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Synthesis of pterocarpans through palladium-catalyzed oxyarylation of alkoxy-2*H*-chromenes with *o*-iodophenols

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ABSTRACT

The oxyarylation of alkoxy-2*H*-chromenes (**1a**-**e**) with *o*-iodophenols substituted by electron-withdrawing (CHO) and electron-donating (OMe) groups is studied under two experimental conditions: a) $Pd(OAc)_2$, Ag_2CO_3 in PEG-400 at 140 °C, 10 min and b) oxime-based palladacycle, DIPEA, in PEG-400 at 150 °C, 3–4 h. Pterocarpans are obtained in moderate to good chemical yields.

1. Introduction

The oxyarylation reaction was discovered by Horino and Inoue in 1971 and represented an unparalleled tool for obtaining polyfunctionalized compounds bearing benzofuran-scaffolds [1a–c]. The oxyarylation of alkoxy-2*H*-chromenes with alkoxy-o-mercury substituted phenols was used in the synthesis of natural pterocarpans, coumestans and analogues [2] (Fig. 1) [2a-d] subgroups of the isoflavonoids comprising several bioactive products. Under these conditions the mercury-palladium exchange as well as the carbo-palladation step occurs at room temperature and the precursors are easily prepared from available alkoxy phenols bearing different patterns of oxygenation [2a-d], but the stoichiometric use of palladium salts and the need of organomercurial intermediates are severe limitations. However, these conditions are still eventually used to prepare compounds substituted by alkoxy groups at the D-ring [2e].

In 1995, Larock and co-workers [3] reported the first examples of the palladium-catalyzed synthesis of non-natural pterocarpans through the oxyarylation of 6-MeO-2*H*-chromen with *o*-iodophenols in the presence of 5 mol% of $Pd(OAc)_2$ and 10 mol% of PPh_3. Under these conditions, moderate yields of pterocarpans were obtained with *o*-iodophenols substituted by electron-withdrawing groups (Fig. 1). However, the presence of a methoxy group at *o*-iodophenol lead to adducts in lower yields.

Antus and Kiss reported the oxyarylation of 6-MeO-2*H*-chromene with *o*-iodophenol in the presence of silver carbonate as base, in acetone (Fig. 1) [4]. Costa and Nájera broadened the scope of this reaction using 2*H*-chromene and 6-Cl-2*H*-chromene as olefins and *p*-substituted *o*-iodophenols under MW heating. Moderate to good yields of non-natural pterocarpans were obtained when these phenols were substituted by electron-withdrawing groups (Fig. 1) but low yield was observed when dihydronaphthalene was oxyarylated with electron-rich 5-methoxy-*o*-iodophenol [5,6]. A cationic mechanism for these oxyarylations was firstly proposed by Antus [6a] and confirmed by electrospray mass spectrometry studies [6b]. The cationic mechanism was also suggested for other

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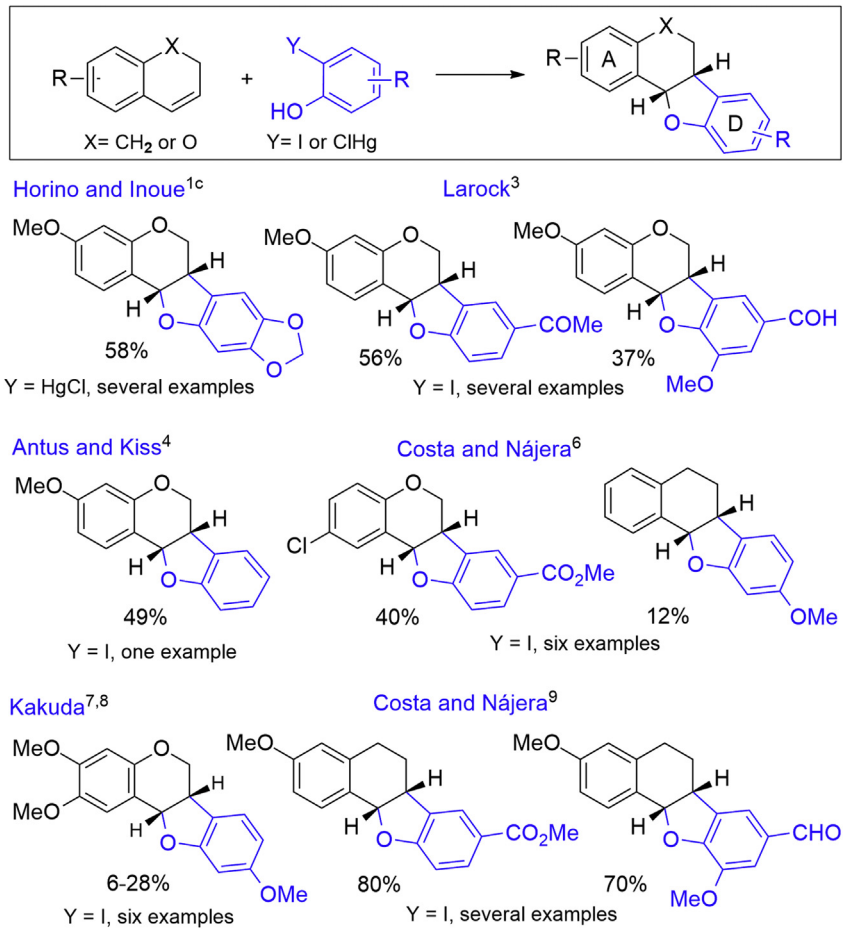


Fig. 1. Selected examples of oxyarylation of 2*H*-chromenes.

oxyarylations [6c,6d,6e]. These reactions were also accomplished in the absence of a Lewis acid, using an oxime-palladacycle as pre-catalyst [5]. Low yield in the oxyarylation of 6,7-dimethoxy-2*H*-chromene with 5-methoxy-*o*-iodophenol was also reported by Kakuda [7] in the synthesis of antiproliferative pterocarpans isolated from the Brazilian flora [8] (Fig. 1). Costa and Nájera reported the oxyarylation of alkoxy-1,2-dihydronaphthalenes with *o*-iodophenol substituted by electron-withdrawing groups at the *para* position, leading to adducts in good to excellent yields when PEG-400 was used as solvent [9]. In this solvent, it was observed the *in situ* generation of palladium nanoparticles, faster reactions (10 min for $Pd(OAc)_2$ and 3–4 h for an oxime-based palladacycle) and better chemical yields when compared to the use of acetone as solvent under MW heating [5].

