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Nano $CoFe_2O_4$ supported antimony(III) as an efficient and recyclable catalyst for one-pot three-component synthesis of multisubstituted pyrroles†

Bao-Le Li, Hai-Chuan Hu, Li-Ping Mo and Zhan-Hui Zhang*

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A novel magnetic nano-$CoFe_2O_4$ supported Sb ([$CoFe_2O_4$@SiO_2–DABCO–Sb]) was successfully constructed, which exhibited high catalytic activity for one-pot three-component synthesis of multisubstituted pyrroles in the reaction of amines, nitroolefin and 1,3-dicarbonyl compounds. The magnetic heterogeneous catalyst could be easily recovered using an external magnet and reused many times without significant loss of catalytic activity.

Introduction

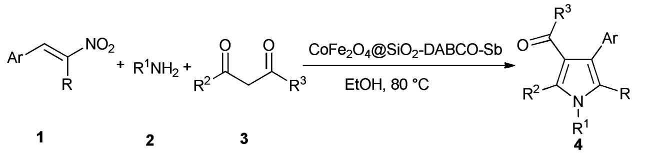
The development of environmentally benign, sustainable and efficiently reusable catalysts is considered as a key point of green chemistry for providing both economic and ecological benefits.[1] From this aspect, nanocatalysts have received a lot of attention because of their unusual properties of a larger surface area to volume ratio which enhanced the contact between reactants and catalyst. They may effectively bridge the gap between homogeneous and heterogeneous catalysis due to their high dispersion properties, good catalytic activity and selectivity. Specifically, magnetic nanocatalysts are the most interesting owing to their easy and efficient isolation and recovery with an external magnetic field, which avoids loss of the catalyst associated with filtration or centrifugation and they have been widely applied in organic reactions.[2–5] Among various magnetic nanoparticles, cobalt ferrite ($CoFe_2O_4$) is a well-known magnetic material with the properties of high magnetocrystalline anisotropy, moderate saturation magnetization, excellent chemical stability, low toxicity, readily accessibility and inexpensiveness which make it a promising material as catalysts support.[6] Recently, antimony(III) chloride has been applied in organic synthesis due to its accessibility and easier to handle than other metal halides.[7] However, antimony trichloride reacts violently with water because of its property of hygroscopic in the air. The immobilization of antimony(III) chloride on magnetic nanoparticles may overcome this defect, simplified process set-ups, and eventually allowed straightforward catalyst recovery and further reuse.

Pyrrole is one of the most important simple heterocycles owing to its antitumor, anti-inflammatory, antibacterial, antioxidant, and antifungal properties.[8] Furthermore, the pyrrole ring has been frequently found in a broad range of natural products and biologically active compounds.[9] In addition, pyrrole derivatives are also particularly important in materials science.[10] These utilities continue to drive the interest in the development of new synthetic methods for pyrroles. The traditional routes to their preparation are multistep reactions, as illustrated by the Paal–Knorr cyclization of 1,4-dicarbonyls with ammonia or primary amines.[11] This methods suffer from several drawbacks, such as stepwise reactions, narrow substrate scope, and lacking the variation of substituents on the pyrrole ring due to the unity of starting materials. For all these reasons, the search for new atom-economical and green synthetic methods, which avoid the use of special reagents, cost, time, and steps from readily available and inexpensive materials for the synthesis of functionalized pyrrole derivatives has attracted much attention.[12,13] Very recently, multicomponent coupling reactions (MCRs) which lead to the connection of three or more starting materials in a single synthetic operation with high atom economy and bond-forming efficiency offer significant advantages over classical stepwise methods. For this reasons, the development of new multicomponent reactions is rapidly becoming one of the important tools in modern organic synthesis.[14] Combining both advantages of multicomponent reaction and the magnetic supported nanocatalysts, the development of a new atom-efficient and environmentally friendly synthetic procedure for the efficient preparation of structurally diverse pyrroles is therefore an interesting challenge.

In conjunction with our studies on the design of magnetic nanocatalysts[15] and sustainable synthesis development,[16] we wish to report here a novel magnetic nanoparticle-supported Sb ([$CoFe_2O_4$@SiO_2–DABCO–Sb]) and its application for the synthesis of N-protected functionalized pyrroles *via* three-component reactions of amines, nitroolefin and 1,3-dicarbonyl compounds (Scheme 1).

College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China. E-mail: zhanhui@mail.nankai.edu.cn; Fax: +86 31180787431

† Electronic supplementary information (ESI) available: ^1H NMR and ^{13}C NMR spectra of all compounds. CCDC 964609. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra47855f



Scheme 1 Synthesis of functionalized pyrroles in the presence of $CoFe_2O_4$@SiO_2–DABCO–Sb.

Results and discussion

Firstly, we prepared $CoFe_2O_4$ nanoparticles as described in our previous work[15d] by a chemical co-precipitation technique using $FeCl_3\cdot6H_2O$ and $CoCl_2\cdot6H_2O$ as precursors. $CoFe_2O_4$ nanoparticles were easily coated with a layer of SiO_2 though chemical bonds by sonication of $CoFe_2O_4$ suspension in a 1 L solution with the molar composition of $292NH_4OH : 1\ CTABr : 2773H_2O$ and tetraethyl orthosilicate (TEOS).[17] The obtained $CoFe_2O_4$@SiO_2 was then treated with an excess amount of 3-chloropropyltrimethoxysilane and triethylamine in dry toluene at 110 °C to give $CoFe_2O_4$@SiO_2 bonded 3-propylchloride.[18] Then, 3-chloropropyl $CoFe_2O_4$@SiO_2 reacted with 1,4-diazabicyclo[2.2.2]octane (DABCO) in refluxing acetone to afford $CoFe_2O_4$@SiO_2–DABCO. Finally, $CoFe_2O_4$@SiO_2–DABCO and antimony trichloride was added in a round-bottomed flask contained acetone under reflux conditions to yield MNPs supported Sb catalyst ([$CoFe_2O_4$@SiO_2–DABCO–Sb])[19] (Scheme 2).

As determined by inductively coupled plasma mass spectrometry (ICP-MS), the content of antimony in the $CoFe_2O_4$@SiO_2–DABCO–Sb catalyst was 6.32 wt%, which provides direct evidences for the fact that antimony was immobilized onto the silica-coated magnetic nanoparticles. The EDS elemental analysis indicated the presence of Fe, Co, Si, Cl, O, C, N and Sb (Fig. 1). Fig. 2 shows Fourier transform infrared (FT-IR) spectrum of $CoFe_2O_4$@SiO_2 and $CoFe_2O_4$@SiO_2–DABCO–Sb. The presence of Co–O and Fe–O bonds in the magnetic particles was confirmed by the characteristic peak appeared at 597 cm^{-1}, which are the evidence to verify the presence of magnetic nanoparticles. The obvious broad peak near 1200 cm^{-1} is anti symmetric Si–O–Si stretching. Two bands are present at 797 and 462 cm^{-1} assignable to symmetric Si–O–Si stretching and bending modes respectively. The band that presents at near 2948 cm^{-1} provides direct evidences to support the existence of stretching of alkyl C–H. New peaks near 1474 cm^{-1} is due to CH_2, and a characteristic broad absorbance at 1000–1200 cm^{-1} shows the existence of C–N stretching, which clearly indicates the presence of DABCO. As shown in Fig. 3, the SEM of the magnetic $CoFe_2O_4$@SiO_2–DABCO–Sb catalyst demonstrates

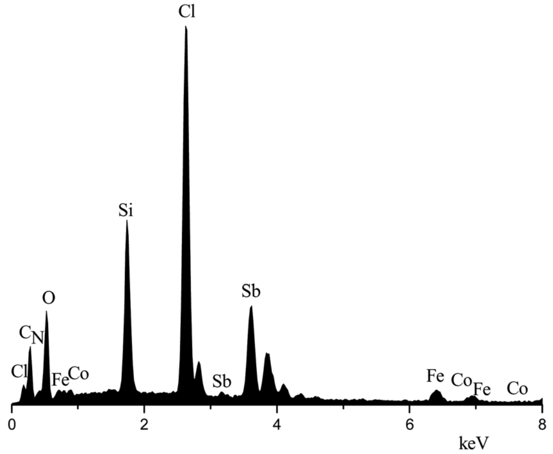


Fig. 1 EDS spectrum of $CoFe_2O_4$@SiO_2–DABCO–Sb.

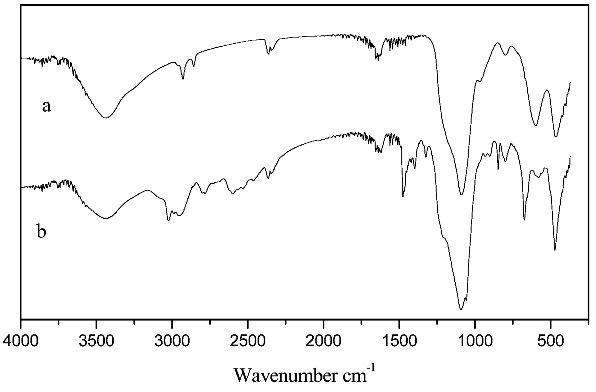
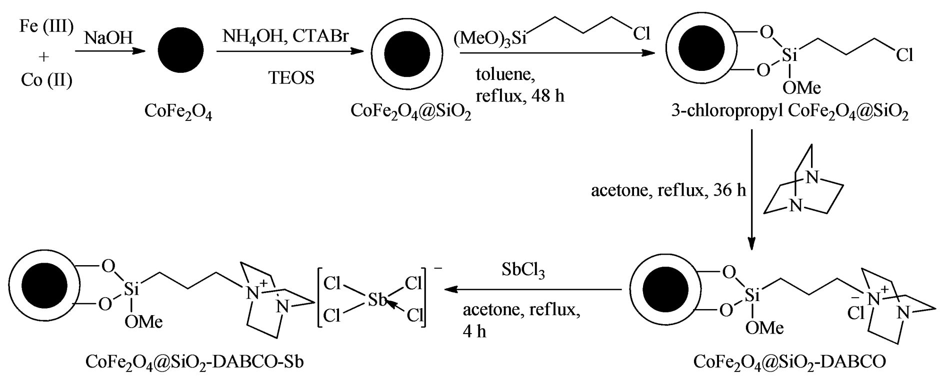


Fig. 2 IR spectra of the (a) $CoFe_2O_4$@SiO_2 and (b) $CoFe_2O_4$@SiO_2–DABCO–Sb.



