

METHODOLOGY

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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-octahydroxanthene. 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**,

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Table 1 Optimisation of condition for reaction between dimedone and 4-NO₂-benzaldehyde in the presence of SmCl₃

Entry ^a	Solvent	SmCl ₃ mol %	Time	Temp ^o C	Yield ^b %	
					3a	4a
1	Water	10	15 min	RT	91	Nil
2	Water	10	24 h	RT	95	Nil
3	Water	20	24 h	100	95	Nil
4	No solvent	10	24 h	100	60	40
5	No Solvent	10	24 h	120	40	60
6	No Solvent	20	8 h	120	Nil	98 ^c

^a All reactions were performed using 4-nitrobenzaldehyde (1 mmol), dimedone (2 mmol) and SmCl₃, ^bisolated 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-phenyl-1,8-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.

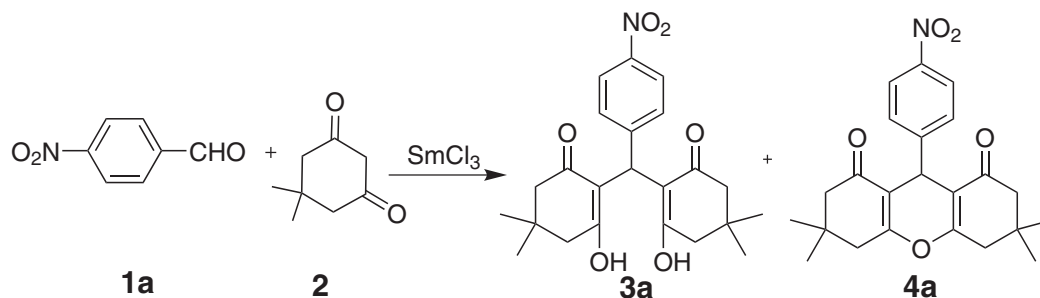
In case of formation of open chain compounds **3a** to **3o**, irrespective of whether it has electron donating or withdrawing substituents on the aromatic ring all the starting materials underwent reaction within 30 min.

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 be 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.

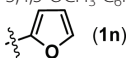
In case of furfuraldehyde (**1n**) and cinnamaldehyde (**1o**) the open chain compounds **3n** and **3o** were obtained in excellent yield where as the corresponding cyclised products **4n** and **4o** was obtained only in minor quantity along with a mixture of side products. In order to improve the 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



Scheme 1 Optimisation of condition for reaction between dimedone and 4-NO₂-benzaldehyde in the presence of SmCl₃.

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)	
					Found	Reported	Found	Reported
1	C ₆ H ₅ - (1a)	3a/4a	20/9	97/98	186-188	192-194 [35]	203-205	204-206 [36]
2	2-NO ₂ -C ₆ H ₅ - (1b)	3b/4b	30/10	91/98	244-246	248-252 [24]	246-248	248-249 [36]
3	3-NO ₂ -C ₆ H ₅ - (1c)	3c/4c	30/10	91/97	201-203	201-203 [35]	171-173	170-172 [36]
4	4-NO ₂ -C ₆ H ₅ - (1d)	3d/4d	30/8	91/97	194-196	195-197 [35]	225-226	221-223 [36]
5	2-Br-C ₆ H ₅ - (1e)	3e/4e	25/8	97/98	238-240	241-243 [37]	226-229	226-229 [38]
6	2-Cl-C ₆ H ₅ - (1f)	3f/4f	20/8	95/98	200-202	202-204 [35]	230-232	225-227 [36]
7	4-Cl-C ₆ H ₅ - (1g)	3g/4g	20/9	95/97	142-144	145-147 [35]	230-233	229-230 [36]
8	4-CH ₃ -C ₆ H ₅ - (1h)	3h/4h	30/8	95/98	139-141	141-143 [35]	212-214	210-211 [36]
9	4-OCH ₃ -C ₆ H ₅ - (1i)	3i/4i	30/10	82/97	146-148	146-148 [35]	242-245	242-243 [39]
10	4-OH-C ₆ H ₅ - (1j)	3j/4j	30/9	88/98	188-190	201-203 [35]	244-246	247-248 [36]
11	4-OH,3-OCH ₃ -C ₆ H ₅ - (1k)	3k/4k	15/8	94/98	193-195	193-195 [35]	227-228	224-225 [40]
12	3,4-OCH ₃ -C ₆ H ₅ - (1l)	3l/4l	25/9	96/97	178-180	187-189 [35]	179-181	170-172 [40]
13	3,4,5-OCH ₃ -C ₆ H ₅ - (1m)	3m/4m	15/10	93/98	203-205	205-208 [38]	186-188	182-183 [36]
14	 (1n)	3n/4n	20/24	93/20	139-141	142-144 [37]	-	-
15	C ₆ H ₅ CH = CH- (1o)	3o/4o	14/-	96/-	213-215	215-216 [6]	-	-

