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DDQ catalyzed benzylic acetoxylation of arylalkanes: a case of exquisitely controlled oxidation under sonochemical activation☆

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Abstract—Acetoxylated arylalkanes are selectively obtained via sonochemical activation of DDQ catalyzed benzylic oxidation of arylalkanes in the presence of anhydrous acetic acid. The method gives an exquisite control of benzylic acetoxylation under ultrasound, in contrast to the uncontrolled oxidation observed under conventional heating or microwave activation. In addition, the developed method could be a useful strategy for the synthesis of industrially important enantiopure benzyl alcohols due to the easy amenability of obtained acetoxylated products toward chiral resolution.

1. Introduction

The selective C–H bond activation of hydrocarbons constitutes one of the most versatile albeit challenging pursuits of organic synthesis.[1] In particular, the controlled benzylic oxidation[2] of arylalkane derivatives has remained a prominent area of interest due to the immense industrial importance and synthetic utility of the corresponding oxidation products like benzyl alcohols[3] or acetates.[4]

There have been a few reports disclosing the enantioselective benzylic hydroxylation of arylalkanes, however, a majority of the above methods provide the hydroxylated product in poor yield and selectivity.[5] In this context, the realization of an efficient protocol for benzylic acetoxylation assumes significance, since the corresponding acetoxylated products not only possess important applications in the fine chemical industry,[2a] but also serve as convenient synthons for the synthesis of enantiopure benzyl alcohols.[4h,6] In addition, the benzyl acetate moiety constitutes the core structure of a number of natural products and biologically active compounds.[4g,7]

However, the development of an efficient protocol for the controlled acetoxylation of arylalkanes has been constrained by the extreme susceptible of the acetoxy function toward over-oxidation or other side reactions.[8] Although some reports for the synthesis of acetoxylated arylalkanes[8b–c,9] have emerged in recent times, a number of limitations remain. For instance, a majority of the acetoxylation protocols in the literature involve the indispensable usage of a halide[8b,9] or nitrate ion source,[8c] which renders the associated work up procedures to be tedious. In addition, some of the reported methods also provide low product selectivity, as well as the requirement for delicate reaction conditions, expensive reagents, and long reaction times.[8b–c] Thus, there has been a persistent requirement of an efficient method for the controlled benzylic acetoxylation of arylalkanes.

Ultrasound and Microwave have been widely recognized as important enabling technologies in organic synthesis due to a range of ensuing benefits like improved yields, shorter reaction times, and enhanced selectivity.[10] Although it has been widely presumed that ultrasound and microwave provide differential assistance to competing reaction pathways,[11] there has been a dearth of reports wherein the comparative efficacy of ultrasound and microwave toward selective formation of competing products has been clearly discerned.

In this context, we herein wish to report an efficient and exquisitely controlled DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone)[12] catalyzed benzylic acetoxylation protocol in the presence of an anhydrous acetic acid under sonochemical activation in contrast to the uncontrolled oxidation observed under conventional heating or microwave activation.

2. Results and discussion

As part of our ongoing efforts toward the synthesis of important bioactive molecules, we have had an interest in exploring the versatility of DDQ-mediated oxidation of arylalkanes.[13] DDQ has been widely recognized as an effective[12] and recyclable[14] oxidizing reagent for a variety

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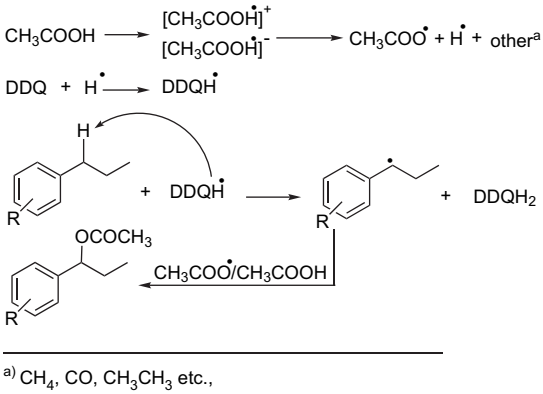
of organic transformations. In this context, we had earlier observed the remarkable differential oxidizing ability of DDQ under varying reaction conditions. Thus, we observed that while the reaction of arylalkanes with 1.25 or 3.1 equiv of DDQ in dry dioxane provided arylalkenes[13b] or arylalkenal,[13e] respectively, the use of 2.2 equiv of DDQ under aqueous conditions led to the formation of corresponding arylalkanones.[13c] We were quite fascinated by this tunable oxidizing ability of DDQ, and sought to exploit the same for the selective acetoxylation of arylalkanes.

