

ORIGINAL PAPER

Efficient one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by niobium pentachlorideAloisio de Andrade Bartolomeu*, Manoel Lima de Menezes,
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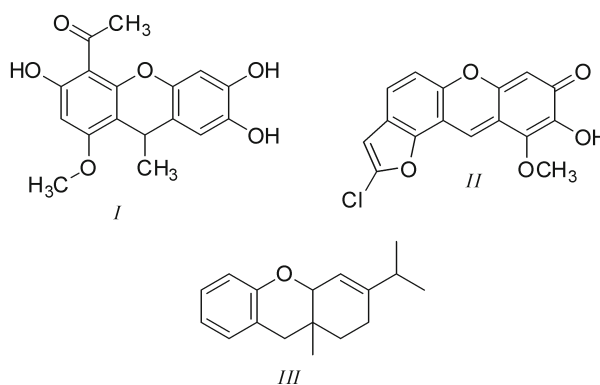
A simple and efficient procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives through one-pot condensation of 2-naphthol with aryl aldehydes in the presence of niobium pentachloride is described. The reactions were carried out using 25 mole % of NbCl₅, at ambient temperature, and in acceptable reaction times, affording excellent yields of the products.

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Keywords: niobium pentachloride, Lewis acid, one-pot condensation, 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives

Introduction

The synthesis of xanthenes and their derivatives has received significant attention due to their various pharmacological activities, such as antibacterial and antifungal (Limsuwan et al., 2009; Omolo et al., 2011), analgesic and anti-inflammatory (Hafez et al., 2008; Banerjee et al., 2011), anti-viral (Jamison et al., 1990; Naidu et al., 2012), antioxidant (Nishiyama et al., 1998), anti-cancer (Chatterjee et al., 1996; Song et al., 2013), cytotoxic (Bhattacharya et al., 2009) and anti-proliferative properties (Kumar et al., 2010). These compounds have also been employed as sensitizers in photodynamic therapy (Neckers, 1989; Gutiérrez & García, 1998; Chang et al., 2008), in the food industry as additives (Tanaka, 2001; Chequer et al., 2012; Odo et al., 2012; Qi et al., 2012), in laser technologies (Ahmad et al., 2002; De et al., 2005) and as fluorescent materials for the visualisation of biomolecules (Knight & Stephens, 1989; Liu et al., 2001; Hilderbrand & Weissleder, 2007). In addition, xanthenes and their derivatives can be used as sensitizers in dye-sensitised solar cells (DSSCs) (Hara et al., 2000; Pradhan et al., 2007; Guillén et al., 2008; Sharma et al., 2009) and as

**Fig. 1.** Examples of natural xanthenes.

hole-transporting materials in organic light-emitting devices (OLEDs) (Chu et al., 2012).

Xanthenes are rare in natural plants and have been isolated from only two plant families, Compositae and Fabaceae (Ravindranath & Seshadri, 1973; Thangadurai et al., 2001; Cao et al., 2007, 2008; Huang et al., 2010). Compounds *I*, *II* and *III* are examples of natural xanthenes (Fig. 1). Blumeaxanthene (*I*)

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and blumeaxanthene II (*II*) have been isolated from *Blumea riparia* DC (Compositae), a Chinese medicinal herb traditionally used to treat gynecological disorders (Huang et al., 2010) and the 3-isopropyl-9a-methyl-1,2,4a,9a-tetrahydroxanthene (*III*) has been isolated from *Indigofera longiracemosa* Boiv. Ex. Baill. (Fabaceae) for use in traditional Indian medicine as an antidote for all snake venoms (Thangadurai et al., 2001).

Due to the applicability of the xanthenes and benzoxanthenes, several synthetic protocols have been reported, including the reaction of alkylphenoxy-magnesium halides with triethylorthoformate (Casiraghi et al., 1973), the palladium-catalysed cyclisation of polycyclic aryltriflate esters (Wang & Harvey, 2002), the cyclocondensation reaction between 2-tetralone and 2-hydroxyarylaldehydes under acidic conditions (Jha & Beal, 2004), and the reaction of the condensation of cyclic 1,3-diketones with aryl aldehydes catalysed by molybdate sulphonic acid (Karami et al., 2013). Furthermore, 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives can be prepared by the condensation reaction of 2-naphthol with aryl aldehydes in the presence of different Lewis acids (Ding et al., 2007; Wang et al., 2008; Urinda et al., 2009; Wang et al., 2010; Soleimani et al., 2011; Tabatabaieian et al., 2011; Mirjalili et al., 2011; Zolfigol et al., 2012; Rao et al., 2012; Cao et al., 2013) and Brønsted acids (Gong et al., 2009; Hajipour et al., 2010; Rahmatpour, 2011; Ghassamipour & Sardarian, 2012; Prasad et al., 2012; Zare et al., 2012).

