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ScienceDirect
Tetrahedron
Tetrahedron 64 (2008) 1204–1212
www.elsevier.com/locate/tet

Direct palladium/carboxylic acid-catalyzed C-allylation of cyclic 1,3-diones with allylic alcohols in water

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Received 7 September 2007; received in revised form 14 November 2007; accepted 23 November 2007

Abstract

The direct activation of C–O bonds in allylic alcohols in water as a suspension medium by palladium complexes has been accelerated by carrying out the reactions in the presence of a carboxylic acid. The palladium-catalyzed allylation of cyclic 1,3-diones using allylic alcohols directly gave the corresponding *C*-allylated products in good yields.

Keywords: Palladium-catalyzed; Water; Cyclic 1,3-diones; Allylic alcohols

1. Introduction

The palladium-catalyzed allylation is a powerful tool for C–C, C–N, and C–O bond formation, which has been widely applied to organic chemistry.[1–3] The processes have been shown to proceed by attack of nucleophiles on intermediate η^3-allylpalladium(II) complexes generated by oxidative addition of allylic compounds including halides,[4–6] esters,[7–15] carbonates,[16–20] carbamates,[21,22] phosphates,[23,24] and related derivatives[25–28] to a Pd(0) complex. Because these substrates are synthesized from the corresponding allylic alcohols, palladium-catalyzed conversion of allylic alcohols directly into allylation products is highly beneficial, especially from the viewpoint of the atom economy.[29,30] For achieving the palladium-catalyzed direct cleavage of C–O bond in allylic alcohols, various processes have been reported.[31] These processes include conversion of allylic alcohols into the esters of inorganic acids (e.g., As_2O_3,[32] B_2O_3,[33] CO_2[1]) or employment of a Lewis acid (e.g., BEt_3,[34,35] BF_3,[36] BPh_3,[37] $SnCl_2$[38,39]). However, there have been only limited and sporadic reports dealing with the direct cleavage of the C–O bond in allylic alcohols on interaction with a transition metal complex.[40–43] Successful applications using allylic alcohols directly in catalytic processes are even more limited. This apparently stems from the poor capability of a nonactivated hydroxyl to serve as a leaving group.[37] Ozawa et al. reported that (π-allyl)palladium complexes bearing diphosphinidenecyclobutene ligands effectively catalyze C- and N-allylation using allylic alcohols without OH activators.[44] However, the addition of pyridine as a base was required for the C-allylation of active methylene compounds to enhance their nucleophilicity. Patil and Yamamoto disclosed the direct palladium-catalyzed allylic substitution of allylic alcohols by carbon pronucleophiles.[45] We have reported our attempts and some successful applications of a process involving the C–O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes in the presence of $Ti(O^iPr)_4$ in benzene.[46–49] Organic reactions in water have recently attracted much attention, because water is a safe and economical substitute for conventional organic solvent.[50–54] Thus, development of atom-economical reactions in water is one of the most important goals of synthetic chemistry. Due to our continuing interest in the palladium-catalyzed allylation of anilines, we have recently disclosed a new catalytic system for palladium/carboxylic acid-catalyzed allylation of anilines with allylic alcohols in water as a suspension medium.[55] Herein, we will

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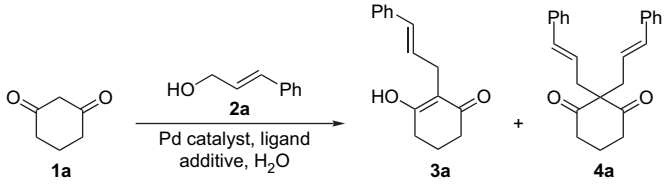
doi:10.1016/j.tet.2007.11.082

describe a novel catalysis of palladium complex, which mediates C-allylation of cyclic 1,3-diones with allylic alcohols using water as solvent.

2. Results and discussion

The palladium-catalyzed allylation of cyclic 1,3-diones with cinnamyl alcohol was investigated under various conditions (Scheme 1). When a mixture of 1,3-cyclohexadione (**1a**, 1 mmol) and cinnamyl alcohol (**2a**, 0.8 mmol) was heated in the presence of catalytic amounts of $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), and 1-adamantanecarboxylic acid (1-$AdCO_2H$) (0.5 mmol) in water at 50 °C for 15 min, 2-cinnamyl-1,3-cyclohexadione (**3a**) was formed in only 3% yield (entry 1 in Table 1). The reaction, under reflux, increased the yields of products **3a** and 2,2-dicinnamyl-1,3-cyclohexadione (**4a**) to 21 and 78%, respectively (entry 2). It was confirmed that the yield was decreased in the absence of PPh_3 (entry 3). The reaction did not occur in the absence of the palladium species as a catalyst (entry 4). As expected, increasing the relative amount of 1,3-cyclohexadione favored the formation of the desired diallylated product **4a** (entries 5 and 6). The reaction gave only 40% yield without water as solvent (entry 7). The absence of a carboxylic acid gave moderate yields of products (entry 8). The effect of water may activate allyl alcohol via hydration of the hydroxyl group for the smooth generation of the π-allylpalladium intermediate.[56] Other carboxylic acids such as $PhOCH_2CO_2H$ (entry 9), lauric acid (entry 10), and 4-octylbenzoic acid (entry 12) were also effective for the allylation. $PhCO_2H$ (entry 13), CH_3CO_2H (entry 15), and dodecylbenzenesulfonic acid (DBSA) (entry 16) gave moderate yields of products. Ph_2CHCO_2H (entry 11) and 4-aminobenzoic acid (entry 14) retarded the allylation. Strong acids such as C_6F_5OH (entry 17) also enhanced the substitution reaction.



Scheme 1. Allylation of 1,3-cyclohexadione (**1a**) with cinnamyl alcohol (**2a**).

A comparative study of different palladium catalysts and phosphine ligands in water was undertaken (Table 2). Among the palladium catalysts including $Pd(OAc)_2$ (entry 1), $Pd(acac)_2$ (entry 2), $PdCl_2$(1,10-phen) (entry 3), $Pd(OCOCF_3)_2$ (entry 4), $PdCl_2(MeCN)_2$ (entry 5), $PdCl_2(PhCN)_2$ (entry 6), $PdCl_2$ (entry 7), $Pd(propionate)_2$ (entry 8), $Pd(hfacac)_2$ (entry 9), $Pd_2(dba)_3$ (entries 10 and 11), and $Pd(PPh_3)_4$ (entry 12) were used. $Pd(OAc)_2$, $PdCl_2$, $Pd(hfacac)_2$, and $Pd(PPh_3)_4$ were found to be the superior. However, using $Pd_2(dba)_3$ with extra PPh_3 as catalyst increased the yield of products (entry 11). The catalytic reactivity of the phosphine ligands is likely due to improved catalyst stability. In the presence

