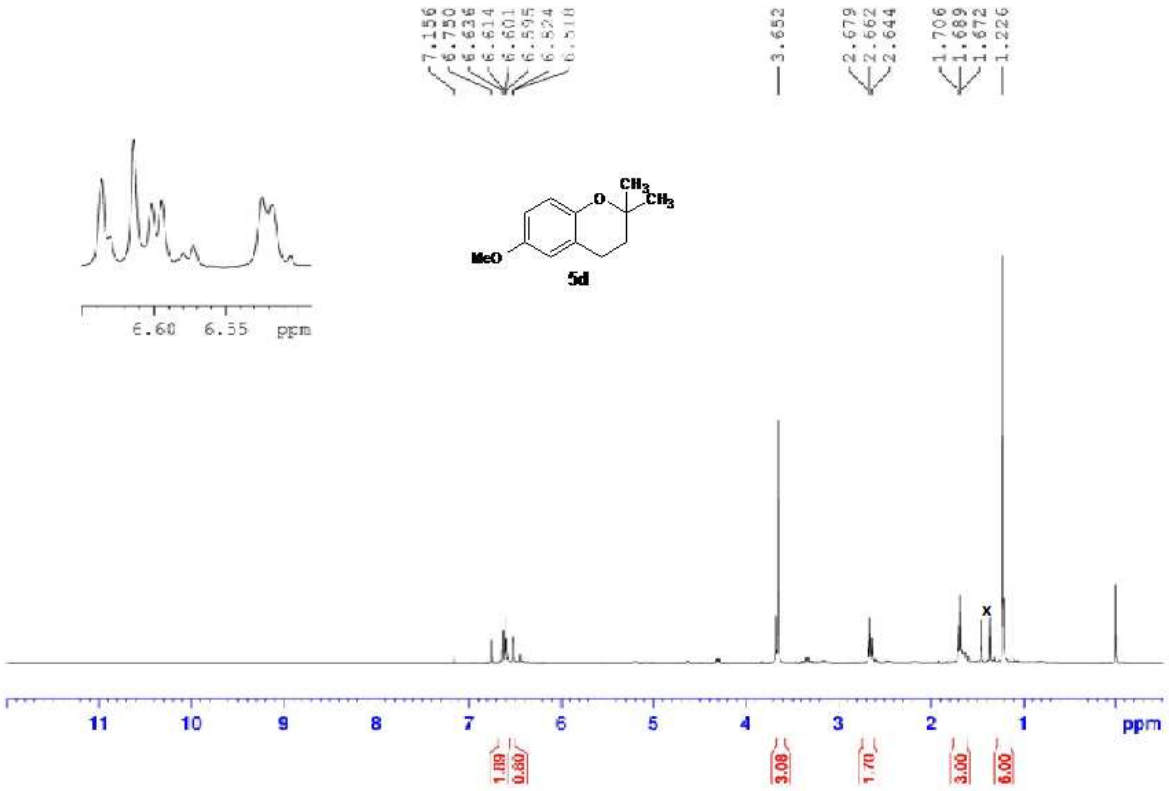

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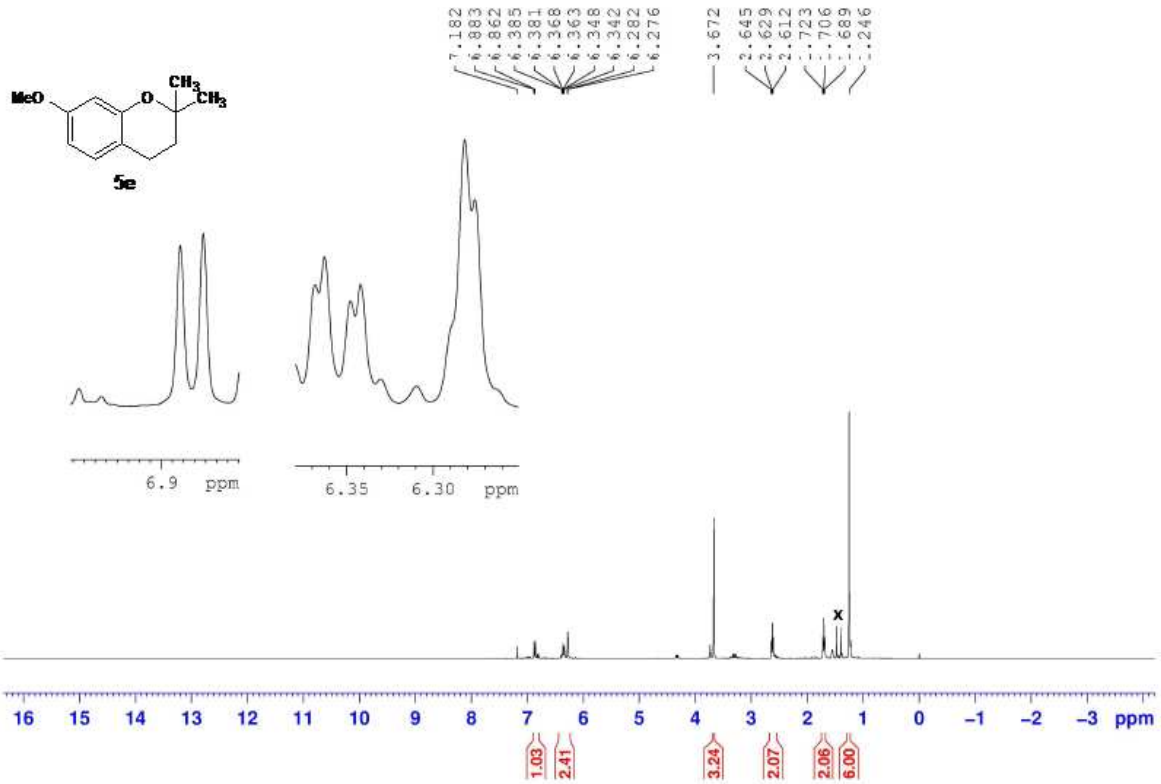
