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低共熔溶剂 1,3-二甲基脲/*L*-(+)-酒石酸中(*E*)-2-苯乙烯基喹啉-3-羧酸类衍生物的绿色合成

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摘要 利用环境友好且无毒无害的1,3-二甲基脲(DMU)/*L*-(+)-酒石酸(LTA) (*n*∶*n*=7∶3)形成的低共熔溶剂(DES)作为反应介质和催化剂使 2-甲基喹啉-3-羧酸与芳醛直接进行有效的乙烯化反应, 成功实现了(*E*)-2-苯乙烯基喹啉-3-羧酸类衍生物的绿色合成. 所开发的合成方法具有温和且环境友好的反应条件, 实验操作简便, 后处理简单和收率高等优点, 具有很好的实际应用价值.

关键词 绿色合成; 2-苯乙烯基喹啉; 1,3-二甲基脲; *L*-(+)-酒石酸; 低共熔溶剂

Deep Eutectic Solvent of 1,3-Dimethylurea/*L*-(+)-Tartaric Acid for the Green Synthesis of (*E*)-2-Styrylquinoline-3-carboxylic Acid Derivatives

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Abstract A green, efficient and catalyst-free synthesis of (*E*)-2-styrylquinoline-3-carboxylic acid derivatives via direct olefination of 2-methylquinoline-3-carboxylic acid with aromatic aldehydes has been accomplished successfully by using environmentally benign and non-toxic deep eutectic solvent (DES) of 1,3-dimethylurea (DMU)/*L*-(+)-tartaric acid (LTA) (*n*∶*n*=7∶3) as a dual catalyst and reaction medium. The synthetic strategy has the attractive features such as mild and environmentally benign reaction conditions, experimental simplicity, easy work-up procedure and good yields, which would contribute to the usefulness of this method.

Keywords green synthesis; 2-styrylquinoline; 1,3-dimethylurea; *L*-(+)-tartaric acid; deep eutectic solvent

1 Introduction

Among quinoline derivatives, 2-styrylquinoline (SQ) structure forms an important type of structural motif and represents an elite scaffold and a wonderful pharmacophore in drug discovery.[1] Many members of this family such as FZ-41 (**I**), VUF5017 (**II**), and WK14 (**III**) as shown in Figure 1 have been widely applied as antiproliferative,[2] antiviral,[3] anti-human immunodeficiency virus (HIV),[4] antimicrobial[5] agents and antagonist.[6] Especially, recent studies have revealed that some carboxyl-containing 2-styrylquinolines (**IV**) were found to display potent biological activities. For example, 2-styrylquinoline-4-carboxylic acid derivatives were found to improve significantly the toxic effect against *Leishmania* (*Leishmania*) *amazonensis* and were considered to be the most promising antileishmanial agents due to the parasite killing effect in intracellular forms inside infected macrophages.[7] In this regard, Mittal and coworker[8] reported that (*E*)-4-phenyl-2-styrylquinoline-3-carboxylic acids (**V**) could be used as effective antiproliferative agents with excellent selectivity toward cancer tissue, the selectivity of which will enhance concentration in the cancer cells and will reduce the absorption in the non-cancerous cells, enabling these molecules much less toxic. Owing to their striking biological activities, we envisioned that the development of a new and facile synthetic approach for this class of 2-styrylquinoline derivatives would be highly attractive.

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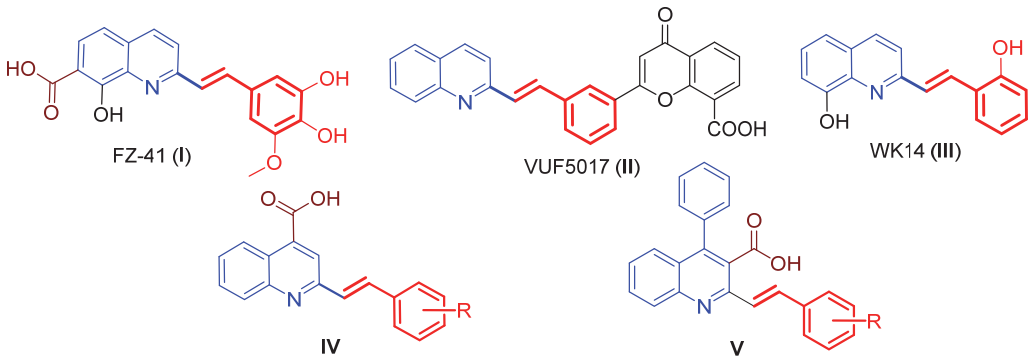
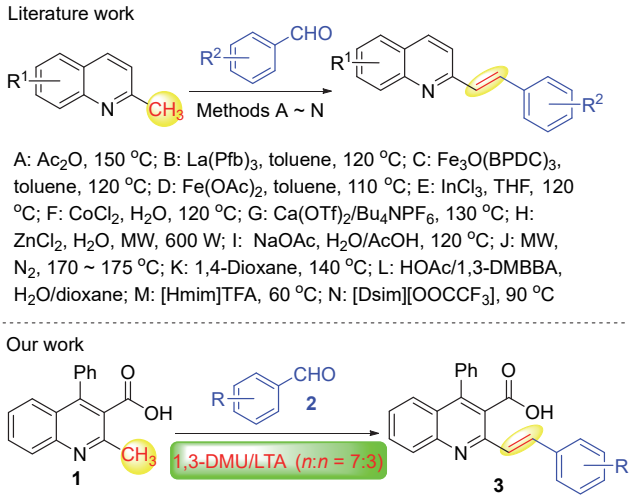


