Tetrahedron Letters 52 (2011) 5951–5955

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

An efficient synthesis of 6*H*,7*H*-chromeno[4,3-*b*]chromenes and 6,7-dihydrothio chromeno[3,2-*c*]chromenes as 9-substituted xanthene like analogs ☆

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ARTICLE INFO

Article history:
Received 22 June 2011
Revised 20 August 2011
Accepted 23 August 2011
Available online 5 September 2011

ABSTRACT

An efficient synthetic route with good overall yields to access 7-aryl/heteroaryl/alkyl substituted 6*H*,7*H*-chromeno[4,3-*b*]chromene, and 6,7-dihydrothiochromeno[3,2-*c*]chromene scaffolds has been developed. The route to these xanthene-like analogs involves a three-step reaction sequence: (1) Michael addition of readily available phenol and thiophenol to 4-chloro-2,2-dimethyl-2*H*-chromene-3-carbaldehyde, (2) Grignard reaction of different aryl, heteroaryl and alkyl magnesium bromides on the resulting carbaldehydes followed by (3) $FeCl_3$ catalyzed spontaneous intramolecular Friedel–Craft's reaction on the diarylmethyl carbinols.

Xanthenes and related compounds have been of significant interest because of their broad spectrum of pharmaceutical importance, such as analgesic,[1] anti-bacterial,[2] anti-inflammatory,[3] and anti-viral activities.[4] These compounds are being used as antagonists for the paralyzing action of zoxazolamine[5] and in photodynamic therapy (PDT).[6] Many benzoxanthene derivatives are potent nonpeptidic inhibitors of recombinant human calpain I,[7] and novel CCR1 receptor antagonists.[8] It is also worth mentioning that xanthenes and the related condensed ring systems are being used as dyes and fluorescent materials because of their useful spectroscopic properties.[9] Examples include fluorescein, rosamine, and fluorone (Fig. 1). Fluorone derivatives have wide applications, such as in the detection of a variety of metal ions,[10] sugars,[11] phosphorylated molecules,[12] HIV-1 nucleocapsid protein,[13] reactive oxygen species,[14] in screening assays for mitochondrial permeability,[15] telomerase inhibition,[16] and acetylcholinesterase inhibition.[17] Furthermore, these heterocycles have also been utilized in laser technologies,[18] as pH sensitive fluorescent materials for the visualization of biomolecules,[19] cosmetics, potential agrochemicals, pigments.[20] Moreover, this prototype is also common in several bioactive natural products.[21]

The importance and utility of this family of compounds have led to the development of several synthetic strategies for accessing xanthene scaffolds.[22] Very recently, some elegant synthetic protocols for xanthones have been reported. Larock and co-workers[23] reported an aryl to imidoyl palladium migration involving intramolecular C–H activation to access xanthone skeletons. Domínguez and co-workers[24] employed Cu-mediated intramolecular *O*-arylation of *o*-halobenzophenones and applied S_NAr reactions with KOH as base under aqueous condition to synthesize xanthone scaffolds.

Careful analysis of reaction conditions suggests that the above methods have several drawbacks, such as the use of unfavorable reaction conditions (strong acidic media with high temperature), stoichiometric amounts of reaction promoters, and the moisture sensitiveness of the reported catalysts. This warrants new, ample scope for the development of new synthetic protocols toward xanthene scaffolds. We are currently engaged in the design and synthesis of symmetrical and unsymmetrical trisubstituted methanes (TRSMs) for the development of new anti-tubercular and anti-cancer agents by intermolecular diarylmethylation of electron-rich

