

# Facile and efficient synthesis of xanthenedione derivatives promoted by niobium pentachloride

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Xanthenedione derivatives were synthesised in one-pot reactions between arylaldehyde derivatives and 1,3-cyclohexanedione promoted by niobium pentachloride. This new method is simple, cost-effective, high-yielding with a good variety of substrates generality, and can be conducted within reasonable reaction times.

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**Keywords:** niobium pentachloride, Lewis acid, xanthenedione derivatives, one-pot reactions

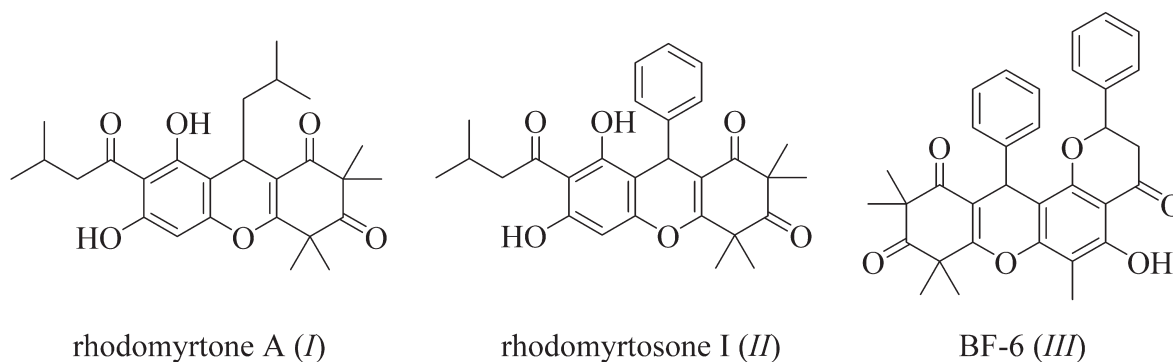
## Introduction

Among the various classes of natural compounds, xanthene derivatives have received special attention since many of these compounds have biological and therapeutic properties (Chibale et al., 2003; El-Brashy et al., 2004). Xanthene derivatives are recognised for their use as sensitising dyes (Bhowmik & Ganguly, 2005), in photodynamic therapy to destroy tumour cells (Ormond & Freeman, 2013), in laser technologies (Ahmad et al., 2002) and in pH-sensitive fluorescent materials for the visualisation of biomolecules (Knight & Stephens, 1989). Research has focused on secondary metabolites of the genus *Allanblackia* (Locksley & Murray, 1971; Nkengfack et al., 2002) and the significant increase in the number of studies stems from the fact that many of these secondary metabolites, such as xanthenes, benzophenones and pentacyclic triterpenes, exhibit biological, pharmacological, anti-inflammatory, antimicrobial, antifungal, HIV-inhibitory and cytotoxic properties (Fuller et al., 1999; Peres et al., 2000; Peres & Nagem, 1997). The plants of the genus *Allanblackia*, which belong to the family *Clusiaceae*, are found in large forests in the west and south of the province of Cameroon, where they are used to treat respiratory diseases, toothache and diarrhoea (Fobane et al., 2014). Rhodomyrtonone A (*I*)

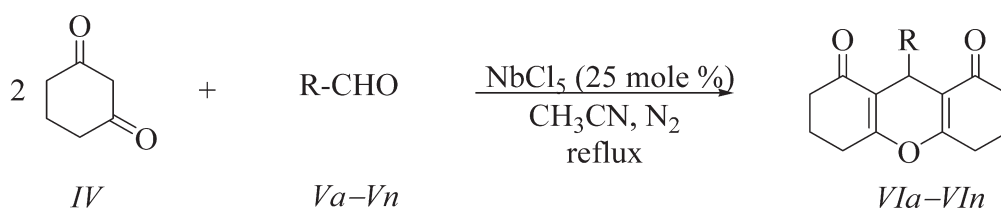
and rhodomyrtonone I (*II*) extracted from *Rhodomyrthus tomentosa* (Hiranrat et al., 2012; Hiranrat & Mahabusarakam, 2008; Limsuwan et al., 2009; Sianglum et al., 2011; Visutthi et al., 2011), together with the compound known as BF-6 (*III*) extracted from the leaves of *Baeckea frutescens* (Makino & Fujimoto, 1999) are examples of natural xanthenediones (Fig. 1).

