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Epoxide as precatalyst for metal-free catalytic transesterification

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ABSTRACT

Transesterification of methyl esters was accelerated by an *in situ*-generated metal-free catalyst comprising a quaternary alkylammonium salt and an epoxide. The combination of a quaternary alkylammonium acetate and glycidol is optimal, and various esters were synthesized from methyl esters with alcohols in good to excellent yield. Analysis of the catalyst solution revealed that basic species are generated by the ring-opening reaction of epoxide.

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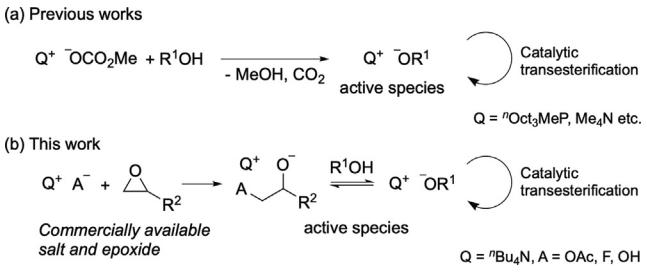
Introduction

Metal-free catalysis has emerged as a viable method over the last few decades due to the low cost compared with common metal catalysts and the absence of metal contamination in the reaction products [1–3]. Catalytic transesterification of abundant esters is considered as a useful method for the efficient synthesis of various esters [4–6], and recent developments of metal-free catalysis have overcome drawbacks of metal-based catalysts and expanded the scope of substrates to those having a chelating moiety that may deactivate a metal center [7–15]. Nolan et al. reported that the *N*-heterocyclic carbene works as a nucleophilic catalyst for transesterification under mild conditions [12]. More recently, organic methyl carbonate salts were reported as catalysts for the transesterification of alkyl carbonate and methyl esters (Scheme 1a) [13–15]. Facile decomposition of methyl carbonate accompanied by CO_2 uptake resulted in the generation of active basic species. While those catalysts are easy to handle and efficient enough to afford product esters, a simpler and more accessible system is desired for a wide range of applications, including industrial use.

Epoxides are useful precursors for value-added alcohols by the ring-opening reaction due to the strained three-membered ring [16]. We hypothesized that such an energetically favored ring-opening process could serve as a simple metal-free catalyst generator (Scheme 1b). Quaternary alkylammonium halide reacts with ethylene oxide to generate anion species, followed by an attack to the carbonyl groups of substrates [17], and this basic reactivity is currently applied to catalytic carbonate synthesis [18–20]. We recently found that the catalytic transformation of glycidol to glycidyl esters is mildly promoted by quaternary alkyl ammonium chloride, in which chloride anions attack the epoxide to produce an active anion catalyst [21]. Herein, we reveal the interesting role of epoxide as an anion precatalyst for general catalytic transesterification.



Scheme 1. Concept of this work.

Results and discussion

For transesterification of methyl benzoate (**1a**) with 1 eq of 1-hexanol (**2a**) in hexane under azeotropic reflux conditions (heater temperature: 80 °C) for 2 h, the addition of 5 mol% (^{n}Bu)$_4$NOAc with 5 mol% glycidol resulted in the formation of hexyl benzoate (**3aa**) in 91% yield (Table 1, entry 1). No other commercially

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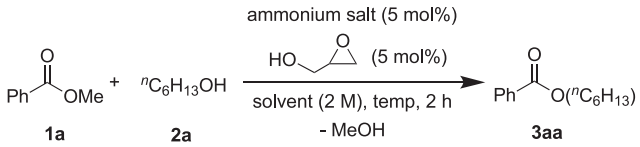
Table 1
Catalytic transesterification of **1a** with **2a**.[a]



