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Indium-mediated one-pot pyrrole synthesis from nitrobenzenes and 1,4-diketones

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ABSTRACT

One-pot reduction-triggered heterocyclizations of nitrobenzene derivatives with 1,4-diketones were investigated. In the presence of indium/AcOH in toluene at 80 °C, reaction of nitrobenzenes with 2,5-hexadione produced moderate to excellent yields (40–98%) of the corresponding pyrroles within 1.5–24 h depending on the substituents of the starting materials. Similarly, the reaction of nitrobenzenes with 1-phenyl-1,4-pantanedione in the presence of indium/AcOH in toluene at reflux afforded the corresponding pyrroles within 0.5–24 h with 60–98% yields.

1. Introduction

The pyrrole heterocyclic unit is a key structural moiety in various natural products and synthetic medicinal agents. Pyrroles and their derivatives represent one of the most pharmaceutically important class of *N*-heterocyclic compounds because of their remarkable anti-bacterial, anti-viral, anti-inflammatory, anti-tumoral, and antioxidant activities.[1] Moreover, polypyrroles have been applied as conducting polymers,[2] and pyrrolic macrocycles as anion receptors, such as calix[4]pyrroles.[3]

Because of the wide-ranging applications of pyrroles, many synthetic chemists have focused on developing more efficient synthesis methods. Since the initial success of the Paal–Knorr condensation of 1,4-dicarbonyls with ammonia or primary amines,[4] the use of 1,4-dicarbonyls has become one of the most versatile and widely applied methods among the many strategies that have been developed.[5] Besides the Paal–Knorr type condensation reaction, various synthetic methods have been developed to synthesize pyrroles, including Hantzsch synthesis,[6] tandem reaction,[7] rearrangement of *o*-vinyl oximes,[8] [3+2] cycloaddition of 1,3-dipolar reagents with alkynes,[9] hydroamination of diynes,[10] and olefin cross-metathesis,[11] to mention but a few.[12] Nevertheless, none of these methods involve one-pot reductive condensation reactions starting from nitroarenes and 1,4-dicarbonyls, which could potentially result in the efficient production of pyrroles if the reaction timing of the reduction and condensation reactions is suitably controlled.

We have performed extensive studies to develop new and efficient one-pot reductive organic transformations,[13] including various indium-mediated reductive heterocyclizations, via the reductive cyclization reaction of nitroarenes to nitrogen-containing heterocycles, such as 2,1-benzisoxazoles,[13a] benzimidazoles,[13e] quinolines,[13f] indazoles,[13g,h] indoles,[13i,j] and oxazoles.[13k] We were confident that the same concept could be applied to the synthesis of pyrroles from nitroarenes and 1,4-dicarbonyls, as the reaction path should be similar to the heterocyclization reactions discussed above. If successful, reduction of nitroarenes followed by the Paal–Knorr type condensation reaction could occur in a single step, allowing efficient synthetic transformation. Herein we report the development of a one-pot synthesis method involving indium reduction-triggered intermolecular heterocyclization to create pyrroles starting from nitroarenes with 1,4-dicarbonyls, and we discuss mechanistic considerations in detail.

2. Results and discussion

In an effort to determine the appropriate reaction system, we carried out primary control experiments using nitrobenzene and 2,5-hexadione as representative model substrates. We initially examined various reaction conditions to determine the best reaction conditions using indium and acid additives in various solvent systems (Table 1). Reactions of nitrobenzene and 2,5-hexadione in the presence of indium/acetic acid in various solvents, such as methanol, ethyl acetate (EA), tetrahydrofuran (THF), acrylonitrile, benzene, and toluene were examined to determine the best medium. Use of a protic solvent, such as methanol or water was not very successful with regard to

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0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
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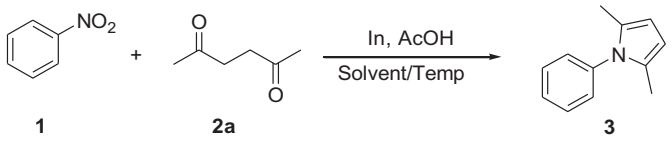
Table 1
Indium-mediated reductive heterocyclization of nitrobenzene (1 mmol) with 2,5-hexadione under different reaction conditions



Entry	Molar equiv					Solvent (mL)/Temp (°C)	Time (h)	Yield[a] (%) **3**
	1	**2a**	In	AcOH	$InCl_3$			
1	1	1	3	10	—	EA(5)/reflux	5	86
2	1	1	4	10	—	EA(5)/reflux	5	88
3	1	1	5	10	—	EA(5)/reflux	5	82
4	1	2	4	10	—	EA(5)/reflux	5	79
5	1	1	4	10	—	THF(5)/reflux	24	59
6	1	1	4	10	—	THF/H_2O(3:3)/70	8	84
7	1	1	4	10	—	MeOH(5)/reflux	2	70
8	1	1	5	—	1	MeOH(5)/reflux	4	25[b]
9	1	2	5	—	2	MeOH(5)/reflux	4	27[b]
10	1	1	4	10	—	CH_3CN(5)/80	5	88
11	1	1	4	10	—	Benzene(5)/reflux	0.5	89
12	1	1	4	10	—	Toluene(5)/80	4	90
13	1	1	4	10	—	Toluene(5)/reflux	0.5	86
14	1	1	4	—	1	Toluene(5)/80	24	—[b]
15	1	1	3	10	—	Toluene(5)/80	4	88
16	1	1	5	10	—	Toluene(5)/80	4	86