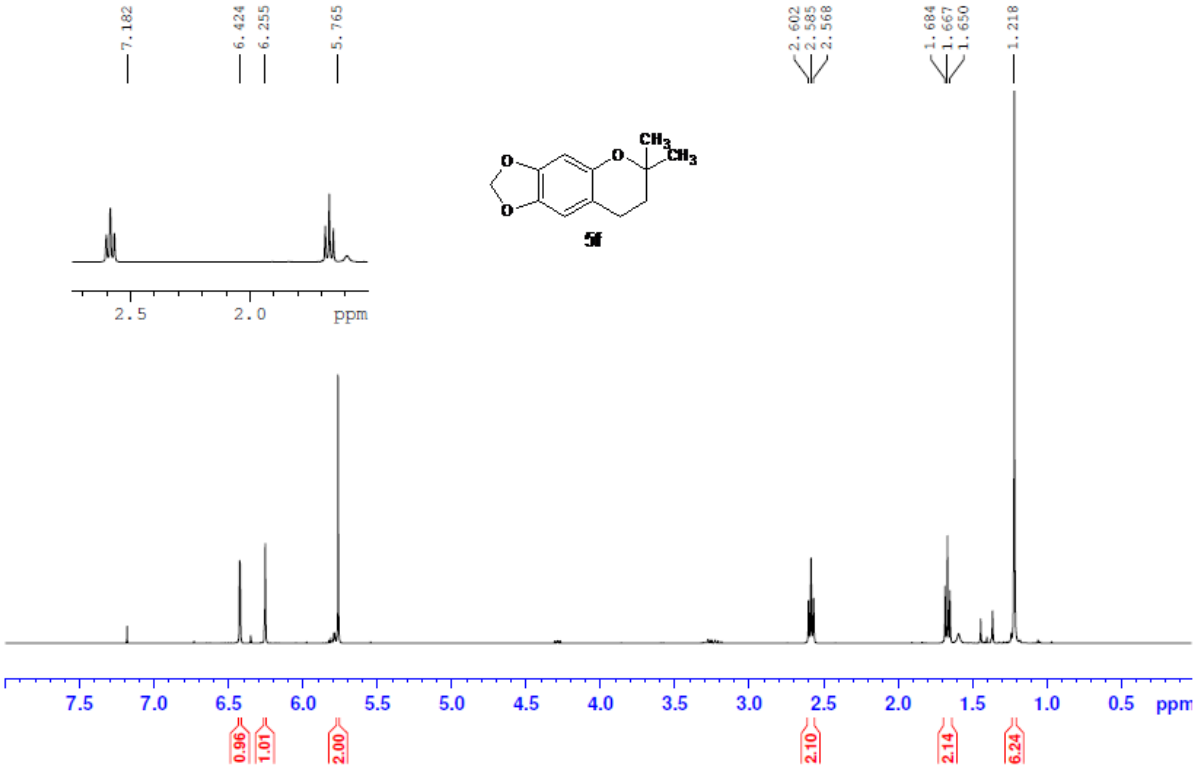


^{1}H NMR of compound 5f



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