Molybdenum(II)-Catalyzed Allylation of Electron-Rich Aromatics and Heteroaromatics

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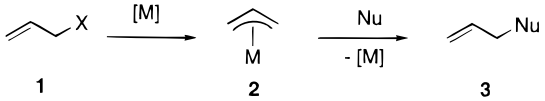
The stable, readily available molybdenum(II) complexes $[Mo(CO)_4Br_2]_2$ (**B**) and $Mo(CO)_3(MeCN)_2(SnCl_3)Cl$ (**C**) have been found to catalyze C−C bond-forming allylic substitution with electron-rich aromatics (e.g., **15** + PhOMe → **62**) and heteroaromatics (e.g., **15** + **36** → **88**) as nucleophiles under mild conditions (room temperature, 30 min−3 h). Remarkable is the *para*-selectivity for anisole, whereas phenol tends to favor *ortho*-substitution in certain instances. Mechanistic and stereochemical experiments are indicative of Lewis-acid catalysis rather than a metal template-controlled process.

Introduction

Allylic substitution catalyzed by palladium(0) and other transition metal complexes (Mo, W, Fe, Co, Ni) is a well-established methodology in organic synthesis.[1] This now classical reaction is generally stereospecific and, in the case of Pd(0) and malonate-type nucleophiles, normally occurs via a double inversion of configuration (*inv-inv*), involving η^3-complexes **2** (M = Pd)[2] as intermediates (Scheme 1). With organometallics and a Pd(0)[3] or Ni(0)[4] catalyst, an *inv-ret* pathway is observed, resulting in an overall inversion. The complementary *ret-inv* mechanism has been reported for substrates capable of precoordination of Pd(0)[5−7] and for stoichiometric, Mo(0)-mediated reactions involving isolation of the η^3-complexes **2**.[8] Finally, the *ret-ret* alternative has been demonstrated for the Mo(0)-catalyzed reaction[9,10] (in contrast to the stoichiometric procedure). On the other hand, allylic substitution catalyzed by strong Lewis acids proceeds via uncoordinated allylic cations, which results in stereochemical scrambling.

Scheme 1



The Pd(0)-catalyzed allylic substitution has mainly been developed to construct C−C bonds,[1−3,5−7] although formation of C−H, C−O, and C−N bonds has also been reported.[1,2g−i,5b] Recently, Sinou[11] has shown that phenols and naphthols can be used as O-nucleophiles to obtain arylallyl ethers, such as **5**, provided carbonates (**4**), rather than acetates, are employed as allylic substrates (Scheme 2). At higher temperature, the primarily formed β-naphthoxy derivative **5** undergoes a rearrangement to afford the thermodynamic product **6**,[11] so that the reaction can, a priori, be employed either as a C−O or C−C bond-forming process.

In the adjacent paper,[12] we have detailed the preparation of molybdenum(II) complexes **A**−**C** (Scheme 3) and their tungsten(II) congeners and demonstrated their utilization as Lewis-acidic catalysts in allylic substitution.[13−16] Complexes **A**−**C** proved to catalyze both C−O and C−C bond formation. Thus, allylic acetate **7** reacted with

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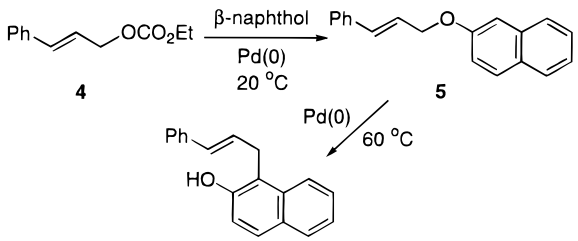
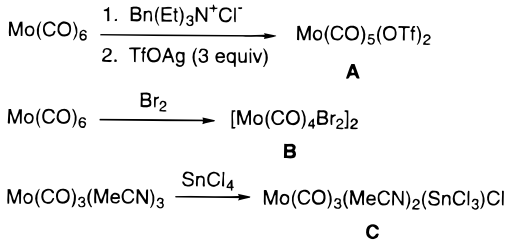
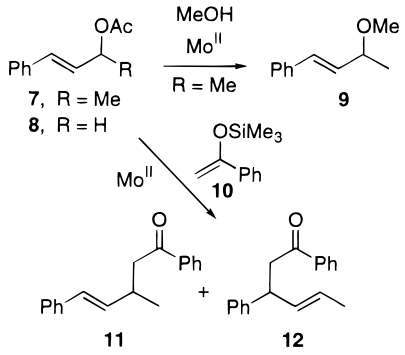
Scheme 2



Scheme 3



Scheme 4



MeOH[12,13] in the presence of either of the complexes **A**−**C** (2−5 mol %) at room temperature to give the corresponding methoxy-derivative **9** (Scheme 4). By contrast, cinnamyl acetate **8** proved inert, suggesting that only those allylic substrates that are capable of a fair degree of stabilization of the allylic cation can be successfully employed. The C−C bond formation with silyl enol ethers as nucleophiles (e.g., **10**) occurred under very mild conditions even more readily (Scheme 4).[12,13] Although this particular reaction was not regioselective, producing a ~1:1 mixture of **11** and **12**, we have described a number of highly regioselective examples.[12]

Results and Discussion

The electron-rich double bond in enol ethers, such as **13** (Chart 1), proved sufficiently nucleophilic to effect

Chart 1

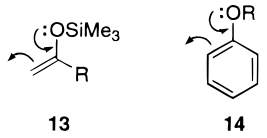
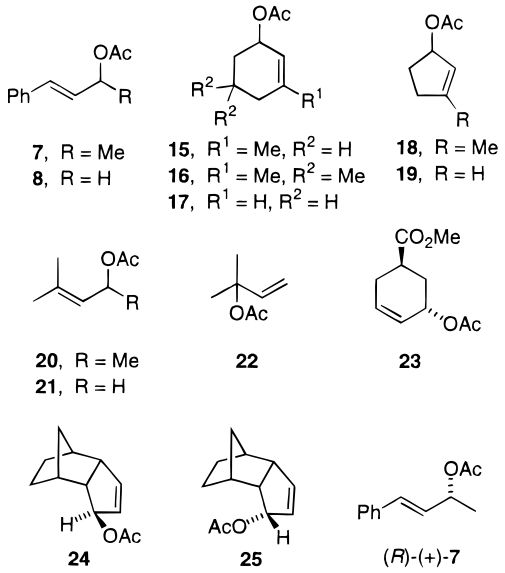


Chart 2



allylic substitution in the presence of Mo(II) catalysts **A**−**C**.[12] It is, therefore, tempting to raise the question of whether aromatics, such as anisole (**14**; R = Me), can be regarded as alkyl vinyl ethers and would react with an allylic substrate. Furthermore, would phenol (**14**; R = H) serve as a nucleophilic enol? If successful, what would be the regioselectivity regarding both the allylic substrate and the aromatic ring, and what chemoselectivity can be expected for phenol in view of the Sinou work (Scheme 2):[11] O- or C-allylation? Finally, if C−C bond formation is attained, would this be an example of direct, Friedel−Crafts-type aromatic substitution or a two-step process as that in the Scheme 2? Note that in classical Friedel−Crafts reactions[17,18] and related processes, the Lewis-acidic catalyst has to be used, as a rule, in stoichiometric amounts owing to its trapping by coordination to the product, which makes it unavailable for another catalytic cycle. Hence, effective dissociation of the catalyst from the product is crucial, and attempts at developing a new system should focus on this step.

To address these issues, we have employed a series of allylic substrates (Chart 2) and a set of representative, electron-rich aromatic and heteroaromatic compounds

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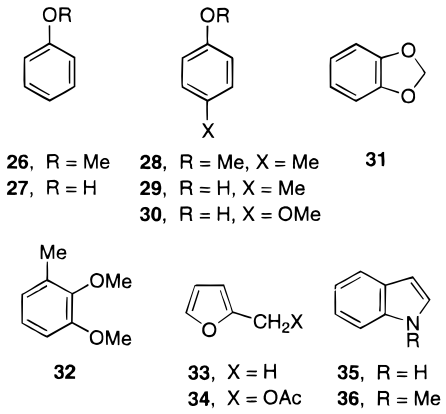
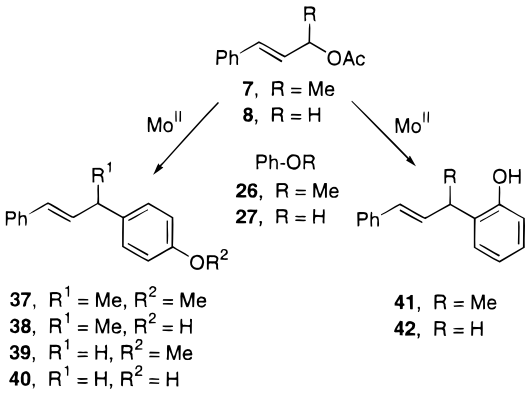
Chart 3



Scheme 5



(Chart 3). Since the initial experiments with complex **A** turned out to give poor conversions,[13c] we have focused on complexes **B** and **C**.

General Reactivity. At the outset, we have utilized the readily available allylic acetate **7**, which previously proved fairly reactive toward a range of silyl enol ethers;[12] anisole **26** and phenol **27** were selected as nucleophilic probes (Scheme 5).

In the presence of dibromo complex **B** (5 mol %), **7** turned out to react with anisole at room temperature, affording **37** as the sole product in 91% isolated yield (Table 1, entry 1).[19] Note that **37** was formed with high selectivity by connecting the *p*-position of the aromatic ring to the methyl terminus of the allylic system.[20] Phenol proved slightly less selective, giving a ~7:1 mixture of *p*- and *o*-products **38** and **41** (Table 1, entry 2). Allylation with cinnamyl acetate **8** followed the same pattern: anisole furnished solely the *p*-isomer **39** (Table 1, entry 10), whereas phenol gave a ~5:1 mixture of *p*- and *o*-products **40** and **42** (Table 1, entry 11). In both cases, only attack at the less substituted terminus of the allylic moiety was observed and the *trans*-configuration of the double bond was preserved.

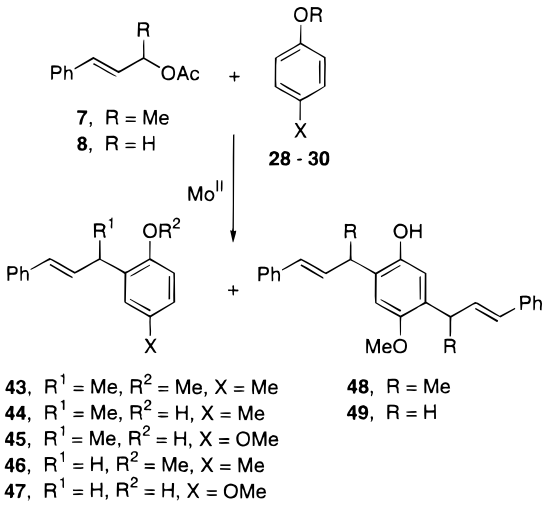
The unusually high *p*-selectivity, observed both with anisole and phenol, raised the question of what would be the result of blocking the *p*-position. To address this issue, we have employed *p*-substituted aromatics **28**−**30** (Scheme 6). With **7**, both *p*-methylanisole **28** and *p*-cresol **29** turned out to produce the corresponding *o*-isomers **43**

Table 1. Allylation of Aromatics with 7 and 8 Catalyzed by Complex B[a]

entry	allylic compd	aromatic compd	time	product(s)	product ratio[b]	yield (%)[c]
1	**7**	Ph-OMe	1 h	**37**		91
2	**7**	Ph-OH	30 min	**38** + **41**	88:12	94
3	**7**	**28**	4 h	**43**[d]	*d*	61
4	**7**	**29**	1 h	**44**		56
5	**7**	**30**	30 min	**45** + **48**	34:66	61
6	**7**	**33**	30 min	**54** + **56**	84:16	90
7	**7**	**35**	2 h	**58** + **60**	80:20	52
8	**7**	**36**	4 h	**59** + **61**	85:15	86
9	(*R*)-**7**	Ph-OMe	1 h	(±)-**37**		90
10	**8**	Ph-OMe	4 h	**39**		68
11	**8**	Ph-OH	1 h	**40** + **42**	83:17	71
12	**8**	**28**	6 h[e]	**46**		30[f]
13	**8**	**30**	3 h	**47** + **49**	81:19	78
14	**8**	**31**	6 h	**50** + **51**	79:21	70
15	**8**	**32**	6 h	**52** + **53**	77:23	57
16	**8**	**33**	5 h	**55** + **57**	75:25	44

[a] The reactions were carried out on 0.5 mmol scale in CH_2Cl_2 with 5 mol % of the catalyst at room temperature under inert atmosphere unless stated otherwise. [b] The product ratios were determined by ^{1}H NMR spectra of the crude mixtures. [c] Isolated yield. [d] Contained ~2% of a bis-allylated byproduct. [e] 2 mol % of the catalyst. [f] Traces of a mixture of bis-allylated products were also detected.

Scheme 6



and **44**, respectively (Table 1, entries 3 and 4).[20] In the case of the doubly activated nucleophile **30**, preferential formation of the isomer **45** (corresponding to *o*-substitution with respect to the hydroxy group) was observed. However, in this instance, bis-allylated derivative **48** was isolated as the major product (Table 1, entry 5),[21] reflecting the enhanced reactivity of the aromatic ring. Formation of the latter derivative could be partially (but not entirely) suppressed by using an excess of **30** (typically 5 equiv). Cinnamyl acetate **8** exhibited similar reactivity toward both **28** and **30**, affording **46** and **47**, respectively, contaminated with the bis-allylated byproduct **49** in the latter case (Table 1, entries 12 and 13).[20]

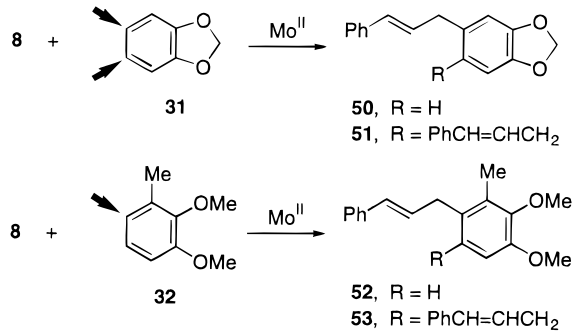
The bis-allylation complicates the reaction of a highly activated aromatic ring (i.e., one with two oxygen groups attached) if a highly reactive allylic partner is utilized

(19) This particular reaction is also completed at −10 °C in 30 min.

(20) The products structure was corroborated by NMR spectrometry, including 2D-NMR experiments (e.g., NOESY) in more complicated cases. For details, see the Experimental Section.

(21) The bis(allyl) derivative was obtained as a ~1:1 mixture of diastereoisomers, which could not be separated and fully characterized. However, the HRMS and NMR data are fully supportive of its structure. Moreover, the latter problem was avoided by utilizing cinnamyl acetate (**8**).

