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Synthesis of alkyl-substituted pyrroles by three-component coupling of carbonyl compound, amine and nitro-alkane/alkene on a solid surface of silica gel/alumina under microwave irradiation

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Abstract—Efficient synthesis of highly substituted alkylpyrroles and fused pyrroles has been achieved by a three-component coupling of (a) α,β-unsaturated aldehyde/ketone, amine and nitroalkane and (b) α,β-unsaturated nitroalkene, aldehyde/ketone and amine on the surface of silica gel and alumina without any solvent under microwave irradiation.

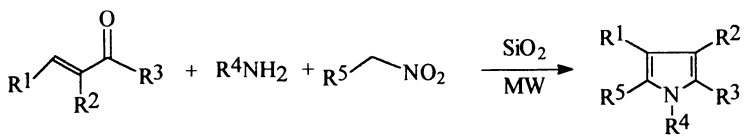
1. Introduction

The synthesis of pyrroles has remained an extremely attractive domain in heterocyclic chemistry as they constitute the core unit of many natural products[1] and serve as the building blocks for porphyrin synthesis.[2] Several alkylpyrrole derivatives have also been shown to possess remarkable biological activity.[3] Although there are quite a number of methods available for the synthesis of pyrroles,[4] most of them involve multistep synthetic operations which lower the overall yield. Recently, a few one-step procedures[5] have been reported; however these are not very satisfactory with regard to reaction conditions (long reaction period), yield, generality and scope of substitution at the ring. Thus, there is a need for a simple, efficient and more general method for the synthesis of this useful heterocyclic nucleus.

The art of performing efficient chemical transformation coupling three or more components in a single operation by a reusable catalyst avoiding toxic reagents, large amount of solvents and expensive purification techniques, represents a fundamental target of the modern organic synthesis.[6] As a part of our program to achieve this goal utilising surface mediated reactions,[7] we wish to report here an efficient microwave-assisted one-pot synthesis of pyrroles by two alternative routes: (a) coupling of an α,β-unsaturated carbonyl compound, an amine and a nitroalkane on the surface of silica gel[8] (Scheme 1) and (b) coupling of a carbonyl compound, an amine and an α,β-unsaturated nitroalkene on the surface of alumina (Scheme 2).

2. Results and discussion

In a typical general procedure for route **a**, a mixture of α,β-unsaturated aldehyde or ketone, an amine and nitroalkane adsorbed on the surface of silica gel was irradiated by microwave in a domestic microwave oven for a certain period of time as required to complete the reaction. Elution of the reaction mixture with ether followed by evaporation of solvent furnished the crude product which was purified by column chromatography. The reaction delineated in route **b** is also carried out under similar conditions however on the surface of alumina. Although, either silica gel or alumina can be used as a surface for these transformations, silica gel for route **a** and alumina for route **b** are chosen for better performance with regard to yield in respective cases.



Scheme 1.

Keywords: pyrrole; microwave; silica gel; alumina.

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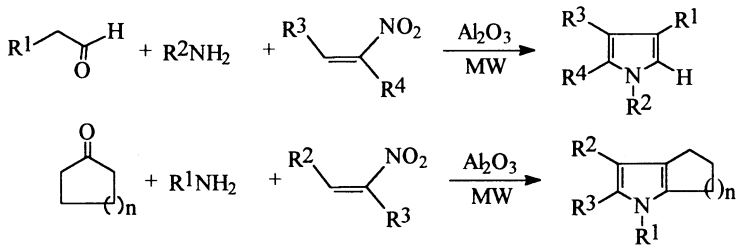
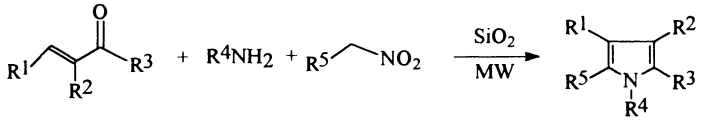
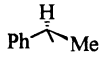
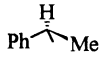


Scheme 2.

Table 1. Synthesis of pyrroles from coupling of conjugated carbonyl compounds, amines and nitroalkanes



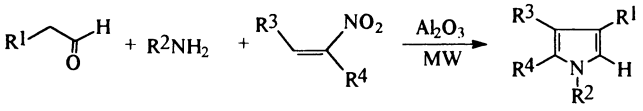
Entry	R^1	R^2	R^3	R^4	R^5	Time (min)	Yield (%)[a]
1	Ph	H	H	$PhCH_2$	Me	5	60
2	Ph	H	H	$PhCH_2$	Et	8	62
3	Ph	H	Ph	$PhCH_2$	Me	10	65
4	Ph	H	Me	$PhCH_2$	Me	8	64
5	Ph	H	Me	$PhCH_2$	Et	10	66
6	H	H	Me	$PhCH_2$	Me	5	60
7	H	H	Me		Me	5	60
8	Ph	H	H		Me	5	62
9	Ph	H	Me		Me	10	66
10	Ph	H	H	Me_2CH	Me	5	64
11		H	Me	Me_2CH	Me	5	68
12		H	Me	$PhCH_2$	Me	5	72
13		H	Me	*n*-Bu	Et	10	68
14	*n*-Pr	Et	H	$PhCH_2$	Me	5	60
15	*n*-Pr	Et	H		Me	5	65
16	Ph	H	H	*n*-Pr	Me	10	62
17	Ph	H	H	*n*-Bu	Me	8	61
18	Ph	H	Me	*n*-Bu	Me	10	65
19	$-(CH_2)_4-$		Me	*n*-Bu	Me	8	65

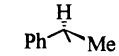
[a] Yields refer to those of pure isolated products

A wide range of structurally varied α,β-unsaturated aldehydes and ketones including aromatic, aliphatic and heterocyclic units were coupled with a variety of aliphatic and aromatic amines and nitroalkane by this procedure through a single step operation to produce the corresponding alkyl substituted pyrroles as summarized in Table 1. The reaction with nitromethane does not proceed at all; however higher homologues like nitroethane and nitropropane underwent smooth reactions. This procedure can put the desired alkyl substituents at any selected position of the pyrrole ring with proper choice of coupling components and thus this route provides easy access to alkyl-substituted pyrroles. A chiral amine has also been used to furnish pyrrole derivatives (entries 8,9) attached with a chiral moiety which can be of much importance for further manipulation.