Entry	Ammonium salt	Solvent	Temp [°C]	Yield [%]
1	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	Reflux (heater temp: 80 °C)	91
2	$(^n\mathrm{Bu})_4\mathrm{NF}$	Hexane	Reflux	82
3	$(^n\mathrm{Bu})_4\mathrm{NCl}$	Hexane	Reflux	6
4	$(^n\mathrm{Bu})_4\mathrm{NBr}$	Hexane	Reflux	1
5	$(^n\mathrm{Bu})_4\mathrm{NI}$	Hexane	Reflux	0
6	$(^n\mathrm{Bu})_4\mathrm{NNO_3}$	Hexane	Reflux	1
7	$(^n\mathrm{Bu})_4\mathrm{NOH}$	Hexane	Reflux	80
8	$(^n\mathrm{Bu})_3\mathrm{N}$	Hexane	Reflux	38
9[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	Reflux	99 (99)[c]
10[b,d]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	Reflux	77
11[b,d]	$\mathrm{Me_4NOAc}$	Hexane	Reflux	70
12[b,f]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	Reflux	0
13	none[g]	Hexane	Reflux	0
14[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	40	1
15[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Hexane	65	26
16[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	Toluene	65	8
17[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	$\mathrm{CH_3CN}$	65	14
18[b]	$(^n\mathrm{Bu})_4\mathrm{NOAc}$	THF	65	11

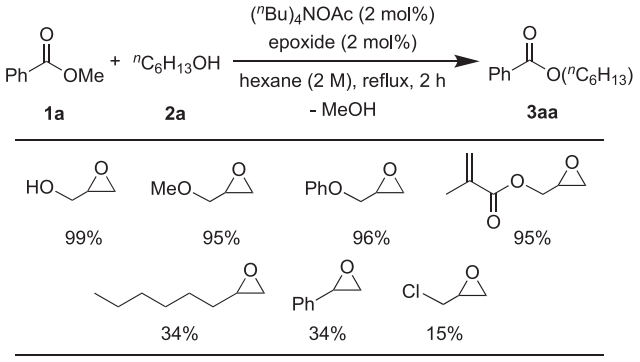
[a] Conditions: **1a** (1 mmol), **2a** (1 mmol), ammonium salt (5 mol%), epoxide (5 mol%), solvent (2 M), 2 h. Yields were determined by GC using biphenyl as an internal standard. Average values of two runs are shown.
[b] Ammonium salt (2 mol%), epoxide (2 mol%).
[c] Yield of isolated product.
[d] Reaction time was 0.5 h.
[f] Without glycidol.
[g] With only glycidol (2 mol%).

available salt, such as halide, nitrate, and hydroxide, exhibited higher activity (entries 2–7). Only fluoride and hydroxide salt acted as a catalyst to give **3aa** in 82% and 80% yield, respectively, and hence the basicity of the anions might relate to the catalytic activity. $(^n\mathrm{Bu})_3\mathrm{N}$ showed low catalytic activity, giving **3aa** in 38% yield (entry 8). Reduction of the amount of catalyst and glycidol positively affected the product yield (entry 9). The activity of ammonium acetate with a shorter *N*-alkyl chain, $\mathrm{Me_4NOAc}$ was comparable to that of $(^n\mathrm{Bu})_4\mathrm{NOAc}$ under a shortened reaction time (entries 10 and 11). The reaction without glycidol, and without $(^n\mathrm{Bu})_4\mathrm{NOAc}$ showed no catalytic activity (entries 12 and 13). Catalytic reactions at a lower temperature had severely decreased yields, indicating that the removal of liberated methanol is key to the equilibrium reaction toward the desired product (entries 14 and 15). Solvents screening revealed that 0.5 mL (2 M) of hexane was best (entries 16–18).

Upon identifying the optimized ammonium salt catalyst and reaction conditions, we screened an epoxide catalyst (Table 2). Glycidyl compounds, such as glycidyl methyl ether, glycidyl phenyl ether, and glycidyl methacrylate, also produced yields comparable to glycidol. In contrast, the addition of 1,2-epoxyoctane, styrene oxide, and epichlorohydrin led to yields of **3aa** of only 34%, 34%, and 15%, respectively. The epoxide functional group comprising a glycidyl moiety (-$\mathrm{OCH_2}$-epoxide) was more efficient for this system than aliphatic and aromatic epoxides.

