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• **Graphical Abstract:**

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Hai-Chuan Hu, Yu-Heng Liu, Bao-Le Li, Zhen-Shui Cui and Zhan-Hui Zhang*

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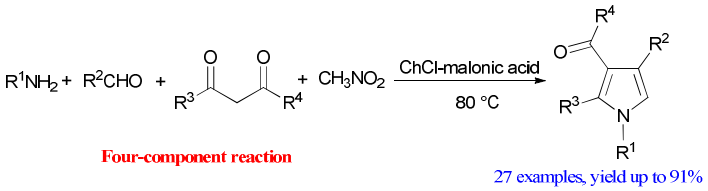

Deep eutectic solvent based on choline chloride and malonic acid as an efficient and reusable catalytic system for one-pot synthesis of functionalized pyrroles

Hai-Chuan Hu[a], Yu-Heng Liu[b], Bao-Le Li[a], Zhen-Shui Cui[a] and Zhan-Hui Zhang*[,a]

Deep eutectic solvent (DES) based on choline chloride and malonic acid was prepared easily with high purity at low cost. It has been applied as dual catalyst and reaction medium for synthesis of functionalized pyrroles by one-pot, four-component reaction of amines, aldehydes, 1,3-dicarbonyl compounds and nitromethane. This green solvent could be recycled and reused three times without loss of its efficiency.

Introduction

Developing new environmentally benign solvents is one of the key subjects in chemistry industry. During the past years, ionic liquids (ILs) as a class of green solvents have been applied in many fields such as separation technology,[1] biocatalysis[2] and organic synthesis[3] because of their distinctive properties such as low vapor pressure, non-volatility, good stability and recyclability. However, recent examples have also demonstrated the disadvantage of using ILs as solvents, such as high cost, difficult preparation and some toxic properties.[4] Therefore, developing a simple synthetic and greener alternative solvent has very important practical significance. In recent years, low-cost eutectic mixtures include deep eutectic solvents (DESs) based on choline chloride (ChCl) first introduced by Abbott and co-workers,[5] low-melting mixture (LMM) of sugar,

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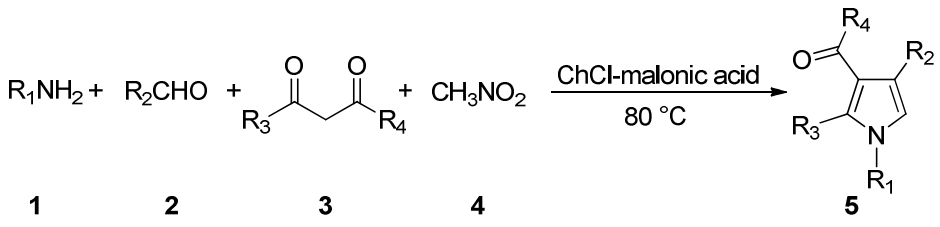
urea and inorganic salts first described by König and co-workers,[6] natural deep eutectic solvents (NADES) first described by Choi and co-workers,[7] low-transition temperature mixtures (LTTMs) descried by Kroon and co-workers,[8] and deep eutectic ionic liquids (DEILs) reported by Hillman' group[9] with similar physical properties and phase bahavior to ILs, are gaining increasing attention in chemistry fields. Compared with ILs, the synthetic process of these eutectic mixtures is relatively simple, which only by mixing two or more compounds under heating until a homogenous liquid is formed without any purification with 100% atom untilzation rate.[10] In addition, the synthetic materials of these eutectic mixtures are abundant, low-toxic, relatively cheap, and biodegradable, which makes them particularly desirable for large-scale applications successfully in industrial production.[11] To date, they have been applied to many chemical processing such as extraction,[12] polymerizations,[13] biomass processing,[14] materials synthesis[15] and organic reactions.[16]

The pyrrole nucleus is one of the most relevant simple heterocycles found in a large number of natural products, agrochemicals, and pharmaceuticals.[17] Many pyrrole-containing compounds possess potent biological activity.[18-19] Furthermore, pyrrole derivatives are particularly important in materials science.[20] Consequently, the preparation of pyrroles has received considerable attention and a number of synthetic routes have been reported, such as Hantzsch,[21] Paal–Knorr,[22] and Clauson-Kaas reactions.[23] Multicomponent reactions (MCRs) have been extensively used in organic synthesis. Up to date, MCRs have emerged as vital tools for the preparation of substituted and functionalized pyrrole derivatives from simple materials.[24] In 2010, Jana and co-workers reported one-pot, four-component coupling reactions of 1,3-dicarbonyl compounds, amines, aromatic aldehydes, and nitroalkanes for the synthesis of highly functionalized pyrroles catalyzed by $FeCl_3$. However, this method suffers from the shortcoming of long reaction time, low yield of products and tedious work-up procedure.[25] In the past several years, great efforts have been made in this area in order to develop a simple and efficient method to improve this conversion. Khan,[26] Saeidian,[27] Jeong,[28] and Zhang[29] have reported some metal-catalyzed methods for this conversion. Despite the

advances achieved, all of these methods used transition metals, and these bring great difficulties form the separation and purification of the target products, especially in the synthesis of pharmaceutical molecules. To solve these problems, a series of metal-free catalyzed methods for this transformation have been reported, for example, the use of I_2,[30] Amberlyst-15,[31] bromodimethylsulfonium bromide (BDMS),[32] and ionic liquid.[33] However, the major limitation of these methods lies in the variable amines that must be aliphatic amines or benzylamines. Montmorillonite clay,[34] gluconic acid aqueous solution (GAAS)[35] and 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim]HSO_4)[36] have also been used for this four-component reaction. However, these methods required long reaction times. Thus, the development of a simple, more efficient method for the synthesis of pyrroles remains an attractive goal.

