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Application of Nazarov cyclization to access [6-5-6] and [6-5-5]tricyclic core embedded New Heterocycles : An easy entry to structures related to Taiwaniaquinoids†

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A concise and general route to synthesize new class of [6-5-6] tricyclic core embedded polyheterocycles has been accomplished using diastereoselective Nazarov cyclization with an overall yield of 35-40%. Versatility of this synthetic route has also been demonstrated by accessing a variety of [6-5-5] tricyclic core incorporated polycycles. It was observed that the efficiency of cyclization depends upon the impact of polarization on the reacting systems. Amongst the various Lewis and Bronsted acids screened for cyclization, Triflic acid was found to be the most effective catalyst.

Introduction

[6-5-6]ABC tricyclic skeleton, which is rather uncommon, has been known to be found in several natural products, among which members of taiwaniaquinoids holds special mention (Fig **1**).[1a-c] Taiwaniaquinol B, isolated from Taiwanese pine tree *Taiwania cryptomerioide,* is one such *6-nor-5(6→7)abeo-abietane* type diterpenoid containing the uncommon fused [6-5-6] tricyclic carbon skeleton.[2] Several members of the taiwaniaquinoids have shown activity as aromatase inhibitors and are currently under evaluation for their potential as drug leads in the treatment of estrogen-dependent cancers.[3,4] Thus, the distinctive [6-5-6] fused ring system has received considerable attention by synthetic organic chemists, and several total synthesis of such norditerpenoids has appeared in the last few years.[5]

Nazarov reaction[6] is considered as one of the most versatile reactions to construct cyclopentenone fused carbocycles. Although the concept of polarized Nazarov substrate[7] *i.e.* divinyl ketone **1** has been exploited to construct simple functionalized cyclopentenone **3** *via* intermediate **2** under mild reaction conditions (Scheme 1), its utilization for the construction of [6-5-6] tricyclic skeleton fused heteropolycycles is rather limited.[8] Trauner *et al* utilized the Nazarov chemistry efficiently to synthesize several members of Taiwaniaquinoid family containing [6-5-6] tricyclic skeleton including Taiwaniaquinol B using trimethylsilyl triflate(TMSOTf) in nitromethane.[9] Fillion *et al* reported synthesis of Taiwaniaquinol B, applying domino acylation/alkylation as a key step.[5a]Approaches based on palladium catalyzed alkylation[5b] and intramolecular Heck reactions[5c-e] to assemble the [6-5-6] tricyclic skeleton containing natural products have also been well delineated by several groups. How ever, as such, no general and efficient method to assemble heterocycles with hetroatom impregnated [6-5-6] tricyclic skeleton is reported so far.

Therefore, a mild and expedient method for the construction of heteroatom embedded [6-5-6] tricyclic skeletons is highly desirable. In the quest for attaining novel molecules with interesting properties, we envisaged to encompass the polarized Nazarov concept to access diversified [6-5-6] tricyclic skeletons. Further cognizing the fact that the *cis* ring fusion preferences in the cyclic systems could direct the protonation in diastereoselective Nazarov product,[10,11] we endeavored to design a new class of polarized Nazarov substrate **4** by casting

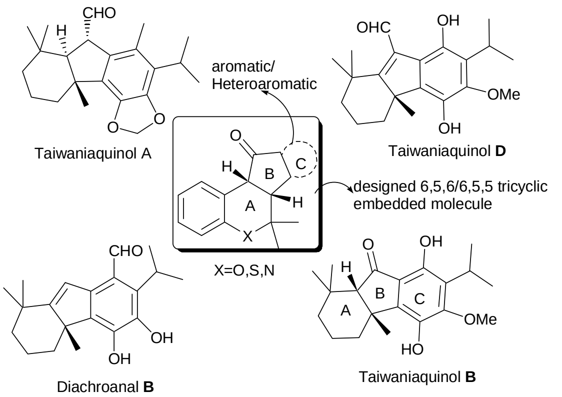
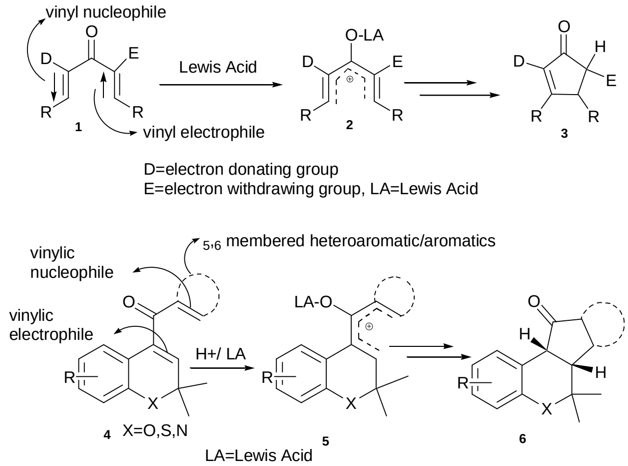


Fig 1 Representative natural [6-5-6] tricyclic skeleton and our designed novel]6-5-6]/[6-5-5] skeleton embedded polycycles

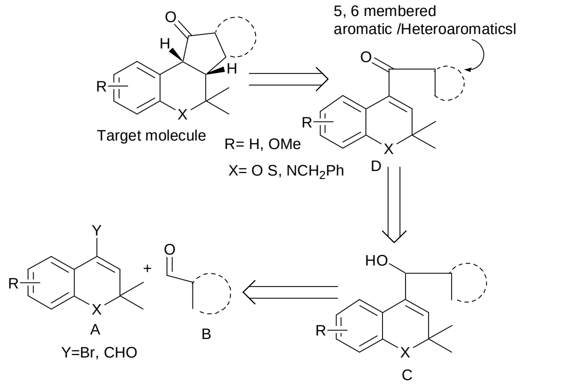


Scheme 1 A general Polarized Nazarov Reaction and our designed polarized substrate **4**

aromatics/heteroaromatics[12] as vinyl nucleophiles to access a variety of novel benzene annulated [6-5-6]/[6-5-5] tricylic heteropolycycles **6** *via* intermediate **5.**

Results and Discussion

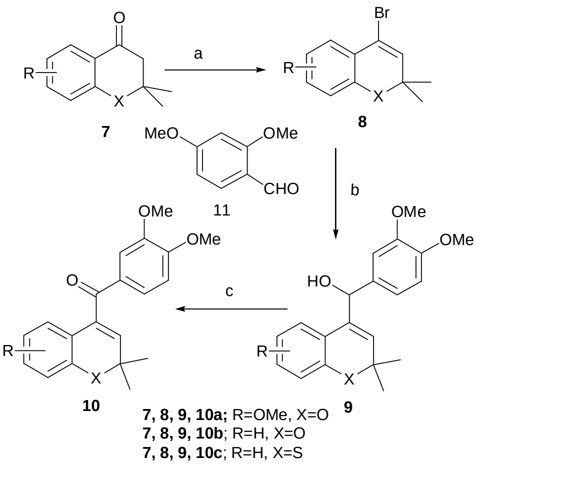
The general retrosynthetic analysis of the target molecule depicted that the Nazarov substrates **D** could be assembled by oxidizing the alcohol C which would be procured through the coupling of suitable bromo substrates **A** with different aromatic and heteroaromatic aldehydes **B** (Scheme 2).



Scheme 2 Retrosynthetic analysis of Target molecule

Towards the realization of our goal, we first embarked upon the syntheses of benzo annulated [6-5-6]tricyclic skeleton embedded polyheterocycles. Synthesis of the Nazarov substrates **10a-c** were achieved as outlined in Scheme **2**. Chromanones/thiochromanones **7** were treated with PBr_3 in dry benzene at 60^{o}C to furnish the bromo compounds **8a-c** in good yields (60-64%)[13]. **8a-c** were further treated with *n*-BuLi under inert atmosphere at -78^{o}C in dry THF and reacted with commercially available veratraldehyde **11** to obtain the corresponding divinyl alcohols **9a-c** in reasonable yields (55-60%). MnO_2 oxidation of allylic alcohols **9a-c** furnished the coveted Nazarov substrate **10a-c** in high yields (80-85%).

In an effort to optimize the best catalyst for the Nazarov cyclization to obtain the [6-5-6] tricyclic core of **12a-c,**

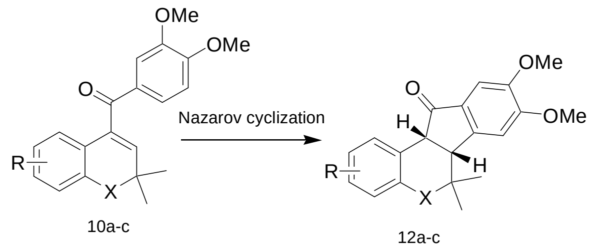


Scheme 3 Synthesis of Nazarov substrates **10a-c.**

^{a}*Reagents and Conditions*: (a) PBr_3, dry benzene, 60 ºC , 24h, 60-64%. (b) (i) *n*-BuLi, dry THF, -78 ºC, N_2, 5-10 mints. ii) **11**, -78 ºC to r.t, 2h, 55-60%. (c) MnO_2, dry ether, rt, 1h, 80-85%.

