A highly efficient green synthesis of 1, 8-dioxo-octahydroxanthenes

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Abstract
SmCl3 (20 mol%) has been used as an efficient catalyst for reaction between aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione at 120°C to give 1,8-dioxo-octahydroxanthene derivatives in high yield. The same reaction in water, at room temperature gave only the open chain analogue of 1,8-dioxo-octahydroxanthene. Use of eco-friendly green Lewis acid, readily available catalyst and easy isolation of the product makes this a convenient method for the synthesis of either of the products.

Background
1,8-dioxo-octahydroxanthenes are important class of oxygen heterocycle in which a phenyl substituted pyran ring is fused on either side with two cyclohexenone rings. Presence of conjugated bis-dienone functionality makes these compounds sensitive to attack by nucleophiles and light energy. In the recent past, there is a renewed interest in the synthesis of this class of compounds as number of its applications increased, both in the field of medicinal chemistry and material science. 1,8-dioxo-octahydroxanthenes shows useful biological activities such as anti-inflammatory, antibacterial, antiviral activities [1], finds use in biodegradable agrochemicals [2,3], cosmetics and pigments [4], fluorescent materials [5], photodynamic therapy [6], luminescent sensors [7], and in laser technologies [8]. The formation of intermediate, 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one), in the synthesis of 1,8-dioxo-octahydroxanthenes can take place even without a catalyst [9]. However, there is always need for a catalyst in the cyclization step to get the cyclized compound [9-12]. A variety of reagents, mainly acids, have been employed to accomplish this transformation [11,13-27]. However many of these reagents has its own disadvantages, such as use of expensive reagents, high catalyst loading and low yield.

On exposure to water, conventional Lewis acids such as AlCl3, ZnCl2, BCl3 etc., decomposes whereas lanthanide Lewis acids shows high hydrolytic stability. In fact, several organic reactions catalysed by lanthanide Lewis acids are carried out in water [28]. The catalysts can be recovered and reused without loss of much activity, thus considered to be green Lewis acids. SmCl3 is one of the readily available inexpensive Lewis acids which is ranked as “hard” according to the hard soft acids and bases (HSAB) concept [29]. SmCl3 is an excellent catalyst used in several important organic transformations such as selective removal of acid sensitive protecting groups like Boc, THP and TBDMS in the presence of one another [30], C-acylation of 1, 3-dicarbonyl compounds and malononitrile [31], and in the formation of ether from allylic alcohols [32]. SmCl3 is also used in electro reductive alkylation of ketones [33] and cleavage of allyl ethers [34]. Considering that there is a need for the use of more useful greener acid catalyst we examined SmCl3, a water resistant, reusable, lanthanide Lewis acid for the synthesis of 1,8-dioxo-octahydroxanthenes. Here in we report a highly efficient and clean synthesis of 1,8-dioxo-octahydroxanthenes using SmCl3.

Results and Discussion
Reaction between 4-NO2-benzaldehyde (1d, 1 mole) and dimedone (2, 2 mole) in presence of SmCl3 was identified as the test reaction and different reaction parameters were studied for the formation of corresponding 1,8-dioxo-octahydroxanthenone. Considering the fact that SmCl3 is a water resistant Lewis acid the reaction was carried out in water at room temperature (RT). The reaction was complete in 15 min. However, it was only, the open chain, compound 2,2''-((4-nitrophenyl)methylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-enone) (3d,
Table 1 Optimisation of condition for reaction between dimedone and 4-NO2-benzaldehyde in the presence of SmCl3

| Entry | Solvent   | SmCl3 mol % | Time  | Temp°C | Yield b % |
|-------|-----------|-------------|-------|--------|-----------|
| 1     | Water     | 10          | 15 min| RT     | 91        |
| 2     | Water     | 10          | 24 h  | RT     | 95        |
| 3     | Water     | 20          | 24 h  | 100    | 95        |
| 4     | No solvent| 10          | 24 h  | 100    | 95        |
| 5     | No Solvent| 10          | 24 h  | 120    | 95        |
| 6     | No Solvent| 20          | 8 h   | 120    | 98        |

a All reactions were performed using 4-nitrobenzaldehyde (1 mmol), dimedone (2 mmol) and SmCl3. b Isolated yield, c the catalyst was recovered and reused for four times to get 97%, 96%, 96% and 96% of the product.