Scheme 7

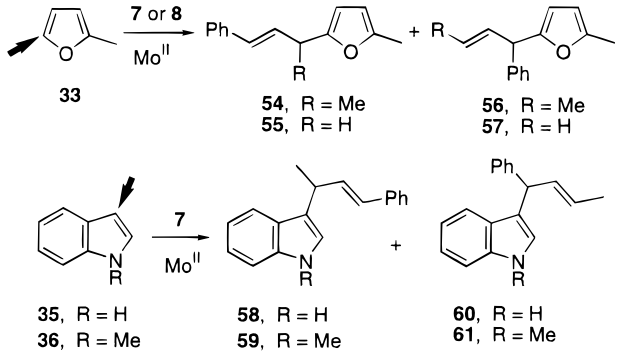


(Table 1, entry 5). Thus, 1,2-(methylenedioxy)benzene (**31**) was found to mainly afford an inseparable diastereoisomeric mixture of bis-allylated products on reaction with **7**. By contrast, employing the less reactive cinnamyl acetate **8** (Scheme 7) resulted in a substantial reduction of the rate of the second allylation so that **50** could be isolated as the major product, whereas **51** was formed only in a minute amount (Table 1, entry 14). Note that, in this formation of **50** and **51**, each allyl group was introduced into the *p*-position with respect to one of the oxygen atoms of the aromatic ring in **31**.[20] Similarly, a ~3:1 mixture of mono- and bis-allylated products **52** and **53** was obtained on reaction of **8** with 3-methylveratrole (**32**) (Table 1, entry 15); again, in **53**, allyl groups are located *para* to each of the MeO groups.[20]

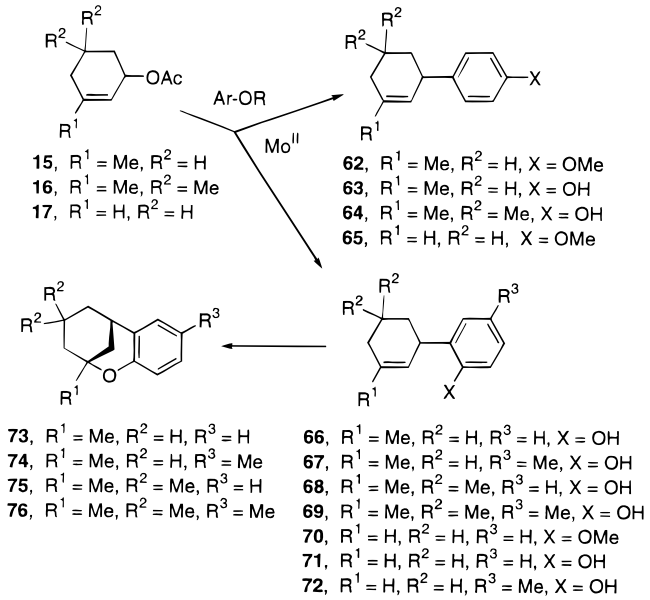
As shown above, electron-rich aromatics proved to be excellent reaction partners. By contrast, aromatics with an adjacent electron-withdrawing group, such as Ph−Cl, Ph−COMe, Ph−NO_2, and *m*-chlorophenol were inert, which is consistent with the assumed nucleophilic role of the aromatic ring in these reactions. A methyl group alone on the ring is apparently too weak to promote the reaction, for toluene also proved inert (at room temperature). Surprisingly, no reaction was observed with Ph−OAc, Ph−NHCOMe, and Ph−NMe_2 although these substituents are normally regarded as activating the aromatic ring. This lack of reactivity can be attributed to inactivation of the catalyst by preferential coordination of the metal to the Lewis-basic functional group (carbonyl or nitrogen, respectively). The latter coordination is evidenced by IR spectroscopy: thus, for instance, adding an equimolar amount of **B** to a solution of **8** in CH_2Cl_2 caused a shift of ν(C=O) by 25 cm^{-1} (from 1740 to 1715 cm^{-1}). Similarly, a shift by 10 cm^{-1} was observed for benzaldehyde (from 1700 to 1690 cm^{-1}). Furthermore, in both instances, the relative intensities in the ν(C=O) region of the complex have also changed: of the three maxima at 1960 (vs), 2040 (s), and 2100 (w) cm^{-1}, the latter was moderately increased, indicating a change in the symmetry of the coordination sphere of the metal. With acetamide as a model for amidic group, formation of a precipitate was observed within 5 min after adding complex **B**, demonstrating a strong coordination. This behavior clearly shows that while coordination to the acetate leaving group is essential for the allylic substitution to occur, the presence of another competing Lewis-basic group in the molecule of one of the reaction partners can engage the catalyst and prevent the reaction.

In view of the high reactivity of the electron-rich aromatics, it was desirable to explore the potential application of this method in heteroaromatic chemistry. To this end, furan and indole derivatives **33**−**36** were

Scheme 8



Scheme 9



employed as representative model compounds (Scheme 8). 2-Methylfuran (**33**) was found to readily react with **7**, producing mainly **54** as the result of connecting the most reactive 5-position[20] of the furan ring with the methyl terminus of the allyl moiety (Table 1, entry 6); **8** gave a mixture of **55** and **57** (Table 1, entry 16). In the case of indole **35** and its *N*-methyl derivative **36**, the electrophilic attack occurred exclusively at the expected 3-position[20] (Table 1, entries 7and 8). Again, the reaction exhibited high preference for the methyl terminus of the allylic moiety, affording **58** and **59**, respectively, in preference to their regioisomers **60** and **61**.[22] By contrast, benzothiazole proved inert (presumably owing to deactivation of the catalyst by coordination), whereas pyrrole produced an intractable mixture. Carbazole, whose "indole β-position" is blocked by the annulated ring, was also inert.

To establish the scope of this novel catalysis in aromatic electrophilic substitution, we have examined the reactivity of additional allylic acetates, namely **15**−**22** (Chart 2), toward our set of electron-rich aromatics (Chart 3).

The reaction of **15** with anisole, carried out in the presence of complex **B**, produced the expected *p*-isomer **62** (Scheme 9) at room temperature in 30 min (Table 2, entries 1 and 2). The less reactive cyclohexenyl acetate

(22) In contrast to the ready reaction of both **35** and **36** with **7**, practically no reaction with **8** was detected.

Table 2. Catalytic Allylation of Aromatics with 15−25[a]

entry	allylic compd	aromatic compd	catalyst	time	product(s)	product ratio[b]	yield (%)[c]
1	**15**	Ph−OMe	**B**	30 min	**62**		42
2	**15**	Ph−OMe	**B**	3 h[d]	**62**		50
3	**15**	Ph−OH	**B**	20 min	**63** + **73**	36:64	59
4	**15**	Ph−OH	**C**	20 min	**63** + **66** + **73**	11:43:46	44
5	**15**	**29**	**B**	30 min	**74**		77
6	**15**	**34**	**B**	30 min	**87**		65
7	**15**	**36**	**B**	30 min	**88**		85
8	**16**	Ph−OH	**B**	30 min	**64** + **75**	36:64	22[e]
9	**16**	**29**	**B**	30 min	**76**		80
10	**16**	**36**	**B**	30 min	**89**		70
11	**17**	Ph−OMe	**B**	2 h	**65** + **70**	57:43	56
12	**17**	Ph−OMe	**C**	1.5 h	**65** + **70**	54:46	73
13	**17**	Ph−OH	**B**	30 min	**71**[f]	90:10[g]	79
14	**17**	Ph−OH	**C**	30 min	**71**[f]	95:5[g]	83
15	**17**	**29**	**C**	2 h	**72**[f]	84:16[g]	91
16	**19**	Ph−OMe	**B**	2 h	**77**[f]	80:20[g]	50
17	**19**	Ph−OH	**B**	20 min	**78**[f]	87:13[g]	41[e]
18	**19**	**31**	**B**	2 h	**79**		47
19	**19**	**32**	**B**	2 h	**80**		74
20	**20**	Ph−OMe	**B**	2 h	**81**[f]		24[e]
21	**20**	Ph−OH	**B**	2 h	**85**[f,h]	95:5[g]	19[e]
22	**21**	Ph−OMe	**B**	1 h	**82**[i]	73:27[j]	42
23	**21**	Ph−OH	**B**	1 h	**86**[f]	90:10	27[e]
24	**22**	Ph−OMe	**B**	1.5 h	**82**[i]	>95:5[j]	47
25	**22**	Ph−OH	**B**	2 h	**86**[f]	80:20	48
26	**23**	Ph−OH	**B**	4 h	**90** + **91**[k]	90:10	59
27	**23**	Ph−OH	**C**	4 h	**90** + **91**[l]	90:10	50
28	**24**	Ph−OMe	**B**	1 h	**93**[m]		75
29	**24**	Ph−OH	**B**	30 min	**92**[m]		51
30	**25**	Ph−OMe	**B**	6 h	**93**		72

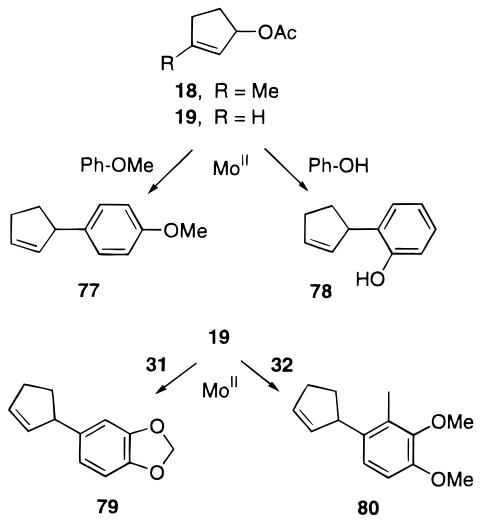
[a] The reactions were carried out on 0.5 mmol scale in CH_2Cl_2 with 5 mol % of the catalyst at room temperature under inert atmosphere unless stated otherwise. [b] The product ratios were determined by ^1H NMR spectra of the crude mixtures. [c] Isolated yield. [d] At −10 °C. [e] The low yield is mainly due to the competing elimination. [f] Contained bis-allylated byproduct(s). [g] The mono-/bis-allylation ratio. [h] The intermediate acyclic product was detected by TLC but not isolated; the reaction was quenched after the cyclization had been completed. [i] Contained *ortho*-isomer as byproduct. [j] The *para*/*ortho* ratio. [k] Contained the corresponding *cis*-isomers as byproducts, which were not fully characterized; the trans/cis ratio was 81:19 for **90** and 75:25 for **91**. [l] The trans/cis ratio for **90** was 75:25. [m] A 10-fold excess of the aromatic nucleophile was used in order to suppress the bis-allylation.

17 afforded a ∼3:2 mixture of *p*- and *o*-isomers **65** and **70** (Table 2, entry 11); bimetallic catalyst **C** showed the same behavior (Table 2, entry 12).

In contrast to anisole, phenol exhibited enhanced proportion of the *o*-product on reaction with **15**, giving rise to a mixture of the *p*- and *o*-allylated phenols **63** and **66** and the bridged heterocycle **73** (Table 2, entries 3 and 4); the latter cyclic ether apparently originates from a ring closure reaction of the intermediate *o*-substituted phenol **66**. With the *p*-position blocked, as in *p*-cresol **29**, the initially generated *o*-substituted product **67** (not isolated) was cyclized to **74** in good yield (Table 2, entry 5). Isophoryl acetate **16** reacted in an analogous way with both phenol **27** and *p*-cresol **29**, affording a mixture of *p*-allylated phenol **64** and the ring-closed heterocycle **75**, in the former case (Table 2, entry 8) and cylic ether **76** as the sole product, in the latter (Table 2, entry 9); the ring-opened intermediates **68** and **69**, respectively, could not be isolated. On the other hand, the reaction of cyclohexenyl acetate **17** with either phenol **27** or *p*-cresol **29** stopped at the stage of the *o*-substituted product **71** or **72**, respectively (Table 2, entries 13−15), accompanied by a small amount of bis-allylated byproducts, as revealed by GCMS.

Of the five-membered ring allylic substrates **18** and **19**, the former gave almost exclusively elimination products, whereas the latter followed the pattern of its cyclohexene-derived counterparts (Scheme 10). Thus, reaction of **19** with anisole afforded mainly *p*-substituted product **77** (Table 2, entry 16), while reaction with phenol gave rise to *o*-substituted product **78** (Table 2, entry 17);

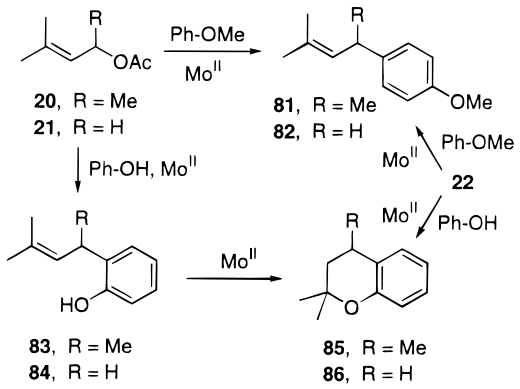
Scheme 10



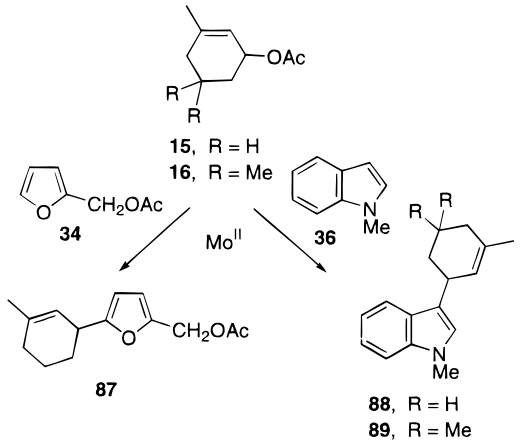
in both cases, small amounts of bis-allylated byproducts were detected. However, the isolated yields were lower than those in the cyclohexene series, owing to the larger proportion of competing elimination of the allylic substrate. The doubly activated aromatics **31** and **32** gave acceptable yields of the corresponding substitution products **79** and **80**, respectively (Table 2, entries 18 and 19).

The aliphatic allylic acetate **20** (Scheme 11) turned out to be less efficient than the other members of the series (**7**−**19**), mainly due to preferential elimination. Nevertheless, the reaction with anisole furnished the *p*-sub-

Scheme 11



Scheme 12

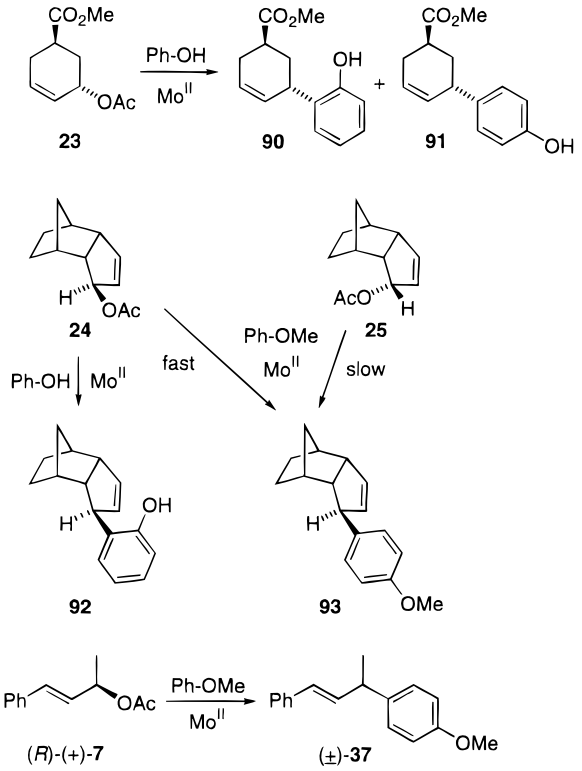


stitution product **81** in 24% yield (Table 2, entry 20). With phenol, an initial formation of **83** was observed by TLC, followed by cyclization to produce the benzopyran derivative **85** (Table 2, entry 21). Prenyl acetate **21** exhibited similar behavior, giving **82** with anisole (Table 2, entry 22), whereas the cyclic product **86** resulted from the reaction with phenol (Table 2, entry 23); the ring-opened intermediate **84** could not be isolated. Notably higher yields were obtained when the allylic isomer **22** was utilized as electrophile (Table 2, entries 24 and 25).