Xanthene derivatives can be prepared by several methods: cyclodehydration (Bekaert et al., 1992), the trapping of benzynes by phenols (Knight & Little, 2001), the palladium-catalysed cyclisation of polycyclic aryltriflate esters (Wang & Harvey, 2002), a simple and efficient procedure for the synthesis of xanthene derivatives through one-pot condensation of 2-naphthol with aryl aldehydes in the presence of niobium pentachloride (Bartolomeu et al., 2014), the condensation of cyclohexane-1,3-diones and aromatic aldehydes in the presence of solid acids  $Y(NO_3)_3 \cdot 6H_2O$  and  $SnCl_2 \cdot 2H_2O$  (Karami et al., 2013a), amongst others (Horning & Horning, 1946; John et al., 2006; Saini et al., 2006; Zhang & Tao 2008; Zhang & Liu, 2008; Wang et al., 2008; Urinda et al., 2009; Lü et al., 2009; Maleki et al., 2011; Soleimani et al., 2011; Pramanik & Bhar, 2012; Dharma Rao et al., 2012; Karami et al., 2013b, 2013a, 2014; Li et al., 2013; Cao et al., 2013; Shirini et al., 2013; Napoleon & Khan 2014; Napoleon et al., 2014; Iniyavan et al.,

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**Fig. 1.** Examples of natural xanthenediones.



**Fig. 2.** Synthesis of xanthenedione derivatives.

2014; Shirini et al., 2014, 2015; Preetam et al., 2015; Ilangoan et al., 2011). However, some of these methods involve long reaction times, extreme reaction conditions, expensive reagents and unsatisfactory yields, hence the improvement of these syntheses has been the target of several studies. One-pot reactions are effective for carrying out numerous transformations and forming several bonds in a single pot while, at the same time, eliminating several purification steps, minimising chemical waste generation and saving time. Such advantages have significant relevance in modern synthetic methodology (D'Souza & Müller, 2007; Isambert & Lavilla, 2008).

As part of the present investigation of the use of  $\text{NbCl}_5$  as a promoter in organic reactions, this work describes a new route for the preparation of xanthenedione derivatives (*VIa-VIn*) through a one-pot reaction between aldehyde derivatives (*Va-Vn*) and 1,3-cyclohexanedione (*IV*) promoted by niobium pentachloride (Fig. 2).

Niobium pentachloride is a stronger Lewis acid currently attracting interest as a reagent in organic synthesis; it has found applications as an effective catalyst in a variety of organic reactions (Andrade, 2004; Guo et al., 2011; Hou et al., 2010b, 2010a, 2011a, 2011b; Lacerda et al., 2012; Oshiro et al., 2015; Bartolomeu et al., 2014, 2015).

## Experimental

The solvents were distilled with  $\text{CaH}_2$ . All chemicals were purchased from Sigma-Aldrich (USA) and used without further purification, with the exception of  $\text{NbCl}_5$ . The  $\text{NbCl}_5$  used was supplied by

Companhia Brasileira de Metalurgia e Mineração (CBMM, Brasil) and re-crystallised by sublimation following the procedure detailed in the supplementary data; this method is described in the literature (Alves, 1986). Thin-layer chromatography was performed on 0.2 mm Merck 60F254 silica gel aluminium sheets (Germany), with visualisation using a vanillin/methanol/water/sulphuric acid mixture. Infrared (IR) spectra were recorded using a Bruker Vertex 70 Fourier Transform Spectrometer (Germany) equipped with a Bruker Platinum ATR unit (Germany). A Bruker DRX 400 spectrometer was employed for generating the NMR spectra ( $\text{CDCl}_3$  as a solvent) using tetramethylsilane as internal reference. HR-MS analyses were performed on an LCMS-IT-TOF mass spectrometer (Shimadzu, Japan). The melting points of the synthesised compounds were determined by differential scanning calorimetry (DSC). DSC measurements were performed using a Mettler-Toledo model DSC 1 stare system.

