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Synthesis of Oxygen Heterocycles via Pd-Catalyzed Cross-Coupling of Unsaturated Phenols and Vinylic Halides or Triflates

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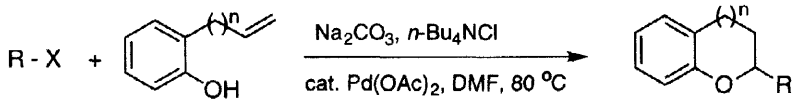
Abstract: The palladium-catalyzed cross-coupling of *o*-allylic and *o*-vinylic phenols with vinylic halides and triflates produces substituted dihydrobenzopyrans and dihydrobenzofurans respectively in good to high yields. The proposed mechanism involves vinylpalladium addition to the olefin, rearrangement to a π-allylpalladium intermediate and subsequent intramolecular nucleophilic displacement of palladium. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: alkenyl halides; coupling reactions; palladium; phenols.

Catalytic transformations involving π-allylpalladium intermediates have found widespread utility in a number of important chemical processes.[1] The increased use of these complexes in the cyclization of suitable substrates has paralleled the exploration of new strategies, other than allylic ionization, for their preparation.[2] Recent work in this area in our and other groups has focused on the possibility of utilizing π-allylpalladium species derived from the cross-coupling of aryl and vinylic halides or triflates with olefinic compounds in the construction of heterocycles. For example, aryl halides containing heteroatom or carbon nucleophiles in the ortho position have been reacted with 1,2-,[3] 1,3-[4] and 1,4-dienes[5] or vinylic cyclopropanes and cyclobutanes[6] to afford five- and six-membered ring hetero- and carbocycles. A complementary, mechanistically-related heterocyclization method has been achieved by the reaction of vinylic halides or triflates with alkenes containing proximate nucleophiles, such as alkenoic acids,[7] *o*-alkenyl anilides[8] and unsaturated sulfonamides.[9] As part of our ongoing studies, we anticipated that the Pd-catalyzed cross-coupling of vinylic halides or triflates with *o*-alkenyl phenols might afford an expeditious route to a variety of oxygen heterocycles.[10] We now report the full details of this study, which provides a convenient new route to dihydrobenzopyrans (**3**) and dihydrobenzofurans (**4**) (eq. 1).



1 **2**

R = vinylic; X = I, Br, O_3SCF_3

3 (n = 1)
4 (n = 0)

(1)

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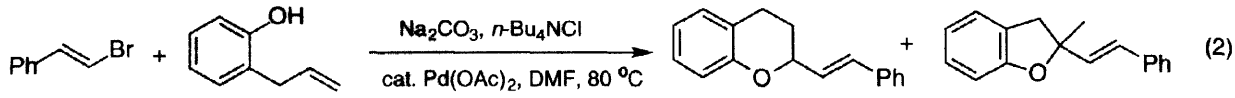
RESULTS AND DISCUSSION

On the basis of our previous experience with related reactions, our first attempts to effect the cross-coupling of an unsaturated phenol and a vinylic substrate were made by reacting 1 equiv of β-bromostyrene (**1a**, 0.25 mmol) with 1 equiv of commercially available *o*-allylphenol (**2a**) in the presence of Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.1 equiv) and 5 mol % of $Pd(OAc)_2$ in DMF (2 mL) (eq. 2). The reaction (80 °C, 24 h) afforded the



(2)

1a **2a** **3a** **5a**

desired 3,4-dihydro-2[(*E*)-β-styryl]-2H-1-benzopyran (**3a**) together with 2,3-dihydro-2-methyl-2[(*E*)-β-styryl]-benzofuran (**5a**) in 66% overall yield as a 91/9 inseparable mixture according to ^1H NMR spectroscopic data. Increasing the amount of phenol (**2a**) to 2 equiv led to a better yield (90 %). These latter conditions were successfully utilized for the reaction of other vinylic halides and triflates with *o*-allylphenol (**2a**) (Table 1, entries 1-20). In some cases, however, vinylic triflates required a different experimental procedure, employing 3.5 equiv of $KHCO_3$, 1.1 equiv of *n*-Bu_4NCl and 5 mol % of $Pd(OAc)_2$ in MeCN at 80 °C (Table 1, entries 13, 17, 19 and 20). Acyclic, cyclic, terminal and internal vinylic halides and triflates have all been employed in this cross-coupling process with little variation in yield. As anticipated (see the later discussion of mechanism), *(E)*- and *(Z)*-1-halo-1-alkenes both give exclusively the *(E)*-substituted product (entries 3 and 4). The yields with iodides, bromides and triflates are generally comparable. Shorter reaction times have usually been observed in the reactions employing vinylic triflates. The major by-product observed in the reactions of vinylic halides is the dihydrobenzofuran derivative (**5**) (entries 1-8). This type of side product is never observed in the reactions of the more hindered cyclic vinylic triflates (entries 10-20) or 4-phenyl-cyclohex-1-enyl iodide (entry 9). Good results were also obtained with *o*-methallylphenol (**2b**), which produces the corresponding cross-coupled products in relatively high yields and, as predictable (see the later discussion of mechanism), with complete regioselectivity (Table 1, entries 21-24). The reactions of vinylic halides with *o*-crotylphenol (**2c**) gave mixed results as expected for addition to the more hindered double bond. Only β-iodo- and β-bromostyrene gave good yields of the desired product, although it was produced as an inseparable mixture of six- and five-membered rings in a 4-5/1 ratio (Table 1, entries 25 and 26). Other vinylic halides, such as *(E)*-1-iodo-hexene (**1c**) and 1-iodo-2-methyl-propene (**1f**), produced only low yields of the corresponding cyclization products (Table 1, entries 27 and 28). With 1-iodo-2-methyl-propene, the reaction with 5 equiv of phenol **2c** resulted in a better yield (compare entries 28 and 29).

Consistent with our previous studies, the present reaction appears to proceed as depicted in Scheme 1. Oxidative addition of the vinylic halide or triflate **1** to Pd(0) and subsequent addition of the resulting vinylic palladium complex to the carbon-carbon double bond, followed by β-hydride elimination from the resultant σ-alkyl intermediate **6**, gives the η^2-diene complex **7**. The regioselective readdition of HPdX to the carbon-carbon double bond of complex **7** leads to a σ-allylpalladium intermediate **9**, which can rearrange to the π-allylpalladium complex **10**. Subsequent intramolecular nucleophilic attack of the phenoxy group on the π-allylpalladium intermediate results in the observed dihydrobenzopyran **3** or dihydrobenzofuran **4** and regeneration of the Pd(0)

Table 1. Pd-Catalyzed Cross-Coupling of Unsaturated Phenols with Vinylic Halides or Triflates.[a]