The reaction of **15** with the furan derivative **34** proceeded readily, furnishing the expected substitution product **87** in high yield (Scheme 12; Table 2, entry 6), and so did the reactions of **15** and **16** with *N*-methylindole (**36**), which afforded the β-substituted indole derivatives **88** and **89**, respectively (Table 2, entries 7 and 10).

Stereochemistry. To establish the stereochemistry of the allylation process with respect to the allylic electrophile, we first investigated the reactivity of allylic acetate **23** (Scheme 13). Its reaction with phenol catalyzed by complex **B** proceeded readily at ambient temperature, giving a 90:10 mixture of *o*- and *p*-isomers **90** and **91** (Table 2, entry 26), separated by semipreparative HPLC. ^{1}H NMR spectroscopy revealed that the products were contaminated by the corresponding *cis*-isomers (the *trans*/*cis* ratios were 81:19 for **90** and 75:25 for **91**), which could not be separated. The same reaction catalyzed by complex **C** also afforded a 90:10 mixture of **90** and **91** (Table 2, entry 27), in which the content of the *cis*-isomer was similar to the later case (75:25). In contrast to this ready reaction, the *cis*-epimer of **23** reacted sluggishly, giving mainly elimination products. Apparently, the pseudoaxial disposition of the leaving group in the *trans*-epimer **23**,

Scheme 13



allowing an overlap of π and σ^* orbitals in the transition state at low energy cost, is the prerequisite for the reaction to occur readily.

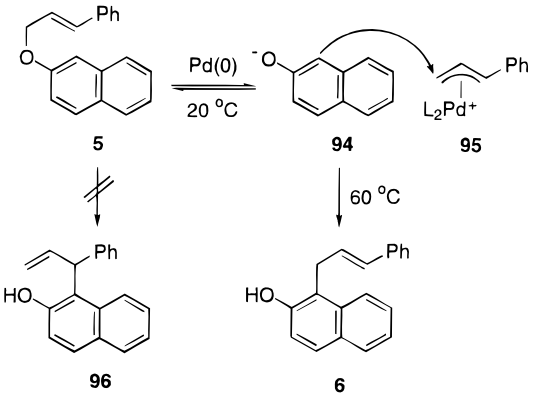
The epimeric pair of bicyclic allylic acetates **24** and **25**, first introduced by Fiaud,[23] has previously been employed to establish the steric course of Pd(0)- and Mo(0)-catalyzed allylic substitution.[5a,9,23] The advantage of this system is the steric bias, which renders the *endo*-face inaccessible by both the catalyst and the nucleophile.[5a,b,9,23] In agreement with the previously observed reactivity toward Mo(0)[9] and Mo(II),[12] *exo*-acetate **24** turned out to react readily with either phenol or anisole, affording the respective *exo*-products **92** and **93** (Table 2, entries 28 and 29). Note, again, the selective *ortho*-substitution for phenol (**92**) and the *para*-attachment for anisole (**93**). The *endo*-epimer **25** also furnished **93** on reaction with anisole (Table 2, entry 30), although in a somewhat slower process (6 h vs 1 h; compare entries 28 and 30), which is in agreement with the previously observed reactivity toward silyl enol ethers.[12]

The reaction of the enantiomerically pure allylic acetate (*R*)-(+)-**7**[5b] with anisole produced racemic **37** in excellent yield (Table 1, entry 9), demonstrating the nonstereospecific nature of these Mo(II)-catalyzed allylation reactions; the role of Mo(II) catalyst can thus be defined as that of a very selective Lewis acid, which is in line with our previous observations.[12]

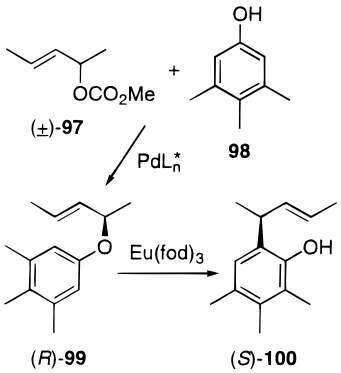
Mechanistic Considerations. The Pd(0)-catalyzed reaction of ethyl cinnamyl carbonate **4** with β-naphthol (Scheme 2) has been shown by Sinou[11] to give first the O-allylated kinetic product **5**, which is rearranged at higher temperature to the thermodynamic C-alkylated product **6**. Although the latter rearrangement could be conjectured as occurring via Claisen rearrangement (Scheme 14), Sinou has demonstrated that this is not the

(23) Fiaud, J.-C.; Legros, J.-Y. *J. Org. Chem.* **1987**, *52*, 1907.

Scheme 14



Scheme 15



case, since the Claisen rearrangement should give **96** rather than **6**. According to his interpretation, ArO serves as a leaving group in the presence of Pd(0), which allows for generation of the corresponding π-allyl complex **95** together with naphthoxide (**94**), whose recombination eventually leads to **6**. Interestingly, this reactivity appears to be confined to naphthoxy derivatives; the corresponding phenoxy systems were inert under the same conditions.

Recently, Trost has also examined the rearrangements of arylallyl ethers, such as (*R*)-**99**, obtained on the reaction of racemic allylic carbonate **97** with phenol **98**, catalyzed by a chiral Pd(0) complex (Scheme 15). Whereas Pd catalysts proved ineffective in his systems, he found that (*R*)-**99** underwent Claisen rearrangement by the action of $Eu(fod)_3$ at 50 °C; formation of (*S*)-**100** as the main product is compatible with the involvement of a chairlike transition state.[24]

In light of these reports, it was of interest to elucidate the mechanism of our Mo(II)-catalyzed C−C bond-forming reactions. Although we were unable to intercept the O-allylation product, its formation as a short-lived intermediate could not be a priori excluded. Furthermore, the Mo(II)-catalyzed reaction with MeOH as a prototype O-nucleophile (**7** + MeOH → **9**; Scheme 4) has been shown by us to occur with complete racemization.[12] Hence, if the O-allylated species were the intermediate, racemization would occur in the first step, leaving the question of the stereochemistry of the putative rearrangement to the C-allylated product open. To address these issues, an enantiopure O-allyl derivative of known configuration was required. Sinou has demonstrated an overall retention (via *inv-inv* mechanism) for O-allylation, using the *cis*-epimer of **23**.[11,25] With this stereochemistry in mind, we have reacted allylic carbonate (*R*)-(+)-**101** (synthesized from the corresponding alcohol of 95% ee[5b]) with phenol to obtain (*R*)-(+)-**102** (75%).[26,27] Similarly, the Pd(0)-catalyzed reaction of (*R*)-(+)-**101** with β-naphthol afforded the naphthoxy derivative (*R*)-(+)-**104** (86%).[26] Whereas the O-allylated derivatives (+)-**102** and (+)-**104** proved inert to Pd catalysts, their rearrangement to the respective C-allylated products **38**/**41** (1:1) and **105** was accomplished on treatment with a catalytic amount of complex **B** (room temperature, 20 or 8 h). However, the latter transformations turned out to be much slower than the direct C−C bond-forming allylation (note that 30 min is required for the reaction of **7** with PhOH: Table 1, entry 2), and the respective products **38**/**41** and **105** proved to be racemic. Moreover, free phenol and β-naphthol (~5%), respectively, were detected in the crude reaction mixtures by GCMS. Similar results were obtained with other Lewis acids, such as $(TfO)_3Yb$ (rt, overnight). An entirely different picture was obtained when $Eu(fod)_3$ was employed as the Lewis acid. In consonance with Trost's findings, the product of Claisen rearrangement **103** (80 °C, 12 h in dichloroethane; ~75% conversion)[28] was formed and proved to be of 76% ee as revealed by HPLC on Chiralcel OD-H column. The naphthyl derivative **104** reacted similarly with $Eu(fod)_3$ to afford the corresponding product of Claisen rearrangement **106** (80 °C, 12 h in dichloroethane; >95% conversion; 82% ee). Each of **103** and **106** was obtained as a ~4:1 mixture of *trans*/*cis*-isomers.

In another experiment (Scheme 17), cyclohexenyl phenyl ether **107**, synthesized from cyclohex-1-en-2-ol and phenol via the Mitsunobu reaction (DEAD, Ph_3P; 77%),[29] was converted into the C-alkylated *ortho*-product **71** (36%) and its *p*-isomer (10%) on treatment with **B** (5 mol %); unreacted **107** (15%), free phenol (~5%), and some elimination products were also detected in the crude reaction mixture. Again, the reaction was much slower than the direct allylation of phenol with cyclohexenyl acetate **17** (20 h vs 30 min), lending more credence to the above finding that the Mo(II)-catalyzed transformation of the allyl ether into the C-allylated product is an interrather than intramolecular process.

The above results rule out the involvement of Claisen rearrangement in the Mo(II)-catalyzed allylation of free phenols and demonstrate that, although some of the final product may arise from the initially generated O-ally-

(24) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 815. (b) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 9074.

(25) Note that the stereochemical course of the O-allylation could not be established with the Trost system[24] as the carbonate **97** forms a *meso*-π-allyl complex.

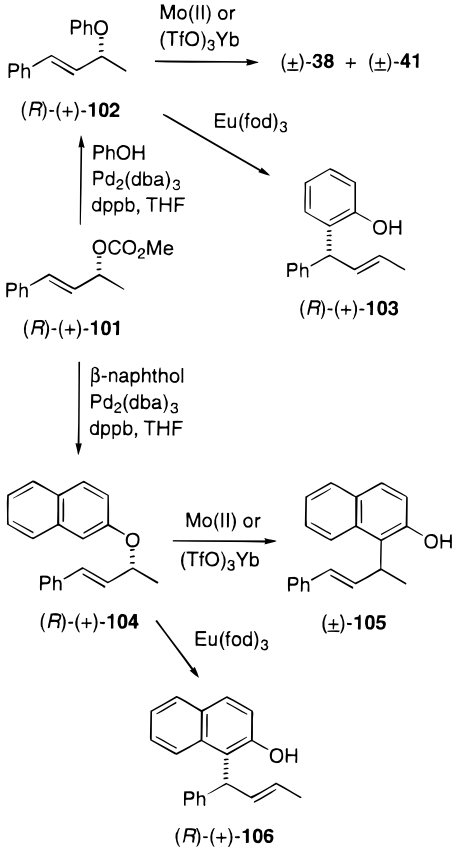
(26) The (*R*)-configuration for (+)-**102** ($[\alpha]_D$ +81.7; *c* 2.1 in $CHCl_3$) and (+)-**104** ($[\alpha]_D$ +233.3; *c* 2.0 in $CHCl_3$) is assumed in view of the double inversion mechanism demonstrated for this type of reaction by Sinou[11] but not rigorously proven. Note that other O-nucleophiles are also known to react via the *inv-inv* mechanism; for an overview, see the references list in ref 5b. The ee for the latter aryloxy compounds could not be determined since their maximum optical rotations are unknown and we failed to separate the enantiomers of the corresponding racemates on the available chiral columns.

(27) Interestingly, the Mitsunobu reaction of (±)-4-phenyl-but-3-en-2-ol with PhOH (DEAD, Ph_3P, THF, rt, 4 h) gave a 67:33 mixture of (±)-**102** and its allylic isomer.

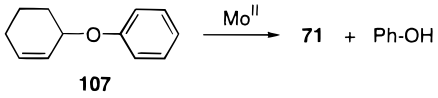
(28) The spectral characteristics for (*R*)-**103** are identical to those reported for the corresponding racemate. The (*R*)-configuration for both **103** and **106** is assumed in view of the prevailing chairlike transition state for the Claisen rearrangement, proposed by Trost.[24] For (±)-**103**, see: Albergola, A.; Gonzalez-Ortega, A.; Pedrosa, R.; Vicente, M. *Synthesis* **1984**, 238.

(29) For review, see: (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Shull, B. K.; Sakai, T.; Nichols, J. B.; Koreeda, M. *J. Org. Chem.* **1997**, *62*, 8294.

Scheme 16



Scheme 17



lated intermediate, this is not the main reaction channel for the catalytic C-allylation. The stereospecific Claisen rearrangement of O-allyl derivatives, reported by Trost,[24] appears to be unique to Eu(III); other Lewis-acid catalysts, such as Mo(II) or Yb(III), drive the reaction toward dissociation followed by recombination.

***Ortho-/Para*-Selectivity.** The stereochemical investigation pointed to the Mo(II)-initiated ionization of the allylic acetate to generate the corresponding allylic cation, which then attacks the electron-rich aromatic ring. This scenario should lead to the classical distribution of *ortho*- and *para*-isomers. However, anisole exhibited almost exclusive preference for the *para*-substitution in most reactions (Table 1, entries 1, 9, and 10; Table 2, entries 1, 2, 16, 20, 22, 24, 28, and 30) except in one case (Table 2, entries 11 and 12). Phenol, on the other hand, exhibited high preference for the formation of *ortho*-isomers, especially with cyclic allylic acetates (Table 2, entries 3, 4, 8, 13, 14, 17, 21, 23, 25, 26, and 29), whereas *para*-substitution was favored in the case of the cinnamyl system (Table 1, entries 2 and 11). Since steric effects alone, i.e., OCH_3 vs OH, can hardly be taken responsible for such a dramatic change of regioselectivity, there must be other factors operating in these reactions. Note that the metal is apparently not involved in coordination of the allylic cation via an η^3-complex as evidenced by scrambling of the original stereochemical information (vide supra). Moreover, phenol, a potentially bidentate nucleophile, has been shown to also react by direct C-alkylation rather than via the O-allylated intermediate, so that the difference between the regioselectivity of anisole vs phenol must, indeed, originate from another effect.

