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Polyether-substituted thiazolium ionic liquid catalysts – a thermoregulated phase-separable catalysis system for the Stetter reaction

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A series of polyether-substituted thiazolium ionic liquids have been synthesized and used as catalysts in the Stetter reaction. The ionic liquids are a thermoregulated phase-separable catalysis (TPSC) system, because they possess the properties of critical solution temperature (CST) and inverse temperature-dependent solubility in toluene–heptane. The results showed that the novel TPSC system exhibits high recycling efficiency, and provides a potential route for a environmentally benign Stetter reaction.

1. Introduction

The Stetter reaction is one of the most important reactions in organic synthesis. It is widely used in stereoselective synthesis,[1,2] heterocyclic synthesis,[3,4] total synthesis of natural products,[5,6] electrochemical materials synthesis,[7] and so on. Thiazolium salts,[8] cyanide ions,[9] triazolium salts[10-12] and tributylphosphine[13] can be used as catalysts for the Stetter reaction. Generally, Stetter reactions are carried out under heterogeneous conditions with low reaction rates. Homogeneous catalysts are of higher catalytic activity, but it is difficult to separate the catalyst from the reaction mixture. So far, intensive work has been focused on developing efficient catalytic systems for heterogenization of homogeneous catalysts.[14] Recently, based on the critical solution temperature (CST) of nonionic tensioactive phosphine ligands, a novel catalytic system (termed thermoregulated phase-separable catalysis (TPSC)), in which the catalyst itself becomes one phase at room temperature and entirely dissolves in the organic phase at higher reaction temperature, has been developed by Jin and Wang.[15] By simple decantation, products can be easily separated from the catalyst upon cooling of the reaction solution. So TPSC combines the advantages of one-phase homogeneous catalysis with an easy means of catalyst separation.

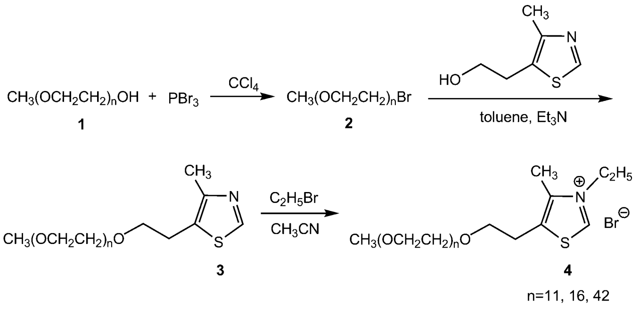
It is well known that room-temperature ionic liquids (RTILs) with many unique properties have provided a class of superior reaction media in synthesis.[16-20] Grée and his group were the first to use imidazolium-type RTILs as Stetter reaction media.[21] Thiazolium salts and Et_3N are efficient catalysts for Stetter reactions performed in RTILs, but it is impossible for the catalyst to be recycled. Yang has reported the first example of a microwave-assisted intramolecular Stetter reaction in RTILs.[22] Although the thiazolium catalyst in RTILs is recyclable and reusable, this paper reported that the catalyst could only be efficiently recycled twice. In addition, immobilized thiazolium and triazolium catalysts have been synthesized to improve the recycling of Stetter catalysts.[23] However, they were only recycled twice, and no further studies on the recycling efficiency were carried out. To the best of our knowledge, no other articles about the recycling of Stetter catalysts have been published.

In this paper, a series of thermoregulated thiazolium ionic liquids catalysts for use in the Stetter reaction were designed and synthesized by introducing a polyether chain to the thiazole compound. It was found that the catalysts possessed the properties of CST and inverse temperature-dependent solubility in toluene–heptane. The catalysts were successfully applied in the Stetter reactions of ethyl acrylate with furfural or butanal. Thus, a novel TPSC system of polyether-substituted thiazolium ionic liquids catalyst has been developed for resolving the problem associated with the separation and reuse of Stetter catalysts.

2. Results and discussion

2.1 Synthesis of thermoregulated thiazolium ionic liquid catalysts

The process for synthesis of the thermoregulated thiazolium ionic liquid catalysts **4** is shown in Scheme 1. Firstly, poly(ethylene glycol) monomethyl ethers **1** with different numbers of polymerized ethylene oxide units (n = 11, 16, 42) was reacted with PBr_3 to obtain bromine-substituted poly(ethylene



Scheme 1 The synthesis of the thermoregulated thiazolium ionic liquid catalysts.

