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ARTICLE

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 unnatural 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 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.

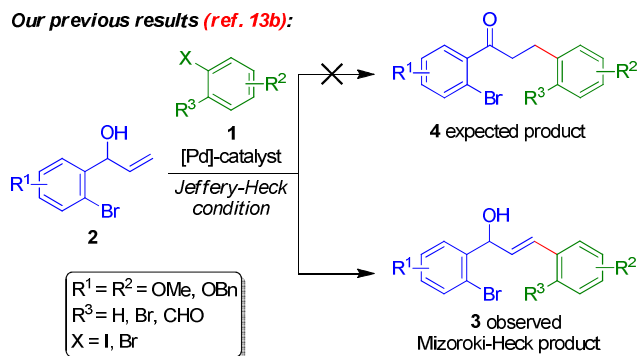
Introduction

Development of new synthetic methods based on one-pot or sequential one-pot are considered as important methods for the synthesis of organic compounds.¹ Particularly, the sequential one-pot processes involve in multiple reactions promoted by a metal-catalyst in a sequential fashion.² On the other hand, such transformations could also be feasible via sequential addition of reagents to accomplish a set of reactions.³ On the other hand, 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.⁴ These sort of processes can be classified into pseudo-domino, cascade⁵ and tandem-processes. Usually, the one-pot methods have certain advantages over conventional methods. For example, they reduce the waste formation save time, energy, resources and increase the efficacy.⁶ 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. Since many cyclic systems constitute core or part-structures of biologically active natural or unnatural compounds.

Recently, transition-metal mediated one-pot processes have gained much attention due their procedural advantages.^{7,8} Among them, the domino Heck reactions under [Pd]-catalysis are well known.⁹⁻¹¹ While the reports on Heck coupling followed by reduction are limited.¹² In continuation of our interest in the development of synthetic methods by [Pd]-catalysis,¹³ we have observed the selective formation of β -aryl

allylic alcohols **3** in a highly regio- and stereoselective manner.^{13b} 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.¹⁴ 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.

Our previous results (ref. 13b):



Scheme 1. Synthesis of β -aryl allylic alcohols **3**

Amongst the β -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., $R^3 = \text{CHO}$ and $X = \text{Br}$). Therefore, herein, we report a short and efficient synthesis of interesting cyclic ethers 1,3-dihydroisobenzofurans **6** by

employing reduction and acid mediated intramolecular cyclization protocol on β -aryl allylic alcohols 3.

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

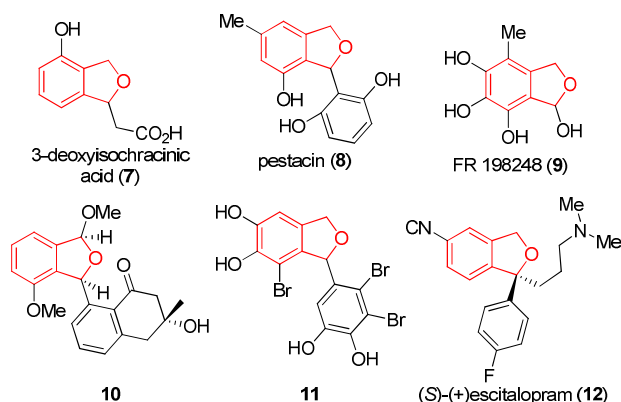
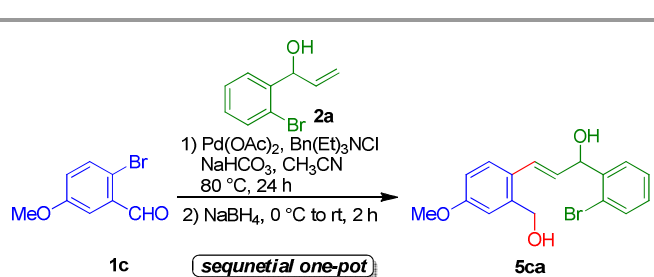


Figure 1: Representative examples of naturally occurring phthalans.

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 β -aryl allylic alcohols **3** and in-situ reduction of the aldehyde functionality. Thus, the [Pd]-catalyzed coupling of 2-bromobenzaldehyde **1c** with the *ortho*-bromo aryl allylic alcohol **1a** followed by reduction of **3ca** with NaBH₄ gave the desired diol **5ca** in very good yield (Scheme 2). The idea behind this hypothesis is to minimize the number of steps, to minimize 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 CDCl₃ and hence, proceeded to the next reaction.



Scheme 2: Synthesis of diol 5.

With the required diol **5ca** in hand, next, the acid promoted cyclization was explored under different sets of conditions and the results are summarized in the Table 1. Thus, the reaction carried out with the Lewis acid (BF₃·Et₂O) at 0 °C and as well as at –10 °C lead to the decomposition of the starting material (Table 1, entries 1 and 2). Therefore, the reaction at 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). On the other hand, exploring the reaction with different acids such as protic acid (*p*-TSA) or Lewis acid (AlCl₃), furnished the product **6ca** in moderate to very good yield (Table 1, entries 5-7), whereas the reaction with H₂SO₄, gave the product in poor yield (20%, Table 1, entries 8).

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

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

^aReaction conditions: All the reactions carried out with diol **5ca** (0.10 mmol) in DCM. ^bIsolated yields of chromatographically pure products.

Having established the reaction conditions for the synthesis of 1,3-dihydroisobenzofuran **6**, we thought that the method can be made still 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., on the crude diol which was obtained the after work-up followed by concentrated under reduced pressure) and furnished the product in 48% overall yield (Scheme 3). The structure of the cyclic ether **6ca** was confirmed from the spectroscopic data. ¹H-NMR data unambiguously confirmed the geometry of the double bond as *trans* one by calculating the coupling constant ($J = 15.5$ to 15.6 Hz, see; experimental section and supporting information). Therefore, the other possibility for the formation of seven membered cyclic ether **7ca** was ruled out, because it must contain *cis* double bond. In addition, the formation of five membered cyclic ether **6ca** is geometrically favoured over the seven membered one.

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

Now with the optimized reaction conditions in hand, to check the scope and limitations of the method, we have 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 the figure 2. It is worth mentioning that although the yields of the cyclic ether products **6** are moderate, but they actually represent the overall yield of three individual reactions. Therefore, each step contributes for at least 75% yield and hence the method is still stands efficient.

