Tetrahedron 64 (2008) 9962–9976

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An unexpected reaction of phosphorous tribromide on chromanone, thiochromanone, 3,4-dihydro-2*H*-benzo[*b*]thiepin-5-one, 3,4-dihydro-2*H*-benzo[*b*]oxepin-5-one and tetralone derived allylic alcohols: a case study☆

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ARTICLE INFO

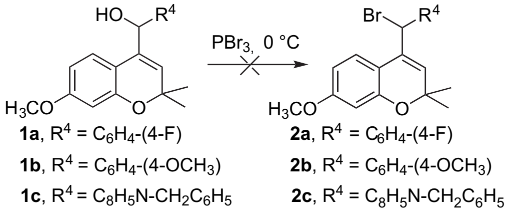
Article history:
Received 28 March 2008
Received in revised form 29 July 2008
Accepted 30 July 2008
Available online 5 August 2008

ABSTRACT

Treatment of chromanone, thiochromanone, tetralone and benzo[*b*]thiepinone derived allylic alcohols with phosphorous tribromide furnished unexpected products instead of desired bromo derivatives. Reaction of 7-methoxy-2,2-dimethylchromenyl-aryl-methanols and 7-methoxy-2,2-dimethylthiochromenyl-aryl-methanols with PBr_3 gave saturated carbonyls and exocyclic olefins depending on the substituents at R^4, whereas allylic alcohols without 7-methoxy substituent furnished rearranged products. Several related analogs varying in ring size, heteroatom in the ring and substituents at various positions were synthesized and studied. Reactions of other phosphorous-based reagents like PPh_3, PPh_3/I_2 and PPh_3Br_2 on allylic alcohols were also attempted. A case study is presented here.

1. Introduction

The reaction of allylic alcohols with phosphorus tribromide to furnish bromo derivatives is an important transformation in organic synthesis.[1] In this reaction, the hydroxy of allylic alcohol is replaced by bromide through stereo- and regioselective manner leading to the formation of corresponding bromo derivatives or the allylic alcohol rearranges into the terminal bromides involving migration of the double bond.[2] Recently in an effort towards accessing chromene containing bioactive agents,[3] we needed advanced intermediates **2a**–**c**, which could be obtained from carbinols **1a**–**c** on treatment with PBr_3. But instead of furnishing bromo derivatives **2a**–**c**, to our surprise, carbinols **1a**–**c** underwent isomerization to give saturated carbonyls **3**, **4** and exocyclic olefins **5**, **6** (Schemes 1 and 2). From close analysis of the structures of allylic alcohols **1a**–**c** and the ratio of their products, it was apparent that reaction was dependent on the substituents of allylic alcohols as **1a** containing *para* fluoro-phenyl group (−R effect) furnished saturated ketone **3** (77%) whereas **1b** containing *para* methoxyphenyl group (+R effect) gave saturated ketone **4** (67%) and exocyclic olefin **5** (15%) while **1c** furnished exocyclic olefin **6** (32%).



Scheme 1.

2. Results and discussion

This unusual transformation of allylic alcohols to saturated carbonyls and exocyclic olefins encouraged us to study the reaction of PBr_3 on a set of allylic alcohols as this type of disproportionation reactions are highly important in organic synthesis[4] and very few one-step synthetic methods are reported in the literature for such transformations.[5]

Thus, a series of substituted allylic alcohols were treated with PBr_3 and saturated carbonyls and exocyclic olefins were isolated from the reactions, Table 1. As stated above, allylic alcohols possessing R^4 groups with +R resonance effects gave good yields of exocyclic olefins while R^4 group with −R resonance effects gave good yields of saturated ketones. Increasing the number of OCH_3 groups and incorporation of $N(CH_3)_2$ group on R^4 (high +R effect) improved the yield of the exocyclic olefins[6a] while incorporation of

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☆ CDRI communication number 6996.

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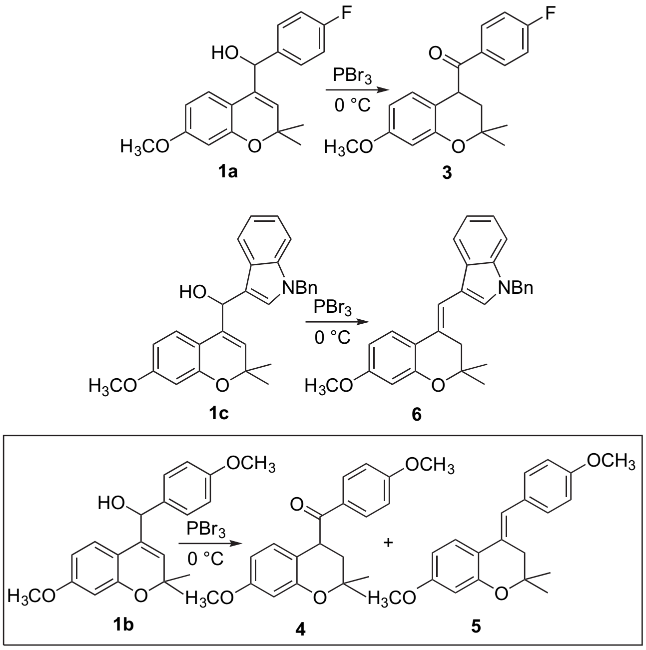
doi:10.1016/j.tet.2008.07.106



Scheme 2.

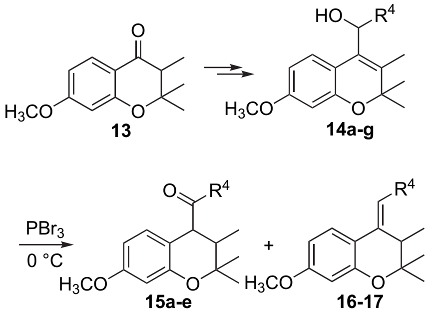
Table 1
Transformation of allylic alcohols into saturated carbonyls and exocyclic olefins using PBr_3

Entry	Allylic alcohol	R^4	Ketone	Yield (%)	Olefin	Yield (%)
1	**1d**	C_6H_5	**2d**	73	—	—
2	**1e**	C_6H_4-(2-OCH_3)	**2e**	65	7	19
3	**1f**	C_6H_4-(3-OCH_3)	**2f**	78	—	—
4	**1g**	C_6H_3-(2,4-OCH_3)	**2g**	20	8	56
5	**1h**	C_6H_2-(2,4,6-OCH_3)	**2h**	—	9	65
6	**1i**	(2-Thienyl)	**2i**	58	10	18
7	**1j**	(2-Furyl)	**2j**	67	—	—
8	**1k**	CH=CH–C_6H_5	**2k**	—	11	25
9	**1l**	C_6H_4-{4-$N(CH_3)_2$}	**2l**	—	12	67
10	**1m**	C_6H_4-(2-Cl)	**2m**	60	—	—
11	**1n**	(3-NO_2)	**2n**	82	—	—
12	**1o**	C_6H_4-(4-CN)	**2o**	74	—	—
13	**1p**	C_6H_4-{4-$CH(CH_3)_2$}	**2p**	69	—	—
14	**1q**	$C_{10}H_7$	**2q**	75	—	—
15	**1r**	C_2H_5	**2r**	61	—	—
16	**1s**	C_3H_7	**2s**	63	—	—
17	**1t**	CH=$CHCH_3$	**2t**	69	—	—
18	**1u**	C_6H_4-(4-Cl)	**2u**	60	—	—

CN, F, NO_2, Cl group (high −R effect) increases the yield of saturated ketones,[6b] Scheme 2.

2.1. Reaction of PBr_3 on tetrasubstituted allylic alcohols

Further to elaborate this methodology, we were interested to explore the reaction of PBr_3 on tetrasubstituted allylic alcohols. From the literature reports it was observed that the isomerization of allylic alcohols using known methods depends largely upon the substitution on the double bond.[5a] The reaction becomes more difficult as the number of substituents on double bond increases. A handful of examples are known for the transposition of trisubstituted and conjugated allylic alcohols into saturated carbonyls.[7] Not a single example of conversion of tetrasubstituted allylic alcohols into saturated carbonyls by using metal catalyst or any other regents in one step is known; perhaps due to steric hindrance present in double bond having four substituents. To explore the possibility of this reaction, tetrasubstituted allylic alcohols were synthesized from 3-methyl substituted chromanone **13**[8] and were treated with PBr_3. To our delight, the saturated ketones **15a**–**e** and exocyclic olefins **16**, **17** were isolated in good yields, Scheme 3 and Table 2.



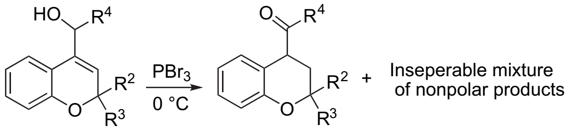
Scheme 3.

Table 2
Transformation of tetrasubstituted allylic alcohols **14a–g** to saturated ketones **15a–e** and exocyclic olefins **16**, **17**

Entry	Alcohol	R^4	Ketone	Yield (%)	Olefin	Yield (%)
1	**14a**	C_6H_5	**15a**	84	—	—
2	**14b**	C_6H_4-(3-OCH_3)	**15b**	79	—	—
3	**14c**	C_6H_4-(4-F)	**15c**	83	—	—
4	**14d**	C_3H_7	**15d**	75	—	—
5	**14e**	C_6H_4-(4-Cl)	**15e**	87	—	—
6	**14f**	C_6H_4-(4-OCH_3)	—	—	16	71
7	**14g**	C_6H_4-{4-$N(CH_3)_2$}	—	—	17	73

2.2. Reaction of PBr_3 on chromanone and 2-isopropyl-chromanone and 2,2-dimethylchromanone derived allylic alcohols

In continuation of our study, PBr_3 was reacted with chromene containing allylic alcohols **18** without dimethyl and **20a**,**b** with 2-isopropyl substituents. While minor amount of saturated carbonyls **19** and **21a**,**b**, respectively, were obtained, the reaction gave mostly inseparable mixture of non-polar products. The allylic alcohols were also not much stable perhaps due to the presence of a proton adjacent to oxygen. On the contrary, on treatment of PBr_3 the allylic alcohol **22** without 7-methoxy substituent and proton adjacent to oxygen, furnished saturated carbonyl **23**, Scheme 4 and Table 3.



Scheme 4.

Table 3
Transformation of allylic alcohols **18**, **20a**,**b**, **22** to saturated ketones **19**, **21a**,**b**, **23** using PBr_3

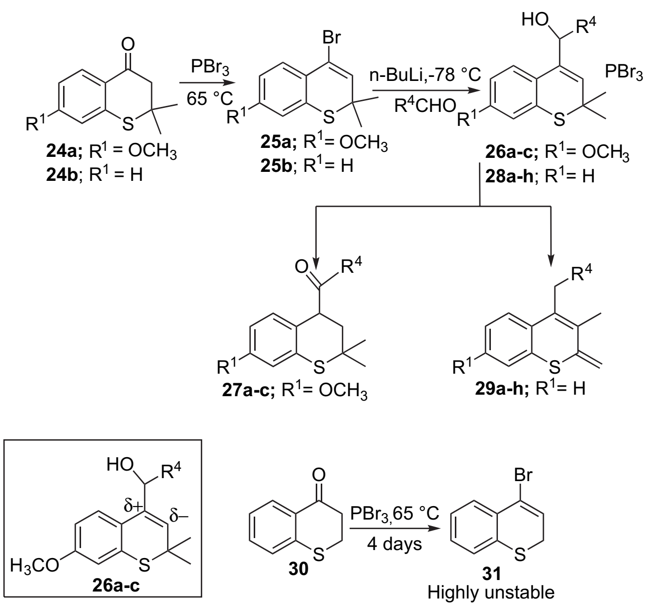
Entry	Alcohol	R^2, R^3, R^4	Ketone	Yield (%)
1	**18**	R^2=R^3=H, R^4=C_6H_4-(3-OCH_3)	**19**	20
2	**20a**	R^2=H, R^3=Isopropyl, R^4=C_6H_5	**21a**	15
3	**20b**	R^2=H, R^3=Isopropyl, R^4=C_6H_4-(3-OCH_3)	**21b**	26
4	**22**	R^2=R^3=Me, R^4=C_6H_4-(4-Cl)	**23**	30

Table 4
List of final products **27a–c** and **29a–h** during treatment of PBr_3 on allylic alcohols **26a–c**, **28a–h** containing thiochromene ring

Entry	Alcohol	R^1, R^4	Ketone	Yield (%)	Rearranged product	Yield (%)
1	**26a**	OCH_3, C_6H_4-(4-Cl)	**27a**	50	—	—
2	**26b**	OCH_3, C_6H_5	**27b**	51	—	—
3	**26c**	OCH_3, C_6H_4-(3-NO_2)	**27c**	60	—	—
4	**28a**	H, C_6H_4-(3-NO_2)	—	—	**29a**	63
5	**28b**	H, C_6H_4-(4-OCH_3)	—	—	**29b**	53
6	**28c**	H, C_6H_4-{4-$N(CH_3)_2$}	—	—	**29c**	59
7	**28d**	H, C_6H_5	—	—	**29d**	52
8	**28e**	H, C_6H_4-(4-Cl)	—	—	**29e**	62
9	**28f**	H, C_6H_4-(4-CN)	—	—	**29f**	65
10	**28g**	H, C_6H_3-(2,4-Cl)	—	—	**29g**	61
11	**28h**	H, C_6H_4-(4-CH_3)	—	—	**29h**	57

2.3. Reaction of PBr_3 on 2,2-dimethyl-thiochromanone and thiochromanone derived allylic alcohols

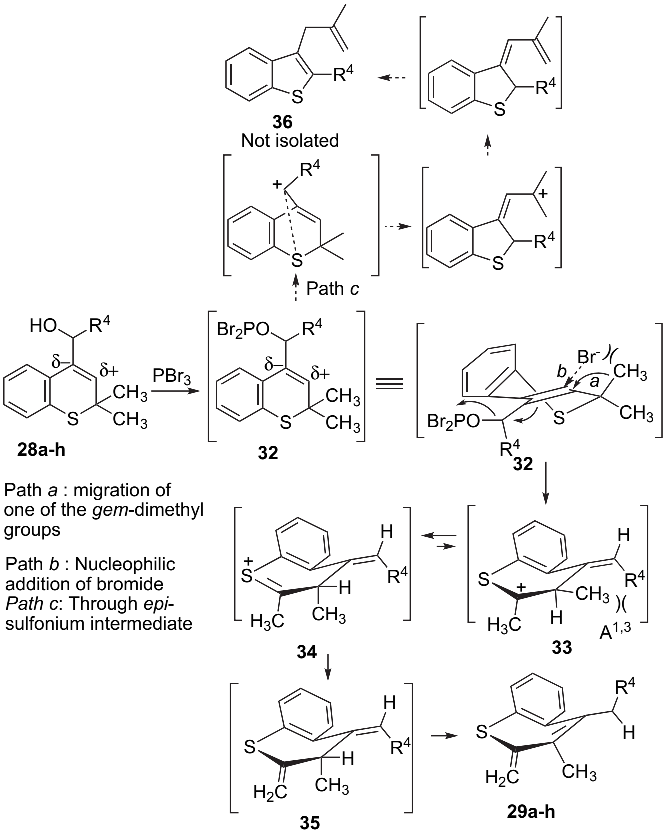
We further wanted to observe the role of heteroatom in this transformation reaction of allylic alcohols and thus 7-methoxy-2, 2-dimethyl-thiochroman-4-one **24a** was converted into bromo derivative **25a**, which on subsequent reaction with *n*-BuLi and R^4CHO afforded allylic alcohols **26a–c** following reported procedures.[4,9] The resulting compounds **26a–c** with 7-methoxy substituent on reaction with PBr_3 at 0 °C furnished saturated ketones **27a–c** in good yields (Table 4). On the contrary, on treatment with PBr_3, the allylic alcohols without 7-methoxy substituent **28a–h**, furnished rearranged products **29a–h** instead of giving saturated carbonyls. On the other hand, thiochromanone derived bromo derivative **31** was not stable and further reaction was not performed on it, Scheme 5.



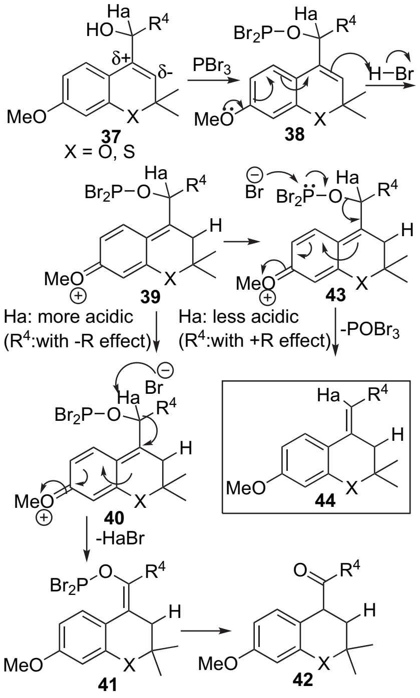
Scheme 5.

2.4. Plausible reaction mechanism for the formation of rearranged products

The sulfur of **26a–c** having vacant 3d orbital might induce inverse polarization on double bond through attracting the electron cloud of benzene ring. On the other hand, the electron-donating effect of OCH_3 at benzene nucleus nullifies the effect of sulfur and causes the polarization of double bond of **26a–c** (Schemes 5–7) similar to the one observed in chroman containing allylic alcohols.[6a,b] Thus it was observed that donating effect of OCH_3 in **26a–c** plays a role in retaining the polarization of double bond, which eventually furnished the saturated ketones **27a–c** (Scheme 7). Further to ascertain the role of 7-OCH_3 at benzene ring on polarization of double bond,



Scheme 6.



