JOC The Journal of Organic Chemistry

Article

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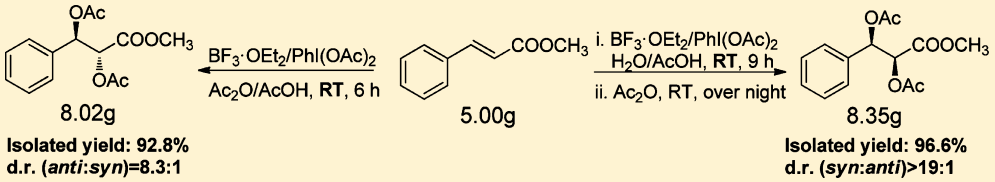
BF_3·OEt_2-Promoted Diastereoselective Diacetoxylation of Alkenes by $PhI(OAc)_2$

Wenhe Zhong, Jun Yang, Xiangbao Meng,* and Zhongjun Li*

The State Key Laboratory of Natural and Biomimetic Drugs, Department of Chemical Biology, School of Pharmaceutical Sciences, Peking University, Beijing 100191, P. R. China

Supporting Information

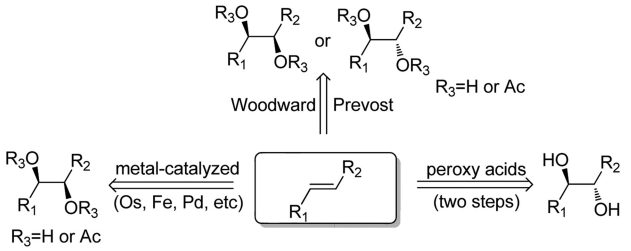


ABSTRACT: Selective *syn* and *anti* diacetoxylations of alkenes have been achieved using a $PhI(OAc)_2/BF_3$·OEt_2 system in the presence and absence of water, respectively. A broad range of substrates including electron-deficient alkenes (such as *α,β*-unsaturated esters) could be elaborated efficiently at room temperature with this methodology, furnishing the desired products in good to excellent yields and diastereoselectivity. In particular, a multigram-scale diastereoselective diacetoxylation of methyl cinnamate (5.00 g) was also accomplished in a few hours, maintaining the same efficiency as small-scale reaction. This novel methodology provides an alternative approach for the preparation of various 1,2-diols.

INTRODUCTION

The dioxygenation of alkenes presents an attractive approach for the preparation of various 1,2-diols, and the diastereoselective dioxygenation continues to be a fascinating area of research in organic synthesis (Scheme 1).[1] The *syn* vicinal diols

Scheme 1. Approaches for the Diastereoselective Dioxygenation of Alkenes



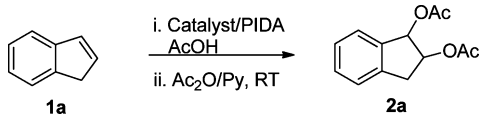
are mostly prepared by metal-catalyzed dioxygenation of alkenes. One typical method is OsO_4-catalyzed *syn*-dihydroxylation of alkenes, as well as its asymmetric version developed by Sharpless et al., which has been elegantly demonstrated and widely used in organic synthesis.[2] Because of the high cost and toxicity of OsO_4, efforts are continuously made to develop alternative metal catalysts.[3] The *anti* vicinal diols are commonly produced through a two-step procedure: epoxidation of alkenes by using peroxy acids followed by a ring-opening reaction.[4] In addition, the Woodward–Prevost reaction is another general method to achieve diastereoselective dioxygenation of alkenes,[5] but the use of a stoichiometric amount of expensive silver salts limits its application on an industrial scale. Because of the high cost of metal catalysts and potential environmental pollution, there is an increasing interest in developing metal-free alkene dioxygenation procedure. However, it remains a challenging task, and examples are still scarce.[6,7] Sudalai et al.[8] developed a metal-free version of the Woodward–Prevost reaction without the use of silver salts, but a high temperature was still necessary. Very recently, Gade et al.[9] reported that triflic acid was able to efficiently catalyze dioxygenation of alkenes using $PhI(OAc)_2$ as oxidant; meanwhile, Fujita et al.[10] first developed enantioselective variants of the Woodward and Prevost reactions by employing a chiral hypervalent iodine(III)/BF_3·OEt_2 system. An optically active 1,3-dioxolan-2-yl cation was formed mediated by chiral hypervalent iodine(III) and then attacked by water or trimethylsilyl acetate to provide *syn* and *anti* products, respectively. The dioxygenate products were obtained in moderate yields with good enantioselectivity, but the reactions presently were limited to styrene type substrates and needed to be conducted at a very low temperature. Considering the good oxidizing properties of hypervalent iodine compounds, we reasoned that using hypervalent iodine compounds instead of I_2/silver salts system in the Woodward–Prevost reaction may offer a convenient and practical approach to the synthesis of valuable 1,2-diols.

Over the past two decades, hypervalent iodine reagents have been widely used in organic synthesis, mostly because of their oxidizing properties, low toxicity, and availability.[11] Although the preparation of *syn* dioxygenate alkenes using hypervalent iodine(III) reagents has been described,[12] those methods are limited to some active substrates. For example, the dioxygenation of stilbenes with phenyliodine(III) bis(trifluoroacetate)

Received: August 24, 2011
Published: November 17, 2011

   dx.doi.org/10.1021/jo201752y | J. Org. Chem. 2011, 76, 9997–10004

Table 1. Optimization of Reaction Conditions for the Indene Diacetoxylation with $PhI(OAc)_2$



1a 2a

entry[a]	catalyst	mol %[b]	yield[c] (%)	dr (*syn*/*anti*)[d]
1	$BF_3{\cdot}OEt_2$	10	93	>19:1
2	$BF_3{\cdot}OEt_2$	10	76	7.7:1[e]
3	$BF_3{\cdot}OEt_2$	10	80	>19:1[f]
4	$BF_3{\cdot}OEt_2$	5	71	>19:1
5	$BF_3{\cdot}2AcOH$	10	62	11:1[g]
6	TfOH	5	76	4.3:1
7	TfOH	10	81	2:1
8	$HBF_4{\cdot}OEt_2$	5	77	10:1
9	$Cu(OTf)_2$	10	74	5.6:1
10	$Zn(OTf)_2$	10	65	3.6:1
11	$Sc(OTf)_2$	10	72	1.7:1
12[h]	$BF_3{\cdot}OEt_2$	5	86	1:15
13[h]	TfOH	5	72	1:6.3