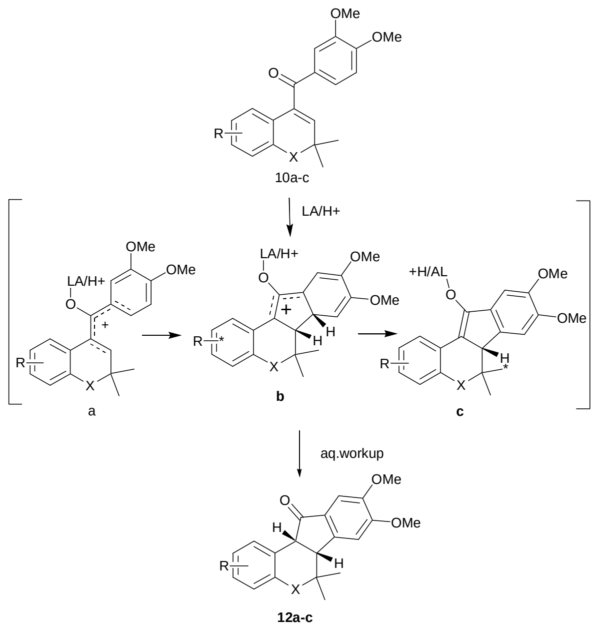
substrates **10a-c** were reacted with various catalytic Lewis and Bronsted acids in dichloromethane at room temperature (Table 1). It was observed that the Nazarov substrates **10a-c** cyclized to furnish the [6-5-6] tricyclic embedded heteropolycycles **12a-c** in high yields (87-91%) at room temperature with just one equivalent of Triflic acid in a very short reaction time. Besides triflic acid, other Bronsted acids such as H_2SO_4, CF_3COOH and *p*-TsOH also gave the cyclized product albeit in low yields (65-85%) and longer reaction time. Well known Lewis acids like $AlCl_3$, $FeCl_3$, $BF_3.Et_2O$ did not show very good reactivity and remained low yielding even after increase in the catalyst loading (47-62%).

Table 1 Catalyst optimization for Nazarov cyclization



Entry	Substrate	catalyst	condition	Time (h)	Yield
1	**10a**	**CF_3SO_3H**	**DCM, rt**	**1.5**	**91%**
2	**10a**	H_2SO_4	DCM, rt	3	85%
3	**10c**	CF_3COOH	DCM, rt	2.5	82%
4	**10b**	p-TsOH	DCM, rt	12	65%
5	**10b**	$AlCl_3$	DCM, rt	10	62%
6	**10c**	$FeCl_3$	DCM, rt	16	45%
7	**10a**	$BF_3.Et_2O$	DCM, rt	14	47%
8	**10c**	$Sc(OTf)_3$	DCM, rt	48	28%

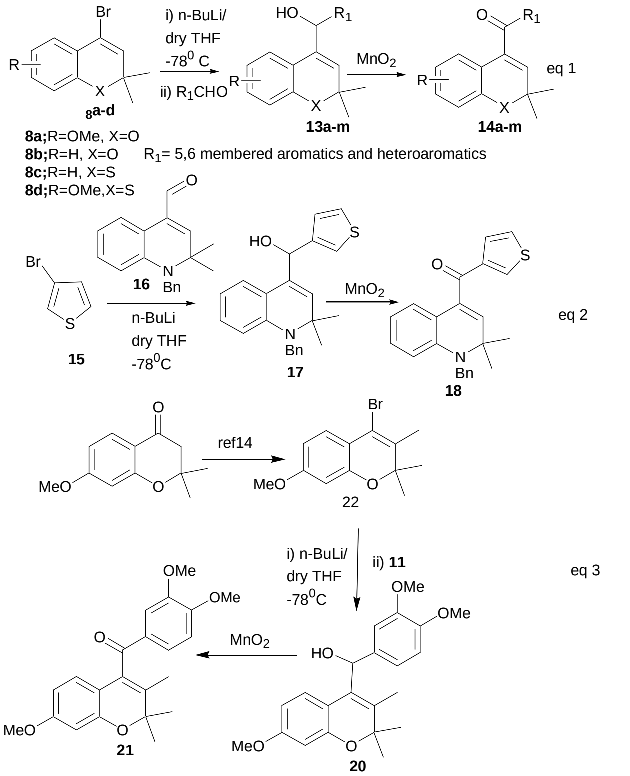
Use of milder Lewis acid like $Sc(OTf)_3$ also did not improve the reactivity significantly, as substantial amount of substrate was left unreacted even after 48 hrs (28% yield) (Table 1). The *syn* stereochemistry established by NOESY experiments in the products **12a-c** reflects the greater stablity of *cis* fused



Scheme 4 Aromatic Nazarov cyclization Process.

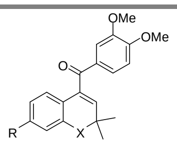
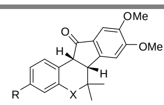
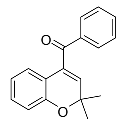
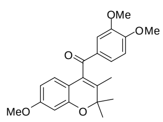
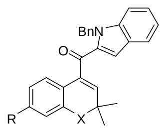
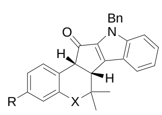
cyclopentenone [6-5-6] tricyclic systems. This is due to the enol protonation step of one of the intermediates **c** in Nazarov cyclization process (Scheme 4) during the aqueous workup which gave thermodynamically favourable cis fused products. However, it was delightful to achieve products with excellent diastereoselectivity (>99%) with no trace of other isomer detected even in the HPLC analysis. Change of solvent from DCM to dry benzene did not change the yields. With the best optimized reaction conditions at hand, we set out to explore the generality of the synthetic pathway to synthesize new molecular entities embedded with [6-5-6] tricyclic systems.Thus **14a (**eq 1**)** and **21 (**eq 3**)** were synthesized **(Scheme 5)** from bromo substrates **8b** and **22** with benzaldehyde and veratraldehyde respectively, following similar reaction conditions as given in Scheme **3.** But to our dismay **14a** failed to give the cyclized product under the optimized cyclization reaction conditions indicating that activated aromatic rings are required for cyclization of such class of Aromatic Nazarov substrates (entry 2, Table 2). In order to achieve [6-5-6] tricyclic system with a quarternary stereocenter, our attempt to cyclize **21** turned futile presumably due to the steric hindrance caused by substituted methyl group in the reaction intermediate (entry 3,Table 2). Further increase in catalytic loading and temperature only led to decomposition of the starting material.

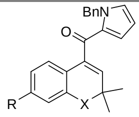
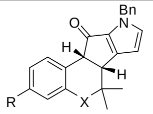
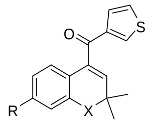
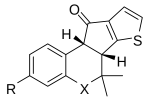
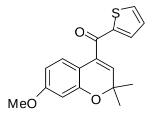
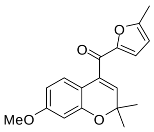
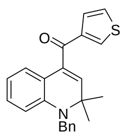
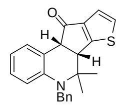
Thereafter we turned our attention to further explore this synthetic methodology to attain a varied class of heteroatom impregnated [6-5-5]ABC tricycle skeleton. Towards this objective various heteroaromatic Nazarov substrates **14b-m** and **18** (Table 2) were synthesized essentially following the similar reaction condition as depicted in eq. 1 and eq. 2 (Scheme 5). The intermediate aldehyde **16** in eq. 2 which is required for the synthesis of substrate **18** was synthesized following standard reaction conditions(see supporting information for the scheme).[15,16] Synthesized substrates (**14a-m, 18**) were then surveyed under one of the best optimized reaction conditions (triflic acid in DCM) for the desired cyclized products.



Scheme 5 Synthesis of new Aromatic / Heteroaromatic Nazarov substrates following similar reaction conditions as Scheme **3**

Table 2 Results of Nazarov Reaction on Aryl and Heteroaryl Polarized Substrates[a]

Entry	substrate	time	temperature	product	dr[b] (%)	yield (%)
1	 **10a,b,c**	1.5 h. 1 h 1.2 h	**rt** **rt** **rt**	 **12a,b,c** **12a**R=OMe, X=O **12b** R=H, X=O **12c** R=H, X=S	>99 >99 >99	90 91 87
2	 **14a**	>24.h	**rt/60 °C**	No reaction	---	---
3	 **21**	>24.h	**rt/60 °C**	No reaction	---	---
4	 **14b,c,d,e**	1 min. 1 min I min 1 min	**rt** **rt** **rt** **rt**	 **15b,c,d,e** **15b** R=OMe,X=O **15c** R=OMe, X=S **15d** R=H, X=O **15e**R=H, X=S	>99 >99 >99 >99	90 92 92 91
		45 min	**rt**	**15f R**=OMe, X=O		

5	 **14f,g,h**	35 min 40 min 1.5 h	**rt** **rt** **rt**	 **15f,g,h**	**15g** R=OMe, X=S **15h** R=H, X=O **15i** R=OMe, X=O	>99 >99 >99	85 88 87
6	 **14i,j,k**	1 h 1.3.h	**rt** **rt**	 **15i,j,k**	**15j** R=H, X=S **15k** R=H, X=O	>99 >99 >99	84 88 81
7	 **14l**	>24.h	**rt/60 °C**	No reaction		---	---
8	 **14m**	>24.h	**rt/60 °C**	No reaction		---	---
9	 **18**	1.5h	**rt**	 **19**		>99	85

a= DCM is used as solvent in all reactions; **b**= determined by NMR/HPLC

Observation of summarized results (Table 2) emphasized that aryl and heteroaryls represented the electron donating vinyl nucleophile in polarized Nazarov cyclization. It also provided information about the extent of polarization in these relatively new class of aromatic/heteroaromatic Nazarov substrates as the 2-substituted thiophene and furan substrates **14l** and **14m** failed to cyclize whereas 3-substituted thiophene substrates **14i, 14j, 14k** and **18** gave cyclized products **15i, 15j, 15k** and **19** in varying yields (84, 88, 81 and 85% respectively) under the similar reaction conditions. Increasing temperature and catalyst loading gave only uncharacterizable products. In contrast, 2-substituted pyrrole based substrates **14f, 14g,** and **14h** furnished **15f, 15g**, and **15h** in good yields (85, 88, and 87% respectively**)**. Indole based Nazarov substrates **14b, 14c, 14d, 14e** gave the desired [6-5-5] tricycle skeleton embedded novel pentacyclic molecules **15b, 15c, 15d, 15e** under similar reaction conditions in a minute with very high yields (90, 92, 92, 91% respectively).