### General procedure for syntheses of xanthenedione derivatives (*VIa-VIn*)

To a solution of  $\text{NbCl}_5$  (67.5 mg, 0.25 mmol) in anhydrous  $\text{CH}_3\text{CN}$  (2.0 mL), maintained under  $\text{N}_2$  atmosphere (Table 1), a solution of 1,3-cyclohexanedione (*IV*; 224 mg, 2.0 mmol) and the respective arylaldehyde (*Va-Vn*; 1.0 mmol) in anhydrous  $\text{CH}_3\text{CN}$  (3.0 mL) were added. The reaction mixture was stirred under reflux for 2 h. Next, the reaction mixture was poured into water (10.0 mL) at  $0^\circ\text{C}$  and the precipitate was filtered and washed with a mixture of acetone/water ( $\varphi_r = 1 : 1$ ). The products were dissolved

**Table 1.** Optimisation of one-pot reaction between *IV* and *Va* promoted by  $\text{NbCl}_5^{a,b}$ 

Entry	$\text{NbCl}_5$ (mole %)	Solvent	Time (h)	Yield <sup>c</sup> (%)
1 <sup>a</sup>	0	DCM	24	–
2 <sup>a</sup>	10	DCM	2	15
3 <sup>a</sup>	25	DCM	2	22
4 <sup>a</sup>	50	DCM	2	19
5 <sup>a</sup>	0	DCE	24	–
6 <sup>a</sup>	10	DCE	2	18
7 <sup>a</sup>	25	DCE	2	45
8 <sup>a</sup>	50	DCE	2	33
9 <sup>a</sup>	0	$\text{CH}_3\text{CN}$	24	–
10 <sup>a</sup>	25	$\text{CH}_3\text{CN}$	2	90
11 <sup>a</sup>	50	$\text{CH}_3\text{CN}$	2	77
12 <sup>b</sup>	10	$\text{CH}_3\text{CN}$	2	25
13 <sup>b</sup>	25	$\text{CH}_3\text{CN}$	2	87
14 <sup>b</sup>	50	$\text{CH}_3\text{CN}$	2	75

a) Reaction conditions: 1,3-cyclohexanedione (*IV*) (2.0 mmol), benzaldehyde (*Va*) (1.0 mmol) and  $\text{NbCl}_5$  (0–50 mole %) in dichloromethane (DCM; 3.0 mL), 1,2-dichloroethane (DCE; 3.0 mL) or  $\text{CH}_3\text{CN}$  (3.0 mL) under reflux, in an  $\text{N}_2$  atmosphere; b) reaction conditions: *IV* (2.0 mmol), *Va* (1.0 mmol) and  $\text{NbCl}_5$  (25–50 mole %) in  $\text{CH}_3\text{CN}$  (3.0 mL) under reflux, in an  $\text{N}_2$  atmosphere; c) isolated yields by re-crystallisation.