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Table 1 The solubility of catalysts **4** in toluene–heptane

		Toluene–heptane (v/v)			
n	Toluene	1 : 1	1 : 1.2	1 : 1.5	1 : 2
11	Soluble	Slightly soluble	Insoluble; insoluble on heating	Insoluble; insoluble on heating	Insoluble; soluble on heating; inverse
16	Soluble	Insoluble; soluble on heating; inverse	Insoluble; insoluble on heating	Insoluble; insoluble on heating	Insoluble; insoluble on heating
42	Soluble	Slightly soluble	Insoluble; soluble on heating; inverse	Insoluble; insoluble on heating	Insoluble; insoluble on heating

glycol) monomethyl ethers **2**. Then, compounds **2** were reacted with 4-methyl-5-(hydroxyethyl)thiazole in the presence of Et_3N to produce polyether-substituted compounds **3**. Lastly, the thermoregulated thiazolium ionic liquid catalysts **4** with different polyether chain lengths were obtained by the reaction of compounds **3** with bromoethane. Catalysts **4** are pale yellow, viscous liquids at room temperature. The viscosity increases with the length of the polyether chain. The structures of compounds **3** and **4** were determined by NMR. In the ^1H NMR spectrum of catalysts **4**, there is clearly the resonance of the CH-acidic thiazolium proton at about $\delta = 10$, which indicates the existence of the heterazolium precursor of the active carbene species.

2.2 Critical solution temperature (CST) of thermoregulated thiazolium ionic liquid catalysts

The critical solution temperature (CST) is the temperature at which a mixture of two liquids, immiscible at ordinary temperature, ceases to separate into two phases. The upper critical solution temperature (UCST) is the critical temperature above which a mixture is miscible in all proportions. The CST properties of polyether-substituted nonionic phosphine ligands in nonpolar aprotic solvents has been reported.[24] We have discovered that the polyether-substituted thiazolium ionic liquid catalysts **4** (n = 11, 16, 42) also possess the property of CST (UCST) in mixture of toluene and heptane. The results of the solubility of catalysts **4** are shown in Table 1.

According to Table 1, the catalysts **4** (n = 11, 16, 42) exhibit good thermoregulated solubility in toluene–heptane (v/v)=1 : 2, 1 : 1 and 1 : 1.2, respectively. Moreover, inverse temperature-dependent solubility and the property of UCST of catalysts **4** have been found. The relationship between the solubility and temperature is shown in Fig. 1. It can be seen that catalyst **4** (n = 16) exhibits the best property of CST. At room temperature, catalyst **4** (n = 16) is hardly soluble, but when the temperature raises to about 60 °C, the solubility increases markedly. Above 60 °C, the catalyst can completely dissolve in the solvent mixture and the whole system becomes one phase. Therefore, catalyst **4** (n = 16) has a CST of 60 °C in toluene–heptane (v/v=1 : 1).

2.3 General principle of TPSC of polyether-substituted thiazolium ionic liquid catalysts

The CST and inverse temperature-dependent solubility in toluene–heptane enable the polyether-substituted thiazolium ionic liquid catalysts **4** to meet the requirements of a TPSC. The general principle of TPSC is illustrated in Fig. 2. At room temperature, the ionic liquid catalyst is insoluble in organic solvent, and the system is biphasic. When heated to temperatures above the CST, the ionic liquid catalyst is completely soluble in organic solvent, and the system becomes homogeneous. After reaction, upon cooling to a temperature lower than the CST, the system becomes biphasic again, accompanied by separation of the products in the organic phase from the ionic liquid catalyst. After simple decantation, the lower ionic liquid catalyst can be recycled.