As a part of our ongoing research program aimed at developing multicomponent reactions[37] and environmental benign synthetic methodologies,[38] herein we wish to report a simple, practical and metal-free method for the construction of *N*-protected functionalized pyrroles by one-pot, four-component reaction of amines, aldehydes, 1,3-dicarbonyl compounds and nitromethane in choline chloride-malonic acid (Scheme 1).



Scheme 1 Synthesis of fuctionalized pyrroles using ChCl-malonic acid

Results and discussion

The preparation of choline chloride-malonic acid based DES was performed by stirring ChCl (1 mol) and malonic acid (1 mol) at 80 ºC until a homogenous liquid was formed. This method gave DES with 100% atom economy since it completely forms a eutectic mixture with no by-product formation. Thermal stability of ChCl-malonic acid was investigated by TG analysis in the N_2

atmosphere, which showed that there were two steps of weight loss (Figure 1). The weight loss at temperatures below 110 ^{o}C was due to the removal of water. The weight loss of the ChCl-malonic acid system was nearly 43.6% in the temperature range 110-160 ^{o}C, which was attributed to the complete decomposition of malonic acid. In addition, there is less weight loss when ChCl-malonic acid was heated for 5 h at100 ^{o}C, which indicaties that this DES is stable under 100 ^{o}C. It was hence tempting and logical to study its potential as a green solvent in organic synthesis.

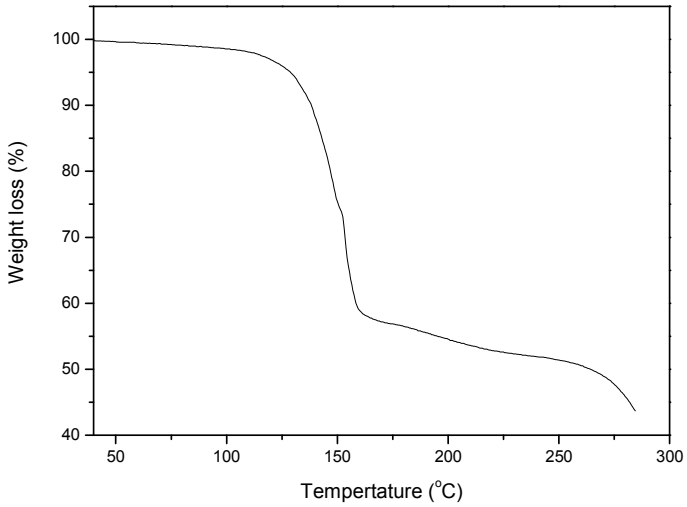


Fig. 1 TG analysis of ChCl-malonic acid

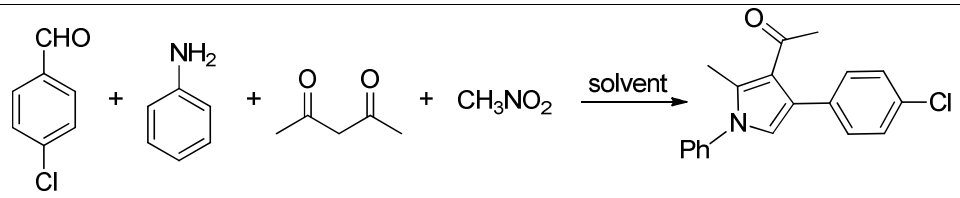
To optimize the reaction conditions, the model reaction of aniline, 4-chlorobenzaldehyde, acetylacetone and nitromethane was investigated and the results are recorded in Table 1. To initiate our study, the model reaction was performed in the absence of catalyst under solvent-free condition and only a trace amount of the desired product was detected after prolonged reaction time (Table 1, entry 1). The commerical available ionic liquids such as bmimBF_4 and bmimPF_6 were explored, no improvement was observed. Recently, Handy and Lavender reported that ChCl/urea DES could been used as effective solvent/catalyst for synthesis of pyrrole via the Paal-Knorr reaction,[39] however, this four-component reaction could not proceed at all in this DES (entry 4). Furthermore, the use of some ChCl based on DESs such as ChCl + oxalic acid/tartaric acid/citric acid provided

the desired product in very low yields. When the reaction was performed in ChCl: $FeCl_3$ or ChCl:$ZnBr_2$, the yields of product were significantly improved. This finding encouraged us to test other DESs. Previously, Abbott and co-workers reported that DESs can be formed between ChCl and dicarboxylic acids such as malonic or succinic acid, and their physical properties of these DESs such as viscosity, conductivity and surface tension were also investigated.[5b] Subsequently, the model reaction was undertaken in ChCl + itaconic acid/ fumaric acid/ malic acid/ succinic acid/ malonic acidd. To our delight, ChCl-malonic acid was found to be a more efficient medium and provided desired product in remarkably high yield (88% yield, entry 14). The difference in the catalytic efficiency of these DESs may be due to their varying acidity. A lower reaction temperature of 60 ^oC decreased the yield to 52% (Table 1, entry 17), but a higher reaction temperature (90 ^oC) did not make a significant effect in the yield of product (Table 1, entry 18). The reaction in the presence of individual component such as ChCl and malonic acid instead of DES was also investigated. It was found that 12% yield of product was obtained when only malonic acid was used wheres no reaction was observed in the case of ChCl in the absence of malonic acid, which indicated that neither ChCl nor malonic acid promotes the reaction alone. The co-existence of ChCl and malonic acid has shown the synergetic effect on the reaction, which is perhaps the main reason for the high catalytic activity of the DES. This result is consistent with ChCl/oxalic acid system.[16j] Malonic acid only forms deep eutectic solvent with choline chloride, and it does not participate in the reaction. Finally, we examined the reaction with various amount of ChCl-malonic acid. The reaction proceeded smoothly to give the desired product **5m** in 88% yield when 0.5 g and 1.0 g ChCl-malonic acid was used. A slightly lower yield was achieved using 1.5 g ChCl-malonic acid. Thus, the most suitable reaction conditions for the model reaction were established (Table 1, entry 14).