**Table 2.** Results for synthesis of xanthenedione derivatives (*VIa–VI<sub>n</sub>*)

Compound R	Appearance	Yield (%) <sup>a</sup>	$\Delta H_{\text{fusion}}$ ( $\text{J g}^{-1}$ )	Purity (%)	M.p./°C		
					Found	Reported <sup>b</sup>	
<i>Va</i>	$\text{C}_6\text{H}_5$	white solid	87 ( <i>VIa</i> )	–135.86	99	263.9	261–264 (Shirini et al., 2013)
<i>Vb</i>	4- $\text{CH}_3\text{C}_6\text{H}_4$	white solid	77 ( <i>VIb</i> )	–127.38	98	253.1	249–251 (Shirini et al., 2013)
<i>Vc</i>	4- $\text{COOH}\text{C}_6\text{H}_4$	white solid	66 ( <i>VIc</i> ) <sup>c</sup>	–75.79	99	281.8	–
<i>Vd</i>	4- $\text{OCH}_3\text{C}_6\text{H}_4$	white solid	73 ( <i>VI<sub>d</sub></i> )	–103.81	99	193.4	203–204 (Shirini et al., 2013)
<i>Ve</i>	2- $\text{OCH}_3\text{C}_6\text{H}_4$	white solid	65 ( <i>VI<sub>e</sub></i> )	–74.24	96	212.2	216–218 (Maleki et al., 2012)
<i>Vf</i>	4-OH-3- $\text{OCH}_3\text{C}_6\text{H}_3$	white solid	80 ( <i>VI<sub>f</sub></i> )	–118.16	98	239.0	225–227 (John et al., 2006)
<i>Vg</i>	3- $\text{NO}_2\text{C}_6\text{H}_4$	white solid	57 ( <i>VI<sub>g</sub></i> )	–89.98	99	281.2	281–283 (Shirini et al., 2013)
<i>Vh</i>	4- $\text{NO}_2\text{C}_6\text{H}_4$	white solid	61 ( <i>VI<sub>h</sub></i> )	–82.34	98	255.3	248–250 (Shirini et al., 2013)
<i>Vi</i>	4- $\text{BrC}_6\text{H}_4$	white solid	64 ( <i>VI<sub>i</sub></i> )	–73.43	99	251.1	283–285 (Shirini et al., 2013)
<i>Vj</i>	2- $\text{BrC}_6\text{H}_4$	white solid	55 ( <i>VI<sub>j</sub></i> )	–65.57	97	250.0	255–256 (Li et al., 2013)
<i>Vk</i>	4- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4$	white solid	70 ( <i>VI<sub>k</sub></i> )	–84.72	98	211.6	196–198 (Iniyavan et al., 2015)
<i>Vl</i>	$\text{C}_4\text{H}_3\text{S}$	white solid	69 ( <i>VI<sub>l</sub></i> ) <sup>c</sup>	–71.01	98	210.1	–
<i>Vm</i>	4-( $\text{CH}_3$ ) <sub>2</sub> $\text{NC}_6\text{H}_4$	white solid	54 ( <i>VI<sub>m</sub></i> )	–77.81	98	233.2	218–220 (Napoleon et al., 2014)
<i>Vn</i>	4- $\text{COH-C}_6\text{H}_4$	white solid	78 ( <i>VI<sub>n</sub></i> )	–	–	> 325.0	> 300.00 (Kaya et al., 2011)

a) Yields of isolated products by re-crystallisation; b) products known in the literature and their melting points were compared with values already reported; c) product not described in the literature.

in 10.0 mL of hot ethanol, and cooled in a freezer to afford the compounds (*VIa–VI<sub>n</sub>*). The full experimental details and spectroscopic characterisations (<sup>1</sup>H and <sup>13</sup>C NMR, DSC, infrared and mass spectrometry) for compounds (*VIa–VI<sub>m</sub>*) can be found in the Supplementary Data section of this article's web page.

## Results and discussion

First, the one-pot reaction between *IV* (2.0 mmol) and benzaldehyde (*Va*; 1.0 mmol), in the presence of different concentrations (0 mole %, 10 mole %, 25 mole % or 50 mole %) of niobium pentachloride and different types of anhydrous solvents (acetonitrile, dichloromethane and 1,2-dichloroethane), was used as a model in order to develop a protocol for optimising

the reaction conditions. The reaction was conducted by heating under reflux, in an  $\text{N}_2$  atmosphere (Table 1, entries 1–11) or in an air atmosphere (Table 1, entries 12–14). The results are summarised in Table 1.

The results in Table 1 show that the reactions with 0 mole % and 10 mole % of  $\text{NbCl}_5$  lead to no or insignificant yields, independent of the solvent used. The use of 25 mole % of  $\text{NbCl}_5$  afforded the best yields in the three solvents tested, of which the acetonitrile showed the best yields (87 % in 2 h) (Table 1, entry 13). With 50 mole % of  $\text{NbCl}_5$ , the product started to degrade and other products were formed, resulting in a reduction in yield (Table 1, entries 11 and 14). From these results, a time of 2 h, 25 mole % of  $\text{NbCl}_5$  and air atmosphere (Table 1, entry 13) were established as optimal for the other reactions performed.

