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Gold- and silver-catalyzed allylic alkylation of 1,3-dicarbonyl compounds with allylic alcohols

Prasath Kothandaraman, Weidong Rao, Xiaoxiang Zhang, Philip Wai Hong Chan *

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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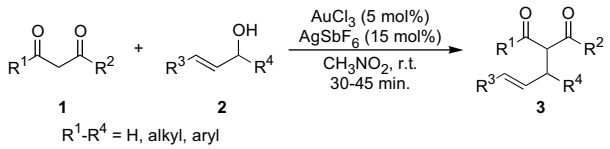
ABSTRACT

A highly efficient gold- and silver-catalyzed allylic alkylation of 1,3-dicarbonyl compounds with allylic alcohols has been developed. The reaction was shown to proceed expediently for a wide variety of 1,3-dicarbonyl compounds and allylic alcohols, including 1° and terminal ones, under very mild conditions at room temperature in good to excellent yields (55–96%).

1. Introduction

Allylic alkylations of 1,3-dicarbonyl compounds are an important type of carbon–carbon bond formation reaction that provide a convenient strategy for the construction of complex molecular structures from simple building blocks.[1] Generally, the reactions have relied on the use of preformed electrophiles such as allylic halides, carbonates, acetates, triflates, and related compounds with good leaving group ability. However, with the recent shift in green chemistry toward developing new methods that make use of inexpensive and readily available electrophiles that follow the principles of atom-economy,[2] the establishing of alternative allylic alkylation strategies has been actively pursued.[3–13] One such strategy has been the use of allylic alcohols as the allylating reagent in the presence of Pd, Co, and Cu salts as the catalyst.[4] More recently, Lewis and Brønsted acids such as $BF_3{\cdot}OEt_2$,[5] $InCl_3$,[6] $FeCl_3$,[7] LnOTf (Ln=La, Yb, Sc, Hf),[8] $Bi(OTf)_3$,[9] *p*-toluenesulfonic acid,[10] molecular iodine,[11] and H-Montmorillonite[12] have also been reported to catalyze these reactions. Although shown to be efficient, producing H_2O as the only side product, catalytic systems that can mediate allylic alkylation of 1,3-dicarbonyl compounds with a broad range of allylic alcohols have remained sparse. In this regard, we envisioned that gold catalysis would form the basis for developing a new approach for allylic alkylations of 1,3-dicarbonyl compounds with allylic alcohols irrespective of the nature of the pre-electrophile.

Gold complexes have emerged as an efficient and versatile class of Lewis acid catalysts for a wide variety of stereoselective C–X (X=C, N, O, S) bond formations.[13–19] While much of the current works have focused on the interaction of the gold catalyst with the π-bonds of alkenes, alkynes, and allenes, their applications to reactions with other functional groups have also gathered momentum in recent years. A notable example is that by Campagne and co-workers who reported the propargylation of allylsilanes with propargylic alcohols in the presence of $HAuCl_4{\cdot}2H_2O$ as catalyst could be accomplished in good to excellent yields and selectivity.[14] Following this seminal work, we[15] and the respective groups of Beller[16] and Dyker[17] reported similar efficient approaches for Friedel–Crafts allylic alkylations, benzylations, and propargylations of aromatic compounds with allylic, propargylic, and benzylic alcohols. Methods for the allylic alkylation, benzylation and propargylation of anilines, azides and sulfonamides with allylic, benzylic and propargylic alcohols that make use of gold catalysis have also been recently communicated.[18] To our knowledge, however, a gold-catalyzed protocol for the allylic alkylation of 1,3-dicarbonyl compounds with allylic alcohols is not known. As part of an ongoing program examining the utility of alcohols as building blocks in organic synthesis,[20] we report herein the allylic alkylation of 1,3-dicarbonyl compounds with allylic alcohols catalyzed by $AuCl_3$ with $AgSbF_6$ as a co-catalyst (Scheme 1). The reactions were shown to proceed smoothly in good to excellent product yields up to 96% for a wide variety of starting materials under mild conditions at room temperature.



Scheme 1.

* Corresponding author. Tel.: +65 6316 8760; fax: +65 6791 1961.
E-mail address: waihong@ntu.edu.sg (P.W.H. Chan).

