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Competitive pathways in Pd-catalyzed synthesis of arylphenols

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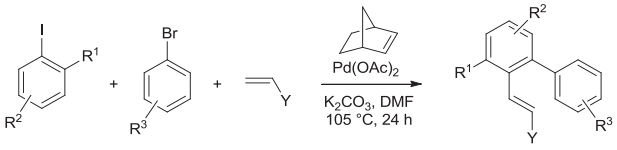
ABSTRACT

Novel developments are described, which have been achieved in the framework of the studies of sequential palladium-catalyzed reactions, involving palladacycle formation with norbornene or norbornadiene via aromatic C–H activation. The use of *o*-bromophenols as partners of iodobenzenes has led to ring formation after norbornene deinsertion, or to arylphenols, containing a pendant norbornenyl or norbornadienyl group or to vinylarylphenols. The availability of a reductive elimination step drives the reaction course toward a preferential product.

1. Introduction

Direct C–H activation of Csp^2 and Csp^3 bonds has opened a variety of synthetic pathways involving C–C bond formation.[1] Our studies in this area have been aimed at working out new methods to achieve ordered reaction sequences by means of palladium and norbornene joint catalysis involving palladacycle formation through C–H bond activation. We have previously shown that biphenyl derivatives can be prepared by reaction of *ortho*-substituted iodoarenes with bromoarenes, followed by a variety of irreversible intermolecular steps, such as Heck and Suzuki coupling leading to the final organic products.[2] The key for the success of these reactions is the use of iodoarenes, containing electron-releasing substituents, in conjunction with bromoarenes, bearing electron-withdrawing groups. If the latter substituents are present in iodoarenes, they render iodoarene reactivity too high, so that secondary reactions, not involving the bromoarene, predominate. Bromoarenes with donor substituents cannot be generally used because of their low reactivity.

Using this methodology some years ago we worked out a procedure leading to biaryl-bonded palladium complexes, which were caused to react further with olefins, in particular methyl acrylate, to terminate the process with liberation of palladium(0) (Scheme 1).[2c]



Scheme 1. Palladium/norbornene catalyzed synthesis of *o*-vinylbiaryl derivatives.

In continuation of this work we observed that also other bromoarenes, not containing electron-withdrawing substituents but having chelating properties, such as bromophenols, could be used as partners of the iodoarenes.[3] Our research thus led us to the synthesis of an important class of compounds, containing the base structure of cannabinoids. The one-pot reaction of an *ortho*-substituted iodoarene with an *o*-bromophenol and an electron poor olefin, such as an acrylic ester in the presence of $Pd(OAc)_2$ and norbornene as catalysts, potassium carbonate as a base in DMF as solvent at 80 °C for 24 h afforded the corresponding dibenzopyran derivative in good to excellent yields (Scheme 2). This result was achieved because the base present in the reaction mixture acted as a third catalyst to cause the phenolic group to

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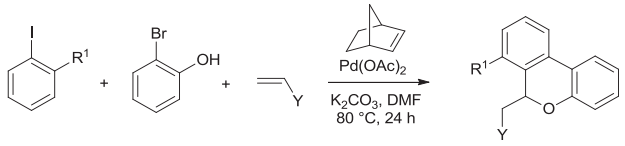
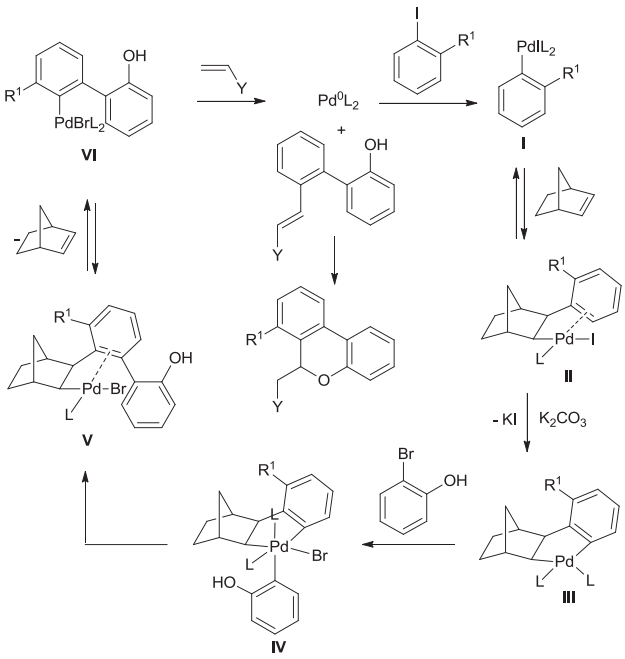
add to the double bond of the arylacrylate formed according to an intramolecular Michael reaction.[3]



Scheme 2. Synthesis of dibenzopyran derivatives.

The following Schemes 2 and 3 show the stoichiometry of the reaction and the corresponding reaction pathway, which is supported by the isolation of products and intermediates.[3,2a,b]



Scheme 3. Proposed reaction pathway to dibenzopyrans (L=solvent or any coordinating species present in the reaction mixture).

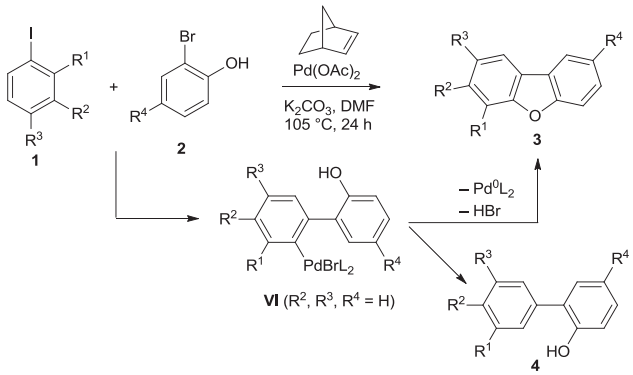
The initial oxidative addition of the iodoarene to the in situ formed palladium(0) species[4] is followed by stereoselective norbornene insertion into the arylpalladium bond of **I** leading to complex **II** with the aryl ring and the palladium group *cis* and *exo* to the norbornyl moiety.[5] This species, containing the palladium center weakly bound to the aromatic ring, readily undergoes palladacycle formation[6] through activation of the aromatic *ortho* C–H bond.[7] The subsequent oxidative addition of bromophenol to the palladium(II) metallacycle **III** to form palladium(IV) complex **IV**,[8] is followed by selective migration of the phenolic unit onto the aromatic site of the metallacycle to give the palladium(II) species **V**.[9] Norbornene deinsertion, likely due to the steric hindrance created by the two *ortho* substituents, affords the *o*-biarylpalladium bromide **VI**, which readily reacts with the terminal electron-poor olefin according to the Heck coupling. The resulting organic product undergoes Michael-type reaction to the dibenzopyran derivative. Both norbornene insertion (from **I** to **II**) and deinsertion (from **V** to **VI**) are equilibrium steps. It is worth noting that the deinsertion step is favored by the irreversible Heck coupling to yield the organic product and regenerate the palladium(0) catalyst.

Considering Scheme 3 the question arose of what would happen in the absence of the added olefin. Another pathway leading to reaction of the hydroxyl function with the palladium-bonded biaryl of complex **VI** seemed to be possible and we set out to gain insight on this point. The situation appeared much more complex than expected, however, because the presence of the phenolic group allowed competitive ways to be at work.

In the present paper we shall analyze the iodoarene/bromophenol/norbornene/palladium system and we shall see that the reaction can be driven toward different products by suitable termination steps.