The optimized combination of catalysts, $(^n\mathrm{Bu})_4\mathrm{NOAc}$ and glycidol, was used to synthesize various esters from corresponding methyl esters and alcohols (Table 3). Aromatic esters with electron-withdrawing as well as electron-donating functional groups at the *para*-position were quantitatively converted to *n*-hexyl esters (**3ba**-**3ea**). *Ortho*-substituted aromatic ester **1f** was also converted to the corresponding ester **3fa**. This system is applicable for the transformation of aliphatic esters, and methyl 1-phenylacetate (**1g**) was converted to ester**3ga** in 87% yield. For sterically-hindered substrates, slightly higher catalyst loading, $(^n\mathrm{Bu})_4\mathrm{NOAc}$ (5 mol%), was necessary. The reaction with methyl cyclohexanecarboxylate (**1h**) and methyl pivalate (**1j**) afforded **3hb** and **3ib** in 97% and 72% yield, respectively. Secondary alcohols were also available as an alcohol part of the product ester. 2-Hexyl benzoate **3ac** was obtained in 92% yield after refluxing for 16 h. Allylic alcohol (**2d**) reacted efficiently while keeping an olefin moiety intact, affording **3ad** in 93% yield. Notably, esters with a chelating group, such as methyl salicylate **1j**, methyl picolinate **1k**, and methyl 2-thiophenecarboxylate **1l**, were applicable to this catalysis, and the corresponding esters **3jb**, **3ka**, and **3la** were isolated in excellent yields (97%–98%). This catalyst system has similar

Table 2
Screening of epoxide.[a]



[a] Conditions : **1a** (1 mmol), **2a** (1 mmol), ammonium salt (2 mol%), epoxide (2 mol

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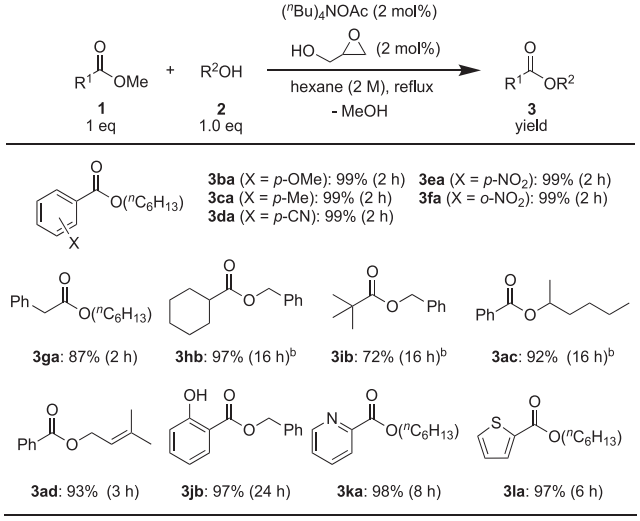
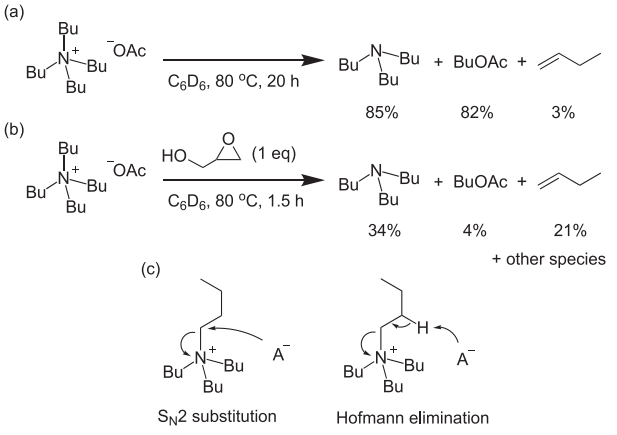
Table 3
Catalytic transesterification of various substrates.[a]