[a]1.0 mmol scale (0.2 M solution), 1.0 equiv of PIDA, 2.0 equiv of H_2O, rt; then 3 mL of pyridine and 0.5 mL of Ac_2O, rt. [b]Catalyst loading. [c]Isolated yield. [d]Determined by ^{1}HNMR integration. [e]1.0 equiv of H_2O was used. [f]4.0 equiv of H_2O was used. [g]The solvent was CH_2Cl_2. [h]0.2 mL of Ac_2O was added instead of H_2O. PIDA = $PhI(OAc)_2$.

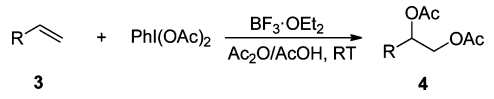
(PIFA)[12a] or [hydroxy(tosyloxy)iodo]benzene (Koser's reagent)[12c] was performed over 10 days. Herein, we report a convenient and practical procedure for the diastereoselective diacetoxylation of alkenes mediated by $PhI(OAc)_2/BF_3{\cdot}OEt_2$ system under mild conditions.

RESULTS AND DISCUSSION

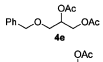
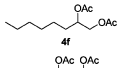
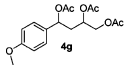
Compared with PIFA or Koser's reagent, (diacetoxyiodo)-benzene [$PhI(OAc)_2$] is more easily available and stable. Therefore, our initial experiments focused on searching an efficient catalyst capable of activating $PhI(OAc)_2$ to allow the direct oxidation of the olefins. We found that when indene was exposed to $PhI(OAc)_2$ in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$[13] in AcOH, a mixture of *anti*-diacetate products and *syn*-hydroxyacetate products was obtained efficiently at room temperature. We thought that trace amounts of water may be present in the solvent and responsible for the formation of hydroxyacetate product. Indeed, after addition of 2 equiv of H_2O to the reaction, only the hydroxyacetate product was isolated with a high *syn* diastereoselectivity. When water was reduced to 1 equiv, a decreased diastereoselectivity was observed (Table 1, entry 2). However, too much water led to a small loss of product yield (entry 3). Additionally, Brønsted acids, such as TfOH[9] and HBF_4[14] (entries 5−7), were efficient for this transformation as well, albeit with decreased yield and diastereoselectivity. Metal salts, such as $Cu(OTf)_2$, $Zn(OTf)_2$ and $Sc(OTf)_3$, were also screened as Lewis acids. Less satisfying results were generally obtained, with low yields as well as poor diastereoselectivity (entries 8−10). Attempts to conduct this reaction without using any catalysts led to a low yield.[15] Moreover, further studies surveying the effect of different solvents indicated that acetic acid yielded the best result (see the Supporting Information). Using the same reagents, *anti*-diacetate product was formed with excellent diasteroselectivity and in good yields under anhydrous conditions, in which trace amounts of water were removed by the addition of acetic anhydride (entry 11). Moreover, TfOH also promoted this olefin *anti*-diacetoxylation modification, albeit with lower yield and diastereoselectivity (entry 12), comparing with $BF_3{\cdot}OEt_2$. These results clearly show that diacetoxylation of alkene mediated by the $PhI(OAc)_2/BF_3{\cdot}OEt_2$ system can provide rapid access to vicinal diol with good diastereoselectivity and high yield.

After optimizing the reaction conditions, we studied the generality of this methodology. As summarized in Table 2, the

Table 2. $BF_3{\cdot}OEt_2$-Catalyzed Diacetoxylation of Terminal Olefins with $PhI(OAc)_2$



3 4

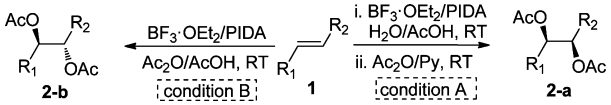
Entry[a]	Product	Time(h)	Yield[%][b]
1		2	98
2		2	84
3		2	91
4		2	90
5[c]		20	74
6[d]		8	94
7		24	78[e]

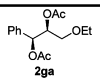
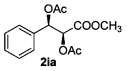
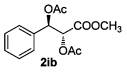
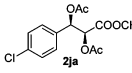
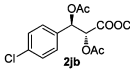
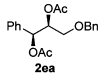
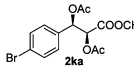
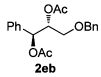
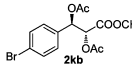
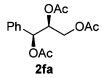
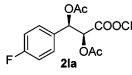
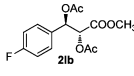
[a]Reaction conditions: **3** (1.0 mmol), AcOH (5 mL), Ac_2O (0.2 mL), $PhI(OAc)_2$ (1.0 equiv), $BF_3{\cdot}OEt_2$ (0.1 equiv). [b]Yield of isolated product. [c]Run at 50 °C. [d]0.4 equiv of $BF_3{\cdot}OEt_2$ was used. [e]dr =1.7:1. tBu = tertiary butyl.