The structure and stereochemistry of the synthesized cyclic molecules were determined through incisive analysis of ^{1}H, ^{13}C NMR, ^{1}H-^{1}H COSY, HSQC spectra. The *cis* relationship between two vicinal protons in the final products was first revealed by the coupling constant (J = 6-7 Hz) from ^{1}H NMR. This stereochemical assignment was further reinforced by NOESY experiments.

In conclusion we have reported an easy, general and expedient route to access variety of uncommon hetero [6-5-6]ABC tricyclic cores analogous to Taiwaniaquinoids as well as several hetero [6-5-5] tricyclic systems *via* diastereoselective Nazarov cyclization. This is first such aromatic Nazarov system which showed excellent diastereo and regioselectivity under very mild reaction conditions, providing high yielding functionalized scaffolds that could serve as a valuable building block towards Diversity Oriented Synthesis. Their bioevaluation and the asymmetric version of Nazarov reaction on this system is currently underway in our lab and will be reported in due course of time.

Experimental

General Methods

All dry reactions were carried out under argon or nitrogen. Commercial reagents were used without further purification unless otherwise stated. Reactions were monitored on silica gel TLC plates (coated with TLC grade silica gel, obtained from Merck). Detecting agent used (for TLC) were iodine vapors. Column chromatography was performed over silica gel (100-200 mesh) procured from Qualigens (India). Mass spectra were recorded using electron spray ionization (ESI-MS) or Fast atom bombardment spectra (FAB-MS) on a JEOL SX 102 spectrometer using Argon/xenon as the FAB gas. Melting points were determined on COMPLAB melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-200 (operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C) or DPX-300 (operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer using $CDCl_3$ and CCl_4 as solvent. Tetramethylsilane (0.00 ppm) served as an internal standard in 1H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. Coupling constants (J values) are given in hertz (Hz). Chemical shifts are expressed in parts per million.

Experimental Procedures and Characterization Data

Typical Procedure to Prepare Allyl Alcohols

(1-Benzyl-1H-indol-2-yl)(7-methoxy-2, 2-dimethyl-2H-chromen-4-yl) methanol (13b)

To a stirred solution of bromo substrate **8a** (500 mg, 1.85 mmol) in anhydrous THF (20 mL) at -78°C and under N_2, *n*- BuLi (1.6 M in hexane,1.2 ml, 1.85 mmol) was added. The resulting yellow solution was stirred at -78°C for 5-10 minutes after which N-benzyl indole 2-carboxaldehyde (393 mg, 1.66 mmol) in THF (2mL) were added at the same temperature and stirred at room temperature for 1h. After quenching with water, THF was removed in vacuo. The mixture was extracted with ethyl acetate (3 × 20 ml), washed with brine and dried over Na_2SO_4. The concentrated extract was subjected to column chromatography on silica gel and elution with 20% ethyl acetate in hexane furnished alcohol **13b** (418 mg, 54%) as viscous green oil, R_f = 0.51 (AcOEt/hexane, 20:80); IR (Neat): 3417, 3010, 2330, 1211, 759, 670 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 (d, 1H, *J* = 7.5), 7.33-7.02 (m, 8H), 6.47 (d, 2H, *J* = 7.7), 6.37 (d, 1H, *J* = 2.5), 6.14-6.10 (m, 1H), 5.71 (s, 1H) , 5.67 (s, 1H), 5.54 (s, 2H), 3.71 (s, 3H), 2.00 (s, 1H), 1.46 (s, 3H), 1.43 (s, 3H); MS (FAB): *m/z* 410 $[M-OH]^+$; Anal. Calcd. for $C_{28}H_{27}NO_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 78.95; H, 6.34; N, 3.35.

(1-Benzyl-1H-indol-2-yl)(7-methoxy-2, 2-dimethyl-2H-thiochromen-4-yl) methanol (13c)

As described for **13b, 8d** (500 mg, 1.75 mmol) in THF (20ml) , *n*-BuLi (1.1 ml, 1.75 mmol) , N-benzyl indole 2-carboxaldehyde (372 mg, 1.57 mmol) in THF (2mL) furnished **13c** (410mg, 53%) as viscous colorless oil, R_f = 0.53 (AcOEt/hexane, 20:80); IR (Neat): 3409, 3020, 2360, 1216, 762, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, 1H, *J* = 7.8), 7.52 (d, 1H, *J* = 8.8), 7.30-7.24 (m, 4H), 7.15-7.04 (m, 6H), 6.81 (d, 1H, *J* = 1.1), 6.64 (dd, 1H, J_1 = 2.5, J_2 = 8.7) , 6.72 (d, 1H, *J* = 2.5), 5.39 (s, 2H), 3.78 (s, 3H), 1.26 (s, 3H) , 0.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 150.1, 149.1, 140.6, 137.3, 134.8, 128.8, 127.5, 126.5, 126.2, 124.8, 123.0, 120.1, 120.0, 118.8, 17.5, 112.9, 112.3, 110.3, 55.3, 55.1, 48.9, 48.3, 29.6, 22.8; MS (ESI): *m/z* 424 $[M-OH]^+$; Anal. Calcd. for $C_{28}H_{27}NO_2S$: C, 76.16; H, 6.16; N, 3.17. Found: C, 76.09; H, 6.24; N, 3.28.

(1-Benzyl-1H-indol-2-yl)(2,2-dimethyl-2H-chromen-4-yl)methanol (13d)

As described for **13b, 8b** (500 mg, 2.09 mmol) in THF (20ml) , *n*-BuLi (1.3 ml, 2.09 mmol) , N-benzyl indole 2-carboxaldehyde (594 mg, 1.88 mmol) in THF (2mL) furnished **13d** (471mg, 57%) as viscous colorless oil, R_f = 0.54 (AcOEt/hexane, 20:80); IR (Neat): 3429, 3021, 2359, 1620, 1218, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, 2H, *J* = 7.7), 7.35-7.20 (m, 5H), 7.16-7.03 (m, 4H), 6.58 (d, 2H, *J* = 4.1), 6.49 (s, 1H), 5.89 (d, 1H, *J* = 1.1), 5.74 (s, 1H), 5.61 (d, 1H, *J* = 16.9), 5.53 (d, 1H, *J* = 16.8), 2.02 (s, br,1H), 1.51 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ ,152.7, 139.5, 138.2, 137.8, 129.0, 128.8, 127.6, 127.5, 127.2, 126.2, 123.5, 122.4, 121.1, 120.4, 120.2, 119.8, 116.6, 109.6,102.6, 75.9, 65.3, 46.9, 27.7, 27.6; MS (ESI): *m/z* 396 $[M+1]^+$, 378 $[M-OH]^+$; Anal. Calcd. for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.92; H, 6.45; N, 3.61.

(1-Benzyl-1H-pyrrol-2-yl)(2,2-dimethyl-2H-chromen-4-yl)methanol (13f)

As described for **13b, 8a** (500 mg, 1.85 mmol) in THF (20ml) , *n*-BuLi (1.2 ml, 1.85 mmol) , N-benzylpyrrole 2-carboxaldehyde (308 mg, 1.67 mmol) in THF (2mL) furnished **13f** (339 mg, 53%) as viscous colorless oil, R_f = 0.45 (AcOEt/hexane, 20:80); IR (Neat): 3419, 3021, 2360, 1211, 761, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.23 (m, 3H), 7.12-7.10 (m, 2H), 7.03-6.97 (m, 1H), 6.76-6.74 (m, 2H), 6.57-6.52 (m, 1H), 6.40 (dd, 1H, J_1 = 1.4 , J_2 = 7.7), 6.07-6.01 (m, 2H), 5.82 (d, 1H, *J* = 1.2), 5.48 (s, 1H) , 5.35 (d, 1H, *J* = 16.0), 5.17 (d, 1H, *J* = 16.0), 1.83 (s, br, 1H), 1.44 (s, 3H), 1.42 (s, 3H); MS (ESI): *m/z* 328 $[M-OH]^+$; Anal. Calcd. for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 79.88; H, 6.79; N, 3.93

(3,4-Dimethoxyphenyl)(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)methanol (9a)

As described for **13b, 8a** (500 mg, 1.85 mmol) in THF (20ml) , *n*-BuLi (1.2 ml, 1.85 mmol), veratraldehyde (276 mg, 1.66 mmol) in THF (2mL) furnished **9a** (364 mg, 55%) as viscous colorless oil, R_f = 0.61 (AcOEt/hexane, 20:80); IR (Neat): 3431, 2360, 1560, 1217,761, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3+CCl_4$): δ 6.95-6.91 (m, 2H), 6.87 (d, 1H, *J* = 8.6), 6.80 (d, 1H, *J* = 7.9), 6.36 (d, 1H, *J* = 2.5), 6.26 (dd, 1H, J_1 = 2.6 , J_2 = 8.6), 5.68 (s, 1H), 5.53 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.72 (s, 3H), 2.03 (s, br,1H), 1.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3+CCl_4$): δ 160.4, 154.5, 149.2, 148.8, 134.4, 133.3, 124.8, 124.8, 119.5, 113.4, 111.2, 110.3, 106.5, 102.2, 76.0, 72.6, 55.8, 5.7, 55.0, 27.9; MS (ESI): *m/z* 339 $[M-OH]^+$; Anal. Calcd. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.65; H, 6.85.

