JOC The Journal of Organic Chemistry

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$Zn(OTf)_2$-Promoted Chemoselective Esterification of Hydroxyl Group Bearing Carboxylic Acids

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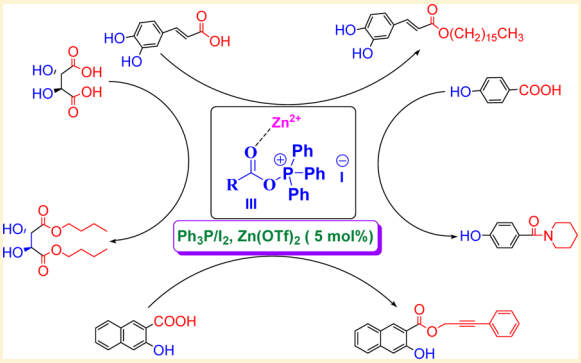
Supporting Information

ABSTRACT: Selective esterification of aliphatic and aromatic carboxylic acids with various alcohols is studied using triphenylphosphine, I_2, and a catalytic amount of $Zn(OTf)_2$. Use of this catalyst allows the formation of esters at a faster rate with good to excellent yield by activating the in situ generated acyloxyphosphonium ion intermediate. During the esterification process, both their aromatic and aliphatic hydroxyl groups are fully preserved from transesterification. The results show that the bulkiness and the reactivity of this doubly activated intermediate **III** control the selectivity and the rate of the reaction, respectively. The method is also useful for direct amidation reactions.



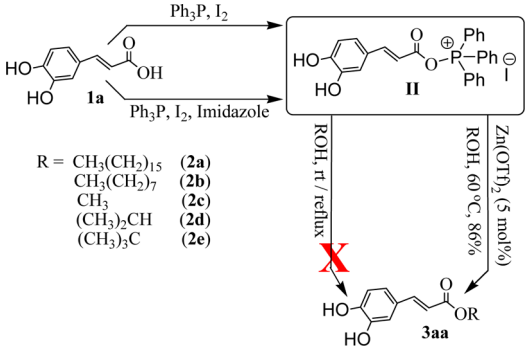
INTRODUCTION

Esterification is one of the essential chemical reactions that have been widely used in the chemical and pharmaceutical industries.[1] This basic chemical transformation has been already accomplished by several chemical methods, but only a few methods offer direct esterification, functional group tolerance, and selective and mild reaction conditions.[2] Hence, there is a clear and unmet need for improved, regioselective, and chemoselective esterification methods.[3] The biologically active ester derivatives like epicatechin gallate, epigallocatechin gallate, caffeic acid, phenethyl ester, and others are good example of such class of complex compounds. Chemoselective synthesis of these compounds in fewer steps using regular esterification reaction conditions are very difficult because of the requirement of other functional group protection or the use of harsh reaction condition and/or a large excess of reactants.[4]

There have been continuous efforts in recent years aimed at developing mild reaction protocols for chemoselective esterification with improved efficiency. Robles and co-workers reported a mild and selective esterification reaction method (Scheme 1)[3c] based on the Garegg–Samuelsson reaction conditions.[3a] Recently, Zhang and co-workers reported the use of hypervalent iodine reagent iodosodilactone as an efficient coupling reagent for direct esterification/amidation with triphenylphosphine and 4-dimethylaminopyridine.[3d] The mechanistic studies showed the generation of acyloxyphosphonium ion as the key intermediate for the formation of ester/amide.

Earlier, Mukaiyama and co-workers reported that oxidative activation of triphenylphosphine by di(2-pyridyl)disulfide causes generation of acyloxyphosphonium ion intermediate from carboxylic acids, followed by reaction with alcohols or amines gives corresponding esters and amides.[3b] All these methods use in situ activation of acid for direct esterification/amidation. Although very attractive, the activation is not always strong and/or selective enough for the complex substrates. Therefore, the key feature for further development of mild and selective esterification methods is that the acid should be activated to more reactive species.

Scheme 1. Model Reaction of $Zn(OTf)_2$-Catalyzed Esterification of Carboxylic Acids

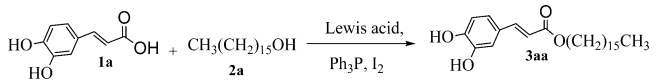


In this context, here we describe a significant improvement of these methods that is mild, highly efficient, and chemoselective using triphenylphosphine, I_2, and a catalytic amount of $Zn(OTf)_2$ as an activator. Hypothetically, there could be a possibility of the reaction proceeding via in situ generation of the zinc-coordinated acyloxyphosphonium ion intermediate, which might increase the electrophilicity well enough to facilitate the intermolecular attack of the alcohol or amine at a faster rate (within 3–5 h) to produce the corresponding ester/amide with good to excellent yield. The reaction

Received: November 20, 2012
Published: January 25, 2013

   dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386–2396

Table 1. Screening of Lewis Acids and Solvent System for the Esterification Reaction[a]



entry	Lewis acid (mol %)	phosphine/I_2	solvent	temp (°C)	time (h)	yield[c] (%)
1	$Zn(OTf)_2$; (1)	Ph_3P/I_2	CH_3CN	100[b]	24	23
2	$Zn(OTf)_2$; (2)	Ph_3P/I_2	CH_3CN	80	12	41
3	**$Zn(OTf)_2$; (5)**	**Ph_3P/I_2**	**CH_3CN**	**60**	**4**	**86**
4	$Zn(OTf)_2$; (5)	Ph_3P/I_2	CH_3CN	80	4	87
5	$Zn(OTf)_2$; (5)	Ph_3P/I_2	CH_3CN	rt	24	ND
6	$Zn(OTf)_2$; (5)	–	CH_3CN	60	24	ND
7	–	Ph_3P/I_2	CH_3CN	60	24	ND
8	$Zn(OTf)_2$; (5)	Ph_3P/I_2	CH_2Cl_2	60[b]	48	26
9	$Zn(OTf)_2$; (5)	Ph_3P/I_2	THF	60	30	20
10	$Zn(OTf)_2$; (5)	Ph_3P/I_2	DMF	60	24	13
11	$Zn(OTf)_2$; (5)	Ph_3P/I_2	toluene	60	24	10
12	$Zn(OAc)_2$; (5)	Ph_3P/I_2	CH_3CN	80	28	10
13	$ZnCl_2$; (5)	Ph_3P/I_2	CH_3CN	80	24	8
14	$Zn(ClO_4)_2{\cdot}6H_2O$; (5)	Ph_3P/I_2	CH_3CN	100[b]	24	7
15	$Cu(OTf)_2$; (5)	Ph_3P/I_2	CH_3CN	100[b]	20	6
16	$FeCl_3$; (5)	Ph_3P/I_2	CH_3CN	80	24	5

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), Lewis acid (1−5 mol %), and alcohol (1.1 equiv) in dry acetonitrile. [b]Reactions were performed under the sealed tube conditions. [c]Isolated yield. ND: not detectable.

condition is functional group tolerant and useful for selective esterification of primary over secondary alcohols. In addition, this method also shows the use of several structurally complex and biologically active alcohol and acid conversion to their corresponding esters, which are proven as a difficult substrate for direct esterification.

RESULT AND DISCUSSION

It is well documented that the Lewis acid catalyzed esterification is very efficient due to the enhancement of electrophilicity of carboxylic acids and anhydrides.[7] Consequently, considerable attention has been directed toward the investigation of a wide variety of Lewis acids such as $CoCl_2$, $InCl_3$, $TiCl_4$, $AgClO_4$, $ZnCl_2$, $CeCl_3$, $Yb(OTf)_3$, $HfCl_4{\cdot}(THF)_2$, and others for their role is esterification.[5] Recently, a catalytic amount of $Zn(OTf)_2$ was used for amide cleavage and esterification of β-hydroxyethylamides.[6a] It was also used for the microwave-irradiated esterification of simple acids and alcohols.[6b] However, to the best of our knowledge, there is no previous report of zinc-catalyzed chemoselective esterification/amidation using Ph_3P/I_2. Although the chemoselective esterifications of phenolic acids and alcohols have been successfully achieved by a few methods, the reaction conditions are either harsh or their purifications are troublesome,[7] whereas the reported Lewis acid catalyzed esterification for most of these phenolic acids/alcohols are very slow and yields are poor to moderate only.[8]

We hypothesized that the combination of in situ carboxylic acid activation followed by the Lewis acid activation of this activated ester intermediate would give us an otherwise unattainable enhanced reactivity. Therefore, to check the feasibility of the Lewis acid catalyzed esterification, caffeic acid (**1a**) and cetyl alcohol (**2a**) were chosen as a substrate for the model reaction, using Ph_3P (2.0 equiv), I_2 (2.0 equiv), a catalytic amount of (5 mol %) $Zn(OTf)_2$ in CH_3CN solvent at 60 °C (Table 1, entry 3). To our delight, we obtained the ester **3aa** with excellent yield of 86% (within 4 h) using this double activation method. Interestingly, the ester **3aa** was not obtained by either only Lewis acid or Robles's protocol using Ph_3P (1.5 equiv), I_2 (1.5 equiv) and imidazole (3.3 equiv), showing the viability of our method of esterification (Scheme 1).[3c]

Encouraged by this excellent result, we decided to optimize the reaction conditions studying several Lewis acids, solvents, and temperature (Table 1). The best result was obtained with 5 mol % of $Zn(OTf)_2$ catalyst with CH_3CN as solvent. However, the use of lower amount of the catalyst resulted in poor yields (Table 1, entries 1 and 2). The reaction was sluggish at lower temperature (entry 5), and there was no significant improvement of ester formation at higher temperature (entry 4).

