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Pd-Catalyzed direct arylation approach to the 6*H*-dibenzo[*c,h*]chromenes : Total synthesis of arnottin I†

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Abstract : An efficient synthesis of 6*H*-dibenzo[*c,h*]chromenes has been achieved from 2-bromobenzyl-α-naphthyl ethers via a Pd-catalyzed intramolecular direct-arylation using easily available $Pd(PPh_3)_4$ or $Pd(OAc)_2/PPh_3$ at elevated temperature. The reaction affords biaryl-coupling products in good to excellent yields in 6–9 h (up to 94% yields). A tentative mechanism has been proposed to understand the reaction pathway. Applying the methodology, a straightforward and concise total synthesis of arnottin I has been demonstrated by converting the biaryl-coupling products to the 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one using pyridinium chlorochromate (PCC) mediated oxidation.

Keywords : Direct biaryl-coupling, Pd-catalyzed, 6*H*-dibenzo[*c,h*]chromenes, oxidation, 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one, arnottin I.

Introduction

In recent years, strategies for the synthesis of natural products that rely on transition metal-catalyzed cross-coupling reactions predominate in the literature over other approaches[1]. In this regard, intramolecular transition-metal-catalyzed arene C–H bond functionalization reactions have emerged as versatile tools for the atom- and step-economical assembly of aromatic compounds and has been utilized in the total synthesis of various natural products[2]. These reactions substitute one of the preactivated arenes with a simple arene (Scheme 1) which ultimately leads to the discovery of 'ideal synthesis'[3]. Despite the associated advantages, several important challenges still remain to be overcome. For example, the predominant of direct arylation reactions employ aryl iodides as coupling partners[4]. For more reactive aryl iodides, moderately electron-rich monodentate phosphines such as PPh_3 are typically used. In case of aryl bromides and chlorides, more sterically bulky and electron-rich trialkylphosphine or Buchwald's biphenylphosphines are required[5,2c-e].

The impetus for the synthesis of biaryl compounds lies in their exhaustive use as building blocks of many alkaloids and carbocyclic natural products[6]. Especially, those having 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one skeleton constitute the basic skeleton of wide range of biologically active metabolites of certain *Streptomyces* species[7–11]. Gilvocarcins (**1b-c**)[7] and other related compounds, such as ravidomycin (**1d**)[8] and chrysomycins (**1e-f**)[9], are metabolites of certain *Streptomyces* species and belong to a class of aryl *C*-glycoside antibiotics[10] (Fig. 1). The coumarin-based natural product arnottin I (**1a**), having a 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one skeleton is found in gilvocarcin-type antibiotics[11]. Arnottin I (**1a**) is a non-alkaloidal minor component isolated from the bark of *Xanthoxylum arnottianum* Maxim, which belongs to the family *Rutaceae*[11a]. These natural products sharing a common tetracyclic aromatic nucleus, 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one with the C-4 position attached with a sugar moiety have greatly attracted the synthetic chemists. Defucogilvocarcins[12] having a similar chromophore have also been extensively studied (Fig. 1). In this regard, mainly the regioselective synthesis of highly substituted 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one comes up as a major challenge.

†**In honour of Professor Sunil Kumar Talapatra on the occasion of his 80th birthday.**

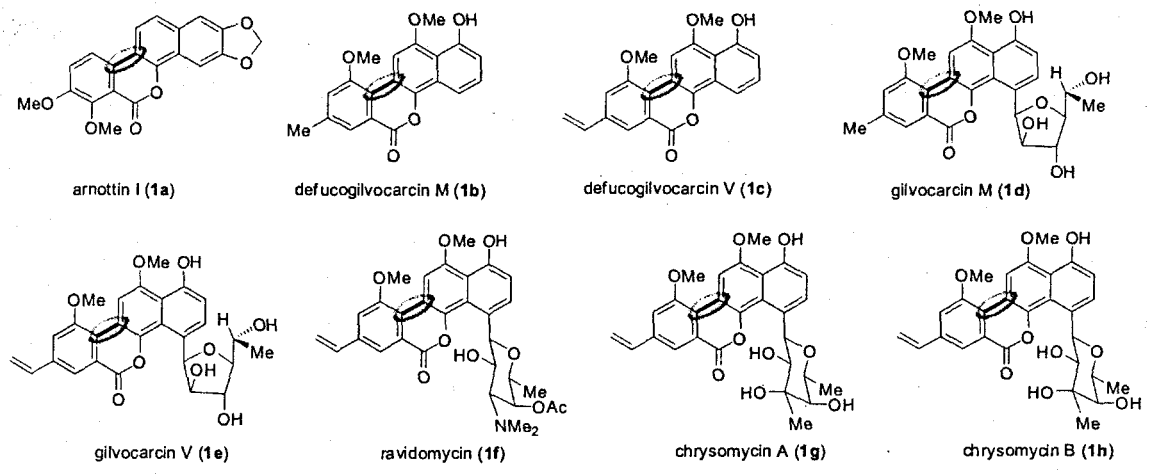


Fig. 1. Natural products sharing 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one structure (**1a-h**).

We envisioned that 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one can be achieved from a benzylic oxidation of 6*H*-dibenzo[*c*,*h*]chromenes[13]. In the literature, 6*H*-dibenzo[*c*,*h*]chromenes have been synthesized via an efficient direct arylation strategy independently developed by Shi and co-workers using base-promoted organo-catalytic homolytic-aromatic-substitution (HAS) reactions[13a,14] and by Fagnou and co-workers via Pd-catalyzed direct arylation which requires expensive palladiun source such as $Pd(OPiv)_2$ and phosphine such as $P(4\text{-F-Ph})_3$ as ligands[15]. However, simple, mild and versatile preparations of 6*H*-dibenzo[*c*,*h*]chromenes with specific substitution patterns are still highly desirable. Herein, we report a simple and efficient protocol for the synthesis of 6*H*-dibenzo[*c*,*h*]chromenes by the palladium-catalyzed intramolecular biaryl-coupling from 2-bromobenzyl α-naphthyl ethers using easily available $Pd(PPh_3)_4$ or $Pd(OAc)_2$/PPh_3. Our goal behind synthesizing 6*H*-dibenzo[*c*,*h*]-chromenes is that these biaryl-coupling products could be converted to 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one using pyridinium chlorochromate (PCC)-mediated oxidation[13], which in fact demonstrates an efficient total synthesis of arnottin I (**1a**).