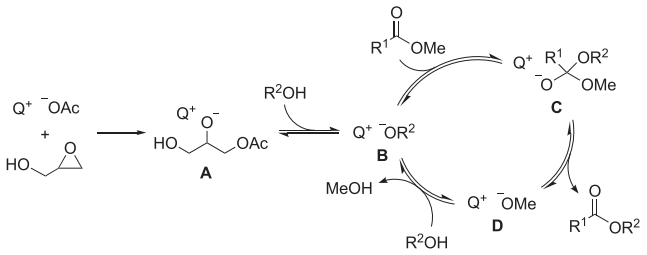
[a] Conditions : ester (1 mmol), alcohol (1 mmol), (^{n}Bu)$_4$NOAc (2 mol%), glycidol (2 mol%), solvent (2 M). Yields of isolated product are shown. [b] (^{n}Bu)$_4$NOAc

feature to the reported metal-free catalyst in terms of the substrate scope [15].

The role of epoxide in this catalysis was elaborated by analyzing the reaction solution with NMR spectroscopy. First, we conducted a thermal decomposition of (^{n}Bu)$_4$NOAc in C_6D_6 (Scheme 2(a)). After heating the solution at 80 °C for 20 h, tributylamine (85%), butyl acetate (82%), and 1-butene (3%) were observed as decomposed products. The formation of butyl acetate indicated that S_N2 substitution by acetate took place at the α-carbon of the ammonium cation, and 1-butene was likely generated by the abstraction of the β-C-H moiety of the ammonium cation by anions (Hofmann elimination, Scheme 2(c)) [22]. Therefore, the acetate anion of (^{n}Bu)$_4$NOAc prefers the nucleophilic attack over proton abstraction. The decomposition pathway was altered when 1 eq of glycidol was added to the (^{n}Bu)$_4$NOAc solution. The yield of 1-butene was increased (21%), and in contrast, the formation of butyl acetate was suppressed (4%), indicating that a more basic species is formed in the solution (Scheme 2(b)). Although the immediate oligomerization of glycidol hampered the characterization of the ring-opened products [23,24], the reaction between acetate and glycidol



Scheme 2. (a) Thermal decomposition of (^{n}Bu)$_4$NOAc, (b) that with 1 eq of glycidol. (c) Major decomposition pathways of alkyl ammonium salt.



Scheme 3. Possible reaction mechanism. Q indicates ^{n}Bu$_4$N.

proceeded to form alkoxide species, which are a catalytically active species.

The mechanism of the catalytic transesterification is essentially the same as that previously reported for glycidyl ester synthesis [21] and the methyl carbonate catalyst system [15]. As shown in Scheme 3, the reaction begins with a nucleophilic attack of acetate to glycidol, affording ring-opened species **A**. The basicity of the ring-opened species is high enough to abstract the proton of the substrate alcohol. Alkoxide **B** reacts with the carbonyl group of methyl ester, and the alcohol part of the ester is replaced to give desired ester through tetrahedral intermediate **C**. Finally, the methoxide species **D** abstracts a proton of substrate alcohol to generate **B** and MeOH, which would be azeotropically removed from the reaction mixture. The cycle may enter **A** from **B** and **D** by the proton abstraction of diol species derived from epoxide. In any cases, the key step is the ring-opening of epoxide, and thus generated alkoxide species work under equilibrium fashion.

Conclusion

Here, we demonstrated that an epoxide acts as an efficient precatalyst for transesterification by alkyl ammonium salts. This facile ring-opening reaction of glycidol and related compounds could be utilized for *in situ*-generation of an active anion catalyst. The use of a readily available organic salts and epoxides may serve as practical metal-free catalysts. Further applications of the catalyst and studies of the reaction mechanism are underway in our laboratory.

Experimental section

General procedure

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on Bruker 600 MHz NMR spectrometer. All spectra were recorded at 25 ± 1 °C. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0 ppm for ^{1}H, and $CDCl_3$ at 77.0 ppm for ^{13}C unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using an InertCap-1 column (0.25 mm × 30 m, GL Sciences Inc.). All samples were analyzed and quantified by using biphenyl or undecane as an internal standard. High resolution mass spectroscopies were recorded on a Bruker micrOTOFII spectrometer using ESI mode. Elemental analyses were measured with a Thermo Fisher Scientific Inc. Flash2000 instrument. All chemicals were purchased from chemical suppliers. Hydrate form of ^{n}Bu$_4$NF (TCI) and 54% aqueous solution of ^{n}Bu$_4$NOH (Sigma-Aldrich) were used without any purification. ^{n}Bu$_4$NOAc was purified by recrystallization in hot toluene solution under an inert atmosphere to remove water. Glycidol was distilled under an atmospheric pressure before to use in order to remove oligomers. Other chemicals were used as received. Catalytic reactions were performed using ChemiStation (Tokyo Rika Inc.) equipped with thermostated apparatus.