results demonstrate that a variety of terminal alkenes can be oxidized smoothly to produce the diacetate products in high yields. Styrene derivatives bearing electron-donating (Table 2, entries 2 and 4) or electron-withdrawing (entry 3) groups were elaborated efficiently. Allyl benzyl ether was also oxidized to the diacetate in good yield, albeit at elevated temperature (entry 5). Notably, diacetoxylation of a simple aliphatic alkene also

dx.doi.org/10.1021/jo201752y | J. Org. Chem. 2011, 76, 9997−10004

Table 3. Diastereoselective Diacetoxylation of Internal Olefins



Entry[a]	Product	Yield[%][b]	dr (*syn*:*anti*)[c]	Entry[a]	Product	Yield[%][b]	dr (*syn*:*anti*)[c]
1	 **2aa**	93	>19:1	12	 **2ga**	78	>99:1
2	 **2ab**	91	<1:19	13	 **2gb**	71	1:12.5[e]
3	 **2ba**	80	9.1:1	14	 **2ha**	99	14:1
4	 **2bb**	90	1:17	15	 **2hb**	36	1:5.7
5	 **2ca**	74	>99:1[d]	16	 **2ia**	99	>19:1[f]
6	 **2cb**	62	>99:1	17	 **2ib**	94	1:9.1[g]
7	 **2da**	76	12.5:1	18	 **2ja**	98	>19:1[f]
8	 **2db**	72	1:1.4	19	 **2jb**	93	1:6.3[g]
9	 **2ea**	70	>99:1	20	 **2ka**	100	>19:1[f]
10	 **2eb**	67	1:12.5[e]	21	 **2kb**	87	1:7.1[g]
11	 **2fa**	71	>19:1	22	 **2la**	99	11:1[f]
				23	 **2lb**	97	1:3.4[g]

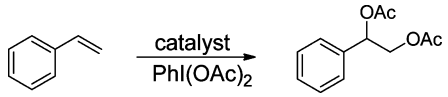
[a]Conditions A: **1** (1.0 mmol), AcOH (5 mL), H_2O (2.0 equiv), PIDA (1.0 equiv), $BF_3{\cdot}OEt_2$ (0.1 equiv); then 0.5 mL of Ac_2O/3 mL of pyridine, rt. Conditions B: **1** (1.0 mmol), AcOH (5 mL), Ac_2O (0.2 mL), PIDA (1.0 equiv), $BF_3{\cdot}OEt_2$ (0.1 equiv). [b]Isolated yield. [c]Determined by ^{1}HNMR integration. [d]Not treated with Ac_2O. [e]Run at 50 °C. [f]3.0 equiv of $BF_3{\cdot}OEt_2$ and 1.2 equiv of PIDA were used. [g]3.0 equiv of $BF_3{\cdot}OEt_2$ and 1.5 equiv of PIDA were used. PIDA = $PhI(OAc)_2$. Py=pyridine.

proceeded smoothly at ambient temperature with excellent yields by increasing the catalyst loading (entry 6). An anisole derivative (entry 7), which is sensitive to some hypervalent iodine reagents, was well tolerated as well.[16]

Subsequently, a series of internal olefins were subjected to oxidation to explore the scope and diastereoselectivity of this methodology further. Our initial studies showed that *syn* and *anti* dioxygenate products were formed by adding water to (conditions A) and removing water from (conditions B) the reaction, respectively. Most olefin substrates underwent dioxygenation to produce a regioisomeric mixture of hydroxyacetate products in wet AcOH. To simplifying the purification process, AcOH was removed under vacuum at the end of the reaction, and the residue was treated with Ac_2O in pyridine to give diacetate products. As shown in Table 3, diacetoxylation of the tested internal olefins was mostly achieved in good to excellent yields along with high diastereoselectivity. Because of the inherent strain of the ring, indene (**2a**) and 1,2-dihydronaphthalene (**2b**) were efficiently oxidized to the *syn* and *anti* diacetate products in excellent yields as well as diastereoselectivity (Table 3, entries 1 and 2). Products **2ca** and **2cb**[17] were obtained in the *cis* configuration exclusively. By increasing the loading of $BF_3{\cdot}OEt_2$ to 0.4 equiv, *trans*-stilbene was consumed within 2 h in wet AcOH, producing a good yield of *syn*-diastereoisomer with high selectivity; however, a poor diastereoselectivity was observed in dry AcOH. Cinnamyl alcohol (entry 6) and its ether derivatives afforded their corresponding *syn* dioxygenate products in excellent diastereoselective ratios (up to 99:1), and their *anti*-diacetate products were also selectively obtained under anhydrous condition (entries 5−7). Cyclopentene was well-tolerated in wet condition, and the *cis* products were achieved in excellent yield along with high diastereoselectivity (entry 8). However, attempts to prepare the *trans* products led to a low yield. When *trans*-methyl cinnamate was treated under the standard conditions, only trace amounts of product were detected. But dioxygenation of *trans*-methyl cinnamate proceeded smoothly in the presence of 3.0 equiv of $BF_3{\cdot}OEt_2$ under wet conditions, generating excellent yield (up to 99%) and high diastereoselectivity. Other *trans*-methyl cinnamate derivatives (entries 10−12) behaved similarly to methyl cinnamate in product yield as well as diastereoselectivity. Additionally, high yields of their

dx.doi.org/10.1021/jo201752y | *J. Org. Chem.* 2011, 76, 9997−10004

Table 4. Effect of Proton-Trapping on the Diacetoxylation of Styrene



entry[a]	catalyst	additive	time (h)	yield (%)
1	TfOH (10%)		2	91[b]
2	TfOH (10%)	DTBMP (12%)	24	trace
3	$BF_3{\cdot}OEt_2$ (10%)		2	97[b]
4	$BF_3{\cdot}OEt_2$ (10%)	DTBMP (12%)	24	trace

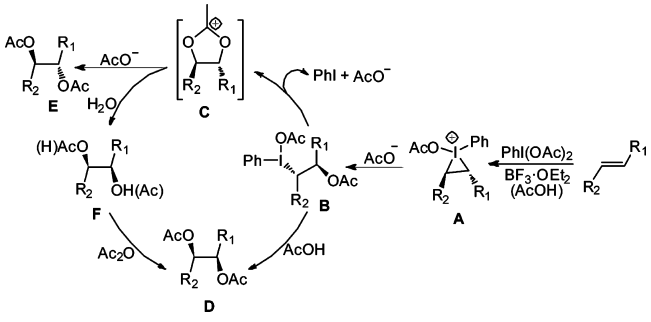
[a]Reaction conditions: styrene (1.0 mmol), AcOH (5 mL), $PhI(OAc)_2$ (1.0 equiv), rt. [b]Isolated yield. DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine.

anti-diacetate products were obtained along with moderate to good diastereoselectivity.