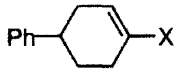
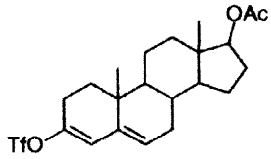
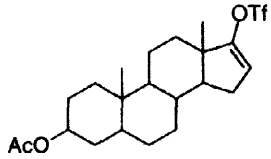
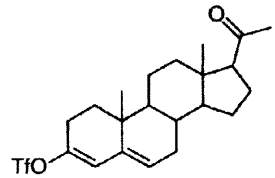
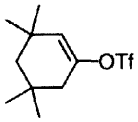
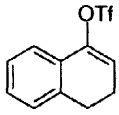
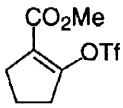
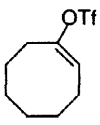
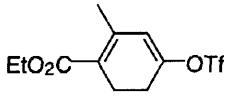
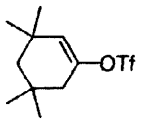
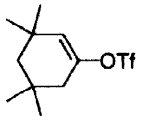
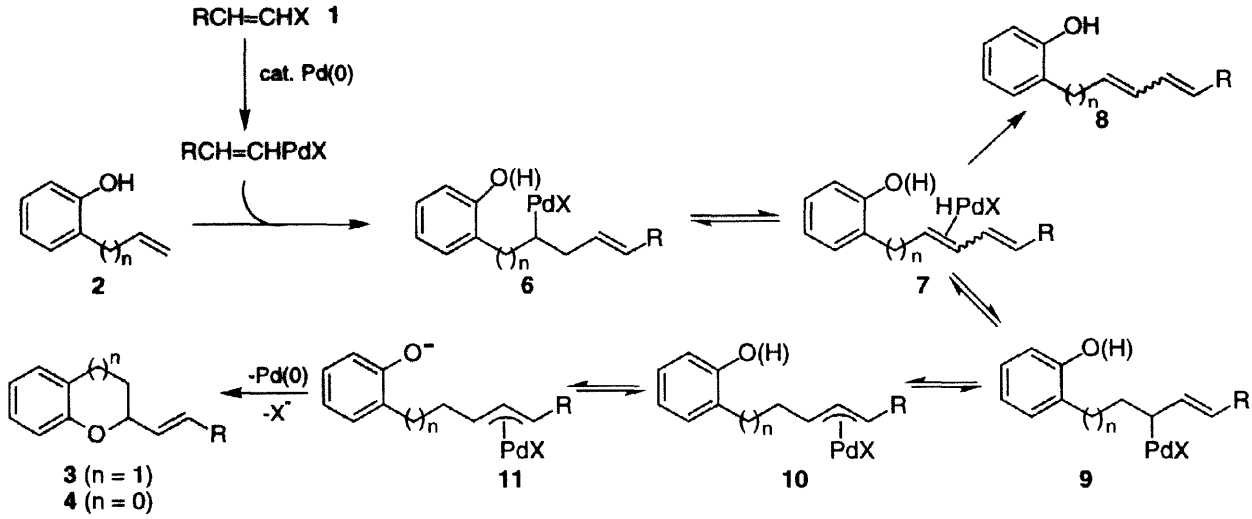
Entry	Vinylic halide or triflate (1)	Phenol (2)	Time (h)	Product(s)	% Yield[b,c]
1	*(E)*-PhCH=CHBr (**1a**)	*o*-$HOC_6H_4CH_2CH=CH_2$ (**2a**)	24	**3a** (**5a**)	82 (8)
2	*(E)*-PhCH=CHI (**1b**)		48		76 (8)
3	*(E)*-*n*-BuCH=CHI (**1c**)		36	**3b** (**5b**)	62 (10)
4	*(Z)*-*n*-BuCH=CHI (**1d**)		36		58 (9)
5	*(E)*-*t*-BuCH=CHBr (**1e**)		48	**3c** (**5c**)	14 (1)
6					32 (3)[d]
7	$(CH_3)_2C$=CHI (**1f**)		36	**3d** (**5d**)	68 (7)
8	*n*-BuCI=CH_2 (**1g**)		24	**3e** (**5e**)	57 (6)
9	 X = I (**1h**)		6	**3f**	55
10	X = OTf (**1i**)		8		53
11	 (**1j**)		5	**3g**	56
12	 (**1k**)		24	**3h**	50
13	 (**1l**)		1.5	**3i**	59[e]
14	 (**1m**)		3	**3j**	76
15	 (**1n**)		2	**3k** (**8k**)	29 (60)[e]
16	 (**1o**)		0.5	**3l**	8
17			1.0		63[e]
18	 (**1p**)		4	**3m**	28
19			2		41[e]
20	 (**1q**)		1	**3n**	58[e]

Table 1. (continued)

Entry	Vinylic halide or triflate (1)	Phenol (2)	Time (h)	Product(s)	% Yield[b,c]
21	*(E)*-PhCH=CHBr (**1a**)	*o*-$HOC_6H_4CH_2C(CH_3)=CH_2$ (**2b**)	24	**3o**	75[f]
22	*(E)*-PhCH=CHI (**1b**)		24		75[g]
23	*(E)*-*t*-BuCH=CHBr (**1e**)		24	**3p**	83[h]
24	$(CH_3)_2C$=CHI (**1f**)		24	**3q**	60[i]
25	*(E)*-PhCH=CHBr (**1a**)	*o*-$HOC_6H_4CH_2CH=CHCH_3$ (**2c**)	72	**3r** (**5r**)	56 (11)
26	*(E)*-PhCH=CHI (**1b**)		72		40 (10)
27	*(E)*-*n*-BuCH=CHI (**1c**)		24	**3s** (**5s**)	33 (4)
28	$(CH_3)_2C$=CHI (**1f**)		24	**3t** (**5t**)	25 (3)
29					49 (4)[d]
30	*(E)*-PhCH=CHBr (**1a**)	*o*-$HOC_6H_4CH=CH_2$ (**2d**)	24	**4a** (**15**)	56 (5)[j]
31			48		49 (3)[j,k]
32	*(E)*-PhCH=CHI (**1b**)		24		54 (18)[j,k]
33	*(E)*-*n*-BuCH=CHI (**1c**)		36	–	–
34	*(E)*-*t*-BuCH=CHBr (**1e**)		24	**4b**	40
35			48		53[k]
36	 (**1m**)		2	**4c** (**8c**)	20 (77)
37	*(E)*-PhCH=CHBr (**1a**)	*o*-$HOC_6H_4CH=CHCH_3$ (**2e**)	48	**4d**	36
38					54[k]
39	*(E)*-*t*-BuCH=CHBr (**1e**)		48	**4e**	20
40	 (**1m**)		5	**4f** (**8f**)	19 (23)

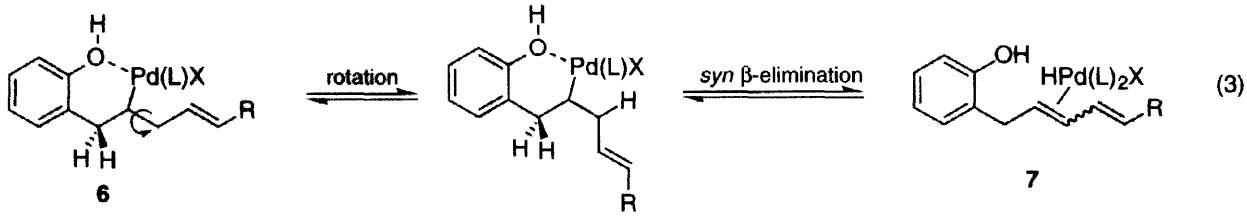
[a] Unless otherwise stated, reactions were carried out under an argon atmosphere at 80 °C in DMF for an appropriate time interval using the following molar ratios: **1**: **2**: Na_2CO_3: *n*-Bu_4NCl: $Pd(OAc)_2$ = 1 : 2 : 3.5 : 1.1 : 0.05. [b] Yields are given for isolated compounds. [c] Figures in parentheses refer to the yield of the indicated by-product in the mixture, calculated by ^1H NMR spectral analysis. [d] 5 Equiv of phenol **2c** were used. [e] The reaction was carried out using $KHCO_3$ (3.5 equiv.) as the base and MeCN as the solvent. [f] *Cis/trans* ratio is 77/23 (see ref. 12). [g] *Cis/trans* ratio is 71/29 (see ref. 12). [h] *Cis/trans* ratio is 70/30 (see ref. 12). [i] *Cis/trans* ratio is 50/50 (see ref. 11). [j] The number in parentheses refers to the yield of 2-benzyl-2H-1-benzopyran (**15**), calculated by ^1H NMR spectral analysis. [k] The reaction was carried out using K_2CO_3 (3.5 equiv) as the base and MeCN as the solvent.

