Acylation of Alcohols and Amines with Vinyl Acetates Catalyzed by $Cp^*_2Sm(thf)_2$

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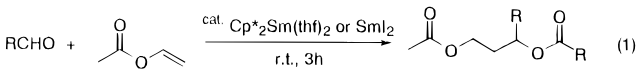
$Cp^*_2Sm(thf)_2$ was found to be an efficient catalyst for the acylation of alcohols and amines with esters under mild conditions. In the present acylation, vinyl and isopropenyl acetates served as good acylating agents. Thus, a variety of alcohols and amines underwent acylation with vinyl and isopropenyl acetates in the presence of $Cp^*_2Sm(thf)_2$ to give the corresponding esters and amides in good to excellent yields. This catalytic acylation of alcohols and amines offers an additional useful method by the use of various esters, instead of acid anhydrides and acid chlorides, as acylating agents under very mild conditions.

The acylation of hydroxy and amino groups is one of the most widely used transformations in organic synthesis, and a variety of acylating agents have been developed. Acid halides and acid anhydrides are usually employed as the acylating agents in the presence of protic or Lewis acid catalysts.[1] Recently, pyridine derivatives,[2] such as 4-(dimethylamino)pyridine and 4-pyrrolidinopyridine, and tributylphosphine[3] were used as efficient catalysts for the acylation of alcohols with acetic anhydride. More recently, $Sc(OTf)_3$[4] and $La(OPr^i)_3$[5] have been reported to promote the efficient acylation of alcohols with acetic anhydride at room temperature and the transesterification of benzoates with alcohols under moderate conditions (60−100 °C), respectively. Tetrabutylammonium salt[6] and cyanide anion[7] are also used in the acylation of amines with esters.

Since the first introduction of a useful method for the generation of samarium(II) diiodide (SmI_2) by Kagan and co-workers,[8] samarium(II) complexes have been widely used in organic synthesis.[9] However, only a few reactions using catalytic amounts of Sm(II) complexes were investigated. For example, SmI_2 has been reported to catalyze the intramolecular Tishchenko reaction,[10] epoxide rearrangements,[11] Michael and aldol reactions,[12] and Diels−Alder reactions.[13] Samarium(II) complexes such as $Cp^*_2Sm(thf)_2$ have also proved to be a useful catalyst in hydrogenation[14] and hydroboration of alkenes[15,16] and hydroamination/cyclization of amines.[14a,15]

In a previous paper, we reported that $Cp^*_2Sm(thf)_2$ and SmI_2 catalyze a new type of 1:2 cross coupling reaction of vinyl esters with aldehydes under mild conditions (eq 1).[17] In the course of this study, we found that $Cp^*_2Sm(thf)_2$ can be applied as an efficient catalyst for the acylations of alcohols and amines with esters.



(1)

Based on the fact that vinyl acetate (**1**) was activated by $Cp^*_2Sm(thf)_2$ in the coupling reaction with aldehydes, **1** was chosen as an acylation agent and allowed to react with octanol (**2**) under the influence of $Cp^*_2Sm(thf)_2$ under several reaction conditions (Table 1). A stoichiometric reaction of **1** with **2** in the presence of $Cp^*_2Sm(thf)_2$ catalyst at room temperature for 3 h resulted in octyl acetate (**3**) in 86% yield (run 1). However, when **2** was allowed to react with 2 equiv of **1** under the same reaction conditions, **3** was formed in quantitative yield (run 2). Surprisingly, even at 0 °C the acylation of **2** with **1** was smoothly promoted by $Cp^*_2Sm(thf)_2$ forming **3** quantitatively (run 3). The acylation was found to be

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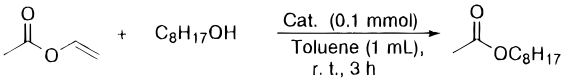
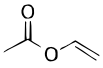
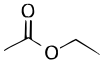
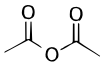
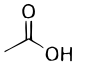
Table 1. Acylation of Octanol (2) with Vinyl Acetate (1) by Cp*$_2$Sm(thf)$_2$ Complex under Various Conditions



