Palladium-Catalyzed Reaction of Aryl Bromides with 7-Hydroxy-1,3-Dienes

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Palladium-catalyzed reaction of aryl bromides with 7-hydroxy-1,3-dienes proceeded in different reaction paths depending on the structure of the starting substrates. With cyclic 7-hydroxy-1,3-dienes, the reaction proceeded via insertion of the olefin into the Pd−O bond of a postulated Pd(Ar)(OR)-olefin complex to give a (η^1-allyl)palladium intermediate, which underwent $\eta^1-\eta^3-\eta^1$ allylic rearrangement followed by C−C bond-forming reductive elimination to afford overall 1,4-alkoxyarylation products, while with acyclic 7-hydroxy-1,3-dienes, the reaction produced 1,2-alkoxyarylation products under the same reaction conditions. The 1,2-alkoxyarylation products resulted from insertion of the olefin into either the Pd−C or the Pd−O bond of the postulated Pd(Ar)(OR)-olefin complex followed by reductive elimination.

Introduction

The palladium-catalyzed intramolecular addition reactions of alcohols with alkenes,[1] alkynes,[1a,2] 1,3-dienes,[3] and allenes[4] have been intensively studied, since they are often associated with high stereo- and regioselectivities. Furthermore, palladium can usually be used in catalytic amounts, tolerates a wide variety of functional groups, and proceeds under mild reaction conditions. Both Pd(0) and Pd(II) complexes are used to initiate catalytic cycles. Olefin complexes of Pd(II) are easily generated and highly reactive. Thus, they were among the first used to catalyze useful organic transformations and are among the most extensively developed. In general, Pd(0), from reductive elimination, is the product of the reaction. Therefore, for catalysis, an oxidant is needed to oxidize Pd(0) back to Pd(II) in the presence of reactants and products.[5] On the other hand, synthetically useful Pd(0) chemistry is based on the oxidative addition of vinyl, aryl, or allylic halides or triflates to Pd(0) to the corresponding Pd(II) species. Among them, the addition of arylpalladium(II) species to 1,3-dienes is known to afford π-allylpalladium intermediates,[6] and extensive work on the inter- and intramolecular displacement of palladium from π-allylpalladium compounds by carbon-[7] and hetero-nucleophiles[8] has been studied. Recently, Wolfe has demonstrated that $Pd_2(dba)_3$/dpe-phos[9]-catalyzed reaction of aryl and vinyl bromides with γ-hydroxy alkenes in the presence of NaO*t*Bu produced tetrahydrofurans resulting from intramolecular olefin insertion into a postulated Pd(Ar)-(OR)-olefin intermediate.[10] Insertion of the olefin into either the Pd−O or the Pd−C bond of the intermediate would both lead to tetrahydrofurans with high stereoselectivities. Herein, we wish to report on stereocontrolled palladium-catalyzed alkoxyarylation reactions of 7-hydroxy-1,3-dienes. Depending on the structure of the starting dienols, different types of products are formed.

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(9) dpe-phos = bis(2-diphenylphosphinophenyl) ether.

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With cyclic 7-hydroxy-1,3-dienes the reaction underwent insertion of the olefin into the Pd−O bond of a postulated Pd(Ar)(OR)-olefin complex to give a η^1-allylpalladium intermediate, which led to an overall 1,4-alkoxyarylation product after $\eta^1-\eta^3-\eta^1$ allylic rearrangement followed by C−C bond-forming reductive elimination, while with acyclic 7-hydroxy-1,3-dienes, the reaction produced 1,2-alkoxyarylation products under the same reaction conditions. The 1,2-alkoxyarylation products derived from insertion of the olefin into either the Pd−C or the Pd−O bond of the postulated Pd(Ar)(OR)-olefin complex followed by reductive elimination.