Several metallic Lewis acids (Saini et al., 2006; Wang et al., 2008, 2010; Urinda et al., 2009; Soleimani et al., 2011; Tabatabaieian et al., 2011; Mirjalili et al., 2011; Rao et al., 2012; Zolfigol et al., 2012; Cao et al., 2013) have been employed as catalysts in this type of reaction whilst, in the current work, studies on the use of niobium pentachloride (NbCl₅) as a catalyst in these one-pot reactions are reported. NbCl₅ forms chloro-bridged dimers in its solid state in which each niobium atom is surrounded by a distorted octahedron of chlorine atoms. NbCl₅ is highly electrophilic and can act as a Lewis acid, promoting several organic transformations (Batista et al., 1997; Kobayashi et al., 2000; Constantino et al., 2001, 2004, 2005, 2007; Andrade, 2004; da Silva-Filho et al., 2005, 2008; Andrade & Rocha, 2006; Wang et al., 2007; Polo et al., 2008; Cai et al., 2010; Hou et al., 2010, 2011; da Silva et al., 2012; dos Santos & da Silva, 2012; Lacerda et al., 2012; Liu et al., 2013; Martins et al., 2013; dos Santos et al., 2013; Bian et al., 2014; Nasserri et al., 2014).

Experimental

All reactions were performed under an atmosphere of N₂. CH₂Cl₂ was distilled from CaH₂. All chemicals were purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification.

Table 1. Optimisation of reaction between 2-naphthol (*IV*) and benzaldehyde^a (*Va*)

Entry	Amount of catalyst/mole %	Time/h	Yield ^b /%
1	0	120	5
2	10	48	60
3	25	48	90
4	50	24	75

a) Reaction conditions: 2-naphthol (1.0 mmol), benzaldehyde (0.5 mmol) and NbCl₅ (0–50 mole %) in CH₂Cl₂ at ambient temperature; b) yield of isolated products.

NbCl₅ used was re-crystallised by sublimation following the procedure detailed in the literature (Alves, 1986). Thin-layer chromatography was performed on 0.2 mm Merck 60 F₂₅₄ silica gel aluminium sheets, which were visualised with an ammonium cerium(IV) sulphate/phosphomolybdic acid/sulphuric acid/water mixture. Infrared (IR) spectra were recorded on a Bruker Vertex 70 Fourier Transform spectrometer using a Bruker Platinum ATR unit. Bruker DPX 300, DRX 400 and DRX 500 spectrometers were employed for the NMR spectra (CDCl₃ solutions) using TMS as internal reference for ¹H and CDCl₃ as an internal reference for ¹³C NMR spectra. MS analyses were performed on a PerkinElmer Clarus 680 GC equipped with a Clarus SQ 8T mass spectrometer. The melting point of compounds were determined by DSC analyses. DSC measurements were performed using a PerkinElmer DSC 8500 with power compensation.

General procedure for one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives

To a solution of NbCl₅ (25 mole %) in anhydrous CH₂Cl₂ (2.0 mL), maintained at ambient temperature under N₂ atmosphere, were added a solution of 2-naphthol (*IV*) (1.0 mmol) and the respective aldehyde (*Va–Vu*) (0.5 mmol) in anhydrous CH₂Cl₂ (4.0 mL). Once the addition was completed, stirring was continued at the same temperature for 24 or 48 h (Table 2). The reaction mixture was quenched with H₂O addition (3.0 mL) and the product was extracted with CH₂Cl₂ (10.0 mL). The organic layer was separated and washed with saturated aqueous NaHCO₃ (3 × 10.0 mL), brine (2 × 10.0 mL), dried over anhydrous MgSO₄, filtered and the solvent from the filtrate evaporated under vacuum. The residue was re-crystallised from ethanol to afford pure products (*VIa–VIu*). The full experimental details and spectroscopic characterisations (¹H and ¹³C NMR, infrared and mass spectrometry) for compounds *VIa–VIu* can be found in the Supplementary Content section of this article's web page.