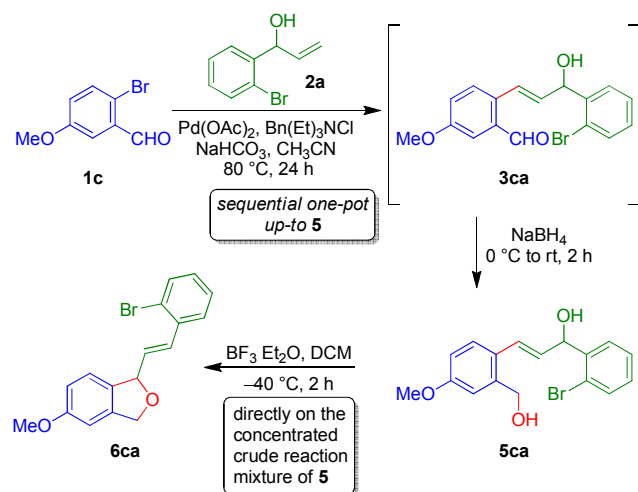
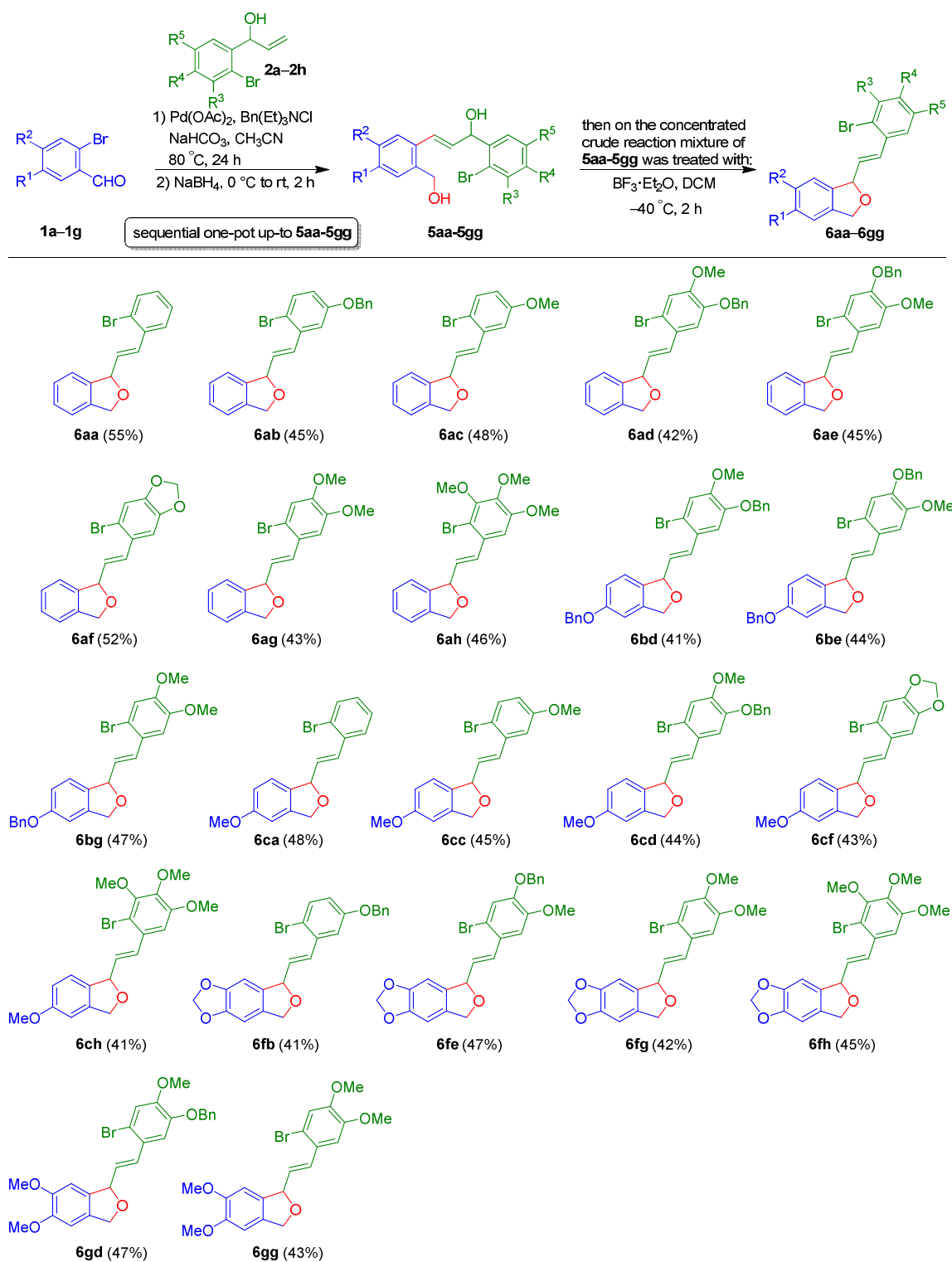


Figure 2: Synthesis of 1, 3-dihydroisobenzofurans **6aa-6gg** from 2-bromobenzaldehydes **1a-1g** and aryl allylic alcohols **2a-2h**.

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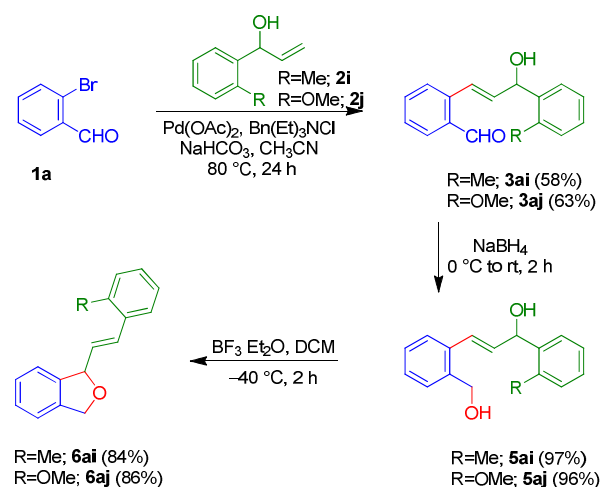


^aReaction conditions: All the reactions carried out with 2-bromobenzaldehydes **1a-1g** (0.50 mmol). ^bIsolated yields of chromatographically pure products.

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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 along with the Mizoroki-Heck product.^{13b} 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 the diol **5** (Scheme 4).



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

Experimental Section

General Considerations

IR spectra were recorded on a Bruker Tensor 37 (FT-IR) spectrophotometer. ¹H-NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl₃; chemical shifts (δ 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 CHCl₃ ($\delta_{\text{H}} = 7.25$ ppm). ¹³C-NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at 295 K in CDCl₃; chemical shifts (δ in ppm) are reported relative to CHCl₃ [$\delta_{\text{C}} = 77.00$ ppm (central line of triplet)]. In the ¹³C-NMR, the nature of carbons (C, CH, CH₂ and CH₃) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH₂) and q = quartet (for CH₃). In the ¹H-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 ¹H, ¹³C 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 measured

using Oxford Super Nova instrument. All small scale dry reactions were carried out using 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 solvents were distilled prior use; petroleum ether with a boiling range of 60 to 80 °C, diethyl ether, dichloromethane (DCM), ethyl acetate, THF (with purity 99%), acetonitrile (with purity 99.9%), purchased from locally available commercial sources were used. All aromatic aldehydes (with purity 98%), bromine (with purity 99%), iodine (with purity 99%), Bn(Et)₃NCl (with purity 99%), Pd(OAc)₂ (with purity 98%), 3-iodoanisole (with purity 99%), 2-bromoiodobenzene (with purity 99%), NaBH₄ (with purity 99%), K₂CO₃ (with purity 99%), and NaHCO₃ (with purity 99.5%) were purchased from Sigma-Aldrich, whereas vinylmagnesium bromide (with purity 99%), BF₃·Et₂O (with purity 48%) and iodobenzene (with purity 99%) were purchased from other commercial sources and used as received. The bases NaHCO₃ dried at 150–170 °C over oil bath. Diethyl ether and toluene were dried over sodium/ benzophenone. DCM and DCE, dried over calcium hydride. Acetonitrile dried over P₂O₅. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

The following *ortho*-bromobenzaldehydes **1a–1h** except **1a** were synthesized from corresponding aromatic aldehydes using literature reported bromination method.¹⁷ Bromo aryl allylic alcohols **2a**¹⁸, **2g** and **2h**¹⁹ except 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, was added 1.0 M vinylmagnesium bromide (20 mmol, 1.0 M in THF), and the resultant reaction mixture slowly allowed to reach the room temperature and stirred for 1.5 h. The reaction mixture was quenched with saturated aq. NH₄Cl solution and extracted with diethyl ether (3 × 30 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na₂SO₄ 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 the *ortho*-bromo aryl allylic alcohol **2a–2h** (80–92%).