Scheme 2 Synthesis of $CoFe_2O_4$@SiO_2–DABCO–Sb.

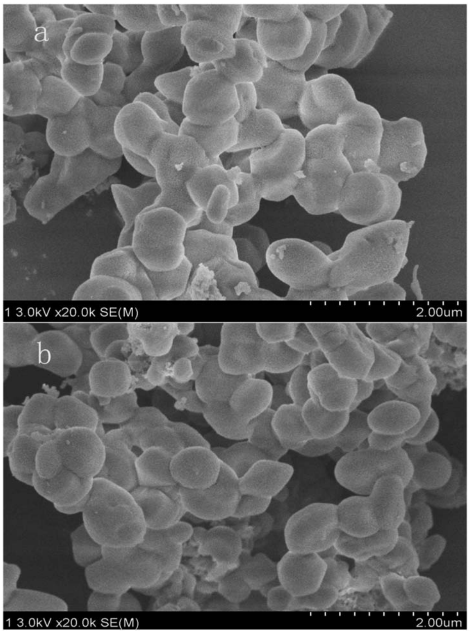


Fig. 3 SEM image of $CoFe_2O_4$@SiO_2–DABCO–Sb (a) "fresh" catalyst and (b) "recovered" catalyst after the fifth run.

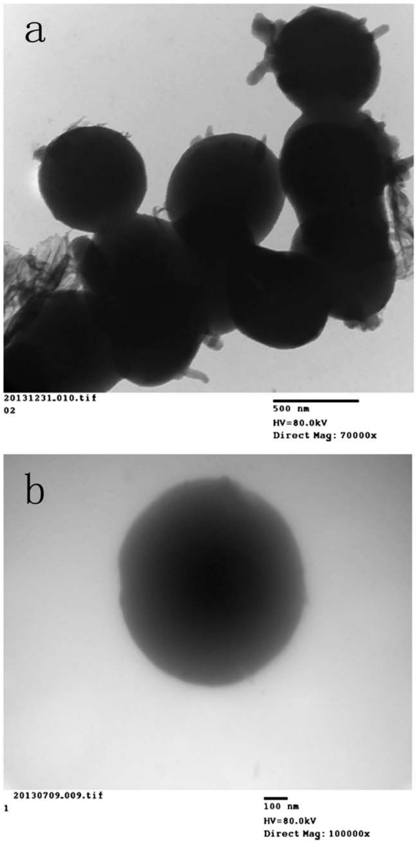


Fig. 4 TEM images of (a) $CoFe_2O_4$@SiO_2–DABCO–Sb (b) a typically core–shell structure of $CoFe_2O_4$@SiO_2 NPs.

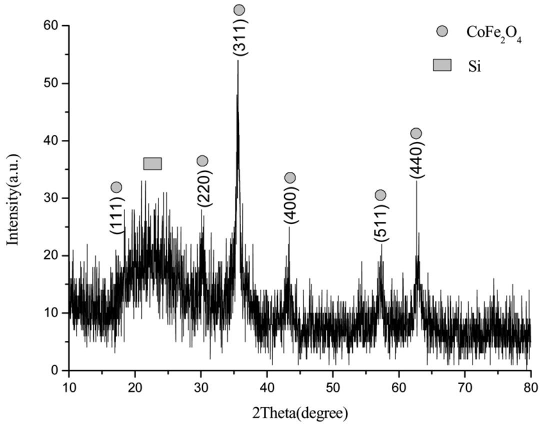


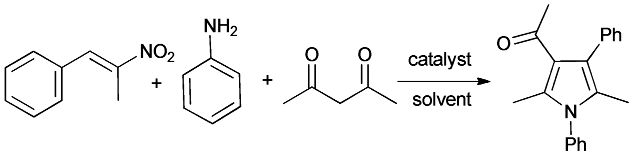
Fig. 5 XRD pattern of $CoFe_2O_4$@SiO_2–DABCO–Sb.

that the particles is spherical or quasi-spherical shape with a mean particle diameter of 1.00 μm, which was also in a good agreement with the results from TEM (Fig. 4). In addition, the TEM image apparently shows the core–shell structure, giving the indirect evidence to verify the formation of silica shell on the surface of cobalt ferrite (Fig. 4b). The powder X-ray diffraction pattern of prepared catalyst $CoFe_2O_4$@SiO_2–DABCO–Sb in Fig. 5 was confirmed that the sample is typical $CoFe_2O_4$ crystals phases. It displays diffraction peaks at around 18.4°, 30.1°, 35.6°, 43.3°, 57.3° and 62.6° corresponding to the (111), (220), (311), (400), (511) and (440), which can be well indexed to the cubic spinel phase of $CoFe_2O_4$ in accordance with literature data (JCPDS 22-1086).

The activity of the immobilized antimony catalyst was initially evaluated for the model reaction of (*E*)-(2-nitroprop-1-en-1-yl)benzene (1 mmol), aniline (1 mmol) and acetylacetone (1 mmol) in ethanol at 80 °C. The reaction, as shown in Table 1, proceeded very slowly in the absence of catalyst and only a trace of desired product was found after heating for more than 12 h (Table 1, entry 1). Gratifyingly, $CoFe_2O_4$@SiO_2–DABCO–Sb exhibited very high activity, leading to the formation of 1-(2,5-dimethyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone (**4b**) in 80% yield in ethanol at 80 °C (Table 1, entry 17). Solvent screening revealed a significant solvent effect. When shifting the solvent to water, THF, methanol, CH_3CN or toluene, **4b** was obtained in 30, 45, 40, 70, or 38% yield, respectively (Table 1, entries 7–11). The EtOH–H_2O (1 : 1) system was also examined for this reaction, showing lower yield of the product (Table 1, entry 12). Among all these solvents, ethanol was found to be the best one and afforded the highest yield. Furthermore, the reaction was investigated under solvent-free condition, the yield of product was not improved (Table 1, entry 13). Finally, reaction temperature and catalyst amount were further examined in ethanol. Decreasing the reaction temperature from 80 °C to 60 °C, the yield suffered an obvious decrease (52%, Table 1, entry 14). Lowering the catalyst loading to 0.5%, the yield decreased to 64%, whereas an increasing in catalyst concentration to 1 mol% did not produce better results.

Besides, the reactivities of different magnetical nano catalysts such as nano γ-Fe_2O_3@SiO_2–TfOH,[15c] γ-Fe_2O_3@HAP–SO_3H,[15a] γ-Fe_2O_3@SiO_2–NHC–Cu(II),[11d] γ-Fe_2O_3@SiO_2–NHC–

Table 1 Reaction of (*E*)-(2-nitroprop-1-en-1-yl)benzene, aniline and acetylacetone in different conditions[a]



Entry	Catalyst	Solvent	Temperature [°C]	Yield [%]
1	No	EtOH	80	Trace
2	γ-Fe_2O_3@SiO_2–TfOH	EtOH	80	46
3	γ-Fe_2O_3@HAP–SO_3H	EtOH	80	48
4	γ-Fe_2O_3@SiO_2–NHC–Cu(II)	EtOH	80	57
5	γ-Fe_2O_3@SiO_2–NHC–Zn(II)	EtOH	80	60
6	$CoFe_2O_4$@SiO_2	EtOH	80	40
7	$CoFe_2O_4$@SiO_2–DABCO–Sb	H_2O	80	30
8	$CoFe_2O_4$@SiO_2–DABCO–Sb	THF	80	45
9	$CoFe_2O_4$@SiO_2–DABCO–Sb	MeCN	Reflux	40
10	$CoFe_2O_4$@SiO_2–DABCO–Sb	MeOH	Reflux	70
11	$CoFe_2O_4$@SiO_2–DABCO–Sb	Toluene	80	38
12	$CoFe_2O_4$@SiO_2–DABCO–Sb	EtOH–H_2O (1 : 1)	80	36
13	$CoFe_2O_4$@SiO_2–DABCO–Sb	Solvent-free	80	78
14	$CoFe_2O_4$@SiO_2–DABCO–Sb	EtOH	60	52
15	$CoFe_2O_4$@SiO_2–DABCO–Sb (0.1 mol%)	EtOH	80	64
16	$CoFe_2O_4$@SiO_2–DABCO–Sb (0.3 mol%)	EtOH	80	75
17	$CoFe_2O_4$@SiO_2–DABCO–Sb (0.5 mol%)	EtOH	80	80
18	$CoFe_2O_4$@SiO_2–DABCO–Sb (1 mol%)	EtOH	80	80
19	$CoFe_2O_4$@SiO_2–DABCO–Sb (0.5 mol%)	EtOH	80	82[b]

[a] Reaction condition: (*E*)-(2-nitroprop-1-en-1-yl)benzene (1 mmol), aniline (1 mmol) and acetylacetone (1 mmol), catalyst (0.5 mol%), solvent (1 ml), 12 h. [b] 50 mmol scale.