Table 1
Allylation of 1,3-cyclohexadione (**1a**) with cinnamyl alcohol (**2a**): temperature and acid effects[a]

Entry	Additive	Yield (%)[b] (**3a**+**4a**)	Yield (%)[b] of **3a**	Yield (%)[b] of **4a**
1[c]	1-$AdCO_2H$	3	3	
2	1-$AdCO_2H$	99	21	78
3[d]	1-$AdCO_2H$	6	6	
4[e]	1-$AdCO_2H$	0		
5[f]	1-$AdCO_2H$	99	17	82
6[g]	1-$AdCO_2H$	99[h]	1	98
7[i]	1-$AdCO_2H$	40	16	24
8[j]	—	62	26	36
9	$PhOCH_2CO_2H$	91	20	71
10	$CH_3(CH_2)_{10}CO_2H$	89	5	84
11	Ph_2CHCO_2H	33	8	25
12	4-Oct$C_6H_4CO_2H$	88	15	73
13	$PhCO_2H$	58	32	26
14	$H_2NC_6H_4CO_2H$	28	12	16
15	CH_3CO_2H	73	18	55
16	DBSA	49	11	38
17	C_6F_5OH	99	4	95

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), and additive (0.5 mmol) in water (5 mL) were refluxed for 15 min.
[b] Isolated yield was based on **2a**.
[c] Stirred at 50 °C for 15 min.
[d] Without PPh_3.
[e] Without $Pd(OAc)_2$.
[f] Compound **2a** (1.2 mmol) was used.
[g] Compound **2a** (4 mmol) was used.
[h] Isolated yield was based on **1a**.
[i] Without water.
[j] Without additive.

of various monodentate ligands including PPh_3, Bu_3P, $(2\text{-}MeC_6H_4)_3P$, $(2\text{-furyl})_3P$, $(2\text{-pyridyl})Ph_2P$, $(3\text{-}MeC_6H_4)_3P$, $(4\text{-}MeC_6H_4)_3P$, $(4\text{-}MeOC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$, $[2,6\text{-}(MeO)_2C_6H_3]_3P$, and $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$ (entries 1 and 13–23) showed that PPh_3 (entry 1), $(2\text{-furyl})_3P$ (entry 15), $(2\text{-pyridyl})Ph_2P$ (entry 16), $(3\text{-}MeC_6H_4)_3P$ (entry 17), $(4\text{-}MeC_6H_4)_3P$ (entry 18), and $(4\text{-}FC_6H_4)_3P$ (entry 20) were the most effective ligands. The bidentate ligands such as dppp, dppb, and dpph could give good results (entries 24–26). (±)-BINAP afforded low yields of products (entry 27).

Results for C-allylation of a number of cyclic 1,3-diones (**1b–i**) with cinnamyl alcohol (**2a**) using $Pd(OAc)_2$, PPh_3, and 1-$AdCO_2H$ in water are summarized in Table 3. Dimedone (**1b**) underwent mono- and diallylation, while the addition of 1-$AdCO_2H$ provided mono- and diallylated products in quantitatively yields (entry 1). 2,4-Quinolinediol (**1c**) also reacted to give the *C*-allylated products in good yields (entry 2). With 3-hydroxy-1*H*-phenalen-1-one (**1d**), only the diallylated product 2,2-dicinnamyl-2*H*-phenalen-1,3-dione (**4d**) was obtained, however, in a very low yield (entry 3). The reaction gave 36% yield under reflux for 30 min (entry 4). Cyclic 1,3-diones **1e** and **1f** also afforded only diallylated product in high yields (entries 5 and 6). Using $Pd(OAc)_2$ as catalyst was more effective than $PdCl_2$ (entry 7). 4-Hydroxycoumarin (**1g**) gave monoallylated products **3g** and **5** in 68 and 6%, respectively (entry 8). Compound **5** may be produced via

Table 2
Allylation of 1,3-cyclohexadione (**1a**) with cinnamyl alcohol (**2a**): palladium and phosphine ligand effects[a]

Entry	Palladium	Ligand	Yield (%)[b] (**3a**+**4a**)	Yield (%)[b] of **3a**	Yield (%)[b] of **4a**
1	$Pd(OAc)_2$	PPh_3	99	21	78
2	$Pd(acac)_2$	PPh_3	70	3	67
3	$PdCl_2$(1,10-phen)	PPh_3	77	11	66
4	$Pd(OCOCF_3)_2$	PPh_3	59	8	51
5	$PdCl_2(MeCN)_2$	PPh_3	52	8	44
6	$PdCl_2(PhCN)_2$	PPh_3	74	3	71
7	$PdCl_2$	PPh_3	95	8	87
8	$Pd(propionate)_2$	PPh_3	81	6	75
9	$Pd(hfacac)_2$[c]	PPh_3	99	30	69
10	$Pd_2(dba)_3$	—	2	2	
11	$Pd_2(dba)_3$	PPh_3	87	2	85
12	$Pd(PPh_3)_4$	—	99	13	86
13	$Pd(OAc)_2$	Bu_3P	5	5	
14	$Pd(OAc)_2$	$(2\text{-}MeC_6H_4)_3P$	44	5	39
15	$Pd(OAc)_2$	$(2\text{-Furyl})_3P$	99	3	96
16	$Pd(OAc)_2$	$(2\text{-Pyridyl})Ph_2P$	99	2	97
17	$Pd(OAc)_2$	$(3\text{-}MeC_6H_4)_3P$	99	16	83
18	$Pd(OAc)_2$	$(4\text{-}MeC_6H_4)_3P$	99	9	90
19	$Pd(OAc)_2$	$(4\text{-}MeOC_6H_4)_3P$	87	6	81
20	$Pd(OAc)_2$	$(4\text{-}FC_6H_4)_3P$	99	7	92
21	$Pd(OAc)_2$	$(4\text{-}ClC_6H_4)_3P$	96	3	93
22	$Pd(OAc)_2$	$[2,6\text{-}(MeO)_2C_6H_3]_3P$	3	3	
23	$Pd(OAc)_2$	$[2,4,6\text{-}(MeO)_3C_6H_2]_3P$	4	4	
24	$Pd(OAc)_2$	dppp[d]	80	11	69
25	$Pd(OAc)_2$	dppb[e]	80	33	47
26	$Pd(OAc)_2$	dpph[f]	81	47	34
27	$Pd(OAc)_2$	(±)-BINAP[g]	6	6	

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), Pd catalyst (0.05 mmol), ligand (0.2 mmol), and 1-$AdCO_2H$ (0.5 mmol) in water (5 mL) were refluxed for 15 min.
[b] Isolated yield was based on **2a**.
[c] Palladium hexafluoroacetylacetonate.
[d] 1,3-Bis(diphenylphosphino)propane.
[e] 1,4-Bis(diphenylphosphino)butane.
[f] 1,6-Bis(diphenylphosphino)hexane.
[g] (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.

