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Dual functions of N,N-dimethylethanolamnium-based ionic liquids for the Knoevenagel reactions at room temperature

Anlian Zhu, Ruixia Liu, Lingjun Li, Liangyun Li, Lan Wang, Jianji Wang*

School of Chemical and Environmental Sciences, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, PR China

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ABSTRACT

In this work, the hydrogen bond formation ability of cation and anion of the ILs was determined by using the solvatochromic method and was found to be responsible for their catalytic activity in the Knoevenagel reactions. The enhancement in the hydrogen bond donor ability of the cations and the hydrogen bond acceptor ability of the anions can both lead to the increase in the catalytic activity of the ILs. From the proposed reaction mechanism, it was deduced that the cations of the ILs can form hydrogen bond with aldehyde to activate the C=O bond as electrophile, and the anions of the ILs can promote active methylene compound to produce carboanion as nucleophile, showing dual function activation effect in the catalytic processes. In addition, the optimized N,N-dimethylethanolamnium acetate as dual function activator for the Koevenagel reactions benefits from wide substrates tolerance, ambient reaction temperature, easy work-up procedure, and easy reuse of the IL.

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1. Introduction

Ionic liquids (ILs) have attracted great interest in the area of green chemistry due to their favorable properties such as negligible vapor pressure, wide liquid range, excellent salvation ability and feasible designablility [1]. As novel intriguing functional materials, they have been widely applied in organic synthesis and catalysis [2-8], energy storage [9,10], extraction and separation [11,12], biomass conversion and utilization [13,14] and among others, and the applicable fields of ILs could be widened with more and more new functional ILs being designed and synthesized. However, rational design of ILs for a peculiar application is still in its infancy, and thus the related studies on the relationship between the functions of ILs and their structures are in a great necessary. It has been found that the cation and anion of ILs have synergetic effect in catalyzing various organic reactions [6,13-21]. For example, Chakraborti et al. [18-21] reported the importance of both the cation and the anion of ILs in imparting catalytic potential to 1-methyl-3-alkylimidizoluma-based ILs in promoting various organic reactions. The role of the ILs has been envisaged as cooperative "electrophile-nucleophile dual activation" through hydrogen-bonded networks. The results of various spectroscopic studies, such as IR and ¹H NMR, suggested that hydrogen bond donor ability of C-2 hydrogen of the imidazolium

cation and hydrogen bond acceptor property of the anion would be essential for the catalytic potential of these ILs, and have been substantiated by identification of the hydrogen-bonded supramolecular catalytic species through MALDI-TOF-TOF and ESI-MS studies.

In the present work, a series of ILs based on N,Ndimethylethanolamnium (DMEA) moiety with different counter anions have been synthesized, and the hydrogen bond donor ability and the hydrogen bond acceptor ability of the ILs have been estimated. The catalytic activity of these ILs on Knoevenagel reactions has been investigated and the relationship between the catalytic activity and the hydrogen bond formation ability of cation and anion of the ILs has been discussed from the view-point of their dual activation effect on electrophiles and nucleophiles. On the other hand, this kind of ILs have shown excellent performance in catalyzing Knoevenagel reactions with wide substrates tolerance, easy separation and work-up procedures, feasible reutilization of the ILs and benign reaction conditions.

2. Experimental

2.1. Chemicals and instruments

Acetic acid (Ac), propanoic acid (Pr), butanoic acid (Bu), isobutanoic acid (i-Bu), and lactic acid (Lac) were all AR grade and purchased from Aladdin Reagents Company. N,N'dimethylaminoethanol (AR grade) was obtained from Beijing Chemical Reagent Company and distilled at reduced pressure



^{*} Corresponding author. Tel.: +86 0373 3325805; fax: +86 0373 3329030. *E-mail address:* jwang@henannu.edu.cn (J. Wang).

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Scheme 1. Synthesis of protic N,N'-dimethylaminoethanol-based ionic liquids.

before use. Strong basic ion exchange resin (Ambersep 900 OH), 4-nitroaniline and N,N-diethyl-4-nitroaniline were purchased from Alfa Aesar, and 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)phenolate (Reichardt's dye 33) was obtained from Aldrich. Aldehydes, ethyl cyanoacetate, malononitrile and other reagents were analytical grade, and the water used in this work was twice deionized. All of the commercially available reagents were used as received unless indicated otherwise.