In this paper, we report the synthesis of pterocarpans (**3**) through a catalytic oxyarylation of 2*H*-chromenes (**1**) with *o*-iodophenols (**2**) under appropriate reaction conditions (Fig. 2).

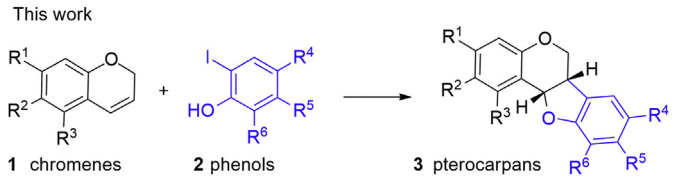
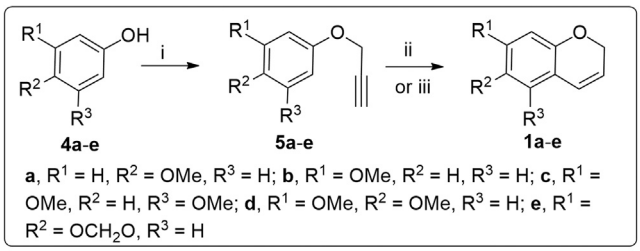


Fig. 2. Synthesis of pterocarpans (**3**) through a catalytic oxyarylation of 2*H*-chromenes (**1**) with *o*-iodophenols (**2**).

2. Results and discussion

The synthesis of 2*H*-chromenes (**1a-e**) is shown in Scheme 1. Firstly, the O-alkylation of phenols **4a-e** was carried out with propargyl bromide to furnish compounds **5a-e** in excellent yields. Among the approaches available to prepare 2*H*-chromenes, the thermic cyclization of *O*-propargylated phenol ethers **5** is less costly and can lead to **1** with several oxygenated substituents at the aromatic ring [10a,b]. The use of microwave heating in PEG-400



i) K_2CO_3 1.5 equiv, Propargyl bromide (1.2 equiv), acetone, r.t. 24 h,75-90%

ii) PEG-400, MW 300W ,170 °C, 15 min
1a (60%) **1b** (48%) **1c** (56%) **1d** (42%) **1e** (50%)

iii) PEG-400, 220 °C, 2 h
1a 56%) **1b** (42%) **1c** (50%) **1d** (44%) **1e** (47%)

Scheme 1. Synthesis of 2*H*-chromenes **1a-e**.

(170 °C, 15 min) allowed the preparation of 2*H*-chromenes **1a** and **1c** from symmetric **5a** and **5c** in 60% and 56% yield, respectively, after flash chromatography. Unfortunately, **1b** was obtained from **5b** as a 1:1 mixture with a regioisomer (structure not shown, see supplementary material). Although **1b** could be obtained in moderate yield in pure form (48%), it was laborious to purify by chromatography. In contrast, the cyclization of **5d** and **5e** was more regioselective and small amounts of the corresponding regioisomers of **1d** and **1e** could be easily removed by flash chromatography. Even though, under thermal conditions (*N*,*N*-diethylaniline or xylene under reflux) the reported reactions time were too long [10a,b], in our hands, using PEG-400 as solvent at 220 °C, 2*H*-chromenes were prepared in 1.5 h, in similar reasonable chemical yields and these conditions are useful for gram-scale reactions (Scheme 1).

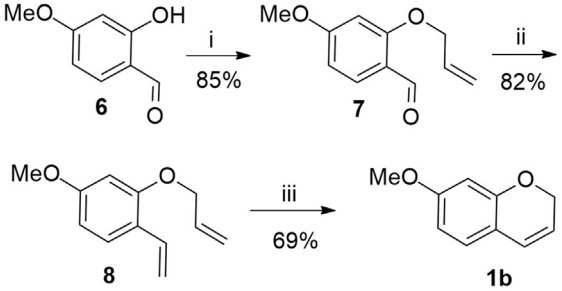
An alternative route to prepare **1b** is shown in Scheme 2. When aldehyde **6** was allowed to react with allyl bromide intermediate **7** was obtained and was then submitted to a Wittig olefination to produce **8** in 82% yield. In the presence of Grubbs 2nd generation catalyst, a metathesis reaction took place, leading to **1b** in 69% (48% overall yield) [11].

This approach could be eventually used to prepare other 2*H*-chromenes. On the other hand, *o*-iodophenols **2a** and **2e** are commercially available, while **2b-d** were prepared by iodination of the corresponding phenols [12,13].

Next, we examined the oxyarylation of **1a-e** with *o*-iodophenol (**2a**) (Scheme 3) and based on our previous experience [5,9], two experimental conditions were selected for this study, Conditions A: $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (1.1 equiv) in PEG-400 at 140 °C and Conditions B: oxime-based palladacycle (5 mol%), Cy_2NH (3 equiv), in PEG-400 at 150 °C.