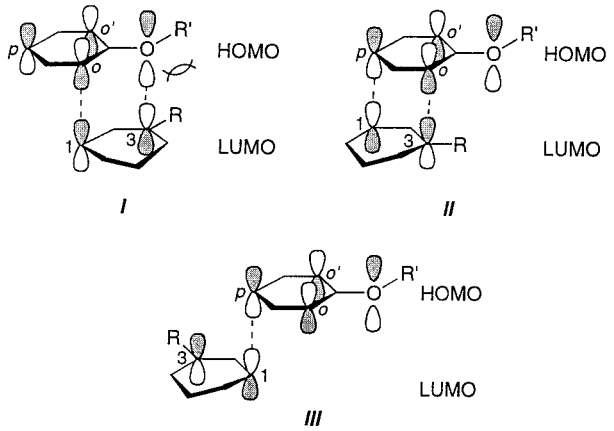


Figure 1. Orbital interactions between the allylic cations derived from **15** (R = Me) or **17** (R = H) with **26** (R′ = Me) or **27** (R′ = H).

To shed light on the differences in regioselectivity of the reactions of allylic substrates, such as **15**, with PhOMe (**26**) vs PhOH (**27**), let us consider the HOMO−LUMO interactions (Figure 1). In the reaction of PhOH with **15**, the HOMO of PhOH should interact with the LUMO of the allylic cation derived from **15** (R = Me). For bond formation between the *ortho*-carbon of PhOH (R′ = H) and the less substituted terminus (1) of the latter cation (***I***), an additional stabilizing interaction can be identified between the orbital located on the oxygen atom of PhOH and the 3-position of the cation. The formation of the *para*-isomer can either occur without the secondary interactions (***III***) or, perhaps, via ***II***, in which the bond-forming interaction between the *p*-carbon of PhOH and the less substituted carbon of the cation (C-1) is supplemented by the stabilizing interaction of the *ortho*-orbital of PhOH with the orbital in the 3-position of the cation. Since the negative charge in PhOH is mainly residing on the oxygen, the O−C interaction in ***I*** should be more significant than the C−C interaction in ***II***, which is in agreement with the preferential formation of the *ortho*-isomer. Note that considering purely Coulombic interactions would lead to the same conclusions. A dramatically different scenario is encountered in the reaction of **15** with PhOMe, where severe eclipsed interaction between the two methyls would render the transition state ***I*** (R = R′ = Me) much higher in energy, so that an alternative (***II*** or ***III***) becomes favored. The reactivity of **17** lends further credence to this model: in this instance, the repulsive interaction in the transition state ***I*** is absent (R = H), allowing the formation of the *ortho*-substituted product, which is in perfect agreement with the experiment that gives a ∼3:2 *p*/*o*-ratio (Table 2, entries 11 and 12).

A similar analysis can be applied to the reaction of the cinnamyl electrophile **8** with the same pair of nucleophiles (Figure 2). The transition states ***IV*** and ***V*** are apparently less stabilized by additional interactions than their counterparts ***I*** and ***II***, since the charge in the benzylic position (3) is further delocalized to the aromatic ring of the cinnamyl unit. Moreover, a steric clash between OH/OMe and the Ph group can be identified in ***IV***. As a result, transition state ***VI*** can be regarded as more likely, which is in agreement with the experimen-

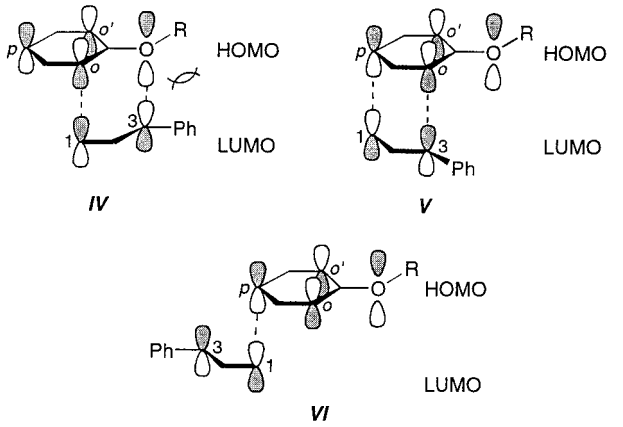
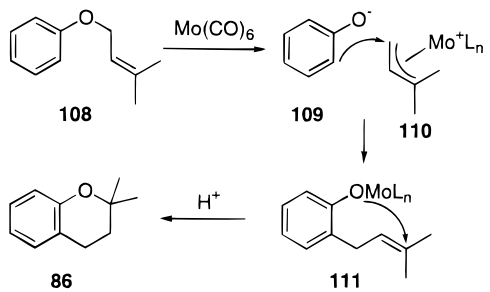


Figure 2. Orbital interactions between the allylic cations derived from **8** with **26** (R = Me) or **27** (R = H).

Scheme 18



tally observed shift of the preference to the *p*-substitution even for PhOH (Table 1, entries 1, 2, and 9−11).

Epilogue

While this work was in progress, two papers appeared reporting on the transition metal-catalyzed Friedel−Crafts-type allylation of aromatics, such as toluene, xylene, and anisole, with allylic esters, chlorides, or alcohols.[30,31] However, neither $Mo(CO)_6$ (10 mol %)[30] nor Cp*RuCl(SPr^i)−Ru(OH$_2$)(SPr^i)Cp* (5 mol %),[31] employed as catalysts, was as selective as our Mo(II) complexes and the reaction condition were rather harsh (typically 80−140 °C for 6−72 h).

In another recent paper, $Mo(CO)_6$ has been shown to catalyze the conversion of prenyl phenyl ether (**108**) (110 °C for 55 h) into dimethylchromane (**86**) (65%); interestingly, free phenol (5−10%) was detected in the crude reaction mixture (Scheme 18).[32] In light of our findings, one can envisage the following mechanism: on reaction with the catalyst, the PhO$^-$ group departs with concomitant formation of π-prenyl complex **110**, which then recombines with the phenoxide (**109**) to give the C-allylated intermediate **111**, whose 6(*O*)^n-*endo*-*Trig* cyclization,[33] analogous to that described in Scheme 9, affords the final chroman **86** by obeying the Markovnikov, rather than Baldwin, rule.

Conclusions

We have developed a new, extremely mild method for C-allylation of electron-rich aromatics and heteroaromatics, catalyzed by the readily available Mo(II) complexes $[Mo(CO_4Br_2]_2$ (**B**) or $Mo(CO)_3(MeCN)_2(SnCl_3)Cl$ (**C**), which have not been used in catalytic chemistry before. The *para*-selectivity, observed with anisole (**26**) and its congeners, is remarkable. Since selected heteroaromatics, such as the furan and indole derivatives **34** and **36**, undergo the reaction as easily as other aromatics, complexes **B** and **C** are likely to become a valuable addition to the menu of the Friedel−Crafts-type catalysts for allylation of aromatics. The salient features of our method are the low catalyst loading (≤2 mol %) and the mild conditions (room temperature or lower for 30 min − 2 h). In the overall reaction outcome, the reactivity of catalysts **B** and **C** seems to parallel that of $LiCo(B_9C_2H_{11})_2$ (lithium cobalt bis(dicarbollide)) and related Li$^+$ reagents.[34]

Experimental Section

General Methods. Melting points were determined on a Kofler block and are uncorrected. The NMR spectra were recorded in $CDCl_3$, ^{1}H at 250 MHz and ^{13}C at 62.9 MHz with chloroform-d_1 (δ 7.26, ^{1}H; δ 77.0, ^{13}C) as internal standard; 2D-techniques were used to establish the structures and to assign the signals. The IR spectra were recorded for a thin film between KBr plates unless otherwise stated. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. The GC-MS analysis was performed with RSL-150 column (25m × 0.25 mm). Chiral HPLC analyses were carried out on Chiralpak AD (Daicel) and Chiracel OD (Daicel) columns with a 10 mm guard column (silica), using UV detection at 254 nm. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. The catalysts were prepared by literature methods: $[Mo(CO)_4Br_2]_2$ (**B**);[12,15] $Mo(CO)_3(MeCN)_2(SnCl_3)Cl$ (**C**).[12,16] Cinnamyl acetate (**8**) was purchased from Lancaster Synthesis Ltd. Other allylic acetates are known compounds[35] and were prepared by stirring the corresponding allylic alcohols with a mixture of acetic anhydride and triethylamine and a catalytic amount of (dimethylamino)pyridine in diethyl ether. Carbonate (*R*)-(+)-**101**[36] was prepared according to the literature procedure[11] from the corresponding alcohol[5b] (95% ee). All aromatic and heteroaromatic compounds were purchased and used without further purification. Some of the products are known compounds.[37] Yields are given for isolated product showing one spot on a TLC plate and no impurities detectable in the NMR spectrum.

General Procedure for Allylic Substitution Using Catalysts B or C. To a stirred solution of an allylic acetate (1 equiv) and a nucleophile (1.1−1.3 equiv) in CH_2Cl_2 (5 mL) at room temperature was added 2−5 mol % of the catalyst (**B**

(30) Shimizu, I.; Sakamoto, T.; Kawaragi, S.; Maruyama, Y.; Yamamoto, A. *Chem. Lett.* **1997**, 137.

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(35) Allylic acetates references are as follows. **7**: (a) Goering, H. L.; Seits, E. P., Jr.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5304. **15**: (b) Ishida, T.; Asakawa, Y.; Okano, M.; Aratani, T. *Tetrahedron Lett.* **1977**, *18*, 2437. **16** and **17**: (c) Lessard, J.; Tan, P. V. M.; Martino, R.; Sanders, J. K. *Can. J. Chem.* **1977**, *55*, 1015. **18**: (d) Masatoshi, A.; *Bull. Chem. Soc. Jpn.* **1990**, *63*, 721. (e) Shono, T.; Ikeda, A. *J. Am. Chem. Soc.* **1972**, *94*, 7892. **19**: (f) Hansson, S.; Heumann, A.; Rein, T.; Åkermark, B. *J. Org. Chem.* **1990**, *55*, 975. **20**: (g) Michejda, C. J.; Comnick R. W. *J. Org. Chem.* **1975**, *40*, 1046. **21**: (h) Suga, K.; Watanabe, S.; Hijikata, K. *Aust. J. Chem.* **1971**, *24*, 197. **22**: (i) Bergstrom, D. E.; Ruth, J. L.; Warwick, P. *J. Org. Chem.* **1981**, *46*, 1432. **23**: (j) Trost, B.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. **24** and **25**: ref 3g. Enantiomerically pure acetate (*R*)-(+)-**7** was obtained by acetylation of the enantiomerically pure alcohol which, in turn, was obtained from the racemate by Sharpless epoxidation in kinetic resolution mode and had $[\alpha]_D$ +24.5 (*c* 2.5, $CHCl_3$).[5b,12]

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or **C**) in one portion. The mixture was stirred under nitrogen until the reaction was complete (as evidenced by TLC), then diluted with ether (20 mL), and washed successively with 5% aqueous $NaHCO_3$ and water. The organic phase was dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (15 × 2 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent.

1-Phenyl-3-(4′-methoxyphenyl)-1-butene (37). Acetate **7** (100 mg, 0.53 mmol) was reacted with anisole (**26**) (70 mg, 0.65 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give **37** (114 mg, 91%) as a colorless oil (Table 1, entry 1): ^{1}H NMR δ 1.43 (d, J = 6.9 Hz, 3 H, Me), 3.58 (m, 1 H, 3-H), 3.76 (s, 3 H, OMe), 6.37 (m, 2 H, 1-H, 2-H), 6.85 (d, J = 8.8 Hz, 2 H, 3′-H, 5′-H), 7.17 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H), 7.20−7.36 (m, 5 H, Ph); ^{13}C NMR δ 21.3 (Me), 41.7 (3-CH), 55.2 (OMe), 113.8 (3′,5′-CH), 126.1, 127.0, 128.2, 128.3, 128.5, 135.6 (1-CH), 137.6 and 137.7 (1′-C and 1″-C), 158.0 (4′-C); MS (EI) m/z (%) 238 (71, M$^{\bullet+}$), 223 (100).

1-Phenyl-3-(4′-hydroxyphenyl)-1-butene (38) and 1-Phenyl-3-(2′-hydroxyphenyl)-1-butene (41). Acetate **7** (100 mg, 0.53 mmol) was reacted with phenol (**27**) (60 mg. 0.64 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford an 18:82 mixture of **38** and **41** (111 mg, 94%) as a colorless oil (Table 1, entry 2): MS (EI) m/z (%) 224 (73, M$^{\bullet+}$), 209 (100). **38:** ^{1}H NMR δ (measured in a mixture with the *ortho*-isomer) 1.41 (d, J = 6.9 Hz, 3 H, Me), 3.56 (m, 1 H, 3-H), 5.08 (br s, 1 H, OH), 6.36 (m, 2H, 1-H, 2-H), 6.75 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.11 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 7.17−7.36 (m, 5 H, Ph); ^{13}C NMR δ 21.8 (Me), 42.1 (3-CH), 115.8 (3′,5′-CH), 126.6, 127.5, 128.8, 129.0, 130.2, 136.1 (1-CH), 138.1 and 138.3 (1′, 1″-C), 154.3 (4′-C). **41:** ^{1}H NMR δ (measured in a mixture with the *para*-isomer) 1.47 (d, J = 7.0 Hz, 3 H, Me), 3.88 (m, 3 H, 3-H), 5.08 (br s, 1 H, OH), 6.47 (m, 2 H, 1-H, 2-H), 6.87−7.4 (m, 2 H, 4′-H, 6′-H).

1-Phenyl-3-(4′-methoxyphenyl)-1-propene (39).[37a,b] Acetate **8** (100 mg, 0.57 mmol) was reacted with anisole (**26**) (70 mg, 0.65 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **39** (87 mg, 68%) as a colorless oil (Table 1, entry 10): ^{1}H NMR δ 3.46 (d, J = 6.0 Hz, 2 H, 3-H), 3.76 (s, 3 H, OMe), 6.31 (dt, J = 15.9, 6.0 Hz, 1 H, 2-H), 6.42 (d, J = 16.0 Hz, 1 H, 1-H) 6.84 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.13 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 7.17−7.35 (m, 5 H, Ph), ^{13}C NMR δ 38.9 (3-CH_2), 55.7 (OMe), 114.4 (3′,5′-CH), 126.6, 127.5, 129.0, 130.1, 130.2, 131.2 (1-CH), 132.6 and 138.0 (1′-C and 1″-C), 158.6 (4′-C); MS (EI) m/z (%) 224 (100, M$^{\bullet+}$).

1-Phenyl-3-(4′-hydroxyphenyl)-1-propene (40)[37b,c] **and 1-Phenyl-3-(2′-hydroxy-phenyl)-1-propene (42).**[37c] Acetate **8** (100 mg, 0.57 mmol) was reacted with phenol (**27**) (60 mg, 0.64 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to produce a 17:83 mixture of **40** and **42** (85 mg, 71%) as a colorless oil (Table 1, entry 11): MS (EI) m/z (%) 210 (100, M$^{\bullet+}$). **40:** ^{1}H NMR δ (measured in a mixture with the *ortho*-isomer) 3.46 (d, J = 6.0 Hz, 2 H, 3-H), 5.01 (s, 1 H, OH), 6.31 (dt, J = 15.9, 6.0 Hz, 1 H, 2-H), 6.42 (d, J = 16.0 Hz, 1 H, 1-H), 6.84 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.13 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 7.17−7.35 (m, 5 H, Ph); ^{13}C NMR δ 38.9 (3-CH_2), 115.8 (3′,5′-CH), 126.6, 127.5, 129.0, 130.1, 130.3, 131.2 (1-CH), 132.8 and 138.0 (1′-C and 1″-C), 154.3 (4′-C). **42:** ^{1}H NMR δ (measured in a mixture with the *para*-isomer) 3.57 (d, J = 6.0 Hz, 2 H, 3-H), 4.93 (s, 1 H, OH), 6.38 (dt, J = 15.8 and 6.0 Hz, 1 H, 2-H), 6.51 (d, J = 16.0 Hz, 1 H, 1-H), 6.81 (d, J = 8.2 Hz, 6′-H), 6.88 (t, J = 7.2, 1 H, 4′-H), 7.11−7.37 (m; 7H, 3′-H, 5′-H, 2″-H, 6″-H).