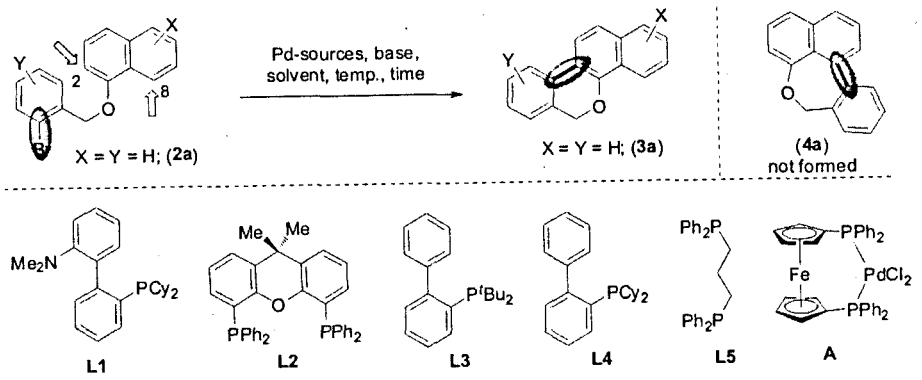
Results and discussion

Direct biaryl-coupling reactions through selective functionalization via C–H bond activation have emerged as an extremely useful exploratory synthetic strategy in contemporary organic synthesis. This strategy has been utilized in the total synthesis of various natural products[2]. However, in most of the cases, direct intramolecular biaryl-coupling requires expensive phosphine ligands[2c-e]. As part of our ongoing studies toward the synthesis of arnottin I (**1a**) as well as other related natural products sharing 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one (Fig. 1), we investigated the direct-arylation strategy for the synthesis of 6*H*-dibenzo[*c*,*h*]chromenes using 10 mol% of $Pd(PPh_3)_4$ or $Pd(OAc)_2/PPh_3$. Initially, we started examining the Pd-catalyzed direct biaryl-coupling of 2-bromobenzyl-α-naphthyl ether **2a** using 5 mol% of $Pd(OAc)_2$ and ligands **L1-L5** in the presence of 2 equiv. of K_2CO_3 in dimethylacetamide (DMA) at 140 °C for 7–9 h. It was found that, these reactions afforded product 6*H*-dibenzo[*c*,*h*]chromene **3a** in 90–94% yields (entries 1–5, Table 1). Interestingly, 10 mol% $Pd(PPh_3)_4$ can efficiently catalyze the direct coupling in 94% yields in 8 h (entry 6). K_2CO_3 was found to be more efficient than other bases such as Na_2CO_3, Cs_2CO_3 and KO^{t}Bu (entries 7–9). Optimization studies with different solvents showed that DMA is better choice than DMF and DMSO (entries 9–11).

Further optimization studies revealed that 5 mol% and 10 mol% of $Pd(OAc)_2$-PPh_3 afforded product **3a** in 88% and 93% yields, respectively (entries 14 and 19). We also found that 5 mol% each of $Pd(dppf)_2Cl_2$ and $Pd(PPh_3)_4$ afforded product **3a** in 91% and 89% of yields, respectively (entries 16 and 20). Although, 10 mol% each of $Pd_2(dba)_3$, $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ efficiently catalyzed the biaryl-coupling and led to 96%, 86% and 93% conversion, respectively, these reactions were always as-

sociated with unwanted debrominated products (entries 12, 17–18). Thus, based on above studies, 10 mol% $Pd(PPh_3)_4$ (condition **A**) and 10 mol% $Pd(OAc)_2$ in combination with 20 mol% of PPh_3 (condition **B**) were chosen for further substrate scope. It is interesting to note that the direct biaryl-coupling of **2a** presented here is highly regioselective. There are two reacting centers in the bromoarene **2a**, viz. C-2 and C-8 positions (Table 1). However, the coupling took place only at C-2 position. Notably, the literature on direct biaryl-coupling of *N*-acylated 2-bromobenzyl-α-naphthylamines generally affords mixture of two regio-isomers[16]. This indicates that the directing heteroatom might play a crucial role in Pd-catalyzed direct arylations.

Table 1. Optimization of direct biaryl-coupling



Entry	Pd-ligand complex (mol%)	Base (2 equiv.)	Solvent	Temp. (°C)	Time (h)	Yield[a,b] (%)
1.	5 mol% $Pd(OAc)_2$ - 10 mol% **L1**	K_2CO_3	DMA	140	7	94
2.	5 mol% $Pd(OAc)_2$ - 5 mol% **L2**	K_2CO_3	DMA	140	9	91
3.	5 mol% $Pd(OAc)_2$ - 10 mol% **L3**	K_2CO_3	DMA	140	8	93
4.	5 mol% $Pd(OAc)_2$ - 10 mol% **L4**	K_2CO_3	DMA	140	9	92
5.	5 mol% $Pd(OAc)_2$ - 5 mol% **L5**	K_2CO_3	DMA	140	7	90
6.	10 mol% $Pd(PPh_3)_4$	K_2CO_3	DMA	140	8	94[c]
7.	10 mol% $Pd(PPh_3)_4$	Na_2CO_3	DMA	140	9	89
8.	10 mol% $Pd(PPh_3)_4$	Cs_2CO_3	DMA	140	8	90
9.	10 mol% $Pd(PPh_3)_4$	KO^{t}Bu	DMA	140	7	87
10.	10 mol% $Pd(PPh_3)_4$	K_2CO_3	DMF	110	9	56
11.	10 mol% $Pd(PPh_3)_4$	K_2CO_3	DMSO	120	8	52
12.	10 mol% $Pd_2(dba)_3$	K_2CO_3	DMA	140	8	96[d]
13.	10 mol% $Pd(OAc)_2$ - 20 mol% PPh_3	K_2CO_3	DMF	110	6	64
14.	10 mol% $Pd(OAc)_2$ - 20 mol% PPh_3	K_2CO_3	DMA	140	7	93[e]
15.	5 mol% $Pd(OAc)_2$ - 10 mol% PCy_3	K_2CO_3	DMA	140	6	92
16.	5 mol% **A**	K_2CO_3	DMA	140	8	91
17.	10 mol% $Pd(PPh_3)_2Cl_2$	K_2CO_3	DMA	140	7	86[f]
18.	10 mol% $Pd(OAc)_2$	K_2CO_3	DMA	140	9	93[d]
19.	5 mol% $Pd(OAc)_2$ - 10 mol% PPh_3	K_2CO_3	DMA	140	9	88
20.	5 mol% $Pd(PPh_3)_4$	K_2CO_3	DMA	140	9	89

[a]All the reactions were performed under inert atmosphere in 0.25 mmol scale of **2a** in 2 mL of solvent at indicated temperature. [b]Isolated yields after column purification. [c]Condition **A**. [d]Biaryl-coupling : debrominated product = 2 : 3. [e]Condition **B**. [f]Biaryl-coupling : debrominated product = 3 : 1.

With optimized conditions **A** and **B** (Table 1) in hand, we then surveyed the substrate scope of 2-bromobenzyl α-naphthyl ethers **2** and the results are summarized in Table 2. As most of the 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one-based natural products contain electron-rich functional groups (Fig. 1), we synthesized various starting materials **2a-g** having electron-rich 2-bromobenzyl counterpart (vide Experimental). In case of 10 mol% $Pd(PPh_3)_4$ (condition **A**) and 10 mol% $Pd(OAc)_2$-PPh_3 (condition **B**), we observed the reactions took only 6–9 h for the completion. Interestingly, both conditions **A** and **B** afforded 6*H*-dibenzo[*c*,*h*]chromenes **3a-h** in good to excellent yields (69–94%) at elevated temperature.

