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N,O-ligand accelerated zinc-catalyzed transesterification of alcohols with vinyl esters

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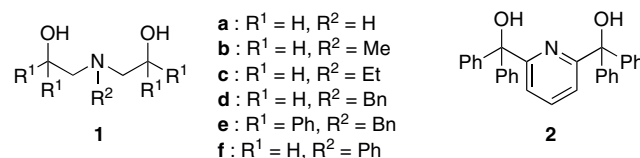
Abstract

N-Phenyldiethanolamine (**1f**) is an efficient ligand for zinc-catalyzed transesterification of alcohols with vinyl acetate ($R^3 = Me$) at room temperature. In the case of using other vinyl esters ($R^3 = Et$, *n*-Pr, Ph), the corresponding products were easily obtained in the presence of pyridine-type ligand **2** instead of aminoalcohol **1f**.
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Keywords: Zinc catalyst; Alcohol; Ester; Transesterification

1. Introduction

Transesterification is a convenient method for preparation of versatile esters from inexpensive alcohols and esters [1]. Acidic [2] or basic [3] catalysts are commonly used to promote this reaction in heating, but they sometimes exhibit low chemoselectivity, and labile functional groups can be damaged. They may also lead to the formation of side products. Recently, the Nolan groups and the Hedrick groups independently reported transesterification of alcohols using *N*-heterocyclic carbene type catalysts [4]. In this case, not only vinyl esters but also alkyl esters such as ethyl acetate and methyl benzoate were effective acylation reagents at room temperature. On the other hand, organometallic catalysts such as $Cp_2^*Sm(thf)_2$ [5] distannoxanes [6], and tin(IV) amide with fluorous tag [7], or the basic iminophosphoranes [8], iodine [9], ammonium triflate derivatives [10] are better than simple acids, however they still require heating conditions or long times to complete the reaction. We report here an efficient method of transesterification using Et_2Zn with **1** or **2** as ligands with vinyl esters as acylation reagents under mild conditions [11].

a : R^1 = H, R^2 = H
b : R^1 = H, R^2 = Me
c : R^1 = H, R^2 = Et
d : R^1 = H, R^2 = Bn
e : R^1 = Ph, R^2 = Bn
f : R^1 = H, R^2 = Ph

2. Results and discussion

We investigated the effect of ligands for the zinc-promoted transesterification of benzyl alcohol with vinyl acetate in toluene as a solvent at room temperature (Table 1). Without a ligand and Et_2Zn, the reaction did not occur (Entry 1). Using Et_2Zn as a catalyst, the reaction occurred, but we obtained benzyl acetate in a low yield (Entry 2). We next investigated effect of ligands **1** and **2**. The zinc complex from 5 mol% of ligand and 10 mol% of Et_2Zn was used as a catalyst. Using ligands **1a–c** led to lower yields compared to the case without ligands (Entry 2 vs. Entries 3–5). *N*-benzyldiethanolamine (**1d**), its derivative **1e** and pyridine-type ligand **2** led to moderate yields (Entries 6, 7 and 9). When *N*-phenyldiethanolamine (**1f**) was employed, the reaction yielded the desired product quantitatively in 1 h (Entry 8).

In the presence of **1f** as a ligand, the effect of solvents was examined. Using hexane as a solvent, instead

Table 1
Optimization of reaction conditions on the transesterification of benzyl alcohol with vinyl acetate[a]
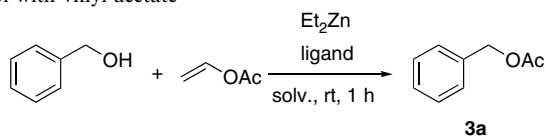
Entry	Ligand (mol%)	mol% of Et$_2$Zn	Solvent	Yield (%)[b]
1	–	–	PhMe	0
2	–	10	PhMe	30
3	**1a** (5)	10	PhMe	4
4	**1b** (5)	10	PhMe	8
5	**1c** (5)	10	PhMe	16
6	**1d** (5)	10	PhMe	46
7	**1e** (5)	10	PhMe	52
8	**1f** (5)	10	PhMe	99 (90)[c]
9	**2** (5)	10	PhMe	(76)[c]
10	**1f** (5)	10	Hexane	81
11	**1f** (5)	10	THF	27
12	**1f** (5)	10	MeCN	7
13	**1f** (5)	10	AcOEt	16
14	**1f** (5)	10	CHCl$_3$	1