Figure 1 Structures of some bioactive 2-styrylquinlines **I**～**V**

As the 2-methylquinoline derivatives could be readily converted into the enamine tautomeric form via methyl C(sp^3)—H activation by the adjacent nitrogen atom under various catalytic conditions,[9] the direct olefination of 2-methylquinolines by the Knoevenagel-type condensation reaction with aromatic aldehydes appears to be the most simple and straightforward approach for 2-styrylquinoline in comparison with other possible methods like the Witting reactions using expensive 2-quinolinecarboxaldehydes[10] and reductive olefinations of quinoline *N*-oxides with olefins.[11] The classic approach for the direct olefination of 2-methylquinolines with aldehydes involves the use of acetic anhydride as reaction medium.[12] But the protocol is plagued by constraints like high reaction temperature, the use of a large excess of aldehydes and low product yields. Due to the great significance of the methyl C(sp^3)—H activation of 2-methylquinoline in the synthesis of 2-styrylquinoline, great efforts have been devoted during the past decades to develop more convenient and effective synthetic methods, such as the use of metal catalyst like La(Pfb)$_3$,[13] $Fe_3O(BPDC)_3$,[14] or $Fe(OAc)_2$[15] in toluene, $InCl_3$ in tetrahydrofuran (THF),[16] $CoCl_2$ in H_2O,[17] $Ca(OTf)_2/Bu_4NPF_6$ under solvent free condition,[18] $ZnCl_2$ under microwave irradiation,[19] the utilization of NaOAc as base in water-acetic acid binary solvents,[5] solvent-free microwave irradiation under inert gas atmosphere (N_2) at high temperatures (170～175 ℃),[20] the employment of 1,4-dioxane as reaction media under catalyst-free condition at 140 ℃,[21] and the combination of 1,3-dimethylbarbituric acid (1,3-DMBBA) and HOAc as synergistic catalysts[22] as listed in Scheme 1. Although these elegant methods for the direct olefination of 2-methylquinolines have emerged, they were invariably associated with certain limitations in terms of harsh reaction conditions, toxic chemical reagents, expensive or unavailable catalysts, and volatile, flammable and harmful organic solvents. In addition, 2-styrylquinolines could also be facilely accessed by using 1-methylimidazolium trifluoroacetate ([Hmim]-TFA)[23] or Brønsted acidic imidazolium ionic liquids as the reaction medium,[24] which involved the *in situ* generation of 2-methylquinoine from *o*-aminoketone and *β*-ketoester followed by its olefination reaction with aromatic aldehydes. But the high cost and environmental toxicity



Scheme 1 Various synthetic methods for 2-styrylquinoline derivatives

of these ionic liquids have limited their practical application.

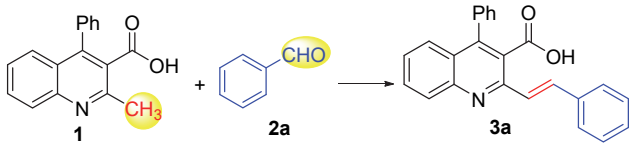
Nowadays, in light of the stringent environmental requirements and safety consideration in the chemical production, increasing research effort has been focused on the development of sustainable and environmentally benign reaction procedures to replace those efficient but somewhat outdated methods, particularly, to replace volatile, flammable and harmful organic solvents.[25] In this regard, Fu *et al.*[26] reported the synthesis of 2-alkenylazaarenes via dehydrative coupling of 2-methylazaarenes with aldehydes 'on water'. However, the poor solubility of water as solvent is a major limitation to its wide application in organic reaction. In the past decade, deep eutectic solvents (DESs), as an emerging class of unconventional solvents derived from the combination of two or three safe and cheap components of Lewis or Brønsted acids and bases through hydrogen bond formation, have attracted enormous attention due to their unique properties including wide liquid range, negligible vapor pressure, low toxicity, non-flammability, high solvation capacity, high biodegradability, low cost of components and convenient preparation,[27] thereby rendering them widely acknowledged as an excellent alternative to volatile organic solvents in the development of en-

vironmentally friendly organic reactions.[28-30] For example, Zhang's group have developed the application of choline chloride (ChCl)/urea,[31] choline chloride/lactic acid (ChCl/Lac),[32] and choline chloride/glycerol (ChCl/Gly)[33] as a biodegradable, recycled and reusable media in the green synthesis of heterocyclic compounds. In light of these findings, we would like to report, herein, an environmentally benign synthesis of (*E*)-2-styrylquinoline-3-carboxylic acid derivatives by using 1,3-dimethylurea (DMU)/*L*-(+)-tartaric acid (LTA) as a safe, eco-friendly and unconventional reaction medium. To the best of our knowledge, the synthesis of such quinoline derivatives using deep eutectic solvents (DESs) as the reaction medium has not been achieved so far.

2 Results and discussion

Initially, the model reaction of 2-methylquinoline-3-carboxylic acid (**1**), which was readily obtained by the method of literature,[34] with benzaldehyde (**2a**) was investigated by using the widely used DES, namely ChCl/urea (n∶n=1∶2) as the reaction medium at 80 ℃,[35] but no formation of the desired product was observed and the starting materials were recovered unchanged (Entry 1, Table 1). The use of ChCl/polyethylene glycol (n∶n=1∶2)[36] or ChCl/glycerol (n∶n=1∶2)[33] as solvent was also unfruitful (Table 1, Entries 2 and 3). In 2014, Sanap *et al.*[37] reported the direct C-3 alkenylation of indoles in the DES of ChCl-oxalic acid. Interestingly, following the purported approach the yield of the desired product **3a** could be improved to 38% (Entry 4, Table 1), but this was still not satisfactory as it was expected. Moreover, further changing the reaction conditions such as temperatures and molar ratio resulted in no further improvement in the product yield. This finding encouraged us to test other acidic DESs to pick a suitable solvent for the reaction. Thus, a series of renewable carboxylic acid containing DESs were screened, such as ChCl-malonic acid,[38] ChCl/citric acid,[39] DMU/citric acid,[40] ChCl/*L*-(+)-tartaric acid (ChCl/LTA),[41] and DMU/*L*-(+)-tartaric acid (DMU/LTA),[42] which were obtained according to the literature procedure (Table 1, Entries 5～9). To our great delight, using DMU/*L*-(+)-tartaric acid DES (n∶n=3∶1) was found to be very suitable to prompt the reaction proceeding efficiently, giving the corresponding product **3a** in a remarkably high yield of 69% within 8 h (Table 1, Entry 9). This promising result further interested us to determine the optimum reaction conditions by examining the effect of different reaction temperature and molar ratio of the DES on the product yield. And it was found that the best result could be achieved when a 7∶3 molar ratio of DMU/LTA[43] as the reaction medium at 80 ℃ in terms of reaction rate and yield (Table 1, Entry 12). In order to

Table 1 Reaction of 2-methylquinoline-3-carboxylic acid (**1**) with benzaldehyde (**2a**) in different medium[a]