1-Phenyl-3-(2′-methoxy-5′-methylphenyl)-1-butene (43). Acetate **7** (100 mg, 0.53 mmol) was reacted with 4-methylanisole (**28**) (85 mg, 0.70 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford **43** (81 mg, 61%) as a colorless oil (Table 1, entry 3): ^{1}H NMR δ 1.40 (d, J = 6.9 Hz, 3 H, 4-Me), 2.26 (s, 3 H, 5′-Me), 3.79 (s, 3 H, OMe), 4.06 (m, 1 H, 3-H), 6.41 (m, 2 H, 1-H, 2-H), 6.75 (d, J = 8.8 Hz, 1 H, 3′-H), 7.03 (m, 2 H, 4′-H, 6′-H), 7.12−7.40 (m, 5 H, Ph); ^{13}C NMR δ 20.5 (Me), 21.0 (Me), 35.6 (3-CH), 56.1 (OMe), 111.1 (CH), 126.5 (2′,6′-CH), 127.2 (CH), 127.8 (CH), 128.5 (CH), 128.7 (CH), 128.8 (3′,5′-CH), 130.2 (C), 134.3 (C), 135.5(CH), 138.4 (C), 158.0 (2″−C); MS (EI) m/z (%) 252 (89, M$^{\bullet+}$), 237 (100).

1-Phenyl-3-(2′-hydroxy-5′-methylphenyl)-1-butene (44). Acetate **7** (100 mg, 0.53 mmol) was reacted with *p*-cresol (**29**) (70 mg, 0.65 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **44** (70 mg, 56%) as a colorless oil (Table 1, entry 4): ^{1}H NMR δ 1.46 (d, J = 6.9 Hz, 3 H, 4-Me), 2.26 (s, 3 H, 5′-Me), 3.86 (qd; J = 6.9, 5.0 Hz, 1 H, 3-H), 5.01 (s, 1 H, OH), 6.40 (dd, J = 16.0, 5.0 Hz, 1 H, 2-H), 6.49 (d, J = 16.0 Hz, 1 H, 1-H), 6.67 (d, J = 8.2 Hz, 1 H, 3′-H), 6.89 (dd, J = 8.2, 1.9 Hz, 1 H, 4′-H), 6.98 (d, J = 1.9 Hz, 1 H, 6′-H), 7.15−7.37 (m, 5 H, Ph); MS (EI) m/z (%) 238 (85, M$^{\bullet+}$), 91 (100).

1-Phenyl-3-(2′-hydroxy-5′-methoxyphenyl)-1-butene (45) and 2,5-Bis(1′-phenyl-1′-buten-3′-yl)-4-methoxyphenol (48). Acetate **7** (100 mg, 0.53 mmol) was reacted with 4-methoxyphenol (**30**) (90 mg, 0.72 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give a 34:66 mixture of **45** and **48** (81 mg, 61%) as a colorless oil (Table 1, entry 5). The two compounds were separated by column chromatography on silica (20 × 2.5 cm) with a hexanes−ethyl acetate mixture (9:1) as an eluent. The slower moving component was identified as **45:** ^{1}H NMR δ 1.47 (d, J = 7.2 Hz, 3 H, 4-Me), 3.76 (s, 3 H, OMe), 3.87 (m, 1 H, 3-H), 4.84 (s, 1 H, OH), 6.39 (dd, J = 16.0, 5.7 Hz, 1 H, 2-H), 6.49 (d, J = 16.3 Hz, 1 H, 1-H), 6.66 (dd, J = 8.8, 1.9 Hz, 1 H, 4′-H), 6.74 (d; J = 8.8 Hz, 1 H, 3′-H), 6.78 (d, J = 1.9 Hz, 1 H, 6′-H), 7.15−7.37 (m, 5 H, Ph); MS (EI) m/z (%) 254 (58, M$^{\bullet+}$), 150 (100). The faster moving component was identified as **48:** ^{1}H NMR (recorded for a ∼1:1 mixture of diastereoisomers) δ 1.38 and 1.47 (2 × d, J = 7.2 and 6.9 Hz, respectively, 2 × 3 H, 4′-Me and 4″-Me), 3.80 (s, 3 H, OMe), 3.86 and 4.02 (2 × m, 2 × 1 H, 3′-H and 3″-H), 4.81 (s, 1 H, OH), 6.36−6.54 (m, 4 H, 1′-H, 1″-H, 2′-H, 2″-H), 6.61 and 6.71 (2 × s, 2 × 1 H, 3-H and 6-H), 7.16−7.37 (m, 10 H, 2 × Ph); MS (EI) m/z (%) 384 (62, M$^{\bullet+}$), 369 (100).

1-Phenyl-3-(2′-methoxy-5′-methylphenyl)-1-propene (46).[37d] Acetate **8** (100 mg, 0.57 mmol) was reacted with 4-methylanisole (**28**) (85 mg, 0.70 mmol) in the presence of catalyst **B** (2 mol %) in CH_2Cl_2 (5 mL) to produce **46** (40 mg, 30%) as a colorless oil (Table 1, entry 12): ^{1}H NMR δ 2.26 (s, 3 H, 5′-Me), 3.50 (d, J = 5.5 Hz, 2 H, 3-H), 3.81 (s, 3 H, OMe), 6.34 (dt, J = 15.7, 5.6 Hz, 1 H, 2-H), 6.43 (d, J = 15.7 Hz, 1 H, 1-H), 6.76 (d, J = 8.8 Hz, 1 H, 3′-H), 6.98 (m, 2 H, 4′-H, 6′-H), 7.14−7.37 (m, 5 H, Ph); MS (EI) m/z (%) 238 (100, M$^{\bullet+}$).

1-Phenyl-3-(2′-hydroxy-5′-methoxyphenyl)-1-propene (47)[37e,f] **and 2,5-Bis-(1′-phenyl-1′-buten-3′-yl)-4-methoxyphenol (49).** Acetate **8** (100 mg, 0.57 mmol) was reacted

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with 4-methoxyphenol (**30**) (100 mg, 0.80 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford an 81:19 mixture of **47** and **49** (101 mg, 78%) as a colorless oil (Table 1, entry 13). The two compounds were separated by column chromatography on silica (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent. The slower moving component was identified as **47:** ^{1}H NMR δ 3.53 (d, J = 6.3 Hz, 2 H, 3-H), 3.75 (s, 3 H, OMe), 4.62 (br s, 1 H, OH), 6.36 (dt, J = 16.0, 6.3 Hz, 1 H, 2-H), 6.50 (d, J = 16.0 Hz, 1 H, 1-H), 6.66−6.77 (m, 3 H, 3′-H, 4′-H, 6′-H), 7.17−7.37 (m, 5 H, Ph); MS (EI) m/z (%) 240 (100, $M^{\bullet+}$). The faster moving component was identified as **49:** ^{1}H NMR δ 3.47 and 3.53 (2 × d, J = 6.0 Hz, 2 × 2 H, 3′-H and 3″-H), 3.79 (s, 3 H, OMe), 4.57 (s, 1 H, OH), 6.28−6.53 (m, 4 H, 1′,1″,2′,2″-H), 6.68 (s, 2 H, 3-H and 6-H), 7.15−7.20 (m, 10 H, 2 × Ph); MS (EI) m/z (%) 356 (100, $M^{\bullet+}$).

1-Phenyl-3-(1′,3′-benzodioxol-5′-yl)-1-propene (50) and 5,6-Bis(1′-phenyl-1′-propen-3′-yl)-1,3-benzodioxole (51). Acetate **8** (100 mg, 0.57 mmol) was reacted with 1,3-benzodioxole (**31**) (80 mg, 0.66 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give a 79:21 mixture of **50** and **51** (90 mg, 70%) as a colorless oil (Table 1, entry 14). The two compounds were separated by column chromatography on silica (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent. The slower moving component was identified as **50:** ^{1}H NMR δ 3.45 (d, J = 6.6 Hz, 2 H, 3-H), 5.91 (s, 2 H, OCH_2O), 6.29 (dt, J = 15.7, 6.6 Hz, 1 H, 2-H), 6.43 (d, J = 15.7 Hz, 1 H, 1-H), 6.67 (dd, J = 7.9, 1.6 Hz, 1 H, 6′-H), 6.72−6.76 (m, 2 H, 4′-H, 7′-H), 7.15−7.37 (m, 5 H, Ph); MS (EI) m/z (%) 238 (100, $M^{\bullet+}$). The faster moving component was identified as **51:** ^{1}H NMR δ 3.49 (d, J = 5.0 Hz, 4 H, 3′-H and 3″-H), 5.91 (s, 2 H, OCH_2O), 6.22−6.42 (m, 4 H; 1′,1″,2′,2″-H), 6.73 (s, 2 H, 4-H and 7-H), 7.17−7.33 (m, 10 H, 2 × Ph); MS (EI) m/z (%) 354 (63, $M^{\bullet+}$), 250 (100).

1-Phenyl-3-(3′,4′-dimethoxy-2′-methylphenyl)-1-propene (52) and 4,5-Bis(1′-phenyl-1′-propen-3′-yl)-1,2-dimethoxy-3-methylbenzene (53). Acetate **8** (100 mg, 0.57 mmol) was reacted with 1,2-dimethoxy-3-methylbenzene (**32**) (100 mg, 0.65 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give a 77:23 mixture of **52** and **53** (81 mg, 57%) as a colorless oil (Table 1, entry 15). The two compounds were separated by column chromatography on silica (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent. The slower moving component was identified as **52:** ^{1}H NMR δ 2.24 (s, 3 H, 2′-Me), 3.46 (d, J = 4.7 Hz, 2 H, 3-H), 3.78 (s, 3 H, 3′-OMe), 3.83 (s, 3 H, 4′-OMe), 6.23−6.38 (m, 2 H, 1-H and 2-H), 6.71 (d, J = 8.2, 5′-H), 6.89 (d, J = 8.4 Hz, 6′-H), 7.14−7.35 (m, 5 H, Ph); NOESY NMR δ 2.24 (2′-Me) ↔ 3.46 (3-H), 2.24 (2′-Me) ↔ 6.32 (1- and 2-H), 2.24 (2′-Me) ↔ 3.78 (3′- OMe), 3.46 (3-H) ↔ 6.89 (6′-H), 3.83 (4′-OMe) ↔ 6.71 (5′-H); MS (EI) m/z (%) 268 (100, $M^{\bullet+}$). The faster moving component was identified as **53:** ^{1}H NMR δ 2.27 (s, 3 H, 3-Me), 3.54 (d, J = 4.7 Hz, 4 H, 3′-H and 3″-H), 3.78 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 6.17−6.37 (m; 4 H; 1′-H, 1″-H, 2′-H, 2″-H), 6.68 (s, 1 H, 6-H), 7.14−7.33 (m, 10 H, 2 × Ph); MS (EI) m/z (%) 384 (100, $M^{\bullet+}$).

1-Phenyl-3-(2′-methylfuran-5′-yl)-1-butene (54) and 4-Phenyl-4-(2′-methylfuran-5′-yl)-2-butene (56). Acetate **7** (100 mg, 0.53 mmol) was reacted with 2-methylfuran (**33**) (82 mg, 1.00 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish an inseparable 84:16 mixture of **54** and **56** (100 mg, 90%) as a colorless oil (Table 1, entry 6): MS (EI) m/z (%) 212 (100, $M^{\bullet+}$). **54:** ^{1}H NMR δ (measured in a mixture with the **56**)1.31 (d, J = 6.9 Hz, 3 H, 4-Me), 2.14 (s, 3 H, 2′-Me), 3.51 (p, J = 6.9 Hz, 1 H, 3-H), 5.76 and 5.80 (2 × m, 2 × 1 H, 3′-H and 4′-H), 6.16 (dd; J = 15.7, 7.2 Hz, 1 H, 2-H), 6.32 (d, J = 16.0 Hz, 1 H, 1-H), 7.01−7.48 (m, 5 H, Ph). **56:** ^{1}H NMR δ (measured in a mixture with the **54**) 1.59 (d, J = 6.6 Hz, 3 H, 1-Me), 2.11 (s, 3 H, 2′-Me), 4.51 (d, J = 7.6 Hz, 1 H, 4-H), 5.43 (m, 1 H, 2-H), 5.69 (m, 1 H, 3-H).

1-Phenyl-3-(2′-methylfuran-5′-yl)-1-propene (55)[37g] and 3-Phenyl-3-(2′-methyl-furan-5′-yl)-1-propene (57).[37g] Acetate **8** (100 mg, 0.57 mmol) was reacted with 2-methylfuran (**33**) (60 mg, 0.73 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to produce an inseparable 75:25 mixture of **55** and **57** (50 mg, 44%) as a colorless oil (Table 1, entry 16): MS (EI) m/z (%) 198 (100, $M^{\bullet+}$). **55:** ^{1}H NMR δ 2.26 (s, 3 H, 2′-Me), 3.49 (d, J = 6.6 Hz, 2 H, 3-H), 5.87 and 5.92 (2 × m, 2 × 1 H, 3′-H and 4′-H), 6.29 (dt, J = 15.7, 6.6 Hz; 1 H; 2-H), 6.48 (d, J = 16.0 Hz, 1 H, 1-H), 7.17−7.38 (m, 5 H, Ph). **57:** ^{1}H NMR δ (measured in a mixture with the isomer **55**) 2.23 (s, 3 H, 2′-Me), 4.67 (d, J = 7.2 Hz, 1 H, 3- H), 5.03 (d, J = 17.0 Hz, 1 H, 1*E*-H), 5.18 (d, J = 10.1 Hz, 1 H, 1*Z*-H), 5.86 and 5.90 (2 × m, 2 × 1 H, 3′-H and 4′-H), 6.19 (ddd; J = 17.0, 10.1, 7.2 Hz; 1 H; 2-H).