Results and Discussion

The starting 7-hydroxy-1,3-dienes **1a**−**e** (Table 1) were prepared from addition of 2.5 equiv of methyl (**1a**, **1d**, and **1e**), phenyl (**1b**), or benzylic (**1c**) Grignard reagents to the corresponding ester-functionalized 1,3-dienes.[11] Our alkoxyarylation study began with **1a** (entry1, Table 1). Reaction of cyclic 7-hydroxy-1,3-diene **1a** with bromobenzene using Wolfe's protocols (NaO*t*Bu and catalytic $Pd_2(dba)_3$/dpe-phos)[10] resulted in recovery of the starting dienol. However, we have found that Pd-$(PPh_3)_4$ with dpe-phos was an efficient catalyst for reaction of bromobenzene with **1a**. Thus, treatment of **1a** with 2.0 equiv of bromobenzene, 2.0 equiv of NaO*t*-Bu, 2 mol % of $Pd(PPh_3)_4$, and 2 mol % (dpe-phos) in THF at 65 °C under nitrogen for 2 h afforded a major product in 55% yield, identified as 2,2-dimethyl-5-phenylhexahydrobenzofuran **2a** (entry 1, Table 1). NOE experiments provided the initial evidence for support of all *syn* relationships among hydrogen atoms at C(a), C(b), and C(c) of **2a**. It is important to note that three stereogenic centers of **2a** are created; however, only the single diastereomer shown was isolated. The high diastereoselectivity observed in the formation of **2a** suggested that the reaction proceeded via the Pd(Ar)-(OR)-olefin intermediate **3** (Scheme 1) as proposed by Wolfe.[10] Intermediate **3**, which was presumably derived from chelation/direction by the substrate, could undergo insertion of the olefin into the Pd−O bond to give η^1-allylpalladium intermediate **4** (path A, Scheme 1). Intermediate **4** may undergo $\eta^1-\eta^3-\eta^1$ allylic rearrangement to the η^1-allylpalladium intermediate **5**. Intermediate **5** led to 1,4-alkoxyarylation product **2a** after C−C bond-forming reductive elimination (Table 1, entry 1) with concomitant regeneration of the Pd(0) catalyst. Alternatively, insertion of the olefin into the Pd−C bond of intermediate **3** would give the metallobicyclic intermediate **6** (path B, Scheme 1). Intermediate **6** led to 1,2-alkoxyarylation product **7** after C−O bond-forming reductive elimination. However, compound **7** was not observed. It is reasonable to state that the sterically congested bicyclic intermediate **6** may undergo β-Ph elimination to regenerate **3**, which led to the formation of 1,4-alkoxyarylation product **2a** via path A. The β-Ph elimination can be considered as the reverse of the olefin insertion step of the Heck reaction. It must be mentioned that arylpalladation reactions are not reversible in most cases; the known examples involve systems in which the (aryl)(alkyl)palladium intermediate does not have *syn*-β-hydrogen atoms.[12] Since intermediate **6** does not have β-hydrogen atoms *syn* to the palladium, the β-Ph elimination would likely proceed. Under the same reaction conditions, reaction of **1a** with 4-bromotoluene, 4-bromoanisole, and 2-bromonaphthalene afforded 1,4-alkoxyarylation products **2b** (62%), **2c** (84%), and **2d** (56%), respectively, as the major product in each case (Table 1, entries 2−4). The main side products observed in these reactions are dehalogenated arenes. Among them, use of an electron-rich aryl bromide (e.g., 4-bromoanisole) led to a significant increase in chemical yield in the preparation of hexahydrobenzofuran product **2c** (Table 1, entry 3). The structure of **2c** was accomplished by X-ray diffraction analysis. The all *syn* relative stereochemistry of **2c**, derived from *syn*-addition of the oxygen and the aryl group across the conjugated diene, further supports the proposed chelation/direction mechanism in Scheme 1. However, 1,4-alkoxyarylation/double-bond migration products **2e**−**g** (36−54% yields, entries 5−7, Table 1) were obtained when electron-deficient aryl bromides were employed as the coupling partners. Moreover, reactions of **1a** with β-bromostyrene (Table 1, entry 8) and 2-bromopyridine (entry 9, Table 1) also provided 1,4-alkoxyarylation/double-bond migration products **2h** (65%) and **2i** (48%), respectively. Interestingly, a different reaction path was observed in reactions of cyclic 7-hydroxy-1,3-dienes bearing two bulky substituents at the 7-position. For example, substrates **1b** and **1c**, which are substituted with diphenyl (**1b**) or dibenzyl (**1c**) groups at the 7-position, produced tetrahyrobenzofurans **2j** (65%, Table 1, entry 10) and **2k** (58%, entry 11, Table 1), respectively. Compounds **2j** and **2k** apparently derived from β-hydride elimination from η^1-allylpalladium intermediate **5** (Scheme 1). This result indicated that the rate of β-hydride elimination from **5** occurred more rapidly than that of C−C bond-forming reductive elimination when substrates carry two bulky groups at the 7-position.

Next, the analogous reactions of acyclic 7-hydroxy-1,3-dienes **1d**−**e** were examined, and the results are listed in entries 12−15, Table 1. Interestingly, reactions of **1d**,**e** with aryl bromides using the same reaction conditions provided 1,2-alkoxyarylation products **2l**−**o** (48−65% yields). The *syn*-1′,2-stereochemistry of tetrahydrofurans **2l**−**o** was assigned on the basis of comparison of the ^{13}C NMR chemical shifts to those of related compounds found in the literature.[13] The formation of 1,2-alkoxyarylation products from acyclic substrates may suggest that insertion of the olefin into the Pd−C bond of the Pd(Ar)(OR)-olefin **8** provided six-membered-ring metallocyclic intermediate **9** (path A, Scheme 2). Intermediate **9** may undergo C−O bond-forming reductive elimination to afford tetrahydrofurans **2l**−**o** with regeneration of the Pd(0) catalyst. Alternatively, insertion of the olefin into the Pd−O bond of **8** occurred to provide η^1-allylpalladium intermediate **10**. Intermediate **10** led to **2l**−**o** after C−C bond-forming reductive elimination (Scheme 2, path B). Moreover, the