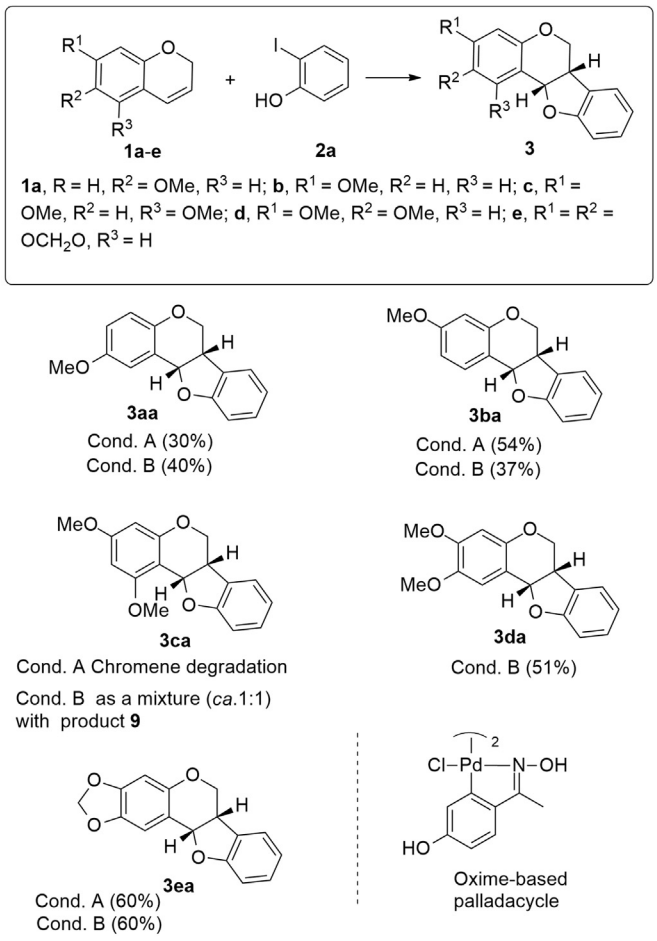
Concerning oxyarylations of 2*H*-chromenes **1a-e** with *o*-iodophenol (**2a**) under Conditions A (Scheme 3), reactions were very fast (ca. 10 min) and pterocarpans **3aa**, **3ba**, **3da** and **3ea** were regioselectively obtained in moderate to good yields. However, 2*H*-chromene **1c** was unstable in the presence of silver carbonate, even at rt, and the expected adduct **1ca** was not formed under these reaction conditions. Under Conditions B (Scheme 3), oxyarylations of **1a**,**b**,**d**,**e** with **2a** were slower and 3–4 h of reaction time was required to obtain the corresponding pterocarpans **3aa**, **3ba**, **3da** and **3ea** in moderate to good yields. However, the oxyarylation of **1c** with **2a** under Conditions B led to the expected pterocarpan **3ca** along with a secondary product **9** (Scheme 4). After 4 h of reaction it was possible to identify by ^{1}H NMR the presence of products **3ca** and **9**, as a ~1:1 mixture. The mixture of **3ca** and **9** was separated and their structures established. We have tried to favor the formation of **3ca** using phosphine ligands. After some screening experiments, a 66:37 mixture of **3ca**:**9** was formed in the presence of SPhos (Scheme 4) and **3ca** could be obtained in pure form by flash chromatography, in 51% yield, along with 22% of **9**.

It is worth to mention that while in adducts **3** the oxygen of the *o*-iodophenol (**2**) appears attached to the benzylic carbon of the olefin (**1**), in **9** is the aromatic ring of the *o*-iodophenol which is attached this carbon. This suggests that these products may be

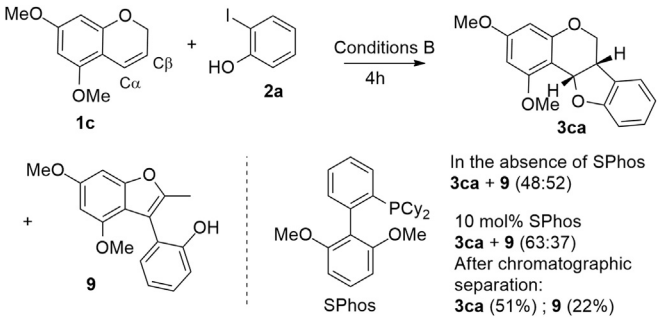


i) Allyl bromide (1.3 equiv), K_2CO_3 (2.5 equiv), acetone, rt, 18 h
ii) Ph_3PMeI (1.2 equiv), NaH (1.5 equiv), THF, 0 °C to rt, 6 h
iii) Grubbs 2nd G (1 mol%), DCM, rt, 18 h

Scheme 2. Alternative synthesis of 2*H*-chromene **1b**.



Scheme 3. Oxyarylation of **1a-e** with **2a**. Synthesis of pterocarpans.



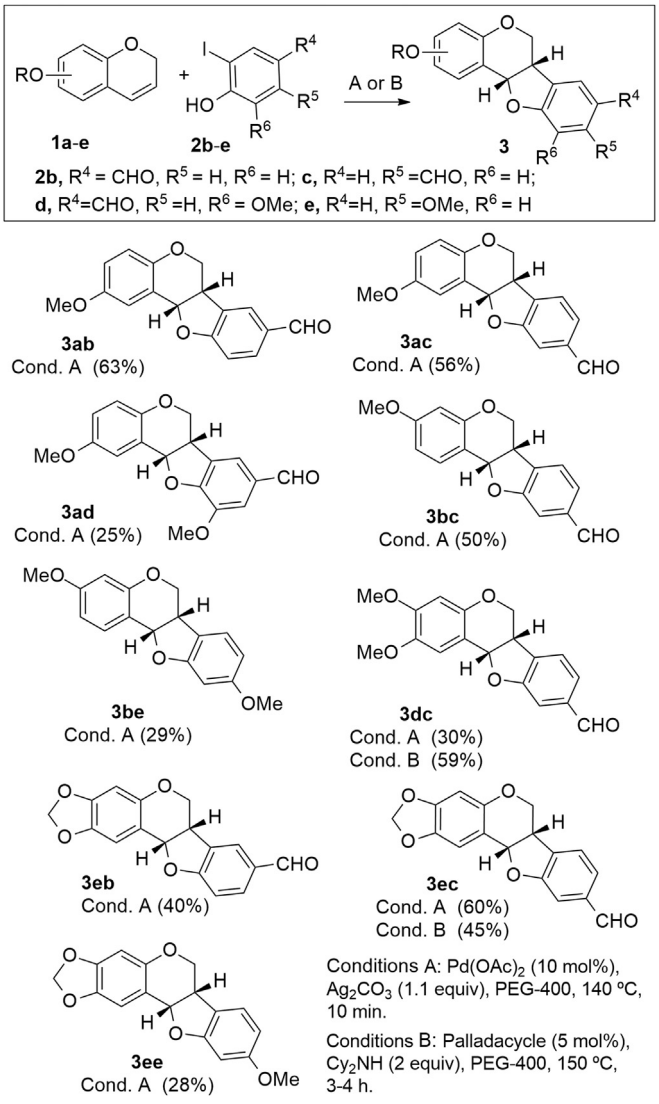
Scheme 4. Effect of SPhos in the regioselectivity of the oxyarylation of **1c** with **2a**.