Table 1, Scheme 1, entry 1) obtained as the sole product, in very good yield. Formation of the open chain compound was confirmed from 1H-NMR spectra of 3d which shows a peak corresponding to phenyl methylene proton at δ 5.54. The reaction mixture when left at RT for 24 h in water (entry 2) or heated at 100°C in water for 24 h (entry 3) gave only the open chain compound 3d. Heating a neat reaction mixture with SmCl3 (10 mol %, entry 4) at 100°C, for 24 h gave cyclised product 4d in 40% yield. However, heating the neat reaction mixture in presence of SmCl3 (20 mol%) at 120°C for 8 h, led to the formation of cyclised product 4d in excellent yield (entry 5, 98%).

Based on these results it was concluded that use of SmCl3 (10 mol %) in water, at room temperature and SmCl3 (20 mol %) without solvent at 120°C would be the useful conditions for the formation of open chain compound 3d and the 9-phenyl1,8-dioxo-octahydroxanthane (4d) respectively. A series of examples illustrating versatility of this method was studied using aromatic, hetero aromatic and aliphatic aldehydes (Scheme 2) and the results are summarized in Table 2.

In case of formation of open chain compounds 3a to 3o, irrespective of whether it has electron donating or withdrawing substituents on the aromatic ring all the starting materials underwent reaction within 30 min. However, wide difference in reaction rate could be observed, in the formation of xanthenediones 4a to 4m. Among the different nitro benzaldehydes studied, 4-nitro-benzaldehyde (1d) underwent reaction faster (8 h) compared to 3-nitro-benzaldehyde (1c, 10 h, entry 3) and 2-nitro-benzaldehyde (1b, 13 h) to give the product 4b, 4c and 4d respectively. Steric hindrance of the 2-nitro group may the reason for slow reaction rate. In case of halo substituted benzaldehydes 1e-1g, the mesomerically electron donating character was predominant hence the reaction took place fast (entry 5, 6 and 7) compared to substrates with electron withdrawing substituents.

The effect of 4-CH3 substituent was so mild that the 4-CH3-benzaldehyde (1h) did not make any difference in reaction rate (entry 8, 5 h) compared to unsubstituted benzaldehyde (1a). In case of benzaldehydes 1i and 1j (entry 9, and 10), containing just one electron donating substituent, the rate of reaction was fast compared to compounds with electron withdrawing substituents. A significant increase in the rate of the reaction could be observed when more than one electron donating groups (entry 11, 12 and 13) are present. The reaction condition was tolerant to ether, phenolic -OH group.

In case of furfuraldehyde (1n) and cinnamaldhyde (1o) the open chain compounds 3n and 3o were obtained in excellent yield where as the corresponding cyclised products 4n and 4o was obtained only in minor quantity along with a mixture of side products. In order to improve the yield of cyclised products 4n and 4o, different reaction conditions were tried by varying the quantity of the catalyst from 20 mol % to 100 mol % and the reaction temperature from ambient to 85°C. None of the reaction conditions gave better result. Polymerisable nature of the furyl ring and cinnamoyl group may be the reason for low yield of the product. Spectral data and melting point observed for all the products were comparable with data reported in the literature (please check additional files 1 and 2).

In order to know the efficiency of SmCl3 the data reported in the literature for the synthesis of compound...
form intermediate with another molecule of dimedone to give rise to the cyclic compound. The presence of water as solvent may further undergo dehydration reaction to give the cyclised product. After completion of the reaction it was cooled to room temperature and water (5 mL) was added, solid separated was filtered washed with water (5 mL) and dried under vacuum to get the desired xanthandione derivative. The combined aqueous layer was washed with EtOAc to remove any other organic impurities, concentrated and dried under vacuum at 120°C for 2 h to recover the catalyst in almost quantitative yield.