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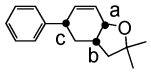
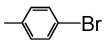
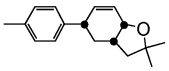
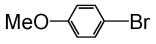
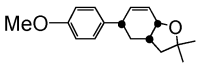
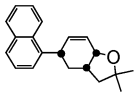
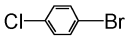
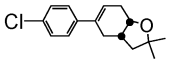
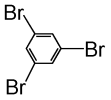
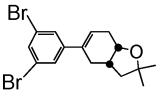
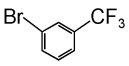
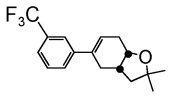
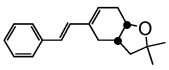
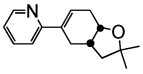
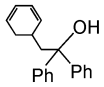
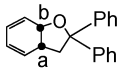
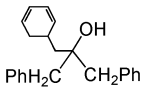
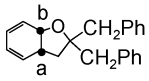
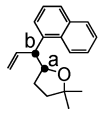
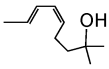
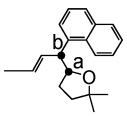
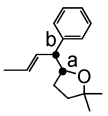
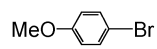
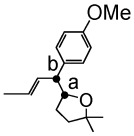
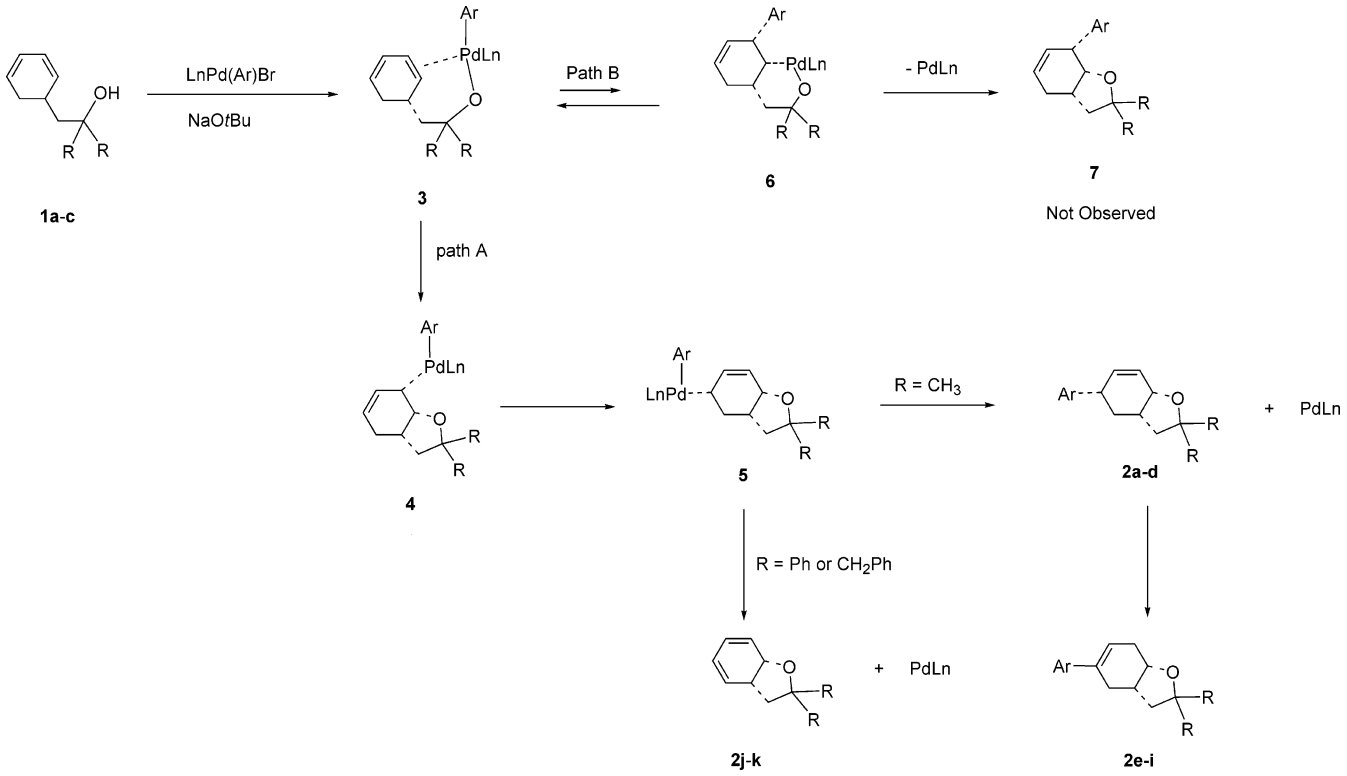
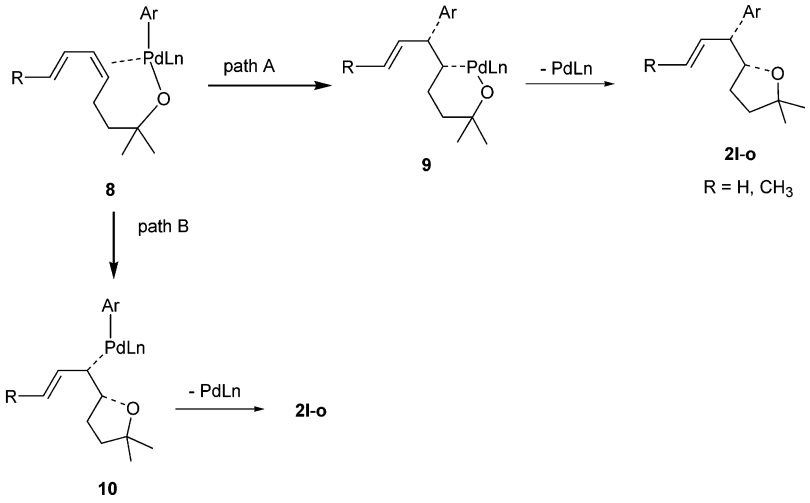
Table 1. Palladium-Catalyzed Intramolecular Reaction of 7-Hydroxy-1,3-diene with Aryl Bromides (2.0 mol) Using $Pd(PPh_3)_4$ (2.0 mol %), dpe-phos (2.0 mol %), and NaO*t*Bu (2.0 mol) in Refluxing THF for 2 h

entry	1,3-diene alcohol	aryl bromide	product		Yield (%)
1	 **1a**			**2a**	55
2	**1a**			**2b**	62
3	**1a**			**2c**	84
4	**1a**			**2d**	56
5	**1a**			**2e**	54
6	**1a**			**2f**	40
7	**1a**			**2g**	36
8	**1a**			**2h**	65
9	**1a**			**2i**	48
10	 **1b**			**2j**	65
11	 **1c**			**2k**	58
12	 **1d**			**2l**	48
13	 **1e**			**2m**	52
14	**1e**			**2n**	48
15	**1e**			**2o**	65