[a] Reaction conditions: PhCH$_2$OH (1 mmol), vinyl acetate (5 mmol), ligand, Et$_2$Zn in hexane (1.0 M), solvent (2 mL).
[b] Determined by ^{1}H NMR.
[c] Values in parenthesis are isolated yields.

of toluene, led to also good yield (Entry 8 vs. Entry 10). By contrast, polar solvents such as THF, acetonitrile, ethyl acetate, and chloroform were less effective (Entries 11–14). Thus, non-polar solvents were more suitable for this reaction.

Under optimized reaction conditions, transesterifications of vinyl acetate with various primary alcohols bearing a variety of functional groups were carried out at room temperature, and the results are summarized in Table 2.

4-Methoxybenzyl alcohol and 4-chlorobenzyl alcohol were smoothly converted into the corresponding acetates (Entries 1 and 2). The reaction of the benzylic alcohol with ester moiety in its molecule required a longer reaction time, but no side product was identified (Entry 3). This means that the methyl ester moiety is less reactive compared to the vinyl acetate and does not take part in the transesterification. *ortho-*, *meta-*, and *para-*methylbenzyl alcohols were also treated with vinyl acetate, which led to high yields. No steric effect was observed, nor did any electronic influence result from the difference of the position of the methyl group (Entries 4–6). 1-Naphthalenemethanol was also easily acylated into the desired ester (Entry 7). Allylic alcohols such as cinnamyl alcohol and geraniol also led to good yields (Entries 8 and 9). Phenethyl alcohol, 2-phenyl-1-propanol, and 3-phenyl-1-propanol reacted equally well, giving the corresponding acetates in good yields (Entries 10–12). Saturated linear alcohol such as decanol, was effectively acylated in a high yield (Entry 13). The transesterification of alcohols bearing acid-sensitive functional groups, such as 2-hydroxymethyl-1,4-benzodioxane, led to the desired products

(Entry 14). There was no side product but the reaction required much a longer reaction time.

Based on the result of the acylation of various primary alcohols with vinyl acetate, we tested the transesterification of steric hindered secondary alcohols with vinyl acetate (Table 3). In the presence of 10 mol% of **1f** and 20 mol% of Et$_2$Zn at room temperature, benzylic secondary alcohols, such as 1-phenylethanol and 1-(2-naphthyl)ethanol, produced moderate to good yields (Entries 1 and 2). Allylic secondary alcohol such as *trans*-piperitol and saturated secondary alcohols such as borneol and menthol also led to good yields in the presence of 20 mol% of **1f** and 40 mol% of Et$_2$Zn (Entries 3–5). When pyridine-type ligand **2** was used, the desired product obtained in moderate yield (Entry 6).

We next attempted esterification with other vinyl esters such as vinyl propionate, butyrate, and benzoate [12] (Table 4). In the case of vinyl propionate, the benzyl esters were obtained low yield using 5 mol% of **1f** and 10 mol% of Et$_2$Zn (Entry 1). When the reaction was carried out in the presence of pyridine-type ligand **2** instead of aminoalcohol **1f**, the corresponding product was obtained in good yield (Entry 2). Under this condition, other benzyl esters and cinnamyl esters were easily prepared in good yields. (Entries 3–7).

In summary, we found that various esters were easily obtained from alcohols and vinyl esters in the presence of catalytic amount of Et$_2$Zn with **1f** or **2** as a ligand at room temperature.
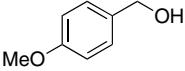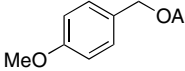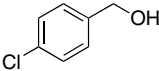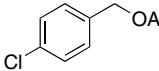
3. Experimental
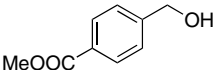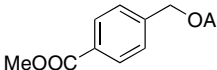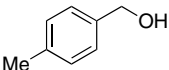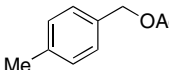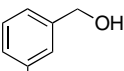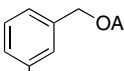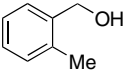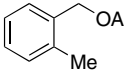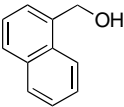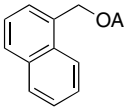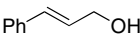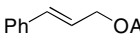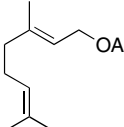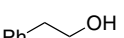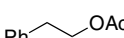
3.1. General methods