To demonstrate the industrial applicability of this protocol, the model reaction was carried out on a large scale (50 mmol). The reaction was completed in 1 h and afforded the corresponding

product in 89% yield (Table 1, entry 21).

Table 1 Reaction of 4-chlorobenzaldehyde, aniline, acetylacetone and nitromethane in various DESs[a]



Entry	Catalyst	Temperature (^{o}C)	Yield (%)
1[b]	no	80	trace
2	bmimBF_4	80	trace
3	bmimPF_6	80	trace
4	ChCl: urea (1:2)	80	trace
5	ChCl: L-(+)-tartaric acid (2:1)	80	12
6	ChCl: citric acid (2:1)	80	18
7	ChCl: oxalic acid (1:1)	80	20
8	ChCl: $FeCl_3$ (1:2)	80	49
9	ChCl: $ZnBr_2$ (1:2)	80	70
10	ChCl: itaconic acid (1:1)	80	78
11	ChCl: fumaric acid (1:1)	80	80
12	ChCl: malic acid (1:1)	80	71
13	ChCl: succinic acid (1:1)	80	65
14	ChCl: malonic acid (1:1)	80	88
15	ChCl: malonic acid (1:1) 1.0 g	80	88
16	ChCl: malonic acid (1:1) 1.5 g	80	86
17	ChCl: malonic acid (1:1)	60	52
18	ChCl: malonic acid (1:1)	90	88
19	ChCl	80	0
20	malonic acid	80	12
21[c]	ChCl: malonic acid (1:1)	80	89

[a] Reaction condition: 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol), acetylacetone (1 mmol), nitromethane (3 mmol), ChCl: second component ratio in (mol:mol), solvent (0.5 g), 60 min. [b] The reaction time up to 12 h. [c] The reaction was carried out in 50 mmol scale.

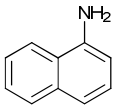
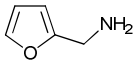
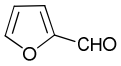
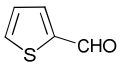
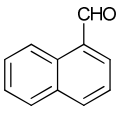
With these findings in hand, we examined this method to a wider range of amines, aldehydes, and 1,3-dicarbonyl compounds and the results was depicted in Table 2. Firstly, diverse amines were investigated. The results demonstrated that a wide range of anilines, regardless of electron-donating or electron-withdrawing groups on the benzene ring, could undergo the reaction smoothly to afford the expected products in moderate to good yields. Anilines bearing a weakly electron-withdrawing were a little bit less efficient in the reaction. A decrease in reactivity was observed when *ortho*-substitution substrate was used (Table 2, entry 5), thus revealing a strong steric effect. Noticeably, the notoriously difficult 4-nitroaniline was also successfully converted into the corresponding product **5i** (Table 2, entry 9). It is worth mentioning that the reaction time was shortened obviously compared with previous reported method.[35] In addition, this reaction was amenable to polycyclic aromatic substrate such as naphthylamine, and the corresponding product **5g** was obtained in high yield (Table 2, entry 10). Amine containing heteroaromatic group such as furan-2-ylmethanamine was also subjected to the standard reaction conditions, very valuable product **5k** was obtained in good yield (Table 2, entry 11). Moreover, prop-2-en-1-amine could be employed as a facile substrate and provided the corresponding products in good yields (Table 2, entries 18 and 19). Also, it was found that different kinds of aliphatic amines reacted successfully to afford the desired products under the same reaction conditions in apparently shorter reaction time (Table 2, entries 12 and 13).

Next, the substrate scope of aldehydes with a variety of substituents was also investigated in this 4CRs. The aromatic ring of benzaldehyde bearing electron-withdrawing or electron-donating groups afforded the desired products in high yields, showing no significant influence on the reaction time and the yield of the products. Notably, heteroaromatic aldehydes such as 2-furaldehyde and 2-thiophenealdehyde were tolerated and furnished the corresponding products **5r** and **5s** in excellent yields. 1-Naphthaldehyde also afforded the product **5t** in 80 % yield. Unfortunately, alkyl aldehyde

such as cyclohexanecarboxaldehyde or benzylic aldehyde provided inseparable complex mixtures under similar reaction conditions.

Encouraged by the good results with acetylacetone, we further expand the reaction scope. A variety of 1,3-dicarbonyl compounds such as methyl acetoacetate, ethyl acetoacetate, 2-methoxyethyl acetoacetate, allyl acetoacetate, *tert*-butyl 3-oxobutanoate, isobutyl 3-oxobutanoate and methyl 3-oxopentanoate were applied to this 4CRs, the desired products were isolated in high yields (Table 2, entries 21-27).