Scheme 7.

PBr_3 reaction was performed on allylic alcohols **28a–h** without 7-OCH_3 substituent.

This reaction can be thought to proceed via an intermediate **32** formed during the reaction of **28a–h** with PBr_3 followed by elimination of HBr. The double bond in **28a–h** is not similarly polarized owing to absence of 7-OCH_3 as it was observed in **26a–c** (Scheme 7). Moreover, the tendency of leaving group ability of $OPBr_2$ and the ability of accommodating electron cloud in vacant 3d orbital of sulfur atom in **32** caused the inverse polarization of double bond in **32**. This resulted into an additional +ve charge on trisubstituted carbon atom of double bond where nucleophilic addition of bromide anion (path *b*) can take place or one of the *gem*-dimethyl groups can migrate (path *a*) or the reaction may follow through *epi*-sulfonium intermediate[11d–f] to furnish **36** (path *c*) (Scheme 6). Close inspection of six membered half-chair like transition state[5] of **32** revealed that the nucleophilic approach of bromide ion was obstructed due to the steric hindrance of one of the *gem*-dimethyl groups at pseudoaxial (á) position. Thus the reaction followed path *a* and migratory aptitude of á-methyl prevailed over nucleophilic attack of bromide ion and afforded **33**. Moreover, the driving force of migration of one of the *gem*-dimethyl groups is the formation of sulfonium ion due to the lone pair participation of sulfur atom in the stabilization of an intermediate positive charge on carbon atom bearing methyl group in **34**. Further, **33** with methyl at equatorial rearranged to **34** with methyl at axial due to the existence of severe 1,3-allylic strain ($A^{1,3}$)[10,11] between equatorial-methyl and R^4 in **33**. Compound **34** got deprotonated to furnish **35**, which again rearranged for an extended double bond delocalization in presence of acidic medium (PBr_3/benzene) to furnish **29a–h**. The possibility of formation of **36** has been ruled out from the incisive analysis of COSY, NOESY and HMBC spectra of the rearranged product (Fig. 1).

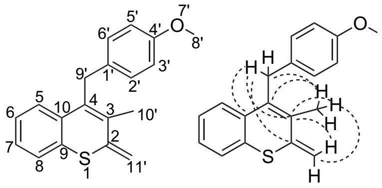


Figure 1. HMBC correlation of compound **29b**.

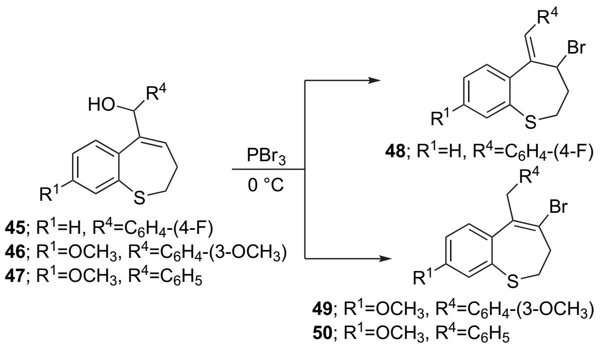
2.5. Plausible reaction mechanism for the formation of saturated carbonyls and exocyclic olefins from allylic alcohols containing 7-methoxy and 2,2-dimethyl substituents

Based on the preliminary published results,[6] a probable mechanism was proposed where addition of HBr was shown on the double bond. It has been now observed from the detailed results furnished above that 7-methoxy substituent plays an important role towards the transformation of allylic alcohols to saturated carbonyls or exocyclic olefins or other rearranged products. Thus a revised mechanism is discussed where role of 7-methoxy is explained.

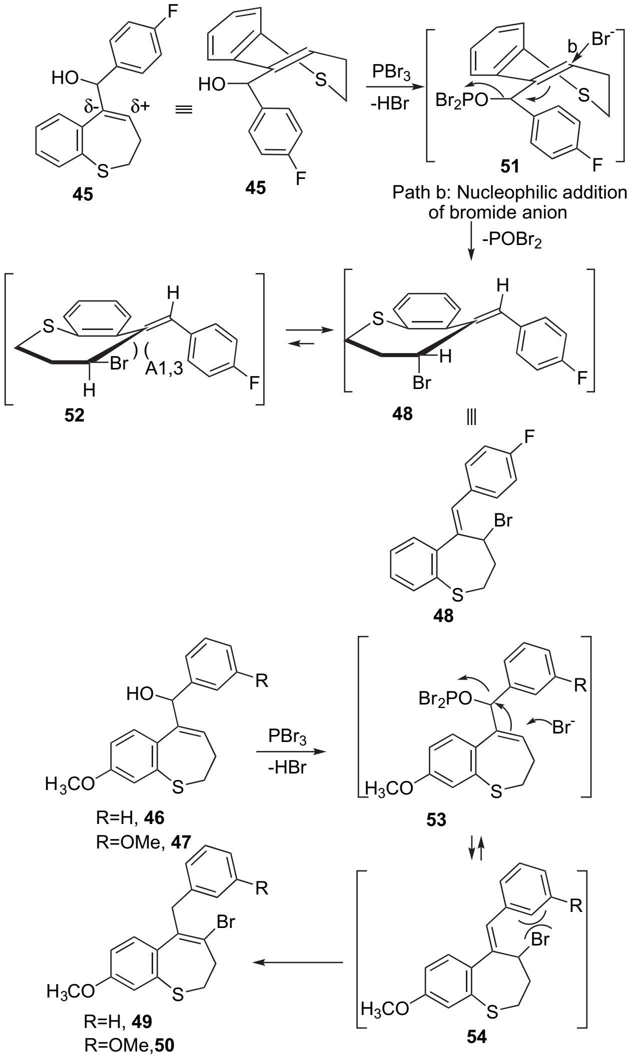
Treatment of **37** with PBr_3 furnished **38** with formation of HBr. The double bond in **38** got protonated due to the extended conjugation of 7-methoxy in aromatic ring giving rise to a quinonoid structure like **39**. In the presence of electronegative substituents in R_4, H_a proton is more acidic and thus bromide anion in the solution abstracts it giving rise to **40**, which on hydrolysis furnished saturated carbonyl **41**. On the other hand, in presence of electron-donating substituents in R_4, acidity of proton H_a is reduced and thus bromide anion attacks $POBr_2$ group resulting into formation of $POBr_3$ and exocyclic olefin **44**.

2.6. Reaction of PBr_3 on benzo[*b*]thiepinone and 8-methoxybenzo[*b*]thiepinone derived allylic alcohols

We became interested in executing the reaction of PBr_3 on benzo[*b*]thiepinone[12] derived allylic alcohols without *gem*-dimethyl substituents. On treatment with PBr_3, **45–47** furnished bromo derivative **48–50**. Reaction of **45** with PBr_3 gave a twist-chair[13] like intermediate **51** with elimination of HBr. Nucleophilic addition of bromide anion and migration of double bond gave **49**.



Scheme 8.



Scheme 9.

Table 5
Formation of bromo derivatives **48**–**50** from alcohols **45**–**47**

Entry	Alcohol	R^1, R^4	Product	Yield (%)
1	**45**	H, C_6H_4-(4-F)	**48**	51
2	**46**	OCH_3, C_6H_4-(3-OCH_3)	**49**	53
3	**47**	OCH_3, C_6H_5	**50**	57

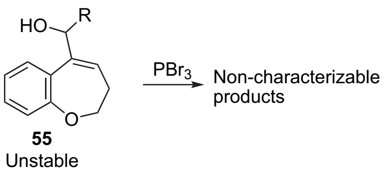
On the other hand, allylic alcohols **46** and **47** with 7-methoxy substituent afforded bromide **54** through migration of double bond and elimination of $POBr_2$. Isomerization of exocyclic double bond to endocyclic leads to **49** and **50** perhaps due to $A^{1,3}$ strain[10,11] and increased electron density on R^4 from +R effect of 8-methoxy of **54** (Schemes 8 and 9 and Table 5).

2.7. Plausible reaction mechanism

See Scheme 9.

2.8. Reaction of PBr_3 on benzo[*b*]oxepinone derived allylic alcohols

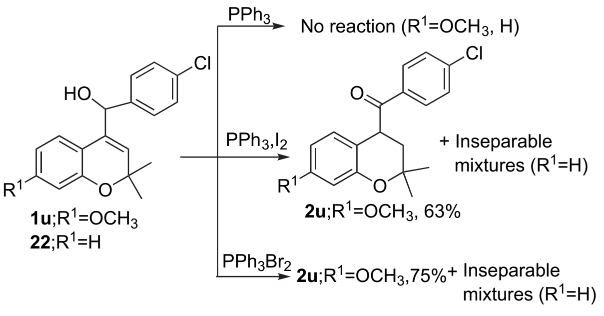
Similar reaction of PBr_3 on allylic alcohols **54** derived from benzo[*b*]oxepinone[12] gave non-characterizable products and allylic alcohols **55** was also unstable, Scheme 10.



Scheme 10.

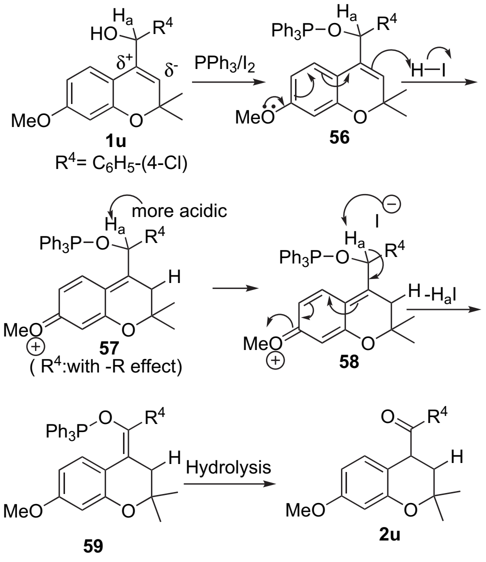
2.9. Reaction of allylic alcohols with other reagents based on phosphorous

The allylic alcohols were also treated with other phosphorous derived reagents to study their properties. Towards this objective, alcohols **1u** and **22** was reacted with triphenyl phosphine, combination of triphenyl phosphine and iodine and triphenylphosphinedibromide in THF as solvent. On treatment with PPh_3/I_2 and PPh_3Br_2 **1u** containing 7-methoxy gave saturated carbonyl **2u**. On reaction with PPh_3/I_2 and PPh_3Br_2 alcohol **22** without 7-methoxy gave inseparable mixture of products. The alcohols **1u** and **22** were intact on treatment of PPh_3 on them, Scheme 11.



Scheme 11.

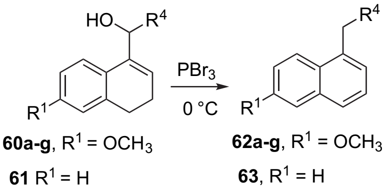
Reaction may be thought to proceed via an intermediate **56** formed from the reaction of **1u** with PPh_3/I_2. The double bond in **56** gets protonated due to the presence of 7-methoxy to furnish **57**. Finally abstraction of proton by iodide and followed by hydrolysis furnished saturated carbonyl **2u**, Scheme 12.



Scheme 12.

2.10. Reaction of PBr_3 on tetralone and 6-methoxytetralone derived allylic alcohols

Further to elaborate the reaction of PBr_3 on allylic alcohols, we became interested to decrease the polarizability of the unsymmetrically substituted double bond by replacing the heteroatom of the ring with the carbon atom. Surprisingly the allylic alcohols **60a**–**g** rearranged to the 1-arylmethylnaphthalenes **62a**–**g** via aromatization of ring B (Scheme 13).[14]



Scheme 13.

In conclusion, we have demonstrated the effect of R^1 and R^4 and heteroatom substituent on polarization of the double bond in allylic alcohols **A** (abstract) leading to the formation of saturated ketones, exocyclic olefins, methyl migrated products **29a**–**h**, bromo derivatives **48**–**50** and 1-arylmethylnaphthalenes **62a**–**g** and **63**. The chromene containing allylic alcohols having high electron-donating substituent at R^1 and R^4 furnished exocyclic olefins. While saturated carbonyls are obtained when high electron-withdrawing substituent at R^1 and R^4 are present in the allylic alcohols containing chromene ring. The thiochromene containing allylic alcohols **26a**–**c** having OCH_3 at R^1 and electron-withdrawing substituent at R^4 furnished saturated carbonyls **27a**–**c**. When electron-donating group (OCH_3) is absent at R^1 like in **28a**–**h**, the reaction involves a sequence of rearrangement reactions.

3. Experimental section

3.1. General

All melting points were recorded in open capillaries on Remi MP-1, 4/98 melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer RX_1 and FTIR 8201 PC Shimadzu spectrophotometers and values are expressed in cm^{-1}.

Solid samples were recorded as KBr wafers and liquid samples as their film between NaCl plates. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were generally recorded on Advance DPX200 Bruker 200 MHz and Advance DRX200 Bruker 300 MHz spectrometer unless otherwise mentioned. NMR samples were generally made in chloroform-*d* solvent and chemical shifts were reported in δ scale in parts per million (ppm) using tetramethylsilane (TMS, Me$_4$Si) as the internal standard. FABMS spectra are recorded on JEOL SX 102 Mass Spectrometer using Argon/Xenon (6 kV, 10 mA) as the FAB gas. Elemental analyses were performed on Vario EL III and Carlo Erba 1108 CHN Analyzer. All the compounds were dried in abderhalden. Analytical thin layer chromatography (TLC) was carried out on (10 cm×5 cm) glass plates coated with Merck's silica gel G or GF$_{254}$ (containing 13% calcium sulfate as binder) or Merck's aluminium oxide 60 GF$_{254}$ neutral or 60 HF$_{254}$ basic.

3.2. General procedure to prepare allylic alcohols

The alcohols were prepared from their corresponding chromanone, thiochromanone, benzo[*b*]thiepinone and tetralone derivatives via a two-step reaction sequence as reported earlier.[6]

3.2.1. (4-Fluoro-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol **1a**

Yield=51% as yellow semi solid. IR (Neat): 3420, 1612, 1506, 1277, 1223, 1147, 836, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.34–7.27 (m, 2H, Ar*H*), 6.93–6.89 (m, 2H, Ar*H*), 6.80 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.31 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.20 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.57 (s, 1H, 3-*H*), 5.52 (s, 1H, C*H*OH), 3.63 (s, 3H, OC*H*$_3$), 2.24 (br s, 1H, CHO*H*), 1.37 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.9, 155.0, 137.8, 133.5, 129.2, 125.8, 125.2, 116.1, 115.7, 113.6, 106.0, 102.8, 76.6, 72.7, 55.6, 28.2. MS (FAB): *m*/*z* (%): 314 (40, [M$^+$]), 299 (100, [M$^+$−CH$_3$]), 297 (30, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{19}FO_3$: C, 72.60; H, 6.09. Found: C, 72.69; H, 6.17.

3.2.2. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-(4-methoxy-phenyl)-methanol **1b**

Yield=70% as yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3420, 2974, 1612, 1507, 1249, 1169, 1146, 1030, 754 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.32 (d, 2H, *J*=8.6 Hz, Ar*H*), 6.89–6.83 (m, 3H, Ar*H*), 6.38 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.27 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.70 (s, 1H, 3-*H*), 5.56 (s, 1H, C*H*OH), 3.76 (s, 3H, OC*H*$_3$), 3.70 (s, 3H, OC*H*$_3$), 2.35 (br s, 1H, CHO*H*), 1.46 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.7, 159.6, 154.9, 134.5, 133.7, 128.8, 125.3, 125.2, 114.4, 114.1, 106.8, 102.7, 76.7, 72.6, 55.5, 28.2. MASS (FAB): *m*/*z* (%): 326 (50, [M$^+$]), 311 (100, [M$^+$−CH$_3$]), 309 (55, [M$^+$−OH]). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.75; H, 6.67.

3.2.3. (1-Benzyl-1H-indol-3-yl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol **1c**

Yield=50% as yellow oil; R_f=0.4 (15% ethyl acetate in hexane). IR (Neat): 3435, 1619, 1507, 1267, 1229, 1143, 757 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.58 (d, 1H, *J*=7.9 Hz, Ar*H*), 7.49 (d, 1H, *J*=8.8 Hz, Ar*H*), 7.24–6.84 (m, 7H, Ar*H*), 6.94–5.77 (m, 4H, Ar*H*, C*H*OH, 3-*H*), 5.20 (s, 2H, C*H*$_2$C$_6$H$_5$), 3.68 (s, 3H, OC*H*$_3$), 2.19 (br s, 1H, CHO*H*), 1.39 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.6, 155.0, 137.8, 137.3, 131.5, 129.1, 128.6, 127.6, 126.5, 125.6, 125.5, 122.1, 120.6, 119.9, 115.4, 110.2, 106.7, 102.4, 76.8, 73.1, 71.6, 55.5, 50.4, 28.3. MS (FAB): *m*/*z* (%): 425 (70, [M$^+$]), 408 (100, [M$^+$−OH]). Anal. Calcd for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 78.96; H, 6.38; N, 3.36.