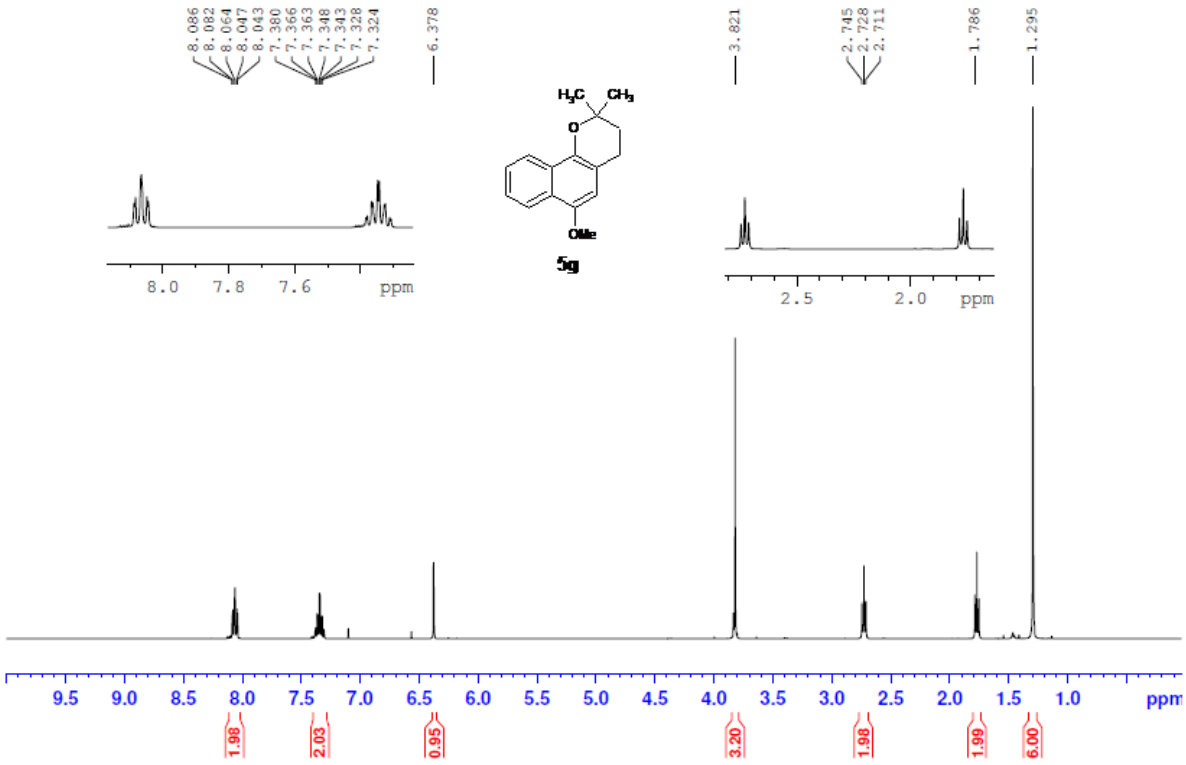
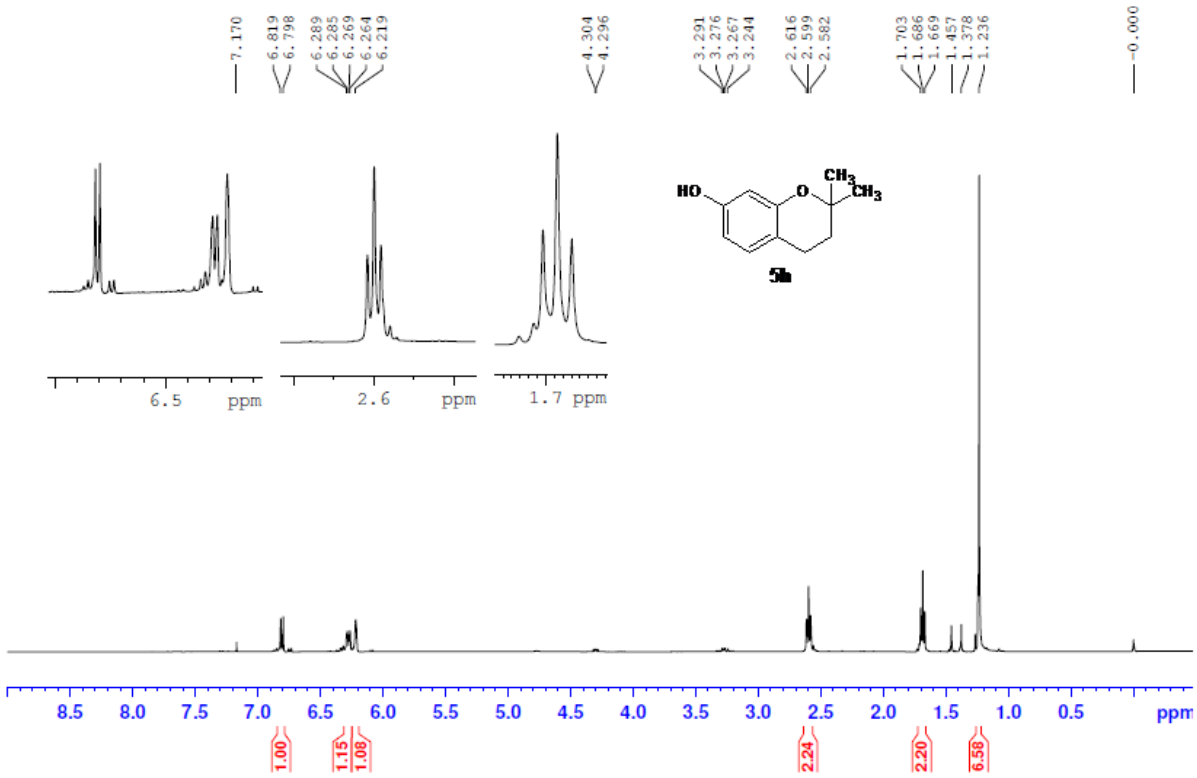


^{1}H NMR of compound 5h