**Table 3.** Spectral data of compounds (*VIa–VIi*)

Compound	Spectral data
<i>VIa</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2948, 2889, 1650, 1618, 1494, 1450, 1421, 1359, 1200, 1172, 1130, 1012, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.33–7.29 (m, 2H), 7.23 (dd, $J = 6.9$ Hz (2 $\times$ ), 2H), 7.13 (m, 1H), 4.83 (s, 1H), 2.70–2.52 (m, 4H), 2.41–2.30 (m, 4H), 2.08–1.96 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.5, 163.9, 144.3, 128.4, 128.1, 126.4, 116.9, 36.9, 31.6, 27.1, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_3$ [ $\text{M} + \text{Na}$ ] $^+$ : 317.1148, found 317.1129
<i>VIb</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 3030, 2952, 2892, 1650, 1614, 1510, 1452, 1417, 1355, 1338, 1232, 1197, 1172, 1012, 954 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.19 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 8.1$ Hz, 2H), 4.78 (s, 1H), 2.68–2.52 (m, 4H), 2.41–2.30 (m, 4H), 2.29–2.25 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.6, 163.8, 141.5, 135.9, 128.8, 128.2, 117.0, 37.0, 31.2, 27.1, 21.1, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_3$ [ $\text{M} + \text{Na}$ ] $^+$ : 331.1305, found 331.1308
<i>VIc</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 3531, 2948, 2887, 1720, 1670, 1650, 1604, 1427, 1361, 1272, 1203, 1174, 1130, 1110, 1014, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.55 (d, $J = 8.3$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 4.45 (s, 1H), 2.39–2.27 (m, 4H), 2.04–1.97 (m, 4H), 1.77–1.64 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.4, 168.0, 164.5, 149.3, 129.4, 128.9, 128.3, 115.9, 36.8, 31.7, 26.9, 20.1 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_5$ [ $\text{M} + \text{Na}$ ] $^+$ : 361.1046, found 361.1032
<i>VI d</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2956, 2889, 2838, 1650, 1616, 1510, 1459, 1440, 1427, 1378, 1357, 1334, 1257, 1234, 1201, 1168, 1132, 1029, 956 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.22 (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 4.77 (s, 1H), 3.74 (s, 3H), 2.68–2.53 (m, 4H), 2.42–2.29 (m, 4H), 1.95–2.09 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.6, 163.7, 158.0, 136.7, 129.3, 117.1, 113.5, 55.1, 36.9, 30.8, 27.1, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_4$ [ $\text{M} + \text{Na}$ ] $^+$ : 347.1254, found 347.1252
<i>VIe</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2943, 2873, 2831, 1650, 1620, 1488, 1467, 1454, 1429, 1382, 1357, 1334, 1290, 1245, 1207, 1176, 1134, 1116, 1045, 1027, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.39 (dd, $J = 7.6$ Hz, 1.8 Hz, 1H), 7.19–7.04 (m, 1H), 6.88 (ddd, $J = 7.5$ Hz, 7.5 Hz, 1.0 Hz, 1H), 6.80 (d, $J = 8.3$ Hz, 1H), 4.91 (s, 1H), 3.81 (s, 3H), 2.65–2.47 (m, 4H), 2.36–2.25 (m, 4H), 2.05–1.91 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.7, 164.3, 158.0, 131.9, 131.5, 127.8, 120.5, 115.3, 111.6, 55.7, 37.0, 29.2, 27.1, 20.4 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_4$ [ $\text{M} + \text{Na}$ ] $^+$ : 347.1254, found 347.1242
