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Zirconocene dichloride catalysed one-pot synthesis of pyrroles through nitroalkene-enamine assembly†

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Zirconocene dichloride in an environment-friendly ethanol medium was found to be an efficient catalyst for the synthesis of multi-substituted pyrroles by involving multi-component reactions of amines, β-dicarbonyl compounds and nitroalkenes. The reactions undergo completion easily with high yields and no side-products, allowing the purification of pyrroles in hassle-free and economical manner.

Introduction

Pyrroles constitute numerous natural products and pharmaceuticals[1,2] (Fig. 1). The scaffold has also found use in material science and supramolecular chemistry.[3] Recent years witnessed a shift from conventional methods to multi-component reactions.[4] This has helped to overcome several drawbacks such as non-availability of suitable starting materials for desired substitutions, functional group tolerance, multi-step synthesis, and regioselectivity issues. Based on our interests in bioactive heterocycles and metal-mediated reactions,[5] we sought a highly efficient, low-cost, non-toxic catalyst for a multi-component reaction toward the synthesis of pyrroles. Several researchers have investigated metal-mediated formation of C–C/C–N bonds in pyrrole synthesis,[6] and various metal salts have demonstrated high efficiencies.[7–19]

Examination of the previous studies illustrates general reaction patterns involving either a cycloisomerization or a cycloaddition in the synthesis of pyrroles. The vast numbers of methods available provide chemists with an arsenal of strategies to choose, depending on the starting materials available or the products desired. One of the interesting strategies available for the synthesis of pyrroles involves the reaction between enamines and nitroalkenes.[11a–c,12,20] Among the several methods that encompass this strategy, a few deserve mention on the basis of the reagents/conditions employed. A three-component reaction has been reported for the synthesis of pyrroles from amines and nitrostyrenes using (diacetoxyiodo)benzene at reflux temperature in ethanol.[20d] The synthesis of highly functionalized pyrroles have been achieved by coupling reactions of 1,3-dicarbonyl compounds, amines, aromatic aldehydes and nitroalkanes using iron(III) salts as catalysts.[11a] High-speed vibration milling of ketones with *N*-iodosuccinimide, amines, β-dicarbonyl compounds, cerium(IV) ammonium nitrate and silver nitrate affords polysubstituted pyrroles.[13d] A four-component protocol using ionic liquid media involves primary amines, aldehydes, nitromethane and β-diketones for the synthesis of functionalized pyrroles.[20e] One-pot, four-component condensation reactions of aromatic aldehydes, benzyl amines, β-ketoesters and nitroalkanes in the presence of $NiCl_2 \cdot 6H_2O$ yields tetrasubstituted pyrroles.[12] A multi-component synthesis of substituted pyrroles promoted by $CeCl_3 \cdot 7H_2O$ under microwave irradiation of β-nitrostyrene, β-diketones and aryl amines is also known to afford good yields of pyrroles.[13c] $Yb(OTf)_3$ effectively promotes the coupling reaction of amines, 1,3-diketones and phenacyl bromide in a one-pot reaction.[19] Although this strategy has been well explored during the past few years, the reactions in many cases are undermined by long duration, low-to-moderate yields, poor atom economy, high cost, environmentally non-benign solvents, regio-/chemo-selectivity issues, toxicity, functional group incompatibility, and tedious work-up and isolation procedures. Contemplating on this, we decided to investigate the reaction for an efficient, commercially available, high yielding and inexpensive catalyst in an eco-friendly condition.

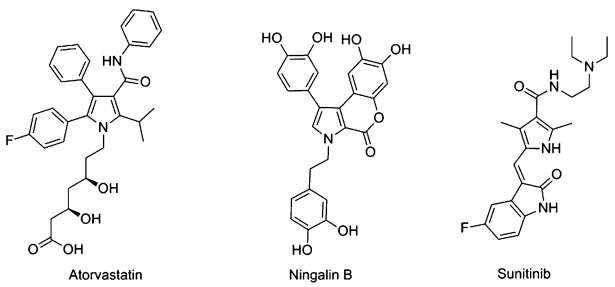

Fig. 1 A few pyrrole-based biologically active molecules.

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Our investigations revealed the potential of zirconocene dichloride (Cp_2ZrCl_2) in an ethanol medium as one of the most effective catalysts for the *in situ* formation of enamines and their subsequent reaction with nitroalkenes to afford pyrroles with multiple substituents.

Results and discussion

A one-pot, three-component reaction between aniline, 3-oxo-*N*-phenylbutanamide and β-nitrostyrene was envisaged to provide access to a multi-substituted pyrrole[13c,20] (Scheme 1). With these substrates, the reactions would proceed through the two key steps of enamine formation from the amine and β-ketoamide and a subsequent Michael addition of the resulting enamine to the β-nitrostyrene. We anticipated that a suitable catalyst would promote both of these reactions in succession to afford pyrrole derivatives without any impediment. Although the commercially available starting materials have been carefully chosen to address the substitution, the difficulty was to identify a catalyst that would promote both of these reactions effectively in sequence. To provide an environmentally benign reaction condition, EtOH was employed as the solvent, considering the polar nature of the transition state that would be encountered. The search for a cost-effective, mild and efficient metal catalyst was initiated. The screening of the relatively inexpensive transition metal salts, such as chlorides of nickel, iron, copper, titanium and zirconium, at a catalytic concentration of 5 mol% gave modest yields, up to a maximum of 61% with $ZrCl_4$ in 7 h, providing impetus for further evaluation (Table 1). A variation of the ligand was then tried by replacing $ZrCl_4$ with $CpZrCl_3$. Encouraging enough was the result when a 5 mol% concentration of $CpZrCl_3$ under the reflux condition afforded the desired product in 69% yield while the time of the reaction was reduced to 4 h. This prompted us to carry out the reaction under similar conditions with the dicyclopentadienyl derivative Cp_2ZrCl_2, and gratifyingly, the yield increased to 78%. More significantly, the reaction underwent completion in 1.5 h. On the contrary, a similar reaction with Cp_2TiCl_2 gave poor yield, even after 15 h.