1 2 3

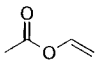
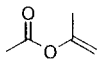
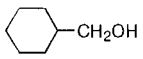
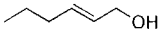
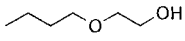
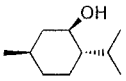
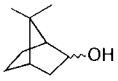
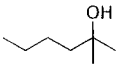
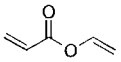
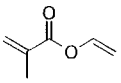
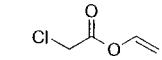
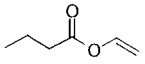
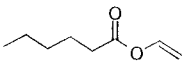
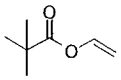
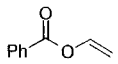
Run	Catalyst	Acylating Agent	Ratio[a]	Yield / %[b]
1	Cp*$_2$Sm(thf)$_2$	 (1)	1 / 1	86
2	Cp*$_2$Sm(thf)$_2$	**1**	1 / 2	> 99
3[c]	Cp*$_2$Sm(thf)$_2$	**1**	1 / 2	> 99
4[d]	Cp*$_2$Sm(thf)$_2$	**1**	1 / 2	92
5	Cp*$_2$Sm(thf)$_2$	**1**	2 / 1	(> 99)[e]
6[f]	SmI_2	**1**	1 / 2	18
7	Cp*$_2$Sm(thf)$_2$		1 / 2	66
8	Cp*$_2$Sm(thf)$_2$		1 / 2	40
9	Cp*$_2$Sm(thf)$_2$		1 / 2	No reaction

[a] Ratio of **2** / acylating agent (mmol / mmol) [b] GLC yields based on **2**. [c] 0 °C for 3 h. [d] Cp*$_2$Sm(thf)$_2$ (1 mol%) was used. [e] Number in parentheses is yield based on **1**. [f] THF was used as a solvent instead of toluene.

induced even in the presence of 1 mol % of Cp*$_2$Sm(thf)$_2$ (run 4). Using of 2 equiv of **2** with respect to **1**, **3** was also obtained in almost quantitative yield (run 5). SmI_2 was less active than Cp*$_2$Sm(thf)$_2$ complex (run 6). On the other hand, the acylation of **2** with ethyl acetate gave **3** in moderate yield (run 7). When acetic anhydride was employed instead of **1**, **3** was formed in low yield (run 8). This is believed to be due to the simultaneous formation of acetic acid in addition to **3**. Actually, the acylation of **2** with acetic acid in the presence of Cp*$_2$Sm(thf)$_2$ resulted in the decomposition of the samarium complex, and no ester was formed (run 9).

Table 2 shows the acylation of various alcohols with **1** by the Cp*$_2$Sm(thf)$_2$ catalyst. The acylation of primary alcohols with **1** could be achieved in excellent yields at room temperature for 3 h (runs 1 and 3−6). Secondary alcohol such as 2-octanol (**4**) was acetylated with **1** with more difficulty under these conditions to give 2-octyl acetate in 54% yield (run 7). However, when isopropenyl acetate (**5**) was employed as the acylation agent in place of **1**, 2-octyl acetate was obtained in 95% yield (run 8). It is interesting that sterically hindered terpene alcohols such as *l*-menthol and borneol were also acetylated with **5** at room temperature to give the corresponding acetates in quantitative yields (runs 9 and 10). The catalytic activity of SmI_2 was found to be comparable to that of the Cp*$_2$Sm(thf)$_2$ complex, when using **5** as the acylating agent (run 2). However, a tertiary alcohol, 2-methyl-2-hexanol (**6**), was found to be a sluggish substrate even when **5** was used as the acylating agent (run 12). The acylation of **2** with a wide variety of vinyl esters could be accomplished by the use of Cp*$_2$Sm(thf)$_2$ as the catalyst (runs 13−19). For example, vinyl acrylate and vinyl methacrylate with **1** produced the corresponding esters in quantitative yields without the polymerization of esters (runs 13 and 14). These transformations seem

Table 2. Acylation of a Variety of Alcohols with 1 and Several Vinyl Esters by Sm(II) Complexes[a]