¹H NMR spectra were recorded on a BRUKER AV-400 instrument at room temperature by using TMS as internal standard. Melting points were taken from a XRC-1 Microscopic Melting Point Measurer (Sichuan University instrument factory) without correction. The UV-vis spectra were determined by a TU-1021 spectrometer (Beijing Persee Instrument Company) with a standard 5 mm cell, and the temperature was controlled to 25.0 ± 0.1 °C with a DC-2006 low temperature thermostat (Shanghai Hengping Instrument & Meter Factory, China).

2.2. Synthesis and characterization of the ILs

Protic ILs were synthesized simply by neutralization of N,N'-dimethylaminoethanol with corresponding carboxyl acids (Scheme 1, path (a)). In a typical reaction, 0.1 mol N,N'-dimethylaminoethanol dissolved in 10 ml methanol was put into a 100 ml flask, and 0.1 mol carboxyl acid was slowly added under stirring. The solution was stirred at room temperature for 24 h to complete the reaction, and then the methanol was removed at 50 °C under reduced pressure to give a pale yellow and viscous liquid.

[Choline][Ac] was synthesized by the neutralization reaction of acetic acid with [Choline][OH] prepared from the ionic exchange of [Choline][Cl] by strong basic ionic exchange resin (Scheme 1, path (b)). For the preparation of [C4-choline][Ac] (Scheme 1, path (c)), the following produce was closely followed. Into a 100 ml flask containing 0.1 mol N,N'-dimethylaminoethanol in ethanol at 80 °C, 0.11 mol chlorobutane was dropped under stirring through a dropping funnel for 10 h to get [C4-choline][Cl], which was ionic exchanged into [C4-choline][OH]. Then, [C4-choline][OH] was neutralized with acetic acid to give [C4-choline][Ac]. Both of the prepared ILs were pale yellow and viscous liquids at room temperature. The purity for all of the ILs is higher than 99% as determined by ¹H NMR.

2.3. General procedures for Knoevenagel reactions and reutilization of the ILs

In a typical experiment, 0.5 mmol aldehyde, equivalent active methylene compounds and a given amount of ILs were mixed in a

Table 1
Catalytic performance of different ILs for the Knoevenagel reactions.

Entry	IL (molar ratio of IL to substrate)	Time	Isolated yield (%)	
1	[DMEA][Ac] (0.2:1)	1.5 h	85	
2	[DMEA][Ac] (0.5:1)	40 min	97	
3	[DMEA][Ac] (1:1)	25 min	99	
4	[DMEA][Ac] (1.5:1)	25 min	99	
5	[DMEA][Pr] (1:1)	25 min	90	
6	[DMEA][Bu] (1:1)	25 min	85	
7	[DMEA][i-Bu] (1:1)	25 min	85	
8	[DMEA][Lac] (1:1)	25 min	60	
9	[DMEA][Ac] (0.1:1)	6 h	80	
10	[Choline][Ac] (0.1:1)	6 h	85	
11	[C ₄ -Choline][Ac] (0.1:1)	5 h	99	
12	DMEA	3.5 h	70	
13	[AM][Ac]	3.5 h	60	
14 ^a	[DMEA][Ac] (1:1)	25 min	98	

^a The fifth reuse of the recovered ionic liquid.

flask and stirred for a desired time at room temperature. The reactions were monitored by TLC. At the end of the reactions, water was added to the mixtures. The ILs dissolved in water can be recycled for at least five times without significant activity decrease after simple drying process. Most of the products can be obtained from simple filtration after the water was added to the reaction mixtures, and no further purification was required. All of the products were previously reported, they were characterized by melting point and ¹H NMR spectroscopy measurements.