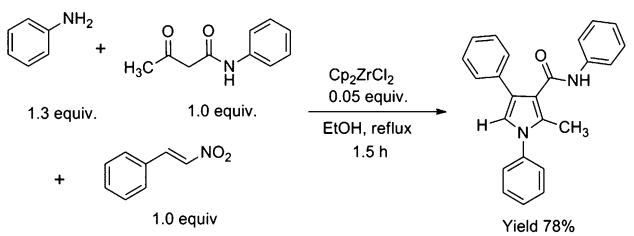
A study to optimize the concentration of Cp_2ZrCl_2 indicated 5 mol% to be the best, whereas the yields did not improve at increased concentrations. At concentrations below optimum, the reaction did not undergo completion, yet a trace amount of the product was observed even in the absence of the catalyst. An independent study carried out to examine the effect of solvents revealed that the polar protic solvent EtOH itself was the most suitable medium for the reaction. The scope of the reaction was examined by varying the substituents on the reacting partners (Table 2). Electron-donating and electron-withdrawing groups on the aryl amines did not significantly deter the yields. Aliphatic amines were found to be slightly lower yielding and less reactive than the aromatic counterparts (Scheme 2).

Table 1 Standardization of reaction conditions[a]

No.	Catalyst	Solvent	Time (h)	Yield[b] (%)
1	$NiCl_2 \cdot 6H_2O$	EtOH	8	48
2	$FeCl_3$	EtOH	13	43
3	CuCl	EtOH	24	37
4	$TiCl_4$	EtOH	7	53
5	$ZrCl_4$	EtOH	7	61
6	$CpZrCl_3$	EtOH	4	69
7	**Cp_2ZrCl_2**	**EtOH**	**1.5**	**78**
8	Cp_2TiCl_2	EtOH	15	50
9	Cp_2ZrCl_2[c]	EtOH	1.5	55
10	Cp_2ZrCl_2[d]	EtOH	1.5	79
11	—	EtOH	10	Trace
12	Cp_2ZrCl_2	H_2O	7	52
13	Cp_2ZrCl_2	THF	24	37
14	Cp_2ZrCl_2	Acetone	10	35
15	Cp_2ZrCl_2	CH_2Cl_2	13	40
16	Cp_2ZrCl_2	CCl_4	8	48
17	Cp_2ZrCl_2	DMSO	4	57
18	Cp_2ZrCl_2	DMF	12	40

[a] Amine (1.3 equiv.), 1,3-dicarbonyl compound (1.0 equiv.), nitroalkene (1.0 equiv.), catalyst (0.05 equiv.), reflux. [b] Isolated yield. [c] Catalyst (0.025 equiv.). [d] Catalyst (0.10 equiv.).

The β-dicarbonyl compounds dictated the substitution at the 2nd and 3rd positions of the pyrrole, whereas the amines could decipher the N1 substituent. The reaction tolerated β-ketoesters and β-diketones very well in place of β-ketoamides. The substitutions at the β and α-positions of nitroalkenes were reproduced at the 4th and 5th positions, respectively. The reactions of penta-substituted pyrroles took a longer time to complete, suggestive of the steric encumbrance faced during the cyclocondensation. No significant side-product was observed during the course of the reactions. This allowed for the easy purification of the desired products by elution through a column of silica gel using hexane–ethyl acetate mixture as the eluent to remove the trace amounts of impurities/starting materials observed in some instances. A plausible mechanism[11e] for the reactions is outlined in Fig. 2. Cp_2ZrCl_2 coordinates to the electrophilic carbonyl oxygen of the dicarbonyl compound **B** ensuring a nucleophilic attack by the amine **A** to afford the imine **C**, which tautomerizes to the enamine **D**. The enamine renders a nucleophilic attack on the electrophilic nitroalkene **E**, coordinated to zirconocene dichloride. The resulting intermediate **F** tautomerizes to the corresponding enamine and facilitates an intramolecular attack through the nitrogen atom on the iminium ion stabilized by zirconocene chloride. This affords the dihydro-1*H*-pyrrole intermediate **G**, which undergoes an elimination reaction to gain aromaticity with the consequent formation of substituted pyrrole **H**. Cp_2ZrCl_2 displays the role of a mild and efficient catalyst

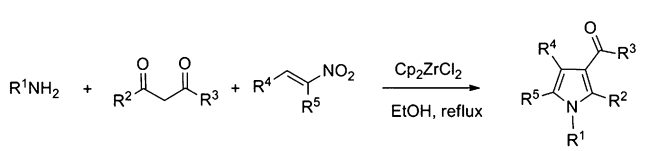


Scheme 1 Cp_2ZrCl_2 catalysed one-pot synthesis of pyrrole.

Table 2 Synthesis of pyrroles using Cp_2ZrCl_2 catalyst[a]