All the experiments were carried out under an argon atmosphere. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are reported in δ ppm referenced to an internal SiMe$_4$ standard for ^{1}H and ^{13}C NMR. Mass spectra were recorded on a GCMS-QP 5050, JEOL JMS-AX500, or JEOL JMS-HX110. **1a–c** and **1f** are commercially available. **1d** [13] and **2** [14] were similarly prepared according to the literature methods.

3.2. Preparation of aminoalcohol 1e

A solution of phenylmagnesium bromide (30 mmol) in THF (23 mL) was added to diethyl *N*-benzyliminodiacetate (1.53 g, 6.0 mmol) in THF (15 mL) at room temperature. The mixture was stirred for overnight. The mixture was added sat. NH$_4$Cl aq. and diluted with ethyl acetate. The organic layer was washed with brine, dried over MgSO$_4$, and concentrated under reduced pressure. The crude product was purified by recrystallization from hexane–chloroform: 0.298 g, 0.60 mmol, 10% as a white solid; m.p. 147–150 °C; ^{1}H NMR (DMSO-*d*) δ: 3.26 (s, 2H), 3.43 (s, 4H), 5.87 (s, 2H), 6.75–6.85 (m, 2H), 7.09–7.33 (m, 23H);

Table 2
Transesterification of primary alcohols with vinyl acetate[a]

Entry	Alcohol	Time (h)	Product	Yield (%)[b]
1	MeO—C6H4—CH2OH	3	MeO—C6H4—CH2OAc **3b**	78
2	Cl—C6H4—CH2OH	2	Cl—C6H4—CH2OAc **3c**	90
3[c]	MeOOC—C6H4—CH2OH	24	MeOOC—C6H4—CH2OAc **3d**	64
4	Me—C6H4—CH2OH	3	Me—C6H4—CH2OAc **3e**	87
5	Me—C6H4—CH2OH	3	Me—C6H4—CH2OAc **3f**	88
6	Me—C6H4—CH2OH	3	Me—C6H4—CH2OAc **3g**	92
7	naphthyl—CH2OH	2.5	naphthyl—CH2OAc **3h**	97
8	Ph—CH=CH—CH2OH	5	Ph—CH=CH—CH2OAc **3i**	95
9[c]	geraniol	4	geranyl OAc **3j**	97
10	Ph—CH2CH2OH	4	Ph—CH2CH2OAc **3k**	96

Table 2 (*continued*)

Entry	Alcohol	Time (h)	Product	Yield (%)[b]
11	Ph—CH(CH₃)CH₂OH	5	**3l** Ph—CH(CH₃)CH₂OAc	91
12	Ph—CH₂CH₂CH₂OH	6	**3m** Ph—CH₂CH₂CH₂OAc	90
13[c]	⟨⟩₈ OH	5	**3n** ⟨⟩₈ OAc	97
14	benzodioxane-CH₂OH	24	**3o** benzodioxane-CH₂OAc	79

[a] Reaction conditions: alcohol (1 mmol), vinyl acetate (5 mmol), ligand **1f** (5 mol%), Et₂Zn (10 mol%) in hexane (1.0 M, 0.1 mL), PhMe (2 mL), rt.
[b] Isolated yields.
[c] 10 mol% of **1f** and 20 mol% of Et₂Zn were used under 0.5 mmol scale reaction.