It is worth to mention that while in adducts **3** the oxygen of the *o*-iodophenol (**2**) appears attached to the benzylic carbon of the olefin (**1**), in **9** is the aromatic ring of the *o*-iodophenol which is attached this carbon. This suggests that these products may be

originated from regioisomeric mechanistic pathway (see mechanistic discussion).

In Scheme 5 are shown the results obtained for the oxyarylation of olefins **1a-e** with substituted *o*-iodophenols **2b-e**. Under Conditions A, 2*H*-chromene **1a** reacted with electron-poor *o*-iodophenols **2b** and **2c** leading respectively, to **3 ab** and **3ac** in moderate to good yields. The simultaneous presence of a methoxy group and an aldehyde group at the structure of *o*-iodophenol, as in **2d**, lead to a decrease in the yield of adduct **3ad** to 25%. The oxyarylation of 2*H*-chromen **1b** with **2c** led to **3bc** in 50% yield. Finally, in the oxyarylation of this 2*H*-chromen with electron-rich *o*-iodophenol **2e** (absence of electron-withdrawing group) under the same reaction conditions led to natural pterocarpan **3be** in moderate 29% yield.

2*H*-Chromene **1d** led to **3dc** under both reaction conditions, but better yield (59%) was obtained under Conditions B. Finally, under Conditions A, 2*H*-chromene **1e** was oxyarylated with **2b** leading the expected adduct **3eb** in 40% yield. The oxyarylation of this 2*H*-chromene with **2c** led to pterocarpan **3ec** in moderate yield under Conditions A and B. Also, in this case oxyarylation with electron-rich *o*-iodophenol **2e** led to **3ee** in moderate 28% yield under conditions A.



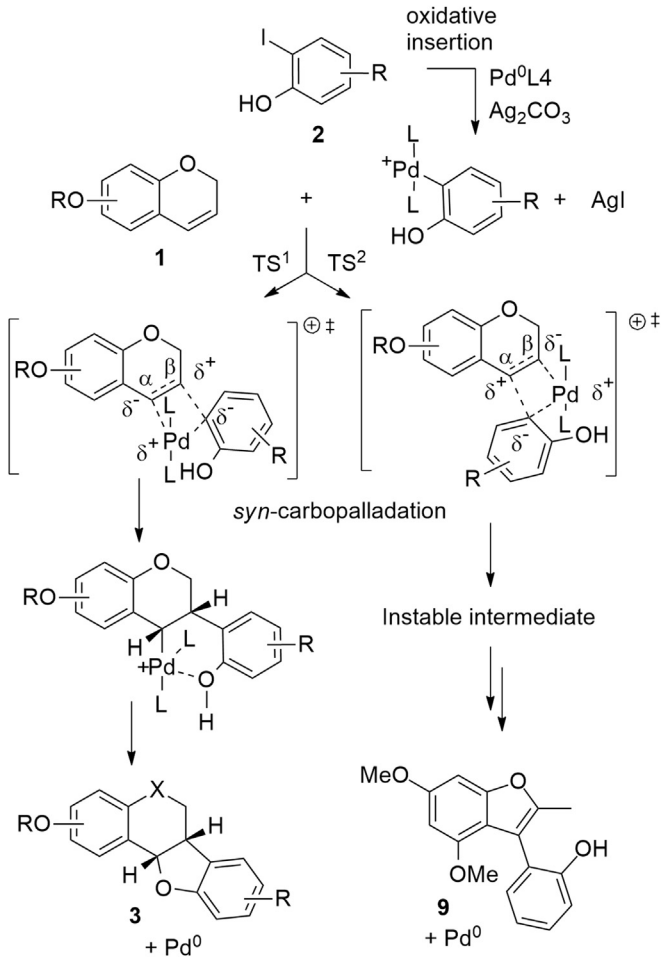
Scheme 5. Oxyarylation of **1a-e** with **2b-e**.

3. Mechanistic considerations

Based on the literature and in our previous results we propose that under Conditions A (TS^1) a cationic mechanism is operating [14–16]. The oxyarylation reaction would starts with the attack of an electrophilic cationic palladium specie ($ArPd^+$) to the double bound of 2*H*-chromene 1 (Scheme 6). This step would be fast for our electron-rich olefins originating a σ-complex, which can lead to a positive transition state precursor of adducts, were a partial positive charge is developed at the β-carbon and is not stabilized by the aromatic ring at 2*H*-chromene moiety (TS^1). The resulting palladacycle intermediate undergoes a reductive elimination of the Pd^0 and the formation of the ether linkage in **3** with retention of the configuration at the benzylic carbon.

As under Conditions A the oxyarylations of 2*H*-chromenes **1** with iodophenols **2** afforded exclusively **3**, the regiochemistry under these conditions seems to be controlled mainly by steric interactions between the incoming aryl group and the aromatic group at the olefin in the transition state, as occurs in the Heck reaction [15,16].

It is worth to mention that the regioselectivity in the arylation of substituted styrenes with cationic arylpalladium species was previously addressed by Fristrup and co-workers [17]. They observed that the rate of formation of stilbenes, the main products in these Heck reactions, is not dependent on the electronic effect of the substituent at the styrene moiety. In the proposed TS leading to the



Scheme 6. Mechanistic rationalization for the oxyarylation of **1** with **2** under Conditions A.

main product, a partial positive charge is developed at the β-carbon and ρ = 0. However, the rate of the regioisomeric products increased for electron-releasing groups. In this case, in the corresponding TS a partial positive charge is developed at the benzylic carbon and, as consequence, ρ = −0.74. These results [17] support our mechanistic rationalization.