General procedure-2 for the synthesis of 1,3-dihydroisobenzofurans (6aa–6gg): In an oven dried Schlenk under nitrogen atmosphere, were added Pd(OAc)₂ (5 mol%), Bn(Et)₃NCl (0.50 mmol), NaHCO₃ (1 mmol), 2-bromobenzaldehydes **1a–1g** (0.50 mmol) and *ortho*-bromo aryl allylic alcohol **2a–2h** (0.60 mmol) followed by dry acetonitrile (4 mL). The resulted reaction mixture was stirred for 24 h at 80 °C. Allowed the reaction to 0 °C where added NaBH₄ (1.50 mmol), stirred for two hours at rt. The reaction mixture was quenched with saturated aq. NH₄Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Traces of solvents removed under high vacuum, to the above crude dry DCM 20 mL was added cooled the reaction to –40 °C, BF₃·Et₂O (2.5 mmol) added, stir the reaction for 2 h at the same temperature. The reaction mixture was then quenched with saturated aqueous NaHCO₃ solution and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were dried over anhydrous Na₂SO₄, 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 & 6aj): In an oven dried Schlenk under nitrogen atmosphere, were added Pd(OAc)₂ (5 mol%), Bn(Et)₃NCl (0.50 mmol), NaHCO₃ (1 mmol), 2-bromobenzaldehydes **1a** (0.50 mmol) and *ortho*-bromo aryl allylic alcohol **2i–2j** (0.60 mmol) followed by dry acetonitrile (4 mL). The resulted reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was quenched using saturated aq. NH₄Cl solution and compound was extracted in ethyl acetate, concentrated under reduced pressure. The aldehyde **3** was isolated by silica gel column chromatography (petroleum ether/ethyl acetate). The aldehyde **3** was subjected to 0 °C and added NaBH₄ (1.50 mmol), stirred for two hours at rt. The reaction mixture was quenched with saturated aq. NH₄Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with saturated NaCl solution, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Traces of solvents removed under high vacuum, to the above crude dry DCM 20 mL was added cooled the reaction to –40 °C, BF₃·Et₂O (2.5 mmol) added, stir the reaction for 2 h at the same temperature. The reaction mixture was then quenched with saturated aqueous NaHCO₃ solution and the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were dried over anhydrous Na₂SO₄, 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 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⁻¹): $\nu_{max}=3371$, 3032, 2920, 1592, 1571, 1462, 1291, 1380, 1291, 1233, 1163, 1010, 927, 736, 697 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=7.50$ – 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=CH₂), 5.54 (d, 1H, $J=5.4$ Hz, ArCH-OH), 5.40 (td, 1H, $J=15.6$ and 1.5 Hz, C=CH_aH_b), 5.22 (td, 1H, $J=10.3$ and 1.5 Hz, C=CH_aH_b), 5.04 (s, 2H, PhCH₂O), 2.25 (d, 1H, $J=3.9$ Hz, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=158.4$ (s, Ar-C), 142.5 (s, Ar-C), 138.1 (d, CH=CH₂), 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=CH₂), 114.2 (d, Ar-CH), 112.9 (s, Ar-C), 73.4 (d, Ar-CHOH), 70.2 (t, PhCH₂) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₆H₁₄BrO]⁺=[(M+H)–H₂O]⁺: 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 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 cm⁻¹): $\nu_{max}=3380$, 2922, 2851, 1593, 1572, 1468, 1416, 1290, 1233, 1161, 1047, 1013, 928, 807, 771 cm⁻¹. ¹H NMR (CDCl₃, 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, CH=CH₂), 5.53 (d, 1H, $J=5.4$ Hz, ArCH-OH), 5.38 (td, 1H, $J=17.1$ and 1.5 Hz, C=CH_aH_b), 5.21 (dd, 1H, $J=10.3$ and 1.5 Hz, C=CH_aH_b), 3.78 (s, 3H, Ar-OCH₃), 2.34 (br. s, 1H, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=159.3$ (s, Ar-C), 142.4 (s, Ar-C), 138.1 (d, CH=CH₂), 133.3 (d, Ar-CH), 115.7 (t, CH=CH₂), 115.2 (d, Ar-CH), 113.0 (d, Ar-CH), 112.7 (s, Ar-C), 73.4 (d, Ar-CHOH), 55.4 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₆H₁₀BrO]⁺=[(M+H)–H₂O]⁺: 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 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 cm⁻¹): $\nu_{max}=3392$, 2933, 2847, 1599, 1497, 1454, 1381, 1251, 1120, 1155, 1120, 1039, 1023, 861, 834, 696, 665 cm⁻¹. ¹H NMR (CDCl₃, 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, CH=CH₂), 5.51 (d, 1H, $J=5.4$ Hz, ArCH-OH), 5.38 (td, 1H, $J=15.6$ and 1.5 Hz, C=CH_aH_b), 5.20 (td, 1H, $J=10.3$ and 1.5 Hz, C=CH_aH_b), 5.09 (s, 2H, PhCH₂O), 3.38 (s, 3H, Ar-OCH₃), 2.29 (d, 1H, $J=2.9$ Hz, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=149.4$ (s, Ar-C), 148.1 (s, Ar-C), 138.5 (d, CH=CH₂), 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, CH=CH₂), 112.1 (s, Ar-C), 110.7 (d, Ar-CH), 73.3 (d, Ar-CHOH), 71.2 (t, PhCH₂), 56.0 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₇H₁₆BrO₂]⁺=[(M+H)–H₂O]⁺: 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 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 cm⁻¹): $\nu_{max}=3404$, 3032, 3008, 2932, 1600, 1502, 1502, 1439, 1379, 1257, 1156, 1120, 1029, 925, 863, 777 cm⁻¹. ¹H NMR (CDCl₃, 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, CH=CH₂), 5.49 (d, 1H, $J=5.4$ Hz, ArCH-OH), 5.35 (td, 1H, $J=15.6$ and 1.5 Hz, C=CH_aH_b), 5.31 (td, 1H, $J=10.3$ and 1.5 Hz,

C=CH_aH_b), 5.11 (d, 1H, *J*=12.2 Hz, PhCH_aH_bO), 5.10 (d, 1H, *J*=12.2 Hz, PhCH_aH_bO), 3.85 (s, 3H, Ar-OCH₃), 2.10 (d, 1H, *J*=2.4 Hz, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=149.6 (s, Ar-C), 147.8 (s, Ar-C), 138.4 (d, CH=CH₂), 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, CH=CH₂), 113.1 (s, Ar-C), 112.9 (d, Ar-CH), 73.2 (d, Ar-CHOH), 71.1 (t, PhCH₂), 56.2 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₇H₁₆BrO₂]⁺=[(M+H)-H₂O]⁺: 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 colorless viscous liquid. [TLC control *R_f*(**1f**)=0.60, *R_f*(**2f**)=0.50 (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=3346, 2897, 1501, 1471, 1407, 1230, 1107, 1035, 930, 840, 798 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=6.98 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 5.95 (d, 1H, *J*=5.4 Hz, OCH_aH_bO), 5.94 (d, 1H, *J*=5.4 Hz, OCH_aH_bO), 5.93 (ddd, 1H, *J*=15.6, 10.3 and 5.4 Hz, CH=CH₂), 5.51 (d, 1H, *J*=5.4 Hz, ArCH-OH), 5.37 (td, 1H, *J*=15.6 and 1.5 Hz, C=CH_aH_b), 5.20 (td, 1H, *J*=10.3 and 1.5 Hz, C=CH_aH_b), 2.26 (d, 1H, *J*=2.9 Hz, OH) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=147.8 (s, Ar-C), 147.7 (s, Ar-C), 138.4 (d, CH=CH₂), 134.8 (s, Ar-C), 115.3 (t, CH=CH₂), 112.8 (s, Ar-C), 112.5 (d, Ar-CH), 107.7 (d, Ar-CH), 101.7 (t, OCH₂O), 73.3 (d, Ar-CHOH) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₀H₉BrNaO₃]⁺=[M+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 yellow viscous liquid. [TLC control *R_f*(**1a**)=0.80, *R_f*(**2a**)=0.70 and *R_f*(**6aa**)=0.85 (petroleum ether/ethyl acetate 95:5, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2922, 2852, 1588, 1465, 1437, 1357, 1284, 1246, 1158, 1122, 1107, 1021, 963, 747, 698, 665 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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, PhCH(O)CH=CH], 5.22 (d, 1H, *J*=11.7 Hz, PhCH_aH_bOCHCH=CH), 5.14 (d, 1H, *J*=11.7 Hz, PhCH_aH_bOCHCH=CH) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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, Ph-CHCH=CH), 72.9 (t, Ph-CH₂OCHCH=CH) ppm. HR-MS (ESI⁺): *m/z* calculated for [C₁₆H₁₃BrNaO]⁺=[M+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 pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5, *R_f*(**1a**)=0.80, *R_f*(**2b**)=0.50 and *R_f*(**6ab**)=0.65 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2922, 2852, 1590, 1563, 1459, 1286, 1238, 1173, 1028, 1013, 963, 739, 697 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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,