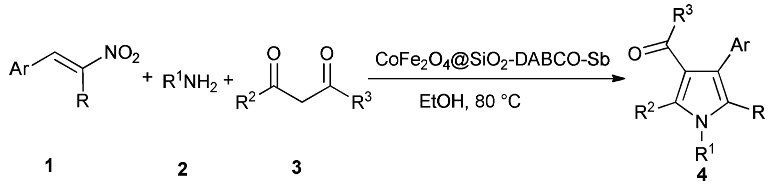
Zn(II),[11d] and $CoFe_2O_4$@SiO_2 were investigated. It was observed that $CoFe_2O_4$@SiO_2–DABCO–Sb served as the best catalyst to provide **4b** in optimum yield. Therefore, the optimal conditions were established as follows: use of 0.5 mol% $CoFe_2O_4$@SiO_2–DABCO–Sb as the catalyst and ethanol as the solvent to perform the reaction at 80 °C. To exploit the potential of the current catalytic system, the model reaction was scaled up to 50 mmol. As expected, the desired product could be obtained in 82% yield (Table 1, entry 19).

Having identified the optimized reaction conditions, the scope and limitations of this three-component reaction were next explored by variation of substituents R and Ar of the nitroolefin component. Satisfactorily as shown in Table 2, when R is hydrogen in nitroolefins, the reaction was completed in 0.25 h to afford **4a** in 93% yield (Table 2, entry 1). The alkyl group of nitroolefins exhibited an influence for this three-component reaction. The reaction with methyl-substituted nitroolefins was slower, but high yield of product was also maintained (Table 2, entry 2). Early experiments using the conditions reported by Silveira showed that $CeCl_3 \cdot 7H_2O$ promoted this reaction to give **4b** in only 45% yield.[20] Nitroolefins with ethyl group smoothly produced the corresponding products **4l–4n**, although longer reaction times were required as the steric hindrance of R increased. Aryl groups with electron-rich or electron-poor substituents in nitroolefins revealed little impact on the reaction times and the yields of the products. Furthermore, the substrates with heteroaryl groups such as 2-furyl and 2-thienyl groups afforded **4i**, **4j** and **4n**, **4o** respectively in high yield. Moreover, examination of nitroolefin with a larger aromatic group, such as naphthyl, was also applied to this reaction to afford the desired product **4k**, albeit in relatively lower yield.

Next, we set out to test the reactivity of various substituted amines. As depicted in Table 2, most of aniline with electron-donating or weakly electron-withdrawing substituents were found to be applicable to this reaction and gave the expected products in high to excellent yields. The nature of the substituent on the benzene ring of aniline had a slight impact on the yields. For example, for substrates with a methyl or methoxy group attached on the benzene ring, the corresponding products were obtained in yields of 82% and 88%, respectively (Table 2, entries 19 and 20). Aniline with strongly electron-withdrawing group such as trifluoromethyl decreased the reactivity and gave lower but still acceptable yield. However, the target product could not be obtained when a strong electron-withdrawing group such as nitro was present. Moreover, amines containing heteroaromatic groups such as furan-2-ylmethanamine also underwent the reaction, affording the desired products **4ab** and **4as** in high yield. Also, 9*H*-fluoren-2-amine was well tolerated to give **4r** and **4ac** in good yield. Additionally, different kinds of aliphatic amines gave the desired products in excellent yield.

To further explore the substrate scope, we then extended the scope of this reaction to several β-ketoesters such as methyl

Table 2 Synthesis of functionalized pyrroles **4**



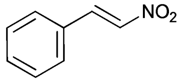
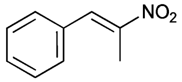
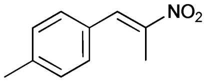
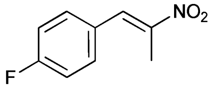
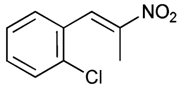
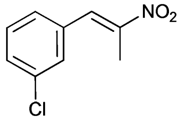
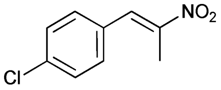
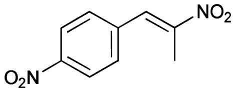
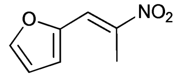
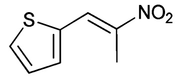
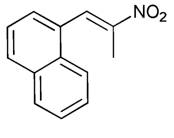
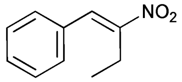
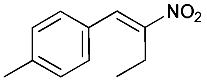
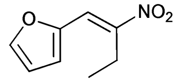
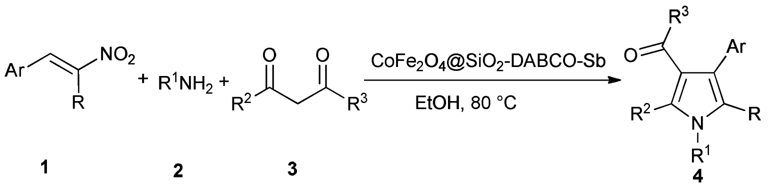
Entry	Nitroolefin	Amine	R^2	R^3	Product	Time (h)	Yield[a] (%)	mp (°C)
1		$PhNH_2$	Me	Me	**4a**	0.25	93	106–107
2		$PhNH_2$	Me	Me	**4b**	12	80	102–103
3		$PhNH_2$	Me	Me	**4c**	12	87	Oil
4		$PhNH_2$	Me	Me	**4d**	14	86	127–128
5		$PhNH_2$	Me	Me	**4e**	16	75	Oil
6		$PhNH_2$	Me	Me	**4f**	16	78	108–110
7		$PhNH_2$	Me	Me	**4g**	14	85	146–147
8		$PhNH_2$	Me	Me	**4h**	16	75	Oil
9		$PhNH_2$	Me	Me	**4i**	15	88	101–102
10		$PhNH_2$	Me	Me	**4j**	15	82	81–82
11		$PhNH_2$	Me	Me	**4k**	12	47	133–134
12		$PhNH_2$	Me	Me	**4l**	20	80	Oil
13		$PhNH_2$	Me	Me	**4m**	20	80	Oil
14		$PhNH_2$	Me	Me	**4n**	20	76	Oil

Table 2 (*Contd.*)



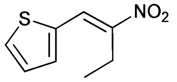
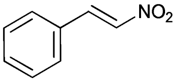
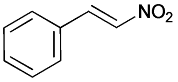
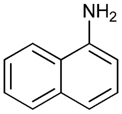
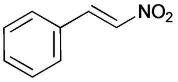
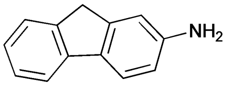
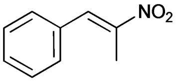
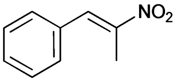
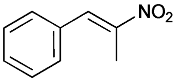
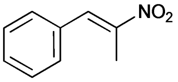
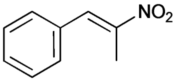
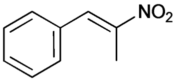
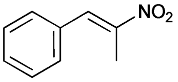
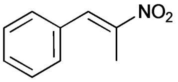
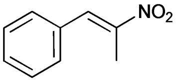
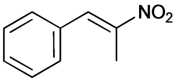
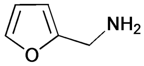
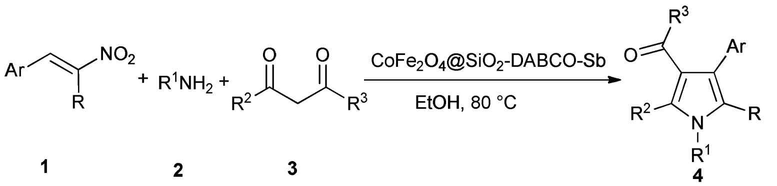
Entry	Nitroolefin	Amine	R^2	R^3	Product	Time (h)	Yield[a] (%)	mp (°C)
15		$PhNH_2$	Me	Me	**4o**	20	78	Oil
16		4-$CMe_3C_6H_4NH_2$	Me	Me	**4p**	0.5	92	146–148
17			Me	Me	**4q**	1	75	142–143
18			Me	Me	**4r**	1	80	148–149
19		4-$CH_3C_6H_4NH_2$	Me	Me	**4s**	12	82	112–113
20		4-$OCH_3C_6H_4NH_2$	Me	Me	**4t**	12	88	130–132
21		4-$FC_6H_4NH_2$	Me	Me	**4u**	14	82	95–96
22		4-$ClC_6H_4NH_2$	Me	Me	**4v**	15	75	Oil
23		2-$BrC_6H_4NH_2$	Me	Me	**4w**	16	70	Oil
24		3-$BrC_6H_4NH_2$	Me	Me	**4x**	16	72	Oil
25		4-$BrC_6H_4NH_2$	Me	Me	**4y**	15	77	106–107
26		4-$CF_3C_6H_4NH_2$	Me	Me	**4z**	16	51	Oil
27		4-$OCF_3C_6H_4NH_2$	Me	Me	**4aa**	14	85	125–126
28			Me	Me	**4ab**	6	90	120–121

Table 2 (*Contd.*)