We then turned our attention to the synthesis of few

Table 2. Substrates scope of Pd-catalyzed synthesis of 6*H*-dibenzo[*c*,*h*]chromenes

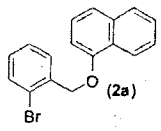
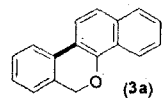
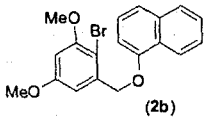
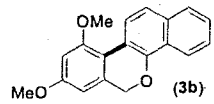
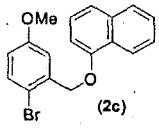
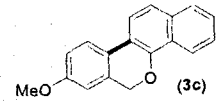
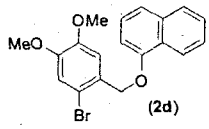
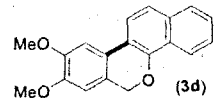
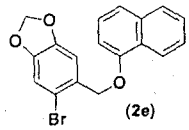
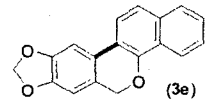
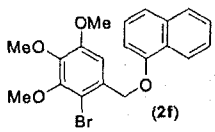
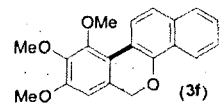
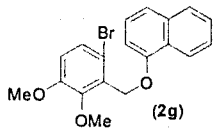
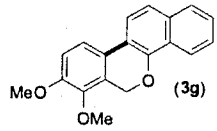
	 (2a)			 (3a)	
1.	**2a**	**A** : 10 mol% $Pd(PPh_3)_4$	8 h	**3a**	84%
2.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	7 h		93%
	 (2b)			 (3b)	
3.	**2b**	**A** : 10 mol% $Pd(PPh_3)_4$	9 h	**3b**	72%
4.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	7 h		65%
	 (2c)			 (3c)	
5.	**2c**	**A** : 10 mol% $Pd(PPh_3)_4$	8 h	**3c**	87%
6.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	6 h		90%
	 (2d)			 (3d)	
7.	**2d**	**A** : 10 mol% $Pd(PPh_3)_4$	7 h	**3d**	85%
8.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	9 h		88%
	 (2e)			 (3e)	
9.	**2e**	**A** : 10 mol% $Pd(PPh_3)_4$	8 h	**3e**	81%
10.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	9 h		85%
	 (2f)			 (3f)	
11.	**2f**	**A** : 10 mol% $Pd(PPh_3)_4$	7 h	**3f**	69%
12.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	8 h		75%

Table-2 (contd.)

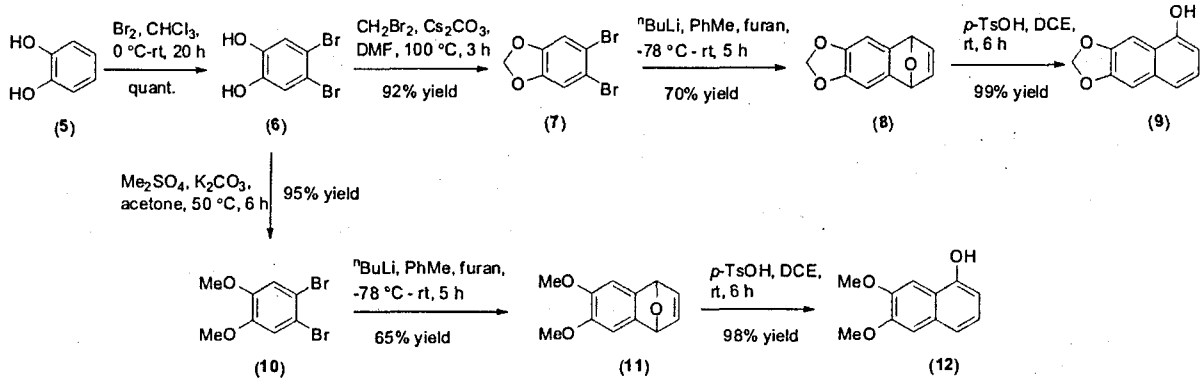
	 (2g)			 (3g)	
13.	**2g**	**A** : 10 mol% $Pd(PPh_3)_4$	9 h	**3g**	78%
14.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	7 h		79%

substrates based on 6,7-dimethoxy and 6,7-methylenedioxy-α-naphthols (**9** and **12**) (Scheme 1). Towards this end, we synthesized α-naphthols **9** and **12** in few steps following a modified literature procedure, as shown in Scheme 1[17]. The synthesis commenced with bis-bromination of pyrocatechol **5** to afford 4,5-dibromo catechol **6**[18] in quantitative yields, which was then converted to 4,5-dibromo-1,2-methylenedioxybenzene **7** with dibromomethane in the presence of Cs_2CO_3 in 92% yield. The latter was then treated with ^nBuLi to form a reactive benzyne intermediate which then follows a Diels-Alder reaction with furan to afford oxabenzonorbornadiene **8**. Finally, 6,7-methylenedioxy-α-naphthol **9** was synthesized from **8** via an acid-catalyzed isomerization (63.8% overall yield from pyrocatechol)[17]. Following similar type of sequences, we also synthesized 6,7-dimethoxy-α-naphthol **12** in 60.5% overall yield from pyrocatechol.

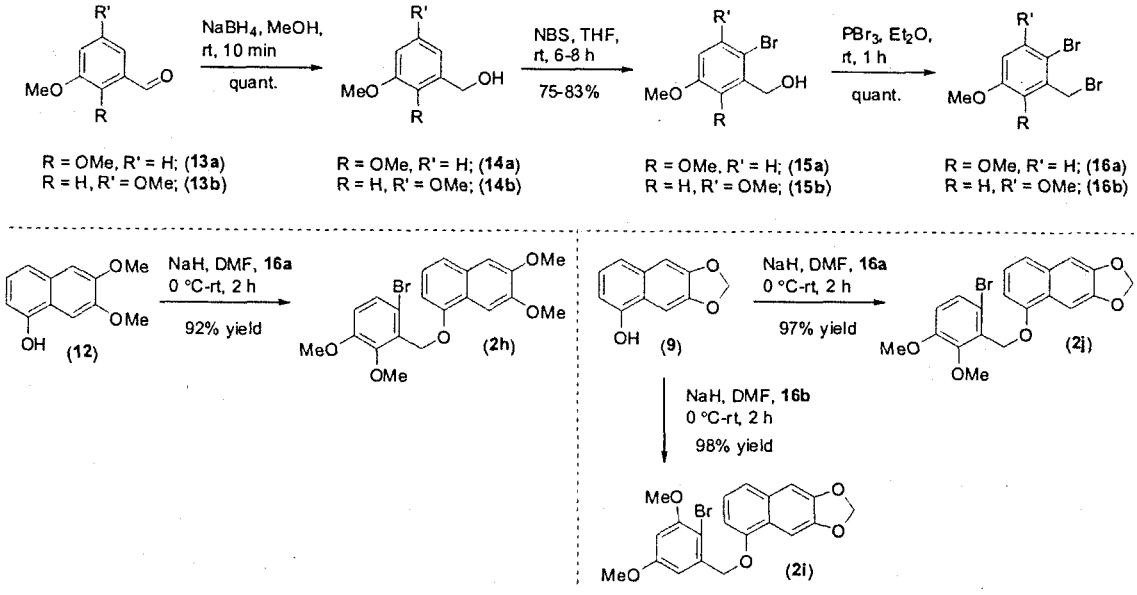
On the other hand, 2-bromobenzyl bromides **16a-b** were prepared in 75–83% overall yields from corresponding aldehydes **13a-b** following three steps, viz. $NaBH_4$ reduction to afford benzylalcohols **14a-b**, bromination of **14a-b** using *N*-bromo succinimide to synthesize 2-bromobenzylalcohols **15a-b**, followed by treatment with phosphorous tribromide to afford 2-bromobenzylbromides **16a-b** (Scheme 2). These 2-bromobenzylbromides were then reacted with 6,7-methylenedioxy-α-naphthol **9** and 6,7-dimethoxy-α-naphthol **12** in the presence of NaH to afford substrates **2h-j** (Scheme 2).

With 2-bromobenzyl-α-naphthyl ether **2h-j** in hand, we then explored direct biaryl-coupling under the optimized conditions. To our delight, conditions **A** and **B** afforded 6*H*-dibenzo[*c*,*h*]chromenes **3h-j** in good to excellent yields, where Pd^0-efficiently catalyzed the biaryl-coupling (Table 3). The results in Table 3 clearly depict that 2-bromobenzyl-α-naphthyl ether **2h-j** having highly electron-rich environment can easily undergo direct biarylation at elevated temperature to afford 6*H*-dibenzo[*c*,*h*]chromenes **3h-j** in good yields (71–79%). Especially, the substitution patterns present in the aromatic rings of 6*H*-dibenzo[*c*,*h*]chromenes of the types **3h** and **3j** are found in various alkaloids sharing 5,6-dihydrobenzo[*c*]phenanthridines such as dihydronitidine, dihydroavicine and chelerythrine[19].