Table 3
Allylation of cyclic 1,3-diones (**1b–i**) with cinnamyl alcohol (**2a**)[a]

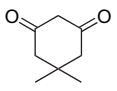
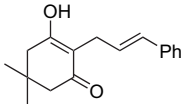
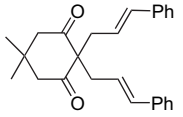
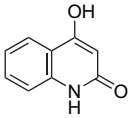
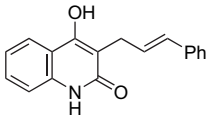
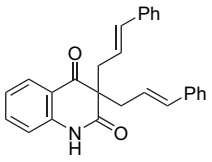
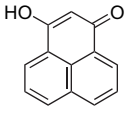
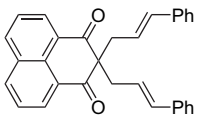
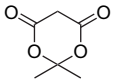
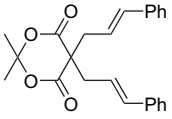
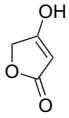
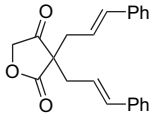
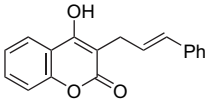
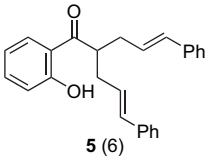
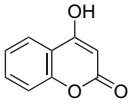
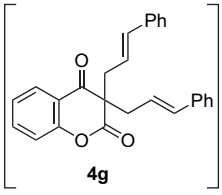
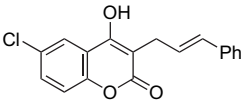
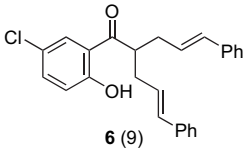
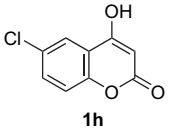
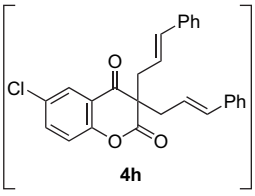
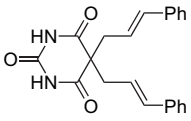
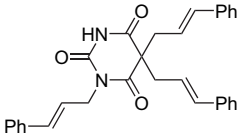
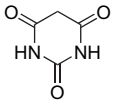
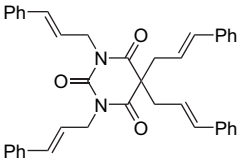
Entry	**1**	Yields[b] (%)	
1	 **1b**	 **3b** (73)	 **4b** (26)
2	 **1c**	 **3c** (59)	 **4c** (29)
3	 **1d**	 **4d** (9)	

Table 3 (*continued*)

Entry	1	Yields[b] (%)
4[c]	**1d**	**4d** (36)
5	 **1e**	 **4e** (99)
6	 **1f**	 **4f** (98)
7[d]	**1f**	**4f** (62)
		 **3g** (68)
		 **5** (6)
8	 **1g**	 **4g**
		 **3h** (31)
		 **6** (9)
9	 **1h**	 **4h**
		 **4i** (10)
		 **7** (40)
10	 **1i**	 **8** (47)

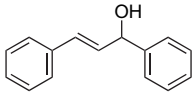
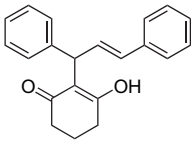
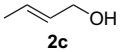
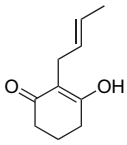
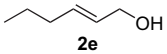
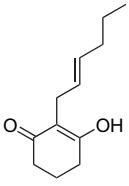
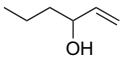
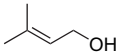
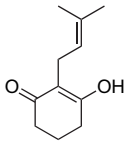
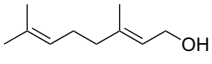
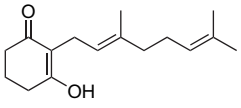
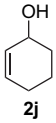
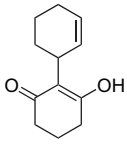
[a] Reaction conditions: **1** (1 mmol), **2a** (0.8 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), and 1-$AdCO_2H$ (0.5 mmol) in water (5 mL) were refluxed for 15 min.

[b] Isolated yield was based on **2a**.

[c] Refluxed for 30 min.

[d] $PdCl_2$ was used.

Table 4
Reaction of 1,3-cyclohexadione (**1a**) with allylic alcohols **2**[a]

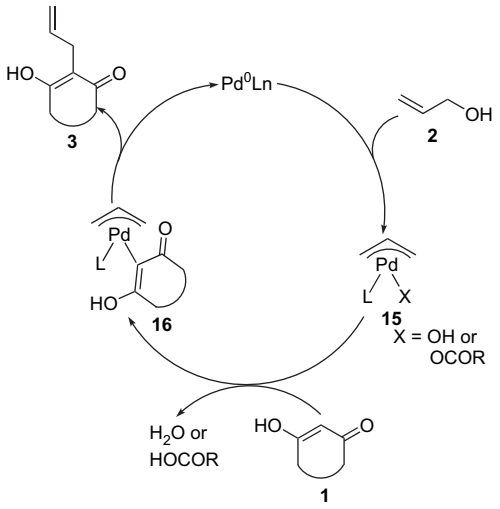
Entry	2	Yields[b] (%)
1	 **2b**	 **9** (52)
2	 **2c**	 **10** (33) (*E*/*Z* = 80/20)[c]
3	 **2d**	**10** (43) (*E*/*Z*=82:18)[c]
4	 **2e**	 **11** (57)
5	 **2f**	**11** (38)
6	 **2g**	 **12** (13)
7	 **2h**	**12** (12)
8	 **2i**	 **13** (24)
9	 **2j**	 **14** (66)

[a] Reaction conditions: **1a** (1.0 mmol), **2** (0.8 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), 1-adamantanecarboxylic acid (0.5 mmol), and water (5 mL) were refluxed for 30 min.
[b] Isolated yield was based on **2**.
[c] Determined by GC.

diallyated product **4g**, which was hydrolyzed and then decarboxylated to compound **5**. 6-Chloro-4-hydroxycoumarin (**1h**) reacted as **1g**, affording the corresponding products **3h** and **6** in 31 and 9%, respectively (entry 9). Allylation of **1i** gave mixtures of di-, tri-, and tetraallylated pyrimidine **4i**, **7**, and **8** in yields of 10, 40, and 47%, respectively (entry 10).