Scheme 1



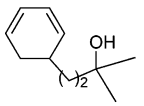
Scheme 2



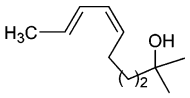
syn diastereoselectivity found for **2l**−**o** can be explained by both reaction paths in Scheme 2.[14] The isolation of only 1,2-alkoxyarylation products from acyclic precursors may suggest that the C−C bond-forming reductive elimination occurs from intermediate **10** at a rate that was faster than $\eta^1-\eta^3-\eta^1$ allylic rearrangement (path B, Scheme 1). The difference in formation of alkoxyarylation products (1,4- vs 1,2-alkoxyarylation) between cyclic and acyclic substrates could be explained as follows. The $\eta^1-\eta^3-\eta^1$ allylic isomerization may be faster in the cyclic intermediate **4** than the acyclic intermediate **10** for steric reasons. For example, intermediate **10** has more conformational flexibility to minimize unfavorable interactions via the σ-bond (Pd−C) rotation, whereas in **4**, the palladium fragment is on the concave face of a bicyclic ring system, and the $\eta^1-\eta^3-\eta^1$ allylic isomerization would place the palladium further away from the tertiary carbon center to furnish **5**. The η^1-allylpalladium intermediate **5** led to 1,4-alkoxyarylation products **2a**−**i** or alkoxylation/β-hydride elimination products **2j**−**k**.

Attempted synthesis of larger rings using longer tethers failed to give six-membered-ring heterocycles. For example, intramolecular alkoxyarylation reaction of 8-hydroxy-1,3-dienes **11** and **12** resulted in the recovery of starting dienols. Moreover, the Pd-catalyzed reaction of the primary alcohol **13** with bromobenzene failed to provide any tetrahydrofurans under the same reaction conditions. The main product in this reaction is aldehyde resulting from oxidation of the starting dienol.

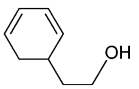
(14) The *anti*-1′,2-stereochemistry of tetrahydrofurans was obtained by *syn*-addition of the oxygen and the aryl group across the *E*-form carbon−carbon double bond. (See ref 10.)



11



12



13

In conclusion, the palladium-catalyzed reaction of aryl bromides with 7-hydroxy-1,3-dienes underwent various reaction paths depending on the structure of the starting substrates. With cyclic 7-hydroxy-1,3-dienes, insertion of the olefin into the Pd−O bond of the initially formed Pd(Ar)(OR)-olefin complex was predominant, and the reaction led to 1,4-alkoxyarylation or alkoxylation/*β*-hydride elimination products. In contrast to the reactions of cyclic precursors, reactions of acyclic 7-hydroxy-1,3-dienes proceeded with insertion of the olefin into either the Pd−C or the Pd−O bond of the Pd(Ar)-(OR)-olefin intermediate to afford 1,2-oxyarylation products after reductive elimination.

Experimental Section

General Considerations. All reactions were run under an argon atmosphere in oven-dried glassware unless otherwise indicated. 7-Hydroxy-1,3-dienes **1a**−**e** were synthesized by addition of 2.5 molar equiv of methyl, phenyl, or benzylic Grignard reagents to the corresponding ester-functionalized 1,3-dienes.[11] Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Tetrahydrofuran (THF) was predried by molecular sieves and then by passing through an Al_2O_3 column.[15] Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230−400 mesh) using the indicated solvents.[16] ^{1}H nuclear magnetic resonance (NMR) spectra were obtained with a Bruker-AC 500 (500 MHz) spectrometer. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with a Bruker-AC 500 (125 MHz) spectrometer with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and were reported as mass/charge *(m/e)* with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure for Palladium-Catalyzed Reaction of Aryl Bromides with 7-Hydroxy 1,3-Dienes. To an oven-dried 100 mL round-bottom flask equipped with a stirrer bar and a condenser and capped with a rubber septum were added dpe-phos[9] (10.8 mg, 0.02 mmol), $Pd(PPh_3)_4$ (23.0 mg, 0.02 mmol), bromobenzene (0.31 g, 2.0 mmol), and NaO*t*Bu (0.19 g, 2.0 mmol). The apparatus was evacuated (oil pump) and filled with nitrogen three times. To the reaction mixture was then added via syringe 7-hydroxy 1,3-diene **1a** (0.15 g, 1.0 mmol) in 30 mL of THF. The resulting mixture was heated at reflux under nitrogen. The reaction was monitored by TLC and was quenched with saturated aqueous ammonium chloride solution (20 mL) at 30 °C after no **1a** was detected (ca. 2 h). The reaction mixture was diluted with 100 mL of ether. The resulting solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), filtered, and concentrated in vacuo to give the crude mixture.

(15) Pangborn A. B.; Giardello M. A.; Grubbs R. H.; Rosen R. K.; Timmers F. J. *Organometallics* **1996**, *15*, 1518.
(16) Still, W. C.; M. Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(±)-(3a*S*,5*S*,7a*S*)-2,2-Dimethyl-5-phenyl-2,3,3a,4,5,7a-hexahydrobenzo[*b*]furan (2a). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with bromobenzene (0.31 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2a** (0.13 g, 0.55 mmol, 55%) as a colorless liquid: IR (CH_2Cl_2) 3056, 2987, 2305, 1603, 1551, 1272 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.28 (m, 5 H), 7.19 (m, 2 H), 6.04 (m, 2 H), 4.25 (m, 1 H), 3.24 (dd, *J* = 11.6, 2.1 Hz, 1 H), 2.35 (m, 1 H), 2.11 (dd, *J* = 12.9, 8.7 Hz, 1 H), 1.79 (dt, *J* = 12.5, 4.4 Hz, 1 H), 1.47 (m, 2 H), 1.34 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 145.49, 136.04, 129.34, 128.41, 128.19, 127.30, 126.31, 126.20, 79.89, 71.97, 45.58, 42.95, 38.25, 36.86, 30.27, 28.30; MS (EI) *m/e* 228.3 (M$^+$, 21), 165.2 (12), 155.2 (2), 124.2 (100), 91.1 (18), 79.1 (4), 77.1 (11); HRMS (EI) *m/e* calcd for $C_{16}H_{20}O$ 228.1515, found 228.1512.