Gade et al.[9] have demonstrated that protons act as the active catalysts in the metal salts (Lewis acids) catalyzed dioxygenation of alkenes using $PhI(OAc)_2$ as the oxidant. Although it has been proposed that $BF_3{\cdot}OEt_2$ activated hypervalent iodine(III) compounds through a Lewis acid coordination pathway,[18] it is still possible that a strong Brønsted acid produced by the $BF_3{\cdot}OEt_2$/AcOH system catalyzes the reaction. In order to identify the catalytically active species, a proton-trapping experiment was carried out. As shown in Table 4, $BF_3{\cdot}OEt_2$ was able to catalyze the diacetoxylation of styrene within 2 h. But after a proton-trapping reagent (DTBMP)[19] was added into the solution, the reaction was dramatically inhibited. These results indicated that the proton was also crucial for catalyzing the dioxygenation of alkenes in our system. However, $BF_3{\cdot}OEt_2$ performed better in catalyzing diastereoselective diacetoxylation of alkenes than the Brønsted acid (TfOH or HBF_4), not only in the product yields but also in the diastereoselectivity (Table 1, entries 1, 5, and 7; entries 11 and 12).

For the I_2/silver salt mediated Woodward–Prevost reaction mechanism, we inferred that the important intermediate acetoxonium is formed during the oxidation of alkenes mediated by hypervalent iodine(III), which was also proposed in previous literature.[9,10,20] On the basis of our studies, a mechanism is proposed in Scheme 2. $PhI(OAc)_2$ is first

Scheme 2. Proposed Mechanism for $PhI(OAc)_2/BF_3{\cdot}OEt_2$-Mediated Diastereoselective Dioxygenation of Alkenes



activated by the $BF_3{\cdot}OEt_2$-HOAc system and reacts with the alkene to form intermediate **A**, followed by reaction with acetate to form species **B**. The intermediate **B** might undergo S_N2-type nucleophilic substitution by acetic acid to generate *syn*-diacetoxylation products, in agreement with the observation that *syn*-diacetate products are formed under anhydrous conditions in some cases. However, species **B** likely prefers to undergo intramolecular cyclization to form acetoxonium **C**, which is hydrolyzed in the presence of water to generate the *syn*-hydroxyacetate product **F**.[3k,5a] In the absence of water, the *anti*-diacetate product **E** is formed via the ring-opening of acetoxonium **C** by acetate.

In order to demonstrate the synthetic usefulness of this method, a scale-up reaction was performed (Figure 1). Methyl

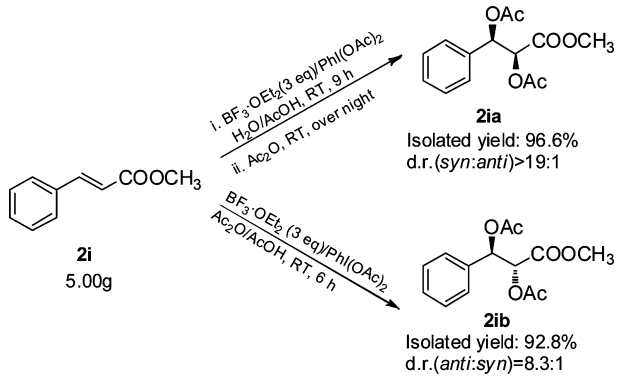


Figure 1. Multigram-scale diacetoxylation of methyl cinnamate.

cinnamate (**2i**) (5.00 g, 30.9 mmol) was consumed completely in the presence of 2.0 equiv of H_2O at room temperature after 9 h. After the reaction mixture was treated with Ac_2O, 8.35 g of **2ia** was obtained (96.6% isolated yield) with excellent diastereoselectivity [dr (*syn*/*anti*) > 19:1], which is consistent with the result of small-scale reaction. *Anti*-diacetoxylation of methyl cinnamate (**2i**) in a 5.00 g scale was also performed to furnish the desired product efficiently, further demonstrating the efficiency of this methodology.

In conclusion, we have successfully developed a convenient and efficient method for the diastereoselective diacetoxylation of alkenes mediated by $PhI(OAc)_2/BF_3{\cdot}OEt_2$. By using the Woodward–Prevost strategy, the selective preparation of *syn* and *anti* diastereomers can be controlled by adding water to and removing water from the reaction, respectively. A broad range of substrates are compatible with this methodology, and even electron-deficient alkenes (such as α,β-unsaturated esters) can be smoothly dioxygenated at room temperature. Comparing with metal-related procedures, our method uses environmentally benign and low cost $PhI(OAc)_2$ as the oxidant and can be scaled up easily. We anticipate this metal-free methodology will provide an alternative protocol for the preparation of various vicinal diols.

EXPERIMENTAL SECTION

General Procedure A (*Syn* Diacetoxylation of Alkenes). To a solution of alkene (1.0 mmol) and $PhI(OAc)_2$ (322 mg, 1.0 mmol) in AcOH (5.0 mL) and H_2O (36 μL, 2.0 mmol) was added $BF_3{\cdot}OEt_2$ (13 μL, 0.1 mmol). The reaction mixture was stirred at room temperature

dx.doi.org/10.1021/jo201752y | J. Org. Chem. 2011, 76, 9997–10004

for a desired period of time. Then 0.2 equiv of NaOAc was added into the reaction solution, and the solvent was removed under vacuum. The residue was dissolved in pyridine (3 mL) and treated with Ac_2O (0.5 mL) overnight at room temperature. After the solvent was removed under vacuum, the residue was purified by flash chromatography to afford the product.

General Procedure B (*Anti* Diacetoxylation of Alkenes). To a solution of $PhI(OAc)_2$ (322 mg, 1.0 mmol) in AcOH (5.0 mL) and Ac_2O (0.2 mL) was added $BF_3{\cdot}OEt_2$ (13 μL, 0.1 mmol), and the mixture was stirred at room temperature under Ar atmosphere for 30 min before alkene (1.0 mmol) was added. The resulting mixture was stirred at room temperature for a desired period of time and then quenched by 0.2 equiv of NaOAc. After the solvent was removed under vacuum, the residue was purified by flash chromatography to afford the product.