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Procedure for catalytic transesterification

In the test tube (volume: 15 mL), catalyst (0.050 mmol) was suspended in hexane (0.5 mL). Methyl ester (1.0 mmol), alcohol (1.0 mmol), and epoxide (0.050 mmol) were added in this order. The test tube was placed in the ChemiStation apparatus whose temperature setting was stabilized, and magnetically stirred for 2 h under azeotropic reflux condition (heater temp: 80 °C for hexane). Resulting reaction mixture was diluted with CH_3CN (3 mL), and collected in the vial. Extra CH_3CN (3 mL) was used for a collection of residual chemicals in a test tube. To a combined solution was then added measured amount of biphenyl or undecane (as an internal standard for GC analysis), and an aliquot was used for GC measurement. The conversion of substrate and the yield of products were determined by GC-FID. For the isolation of product esters, silica-gel column chromatography was carried out using EtOAc and Hexane as eluent. The reaction setup was displayed in Fig. S1. As some of alkylammonium salts are hydroscopic, the initial experiments are performed under N_2 flow condition (Fig. S1, right). After confirming that same results are given under an open-air condition (Fig. S1, left), the operations were performed under an open-air condition because of simple operation.

Characterization of isolated products

Hexyl benzoate (3aa)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.32–1.36 (4 H, m, —C*H*$_2$—), 1.42–1.48 (2 H, m, —C*H*$_2$—), 1.74–1.79 (2 H, m, —C*H*$_2$—), 4.32 (2 H, t, J = 6.7 Hz, C*H*$_2$—OCO), 7.42–7.45 (2 H, m, Ar*H*), 7.54–7.57 (1 H, m, Ar*H*), 8.04–8.06 (2 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.7, 28.7, 31.5, 65.1, 128.3, 129.5, 130.5, 132.8, 166.7; HRMS (ESI positive, CH_3CN): calcd for C13H18O2 + Na: 229.1199, found: 229.1232.

Hexyl 4-methoxybenzoate (3ba)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.32–1.35 (4 H, m, —C*H*$_2$—), 1.41–1.46 (2 H, m, —C*H*$_2$—), 1.72–1.77 (2 H, m, —C*H*$_2$—), 3.86 (3 H, s, OMe), 4.28 (2 H, t, J = 6.7 Hz, C*H*$_2$—OCO), 6.92 (2 H, d like, J = 9.0 Hz, Ar*H*), 8.00 (2 H, d like, J = 9.0 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.7, 28.7, 31.5, 55.4, 64.8, 113.5, 123.0, 131.5, 163.2, 166.5; HRMS (ESI positive, CH_3CN): calcd for C14H20O3 + Na: 259.1305, found: 259.1273.

Hexyl 4-methylbenzoate (3ca)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.32–1.35 (4 H, m, —C*H*$_2$—), 1.41–1.46 (2 H, m, —C*H*$_2$—), 1.73–1.78 (2 H, m, —C*H*$_2$—), 2.41 (3 H, s, Me), 4.29 (2 H, t, J = 6.7 Hz, C*H*$_2$—OCO), 7.23 (2 H, d like, J = 7.9 Hz, Ar*H*), 7.93 (2 H, d like, J = 8.2 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 21.6, 22.5, 25.7, 28.7, 31.5, 64.9, 127.8, 129.0, 129.5, 143.4, 166.8; HRMS (ESI positive, CH_3CN): calcd for C8H20N4O3 + Na: 243.1428, found: 243.1391.