PhCH(O)CH=CH], 5.22 (dd, 1H, *J*=12.2 and 2.4 Hz, PhCH_aH_bOCHCH=CH), 5.13 (dd, 1H, *J*=12.2 and 1.0 Hz, PhCH_aH_bOCHCH=CH), 4.98 (s, 2H, PhCH₂O) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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, Ph-CHCH=CH), 72.8 (t, Ph-CH₂OCHCH=CH) 70.1 (t, PhCH₂O) ppm. HR-MS (ESI⁺): *m/z* calculated for [C₂₃H₁₈⁷⁹BrO]⁺=[(M+H)-H₂O]⁺: 389.0536; found 389.0545 and [C₂₃H₁₈⁸¹BrO]⁺=[(M+H)-H₂O]⁺: 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 pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5, *R_f*(**1a**)=0.75, *R_f*(**2c**)=0.35 and *R_f*(**6ac**)=0.50 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2959, 2929, 1592, 1571, 1464, 1287, 1236, 1161, 1014, 802, 754, 733, 599 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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_aH_bOCHCH=CH), 5.08 (d, 1H, *J*=12.3 Hz, PhCH_aH_bOCHCH=CH), 3.68 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 55.4 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): *m/z* calculated for [C₁₇H₁₄BrO]⁺=[(M+H)-H₂O]⁺: 313.0223; found 313.0212, [C₁₇H₁₄⁸¹BrO]⁺=[(M+H)-H₂O]⁺: 315.0202; found 315.0189 and [C₁₇H₁₉BrNO₂]⁺=[M+NH₄]⁺: 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 brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, *R_f*(**1a**)=0.80, *R_f*(**2d**)=0.20 and *R_f*(**6ad**)=0.30 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2918, 2850, 1595, 1502, 1461, 1385, 1260, 1200, 1166, 1024, 861, 750, 697 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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_aH_bOCHCH=CH), 5.14 (d, 1H, *J*=12.2 Hz, PhCH_aH_bOCHCH=CH), 5.10 (s, 2H, PhCH₂O) 3.83 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 71.1 (t, PhCH₂O), 56.1 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₄H₂₁BrNaO₃]⁺=[M+Na]⁺:459.0566; found 459.0583 and [C₂₄H₂₁BrNaO₃]⁺=[M+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 brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1a**)=0.80, R_f(**2e**)=0.20 and R_f(**6ae**)=0.35 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2957, 2920, 2851, 1503, 1462, 1441, 1379, 1261, 1206, 1163, 1026, 743 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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_aH_bOCHCH=CH), 5.13 (d, 1H, J=12.2 Hz, PhCH_aH_bOCHCH=CH), 5.06 (s, 2H, PhCH₂O) 3.86 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 71.3 (t, PhCH₂O), 56.2 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₄H₂₂BrO₃]⁺=[M+H]⁺:437.0747; found 437.0735 and [C₂₄H₂₂⁸¹BrO₃]⁺=[M+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 pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1a**)=0.80, R_f(**2f**)=0.30 and R_f(**6af**)=0.65 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2901, 2852, 1502, 1474, 1412, 1247, 1229, 1116, 1034, 978, 961, 933, 863, 838, 750 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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, OCH₂O), 5.78 [d, 1H, J=7.8 Hz, PhCH(O)CH=CH], 5.22 (dd, 1H, J=12.2 and 2.4 Hz, PhCH_aH_bOCHCH=CH), 5.13 (d, 1H, J=12.2 Hz, PhCH_aH_bOCHCH=CH) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH) ppm. HR-MS (ESI⁺): m/z calculated for [C₁₇H₁₃BrNaO₃]⁺=[M+Na]⁺:366.9940; found 366.9938 and [C₁₇H₁₃⁸¹BrNaO₃]⁺=[M+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 yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1a**)=0.80, R_f(**2g**)=0.15 and R_f(**6ag**)=0.30 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2928, 2847, 1502, 1462, 1439, 1380, 1256, 1160, 1024, 751 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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_aH_bOCHCH=CH), 5.13 (d, 1H, J=12.2 Hz, PhCH_aH_bOCHCH=CH), 3.83 (s, 3H, Ar-OCH₃), 3.81 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 56.0 (q, Ar-OCH₃), 56.9 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₁₈H₁₇BrNaO₃]⁺=[M+Na]⁺: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 yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1a**)=0.80, R_f(**2h**)=0.10 and R_f(**6ah**)=0.25 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2923, 2851, 1559, 1480, 1426, 1391, 1325, 1201, 1166, 1106, 1009, 926, 753 cm⁻¹. ¹H-NMR (CDCl₃, 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_aH_bOCHCH=CH), 5.14 (d, 1H, J=12.2 Hz, PhCH_aH_bOCHCH=CH), 3.88 (s, 3H, Ar-OCH₃), 3.87 (s, 3H, Ar-OCH₃), 3.82 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-CH₂OCHCH=CH), 61.1 (q, Ar-OCH₃), 61.0 (q, Ar-OCH₃), 56.1 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₁₉H₁₈BrO₃]⁺=[(M+H)-H₂O]⁺: 373.0434; found 373.0416 and [C₁₉H₁₈⁸¹BrO₃]⁺=[(M+H)-H₂O]⁺: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 yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1b**)=0.70, R_f(**2d**)=0.30 and R_f(**6bd**)=0.50 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2956, 2922, 2852, 1600, 1500, 1455, 1383, 1260, 1166, 1025, 737, 697 cm⁻¹. ¹H-NMR (CDCl₃, 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_aH_bOCHCH=CH), 5.12 (d, 1H, J=12.7 Hz, ArCH_aH_bOCHCH=CH), 5.10 (s, 2H, PhCH₂O), 5.08 (s, 2H, PhCH₂O), 3.83 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-CH₂OCHCH=CH), 71.1 (t, PhCH₂O), 70.3 (t, PhCH₂O), 56.0 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₃₁H₂₈BrO₄]⁺=[M+H]⁺: 543.1165; found 543.1140 and [C₃₁H₂₈⁸¹BrO₄]⁺=[M+H]⁺: 545.1145; found 545.1130, [C₃₁H₂₇BrNaO₄]⁺=[M+Na]⁺: 565.0985; found 565.0959 and [C₃₁H₂₇⁸¹BrNaO₄]⁺=[M+Na]⁺: 567.0964; found 567.0977.

5-(Benzyloxy)-1-[(E)-2-[4-(benzyloxy)-2-bromo-5-methoxyphenyl]vinyl]-1,3-dihydro-2-benzofuran (6be): GP-2 was carried out and the product **6be** (119 mg, 44%) was furnished as brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1b**)=0.70, R_f(**2e**)=0.30 and R_f(**6be**)=0.55 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2923, 2852, 1600, 1502, 1455, 1439, 1380, 1259, 1163, 1026, 737, 697 cm⁻¹. ¹H-NMR (CDCl₃, 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_aH_bOCHCH=CH), 5.10 (d, 1H, J=12.2 Hz, ArCH_aH_bOCHCH=CH), 5.07 (s, 2H, PhCH₂O), 5.07 (s, 2H, PhCH₂O), 3.83 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-CH₂OCHCH=CH), 71.1 (t, PhCH₂O), 70.3 (t, PhCH₂O), 56.1 (s, 3H, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₃₁H₂₈BrO₄]⁺=[M+H]⁺: 543.1165; found 543.1142 and [C₃₁H₂₈⁸¹BrO₄]⁺=[M+H]⁺: 545.1145; found 545.1126, [C₃₁H₂₇BrNaO₄]⁺=[M+Na]⁺: 565.0985; found 565.0962 and [C₃₁H₂₇⁸¹BrNaO₄]⁺=[M+Na]⁺: 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 brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1b**)=0.70, R_f(**2g**)=0.15 and R_f(**6bg**)=0.40 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2922, 2851, 1600, 1503, 1462, 1439, 1259, 1162, 1027, 801, 737, 697 cm⁻¹. ¹H-NMR (CDCl₃, 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_aH_bOCHCH=CH), 5.09 (d, 1H, J=12.2 Hz, ArCH_aH_bOCHCH=CH), 5.07 (s, 2H, PhCH₂O), 3.86 (s, 3H, Ar-OCH₃), 3.83 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-