Table 3
Transesterification of secondary alcohols with vinyl acetate[a]
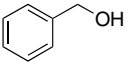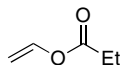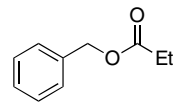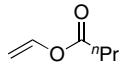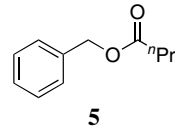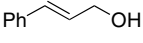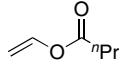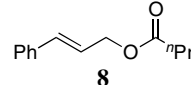
Entry	Alcohol	Ligand **1f**/Et₂Zn (mol%)	Product	Yield (%)[b]
1	Ph—CH(CH₃)OH	10/20	**3p** Ph—CH(CH₃)OAc	71
2	naphthyl-CH(CH₃)OH	10/20	**3q** naphthyl-CH(CH₃)OAc	85
3	menthenol (isopropyl cyclohexenol)—OH	20/40	**3r** —OAc	79
4	borneol—OH	20/40	**3s** —OAc	86
5	menthol—OH	20/40	**3t** —OAc	91
6[c]		20/40		73

[a] Reaction conditions: alcohol (1 mmol), vinyl acetate (5 mmol), ligand **1f**, Et₂Zn in hexane (1.0 M), PhMe (2 mL), rt, 24 h.
[b] Isolated yields.
[c] This reaction was carried out using **2** instead of **1f**.

Table 4
Transesterification of alcohols with vinyl esters[a]

Entry	Alcohol	Vinyl ester	Ligand	Time (h)	Product	Yield (%)[b]
1			**1f**	3	**4**	47[c]
2			**2**	2.5		90
3			**2**	2.5	**5**	88
4			**2**	5	**6**	92
5				3	**7**	90
6	Ph⌒⌒OH		**2**	3	**8**	94
7				4	**9**	92

[a] Reaction conditions: alcohol (1 mmol), vinyl acetate (5 mmol), ligand (5 mol%), Et_2Zn (10 mol%) in hexane (1.0 M, 0.1 mL), PhMe (2 mL), rt.
[b] Isolated yields.
[c] Determined by ^1H NMR.

^{13}C NMR (DMSO-*d*) δ: 59.4, 64.9, 77.0, 126.5, 126.7, 127.1, 128.1, 128.4, 129.3, 139.1, 147.6; FAB-MS *m/z* (rel. intensity) 500 (M^++1, 43); HRMS (FAB-MS) *m/z*. Calc. for $C_{35}H_{34}O_2N$+H 500.2590. Found 500.2623.

3.3. General procedure of transesterification of alcohol with vinyl ester

Under an atmosphere of argon, Et_2Zn (0.1 mmol) in hexane (1.0 M, 0.1 mL) was added to the solution of ligand **1** or **2** (0.05 mmol) in PhMe (1 mL) and the mixture was stirred for 0.5 h at room temperature. A mixture of alcohol (1 mmol) and vinyl ester (5 mmol) in PhMe (1 mL) was added to the reaction mixture. After being stirred for corresponding period, the reaction mixture was diluted with diethyl ether and quenched with water. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

3.3.1. Benzyl acetate (3a) [15]
90% as a colorless liquid; ^1H NMR ($CDCl_3$) δ: 2.08 (s, 3H), 5.09 (s, 2H), 7.25–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ: 20.7, 66.0, 128.02, 128.05, 128.3, 135.8, 170.6; EI-MS *m/z* (rel. intensity) 150 (M^+, 35).

3.3.2. 4-Methoxybenzyl acetate (3b) [16]
78% as a colorless liquid; ^1H NMR ($CDCl_3$) δ: 2.07 (s, 3H), 3.80 (s, 3H), 5.04 (s, 2H), 6.83–6.94 (m, 2H), 7.22–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 21.1, 55.3, 66.1, 114.0, 128.1, 130.2, 159.7, 171.0; EI-MS *m/z* (rel. intensity) 180 (M^+, 43).

3.3.3. 4-Chlorobenzyl acetate (3c) [17]

90% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.10 (s, 3H), 5.06 (s, 2H), 7.23–7.38 (m, 4H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 65.4, 128.7, 129.6, 134.1, 134.4, 170.7; EI-MS m/z (rel. intensity) 184 (M$^+$, 31).