Hexyl 4-cyanobenzoate (3da)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.32–1.36 (4 H, m, —C*H*$_2$—), 1.41–1.46 (2 H, m, —C*H*$_2$—), 1.75–1.80 (2 H, m, —C*H*$_2$—), 4.35 (2 H, t, J = 6.7 Hz, C*H*$_2$—OCO), 7.74 (2 H, d like, J = 8.6 Hz, Ar*H*), 8.14 (2 H, d like, J = 8.7 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.6, 28.5, 31.4, 65.9, 116.2, 118.0, 130.0, 132.2, 134.3, 165.0; HRMS (ESI positive, CH_3CN): calcd for C14H17O2 + Na:254.11515, found: 254.11646.

Hexyl 4-nitrobenzoate (3ea)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.91 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.33–1.36 (4 H, m, —C*H*$_2$—), 1.42–1.47 (2 H, m, —C*H*$_2$—), 1.76–1.81 (2 H, m, —C*H*$_2$—), 4.37 (2 H, t, J = 6.8 Hz, C*H*$_2$—OCO), 8.21 (2 H, d like, J = 8.9 Hz, Ar*H*), 8.29 (2 H, d like, J = 8.9 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.6, 28.5, 31.4, 66.1, 123.5, 130.6, 135.9, 150.5, 164.7; Elemental analysis calcd (%) for C13H17NO4: C 62.14 H 6.82 N 5.57, found: C 61.76 H 6.87 N 5.62.

Hexyl 2-nitrobenzoate (3fa)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.89 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.30–1.34 (4 H, m, —C*H*$_2$—), 1.36–1.41 (2 H, m, —C*H*$_2$—), 1.69–1.74 (2 H, m, —C*H*$_2$—), 4.32 (2 H, t, J = 6.8 Hz, C*H*$_2$-OCO), 7.61–7.64 (1 H, m, Ar*H*), 7.67 (1 H, td, J = 7.5, 1.3 Hz, Ar*H*), 7.75 (1 H, dd, J = 7.6, 1.5 Hz, Ar*H*), 7.90 (1 H, dd, J = 8.0, 1.1 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.5, 28.2, 31.3, 66.7, 123.8, 127.9, 129.9, 131.6, 132.8, 148.3, 165.5; HRMS (ESI positive, CH_3-CN): calcd for C13H17O4 + Na: 274.10498, found: 274.10132.

Hexyl 2-phenylacetate (3ga)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.80 (3 H, t like J = 7.0 Hz, —C*H*$_3$), 1.17–1.26 (6 H, m, —C*H*$_2$—), 1.50–1.55 (2 H, m, —C*H*$_2$—), 3.54 (2 H, s, PhC*H*$_2$—), 4.00 (2 H, t, J = 6.8 Hz, C*H*$_2$—OCO), 7.17–7.26 (5 H, d like, J = 8.9 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.9, 22.5, 25.5, 28.5, 31.3, 41.5, 65.0, 127.0, 128.5, 129.2, 134.2, 171.6; HRMS (ESI positive, CH_3CN): calcd for C14H20O2: 243.13555, found: 243.13752.

Benzyl cyclohexanecarboxylate (3hb)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.18–1.31 (3 H, m, Cy*H*), 1.43–1.50 (2 H, m, Cy*H*), 1.62–1.66 (1 H, m, Cy*H*), 1.73–1.76 (2 H, m, Cy*H*), 1.91–1.95 (2 H, m, Cy*H*), 2.35 (1 H, tt, J = 11, 3.6 Hz, Cy*H*), 5.11 (2 H, s, —C*H*$_2$Ph), 7.30–7.38 (5 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.4, 25.7, 29.0, 43.2, 65.9, 127.9, 128.0, 128.5, 136.3, 175.9; Elemental analysis calcd (%) for C14H18O2: C 77.03 H 8.31, found: C 76.72 H 8.40.