2.4. Determinations of the hydrogen bond donor and acceptor parameters

The hydrogen bond formation ability of the ILs was evaluated from the hydrogen bond donor ability and the hydrogen bond acceptor ability of the ILs by using the solvatochromic method established by Kamlet and Taft [22-24]. For this purpose, Reichardt's dyes, 4-nitroaniline and N,Ndiethyl-4-nitroaniline were selected as a set of solvatochromic probes. A less basic probe, 2,6-dichloro-4-(2,4,6-triphenyl-1pyridinio)phenolate (Reichardt's dye 33, pKa=4.78), was used to determine polarity of the ILs due to the strong acidity of these protic ILs. The procedure for the measurements of the Kamlet-Taft parameters of the ionic liquids was as follows. To 2 ml ionic liquid, each probe dye was added as a concentrated dry dichloromentane solution, and the concentration of probe dyes in the ILs was kept at about 1×10^{-4} moll⁻¹ for Reichardt's dye 33, and 5×10^{-5} mol l⁻¹ for both N,N-diethyl-4-nitroaniline and 4nitroaniline to avoid aggregation of the dyes. The dichloromentane was then carefully removed by vacuum drying at 40°C for 8 h. These ionic liquids solutions were placed into quartz cells with 5 mm light-path length. Temperature of the quartz sample cell was maintained at 25 °C by water circulation. From the wavelength at the maximum absorption (λ_{max}) determined, values of

Table 2

The α and β values of the ILs at 25 °C.

Entry	IL	α	β
1	[DMEA][Ac]	1.08	0.71
2	[DMEA][Pr]	0.99	0.82
3	[DMEA][Lac]	0.82	0.64
4	[DMEA][Bu ⁻]	1.14	0.61
5	[DMEA][i-Bu ⁻]	1.11	0.65
6	[Choline][Ac]	0.57	0.75
7	[C4-choline][Ac]	0.53	0.96

the solvent parameters were calculated by using the following equations [25,26]:

$$\nu_{dye} = \frac{1}{\lambda_{\max(dye)} \times 10^{-4}} \tag{1}$$

$$E_T(30) = 0.9986 \left(\frac{28592}{\lambda_{\max(\text{Reichardt's dye 33})}}\right) - 8.6878$$
(2)

$$\pi^* = 0.314(27.52 - \nu_{(N,N-diethyl-4-nitroaniline)})$$
(3)

$$\alpha = 0.0649 E_T(30) - 2.03 - 0.72 \pi^* \tag{4}$$

$$\beta = \frac{1.035\nu_{\text{(N,N-diethyl-4-nitroaniline)}} + 2.64 - \nu_{\text{(4-nitroaniline)}}}{2.80} \tag{5}$$

In these equations, E_T (30), π^* , α and β stand for polarity, dipolarity/polarizability, hydrogen bond donor ability (acidity) and hydrogen bond acceptor ability (basicity) of the ILs, respectively.

3. Results and discussion

3.1. The catalytic activity of different ILs on the Knoevenagel reactions

This work was originated from the discovery that ionic liquid N,N-dimethylethanolamnium acetate is able to catalyze the



Fig. 1. The plausible reaction mechanism for [DMEA][Ac] promoted Knoevenagel reactions.

Knoevenagel reaction between 4-nitrobenzaldehyde and ethyl cyanoacetate, and its catalytic performance was affected by the molar ratio of the IL to the substrates (Table 1, entries 1-4). It was shown that catalytic activity of the IL increased with increasing molar ratio of the IL to substrates from 0.2 to 1, but with the further increase of the molar ratio, the catalytic performance was kept at the same level. Then catalytic activity of the ILs with N,Ndimethylethanolamnium cation but different carboxyl acid anions for the Knoevenagel reaction between 4-nitrobenzaldehyde and ethyl cyanoacetate was investigated at the mole ratio of 1:1 and the results were also collected in Table 1 (Table 1, entries 5-8). It was found that the catalytic performance of the ILs was significantly affected by anions of the ILs, and the ILs with acetate anion has the highest catalytic activity. Therefore, the ILs composed of the same acetate anion but different cations were also investigated for the catalysis of a model Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate (Table 1, entries 9–11) at the molar ratio of 1:1. In the experiment, it was found that with the increase of the carbon chain length linked on the nitrogen atom of cation of the ILs, the reactions could be promoted significantly but suffered from low isolated yields because of the low selectivity. However, when the molar ratio of the ILs to substrates was decreased to 0.1:1, [Choline][Ac] and [C₄-Choline][Ac] could give satisfactory results, especially [C₄-Choline][Ac] could give almost quantitative isolated yields within prolonged reaction time. This suggests that catalytic activity of the ILs increases with the prolonged carbon chain length of cations. However, the attempt to promote the same reaction was not successful in N,N-dimethylethanolamnium because too many side-reactions took place. This indicates that ionic nature of the IL is also important for this reaction. In addition, under the catalysis of ammonium acetate ([AM][Ac]), the same reaction gave only 60% conversion after 3 h, which suggests that introduce of hydroxyl group in the cation benefits to the excellent performance of DMEAbased ionic liquids.