[a] Isolated yield.
[b] Starting materials were remained.

yield or reaction time; in contrast, use of aprotic nonpolar solvents, such as ethyl acetate, acrylonitrile, benzene, or toluene was more promising in terms of a high yield of the desired product, pyrroles. Interestingly, trial experiments of heterocyclization of nitrobenzene and 2,5-hexadione in the presence of indium and indium(III) chloride Lewis acid worked poorly (entries 8, 9) or did not work at all (entry 14). Acetic acid worked fairly well and therefore we used acetic acid as an acid additive for our reactions. After more control experiments to determine the optimal molar ratios of substrates, indium, and acetic acid, we found that the most optimized reaction conditions were nitrobenzene (1 equiv)/2,5-hexadione (1 equiv)/indium (4 equiv)/AcOH (10 equiv) in toluene at 80 °C (entry 12).

To elucidate the reaction path clearly, we used GC and GC–MS analysis to monitor intermediates that formed during heterocyclization to create 2,5-dimethyl-1-phenyl-1*H*-pyrrole (**3**) using nitrobenzene and 2,5-hexadione performed at 50 °C, a lower reaction temperature than the optimized reaction condition. By decreasing the reaction temperature, we were able to slow down the reaction, which made it possible for us to effectively monitor the formation of intermediates and changes in their distribution. Data obtained from the control experiments are shown in Fig. 1. At this lower reaction temperature, the concentration of nitrobenzene substrate was reduced by 50% within 10 min, while only 28% of another substrate, 2,5-hexadione, disappeared. At that time, 22% of aniline and 16% of the desired pyrrole product were obtained. The reaction time required for 50% consumption of 2,5-hexadione was about 25 min, which is relatively slower than the reaction time required for the transformation of nitrobenzene to aniline. Therefore, the concentration of the aniline in the reaction batch was increased for 20–30 min and then gradually decreased thereafter. In the meantime, possible intermediates of 5-(phenylimino)hexan-2-one (**A**) or 5-(phenylamino)hex-4-en-2-one (**B**) were observed as traces on GC–MS analysis. Even though both of these compounds are possible intermediates, we presume intermediate **A** to be a more convincing intermediate than intermediate **B**, because **B** needs to be isomerized to the thermodynamically disfavored *Z*-form for the formation of the cyclic pyrrole product. A plausible mechanism based on our control experiments, kinetic studies, and our previous work is proposed in Scheme 1.

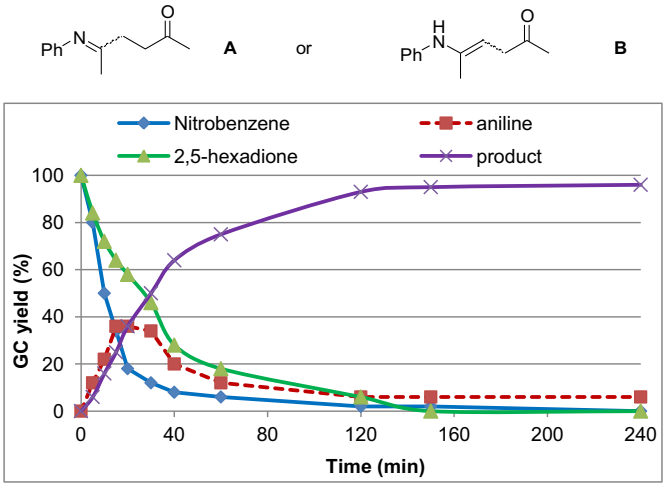
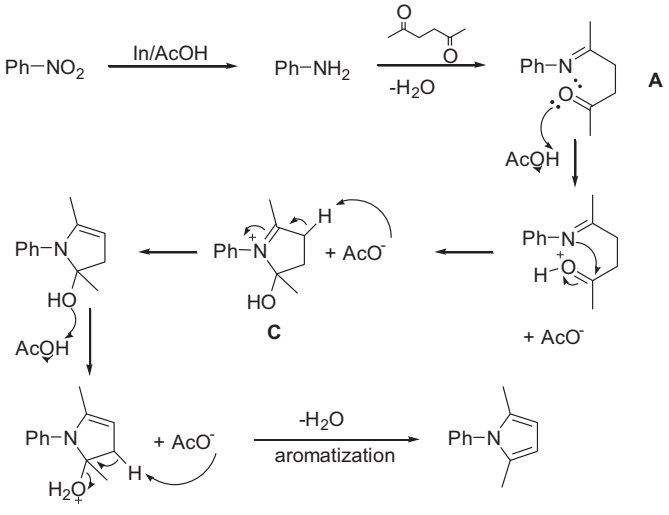


Fig. 1. Heterocyclization reaction to produce 2,5-dimethyl-1-phenyl-1*H*-pyrrole (**3**) using nitrobenzene and 2,5-hexadione at 50 °C as monitored by GC and GC–MS.

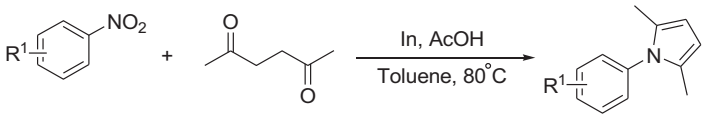


Scheme 1.