Results for allylation of 1,3-cyclohexadione with both aromatic and aliphatic allylic alcohols **2b–j** using $Pd(OAc)_2$, PPh_3, and 1-$AdCO_2H$ are summarized in Table 4. In addition to the parent cinnamyl alcohol (**2a**), *trans*-1,3-diphenyl-2-propen-1-ol (**2b**) reacted to give the allylating product **9** in moderate yields (entry 1). Steric factors affected the yield. In contrast to the previous systems for allylic substitution, reactions of aliphatic allylic alcohols occurred with only low yields (entries 2–9). Treatment of 1,3-cyclohexadione (**1a**) with crotyl alcohol (**2c**) gave only stereoisomeric product **10** in the yield of 33% (entry 2). The formation of regioisomeric product was not observed. The 80:20 *E*/*Z* ratio of **10** was determined by ^1H NMR. Product *E* alkene arose from the more thermodynamically stable *syn* π-allyl complex. Both regioisomeric alcohols **2c** and **2d** gave identical product **10** in similar *E*/*Z* ratios (entry 3). The loss of the stereochemistry of the starting alcohol **2c** is due to a rapid $\sigma \leftrightarrows \eta^3 \leftrightarrows \sigma$ interconversion of the π-allyl intermediate compared to the rate of alkylation of this intermediate. With the unsymmetrical allylic alcohols **2**, the major products were obtained from approach of **1** at the less sterically hindered primary site. Both regioisomeric alcohols **2e** and **2f** reacted with 1,3-cyclohexadione to give only more highly substituted alkene **11** (entries 4 and 5). Similarly, 3-methyl-2-buten-1-ol (**2g**) and its regioisomer **2h**, 2-methyl-3-buten-2-ol yielded only monoallylated product **12** (entries 6 and 7). Using geraniol (**2i**) as allylating reagent gave only monoallylated product **13** in 24% yield (entry 8). The secondary alcohol **2j** gave 66% yields (entry 9).

Although a detailed mechanistic study for the allylation of cyclic 1,3-diones **1** with allylic alcohols **2** has not been undertaken, the reaction most likely proceeds via the pathway outlined in Scheme 2, in which the substituent on allylic alcohol



Scheme 2. Proposed mechanism of the allylation of cyclic 1,3-diones **1** with allylic alcohols **2**.

is omitted. Oxidative addition of alcohol **2** or protonated alcohol, formed by the acid, to Pd(0) species affords the π-allylpalladium intermediate (**15**). The formation of π-allylpalladium may be accelerated by the acid, possibly by protonation to increase the leaving group ability of the OH group of allyl alcohol.[57] Formation of a π-allylpalladium with carboxylic acid could be the key for the rate enhancement by the acid.[58] Intermolecular nucleophilic substitution of pronucleophiles **1** takes place at the π-allyl system to give intermediate **16**, which undergoes reductive elimination to produce 2-allylated-1,3-diones. In the presence of cyclic 1,3-diones, which may be relatively reactive toward the palladium center, **15** should be predominantly transformed to **16** to afford allylated compound.

3. Conclusions

In summary, we have developed a catalytic system that enables reactions of cyclic 1,3-diones with allylic alcohols as allylating agents in water. This is a simple and efficient route for C–C bond formation. The effect of addition of a carboxylic acid to promote the palladium-catalyzed allyl–OH bond cleavage remarkably enhanced both the reaction rate and the yield. The alkylation of aromatic allylic alcohol worked well with cyclic 1,3-diones, giving generally good to high yields of the corresponding allylic 1,3-diones.

4. Experimental section

4.1. General considerations: general method

All melting points were uncorrected. IR absorption spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrophotometer. Proton and carbon-13 NMR spectra were measured with a Unity-400 or Mercury Plus-400 spectrometer. Carbon multiplicities were obtained from DEPT experiments. Chemical shifts (δ) and coupling constants (Hz) were measured with respect to TMS or chloroform-d_1. MS and high-resolution mass spectra (HRMS) were taken on a Thermo-Finnigan trace GC or JEOL TMSD-100 instrument, with a direct inlet system. Elemental analyses were carried out on a Heraeus CHN-O-Rapid elemental analyzer.

4.2. General procedure for the palladium-catalyzed allylation of cyclic 1,3-diones

4.2.1. Reaction with 1,3-cyclohexadione (*1a*)

Cinnamyl alcohol (**2a**) (107 mg, 0.8 mmol) and 1-adamantanecarboxylic acid (90 mg, 0.5 mmol) were suspended in water (5 mL) at rt, and then $Pd(acac)_2$ (11 mg, 0.05 mmol), PPh_3 (52 mg, 0.2 mmol), and 1,3-cyclohexadione (112 mg, 1 mmol) were added. The whole mixture was heated under reflux conditions for 15 min. After the mixture was cooled to rt, water and brine were added. The organic materials were extracted with dichloromethane, dried over magnesium sulfate, and concentrated under vacuum. Column chromatography (ethyl acetate/*n*-hexane 1:4) of the residue afforded **3a** and **4a** in 21 and 79% yields, respectively.

4.2.2. 2-Cinnamyl-1,3-cyclohexadione (*3a*)

White crystals. Mp 161–162 °C (methanol/hexane) (160–162 °C[59]). IR (KBr) ν: 3421, 2948, 1577 cm^{-1}. ^1H NMR (CD_3OD) δ: 1.96 (quin, J=6.4 Hz, 2H, CH_2), 2.44 (t, J=6.4 Hz, 4H, $CH_2\times2$), 3.13 (d, J=6.8 Hz, 2H, CH_2), 6.18 (dt, J=6.8, 16.0 Hz, 1H, vinyl H), 6.33 (d, J=16.0 Hz, 1H, vinyl H), 7.10–7.14 (m, 1H, ArH), 7.20–7.29 (m, 4H, ArH). ^{13}C NMR (CD_3OD) δ: 22.0 (CH_2), 26.1 (CH_2), 33.8 (CH_2), 114.8 (C), 126.9 (CH), 127.6 (CH), 129.3 (CH), 129.4 (CH), 130.6 (CH), 139.4 (C). EIMS *m/z*: 228 (M^+), 200, 172, 157, 144, 138, 130, 115, 104, 91. HRESI-MS calcd for $C_{15}H_{17}O_2$ $[M+1]^+$ 229.1228, found 229.1227.

4.2.3. 2,2-Dicinnamyl-1,3-cyclohexadione (*4a*)

White crystals. Mp 109–110 °C (chloroform/hexane) (110–111 °C[59]). IR (KBr) ν: 3398, 2925, 1693 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.85 (quin, J=6.8 Hz, 2H, CH_2), 2.54 (t, J=6.8 Hz, 4H, $CH_2\times2$), 2.72 (d, J=7.6 Hz, 2H, CH_2), 5.96 (dt, J=7.6, 15.6 Hz, 1H, vinyl H), 6.39 (d, J=15.6 Hz, 1H, vinyl H), 7.18–7.31 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$) δ: 16.4 (CH_2), 40.2 (CH_2), 40.4 (CH_2), 68.6 (C), 123.6 (CH), 126.2 (CH), 127.5 (CH), 128.5 (CH), 134.3 (CH), 136.7 (C), 210.9 (C). EIMS *m/z*: 344 (M^+), 326, 308, 282, 254, 243, 235, 227, 220, 205, 198, 179, 167, 156, 141, 128, 118, 115, 92, 91. HRESI-MS calcd for $C_{24}H_{25}O_2$ $[M+1]^+$ 345.1854, found 345.1852.