Under Conditions B, oxyarylation of **1** with **2** were also regioselective for the majority of 2*H*-chromenes, leading to pterocarpans **3**. The exception was the oxyarylation of **1c** with **2a**, which furnished a mixture of **3ca** and **9** (*ca.* 1:1, in the absence of ligands). Once it is known that palladium catalyzed reactions in water can go through a cationic mechanism, even in the absence of a silver salt [14] and since PEG-400 is relatively polar and the temperature employed is high (150 °C), we can accept a cationic mechanism under these reaction conditions. It is worth to mention that in this case the partial positive charge at the benzylic carbon is stabilized by resonance by the two methoxy groups, but the possible regioisomer of adduct **3ca** was not observed in the reaction medium. Following the reaction by TLC one can observe the formation of a possible intermediate which is not present at the end of the reaction, which is transformed in **9**. Unfortunately, we didn't succeed to purify this compound and establish its structure.

Theoretical studies (DFT) were undergone to try to corroborate our proposed mechanistic rationalization but, unfortunately, the results obtained were not conclusive.

4. Conclusions

Pterocarpans could be prepared in moderate to good yield by oxyarylation of 2*H*-chromenes with *o*-iodophenols using two experimental conditions: a) $Pd(OAc)_2$, Ag_2CO_3 in PEG-400 at 140 °C, 10 min and b) oxime-based palladacycle, DIPEA, in PEG-400 at 150 °C, 3–4 h. Aldehydes are only scarce used in oxyarylation reactions [9,18]. In the prepared pterocarpans, these groups can be used as precursor of other chemical functionalities or to connect the structure to another bioactive compound or to a carrier group [19]. Work is now in progress to better evaluate the mechanism of these oxyarylations and to study the antiproliferative effect of the synthesized compounds.

5. Experimental section

All commercially available reagents and solvents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 or 500 MHz for ^{1}H NMR and 101 or 126 MHz for ^{13}C NMR using TMS as internal standard (0.00 ppm). The following abbreviations are used to describe peak patterns where appropriate. All coupling constants (J) are given in Hz and chemical shifts in ppm. 13C NMR spectra were referenced to $CDCl_3$ at 77.16 ppm. Low-resolution electron impact (GC-EI) mass spectra were obtained at 70 eV with a Shimadzu QP-5000 instrument, and HRMS (GC-EI) were recorded with a Finnigan MAT 95 S instrument. Analytical TLC was performed with Schleicher & Schuell F1400/LS silica gel plates, and the spots were visualized under UV light (λ = 254 nm). For flash chromatography, Merck silica gel 60 (0.040–0.063 mm) was employed.

5.1. General procedure for the preparation of aryl propargyl ethers

To a mixture of phenols **4a**–**d** (1 mmol), K_2CO_3 (1.5 mmol) and acetone (2.0 mL) was slowly added propargyl bromide (1.2 mmol) under magnetic stirring at rt. After 18 h, the reaction was diluted with EtOAc (15 mL), the organic layer was washed with H2O (5 mL) and brine (3 × 5 mL), dried over anhydrous sodium sulfate, and filtered. The solvent was evaporated in vacuo and the resulting oil was pure enough to ne next step.

5.1.1. 1-Methoxy-4-(prop-2-yn-1-yloxy)benzene (**6a**) [20]

Yellow oil, (97.3 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (d, *J* = 9.2 Hz, 2H), 6.86 (d, *J* = 9.4 Hz, 2H), 4.62 (d, *J* = 2.7 Hz, 2H), 3.74 (s, 3H), 2.59 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3): δ 154.4, 151.7, 116.16, 114.6, 79.1, 75.6, 56.5, 55.5.

5.1.2. 1-Methoxy-3-(prop-2-yn-1-yloxy)benzene (**6b**) [20]

Yellow oil, (126.5 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (t, *J* = 8.6 Hz, 1H), 6.59–6.53 (m, 3H), 4.67–4.65 (m, 2H), 3.78 (s, 3H), 2.52 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.5, 158.5, 129.6, 106.9, 101.2, 78.3, 75.3, 55.5, 55.0.

5.1.3. 1,3-Dimethoxy-5-(prop-2-yn-1-yloxy)benzene (**6c**) [21]

Yellow oil, (153.8 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.15 (s, 1H), 6.12 (s, 1H), 4.64 (d, *J* = 2.4 Hz, 1H), 3.76 (s, 3H), 2.52 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 161.4, 159.3, 93.7, 78.3, 75.5, 55.8, 55.3.

5.1.4. 1,2-Dimethoxy-4-(prop-2-yn-1-yloxy)benzene (**6d**) [22]

Yellow oil, (157.6 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.74 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 2.8 Hz, 1H), 6.45 (dd, *J* = 8.7, 2.8 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 2H), 3.80 (d, *J* = 8.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.2, 150.0, 144.2, 111.8, 104.55, 101.4, 79.0, 75.5, 56.5, 55.9.

5.1.5. 5-(Prop-2-yn-1-yloxy)benzo[d] [1,3]dioxole (**6e**) [23]

Yellow oil, (158.6 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.73 (d, *J* = 8.5 Hz, 7H), 6.59 (d, *J* = 2.4 Hz, 7H), 6.43 (dd, *J* = 8.5, 2.5 Hz, 7H), 5.95–5.93 (m, 14H), 4.63 (d, *J* = 2.3 Hz, 15H), 2.53 (t, *J* = 2.1 Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 152.8, 148.1, 142.2, 107.8, 106.3, 101.1, 98.6, 78.5, 75.3, 56.8.

5.2. Typical procedure for the preparation of 2H-chromenes

In a sealed reaction tube with a magnetic stirring bar was added 1 mmol of 6a-d and PEG 400 (1.0 mL). Then the reaction tube was sealed with the cap and stirred at 170 °C for 15 min at 300w in a microwave synthesizer (CEM Discover®SP), The reaction was extracted with 15 mL of EtOAc, the organic layer was washed with distilled H_2O (5 mL) and brine (3 × 5 mL), the organic phase was dried with anhydrous MgSO4, filtered and evaporated under vacuum. The pure compounds was obtained after flash chromatography (EtOAc/hexane; from 5/95).

5.3. Typical procedure B for the preparation of 2H-chromenes

In a sealed reaction tube with a magnetic stirring bar was added 1 mmol of 6a-d and PEG 400 (1.0 mL). Then the reaction tube was sealed with the cap and stirred at 220 °C for 1 h and, The reaction was extracted with 15 mL of EtOAc, the organic layer was washed with distilled H_2O (5 mL) and brine (3 × 5 mL), the organic phase was dried with anhydrous MgSO4, filtered and evaporated under vacuum. The pure compounds was obtained after flash chromatography (EtOAc/hexane; from 5/95).