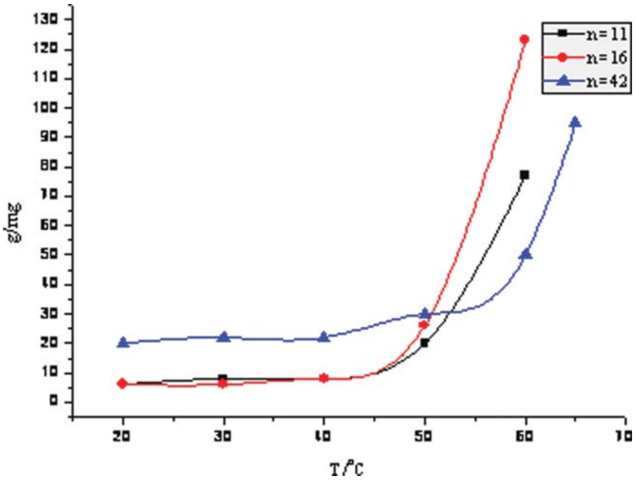


Fig. 1 The relationship between the solubility of catalysts **4** in toluene–heptane and temperature (n = 11, toluene–heptane (v/v)=1 : 2; n = 16, toluene–heptane (v/v)=1 : 1; n = 42, toluene–heptane (v/v)=1 : 1.2).

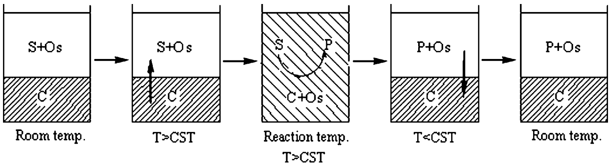


Fig. 2 The general principle of TPSC of polyether-substituted thiazolium ionic liquids catalyst. (S: substrate; Os: organic solvent; C: ionic liquids catalyst; P: product).

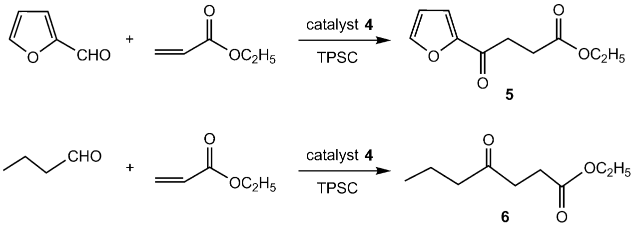
2.4 Optimization of reaction conditions in the novel TPSC system

The novel TPSC system of the polyether-substituted thiazolium ionic liquid catalyst has been successfully used in Stetter reactions of ethyl acrylate with furfural or butanal (Scheme 2).

The results of the Stetter reaction of ethyl acrylate with furfural in the novel TPSC system are shown in Table 2. The % conversion and yield were determined by GC. According to entries 1–3, the length of the polyether chain of catalyst **4**

Table 2 Stetter reaction of ethyl acrylate with furfural in the novel TPSC system

Entry	*n*	Catalyst (mol%)	Toluene: heptane (v/v)	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)
1	11	15	1 : 2	80	12	99.2	43.0
2	16	15	1 : 1	80	12	99.0	42.8
3	42	15	1 : 1.2	85	12	95.4	35.1
4	16	15	1 : 1	40	12	88.7	28.4
5	16	15	1 : 1	60	12	92.2	28.5
6	16	15	1 : 1	90	12	99.5	36.7
7	16	5	1 : 1	80	12	87.2	28.2
8	16	10	1 : 1	80	12	90.5	32.8
9	16	20	1 : 1	80	12	99.3	39.8
10	16	15	1 : 1	80	5	85.8	27.4
11	16	15	1 : 1	80	10	95.7	37.4
12	16	15	1 : 1	80	15	99.0	41.1



Scheme 2 Stetter reactions of ethyl acrylate with furfural and butanal.

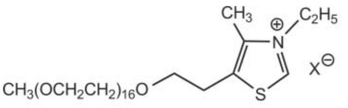
affects the catalytic property. When *n* = 11–16, the conversion of furfural and yield of **5** vary little, and the conversion is above 99.0%. When *n* is increased to 42, the conversion decreases. This is possibly due to the diffusion control from the presence of the bulkier catalyst. Larger mass transfer resistance results in a lower reaction rate. Moreover, the larger spatial effect of the catalyst means it can not contact well with the reaction substrates. In addition, when *n* = 11, the color of the upper organic layer after reaction and cooling to room temperature indicates a small loss of ionic liquid catalyst, which will influence the recycling efficiency of the catalyst. Therefore, *n* = 16 seems to give the best result. The conversion and yield of the Stetter reaction increased with increasing temperature (entries 4, 5 and 2). When the temperature is higher than the CST (60 °C), the conversion of furfural and yield of **5** reach 99.0% and 42.8%, respectively. The obvious increase of conversion indicates that the reaction occurs in the homogeneous phase. The result provides further proof for TPSC. However, further increase of temperature results in lower selectivity for product **5** because of side reactions such as polymerization of ethyl acrylate and condensation of furfural (entry 6). The conversion and yield increase with increasing the amount of thiazolium ionic liquid catalyst **4** from 5 to 15 mol% (entry 7, 8 and 2). The use of 20 mol% of catalyst cannot give much improved conversion and yield (entry 9). When the reaction time is over 5 h, the conversion of furfural and yield of **5** increase significantly (entry 10, 11 and 2). But upon prolonging the reaction time, no significant increase of conversion and yield is obtained (entry 12). Compared with the corresponding reaction catalyzed by thiazolium salt,[8,9] the reaction time could be significantly shortened, because the reaction is homogeneous.