4.2.4. 2-Cinnamyl-5,5-dimethyl-1,3-cyclohexadione (*3b*)

White crystals. Mp 166–167 °C (methanol/hexane) (165–167 °C[60]). IR (KBr) ν: 3446, 2958, 1558 cm^{-1}. ^1H NMR (CD_3OD) δ: 1.08 (s, 6H, $CH_3\times2$), 2.33 (s, 4H, $CH_2\times2$), 3.13 (dd, J=1.2, 6.4 Hz, 2H, CH_2), 6.18 (dt, J=6.4, 15.6 Hz, 1H, vinyl H), 6.33 (d, J=16.0 Hz, 1H, vinyl H), 7.10–7.15 (m, 1H, ArH), 7.21–7.28 (m, 4H, ArH). ^{13}C NMR (CD_3OD) δ: 26.3 (CH_2), 28.4 (CH_3), 32.0 (C), 47.4 (CH_2), 112.7 (C), 126.4 (CH), 127.0 (CH), 128.9 (CH), 129.8 (CH), 130.1 (CH), 138.7 (C). EIMS *m/z*: 256 (M^+), 254, 239, 221, 212, 199, 170, 155, 141, 128, 115, 102, 91, 77. HRESI-MS calcd for $C_{17}H_{21}O_2$ $[M+1]^+$ 257.1541, found 257.1540.

4.2.5. 2,2-Dicinnamyl-5,5-dimethyl-1,3-cyclohexadione (*4b*)

Yellow crystals. Mp 148–149 °C (chloroform/hexane) (149 °C[61]). IR (KBr) ν: 3447, 2954, 1693 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.95 (s, 6H, $CH_3\times2$), 2.57 (s, 4H, $CH_2\times2$), 2.70 (dd, J=1.2, 7.6 Hz, 4H, $CH_2\times2$), 6.01 (dt, J=7.6, 16.0 Hz, 2H, vinyl H), 6.43 (d, J=16.0 Hz, 2H, vinyl H), 7.18–7.31 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$) δ: 28.7 (CH_3), 30.7 (C), 38.4 (CH_2), 52.3 (CH_2), 68.5 (C), 123.8 (CH), 126.2 (CH), 127.4 (CH), 128.5 (CH), 134.4 (CH), 136.9 (C), 209.0 (C). EIMS *m/z*: 372 (M^+), 354, 336, 321, 299, 281, 263, 255, 243, 225, 220, 207, 205, 199, 179, 167, 154, 142, 128, 117, 115, 105, 92. HRESI-MS calcd for $C_{26}H_{29}O_2$ $[M+1]^+$ 373.2167, found 373.2169.

*4.2.6. 3-Cinnamyl-4-hydroxyquinoline-2(1H)-one (**3c**)*

Yellow crystals. Mp 221–222 °C (methanol/hexane). IR (KBr) ν: 3024, 1602 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.56 (d, J=5.2 Hz, 2H, CH_2), 6.36 (dt, J=5.6, 16.0 Hz, 1H, vinyl H), 6.43 (d, J=16.0 Hz, 1H, vinyl H), 7.10–7.14 (m, 1H, ArH), 7.20–7.35 (m, 6H, ArH), 7.51 (ddd, J=1.6, 7.2, 8.4 Hz, 1H, ArH), 7.99 (dd, J=1.2, 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ: 27.3 (CH_2), 110.0 (C), 116.4 (CH), 117.3 (C), 123.2 (CH), 123.9 (CH), 127.0 (CH), 127.9 (CH), 128.1 (CH), 129.4 (CH), 131.2 (CH), 131.6 (CH), 138.6 (C), 139.2 (C), 160.9 (C), 166.4 (C). EIMS *m/z*: 277 (M^+), 246, 230, 187, 186, 168, 146, 130, 115, 91. HRESI-MS calcd for $C_{18}H_{16}NO_2$ $[M+1]^+$ 278.1181, found 278.1182.

*4.2.7. 3,3-Dicinnamylquinoline-2,4(1H,3H)-dione (**4c**)*

Colorless oil. IR (KBr) ν: 3059, 1659 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.86–2.98 (m, 4H, $CH_2\times2$), 5.99 (dt, J=7.6, 15.6 Hz, 2H, vinyl H), 6.43 (d, J=16.0 Hz, 2H, vinyl H), 6.88 (d, J=8.0 Hz, 1H, ArH), 7.08–7.29 (m, 11H, ArH), 7.42–7.47 (m, 1H, ArH), 7.94 (d, J=8.0 Hz, 1H, ArH), 9.31 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 41.3 (CH_2), 62.3 (C), 116.2 (CH), 119.5 (C), 123.2 (CH), 123.6 (CH), 126.2 (CH), 127.3 (CH), 127.4 (CH), 128.3 (CH), 134.3 (CH), 136.2 (CH), 136.8 (C), 140.7(C), 173.7 (C), 196.5 (C). EIMS *m/z*: 393 (M^+), 378, 364, 316, 302, 277, 276, 258, 248, 230, 219, 203, 186, 176, 175, 157, 146, 129, 117, 115, 91, 77. HRESI-MS calcd for $C_{27}H_{24}NO_2$ $[M+1]^+$ 394.1807, found 394.1809.

*4.2.8. 2,2-Dicinnamyl-2H-phenalene-1,3-dione (**4d**)*

Deep yellow oil. IR (KBr) ν: 2921, 1668 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.97 (d, J=7.6 Hz, 4H, $CH_2\times2$), 6.00 (dt, J=7.6, 15.6 Hz, 2H, vinyl H), 6.40 (d, J=16.0 Hz, 2H, vinyl H), 7.09–7.19 (m, 10H, ArH), 7.72 (t, J=8.0 Hz, 2H, ArH), 8.18 (d, J=8.4 Hz, 2H, ArH), 8.47 (d, J=7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 40.1 (CH_2), 67.2 (C), 124.0 (CH), 126.1 (CH), 126.6 (CH), 127.2 (CH), 127.5 (C), 128.3 (CH), 128.9 (CH), 131.4 (C), 132.9 (C), 134.1 (CH), 134.4 (CH), 137.0 (C), 197.7 (C). EIMS *m/z*: 428 (M^+), 410, 392, 352, 337, 312, 311, 293, 283, 265, 252, 221, 211, 210, 205, 183, 165, 155, 127, 117, 115, 91, 77. HRESI-MS calcd for $C_{31}H_{25}O_2$ $[M+1]^+$ 429.1854, found 429.1851.