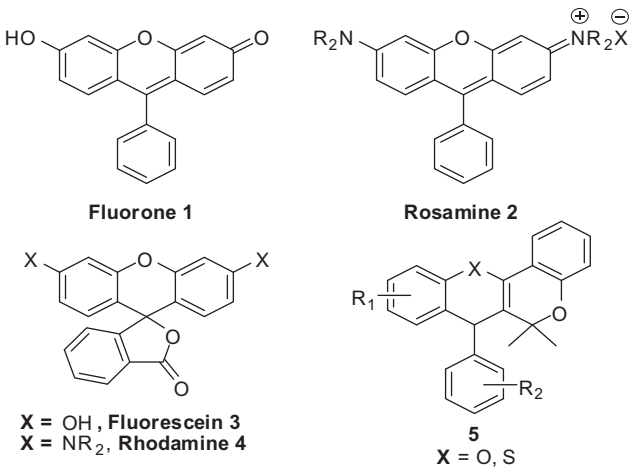

Figure 1. Structures of some common xanthene dyes (**1**–**4**) and target molecule (**5**).

☆ CDRI communication number 8119.

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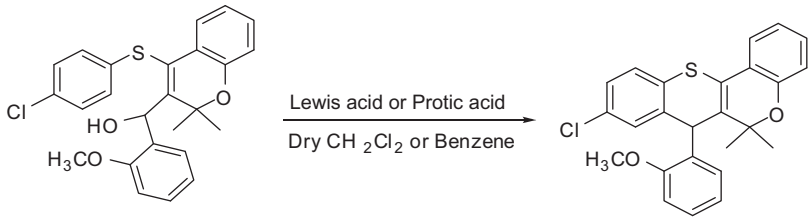
doi:10.1016/j.tetlet.2011.08.127

Table 1
Optimization studies for the synthesis of **11i.**



10i **11i**

Entry	Catalyst	Conditions	Yield[a] (%)
1	Conc. H_2SO_4 (Catalytic)	Dry benzene, reflux, 20 min	32
2	Anhyd. $AlCl_3$ (1.2 equiv)	Dry CH_2Cl_2, 0 °C to rt, 12 min	51
3	TfOH (10 mol %)	Dry CH_2Cl_2, 0 °C to rt, 10 min	45
4	Anhyd. $FeCl_3$ (1.2 equiv)	Dry CH_2Cl_2, 0 °C to rt, 2–5 min	68
5	$Sc(OTf)_3$ (10 mol %)	Dry CH_2Cl_2, 0 °C to rt, 12 min	52
6	Anhyd. $FeCl_3$ (10 mol %)	Dry CH_2Cl_2, 0 °C to rt, 2–5 min	77
7	BF_3–OEt_2 (10 mol %)	Dry CH_2Cl_2, 0 °C to rt, 8 min	48

[a] Isolated yield of **11i** after silica gel column chromatography.

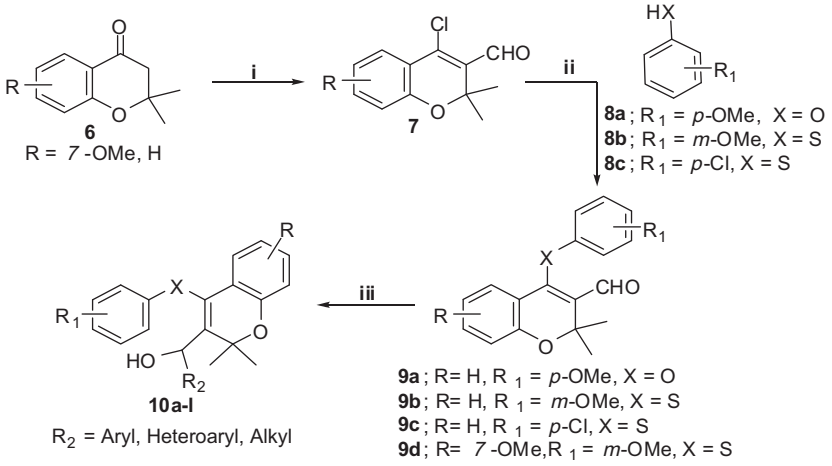
arenes using diaryl carbinols as alkylating agents.[25,26] In continuation, we became interested in synthesizing 9-substituted xanthenes as conformationally constrained triarylmethanes (TRAMs) for which not many methods are available.[27,28] In this context, we envision a versatile and efficient method of synthesizing xanthene motifs like **5** with distinct skeletal frameworks involving Grignard reaction and Lewis acid catalyzed intramolecular Friedel–Craft's arylation as the key synthetic steps (Scheme 1).