From Table 2, it can be seen that the yield of product **5** is only 42.8% under the optimum conditions (Table 2, entry 2).

Table 3 Stetter reaction of ethyl acrylate with furfural catalyzed by different catalysts

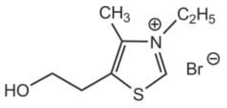
Entry	Catalyst	Anion	Conversion (%)	Yield (%)
1	**7**	Cl^-	97.4	38.7
2	**4** (*n* = 16)	Br^-	99.0	42.8
3	**8**	I^-	99.2	35.6
4	**9**	BF_4^-	99.1	41.7
5	**10**	PF_6^-	98.7	40.8
6	**11**	Br^-	96.5	37.5

To increase the selectivity of the Stetter product, the thiazolium ionic liquid catalysts **7–10** were synthesized with different anions and used in the Stetter reaction of ethyl acrylate with furfural under the same reaction conditions as catalyst **4** (*n* = 16). The catalyst **7** was synthesized according to the same synthesis route as catalyst **4** (*n* = 16) by using chloroethane instead of bromoethane. The catalysts **8–10** were obtained by anion exchange reaction of catalyst **4** (*n* = 16) using a corresponding sodium salt. A thiazolium salt catalyst **11** without a polyether chain was also used to catalyze the Stetter reaction of ethyl acrylate with furfural in DMF. The obtained results are shown in Table 3. The results showed that catalyst **4** (*n* = 16) gave the highest yield, and catalyst **8** with I^- gave the lowest yield (entry 3). BF_4^- or PF_6^- did not improve the selectivity of the Stetter products (entries 4 and 5) compared with Br^-. According to entries 2 and 6, the thiazolium ionic liquid catalyst **4** (*n* = 16) gave a higher conversion and yield than the thiazolium salt catalyst **11**. This is due to the advantage of the novel TPSC system over a conventional reaction system. In all, catalyst **4** (*n* = 16) is the best catalyst for Stetter reactions of ethyl acrylate with furfural.



7-10

X=Cl, I, BF_4, PF_6



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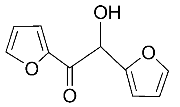
Why is the selectivity of the Stetter product relatively low? In general, intramolecular Stetter reactions can give relatively high selectivity, but it is difficult for intermolecular Stetter reactions to achieve high selectivity. To the best of our knowledge, the highest yield is 67% in the Stetter reaction of *p*-fluorobenzaldehyde with methyl acrylate.[21] The lower selectivity or yield is mainly due to the reaction of the catalytic carbanion with a second aldehyde molecule, which affords a condensation byproduct.[25] In addition, the polymerization of ethyl acrylate could occur at higher temperature, although hydroquinone is added as an inhibitor. The main byproducts of compounds **12–14** were determined by GC-MS in a Stetter reaction of ethyl acrylate with furfural. Compound **12** is a self-condensation product of furfural catalyzed by a thiazolium carbanion. Compound **13** may be afforded by the reaction of furfural with ethanol derived from the hydrolysis of ethyl acrylate. Acrylic acid derived from ethyl acrylate hydrolysis could react with another molecule of ethyl acrylate by a Diels–Alder reaction to afford compound **14**. The yield of compounds **12–14** were 31.2%, 11.6% and 8.3%, respectively.