Entry	R^1	R^2	R^3	R^4	R^5	Product	Yield[b] (%)	Time[c] (h)
1	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(i)**	78	1.5
2	$-C_6H_4$–OMe-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(ii)**	73	3
3	$-C_6H_4$–Me-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(iii)**	74	1.5
4	$-C_6H_4$–Cl-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(iv)**	76	1.5
5	$-C_6H_4$–Br-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(v)**	78	1.5
6	$-C_3H_7$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(vi)**	67	6
7	$-CH_2C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	–H	**4a(vii)**	69	6
8	$-C_6H_5$	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(i)**	77	1.5
9	$-C_6H_4$–Me-*p*	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(ii)**	74	1.5
10	$-C_6H_4$–Br-*p*	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(iii)**	75	1.5
11	$-C_3H_7$	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(iv)**	67	6
12	$-CH_2C_6H_5$	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(v)**	69	6
13	$-CH_2C_6H_4$–OMe-*p*	$-CH_3$	$-OC_2H_5$	$-C_6H_5$	–H	**4b(vi)**	70	6
14	$-C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_5$	–H	**4c(i)**	76	1.5
15	$-C_6H_4$–Me-*p*	$-CH_3$	$-CH_3$	$-C_6H_5$	–H	**4c(ii)**	74	1.5
16	$-C_6H_4$–Br-*p*	$-CH_3$	$-CH_3$	$-C_6H_5$	–H	**4c(iii)**	75	1.5
17	$-C_3H_7$	$-CH_3$	$-CH_3$	$-C_6H_5$	–H	**4c(iv)**	70	6
18	$-CH_2C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_5$	–H	**4c(v)**	74	6
19	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–OMe-*p*	–H	**4d(i)**	76	3
20	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–Cl-*p*	–H	**4d(ii)**	72	1.5
21	$-C_6H_4$–Me-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–OMe-*p*	–H	**4d(iii)**	77	3
22	$-C_6H_4$–Me-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–Cl-*p*	–H	**4d(iv)**	74	1.5
23	$-C_6H_4$–Br-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–OMe-*p*	–H	**4d(v)**	72	3
24	$-C_6H_4$–Br-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–Cl-*p*	–H	**4d(vi)**	71	1.5
25	$-C_6H_4$–OMe-*p*–	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–OMe-*p*	–H	**4d(vii)**	67	3
26	$-C_6H_4$–Cl-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_4$–OMe-*p*	–H	**4d(viii)**	68	3
27	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_3$–OH-*p*,–OMe-*m*	–H	**4d(ix)**	70	3
28	$-C_6H_5$	$-CH(CH_3)_2$	$-NHC_6H_5$	$-C_6H_5$	–H	**4d(x)**	75	1.5
29	$-C_6H_5$	$-CH(CH_3)_2$	$-NHC_6H_5$	$-C_6H_4$–Me-*p*	–H	**4d(xi)**	73	1.5
30	$-C_6H_5$	$-CH(CH_3)_2$	$-NHC_6H_5$	$-C_6H_4$–F-*p*	–H	**4d(xii)**	74	1.5
31	$-C_6H_5$	$-CH_3$	$-OC_2H_5$	$-C_6H_4$–OMe-*p*	–H	**4e(i)**	73	3
32	$-C_6H_5$	$-CH_3$	$-OC_2H_5$	$-C_6H_4$–Cl-*p*	–H	**4e(ii)**	72	1.5
33	$-C_6H_5$	$-CH_3$	$-OC_2H_5$	$-C_6H_3$–OH-*p*,–OMe-*m*	–H	**4e(iii)**	69	3
34	$-C_6H_4$–Me-*p*	$-C_6H_5$	$-OC_2H_5$	$-C_6H_5$	–H	**4e(iv)**	67	6
35	$-C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_4$–OMe-*p*	–H	**4e(v)**	74	3
36	$-C_6H_5$	$-CH_3$	$-CH_3$	$-C_6H_4$–Cl-*p*	–H	**4e(vi)**	71	1.5
37	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-CH_3$	**4f(i)**	70	6
38	$-C_6H_4$–OMe-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-CH_3$	**4f(ii)**	69	6
39	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-C_6H_5$	**4f(iii)**	69	10
40	$-CH_2C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-C_6H_5$	**4f(iv)**	68	10
41	$-C_6H_5$	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-C_6H_4$–F-*p*	**4f(v)**	67	10
42	$-C_6H_4$–OMe-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-C_6H_4$–F-*p*	**4f(vi)**	68	10
43	$-C_6H_4$–Me-*p*	$-CH_3$	$-NHC_6H_5$	$-C_6H_5$	$-C_6H_4$–F-*p*	**4f(vii)**	67	10

[a] Amine (1.3 equiv.), 1,3-dicarbonyl compound (1.0 equiv.), nitroalkene (1.0 equiv.). [b] Isolated yield. [c] Reaction time.



Scheme 2 Synthesis of multi-substituted pyrroles.

during the course of the reactions, which involve the formation of enamine, the reaction of enamine with nitroalkene and, finally, cyclocondensation, favoring the reaction kinetics to afford the product efficiently under mild conditions.

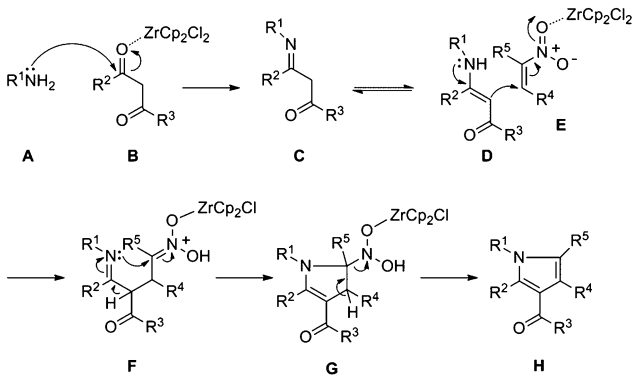


Fig. 2 Plausible reaction mechanism.

Conclusions

In summary, the inexpensive Cp_2ZrCl_2 was found to be an efficient catalyst for the synthesis of multi-substituted pyrroles by involving multi-component reactions of amines, β-dicarbonyl compounds and nitroalkenes. The reactions were carried out under environmentally benign conditions in an ethanol medium. Various functional groups were tolerated, and choice of the substituents allowed the formation of desired multi-substituted pyrroles. The operationally simple procedure affords the products easily with good yields. No significant side products were observed from the reactions, simplifying the purification. Regioselectivity was in coherence with the suggested reaction mechanism. We believe that this simple, cost-effective, highly efficient, catalytic, one-pot procedure could be a valuable addition and/or a viable alternative to the existing methods for the synthesis of multi-substituted pyrroles.

Experimental section

Representative procedure for the synthesis of pyrrole 4a(i)

A mixture of aniline (68 mg, 0.73 mmol, 1.3 equiv.), 3-oxo-*N*-phenylbutanamide (100 mg, 0.56 mmol, 1.0 equiv.), β-nitrostyrene (84 mg, 0.56 mmol, 1.0 equiv.) and Cp_2ZrCl_2 (8.0 mg, 0.028 mmol, 0.05 equiv.) in ethanol (5 mL) was refluxed at 80 °C. After completion of the reaction (1.5 h), as monitored by TLC, the solvent was evaporated. The residue was dissolved in ethyl acetate and washed with water. The organic layer was dried, concentrated and purified by eluting through a column of silica gel using hexane–ethyl acetate mixture (95 : 5) as the eluent to give 155 mg (78%) yield of **4a(i)**.