The requisite aryl, heteroaryl, and alkyl substituted methanols **10a–l** were synthesized by the reaction between Grignard reagents, generated from commercially available aryl, heteroaryl and alkyl bromo derivatives, and carbaldehydes **9a–d,** which in turn were easily generated from the intermolecular Michael addition[29] of phenols or thiophenols **8a–c** on 4-chloro-2,2-dimethyl-2*H*-chromene-3-carbaldehydes **7** with 65–71% yields. The carbaldehyde **7** was readily synthesized from corresponding 4-chromanone **6** via the Vilsmeier–Haack–Arnold reaction[30] (Scheme 1).

In our initial endeavor, we examined the cyclization reaction of carbinol **10i** to the corresponding xanthene derivative **11i** in the presence of conc. H_2SO_4 (Table 1, Entry 1). Thus, a solution of **10i** in dry benzene along with a catalytic amount of conc. H_2SO_4 was heated at reflux temperature, leading to partial decomposition of the starting material and hence the yield of the expected product was only 32%. To further improve the yield and optimize the standard reaction conditions, the same reaction was carried out in the presence of several protic and Lewis acid catalysts, such as TfOH, anhydrous $AlCl_3$, BF_3–OEt_2, and $Sc(OTf)_3$. Finally, it was found that **10i** could be transformed into **11i** in high yield by treating a solution of **10i** in dry CH_2Cl_2 at 0 °C to rt using a catalytic amount of anhydrous $FeCl_3$ (10 mol %) (Entry 6).[32]

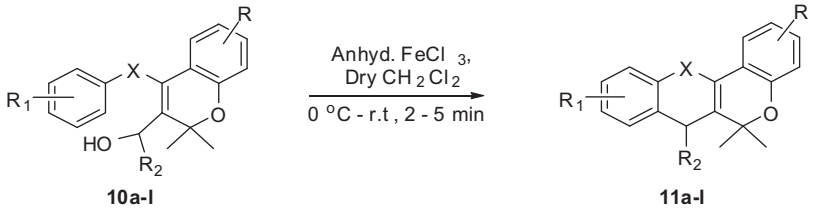
On the basis of these facts and the above optimization protocols, we treated all the resulting diarylmethyl carbinols **10a–l** with $FeCl_3$ (10 mol %) in anhydrous dichloromethane (CH_2Cl_2) at 0 °C to rt to furnish the corresponding desired substituted xanthene scaffolds **11a–l** (Table 2).[31]