Table 2 SmCl₃ catalysed synthesis of 9-aryl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione derivatives or its open chain form

| S.No | Ar          | Product     | Time (min/h) | Yield (%) | Melting Point°C (3) | Melting Point°C (4) |
|------|-------------|-------------|--------------|-----------|---------------------|---------------------|
| 1    | C₆H₅(1a)   | 3a/4a       | 20/9         | 97/98     | 186-188             | 192-194 (35)        |
| 2    | 2-NO₂-C₆H₅(1b) | 3b/4b     | 30/10        | 91/98     | 244-246             | 248-252 (24)        |
| 3    | 3-NO₂-C₆H₅(1c) | 3c/4c      | 30/10        | 91/97     | 201-203             | 201-203 (35)        |
| 4    | 4-NO₂-C₆H₅(1d) | 3d/4d     | 30/8         | 91/97     | 194-196             | 195-197 (35)        |
| 5    | 2-Br-C₆H₅(1e) | 3e/4e      | 25/8         | 97/98     | 238-240             | 241-243 (37)        |
| 6    | 2-Cl-C₆H₅(1f) | 3f/4f      | 20/8         | 95/98     | 200-202             | 202-204 (35)        |
| 7    | 4-Cl-C₆H₅(1g) | 3g/4g      | 20/9         | 95/97     | 142-144             | 145-147 (35)        |
| 8    | 4-CH₃-C₆H₅(1h) | 3h/4h     | 30/8         | 95/98     | 139-141             | 141-143 (35)        |
| 9    | 4-OCH₃-C₆H₅(1i) | 3i/4i      | 30/10        | 82/97     | 146-148             | 146-148 (35)        |
| 10   | 4-OH-C₆H₅(1j)  | 3j/4j      | 30/9         | 88/98     | 188-190             | 201-203 (35)        |
| 11   | 4-CH₃-OCH₃-C₆H₅(1k) | 3k/4k | 15/8        | 94/98     | 193-195             | 193-195 (35)        |
| 12   | 3,4-OCH₂-C₆H₅(1l) | 3l/4l     | 25/9         | 96/97     | 178-180             | 187-189 (35)        |
| 13   | 3,4S-OCH₂-C₆H₅(1m) | 3m/4m   | 15/10        | 93/98     | 203-205             | 205-208 (38)        |
| 14   | C₆H₅CH = CH(1o) | 3n/4n     | 20/24        | 93/20     | 139-141             | 142-144 (37)        |
| 15   | C₆H₅SH = CH(1o) | 3o/4o     | 14/-         | 96/-      | 213-215             | 215-216 (6)         |

Experimental

General Procedure for the Preparation of 2, 2'-aryl/alkylmethylene bis(3-hydroxy-5, 5'-dimethyl-2-cyclohexene-1-one) (3d)

To a mixture of an aldehyde (1 mole) and 5, 5-dimethyl-1,3-cyclohexanedione (2 mole) in water SmCl₃ (10 mol %) was added and stirred at ambient temperature, till the reaction goes to completion. Progress of the reaction was monitored by TLC (Silica gel, 9:1, Hexane:EtOAc). After completion of the reaction, the solid separated was washed with water and dried to get the product.

General Procedure for the Preparation of 3,3,6,6-Tetramethyl-9-aryl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (4)

To a solution of an aldehyde (1 mole) and 5,5-dimethyl-1,3-cyclohexanedione (2 mole), SmCl₃ (20 mol%) was added and stirred at 120°C. The progress of the reaction was monitored by TLC (Silica gel, 7:3, Hexane:EtOAc). After completion of the reaction it was cooled to room temperature and water (5 mL) was added, solid separated was filtered washed with water (5 mL) and dried under vacuum to get the desired xanthandione derivative. The combined aqueous layer was washed with EtOAc to remove any other organic impurities, concentrated and dried under vacuum at 120°C for 2 h to recover the catalyst in almost quantitative yield.