1 2 3 4

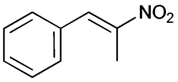
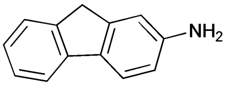
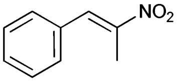
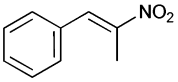
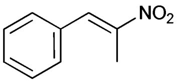
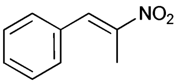
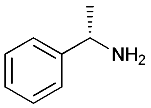
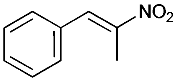
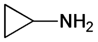
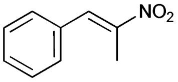
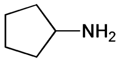
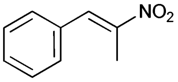
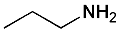
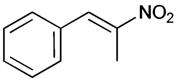
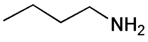
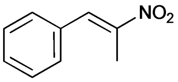
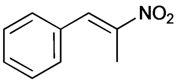
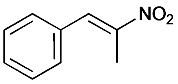
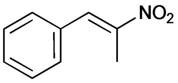
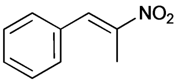
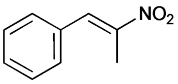
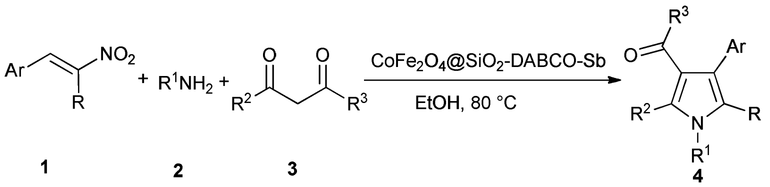
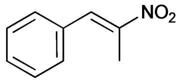
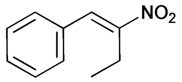
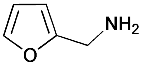
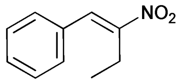
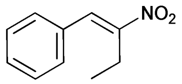
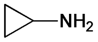
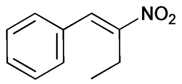
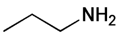
Entry	Nitroolefin	Amine	R^2	R^3	Product	Time (h)	Yield[a] (%)	mp (°C)
29			Me	Me	**4ac**	14	73	153–155
30		$H_2C{=}CHCH_2NH_2$	Me	Me	**4ad**	6	91	Oil
31		$PhCH_2NH_2$	Me	Me	**4ae**	6	90	Oil
32		$PhCH_2CH_2NH_2$	Me	Me	**4af**	6	92	124–125
33			Me	Me	**4ag**	6	87	92–93
34			Me	Me	**4ah**	6	89	Oil
35			Me	Me	**4ai**	12	72	61–62
36			Me	Me	**4aj**	6	88	Oil
37			Me	Me	**4ak**	6	86	Oil
38		$PhNH_2$	Me	OMe	**4al**	8	82	108–109
39		$PhNH_2$	Me	OEt	**4am**	8	85	83–84
40		$PhNH_2$	Me	OCH_2CH_2OMe	**4an**	8	80	72–73
41		$PhNH_2$	Me	$OCH_2CH{=}CH_2$	**4ao**	10	78	Oil
42		$PhNH_2$	Et	OMe	**4ap**	10	76	100–101
43		$PhNH_2$	Me	$OCMe_3$	**4aq**	8	83	96–97

Table 2 (*Contd.*)



Entry	Nitroolefin	Amine	R^2	R^3	Product	Time (h)	Yield^a (%)	mp (°C)
44		PhNH$_2$	Me	OCH$_2$CH(CH$_3$)$_2$	**4ar**	8	81	70–71
45			Me	Me	**4as**	12	89	103–104
46		PhCH$_2$NH$_2$	Me	Me	**4at**	12	86	Oil
47			Me	Me	**4au**	12	82	Oil
48			Me	Me	**4av**	12	83	Oil

^{a} Isolated yield.

acetoacetate, ethyl acetoacetate, 2-methoxyethyl acetoacetate, allyl acetoacetate, *tert*-butyl-3-oxobutanoate, isobutyl-3-oxobutanoate and methyl-3-oxopentanoate. In general, β-ketoesters were also found to be suitable reaction partners in this reaction and gave the desired products in high yields (Table 2, entries 38–44). Thus, these successful results greatly proved that this procedure was extendable to various substrates in three-component reactions, generating moderate to high yields of the functionalized pyrroles.

The structures of the prepared products were identified from their IR, ^{1}H NMR, ^{13}C NMR spectra and elemental analysis. The structure of the corresponding product **4o** has also been elucidated by single-crystal X-ray crystallographic analysis (Fig. 6).

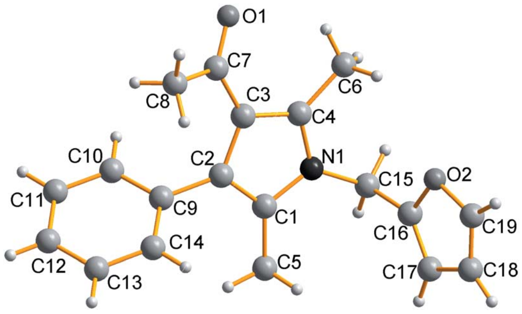


Fig. 6 Single-crystal X-ray structural of compound **4o** (CCDC 964609).

The magnetic CoFe$_2$O$_4$@SiO$_2$–DABCO–Sb catalyst exhibited high reactivity in the reaction of synthesis of multisubstituted pyrroles owing to its high dispersion in EtOH and easy accessibility to the active sites. Upon completion of the reaction, the catalyst can be easily removed using an external magnetic from the reaction mixture, avoiding a filtration step. The recover catalyst was washed with ethyl acetate, air-dried and then reused directly in model reaction for the next round without further purification. The results showed that the catalyst can be recycled for up to five times with essentially no loss of catalytic activity, which indicates that the prepared catalyst possessed excellent activity and reusability (Table 3). Furthermore, the SEM image of recovered catalysts after fifth cycle does not show any significant change in the shape and size of the magnetic nanoparticles, which provides hard evidence to demonstrate that MNPs-supported Sb catalyst was high chemical stable (Fig. 3).

Table 3 Recycling of the catalyst

Entry	Recycle	Yield^a (%)
1	1st	80
2	2nd	80
3	3rd	78
4	4th	78
5	5th	76

^{a} Isolated yield.

Conclusions

In summary, a new type of magnetically separable and easily recyclable heterogeneous Sb catalyst have been successfully prepared by immobilizing Sb onto DABCO-modified MNPs, which has demonstrated a promising catalytic activity for the one-pot three-component coupling reaction of amines, nitroolefin and 1,3-dicarbonyl compounds. This environmentally friendly, atom-economical and efficient methodology allows preparation of various multisubstituted pyrroles with good to excellent yields starting from readily available materials under mild conditions. This magnetic nanoparticle $CoFe_2O_4$ supported Sb catalyst can easily be separated and recovered from the reaction mixture by decantation using an external magnet. And no significant loss of activity occurred after five consecutive cycles, indicating great potential in large-scale industrial processes.

Experimental section

All solvents and chemicals were obtained commercially and were used as received. IR spectra were recorded using KBr pellets or as liquid films on KBr pellets with a Bruker-TENSOR 27 spectrometer. X-ray diffraction analysis was carried out using a PANalytical X'Pert Pro X-ray diffractometer. Surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument. Transmission electron microscope (TEM) observation was performed using Hitachi H-7650 microscope at 80 kV. Elemental compositions were determined with a Hitachi S-4800 scanning electron microscope equipped with an INCA 350 energy dispersive spectrometer (SEM-EDS) presenting a 133 eV resolution at 5.9 keV. The ICP-MS analyses were carried out with an X Series 2 spectrometer. Melting points were measured on an X-4 digital melting point apparatus are uncorrected. NMR spectra were recorded with a Bruker DRX-500 spectrometer at 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR using $CDCl_3$ as the solvent and TMS as an internal standard. Elemental analyses were performed on a Vario EL III CHNOS elemental analyzer.

Preparation of $CoFe_2O_4$@SiO_2–DABCO–Sb magnetic nanoparticles

$CoFe_2O_4$ NPs were prepared by a chemical co-precipitation technique using $FeCl_3\cdot 6H_2O$ and $CoCl_2\cdot 6H_2O$ as precursors according to our previously reported procedure.[15d] Coating of a layer of silica on the surface of the $CoFe_2O_4$ NPs was prepared according to the procedure of Chen *et al.*[17] The $CoFe_2O_4$ NPs (0.5 g) were dispersed in a 1 L solution with the molar composition of $292NH_4OH : 1\ CTABr : 2773H_2O$ under vigorous mixing. Tetraethyl orthosilicate was then added successively. After stirring for 24 h at room temperature, the black $CoFe_2O_4$ NPs were collected with a permanent magnet, followed by washing three times with ethanol, diethyl ether and drying at 100 °C in a vacuum for 24 h. The obtained $CoFe_2O_4$@SiO_2 (0.5 g) was added to the solution of 3-chloropropyltrimethoxysilane (5 mmol) and triethylamine (0.25 ml) in dry toluene (20 ml) and refluxed for 48 h. After the reaction finished, the 3-chloropropyl $CoFe_2O_4$@SiO_2 NPs were separated by a permanent magnet, washed with double-distilled water and anhydrous ethanol, and dried at 100 °C for 5 h to give the 3-chloropropyl $CoFe_2O_4$@SiO_2.

For the preparation of $CoFe_2O_4$@SiO_2–DABCO: 3-chloropropyl $CoFe_2O_4$@SiO_2 (0.5 g) and DABCO (0.56 g, 5 mmol) were added in a 50 ml round-bottomed flask contained dry acetone (30 ml) and refluxed for 36 h. The solid was collected using a permanent magnet, followed by washing with acetone, ethanol, and methanol in turn. Finally, the obtained $CoFe_2O_4$@SiO_2–DABCO was dried under vacuum at 60 °C for 24 h.

The obtained $CoFe_2O_4$@SiO_2–DABCO (0.25 g) were added to the solution of antimony(III) chloride (0.225 g) in dry acetone (10 ml) in a 25 ml round-bottomed flask equipped with a reflux condenser, and refluxed for 12 h. The resulting solid was collected using a permanent magnet, followed by washing three times with acetone and dried under vacuum at 50 °C for 12 h to give $CoFe_2O_4$@SiO_2–DABCO–Sb as a black powder.

General procedure for synthesis of functionalized pyrroles 4

To a mixture of amines (1 mmol), nitroolefin (1 mmol) and 1,3-dicarbonyl compound (1 mmol) in EtOH (1 ml), $CoFe_2O_4$@SiO_2–DABCO–Sb (0.5 mol%) was added. The reaction mixture was stirred at 80 °C (monitored by TLC). After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was separated magnetically, washed with ethyl acetate, and used for subsequent cycles after drying under vacuum. The crude products were obtained by evaporation of the solvent and purified 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 (4a). White solid, 106–107 °C; IR (KBr): 3037, 2928, 1657, 1498, 1412, 1228, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.08 (s, 3H), 2.41 (s, 3H), 6.67 (s, 1H), 7.30–7.34 (m, 3H), 7.38–7.39 (m, 4H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.1, 120.6, 122.6, 126.2, 126.3, 126.8, 128.1, 128.3, 129.3, 129.3, 135.3, 136.0, 138.7, 197.6 ppm. Anal. calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.72; H, 6.04; N, 4.95; ESI-MS: $m/z = 276\ (M + 1)^+$.