In the alternative route coupling of an aldehyde with an amine and α,β-unsaturated nitroalkene on the surface of alumina under microwave irradiation produced 1,3,4,5-alkyl-substituted pyrroles. The results are presented in

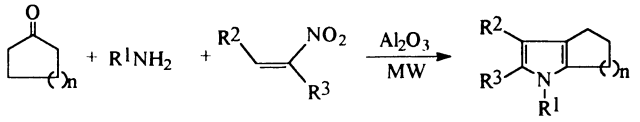
Table 2. Synthesis of pyrroles from coupling of aldehydes, amines and α,β-unsaturated nitroalkenes

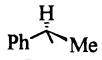
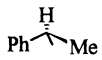


Entry	R^1	R^2	R^3	R^4	Time (min)	Yield (%)[a]
1	Me	*n*-Pr	Ph	Me	15	74
2	Me	*n*-Bu	Ph	Me	15	71
3	Me	Me_2CH	Ph	Me	15	78
4	Me	$PhCH_2$	Ph	Me	13	75
5	Me		Ph	Me	13	75
6	Et	*n*-Pr	Ph	Me	15	72
7	Et	*n*-Bu	Ph	Me	15	71
8	Me	*n*-Bu	*p*-ClC_6H_4	Me	13	76
9	Me	$PhCH_2$	*p*-ClC_6H_4	Me	13	78
10	Me	Me_2CH	*p*-ClC_6H_4	Me	13	80
11	Me	Me_2CH	*p*-ClC_6H_4	Et	15	81
12	Me	*n*-Bu	*p*-ClC_6H_4	Et	15	77

[a] Yields refer to those of pure isolated products

Table 3. Synthesis of pyrroles from coupling of ketone, amines and α,β-unsaturated nitroalkenes



Entry	*n*	R^1	R^2	R^3	Time (min)	Yield (%)[a]
1	1	*n*-Bu	Ph	Me	15	78
2	2	*n*-Bu	Ph	Me	15	84
3	2	$PhCH_2$	Ph	Me	15	81
4	2		Ph	Me	13	79
5	3	*n*-Bu	Ph	Me	15	78
6	4	*n*-Bu	Ph	Me	13	74
7	1	$PhCH_2$	*p*-ClC_6H_4	Me	15	78
8	2	Me_2CH	*p*-ClC_6H_4	Me	15	85
9	2	$PhCH_2$	*p*-ClC_6H_4	Me	15	82
10	2		*p*-ClC_6H_4	Me	15	80
11	2	*n*-Bu	*p*-ClC_6H_4	Me	13	78
12	1	$PhCH_2$	*p*-ClC_6H_4	Et	13	79
13	2	$PhCH_2$	*p*-ClC_6H_4	Et	15	82
14	2	Me_2CH	*p*-ClC_6H_4	Et	13	86
15	2	$PhCH_2$	*p*-FC_6H_4	Me	15	82

[a] Yields refer to those of pure isolated products

Table 2. In this synthesis substitution at the α-position of nitroalkene is essential without which the reaction takes a different course which is being investigated separately and will be disclosed in the future. Open-chain ketones in place of aldehydes also lead to different products the identities of which are yet to be established. However, very interestingly cyclic ketones under similar treatment provided fused pyrroles. The results are reported in Table 3.

In general, the reactions are very fast and clean. The yields are reasonably good for a three-component coupling reaction. None of these operations involves any strong acid, base and solvent. Moreover, silica gel and alumina used can be recycled after being washed with methanol and dried. Conventional heating in dry media in place of microwave leads to messy product with formation of tarry material. However, prolonged reflux in THF solution in presence of silica gel or alumina affords the corresponding pyrroles in much lower yields.

Presumably, the imine formed by the initial reaction of a carbonyl compound and amine on the surface of silica gel or alumina[9] undergoes coupling with nitroalkane leading to pyrrole nucleus following the course outlined by Ishii in a similar synthesis.[5a,c]

3. Conclusion

In conclusion, the present microwave-assisted one-pot procedure on the surface of silica gel and alumina provides an efficient methodology for the synthesis of alkyl-substituted pyrroles and fused pyrroles from easily available starting materials by a simple three-component coupling reaction. The notable advantages of this procedure are: (a) reasonably good yields; (b) fast reaction; (c) mild reaction conditions; (d) choice of appropriate substituents on the pyrrole ring; (e) general applicability and (f) above all, green synthesis avoiding toxic reagents and solvents. Thus, it provides a better and more practical alternative to the existing methodologies[3,4] for the synthesis of pyrroles and we believe, our procedure will find important applications in the synthesis of pyrroles to cater the needs of academia as well as pharmaceutical industries.

4. Experimental

4.1. General

Melting points were determined on a glass disk with an electrical bath and are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were run in $CDCl_3$ solutions. IR spectra were taken as KBr plates for solids and as neat for liquids. Elemental analyses were done by a Perkin Elmer autoanalyzer. Silica gel (HF 254, E-Merck, India) was used as available. Alumina (neutral, Brockmann activity 1 for column chromatography) was activated by heating at 180°C for 4 h under vacuum (0.05 mm of Hg) before use. The starting materials are all commercially available and were distilled before use. A domestic microwave oven (BPL-Sanyo, India; multipower; power source; 230V, 50 Hz; microwave frequency: 2450 MHz) was used for all reactions.

4.2. General procedure for the synthesis of pyrroles. Route a

4.2.1. *N*-Benzyl-2-methyl-3-phenylpyrrole (entry 1, Table 1). A mixture of cinnamaldehyde (264 mg, 2 mmol), benzyl amine (214 mg, 2 mmol) and nitroethane (450 mg, 6 mmol) was uniformly adsorbed on the surface of silica gel (3 g) stirring for five minutes in a pyrex round bottomed flask at room temperature under moisture guard of anhydrous $CaCl_2$. The flask was then placed on a bed of silica gel in a porcelain basin and irradiated by microwave in a domestic microwave oven at 120 W for five minutes (TLC). The reaction mass was eluted with ether and the ether extract was evaporated to leave the crude product which was purified by column chromatography over silica gel (hexane–ether 98:2) to afford the pure product (296 mg, 60%) as a colourless oil, IR 3058, 3030, 1701, 1602, 1550 cm^{-1}; ^1H NMR δ 7.41–7.01 (m, 8H), 7.00 (d, J=7.2 Hz, 2H), 6.64 (d, J=2.7 Hz, 1H), 6.32 (d, J=2.7 Hz, 1H), 4.99 (s, 2H), 2.22 (s, 3H); ^{13}C NMR δ 138.7, 138.1, 129.3 (2), 128.9 (2), 128.5 (2), 127.9 (2), 125.7 (2), 125.6, 123.1, 121.2, 108.3, 51.2, 11.4. Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.32; H, 6.85; N, 5.54.