3.3.4. Methyl 4-(acetoxymethyl)benzoate (3d)

64% as colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.13 (s, 3H), 3.92 (s, 3H), 5.15 (s, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 8.03 (dd, $J = 1.7$ and 6.6 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ: 23.2, 54.5, 67.8, 130.0, 132.18, 132.23, 143.3, 169.0, 173.0; FAB-MS m/z (rel. intensity) 209 (M$^+$+1, 100); HRMS (FAB-MS) m/z. Calc. for C$_{11}$H$_{12}$O$_4$+H 209.0814. Found 209.0824.

3.3.5. 4-Methybenzyl acetate (3e) [18]

87% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.08 (s, 3H), 2.34 (s, 3H), 5.06 (s, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 21.2, 66.3, 128.5, 129.3, 132.9, 138.1, 170.9; EI-MS m/z (rel. intensity) 164 (M$^+$, 50).

3.3.6. 3-Methybenzyl acetate (3f) [19]

88% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.09 (s, 3H), 2.35 (s, 3H), 5.06 (s, 2H), 7.07–7.31 (m, 4H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 21.4, 66.4, 125.4, 128.5, 129.0 (C × 2), 135.8, 138.3, 170.9; EI-MS m/z (rel. intensity) 164 (M$^+$, 39).

3.3.7. 2-Methybenzyl acetate (3g) [20]

92% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.09 (s, 3H), 2.35 (s, 3H), 5.12 (s, 2H), 7.12–7.39 (m, 4H); ^{13}C NMR (CDCl$_3$) δ: 18.9, 21.0, 64.7, 126.0, 128.6, 129.2, 130.4, 133.8, 137.0, 171.0; EI-MS m/z (rel. intensity) 164 (M$^+$, 0.7).

3.3.8. (1-Naphthalenyl)methyl acetate (3h) [21]

97% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.10 (s, 3H), 5.56 (s, 2H), 7.42–7.60 (m, 4H), 7.78–7.92 (m, 2H), 7.95–8.05 (m, 1H); ^{13}C NMR (CDCl$_3$) δ: 21.1, 64.6, 123.6, 125.3, 126.0, 126.6, 127.5, 128.8, 129.4, 131.5, 131.6, 133.8, 171.0; EI-MS m/z (rel. intensity) 200 (M$^+$, 60).

3.3.9. Cinnamyl acetate (3i) [15]

96% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.03 (s, 3H), 4.66 (dd, $J = 1.2$ and 6.5 Hz, 2H), 6.22 (td, $J = 6.5$ and 15.9 Hz, 1H), 6.58 (d, $J = 15.9$ Hz, 1H), 7.11–7.39 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 65.1, 123.1, 126.6, 128.1, 128.6, 134.2, 136.2, 170.8; FAB-MS m/z (rel. intensity) 176 (M$^+$, 32).

3.3.10. Geranyl acetate (3j) [15]

97% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.60 (s, 3H), 1.68 (s, 3H), 1.71 (s, 3H), 1.99–2.17 (m, 4H), 2.06 (s, 3H), 4.72 (d, $J = 7.1$ Hz, 2H), 5.03–5.15 (m, 1H), 5.30–5.39 (m, 1H); ^{13}C NMR (CDCl$_3$) δ: 16.4, 17.7, 21.0, 25.7, 26.3, 39.5, 61.4, 118.2, 123.7, 131.8, 142.2, 171.1; EI-MS m/z (rel. intensity) 196 (M$^+$, 0.08).

3.3.11. Phenethyl acetate (3k) [15]

96% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 2.01 (s, 3H), 2.92 (t, $J = 7.1$ Hz, 3H), 4.26 (t, $J = 7.1$ Hz, 2H), 7.08–7.36 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 35.1, 64.9, 126.6, 128.5, 128.9, 137.8, 171.0; EI-MS m/z (rel. intensity) 165 (M$^+$+1, 0.03).

3.3.12. 2-Phenylpropyl acetate (3l) [22]

91% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.30 (d, $J = 7.0$ Hz, 3H), 2.00 (s, 3H), 3.09 (sextet, $J = 7.0$ Hz, 1H), 4.04–4.21 (m, 2H), 7.10–7.39 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 18.1, 20.9, 38.9, 69.4, 126.7, 127.3, 128.5, 143.2, 171.1; EI-MS m/z (rel. intensity) 178 (M$^+$, 22).