1. 2, 2'-(4-nitrophenylmethylene)bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) (3d)

The reaction was carried out according to the general experimental procedure using 4-nitrobenzaldehyde (100 mg, 0.0006 mole), 5,5-dimethyl-1,3-cyclohexanedione (170 mg, 0.0013 mole) and SmCl₃ (16.9 mg, 10 mol%) in water (1 mL). Conditions: room temperature, 30 minutes. The title compound 3d was obtained (251 mg, 91%) as a solid. The spectral data for the compound 3d was in agreement with the values already reported in the literature [35].

Mp: 194-196°C. 1H NMR (400 MHz, CDCl₃): δ 1.04 (s, 6H, 2 × CH₃), 1.16 (s, 6H, 2 × CH₃), 2.24-2.44 (m, 8H, 4 × CH₂), 5.57 (s, 1H, CH), 7.03-7.51 (m, 4H, Ar), 11.87 (s, 1H, OH).
2. 2,2′-(4-methoxyphenylmethylene)bis[3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one] (3i)

The reaction was carried out according to the general experimental procedure using 4-methoxybenzaldehyde (100 mg, 0.0007 mole), 5,5-dimethyl-1,3-cyclohexane-dione (188 mg, 0.0014 mole) and SmCl₃ (18.8 mg, 10 mol%) in water (1 mL). Conditions: room temperature, 30 minutes. The title compound 3i was obtained (242 mg, 82%) as a solid. The spectral data for the compound 3i was in agreement with the values already reported in the literature [35].

Mp: 146-148°C. 1H NMR (400 MHz, CDCl₃): δ 1.02 (s, 6H, 2 × CH₃), 1.15 (s, 6H, 2 × CH₃), 2.21-2.40 (m, 8H, 4 × CH₂), 3.70 (s, 3H, OCH₃), 5.41 (s, 1H, CH), 6.75 (d, J = 8.8 Hz, 2H, Ar), 6.93 (d, J = 8.0 Hz, 2H, Ar), 11.84 (s, 1H, OH).

3. 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4d)

The reaction was carried out according to the general experimental procedure using 4-nitrobenzaldehyde (100 mg, 0.0006 mole), 5,5-dimethyl-1,3-cyclohexane-dione (170 mg, 0.0013 mole) and SmCl₃ (33.9 mg, 20 mol%). Conditions: 120°C, 8 h. The title compound 4d was obtained (257 mg, 97%) as a solid. The spectral data for the compound 4d was in agreement with the values already reported in the literature [34]. Mp: 225-226°C. The same reaction was repeated with the recovered catalyst for four times to get 97%, 96%, 96% and 96% of the product.

1H NMR (400 MHz, CDCl₃): δ 0.99 (s, 6H, 2 × CH₃), 1.11 (s, 6H, 2 × CH₃), 2.18 (q, J = 19.6 Hz, 4H, 2 × CH₂), 2.49 (s, 4H, 2 × CH₂), 4.82 (s, 1H, CH), 7.47 (d, J = 19.6 Hz, 2H, Ar), 7.47 (d, J = 5.2 Hz, 2H, Ar).

4. 9-(4-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (4j)

The reaction was carried out according to the general experimental procedure using 4-hydroxybenzaldehyde (100 mg, 0.0008 mole), 5,5-dimethyl-1,3-cyclohexane-dione (210 mg, 0.0016 mole) and SmCl₃ (42 mg, 20 mol %). Conditions: 120°C, 9 h. The title compound 4j was obtained (298 mg, 98%) as a solid. The spectral data for the compound 4j was in agreement with the values already reported in the literature [36]. Mp: 244-246°C.

1H NMR (400 MHz, CDCl₃): δ 0.99 (s, 6H, 2 × CH₃), 1.09 (s, 6H, 2 × CH₃), 2.21 (q, J = 8.8 Hz, 4H, 2 × CH₂), 2.45 (s, 4H, 2 × CH₂), 4.67 (s, 1H, CH), 6.61 (d, J = 8 Hz, 2H, Ar), 7.11 (d, J = 8 Hz, 2H, Ar).