CH₂OCHCH=CH), 70.3 (t, PhCH₂O), 56.1 (q, Ar-OCH₃), 55.9 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₅H₂₄BrO₄]⁺=[M+H]⁺: 467.0852; found 467.0824 and [C₂₅H₂₄⁸¹BrO₄]⁺=[M+H]⁺: 469.0832; found 469.0817, [C₂₅H₂₃BrNaO₄]⁺=[M+Na]⁺: 489.0672; found 489.0646 and [C₂₅H₂₃⁸¹BrNaO₄]⁺=[M+Na]⁺: 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 yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1c**)=0.70, R_f(**2a**)=0.40 and R_f(**6ca**)=0.50 UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2956, 2924, 2854, 1610, 1493, 1466, 1275, 1117, 1025, 821, 748, 665 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=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_aH_bOCHCH=CH), 5.09 (d, 1H, J=12.2 Hz, ArCH_aH_bOCHCH=CH), 3.81 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 55.6 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₇H₁₅BrNaO₂]⁺=[M+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 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 cm⁻¹): ν_{max}=2957, 2922, 2852, 1594, 1465, 1284, 1241, 1016, 804 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ=7.42 (d, 1H, J=8.8 Hz, Ar-H), δ=7.10 (d, 1H, J=8.3 Hz, Ar-H), δ=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_aH_bOCHCH=CH), 5.10 (d, 1H, J=12.2 Hz, ArCH_aH_bOCHCH=CH), 3.81 (s, 3H, Ar-OCH₃), 3.76 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ=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-CH₂OCHCH=CH), 55.6 (s, Ar-OCH₃), 55.5 (s, Ar-OCH₃) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₈H₁₆BrO₂]⁺=[M+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 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 cm⁻¹): ν_{max}=2924, 2853, 1597, 1497, 1465, 1261, 1201, 1166, 1117, 1029, 813, 743, 698 cm⁻¹. ¹H-NMR (CDCl₃,

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_aH_bOCHCH=CH), 5.10 (s, 2H, PhCH₂O), 5.09 (d, 1H, $J=12.2$ Hz, ArCH_aH_bOCHCH=CH), 3.83 (s, 3H, Ar-OCH₃), 3.81 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-CH₂OCHCH=CH), 71.1 (t, PhCH₂O), 56.1 (q, Ar-OCH₃), 55.5 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₅H₂₄BrO₄]⁺=[M+H]⁺: 467.0852; found 467.0826 and [C₂₅H₂₄⁸¹BrO₄]⁺=[M+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 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 cm⁻¹): $\nu_{max}=2921$, 2852, 1605, 1500, 1474, 1235, 1106, 1036, 932, 870, 822 cm⁻¹. ¹H-NMR (CDCl₃, 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, OCH₂O), 5.72 [d, 1H, $J=7.8$ Hz, ArCH(O)CH=CH], 5.17 (dd, 1H, $J=12.2$ and 2.4 Hz, ArCH_aH_bOCHCH=CH), 5.08 (d, 1H, $J=12.2$ Hz, ArCH_aH_bOCHCH=CH), 3.81 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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, OCH₂O), 84.7 (d, Ar-CHCH=CH), 72.7 (t, Ar-CH₂OCHCH=CH), 55.5 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₁₈H₁₆BrO₄]⁺=[M+H]⁺: 375.0226; found 375.0212 and [C₁₈H₁₆⁸¹BrO₄]⁺=[M+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 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 cm⁻¹): $\nu_{max}=2923$, 2852, 1563, 1481, 1463, 1427, 1392, 1326, 1274, 1200, 1165, 1107, 1031, 1011, 926, 813 cm⁻¹. ¹H-NMR (CDCl₃, 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_aH_bOCHCH=CH), 5.09 (d, 1H, $J=12.2$ Hz, ArCH_aH_bOCHCH=CH), 3.88 (s, 3H, Ar-OCH₃), 3.87 (s, 3H, Ar-OCH₃), 3.82 (s, 3H, Ar-OCH₃), 3.80 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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-CH₂OCHCH=CH), 61.1 (q, Ar-OCH₃), 60.9 (q, Ar-OCH₃), 56.1 (q, Ar-OCH₃), 55.5 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₀H₂₁BrNaO₅]⁺=[M+Na]⁺: 443.0465; found 443.0448.

5-[(E)-2-[5-(Benzyloxy)-2-bromophenyl]vinyl]-5,7-dihydrofuro[3,4-f][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, $R_f(1f)=0.30$, $R_f(2b)=0.45$ and $R_f(6fb)=0.40$ UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2920$, 2851, 1591, 1501, 1464, 1378, 1278, 1239, 1173, 1122, 1039, 939, 851, 737, 698 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): $\delta=7.50$ –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, OCH_aH_bO), 5.97 (d, 1H, $J=2.9$ Hz, OCH_aH_bO), 5.70 (d, 1H, $J=7.8$ Hz, ArCH(O)CH=CH), 5.12 (dd, 1H, $J=11.7$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 5.04 (d, 1H, $J=11.7$ Hz, ArCH_aH_bOCHCH=CH), 5.01 (s, 2H, PhCH₂O) ppm. ¹³C-NMR (CDCl₃, 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, OCH₂O), 84.9 (d, Ar-CHCH=CH), 72.9 (t, Ar-CH₂OCHCH=CH), 70.2 (t, PhCH₂O) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₄H₁₉BrNaO₄]⁺=[M+Na]⁺: 473.0359; found 473.0330 and [C₂₄H₁₉⁸¹BrNaO₄]⁺=[M+Na]⁺: 475.0338; found 475.0317.

5-[(E)-2-[4-(Benzyloxy)-2-bromo-5-methoxyphenyl]vinyl]-5,7-dihydrofuro[3,4-f][1,3]benzodioxole (6fe): GP-2 was carried out and the product **6fe** (113 mg, 47%) was furnished as brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20, $R_f(1f)=0.70$, $R_f(2e)=0.30$ and $R_f(6fe)=0.50$ UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2956$, 2924, 2853, 1598, 1502, 1439, 1259, 1162, 1033, 852, 803, 735, 698 cm⁻¹. ¹H-NMR (CDCl₃, 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, OCH₂O), 5.67 (d, 1H, $J=7.8$ Hz, ArCH(O)CH=CH), 5.11 (dd, 1H, $J=11.7$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 5.07 (s, 2H, PhCH₂O), 5.02 (dd, 1H, $J=11.7$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 3.85 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 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, OCH₂O), 85.1 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH₂OCHCH=CH), 71.2 (t, PhCH₂O), 56.2 (q, Ar-OCH₃) ppm. HR-MS (ESI⁺): m/z calculated for [C₂₅H₂₂BrO₅]⁺=[M+H]⁺: 481.0645; found 481.0615 and [C₂₅H₂₂⁸¹BrO₅]⁺=[M+H]⁺: 483.0625;

found 483.0602, $[C_{25}H_{21}BrNaO_5]^+=[M+Na]^+$: 503.0465; found 503.0438 and $[C_{25}H_{21}Br^{81}NaO_5]^+=[M+Na]^+$: 505.0444; found 505.0422.

5-[(E)-2-(2-Bromo-4,5-dimethoxyphenyl)vinyl]-5,7-dihydrofuro[3,4-f][1,3]benzodioxole (6fg): GP-2 was carried out and the product **6fg** (85 mg, 42%) was furnished as 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 cm^{-1}): $\nu_{max}=2924$, 2852, 1600, 1503, 1473, 1380, 1261, 1208, 1163, 1035, 937, 860, 736, 698, 665 cm^{-1} . 1H -NMR ($CDCl_3$, 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_aH_bO), 5.96 (d, 1H, $J=2.9$ Hz, OCH_aH_bO), 5.69 (d, 1H, $J=7.8$ Hz, ArCH(O)CH=CH), 5.11 (dd, 1H, $J=11.7$ and 2.0 Hz, ArCH_aH_bOCHCH=CH), 5.02 (dd, 1H, $J=11.7$ and 2.0 Hz, ArCH_aH_bOCHCH=CH), 3.86 (s, 3H, Ar-OCH₃), 3.83 (s, 3H, Ar-OCH₃) ppm. ^{13}C -NMR ($CDCl_3$, 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_2O), 85.2 (d, Ar-CHCH=CH), 72.8 (t, Ar-CH₂OCHCH=CH), 56.1 (q, Ar-OCH₃), 56.0 (q, Ar-OCH₃) ppm. HR-MS (ESI^+): m/z calculated for $[C_{19}H_{17}BrNaO_5]^+=[M+Na]^+$: 427.0152; found 427.0127 and $[C_{19}H_{17}^{81}BrNaO_5]^+=[M+Na]^+$: 429.0137; found 429.0121, HR-MS (ESI^+) m/z calculated for $[C_{19}H_{18}BrO_5]^+=[M+H]^+$: 405.0332; found 405.0304 and $[C_{19}H_{18}^{81}BrO_5]^+=[M+H]^+$: 407.0312; found 407.0294.

