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# Sequential one-pot approach for the synthesis of functionalized phthalans *via* Heck-reduction–cyclization (HRC) reactions†

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An efficient and practical method is described for the direct synthesis of 1,3-dihydroisobenzofurans, an important structural motif present in biologically active natural or synthetic compounds. The reaction was performed in an almost one-pot fashion *via* controlled [Pd]-catalyzed intermolecular Mizoroki–Heck coupling between 2-bromobenzaldehydes and allylic alcohols followed by reduction and treatment of crude diol with a Lewis acid to give 1,3-dihydroisobenzofurans. Significantly, the method enabled the synthesis of 1,3-dihydroisobenzofurans with simple to dense functionalities on the aromatic rings.

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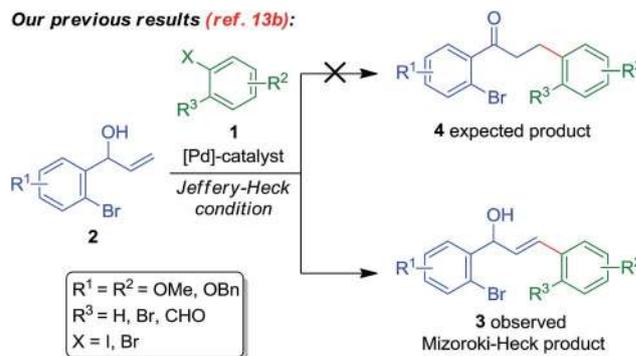
## Introduction

Development of new synthetic methods based on one-pot synthesis or sequential one-pot synthesis are considered as important methods for the synthesis of organic compounds.<sup>1</sup> Particularly, the sequential one-pot processes involved in multiple reactions are promoted by a metal-catalyst in a sequential fashion.<sup>2</sup> Moreover, such transformations could also be feasible *via* the sequential addition of reagents to accomplish a set of reactions.<sup>3</sup> In addition, it would also be possible to develop such one-pot methods using a metal-catalyst to complete the initial reaction followed by the treatment of the resultant intermediate product with a reagent or *vice versa*.<sup>4</sup> These types of processes can be classified into pseudo-domino, cascade<sup>5</sup> and tandem-processes. Usually, the one-pot methods have certain advantages over conventional methods. For example, they reduce waste formation, save time, energy, resources and increase the efficacy.<sup>6</sup> In general, the overall yields of such processes are found to be higher than those from the corresponding step-wise methods. Thus, the sequential one-pot processes that construct multiple bonds are of immense importance, particularly for the synthesis of cyclic structures because many cyclic systems constitute core or part-structures of biologically active natural or synthetic compounds.

Recently, transition-metal mediated one-pot processes have gained considerable attention due to their procedural advantages.<sup>7,8</sup> Among them, the domino Heck reactions under [Pd]-catalysis are well known,<sup>9–11</sup> although the reports on Heck coupling followed by reduction are limited.<sup>12</sup> In continuation of

our interest in the development of synthetic methods by [Pd]-catalysis,<sup>13</sup> we have observed the selective formation of  $\beta$ -aryl allylic alcohols **3** in a highly regio- and stereo-selective manner.<sup>13b</sup> Surprisingly, this is not the expected product **3** under conventional Jeffery-Heck conditions. After a careful study of the literature, we realized that the usual Heck reaction followed by double bond isomerization to give the carbonyl compounds was observed for those substrates having no *ortho*-substituents on the aromatic ring of the allylic alcohols.<sup>14</sup> Therefore, it was thought that the bromo substituent at the *ortho*-position on the aromatic moiety of the allylic alcohol plays a major role to confine the rotation around C–C bond of the PdCH–CH(OH)Ar intermediate (Scheme 1).

Amongst the  $\beta$ -aryl allylic alcohols **3**, those with aldehyde functionality on the aromatic ring appear to be a potential synthetic precursor for the synthesis of oxygen containing heterocyclic compounds (*i.e.*, R<sup>3</sup> = CHO and X = Br). Therefore, herein, we report a short and efficient synthesis of interesting cyclic ethers 1,3-dihydroisobenzofurans **6** by employing



Scheme 1 Synthesis of  $\beta$ -aryl allylic alcohols **3**.

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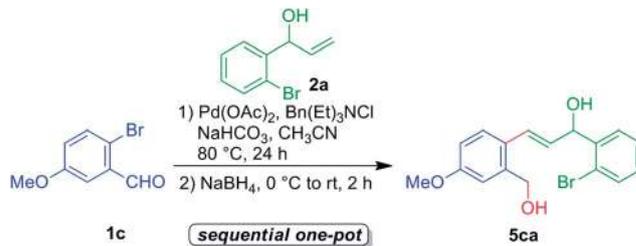
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reduction and acid mediated intramolecular cyclization protocol on  $\beta$ -aryl allylic alcohols **3**.

Oxygen containing heterocyclic compounds are widely assayed for their substantial therapeutic applications such as tetrahydroisobenzofuran motifs.<sup>15,16</sup> They are pervasive structural elements in biologically relevant small molecules (Fig. 1). For example, 3-deoxyisochracinic acid **8** that was isolated from *Cladosporium* species shows antibacterial activity by inhibiting the growth of *Bacillus subtilis*.<sup>15a</sup> The cyclic ether pestacin **9** was obtained from microorganism *Pestalotiopsis microspora*, which exhibits antifungal, antimycotic and antioxidant activities.<sup>15b</sup> FR 198248 **10** was isolated from *Aspergillus flavipes*, which shows antibacterial activity and inhibitory activity against *Staphylococcus aureus* peptide deformylase and also exhibits anti-influenza activity.<sup>15c-e</sup> 1,4-Dimethoxy-3-(3*R*-hydroxy-3*R*-methyl-1-tetralone)-1(3*H*)-isobenzofuran **11** was isolated from the broth of marine *Streptomyces* species M268 and identified to be cytotoxic against human cancer cell lines HL-60, A549 and BEL-7402.<sup>15f</sup> 7-Bromo-1-(2,3-dibromo-4,5-dihydroxyphenyl)-5,6-dihydroxy-1,3-dihydroisobenzofuran **12** was isolated from a brown alga *Leathesia nana*, and it shows potential action on malignant tumors and cardiovascular diseases.<sup>15g</sup> The (*S*)-(+)-enantiomer **13**, known as escitalopram, seems to be more potent than the other (*S*)-(–)-enantiomer.<sup>15h-i</sup>

We thought that the process can be made more efficient by developing a sequential one-pot method for the direct synthesis of diol **5** starting from aryl allylic alcohols **2** and 2-bromobenzaldehydes **1**. This can be achieved by [Pd]-catalysed coupling for the formation of  $\beta$ -aryl allylic alcohols **3** and *in situ* reduction of the aldehyde functionality. Thus, the [Pd]-catalyzed coupling of 2-bromobenzaldehyde **1c** with *ortho*-bromo aryl allylic alcohol **1a** followed by the reduction of **3ca** with NaBH<sub>4</sub> gave the desired diol **5ca** in a very good yield (Scheme 2). The idea behind this hypothesis is to minimize the number of steps and waste and to improve the overall yield of the reaction over the step-wise approach. However, the diol **5ca** was not characterized due to its insolubility in CDCl<sub>3</sub>, and hence it proceeded to the next reaction.

With the required diol **5ca** in hand, the acid promoted cyclization was subsequently explored under different sets of



Scheme 2 Synthesis of diol **5**.

conditions, and the results are summarized in Table 1. Thus, the reaction carried out with a Lewis acid (BF<sub>3</sub>·Et<sub>2</sub>O) at 0 °C, as well as at –10 °C, leads to the decomposition of the starting material (Table 1, entries 1 and 2). Therefore, the reaction at a further low temperature (–20 °C), furnished the product **6ca** in poor yield (30%, Table 1, entry 3). Interestingly, a further drop of temperature (–40 °C) gave the product **6ca** in excellent yield (95%, Table 1, entry 4). However, exploring the reaction with different acids such as protic acid (*p*-TSA) or Lewis acid (AlCl<sub>3</sub>) furnished the product **6ca** in moderate to very good yields (Table 1, entries 5–7), whereas the reaction with H<sub>2</sub>SO<sub>4</sub> gave the product in poor yield (20%, Table 1, entries 8).

Having established the reaction conditions for the synthesis of 1,3-dihydroisobenzofuran **6**, we thought that the method can still be made more efficient by performing cyclization directly on crude diol **5ca** without the column purification. Interestingly, the reaction was found to be smooth on the crude diol **5ca** (*i.e.*, the crude diol, which was obtained after work-up followed by concentration under reduced pressure) and furnished the product in the overall yield of 48% (Scheme 3). The structure of the cyclic ether **6ca** was confirmed from the spectroscopic data. <sup>1</sup>H-NMR data unambiguously confirmed the geometry of the double bond as *trans* by calculating the coupling constant ( $J = 15.5$  to  $15.6$  Hz, see Experimental section and ESI†). Therefore, the other possibility for the formation of seven membered cyclic ether **7ca** was ruled out because it must contain a *cis* double bond. In addition, the formation of five membered cyclic ether **6ca** is geometrically favoured over the seven membered one.

Now, with the optimized reaction conditions in hand, to check the scope and limitations of the method, we investigated this sequential one-pot method on various 2-bromobenzaldehydes **1a–1g** in conjunction with *ortho*-bromo aryl allylic alcohols **2a–2h**. Quite interestingly, the method was amenable on various systems possessing dense functionalities on both the aromatic rings and furnished the products **6aa–6gg** in moderate yields (41–55%), as summarized in Fig. 2. It is worth mentioning that although the yields of the cyclic ether products **6** are moderate, they actually represent the overall yield of three individual reactions. Therefore, each step contributes to at least 75% yield, and thus the method still stands efficient.

After the successful synthesis of 1,3-dihydroisobenzofurans, we planned to increase the scope of this protocol by employing the allylic alcohols possessing a methyl/methoxy group in the *ortho* position. During the sequential one-pot approach, we observed the formation of the regular Jeffery-Heck product

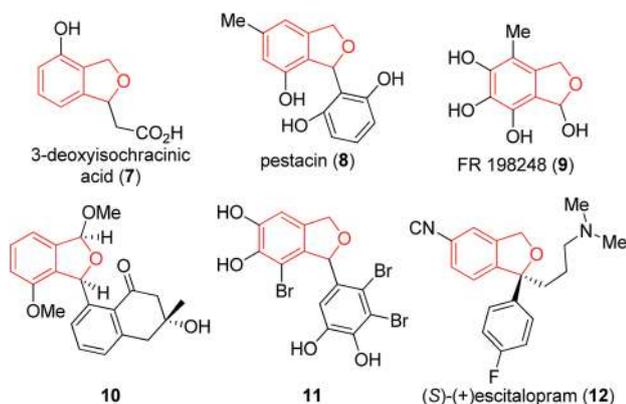
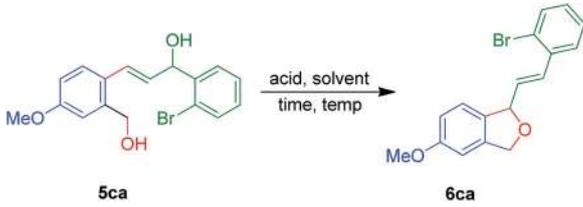
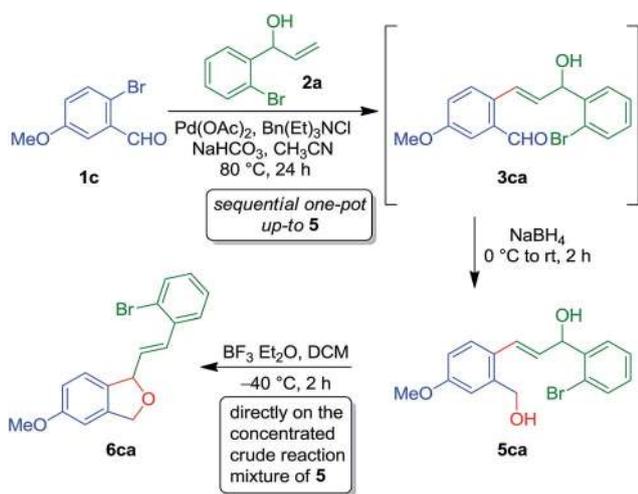


Fig. 1 Representative examples of naturally occurring phthalans.