5.3.1. 6-Methoxy-2H-chromene (**1a**) [20]

Yellow oil, (89.2 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.65 (d, *J* = 8.7 Hz, 1H), 6.59 (s, 1H), 6.47 (d, *J* = 3.0 Hz, 1H), 6.31 (s, 1H), 5.73 (dt, *J* = 9.8, 3.6 Hz, 1H), 4.67 (dd, *J* = 3.6, 1.9 Hz, 2H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.4, 159.4, 93.7, 78.5, 75.6, 55.8, 55.3.

*5.3.2. 7-Methoxy-2H-chromene (**1b**) [20]*

Yellow oil, (72.9 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.89 (d, J = 8.3 Hz, 1H), 6.44 (dd, J = 8.3, 2.5 Hz, 1H), 6.39 (t, J = 5.1 Hz, 2H), 5.64 (dt, J = 9.7, 3.6 Hz, 1H), 4.81 (dd, J = 3.5, 1.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.4, 155.2, 127.2, 124.2, 118.86, 115.6, 106.8, 101.6, 65.5, 55.3.

*5.3.3. 5,7-Dimethoxy-2H-chromene (**1c**) [21]*

Yellow oil, (124.9 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.69 (d, J = 9.8 Hz, 1H), 6.04 (d, J = 1.3 Hz, 1H), 5.59 (d, J = 9.9 Hz, 1H), 4.73 (dd, J = 3.7, 1.7 Hz, 1H), 3.79 (s, 1H), 3.77 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 160.9, 156.1, 155.9, 119.4, 116.5, 105.4, 93.5, 91.8, 65.3, 55.5, 55.3.

*5.3.4. 6,7-Dimethoxy-2H-chromene (**1d**) [22]*

Yellow oil, (86.4 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.52 (s, 1H), 6.42 (s, 1H), 6.35 (d, J = 9.7 Hz, 1H), 5.66 (s, 1H), 4.73 (s, 2H), 3.83 (d, J = 6.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.5, 150.5, 145.5, 126.4, 121.2, 116.4, 112.0, 102.6, 67.4, 58.5, 57.9.

*5.3.5. 6H- [1,3]Dioxolo[4,5-g]chromene (**1e**) [22]*

Yellow oil, (96.8 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.39 (s, 1H), 6.31 (s, 1H), 6.23 (d, J = 9.7 Hz, 1H), 5.80 (s, 2H), 5.58 (dt, J = 9.7, 3.7 Hz, 1H), 4.62 (dd, J = 3.6, 1.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.4, 147.4, 141.8, 124.7, 119.0, 115.5, 105.9, 100.9, 98.5, 65.3.

5.4. General procedure for the oxyarylation of 2H-chromenes

Conditions A: In a reaction tube were added the 2*H*-chromene (1a-f) (0.25 mmol) and the 2-iodophenol (2a-e) (2 equiv.), dicyclohexylamine (0.5 mmol, 0.099 mL), *p*-hydroxyacetophenone oxime derived palladacycle (7 mg, 5 mol%) and PEG 400 (2 mL) and stirred at 150 °C. The reaction was monitored till completion by TLC. The reaction mixture was extracted with EtOAc (5 mL), washed with brine (5 × 10 mL) and then 1 M HCl solution was added to pH 2. The organic phase was dried with anhydrous $MgSO_4$, filtered and evaporated under vacuum. Pure compounds were obtained after flash chromatography (from 1:9, EtOAc/hexane).

Conditions B: In a reaction tube were added the 2*H*-chromene (1a-f) (0.25 mmol) and the 2-iodophenol (2a-e) (2 equiv.), Ag2CO3 (0.28 mmol), Pd(OAc)2 (10 mol%) and PEG 400 (2 mL) and the reaction mixture was stirred at 140 °C. The reaction was monitored till completion by TLC and the same work-up as above was performed.

*5.4.1. 2-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene (**3aa**)*

White solid, (20.3 mg, 40% yield) mp 55 °C. IR (KBr) ν_{max}: 2972, 2911, 1642, 1430, 1250 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, J = 7.3 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 2.3 Hz, 1H), 6.94–6.82 (m, 4H), 5.49 (d, J = 6.3 Hz, 1H), 4.25 (q, J = 10.9 Hz, 1H), 3.80 (s, 3H), 3.69–3.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.2, 154.3, 149.5, 129.2, 127.1, 124.8, 121.0, 120.4, 118.4, 117.4, 114.0, 110.2, 77.9, 66.6, 55.8, 40.5. HRMS (EI) calculated for $C_{16}H_{14}O_3$: 254.0943; found: 254,0932.

*5.4.2. 3-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene (**3ba**) [23]*

White solid, (27.4 mg, 54% yield) mp 55–57 °C. IR (KBr) ν_{max}: 2953, 2889, 1630, 1480, 1258 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30–7.24 (m, 2H), 7.22–7.16 (m, 1H), 6.91 (dd, J = 8.3, 6.7, 3.0 Hz, 2H), 6.58 (t, J = 8.3 Hz, 2H), 5.68 (d, J = 6.6 Hz, 1H), 4.25 (dd, J = 11.0, 5.0, 0.8 Hz, 1H), 3.95 (s, 3H), 3.66 (t, J = 11.1 Hz, 1H), 3.54–3.46 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.2, 159.5, 156.6, 130.6, 129.2, 127.0, 124.6, 120.8, 110.63, 109.9, 108.8, 103.2, 74.7, 66.1, 56.2, 39.6. HRMS (EI) calculated for $C_{16}H_{14}O_3$: 254.0943; found: 254.0938.