2-Methyl-*N*-1,4-triphenyl-1*H*-pyrrole-3-carboxamide, 4a(i)

White solid m.p. = 132–134 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3348, 1651, 1594, 1433, 1316; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.55 (m, 10H), 7.24 (d, J = 6.2 Hz, 4H), 7.17 (brs, 1H), 7.02–7.06 (m, 1H), 6.79 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.95, 138.94, 138.46, 135.67, 134.52, 129.61, 129.36, 128.90, 128.86, 128.08, 127.49, 126.30, 123.58, 123.46, 120.20, 119.34, 115.22, 12.47; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{24}H_{20}N_2NaO$, 375.1473, found 375.1479.

1-(4-Methoxyphenyl)-2-methyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4a(ii)

Reddish brown solid; m.p. = 160–162 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3324, 1648, 1595, 1437, 1316; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.53 (m, 6H), 7.20–7.30 (m, 5H), 7.15 (brs, 1H), 7.00–7.04 (m, 3H), 6.72 (s, 1H), 3.89 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.02, 159.25, 138.47, 136.00, 134.57, 131.77, 129.61, 128.89, 128.81, 127.52, 127.44, 123.43, 123.24, 120.45, 119.29, 114.74, 114.44, 55.60, 12.39; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO_2$, 405.1579, found 405.1578.

2-Methyl-*N*,4-diphenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxamide, 4a(iii)

Brownish solid; m.p. = 98–100 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3335, 1648, 1516, 1432, 1311; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 7.2 Hz, 1H), 7.20–7.30 (m, 8H), 7.15 (brs, 1H), 7.02 (t, J = 6.4 Hz, 1H), 6.75 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.99, 138.46, 138.08, 136.35, 135.76, 134.56, 129.91, 129.61, 128.88, 128.79, 127.43, 126.08, 123.42, 123.37, 120.26, 119.30, 114.95, 21.13, 12.44; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO$, 389.1630, found, 389.1637.

1-(4-Chlorophenyl)-2-methyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4a(iv)

White solid; m.p. = 191–193 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3330, 1646, 1520, 1438, 1311; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.52 (m, 7H), 7.32 (d, J = 8.6 Hz, 2H), 7.19–7.26 (m, 4H), 7.13 (brs, 1H), 7.03 (t, J = 6.9 Hz, 1H), 6.74 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77, 138.33, 137.38, 135.54, 134.22, 134.01, 129.61, 129.58, 128.96, 128.84, 127.65, 127.51, 123.88, 123.58, 120.01, 119.34, 115.55, 12.47; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{24}H_{19}ClN_2NaO$, 409.1084, found 409.1084.

1-(4-Bromophenyl)-2-methyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4a(v)

White solid; m.p. = 140–142 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3315, 1641, 1594, 1436, 1315; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.39–7.52 (m, 5H), 7.20–7.25 (m, 6H), 7.13 (brs, 1H), 7.03 (t, J = 6.9 Hz, 1H), 6.74 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.75, 138.31, 137.89, 135.48, 134.20, 132.60, 129.58, 128.96, 128.83, 127.81, 127.65, 123.92, 123.58, 121.94, 119.94, 119.34, 115.60, 12.47; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{24}H_{19}BrN_2NaO$, 453.0578, found 453.0576.

2-Methyl-*N*,4-diphenyl-1-propyl-1*H*-pyrrole-3-carboxamide, 4a(vi)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 3407, 1660, 1528, 1436, 1313; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.48 (m, 5H), 7.18–7.25 (m, 4H), 7.09 (brs, 1H), 6.99–7.03 (m, 1H), 6.59 (s, 1H), 3.85 (t, J = 7.7 Hz, 2H), 2.63 (s, 3H), 1.79–1.87 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.16, 138.58, 134.98, 130.50, 129.61, 128.79, 128.75, 127.20, 123.27, 122.60, 119.25, 119.12, 113.98, 48.34, 24.17, 11.29, 11.12; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{21}H_{22}N_2NaO$, 341.1630, found 341.1650.

1-Benzyl-2-methyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4a(vii)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 3390, 1660, 1529, 1432, 1220; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.50 (m, 8H), 7.19–7.26 (m, 4H), 7.13 (d, J = 6.8 Hz, 2H), 7.00–7.04 (m, 1H), 6.65 (s, 1H), 5.12 (s, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.03, 138.51, 136.75, 135.52, 134.76, 129.64, 128.96, 128.82, 128.78, 127.84, 127.32, 126.67, 123.37, 123.04, 119.74, 119.29, 114.56, 50.44, 11.23; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO$, 389.1630, found 389.1641.

Ethyl 2-methyl-1,4-diphenyl-1*H*-pyrrole-3-carboxylate, 4b(i)

Reddish liquid; IR (cm^{-1}): $\bar{\upsilon}$ = 2980, 1694, 1597, 1408, 1222; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.53 (m, 5H), 7.34–7.38 (m, 4H), 7.26–7.30 (m, 1H), 6.74 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 2.48 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 139.00, 136.58, 135.60, 129.33, 129.27, 128.07, 127.56, 126.63, 126.34, 126.27, 120.84, 111.76, 59.48, 14.08, 12.66; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_2$, 328.1313, found 328.1324.

Ethyl 2-methyl-4-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate, 4b(ii)

Off-white solid; m.p. = 62–65 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2926, 1695, 1518, 1407, 1221; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.43 (m, 2H), 7.19–7.35 (m, 7H), 6.68 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89, 138.07, 136.69, 136.46, 135.68, 129.89, 129.27, 127.55, 126.44, 126.22, 126.14, 120.92, 111.50, 59.45, 21.11, 14.09, 12.63; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_2$, 342.1470, found 342.1498.