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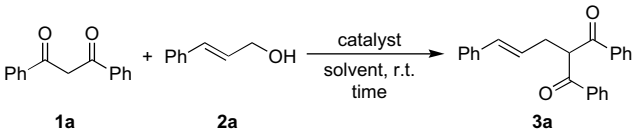
Table 1
Optimization of the reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Time (h)	Yield[b] (%)
1	$AuCl_3/AgSbF_6$	$MeNO_2$	0.5	84
2	$AuCl_3/AgSbF_6$	CH_2Cl_2	3	58
3	$AuCl_3/AgSbF_6$	MeCN	16	15
4	$AuCl_3/AgSbF_6$	1,4-Dioxane	16	32
5	$AuCl_3/AgSbF_6$	C_6H_6	18	23
6	$AuCl_3/AgSbF_6$	PhMe	18	12
7	$AuCl_3$/AgOTf	$MeNO_2$	0.5	75
8	AuCl/AgOTf	$MeNO_2$	0.5	72
9	Ph_3PAuCl/AgOTf	$MeNO_2$	24	—[c]
10	$AuCl_3$	$MeNO_2$	16	28
11	AuCl	$MeNO_2$	18	26
12	Ph_3PAuCl	$MeNO_2$	24	—[c]
13	$AgSbF_6$	$MeNO_2$	24	29
14	$Cu(OTf)_2$	$MeNO_2$	0.5	62
15	$In(OTf)_3$	$MeNO_2$	24	64
16	$ZnCl_2$	$MeNO_2$	24	25
17	TFA	$MeNO_2$	16	47
18	*p*-TsOH·H_2O	$MeNO_2$	0.5	68
19	H_2SO_4	$MeNO_2$	16	45
20	TfOH	$MeNO_2$	24	20
21	HCl	$MeNO_2$	24	22

[a] All reactions were performed at room temperature with catalyst/**1a**/**2a** ratio=1:80:20.
[b] Isolated yield.
[c] No reaction.

2. Results and discussion

At the outset of this study, we purposely chose to focus our attention to develop a catalytic system that would effect allylic alkylations of 1,3-dicarbonyl compounds with less reactive primary allylic alcohols. With this in mind, we chose to examine the allylic alkylation of 1,3-diphenylpropane-1,3-dione **1a** with (*E*)-3-phenylprop-2-en-1-ol **2a** as the model substrates to establish the reaction conditions (Table 1). This revealed treatment of 4 equiv of **1a** with **2a** (1 equiv) and 5 mol % of $AuCl_3$ and 15 mol % of $AgSbF_6$ as catalyst in CH_3NO_2 at room temperature for 0.5 h gave the best result. Under these conditions, 2-cinnamyl-1,3-diphenylpropane-1,3-dione **3a** was furnished in 84% yield (entry 1) that was comparable to those obtained with other catalytic systems previously reported for this reaction.[21] Retention of trans-stereochemistry in the allylated product, which was afforded as a single regioisomer, was also confirmed by comparison with NOE spectroscopic data obtained for closely related adducts (see below) and known literature data.[11] A lower product yield of 58%, on the other hand, was obtained when the reaction was repeated with CH_2Cl_2 instead of $MeNO_2$ as the solvent (entry 2). In contrast, the analogous reactions conducted in other polar solvents such as MeCN and 1,4-dioxane were less effective and gave markedly lower product yields of 15 and 32%, respectively (entries 3 and 4). Significantly lower product yields of 12 and 23% were also found for the respective reactions in non-polar solvents C_6H_6 and PhMe (entries 5 and 6). Examination of other different gold and silver combinations revealed that changing the silver source to AgOTf or switching the gold catalyst from $AuCl_3$ to AuCl gave **3a** in lower yields of 72–75% (entries 7 and 8). A similar outcome was found when reactions employing other single metal Lewis acid or Brønsted catalysts were examined. In our hands, while reactions with either $Cu(OTf)_2$ or $In(OTf)_3$ as catalyst gave low product yields of 62–64%, those mediated by AuCl, $AuCl_3$, $AgSbF_6$ or $ZnCl_2$ afforded **3a** in yields of 29% or less (entries 10–16). Notably, the low catalytic activity observed for the analogous $AgSbF_6$-catalyzed reaction also provided evidence that the cationic Au(III) complex was the active species (entry 13). In addition, the only Lewis acid catalysts that were found to lead to no reaction on the basis of TLC analysis was Ph_3PAuCl or Ph_3PAuCl in combination with AgOTf (entries 9 and 12). In the case of a survey of reactions catalyzed by Brønsted acids, only those mediated by *p*-TsOH·H_2O, TFA, or H_2SO_4 were found to give **3a** in moderate to good yields of 45–68% (entries 17–19). In the latter two cases, however, extended reaction times of 16 and 24 h were required. In contrast, much lower product yields of 20–22% could only be accomplished for the analogous reactions catalyzed by TfOH or HCl even after increasing reaction times to 24 h (entries 20 and 21).