3.3.13. 3-Phenylpropyl acetate (3m) [23]

90% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.88–2.02 (m, 2H), 2.05 (s, 3H), 2.63–2.74 (m, 2H), 4.10 (q, $J = 6.6$ Hz, 2H), 7.11–7.23 (m, 3H), 7.23–7.34 (m, 2H); ^{13}C NMR (CDCl$_3$) δ: 21.0, 30.2, 32.2, 63.8, 126.0, 128.4, 128.4, 141.2, 171.2; EI-MS m/z (rel. intensity) 178 (M$^+$, 0.11).

3.3.14. Decyl acetate (3n) [24]

97% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.88 (t, $J = 6.8$ Hz, 3H), 1.18–1.41 (m, 14H), 1.62 (quintet, $J = 7.0$ Hz, 2H), 2.05 (s, 3H), 4.05 (t, $J = 6.8$ Hz, 2H) ; ^{13}C NMR (CDCl$_3$) δ: 14.5, 21.4, 23.1, 26.3, 29.0, 29.66, 29.71, 29.9, 32.3, 65.1, 171.7; EI-MS m/z (rel. intensity) 201 (M$^+$+1, 1).

3.3.15. 2-Acetoxymethyl-1,4-benzodioxane (3o) [25]

79% as a yellow liquid; ^{1}H NMR (CDCl$_3$) δ: 2.07 (s, 3H), 4.01 (dd, $J = 6.8$ and 11.4 Hz, 1H), 4.17–4.42 (m, 4H), 6.67–6.95 (m, 4H) ; ^{13}C NMR (CDCl$_3$) δ: 20.8, 62.6, 65.1, 70.9, 117.3, 117.5, 121.7, 142.8, 143.0, 170.6; EI-MS m/z (rel. intensity) 208 (M$^+$, 37).

3.3.16. 1-Phenylethyl acetate (3p) [15]

71% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.53 (d, $J = 6.6$ Hz, 3H), 2.06 (s, 3H), 5.88 (q, $J = 6.6$ Hz, 1H), 7.21–7.42 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 21.3, 22.2, 72.3, 126.1, 127.9, 128.5, 141.7, 170.3; EI-MS m/z (rel. intensity) 164 (M$^+$, 24).

3.3.17. 1-(2-Naphthyl)ethyl acetate (3q) [26]

85% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.62 (d, $J = 6.6$ Hz, 3H), 2.09 (s, 3H), 6.05 (q, $J = 6.6$ Hz, 1H), 7.41–7.53 (m, 3H), 7.71–7.92 (m, 4H); ^{13}C NMR (CDCl$_3$) δ: 21.4, 22.2, 72.4, 124.1, 125.0, 126.0, 126.2, 127.7, 128.0, 128.4, 133.0, 133.2, 139.0, 170.4; EI-MS m/z (rel. intensity) 214 (M$^+$, 25).

3.3.18. trans-Piperityl acetate (3r) [27]

79% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.84 (d, $J = 6.9$ Hz, 3H), 0.95 (d, $J = 6.9$ Hz, 3H), 1.33–1.56 (m, 2H), 1.63–1.80 (m, 5H), 1.92–2.02 (m, 2H), 2.06 (s, 3H), 5.21–5.36 (m, 2H); ^{13}C NMR (CDCl$_3$) δ: 17.9,

20.9, 21.1, 21.5, 23.2, 26.8, 29.5, 43.9, 72.1, 120.8, 139.8, 171.2; EI-MS m/z (rel. intensity) 196 (M$^+$, 2).

3.3.19. Bornyl acetate (3s) [15]

86% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.83 (s, 3H), 0.87 (s, 3H), 0.90 (s, 3H), 0.97 (dd, $J = 3.5$ and 13.7 Hz, 1H), 1.16–1.38 (m, 2H), 1.61–1.82 (m, 2H), 1.86–2.00 (m, 1H), 2.06 (s, 3H), 2.28–2.42 (m, 1H), 4.88 (ddd, $J = 1.3$, 5.6 and 10.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ: 13.4, 18.8, 19.6, 21.2, 27.0, 28.0, 36.7, 44.8, 47.7, 48.6, 79.8, 171.4; EI-MS m/z (rel. intensity) 196 (M$^+$, 1.5).