Table 1 Optimization table for the synthesis of 1,3-dihydroisobenzofuran **6ca** from the diol **5ca**


Entry <sup>a</sup>	Acid (equiv)	Solvent (5 mL)	Temp (°C)	Time min	Yield <sup>b</sup> of <b>6ca</b> (%)
1	BF <sub>3</sub> ·Et <sub>2</sub> O (2.0)	DCM	0	15	—
2	BF <sub>3</sub> ·Et <sub>2</sub> O (4.0)	DCM	−10	15	—
3	BF <sub>3</sub> ·Et <sub>2</sub> O (5.0)	DCM	−20	15	30
4	BF <sub>3</sub> ·Et <sub>2</sub> O (5.0)	DCM	−40	120	95
5	<i>p</i> -TSA (3.0)	DCM	−40	60	50
6	AlCl <sub>3</sub> (1.2)	DCM	−40	10	70
7	AlCl <sub>3</sub> (1.2)	DCE	−40	10	80
8	H <sub>2</sub> SO <sub>4</sub> (3.0)	DCM	−40	30	20

<sup>a</sup> Reaction conditions: all the reactions carried out with diol **5ca** (0.10 mmol) in DCM. <sup>b</sup> Isolated yields of chromatographically pure products.

Scheme 3 Sequential one-pot method for the synthesis of **6ca**.

along with the Mizoroki–Heck product.<sup>13b</sup> This (Jeffery–Heck product) interfered in the further steps and hindered the isolation of clean products. Thus, we proceeded in a step-wise approach and achieved the targeted 1,3-dihydroisobenzofurans **6ai** and **6aj** in a moderate overall yield (47% and 52%). It is worth mentioning that in these cases, we were also able to characterise diol **5** (Scheme 4).

## Experimental section

### General considerations

IR spectra were recorded on a Bruker Tensor 37 (FT-IR) spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl<sub>3</sub>; chemical shifts ( $\delta$  in ppm) and coupling constants ( $J$  in Hz) are reported in

standard fashion with reference to either internal standard tetramethylsilane (TMS) ( $\delta_{\text{H}} = 0.00$  ppm) or CHCl<sub>3</sub> ( $\delta_{\text{H}} = 7.25$  ppm). <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer at 295 K in CDCl<sub>3</sub>; chemical shifts ( $\delta$  in ppm) are reported relative to CHCl<sub>3</sub> [ $\delta_{\text{C}} = 77.00$  ppm (central line of triplet)]. In <sup>13</sup>C-NMR, the nature of carbons (namely, C, CH, CH<sub>2</sub> and CH<sub>3</sub>) was determined by recording the DEPT-135 spectra, and it is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH<sub>2</sub>) and q = quartet (for CH<sub>3</sub>). In <sup>1</sup>H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br. s = broad singlet, septd = septet of doublets. The assignment of signals was confirmed by <sup>1</sup>H, <sup>13</sup>C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. X-ray crystal structure data were obtained using an Oxford Super Nova instrument. All the small scale dry reactions were carried out using the standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were generally run under an argon or nitrogen atmosphere. All the solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C, diethyl ether, dichloromethane (DCM), ethyl acetate, THF (with purity 99%), and acetonitrile (with purity 99.9%), which were purchased from locally available commercial sources were used. All aromatic aldehydes (with purity 98%), bromine (with purity 99%), iodine (with purity 99%), Bn(Et)<sub>3</sub>NCl (with purity 99%), Pd(OAc)<sub>2</sub> (with purity 98%), 3-iodoanisole (with purity 99%), 2-bromiodobenzene (with purity 99%), NaBH<sub>4</sub> (with purity 99%), K<sub>2</sub>CO<sub>3</sub> (with purity 99%), and NaHCO<sub>3</sub> (with purity 99.5%) were purchased from Sigma-Aldrich, whereas vinylmagnesium bromide (with purity 99%), BF<sub>3</sub>·Et<sub>2</sub>O (with purity 48%) and iodobenzene (with purity 99%) were purchased from

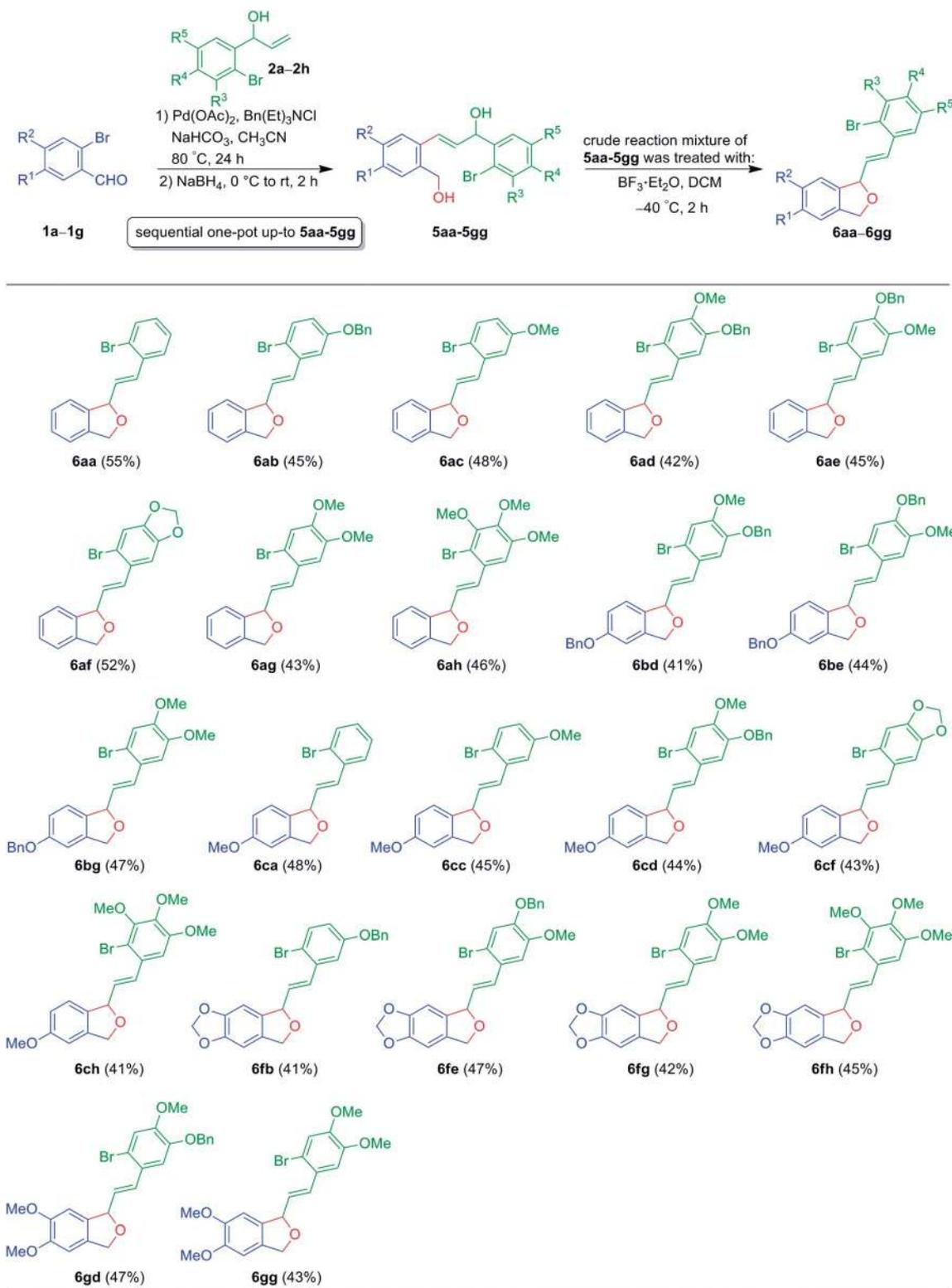
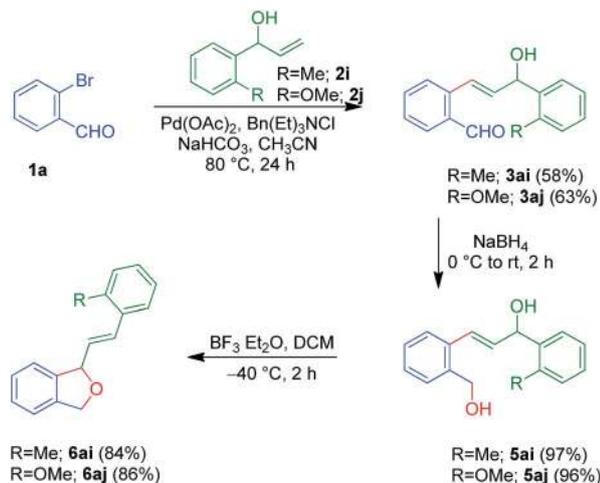


Fig. 2 Synthesis of 1,3-dihydroisobenzofurans **6aa-6gg** from 2-bromobenzaldehydes **1a-1g** and aryl allylic alcohols **2a-2h**. All reactions were carried out with 2-bromobenzaldehydes **1a-1g** (0.50 mmol). Isolated yields of chromatographically pure products in parentheses.

other commercial sources and used as received. The base  $\text{NaHCO}_3$  was dried at  $150-170^\circ\text{C}$  over an oil bath. Diethyl ether and toluene were dried over sodium/benzophenone, DCM and DCE were dried over calcium hydride, and acetonitrile was dried

over  $\text{P}_2\text{O}_5$ . Acme's silica gel (60-120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).



Scheme 4 Step-wise approach for the synthesis of 1,3-dihydroisobenzofurans **6ai** and **6aj** from 2-bromobenzaldehyde **1a** and aryl allylic alcohols **2i** and **2j**.

*ortho*-Bromobenzaldehydes **1a–1h** except **1a** were synthesized from corresponding aromatic aldehydes using a bromination method reported in the literature.<sup>17</sup> Among the bromo aryl allylic alcohols, **2a**,<sup>18</sup> **2g**<sup>13b</sup> and **2h**<sup>13b</sup> were reported in literature.

**General procedure-1 for the synthesis of *ortho*-bromo aryl allylic alcohols (2a–2h).** To a magnetically stirred solution of 2-bromobenzaldehydes **1a–1h** (10 mmol) in THF (20 mL), in a round bottom flask at 0 °C, under nitrogen atmosphere, 1.0 M of vinylmagnesium bromide (20 mmol, 1.0 M in THF) was added, and the resultant reaction mixture was slowly allowed to reach room temperature and stirred for 1.5 h. The reaction mixture was quenched with saturated aq. NH<sub>4</sub>Cl solution and extracted with diethyl ether (3 × 30 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate 90 : 10 to 80 : 20) furnished *ortho*-bromo aryl allylic alcohols **2a–2h** (80–92%).

**General procedure-2 for the synthesis of 1,3-dihydroisobenzofurans (6aa–6gg).** In an oven-dried Schlenk flask under nitrogen atmosphere, Pd(OAc)<sub>2</sub> (5 mol%), Bn(Et)<sub>3</sub>NCl (0.50 mmol), NaHCO<sub>3</sub> (1 mmol), 2-bromobenzaldehydes **1a–1g** (0.50 mmol) and *ortho*-bromo aryl allylic alcohol **2a–2h** (0.60 mmol) were added, followed by the addition of dry acetonitrile (4 mL). The resulting reaction mixture was stirred for 24 h at 80 °C. Then, the reaction mixture was cooled to 0 °C and NaBH<sub>4</sub> (1.50 mmol) was added to it, and the mixture was stirred for two hours at room temperature. The reaction mixture was quenched with saturated aq. NH<sub>4</sub>Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Traces of solvents were removed under high vacuum, and to the obtained crude, 20 mL of dry DCM was added, and then the mixture was cooled to –40 °C, BF<sub>3</sub>·Et<sub>2</sub>O (2.5 mmol) was added, and the reaction was

stirred for 2 h at the same temperature. The reaction mixture was then quenched with saturated aqueous NaHCO<sub>3</sub> solution, and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **6aa–6gg** (40–55%).