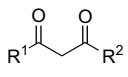
To define the scope of the $AuCl_3/AgSbF_6$-catalyzed reactions, we applied this process to a series of substituted 1,3-dicarbonyl compounds **1a**–**e** and allylic alcohols **2a**–**j** (Table 2). This revealed the allylic alkylation of **1a** with primary allylic alcohols bearing either an electron-withdrawing or electron-donating group proceeded in excellent yields (entries 1–3). Similarly, the analogous reaction of other 1,3-dicarbonyl compounds with electron-rich and electron-deficient 2° allylic alcohols afforded the corresponding allylated adducts in yields of 55–93% (entries 4–11). Notably, this included the allylic alkylation of less acidic β-ketoesters **1c** and **1d** with **2f** or **2g**, which gave **3f**–**g** and **3k**–**l** in excellent yields (entries 5 and 6 and 10 and 11). Likewise, we were pleased to find allylic alkylations **1a** with less reactive terminal allylic alcohols **2h**–**j** proceeded well and gave the corresponding products **3m**–**o** in excellent yields of 82–86% (entries 12–14). The allylated products **3m** and **3n** were also obtained as single regioisomers on the basis of NOE measurements of these adducts (see Supplementary data for details). The present procedure was also shown to work well for the allylic alkylation of cyclic 1,3-diketone **1e** with **2g**, giving **3h** in good yield as its enol ether (entry 7). Similarly, 1,5-diene alcohol **2k** was found to be good allylating source, affording the product in 70% yield (entry 15). However, poor regioselectivities were found for reactions with allylic alcohols containing two different substituents such as an aryl and alkyl group as in **2l** and **2m** (entries 16 and 18). In each of these reactions, the corresponding allylated products were furnished in good to excellent yields but also as inseparable mixture of regioisomers. The allylic alkylation of **1b** with **2l** was the only instance where product **3r** was furnished as a single regioisomer in 83% yield (entry 17), which is consistent with our earlier findings for reactions with 1° and terminal allylic alcohols.

Although the above experimental results do not provide a clear perspective on the mechanism of the present procedure, we tentatively propose the reaction to proceed in a manner similar to that put forward by us[11] and Campagne.[14] This could involve combination of the gold and silver catalyst to give a more electrophilic Au(III) complex as postulated by Li and co-workers.[19] This newly formed active species subsequently activates the allylic alcohol thereby making the hydroxyl group a better leaving group. The regioselectivities obtained in these reactions may be due to subsequent attack at the sterically less hindered carbon center of this presumed activated intermediate.

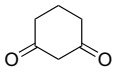
3. Conclusion

In summary, we have demonstrated a practical and straightforward method for the allylic alkylation of 1,3-dicarbonyl compounds under mild conditions at room temperature that proceeded in good to excellent yields. The present protocol is applicable to a variety of 1,3-dicarbonyl compounds and allylic alcohols containing electron-withdrawing and electron-donating, and sterically demanding substrate combinations. The reactivity of gold catalysis to mediate this useful carbon–carbon bond formation was

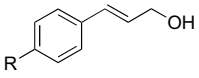
Table 2
$AuCl_3/AgSbF_6$-catalyzed allylic alkylation of 1,3-dicarbonyl compounds **1a–e** with allylic alcohols **2a–m**[a]



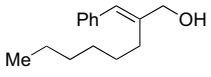
1b, $R^1 = R^2 = Me$
1c, $R^1 = Me$, $R^2 = OEt$
1d, $R^1 = Ph$, $R^2 = OEt$



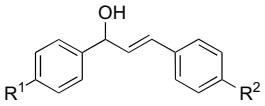
1e



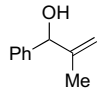
2b, R = Br
2c, R = Me



2d

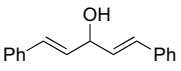


2e, $R^1 = R^2 = H$
2f, $R^1 = R^2 = Br$
2g, $R^1 = R^2 = Me$

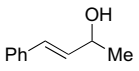


2h

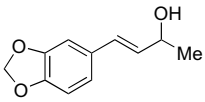
2i, R = Me
2j, R = Ph



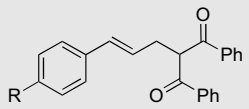
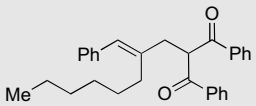
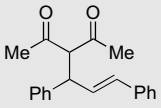
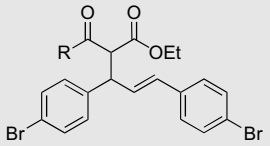
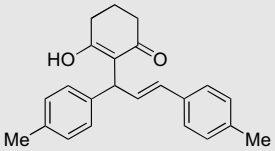
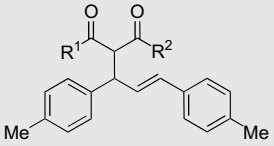
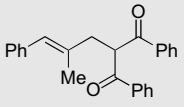
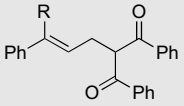
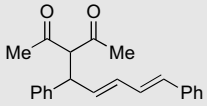
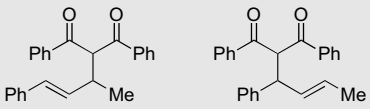
2k



2l

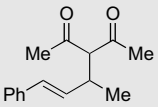
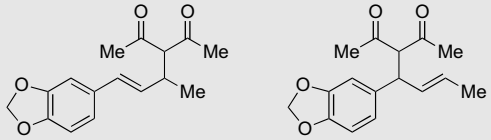