Initially, a mixture of 1-(3,4-dioxymethylenephenyl)propane (**1a**), DDQ (1.1 equiv), and dry acetic acid was stirred under a nitrogen atmosphere at room temperature (18 h) or refluxed for 6 h. The method provided the expected 1-(3,4-dioxymethylenephenyl)propyl acetate (**1b**) in low yield (39%) along with a number of side products such as 1-(3,4-dioxymethylenephenyl)prop-1-ene,[13b] (10%), and 1-(3,4-dioxymethylenephenyl)propan-1-one[13c] (17%). We were quite intrigued by the above observation, especially in view of the fact that an earlier report had disclosed the DDQ catalyzed benzylic acetoxylation of the cyclic side chain of polyaromatic rings along with the possibility of formation of olefinic and ketonic products.[15] Evidently, the open propyl side chain of **1a** was incompatible with our objective of controlled oxidation under the above reaction conditions. We further presumed that the initial excessive exposure of the substrate toward DDQ (1.1 equiv) might have triggered competing reaction pathways leading to the formation of side products like 1-(3,4-dioxymethylenephenyl)prop-1-ene and 1-(3,4-dioxymethylenephenyl)propan-1-one in addition to the desired 1-(3,4-dioxymethylenephenyl)propyl acetate (**1b**). Consequently, the reaction mixture was subjected to a step-wise addition of DDQ into a dilute solution of **1a** in acetic acid, which led to an increase in the yield of **1b** (46%), but the formation of side products was still a limiting factor.

In our quest for a reduction in the number of side products, we shifted our attention toward the use of alternative sources of energy like ultrasound and microwave, as they have been known to increase the yield of the product by preferentially accelerating one of the competing reaction pathways while reducing the reaction time. Thus, the above reaction was conducted under ultrasonic irradiation and gratifyingly, **1b** was obtained in 82% yield after 70 min (Scheme 1). Later on, we decided to investigate the effect of microwave on the above reaction. However, the microwave irradiation was found to be a leveling energy source toward the formation of either acetoxylated or dehydrogenated product, as both **1b** and 1-(3,4-dioxymethylenephenyl)prop-1-ene[13b] were formed in comparative yields (Scheme 1).

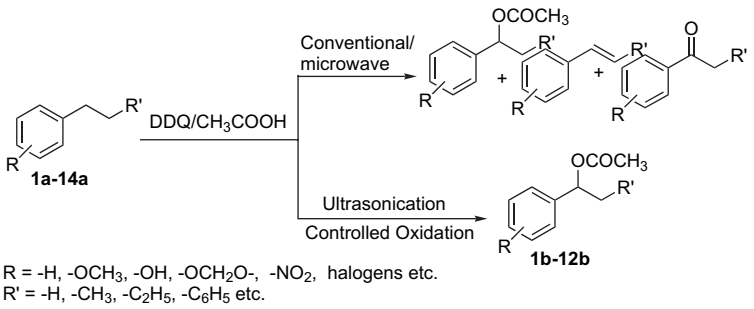
The unique specificity of ultrasound over conventional and microwave conditions impelled us to seek the underlying mechanistic rationale. It has been widely recognized that the DDQ catalyzed oxidation of arylalkanes generally proceeds through an initial hydride ion abstraction leading to the formation of ionic intermediates.[12,15c] We hypothesized that the conventional or microwave[10b] heating of our reaction mixture might also support the initial hydride ion abstraction to form the ionic intermediates, which in turn get implicated in competing reaction pathways leading to the formation of side products like arylalkenes and arylketones in addition to the expected acetoxylated product **1b**.

We were also quite aware of the fact that a key feature of ultrasound-assisted reactions is the enhancement of radical mechanisms.[16] Therefore, we ascribed the exclusive formation of **1b** under sonication to the involvement of a free radical intermediate (Scheme 2).