Based on the previously reported mechanism by Echavarren and Maseras[15a,20], a possible mechanism has been proposed via a carbonate-assisted palladation, as outlined in Scheme 2. Under the catalysis using Pd^0-species,



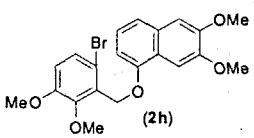
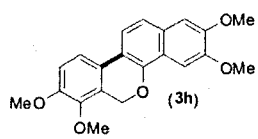
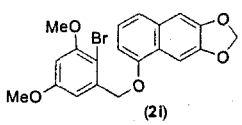
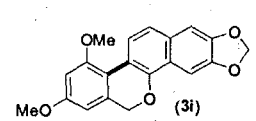
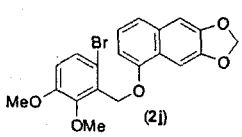
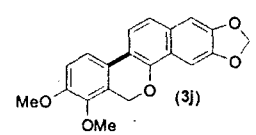
Scheme 1. Synthesis of α-naphthol derivatives **9** and **12**.

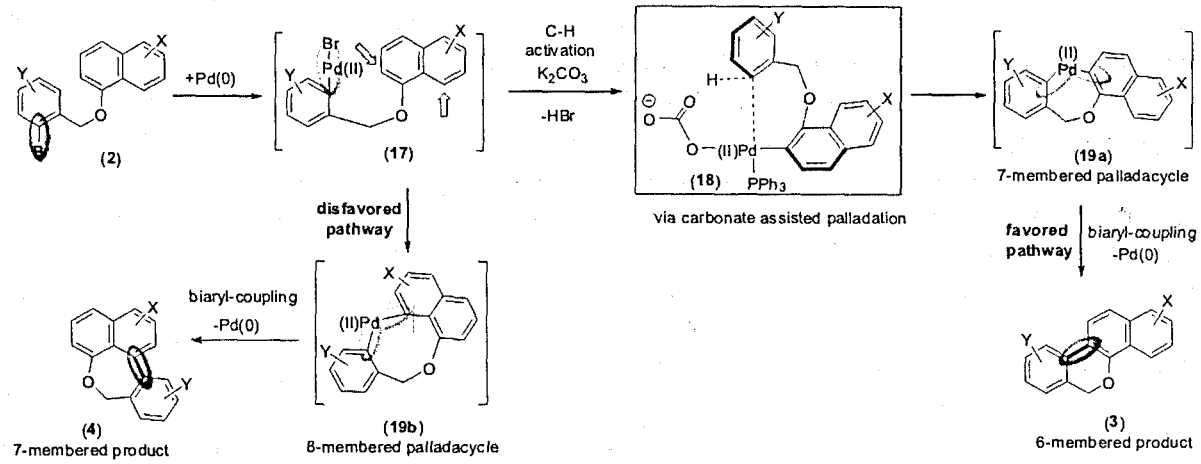


Scheme 2. Synthesis of 2-bromobenzyl-α-naphthyl ether derivatives **2h-j**.

substrates of the type 2-bromobenzyl-α-naphthyl ethers **2** could provide intermediate **17** after oxidative addition (Scheme 3). Intermediate **17** has a potential to undergo C–H activation in the presence of K_2CO_3 at C-2 position to form intermediate **19a** (a 7-membered palladacycle)[21] via carbonate-assisted palladation, as described by Echavarren and Maseras, which in turn could afford expected 6*H*-dibenzo[*c*,*h*]chromenes **3** upon reductive elimination. On the other hand, intermediate **17** could follow C–H activation at C-8 position to form intermediate **19b** (a 8-membered palladacycle), which could afford 7-membered biaryl product **4**. We believe that the formation of products probably follows a more stable palladacycle formed during the course of the reaction.

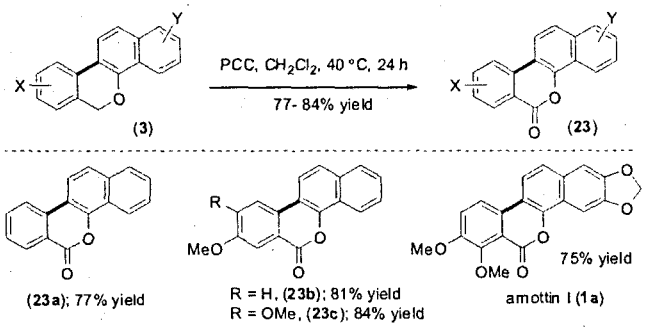
Table 3. Substrates scope of Pd-catalyzed biaryl synthesis

	 (2h)			 (3h)	
1.	**2h**	**A** : 10 mol% $Pd(PPh_3)_4$	8 h	3h	77%
2.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	7 h		71%
	 (2i)			 (3i)	
3.	**2i**	**A** : 10 mol% $Pd(PPh_3)_4$	7 h	**3i**	75%
4.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	8 h		78%
	 (2j)			 (3j)	
5.	**2j**	**A** : 10 mol% $Pd(PPh_3)_4$	8 h	**3j**	79%
6.		**B** : 10 mol% $Pd(OAc)_2/PPh_3$	9 h		72%



Scheme 3. Proposed mechanism of direct biaryl-coupling catalyzed by Pd^0.

Further, to show the versatility of our approach, few 6*H*-dibenzo[*c*,*h*]chromenes **17a-c** were oxidized in the presence of pyridinium chlorochromate (PCC) under refluxing dichloromethane (Scheme 4)[13]. Gratifyingly, we could synthesize 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-ones **23a-c** in 77–84% of yields, respectively. In the event, we have also completed the total synthesis of arnottin I **1a** in 75% yields from **3j** (Table 3).



Scheme 4. Synthesis of lactone via benzylic oxidation and synthesis of arnottin I (**1a**).

In summary, we have developed an efficient intramolecular direct biaryl-coupling approach to the 6*H*-dibenzo[*c*,*h*]chromenes **3** from a direct biaryl-coupling using easily available $Pd(PPh_3)_4$ or $Pd(OAc)_2/PPh_3$ under the Pd^0-catalyzed conditions. Our methodology provides an efficient entry to the various 6*H*-dibenzo[*c*,*h*]-chromenes **3** (up to 94% yield) at elevated temperature. These compounds could serve as advanced intermediates for the synthesis of 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-ones, commonly found in a wide range of metabolites. Our methodology also paved the way for the regiodefined total synthesis of arnottin I (**1a**). Further exploration of this direct biaryl-coupling reactions as well as application of this strategy in the total synthesis of natural products sharing 6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one is currently under active investigation in our laboratory.

Experimental

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O) was distilled over sodium/benzophenoneketyl. *N*,*N*-Dimethylacetamide (DMA) was distilled over calcium hydride. All other solvents and reagents were used as received, unless otherwise noted.

Thin layer chromatography was performed using Merck Silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel from Merck (particle size 100–200 mesh) was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (An ISO 9001 : 2000) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported

in ppm relative to the residual solvent signal (δ 7.26 for ^{1}H NMR and δ 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows : chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows : s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) from Perkin-Elmer spectrometer and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High resolution mass spectra and X-ray crystal data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER), Bhopal.