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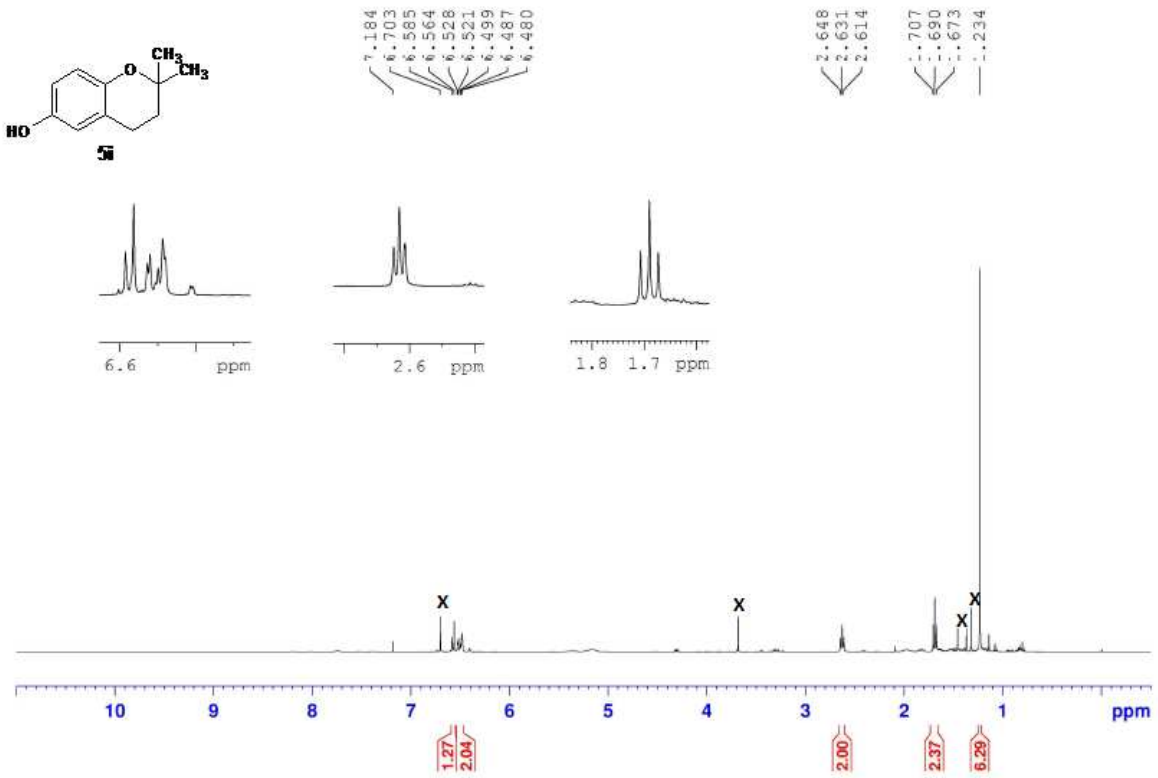

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