(3,4-Dimethoxyphenyl)(2,2-dimethyl-2H-chromen-4-yl)methanol (9b)

As described for **13b, 8b** (500 mg, 2.09 mmol) in THF (20ml), *n*-BuLi (1.3 ml, 2.09 mmol),veratraldehyde (312 mg, 1.88 mmol) in THF (2mL) furnished **9b** (409 mg, 60%) as viscous colorless oil, R_f = 0.59 (AcOEt/hexane, 20:80); IR (Neat): 3414, 3021, 2358, , 1591, 1216,758, 668 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3+CCl_4$): δ 7.00-6.94 (m, 1H), 6.91-6.85 (m, 3H), 6.75-6.60 (m, 3H), 5.70 (s, 1H), 5.52 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 1.86 (s, br,1H), 1.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3+CCl_4$): δ 153.1, 149.2, 148.9, 134.2, 133.4, 129.0, 127.5, 123.9, 120.5, 120.2, 119.5, 116.8, 111.1, 110.2, 75.7, 72.5, 55.8, 55.7, 27.9; MS (ESI): *m/z* 309 $[M-OH]^+$; Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.71; H, 6.90.

(3,4-Dimethoxyphenyl)(2,2-dimethyl-2H-thiochromen-4-yl)methanol (9c)

As described for **13b, 8c** (500 mg, 1.96 mmol) in THF (20ml) , *n*-BuLi (1.2 ml, 1.96 mmol), veratraldehyde (293 mg, 1.76 mmol) in THF (2mL) furnished **9c** (395 mg, 59%) as viscous colorless oil, R_f = 0.48 (AcOEt/hexane, 20:80); IR (Neat): 3430, 3020, 2331, 1571, 1212, 760, 660 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3+CCl_4$): δ 7.30-7.27 (m, 1H), 7.19 (dd, 1H, J_1 = 1.0 , J_2 = 7.8), 7.09-7.03 (m, 1H), 6.99-6.91 (m, 3H), 6.81-6.79 (m, 1H), 6.12 (s, 1H), 5.66 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.10 (s, br,1H), 1.49 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz,

$CDCl_3$+CCl_4): δ 149.1, 148.6, 137.0, 134.8, 133.1, 132.8, 130.8, 127.9, 127.4, 127.3, 125.4, 119.4, 111.1, 110.2, 55.7, 55.6, 40.2, 28.9. MS (ESI): *m/z* 325[M-OH]$^+$; Anal. Calcd. for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.22; H, 6.57.

(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)(thiophen-3-yl)methanone (13i)

As described for **13b, 8a** (500 mg, 1.85 mmol) in THF (20ml), *n*-BuLi (1.2 ml, 1.85 mmol), thiophene 3-carboxaldehyde (186 mg, 1.66 mmol) in THF (2mL) furnished **13i** (320 mg, 57%) as viscous colorless oil, R_f = 0.50(AcOEt/hexane, 20:80); IR (Neat): 3434, 3020, 1217, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.06 (dd, 1H, J_1 = 1.3 , J_2 = 4.9), 6.96 (d, 1H, *J* = 8.6), 6.39 (d, 1H, *J* = 2.5), 6.31 (dd, 1H, J_1 = 2.5 , J_2 = 8.5), 5.65 (s, 2H), 3.74 (s, 3H), 2.26 (s, br, 1H), 1.47 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.5, 154.5, 143.4, 133.4, 126.6, 124.8, 124.7, 122.4, 113.3, 106.5, 102.3, 76.1, 69.3, 55.0, 27.9, 27.8; MS (ESI): *m/z* 285 [M-OH]$^+$; Anal. Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.42; H, 5.91.

(2,2-Dimethyl-2H-thiochromen-4-yl)thiophen-3-ylmethanol (13j)

As described for **13b, 8c** (500 mg, 1.96 mmol) in THF (20ml), *n*-BuLi (1.2 ml, 1.96 mmol), thiophene 3-carboxaldehyde (197 mg, 1.76 mmol) in THF (2mL) furnished **13j** (305 mg, 54%) as viscous colorless oil, R_f = 0.52 (AcOEt/hexane, 20:80); IR (Neat): 3443, 3020, 2330, 1211, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$ +CCl_4): δ 7.22-7.16 (m, 3H), 7.12-7.11 (m, 1H), 7.02-6.88 (m, 3H), 5.98 (s, 1H), 5.68 (s, 1H), 1.96 (s, br, 1H), 1.39 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ +CCl_4): δ 144.0, 137.3, 133.3, 132.8, 130.7, 128.0, 127.5, 126.7, 125.3, 125.1, 122.4, 71.1, 40.2, 29.1, 29.0; MS (ESI): *m/z* 271 [M-OH]$^+$; Anal. Calcd. for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.54; H, 5.51.

(2,2-Dimethyl-2H-chromen-4-yl)(thiophen-3-yl)methanol (13k)

As described for **13b, 8b** (500 mg, 2.09 mmol) in THF (20ml), *n*-BuLi (1.3ml, 2.09 mmol), thiophene 3-carboxaldehyde (210 mg, 1.88 mmol) in THF (2mL) furnished **13k** (313 mg, 55%) as viscous colorless oil, R_f = 0.53 (AcOEt/hexane, 20:80); IR (Neat): 3404, 3021, 2359, 1216, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.14-7.06 (m, 3H), 6.85-6.73 (m, 2H), 5.81 (s, 1H), 5.72 (s, 1H), 2.38 (s, br, 1H), 1.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 143.2,133.4, 129.0, 127.4, 126.5, 126.1, 123.7, 122.6, 120.4, 120.1, 116.7, 75.7, 68.9, 27.7, 27.6; MS (ESI): *m/z* 255 [M-OH]$^+$; Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.67; H, 6.05.

(2, 2-dimethyl-2H-chromen-4-yl)(Phenyl) methanol (13a)

As described for **13b, 8b** (500 mg, 1.85 mmol) in THF (20ml), *n*-BuLi (1.2 ml, 1.85 mmol), benzaldehyde (176 mg, 1.66 mmol) in THF (2mL) furnished **13a** (322 mg, 58%) as viscous colorless oil, R_f = 0.56(AcOEt/hexane, 20:80); IR (Neat): 3430, 3019, 2360, 1210, 759, 669 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 1H, *J* = 1.6), 7.45 (d, 1H, *J* = 1.0), 7.41-7.29 (m, 3H), 7.12-7.03 (m, 2H), 6.83 (dd, 1H, J_1 = 1.0, J_2 = 8.0), 6.75 (m, 1H), 5.84 (d, 1H, *J* = 1.2), 5.69 (d, 1H, *J* = 2.5), 2.17 (d, 1H, *J* = 3.8), 1.50 (s, 3H), 1.50 (s, 3H); MS (ESI): *m/z* 249 [M-OH]$^+$; Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; Found: C, 81.19; H, 6.91.

(7-methoxy-2, 2-dimethyl-2H-chromen-4-yl)(5-methylfuran-2-yl) methanol (13m)

As described for **13b, 8a** (500 mg, 1.85 mmol) in THF (20ml), *n*-BuLi (1.2 ml, 1.85 mmol), 5-methyl furfural (183 mg, 1.66 mmol) in THF (2mL) furnished **13m** (312 mg, 56%) as viscous colorless oil, R_f = 0.52(AcOEt/hexane, 20:80); IR (Neat): 3432, 3023, 2360, 1213, 760, cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 (d, 1H, *J* = 8.4), 6.43 (d, 1H, *J* = 2.5), 6.36 (dd, 1H, J_1 = 2.5, J_2 = 8.5), 6.07 (d, 1H, *J* = 2.8), 5.89 (d, 1H, *J* = 2.1), 5.77 (d, 1H, *J* = 0.8), 5.65 (s, 1H), 3.77 (s, 3H), 2.31 (s, 3H), 2.17 (s, br, 1H), 1.47 (s, 6H); MS (ESI): *m/z* 283 [M-OH]$^+$; Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71; Found: C, 72.90; H, 6.59.

(3, 4-dimethoxyphenyl)(7-methoxy-2, 2, 3-trimethyl-2H-chromen-4-yl) methanol (20)

As described for **13b, 22** (500 mg, 1.76 mmol) in THF (20ml), *n*-BuLi (1.1 ml, 1.76 mmol), veratraldehyde (263 mg, 1.58 mmol) in THF (2mL) furnished **20** (379 mg, 58%) as viscous colorless oil, R_f = 0.44 (AcOEt/hexane, 20:80); IR (Neat): 3430, 3021, 2323, 1213, 759, 661 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (s, 1H), 6.96 (d, 1H, *J* = 8.6), 6.86-6.77 (m, 3H), 6. 36 (d, 1H, *J* = 2.2), 6. 24 (dd, 1H, J_1 = 2.0 , J_2 = 8.5), 5.96 (s, 1H), 3.85 (s, 6H), 3.72 (s, 3H), 1.86 (s, 3H), 1.48 (s, 3H), 1.41 (s, 3H); MS (ESI): *m/z* 353 [M-OH]$^+$; Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07; Found: C, 71.45; H, 6.96.

(1-Benzyl-2,2-dimethyl-1,2-dihydroquinolin-4-yl)thiophen-3-ylmethanol (17)

As described for **13b, 15** (500 mg, 3.06 mmol) in THF (20ml), *n*-BuLi (1.9 ml, 3.06 mmol), **16** (762 mg, 2.75 mmol) in THF (2mL) furnished **17** (631 mg, 57%) as viscous colorless oil, R_f = 0.49(AcOEt/hexane, 20:80); IR (Neat): 3433, 3021, 2359, 1210, 760, 671 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.10 (m, 7H), 7.07-7.05 (m, 1H), 6.93 (d, 1H, *J* = 6.8), 6.82-6.76 (m, 1H), 6.39 (t, 1H, *J* = 7.3), 6.22 (d, 1H, *J* = 8.2), 5.70 (s, 1H), 5.64 (s, 1H), 4.51-4.38 (m, 2H), 1.99 (s, br, 1H), 1.35 (s, 3H), 1.33 (s, 3H); MS (ESI): *m/z* 344 [M-OH]$^+$; Anal. Calcd. for $C_{23}H_{23}NOS$: C, 76.42; H, 6.41; N, 3.87. Found: C, 76.33; H, 6.56; N, 3.75.