4,5-Dibromobenzene-1,2-diol (**6**) :

A round-bottom flask was charged with pyrocatechol (15 g; 136 mmol; 1.0 equiv.) in $CHCl_3$ (150 mL per mmol). To this reaction mixture Br_2 (13.9 mL; 272 mmol; 2.0 equiv.) was added at 0 °C using dropping funnel. The reaction mixture was stirred for 20 h. After completion of reaction (monitored by TLC) reaction mixture was evaporated to dryness. Then the crude product was directly treated for next step.

5,6-Dibromobenzo[d][1,3]dioxole (**7**) :

A round-bottom flask was charged with 4,5-dibromobenzene-1,2-diol (1.0 equiv. (generally in 10 g scale)) in DMF (2 mL per mmol). To this reaction mixture was added Cs_2CO_3 (1.5 equiv.) and CH_2Br_2 (1.5 equiv.) at RT. The reaction mixture was stirred at 100 °C for 3 h. After completion of reaction (monitored by TLC) the solid part was filtered and to the organic part 100 mL water was added. The aqueous layer was extracted with EtOAc (50 ml × 2). The organic layer was collected and dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (9 : 1 hexanes/EtOAc) to afford pure (**7**).

1,2-Dibromo-4,5-dimethoxybenzene (**10**) :

A round-bottom flask was charged with 4,5-dibromobenzene-1,2-diol (1.0 equiv. (generally in 10 g scale)) in acetone (2 mL per mmol). To this reaction mixture was added K_2CO_3 (4.0 equiv.) and Me_2SO_4 (3.0 equiv.) and was stirred at 50 °C for 3 h. After completion of reaction (monitored by TLC) the reaction mixture was evaporated to dryness in rotary-evaporator. 50 ml water and DCM was added to reaction mixture. The organic layer was extracted and dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (9 : 1 hexanes/EtOAc) to afford pure (**10**) :

General procedure for synthesis of α-naphthol derivatives (**9**) *and* (**12**) :

Step 1 : A flame dried round-bottom flask was charged with 1,2-dibromobenzene derivative (1.0 equiv. (generally in 5 g scale)) and furan (5.0 equiv.) in toluene (3 mL per mmol) and cooled to –78 °C. To this reaction mixture was added ^{n}BuLi, 2.6 *M* in dry THF (1.1 equiv.) using a syringe pump. After additional the solution was warmed up to –40 °C, the reaction mixture was stirred until completion (monitoring by TLC), the reaction was quenched with 50 mL water. The aqueous layer was extracted with EtOAc (40 ml × 3). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (9 : 1 hexanes/EtOAc) to afford pure (**8**) and (**11**).

Step 2 : A round-bottom flask was charged with 1,4-dihydro-1,4-epoxynaphthalene derivatives (**8**) and (**11**) (1.0 mmol; 1.0 equiv.) in DCE (3 mL per mmol). After 5 min of stirring at RT, *p*-TSA (0.2 mmol; 0.2 equiv.) was added to the reaction mixture. The stirring was continued for 6 h. After completion of reaction (monitored by TLC, showing complete consumption of starting materials) the reaction mixture was poured into a separatory funnel and washed with water (15 mL). The aqueous layer was further extracted with CH_2Cl_2 (10 mL × 2). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The crude product was charged for next step.

General procedure for synthesis of 2-bromobenzyl-α-naphthyl ether derivatives **2h-j** :

In an oven-dried round-bottom flask, α-naphthols (5.00 mmol; 1.0 equiv.) was taken in *N,N*-dimethylformamide (20 mL) under inert atmosphere and the reaction vessel was cooled to 0 °C. To this reaction mixture NaH (6.00 mmol; 1.2 equiv.) was added portion-wise and it was stirred for another 5 min. A solution of 2-bromobenzylbromides (5.50 mmol; 1.1 equiv.) in *N,N*-dimethylformamide (2 mL) was added drop-wise to the

reaction mixture at 0 °C. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH_4Cl (5 mL) and then diluted with 30 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 30 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (10 : 1 hexanes/EtOAc) to afford **2a-j**.

1-((2-Bromobenzyl)oxy)naphthalene (**2a**) : 93% yield as light white colored solid, R_f 0.55 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.42–8.40 (1H, m), 7.85–7.83 (1H, m), 7.70 (1H, d, *J* 7.63 Hz), 7.63 (1H, d, *J* 7.87 Hz), 7.55–7.50 (2H, m), 7.48 (1H, d, *J* 8.27 Hz), 7.41–7.36 (2H, m), 7.26 (1H, t, *J* 7.63 Hz), 6.90 (1H, d, *J* 7.56 Hz), 5.34 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.1, 136.4, 134.6, 132.7, 129.2, 128.8, 127.63, 127.56, 126.5, 125.9, 125.7, 125.4, 122.3, 122.1, 120.8, 105.4, 69.4; IR (film) υ_{max} : 2924, 2853, 1581, 1401, 1276, 1269, 1244, 1103, 1022, 871, 789, 768,751 cm^{-1}; m.p. 97–100 °C.

1-((2-Bromo-3,5-dimethoxybenzyl)oxy)naphthalene (**2b**) : 91% yield as light yellow color solid, R_f 044 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.38–8.36 (1H, m), 7.82–7.80 (1H, m), 7.50–7.48 (2H, m), 7.45 (1H, d, *J* 8.32 Hz), 7.36 (1H, t, *J* 7.95 Hz), 6.90 (1H, d, *J* 2.64 Hz), 6.87 (1H, d, *J* 7.61 Hz), 6.47 (1H, d, *J* 2.64 Hz), 5.31 (2H, s), 3.90 (3H, s), 3.78 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 160.0, 156.7, 154.1, 138.5, 134.6, 127.6, 126.5, 125.9, 125.7, 125.4, 122.0, 120.8, 105.6, 104.9, 102.2, 98.9, 69.8, 56.4, 55.6; IR (film) υ_{max} : 3051, 3007, 2940, 2840, 1589, 1455, 1402, 1369, 1331, 1269, 1227, 1201, 1161, 1089, 1067, 1022, 957, 829, 790, 770 cm^{-1}; m.p. 122–124 °C.

1-((2-Bromo-5-methoxybenzyl)oxy)naphthalene (**2c**) : 89% yield as grey color solid, R_f 0.57 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.41–8.39 (1H, m), 7.85–7.83 (1H, m), 7.55–7.47 (4H, m), 7.39 (1H, t, *J* 7.9 Hz), 7.29 (1H, d, *J* 3.01 Hz), 6.90 (1H, d, *J* 7.54 Hz), 6.78 (1H, dd, *J* 8.81, 3.11 Hz), 5.29 (2H, s), 3.80 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 159.2, 154.1, 137.5, 134.6, 133.2, 127.6, 126.5, 125.9, 125.7, 125.4, 122.1, 120.9, 114.7, 114.5, 112.4, 105.5, 69.5, 55.5.

1-((2-Bromo-4,5-dimethoxybenzyl)oxy)naphthalene (**2d**) : 86% yield as light yellowish solid, R_f 0.57 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.34–8.32 (1H, m), 7.82–7.80 (1H, m), 7.50–7.44 (3H, m), 7.37 (1H, t, *J* 7.91 Hz), 7.17 (1H, s), 7.08 (1H, s), 6.90 (1H, d, *J* 7.51 Hz), 5.25 (2H, s), 3.89 (3H, s), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.2, 149.2, 148.8, 138.6, 128.4, 127.6, 126.5, 125.9, 125.8, 125.3, 122.0, 120.8, 119.5, 112.8, 112.0, 105.6, 69.6, 56.2, 56.1; IR (film) υ_{max} : 3054, 2935, 2840, 1597, 1581, 1506, 1463, 1391, 1266, 1239, 1211, 1163, 1096, 1069, 1033, 965, 855, 792, 771 cm^{-1}; m.p. 103–105 °C.