*5.4.3. 1,3-Dimethoxy-6a,11a-dihydro-6H-benzofuro[3,2-c] chromene (**3ca**)*

White solid, (28.9 mg, 51% yield) mp 122 °C. IR (KBr) ν_{max}: 2965, 2911, 1610, 1471, 1230 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (dd, J = 7.3, 0.6 Hz, 1H), 7.16 (td, J = 7.9, 1.3 Hz, 1H), 6.88 (dd, J = 8.2, 6.7, 2.9 Hz, 2H), 6.16 (d, J = 2.3 Hz, 1H), 6.10 (d, J = 2.3 Hz, 1H), 5.61 (d, J = 6.5 Hz, 1H), 4.26–4.20 (m, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 3.65 (t, J = 11.1 Hz, 1H), 3.47–3.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.8, 160.9, 159.5, 157.4, 129.1, 127.0, 124.5, 120.6, 110.5, 101.6, 93.3, 92.5, 74.8, 66.2, 56.0, 55.4, 39.4. HRMS (EI) calculated for $C_{17}H_{16}O_4$: 284.1049; found: 284.1039.

*5.4.4. 2,3-Dimethoxy-6a,11a-dihydro-6H-benzofuro[3,2-c] chromene (**3da**)*

White solid, (28.9 mg, 51% yield) mp 110 °C. IR (KBr) ν_{max}: 2942, 1612, 1310,1280 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J = 7.3 Hz, 1H), 7.19 (td, J = 7.8, 1.3 Hz, 1H), 6.99 (s, 1H), 6.91 (td, J = 7.5, 0.8 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.49 (s, 1H), 5.48 (d, J = 6.5 Hz, 1H), 4.36–4.14 (m, 1H), 3.90 (s, 3H), 3.85 (s, 4H), 3.75–3.47 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.3, 150.6, 149.9, 144.3, 129.2, 127.2, 124.8, 121.0, 112.25, 110.6, 110.2, 100.8, 77.9, 66.5, 56.4, 56.0, 40.3. HRMS (EI) calculated for $C_{17}H_{16}O_4$: 284.1049; found: 284.1039.

*5.4.5. Dihydro-6H-benzofuro[3,2-c] [1,3],dioxolo[4,5-g]chromene (**3ea**)*

White solid, (32.1 mg, 60% yield) mp 100–103 °C. IR (KBr) ν_{max}: 2952, 2931, 1594, 1538, 1350 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, J = 7.8 Hz, 1H), 7.22–7.15 (m, 1H), 6.95 (s, 1H), 6.91 (td, J = 7.4, 0.9 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H), 5.94 (dd, J = 12.1, 1.3 Hz, 2H), 5.45 (d, J = 6.6 Hz, 1H), 4.25 (dd, J = 9.3, 3.4 Hz, 1H), 3.61 (dd, J = 6.7, 4.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.3, 150.6, 149.9, 144.3, 129.2, 127.2, 124.8, 121.0, 112.2, 110.6, 110.2, 100.8, 77.9, 66.6, 56.4, 56.0, 40.3. HRMS (EI) calculated for $C_{16}H_{12}O_4$: 268.0736; found: 268.0714.

*5.4.6. 2-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene-8-carbaldehyde (**3 ab**)*

White solid, (35.5 mg, 63% yield) mp 133–135 °C. IR (KBr) ν_{max}: 3021, 2985, 1692, 1448, 1315 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.82 (s, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.03 (s, 1H), 6.94 (d, J = 8.3 Hz, 1H), 6.87 (s, 1H), 5.67 (d, J = 7.4 Hz, 1H), 4.30 (dd, J = 10.8, 4.7 Hz, 1H), 3.81 (s, 2H), 3.66 (dd, J = 23.0, 12.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.3, 164.6, 154.4, 149.5, 134.0, 130.8, 128.6, 125.6, 119.6, 118.5, 117.5, 113.9, 110.3, 79.5, 66.3, 55.7, 39.8, 30.1, 29.1. HRMS (EI) calculated for $C_{17}H_{14}NaO_4$: 305.0789; found: 305.0784.

*5.4.7. 2-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene-9-carbaldehyde (**3ac**)*

White solid, (31.6 mg, 56% yield) mp 135–137 °C. IR (KBr) ν_{max}: 3044, 2996, 1695, 1460, 1322 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.45 (s, 1H), 7.38 (s, 1H), 7.12 (s, 1H), 6.88 (s, 2H), 5.76 (d, J = 7.3 Hz, 1H), 4.32 (dd, J = 10.5, 4.3 Hz, 1H), 3.95 (s, 2H), 3.85–3.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.6, 154.4, 149.4, 128.5, 126.7, 121.1, 119.2, 118.6, 117.7, 113.8, 109.9, 80.1, 66.1, 55.7, 40.0. HRMS (ESI) calculated for $C_{17}H_{14}NaO_4$: 305.0789; found: 305.0784.

*5.4.8. 2,10-Dimethoxy-6a,11a-dihydro-6H-benzofuro[3,2-c] chromene-8-carbaldehyde (**3ad**)*

White solid, (15.6 mg, 25% yield) mp 145 °C. IR (KBr) ν_{max}: 3072, 2974, 1671, 1482, 1318 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H), 7.45 (s, 1H), 7.38 (s, 1H), 7.12 (s, 1H), 6.88 (s, 2H), 5.76 (d,

J = 7.3 Hz, 1H), 4.32 (dd, J = 10.5, 4.3 Hz, 1H), 3.95 (s, 2H), 3.85–3.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.3, 154.3, 153.4, 149.4, 145.3, 131.6, 128.7, 120.8, 119.3, 118.4, 117.8, 113.9, 112.3, 80.2, 66.3, 56.1, 55.8, 40.3. HRMS (ESI) calculated for $C_{18}H_{16}NaO_5$: 335.0889; found: 335.0889.

*5.4.9. 3-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene-9-carbaldehyde (**3bc**)*

White solid, (28.2 mg, 50% yield) mp 140 °C. IR (KBr) ν_{max}: 3015, 2980, 1683, 1475, 1312 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 7.46 (dd, J = 7.4, 1.4 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.32–7.30 (m, 1H), 6.67 (dd, J = 8.6, 2.5 Hz, 1H), 6.47 (d, J = 2.5 Hz, 1H), 5.62 (d, J = 6.8 Hz, 1H), 4.35–4.28 (m, 1H), 3.80 (s, 2H), 3.76 (d, J = 10.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.5, 161.2, 160.1, 156.5, 138.0, 134.5, 131.8, 125.0, 124.2, 111.6, 109.4, 101.6, 78.3, 65.7, 55.3, 40.3, 29.6. HRMS (ESI) calculated for $C_{17}H_{14}NaO_4$:305.0789; found: 305.0788.