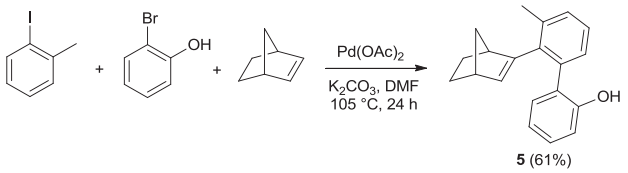
2. Results and discussion

We expected that the reaction between iodides **1** and bromophenols **2**, when carried out in the absence of an electron-poor olefin, such as methyl acrylate, could give rise to dibenzofurans **3** as a result of the attack of the phenolic hydroxyl on the arylpalladium bond of complex **VI** (Scheme 4).



Scheme 4. Formation of dibenzofurans.

Under the adopted conditions dibenzofuran **3** was obtained only to a limited extent (conditions for improving yields will be shown later in this text), the main product being a hydroxybiphenyl, still bonded to the dehydrogenated norbornyl group. Thus the reaction of *o*-iodotoluene and *o*-bromophenol with norbornene in the presence of $Pd(OAc)_2$ as catalyst, potassium carbonate as a base in DMF as solvent at 105 °C for 24 h gave dibenzofuran **3** (R^1=Me; R^2, R^3, R^4=H) in only 5% yield together with the arylphenol resulting from hydrogenolysis of complex **VI** (**4**; 2%) (Scheme 4), the main product being compound **5** (61% yield, Scheme 5). Formation of compound **5** meant that (a) norbornene was not deinserted, as usually observed; (b) there was a new type of termination, based on β-hydrogen elimination from the palladium-bonded norbornyl group.

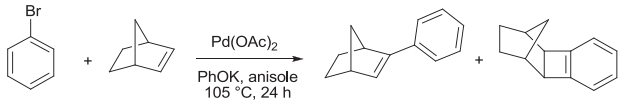


Scheme 5. Palladium-catalyzed reaction of *o*-iodotoluene, *o*-bromophenol with norbornene.

Observation (a) arises the question of why norbornene was not eliminated, contrary to what usually observed. It can be readily answered considering the coordinating effect of the phenolic group on the norbornyl-bonded palladium, possibly through formation of an eight-membered oxapalladacycle. Other type of oxapalladacycle complexes have been reported.[10]

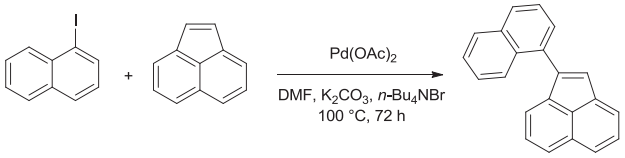
The latter observation (b) also leads to the question of why β-hydrogen elimination occurred on the palladium-bonded norbornyl. As Sicher first observed many years ago[11] this elimination in

the rigid norbornane system cannot occur intramolecularly because the correct stereochemical arrangement cannot be reached. We could show, however, that this becomes possible using an alkali phenoxide in a bimolecular reaction (Scheme 6).[12]



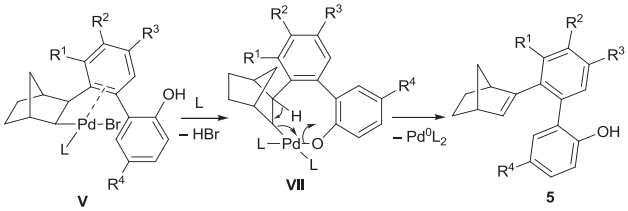
Scheme 6. Effect of PhOK in a palladium-catalyzed reaction of bromobenzene with norbornene.

Another instance of β-hydrogen elimination occurring in a rigid molecule has been reported by Dyker,[13] who caused 1-iodonaphthalene to react with acenaphthylene and obtained 1-(naphthalene-1-yl)acenaphthylene (Scheme 7). This is a special case, however, where double bond formation is favored by the particular aromatic structure of the molecule formed.



Scheme 7. β-Hydrogen elimination in the rigid structure of the acenaphthylene.

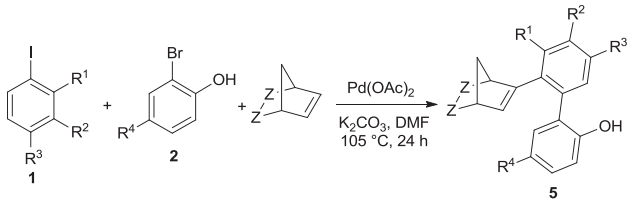
The formation of the double bond in the norbornenylarylphenol of Scheme 5 clearly appears to be analogous to that shown in Scheme 6. One can wonder, however, why a bimolecular β-hydrogen elimination did not occur earlier, when the arylnorbornylpalladium complex was present together with bromophenoxide. Apparently the latter is not able to abstract a proton at this stage and the system acquires the ability to do so only when the phenoxide can act intramolecularly. The process is depicted in Scheme 8 starting from intermediate **V** (Scheme 3), which, in place of undergoing norbornene deinsertion, retains norbornene through coordination of the hydroxyl group to palladium, possibly as in complex **VII**.



Scheme 8. Oxapalladacycle formation preventing norbornene deinsertion and favoring β-H elimination.

We observed a similar behavior with norbornadiene, which was previously shown to give rise to analogous palladium complexes.[14] Table 1 shows some norbornenyl- and norbornadienyl-substituted arylphenols, obtained in satisfactory yields as a mixture of two diastereoisomers. The molar ratio of the latter (determined by NMR) was 1.4:1 working at 105 °C in the case of norbornenyl-substituted arylphenols while the corresponding norbornadienyl derivatives were in the 1.1:1 molar ratio.

Table 1
Reaction of *o*-substituted iodoarenes and *o*-bromophenols with norbornene (Z–Z=CH_2–CH_2) or norbornadiene (Z–Z=CH=CH) in the presence of $Pd(OAc)_2$ and K_2CO_3 in DMF at 105 °C[a]



Entry	R^1	R^2	R^3	R^4	Z–Z	Yield of **5** (%)[b,c]
1	Me	H	H	H	CH_2–CH_2	61
2	Me	H	Me	H	CH_2–CH_2	62
3	Me	H	H	Me	CH_2–CH_2	71
4[d]	Me	H	OMe	H	CH_2–CH_2	64
5[e]	Me	OMe	OMe	H	CH_2–CH_2	74
6[f]	(CH=CH)$_2$		H	H	CH_2–CH_2	45
7	(CH=CH)$_2$		Me	H	CH_2–CH_2	56
8	(CH=CH)$_2$		OMe	H	CH_2–CH_2	60
9[g]	CF_3	H	H	H	CH_2–CH_2	45
10	Me	H	H	H	CH=CH	75
11	Me	H	H	Me	CH=CH	72
12	(CH=CH)$_2$		H	H	CH=CH	62

[a] Reaction conditions: molar ratio of the reaction components in the order reported in the title 25:25:30 (60 for norbornadiene):1:80; 105 °C for 24 h. DMF as solvent, under N_2; 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF.
[b] Isolated yield based on the amount of iodoarene put in reaction.
[c] Unless otherwise indicated benzofurans **3** and the corresponding arylphenols are each present in the range 2–10%. Other by-products, mainly derived from reaction of aryl iodide with norbornene/norbornadiene, have been reported previously.[2a,c,15]
[d] 48 h.
[e] 66 h.
[f] 16% yield of **3** (R^1, R^2=(CH=CH)$_2$; R^3, R^4=H).
[g] 45% yield of **3** (R^1=CF_3; R^2, R^3, R^4=H).