catalyst. The depicted mechanism is strongly supported by the exclusive formation of *(E)*-substituted products, either from *(E)*- or *(Z)*-1-halo-1-alkenes, as a result of the known thermodynamic preference for *syn-syn*-π-allylpalladium formation (Table 1, entries 3 and 4). Intermediate **7** is assumed to completely rearrange to **9**, rather than undergo nucleophilic attack of the phenol or phenoxide on the complexed olefin in **7**, since the latter process (for n = 1) would be expected to produce heterocycles containing one less carbon in the ring than those actually obtained in the reaction. Vinylic substitution products **8**, derived from the irreversible elimination of palladium hydride from the complex **7**, have been isolated in only a few cases and generally in low yield. Only the reaction of triflate **1n** with *o*-allylphenol (**2a**) gave vinylic substitution as the main product (Table 1, entry 15). We have recently observed that free dienes analogous to **8** may be present in related nitrogen cyclizations leading to unexpected nitrogen heterocycles.[12] In the present reaction a mechanism involving the free diene would be expected to produce regioisomeric π-allylpalladium intermediates and products and we have no evidence of their formation. Consequently, we conclude that this mechanism is not operating here.



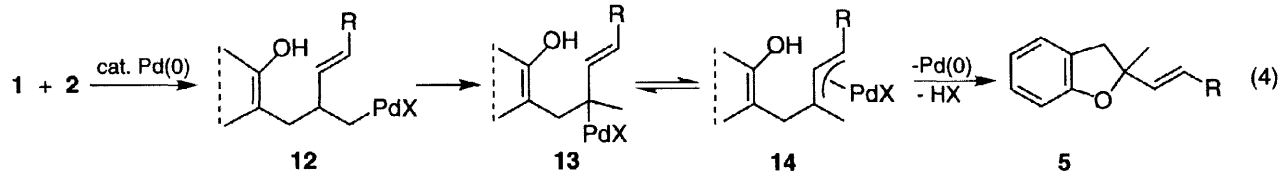
Scheme 1

The high regioselectivity observed in the *syn* β-elimination of HPdX from **6** can be tentatively accounted for by assuming that coordination of the phenolic (or phenoxy) group to the palladium in the σ-alkylpalladium adduct makes it difficult to achieve the conformation required for *syn* elimination of palladium and one of the benzylic hydrogens and thus directs elimination of the hydrido-palladium species towards the η^2-diene complex (**7**) (eq. 3). On the other hand, since *syn* β-elimination of HPdX appears to be reversible under our conditions, elimination of one of the benzylic hydrogens, followed by readdition and migration of palladium along the carbon chain resulting again in the π-allylpalladium complex **11** cannot *a priori* be excluded.



(3)

This process usually shows good regioselectivity in the step involving carbopalladation of the carbon-carbon double bond. Only low yields of the dihydrofuran derivatives **5**, derived from addition of the σ-vinylic palladium complex to the carbon-carbon double bond with the opposite regiochemistry, as noted earlier in similar reactions,[13] have sometimes been observed (eq. 4). The regiochemistry is accounted for by preferential



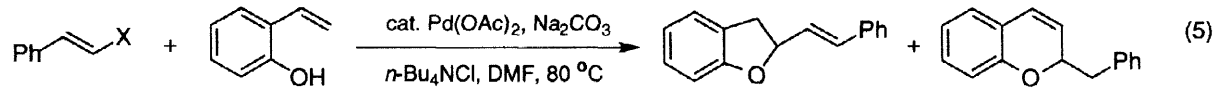
(4)

formation of the new carbon-carbon bond on the less hindered end of the starting alkene. The complete regioselectivity observed with *o*-methallylphenol (**2b**) (Table 1, entries 20-23), as expected for the carbopalladation of an α,α-disubstituted double bond, is in agreement with this view. The substitution pattern

of the transferred vinylic unit also seems to play a role. The greater regioselectivity obtained with vinylic triflates is probably related to the increased steric bulk of the vinylic unit (all the triflates tested are cyclic compounds), since it can reasonably be presumed that the nature of the anion of the vinylic palladium intermediate does not affect the regiochemical course of the reaction to a large extent. The nearly identical results obtained in the reactions of 4-phenyl-cyclohex-1-enyl triflate and 4-phenyl-cyclohex-1-enyl iodide (Table 1, compare entries 9 and 10) support this hypothesis. Coordination of the *o*-phenolic oxygen to palladium may also favor formation of intermediate **6** over **12**.

In light of the successful cross-coupling of *o*-allylic phenols, we have also examined analogous reactions of *o*-vinylic phenols, in order to extend the present methodology to the synthesis of dihydrobenzofurans (**4**) (Table 1, entries 30-40). The reaction of β-bromostyrene (**1a**, 0.25 mmol) with 2 equiv of *o*-vinylphenol (**2d**) in the presence of Na_2CO_3 (3.5 equiv), *n*-Bu_4NCl (1.1 equiv) and 5 mol % of $Pd(OAc)_2$ in DMF (2 mL) at 80 °C gave 2[(*E*)-β-styryl]-2,3-dihydrobenzofuran (**4a**) in satisfactory yield (56 %, 24 h) (Table 1, entry 30). However, the above conditions gave mixed results when applied to other vinylic halides and triflates and to more substituted *o*-vinylic phenols. Therefore, we examined the possible effects of different bases and solvents on the reaction outcome and, after a systematic screening, we have been able to arrive at new conditions (3.5 equiv of K_2CO_3, 1.1 equiv of *n*-Bu_4NCl, 5 mol % of $Pd(OAc)_2$ in MeCN at 80 °C), which in a few cases gave us better results (compare, for example, entries 34 and 35 or 37 and 38). However, no consistent advantages have been observed when these latter conditions have been applied. Thus, for reasons that escape us, (*E*)-1-iodo-1-hexene (**1c**) gave an intractable mixture of products when reacted with *o*-vinylphenol (entry 33).

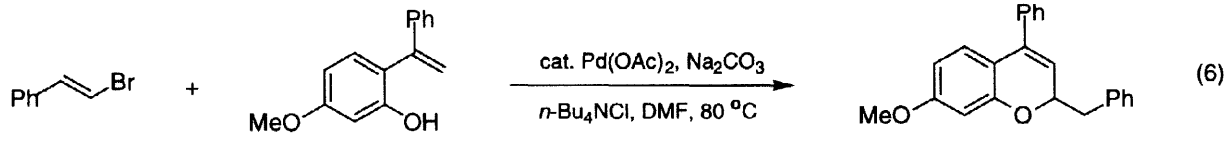
To our surprise, in the reaction of *o*-vinylphenol with β-bromo- and β-iodostyrene, the formation of a small amount (5 to 18%) of 2-benzyl-2H-1-benzopyran (**15**) was observed, together with the desired product (Table 1, entries 30-32) (eq. 5). Exposure of β-bromostyrene (**1a**) to 5-methoxy-2-(α-styryl)phenol



(5)