*syn-Acetic Acid 2-Acetoxyindan-1-yl Ester (**2aa**).*[3k] General procedure A, the reaction was performed at room temperature for 5 h, and compound **2aa** was isolated in 93% yield (colorless oil) (*syn*/*anti* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.25 (m, 4H), 6.22 (d, *J* = 5.6 Hz, 1H), 5.57−5.52 (m, 1H), 3.24 (dd, *J* = 6.8, 16 Hz, 1H), 3.13 (dd, *J* = 6.0, 16.0 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 140.1, 138.1, 129.5, 127.3, 125.7, 124.9, 75.0, 73.2, 35.8, 20.8, 20.7.

*anti-Acetic Acid 2-Acetoxyindan-1-yl Ester (**2ab**).*[3k] General procedure B, the reaction was performed at room temperature for 3 h, and compound **2ab** was isolated in 91% yield (colorless oil) (*anti*/*syn* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.24 (m, 4H), 6.25 (d, *J* = 3.6 Hz, 1H), 5.47−5.43 (m, 1H), 3.52 (dd, *J* = 7.2, 16.8 Hz, 1H), 2.90 (dd, *J* = 4.4, 16.4 Hz, 1H), 2.11(s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 140.6, 138.3, 129.5, 127.4, 125.6, 124.9, 80.7, 78.7, 36.8, 21.0, 20.9.

*syn-Acetic Acid 1-Acetoxy-1,2,3,4-tetrahydronaphthalen-2-yl Ester (**2ba**).*[3k] General procedure A, the reaction was performed at room temperature for 5 h, and compound **2ba** was isolated in 80% yield (colorless oil) (*syn*/*anti* = 9.1:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.15 (m, 4H), 6.18 (d, *J* = 3.2 Hz, 1H), 5.25 (dt, *J* = 3.6, 11.2 Hz, 1H), 3.04 (dt, *J* = 5.2, 17.2 Hz, 1H), 2.96−2.88 (m, 1H), 2.27−2.19 (m, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.02−1.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 136.4, 132.7, 130.0, 128.7, 128.6, 126.4, 70.1, 69.3, 27.1, 23.3, 21.1, 21.0.

*anti-Acetic Acid 1-Acetoxy-1,2,3,4-tetrahydronaphthalen-2-yl Ester (**2bb**).*[3k] General procedure B, the reaction was performed at room temperature for 5 h, and compound **2bb** was isolated in 90% yield (colorless oil) (*syn*/*anti* = 1:17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.14 (m, 4H), 6.06 (d, *J* = 6.0 Hz, 1H), 5.21−5.16 (m, 1H), 2.91 (t, *J* = 6.8 Hz, 2H), 2.20−2.14 (m, 1H), 2.11 (s, 3H), 2.06−1.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 136.6, 132.7, 129.0, 128.5, 128.2, 126.4, 71.4, 71.0, 25.6, 24.9, 21.1, 21.0.

*cis-Acetic Acid 2-Hydroxy-2-phenylcyclohexyl Ester (**2ca**).*[3k] General procedure A, 10 h at room temperature, compound **2ca** was isolated in 74% yield (white solid) (*cis*/*trans* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.29 (dd, *J* = 5.2, 10.8 Hz, 1H), 2.25 (br, 1H), 1.92−1.83 (m, 4H), 1.80 (s, 3H), 1.78−1.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 145.9, 128.1, 126.8, 124.6, 76.2, 75.1, 39.6, 27.1, 24.1, 20.9, 20.7.

*cis-Acetic Acid 2-Acetoxy-2-phenylcyclohexyl Ester (**2cb**).*[3n] General procedure B, 2 h at room temperature, compound **2cb** was isolated in 62% yield (white solid) (*cis*/*trans* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.21 (m, 5H), 4.75 (dd, *J* = 4.4, 11.2 Hz, 1H), 3.02−2.98 (br, 1H), 2.18 (s, 3H), 2.13−1.89 (m, 3H), 1.84 (s, 3H), 1.80−1.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.9, 140.2, 127.6, 127.0, 125.1, 83.4, 76.9, 30.9, 27.3, 23.7, 21.6, 20.5 (one carbon is missing due to overlapping).

*syn-Acetic Acid 2-Acetoxy-1,2-diphenylethyl Ester (**2da**).*[3k] General procedure A, the reaction was performed in 10 mL AcOH at room temperature for 2 h by using 0.4 equiv of $BF_3{\cdot}OEt_2$, and compound **2da** was isolated in 76% yield (white solid) (*syn*/*anti* = 12.5:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.13 (m, 5H), 6.05 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 136.1, 128.3, 128.1, 127.4, 77.1, 20.9.

*anti-Acetic Acid 2-Acetoxy-1,2-diphenylethyl Ester (**2db**).*[3k] General procedure B, the reaction was performed in 10 mL AcOH at room temperature for 1 h by using 0.4 equiv of $BF_3{\cdot}OEt_2$, and compound **2db** was isolated in 72% yield (white solid) (*syn*/*anti* = 1:1.4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.27 (m, 3.4H), 7.22−7.13 (m, 6.6H), 6.09 (s, 1H), 6.05 (s, 0.72H), 2.08 (s, 2.5H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.5, 136.1, 136.0, 128.3, 128.2, 128.1, 128.0, 127.5, 127.5, 77.1, 76.4, 20.9, 20.8.

*syn-Acetic Acid 2-Acetoxy-3-benzyloxy-1-phenylpropyl Ester (**2ea**).*[3k] General procedure A, 12 h at room temperature, compound **2ea** was isolated in 70% yield (colorless oil) (*syn*/*anti* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.26 (m, 10H), 6.05 (d, *J* = 7.2 Hz, 1H), 5.39−5.34 (m, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.4 Hz, 1H), 3.49 (dd, *J* = 4.0, 10.8 Hz, 1H), 3.31 (dd, *J* = 4.8, 10.8 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.7, 137.6, 136.6, 128.5, 128.4, 128.3, 127.7, 127.2, 74.1, 73.7, 73.2, 68.0, 20.9, 20.8.