*5.4.10. 3,9-Dimethoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene (**3be**)*

White solid, (16.4 mg, 29% yield) mp 130–135 °C. IR (KBr) ν_{max}: 3008, 2890, 1710, 1461, 1310 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 8.5 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 6.57 (dd, J = 8.5, 2.5 Hz, 1H), 6.38 (dd, J = 8.7, 3.9, 2.4 Hz, 3H), 5.44 (d, J = 6.8 Hz, 1H), 4.18 (dd, J = 10.7, 4.8 Hz, 1H), 3.72 (s, 2H), 3.69 (s, 3H), 3.56 (t, J = 10.9 Hz, 1H), 3.51–3.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.0, 160.9, 160.6, 156.5, 131.8, 124.6, 119.0, 112.3, 109.1, 106.3, 101.5, 101.5, 96.8, 96.8, 78.5, 66.5, 55.4. HRMS (ESI) calculated for $C_{17}H_{16}NaO_4$: 307.0946; found: 307.0941.

*5.4.11. 6a,11a-Dihydro-6H-benzofuro[3,2-c] [1,3],dioxolo[4,5-g]chromene-9-carbaldehyde (**3ec**)*

White solid, (35.5 mg, 60% yield) mp 141–143 °C. IR (KBr) ν_{max}: 3059, 2950, 1690, 1490, 1295 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 7.46 (dd, J = 7.5, 1.1 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.31 (s, 1H), 6.94 (s, 1H), 6.46 (s, 1H), 6.46 (s, 1H), 6.46 (s, 1H), 5.95 (dd, J = 11.9, 1.2 Hz, 2H), 5.56 (d, J = 6.1 Hz, 1H), 4.28 (dd, J = 9.8, 6.2 Hz, 1H), 3.84 (t, J = 6.0 Hz, 1H), 3.70 (dd, J = 5.4, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.6, 160.1, 151.0, 149.1, 142.4, 138.2, 134.5, 125.2, 124.5, 111.4, 109.6, 108.8, 101.5, 99.0, 78.9, 66.1, 40.5. HRMS (EI) calculated for $C_{17}H_{12}O_5$: 296.0685; found: 296.0675.

*5.4.12. 2,3-Dimethoxy-6a,11a-dihydro-6H-benzofuro[3,2-c]chromene-9 carbaldehyde (**3dc**)*

White solid, (36.8 mg, 59% yield) mp 136 °C. IR (KBr) ν_{max}: 3019, 2974, 2948, 1690, 1325 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.94 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.33 (s, 1H), 7.27 (d, J = 0.9 Hz, 1H), 6.99 (s, 1H), 6.49 (s, 1H), 5.60 (d, J = 6.5 Hz, 1H), 4.31 (d, J = 5.7 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.73–3.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.7, 160.1, 150.8, 149.9, 144.6, 138.1, 134.7, 125.23, 124.6, 112.1, 110.0, 109.5, 100.9, 78.7, 66.0, 56.4, 56.0, 40.5. HRMS (EI) calculated for $C_{18}H_{16}O_5$: 312.0998; found: 312.0989.

*5.4.13. 6a,11a-Dihydro-6H-benzofuro[3,2-c] [1,3],dioxolo[4,5-g]chromene-8-carbaldehyde (**3eb**)*

White solid, (23.7 mg, 40% yield) mp 125 °C. IR (KBr) ν_{max}: 3005, 2981, 2923, 1695, cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.81 (s, 1H), 7.78 (d, J = 1.6 Hz, 1H), 7.69 (dd, J = 8.3, 1.7 Hz, 1H), 6.89 (d, J = 9.5 Hz, 2H), 6.42 (s, 1H), 6.03–5.72 (m, 3H), 5.57 (d, J = 7.0 Hz, 1H), 4.37–4.16 (m, 1H), 3.79–3.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.1, 164.3, 150.8, 148.8, 142.5, 133.8, 130.4, 128.3, 125.2, 110.7, 110.1, 108.3, 101.1, 98.7, 79.5, 66.0, 39.2. HRMS (ESI) calculated for $C_{17}H_{12}NaO_5$: 319.0582; found: 319.0557.

*5.4.14. 9-Methoxy-6a,11a-dihydro-6H-benzofuro[3,2-c][1,3],dioxolo[4,5 g]chromene (**3ee**)*

White solid, (16.7 mg, 28% yield) mp 140 °C. IR (KBr) ν_{max}: 2894, 1613, 1415, 1277 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, J = 8.9 Hz, 1H), 6.93 (s, 1H), 6.45 (d, J = 6.9 Hz, 2H), 5.93 (dd, J = 11.8, 1.1 Hz, 2H), 5.45 (d, J = 6.5 Hz, 1H), 4.33–4.11 (m, 1H), 3.77 (s, 3H), 3.71–3.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.0, 160.4, 150.9, 148.7, 142.5, 124.7, 118.9, 111.8, 108.7, 106.3, 101.2, 98.8, 96.8, 78.9, 66.7, 55.4, 39.5. HRMS (EI) calculated for $C_{17}H_{14}O_5$: 299.0919; found: 299.0914.

*5.4.15. 3,5-Dimethoxy-2-(3-methylbenzofuran-2-yl)phenol (**9**)*

White solid, (18.1 mg, 22% yield) mp 135 °C. IR (KBr) ν_{max}: 3420, 2932,2846 1596, 1479 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (dd, J = 9.0, 5.7, 1.6 Hz, 1H), 7.23 (dd, J = 7.6, 1.6 Hz, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.33 (d, J = 1.9 Hz, 1H), 5.39 (s, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.8, 156.2, 154.1, 153.5, 150.9, 131.6, 129.2, 120.4, 120.3, 116.0, 111.6, 110.3, 94.5, 88.4, 55.9, 55.7, 12.5. HRMS (EI) calculated for $C_{17}H_{16}O_4$: 284.1049; found: 284.1042.0.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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