1-(2,5-Dimethyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone (4b). White solid, mp 102–103 °C; IR (KBr): 2920, 1641, 1496, 1383, 1165, 952, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 1.93 (s, 3H), 2.28 (s, 3H), 7.25–7.32 (m, 5H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 13.0, 31.0, 121.8, 122.1, 126.6, 126.7, 128.1, 128.2, 128.6, 129.4, 130.5, 134.9, 136.9, 137.6, 197.3 ppm; anal. calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84; found: C, 82.92; H, 6.47; N, 4.71; ESI-MS: $m/z = 290\ (M + 1)^+$.

1-(2,5-Dimethyl-1-phenyl-4-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanone (4c). Yellow sticky liquid; IR (KBr): 2920, 1653, 1518, 1458, 1383, 1165, 950, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.84 (s, 3H), 1.95 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 7.18–7.21 (m, 4H), 7.25 (d, $J = 7.5$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 13.0, 21.2, 31.0, 121.8, 122.0, 126.6, 128.2, 128.6, 128.9, 130.3, 133.8, 134.8, 136.1, 137.6, 197.5 ppm; anal. calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62; found: C, 83.02; H, 6.79; N, 4.58; ESI-MS: $m/z = 304\ (M + 1)^+$.

1-(4-(4-Fluorophenyl)-2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4d). Yellow solid, mp 127–128 °C; IR (KBr): 2922, 1649, 1514, 1415, 1383, 1215, 954, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.82 (s, 3H), 1.94 (s, 3H), 2.28 (s, 3H), 7.09 (t, J = 8.5 Hz, 2H), 7.24–7.28 (m, 4H), 7.47 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.0, 13.0, 31.0, 115.1 (d, $^2J_{CF}$ = 21.2 Hz), 120.9, 121.7, 126.8, 128.1, 128.7, 129.5, 131.9 (d, $^3J_{CF}$ = 7.5 Hz), 132.8 (d, $^4J_{CF}$ = 3.2 Hz), 135.0, 137.5, 161.8 (d, $^1J_{CF}$ = 244.1 Hz), 196.9 ppm; anal. calcd for $C_{20}H_{18}FNO$: C, 78.15; H, 5.90; N, 4.56; found: C, 78.01; H, 5.76; N, 4.45; ESI-MS: *m*/*z* = 308 (M + 1)$^+$.

1-(4-(2-Chlorophenyl)-2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4e). Yellow sticky liquid; IR (KBr): 2920, 1647, 1516, 1406, 1384, 1168, 950, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.76 (s, 3H), 1.91 (s, 3H), 2.32 (s, 3H), 7.24–7.34 (m, 5H), 7.45–7.49 (m, 2H), 7.51 (t, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.1, 13.3, 30.1, 119.0, 121.3, 126.6, 127.2, 128.1, 128.3, 128.6, 128.7, 129.5, 132.8, 135.0, 135.3, 136.0, 137.4, 196.2 ppm; anal. calcd for $C_{20}H_{18}ClNO$: C, 74.18; H, 5.60; N, 4.33; found: C, 74.09; H, 5.47; N, 4.19; ESI-MS: *m*/*z* = 324 (M + 1)$^+$.

1-(4-(3-Chlorophenyl)-2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4f). Yellow solid, mp 108–110 °C; IR (KBr): 2920, 1647, 1595, 1516, 1383, 1168, 952, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.84 (s, 3H), 1.97 (s, 3H), 2.27 (s, 3H), 7.19 (d, J = 7.5 Hz, 1H), 7.23–7.34 (m, 5H), 7.47 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.1, 13.0, 31.0, 120.7, 121.7, 126.7, 127.0, 128.1, 128.7, 128.8, 129.4, 129.5, 130.4, 134.0, 135.2, 137.3, 138.9, 196.7 ppm; anal. calcd for $C_{20}H_{18}ClNO$: C, 74.18; H, 5.60; N, 4.33; found: C, 74.08; H, 5.44; N, 4.25; ESI-MS: *m*/*z* = 324 (M + 1)$^+$.

1-(4-(4-Chlorophenyl)-2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4g). Yellow solid, mp 146–147 °C; IR (KBr): 2914, 1647, 1489, 1383, 1166, 1087, 952, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.85 (s, 3H), 1.98 (s, 3H), 2.30 (s, 3H), 7.26–7.28 (m, 4H), 7.40 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.1, 13.0, 31.1, 120.8, 121.7, 126.9, 128.1, 128.4, 128.7, 129.5, 131.7, 132.5, 135.1, 135.4, 137.4, 196.8 ppm; anal. calcd for $C_{20}H_{18}ClNO$: C, 74.18; H, 5.60; N, 4.33; found: C, 74.06; H, 5.48; N, 4.25; ESI-MS: *m*/*z* = 324 (M + 1)$^+$.

1-(2,5-Dimethyl-4-(4-nitrophenyl)-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4h). Yellow sticky liquid; IR (KBr): 2922, 1647, 1527, 1348, 1174, 954, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.86 (s, 3H), 2.01 (s, 3H), 2.29 (s, 3H), 7.25 (d, J = 7.0 Hz, 2H), 7.49–7.58 (m, 4H), 7.64 (d, J = 7.5 Hz, 1H), 8.18 (d, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.1, 13.2, 31.1, 119.8, 121.5, 121.6, 125.0, 127.6, 128.1, 129.0, 129.6, 135.6, 136.7, 137.2, 138.8, 195.9 ppm; anal. calcd for $C_{20}H_{18}N_2O_3$: C, 71.84; H, 5.43; N, 8.38; found: C, 71.76; H, 5.32; N, 8.25; ESI-MS: *m*/*z* = 335 (M + 1)$^+$.

1-(4-(Furan-2-yl)-2,5-dimethyl-1-phenyl-1*H*-pyrrol-3-yl)ethanone (4i). White solid, mp 101–102 °C; IR (KBr): 2922, 1643, 1516, 1383, 1172, 1076, 954, 705 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.93 (s, 3H), 2.05 (s, 3H), 2.27 (s, 3H), 6.32 (d, J = 3.0 Hz, 1H), 6.48 (s, 1H), 7.21 (d, J = 7.0 Hz, 2H), 7.45–7.52 (m, 4H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.3, 12.9, 29.4, 109.1, 111.0, 111.4, 121.1, 128.0, 128.8, 129.4, 129.5, 135.7, 137.2, 141.9, 148.9, 196.5 ppm; anal. calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01; found: C, 77.28; H, 6.07; N, 4.85; ESI-MS: *m*/*z* = 280 (M + 1)$^+$.

1-(2,5-Dimethyl-1-phenyl-4-(thiophen-2-yl)-1*H*-pyrrol-3-yl)-ethanone (4j). Yellow solid, mp 81–82 °C; IR (KBr): 2918, 1647, 1498, 1383, 1261, 1076, 945, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.88 (s, 3H), 2.05 (s, 3H), 2.27 (s, 3H), 6.94 (dd, J = 1.0, 3.5 Hz, 1H), 7.07 (dd, J = 3.5, 5.0 Hz, 1H), 7.23 (d, J = 7.0 Hz, 2H), 7.33 (dd, J = 1, 5.0 Hz, 1H), 7.45–7.52 (m, 3H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.2, 13.1, 30.3, 113.5, 122.3, 125.8, 127.1, 127.9, 128.1, 128.8, 128.9, 129.5, 135.3, 137.3, 137.6, 196.8 ppm; anal. calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74; found: C, 73.02; H, 5.65; N, 4.59; ESI-MS: *m*/*z* = 296 (M + 1)$^+$.

1-(2,5-Dimethyl-4-(naphthalen-1-yl)-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4k). Yellow solid, mp 133–134 °C; IR (KBr): 2918, 1647, 1498, 1383, 1276, 949, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.63 (s, 3H), 1.71 (s, 3H), 2.39 (s, 3H), 7.32 (d, J = 7.5 Hz, 2H), 7.43–7.55 (m, 7H), 7.82 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 11.2, 13.4, 30.1, 119.5, 122.3, 125.5, 125.8, 126.2, 126.3, 127.5, 128.2, 128.3, 128.6, 128.7, 129.1, 129.5, 133.6, 133.7, 134.8, 135.6, 137.6, 196.9 ppm; anal. calcd for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13; found: C, 84.81; H, 6.19; N, 4.02; ESI-MS: *m*/*z* = 340 (M + 1)$^+$.

1-(5-Ethyl-2-methyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone (4l). Yellow sticky liquid; IR (KBr): 2929, 1653, 1496, 1253, 1166, 1028, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.71 (t, J = 7.5 Hz, 3H), 1.89 (s, 3H), 2.26 (s, 3H), 2.27 (q, J = 7.5 Hz, 2H), 7.28–7.33 (m, 5H), 7.39 (t, J = 8.0 Hz, 2H), 7.46–7.53 (m, 3H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.9, 14.9, 17.9, 31.0, 121.7, 121.9, 126.7, 128.2, 128.5, 128.7, 129.3, 130.6, 132.9, 135.1, 137.0, 137.6, 197.2 ppm; anal. calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62; found: C, 82.99; H, 6.79; N, 4.55; ESI-MS: *m*/*z* = 304 (M + 1)$^+$.

1-(5-Ethyl-2-methyl-1-phenyl-4-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanone (4m). Yellow sticky liquid; IR (KBr): 2929, 1653, 1498, 1363, 1165, 950, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.71 (t, J = 7.5 Hz, 3H), 1.91 (s, 3H), 2.26 (s, 3H), 2.27 (q, J = 7.5 Hz, 2H), 2.39 (s, 3H), 7.18–7.22 (m, 4H), 7.27–7.29 (m, 2H), 7.45–7.52 (m, 3H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.9, 14.9, 18.0, 21.2, 31.0, 121.7, 121.8, 128.5, 128.6, 128.9, 129.3, 130.4, 132.9, 133.9, 135.0, 136.2, 137.6, 197.3 ppm; anal. calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41; found: C, 82.90; H, 7.28; N, 4.27; ESI-MS: *m*/*z* = 318 (M + 1)$^+$.