Ethyl 1-(4-bromophenyl)-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate, 4b(iii)

Reddish solid; m.p. = 102–104 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2974, 1693, 1525, 1396, 1275; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.22 (d, J = 8.5 Hz, 2H), 6.70 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.71, 137.96, 136.40, 135.33, 132.58, 129.24, 127.88, 127.63, 126.98, 126.44, 121.95, 120.58, 112.18, 59.61, 14.09, 12.68; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{18}BrNNaO_2$, 406.0419, found 406.0419.

Ethyl 2-methyl-4-phenyl-1-propyl-1*H*-pyrrole-3-carboxylate, 4b(iv)

Yellowish liquid; IR (cm^{-1}): $\bar{\upsilon}$ = 2968, 1693, 1525, 1418, 1280; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.39 (m, 5H), 6.54 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.81 (t, J = 7.4 Hz, 2H), 2.54 (s, 3H), 1.73–1.83 (m, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.97, 136.06, 135.91, 129.25, 127.46, 125.99, 125.77, 119.72, 110.37, 59.27, 48.40, 24.12, 14.05, 11.35, 11.25; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{17}H_{21}NNaO_2$, 294.1470, found 294.1492.

Ethyl 1-benzyl-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate, 4b(v)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 2928, 1693, 1526, 1417, 1282; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12–7.43 (m, 8H), 7.11 (d, J = 6.8 Hz, 2H), 6.62 (s, 1H), 5.10 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.90, 136.77, 136.43, 135.88, 129.30, 128.94, 127.80, 127.51, 126.58, 126.23, 126.13, 120.42, 111.08, 59.39, 50.54, 14.07, 11.49; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_2$, 342.1470, found 342.1470.

Ethyl 1-(4-methoxybenzyl)-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate, 4b(vi)

Yellowish liquid; IR (cm^{-1}): $\bar{\upsilon}$ = 3445, 1639, 1514, 1250, 1179; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.40 (m, 5H), 7.04 (d, J = 8.7 Hz, 2H), 6.87–6.89 (m, 2H), 6.57 (s, 1H), 5.01 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 2.50 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.91, 159.20, 136.32, 135.89, 129.26, 128.65, 128.05, 127.48, 126.07, 120.23, 114.28, 110.95, 59.36, 55.32, 50.04, 14.05, 11.51; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{22}H_{23}NNaO_3$, 372.1576, found 372.1576.

1-(2-Methyl-1,4-diphenyl-1*H*-pyrrol-3-yl)ethanone, 4c(i)

Reddish solid; m.p. = 107–109 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2923, 1638, 1495, 1406, 1231; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.54 (m, 3H), 7.41 (d, J = 4.4 Hz, 4H), 7.33–7.40 (m, 3H), 6.70 (s, 1H), 2.44 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.69, 138.78, 136.03, 135.31, 129.36, 129.34, 128.30, 128.12, 126.83, 126.32, 126.26, 122.59, 120.62, 31.12, 12.91; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{19}H_{17}NNaO$, 298.1208, found 298.1228.

1-(2-Methyl-4-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-3-yl)ethanone, 4c(ii)

White solid; m.p. = 87–89 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2923, 1654, 1517, 1405, 1221; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 4.3 Hz, 4H), 7.27–7.32 (m, 3H), 7.19–7.22 (m, 2H), 6.64 (s, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.65, 138.13, 136.23, 136.13, 135.44, 129.92, 129.35, 128.27, 126.78, 126.17, 126.05, 122.41, 120.70, 31.10, 21.11, 12.88; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO$, 312.1364, found 312.1382.

1-(1-(4-Bromophenyl)-2-methyl-4-phenyl-1*H*-pyrrol-3-yl) ethanone, 4c(iii)

White solid; m.p. = 122–124 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2924, 1654, 1494, 1409, 1221; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.6 Hz, 2H), 7.39–7.41 (m, 5H), 7.24 (d, J = 8.7 Hz, 2H), 6.66 (s, 1H), 2.42 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.64, 137.78, 135.76, 135.09, 132.60, 129.30, 128.35, 127.79, 126.98, 126.66, 122.93, 122.00, 120.34, 31.12, 12.85; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{19}H_{16}BrNNaO$, 376.0313, found 376.0321.

1-(2-Methyl-4-phenyl-1-propyl-1*H*-pyrrol-3-yl)ethanone, 4c(iv)

Color-less liquid; IR (cm^{-1}): $\bar{\upsilon}$ = 2926, 1649, 1509, 1414, 1276; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.38 (m, 5H), 6.52 (s, 1H), 3.82 (t, J = 7.4 Hz, 2H), 2.51 (s, 3H), 2.04 (s, 3H), 1.77–1.83 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.57, 136.53, 134.76, 129.37, 128.19, 126.58, 125.60, 121.60, 119.53, 48.19, 31.01, 24.05, 11.50, 11.28; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{16}H_{19}NNaO$, 264.1364, found 264.1378.

1-(1-Benzyl-2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone, 4c(v)

Color-less oil; IR (cm^{-1}): $\bar{\upsilon}$ = 2925, 1651, 1510, 1413, 1354; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.39 (m, 8H), 7.12 (d, J = 7.1 Hz, 2H), 6.57 (s, 1H), 5.09 (s, 2H), 2.47 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.63, 136.58, 136.32, 135.16, 129.37,

128.95, 128.22, 127.87, 126.71, 126.68, 125.93, 122.09, 120.12, 50.32, 31.08, 11.58; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO$, 312.1364, found 312.1372.

4-(4-Methoxyphenyl)-2-methyl-*N*,1-diphenyl-1*H*-pyrrole-3-carboxamide, 4d(i)

Brown solid; m.p. = 107–109 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3390, 2918, 1596, 1497, 1247; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 3H), 7.36 (d, J = 7.2 Hz, 2H), 7.25–7.27 (m, 4H), 6.99–7.05 (m, 3H), 6.72 (s, 1H), 3.87 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.05, 159.15, 138.95, 138.49, 135.57, 130.81, 129.34, 128.81, 128.01, 126.63, 126.28, 123.44, 123.12, 120.08, 119.38, 115.08, 114.35, 55.41, 12.54; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO_2$, 405.1579, found 405.1580.