Typical Procedure for the Oxidation of Allylic alcohols

2H-Chromen (1-Benzyl-1H-indol-2-yl) (7-methoxy-2, 2-dimethyl--4-yl) methanone (**14b**)

To a stirred solution of substrate **13b** (300 mg, 0.70 mmol) in dry ether (50 ml) at room temperature, was added activated MnO_2 (613 mg, 7.05 mmol) and the reaction was stirred for 2h. It was filtered through celite, concentrated in vacuo and was subjected to column chromatography on silica gel and elution with 10% ethyl acetate in hexane furnished the desired product **14b** (229 mg, 77%) as colorless semi solid, R_f =

0.61(AcOEt/hexane, 10:90); IR (KBr): 3018, 2920, 1614, 1276, 1142, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 1H, *J* = 8.0), 7.42-7.32 (m, 2H), 7.24-7.08 (m, 8H), 6.44-6.36 (m, 2H), 5.88 (s, 1H), 5.87 (s, 2H), 3.76 (s, 3H), 1.50 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.4, 161.1, 154.0, 140.5, 138.2, 134.9, 133.4, 132.6, 128.5, 127.2, 126.6, 126.5, 126.3, 125.8, 123.2, 121.1, 115.8, 112.3, 110.9, 107.0, 102.3, 75.7, 55.2, 48.0, 27.2. MS (ESI): *m/z* 424 $[M+1]^+$, 91 $[C_6H_5CH_2]^+$; Anal. Calcd. for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.49; H, 5.88; N, 3.40.

(1-Benzyl-1H-indol-2-yl)(7-methoxy-2, 2-dimethyl-2H-thiochromen-4-yl) methanone (14c)

As described for **14b, 13c** (300 mg, 0.68 mmol) in dry ether (50ml), MnO_2 (591 mg, 6.80 mmol) furnished **14c** (236 mg,79%) as colorless semi solid, R_f = 0.64(AcOEt/hexane, 10:90); IR (KBr): 2925, , 2358, 1710, 1594, 1210, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 1H, *J* = 7.7), 7.46-7.24 (m, 5H), 7.20-7.05 (m, 5H) , 6.90 (d, 1H, *J* = 3.6 Hz), 6.56 (dd, 1H, J_1 = 2.6 , J_2 = 3.6), 6.06 (s, 1H), 5.92 (s, 2H), 3.80 (s, 3H), 1.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.3, 159.2, 140.5, 138.3, 137.8, 135.7, 135.1, 133.9, 128.5, 128.1, 127.2, 126.6, 126.4, 125.9, 123.3, 123.2, 121.0, 116.2, 112.6, 111.6, 110.8, 55.2, 48.0, 40.8, 28.5; MS (ESI): *m/z* 440 $[M+1]^+$; Anal. Calcd. for $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.59; H, 5.82; N, 3.25.

(1-Benzyl-1H-indol-2-yl)(2,2-dimethyl-2H-chromen-4-yl)methanone (14d)

As described for **14b, 13d** (300 mg, 0.76 mmol) in dry ether (50ml), MnO_2 (659 mg, 7.59 mmol) furnished **14d** (241 mg, 81%) as colorless semi solid, R_f = 0.62(AcOEt/hexane, 10:90); IR (KBr): 3020, 2360, 1730, 1637, 1260, 1216, 761, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, 1H, *J* = 8.0), 7.43-7.39 (m, 2H), 7.28-7.7.12 (m, 9H), 6.90-6.81 (m, 2H), 6.02 (s, 1H), 5.92 (s, 2H), 1.55 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.3, 152.6, 140.6, 138.2, 134.9, 133.7, 129.9, 128.5, 127.2, 126.6, 125.9, 125.4, 123.2, 121.1, 120.9, 119.1, 117.0, 116.0, 110.9, 75.3, 48.1, 27.2; MS (ESI): *m/z* 394 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 82.35; H, 5.97; N, 3.65.

(1-Benzyl-1H-indol-2-yl)(2,2-dimethyl-2H-thiochromen-4-yl)methanone (14e)

As described for **14b, 13e** (300 mg, 0.73mmol) in dry ether (50ml), MnO_2 (633 mg, 7.29 mmol) furnished **14e** (250 mg, 84%) as colorless semi solid, R_f = 0.67(AcOEt/hexane, 10:90); IR (KBr): ν 3020, 2925, 2360, 1726, 1638, 1216,761, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, 1H, *J* = 7.8 Hz), 7.43-7.34 (m, 3H), 7.29-7.27 (m, 3H) ,7.19-7.09 (m, 6H), 7.01-6.99 (m, 1H), 6.17(s, 1H), 5.92 (s, 2H), 1.51(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.1, 140.6, 138.3, 137.8, 135.1, 132.2, 130.1, 128.5, 128.3, 127.9, 127.2, 126.9, 126.7, 126.6, 125.9, 125.4, 123.3, 121.1, 116.4, 48.0, 40.4, 28.5; MS (ESI): *m/z* 410 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{23}NOS$: C, 79.18; H, 5.66; N, 3.42. Found: C, 79.27; H, 5.71; N, 3.33 .

(1-Benzyl-1H-pyrrol-2-yl)(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)methanone (14f)

As described for **14b, 13f** (300 mg, 0.80 mmol) in dry ether (50ml), MnO_2 (695 mg, 8.00 mmol) furnished **14f** (244 mg, 81%) as colorless semi solid, R_f = 0.67 (AcOEt/hexane, 10:90); IR (KBr): 3021, 2361,1730, 1606, 1216, 1045, 761 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.17 (m, 5H), 7.11 (d, 1H, *J* = 8.4), 7.03-7.01 (m, 2H), 6.92 (dd, 1H, J_1 = 1.5 , J_2 = 3.9), 6.45-6.36 (m, 2H), 6.20-6.17 (m, 1H), 5.77 (s, 1H), 5.67 (s, 2H), 3.76 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 160.9, 154.0, 138.0, 133.3, 131.6, 130.4, 130.2, 128.5, 127.5, 127.2, 126.1, 123.5, 112.6, 198.6, 106.8, 102.2, 75.6, 55.2, 52.5, 27.3; MS (ESI): *m/z* 374 $[M+1]^+$; Anal. Calcd. for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.10; H, 6.31; N, 3.81.

(1-Benzyl-1H-pyrrol-2-yl)(7-methoxy-2,2-dimethyl-2H-thiochromen-4-yl)methanone (14g)

As described for **14b, 13g** (300 mg, 0.76 mmol) in dry ether (50ml), MnO_2 (667 mg, 7.67 mmol) furnished **14g** (253 mg,85%) as colorless semi solid, R_f = 0.66(AcOEt/hexane, 10:90); IR (KBr) :3020, 2359,1681, 1220, 759, 670 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.14 (m, 5H), 7.01-6.96 (m, 2H), 6.82 (d, 1H, *J* = 2.4), 6.77-6.75 (m, 1H), 6.55-6.49 (m, 1H), 6.14-6.11 (m, 1H), 5.89 (s, 1H), 5.64 (s, 2H), 3.75 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.5, 159.0, 138.0, 137.5, 133.7, 133.6, 131.4, 130.6, 128.5, 127.9, 127.2, 123.9, 123.4, 112.3, 111.5, 108.6, 55.2, 52.5, 40.6, 28.6; MS (ESI): *m/z* 390 $[M+1]^+$; Anal. Calcd. for $C_{24}H_{23}NO_2S$: C, 74.00; H, 5.95; N, 3.60. Found: C, 74.07; H, 5.88 ; N, 3.52.

(3,4-Dimethoxyphenyl)(7-methoxy-2,2-dimethyl-2H-chromen-4-yl)methanone (10a)

As described for **14b, 9a** (300 mg, 0.84 mmol) in dry ether (50ml), MnO_2 (732 mg, 8.42 mmol) furnished **10a** (244 mg, 82%) as colorless semi solid, R_f = 0.71(AcOEt/hexane, 10:90); IR (KBr): ν 3021, 2361, 1730, 1217,761, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, 1H, *J* = 1.8z), 7.48 (dd, 1H, J_1 = 1.8 , J_2 = 8.3) , 7.12 (d, 1H, *J* = 8.4), 6.85 (d, 1H, *J* = 8.3), 6.44-6.37 (m, 2H), 5.70 (s, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.79 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 161.0, 153.9, 153.4, 148.9, 132.5, 131.2, 129.9, 126.3, 125.3, 112.4, 111.2, 109.7, 106.9, 102.3, 75.7, 55.9, 55.8, 55.1; MS (ESI): *m/z* 355 $[M+1]^+$; Anal. Calcd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.29; H, 6.17.

(3,4-Dimethoxyphenyl)(2,2-dimethyl-2H-chromen-4-yl)methanone (10b)

As described for **14b, 9b** (300 mg, 0.92 mmol) in dry ether (50ml), MnO_2 (800 mg, 6.80 mmol) furnished **10b** (253 mg, 85%) as colorless semi solid, R_f = 0.72 (AcOEt/hexane, 10:90); IR (KBr): 3020, 2361, 1724, 1591, 1216, 760, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, 1H, *J* = 1.9), 7.50 (dd, 1H, J_1 = 2.0, J_2 = 8.3), 7.20-7.14 (m, 2H), 6.88-6.80 (m, 3H), 5.87 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 1.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 153.7, 152.5, 149.09, 133.7, 132.9, 130.0, 129.9, 125.5, 125.4, 121.0, 119.3, 117.0, 111.3, 109.9, 75.4, 56.1, 55.9, 27.3. MS(ESI): *m/z* 325 $[M+1]^+$. Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.17; H, 6.15.