Table 2 Synthesis of multisubstituted pyrroles **5**

Entry	Aldehyde	Amine	R^3	R^4	Product	Time/h	Yield/%[a]	Ref.
1	PhCHO	$PhNH_2$	Me	Me	**5a**	1.0	90	25
2	PhCHO	4-$CH_3C_6H_4NH_2$	Me	Me	**5b**	1.0	90	35
3	PhCHO	4-$C(CH_3)_3C_6H_4NH_2$	Me	Me	**5c**	1.0	91	35
4	PhCHO	4-$FC_6H_4NH_2$	Me	Me	**5d**	1.0	87	34
5	PhCHO	2-$ClC_6H_4NH_2$	Me	Me	**5e**	1.8	56	
6	PhCHO	3-$ClC_6H_4NH_2$	Me	Me	**5f**	1.2	80	24c
7	PhCHO	4-$ClC_6H_4NH_2$	Me	Me	**5g**	1.0	89	26
8	PhCHO	4-$BrC_6H_4NH_2$	Me	Me	**5h**	1.0	86	35
9	PhCHO	4-$NO_2C_6H_4NH_2$	Me	Me	**5i**	1.5	52	35
10	PhCHO		Me	Me	**5j**	1.5	60	24c
11	PhCHO		Me	Me	**5k**	0.5	80	
12	PhCHO	$PhCH_2NH_2$	Me	Me	**5l**	0.5	82	24c
13	PhCHO		Me	Me	**5m**	0.5	85	35
14	4-$CH_3C_6H_4CHO$	$PhNH_2$	Me	Me	**5n**	1.0	90	35
15	4-ClC_6H_4CHO	$PhNH_2$	Me	Me	**5o**	1.0	88	35
16	4-$NO_2C_6H_4CHO$	$PhNH_2$	Me	Me	**5p**	1.5	78	35
17	4-$CF_3C_6H_4CHO$	$PhNH_2$	Me	Me	**5q**	1.5	75	35
18		H_2C=$CHCH_2NH_2$	Me	Me	**5r**	1.5	70	
19		H_2C=$CHCH_2NH_2$	Me	Me	**5s**	1.5	72	
20		$PhNH_2$	Me	Me	**5t**	1.5	81	29
21	PhCHO	$PhNH_2$	Me	OMe	**5u**	1.5	80	35

22	PhCHO	$PhNH_2$	Me	OEt	**5v**	1.5	85	35
23	PhCHO	$PhNH_2$	Me	OCH_2CH_2OMe	**5w**	1.5	80	35
24	PhCHO	$PhNH_2$	Me	$OCH_2CH{=}CH_2$	**5x**	1.5	76	35
25	PhCHO	$PhNH_2$	Me	$OC(CH_3)_3$	**5y**	2.0	83	
26	PhCHO	$PhNH_2$	Me	$OCH_2CH(CH_3)_2$	**5z**	2.0	80	
27	PhCHO	$PhNH_2$	Et	OMe	**5aa**	2.0	78	29

[a] Isolated yield.

The structures of the products were determined by their FTIR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis. Furthermore, the structure of compound **5c** was unambiguously confirmed by single crystal X-ray analysis (Fig. 2).

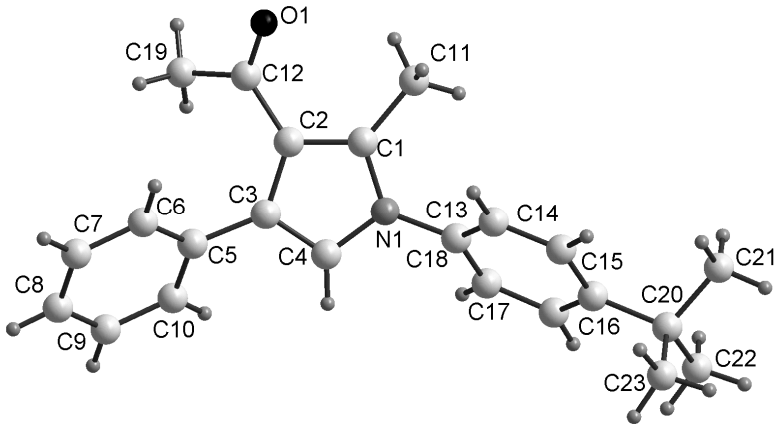
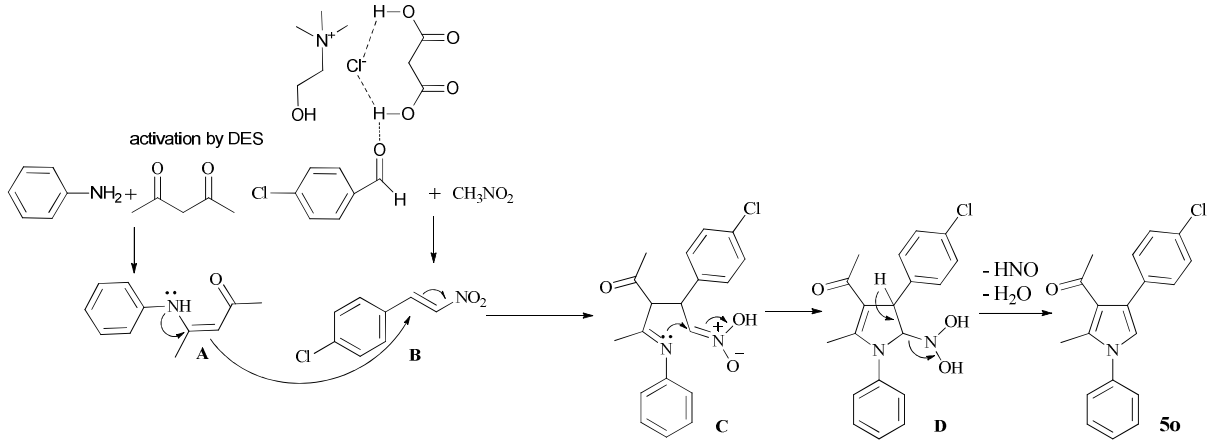