1-(5-Ethyl-4-(furan-2-yl)-2-methyl-1-phenyl-1*H*-pyrrol-3-yl)-ethanone (4n). Yellow sticky liquid; IR (KBr): 2931, 1647, 1508, 1432, 1151, 1010, 704 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.82 (t, J = 7.5 Hz, 3H), 2.03 (s, 3H), 2.24 (s, 3H), 3.35 (q, J = 7.5 Hz, 2H), 6.33 (d, J = 3.0 Hz, 1H), 6.47–6.48 (m, 1H), 7.23–7.25 (m, 2H), 7.46–7.53 (m, 4H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.8, 15.0, 18.3, 29.4, 109.2, 110.8, 110.9, 121.1, 128.3, 128.9, 129.4, 135.8, 137.1, 141.9, 148.8, 196.5 ppm; anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77; found: C, 77.62; H, 6.42; N, 4.59; ESI-MS: *m*/*z* = 194 (M + 1)$^+$.

1-(5-Ethyl-2-methyl-1-phenyl-4-(thiophen-2-yl)-1*H*-pyrrol-3-yl)-ethanone (4o). Yellow sticky liquid; IR (KBr): 2931, 1647, 1558, 1508, 1288, 1074, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.78 (t, J = 7.5 Hz, 3H), 2.03 (s, 3H), 2.25 (s, 3H), 2.32 (q, J = 7.5 Hz, 2H), 6.96 (dd, J = 1.5, 3.5 Hz, 1H), 7.08 (dd, J = 3.5, 5.5 Hz, 1H), 7.26–7.27 (m, 2H), 7.34 (dd, J = 1.5, 5.5 Hz, 1H), 7.46–7.53 (m, 3H) ppm; ^{13}C NMR (CDCl$_3$, 125 MHz) δ 12.9, 15.1, 18.2, 30.2, 112.9, 122.2, 125.8, 127.0, 128.1, 128.4, 128.8, 129.4, 135.1, 135.5, 137.3, 137.5, 196.9 ppm; anal. calcd for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53; found: C, 73.59; H, 6.00; N, 4.51; ESI-MS: $m/z = 310\ (M + 1)^+$.

1-(1-(5-(*tert*-Butyl)phenyl)-2-methyl-5-phenyl-1*H*-pyrrol-3-yl)ethanone (4p). White solid, 146–148 °C; IR (KBr): 2929, 1650, 1512, 1408, 1220, 843, 756, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 9H), 2.07 (s, 3H), 2.41 (s, 3H), 6.65 (s, 1H), 7.25 (d, $J =$ 8.5 Hz, 2H), 7.30–7.32 (m, 1H), 7.37–7.38 (m, 4H), 7.58 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.9, 31.1, 31.3, 34.7, 120.7, 122.4, 125.7, 126.1, 126.2, 126.7, 128.2, 129.3, 135.4, 136.1, 136.1, 151.2, 197.6 ppm; anal. calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23; found: C, 83.28; H, 7.56; N, 4.15; ESI-MS: $m/z = 332\ (M + 1)^+$.

1-(2-Methyl-1-(naphthalen-1-yl)-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4q). White solid, 142–143 °C; IR: 3130, 2929, 1657, 1506, 1438, 1257, 1234, 1128, 806, 777; ^1H 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),7.38–7.48 (m, 6H), 7.50–7.53 (m, 1H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.96 (t, $J = 9.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.4, 31.2, 121.7, 121.8, 122.9, 125.2, 125.3, 126.1, 126.8, 126.9, 127.6, 128.2, 128.3, 129.3, 129.4, 130.6, 134.1, 135.3, 136.1, 137.0, 197.7 ppm; anal. calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30; found: C, 84.79; H, 5.81; N, 4.15; ESI-MS: $m/z = 326\ (M + 1)^+$.

1-(1-(9*H*-Fluoren-2-yl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4r). White solid, 148–149 °C; IR (KBr): 3035, 2920, 1657, 1512, 1404, 772, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.09 (s, 3H), 2.45 (s, 3H), 3.98 (s, 2H), 6.72 (s, 1H), 7.31–7.43 (m, 8H), 7.50 (s, 1H), 7.58 (d, $J = 7.5$ Hz, 1H), 7.82 (d, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 13.1, 31.2, 36.9, 120.2, 120.3, 120.8, 122.5, 123.0, 125.0, 125.2, 126.3, 126.8, 127.1, 127.3, 128.3, 129.4, 135.5, 136.1, 137.2, 140.5, 141.7, 143.4, 145.3, 197.6 ppm; anal. calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85; found: C, 85.86; H, 5.69; N, 3.78; ESI-MS: $m/z = 364\ (M + 1)^+$.

1-(2,5-Dimethyl-4-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanone (4s). Yellow solid, mp 112–113 °C; IR (KBr): 2920, 1647, 1508, 1383, 1166, 950, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.84 (s, 3H), 1.93 (s, 3H), 2.28 (s, 3H), 2.43 (s, 3H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.29–7.31 (m, 5H), 7.39 (t, $J = 7.5$ Hz, 2H), ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 12.8, 20.9, 30.7, 121.4, 121.7, 126.3, 126.5, 127.6, 127.9, 129.8, 130.2, 134.6, 134.8, 136.7, 138.3, 197.0 ppm; anal. calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62; found: C, 83.1; H, 6.79; N, 4.52; ESI-MS: $m/z = 304\ (M + 1)^+$.

1-(1-(4-Methoxyphenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4t). Yellow solid, mp 130–132 °C; IR (KBr): 2902, 1654, 1514, 1383, 1247, 958, 707 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.84 (s, 3H), 1.93 (s, 3H), 2.28 (s, 3H), 3.87 (s, 3H), 7.01 (d, $J = 9.0$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 7.29–7.31 (m, 3H), 7.39 (t, $J = 7.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 13.0, 30.9, 55.5, 114.6, 121.6, 121.9, 126.5, 127.0, 128.2, 129.1, 130.1, 130.5, 135.2, 136.9, 159.5, 197.2 ppm; anal. calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; found: C, 78.88; H, 6.45; N, 4.32; ESI-MS: $m/z = 320\ (M + 1)^+$.

1-(1-(4-Fluorophenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4u). Yellow solid, mp 95–96 °C; IR (KBr): 2918, 1647, 1508, 1383, 1222, 952, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.84 (s, 3H), 1.92 (s, 3H), 2.27 (s, 3H), 7.19–7.24 (m, 4H), 7.28–7.33 (m, 3H), 7.39 (t, $J = 7.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 12.9, 30.9, 116.3 (d, $^2J_{CF} = 22.7$ Hz), 121.9, 122.2, 126.7, 128.2, 129.9 (d, $^3J_{CF} = 8.7$ Hz), 130.4, 133.5 (d, $^4J_{CF} = 3.3$ Hz), 134.9, 136.7, 162.3 (d, $^1J_{CF} = 247.5$ Hz), 197.4 ppm; anal. calcd for $C_{20}H_{18}FNO$: C, 78.15; H, 5.90; N, 4.56; found: C, 78.06; H, 5.81; N, 4.49; ESI-MS: $m/z = 308\ (M + 1)^+$.

1-(1-(4-Chlorophenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4v). Yellow sticky liquid; IR (KBr): 2920, 1647, 1496, 1384, 1166, 952, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 1.92 (s, 3H), 2.28 (s, 3H), 7.21 (d, $J = 8.5$ Hz, 2H), 7.28–7.32 (m, 3H), 7.39 (t, $J = 7.0$ Hz, 1H), 7.48 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 13.0, 30.9, 122.1, 122.4, 126.5, 126.7, 128.2, 129.5, 129.7, 130.4, 134.6, 134.7, 136.1, 136.6, 197.3 ppm; anal. calcd for $C_{20}H_{18}ClNO$: C, 74.18; H, 5.60; N, 4.33; found: C, 74.05; H, 5.48; N, 4.26; ESI-MS: $m/z = 324\ (M + 1)^+$.

1-(1-(2-Bromophenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4w). Yellow sticky liquid; IR (KBr): 2918, 1508, 1481, 1383, 1273, 1166, 952, 706 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.79 (s, 3H), 1.94 (s, 3H), 2.23 (s, 3H), 7.29–7.41 (m, 7H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.6, 12.6, 31.0, 121.7, 122.2, 123.8, 126.3, 126.6, 128.1, 128.5, 130.3, 130.5, 130.6, 133.6, 134.8, 136.8, 137.2, 197.3 ppm; anal. calcd for $C_{20}H_{18}BrNO$: C, 65.23; H, 4.93; N, 3.80; found: C, 62.20; H, 4.87; N, 3.69; ESI-MS: $m/z = 368\ (M + 1)^+$.

1-(1-(3-Bromophenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone hydrobromide (4x). Yellow sticky liquid; IR (KBr): 2920, 1647, 1508, 1479, 1383, 1273, 1166, 952, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.86 (s, 3H), 1.92 (s, 3H), 2.29 (s, 3H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.28–7.33 (m, 3H), 7.40 (t, $J = 8.0$ Hz, 3H), 7.45 (s, 1H), 7.61 (d, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 13.0, 31.0, 122.1, 122.4, 122.8, 126.5, 126.7, 127.0, 128.3, 130.4, 130.7, 131.4, 131.9, 134.7, 136.6, 138.9, 197.3 ppm; anal. calcd for $C_{20}H_{18}BrNO$: C, 65.23; H, 4.93; N, 3.80; found: C, 65.04; H, 4.81; N, 3.69; ESI-MS: $m/z = 368\ (M + 1)^+$.