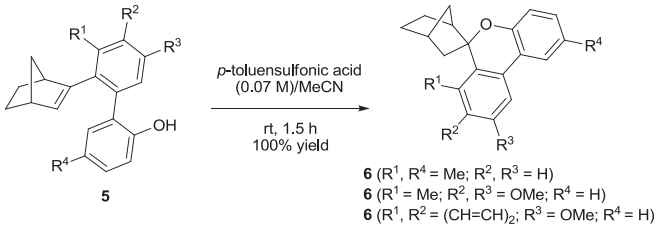
We can observe that the reaction works satisfactorily with various substrates both with norbornene and norbornadiene. Yields of dibenzofurans **3** were in general modest and only using the *o*-CF_3 group in the iodoarene could a satisfactory yield be obtained.[16] This result is likely due to the presence of an electron-withdrawing group in complex **VI** (Scheme 4) favoring the final cyclization step. Table 2 shows that although dibenzofuran formation through C–O coupling remains difficult in most cases,[17] it is enhanced by raising the temperature and decreasing the ratio between norbornene and palladium to half the stoichiometric amount, thus favoring norbornene expulsion.

Table 2
Reaction of *o*-substituted iodoarenes and *o*-bromophenols in the presence of norbornene, $Pd(OAc)_2$ and K_2CO_3 in DMF at 120 °C[a]

Entry	R^1	R^2	R^3	R^4	Yield of **3** (%)[b]	Yield of **5** (%)[b,c]
1	Me	H	H	H	45	36
2	(CH=CH)$_2$		H	H	24	37
3	CF_3	H	H	H	75	15

[a] Reaction condition: molar ratio of the reaction components in the order reported in the title 25:25:12:1:80; 120 °C for 24 h. DMF as solvent, under N_2; 2.2×10^{-3} mmol $Pd(OAc)_2$/mL DMF.
[b] Isolated yield based on the amount of iodoarene put in reaction.
[c] Two diastereoisomers in 1.1:1 molar ratio.

Going back to Scheme 8 we could expect a termination step consisting of reductive elimination leading to the formation of a ring joining the phenolic to the norbornyl group in oxapalladacycle **VII**. We did not observe this process, but ascertained that in the presence of a catalytic amount of acid, such as the *p*-toluenesulfonic one it is possible to convert these norbornenyl-substituted phenols quantitatively into oxaspiro compounds (Scheme 9).



Scheme 9. Acid-catalyzed quantitative conversion of **5** into oxaspiro compounds **6**.

The X-ray structure of compound **6** (R^1=Me; R^2, R^3=OMe; R^4=H) reveals the presence of only one stereoisomer (Fig. 1). It is further supported by NMR determinations.

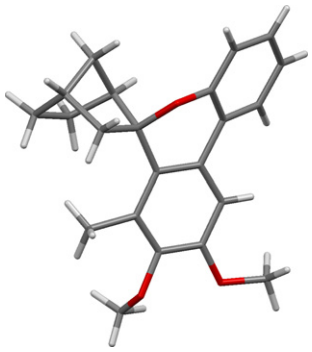
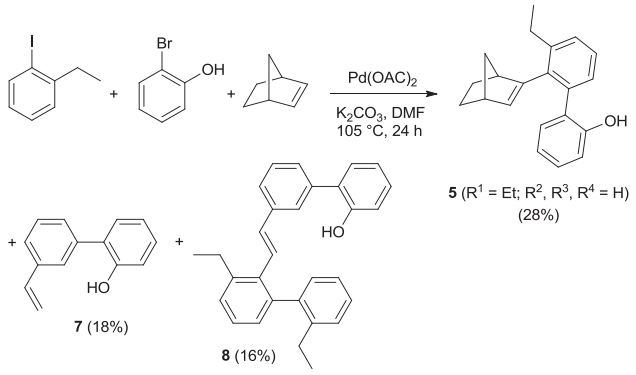


Fig. 1. X-ray structure of compound **6** (R^1=Me; R^2, R^3=OMe; R^4=H).

Another surprising result consisted of the unexpected dehydrogenation of alkyl groups present in the *ortho* position of the starting iodoarene (Scheme 10). The reaction of *o*-iodoethylbenzene and *o*-bromophenol with norbornene, under the conditions reported in Table 1, gave compound **5** (R^1=Et; R^2, R^3, R^4=H) together with the vinylphenylphenol **7** and compound **8** in 28%, 18%, and 16% yield, respectively. Compound **8** results from a secondary reaction, which takes place by arylation of the first formed vinyl group by another molecule of palladium-bonded biaryl.

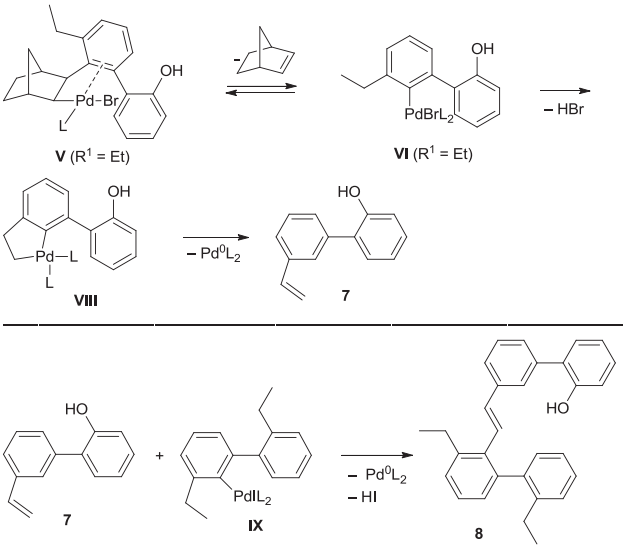


Scheme 10. Dehydrogenation of an aryl-bonded ethyl group.

The reaction proceeds as in Scheme 3 until complex **V** (R^1=Et) is formed. At this point the steric hindrance generated by the presence of the two ortho substituents causes norbornene deinsertion and the resulting arylpalladium bromide **VI** (R^1=Et) forms the palladacycle ring **VIII**, which undergoes reductive elimination to vinylphenylphenol **7**. A secondary Heck type reaction with complex **IX** leads to compound **8**. The combined yields of **7** and **8** shows that dehydrogenation represents the majority of the reaction outcome.

Dehydrogenation of alkyl groups in iodoarenes had been reported[18] but we did not expect that it could occur after the formation of the biphenyl structure, with the hydroxyl group still free to undergo intramolecular cyclization. Apparently dibenzofuran ring formation is rather difficult and subject to competitive reactions.[17]

A general consideration is appropriate at this point. The elimination of norbornene from the (*o*-hydroxyphenyl)arylnorbornylpalladium complex (**V**, Scheme 3) resulting from aryl coupling depends on the availability of irreversible steps leading to a final product with concomitant liberation of palladium(0). If we compare Schemes 5 and 11 where the starting iodoarenes differ only by a methylene group we notice that in the latter norbornene is deinserted (from **V** to **VI** (R^1=Et)) to a significant extent because there is the possibility of hydrogen elimination from the ethyl group, which is absent in the case of Scheme 5. In the latter case the norbornyl group is preserved and undergoes another type of elimination, leading to norbornenylbiphenylphenol **5** predominantly. Similarly the addition of methyl acrylate (Scheme 2) causes the complete elimination of norbornene to allow the biarylpalladium complex thus formed to undergo the irreversible step consisting of a Heck reaction. Norbornene elimination to form dibenzofurans does not occur so easily because ring formation by C–O coupling is more difficult and requires less norbornene and higher temperature.



Scheme 11. Proposed pathways for ethyl dehydrogenation and vinyl arylation.

3. Conclusions

In conclusion the reactions of bromoarenes containing a phenolic function with iodoarenes under palladium/norbornene catalysis, involving palladacycle formation via C–H activation, offer versatile systems allowing to steer reactivity in different directions.