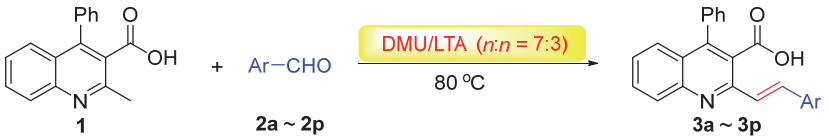
Entry	Reaction medium (molar ratio)	Temp./℃	Time/h	Yield[b]/%
1	ChCl/urea (1∶2)	80	8	NR[c]
2	ChCl/PEG (1∶2)	80	10	NR[c]
3	ChCl/glycerol (1∶2)	80	10	11
4	ChCl/oxalic acid (1∶1)	80	8	38
5	ChCl-malonic acid (1∶1)	90	8	26
6	ChCl/citric acid (2∶1)	90	8	41
7	DMU/citric acid (3∶2)	90	8	33
8	ChCl/LTA (1∶1)	90	8	45
9	DMU/LTA (3∶1)	80	8	69
10	DMU/LTA (2∶1)	80	8	74
11	DMU/LTA (1∶1)	80	8	52
12	**DMU/LTA (7∶3)**	**80**	**6**	**84**
13	DMU/LTA (7∶3)	70	6	78
14	DMU/LTA (7∶3)	90	6	81
15	Ac_2O	150	30	46
16	LTA in CH_2Cl_2	85	24	15
17	DMU/LTA[d]	80	6	84
18	DMU/LTA[e]	80	6	81
19	DMU/LTA[f]	80	6	79
20	DMU/LTA[g]	80	6	67

[a] Reaction conditions: substrate **1** (0.5 mmol), benzaldehyde (**2a**) (0.55 mmol) and DMU/LTA (2 g); [b] Isolated yield; [c] NR means no reaction; [d] Reaction in the 1st recovered DES solvent; [e] Reaction in the 2nd recovered DES solvent; [f] Reaction in the 3rd recovered DES solvent; [g] Reaction in the 4th recovered DES solvent.

highlight the advantages of the DES solvent, the model reaction in organic solvent such as Ac_2O[2] as described in literature was also conducted, from which the product **3a** was obtained only in 46% yield (Table 1, Entry 15). Thus, the use of DMU/LTA as the green reaction medium not only avoids the disadvantages of conventional organic solvents, but also results in greatly enhanced reactivity. In addition, we also carried out the model reaction by using *L*-(+)-tartaric acid as Brønsted acid catalyst in CH_2Cl_2 at refluxing temperature. However, it was found that the product formed from the reaction was only in a very low amount as observed by thin-layer chromatography (TLC) after 24 h (Table 1, Entry 16), which suggested that the reaction gave a good yield due to DMU/LTA as reaction medium and not due to its individual *L*-(+)-tartaric acid component. The reason for the effectiveness of DMU/LTA might be due to its good solubility, high stability and positive synergic effect on the reaction through extensive hydrogen bonding. Finally, the recyclability of the DMU/LTA for the model reaction was investigated by subjecting the fresh substrates **1** and **2a** to the recovered DMU/LTA, obtained by evaporating the aqueous layer under vacuum after product removal without further purification to repeat the model reaction. Moreover, the recovered DMU/LTA was found to be re-used up to three consecutive runs without significant decrease in **3a** yield (Table 1, Entries 17～19), though a slight darkening of the eutectic mixture was observed after recycling.[44-45] However, starting from the fourth cycle, a significant drop in the product yield was noticed (Table 1, Entry 20). Thus, this procedure using DMU/LTA as medium offers notable advantages, such as experimental simplicity, metal-free, mild and environmentally benign reaction conditions, easy work-up and satisfactory yields in comparison with reported methods,[11-21] which would contribute to the usefulness of this method.

To demonstrate the synthetic potential by applying DMU/LTA as the privileged reaction medium in the Knoevenagel-type condensation reaction, the reaction was extended to other substituted aromatic aldehydes in a similar fashion. Satisfactorily, these aldehydes were equally amenable to the reaction process without any experimental difficulties, successfully delivering the corresponding **3b**～**3l** in satisfactory yields of 62%～87% as listed in Table 2. It is worthy to note that in all cases the newly-formed olefin groups remain unaffected under the reaction conditions. Moreover, the electronic nature of the substituent present in the aromatic aldehydes appeared not to affect the transformation, neither in product yield nor in reaction rate. For example, the compound **3b** with electron-donating methyl group and **3l** bearing electron-withdrawing CN group were

Table 2 Yields and physical properties of the newly-synthesized **3a**～**3p**[a]



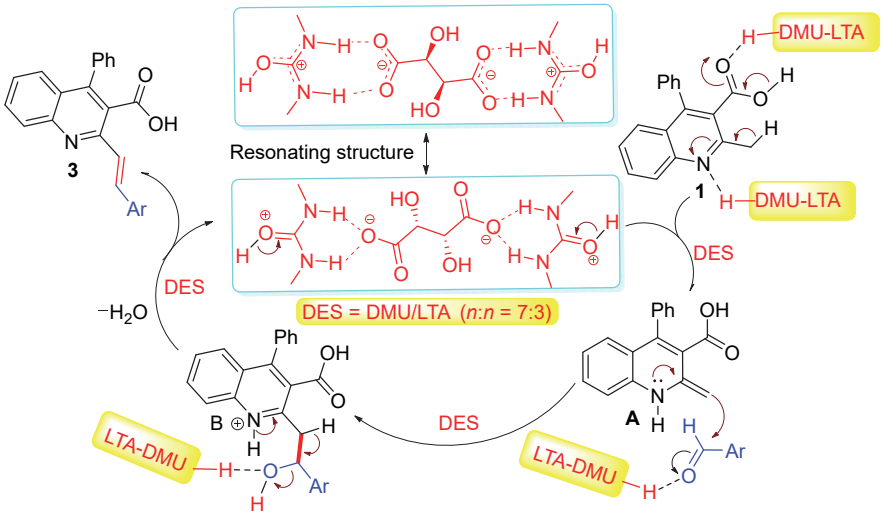
Entry	Compd.	Ar	Yield[b]/%	m.p./℃
1	**3a**	C_6H_5	84	218～220
2	**3b**	4-MeC_6H_4	81	198～199
3	**3c**	3-$MeOC_6H_4$	80	184～185
4	**3d**	2,3-$(MeO)_2C_6H_3$	62	192～194
5	**3e**	2,4-$(MeO)_2C_6H_3$	66	221～222
6	**3f**	2,4,5-$(MeO)_3C_6H_2$	63	239～241
7	**3g**	3,4,5-$(MeO)_3C_6H_2$	76	211～213
8	**3h**	4-ClC_6H_4	85	257～258
9	**3i**	3,5-$Cl_2C_6H_3$	84	198～200
10	**3j**	3-BrC_6H_4	79	190～192
11	**3k**	4-BrC_6H_4	87	238～240
12	**3l**	4-CNC_6H_4	78	261～263
13	**3m**		82	175～178
14	**3n**		76	197～198
15	**3o**		81	181～182
16	**3p**		84	195～196

[a] **1** (0.5 mmol), **2a**～**2p** (0.55 mmol), DES of 1,3-DMU/*L*-tartaric acid (*n*∶*n*=7∶3) (2 g), and the olefinization reaction at 80 ℃ for 6～8 h. [b] Isolated yields.