1-(1-(4-Bromophenyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4y). Yellow solid, mp 106–107 °C; IR (KBr): 2922, 1658, 1519, 1489, 1384, 1263, 1168, 952, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 1.92 (s, 3H), 2.28 (s, 3H), 7.15 (d, $J = 8.5$ Hz, 2H), 7.28–7.33 (m, 3H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 13.0, 31.0, 122.1, 122.4, 122.7, 126.5, 126.7, 128.2, 129.8, 130.4, 132.7, 134.7, 136.6, 197.4 ppm; anal. calcd for $C_{20}H_{18}BrNO$: C, 65.23; H, 4.93; N, 3.80; found: C, 65.07; H, 4.85; N, 3.72; ESI-MS: $m/z = 368\ (M + 1)^+$.

1-(2,5-Dimethyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)ethanone (4z). Yellow sticky liquid; IR (KBr): 2926, 1660, 1516, 1442, 1386, 1265, 960, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.86 (s, 3H), 1.93 (s, 3H), 2.29 (s, 3H), 7.29–7.34 (m, 3H), 7.41 (t, $J = 8.0$ Hz, 4H), 7.80 (t, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 13.0, 30.9, 122.4, 122.7, 123.6 (q, $^1J_{FC} = 270.7$ Hz), 126.3, 126.7 (q, $^3J_{FC} = 3.3$ Hz), 126.8, 128.3, 128.7, 130.4, 130.9 (q, $^2J_{FC} = 36.0$ Hz), 134.5, 136.4, 140.8, 197.3 ppm; anal. calcd for $C_{21}H_{18}F_3NO$: C, 70.58; H, 5.08; N, 3.92; found: C, 70.50; H, 4.89; N, 3.82; ESI-MS: $m/z = 358\ (M + 1)^+$.

1-(2,5-Dimethyl-4-phenyl-1-(4-(trifluoromethoxy)phenyl)-1*H*-pyrrol-3-yl)ethanone (4aa). White solid, mp 125–126 °C; IR (KBr): 2926, 1660, 1508, 1410, 1384, 1269, 956, 705 cm^{-1}; ^1H

NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 1.92 (s, 3H), 2.28 (s, 3H), 7.29–7.33 (m, 5H), 7.36–7.41 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 12.9, 30.9, 119.4 (q, $^1J_{FC} = 256.6$ Hz), 121.8, 122.1, 122.4, 126.5, 126.7, 128.2, 129.7, 130.4, 134.7, 136.0, 136.6, 149.0, 197.3 ppm; anal. calcd for $C_{21}H_{18}F_3NO_2$: C, 67.55; H, 4.86; N, 3.75; found: C, 67.45; H, 4.80; N, 3.69; ESI-MS: $m/z = 374$ $(M + 1)^+$.

1-(1-(Furan-2-ylmethyl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)-ethanone (4ab). White solid, mp 120–121 °C; IR (KBr): 2922, 1643, 1518, 1406, 1383, 1292, 941, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 2.13 (s, 3H), 2.58 (s, 3H), 5.00 (s, 2H), 6.14 (d, $J = 7.5$ Hz, 1H), 6.32 (dd, $J = 2.0$ Hz, 3.0 Hz, 1H), 7.22–7.24 (m, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.35–7.38 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.3, 11.7, 31.0, 40.6, 107.9, 110.4, 121.6, 122.2, 125.9, 126.6, 128.1, 130.6, 134.1, 137.0, 142.6, 149.9, 197.2 ppm; anal. calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77; found: C, 77.72; H, 6.47; N, 4.68; ESI-MS: $m/z = 294$ $(M + 1)^+$.

1-(1-(9*H*-Fluoren-2-yl)-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)-ethanone (4ac). Yellow solid, mp 153–155 °C; IR (KBr): 2922, 1654, 1518, 1489, 1357, 1265, 952, 709 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.89 (s, 3H), 1.95 (s, 3H), 2.32 (s, 3H), 3.99 (s, 2H), 7.27–7.44 (m, 9H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 13.2, 31.1, 36.9, 120.3, 120.5, 121.8, 122.2, 124.9, 125.2, 126.6, 126.9, 126.9, 127.1, 127.4, 128.3, 130.6, 135.2, 136.0, 137.0, 140.5, 142.2, 143.5, 144.5, 197.3 ppm; anal. calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71; found: C, 85.88; H, 6.01; N, 3.56; ESI-MS: $m/z = 378$ $(M + 1)^+$.

1-(1-Allyl-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4ad). Yellow sticky liquid; IR (KBr): 2920, 1647, 1516, 1406, 1384, 1155, 941, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.86 (s, 3H), 2.03 (s, 3H), 2.48 (s, 3H), 4.46 (s, 2H), 4.83 (d, $J = 17.0$ Hz, 1H), 5.18 (d, $J = 10.5$ Hz, 1H), 5.87–5.94 (m, 1H), 7.23 (d, $J = 7.0$ Hz, 2H), 7.29 (t, $J = 7.0$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.0, 11.4, 31.0, 45.7, 116.4, 121.3, 122.1, 125.7, 126.5, 128.1, 130.6, 132.6, 134.0, 137.1, 197.2 ppm; anal. calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53; found: C, 80.57; H, 7.48; N, 5.47; ESI-MS: $m/z = 254$ $(M + 1)^+$.

1-(1-Benzyl-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4ae). Yellow sticky liquid; IR (KBr): 2918, 1647, 1516, 1406, 1155, 945, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.90 (s, 3H), 2.00 (s, 3H), 2.47 (s, 3H), 5.11 (s, 2H), 6.97 (d, $J = 7.5$ Hz, 2H), 7.26–7.35 (m, 6H), 7.38 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.3, 11.8, 31.1, 46.9, 121.6, 122.4, 125.7, 126.0, 126.6, 127.5, 128.2, 128.9, 130.6, 134.2, 136.8, 137.1, 197.3 ppm; anal. calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62; found: C, 83.02; H, 6.91; N, 4.49; ESI-MS: $m/z = 304$ $(M + 1)^+$.

1-(2,5-Dimethyl-1-phenethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4af). White solid, mp 124–125 °C; IR (KBr): 2939, 1639, 1510, 1410, 1151, 1026, 952, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.86 (s, 3H), 1.93 (s, 3H), 2.49 (s, 3H), 2.94 (t, $J = 7.5$ Hz, 2H), 4.04 (t, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.24–7.32 (m, 4H), 7.37 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.2, 11.8, 31.0, 36.9, 45.3, 121.5, 122.2, 125.6, 126.5, 127.0, 128.2, 128.7, 128.8, 130.6, 133.7, 137.2, 137.7, 197.1 ppm; anal. calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41; found: C, 83.07; H, 7.22; N, 4.25; ESI-MS: $m/z = 318$ $(M + 1)^+$.

(*S*)-1-(2,5-Dimethyl-4-phenyl-1-(1-phenylethyl)-1*H*-pyrrol-3-yl)-ethanone (4ag). Yellow solid, mp 92–93 °C; IR (KBr): 2920, 1645, 1518, 1396, 1269, 950, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.86 (s, 3H), 1.88 (s, 3H), 1.92 (d, $J = 7.5$ Hz, 3H), 2.41 (s, 3H), 5.64 (q, $J = 7.0$ Hz, 1H), 7.12 (d, $J = 7.5$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.28 (t, $J = 6.5$ Hz, 2H), 7.33–7.38 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.5, 12.6, 18.8, 31.2, 52.7, 122.0, 122.9, 125.9, 126.5, 127.2, 128.1, 128.7, 130.7, 134.0, 137.2, 140.9, 197.7 ppm; anal. calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41; found: C, 83.07; H, 7.21; N, 4.30; ESI-MS: $m/z = 318$ $(M + 1)^+$.

1-(1-Cyclopropyl-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4ah). Yellow sticky liquid; IR (KBr): 2924, 1647, 1516, 1465, 1384, 1151, 950, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.96 (q, $J = 5.5$ Hz, 2H), 1.14 (q, $J = 7.0$ Hz, 2H), 1.83 (s, 3H), 2.14 (s, 3H), 2.59 (s, 3H), 2.93–2.98 (m, 1H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.1, 11.3, 13.0, 26.0, 31.0, 121.3, 121.9, 126.5, 127.9, 128.1, 130.5, 136.5, 137.1, 197.1 ppm; anal. calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53; found: C, 80.48; H, 7.39; N, 5.49; ESI-MS: $m/z = 254$ $(M + 1)^+$.

1-(1-Cyclopentyl-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4ai). Yellow solid, mp 61–62 °C; IR (KBr): 2924, 1647, 1508, 1406, 1383, 1161, 950, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.65–1.75 (m, 4H), 1.82 (s, 3H), 1.92–2.05 (m, 4H), 2.11 (s, 3H), 2.57 (s, 3H), 4.63–4.70 (m, 1H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.8, 12.9, 25.2, 31.1, 56.3, 121.9, 122.9, 125.7, 126.5, 128.1, 130.6, 133.9, 137.3, 197.5 ppm; anal. calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98; found: C, 81.10; H, 8.15; N, 4.79; ESI-MS: $m/z = 282$ $(M + 1)^+$.

1-(2,5-Dimethyl-4-phenyl-1-propyl-1*H*-pyrrol-3-yl)ethanone (4aj). Yellow sticky liquid; IR (KBr): 2933, 1647, 1506, 1408, 1383, 1155, 950, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.99 (t, $J = 7.5$ Hz, 3H), 1.67–1.74 (m, 2H), 1.84 (s, 3H), 2.06 (s, 3H), 2.52 (s, 3H), 3.77 (t, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 7.5$ Hz, 2H), 7.28 (t, $J = 7.0$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.3, 11.3, 11.8, 23.8, 30.9, 45.3, 121.2, 122.1, 125.4, 126.4, 128.1, 130.6, 133.7, 137.2, 197.1 ppm; anal. calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49; found: C, 79.89; H, 8.21; N, 5.39; ESI-MS: $m/z = 256$ $(M + 1)^+$.