The empirical Kamlet–Taft parameters including the hydrogen bond donor acidity α and hydrogen bond acceptor basicity β determined experimentally were collected in Table 2 (entries 1–5). It can be seen that for the ILs with the same cation of [DMEA], the α

Table 3

1mmol

Knoevenagel reactions of different aldehydes with active methylene compounds.

1mmo



			•			
Entry	R_1	R ₂	Reaction time	Isolated yield (%)	mp (°C)	Lit. mp (°C)
1 ^a	$4-NO_2C_6H_4$	CN	20 min	97	158	157 [27]
2 ^b	C ₆ H ₅	CN	1 min	97	80-81	80-81 [28]
3 ^a	$3-NO_2C_6H_4$	CN	20 min	92	101-102	100-102 [29]
4 ^a	$4-OHC_6H_4$	CN	2 min	99	188	188 [30]
5 ^b	$4-OHC_6H_4$	CN	2 min	93	188	188 [30]
6 ^a	4-ClC ₆ H ₄	CN	30 min	95	159-160	160-161 [27]
7 ^b	4-ClC ₆ H ₄	CN	30 min	65	159-160	160-161 [27]
8 ^b	$4-FC_6H_4$	CN	2 min	99	-	-
9 ^a	C ₆ H ₄ CH=CH	CN	30 min	83	114-115	-
10 ^b	C ₆ H ₄ CH=CH	CN	30 min	70	114-115	-
11 ^b	CH ₃ OC ₆ H ₄	CN	1 h	97	114	113-114 [27]
	\square					
12 ^b	0	CN	2 min	98	65-66	70[28]
13 ^b	$2-OHC_6H_4$	CN	20 min	94.2	159-160	_ ` `
14 ^b	C ₆ H ₁₃	CN	3 min	95	-	-
15 ^b	$4-(OH)C_6H_3-3-(OCH_3)$	CN	5 min	90	138	-
16 ^b	N	CN	2 min	95	214	-
17 ^a	$4-NO_2C_6H_4$	COOC ₂ H ₅	25 min	95	167-168	168 [28]
18 ^b	C ₆ H ₅	COOC ₂ H ₅	30 min	99	44-46	47-48 [28]
19 ^a	$3-NO_2C_6H_4$	COOC ₂ H ₅	30 min	98	127-128	130-131 [28]
20 ^a	4-ClC ₆ H ₄	COOC ₂ H ₅	20 min	99	90	92-94 [31]
21 ^b	$4-FC_6H_4$	COOC ₂ H ₅	30 min	94	98	94-96 [28]
22 ^b	0	COOC ₂ H ₅	5 min	95	88	84~86[28]
23 ^b	C ₆ H ₄ CH=CH	COOC ₂ H ₅	5 min	98	111-112	-
24 ^b	2-OHC ₆ H ₄	COOC ₂ H ₅	30 min	95	-	-
25 ^a	$4-OHC_6H_4$	COOC ₂ H ₅	5 min	91	167-168	169-171 [28]
26 ^a	$4-(OH)C_6H_3-3-(OCH_3)$	COOC ₂ H ₅	30 min	80	98	
27 ^a	IN	COOC ₂ H ₅	2 min	95	97–98	-
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^a The ratio of the IL to the substrates is 1:1.

^b The ratio of the IL to the substrates is 0.2:1.

values decrease in the sequence: Bu > i-Bu > Ac > Pr > Lac, suggesting that the hydrogen bond donor ability of such ILs can be modulated by the nature of the anions, although the relationship between the α values and the catalytic performance of the ILs is not clear. The other parameter hydrogen bond acceptor basicity β is found to decrease in the order: $Pr > Ac > i-Bu \approx Lac > Bu$. This sequence is almost the same as the sequence of the catalytic activity of the ILs for the Knoevenagel reactions except those with Ac and Pr as the anions, indicating that the increase in hydrogen bond acceptor ability of the anions would lead to the increase in catalytic activity. The irregular behavior of Ac and Pr anions in the catalytic performance suggests that the hydrogen bond acceptor ability of the anions is not the only factor influencing the Knoevenagel reactions, and the hydrogen bond donor ability of the cations should have synergetic effect on the catalytic reactions because the α values of [DMEA][Ac] is larger than that of [DMEA][Pr], which may be the reason for the higher catalytic activity of the former IL. Furthermore, the Kamlet-Taft parameters of the ILs with the same Ac anion but different cations have also been determined and the results are collected in Table 2 (entries 1, 6 and 7). It was found that the α and β values can be influenced by the change of the cations, and the α values decrease in the sequence of DMEA > Choline > C4-Choline, which is not in accordance with the catalytic activity. However, the β values increase in the same sequence of the catalytic activity, which indicates that the hydrogen bond acceptor ability of the ILs is the main factor controlling their catalytic activities.