*4.2.9. 3-Cinnamyl-4-hydroxy-2H-chromen-2-one (**3g**)*

Yellow crystals. Mp 285–286 °C (methanol/hexane). IR (KBr) ν: 3220, 1668 cm^{-1}. ^1H NMR (CD_3OD) δ: 3.48 (dd, J=1.6, 6.0 Hz, 2H, CH_2), 6.31 (dt, J=6.0, 16.0 Hz, 1H, vinyl H), 6.45 (d, J=16.0 Hz, 1H, vinyl H), 7.10–7.36 (m, 7H, ArH), 7.57–7.61 (m, 1H, ArH), 7.93–7.96 (m, 1H, ArH). ^{13}C NMR (CD_3OD) δ: 27.8 (CH_2), 104.1 (C), 117.4 (CH), 117.8 (C), 124.4 (CH), 125.2 (CH), 127.1 (CH), 128.0 (CH), 129.3 (CH), 129.5 (CH), 131.8 (CH), 133.0 (CH), 138.9 (C), 153.8 (C), 162.8 (C), 166.1 (C). EIMS *m/z*: 278 (M^+), 249, 231, 213, 202, 188, 187, 157, 128, 121, 115, 91, 77. HRESI-MS calcd for $C_{18}H_{15}O_3$ $[M+1]^+$ 279.1021, found 279.1021.

*4.2.10. (4E)-2-Cinnamyl-1-(2-hydroxyphenyl)-5-phenylpent-4-en-1-one (**5**)*

Colorless oil. IR (KBr) ν: 3026, 1632 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.49–2.56 (m, 2H, CH×2), 2.69–2.77 (m, 2H, CH×2), 3.75 (quin, J=6.8 Hz, 1H, CH), 6.14 (dt, J=7.2, 15.6 Hz, 2H, vinyl H), 6.43 (d, J=15.6 Hz, 2H, vinyl H), 6.90 (ddd, J=1.2, 7.2, 8.0 Hz, 1H, ArH), 7.00 (dd, J=1.2, 8.4 Hz, 1H, ArH), 7.17–7.30 (m, 10H, ArH), 7.47 (ddd, J=1.6, 7.2, 8.4 Hz, 1H, ArH), 7.82 (dd, J=1.6, 8.0 Hz, 1H, ArH), 12.55 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 35.3 (CH_2), 45.9 (CH), 118.8 (CH), 118.9 (CH), 119.0 (C), 126.1 (CH), 126.6 (CH), 127.3 (CH), 128.5 (CH), 129.8 (CH), 132.6 (CH), 136.5 (CH), 137.1 (C), 163.1 (C), 208.6 (C). EIMS *m/z*: 368 (M^+), 350, 277, 251, 233, 218, 205, 183, 149, 131, 121, 115, 93, 91. Anal. Calcd for $C_{26}H_{24}O_2\cdot H_2O$: C, 84.75; H, 6.57. Found: C, 84.38; H, 7.00.

*4.2.11. 6-Chloro-3-cinnamyl-4-hydroxy-2H-chromen-2-one (**3h**)*

Brown crystals. Mp 200–201 °C (methanol/hexane). IR (KBr) ν: 3287, 1670 cm^{-1}. ^1H NMR (CD_3OD) δ: 3.47 (dd, J=1.6, 6.0 Hz, 2H, CH_2), 6.30 (dt, J=6.0, 16.0 Hz, 1H, vinyl H), 6.46 (d, J=15.6 Hz, 1H, vinyl H), 7.13–7.17 (m, 1H, ArH), 7.22–7.26 (m, 2H, ArH), 7.30–7.35 (m, 3H, ArH), 7.57 (dd, J=2.4, 8.8 Hz, 1H, ArH), 7.92 (d, J=2.4 Hz, 1H, ArH). ^{13}C NMR (CD_3OD) δ: 28.5 (CH_2), 104.1 (C), 118.2 (CH), 119.8 (C), 123.8 (CH), 126.5 (CH), 127.4 (CH), 127.4 (CH), 128.7 (C), 128.9 (CH), 130.8 (CH), 131.2 (CH), 138.0 (C), 151.7 (C), 161.5 (C), 163.5 (C). EIMS *m/z*: 314 (M^++2), 312 (M^+), 297, 277, 265, 223, 221, 209, 202, 157, 155, 130, 128, 115, 91. HRESI-MS calcd $C_{18}H_{14}O_3Cl$ $[M+1]^+$ 313.0631, found 313.0630.

*4.2.12. (4E)-1-(5-Chloro-2-hydroxyphenyl)-2-cinnamyl-5-phenylpent-4-en-1-one (**6**)*

Colorless oil. IR (KBr) ν: 3026, 1638 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.47–2.54 (m, 2H, CH×2), 2.66–2.73 (m, 2H, CH×2), 3.64 (quin, J=6.8 Hz, 1H, CH), 6.11 (dt, J=7.6, 15.6 Hz, 2H, vinyl H), 6.42 (d, J=15.6 Hz, 2H, vinyl H), 6.93 (d, J=8.0 Hz, 1H, ArH), 7.16–7.30 (m, 10H, ArH), 7.37 (dd, J=2.8, 8.8 Hz, 1H, ArH), 7.75 (d, J=2.8 Hz, 1H, ArH), 12.43 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 35.1 (CH_2), 46.1 (CH), 119.5 (C), 120.4 (CH), 123.6 (C), 126.1 (CH), 126.1 (CH), 127.3 (CH), 128.5 (CH), 129.0 (CH), 132.9 (CH), 136.3 (CH), 136.9 (C), 161.5 (C), 207.8 (C). EIMS *m/z*: 402 (M^+), 386, 384, 311, 287, 285, 267, 243, 232, 217, 204, 180, 157, 155, 143, 129, 117, 115, 99, 91. Anal. Calcd for $C_{26}H_{23}ClO_2$: C, 77.51; H, 5.75. Found: C, 77.57; H, 5.79.

*4.2.13. 5,5-Dicinnamylpyrimidine-2,4,6(1H,3H,5H)-trione (**4i**)*

White crystals. Mp 220–221 °C (methanol/hexane) (226–228 °C[59]). IR (KBr) ν: 3447, 1638 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.88 (dd, J=0.8, 7.6 Hz, 4H, $CH_2\times2$), 6.14 (dt, J=7.6, 15.6 Hz, 2H, vinyl H), 6.53 (d, J=15.6 Hz, 2H, vinyl H), 7.20–7.38 (m, 10H, ArH), 10.42 (br s, 2H, NH×2). ^{13}C NMR ($CDCl_3$) δ: 42.7 (CH_2), 58.0 (C), 123.8 (CH), 127.8

(CH), 129.2 (CH), 130.1 (CH), 136.5 (CH), 138.3 (C), 150.5 (C), 173.2 (C). EIMS *m/z*: 360 (M^+), 342, 324, 282, 269, 243, 232, 220, 219, 205, 183, 180, 179, 170, 155, 143, 142, 129, 117, 115, 91, 77. HRESI-MS calcd for $C_{22}H_{21}N_2O_3$ $[M+1]^+$ 361.1552, found 361.1554.