3.2.4. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-phenyl-methanol **1d**

Yield=70% as yellow semi solid; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3429, 2973, 1614, 1502, 1277, 1146, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.33–7.22 (m, 5H, Ar*H*), 6.82 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.29 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.17 (dd, 1H, J_1=8.5 Hz, J_2=2.6 Hz, Ar*H*), 5.55 (s, 1H, 3-*H*), 5.48 (s, 1H, C*H*OH), 3.58 (s, 3H, −OC*H*$_3$), 2.29 (br s, 1H, CHO*H*), 1.35 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 155.0, 142.0, 133.5, 129.0, 128.4, 127.4, 125.7, 125.2, 113.8, 106.8, 102.6, 73.4, 55.6, 28.2. MS (FAB): *m*/*z* (%): 296 (40, [M$^+$]), 281 (100, [M$^+$−CH$_3$]), 279 (40, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found C, 77.11; H, 6.86.

3.2.5. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-(2-methoxy-phenyl)-methanol **1e**

Yield=64% as a yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3473, 2972, 1612, 1499, 1282, 1245, 1146, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.16–7.11 (m, 2H, Ar*H*), 6.83–6.75 (m, 3H, Ar*H*), 6.31 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.20 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.91 (s, 1H, 3-*H*), 5.59 (s, 1H, C*H*OH), 3.80 (s, 3H, OC*H*$_3$), 3.62 (s, 3H, OC*H*$_3$), 2.85 (br s, 1H, CHO*H*), 1.37 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.7, 157.4, 154.7, 132.6, 130.0, 129.6, 128.4, 125.1, 121.3, 114.4, 111.0, 106.8, 102.5, 76.8, 67.3, 55.9, 55.6, 28.2. MS (FAB): *m*/*z* (%): 326 (30, [M$^+$]), 311 (100, [M$^+$−CH$_3$]), 309 (40, [M$^+$−OH]). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.67; H, 6.74.

3.2.6. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-(3-methoxy-phenyl)-methanol **1f**

Yield=65% as a yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3434, 2970, 1610, 1270, 1147, 1040, 768 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.13 (t, 1H, *J*=8.4 Hz, Ar*H*), 7.08–6.80 (m, 3H, Ar*H*), 6.71–6.67 (m, 1H, Ar*H*), 6.27 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.16 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.54 (s, 1H, 3-*H*), 5.42 (s, 1H, C*H*OH), 3.65 (s, 3H, OC*H*$_3$), 3.57 (s, 3H, OC*H*$_3$), 2.62 (br s, 1H, CHO*H*), 1.34 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 160.2, 154.9, 143.8, 133.9, 133.5, 130.0, 125.7, 125.4, 119.8, 113.7, 113.0, 106.8, 102.7, 76.6, 73.2, 55.5, 28.2. MS (FAB): *m*/*z* (%): 326 (20, [M$^+$]), 311 (100, [M$^+$−CH$_3$]), 309 (35, [M$^+$−OH]). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.47; H, 6.69.

3.2.7. (2,4-Dimethoxy-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromene-4-yl)-methanol **1g**

Yield=64% as a light yellow semi-solid, R_f=0.4 (15% ethyl acetate in hexane). IR (Neat): 3422, 2929, 1611, 1151, 1043, 792 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.09 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.84 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.49–6.29 (m, 4H, Ar*H*), 5.93 (s, 1H, 3-*H*), 5.74 (s, 1H, C*H*OH), 3.87 (s, 3H, OC*H*$_3$), 3.74 (s, 3H, OC*H*$_3$), 3.71 (s, 3H, OC*H*$_3$), 2.59 (br s, 1H, CHO*H*), 1.46 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.0, 160.6, 158.5, 154.7, 132.8, 129.1, 125.1, 124.8, 122.9, 144.4, 106.8, 104.8, 102.5, 99.0, 76.8, 66.7, 55.9, 55.7, 55.5, 28.5, 28.3. MS (FAB): *m*/*z* (%): 356 (25, [M$^+$]), 341 (100, [M$^+$−CH$_3$]), 339 (90, [M$^+$−OH]). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.89; H, 6.84.

3.2.8. (7-Methoxy-2,2-dimethyl-2H-chromene-4-yl)-(2,4,6-trimethoxy-phenyl)-methanol **1h**

Yield=63% as light yellow semi solid; R_f=0.4 (20% ethyl acetate in hexane). IR (Neat): 3551, 3013, 1611, 1217, 1147, 761 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.48 (d, 1H, *J*=8.4 Hz, Ar*H*), 6.46–6.37 (m, 2H, Ar*H*), 6.15 (s, 2H, Ar*H*), 6.05 (s, 1H, 3-*H*), 5.15 (s, 1H, C*H*OH), 3.81 (s, 3H, OC*H*$_3$), 3.79 (s, 3H, OC*H*$_3$), 3.76 (s, 3H, OC*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 1.35 (d, 6H, *J*=5.6 Hz, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.1, 160.5, 159.2, 154.8, 133.0, 125.8, 124.4, 115.2, 110.5, 106.7, 102.4, 91.7, 76.5, 65.9, 56.1, 55.7, 28.2. MS (FAB): *m*/*z* (%): 386 (50, [M$^+$]), 371 (100, [M$^+$−CH$_3$]), 369 (40, [M$^+$−OH]). Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.29; H, 6.85.

3.2.9. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-thiophen-2-yl-methanol **1i**

Yield=54% as a dark yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3439, 2975, 1614, 1503, 1276, 1196, 1069, 762 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.25 (dd, 1H, J_1=4.7 Hz, J_2=1.0 Hz, Ar*H*), 7.02–6.91 (m, 3H, Ar*H*), 6.39 (d, 1H, J=2.5 Hz, Ar*H*), 6.31 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.82 (s, 1H, 3-*H*), 5.78 (s, 1H, C*H*OH), 3.71 (s, 3H, OC*H*$_3$), 2.35 (br s, 1H, CHO*H*), 1.46 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.9, 154.9, 146.6, 133.7, 127.3, 126.0, 125.0, 113.6, 107.0, 102.7, 76.7, 71.2, 69.0, 55.6, 28.2. MS (FAB): *m/z* (%): 302 (40, [M$^+$]), 287 (100, [M$^+$−CH$_3$]), 285 (60, [M$^+$−OH]). Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.46; H, 6.09.

3.2.10. Furan-2-yl-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol ***1j***

Yield=58% as a dark yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3434, 2974, 1614, 1503, 1276, 1145, 746 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.30 (s, 1H, Ar*H*), 6.87 (d, 1H, J=8.4 Hz, Ar*H*), 6.33–6.20 (m, 3H, Ar*H*), 6.12 (d, 1H, J=3.2 Hz, Ar*H*), 5.63 (s, 1H, 3-*H*), 5.59 (s, 1H, C*H*OH), 3.65 (s, 3H, OC*H*$_3$), 2.48 (br s, 1H, CHO*H*), 1.36 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.9, 155.1, 154.8, 142.8, 131.1, 125.5, 124.7, 113.8, 110.8, 108.2, 106.9, 102.7, 76.6, 66.9, 55.6, 28.1. MS (FAB): *m/z* (%): 286 (50, [M$^+$]), 271 (100, [M$^+$−CH$_3$]), 269 (70, [M$^+$−OH]). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.40; H, 6.31.

3.2.11. 1-(7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-3-phenyl-prop-2-en-1-ol ***1k***

Yield=52% as a yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3430, 2928, 1612, 1277, 1146, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.40–7.24 (m, 6H, Ar*H*), 6.72 (d, 1H, J=15.9 Hz, CH=C*H*C$_6$H$_5$), 6.44–6.37 (m, 3H, Ar*H*, C*H*=CHC$_6$H$_5$), 5.64 (s, 1H, 3-*H*), 5.23 (d, 1H, J=5.9 Hz, C*H*OH), 3.74 (s, 3H, OC*H*$_3$), 2.19 (br s, 1H, CHO*H*), 1.42 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.0, 155.0, 136.9, 133.5, 132.1, 130.4, 128.9, 128.2, 127.0, 125.2, 125.1, 113.9, 107.0, 102.8, 76.6, 71.8, 55.6, 28.1. MS (FAB): *m/z* (%): 322 (30, [M$^+$]), 307 (100, [M$^+$−CH$_3$]), 305 (95, [M$^+$−OH]). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.34; H, 6.81.

3.2.12. (4-Dimethylamino-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol ***1l***

Yield=59% as yellow solid; mp 90 °C (dichloromethane); R_f=0.4 (15% ethyl acetate in hexane). IR (KBr): 2429, 2972, 1613, 1521, 1146, 757 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.20 (d, 2H, J=8.8 Hz, Ar*H*), 6.80 (d, 1H, J=8.5 Hz, Ar*H*), 6.61 (d, 2H, J=8.8 Hz, Ar*H*), 6.30 (d, 1H, J=2.5 Hz, Ar*H*), 6.20 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.69 (s, 1H, 3-*H*), 5.47 (s, 1H, C*H*OH), 3.63 (s, 3H, OC*H*$_3$), 2.86 {s, 6H, N(C*H*$_3$)$_2$}, 1.38 (s, 3H, 2-C*H*$_3$), 1.18 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 154.9, 144.6, 134.7, 129.9, 128.6, 125.2, 124.6, 113.0, 106.8, 102.5, 72.8, 55.5, 40.9, 30.1, 28.3. MS (FAB): *m/z* (%): 339 (40, [M$^+$]), 322 (100, [M$^+$−OH]). Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.20; H, 7.45; N, 4.19.

3.2.13. (2-Chloro-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol ***1m***

Yield=60% as a yellow oil; R_f=0.4 (15% ethyl acetate in hexane). IR (Neat): 3434, 2969, 1614, 1503, 1276, 1199, 1146, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.39–7.29 (m, 2H, Ar*H*), 7.17–7.12 (m, 2H, Ar*H*), 6.83 (d, 1H, J=8.5 Hz, Ar*H*), 6.33–6.23 (m, 2H, Ar*H*), 5.99 (s, 1H, 3-*H*), 5.46 (s, 1H, C*H*OH), 3.64 (s, 3H, OC*H*$_3$), 2.36 (br s, 1H, CHO*H*), 1.34 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.9, 154.9, 139.3, 133.9, 132.5, 130.0, 129.7, 128.8, 127.6, 125.8, 124.6, 113.9, 107.0, 102.8, 76.9, 68.9, 55.6, 28.1. MS (FAB): *m/z* (%): 330 (20, [M$^+$]), 315 (100, [M$^+$−CH$_3$]), 313 (15, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{19}ClO_3$: C, 68.98; H, 5.79. Found: C, 69.11; H, 5.76.

3.2.14. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-(3-nitro-phenyl)-methanol ***1n***

Yield=53% as a dark yellow oil; R_f=0.5 (25% ethyl acetate in hexane). IR (Neat): 3453, 1613, 1530, 1351, 1146, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.34 (s, 1H, Ar*H*), 8.10 (d, 1H, J=1 Hz, Ar*H*), 7.75 (d, 1H, J=7.6 Hz, Ar*H*), 7.51 (t, 1H, J=7.9 Hz, Ar*H*), 6.95 (d, 1H, J=8.5 Hz, Ar*H*), 6.39 (d, 1H, J=2.5 Hz, Ar*H*), 6.30 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.70 (s, 1H, 3-*H*), 5.62 (s, 1H, C*H*OH), 3.72 (s, 3H, OC*H*$_3$), 2.42 (br s, 1H, CHO*H*), 1.46 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.2, 155.2, 148.8, 144.2, 133.2, 129.8, 127.1, 125.2, 123.1, 122.2, 113.0, 107.1, 103.0, 76.5, 73.0, 55.6, 28.1. MS (FAB): *m/z* (%): 341 (45, [M$^+$]), 326 (100, [M$^+$−CH$_3$]), 324 (20, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.81; H, 5.68; N, 4.07.

3.2.15. 4-[Hydroxy-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methyl]-benzonitrile ***1o***

Yield=55% as a yellow oil; R_f=0.5 (20% ethyl acetate in hexane). IR (Neat): 3450, 2969, 1613, 1503, 1277, 1199, 1146, 760 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.52 (d, 2H, J=8.2 Hz, Ar*H*), 7.46 (d, 2H, J=8.2 Hz, Ar*H*), 6.84 (d, 1H, J=8.5 Hz, Ar*H*), 6.30 (d, 1H, J=2.4 Hz, Ar*H*), 6.21 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.54 (s, 1H, 3-*H*), 5.46 (s, 1H, C*H*OH), 3.63 (s, 3H, OC*H*$_3$), 1.35 (s, 6H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.1, 155.1, 147.5, 133.2, 132.7, 127.8, 127.1, 125.3, 119.1, 113.2, 111.7, 107.0, 102.9, 76.5, 73.2, 55.6, 28.0. MS (FAB): *m/z* (%): 321 (50, [M$^+$]), 306 (100, [M$^+$−CH$_3$]), 304 (20, [M$^+$−OH]). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.81; H, 5.93; N, 4.42.

3.2.16. (4-Isopropyl-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)-methanol ***1p***

Yield=65% as a yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3436, 2964, 1614, 1504, 1277, 1198, 1146, 1069, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.35 (d, 2H, J=8.1 Hz, Ar*H*), 7.25–7.15 (m, 2H, Ar*H*), 6.92 (d, 1H, J=8.5 Hz, Ar*H*), 6.39 (d, 1H, J=2.5 Hz, Ar*H*), 6.29 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 5.72 (s, 1H, 3-*H*), 5.60 (s, 1H, C*H*OH), 3.71 (s, 3H, OC*H*$_3$), 2.88 {sept, 1H, C*H*(CH$_3$)$_2$}, 2.12 (br s, 1H, CHO*H*), 1.47 (s, 6H, 2-C*H*$_3$), 1.23 {d, 6H, J=6.9 Hz, CH(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 154.9, 149.1, 139.4, 133.5, 127.4, 127.1, 125.3, 113.9, 106.8, 102.6, 73.1, 55.5, 34.2, 28.3, 24.3. MS (FAB): *m/z* (%): 338 (20, [M$^+$]), 323 (100, [M$^+$−CH$_3$]), 321 (30, [M$^+$−OH]). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.12; H, 7.71.

3.2.17. (7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-naphthalen-1-yl-methanol ***1q***

Yield=54% as a yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3434, 2958, 1614, 1277, 1210, 1145, 1068, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.45–8.36 (m, 1H, Ar*H*), 8.04 (d, 1H, J=8.2 Hz, Ar*H*), 7.91–7.81 (m, 2H, Ar*H*), 7.58–7.45 (m, 3H, Ar*H*), 6.96 (d, 1H, J=8.2 Hz, Ar*H*), 6.45–6.40 (m, 2H, Ar*H*), 5.64 (s, 1H, 3-*H*), 5.59 (s, 1H, C*H*OH), 3.76 (s, 3H, OC*H*$_3$), 2.15 (br s, 1H, CHO*H*), 1.35 (s, 6H, 2-C*H*$_3$). MS (FAB): *m/z* (%): 346 (30, [M$^+$]), 331 (100, [M$^+$−CH$_3$]), 329 (40, [M$^+$−OH]). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.65; H, 6.43.

3.2.18. 1-(7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-propan-1-ol ***1r***

Yield=66% as a yellow oil; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 3467, 2968, 1613, 1503, 1276, 1146, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.05 (d, 1H, J=8.7 Hz, Ar*H*), 6.34–6.26 (m, 2H, Ar*H*), 5.61 (s, 1H, 3-*H*), 4.86 (s, 1H, C*H*OH), 3.67 (s, 3H, OC*H*$_3$), 2.02–1.95 (m, 2H, C*H*$_2$CH$_3$), 1.69 (br s, 1H, CHO*H*), 1.36 (s, 6H, 2-C*H*$_3$), 0.89 (t, 3H, J=7.5 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.7, 154.8, 135.0, 132.1, 131.3, 124.9, 114.2, 106.7, 102.5, 76.0, 55.6, 28.2, 21.5, 12.4. MS (FAB): *m/z* (%): 248 (50, [M$^+$]), 233 (100, [M$^+$−CH$_3$]), 231 (25, [M$^+$−OH]). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.62; H, 8.19.

3.2.19. 1-(7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-butan-1-ol ***1s***

Yield=64% as a yellow oil; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 3487, 2965, 1613, 1503, 1272, 1199, 1159, 1127, 758 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.17 (d, 1H, *J*=9.2 Hz, Ar*H*), 6.45–6.40 (m, 2H, Ar*H*), 5.54 (s, 1H, 3-*H*), 4.61–4.55 (m, 1H, C*H*OH), 3.75 (s, 3H, OCH_3), 1.96 (br s, 1H, CHO*H*), 1.71–1.63 (m, 2H, $CH_2CH_2CH_3$), 1.53–1.44 (m, 2H, $CH_2CH_2CH_3$), 1.39 (d, 6H, *J*=4.8 Hz, 2-CH_3), 0.93 (t, 3H, *J*=7.2 Hz, $CH_2CH_2CH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.8, 155.0, 134.9, 124.4, 123.7, 114.1, 106.9, 102.8, 76.4, 71.0, 55.5, 38.8, 28.2, 28.0, 19.4, 14.0. MS (FAB): *m*/*z* (%): 262 (60, [M^+]), 247 (100, [M^+-CH_3]), 245 (30, [M^+-OH]). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.13; H, 8.41.

3.2.20. 1-(7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)-but-2-en-1-ol ***1t***

Yield=65% as a yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3455, 2974, 1613, 1503, 1276, 1199, 1147, 758 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.19 (d, 2H, *J*=9.2 Hz, Ar*H*), 6.44–6.39 (m, 2H, Ar*H*), 5.80–5.60 (m, 2H, $CH{=}CHCH_3$), 5.59 (s, 1H, 3-*H*), 5.01 (d, 1H, *J*=6.0 Hz, C*H*OH), 3.76 (s, 3H, OCH_3), 1.71 (d, 3H, *J*=6.0 Hz, $CH{=}CHCH_3$), 1.41 (s, 6H, 2-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.9, 155.0, 133.6, 132.2, 129.1, 125.0, 124.4, 114.0, 106.9, 102.7, 76.5, 71.7, 55.6, 28.2, 18.1. MS (FAB): *m*/*z* (%): 260 (30, [M^+]), 245 (100, [M^+-CH_3]), 243 (30, [M^+-OH]). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.78; H, 7.67.