**General procedure-3 for the synthesis of 1,3-dihydroisobenzofurans (6ai and 6aj).** In an oven-dried Schlenk flask under nitrogen atmosphere, Pd(OAc)<sub>2</sub> (5 mol%), Bn(Et)<sub>3</sub>NCl (0.50 mmol), NaHCO<sub>3</sub> (1 mmol), 2-bromobenzaldehydes **1a** (0.50 mmol) and *ortho*-bromo aryl allylic alcohol **2i–2j** (0.60 mmol) were added, followed by the addition of dry acetonitrile (4 mL). The resulting reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was quenched using saturated aq. NH<sub>4</sub>Cl solution, and then compound was extracted in ethyl acetate and concentrated under reduced pressure. The aldehyde **3** was isolated by silica gel column chromatography (petroleum ether/ethyl acetate). The aldehyde **3** was cooled to 0 °C and NaBH<sub>4</sub> (1.50 mmol) was added and stirred for two hours at room temperature. The reaction mixture was quenched with saturated aq. NH<sub>4</sub>Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Traces of solvents were removed under high vacuum, and to the obtained crude, 20 mL of dry DCM was added, and then the mixture was cooled to –40 °C, BF<sub>3</sub>·Et<sub>2</sub>O (2.5 mmol) was added, and the reaction mixture was stirred for 2 h at the same temperature. The reaction mixture was then quenched with saturated aqueous NaHCO<sub>3</sub> solution and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification of the residue on a silica gel column chromatography (petroleum ether/ethyl acetate) furnished the products **6ai** & **6aj** (47–52%).

**1-[5-(Benzyloxy)-2-bromophenyl]prop-2-en-1-ol (2b).** GP-1 was carried out and the product **2b** (2.80 g, 88%) was furnished as a pale yellow liquid. [TLC control  $R_f(\mathbf{1b}) = 0.60$ ,  $R_f(\mathbf{2b}) = 0.40$  (petroleum ether/ethyl acetate 90 : 10, UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\text{max}} = 3371, 3032, 2920, 1592, 1571, 1462, 1291, 1380, 1291, 1233, 1163, 1010, 927, 736, 697$  cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.50\text{--}7.28$  (m, 6H, Ar-H), 7.19 (d, 1H,  $J = 2.9$  Hz, Ar-H), 6.78 (dd, 1H,  $J = 8.8$  and 2.9 Hz, Ar-H), 5.99 (ddd, 1H,  $J = 15.6, 10.3$  and 5.4 Hz, CH=CH<sub>2</sub>), 5.54 (d, 1H,  $J = 5.4$  Hz, ArCH-OH), 5.40 (td, 1H,  $J = 15.6$  and 1.5 Hz, C=CH<sub>a</sub>H<sub>b</sub>), 5.22 (td, 1H,  $J = 10.3$  and 1.5 Hz, C=CH<sub>a</sub>H<sub>b</sub>), 5.04 (s, 2H, PhCH<sub>2</sub>O), 2.25 (d, 1H,  $J = 3.9$  Hz, OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 158.4$  (s, Ar-C), 142.5 (s, Ar-C), 138.1 (d, CH=CH<sub>2</sub>), 136.4 (s, Ar-C), 133.3 (d, Ar-CH), 128.6 (d, 2C, Ar-CH), 128.1 (d, Ar-CH), 127.5 (d, 2C, Ar-CH), 115.9 (d, Ar-CH), 115.7 (t, CH=CH<sub>2</sub>), 114.2 (d, Ar-CH), 112.9 (s, Ar-C), 73.4 (d, Ar-CHOH), 70.2 (t, PhCH<sub>2</sub>) ppm. HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for [C<sub>16</sub>H<sub>14</sub>BrO]<sup>+</sup> = [(M + H)–H<sub>2</sub>O]<sup>+</sup>: 301.0223; found 301.0213.

**1-(2-Bromo-5-methoxyphenyl)prop-2-en-1-ol (2c).** GP-1 was carried out and the product **2c** (2.20 mg, 92%) was furnished as a pale yellow liquid. [TLC control  $R_f(\mathbf{1c}) = 0.80$ ,  $R_f(\mathbf{2c}) = 0.50$  (petroleum ether/ethyl acetate 80 : 20, UV detection)]. IR

(MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 3380, 2922, 2851, 1593, 1572, 1468, 1416, 1290, 1233, 1161, 1047, 1013, 928, 807, 771 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.39$  (d, 1H,  $J = 8.8$  Hz, Ar-H), 7.07 (d, 1H,  $J = 3.4$  Hz, Ar-H), 6.69 (dd, 1H,  $J = 8.8$  and 3.4 Hz, Ar-H), 5.99 (ddd, 1H,  $J = 17.1, 10.3$  and 5.4 Hz,  $\text{CH}=\text{CH}_2$ ), 5.53 (d, 1H,  $J = 5.4$  Hz, ArCH-OH), 5.38 (td, 1H,  $J = 17.1$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.21 (dd, 1H,  $J = 10.3$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 3.78 (s, 3H, Ar-OCH<sub>3</sub>), 2.34 (br. s, 1H, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 159.3$  (s, Ar-C), 142.4 (s, Ar-C), 138.1 (d,  $\text{CH}=\text{CH}_2$ ), 133.3 (d, Ar-CH), 115.7 (t,  $\text{CH}=\text{CH}_2$ ), 115.2 (d, Ar-CH), 113.0 (d, Ar-CH), 112.7 (s, Ar-C), 73.4 (d, Ar-CHOH), 55.4 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{10}\text{H}_{10}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 224.9910; found 224.9903.

1-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]prop-2-en-1-ol (**2d**).

**GP-1** was carried out and the product **2d** (2.96 g, 85%) was furnished as a brownish viscous liquid. [TLC control  $R_f(\mathbf{1d}) = 0.60$ ,  $R_f(\mathbf{2d}) = 0.30$  (petroleum ether/ethyl acetate 90 : 10, UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 3392, 2933, 2847, 1599, 1497, 1454, 1381, 1251, 1120, 1155, 1120, 1039, 1023, 861, 834, 696, 665 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.42$  (dd, 2H,  $J = 7.3$  and 6.8 Hz, Ar-H), 7.37 (t, 2H,  $J = 7.3$  Hz, Ar-H), 7.31 (ddd, 1H,  $J = 7.3$  and 6.8 Hz, Ar-H), 7.03 (s, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 5.98 (ddd, 1H,  $J = 15.6, 10.3$  and 4.9 Hz,  $\text{CH}=\text{CH}_2$ ), 5.51 (d, 1H,  $J = 5.4$  Hz, ArCH-OH), 5.38 (td, 1H,  $J = 15.6$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.20 (td, 1H,  $J = 10.3$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.09 (s, 2H,  $\text{PhCH}_2\text{O}$ ), 3.38 (s, 3H, Ar-OCH<sub>3</sub>), 2.29 (d, 1H,  $J = 2.9$  Hz, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 149.4$  (s, Ar-C), 148.1 (s, Ar-C), 138.5 (d,  $\text{CH}=\text{CH}_2$ ), 136.3 (s, Ar-C), 134.0 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.0 (d, Ar-CH), 127.3 (d, 2C, Ar-CH), 117.6 (d, Ar-CH), 115.3 (t,  $\text{CH}=\text{CH}_2$ ), 112.1 (s, Ar-C), 110.7 (d, Ar-CH), 73.3 (d, Ar-CHOH), 71.2 (t,  $\text{PhCH}_2$ ), 56.0 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{16}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 331.0328; found 331.0332.

1-[4-(Benzyloxy)-2-bromo-5-methoxyphenyl]prop-2-en-1-ol (**2e**).

**GP-1** was carried out and the product **2e** (2.79 g, 80%) was furnished as a brownish viscous liquid. [TLC control  $R_f(\mathbf{1e}) = 0.60$ ,  $R_f(\mathbf{2e}) = 0.30$  (petroleum ether/ethyl acetate 90 : 10, UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 3404, 3032, 3008, 2932, 1600, 1502, 1502, 1439, 1379, 1257, 1156, 1120, 1029, 925, 863, 777 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.42$  (d, 2H,  $J = 7.3$  Hz, Ar-H), 7.35 (dd, 2H,  $J = 7.3$  and 6.8 Hz, Ar-H), 7.29 (t, 1H,  $J = 7.3$  Hz, Ar-H), 7.06 (s, 1H, Ar-H), 7.00 (s, 1H, Ar-H), 5.90 (ddd, 1H,  $J = 15.6, 10.3$  and 4.9 Hz,  $\text{CH}=\text{CH}_2$ ), 5.49 (d, 1H,  $J = 5.4$  Hz, ArCH-OH), 5.35 (td, 1H,  $J = 15.6$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.31 (td, 1H,  $J = 10.3$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.11 (d, 1H,  $J = 12.2$  Hz,  $\text{PhCH}_a\text{H}_b\text{O}$ ), 5.10 (d, 1H,  $J = 12.2$  Hz,  $\text{PhCH}_a\text{H}_b\text{O}$ ), 3.85 (s, 3H, Ar-OCH<sub>3</sub>), 2.10 (d, 1H,  $J = 2.4$  Hz, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 149.6$  (s, Ar-C), 147.8 (s, Ar-C), 138.4 (d,  $\text{CH}=\text{CH}_2$ ), 136.5 (s, Ar-C), 133.4 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 128.0 (d, Ar-CH), 127.6 (d, 2C, Ar-CH), 115.7 (d, Ar-CH), 115.3 (t,  $\text{CH}=\text{CH}_2$ ), 113.1 (s, Ar-C), 112.9 (d, Ar-CH), 73.2 (d, Ar-CHOH), 71.1 (t,  $\text{PhCH}_2$ ), 56.2 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{16}\text{BrO}_2]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 331.0328; found 331.0334.

1-(6-Bromo-1,3-benzodioxol-5-yl)prop-2-en-1-ol (**2f**). **GP-1** was carried out and the product **2f** (2.0 g, 80%) was furnished as a colorless viscous liquid. [TLC control  $R_f(\mathbf{1f}) = 0.60$ ,  $R_f(\mathbf{2f}) = 0.50$

(petroleum ether/ethyl acetate 80 : 20, UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 3346, 2897, 1501, 1471, 1407, 1230, 1107, 1035, 930, 840, 798 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 6.98$  (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 5.95 (d, 1H,  $J = 5.4$  Hz,  $\text{OCH}_a\text{H}_b\text{O}$ ), 5.94 (d, 1H,  $J = 5.4$  Hz,  $\text{OCH}_a\text{H}_b\text{O}$ ), 5.93 (ddd, 1H,  $J = 15.6, 10.3$  and 5.4 Hz,  $\text{CH}=\text{CH}_2$ ), 5.51 (d, 1H,  $J = 5.4$  Hz, ArCH-OH), 5.37 (td, 1H,  $J = 15.6$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 5.20 (td, 1H,  $J = 10.3$  and 1.5 Hz,  $\text{C}=\text{CH}_a\text{H}_b$ ), 2.26 (d, 1H,  $J = 2.9$  Hz, OH) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 147.8$  (s, Ar-C), 147.7 (s, Ar-C), 138.4 (d,  $\text{CH}=\text{CH}_2$ ), 134.8 (s, Ar-C), 115.3 (t,  $\text{CH}=\text{CH}_2$ ), 112.8 (s, Ar-C), 112.5 (d, Ar-CH), 107.7 (d, Ar-CH), 101.7 (t,  $\text{OCH}_2\text{O}$ ), 73.3 (d, Ar-CHOH) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{10}\text{H}_9\text{BrNaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 278.9627; found 278.9639.

1-[(E)-2-(2-Bromophenyl)vinyl]-1,3-dihydro-2-benzofuran (**6aa**).