(±)-(3a*S*,5*S*,7a*S*)-2,2-Dimethyl-5-(4-methylphenyl)-2,3,-3a,4,5,7a-hexahydrobenzo[*b*]furan (2b). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 4-bromotoluene (0.34 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2b** (0.15 g, 0.62 mmol, 62%) as a colorless liquid: IR (CH_2Cl_2) 3051, 2986, 1602, 1551, 1422, 1268 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.09 (m, 4 H), 6.03 (m, 2 H), 4.24 (m, 1 H), 3.21 (d, *J* = 7.7 Hz, 1 H), 2.34 (m, 1 H), 2.31 (s, 3 H) 2.10 (dd, *J* = 12.9, 8.7 Hz, 1 H), 1.77 (dt, *J* = 12.6, 4.4 Hz, 1 H), 1.46 (m, 2 H), 1.34 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 142.49, 136.28, 135.65, 129.09, 127.16, 126.17, 79.82, 71.98, 45.60, 42.52, 38.27, 36.96, 30.27, 28.30, 20.90; MS (EI) *m/e* 242.5 (M$^+$, 22), 219.4 (2), 185.4 (3), 169.3 (29), 131.3 (23), 124.3 (100), 109.2 (25), 91.2 (14); HRMS (EI) *m/e* calcd for $C_{17}H_{22}O$ 242.1670, found 242.1671.

(±)-(3a*S*,5*S*,7a*S*)-5-(4-Methoxyphenyl)-2,2-dimethyl-2,3,-3a,4,5,7a-hexahydrobenzo[*b*]furan (2c). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 4-bromoanisole (0.37 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2c** (0.22 g, 0.84 mmol, 84%) as a white solid: mp 76−77 °C; IR (CH_2Cl_2) 3056, 2986, 2685, 1600, 1551, 1421, 1258 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.12 (d, *J* = 8.65 Hz, 2 H), 6.84 (d, *J* = 8.65 Hz, 2 H), 6.03 (m, 2 H), 4.24 (m, 1 H), 3.77(s, 3 H), 3.20 (d, *J* = 11.6 Hz, 1 H), 2.33 (m, 1 H), 2.11 (dd, *J* = 12.9, 8.7 Hz, 1 H), 1.77 (dt, *J* = 12.6, 4.4 Hz, 1 H), 1.48 (dd, *J* = 12.9, 2.2 Hz, 1 H), 1.42 (d, *J* = 7.5 Hz, 1 H), 1.34 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 157.99, 137.61, 136.44, 128.17, 126.08, 113.79, 79.83, 71.93, 55.11, 45.56, 42.07, 38.23, 37.01, 30.27, 28.28; MS (EI) *m/e* 258.4 (M$^+$, 52), 201.2 (17), 185.2 (34), 174.2 (28), 160.2 (47), 147.2 (50), 134.2 (96), 124.2 (100), 91.1 (19); HRMS (EI) *m/e* calcd for $C_{17}H_{22}O_2$ 258.1620, found 258.1617. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 and hexanes.

(±)-(3a*S*,5*S*,7a*S*)-2,2-Dimethyl-5-(1-naphthyl)-2,3,3a,4,5,-7a-hexahydrobenzo[*b*]furan (2d). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 1-bromonaphthalene (0.41 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetates in hexanes) to give **2d** (0.16 g, 0.56 mmol, 56%) as a colorless liquid: IR (CH_2Cl_2) 3051, 2986, 2686, 1598, 1509, 1422, 1272 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.13 (d, *J* = 8.1 Hz, 1 H), 7.89 (d, *J* = 8.1 Hz, 1 H), 7.75 (d, *J* = 7.9 Hz, 1 H), 7.49 (m, 4 H), 6.23 (d, *J* = 10.2 Hz, 1 H), 6.18 (dt, *J* = 9.9, 3.2 Hz, 1 H), 4.36 (m, 1 H), 4.10 (d, *J* = 6.7 Hz, 1 H), 2.52 (m, 1 H), 2.17 (dd, *J* = 12.9, 8.7 Hz, 1 H), 2.02 (dt, *J* = 11.4, 2.9 Hz, 1 H), 1.75 (m, 1 H), 1.51 (dd, *J* = 13.0, 2.3 Hz, 1 H), 1.37 (s, 3 H), 1.32 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 141.22, 136.57, 133.95, 131.28, 128.98, 126.86, 126.37, 125.79, 125.71, 125.37, 79.96, 72.24, 45.67, 38.57, 35.66, 30.32, 28.39; MS (EI) *m/e* 278.4 (M$^+$, 100), 205.3 (49), 167.2 (88), 165.2 (76), 154.2 (73), 152.2 (50), 141.2 (24), 124.2(80), 109.2(21); HRMS (EI) *m/e* calcd for $C_{20}H_{22}O$ 278.1670, found 278.1665.

(±)-(3a*S*,7a*S*)-5-(4-Chlorophenyl)-2,2-dimethyl-2,3,-3a,4,7,7a-hexahydrobenzo[*b*]furan (2e). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 1-bromo-4-chlorobenzene (0.39 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2e** (0.14 g, 0.54 mmol, 54%) as a colorless liquid: IR (CH_2Cl_2) 3053, 2987, 2685, 1685, 1602, 1551, 1421 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 4 H), 6.10 (t, J = 4.2 Hz, 1 H), 4.27 (m, 1 H), 2.62 (m, 1 H), 2.47 (dd, J = 15.6, 6.4 Hz, 1 H), 2.41 (m, 2 H), 2.32 (dd, J = 15.7, 5.8 Hz, 1 H), 1.95 (dd, J = 12.2, 7.9 Hz, 1 H), 1.48 (dd, J = 12.2, 7.4 Hz, 1 H), 1.31 (s, 3 H), 1.22 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.50, 136.87, 132.40, 128.34, 126.43, 123.49, 79.43, 74.66, 45.20, 37.41, 30.09, 29.21, 27.25; MS (EI) *m/e* 262.3 (M^+, 2), 222.2 (5), 206.2 (6), 153.2 (6), 141.1 (11), 139.1 (26), 98.1 (100), 83.1 (11); HRMS (EI) *m/e* calcd for $C_{16}H_{19}ClO$ 262.1124, found 262.1130.