1a,b **2d** **4a** **15**

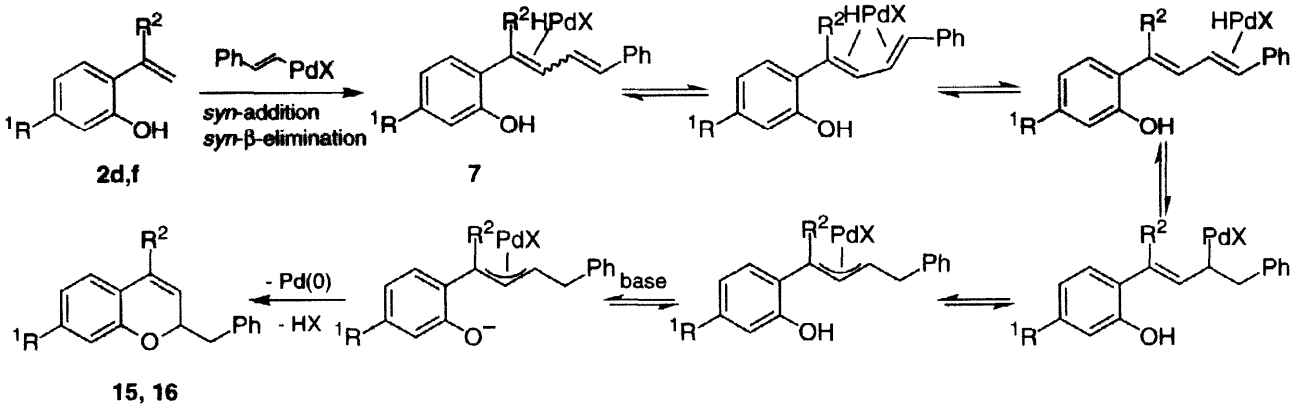
(**2f**) under our usual reaction conditions produced a messy reaction mixture, which nonetheless contained 2-benzyl-4-phenyl-7-methoxy-2H-1-benzopyran (**16**) as the main product (43 % yield, 3 h), along with other unidentified products (eq. 6).



(6)

1a **2f** **16**

The mechanism given above is not adequate to explain the formation of these products and, while we have not attempted any mechanistic work on this reaction, a possible rationale involves isomerization of the η^2-diene complex **7** by transfer of the HPdX moiety from one double bond to the other, as has sometimes been observed in Heck reactions (Scheme 2).[14] While we have tried to take synthetic advantage of this unusual reaction, since it suggests a promising new cyclization strategy, all our attempts to improve the yield of compound **16** gave unsatisfactory results. Further work on this process is needed.



Scheme 2

In conclusion, the methodology described in the present paper provides a simple, convenient entry into 2-vinylsubstituted dihydrobenzopyrans and dihydrobenzofurans from unsaturated halides or triflates and vinylic or allylic phenols. In this chemistry, the ability of palladium to migrate along the carbon chain without noticeable formation of vinylic substitution products upon appropriate choice of catalyst, base and additive affords a novel, new route to a variety of interesting oxygen heterocycles.

EXPERIMENTAL SECTION

General. Proton and carbon NMR spectra were recorded on a Nicolet NT-300 (at 300 MHz and 75.5 MHz, respectively) or on a Bruker AC 200 (at 200 MHz and 50.3 MHz, respectively). Infrared spectra were recorded with a Nicolet 5DX FT/IR or with a Beckman 4250 spectrometer. MS spectra were recorded with a Hewlett Packard HP 5980A spectrometer equipped with a Data System 5934A. High resolution mass spectral analyses were performed on a Kratos MS-50 spectrometer. Reaction products were purified on axially compressed columns, packed with 25-40μ SiO_2 (Macherey Nagel), connected to a Gilson solvent delivery system and a Gilson refractive index detector, or by flash column chromatography with 40-63μ SiO_2 (Merck).

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Palladium acetate was donated by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. or purchased from Aldrich and was used without further purification. All vinylic halides[15] and triflates,[16] *o*-crotylphenol (**2b**),[17] *o*-methallylphenol (**2c**),[17] *o*-vinylphenol (**2d**)[18] and 4-methoxy-2-(α-styryl)phenol (**2f**)[19] were synthesized by literature procedures.

General procedure for the palladium-catalyzed reactions with Na_2CO_3 as the base (procedure A). To a mixture of $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), 2.0 equiv of the *o*-allylic or *o*-vinylic phenol, 3.5 equiv of Na_2CO_3, 1.2 equiv of *n*-Bu_4NCl in 2 mL of DMF in a 1 dram vial was added 1 equiv of the vinylic halide or triflate (0.25 mmol). The vial was flushed with nitrogen and capped with a screw-cap containing a teflon liner. After heating at 80 °C for an appropriate time interval, the reaction mixture was diluted with ether and washed with saturated NH_4Cl, followed by water. The organic layer was dried over $MgSO_4$, filtered, concentrated and purified by flash column chromatography (vinylic halide reactions) or preparative HPLC (vinylic triflate reactions).

Palladium-catalyzed reactions with $KHCO_3$ as the base (procedure B). To a mixture of $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), $KHCO_3$ (0.875 mmol, 3.5 equiv), *n*-Bu_4NCl (0.30 mmol, 1.2 equiv) and *o*-allylphenol (0.5 mmol, 2 equiv) in 1.5 mL of MeCN, 0.25 mmol (1 equiv) of the corresponding vinylic triflate were added. The mixture was stirred under argon at 80 °C for an appropriate time and then, after the usual work-up, was purified by HPLC.

Palladium-catalyzed reactions with K_2CO_3 as the base (procedure C). To a 1 dram vial were added $Pd(OAc)_2$ (0.0125 mmol, 5 mol %), the corresponding vinylic halide (0.25 mmol), K_2CO_3 (0.875 mmol), *n*-Bu_4NCl (0.30 mmol), MeCN (1.5 mL) and the *o*-vinylic phenol (0.5 mmol). The vial was capped with a screw cap containing a Teflon liner. After heating at 80 °C for an appropriate time, the mixture was extracted (ether and saturated NH_4Cl), dried, concentrated and purified by flash column chromatography (silica gel, hexane/EtOAc as eluents).

The following dihydrobenzopyrans (**3**) and dihydrobenzofurans (**4**) were prepared according to the indicated procedures.

3,4-Dihydro-2-[*(E)*-β-styryl]-2H-1-benzopyran (3a) and 2,3-dihydro-2-methyl-2-[*(E)*-β-styryl]-benzofuran (5a) (entries 1 and 2, procedure A): oily mixture; IR ($CDCl_3$) 2952, 1608, 1229 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88-2.01 (m, 1 H), 2.01-2.18 (m, 1 H), 2.76-2.96 (m, 2 H), 4.68-4.75 (m, 1 H), 6.34 (dd, 1 H, *J* = 15.9 Hz, 6.0 Hz), 6.71 (d, 1 H, *J* = 15.9 Hz), 6.82-6.89 (m, 2 H), 7.05-7.16 (m, 2 H), 7.22-7.43 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.4, 28.0, 76.2, 116.9, 120.2, 121.8, 126.6, 127.3, 127.8, 128.5, 128.7, 130.0, 131.5, 136.5, 154.5; HRMS of the mixture *m/z* 236.1199 (calcd. 236.1201 for $C_{17}H_{16}O$). The presence of 2,3-dihydro-2-methyl-2-[(*E*)-β-styryl]-benzofuran (**5a**) was revealed in the ^1H NMR spectrum by the following signals: δ 1.65 (s), 3.14 (d, *J* = 15.3 Hz), 3.27 (d, *J* = 15.3 Hz).

2-[*(E)*-1-Hexenyl]-3,4-dihydro-2H-1-benzopyran (3b) and 2-[*(E)*-1-hexenyl]-2,3-dihydro-2-methylbenzofuran (5b) (entries 3 and 4, procedure A): oily mixture; IR ($CDCl_3$) 2955, 1610, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, *J* = 6.9 Hz), 1.25-1.45 (m, 4 H), 1.77-2.11 (m, 4 H), 2.71-2.93 (m, 2 H), 4.44-4.50 (m, 1 H), 5.61 (ddt, 1 H, *J* = 15.3, 6.6, 1.2 Hz), 5.81 (dt, 1 H, *J* = 15.3, 6.6 Hz), 6.78-6.85 (m, 2 H), 7.02-7.13 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.3, 24.5, 28.1, 31.2, 32.1, 76.5, 116.8, 120.0, 121.8, 127.2, 129.3, 129.5, 133.8, 154.7; HRMS of the mixture *m/z* 216.1518 (calcd. 216.1514 for $C_{15}H_{20}O$). The presence of 2-[(*E*)-1-hexenyl]-2,3-dihydro-2-methylbenzofuran (**5b**) was revealed in the ^1H NMR spectrum by the following signals: δ 1.53 (s), 3.02 (d, *J* = 15.6 Hz), 3.16 (d, *J* = 15.6 Hz).