<i>VI f</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 3313, 2950, 2925, 1662, 1641, 1618, 1510, 1467, 1454, 1434, 1380, 1359, 1272, 1230, 1203, 1170, 1151, 1118, 1039, 1012, 956 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.08 (d, $J = 2.0$ Hz, 1H), 6.75 (d, $J = 8.1$ Hz, 1H), 6.55 (dd, $J = 8.1$ Hz, 2.0 Hz, 1H), 5.49 (s, 1H), 4.74 (s, 1H), 3.92 (s, 3H), 2.68–2.53 (m, 4H), 2.44–2.31 (m, 4H), 2.07–1.95 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.8, 163.8, 145.9, 144.1, 136.6, 119.7, 117.0, 113.9, 112.4, 55.9, 37.0, 31.0, 27.1, 20.2 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_5$ [ $\text{M} + \text{Na}$ ] $^+$ : 363.1203, found 363.1202
<i>VI g</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2954, 2890, 2823, 1650, 1620, 1521, 1415, 1384, 1348, 1253, 1234, 1201, 1170, 1130, 1080, 1014, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 8.06–7.96 (m, 2H), 7.84 (ddd, $J = 7.8$ Hz, 1.3 Hz (2 $\times$ ) Hz, 1H), 7.44–7.38 (m, 1H), 4.89 (s, 1H), 2.76–2.56 (m, 4H), 2.42–2.29 (m, 4H), 2.12–1.94 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.6, 164.6, 148.3, 146.4, 135.9, 128.7, 122.6, 121.7, 115.7, 36.8, 31.9, 27.1, 20.2 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_5$ [ $\text{M} + \text{Na}$ ] $^+$ : 362.0999, found 362.0988
<i>VI h</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2946, 2925, 2871, 1656, 1606, 1593, 1517, 1458, 1425, 1384, 1346, 1247, 1232, 1199, 1170, 1126, 1058, 1012, 956 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 8.10 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 4.88 (s, 1H), 2.70–2.59 (m, 4H), 2.39–2.30 (m, 4H), 2.02–1.96 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.4, 164.5, 151.6, 141.4, 133.6, 129.4, 128.0, 126.9, 123.4, 115.8, 36.8, 32.2, 27.1, 20.2 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_5$ [ $\text{M} + \text{H}$ ] $^+$ : 340.1179, found 340.1188
<i>VI i</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2987, 2900, 1656, 1616, 1486, 1458, 1417, 1405, 1382, 1357, 1230, 1201, 1168, 1126, 1070, 1088, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.34 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 4.76 (s, 1H), 2.67–2.51 (m, 4H), 2.41–2.30 (m, 4H), 2.09–1.93 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.5, 164.0, 143.4, 131.2, 130.2, 120.3, 116.4, 36.8, 31.4, 27.1, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{19}\text{H}_{17}\text{BrO}_3$ [ $\text{M} + \text{H}$ ] $^+$ : 373.0434, found 373.0454
<i>VI j</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2985, 2950, 2877, 1660, 1620, 1467, 1429, 1378, 1357, 1336, 1234, 1199, 1176, 1130, 1010, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.46–7.41 (m, 2H), 7.24–7.18 (m, 1H), 7.02–6.96 (m, 1H), 5.02 (s, 1H), 2.66–2.54 (m, 4H), 2.37–2.30 (m, 4H), 2.04–1.99 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.6, 164.4, 141.4, 133.5, 128.0, 126.9, 115.0, 36.9, 34.0, 27.1, 20.2, 0.0 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{19}\text{H}_{17}\text{BrO}_3$ [ $\text{M} + \text{H}$ ] $^+$ : 373.0434, found 373.0461
<i>VI k</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2983, 2906, 1660, 1618, 1483, 1450, 1432, 1380, 1357, 1228, 1201, 1174, 1126, 1088, 956 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.57–7.51 (m, 2H), 7.49–7.36 (m, 6H), 7.34–7.28 (m, 1H), 4.87 (s, 1H), 2.75–2.49 (m, 4H), 2.47–2.32 (m, 4H), 2.14–1.96 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.6, 163.9, 143.4, 141.2, 139.3, 128.8, 128.6, 127.0, 126.9, 116.8, 36.9, 31.3, 27.2, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}_3$ [ $\text{M} + \text{H}$ ] $^+$ : 371.1642, found 371.1654