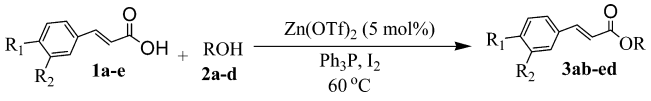
Exclusion of either Ph_3P/I_2 or $Zn(OTf)_2$ did not result in a detectable amount of the desired ester (entries 6 and 7). In the meantime, esterification of palmitic acid with ethanol in the absence of $Zn(OTf)_2$ resulted the desired ester with moderate yield (50%). Thus, both Ph_3P/I_2 and $Zn(OTf)_2$ are indispensable for chemoselctive esterification of less reactive 3,4-dihydroxybenzoic acid. In addition, a set of solvents was also studied, resulting lower yield than with CH_3CN (entries 8−11). The catalytic amount of other nontoxic Lewis acids such as $Cu(OTf)_2$, $FeCl_3$, $InCl_3$, $BF_3{\cdot}OEt_2$, and $AlCl_3$ resulted poor or no yield even at high temperature under similar experimental conditions (Table 1, entries 15 and 16; results are not shown for $InCl_3$, $BF_3{\cdot}OEt_2$, and $AlCl_3$). We also observed that, in the presence of the lower amount of Ph_3P/I_2 (less than 2.0 equiv), the activated intermediate can suffer the attack of a second molecule of the acid to generate significant amounts of anhydride and Ph_3PO.[3c] Therefore, Ph_3P/I_2 (2.0 equiv) and $Zn(OTf)_2$ (5 mol %) in CH_3CN solvent are the best reaction conditions at 60 °C.

We also determine the scope of this methodology for esterification/amidation by analyzing the reactivity of various acids, alcohols, and amines using these optimized reaction conditions. We first tested the esterification of cinnamic acids (**1a−e**) with primary (**2a−c**), secondary (**2d**), and tertiary alcohol (**2e**). The esterification of caffeic acids with primary alcohols produced the desired ester with good to excellent yields (86−90%). The reaction with the secondary alcohol (**2c**)

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

resulted moderate to good yields (70−75%) only but failed with the hindered tertiary alcohol (Table 2).

Table 2. Esterification of Cinnamic Acids under Optimized Reaction Conditions[a]



entry	acid	alcohol	time (h)	product	yield[b] (%)
1	**1a**: R_1 = OH, R_2= OH	**2b**	4	**3ab**	86
2	**1a**: R_1 = OH, R_2= OH	**2d**	5	**3ad**	70
3	**1a**: R_1 = OH, R_2= OH	**2e**	12	**3ae**	ND
4	**1b**: R_1 = OH, R_2= OMe	**2a**	4	**3ba**	86
5	**1b**: R_1 = OH, R_2= OMe	**2b**	4	**3bb**	86
6	**1b**: R_1 = OH, R_2= OMe	**2d**	5	**3bd**	73
7	**1c**: R_1 = OMe, R_2 = OH	**2a**	4	**3ca**	86
8	**1c**: R_1 = OMe, R_2 = OH	**2b**	4	**3cb**	86
9	**1c**: R_1 = OMe, R_2 = OH	**2c**	3.5	**3cc**	90
10	**1c**: R_1 = OMe, R_2 = OH	**2d**	5	**3cd**	73
11	**1d**: R_1 = OH, R_2= H	**2a**	3.5	**3da**	90
12	**1d**: R_1 = OH, R_2= H	**2b**	3.5	**3db**	90
13	**1d**: R_1 = OH, R_2= H	**2d**	5	**3dd**	73
14	**1e**: R_1 = H, R_2= OH	**2a**	3.5	**3ea**	90
15	**1e**: R_1 = H, R_2= OH	**2b**	3.5	**3eb**	90
16	**1e**: R_1 = H, R_2= OH	**2c**	3.5	**3ec**	90
17	**1e**: R_1 = H, R_2= OH	**2d**	5	**3ed**	75

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), $Zn(OTf)_2$ (5 mol %), and alcohol (1.1 equiv) in dry acetonitrile. [b]Isolated yield. ND: not detectable.

The chemoselectivity was established by performing reactions between various hydroxyl group bearing aromatic and aliphatic carboxylic acids and different types of alcohols (Table 3, entries 1−18). The overall yields of these esters are generally good, except for secondary alcohol and gallic acid. Similar results were also obtained for the esterification aliphatic acids with secondary benzylic alcohols (Table 3, entries 17 and 18). The α-hydroxycarboxylic acid (L-tartaric acid) also produced an excellent yield of 98%.[9a] Treatment of unsymmetrical diol using these optimized reaction conditions resulted in exclusively regioselective esterification of primary alcohol (Table 3, entry 11) in the presence of secondary alcohol, showing the high selectivity of this method. Likewise, selective esterification of aliphatic acid in the presence of aromatic acid was also observed (Table 3, entry 12).

To investigate the compatibility of different protecting groups under these reaction conditions, we performed esterification with the protected acids/alcohols. It has already been reported that the presence of acid-sensitive protecting groups do not produce the desire ester with better yield due to either deprotection or labile functional groups suffer nucleophilic attack.[9b] However, we could not find any deprotected/decomposed compound in the case of Ts-, Boc-, Tr-, TBDPS-, TBDMS-, and acetonide- protecting groups of acids/alcohols (Table 3, entries 9−11 and 13−16). The yields of the esterification reactions of protected acids/alcohols were also excellent (89−97%), showing a good selectivity for these compounds.

We also investigated the role of electron-donating and electron-withdrawing functional groups on the selective esterification (Table 4, entries 1−5). The results clearly showed that the presence of $Zn(OTf)_2$ in the reaction medium surmounts the direct effect of these functional groups on esterification. The reactions with secondary alcohols were sluggish, as expected. The esterification is also compatible and selective with the presence of both terminal and internal alkenes and alkynes, and no addition of I_2 over these multiple bonds was observed (Table 3, entries 3 and 7; Table 4, entries 1, 2 and 4). Other functional groups present in carboxylic acids and alcohols such as carbonyl, nitro, bromo, and methoxy were also unaffected under the adopted reaction condition.

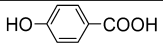
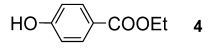
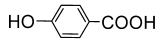
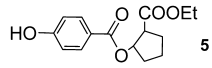
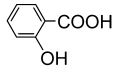
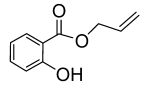
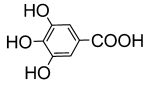
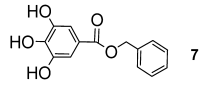
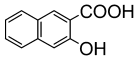
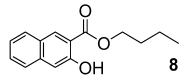
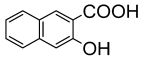
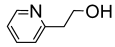
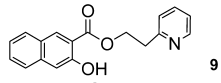
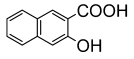
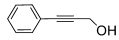
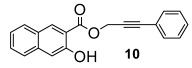
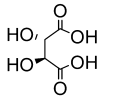
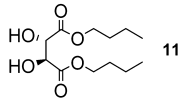
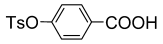
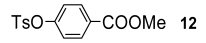
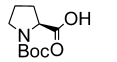
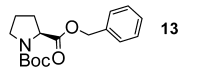
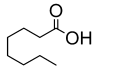
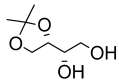
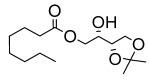
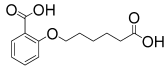
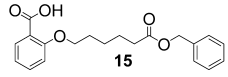
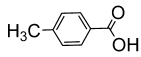
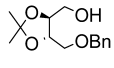
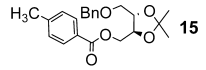
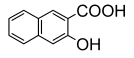
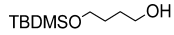
After studying the usefulness of our method of chemoselective esterification for various acids and alcohols, we decided to establish the applicability of this method for the synthesis of biologically active molecules/intermediates. The esterfication of saturated fatty acids (palmitic acid and octanoic acid), unsaturated fatty acid (oleic acid), (+)-menthol, cholesterol, indole-3-propionic acid, quinoline-2-carboxylic (Table 5, entries 1−9), and gallic acid (Table 3, entry 4) resulted in a corresponding ester with moderate to excellent yield, which is very important in the synthesis of complex molecules. This could be due the mild reaction conditions, avoiding possible decomposition or simultaneous reactions with other functional groups within the same molecule. The esterification yields were higher for primary alcohols compared to secondary and tertiary alcohols, as expected. Significantly, when chiral carboxylic acids and alcohols were used, retention of the stereochemistry was also observed. The chiral ester **13** and **21** showed >99% ee as measured by HPLC (Figure S38−S41, Supporting Information).

To extend the use of this methodology beyond esterification, we tested amidation reaction. The amidation of various carboxylic acids with *n*-butylamine, benzylamine, (pyridin-2-yl)methanamine, *N*′,*N*′-dimethylethane-1,2-diamine and piperidine under the optimized reaction condition of esterification resulted the desired amide with good to excellent yields of 75−98% (Table 6, entries 1−8). Therefore, this reaction condition is a good alternative to the methods known for amidation. It is worth noting that adopted reaction condition worked well for several hetercylic substrates (Table 3, entries 6 and 10; Table 5 entries 5, 6, 8, and 9; Table 6, entries 4−8).

The results obtained in our study suggest that the reaction between Ph_3P and I_2 yielded the triphenylphosphonium iodide intermediate (**I**), and subsequent attack of carboxylic acid generates the acyloxyphosphonium ion intermediate (**II**), in accordance with the Garegg−Samuelsson reaction mechanism,[3a,10] whereas addition of $Zn(OTf)_2$ to intermediate (**II**) proposed the formation of zinc-coordinated active intermediate (**III**) as reported earlier.[6a] This could enhance the electrophilicity toward a carbonyl center of acyloxyphosponium ion intermediate (**III**) and facilitate the nucleophilic attack of the alcohol. This is the key step for selectivity of our esterification reaction (Scheme 2). The generation of these proposed intermediates in the reaction mixture was studied by ^{13}C NMR and ^{31}P NMR spectroscopy as shown in the Figure 1 (for full spectra, see Figures S1 and S2, Supporting Information). The NMR spectra were collected after addition of each reagent with a sufficient time gap.[10a] The observed changes in their chemical shifts (as shown in Tables S1 and S2, Supporting Information) indicate the formation of intermediate **I**[10b] and **II**. The downfield shift of the ^{31}P NMR signal ($\Delta\delta$ = 3.0 ppm) and the ^{13}C NMR signal for the C═O group ($\Delta\delta$ = 0.5 ppm), after addition of $Zn(OTf)_2$ to the intermediate **II**, indicate the formation of intermediate **III**. These spectral changes also

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

Table 3. Chemoselective Esterification of Carboxylic Acids and Alcohols under Optimized Reaction Conditions[a]

Entry	Acid	Alcohol	Time (h)	Product	Yield (%)[b]
1			4	 **4**	91
2			5	 **5**	69
3			4	 **6**	87
4			4	 **7**	65
5			4	 **8**	90
6			4	 **9**	88
7			4	 **10**	81
8			4	 **11**	98[c]
9		**2c**	4	 **12**	89
10			4	 **13**	89
11			3.5	 **14**	97
12			4	 **15**	96
13			4	 **15**	95
14			4	**17**	97
15			5	**18**	75
16			4	**19**	98
17			6	**20**	61
18			6	**21**	70

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), $Zn(OTf)_2$ (5 mol %), and alcohol (1.1 equiv) in dry acetonitrile. [b]Isolated yield. [c]Ph_3P (4.0 equiv), I_2 (4.0 equiv), $Zn(OTf)_2$ (10 mol %), and alcohol (2.2 equiv) in dry acetonitrile.

propose the coordination of zinc ion to the C═O group of intermediate **III**.