Fig. 2 Single-crystal X-ray structural of compound **5c** (CCDC 1008451)

Based on the literatures,[34] the product formation for this four-component reaction can be mechanistically rationalized via a domino reaction pathway (Scheme 2). We propose that choline chloride-malonic acid DES catalyzes the reaction via hydrogen-bonding activation of carbonyl group of acetylacetone and increases its electrophilicity, thereby facilitating the attack of aniline to generate the enaminone **A**. Similarly, it also forms hydrogen bond with the oxygen of carbonyl group of 4-chlorobenzaldehyde to facilitate the Knoevenagel condensation with nitromethane to produce intermediate **B**. The presence of intermolecular hydrogen bonding plays an important role and provides additional attractive forces between molecules. The DES also might assist in

improving the reactivity of enaminone **A**, which participates in the Michael addition with **B** to give intermediate **C**. This can be verified by the fact that intermediate **A** and **B** could be isolated in the present reaction process. In addition, product **5o** can be obtained by two-component reaction of **A** and **B** in this DES. Subsequently, an intramolecular cyclization of intermediate **C** involving the attack by the imine nitrogen to the nearby –C=N(O)OH moiety affords intermediate **D**. Finally the intermediate **D** undergoes aromatization by the elimination of nitroxyl (HNO) and water molecule to lead the final product **5o**.



Scheme 2 Plausible mechanism for the synthesis of pyrrole **5o**

Deep eutectic solvents as a novel reaction media have been used to the development of a green protocol for the simple and efficient preparation of various heterocyclic compounds owing to its atom economy and ease of recovery and reuse. Thus, the reusability of the DESs was investigated by using aniline, 4-chlorobenzaldehyde, acetylacetone and nitromethane as starting materials under optimized conditions (Table 3). Upon completion of the reaction, water was added to the reaction mixture. The DES was dissolved in water and the crude product was obtained by extraction with EtOAc. The DES was recovered by evaporating water at 80 ^{o}C under vacuum and recycled for the next batch. The result of the reusability of the DES was illustrated in Table 3. The DES can be recycled for up to five times without significant loss in yield, which shows that this DES possessed excellent activity and reusability.

Table 3 Recycling of the solvent

Entry	Reaction runs	Yield (%)[a]
1	1 st	88
2	2 nd	88
3	3 rd	87
4	4 th	85
5	5 th	84

[a] Isolated yield.

Finally, in order to show the merit of the present method, we have compared our result with the most recently reported catalytic systems in the literatures. As can be seen in Table 4, it is clear that the present protocol is superior in terms of reaction time and product yield.

Table 4 Comparison of our result with previously reported systems

Entry	Catalyst	Reaction conditions	Product	Time	Yield (%)
1	$FeCl_3$ (10 mol%)	Reflux	**5a**	14 h	54[25]
2	$NiCl_2{\cdot}6H_2O$ (10 mol%)	Reflux	**5a**	10 h	52[26]
3	Silica supported tungsticacid (10 mol%)	Reflux	**5y**	4 h	79[28]
4	Magnetic nanoparticle $CoFe_2O_4$ supported Mo (1.0 mol%)	90 ºC	**5a**	4 h	90[29]
5	I_2 (10 mol%)	90ºC	**5l**	6 h	85[30]
6	Amberlyst-15 (10 wt%)	Ultrasound	**5u**	4 h	72[31]
7	BDMS (10 mol%)	Room temperature	**5u**	9 h	70[32]
8	Montmorillonite clay K-10 (10 mol%)	60 ºC	**5a**	6 h	70[34]
9	GAAS (5 ml)	100 ºC	**5a**	7 h	87[35]
10	$[bmim]HSO_4$ (20 mol%)	90 ºC	**5a**	3 h	90[36]
11	ChCl/malonic acid (0.1g)	80 ºC	**5a**	1 h	90 (this work)

Conclusions

In conclusion, we have developed a simple, green, and highly efficient procedure for synthesis of diversely substituted pyrroles by one-pot, four-component coupling reaction of amines, aldehydes,

1,3-dicarbonyl compounds and nitromethane. The reaction proceeded in deep eutectic solvent and provided the corresponding products in good to excellent yields. The good catalytic potency and excellent recyclability of choline chloride-malonic acid make this protocol more useful for preparation of multisubstituted pyrroles in large scale over reported methodologies.

Experimental section

General information

All solvents and chemicals were obtained commercially and were used without further purification. Melting points were measured on an X-4 digital melting point apparatus and were corrected with benzoic acid. IR spectra were obtained as KBr pellets or as liquid films on KBr pellets with a Bruker-TENSOR 27 spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker DRX-500 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Elemental analyses were determined on a Vario EL III CHNOS elemental analyzer.

Preparation of deep eutectic solvents

A mixture of choline chloride and the second component was heated until a clear liquid appeared, then allowed to cool at room temperature and used without further purification.