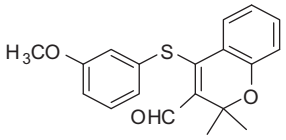
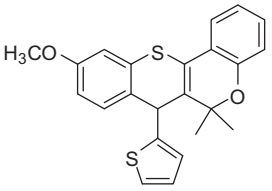
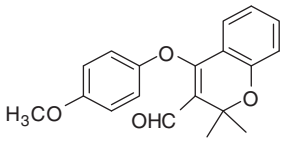
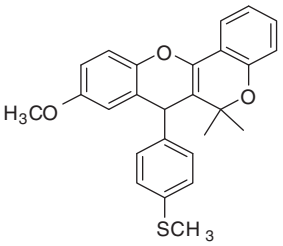
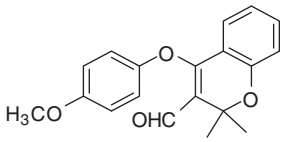
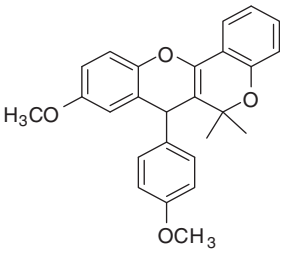
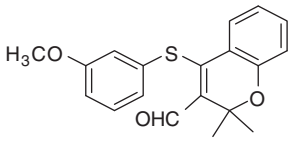
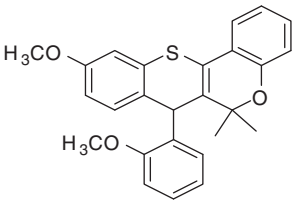
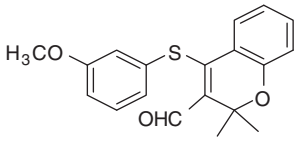
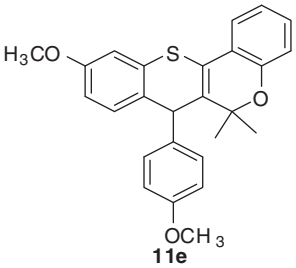
After optimizing the reaction conditions and with final products at hand, we explored the conversion of carboxaldehydes **9a** and **9b** directly to indole containing xanthene like scaffolds (compounds **11m** and **11n**) through a one-pot scalable synthetic step. Toward this objective, the carbaldehydes **9a–b** on reaction with $POCl_3$ and indole in dry CH_2Cl_2 furnished **11m** and **11n**[33] in 55% and 64% yield, respectively (Scheme 2). However, this reaction was performed two times on gram scale (**9a**: 3.544 mmol, 54% and 3.705 mmol, yield: 52%; **9b**: 3.676 mmol, yield: 53%, and 3.060 mmol, yield: 56%) and the yield varies from 52–56%. In this reaction, a small amount of the unsubstituted side products **12m** and **12n** were also formed through $FeCl_3$ catalyzed carbon–carbon bond cleavage[27,28] (9 and 17% respectively).



Scheme 1. Reagents and conditions: (i) $POCl_3$, dry DMF, 0 °C to rt, 72–75% (ii) NaH, dry THF, 0 °C to rt, 2–3 h, 65–71%; (iii) R_2-Br, Mg/I_2, dry THF, rt, 1 h, 62–71%.

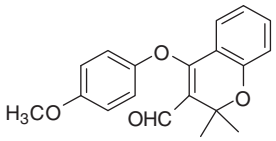
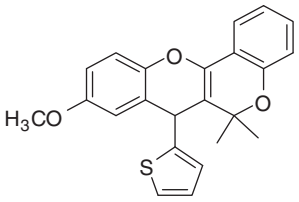
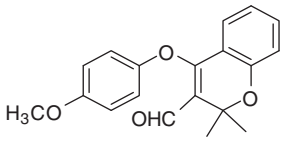
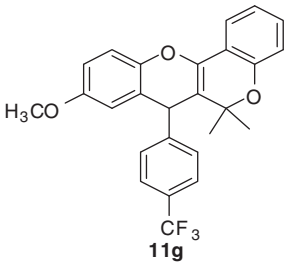
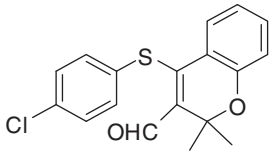
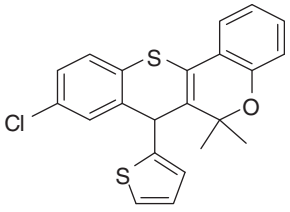
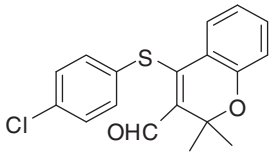
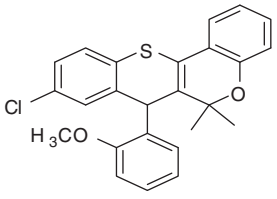
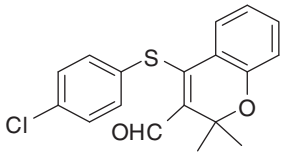
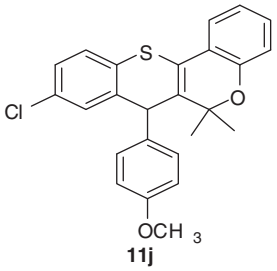
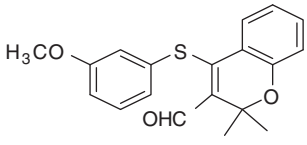
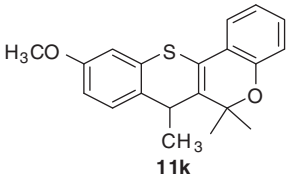
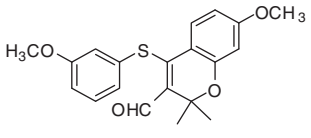
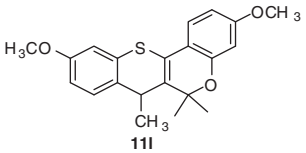
Table 2
Synthesis of unsymmetrical 9-substituted xanthene like scaffolds **11a–l**