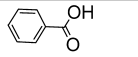
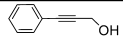
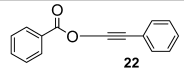
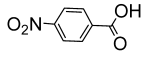
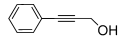
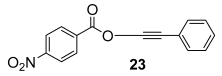
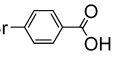
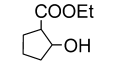
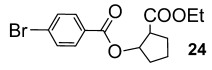
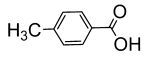
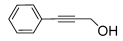
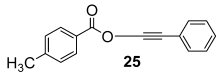
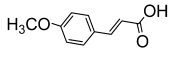
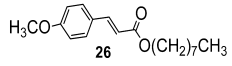
Selectivity of esterification under this optimized reaction conditions can be explained by the formation of much hindered intermediate **III**. When this intermediate suffers attack by more hindered secondary and tertiary alcohols, a bigger steric repulsion between the ligands of phosphine and substituent of the alcohols minimizes the probability of nucleophilic addition.[11] Under this optimized reaction condition, the phenolic hydroxyl group present on either substrate would not essentially take part in the reactions, even though Ph_3P and I_2 have been largely employed for the synthesis of iodoalkanes. Therefore, the reaction mechanism rules out phenolic carbons as substrate for S_N2-type reactions, while the generation of the nucleophilic species due to deprotection, a relatively weak base, secures that carboxylate rather than phenolates are formed, in the presence of stoichiometric amounts of reagents. This could be the main reason behind the selectivity of esterification.

■ CONCLUSION

Therefore, we have developed a mild, safe, and highly chemoselective esterification/amidation reaction method for

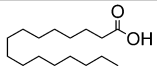
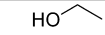
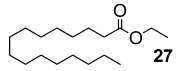
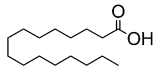
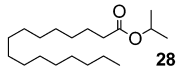
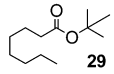
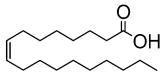
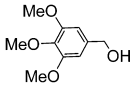
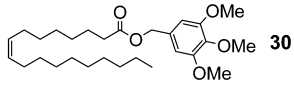
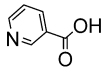
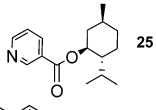
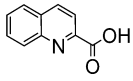
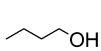
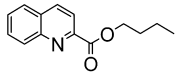
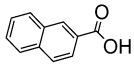
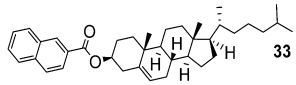
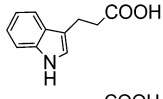
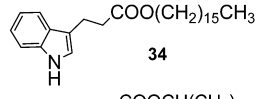
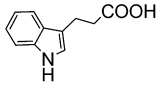
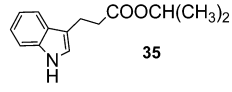
dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

Table 4. Substrate Scope of Esterification under Optimized Reaction Conditions[a]

Entry	Acid	Alcohol	Time (h)	Product	Yield (%)[b]
1			3.5	 22	96
2			3.5	 23	98
3			5	 24	76
4			4	 25	95
5		**2b**	4	 26	93

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), $Zn(OTf)_2$ (5 mol %), and alcohol (1.1 equiv) in dry acetonitrile. [b]Isolated yield.

Table 5. Synthesis of Biologically Active Esters[a]

Entry	Acid	Alcohol	Time (h)	Product	Yield (%)[b]
1			3.5	 27	98
2		2d	5	 28	77
3		2e	6	 29	20
4			3.5	 30	98
5			5	 25	73
6			3.5	 32	96
7		Cholesterol	5	 33	72
8		**2a**	4	 34	97
9		**2d**	5	 35	80

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), $Zn(OTf)_2$ (5 mol %), and alcohol (1.1 equiv) in dry acetonitrile. [b]Isolated yield.

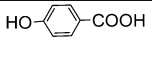
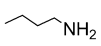
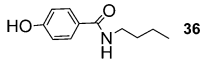
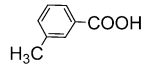
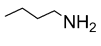
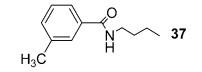
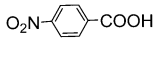
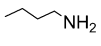
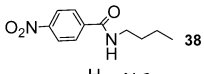
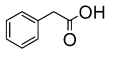
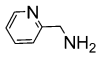
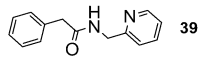
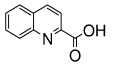
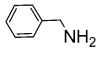
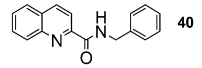
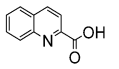
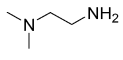
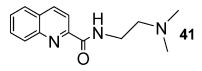
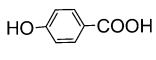
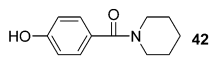
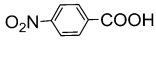
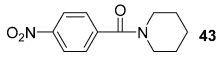
aromatic and aliphatic carboxylic acids in the presence of triphenylphosphine, I_2, and zinc triflate. In particular, we have demonstrated the utility of zinc ion assisted activation of acyloxyphosphonium ion intermediate in the selective esterification of hydroxyl group bearing carboxylic acids. In addition, we have shown selective esterification of primary alcohols in the presence of sterically hindered alcohols and selective esterification of aliphatic carboxylic acid over aromatic carboxylic acid, which may be of interest in the synthesis of polyfunctionalized substrates. We believe this facile and efficient protocol will serve as a useful alternative to the existing esterification methods and will decrease the burden of protecting groups in the synthesis of several complex molecules, which constitutes an important objective in modern organic chemistry.

EXPERIMENTAL SECTION

General Information. All reagents were purchased from different commercial sources and used directly without further purification. Dry solvents were obtained according to the reported procedures. Column chromatography was performed using 60−120 mesh silica gel. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F254 (0.25 mm). ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz, respectively. Coupling constants (J values) are reported in hertz, and chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane using residual chloroform (δ = 7.24 for ^{1}H NMR, δ = 77.23 for ^{13}C NMR) as an internal standard. ^{31}P NMR spectra

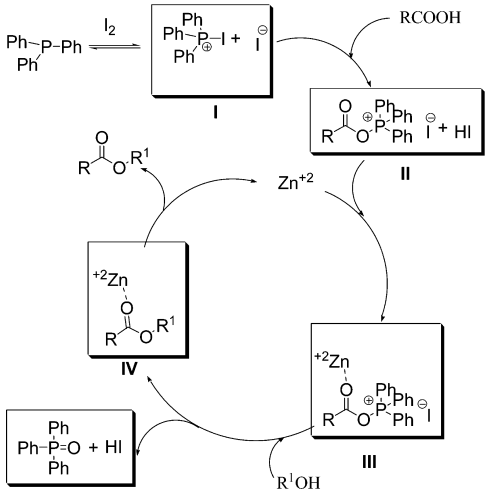
dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

Table 6. Amidation of Carboxylic Acids under Optimized Reaction Conditions[a]

Entry	Acid	Amine	Time (h)	Product	Yield (%)[b]
1			4	 **36**	85
2			4	 **37**	94
3			4	 **38**	98
4			4	 **39**	95
5			4	 **40**	95
6			4	 **41**	98
7			6	 **42**	75
8			6	 **43**	78

[a]Performed with carboxylic acid (1.0 equiv), Ph_3P (2.0 equiv), I_2 (2.0 equiv), $Zn(OTf)_2$ (5 mol %), and amine (1.1 equiv) in dry acetonitrile. [b]Isolated yield.

Scheme 2. Possible Reaction Mechanism for the $Zn(OTf)_2$-Mediated Esterification



were recorded in $CDCl_3$ and calibrated to external standard 85% H_3PO_4. Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), m (multiplet), and br (broadened). Melting points were determined using a melting point apparatus and are uncorrected. Mass spectra were recorded using a Q-TOF mass spectrometry system, and data were analyzed using the built-in software. Infrared (IR) spectra were recorded in KBr using a FT-IR spectrophotometer from 4000 to 450 cm^{-1}. Optical rotations were measured on a polarimeter at room temperature. HPLC spectra were recorded by using a Chiralcel OD column and *n*-hexane/2-propanol as the eluent.

General Procedure for the $Zn(OTf)_2$-Catalyzed Esterification/Amidation of Carboxylic Acids. To a stirring solution of I_2 (2.0 equiv) and triphenylphosphine (2.0 equiv) in dry acetonitrile (10 mL) was added carboxylic acid (1.0 equiv) under a N_2 atmosphere, the reaction mixture was stirred for 10 min, and then (5 mol %) of $Zn(OTf)_2$ was added. Stirring was continued for 30 min at 60 °C, and then alcohol/amine (1.1 equiv) in dry acetonitrile was added. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in ethylacetate and washed with saturated $NaHCO_3$ followed by brine solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography with silica gel and a gradient solvent system of ethylacetate to hexane yielded the target compound. Synthesized compounds were properly characterized by NMR, HRMS (ESI), and melting points.