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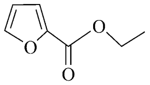

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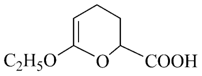

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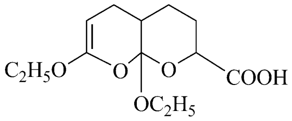
Our novel TPSC system was also used in the Stetter reaction of aliphatic aldehydes. The reaction of butanal with ethyl acrylate was investigated. The optimum reaction conditions were found to be using 15 mol% ionic liquid catalyst **4** (n = 16), toluene–heptane (v/v=1 : 1) as the solvent, with a reaction temperature of 80 °C and a reaction time of 12 h. Under the above conditions, the conversion of butanal and the yield of **6** were 99.5% and 37.3% respectively. The selectivity of the Stetter product is low, but higher than that of the corresponding reaction catalyzed by the thiazolium salt.[9] The main byproducts determined by GC-MS are compounds **14–16**. Compounds **14** and **15** are the polymerization products of ethyl acrylate. Compound **15** is the product of the Diels–Alder reaction between compound **14** and ethyl acrylate. Compound **16** is the self-condensation product of butanal catalyzed by the thiazolium carbanion. Under the above conditions, the yields of compounds **14–16** were 15.4%, 8.7% and 32.6% respectively.



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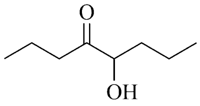

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2.5 Recycling of the thermoregulated thiazolium ionic liquid catalyst

After the reaction, the organic phase was separated from the ionic liquid catalyst by simple decantation. The ionic liquid catalyst was directly recycled by addition of fresh solvents and substrates. Table 4 shows the recycling efficiency of the catalyst **4** (n = 16) in the Stetter reaction of furfural with ethyl acrylate.

According to Table 4, there is no obvious decrease in the conversion of furfural and yield of **5** after the catalyst is reused six times. However, a slight decrease in catalytic activity is observed after the catalyst is reused seven times. In the Stetter reaction of butanal with ethyl acrylate, the ionic liquid catalyst **4** (n = 16) can be reused five times without obvious loss of catalytic activity. The catalyst, after being reused five times, was characterised using ^{1}H NMR. The resonance at $\delta = 9.5$ indicates the presence of the active proton of the thiazole ring. Therefore, the catalytic activity of catalyst **4** can be retained to some extent.

Table 4 Recycling efficiency of the catalyst **4** (n = 16) in the Stetter reaction of furfural with ethyl acrylate

Recycle number	Conversion (%)	Yield of **5** (%)
1	99.0	42.3
2	99.2	42.2
3	99.0	42.2
4	98.7	41.2
5	98.5	40.9
6	98.8	41.2
7	97.5	38.9
8	95.0	35.5

3. Conclusion

A new type of thermoregulated thiazolium ionic liquid catalyst for the Stetter reaction was synthesized by introducing a polyether chain to the thiazole compound. This novel thermoregulated phase-separable catalysis (TPSC) system has been developed for resolving the problems associated with separation and reuse of Stetter catalysts. We also successfully applied it for the Stetter reaction of ethyl acrylate with furfural or butanal. Two Stetter reactions were fully investigated, and the reaction conditions were optimized. Though the yield is low under the optimum reaction conditions, the novel TPSC system exhibits good recycling efficiency. There is no obvious decrease in the conversion of furfural and yield after the catalyst is reused six times. In the Stetter reaction of butanal with ethyl acrylate, the catalyst can be reused five times without obvious loss of catalytic activity. Therefore, this novel TPSC system provides a potential route for an environmentally benign Stetter reaction.

4. Experimental

4.1 Materials and product analysis

All chemicals were used as purchased and were of reagent grade. The solvents were dried by standard procedures and used freshly distilled. The reaction products were analyzed by a gas chromatograph (SP6800A) equipped with a flame ionization detector, a capillary column (OV-17, 30 m × 0.25 μm × 0.25 mm). ^{1}H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were recorded with a Bruker AV 500 MHz spectrometer.

4.2 Bromine-substituted poly(ethylene glycol) monomethyl ether (2)

All the glass vessels were dried before use. Poly(ethylene glycol) monomethyl ether **1** (7.5 g, 10 mmol) and 20 mL CCl_4 were added to a 100 mL four-neck flask equipped with a thermometer, a reflux condenser and a dropping funnel. With stirring, fresh distilled PBr_3 (4.05 g, 15 mmol) in 30 mL CCl_4 was added dropwise. During the dropwise addition, the reaction temperature was kept at 30–40 °C. After finishing the addition, the temperature was elevated to 65–70 °C and the reaction solution was stirred for 4–5 h. Then, the product was separated from the reaction mixture with a separatory funnel, followed by washing with CCl_4 to obtain a pale yellow solution of **2**. Yield: 3.12 g (38.4%).