Initially, nitrobenzene is reduced to aniline by indium/AcOH via single electron transfers (SETs) and proton transfers (PTs). The in situ-formed aniline couples with 2,5-hexadione to form the imine intermediate (**A**). As soon as the imine is formed, an AcOH-assisted intramolecular cyclization reaction may occur by attack of the imine nucleophile toward the adjacent protonated-keto electrophile to form the five-membered ring intermediate (**C**). Deprotonation of the α-proton of the iminium ion in intermediate (**C**) followed by aromatization caused by dehydration produces the desired pyrrole product. Similar result was obtained when aniline, an intermediate of our reaction, and 2,5-hexadione were reacted in the presence of AcOH in toluene without indium at 80 °C, which strongly supported our proposed reaction path of aniline to pyrrole in Scheme 1.

Using the optimized reaction conditions with indium (4 equiv)/AcOH (10 equiv) in toluene at 80 °C, heterocyclizations of variously substituted nitrobenzenes with 2,5-hexadione were examined to verify our one-pot synthesis method. In most cases, heterocyclization for pyrrole ring formation was successful with an excellent yield. Most reactions of *m*- or *p*-alkylnitrobenzenes or *m*- or *p*-alkoxynitrobenzenes with 2,5-hexadione were completed within 2.5–4 h and produced excellent yields (90–98%) of the corresponding pyrroles (Table 2, entries 4–6, 8, 9). Reaction time of

Table 2
Indium-acetic acid-mediated reductive heterocyclization of nitroarenes (1 mmol) with 2,5-hexadione (1 equiv) in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene (5 mL) at 80 °C



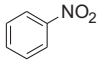
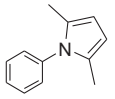
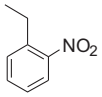
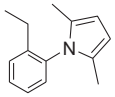
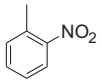
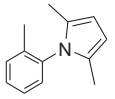
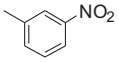
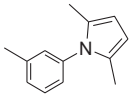
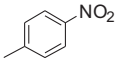
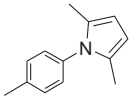
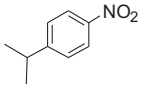
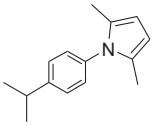
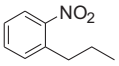
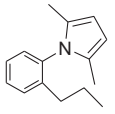
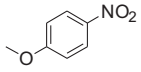
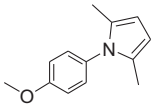
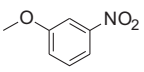
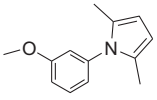
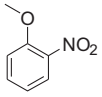
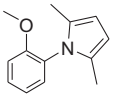
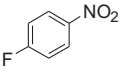
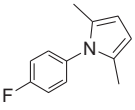
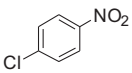
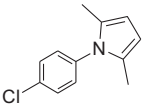
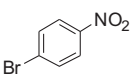
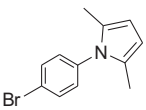
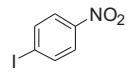
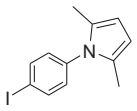
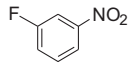
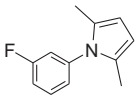
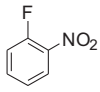
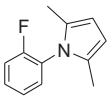
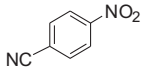
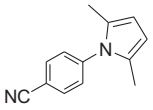
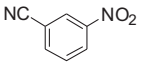
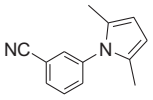
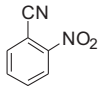
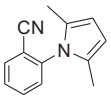
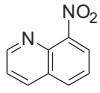
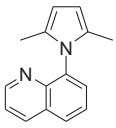
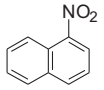
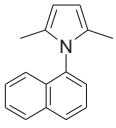
Entry	Substrate	Time (h)	Product		Yield[a] (%)
1		4		**(3)**	90
2		4		**(4)**	92
3		4		**(5)**	93
4		3		**(6)**	97
5		2.5		**(7)**	98
6		5		**(8)**	92
7		8		**(9)**	93
8		1.5		**(10)**	95
9		4		**(11)**	95
10		6		**(12)**	94
11		2		**(13)**	91
12		6		**(14)**	94
13		8		**(15)**	97[b]

Table 2 (*continued*)

Entry	Substrate	Time (h)	Product	Yield[a] (%)
14		9	 **(16)**	90[b]
15		10	 **(17)**	87
16		13	 **(18)**	86
17		24	 **(19)**	40[e]
18		24	 **(20)**	84
19		24	 **(21)**	42[c,e] 48[c,d,e]
20		24	 **(22)**	80
21		6	 **(23)**	96

[a] Isolated yield.
[b] A dehalogenated product was observed.
[c] Byproducts were observed.
[d] Reflux condition.
[e] Starting materials were remained.