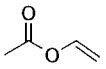
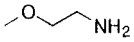
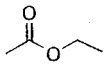
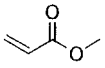
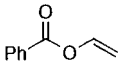
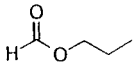
Run	Alcohol	Vinyl Ester	Ester/ Yield, %[b, c]
1	$C_8H_{17}OH$ (**2**)	 (**1**)	> 99 (18)
2	**2**	 (**5**)	> 99 (> 99)
3	$PhCH_2OH$	**1**	96
4		**1**	> 99
5		**1**	88
6		**1**	> 99
7	2-octanol (**4**)	**1**	54
8	**4**	**5**	95 (92)
9		**5**	>99
10		**5**	>99
11	 (**6**)	**1**	11 (-)
12	**6**	**5**	51 (-)
13	**2**		> 99 (17)
14	**2**		>99 (23)
15	**2**		> 99 (79)
16	**2**		> 99 (62)
17	**2**		> 99 (58)
18	**2**		> 99 (32)
19	**2**		>99 (15)

[a] Alcohol (1 mmol) was allowed to react with vinyl ester (2 mmol) in the presence of Cp*$_2$Sm(thf)$_2$ (0.1 mmol) in toluene (1 mL) at room temperature for 3 h. [b] Based on alcohol used. [c] Number in parentheses is yield when using SmI_2 (0.1 mmol) in THF (1 mL) as catalyst.

to be of interest, since acid halides and acid anhydrides of vinyl acrylate or vinyl methacrylate are not readily available. It is important to note that octyl pivaloate and octyl benzoate were easily obtained by the reaction of **2** with the corresponding vinyl esters in quantitative yields, because the pivaloate and benzoate esters are the most commonly used esters to protect alcohols (runs 18 and 19).

The catalytic acylation of amino groups was also achieved using Cp*$_2$Sm(thf)$_2$ as the catalyst. Table 3 shows representative results for the acylation of various amines with vinyl acetate **1** catalyzed by Cp*$_2$Sm(thf)$_2$.

Table 3. Acylation of Various Amines with Esters Catalyzed by Sm(II) Complexes[a]

Run	Amine	Ester	Amide/ Yield, %[b]
1	$C_8H_{17}NH_2$ (**7**)	 (**1**)	>99 (>99)[c]
2[d]	**7**	**1**	51
3	$PhCH_2NH_2$	**1**	> 99
4	$PhNH_2$	**1**	No reaction
5		**1**	80
6	$(C_4H_9)_2NH$	**1**	No reaction
7		**1**	> 99
8		**1**	> 99
9	**7**	 (**9**)	60 (33)[c]
10	**7**		86 (58)[c]
11	**7**		16
12	**7**		98
13	**7**	 (**11**)	> 99 (>99)[c]
14	$PhNH_2$	**11**	80
15	$(C_4H_9)_2NH$	**11**	> 99

[a] Amine (2 mmol) was allowed to react with ester (1 mmol) in the presence of $Cp^*_2Sm(thf)_2$ (0.1 mmol) in toluene (1 mL) at room temperture for 3 h. [b] Based on ester used. [c] Number in parentheses is yield using SmI_2 (0.1 mmol) in THF (1 mL) as catalyst. [d] **7** (1 mmol) was used.

The acylation of octylamine (**7**) with **1** in the presence of $Cp^*_2Sm(thf)_2$ or SmI_2 at room temperature afforded *N*-octylacetamide (**8**) in good yield (run 1). A stoichiometric reaction of **7** with **1** in the presence of a catalytic amount of $Cp^*_2Sm(thf)_2$ afforded **8** in 51% yield (run 2). By the use of 2 equiv of **7** with respect to **1**, **8** was obtained in excellent yield. Benzylamine was also subjected to the acetylation with **1** to give the corresponding amide in quantitative yield (run 3). In the acylation of **7** with **1**, SmI_2 also served as an efficient catalyst (run 1). However, aniline did not react with **1** under these conditions (run 4). Amines bearing an ether function such as 2-methoxyethylamine were also acylated to afford the corresponding amide in good yield (run 5). The acylation of a secondary aliphatic amine such as dibutylamine with **1** was difficult to carry out by the present method (run 6). However, the same procedure for cyclic amines such as pyrrolidine and piperidine produced *N*-acetylpyrrolidine and *N*-acetylpiperidine, respectively, in quantitative yields (runs 7 and 8). In another approach for the introduction of an acetyl group on the amino groups, ethyl acetate (**9**) was employed in place of vinyl acetate **1**. The reaction of **7** with **9** under the influence of $Cp^*_2Sm(thf)_2$ produced amide **8** in 60% yield, but SmI_2 gave **8** in low yield (33%) (run 9). When methyl acrylate was used as an ester, the yield of amide attained 86% by $Cp^*_2Sm(thf)_2$ and to 58% by SmI_2 (run 10). In contrast to methyl benzoate which reacted sluggishly with **7** to give *N*-octylbenzamide (**10**) in poor yield (16%), vinyl benzoate reacted with ease forming **10** in 98% yield (runs 11 and 12).