Benzyl pivalate (3ib)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.23 (9 H, s, —C(CH_3)$_3$), 5.11 (2 H, s, C*H*$_2$Ph), 7.30–7.38 (5 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.2, 38.8, 66.0, 127.6, 127.9, 128.5, 136.4, 178.4; HRMS (ESI positive, CH_3CN): calcd for C12H16O2 + Na: 215.1043, found: 215.1079.

2-Hexyl benzoate (3ac)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like J = 7.1 Hz, —C*H*$_3$), 1.34 (3 H, d, 6.2 Hz, —CHC*H*$_3$), 1.32–1.42 (4 H, m, —C*H*$_2$—), 1.60–1.64 (1 H, m, —C*H*$_2$—), 1.71–1.78 (1 H, m, —C*H*$_2$—), 5.16 (1 H, sextet like, J = 6.3 Hz, C*H*—OCO), 7.42–7.45 (2 H, m, Ar*H*), 7.53–7.56 (1 H, m, Ar*H*), 8.03–8.05 (2 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.1, 25.6, 27.6, 35.8, 71.7, 128.3, 129.5, 130.9, 132.7, 166.2; HRMS (ESI positive, CH_3CN): calcd for C13H18O2 + Na: 229.1199, found: 229.1237.

3-methyl-2-butenyl benzoate (3ad)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.77 (3 H, s, —C*H*$_3$), 1.79 (3 H, s, —C*H*$_3$), 4.82 (2 H, d, J = 7.2 Hz, —C*H*$_2$—), 5.48 (1 H, t sept, J = 7.2, 1.4 Hz, —CH$_2$C*H*=C—), 7.40–7.45 (2 H, m, Ar*H*), 7.51–7.55 (1 H, m, Ar*H*), 8.04–8.06 (2 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.0, 25.7, 61.8, 118.7, 128.2, 129.5, 130.5, 132.7, 139.0, 166.6; HRMS (ESI positive, CH_3CN): calcd for C12H14O2 + Na: 213.0882, found: 213.0886.

Benzyl salicylate (3jb)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.39 (2 H, s, C*H*$_2$Ph), 6.87 (1 H, t like, J = 7.6 Hz, Ar*H*), 6.99 (1 H, d like, J = 8.7 Hz, Ar*H*), 7.35–7.47 (6 H, m, Ar*H*), 7.89 (1 H, dd, J = 8.0, 1.7 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 67.0, 112.4, 117.6, 119.2, 128.3, 128.5, 128.7, 130.0, 135.3, 135.8, 161.7, 169.9; HRMS (ESI positive, CH_3CN): calcd for C14H12O3 + Na: 251.06787 found: 251.06474.

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Hexyl 2-pyridinecarboxylate (3ka)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.89 (3 H, t like, J = 7.0 Hz, —C*H*$_3$), 1.31–1.36 (4 H, m, —C*H*$_2$—), 1.41–1.46 (2 H, m, —C*H*$_2$—), 1.80–1.85 (2 H, m, —C*H*$_2$—), 4.41 (2 H, t, J = 7.0 Hz, C*H*$_2$—OCO), 7.47–7.49 (1 H, m, Py*H*), 7.84–7.87 (1 H, m, Py*H*), 8.12–8.14 (1 H, m, Py*H*), 8.77–8.78 (1 H, m, Py*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.6, 28.6, 31.4, 66.2, 125.1, 126.8, 137.1, 148.2, 149.8, 165.2; HRMS (ESI positive, CH_3CN): calcd for C12H17O2 + Na: 230.11515, found: 230.11802.

Hexyl 2-thiophenecarboxylate (3la)

^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.90 (3 H, t like, J = 7.1 Hz, —C*H*$_3$), 1.31–1.35 (4 H, m, —C*H*$_2$—), 1.40–1.45 (2 H, m, —C*H*$_2$—), 1.72–1.76 (2 H, m, —C*H*$_2$—), 4.29 (2 H, t, J = 6.7 Hz, C*H*$_2$—OCO), 7.10 (1 H, dd, J = 5.0, 3.8 Hz, thiophene*H*), 7.54 (1 H, dd, J = 5.0, 1.3 Hz, thiophene*H*), 7.79 (1 H, dd, J = 3.7, 1.3 Hz, thiophene*H*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.0, 22.5, 25.6, 28.6, 31.4, 65.3, 127.7, 132.1, 133.2, 134.1, 162.4; Elemental analysis calcd (%) for C11H16O2S: C 62.23 H 7.60, found: C 62.79 H 7.83.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.06.056.