Scheme 2.

In order to verify this hypothesis, **1a** was reacted with 1.1 equiv of DDQ/AcOH in the presence of free radical initiator like benzoyl peroxide. To our pleasant delight, the addition of benzoyl peroxide remarkably accelerated the rate of acetoxylation and provided **1b** in 81% yield within 30 min. Interestingly, the replacement of benzoyl peroxide with a free radical scavenger like ascorbic acid leads to a complete inhibition of the reaction, thus emphatically supporting our premise of a free radical acetoxylation pathway.



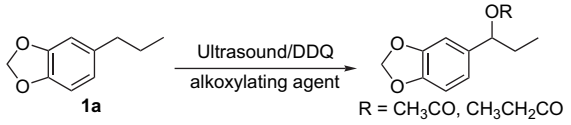
Scheme 1.

For comparative studies, different oxidizing agents such as cerium ammonium nitrate (CAN), palladium acetate, selenium dioxide, chromium trioxide, mercuric acetate, and $KMnO_4$ (10 equiv) were used instead of DDQ under similar reaction conditions with sonochemical activation. However, none of the oxidants provided acetoxylated product (**1b**) except $KMnO_4$, which conferred **1b** in 16% yield with 1-(3,4-dioxymethylenephenyl)prop-1-one[13c] (32%) as the major product. Hence, it may be concluded that the specific conjunction of DDQ with ultrasound imparts the pronounced control of benzylic acetoxylation of arylalkanes observed in our case. It may be mentioned here that, although the DDQ catalyzed benzylic oxidation has been previously explored,[15,17] we did not come across a literature report for the ultrasound-assisted controlled benzylic acetoxylation of arylalkanes using DDQ as an oxidizing agent.

Later on, the developed method was explored with other trapping reagents like formic acid, propionic acid, acetic anhydride, vinyl acetate, and trifluoroacetic acid (Table 1). However, only acetic anhydride was found to provide **1b** in comparative yield. A number of side products got formed with formic acid as an alkoxylating agent, and the product was obtained in traces. In the case of trifluoroacetic acid, the decreased basic strength of the acetate ion, due to the presence of the three fluorines, probably led to non-formation of the product. Again, the yield of the product was poor with propionic acid (34%), which might be due to the bulkier nature of propionate ions. Surprisingly, the treatment of vinyl acetate, a well known acylating agent, with **1a** provided dehydrogenated product 1-(3,4-dioxymethylenephenyl)prop-1-ene[13b] instead of the acetoxylated product **1b**.

To underline the substrate scope of the process, the developed method was extended to a number of substituted arylalkanes (Table 2). It is clear that the presence of methoxy substituents increased the yield of **1b**. The low yield of product in the case of hydroxy substituted (entry 6) phenylpropane might be due to the formation of a complex between DDQ and the hydroxyl group.[18] Further, the presence of electron withdrawing substituents at the aromatic ring (entries 13 and 14) hindered the progress of the reaction and thus no product could be isolated with nitro or bromo dihydrosafrole as substrate. In the case of biactive bibenzyl[19] (entry 10), containing two benzylic sites, selective acetoxylation was found to occur in accordance with the formation of more stable free radical. Interestingly, safrole and methyl chavicol (entries 11 and 12) didn't provide the expected benzyl acetate under the above conditions and instead, rearranged products[20] (compounds **11b** and **12b** in entries 11 and 12) were obtained along with the corresponding cinnamaldehydes.[21] Thus the controlled oxidizing ability of the developed protocol selectively provided the important acetoxylated arylalkanes (**1b**–**12b**). It may be mentioned here that the above method also constitutes a convenient and efficient strategy toward the synthesis of immensely important enantiopure benzyl alcohols[3] due to the easily amenable nature of obtained acetoxylated products toward enantiomeric resolution.[6]

Table 1. Effect of different alkoxylating agents on **1a**



Sr. no	Alkoxylating agent	Reaction time (min)	Yield (%)
1	CH_3COOH	70	82
2	HCOOH	70	Traces
3	CH_3CH_2COOH	120	34
4	$(CH_3CO)_2O$	80	78
5	$CH_2{=}CHOCOCH_3$	120	*nd*
6	CF_3COOH	120	*nd*
7	$C_6H_5CH_2COOH$[a]	120	*nd*

nd=not detected.
[a] Phenylacetic acid of 1.5 equiv was taken and dry dioxane was used as solvent.