4.3 Polyether-substituted thiazole (3)

Bromine-substituted poly(ethylene glycol) monomethyl ether **2** (8.13 g, 10 mmol), 4-methyl-5-(hydroxyethyl)thiazole (1.43 g, 10 mmol), Et_3N (1.01 g, 10 mmol) and toluene (40 mL) were added to a 100 mL round-bottomed flask with a reflux condenser. The resulting mixture was stirred and heated under reflux for 6 h. Then, the mixture was cooled to room temperature. Et_3N salt was separated from the solution by filtration, and the solvent was removed under atmospheric distillation to obtain compound **3**. Yield: 5.91 g (67.6%); ^{1}H NMR (500 MHz, D_2O): $\delta = 2.29$ (s, 3H), 2.95 (t, $J = 7.0$ Hz, 2H), 3.52 (s, 3H), 3.55–3.64 (m, 64H), 3.66 (t, $J = 7.1$ Hz, 2H), 8.71 (s, 1H); ^{13}C NMR (125 MHz, D_2O): $\delta = 16.86$, 30.22, 60.35, 68.77–71.72, 125.00, 137.14, 138.35.

4.4 Thermoregulated thiazolium ionic liquid catalyst (4)

Polyether-substituted thiazole **3** (5.91 g, 6.7 mol), bromoethane (0.74 g, 6.7 mol), and dried acetonitrile (20 mL) were mixed in a 100 mL round-bottomed flask with a reflux condenser (potassium hydroxide drying tube) and heated under reflux for 24 h. After cooling, the acetonitrile was removed to give the product **4**. Yield: 4.75 g (72%); ^{1}H NMR (500 MHz, D_2O): $\delta =$ 1.60 (t, $J = 7.3$ Hz, 3H), 2.36 (s, 3H), 2.98 (t, $J = 7.0$ Hz, 2H), 3.45 (s, 3H), 3.47–3.69 (m, 64H), 3.70 (t, $J = 7.0$ Hz, 2H), 4.52 (q, $J = 7.2$ Hz, 2H), 9.50 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 14.76, 18.29, 30.39, 53.06, 61.34, 70.01–72.53, 128.23, 148.79, 148.94.

4.5 Stetter reactions of furfural or butanal with ethyl acrylate catalyzed by thermoregulated thiazolium ionic liquid catalyst 4

Freshly distilled furfural or butanal (0.05 mol) and ethyl acrylate (0.05 mol), Et_3N (15 mol%), hydroquinone (3.6 mol%), thermoregulated thiazolium ionic liquid catalyst **4** (15 mol%), and 40 mL toluene–heptane mixture (v/v=1 : 1) were added to a 100 mL round-bottomed flask with a reflux condenser. The resulting mixture was heated to the given temperature and stirred for a given time. After completion of the reaction, the mixture was cooled to room temperature. By simple decantation, the upper organic phase (containing products) was separated from the catalyst. Then, the organic phase was washed with water, and dried over $MgSO_4$. The solvent was removed by atmospheric distillation. (a) The residue was recrystallized from ethanol to obtain product **5**. m.p. 52–53 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.3$ Hz, 3H), 2.74 (t, $J = 6.8$ Hz, 2H), 3.16 (t, $J = 6.8$ Hz, 2H), 4.14 (q, $J = 7.2$ Hz, 2H), 6.54 (t, $J =$ 7.2 Hz, 1H), 7.24 (d, $J = 6.9$ Hz, 1H), 7.59 (d, $J = 7.0$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.19$, 27.89, 33.07, 60.72, 112.25, 117.06, 146.37, 152.43, 172.69, 187.38. (b) The residue was distilled under vacuum to obtain product **6** (88–90 °C/13 mmHg). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.5$ Hz, 3H), 1.13 (t, $J = 7.2$ Hz, 3H), 1.52 (m, 2H), 2.33 (t, $J = 7.0$ Hz, 2H), 2.62 (t, $J = 6.9$ Hz, 2H), 2.47 (t, $J = 7.0$ Hz, 2H), 4.03 (q, $J = 7.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 13.63$, 14.08, 17.20, 24.95, 36.97, 44.60, 60.53, 172.82, 209.09.

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