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Synthesis of Substituted Benzenes and Phenols by Ring-Closing Olefin Metathesis

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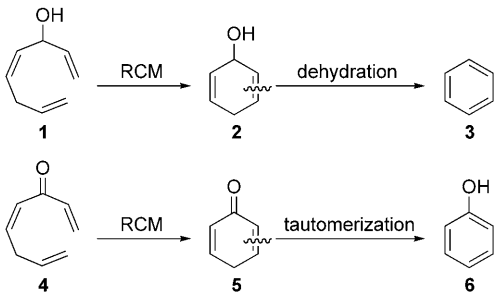
Abstract: New synthetic approaches to substituted aromatic compounds are reported. Ring-closing olefin metathesis (RCM)/dehydration and RCM/tautomerization are the key processes in the synthesis of substituted benzenes **3** and phenols **6**, respectively. Readily accessible 1,5,7-trien-4-ols **7**, which are the precursors of benzenes, were prepared from β-halo-α,β-unsaturated aldehydes **11** or β-halo-α,β-unsaturated esters **19** by utilizing reliable transformations in which cross-coupling with vinylic metal reagents **12** and allylation with allylic metal reagents **13** were employed as carbon–carbon bond forming reactions. RCM of **7**, followed by dehydration, afforded a wide variety of substituted benzenes **3**. In addition, RCM of 1,5,7-trien-4-ones **9**, which were prepared by oxidation of **7**, furnished various substituted phenols **6** by automatic tautomerization.

Keywords: arenes · cyclization · dehydration · metathesis · tautomerization

Introduction

The demand for functionalized aromatic compounds is growing rapidly in many research fields. Therefore, the efficient synthesis of the desired aromatic compounds is a critical issue in organic synthesis.[1] Electrophilic aromatic substitution is predominantly used for the synthesis of substituted aromatic compounds at both laboratory and industrial levels. It is, however, quite difficult to synthesize the desired aromatic compounds only with this transformation. The introduction of a substituent to an existing aromatic ring, which is one of the features of electrophilic aromatic substitution, gives rise to induction of plural orientation on the aromatic ring in most cases. Hence, it is often difficult to control substitution sites regioselectively with this reaction, as required by synthetic chemists. The direct construction of aromatic rings from acyclic precursors in which substituents are arranged at predetermined positions presents a potential advantage in terms of selective synthesis of complex aromatic compounds.[2] Recently, ring-closing olefin metathesis (RCM), which has seen much improvement with the development of readily available ruthenium carbene complexes, has begun to be applied in this strategy.[3–5] RCM is one of the most powerful reactions to form carbon-carbon double bonds of cyclic compounds due to its operational simplicity, high chemoselectivity, and remarkable functional group tolerance.[6,7] Therefore, it seems quite reasonable to apply this reaction to the synthesis of aromatic compounds.

In the last few years, we have focused our efforts on the development of a new method for the synthesis of aromatic compounds with RCM,[8] and found that substituted benzenes **3** and phenols **6** can be obtained from tandem RCM/dehydration of 1,4,7-trien-3-ols **1** and RCM/tautomerization of 1,4,7-trien-3-ones **4**, respectively (Scheme 1). The key point of these processes is the adoption of cyclohexa-2,5-di-



Scheme 1. Substituted benzenes **3** and phenols **6** from tandem RCM/dehydration of 1,4,7-trien-3-ols **1** and RCM/tautomerization of 1,4,7-trien-3-ones **4**.

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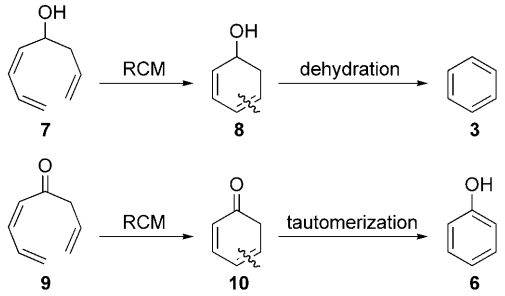
enols **2** and cyclohexa-2,5-dienones **5** as target intermediates of RCM. Although these processes yield various substituted benzenes and phenols, they lack generality because precursors **1** and **4** could not be readily prepared. On the other hand, cyclohexa-2,4-dienols **8** and cyclohexa-2,4-dienones **10** are also regarded as precursors of benzenes and phenols with these routes (Scheme 2). Therefore, it is anticipated that the RCM/dehydration of 1,5,7-trien-4-ols **7** and the RCM/tautomerization of 1,5,7-trien-4-ones **9** would give benzenes **3** and phenols **6**, respectively.

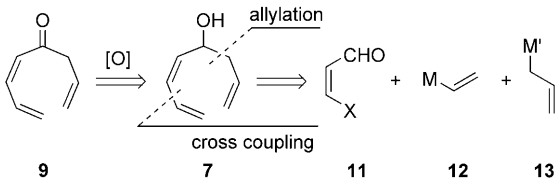


Scheme 2. 1,5,7-Trien-4-ols **7** and 1,5,7-trien-4-ones **9** give benzenes **3** after RCM/dehydration and phenols **6** after RCM/tautomerization, respectively.

Herein we present the results of investigation of the synthesis of substituted benzenes and phenols with these routes. Because of the accessibility of **7** and **9**, the synthetic routes have great generality for the preparation of various aromatic compounds. First, we will describe the preparation of precursors **7** and **9**. Then, we will discuss in detail the synthesis of benzenes **3** and phenols **6** with RCM.

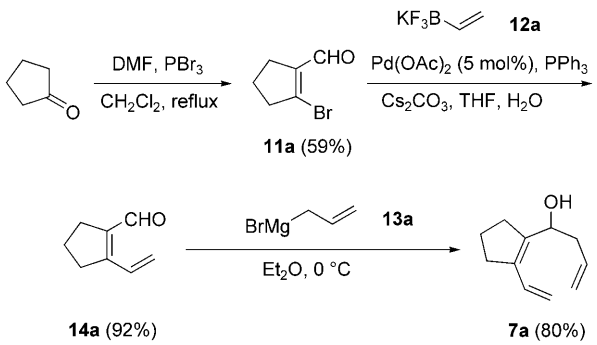
Results and Discussion

Our retrosynthetic analysis revealed that substrates **7** and **9** could be synthesized from three basic segments (Scheme 3). A combination of the cross-coupling reaction of β-halo-α,β-unsaturated aldehydes **11** with vinylic metal reagents **12** and the allylation of the resulting coupling products with allylic metal reagents **13** would lead to trienes **7**, which are the precursors of benzenes. In addition, oxidation of **7** at the alcohol position would be expected to furnish **9** for the synthesis of phenols. If the three basic segments containing various substituents are employed with this route, it is predicted that a wide variety of compounds **7** and **9** would be prepared.



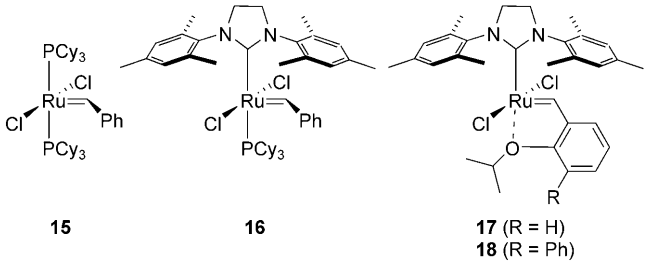
Scheme 3. Retrosynthetic analysis of substrates **7** and **9**.

The synthetic route to 1-(1-hydroxy-3-butenyl)-2-vinylcyclopentene (**7a**) is given in Scheme 4 as a representative example of the preparation of **7**. We started with an examination of the preparation of **11a** from cyclopentanone according to a procedure in the literature.[9] Suzuki–Miyaura coupling[10] between **11a** and potassium trifluorovinylborate (**12a**) in the presence of 5 mol% $Pd(OAc)_2$ as the precatalyst, PPh_3 as the ligand, and Cs_2CO_3 as the base in THF/H_2O afforded dienal **14a** in high yield. Then, the reaction of **14a** with allyl Grignard reagent **13a** in Et_2O gave the desired product **7a**.



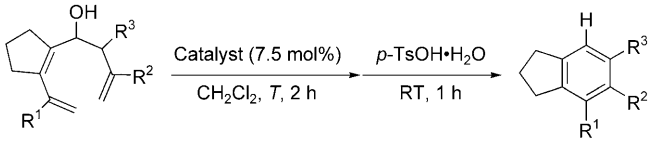
Scheme 4. A representative example of the preparation of **7**.

In this work, we employed the following ruthenium carbene catalysts for RCM: Grubbs first-generation catalyst **15**,[11] Grubbs second-generation catalyst **16**,[12] Hoveyda–Grubbs catalyst **17**,[13] and substituted Hoveyda–Grubbs catalyst **18**.[14]

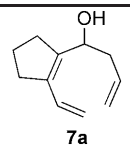
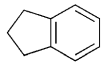
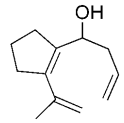
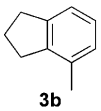
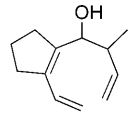
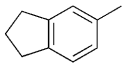
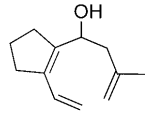
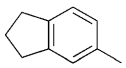
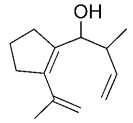
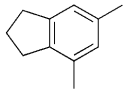
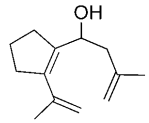
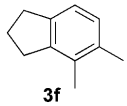


To our delight, when we carried out RCM of **7a** using Grubbs first-generation catalyst **15** at room temperature followed by dehydration with a catalytic amount of *p*-toluenesulfonic acid, the corresponding benzene **3a** was quantitatively obtained (Table 1, entry 1). Then, we prepared a variety of methyl-substituted compounds **7** (**7b–f**) using the above-mentioned route and conducted RCM/dehydration reactions to examine the effect of substituents in the vicinity of the RCM-reactive double bonds on the reactivity (Table 1, entries 2–11). Under the same reaction conditions, introduction of a methyl group at the R^1 or R^3 position retarded the conversion of the reaction to approximately half that of **7a** (Table 1, entry 1 vs. entries 2 and 4), whereas in-

Table 1. Synthesis of benzenes **3** by RCM/dehydration.[a]



7 **3**

Entry	Substrate	Product	Catalyst	*T* [°C]	Yield [%][b]
1	 **7a**	 **3a**	**15**	RT	>99
2	 **7b**	 **3b**	**15**	RT	48
3			**16**	RT	96
4	 **7c**	 **3c**	**15**	RT	44
5			**16**	RT	97
6	 **7d**	 **3c**	**15**	RT	trace
7			**16**	RT	94
8	 **7e**	 **3e**	**15**	RT	24
9			**16**	RT	92
10	 **7f**	 **3f**	**16**	40	0
11[c]			**16**	100	91

[a] Ring-closing olefin metathesis was carried out with 1,5,7-trien-4-ol **7** and ruthenium catalyst (**15** or **16**, 7.5 mol%) in CH_2Cl_2 for 2 h. The reaction mixture was treated with *p*-toluenesulfonic acid (10 mol%) at room temperature for 1 h. [b] NMR yield by ^1H NMR analysis by using 1,4-bis(trimethylsilyl)benzene as the internal standard. [c] The reaction was carried out in toluene.

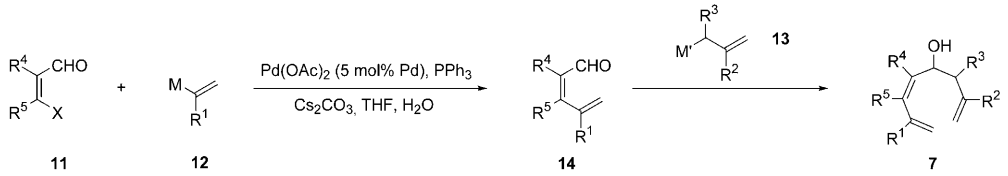
troduction of a methyl group at the R^2 position further decreased the reactivity (Table 1, entry 6). More active Grubbs second-generation catalyst **16** was, however, sufficient to drive the reactions to completion under the same conditions (Table 1, entries 3, 5, and 7). As we had anticipated, simultaneous introduction of two methyl groups at the R^1 and R^3 positions decreased the reactivity synergistically (Table 1, entry 8), but catalyst **16** promoted the reaction at room temperature (Table 1, entry 9). Substrate **7f** containing two methyl groups at the R^1 and R^2 positions was an exception: the reaction of **7f** did not proceed at all even when **16** was used at 40°C (Table 1, entry 10) and a high reaction temperature (100°C) was required to complete the reaction (Table 1, entry 11).

After acquiring basic data, we next examined the generality of this synthetic route. The results of cross-coupling between **11** and **12**, and allylation of coupled products **14** with **13** to yield **7** are summarized in Table 2. For the cross-coupling, we employed Suzuki–Miyaura coupling. The reaction proceeded cleanly under standard conditions by using $Pd(OAc)_2$, PPh_3, and Cs_2CO_3 in THF/H_2O to furnish various products **14** in good to excellent yields. Coupled products **14c–e** were used directly without isolation for the subsequent allylation, because we were concerned about their stability during the purification step. For the subsequent allylation, readily available allylborane, allyl Grignard, and allylstannane reagents were employed. In the reaction with allylborane, solvent-free conditions could be utilized to obtain the corresponding homoallylic alcohols **7** in high yields.[15] We examined only one example of the allylation with allylstannane, which requires the addition of a Lewis acid to promote the reaction (Table 2, entry 8). When we used $MgBr_2$ as the Lewis acid for the reaction of **14g** with **13e**, a mixture of **7n** and **7n** substituted with bromide at the allylic chloride position was obtained. After screening for the optimal conditions, we found that $BF_3{\cdot}Et_2O$ was the optimal Lewis acid for this reaction, affording pure **7n** in good yield.

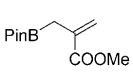
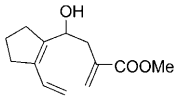
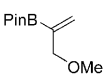
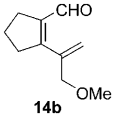
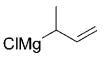
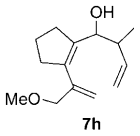
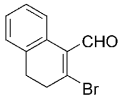
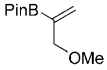
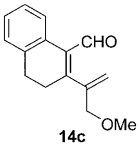
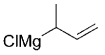
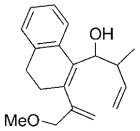
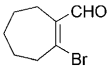
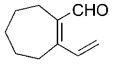
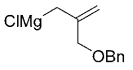
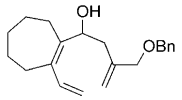
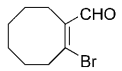
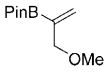
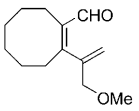
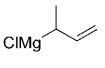
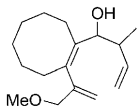
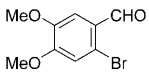
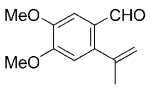
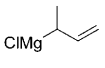
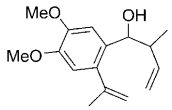
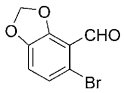
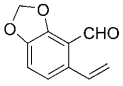
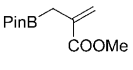
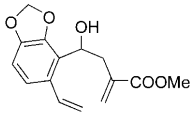
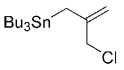
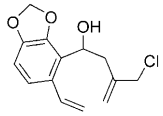
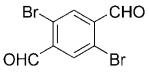
α,β-Unsaturated esters **19** can be used instead of aldehydes **11** and are also good candidates for the starting material for the preparation of **7**. Table 3 shows the results of the conversion of **19** to **7**. This synthetic route employs the following reactions: the Suzuki–Miyaura coupling between **19** and **12**, the reduction of esters **20** to alcohols **21** with diisobutylaluminum hydride (DIBAL-H), the oxidation of the resulting alcohols **21** to aldehydes **14** with MnO_2, and the allylation of **14** with allyl Grignard reagents to yield **7**.[16] Although various 1,5,7-trien-4-ols **7** were successfully prepared with this route, it should be mentioned that *E*/*Z* isomerization was observed in the cross-coupling reaction between alkenyl triflate **19d** and potassium isopropenyltrifluoroborate (**12c**). When the reaction of **12c** and geometrically pure (*Z*)-**19d** was carried out in the presence of a palladium catalyst in THF/H_2O at reflux temperature, a 1:4 *E*/*Z* mixture of **20d** was obtained. Decreasing the temperature to room temperature improved the *E*/*Z* ratio to 1:20 and the isomers could be separated by silica-gel column chromatography (Table 3, entry 4). Interestingly, no such *E*/*Z* isomerization was observed in a similar reaction of alkenyl iodide **19b** or **19c** even at elevated temperatures (Table 3, entries 2 and 3).