3. Conclusion

In conclusion, we disclose a DDQ catalyzed benzylic acetoxylation protocol wherein the application of ultrasound imparted exquisite control of the oxidation process as compared to conventional or microwave activation. The developed method provides a convenient and selective access to immensely important acetoxylated arylalkanes in lieu of the prevalent methods involving the formation of several competing oxidized products. In addition, the developed method could be a useful strategy for the synthesis of industrially important enantiopure benzylic secondary alcohols through chiral resolution of obtained acetoxylated products.

4. Experimental section

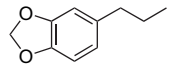
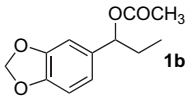
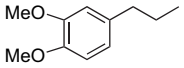
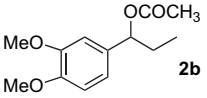
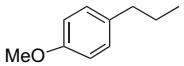
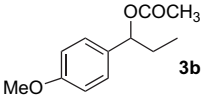
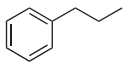
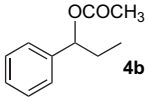
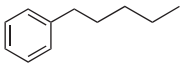
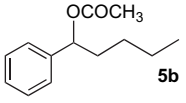
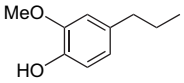
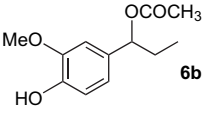
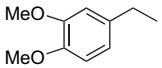
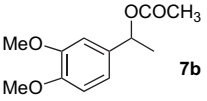
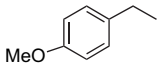
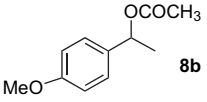
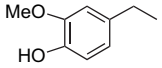
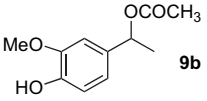
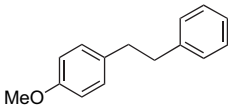
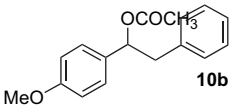
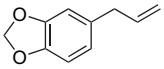
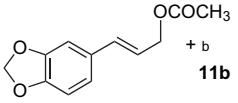
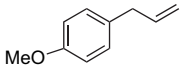
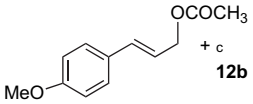
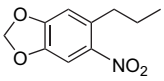
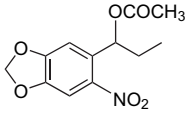
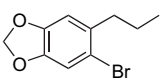
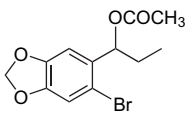
4.1. General methods

Commercial reagents and solvents were of analytical grade and were purified by standard procedures prior to use. Sonics vibra cell© ultrasonicator (20 kHz, 400 W) was used for all the given reaction. A CEM Discover© focused microwave (2450 MHz, 300 W) was used wherever mentioned. ^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker Avance-300 spectrometer. GC–MS were determined using a Shimadzu-2010 spectrometer. HRMS spectra were determined using micromass Q-TOF ultima spectrometer.

4.2. Acetoxylation of phenylalkanes under ultrasonication

A mixture of arylalkane (**1a**–**14a**, 6.0 mmol) and dry acetic acid (40 mL) were taken in a 100 mL glass beaker. To this reaction mixture, DDQ (6.6 mmol) was added in three parts, each after 5 min of sonication (pulse length: 3 s, duty: 35%, probe: microtip). Thereafter, the reaction mixture was sonicated for the time given in Tables 1 and 2 with a gap of 2 min after each 20 min of irradiation. After completion of the reaction (color changed from green to red), the reaction mixture was filtered to remove the precipitate of $DDQH_2$ and water was added to the filtrate. The aqueous layer was extracted with dichloromethane (3×20 mL), the organic layer was dried over sodium sulfate, and the solvent was removed under vacuum to afford the crude product, which was