**GP-2** was carried out and the product **6aa** (83 mg, 55%) was furnished as a yellow viscous liquid. [TLC control  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2a}) = 0.70$  and  $R_f(\mathbf{6aa}) = 0.85$  (petroleum ether/ethyl acetate 95 : 5, UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2922, 2852, 1588, 1465, 1437, 1357, 1284, 1246, 1158, 1122, 1107, 1021, 963, 747, 698, 665 \text{ cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.53$  (dd, 1H,  $J = 7.8$  and 1.5 Hz, Ar-H), 7.50 (dd, 1H,  $J = 7.8$  and 1.5 Hz, Ar-H), 7.35–7.15 (m, 5H, Ar-H), 7.10 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 7.08 (ddd, 1H,  $J = 9.3, 7.8$  and 1.5 Hz, Ar-H), 6.21 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.80 [d, 1H,  $J = 7.8$  Hz,  $\text{PhCH}(\text{O})\text{CH}=\text{CH}$ ], 5.22 (d, 1H,  $J = 11.7$  Hz,  $\text{PhCH}_a\text{H}_b\text{-OCHCH}=\text{CH}$ ), 5.14 (d, 1H,  $J = 11.7$  Hz,  $\text{PhCH}_a\text{H}_b\text{-OCHCH}=\text{CH}$ ) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 140.6$  (s, Ar-C), 139.1 (s, Ar-C), 136.4 (s, Ar-C), 132.9 (d, Ar-CH), 132.0 (d, Ar-CH), 130.5 (d, Ar-CH-CH=CH-Ar), 129.1 (d, Ar-CH-CH=CH-Ar), 127.8 (d, Ar-CH), 127.5 (d, Ar-CH), 127.4 (d, Ar-CH), 127.3 (d, Ar-CH), 123.8 (s, Ar-C), 122.0 (d, Ar-CH), 121.1 (d, Ar-CH), 85.0 (d,  $\text{Ph-CHCH}=\text{CH}$ ), 72.9 (t,  $\text{Ph-CH}_2\text{OCHCH}=\text{CH}$ ) ppm. HR-MS ( $\text{ESI}^+$ ):  $m/z$  calculated for  $[\text{C}_{16}\text{H}_{13}\text{BrNaO}]^+ = [\text{M} + \text{Na}]^+$ : 323.0042; found 323.0041.

1-[(E)-2-[5-(Benzyloxy)-2-bromophenyl]vinyl]-1,3-dihydro-2-benzofuran (**6ab**). **GP-2** was carried out and the product **6ab** (92 mg, 45%) was furnished as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 95 : 5,  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2b}) = 0.50$  and  $R_f(\mathbf{6ab}) = 0.65$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2922, 2852, 1590, 1563, 1459, 1286, 1238, 1173, 1028, 1013, 963, 739, 697 \text{ cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.41$  (d, 1H,  $J = 8.3$  Hz, Ar-H), 7.39–7.20 (m, 8H, Ar-H), 7.19 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 7.14 (d, 1H,  $J = 2.9$  Hz, Ar-H), 7.05 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.73 (dd, 1H,  $J = 8.8$  and 2.9 Hz, Ar-H), 6.19 (dd, 1H,  $J = 15.6$  and 7.3 Hz, ArCH=CH), 5.80 [d, 1H,  $J = 7.3$  Hz,  $\text{PhCH}(\text{O})\text{CH}=\text{CH}$ ], 5.22 (dd, 1H,  $J = 12.2$  and 2.4 Hz,  $\text{PhCH}_a\text{H}_b\text{-OCHCH}=\text{CH}$ ), 5.13 (dd, 1H,  $J = 12.2$  and 1.0 Hz,  $\text{PhCH}_a\text{H}_b\text{-OCHCH}=\text{CH}$ ), 4.98 (s, 2H,  $\text{PhCH}_2\text{O}$ ) ppm.  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 158.0$  (s, Ar-C), 140.5 (s, Ar-C), 139.1 (s, Ar-C), 137.1 (s, Ar-C), 136.4 (s, Ar-C), 133.4 (d, Ar-CH), 132.1 (d, Ar-CH), 130.5 (d, Ar-CH), 128.5 (d, 2C, Ar-CH), 128.0 (d, Ar-CH-CH=CH-Ar), 127.8 (d, Ar-CH-CH=CH-Ar), 127.5 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 122.0 (d, Ar-CH), 121.1 (d, Ar-CH), 116.2 (d, Ar-CH), 114.8 (s, Ar-C), 113.3 (d, Ar-CH), 84.8 (d,  $\text{Ph-CHCH}=\text{CH}$ ), 72.8 (t,  $\text{Ph-CH}_2\text{OCHCH}=\text{CH}$ ) 70.1 (t,  $\text{PhCH}_2\text{O}$ ) ppm. HR-MS ( $\text{ESI}^+$ ):  $m/z$  calculated for  $[\text{C}_{23}\text{H}_{18}^{79}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 389.0536; found 389.0545 and  $[\text{C}_{23}\text{H}_{18}^{81}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 391.0515; found 391.0529.

1-[(E)-2-(2-Bromo-5-methoxyphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6ac**). GP-2 was carried out and the product **6ac** (80 mg, 48%) was furnished as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 95 : 5,  $R_f(\mathbf{1a}) = 0.75$ ,  $R_f(\mathbf{2c}) = 0.35$  and  $R_f(\mathbf{6ac}) = 0.50$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2959, 2929, 1592, 1571, 1464, 1287, 1236, 1161, 1014, 802, 754, 733, 599 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.35$  (d, 1H,  $J = 8.8$  Hz, Ar-H), 7.30–7.05 (m, 4H, Ar-H), 7.01 (d, 1H,  $J = 15.5$  Hz, ArCH=CH), 6.97 (d, 1H,  $J = 2.2$  Hz, Ar-H), 6.62 (dd, 1H,  $J = 8.7$  and 3.0 Hz, Ar-H), 6.13 (dd, 1H,  $J = 15.5$  and 7.5 Hz, ArCH=CH), 5.74 [d, 1H,  $J = 7.5$  Hz, PhCH(O)CH=CH], 5.16 (dd, 1H,  $J = 12.3$  and 2.2 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.08 (d, 1H,  $J = 12.3$  Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.68 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 158.9$  (s, Ar-C), 140.5 (s, Ar-C), 139.1 (s, Ar-C), 140.0 (s, Ar-C), 133.4 (d, Ar-CH), 132.0 (d, Ar-CH), 130.7 (d, Ar-CH), 127.8 (d, Ar-CH-CH=CH-Ar), 127.5 (d, Ar-CH-CH=CH-Ar), 122.0 (d, Ar-CH), 121.1 (d, Ar-CH), 115.7 (d, Ar-CH), 114.5 (s, Ar-C), 112.0 (d, Ar-CH), 84.9 (d, Ph-CHCH=CH), 72.9 (t, Ph-CH<sub>2</sub>OCHCH=CH), 55.4 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{14}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 313.0223; found 313.0212,  $[\text{C}_{17}\text{H}_{14}^{81}\text{BrO}]^+ = [(\text{M} + \text{H}) - \text{H}_2\text{O}]^+$ : 315.0202; found 315.0189 and  $[\text{C}_{17}\text{H}_{19}\text{BrNO}_2]^+ = [\text{M} + \text{NH}_4]^+$ : 348.0594; found 348.0587.

1-[(E)-2-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]vinyl]-1,3-dihydro-2-benzofuran (**6ad**). GP-2 was carried out and the product **6ad** (92 mg, 42%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2d}) = 0.20$  and  $R_f(\mathbf{6ad}) = 0.30$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2918, 2850, 1595, 1502, 1461, 1385, 1260, 1200, 1166, 1024, 861, 750, 697 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.43$  (d, 2H,  $J = 7.3$  Hz, Ar-H), 7.38 (dd, 2H,  $J = 7.3$  and 6.8 Hz, Ar-H), 7.35–7.25 (m, 4H, Ar-H), 7.22 (dd, 1H,  $J = 7.8$  and 2.0 Hz, Ar-H), 7.06 (s, 1H, Ar-H), 7.04 (s, 1H, Ar-H), 7.03 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.13 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.81 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.25 (dd, 1H,  $J = 12.2$  and 2.4 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.14 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10 (s, 2H, PhCH<sub>2</sub>O) 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 149.1$  (s, Ar-C), 148.6 (s, Ar-C), 140.7 (s, Ar-C), 139.2 (s, Ar-C), 136.2 (s, Ar-C), 130.7 (d, Ar-CH-CH=CH-Ar), 130.0 (d, Ar-CH-CH=CH-Ar), 128.8 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.1 (d, Ar-CH), 127.8 (d, Ar-CH), 127.5 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 122.1 (d, Ar-CH), 121.1 (d, Ar-CH), 117.6 (d, Ar-CH), 114.4 (s, Ar-C), 109.6 (d, Ar-CH), 85.2 (d, Ph-CHCH=CH), 72.8 (t, Ph-CH<sub>2</sub>OCHCH=CH), 71.1 (t, PhCH<sub>2</sub>O), 56.1 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{24}\text{H}_{21}\text{BrNaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 459.0566; found 459.0583 and  $[\text{C}_{24}\text{H}_{21}\text{BrNaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 461.0546; found 461.0561.

1-[(E)-2-[4-(Benzyloxy)-2-bromo-5-methoxyphenyl]vinyl]-1,3-dihydro-2-benzofuran (**6ae**). GP-2 was carried out and the product **6ae** (100 mg, 45%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2e}) = 0.20$  and  $R_f(\mathbf{6ae}) = 0.35$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2957, 2920, 2851, 1503, 1462, 1441, 1379, 1261, 1206, 1163, 1026, 743 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.40$  (d, 2H,  $J = 6.8$  Hz, Ar-H), 7.34 (dd, 2H,  $J = 7.3$

and 6.8 Hz, Ar-H), 7.31–7.24 (m, 4H, Ar-H), 7.20 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 7.08 (s, 1H,  $J = 9.3$  Hz, Ar-H), 7.03 (s, 1H,  $J = 9.3$  Hz, Ar-H), 7.00 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.02 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.78 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.23 (dd, 1H,  $J = 12.2$  and 2.4 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.13 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.06 (s, 2H, PhCH<sub>2</sub>O) 3.86 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 150.2$  (s, Ar-C), 147.7 (s, Ar-C), 140.8 (s, Ar-C), 139.2 (s, Ar-C), 136.5 (s, Ar-C), 130.6 (d, Ar-CH-CH=CH-Ar), 129.9 (d, Ar-CH-CH=CH-Ar), 128.6 (d, 2C, Ar-CH), 128.4 (s, Ar-C), 128.1 (d, Ar-CH), 127.8 (d, Ar-CH), 127.6 (d, 2C, Ar-CH), 127.5 (d, Ar-CH), 122.1 (d, Ar-CH), 121.1 (d, Ar-CH), 115.8 (d, Ar-CH), 115.2 (s, Ar-C), 112.1 (d, Ar-CH), 85.2 (d, Ph-CHCH=CH), 72.9 (t, Ph-CH<sub>2</sub>OCHCH=CH), 71.3 (t, PhCH<sub>2</sub>O), 56.2 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{24}\text{H}_{22}\text{BrO}_3]^+ = [\text{M} + \text{H}]^+$ : 437.0747; found 437.0735 and  $[\text{C}_{24}\text{H}_{22}^{81}\text{BrO}_3]^+ = [\text{M} + \text{H}]^+$ : 439.0726; found 439.0732.