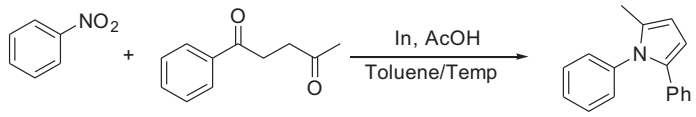
sterically more hindered *ortho*-propyl-substituted nitrobenzene (entry 7) with 2,5-hexadione was delayed compared to those of *ortho*-methyl- or *ortho*-ethyl-substituted nitrobenzenes (entries 2 and 3); however, excellent yields of the desired pyrrole derivatives were produced. When reflux condition was applied, it was completed within 1 h with an excellent yield (93%).

Reaction time delay was also observed when nitrobenzenes were substituted with a halogen, regardless of the position of the halo-substituent, with excellent yields maintained (entries 11–16). Moreover, reactions of some cyano-substituted nitrobenzenes with 2,5-hexadione proceeded very slowly (entries 17–19). In the case of *o*-cyanonitrobenzene or *p*-cyanonitrobenzene with 2,5-hexadione, poor yields of the corresponding pyrroles were obtained, even after 24 h of reaction, possibly because the cyano substituent had a conjugative effect on the 2-nitrobenzene ring, i.e., reaction of resonance-stabilized cyano group-substituted nitrobenzenes was to a large extent retarded compared to those of alkyl- or methoxy-substituted nitrobenzene substrates. However, reductive transformation from cyanonitrobenzenes to cyanoanilines was fast and none of the starting nitroarene remained after 1 h. In the case of the 1-cyano-4-nitrobenzene/2,5-hexadione reaction, the reaction mixture contained ~36% 4-cyanoaniline and ~16% pyrrole product with ~48% 2,5-hexadione substrate remaining after 1 h. In addition, a trace amount of imine or enamine (analogues of **A** or **B**) was detected on GC–MS analysis. Therefore, we believe that the imine formation step and/or cyclization step are/is responsible for retardation of the reaction, as in both these steps, the nucleophilic nitrogen lone pair of aniline and/or imine intermediate is stabilized, which could slow down imine formation and/or cyclization.

To extend the methodology to other 1,4-diketone derivatives, heterocyclizations of variously substituted nitrobenzenes with 1-phenyl-1,4-pantanedione were examined under the optimized reaction conditions that we used for heterocyclization of variously substituted nitrobenzenes with 2,5-hexadione. Unfortunately, heterocyclization of nitrobenzene with 1-phenyl-1,4-pantanedione

with indium (4 equiv)/AcOH (10 equiv) in toluene at 80 °C was not successful, with a long reaction time and poor yield firstly (Table 3, entry 1). However, we found that the long reaction time could be decreased and the yield increased by changing the reaction temperature from 80 °C to reflux in several control experiments (entry 4).

Table 3
Indium-mediated reductive heterocyclization of nitrobenzene (0.5 mmol) with 1-phenyl-1,4-pantanedione under different reaction conditions



1 **24** **25**

Entry	Molar equiv				Solvent (mL)/ Temp (°C)	Time (h)	Yield[a] (%) **25**
	1	**24**	In	AcOH			
1	1	1	4	10	Toluene(2.5)/80	8	43[b]
2	1	1	4	10	Toluene(2.5)/80	24	30[b]
3	1	1.5	4	10	Toluene(2.5)/reflux	2	76
4	1	1	4	10	Toluene(2.5)/reflux	1	85

[a] Isolated yield.
[b] Starting materials were remained.

Heterocyclizations of variously substituted nitrobenzenes with 1-phenyl-1,4-pantanedione were examined to extend our method using modified optimum conditions; results are shown in Table 4. A similar trend was observed for these cyclization reactions and the reactions of nitrobenzenes with 2,5-hexadione. In most cases, excellent yields were obtained within 1–4 h; reactions of most alkyl- or methoxy-substituted nitrobenzenes were completed within 2 h except for 1-nitro-2-propylbenzene, while halobenzenes showed delayed reaction times of 2–4 h. For *o*- or *p*-cyano-substituted nitrobenzenes, reactions slowed down more drastically and it took 24 h, even under toluene reflux conditions, to obtain a reduced yield of the corresponding pyrrole products, especially for 1-cyano-4-nitrobenzene (75%, entry 17) and 1-cyano-2-nitrobenzene (60%, entry 19), similar to the 2,5-hexadione cases.

3. Conclusions

In conclusion, we developed a simple and efficient method for the one-pot reduction-triggered heterocyclization of nitrobenzenes and 1,4-diketones to produce pyrroles. In the presence of indium/AcOH in toluene at 80 °C, nitrobenzenes and 2,5-hexadione produced the corresponding pyrrole with moderate to excellent yields. Similarly, the reaction of nitrobenzenes with 1-phenyl-1,4-pantanedione in the presence of indium/AcOH in toluene at reflux afforded the corresponding pyrrole with an excellent yield (60–98%). The presence of a cyano group on nitrobenzene at the *para* or *ortho* positions strongly delayed reactions for up to 24 h in both cases, presumably because of resonance contribution of the cyano group to the imine formation step and/or cyclization step.