1-Phenyl-3-(indol-3′-yl)-1-butene (58) and 4-Phenyl-4-(indol-3′-yl)-2-butene (60). Acetate **7** (100 mg, 0.53 mmol) was reacted with indole (**35**) (70 mg, 0.60 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to produce an inseparable 67:33 mixture of **58** and **60** (67 mg, 52%) as a colorless oil (Table 1, entry 7): MS (EI) m/z (%) 247 (81, $M^{\bullet+}$), 117 (100). **58:** ^{1}H NMR δ (measured in a mixture with isomer **60**) 1.54 (d, J = 6.9 Hz, 3 H, 4-Me), 3.91 (p, J = 6.9 Hz, 1 H, 3-H), 6.45 (m, 2 H, 1-H and 2-H), 6.90 (d, J = 2.2 Hz, 1 H, 2′-H), 6.97−7.39 (m, 9 H, arom). **60:** ^{1}H NMR δ (measured in a mixture with isomer **58**) 1.70 (d, J = 6.6 Hz, 3 H, 1-Me), 4.87 (d, J = 7.6 Hz, 1H, 4-H), 5.51 (dq, J = 15.1, 6.3 Hz 1 H; 2-H), 5.94 (dd; J = 15.1, 7.6 Hz; 1 H; 3-H), 6.77 (d, J = 1.6 Hz, 1 H, 2′-H), 6.90−4.39 (arom, obscured by the signals corresponding to **58**).

1-Phenyl-3-(1′-methylindol-3′-yl)-1-butene (59) and 4-Phenyl-4-(1′-methylindol-3′-yl)-2-butene (61). Acetate **7** (100 mg, 0.53 mmol) was reacted with 1-methylindole (**36**) (80 mg, 0.61 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford an inseparable 85:15 mixture of **59** and **61** (118 mg, 86%) as a colorless oil (Table 1, entry 8): MS (EI) m/z (%) 261 (18, $M^{\bullet+}$), 158 (100). **59:** ^{1}H NMR δ (measured in a mixture with isomer **61**) 1.43 (d, J = 6.9 Hz, 3 H, 4-Me), 3.52 (s, 3 H, NMe), 3.80 (p, J = 6.6 Hz, 1 H, 3-H), 6.35 (m, 2 H, 1-H and 2-H), 6.69 (s, 1 H, 2′-H), 6.90−7.37 (m, 9 H, arom). **61:** ^{1}H NMR δ (measured in a mixture with isomer **59**) 1.60 (d, J = 6.6 Hz, 3 H, 1-Me), 3.51 (s, 3 H, NMe), 4.76 (d, J = 7.2 Hz, 1 H, 4-H), 5.51 (dq, J = 15.1, 6.3 Hz, 1 H, 2-H), 5.94 (dd, J = 15.1, 7.5 Hz, 1 H, 3-H), 6.63 (s, 1 H, 2′-H).

1-Methyl-3-(4′-methoxyphenyl)cyclohexene (62). Acetate **15** (100 mg, 0.65 mmol) was reacted with anisole **26** (100 mg, 0.93 mmol) at −10 °C in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give **62** (65 mg, 50%) as a colorless oil (Table 2, entry 2): ^{1}H NMR δ 1.36−2.02 (m, 6 H, 3 × CH_2), 1.73 (s, 3 H, 1-Me), 3.31 (m, 1 H, 3-H), 3.77 (s, 3 H, OMe), 5.41 (br s, 1 H, 2-H), 6.82 (d, J = 8.5 Hz, 2 H 3′-H, 5′-H), 7.11 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H); ^{13}C NMR δ 22.0, 30.4, 32.9 (4,5,6-CH_2), 24.4 (1-Me), 41.7 (3-CH), 55.7 (OMe), 114.0 (3′,5′-CH), 125.2 (2-CH), 129.0 (2′,6′-H), 135.5 and 139.8 (1-C and 1′-C), 158.2 (4′-C); MS (EI) m/z (%) 202 (98, $M^{\bullet+}$), 187 (100).

1-Methyl-3-(4′-hydroxyphenyl)cyclohex-1-ene (63), 1-Methyl-3-(2′-hydroxyphenyl)cyclohex-1-ene (66), and 3,4,5,6-Tetrahydro-2-methyl-2,6-methano-2*H*-1-benzocin (73).[37l] Acetate **15** (100 mg, 0.65 mmol) was reacted with phenol (**27**) (330 mg, 3.51 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL). Column chromatography of the crude product on silica gel (15 × 2 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent afforded (in the order of elution) **63** (46 mg, 38%) and **73** (26 mg, 21%) as colorless oils (Table 2, entry 3). The same reaction with catalyst **C** (5 mol %) afforded **73** (25 mg, 20%) and a 1:4 mixture of **63** and **66** (29 mg, 24%). (Table 2, entry 4). The latter mixture was separated by preparative HPLC on Partisil 10 column with a 95:5 mixture hexanes−ethyl acetate (Table 1, entry 4). **63:** ^{1}H NMR δ 1.25−1.95 (m, 6 H, 3 × CH_2), 1.61 (s, 3 H, 1-Me), 3.18 (m, 1 H, 3-H), 5.28 (br s, 2 H, 2-H and OH), 6.65 (d, J = 8.5 Hz, 2H, 3′-H, 5′-H), 6.94 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H); ^{13}C NMR δ 21.9, 30.3, 32.9 (4,5,6-CH_2), 24.4 (1-Me), 41.7 (3-CH), 115.4 (3′,5′-CH), 125.1 (2-CH), 129.2 (2′,6′-CH), 135.6 and 140.0 (1-C and 1′-C), 153.9 (4′-C); MS (EI) m/z (%) 188 (96, $M^{\bullet+}$), 120 (100). **66:** ^{1}H NMR δ 1.52−2.10 (m, 6 H, 3 × CH_2), 1.70 (s, 3 H, 1-Me), 3.48 (m, 1 H, 3-H), 5.51 (s, 1 H, OH), 5.58 (s, 1H, 2-H), 6.82 (m, 2H, 3′-H, 5′-H), 7.10 (m, 2 H, 2′-H, 6′-H). **73:** ^{1}H NMR δ 1.35 (s, 3 H, 2-Me), 1.43−1.81 (m, 8 H, 4 × CH_2), 3.04 (m, 1 H, 6-H), 6.78 (m, 2 H, 8-H and 10-H), 6.98 (d, J = 7.6

Hz, 1 H, 7-H), 7.09 (t, J = 6.9 Hz, 1 H, 9-H);^{13}C NMR δ 18.7, 33.0, 36.3, and 39.8 (3,4,5,11-CH_2), 29.8 (2-Me), 33.4 (6-CH), 75.1 (2-C), 115.4 (10-CH), 119.5 (8-CH), 126.4 (6a-C), 127.7 and 128.5 (7- and 9-CH), 157.9 (10a−C); MS (EI) *m*/*z* (%) 188 (77, M$^{\bullet+}$), 120 (100).

1,5,5-Trimethyl-3-(4′-hydroxyphenyl)cyclohex-1-ene (64) and 3,4,5,6-Tetrahydro-2,4,4-trimethyl-2,6-methano-2*H*-1-benzocin (75). Acetate **16** (100 mg, 0.55 mmol) was reacted with phenol (**27**) (150 mg, 1.60 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL). Column chromatography of the crude product on silica gel (15 × 2 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent afforded (in the order of elution) **64** (10 mg, 8%) and **75** (17 mg, 14%) as colorless oils (Table 2, entry 8). **64:** ^{1}H NMR δ 0.96 (s, 6 H, 2 × 5-Me), 1.50−1.90 (m, 4 H, 4-H and 6-H), 1.71 (s, 3 H, 1-Me), 3.30 (m, 1 H, 3-H), 4.91 (br s, 1 H, OH), 5.36 (br s, 1 H, 2-H), 6.76 (d, J = 8.5 Hz, 2 H, 3′-H,5′-H), 7.06 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H); ^{13}C NMR δ 23.0 and 24.2 (2 × 5-Me), 29.4 (5-C), 30.8 (1-Me), 39.0 (3-CH), 43.0 and 45.3 (4- and 6-CH_2), 114.1 (3′,5′-CH), 122.6 (2-CH), 127.7 (2′,6′-CH), 133.7 and 138.7 (1-C and 1′-C), 152.6 (4′-C); MS (EI) *m*/*z* (%) 216 (62, M$^{\bullet+}$), 98 (100). **75:** ^{1}H NMR δ 0.54 (s, 3 H, 4-Me_a), 0.89 (s, 3 H, 4-Me_b), 1.40 (s, 3 H, 2-Me), 1.54−1.92 (m, 6 H, 3 × CH_2), 3.03 (p, J = 3.3 Hz, 1 H, 6-H), 6.70 (d, J = 8.2 Hz, 1 H, 10-H), 6.77 (t, J = 7.4 Hz, 1 H, 8-H), 7.07 (m, 2 H, 7-H and 9-H); ^{13}C NMR δ 29.6, 30.6, and 33.1 (2, 4,4-Me), 29.9 (4-C), 37.2 (6-CH), 36.3, 45.7, and 52.0 (3,5,11-CH_2), 75.5 (2-C), 115.7 (10-CH), 119.5 (8-CH), 127.9 and 128.5 (7- and 9-CH), 128.1 (6a), 156.1 (10a); MS (EI) *m*/*z* (%) 216 (90, M$^{\bullet+}$) 145 (100).

3-(4′-Methoxyphenyl)cyclohex-1-ene (65)[37h] **and 3-(2′-Methoxyphenyl)cyclohex-1-ene (70).**[37i] Acetate **17** (100 mg, 0.71 mmol) was reacted with anisole (**26**) (150 mg, 1.39 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to produce a 57:43 mixture of **65** and **70** (75 mg, 56%) as a colorless oil (Table 2, entry 11). The two compounds were separated by column chromatography on silica gel (20 × 2.5 cm) with a 95:5 hexanes−ethyl acetate mixture (95:5) as eluent. The slower moving component was identified as **65:** ^{1}H NMR δ 1.45−2.12 (m, 6 H, 3 × CH_2), 3.34 (m, 1 H, 3-H), 3.78 (s, 3 H, OMe), 5.69 (dd, J = 10.1, 1.9 Hz, 1 H, 2-H), 5.86 (ddd, J 10.1, 6.0, 3.5 Hz, 1 H, 1-H), 6.84 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.13 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H); MS (EI) *m*/*z* (%) 188 (M$^+$, 100). The faster moving component was identified as **70:** ^{1}H NMR δ 1.47−2.07 (m, 6 H; 3 × CH_2), 3.82 (s, 3 H, OMe), 3.85 (m, 1 H, 3-H), 5.66 (dd, J = 10.1, 2.5 Hz, 1 H, 2-H), 5.90 (ddd, J = 10.1, 6.0, 3.8 Hz, 1 H, 1-H), 6.89 (m, 2 H, 3′-H, 5′-H), 7.18 (m, 2 H, 4′-H, 6′-H); MS (EI) *m*/*z* (%) 188 (100, M$^{\bullet+}$).

3-(2′-Hydroxyphenyl)cyclohexene (71).[37j] Acetate **17** (100 mg, 0.71 mmol) was reacted with phenol (**27**) (200 mg, 2.13 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford a 90:10 mixture of **71** and a bis-allylated product (93 mg, 79%) as a colorless oil (Table 2, entry 13). GS-MS showed the molecular ions for the two products to be 174 and 254. The same reaction with catalyst **C** (5 mol %) gave rise to a 95:5 mixture of **71** and a bis-allylated product (101 mg, 83%) (Table 2, entry 14). Column chromatography of the former mixture on silica gel (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent furnished **71** (90 mg): ^{1}H NMR δ 1.48−2.17 (m, 6 H, 3 × CH_2), 3.58 (m, 1 H, 3-H), 5.46 (s, 1 H, OH), 5.80 (dm, J = 10.1 Hz, 1 H, 2-H), 6.04 (ddd, J = 10.1, 6.0, 3.2 Hz, 1 H, 1-H), 6.71−6.96 (m, 3 H, 3′-H, 5′-H, 6′-H), 7.10 (m, 1 H, 4′-H); MS (EI) *m*/*z* (%) 174 (100, M$^{\bullet+}$).

3-(2′-Hydroxy-5′-methylphenyl)cyclohex-1-ene (72)[37k] **and 2,6-Bis(cyclohex-2′-en-1′-yl)-4-methylphenol.** Acetate **17** (130 mg; 0.92 mmol) was reacted with *p*-cresole (**29**) (385 mg, 3.56 mmol) in the presence of catalyst **C** (5 mol %) in CH_2Cl_2 (5 mL) to produce an 84:16 mixture of **72** and 2,6-bis(2′-cyclohexenyl)-4-methylphenol (150 mg, 91%) as a colorless oil (Table 2, entry 15). The two compounds were separated by column chromatography on silica (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent. The slower moving component was identified as **72:** ^{1}H NMR δ 1.58−2.14 (m, 6 H; 3 × CH_2), 2.24 (s, 3 H, 5′-Me), 3.54 (m, 1 H, 3-H), 5.35 (s, 1 H, OH), 5.79 (dd, J = 10.1, 2.1 Hz, 1 H, 2-H), 6.01 (ddd, J = 10.1, 6.0, 3.5 Hz, 1 H, 1-H), 6.67 (d, J = 7.9 Hz, 1 H, 3′-H), 6.87 (m, 2 H, 4′-H and 6′-H); MS (EI) *m*/*z* (%) 188 (100, M$^{\bullet+}$). The faster moving component was identified as 2,6-bis-(cyclohex-2′-en-1′-yl)-4-methylphenol: ^{1}H NMR δ 1.55−2.12 (m, 12 H, 6 × CH_2), 2.24 (s, 3 H, 4-Me), 3.58 (m, 2 H, 1′-H, 1″-H), 5.59 (s, 1 H, OH), 5.79 (d, J = 10.1, 2 H, 2′-H, 2″-H), 6.00 (ddd, J = 10.1, 6.0, 3.5 Hz, 1 H, 3′-H, 3″-H), 6.80 (s, 2 H, 3-H and 5-H); MS (EI) *m*/*z* (%) 268 (100, M$^{\bullet+}$).

3,4,5,6-Tetrahydro-2,8-dimethyl-2,6-methano-2*H*-1-benzocin (74). Acetate **15** (100 mg, 0.65 mmol) was reacted with *p*-cresol (**29**) (710 mg, 6.57 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford **74** (101 mg, 77%) as a colorless oil (Table 2, entry 5): ^{1}H HMR δ 1.38 (s, 3 H, 2-Me), 1.48−1.97 (m, 8H, 4 × CH_2), 2.29 (s, 3 H, 8-Me) 3.02 (p, J = 3.1 Hz, 1 H, 6-H), 6.72 (d, J = 8.2 Hz, 1 H, 10-H), 6.83 (d, J = 1.9 Hz, 1 H, 7-H), 6.94 (dd, J = 8.2 Hz, J = 1.9 Hz, 1 H, 9-H); ^{13}C NMR δ 18.8, 33.1, 36.5, 40.0 (3,4,5,11-CH_2), 20.9 (8-Me), 29.9 (2-Me), 33.5 (6-CH), 74.9 (2-C), 115.2 (10-CH), 126.1 and 128.4 (6a- and 8-C), 128.5 and 129.0 (7- and 9-CH), 154.9 (10a−C); IR ν 3020, 2980, 2925, 2870, 2850, 1620, 1590, 1490, 1450 cm^{-1}; MS (EI) *m*/*z* (%) 202 (100, M$^{\bullet+}$).