4. Experimental section

4.1. General

Most starting materials were commercially available and were used without further purification. 2,5-Norbornadiene was distilled through a Vigreux column prior to use. 4-Methoxy-2-methyliodobenzene was prepared starting from the corresponding aniline by diazotization procedure.[19] 3,4-Dimethoxy-2-methyliodobenzene,[20] 1-iodo-4-methylnaphthalene,[21] and 1-iodo-4-methoxynaphthalene[22] were prepared according to reported procedures.

All reactions were carried out under nitrogen using standard Schlenk techniques. DMF was dried and stored over 4 Å molecular sieves under nitrogen. Gas chromatography analyses were performed with an Agilent Technologies 7820A GC System using a 30 m SE-30 capillary column. Flash column chromatography was carried out on Merck Kieselgel 60 and TLC on Merck $60F_{254}$ plates. Mass spectra (EI) were obtained with a Hewlett Packard instrument working at 70 eV ionization energy. NMR spectra were recorded in $CDCl_3$ on Bruker AC-300 and AVANCE 300 spectrometers, unless otherwise indicated. Chemical shifts are reported in parts per million using the solvent as internal reference (7.26 and 77.00 ppm, respectively for ^1H and ^{13}C). The reported assignments are based on 2D experiments (COSY and NOESY). Melting points were determined with an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

4.2. General procedure for the reaction of *ortho*-substituted aryl iodides with 2-bromophenols and norbornene/norbornadiene

A Schlenk-type flask, equipped with a magnetic stirring bar, was charged under nitrogen with K_2CO_3 (246 mg, 1.78 mmol) and with a DMF solution (5 mL) of $Pd(OAc)_2$ (5 mg, 0.022 mmol). A DMF solution (5 mL) of the *ortho*-substituted aryl iodide (0.56 mmol), the 2-bromophenol (0.56 mmol), and norbornene (63 mg, 0.67 mmol) or norbornadiene (123 mg, 1.34 mmol) was then added. The resulting mixture was stirred in an oil bath at 105 °C for 24–66 h. After cooling to room temperature, the mixture was diluted with EtOAc (30 mL) and washed with a saturated solution of NaCl (3×25 mL). The organic layer was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the products were isolated by flash column chromatography on silica gel using mixtures of hexane–EtOAc as eluent.

4.3. Characterization data

*4.3.1. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-3′-methyl-[1,1′-biphenyl]-2-ol (**5**, R^1=Me, R^2, R^3, R^4=H, Z–Z=CH_2–CH_2; Table 1, entry 1).* From 2-iodotoluene (122 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 61% (94 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^1H NMR: δ 7.29–7.17 (m, 4H (A), 3H (B)), 7.15–7.08 (m, 1H (A), 1H (B)), 7.04 (d, J=7.0 Hz, 1H (B)), 7.00–6.81 (m, 2H (A), 2H (B)), 6.02, 5.84 (2 d, J=2.8 Hz, 1H (A), 1H (B), =CH), 4.97, 4.90 (2 br s, 1H (A), 1H (B), OH), 2.89, 2.79 (2 br s, 1H (A), 1H (B), H4), 2.55, 2.48 (2 br s, 1H (B), 1H (A), H1), 2.33, 2.30 (2s, 3H (B), 3H (A)), 1.71–1.37 (m, 2H (A), 2H (B), H5*exo*, H6*exo*), 1.22–0.78 (m, 4H (A), 4H (B), H7*syn*, H7*anti*, H5*endo*, H6*endo*); ^{13}C NMR: δ 152.8, 152.3, 145.4, 144.8, 138.3, 137.7, 137.2, 136.4, 135.3, 135.0, 133.7, 132.7, 132.5, 131.1, 130.8, 130.5, 130.2, 130.1, 129.3, 129.2, 129.0, 128.8, 127.7, 127.4, 126.9, 120.1, 119.6, 116.1, 114.8, 48.8, 48.3, 47.7, 43.0, 42.8, 26.0, 25.9, 24.0, 23.9, 21.0, 20.8; MS (EI, 70 eV): M^+ 276 (53), m/z 261 (78), 248 (30), 233 (30), 219 (43), 195 (41), 178 (20), 165 (21). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.23; H, 7.32.

*4.3.2. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-3′,5′-dimethyl-[1,1′-biphenyl]-2-ol (**5**, R^1, R^3=Me, R^2, R^4=H, Z–Z=CH_2–CH_2; Table 1, entry 2).* From 2,4-dimethyliodobenzene (130 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 62% (101 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^1H NMR: δ 7.29–7.17 (m, 2H (A), 1H (B)), 7.12–7.08 (br s, 1H (A), 1H (B)), 7.04 (dd, J=7.2, 1.7 Hz, 1H (B)), 7.00–6.81 (m, 3H (A), 3H (B)), 6.00, 5.82 (2 d, J=3.0 Hz, 1H (A), 1H (B), =CH), 5.04, 4.98 (2 br s, 1H (A), 1H (B), OH), 2.88, 2.79 (2 br s, 1H (A), 1H (B), H4), 2.54, 2.47 (2 br s, 1H (B), 1H (A), H1), 2.35 (br s, 3H (A), 3H (B), CH_3), 2.30, 2.27 (2s, 3H (B), 3H (A), CH_3), 1.71–1.37 (m, 2H (A), 2H (B), H5*exo*, H6*exo*), 1.22–0.78 (m, 4H (A), 4H (B), H7*syn*, H7*anti*, H5*endo*, H6*endo*); ^{13}C NMR: δ 152.8, 152.3, 145.4, 144.7, 137.8, 137.2, 137.1, 136.7, 136.3, 135.1, 134.9, 133.8, 133.6, 133.1, 131.14, 131.07, 130.9, 130.7, 129.5, 129.0, 128.8, 128.7, 128.3, 120.1, 119.6, 116.1, 114.7, 48.7, 48.3, 47.8, 43.0, 42.8, 26.03, 25.97, 24.0, 23.9, 20.94, 20.89, 20.77; MS (EI, 70 eV): M^+ 290 (38), m/z 275 (84), 247 (100), 233 (43), 222 (52), 209 (62), 189 (40), 165 (53), 152 (32). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.58; H, 7.57.

*4.3.3. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-3′,5-dimethyl-[1,1′-biphenyl]-2-ol (**5**, R^1=Me, R^2, R^3=H, R^4=Me, Z–Z=CH_2–CH_2; Table 1, entry 3).* From 2-iodotoluene (122 mg, 0.56 mmol), 2-bromo-4-methylphenol (105 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 71% (115 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^1H NMR: δ 7.29–7.21 (m, 2H (A), 2H (B)), 7.16–7.10 (m, 1H (A), 1H (B)), 7.08–6.98 (m, 2H (A), 1H (B)), 6.87–6.78 (m, 1H (A), 2H (B)), 6.04, 5.84 (2d, J=3.0 Hz, 1H (A), 1H (B)), 4.91, 4.82 (2 br s, 1H (A), 1H (B)), 2.91, 2.81 (2 br s, 1H (A), 1H (B)), 2.58, 2.51 (2 br s, 1H (B), 1H (A)), 2.34, 2.33, 2.30, 2.25 (4s, 3H (B), 3H (A), 3H (A), 3H (B)), 1.74–1.40 (m, 2H (A), 2H (B)), 1.31–0.78 (m, 4H (A), 4H (B)); ^{13}C NMR: δ 150.4, 149.9, 145.6, 144.7, 137.7, 137.5, 136.4, 136.2, 135.3, 134.9, 133.7, 132.2, 131.4, 131.2, 130.1, 129.9, 129.4, 129.2, 129.0, 128.7, 128.5, 128.1, 127.5, 127.4, 127.3, 126.8, 116.0, 114.4, 48.8, 48.1, 47.5, 43.0, 42.7, 25.9, 25.8, 23.9, 23.7, 20.9, 20.8, 20.5, 20.2; MS (EI, 70 eV): M^+ 290 (29), m/z 275 (100), 247 (55), 245 (52), 233 (49), 222 (34), 209 (54), 178 (21), 165 (23). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 87.12; H, 7.71.