4d, using different type of the catalysts was compared with SmCl₃. The data on catalysts ranging from neutral salts, protic acids, and Lewis acids (Table 3, Scheme 3) were used for the comparison. This clearly shows that SmCl₃ is a better catalyst for preparation of 1,8-dioxo-octahydroxanthanes in terms of high yield of the product, short reaction time and simple workup procedure.

Considering the Lewis acidic nature of SmCl₃ a possible mechanism is proposed (Scheme 4). Reaction of dimedone in its enol form is expected to react with aromatic aldehyde, under the influence of SmCl₃, to give rise to *ortho*-quinone methides (*o*-QMs) **III** by Knoevenagel adduct formation. The intermediate **III** may further undergo Michael addition with another molecule of dimedone to form intermediate **IV**. The presence of water as solvent might not have facilitated dehydration reaction to give the cyclised product **4**. However, when reaction was carried out in the absence of water a facile dehydration reaction took place to give rise to the cyclic compound **4**.

Experimental

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

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 filtered, washed with water and dried to get the product.

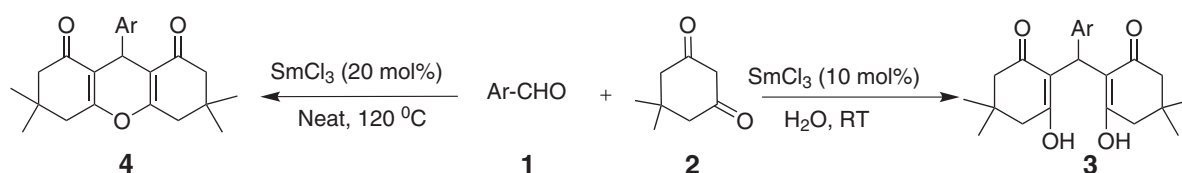
General Procedure for the Preparation of 3,3,6,6-Tetramethyl-9-aryl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (4)

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).



Scheme 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.

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-cyclohexanedione (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-cyclohexanedione (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)

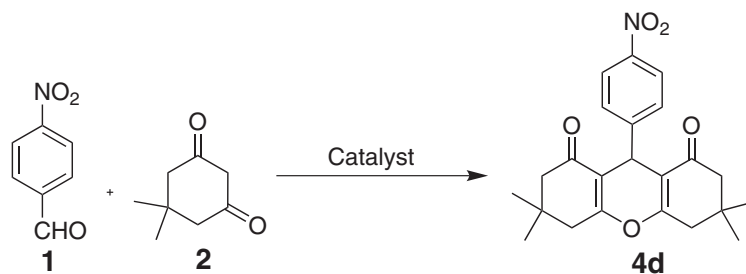
The reaction was carried out according to the general experimental procedure using 4-hydroxybenzaldehyde (100 mg, 0.0008 mole), 5,5-dimethyl-1,3-cyclohexanedione (210 mg, 0.0016 mole) and SmCl₃ (42 mg, 20 mol%). Conditions: 120 °C, 9 h. The title compound **4j** was obtained (298 mg, 98%) as a solid. 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