5-Bromo-6-[(E)-2-(1,3-dihydro-2-benzofuran-1-yl)vinyl]-1,3-benzodioxole (**6af**). GP-2 was carried out and the product **6af** (90 mg, 52%) was furnished as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2f}) = 0.30$  and  $R_f(\mathbf{6af}) = 0.65$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2901, 2852, 1502, 1474, 1412, 1247, 1229, 1116, 1034, 978, 961, 933, 863, 838, 750 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.35$ –7.23 (m, 3H, Ar-H), 7.19 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 7.03 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.99 (d, 2H,  $J = 2.4$  Hz, Ar-H), 6.07 (dd, 1H,  $J = 15.5$  and 7.8 Hz, ArCH=CH), 5.94 (s, 2H, OCH<sub>2</sub>O), 5.78 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.22 (dd, 1H,  $J = 12.2$  and 2.4 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.13 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 148.1$  (s, Ar-C), 147.6 (s, Ar-C), 140.7 (s, Ar-C), 139.1 (s, Ar-C), 130.5 (d, Ar-CH-CH=CH-Ar), 130.3 (d, Ar-CH-CH=CH-Ar), 129.6 (s, Ar-C), 127.8 (d, Ar-CH), 127.4 (d, Ar-CH), 122.0 (d, Ar-CH), 121.1 (d, Ar-CH), 115.0 (s, Ar-C), 112.6 (d, Ar-CH), 106.4 (d, Ar-CH), 101.7 (d, Ar-CH), 85.0 (d, Ph-CHCH=CH), 72.8 (t, Ph-CH<sub>2</sub>OCHCH=CH) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{13}\text{BrNaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 366.9940; found 366.9938 and  $[\text{C}_{17}\text{H}_{13}^{81}\text{BrNaO}_3]^+ = [\text{M} + \text{Na}]^+$ : 368.9920; found 368.9918.

1-[(E)-2-(2-Bromo-4,5-dimethoxyphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6ag**). GP-2 was carried out and the product **6ag** (78 mg, 43%) was furnished as a yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(\mathbf{1a}) = 0.80$ ,  $R_f(\mathbf{2g}) = 0.15$  and  $R_f(\mathbf{6ag}) = 0.30$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2928, 2847, 1502, 1462, 1439, 1380, 1256, 1160, 1024, 751 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.30$ –7.15 (m, 4H, Ar-H), 7.00 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.99 (s, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 6.10 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.78 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.21 (dd, 1H,  $J = 12.2$  and 2.4 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.13 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.83 (s, 3H, Ar-OCH<sub>3</sub>), 3.81 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 149.4$  (s, Ar-C), 148.4 (s, Ar-C), 140.6 (s, Ar-C), 139.1 (s, Ar-C), 130.6 (d, Ar-CH-CH=CH-Ar), 129.8 (d, Ar-CH-CH=CH-Ar), 128.2 (s, Ar-C), 127.7 (d, Ar-CH), 127.4 (d, Ar-CH), 122.0 (d, Ar-CH), 121.0 (d, Ar-CH), 115.2 (d, Ar-CH), 114.5 (s, Ar-C), 109.0 (d, Ar-CH), 85.2 (d, Ph-CHCH=CH), 72.8 (t, Ph-CH<sub>2</sub>OCHCH=CH), 56.0 (q, Ar-OCH<sub>3</sub>),

56.9 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>18</sub>H<sub>17</sub>BrNaO<sub>3</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 383.0253; found 383.0254.

1-[(*E*)-2-(2-Bromo-3,4,5-trimethoxyphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6ah**). GP-2 was carried out and the product **6ah** (90 mg, 46%) was furnished as a yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10, R<sub>f</sub>(**1a**) = 0.80, R<sub>f</sub>(**2h**) = 0.10 and R<sub>f</sub>(**6ah**) = 0.25 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>): ν<sub>max</sub> = 2923, 2851, 1559, 1480, 1426, 1391, 1325, 1201, 1166, 1106, 1009, 926, 753 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.45–7.15 (m, 4H, Ar-H), 7.10 (d, 1H, *J* = 15.6 Hz, ArCH=CH), 6.87 (s, 1H, Ar-H), 6.13 (dd, 1H, *J* = 15.6 and 7.8 Hz, ArCH=CH), 5.81 [d, 1H, *J* = 7.8 Hz, PhCH(O)CH=CH], 5.23 (dd, 1H, *J* = 12.2 and 2.4 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.14 (d, 1H, *J* = 12.2 Hz, PhCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 3.87 (s, 3H, Ar-OCH<sub>3</sub>), 3.82 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 152.7 (s, Ar-C), 150.8 (s, Ar-C), 143.0 (s, Ar-C), 140.6 (s, Ar-C), 139.1 (s, Ar-C), 131.9 (s, Ar-C), 131.2 (d, Ar-CH-CH=CH-Ar), 130.9 (d, Ar-CH-CH=CH-Ar), 127.8 (d, Ar-CH), 127.5 (d, Ar-CH), 122.1 (d, Ar-CH), 121.1 (d, Ar-CH), 110.8 (s, Ar-C), 105.6 (d, Ar-CH), 85.1 (d, Ph-CHCH=CH), 72.9 (t, Ph-CH<sub>2</sub>OCHCH=CH), 61.1 (q, Ar-OCH<sub>3</sub>), 61.0 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>19</sub>H<sub>18</sub>BrO<sub>3</sub>]<sup>+</sup> = [(M + H)–H<sub>2</sub>O]<sup>+</sup>: 373.0434; found 373.0416 and [C<sub>19</sub>H<sub>18</sub><sup>81</sup>BrO<sub>3</sub>]<sup>+</sup> = [(M + H)–H<sub>2</sub>O]<sup>+</sup>: 375.0413; found 375.0401.

5-(Benzyloxy)-1-[(*E*)-2-[5-(benzyloxy)-2-bromo-4-methoxy phenyl]vinyl]-1,3-dihydro-2-benzofuran (**6bd**). GP-2 was carried out and the product **6bd** (111 mg, 41%) was furnished as a yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10, R<sub>f</sub>(**1b**) = 0.70, R<sub>f</sub>(**2d**) = 0.30 and R<sub>f</sub>(**6bd**) = 0.50 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>): ν<sub>max</sub> = 2956, 2922, 2852, 1600, 1500, 1455, 1383, 1260, 1166, 1025, 737, 697 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.50–7.25 (m, 10H, Ar-H), 7.11 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.06 (s, 1H, Ar-H), 7.05 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.00 (d, 1H, *J* = 15.6 Hz, ArCH=CH), 6.92 (d, 1H, *J* = 7.8 Hz, Ar-H), 6.87 (s, 1H, Ar-H), 6.10 (dd, 1H, *J* = 15.6 and 7.8 Hz, ArCH=CH), 5.75 [d, 1H, *J* = 7.8 Hz, ArCH(O)CH=CH], 5.18 (dd, 1H, *J* = 12.7 and 2.0 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.12 (d, 1H, *J* = 12.7 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10 (s, 2H, PhCH<sub>2</sub>O), 5.08 (s, 2H, PhCH<sub>2</sub>O), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 159.1 (s, Ar-C), 149.1 (s, Ar-C), 148.6 (s, Ar-C), 140.9 (s, Ar-C), 136.8 (s, Ar-C), 136.2 (s, Ar-C), 133.0 (s, Ar-C), 130.4 (d, Ar-CH-CH=CH-Ar), 130.3 (d, Ar-CH-CH=CH-Ar), 128.8 (s, Ar-C), 128.6 (d, 3C, Ar-CH), 128.1 (d, Ar-CH), 128.0 (d, Ar-CH), 127.4 (d, 5C, Ar-CH), 122.9 (d, Ar-CH), 117.6 (d, Ar-CH), 114.6 (d, Ar-CH), 114.3 (s, Ar-C), 109.6 (d, Ar-CH), 107.3 (d, Ar-CH), 84.9 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 71.1 (t, PhCH<sub>2</sub>O), 70.3 (t, PhCH<sub>2</sub>O), 56.0 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>31</sub>H<sub>28</sub>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 543.1165; found 543.1140 and [C<sub>31</sub>H<sub>28</sub><sup>81</sup>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 545.1145; found 545.1130, [C<sub>31</sub>H<sub>27</sub>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 565.0985; found 565.0959 and [C<sub>31</sub>H<sub>27</sub><sup>81</sup>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 567.0964; found 567.0977.

5-(Benzyloxy)-1-[(*E*)-2-[4-(benzyloxy)-2-bromo-5-methoxy phenyl]vinyl]-1,3-dihydro-2-benzofuran (**6be**). GP-2 was carried out and the product **6be** (119 mg, 44%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10, R<sub>f</sub>(**1b**) = 0.70, R<sub>f</sub>(**2e**) = 0.30 and R<sub>f</sub>(**6be**) = 0.55 UV

detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>): ν<sub>max</sub> = 2923, 2852, 1600, 1502, 1455, 1439, 1380, 1259, 1163, 1026, 737, 697 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.50–7.20 (m, 10H, Ar-H), 7.09 (s, 1H, Ar-H), 7.05 (d, 1H, *J* = 7.8 Hz, Ar-H), 7.03 (s, 1H, Ar-H), 6.98 (d, 1H, *J* = 15.6 Hz, ArCH=CH), 6.91 (dd, 1H, *J* = 8.3 and 2.0 Hz, Ar-H), 6.86 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.09 (dd, 1H, *J* = 15.6 and 7.8 Hz, ArCH=CH), 5.74 [d, 1H, *J* = 7.8 Hz, ArCH(O)CH=CH], 5.17 (dd, 1H, *J* = 12.2 and 2.0 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10 (d, 1H, *J* = 12.2 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.07 (s, 2H, PhCH<sub>2</sub>O), 5.07 (s, 2H, PhCH<sub>2</sub>O), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 159.1 (s, Ar-C), 150.2 (s, Ar-C), 148.6 (s, Ar-C), 140.9 (s, Ar-C), 136.8 (s, Ar-C), 136.2 (s, Ar-C), 133.1 (s, Ar-C), 130.5 (d, Ar-CH-CH=CH-Ar), 130.2 (d, Ar-CH-CH=CH-Ar), 128.7 (d, 2C, Ar-CH), 128.6 (d, 2C, Ar-CH), 128.1 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 127.4 (d, 2C, Ar-CH), 127.4 (d, 2C, Ar-CH), 122.9 (d, Ar-CH), 117.5 (d, Ar-CH), 114.6 (s, Ar-C), 114.4 (d, Ar-CH), 109.5 (d, Ar-CH), 107.3 (d, Ar-CH), 84.8 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 71.1 (t, PhCH<sub>2</sub>O), 70.3 (t, PhCH<sub>2</sub>O), 56.1 (s, 3H, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>31</sub>H<sub>28</sub>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 543.1165; found 543.1142 and [C<sub>31</sub>H<sub>28</sub><sup>81</sup>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 545.1145; found 545.1126, [C<sub>31</sub>H<sub>27</sub>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 565.0985; found 565.0962 and [C<sub>31</sub>H<sub>27</sub><sup>81</sup>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 567.0964; found 567.0987.

5-(Benzyloxy)-1-[(*E*)-2-(2-bromo-4,5-dimethoxyphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6bg**). GP-2 was carried out and the product **6bg** (108 mg, 47%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10, R<sub>f</sub>(**1b**) = 0.70, R<sub>f</sub>(**2g**) = 0.15 and R<sub>f</sub>(**6bg**) = 0.40 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>): ν<sub>max</sub> = 2922, 2851, 1600, 1503, 1462, 1439, 1259, 1162, 1027, 801, 737, 697 cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.42 (dd, 2H, *J* = 8.3 and 1.5 Hz, Ar-H), 7.38 (ddd, 2H, *J* = 8.3, 5.8 and 1.5 Hz, Ar-H), 7.33 (ddd, 1H, *J* = 8.3, 5.8 and 1.5 Hz, Ar-H), 7.11 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.02 (d, 1H, *J* = 15.6 Hz, ArCH=CH), 7.01 (s, 1H, Ar-H), 7.00 (s, 1H, Ar-H), 5.91 (dd, 1H, *J* = 8.3 and 2.4 Hz, Ar-H), 6.86 (d, 1H, *J* = 2.0 Hz, Ar-H), 6.09 (dd, 1H, *J* = 15.6 and 7.8 Hz, ArCH=CH), 5.75 [d, 1H, *J* = 7.8 Hz, ArCH(O)CH=CH], 5.18 (dd, 1H, *J* = 12.2 and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.09 (d, 1H, *J* = 12.2 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.07 (s, 2H, PhCH<sub>2</sub>O), 3.86 (s, 3H, Ar-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 159.1 (s, Ar-C), 149.4 (s, Ar-C), 148.5 (s, Ar-C), 140.9 (s, Ar-C), 136.8 (s, Ar-C), 133.1 (s, Ar-C), 130.4 (d, Ar-CH-CH=CH-Ar), 130.1 (d, Ar-CH-CH=CH-Ar), 128.5 (d, 2C, Ar-CH), 128.3 (s, Ar-C), 128.0 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 122.9 (d, Ar-CH), 115.2 (d, Ar-CH), 114.6 (d, Ar-CH), 114.5 (s, Ar-C), 109.1 (d, Ar-CH), 107.3 (d, Ar-CH), 84.9 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 70.3 (t, PhCH<sub>2</sub>O), 56.1 (q, Ar-OCH<sub>3</sub>), 55.9 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>25</sub>H<sub>24</sub>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 467.0852; found 467.0824 and [C<sub>25</sub>H<sub>24</sub><sup>81</sup>BrO<sub>4</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 469.0832; found 469.0817, [C<sub>25</sub>H<sub>23</sub>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 489.0672; found 489.0646 and [C<sub>25</sub>H<sub>23</sub><sup>81</sup>BrNaO<sub>4</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 491.0651; found 491.0649.