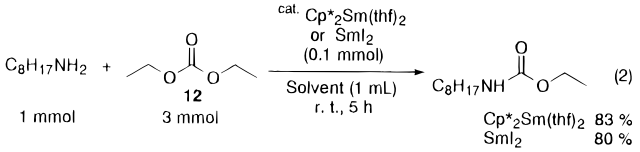
Table 4. Acylation of Octanol (2) and Octyl Amine (7) with Vinyl Acetate (1) by Several Samarium Complexes[a]

			yield, %	
run	catalyst	solvent	**3**	**8**
1	$Cp^*_2Sm(thf)_2$	toluene	>99	>99
2	SmI_2	THF	18	>99
3	SmI_3	THF	54	>99
4	$Sm(OPr^i)_3$	THF	>99	60
5	$Sm(OTf)_3$	THF	13	8
6	$Al(OPr^i)_3$	THF	30	trace
7	H_2SO_4	THF	12	–

[a] The reaction was carried out under the same conditions as in Table 2 for **2** and Table 3 for **7**.

The method can be successfully extended to the preparation of formamides by the use of formates (runs 13–15 in Table 3). Thus, the reaction of octylamine **7** with propyl formate (**11**) in the presence of $Cp^*_2Sm(thf)_2$ or SmI_2 afforded *N*-octylformamide in quantitative yield (run 13). Although the acylation of dibutylamine and aniline with ester **1** was difficult to carry out, these amines were formylated with **11** in the presence of $Cp^*_2Sm(thf)_2$ to give formamides in relative good yields (runs 14 and 15).

Diethyl carbonate (**12**) was also used as an acylating agent. A stoichiometric reaction of **7** with **12** under the influence of $Cp^*_2Sm(thf)_2$ at room temperature for 5 h produced carbamate in 83% yield. SmI_2 also promoted this reaction (eq 2).



In order to obtain some information on the nature of the actual samarium species involved in the promotion of the acylation reaction, the catalytic activity of several samarium complexes was examined. The acylation of octanol **2** and octylamine **7** with **1** under the standard set of conditions was investigated and the results are shown in Table 4. Although protic and Lewis acids are known to catalyze the acylation of alcohols with acid anhydrides, the acylation of **2** with **1** by these acids gave unsatisfactory results (runs 6 and 7). The potential of representative Sm(III) compounds, such as SmI_3, $Sm(OTf)_3$, and $Sm(OPr^i)_3$, in this reaction was also examined under these conditions (runs 3–5). It was found that the catalytic activity of $Sm(OTf)_3$ was considerably lower than that of the $Cp^*_2Sm(thf)_2$ complex. However, SmI_3 acted as a good acylating catalyst for amine **7** with **1** but not for the alcohol **2**. In contrast, $Sm(OPr^i)_3$ was efficient for the acylation of alcohol **2** but not amine **7**, though $Cp^*_2Sm(thf)_2$ was very active for both substrates.

On the basis of these results, it is probable that the active species in the present reaction is the samarium(III) complex derived from $Cp^*_2Sm(thf)_2$ and **1**, alcohol, or amine. Indeed, when vinyl acetate **1** was added to a solution of $Cp^*_2Sm(thf)_2$ in toluene, the color immediately changed from violet to yellow. This color change may be

related to the formation of a new samarium species in which vinyl acetate **1** is coordinated or bonded to the $Cp^*_2Sm(thf)_2$. The addition of alcohol **1** to the resulting complex gave an almost transparent solution, which finally became colloidal. Furthermore, the order of addition of **1** and **2** to the $Cp^*_2Sm(thf)_2$ solution was not essential in the yield of product **3**. These observations may suggest that a samarium(III) species generated during the reaction of $Cp^*_2Sm(thf)_2$ with **1** or alcohol catalyzes the present acylation. The isolation of the complex by the independent reactions of $Cp^*_2Sm(thf)_2$ with **1** and alcohol **2** was attempted, but we have not succeeded in obtaining a samarium complex.