2m

Entry	Substrates	Time (h)	Product		Yield[b] (%)
1	**1a**+**2b**	0.75		**3b**, R=Br	79
2	**1a**+**2c**	0.5		**3c**, R=Me	83
3	**1a**+**2d**	0.5		**3d**	96
4	**1b**+**2e**	0.5		**3e**	91
5	**1c**+**2f**	0.75		**3f**, R=Me	87[c]
6	**1d**+**2f**	0.75		**3g**, R=Ph	87[d]
7	**1e**+**2g**	0.75		**3h**	82
8	**1a**+**2g**	0.5		**3i**, R^1=R^2=Ph	91
9	**1b**+**2g**	0.5		**3j**, R^1=R^2=Me	93
10	**1c**+**2g**	0.5		**3k**, R^1=Me, R^2=OEt	93[c]
11	**1d**+**2g**	0.5		**3l**, R^1=Ph, R^2=OEt	91[c]
12	**1a**+**2h**	0.5		**3m**	86
13	**1a**+**2i**	0.5		**3n**, R=Me	82
14	**1a**+**2j**	0.5		**3o**, R=Ph	86
15	**1b**+**2k**	0.5		**3p**	70
16	**1a**+**2l**	0.5		**3q**	87[e]

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrates	Time (h)	Product		Yield[b] (%)
17	**1b**+**2l**	0.5		**3r**	83
18	**1b**+**2m**	0.5		**3s**	55[f]

[a] All reactions were performed at room temperature with $AuCl_3/AgSbF_6$/**1a**/**2a** ratio=1:3:80:20.
[b] Isolated yield.
[c] Isolated as an inseparable mixture of diastereomers in a ratio=1:1.
[d] Isolated as an inseparable mixture of diastereomers in a ratio=3:1.
[e] Isolated as an inseparable mixture of regioisomers in a ratio=3:1.
[f] Isolated as an inseparable mixture of regioisomers, the ratio of which could not be determined by ^{1}H NMR analysis due to overlapping peaks.

exemplified by short reaction times and high product yields obtained for reactions with 1° and terminal allylic alcohols. The superior catalytic activity exhibited by the present $AuCl_3/AgSbF_6$-mediated method may also provide an explanation for the poor regioselectivities observed.

4. Experimental

4.1. General remarks

All reactions were performed under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using Merck 60 F_{254} precoated silica gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 and a gradient solvent system (EtOAc/*n*-hexane as eluant). Unless otherwise stated, ^{1}H and ^{13}C NMR spectra were measured on Bruker Avance 400 MHz spectrometer. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Infrared spectra were recorded on Shimadzu IR Prestige-21 FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. Low resolution mass spectra were determined on a Finnigan LCQ XP MAX mass spectrometer. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT95XP LC/HRMS mass spectrometer.

4.2. General procedure for optimizing the Lewis and Brønsted acid-catalyzed allylic alkylation of 1a with 2a

To a solution of $MeNO_2$ (2 mL) containing the Lewis or Brønsted acid catalyst (5 mol %) under an argon atmosphere was added **2a** (0.3 mmol), followed by the slow addition of **1a** (1.2 mmol) dissolved in $MeNO_2$ (2 mL). The mixture was stirred at room temperature and monitored by TLC analysis. On completion, the reaction mixture was filtered through Celite® and washed with EtOAc (15 mL). The organic solvent was removed under reduced pressure and the resultant residue obtained was subjected to purification by flash column chromatography to give **3a**.

4.3. General procedure for $AuCl_3/AgSbF_6$-catalyzed allylic alkylation of 1,3-dicarbonyl compounds 1a–e with allylic alcohols 2a–m

To a solution of $MeNO_2$ (2 mL) containing $AuCl_3$ (5 mol %), $AgSbF_6$ (15 mol %) under an argon atmosphere was added **2** (0.3 mmol), followed by the slow addition of **1** (1.2 mmol) dissolved in $MeNO_2$ (2 mL). The mixture was stirred at room temperature and monitored by TLC analysis. On completion, the reaction mixture was filtered through Celite® and washed with EtOAc (15 mL). The organic solvent was removed under reduced pressure and the resultant residue obtained was subjected to purification by flash column chromatography to give the title compound **3**.

*4.3.1. 2-Cinnamyl-1,3-diphenylpropane-1,3-dione (**3a**)*[4e,9,22]

Yellow solid; yield: 84%; ^{1}H NMR δ 7.98 (m, 4H), 7.54 (m, 2H), 7.43 (m, 4H), 7.23 (m, 5H), 6.48 (d, 1H, *J*=15.6 Hz), 6.21 (m, 1H), 5.34 (t, 1H, *J*=6.7 Hz), 3.0 (t, 2H, *J*=6.8 Hz); ^{13}C NMR δ 195.6, 137.0, 136.0, 133.6, 132.5, 129.0, 128.6, 128.5, 127.4, 126.8, 126.2, 57.1, 33.0; MS (ESI) *m*/*z* 363 $[M+Na]^+$, 341 $[M+H]^+$.

*4.3.2. 2-(4-Bromocinnamyl)-1,3-diphenylpropane-1,3-dione (**3b**)*

Colorless oil; yield: 79%; ^{1}H NMR δ 7.98 (m, 4H), 7.58 (m, 2H), 7.46 (m, 4H), 7.38 (d, 2H, *J*=8.4 Hz), 7.12 (d, 2H, *J*=8.6 Hz), 6.39 (d, 1H, *J*=16.0 Hz), 6.22 (m, 1H), 5.35 (t, 1H, *J*=6.8 Hz), 3.0 (t, 2H, *J*=6.4 Hz); ^{13}C NMR δ 195.5, 136.0, 135.9, 133.7, 131.5, 131.3, 129.0, 128.6, 127.7, 127.6, 121.0, 57.0, 32.9; IR (neat, cm^{-1}) 3062, 2926, 1694, 1668, 1596, 1486, 1447, 1271, 1071, 616; HRMS (ESI) calcd for $C_{24}H_{19}O_2BrNa$: 441.0466, found: 441.0484.