3.2. Plausible catalytic mechanism

Based on the different catalytic activities observed for the studied ILs on the Knoevenagel reactions and their relationship with the hydrogen bond forming ability of the ILs, a plausible reaction mechanism was proposed and illustrated in Fig. 1. It was deduced that the reaction was originated from the dehydrogenation of the active methylene compounds to form the carboanion attacked by the anion of the ILs, and then the carboanion attacked the C=O bond which was activated by the formation of hydrogen bond with cation of the ILs to give the intermediate α -cyano-alcohols, which was then attacked by the anions of the ILs to form the dehydration productions. In this catalytic procedure, anions of the ILs act as an activator for the nucleophiles to produce carboanions, and cations of the ILs act as an activator for the electrophiles to increase the polarization of C=O bond. Therefore, it is reasonable to state that the increased hydrogen bond acceptor ability of the anions will benefit to the production of the carboanion and thus to the increased catalytic activity. The increased hydrogen bond donor ability of the cations would increase the polarization of C=O bonds which become easy to be attacked by the carboaions. As a result, the increased hydrogen bond formation ability of the cations and the anions results in the dual functions for the activation of the substrates and contributes to the increased catalytic activities of the ILs.

3.3. Knoevenagel reactions between different aldehydes and active methylene compounds

As discussed above, [C4-Choline][Ac] has the highest catalytic activity for the Knoevenagel reactions. However, considering the fact that its preparation procedure is tedious and then the cost is much higher, the Knoevenagel reactions of different aldehydes with active methylene compounds were further investigated by using [DMEA][Ac] as promotor. As the ratio of the IL to the substrates is kept at 1:1 for the solid aldehydes and at 0.2:1 for the liquid aldehydes (see Table 3), the

reactions involving various aldehydes, including aromatic aldehydes with electro-donating groups as well as electro-withdrawing groups, allyl aldehydes, and aliphatic aldehydes could all give satisfactory isolated yields within 1 h. The reactions involving heterocyclic aldehydes also showed excellent reaction activity in this system such as furaldehyde and pyridine-4-carboxaldehyde, and almost quantitative isolated yields were obtained within 5 min for their reactions with malononitrile and ethyl cyanoacetate.

4. Conclusion

A series of ionic liquids based on N,N-dimethylethanolamnium moiety were synthesized and found to be efficient for the promotion of Knoevenagel reactions at ambient temperature, and the substrates tolerance was considerably wide because aromatic aldehydes with electro-donating groups as well as electro-withdrawing groups, allyl aldehydes, aliphatic aldehydes and heterocyclic aldehydes can all react with malononitrile and ethyl cyanoacetate fluently and give good to excellent isolated yields. This reaction system also benefit from the ambient reaction temperature. easy preparation procedure, and the reuse of the ILs. Furthermore, it was found that the catalytic activity of the ILs was relevant to the hydrogen bond forming ability of the ILs, and the increase in the hydrogen bond donor ability of the cations would increase the catalytic activity of the ILs. However, the hydrogen bond acceptor ability of the anions played a more important role in the catalytic activity of the ILs compared with the hydrogen bond donor ability of the cations. These findings would be useful for the better understanding of the synergetic effect of ILs in catalytic reactions and for the rational design of the ILs for the particular reactions from structure-activity relationships of the ILs.

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Appendix A.

Selected data for typical compounds are given below:

[DMEA][Ac]: ¹H NMR (400 MHz; D_2O): 1.729(s, 3H, C<u>H</u>₃COO⁻), 2.683(s, 6H, (CH₃)₂N), 3.039–3.066 (q, 2H), 3.645–3.671 (q, 2H);

[Choline][Ac]: ¹H NMR (400 MHz; D₂O): 1.700(s, 3H, C<u>H</u>₃COO⁻), 2.989(s, 9H, (CH₃)₃N), 3.294–3.319(q, 2H), 3.829–3.859(q, 2H);

Products data



¹H NMR (400 MHz, CDCl₃): 7.878(s, 1H), 8.065–8.087(d, 2H), 8.382–8.404(d, 2H); mp 158 °C, ref. 160–162 °C.