With a wide variety of the desired precursors in hand, we tried to synthesize substituted benzenes **3** by RCM/dehydration of **7**. The results are presented in Table 4. All RCM reactions were conducted with Grubbs second-generation catalyst **16**. The formation of condensed benzenes containing five- to eight-membered aliphatic rings was accomplished without any problems (Table 4, entries 1–5). Likewise, substituted naphthalenes **3l–n** were produced in high yields under similar conditions (Table 4, entries 6–8). The construc-

Table 2. Preparation of 1,5,7-trien-4-ols **7**, precursors of benzenes **3**, from β-halo-α,β-unsaturated aldehydes **11** by Suzuki–Miyaura coupling and allylation.[a]

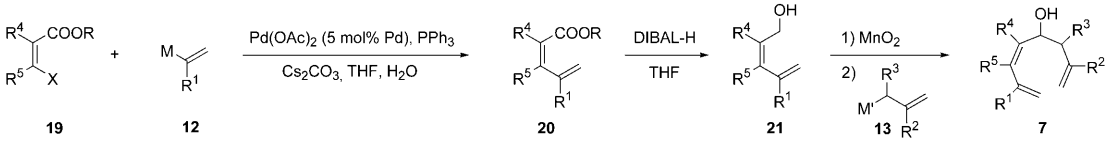


11 12 14 7

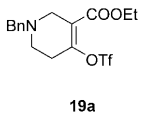
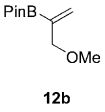
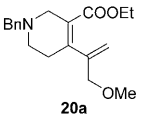
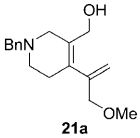
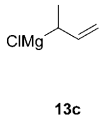
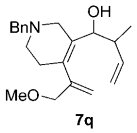
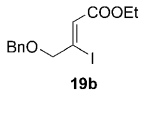
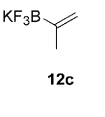
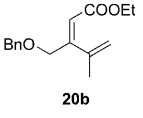
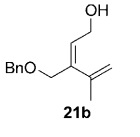
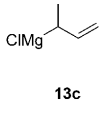
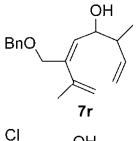
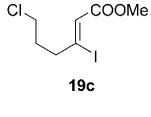
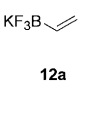
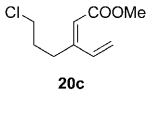
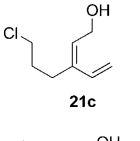
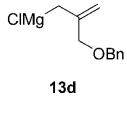
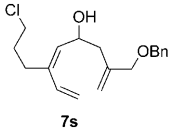
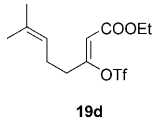
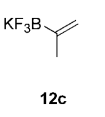
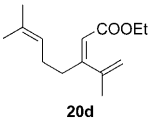
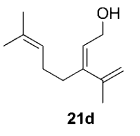
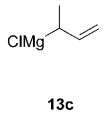
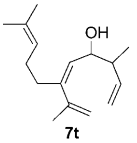
Entry	11	12	Conditions	14	Yield [%] of 14[b]	13	7	Yield [%] of 7[b]
1	 **11a**	 **12a**	50 °C, 3 h	 **14a**	92	 **13b**	 **7g**	91
2	 **11a**	 **12b**	50 °C, 3 h	 **14b**	78	 **13c**	 **7h**	88
3	 **11b**	 **12b**	50 °C, 2 h	 **14c**	n.i.[c]	 **13c**	 **7i**	31 (2 steps)
4	 **11c**	 **12a**	50 °C, 2 h	 **14d**	n.i.[c]	 **13d**	 **7j**	67 (2 steps)
5	 **11d**	 **12b**	50 °C, 2 h	 **14e**	n.i.[c]	 **13c**	 **7k**	83 (2 steps)
6	 **11e**	 **12c**	50 °C, 3 h	 **14f**	> 99	 **13c**	 **7l**	90
7	 **11f**	 **12a**	50 °C, 3 h	 **14g**	96	 **13b**	 **7m**	88
8	–	–	–	–	–	 **13e**	 **7n**	78
9	 **11g**	 **12c**	reflux, 3 h, 10 mol % Pd	**14h**	84	**13f**	**7o**	> 99
10	**11h**	**12a**	50 °C, 3 h	**14i**	82	**13b**	**7p**	96

[a] Suzuki–Miyaura coupling was carried out with halo-aldehyde **11** and vinylborane **12** in the presence of $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %), and Cs_2CO_3 (3 equiv) in THF/H_2O (5:1). Allylation was carried out with **14** and allylic metal reagent **13** under various conditions (See Experimental Section for details). [b] Yield of isolated product after silica-gel chromatography. [c] n.i. = Not isolated.

Table 3. Preparation of 1,5,7-trien-4-ols **7**, precursors of benzenes **3**, from α,β-unsaturated esters **19** by Suzuki–Miyaura coupling, reduction with DIBAL-H, oxidation with MnO_2, and allylation.[a]



19 **12** **20** **21** **13** **7**

Entry	**19**	**12**	Conditions	**20**	Yield [%] of **20**[b]	**21**	Yield [%] of **21**[b]	**13**	**7**	Yield [%] of **7**[b]
1	 **19a**	 **12b**	reflux, 12 h	 **20a**	86	 **21a**	69	 **13c**	 **7q**	72 (2 steps)
2	 **19b**	 **12c**	reflux, 24 h	 **20b**	70	 **21b**	90	 **13c**	 **7r**	67 (2 steps)
3	 **19c**	 **12a**	60 °C, 12 h	 **20c**	73	 **21c**	94	 **13d**	 **7s**	70 (2 steps)
4	 **19d**	 **12c**	RT, 15 h	 **20d**	56[c]	 **21d**	95	 **13c**	 **7t**	73 (2 steps)

[a] Suzuki–Miyaura coupling was carried out with halo-ester **19** and vinylborane **12** in the presence of $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), and Cs_2CO_3 (3 equiv) in THF/H_2O (5:1). Reduction of **20** to **21** was carried out with DIBAL-H (2 equiv) in THF at −78 °C for 30 min. Oxidation of **21** to **14** was carried out with MnO_2 (20–30 equiv) in CH_2Cl_2 at RT for 0.5–1 h. Allylation was carried out with **14** and allylic Grignard reagent **13** under various conditions (See Experimental Section for details). [b] Yield of isolated product after silica-gel chromatography. [c] An *E*/*Z*-mixture of **20d** (1:20) was obtained.

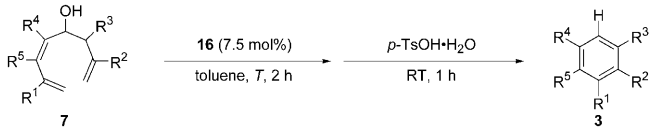
tion of two rings from **7o** led to the formation of substituted anthracene **3o** (Table 4, entry 9). To demonstrate the functional group tolerance of this synthesis, substrates **7p** and **7q** containing heteroatoms were converted into the corresponding benzothiophene **3p** and 1,2,3,4-tetrahydroisoquinoline **3q**, respectively (Table 4, entries 10 and 11). In addition, single-ring benzenes **3r–t** containing the benzyloxy, halogen, or olefin functionality were also prepared in satisfactory yields (Table 4, entries 12–14).

Our attention was next turned to the formation of substituted phenols **6**. First, we prepared 1,5,7-trien-4-one **9a** as a test precursor from 1,5,7-trien-4-ol **7a** by Dess–Martin oxidation (Scheme 5).

Table 5 summarizes the results of the synthesis of **6a** from **9a** by RCM/tautomerization by using various ruthenium carbene catalysts **15–18**. A large difference in reactivity was noted between **7a** and **9a**. Whereas the reaction of 1,5,7-trien-4-ol **7a** in the presence of 7.5 mol% Grubbs first-generation catalyst **15** at room temperature gave substituted benzene **3a** quantitatively, the reaction of 1,5,7-trien-4-one **9a** under similar conditions gave the corresponding phenol **6a** in only 3% yield (Table 1, entry 1 vs. Table 5, entry 1). This result is consistent with the fact that electron-deficient dienic systems are less reactive than normal dienic systems in RCM reactions.[17] Although Grubbs second-generation catalyst **16** could not improve the yield effectively at room temperature (Table 5, entry 2), a satisfactory result was obtained when the temperature was increased to 40 °C (Table 5, entry 3). On the other hand, phosphine-free ruthenium carbene catalysts **17** and **18** exhibited sufficient reactivity even at room temperature (Table 5, entries 4–7). It was, therefore, concluded that **17** and **18** are the most suitable catalysts for precursors **7**. When the loading of catalyst **18** was decreased to 5.0 or 2.5 mol%, the reaction still efficiently furnished the product in good yield at 40 °C (Table 5, entries 8 and 9). Because of the commercial availability and remarkable stability of Hoveyda–Grubbs catalyst **17**, we chose to use it for the following RCM of **9**.

The effect of introducing methyl substituents on the reactivity was next examined by using substrates **9b–f** (Table 6). By analogy with the results for 1,5,7-trien-4-ols **7** in Table 1, the reactivity of **9** was decreased by a larger extent when a methyl group was introduced at the R^2 position than when it was introduced at the R^1 or R^3 position (Table 6, entries 1–4). When methyl groups were introduced at the R^1 and R^2 positions at the same time, the reaction in the presence of **17** in dichloromethane at 40 °C did not occur at all (Table 6, entry 6). However, increasing the temperature to 80 °C and

Table 4. Synthesis of benzenes **3** by RCM/dehydration.[a]



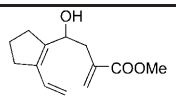
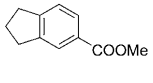
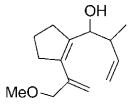
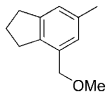
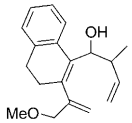
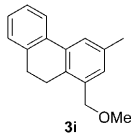
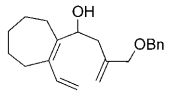
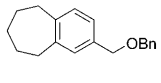
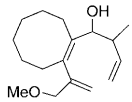
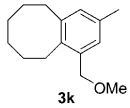
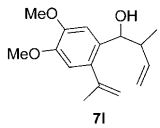
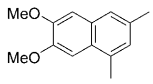
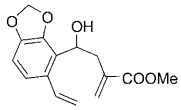
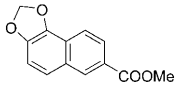
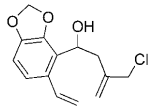
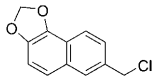
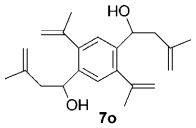
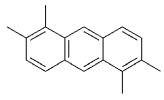
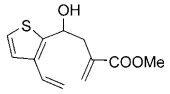
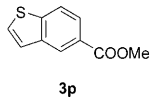
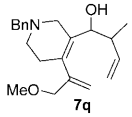
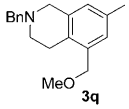
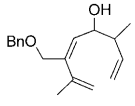
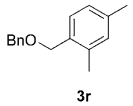
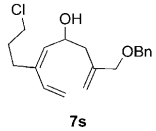
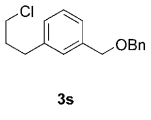
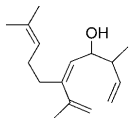
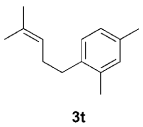
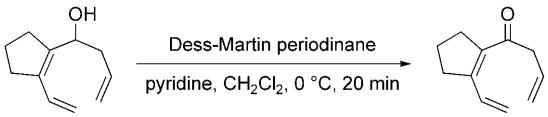
Entry	Substrate	*T* [°C]	Product	Yield [%][b]
1	 **7g**	80	 **3g**	82
2	 **7h**	80	 **3h**	91
3	 **7i**	80	 **3i**	86
4	 **7j**	80	 **3j**	86
5	 **7k**	80	 **3k**	98
6	 **7l**	80	 **3l**	92
7	 **7m**	100	 **3m**	82
8	 **7n**	80	 **3n**	88
9	 **7o**	100	 **3o**	78
10	 **7p**	80	 **3p**	73
11	 **7q**	80	 **3q**	82
12[c]	 **7r**	RT	 **3r**	91

Table 4. (Continued)

Entry	Substrate	*T* [°C]	Product	Yield [%][b]
13	 **7s**	80	 **3s**	81
14[c]	 **7t**	RT	 **3t**	75

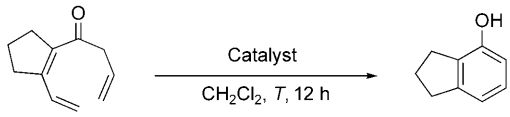
[a] Ring-closing olefin metathesis was carried out with 1,5,7-trien-4-ol **7** and ruthenium catalyst (**16**, 7.5 mol%) in toluene for 2 h. The reaction mixture was treated with *p*-toluenesulfonic acid (10 mol%) at room temperature for 1 h. [b] Yield of isolated product after silica-gel chromatography. [c] The reaction was carried out in CH_2Cl_2.



7a **9a** (74%)

Scheme 5. Preparation of **9a** from **7a** by Dess–Martin oxidation.

Table 5. Synthesis of phenol **6a** by RCM/tautomerization.[a]



9a **6a**

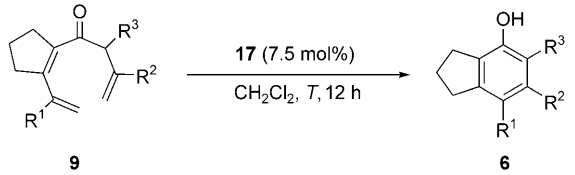
Entry	Catalyst [mol%]	*T* [°C]	Yield [%][b]
1	**15** (7.5)	RT	3
2	**16** (7.5)	RT	19
3	**16** (7.5)	40	81
4	**17** (7.5)	RT	82
5	**17** (7.5)	40	88
6	**18** (7.5)	RT	84
7	**18** (7.5)	40	95
8	**18** (5.0)	40	85
9	**18** (2.5)	40	83

[a] Ring-closing olefin metathesis was carried out with 1,5,7-trien-4-one **9a** and ruthenium catalyst (**15**, **16**, **17**, or **18**) in CH_2Cl_2 for 12 h. [b] Yield of isolated product after silica-gel chromatography.

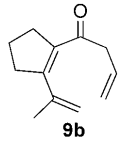
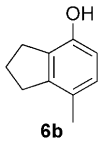
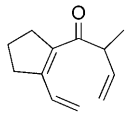
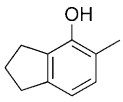
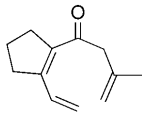
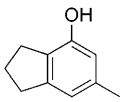
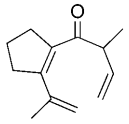
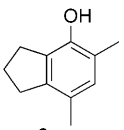
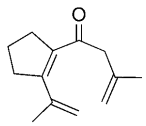
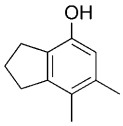
changing the solvent to toluene gave the corresponding phenol **6f** in high yield (Table 6, entry 7).

Table 7 shows the results of the Dess–Martin oxidation of 1,5,7-trien-4-ols **7** to yield 1,5,7-trien-4-ones **9**. All reactions proceeded well and various trienones **9** were prepared. A unique characteristic was found in **9k**, containing a cyclooctene ring, which existed in equilibrium with 2*H*-pyran **22k** (Scheme 6).[18] By integrating well-resolved signals in the ^{1}H NMR spectra of the mixture, the equilibrium ratio of **9k** to **22k** was determined to be 2.8:1 at room temperature. No such equilibrium was observed in the other 1,5,7-trien-4-ones **9**.