3,4-Dihydro 2-[*(E)*-3,3-dimethyl-1-butenyl]-2H-1-benzopyran (3c) and 2,3-dihydro-2-[*(E)*-3,3-dimethyl-1-butenyl]-2-methylbenzofuran (5c) (entries 5 and 6, procedure A): oily mixture; IR ($CDCl_3$) 2959, 1582, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 1.77-1.90 (m, 1 H), 1.97-2.06 (m, 1 H), 2.71-2.93 (m, 2 H), 4.43-4.49 (m, 1 H), 5.52 (dd, 1 H, *J* = 15.9, 6.9 Hz), 5.82 (dd, 1 H, *J* = 15.6, 0.6 Hz), 6.80-6.85 (m, 2 H), 7.03-7.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.7, 28.4, 29.5, 33.0, 76.9, 116.9, 120.0, 121.9, 124.4, 127.2, 129.4, 129.5, 144.2; HRMS of the mixture *m/z* 216.1518 (calcd. 216.1514 for $C_{15}H_{20}O$). The presence of 2,3-dihydro-2-[(*E*)-3,3-dimethyl-1-butenyl]-2-methylbenzofuran (**5c**) was revealed in the ^1H NMR spectrum by the following signals: δ 1.00 (s), 1.52 (s), 3.01 (d, *J* = 15.3 Hz), 3.17 (d, *J* = 14.7 Hz).

3,4-Dihydro-2-(2-methyl-1-propenyl)-2H-1-benzopyran (3d) and 2,3-dihydro-2-methyl-2-(2-methyl-1-propenyl)-benzofuran (5d) (entry 7, procedure A): oily mixture; IR ($CDCl_3$) 2930, 1607,

1232 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (d, 3 H, J = 1.2 Hz), 1.79 (d, 3 H, J = 0.9 Hz), 1.81-2.00 (m, 2 H), 2.70-2.94 (m, 2 H), 4.69-4.77 (m, 1 H), 5.34-5.38 (m, 1 H), 6.75-6.85 (m, 2 H), 7.03-7.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.4, 24.8, 26.0, 28.1, 73.0, 116.9, 120.0, 121.8, 124.6, 127.2, 130.0, 137.1, 154.9; HRMS of the mixture *m/z* 188.1204 (calcd. 188.1201 for $C_{13}H_{16}O$). The presence of 2,3-dihydro-2-methyl-2-(2-methyl-1-propenyl)-benzofuran (**5d**) was revealed in the ^1H NMR spectrum by the following signals: δ 3.10 (d, J = 15.3 Hz), 3.29 (d, J = 15.3 Hz), 5.53-5.57 (m).

2-(1-Hexen-2-yl)-3,4-dihydro-2H-1-benzopyran (3e) and 2-(1-hexen-2-yl)-2,3-dihydro-2-methylbenzofuran (5e) (entry 8, procedure A): oily mixture; IR ($CDCl_3$) 2958, 1608, 1234 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7.2 Hz), 1.30-1.50 (m, 4 H), 1.83-2.23 (m, 4 H), 2.71-2.93 (m, 2 H), 4.46 (m, 1 H), 4.96 (d, 1 H, J = 1.2 Hz), 5.14 (s, 1 H), 6.80-6.86 (m, 2 H), 7.03-7.11 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 22.7, 24.9, 26.7, 30.2, 31.7, 78.4, 110.6, 116.8, 120.0, 121.9, 127.3, 129.4, 148.8, 155.0; HRMS of the mixture *m/z* 216.1520 (calcd. 216.1514 for $C_{15}H_{20}O$). The presence of 2-(1-hexen-2-yl)-2,3-dihydro-2-methylbenzofuran (**5e**) was revealed in the ^1H NMR spectrum by the following signals: δ 4.79 (s), 5.18 (s).

3,4-Dihydro-2-(4-phenylcyclohex-1-enyl)-2H-1-benzopyran (3f) (entries 9 and 10, procedure A): mp 97-8 °C; IR (KBr) 2926, 655, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60-2.50 (m, 8 H), 2.65-3.01 (m, 3 H), 4.35-4.45 (m, 1 H), 5.81-5.95 (m, 1 H), 6.71-7.35 (m, 9 H) ; ^{13}C NMR ($CDCl_3$) δ 24.8, 25.1, 26.4, 29.7, 33.3, 40.0, 79.2, 116.7, 121.9, 122.0, 123.2, 124.2, 126.9, 127.2, 128.4, 129.5, 137.4, 146.9, 155.0 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 290 (M^+, 100), 183 (62), 107 (100). Anal. calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64 ; found: C, 86.91; H, 7.74.

2-(17β-Acetoxyandrosta-3,5-dien-3-yl)-3,4-dihydro-2H-1-benzopyran (3g) (entry 11, procedure A): mp 154-56 °C; IR (KBr) 2923, 1772, 1169 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 0.98 (s, 3 H), 2.05 (s, 3 H), 4.50-4.35 (m, 1 H), 4.60 (t, 1 H, J = 8.3 Hz), 5.48 (bs,1 H), 6.02 (s, 1 H), 6.70-7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.0, 19.0, 20.6, 22.7, 23.5, 24.6, 25.3, 26.6, 27.6, 29.7, 31.6, 34.0, 35.2, 36.8, 42.5, 48.3, 51.2, 79.4, 82.8, 116.9, 121.9, 122.0, 123.6, 124.8, 127.2, 129.4, 135.3, 141.1, 155.2, 171.2 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 446 (M^+, 100), 431 (21). Anal. calcd. for $C_{30}H_{38}O_3$: C, 80.68; H, 8.58; found: C, 80.77; H, 8.64.

2-(3β-Acetoxyandrost-16-en-17-yl)-3,4-dihydro-2H-1-benzopyran (3h) (entry 12, procedure A): oil; IR (KBr) 2926, 1737, 1237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 3 H), 0.90 (s, 1.5 H), 0.95 (s, 1.5 H), 2.05 (s, 3 H), 2.65-3.00 (m, 2 H), 4.45-4.85 (m, 2 H), 5.60-5.80 (m, 1 H), 6.70-7.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 16.9, 20.9, 21.4, 24.8, 26.9, 27.4, 28.4, 31.1, 31.72, 34.0, 35.1, 35.6, 36.4, 44.7, 46.6, 54.7, 57.2, 73.4, 73.6, 116.7, 119.8, 121.8, 125.5, 126.1, 127.00, 129.3, 154.9, 170.6 (several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 448 (M^+, 23), 315 (28), 107 (100). Anal. calcd. for $C_{30}H_{40}O_3$: C, 80.32; H, 8.99; found: C, 80.21; H, 8.85.

2-(17β-Acetylandrosta-3,5-dien-3-yl)-3,4-dihydro-2H-1-benzopyran (3i) (entry 13, procedure B): oil; IR (KBr) 2926, 1767, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.50 (s, 3 H), 0.80 (s, 1.5 H), 0.85 (s, 1.5 H), 2.00 (s, 3 H), 4.15-4.45 (m, 2 H), 5.20-5.40 (m, 1 H), 5.85 (s, 1 H), 6.55-7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.0, 22.7, 24.2, 24.4, 25.1, 26.2, 29.6, 31.4, 31.7, 33.5, 34.6, 35.0, 38.7, 44.0, 46.06, 56.9, 63.5, 79.4, 115.9, 119.9, 121.8, 124.0, 125.7, 126.7, 127.6, 135.1, 140.9, 154.8, 210.23

(several signals overlap, because the product is a mixture of diastereoisomers); MS *m/z* (relative intensity) 430 (M^+, 100). Anal. calcd. for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89; found: C, 83.72; H, 8.97.