5-Bromo-6-((naphthalen-1-yloxy)methyl)benzo[d]-[1,3]dioxole (**2e**) : 88% yield as white solid, R_f 0.7 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.36–8.33 (1H, m), 7.82–7.80 (1H, m), 7.51–7.45 (3H, m), 7.37 (1H, t, *J* 7.94 Hz), 7.15 (1H, s), 7.06 (1H, s), 6.86 (1H, d, *J* 7.55 Hz), 5.98 (2H, s), 5.22 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.0, 148.0, 147.7, 134.6, 129.7, 127.6, 126.5, 125.8, 125.7, 125.4, 122.1, 120.8, 112.9, 112.7, 108.9, 105.4, 101.9, 69.5; IR (film) υ_{max} : 3055, 2898, 1599, 1580, 1503, 1480, 1392, 1268, 1239, 1102, 1071, 1039, 933, 860, 834, 790, 770, 733 cm^{-1}.

1-((2-Bromo-3,4,5-trimethoxybenzyl)oxy)naphthalene (**2f**) : 83% yield as gel compound, R_f 0.9 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.36–8.34 (1H, m), 7.83–7.81 (1H, m), 7.51–7.46 (3H, m), 7.38 (1H, t, *J* 7.93 Hz), 7.07 (1H, s), 6.90 (1H, d, *J* 7.56 Hz), 5.28 (2H, s), 3.95 (3H, s), 3.91 (3H, s), 3.83 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.1, 153.0, 151.0, 134.6, 132.0, 127.6, 126.5, 125.9, 125.8, 125.4, 122.0, 120.9, 108.5, 107.7, 105.7, 69.8, 61.2, 61.1, 56.2. IR (film) υ_{max} : 3053, 2935, 1579, 1460, 1396, 1333, 1268, 1238, 1198, 1166, 1106, 1010, 994, 791, 770 cm^{-1}.

1-((6-Bromo-2,3-dimethoxybenzyl)oxy)naphthalene (**2g**) : 90% yield as white color solid, R_f 0.40 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) : δ 8.24 (1H, d, *J* 8.33 Hz), 7.80 (1H, d, *J* 8.12 Hz), 7.48–7.40 (4H, m), 7.37 (1H, d, *J* 8.85 Hz), 7.07 (1H, dd, *J* 7.06, 0.93 Hz), 6.86 (1H, d, *J* 8.84 Hz), 5.35 (2H, s), 3.88 (3H, s), 3.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.8, 152.4, 149.8, 134.6, 130.4, 128.1, 127.4, 126.4, 126.0, 125.9, 125.1, 122.4, 120.5, 116.4, 114.0, 105.3, 65.1, 62.2,

56.0; IR (film) υ_{max} : 3053, 2939, 1580, 1476, 1402, 1268, 1241, 1177, 1095, 1066, 1017, 852, 793, 711 cm^{-1}; m.p. 115–118 °C.

1-((6-Bromo-2,3-dimethoxybenzyl)oxy)-6,7-dimethoxynaphthalene (**2h**) : 84% yield as gel compound, R_f 0.40 (20% EtOAc in hexanes); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.54 (1H, s), 7.38–7.30 (3H, m), 7.01 (1H, s), 7.02 (1H, dd, *J* 7.09, 1.03 Hz), 6.86 (1H, d, *J* 8.84 Hz), 5.35 (2H, s), 3.99 (3H, s), 3.93 (3H, s), 3.88 (3H, s), 3.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 153.9, 152.4, 149.8, 149.7, 148.9, 130.49, 130.47, 128.1, 124.3, 121.2, 119.4, 116.4, 113.9, 105.2, 101.5, 65.5, 62.1, 56.0, 55.96, 55.8; IR (film) υ_{max} : 3055, 2937, 2836, 2068, 1603, 1581, 1584, 1485, 1376, 1260, 1158, 1085, 1011, 970, 840, 813, 779, 738 cm^{-1}.

5-((2-Bromo-3,5-dimethoxybenzyl)oxy)naphtho[2,3-d][1,3]dioxole (**2i**) : 89% yield as light yellow color solid, R_f 0.65 (20% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.65 (1H, s), 7.29 (1H, d, *J* 8.16 Hz), 7.22 (1H, t, *J* 7.92 Hz), 7.01 (1H, s), 6.85 (1H, d, *J* 2.25 Hz), 6.78 (1H, d, *J* 7.34 Hz), 6.48 (1H, d, *J* 2.66 Hz), 6.04 (2H, s), 5.28 (2H, s), 3.91 (3H, s), 3.79 (3H, s), 1.56 (H_2O); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 160, 156.7, 153.7, 148.0, 147.3, 138.5, 131.8, 124.5, 122.1, 120.1, 105.0, 103.8, 102.2, 101.0, 99.0, 98.9, 77.24, 69.9, 56.4, 55.6; IR (film) υ_{max} : 2922, 2844, 1589, 1463, 1334, 1246, 1199, 1163, 1127, 1037, 941, 832, 744 cm^{-1}; m.p. 122–124 °C.

5-((6-Bromo-2,3-dimethoxybenzyl)oxy)naphtho[2,3-d][1,3]dioxole (**2j**) : 91% yield as solid, R_f 0.323 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.53 (1H, s), 7.37 (1H, d, *J* 8.82 Hz), 7.30–7.28 (2H, m), 7.09 (1H, s), 6.99–6.97 (1H, m), 6.87 (1H, d, *J* 8.85 Hz), 5.97 (2H, s), 5.30 (2H, s), 3.88 (3H, s), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 154.4, 152.4, 149.7, 147.9, 147.1, 131.7, 130.5, 128.1, 124.5, 122.2, 119.9, 116.4, 114.0, 104.8, 103.7, 100.7, 99.3, 65.1, 66.2, 56.0; IR (film) υ_{max} : 2936, 1610, 1520, 1464, 1418, 1368, 1245, 1185, 1123, 1085, 1040, 1013, 943, 861, 739 cm^{-1}.

General procedure for direct biaryl-coupling :

In an oven-dried Schlenk flask, 2-halide aromatic substrates (0.50 mmol; 1.0 equiv.), potassium carbonate (1.0 mmol; 2.0 equiv.) and tetrakis(triphenylphosphine)-palladium(0) (0.05 mmol; 10 mol%) (or 10 mol% of $Pd(OAc)_2$ and 20 mol% of PPh_3) were taken in *N,N*-dimethylacetamide (5 mL) under argon atmosphere and the reaction mixture was purged with argon for approximately 5 min. The Schlenk flask was closed and heated at 140 °C for indicated time (3–10 h). Upon completion of the reactions (TLC), the reaction mixture was diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude cyclized products were purified by flash chromatography to afford pure biaryl-coupling products **3a-j**.