obtained in comparable yields of 81% and 78%, respectively, showing little distinction (Table 2, Entries 2 and 12). Conversely, the site of substituent present in the aromatic aldehydes had somewhat steric hindrance effect on the product yields. It was observed that the reaction with *ortho*-substituted aromatic aldehydes generally gave the corresponding products **3d**, **3e**, and **3f** in relatively lower yields with longer reaction time (Table 2, Entries 4～6). Particularly, the reaction with di-*ortho* substituted aromatic aldehydes such as 2,6-dimethyl-, 2,6-dimethoxy- and 2,6-dihalobenzaldehydes was found to be scarcely proceeded, from which the desired products were detected only in negligible amount that did not warrant isolation. In order to further diversify our synthetic work, it would be interesting in seeing whether heteroaryl aldehydes would exhibit a similar reactivity. To our delight, the chosen furan-2-carbaldehyde, thiophene-2-carbaldehyde, picolinaldehyde and nicotinaldehyde were viable substrates for this transformation, invariably furnishing the corresponding 2-hetaryvinylquinolines **3m**～**3p** in comparable yields (Table 2, Entries 13～16). However, the reaction with aliphatic aldehydes such as butyraldehyde, *iso*-butyraldehyde and cyclohexanecarboxaldehyde was found to be fraught with difficulties associated with combination of starting materials and numerous products, from which the desired alkenylation products could not be separated in any appreciable yield.

Theoretically, the structures of these newly-synthesized targeted compounds should exist as (*E*)- and/or (*Z*)-geometry due to the presence of the exocyclic vinyl double bond. The most diagnostic evidence for the geometry of vinyl moiety was the characteristic resonances of the arising two vinylic proton CH=CH doublets at δ 7.08～7.45 and 7.94～8.33 with large spin-spin coupling constants J_{ab}≈16.0 Hz in their ^{1}H NMR spectra, which was indicative of the *E*-configuration for the exocyclic vinyl moiety. It is worthy to mention that by a simple literature survey it was found that most of 2-styrylquinoline derivatives were reported to exhibit selectively the *E*-configuration, regardless of the presence or absence of substituent at the 3-position of quinoline ring or the styryl moiety. Thus, it would be that the reason for the *E*-configuration might be more thermodynamically stable for the (*E*)-isomer than its (*Z*)-isomer.

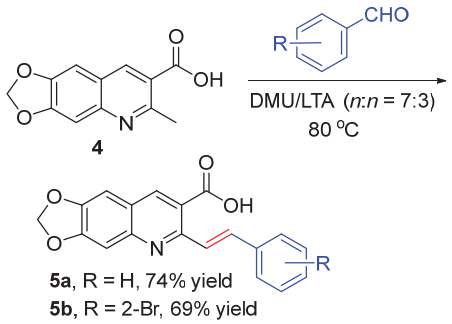
On the basis of the reports from Krishnakumar *et al.*,[44] who determined the structure, thermal stability and pH value of DMU/LTA (*n* ∶ *n*=7 ∶ 3) and from Alvi *et al.*,[45] who recently described the resonance structure of the DES as a proton source, a proposed reaction mechanism for the synthesis of the title compounds was outlined in Scheme 2. First, the ability of the acidic DMU/LTA (*n* ∶ *n*=7 ∶ 3) (pH=3.7) to N-protonation might play an important role for activation of the 2-methylquinoline-3-carboxylic acids to generate the enamine intermediate **A**. Moreover, the presence of the electron-withdrawing carboxylic acid group at the 3-position of quinoline ring might be conducive to this transformation. In order to verify the hypothesis, a control experiment was carried out to investigate whether 2-methylquinoline could show a similar chemical behavior with **1** under the same reaction conditions. It was observed that the reaction of 2-methylquinoline with aromatic aldehydes did not proceed smoothly, frustrating by the very poor yields of the resulting products, and the desired products could not be isolated in appreciable yields. Thus, the experimental results may adequately support our assumption. Subsequently, the formed intermediate **A** could be behaved as a nucleophile to attack the aromatic aldehydes, producing the intermediate **B**. In this nucleophilic addition reaction, the DES might also assist in improving the electrophilic reactivity of the aldehydes by hydrogen-bond with its carbonyl group. Finally, the generated hydroxyl group was undergone dehydration reaction to give the product **3**. In view of the entire reaction process, DES played dual roles of solvent and catalyst. In addition, it was worthy to note that although the structure of DMU/LTA was determined to be a 2 ∶ 1 molar ratio



Scheme 2 Proposed mechanistic pathway for synthesis of **3**

through hydrogen bonding, from the reaction result the 7∶3 molar ratio of DMU/LTA was superior to that of 2∶1. It was speculated that the presence of slightly excessive 1,3-dimethylurea might be acted as proton acceptor favoring the deprotonation in the transition state of **B** and thus promoting the generation of final product **3**. However, the present explanation is still in its infancy, and the real reaction mechanism has not yet been elucidated clearly. More studies toward the mechanism and the scope of this novel transformation represent an intriguing goal which is currently being actively pursued in our laboratory.

It has been reported that the derivatives of [1,3]dioxolo-[4,5-*g*]quinoline-3-carboxylic acid have been an attractive synthetic target owing to their potent antibacterial activity.[46] Thus, in view of their striking biological activities, the readily available 6-methyl-[1,3]dioxolo[4,5-*g*]quinoline-7-carboxylic acid (**4**) was further subjected to the DMU/LTA-promoted olefinization reaction sequence as shown in Scheme 3. As expected, both substrates were equally suitable to the reaction conditions, giving rise to the corresponding 6-styryl-substituted [1,3]dioxolo[4,5-*g*]-quinoline-3-carboxylic acids **5a** and **5b** in satisfactory yields of 74% and 69%, respectively. Work is currently ongoing, mainly focusing on the extension of the product scope and their biological activity assessment.



Scheme 3 Synthesis of 6-styryl-substituted [1,3]dioxolo[4,5-*g*]-quinoline-3-carboxylic acids **5a** and **5b**

3 Conclusions

In summary, the application of environmentally benign and non-toxic DES of DMU/LTA as mildly acidic reaction medium has been developed for the green synthesis of a series of structurally intriguing (*E*)-4-phenyl-2-styryl-quinoline-3-carboxylic acids via the direct olefination of 2-methylquinoline-3-carboxylic acids with aromatic aldehydes. The recyclability and biodegradability of the DMU/LTA make this methodology highly sustainable and reliable. The merits of the synthetic protocol described here include experimental simplicity, the use of inexpensive reagents, easy work-up procedure and satisfactory yields, which would contribute to the usefulness of this method. Currently, work is ongoing, mainly focusing on the further elaboration and application of these compounds, which represent an intriguing goal being contemplated, and these results will be a part of future reports.