(3,4-Dimethoxyphenyl)-(2,2-dimethyl-2H-thiochromen-4-yl)methanone (10c)

As described for **14b, 9c** (300 mg, 0.87 mmol) in dry ether (50ml), MnO_2 (762 mg, 8.77 mmol) furnished **10c** (235 mg, 79%) as colorless semi solid, R_f = 0.75 (AcOEt/hexane, 10:90); IR (KBr): 3021, 2361, 1732, 1268, 1217, 758, 668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 7.45 (d, 1H, J = 1.8), 7.34-7.30 (m, 2H), 7.16-7.11 (m, 2H), 7.03-6.98 (m, 1H), 6.78 (d, 1H, J=8.4), 6.01 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 195.1, 153.6, 149.1, 137.9, 136.5, 132.1, 130.2, 130.0, 128.3, 128.0, 126.9, 125.6, 125.5, 111.6, 110.0, 55.9, 55.8, 40.5, 28.6; MS (ESI): m/z 341 $[M+1]^+$; Anal. Calcd. for $C_{20}H_{20}O_3S$: C, 70.56; H, 5.92. Found: C, 70.65; H, 6.02.

(7-Methoxy-2,2-dimethyl-2H-chromen-4-yl)thiophen-3-ylmethanone (14i)

As described for **14b, 13i** (300 mg, 0.99 mmol) in dry ether (50ml), MnO_2 (863 mg, 9.93 mmol) furnished **14i** (223 mg, 75%) as colorless semi solid, R_f = 0.68 (AcOEt/hexane, 10:90); IR (KBr): 3020, 236, 1731, 1651, 1614, 1218, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (dd, 1H, J_1 = 1.1, J_2 = 2.9), 7.55 (dd, 1H, J_1 = 1.1 , J_2 = 5.0), 7.33-7.30 (m,1H), 7.26-7.23 (m, 1H), 6.41-6.37 (m, 2H), 5.86 (s, 1H), 3.77 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.2, 161.4, 154.2, 142.0, 134.2, 133.5, 131.9, 128.2, 126.5, 126.2, 112.0, 107.1, 102.6, 75.6, 55.2, 27.4; MS (ESI): m/z 301 $[M+1]^+$; Anal. Calcd. for $C_{17}H_{16}O_3S$: C,67.98; H, 5.37. Found: C, 68.06; H, 5.48.

(2,2-Dimethyl-2H-thiochromen-4-yl) thiophen-3-ylmethanone (14j)

As described for **14b, 13j** (300 mg, 1.04 mmol) in dry ether (50ml), MnO_2 (905 mg, 10.4 mmol) furnished **14j** (229 mg, 77%) as colorless semi solid , R_f = 0.65 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$): δ 7.78-7.77 (m, 1H), 7.42-7.41 (m, 1H), 7.28-7.25 (m, 1H), 7.22-7.18 (m, 2H), 7.12-7.06 (m, 1H), 7.00-6.95 (m, 1H), 6.07 (s, 1H), 1.42 (s, 6H); MS (ESI): m/z 303 $[M+NH_4]^+$; Anal. Calcd. for $C_{16}H_{14}OS_2$: C, 67.10; H, 4.93. Found: C, 67.16; H, 5.03.

(2, 2-Dimethyl-2H-chromen-4-yl)(thiophen-3-yl)methanone (14k)

As described for **14b, 13k** (300 mg, 1.10 mmol) in dry ether (50ml), MnO_2 (958 mg, 11.0 mmol) furnished **14k** (232 mg, 77%) as colorless semi solid, R_f = 0.63 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$): δ 7.90-7.89 (m, 1H), 7.51-7.49 (m, 1H), 7.28-7.25 (m, 1H), 7.22-7.18 (m, 2H), 7.12-7.06 (m, 1H), 7.00-6.95 (m, 1H), 5.92 (s, 1H), 1.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 161.0, 153.9, 153.4, 148.9, 132.5, 131.2, 129.9, 126.3, 125.3, 112.4, 111.2, 109.7, 106.9, 102.3, 75.7, 55.9, 55.8, 55.1, 27.2 ; MS (ESI): m/z 271 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 71.16; H, 5.13.

1-Benzyl-2,2-dimethyl-1,2-dihydroquinoline-4-carbaldehyde (16)

To a stirred solution of N-benzyl-2,2,4-trimethyl-1,2-dihydroquinoline (580 mg, 2.196 mmol) in anhydrous dioxane (44 ml) was added SeO_2 (365.66 mg, 3.295 mmol). It was then heated to reflux and stirred for 2 h. The mixture was filtered through celite, concentrated in vacuo and was subjected to column chromatography on silica gel and elution with 10% ethyl acetate in hexane furnished the desired product **16 (**250 mg, 41-45%) as a viscous yellow oil. R_f = 0.55 ; ^1H NMR (300 MHz, $CDCl_3$): δ 9.70 (s, 1H), 8.14 (dd, 1H, J_1 = 1.2 , J_2 = 7.7), 7.23-7.13 (m, 5H), 6.95-6.90 (m, 1H), 6.62-6.57 (m, 1H), 6.29 (d, 1H, J = 8.3), 6.20 (s, 1H), 4.45 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 151.6, 143.7, 138.9, 132.4, 130.0, 128.6, 126.7, 126.0, 125.7, 116.9, 116.7, 112.9, 57.4, 47.8, 27.3; MS (ESI): m/z 278 $[M+1]^+$; Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.19; H, 6.81; N, 4.95.

(2,2-dimethyl-2H-chromen-4-yl)(phenyl)methanone (14a)

As described for **14b, 13a** (300 mg, 1.18 mmol) in dry ether (50ml), MnO_2 (1.03 g, 11.8 mmol) furnished **14a** (235 mg, 79%) as colorless semi solid, R_f = 0.65 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$+CCl_4): δ 7.92-7.90(m, 2H), 7.63-7.58 (m, 1H), 7.50-7.45 (m, 2H), 7.30 (dd, 1H, J_1 = 1.5, J_2 = 7.6), 7.23-7.14 (m, 1H), 6.91-6.83 (m, 2H), 5.95 (s, 1H), 1.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.1, 152.6, 137.2, 135.6, 133.2, 132.8, 130.0, 129.9, 128.5, 125.7, 121.0, 119.1, 117.0, 75.4, 27.3; MS (ESI): m/z 252 $[M+1]^+$; Anal. Calcd. for $C_{17}H_{15}O_2$: C, 81.25; H, 6.02. Found: C, 81.16; H, 5.93.

(7-methoxy-2, 2-dimethyl-2H-chromen-4-yl)(thiophen-2-yl) methanone (14l)

As described for **14b, 13l** (300 mg, 0.99 mmol) in dry ether (50ml), MnO_2 (863 mg, 9.93 mmol) furnished **14l** (235 mg, 79%) as colorless semi solid, R_f = 0.65 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$): δ 7.72-7.68 (m, 2H), 7.30 (d, 1H, J = 7.9), 7.15-7.12 (m, 1H), 6.46-6.42 (m, 2H), 5.96 (s, 1H), 3.79 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.9, 161.3, 154.1, 144.0, 134.8, 134.6, 132.6, 132.0, 128.0, 126.3, 111.8, 107.1, 102.5, 75.7, 55.3, 27.2; MS (ESI): m/z 301 $[M+1]^+$; Anal. Calcd. for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 68.10; H, 5.29.

(7-methoxy-2, 2-dimethyl-2H-chromen-4-yl)(5-methylfuran-2-yl)methanone (14m)

As described for **14b, 13m** (300 mg, 1.0 mmol) in dry ether (50ml), MnO_2 (869 mg, 10.0 mmol) furnished **14m** (238 mg, 80%) as colorless semi solid, R_f = 0.69 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, 1H, J = 9.0), δ 7.04 (d, 1H, J = 3.4), 6.44-6.40 (m, 2H), δ 6.15 (d, 1H, J = 3.0), 5.94 (s, 1H), 3.76 (s, 3H), 2.42 (s, 3H), 1.50 (s, 6H); MS (ESI): m/z 299 $[M+1]^+$; Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.36; H, 5.93.

(3,4-dimethoxyphenyl)(7-methoxy-2,2,3-trimethyl-2H-chromen-4-yl)methanone (21)

As described for **14b, 20** (300 mg, 0.81 mmol) in dry ether (50ml), MnO_2 (705 mg, 8.10 mmol) furnished **14m** (226 mg, 76%) as colorless semi solid, R_f = 0.71 (AcOEt/hexane, 10:90); ^1H NMR (300 MHz, $CDCl_3$): δ 7.58(d, 1H, J = 1.58), 7.44 (dd, 1H, J_1 = 1.7, J_2 = 8.3), 6.80 (d, 1H, J = 8.4), 6.59 (d, 1H, J = 8.4), 6.40 (d, 1H, J = 2.4), 6.27 (dd, 1H, J_1 = 2.5, J_2 = 8.5), 3.94 (s, 3H), 3.91 (s, 3H) , 3.74 (s, 3H), 1.67 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ95.9, 160.3, 153.8, 152.7, 149.3, 131.2, 129.9, 129.5, 125.4, 125.2, 114.5, 110.2, 107.0, 78.4, 55.9, 55.8, 55.0, 25.4, 15.6; MS (ESI): m/z 369 $[M+1]^+$; Anal.

Calcd. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.63; H, 6.68.