This procedure is followed for the synthesis of all pyrroles listed in Table 1. The known compounds (entries 14, 17, 18, 19) have been identified by comparison of spectral data and mp with those reported.[5a] The mp, spectral and analytical data of all new compounds are presented below in order of their entries.

4.2.2. *N*-Benzyl-2-ethyl-3-phenylpyrrole (entry 2). Colourless oil; IR (neat) 3030, 2966, 2931, 1600, 1498, 1454, 1353, 1249, 727 cm^{-1}; ^1H NMR δ 7.42–7.17 (m,

8H), 7.00 (d, J=6.9 Hz, 2H), 6.57 (d, J=3.0 Hz, 1H), 6.29 (d, J=3.0 Hz, 1H), 5.05 (s, 2H), 2.65 (q, J=7.5 Hz, 2H), 1.12 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 139.0, 138.1, 131.6, 129.2 (2), 128.8 (2), 128.3 (2), 127.9, 126.8, 125.7, 122.6 (2), 121.1, 108.6, 50.8, 18.4, 15.7. Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.21; H, 7.26; N, 5.31.

4.2.3. *N*-Benzyl-3,5-diphenyl-2-methylpyrrole (entry 3). Colourless cubic crystal, mp 103–105°C; IR (KBr) 3039, 2927, 1600, 1448, 1348, 758, 700 cm^{-1}; ^{1}H NMR δ 7.47 (d, J=7.1 Hz, 2H), 7.36–7.24 (m, 11H), 7.00 (d, J=7.1 Hz, 2H), 6.45 (s, 1H), 5.20 (s, 2H), 2.27 (s, 3H); ^{13}C NMR δ 138.8, 137.1, 134.3, 133.4, 128.9, 128.8 (2), 128.7 (2), 128.4 (2), 128.3, 128.0, 127.6, 127.0, 126.9, 126.6 (2), 125.6, 125.2, 122.4, 108.5, 47.9, 11.3. Anal. Calcd for $C_{24}H_{21}N$: C, 89.13; H, 6.54; N, 4.33. Found: C, 89.01; H, 6.45; N, 4.21.

4.2.4. *N*-Benzyl-2,5-dimethyl-3-phenylpyrrole (entry 4). Colourless cubic crystal, mp 52–54°C; IR (KBr) 3035, 2931, 1604, 1456, 1346, 748, 702 cm^{-1}; ^{1}H NMR δ 7.43–7.21 (m, 8H), 6.78 (d, J=7.4 Hz, 2H), 6.10 (s, 1H), 5.05 (s, 2H), 2.25 (s, 3H), 2.18 (s, 3H); ^{13}C NMR δ 138.8, 138.1, 129.2 (2), 128.8 (2), 128.7 (2), 128.4, 128.3 (2), 126.1, 125.4, 124.8, 121.4, 106.9, 47.4, 12.8, 11.6. Anal. Calcd for $C_{19}H_{19}N$; C, 87.31; H, 7.33; N, 5.36. Found: C, 87.20; H, 7.29; N, 5.29.

4.2.5. *N*-Benzyl-2-ethyl-5-methyl-3-phenylpyrrole (entry 5). Colourless oil; IR (neat) 2966, 2931, 1602, 1527, 1452, 1350, 761, 727, 698 cm^{-1}; ^{1}H NMR δ 7.42–6.88 (m, 8H), 6.86 (d, J=6.9 Hz, 2H), 6.08 (s, 1H), 5.04 (s, 2H), 2.63 (q, J=7.5 Hz, 2H), 2.10 (s, 3H), 1.12 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 139.2, 138.2, 131.0, 129.2 (2), 128.8 (2), 128.3 (2), 127.6, 126.0 (2), 125.2, 124.9, 121.3, 107.4, 47.3, 18.8, 16.3, 12.8. Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.11; H, 7.61; N, 4.99.

4.2.6. *N*-Benzyl-2,5-dimethylpyrrole (entry 6). Colourless oil; IR (neat) 2995, 2912, 1652, 1434, 1406, 1056, 1029, 731 cm^{-1}; ^{1}H NMR δ 7.31–7.20 (m, 3H), 6.88 (d, J=6.9 Hz, 2H), 5.85 (s, 2H), 4.85 (s, 2H), 2.13 (s, 6H); ^{13}C NMR δ 139.0, 129.1 (2), 128.4, 127.4, 126.9, 126.1 (2), 105.8 (2), 47.1, 12.9 (2). Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.54. Found: C, 84.14; H, 8.05; N, 7.42.

4.2.7. *N*-Cyclohexyl-2,5-dimethylpyrrole (entry 7). Colourless oil; IR (neat) 2985, 2044, 1620, 1326, 1187, 906, 733 cm^{-1}; ^{1}H NMR δ 5.73 (s, 2H), 3.91 (m, 1H), 2.29 (s, 6H), 1.95–1.21 (m, 10H); ^{13}C NMR δ 128.3 (2), 106.4 (2), 56.8, 32.8 (2), 27.1 (2), 26.1 (2), 14.9. Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.16; H, 10.72; N, 7.79.

4.2.8. 2-Methyl-*N*-(α)-methylbenzyl-3-phenylpyrrole (entry 8). Colourless oil; IR (neat) 3028, 2979, 1600, 1496, 1448, 1309, 975, 761, 700 cm^{-1}; ^{1}H NMR δ 7.41–7.27 (m, 8H), 7.02 (d, J=8.2 Hz, 2H), 6.61 (d, J=3.0 Hz, 1H), 6.35 (d, J=3.0 Hz, 1H), 5.33 (q, J=7.0 Hz, 1H), 2.20 (s, 3H), 1.83 (d, J=7.0 Hz, 3H); ^{13}C NMR δ 144.0, 137.9, 130.9, 129.4 (2), 128.6, 128.5, 127.9, 127.6 (2),126.1, 125.8, 122.8, 122.6, 117.1, 107.9, 55.6, 22.9, 11.3. Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.19; H, 7.26; N, 5.27.