In conclusion, an efficient catalytic acylation method using vinyl esters as acylating agents under mild conditions has been developed. A variety of alcohols and amines were acylated to the corresponding esters and amides, respectively, in good yields under mild conditions.

Experimental Procedures

General Procedure. ^{1}H and ^{13}C NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared spectra (IR) were measured using a NaCl plate. GLC analyses were performed with a flame ionization detecter using 1 mm × 30 m capillary column (OV-1). Mass spectra were determined at an ionizing voltage of 70 eV. Elemental samarium, pentamethylcyclopentadiene, 1,2-diiodoethane, $Al(OPr^i)_3$, and H_2SO_4 were purchased from commericial sources and used without purification. Toluene, THF, vinyl esters, esters, alcohols, and amines were purchased from commericial origin and distilled prior to use. Potassium hydride (36 wt % dispersion in mineral oil) was purchased from commercial sources and purified by washing with hexane. $Cp^*_2Sm(thf)_2$,[18] $Sm(OTf)_3$,[19] and $Sm(OPr^i)_3$[20] were synthesized according to literature methods. THF solution of SmI_2[21] and SmI_3[22] were prepared by literature methods.

General Procedure for the $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Alcohols with Esters. Into a Schlenk tube containing toluene solution (1 mL) of $Cp^*_2Sm(thf)_2$ (0.1 mmol) was slowly added ester (1 mmol) followed by alcohol (2 mmol) at 0 °C under argon. The reaction mixture was stirred at rt under argon atmosphere. When the reaction was complete, diethyl ether containing water (10 mL) was added to the solution, and the catalyst was removed by filtration. Removal of the solvent under reduced pressure afforded a yellow liquid, which was purified by column chromatography on silica gel with *n*-hexane/AcOEt (10/1 v/v) as eluent to give the corresponding ester.

General Procedure for the SmI_2-Catalyzed Acylation of Alcohols with Esters. A THF solution of SmI_2 was prepared by Kagan's method.[21] Ester (1 mmol) and alcohol (2 mmol) were added to the THF solution (1 mL) of SmI_2 (0.1 mmol), and the solution was stirred at rt for 3 h. The same workup described in the general procedure was used in the $Cp^*_2Sm(thf)_2$-catalyzed acylation of alcohols with esters.

Octyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.2 Hz, 3H), 1.20−1.42 (m, 10H), 1.62 (quintet, J = 6.8 Hz, 2H), 2.04 (d, J = 1.6 Hz, 3H), 4.05 (dt, J = 1.0, 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 20.9, 22.6, 25.9, 28.6, 29.1, 29.2, 31.7, 64.6, 171.1. IR (neat) 1040, 1237, 1365, 1467, 1745, 2856, 2927 cm^{-1}.

2-Octyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.20 (d, J = 7.3 Hz, 3H), 1.23−1.36 (m, 10H), 2.02 (s, 3H), 4.89 (sextet, J = 6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 19.9, 21.3, 22.5, 25.3, 29.1, 31.7, 35.9, 71.0, 170.7. IR (neat) 609, 734, 1020, 1123, 1244, 1371, 1465, 1739, 2859, 2931 cm^{-1}.

***l*-Menthyl acetate:** ^{1}H NMR ($CDCl_3$) δ 0.77 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H), 0.72−1.15 (m, 2H), 1.30−2.07 (m, 7H), 2.03 (s, 3H), 4.68 (td, J = 4.3, 10.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 16.6, 21.0, 21.6, 22.3, 23.7, 26.5, 31.6, 34.5, 41.2, 47.2, 74.4, 170.9. IR (neat) 1024, 1246, 1369, 1454, 1737, 2870, 2955 cm^{-1}.

Bornel acetate: ^{1}H NMR ($CDCl_3$) δ 0.78−2.08 (m, 8H), 0.84 (s, 3H), 0.87 (s, 3H), 0.91 (s, 3H), 2.29−2.41 (m, 1H), 2.60 (d, J = 0.5 Hz, 3H), 4.66 (dd, J = 3.8, 4.1 Hz, 0.3H), 4.88 (dt, 2.8, 9.7 Hz, 0.7H). ^{13}C NMR ($CDCl_3$) δ 11.3, 13.4, 18.8, 19.7, 19.8, 20.1, 21.2, 22.8, 27.0, 28.0, 33.7, 36.7, 38.7, 44.8, 45.0, 46.8, 47.7, 48.5, 48.6, 79.8, 80.9, 170.6, 171.4. IR (neat) 1033, 1048, 1247, 1362, 1455, 1737, 2879, 2954 cm^{-1}.