Typical Procedure for the Aromatic Nazarov cyclization

11-Benzyl-3-methoxy-6,6-dimethyl-6a,11-dihydro-6H,12aH-5-oxa-11-azabenzo[5,6]pentaleno[2,1-b]naphthalen-12-one(15b)

To a stirred solution of substrate **14b** (200 mg, 0.47 mmol) in anhydrous DCM (20 ml) at room temperature, was added triflic acid (CF_3SO_3H, 0.04 ml, 0.47 mmol) at the same temperature and was stirred vigorously till the completion of reaction. It was then neutralized by saturated Na_2CO_3 solution at 0^{o}C, extracted with DCM (3 × 10 ml), dried over anhydrous Na_2SO_4. After the evaporation, the residue was subjected to column chromatography on silica gel and elution with 10% ethyl acetate in hexane furnished the cyclized product **15b** (180 mg, 90%) as colorless semi solid, R_f = 0.51 (AcOEt/hexane, 10:90); IR (KBr): 1716, 1217 ,1027, 766 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, 1H, *J* = 8.2), 7.73 (dd, 1H, J_1 = 0.5 , J_2 = 8.6), 7.42-7.33 (m, 2H), 7.26-7.18 (m, 6H), 6.64 (dd, 1H, J_1 = 2.5, J_2 = 8.5), 6.48 (d, 1H, *J* = 2.5), 5.62 (d, 1H, *J* = 15.7), 5.52 (d, 1H, *J* = 15.6), 4.03 (d, 1H, *J* = 5.9), 3.91 (d, 1H, *J* = 5.9), 3.77 (s, 3H), 1.78 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 159.6, 153.3, 144.0, 141.8, 138.4, 137.1, 129.9, 128.7, 127.6, 127.1, 126.8, 123.2, 122.5, 120.9, 113.1, 112.0, 107.8, 102.5, 77.9, 55.2, 50.7, 47.5, 43.6, 29.0, 21.7 . MS (ESI): *m/z* 424[M+1]$^+$, 91 [$C_6H_5CH_2$]$^+$; Anal. Calcd. for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.37; H, 5.88; N, 3.39.

11-Benzyl-3-methoxy-6,6-dimethyl-6a,11-dihydro-6H,12aH-5-thia-11-azabenzo[5,6]pentaleno[2,1-b]naphthalen-12-one (15c)

As described for **15b, 14c** (200 mg, 0.45 mmol) in anhydrous DCM (20ml), triflic acid (0.04 ml,0.45 mmol) furnished **15c** (184 mg, 92%) as colorless white solid, m.p. 165-170 ^{o}C; R_f = 0.53 (AcOEt/hexane, 10:90); IR (KBr): 2926, 2361, 1692, 1594, 1216, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, 1H, *J* = 8.0), 7.63 (d, 1H, *J* = 9.2), 7.41-7.32 (m, 2H), 7.27-7.17 (m, 6H), 6.82-6.78 (m, 2H), 5.63 (d, 1H, *J* = 15.8), 5.53(d, 1H, *J* = 15.9), 4.19 (d, 1H, *J* = 5.9), 4.08 (d, 1H, *J* = 6.0), 3.79 (s, 3H), 1.58 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.4, 158.4, 143.9, 141.5, 138.9, 137.1, 134.4, 131.2, 128.6, 127.6, 127.2, 126.6, 125.2, 124.2, 123.1, 120.9, 113.4, 111.9, 111.8, 57.2, 55.2, 49.2, 47.6, 47.5, 26.0; MS (ESI): *m/z* 440 [M+1]$^+$; Anal. Calcd. for $C_{28}H_{25}NO_2S$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.59; H, 5.81; N, 3.11.

11-Benzyl-6,6-dimethyl-6a,11-dihydro-6H,12aH-5-oxa-11-azabenzo[5,6]pentaleno[2,1-b]naphthalene (15d)

As described for **15b, 14d** (200 mg, 0.50 mmol) in anhydrous DCM (20ml), triflic acid (0.045 ml,0.50 mmol) furnished **15d** (183 mg, 92%) as colorless white solid, m.p. 160-165 ^{o}C; R_f =0.56 (AcOEt/hexane, 10:90); IR (KBr): 2923, 2855, 2361, 1692, 1461, 1217, 759, cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.80 (m, 2H), 7.42-7.34 (m, 2H), 7.26-7.15 (m, 7H) , 7.06-7.01 (m, 1H) ,6.90 (dd, 1H, J_1 = 0.9 , J_2 = 8.0), 5.63 (d, 1H, *J* = 15.6), 5.53 (d, 1H, *J* = 15.7), 4.09 (d, 1H, *J* = 5.8), 3.93 (d, 1H, *J* = 6.0), 1.79 (s, 3H), 0.70 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3, 152.4, 144.1, 141.9, 138.3, 137.0, 129.3, 128.7, 127.9, 127.6, 127.1, 126.8, 123.2, 122.5, 121.1, 121.0, 122.0, 77.6, 51.1, 47.5, 43.7, 29.0, 21.6; MS (ESI): *m/z* 394 [M+1]$^+$; Anal. Calcd. for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 82.38; 5.95; N, 3.63

11-Benzyl-6,6-dimethyl-6a,11-dihydro-6H,12aH-5-thia-11-azabenzo[5,6]pentaleno[2,1-b]naphthalen-12-one (15e)

As described for **15b, 14e** (200 mg, 0.48 mmol) in anhydrous DCM (20ml), triflic acid (0.04 ml,0.48 mmol) furnished **15e** (182 mg, 91%) as colorless semi solid, R_f = 0.58 (AcOEt/hexane, 10:90); IR (KBr): 3020, 2360,1691, 1595, 1216, 761, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 1H, *J* = 8.0), 7.71 (d, 1H, *J* = 6.8) , 7.42-7.33 (m, 2H), 7.24-7.18 (m, 9H), 5.63 (d, 1H, *J* = 15.6), 5.54 (d, 1H, *J* = 15.6), 4.24 (d, 1H, *J* = 6.0), 4.11 (d, 1H, *J* = 6.0), 1.57 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.9, 143.9, 141.6, 139.0, 137.1, 133.4, 133.1, 130.4, 128.7, 128.5, 127.6, 127.2, 127.1, 126.7, 125.5, 124.2, 123.1, 120.9, 111.9, 57.9, 49.4, 47.5, 29.6, 26.0; MS (ESI): *m/z* 410 [M+1]$^+$; Anal. Calcd. for $C_{27}H_{23}NOS$: C, 79.18; H, 5.66; N,3.42. Found: C, 79.30; H, 5.75; N, 3.35.

(9-Benzyl-3-methoxy-6,6-dimethyl-6a,9-dihydro-6H,10aH-5-oxa-9-azapentaleno[2,1-a]naphthalen-10-one (15f)

As described for **15b, 14f** (200 mg, 0.53 mmol) in anhydrous DCM (20ml), triflic acid (0.045 ml,0.53 mmol) furnished **15f** (170 mg, 85%) as colorless semi solid, R_f =0.49 (AcOEt/hexane, 10:90); IR (KBr): 3020, 2361, 1709, 1216, 1104, 761 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, 1H, *J* = 8.6), 7.30-7.21 (m, 5H), 7.01 (d, 1H, *J* = 2.4), 6.58 (dd, 1H, J_1 = 2.5 , J_2 = 8.4), 6.40 (d, 1H, *J* = 2.4), 6.17 (d, 1H, *J* = 2.3), 5.30 (d, 1H, *J* = 14.7), 5.20 (d, 1H, *J* = 14.6), 3.93 (d, 1H, *J* = 6.2), 3.77 (s, 3H), 3.49 (d, 1H, *J* = 6.2 Hz), 1.50 (s, 3H), 1.01 (s, 3H); MS (ESI): *m/z* 374 [M+1]$^+$;Anal. Calcd. for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.26; H, 6.14; N, 3.86.

9-Benzyl-3-methoxy-6,6-dimethyl-6a,9-dihydro-6H,10aH-5-thia-9-azapentaleno[2,1-a]naphthalen-10-one (15g)

As described for **15b, 14g** (200 mg, 0.51 mmol) in anhydrous DCM (20ml), triflic acid (0.045 ml,0.51 mmol) furnished **15g** (175 mg, 88%) as colorless semi solid, R_f =0.53 (AcOEt/hexane, 10:90); IR(KBr) 3021, 2360, 1731, 1218, 763, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 1H), 7.33-7.25 (m, 5H), 7.05 (d, 1H, *J* = 2.4), 6.81-6.74 (m, 2H), 6.20 (d, 1H, *J* = 2.4), 5.32 (d, 1H, *J* = 14.8), 5.18 (d, 1H, *J* = 14.7), 4.09 (d, 1H, *J* = 6.7), 3.78 (s, 3H), 3.65 (d, 1H, *J* = 6.3), 1.46 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.8, 158.2, 150.3, 137.0, 134.4, 133.9, 133.9, 131.2, 128.8, 127.9, 124.8, 113.5, 111.9, 107.3, 56.8, 55.2, 50.9, 48.7, 46.1, 29.0, 25.9; MS (ESI): *m/z* 390 [M+1]$^+$; Anal. Calcd. for $C_{24}H_{23}NO_2S$: C, 74.00; H, 5.95; N, 3.60. Found: C, 74.08; H, 6.02; N, 3.53.

9-Benzyl-6,6-dimethyl-6a,9-dihydro-6H,10aH-5-oxa-9-azapentaleno[2,1-a]naphthalen-10-one (15h)

As described for **15b, 14h** (200 mg, 0.58 mmol) in anhydrous DCM (20ml), triflic acid (0.046 ml,0.58 mmol) furnished **15h** (174 mg, 87%) as colorless semi solid, R_f =0.45(AcOEt/hexane, 10:90); IR (KBr): 3021, 2361, 1667, 1595, 1216, 763, 670 cm^{-1} ;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 1H, *J* = 7.6), 7.30-7.21 (m, 5H), 7.16-7.11 (m, 1H), 7.03-6.96 (m, 2H), 6.83 (dd, 1H, J_1 = 1.0 , J_2 = 8.1), 6.18 (d, 1H, *J* = 2.4), 5.31 (d, 1H, *J* = 14.8), 5.21 (d, 1H, *J* = 14.7), 3.99 (d, 1H, *J* = 6.2), 3.52 (d, 1H, *J* = 6.2), 1.51 (s, 3H), 1.00 (s, 3H). MS (ESI): *m/z* 344 $[M+1]^+$; Anal. Calcd for $C_{23}H_{21}$ NO_2: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.56; H, 6.28; N,3.98.