4.2.9. 2,5-Dimethyl-*N*-(α)-methylbenzyl-3-phenylpyrrole (entry 9). Colourless cubic crystal, mp 46–48°C; IR (KBr) 2991, 2912, 1658, 1436, 1406, 1056, 1029, 702 cm^{-1}; ^{1}H NMR δ 7.39–7.07 (m, 10H), 6.03 (s, 1H), 5.54 (q, J=7.2 Hz, 1H), 2.19 (s, 3H), 2.11 (s, 3H), 1.95 (d, J=7.2 Hz, 3H); ^{13}C NMR δ 142.2, 137.6, 128.4 (2), 128.1 (2), 127.8 (2), 126.8, 125.9, 125.6, 124.7, 124.6, 124.5, 121.2, 107.0, 52.6, 19.3, 13.6, 12.2. Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.11; H, 7.61; N, 4.99.

4.2.10. *N*-Isopropyl-2-methyl-3-phenylpyrrole (entry 10). Colourless cubic crystal, mp 74–76°C; IR (KBr) 2976, 2931, 1598, 1552, 1496, 1452, 1342, 1234, 763, 700 cm^{-1}; ^{1}H NMR δ 7.40–7.17 (m, 5H), 6.74 (d, J=2.9 Hz, 1H), 6.28 (d, J=2.9 Hz, 1H), 4.35–4.26 (m, 1H), 2.35 (s, 3H), 1.43 (d, J=6.7 Hz, 6H); ^{13}C NMR δ 137.6, 128.2 (2), 124.9 (2), 124.2, 121.7, 114.8 (2), 107.5, 47.1, 23.6 (2), 10.8. Anal. Calcd. For $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.25; H, 8.52; N, 6.91.

4.2.11. *N*-Isopropyl-3-(2-furfuryl)-2,5-dimethylpyrrole (entry 11). Colourless oil; IR (neat) 2974, 2933, 1622, 1311, 1199, 910, 731 cm^{-1}; ^{1}H NMR δ 7.46 (s, 1H), 6.52–6.50 (m, 1H), 6.27 (d, J=3.2 Hz, 1H), 6.17 (s, 1H), 5.54 (m, 1H), 2.51 (s, 3H), 2.41 (s, 3H), 1.59 (d, J=6.2 Hz, 6H); ^{13}C NMR δ 153.0, 140.1, 128.1, 125.1, 112.1, 111.3, 106.1, 103.2, 47.7, 22.6 (2), 14.5, 12.9. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.70; H, 8.32; N, 6.80.

4.2.12. *N*-Benzyl-3-(2-furfuryl)-2,5-dimethylpyrrole (entry 12). Colourless oil; IR (neat) 2976, 2918, 1624, 1452, 1338, 908, 727 cm^{-1}; ^{1}H NMR δ 7.35–7.24 (m, 5H), 6.91 (d, J=6.9 Hz, 1H), 6.40–6.39 (m, 1H), 6.19–6.16 (m, 2H), 5.03 (s, 2H), 2.31 (s, 3H), 2.16 (s, 3H); ^{13}C NMR δ 152.8, 140.0, 138.4, 129.2 (2), 128.5, 128.1, 127.5, 126.0, 125.2, 112.0, 111.3, 104.9, 102.8, 47.1, 12.6, 11.7. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.12; H, 6.71; N, 5.51.

4.2.13. *N*-Butyl-2-ethyl-3-(2-furfuryl)-5-methylpyrrole (entry 13). Colourless oil; IR (neat) 2962, 2871, 1620, 1463, 1340, 910, 779, 732 cm^{-1}; ^{1}H NMR δ 7.42 (s, 1H), 6.48–6.47 (m, 1H), 6.24 (d, J=3.0 Hz, 1H), 6.17 (s, 1H), 3.84 (t, J=7.8 Hz, 2H), 2.91 (q, J=7.5 Hz, 2H), 2.32 (s, 3H), 1.76–1.67 (m, 2H), 1.52–1.45 (m, 2H), 1.31 (t, J=7.5 Hz, 3H), 1.07 (t, J=7.8 Hz, 3H); ^{13}C NMR δ 152.9, 139.9, 130.9, 127.6, 111.3, 111.0, 104.9, 102.3, 43.7, 34.1, 20.6, 19.2, 15.4, 14.3, 12.8. Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.79; H, 9.09; N, 5.99.

4.2.14. *N*-Cyclohexyl-4-ethyl-2-methyl-3-propylpyrrole (entry 15). Colourless oil; IR (neat) 3011, 2981, 1629, 1497, 1301, 970, 711 cm^{-1}; ^{1}H NMR δ 6.33 (s, 1H), 3.94–3.85 (m, 1H), 2.39 (q, J=7.5 Hz, 2H), 2.31 (t, J=7.3 Hz, 2H), 2.24 (s, 3H), 1.95–1.21 (m, 12H), 1.12 (t, J=7.5 Hz, 3H), 6.94 (t, J=2.4 Hz, 3H); ^{13}C NMR δ 128.1, 127.6, 118.9, 115.5, 56.7, 31.8 (2), 26.2 (2), 25.1, 24.6, 23.5,

22.5, 14.2, 13.8, 11.7. Anal. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.66; N, 6.00. Found: C, 82.21; H, 11.57; N, 5.92.

4.2.15. 2-Methyl-3-phenyl-*N*-propylpyrrole (entry 16). Colourless oil; IR (neat) 2973, 2932, 1699, 1687, 1362, 1190, 713 cm^{-1}; ^1H NMR δ 7.40–7.17 (m, 5H), 6.64 (d, J=3.0 Hz, 1H), 6.26 (d, J=3.0 Hz, 1H), 3.85 (t, J=7.4 Hz, 2H), 2.33 (s, 3H), 1.92–1.86 (m, 2H), 1.07 (t, J=7.4 Hz, 3H); ^{13}C NMR δ 137.6, 130.4 (2), 129.2 (2), 128.2, 125.6, 122.2, 118.1, 116.3, 47.6, 25.2, 11.4, 10.8. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.21; H, 5.51; N, 6.92.