3.2.21. (4-Chloro-phenyl)-(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)methanol ***1u***

Yield=60% as yellow oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3406, 2924, 1593, 1216, 759 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.28 (m, 4H, Ar*H*), 6.89 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.38 (s, 1H, Ar*H*), 6.31–6.27 (m, 1H, Ar*H*), 5.62 (s, 1H, Ar*H*), 5.58 (s, 1H), 3.71 (s, 3H, OCH_3), 2.21 (br s, 1H, O*H*), 1.45 {s, 6H, $(CH_3)_2$}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.9, 155.0, 140.5, 134.1, 133.4, 129.2, 128.8, 126.1, 125.2, 113.5, 106.9, 102.8, 76.7, 72.9, 55.6, 28.2, 28.1. MS (FAB): *m*/*z* (%): 331 (30, [M^++H]). Anal. Calcd for $C_{19}H_{19}ClO_3$: C, 68.98; H, 5.79. Found: C, 68.91; H, 5.85.

3.2.22. (7-Methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-phenyl-methanol ***14a***

Yield=67% as a white solid; mp 135 °C (dichloromethane); R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 3471, 2985, 2362, 1606, 1503, 1361, 1198, 1029, 704 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45–7.25 (m, 5H, ArH), 6.97 (d, 1H, *J*=8.6 Hz, ArH), 6.40 (d, 1H, *J*=2.6 Hz, ArH), 6.24 (dd, 1H, J_1=8.6 Hz, J_2=2.6 Hz, ArH), 6.06 (s, 1H, C*H*OH), 3.69 (s, 3H, OCH_3), 2.27 (br s, 1H, CHO*H*), 1.87 (s, 3H, $=CCH_3$), 1.42 {s, 3H, $C(CH_3)_2$}, 1.40 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.0, 154.5, 142.7, 134.4, 128.8, 128.1, 127.3, 126.4, 125.7, 114.7, 106.8, 102.8, 79.1, 70.4, 55.5, 25.8, 25.2, 14.6. MS (FAB): *m*/*z* (%): 310 (70, [M^+]), 295 (100, [M^+-CH_3]), 293 (50, [M^+-OH]). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.47; H, 7.17.

3.2.23. (3-Methoxy-phenyl)-(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-methanol ***14b***

Yield=60% as a light yellow liquid; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 3465, 3013, 1610, 1503, 1263, 1217, 1159, 767 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.25–7.19 (m, 1H, ArH), 7.03–6.90 (m, 3H, ArH), 6.80–6.79 (m, 1H, ArH), 6.39 (d, 1H, *J*=2.5 Hz, ArH), 6.25 (dd, 1H, J_1=8.6 Hz, J_2=2.6 Hz, ArH), 6.01 (s, 1H, C*H*OH), 3.77 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 1.86 (s, 3H, $=CCH_3$), 1.48 {s, 3H, $C(CH_3)_2$}, 1.41 {s, 3H, $C(CH_3)_2$}. MS (FAB): *m*/*z* (%): 340 (90, [M^+]), 325 (100, [M^+-CH_3]), 323 (60, [M^+-OH]). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.03; H, 7.07.

3.2.24. (4-Fluoro-phenyl)-(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-methanol ***14c***

Yield=52% as pale yellow oil; R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 3453, 2961, 1613, 1503, 1160, 758 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.64 (d, 1H, *J*=8.2 Hz, ArH), 6.45–6.39 (m, 2H, Ar*H*), 4.93 (t, 1H, *J*=7.3 Hz, C*H*OH), 3.75 (s, 3H, OCH_3), 2.01 (br s, 1H, CHO*H*), 1.88–1.84 (m, 2H, $CHCH_2CH_2CH_3$), 1.81 (s, 3H, $=CCH_3$), 1.51–1.67 (m, 2H, $CHCH_2CH_2CH_3$), 1.41 {s, 3H, $C(CH_3)_2$}, 1.27 {s, 3H, $C(CH_3)_2$}, 0.90 (t, 3H, *J*=7.2 Hz, $CHCH_2CH_2CH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 159.8, 154.3, 132.6, 128.6, 126.3, 115.4, 106.7, 102.7, 78.7, 55.5, 28.2, 26.0, 25.0, 19.9, 14.4. MS (FAB): *m*/*z* (%): 276 (80, [M^+]), 261 (100, [M^+-CH_3]), 259 (20, [M^+-OH]). Anal. Calcd for $C_{20}H_{21}FO_3$: C, 73.15; H, 6.45. Found: C, 73.12; H, 6.48.

3.2.25. (4-Chloro-phenyl)-(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-methanol ***14e***

Yield=66% as a white solid; mp 130 °C (dichloromethane); R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 3465, 2978, 1611, 1576, 1501, 1157, 1085, 811 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.37–7.25 (m, 4H, Ar*H*), 6.94 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.39 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.25 (dd, 1H, J_1=8.6 Hz, J_2=2.5 Hz, Ar*H*), 6.00 (s, 1H, C*H*OH), 3.73 (s, 3H, OCH_3), 2.37 (br s, 1H, CHO*H*), 1.85 (s, 3H, $=CCH_3$), 1.46 {s, 3H, $C(CH_3)_2$}, 1.41 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.1, 154.5, 141.2, 134.7, 133.1, 128.9, 127.8, 127.2, 126.3, 114.4, 106.9, 102.9, 79.0, 69.9, 55.6, 25.7, 25.2, 14.6. MS (FAB): *m*/*z* (%): 344 (90, [M^+]), 331 (60, [M^+-CH_3]), 329 (100, [M^+-OH]). Anal. Calcd for $C_{20}H_{21}ClO_3$: C, 69.66; H, 6.14. Found: C, 69.57; H, 6.05.

3.2.26. (4-Methoxy-phenyl)-(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-methanol ***14f***

Yield=62% as a pale yellow viscous oil; R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 3474, 2931, 1599, 1507, 1166, 1020, 831 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33 (d, 2H, *J*=8.8 Hz, Ar*H*), 6.98 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.87 (d, 2H, *J*=8.8 Hz, Ar*H*), 6.40 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.26 (dd, 1H, J_1=8.6 Hz, J_2=2.5 Hz, Ar*H*), 6.01 (s, 1H, C*H*OH), 3.79 (s, 3H, OCH_3), 2.24 (br s, 1H, CHO*H*), 1.86 (s, 3H, $=CCH_3$), 1.48 {s, 3H, $C(CH_3)_2$}, 1.42 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.0, 159.0, 154.5, 134.7, 134.2, 128.0, 127.1, 126.5, 114.7, 114.2, 106.8, 102.8, 79.1, 70.2, 55.6, 25.8, 25.21, 14.6. MS (FAB): *m*/*z* (%): 340 (50, [M^+]), 323 (100, [M^+-OH]). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.22; H, 7.09.

3.2.27. (4-Dimethylamino-phenyl)-(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)-methanol ***14g***

Yield=59% as a white solid; mp 142 °C (dichloromethane); R_f=0.5 (15% ethyl acetate in hexane). IR (KBr): 3444, 2926, 1594, 1351, 1160, 765 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.27 (d, 1H, *J*=8.4 Hz, Ar*H*), 7.03 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.71 (d, 1H, *J*=8.8 Hz, Ar*H*), 6.40 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.27 (dd, 1H, J_1=8.6 Hz, J_2=2.5 Hz, Ar*H*), 5.98 (s, 1H, C*H*OH), 3.70 (s, 3H, OCH_3), 2.92 (s, 6H, N–$(CH_3)_2$), 1.84 (s, 3H, $=CCH_3$), 1.48 {s, 3H, $C(CH_3)_2$}, 1.40 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (50 MHz, $CDCl_3$): δ 159.9, 154.4, 150.1, 133.9, 130.4, 128.1, 126.9, 126.6, 115.1, 113.0, 106.8, 102.8, 79.1, 70.5, 55.6, 41.0, 30.1, 25.9, 25.1, 14.6. MS (FAB): *m*/*z* (%): 354 (100, [M^+]). Anal. Calcd for $C_{22}H_{27}NO_3$: C, 74.76; H, 7.70; N, 3.96. Found: C, 74.70; H, 7.68; N, 4.02.

3.2.28. (2H-Chromen-4-yl)-(3-methoxy-phenyl)-methanol ***18***

Yield=48% as yellow oil; R_f=0.5 (15% ethyl acetate in hexane). The compound was not stable and used as such for the next step.

3.2.29. (2-Isopropyl-2H-chromen-4-yl)-phenyl-methanol ***20a***

Yield=(58%) as a dark yellow viscous oil; R_f=0.5 (10% ethyl acetate in hexane). The compound was not stable and used as such for the next step.

3.2.30. (2-Isopropyl-2H-chromen-4-yl)-(3-methoxy-phenyl)-methanol ***20b***

Yield=55% as a dark yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (neat): 3438, 1604, 1488, 1217, 766 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.30–7.23 (m, 1H, Ar*H*), 7.09–7.01 (m, 4H, Ar*H*), 6.85–6.72 (m, 3H, Ar*H*), 5.91 (d, 1H, *J*=3.4 Hz, =C*H*), 5.66 (s, 1H, C*H*OH), 4.67–4.62 {m, 1H, C*H*CH(CH$_3$)$_2$}, 3.78 (s, 3H, OC*H*$_3$), 2.15 (br s, 1H, CHO*H*), 2.12–2.00 {m, 1H, C*H*(CH$_3$)$_2$}, 1.03 {d, 6H, CH(C*H*$_3$)$_2$}. MS (FAB): *m*/*z* (%): 309 (80, [M$^+$]), 293 (100, [M$^+$−OH]), 267 (100, [M$^+$−CH(CH$_3$)$_2$]). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.45; H, 7.11.

3.2.31. (4-Chloro-phenyl)-(2,2-dimethylchroman-4-yl)-methanol ***22***

Yield=67% as yellow oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3406, 2924, 1593, 1216, 759 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): *δ* 7.29–7.20 (m, 4H, Ar*H*), 6.99–6.93 (m, 1H, Ar*H*), 6.92–6.89 (m, 1H, Ar*H*), 6.73–6.64 (m, 2H, Ar*H*), 5.67 (s, 1H), 5.54 (s, 1H), 1.37 {s, 6H, (CH$_3$)$_2$}. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 151.9, 138.7, 132.5, 131.8, 127.9, 125.6, 127.2, 122.6, 119.3, 118.6, 115.6, 98.7, 74.5, 71.0, 26.5, 26.4. MS (ESI): *m*/*z* (%): 325 (100, [M$^+$+Na]), 285 (30, [M$^+$−OH]). Anal. Calcd for $C_{18}H_{19}ClO_2$: C, 71.40; H, 6.32. Found: C, 71.33; H, 6.23.

3.2.32. (4-Chloro-phenyl)-(7-methoxy-2,2-dimethyl-2H-thiochromen-4-yl)-methanol ***26a***

Yield=53% as brown viscous yellow oil; *R$_f$*=0.6 (15% ethyl acetate in hexane). IR (Neat): 3417, 2364, 1596, 1277, 1224, 1051, 770 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.28–7.18 (m, 5H, Ar*H*), 7.06 (d, 1H, *J*=8.7 Hz, Ar*H*), 6.75 (d, 1H, *J*=2.4 Hz, Ar*H*), 6.44 (dd, 1H, *J*$_1$=8.7 Hz, *J*$_2$=2.4 Hz, Ar*H*), 5.83 (s, 1H, =C*H*), 5.58 (s, 1H, C*H*OH), 3.67 (s, 3H, OC*H*$_3$), 2.20 (br s, 1H, CHO*H*), 1.37 {s, 6H, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): 157.5, 139.6, 135.3, 133.8, 132.4, 130.3, 127.6, 127.2, 125.6, 122.4, 111.77, 110.2, 73.2, 54.2, 39.6, 27.9. MS (FAB): *m*/*z* (%): 346 (40, [M$^+$]), 329 (100, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{19}ClO_2S$: C, 65.79; H, 5.52. Found: C, 65.66; H, 5.61.

3.2.33. (7-Methoxy-2,2-dimethyl-2H-thiochromen-4-yl)-phenyl-methanol ***26b***

Yield=48% as a yellow viscous yellow oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3441, 2366, 1500, 1351, 670 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.34–7.17 (m, 5H, Ar*H*), 7.08 (d, 1H, *J*=8.7 Hz, Ar*H*), 6.75 (d, 1H, *J*=2.4 Hz, Ar*H*), 6.44 (dd, 1H, *J*$_1$=8.7 Hz, *J*$_2$=2.4 Hz, Ar*H*), 5.87 (s, 1H, =C*H*), 5.61 (s, 1H, C*H*OH), 3.65 (s, 3H, OC*H*$_3$), 2.09 (br s, 1H, CHO*H*), 1.37 {s, 6H, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 158.9, 142.5, 136.9, 135.1, 131.3, 129.0, 128.2, 127.3, 127.0, 124.2, 113.1, 111.6, 75.1, 55.6, 41.0, 29.5. MS (FAB): *m*/*z* (%): 312 (50, [M$^+$]), 295 (100, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 73.09; H, 6.39.

3.2.34. (7-Methoxy-2,2-dimethyl-2H-thiochromen-4-yl)-(3-nitro-phenyl)-methanol ***26c***

Yield=53% as a brown oil; *R$_f$*=0.5 (25% ethyl acetate in hexane). IR (Neat): 3434, 2970, 1718, 1610, 1270, 1148, 1051, 771 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 8.22 (s, 1H, Ar*H*), 8.02 (d, 1H, *J*=2.5 Hz, Ar*H*), 7.58 (d, 1H, *J*=7.7 Hz, Ar*H*), 7.38 (t, 1H, *J*=7.9 Hz, Ar*H*), 7.07 (d, 1H, *J*=8.7 Hz, Ar*H*), 6.70 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.40 (dd, 1H, *J*$_1$=8.7 Hz, *J*$_2$=2.5 Hz, Ar*H*), 5.78 (s, 1H, =C*H*), 5.62 (s, 1H, C*H*OH), 3.66 (s, 3H, OC*H*$_3$), 2.52 (br s, 1H, CHO*H*), 1.38 {s, 6H, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 159.1, 148.8, 144.7, 136.5, 135.5, 133.1, 132.9, 129.8, 127.1, 123.3, 123.0, 122.1, 113.3, 111.8, 74.9, 55.6, 41.0, 29.3. MS (FAB): *m*/*z* (%): 357 (60, [M$^+$]), 342 (100, [M$^+$−CH$_3$]), 340 (50, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92. Found: C, 63.91; H, 5.43; N, 3.78.

3.2.35. (2,2-Dimethyl-2H-thiochromen-4-yl)-(3-nitro-phenyl)-methanol ***28a***

Yield=52% as brown oil; *R$_f$* 0.5 (20% ethyl acetate in hexane). IR (Neat): 3431, 2925, 2362, 1529, 1349, 768 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 8.25 (s, 1H, Ar*H*), 8.05 (d, 1H, *J*=8.1 Hz, Ar*H*), 7.59 (d, 1H, *J*=7.6 Hz, Ar*H*), 7.44–7.36 (m, 1H, Ar*H*), 7.18 (t, 2H, *J*=9.2 Hz, Ar*H*), 7.04–6.89 (m, 1H, Ar*H*), 5.94 (s, 1H, =C*H*), 5.69 (s, 1H, C*H*OH), 2.35 (br s, 1H, CHO*H*), 1.39 {s, 6H, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 149.2, 145.7, 137.2, 135.6, 134.7, 133.2, 131.1, 131.0, 129.2, 129.3, 126.3, 126.1, 123.8, 123.3, 96.5, 73.0, 40.5, 28.7. MS (FAB): *m*/*z* (%): 327 (40, [M$^+$]), 312 (100, [M$^+$−CH$_3$]), 310 (80, [M$^+$−OH]). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.03; H, 5.23; N, 4.28. Found: C, 65.91; H, 5.29; N, 4.34.

3.2.36. (2,2-Dimethyl-2H-thiochromen-4-yl)-(4-methoxy-phenyl)-methanol ***28b***

Yield=49% as brown viscous oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3379, 2923, 2361, 1612, 1352, 770 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.24 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.16–7.12 (m, 1H, Ar*H*), 7.02–6.90 (m, 3H, Ar*H*), 6.79 (d, 2H, *J*=8.6 Hz, Ar*H*), 6.06 (s, 1H, =C*H*), 5.60 (s, 1H, C*H*OH), 3.74 (s, 3H, OC*H*$_3$), 1.45, 1.43 {s, 6H, (C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 159.4, 137.5, 134.8, 133.5, 133.1, 131.2, 129.4, 128.8, 128.3, 127.7, 125.8, 125.4, 114.8, 114.4, 74.2, 55.6, 40.7, 30.1. MS (FAB): *m*/*z* (%): 312 (40, [M$^+$]), 306 (100, [M$^+$−CH$_3$]), 304 (20, [M$^+$−OH]). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 73.14; H, 6.51.