General procedure for synthesis of functionalized pyrroles 5

A mixture of aldehyde (1 mmol), amine (1 mmol), 1,3-dicarbonyl compound (1 mmol), CH_3NO_2 (3 mmol) in ChCl-malonic acid (0.5 g) was stirred at 80 ^{o}C (monitored by TLC). Upon completion of the reaction, the reaction mixture was cooled to room temperature and water (5 mL) was added. The ChCl-malonic acid was dissolved in water and the products were extracted with EtOAc (3 × 5mL). Pure products were obtained by evaporation of the solvent, followed by recrystallization from ethanol or by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

1-(2-Methyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone (5a). White solid, mp 106-107 °C; ^{1}H

NMR ($CDCl_3$, 500 MHz) δ 2.08 (s, 3H), 2.41 (s, 3H), 6.68 (s, 1H), 7.31-7.35 (m, 3H), 7.38-7.39 (m, 4H), 7.43 (t, J = 7.5 Hz, 1H), 7.49-7.51 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.2, 120.6, 122.6, 126.3, 126.3, 126.9, 128.1, 128.3, 129.4, 129.4, 135.3, 136.0, 138.8, 197.7 ppm.

1-(2-Methyl-4-phenyl-1-(p-tolyl)-1*H*-pyrrol-3-yl)ethanone (5b). White solid, mp 109-111 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 6.64 (s, 1H), 7.21 (d, J = 8.5 Hz, 2H), 7.26-7.32 (m, 3H), 7.37-7.38 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 21.1, 31.1, 120.7, 122.4, 126.1, 126.2, 126.8, 128.3, 129.4, 129.9, 135.4, 136.1, 136.2, 138.1, 197.6 ppm.

1-(1-(4-(*tert*-butyl)phenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5c). White solid, mp 148-149 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 9H), 2.08 (s, 3H), 2.41 (s, 3H), 6.66 (s, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.29-7.34 (m, 1H), 7.38-7.39 (m, 4H), 7.49 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.0, 31.1, 31.4, 34.8, 120.7, 122.4, 125.8, 126.2, 126.3, 126.8, 128.3, 129.4, 135.5, 136.1, 136.2, 151.3, 197.7 ppm.

1-(1-(4-Fluorophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5d). White solid, mp 126-127 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 2.38 (s, 3H), 6.63 (s, 1H), 7.16 (t, J = 8.0 Hz, 2H), 7.29-7.31 (m, 3H), 7.36-7.37 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 31.1, 116.4 (d, $^2J_{CF}$ = 22.8 Hz), 120.7, 122.6, 126.4, 126.9, 128.1 (d, $^3J_{CF}$ = 8.4 Hz), 128.3, 129.3, 134.8(d, $^4J_{CF}$ = 2.9 Hz), 135.4, 135.9, 162.1 (d, $^1J_{CF}$ = 247.1 Hz), 197.5 ppm.

1-(1-(2-Chlorophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5e). Pale yellow solid, mp 98-99 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.28 (s, 3H), 6.56 (s, 1H), 7.34-7.29 (m, 1H), 7.44-7.35 (m, 7H), 7.57-7.55 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.3, 31.1, 76.8, 77.0, 77.3, 120.3, 121.9, 126.3, 126.8, 127.6, 128.2, 129.5, 129.6, 130.2, 130.5, 132.6,136.0,136.4,136.5,197.5 ppm; Anal. Calcd for $C_{19}H_{16}ClNO$: C, 73.66; H, 5.21; N, 4.52; Found: C, 73.42; H, 5.01; N, 4.70; ESI-MS: m/z = 310 $(M+1)^+$.

1-(1-(3-Chlorophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5f). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 2.41 (s, 3H), 6.65 (s, 1H), 7.23-7.27 (m, 1H),

7.30-7.44 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.1, 98.5, 120.4, 122.6, 123.0, 124.5, 125.4, 126.5, 126.7, 127.0, 128.4, 129.3, 130.4, 135.0, 135.1, 135.7, 139.9, 197.6 ppm.

1-(1-(4-Chlorophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5g). Yellow solid, mp 127- 128 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 2.40 (s, 3H), 6.64 (s, 1H), 7.28 (d, J = 8.5 Hz, 2H), 7.31-7.40 (m, 5H), 7.47 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 31.1, 120.4, 122.9, 126.6, 126.9, 127.5, 128.3, 129.3, 129.6, 134.1, 135.1, 135.8, 137.3, 197.6 ppm.

1-(1-(4-Bromophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5h). White solid, mp 141-143 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.06 (s, 3H), 2.40 (s, 3H), 6.63 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.31-7.39 (m, 5H), 7.61 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 12.9, 31.1, 120.4, 122.0, 122.9, 126.7, 127.0, 127.8, 128.4, 129.3, 132.6, 135.1, 135.8, 137.8, 197.6 ppm.

1-(2-Methyl-1-(4-nitrophenyl)-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5i). Yellow solid, mp 171- 172 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.07 (s, 3H), 2.46 (s, 3H), 6.72 (s, 1H), 7.33-7.42 (m, 5H), 7.54 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.1, 31.2, 119.9, 124.1, 125.0, 126.5, 127.3, 127.5, 128.5, 129.2, 134.7, 135.3, 144.1, 146.8, 197.7 ppm.