Table 2. Controlled oxidation of arylalkanes into corresponding acetoxylated products under sonochemical activation

Entry	Substrate (**a**)	Reaction time (min)	Product (**b**)	Yield (%)	Ref.[a]
1		70	 **1b**	82	7a,b
2		70	 **2b**	81	7c,d,4j
3		70	 **3b**	74	4c,8b
4		90	 **4b**	64	4c
5		90	 **5b**	62	—
6		70	 **6b**	31	7f
7		70	 **7b**	80	7c,h
8		70	 **8b**	75	4c
9		70	 **9b**	26	7e
10		70	 **10b**	79	19a,b
11		70	 + b **11b**	38 (42)	20
12		70	 + c **12b**	34 (39)	4g
13		120		*nd*	—
14		120		*nd*	—

General conditions: (pulse length: 3 s, duty: 35%, probe: microtip), substrate **1a**–**14a** (6.0 mmol), dry acetic acid (40 mL), DDQ (6.6 mmol); *nd*=not detected.

[a] Literature reference of the compounds; number in parenthesis denotes yield of the side product.

[b] 3,4-Dioxymethylenecinnamaldehyde.

[c] 4-Methoxycinnamaldehyde.

chromatographed on neutral alumina column with 1:10 mixture of dichloromethane in hexane to yield the products (**1b–12b**).

4.3. Spectral data of title compounds

4.3.1. 1-(3,4-Dioxymethylenephenyl)propyl acetate[7a,b,d] (1b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 6.75–6.69 (3H, m), 5.86 (2H, s), 5.50 (1H, t, *J* 6.9 Hz), 1.98 (3H, s), 1.86–1.63 (2H, m), 0.81 (3H, t, *J* 7.3 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.4, 147.7, 147.1, 134.4, 120.4, 108.0, 107.0, 101.0, 77.3, 29.2, 21.3, and 9.9.

4.3.2. 1-(3,4-Dimethoxyphenyl)propyl acetate[4j,7c,d] (2b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 6.81–6.74 (3H, m), 5.53 (1H, t, *J* 6.9 Hz), 3.80 (3H, s), 3.77 (3H, s), 1.97 (3H, s), 1.88–1.65 (2H, m), 0.80 (3H, t, *J* 7.3 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.4, 148.8, 148.6, 133.0, 119.2, 110.9, 109.9, 77.1, 55.8, 29.1, 21.3, and 10.0.

4.3.3. 1-(4-Methoxyphenyl)propyl acetate[4c,8b] (3b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 7.21 (2H, d, *J* 8.5 Hz), 6.81 (2H, d, *J* 8.5 Hz), 5.57 (1H, t, *J* 6.9 Hz), 3.72 (3H, s), 1.98 (3H, s), 1.90–1.67 (2H, m), 0.81 (3 H, t, *J* 7.7 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.5, 159.2, 132.6, 128.0, 113.7, 77.1, 55.2, 29.0, 21.3, and 10.0.

4.3.4. 1-Phenylpropyl acetate[4c] (4b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 7.25–7.19 (5H, m), 5.61 (1H, t, *J* 6.9 Hz), 2.00 (3H, s), 1.88–1.71 (2H, m), 0.83 (3H, t, *J* 7.3 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.1, 140.5, 128.4, 127.8, 126.5, 77.4, 28.5, 21.3, and 10.7.

4.3.5. 1-Phenylpentyl acetate (5b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 7.27–7.20 (5H, m), 5.68 (1H, t, *J* 6.9 Hz), 2.04 (3H, s), 1.91–1.74 (2H, m), 1.62–1.54 (4H, m), 0.89 (3H, t, *J* 7.3 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.3, 140.8, 128.8, 127.9, 126.2, 76.9, 30.5, 30.1, 22.9, and 12.7.

4.3.6. 1-(4-Hydroxy-3-methoxyphenyl)propyl acetate[7f] (6b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 6.89–6.85 (3H, m), 5.66 (1H, s), 5.53 (1H, t, *J* 6.9 Hz), 3.80 (3H, s), 1.97 (3H, s), 1.86–1.71 (2H, m), 0.81 (3H, t, *J* 7.3 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.5, 146.4, 145.3, 132.4, 121.0, 114.2, 109.8, 77.5, 55.9, 29.1, 21.3, and 10.0.