3.2.37. (4-Dimethylamino-phenyl)-(2,2-dimethyl-2H-thiochromen-4-yl)-methanol ***28c***

Yield=51% as a dark brown oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3405, 2922, 1611, 1520, 1354, 761 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.18–7.04 (m, 4H, Ar*H*), 6.90–6.83 (m, 2H, Ar*H*), 6.54 (d, 2H, *J*=8.6 Hz, Ar*H*), 6.04 (s, 1H, =C*H*), 5.48 (s, 1H, C*H*OH), 2.82 {s, 6H, −N(C*H*$_3$)$_2$}, 2.02 (br s, 1H, CHO*H*), 1.38 {d, 6H, *J*=4.6 Hz, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 159.3, 137.5, 134.8, 133.6, 129.4, 128.8, 128.3, 127.9, 127.7, 126.5, 125.8, 125.4, 114.3, 113.1, 74.2, 40.7, 38.2, 30.1. MS (FAB): *m*/*z* (%): 325 (50, [M$^+$]), 308 (100, [M$^+$−OH]). Anal. Calcd for $C_{20}H_{23}NOS$: C, 73.81; H, 7.12; N, 4.30. Found: C, 73.97; H, 7.17; N, 4.23.

3.2.38. (2,2-Dimethyl-2H-thiochromen-4-yl)-phenyl-methanol ***28d***

Yield=56% as a yellow oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3530, 2958, 1502, 1359, 1005, 688 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.42–7.24 (m, 7H, Ar*H*), 7.19–6.91 (m, 2H, Ar*H*), 6.09 (s, 1H, =C*H*), 5.82 (s, 1H, C*H*OH), 2.15 (br s, 1H, CHO*H*), 1.46 {d, 6H, *J*=8.6 Hz, C(C*H*$_3$)$_2$}. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 142.2, 136.9, 133.2, 133.1, 130.7, 128.5, 127.9, 127.7, 127.3, 126.9, 125.4, 125.0, 74.4, 40.2, 29.0, 28.9. MS (FAB): *m*/*z* (%): 282 (50, [M$^+$]), 265 (100, [M$^+$−OH]). Anal. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42. Found: C, 76.41; H, 6.49.

3.2.39. (4-Chloro-phenyl)-(2,2-dimethyl-2H-thiochromen-4-yl)-methanol ***28e***

Yield=68% as a colourless viscous oil; *R$_f$*=0.5 (15% ethyl acetate in hexane). IR (Neat): 3430, 1601, 1463, 1436, 1257, 1218, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.31–7.17 (m, 6H, ArH), 7.07–6.96 (m, 2H, ArH), 6.03 (s, 1H, =CH), 5.68 (d, 1H, *J*=2.8 Hz, CHOH), 2.27 (d, 1H, *J*=2.8 Hz, CHOH), 1.45 {s, 3H, C(CH$_3$)$_2$}, 1.43 {s, 3H, C(CH$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 140.9, 137.1, 134.1, 133.9, 133.6, 130.8, 129.1, 128.7, 128.4, 128.0, 125.7, 125.5, 40.6, 29.3. MS (FAB): *m*/*z* (%): 316 (100, [M$^+$]). Anal. Calcd for $C_{18}H_{17}ClOS$: C, 68.23; H, 5.41. Found: C, 68.31; H, 5.46.

3.2.40. 4-[(2,2-Dimethyl-2H-thiochromen-4-yl)-hydroxy-methyl]-benzonitrile ***28f***

Yield=64% as a pale yellow semi-solid; *R$_f$*=0.5 (20% ethyl acetate in hexane). IR (Neat): 3433, 2231, 1606, 1217, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): *δ* 7.61–7.48 (m, 4H, ArH), 7.30–7.21 (m, 2H, ArH), 7.11–6.96 (m, 2H, ArH), 5.98 (s, 1H, =CH), 5.73 (d, 1H, *J*=2.4 Hz, CHOH), 2.59 (br s, 1H, CHOH), 1.44 {s, 3H, C(CH$_3$)$_2$}, 1.43 {s, 3H, C(CH$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): *δ* 147.8, 136.8, 135.3, 133.8, 132.7, 130.4, 128.5, 128.2, 127.7, 125.8, 125.5, 119.1, 111.7, 75.0, 40.6, 29.2. MS (FAB): *m*/*z* (%): 307 (100, [M^+]). Anal. Calcd for $C_{19}H_{17}NOS$: C, 74.23; H, 5.57; N, 4.56. Found: C, 74.31; H, 5.53; N, 4.61.

3.2.41. *(2,4-Dichloro-phenyl)-(2,2-dimethyl-2H-thiochromen-4-yl)-methanol* ***28g***

Yield=63% as a pale yellow semi-solid; R_f=0.5 (20% ethyl acetate in hexane). IR (Neat): 3404, 1587, 1466, 1217, 759 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.32–6.96 (m, 7H, ArH), 6.07 (s, 1H, =CH), 5.84 (s, 1H, CHOH), 2.24 (br s, 1H, CHOH), 1.36 {s, 3H, $C(CH_3)_2$}, 1.31 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (50 MHz, $CDCl_3$): δ 138.4, 136.1, 134.7, 134.6, 133.6, 131.0, 129.8, 128.5, 128.0, 127.9, 125.8, 124.8, 69.8, 40.1, 29.2. MS (FAB): *m*/*z* (%): 350 (100, [M^+]). Anal. Calcd for $C_{18}H_{16}Cl_2OS$: C, 61.54; H, 4.59. Found: C, 61.48; H, 4.55.

3.2.42. *(2,2-Dimethyl-2H-thiochromen-4-yl)-p-tolyl-methanol* ***28h***

Yield=61% as a pale yellow viscous oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3399, 1594, 1437, 760 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.30–6.95 (m, 8H, ArH), 6.11 (s, 1H, =CH), 5.69 (d, 1H, *J*=3.4 Hz, CHOH), 2.31 (s, 3H, CH_3), 2.07 (d, 1H, *J*=3.4 Hz, CHOH), 1.47 {s, 3H, $C(CH_3)_2$}, 1.45 {s, 3H, $C(CH_3)_2$}. ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6, 138.0, 137.2, 133.5, 133.3, 131.2, 130.2, 129.7, 129.3, 128.3, 127.7, 127.4, 125.7, 125.4, 74.6, 40.6, 29.4, 21.5. MS (FAB): *m*/*z* (%): 295 (100, [M^+-H]). Anal. Calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80. Found: C, 76.91; H, 6.75.

3.2.43. *(2,3-Dihydro-benzo[b]thiepin-5-yl)-(4-fluoro-phenyl)-methanol* ***45***

Yield=59% as light yellow viscous oil; R_f=0.5 (15% ethyl acetate in hexane). IR (neat): 3399, 2926, 2362, 1604, 1508, 1222, 765 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.48–7.44 (m, 1H, Ar*H*), 7.36–7.28 (m, 2H, Ar*H*), 7.16–7.14 (m, 2H, Ar*H*), 7.08–7.04 (m, 1H, Ar*H*), 6.91–6.82 (m, 2H, Ar*H*), 6.35 (t, 1H, *J*=7.8 Hz, =C*H*), 5.52 (s, 1H, C*H*OH), 3.37–3.26 (m, 2H, SCH_2CH_2), 2.48 (br s, 1H, CHO*H*), 2.21–1.98 (m, 2H, SCH_2CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.0, 160.1, 144.3, 143.6, 138.1, 135.6, 134.4, 129.6, 129.3, 129.1, 128.6, 128.2, 128.0, 115.6, 115.2, 76.6, 43.6, 26.2. MS (FAB): *m*/*z* (%): 286 (100, [M^+]). Anal. Calcd for $C_{17}H_{15}FOS$: C, 71.30; H, 5.28. Found: C, 71.38; H, 5.23.

3.2.44. *(E)-(8-Methoxy-2,3-dihydrobenzo[b]thiepin-5-yl)-(3-methoxyphenyl)methanol* ***46***

Yield=64% as light yellow viscous oil; R_f=0.4 (15% ethyl acetate in hexane). IR (Neat): 3429, 2931, 2839, 1595, 1485, 1283, 1045, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 7.19–7.11 (m, 2H, Ar*H*), 7.03–6.99 (m, 2H, Ar*H*), 6.80–6.73 (m, 2H, Ar*H*), 6.40 (t, 1H, *J*=8.7 Hz, Ar*H*), 5.58 (s, 1H), 3.76 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.45–3.35 (m, 2H), 2.25–2.15 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): 160.0, 158.6, 144.2, 143.9, 135.7, 129.6, 129.2, 129.0, 128.7, 120.2, 119.9, 114.7, 113.9, 112.5, 55.7, 43.5, 26.4. MS (FAB): *m*/*z* (%): 329 (90, M+1), 311 (45, M−17). Anal. Calcd for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14. Found: C, 69.57; H, 6.17.

3.2.45. *(E)-(8-Methoxy-2,3-dihydrobenzo[b]thiepin-5-yl)-(phenyl)methanol* ***47***

Yield=62% as light yellow viscous oil; R_f=0.5 (15% ethyl acetate in hexane). IR (Neat): 3423, 2928, 2368, 1594, 1487, 1286, 1228, 1046, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.38–7.34 (m, 2H, Ar*H*), 7.25–7.03 (m, 5H, Ar*H*), 6.69 (dd, 1H, J_1=2.64 Hz, J_2=8.5 Hz, Ar*H*), 6.29 (t, 1H, *J*=7.7 Hz, Ar*H*), 5.51 (s, 1H), 3.66 (s, 3H, OCH_3), 3.35–3.26 (m, 2H), 2.18–1.95 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 159.6, 144.2, 143.9, 135.7, 129.6, 129.5, 128.8, 128.2, 127.7, 114.7, 113.9, 112.5, 75.7, 55.7, 43.5, 26.4. MS (FAB): *m*/*z* (%): 281 (100, M−17). Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.57; H, 6.01.

3.3. General procedure of the PBr_3 reaction on allylic alcohols

Compound (0.1 mmol) was taken in dry benzene (2 ml) and cooled at 0 °C. PBr_3 (1 equiv) was added to this stirred solution and the reaction was monitored by TLC. After consumption of the starting material the reaction mixture was poured into ice-water and extracted with ethyl acetate. The organic layer was dried on Na_2SO_4 and concentrated. The crude was chromatographed through silica gel column to furnish the product. In case of substrates containing basic nitrogen the reaction mixture was neutralized by using $NaHCO_3$ after pouring it to ice.

3.3.1. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-phenyl-methanone* ***2d***

Yield=73% as light yellow viscous oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 1683, 1618, 1504, 1208, 1127, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.96–7.91 (m, 2H, Ar*H*), 7.57–7.42 (m, 3H, Ar*H*), 6.79 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 6.43–6.37 (m, 2H, Ar*H*), 4.75–4.66 (m, 1H, 4-*H*), 3.75 (s, 3H, OCH_3), 2.16–2.10 (m, 2H, 3-*H*), 1.43 (s, 3H, 2-CH_3), 1.35 (s, 3H, 2-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.9, 160.3, 155.0, 137.0, 133.5, 129.9, 129.2, 129.1, 112.1, 108.0, 102.7, 74.5, 55.6, 42.4, 37.9, 29.8, 24.9. MS (FAB): *m*/*z* (%): 297 (15, [M^++H]), 191 (100, [$M^+-COC_6H_5$]). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.86; H, 6.81.

3.3.2. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-(2-methoxy-phenyl)-methanone* ***2e***

Yield=65% as light yellow semi solid; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 2974, 1679, 1616, 1163, 1128, 758 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.61–7.47 (m, 2H, Ar*H*), 7.06–6.89 (m, 3H, Ar*H*), 6.46–6.37 (m, 2H, Ar*H*), 4.77 (m, 1H, 4-*H*), 3.87 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.08–1.99 (m, 2H, 3-*H*), 1.37 (s, 3H, 2-CH_3), 1.29 (s, 3H, 2-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 205.5, 159.9, 158.3, 155.1, 133.7, 130.8, 130.4, 129.6, 121.4, 112.7, 112.0, 107.6, 102.4, 74.6, 55.9, 55.6, 45.6, 37.3, 29.3, 25.4. MS (FAB): *m*/*z* (%): 327 (40, [M^++H]), 191 (100, [$M^+-COC_6H_4OCH_3$]), 135 (30, [$M^+-C_{12}H_{15}O_2$]). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.56; H, 6.80.

3.3.3. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-(3-methoxy-phenyl)-methanone* ***2f***

Yield=78% as yellow viscous oil; R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 2974, 1683, 1616, 1584, 1504, 1262, 1164, 757 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44–7.39 (m, 2H, Ar*H*), 7.27 (t, 1H, *J*=7.6 Hz, Ar*H*), 7.02 (dd, 1H, J_1=8.3 Hz, J_2=2.5 Hz, Ar*H*), 6.70 (d, 1H, *J*=8.9 Hz, Ar*H*), 6.33–6.28 (m, 2H, Ar*H*), 4.64–4.55 (m, 1H, 4-*H*), 3.72 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 2.06–1.95 (m, 2H, 3-*H*), 1.33 (s, 3H, 2-CH_3), 1.25 (s, 3H, 2-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.6, 160.3, 155.0, 138.4, 130.1, 129.9, 121.7, 120.0, 113.6, 112.2, 108.0, 102.7, 74.5, 55.8, 55.6, 42.4, 37.9, 29.9, 24.9. MS (FAB): *m*/*z* (%): 327 (50, [M^++H]), 191 (100, [$M^+-COC_6H_4OCH_3$]), 135 (30, [$M^+-C_{12}H_{15}O_2$]). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.53; H, 6.75.

3.3.4. *(2,4-Dimethoxy-phenyl)-(7-methoxy-2,2-dimethyl-chroman-4-yl)-methanone* ***2g***

Yield=20% as yellow viscous oil; R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 2927, 1659, 1610, 1445, 1265, 1160, 780 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.76 (d, 1H, *J*=8.6 Hz, Ar*H*), 6.87 (d, 1H, *J*=8.3 Hz, Ar*H*), 6.59–6.37 (m, 4H, Ar*H*), 4.74–4.94 (m, 1H, 4-*H*), 3.87 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 2.07–1.99 (m, 2H, 3-*H*), 1.25 (s, 6H, 2-CH_3). MS (FAB): *m*/*z* (%): 357 (50, [M^++H]), 191 (50, [$M^+-COC_6H_3(OCH_3)_2$]), 165 (100, [$M^+-C_{12}H_{15}O_2$]). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.88; H, 6.73.

3.3.5. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-thiophene-2-yl-methanone* ***2i***

Yield=58% as yellow oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 2977, 1658, 1506, 1204, 1165, 1127, 752 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.65–7.57 (m, 2H, Ar*H*), 7.12–7.07 (t, 1H, *J*=4.2 Hz, Ar*H*), 6.84 (d, 1H, *J*=9.2 Hz, Ar*H*), 6.42–6.39 (m, 2H, Ar*H*), 4.53–4.44 (m, 1H, 4-*H*), 3.75 (s, 3H, OC*H*$_3$), 2.22–2.06 (m, 2H, 3-*H*), 1.46 (s, 3H, 2-C*H*$_3$), 1.33 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 194.8, 160.5, 155.0, 143.7, 134.5, 133.2, 130.1, 128.6, 111.8, 108.1, 102.7, 74.5, 55.6, 44.4, 38.3, 29.9, 24.5. MS (FAB): *m*/*z* (%): 303 (60, [M$^+$+H]), 191 (100, [M$^+$−CO–C$_4$H$_3$S]). Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 66.48; H, 5.97.

3.3.6. *Furan-2-yl-(7-methoxy-2,2-dimethyl-chroman-4-yl)-methanone* ***2j***

Yield=67% as yellow viscous oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 1672, 1619, 1505, 1464, 1163, 1128, 769 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.60 (d, 1H, *J*=1.6 Hz, Ar*H*), 7.11 (d, 1H, *J*=4.1 Hz, Ar*H*), 6.78 (d, 1H, *J*=9.1 Hz, Ar*H*), 6.54–6.51 (m, 1H, Ar*H*), 6.43–6.38 (m, 2H, Ar*H*), 4.55–4.46 (m, 1H, 4-*H*), 3.74 (s, 3H, OC*H*$_3$), 2.22–2.00 (m, 2H, 3-*H*), 1.44 (s, 3H, 2-C*H*$_3$), 1.32 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 190.7, 160.3, 155.1, 152.6, 147.0, 129.9, 118.9, 112.8, 111.6, 108.0, 102.6, 74.5, 55.6, 42.8, 37.5, 29.8, 24.5. MS (FAB): *m*/*z* (%): 287 (20, [M$^+$+H]), 191 (100, [M$^+$−CO−C$_4$H$_3$O]). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.38; H, 6.33.

3.3.7. *(2-Chloro-phenyl)-(7-methoxy-2,2-dimethyl-chroman-4-yl)-methanone* ***2m***

Yield=60% as light yellow semi solid; R_f=0.5 (12% ethyl acetate in hexane). IR (Neat): 2976, 1678, 1609, 1440, 1268, 1159, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.41–7.19 (m, 4H, Ar*H*), 6.95 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.44–6.31 (m, 2H, Ar*H*), 4.55–4.50 (m, 1H, 4-*H*), 3.69 (s, 3H, OC*H*$_3$), 1.98–1.84 (m, 2H, 3-*H*), 1.32 (s, 3H, 2-C*H*$_3$), 1.20 (s, 3H, 2-C*H*$_3$). MS (FAB): *m*/*z* (%): 332 (40, [M$^+$+H]), 281 (100, [M$^+$−CH$_3$, −Cl]). Anal. Calcd for $C_{19}H_{19}ClO_3$: C, 68.98; H, 5.79. Found: C, 68.89; H, 5.88.