*4.3.3. 2-(4-Methylcinnamyl)-1,3-diphenylpropane-1,3-dione (**3c**)*

Colorless oil; yield: 83%; ^{1}H NMR δ 7.99 (m, 4H), 7.57 (m, 2H), 7.46 (m, 4H), 7.17 (d, 2H, *J*=8.0 Hz), 7.07 (d, 2H, *J*=8.2 Hz), 6.44 (d, 1H, *J*=15.6 Hz), 6.17 (m, 1H), 5.35 (t, 1H, *J*=6.4 Hz), 3.01 (t, 2H, *J*=6.8 Hz), 2.32 (s, 3H); ^{13}C NMR δ 195.5, 137.1, 135.9, 134.2, 133.6, 132.3, 129.1, 128.94, 128.8, 128.6, 126.0, 125.7, 57.2, 33.02, 21.17; IR (neat, cm^{-1}) 3024, 2921, 2855, 1685, 1597, 1513, 1448, 1201, 967, 689; HRMS (ESI) calcd for $C_{25}H_{22}O_2Na$: 377.1517, found: 377.1509.

*4.3.4. (E)-2-(2-Benzylideneoctyl)-1,3-diphenylpropane-1,3-dione (**3d**)*

Colorless oil; yield: 96%; ^{1}H NMR (300 MHz) δ 7.98 (m, 4H), 7.54 (m, 2H), 7.42 (m, 4H), 7.22 (m, 3H), 7.01 (d, 2H, *J*=7.2 Hz), 6.24 (s, 1H), 5.46 (t, 1H, *J*=6.6 Hz), 3.02 (d, 2H, *J*=5.7 Hz), 2.16 (t, 2H, *J*=8.4 Hz), 1.42 (m, 2H), 1.22 (m, 6H), 0.82 (t, 3H, *J*=6.3 Hz); ^{13}C NMR δ 195.7, 162.3, 139.9, 137.7, 136.2, 133.5, 128.9, 128.6, 128.5, 128.0, 127.5, 126.2, 56.1, 36.2, 31.5, 30.9, 29.3, 28.2, 22.5, 14.0; IR (neat, cm^{-1}) 3062, 2926, 1693,1676, 1447, 1268, 665; HRMS (ESI) calcd for $C_{30}H_{32}O_2Na$: 447.2300, found: 447.2287.

*4.3.5. (E)-3-(1,3-Diphenylallyl)pentane-2,4-dione (**3e**)*[23]

White solid; yield: 91%; ^{1}H NMR δ 7.20 (m, 10H), 6.40 (d, 1H, *J*=15.8 Hz), 6.16 (m, 1H), 4.28 (m, 2H), 2.24 (s, 3H), 1.92 (s, 3H); ^{13}C

NMR δ 202.8, 202.7, 200.1, 136.5, 131.6, 129.2, 129.0, 128.5, 128.4, 128.4, 127.9, 127.7, 127.2, 126.3, 126.9, 74.5, 49.1, 30.0, 29.7; MS (ESI) *m*/*z* 315 $[M+Na]^+$, 293 $[M+H]^+$.

4.3.6. (E)-Ethyl-2-acetyl-3,5-bis(4-bromophenyl)pent-4-enoate (**3f**)

White solid; yield 87%; mp 79–81 °C; ^{1}H NMR δ 7.42 (m, 8H), 7.13 (m, 8H), 6.38–6.14 (m, 4H), 4.22 (q, 2H, *J*=8.2 Hz), 4.16 (q, 2H, *J*=7.15 Hz), 4.05 (q, 2H, *J*=6.04 Hz), 3.93 (q, 4H, *J*=7.12 Hz), 2.27 (s, 3H), 2.06 (s, 3H), 1.18 (t, 3H, *J*=7.1 Hz), 1.0 (t, 3H, *J*=7.1 Hz); ^{13}C NMR δ 201.1, 200.7, 167.6, 167.2, 139.1, 139.1, 135.5, 135.3, 132.0, 131.8, 131.6, 131.1, 130.8, 129.7, 129.6, 129.5, 127.9, 127.8, 121.5, 121.1, 121.0, 65.0, 64.9, 61.8, 61.6, 48.0, 47.8, 30.0, 29.9, 14.1, 13.8; IR (neat, cm^{-1}) 2981, 1741, 1710, 1487, 1246, 1010; HRMS (ESI) calcd for $C_{21}H_{20}O_3Br_2Na$: 500.9677, found: 500.9682.