3,8,9-Trimethoxy-6,6-dimethyl-6a,11a-dihydro-6H-indeno[1,2-c]chromen-11-one (12a)

As described for **15b, 10a** (200 mg, 0.56 mmol) in anhydrous DCM (20ml), triflic acid (0.05 ml,0.56 mmol) furnished **12a** (180 mg, 90%) as colorless semi solid, R_f =0.64 (AcOEt/hexane, 10:90); IR (KBr): 3018, 2925, 2360, 1708, 1591, 1462, 1219, 1035, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+CCl_4): δ 7.65 (d, 1H, *J* = 8.5), 7.24 (s, 1H), 6.98 (s, 1H), 6.61 (dd, 1H, J_1 = 2.5 , J_2 = 8.5) , 6.41 (d, 1H, *J* = 2.5), 4.00 (s, 3H), 3.94 (s, 3H), 3.77 (s, 3H), 3.66 (d, 1H, *J* = 5.9), 3.59 (d, 1H, *J* = 5.9), 1.67 (s, 3H), 0.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 201.2, 159.6, 154.9, 153.1, 150.2, 147.0, 130.4, 129.8, 112.4, 107.9, 107.8, 105.0, 102.3, 56.2, 56.1, 55.1, 47.3, 46.7, 28.4, 20.6; MS (ESI): *m/z* 355 $[M+1]^+$; Anal. Calcd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.25; H, 6.34.

(8,9-Dimethoxy-6,6-dimethyl-6a,11a-dihydro-6H-indeno[1,2-c]chromen-11- one (12b)

As described for **15b, 10b** (200 mg, 0.61 mmol) in anhydrous DCM (20ml), triflic acid (0.05 ml,0.61mmol) furnished **12b** (182 mg, 91%) as colorless semi solid, R_f =0.65 (AcOEt/hexane, 10:90); IR (KBr): 3020, 2360, 1710, 1591, 1219, 1032, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (dd, 1H, J_1 = 1.1 , J_2 = 7.6), 7.28 (s, 1H), 7.21-7.15 (m, 1H), 7.05 (dd, 1H, J_1 = 1.1 , J_2 = 7.4), 7.01 (s, 1H), 6.90-6.87 (m, 1H), 4.01 (s, 3H), 3.94 (s, 3H), 3.72 (d, 1H, *J* = 5.9), 3.67 (d, 1H, *J* = 5.9), 1.70 (s, 3H), 0.56 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.0, 154.8, 152.2, 150.0, 147.1, 129.8, 129.5, 127.8, 121.1, 120.2, 117.1, 107.8, 104.9, 77.2, 56.3, 56.1, 47.2, 47.1, 28.3, 20.4; MS (ESI): *m/z* 325$[M+1]^+$; Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 73.95; H, 6.13.

8,9-Dimethoxy-6,6-dimethyl-6a,11a-dihydro-6H-5-thiabenzo[a]fluoren-11-one (12c)

As described for **15b, 10c** (200 mg, 0.58 mmol) in anhydrous DCM (20 ml), triflic acid (0.046 ml,0.58 mmol) furnished **12c** (173 mg, 87%) as colorless semi solid, R_f = 0.67 (AcOEt/hexane, 10:90); IR (KBr): 3021, 2360, 1730, 1217, 1044, 764 cm^{-1}; ^{1}H NMR (300 MHz,$CDCl_3$+CCl_4): δ 7.75 (d, 1H, *J* = 7.5), 7.25-7.12 (m, 4H), 6.97 (s, 1H), 4.00 (s, 3H), 3.94 (s, 3H) , 3.89 (d, 1H, *J* = 5.9), 3.86 (d, 1H, *J* = 5.9), 1.54 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$+CCl_4): δ 200.2, 154.4, 150.2, 146.2, 132.7, 131.5, 131.0, 129.8, 127.8, 125.3, 109.0, 104.7, 56.2, 56.0, 53.1, 52.1, 45.7, 28.58, 24.0; MS (ESI): *m/z* 341 $[M+1]^+$;Anal. Calcd. for $C_{20}H_{20}O_3S$: C, 70.56; H, 5.92. Found: C, 70.44; H, 6.01.

3-Methoxy-6,6-dimethyl-6a,10a-dihydro-6H-5-oxa-7-thiapentaleno[2,1-a]naphthalen-10-one (15i)

As described for **15b, 14i** (200 mg, 0.67 mmol) in anhydrous DCM (20ml), triflic acid (0.06 ml,0.67 mmol) furnished **15i** (168 mg, 84%) as colorless semi solid, R_f =0.48 (AcOEt/hexane, 10:90); IR (KBr): 3019, 2360, 1714, 1584, 1215, 760, 669 cm^{-1} ; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, 1H, J_1 = 0.6 , J_2 = 8.5), 7.29 (d, 1H, *J* = 5.0), 7.13 (d, 1H, *J* = 5.2), 6.51 (dd, 1H, J_1 = 2.5 , J_2 = 8.5), 6.30 (d, 1H, *J* = 2.5), 3.93 (d, 1H, *J* = 6.5), 3.71 (d, 1H, *J* = 6.6), 3.68 (s, 3H), 1.51 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 166.7, 159.7, 152.9, 146.1, 131.0, 129.8, 120.3, 111.7, 108.3, 102.6, 76.0, 55.1, 51.2, 47.2, 27.2, 22.5; MS (ESI): *m/z* 301 $[M+1]^+$. Anal. Calcd. for $C_{17}H_{16}O_3$ S : C, 67.98; H, 5.37; . Found: C, 68.07; H, 5.31.

6,6-Dimethyl-6a,11a-dihydro-6H,7H-5,8-dithiacyclopenta[b]phenanthren-11-one (15j)

As described for **15b, 14j** (200 mg, 0.70 mmol) in anhydrous DCM (20ml), triflic acid (0.062 ml, 0.70 mmol) furnished **15j** (176 mg, 88%) as colorless semi solid, m.p.95-100^{o}C; Yield: 88%, R_f =0.47 (AcOEt/hexane, 10:90); IR (KBr): 3015, 2351, 1704, 1586, 1219, 760, 669 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, 1H, *J* = 7.5), 7.27 (d, 1H, *J* = 5.0), 7.17-7.04 (m, 4H), 4.13 (d, 1H, *J* = 6.6), 3.87 (d, 1H, *J* = 6.6), 1.44 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 167.1, 146.7, 132.1, 131.0, 130.8, 130.3, 128.4, 127.0, 125.7, 120.1, 57.1, 52.3, 44.5, 28.3, 25.4; MS (ESI): *m/z* 303 $[M+NH_4]^+$; Anal. Calcd. for $C_{16}H_{14}OS_2$: C, 67.10; H, 4.93. Found: C, 67.02; H, 5.01.

6,6-Dimethyl-6a,10a-dihydro-6H-5-oxa-7-thiapentaleno[2,1-a]naphthalen-10-one (15k)

As described for **15b, 14k** (200 mg, 0.74 mmol) in anhydrous DCM (20ml), triflic acid (0.065 ml, 0.74 mmol) furnished **15k** (162 mg, 81%) as colorless white solid, m.p. 170-175 ^{o}C ; R_f = 0.46 (AcOEt/hexane, 10:90); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, 1H, *J* = 7.6), 7.38 (d, 1H, *J* = 5.7), 7.21 (d, 1H, *J* = 5.0), 7.17-7.12 (m, 1H), 7.06-6.98 (m, 1H), 6.88 (dd, 1H, J_1 = 1.1, J_2 = 8.0), 4.09 (d, 1H, *J* = 6.5), 3.83 (d, 1H, *J* = 6.5), 1.60 (s, 3H), 0.98 (s, 3H) ;^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 167.1, 152.1, 145.9, 131.3, 129.2, 128.1, 121.5, 120.1, 119.8, 117.5, 75.9, 51.58, 47.23, 27.1, 22.4 ; MS (ESI): *m/z* 271 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22. Found: C, 70.95; H, 5.11.

5-Benzyl-6,6-dimethyl-5,6,6a,10a-tetrahydro-7-thia-5-azapentaleno[2,1-a]naphthalen-10-one (19)

As described for **15b, 18** (200 mg, 0.56 mmol) in anhydrous DCM (20ml), triflic acid (0.05 ml, 0.56 mmol) furnished **19** (170 mg, 85%) as dark solid, m.p.100-105^{o}C; R_f= 0.49 (AcOEt/hexane, 10:90); IR (Neat): 3021, 2360, 1731, 1216, 761, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, 1H, *J* = 7.4), 7.37 (d, 1H, *J* = 5.1), 7.28-7.16 (m, 6H), 7.02-6.97 (m, 1H), 6.83-6.78 (m, 1H), 6.45 (d, 1H, *J* = 8.2), 4.59 (d, 1H, *J* = 17.5), 4.37 (d, 1H, *J* = 17.5), 4.24 (d, 1H, *J* = 6.5), 3.82 (d, 1H, *J* = 6.5), 1.43 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.2, 168.2, 146.8, 144.2, 140.2, 131.0, 129.2, 128.5, 127.7, 126.6, 126.0, 120.3, 118.6, 118.1, 114.3, 56.4, 53.8, 51.4, 49.4, 25.0, 24.2; MS (ESI): *m/z* 360 $[M+1]^+$; Anal. Calcd. for $C_{23}H_{21}$ NOS: C, 76.84; H, 5.89; N, 3.90. Found: C, 76.93; H, 5.97; N, 4.01.

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