4 Experimental section

4.1 Materials and instruments

The chemicals used in this report were obtained from Energy Chemical and were used without further purification. Melting points were determined using a WRS-1B melting point apparatus. The ^{1}H (400 or 600 MHz) NMR and ^{13}C (100 or 150 MHz) NMR spectra were recorded on an Agilent 400-MR spectrometer using DMSO-d_6 as the solvent. The reported chemical shifts (δ values) are given downfield from tetramethylsilane (TMS) as the internal standard. Elemental analyses were carried out on an EA 2400II elemental analyzer (PerkinElmer, Waltham, MA). The progress of reactions was monitored by TLC on silica gel GF254 using ethyl acetate/petroleum ether (V∶V=1∶10) as eluent.

4.2 Synthesis

4.2.1 Procedure for the preparation of deep eutectic solvent

The deep eutectic solvent 1,3-dimethylurea/*L*-(+)-tartaric acid was prepared as follows:[44] a mixture of 1,3-dimethylurea and *L*-(+)-tartaric acid with a molar ratio of 7∶3 was heated at 100 ℃ in air with stirring until a clear colourless liquid was obtained. After cooling to room temperature and vacuum drying for 5 h, the resulting 1,3-dimethylurea/*L*-(+)-tartaric acid deep eutectic solvent was sealed for later use.

4.2.2 General procedure for the synthesis of (*E*)-2-styrylquinoline-3-carboxylic acids (**3a**～**3p** and **5a**～**5b**)

In a typical experiment, 2 g of *L*-(+)-tartaric acid-DMU (n/n=3/7) mixture was heated to 70 ℃ to obtain a clear melting mixture. To this melt, 2-methyl-4-phenyl-quinoline-3-carboxylic acid (**1**) or 6-methyl[1,3]dioxolo-[4,5-*g*]quinoline-7-carboxylic acid (**4**) (0.5 mmol) and respective aromatic aldehydes (**2a**～**2l**) or heteroaromatic aldehydes (**2m**～**2p**) (0.55 mmol) were added, and the resulting reaction mixture was stirred at 80 ℃ for 6～8 h (as monitored by TLC). After the reaction was completed, the mixture was diluted with an equal volume of water and extracted using EtOAc (5 mL×3). The deep eutectic solvent could be easily isolated after removing H_2O from the aqueous layer under vacuum, and could be further used for the next run reaction. The combined organic layer was dried over Na_2SO_4 followed by evaporation of the solvent under reduced vacuum and washed with EtOH or column chromatography over silica gel using petroleum ether/EtOAc (V∶V=1∶1) as eluent to afford the desired **3a**～**3p** and **5a**～**5b**. The yields, physical properties and the spectral and analytical data are given below.

(*E*)-4-Phenyl-2-styrylquinoline-3-carboxylic acid (**3a**): Yellow solid, yield 84%. m.p. 218～220 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.29 (br s, 1H, COOH), 8.15 (d, J=8.4 Hz, 1H, ArH), 8.10 (d, J=15.6 Hz, 1H, CH=CH), 7.84 (t, J=7.6 Hz, 1H, ArH), 7.70 (d, J=7.2 Hz, 2H, ArH), 7.53～7.59 (m, 4H, ArH), 7.42～7.48 (m, 6H, ArH),

7.38 (d, J=15.6 Hz, 1H, CH=CH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.4, 150.1, 147.5, 145.3, 136.2, 136.1, 135.4, 131.1, 129.8, 129.6, 129.5, 129.1, 128.8, 127.8, 127.6, 126.4, 125.7, 124.5; IR (KBr) v: 3446, 3072, 2968, 1715, 1590, 1453, 1428, 1234, 1195, 1118, 834 cm^{-1}; Anal. calcd for $C_{24}H_{17}NO_2$: C 82.03, H 4.88, N 3.99; found C 81.82, H 5.07, N 3.82.

(*E*)-2-(4-Methylstyryl)-4-phenylquinoline-3-carboxylic acid (**3b**): Yellow solid, yield 81%. m.p. 198～199 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.58 (br s, 1H, COOH), 8.14 (d, J=8.0 Hz, 1H, ArH), 8.07 (d, J=15.6 Hz, 1H, CH=CH), 7.84 (t, J=7.2 Hz, 1H, ArH), 7.53～7.63 (m, 6H, ArH), 7.42～7.47 (m, 3H, ArH), 7.32 (d, J=16.0 Hz, 1H, CH=CH), 7.27 (d, J=7.6 Hz, 2H, ArH), 2.35 (s, 3H, Me); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.4, 147.5, 145.2, 139.3, 136.1, 135.5, 133.5, 131.1, 130.1, 129.8, 129.5, 129.0, 128.8, 128.6, 127.8, 127.5, 126.9, 126.4, 125.6, 123.4, 21.4; IR (KBr) v: 3447, 3055, 2958, 1707, 1583, 1515, 1454, 1372, 1271, 1188, 1154, 832 cm^{-1}; Anal. calcd for $C_{25}H_{19}NO_2$: C 82.17, H 5.24, N 3.83; found C 81.96, H 5.41, N 3.68.

(*E*)-2-(3-Methoxystyryl)-4-phenylquinoline-3-carboxylic acid (**3c**): Yellow solid, yield 80%. m.p. 184～185 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.62 (br s, 1H, COOH), 8.14 (d, J=8.4 Hz, 1H, ArH), 8.05 (d, J=15.6 Hz, 1H, CH=CH), 7.84 (t, J=7.6 Hz, 1H, ArH), 7.55～7.62 (m, 4H, ArH), 7.47 (d, J=8.4 Hz, 1H, ArH), 7.38～7.44 (m, 3H, ArH), 7.36 (d, J=15.6 Hz, 1H, CH=CH), 7.28 (d, J=7.6 Hz, 1H, ArH), 7.24 (s, 1H, ArH), 6.98 (d, J=8.0 Hz, 1H, ArH), 3.83 (s, 3H, OMe); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.4, 160.1, 150.1, 147.5, 145.3, 137.7, 136.1, 135.4, 131.1, 130.5, 129.8, 129.5, 129.1, 128.8, 128.4, 127.7, 126.4, 125.7, 124.8, 119.8, 115.3, 113.3, 55.6; IR (KBr) v: 3445, 3070, 2923, 1712, 1576, 1577, 1503, 1453, 1417, 1354, 1236, 1129, 928 cm^{-1}; Anal. calcd for $C_{25}H_{19}NO_3$: C 78.72, H 5.02, N 3.67; found C 79.00, H 4.83, N 3.46.