2-Methyl-2-hexyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 6.8 Hz, 3H), 1.18−1.38 (m, 4H), 1.42 (s, 6H), 1.63−1.76 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 14.1, 22.5, 23.0, 26.0, 26.1, 40.5, 82.5, 170.5. IR (neat) 503, 606, 652, 756, 877, 949, 1047, 1242, 1367, 1446, 1739, 2960 cm^{-1}.

Benzyl acetate: ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H), 5.09 (s, 2H), 7.26−7.36 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 20.8, 66.1, 128.1, 128.4, 135.8, 170.6. IR (neat) 697, 750, 1027, 1228, 1380, 1456, 1739 cm^{-1}.

Cyclohexylmethyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.86−1.06 (m, 2H), 1.12−1.36 (m, 3H), 1.55−1.82 (m, 6H), 2.05 (d, J = 1.1 Hz, 3H), 3.88 (d, J = 6.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 20.9, 25.6, 26.3, 29.6, 37.0, 69.6, 171.2. IR (neat) 1037, 1242, 1363, 1450, 1745, 2853, 2925 cm^{-1}.

***trans*-2-Hexenyl acetate:** ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3H), 1.41 (sextet, J = 7.0 Hz, 2H), 2.03 (q, J = 7.0 Hz, 2H), 2.05 (d, J = 1.4 Hz, 3H), 4.51 (d, J = 6.2 Hz, 2H), 5.56 (dt, J = 7.1, 14.8 Hz, 1H), 5.77 (dt, J = 7.1, 14.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 13.5, 20.9, 22.0, 34.2, 65.2, 123.9, 136.3, 170.8. IR (neat) 969, 1026, 1234, 1362, 1455, 1738, 2961 cm^{-1}.

3-Oxyhexyl acetate: ^{1}H NMR ($CDCl_3$) δ 0.92 (dt, J = 1.5, 7.1 Hz, 3H), 1.37 (sextet, J = 7.1 Hz, 2H), 1.57 (quientet, J = 7.1 Hz, 2H), 2.08 (d, J = 1.9 Hz, 3H), 3.47 (dt, J = 1.9, 7.1 Hz, 2H), 3.62 (dt, J = 1.9, 4.8 Hz, 2H), 4.21 (dt, = 1.7, 4.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.7, 19.1, 20.8, 31.5, 63.5, 68.4, 71.0, 170.9. IR (neat) 1056, 1129, 1243, 1371, 1742, 2959 cm^{-1}.

Octyl acrylate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.19−1.44 (m, 10H), 1.68 (sixtet, J = 6.6 Hz, 2H), 5.81 (d, J = 10.3 Hz, 1H), 6.12 (dd, J = 10.3, 17.5 Hz, 1H), 6.39 (d, J = 17.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 28.6, 29.1, 29.2, 31.7, 64.7, 128.6, 130.3, 166.3. IR (neat) 810, 985, 1193, 1270, 1408, 1732, 2927 cm^{-1}.

Octyl methacrylate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.2 Hz, 3H), 1.19−1.44 (m, 10H), 1.68 (quintet, J = 6.9 Hz, 2H), 1.95 (d, J = 0.8 Hz, 3H), 4.14 (t, J = 6.8 Hz, 2H), 5.53 (s, 1H), 6.09 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 18.2, 22.6, 25.9, 28.6, 29.1, 29.2, 31.7, 64.8, 125.0, 136.5, 167.5. IR (neat) 652, 1163, 1455, 1639, 1716, 2929 cm^{-1}.

Octyl 1-chloroacetate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.22−1.42 (m, 10H), 1.67 (quintet, J = 7.0 Hz, 2H), 4.06 (s, 2H), 4.18 (t, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.7, 28.4, 29.1, 31.7, 40.8, 66.3, 167.3. IR (neat) 1247, 1463, 1739, 2856, 2927 cm^{-1}.