¹H NMR (400 MHz, CDCl₃): 7.530–7.568(t, 2H), 7.621–7.659(t, 1H), 7.783(s, 1H), 7.905–7.923(d, 2H); mp 80–81 °C, ref. 82 °C.



¹HNMR (400 MHz, CDCl₃): 7.515–7.536(d, 2H), 7.731(s, 1H), 7.848–7.870(d, 2H); mp 158–160 °C, ref. 160–161 °C



 ^{1}H NMR (400 MHz, CDCl₃): 6.954–6.975(d, 2H), 7.651(s, 1H), 7.869–7.891(d, 2H); mp 188 °C, ref. 188 °C.



¹H NMR (400 MHz, CDCl₃): 3.918(s, 3H), 7.006–7.028(d, 2H), 7.654(s, 1H), 7.904–7.927(d, 2H); mp 113–114 °C, ref. 115–116 °C.



¹HNMR (400 MHz, CDCl₃): 6.715–6.724(t, 1H), 7.364–7.373(s, 1H), 7.513(s, 1H), 7.805–7.808(d, 1H).



 ^{1}H NMR (400 MHz, CDCl_3): 7.078–7.099(d, 1H), 7.148–7.166(t, 1H), 7.307–7.327(d, 1H), 7.443–7.478(t, 1H), 7.697(s, 1H); mp 158–160 °C.



¹H NMR (400 MHz, CDCl₃): 1.407–1.442(t, 3H), 4.299–4.454(q, 2H), 7.713–7.751(m, 1H), 8.123–8.365(m, 4H); mp 167–168 °C, ref. 168 °C.



¹H NMR (400 MHz, CDCl₃): 1.408–1.443(t, 3H), 4.400–4.454(q, 2H), 7.720–7.761(m, 1H), 8.310(s, 1H), 8.395–8.431(d, 2H), 8.700(s, 1H); mp 127–128 °C, ref. 131–133 °C.



 ^{1}H NMR (400 MHz, CDCl_3): 1.389–1.425(t, 3H), 4.367–4.420(q, 2H), 7.492–7.585(m, 3H), 7.988–8.006(d, 2H), 8.259(s, 1H); mp 46 °C, ref. 49 °C.



 ^{1}H NMR (400 MHz, CDCl_3): 1.386–1.422(t, 3H), 4.366–4.419(q, 2H), 7.474–7.496(d, 2H), 7.928–7.950(d, 2H), 8.201(s, 1H); mp 90 $^{\circ}\text{C}.$



 ^{1}H NMR (400 MHz, CDCl₃): 1.381–1.417(t, 3H), 4.353–4.406(q, 2H), 6.093–6.130(m, 1H), 6.966–6.987(d, 2H), 7.954–7.976(d, 2H), 8.195(s, 1H); mp 167–168 °C, ref. 169–171 °C.



¹H NMR (400 MHz, CDCl₃): 1.367–1.402(t, 3H), 4.335–4.389(q, 2H), 6.657–6.6666(t, 1H), 7.392–7.401(d, 1H), 7.751–7.753(d, 1H), 8.020(s, 1H); mp 88 °C, ref. 83 °C.



 ^{1}H NMR (400 MHz, CDCl_3): 1.520–1.556(t, 3H), 4.479–4.533(q, 2H), 7.422–7.457(d, 2H), 7.580–7.590(t, 3H), 7.741–7.765(d, 2H), 8.155–8.182(m, 1H); mp 111–112 °C.



¹HNMR (400 MHz, CDCl₃): 1.377–1.413(t, 3H), 3.987(s, 3H), 4.347-4.401(q, 2H), 6.212(s, 1H), 6.993-7.013(d, 1H), 7.384-7.409(m, 1H), 7.854-7.858(d, 1H), 8.145(s, 1H); mp 98 °C.



¹HNMR (400 MHz, CDCl₃): 1.555–1.591(t, 3H), 4.547–4.601(q, 2H), 7.902-7.917(d, 2H), 8.350(s, 1H) 8.969-8.984(d, 2H), mp 97-98°C.

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