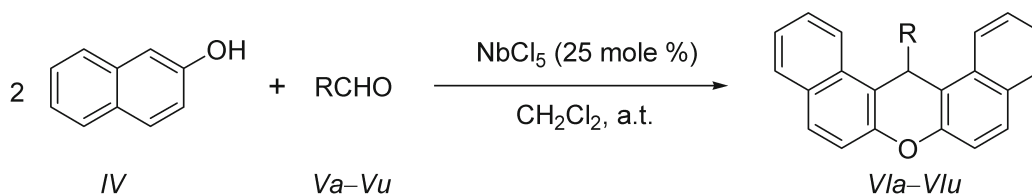
Results and discussion

The reaction between 2-naphthol (*IV*) and ben-

Table 2. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by NbCl₅

Product	R	Time/h	Yield ^a /%	M.p./ °C	
				Found	Reported ^b
<i>VIa</i>	C ₆ H ₅	48	90	190	190–191 (Ding et al., 2007)
<i>VIb</i>	4-FC ₆ H ₄	48	91	247	245 (Poupelin et al., 1978a)
<i>VIc</i>	3-FC ₆ H ₄	48	93	222	220 (Poupelin et al., 1978a)
<i>VI d</i>	2-FC ₆ H ₄	24	95	233	234 (Poupelin et al., 1978a)
<i>VIe</i>	4-ClC ₆ H ₄	48	95	295	295 (Rostamizadeh et al., 2008)
<i>VI f</i>	3-ClC ₆ H ₄	48	96	200	199–200 (Kumari et al., 2008)
<i>VI g</i>	2-ClC ₆ H ₄	24	96	220	221 (Poupelin et al., 1978a)
<i>VI h</i>	4-BrC ₆ H ₄	48	97	300	300–302 (Jin et al., 2006)
<i>VI i</i>	3-BrC ₆ H ₄	48	97	195	194–195 (Rostamizadeh et al., 2008)
<i>VI j</i>	2-BrC ₆ H ₄	24	96	215	216–217 (Nasr-Esfahani & Abdizadeh, 2013)
<i>VI k</i>	4-OCH ₃ C ₆ H ₄	48	70	201	202–203 (Gong et al., 2009)
<i>VI l</i>	3-OCH ₃ C ₆ H ₄	24	91	182	180–181 (Bhattacharya & Rana, 2007)
<i>VI m</i>	2-OCH ₃ C ₆ H ₄	24	93	261	258–259 (Mirjalili et al., 2011)
<i>VI n</i>	4-NO ₂ C ₆ H ₄	24	98	329	326–328 (Tabatabaieian et al., 2011)
<i>VI o</i>	3-NO ₂ C ₆ H ₄	24	97	225	224–226 (Ding et al., 2007)
<i>VI p</i>	4-CH ₃ C ₆ H ₄	24	95	233	233–234 (Rostamizadeh et al., 2008)
<i>VI q</i>	3-CH ₃ C ₆ H ₄	24	96	201	197–198 (Mirjalili et al., 2011)
<i>VI r</i>	2-CH ₃ C ₆ H ₄	24	98	208	208 (Poupelin et al., 1978a)
<i>VI s</i>	4-[(CH ₃) ₃ C]C ₆ H ₄	24	92	302	303 (Prasad & Nath, 2012)
<i>VI t</i>	4-C ₆ H ₅ C ₆ H ₄	48	96	285	281 (Poupelin et al., 1978b)
<i>VI u</i>	4-SCH ₃ C ₆ H ₄	48	88	213	216 (Hunnur et al., 2008)

a) Yield of isolated products; b) all products are known and their melting points were compared with values already reported.

**Fig. 2.** NbCl₅-promoted synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes.

zaldehyde (*Va*) was used as a reaction model in order to develop a protocol for the optimisation of the reaction conditions. The results are summarised in Table 1, where it can be seen that this reaction was strongly influenced by the amount of catalyst. The best results were obtained using 25 mole % of catalyst in 48 hours (Table 1, entry 3) and 50 mole % in 24 hours (Table 1, entry 4). Accordingly, 25 mole % of catalyst was selected for use in these reactions due to its low concentration, which resulted in excellent yields.