4-(4-Chlorophenyl)-2-methyl-*N*,1-diphenyl-1*H*-pyrrole-3-carboxamide, 4d(ii)

Reddish sticky liquid; IR (cm^{-1}): $\bar{\upsilon}$ = 3312, 1642, 1594, 1494, 1439; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, J = 7.7 Hz, 2H), 7.44–7.47 (m, 3H), 7.40 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.25–7.29 (m, 3H), 7.07–7.09 (m, 2H), 6.78 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ163.94, 138.75, 138.21, 135.48, 133.21, 132.87, 130.40, 129.43, 129.02, 128.94, 128.22, 126.23, 123.81, 122.34, 120.33, 119.47, 115.35, 12.34; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{24}H_{19}ClN_2NaO$, 409.1084, found 409.1083.

4-(4-Methoxyphenyl)-2-methyl-*N*-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxamide, 4d(iii)

Deep yellow solid; m.p. = 133–135 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3390, 2918, 1662; 1516, 1438, 1313; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.44 (m, 2H), 7.21–7.29 (m, 9H), 6.96–7.03 (m, 3H), 6.67 (s, 1H), 3.85 (s, 3H), 2.51 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.09, 159.13, 138.55, 138.02, 136.43, 135.68, 130.83, 129.90, 128.81, 126.74, 126.09, 123.95, 123.39, 120.16, 119.37, 114.87, 114.35, 55.42, 21.12, 12.50; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{26}H_{24}N_2NaO_2$, 419.1735, found 419.1737.

4-(4-Chlorophenyl)-2-methyl-*N*-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxamide, 4d(iv)

White solid; m.p. = 182–184 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3302, 2918, 1638, 1517, 1432; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.4 Hz, 11.9 Hz, 4H), 7.24–7.33 (m, 8H), 7.08 (brs, 2H), 6.76 (s, 1H), 2.51 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.92, 138.29, 138.24, 136.25, 135.61, 133.19, 133.00, 130.43, 129.96, 128.99, 128.92, 126.04, 123.73, 122.17, 120.40, 119.44, 115.15, 21.11, 12.27; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{21}ClN_2NaO$, 423.1240, found 423.1255.

1-(4-Bromophenyl)-4-(4-methoxyphenyl)-2-methyl-*N*-phenyl-1*H*-pyrrole-3-carboxamide, 4d(v)

White sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 3397, 2836, 1661, 1595, 1492, 1314; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.25–7.28 (m, 7H), 7.03–7.06 (m, 1H), 7.01 (d, J = 8.7 Hz, 2H), 6.70 (s, 1H), 3.89 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.82, 159.26, 138.41, 137.97, 135.67, 135.41, 132.57, 130.80, 128.83, 127.82, 126.36, 123.52, 121.87, 119.83, 119.39, 115.54, 114.40, 55.43, 12.50; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{21}BrN_2NaO_2$, 483.0684, found 483.0684.

1-(4-Bromophenyl)-4-(4-chlorophenyl)-2-methyl-*N*-phenyl-1*H*-pyrrole-3-carboxamide, 4d(vi)

White solid; m.p. = 205–207 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3291, 2918, 1638, 1495, 1314; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.65 (m, 2H), 7.38–7.44 (m, 4H), 7.22–7.27 (m, 6H), 7.06 (q, J = 4.7 Hz, 9.1 Hz, 1H), 7.03 (brs, 1H), 6.72 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.66, 138.13, 137.77, 133.43, 132.66, 132.62, 130.41, 129.07, 128.96, 127.77, 125.98, 123.87, 122.72, 122.11, 120.06, 119.46, 115.78, 12.31; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{24}H_{18}BrClN_2NaO$, 487.0189, found 487.0184.

1,4-Bis(4-methoxyphenyl)-2-methyl-*N*-phenyl-1*H*-pyrrole-3-carboxamide 4d(vii)

Brown solid; m.p. = 132–135 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3319, 2836, 1642, 1593, 1438, 1315; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.47 (m, 2H), 7.23–7.30 (m, 7H), 6.99–7.06 (m, 5H), 6.68 (s, 1H), 3.89 (d, J = 4.5 Hz, 6H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.10, 159.20, 159.09, 138.53, 135.91, 131.83, 130.82, 128.81, 127.52, 126.71, 123.39, 122.79, 120.32, 119.34, 114.62, 114.42, 114.33, 55.59, 55.41, 12.43; ESI-HRMS (*m*/*z*): $[M + H]^+$ calcd. for $C_{26}H_{25}N_2O_3$, 413.1865, found: 413.1855.

1-(4-Chlorophenyl)-4-(4-methoxyphenyl)-2-methyl-*N*-phenyl-1*H*-pyrrole-3-carboxamide, 4d(viii)

White solid m.p. = 101–103 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3306, 2837, 1639, 1594, 1435, 1316; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.50 (m, 4H), 7.24–7.32 (m, 7H), 6.99–7.04 (m, 3H), 6.68 (s, 1H), 3.87 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.82, 159.25, 138.40, 137.45, 135.46, 133.94, 130.79, 129.56, 128.81, 127.50, 126.37, 123.50, 123.45, 119.88, 119.38, 115.47, 114.39, 55.41, 12.47; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{21}ClN_2NaO_2$, 439.1189, found 439.1188.

4-(4-Hydroxy-3-methoxyphenyl)-2-methyl-*N*,1-diphenyl-1*H*-pyrrole-3-carboxamide, 4d(ix)

Reddish brown solid, m.p. = 160–162 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3392, 2959, 1647, 1532, 1439, 1316; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.54 (m, 7H), 7.26–7.28 (m, 3H), 6.99–7.06 (m, 4H), 6.75 (s, 1H), 5.80 (brs, 1H), 3.80 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.09, 146.72, 145.29, 138.90, 138.45, 135.62, 129.36, 129.03, 128.88, 128.07, 126.28, 123.52, 123.48, 122.40, 120.10, 119.29, 115.02, 114.80, 112.32, 55.94, 12.53; ESI-HRMS (*m*/*z*): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO_3$, 421.1528, found 421.1529.