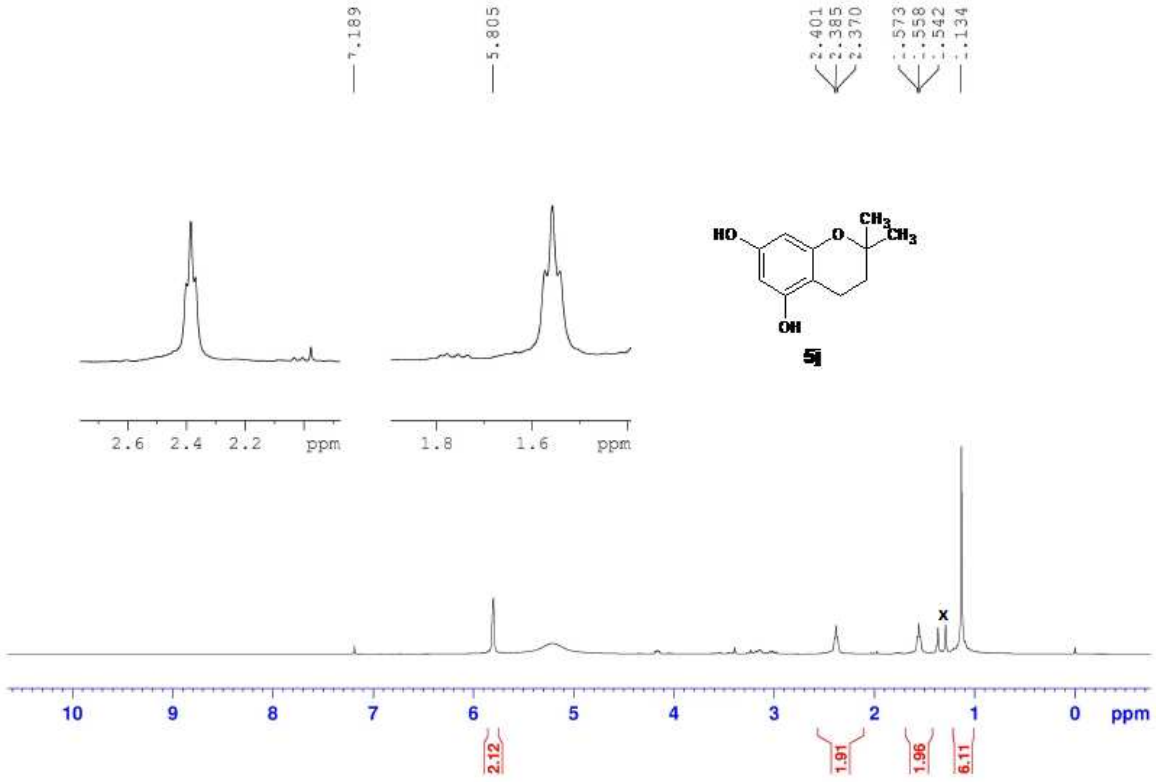

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