After optimisation of the reaction conditions, other benzaldehydes (*Vb–Vu*) were examined in the presence of 25 mole % of NbCl₅. These one-pot reactions were carried out under an inert atmosphere of N₂, at ambient temperature and using anhydrous CH₂Cl₂ as solvent. The products obtained were purified by recrystallisation in ethanol and characterised by spectroscopic (¹H NMR, ¹³C NMR and FTIR) and spectrometric (GC-MS) methods. The results are summarised in Fig. 2 and Table 2. In general, the results given in Table 2 show that excellent yields of 14-aryl-

14*H*-dibenzo[*a,j*]xanthene derivatives were obtained under mild conditions in 24 or 48 hours. Furthermore, it was observed that this protocol permitted the use of aryl aldehydes containing electron-withdrawing and electron-donating groups.

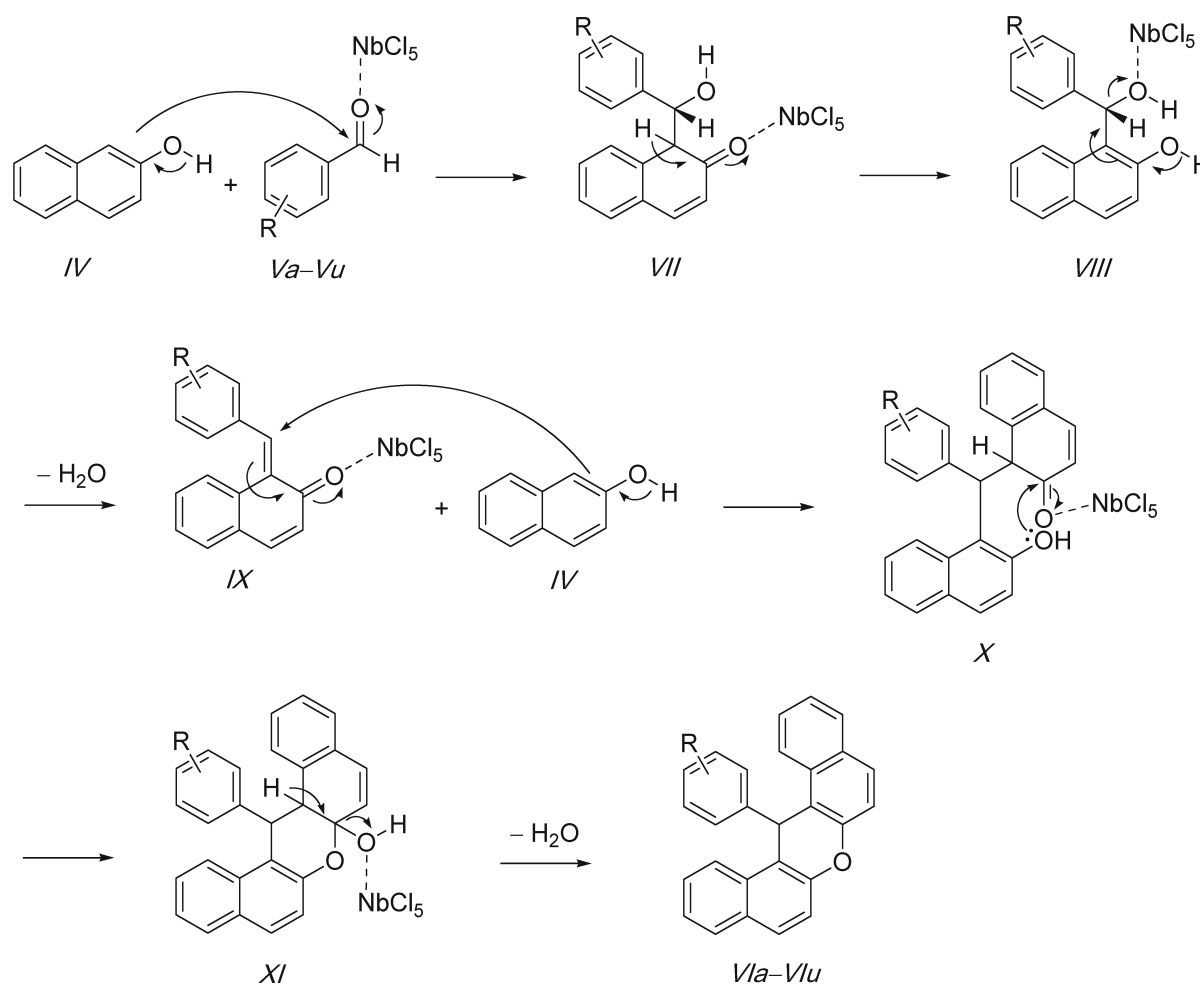
In Table 3, the result obtained in this work (Entry 1) for the synthesis of 14-(4-chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene (*VIe*) is compared with other studies detailed in the literature (Khosropour et al., 2005; Das et al., 2006; Nagarapu et al., 2007; Dabiri et al., 2008a, 2008b; Urinda et al., 2009; Wang et al., 2010; Rahmatpour & Aalaie, 2011; Zolfigol et al., 2012). The results presented in Table 3 show that, regardless of the catalyst used, in the presence or absence of solvent, high temperatures are necessary to obtain good yields of xanthene *VIe*. When compared with other catalysts, NbCl₅ proved to be the only one capable of promoting this one-pot reaction with good yields at ambient temperature.