6H-Dibenzo[c,h]chromene (**3a**) : White color solid, R_f 0.40 (in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.35–8.32 (1H, m), 7.89–7.83 (2H, m), 7.77 (1H, d, *J* 7.75 Hz), 7.57 (1H, d, *J* 8.72 Hz), 7.54–7.52 (2H, m), 7.44 (2H, t, *J* 7.57 Hz), 7.33 (2H, t, *J* 7.46 Hz), 7.23 (2H, d, *J* 7.37 Hz), 5.35 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 150.4, 134.5, 130.8, 130.7, 128.6, 127.7, 127.4, 126.7, 125.9, 125.4, 124.7, 122.3, 122.0, 121.6, 121.0, 117.2, 69.0; IR (film) υ_{max} : 2943, 2853, 1581, 1401, 1278, 1257, 1191, 1094, 1062, 1024, 871, 789, 768, 751 cm^{-1}; HRMS (ESI) *m/z* 233.1652 $[M + H]^+$; calcd. for $[C_{17}H_{12}O + H]^+$: 233.0961; m.p. 93 °C [lit. E. Motti, N. D. Ca, A. Piersimoni, Z. M. Zhou and M. Catellani, *Org. Lett.*, 2012, **14**, 5792].

8,10-Dimethoxy-6H-dibenzo[c,h]chromene (**3b**) : Light yellow solid, R_f 0.40 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.39–8.38 (1H, m), 7.82–7.80 (1H, m), 7.51–7.48 (1H, m), 7.46–7.44 (1H, m), 7.63 (1H, t, *J* 7.81 Hz), 6.90–6.86 (2H, m), 6.47 (1H, d, *J* 2.63 Hz), 5.31 (2H, s), 3.90 (3H, s), 3.78 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 160.0, 154.1, 138.5, 134.6, 127.6, 126.5, 125.9, 125.7, 125.4, 122.0, 120.8, 105.6, 104.9, 102.2, 98.9, 69.8, 56.4, 55.6; HRMS (ESI) *m/z* 293.1172 $[M+H]^+$; calcd. for $[C_{19}H_{16}O_3 + H]^+$: 293.1172.

8-Methoxy-6H-dibenzo[c,h]chromene (**3c**) : Light yellow color solid, R_f 0.46 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.25–8.23 (1H, m), 7.79 (2H, d, *J* 8.64 Hz), 7.67 (1H, d, *J* 8.57 Hz), 7.52 (1H, d, *J* 8.59 Hz), 7.50–7.43 (2H, m), 6.95 (1H, dd, *J* 8.51, 2.56 Hz), 6.7 (1H, d, *J* 2.46 Hz), 5.28 (2H, s), 3.87 (3H, s), 1.55 (H_2O peak); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 159.3,

149.2, 133.9, 132.4, 127.6, 126.2, 125.7, 125.4, 123.6, 122.0, 121.5, 120.7, 117.2, 113.9, 110.3, 68.9, 55.5; IR (film) υ_{max} : 2919, 2848, 1599, 1442, 1240, 1101, 1082, 1036, 917, 862, 805, 746 cm^{-1}.

8,9-Dimethoxy-6H-dibenzo[c,h]chromene (**3d**) : Grey color solid, R_f 0.18 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.27–8.24 (1H, m), 7.81–7.75 (2H, m), 7.53 (1H, d, *J* 8.57 Hz), 7.49–7.46 (2H, m), 7.25 (1H, s), 6.73 (1H, s), 5.26 (2H, s), 3.99 (3H, s), 3.93 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 149.4, 149.3, 148.8, 133.9, 127.6, 126.3, 125.8, 125.4, 123.5, 123.3, 122.1, 121.5, 120.6, 117.3, 108.1, 105.7, 68.6, 56.2, 56.1; IR (film) υ_{max} : 2932, 2844, 1599, 1452, 1371, 1248, 1211, 1146, 1052, 858, 818, 758 cm^{-1}.

6H-[1,3]Dioxolo[4',5':4,5]benzo[1,2-c]benzo[h]-chromene (**3e**) : White color solid, R_f 0.59 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.26–8.23 (1H, m), 7.80–7.78 (1H, m), 7.69 (1H, d, *J* 8.64 Hz), 7.53–7.46 (3H, m), 7.23 (1H, s), 6.71 (1H, s), 6.00 (2H, s), 5.20 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 149.5, 148.2, 147.0, 134.0, 127.6, 126.4, 125.8, 125.2, 125.1, 124.6, 122.1, 121.6, 120.8, 117.4, 105.5, 103.0, 101.2, 68.9; IR (film) υ_{max} : 3053, 2899, 1485, 1378, 1349, 1262, 1237, 1111, 1095, 1040, 1009, 946, 861, 808, 750 cm^{-1}; HRMS (ESI) *m/z* 275.0674 $[M-H]^+$; calcd. for $[C_{18}H_{12}O_3-H]^+$: 275.0703; m.p. 125–128 °C.

8,9,10-Trimethoxy-6H-dibenzo[c,h]chromene (**3f**) : White color solid, R_f 0.31 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.45 (1H, d, *J* 8.77 Hz), 8.28–8.25 (1H, m), 7.81–7.79 (1H, m), 7.53 (1H, d, *J* 8.86 Hz), 7.48–7.46 (2H, m), 6.60 (1H, s), 5.12 (2H, s), 3.95 (3H, s), 3.92 (3H, s), 3.84 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 152.9, 151.4, 149.9, 142.9, 133.6, 128.4, 127.4, 126.3, 125.4, 125.1, 124.7, 122.1, 121.1, 117.2, 116.2, 104.5, 69.2, 61.2, 60.7, 56.2; IR (film) υ_{max} : 2923, 2844, 1595, 1445, 1384, 1349, 1270, 1233, 1189, 1094, 1034, 1012, 978, 945, 902, 825 cm^{-1}; HRMS (ESI) *m/z* 321.1090 $[M-H]^+$; calcd. for $[C_{20}H_{18}O_4-H]^+$: 321.1121.

7,8-Dimethoxy-6H-dibenzo[c,h]chromene (**3g**) : Yellowish solid, R_f 0.48 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.27 (1H, d, *J* 7.87 Hz), 7.80–7.76 (2H, m), 7.52–7.43 (4H, m), 6.95 (1H, d, *J* 8.49 Hz), 5.42 (2H, s), 3.92 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 152.2, 149.2, 144.4, 134.0, 127.6, 126.3, 125.8, 125.4, 125.0, 124.3, 122.1, 121.5, 120.8, 117.9, 117.0, 111.9, 63.8, 61.0, 55.9; IR (film) υ_{max} : 2932, 2840, 1583, 1496, 1463, 1390, 1356, 1274, 1231, 1097, 1070, 998, 804, 750 cm^{-1}; HRMS (ESI) *m/z* 291.0989 $[M-H]^+$; calcd. for $[C_{19}H_{16}O_3-H]^+$: 291.1016; m.p. 120–122 °C.

2,3,7,8-Tetramethoxy-6H-dibenzo[c,h]chromene (**3h**) : Light yellow color solid, R_f 0.40 (20% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.61 (1H, d, *J* 8.43 Hz), 7.53 (1H, s), 7.39 (1H, d, *J* 8.52 Hz), 7.34 (1H, d, *J* 8.48 Hz), 7.08 (1H, s), 6.91 (1H, d, *J* 8.51 Hz), 5.39 (2H, s), 4.04 (3H, s), 3.99 (3H, s), 3.90 (3H, s), 3.89 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 151.9, 149.8, 149.4, 148.3, 144.4, 129.9, 124.7, 124.6, 120.4, 120.0, 119.2, 117.6, 115.9, 111.9, 106.5, 101.0, 63.8, 60.9, 55.94, 55.85, 55.84; IR (film) υ_{max} : 2960, 2823, 2860, 1611, 1473, 1257, 1221, 1160, 1095, 1065, 1028, 1008, 949, 865, 845, 815, 795 cm^{-1}; HRMS (ESI) *m/z* 353.1407 $[M-H]^+$; calcd. for $[C_{21}H_{20}O_5-H]^+$: 353.1384; m.p. 169–171 °C.