*4.3.4. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-5′-methoxy-3′-methyl-[1,1′-biphenyl]-2-ol (**5**, R^1=Me, R^3=OMe, R^2, R^4=H, Z–Z=CH_2–CH_2; Table 1, entry 4).* From 4-methoxy-2-methyliodobenzene (139 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 64% (110 mg) yield. Eluent: hexane/EtOAc 95:5. Mp (hexane): 94 °C. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^1H NMR: δ 7.34–7.20 (m, 2H (A), 1H (B)), 7.09 (d, J=6.9 Hz, 1H (B)), 7.05–6.83 (m, 3H (A), 3H (B)), 6.76–6.68 (m, 1H (A), 1H (B)), 6.02, 5.84 (2d, J=2.4 Hz, 1H (A), 1H (B)), 5.16 (br s, 1H (A), 1H (B)), 3.84, 3.83 (2s, 3H (A), 3H (B)), 2.92, 2.82 (2 br s, 1H (A), 1H (B)), 2.56, 2.48 (2 br s, 1H (B), 1H (A)), 2.35, 2.32 (2s, 3H (B), 3H (A)), 1.76–1.40 (m, 2H (A), 2H (B)), 1.31–0.80 (m, 4H (A), 4H (B)); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 158.0, 152.7, 152.2, 145.1, 144.5, 139.3, 138.5, 138.0, 136.4, 134.9, 133.5, 130.9, 130.8, 130.6, 129.4, 129.2, 129.1, 128.8, 128.5, 120.2, 119.6, 116.2, 116.02, 115.98, 114.8, 113.6, 112.6, 55.2, 48.6, 48.5, 48.3, 47.8, 43.0, 42.7, 26.04, 25.96, 23.9, 23.8, 21.2, 21.1; MS (EI, 70 eV): M^+ 306 (69), m/z 291 (63), 289 (24), 278 (28), 263 (46), 261 (100), 249 (22), 238 (23), 225 (18), 165 (13). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.65; H, 7.30.

*4.3.5. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-4′,5′-dimethoxy-3′-methyl-[1,1′-biphenyl]-2-ol (**5**, R^1=Me, R^2, R^3=OMe, R^4=H, Z–Z=CH_2–CH_2; Table 1, entry 5).* From 3,4-dimethoxy-2-methyliodobenzene (156 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 74% (139 mg) yield. Eluent: hexane/EtOAc 9:1. Mp (hexane): 118 °C. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^1H NMR: δ 7.32–7.18 (m, 2H (A), 1H (B)), 7.06 (d, J=6.9 Hz, 1H (B)), 7.02–6.83 (m, 3H (A), 3H (B)), 6.72 (br s, 1H (A), 1H (B)), 5.98, 5.81 (2d, J=2.7 Hz, 1H (A), 1H (B)), 5.16 (br s, 1H (A), 1H (B)), 3.88, 3.86 (2s, 6H (A), 6H (B)), 2.90, 2.80 (2 br s, 1H (A), 1H (B)), 2.59, 2.49 (2 br s, 1H (B), 1H

(A)), 2.27, 2.23 (2s, 3H (B), 3H (A)), 1.75–1.36 (m, 2H (A), 2H (B)), 1.34–0.73 (m, 4H (A), 4H (B)); ^{13}C NMR: δ 153.0, 152.3, 151.7, 151.2, 147.0, 145.1, 144.4, 134.9, 133.5, 132.6, 132.0, 131.8, 131.0, 130.8, 130.5, 130.2, 129.3, 129.0, 128.7, 128.6, 120.0, 119.5, 116.1, 114.7, 112.3, 111.4, 60.0, 55.6, 48.6, 48.3, 47.8, 42.9, 42.7, 26.0, 25.8, 23.74, 23.65, 13.8, 13.7; MS (EI, 70 eV): M^+ 336 (79), *m*/*z* 321 (100), 308 (31), 291 (65), 277 (19), 255 (26), 178 (13), 165 (18). Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.79; H, 7.26.

*4.3.6. 2-(1-(Bicyclo[2.2.1]hept-2-en-2-yl)naphthalen-2-yl)phenol (**5**, R^1, R^2=(CH=CH)$_2$, R^3, R^4=H, Z–Z=CH$_2$–CH$_2$; Table 1, entry 6).* From 1-iodonaphthalene (142 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 45% (87 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 8.10–7.97 (m, 1H (B), 1H (A)), 7.94–7.80 (m, 2H (A), 2H (B)), 7.59–7.49 (m, 2H (A), 2H (B)), 7.44 (d, *J*=8.4 Hz, 1H (A), 1H (B)), 7.35–7.27 (m, 2H (A), 2H (B)), 7.16 (d, *J*=7.8 Hz, 1H (B)), 7.13–6.92 (m, 2H (A), 1H (B)), 6.30, 6.12 (2 d, *J*=2.8 Hz, 1H (A), 1H (B)), 5.12, 4.90 (2 s, 1H (A), 1H (B), OH), 3.05, 2.95 (2 br s, 1H (A), 1H (B)), 2.77, 2.65 (2 br s, 1H (B), 1H (A)), 1.89–1.49 (m, 2H (A), 2H (B)), 1.49–0.89 (m, 4H (A), 4H (B)); ^{13}C NMR: δ 153.0, 152.3, 144.2, 143.5, 136.5, 136.4, 134.8, 133.8, 133.3, 132.9, 132.0, 131.3, 130.9, 129.2, 129.0, 128.7, 128.1, 128.0, 127.8, 127.6, 126.6, 126.5, 126.4, 126.1, 125.9, 120.2, 119.9, 116.2, 114.9, 49.2, 49.1, 48.7, 48.5, 43.3, 43.1, 26.2, 26.0, 23.8; MS (EI, 70 eV): M^+ 312 (100), *m*/*z* 295 (9), 284 (44), 267 (49), 255 (31), 231 (28), 215 (13), 202 (13). Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: C, 88.67; H, 6.51.

*4.3.7. 2-(1-(Bicyclo[2.2.1]hept-2-en-2-yl)-4-methylnaphthalen-2-yl) phenol (**5**, R^1, R^2=(CH=CH)$_2$, R^3=Me, R^4=H, Z–Z=CH$_2$–CH$_2$; Table 1, entry 7).* From 1-iodo-4-methylnaphthalene (150 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 56% (109 mg) yield. Eluent: hexane/EtOAc 97:3. Mp (hexane): 131 °C. A 1.7:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 8.14–8.03 (m, 2H (A), 2H (B)), 7.64–7.51 (m, 2H (A), 2H (B)), 7.36–7.26 (m, 3H (A), 2H (B)), 7.17 (dd, *J*=7.5, 1.2 Hz, 1H (B)), 7.08–6.98 (m, 2H (A), 1H (B)), 6.95 (t further split, *J*=7.5 Hz, 1H (B)), 6.27, 6.10 (2d, *J*=2.7 Hz, 1H (A), 1H (B)), 5.14, 4.95 (2 br s, 1H (A), 1H (B)), 3.05, 2.95 (2 br s, 1H (A), 1H (B)), 2.78 (br s, 1H (B)), 2.76 (s, 3H (A), 3H (B)), 2.67 (br s, 1H (A)), 1.86–1.41 (m, 2H (A), 2H (B)), 1.39–0.91 (m, 4H (A), 4H (B)); ^{13}C NMR: δ 152.9, 152.3, 144.3, 143.5, 136.3, 135.1, 134.8, 134.3, 134.0, 133.3, 133.1, 132.9, 132.5, 132.4, 132.1, 131.4, 131.1, 130.8, 129.5, 129.2, 129.1, 128.9, 128.7, 128.5, 127.1, 126.5, 126.2, 126.02, 125.97, 125.95, 124.15, 124.12, 120.1, 119.8, 116.1, 114.8, 49.1, 49.0, 48.8, 48.6, 43.2, 43.1, 26.1, 26.0, 23.7, 23.6, 19.4, 19.3; MS (EI, 70 eV): M^+ 326 (100), *m*/*z* 311 (10), 298 (29), 283 (39), 281 (47), 269 (26), 257 (15), 245 (29), 239 (12). Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.02; H, 6.86.