Characterization of the Synthesized Compounds. *(E)-Hexadecyl 3-(3,4-dihydroxyphenyl)acrylate (**3aa**):*[12a,b] white solid (97 mg, 86%); mp 105−107 °C (lit.[12a] mp 105−107 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm} 7.48 (d, 1H, *J* = 16.0 Hz), 7.04 (s, 1H), 6.88 (d, 1H, *J* = 8.0 Hz), 6.80(d, 1H, *J* = 8.0 Hz), 6.19 (d, 1H, *J* = 16.0 Hz), 4.13 (t, 2H, *J* = 6.8 Hz), 1.69−1.59 (m, 2H), 1.25 (m, 26H), 0.87 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ_{ppm} 166.7, 147.2, 144.6, 143.9, 125.1, 120.3, 114.8, 113.5, 113.4, 63.1, 30.7, 28.5, 28.1, 27.7, 24.8, 21.5, 13.1; HRMS (ESI) calcd for $C_{25}H_{41}O_4$ $[M + H]^+$ 405.3005, found 405.3006.

*(E)-Octyl 3-(3,4-dihydroxyphenyl)acrylate (**3ab**):*[12a,b] white solid (70 mg, 86%); mp 65−66 °C (lit.[12a] mp 64−66 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.54 (d, 1H, *J* = 16.0 Hz), 7.09 (s, 1H), 6.92 (d, 1H, *J* = 8.0 Hz), 6.85 (d, 1H, *J* = 8.0 Hz), 6.23 (d, 1H, *J* = 16.0 Hz), 4.16 (t, 2H, *J* = 6.8 Hz), 1.70−1.65 (m, 2H), 1.38−1.28 (br s, 10H), 0.79 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ_{ppm} 166.6, 147.1, 144.5, 143.9, 125.1, 120.4, 114.8, 113.5, 113.4, 63.1, 30.6, 28.1, 28.0, 27.6, 24.8, 21.4, 13.0; HRMS (ESI) calcd for $C_{17}H_{25}O_4$ $[M + H]^+$ 293.1753, found 293.1757.

*(E)-Isopropyl 3-(3,4-dihydroxyphenyl)acrylate (**3ad**):*[12c] colorless oil (43 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.54 (d, 1H, *J* = 16.0 Hz), 7.11 (s, 1H), 6.97 (d, 1H, *J* = 8.0 Hz), 6.81 (d, 1H, *J* = 8.0 Hz), 6.24 (d, 1H, *J* = 16.0 Hz), 5.13−5.02 (m, 1H), 1.36 (d, 6H, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ_{ppm} 166.0, 147.1, 144.5, 143.9, 125.1, 120.4, 114.8, 113.5, 113.4, 68.3, 22.5; HRMS (ESI) calcd for $C_{12}H_{15}O_4$ $[M + H]^+$ 223.0970, found 223.0974.

*(E)-Hexadecyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (**3ba**):*[12a] white solid (93 mg, 86%); mp 65−66 °C (lit.[12a] mp 65−67 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.56 (d, 1H, *J* = 16.0 Hz), 7.11 (s, 1H), 7.00 (d, 1H, *J* = 8.4 Hz), 6.81 (d, 1H, *J* = 8.4 Hz), 6.27 (d, 1H, *J* = 16.0 Hz), 5.73 (br s, 1H), 4.15 (t, 2H, *J* = 6.6 Hz), 3.89 (s, 3H), 1.68−1.65 (m, 2H), 1.27−1.23 (br s, 26H), 0.85 (t, 3H, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.6, 148.7, 146.1, 144.6, 128.4, 121.9, 116.7, 113.3, 110.8, 64.8, 56.2, 32.1, 29.9, 29.6, 29.0, 26.2, 22.9, 14.3; HRMS (ESI) calcd for $C_{26}H_{43}O_4$ $[M + H]^+$ 419.3161, found 419.3160.

*(E)-Octyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (**3bb**):*[12a] colorless oil (63 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.56 (d, 1H, *J* = 16.0 Hz), 7.11 (s, 1H), 7.00 (d, 1H, *J* = 8.4 Hz), 6.81 (d, 1H, *J* = 8.4 Hz), 6.02 (d, 1H, *J* = 16.0 Hz), 5.73 (br s, 1H), 4.15 (t, 2H, *J* = 6.8 Hz), 3.89 (s, 3H), 1.70−1.63 (m, 2H), 1.36−1.23 (br s, 10H), 0.86 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.7, 148.8,

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

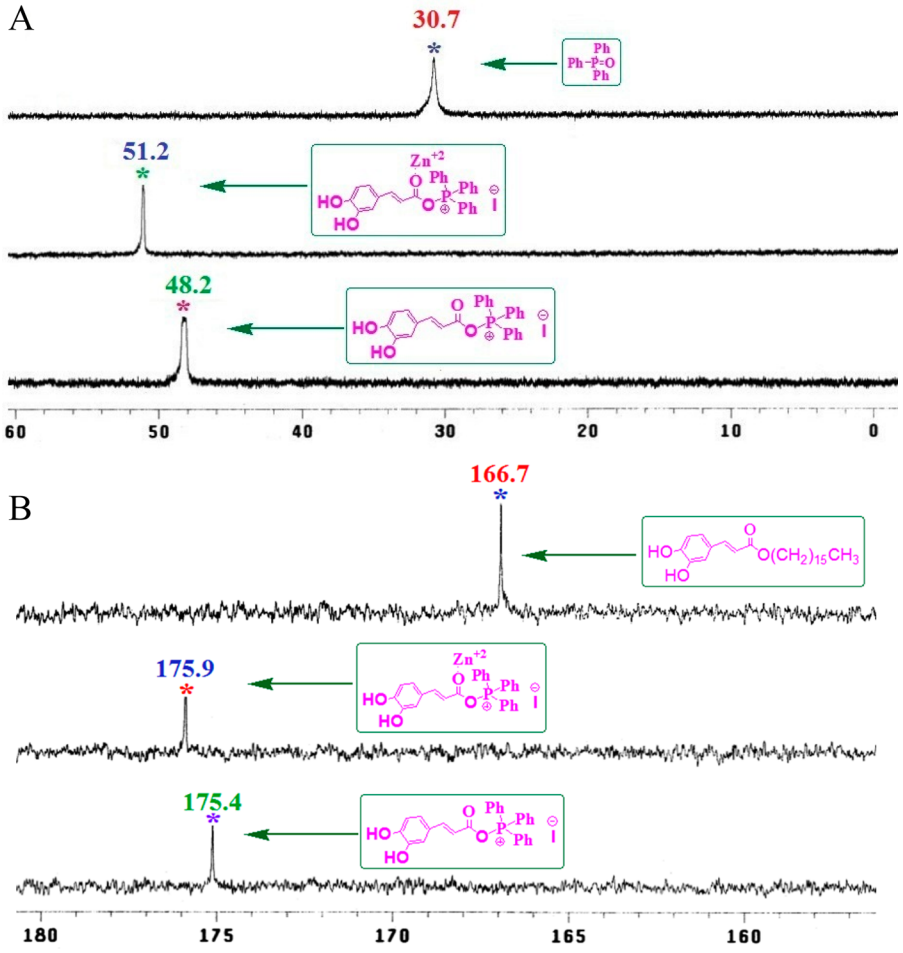


Figure 1. Monitoring the progress of reaction by ^{31}P NMR (A) and ^{13}C NMR spectra (B) in $CDCl_3$.

146.0, 144.6, 128.2, 121.9, 116.3, 113.3, 110.7, 64.8, 56.0, 31.9, 29.8, 29.3, 28.9, 26.1, 22.8, 14.2; HRMS (ESI) calcd for $C_{18}H_{27}O_4$ $[M + H]^+$ 307.1909, found 307.1911.

(E)-Isopropyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (**3bd**):[12d] colorless oil (45 mg, 73%); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.49 (d, 1H, J = 16.0 Hz), 7.05 (s, 1H), 6.93 (d, 1H, J = 8.4 Hz), 6.75 (d, 1H, J = 8.4 Hz), 6.19 (d, 1H, J = 16.0 Hz), 5.78 (br s, 1H), 5.08−5.02 (m, 1H), 3.82 (s, 3H), 1.23 (d, 6H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.1, 148.7, 146.1, 144.4, 128.3, 121.8, 116.9, 113.3, 110.8, 67.8, 56.1, 22.1; HRMS (ESI) calcd for $C_{13}H_{17}O_4$ $[M + H]^+$ 237.1127, found 237.1127.

(E)-Hexadecyl 3-(3-hydroxy-4-methoxyphenyl)acrylate (**3ca**):[12a] white solid (93 mg, 86%); mp 69−70 °C (lit.[12a] mp 69−70 °C); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.58 (d, 1H, J = 16.0 Hz), 7.04 (d, 1H, J = 8.0 Hz), 7.00 (s, 1H), 6.88 (d, 1H, J = 8.0 Hz), 6.27 (d, 1H, J = 16.0 Hz), 6.04 (br s, 1H), 4.16 (t, 2H, J = 6.8 Hz), 3.89 (s, 3H), 1.69−1.61 (m, 2H), 1.28−1.18 (m, 26H), 0.85 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.7, 148.2, 147.02, 144.9, 127.2, 123.2, 115.8, 115.0, 109.5, 64.8, 56.1, 32.1, 29.9, 29.5, 29.0, 26.2, 22.9, 14.3; HRMS (ESI) calcd for $C_{26}H_{43}O_4$ $[M + H]^+$ 419.3161, found 419.3162.