Octyl butanoate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H), 1.22−1.38 (m, 10H), 1.57 (quintet, J = 7.3 Hz, 2H), 1.66 (sextet, J = 7.2 Hz, 2H), 2.28 (t, J = 7.4 Hz, 2H), 4.08 (t, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 13.6, 14.0, 18.4, 22.6, 25.9, 28.6, 29.2, 31.7, 36.2, 64.3, 173.7. IR (neat) 1015, 1107, 1176, 1379, 1467, 1738, 2857, 2929 cm^{-1}.

Octyl hexanoate: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 6.8 Hz, 3H), 1.18−1.42 (m, 12H), 1.50−1.70 (m, 6H), 2.29 (t, J = 7.7 Hz, 2H), 4.06 (t, J = 6.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.1, 14.3, 22.6, 22.9, 25.0, 26.2, 28.9, 29.5, 31.6, 32.0, 34.6, 64.6, 174.2. IR (neat) 1099, 1172, 1467, 1732, 2925 cm^{-1}.

Octyl pivaloate: ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 6.5 Hz, 3H), 1.12 (s, 9H), 1.14−1.32 (m, 12H), 3.98 (t, J = 6.5 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 25.9, 27.2, 28.6, 29.1, 29.4, 31.7, 38.7, 64.4, 178.6. IR (neat) 1157, 1284, 1481, 1700, 1734, 2927 cm^{-1}.

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Octyl benzoate: ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 6.2 Hz, 3H), 1.12−1.41 (m, 10H), 1.67 (quintet, J = 6.8 Hz, 2H), 4.22 (dt, J = 1.4 and 6.6 Hz, 2H), 7.33 (dt, J = 1.4, 7.4 Hz, 2H), 7.44 (dt, J = 1.5, 7.4 Hz, 1H), 7.95 (dd, J = 1.5, 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.3, 22.9, 26.3, 29.0, 29.4, 29.5, 32.1, 65.4, 128.6, 129.8, 130.9, 133.0, 166.9. IR (neat) 710, 1112, 1273, 1451, 1722, 2927 cm^{-1}.

General Procedure for the $Cp^*_2Sm(thf)_2$-Catalyzed Acylation of Amines with Esters. Into a Schlenk tube containing toluene solution (1 mL) of $Cp^*_2Sm(thf)_2$ (0.1 mmol) was slowly added ester (1 mmol) followed by amine (2 mmol) at 0 °C under argon. The reaction mixture was stirred at rt under argon. The same workup described in the general procedure was used for the $Cp^*_2Sm(thf)_2$-catalyzed acylation of alcohols with esters.

***N*-Octylacetoamide:** ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 3.3 Hz, 3H), 1.21−1.41 (m, 10H), 1.45−1.59 (m, 2H), 1.99 (d, J = 1.6 Hz, 3H), 3.23 (q, J = 6.5 Hz, 2H), 6.40 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 23.0, 26.8, 29.0, 29.1, 29.4, 31.6, 39.5, 170.1. IR (neat) 603, 722, 1294, 1369, 1436, 1655, 2926, 3086, 3288 cm^{-1}.

***N*-Benzylacetamide:** ^{1}H NMR ($CDCl_3$) δ 1.89 (s, 3H), 4.30 (d, J = 5.7 Hz, 2H), 6.19 (brs, 1H), 7.16−7.26 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 23.0, 43.5, 127.3, 127.7, 128.6, 138.2, 170.0. IR (neat) 503, 696, 745, 1553, 1644, 3294 cm^{-1}.

***N*-(3-Oxybutyl)acetamide:** ^{1}H NMR ($CDCl_3$) δ 1.97 (d, J = 6.5 Hz, 3H), 3.33 (d, J = 7.0 Hz, 3H), 3.38−3.45 (m, 4H), 6.53 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 22.8, 39.0, 58.4, 70.9, 170.3. IR (neat) 603, 1128, 1198, 1294, 1372, 1434, 1556, 1661, 2880, 2930, 3294 cm^{-1}.

1-Acetylpiperidine: ^{1}H NMR ($CDCl_3$) δ 1.81 (q, J = 6.7 Hz, 2H), 1.91 (q, J = 6.7 Hz, 2H), 1.98 (s, 3H), 3.36 (t, J = 6.7 Hz, 2H), 3.37 (t, J = 6.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 22.1, 24.2, 25.8, 45.1, 47.0, 168.8. IR (neat) 615, 1454, 1632, 2875, 2970, 3471 cm^{-1}.