Table 6. Synthesis of phenols **6** by RCM/tautomerization.[a]



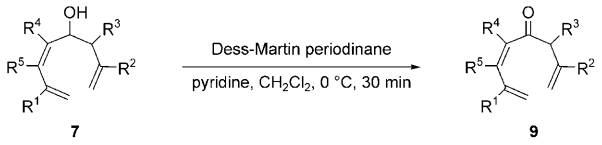
9 **6**

Entry	Substrate	Product	T [°C]	Yield [%][b]
1	 **9b**	 **6b**	40	91
2	 **9c**	 **6c**	40	91
3	 **9d**	 **6d**	40	22
4[c]			80	86
5	 **9e**	 **6e**	40	88
6	 **9f**	 **6f**	40	0
7[c]			80	92

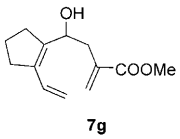
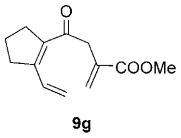
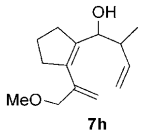
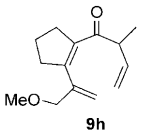
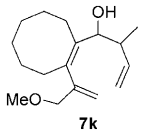
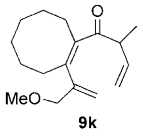
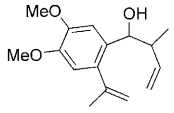
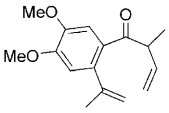
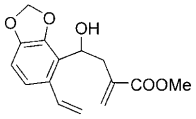
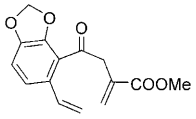
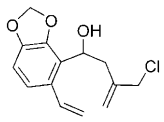
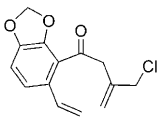
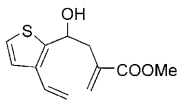
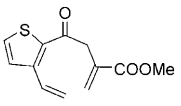
[a] Ring-closing olefin metathesis was carried out with 1,5,7-trien-4-one **9** and ruthenium catalyst **17** (7.5 mol%) in CH_2Cl_2 for 12 h. [b] Yield of isolated product after silica-gel chromatography. [c] The reaction was carried out in toluene.

As the final experiment of this study, we conducted RCM/tautomerization of the obtained compound **9** in the presence of Hoveyda–Grubbs catalyst **17** (Table 8). A variety of phenol derivatives **6** were successfully formed in high yields, as expected. The reaction of the equilibrium mixture of **9k** and **22k** furnished the corresponding product **6k** cleanly (Table 8, entry 3). Even when ester, allyl chloride, benzyl chloride, or sulfur functionality was present in the substrate or the product, the reaction proceeded without any problems, giving only the desired product. It should be noted that tolerance of the catalyst to the phenol hydroxyl group of the products contributes to the success of this RCM/tautomerization process.

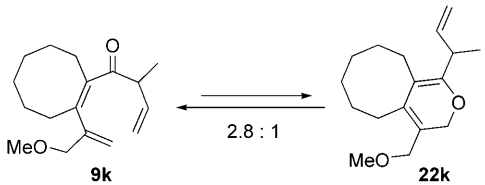
Table 7. Preparation of 1,5,7-trien-4-ones **9**, precursors of phenols **6**, from 1,5,7-trien-4-ols **7** by Dess–Martin oxidation.[a]



7 **9**

Entry	Substrate	Product	Yield [%][b]
1	 **7g**	 **9g**	86
2	 **7h**	 **9h**	66
3	 **7k**	 **9k**	68[c]
4	 **7l**	 **9l**	79
5	 **7m**	 **9m**	79
6	 **7n**	 **9n**	77
7	 **7p**	 **9p**	56

[a] Reaction was carried out with 1,5,7-trien-4-ol **7**, Dess–Martin periodinane (2 equiv), and pyridine (4 equiv) in CH_2Cl_2 at 0 °C for 30 min. [b] Yield of isolated product after silica-gel chromatography. [c] Equilibrium mixture of **9k** and **22k** (2.8:1) was obtained.



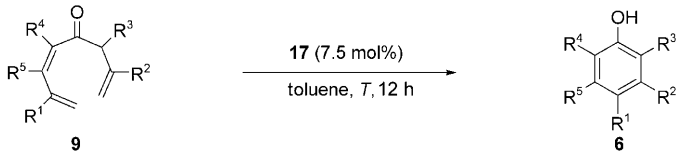
9k **22k**

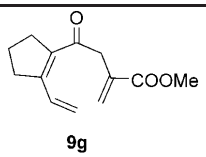
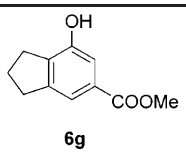
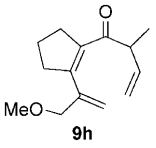
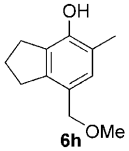
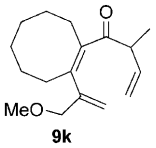
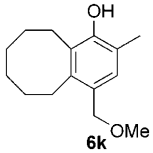
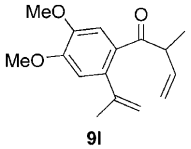
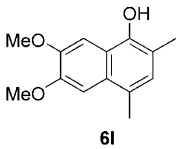
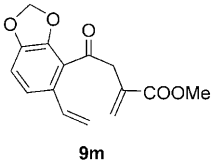
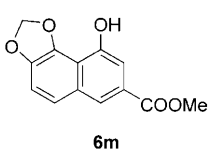
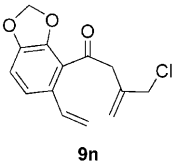
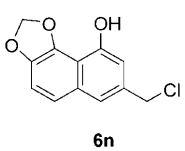
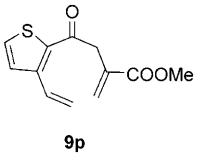
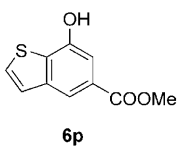
Scheme 6. Equilibrium between **9k** and **22k**.

Conclusion

We have developed an efficient synthetic approach to substituted benzenes and phenols by utilizing ruthenium-catalyzed RCM/dehydration and RCM/tautomerization as the respective key process. Because the presented synthetic routes in-

Table 8. Synthesis of phenols **6** by RCM/tautomerization.[a]



Entry	Substrate	T [°C]	Product	Yield [%][b]
1	 **9g**	80	 **6g**	95
2	 **9h**	80	 **6h**	85
3	 **9k**	80	 **6k**	98
4[c]	 **9l**	40	 **6l**	84
5	 **9m**	80	 **6m**	81
6	 **9n**	80	 **6n**	80
7	 **9p**	80	 **6p**	70

[a] Ring-closing olefin metathesis was carried out with 1,5,7-trien-4-one **9** and ruthenium catalyst **17** (7.5 mol%) in toluene for 12 h. [b] Yield of isolated product after silica-gel chromatography. [c] The reaction was carried out in CH_2Cl_2.

volve highly reliable and mild transformations at all steps, it is possible to synthesize a wide variety of substituted benzenes **3** and phenols **6** containing various functionalities with these routes.

It is reasonable to say that modern synthetic organic chemistry has sufficient flexibility to construct acyclic compounds with more selectivity than aromatic compounds. Therefore, the direct construction of aromatic rings from acyclic precursors would provide one possible solution to the difficulty of responding to the growing demand for complex aromatic compounds. Combinations of the cyclization of acyclic precursors prepared in a selective manner and subsequent aromatization provide an effective means to access the desired aromatic compounds without the formation of inseparable regioisomers. Because ruthenium-catalyzed RCM has become one of the most powerful cyclization reactions, application of this reaction to the synthesis of aromatic compounds is expected to increase its importance in organic synthesis.

Experimental Section

General: All anaerobic and moisture-sensitive manipulations were carried out by using standard Schlenk techniques under predried nitrogen or by using glove box techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) or a LA-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR spectroscopy and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectroscopy.

Materials: THF and Et_2O were distilled from sodium benzophenone-ketyl under nitrogen prior to use. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Ruthenium complexes, Grubbs first-generation catalyst **15**,[11b] Grubbs second-generation catalyst **16**,[12b] Hoveyda–Grubbs catalyst **17**,[19] and substituted Hoveyda–Grubbs catalyst **18**[19] were prepared according to the reported procedures. β-Halo-α,β-unsaturated aldehydes **11a–d**,[9] **11g**,[20] and α,β-unsaturated esters **19a**,[21] **19b**,[22] **19c**,[23] and **19d**[24] were prepared according to the reported procedures. β-Halo-α,β-unsaturated aldehydes **11e**, **11f**, and **11h** were used as received. Potassium vinyl trifluoroborate **12a**[10] and potassium isopropenyltrifluoroborate **12c**[25] were prepared according to the reported procedures. Vinylboronic acid pinacol ester **12b** was prepared according to the reported procedure.[26] Allylic metal reagents **13a**,[27] **13b**,[15] **13c**,[27] **13d**,[28] **13e**,[29] and **13f**[30] were prepared according to the reported procedures. Dess–Martin periodinane[31] and activated MnO_2[32] were prepared according to the reported procedures. Palladium acetate, triphenylphosphine, cesium carbonate, pyridine, and *p*-toluenesulfonic acid were used as received.

General procedure A: preparation of unsaturated aldehydes 14: A mixture of potassium vinyl trifluoroborate (17.9 mmol), $Pd(OAc)_2$ (0.70 mmol), PPh_3 (1.40 mmol), Cs_2CO_3 (41.3 mmol), and β-halo-α,β-unsaturated aldehyde **11** (13.8 mmol) in THF (40 mL) and water (8 mL) was heated to 50 °C and stirred for 2–3 h. After cooling to room temperature, the mixture was diluted with water and extracted with ether three times. The organic layers were combined, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was evaporated under reduced pressure. The residue was purified by silica-gel column chromatography to give unsaturated aldehyde **14**.

2-Vinylcyclopentene-1-carbaldehyde (14a): The reaction was carried out by following the general procedure A and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (92% yield). ^{1}H NMR ($CDCl_3$): δ = 1.91 (quint, J = 7.6 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H), 5.55 (d, J = 11.0 Hz, 1H), 5.56 (d, J = 16.8 Hz, 1H), 7.27 (dd, J = 16.8, 11.0 Hz, 1H), 10.21 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 20.89, 30.77, 34.01, 121.99, 128.37, 139.61, 157.69, 187.56 ppm; HRMS (EI): m/z calcd for $C_8H_{10}O$: 122.0732 [M^+]; found: 122.0731.

2-Isopropenylcyclopentene-1-carbaldehyde: The reaction was carried out by following the general procedure A and the product was purified by

silica-gel column chromatography (hexane/EtOAc 10:1) (73% yield). ^{1}H NMR ($CDCl_3$): δ=1.90 (quint, J=7.7 Hz, 2H), 1.96 (s, 3H), 2.63 (tt, J=8.0, 1.9 Hz, 2H), 2.73 (tt, J=7.7, 2.2 Hz, 2H), 5.08 (s, 1H), 5.21 (dq, J=1.6, 1.5 Hz, 1H), 9.89 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=21.36, 21.76, 30.55, 37.63, 76.68, 77.00, 77.32, 118.61, 139.89, 139.70, 164.29, 189.66 ppm; HRMS (EI): m/z calcd for $C_9H_{12}O$: 136.0888 [M^+]; found: 136.0883.

2-(1-Methoxymethylvinyl)cyclopentene-1-carbaldehyde (14b): The reaction was carried out by following the general procedure A and the product was purified by silica-gel column chromatography (hexane/EtOAc 20:1) (84% yield). ^{1}H NMR ($CDCl_3$): δ=1.92 (quint, J=7.9 Hz, 2H), 2.65 (tt, J=7.6, 1.9 Hz, 2H), 2.76 (tt, J=7.6, 1.9 Hz, 2H), 3.34 (s, 3H), 4.07 (dd, J=1.2, 0.6 Hz, 2H), 5.29 (d, J=1.9 Hz, 1H), 5.42 (dd, J=3.1, 1.5 Hz, 1H), 9.90 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=21.32, 30.53, 37.39, 57.94, 74.00, 119.63, 140.38, 141.66, 161.31, 189.50 ppm; HRMS (EI): m/z: $C_{10}H_{14}O_2$ 166.0994 [M^+]; found: 166.0991.

2-Isopropenyl-4,5-dimethoxybenzaldehyde (14f): The reaction was carried out by following the general procedure A and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (>99% yield). M.p. 50–51°C; ^{1}H NMR ($CDCl_3$): δ=2.17 (dd, J=1.4, 0.7 Hz, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 4.92 (dq, J=1.7, 1.5 Hz, 1H), 5.42 (quint, J=1.7 Hz, 1H), 6.75 (s, 1H), 7.44 (s, 1H), 10.07 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=25.26, 55.91, 56.01, 108.48, 110.05, 118.87, 126.51, 140.97, 143.22, 148.28, 153.35, 190.65 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{15}O_3$: 207.1021 [M^++H]; found: 207.1025.

5-Vinylbenzo[1,3]dioxole-4-carbaldehyde (14g): The reaction was carried out by following the general procedure A and the product was purified by silica-gel column chromatography (hexane/EtOAc=10/1) (96% yield). M.p. 94–96°C; ^{1}H NMR ($CDCl_3$): δ=5.37 (dd, J=11.2, 1.5 Hz, 1H), 5.56 (dd, J=17.6, 1.2 Hz, 1H), 6.13 (s, 2H), 6.96 (d, J=8.3 Hz, 1H), 7.02 (d, J=8.3 Hz, 1H), 7.37 (dd, J=17.4, 11.0 Hz, 1H), 10.36 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=102.71, 113.10, 116.66, 117.66, 120.60, 133.53, 133.69, 148.12, 150.49, 188.64 ppm; HRMS (FAB): m/z calcd for $C_{10}H_9O_3$: 177.0552 [M^++H]; found: 177.0553.

2,5-Diisopropenylbenzene-1,4-dicarbaldehyde (14h): The reaction was carried out by following the general procedure A in the presence of 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3 at reflux temperature for 3 h and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (84% yield). M.p. 64–65°C; ^{1}H NMR ($CDCl_3$): δ=2.22 (s, 6H), 4.95 (s, 2H), 5.50 (t, J=1.5 Hz, 2H), 7.90 (s, 2H), 10.25 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ=24.54, 119.95, 127.96, 136.39, 140.56, 145.79, 191.44 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{15}O_2$: 215.1072 [M^++H]; found: 215.1081.

3-Vinylthiophene-2-carbaldehyde (14i): The reaction was carried out by following the general procedure A and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (82% yield); ^{1}H NMR ($CDCl_3$): δ=5.58 (dd, J=12.2, 1.0 Hz, 1H), 5.83 (dd, J=17.6, 1.0 Hz, 1H), 7.25 (dd, J=17.6, 11.0 Hz, 1H), 7.33 (d, J=5.1 Hz, 1H), 7.64 (dt, J=5.2, 0.7 Hz, 1H), 10.13 ppm (d, J=1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=119.90, 126.65, 127.52, 134.12, 137.70, 146.84, 181.94 ppm; HRMS (EI): m/z calcd for $C_7H_6O_3$: 138.0139 [M^+]; found: 138.0134.

General procedure B: preparation of unsaturated esters 20: A mixture of potassium vinyltrifluoroborate (2.60 mmol), $Pd(OAc)_2$ (0.10 mmol), PPh_3 (0.20 mmol), Cs_2CO_3 (6.00 mmol), α,β-unsaturated ester **19** (2.00 mmol) in THF (15 mL), and water (3 mL) was heated to reflux temperature and stirred for several hours. After cooling to room temperature, the mixture was diluted with water and extracted with ether three times. The organic layers were combined, washed with brine, and dried over Na_2SO_4. After filtration, the filtrate was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography to give unsaturated ester **20**.

1-Benzyl-4-(1-methoxymethylvinyl)-1,2,5,6-tetrahydropyridine-3-carboxylic acid ethyl ester (20a): The reaction was carried out at reflux temperature for 12 h by following general procedure B, and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (86% yield). ^{1}H NMR ($CDCl_3$): δ=1.23 (t, J=7.0 Hz, 3H), 2.37 (tt, J=5.5, 5.5 Hz, 2H), 2.54 (t, J=5.5 Hz, 2H), 3.28 (t, J=2.5 Hz, 2H), 3.36 (s, 3H), 3.63 (s, 2H), 4.03 (s, 2H), 4.12 (q, J=7.1 Hz, 2H), 4.93 (d, J=0.6 Hz, 1H), 5.13 (q, J=1.5 Hz, 1H), 7.24–7.28 (m, 1H), 7.31–7.37 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): δ=13.91, 32.78, 48.61, 52.92, 58.19, 60.19, 62.09, 74.61, 112.09, 124.79, 127.09, 128.22, 129.05, 137.75, 146.43, 147.33, 166.59 ppm; HRMS (FAB): m/z calcd for $C_{19}H_{26}NO_3$: 316.1913 [M^++H]; found: 316.1917.