4.3.7. 1-(3,4-Dimethoxyphenyl)ethyl acetate[7c,h] (7b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 6.83–6.71 (3H, m), 5.76 (1H, q, *J* 6.6 Hz), 3.79 (3H, s), 3.75 (3H, s), 1.95 (3H, s), 1.43 (3H, d, *J* 6.6 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.5, 146.5, 145.4, 133.5, 119.3, 114.3, 109.6, 72.4, 55.9, 22.0, and 21.4.

4.3.8. 1-(4-Methoxyphenyl)ethyl acetate[4c] (8b). Colorless oil; δ_H (300 MHz, $CDCl_3$) 7.18 (2H, d, *J* 8.5 Hz), 6.78 (2H, d, *J* 8.5 Hz), 5.75 (1H, q, *J* 6.5 Hz), 3.76 (3H, s), 1.98 (3H, s), 1.43 (3H, d, *J* 6.5 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.4, 158.7, 134.6, 128.0, 114.1, 72.1, 55.2, 21.8, and 21.2.

4.3.9. 1-(4-Hydroxy-3-methoxyphenyl)ethyl acetate[7e] (9b). White crystalline solid; mp 71–73 °C; δ_H (300 MHz, $CDCl_3$) 6.89–6.87 (3H, m), 5.64 (1H, s), 5.87 (1H, q, *J* 6.5 Hz), 3.90 (3H, s), 2.06 (3H, s), 1.54 (3H, d, *J* 6.5 Hz); δ_C (75.4 MHz, $CDCl_3$) 170.3, 146.9, 145.7, 134.3, 118.4, 111.0, 109.7, 72.2, 55.8, 21.9, and 21.3.

4.3.10. 1-(4-Methoxyphenyl)-2-(phenyl)ethyl acetate[19a,b] (10b). White solid; mp 82–85 °C (lit.[19b] 82.4–83.0 °C); δ_H (300 MHz, $CDCl_3$) 7.18–7.15 (5H, m), 7.06 (2H, d, *J* 6.6 Hz), 6.80 (2H, d, *J* 8.5 Hz), 5.87 (1H, t, *J* 7.4 Hz), 3.73 (3H, s), 3.18–2.94 (2H, m), 1.94 (3H, s); δ_C (75.4 MHz, $CDCl_3$) 170.1, 159.3, 137.2, 132.1, 129.5, 128.2, 128.1, 127.7, 127.5, 126.5, 113.7, 76.4, 55.2, 42.8, and 21.2.

4.3.11. 1-(3,4-Dioxymethylenephenyl)cinnamyl acetate[20] (11b). Yellowish oil; δ_H (300 MHz, $CDCl_3$) 6.85 (1H, s), 6.76 (1H, d, *J* 6.8 Hz), 6.69 (1H, d, *J* 6.8 Hz), 6.51 (1H, d, *J* 16.1 Hz), 6.09–5.99 (1H, m), 5.88 (2H, s), 4.63 (2H, d, *J* 6.3 Hz), 2.02 (3H, s); δ_C (75.4 MHz, $CDCl_3$) 170.8, 148.0, 147.6, 134.0, 130.6, 121.5, 121.1, 108.3, 105.8, 101.1, 65.1, and 21.3.

4.3.12. 1-(4-Methoxyphenyl)cinnamyl acetate[4g] (12b). Yellowish oil; δ_H (300 MHz, $CDCl_3$) 7.24 (2H, d, *J* 8.5 Hz), 6.88 (2H, d, *J* 8.5 Hz), 6.56 (1H, d, *J* 16.1 Hz), 6.13–6.05 (1H, m), 4.64 (2H, d, *J* 6.1 Hz), 3.74 (3H, s), 2.02 (3H, s); δ_C (75.4 MHz, $CDCl_3$) 170.9, 159.6, 134.0, 131.7, 127.9, 120.8, 114.6, 65.4, 55.4, and 21.0.

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Supplementary data

Spectral data of some representative compounds were provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.07.018.

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