4.3.7. (E)-Ethyl-2-benzoyl-3,5-bis(4-bromophenyl)pent-4-enoate (**3g**)

White solid; yield 87%; mp 118–121 °C; ^{1}H NMR δ 7.93 (m, 2H), 7.91 (m, 1H), 7.50 (m, 6H), 7.33 (m, 6H), 6.99 (m, 2H), 6.12 (m, 2H), 4.93 (d, 1H, *J*=10.8 Hz), 4.52 (m, 1H), 4.10 (m, 1H), 3.89 (m, 2H), 1.11 (t, 1H, *J*=6.9 Hz), 0.93 (t, 3H, *J*=6.9 Hz); ^{13}C NMR δ 192.8, 192.1, 167.7, 167.2, 139.7, 139.1, 136.6, 136.3, 135.6, 135.5, 133.8, 133.7, 131.8, 131.8, 131.6, 131.4, 131.0, 130.9, 130.1, 130.0, 129.8, 129.6, 128.8, 128.7, 128.5, 127.8, 121.4, 121.3, 121.1, 120.8, 61.8, 61.6, 59.5, 59.3, 48.2, 48.1, 14.1, 13.7; IR (neat, cm^{-1}) 3064, 2980, 1720, 1678, 1487, 1259, 1010; HRMS (ESI) calcd for $C_{26}H_{22}O_3Br_2Na$: 562.9833, found: 562.9830.

4.3.8. (E)-2-(1,3-Di-p-tolylallyl)-3-hydroxycyclohex-2-enone (**3h**)

Colorless oil; yield 82%; ^{1}H NMR (300 MHz) δ 7.28 (m, 3H), 7.11 (m, 5H), 6.54 (dd, 1H, *J*=16.2, 6.3 Hz), 6.32 (d, 1H, *J*=14.4 Hz), 5.29 (d, 1H, *J*=6.3 Hz), 2.53 (t, 2H, *J*=6.3 Hz), 2.44 (t, 2H, *J*=6.9 Hz), 2.38 (s, 6H), 2.02 (m, 2H); ^{13}C NMR δ 197.2, 172.3, 162.3, 137.9, 137.5, 136.6, 133.8, 132.3, 129.7, 129.4, 129.2, 129.1, 129.0, 127.9, 126.3, 117.1, 40.8, 36.5, 29.4, 21.1, 21.0, 20.6; IR (neat, cm^{-1}) 3023, 2947, 2922, 2871, 1605, 1378, 1268, 1178; HRMS (ESI) calcd for $C_{23}H_{25}O_2$: 333.1855, found: 333.1842.

4.3.9. (E)-2-(1,3-Di-p-tolylallyl)-1,3-diphenylpropane-1,3-dione (**3i**)

White solid; yield: 91%; mp 159–163 °C; ^{1}H NMR (300 MHz) δ 7.98 (m, 2H), 7.82 (m, 2H), 7.52 (m, 1H), 7.46 (m, 3H), 7.32 (m, 2H), 7.20 (d, 2H, *J*=10.8 Hz), 7.01 (d, 2H, *J*=10.4 Hz), 6.96 (m, 4H), 6.19 (m, 2H), 5.89 (d, 1H, *J*=6.8 Hz), 4.77 (m, 1H), 2.25 (s, 3H), 2.23 (s, 3H); ^{13}C NMR δ 194.6, 193.8, 138.0, 137.3, 137.0, 136.9, 136.3, 134.1, 133.3, 133.1, 131.5, 129.3, 129.0, 128.9, 128.8, 128.82, 128.5, 128.1, 126.1, 62.8, 49.6, 21.1, 20.9; IR (neat, cm^{-1}) 3052, 2976, 2867, 1603, 1367, 1256, 1167; HRMS (ESI) calcd for $C_{32}H_{28}O_2Na$: 467.1987, found: 467.1985.

4.3.10. (E)-3-(1,3-Di-p-tolylallyl)pentane-2,4-dione (**3j**)

White solid; yield: 93%; mp 77–80 °C; ^{1}H NMR (300 MHz) δ 7.30 (m, 4H), 7.05 (m, 4H), 6.34 (d, 1H, *J*=15.9 Hz), 6.1 (dd, 1H, *J*=15.3, 7.8 Hz), 4.27 (m, 2H), 2.30 (s, 6H), 2.23 (s, 3H), 1.92 (s, 3H); ^{13}C NMR δ 203.0, 202.9, 137.5, 137.2, 136.8, 133.8, 131.3, 129.7, 129.4, 129.3, 129.2, 129.0, 128.5, 128.3, 127.8, 127.2, 126.3, 67.1, 48.9, 30.0, 29.8, 21.1, 21.0; IR (neat, cm^{-1}) 3042, 2985, 1690, 1682, 1437, 935; HRMS (ESI) calcd for $C_{22}H_{24}O_2Na$: 343.1674, found: 343.1675.