4.2.16. *N*-Benzyl-2,4-dimethyl-3-phenylpyrrole (route b) (entry 4, Table 2). A mixture of propionaldehyde (116 mg, 2 mmol), benzyl amine (214 mg, 2 mmol) and a solution of α-methyl-β-nitrostyrene (326 mg, 2 mmol) in THF (2 mL) was uniformly adsorbed on the surface of alumina by stirring for five minutes and then THF was removed completely under reduced pressure. The residual solid mass was then irradiated by microwave as described in the previous experiment for 13 minutes. Usual work and purification provided the pure pyrrole (392 mg, 75%) as a colourless oil, IR 2930, 2878, 1701, 1531 cm^{-1}; ^1H NMR δ 7.39–7.04 (m, 10H), 6.47 (s, 1H), 5.0 (s, 2H), 2.13 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 138.3, 136.8, 130.4, 130.0, 129.8 (2), 128.8 (2), 128.1 (2), 127.9, 125.3 (2), 122.3, 118.4, 116.4, 50.3, 11.0, 10.5. Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.20; H, 7.26; N, 5.22.

This procedure is followed for the synthesis of all pyrroles listed in Table 2. The mp, spectral and analytical data of all new compounds are summarized below in order of their entries.

4.2.17. 2,4-Dimethyl-3-phenyl-*N*-propylpyrrole (entry 1). Colourless oil; IR (neat) 2972, 2930, 1709, 1685, 1192, 732 cm^{-1}; ^1H NMR δ 7.52–7.33 (m, 5H), 6.57 (s, 1H), 3.86 (t, J=7.3 Hz, 2H), 2.33 (s, 3H), 2.25 (s, 3H), 1.92–1.84 (m, 2H), 1.07 (t, J=7.4 Hz, 3H); ^{13}C NMR δ 137.5, 130.4 (2), 129.1, 128.4 (2), 125.6, 122.2, 118.1, 116.3, 48.8, 25.1, 11.9, 11.4, 11.0. Anal. Calcd for $C_{15}H_{19}N$: C, 84.86; H, 8.98; N, 6.57. Found: C, 84.72; H, 8.92; N, 6.51.

4.2.18. *N*-Butyl-2,4-dimethyl-3-phenylpyrrole (entry 2). Colourless oil; IR (neat) 2971, 2959, 1526, 1352, 1081, 831 cm^{-1}; ^1H NMR δ 7.39–7.18 (m, 5H), 6.44 (s, 1H), 3.74 (t, J=7.2 Hz, 2H), 2.04 (s, 3H), 1.73 (s, 3H), 1.73–1.70 (m, 2H), 1.42–1.37 (m, 2H), 0.95 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 136.9, 130.1 (2), 130.0, 128.4, 127.8 (2), 125.1, 116.1, 115.8, 46.3, 33.4, 20.0, 13.7, 11.7, 10.3. Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.41; H, 9.25; N, 6.04.

4.2.19. 2,4-Dimethyl-*N*-isopropyl-3-phenylpyrrole (entry 3). Colourless oil; IR (neat) 2974, 2931, 1685, 1363, 1193, 759 cm^{-1}; ^1H NMR δ 7.41–7.18 (m, 5H), 6.53 (s, 1H), 4.26 (m, 1H), 2.21 (s, 3H), 2.10 (s, 3H), 1.41 (d, J=6.6 Hz, 6H); ^{13}C NMR δ 137.4, 130.9 (2), 130.7, 130.5, 130.4, 129.2 (2), 125.2, 116.5, 47.2, 24.0 (2), 12.8, 11.6. Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.35; H, 8.92; N, 6.51.

4.2.20. 2,4-Dimethyl-*N*-(α)-methylbenzyl-3-phenylpyrrole (entry 5). Colourless oil; IR (neat) 2973, 2940, 1701, 1482, 1369, 1082, 731 cm^{-1}; ^1H NMR δ 7.42–7.22 (m, 8H), 7.09 (d, J=7.2 Hz, 2H), 6.70 (s, 1H), 5.32 (q, J=7.2 Hz, 1H), 2.20 (s, 3H), 2.12 (s, 3H), 1.85 (d, J=7.2 Hz, 3H); ^{13}C NMR δ 143.7, 136.7, 129.9 (2), 128.9 (2), 128.5 (2), 127.8 (2), 127.0, 125.8, 125.1 (2), 124.9, 116.0, 114.6, 54.8, 22.3, 11.2, 10.7. Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.04; H, 7.58; N, 4.97.

4.2.21. 4-Ethyl-2-methyl-3-phenyl-*N*-propylpyrrole (entry 6). Colourless oil; IR (neat) 3029, 2952, 1665, 1482, 1089, 731 cm^{-1}; ^1H NMR δ 7.37–7.18 (m, 5H), 6.48 (s, 1H), 3.84 (t, J=7.3 Hz, 2H), 2.48 (q, J=7.5 Hz, 2H), 2.17 (s, 3H), 1.91–1.82 (m, 2H), 1.07 (t, J=7.4 Hz, 3H), 0.95 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 137.5, 130.4 (2), 128.2 (2), 125.3, 125.1, 123.4, 121.3, 117.1, 47.4, 24.9, 21.5, 20.1, 11.4, 11.0. Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.42; H, 9.22; N, 6.09.

4.2.22. *N*-Butyl-4-ethyl-2-methyl-3-phenylpyrrole (entry 7). Colourless oil; IR (neat) 3030, 2926, 1625, 1476, 1091, 731 cm^{-1}; ^1H NMR δ 7.38–7.18 (m, 5H), 6.45 (s, 1H), 3.78 (t, J=7.5 Hz, 2H), 2.48 (q, J=7.5 Hz, 2H), 2.17 (s, 3H), 1.75–1.67 (m, 2H), 1.43–1.37 (m, 2H), 1.10 (t, J=7.5 Hz, 3H), 0.96 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 137.5, 130.5 (2), 128.1 (2), 125.6, 125.5, 123.7, 121.5, 116.8, 46.9, 33.9, 20.5, 19.3, 15.2, 14.2, 10.8. Anal. Calcd for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.43; H, 9.51; N, 5.72.

4.2.23. *N*-Butyl-3-(4-chlorophenyl)-2,4-dimethylpyrrole (entry 8). Colourless oil; IR (neat) 2957, 2931, 1647, 1605, 1382, 702 cm^{-1}; ^1H NMR δ 7.43 (d, J=8.4 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 6.47 (s, 1H), 3.80 (t, J=7.3 Hz, 2H), 2.21 (s, 3H), 2.03 (s, 3H), 1.73–1.68 (m, 2H), 1.42–1.36 (m, 2H), 0.94 (t, J=7.3 Hz, 3H); ^{13}C NMR δ 135.9, 132.1, 131.1 (2), 130.3 (2), 129.3, 125.6, 118.2, 116.1, 46.8, 33.8, 20.4, 13.3, 11.3, 10.9. Anal. Calcd for $C_{16}H_{20}NCl$: C, 73.41; H, 7.70; N, 5.35. Found: C, 73.29; H, 7.59; N, 5.29.