1-(2-Methyl-1-(naphthalen-1-yl)-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5j). White solid, mp 143-144 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.15 (s, 3H), 2.22 (s, 3H), 6.71 (s, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.38-7.49 (m, 6H), 7.51-7.59 (m, 3H), 7.97 (t, J = 9.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.4, 31.2, 121.8, 121.9, 122.9, 125.3, 125.4, 126.1, 126.8, 126.9, 127.6, 128.3, 128.3, 129.4, 129.5, 130.6, 134.1, 135.3, 136.1, 137.1, 197.8 ppm.

1-(1-(Furan-2-ylmethyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5k). White solid, mp 77-78 °C; IR (KBr): 2926, 1637, 1604, 1500, 1168, 943 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.00 (s, 3H), 2.54 (s, 3H), 4.98 (s, 2H), 6.25 (d, J = 8.0 Hz, 1H), 6.34 (dd, J = 2.5, 2.0 Hz, 1H), 6.53 (s, 1H), 7.28-7.30 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.38 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 30.9, 43.1, 108.4, 110.4, 119.3, 121.8, 125.7, 126.5, 128.0, 129.1, 134.6, 136.0, 142.8, 149.2, 197.4 ppm; Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01; Found: C, 77.32; H, 6.02; N, 4.98;

ESI-MS: m/z = 280 $(M+1)^+$.

1-(1-Benzyl-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5l). White solid, mp 87-88 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.04 (s, 3H), 2.44 (s, 3H), 5.06 (s, 2H), 6.54 (s, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.26-7.37 (m, 8H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.6, 31.1, 50.3, 120.2, 122.1, 125.9, 126.7, 127.9, 128.3, 129.0, 129.4, 135.2, 136.4, 136.7, 197.5 ppm.

1-(1-Cyclopropyl-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (5m). White solid，mp 80-81 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94-0.97 (m, 2H), 1.00-1.06 (m, 2H), 2.00 (s, 3H), 2.58 (s, 3H), 3.13-3.17 (m, 1H), 6.50 (s, 1H), 7.26-7.36 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 6.9, 12.2, 28.2, 31.1, 119.6, 122.0, 125.1, 126.7, 128.3, 129.4, 136.5, 137.4, 197.5 ppm.

1-(2-Methyl-1-phenyl-4-(p-tolyl)-1*H*-pyrrol-3-yl)ethanone (5n). White solid, mp 92-93 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.38 (s, 3H), 2.41 (s, 3H), 6.65 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.32 (d, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.0, 21.2, 31.2, 120.5, 122.6, 126.2, 126.3, 128.1, 129.0, 129.2, 129.4, 133.0, 135.2, 136.5, 138.8, 197.8 ppm.

1-(4-(4-Chlorophenyl)-2-methyl-1-phenyl-1*H*-pyrrol-3-yl)ethanone (5o). White solid, mp 105-106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.10 (s, 3H), 2.40 (s, 3H), 6.66 (s, 1H), 7.30-7.37 (m, 6H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.0, 31.2, 120.8, 122.5, 125.0, 126.3, 128.3, 128.5, 129.4, 130.5, 132.8, 134.5, 135.5, 138.6, 197.2 ppm.

1-(2-Methyl-4-(4-nitrophenyl)-1-phenyl-1*H*-pyrrol-3-yl)ethanone (5p). Brown sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (s, 3H), 2.40 (s, 3H), 6.78 (s, 1H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.51-7.54 (m, 4H), 8.25 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.3, 121.7, 122.5, 123.7, 124.1, 126.3, 128.6, 129.5, 129.6, 136.1, 138.3, 143.0, 146.5, 196.7 ppm.

1-(2-Methyl-1-phenyl-4-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)ethanone (5q). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.41 (s, 3H), 6.72 (s, 1H), 7.33 (d, *J* = 7.5

Hz, 2H), 7.45 (t, J = 7.0 Hz, 1H), 7.51 (m, 4H), 7.64 (d, J = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.2, 121.2, 122.5, 124.4 (q, $^1J_{FC}$ = 270.5 Hz), 125.2 (q, $^3J_{FC}$ =3.6 Hz), 126.3, 128.4, 129.0, 129.4 (q, $^2J_{FC}$ =12.5 Hz), 135.7, 138.5, 139.8, 197.0 ppm.

1-(1-Allyl-4-(furan-2-yl)-2-methyl-1*H*-pyrrol-3-yl)ethanone (5r). Yellow sticky liquid; IR (KBr): 2924, 1654, 1560, 1419, 1190, 1010, 937 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.15 (s, 3H), 2.46 (s, 3H), 4.45 (dt, J = 5.0, 1.5 Hz, 2H), 5.02 (d, J = 17.0 Hz, 1H), 5.23 (d, J = 10.0 Hz, 1H), 5.87-5.94 (m, 1H), 6.35 (d, J = 3.0 Hz, 1H), 6.46 (dd, J = 3.0, 2.0 Hz, 1H), 6.67 (s, 1H), 7.44 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.4, 29.8, 41.0, 107.7, 111.0, 114.6, 117.7, 120.9, 132.5, 135.5, 141.6, 149.1, 196.5 ppm; Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; Found: C, 73.30; H, 6.51; N, 5.99; ESI-MS: m/z = 230 $(M+1)^+$.