1-Acetylpyrrolidine: ^{1}H NMR ($CDCl_3$) δ 1.48−1.70 (m, 6H), 2.08 (s, 3H), 3.39 (t, J = 5.4 Hz, 2H), 3.54 (t, J = 5.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.4, 24.4, 25.4, 26.3, 42.4, 47.4, 168.7. IR (neat) 752, 988, 1268, 1445, 1651, 2856, 2936, 3476 cm^{-1}.

***N*-Octylacrylamide:** ^{1}H NMR ($CDCl_3$) δ 0.90−0.99 (m, 3H), 1.20−1.30 (m, 8H), 1.42−1.62 (m, 2H), 3.19−3.42 (m, 1H), 3.42−3.56 (m, 1H), 5.60−5.66 (m, 1H), 6.16−6.34 (m, 2H), 6.42−6.83 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9, 15.1, 22.5, 26.9, 29.1, 29.2, 29.4, 31.6, 39.5, 65.7, 125.6, 131.0, 165.6. IR (neat) 723, 953, 1245, 1463, 1556, 1651, 2926, 3281 cm^{-1}.

***N*-Octylbenzamide:** ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5 Hz, 3H), 1.16−1.43 (m, 10H), 1.60 (quintet, J = 7.3 Hz, 2H), 3.42 (q, J = 6.7 Hz, 2H), 6.43 (brs, 1H), 7.36−7.49 (m, 3H), 7.77 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 27.0, 29.1, 29.2, 29.6, 31.7, 40.1, 126.8, 128.4, 131.2, 134.8, 167.5. IR (neat) 692, 715, 1285, 1466, 1532, 1632, 2849, 2919, 3338 cm^{-1}.

***N*-Octylformamide:** ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.3 Hz, 3H), 1.21−1.38 (m, 10H), 1.45−1.60 (m, 2H), 3.19−3.31 (m, 2H), 6.10 (brs, 1H), 8.14 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 26.3, 26.7, 29.0, 29.1, 29.4, 31.1, 31.7, 38.1, 41.8, 161.3, 164.8. IR (neat) 722, 1382, 1463, 1538, 1661, 2924, 3281 cm^{-1}.

***N*-Phenylformamide:** ^{1}H NMR ($CDCl_3$) δ 7.06−7.18 (m, 4H), 7.53−7.57 (m, 1H), 8.30 (s, 0.5H), 8.59 (brs, 1H), 8.68 (d, J = 11.6 Hz, 0.5 H), 9.23 (brs). ^{13}C NMR ($CDCl_3$) δ 118.6, 120.1, 124.6, 125.0, 128.8, 129.5, 136.7, 136.9, 159.7, 163.1. IR (neat) 659, 754, 1314, 1401, 1444, 1688, 3136 cm^{-1}.

***N*,*N*-Dibutylformamide:** ^{1}H NMR ($CDCl_3$) δ 0.83−0.88 (m, 6H), 1.15−1.33 (m, 4H), 1.37−1.52 (m, 4H), 3.11−3.22 (m, 4H), 8.00 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 13.5, 13.7, 19.5, 20.0, 29.2, 30.6, 41.9, 47.2, 163.4. IR (neat) 1119, 1213, 1427, 1457, 1675, 2872, 2931, 2958 cm^{-1}.

***N*-Octylethoxyformamide:** ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 6.8 Hz, 3H), 1.10−1.28 (m, 13 H), 1.29−1.45 (m, 2H), 3.08 (q, J = 6.8 Hz, 2H), 4.03 (q, J = 6.8 Hz, 2H), 4.81 (brs, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 14.2, 14.6, 22.6, 22.8, 26.7, 29.1, 30.0, 31.7, 60.5, 63.7, 156.6. IR (neat) 1041, 1260, 1533, 1700, 2855, 2927, 3340 cm^{-1}.

General Procedure for the SmI_2-Catalyzed Acylation of Amines with Esters. A THF solution of SmI_2 was prepared by Kagan's method.[21] Ester (1 mmol) and amine (2 mmol) were added to the THF solution (1 mL) of SmI_2 (0.1 mmol), and the solution was stirred at rt for 3 h. The same workup described in the general procedure was used in the $Cp^*_2Sm(thf)_2$-catalyzed acylation of alcohols with esters.

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