*4.3.8. 2-((1-Bicyclo[2.2.1]hept-2-en-2-yl)-4-methoxynaphthalen-2-yl)phenol (**5**, R^1, R^2=(CH=CH)$_2$, R^3=OMe, R^4=H, Z–Z=CH$_2$–CH$_2$; Table 1, entry 8).* From 1-iodo-4-methoxynaphthalene (159 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 60% (115 mg) yield. Eluent: hexane/EtOAc 95:5. Mp (hexane): 137 °C. A 1.7:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 8.36–8.28 (m, 1H (A), 1H (B)), 8.02–7.89 (m, 1H (B), 1H (A)), 7.56–7.48 (m, 2H (A), 2H (B)), 7.36–7.25 (m, 2H (A), 1H (B)), 7.15 (dd, *J*=7.2, 1.2 Hz, 1H (B)), 7.06–6.95 (m, 2H (A), 1H (B)), 6.92 (t further split, *J*=7.5 Hz, 1H (B)), 6.74 (s, 1H (A), 1H (B)), 6.21, 6.01 (2d, *J*=2.7 Hz, 1H (A), 1H (B)), 5.19, 4.96 (2 br s, 1H (A), 1H (B)), 4.00, 3.98 (2s, 3H (A), 3H (B)), 3.00, 2.89 (2 br s, 1H (A), 1H (B)), 2.71, 2.58 (2 br s, 1H (B), 1H (A)), 1.81–1.36 (m, 2H (A), 2H (B)), 1.34–0.74 (m, 4H (A), 4H (B)); ^{13}C NMR: δ 154.7, 154.5, 152.9, 152.1, 144.0, 143.3, 136.0, 134.8, 133.7, 132.9, 131.7, 130.9, 130.6, 129.5, 129.1, 128.8, 128.6, 127.0, 126.8, 126.1, 125.6, 125.3, 125.2, 121.9, 120.1, 119.7, 116.1, 114.8, 106.6, 105.6, 55.4, 48.8, 48.7, 48.6, 48.4, 43.1, 42.9, 26.1, 26.0, 23.6; MS (EI, 70 eV): M^+ 342 (86), *m*/*z* 313 (26), 301 (15), 285 (31), 273 (44), 261 (100), 202 (22). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.37; H, 6.43.

*4.3.9. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-3′-trifluoromethyl-[1,1′-biphenyl]-2-ol (**5**, R^1=CF$_3$, R^2, R^3, R^4=H, Z–Z=CH$_2$–CH$_2$; Table 1, entry 9).* From 1-iodo-2-(trifluoromethyl)benzene (152 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 45% (83 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 7.80–7.72 (m, 1H (A), 1H (B)), 7.49–7.39 (m, 2H (A), 2H (B)), 7.33–7.21 (m, 1H (A), 1H (B)), 7.18 (dd, *J*=7.5, 1.5 Hz, 1H (A)), 7.06–6.85 (m, 2H (A), 3H (B)), 6.21, 6.06 (2 br s, 1H (A), 1H (B), =CH), 4.80, 4.73 (2 br s, 1H (A), 1H (B), OH), 2.84, 2.76 (2m, 1H (A), 1H (B), H4), 2.57, 2.53 (2m, 1H (B), 1H (A), H1), 1.68–1.48 (m, 1H (A), 1H (B), H5*exo*), 1.42–1.22 (m, 1H (A), 1H (B), H6*exo*), 1.20–0.80 (m, 4H (A), 4H (B), H5*endo*, H6*endo*, H7*syn*, H7*anti*); ^{13}C NMR: δ 152.5, 152.3, 142.6, 142.1, 137.0 (q, $J_{C,F}$=2.5 Hz), 135.9 (q, $J_{C,F}$=1.9 Hz), 134.9, 134.1, 131.6, 131.0, 129.7, 129.4, 128.3, 127.5, 127.1, 126.4, 126.3 (2 q, $J_{C,F}$=5.7 Hz), 124.0, 123.9 (2 q, $J_{C,F}$=273.8 Hz), 120.5, 120.1, 116.7, 115.3, 50.1, 49.9, 49.0, 48.6, 42.9, 42.7, 25.2, 25.1, 23.4, 23.3; MS (EI, 70 eV): M^+ 330 (63), *m*/*z* 302 (84), 285 (70), 261 (50), 249 (53), 233 (100), 215 (50), 202 (25). Anal. Calcd for $C_{20}H_{17}F_3O$: C, 72.72; H, 5.19. Found: C, 73.00; H, 5.16.

*4.3.10. 2′-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)-3′-methylbiphenyl-2-ol (**5**, R^1=Me, R^2, R^3, R^4=H, Z–Z=CH=CH; Table 1, entry 10).* From 2-iodotoluene (122 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornadiene (123 mg, 1.34 mmol), product **5** was obtained in 75% (115 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.1:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: 7.33–7.06 (m, 5H (A), 5H (B)), 7.00–6.85 (m, 2H (A), 2H (B)), 6.67, 6.60 (2m, 1H (A), 1H (B)), 6.55–6.49 (m, 1H (A), 1H (B)), 6.45 (d, *J*=2.7 Hz, 1H (B)), 6.21 (m, 1H (A)), 4.95, 4.85 (2 br s, 1H (A), 1H (B)), 3.57 (br s, 1H (A), 1H (B)), 3.22 (br s, 1H (A), 1H (B)), 2.29 (s, 3H (B)), 2.22 (s, 3H (A)), 1.89, 1.83 (2 d, *J*=5.7 Hz, 2H (B)), 1.79, 1.70 (2 d, *J*=5.7 Hz, 2H (A)); ^{13}C NMR: δ 154.6, 154.3, 152.5, 142.9, 142.7, 142.6, 141.8, 140.2, 140.1, 138.82, 138.77, 136.9, 136.6, 135.6, 135.0, 130.9, 130.7, 130.1, 130.0, 128.94, 128.88, 128.83, 128.6, 128.3, 128.2, 127.2, 127.1, 120.1, 119.9, 115.4, 115.3, 73.7, 56.6, 56.4, 50.9, 50.7, 21.3, 21.2; MS (EI, 70 eV): M^+ 274 (12), *m*/*z* 259 (10), 208 (100), 189 (11), 178 (16), 165 (33). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.33; H, 6.64.