5-[(E)-2-(2-Bromo-3,4,5-trimethoxyphenyl)vinyl]-5,7-dihydrofuro[3,4-f][1,3]benzodioxole (6fh): GP-2 was carried out and the product **6fh** (98 mg, 45%) was furnished as 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 cm^{-1}): $\nu_{max}=2928$, 2854, 1566, 1503, 1482, 1394, 1329, 1264, 1198, 1164, 1107, 1037, 1010, 934, 814, 739 cm^{-1} . 1H -NMR ($CDCl_3$, 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_aH_bO), 5.95 (d, 1H, $J=2.9$ Hz, OCH_aH_bO), 5.69 (d, 1H, $J=7.8$ Hz, ArCH(O)CH=CH), 5.11 (dd, 1H, $J=11.7$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 5.03 (dd, 1H, $J=11.7$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 3.88 (s, 3H, Ar-OCH₃), 3.87 (s, 3H, Ar-OCH₃), 3.83 (s, 3H, Ar-OCH₃) ppm. ^{13}C -NMR ($CDCl_3$, 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_2O), 85.0 (d, Ar-CHCH=CH), 72.9 (t, Ar-CH₂OCHCH=CH), 61.1 (q, Ar-OCH₃), 60.9 (q, Ar-OCH₃), 56.1 (q, Ar-OCH₃) ppm. HR-MS (ESI^+): m/z calculated for $[C_{20}H_{19}BrNaO_6]^+=[M+Na]^+$: 457.0257; found 457.0257 and $[C_{20}H_{19}^{81}BrNaO_6]^+=[M+Na]^+$: 459.0237; found 459.0236.

1-[(E)-2-[5-(Benzyloxy)-2-bromo-4-methoxyphenyl]vinyl]-5,6-dimethoxy-1,3-dihydro-2-benzofuran (6gd): GP-2 was carried out and the product **6gd** (116 mg, 47%) was furnished as 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 cm^{-1}): $\nu_{max}=2926$, 2853, 1598, 1503, 1463, 1384, 1261, 1203, 1166, 1032, 859, 737, 698 cm^{-1} . 1H -NMR ($CDCl_3$, 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_aH_bOCHCH=CH), 5.10 (s, 2H, PhCH₂O), 5.07 (dd, 1H, $J=11.2$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 3.88 (s, 3H, Ar-OCH₃), 3.86 (s, 3H, Ar-OCH₃), 3.83 (s, 3H, Ar-OCH₃) ppm. ^{13}C -NMR ($CDCl_3$, 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-CH₂OCHCH=CH), 71.1 (t, PhCH₂O), 56.2 (q, Ar-OCH₃), 56.1 (q, Ar-OCH₃), 56.0 (q, Ar-OCH₃) ppm. HR-MS (ESI^+): m/z calculated for $[C_{26}H_{25}BrNaO_5]^+=[M+Na]^+$: 519.0778; found 519.0753 and $[C_{26}H_{25}^{81}BrNaO_5]^+=[M+Na]^+$: 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 brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 70:30, $R_f(\mathbf{1g})=0.65$, $R_f(\mathbf{2g})=0.45$ and $R_f(\mathbf{6gg})=0.35$ UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{max}=2924$, 2852, 1600, 1504, 1462, 1264, 1210, 1163, 1121, 1029, 863 cm^{-1} . 1H -NMR ($CDCl_3$, 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_aH_bOCHCH=CH), 5.07 (dd, 1H, $J=11.2$ and 2.9 Hz, ArCH_aH_bOCHCH=CH), 3.88 (s, 3H, Ar-OCH₃), 3.86 (s, 6H, Ar-OCH₃), 3.83 (s, 3H, Ar-OCH₃) ppm. ^{13}C -NMR ($CDCl_3$, 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-CH₂OCHCH=CH), 56.2 (q, Ar-OCH₃), 56.1 (q, Ar-OCH₃), 56.0 (q, Ar-OCH₃), 55.9 (q, Ar-OCH₃) ppm. HR-MS (ESI^+): m/z calculated for $[C_{20}H_{21}BrNaO_5]^+=[M+Na]^+$: 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 yellow colored viscous liquid. [TLC control (petroleum ether/ethyl acetate 70:30, $R_f(\mathbf{3ai})=0.70$, $R_f(\mathbf{5ai})=0.30$ UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{max}=3330$, 1485, 1459, 1006, 967, 753, 564 cm^{-1} . 1H -NMR ($CDCl_3$, 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_aH_bOH), 4.62 (d, 1H, $J=12.2$ Hz, PhCH_aH_bOH), 3.76 (br.s, 1H, OH), 3.29 (br.s, 1H, OH), 2.35 (s, 3H, Ar-CH₃) ppm. ^{13}C -NMR ($CDCl_3$, 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-CH₂OH), 19.1 (q, Ar-CH₃) ppm.

(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 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⁻¹): ν_{max} =3320, 1597, 1489, 1461, 1244, 1023, 753 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ =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, ArCH₂OH), 3.77 (s, 3H, Ar-OCH₃), 3.64 (br.s, 2H, 2 × OH) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ =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-CH₂OH), 55.4 (q, Ar-OCH₃) ppm.

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 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⁻¹): ν_{max} =2924, 2853, 1731, 1460, 1029, 965, 747, 697 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ =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_aH_bOCHCH=CH), 5.14 (d, 1H, J =12.2 Hz, PhCH_aH_bOCHCH=CH), 2.39 (s, 3H, Ar-CH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ =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-CH₂OCHCH=CH), 19.9 (q, Ar-CH₃) ppm.

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 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⁻¹): ν_{max} =2904, 2838, 1489, 1461, 1244, 1028, 749, 697 cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ =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_aH_bOCHCH=CH), 5.13 (d, 1H, J =12.2 Hz, PhCH_aH_bOCHCH=CH), 3.86 (s, 3H, Ar-OCH₃) ppm. ¹³C-NMR (CDCl₃, 100 MHz): δ =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-CH₂OCHCH=CH), 55.4 (q, Ar-OCH₃) ppm.

Conclusions

In summary, we have developed an efficient and practical method for the direct synthesis of important 1, 3-dihydroisobenzofurans, an important structural motif present in biologically active natural or unnatural 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 BF₃·Et₂O gave the 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, but actually represents the overall yield of three individual reactions.

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Notes and references

- A. –L. Ulaczyk and D. G. Hall, *Curr. Opin. Chem. Biol.*, 2005, **9**, 266–276.
 - P. J. Parsons, C. S. Penkett and A. J. Shell, *Chem. Rev.*, 1996, **96**, 195–206.
 - L. F. Tietze, *Chem. Rev.*, 1996, **96**, 115–136.
 - A. B. Dounay and L. E. Overman, *Chem. Rev.*, 2003, **103**, 2945–2963.
 - L. F. Tietze, H. Ila and H. P. Bell, *Chem. Rev.*, 2004, **104**, 3453–3516.
 - A. Domling, *Chem. Rev.*, 2006, **106**, 17–89.
 - G. Zeni and R. C. Larock, *Chem. Rev.*, 2006, **106**, 4644–4680.
 - D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174–238.
 - B. B. Toure and D. G. Hall, *Chem. Rev.* 2009, **109**, 4439–4486.
 - J. Le Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170–1214.
 - B. Liégault, J.-L. Renaud and C. Bruneau, *Chem. Soc. Rev.*, 2008, **37**, 290–299.
- X. Zhang, A. Liu and W. Chen, *Org. Lett.*, 2008, **10**, 3849–3852.
 - J. Chae, J. Yun and S. L. Buchwald, *Org. Lett.*, 2004, **6**, 4809–4812.