3,4,5,6-Tetrahydro-2,4,4,8-tetramethyl-2,6-methano-2*H*-1-benzocin (76). Acetate **16** (294 mg, 1.62 mmol) was reacted with *p*-cresol (**29**) (2.06 g, 19.07 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **76** (298 mg, 80%) as a colorless oil (Table 2, entry 9): ^{1}H NMR δ 0.58 (s, 3 H, 4-Me_a), 0.90 (s, 3 H, 4-Me_b), 1.4 (s, 3 H, 2-Me), 1.45−1,89 (m, 6 H, 3 × CH_2), 2.27 (s, 3 H, 8-Me), 3.0 (p, J = 3.5 Hz, 1 H, 4-H), 6.63 (d, J = 8.2 Hz, 1 H, 10-H), 6.87 (d, J = 2.2 Hz, 1 H, 7-H), 6.94 (dd, J = 8.2, 2.2 Hz, 1 H, 9-H); ^{13}C NMR δ 20.9 (8-Me), 29.7, 30.6 and 33.1 (2,4,4-Me), 30.0 (4-C), 36.5, 45.7 and 52.1 (3,5,11-CH_2), 37.2 (6-CH), 75.3 (2-C), 115.4 (10-CH), 127.5 and 128.5 (6a- and 8-C), 128.8 and 129.0 (7- and 9-CH), 153.9 (10a); IR ν 3060, 3010, 2980−2860, 2840, 1620, 1590, 1500, 1460 cm^{-1}; MS (EI) *m*/*z* (%) 230 (100, M$^{\bullet+}$).

3-(4′-Methoxyphenyl)cyclopent-1-ene (77).[37h] Acetate **19** (100 mg, 0.79 mmol) was reacted with anisole (**26**) (150 mg, 1.39 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give an 80:20 mixture of **77** and bis-allylated products (64 mg, 50%) as a colorless oil (Table 2, entry 16). The GS-MS analysis of the crude product mixture showed the presence of two compounds (11% and 9%) with the molecular ion 240 corresponding to the isomeric bis-allylated products. Pure **77** was obtained from that mixture by column chromatography on silica gel (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent: ^{1}H NMR δ 1.58−1.68 and 2.11−2.45 (2 × m, 4 H, 2 × CH_2), 3.73 (s, 3 H, OMe), 3.79 (m, 1 H, 3-H), 5.70 (ddd, J = 5.7, 3.8, 1.9 Hz, 1 H, 2-H), 5.85 (ddd, J = 5.7, 4.4, 2.2 Hz, 1 H, 1-H), 6.78 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.05 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H); MS (EI) *m*/*z* (%) 174 (100, M$^{\bullet+}$).

3-(2′-Hydroxyphenyl)cyclopent-1-ene (78).[37i] Acetate **19** (100 mg, 0.79 mmol) was reacted with phenol (**27**) (200 mg, 2.13 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give an 87:13 mixture of **78** and a bis-allylated products (48 mg, 41%) as a colorless oil (Table 2, entry 17). The GS-MS analysis of the crude product mixture showed the presence of two compounds (8% and 5%) with the molecular ion 226 corresponding to the isomeric bis-allylated products. Pure **78** was obtained from that mixture by column chromatography on silica gel (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent: ^{1}H NMR δ 1.53−1.84 and 2.36−2.57 (2 × m, 4 H, 4-H, 5-H), 4.05 (m, 1 H, 3-H), 5.28 (br s, 1 H, OH), 5.89 (m, 1 H, 2-H), 6.07 (m, 1 H, 1-H), 6.71−7.26 (m, 4H, 3′-H, 6′-H); MS (EI) *m*/*z* (%) 160 (100, M$^{\bullet+}$).

3-(1′,3′-Benzodioxol-5′-yl)-cyclopent-1-ene (79). Acetate **19** (100 mg, 0.79 mmol) was reacted with 1,3-benzodioxole (**31**) (150 mg, 1.23 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **79** (70 mg, 47%) as a colorless oil (Table 2, entry 18): ^{1}H NMR δ 1.51−1.63 and 2.20−2.40 (2 × m, 4 H, 4-H, 5-H), 3.72 (m, 1 H, 3-H), 5.64 (m, 2 H, 1-H, 2-H), 5.81 (s, 2 H, OCH_2O), 6.55 (dd, J = 7.9, 1.6 Hz, 1 H, 6′-H), 6.58 (d, J = 1.6 Hz, 1 H, 4′-H), 6.63 (d, J = 7.9 Hz, 1 H, 7′-H); MS (EI) *m*/*z* (%) 188 (100, M$^{\bullet+}$).

3-(3′,4′-Dimethoxy-2′-methylphenyl)-cyclopent-1-ene (80). Acetate **19** (100 mg, 0.79 mmol) was reacted with 1,2-dimethoxy-3-methylbenzene (**32**) (160 mg, 1.05 mmol) in the

presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **80** (128 mg, 74%) as a colorless oil (Table 2, entry 19): ^{1}H NMR δ 1.50−1.65 and 2.35−2.46 (2 × m, 4 H, 4-H, 5-H), 2.27 (s, 3 H, 2′-Me), 3.77 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 4.01 (m, 1 H, 3-H), 5.73 (ddd, J = 5.7, 4.1, 1.9 Hz,1 H, 2-H), 5.92 (ddd, J = 5.7, 4.3, 2.0 Hz, 1 H, 1-H), 6.68 (d, J = 8.5 Hz, 1 H, 5′-H), 6.81 (d, J = 8.5 Hz, 1 H, 6′-H); MS (EI) m/z (%) 218 (30, $M^{\bullet+}$), 152 (100).

2-Methyl-4-(4′-methoxyphenyl)-2-butene (81).[37m] Acetate **20** (100 mg, 0.70 mmol) was reacted with anisole (**26**) (100 mg, 0.93 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **81** (32 mg, 24%) as a colorless oil (Table 2, entry 20): ^{1}H NMR δ 1.27 (d, J = 6.9 Hz, 3 H, 5-CH_3), 1.67 and 1.69 (2 × d, J = 1.5 and 1.2 Hz, 2 × 3 H, 1- and 2-CH_3), 3.61 (m, 1 H, 4-H), 3.78 (s, 3 H, OMe), 5.24 (dm, J = 9.1 Hz, 1 H, 3-H), 6.83 (d, J = 8.5 Hz, 2 H, 3′-H and 5′-H), 7.14 (d, J = 8.5 Hz, 2 H, 2′-H and 6′-H); MS (EI) m/z (%) 190 (28, $M^{\bullet+}$), 175 (100).

2-Methyl-4-(4′-methoxyphenyl)-2-butene (82).[37n−s] **Method A.** Acetate **21** (100 mg, 0.78 mmol) was reacted with anisole (**26**) (100 mg, 0.93 mmol) in the presence of the catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish a 73:27 mixture of **82** and the corresponding *ortho*-isomer (57 mg, 42%) as a colorless oil (Table 2, entry 22). Pure **82** was obtained from that mixture by column chromatography on silica gel (20 × 2.5 cm) with a 95:5 hexanes−ethyl acetate mixture as an eluent: ^{1}H NMR δ 1.71 (s, 3 H, Me), 1.73 (s, 3 H, Me), 3.27 (d, J = 7.2 Hz, 2 H, 4-H), 3.77 (s, 3 H, OMe), 5.24 (br t, J = 7.2 Hz, 1 H, 3-H), 6.82 (d, J = 8.8 Hz, 2 H, 3′-H and 5′-H), 7.18 (d, J = 8.5 Hz, 2 H, 2′-H and 6′-H); MS (EI) m/z (%) 176 (36, $M^{\bullet+}$), 121 (100).

Method B. The reaction of **22** with anisole (**26**) was carried out as described in method A to afford **82** (65 mg, 47%; Table 2, entry 24). The GC-MS analysis of the product showed the presence of the *ortho* isomer (less than 5%).

3,4-Dihydro-2,2,4-trimethyl-2*H*-benzopyran (85).[37t] Acetate **20** (80 mg, 0.56 mmol) was reacted with phenol (**27**) (260 mg, 2.77 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give an 95:5 mixture of **85** and bis-allylated products (19 mg, 19%) as a colorless oil (Table 2, entry 21). The GS-MS analysis of the crude product mixture showed the presence of two compounds (3% and 2%) with the molecular ions 258 corresponding to the isomeric bis-allylated products. Pure **85** was obtained from that mixture by column chromatography on silica gel (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent: ^{1}H NMR δ 1.25 (s, 3 H, Me), 1.41 (s, 3 H, Me), 1.33 (d, J = 6.6 Hz, 3 H, 4-Me), 1.70 (m, 2 H, CH_2), 2.95 (m, 1 H, 4-H), 6.76 (d, J = 8.2 Hz, 1 H, 8-H), 6.85 (t, J = 7.5 Hz, 1 H, 6-H), 7.08 (dd; J = 8.2, 7.3 Hz; 1 H, 7-H), 7.23 (d, J = 7.5 Hz, 1 H, 5-H); ^{13}C NMR δ 20.7 and 25.0 (2 × 2-Me), 26.7 (4-CH), 30.5 (4-Me), 43.1 (3-CH_2), 74.7 (2-C), 117.6 and 120.2 (6- and 8-CH), 127.5 and 127.7 (5- and 7-CH), 126.7 (4a−C), 153.9 (8a−C); MS (EI) m/z (%) 176 (46, $M^{\bullet+}$), 121 (100).

3,4-Dihydro-2,2-dimethyl-2*H*-benzopyran (86).[37h] **Method A.** Acetate **21** (100 mg, 0.78 mmol) was reacted with phenol (**27**) (150 mg, 1.60 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford a 90:10 mixture of **86** and a bis-allylated product (32 mg, 27%) as a colorless oil (Table 2, entry 23). Pure **86** was obtained from that mixture by column chromatography on silica gel (20 × 2.5 cm) with a 9:1 hexanes−ethyl acetate mixture as an eluent: ^{1}H NMR δ 1.33 (s, 6 H, 2 × 2-CH_3), 1.80 (m, 2 H, 3-H), 2.77 (t, J = 6.9 Hz, 2 H, 4-H), 6.71−7.11 (m, 4 H, arom); ^{13}C NMR δ 22.9 (3-CH_2), 27.3 (2 × 2-Me), 33.2 (4-CH_2), 74.5 (2-C), 117.7 and 120.0 (6- and 8-CH), 121.3 (4a-C), 127.7 and 129.8 (5- and 7-CH), 154.4 (8a-C).

Method B. The reaction of **22** with phenol (**27**) was carried out as described in method A to afford an 80:20 mixture of **86** and a bis-allylated product (55 mg, 48%) as a colorless oil (Table 2, entry 25), identical with the product obtained from **21** and **27** (see above).

5-(3′-Methylcyclohex-2′-en-1′-yl)furfuryl Acetate (87). Acetate **15** (120 mg, 0.78 mmol) was reacted with furfuryl acetate (**34**) (140 mg, 1.0 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to yield **87** (120 mg, 65%) as a colorless oil (Table 2, entry 6): ^{1}H NMR δ 1.56−1.94 (m, 6 H, 3 × CH_2), 1.70 (s, 3 H, 3′-Me), 2.07 (s, 3 H, MeCO), 3.42 (m, 1 H, 1′-H), 5.00 (s, 2 H, OCH_2), 5.47 (m, 1 H, 2′-H), 5.94 (d, J = 3.2 Hz, 1 H, 4-H), 6.29 (d, J = 3.2 Hz, 1 H, 3-H); ^{13}C NMR δ 21.2 (CH_3CO), 24.3 (3′-CH_3), 21.3, 28.2 and 30.3 (4′,5′,6′-CH_2), 35.7 (1′-CH), 58.8 (OCH_2), 105.8 and 111.7 (3,4-CH), 121.3 (2′-CH), 136.5 (C), 148.0 (C), 161.0 (C), 171.1 (CO); MS (EI) m/z (%) 234 (12, $M^{\bullet+}$), 79 (100).

1-Methyl-3-(1′-methylindol-3′-yl)cyclohex-1-ene (88). Acetate **15** (100 mg, 0.65 mmol) was reacted with 1-methylindole (**36**) (100 mg, 0.76 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **88** (125 mg, 85%) as a colorless oil (Table 2, entry 7): ^{1}H NMR δ 1.63−2.01 (m, 6 H, 3 × CH_2), 1.73 (s, 3 H, 1-Me), 3.64 (s, 3 H, NMe), 3.67 (m, 1 H, 3-H), 5.57 (m, 1 H, 2-H), 6.74 (s, 1 H, 2′-H), 7.06 (t, J = 7.9 Hz, 1 H, 5′-H), 7.22 (m, 2 H, 6′-H and 7′-H), 7.61 (d, J = 7.9 Hz, 1 H, 4′-H); MS (EI) m/z (%) 225 (100, $M^{\bullet+}$).

1,5,5-Trimethyl-3-(1′-methylindol-3′-yl)cyclohex-1-ene (89). Acetate **16** (141 mg, 0.78 mmol) was reacted with 1-methylindole (**36**) (514 mg, 3.92 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to furnish **89** (143 mg, 70%) as a colorless oil (Table 2, entry 10): ^{1}H HMR δ 0.95 (s, 3 H, 5-Me_a), 1.02 (s, 3 H, 5-Me_b), 1.45−1.95 (m, 4 H, 4-H and 6-H), 1.70 (s, 3 H, 3-Me), 3.65 (s, 3 H, NMe), 5.50 (br s, 1 H, 2-H), 6.70 (s, 1 H, 2′-H), 7.02 (m, 1 H, 5′-H), 7.19 (m, 2 H, 6′- and 7′-H), 7.68 (d, J = 9.0 Hz, 1 H, 4′-H); ^{13}C NMR δ 24.4 and 25.8 (2 × 5-Me), 30.8 (5-C), 32.0 (1-Me), 32.4 (NMe), 33.0 (3-CH), 44.5 and 44.7 (4- and 6-CH_2), 109.7 (CH), 118.9 (CH), 120.0 (CH), 120.5 (C), 121.9 (CH), 124.4 (CH), 125.6 (CH), 127.6 (C), 133.3 (C), 137.8 (C); MS (EI) m/z (%) 262 (100, $M^{\bullet+}$).