3,4-Dihydro-2-(3,3,5,5-tetramethylcyclohex-1-enyl)-2H-1-benzopyran (3j) (entry 14, procedure A): oil; IR (KBr) 2902, 1452, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.96 (s, 3 H), 1.00 (s, 6 H), 1.35 (s, 2 H), 1.65-2.01 (m, 4 H), 2.60-2.95 (m, 2 H), 4.31-4.34 (m, 1 H), 5.50 (s, 1 H), 6.71-7.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 25.0, 26.4, 29.8, 29.9, 30.2, 30.5, 31.5, 32.4, 38.0, 50.0, 79.7, 102.6, 116.8, 121.9, 123.0, 127.1, 129.3, 133.4, 155.2; MS *m/z* (relative intensity) 270 (M^+, 26), 163 (74), 133 (50), 107 (100). Anal. calcd. for $C_{19}H_{26}O$: C, 84.39; H, 9.69; found: C, 84.47; H, 9.76.

3,4-Dihydro-2-(3,4-dihydronaphth-1-yl)-2H-1-benzopyran (3k) (entry 15, procedure B): oil; IR (KBr) 2934, 1237, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95-2.40 (m, 4 H), 2.60-3.10 (m, 4 H), 5.03 (dd, 1 H, J = 2.3, 8.0 Hz), 6.26 (t, 1 H, J = 4.0 Hz), 6.75-7.40 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 25.0, 27.0, 28.6, 109.7, 116.9, 120.3, 122.9, 124.5, 125.2, 126.1, 126.4, 126.9, 127.9, 128.1, 129.6, 133.0, 136.8, 155.0; MS *m/z* (relative intensity) 262 (M^+, 83), 155 (100), 107 (21). Anal. calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92; found: C, 86.86; H, 6.80.

1-(3,4-Dihydronaphth-1-yl)-3-(*o*-hydroxyphenyl)-(*E*)-1-propene (8k) (entry 15, procedure B): oil; IR (KBr) 3230, 1620, 811 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (m, 2 H), 2.81 (t, 2 H, J = 8.0 Hz), 3.41 (d, 2 H, J = 7.0 Hz), 5.37 (bs, 1 H), 5.98 (t, 1 H, J = 4.0 Hz), 6.35 (dt, 1 H, J = 19.0, 7.0 Hz), 6.85-7.00 (m, 4 H), 7.05-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 28.1, 29.7, 115.4, 118.7, 122.2, 124.2, 126.1, 127.0, 127.7, 129.9, 132.1, 132.3, 134.9, 136.5, 138.6, 160.1; MS *m/z* (relative intensity) 262 (M^+, 22), 133 (45). Anal. calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92; found: C, 87.98; H, 6.83.

2-(2-Carbomethoxycyclopenten-1-yl)-3,4-dihydro-2H-1-benzopyran (3l) (entries 16 and 17, procedures A and B): oil; IR (KBr) 1737, 1237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70-2.15 (m, 4 H), 2.40-3.10 (m, 6 H), 3.77 (s, 3 H), 5.54-5.57 (m, 1 H), 6.50-7.15 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.4, 25.0, 26.3, 33.6, 51.2, 73.5, 116.5, 120.0, 121.8, 127.1, 128.2, 129.4, 154.7, 158.9, 165.6; MS *m/z* (relative intensity) 258 (M^+, 20), 151 (100). Anal. calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02; found: C, 74.34; H, 6.95.

2-(Cycloct-1-enyl)-3,4-dihydro-2H-1-benzopyran (3m) (entries 18 and 19, procedures A and B): oil; IR (KBr) 2934, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40-1.75 (m, 8 H), 1.75-2.10 (m, 2 H), 2.10-2.45 (m, 4 H), 2.65-3.10 (m, 2 H), 4.39-4.43 (m, 1 H), 5.74 (t, 1 H, J = 10.0 Hz), 6.70-7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 25.3, 25.8, 25.9, 26.3, 26.4, 26.9, 29.1, 30.0, 80.8, 116.2, 119.8, 121.9, 127.1, 127.5, 129.4, 140.0, 155.3; MS *m/z* (relative intensity) 242 (M^+, 28), 107 (100). Anal. calcd. for $C_{17}H_{22}O$: C, 84.25; H, 9.15; found: C, 84.32; H, 9.23.

2-(4-Carbethoxy-3-methylcyclohexa-1,3-dienyl)-3,4-dihydro-2H-1-benzopyran (3n) (entry 20, procedure B): oil; IR (KBr) 2934, 1704, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, 3 H, J = 8.2 Hz), 1.80-2.60 (m, 6 H), 2.20 (s, 3 H), 2.65-3.00 (m, 2 H), 4.22 (q, 2 H, J = 8.2 Hz), 4.53-4.56 (m, 1 H), 6.00 (s, 1 H), 6.70-7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 20.5, 23.3, 24.0, 24.5, 26.2, 59.8, 79.7, 116.6, 121.0, 121.6, 126.0, 127.3, 129.4, 142.7, 143.8, 154.5, 168.2; MS *m/z* (relative intensity) 298 (M^+, 100), 225 (80), 107 (79). Anal. calcd. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43; found: C, 76.41; H, 7.48.

3,4-Dihydro-3-methyl-2-[(*E*)-β-styryl]-2H-1-benzopyran (3o) (entries 21 and 22, procedure A): oil; IR ($CDCl_3$) 2969, 1608, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, 3 H, J = 6.9 Hz), 1.75-2.08 (m, 0.23 H), 2.20-2.35 (m, 0.77 H), 2.54 (dd, 0.77 H, J = 16.5, 7.2 Hz), 2.85 (dd, 0.23 H, J = 15.9, 4.8 Hz), 4.28 (t,

0.23 H, J = 8.1 Hz), 4.70-4.76 (m, 0.77 H), 6.27 (dd, 1 H, J = 15.9, 6.6 Hz), 6.69 (d, 1 H, J = 16.2 Hz), 6.38-6.89 (m, 2 H), 7.04 (d, 1 H, J = 7.5 Hz) (several peaks can't be assigned due overlap); ^{13}C NMR ($CDCl_3$) δ 30.9, 31.7, 116.5, 116.6, 116.9, 120.3, 121.0, 121.8, 125.9, 126.5, 126.6, 127.3, 127.4, 127.9, 128.5, 129.3, 130.0, 132.5, 133.4, 136.6, 153.7; HRMS of the mixture *m/z* 250.1365 (calcd. 250.1358 for $C_{18}H_{18}O$).

3,4-Dihydro-2-[*(E)*-3,3-dimethyl-1-butenyl]-3-methyl-2H-1-benzopyran (3p) (entry 23, procedure A): oil; IR ($CDCl_3$) 2962, 1610, 1232 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 2.1 H, J = 7.2 Hz), 0.96 (d, 0.9 H, J = 6.9 Hz), 1.03 (s, 6.3 H), 1.07 (s, 2.7 H), 1.80-1.93 (m, 0.3 H), 2.11-2.22 (m, 0.7 H), 2.48-2.54 (m, 1 H), 2.80 (dd, 0.3 H, J = 16.5, 5.1 Hz), 2.90 (dd, 0.7 H, J = 16.2, 5.4 Hz), 4.03 (t, 0.3 H, J = 8.7 Hz), 4.51 (dd, 0.7 H, J = 6.9, 2.7 Hz), 5.44 (dd, 1 H, J = 15.6, 6.9 Hz), 5.79 (dd, 0.7 H, J = 15.6, 0.6 Hz), 5.81 (d, 0.3 H, J = 15.6 Hz), 6.80-6.88 (m, 2 H), 7.00-7.15 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.4, 29.5, 29.6, 30.7, 31.8, 33.2, 33.5, 79.7, 83.3, 116.5, 116.7, 120.0, 121.1, 123.4, 127.2, 129.2, 129.9, 145.3, 146.3, 153.9, 154.4; HRMS of the mixture *m/z* 230.1677 (calcd. 250.1358 for $C_{16}H_{22}O$).