4. Experimental section

4.1. General considerations

Most chemical reagents were purchased from Sigma–Aldrich Co. (St. Louis, Missouri, USA) and were used without further purification. Solvents were purchased and dried using standard methods. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively (JEOL, Tokyo, Japan). Chemical shifts are reported in parts per million relative to the residual solvent as an internal standard. GC–MS spectra were recorded on an Agilent 6890N GC connected to an Agilent 5975 mass selective detector (Hewlett–Packard Co., Palo Alto, California, USA). Infrared (IR) spectra were recorded using an MB104 FTIR (ABB Bomem, Inc., Zurich, Switzerland). The elemental analysis data were obtained by the Thermo Scientific Flash 2000 (Thermo Fisher Scientific, USA). Melting points were determined on an electrothermal apparatus and were uncorrected. All the major products were isolated by flash column chromatography on silica gel (230–400 mesh ATSM, purchased from Merck & Co., Inc. (Whitehouse Station, New Jersey, USA)) using a mixed solvent eluent (ethyl acetate/hexane).

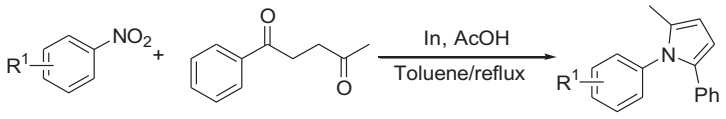
4.2. General procedure for the indium-mediated reductive reaction of nitrobenzenes with 2,5-hexadione or 1-phenyl-1,4-pantanedione to obtain pyrroles

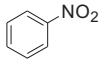
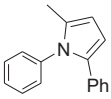
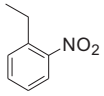
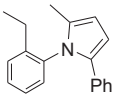
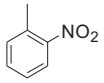
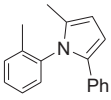
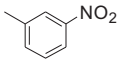
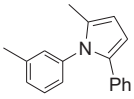
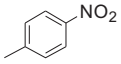
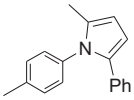
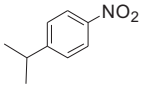
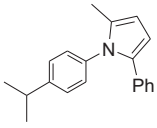
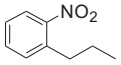
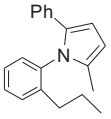
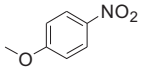
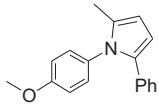
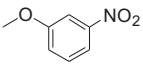
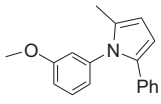
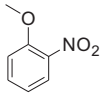
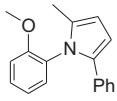
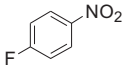
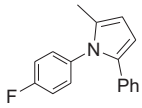
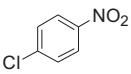
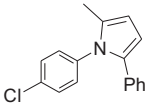
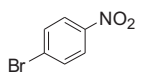
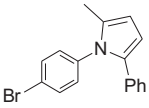
Nitrobenzene derivative (1.0 mmol) was added to a mixture of indium powder (460 mg, 4.0 mmol), and acetic acid (0.572 mL, 10 mmol) in toluene (2 mL), followed by the addition of 2,5-hexadione or 1-phenyl-1,4-pentanedione (1.0 mmol) in toluene (3 mL). The reaction mixture was stirred at 80 °C for 2,5-hexadione (or reflux for 1-phenyl-1,4-pentadione) under a nitrogen atmosphere. After the reaction was completed, the reaction mixture was diluted with ethyl acetate (30 mL), filtered through Celite, poured into 10% $NaHCO_3$ (30 mL), and then extracted with ethyl acetate (30 mL×3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was eluted with hexane for most derivatives or ethyl acetate/hexane (v/v=5:95) for benzonitrile derivatives through a neutral silica gel column to give the corresponding pyrroles. The structures of the pyrroles were characterized by ^{1}H NMR, ^{13}C NMR, FTIR, and GC–MS, and were mostly known compounds. If it is an unknown compound, elemental analysis data were reported additionally.

*4.2.1. 2,5-Dimethyl-1-phenyl-1H-pyrrole (**3**).*[12e,14a,b] Yield 90%. Pale brown solid, mp 49–50 °C (lit.[14a] mp 50.1–50.3 °C). TLC (20% ethyl acetate/hexane) R_f 0.58; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.40–7.38 (m, 1H), 7.21 (dd, 2H, J=8.2, 1.3 Hz), 5.90 (s, 2H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 128.9, 128.8, 128.2, 127.6, 105.6, 12.9; IR (KBr) 3055, 2972, 1596, 1496, 1402 cm^{-1}; GC–MS *m*/*z* (rel intensity) 171 (M^+, 100), 154 (13), 77 (15), 51 (8).

*4.2.2. 1-(2-Ethylphenyl)-2,5-dimethyl-1H-pyrrole (**4**).*[14c] Yield 92%. Yellow liquid. TLC (20% ethyl acetate/hexane) R_f 0.69; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.37 (m, 2H), 7.30–7.24 (m, 1H), 7.13 (d, 1H, J=7.6 Hz), 5.91 (s, 2H), 2.25 (q, 2H, J=7.6 Hz), 1.92 (s, 6H), 1.09 (t, 3H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.4, 129.0, 128.9, 128.52, 128.48, 126.5, 105.2, 23.3, 13.9, 12.6; IR (KBr) 3037, 2972,