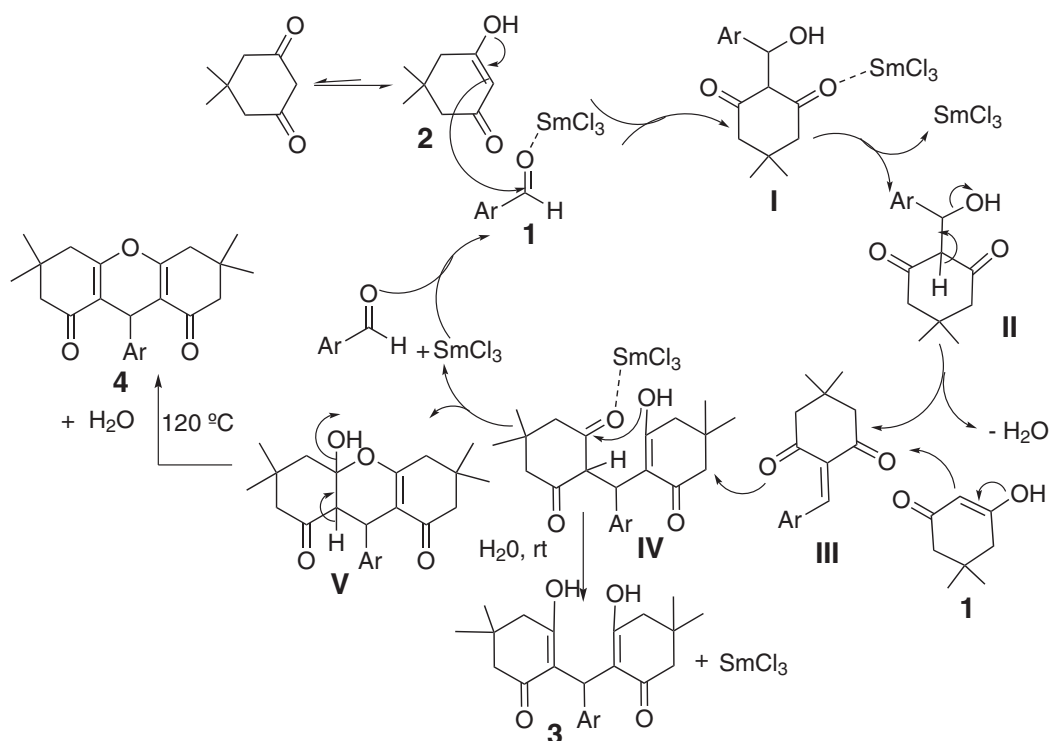
In conclusion, SmCl₃, a water resistant Lewis acid was used for the synthesis of 3,3,6,6-tetramethyl-9-aryl-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione derivatives or its open chain analogue depending upon the reaction condition. Water was used as the green solvent, and the catalyst could be recovered 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 xanthenedione 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 xanthenediones. Further studies on the use of xanthenediones 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	NaHSO ₄ -SiO ₂	10	7.5 h	91	[18]
2	TBAHS	10	3.5 h	94	[39]
3	DABCO-Br	10	2.5 h	90	[41]
4	KAl(SO ₄) ₂ ·12H ₂ O	50	4.0 h	90	[19]
5	EPZ 10	10	3.0 h	95	[42]
6	Yb(OTf) ₃ /[BPy] BF ₄	1/2 mL	5.0 h	89	[25]
7	ZnO-CH ₃ COCl	30	16.0 h	96	[43]
8	LiBr	15	1.0 h	84	[17]
9	Sulfamic acid	10	11.0 h	94	[15]
10	SmCl ₃	20	8.0 h	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 SmCl_3 .



Scheme 4 Proposed mechanism for the SmCl_3 catalyzed 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.

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