*anti-Acetic Acid 2-Acetoxy-3-benzyloxy-1-phenylpropyl Ester (**2eb**).* General procedure B, 2 h at 50 °C, **2eb** was isolated in 67% yield (colorless oil) (*syn*/*anti* = 1:12.5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 10H), 6.04 (d, *J* = 5.6 Hz, 1H), 5.44−5.40 (m, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 3.60 (dd, *J* = 6.0, 10.8 Hz, 1H), 3.52 (dd, *J* = 4.0, 10.4 Hz, 1H), 2.05 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.4, 137.6, 136.2, 128.3, 128.2, 128.2, 127.7, 127.1, 73.5, 73.1, 73.0, 67.5, 20.9, 20.8; HRMS (ESI) calcd for $C_{20}H_{22}O_5Na$ [M + Na]$^+$ 365.13594, found 365.13584.

*syn-Acetic Acid 2,3-Diacetoxy-1-phenylpropyl Ester (**2fa**) from trans-Cinnamyl Alcohol.* General procedure A, 24 h at room temperature, **2fa** was isolated in 71% yield (colorless oil) (*syn*/*anti* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.34 (m, 5H), 5.98 (d, *J* = 7.2 Hz, 1H), 5.46−5.42 (m, 1H), 4.27 (dd, *J* = 3.6, 12.0 Hz, 1H), 3.81 (dd, *J* = 6.0, 12.4 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.9, 169.6, 135.9, 128.8, 128.6, 127.1, 73.8, 72.2, 62.1, 20.8, 20.7, 20.6; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ [M + Na]$^+$ 317.09956, found 317.09940.

*syn-Acetic Acid 2-Acetoxy-3-ethyl-1-phenylpropyl Ester (**2ga**).* General procedure A, 16 h at room temperature, **2ga** was isolated in 78% yield (colorless oil) (*syn*/*anti* > 99:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (m, 5H), 6.03 (d, *J* = 7.6 Hz, 1H), 5.35−5.31 (m, 1H), 3.46−3.41 (m, 2H), 3.33−3.29 (m, 1H), 3.23 (dd, *J* = 5.2, 11.2 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.6, 136.7, 128.5, 128.4, 127.2, 74.2, 73.8, 68.4, 66.7, 20.9, 20.8, 14.9; HRMS (ESI): calcd for $C_{15}H_{20}O_5Na$ [M + Na]$^+$ 303.12029, found 303.12004.

*anti-Acetic Acid 2-Acetoxy-3-ethyl-1-phenylpropyl Ester (**2gb**).* General procedure B, 2 h at 50 °C, **2gb** was isolated in 71% yield (colorless oil) (*syn*/*anti* = 1:12.5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.33 (m, 5H), 6.05 (d, *J* = 5.2 Hz, 1H), 5.43−5.38 (m, 1H), 3.56 (dd, *J* = 6.4, 10.8 Hz, 1H), 3.50−3.44 (m, 3H), 2.13 (s, 3H), 2.01 (s, 3H), 1.17 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.5, 136.2, 128.3, 127.1, 73.6, 73.2, 68.0, 66.7, 20.9, 20.8, 15.0; HRMS (ESI) calcd for $C_{15}H_{20}O_5Na$ [M + Na]$^+$ 303.12029, found 303.12003.

*cis-1,2-Cyclopentanediol Diacetate (**2ha**).*[21] General procedure A, 48 h at room temperature, **2ha** was isolated in 99% yield (colorless oil) (*cis*/*trans* = 14:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17−5.12 (m, 1H), 2.05 (s, 3H), 2.02−1.61 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 74.0, 28.1, 20.8, 19.0.

*trans-1,2-Cyclopentanediol Diacetate (**2hb**).* General procedure B, 48 h at room temperature, **2hb** was isolated in 36% yield (colorless oil) (*cis*/*trans* = 1:5.7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08−5.05 (m, 1H), 2.16−2.06 (m, 1H), 2.04 (s, 3H), 1.81−1.73 (m, 1H), 1.67−1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 78.9, 30.3, 21.4, 21.0.

*syn-3-Methoxy-3-oxo-1-phenylpropane-1,2-diyl Diacetate (**2ia**).*[22] To the solution of *trans*-methyl cinanmate (1.0 mmol) and $PhI(OAc)_2$ (1.2 mmol) in AcOH (5.0 mL) and H_2O (36 μL, 2.0 mmol) was added $BF_3{\cdot}OEt_2$ (3.0 mmol). The reaction mixture was

dx.doi.org/10.1021/jo201752y | *J. Org. Chem.* 2011, 76, 9997−10004

stirred at room temperature for 8 h. Then 0.5 mL of acetic anhydride was added, and the resulting mixture was stirred at room temperature overnight. The reaction was quenched by adding 3.0 equiv of NaOAc. After the solvent was removed under vacuum, the residue was purified by flash chromatography to afford **2ia** in 99% yield (colorless oil) (*syn*/*anti* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.33 (m, 5H), 6.27 (d, J = 4.0 Hz, 1H), 5.33 (d, J = 4.0 Hz, 1H), 3.70 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.3, 167.4, 135.4, 128.6, 128.4, 126.6, 74.0, 73.6, 52.4, 20.7, 20.2.

*anti-3-Methoxy-3-oxo-1-phenylpropane-1,2-diyl Diacetate (**2ib**).* To the solution of $PhI(OAc)_2$ (1.0 mmol) in AcOH (1.0 mL) and Ac_2O (0.1 mL) was added $BF_3{\cdot}OEt_2$ (3.0 mmol), and the mixture was stirred at room temperature under Ar atmosphere for 30 min before *trans*-methyl cinanmate (1.0 mmol) was added. The resulting mixture was stirred at room temperature for 4 h, and the second batch of $PhI(OAc)_2$ (0.5 mmol) was added. The reaction mixture was further stirred for 2.5 h and then quenched by adding 3.0 equiv of NaOAc. After the solvent was removed under vacuum, the residue was purified by flash chromatography to afford **2ib** in 94% yield (colorless oil) (*syn*/ = 1:9.1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (br, 5H), 6.21 (d, J = 5.2 Hz, 1H), 5.48 (d, J = 5.2 Hz, 1H), 3.71 (s, 3H), 2.12−2.11 (br, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.2, 167.1, 135.0, 128.6, 128.2, 127.2, 73.3, 73.2, 52.2, 20.6, 20.2; HRMS (ESI) calcd for $C_{14}H_{16}O_6Na$ $[M + Na]^+$ 303.08391, found 303.08388.