- J. Yun and S. L. Buchwald, *Org. Lett.*, 2001, **3**, 1129–1131. d) B. H. Lipshutz, W. Chrisman, K. Noson, P. Papa, J. A. Sclafani, R. W. Vivian and J. M. Keith, *Tetrahedron*, 2000, **56**, 2779–2788. e) C.-H. Cho, I.-S. Kim and K. Park, *Tetrahedron*, 2004, **60**, 4589–4599. f) S. Paul, S. Samanta and J. K. Ray, *Tetrahedron Lett.*, 2010, **51**, 5604–5608. g) M. Ghosh, A. Ahmed, S. Dhara and J. K. Ray, *Tetrahedron Lett.*, 2013, **54**, 4837–4840. h) Y. Tian, J. Qi, C. Sun, D. Yin, X. Wang and Q. Xiao, *Org. Biomol. Chem.*, 2013, **11**, 7262–7266. i) S. U. Son, K. H. Park and Y. K. Chung, *J. Am. Chem. Soc.*, 2002, **124**, 6838–6839. j) E. M. Beccalli, G. Broggini, M. Martinelli, N. Masciocchi and S. Sottocornola, *Org. Lett.*, 2006, **8**, 4521–4524. k) H. A. Oskooie, M. M. Heravi and F. K. Behbahani, *Molecules*, 2007, **12**, 1438–1446. l) R. Sanz, V. Guilarte and M. P. Castroviejo, *Synlett*, 2008, **19**, 3006–3010.
- a) A. Bruggink, R. Schoevaert and T. Kieboom, *Org. Process Res. Dev.*, 2003, **7**, 622–640. b) S. P. Maddaford, N. G. Andersen, W. A. Cristofoli and B. A. Keay, *J. Am. Chem. Soc.*, 1996, **118**, 10766–10773. c) L. E. Overman and M. D. Rosen, *Angew. Chemie.*, 2000, **112**, 4768–4771; *Angew. Chem. Int. Ed.*, 2000, **39**, 4596–4599. d) R. Grigg, P. Fretwell, C. Meerholtz and V. Sridharan, *Tetrahedron*, 1994, **50**, 359–370. e) M. R. Fielding, R. Grigg, V. Sridharan, M. Thornton-pett and C. J. Urch, *Tetrahedron*, 2001, **57**, 7737–7748. f) L. Shi, C. K. Narula, K. T. Mak, L. Kao, Y. Xu and R. F. Heck, *J. Org. Chem.*, 1983, **48**, 3894–3900. g) G. Cuny, M. Bois-Choussy and J. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 14475–14484. h) H. Zhang and R. C. Larock, *J. Org. Chem.*, 2003, **68**, 5132–5138. i) A. Arcadi, S. Cacchi, G. Fabrizi and F. Marinelli, *Synlett*, 2000, 394–396. j) G. Dyker, *J. Org. Chem.*, 1993, **58**, 6426–6428. k) X. Xu, Y. Qian, L. Yang and W. Hu, *Chem. Commun.*, 2011, **47**, 797–799. l) X. Xu, W.-H. Hu, P. Y. Zavalij and M. P. Doyle, *Angew. Chem.*, 2011, **123**, 11348–11351; *Angew. Chem. Int. Ed.*, 2011, **50**, 11152–11155. m) P. Wipf, C. R. J. Stephenson and K. Okumura, *J. Am. Chem. Soc.*, 2003, **124**, 14694–14695. n) V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathen and B. Lakshmi, *Acc. Chem. Res.*, 2003, **36**, 899–907. o) J. Zhu, *Eur. J. Org. Chem.*, 2003, **7**, 1133–1144. p) W. Hu, X. Xu, J. Zhou, W.-J. Liu, H. Huang, J. Hu, L. Yang and L.-Z. Gong, *J. Am. Chem. Soc.*, 2008, **130**, 7782–7783. q) P. Truong, X. Xu and M. P. Doyle, *Tetrahedron Lett.*, 2011, **52**, 2093–2096.
 - a) A. Ahmed, S. Dhara and J. K. Ray, *Tetrahedron Lett.*, 2013, **54**, 1673–1676. b) J. M. A. Miguez, L. A. Adrio, A. Sousa-pedrares, J. M. Vila and K. K. Hii, *J. Org. Chem.*, 2007, **72**, 7771–7774. c) S. T. Handy, T. Wilson and A. Muth, *J. Org. Chem.*, 2007, **72**, 8496–8500. d) S. A. Springfield, K. Marcantonio, S. Ceglia, J. Albaneze-walker, P. G. Dormer, T. D. Nelson and J. A. Murry, *J. Org. Chem.*, 2003, **68**, 4598–4599.
 - a) M. Shiri, *Chem. Rev.*, 2012, **112**, 3508–3549. b) H. Lebel, C. Ladjeil and L. Brthous, *J. Am. Chem. Soc.*, 2007, **129**, 13321–13326. c) M. Miura, T. Tsuda, T. Satoh, S. Pivsa-Art and M. Nomura, *J. Org. Chem.*, 1998, **63**, 5211–5215.
 - E-i. Negishi, C. Copéret, S. Ma, S.-Y. Liou and Liu, *F. Chem. Rev.*, 1996, **96**, 365–393.
 - For some recent domino one-pot Pd-catalyzed transformations, see: a) C. Chowdhury, S. Mukherjee, B. Chakraborty and B. Achari, *Org. Biomol. Chem.*, 2011, **9**, 5856–5862. b) J. Lubkoll, A. Millemaggi, A. Perry and R. J. K. Taylor, *Tetrahedron*, 2010, **66**, 6606–6612. c) M. L. N. Rao and P. Dasgupta, *Tetrahedron Lett.*, 2012, **53**, 162–165. d) B. Laleu and M. Lautens, *J. Org. Chem.*, 2008, **73**, 9164–9167. e) N. Selander, K. J. Szabó, *J. Org. Chem.*, 2009, **74**, 5695–5698. f) Y. Cheng, Z. Duan, L. Yu, Z. Li, Y. Zhu and Y. Wu, *Org. Lett.*, 2008, **10**, 901–904. g) G. Satyanarayana and M. E. Maier, *Org. Lett.*, 2008, **10**, 2361–2364. h) I. Kim and K. Kim, *Org. Lett.*, 2010, **12**, 2500–2503. i) G. Satyanarayana and M. E. Maier, *Eur. J. Org. Chem.*, 2008, 5543–5552. j) O. Leogane and H. Lebel, *Angew. Chem.*, 2008, **120**, 356–358. *Angew. Chem. Int. Ed.*, 2008, **47**, 350–352. k) J. Barluenga, A. Mendoza, F. Rodríguez and J. F. Fañanás, *Angew. Chem.*, 2009, **121**, 1672–1675. *Angew. Chem. Int. Ed.*, 2009, **48**, 1644–1647. l) Y. Liang, T. Meng, H.-J. Zhang and Z. Xi, *Synlett*, 2011, 911–914. m) T. Toyoshima, Y. Mikano, T. Miura and M. Murakami, *Org. Lett.*, 2010, **12**, 4584–4587. n) A. Schweinitz, A. Chtchemelinine and A. Orellana, *Org. Lett.*, 2011, **13**, 232–235. o) F. Jafarpour and N. Jalalimanesh, *Tetrahedron*, 2012, **68**, 10286–10292. p) C. S. Cho, D. K. Lim, J. Q. Zhang, T.-J. Kim and S. C. Shim, *Tetrahedron Lett.*, 2004, **45**, 5653–5656. q) A. S. K. Hashmi, M. Ghanbari, M. Rudolph and F. Rominger, *Chemistry - A European Journal*, 2012, **18**, 8113–8119. r) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Ackermann, J. D. B. Becker, M. Rudolph, C. Scholz and F. Rominger, *Adv. Synth. Catal.*, 2012, **354**, 133–137. s) A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Rudolph, T. D. Ramamurthi and F. Rominger, *Angew. Chem.*, 2009, **121**, 8392–8395. *Angew. Chem. Int. Ed.*, 2009, **48**, 8243–8246.
 - For some recent sequential one-pot Pd-catalyzed transformations, see: a) R.-J. Song, Y. Liu, R.-J. Li and J.-H. Li, *Tetrahedron Lett.*, 2009, **50**, 3912–3916. b) L. Nassar-Hardy, S. Fabre, A. M. Amer, E. Fouquet and F.-X. Felpin, *Tetrahedron Lett.*, 2012, **53**, 338–341. c) Y. Zhou, Y. Zhao, X. Dai, J. Liu, L. Li and H. Zhang, *Org. Biomol. Chem.*, 2011, **9**, 4091–4097. d) J.-Y. Lee and P. Ho Lee, *J. Org. Chem.*, 2008, **73**, 7413–7416. e) T. Matsuda, M. Shigeno and M. Murakami, *Org. Lett.*, 2008, **10**, 5219–5221. f) Y. Zhao, Y. Zhou, L. Liang, X. Yang, F. Du, L. Li and H. Zhang, *Org. Lett.*, 2009, **11**, 555–558. g) J. Peng, D. Jiang, W. Lin and Y. Chen, *Org. Biomol. Chem.*, 2007, **5**, 1391–1396.
 - For reviews on domino Heck reactions, see: a) E. Negishi, C. Copret, S. Ma, S.-Y. Liou and F. Liu, *Chem. Rev.*, 1996, **96**, 365–394. b) I. P. Beletskaya and A. V. Chepravok, *Chem. Rev.*, 2000, **100**, 3009–3066. c) A. B. Dounay and L. E. Overman, *Chem. Rev.*, 2003, **103**, 2945–2964. d) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, **2005**, **105**, 2527–2572. e) G. Zeni and R. C. Larock, *Chem. Rev.*, 2006, **106**, 4644–4680.
 - For recent domino Heck cyclizations, see: a) R. T. Ruck, M. A. Huffman, M. M. Kim, M. Shevlin, W. V. Kandur and I. W. Davies, *Angew. Chem.*, 2008, **120**, 4789–4792. *Angew. Chem. Int. Ed.*, 2008, **47**, 4711–4714. b) G. Satyanarayana, C. Maichle-Mössmerzb and M. E. Maier, *Chem. Commun.*, 2009, 1571–1573. c) Y. Hu, C. Yu, D. Ren, Q. Hu, L. Zhang and D. Cheng, *Angew. Chem.*, 2009, **121**, 5556–5559. *Angew. Chem. Int. Ed.*, 2009, **48**, 5448–5451. d) L. F. Tietze, A. Düfert, F. Lotz, L. Sölter, K. Oum, T. Lenzer, T. Beck and R. Herbst-Irmer, *J. Am. Chem. Soc.*, 2009, **131**, 17879–17884.
 - For recent domino Heck couplings, see: a) O. Rene, D. Lapointe and K. Fagnou, *Org. Lett.*, 2009, **11**, 4560–4563. b) Z. Lu, C. Hu, J. Guo, J. Li, Y. Cui and Y. Jia, *Org. Lett.*, 2010, **12**, 480–483. c) M. Hussain, S.-M. T. Toguem, R. Ahmad, D. T. Tung, I. Knepper, A. Villinger and P. Langer, *Tetrahedron*, 2011, **67**, 5304–5318. d) I. Ullah, M. Nawaz, A. Villinger and P. Langer, *Tetrahedron Lett.*, 2011, **52**, 1888–1890.
 - F.-X. Felpin, O. Ibarguren, L. Nassar-hardy and E. Fouquet, *J. Org. Chem.*, 2009, **74**, 1349–1352.
 - a) A. G. K. Reddy, J. Krishna and G. Satyanarayana, *Synlett*, 2011, 1756–1760. b) J. Krishna, A. G. K. Reddy, B. V. Ramulu, L. Mahendar and G. Satyanarayana, *Synlett*, 2012, **23**, 375–380. c) A. G. K. Reddy and G. Satyanarayana, *Tetrahedron*, 2012, **68**, 8003–8010. d) A. G. K. Reddy, J. Krishna and G. Satyanarayana, *Tetrahedron Lett.*, 2012, **53**, 5635–5640. e) J. Krishna, A. G. K. Reddy, G. Satyanarayana, *Synlett*, 2013, **24**, 967–972. f) A. G. K. Reddy, J. Krishna and G. Satyanarayana, *Tetrahedron*, 2013, **69**, 10098–10107. g) B. Suchand, J. Krishna, B. V. Ramulu, D. Dibyendu, A. G. K. Reddy, L. Mahendar and G. Satyanarayana, *Tetrahedron Lett.* 2012, **53**, 3861–3864. h) B. V. Ramulu, L. Mahendar, J. Krishna, A. G. K. Reddy, B. Suchand and G. Satyanarayana, *Tetrahedron*, 2013, **69**, 8305–8315. i) J. Krishna, A. G. K. Reddy, G. Satyanarayana, *Tetrahedron, Lett.* 2014, **55**, 861–864. j) J. Krishna, A. G. K. Reddy, G. Satyanarayana, *Synth. Commun.*, 2014, **44**, 2103–2111. k) L. Mahendar, J. Krishna, A. G. K. Reddy, B. V. Ramulu and G. Satyanarayana, *Org. Lett.*, 2012, **14**, 628–631. l) L. Mahendar and G. Satyanarayana, *J. Org. Chem.*, 2014, **79**, 2059–2074. m) L. Mahendar, A. G. K. Reddy, J. Krishna and G. Satyanarayana, *J. Org. Chem.*, 2014, **79**, 8566–8576.