3-Benzyloxymethyl-4-methylpenta-2,4-dienoic acid ethyl ester (20b): The reaction was carried out at reflux temperature for 12 h by following general procedure B, and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (70% yield); ^{1}H NMR ($CDCl_3$): δ=1.27 (t, J=7.0 Hz, 3H), 1.95 (dd, J=1.5, 0.9 Hz, 3H), 4.06 (d, J=1.9 Hz, 2H), 4.15 (q, J=7.4 Hz, 2H), 4.57 (s, 2H), 4.76 (dq, J=1.5, 0.9 Hz, 1H), 5.02 (quint, J=1.5 Hz, 1H), 5.97 (t, J=1.8 Hz, 1H), 7.28–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=13.99, 22.00, 59.79, 72.19, 72.48, 113.32, 114.62, 127.45, 127.63, 128.30, 137.56, 142.51, 157.20, 165.67 ppm; HRMS (FAB): m/z calcd for $C_{16}H_{21}O_3$: 261.1491 [M^++H]; found: 261.1500.

6-Chloro-3-vinyl-2-hexenoic acid methyl ester (20c): The reaction was carried out at 60°C for 12 h by following the general procedure B, and the product was purified by silica-gel column chromatography (hexane/EtOAc 20:1) (73% yield). ^{1}H NMR ($CDCl_3$): δ=1.93–2.02 (m, 2H), 2.53 (t, J=7.7 Hz, 2H), 3.56 (t, J=6.5 Hz, 2H), 3.72 (s, 3H), 5.48 (d quint, J=11.1, 0.6 Hz, 1H), 5.64 (dd, J=18.2, 0.6 Hz, 1H), 5.76 (d, J=0.9 Hz, 1H), 7.71 ppm (dd, J=17.9, 11.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=30.37, 31.53, 44.18, 51.07, 117.61, 120.49, 132.50, 153.10, 166.24 ppm; HRMS (FAB): m/z calcd for $C_9H_{14}ClO_2$: 189.0682 [M^++H]; found: 189.0679.

3-Isopropenyl-7-methyl-2,6-octadienoic acid ethyl ester (20d): The reaction was carried out at room temperature for 15 h by following the general procedure B, and the product was purified by silica-gel column chromatography (hexane/EtOAc 20:1) (56% yield). ^{1}H NMR ($CDCl_3$): δ=1.26 (t, J=7.1 Hz, 3H), 1.60 (s, 3H), 1.68 (d, J=1.0 Hz, 3H), 1.93 (s, 3H), 2.07–2.16 (m, 2H), 2.21–2.25 (m, 2H), 4.13 (q, J=7.1 Hz, 2H), 4.69 (s, 1H), 4.96 (quint, J=1.6 Hz, 1H), 5.08 (t septet, J=7.1, 1.2 Hz, 1H), 5.61 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=14.05, 17.61, 22.03, 25.55, 25.77, 38.31, 59.64, 111.87, 115.55, 122.92, 132.34, 144.96, 161.69, 165.89 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{23}O_2$: 223.1698 [M^++H]; found: 223.1691.

General procedure C: preparation of unsaturated alcohol 21: Diisobutylaluminum hydride (0.97 M in hexane, 3.22 mmol) was added dropwise to a solution of ester **20** (1.61 mmol) in dry THF (5 mL) at −78°C. The mixture was stirred at the same temperature for 30 min and then warmed up to room temperature. It was treated with saturated potassium and sodium tartrate (Rochelle salt) and stirred for 30 min. After extraction with EtOAc three times, the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give unsaturated alcohol **21**.

[1-Benzyl-4-(1-methoxymethylvinyl)-1,2,5,6-tetrahydropyridin-3-yl]-methanol (21a): The reaction was carried out by following the general procedure C and the product was purified by silica-gel column chromatography (EtOAc) (69% yield); ^{1}H NMR ($CDCl_3$): δ=2.22–2.23 (m, 2H), 2.56 (t, J=5.8 Hz, 2H), 2.67 (br s, 1H), 3.16 (t, J=2.2 Hz, 2H), 3.45 (s, 3H), 3.63 (s, 2H), 3.90 (s, 2H), 3.98 (s, 2H), 4.96 (d, J=2.1 Hz, 1H), 5.20 (d, J=1.6 Hz, 1H), 7.24–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=29.88, 49.28, 54.48, 58.33, 61.25, 62.55, 74.45, 115.67, 127.10, 128.20, 129.28, 132.13, 133.25, 137.58, 145.08 ppm; HRMS (FAB): m/z calcd for $C_{17}H_{24}NO_2$: 274.1807 [M^++H]; found: 274.1805.

3-Benzyloxymethyl-4-methyl-2,4-pentadien-1-ol (21b): The reaction was carried out by following the general procedure C and the product was purified by silica-gel column chromatography (hexane/EtOAc 3:1) (90% yield). ^{1}H NMR ($CDCl_3$): δ=1.36 (br s, 1H), 1.86 (dd, J=1.6, 1.0 Hz, 3H), 4.05 (d, J=0.9 Hz, 2H), 4.27 (d, J=6.5 Hz, 2H), 4.51 (s, 2H), 4.76 (dq, J=2.2, 0.9 Hz, 1H), 5.09 (dq, J=2.2, 1.6 Hz, 1H), 5.71 (tt, J=6.8, 1.2 Hz, 1H), 7.27–7.37 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=21.87, 59.50, 71.64, 72.51, 115.81, 127.47, 127.76, 128.20, 137.95, 141.49 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{18}KO_2$: 257.0994 [M^++K]; found: 257.0952.

6-Chloro-3-vinyl-2-hexen-1-ol (21c): The reaction was carried out by following the general procedure C and the product was purified by silica-gel column chromatography (hexane/EtOAc 3:1) (94% yield); ^{1}H NMR ($CDCl_3$): δ=1.25 (br s,1H), 1.92–1.98 (m, 2H), 2.39 (t, J=7.4 Hz, 2H),

3.56 (t, $J=6.4$ Hz, 2H), 4.32 (d, $J=6.7$ Hz, 2H), 5.22 (dt, $J=11.0$, 1.6 Hz, 1H), 5.33 (d, $J=17.4$ Hz, 1H), 5.62 (t, $J=7.1$ Hz, 1H), 6.61 ppm (ddd, $J=17.4$, 11.0, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=30.20$, 31.25, 44.61, 58.23, 115.64, 129.01, 131.71, 137.57 ppm; HRMS (FAB): m/z calcd for $C_8H_{12}Cl$: 143.0628 [M^+-OH]; found: 143.0629.

3-Isopropenyl-7-methylocta-2,6-dien-1-ol (21d): The reaction was carried out by following the general procedure C and the product was purified by silica-gel column chromatography (hexane/EtOAc 8:1) (95% yield); ^{1}H NMR ($CDCl_3$): $\delta=1.20$ (br s, 1H), 1.60 (s, 3H), 1.68 (d, $J=1.0$ Hz, 3H), 1.81 (t, $J=0.9$ Hz, 3H), 2.02–2.07 (m, 2H), 2.11–2.15 (m, 2H), 4.17 (d, $J=6.8$ Hz, 2H), 4.63 (dq, $J=2.4$, 0.9 Hz, 1H), 4.99 (dq, $J=3.1$, 1.5 Hz, 1H), 5.09 (t heptet, $J=6.8$, 1.2 Hz, 1H), 5.42 ppm (tt, $J=6.8$, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=17.67$, 22.12, 25.63, 26.64, 36.00, 60.02, 114.46, 123.79, 124.34, 131.68, 143.21, 146.08 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{19}$: 163.1487 [M^+-OH]; found: 163.1485.

General procedure D: preparation of unsaturated aldehydes: MnO_2 (50.0 mmol) was added in one portion to a solution of **21** (1.73 mmol) in dichloromethane (15 mL) under air. The mixture was stirred for 2.5 h at room temperature and then was filtered through Celite. The residual solid was washed thoroughly with dichloromethane and the filtrate was concentrated under reduced pressure. The crude aldehyde was characterized by ^{1}H NMR and used without further purification.

1-Benzyl-4-(1-methoxymethylvinyl)-1,2,5,6-tetrahydropyridine-3-carbaldehyde: The reaction was carried out by following the general procedure D. ^{1}H NMR ($CDCl_3$): $\delta=2.49$–2.51 (m, 2H), 2.57 (t, $J=5.2$ Hz, 2H), 3.27 (t, $J=2.5$ Hz, 2H), 3.35 (s, 3H), 3.65 (s, 2H), 4.04 (t, $J=0.6$ Hz, 2H), 5.14–5.15 (m, 1H), 5.45 (q, $J=1.2$ Hz, 1H), 7.24–7.36 (m, 5H), 9.79 ppm (s, 1H).

3-Benzyloxymethyl-4-methyl-2,4-pentadienal: The reaction was carried out by following the general procedure D; ^{1}H NMR ($CDCl_3$): $\delta=1.96$ (dd, $J=1.2$, 1.0 Hz, 3H), 4.20 (d, $J=1.4$ Hz, 2H), 4.55 (s, 2H), 5.05 (dd, $J=1.7$, 1.0 Hz, 1H), 5.30 (quint, $J=1.5$ Hz, 1H), 6.18 (dt, $J=8.0$, 1.5 Hz, 1H), 7.25–7.39 (m, 5H), 9.83 ppm (d, $J=8.0$ Hz, 1H).

6-Chloro-3-vinyl-2-hexenal: The reaction was carried out by following the general procedure D; ^{1}H NMR ($CDCl_3$): $\delta=1.94$–2.04 (m, 2H), 2.56–2.60 (m, 2H), 3.58 (t, $J=6.1$ Hz, 2H), 5.61 (dq, $J=11.0$, 0.7 Hz, 1H), 5.70 (dt, $J=17.1$, 0.6 Hz, 1H), 5.94 (d quint, $J=8.0$, 0.6 Hz, 1H), 7.19 (ddd, $J=17.4$, 11.0, 0.6 Hz, 1H), 10.15 ppm (d, $J=7.9$ Hz, 1H).

3-Isopropenyl-7-methyl-2,6-octadienal: The reaction was carried out by following the general procedure D; ^{1}H NMR ($CDCl_3$): $\delta=1.60$ (s, 3H), 1.68 (d, $J=1.3$ Hz, 3H), 1.94 (dd, $J=1.6$, 1.0 Hz, 3H), 2.14 (q, $J=7.3$ Hz, 2H), 2.33 (dd, $J=9.5$, 6.7 Hz, 2H), 4.94 (dq, $J=1.8$, 0.9 Hz, 1H), 5.07 (t heptet, $J=7.0$, 1.5 Hz, 1H), 5.23 (quint, $J=1.6$ Hz, 1H), 5.88 (dt, $J=8.0$, 1.2 Hz, 1H), 9.75 ppm (d, $J=7.9$ Hz, 1H).

General procedure E: **preparation of 1,5,7-trien-4-ols 7**: To a stirred solution of **14** (6.93 mmol) in THF (20 mL) was added allyl Grignard reagent (0.58 M solution in THF, 13.9 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. The mixture was then quenched by addition of saturated aqueous NH_4Cl solution, extracted with EtOAc three times, and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give 1,5,7-trien-4-ols **7**.

General procedure F: preparation of homoallylic alcohols 7 by allylboration: Allylboronic acid pinacol ester **13b** (0.866 mmol) was added to **14** (0.722 mmol) with stirring at room temperature. The reaction mixture was stirred for 48 h without solvent and then quenched by addition of $CHCl_3$ and the crude material was purified by silica-gel column chromatography to give 1,5,7-trien-4-ols **7**.

General procedure G: preparation of homoallylic alcohols 7 by allylstannation: $BF_3{\cdot}OEt_2$ (1.47 mmol) was added to a stirred solution of **14** (1.05 mmol) in dichloromethane (5 mL) at −78 °C. 2-Chloromethyl-3-tributylstannylpropene **13e** was then added to the mixture. The resulting mixture was stirred for 30 min and then quenched by addition of water at −78 °C. The mixture was warmed to room temperature, extracted with EtOAc, and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure and the residue was purified by silica-gel column chromatography to give 1,5,7-trien-4-ol **7**.

1-(1-Hydroxy-3-butenyl)-2-vinylcyclopentene (7a): The reaction was carried out in Et_2O by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (80% yield). ^{1}H NMR ($CDCl_3$): $\delta=1.68$ (br s, 1H), 1.79–1.91 (m, 2H), 2.27–2.33 (m, 1H), 2.38–2.44 (m, 2H), 2.52 (t, $J=7.6$ Hz, 2H), 2.59–2.65 (m, 1H), 4.72 (dd, $J=6.4$, 6.1 Hz, 1H), 5.08–5.17 (m, 4H), 5.76 (dddd, $J=17.1$, 14.3, 7.6, 6.4 Hz, 1H), 6.72 ppm (dd, $J=17.1$, 10.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=21.34$, 31.91, 32.71, 40.21, 67.23, 114.54, 117.62, 130.17, 134.43, 136.76, 142.27 ppm; HRMS (FAB): m/z calcd for $C_{11}H_{15}$: 147.1174 [M^+-OH]; found: 147.1170.

1-(1-Hydroxy-3-butenyl)-2-isopropenylcyclopentene (7b): The reaction was carried out in Et_2O by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (80% yield); ^{1}H NMR ($CDCl_3$): $\delta=1.60$ (br s, 1H), 1.82 (quint, $J=7.6$ Hz, 2H), 1.84 (t, $J=1.2$ Hz, 3H), 2.20–2.30 (m, 1H), 2.32–2.55 (m, 5H), 4.67 (dd, $J=8.3$, 5.4 Hz, 1H), 4.76 (d, $J=1.7$ Hz, 1H), 4.93 (dq, $J=2.4$, 1.5 Hz, 1H), 5.09 (ddt, $J=11.5$, 2.0, 1.0 Hz, 1H), 5.14 (dq, $J=17.4$, 1.7 Hz, 1H), 5.78 ppm (dddd, $J=16.8$, 10.2, 7.8, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=21.78$, 22.43, 31.25, 36.38, 40.50, 67.72, 113.39, 117.44, 134.82, 138.60, 141.08, 141.55 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{17}O$: 177.1279 [M^+-H]; found: 177.1276.

1-(1-Hydroxy-2-methyl-3-butenyl)-2-vinylcyclopentene (7c): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (diastereomeric mixture: 88% yield). The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): $\delta=0.84$ (d, $J=6.7$ Hz, 1.5H), 1.11 (d, $J=6.7$ Hz, 1.5H), 1.65 (br s, 0.5H), 1.76–1.89 (m, 2.5H), 2.31–2.67 (m, 5H), 4.31 (d, $J=9.5$ Hz, 0.5H), 4.41 (d, $J=8.2$ Hz, 0.5H), 4.97 (ddd, $J=10.4$, 1.9, 0.9 Hz, 0.5H), 5.03 (dt, $J=17.4$, 1.6 Hz, 0.5H), 5.08–5.21 (m, 3H), 5.62 (ddd, $J=18.0$, 10.4, 7.7 Hz, 0.5H), 5.78 (ddd, $J=18.6$, 10.1, 8.5 Hz, 0.5H), 6.69 (dd, $J=17.1$, 2.5 Hz, 0.5H), 6.72 ppm (dd, $J=17.4$, 2.1 Hz, 0.5H); ^{13}C NMR ($CDCl_3$): $\delta=16.04$, 16.48, 21.51, 21.64, 31.92, 32.67, 32.72, 32.82, 42.80, 43.61, 71.00, 71.88, 114.49, 114.61, 114.69, 116.74, 130.41, 130.51, 137.58, 138.65, 140.01, 140.85, 141.34, 141.86 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{17}O$: 177.1279 [M^+-H]; found: 177.1276.