*syn-3-Methoxy-3-oxo-1-(4-Chlorophenylpropane)-1,2-diyl Diacetate (**2ja**).* Employing the same procedure as **2ia**, 16 h at room temperature, compound **2ja** was isolated in 98% yield (colorless oil) (*syn*/*anti* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 4H), 6.23 (d, J = 4.0 Hz, 1H), 5.30 (d, J = 4.0 Hz, 1H), 3.72 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.3, 167.3, 134.7, 134.1, 128.7, 128.2, 73.8, 73.1, 52.7, 20.7, 20.3; HRMS (ESI) calcd for $C_{14}H_{15}ClO_6Na$ $[M + Na]^+$ 337.04494, found 337.04442.

*anti-3-Methoxy-3-oxo-1-(4-Chlorophenylpropane)-1,2-diyl Diacetate (**2jb**).* Employing the same procedure as **2ib**, **2jb** was isolated in 93% yield (colorless oil) (*syn*/*anti* = 1:6.3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.26 (m, 4H), 6.18 (d, J = 5.2 Hz, 1H), 5.47 (d, J = 5.2 Hz, 1H), 3.72 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.0, 166.9, 134.5, 133.6, 128.6, 128.4, 73.0, 72.5, 52.3, 20.5, 20.2; HRMS (ESI) calcd for $C_{14}H_{15}ClO_6Na$ $[M + Na]^+$ 337.04494, found 337.04477.

*syn-3-Methoxy-3-oxo-1-(4-bromophenylpropane)-1,2-diyl Diacetate (**2ka**).* Employing the same procedure as **2ia**, 20 h at room temperature, compound **2ka** was isolated in 100% yield (colorless oil) (*syn*/*anti* > 19:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.22 (d, J = 4.0 Hz, 1H), 5.30 (d, J = 4.0 Hz, 1H), 3.72 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.3, 167.2, 134.6, 131.6, 128.4, 122.8, 73.7, 73.1, 52.6, 20.7, 20.3; HRMS (ESI) calcd for $C_{14}H_{15}BrO_6Na$ $[M + Na]^+$ 380.99442, found 380.99447.

*anti-3-Methoxy-3-oxo-1-(4-bromophenylpropane)-1,2-diyl Diacetate (**2kb**).* Employing the same procedure as **2ib**, compound **2kb** was isolated in 87% yield (colorless oil) (*syn*/*anti* = 1:7.1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.16 (d, J = 4.8 Hz, 1H), 5.46 (d, J = 4.8 Hz, 1H), 3.72 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.0, 166.9, 134.1, 131.4, 128.9, 122.8, 73.0, 72.6, 52.3, 20.6, 20.3; HRMS (ESI) calcd for $C_{14}H_{15}BrO_6Na$ $[M + Na]^+$ 380.99442, found 380.99429.

*syn-3-Methoxy-3-oxo-1-(4-fluorophenylpropane)-1,2-diyl Diacetate (**2la**).* Employing the same procedure as **2ia**, 12 h at room temperature, compound **2la** was isolated in 99% yield (colorless oil) (*syn*/*anti* = 11:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.34 (m, 2H), 7.05 (t, J = 8.4 Hz, 2H), 6.24 (d, J = 4.0 Hz, 1H), 5.30 (d, J = 4.0 Hz, 1H), 3.70 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.2, 167.2, 162.6 (d, J = 246.1 Hz), 131.3 (d, J = 3.3 Hz), 128.6 (d, J = 8.3 Hz), 115.3 (d, J = 21.6 Hz), 73.8, 73.0, 52.4, 20.6, 20.1; HRMS (ESI) calcd for $C_{14}H_{15}FO_6Na$ $[M + Na]^+$ 321.07449, found 321.07432.

*anti-3-Methoxy-3-oxo-1-(4-fluorophenylpropane)-1,2-diyl Diacetate (**2lb**).* Employing the same procedure as **2ib**, compound **2 lb** was isolated in 97% yield (colorless oil) (*syn*/*anti* = 1:3.4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H), 7.07 (t, J = 8.4 Hz, 2H), 6.19 (d, J = 5.2 Hz, 1H), 5.47 (d, J = 5.2 Hz, 1H), 3.71 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.1, 167.0, 162.7 (d, J = 246.1 Hz), 130.92 (d, J = 3.2 Hz), 129.2 (d, J = 8.3 Hz), 115.2 (d, J = 21.6 Hz), 73.1, 72.5, 52.2, 20.6, 20.2; HRMS (ESI) calcd for $C_{14}H_{15}FO_6Na$ $[M + Na]^+$ 321.07449, found 321.07376.

General Procedure C (Diacetoxylation of Terminal Alkenes). To the solution of alkene (1.0 mmol) and $PhI(OAc)_2$ (322 mg, 1.0 mmol) in AcOH (5.0 mL) and Ac_2O (0.2 mL) was added $BF_3{\cdot}OEt_2$ (13 μL, 0.1 mmol). The resulting mixture was stirred at corresponding temperature for the desired time and then quenched by adding 0.2 equiv of NaOAc. After the solvent was removed under vacuum, the residue was purified by flash chromatography to afford the product.

*1-Phenylethane-1,2-diyl Diacetate (**4a**).*[3k] General procedure C, 2 h at room temperature, **4a** was isolated in 98% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 5H), 6.02 (dd, J = 4.0, 8.0 Hz, 1H), 4.34 (dd, J = 4.0, 12.0 Hz, 1H), 4.28 (dd, J = 8.0, 12.0 Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 169.9, 136.4, 128.5, 128.5, 126.6, 73.2, 66.0, 21.0, 20.6.