3,4-Dihydro-3-methyl-2-(2-methylpropenyl)-2H-1-benzopyran (3q) (entry 24, procedure A): oil; IR ($CDCl_3$) 2969, 1610, 1234 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (d, 1.5 H, J = 7.2 Hz), 1.73 (d, 1.5 H, J = 0.9 Hz), 1.77 (s, 3 H), 2.10-2.21 (m, 1 H), 2.48-2.53 (m, 0.5 H), 2.53-2.58 (m, 0.5 H), 2.82 (dd, 0.5 H, J = 16.5, 5.1 Hz), 2.90 (dd, 0.5 H, J = 16.2, 5.7 Hz), 4.37 (t, 0.5 H, J = 9.0 Hz), 4.82 (dd, 0.5 H, J = 9.0, 3.0 Hz), 5.28 (dt, 0.5 H, J = 9.3, 1.2 Hz), 5.34 (dt, 0.5 H, J = 9.0, 1.5 Hz), 6.78-6.86 (m, 2 H), 7.01-7.14 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.7, 18.8, 26.1, 26.2, 30.6, 30.7, 31.7, 31.8, 33.6, 33.7, 75.4, 78.2, 116.5, 116.8, 120.0, 121.1, 121.2, 122.1, 123.8, 127.1, 129.2, 130.7, 136.2, 137.6, 138.3, 153.9, 154.6; HRMS of the mixture *m/z* 202.1359 (calcd. 250.1358 for $C_{14}H_{18}O$).

3,4-Dihydro-2-methyl-2-[*(E)*-β-styryl]-2H-1-benzopyran (3r) and 2,3-dihydro-2-ethyl-2[*(E)*-β-styryl]-benzofuran (5r) (entries 25 and 26, procedure A): oily mixture; IR ($CDCl_3$) 2973, 1610, 1238 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 3 H), 1.85-2.06 (m, 2 H), 2.65-2.76 (m, 2 H), 6.23 (d, 1 H, J = 16.2 Hz), 6.52 (d, 1 H, J = 15.9 Hz), 6.82 (td, 1 H, J = 7.5, 0.6 Hz), 6.91 (d, 1 H, J = 8.4 Hz), 7,01, d, 1 H, J = 7.2 Hz), 7.12 (t, 1 H, J = 8.1 Hz), 7.19-7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.7, 32.3, 40.5, 116.9, 119.9, 121.4, 126.4, 127.4, 127.5, 128.5, 128.8, 129.4, 133.1, 136.7, 153.9; HRMS of the mixture *m/z* 250.1362 (calcd. 250.1358 for $C_{18}H_{18}O$). The presence of 2,3-dihydro-2-ethyl-2[*(E)*-β-styryl]-benzofuran (**5r**) was revealed in the ^{1}H NMR spectrum by the following signals: δ 1.01 (t, J = 7.5 Hz), 3.20 (bs), 6.29 (d, J = 16.2 Hz), 6.65 (d, J = 15.9 Hz).

2-[*(E)*-1-Hexenyl]-3,4-dihydro-2-methyl-2H-1-benzopyran (3s) and 2-ethyl-2[*(E)*-1-hexenyl]-2,3-dihydrobenzofuran (5s) (entry 27, procedure A): oily mixture; IR ($CDCl_3$) 2957, 1609, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 3 H, J = 7.2 Hz), 1.17-1.34 (m, 4 H), 1.41 (s, 3 H), 1.75-2.10 (m, 4 H), 2.63-2.73 (m, 2 H), 5.47 (d, 1 H, J = 15.6 Hz), 5.58 (dt, 1 H, J = 15.6, 6.3 Hz), 6.76-6.84 (m, 2 H), 7.00-7.12 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.1, 22.6, 27.3, 29.8, 31.4, 32.0, 32.3, 76.3, 116.9, 119.6, 121.5, 127.2, 129.3, 130.0, 133.2, 154.1; HRMS of the mixture *m/z* 230.1670 (calcd. 230.1671 for $C_{16}H_{22}O$). The presence of 2-ethyl-2[*(E)*-1-hexenyl]-2,3-dihydrobenzofuran (**5s**) was revealed in the ^{1}H NMR spectrum by the following signals: δ 0.94 (t, J = 7.5 Hz), 3.09 (bs), 5.70 (dt, J = 15.6, 6.6 Hz).

3,4-Dihydro-2-methyl-2-(2-methylpropenyl)-2H-1-benzopyran (3t) and 2-ethyl-2,3-dihydro-2-(2-methylpropenyl)-benzofuran (5t) (entries 28 and 29, procedure A): oily mixture; IR ($CDCl_3$)

1219 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 3 H), 1.64 (d, 3 H, *J* = 0.9 H), 1.79 (d, 3 H, *J* = 1.2 Hz), 1.71-1.81 (m, 1 H), 1.93-2.05 (m, 1 H), 2.64-2.87 (m, 2 H), 5.15-5.18 (m, 1 H), 6.77-6.84 (m, 2 H), 7.01-7.10 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.6, 22.6, 27.3, 27.5, 33.4, 76.4, 117.1, 119.7, 121.8, 127.0, 128.0, 129.3, 135.5, 154.0; HRMS of the mixture *m/z* 202.1359 (calcd. 202.1358 for $C_{14}H_{18}O$). The presence of 2-ethyl-2,3-dihydro-2-(2-methylpropenyl)-benzofuran (**5t**) was revealed in the ^1H NMR spectrum by the following signals: δ 0.95 (t, *J* = 7.2 Hz), 3.10-3.30 (m), 5.47 (s).

2,3-Dihydro-2-[*(E)*-β-styryl]-benzofuran (4a) and 2-benzyl-2H-1-benzopyran (15) (entries 30-32, procedures A and C): oily mixture; IR ($CDCl_3$) 2954, 1598, 1229 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.09 (dd, 1 H, *J* = 15.6, 7.8 Hz), 3.44 (dd, 1 H, *J* = 16.2, 8.4 Hz), 5.36 (dtd, 1 H, *J* = 15.3, 8.1, 0.6 Hz), 6.36 (dd, 1 H, *J* = 15.6 Hz, 7.2 Hz), 6.71 (d, 1 H, *J* = 15.6 Hz), 6.81-6.89 (m, 2 H), 7.10-7.20 (m, 2 H), 7.24-7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 36.4, 83.5, 109.5, 120.5, 124.9, 126.5, 126.7, 128.0, 128.1, 128.4, 128.6, 132.3, 136.3, 159.4; HRMS of the mixture *m/z* 222.1051 (calcd. 222.1045 for $C_{16}H_{14}O$). The presence of 2-benzyl-2H-1-benzopyran (**15**) was revealed in the ^1H NMR spectrum by the following signals: δ 2.91 (dd, *J* = 13.8, 6.3 Hz), 4.96-5.08 (m), 5.68 (dd, *J* = 9.9, 3.6 Hz), 6.41 (d, *J* = 9.6 Hz).