Table 3. (continued)

Compound	Spectral data
<i>VII</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 3301, 2948, 2885, 1650, 1616, 1450, 1421, 1382, 1350, 1315, 1284, 1205, 1172, 1132, 1012, 958 $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.05 (dd, $J = 5.1$ Hz, 1.3 Hz, 1H), 6.93 (dd, $J = 3.5$ Hz, 0.5 Hz, 1H), 6.84 (dd, $J = 5.1$ Hz, 3.5 Hz, 1H), 5.19 (s, 1H), 2.72–2.60 (m, 4H), 2.54–2.41 (m, 4H), 2.10–2.01 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.4, 164.2, 148.4, 126.8, 125.0, 123.5, 116.4, 36.9, 27.1, 26.1, 20.6 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{S} [\text{M} + \text{Na}]^+$ : 323.0712, found 323.0706
<i>VI<sub>m</sub></i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2941, 2889, 2804, 1718, 1689, 1656, 1612, 1521, 1456, 1452, 1386, 1357, 1226, 1174, 1124, 1066, 1010, 954. $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.19–7.13 (m, 2H), 6.63–6.59 (m, 2H), 4.72 (s, 1H), 2.87 (s, 6H), 2.67–2.55 (m, 4H), 2.38–2.31 (m, 4H), 2.04–1.95 (m, 4H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.7, 163.5, 149.2, 132.7, 130.4, 129.3, 128.9, 117.3, 112.4, 112.2, 111.6, 40.6, 40.4, 37.0, 27.2, 20.3 HRMS (ESI), $m/z$ : Calcd. for $\text{C}_{21}\text{H}_{23}\text{NO}_3 [\text{M} + \text{H}]^+$ : 338.1751, found 338.1747
<i>VI<sub>n</sub></i>	IR, $\tilde{\nu}/\text{cm}^{-1}$ : 2948, 1669, 1619, 1504, 1453, 1359, 1233, 1175, 1130, 958, 809, 615. $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 400 MHz), $\delta$ : 7.08 (s, 4H), 4.73 (s, 2H), 2.67–2.50 (m, 8H), 2.41–2.26 (m, 8H), 2.04–1.98 (m, 8H) $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz), $\delta$ : 196.7, 164.0, 141.9, 128.0, 117.0, 36.9, 30.8, 27.1, 20.1

After optimisation of the reaction conditions, other arylaldehydes (*Vb–Vn*) were allowed to react in the presence of 25 mole % of  $\text{NbCl}_5$  and anhydrous  $\text{CH}_3\text{CN}$ . The products obtained were purified by re-crystallisation in ethanol and characterised by spectroscopic and spectrometric methods ( $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, IR and MS). The spectral data were compared with those in the literature (John et al., 2006; Li et al., 2013; Iniyavan et al., 2015; Shirini et al., 2015, 2014, 2013; Pramanik & Bhar, 2012; Napoleon & Khan, 2014; Maleki et al., 2012). The results are summarised in Tables 2 and 3.

The results in Table 2 show that, by using 25 mole % equivalent of  $\text{NbCl}_5$  and a reaction time of 2 h, it was possible to obtain xanthenedione derivatives (*VI<sub>a</sub>–VI<sub>n</sub>*) with good yields (55–87 %). Large yield differences were not observed by changing the benzaldehyde derivative and the compound (*VI<sub>c</sub>*) is not described in the literature. Through differential scanning calorimetric analysis (DSC), it was possible to determine the melting points, purity and enthalpy of fusion of the synthesised compounds, in accordance with the ASTM method (ASTM, 2014). The method employed for re-crystallisation afforded the products of high purity (above 97 %, with the exception of compound *VI<sub>c</sub>*).

To promote a scale-up in the process of synthesising xanthenedione derivatives, two reactions were also effected using 10.0 mmol of arylaldehyde (*V<sub>a</sub>* or *V<sub>c</sub>*) in the presence of 2.5 mmol of  $\text{NbCl}_5$ . The yields obtained were similar to the experiments performed with (1.0 mmol), 85 % for product *VI<sub>a</sub>* and 67 % for product *VI<sub>c</sub>*, after re-crystallisation. These results showed that niobium pentachloride is an excellent catalyst for the scale-up process and large-scale applications of these xanthenedione derivatives.

In summary, a simple and efficient procedure for the synthesis of xanthenedione derivatives is described. The reactions were carried out using

25 mole % of  $\text{NbCl}_5$  and acetonitrile as a solvent under reflux, in an air atmosphere, for 2 h, affording good yields of the products.

## Conclusions

A simple and efficient procedure was developed for preparing a variety of 9-aryl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione derivatives by the reactions of various arylaldehydes with 1,3-cyclohexanedione in the presence of niobium pentachloride and anhydrous acetonitrile as solvent under reflux, in an air atmosphere, for 2 hours, affording good yields of the products.

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## Supplementary data

Supplementary data associated with this article can be found in the online version of this paper (DOI: 10.1515/chempap-2016-0098).

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