*1-p-Tolylethane-1,2-diyl Diacetate (**4b**).*[22] General procedure C, 2 h at room temperature, **4b** was isolated in 84% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.98 (dd, J = 4.4, 7.2 Hz, 1H), 4.34−4.25 (m, 2H), 2.34 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.0, 138.4, 133.5, 129.3, 126.6, 73.2, 66.0, 21.1, 21.0, 20.7.

*1-(4-Fluorophenyl)ethane-1,2-diyl Diacetate (**4c**).*[3k] General procedure C, 2 h at room temperature, **4c** was isolated in 91% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 5.6, 8.4 Hz, 2H), 7.05 (t, J = 8.4 Hz, 2H), 5.99 (dd, J = 4.0, 7.2 Hz, 1H), 4.33−4.24 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 169.7, 162.6 (d, J = 245.8 Hz), 132.3 (d, J = 3.2 Hz), 128.4 (d, J = 8.3 Hz), 115.4 (d, J = 21.5 Hz), 72.5, 65.7, 20.8, 20.5.

*1-[4-(tert-Butyl)phenyl]ethane-1,2-diyl Diacetate (**4d**).* General procedure C, 2 h at room temperature, **4d** was isolated in 90% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.01 (dd, J = 4.0, 8.0 Hz, 1H), 4.33 (dd, J = 4.0, 12.0 Hz, 1H), 4.28 (dd, J = 8.0, 12.0 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 151.5, 133.4, 126.4, 125.4, 73.0, 66.0, 34.5, 31.2, 21.0, 20.6; HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ $[M + Na]^+$ 301.14103, found 301.14073.

*Acetic Acid 2-Acetoxy-3-benzyloxypropyl Ester (**4e**).*[3k] General procedure C, 20 h at 50 °C, **4e** was isolated in 74% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (m, 5H), 5.24−5.19 (m, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.34 (dd, J = 4.0, 12.0 Hz, 1H), 4.19 (dd, J = 6.4, 12.0 Hz, 1H), 3.59 (d, J = 5.2 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.2, 137.6, 128.3, 127.7, 127.6, 73.2, 70.2, 68.0, 62.7, 20.9, 20.6.

*Acetic Acid 2-Acetoxydecyl Ester (**4f**).*[3k] General procedure C, the reaction was performed at room temperature for 8 h by using 0.4 equiv of $BF_3{\cdot}OEt_2$, and **4f** was isolated in 94% yield (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10−5.04 (m, 1H), 4.23 (dd, J = 3.2, 12.0 Hz, 1H), 4.03 (dd, J = 6.4, 12.0 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 1.57−1.56 (br, 2H), 1.30−1.28 (m, 8H), 0.89 (t, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.4, 71.5, 65.0, 31.5, 30.6, 28.9, 25.0, 22.4, 20.9, 20.6, 13.9.

*4-(4-Methoxyphenyl)butane-1,2,4-triyl Triacetate (**4g**).* General procedure C, 24 h at room temperature, **4g** was isolated in 78% yield (colorless oil) (dr = 1.7:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.23 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.80−5.75 (m, 1H), 5.26−5.20 (m, 0.6H), 4.97−4.92 (m, 0.4H), 4.26 (td, J = 3.6, 12.0 Hz, 1H), 4.03 (dd, J = 5.6, 12.0 Hz, 1H), 3.79 (s, 3H), 2.34−2.07 (m, 2H), 2.05−2.03 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.0, 169.9, 159.5, 159.4, 131.9, 131.3, 127.9, 127.8, 114.0, 113.9, 72.4, 71.1, 68.6, 67.8, 65.0, 64.6, 55.2, 55.1, 37.1, 37.0, 21.1, 21.0, 20.8, 20.7, 20.6;

HRMS (ESI) calcd for $C_{17}H_{22}O_7Na$ $[M + Na]^+$ 361.12577, found 361.12553.

Multigram Scale Diacetoxylation of Methyl Cinnamate. - *Syn-Diacetoxylation.* To a solution of *trans*-methyl cinanmate (5.00 g, 30.9 mmol) and $PhI(OAc)_2$ (11.9 g, 37 mmol) in AcOH (50 mL) and H_2O (1.12 mL, 62 mmol) was added $BF_3{\cdot}OEt_2$ (7.8 mL, 62 mmol). The reaction mixture was stirred at room temperature for 9 h. Then 10 mL of acetic anhydride was added and the resulting mixture was stirred at room temperature overnight. The reaction was quenched by adding 500 mg of NaOAc and diluted with 250 mL of ethyl acetate. The mixture was subsequently washed with saturated aqueous NaCl (4 × 200 mL) and saturated aqueous $NaHCO_3$. The organic phase was dried over $MgSO_4$, and filtered. The filtrate was evaporated and then the residue was purified by flash chromatography to afford **2ia** in 96.6% yield (*syn*: *anti* > 19:1).

Anti-diacetoxylation. To a solution of $PhI(OAc)_2$ (9.95 g, 31 mmol) in AcOH (30 mL) and Ac_2O (3.0 mL) was added $BF_3{\cdot}OEt_2$ (11.3 mL, 90 mmol), and the mixture was stirred at room temperature under Ar atmosphere for 0.5 h before *trans*-methyl cinanmate (5.00 g, 30.9 mmol) was added. The resulting mixture was stirred at room temperature for 4 h, and the second batch of $PhI(OAc)_2$ (4.83 g, 15 mmol) was added. The reaction mixture was further stirred for 2 h and then quenched by adding 500 mg of NaOAc. The mixture was diluted with 250 mL of ethyl acetate and washed with saturated aqueous NaCl (3 × 200 mL) and saturated aqueous $NaHCO_3$ consecutively. The organic layer was dried over $MgSO_4$, and filtered. The filtrate was evaporated, and then the residue was purified by flash chromatography to afford **2ib** in 92.8% yield (*anti*/*syn* = 8.3:1).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General procedures and characterization data (^1H and ^{13}C NMR spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: (X.M.) xbmeng@bjmu.edu.cn, (Z.L.) zjli@bjmu.edu.cn.

■ ACKNOWLEDGMENTS

This work was supported by grants from the National Natural Science Foundation of China (NSFC Nos. 21072017 and 20732001) and the National Basic Research Program of China (Grant No. 2012CB822100).

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