1-(1-Hydroxy-3-methyl-3-butenyl)-2-vinylcyclopentene (7d): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (80% yield). ^{1}H NMR ($CDCl_3$): $\delta=1.78$ (s, 4H), 1.85 (quint, $J=8.0$ Hz, 2H), 2.19 (dd, $J=13.7$, 4.6 Hz, 1H), 2.37 (ddd, $J=13.9$, 9.0, 0.7 Hz, 1H), 2.44–2.66 (m, 4H), 4.80–4.84 (m, 2H), 4.87 (t, $J=1.7$ Hz, 1H), 5.09–5.15 (m, 2H), 6.73 ppm (dd, $J=17.3$, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=21.38$, 22.27, 31.94, 32.78, 44.28, 65.49, 113.53, 114.57, 130.15, 136.64, 142.16, 142.39 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{17}O$: 177.1279 [M^+-H]; found: 177.1276.

1-(1-Hydroxy-2-methyl-3-butenyl)-2-isopropenylcyclopentene (7e): The reaction was carried out by following the general procedure E and the products were purified by silica-gel column chromatography (hexane/EtOAc 10:1) (diastereomeric mixture: 86% yield); The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): $\delta=0.85$ (d, $J=6.8$ Hz, 1.5H), 1.12 (d, $J=6.8$ Hz, 1.5H), 1.51 (br s, 0.5H), 1.75 (br s, 0.5H), 1.78–1.87 (m, 2H), 1.81(s, 1.5H), 1.85 (s, 1.5H), 2.28–2.61 (m, 5H), 4.27 (dd, $J=9.5$, 2.2 Hz, 0.5H), 4.34 (dd, $J=8.8$, 4.2 Hz, 0.5H), 4.80 (dd, $J=13.4$, 1.7 Hz, 1H), 4.91–4.93 (m, 1H), 5.00 (dt, $J=10.5$, 1.0 Hz, 0.5H), 5.02 (dt, $J=17.6$, 1.4 Hz, 0.5H), 5.14 (dd, $J=10.2$, 1.7 Hz, 0.5H), 5.17 (dd, $J=17.4$, 1.7 Hz, 0.5H), 5.62 (ddd, $J=17.8$, 10.5, 7.6 Hz, 0.5H), 5.76 ppm (ddd, $J=17.3$, 10.2, 8.8 Hz, 0.5H); ^{13}C NMR ($CDCl_3$): $\delta=16.21$, 16.64, 21.85, 21.98, 22.46, 22.49, 30.90, 31.46, 36.31, 36.45, 42.37, 43.27, 71.30, 72.23, 113.20, 113.22, 114.03, 116.39, 136.78, 138.08, 140.38, 141.54, 141.70, 141.96, 143.22 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{19}O$: 191.1436 [M^+-H]; found: 191.1440.

1-(1-Hydroxy-3-methyl-3-butenyl)-2-isopropenylcyclopentene (7f): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (89% yield). ^{1}H NMR ($CDCl_3$): $\delta=1.67$ (br s, 1H), 1.77 (s,

3H), 1.82 (quint, $J=7.6$ Hz, 2H), 1.85 (t, $J=1.4$ Hz, 3H), 2.18 (dd, $J=13.7$, 3.9 Hz, 1H), 2.35–2.63 (m, 5H), 4.76–4.81 (m, 3H), 4.87 (dq, $J=3.4$, 1.7 Hz, 1H), 4.95 ppm (dq, $J=2.9$, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=$ 21.76, 22.20, 22.34, 22.38, 31.20, 36.35, 44.54, 65.84, 113.25, 113.28, 138.83, 140.77, 141.61, 142.54 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{19}O$: 191.1436 [M^+-H]; found: 191.1432.

1-(1-Hydroxy-3-methoxycarbonyl-3-butenyl)-2-vinylcyclopentene (7g): The reaction was carried out by following the general procedure F and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1 to 3:1) (91% yield). ^{1}H NMR ($CDCl_3$): $\delta=1.84$ (quint, $J=7.7$ Hz, 2H), 2.12 (br s, 1H), 2.42–2.67 (m, 6H), 3.77 (s, 3H), 4.88 (dd, $J=8.3$, 4.9 Hz, 1H), 5.08 (d, $J=4.0$ Hz, 1H), 5.12 (d, $J=10.8$ Hz, 1H), 5.66 (d, $J=1.0$ Hz, 1H), 6.23 (d, $J=1.5$ Hz, 1H), 6.69 ppm (dd, $J=17.3$, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=21.41$, 31.85, 32.72, 38.97, 52.05, 67.17, 114.70, 127.82, 130.17, 136.77, 136.95, 142.11, 167.83 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{17}O_2$: 205.1229 [M^+-OH]; found: 205.1229.

1-(1-Hydroxy-2-methyl-3-butenyl)-2-(1-methoxymethylvinyl)-cyclopentene (7h): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 4:1) (diastereomeric mixture: 88% yield). The following data are for a mixture of two diastereomers (0.53:0.47); ^{1}H NMR ($CDCl_3$): $\delta=0.87$ (d, $J=6.7$ Hz, 1.41H), 1.13 (d, $J=6.7$ Hz, 1.59H), 1.82 (quint, $J=7.7$ Hz, 1.06H), 1.86 (quint, $J=7.6$ Hz, 0.94H), 1.95 (br s, 1.00H), 2.32–2.62 (m, 5.00H), 3.32 (s, 1.41H), 3.33 (s, 1.59H), 3.92–3.99 (m, 2.00H), 4.19 (d, $J=9.5$ Hz, 0.47H), 4.23 (d, $J=8.9$ Hz, 0.53H), 4.96 (ddd, $J=10.4$, 1.9, 0.9 Hz, 0.47H), 4.99 (d, $J=2.1$ Hz, 0.53H), 5.04 (d, $J=2.2$ Hz, 0.47H), 5.05 (dt, $J=17.7$, 1.3 Hz, 0.53H), 5.13 (ddd, $J=10.1$, 1.9, 0.6 Hz, 0.47H), 5.17 (ddd, $J=17.7$, 1.9, 0.9 Hz, 0.47H), 5.19 (dt, $J=3.4$, 1.2 Hz, 0.53H), 5.21 (dt, $J=2.2$, 1.2 Hz, 0.53H), 5.64 (ddd, $J=17.7$, 10.7, 7.6 Hz, 0.53H), 5.78 ppm (ddd, $J=18.6$, 10.1, 8.6 Hz, 0.47H); ^{13}C NMR ($CDCl_3$): $\delta=16.35$, 16.63, 21.88, 21.98, 30.97, 31.50, 36.43, 36.50, 41.87, 42.82, 57.85, 57.88, 71.17, 71.78, 74.67, 74.84, 114.01, 114.64, 114.97, 115.95, 138.46, 139.78, 139.93, 140.45, 141.22, 141.59, 142.24, 142.30 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{21}O$: 205.1592 [M^+-OH]; found: 205.1599.

1-[2-(1-Methoxymethylvinyl)-3,4-dihydronaphthalen-1-yl]-2-methyl-3-buten-1-ol (7i): The reaction was carried out by following the general procedure E and the products were purified by silica-gel column chromatography (hexane/EtOAc 10:1) (diastereomeric mixture; 31% yield (2 steps)). The following data are for a mixture of two diastereomers (0.53:0.47); ^{1}H NMR ($CDCl_3$): $\delta=0.71$ (d, $J=6.6$ Hz, 1.59H), 1.19 (d, $J=6.6$ Hz, 1.41H), 2.16–2.41 (m, 3.00H), 2.60–2.95 (m, 3.00H), 3.36 (s, 1.53H), 3.39 (s, 1.47H), 3.94 (s, 0.94H), 3.99 (s, 1.06H), 4.50 (d, $J=10.2$ Hz, 0.47H), 4.51 (d, $J=10.2$ Hz, 0.53H), 4.60 (dt, $J=17.6$, 2.0 Hz, 0.47H), 4.73 (ddd, $J=10.7$, 2.0, 1.0 Hz, 0.53H), 5.01 (t, $J=0.7$ Hz, 0.47H), 5.08 (s, 0.53H), 5.15 (dd, $J=10.2$, 1.4 Hz, 0.47H), 5.21 (dq, $J=17.4$, 1.0 Hz, 0.53H), 5.27 (q, $J=2.0$ Hz, 0.47H), 5.32 (q, $J=1.7$ Hz, 0.53H), 5.46 (ddd, $J=17.6$, 10.5, 7.6 Hz, 0.47H), 5.83 (ddd, $J=17.4$, 10.3, 8.3 Hz, 0.53H), 7.12 –7.22 (m, 3.00H), 7.97 (d, $J=7.9$ Hz, 0.47H), 8.03 ppm (d, $J=7.6$ Hz, 0.53H); ^{13}C NMR ($CDCl_3$): $\delta=16.63$, 17.03, 28.66, 28.81, 29.40, 29.46, 40.48, 41.55, 58.48, 74.89, 74.91, 75.65, 113.67, 114.66, 114.79, 115.86, 125.80, 125.95, 126.00, 126.13, 126.32, 126.48, 126.99, 127.09, 132.38, 133.26, 133.68, 133.86, 136.79, 139.43, 140.47, 141.10, 142.16, 146.61, 146.75 ppm; HRMS (FAB): m/z calcd for $C_{19}H_{23}O$: 267.1749 [M^+-OH]; found: 267.1751.

1-(1-Hydroxy-3-benzyloxymethyl-3-butenyl)-2-vinylcycloheptene (7j): The reaction was carried out by following the general Procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (67% yield (2 steps)); ^{1}H NMR ($CDCl_3$): $\delta=1.42$–1.54 (m, 4H), 1.70–1.81 (m, 2H), 2.26 (dd, $J=14.5$, 3.4 Hz, 1H), 2.33–2.41 (m, 6H), 4.01 (dd, $J=19.4$, 2.0 Hz, 2H), 4.54 (d, $J=1.2$ Hz, 2H), 4.96–5.01 (m, 2H), 5.08 (s, 1H), 5.17–5.22 (m, 2H), 6.76 (dd, $J=17.6$, 11.1 Hz, 1H), 7.27–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): $\delta=26.00$, 27.22, 27.38, 28.40, 32.42, 40.32, 68.75, 72.34, 73.40, 112.44, 116.05, 127.70, 127.79, 128.42, 133.86, 136.95, 137.86, 142.91, 142.93 ppm; HRMS (FAB): m/z calcd for $C_{21}H_{28}O_2K$: 351.1726 [M^++K]; found: 351.1717.

1-(1-Hydroxy-2-methyl-3-butenyl)-2-(1-methoxymethylvinyl)-cyclooctene (7k): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (83% yield (2 steps)); The following data are for a mixture of two diastereomers (0.53:0.47); ^{1}H NMR ($CDCl_3$): $\delta=0.89$ (d, $J=6.8$ Hz, 1.59H), 1.11 (d, $J=6.6$ Hz, 1.41H), 1.45–1.72 (m, 8.00H), 1.83 (d, $J=3.2$ Hz, 0.47H), 1.86 (d, $J=2.2$ Hz, 0.53H), 2.14–2.49 (m, 5.00H), 3.34 (s, 1.41H), 3.35 (s, 1.59H), 3.79 (d, $J=12.3$ Hz, 0.53H), 3.81 (dt, $J=13.0$, 1.2 Hz, 0.47H), 3.85–3.89 (m, 1.00H), 4.11–4.17 (m, 1.00H), 4.71 (dt, $J=2.2$, 1.2 Hz, 0.47H), 4.73 (dt, $J=2.2$, 1.2 Hz, 0.53H), 4.89 (ddd, $J=10.4$, 2.6, 1.0 Hz, 0.53H), 4.96 (dt, $J=17.4$, 1.5 Hz, 0.47H), 5.05 (dd, $J=10.2$ Hz, 1.06H), 5.10 (d quint, $J=14.5$, 1.4 Hz, 0.94H), 5.60 (ddd, $J=17.4$, 10.4, 7.2 Hz, 0.47H), 5.71 ppm (ddd, $J=18.6$, 10.1, 8.4 Hz, 0.53H); ^{13}C NMR ($CDCl_3$): $\delta=17.17$, 17.47, 25.39, 25.66, 26.00, 26.05, 26.80, 26.94, 27.99, 28.14, 30.25, 30.71, 30.94, 40.52, 41.91, 58.41, 74.71, 74.95, 75.68, 76.65, 76.70, 76.75, 77.03, 113.01, 113.45, 114.02, 115.59, 136.58, 137.39, 137.82, 138.53, 141.31, 142.18, 146.42, 146.60 ppm; HRMS (FAB): m/z calcd for $C_{17}H_{27}O$: 247.2062 [M^+-OH]; found: 247.2071.

1-(2-Isopropenyl-4,5-dimethoxyphenyl)-2-methyl-3-buten-1-ol (7l): The reaction was carried out by following the general procedure E and the products were purified by silica-gel column chromatography (hexane/EtOAc 3:1) (diastereomeric mixture: 90% yield); The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): $\delta=0.77$ (d, $J=6.8$ Hz, 1.5H), 1.11 (d, $J=6.6$ Hz, 1.5H), 1.75 (br s, 0.5H), 2.03 (s, 1.5H), 2.05 (s, 1.5H), 2.06 (br s, 0.5H), 2.50 (sextet, $J=7.1$ Hz, 0.5H), 2.59 (sextet, $J=6.8$ Hz, 0.5H), 3.86 (s, 1.5H), 3.87 (s, 1.5H), 3.89 (s, 1.5H), 3.91 (s, 1.5H), 4.55 (d, $J=8.8$ Hz, 0.5H), 4.73 (d, $J=7.1$ Hz, 0.5H), 4.84 (dd, $J=9.3$ Hz, 1H), 4.95–5.00 (m, 1H), 5.18–5.27 (m, 2H), 5.68 (ddd, $J=17.3$, 10.5, 6.6 Hz, 0.5H), 5.85 (ddd, $J=18.8$, 10.3, 8.6 Hz, 0.5H), 6.59 (s, 0.5H), 6.61 (s, 0.5H), 6.96 (s, 0.5H), 7.01 ppm (s, 0.5H); ^{13}C NMR ($CDCl_3$): $\delta=14.47$, 17.03, 25.82, 25.89, 44.16, 46.42, 55.82, 55.93, 73.37, 73.63, 108.88, 109.39, 110.67, 110.78, 114.79, 115.85, 116.78, 130.84, 130.84, 131.56, 135.55, 136.46, 140.79, 141.39, 144.64, 144.76, 147.72, 147.90, 147.93, 148.27 ppm; HRMS (FAB): m/z calcd for $C_{16}H_{22}O_3$: 262.1569 [M^+]; found: 262.1576.

1-(5-Vinyl-4-benzo[1,3]dioxolyl)-3-methoxycarbonyl-3-buten-1-ol (7m): The reaction was carried out in CH_2Cl_2 (0.5 mL) by following the general procedure F, and the product was purified by silica-gel column chromatography (hexane/EtOAc = 5:1 to 2:1) (88% yield); ^{1}H NMR ($CDCl_3$): $\delta=2.78$ (ddd, $J=13.9$, 4.6, 0.9 Hz, 1H), 2.79 (d, $J=8.0$ Hz, 1H), 2.88 (ddd, $J=14.2$, 9.2, 0.9 Hz, 1H), 3.76 (s, 3H), 5.16 (ddd, $J=8.0$, 4.3, 4.3 Hz, 1H), 5.25 (dd, $J=10.8$, 1.2 Hz, 1H), 5.49 (dd, $J=17.6$, 1.5 Hz, 1H), 5.65 (dd, $J=2.2$, 0.9 Hz, 1H), 5.99 (dd, $J=4.6$, 1.6 Hz, 2H), 6.24 (d, $J=1.2$ Hz, 1H), 6.73 (d, $J=8.3$ Hz, 1H), 6.98 (d, $J=8.0$ Hz, 1H), 6.98 ppm (dd, $J=17.6$, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=39.73$, 51.80, 68.08, 100.97, 107.62, 115.44, 120.02, 122.96, 128.15, 130.50, 133.82, 136.44, 144.70, 146.99, 167.55 ppm; HRMS (FAB): m/z calcd for $C_{15}H_{16}KO_5$: 315.0635 [M^++K]; found: 315.0639.