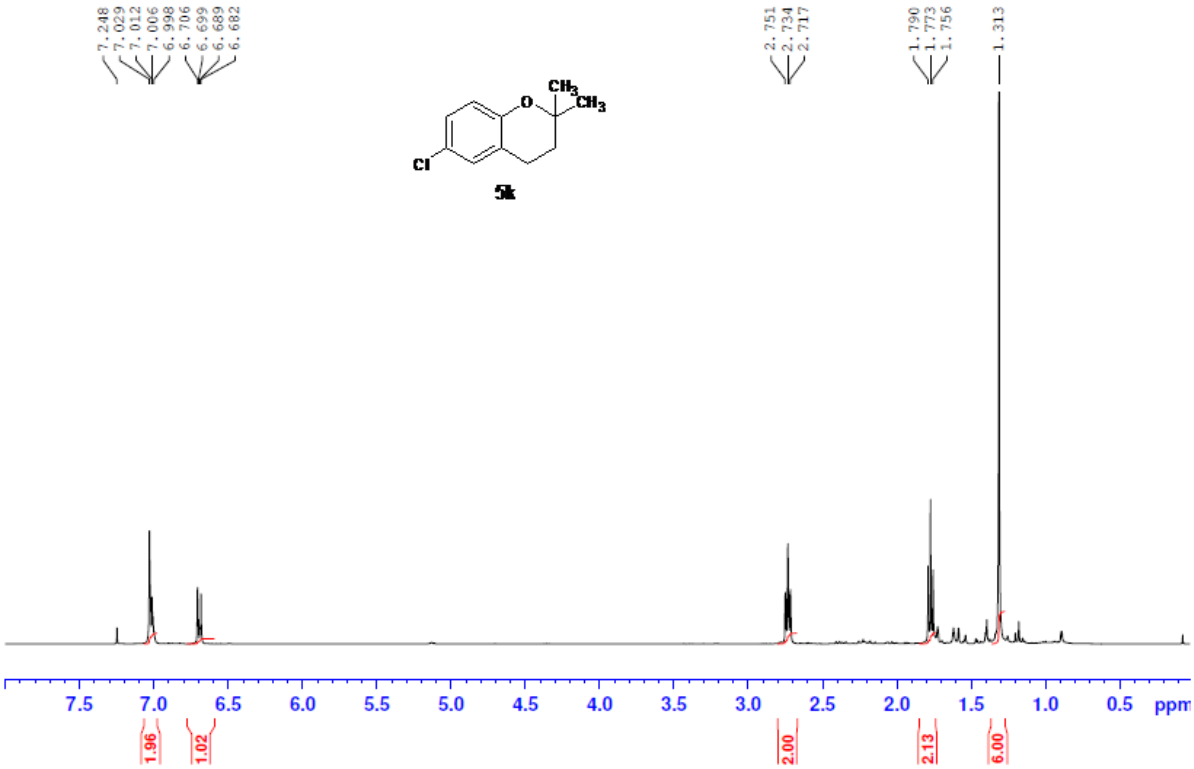

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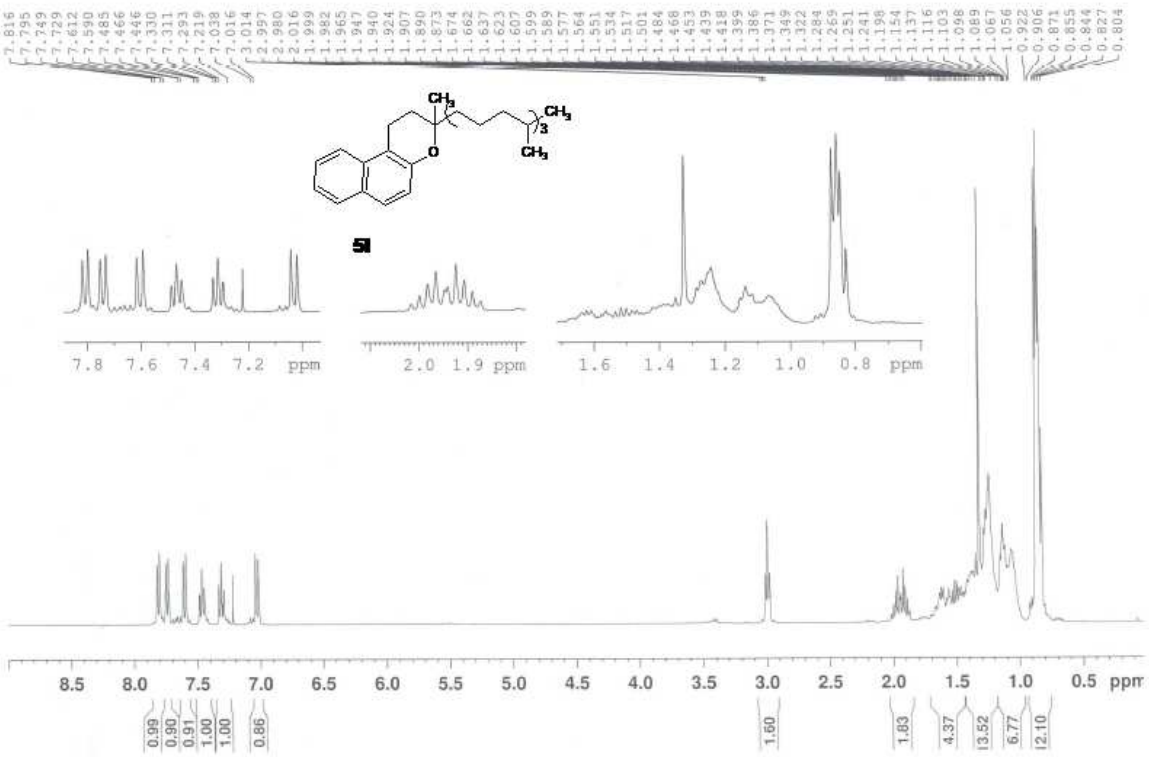