Conclusion

In conclusion, SmCl₃, a water resistant Lewis acid was used for the synthesis of 3,3,6,6-tetramethyl-9-aryl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione derivatives or its open chain analogue depending upon the reaction condition. Water was used as the green solvent, and the catalyst could be recovered and reused. The reaction work up is very simple, solid separated from the reaction mixture was filtered washed with water to recover the catalyst and dried to get the desired xanthenedi-one derivatives. This procedure offers several advantages such as use of inexpensive green catalyst, operational simplicity, cleaner reaction and minimal environmental impact, high yield, thus making it one of the attractive and practical protocols for the synthesis of xanthenedi-ones. Further studies on the use of xanthenedi-ones as visible light sensitizers and as better excited state electron donors to TiO₂ for application in dye sensitised solar cells are in progress.

Table 3 Comparison of the efficiency of catalysts reported for the synthesis of 14-(4-nitrophenyl)-14H-dibenzo[a,j]xanthenes and SmCl₃

| Entry | Catalyst       | Mol % | Time (min/ h) | Yield (%) | Ref. |
|-------|----------------|-------|---------------|-----------|------|
| 1     | NaHSO₄-SiO₂    | 10    | 7.5           | 91        | [18] |
| 2     | TBAHS          | 10    | 3.5           | 94        | [39] |
| 3     | DABCO-Br       | 10    | 2.5           | 90        | [41] |
| 4     | KAIO₂.H₂O     | 50    | 4.0           | 90        | [19] |
| 5     | EPZ 10         | 10    | 3.0           | 95        | [42] |
| 6     | Yb(O₂)₁₂(Bpy) BF₄ | 1/2 mL | 5.0         | 89        | [25] |
| 7     | ZnO-CH₃COCI   | 30    | 16.0          | 96        | [43] |
| 8     | LiBr           | 15    | 1.0           | 84        | [17] |
| 9     | Sulfamic acid  | 10    | 11.0          | 94        | [15] |
| 10    | SmCl₃         | 20    | 8.0           | 98        | This paper |
Scheme 3 Comparison of the efficiency of catalysts reported for the synthesis of 14-(4-nitrophenyl)-14H-dibenzo [a, j] xanthenes and SmCl₃.

Scheme 4 Proposed mechanism for the SmCl₃ catalysed synthesis of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxo-2,3,4,5,6,7-hexahydroxanthene and its open chain form.

Additional material

Additional file 1: Supporting Information File 1. This file contains all experimental procedures for the syntheses of compounds not mentioned in the main article 3a-3c, 3e-h, 3j-3o and 4a-4c, 4e-4i, 4k-4m and their analytical data.

Additional file 2: Supporting Information File 2. This contains NMR spectra for all the compounds reported.

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Authors’ contributions
AI has suggested the problem, monitored the progress of the work and finalised the manuscript. SMA and SMu carried out most of the experimental work and contributed to the preparation of the manuscript. SMar helped characterisation of the compounds prepared. All authors have read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.
References

1. Hatakeyama S, Ochi N, Numata H, Takano S: A new route to substituted 3-methoxy carbonyl dihydroxyprans: Enantioselective synthesis of (+)-methyl elonol. J Chem Soc, Chem Commun 1998, 1202-1204.

2. Hafiez EAA, Elagdi MH, Elagamy AGA, El-Tawel FAIA: Nitriles in heterocyclic synthesis: Novel synthesis of benzoox carbonimide and of benzocarbonylimidazol(3,2-c)quinoline derivatives. Heterocycles 1987, 26:903-907.

3. Abdel Galil FM, Riad BY, Sherif SM, Elnagdi MH: Activated nitriles in heterocyclic synthesis: A novel synthesis of 4-azoloyl-2-Amino quinolines. Chem Lett 1982, 112-112.

4. Ellis GP: The chemistry of heterocyclic compounds. In: Chromene, Chromones and Chromone. Volume 2. Edited by: Weissberger A, Taylor ECE. John Wiley: New York; 1977:13.

5. Callan JF, De Silva P, Magri DC: Luminescent sensors and switches in the early 21st century. Tetrahedron 2003, 61:8551-8588.