A possible mechanism for the condensation reaction of 2-naphthol (*IV*) with aryl aldehydes (*Va–Vu*) promoted by NbCl₅ is presented in Fig. 3. The mech-

Table 3. Comparison of efficiency of several catalysts for synthesis of 14-(4-chlorophenyl-14*H*-dibenzo[*a,j*]xanthene (*VIe*)

Entry	Catalyst	Solvent	Temp/°C	Time/h	Yield ^c /%, reference
1	NbCl ₅ ^a	DCM	a.t.	48	95 (This paper)
2	Alum ^b	DCM	a.t.	24	Traces (Dabiri et al., 2008a)
3	PS/AlCl ₃ ^b	DCM	Reflux	6	Traces (Rahmatpour & Aalaie, 2011)
4	PTSA ^b	DCE	Reflux	18	93 (Khosropour et al., 2005)
5	In(OTf) ₃ ^b	H ₂ O	100	7	80 (Urinda et al., 2009)
6	Alum ^b	H ₂ O	100	4	90 (Dabiri et al., 2008a)
7	MK-10 ^a	None	120	2	89 (Dabiri et al., 2008b)
8	PTSA ^b	None	125	2.5	95 (Khosropour et al., 2005)
9	I ₂ ^a	None	90	3	90 (Das et al., 2006)
10	WO ₃ /ZrO ₂ ^b	None	125	2	92 (Nagarapu et al., 2007)
11	FeCl ₃ ^a	None	100	10	96 (Wang et al., 2010)
12	WCl ₆ ^b	None	110	0.1	97 (Zolfigol et al., 2012)

a) 4-Chlorobenzaldehyde/2-naphthol = 0.5 mmol : 1.0 mmol; b) 4-chlorobenzaldehyde/2-naphthol = 1.0 mmol : 2.0 mmol; c) yield of isolated products.

**Fig. 3.** Proposed reaction mechanism for one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes promoted by NbCl₅.

anism for the reaction is assumed to be the same as that proposed by Zolfigol et al. (2012) using WCl₆ as a Lewis acid. Initially, the aryl aldehyde is activated by NbCl₅. Next, the carbonyl group of the activated aldehyde is attacked by 2-naphthol, producing the intermediate **VII**. Intermediate **VIII** is produced by the

hydrogen transfer in **VII**. Subsequently, after elimination of a water molecule, *o*-quinone methide (**IX**) is generated. Intermediate **IX** is activated by NbCl₅ and acts as a Michael acceptor. Subsequently, this intermediate undergoes a Michael addition of another molecule of 2-naphthol and produces **X**, which is then

converted into *XI* by the NbCl₅-promoted ring closing of *X*. Finally, after elimination of a water molecule from *XI*, the dibenzoxanthenes (*VIa–VIu*) are formed.

Conclusions

In conclusion, a simple and efficient procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives under mild conditions was described. The reactions were carried out using 25 mole % of NbCl₅, at ambient temperature, and in acceptable reaction times, affording excellent yields of the products.

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Supplementary data

Supplementary data associated with this article (Efficient one-pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by niobium pentachloride) can be found in the online version of this paper (DOI: 10.2478/s11696-014-0597-8).

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