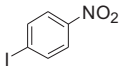
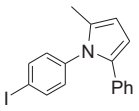
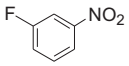
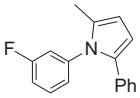
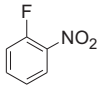
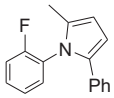
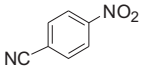
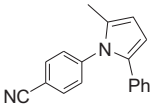
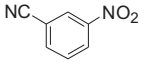
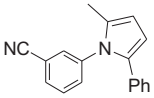
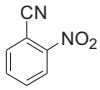
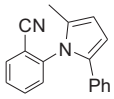
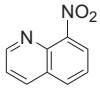
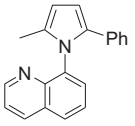
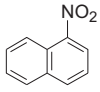
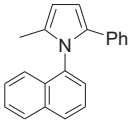
Table 4
Heterocyclization of nitroarenes (0.5 mmol) with 1-phenyl-1,4-pantanedione (1 equiv) in the presence of indium (4 equiv) and acetic acid (10 equiv) in toluene (2.5 mL) at reflux



Entry	Substrate	Time (h)	Product	Yield[a] (%)
1		1.5	 **(25)**	86
2		2	 **(26)**	86
3		1	 **(27)**	94
4		0.5	 **(28)**	94
5		1	 **(29)**	93
6		2	 **(30)**	85
7		3	 **(31)**	97
8		1	 **(32)**	92
9		1	 **(33)**	98
10		1	 **(34)**	94
11		1	 **(35)**	80
12		4	 **(36)**	83
13		2	 **(37)**	81[b]

(*continued on next page*)

Table 4 (*continued*)

Entry	Substrate	Time (h)	Product		Yield[a] (%)
14		3		**(38)**	84[b]
15		2		**(39)**	86
16		2		**(40)**	83
17		24		**(41)**	75[c]
18		24		**(42)**	85
19		24		**(43)**	60[c,d]
20		24		**(44)**	77
21		3		**(45)**	90

[a] Isolated yield.
[b] A dehalogenated product was observed.
[c] Starting materials were remained.
[d] Byproducts were observed.

2935, 1492, 1454, 1402 cm^{-1}; GC–MS *m*/*z* (rel intensity) 199 (M^+, 66), 184 (100), 168 (21), 154 (15), 77 (13), 51 (8).

4.2.3. 2,5-Dimethyl-1-o-tolyl-1H-pyrrole (***5***).[5c] Yield 93%. Brown liquid. TLC (20% ethyl acetate/hexane) R_f 0.72; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.32 (m, 2H), 7.29–7.27 (m, 1H), 7.16 (d, 1H, *J*=7.3 Hz), 5.91 (s, 2H), 1.93 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.1, 130.6, 128.8, 128.3, 128.2, 126.6, 105.2, 17.0, 12.5; IR (KBr) 3031, 2921, 1490, 1400 cm^{-1}; GC–MS *m*/*z* (rel intensity) 185 (M^+, 94), 170 (100), 154 (19), 91 (11), 51 (4).

4.2.4. 2,5-Dimethyl-1-m-tolyl-1H-pyrrole (***6***).[5c] Yield 97%. Brown solid, mp 45–46 °C. TLC (20% ethyl acetate/hexane) R_f 0.61; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, 1H, *J*=8.0 Hz), 7.19 (d, 1H, *J*=8.0 Hz), 7.01 (m, 2H), 5.89 (s, 2H), 2.39 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.94, 138.9, 128.8, 128.74, 128.73, 128.3, 125.2, 105.5, 21.3, 12.9; IR (KBr) 3099, 2974, 2920, 1602, 1519, 1401 cm^{-1}; GC–MS *m*/*z* (rel intensity) 184 (M^+–1, 100), 170 (13), 154 (12), 129 (12), 91 (14), 65 (13), 51 (8).

4.2.5. 2,5-Dimethyl-1-p-tolyl-1H-pyrrole (***7***).[5c] Yield 98%. Pale brown solid, mp 43–44 °C (lit.[5j] mp 45–46 °C). TLC (20% ethyl acetate/hexane) R_f 0.76; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2H, *J*=8.0 Hz), 7.09 (d, 2H, *J*=8.0 Hz), 5.89 (s, 2H), 2.41 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.3, 129.6, 128.8, 127.9, 105.4, 21.1, 12.9; IR (KBr) 3107, 3034, 2985, 2921, 1516, 1406 cm^{-1}; GC–MS *m*/*z* (rel intensity) 184 (M^+–1, 100), 170 (13), 154 (12), 129 (18), 91 (9), 65 (7), 51 (3).

4.2.6. 1-(4-Isopropylphenyl)-2,5-dimethyl-1H-pyrrole (***8***).[14h] Yield 92%. Orange solid, mp 58–60 °C. TLC (20% ethyl acetate/hexane) R_f 0.70; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, 2H, *J*=8.0 Hz), 7.10 (d, 2H, *J*=8.0 Hz), 5.88 (s, 2H), 3.01–2.91 (m, 1H), 2.02 (s, 6H), 1.29 (d, 6H, *J*=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 136.5, 128.9, 127.9, 126.9, 105.3, 33.8, 23.9, 13.0; IR (KBr) 3107, 3039, 2960, 2931, 1500, 1406 cm^{-1}; GC–MS *m*/*z* (rel intensity) 213 (M^+, 100), 198 (18), 170 (21), 157 (10), 129 (9), 77 (6), 51 (3).