(±)-(3a*S*,7a*S*)-5-(3,5-Dibromophenyl)-2,2-dimethyl-2,3,-3a,4,7,7a-hexahydrobenzo[*b*]furan (2f). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 1,3,5-tribromobenzene (0.63 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2f** (0.15 g, 0.40 mmol, 40%) as a colorless liquid: IR (CH_2Cl_2) 3050, 2986, 1712, 1604, 1551, 1421, 1255 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, J = 1.6 Hz, 1 H), 7.41 (s, 1 H), 7.40 (s, 1 H), 6.15 (t, J = 4.3 Hz, 1 H), 4.26 (m, 1 H), 2.61 (m, 1 H), 2.43 (m, 3 H), 2.29 (dd, J = 14.5, 5.6 Hz, 1 H), 1.97 (dd, J = 12.2, 7.9 Hz, 1 H), 1.47 (dd, J = 12.2, 7.3 Hz, 1 H), 1.31 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.64, 135.64, 131.92, 127.10, 125.79, 122.88, 79.49, 74.38, 45.21, 37.32, 30.12, 29.93, 29.29, 27.29; MS (EI) *m/e* 384.3 (M^+, 1), 368.2 (1), 330.1 (3), 277.3 (2), 234.1 (3), 232.1 (3), 168.2 (2), 98.1 (100), 83.1(8); HRMS (EI) *m/e* calcd for $C_{16}H_{18}Br_2O$ 383.9724, found 383.9716.

(±)-(3a*S*,7a*S*)-2,2-Dimethyl-5-[3-(trifluoromethyl)-phenyl]-2,3,3a,4,7,7a-hexahydrobenzo[*b*]furan (2g). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 3-bromobenzotrifluoride (0.45 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2g** (0.11 g, 0.36 mmol, 36%) as a colorless liquid: IR (CH_2Cl_2) 3051, 2987, 2155, 2126, 1603, 1551, 1421, 1273 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1 H), 7.53 (d, J = 7.8 Hz, 1 H), 7.47 (d, J = 7.7 Hz, 1 H), 7.42 (t, J = 7.7 Hz, 1 H), 6.19 (t, J = 4.6 Hz, 1 H), 4.28 (m, 1 H), 2.64 (m, 1 H), 2.52 (dd, J = 15.6, 6.5 Hz, 1 H), 2.44 (m, 2 H), 2.37 (dd, J = 15.6, 6.0 Hz, 1 H), 1.98 (dd, J = 12.2, 7.9 Hz, 1 H), 1.51 (dd, J = 12.2, 7.3 Hz, 1 H), 1.32 (s, 3 H), 1.23 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.81, 136,84, 130.67 (q, J_{C-F} = 32.5 Hz), 128.42, 127.50, 124.74, 124.25 (q, J_{C-F} = 271.3 Hz), 123.30 (q, J_{C-F} = 3.8 Hz), 121.93 (q, J_{C-F} = 3.8 Hz), 79.49, 74.56, 45.24, 37.41, 30.14, 30.09, 29.27, 27.29; MS (EI) *m/e* 296.3 (M^+, 12), 277.3 (5), 240.2 (9), 223.2 (8), 183.2 (6), 159.1 (6), 98.1 (100), 83.1 (7), 69.1 (5); HRMS (EI) *m/e* calcd for $C_{17}H_{19}F_3O$ 296.1388, found 296.1381.

(±)-(3a*S*,7a*S*)-2,2-Dimethyl-5-[(*E*)-2-phenyl-1-ethenyl]-2,3,3a,4,7,7a-hexahydrobenzo[*b*]furan (2h). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with β-bromostyrene (0.37 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution 5 to 10% ethyl acetate in hexanes) to give **2h** (0.17 g, 0.65 mmol, 65%) as a colorless liquid: IR (CH_2Cl_2) 3052, 2986, 2155, 1686, 1591, 1492, 1421, 1267 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.19 (t, J = 7.4 Hz, 1 H), 6.84 (d, J = 16.2 Hz, 1 H), 6.47 (d, J = 16.2 Hz, 1 H), 5.90 (t, J = 4.7 Hz, 1 H), 4.24 (m, 1 H), 2.56 (m, 1 H), 2.40 (m, 3 H), 2.21 (dd, J = 15.7, 5.9 Hz, 1 H), 1.94 (dd, J = 12.2, 7.8 Hz, 1 H), 1.51 (dd, J = 12.2, 7.3 Hz, 1 H), 1.31 (s, 3 H), 1.22 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.74, 136.25, 131.37, 128.53, 127.85, 126.99, 126.18, 125.23, 79.42, 74.93, 45.21, 36.74, 30.08, 29.42, 27.60, 26.43; MS (EI) *m/e* 254.4 (M^+, 31), 214.3 (20), 156.2 (94), 141.2 (54), 131.1 (100), 105.1 (46), 91.1 (43), 77.1(40), HRMS (EI) *m/e* calcd for $C_{18}H_{22}O$ 254.1672, found 254.1671.