(E)-Octyl 3-(3-hydroxy-4-methoxyphenyl)acrylate (**3cb**):[12a] colorless oil (68 mg, 86%); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.59 (d, 1H, J = 16.0 Hz), 7.05 (d, 1H, J = 8.4 Hz), 7.00 (s, 1H), 6.89 (d, 1H, J = 8.4 Hz), 6.27 (d, 1H, J = 16.0 Hz), 5.93 (br s, 1H), 4.16 (t, 2H, J = 6.8 Hz), 3.90 (s, 3H), 1.69−1.64 (m, 2H), 1.36−1.23 (m, 10H), 0.86 (t, 3H, J = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.6, 148.2, 147.0, 144.8, 127.3, 123.2, 115.9, 114.9, 109.6, 64.8, 56.1, 32.0, 29.9, 29.3, 29.0, 26.2, 22.8, 14.3; HRMS (ESI) calcd for $C_{18}H_{27}O_4$ $[M + H]^+$ 307.1909, found 307.1910.

(E)-Methyl 3-(3-hydroxy-4-methoxyphenyl)acrylate (**3cc**):[12e] colorless oil (48 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.60 (d, 1H, J = 16.0 Hz), 7.13 (s, 1H), 7.02 (d, 1H, J = 8.8 Hz), 6.83 (d, 1H, J = 8.8 Hz), 6.29(d, 1H, J = 16.0 Hz), 5.85 (br s, 1H), 3.91 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.9, 148.8, 146.1, 144.9, 128.2, 122.0, 115.9, 113.2, 110.7, 56.2, 51.8; HRMS (ESI) calcd for $C_{11}H_{13}O_4$ $[M + H]^+$ 209.0814, found 209.0812.

(E)-Isopropyl 3-(3-hydroxy-4-methoxyphenyl)acrylate (**3cd**):[12f] colorless oil (45 mg, 73%); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.57 (d, 1H, J = 16.0 Hz), 7.13 (s, 1H), 7.02 (d, 1H, J = 8.0 Hz), 6.83 (d, 1H, J = 8.0 Hz), 6.27 (d, 1H, J = 16.0 Hz), 5.76 (br s, 1H), 5.15−5.10 (m, 1H), 3.92 (s, 3H), 1.30 (d, 6H, J = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.0, 148.6, 146.1, 144.3, 128.4, 121.9, 117.0, 113.2, 110.7, 67.8, 56.2, 22.1; HRMS (ESI) calcd for $C_{13}H_{17}O_4$ $[M + H]^+$ 237.1127, found 237.1127.

(E)-Hexadecyl 3-(4-hydroxyphenyl)acrylate (**3da**):[12a] white solid (107 mg, 90%); mp 84−85 °C (lit.[12a] mp 84−85 °C); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.61 (d, 1H, J = 16.0 Hz), 7.39 (d, 2H, J = 8.8 Hz), 6.84 (d, 2H, J = 8.8 Hz), 6.60 (br s, 1H), 6.27 (d, 1H, J = 16.0 Hz), 4.17 (t, 2H, J = 6.8 Hz), 1.69−1.65 (m, 2H), 1.31−1.23 (m, 26H), 0.85 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.4, 158.4, 145.0, 130.2, 127.1, 116.1, 115.4, 65.1, 32.1, 29.9, 29.6, 29.5, 28.9, 26.2, 22.9, 14.2; HRMS (ESI) calcd for $C_{25}H_{41}O_3$ $[M + H]^+$ 389.3056, found 389.3055.

(E)-Octyl 3-(4-hydroxyphenyl)acrylate (**3db**):[12a] yellow oil (76 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.61 (d, 1H, J = 16.0 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.16 (br, s, 1H), 6.86 (d, 2H, J = 8.4 Hz), 6.28 (d, 1H, J = 16.0 Hz), 4.18(t, 2H, J = 6.8 Hz), 1.71−1.64 (m, 2H), 1.37−1.23 (m, 10H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.7, 158.7, 145.4, 130.2, 126.8, 116.2, 115.0, 65.2, 31.9,

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

29.9, 29.4, 29.3, 28.8, 26.1, 22.8, 14.2; HRMS (ESI) calcd for $C_{17}H_{25}O_3$ $[M + H]^+$ 277.1804, found 277.1805.

*(E)-Isopropyl 3-(4-hydroxyphenyl)acrylate (**3dd**):*[12g] colorless oil (46 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.59 (d, 1H, J = 16.0 Hz), 7.39 (d, 2H, J = 8.4 Hz), 6.83 (d, 2H, J = 8.8 Hz), 6.25 (d, 1H, J = 16.0 Hz), 5.14−5.08 (m, 1H), 1.29 (d, 6H, J = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.9, 158.6, 144.9, 130.2, 127.0, 116.2, 115.8, 68.3, 22.1; HRMS (ESI) calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1025.

*(E)-Hexadecyl 3-(3-hydroxyphenyl)acrylate (**3ea**):*[12a] white solid (107 mg, 90%); mp 83−85 °C (lit.[12a] mp 83−85 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.62 (d, 1H, J = 16.0 Hz), 7.23 (t, 1H, J = 7.8 Hz), 7.10 (d, 1H, J = 8.0 Hz), 7.02 (s, 1H), 6.87 (d, 1H, J = 8.0 Hz), 6.40 (d, 1H, J = 16.0 Hz), 4.20 (t, 2H, J = 6.8 Hz), 1.59−1.55 (m, 2H), 1.26 (br s, 26H), 0.88 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.9, 156.7, 145.1, 136.0, 130.2, 120.7, 118.4, 117.9, 114.9, 65.3, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 28.9, 26.2, 25.9, 22.9, 14.3; HRMS (ESI) calcd for $C_{25}H_{41}O_3$ $[M + H]^+$ 389.3056, found 389.3055.

*(E)-Octyl 3-(3-hydroxyphenyl)acrylate (**3eb**):*[12a] yellow oil (76 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.62 (d, 1H, J = 16.0 Hz), 7.24 (t, 1H, J = 8.0 Hz), 7.08 (d, 1H, J = 8.0 Hz),7.02 (s, 1H), 6.88 (d, 1H, J = 8.0 Hz), 6.41 (d, 1H, J = 16.0 Hz), 5.96 (br s, 1H), 4.20 (t, 2H, J = 6.8 Hz), 1.61 (m, 2H), 1.79−1.66 (m, 10H), 0.87 (t, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.1, 156.7, 145.3, 135.9, 130.2, 120.7, 118.3, 117.9, 114.9, 65.3, 31.9, 29.4, 29.3, 28.8, 26.1, 22.8, 14.3; HRMS (ESI) calcd for $C_{17}H_{25}O_3$ $[M + 1]^+$ 277.1804, found 277.1806.

*(E)-Methyl 3-(3-hydroxyphenyl)acrylate (**3ec**):*[12h] yellow oil (49 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.64 (d, 1H, J = 16.0 Hz), 7.24 (t, 1H, J = 8.0 Hz), 7.07 (d, 1H, J = 7.6 Hz), 7.04 (s, 1H), 6.90 (d, 1H, J = 8.0 Hz), 6.40 (d, 1H, J = 16 Hz), 3.82(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.3, 156.6, 145.5, 135.9, 130.3, 120.8, 118.0, 114.8, 52.2; HRMS (ESI) calcd for $C_{10}H_{11}O_3$ $[M + H]^+$ 179.0708, found 179.0710.

*(E)-Isopropyl 3-(3-hydroxyphenyl)acrylate (**3ed**):*[12i] colorless oil (47 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.58 (d,1H, J = 16.0 Hz), 7.21 (t, 1H, J = 8.0 Hz), 7.07 (d, 1H, J = 8.0 Hz), 6.97 (s, 1H), 6.84 (d, 1H, J = 8.0 Hz), 6.36 (d, 1H, J = 16.0 Hz), 5.15−5.08 (m, 1H), 1.30 (d, 6H, J = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.4, 156.6, 144.9, 136.0, 130.3, 120.7, 118.9, 117.8, 114.8, 68.5, 22.1; HRMS (ESI) calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1022.

*Ethyl 4-hydroxybenzoate (**4**):*[13a] white solid (55 mg, 91%); mp 116−118 °C (lit.[13a] mp 114−117 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.92 (d, 2H, J = 8.4 Hz), 6.86 (d, 2H, J = 8.8 Hz), 4.85 (br s, 1H), 4.33 (q, 2H, J = 7.1 Hz), 1.36 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.3, 160.6, 132.1, 122.7, 115.5, 61.2 14.5; HRMS (ESI) calcd for $C_9H_{11}O_3$ $[M + H]^+$ 167.0708, found 167.0707.

*2-(Ethoxycarbonyl)cyclopentyl 4-hydroxybenzoate (**5**):*[13b] colorless oil (69 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.46 (d, 2H, J = 8.8 Hz), 6.81 (d, 2H, J = 8.4 Hz), 5.68−5.63 (m, 1H), 4.23−4.20 (q, 2H, J = 7.3 Hz), 3.27−3.25 (m, 1H), 2.17−2.00 (m, 2H), 1.96−1.81 (m, 4H), 1.23 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.5, 167.3, 160.6, 131.1, 122.7, 115.5, 79.7, 61.2, 50.3, 33.2, 29.3, 23.1, 14.5; HRMS (ESI) calcd for $C_{15}H_{19}O_5$ $[M + H]^+$ 279.1232, found 279.1234.

*Allyl 2-hydroxybenzoate (**6**):*[13c] white solid (56 mg, 87%); mp 101−102 °C (lit.[13] mp 100−102 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 10.73 (s, 1H), 7.86 (d, 1H, J = 8.0 Hz), 7.44 (t, 1H, J = 8.0 Hz), 6.96 (d, 1H, J = 8.4 Hz), 6.86 (t, 1H, J = 7.8 Hz), 6.01 (m, 1H), 5.42 (dd, 1H, J = 17.2, 1.6 Hz), 5.30 (dd, 1H, J = 17.2, 1.6 Hz), 4.83 (dd, 2H, J = 5.6, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 170.0, 162.0, 136.0, 131.8, 130.1, 119.4, 119.1, 117.8, 112.6, 66.0; ; HRMS (ESI) calcd for $C_{10}H_{11}O_3$ $[M + H]^+$: 179.0708, found 179.0706.

*Benzyl 3,4,5-trihydroxybenzoate (**7**):*[13d] white solid (50 mg, 65%); mp 89−90 °C (lit.[13d] mp 90−90.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.41−7.32 (m, 7H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 166.4, 149.3, 137.7, 136.7, 136.1, 129.1, 128.8, 128.5, 128.3, 126.2, 110.0, 67.1; HRMS (ESI) calcd for $C_{14}H_{13}O_5$ $[M + H]^+$: 261.0763, found 261.0765.