(*E*)-2-(2,3-Dimethoxystyryl)-4-phenylquinoline-3-carboxylic acid (**3d**): Yellow solid, yield 62%. m.p. 192～194 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.53 (br s, 1H, COOH), 8.16～8.27 (m, 4H, ArH and CH=CH), 7.44～7.57 (m, 7H, ArH and CH=CH), 7.11～7.15 (m, 3H, ArH), 3.85 (s, 3H, OMe), 3.84 (s, 3H, OMe); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 167.3, 151.2, 148.2, 145.6, 145.3, 143.1, 133.3, 128.9, 128.7, 127.7, 127.6, 127.5, 126.9, 126.8, 126.6, 125.5, 124.3, 123.9, 123.5, 122.8, 117.0, 111.7, 58.9, 54.0; IR (KBr) v: 3435, 3083, 2889, 1721, 1575, 1527, 1461, 1392, 1248, 1210, 831 cm^{-1}; Anal. calcd for $C_{26}H_{21}NO_4$: C 75.90, H 5.14, N 3.40; found C 75.61, H 5.36, N 3.19.

(*E*)-2-(2,4-Dimethoxystyryl)-4-phenylquinoline-3-carboxylic acid (**3e**): Yellow solid, yield 66%. m.p. 221～222 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.51 (br s, 1H, COOH), 8.25 (d, J=15.6 Hz, 1H, ArH), 8.11 (d, J=8.4 Hz, 1H, ArH), 7.80 (t, J=8.0 Hz, 1H, ArH), 7.50 (d, J=7.6 Hz, 1H, ArH), 7.54～7.59 (m, 4H, ArH), 7.41～7.45 (m, 3H, ArH), 7.33 (d, J=15.6 Hz, 1H, CH=CH), 3.92 (s, 3H, OMe), 3.83 (s, 3H, OMe); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.6, 162.0, 159.3, 151.0, 147.6, 144.9, 135.5, 131.2, 130.9, 129.8, 129.4, 129.3, 129.0, 128.8, 128.7, 127.2, 126.4, 125.4, 122.5, 117.7, 106.5, 99.0, 56.1, 55.8; IR (KBr) v: 3446, 3068, 2895, 1705, 1573, 1510, 1453, 1381, 1234, 1195, 834 cm^{-1}; Anal. calcd for $C_{26}H_{21}NO_4$: C 75.90, H 5.14, N 3.40; found C 76.08, H 4.92, N 3.53.

(*E*)-4-Phenyl-2-(2,4,5-trimethoxystyryl)quinoline-3-carboxylic acid (**3f**): White solid, yield 63%. m.p. 239～241 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.54 (br s, 1H, COOH), 8.33 (d, J=16.0 Hz, 1H, CH=CH), 8.29 (d, J=8.0 Hz, 1H, ArH), 7.91 (d, J=7.6 Hz, 1H, ArH), 7.41 (d, J=16.0 Hz, 1H, CH=CH), 7.58～7.63 (m, 4H, ArH), 7.43～7.49 (m, 3H, ArH), 7.20 (s, 1H, ArH), 6.79 (s, 1H, ArH), 3.93 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.79 (s, 3H, OMe); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 172.4, 154.2, 152.3, 150.7, 143.4, 135.3, 135.0, 134.1, 133.4, 129.7, 129.4, 129.0, 128.9, 127.9, 126.8, 126.7, 125.6, 120.2, 115.7, 112.2, 98.3, 56.8, 56.7, 56.3; IR (KBr) v: 3447, 3046, 2958, 1718, 1582, 1577, 1515, 1454, 1417, 1373, 1296, 1196, 1109, 836 cm^{-1}; Anal. calcd for $C_{27}H_{23}NO_5$: C 73.46, H 5.25, N 3.17; found C 73.61, H 5.07, N 3.34.

(*E*)-4-Phenyl-2-(3,4,5-trimethoxystyryl)quinoline-3-carboxylic acid (**3g**): White solid, yield 76%. m.p. 211～213 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.55 (br s, 1H, COOH), 8.12 (d, J=8.4 Hz, 1H, ArH), 8.04 (d, J=15.6 Hz, 1H, CH=CH), 7.84 (t, J=7.6 Hz, 1H, ArH), 7.53～7.59 (m, 4H, ArH), 7.41～7.46 (m, 3H, ArH), 7.29 (d, J=15.6 Hz, 1H, CH=CH), 7.02 (s, 2H, ArH), 3.87 (s, 6H, 2OMe), 3.72 (s, 3H, OMe); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 178.4, 162.6, 159.3, 156.5, 154.3, 147.9, 145.7, 145.4, 144.5, 140.9, 138.9, 138.6, 137.7, 135.6, 134.6, 114.4, 114.1, 69.6, 65.4; IR (KBr) v: 3443, 3054, 2968, 1723, 1575, 1578, 1505, 1480, 1396, 1239, 1110, 792 cm^{-1}; Anal. calcd for $C_{27}H_{23}NO_5$: C 73.46, H 5.25, N 3.17; found C 73.28, H 5.34, N 3.03.

(*E*)-2-(4-Chlorostyryl)-4-phenylquinoline-3-carboxylic acid (**3h**): Yellow solid, yield 85%. m.p. 257～258 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.59 (br s, 1H, COOH), 8.14 (d, J=8.4 Hz, 1H, ArH), 8.06 (d, J=15.6 Hz, 1H, ArH), 7.84 (t, J=8.06 Hz, 1H, ArH), 7.73 (d, J=8.0 Hz, 2H, ArH), 7.55～7.60 (m, 4H, ArH), 7.51 (d, J=8.4 Hz, 2H, ArH), 7.42～7.48 (m, 3H, ArH), 7.37 (d, J=15.6 Hz, 1H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 167.2, 147.7, 145.3, 143.2, 133.3, 133.0, 132.6, 131.8, 129.0, 127.6, 127.4, 127.3, 126.9, 126.7, 125.6, 124.3, 123.5, 123.1; IR (KBr) v: 3452, 3072, 2962, 1718, 1579, 1490, 1455, 1414, 1372, 1291, 1120, 832 cm^{-1}; Anal. calcd for $C_{24}H_{16}ClNO_2$: C 74.71, H 4.18, N 3.63; found C 74.55, H 4.36, N 3.84.