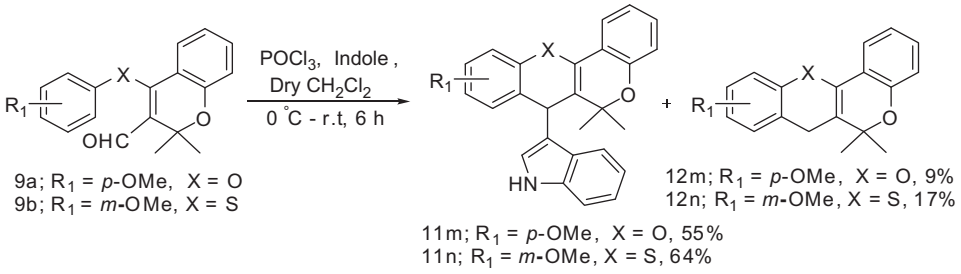
Entry	Aldehydes	Alcohols, Yield (%)	Products	Yield (%)
1		10a, 68	 **11a**	73
2		10b, 63	 **11b**	58
3		10c, 65	 **11c**	71
4		10d, 62	 **11d**	66
5		10e, 64	 **11e**	67

(*continued on next page*)

Table 2 (*continued*)

Entry	Aldehydes	Alcohols, Yield (%)	Products	Yield (%)
6		10f, 66	 **11f**	63
7		10g, 63	 **11g**	59
8		10h, 68	 **11h**	55
9		10i, 70	 **11i**	77
10		10j, 71	 **11j**	61
11		10k, 65	 **11k**	63
12		10l, 67	 **11l**	56

In conclusion, we have demonstrated a convenient and efficient synthetic procedure for the synthesis of structurally diverse 6*H*,7*H*-chromeno[4,3-*b*]chromenes and 6,7-dihydrothiochromeno[3,2-*c*]chromene in good overall yields. Synthesis of these 9-substituted xanthene like heteroatoms containing scaffolds employed a Grignard reaction followed by a Lewis acid catalyzed intramolecular Friedel–Craft's reaction. These diverse xanthene like skeletons may have new interesting biological properties.



Scheme 2. Reagents and conditions: (a) $POCl_3$ (1.5 mol %), dry CH_2Cl_2, 0 °C to rt, 6 h, 55–64%.

Acknowledgments

This research project was partly supported by ICMR and DST, New Delhi, India. Sudipta and Maloy thank the Council of Scientific and Industrial Research (CSIR), India for research fellowships. Instrumental facilities from SAIF, CDRI is acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.127.