*Butyl 3-hydroxynaphthalene-2-carboxylate (**8**):*[13e] yellow oil (59 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 10.43 (br, s, 1H), 8.30 (s, 1H), 7.64 (d, 1H, J = 8.4 Hz), 7.51 (d, 1H, J = 8.4 Hz), 7.33 (t, 1H, J = 7.6 Hz), 7.23 (s, 1H), 7.16 (t, 1H, J = 7.6 Hz), 4.27 (t, 2H, J = 6.6 Hz), 1.75−1.61 (m, 2H), 1.41−1.23 (m, 2H), 0.89 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 170.0, 156.5, 137.9, 132.3, 129.5, 129.3, 127.1, 126.4, 123.9, 114.5, 111.7, 65.7, 30.7, 19.4, 13.9; HRMS (ESI) calcd for $C_{15}H_{17}O_3$ $[M + H]^+$ 245.1178, found 245.1176.

*2-(Pyridin-2-yl)ethyl 3-hydroxynaphthalene-2-carboxylate (**9**):* yellow solid (69 mg, 88%); mp 95−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 10.42 (br, s, 1H), 8.57 (d, 1H, J = 0.8 Hz), 8.35 (s, 1H), 7.73 (d, 1H, J = 8.4 Hz), 7.65−7.61 (m, 2H), 7.45 (t, 1H, J = 7.4 Hz), 7.30−7.23 (m, 3H), 7.17 (t, 1H, J = 6.3 Hz), 4.79 (t, 2H. J = 6.6 Hz), 3.31 (t, 2H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 169.7, 157.6, 156.3, 149.6, 137.9, 136.8, 132.5, 129.3, 129.2, 127.1, 126.3, 124.0, 123.7, 122.0, 114.4, 111.7, 64.8, 37.2; HRMS (ESI) calcd for $C_{18}H_{16}NO_3$ $[M + H]^+$ 294.1130, found 294.1131.

*3-Phenylprop-2-ynyl 3-hydroxynaphthalene-2-carboxylate (**10**):* gray solid (65 mg, 81%); mp 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 10.27 (br, s, 1H), 8.58 (s, 1H), 7.82 (d, 1H, J = 8.4 Hz), 7.68 (d, 1H, J = 8.4 Hz), 7.52−7.48 (m, 3H), 7.36−7.31 (m, 5H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 169.4, 156.4, 138.2, 133.0, 132.2, 129.5, 129.2, 128.5, 127.2, 126.5, 124.2, 122.1, 113.9, 111.9, 87.6, 82.4, 54.1; HRMS (ESI) calcd for $C_{20}H_{15}O_3$ $[M + H]^+$ 303.1021, found 303.1023.

*(2S,3S)-Dibutyl 2,3-dihydroxysuccinate (**11**):*[13f] colorless oil (86 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 4.47 (s, 2H), 4.18 (m, 4H), 3.43 (br s, 2H), 1.60 (m, 4H), 1.33 (m, 4H), 0.87 (t, 6H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 171.8, 72.3, 66.3, 30.6, 19.1, 13.7; HRMS (ESI) calcd for $C_{12}H_{22}O_6Na^+$ $[M + Na]^+$ 285.1314, found 285.1313.

*4-(Methoxycarbonyl)phenyl 4-methylbenzenesulfonate (**12**):*[13g] yellow oil (31 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.90 (d, 2H, J = 8.8 Hz), 7.63 (d, 2H, J = 8.4 Hz), 7.24 (d, 2H, J = 8.0 Hz), 6.99 (d, 2H, J = 8.8 Hz), 3.83 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 166.2, 153.2, 145.9, 132.3, 131.5, 130.1, 129.1, 128.7, 122.5, 52.5, 21.9; HRMS (ESI) calcd for $C_{15}H_{15}O_5S$ $[M + H]^+$ 307.0640, found 307.0639.

*(S)-tert-Butyl Benzyl Pyrrolidine-1,2-dicarboxylate (**13**):*[13h] yellow oil (yield 63 mg, 89%; >99% ee); enantiomeric excess (ee) was analyzed by chiral stationary phase HPLC using a Chiralcel OD column (n-hexane/2-propanol = 98:2, flow rate 0.8 mL/min, λ = 227 nm), chiral compound peak was observed at t_R = 23.187 min; for racemic compound peaks were observed at t_R = 17.178 min and t_R = 22.848 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.41−7.25 (m, 5H), 5.27−5.07 (m, 2H), 4.27 (dd, 1H, J = 4.2 Hz), 3.59−3.31 (m, 2H), 2.27−2.15 (m, 2H), 1.99−1.83 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 172.8, 153.6, 135.5, 128.4, 128.3, 128.1, 127.9, 127.8, 79.6, 66.4, 59.0, 46.1, 30.7, 28.2, 23.4; HRMS (ESI) calcd for $C_{17}H_{23}NO_4Na^+$ $[M + Na]^+$ 328.1525, found 328.1528.

*(S)-2-Hydroxy-2-((S)-2,2-dimethyl-1,3-dioxolane-4-yl)ethyl octanoate (**14**):* yellow oil (97 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 5.14−5.10 (m, 1H), 4.27−4.18 (m, 2H), 4.12−4.07 (m, 1H), 3.99−3.95 (m, 1H), 3.74−3.70 (m, 1H), 2.30 (t, 2H, J = 7.4 Hz), 1.60−1.53 (m, 2H), 1.37 (s, 3H), 1.29 (s, 3H), 1.25−1.20 (br s, 8H), 0.82 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.5, 110.0, 74.6, 70.8, 65.7, 62.9, 34.3, 31.8, 29.2, 29.1, 26.3, 25.5, 25.1, 22.8, 14.2; HRMS (ESI) calcd for $C_{15}H_{28}O_5K^+$ $[M + K]^+$ 327.1574, found 327.1577.

*2-(5-((Benzyloxy)carbonyl)pentyloxy)benzoic acid (**15**):* yellow solid (71 mg, 96%); mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 10.83 (s, 1H), 7.82 (d, 1H, J = 8.0 Hz), 7.45 (t, 1H, J = 7.0 Hz), 7.38−7.32 (m, 5H), 6.98 (d, 1H, J = 8.4 Hz), 6.87 (d, 1H, J = 7.0 Hz), 5.12 (s, 2H), 4.33 (t, 2H, J = 6.4 Hz), 2.40 (t, 2H, J = 7.4 Hz), 1.83−1.78 (m, 2H), 1.76−1.72 (m, 2H), 1.52−1.4 (m, 2H); ^{13}NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.3, 170.2, 156.6, 135.9, 135.7, 129.8, 128.6, 128.3, 128.2, 119.1, 117.6, 112.5, 66.2, 65.1, 34.1, 29.7, 28.3, 25.5, 24.5; IR cm^{-1}: 3083, 2985, 1731, 1698, 1614, 1524, 1416; HRMS (ESI) calcd for $C_{20}H_{23}O_5$ $[M + H]^+$ 343.1545, found 343.1543.

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

*((4S,5S)-5-((Benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-methyl 4-methylbenzoate (**16**):* colorless oil (129 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.91 (d, 2H, J = 8.0 Hz), 7.40−7.35 (m, 2H), 7.32−7.18 (m, 5H), 4.58 (s, 2H), 4.52 (dd, 1H, J = 3.6 Hz), 4.36 (dd, 1H, J = 5.2 Hz), 4.22−4.18 (m, 1H), 4.16−4.12 (m, 1H), 3.69−3.61 (m, 2H), 2.60 (s, 3H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.3, 140.6, 137.9, 132.3, 131.8, 130.8, 129.3, 128.6, 127.9, 127.8, 125.9, 110.1, 76.9, 76.8, 73.8, 70.5, 64.4, 27.2, 21.9; HRMS (ESI) calcd for $C_{22}H_{26}O_5Na^+$ $[M + Na]^+$ 393.1678, found 393.1678.

*4-[tert-Butyldimethylsilyl)oxy]butyl 3-hydroxynapthalene-2-carboxylate (**17**):* light yellow solid (96 mg, 97%); mp 118−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.57 (s, 1H), 7.93 (d, 1H, J = 8.4 Hz), 7.78 (d, 1H, J = 8.4 Hz), 7.55 (t, 2H, J = 7.6 Hz), 7.43 (s, 2H), 4.96−4.90 (m, 2H), 2.67−2.57 (m, 2H), 1.86−1.78 (m, 2H), 1.47−1.39 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 170.4, 160.5, 149.4, 138.8, 136.8, 129.8, 129.2, 127.2, 125.6, 115.7, 110.4, 63.3, 56.1, 29.5, 28.7, 26.7, 26.3, 26.2, 18.6, 15.1; HRMS (ESI) calcd for $C_{21}H_{31}O_4Si$ $[M + H]^+$ 375.1992, found 375.1991.

*2,2,10,10-Tetramethyl-5-(phenoxymethyl)-3,3,9,9-tetraphenyl-4,8-dioxa-3,9-disilaundecan-6-yl octanoate (**18**):* clear viscous oil (208 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.65−7.62 (m, 10H), 7.42−7.30 (m, 10H), 7.28−7.23 (m, 5H), 5.34−5.30 (m, 1H), 4.58 (dd, 2H, J = 11.6, 11.6 Hz), 3.88−3.81 (m, 2H), 3.78−3.74 (m, 1H), 2.21 (t, 2H, J = 7.4 Hz), 1.60−1.53 (m, 2H), 1.25 (br s, 10H), 1.02 (s, 18H), 0.86 (t, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.3, 138.7, 135.8, 135.7, 133.6, 129.9, 128.4, 127.7, 78.4, 73.4, 63.2, 62.3, 34.5, 31.8, 29.9, 29.3, 29.1, 27.0, 25.1, 22.8, 19.4, 14.3; HRMS (ESI) calcd for $C_{51}H_{66}O_5Si_2Na^+$ $[M + Na]^+$ 837.4346, found 837.4347.