1-(5-Vinyl-4-benzo[1,3]dioxolyl)-3-chloromethyl-3-buten-1-ol (7n): The reaction was carried out by following general procedure G and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1 to 4:1) (78% yield); ^{1}H NMR ($CDCl_3$): $\delta=2.48$ (d, $J=7.8$ Hz, 1H), 2.68 (ddd, $J=14.9$, 4.9, 1.0 Hz, 1H), 2.78 (ddd, $J=14.9$, 9.3, 1.0 Hz, 1H), 4.11 (s, 2H), 5.10 (dd, $J=2.2$, 1.3 Hz, 1H), 5.15 (ddd, $J=9.0$, 7.6, 4.9 Hz, 1H), 5.25 (s, 1H), 5.25 (dd, $J=9.8$, 1.4 Hz, 1H), 5.48 (dd, $J=17.3$, 1.5 Hz, 1H), 6.00 (dd, $J=3.4$, 1.5 Hz, 2H), 6.75 (d, $J=8.3$ Hz, 1H), 6.96 (dd, $J=17.3$, 11.0 Hz, 1H), 6.98 ppm (d, $J=8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=$ 40.45, 48.13, 67.88, 101.13, 107.90, 116.01, 117.51, 120.44, 122.97, 130.57, 133.81, 141.73, 144.77, 147.15 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{15}ClO_3$ 266.0710 [M^+]; found: 266.0716.

1,4-Bis-(1-hydroxy-3-methyl-3-butenyl)-2,5-diisopropenylbenzene (7o): The reaction was carried out by following the general procedure E and the products were purified by silica-gel column chromatography (hexane/EtOAc 5:1) (>99% yield). The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): $\delta=1.79$ (s, 6H), 2.04 (br s, 1H), 2.08 (br s, 1H), 2.09 (s, 6H), 2.34 (t, $J=7.1$ Hz, 4H), 4.87–4.88 (m, 4H), 4.91 (t, $J=1.2$ Hz, 2H), 5.03 (t, $J=6.2$ Hz, 2H), 5.24 (t, $J=1.8$ Hz, 2H), 7.30 (s, 1H), 7.31 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta=21.91$, 25.29, 47.90, 47.93, 67.36, 67.47, 77.20, 113.37, 113.48, 115.29, 124.96, 125.01,

139.10, 139.17, 140.89, 140.94, 142.46, 142.50, 144.44, 144.54 ppm; HRMS (FAB): *m/z* calcd for $C_{22}H_{30}KO_2$: 365.1883 [M^++K]; found: 365.1887.

2-(1-Hydroxy-3-methoxycarbonyl-3-butenyl)-3-vinylthiophene (7p): The reaction was carried out by following the general procedure F and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (96% yield). ^{1}H NMR ($CDCl_3$): δ=2.75 (ddd, J=14.1, 8.6, 0.9 Hz, 1H), 2.79 (br s, 1H), 2.83 (ddd, J=14.1, 4.3, 0.9 Hz, 1H), 3.80 (s, 3H), 5.25 (dd, J=10.7, 1.2 Hz, 1H), 5.35–5.37 (m, 1H), 5.57 (dd, J=17.4, 1.3 Hz, 1H), 5.66 (q, J=1.2 Hz, 1H), 6.26 (d, J=1.5 Hz, 1H), 6.77 (dd, J=17.4, 10.7 Hz, 1H), 7.16 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ=42.52, 52.04, 67.17, 114.22, 123.51, 124.92, 128.71, 128.97, 135.08, 135.99, 143.80, 167.80 ppm; HRMS (FAB): *m/z* calcd for $C_{12}H_{14}O_3S$: 238.0664 [M^+]; found: 238.0663.

1-[1-Benzyl-4-(1-methoxymethylvinyl)-1,2,5,6-tetrahydro-3-pyridinyl]-2-methyl-3-buten-1-ol (7q): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (EtOAc) (diastereomeric mixture: 72% yield (2 steps)). The following data are for a mixture of two diastereomers (0.53:0.47); ^{1}H NMR ($CDCl_3$): δ=0.89 (d, J=6.8 Hz, 1.41H), 1.08 (d, J=6.6 Hz, 1.59H), 2.03–2.39 (m, 5.00H), 2.66–2.72 (m, 1.00H), 2.82–2.91 (m, 1.00H), 3.34 (t, J=14.9 Hz, 1.06H), 3.35 (s, 3.00H), 3.51 (t, J=13.9 Hz, 0.94H), 3.70 (d, J=4.1 Hz, 0.53H), 3.73 (d, J=4.2 Hz, 0.47H), 3.84 (t, J=12.4 Hz, 1.06H), 3.91 (t, J=12.5 Hz, 0.94H), 4.12 (s, 0.53H), 4.15 (s, 0.47H), 4.90–4.99 (m, 2.00H), 5.06–5.14 (m, 1.00H), 5.19 (q, J=2.0 Hz, 0.53H), 5.21 (q, J=1.5 Hz, 0.47H), 5.61 (ddd, J=18.1, 10.5, 7.8 Hz, 0.53H), 5.75 (ddd, J=18.6, 10.2, 8.3 Hz, 0.47H), 7.20–7.37 ppm (m, 5.00H); ^{13}C NMR ($CDCl_3$): δ=16.84, 17.10, ?30.46, 30.70, 40.32, 41.19, 49.30, 49.32, 50.42, 50.65, 58.36, 58.38, 62.57, 62.61, 73.38, 73.79, 74.58, 74.70, 114.25, 114.50, 115.17, 115.56, 126.96, 126.98, 128.12, 128.14, 129.07, 129.17, 131.74, 133.06, 133.14, 134.31, 137.80, 137.96, 140.39, 141.83, 145.62, 145.68 ppm; HRMS (FAB): *m/z* calcd for $C_{21}H_{30}NO_2$: 328.2277 [M^++H]; found: 328.2278.

6-Benzyloxymethyl-3,7-dimethyl-1,5,7-octatrien-4-ol (7r): The reaction was carried out by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (diastereomeric mixture: 67% yield (2 steps)). The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): δ=0.99 (d, J=6.8 Hz, 1.5H), 1.05 (d, J=6.8 Hz, 1.5H), 1.53 (br s, 1H), 1.87–1.911 (m, 3H), 2.23 (sextet, J=7.1 Hz, 0.5H), 2.36 (sextet, J=6.6 Hz, 0.5H), 4.03 (d, J=1.2 Hz, 1H), 4.05 (s, 1H), 4.16 (t, J=8.3 Hz, 0.5H), 4.26–4.41 (m, 0.5H), 4.49 (s, 1H), 4.51 (s, 1H), 4.86 (d, J=7.6 Hz, 1H), 5.08–5.18 (m, 3H), 5.49 (t, J=10.8 Hz, 1H), 5.73–5.85 (m, 1H), 7.28–7.35 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=14.86, 16.47, 22.57, 43.71, 44.79, 71.55, 71.67, 71.70, 72.68, 115.44, 116.48, 127.54, 127.72, 127.94, 128.20, 128.31, 138.15, 140.07, 140.42, 141.94, 141.99, 143.00, 143.48 ppm; HRMS (FAB): *m/z* calcd for $C_{18}H_{24}KO_2$: 311.1413 [M^++K]; found: 311.1418.

2-Benzyloxymethyl-9-chloro-6-vinyl-1,5-nonadien-4-ol (7s): The reaction was carried out at -78°C by following the general procedure E and the product was purified by silica-gel column chromatography (hexane/EtOAc 3:1) (70% yield (2 steps)). ^{1}H NMR ($CDCl_3$): δ=1.89–1.96 (m, 2H), 2.33–2.38 (m, 4H), 2.62 (br s, 1H), 3.53 (td, J=6.8, 0.5 Hz, 2H), 3.39–4.01 (m, 2H), 4.54 (s, 2H), 4.70–4.76 (m, 1H), 5.07 (s, 1H), 5.16 (dt, J=11.0, 1.2 Hz, 1H), 5.19 (d, J=1.2 Hz, 1H), 5.31 (d, J=17.8 Hz, 1H), 5.42 (d, J=8.6 Hz, 1H), 6.61 (ddd, J=17.1, 11.2, 0.7 Hz, 1H), 7.32–7.36 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=30.18, 31.32, 42.80, 44.69, 66.17, 72.40, 73.55, 115.58, 116.90, 127.81, 127.85, 128.48, 132.08, 132.78, 136.66, 137.72, 142.29 ppm; HRMS (FAB): *m/z* calcd for $C_{19}H_{25}ClO_2K$ 359.1180 [M^++K]; found: 359.1173.

6-Isopropenyl-3,10-dimethyl-1,5,9-undecatrien-4-ol (7t): The reaction was carried out by following the general procedure E and the products were purified by silica-gel column chromatography (hexane/EtOAc 20:1) (diastereomeric mixture: 73% yield (two steps)). The following data are for a mixture of two diastereomers (0.5:0.5); ^{1}H NMR ($CDCl_3$): δ=0.96 (d, J=7.1 Hz, 1.5H), 1.12 (d, J=7.1 Hz, 1.5H), 1.52 (br s, 0.5H), 1.55 (br s, 0.5H), 1.59 (s, 3H), 1.67 (d, J=1.2 Hz, 3H), 1.81 (quint, J=1.2 Hz, 3H), 1.90–2.24 (m, 4.5H), 2.31–2.36 (m, 0.5H), 4.07 (t, J=8.9 Hz, 0.5H), 4.21 (dd, J=9.6, 5.8 Hz, 0.5H), 4.69 (dt, J=2.4, 0.9 Hz, 0.5H), 4.70 (dq, J=2.5, 0.9 Hz, 0.5H), 4.98 (dq, J=2.4, 1.2 Hz, 1H), 5.05–5.12 (m, 2.5H), 5.13–5.16 (m, 1H), 5.18 (d, J=9.6 Hz, 0.5H), 5.72–5.85 ppm (m, 1.0H); ^{13}C NMR ($CDCl_3$): δ=14.81, 16.49, 17.70, 22.58, 25.64, 26.39, 36.22, 36.25, 43.65, 44.96, 71.87, 71.96, 113.99, 115.11, 116.12, 123.83, 125.40, 125.83, 131.61, 131.62, 140.33, 140.88, 143.59, 143.63, 146.62, 147.08 ppm; HRMS (FAB): *m/z* calcd for $C_{16}H_{25}$: 217.1956 [M^+−OH]; found: 217.1948.

General procedure H: preparation of 1,5,7-trien-4-ones 9: 1,5,7-Trien-4-ol **7** (0.361 mmol) was added to a stirred suspension of Dess–Martin periodinane (0.722 mmol) in dichloromethane (10 mL) and pyridine (1.44 mmol) at 0°C. The reaction mixture was warmed to room temperature and stirred for 30 min. The mixture was then diluted with Et_2O and filtered through Celite. The residual solid was washed with Et_2O thoroughly and the filtrate was concentrated under reduced pressure. Purification by silica-gel flash column chromatography gave the corresponding 1,5,7-trien-4-one **9**.

1-(3-Butenoyl)-2-vinylcyclopentene (9a): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (74% yield); ^{1}H NMR ($CDCl_3$): δ=1.91 (quint, J=7.3 Hz, 2H), 2.68 (t, J=7.3 Hz, 2H), 2.78 (t, J=7.3 Hz, 2H), 3.31 (dt, J=7.1, 1.5 Hz, 2H), 5.12 (dq, J=17.4, 1.5 Hz, 1H), 5.18 (dq, J=10.1, 1.5 Hz, 1H), 5.42 (d, J=10.7 Hz, 1H), 5.47 (ddt, J=17.4, 0.9, 0.6 Hz, 1H), 5.97 (ddt, J=17.4, 10.1, 7.1 Hz, 1H), 7.41 ppm (dd, J=17.4, 10.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.51, 33.36, 34.64, 47.11, 118.25, 121.33, 130.86, 132.03, 136.80, 150.83, 198.38 ppm; HRMS (EI): *m/z* calcd for $C_{11}H_{14}O$: 162.1045 [M^+]; found: 162.1043.

1-(3-Butenoyl)-2-isopropenylcyclopentene (9b): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (82% yield); ^{1}H NMR ($CDCl_3$): δ=1.87 (quint, J=7.8 Hz, 2H), 1.90 (dd, J=1.7, 1.0 Hz, 3H), 2.61–2.71 (m, 4H), 3.39 (dt, J=6.8, 1.5 Hz, 2H), 4.90 (dd, J=2.0, 1.0 Hz, 1H), 5.03 (quint, J=1.7 Hz, 1H), 5.08 (ddd, J=17.3, 3.2, 1.7 Hz, 1H), 5.14 (ddd, J=10.5, 2.9, 1.7 Hz, 1H), 5.93 ppm (ddt, J=17.3, 13.9, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.57, 21.64, 34.75, 38.38, 46.03, 115.31, 117.71, 131.41, 137.54, 141.64, 152.65, 200.63 ppm; HRMS (EI): *m/z* calcd for $C_{12}H_{16}O$: 176.1201 [M^+]; found: 176.1196.

1-(2-Methyl-3-butenoyl)-2-vinylcyclopentene (9c): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (73% yield); ^{1}H NMR ($CDCl_3$): δ=1.19 (d, J=7.1 Hz, 3H), 1.90 (quint, J=4.6 Hz, 2H), 2.66 (dd, J=8.0, 6.8 Hz, 2H), 2.64–2.90 (m, 2H), 3.48 (quint t, J=6.8, 1.0 Hz, 1H), 5.08–5.09 (m, 1H), 5.11–5.12 (m, 1H), 5.38 (d, J=10.8 Hz, 1H), 5.45 (ddt, J=17.8, 1.4, 0.7 Hz, 1H), 5.84 (ddd, J=17.8, 10.0, 7.8 Hz, 1H), 7.35 ppm (dd, J=17.6, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=16.25, 21.68, 33.20, 34.72, 48.99, 116.17, 120.85, 132.06, 137.35, 137.58, 150.77, 201.92 ppm; HRMS (EI): *m/z* calcd for $C_{12}H_{16}O$: 176.1201 [M^+]; found: 176.1200.

1-(3-Methyl-3-butenoyl)-2-vinylcyclopentene (9d): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (89% yield); ^{1}H NMR ($CDCl_3$): δ=1.77 (s, 3H), 1.89 (quint, J=7.4 Hz, 2H), 2.67 (t, J=7.7 Hz, 2H), 2.79 (t, J=7.4 Hz, 2H), 3.24 (s, 2H), 4.76 (dq, J=1.9, 1.0 Hz, 1H), 4.93 (quint, J=1.5 Hz, 1H), 5.41 (d, J=10.8 Hz, 1H), 5.46 (ddq, J=17.0, 1.6, 1.0 Hz, 1H), 7.40 ppm (dd, J=17.9, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.48, 22.64, 33.22, 34.74, 51.19, 114.25, 121.10, 132.00, 137.18, 139.27, 150.64, 198.40 ppm; HRMS (EI): *m/z* calcd for $C_{12}H_{16}O$ [M^+] 176.1201; found: 176.1199.

1-(2-Methyl-3-butenoyl)-2-isopropenylcyclopentene (9e): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (75% yield). ^{1}H NMR ($CDCl_3$): δ=1.17 (d, J=6.8 Hz, 3H), 1.84–1.93 (m, 5H), 2.54–2.77 (m, 4H), 3.66 (quint t, J=6.8, 1.2 Hz, 1H), 4.89 (s, 1H), 4.99 (quint, J=1.8 Hz, 1H), 5.04 (dt, J=4.3, 1.5 Hz, 1H), 5.08 (sextet, J=1.0 Hz, 1H), 5.82 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ=16.44, 21.77, 21.97, 35.62, 37.76, 48.86, 115.49, 115.85, 137.97, 138.03, 141.49, 150.94, 205.19 ppm; HRMS (EI): *m/z* calcd for $C_{13}H_{18}O$ [M^+] 190.1358; found: 190.1357.