3.3.8. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-(3-nitro-phenyl)-methanone* ***2n***

Yield=82% as light yellow solid; mp 70 °C (dichloromethane); R_f=0.5 (20% ethyl acetate in hexane). IR (KBr): 1689, 1615, 1532, 1350, 1210, 1129, 770 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.66 (d, 1H, *J*=7.8 Hz, Ar*H*), 8.32 (dd, 1H, J_1=8.2 Hz, J_2=2.2 Hz, Ar*H*), 8.08 (d, 1H, *J*=7.8 Hz, Ar*H*), 7.56 (t, 1H, *J*=7.9 Hz, Ar*H*), 6.67 (d, 1H, *J*=8.3 Hz, Ar*H*), 6.37–6.29 (m, 2H, Ar*H*), 4.64–4.55 (m, 1H, 4-*H*), 3.67 (s, 3H, OC*H*$_3$), 2.06–2.00 (m, 2H, 3-*H*), 1.36 (s, 3H, 2-C*H*$_3$), 1.28 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 199.7, 160.6, 154.9, 148.9, 137.9, 134.8, 130.4, 129.8, 127.7, 124.1, 111.0, 108.3, 102.9, 74.5, 55.6, 43.3, 37.6, 29.7, 24.8. MS (FAB): *m*/*z* (%): 342 (50, [M$^+$+H]), 191 (100, [M$^+$−COC$_6$H$_4$NO$_2$]). Anal. Calcd for $C_{19}H_{19}NO_5$: C, 66.85; H, 5.61; N, 4.10. Found: C, 66.91; H, 5.52; N, 4.17.

3.3.9. *4-(7-Methoxy-2,2-dimethyl-chroman-4-carbonyl)-benzonitrile* ***2o***

Yield=74% as light brown semi solid; R_f=0.6 (20% ethyl acetate in hexane). IR (Neat): 2973, 1680, 1612, 1507, 1200, 1117, 980 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.95 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.74 (d, 2H, *J*=8.5 Hz, Ar*H*), 6.75 (d, 1H, *J*=8.1 Hz, Ar*H*), 6.45–6.38 (m, 2H, Ar*H*), 4.60–4.59 (m, 1H, 4-*H*), 3.76 (s, 3H, OC*H*$_3$), 2.12–2.05 (m, 2H, 3-*H*), 1.44 (s, 3H, 2-C*H*$_3$), 1.34 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 200.5, 160.6, 154.8, 139.6, 132.9, 129.7, 118.2, 116.7, 111.0, 108.3, 103.0, 74.5, 55.6, 43.7, 37.6, 29.7, 24.7. MS (FAB): *m*/*z* (%): 322 (20, [M$^+$+H]), 191 (100, [M$^+$−CO−C$_6$H$_4$CN]). Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.82; H, 6.04; N, 4.39.

3.3.10. *(4-Isopropyl-phenyl)-(7-methoxy-2,2-dimethyl-chroman-4-yl)-methanone* ***2p***

Yield=69% as yellow viscous oil; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 2966, 1679, 1618, 1504, 1163, 1128, 769 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.89 (d, 2H, *J*=8.3 Hz, Ar*H*), 7.31 (d, 2H, *J*=8.3 Hz, Ar*H*), 6.79 (d, 1H, *J*=7.9 Hz, Ar*H*), 6.42–6.37 (m, 2H, Ar*H*), 4.70–4.64 (m, 1H, 4-*H*), 3.74 (s, 3H, OC*H*$_3$), 3.00–2.93 (m, 1H, C*H*(CH$_3$)$_2$), 2.16–1.97 (m, 2H, 3-*H*), 1.43 (s, 3H, 2-C*H*$_3$), 1.34 (s, 3H, 2-C*H*$_3$), 1.27 {d, 6H, *J*=6.9 Hz, CH(C*H*$_3$)$_2$}. MS (FAB): *m*/*z* (%): 339 (50, [M$^+$+H]), 191 (100, [M$^+$−CO–C$_6$H$_4$–CH–(CH$_3$)$_2$]). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 77.83; H, 7.73.

3.3.11. *(7-Methoxy-2,2-dimethyl-chroman-4-yl)-naphthalen-2-yl-methanone* ***2q***

Yield=75% as white crystalline solid; mp 142 °C (dichloromethane); R_f=0.5 (10% ethyl acetate in hexane). IR (KBr): 2968, 1674, 1593, 1351, 1159, 776 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.42–8.37 (m, 1H, Ar*H*), 8.00 (d, 1H, *J*=8 Hz, Ar*H*), 7.92–7.80 (m, 2H, Ar*H*), 7.59–7.46 (m, 3H, Ar*H*), 6.98 (d, 1H, *J*=8.2 Hz, Ar*H*), 6.49–6.43 (m, 2H, Ar*H*), 4.78–4.69 (m, 1H, 4-*H*), 3.76 (s, 3H, OC*H*$_3$), 2.13–2.03 (m, 2H, 3-*H*), 1.39 (s, 3H, 2-C*H*$_3$), 1.30 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 205.4, 160.3, 155.2, 136.9, 134.4, 132.9, 130.9, 130.3, 128.8, 128.4, 127.2, 127.0, 126.0, 124.8, 111.7, 108.0, 102.7, 74.5, 55.6, 45.3, 37.6, 29.6, 25.1. MS (FAB): *m*/*z* (%): 347 (90, [M$^+$+H]), 191 (100, [M$^+$−COC$_{10}$H$_7$]). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.81; H, 6.42.

3.3.12. *1-(7-Methoxy-2,2-dimethyl-chroman-4-yl)-propan-1-one* ***2r***

Yield=61% as yellow viscous oil; R_f=0.4 (10% ethyl acetate in hexane). IR (Neat): 2975, 1678, 1611, 1442, 1268, 1167, 1128, 761 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.81–6.75 (m, 1H, Ar*H*), 6.48–6.36 (m, 2H, Ar*H*), 3.79–3.75 (m, 1H, 4-*H*), 3.74 (s, 3H, OC*H*$_3$), 2.41–2.33 (m, 2H, COC*H*$_2$CH$_3$), 1.97–1.85 (m, 2H, 3-*H*), 1.42 (s, 3H, 2-C*H*$_3$), 1.27 (s, 3H, 2-C*H*$_3$), 0.87 (t, 3H, *J*=7.3 Hz, COCH$_2$C*H*$_3$). MS (FAB): *m*/*z* (%): 249 (50, [M$^+$+H]), 191 (100, [M$^+$−COCH$_2$CH$_3$]). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.58; H, 8.04.

3.3.13. *1-(7-Methoxy-2,2-dimethyl-chroman-4-yl)-butan-1-one* ***2s***

Yield=63% as yellow viscous oil; R_f=0.5 (12% ethyl acetate in hexane). IR (Neat): 2971, 1705, 1618, 1504, 1163, 1128, 758 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.79 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.48–6.38 (m, 2H, Ar*H*), 3.83–3.87 (m, 1H, 4-*H*), 3.75 (s, 3H, OC*H*$_3$), 2.37 (t, 2H, *J*=7.1 Hz, COC*H*$_2$CH$_2$CH$_3$), 1.95 (d, 2H, *J*=8.9 Hz, 3-*H*), 1.65–1.54 (m, 2H, COCH$_2$C*H*$_2$CH$_3$), 1.42 (s, 3H, 2-C*H*$_3$), 1.24 (s, 3H, 2-C*H*$_3$), 0.87 (t, 3H, *J*=7.3 Hz, COCH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 212.2, 160.4, 155.0, 129.7, 110.8, 108.0, 102.7, 74.3, 55.5, 47.8, 41.5, 36.6, 29.8, 24.5, 17.7, 14.1. MS (FAB): *m*/*z* (%): 263 (40, [M$^+$+H]), 191 (100, [M$^+$−COCH$_2$CH$_2$CH$_3$]). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.37; H, 8.53.

3.3.14. *1-(7-Methoxy-2,2-dimethyl-chroman-4-yl)-but-2-en-1-one* ***2t***

Yield=69% as yellow viscous oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 2978, 1686, 1618, 1505, 1200, 1163, 765 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.97–6.86 (m, 1H, CH=C*H*CH$_3$), 6.72 (d, 2H, *J*=8.3 Hz, C*H*=CHCH$_3$), 6.39–6.31 (m, 2H, Ar*H*), 6.09–6.00 (m, 1H, Ar*H*), 3.82–3.76 (m, 1H, 4-*H*), 3.69 (s, 3H, OC*H*$_3$), 1.90–1.74 (m, 5H, 3-*H*, CH=CHC*H*$_3$), 1.39 (s, 3H, 2-C*H*$_3$), 1.18 (s, 3H, 2-C*H*$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 200.6, 160.4, 155.0, 144.2, 130.1, 128.7, 110.9, 108.0, 102.7, 74.4, 55.5, 46.0, 36.8, 29.8, 24.5, 18.6. MS (FAB): *m*/*z* (%): 261 (40, [M$^+$+H]), 191 (100, [M$^+$−COCH=CHCH$_3$]). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.77; H, 7.73.

3.3.15. *(4-Chloro-phenyl)-(7-methoxy-2,2-dimethylchroman-4-yl)methanone* ***2u***

Yield=60% as colourless oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 3406, 2924, 1593, 1216, 759 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.85 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.41 (d, 2H, *J*=8.5 Hz, Ar*H*), 6.77–6.74 (m, 1H, Ar*H*), 6.43–6.38 (m, 2H, Ar*H*), 4.64–4.58 (m, 1H), 3.78 (s, 3H, OC*H*$_3$), 2.19–1.99 (m, 2H), 1.49 (s, 3H, CH$_3$), 1.39 (s, 3H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.0, 158.7, 153.2, 138.4, 133.4, 129.1, 128.1, 127.8, 110.1, 106.5, 101.2, 98.7, 72.9, 53.9, 41.3, 36.1, 28.4, 28.1, 23.1. MS (ESI): m/z (%): 332 (98, $[M^{+}+2]$), 331 (98, $[M^{+}+1]$). Anal. Calcd for $C_{19}H_{19}ClO_3$: C, 68.98; H, 5.79. Found: C, 69.12; H, 5.76.

3.3.16. (4-Fluoro-phenyl)-(7-methoxy-2,2-dimethyl-chroman-4-yl)-methanone ***3***

Yield=77% white crystalline solid; mp 81 °C (dichloromethane); R_f=0.5 (12% ethyl acetate in hexane). IR (KBr): 2975, 1683, 1617, 1596, 1504, 1161, 845 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.90–7.83 (m, 2H, ArH), 7.06–6.99 (m, 2H, ArH), 6.68 (d, 1H, J=8.7 Hz, ArH), 6.34–6.29 (m, 2H, ArH), 4.56–4.51 (m, 1H, 4-H), 3.66 (s, 3H, OCH$_3$), 2.06–1.96 (m, 2H, 3-H), 1.35 (s, 3H, 2-CH$_3$), 1.26 (s, 3H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 200.1, 160.2, 155.1, 133.1, 132.1, 129.8, 116.4, 116.0, 111.7, 108.1, 102.8, 74.8, 55.6, 42.7, 37.9, 29.8, 24.8. MS (FAB): m/z (%): 315 (70, $[M^{+}+H]$), 191 (100, $[M^{+}-OC_7H_4F)$. Anal. Calcd for $C_{19}H_{19}FO_3$: C, 72.60; H, 6.09. Found: C, 72.67; H, 6.07.

3.3.17. (7-Methoxy-2,2-dimethyl-chroman-4-yl)-(4-methoxy-phenyl)-methanone ***4***

Yield=67% as white solid; mp 105 °C (dichloromethane); R_f=0.6 (15% ethyl acetate in hexane). IR (KBr): 2774, 1674, 1600, 1506, 1261, 1168, 1127 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.86 (d, 2H, J=8.8 Hz, ArH), 6.85 (d, 2H, J=8.8 Hz, ArH), 6.70 (d, 1H, J=8.0 Hz, ArH), 6.33–6.28 (m, 2H, ArH), 4.62–4.52 (m, 1H, 4-H), 3.78 (s, 3H, OCH$_3$), 3.66 (s, 3H, OCH$_3$), 2.09–1.91 (m, 2H, 3-H), 1.35 (s, 3H, 2-CH$_3$), 1.26 (s, 3H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 200.2, 163.9, 160.2, 155.0, 131.6, 130.0, 114.3, 112.6, 107.9, 102.7, 74.6, 55.8, 55.6, 42.1, 38.0, 29.9, 24.9. MS (FAB): m/z (%): 327 (90, $[M^{+}+H]$), 191 (100, $[M^{+}-COC_6H_4OCH_3]$), 135 (100, $[M^{+}-C_{12}H_{15}O_2]$). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.53; H, 6.77.

3.3.18. 7-Methoxy-4-(4-methoxy-benzylidine)-2,2-dimethyl-chroman ***5***

Yield=15% as white crystalline solid; mp 97 °C (dichloromethane); R_f=0.4 (10% ethyl acetate in hexane). IR (KBr): 2972, 1612, 1509, 1248, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.52 (d, 1H, J=8.7 Hz, ArH), 7.22 (d, 2H, J=8.4 Hz, ArH), 6.97 (s, 1H, =CH–Ar), 6.89 (d, 2H, J=8.4 Hz, ArH), 6.51 (d, 1H, J=8.7 Hz, ArH), 6.37 (s, 1H, ArH), 3.82 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 2.69 (s, 2H, 3-H), 1.27 (s, 6H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.0, 158.5, 154.7, 130.9, 129.2, 125.3, 120.9, 115.4, 114.0, 108.4, 101.9, 75.5, 55.6, 37.6, 27.0. MS (FAB): m/z (%): 310 (100, $[M^{+}]$), 295 (80, $[M^{+}-CH_3]$). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.46; H, 7.18.

3.3.19. 1-Benzyl-3-(7-methoxy-2,2-dimethyl-chroman-4-ylidenemethyl)-1H-Indole ***6***

Yield=32% as light yellow viscous oil; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 2971, 2929, 1611, 1164, 754 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.68 (d, 1H, J=7.9 Hz, ArH), 7.57 (d, 1H, J=8.8 Hz, ArH), 7.23–7.03 (m, 10H, ArH, =CH), 6.47 (dd, 1H, J_1=8.6 Hz, J_2=2.5 Hz, ArH), 6.32 (d, 1H, J=2.5 Hz, ArH), 5.28 (s, 2H, CH$_2$C$_6$H$_5$), 3.71 (s, 3H, OCH$_3$), 2.67 (s, 2H, 3-H), 1.22 (s, 6H, 2-CH$_3$). MS (FAB): m/z (%): 410 (100, $[M^{+}+H]$), 409 (70, $[M^{+}]$), 394 (40, $[M^{+}-CH_3]$). Anal. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.23; H, 6.58; N, 3.48.

3.3.20. 7-Methoxy-4-(2-methoxy-benzylidine)-2,2-dimethyl-chroman ***7***

Yield=19% as yellow viscous oil; R_f=0.6 (15% ethyl acetate in hexane). IR (Neat): 2974, 1616, 1507, 1246, 758 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.57 (d, 1H, J=8.7 Hz, ArH), 7.26–7.17 (m, 2H, ArH), 7.11 (s, 1H, =CH–Ar), 7.02–7.63 (m, 2H, ArH), 6.52 (dd, 1H, J_1=8.7 Hz, J_2=2.5 Hz, ArH), 6.38 (d, 1H, J=2.5 Hz, ArH), 3.82 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 2.65 (s, 2H, 3-H), 1.28 (s, 6H, 2-CH$_3$). MS (FAB): m/z (%): 310 (100, $[M^{+}]$), 295 (60, $[M^{+}-CH_3]$). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.27; H, 7.19.

3.3.21. 4-(2,4-Dimethoxy-benzylidine)-7-methoxy-2,2-dimethyl-chroman ***8***

Yield=56% as white solid; mp 150 °C (dichloromethane); R_f=0.4 (15% ethyl acetate in hexane). IR (KBr): 2928, 1612, 1505, 1462, 1288, 1209, 1159, 1041, 760 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.49 (d, 1H, J=8.7 Hz, ArH), 7.04–6.99 (m, 2H, ArH), 6.94 (s, 1H, =CH–Ar), 6.41 (m, 3H, ArH), 6.30 (m, 1H, ArH), 3.75 (s, 3H, OCH$_3$), 3.74 (s, 3H, OCH$_3$), 3.70 (s, 3H, OCH$_3$), 2.56 (s, 2H, 3-H), 1.20 (s, 6H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 160.2, 159.2, 154.6, 131.2, 128.9 125.6, 119.8, 116.9, 108.3, 104.2, 101.8, 98.9, 75.7, 55.9, 55.7, 38.0, 28.5, 27.1. MS (FAB): m/z (%): 340 (100, $[M^{+}]$), 325 (60, $[M^{+}-CH_3]$). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.00; H, 7.12.

3.3.22. 7-Methoxy-2,2-dimethyl-4-(2,4,6-trimethoxy-benzylidene)-chroman ***9***

Yield=65% as white solid; mp 150 °C (dichloromethane); R_f=0.6 (20% ethyl acetate in hexane). IR (KBr): 2930, 1608, 1206, 1127, 761 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.59 (d, 1H, J=8.7 Hz, ArH), 6.65 (s, 1H, =CH), 6.56 (dd, 1H, J_1=8.5 Hz, J_2=2.6 Hz, ArH), 6.36 (d, 1H, J=2.6 Hz, ArH), 6.17 (s, 2H, ArH), 3.84 (s, 3H, OCH$_3$), 3.77 (s, 9H, OCH$_3$), 2.29 (s, 2H, 3-H), 1.29 (s, 6H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 159.2, 154.5, 131.2, 125.8, 115.9, 112.8, 108.6, 108.0, 101.8, 91.1, 76.0, 56.1, 55.7, 39.0, 27.1. MS (FAB): m/z (%): 370 (80, $[M^{+}]$), 355 (100, $[M^{+}-CH_3]$). Anal. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07. Found: C, 71.47; H, 6.99.