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31. *Selected spectral data with experimental procedures.*
Typical procedure for Friedel–Craft's reaction to access 6*H*,7*H*-chromeno[4,3-*b*]chromenes and 6,7-dihydrothiochromeno[3,2-*c*]chromenes:
To a 0.025 molar solution of diarylmethyl carbinol in anhydrous CH_2Cl_2, a catalytic amount (10 mol %) of anhydrous $FeCl_3$ was added at 0 °C and was stirred for 2–5 min. After completion of the reaction water was added and the resulting mixture was extracted with CH_2Cl_2. The crude reaction mixture was purified by silica gel column chromatography (AcOEt/hexane, 4:96) to generate the desired products.
32. 9-chloro-7-(2-methoxyphenyl)-6,6-dimethyl-6,7-dihydro thiochromeno[3,2-*c*]chromene **11i**:
A mixture of carbinol **10i** (115 mg, 0.261 mmol) and $FeCl_3$ (4.233 mg, 0.026 mmol) furnished the product **11i** as a viscous pink oil (yield: 77%, 85 mg). R_f = 0.5 (10% AcOEt/hexane); IR (Neat): 3449, 3070, 2928, 2365, 1597, 1482, 1243, 1031, 764, 672 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.62–7.48 (m, 3H), 7.23–7.12 (m, 4H), 7.09–6.94 (m, 1H), 6.87–6.77 (m, 3H), 5.39 (s, 1H), 3.96 (s, 3H), 1.42 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 155.2, 151.8, 138.0, 132.0, 131.9, 130.6, 129.6, 129.2, 128.8, 128.5, 128.4, 127.8, 126.5, 124.2 123.6, 121.1, 121.0, 116.7, 110.8; 79.6, 55.4, 40.2, 26.0, 25.7. MS (ESI): *m*/*z* 421.2 $[M+1]^+$; Anal. Calcd. for $C_{25}H_{21}ClO_2S$: C, 71.33; H, 5.03. Found C, 71.46; H, 5.15.
33. *3-(10-methoxy-6,6-dimethyl-6,7-dihydrothiochromeno [3,2-c] chromen-7-yl)-1H-indole* ***11n*****:**
To a stirred solution of **9b** (116 mg, 0.355 mmol) in dry CH_2Cl_2 (8 mL) were added indole (63 mg, 0.532 mmol) in dry CH_2Cl_2 (8 mL) and $POCl_3$ (0.005 mmol, 0.481 mL) at 0 °C and the mixture was stirred at room temperature until completion of the reaction (as observed on TLC). After completion of the reaction, the mixture was poured into ice-water and extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. The reaction mixture was concentrated in vauco and purified by silica gel column chromatography (AcOEt/hexane, 10:90), furnished **11n** as a viscous brownish oil (64%, 97 mg). R_f = 0.4 (15% AcOEt/hexane); IR (Neat): 3483, 2924, 2854, 1638, 1487, 1458, 1218, 1035, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ_H 7.87 (br s, 1H), 7.82–7.79 (m, 1H), 7.56–7.52 (m, 1H), 7.46 (d, 1H, *J* = 8.51 Hz), 7.26–7.18 (m, 3H), 7.15–7.09 (m, 2H), 6.99–6.94 (m, 1H), 6.89–6.85 (m, 2H), 6.77–6.74 (m,1H), 5.09 (s, 1H), 3.71 (s, 3H), 1.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 157.9, 151.6, 136.5, 133.7, 132.0, 129.4, 129.3, 129.0, 125.8, 123.8, 122.8, 122.4, 121.8, 121.1, 120.9, 119.5, 118.6, 116.6, 115.4, 113.2, 111.9, 111.3, 79.5, 55.4, 39.7, 26.2, 25.9. MS (ESI): *m*/*z* 426.5 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{23}NO_2S$: C, 76.21; H, 5.45; N, 3.29. Found: C, 76.36; H, 5.56; N, 3.45.