4.2.14. 1,5,5-Tricinnamylpyrimidine-2,4,6(1H,3H,5H)-trione (**7**)

White crystals. Mp 154–155 °C (chloroform/hexane) (157–158 °C[59]). IR (KBr) *ν*: 3422, 1681 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 2.92 (d, *J*=7.6 Hz, 4H, $CH_2\times2$), 4.56 (d, *J*=6.8 Hz, 2H, CH_2), 5.94 (dt, *J*=7.6, 15.6 Hz, 2H, vinyl H), 6.06 (dt, *J*=6.8, 15.6 Hz, 1H, vinyl H), 6.47 (d, *J*=15.6 Hz, 2H, vinyl H), 6.65 (d, *J*=16.0 Hz, 1H, vinyl H), 7.10–7.23 (m, 15H, ArH), 8.82 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) *δ*: 42.0 (CH_2), 42.9 (CH_2), 57.7 (C), 121.1 (CH), 121.7 (CH), 126.3 (CH), 126.5 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 128.5 (CH), 135.2 (CH), 135.8 (CH), 135.9 (C), 136.1 (C), 149.2 (C), 170.8 (C), 171.1 (C). EIMS *m/z*: 476 (M^+), 461, 398, 385, 359, 299, 271, 258, 243, 232, 219, 218, 205, 180, 167, 155, 141, 129, 118, 115, 91. HRESI-MS calcd for $C_{31}H_{29}N_2O_3$ $[M+1]^+$ 477.2178, found 477.2180.

4.2.15. 1,3,5,5-Tetracinnamylpyrimidine-2,4,6(1H,3H,5H)-trione (**8**)

White crystals. Mp 119–120 °C (chloroform/hexane). IR (KBr) *ν*: 3428, 1680 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 2.95 (dd, *J*=0.8, 7.6 Hz, 4H, $CH_2\times2$), 4.61 (dd, *J*=1.2, 6.8 Hz, 4H, $NCH_2\times2$), 5.90 (dt, *J*=7.6, 15.6 Hz, 2H, vinyl H), 6.09 (dt, *J*=6.8, 16.0 Hz, 2H, vinyl H), 6.43 (d, *J*=16.0 Hz, 2H, vinyl H), 6.66 (d, *J*=16.0 Hz, 2H, vinyl H), 7.06–7.24 (m, 20H, ArH). ^{13}C NMR ($CDCl_3$) *δ*: 42.6 (CH_2), 43.6 (CH_2), 57.7 (C), 121.4 (CH), 122.1 (CH), 126.2 (CH), 126.6 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 128.5 (CH), 135.0 (CH), 135.6 (CH), 136.1 (C), 136.1 (C), 150.0 (C), 170.6 (C). EIMS *m/z*: 592 (M^+), 574, 488, 475, 432, 404, 371, 314, 271, 257, 243, 229, 218, 212, 181, 158, 142, 130, 119, 118, 115, 91. HRESI-MS calcd for $C_{40}H_{37}N_2O_3$ $[M+1]^+$ 593.2804, found: 593.2801.

4.2.16. 5,5-Dicinnamyl-2,2-dimethyl-1,3-dioxane-4,6-dione (**4e**)

White crystals. Mp 121–122 °C (chloroform/hexane) (131 °C[59]). IR (KBr) *ν*: 2913, 1742, 1695 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 1.51 (s, 6H, $CH_3\times2$), 2.95 (d, *J*=8.0 Hz, 4H, $CH_2\times2$), 6.08 (dt, *J*=8.0, 15.6 Hz, 2H, vinyl H), 6.53 (d, *J*=15.6 Hz, 2H, vinyl H), 7.19–7.32 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$) *δ*: 29.6 (CH_3), 41.9 (CH_2), 56.1 (C), 105.8 (C), 121.6 (CH), 126.2 (CH), 127.8 (CH), 128.5 (CH), 137.8 (CH), 136.0 (C), 168.5 (C). EIMS *m/z*: 376 (M^+), 359, 341, 319, 301, 290, 273, 255, 244, 217, 206, 205, 199, 181, 167, 155, 141, 129, 117, 115, 104, 91, 77. HRESI-MS calcd for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ 399.1572, found 399.1573.

4.2.17. 3,3-Dicinnamyl-3H,5H-furan-2,4-dione (**4f**)

White crystals. Mp 99–100 °C (chloroform/hexane) (99–100 °C[59]). IR (KBr) *ν*: 2911, 1693 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 2.66–2.75 (m, 4H, $CH_2\times2$), 4.34 (s, 2H, CH_2), 6.02 (dt, *J*=7.6, 15.6 Hz, 2H, vinyl H), 6.49 (d, *J*=15.6 Hz, 2H, vinyl H), 7.20–7.32 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$) *δ*: 38.3 (CH_2), 54.5 (C), 73.2 (CH_2), 120.7 (CH), 126.3 (CH), 128.0 (CH), 128.6 (CH), 136.0 (CH), 136.1 (C), 175.9 (C), 210.2 (C). EIMS *m/z*: 332 (M^+), 304, 286, 241, 223, 219, 205, 192, 181, 167, 155, 141, 129, 118, 115, 91, 77. HRESI-MS calcd for $C_{22}H_{21}O_3$ $[M+1]^+$ 333.1491, found 333.1494.

4.2.18. 2-(But-2-enyl)cyclohexane-1,3-dione (**10**)

White crystals. Mp 112–113 °C (chloroform/hexane). IR (KBr) *ν*: 3403, 2942, 1602 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 1.67 (dq, *J*=1.6, 6.4 Hz, 3H, CH_3), 1.96 (quin, *J*=6.4 Hz, 2H, CH_2), 2.42 (t, *J*=6.0 Hz, 4H, $CH_2\times2$), 3.07 (d, *J*=6.4 Hz, 2H, CH_2), 5.48 (dtq, *J*=1.6, 6.4, 15.2 Hz, 1H, vinyl H), 5.65 (dtq, *J*=1.6, 6.4, 15.2 Hz, 1H, vinyl H). ^{13}C NMR ($CDCl_3$) *δ*: 17.8 (CH_3), 20.6 (CH_2), 25.1 (CH_2), 26.3 (CH_2), 113.3 (C), 127.4 (CH), 129.1 (CH), 175.3 (C), 204.6 (C). EIMS *m/z*: 166 (M^+), 151, 149, 137, 123, 110, 96, 91, 79, 77. HRESI-MS calcd for $C_{10}H_{15}O_2$ $[M+1]^+$ 167.1072, found 167.1072.