(*E*)-2-(3,5-Dichlorostyryl)-4-phenylquinoline-3-carboxylic acid (**3i**): Orange solid, yield 87%. m.p. 198～200 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.37 (br s, 1H, COOH), 8.13 (d, J=8.4 Hz, 1H, ArH), 7.99 (d, J=15.6 Hz, 1H, CH=CH), 7.85 (t, J=7.6 Hz, 1H, ArH), 7.78 (s, 2H, ArH), 7.56～7.59 (m, 5H, ArH), 7.47～7.50 (m,

2H, ArH), 7.45 (d, J=15.6 Hz, 1H, CH=CH), 7.44 (s, 1H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.2, 149.7, 147.4, 145.5, 140.1, 135.4, 135.1, 133.1, 131.2, 129.8, 129.6, 129.0, 128.8, 128.4, 127.9, 126.5, 126.2, 125.9; IR (KBr) v: 3446, 1716, 1577, 1515, 1437, 1374, 1340, 1272, 1126, 834 cm^{-1}; Anal. calcd for $C_{24}H_{15}Cl_2NO_2$: C 68.59, H 3.60, N 3.33; found C 68.38, H 3.79, N 3.11.

(*E*)-2-(3-Bromostyryl)-4-phenylquinoline-3-carboxylic acid (**3j**): Yellow solid, yield 84%. m.p. 190～192 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.59 (br s, 1H, COOH), 8.13 (d, J=8.4 Hz, 1H, ArH), 8.02 (d, J=15.6 Hz, 1H, CH=CH), 7.91 (s, 1H, ArH), 7.85 (t, J=7.6 Hz, 1H, ArH), 7.71 (d, J=8.0 Hz, 1H, ArH), 7.53～7.60 (m, 5H, ArH), 7.47 (d, J=8.4 Hz, 1H, ArH), 7.41～7.45 (m, 3H, ArH), 7.38 (d, J=8.4 Hz, 1H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 167.2, 147.7, 145.3, 143.2, 133.4, 133.3, 132.6, 130.2, 129.0, 127.6, 127.5, 127.4, 126.9, 126.7, 126.6, 125.6, 124.3, 123.6, 123.2, 120.5; IR (KBr) v: 3446, 1719, 1585, 1513, 1457, 1417, 1237, 1111, 786 cm^{-1}; Anal. calcd for $C_{24}H_{16}BrNO_2$: C 66.99, H 3.75, N 3.26; found C 67.20, H 3.56, N 3.09.

(*E*)-2-(4-Bromostyryl)-4-phenylquinoline-3-carboxylic acid (**3k**): Yellow solid, yield 79%. m.p. 238～240 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.59 (br s, 1H, COOH), 8.14 (d, J=8.4 Hz, 1H, ArH), 8.05 (d, J=15.6 Hz, 1H, CH=CH), 7.84 (t, J=7.6 Hz, 1H, ArH), 7.63～7.68 (m, 4H, ArH), 7.55～7.60 (m, 4H, ArH), 7.47 (d, J=8.4 Hz, 1H, ArH), 7.43 (d, J=7.6 Hz, 2H, ArH), 7.38 (d, J=15.6 Hz, 1H, CH=CH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 169.3, 149.8, 147.5, 138.8, 135.4, 134.4, 132.0, 131.5, 131.1, 130.2, 129.8, 129.6, 129.1, 128.8, 127.8, 126.7, 126.5, 126.2, 125.8, 122.8; IR (KBr) v: 3460, 3038, 2980, 1714, 1578, 1497, 1423, 1399, 1290, 1233, 1165, 1126, 1056, 847 cm^{-1}; Anal. calcd for $C_{24}H_{16}BrNO_2$: C 66.99, H 3.75, N 3.26; found C 66.80, H 3.92, N 3.06.

(*E*)-2-(4-Cyanostyryl)-4-phenylquinoline-3-carboxylic acid (**3l**): Orange solid, yield 78%. m.p. 261～263 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.31 (br s, 1H, COOH), 8.12～8.18 (m, 2H, ArH), 8.03 (d, J=7.2 Hz, 2H, ArH), 7.86 (d, J=7.6 Hz, 1H, ArH), 7.82 (d, J=8.0 Hz, 2H, ArH), 7.53～7.59 (m, 4H, ArH), 7.44～7.52 (m, 4H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 172.1, 154.5, 152.2, 150.2, 145.1, 140.2, 139.7, 136.0, 135.9, 135.2, 134.5, 134.4, 133.8, 133.7, 133.5, 132.8, 132.6, 131.5, 131.2, 130.6; IR (KBr) v: 3447, 2228, 1713, 1584, 1514, 1449, 1374, 1267, 1204, 1125, 832 cm^{-1}; Anal. calcd for $C_{25}H_{16}N_2O_2$: C 79.77, H 4.28, N 7.44; found C 79.54, H 4.47, N 7.29.

(*E*)-2-(2-(Furan-2-yl)vinyl)-4-phenylquinoline-3-carboxylic acid (**3m**): Yellow solid, yield 82%. m.p. 175～178 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.59 (br s, 1H, COOH), 8.09 (d, J=8.4 Hz, 1H, ArH), 7.94 (d, J=15.6 Hz, 1H, CH=CH), 7.80～7.84 (m, 2H, ArH), 7.51～7.58 (m, 4H, ArH), 7.40～7.46 (m, 3H, ArH), 7.17 (d, J=15.6 Hz, 1H, CH=CH), 6.91 (dd, J=7.2, 3.8 Hz, 1H, ArH), 6.63～6.67 (m, 1H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 174.2, 157.0, 154.5, 152.3, 149.9, 149.8, 140.1, 135.9, 134.5, 134.3, 134.2, 133.8, 133.6, 132.3, 131.2, 130.3, 128.0, 126.5, 118.8, 117.8; IR (KBr) v: 3462, 1713, 1588, 1511, 1446, 1374, 1340, 1294, 1263, 1204, 1118, 857 cm^{-1}; Anal. calcd for $C_{22}H_{15}NO_3$: C 77.41, H 4.43, N 4.10; found C 77.28, H 4.12, N 4.31.

(*E*)-4-Phenyl-2-(2-(thiophen-2-yl)vinyl)quinoline-3-carboxylic acid (**3n**): Yellow solid, yield 76%. m.p. 197～198 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.65 (br s, 1H, COOH), 8.27 (d, J=15.6 Hz, 1H, CH=CH), 8.10～8.13 (m, 1H, ArH), 7.84 (dd, J=7.6, 7.2 Hz, 1H, ArH), 7.64 (d, J=7.6 Hz, 1H, ArH), 7.51～7.57 (m, 5H, ArH), 7.43～7.48 (m, 3H, ArH), 7.17 (d, J=3.6 Hz, 1H, ArH), 7.08 (d, J=15.6 Hz, 1H, CH=CH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 174.1, 154.5, 152.2, 150.0, 146.2, 140.2, 135.9, 135.5, 134.5, 134.2, 134.0, 133.8, 133.7, 133.5, 133.3, 132.7, 132.3, 131.2, 130.3, 127.9; IR (KBr) v: 3446, 1719, 1583, 1493, 1452, 1417, 1373, 1291, 1263, 1201, 1123, 850 cm^{-1}; Anal. calcd for $C_{22}H_{15}NO_2S$: C 73.93, H 4.23, N 3.92; found C 74.14, H 4.08, N 3.76.