*3-(Trityloxy)propyl 3-nitrobenzoate (**19**):* white solid (137 mg, 98%); mp 85−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.64 (s, 1H), 8.23 (d, 1H, J = 8.0 Hz), 8.16 (d, 1H, J = 7.6 Hz), 7.42−7.34 (m, 6H), 7.21−7.09 (m, 10H), 4.45 (t, 2H, J = 6.2 Hz), 3.22 (t, 2H, J = 5.8 Hz), 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 164.4, 148.2, 147.0, 144.5, 144.1, 135.3, 132.1, 129.6, 128.8, 128.7, 128.0, 127.9, 127.8, 127.3, 127.2, 127.0, 126.9, 124.5, 86.7, 63.3, 59.7, 29.3; HRMS (ESI) calcd for $C_{29}H_{25}NO_5Na^+$ $[M + Na]^+$ 490.1630, found 490.1633.

*Benzhydryl acetate (**20**):*[13i] yellow oil (115 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.20 (t, 4H, J = 7.2 Hz), 7.15 (d, 4H, J = 7.2 Hz), 7.10 (t, 2H, J = 7.0 Hz), 6.77 (s, 1H), 1.96 (s, 3H); ^{13}NMR (100 MHz, $CDCl_3$) δ_{ppm} 169.9, 140.3, 128.5, 127.9, 127.1, 76.9, 21.2; HRMS (ESI) calcd for $C_{15}H_{14}O_2Na^+$ $[M + Na]^+$: 249.0891, found 249.0889.

*(R)-1-Phenylethyl 2-phenylacetate (**21**):*[13j] yellow oil (yield 55 mg, 70%; >99% ee); enantiomeric excess (ee) was analyzed by chiral stationary phase HPLC using a Chiralcel OD column (*n*-hexane/2-propanol = 97:3, flow rate 0.8 mL/min, λ = 254 nm), chiral compound peak observed at t_R = 7.231 min; for racemic compound peaks observed at t_R = 7.189 min and t_R = 7.975 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.32−7.22 (m, 10H), 5.88 (q, 1H, J = 6.6 Hz), 3.62 (s, 2H), 1.50 (d, 3H, J = 6.6 Hz); ^{13}NMR (100 MHz, $CDCl_3$) δ_{ppm} 170.8, 141.6, 134.1, 129.3, 128.6, 128.5, 127.9, 127.1, 126.1, 72.8, 41.7, 22.2; HRMS (ESI) calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1229, found 241.1227.

*3-Phenylprop-2-ynyl benzoate (**22**):*[14a] yellow oil (93 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.10 (d, 2H, J = 8.4 Hz), 7.54 (t, 2H, J = 7.8 Hz), 7.48−7.52 (m, 4H), 7.32−7.26 (m, 2H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 165.9, 133.3, 132.0, 129.9, 129.7, 128.8, 128.5, 128.4, 122.3, 86.7, 83.2, 53.3; HRMS (ESI) calcd for $C_{16}H_{12}O_2Na^+$ $[M + Na]^+$ 259.0735, found 259.0735.

*3-Phenylprop-2-ynyl 4-nitrobenzoate (**23**):*[14b] creamy solid (82 mg, 98%); mp 61−62 °C (lit.[13j] mp 60−62 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.17 (d, 2H, J = 8.8 Hz), 8.14 (d, 2H, J = 8.8 Hz), 7.36 (d, 2H, J = 7.6 Hz), 7.21 (t, 3H, J = 7.6 Hz), 5.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 164.2, 150.8, 135.1, 132.1, 131.1, 129.1, 128.5, 123.7, 122.0, 87.4, 82.5, 54.3; HRMS (ESI) calcd for $C_{16}H_{11}NO_4$ Na^+ $[M + Na]^+$ 304.0586, found 304.0587.

*2-(Ethoxycarbonyl)cyclopentyl 4-bromobenzoate (**24**):* clear oil (65 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.86−7.79 (m, 2H), 7.56−7.46 (m, 2H), 5.58−5.53 (m, 1H), 4.15 (q, 2H, J = 7.2 Hz), 2.97−2.92 (m, 1H), 2.18−2.09 (m, 2H), 1.58−1.78 (m, 4H), 1.23 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 174.1, 165.4, 131.8, 131.2, 129.4, 128.2, 79.4, 60.9, 50.7, 32.8, 29.0, 23.7, 14.3; HRMS (ESI) calcd for $C_{15}H_{17}BrO_4Na^+$ $[M + Na]^+$ 363.0208, found 363.0208.

*3-Phenylprop-2-ynyl 4-methylbenzoate (**25**):* white solid (87 mg, 95%); mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.90 (d, 2H, J = 8.0 Hz), 7.39−7.36 (m, 2H), 7.31 (t, 2H, J = 7.4 Hz), 7.22−7.20 (m, 1H), 7.17−7.13 (m, 2H), 5.03 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 166.9, 140.7, 132.5, 132.1, 131.9, 131.0, 129.1, 128.9, 128.5, 125.9, 122.4, 86.6, 83.4, 53.2, 21.9; HRMS (ESI) calcd for $C_{17}H_{14}O_2Na^+$ $[M + Na]^+$ 273.0891, found 273.0891.

*(E)-Octyl 3-(4-methoxyphenyl)acrylate (**26**):*[14c] yellow oil (76 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.63 (d, 1H, J = 16.0 Hz), 7.46 (d, 2H, J = 8.4 Hz), 6.89 (d, 2H, J = 8.4 Hz), 6.31 (d, 1H, J = 16.0 Hz), 4.18 (t, 2H, J = 6.6 Hz), 3.81 (s, 3H), 1.72−1.65 (m, 2H), 1.28 (br s, 10H), 0.88 (t, 3H, J = 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.4, 161.4, 144.2, 129.7, 127.2, 115.8, 114.3, 64.5, 55.3, 31.9, 29.3, 29.2, 29.1, 28.9, 28.8, 26.0, 22.7, 14.1; HRMS (ESI) calcd for $C_{18}H_{26}O_3$ $[M + H]^+$ 291.1960, found 291.1961.

*Ethyl palmitate (**27**):*[15a] clear oil (55 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 4.05 (q, 2H, J = 7.0 Hz), 2.21 (t, 2H, J = 7.6 Hz), 1.56−1.51 (m, 2H), 1.21−1.15 (br s, 27H), 0.81 (t, 3H, J = 6.6 Hz); ^{13}NMR (100 MHz, $CDCl_3$) δ_{ppm} 174.0, 60.2, 34.5 32.1, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 25.2, 22.9, 14.4, 14.2; HRMS (ESI) calcd for $C_{18}H_{37}O_2$ $[M + H]^+$ 285.2794, found 285.2790.

*Isopropyl palmitate (**28**):*[15b] clear oil (45 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 5.00−4.94 (m, 1H), 2.22 (t, 2H, J = 7.4 Hz), 1.59−1.55 (m, 2H), 1.25−1.22 (br s, 24H), 1.19 (d, 6H, J = 6.4 Hz), 0.84 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 172.7, 66.7, 34.2, 31.5, 29.3, 29.1, 29.0, 28.9, 28.7, 24.6, 22.3, 21.4, 13.7; HRMS (ESI) calcd for $C_{19}H_{39}O_2$ $[M + H]^+$ 299.2950, found 299.2955.

*tert-Butyl octanoate (**29**):*[15c] clear liquid (40 mg, 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 2.50 (t, 2H, J = 7.3 Hz), 1.76−1.66 (m, 2H), 1.37−1.24 (br s, 8H), 0.98 (s, 9H), 0.85 (t, 3H, J = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 172.0, 74.8, 63.9, 34.0, 31.6, 29.1, 28.9, 28.3, 25.0, 22.6, 19.1, 14.0; HR-MS m/z calcd. for $C_{12}H_{24}O_2$$[M + H]^+$ 201.1855, found 201.1850.

*(Z)-3,4,5-Trimethoxybenzyl octadec-8-enoate (**30**):* yellow oil (80 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 6.51 (s, 2H), 5.26−5.25 (m, 2H), 4.96 (s, 2H), 3.78 (s, 6H), 3.75 (s, 3H), 2.30−2.26 (m, 2H), 1.93−1.92 (m, 4H), 1.57−1.55 (m, 2H), 1.22−1.18 (br s, 20H), 0.80 (t, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.7, 153.4, 131.8, 130.1, 129.8, 105.5, 66.4, 60.9, 56.2, 34.4, 32.0, 31.0, 29.8, 29.6, 29.4, 29.3, 27.3, 25.1, 22.8, 14.2; HRMS (ESI) calcd for $C_{28}H_{46}O_5Na^+$ $[M + Na]^+$ 485.3243, found 485.3245.

*(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl nicotinate (**31**):*[15d] yellow oil (78 mg,73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 9.24 (s, 1H), 8.77 (d, 1H, J = 4.8 Hz), 8.31 (d, 1H, J = 8.0 Hz), 7.40 (t, 1H, J = 6.4 Hz), 5.00−4.94 (m, 1H), 2.27−2.11 (m, 1H), 2.00−1.89 (m, 2H), 1.77−1.73 (m, 2H), 1.65−1.55 (m, 2H), 1.19−1.10 (m, 2H), 0.95 (d, 6H, J = 10.0 Hz), 0.81−0.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 164.6, 153.0, 150.7, 137.0, 126.6, 123.2, 75.4, 47.1, 40.8, 34.1, 26.4, 23.5, 21.9, 20.6, 16.4; HRMS (ESI) calcd for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1807, found 262.1805.

*Butyl quinoline-2-carboxylate (**32**):*[15e] yellow oil (64 mg, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.24 (d, 1H, J = 8.8 Hz), 8.20 (d, 1H, J = 8.8 Hz), 8.07 (d, 1H, J = 8.8 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.69 (t, 1H, J = 7.7 Hz), 7.54 (t, 1H, J = 7.6 Hz), 4.42 (t, 2H, J = 6.8 Hz), 1.81−1.72 (m, 2H), 1.47−1.35 (m, 2H), 0.91 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 165.2, 148.1, 147.4, 137.0, 130.5, 130.0, 129.0, 128.3, 127.3, 120.8, 65.8, 30.6, 19.0, 13.6; HRMS (ESI) calcd for $C_{14}H_{16}NO_2$ $[M + H]^+$ 230.1181, found 230.1185.