2-Isopropyl-*N*,1,4-triphenyl-1*H*-pyrrole-3-carboxamide, 4d(x)

White solid; m.p. = 177–180 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3404, 2964, 1663, 1594, 1432, 1315; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.55 (m, 5H), 7.37–7.41 (m, 4H), 7.26–7.33 (m, 5H), 7.10 (brs, 1H), 7.04–7.08 (m, 1H), 6.71 (s, 1H), 3.19–3.26 (m, 1H), 1.39 (d, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.79, 143.12, 139.74,

138.38, 134.41, 129.19, 128.82, 128.74, 128.47, 127.32, 126.88, 123.74, 123.57, 119.99, 119.69, 115.31, 26.60, 21.89; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{26}H_{24}N_2NaO$, 403.1786, found, 403.1787.

2-Isopropyl-*N*,1-diphenyl-4-*p*-tolyl-1*H*-pyrrole-3-carboxamide, 4d(xi)

Yellow solid; m.p. = 162–165 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3398, 2974, 1655, 1592, 1432, 1307; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.52 (m, 3H), 7.36–7.38 (m, 4H), 7.22–7.26 (m, 4H), 7.17 (d, J = 7.8 Hz, 2H), 7.12 (brs, 1H), 7.02–7.06 (m, 1H), 6.65 (s, 1H), 3.17–3.24 (m, 1H), 2.36 (s, 3H), 1.36 (d, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.85, 143.06, 139.81, 138.45, 136.58, 131.39, 129.44, 129.16, 128.80, 128.64, 128.41, 127.33, 123.68, 123.50, 119.89, 119.74, 115.22, 26.60, 21.87, 21.16; ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{27}H_{27}N_2O$, 395.2123, found, 395.2123.

4-(4-Fluorophenyl)-2-isopropyl-*N*,1-diphenyl-1*H*-pyrrole-3-carboxamide, 4d(xii)

White solid; m.p. = 182–185 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3391, 2958, 1654, 1594, 1434, 1313; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.55 (m, 5H), 7.37–7.40 (m, 2H), 7.28–7.30 (m, 4H), 7.05–7.11 (m, 4H), 6.68 (s, 1H), 3.15–3.22 (m, 1H), 1.38 (d, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.81, 142.90, 139.61, 138.25, 130.45, 130.10, 130.03, 129.23, 128.92, 128.53, 127.29, 123.92, 122.50, 119.88, 119.64, 115.75, 115.54, 115.40, 26.57, 21.94; ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{26}H_{24}FN_2O$, 399.1873, found, 399.1873.

Ethyl 4-(4-methoxyphenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate, 4e(i)

White solid; m.p. = 118–120 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2930, 1693, 1524, 1402, 1280; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.52 (m, 3H), 7.33–7.38 (m, 4H), 6.91 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.46 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89, 158.31, 139.02, 136.43, 130.32, 129.32, 128.01, 126.34, 126.22, 120.57, 115.73, 113.06, 111.66, 59.47, 55.28, 14.21, 12.77; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_3$, 358.1419, found 358.1440.

Ethyl 4-(4-chlorophenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate, 4e(ii)

White solid; m.p. = 62–64 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2918, 1698, 1517, 1413, 1221; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.51 (m, 3H), 7.28–7.37 (m, 6H), 6.69 (s, 1H), 4.19 (q, J = 7.1, 2H), 2.45 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 138.88, 136.88, 134.15, 132.17, 130.57, 129.38, 128.21, 127.69, 126.35, 125.50, 120.93, 111.63, 59.54, 14.16, 12.68; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{18}ClNNaO_2$, 362.0924, found 362.0933.

Ethyl 4-(4-hydroxy-3-methoxyphenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate, 4e(iii)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 3434, 1639, 1518, 1405, 1232; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.52 (m, 5H), 6.92–6.99 (m, 3H), 6.70 (s, 1H), 5.67 (brs, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 2.46 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.91, 145.70, 144.37, 138.98, 136.44, 129.34, 128.07, 127.71, 126.46, 126.33, 122.17, 120.65, 113.67, 112.25, 111.70, 59.49, 55.88, 14.25, 12.73; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_4$, 374.1368, Found 374.1390.

Ethyl 2,4-diphenyl-1-*p*-tolyl-1*H*-pyrrole-3-carboxylate, 4e(iv)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 2957, 1708, 1517, 1459, 1378; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.56 (m, 2H), 7.39–7.43 (m, 2H), 7.29–7.34 (m, 6H), 7.09 (d, J = 8.1 Hz, 2H), 7.00–7.03 (m, 2H), 6.96 (s, 1H), 4.07 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44, 137.79, 137.15, 136.77, 135.05, 131.61, 131.07, 129.53, 128.97, 127.86, 127.76, 127.55, 126.64, 126.47, 125.79, 122.03, 113.57, 59.79, 21.01, 13.67; ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{26}H_{24}NO_2$, 382.1807, found, 382.1805.

1-(4-(4-Methoxyphenyl)-2-methyl-1-phenyl-1*H*-pyrrol-3-yl) ethanone, 4e(v)

Reddish solid; m.p. = 107–109 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 2930, 1650, 1598, 1498, 1246; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.52 (m, 3H), 7.30–7.36 (m, 4H), 6.94 (d, J = 8.7 Hz, 2H), 6.65 (s, 1H), 3.86 (s, 3H), 2.42 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.72, 158.70, 138.79, 135.22, 130.41, 129.34, 128.33, 128.06, 126.24, 125.91, 122.59, 120.43, 113.73, 55.29, 31.08, 12.99; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{20}H_{19}NNaO_2$, 328.1313, found 328.1326.

1-(4-(4-Chlorophenyl)-2-methyl-1-phenyl-1*H*-pyrrol-3-yl) ethanone, 4e(vi)

Sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 2923, 1655, 1500, 1412, 1222; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.52 (m, 3H), 7.32–7.39 (m, 6H), 6.69 (s, 1H), 2.42 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.24, 138.62, 135.56, 134.53, 132.80, 130.51, 129.41, 129.10, 128.48, 126.26, 125.58, 122.49, 120.76, 31.17, 12.93; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{19}H_{16}ClNNaO$, 332.0818, found 332.0823.