4.2.24. *N*-Benzyl-3-(4-chlorophenyl)-2,4-dimethylpyrrole (entry 9). Colourless oil; IR (neat) 3030, 2961, 2927, 1670, 1488, 1091, 731 cm^{-1}; ^1H NMR δ 7.39–7.10 (m, 9H), 6.51 (s, 1H), 5.04 (s, 2H), 2.16 (s, 3H), 2.06 (s, 3H); ^{13}C NMR δ 135.8, 131.5, 131.2 (2), 128.9 (2), 128.8, 128.7 (2), 128.6, 128.3, 127.8 (2), 125.7, 125.3, 116.7, 50.8, 11.4, 11.0. Anal. Calcd for $C_{19}H_{18}NCl$: C, 77.15; H, 6.13; N, 4.74. Found: C, 77.01; H, 6.02; N, 4.63.

4.2.25. 3-(4-Chlorophenyl)-*N*-isopropyl-2,4-dimethylpyrrole (entry 10). Colourless oil; IR (neat): 2974, 2931, 1705, 1487, 1363, 1098, 835, 732 cm^{-1}; ^1H NMR δ 7.30 (d, J=8.4 Hz, 2H), 7.17 (d, J=8.4 Hz, 2H), 6.51 (s, 1H), 4.25 (m, 1H), 2.15 (s, 3H), 2.03 (s, 3H), 1.40 (d, J=6.6 Hz, 6H); ^{13}C NMR δ 135.9, 131.6 (2), 131.3 (2), 129.2, 128.5, 125.2, 116.4, 113.5, 47.2, 24.5 (2), 11.5, 10.9. Anal. Calcd for $C_{15}H_{18}NCl$: C, 72.72; H, 7.32; N, 5.65. Found: C, 72.62; H, 7.22; N, 5.52.

4.2.26. 3-(4-Chlorophenyl)-2-ethyl-*N*-isopropyl-4-methylpyrrole (entry 11). Colourless cubic crystal, mp 62–64°C; IR (KBr) 2981, 2964, 1527, 1365, 1085, 837 cm^{-1};

^{1}H NMR δ 7.42 (d, J=8.4 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 6.60 (s, 1H), 4.38 (m, 1H), 2.67 (q, J=7.5 Hz, 2H), 2.12 (s, 3H), 1.54 (d, J=6.6 Hz, 6H), 1.24 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 136.1, 131.6 (2), 131.5, 131.2, 128.5 (2), 120.2, 116.8, 113.5, 46.9, 24.6 (2), 18.2, 16.3, 11.5. Anal. Calcd for $C_{16}H_{20}NCl$: C, 73.45; H, 7.30; N, 5.35. Found: C, 73.31; H, 7.21; N, 5.29.

4.2.27. *N*-Butyl-3-(4-chlorophenyl)-2-ethyl-4-methylpyrrole (entry 12). Colourless oil; IR (neat) 2931, 2871, 1706, 1529, 1365, 1091, 823 cm^{-1}; ^{1}H NMR δ 7.45 (d, J=8.4 Hz, 2H), 7.33 (d, J=8.4 Hz, 2H), 6.56 (s, 1H), 3.90 (t, J=7.5 Hz, 2H), 2.68 (q, J=7.5 Hz, 2H), 2.14 (s, 3H), 1.92–1.87 (m, 2H), 1.53–1.48 (m, 2H), 1.25 (q, J=7.5 Hz, 3H), 1.07 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 136.1, 131.8, 131.6 (2), 128.6 (2), 120.6, 119.5, 118.0, 116.5, 46.5, 34.3, 20.7, 18.2, 15.9, 14.3, 11.3. Anal. Calcd for $C_{17}H_{22}NCl$: C, 74.03; H, 8.04; N, 5.08. Found: C, 73.92; H, 8.01; N, 4.97.

4.2.28. *N*-Benzyl-7-methyl-6-phenyl-2,3,4,5-tetrahydroindole (route b) (entry 3, Table 3). A mixture of cyclohexanone (196 mg, 2 mmol), benzyl amine (214 mg, 2 mmol) and α-methyl-β-nitrostyrene (326 mg, 2 mmol) was treated in the same way as in previous experiment to afford a pure product (488 mg, 81%) as a colourless oil, IR 2974, 2934, 1652, 1557 cm^{-1}; ^{1}H NMR δ 7.46–7.02 (m, 10H), 5.03 (s, 2H), 2.61 (t, J=6 Hz, 2H), 2.25 (t, J=6 Hz, 2H), 2.23 (s, 3H), 1.92–1.76 (m, 4H); ^{13}C NMR δ 139.1, 137.3, 130.2, 129.2 (2), 129.1 (2), 129.0, 128.9 (2), 127.4, 125.3 (2), 119.2, 115.8, 109.6, 47.1, 25.0, 24.4, 23.5, 22.3, 11.1. Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.52; H, 7.58; N, 4.56.

This procedure is followed for the synthesis of all pyrroles listed in Table 3. The mp, spectral and analytical data of all new compounds are presented below in order of their entries.

Although the experimental procedures were based on mmol scale reactions, gram-scale reactions also afforded the corresponding products in analogously good yields.

4.2.29. *N*-Butyl-2-methyl-3-phenylcyclopenta[b]pyrrole (entry 1). Colourless oil; IR (neat) 3036, 2929, 1602, 1458, 1126, 748, 700 cm^{-1}; ^{1}H NMR δ 7.41–7.13 (m, 5H), 3.73 (t, J=7.5 Hz, 2H), 2.76–2.67 (m, 4H), 2.46–2.38 (m, 2H), 2.32 (s, 3H), 1.73–1.61 (m, 2H), 1.42–1.30 (m, 2H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 137.5, 136.5, 128.5, 128.2 (2), 127.8 (2), 125.9, 123.8, 116.7, 45.1, 33.5, 28.5, 25.8, 20.2, 19.8, 13.8, 11.3. Anal. Calcd for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.19; H, 9.09; N, 5.42.