(±)-2-[(3a*S*,7a*S*)-2,2-Dimethyl-2,3,3a,4,7,7a-hexahydrobenzo[*b*]furan-5-yl]pyridine (2i). The crude mixture obtained from reaction of **1a** (0.15 g, 1.0 mmol) with 2-bromopyridine (0.32 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5−10% ethyl acetate in hexanes) to give **2i** (0.11 g, 0.48 mmol, 48%) as a colorless liquid: IR (CH_2Cl_2) 3056, 2987, 2685, 2521, 1733, 1603, 1551, 1422, 1272 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.55 (m, 1 H), 7.60 (td, J = 8.0, 1.9 Hz, 1 H), 7.4 (d, J = 8.1 Hz, 1 H), 7.09 (ddd, J = 7.4, 4.9, 1.0 Hz, 1 H), 6.57 (t, J = 4.7 Hz, 1 H), 4.28 (m, 1 H), 2.72 (dd, J = 9.9, 5.3 Hz, 1 H), 2.61 (m, 1 H), 2.52 (m, 2 H), 2.43 (m, 1 H), 1.98 (dd, J = 12.2, 7.7 Hz, 1 H), 1.55 (dd, J = 12.3, 7.0 Hz, 1 H), 1.31 (s, 3 H), 1.22 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.30, 148.70, 137.87, 135.98, 126.28, 121.28, 119.06, 79.31, 74.71, 45.06, 37.17, 30.10, 29.25, 27.85, 27.37; MS (EI) *m/e* 229.3 (M^+, 28), 200.3 (20), 170.2 (94), 156.2 (54), 132.2 (100), 117.1 (46), 98.1 (43), 78.1(40); HRMS (EI) *m/e* calcd for $C_{15}H_{19}NO$ 229.1466, found 229.1464.

(±)-(3a*R*,7a*S*)-2,2-Diphenyl-2,3,3a,7a-tetrahydrobenzo-[*b*]furan (2j). The crude mixture obtained from reaction of **1b** (0.28 g, 1.0 mmol) with bromobenzene (0.31 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5−10% ethyl acetate in hexanes) to give **2j** (0.18 g, 0.65 mmol, 65%) as a colorless liquid: IR (CH_2Cl_2) 3057, 2986, 2831, 2685, 2521, 2410, 2155, 2126, 1970, 1733, 1603, 1551, 1421, 1251, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8, 2 H), 7.38 (d, J = 7.7 Hz, 2 H), 7.32 (t, J = 7.4 Hz, 2 H), 7.23 (m, 3 H), 7.15 (t, J = 7.3 Hz, 1 H), 5.90 (m, 2 H), 5.79 (m, 2 H), 4.81 (dd, J = 11.3, 3.1 Hz, 1 H), 3.12 (dd, J = 12.0, 7.6 Hz, 1 H), 2.84 (m, 1 H), 2.24 (t, J = 10.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.93, 144.79, 128.82, 128.24, 127.94, 126.90, 126.72, 126.11, 124.85, 122.85, 120.70, 82.39, 73.53, 46.70, 37.12; MS (EI) *m/e* 274.3 (M^+, 5), 256.2 (18), 197.2 (12), 183.2 (80), 165.1 (31), 118.1 (10), 91.1 (46), 77.1 (53); HRMS (EI) *m/e* calcd for $C_{18}H_{18}O$ 274.1358, found 274.1350.

(±)-(3a*R*,7a*S*)-2,2-Dibenzyl-2,3,3a,7a-tetrahydrobenzo-[*b*]furan (2k). The crude mixture obtained from reaction of **1c** (0.30 g, 1.0 mmol) with bromobenzene (0.31 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5−10% ethyl acetate in hexanes) to give **2k** (0.18 g, 0.58 mmol, 58%) as a colorless liquid: IR (CH_2Cl_2) 3057, 2986, 2831, 2685, 2521, 2410, 2305, 2126, 1970, 1733, 1603, 1551, 1494, 1421, 1275, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (m, 10 H), 5.81 (dd, J = 9.7, 5.5 Hz, 1 H), 5.73 (d, J = 4.3 Hz, 1 H), 5.71 (d, J = 4.5 Hz, 1 H), 5.61 (dd, J = 9.7, 4.3 Hz, 1 H), 4.50 (dd, J = 10.1, 3.4 Hz, 1 H), 2.93 (d, J = 13.6 Hz, 1 H), 2.85 (d, J = 13.6 Hz, 2 H), 2.69 (d, J = 13.6 Hz, 1 H), 2.34 (m, 1 H), 2.15 (dd, J = 12.5, 8.7 Hz, 1 H), 1.80 (dd, J = 12.4, 7.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.22, 138.00, 130.80, 130.61, 129.83, 127.90, 127.81, 126.13, 126.10, 125.70, 122.85, 120.85, 81.76, 74.64, 46.55, 44.46, 41.48, 37.50; MS (EI) *m/e* 302.4 (M^+, 0.1), 211.3 (26), 193.2 (17), 92.1 (9), 91.1 (100), 65.1 (7); HRMS (EI) *m/e* calcd for $C_{22}H_{22}O$ 302.1671, found 302.1673.