6. Sirkeçioglu O, Talinli N, Akar A: Chemical aspects of santalin as a medicinal plant. Phytother Res 2001, 15:89-94.

7. Poupelin JP, Saint-Rut G, Foussard-Blanpin O: Synthesis and antinflammatory properties of bis(2-hydroxy-1-naphthyl)methane derivatives. J Monosubstituted derivatives. Eu J Med Chem 1978, 13:67-71.

8. Banerjee A, Mukherjee AK: Aromatic amines of santiinal as a histological stain. J Chem Res (S) 1995, 502.

9. Popelin JP, Saint-Rut G, Foussard-Blanpin O: Synthesis and antinflammatory properties of bis(2-hydroxy-1-naphthyl)methane derivatives. I. Monosubstituted derivatives. J Med Chem 1978, 13:67-71.

10. Jin TS, Wang AQ, Li TS: Solid - state condensation reactions between aldehyde and 5,5-dimethyl-1,3-cyclohexanone by grinding at room temperature. Synth Commun 2005, 35:2339-2345.

11. Shi DJ, Wang YH, Lu ZS, Dai GY: Condensation of aromatic aldehydes with acidic methylene compounds without catalyst. Synth Commun 2000, 30:713-726.

12. Jin TS, Wang AQ, Li TS: Solvent-free synthesis of 1,8-dioxo-octahydroxanthenes. J Mol Catal A: Chem 2011, 355:53-58.

13. Khosropour AR, Khodaei MM, Moghanian H: A Facile, Simple and convenient method for the Synthesis of 14-Aryl or Aryl-14-H-Dibenzo[a,j]xanthenes Catalyzed by P-Dodecyl benzene sulfonic Acid in aqueous Media. Synlett 2004, 866-870.

14. Dai B, Thiruppathi P, Reddy KP, Ravikanth B, Nagarapu L: An efficient synthesis of 1,8-dioxo-octahydroxanthenes using heterogeneous catalyst. Catal Commun 2007, 8:555-558.

15. Rajitha B, Kumar BS, Reddy YT: Suflamic acid: A novel and efficient catalyst for the synthesis of aryl 14H-dibenzo[a,j]xanthenes under conventional heating and microwave irradiation. Tetrahedron Lett 2005, 46:8691-8693.

16. Rajitha B, Kumar BS, Reddy YT: Suflamic acid: A novel and efficient catalyst for the synthesis of aryl 14H-dibenzo[a,j]xanthenes under conventional heating and microwave irradiation. Tetrahedron Lett 2005, 46:8691-8693.

17. Saini A, Kumar S, Sandhu JS: A new LiBr-catalyzed, facile and efficient method for the synthesis of 14-aryl or aryl 14H-dibenzo[a,j] and Tetrahydrobenz(b) pyrans under solvent-free conditions. Synth Commun 2007, 37:259-2525.

18. Nagarapu L, Basavarajanna D, Uma C: Efficient Synthesis of Aroyl 14H-dibenzo[a,j]xanthenes using NaH2SO3 or 5% WO3/ZrO2 as heterogenous catalysts under conventional heating in a solvent free media. Synth Commun 2007, 37:259-2525.

19. Shujiang Tu S, Zhou J, Lu Z, Deng X, Shi D, Wang S: An efficient synthesis of 1,8-dioxo-octahydroxanthenes using tetrabutylammonium hydrogen sulfite. Arkivoc 2007, x-k:252-258.

20. Shujing Tu S, Zhou J, Lu Z, Deng X, Shi D, Wang S: Condensation of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanone under solvent free conditions. Indian J Chem Soc B 2006, 45b:470-474.

21. Li J, Wu Y, Ye T, Yi Y, Jiao N: Synthesis of tetraketones in water and under catalyst-free conditions. Green Chem 2010, 12:216-219.

22. Lu H, Li J, Zhang Z: ZrOCl2.8H2O a highly efficient catalyst for the synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes. J Mol Catal A: Chem 2007, 275:25-29.

23. Bagnoli MA, Heravi MM, Mahdavian GN: A high efficient one pot Knoevenagel condensation, Michael addition and cyclo dehydrayion of dimedone and aldehydes in acetonitrile, aqueous and solvent free conditions: scope and limitations. J Mol Catal A: Chem 2007, 269:53-57.