1-(1-Allyl-2-methyl-4-(thiophen-2-yl)-1*H*-pyrrol-3-yl)ethanone (5s). Yellow sticky liquid; IR (KBr): 2920, 1654, 1560, 1541, 1411, 1265, 991 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12 (s, 3H), 2.45 (s, 3H), 4.44 (dt, J = 5.5, 1.5 Hz, 2H), 5.03 (dd, J = 17.0, 1.0 Hz, 1H), 5.23 (dd, J = 10.5, 1.0 Hz, 1H), 5.87-5.95 (m, 1H), 6.58 (s, 1H), 6.93 (dd, J = 3.5, 1.0 Hz, 1H), 7.03 (dd, J = 5.0, 3.5 Hz, 1H), 7.25 (dd, J = 5.0, 1.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.4, 30.5, 49.0, 117.0, 117.8, 121.0, 122.3, 124.8, 126.9, 127.1, 132.6, 135.3, 137.2, 196.9 ppm; Anal. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71; Found: C, 68.44; H, 6.01; N, 5.68; ESI-MS: m/z = 246 $(M+1)^+$.

1-(2-Methyl-4-(naphthalen-1-yl)-1-phenyl-1*H*-pyrrol-3-yl)ethanone (5t). White solid, mp 114-115 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.70 (s, 3H), 2.53(s, 3H), 6.73 (s, 1H), 7.38-7.52 (m, 9H), 7.84-7.89 (m, 2H), 7.95 (d, J = 8.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.1, 118.8, 119.6, 120.8, 122.5, 124.2, 126.3, 126.7, 127.7, 128.4, 129.4, 130.1, 133.6, 135.6, 136.1, 156.3, 157.5, 197.6 ppm.

Methyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5u). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 3H), 3.70 (s, 3H), 6.71 (s, 1H), 7.26-7.28 (m, 1 H), 7.32-7.36 (m,

4H), 7.41-7.44 (m, 3H), 7.47-7.50 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 50.7, 111.5, 121.0, 126.4, 126.7, 127.8, 128.2, 129.2, 129.4, 135.6 136.8, 139.0,166.3 ppm.

Ethyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5v). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (t, J = 7.0 Hz, 3H), 2.46 (s, 3H), 4.18 (q, J = 7.0 Hz, 2H), 6.71 (s, 1H), 7.25-7.28 (m, 1H), 7.32-7.35 (m, 4H), 7.42-7.43 (m, 3H), 7.47-7.50 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 14.2, 59.5, 111.8, 120.9, 126.4, 126.7, 127.6, 128.1, 129.4, 129.4, 135.7, 136.6, 139.0, 165.9 ppm.

2-Methoxyethyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5w). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 3.25 (s, 3H), 3.47 (t, J = 5.0 Hz, 2H), 4.28 (t, J = 5.0 Hz, 2H), 6.71 (s, 1H), 7.26-7.28 (m, 1 H), 7.32-7.35 (m, 4H), 7.41-7.44 (m, 3H), 7.47-7.50 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 58.7, 62.6, 70.4, 111.5, 121.0, 126.4, 126.9, 127.7, 128.2, 129.4, 135.7, 137.0, 139.0, 165.7 ppm.

Allyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5x). Yellow sticky liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.46 (s, 3H), 4.64 (d, J = 4.5 Hz, 2H), 5.09 (m, 2H), 5.79-5.86 (m, 1H), 6.71 (s, 1H), 7.26-7.28 (m, 1 H), 7.32-7.35 (m, 4H), 7.42-7.43 (m, 3H), 7.48-7.51 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 64.4, 111.5, 117.4, 121.1, 126.4, 126.4, 126.9, 127.8, 128.2, 129.4, 129.4, 132.6, 135.6, 136.9, 139.0, 165.5 ppm.

***tert*-Butyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5y).** Yellow sticky liquid; IR (KBr): 2976, 1691, 1502, 1290, 1138, 1030, 962 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.35 (s, 9H), 2.44 (s, 3H), 6.69 (s, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.31-7.35 (m, 4H), 7.39-7.43 (m, 3H), 7.48 (t, J = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.5, 28.1, 79.7, 120.5, 126.2, 126.3, 126.5, 126.7, 127.6, 128.0, 129.0, 129.3, 136.0, 136.0, 165.5 ppm; Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20; Found: C, 79.23; H, 6.88; N, 4.18; ESI-MS: m/z = 334 $(M+1)^+$.

***iso*-Butyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5z).** Yellow sticky liquid; IR (KBr): 2958, 1697, 1523, 1408, 1224, 1138, 985 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78 (d, J =

7.0 Hz, 6H), 1.76-1.84 (m, 1H), 2.50 (s, 3H), 3.95 (d, J = 6.5 Hz, 2H), 6.72 (s, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.34-7.37 (m, 4H), 7.42-7.46 (m, 3H), 7.50 (t, J = 7.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 19.2, 27.7, 70.0, 111.8, 120.9, 126.3, 126.8, 127.8, 128.1, 129.3, 129.4, 135.8, 136.6, 139.0, 166.0 ppm; Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20; Found: C, 79.23; H, 6.86; N, 4.08; ESI-MS: m/z = 335 $(M+1)^+$.

Methyl 2-ethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (5aa). White solid, mp 100-101 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.10 (t, J = 7.5 Hz, 3H), 2.86 (q, J = 7.5 Hz, 2H), 3.69 (s, 3H), 6.65 (s, 1H), 7.22-7.26(m, 1H), 7.32-7.35(m, 4H), 7.41-7.48 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ14.6, 19.2, 50.5, 110.6, 121.3, 126.3, 126.6, 126.8, 127.6, 128.4, 129.1, 129.3, 135.7, 139.2, 143.0, 166.0 ppm.

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