References

[1] D. Stephan, J. Am. Chem. Soc. 137 (2015) 10018–10032.
[2] T. Hashimoto, K. Maruoka, Chem. Rev. 107 (2007) 5656–5682.
[3] T. James, M. van Gemmeren, B. List, Chem. Rev. 115 (2015) 9388–9409.
[4] J. Otera, Chem. Rev. 93 (1993) 1449–1470.
[5] M. Hatano, K. Ishihara, Chem. Commun. 49 (2013) 1983–1997.
[6] K. Mashima, Y. Hayashi, K. Agura, T. Ohshima, Pure Appl. Chem. 86 (2014) 335–343.
[7] (a) G.A. Grasa, R.M. Kissling, S.P. Nolan, Org. Lett. 4 (2002) 3583–3586;
(b) G.A. Grasa, T. Güveli, R. Singh, S.P. Nolan, J. Org. Chem. 68 (2003) 2812–2819;
(c) R. Singh, R.M. Kissling, M.-A. Letellier, S.P. Nolan, J. Org. Chem. 69 (2004) 209–212.
[8] G.W. Nyce, J.A. Lamboy, E.F. Connor, R.M. Waymouth, J.L. Hedrick, Org. Lett. 4 (2002) 3587–3590.
[9] M. Blümel, J.-M. Noy, D. Enders, M.H. Stenzel, T.V. Nguyen, Org. Lett. 18 (2016) 2208–2211.
[10] K. Ishihara, M. Niwa, Y. Kosugi, Org. Lett. 10 (2008) 2187–2190.
[11] T. Funatomi, K. Wakasugi, T. Misakia, Y. Tanabe, Green Chem. 8 (2006) 1022–1027.
[12] M. Selva, A. Perosa, S. Guidi, L. Cattelan, Beilstein J. Org. Chem. 12 (2016) 1911–1924.
[13] a) M. Selva, M. Noè, A. Perosa, M. Gottardo, Org. Biomol. Chem. 10 (2012) 6569–6578;
b) M. Selva, A. Caretto, M. Noè, A. Perosa, Org. Biomol. Chem. 12 (2014) 4143–4155.
[14] M. Fabris, V. Lucchini, M. Noè, A. Perosa, M. Selva, Chem. Eur. J. 15 (2009) 12273–12282.
[15] M. Hatano, Y. Tabata, Y. Yoshida, K. Toh, K. Yamashita, Y. Ogura, K. Ishihara, Green Chem. 20 (2018) 1193–1198.
[16] C. Wang, L. Luo, H. Yamamoto, Acc. Chem. Res. 49 (2016) 193–204.
[17] J. Buddrus, Angew. Chem. Int. Ed. 11 (1972) 1041–1110.
[18] T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda, J. Hasegawa, J. Am. Chem. Soc. 136 (2014) 15270–15279.
[19] K. Nakano, T. Kamada, K. Nozaki, Angew. Chem. Int. Ed. 45 (2006) 7274–7277.
[20] F.D. Monica, A. Buonerba, A. Grassi, C. Capacchione, S. Milione, ChemSusChem 9 (2016) 3457–3464.
[21] S. Tanaka, T. Nakashima, T. Maeda, M. Ratanasak, J. Hasegawa, Y. Kon, M. Tamura, K. Sato, ACS Catal. 8 (2018) 1097–1103.
[22] W.H. Saunders Jr., T.A. Ashe, J. Am. Chem. Soc. 91 (1969) 4473–4478.
[23] D. Wilms, S.-E. Stiriba, H. Frey, Acc. Chem. Res. 43 (2010) 129–141.
[24] R. Haag, A. Sunder, J.-F. Stumbe, J. Am. Chem. Soc. 122 (2000) 2954–2955.

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