4.2.30. *N*-Butyl-7-methyl-6-phenyl-2,3,4,5-tetrahydroindole (entry 2). Colourless oil; IR (neat) 2973, 2930, 1547, 1487, 1462, 1339, 1087, 733 cm^{-1}; ^{1}H NMR δ 7.38–7.15 (m, 5H), 3.73 (t, J=7.8 Hz, 2H), 2.59 (t, J=6.0 Hz, 2H), 2.51 (t, J=6.0 Hz, 2H), 2.27 (s, 3H), 1.80–1.62 (m, 6H), 1.41–1.36 (m, 2H), 0.97 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 136.8, 130.2, 129.5 (2), 128.0, 127.9 (2), 124.7, 119.3, 114.5, 43.2, 33.2, 23.8, 23.4, 22.6, 22.0, 20.2, 13.8, 10.5. Anal. Calcd for $C_{19}H_{25}N$: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.24; H, 9.30; N, 5.21.

4.2.31. *N*-(α)-methylbenzyl-7-methyl-6-phenyl-2,3,4,5-tetrahydroindole (entry 4). Colourless oil; IR (neat) 2970, 2931, 1701, 1457, 1347, 1049, 732 cm^{-1}; ^{1}H NMR δ 7.40–7.15 (m, 10H), 5.56 (q, J=7.2 Hz, 1H), 2.60–2.48 (m, 4H), 2.22 (s, 3H), 1.85 (d, J=7.2 Hz, 3H), 1.82–1.76 (m, 4H); ^{13}C NMR δ 143.0, 137.4, 130.4, 130.3 (2), 130.1, 129.2 (2), 129.0, 128.9 (2), 126.6 (2), 124.5, 111.5, 53.1, 24.4, 22.9, 23.2, 22.9, 22.5, 12.4. Anal. Calcd for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.42; H, 7.89; N, 4.32.

4.2.32. *N*-Butyl-2-methyl-3-phenylcyclohepta[b]pyrrole (entry 5). Colourless oil; IR (neat) 2956, 2922, 1647, 1602, 1384, 702 cm^{-1}; ^{1}H NMR δ 7.50–7.30 (m, 5H), 3.91 (t, J=7.5 Hz, 2H), 2.85 (t, J=4.8 Hz, 2H), 2.69 (t, J=5.1 Hz, 2H), 2.34 (s, 3H), 2.00–2.71 (m, 8H), 1.59–1.49 (m, 2H), 1.11 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 137.1, 130.9, 130.4 (2), 127.9 (2), 121.9, 120.8, 119.7, 117.6, 43.3, 33.8, 32.2, 28.9, 27.7, 25.7, 24.9, 20.2, 13.9, 10.8. Anal. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67; N, 4.98. Found: C, 85.25; H, 9.61; N, 4.87.

4.2.33. *N*-Butyl-2-methyl-3-phenylcycloocta[b]pyrrole (entry 6). Colourless oil; IR (neat) 2970, 1645, 1444, 1601, 1127, 700 cm^{-1}; ^{1}H NMR δ 7.38–7.14 (m, 5H), 3.47 (t, J=7.5 Hz, 2H), 2.73 (t, J=5.1 Hz, 2H), 2.46 (t, J=5.1 Hz, 2H), 2.18 (s, 3H), 1.72–1.37 (m, 12H), 0.94 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 137.2, 130.7, 130.6 (2), 128.0 (2), 127.9, 127.0, 119.2, 117.5, 43.8, 31.6, 29.5, 28.3, 26.2, 25.8, 24.2, 23.4, 20.2, 13.8, 10.7. Anal. Calcd for $C_{21}H_{29}N$: C, 85.37; H, 9.89; N, 4.74. Found: C, 85.31; H, 9.81; N, 4.62.

4.2.34. *N*-Benzyl-3-(4-chlorophenyl)-2-methylcyclohepta-[b]pyrrole (entry 7). Colourless cubic crystal, mp 83–85°C; IR (KBr) 2937, 2842, 1525, 1382, 1089, 831, 731 cm^{-1}; ^{1}H NMR δ 7.25–7.16 (m, 8H), 6.96 (d, J=7.0 Hz, 2H), 4.90 (s, 2H), 2.68 (t, J=6.8 Hz, 2H), 2.54 (t, J=6.7 Hz, 2H), 2.37–2.28 (m, 2H), 2.13 (s, 3H); ^{13}C NMR δ138.6, 137.7, 136.3, 131.2, 130.6 (2), 129.5 (2), 129.1 (2), 127.7, 127.1, 124.6, 124.5 (2), 116.7, 49.2, 28.9, 26.4, 25.3, 12.0. Anal. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.36; N, 4.87. Found: C, 87.62; H, 7.26; N, 4.81.

4.2.35. 6-(4-Chlorophenyl)-7-methyl-*N*-isopropyl-2,3,4,5-tetrahydroindole (entry 8). Colourless oil; IR (neat) 2974, 2931, 1552, 1488, 1460, 1344, 1089, 736 cm^{-1}; ^{1}H NMR δ 7.27 (d, J=8.4 Hz, 2H), 7.10 (d, J=8.4 Hz, 2H), 4.35 (m, 1H), 2.62 (d, J=6.0 Hz, 2H), 2.36 (d, J=6.0 Hz, 2H), 2.18 (s, 3H), 1.79–1.75 (m, 2H), 1.63–1.60 (m, 2H), 1.42 (d, J=7.2 Hz, 6H); ^{13}C NMR δ 135.7, 131.6 (2), 128.9 (2), 126.7, 121.2, 119.7, 115.9, 111.5, 47.6, 24.0, 23.4, 22.8 (2), 22.0, 12.2. Anal. Calcd for $C_{18}H_{22}NCl$: C, 75.11; H, 7.70; N, 4.87. Found: C, 75.01; H, 7.59; N, 4.82.

4.2.36. *N*-Benzyl-6-(4-chlorophenyl)-7-methyl-2,3,4,5-tetrahydroindole (entry 9). Colourless cubic crystal, mp 95–97°C; IR (KBr) 2937, 2931, 1536, 1381, 1079, 700 cm^{-1}; ^{1}H NMR δ 7.47–7.32 (m, 7H), 7.09 (d, J=7.2 Hz, 2H), 5.13 (s, 2H), 2.67–2.60 (m, 4H), 2.30 (s, 3H), 1.99–1.81 (m, 4H); ^{13}C NMR δ 138.9, 135.9, 131.1 (2), 129.2, 129.1 (2), 128.7 (2), 127.7, 127.6, 126.5, 126.4, 124.5, 119.3, 115.8, 47.1, 25.2, 24.4, 23.2, 22.5, 11.1. Anal. Calcd for $C_{22}H_{22}NCl$: C, 78.67; H, 6.60; N, 4.17. Found: C, 78.52; H, 6.53; N, 4.09.