1-(3-Methyl-3-butenoyl)-2-isopropenylcyclopentene (9f): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (77% yield). ^{1}H NMR ($CDCl_3$): δ=1.75 (s, 3H), 1.87 (quint, J=7.8 Hz, 2H), 1.91 (s, 3H), 2.63 (tt, J=7.6, 2.2 Hz, 2H), 2.69 (tt, J=7.6, 2.2 Hz, 2H), 3.34 (s, 2H), 4.72 (d, J=1.0 Hz, 1H), 4.90–4.91 (m, 2H), 5.02 ppm (quint, J=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.69, 21.75, 22.69, 35.07, 38.43, 50.18, 114.24, 115.36, 137.87, 139.73, 141.77, 152.46, 200.87 ppm; HRMS (EI): m/z calcd for $C_{13}H_{18}O$: 190.1358 [M^+]; found: 190.1362.

1-(3-Methoxycarbonyl-3-butenoyl)-2-vinylcyclopentene (9g): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 5:1) (86% yield). ^{1}H NMR ($CDCl_3$): δ=1.92 (quint, J=7.7 Hz, 2H), 2.69 (t, J=7.7 Hz, 2H), 2.82 (t, J=7.7 Hz, 2H), 3.54 (d, J=0.9 Hz, 2H), 3.75 (s, 3H), 5.41 (d, J=11.1 Hz, 1H), 5.47 (dd, J=17.9, 0.9 Hz, 1H), 5.61 (q, J=1.2 Hz, 1H), 6.34 (d, J=1.2 Hz, 1H), 7.41 ppm (dd, J=17.6, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.40, 33.31, 34.55, 45.35, 51.85, 121.39, 127.95, 131.94, 134.41, 136.30, 151.08, 166.74, 196.79 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{17}O_3$: 221.1178 [M^++H]; found: 221.1172.

1-(2-Methyl-3-butenoyl)-2-(1-methoxymethylvinyl)-cyclopentene (9h): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 15:1) (66% yield). ^{1}H NMR ($CDCl_3$): δ=1.17 (d, J=6.8 Hz, 3H), 1.86–1.93 (m, 2H), 2.6–2.8 (m, 4H), 3.33 (s, 3H), 3.63 (tt, J=7.8, 1.0 Hz, 1H), 4.00 (dd, J=2.2, 1.2 Hz, 2H), 5.06 (d, J=1.2 Hz, 1H), 5.09–5.12 (m, 2H), 5.26 (dt, J=1.5, 1.5 Hz, 1H), 5.79–5.88 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ=16.35, 22.04, 35.80, 38.02, 48.88, 58.21, 74.22, 116.09, 116.40, 137.98, 139.52, 142.53, 147.91, 204.66 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{20}O_2$ 221.1542 [M^++H]; found: 221.1547.

1-(2-Methyl-3-butenoyl)-2-(1-methoxymethylvinyl)-cyclooctene (9k): The reaction was carried out by following the general procedure H and the products were purified by silica-gel flash column chromatography (hexane/EtOAc 20:1) (Mixture of 1,5,7-trien-4-one (**9k**)/2*H*-pyran (**22k**): 68% yield). The following data are for a mixture of **9k** and **22k** (0.74:0.26); ^{1}H NMR ($CDCl_3$): δ=1.12 (d, J=6.8 Hz, 2.22H), 1.19 (d, J=7.1 Hz, 0.78H), 1.30–1.75 (m, 8.00H), 2.19–2.37 (m, 4.00H), 3.28 (s, 0.78H), 3.39 (s, 2.22H), 3.35 (quint, J=7.0 Hz, 0.26H), 3.65 (quint, J=7.1 Hz, 0.74H), 4.01 (dd, J=12.7, 0.5 Hz, 0.74H), 4.05 (s, 0.52H), 4.06 (dd, J=12.0, 0.5 Hz, 0.74H), 4.36 (d, J=3.0 Hz, 0.52H), 4.86 (d, J=1.0 Hz, 0.74H), 5.00 (dt, J=10.2, 1.2 Hz, 0.26H), 5.02–5.09 (m, 0.74H), 5.04 (m, 0.74H), 5.07 (dt, J=17.6, 1.6 Hz, 0.26H), 5.15 (q, J=1.5 Hz, 0.74H), 5.72 (ddd, J=17.9, 10.2, 8.0 Hz, 0.26H), 5.91 ppm (ddd, J=16.7, 8.1, 6.5 Hz, 0.74H); ^{13}C NMR ($CDCl_3$): δ=17.06, 17.86, 24.53, 24.63, 25.52, 25.92, 26.09, 26.51, 28.76, 30.34, 31.19, 31.65, 38.11, 50.96, 57.69, 58.77, 67.25, 69.98, 73.97, 113.62, 113.87, 116.09, 116.96, 117.29, 136.44, 138.56, 140.88, 141.44, 143.38, 146.61, 153.78, 211.06 ppm; HRMS (FAB): m/z calcd for $C_{17}H_{26}O_2$: 262.1933 [M^+]; found: 262.1942.

1-(2-Isopropenyl-4,5-dimethoxyphenyl)-2-methyl-3-buten-1-one (9l): The reaction was carried out by following general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 5:1) (79% yield). ^{1}H NMR ($CDCl_3$): δ=1.23 (d, J=7.1 Hz, 3H), 2.13 (d, J=0.7 Hz, 3H), 3.81 (quint, J=6.8 Hz, 1H), 3.89 (s, 3H), 3.92 (s, 3H), 4.84 (s, 1H), 5.02 (d, J=8.6 Hz, 1H), 5.06 (s, 1H), 5.16 (s, 1H), 5.83 (ddd, J=17.8, 10.8, 7.8 Hz, 1H), 6.75 (s, 1H), 6.95 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=17.13, 23.99, 49.65, 55.91, 56.00, 110.58, 111.51, 116.03, 116.71, 131.23, 136.31, 138.22, 144.60, 147.73, 150.44, 206.76 ppm; HRMS (FAB): m/z calcd for $C_{16}H_{20}O_3$: 260.1412 [M^+]; found: 260.1402.

1-(5-Vinyl-4-benzo[1,3]dioxolyl)-3-methoxycarbonyl-3-buten-1-one (9m): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 3:1) (79% yield). ^{1}H NMR ($CDCl_3$): δ=3.74 (s, 3H), 3.92 (d, J=0.9 Hz, 2H), 5.19 (dd, J=11.1, 1.6 Hz, 1H), 5.51 (dd, J=17.6, 1.2 Hz, 1H), 5.70 (dd, J=2.5, 1.2 Hz, 1H), 6.05 (s, 2H), 6.36 (d, J=1.2 Hz, 1H), 6.88 (d, J=8.0 Hz, 1H), 6.91 (dd, J=17.6, 11.1 Hz, 1H). 7.07 ppm (d, J=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=47.23, 52.02, 101.63, 110.84, 114.92, 119.89, 120.65, 128.74, 131.79, 134.26, 134.95, 146.47, 147.22, 166.74, 197.66 ppm; HRMS (FAB): m/z calcd for $C_{15}H_{14}O_5$: 274.0841 [M^+]; found: 274.0837.

1-(5-Vinyl-4-benzo[1,3]dioxolyl)-3-chloromethyl-3-buten-1-one (9n): The reaction was carried out by following general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 10:1) (77% yield). ^{1}H NMR ($CDCl_3$): δ=3.85 (d, J=0.9 Hz, 2H), 4.19 (d, J=1.0 Hz, 2H), 5.08 (d, J=0.9 Hz, 1H), 5.20 (dd, J=11.0, 1.2 Hz, 1H), 5.33 (d, J=0.9 Hz, 1H), 5.50 (dd, J=17.4, 11.9 Hz, 1H), 6.06 (s, 2H), 6.88 (d, J=8.0 Hz, 1H), 6.90 (ddd, J=16.8, 10.4, 0.6 Hz, 1H), 7.04 ppm (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=47.62, 48.16, 101.70, 110.93, 115.32, 119.02, 119.94, 120.88, 131.77, 134.93, 138.87, 146.56, 147.34, 198.25 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{14}ClO_3$: 265.0631 [M^++H]; found: 265.0636.

2-(3-Methoxycarbonyl-3-butenoyl)-3-vinylthiophene (9p): The reaction was carried out by following the general procedure H and the product was purified by silica-gel flash column chromatography (hexane/EtOAc 10:1) (56% yield). ^{1}H NMR ($CDCl_3$): δ=3.76 (s, 3H), 3.88 (d, J=1.0 Hz, 2H), 5.55 (dd, J=11.0, 1.2 Hz, 1H), 5.71 (dd, J=5.1, 1.2 Hz, 1H), 5.76 (dd, J=17.8, 1.2 Hz, 1H), 6.40 (d, J=1.0 Hz, 1H), 7.36 (d, J=5.1 Hz, 1H), 7.44 (dd, J=5.1, 0.5 Hz, 1H), 7.57 ppm (dd, J=17.8, 11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=44.98, 52.06, 118.80, 127.30, 128.76, 129.91, 130.77, 134.10, 134.47, 145.20, 166.66, 190.10 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{13}O_3S$: 237.0585 [M^++H]; found: 237.0577.

General procedure I: preparation of benzene derivatives 3: Catalyst **15** or **16** (7.5 mol%, 0.017 mmol) was added in one portion to a solution of 1,5,7-trien-4-ol **7** (0.232 mmol) in CH_2Cl_2 (23 mL, 0.01 M) under nitrogen. After stirring for 2 h at room temperature, the reaction mixture was treated with *p*-toluenesulfonic acid (0.023 mmol) and stirred for 1 h at room temperature. The mixture was concentrated under reduced pressure and purified by silica-gel column chromatography or preparative TLC on silica gel to give benzene **3**.

4,6-Dimethylindan (3e): The reaction was carried out by following the general procedure I and the product was purified by silica-gel column chromatography (hexane) (92% NMR yield). ^{1}H NMR ($CDCl_3$): δ=2.05 (quint, J=7.4 Hz, 2H), 2.22 (s, 3H), 2.29 (s, 3H), 2.79 (t, J=7.4 Hz, 2H), 2.88 (t, J=7.7 Hz, 2H), 6.79 (s, 1H), 6.89 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=19.01, 21.10, 24.89, 30.95, 32.96, 122.36, 127.71, 133.44, 135.78, 139.94, 144.01 ppm; HRMS (EI): m/z calcd for $C_{11}H_{14}$: 146.1096 [M^+]; found: 146.1093.

4,5-Dimethylindan (3f): The reaction was carried out in toluene at 100°C by following the general procedure I and the product was purified by silica-gel column chromatography (hexane) (91% NMR yield). ^{1}H NMR ($CDCl_3$): δ=2.05 (quint, J=7.8 Hz, 2H), 2.17 (s, 3H), 2.25 (s, 3H), 2.85 (t, J=7.6 Hz, 2H), 2.91 (t, J=7.6 Hz, 2H), 6.93 (d, J=7.8 Hz, 1H), 6.97 ppm (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=15.94, 19.60, 25.11, 31.90, 33.06, 121.33, 127.77, 132.30, 133.90, 141.41, 143.23 ppm; HRMS (EI): m/z calcd for $C_{11}H_{14}$: 146.1096 [M^+]; found: 146.1091.

5-Methoxycarbonylindan (3g): The reaction was carried out in toluene at 80°C by following the general procedure I, and the product was purified by preparative TLC (hexane/EtOAc 10:1) (82% yield). ^{1}H NMR ($CDCl_3$): δ=2.10 (quint, J=7.6 Hz, 2H), 2.94 (t, J=7.6 Hz, 4H), 3.89 (s, 3H), 7.26 (d, J=8.0 Hz, 1H), 7.82 (dd, J=7.8, 1.5 Hz, 1H), 7.88 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=25.34, 32.49, 32.97, 51.89, 124.13, 125.45, 127.84, 128.15, 144.49, 149.92, 167.50 ppm; The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[33]

4-Methoxymethyl-6-methylindan (3h): The reaction was carried out in toluene at 80°C by following the general procedure I, and the product was purified by silica-gel column chromatography (hexane/EtOAc 20:1) (91% NMR). ^{1}H NMR ($CDCl_3$): δ=2.07 (quint, J=7.6 Hz, 2H), 2.32 (s, 3H), 2.85 (t, J=7.3 Hz, 2H), 2.88 (t, J=7.3 Hz, 2H), 3.39 (s, 3H), 4.38 (s, 2H), 6.97 (s, 1H), 6.99 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=21.09, 25.11, 30.35, 32.63, 58.10, 72.95, 124.41, 126.33, 133.30, 135.83, 139.59, 144.62 ppm; HRMS (EI): m/z calcd for $C_{12}H_{16}O$: 176.1201 [M^+]; found: 176.1207.

1-Methoxymethyl-3-methyl-9,10-dihydrophenanthrene (3i): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 10:1)

(86% yield). ^{1}H NMR ($CDCl_3$): δ=2.39 (s, 3H), 2.83 (s, 4H), 3.40 (s, 3H), 4.50 (s, 2H), 7.11 (s, 1H), 7.19–7.24 (m, 2H), 7.27–7.31 (m, 1H), 7.55 (s, 1H), 7.72 ppm (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=21.25, 23.85, 28.81, 58.09, 73.08, 123.90, 124.42, 126.80, 127.18, 127.80, 129.17, 133.33, 134.76, 134.85, 135.68, 137.31 ppm; HRMS (FAB): m/z calcd for $C_{17}H_{18}O$: 238.1358 [M^+]; found: 238.1355.

2-Benzyloxymethyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (3j): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 10:1) (86% yield). ^{1}H NMR ($CDCl_3$): δ=1.60–1.66 (m, 4H), 1.83–1.85 (m, 2H), 2.76–2.80 (m, 4H), 4.49 (s, 2H), 4.55 (s, 2H), 7.07 (s, 2H), 7.10 (s, 1H), 7.23–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=28.24, 28.30, 32.72, 36.38, 36.67, 72.05, 125.45, 127.54, 127.77, 128.34, 128.69, 129.03, 135.65, 138.40, 142.95, 143.52 ppm; HRMS (FAB): m/z calcd for $C_{19}H_{22}O$: 266.1671 [M^+]; found: 266.1674.

1-Methoxymethyl-3-methyl-5,6,7,8,9,10-hexahydrobenzocyclooctene (3k): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 10:1) (98% yield). ^{1}H NMR ($CDCl_3$): δ=1.28–1.41 (m, 4H), 1.63–1.69 (m, 4H), 2.29 (s, 3H), 2.73 (dd, J=6.3, 6.1 Hz, 2H), 2.80 (dd, J=6.3, 6.4 Hz, 2H), 3.39 (s, 3H), 4.45 (s, 2H), 6.89 (s, 1H), 7.01 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=20.89, 25.99, 26.18, 26.33, 30.79, 32.39, 32.86, 58.06, 73.23, 127.96, 129.83, 135.08, 135.10, 136.06, 142.14 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{19}$: 187.1487 [M^+−OMe]; found: 187.1482.

6,7-Dimethoxy-1,3-dimethylnaphthalene (3l): The reaction was carried out by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 5:1) (92% yield). M.p. 103–104°C; ^{1}H NMR ($CDCl_3$): δ=2.43 (s, 3H), 2.61 (s, 3H), 3.99 (s, 3H), 4.01 (s, 3H), 7.05 (s, 1H), 7.06 (s, 1H), 7.16 (s, 1H), 7.35 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=19.44, 21.39, 55.71, 102.86, 106.39, 123.93, 126.10, 127.26, 129.49, 132.45, 133.35, 148.53, 149.11 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{16}O_2$: 216.1150 [M^+]; found: 216.1142.

Naphtho[1,2-*d*][1,3]dioxole-7-carboxylic acid methyl ester (3m): The reaction was carried out in toluene at 100°C by following the general procedure I and the product was purified by silica-gel column chromatography (hexane/EtOAc 4:1) (82% yield). M.p. 103–105°C; ^{1}H NMR ($CDCl_3$): δ=3.96 (s, 3H), 6.20 (s, 2H), 7.24 (d, J=8.9 Hz, 1H), 7.55 (d, J=8.6 Hz, 1H), 7.81 (ddd, J=9.0, 1.5, 0.9 Hz, 1H), 8.00 (dd, J=1.6 Hz, 1H), 8.56 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ=52.13, 101.99, 111.14, 119.79, 121.34, 123.84, 125.34, 128.81, 131.82, 141.17, 145.34, 167.14 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{10}O_4$: 230.0579 [M^+]; found: 230.0573.