1-[(*E*)-2-(2-Bromophenyl)vinyl]-5-methoxy-1,3-dihydro-2-benzofuran (**6ca**). GP-2 was carried out and the product **6ca** (79 mg, 48%) was furnished as a yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10, R<sub>f</sub>(**1c**) = 0.70, R<sub>f</sub>(**2a**) = 0.40 and R<sub>f</sub>(**6ca**) = 0.50 UV detection)]. IR (MIR-ATR, 4000–600

$\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2956, 2924, 2854, 1610, 1493, 1466, 1275, 1117, 1025, 821, 748, 665 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.54$  (d, 1H,  $J = 7.8$  and 1.5 Hz, Ar-H), 7.51 (d, 1H,  $J = 7.8$  and 1.5 Hz, Ar-H), 7.22 (dd, 1H,  $J = 7.8$  and 1.5 Hz, Ar-H), 7.15–7.00 (m, 3H, Ar-H and ArCH=CH), 6.83 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 6.79 (d, 1H,  $J = 2.4$  Hz, Ar-H), 6.19 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.75 [d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH], 5.18 (dd, 1H,  $J = 12.2$  and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.09 (d, 1H,  $J = 12.2$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.81 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 160.0$  (s, Ar-C), 140.9 (s, Ar-C), 136.4 (s, Ar-C), 132.9 (d, Ar-CH), 132.7 (s, Ar-C), 132.4 (d, Ar-CH), 130.3 (d, Ar-CH-CH=CH-Ar), 129.0 (d, Ar-CH-CH=CH-Ar), 127.4 (d, Ar-CH), 127.3 (d, Ar-CH), 123.8 (s, Ar-C), 122.8 (d, Ar-CH), 113.7 (d, Ar-CH), 106.3 (d, Ar-CH), 84.7 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH<sub>2</sub>OCHCH=CH), 55.6 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{15}\text{BrNaO}_2]^+ = [\text{M} + \text{Na}]$ : 353.0148; found 353.0164.

*1-[(E)-2-(2-Bromo-5-methoxyphenyl)vinyl]-5-methoxy-1,3-dihydro-2-benzofuran (6cc)*. GP-2 was carried out and the product **6cc** (71 mg, 45%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(1c) = 0.70$ ,  $R_f(2c) = 0.50$  and  $R_f(6cc) = 0.60$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2957, 2922, 2852, 1594, 1465, 1284, 1241, 1016, 804 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.42$  (d, 1H,  $J = 8.8$  Hz, Ar-H),  $\delta = 7.10$  (d, 1H,  $J = 8.3$  Hz, Ar-H),  $\delta = 7.04$  (d, 1H,  $J = 3.3$  Hz, Ar-H), 7.02 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.83 (dd, 1H,  $J = 8.3$  and 1.9 Hz, Ar-H), 6.79 (d, 1H,  $J = 1.9$  Hz, Ar-H), 6.69 (dd, 1H,  $J = 8.8$  and 2.9 Hz, Ar-H), 6.18 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.75 [d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH], 5.19 (dd, 1H,  $J = 12.2$  and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10 (d, 1H,  $J = 12.2$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.81 (s, 3H, Ar-OCH<sub>3</sub>), 3.76 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 160.0$  (s, Ar-C), 158.9 (s, Ar-C), 140.9 (s, Ar-C), 137.1 (s, Ar-C), 133.5 (d, Ar-CH), 132.6 (s, Ar-C), 132.4 (d, Ar-CH-CH=CH-Ar), 130.5 (d, Ar-CH-CH=CH-Ar), 122.8 (d, Ar-CH), 115.7 (d, Ar-CH), 114.6 (s, Ar-C), 113.7 (d, Ar-CH), 112.0 (d, Ar-CH), 106.3 (d, Ar-CH), 84.7 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH<sub>2</sub>OCHCH=CH), 55.6 (s, Ar-OCH<sub>3</sub>), 55.5 (s, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ )  $m/z$  calculated for  $[\text{C}_{18}\text{H}_{16}\text{BrO}_2]^+ = [\text{M} + \text{Na}]$ : 343.0328; found 343.0314.

*1-[(E)-2-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]vinyl]-5-methoxy-1,3-dihydro-2-benzofuran (6cd)*. GP-2 was carried out and the product **6cd** (103 mg, 44%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(1c) = 0.70$ ,  $R_f(2d) = 0.30$  and  $R_f(6cd) = 0.40$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2924, 2853, 1597, 1497, 1465, 1261, 1201, 1166, 1117, 1029, 813, 743, 698 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.42$  (d, 2H,  $J = 7.3$  Hz, Ar-H), 7.37 (dd, 2H,  $J = 7.8$  and 7.3 Hz, Ar-H), 7.31 (t, 1H,  $J = 7.3$  Hz, Ar-H), 7.10 (d, 1H,  $J = 8.3$  Hz, Ar-H), 7.06 (s, 1H, Ar-H), 7.04 (s, 1H, Ar-H), 6.99 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.84 (dd, 1H,  $J = 8.3$  and 2.0 Hz, Ar-H), 6.79 (d, 1H,  $J = 2.0$  Hz, Ar-H), 6.10 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.75 [d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH], 5.19 (dd, 1H,  $J = 12.2$  and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10 (s, 2H, PhCH<sub>2</sub>O), 5.09 (d, 1H,  $J = 12.2$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.83 (s, 3H, Ar-OCH<sub>3</sub>), 3.81 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 159.9$  (s, Ar-C), 149.1 (s, Ar-C), 148.6 (s, Ar-C), 140.9 (s, Ar-C), 136.2 (s, Ar-C), 132.7 (s, Ar-

C), 130.4 (d, Ar-CH-CH=CH-Ar), 130.3 (d, Ar-CH-CH=CH-Ar), 128.8 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.1 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 122.9 (d, Ar-CH), 117.5 (d, Ar-CH), 114.3 (s, Ar-C), 113.7 (d, Ar-CH), 109.5 (d, Ar-CH), 106.2 (d, Ar-CH), 84.9 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 71.1 (t, PhCH<sub>2</sub>O), 56.1 (q, Ar-OCH<sub>3</sub>), 55.5 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ ):  $m/z$  calculated for  $[\text{C}_{25}\text{H}_{24}\text{BrO}_4]^+ = [\text{M} + \text{H}]^+$ : 467.0852; found 467.0826 and  $[\text{C}_{25}\text{H}_{24}^{81}\text{BrO}_4]^+ = [\text{M} + \text{H}]^+$ : 469.0832; found 469.0812.

*5-Bromo-6-[(E)-2-(5-methoxy-1,3-dihydro-2-benzofuran-1-yl)vinyl]-1,3-benzodioxole (6cf)*. GP-2 was carried out and the product **6cf** (80 mg, 43%) was furnished as a pale yellow liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(1c) = 0.70$ ,  $R_f(2f) = 0.50$  and  $R_f(6cf) = 0.55$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2921, 2852, 1605, 1500, 1474, 1235, 1106, 1036, 932, 870, 822 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.07$  (d, 1H,  $J = 8.3$  Hz, Ar-H), 6.99 (s, 2H, Ar-H), 6.98 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.82 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 6.77 (d, 1H,  $J = 2.4$  Hz, Ar-H), 6.04 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.94 (s, 2H, OCH<sub>2</sub>O), 5.72 [d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH], 5.17 (dd, 1H,  $J = 12.2$  and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.08 (d, 1H,  $J = 12.2$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.81 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 160.0$  (s, Ar-C), 148.1 (s, Ar-C), 147.6 (s, Ar-C), 140.8 (s, Ar-C), 132.7 (s, Ar-C), 130.6 (d, Ar-CH-CH=CH-Ar), 130.2 (d, Ar-CH-CH=CH-Ar), 129.7 (s, Ar-C), 122.7 (d, Ar-CH), 115.0 (s, Ar-C), 113.7 (d, Ar-CH), 112.6 (d, Ar-CH), 106.4 (d, Ar-CH), 106.2 (d, Ar-CH), 101.7 (t, OCH<sub>2</sub>O), 84.7 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 55.5 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ ):  $m/z$  calculated for  $[\text{C}_{18}\text{H}_{16}\text{BrO}_4]^+ = [\text{M} + \text{H}]^+$ : 375.0226; found 375.0212 and  $[\text{C}_{18}\text{H}_{16}^{81}\text{BrO}_4]^+ = [\text{M} + \text{H}]^+$ : 377.0206; found 377.0189.

*1-[(E)-2-(2-Bromo-3,4,5-trimethoxyphenyl)vinyl]-5-methoxy-1,3-dihydro-2-benzofuran (6ch)*. GP-2 was carried out and the product **6ch** (86 mg, 41%) was furnished as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 80 : 20,  $R_f(1c) = 0.95$ ,  $R_f(2h) = 0.25$  and  $R_f(6ch) = 0.45$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2923, 2852, 1563, 1481, 1463, 1427, 1392, 1326, 1274, 1200, 1165, 1107, 1031, 1011, 926, 813 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.08$  (d, 1H,  $J = 8.8$  Hz, Ar-H), 7.06 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.86 (s, 1H, Ar-H), 6.83 (dd, 1H,  $J = 8.3$  and 2.4 Hz, Ar-H), 6.78 (d, 1H,  $J = 2.4$  Hz, Ar-H), 6.10 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.75 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.18 (dd, 1H,  $J = 12.2$  and 2.4 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.09 (d, 1H,  $J = 12.2$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 3.87 (s, 3H, Ar-OCH<sub>3</sub>), 3.82 (s, 3H, Ar-OCH<sub>3</sub>), 3.80 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 160.0$  (s, Ar-C), 152.6 (s, Ar-C), 150.8 (s, Ar-C), 143.0 (s, Ar-C), 140.8 (s, Ar-C), 132.6 (s, Ar-C), 131.9 (s, Ar-C), 131.5 (d, Ar-CH-CH=CH-Ar), 130.6 (d, Ar-CH-CH=CH-Ar), 122.8 (d, Ar-CH), 113.7 (d, Ar-CH), 110.8 (s, Ar-C), 106.2 (d, Ar-CH), 105.6 (d, Ar-CH), 84.7 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH<sub>2</sub>OCHCH=CH), 61.1 (q, Ar-OCH<sub>3</sub>), 60.9 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 55.5 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS ( $\text{ESI}^+$ ):  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{21}\text{BrNaO}_5]^+ = [\text{M} + \text{Na}]^+$ : 443.0465; found 443.0448.