14. T. Jeffery, *J. Chem. Soc., Chem. Commun.*, 1984, 1287–1289. b) A. Briot, C. Baehr, R. Brouillard, A. Wagner and C. Mioskowski, *J. Org. Chem.*, 2004, **69**, 1374–1377.
15. a) U. Holler, J. B. Gloer and D. T. Wicklow, *J. Nat. Prod.*, 2002, **65**, 876–882. b) J. K. Harper, A. M. Arif, E. J. Ford, G. a. Strobel, J. a. Porco, D. P. Tomer, K. L. O'Neill, E. M. Heider and D. M. Grant, *Tetrahedron*, 2003, **59**, 2471–2476. c) Y.-J. Kwon, C.-J. Zheng and W.-G. Kim, *Biosci. Biotechnol. Biochem.*, 2010, **74**, 390–393. d) Y. Nishihara, S. Takase, E. Tsujii, H. Hatanaka and S. Hashimoto, *J. Antibiot.*, 2001, **54**, 297–303. e) Y. Nishihara, E. Tsujii, Y. Yamagishi, K. Sakamoto, Y. Tsurumi, S. Furukawa, M. Hino, M. Yamashita and S. Hasimoto, *J. Antibiot.*, 2001, **54**, 136–143. f) Z. P. Xie, H. Y. Zhang, F. C. Li, B. Liu, S. X. Yang, H. P. Wang, Y. Pu, Y. Chen and S. Qin, *Chin. Chem. Lett.*, 2012, **23**, 941–944. g) D. Shi, X. Fan, L. Han, F. Xu and Z. Yuan, *Faming Zhuanli Shenqing* 2008, CN 101283998 A 20081015. h) K. Dorell, M. A. Cohen, S. S. Huprikar, J. M. Gorman and M. Jones, *Psychosomatics* 2005, **46**, 91–93 i) N. G. Parker and C. S. Brown, *Ann. Pharmacother.* 2000, **34**, 761–771. j) K. Brösen and C. A. Naranja, *Eur. Neuropsychopharmacol.* 2001, **11**, 275–283. k) D. Baldwin and F. N. Johnson, *Rev. Contemp. Pharmacother.* 1995, **6**, 315–325. l) M. B. Keller, *J. Clin. Psychiatry* 2000, **61**, 896–908.
16. R. Karmakar and P. Pahari and D. Mal, *Chem. Rev.* 2014, **114**, 6213–6284.
17. Chandrasekhar, S.; Reddy, N. R.; Rao, Y. S. *Tetrahedron*, **2006**, *62*, 12098–12107.
18. Muratake, H.; Natsume, M.; Nakai, H. *Tetrahedron*, **2004**, *60*, 11783–11803.
19. Krishna, J.; Reddy, A. G. K.; Mahendar, L.; Ramulu, B. V. *Synlett*, **2012**, *23*, 375–380.