4.2.7. 2,5-Dimethyl-1-(2-propylphenyl)-1H-pyrrole (***9***). Yield 93%. Brown liquid. TLC (20% ethyl acetate/hexane) R_f 0.73; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.36 (m, 2H), 7.29–7.27 (m, 1H), 7.13 (d, 1H, *J*=7.6 Hz), 5.91 (s, 2H), 2.22 (t, 2H, *J*=7.7 Hz), 1.93 (s, 6H), 1.53–1.49 (m, 2H), 0.85 (t, 3H, *J*=7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 137.7, 129.5, 129.1, 128.5, 128.3, 126.5, 105.2, 32.4, 22.7, 14.1,

12.7; IR (KBr) 3101, 3066, 2970, 2935, 1494, 1454 cm^{-1}; GC–MS *m/z* (rel intensity) 213 (M^+, 55), 198 (100), 182 (12), 168 (23), 154 (12), 91 (5), 77 (5), 51 (2); Anal. Calcd for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.45; H, 9.00; N, 6.44.

*4.2.8. 1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole (**10**).*[12e,14b] Yield 95%. Pale yellow solid, mp 55–57 °C (lit.[14b] mp 60–62 °C). TLC (30% ethyl acetate/hexane) R_f 0.55; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 2H, *J*=8.5 Hz), 6.96 (d, 2H, *J*=8.5 Hz), 5.88 (s, 2H), 3.86 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 131.7, 129.2, 128.9, 114.1, 105.2, 55.4, 12.9; IR (KBr) 3064, 2997, 2929, 1514, 1406, 1253 cm^{-1}; GC–MS *m/z* (rel intensity) 201 (M^+, 100), 186 (28), 170 (5), 154 (10), 145 (29), 117 (10), 77 (12), 51 (8).

*4.2.9. 1-(3-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole (**11**).*[14i] Yield 95%. Brown liquid. TLC (20% ethyl acetate/hexane) R_f 0.58; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, 1H, *J*=8.0 Hz), 6.95–6.93 (m, 1H), 6.81–6.79 (m, 1H), 6.75 (t, 1H, *J*=2.2 Hz), 5.89 (s, 2H), 3.82 (s, 3H), 2.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 140.1, 129.6, 128.8, 120.5, 113.9, 113.5, 105.6, 55.4, 12.9; IR (KBr) 3070, 2937, 1601, 1491, 1250 cm^{-1}; GC–MS *m/z* (rel intensity) 200 (M^+-1, 100), 186 (13), 170 (5), 156 (7), 77 (5), 51 (3).

*4.2.10. 1-(2-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole (**12**).*[14i] Yield 94%. White solid, mp 62–63 °C (lit.[14i] mp 65–66 °C). TLC (20% ethyl acetate/hexane) R_f 0.57; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 1H), 7.16 (dd, 1H, *J*=7.9, 1.6 Hz), 7.03–7.01 (m, 2H), 5.91 (s, 2H), 3.77 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 130.2, 129.3, 129.1, 127.6, 120.6, 111.9, 105.1, 55.6, 12.5; IR (KBr) 3097, 3070, 2966, 1599, 1502, 1275 cm^{-1}; GC–MS *m/z* (rel intensity) 201 (M^+, 100), 186 (68), 170 (36), 154 (9), 77 (8), 51 (6).

*4.2.11. 1-(4-Fluorophenyl)-2,5-dimethyl-1H-pyrrole (**13**).*[14j] Yield 91%. Yellow solid, mp 51–52 °C. TLC (30% ethyl acetate/hexane) R_f 0.69; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.11 (m, 4H), 5.89 (s, 2H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J*=247.0 Hz), 134.9 (d, *J*=3.3 Hz), 129.8 (d, *J*=8.7 Hz), 128.8, 115.9 (d, *J*=22.3 Hz), 105.7, 12.9; IR (KBr) 3111, 3057, 2982, 2922, 1510, 1408 cm^{-1}; GC–MS *m/z* (rel intensity) 188 (M^+-1, 100), 174 (12), 147 (10), 133 (8), 95 (13), 75 (8), 51 (3).

*4.2.12. 1-(4-Chlorophenyl)-2,5-dimethyl-1H-pyrrole (**14**).*[5j] Yield 94%. Brown solid, mp 56–57 °C (lit.[5j] mp 62–63 °C). TLC (30% ethyl acetate/hexane) R_f 0.65; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, *J*=8.5 Hz), 7.14 (d, 2H, *J*=8.5 Hz), 5.89 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.5, 129.5, 129.3, 128.7, 106.0, 12.9; IR (KBr) 3089, 3055, 2978, 2922, 1460, 1402 cm^{-1}; GC–MS *m/z* (rel intensity) 204 (M^+-1, 100), 190 (10), 169 (18), 154 (22), 111 (10), 83 (10), 75 (11), 51 (5).

*4.2.13. 1-(4-Bromophenyl)-2,5-dimethyl-1H-pyrrole (**15**).*[5c,14b] Yield 97%. Pale yellow solid, mp 74–75 °C (lit.[14b] mp 74–75 °C). TLC (30% ethyl acetate/hexane) R_f 0.68; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, *J*=8.6 Hz), 7.09 (d, 2H, *J*=8.6 Hz), 5.89 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.3, 129.8, 128.6, 121.5, 106.0, 12.9; IR (KBr) 3080, 3033, 2983, 2935, 1521, 1483, 1402 cm^{-1}; GC–MS *m/z* (rel intensity) 251 (M^++2, 100), 249 (M^+, 100), 234 (6), 169 (28), 154 (50), 129 (28), 84 (13), 50 (7).