*5-[(E)-2-[5-(Benzyloxy)-2-bromophenyl]vinyl]-5,7-dihydrofuro[3,4-ff][1,3]benzodioxole (6fb)*. GP-2 was carried out and the product **6fb**

(92 mg, 41%) was furnished as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90 : 10,  $R_f(\mathbf{1f}) = 0.30$ ,  $R_f(\mathbf{2b}) = 0.45$  and  $R_f(\mathbf{6fb}) = 0.40$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2920, 2851, 1591, 1501, 1464, 1378, 1278, 1239, 1173, 1122, 1039, 939, 851, 737, 698 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.50\text{--}7.27$  (m, 6H, Ar-H), 7.14 (d, 1H,  $J = 2.9$  Hz, Ar-H), 7.01 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.76 (dd, 1H,  $J = 8.8$  and 2.9 Hz, Ar-H), 6.68 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.14 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.97 (d, 1H,  $J = 2.9$  Hz,  $\text{OCH}_a\text{H}_b\text{O}$ ), 5.97 (d, 1H,  $J = 2.9$  Hz,  $\text{OCH}_a\text{H}_b\text{O}$ ), 5.70 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.12 (dd, 1H,  $J = 11.7$  and 2.9 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.04 (d, 1H,  $J = 11.7$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.01 (s, 2H, PhCH<sub>2</sub>O) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 158.1$  (s, Ar-C), 148.0 (s, Ar-C), 147.7 (s, Ar-C), 137.1 (s, Ar-C), 136.4 (s, Ar-C), 133.5 (d, Ar-CH-CH=CH-Ar), 133.4 (s, Ar-C), 132.3 (d, Ar-CH-CH=CH-Ar), 131.9 (s, Ar-C), 130.5 (d, Ar-CH), 128.6 (d, 2C, Ar-CH), 128.1 (d, Ar-CH), 127.4 (d, 2C, Ar-CH), 116.3 (d, Ar-CH), 114.8 (s, Ar-C), 113.3 (d, Ar-CH), 102.6 (d, Ar-CH), 101.6 (d, Ar-CH), 101.5 (t, OCH<sub>2</sub>O), 84.9 (d, Ar-CHCH=CH), 72.9 (t, Ar-CH<sub>2</sub>OCHCH=CH), 70.2 (t, PhCH<sub>2</sub>O) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{24}\text{H}_{19}\text{BrNaO}_4]^+ = [\text{M} + \text{Na}]^+$ : 473.0359; found 473.0330 and  $[\text{C}_{24}\text{H}_{19}^{81}\text{BrNaO}_4]^+ = [\text{M} + \text{Na}]^+$ : 475.0338; found 475.0317.

5- $\{[E]\text{-}2\text{-}[4\text{-}(\text{Benzyloxy})\text{-}2\text{-bromo-5-methoxyphenyl}]\text{vinyl}\}\text{-}5,7\text{-dihydrofuro}[3,4\text{-}f][1,3]\text{benzodioxole}$  (**6fe**). GP-2 was carried out and the product **6fe** (113 mg, 47%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80 : 20,  $R_f(\mathbf{1f}) = 0.70$ ,  $R_f(\mathbf{2e}) = 0.30$  and  $R_f(\mathbf{6fe}) = 0.50$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2956, 2924, 2853, 1598, 1502, 1439, 1259, 1162, 1033, 852, 803, 735, 698 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.41$  (d, 2H,  $J = 7.3$  Hz, Ar-H), 7.34 (dd, 2H,  $J = 7.8$  and 7.3 Hz, Ar-H), 7.30 (t, 1H,  $J = 7.3$  Hz, Ar-H), 7.07 (s, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 6.95 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.68 (s, 1H, Ar-H), 6.60 (s, 1H, Ar-H), 6.96 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.97 (s, 2H, OCH<sub>2</sub>O), 5.67 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.11 (dd, 1H,  $J = 11.7$  and 2.9 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.07 (s, 2H, PhCH<sub>2</sub>O), 5.02 (dd, 1H,  $J = 11.7$  and 2.9 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.85 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 150.2$  (s, Ar-C), 148.0 (s, Ar-C), 147.6 (s, 2C, Ar-C), 136.5 (s, Ar-C), 133.6 (s, Ar-C), 131.9 (s, Ar-C), 130.5 (d, Ar-CH-CH=CH-Ar), 130.0 (d, Ar-CH-CH=CH-Ar), 128.5 (d, 2C, Ar-CH), 128.3 (s, Ar-C), 128.0 (d, Ar-CH), 127.5 (d, 2C, Ar-CH), 115.7 (d, Ar-CH), 115.1 (s, Ar-C), 112.1 (d, Ar-CH), 102.6 (d, Ar-CH), 101.6 (d, Ar-CH), 101.5 (t, OCH<sub>2</sub>O), 85.1 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH<sub>2</sub>OCHCH=CH), 71.2 (t, PhCH<sub>2</sub>O), 56.2 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{25}\text{H}_{22}\text{BrO}_5]^+ = [\text{M} + \text{H}]^+$ : 481.0645; found 481.0615 and  $[\text{C}_{25}\text{H}_{22}^{81}\text{BrO}_5]^+ = [\text{M} + \text{H}]^+$ : 483.0625; found 483.0602,  $[\text{C}_{25}\text{H}_{21}\text{BrNaO}_5]^+ = [\text{M} + \text{Na}]^+$ : 503.0465; found 503.0438 and  $[\text{C}_{25}\text{H}_{21}\text{Br}^{81}\text{NaO}_5]^+ = [\text{M} + \text{Na}]^+$ : 505.0444; found 505.0422.

5- $\{[E]\text{-}2\text{-}(2\text{-Bromo-4,5-dimethoxyphenyl}]\text{vinyl}\}\text{-}5,7\text{-dihydrofuro}[3,4\text{-}f][1,3]\text{benzodioxole}$  (**6fg**). GP-2 was carried out and the product **6fg** (85 mg, 42%) was furnished as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 80 : 20,  $R_f(\mathbf{1f}) = 0.70$ ,  $R_f(\mathbf{2g}) = 0.30$  and  $R_f(\mathbf{6fg}) = 0.55$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2924, 2852, 1600, 1503, 1473,$

1380, 1261, 1208, 1163, 1035, 937, 860, 736, 698, 665  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.00$  (s, 2H, Ar-H), 6.98 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.67 (s, 1H, Ar-H), 6.63 (s, 1H, Ar-H), 6.06 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.97 (d, 1H,  $J = 2.9$  Hz, OCH<sub>a</sub>H<sub>b</sub>O), 5.96 (d, 1H,  $J = 2.9$  Hz, OCH<sub>a</sub>H<sub>b</sub>O), 5.69 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.11 (dd, 1H,  $J = 11.7$  and 2.0 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.02 (dd, 1H,  $J = 11.7$  and 2.0 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.86 (s, 3H, Ar-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 149.5$  (s, Ar-C), 148.5 (s, Ar-C), 148.0 (s, Ar-C), 147.7 (s, Ar-C), 133.6 (s, Ar-C), 131.9 (s, Ar-C), 130.7 (d, Ar-CH-CH=CH-Ar), 130.0 (d, Ar-CH-CH=CH-Ar), 128.2 (s, Ar-C), 115.3 (d, Ar-CH), 114.6 (s, Ar-C), 109.1 (d, Ar-CH), 102.7 (d, Ar-CH), 101.6 (d, Ar-CH), 101.5 (t, OCH<sub>2</sub>O), 85.2 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH<sub>2</sub>OCHCH=CH), 56.1 (q, Ar-OCH<sub>3</sub>), 56.0 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{19}\text{H}_{17}\text{BrNaO}_5]^+ = [\text{M} + \text{Na}]^+$ : 427.0152; found 427.0127 and  $[\text{C}_{19}\text{H}_{17}^{81}\text{BrNaO}_5]^+ = [\text{M} + \text{Na}]^+$ : 429.0137; found 429.0121, HR-MS (ESI<sup>+</sup>)  $m/z$  calculated for  $[\text{C}_{19}\text{H}_{18}\text{BrO}_5]^+ = [\text{M} + \text{H}]^+$ : 405.0332; found 405.0304 and  $[\text{C}_{19}\text{H}_{18}^{81}\text{BrO}_5]^+ = [\text{M} + \text{H}]^+$ : 407.0312; found 407.0294.

5- $\{[E]\text{-}2\text{-}(2\text{-Bromo-3,4,5-trimethoxyphenyl}]\text{vinyl}\}\text{-}5,7\text{-dihydro furo}[3,4\text{-}f][1,3]\text{benzodioxole}$  (**6fh**). GP-2 was carried out and the product **6fh** (98 mg, 45%) was furnished as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80 : 20,  $R_f(\mathbf{1f}) = 0.70$ ,  $R_f(\mathbf{2h}) = 0.20$  and  $R_f(\mathbf{6fh}) = 0.40$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2928, 2854, 1566, 1503, 1482, 1394, 1329, 1264, 1198, 1164, 1107, 1037, 1010, 934, 814, 739 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.05$  (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.86 (s, 1H, Ar-H), 6.68 (s, 1H, Ar-H), 6.64 (s, 1H, Ar-H), 6.07 (dd, 1H,  $J = 15.6$  and 7.8 Hz, ArCH=CH), 5.96 (d, 1H,  $J = 2.9$  Hz, OCH<sub>a</sub>H<sub>b</sub>O), 5.95 (d, 1H,  $J = 2.9$  Hz, OCH<sub>a</sub>H<sub>b</sub>O), 5.69 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.11 (dd, 1H,  $J = 11.7$  and 2.9 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.03 (dd, 1H,  $J = 11.7$  and 2.9 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 3.87 (s, 3H, Ar-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm.  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 152.6$  (s, Ar-C), 150.8 (s, Ar-C), 148.0 (s, Ar-C), 147.7 (s, Ar-C), 143.0 (s, Ar-C), 133.4 (s, Ar-C), 131.9 (s, Ar-C), 131.8 (s, Ar-C), 131.3 (d, Ar-CH-CH=CH-Ar), 130.8 (d, Ar-CH-CH=CH-Ar), 110.8 (s, Ar-C), 105.6 (d, Ar-CH), 102.6 (d, Ar-CH), 101.6 (d, Ar-CH), 101.5 (t, OCH<sub>2</sub>O), 85.0 (d, Ar-CHCH=CH), 72.9 (t, Ar-CH<sub>2</sub>OCHCH=CH), 61.1 (q, Ar-OCH<sub>3</sub>), 60.9 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{19}\text{BrNaO}_6]^+ = [\text{M} + \text{Na}]^+$ : 457.0257; found 457.0257 and  $[\text{C}_{20}\text{H}_{19}^{81}\text{BrNaO}_6]^+ = [\text{M} + \text{Na}]^+$ : 459.0237; found 459.0236.

1- $\{[E]\text{-}2\text{-}[5\text{-}(\text{Benzyloxy})\text{-}2\text{-bromo-4-methoxyphenyl}]\text{vinyl}\}\text{-}5,6\text{-dimethoxy-1,3-dihydro-2-benzofuran}$  (**6gd**). GP-2 was carried out and the product **6gd** (116 mg, 47%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 70 : 30,  $R_f(\mathbf{1g}) = 0.65$ ,  $R_f(\mathbf{2d}) = 0.55$  and  $R_f(\mathbf{6gd}) = 0.40$  UV detection)]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2926, 2853, 1598, 1503, 1463, 1384, 1261, 1203, 1166, 1032, 859, 737, 698 \text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.41$  (d, 2H,  $J = 7.3$  Hz, Ar-H), 7.36 (dd, 2H,  $J = 7.8$  and 7.3 Hz, Ar-H), 7.31 (t, 1H,  $J = 7.3$  Hz, Ar-H), 7.05 (s, 2H, Ar-H), 7.00 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.77 (s, 1H, Ar-H), 6.69 (s, 1H, Ar-H), 6.10 (dd, 1H,  $J = 15.6$  and 8.3 Hz, ArCH=CH), 5.75 (d, 1H,  $J = 8.3$  Hz, ArCH(O)CH=CH), 5.18 (dd, 1H,  $J = 11.7$  and 2.0 Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.10

(s, 2H, PhCH<sub>2</sub>O), 5.07 (dd, 1H,  $J = 11.2$  and  $2.9$  Hz, ArCH<sub>a</sub>H<sub>b</sub>-OCHCH=CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 3.86 (s, 3H, Ar-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 149.3$  (s, Ar-C), 149.1 (s, Ar-C), 149.0 (s, Ar-C), 148.6 (s, Ar-C), 136.2 (s, Ar-C), 132.1 (s, Ar-C), 130.6 (s, Ar-C), 130.6 (d, Ar-CH-CH=CH-Ar), 130.2 (d, Ar-CH-CH=CH-Ar), 128.7 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.1 (d, Ar-CH), 127.3 (d, 2C, Ar-CH), 117.5 (d, Ar-CH), 114.4 (s, Ar-C), 109.5 (d, Ar-CH), 104.9 (d, Ar-CH), 103.9 (d, Ar-CH), 85.6 (d, Ar-CHCH=CH), 73.0 (t, Ar-CH<sub>2</sub>OCHCH=CH), 71.1 (t, PhCH<sub>2</sub>O), 56.2 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 56.0 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>26</sub>H<sub>25</sub>-BrNaO<sub>5</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 519.0778; found 519.0753 and [C<sub>26</sub>H<sub>25</sub><sup>81</sup>BrNaO<sub>5</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 521.0757; found 521.0735.