4.3.11. (E)-Ethyl-2-acetyl-3,5-di-p-tolylpent-4-enoate (**3k**)

Yellow oil; Yield: 93%; ^{1}H NMR δ 7.04 (m, 16H), 6.35 (t, 2H, *J*=15.2 Hz), 6.13 (m, 2H), 4.23 (q, 2H, *J*=8.8 Hz), 4.11 (q, 2H, *J*=7.2 Hz), 4.03 (q, 2H, *J*=7.6 Hz), 3.90 (q, 2H, *J*=7.2 Hz), 2.27 (s, 15H), 2.02 (s, 3H), 1.17 (t, 3H, *J*=6.8 Hz), 0.97 (t, 3H, *J*=7.2 Hz); ^{13}C NMR δ 201.9, 201.7, 168.0, 167.7, 137.4, 137.2, 136.7, 136.6, 134.1, 133.9, 131.5, 131.1, 129.6, 129.3, 129.1, 129.0, 128.7, 128.4, 128.3, 127.8, 126.3, 126.2, 125.9, 65.7, 65.4, 61.5, 61.3, 48.7, 48.4, 40.5, 31.6, 29.9, 29.8, 21.1, 221.0, 14.2, 13.82; IR (neat, cm^{-1}) 3432, 2986, 2378, 1732, 1710, 1482, 1145, 1078, 966, 815; HRMS (ESI) calcd for $C_{23}H_{26}O_3Na$: 373.1780, found: 373.1783.

4.3.12. (E)-Ethyl-2-benzoyl-3,5-di-p-tolylpent-4-enoate (**3l**)

White solid; yield: 91%; mp 97–103 °C; ^{1}H NMR (300 MHz) δ 8.08 (m, 2H), 7.91 (m, 2H), 7.40 (m, 6H), 6.96 (m, 16H), 6.45 (d, 1H, *J*=15.6 Hz), 6.32 (m, 2H), 6.15 (dd, 1H, *J*=15.2, 7.5 Hz), 4.93 (q, 2H, *J*=6.3 Hz), 4.50 (q, 2H, *J*=7.6 Hz), 4.11 (m, 2H), 3.86 (m, 2H), 2.30 (s, 6H), 2.21 (s, 6H), 1.10 (t, 3H, *J*=6.9 Hz), 0.91 (t, 3H, *J*=7.2 Hz); ^{13}C NMR δ 193.3, 192.6, 168.0, 167.6, 138.0, 137.4, 137.2, 137.0, 136.6, 136.6, 136.2, 134.2, 13.1, 133.5, 133.4, 131.3, 131.2, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 127.7, 126.2, 126.1, 61.6, 61.4, 59.9, 59.7, 48.5, 48.4, 21.1, 21.0, 20.9, 14.1, 13.7; IR (neat, cm^{-1}) 3065, 2985, 1720, 1675, 1487, 1445, 1300, 1155, 1072, 977, 806; HRMS (ESI) calcd for $C_{28}H_{28}O_3Na$: 435.1936, found: 435.1937.

4.3.13. 2-(2-Methyl-3-phenylallyl)-1,3-diphenylpropane-1,3-dione (**3m**)

Colorless oil; yield: 86%; ^{1}H NMR δ 7.91 (m, 4H), 7.57 (m, 2H), 7.43 (m, 4H), 7.25 (m, 3H), 7.02 (m, 2H), 6.27 (s, 1H), 5.47 (t, 3H, *J*=6.8 Hz), 3.01 (d, 2H, *J*=6.8 Hz), 1.87 (s, 3H); ^{13}C NMR δ 195.7, 137.7, 136.2, 135.1, 133.5, 128.9, 128.7, 128.6, 127.9, 127.8, 126.2, 56.1, 39.7, 18.2; IR (neat, cm^{-1}) 3084, 3060, 2930, 1700, 1696, 1663, 1596, 1447, 1269, 781, 743, 699; HRMS (ESI) calcd for $C_{25}H_{22}O_2Na$: 377.1517, found: 377.1509.

4.3.14. 2-(3-Methyl-3-phenylallyl)-1,3-diphenylpropane-1,3-dione (**3n**)

Colorless oil; yield 82%; ^{1}H NMR δ 7.99 (m, 4H), 7.54 (m, 2H), 7.43 (m, 4H), 7.23 (m, 4H), 5.74 (t, 1H, *J*=7.2 Hz), 5.32 (t, 1H, *J*=6.8 Hz), 3.01 (t, 2H, *J*=7.2 Hz), 2.0 (s, 3H); ^{13}C NMR δ 195.8, 143.4, 137.4, 136.0, 133.5, 128.9, 128.7, 128.6, 128.1, 126.8, 125.7, 124.3, 56.9, 28.9, 16.0; IR (neat, cm^{-1}) 3058, 2919, 1693, 1669, 1596, 1447, 1322, 1263, 1180; HRMS (ESI) calcd for $C_{25}H_{22}O_2Na$: 377.1517, found: 377.1506.