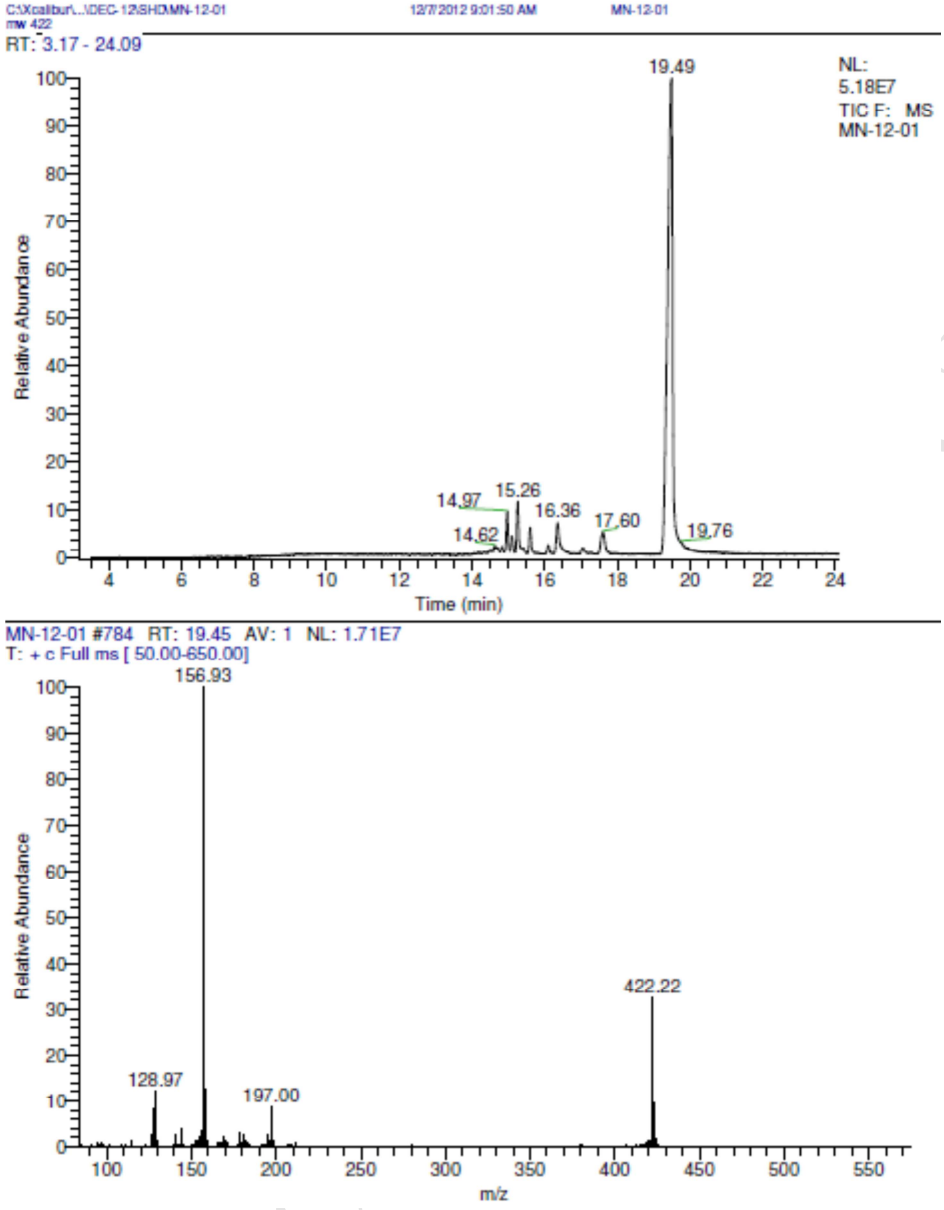
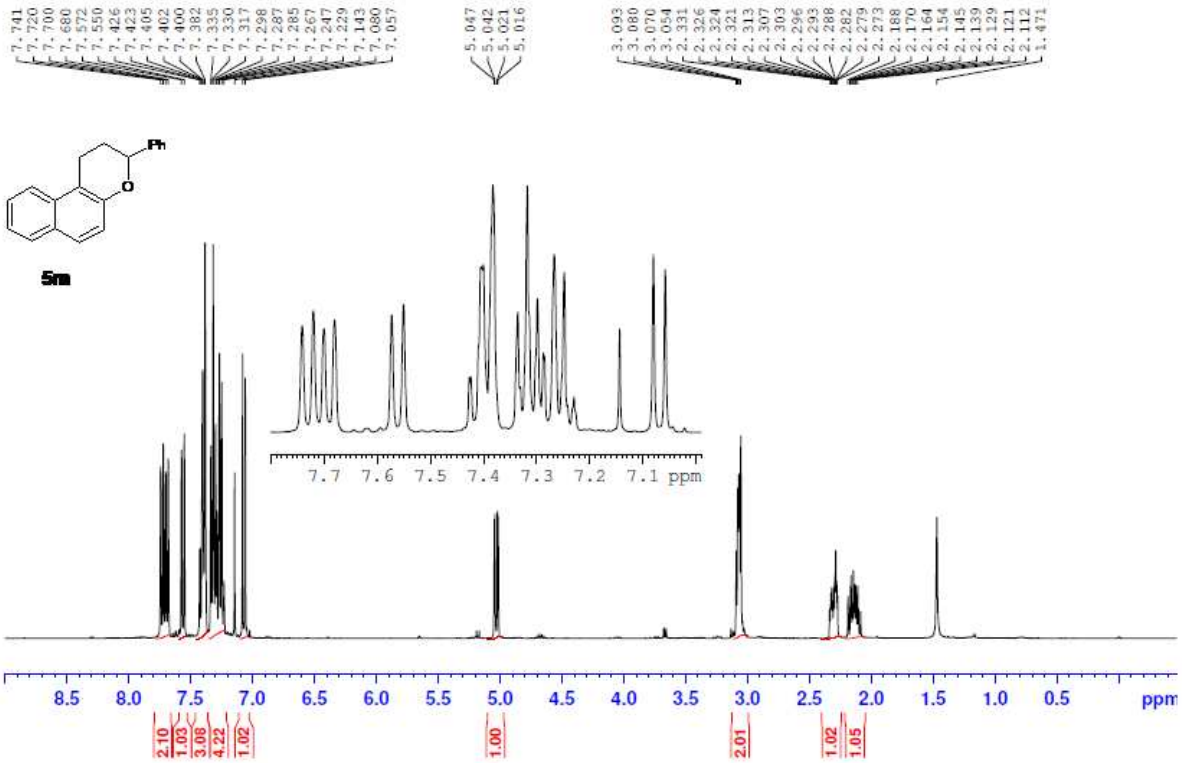


GCMS of compound 5l



^{1}H NMR of compound 5m