*4.3.11. 2′-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)-3′,5-dimethylbiphenyl-2-ol (**5**, R^1=Me, R^2, R^3=H, R^4=Me, Z–Z=CH=CH; Table 1, entry 11).* From 2-iodotoluene (122 mg, 0.56 mmol), 2-bromo-4-methylphenol (105 mg, 0.56 mmol), and norbornadiene (123 mg, 1.34 mmol), product **5** was obtained in 72% (116 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.1:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 7.27–7.17 (m, 2H (A), 2H (B)), 7.14–7.06 (m, 1H (A), 1H (B)), 7.05–6.96 (m, 1H (A), 1H (B)), 6.90–6.84 (m, 1H (A), 1H (B)), 6.80 (d, *J*=8.0 Hz, 1H (A)), 6.74 (d, *J*=8.0 Hz, 1H (B)), 6.64 (m, 1H (A)), 6.54 (m, 1H (B)), 6.50 (d, *J*=2.7 Hz, 1H (A)), 6.45 (m, 1H (A)), 6.40 (d, *J*=2.7 Hz, 1H (B)), 6.16 (m, 1H (B)), 4.79, 4.63 (2 br s, 1H (A), 1H (B)), 3.54 (br s, 1H (A), 1H (B)), 3.20, 3.16 (2 partially overlapped br s, 1H (B), 1H (A)), 2.28 (s, 3H (B)), 2.26 (s, 3H (A), 3H (B)), 2.17 (s, 3H (A)), 1.89, 1.81 (2 d, *J*=5.7 Hz, 2H (B)), 1.76, 1.70 (2 d, *J*=5.7 Hz, 2H (A)); ^{13}C NMR: δ 154.8, 154.4, 150.2, 143.0, 142.7, 142.4, 141.7, 140.2, 140.0, 138.7, 138.5, 136.8, 136.5, 135.9, 135.3, 131.31, 131.26, 130.0, 129.9, 129.3, 129.2, 129.1, 128.9, 128.6, 128.3, 128.2, 128.1, 127.1, 127.0, 115.3, 115.1, 73.7, 56.6,

56.4, 50.9, 50.7, 21.35, 21.28, 20.4; MS (EI, 70 eV): M^+ 288 (9), *m/z* 222 (100), 207 (11), 179 (22), 178 (19), 165 (9). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.21; H, 6.91.

*4.3.12. 2-(1-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)naphthalen-2-yl)phenol (**5**, R^1, R^2,=(CH=CH)$_2$, R^3, R^4=H, Z–Z=CH=CH; Table 1, entry 12).* From 1-iodonaphthalene (142 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornadiene (123 mg, 1.34 mmol), product **5** was obtained in 62% (108 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.1:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 8.04 (d, *J*=7.8 Hz, 1H (B)), 7.98–7.75 (m, 3H (A), 2H (B)), 7.63–7.39 (m, 3H (A), 3H (B)), 7.37–7.17 (m, 2H (A), 2H (B)), 7.09–6.92 (m, 2H (A), 2H (B)), 6.91–6.69 (m, 2H (A), 2H (B)), 6.65 (br s, 1H (A)), 6.25 (br s, 1H (B)), 5.04, 4.89 (2 br s, 1H (A), 1H (B)), 3.73 (br s, 1H (A), 1H (B)), 3.34 (br s, 1H (A), 1H (B)), 2.09, 1.96 (2 d, *J*=5.7 Hz, 2H (B)), 1.91, 1.86 (2 d, *J*=5.7 Hz, 2H (A)); ^{13}C NMR: δ 153.5, 153.2, 152.5, 152.3, 143.1, 142.9, 142.8, 142.1, 141.8, 141.7, 133.3, 132.05, 132.00, 131.9, 131.6, 131.0, 130.8, 129.2, 129.10, 129.05, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 126.8, 126.64, 126.57, 126.4, 126.2, 125.5, 125.4, 120.2, 120.1, 115.6, 115.5, 73.9, 57.3, 57.1, 51.3, 51.1; MS (EI, 70 eV): M^+ 310 (16), *m/z* 243 (100), 215 (15), 213 (10). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.69; H, 5.91.

*4.3.13. 4-Methyldibenzo[b,d]furan[23] (**3**, R^1=Me, R^2, R^3, R^4=H; Table 2, entry 1).* From 2-iodotoluene (122 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (25 mg, 0.27 mmol), product **3** was obtained in 45% (46 mg) yield. Eluent: hexane/EtOAc 95:5.

*4.3.14. Benzo[d]naphtho[1,2-b]furan[23] (**3**, R^1, R^2=(CH=CH)$_2$, R^3, R^4=H; Table 2, entry 2).* From 1-iodonaphthalene (142 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (25 mg, 0.27 mmol), product **3** was obtained in 24% (29 mg) yield. Eluent: hexane/EtOAc 95:5.

*4.3.15. 4-(Trifluoromethyl)dibenzo[b,d]furan (**3**, R^1=CF_3, R^2, R^3, R^4=H; Table 2, entry 3).* From 1-iodo-2-(trifluoromethyl)benzene (152 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (25 mg, 0.27 mmol), product **3** was obtained in 75% (99 mg) yield. Eluent: hexane/EtOAc 95:5. ^{1}H NMR: δ 8.12 (d further split, *J*=7.9 Hz, 1H, H1), 7.97 (d further split, *J*=7.0 Hz, 1H, H9), 7.69, 7.67 (two partly overlapping d, 2H, H3, H6), 7.53 (ddd, *J*=8.5, 7.3, 1.2 Hz, 1H, H7), 7.45–7.36 (m, 2H, H2, H8); ^{13}C NMR: δ 156.4 (C5a), 152.1 (q, $J_{C,F}$=1.9 Hz, C4a), 128.1 (C7), 126.0, 124.3 (C1), 123.9 (q, $J_{C,F}$=4.7 Hz, C3), 123.4 (C8), 123.3 (q, $J_{C,F}$=272.1 Hz, CF_3), 122.9, 122.3 (C2), 120.7 (C9), 115.0 (q, $J_{C,F}$=33.8 Hz, C4), 112.1 (C6); MS (EI, 70 eV): M^+ 236 (100), *m/z* 217 (17), 186 (13), 139 (14). Anal. Calcd for $C_{13}H_7F_3O$: C, 66.11; H, 2.99. Found: C, 66.31; H, 3.03.

*4.3.16. 2,7-Dimethylspiro[benzo[c]chromene-6,2′-bicyclo[2.2.1]heptane] (**6**, R^1, R^4=Me, R^2, R^3=H; Scheme 9).* From the corresponding compound **5** (87 mg, 0.30 mmol) and *p*-toluenesulfonic acid (25 mg, 0.15 mmol) in MeCN (2 mL) at room temperature for 1.5 h, product **6** was obtained quantitatively. Mp (hexane): 114 °C. Eluent: hexane/EtOAc 95:5. ^{1}H NMR: δ 7.61 (d further split, *J*=7.7 Hz, 1H, H10), 7.54 (d, *J*=1.5 Hz, 1H, H1), 7.24 (t, *J*=7.7 Hz, 1H, H9), 7.09 (d further split, *J*=7.5 Hz, 1H, H8), 7.05 (dd, *J*=8.2, 1.9 Hz, 1H, H3), 6.87 (d, *J*=8.1 Hz, 1H, H4), 2.96 (dd, *J*=14.2, 2.1 Hz, 1H, H3′*endo*), 2.59 (s, 3H, CH_3(C7)), 2.52–2.48 (m, 1H, H4′), 2.42 (br d, *J*=5.1 Hz, 1H, H1′), 2.39 (s, 3H, CH_3(C2)), 2.07–1.94 (m, 2H, H7′*syn*, H3′*exo*), 1.60–1.48 (m, 2H, H5′*exo*, H5′*endo*), 1.34–1.17 (m, 1H, H6′*exo*), 1.08–0.96 (m, 2H, H6′*endo*, H7′*anti*); ^{13}C NMR: δ 150.2 (C4a), 134.7 (C7), 133.8 (C6a), 132.5 (C10a), 132.1 (C8), 130.6 (C2), 129.6 (C3), 127.3 (C9), 125.1 (C10b), 123.7 (C1), 122.3 (C10), 117.2 (C4), 88.9 (C2′), 44.3 (C1′), 39.4 (C3′), 36.9 (C4′), 35.6 (C7′), 29.4 (C5′), 24.7 (CH_3(C7)), 21.6 (C6′), 21.0 (CH_3(C2)); MS (EI, 70 eV): M^+ 290 (34), *m/z* 275 (100), 247 (51), 233 (49), 222 (32), 209 (42), 165 (15). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.97; H, 7.61.