3.3.23. 7-Methoxy-2,2-dimethyl-4-thiophen-2-yl-methylene-chroman ***10***

Yield=18% as a white solid; mp 105 °C (dichloromethane); R_f=0.5 (10% ethyl acetate in hexane). IR (KBr): 2962, 1598, 1381, 1162, 1351, 1162, 707 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.53 (d, 1H, J=8.8 Hz, ArH), 7.28–7.24 (m, 1H, ArH), 7.12 (s, 1H, =CH–), 7.07–7.03 (m, 2H, ArH), 6.52 (dd, 1H, J_1=8.8 Hz, J_2=2.6 Hz, ArH), 6.39 (d, 1H, J=2.5 Hz, ArH), 3.79 (s, 3H, OCH$_3$), 2.86 (s, 2H, 3-H), 1.35 (s, 6H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 161.3, 155.0, 141.2, 129.4, 127.7, 127.5, 125.1, 125.0, 114.1, 108.6, 102.2, 71.2, 55.7, 38.2, 27.2. MS (FAB): m/z (%): 286 (100, $[M^{+}]$). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.41; H, 6.32.

3.3.24. 7-Methoxy-2,2-dimethyl-4-(3-phenyl-allylidene)-chroman ***11***

Yield=25% as yellow viscous oil; R_f=0.6 (10% ethyl acetate in hexane). IR (Neat): 2928, 1610, 1498, 1270, 1161, 757 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.46–7.13 (m, 7H, ArH, AlkeneH), 6.72–6.59 (m, 2H, ArH, AlkeneH), 6.24 (dd, 1H, J_1=8.6 Hz, J_2=2.5 Hz, ArH), 6.29 (d, 1H, J=2.5 Hz, ArH), 3.71 (s, 3H, OCH$_3$), 2.61 (s, 2H, 3-H), 1.28 (s, 6H, 2-CH$_3$). MS (FAB): m/z (%): 306 (90, $[M^{+}]$), 291 (20, $[M^{+}-CH_3]$). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.44; H, 7.18.

3.3.25. [4-(7-Methoxy-2,2-dimethyl-chroman-4-ylidenemethyl)-phenyl]-dimethyl-amine ***12***

Yield=67% as light yellow solid; mp 120 °C (dichloromethane); R_f=0.5 (10% ethyl acetate in hexane). IR (KBr): 2971, 2926, 1610, 1520, 1351, 816 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.52 (d, 1H, J=8.8 Hz, ArH), 7.20 (d, 2H, J=8.5 Hz, ArH), 6.96 (s, 1H, =CH–Ar), 6.72 (d, 2H, J=8.5 Hz, ArH), 6.50 (dd, 1H, J_1=8.1 Hz, J_2=2.6 Hz, ArH), 6.37 (d, 1H, J=2.6 Hz, ArH), 3.77 (s, 3H, OCH$_3$), 2.97 {s, 6H, N(CH$_3$)$_2$}, 2.73 (s, 2H, 3-H), 1.27 (s, 6H, 2-CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 160.8, 154.6, 149.0, 130.8, 127.9, 125.2, 121.4, 115.8, 112.9, 108.3, 102.0, 75.6, 55.6, 41.1, 37.7, 27.1. MS (FAB): m/z (%): 323 (100, $[M^{+}]$), 308 (30, $[M^{+}-CH_3]$). Anal. Calcd for $C_{21}H_{25}NO_2$: C, 77.98; H, 7.79; N, 4.33. Found: C, 77.90; H, 7.77; N, 4.27.

3.3.26. (7-Methoxy-2,2,3-trimethyl-chroman-4-yl)-phenyl-methanone ***15a***

Yield=84% as white solid; mp 105 °C (dichloromethane); R_f=0.6 (10% ethyl acetate in hexane). IR (Neat): 2957, 1673, 1617, 1160, 1125, 702 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.81 (d, 2H, *J*=7.4 Hz, Ar*H*), 7.54–7.38 (m, 3H, Ar*H*), 6.72 (d, 1H, *J*=8.4 Hz, Ar*H*), 6.44 (d, 1H, *J*=1.9 Hz, Ar*H*), 6.36 (d, 1H, *J*=8.4 Hz, Ar*H*), 4.19 (d, 1H, *J*=11.3 Hz, ArC*H*), 3.74 (s, 3H, OCH_3), 2.51–2.42 (m, 1H, C*H*CH_3), 1.45 {s, 3H, $C(CH_3)_2$}, 1.21 {s, 3H, $C(CH_3)_2$}, 0.92 (d, 3H, *J*=6.7 Hz, $CHCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 202.67, 160.3, 154.3, 137.6, 133.4, 129.5, 129.1, 113.6, 108.0, 102.7, 78.3, 55.6, 50.9, 40.2, 28.1, 19.6, 15.7. MS (FAB): *m/z* (%): 311 (70, [M$^+$+H]), 310 (40, [M$^+$]), 205 (100, [M$^+$−COC_6H_5]). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.47; H, 7.10.

3.3.27. *(3-Methoxy-phenyl)-(7-methoxy-2,2,3-trimethyl-chroman-4-yl)-methanone* ***15b***

Yield=79% as colourless oil; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 2973, 2935, 1677, 1615, 1548, 1261, 1165, 1037, 761 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.45–7.33 (m, 3H, Ar*H*), 7.12 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.35 (d, 1H, *J*=8.7 Hz, Ar*H*), 6.43 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.35 (dd, 1H, J_1=8.4 Hz, J_2=2.5 Hz, Ar*H*), 4.18 (d, 1H, *J*=11.3 Hz, ArC*H*), 3.81 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.32–2.61 (m, 1H, C*H*CH_3), 1.45 {s, 3H, $C(CH_3)_2$}, 1.25 {s, 3H, $C(CH_3)_2$}, 0.93 (d, 3H, *J*=6.8 Hz, $CHCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 202.5, 160.3, 160.2, 154.4, 139.0, 130.0, 129.1, 122.2, 120.1, 113.6, 108.0, 102.7, 78.4, 55.7, 55.6, 50.8, 40.2, 28.1, 19.6, 15.7. MS (FAB): *m/z* (%): 341 (50, [M$^+$+H]), 205 (100, [M$^+$−$COC_6H_4OCH_3$]). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.00; H, 7.09.

3.3.28. *(4-Fluoro-phenyl)-(7-methoxy-2,2,3-trimethyl-chroman-4-yl)-methanone* ***15c***

Yield=83% as light yellow solid; mp 120 °C (dichloromethane); R_f=0.6 (10% ethyl acetate in hexane). IR (Neat): 2960, 1674, 1618, 1594, 1507, 1161, 1126, 779 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.91–7.84 (m, 2H, Ar*H*), 7.12–7.03 (t, 2H, Ar*H*), 6.69 (d, 1H, *J*=8.7 Hz, ArH), 6.43 (d, 1H, *J*=2.5 Hz, Ar*H*), 6.35 (dd, 1H, J_1=8.4 Hz, J_2=2.5 Hz, Ar*H*), 4.12 (d, 1H, *J*=11.2 Hz, ArC*H*), 3.74 (s, 3H, OCH_3), 2.48–2.39 (m, 1H, C*H*CH_3), 1.45 {s, 3H, $C(CH_3)_2$}, 1.20 {s, 3H, $C(CH_3)_2$}, 0.92 (d, 3H, *J*=6.8 Hz, $CHCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 200.9, 168.5, 163.4, 160.4, 154.2, 133.6, 132.4, 132.2, 128.9, 116.3, 115.9, 113.3, 108.1, 102.8, 78.4, 55.6, 51.3, 40.2, 28.1, 19.5, 15.6. MS (FAB): *m/z* (%): 329 (50, [M$^+$+H]), 205 (100, [M$^+$−COC_6H_4F]). Anal. Calcd for $C_{20}H_{21}FO_3$: C, 73.15; H, 6.45. Found: C, 73.08; H, 6.42.

3.3.29. *1-(7-Methoxy-2,2,3-trimethyl-chroman-4-yl)-propan-1-one* ***15d***

Yield=75% as light yellow viscous oil; R_f=0.5 (7% ethyl acetate in hexane). IR (Neat): 2970, 1703, 1618, 1504, 1267, 1162, 1128, 759 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.63 (d, 1H, *J*=7.9 Hz, Ar*H*), 6.38–6.32 (m, 2H, Ar*H*), 3.67 (s, 3H, OCH_3), 3.26 (d, 1H, *J*=11.2 Hz, ArC*H*), 2.18 (t, 2H, *J*=7.27 Hz, $COCH_2CH_2CH_3$), 2.09–2.05 (m, 1H, C*H*CH_3), 1.55–1.43 (m, 2H, $COCH_2CH_2CH_3$), 1.36 {s, 3H, $C(CH_3)_2$}, 1.01 {s, 3H, $C(CH_3)_2$}, 0.92 (d, 3H, *J*=6.8 Hz, $CHCH_3$), 0.76 (t, 3H, *J*=7.3 Hz, $COCH_2CH_2CH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 212.3, 160.4, 154.6, 128.9, 111.8, 108.0, 102.7, 78.1, 56.0, 55.5, 40.6, 39.0, 28.2, 19.1, 17.7, 15.4, 14.1. MS (FAB): *m/z* (%): 277 (20, [M$^+$+H]), 205 (100, [M$^+$−$COCH_2CH_2CH_3$]). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.12; H, 8.38.

3.3.30. *(4-Chloro-phenyl)-(7-methoxy-2,2,3-trimethyl-chroman-4-yl)-methanone* ***15e***

Yield=87% as light yellow solid; mp 107 °C (dichloromethane); R_f=0.5 (8% ethyl acetate in hexane). IR (Neat): 2977, 2934, 1677, 1616, 1503, 1201, 1162, 1096, 763 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.77 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.37 (d, 2H, *J*=8.5 Hz, Ar*H*), 6.68 (d, 1H, *J*=8.5 Hz, ArH), 6.45 (d, 1H, *J*=2.4 Hz, Ar*H*), 6.35 (dd, 1H, J_1=8.5 Hz, J_2=2.5 Hz, Ar*H*), 4.09 (d, 1H, *J*=11.2 Hz, ArC*H*), 3.74 (s, 3H, OCH_3), 2.46–2.37 (m, 1H, C*H*CH_3), 1.44 {s, 3H, $C(CH_3)_2$}, 1.19 {s, 3H, $C(CH_3)_2$}, 0.92 (d, 3H, *J*=6.7 Hz, $CHCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.2, 160.4, 154.2, 139.8, 135.5, 131.0, 129.3, 128.9, 113.2, 108.1, 102.9, 78.4, 55.6, 51.5, 40.2, 28.1, 19.1, 15.5. MS (FAB): *m/z* (%): 345 (90, [M$^+$+H]), 205 (100, [M$^+$−COC_6H_4Cl]). Anal. Calcd for $C_{20}H_{21}ClO_3$: C, 69.66; H, 6.14. Found: C, 69.77; H, 6.13.

3.3.31. *7-Methoxy-4-(4-methoxy-benzylidene)-2,2,3-trimethyl-chroman* ***16***

Yield=71% as colourless liquid; R_f=0.6 (8% ethyl acetate in hexane). IR (Neat): 2928, 1609, 1509, 1457, 1248, 1157, 1036, 830 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 (d, 1H, *J*=8.7 Hz, Ar*H*), 7.17 (d, 2H, *J*=7.4 Hz, Ar*H*), 6.87–6.75 (m, 3H, Ar*H*, =C*H*–Ar), 6.45 (dd, 1H, J_1=8.7 Hz, J_2=2.5 Hz, Ar*H*), 6.31 (d, 1H, *J*=2.5 Hz, Ar*H*), 3.76 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 2.76–2.70 (m, 1H, C*H*CH_3), 1.44 {s, 3H, $C(CH_3)_2$}, 1.30 {s, 3H, $C(CH_3)_2$}, 1.03 (d, 3H, *J*=6.8 Hz, $CHCH_3$). MS (FAB): *m/z* (%): 329 (50, [M$^+$+H]), 205 (100, [M$^+$−COC_6H_4F]). Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.82; H, 7.56.

3.3.32. *[4-(7-Methoxy-2,2,3-trimethyl-chroman-4-ylidenemethyl)-phenyl]-dimethyl-amine* ***17***

Yield=73% as pale yellow viscous oil; R_f=0.7 (10% ethyl acetate in hexane). IR (Neat): 2920, 1595, 1433, 1348, 1158, 1115, 1056, 613 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 (d, 1H, *J*=8.7 Hz, Ar*H*), 7.17 (d, 1H, *J*=8.8 Hz, Ar*H*), 6.73–6.67 (m, 3H, Ar*H*, =C*H*–Ar), 6.44 (dd, 1H, J_1=8.7 Hz, J_2=2.5 Hz, Ar*H*), 6.30 (d, 1H, *J*=2.5 Hz, Ar*H*), 3.71 (s, 3H, OCH_3), 2.92 {s, 6H, $N(CH_3)_2$}, 2.82–2.78 (m, 1H, C*H*CH_3), 1.30 {s, 3H, $C(CH_3)_2$}, 1.18 {s, 3H, $C(CH_3)_2$}, 1.12 (d, 3H, *J*=6.8 Hz, $CHCH_3$). MS (FAB): *m/z* (%): 338 (100, [M$^+$+H]). Anal. Calcd for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.22; H, 8.09; N, 4.20.

3.3.33. *Chroman-4-yl-(3-methoxy-phenyl)-methanone* ***19***

Yield=55% as yellow oil; R_f=0.6 (10% ethyl acetate in hexane). IR (Neat): 2932, 1682, 1587, 1488, 1455, 1260, 1227, 1010 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.62–7.38 (m, 3H, Ar*H*), 7.18–7.12 (m, 2H, Ar*H*), 6.91–6.82 (m, 3H, Ar*H*), 4.81 (t, 1H, *J*=5.9 Hz, ArC*H*), 4.31–4.21 {m, 2H, OCH_2}, 3.85 (s, 3H, OCH_3), 2.30–2.27 (m, 2H, ArCHCH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 201.1, 160.2, 155.3, 145.6, 137.8, 130.0, 128.7, 121.5, 120.7, 120.1, 117.5, 113.3, 63.6, 55.7, 42.6, 26.3. MS (FAB): *m/z* (%): 269 (100, [M$^+$+H]), 135 (95, −$COC_6H_4OCH_3$). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: M$^+$C, 75.93; H, 6.03.

3.3.34. *(2-Isopropyl-chroman-4-yl)-phenyl-methanone* ***21a***

Yield=15% as yellow oil and mixture of diastereomers; R_f=0.5 (10% ethyl acetate in hexane). IR (Neat): 2964, 1667, 1630, 1589, 1363, 1220, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93–7.89 (m, 2H, ArH), 7.55–7.39 (m, 3H, Ar*H*), 7.08–7.06 (m, 1H, Ar*H*), 6.85–6.70 (m, 3H, Ar*H*), 4.78–4.76 (m, 1H, ArC*H*), 3.86–3.79 {m, 1H, C*H*CH $(CH_3)_2$}, 2.11–2.00 (m, 2H, ArCHCH_2), 1.81–1.79 {m, 1H, C*H*$(CH_3)_2$}, 1.05–0.79 {m, 6H, $CH(CH_3)_2$}. MS (FAB): *m/z* (%): 280 (50, [M$^+$+H]), 175 (60, M$^+$−COC_6H_4). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.26; H, 7.27.

3.3.35. *(2-Isopropyl-chroman-4-yl)-(3-methoxy-phenyl)-methanone* ***21b***

Yield=26% as yellow oil and mixture of diastereomers; R_f=0.5 (5% ethyl acetate in hexane). IR (Neat): 2963, 1683, 1586, 1486, 1458, 1430, 1259, 1143, 756 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.59–7.36 (m, 3H, Ar*H*), 7.16–7.10 (m, 2H, Ar*H*), 6.91–6.75 (m, 3H, Ar*H*), 4.80–4.76 (m, 1H, ArC*H*), 3.96–3.89 {m, 1H, C*H*$CH(CH_3)_2$}, 3.84 (s, 3H, OCH_3), 2.16–2.03 (m, 2H, ArCHCH_2), 1.90–1.84 {m, 1H, C*H*$(CH_3)_2$}, 1.05–0.93 {m, 6H, $CH(CH_3)_2$}. MS (FAB): *m/z* (%): 311 (90, [M$^+$+1]), 135 (50, M$^+$−C_9H_9O). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.32; H, 7.21.

3.3.36. *(4-Chloro-phenyl)-(2,2-dimethylchroman-4-yl)-methanone* ***23***

Yield=30% as colourless oil; R_f=0.6 (10% ethyl acetate in hexane). IR (Neat): 3406, 2924, 1593, 1216, 759 cm^{-1}. ^{1}H NMR

(300 MHz, CDCl$_3$): δ 7.86 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.44 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.19–7.13 (m, 1H, Ar*H*), 6.88 (m, 3H, Ar*H*), 4.72–4.66 (m, 1H), 2.19–2.02 (m, 2H), 1.45 (s, 3H, CH$_3$), 1.35 (s, 3H, CH$_3$). MS (ESI): *m*/*z* (%): 300 (30, M+1), 283 (100, [M$^+$−OH]). Anal. Calcd for $C_{18}H_{17}ClO_2$: C, 71.88; H, 5.70. Found: C, 71.95; H, 5.78.