*(3S,8S,9S,10R,13R,14S,17R)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-Tetradecahydro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-1H-cyclopenta[a]phenanthren-3yl 2-naphthoate (**33**):*[15f] crystalline white solid (113 mg, 72%); mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.60 (s, 1H), 8.06 (d, 1H, J = 8.4 Hz), 7.94 (d, 2H, J = 8.0 Hz), 7.86 (d, 1H, J = 8.4 Hz), 7.54 (t, 2H, J = 9.4 Hz), 5.51−5.43

dx.doi.org/10.1021/jo302502r | J. Org. Chem. 2013, 78, 2386−2396

(m, 1H), 4.94−4.92 (m, 1H), 2.52 (d, 2H, J = 8.0 Hz), 2.03−1.74 (m, 4H), 1.57−1.42 (m, 4H), 1.34−1.11 (m, 18H), 1.08 (s, 3H), 0.92 (d, 3H, J = 6.4 Hz), 0.87 (d, 6H, J = 6.4 Hz), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 166.4, 139.9, 135.7, 132.8, 131.1, 129.6, 128.3, 128.0, 126.8, 125.6, 123.1, 75.0, 56.9, 56.4, 50.3, 42.6, 40.0, 39.8, 38.5, 37.3, 36.9, 36.4, 36.1, 35.2, 32.1, 28.5, 28.2, 24.9, 24.5, 24.1, 23.1, 22.8, 21.3, 19.6, 19.0, 12.1; HRMS (ESI) calcd for $C_{38}H_{52}O_2$ $[M]^+$ 540.3967, found 540.3967.

*Hexadecyl 3-(1H-indol-3-yl)propanoate (**34**):* crystalline white solid (106 mg, 97%); mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.02 (br s, 1H), 7.61 (d, 1H, J = 8.0 Hz), 7.35 (d, 1H, J = 8.0 Hz), 7.19 (t, 1H, J = 7.4 Hz), 7.12 (t, 1H, J = 7.4 Hz), 7.01 (s, 1H), 4.06 (t, 2H, J = 6.8 Hz), 3.10 (t, 2H, J = 7.4 Hz), 2.72 (t, 2H, J = 7.8), 1.60−1.53 (m, 4H), 1.29−1.22 (br s, 24H), 0.88 (t, 3H, J = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.8, 136.5, 127.3, 122.0, 121.6, 119.3, 118.8, 114.9, 111.3, 63.0, 35.2, 32.9, 32.1, 29.9, 29.7, 29.6, 29.5, 29.4, 28.8, 26.1, 25.9, 22.9, 20.9, 14.3; HRMS (ESI) calcd for $C_{27}H_{43}NO_2Na^+$ $[M + Na]^+$ 436.3191, found 436.3190.

*Isopropyl 3-(1H-indol-3-yl)propanoate (**35**):* colorless oil (49 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.03 (br s, 1H), 7.60 (d, 1H, J = 8.0 Hz), 7.30 (d, 1H, J = 8.0 Hz), 7.15 (t, 1H, J = 7.4 Hz), 7.10 (t, 1H, J = 7.4 Hz), 6.94 (s, 1H), 5.04−4.98 (m, 1H), 3.08 (t, 2H, J = 7.8 Hz), 2.67 (t, 2H, J = 7.8 Hz), 1.20 (d, 6H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 173.3, 136.4, 127.3, 122.0, 121.6, 119.3, 118.8, 114.9, 111.3, 67.8, 35.5, 21.9, 20.8; HRMS (ESI) calcd for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338, found 232.1339.

*N-Butyl-4-hydroxybenzamide (**36**):*[16a] clear oil (60 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.54 (d, 2H, J = 8.8 Hz), 6.79 (d, 2H, J = 8.8 Hz), 6.42 (br s, 1H), 3.32 (q, 2H, J = 7.0 Hz), 1.53−1.45 (m, 2H), 1.32−1.24 (m, 2H), 0.83 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.5, 160.7, 128.9, 125.5, 115.8, 40.1, 31.8, 20.3,13.9; HRMS (ESI) calcd for $C_{11}H_{16}NO_2$ $[M + H]^+$ 194.1181, found 194.1179.

*N-Butyl-3-methylbenzamide (**37**):*[16b] yellow oil (66 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.27 (d, 2H, J = 7.2 Hz), 7.17−7.11(m, 2H), 6.16 (br s, 1H), 3.34 (q, 2H, J = 7.0 Hz), 2.38 (s, 3H), 1.55−1.50 (m, 2H), 1.38−1.33 (m, 2H), 0.93 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 170.3, 136.9, 135.8, 130.9, 129.6, 126.7, 125.7, 39.6, 31.7, 20.2, 19.7, 13.8; HRMS (ESI) calcd for $C_{12}H_{18}NO$ $[M + H]^+$ 192.1388, found 192.1388.

*N-Butyl-4-nitrobenzamide (**38**):*[16c] white solid (65 mg, 98%); mp 139−140 °C (lit.[16b] mp 135−140 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.24 (d, 2H, J = 8.8 Hz), 7.90 (d, 2H, J = 8.4 Hz), 6.38 (br s, 1H), 3.44 (q, 2H, J = 6.6 Hz), 1.63−1.56 (m, 2H), 1.42−1.34 (m, 2H), 0.93 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 165.8, 149.5, 140.6, 128.3, 123.7, 40.3, 31.6, 20.2, 13.8; HRMS (ESI) calcd for $C_{11}H_{15}N_2O_3$ $[M + H]^+$: 223.1083, found 223.1080.

*2-Phenyl-N-((pyridin-2-yl)methyl)acetamide (**39**):*[16d] brown color solid (79 mg, 95%); mp 105−106 °C (lit.[16c] mp 105−106 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.46 (d, 1H, J = 4.8 Hz), 7.62 (t, 1H, J = 7.8 Hz), 7.37−7.27 (m, 5H), 7.20 (d, 1H, J = 7.6 Hz), 7.16 (t, 1H, J = 6.2 Hz), 6.76 (br s, 1H), 4.52 (d, 2H, J = 4.8 Hz), 3.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 171.2, 156.7, 148.7, 136.6, 135.0, 129.2, 128.6, 126.9, 122.1, 121.6, 44.5, 43.3; HRMS (ESI) calcd for $C_{14}H_{15}N_2O$ $[M + H]^+$ 227.1184, found 227.1188.

*N-Benzylquinoline-2-carboxamide (**40**):*[16e] crystalline yellow solid (72 mg, 95%); mp 122−123 °C (lit.[16d] mp 123−124 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.63 (br s, 1H), 8.35 (d, 1H, J = 8.4 Hz), 8.30 (d, 1H, J = 8.4 Hz), 8.01 (d, 1H, J = 8.4 Hz), 7.86 (d, 1H, J = 8.4 Hz), 7.3 (t, 1H, 7.8 Hz), 7.60 (t, 1H, J = 7.6 Hz), 7.41 (d, 2H, J = 7.2 Hz), 7.36 (t, 2H, J = 7.4 Hz), 7.30 (d, 1H, J = 7.2 Hz), 4.74 (d, 2H, J = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 164.5, 149.7, 146.5, 138.4, 137.5, 130.1, 129.7, 129.3, 128.7, 127.8, 127.5, 119.0, 43.6; HRMS (ESI) calcd for $C_{17}H_{15}N_2O$ $[M + H]^+$ 263.1184, found 263.1186.

*N-(2-(Dimethylamino)ethyl)quinoline-2-carboxamide (**41**):*[16f] colorless solid (69 mg, 98%); mp 88−89 °C (lit.[16c] mp 87−89 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.26 (d, 1H, J = 8.4 Hz), 8.09 (d, 1H, J = 8.4 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.76 (t, 1H, J = 7.6 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.61 (t, 1H, J = 7.6 Hz), 6.54 (br s, 1H), 4.24−4.18 (m, 2H), 3.56−3.48 (m, 2H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 168.9, 154.1, 146.7, 137.5, 130.4, 129.8, 128.5, 128.0, 127.9, 120.0, 57.2, 49.9, 32.6, 31.0; HRMS (ESI) calcd for $C_{14}H_{18}N_3O$ $[M + H]^+$ 244.1450, found 244.1453.

*(4-Hydroxyphenyl)(piperidin-1-yl)methanone (**42**):*[16g] crystalline white solid (56 mg, 75%); mp 215−216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.25 (d, 2H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz), 4.75 (br s, 1H), 4.42 (br s, 2H), 3.45 (br s, 2H), 1.90−1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 169.5, 158.3, 128.3, 126.4, 114.6, 47.5, 33.3, 28.9, 25.5, 24.0; HRMS (ESI) calcd for $C_{12}H_{15}NO_2$ $[M + H]^+$ 206.1181, found 206.1180.

*(4-Nitrophenyl)(piperidin-1-yl)methanone (**43**):*[16h] crystalline yellow solid (55 mg, 78%); mp 121−122 °C (lit.[16g] mp 120.9−122.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 8.27 (d, 2H, J = 8.0 Hz), 7.56 (d, 2H, J = 8.0 Hz), 3.73 (br s, 2H), 3.23 (br s, 2H), 1.72−1.54 (m, 4H), 1.40−1.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 167.0, 147.5, 142.3, 127.3, 123.2, 47.9, 42.4, 33.3, 25.8, 23.8; HRMS (ESI) calcd for $C_{12}H_{15}N_2O_3$ $[M + H]^+$ 235.1083, found 235.1086.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HRMS and ^{1}H and ^{13}C NMR spectra for all new compounds. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge DBT (BT/PR13309/GBD/27/244/2009) and CSIR (02-0090/12/EMR-II), Government of India, for financial support.

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NOTE ADDED AFTER ASAP PUBLICATION

The version published February 6, 2013 contained bond angle errors in the toc/abstract graphic, Tables 3 and 4, and Supporting Information; the correct versions reposted February 8, 2013.