(±)-(5*R*)-2,2-Dimethyl-5-[(1*R*)-1-(1-naphthyl)-2-propenyl]tetrahydrofuran (2l). The crude mixture obtained from reaction of **1d** (0.14 g, 1.0 mmol) with 1-bromonaphthalene (0.41 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2l** (0.13 g, 0.48 mmol, 48%) as a colorless liquid: IR (CH_2Cl_2) 3051, 2986, 2831, 2685, 1598, 1551, 1509, 1422, 1272 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.71 (dd, J = 9.7, 1.4 Hz, 1 H), 7.46 (m, 4 H), 6.29 (ddd, J = 17.3, 10.3, 7.0 Hz, 1 H), 5.13 (d, J = 10.4 Hz, 1 H), 5.06 (d, J = 17.3 Hz, 1 H), 4.51 (q, J = 7.3 Hz, 1 H), 4.13 (t, J = 7.3 Hz, 1 H), 1.79 (m, 1 H), 1.63 (m, 3 H), 1.28 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 139.54, 138.31, 134.01, 128.87, 126.87, 125.72, 125.51, 125.46,125.30, 123.68, 116.05, 81.61, 81.30, 50.33, 38.17, 30.71, 29.15, 28.19; MS (EI) *m/e* 266.4 (M^+, 20), 205.2 (5), 167.2 (49), 165.2 (58), 141.2 (15), 99.2 (100), 81.1 (61), 67.1(20); HRMS (EI) *m/e* calcd for $C_{18}H_{22}O$ 266.1670, found 266.1678.

(±)-(5*R*)-2,2-Dimethyl-5-[(1*R*,2*E*)-1-(1-naphthyl)-2-butenyl]tetrahydrofuran (2m). The crude mixture obtained from reaction of **1e** (0.15 g, 1.0 mmol) with 1-bromonaphthalene (0.41 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2m** (0.15 g, 0.52 mmol, 52%) as a colorless liquid: IR (CH_2Cl_2) 3056, 2987, 2521, 2155, 1603, 1551, 1422, 1265 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1 H), 7.83 (d, J = 7.6 Hz, 1 H), 7.70 (dd, J = 7.1, 1.8 Hz, 1 H), 7.46 (m, 4 H), 5.92 (ddd, J = 15.4, 7.0, 1.4 Hz, 1 H), 5.45 (m, 1 H), 4.47 (q, J = 7.1 Hz, 1 H), 4.08 (t, J = 7.2 Hz, 1 H), 1.78 (m, 1 H), 1.60 (m, 6 H), 1.27 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.29, 133.99, 132.26 131.91, 128.83, 126.65, 126.62, 125.62, 125.49, 125.47, 125.23, 123.83, 82.00, 81.24, 49.28, 38.20, 30.69, 29.13, 28.27, 18.17; MS (EI) *m/e* 280.4 (M^+, 10), 265.3 (9), 181.2 (36), 165.2 (39), 141.2 (13), 113.2 (23), 99.2 (100), 81.1 (51); HRMS (EI) *m/e* calcd for $C_{20}H_{24}O$ 280.1827, found 280.1830.

(±)-(5*R*)-2,2-Dimethyl-5-[(1*R*,2*E*)-1-phenyl-2-butenyl]-tetrahydrofuran (2n). The crude mixture obtained from reaction of **1e** (0.15 g, 1.0 mmol) with bromobenzene (0.31 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2n** (0.11 g, 0.48 mmol, 48%) as a colorless liquid: IR (CH_2Cl_2) 3052, 2987, 2685, 2521, 2410, 2350, 2126, 1970, 1765, 1732, 1602, 1551, 1422, 1265, 1155 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 5 H), 5.78 (dd, J = 15.5, 7.6 Hz, 1 H), 5.44 (m, 1 H), 4.22 (m, 1 H), 3.24 (t, J = 7.4 Hz, 1 H), 1.76 (m, 1 H), 1.68 (d, J = 6.4 Hz, 3 H), 1.56 (m, 3 H), 1.23 (s, 3 H), 1.20 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.66, 132.00, 128.47, 12812, 126.42, 126.11, 81.57, 80.94, 54.62, 38.09, 30.10, 28.90, 28.14, 18.15; MS (EI) *m/e* 230.3 (M^+, 2), 144.2 (6), 131.2 (36), 129.2 (21), 105.1 (28), 99.1 (100), 91.1 (38), 81.1 (81), 55.1 (15); HRMS (EI) *m/e* calcd for $C_{16}H_{22}O$ 230.1671, found 230.1668.

(±)-(5*R*)-2,2-Dimethyl-5-[(1*R*,2*E*)-1-(4-Methoxyphenyl)-2-butenyl]tetrahydrofuran (2o). The crude mixture obtained from reaction of **1e** (0.15 g, 1.0 mmol) with *p*-methoxybromobenzene (0.37 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **2o** (0.17 g, 0.65 mmol, 65%) as a colorless liquid: IR (CH_2Cl_2) 3050, 2987, 2685, 2521, 2410, 2305, 2126, 1970, 1732, 1608, 1551, 1511, 1422, 1263, 1154 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 4.9, 2 H), 6.82 (d, J = 4.8 Hz, 2 H), 5.75 (ddq, J = 15.3, 7.5, 1.5 Hz, 1 H), 5.43 (dqd, J = 15.3, 6.4, 1.0 Hz, 1 H), 4.19 (dt, J = 6.8, 6.7 Hz, 1 H), 3.77 (s, 3 H), 3.20 (t, J = 7.3, 1 H), 1.74 (m, 1 H), 1.67 (d, J = 6.3 Hz, 3 H), 1.58 (m, 3 H), 1.22 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.96, 134.81, 132.24, 129.21, 126.16, 113.16, 81.71, 80.93, 55.13, 53.65, 38.10, 30.35, 28.19, 28.13, 18.15; MS (EI) *m/e* 260.3 (M^+, 5), 174.2 (7), 162.2 (11), 161.2 (75), 121.1 (11), 99.1 (100), 91.1 (14), 81.1 (69), 55.0 (9); HRMS (EI) *m/e* calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1777.

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Supporting Information Available: Characterization data for 7-hydroxy-1,3-dienes **1a**−**e**, ^1H and ^{13}C NMR spectra for compounds **2b**, **c**, **g**, **h**, **j**, **k**, **m**, and **o**, tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters and crystallographic data in CIF format for compound **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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