1-(1-Butyl-2,5-dimethyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4ak). Yellow sticky liquid; IR (KBr): 2931, 1647, 1512, 1408, 1383, 1155, 952, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.98 (t, $J = 7.5$ Hz, 3H), 1.37–1.44 (m, 2H), 1.62–1.68 (m, 2H), 1.84 (s, 3H), 2.06 (s, 3H), 2.52 (s, 3H), 3.80 (t, $J = 7.0$ Hz, 2H), 7.22 (d, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.0$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.3, 11.8, 13.8, 20.1, 30.9, 32.6, 43.5, 121.2, 122.1, 125.3, 126.4, 128.1, 130.6, 133.7, 137.2, 197.1 ppm; anal. calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20; found: C, 80.18; H, 8.47; N, 5.12; ESI-MS: $m/z = 270$ $(M + 1)^+$.

Methyl-2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4al). Yellow solid, mp 108–109 °C; IR (KBr): 2918, 1685, 1525, 1379, 1165, 1072, 952, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.88 (s, 3H), 2.31 (s, 3H), 3.61 (s, 3H), 7.24–7.30 (m, 5H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 12.8, 50.4, 110.7, 122.4, 126.0, 126.9, 127.5, 128.3, 128.6, 129.5, 130.4, 135.9, 136.4, 137.8, 166.4 ppm; anal. calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59; found: C, 78.47; H, 6.09; N, 4.48; ESI-MS: $m/z = 306\ (M + 1)^+$.

Ethyl-2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4am). Yellow solid, mp 83–84 °C; IR (KBr): 2922, 1681, 1533, 1381, 1280, 974, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.01 (t, $J = 7.0$ Hz, 3H), 1.87 (s, 3H), 2.31 (s, 3H), 4.07 (q, $J = 7.0$ Hz, 2H), 7.23–7.26 (m, 3H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.33 (t, $J = 7.0$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 12.7, 14.0, 59.1, 111.1, 122.4, 125.9, 126.7, 127.4, 128.3, 128.6, 129.5, 130.5, 135.7, 136.5, 137.8, 165.9 ppm; anal. calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; found: C, 78.89; H, 6.56; N, 4.28; ESI-MS: $m/z = 320\ (M + 1)^+$.

2-Methoxyethyl 2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4an). Yellow solid, mp 72–73 °C; IR (KBr): 2922, 1701, 1384, 1274, 1078, 846, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.85 (s, 3H), 2.30 (s, 3H), 3.18 (s, 3H), 3.34 (t, $J = 5.0$ Hz, 2H), 4.17 (t, $J = 5$ Hz, 2H), 7.22–7.26 (m, 3H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 12.7, 58.7, 62.3, 70.3, 110.6, 122.4, 125.9, 126.8, 127.4, 128.3, 128.6, 129.4, 130.5, 136.1, 136.4, 137.8, 165.7 ppm; anal. calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01; found: C, 76.48; H, 6.45; N, 3.92; ESI-MS: $m/z = 350\ (M + 1)^+$.

Allyl-2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4ao). Yellow sticky liquid; IR (KBr): 2920, 1685, 1508, 1384, 1273, 1172, 927, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.88 (s, 3H), 2.32 (s, 3H), 4.55 (d, $J = 5.0$ Hz, 2H), 4.97 (dd, $J = 1.5$, 17.0 Hz, 1H), 5.01 (d, $J = 10.5$ Hz, 1H), 5.68–5.76 (m, 1H), 7.45–7.26 (m, 3H), 7.30 (d, $J = 7.0$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.51 (t, $J = 7.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 12.8, 64.1, 110.7, 116.8, 122.4, 126.0, 126.9, 127.5, 128.3, 128.6, 129.5, 130.5, 132.6, 136.1, 136.4, 137.8, 165.6 ppm; anal. calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23; found: C, 79.70; H, 6.25; N, 4.11; ESI-MS: $m/z = 332\ (M + 1)^+$.

Methyl-2-ethyl-5-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4ap). Yellow solid, mp 100–101 °C; IR (KBr): 2916, 1685, 1523, 1284, 1155, 1072, 983, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.04 (t, $J = 7.0$ Hz, 3H), 1.85 (s, 3H), 2.74 (q, $J = 7.5$ Hz, 2H), 3.61 (s, 3H), 7.24–7.31 (m, 5H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.46–7.52 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 14.7, 19.5, 50.4, 109.8, 122.3, 125.9, 126.9, 127.4, 128.5, 128.7, 129.4, 130.4, 136.4, 137.8, 142.0, 166.1 ppm; anal. calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39; found: C, 78.90; H, 6.55; N, 4.29; ESI-MS: $m/z = 320\ (M + 1)^+$.

***tert*-Butyl-2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4aq).** Yellow solid, mp 96–97 °C; IR (KBr): 2926, 1685, 1541, 1384, 1288, 1159, 1080, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.26 (s, 9H), 1.87 (s, 3H), 2.30 (s, 3H), 7.23–7.26 (m, 3H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 12.4, 28.0, 79.2, 112.7, 122.1, 125.8, 126.4, 127.5, 128.3, 128.5, 129.4, 130.4, 135.2, 136.9, 137.9, 165.5 ppm; anal. calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; found: C, 79.33; H, 7.09; N, 3.92; ESI-MS: $m/z = 348\ (M + 1)^+$.

Isobutyl-2,5-dimethyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (4ar). Yellow solid, mp 70–71 °C; IR (KBr): 2933, 1685, 1527, 1384, 1276, 1078, 949, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.67 (d, $J = 7.0$ Hz, 6H), 1.63–1.68 (m, 1H), 1.86 (s, 3H), 2.33 (s, 3H), 3.82 (d, $J = 6.5$ Hz, 2H), 7.22–7.35 (m, 7H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 12.8, 19.1, 27.6, 69.8, 111.0, 122.4, 126.0, 126.8, 127.5, 128.3, 128.6, 129.5, 130.5, 135.9, 136.7, 137.8, 166.1 ppm; anal. calcd for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03; found: C, 79.23; H, 7.07; N, 3.95; ESI-MS: $m/z = 348\ (M + 1)^+$.

1-(5-Ethyl-1-(furan-2-ylmethyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4as). White solid, mp 103–104 °C; IR (KBr): 2929, 1647, 1498, 1406, 1151, 1010, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.01 (t, $J = 7.5$ Hz, 3H), 1.82 (s, 3H), 2.49 (q, $J = 7.5$ Hz, 2H), 2.55 (s, 3H), 5.02 (s, 2H), 6.09 (t, $J = 2.5$ Hz, 1H), 6.32 (dd, $J = 1.5$, 3.0 Hz, 1H), 7.24–7.26 (m, 2H), 7.30 (t, $J = 7.0$ Hz, 1H), 7.35–7.38 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.7, 15.3, 17.6, 31.0, 40.6, 107.7, 110.4, 121.8, 122.0, 126.7, 128.1, 130.5, 131.8, 134.3, 137.1, 142.4, 150.1, 197.2 ppm; anal. calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56; found: C, 78.11; H, 6.76; N, 6.82; ESI-MS: $m/z = 308\ (M + 1)^+$.

1-(1-Benzyl-5-ethyl-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone (4at). Yellow sticky liquid; IR (KBr): 2931, 1653, 1498, 1398, 1415, 952, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.87 (s, 3H), 2.37 (q, $J = 7.5$ Hz, 2H), 2.42 (s, 3H), 5.13 (s, 2H), 6.94 (t, $J = 7.5$ Hz, 2H), 7.25–7.34 (m, 6H), 7.38 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.8, 15.6, 17.7, 31.1, 46.8, 121.7, 122.2, 125.5, 126.7, 127.4, 128.1, 128.9, 130.6, 132.1, 134.4, 137.1, 137.2, 197.3 ppm; anal. calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41; found: C, 83.29; H, 7.25; N, 4.33; ESI-MS: $m/z = 318\ (M + 1)^+$.

1-(1-Cyclopropyl-5-ethyl-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)-ethanone (4au). Yellow sticky liquid; IR (KBr): 2931, 1647, 1516, 1413, 1163, 1016, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.99 (q, $J = 5.0$ Hz, 2H), 1.08 (t, $J = 7.5$ Hz, 3H), 1.15 (q, $J = 7.0$ Hz, 2H), 1.80 (s, 3H), 2.56 (q, $J = 7.5$ Hz, 2H), 2.58 (s, 3H), 2.97–3.01 (m, 1H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.29 (t, $J = 7.0$ Hz, 2H), 7.36 (d, $J = 7.0$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 8.0, 13.3, 14.8, 18.1, 26.2, 31.0, 121.4, 121.7, 126.6, 128.1, 130.5, 133.8, 136.7, 137.2, 197.1 ppm; anal. calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24; found: C, 80.71; H, 7.75; N, 5.08; ESI-MS: $m/z = 268\ (M + 1)^+$.

1-(5-Ethyl-2-methyl-4-phenyl-1-propyl-1*H*-pyrrol-3-yl)ethanone (4av). Yellow sticky liquid; IR (KBr): 2974, 1647, 1550, 1452, 1288, 952, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.99 (t, $J = 7.5$ Hz, 3H), 1.03 (t, $J = 7.5$ Hz, 3H), 1.68–1.76 (m, 2H), 1.81 (s, 3H), 2.42 (q, $J = 7.5$ Hz, 2H), 2.52 (s, 3H), 3.77 (t, $J = 8.0$ Hz, 3H), 7.23–7.26 (m, 2H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 11.9, 15.5, 17.6, 24.2, 30.9, 45.2, 121.5, 121.8, 126.5, 128.1, 130.6, 131.4, 133.7, 137.4, 197.0 ppm; anal. calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20; found: C, 80.15; H, 8.47; N, 5.02; ESI-MS: $m/z = 270\ (M + 1)^+$.

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