4.3.15. 2-(3,3-Diphenylallyl)-1,3-diphenylpropane-1,3-dione (**3o**)

White solid; yield: 86%; mp 162–165 °C; ^{1}H NMR δ 7.82 (m, 4H), 7.52 (m, 2H), 7.36 (m, 6H), 7.20 (m, 3H), 7.10 (m, 5H), 6.25 (t, 1H, *J*=7.6 Hz), 5.19 (t, 1H, *J*=6.8 Hz), 2.91 (t, 2H, *J*=7.2 Hz); ^{13}C NMR δ 195.7, 143.9, 141.8, 139.6, 135.8, 133.5, 129.9, 129.8, 129.5, 129.0, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.7, 127.4, 127.2, 127.1, 127.0, 125.6, 125.3, 124.9, 57.2, 29.2; IR (neat, cm^{-1}) 3057, 2926, 1694, 1672, 1596, 1494, 1447, 1268, 1180, 1073, 766, 693; HRMS (ESI) calcd for $C_{30}H_{24}O_2Na$: 439.1674, found: 439.1662.

4.3.16. 3-((2E,4E)-1,5-Diphenylpent-2,4-dienyl)pentane-2,4-dione (**3p**)

Colorless oil; yield: 70%; ^{1}H NMR δ 7.20 (m, 10H), 6.61 (dd, 1H, *J*=15.6, 10.3 Hz), 6.55 (d, 1H, *J*=15.6 Hz), 6.20 (m, 1H), 5.76 (dd, 1H, *J*=15.1, 6.6 Hz), 4.23 (m, 2H), 2.25 (s, 3H), 1.90 (s, 3H); ^{13}C NMR δ 202.8, 202.6, 140.0, 137.0, 133.2, 132.7, 132.2, 129.0, 128.6, 128.1, 127.9, 127.6, 127.5, 127.2, 126.3, 49.0, 30.0, 29.7; IR (neat, cm^{-1}) 3052, 2935, 1687, 1665, 1439, 1265, 976, 695; HRMS (ESI) calcd for $C_{22}H_{22}O_2Na$: 341.1517, found: 341.1512.

4.3.17. (E)-1,3-Diphenyl-2-(4-phenylbut-3-en-2-yl)propane-1,3-dione (**3q**)

Colorless oil; yield 87%; ^{1}H NMR δ 8.01 (m, 3H), 7.96 (m, 2H), 7.77 (m, 1H), 7.48 (m, 8H), 7.30 (m, 3H), 7.11 (m, 7H), 6.39 (d, 1H, *J*=16.0 Hz), 6.09 (dd, 1H, *J*=15.6, 8.4 Hz), 5.34 (d, 1H, *J*=8.8 Hz), 4.56 (t, 1H, *J*=9.5 Hz), 3.59 (q, 1H, *J*=8.0 Hz), 1.44 (d, 2H, *J*=6.1 Hz), 1.21 (d, 3H, *J*=6.4 Hz); ^{13}C NMR δ 195.1, 194.9, 194.6, 194.0, 141.6, 137.3, 137.1, 137.0, 136.9, 136.9, 133.5, 133.4, 133.3, 133.1, 132.3, 131.0, 128.9, 128.8, 128.8, 128.7, 128.5, 128.4, 128.1, 127.7, 127.2, 126.6, 126.1, 63.0,

62.6, 50.0, 38.6, 18.9, 17.8; IR (neat cm^{-1}) 3059, 3026, 2966, 1697, 1664, 1593, 1446, 1278, 1197; HRMS (ESI) calcd for $C_{25}H_{22}O_2Na$: 377.1517, found: 377.1503.

*4.3.18. (E)-3-(4-Phenylbut-3-en-2-yl)pentane-2,4-dione (**3r**)*[24]

Colorless oil; yield: 83%; ^1H NMR δ 7.26 (m, 5H), 6.41 (d, 1H, J=16 Hz), 5.96 (dd, 1H, J=16.1, 8.4 Hz), 3.70 (d, 1H, J=10.4 Hz), 3.17 (m, 1H), 2.22 (s, 3H), 2.12 (s, 3H), 1.08 (d, 3H, J=6.8 Hz); ^{13}C NMR δ 203.6, 203.5, 136.7, 130.9, 130.9, 128.5, 127.5, 126.2, 37.9, 30.0, 29.7, 18.8; MS (ESI) m/z 253 $[M+Na]^+$, 231 $[M+H]^+$.

*4.3.19. (E)-3-(4-(Benzo[d][1,3]dioxol-5-yl)but-3-en-2-yl)pentane-2,4-dione (**3s**)*

Yellow liquid; yield 55%; ^1H NMR δ 6.83 (s, 1H), 6.72 (d, 2H, J=9.2 Hz), 6.31 (d, 1H, J=15.7 Hz), 5.92 (s, 2H), 5.76 (dd, 1H, J=15.7, 8.6 Hz), 3.67 (d, 1H, J=10.4 Hz), 3.10 (m, 1H), 2.20 (s, 3H), 2.11 (s, 3H), 1.04 (d, 3H, J=6.6 Hz); ^{13}C NMR δ 203.6, 203.5, 148.0, 147.1, 131.2, 130.5, 129.1, 120.8, 108.2, 105.5, 101.0, 37.8, 30.0, 29.7, 18.9; IR (neat, cm^{-1}) 2966, 1697, 1489, 1444, 1355, 1249,1037; HRMS (ESI) calcd for $C_{16}H_{18}O_4Na$: 297.1103, found: 297.1102.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.11.102.

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