*4.3.17. 8,9-Dimethoxy-7-methylspiro[benzo[c]chromene-6,2′-bicyclo[2.2.1]heptane] (**6**, R^1=Me, R^2, R^3=OMe, R^4=H; Scheme 9).* From the corresponding compound **5** (100 mg, 0.30 mmol) and *p*-toluenesulfonic acid (25 mg, 0.15 mmol) in MeCN (2 mL) at room temperature for 1.5 h, product **6** was obtained quantitatively. Mp (hexane): 165 °C. Eluent: hexane/EtOAc 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J*=7.8, 1.5 Hz, 1H), 7.23 (td, *J*=7.8, 1.2 Hz, 1H), 7.17 (s, 1H), 7.05 (td, *J*=7.5, 1.2 Hz, 1H), 6.97 (dd, *J*=7.8, 1.2 Hz, 1H), 3.95 (s, 3H), 3.80 (s, 3H), 3.00 (dd, *J*=14.1, 1.8 Hz, 1H), 2.55–2.46 (m, 4H), 2.40 (d, *J*=4.8 Hz, 1H), 2.05–1.96 (m, 2H), 1.62–1.45 (m, 2H), 1.35–1.20 (m, 1H), 1.10–0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 151.7, 147.0, 129.8, 128.6, 128.2, 127.3, 125.3, 122.8, 121.4, 117.5, 105.8, 89.0, 60.1, 55.5, 44.6, 39.4, 36.9, 35.6, 29.2, 21.5, 14.5; MS (EI, 70 eV): M^+ 336 (40), *m/z* 321 (100), 295 (9), 281 (7), 255 (44), 253 (28). Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19. Found: C, 78.38; H, 7.26.

*4.3.18. 12′-Methoxyspiro[bicyclo[2.2.1]heptane-2,5′-naphtho[1,2-c]chromene] (**6**, R^1, R^2=(CH=CH)$_2$, R^3=OMe, R^4=H; Scheme 9).* From the corresponding compound **5** (103 mg, 0.30 mmol) and *p*-toluenesulfonic acid (25 mg, 0.15 mmol) in MeCN (2 mL) at room temperature for 1.5 h, product **6** was obtained quantitatively. Mp (hexane): 230 °C. Eluent: hexane/EtOAc 95:5. ^{1}H NMR: δ 8.41 (d, *J*=8.7 Hz, 1H), 8.37 (dd, *J*=8.1, 1.8 Hz, 1H), 7.76 (dd, 7.8, 1.5 Hz, 1H), 7.55–7.41 (m, 2H), 7.29 (td, *J*=7.5, 1.8 Hz, 1H), 7.19 (s, 1H), 7.11 (td, *J*=7.5, 1.2 Hz, 1H), 7.03 (dd, *J*=7.8, 1.2 Hz, 1H), 4.09 (s, 3H), 3.34 (dd, *J*=14.7, 2.1 Hz, 1H), 2.68 (br s, 1H), 2.61 (br s, 1H), 2.22–2.12 (m, 2H), 1.92–1.79 (m, 1H), 1.73–1.58 (m, 1H), 1.38–1.22 (m, 2H), 1.18–1.09 (d further split, *J*=9.6 Hz, 1H); ^{13}C NMR: δ 155.0, 152.9, 133.0, 130.2, 129.0, 126.0, 125.9, 125.4, 124.6, 124.2, 124.1, 123.5, 122.5, 121.6, 117.4, 100.5, 89.0, 55.4, 44.9, 41.4, 37.2, 36.4, 28.5, 21.8; MS (EI, 70 eV): M^+ 342 (99), *m/z* 341 (96), 313 (28), 301 (17), 285 (33), 273 (36), 261 (100), 202 (19). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.29; H, 6.55.

*4.3.19. 2′-(Bicyclo[2.2.1]hept-2-en-2-yl)-3′-ethyl-[1,1′-biphenyl]-2-ol (**5**; Scheme 10).* From 2-iodoethylbenzene (130 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **5** was obtained in 28% (45 mg) yield. Eluent: hexane/EtOAc 95:5. Colorless oil. A 1.4:1 mixture of two stereoisomers indicated as A and B. ^{1}H NMR: δ 7.40–6.80 (m, 7H (A), 7H (B)), 5.99, 5.85 (2 d, *J*=2.9 Hz, 1H (A), 1H (B), =CH), 4.93, 4.91 (2 partially overlapped br s, 1H (A), 1H (B), OH), 2.95, 2.80 (2 br s, 1H (A), 1H (B)), 2.63, 2.60 (2 partially overlapped q, *J*=7.5 Hz, 2H (A), 2H (B), CH_2), 2.56, 2.50 (2 br s, 1H (B), 1H (A)), 1.72–1.38 (m, 2H (A), 2H (B)), 1.33–0.76 (m, 7H (A), 7H (B)); MS (EI, 70 eV): M^+ 290 (32), *m/z* 261 (100), 247 (25), 233 (58), 219 (24), 207 (26), 189 (14). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 87.04; H, 7.56.

*4.3.20. 3′-Vinylbiphenyl-2-ol (**7**; Scheme 10).* From 2-iodoethylbenzene (130 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **7** was obtained in 18% (20 mg) yield. ^{1}H NMR: δ 7.05 (br s, 1H, H2′), 7.49–7.43 (m, 2H), 7.38–7.33 (m, 1H), 7.31–7.22 (m, 2H), 7.04–6.96 (m, 2H), 6.77 (dd, *J*=17.6, 10.9 Hz, 1H), 5.82 (dd, *J*=17.6, 0.6 Hz, 1H), 5.32 (dd, *J*=10.9, 0.6 Hz, 1H), 5.21 (br s, 1H, OH); ^{13}C NMR: δ 152.4, 138.6, 137.3, 136.3, 130.1, 129.4, 129.2, 128.4, 127.9, 126.9, 125.7, 120.8, 115.8, 114.8; MS (EI, 70 eV): M^+ 196 (100), *m/z* 181 (32), 165 (21), 152 (19), 139 (11). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.54; H, 6.19.

*4.3.21. 3′-(2-(2′,3-Diethylbiphenyl-2-yl)vinyl)biphenyl-2-ol (**8**; Scheme 10).* From 2-iodoethylbenzene (130 mg, 0.56 mmol), 2-bromophenol (97 mg, 0.56 mmol), and norbornene (63 mg, 0.67 mmol), product **8**

was obtained in 16% (45 mg) yield. ^{1}H NMR: δ 7.95–6.95 (m, 16H), 6.23 (d, J=17.7 Hz, 1H), 5.14 (1H, br s, OH), 2.83, 2.40 (2 q further split, J=7.60 Hz, 4H, CH_2), 1.28, 1.03 (2 t, J=7.60 Hz, 6H, CH_3); MS (EI, 70 eV): M^+ 404 (100), m/z 375 (47), 346 (16), 221 (85), 193 (54), 178 (35).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 915263. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.UK).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.02.029. These data include MOL files and InChIKeys of the most important compounds described in this article.

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