2,3-Dihydro-2-[*(E)*-3,3-dimethyl-1-butenyl]-benzofuran (4b) (entries 34 and 35, procedures A and C): oil; IR ($CDCl_3$) 2961, 1598, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 2.97 (dd, 1 H, *J* = 15.6, 8.4 Hz), 3.32 (dd, 1 H, *J* = 15.6, 9.0 Hz), 5.13 (q, 1 H, *J* = 8.4 Hz), 5.57 (dd, 1 H, *J* = 15.3, 7.8 Hz), 5.84 (dd, 1 H, *J* = 15.0, 0.9 Hz), 6.78 (d, 1 H, *J* = 7.8 Hz), 6.83 (td, 1 H, *J* = 7.5, 0.6 Hz), 7.08-7.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.4, 33.0, 36.5, 84.5, 109.4, 120.3, 124.1, 124.8, 127.0, 128.0, 145.6, 159.4; HRMS *m/z* 202.1362 (calcd. 202.1358 for $C_{14}H_{18}O$).

2,3-Dihydro-2-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-benzofuran (4c) (entry 36, procedure A): oil; IR (KBr) 1630, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 0.96 (s, 3 H), 1.01 (s, 3 H), 1.03 (s, 3 H), 1.35 (s, 2 H), 1.61-1.89 (m, 2 H), 3.03 (dd, 1 H, *J* = 15.6, 9.2 Hz), 3.26 (dd, 1 H, *J* = 15.6, 9.2 Hz), 5.13 (t, 1 H, *J* = 9.2 Hz), 5.53 (s, 1 H), 6.72-6.79 (m, 2 H), 7.02-7.21 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 29.9, 30.5, 31.4, 31.5, 32.5, 34.3, 36.8, 50.0, 86.9, 109.2, 124.8, 127.1, 128.0, 132.7, 133.6, 160.0; MS *m/z* (relative intensity) 256 (M^+, 39), 149 (59), 121 (100). Anal. calcd. for $C_{18}H_{24}O$: C, 84.31; H, 9.44; found: C, 84.44; H, 9.52.

***(E)*-2-(*o*-Hydroxyphenyl)-1-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-ethylene (8c) (entry 36, procedure A)**: mp 91-2 °C; IR (KBr) 3360, 1632, 240, 829, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (m, 2 H), 2.81 (t, 2 H, *J* = 8.0 Hz), 3.41 (d, 2 H, *J* = 7.0 Hz), 5.37 (bs, 1 H), 5.98 (t, 1 H, *J* = 4.1 Hz), 6.35 (dt, 1 H, *J* = 19.0, 7.0 Hz), 6.85-7.00 (m, 4 H), 7.05-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 28.1, 29.7, 115.4, 118.7, 122.2, 124.2, 126.1, 127.0, 127.7, 129.9, 132.1, 132.3, 134.9, 136.5, 138.6, 160.1; MS *m/z* (relative intensity) 256 (M^+, 22), 133 (45). Anal. calcd. for $C_{18}H_{24}O$: C, 84.31; H, 9.44; found: C, 84.44; H, 9.56.

2,3-Dihydro-2-methyl-2-[*(E)*-β-styryl]-benzofuran (4d) (entries 37 and 38, procedures A and C): oil; IR ($CDCl_3$) 2930, 1597, 1244 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 (s, 3 H), 3.30 (d, 1 H, *J* = 15.6 Hz), 3.44 (d, 2 H, *J* = 15.6 Hz), 6.56 (d, 1 H, *J* = 16.2 Hz), 6.82 (d, 1 H, *J* = 15.9 Hz), 6.98 (m, 2 H), 7.27-7.55 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 26.7, 42.7, 87.6, 109.6, 120.3, 125.1, 126.5, 126.6, 127.7, 128.0, 128.2, 128.6, 133.2, 136.6, 158.8; HRMS *m/z* 236.1208 (calcd. 236.1201 for $C_{17}H_{16}O$).

2,3-Dihydro-2-[*(E)*-3,3-dimethyl-1-butenyl]-2-methyl-benzofuran (4e) (entry 39, procedure A): oil; IR ($CDCl_3$) 2930, 1597, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.52 (s, 3 H), 3.02 (d, 1 H, *J* =

15.3 Hz), 3.17 (d, 1 H, J = 15.6 Hz), 5.61 (d, 1 H, J = 15.9 Hz), 5.75 (d, 1 H, J = 15.9 Hz), 6.74-6.85 (m, 2 H), 7.08-7.14 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.5, 30.6, 34.1, 44.1, 86.3, 106.3, 121.9, 126.6, 127.1, 128.4, 131.8, 135.4, 159.8; HRMS *m/z* 216.1520 (calcd. 216.1514 for $C_{15}H_{20}O$).

2,3-Dihydro-2-methyl-2-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-benzofuran (4f) (entry 40, procedure A): oil; IR (KBr) 2900, 1630, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 0.95 (s, 3 H), 0.98 (s, 3 H), 1.00 (s, 3 H), 1.31 (s, 2 H), 1.49 (s, 3 H), 1.77 (s, 2 H), 2.93 (d, 1 H, J = 15.5 Hz), 3.19 (d, 1 H, J = 15.5 Hz), 5.52 (s, 1 H), 6.81 (t, 2 H, J = 8.2 Hz), 7.11 (t, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 26.0, 29.4, 30.1, 30.6, 31.4, 31.9, 32.3, 38.5, 41.2, 49.7, 89.8, 109.5, 120.0, 125.1, 126.8, 128.0, 129.2, 136.1, 159.0; MS *m/z* (relative intensity) 270 (M$^+$, 20), 199 (29), 163 (37), 107 (100). Anal. calcd. for $C_{19}H_{26}O$: C, 84. 38; H, 9.70; found: C, 84.49; H, 9.83.

***(E)*-1-(*o*-Hydroxyphenyl)-2-(3,3,5,5-tetramethylcyclohex-1-en-1-yl)-propene (8f) (entry 40, procedure A)**: oil; IR (KBr) 3200, 1620, 828 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 1.11 (s, 6 H), 1.41 (s, 2 H), 1.76 (s, 3 H), 2.11 (s, 2 H), 5.04 (s, 1 H), 5.71 (s, 1 H), 6.38 (s, 1 H), 6.80-6.95 (m, 2 H), 7.00-7.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.3, 29.7, 30.1, 32.4, 33.1, 40.7, 50.2, 118.2, 120.8, 123.1, 124.5, 128.8, 132.1, 133.1, 136.1, 137.2, 156.2; MS *m/z* (relative intensity) 270 (M$^+$, 32), 255 (49), 199 (73), 135 (46), 107 (100). Anal. calcd. for $C_{19}H_{26}O$: C, 84.38; H, 9.70; found: C, 84.51; H, 9.83.

2-Benzyl-7-methoxy-4-phenyl-2H-1-benzopyran (16, procedure A): oil; IR ($CDCl_3$) 2969, 1610, 1238 cm^{-1}; ^{1}H NMR: 3.00 (dd, 1 H, J = 6.6, 13.5 Hz), 3.22 (dd, 1 H, J = 7.2, 13.5 Hz), 3.81 (s, 3 H), 5.10 (ddd, 1 H, J = 3.9, 7.2, 6.6 Hz), 5.56 (d, 1 H, J = 3.9 Hz), 6.42 (dd, 1 H, J = 2.4, 8.4 Hz), 6.51 (d, 1 H, J = 2.4 Hz), 6.94 (d, 1 H, J = 8.4 Hz), 7.26-7.36 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 41.3, 55.5, 76.0, 102.5, 106.8, 116.5, 120.5, 126.5, 126.6, 126.7, 127.8, 128.4, 128.5, 128.7, 129.7, 136.5, 137.3, 138.60, 155.0, 160.8; MS *m/z* (relative intensity) 328 (M$^+$, 9), 237 (100).

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