(*E*)-3-(2′-Hydroxyphenyl)-5-carbomethoxy-1-cyclohexene (90) and (*E*)-3-(4′-Hydroxyphenyl)-5-carbomethoxy-1-cyclohexene (91). Acetate **23** (100 mg, 0.51 mmol) was reacted with phenol (**27**) (100 mg, 1.06 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to give a 90:10 mixture of *o*- and *p*-isomers **90** and **91** (69 mg, 59%) as a white solid (Table 2, entry 26): MS (EI) m/z (%) 232 (77, $M^{\bullet+}$), 172 (100). Compounds **90** and **91** were separated by preparative HPLC with a 98:2 hexanes−ethyl acetate mixture as an eluent. **90:** ^{1}H NMR δ 2.08 (m, 2 H, 4-H), 2.38 (m, 2 H, 6-H), 2.61 (m, 1 H, 5-H), 3.65 (s, 3 H, OMe), 3.88 (m, 1 H, 3-H), 5.78 (m, 1 H, 1-H), 5.98 (m, 1 H, 2-H), 6.03 (s, 1 H, OH), 6.76−6.88 (m, 2 H, 3′- and 5′-H), 7.08 (m, 2 H, 4′- and 6′-H). **91:** ^{1}H NMR δ 1.92 (dt, J = 12.9, 3.5 Hz, 1 H, 4-H_a), 2.12 (ddd, J = 12.9, 10.7, 6.0 Hz, 1 H, 4-H_b), 2.34 (m, 2 H, 6-H), 2.59 (m, 1 H, 5-H), 3.50 (m, 1 H, 3-H), 3.65 (s, 3 H, OMe), 4.74 (s, 1 H, OH), 5.74 (m, 1 H, 1-H), 5.93 (m, 1 H, 2-H), 6.77 (d, J = 8.5 Hz, 2 H, 3′-H and 5′-H), 7.08 (d, J = 8.5 Hz, 2 H, 4′-H and 6′-H).

1-(2′-Hydroxyphenyl)-3a,4,5,6,7,7a-hexahydro-(1α,-3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (92). Acetate **24** (100 mg, 0.52 mmol) was reacted with phenol (**27**) (490 mg, 5.21 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford **92** (59 mg, 51%) as a colorless oil (Table 2, entry 29): ^{1}H NMR δ 1.25−1.46 (m, 6 H, 3 × CH_2), 2.37 (m, 3 H, 4-H, 7-H, 7a-H), 3.22 (m, 1 H, 3a-H), 3.88 (br s, 1 H, 1-H), 5.37 (s, 1 H, OH), 5.86 (m, 2 H, 2-H, 3-H), 6.80 (m, 2 H, 3′-H, 5′-H), 7.05 (m, 2 H, 2′-H, 6′-H); ^{13}C NMR δ 23.3 and 25.6 (5,6-CH_2); 39.6, 41.6, 47.4 (4,7,7a-CH), 41.6 (8-CH_2), 52.9 and 53.6 (1,3a-CH); 116.5, 121.0, 127.8, and 129.4 (3′-6′-CH), 132.3 (1′-C), 133.8 and 136.6 (2,3-CH), 154.7 (2′-CH); MS (EI) m/z (%) 226 (22, $M^{\bullet+}$), 159 (100).

1-(4′-Methoxyphenyl)-3a,4,5,6,7,7a-hexahydro-(1α,-3aα,4α,7α,7aα)-4,7-methano-1*H*-indene (93). Acetate **24** (70 mg, 0.36 mmol) was reacted with anisole (**26**) (560 mg, 5.19 mmol) in the presence of catalyst **B** (5 mol %) in CH_2Cl_2 (5 mL) to afford **93 (**66 mg, 75%) as a colorless oil (Table 2, entry 28). The GC-MS analysis of the product showed the presence of bis-allylated compound (∼10%): ^{1}H NMR (taken in a mixture with bis-allylation product) δ 1.25 (m, 6 H, 3 × CH_2), 2.30 (m, 3 H, 4-H, 7-H, 7a-H), 3.15 (m, 1 H, 3a-H), 3.54 (m, 1 H, 1-H), 3.76 (s, 3 H, OMe), 5.70 (m, 2 H, 2-H, 3-H), 6.80 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 7.04 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H); MS (EI) m/z (%) 240 (27, $M^{\bullet+}$), 173 (100).

(*R*)-(+)-1-Phenyl-3-phenoxy-1-butene (102) was prepared by following the literature procedure[11] from carbonate (*R*)-(+)-**101** (360 mg, 1.64 mmol) and phenol (160 mg, 1.7 mmol) in 75% yield (276 mg, 1.23 mmol): $[\alpha]_D$ +81.7 (*c* 2.1,

$CHCl_3$); ^{1}H NMR δ 1.52 (d, J = 6.3 Hz, 3 H, 4-Me), 4.97 (p, J = 6.3 Hz, 1 H, 3-H), 6.28 (dd, J = 16.0, 6.0 Hz, 1 H, 2-H), 6.60 (d, J = 16.3 Hz, 1 H, 1-H), 6.88−7.38 (m, 10 H, arom); ^{13}C NMR δ 22.2 (4-CH_3); 74.9 (3-CH); 116.6 (2″,6″-CH), 121.2 (4″-CH), 127.1 (2″,5″-CH), 128.1 (CH), 129.0 and 129.8 (2′,3′,5′,6′-CH), 131.1 (CH), 131.2 (CH), 137.0 (1′-C), 158.5 (1″-C); MS (FAB) m/z (%) 224 (8, $M^{\bullet+}$), 131 (100).

Rearrangement of (*R*)-(+)-102 in the Presence of Lewis-Acid Catalysts. Method A. A solution of (*R*)-(+)-**102** (70 mg, 0.31 mmol) in CH_2Cl_2 (5 mL) was treated with the catalyst **B** as described in the General Procedure for Allylic Substitution. After 20 h at room temperature, the usual workup afforded a 50:50 mixture of **38** and **41** (29 mg, 42%) identical with the compounds prepared directly from **7** and **27** (see above). GC-MS analysis of the crude product mixture showed the presence of phenol (∼5%). The mixture exhibited no optical rotation.

Method B. A solution of (*R*)-(+)-**102** (60 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was treated with $Yb(OTf)_3$ for 20 h at room temperature to afford a ∼50:50 mixture of **38** and **41** (26 mg, 43%) with no optical rotation.

Method C. Following the literature procedure,[24] a solution of (*R*)-(+)-**102** (70 mg, 0.31 mmol) in CH_2ClCH_2Cl (0.5 mL) was treated with $Eu(fod)_3$ at 80 °C for 12 h to afford **103** (34 mg, 49%) as a 4:1 mixture of *trans*/*cis*-isomers and unreacted starting material (17 mg, 24%).

(*E*)-1-Phenyl-1-(2″-hydroxyphenyl)-2-butene ((*E*)-103): [28,37b] ^{1}H NMR δ (taken in a mixture with the (*Z*)-isomer) 1.75 (d, J = 6.3 Hz, 3 H, 4-Me), 4.86 (m, 2 H, 3-H and OH), 5.49 (qdd, J = 15.4, 6.6, 1.3 Hz, 1 H, 3-H), 5.95 (ddq, J = 15.4, 7.1, 1.6 Hz, 1 H, 2-H), 6.79−7.34 (m, 9 H, arom), in accordance with the literature. HPLC on Chiralcel OD-H column with a 98.5:1.5 hexane−2-propanol mixture showed 76% ee (t_{major} = 25.7 min; the minor enantiomer had t_{minor} = 25.0 min; flow rate 0.5 mL/min).

(*Z*)-1-Phenyl-1-(2″-hydroxyphenyl)-2-butene ((*Z*)-103): ^{1}H NMR δ (taken in a mixture with the (*E*)-isomer) 1.73 (d, J = 6.6 Hz, 3 H, 4-Me), 5.20 (d, 1 H, J = 9.5 Hz, 3-H), 5.49 (qd, J = 10.9, 7.1 Hz, 1 H, 3-H), 5.89 (m, 1 H, 2-H), 6.79−7.34 (m, 9 H, arom). HPLC analysis on Chiralcel OD-H column (98.5:1.5 hexane−2-propanol) of a sample containing mainly the (*E*)-isomer showed ≥80% ee, but the low content of the (*Z*)-isomer did not allow us to determine its ee accurately (t_{major} = 31.5 min; t_{minor} = 30.5 min; flow rate 0.5 mL/min).

(*R*)-(+)-1-Phenyl-3-(2-naphthoxy)-1-butene (104) was prepared by following the literature procedure[11] from carbonate (*R*)-(+)-**101** (150 mg, 0.68 mmol) and 2-naphthol (100 mg, 0.69 mmol) in 86% yield (161 mg, 0.59 mmol): $[\alpha]_D$ +233.3 (*c* 2.0, $CHCl_3$); ^{1}H NMR δ 1.54 (d, J = 6.6 Hz, 3 H, 4-Me), 5.06 (p, J = 6.3 Hz, 1 H, 3-H), 6.30 (dd, J = 16.4, 6.0 Hz, 1 H, 2-H), 6.63 (d, J = 16.1 Hz, 1 H, 1-H), 7.12−7.72 (m, 12 H, arom); ^{13}C NMR δ 22.2 (4-CH_3); 75.0 (3-CH); 109.6 (CH), 120.1 (CH), 124.2 (CH), 126.8 (CH), 127.0 and 129.1 (2′,3′,5′,6′-CH), 127.3 (CH), 128.1 (CH), 128.3 (CH), 129.5 (C), 129.9 (CH), 131.1 (CH), 131.2 (CH), 135.1 (C), 137.0 (C), 156.4 (2″-C); MS (EI) m/z (%) 274 (12, $M^{\bullet+}$), 131 (100).

Rearrangement of (*R*)-(+)-102 in the Presence of Lewis-acid Catalysts. Method A. A solution of (*R*)-(+)-**104** (30 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was treated with the catalyst **B.** After 8 h at room temperature, the usual workup afforded **105** (21 mg, 70%).

1-Phenyl-3-(2″-hydroxynaphthyl)-1-butene (105): ^{1}H NMR δ 1.63 (d, J = 6.9 Hz, 3 H, 4-Me), 4.64 (q, J = 6.9 Hz, 1 H, 3-H), 5.87 (s, 1H, OH), 6.74 (s, 2 H, 1, 2-H), 7.04−8.05 (m, 11 H, arom); ^{13}C NMR δ (acetone-d_6) 19.8 (4-CH_3); 35.3 (3-CH); 119.8 (CH), 123.7 (CH), 124.1 (C), 124.9 (CH), 127.1 (CH), 127.3 and 129.7 (2′,3′,5′,6′-CH), 128.0 (CH), 129.4 (CH), 129.5 (CH), 130.1 (CH), 130.9 (C), 134.4 (C), 136.7 (CH), 139.4 (C), 153.5 (2″-C); MS (EI) m/z (%) 274 (100, $M^{\bullet+}$). GC-MS analysis of the crude product mixture showed the presence of naphthol (∼5%). The product had no optical rotation and HPLC on Chiralcel OD-H column with a 95:5 hexane−2-propanol mixture revealed equal amounts of the two enantiomers (t = 17.2 min and t = 18.4 min; flow rate 0.5 mL/min).

Method B. Analogously, a solution of (*R*)-(+)-**104** (30 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was treated with $Yb(OTf)_3$ for 12 h at room temperature to afford **105** (17 mg, 57%) with no optical rotation detected.

Method C. Following the literature procedure,[24] a solution of (*R*)-(+)-**104** (35 mg, 0.13 mmol) in CH_2ClCH_2Cl (0.5 mL) was treated with $Eu(fod)_3$ for 12 h at 80 °C to afford **106** (16 mg, 46%) as a 4:1 mixture of *trans*/*cis*-isomers. The *trans*-isomer was separated from the mixture by preparative HPLC on Partisil 10 column with a 95:5 mixture hexanes−ethyl acetate.

(*E*)-1-Phenyl-1-(2″-hydroxynaphthyl)-2-butene (106): ^{1}H NMR δ 1.77 (d, J = 6.3 Hz, 3 H, 4-Me), 5.6 (m, 2 H, 1,3-H), 5.83 (s, 1H, OH), 6.20 (ddq, J = 15.4, 6.3, 1.6 Hz, 1 H, 2-H), 7.08−7.93 (m, 11 H, arom); ^{13}C NMR δ 18.4 (4-CH_3); 45.6 (1-CH); 119.7 (CH), 119.8 (C), 123.2 (CH), 123.5 (CH), 127.0 (CH), 127.2 (CH), 128.5 and 129.2 (2′,3′,5′,6′-CH), 129.3 (CH), 129.7 (CH), 130.0 (C), 130.3 (CH), 132.1 (CH), 133.4 (C), 141.9 (C), 153.0 (2″-C); MS (EI) m/z (%) 274 (100, $M^{\bullet+}$). HPLC on Chiralcel OD-H column with a 95:5 hexane−2-propanol mixture showed 82% ee (t_{major} = 15.8 min, t_{minor} = 14.6 min; flow rate 0.5 mL/min).

1-Phenoxycyclohex-1-ene (107).[38] To a stirred solution of cyclohex-2-en-1-ol (500 mg, 5.10 mmol), phenol (**27**) (590 mg, 6.27 mmol), and triphenylphosphine (1.638 g, 6.25 mmol) in THF (30 mL) at −20 °C was added dropwise diethyl azodicarboxylate (1.088 g, 6.25 mmol). The reaction mixture was allowed to warm to room temperature and the stirring continued for 4 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (3 × 20 mL). The hexane solution was concentrated in vacuo and passed through a silica gel column (15 × 2 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent to furnish the ether **107** (680 mg, 77%): ^{1}H NMR δ 1.55−2.18 (m, 6 H, 3 × CH_2), 4.78 (m, 1 H, 3-H), 5.80 (dm, J = 10.1 Hz, 1 H, 2-H), 6.04 (dt, J = 10.1, 3.5 Hz, 1 H, 1-H), 6.90 (m, 3 H, 2′-H, 4′-H, 6′-H), 7.26 (t, J = 8.5 Hz, 2 H, 3′-H, 5′-H); ^{13}C NMR δ 19.5, 25.5, 28.8 (4,5,6-CH_2), 71.2 (3-CH), 116.3 (2′,6′-CH), 121 (4′-CH), 126.9 and 132.5 (1,2-CH), 129.9 (3′,5′-CH), 158.3 (1′-C). MS (EI) m/z (%) 174 (0.7, $M^{\bullet+}$), 80 (100).

Rearrangement of the Ether 107 in the Presence of the Catalyst B. Treatment of **107** (100 mg, 0.57 mmol) with the catalyst **B** (5 mol %) for 20 h afforded a multiproduct mixture. The major components of the mixture were separated by column chromatography on silica gel (15 × 2 cm) with a 9:1 hexanes−ethyl acetate mixture as eluent and identified as follows (in order of elution): the starting material **107** (15 mg, 15%), 1-(2′-hydroxyphenyl)cyclohex-2-ene (**71**) (36 mg, 36%), identical with the compound prepared directly from **17** and **27** (see above), and 3-(4′-hydroxyphenyl)cyclohexene[39] (10 mg, 10%). The GC-MS analysis of the crude product mixture also showed the presence of several poly-allylated products and phenol (∼5%). 1-(4′-Hydroxyphenyl)cyclohex-1-ene:[39] ^{1}H NMR δ 1.50−2.18 (m, 6 H, 3 × CH_2), 3.28 (m, 1 H, 3-H), 4.65 (s, 1 H, OH), 5.68 (dm, J = 10.1 Hz, 1 H, 2-H), 5.86 (ddd, J = 10.1, 6.0, 3.4 Hz, 1 H, 1-H), 6.75 (d, 2 H, 2′-H, 6′-H), 7.07 (d, 2 H, 3′-H, 5′-H).

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Supporting Information Available: MS and HRMS spectral characteristics and elemental analyses for new compounds and ^{1}H and ^{13}C NMR spectra for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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