1-[(E)-2-(2-Bromo-4,5-dimethoxyphenyl)vinyl]-5,6-dimethoxy-1,3-dihydro-2-benzofuran (**6gg**). **GP-2** was carried out and the product **6gg** (90 mg, 43%) was furnished as a brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 70 : 30,  $R_f$ (**1g**) = 0.65,  $R_f$ (**2g**) = 0.45 and  $R_f$ (**6gg**) = 0.35 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max} = 2924, 2852, 1600, 1504, 1462, 1264, 1210, 1163, 1121, 1029, 863$  cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.02$  (s, 1H, Ar-H), 7.01 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 7.00 (s, 1H, Ar-H), 6.77 (s, 1H, Ar-H), 6.69 (s, 1H, Ar-H), 6.09 (dd, 1H,  $J = 15.6$  and  $7.8$  Hz, ArCH=CH), 5.74 (d, 1H,  $J = 7.8$  Hz, ArCH(O)CH=CH), 5.17 (dd, 1H,  $J = 11.2$  and  $2.9$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 5.07 (dd, 1H,  $J = 11.2$  and  $2.9$  Hz, ArCH<sub>a</sub>H<sub>b</sub>OCHCH=CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 3.86 (s, 6H, Ar-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 149.5$  (s, Ar-C), 149.4 (s, Ar-C), 149.1 (s, Ar-C), 148.5 (s, Ar-C), 132.2 (s, Ar-C), 130.7 (s, Ar-C), 130.6 (d, Ar-CH-CH=CH-Ar), 130.1 (d, Ar-CH-CH=CH-Ar), 128.3 (s, Ar-C), 115.3 (d, Ar-CH), 114.6 (s, Ar-C), 109.1 (d, Ar-CH), 105.0 (d, Ar-CH), 104.0 (d, Ar-CH), 85.6 (d, Ar-CHCH=CH), 73.0 (t, Ar-CH<sub>2</sub>OCHCH=CH), 56.2 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 56.0 (q, Ar-OCH<sub>3</sub>), 55.9 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>20</sub>H<sub>21</sub>BrNaO<sub>5</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 443.0465; found 443.0468.

(2E)-3-[2-(Hydroxymethyl)phenyl]-1-(2-methylphenyl)prop-2-en-1-ol (**5ai**). **GP-3** was carried out and the product **5ai** (65 mg, 97%) was furnished as a yellow colored viscous liquid. [TLC control (petroleum ether/ethyl acetate 70 : 30,  $R_f$ (**3ai**) = 0.70,  $R_f$ (**5ai**) = 0.30 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max} = 3330, 1485, 1459, 1006, 967, 753, 564$  cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.52$ –7.46 (m, 1H, Ar-H), 7.44 (d, 1H,  $J = 7.8$  Hz, Ar-H), 7.32–7.10 (m, 6H, Ar-H), 6.98 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.21 (dd, 1H,  $J = 15.6$  and  $5.9$  Hz, ArCH=CH), 5.47 [d, 1H,  $J = 5.9$  Hz, PhCH(OH)CH=CH], 4.63 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OH), 4.62 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OH), 3.76 (br.s, 1H, OH), 3.29 (br.s, 1H, OH), 2.35 (s, 3H, Ar-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 140.4$  (s, Ar-C), 137.5 (s, Ar-C), 135.8 (s, Ar-C), 135.2 (s, Ar-C), 133.2 (d, Ar-CH-CH=CH-Ar), 130.4 (d, Ar-CH), 128.7 (d, Ar-CH-CH=CH-Ar), 128.1 (d, Ar-CH), 127.6 (d, Ar-CH), 127.5 (d, Ar-CH), 126.9 (d, Ar-CH), 126.2 (2 × d, 2C, Ar-CH), 125.9 (d, Ar-CH), 71.4 (d, Ph-CHCH=CH), 63.1 (t, Ph-CH<sub>2</sub>OH), 19.1 (q, Ar-CH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>17</sub>H<sub>18</sub>NaO<sub>2</sub>]<sup>+</sup> = [M + Na]<sup>+</sup>: 277.1199; found 277.1197.

(2E)-3-[2-(Hydroxymethyl)phenyl]-1-(2-methoxyphenyl)prop-2-en-1-ol (**5aj**). **GP-3** was carried out and the product **5aj** (67 mg, 96%) was furnished as a colorless viscous liquid. [TLC control

(petroleum ether/ethyl acetate 70 : 30,  $R_f$ (**3aj**) = 0.80,  $R_f$ (**5aj**) = 0.30 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max} = 3320, 1597, 1489, 1461, 1244, 1023, 753$  cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.39$  (ddd, 2H,  $J = 8.8, 7.8$  and  $1.5$  Hz, Ar-H), 7.32–7.10 (m, 4H, Ar-H), 6.99 (d, 1H,  $J = 16.1$  Hz, ArCH=CH), 6.87 (dd, 1H,  $J = 7.8$  and  $7.3$  Hz, Ar-H), 6.82 (d, 1H,  $J = 8.3$  Hz, Ar-H), 6.43 (dd, 1H,  $J = 16.1$  and  $5.9$  Hz, ArCH=CH), 5.52 [d, 1H,  $J = 5.9$  Hz, PhCH(OH)CH=CH], 4.66 (s, 2H, ArCH<sub>2</sub>OH), 3.77 (s, 3H, Ar-OCH<sub>3</sub>), 3.64 (br.s, 2H, 2 × OH) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 156.7$  (s, Ar-C), 141.1 (s, Ar-C), 138.5 (s, Ar-C), 131.0 (d, Ar-CH-CH=CH-Ar), 130.0 (d, Ar-CH), 128.8 (d, Ar-CH-CH=CH-Ar), 128.3 (d, Ar-CH), 128.1 (d, Ar-CH), 127.8 (d, Ar-CH), 127.0 (d, Ar-CH), 125.5 (s, Ar-C), 125.4 (d, Ar-CH), 120.6 (d, Ar-CH), 110.8 (d, Ar-CH), 73.2 (d, Ph-CHCH=CH), 63.5 (t, Ph-CH<sub>2</sub>OH), 55.4 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 271.1329; found 271.1320.

1-[(E)-2-(2-Methylphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6ai**). **GP-3** was carried out and the product **6ai** (50 mg, 84%) was furnished as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95 : 5,  $R_f$ (**5ai**) = 0.15,  $R_f$ (**6ai**) = 0.80 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max} = 2924, 2853, 1731, 1460, 1029, 965, 747, 697$  cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.45$  (d, 1H,  $J = 8.3$  Hz, Ar-H), 7.36–7.25 (m, 3H, Ar-H), 7.24–7.10 (m, 4H, Ar-H), 6.97 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.16 (dd, 1H,  $J = 15.6$  and  $7.8$  Hz, ArCH=CH), 5.79 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.23 (dd, 1H,  $J = 12.2$  and  $2.4$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OCHCH=CH), 5.14 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OCHCH=CH), 2.39 (s, 3H, Ar-CH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 141.0$  (s, Ar-C), 139.2 (s, Ar-C), 135.7 (s, Ar-C), 135.5 (s, Ar-C), 130.3 (2 × d, 2C, Ar-CH-CH=CH-Ar and Ar-CH), 129.9 (d, Ar-CH), 127.7 (2 × d, 2C, Ar-CH-CH=CH-Ar and Ar-CH), 127.4 (d, Ar-CH), 126.0 (d, Ar-CH), 125.9 (d, Ar-CH), 122.0 (d, Ar-CH), 121.1 (d, Ar-CH), 85.5 (d, Ph-CHCH=CH), 72.8 (t, Ph-CH<sub>2</sub>-OCHCH=CH), 19.9 (q, Ar-CH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>17</sub>H<sub>16</sub>NaO]<sup>+</sup> = [M + Na]<sup>+</sup>: 259.1093; found 259.1099.

1-[(E)-2-(2-Methoxyphenyl)vinyl]-1,3-dihydro-2-benzofuran (**6aj**). **GP-3** was carried out and the product **6aj** (53 mg, 86%) was furnished as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95 : 5,  $R_f$ (**5aj**) = 0.10,  $R_f$ (**6aj**) = 0.70 UV detection)]. IR (MIR-ATR, 4000–600 cm<sup>-1</sup>):  $\nu_{\max} = 2904, 2838, 1489, 1461, 1244, 1028, 749, 697$  cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 7.45$  (dd, 1H,  $J = 7.8$  and  $1.5$  Hz, Ar-H), 7.36–7.15 (m, 5H, Ar-H), 7.09 (d, 1H,  $J = 15.6$  Hz, ArCH=CH), 6.91 (d, 1H,  $J = 7.3$  Hz, Ar-H), 6.87 (d, 1H,  $J = 7.3$  Hz, Ar-H), 6.30 (dd, 1H,  $J = 15.6$  and  $7.8$  Hz, ArCH=CH), 5.78 [d, 1H,  $J = 7.8$  Hz, PhCH(O)CH=CH], 5.23 (dd, 1H,  $J = 12.2$  and  $2.4$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OCHCH=CH), 5.13 (d, 1H,  $J = 12.2$  Hz, PhCH<sub>a</sub>-H<sub>b</sub>OCHCH=CH), 3.86 (s, 3H, Ar-OCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 156.9$  (s, Ar-C), 141.2 (s, Ar-C), 139.2 (s, Ar-C), 129.4 (d, Ar-CH-CH=CH-Ar), 128.9 (d, Ar-CH), 127.6 (d, Ar-CH-CH=CH-Ar), 127.4 (d, Ar-CH), 127.1 (d, Ar-CH), 127.0 (d, Ar-CH), 125.4 (s, Ar-C), 122.1 (d, Ar-CH), 121.0 (d, Ar-CH), 120.5 (d, Ar-CH), 110.8 (d, Ar-CH), 85.9 (d, Ph-CHCH=CH), 72.7 (t, Ph-CH<sub>2</sub>OCHCH=CH), 55.4 (q, Ar-OCH<sub>3</sub>) ppm. HR-MS (ESI<sup>+</sup>):  $m/z$  calculated for [C<sub>17</sub>H<sub>17</sub>O<sub>2</sub>]<sup>+</sup> = [M + H]<sup>+</sup>: 253.1223; found 253.1219.

## Conclusions

In summary, we have developed an efficient and practical method for the direct synthesis of 1,3-dihydroisobenzofurans, an important structural motif present in biologically active natural or synthetic compounds. [Pd]-catalyzed controlled intermolecular Mizoroki–Heck coupling and reduction were performed sequentially. The direct treatment of the resultant crude diol without further purification with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  gave 1,3-dihydroisobenzofurans. Significantly, the method enabled the synthesis of 1,3-dihydroisobenzofurans with simple to electron rich aromatic rings. Importantly, the protocol is also applicable for a wide range of *ortho* substituted allylic alcohols. It is worth mentioning that although the yields of the cyclic ether 1,3-dihydroisobenzofurans are moderate, it actually represents the overall yield of three individual reactions.

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