1,2-Dimethoxy-13H-[1,3]dioxolo[4',5' : 4,5]benzo[1,2-h]benzo[c]chromene (**3i**) : Light yellow color solid, R_f 0.33 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.61 (1H, d, *J* 8.55 Hz), 7.54 (1H, s), 7.41 (1H, d, *J* 8.51 Hz), 7.32 (1H, d, *J* 8.50 Hz), 7.07 (1H, s), 6.94 (1H, d, *J* 8.51 Hz), 6.03 (2H, s), 5.36 (2H, s), 3.91 (3H, s), 3.90 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 151.9, 148.9, 148.0, 147.6, 144.4, 131.2, 124.9, 124.4, 121.8, 120.6, 119.3, 117.7, 116.3, 111.9, 104.0, 101.1, 98.9, 63.7, 61.0, 55.9; IR (film) υ_{max} : 2957, 2923, 2854, 1608, 1463, 1475, 1247, 1231, 1179, 1117, 1084, 1038, 990, 946, 864, 820 cm^{-1}; HRMS (ESI) *m/z* 335.0905 $[M-H]^+$; calcd. for $[C_{20}H_{16}O_5-H]^+$: 335.0914; m.p. 160–163 °C.

2,4-Dimethoxy-13H-[1,3]dioxolo[4',5' : 4,5]benzo[1,2-h]benzo[c]chromene (**3j**) : Light yellow color solid, R_f 0.30 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.29 (1H, d, *J* 8.27 Hz), 7.55 (1H, s), 7.32 (1H, d, *J* 8.79 Hz), 7.08 (1H, s), 6.54 (1H, d, *J* 2.51 Hz), 6.49 (1H, d, *J* 2.17 Hz), 6.02 (2H, s), 5.09 (2H, s), 3.93 (3H, s), 3.86 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 159.8, 157.6, 149.4, 147.8, 147.3, 134.9, 130.5, 124.1, 121.4, 119.8, 116.4, 112.8, 103.7, 101.7, 100.9, 99.0, 98.8, 63.5, 55.6, 55.5; IR (film) υ_{max} : 2924, 1608, 1463, 1335, 1244, 1185, 1158, 1128, 1040, 987, 944,

862, 830, 740 cm^{-1}; HRMS (ESI) *m/z* 337.1043 $[M+H]^+$; calcd. for $[C_{20}H_{16}O_5+H]^+$: 337.1071.

Synthesis of lactone via benzylic oxidation and synthesis of arnottin I (**1a**) :

A round-bottom flask was charged with **3** (0.25 mmol; 1.0 equiv.) in CH_2Cl_2 (5 mL) under inert atmosphere. To this reaction mixture PCC (0.75 mmol; 3.0 equiv.) was added and it was stirred for another 5 min at RT. Then, the reaction mixture was refluxed on an oil-bath maintaining the temperature to 40 °C and stirring continued for 24 h. Upon completion of the reaction (monitoring by TLC), it was cooled to room temperature, concentrated under reduced pressure. The crude products were purified by flash chromatography to afford pure **23a-c** and **1a**.

6H-Dibenzo[c,h]chromen-6-one (**23a**) : Light yellow solid, R_f 0.24 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.53 (1H, d, *J* 7.58 Hz), 8.42 (1H, d, *J* 7.83 Hz), 8.13 (1H, d, *J* 7.70 Hz), 7.99 (1H, d, *J* 8.5 Hz), 7.84–7.81 (2H, m), 7.71 (1H, d, *J* 8.69 Hz), 7.62–7.55 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 161.2, 147.2, 145.3, 134.9, 134.2, 130.6, 128.6, 127.9, 127.6, 127.1, 124.5, 123.8, 122.3, 122.0, 121.1, 119.1, 113.0; HRMS (ESI) *m/z* 247 $[M+H]^+$; calcd. for $[C_{17}H_{10}O_2+H]^+$: 247.0754; m.p. 179–181 °C [lit. (D. Mal, A. K. Jana, P. Mitra and K. Ghosh, *J. Org. Chem.*, 2011, **76**, 3392); m.p. 178–180 °C].

8-Methoxy-6H-dibenzo[c,h]chromen-6-one (**23b**) : Grey colored solid, R_f 0.29 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.49 (1H, d, *J* 8.91 Hz), 8.01 (1H, d, *J* 8.86 Hz), 7.91 (1H, d, *J* 8.71 Hz), 7.81–7.77 (2H, m), 7.67 (1H, d, *J* 8.77 Hz), 7.59–7.51 (2H, m), 7.36 (1H, dd, *J* 8.80, 2.81 Hz), 3.91 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 161.3, 159.8, 146.0, 133.6, 128.7, 127.6, 127.4, 127.0, 124.5, 124.4, 123.8, 123.7, 122.3, 122.0, 119.0, 113.1, 111.1, 55.8; IR (film) υ_{max} : 2921, 1727, 1494, 1290, 1114, 1063, 1028, 924, 889, 827, 806, 772 cm^{-1}; HRMS (ESI) *m/z* 277.0849 $[M+H]^+$; calcd. for $[C_{18}H_{12}O_3+H]^+$: 277.0859.

8,9-Dimethoxy-6H-dibenzo[c,h]chromen-6-one (**23c**) : White color solid, R_f 0.36 (30% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 8.55 (1H, d, *J* 8.03 Hz), 7.91 (1H, d, *J* 8.74 Hz), 7.83 (1H, d, *J* 7.72 Hz), 7.77 (1H, s), 7.70 (1H, d, *J* 8.70 Hz), 7.62–7.54 (2H, m), 7.45 (1H, s), 4.10 (3H, s), 4.01 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 161.1, 155.2, 150.0, 146.8, 133.8, 130.6, 127.6, 127.5, 127.0, 124.3, 123.9, 122.2, 118.9, 114.4, 113.0, 110.5, 103.0, 56.35, 56.33; IR (film) υ_{max} : 2922, 2848, 1704, 1608, 1358, 1228, 1209, 1158, 1115, 1054, 806, 764, 733 cm^{-1}; HRMS (ESI) *m/z* 307.0979 $[M+H]^+$; calcd. for $[C_{19}H_{14}O_4+H]^+$: 307.0965.

1,2-Dimethoxy-13H-[1.3]dioxolo[4',5' : 4,5]benzo[1,2-h]benzo[c]chromen-13-one (**1a**) : Yellow solid, R_f 0.20 (30% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) : δ 7.37 (1H, s), 7.05 (1H, d, *J* 8.82 Hz), 6.79–6.77 (2H, m), 6.68 (1H, d, *J* 9.83 Hz), 6.09–6.07 (3H, m), 4.17 (3H, s), 3.85 (3H, s), 1.25 (hexane peak); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 191.0, 167.5, 154.0, 153.5, 149.1, 148.5, 139.1, 134.5, 130.2, 128.3, 123.1, 119.2, 117.3, 115.5, 107.9, 107.6, 102.4, 62.7, 56.9; IR (film) υ_{max} : 2924, 2848, 1774, 1680, 1601, 1481, 1388, 1274, 1117, 1034, 933, 759 cm^{-1}; HRMS (ESI) *m/z* 349.0719 $[M-H]^+$; calcd. for $[C_{20}H_{14}O_6-H]^+$: 349.0707; m.p. 290–292 °C [lit. (D. Mal, A. K. Jana, P. Mitra and K. Ghosh, *J. Org. Chem.*, 2011, **76**, 3392); m.p. 295–297 °C].

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