2,5-Dimethyl-*N*,1,4-triphenyl-1*H*-pyrrole-3-carboxamide, 4f(i)

Yellow solid; m.p. = 182–184 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3393, 1657, 1594, 1438, 1311; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41–7.57 (m, 8H), 7.30 (d, J = 7.0 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 7.07 (brs, 1H), 6.98 (t, J = 7.3 Hz, 1H), 2.44 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.03, 138.63, 137.71, 135.38, 135.29, 131.04, 129.46, 128.95, 128.71, 128.61, 128.30, 127.48, 126.44, 123.14, 119.45, 119.11, 114.10, 12.62, 11.20; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{25}H_{22}N_2NaO$, 389.1630, found 389.1627.

1-(4-Methoxyphenyl)-2,5-dimethyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4f(ii)

White solid, m.p. = 168–170 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3400, 2838, 1660, 1594, 1436; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.47 (m, 4H) 7.33 (d, J = 7.1 Hz, 1H) 7.16–7.25 (m, 6H) 7.11–7.14 (m, 2H) 7.00–7.04

(m, 1H) 3.89 (s, 3H) 2.27 (s, 3H) 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.05, 159.51, 138.66, 135.61, 135.48, 131.03, 130.37, 129.27, 128.92, 128.69, 127.41, 126.74, 123.08, 119.18, 119.08, 114.57, 113.85, 55.55, 12.57, 11.14; ESI-HRMS (m/z): $[M + Na]^+$ calcd. for $C_{26}H_{24}N_2NaO_2$, 419.1735, found 419.1734.

2-Methyl-*N*,1,4,5-tetraphenyl-1*H*-pyrrole-3-carboxamide, 4f(iii)

White sticky solid; IR (cm^{-1}): $\bar{\upsilon}$ = 3390, 2912, 1660, 1497, 1311; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.37 (m, 7H), 7.15–7.21 (m, 4H), 7.07–7.10 (m, 3H), 6.98–7.01 (m, 4H), 6.87–6.89 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.97, 138.53, 137.81, 136.29, 134.94, 131.48, 131.41, 131.37, 130.88, 128.95, 128.80, 128.79, 128.74, 128.13, 127.58, 127.47, 126.71, 123.30, 121.10, 119.23, 115.02, 12.67; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{30}H_{24}N_2NaO$, 451.1786, found 451.1795.

1-Benzyl-2-methyl-*N*,4,5-triphenyl-1*H*-pyrrole-3-carboxamide, 4f(iv)

White solid; m.p. = 140–143 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3269, 3030, 1648, 1529, 1436, 1319; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.34 (m, 8H), 7.14–7.22 (m, 5H), 7.05–7.09 (m, 5H), 6.94–6.99 (m, 3H), 5.08 (s, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.99, 138.56, 137.67, 135.49, 134.93, 131.65, 131.43, 131.33, 131.12, 128.83, 128.71, 128.62, 128.13, 127.72, 127.31, 127.23, 125.72, 123.22, 120.98, 119.18, 114.84, 47.77, 11.80; ESI-HRMS (m/z): $[M + H]^+$ calcd for $C_{31}H_{27}N_2O$, 443.2123, found, 443.2123.

5-(4-Fluorophenyl)-2-methyl-*N*-1,4-triphenyl-1*H*-pyrrole-3-carboxamide, 4f(v)

Yellow solid; m.p. = 178–180 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3408, 1660, 1594, 1436, 1313; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 8H), 7.07–7.23 (m, 7H), 6.99 (t, J = 7.4 Hz, 1H), 6.84–6.88 (m, 2H), 6.71 (t, J = 8.7 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.86, 162.78, 160.33, 138.48, 137.64, 136.33, 134.75, 132.56, 132.48, 131.34, 130.42, 129.07, 128.87, 128.77, 128.75, 128.27, 127.60, 127.47, 127.44, 123.35, 121.25, 119.23, 115.01, 114.85, 114.63, 12.64; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{30}H_{23}FN_2$-NaO, 469.1692, found 469.1691.

5-(4-Fluorophenyl)-1-(4-methoxyphenyl)-2-methyl-*N*,4-diphenyl-1*H*-pyrrole-3-carboxamide, 4f(vi)

Yellow solid, m.p. = 186–188 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3384, 2840, 1655, 1592, 1436, 1312; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (brs, 5H), 7.21 (t, J = 7.8 Hz, 2H), 6.98–7.12 (m, 6H), 6.87 (d, J = 8.6 Hz, 4H), 6.74 (t, J = 8.6 Hz, 2H), 3.82 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.92, 162.73, 160.28, 159.13, 138.46, 136.63, 134.79, 132.57, 132.49, 131.33, 130.59, 130.27, 129.71, 128.85, 128.75, 127.54, 123.32, 120.99, 119.21, 114.85, 114.71, 114.64, 114.18, 55.43, 12.61; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{31}H_{25}FN_2NaO_2$, 499.1798, found 499.1798.

5-(4-Fluorophenyl)-2-methyl-*N*,4-diphenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxamide, 4f(vii)

Yellow solid, m.p. = 186–188 °C; IR (cm^{-1}): $\bar{\upsilon}$ = 3408, 2923, 1662, 1595, 1315; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (brs, 5H), 6.99–7.22 (m, 10H), 6.85–6.89 (m, 2H), 6.72 (t, J = 8.7 Hz, 2H), 2.52 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.90, 149.36, 138.46, 138.20, 136.45, 134.92, 134.78, 132.54, 132.46, 131.34, 130.41, 129.68, 128.84, 128.74, 128.43, 127.54, 123.31, 121.07, 119.19, 114.82, 114.61, 21.16, 12.63; ESI-HRMS (m/z): $[M + Na]^+$ calcd for $C_{31}H_{25}FN_2NaO$, 483.1849, found 483.1848.

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