3.3.20. Mentyl acetate (3t) [15]

91% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.76 (d, $J = 7.0$ Hz, 3H), 0.82–1.15 (m, 9H), 1.21–1.59 (m, 2H), 1.60–1.75 (m, 2H), 1.79–1.93 (m, 1H), 1.94–2.11 (m, 1H), 2.03 (s, 3H), 4.68 (td, $J = 4.4$ and 10.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ: 16.3, 20.6, 21.2, 21.9, 23.4, 26.2, 31.3, 34.2, 30.9, 46.9, 74.1, 170.6; EI-MS m/z (rel. intensity) 199 (M$^+$+1, 0.01).

3.3.21. Benzyl propanoate (4) [28]

90% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.16 (t, $J = 7.5$ Hz, 3H), 2.38 (q, $J = 7.6$ Hz, 2H), 5.12 (s, 2H), 7.26–7.42 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 9.5, 28.0, 66.6, 128.6, 129.0, 136.5, 174.7; EI-MS m/z (rel. intensity) 164 (M$^+$, 23).

3.3.22. Benzyl butanoate (5) [15]

88% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.94 (t, $J = 7.4$ Hz, 3H), 1.67 (sextet, $J = 7.4$ Hz, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 5.11 (s, 2H), 7.27–7.40 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 14.1, 18.9, 36.6, 66.5, 128.6, 129.0, 136.6, 173.9; EI-MS m/z (rel. intensity) 178 (M$^+$, 23).

3.3.23. Benzyl benzoate (6) [15]

92% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 5.36 (s, 2H), 7.29–7.49 (m, 7H), 7.50–7.60 (m, 1H), 8.02–8.13 (m, 2H); ^{13}C NMR (CDCl$_3$) δ: 66.7, 128.2, 128.3, 128.4, 128.7, 129.8, 130.2, 133.1, 136.1, 166.5; EI-MS m/z (rel. intensity) 212 (M$^+$, 21).

3.3.24. Cinnamyl propanoate (7) [29]

90% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 1.17 (t, $J = 7.5$ Hz, 3H), 2.38 (q, $J = 7.6$ Hz, 2H), 4.73 (dd, $J = 1.1$ and 6.4 Hz, 2H), 6.29 (td, $J = 6.4$ and 15.9 Hz, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 7.17–7.44 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 9.5, 28.0, 65.3, 123.8, 127.0, 128.5, 129.0, 134.5, 136.7, 174.7; EI-MS m/z (rel. intensity) 190 (M$^+$, 14).

3.3.25. Cinnamyl butanoate (8) [30]

94% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 0.97 (t, $J = 7.4$ Hz, 3H), 1.57–1.78 (m, 2H), 2.33 (t, $J = 7.4$ Hz, 2H), 4.73 (d, $J = 6.4$ Hz, 2H), 6.28 (td, $J = 6.4$ and 15.9 Hz, 1H), 6.64 (d, $J = 15.9$ Hz, 1H), 7.19–7.46 (m, 5H); ^{13}C NMR (CDCl$_3$) δ: 14.1, 18.9, 36.6, 65.2, 123.8, 127.0, 128.4, 129.0, 134.5, 136.7, 173.8; EI-MS m/z (rel. intensity) 204 (M$^+$, 13).

3.3.26. Cinnamyl benzoate (9) [31]

92% as a colorless liquid; ^{1}H NMR (CDCl$_3$) δ: 4.98 (dd, $J = 1.2$ and 6.4 Hz, 2H), 6.40 (td, $J = 6.4$ and 15.9 Hz, 1H), 6.74 (d, $J = 15.9$ Hz, 1H), 7.20–7.37 (m, 3H), 7.38–7.50 (m, 4H), 7.51–7.61 (m, 1H), 8.04–8.13 (m, 2H); ^{13}C NMR (CDCl$_3$) δ: 65.6, 123.3, 126.7, 128.1, 128.4, 128.6, 129.7, 130.2, 133.0, 134.3, 136.2, 166.4; EI-MS m/z (rel. intensity) 238 (M$^+$, 5).

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