4.2.37. 6-(4-Chlorophenyl)-7-methyl-*N*-(α)-methylbenzyl-2,3,4,5-tetrahydroindole (entry 10). Colourless oil, IR (neat) 2929, 2848, 1645, 1535, 1450, 1371, 1089, 698 cm^{-1}; ^1H NMR δ 7.47–7.26 (m, 9H), 5.65 (q, J=7.2 Hz, 1H), 2.67–2.55 (m, 4H), 2.29 (s, 3H), 2.05 (d, J=7.2 Hz, 3H), 1.86–1.75 (m, 4H); ^{13}C NMR δ 142.9, 136.0, 131.4, 131.2 (2), 129.3, 129.0, 128.6 (2), 127.5 (2), 126.6 (2), 124.6, 119.8, 116.1, 53.0, 25.5, 24.2, 24.1, 23.4, 20.1, 12.2. Anal. Calcd for $C_{23}H_{24}NCl$: C, 78.95; H, 6.91; N, 4.00. Found: C, 78.81; H, 6.89; N, 3.91.

4.2.38. *N*-Butyl-6-(4-chlorophenyl)-7-methyl-2,3,4,5-tetrahydroindole (entry 11). Colourless oil; IR (neat) 2929, 2956, 1647, 1595, 1488, 1089, 1014, 821 cm^{-1}; ^1H NMR δ 7.49 (d, J=8.4 Hz, 2H), 7.24 (d, J=8.4 Hz, 2H), 3.74 (t, J=7.8 Hz, 2H), 2.60 (t, J=6.0 Hz, 2H), 2.50 (t, J=6.0 Hz, 2H), 2.27 (s, 3H), 1.89–1.67 (m, 6H), 1.47–1.42 (m, 2H), 0.97 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 136.7, 135.2, 131.0 (2), 129.8, 129.2 (2), 126.9, 123.8, 115.3, 43.7, 33.7, 24.3, 23.8, 22.5, 20.8, 20.6, 14.2, 10.9. Anal. Calcd for $C_{19}H_{24}NCl$: C, 75.60; H, 8.01; N, 4.64. Found: C, 75.51; H, 7.96; N, 4.61.

4.2.39. *N*-Benzyl-3-(4-chlorophenyl)-2-ethylcyclopenta-[b]pyrrole (entry 12). Colourless oil; IR (neat) 2964, 2931, 1670, 1521, 1452, 1384, 1091, 829 cm^{-1}; ^1H NMR δ 7.41–7.24 (m, 7H), 7.05 (d, J=6.6 Hz, 2H), 5.04 (s, 2H), 2.79–2.38 (m, 8H), 1.15 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 138.8, 137.8, 136.3, 134.3, 134.1, 130.7 (2), 129.8 (2), 129.3 (2), 129.1, 127.7, 116.2, 49.0, 28.7, 26.4, 25.2, 19.0, 15.9. Anal. Calcd for $C_{22}H_{22}NCl$: C, 78.67; H, 6.60; N, 4.17. Found: C, 78.57; H, 6.51; N, 4.11.

4.2.40. *N*-Benzyl-6-(4-chlorophenyl)-7-ethyl-2,3,4,5-tetrahydroindole (entry 13). Colourless oil; IR (neat) 2929, 2873, 1645, 1531, 1485, 1353, 1095, 1014, 827, 732 cm^{-1}; ^1H NMR δ 7.53–7.11 (m, 9H), 5.14 (s, 2H), 2.70–2.48 (m, 6H), 1.89–1.80 (m, 4H), 1.18 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 139.3, 136.0, 131.4 (2), 131.0, 129.2 (2), 129.1 (2), 128.8, 128.6, 127.5, 126.3 (2), 126.1, 119.0, 116.0, 47.0, 24.3, 23.8, 23.1, 22.5, 18.3, 16.3. Anal. Calcd for $C_{23}H_{24}NCl$: C, 78.95; H, 6.91; N, 4.00. Found: C, 78.81; H, 6.82; N, 3.93.

4.2.41. 6-(4-Chlorophenyl)-7-ethyl-*N*-isopropyl-2,3,4,5-tetrahydroindole (entry 14). Colourless oil; IR (neat) 2972, 2933, 1703, 1647, 1488, 1460, 1350, 1091, 1012, 786 cm^{-1}; ^1H NMR δ 7.29 (d, J=8.4 Hz, 2H), 7.05 (d, J=8.4 Hz, 2H), 4.30 (m, 1H), 2.68 (t, J=6.0 Hz, 2H), 2.53 (t, J=7.5 Hz, 2H), 2.34 (t, J=6.0 Hz, 2H), 1.74–1.61 (m, 4H), 1.42 (d, J=6.9 Hz, 6H), 0.94 (t, J=7.5 Hz, 3H); ^{13}C NMR δ 136.1, 131.5, 131.2 (2), 130.3, 129.6 (2), 128.6, 121.2, 116.6, 47.5, 25.1, 24.3, 23.9, 23.1 (2), 23.1, 18.8, 16.7. Anal. Calcd for $C_{19}H_{24}NCl$: C, 75.60; H, 8.01; N, 4.64. Found: C, 75.48; H, 7.92; N, 4.52.

4.2.42. *N*-Benzyl-6-(4-fluorophenyl)-7-methyl-2,3,4,5-tetrahydroindole (entry 15). Colourless cubic crystal, mp 71–73°C; IR (KBr) 2929, 1639, 1504, 1386, 842, 731 cm^{-1}; ^1H NMR δ 7.35–6.85 (m, 9H), 4.90 (s, 2H), 2.39 (m, 4H), 2.06 (s, 3H), 1.72–1.62 (m, 4H); ^{13}C NMR δ 139.0, 133.3, 131.6 (2), 131.2, 131.1, 129.0, 127.8 (2), 127.4, 126.5, 126.3, 124.2, 115.9, 115.1, 109.7, 47.1, 24.4, 23.8, 23.1, 22.4, 11.4. Anal. Calcd for $C_{22}H_{22}NF$: C, 82.73; H, 6.94; N, 4.39. Found: C, 82.59; H, 6.88; N, 4.27.

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