7-Chloromethylnaphtho[1,2-*d*][1,3]dioxole (3n): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by silica-gel column chromatography (hexane/EtOAc 10:1) (88% NMR yield). M.p. 93–95°C; ^{1}H NMR ($CDCl_3$): δ=4.72 (s, 2H), 6.17 (s, 2H), 7.20 (d, J=8.5 Hz, 1H), 7.40 (d, J=8.6 Hz, 1H), 7.46 (d, J=8.9 Hz, 1H), 7.77 (s, 1H), 7.81 ppm (d, J=8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=46.85, 101.75, 110.93, 119.31, 120.56, 121.91, 126.62, 128.09, 129.58, 132.75, 141.24, 143.88 ppm; HRMS (FAB): m/z calcd for $C_{12}H_9ClO_2$: 220.0291 [M^+]; found: 220.0283.

1,2,5,6-Tetramethylanthracene (3o): The reaction was carried out in toluene at 100°C by following the general procedure I and the product was purified by preparative TLC (hexane/CH_2Cl_2 10:1) (78% yield). M.p. 200–203°C; ^{1}H NMR ($CDCl_3$): δ=2.52 (s, 6H), 2.71 (s, 6H), 7.26 (d, J=9.8 Hz, 2H), 7.81 (d, J=8.5 Hz, 2H), 8.49 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ=14.67, 20.68, 122.52, 122.59, 126.32, 129.02, 130.08, 130.66, 130.88, 131.61 ppm; HRMS (FAB): m/z calcd for $C_{18}H_{18}$: 234.1409 [M^+]; found: 234.1403.

Benzo[*b*]thiophene-5-carboxylic acid methyl ester (3p): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by silica-gel column chromatography (hexane/EtOAc 5:1) (73% yield). ^{1}H NMR ($CDCl_3$): δ=3.96 (s, 3H), 7.42 (d, J=5.6 Hz, 1H), 7.51 (d, J=5.4 Hz, 1H), 7.92 (d, J=8.5 Hz, 1H), 8.0 (dd, J=8.5, 1.5 Hz, 1H), 8.54 ppm (d, J=1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=52.29, 122.47, 124.54, 124.74, 125.66, 126.53, 127.77, 139.43, 144.23, 167.51 ppm; HRMS (FAB): m/z calcd for $C_{10}H_9O_2S$: 193.0323 [M^++H]; found: 193.0317.

2-Benzyl-5-methoxymethyl-7-methyl-1,2,3,4-tetrahydroisoquinoline (3q): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 3:1) (82% yield). ^{1}H NMR ($CDCl_3$): δ=2.27 (s, 3H), 2.78 (t, J=5.8 Hz, 2H), 2.80 (t, J=5.2 Hz, 2H), 3.38 (s, 3H), 3.62 (s, 2H), 3.69 (s, 2H), 4.38 (s, 2H), 6.76 (s, 1H), 6.99 (s, 1H), 7.26–7.35 (m, 3H), 7.39–7.41 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ=21.02, 25.46, 50.71, 56.33, 58.33, 62.66, 72.65, 126.98, 127.30, 127.47, 128.42, 129.27, 135.08, 135.76 ppm; HRMS (FAB): m/z calcd for $C_{19}H_{24}NO$: 282.1858 [M^++H]; found: 282.1860.

1-Benzyloxymethyl-2,4-dimethylbenzene (3r): The reaction was carried out by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 11:1) (91% yield). ^{1}H NMR ($CDCl_3$): δ=2.30 (s, 6H), 4.51 (s, 2H), 4.54 (s, 2H), 6.98 (d, J=7.6 Hz, 1H), 6.99 (s, 1H), 7.21 (d, J=6.8 Hz, 1H), 7.24–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ=18.76, 21.04, 70.42, 72.02, 126.30, 127.53, 127.76, 128.33, 128.94, 131.10, 133.05, 136.75, 137.50, 138.41 ppm; HRMS (FAB): m/z calcd for $C_{16}H_{18}OK$: 265.0995 [M^++K]; found: 265.0999.

1-Benzyloxymethyl-3-(3-chloropropyl)-benzene (3s): The reaction was carried out in toluene at 80°C by following the general procedure I and the product was purified by preparative TLC (hexane/EtOAc 10:1) (81% yield). ^{1}H NMR ($CDCl_3$): δ=2.09 (quint, J=6.6 Hz, 2H), 2.78 (t, J=7.6 Hz, 2H), 3.52 (t, J=6.6 Hz, 2H), 4.53 (s, 2H), 4.57 (s, 2H), 7.12 (d, J=7.6 Hz, 1H), 7.21 (d, J=6.1 Hz, 2H), 7.24–7.39 ppm (m, 6H); ^{13}C NMR ($CDCl_3$): δ=32.68, 33.96, 44.22, 72.07, 72.20, 125.61, 127.63, 127.79, 127.84, 127.92, 128.39, 128.53, 138.20, 138.47, 140.85 ppm; HRMS (FAB): m/z calcd for $C_{17}H_{19}ClKO$: 313.0762 [M^++K]; found: 313.0767.

2,4-Dimethyl-1-(4-methyl-3-pentenyl)-benzene (3t): The reaction was carried out by following the General procedure I and the product was purified by preparative TLC (hexane/EtOAc 30:1) (75% yield). ^{1}H NMR ($CDCl_3$): δ=1.59 (s, 3H), 1.70 (s, 3H), 2.22 (q, J=7.6 Hz, 2H), 2.28 (d, J=2.8 Hz, 6H), 2.57 (t, J=8.6 Hz, 2H), 5.18–5.23 (m, 1H), 6.94 (d, J=7.7 Hz, 1H), 6.96 (s, 1H), 7.02 ppm (d, J=7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=17.60, 19.20, 20.89, 25.68, 28.99, 33.05, 124.01, 126.48, 128.70, 130.87, 131.97, 135.19, 135.69, 137.47 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{19}$: 187.1487 [M^+−H]; found: 187.1490.

General procedure J: preparation of phenol derivatives 6: Catalyst **18** (7.5 mol%, 0.019 mmol) was added to a solution of 1,5,7-trien-4-one **9** (0.247 mmol) in CH_2Cl_2 (25 mL, 0.01 M) in one portion under nitrogen and the solution was stirred for 12 h at 40°C. The mixture was concentrated under reduced pressure and purified by silica-gel column chromatography or preparative TLC on silica gel to give phenol **6.**

4-Indanol (6a): The reaction was carried out by following the general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (83% yield). ^{1}H NMR ($CDCl_3$): δ=2.11 (quint, J=7.7 Hz, 2H), 2.85 (t, J=7.7 Hz, 2H), 2.93 (t, J=7.7 Hz, 2H), 4.54 (s, 1H), 6.61 (dd, J=8.0, 0.6 Hz, 1H), 6.83 (d, J=7.1 Hz, 1H), 7.05 ppm (t, J=7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=24.99, 28.67, 33.19, 112.51, 116.95, 127.69, 129.29, 146.72, 151.87 ppm; The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[34]

7-Methyl-4-indanol (6b): The reaction was carried out by following general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (91% yield). M.p. 86–87°C; ^{1}H NMR ($CDCl_3$): δ=2.11 (quint, J=3.9 Hz, 2H), 2.18 (s, 3H), 2.84 (t, J=7.6 Hz, 2H), 2.86 (t, J=7.6 Hz, 2H), 4.46 (s, 1H), 6.54 (d, J=8.3 Hz, 1H), 6.84 ppm (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=18.41, 24.58, 29.00, 31.94, 112.64, 125.95, 128.24, 128.80, 145.04, 149.90 ppm; HRMS (FAB): m/z calcd for $C_{10}H_{12}O$: 148.0888 [M^+]; found: 148.0881.

5-Methyl-4-indanol (6c): The reaction was carried out by following the general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (91% yield). ^{1}H NMR ($CDCl_3$): δ=2.11 (quint, J=7.6 Hz, 2H), 2.23 (s, 3H), 2.82 (t, J=7.6 Hz, 2H), 2.90 (t, J=7.6 Hz, 2H), 4.48 (s, 1H), 6.73 (d, J=7.6 Hz, 1H), 6.92 ppm (d, J=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=15.30, 25.40, 28.66, 33.00, 116.40, 120.72, 128.81, 129.14, 144.03, 150.12 ppm; The ^{1}H and ^{13}C NMR spectra were consistent with those reported previously.[34]

6-Methyl-4-indanol (6d): The reaction was carried out in toluene at 80 °C by following general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (86% yield). ^{1}H NMR ($CDCl_3$): $\delta = 2.08$ (quint, $J = 4.0$ Hz, 2H), 2.27 (s, 3H), 2.79 (t, $J = 7.4$ Hz, 2H), 2.87 (t, $J = 7.7$ Hz, 2H), 4.60 (s, 1H), 6.44 (s, 1H), 6.66 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 21.15$, 25.20, 28.34, 33.11, 113.33, 117.73, 126.17, 137.89, 146.75, 151.62 ppm; HRMS (FAB): m/z calcd for $C_{10}H_{12}O$: 148.0888 [M^+]; found: 148.0886.

5,7-Dimethyl-4-indanol (6e): The reaction was carried out by following general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (88% yield). M.p. 117–118 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.12$ (quint, $J = 7.4$ Hz, 4H), 2.16 (s, 3H), 2.21 (s, 3H), 2.82 (q, $J = 7.7$ Hz, 2H), 4.31 (s, 1H), 6.75 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 15.28$, 18.35, 25.03, 29.06, 31.75, 121.00, 125.47, 128.57, 129.97, 142.39, 148.12 ppm; HRMS (FAB): m/z calcd for $C_{11}H_{14}O$: 162.1045 [M^+]; found: 162.1049.

6,7-Dimethyl-4-indanol (6f): The reaction was carried out in toluene at 80 °C by following general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (92% yield). M.p. 106–107 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.10$ (q, $J = 7.6$ Hz, 2H), 2.10 (s, 3H), 2.21 (s, 3H), 2.84 (q, $J = 7.3$ Hz, 4H), 4.34 (s, 1H), 6.48 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 15.25$, 19.55, 24.83, 28.89, 32.33, 114.37, 124.42, 126.14, 135.91, 145.29, 149.29 ppm; HRMS (FAB): m/z calcd for $C_{11}H_{14}O$: 162.1045 [M^+]; found: 162.1041.

6-Methoxycarbonyl-4-indanol (6g): The reaction was carried out in toluene at 80 °C by following general procedure J and the product was purified by preparative TLC (hexane/EtOAc 3:1) (95% yield). M.p. 153–155 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.13$ (quint, $J = 7.4$ Hz, 2H), 2.90 (t, $J = 7.4$ Hz, 2H), 2.94 (t, $J = 7.7$ Hz, 2H), 3.90 (s, 3H), 5.84 (s, 1H), 7.42 (s, 1H), 7.49 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 25.02$, 29.11, 32.96, 52.14, 114.19, 118.07, 129.61, 135.60, 146.93, 151.99, 167.72 ppm; HRMS (FAB): m/z calcd for $C_{11}H_{13}O_3$: 193.0856 [M^++H]; found: 193.0856.

7-Methoxymethyl-5-methyl-4-indanol (6h): The reaction was carried out in toluene at 80 °C by following the general procedure J and the product was purified by preparative TLC (hexane/EtOAc 5:1) (85% yield). ^{1}H NMR ($CDCl_3$): $\delta = 2.12$ (quint, $J = 7.3$ Hz, 2H), 2.22 (s, 3H), 2.82 (t, $J = 7.3$ Hz, 2H), 2.91 (t, $J = 7.4$ Hz, 2H), 3.35 (s, 3H), 4.34 (s, 2H), 4.62 (br s, 1H), 6.92 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 15.24$, 25.08, 28.76, 31.12, 57.79, 72.76, 121.09, 125.34, 129.13, 129.70, 142.85, 149.921 ppm; HRMS (FAB): m/z calcd for $C_{12}H_{16}O_2$: 192.1150 [M^+]; found: 192.1157.

4-Methoxymethyl-2-methyl-5,6,7,8,9,10-hexahydro-1-benzocyclooctenol (6k): The reaction was carried out in toluene at 80 °C by following the general procedure J, and the product was purified by preparative TLC (hexane/EtOAc 5:1) (98% yield). M.p. 82–83 °C; ^{1}H NMR ($CDCl_3$): $\delta =$ 1.31–1.39 (m, 4H), 1.62–1.68 (m, 4H), 2.19 (s, 3H), 2.77–2.81 (m, 4H), 3.33 (s, 3H), 4.33 (s, 2H), 4.59 (s, 1H), 6.88 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 15.74$, 24.46, 26.30, 26.42, 27.24, 29.45, 31.15, 57.72, 73.32, 119.83, 126.99, 130.03, 139.33, 151.14 ppm; HRMS (FAB): m/z calcd for $C_{15}H_{22}O_2$: 234.1620 [M^+]; found: 234.1621.

6,7-Dimethoxy-2,4-dimethyl-1-naphthalenol (6l): The reaction was carried out by following general procedure J and the product was purified by silica-gel column chromatography (hexane/EtOAc 3:1) (84% yield). M.p. 129–131 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (s, 3H), 2.53 (s, 3H), 4.02 (s, 3H), 4.03 (s, 3H), 4.83 (br s, 1H), 6.95 (s, 1H), 7.12 (s, 1H), 7.44 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 15.43$, 18.88, 55.70, 55.80, 100.88, 103.13, 114.23, 119.81, 124.63, 127.80, 146.23, 148.68, 148.81 ppm; HRMS (FAB): m/z calcd for $C_{14}H_{16}O_3$: 232.1099 [M^+]; found: 232.1092.

9-Hydroxynaphthol[1,2-*d*][1,3]dioxole-7-carboxylic acid methyl ester (6m): the reaction was carried out in toluene at 80 °C by following general procedure J and the product was purified by silica-gel column chromatography (hexane/EtOAc 4:1 to 2:1) (81% yield). M.p. 199–201 °C; ^{1}H NMR ($CDCl_3$): $\delta = 3.94$ (s, 3H), 6.23 (s, 2H), 6.69 (s, 1H), 7.22 (d, $J = 8.6$ Hz, 1H), 7.41 (d, $J = 1.2$ Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 8.12 ppm (d, $J = 1.2$ Hz, 1H); ^{13}C NMR (D_6-DMSO (DMSO = dimethyl sulfoxide)): $\delta = 52.00$, 101.45, 106.30, 111.46, 114.27, 122.12, 123.59, 125.28, 130.52, 140.77, 145.23, 151.85, 166.32 ppm; HRMS (FAB): m/z calcd for $C_{13}H_{10}O_5$: 246.0528 [M^+]; found: 246.0531.

7-Chloromethylnaphtho[1,2-*d*][1,3]dioxol-9-ol (6n): The reaction was carried out in toluene at 80 °C by following the general procedure J and the product was purified by silica-gel column chromatography (hexane/EtOAc 3:1) (80% yield). M.p. 127–129 °C; ^{1}H NMR ($CDCl_3$): $\delta = 4.64$ (s, 2H), 6.19 (s, 2H), 6.72 (s, 1H), 6.88 (d, $J = 1.5$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 1H), 7.32 (br s, 1H), 7.36 ppm (d, $J = 8.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 46.76$, 102.04, 109.59, 111.32, 111.54, 119.70, 122.39, 131.17, 134.45, 139.33, 143.25, 150.58 ppm; HRMS (FAB): m/z calcd for $C_{12}H_9ClO_3$: 236.0240 [M^+]; found: 236.0237.

7-Hydroxy-benzo[*b*]thiophene-5-carboxylic acid methyl ester (6p): The reaction was carried out in toluene at 80 °C by following the general procedure J and the product was purified by preparative TLC (hexane/EtOAc 3:1) (70% yield). M.p. 188–191 °C; ^{1}H NMR (D_6-acetone): $\delta =$ 3.89 (s, 3H), 7.45 (s, 1H), 7.53 (d, $J = 5.4$ Hz, 1H), 7.75 (d, $J = 5.4$ Hz, 1H), 8.11 (d, $J = 1.2$ Hz, 1H), 9.57 ppm (s, 1H); ^{13}C NMR (D_6-acetone): $\delta = 52.27$, 108.76, 117.97, 125.84, 129.03, 132.93, 142.46, 152.86, 167.49 ppm; HRMS (FAB): m/z calcd for $C_{10}H_8O_3S$: 208.0194 [M^+]; found: 208.0191.

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