4.2.19. 2-(2-Cyclohexen-1-yl)cyclohexane-1,3-dione (**14**)

White crystals. Mp 124–126 °C (chloroform/hexane) (138–139 °C[59]). IR (KBr) *ν*: 3385, 2931, 1602 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 1.33–1.42 (m, 1H), 1.59–2.05 (m, 5H), 2.08–2.14 (m, 2H, CH_2), 2.34–2.45 (m, 4H, $CH_2\times2$), 3.68–3.73 (m, 1H, CH), 3.82 (ddt, *J*=2.4, 2.8, 10.0 Hz, 1H, vinyl H), 6.11 (ddt, *J*=2.4, 3.6, 10.0 Hz, 1H, vinyl H), 7.28 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$) *δ*: 20.6 (CH_2), 21.5 (CH_2), 25.0 (CH_2), 28.2 (CH_2), 29.2 (CH_2), 30.4 (CH), 36.5 (CH_2), 118.2 (C), 130.6 (CH), 132.7 (CH), 172.7 (C), 197.7 (C). EIMS *m/z*: 192 (M^+), 177, 164, 136, 121, 109, 91, 79, 77. HRESI-MS calcd for $C_{12}H_{17}O_2$ $[M+1]^+$ 193.1228, found 193.1227.

4.2.20. 2-(Hex-2-enyl)cyclohexane-1,3-dione (**11**)

Light brown oil. IR (KBr) *ν*: 3447, 2956, 1617 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 0.89 (t, *J*=7.2 Hz, 3H, CH_3), 1.38 (sextet, *J*=7.2 Hz, 2H, CH_2), 1.90–2.03 (m, 4H, $CH_2\times2$), 2.43 (t, *J*=6.4 Hz, 4H, $CH_2\times2$), 3.10 (d, *J*=6.8 Hz, 2H, CH_2), 5.46 (dtt, *J*=1.6, 6.8, 15.2 Hz, 1H, vinyl H), 5.67 (dtt, *J*=1.6, 6.8, 15.2 Hz, 1H, vinyl H). ^{13}C NMR ($CDCl_3$) *δ*: 13.6 (CH_3), 20.6 (CH_2), 22.4 (CH_2), 25.2 (CH_2), 26.4 (CH_2), 34.4 (CH_2), 113.1 (C), 128.1 (CH), 133.1 (CH), 179.8 (C), 204.6 (C). EIMS *m/z*: 194 (M^+), 179, 165, 152, 137, 123, 113, 109, 95, 91, 79, 77. HRESI-MS calcd for $C_{12}H_{19}O_2$ $[M+1]^+$ 195.1385, found 195.1385.

4.2.21. 2-(3-Methylbut-2-enyl)cyclohexane-1,3-dione (**12**)

White crystals. Mp 125–127 °C (chloroform/hexane). IR (KBr) *ν*: 3421, 2939, 1610 cm^{-1}. ^1H NMR ($CDCl_3$) *δ*: 1.71 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.95 (quin, *J*=6.8 Hz, 2H, CH_2), 2.44 (t, *J*=6.8 Hz, 4H, $CH_2\times2$), 3.04 (d, *J*=7.2 Hz, 2H, CH_2), 5.13–5.17 (m, 1H, vinyl H), 6.10 (br s, 1H, OH). ^{13}C NMR ($CDCl_3$) *δ*: 17.4 (CH_3), 20.7 (CH_2), 21.1 (CH_2),

22.1 (CH_2), 25.7 (CH_3), 114.7 (C), 122.2 (CH), 133.9 (C), 186.5 (C), 204.9 (C). EIMS *m/z*: 180 (M^+), 165, 162, 151, 147, 137, 125, 118, 110, 95, 92, 81, 79, 77. HRESI-MS calcd for $C_{11}H_{17}O_2$ $[M+1]^+$ 181.1228, found 181.1227.

*4.2.22. 2-((2E,6E)-3,7-Dimethylocta-2,6-dienyl)cyclohexane-1,3-dione (**13**)*

White crystals. Mp 94–96 °C (chloroform/hexane). IR (KBr) ν: 3430, 2921, 1565 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.59 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.95 (quin, J=6.4 Hz, 2H, CH_2), 2.01–2.13 (m, 4H, $CH_2\times2$), 2.37–2.46 (m, 4H, $CH_2\times2$), 3.07 (d, J=7.6 Hz, 2H, CH_2), 5.02–5.08 (m, 1H, vinyl H), 5.19 (tq, J=1.2, 7.2 Hz, 1H, vinyl H). ^{13}C NMR ($CDCl_3$) δ: 16.1 (CH_3), 17.7 (CH_3), 20.6 (CH_2), 21.1 (CH_2), 25.6 (CH_3), 26.3 (CH_2), 39.6 (CH_2), 39.8 (CH_2), 114.1 (C), 122.0 (CH), 123.7 (CH), 132.0 (C), 137.3 (C), 138.8 (C), 205.0 (C). EIMS *m/z*: 248 (M^+), 233, 215, 205, 187, 178, 163, 149, 137, 121, 107, 91, 81, 79, 77. HRESI-MS calcd for $C_{16}H_{25}O_2$ $[M+1]^+$ 249.1854, found 249.1853.

*4.2.23. 3-Hydroxy-2-((E)-1,3-diphenylallyl)cyclohex-2-enone (**9**)*

Light yellow oil. IR (KBr) ν: 3447, 1581 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.81 (quin, J=6.4 Hz, 2H, CH_2), 2.32 (t, J=6.4 Hz, 4H, $CH_2\times2$), 5.15 (d, J=8.4 Hz, 1H, CH), 6.43 (d, J=15.6 Hz, 1H, vinyl H), 6.87 (dd, J=8.4, 15.6 Hz, 1H, vinyl H), 7.11–7.15 (m, 2H, ArH), 7.23 (t, J=7.6 Hz, 2H, ArH), 7.25 (t, J=7.6 Hz, 2H, ArH), 7.28 (d, J=7.6 Hz, 2H, ArH), 7.36 (d, J=7.6 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.5 (CH_2), 33.0 (CH_2), 42.2 (CH), 117.5 (C), 125.7 (CH), 126.1 (CH), 127.0 (CH), 127.5 (CH), 127.9 (CH), 128.3 (CH), 130.8 (CH), 130.9 (CH), 137.5 (C), 143.1 (C), 171.3 (C), 187.2 (C). EIMS *m/z*: 304 (M^+), 281, 267, 213, 186, 167, 157, 141, 129, 115, 105, 91, 77. HRESI-MS calcd for $C_{21}H_{21}O_2$ $[M+1]^+$ 305.1541, found 305.1539.

Acknowledgements

We gratefully acknowledge the National Science Council of the Republic of China for financial support.

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