3.3.37. (4-Chloro-phenyl)-(7-methoxy-2,2-dimethyl-thiochroman-4-yl)-methanone ***27a***

Yield=50% as light yellow oil; *R*$_f$=0.6 (15% ethyl acetate in hexane). IR (Neat): 2926, 2373, 1650, 1479, 1224, 769 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.81 (d, 2H, *J*=8.3 Hz, Ar*H*), 7.37 (d, 2H, *J*=8.3 Hz, Ar*H*), 7.25 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.71 (d, 1H, *J*=2.4 Hz, Ar*H*), 6.53 (dd, 1H, *J*$_1$=8.5 Hz, *J*$_2$=2.4 Hz, Ar*H*), 4.61–4.52 (m, 1H, ArC*H*), 3.79 (s, 3H, OC*H*$_3$), 2.29–2.07 (m, 2H, ArCHC*H*$_2$), 1.51 {s, 3H, C(C*H*$_3$)$_2$}, 1.42 {s, 3H, C(C*H*$_3$)$_2$}. ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.3, 159.2, 138.9, 134.1, 134.0, 130.4, 130.2, 129.9, 127.5, 127.1, 126.7, 120.8, 114.4, 55.2, 49.0, 42.1, 31.0, 30.2, 28.1. MS (FAB): *m*/*z* (%): 347 (100, [M$^+$+H]). Anal. Calcd for $C_{19}H_{19}ClO_2S$: C, 65.79; H, 5.52. Found: C, 65.73; H, 5.49.

3.3.38. (7-Methoxy-2,2-dimethyl-thiochroman-4-yl)-phenyl-methanone ***27b***

Yield=51% as pale yellow semi solid; *R*$_f$=0.5 (10% ethyl acetate in hexane). IR (Neat): 2931, 2363, 1678, 1596, 1223, 1045, 771 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.83 (d, 2H, *J*=8.5 Hz, Ar*H*), 7.47–7.32 (m, 3H, Ar*H*), 6.78 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.64 (d, 1H, *J*=2.6 Hz, Ar*H*), 6.46 (dd, 1H, *J*$_1$=8.5 Hz, *J*$_2$=2.6 Hz, Ar*H*), 4.61–4.55 (m, 1H, ArC*H*), 3.68 (s, 3H, OC*H*$_3$), 2.23–2.04 (m, 2H, ArCHC*H*$_2$), 1.41 {s, 3H, C(C*H*$_3$)$_2$}, 1.33 {s, 3H, C(C*H*$_3$)$_2$}. ^{13}C NMR (75 MHz, CDCl$_3$): δ 198.3, 159.2, 136.1, 134.5, 133.4, 131.2, 128.9, 127.5, 127.1, 121.8, 114.4, 55.6, 48.7, 42.0, 31.4, 30.2, 28.6. MS (FAB): *m*/*z* (%): 312 (100, [M$^+$]). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 72.91; H, 6.44.

3.3.39. (7-Methoxy-2,2-dimethyl-thiochroman-4-yl)-(3-nitro-phenyl)-methanone ***27c***

Yield=60% as brown viscous oil; *R*$_f$=0.5 (15% ethyl acetate in hexane). IR (KBr): 2925, 1670, 1600, 1348, 1238, 1033, 711 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.65 (s, 1H, Ar*H*), 8.27 (d, 1H, *J*=8.1 Hz, Ar*H*), 8.01 (d, 1H, *J*=7.7 Hz, Ar*H*), 7.51 (t, 1H, *J*=7.9 Hz, Ar*H*), 6.74 (d, 1H, *J*=8.5 Hz, Ar*H*), 6.66 (d, 1H, *J*=2.6 Hz, Ar*H*), 6.45 (dd, 1H, *J*$_1$=8.5 Hz, *J*$_2$=2.6 Hz, Ar*H*), 4.59–4.50 (m, 1H, ArC*H*), 3.67 (s, 3H, OC*H*$_3$), 2.23–1.96 (m, 2H, ArCHC*H*$_2$), 1.40 {d, 6H, *J*=7.3 Hz, C(C*H*$_3$)$_2$}. ^{13}C NMR (50 MHz, CDCl$_3$): δ 199.8, 159.0, 148.9, 137.1, 135.2, 130.4, 130.2, 127.5, 124.6, 122.7, 112.8, 112.4, 55.6, 49.0, 42.7, 31.0, 30.0, 28.8. MS (FAB): *m*/*z* (%): 358 (100, [M$^+$]). Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92. Found: C, 63.97; H, 5.36; N, 3.90.

3.3.40. 3-Methyl-2-methylene-4-(3-nitro-benzyl)-2H-thiochromene ***29a***

Yield=63% as pale yellow oil; *R*$_f$=0.5 (15% ethyl acetate in hexane). IR (Neat): 3451, 2924, 2368, 1529, 1349, 1218, 768 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.97–7.93 (m, 2H, ArH), 7.76–7.71 (m, 1H, ArH), 7.36–7.17 (m, 2H, ArH), 5.23 (s, 1H, =CH$_2$), 5.06 (s, 1H, =CH$_2$), 4.32 (s, 2H, CH$_2$Ar), 2.10 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.9, 143.7, 142.7, 140.2, 139.0, 138.3, 134.4, 129.8, 127.7, 124.9, 124.8, 123.4, 122.8, 122.5, 121.7, 118.1, 32.9, 25.4. MS (FAB): *m*/*z* (%): 309 (60, [M$^+$]). Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53. Found: C, 69.97; H, 4.88; N, 4.47.

3.3.41. 4-(4-Methoxy-benzyl)-3-methyl-2-methylene-2H-thiochromene ***29b***

Yield=53% as white solid; *R*$_f$=0.5 (10% ethyl acetate in hexane). IR (KBr): 3415, 2929, 2362, 1611, 1510, 1247, 1035, 743 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.72–7.69 (m, 1H, ArH), 7.40–7.39 (m, 1H, ArH), 7.21–7.16 (m, 2H, ArH), 6.97–6.92 (m, 2H, ArH), 6.72–6.66 (m, 2H, ArH), 5.19 (s, 1H, =CH$_2$), 5.10 (s, 1H, =CH$_2$), 4.17 (s, 2H, CH$_2$Ar), 3.67 (s, 3H, OCH$_3$), 2.10 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): 158.2, 140.9, 138.8, 138.4, 132.5, 129.9, 129.3, 124.6, 124.5, 123.0, 122.5, 117.7, 114.3, 55.6, 32.4, 25.4. MS (FAB): *m*/*z* (%): 294 (30, [M$^+$]), 279 (100, [M$^+$−CH$_3$]). Anal. Calcd for $C_{19}H_{18}OS$: C, 77.51; H, 6.16. Found: C, 77.55; H, 6.11.

3.3.42. Dimethyl-[4-(3-methyl-2-methylene-2H-thiochromen-4-yl-methyl)-phenyl]-amine ***29c***

Yield=59% as light orange viscous oil; *R*$_f$=0.6 (15% ethyl acetate in hexane). IR (Neat): 3406, 2928, 2367, 1519, 1218, 769 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.72–7.61 (m, 1H, ArH), 7.45–7.32 (m, 1H, ArH), 7.16–7.12 (m, 2H, ArH), 6.86 (d, 2H, *J*=8.6 Hz, ArH), 6.52 (d, 2H, *J*=8.6 Hz, ArH), 5.20–5.12 (m, 2H, =CH$_2$), 4.12 (s, 2H, CH$_2$Ar), 2.80 {s, 6H, N(CH$_3$)$_2$}, 2.11 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 148.2, 138.8, 138.3, 130.1, 128.9, 124.4, 123.2, 122.3, 117.6, 113.8, 41.8, 32.3, 25.4. MS (FAB): *m*/*z* (%): 307 (100, [M$^+$]), 292 (60, [M$^+$−CH$_3$]). Anal. Calcd for $C_{20}H_{21}NS$: C, 78.13; H, 6.88; N, 4.56. Found: C, 78.20; H, 6.94; N, 4.55.

3.3.43. 4-Benzyl-3-methyl-2-methylene-2H-thiochromene ***29d***

Yield=52% as colourless oil; *R*$_f$=0.6 (10% ethyl acetate in hexane). IR (Neat): 3462, 2927, 1596, 1434, 730 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.81–7.77 (m, 1H, ArH), 7.50–7.45 (m, 1H, ArH), 7.28–7.09 (m, 7H, ArH), 5.27 (s, 1H, =CH$_2$), 5.17 (s, 1H, =CH$_2$), 4.31 (s, 2H, CH$_2$Ar), 2.17 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 142.7, 140.9, 140.5, 138.8, 138.4, 129.5, 128.8, 128.4, 126.3, 124.6, 124.5, 123.0, 122.5, 117.7, 33.3, 30.1, 25.4. MS (FAB): *m*/*z* (%): 264 (100, [M$^+$]). Anal. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10. Found: C, 81.74; H, 6.19.

3.3.44. 4-(4-Chloro-benzyl)-3-methyl-2-methylene-2H-thiochromene ***29e***

Yield=62% as colourless viscous oil. IR (Neat): 3406, 2924, 1593, 1216, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.83 (d, 1H, *J*=8 Hz, ArH), 7.50 (d, 1H, *J*=8 Hz, ArH), 7.40–7.20 (m, 2H, ArH), 7.19 (d, 2H, *J*=8 Hz, ArH), 7.10 (d, 2H, *J*=8 Hz, ArH), 5.30 (s, 1H, =CH$_2$), 5.17 (s, 1H, =CH$_2$), 4.29 (s, 2H, CH$_2$Ar), 2.17 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 142.6, 140.2, 138.5, 138.4, 137.8, 131.7, 129.3, 128.5, 124.3, 124.2, 122.4, 122.1, 117.4, 32.2, 25.0. MS (FAB): *m*/*z* (%): 297 (30, [M$^+$−H]). Anal. Calcd for $C_{18}H_{15}ClS$: C, 72.35; H, 5.06. Found: C, 72.22; H, 4.88.

3.3.45. 4-(3-Methyl-2-methylene-2H-thiochromen-4-yl-methyl)-benzonitrile ***29f***

Yield=65% as pale yellow viscous oil. *R*$_f$=0.6 (10% ethyl acetate in hexane). IR (Neat): 3405, 1728, 1608, 1216, 759 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.85 (d, 1H, *J*=8 Hz, ArH), 7.54 (d, 2H, *J*=8 Hz, ArH), 7.42–7.20 (m, 5H, ArH), 5.29 (s, 1H, =CH$_2$), 5.09 (s, 1H, =CH$_2$), 4.35 (s, 2H, CH$_2$Ar), 2.16 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 145.8, 139.9, 138.5, 137.8, 132.3, 128.7, 127.3, 124.5, 124.3, 122.3, 122.1, 117.5, 110.0, 32.9, 29.6, 25.0. MS (FAB): *m*/*z* (%): 288 (40, [M$^+$−H]). Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.22; N, 4.84. Found: C, 78.71; H, 5.28; N, 4.83.

3.3.46. 4-(2,4-Dichloro-benzyl)-3-methyl-2-methylene-2H-thiochromene ***29g***

Yield=61% as colourless viscous oil; *R*$_f$=0.5 (10% ethyl acetate in hexane). IR (Neat): 3422, 1649, 1517, 1216, 761 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.82 (d, 1H, *J*=7.8 Hz, ArH), 7.60 (d, 2H, *J*=8 Hz, ArH), 7.48–7.26 (m, 5H, ArH), 5.26 (s, 1H, =CH$_2$), 5.06 (s, 1H, =CH$_2$), 4.30 (s, 2H, CH$_2$Ar), 2.16 (s, 3H, CH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 143.2, 140.0, 138.4, 138.3, 137.6, 132.5, 129.8, 129.0, 127.1, 124.5, 124.4, 122.3, 122.2, 117.4, 30.2, 24.9. MS (FAB): *m*/*z* (%): 333 (100, [M$^+$−H]). Anal. Calcd for $C_{18}H_{14}Cl_2S$: C, 64.87; H, 4.23. Found: C, 64.93; H, 4.24.

3.3.47. 3-Methyl-4-(4-methyl-benzyl)-2-methylene-2H-thiochromene ***29h***

Yield=57% as brown oil; R_f=0.7 (8% ethyl acetate in hexane). IR (Neat): 3432, 1216, 760 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.80 (d, 1H, *J*=7.8 Hz, ArH), 7.51 (d, 1H, *J*=8 Hz, ArH), 7.38–7.26 (m, 2H, ArH), 7.15–6.90 (m, 4H, ArH), 5.26 (s, 1H, $=CH_2$), 5.18 (s, 1H, $=CH_2$), 4.27 (s, 2H, CH_2Ar), 2.28 (s, 3H, CH_3), 2.17 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0, 141.1, 140.8, 139.2, 138.8, 129.1, 128.7, 128.3, 126.6, 124.5, 124.3, 123.4, 122.9, 117.6, 33.5, 31.2, 23.1. MS (FAB): *m*/*z* (%): 277 (90, $[M^+-H]$). Anal. Calcd for $C_{19}H_{18}S$: C, 81.97; H, 6.52. Found: C, 81.94; H, 6.45.

3.3.48. 4-Bromo-5-(4-fluoro-benzylidene)-2,3,4,5-tetrahydro-benzo[b]thiepine ***48***

Yield=51% as brown viscous oil; R_f=0.7 (10% ethyl acetate in hexane). IR (Neat): 3442, 2360, 1651, 1525, 1217, 1022, 771 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47–7.38 (m, 3H, Ar*H*), 7.18–6.97 (m, 5H, Ar*H*), 6.86 (s, 1H, =C*H*Ar), 4.99–4.94 (m, 1H, C*H*Br), 3.58–3.48 (m, 2H, SCH_2), 2.29–2.21 (m, 1H, SCH_2CH_2), 2.06–1.98 (m, 1H, SCH_2CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 161.3, 140.3, 138.5, 134.4, 134.1, 130.3, 129.8, 128.8, 126.4, 126.1, 125.7, 123.4, 114.3, 113.0, 39.3, 32.4, 31.3. MS (FAB): *m*/*z* (%): 349 (100, $[M^+]$). Anal. Calcd for $C_{17}H_{14}BrFS$: C, 58.46; H, 4.04. Found: C, 58.60; H, 4.11.

3.3.49. (E)-4-Bromo-8-methoxy-5-(3-methoxybenzyl)-2,3-dihydrobenzo[b]thiepine ***49***

Yield=53% as brown viscous oil; R_f=0.7 (10% ethyl acetate in hexane). IR (Neat): 3012, 2937, 2369, 1600, 1477, 1219, 1042, 768 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, 1H, *J*=8.7 Hz, Ar*H*), 7.29 (s, 1H, Ar*H*), 7.18 (t, 1H, *J*=7.8 Hz, Ar*H*), 6.92 (dd, 1H, J_1=2.1 Hz, J_2=9.0 Hz, Ar*H*), 6.72 (t, 3H, *J*=7.8 Hz, Ar*H*), 4.15 (s, 2H, Ar–CH_2), 3.86 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.58–3.51 (m, 2H, SCH_2), 3.44–3.36 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 157.4, 141.0, 139.8, 134.4, 134.0, 130.5, 129.5, 122.8, 120.4, 114.1, 114.0, 111.3, 105.0, 55.5, 55.0, 32.3, 32.1, 31.3. MS (FAB): *m*/*z* (%): 390 (97, M^+), 391 (78, M+1), 392 (100, M+2), 393 (22, M+3). Anal. Calcd for $C_{19}H_{19}BrO_2S$: C, 58.32; H, 4.89. Found: C, 58.37; H, 4.86.

3.3.50. (E)-5-Benzyl-4-bromo-8-methoxy-2,3-dihydrobenzo[b]thiepine ***50***

Yield=57% as pale yellow oil; R_f=0.7 (10% ethyl acetate in hexane). IR (Neat): 3062, 2995, 2835, 2366, 1602, 1478, 1268, 1233, 1059, 760 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, 1H, *J*=8.7 Hz, Ar*H*), 7.24 (t, 3H, *J*=9.6 Hz, Ar*H*), 7.17 (d, 1H, *J*=6.9 Hz, Ar*H*), 7.11 (d, 2H, *J*=7.5 Hz, Ar*H*), 6.89 (dd, 1H, J_1=2.1 Hz, J_2=9.0 Hz, Ar*H*), 4.15 (s, 2H, ArCH_2), 3.83 (s, 3H, OCH_3), 3.49 (t, 2H, *J*=6.2 Hz, SCH_2), 3.38 (d, 2H, *J*=6.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.6, 141.8, 138.4, 134.4, 134.1, 132.5, 128.5, 127.2, 124.8, 114.0, 111.3, 108.0, 55.5, 33.3, 32.6, 31.0. MS (FAB): *m*/*z* (%): 360 (98, M^+), 361 (42, M+1), 362 (100, M+2), 363 (32, M+3). Anal. Calcd for $C_{18}H_{17}BrOS$: C, 59.84; H, 4.74. Found: C, 59.88; H, 4.75.

Acknowledgements

This research project was partly supported by Department of Science and Technology (SR/S1/OC-23/2005), New Delhi, India. Maloy, Shagufta and Ajay thank CSIR for providing fellowships. We thank SAIF, CDRI, Lucknow for providing spectral data and referee for the constructive criticism.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.07.106.

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