24. Su W, Yang D, Jin C: Yb(OTf)3 catalyzed condensation reaction of β-naphthol and aldehyde in ionic liquids: A green synthesis of 14H-dibenzo[a,j]xanthenes. Tetrahedron Lett 2008, 49:3391-3394.

25. Kim BS: Efficient synthesis of xanthenic derivatives utilizing ytterbium(III) triflate. J Korean Chem Soc 2007, 51:298-300.

26. Fan XS, Li YZ, Zhang YX: InCl3-H2O-promoted green preparation of xantheneendiones in ionic liquids. Can J Chem 2005, 83:16-20.

27. Kobayashi Y, Sugiura M, Kitagawa H, Lam WW: Rare-Earth Metal Triflates in Organic Synthesis. Chem Rev 2002, 102:2227-2302.

28. Moliander QA, Dowdy ED: Lanthanaide and Group 3 Metalocene Catalysis in Small Molecule Synthesis. In: Chemistry and Use in Organic Synthesis. Edited by: Shu Kobayashi. Berlin, Springer-Verlag; 1999:119-154.

29. Copin-Rh P, Nilaya S, Muraleedharchan KM: Highly chemoselective esterification reactions and Boc/THP/TBDMS discriminating deprotections under Samarium(III) Catalysis. Org Lett 2011, 13:1932-1935.

30. Shen Q, Huang W, Wang J, Zhou X, SmcLi-catalyzed C-acylation of 1,3-dicarbonyl compounds and malononitrile. Org Lett 2007, 9:4401-4404.

31. Shujiang Tu S, Zhou J, Lu Z, Deng X, Shi D, Wang S: Efficient synthesis of 1,8-dioxo-octahydroxanthenes using tetrabutylammonium hydrogen sulfite. Arkivoc 2007, x-k:252-258.

32. Shujing Tu S, Zhou J, Lu Z, Deng X, Shi D, Wang S: Condensation of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanone under solvent free conditions. Indian J Chem Soc B 2006, 45b:470-474.

33. Li J, Xu Y, Tao X, Zhang ZH: An efficient bismuth trichloride-catalyzed synthesis of 1,8-dioxo-octahydroxanthenes. Phosphorus, Sulfur Silicon Relat Elem 2008, 183:1672-1678.

34. Yu JJ, Wang LM, Liu QQ, Guo FL, Liu Y, Jiao N: Synthesis of tetraketones in water and under catalyst-free conditions. Green Chem 2010, 12:216-219.

35. Karade HN, Sathe M, Kaushik MP: An efficient synthesis of 1,8-dioxo-octahydroxanthenes using tetrabutylammonium hydrogen sulfite. Arkivoc 2007, x-k:252-258.

36. Shujing Tu S, Zhou J, Lu Z, Deng X, Shi D, Wang S: Condensation of aromatic aldehyde with 5,5-dimethyl-1,3-cyclohexanone without catalyst. Synth Commun 2002, 32:3063-3067.

37. Bagnoli MA, Heravi MM, Mahdavian GN: A high efficient one pot Knoevenagel condensation, Michael addition and cyclo dehydrayion of dimedone and aldehydes in acetonitrile, aqueous and solvent free conditions: scope and limitations. J Mol Catal A: Chem 2007, 269:53-57.

38. Su W, Yang D, Jin C: Yb(OTf)3 catalyzed condensation reaction of β-naphthol and aldehyde in ionic liquids: A green synthesis of 14H-dibenzo[a,j]xanthenes. Tetrahedron Lett 2008, 49:3391-3394.

39. Kim BS: Efficient synthesis of xanthenic derivatives utilizing ytterbium(III) triflate. J Korean Chem Soc 2007, 51:298-300.

40. Fan XS, Li YZ, Zhang YX: InCl3-H2O-promoted green preparation of xantheneendiones in ionic liquids. Can J Chem 2005, 83:16-20.

41. Kobayashi Y, Sugiura M, Kitagawa H, Lam WW: Rare-Earth Metal Triflates in Organic Synthesis. Chem Rev 2002, 102:2227-2302.