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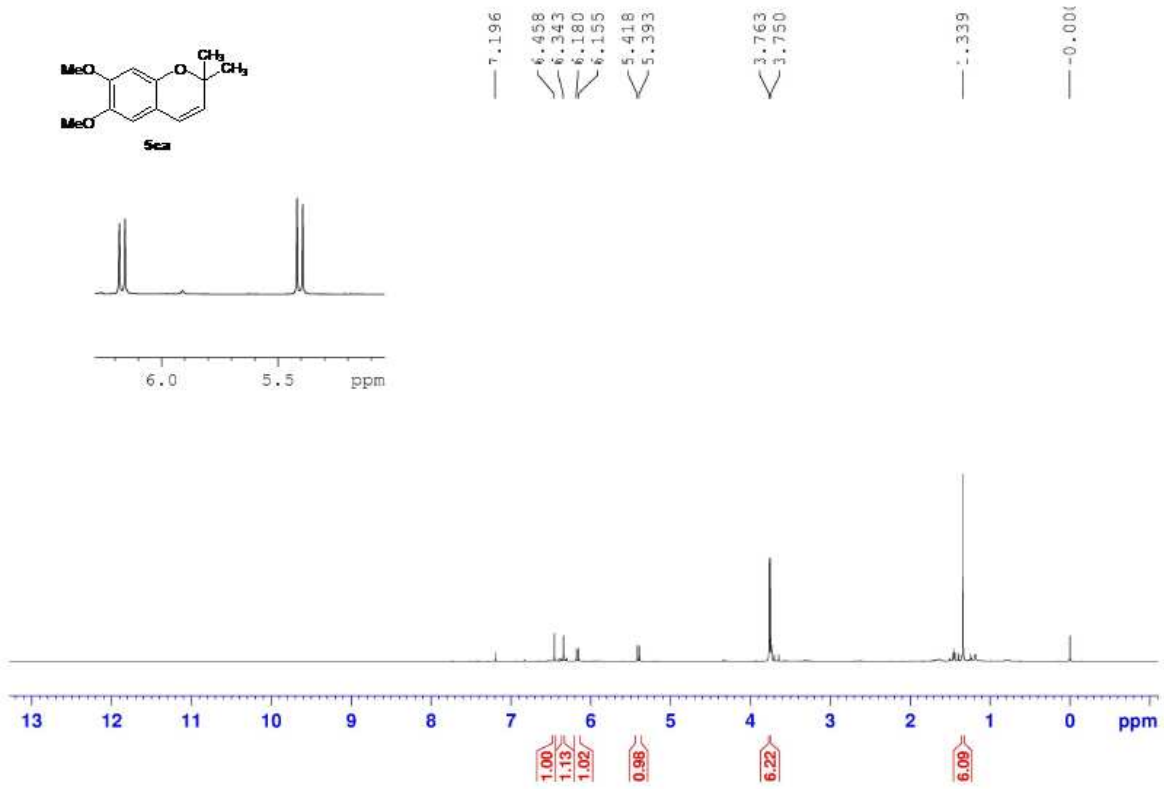

^{1}H NMR of compound 5ga