(*E*)-4-Phenyl-2-(2-(pyridin-2-yl)vinyl)quinoline-3-carboxylic acid (**3o**): Yellow solid, yield 81%. m.p. 181～182 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.64 (br s, 1H, COOH), 8.67 (d, J=3.6 Hz, ArH), 8.16 (d, J=8.4 Hz, 1H, ArH), 8.12 (d, J=15.6 Hz, 1H, ArH), 7.97 (d, J=15.6 Hz, 1H, ArH), 7.87 (dd, J=7.6, 7.6 Hz, 2H, ArH), 7.70 (d, J=7.6 Hz, 1H, ArH), 7.54～7.60 (m, 4H, ArH), 7.44～7.50 (m, 3H, ArH), 7.36～7.39 (m, 1H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 167.2, 151.8, 148.2, 147.5, 145.4, 143.1, 135.5, 133.2, 132.8, 129.0, 127.6, 127.5, 127.2, 126.9, 126.7, 125.8, 125.7, 124.3, 123.7, 122.9, 121.9; IR (KBr) v: 3446, 2915, 1715, 1582, 1508, 1449, 1402, 1380, 1336, 1286, 1240, 1116, 874 cm^{-1}; Anal. calcd for $C_{23}H_{16}N_2O_2$: C 78.39, H 4.58, N 7.95; found C 78.67, H 4.39, N 7.74.

(*E*)-4-Phenyl-2-(2-(pyridin-3-yl)vinyl)quinoline-3-carboxylic acid (**3p**): Yellow solid, yield 84%. m.p. 195～196 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.54 (br s, 1H, COOH), 8.88 (s, 1H, ArH), 8.57 (d, J=4.4 Hz, 1H, ArH), 8.13～8.16 (m, 2H, ArH), 8.09 (d, J=16.0 Hz, 1H, CH=CH), 7.85 (d, J=7.6 Hz, 1H, ArH), 7.55～7.60 (m, 4H, ArH), 7.41～7.50 (m, 5H, ArH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 165.4, 148.0, 147.9, 147.6, 145.6, 144.7, 133.1, 132.0, 130.7, 130.0, 129.4, 127.5, 127.4, 127.0, 126.7, 125.8, 125.0, 124.4, 124.1, 123.4, 122.2; IR (KBr) v: 3461, 1710, 1581, 1581, 1511, 1463, 1406, 1379, 1320, 1132, 874 cm^{-1}; Anal. calcd for $C_{23}H_{16}N_2O_2$: C 78.39, H 4.58, N 7.95; found C 78.18, H 4.35, N 8.11.

(*E*)-6-Styryl-[1,3]dioxolo[4,5-*g*]quinoline-7-carboxylic acid (**5a**): Yellow solid, yield 74%. m.p. 272～273 ℃; ^{1}H NMR (DMSO-d_6, 600 MHz) δ: 13.34 (br s, 1H, COOH), 8.70 (s, 1H, Quino-H), 8.20 (d, J=15.6 Hz, 1H, CH=CH), 7.88 (d, J=15.6 Hz, 1H, CH=CH), 7.65 (t, J=7.8 Hz, 2H, Ben-H), 7.48 (s, 1H, Quino-H), 7.44 (t, J=7.8 Hz, 2H, Ben-H), 7.40 (s, 1H, Quino-H), 7.35 (t, J=7.8 Hz, 1H, Ben-H), 6.26 (s, 2H, OCH_2O); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 102.5, 103.4, 104.5, 121.8, 123.2, 125.8, 127.2, 128.60, 129.0, 133.9, 136.7, 138.5, 147.0, 148.1, 151.1,

152.8, 167.9; IR (KBr) *v*: 3475, 1691, 1623, 1577, 1463, 1402, 1323, 1038, 858 cm^{-1}; Anal. calcd for $C_{19}H_{13}NO_4$: C 71.47, H 4.10, N 4.39; found C 71.23, H 4.37, N 4.18.

(*E*)-6-(2-Bromostyryl)-[1,3]dioxolo[4,5-*g*]quinoline-7-carboxylic acid (**5b**): Yellow solid, yield 69%; m.p. 259～260 ℃; ^1H NMR (DMSO-d_6, 600 MHz) δ: 13.43 (br s, 1H, COOH), 8.72 (s, 1H, Quino-H), 8.17 (d, J=15.6 Hz, 1H, CH=CH), 8.13 (d, J=15.6 Hz, 1H, CH=CH), 7.82 (dd, J=7.8, 1.2 Hz, 1H, Ben-H), 7.71 (d, J=7.8 Hz, 1H, Ben-H), 7.49 (s, 1H, Quino-H), 7.47 (d, J=7.8 Hz, 1H, Ben-H), 7.40 (s, 1H, Quino-H), 7.30 (t, J=7.8 Hz, 1H, Ben-H), 6.27 (s, 2H, OCH_2O); ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 102.5, 103.3, 104.7, 122.0, 123.4, 124.0, 127.5, 128.3, 129.1, 130.1, 131.7, 133.1, 136.4, 138.4, 147.1, 148.2, 150.7, 152.8, 167.8; IR (KBr) *v*: 3448, 1696, 1614, 1585, 1477, 1389, 1298, 1017, 861 cm^{-1}; Anal. calcd for $C_{19}H_{12}BrNO_4$: C 57.31, H 3.04, N 3.52; found C 57.56, H 2.88, N 3.33.

4.2.3 Recycling of the DES of 1,3-dimethylurea/*L*-(+)-tartaric acid

In view of the need for environmental benign methodologies, the recovery and reuse of the DES are essential. The recycling of the DES was investigated by using a representative reaction of 2-methylquinoline-3-carboxylic acid (**1**) and benzaldehyde (**2a**) under optimized conditions. After reaction was complete, water (5 mL) was added to the reaction mixture and shacked vigorously. The resulting solid was extracted using EtOAc (5 mL×3), and the DES was recovered by evaporating the water at 80 ℃ through vacuum rotator evaporator and was reused for the next batch and recycled again. Due to the negligible vapor pressure, there was almost no loss of the amount of DES after 3 consecutive cycles.

Supporting Information ^1H NMR and ^{13}C NMR spectra of compounds **3a**～**3p** and **5a**～**5b** are available free of charge via the Internet at http://sioc-journal.cn/.

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