*4.2.14. 1-(4-Iodophenyl)-2,5-dimethyl-1H-pyrrole (**16**).*[14b] Yield 90%. Yellow solid, mp 67–68 °C (lit.[14b] mp 62–64 °C). TLC (30% ethyl acetate/hexane) R_f 0.69; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, 2H, *J*=8.5 Hz), 6.95 (d, 2H, *J*=8.5 Hz), 5.89 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 130.1, 128.6, 106.1, 92.9, 12.9; IR (KBr) 3074, 3028, 2978, 2933, 1479, 1390 cm^{-1}; GC–MS *m/z* (rel intensity) 297 (M^+, 100), 169 (19), 154 (20), 129 (8), 76 (8), 50 (4).

*4.2.15. 1-(3-Fluorophenyl)-2,5-dimethyl-1H-pyrrole (**17**).*[14j] Yield 87%. Orange solid, mp 62–63 °C. TLC (20% ethyl acetate/hexane) R_f 0.73; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.39 (m, 1H), 7.12–7.10 (m, 1H), 7.01 (d, 1H, *J*=7.8 Hz), 6.95 (dt, 1H, *J*=9.0, 1.8 Hz), 5.90 (s, 2H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J*=247.9 Hz), 140.5 (d, *J*=9.5 Hz), 130.1 (d, *J*=9.1 Hz), 128.7, 124.1 (d, *J*=3.3 Hz), 115.7 (d, *J*=21.9 Hz), 114.8 (d, *J*=20.7 Hz), 106.1, 12.9; IR (KBr) 3055, 2976, 2921, 1604, 1407 cm^{-1}; GC–MS *m/z* (rel intensity) 188 (M^+-1, 100), 174 (12), 95 (11), 75 (8), 51 (3).

*4.2.16. 1-(2-Fluorophenyl)-2,5-dimethyl-1H-pyrrole (**18**).*[14j] Yield 86%. Pale orange liquid. TLC (20% ethyl acetate/hexane) R_f 0.67; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.27 (m, 4H), 5.93 (s, 2H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4 (d, *J*=250.8 Hz), 130.6, 129.7 (d, *J*=7.4 Hz), 129.1, 126.6 (d, *J*=13.2 Hz), 124.4 (d, *J*=3.3 Hz), 116.6 (d, *J*=20.3 Hz), 106.0, 12.4; IR (KBr) 3105, 3072, 2918, 1503, 1400 cm^{-1}; GC–MS *m/z* (rel intensity) 188 (M^+-1, 100), 174 (13), 95 (7), 75 (6), 51 (3).

*4.2.17. 4-(2,5-Dimethyl-1H-pyrrol-1-yl)benzonitrile (**19**).*[5c] Yield 40%. White solid, mp 91–92 °C. TLC (20% ethyl acetate/hexane) R_f 0.52; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 2H, *J*=8.8 Hz), 7.26 (d, 2H, *J*=8.8 Hz), 5.86 (s, 2H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 133.1, 128.9, 128.5, 118.2, 111.4, 107.1, 13.0; IR (KBr) 3061, 2978, 2920, 2228, 1606, 1506, 1402 cm^{-1}; GC–MS *m/z* (rel intensity) 195 (M^+-1, 100), 181 (13), 118 (8), 102 (11), 75 (5).

*4.2.18. 3-(2,5-Dimethyl-1H-pyrrol-1-yl)benzonitrile (**20**).*[14d] Yield 84%. White solid, mp 90–91 °C (lit.[14d] mp 92–94 °C). TLC (20% ethyl acetate/hexane) R_f 0.50; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 1H, *J*=7.3 Hz), 7.60 (t, 1H, *J*=7.3 Hz), 7.52–7.47 (m, 2H), 5.93 (s, 2H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 132.8, 131.6, 131.2, 130.1, 128.5, 117.8, 113.4, 106.8, 12.9; IR (KBr) 3101, 3051, 2978, 2916, 2229, 1583, 1520, 1407 cm^{-1}; GC–MS *m/z* (rel intensity) 195 (M^+-1, 100), 181 (12), 102 (8), 75 (4), 51 (3).

*4.2.19. 2-(2,5-Dimethyl-1H-pyrrol-1-yl)benzonitrile (**21**).*[14k] Yield 42%. Yellow solid, mp 75–76 °C (lit.[14k] mp 83–85 °C). TLC (20% ethyl acetate/hexane) R_f 0.55; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81–7.78 (m, 1H), 7.72 (td, 1H, *J*=7.8, 1.7 Hz), 7.54 (td, 1H, *J*=7.8, 1.2 Hz), 7.37–7.35 (m, 1H), 5.96 (s, 2H), 2.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 133.6, 133.5, 130.1, 128.8, 128.6, 115.9, 113.6, 107.0, 12.6; IR (KBr) 3103, 3068, 2916, 2228, 1595, 1493 cm^{-1}; GC–MS *m/z* (rel intensity) 195 (M^+-1, 100), 181 (28), 102 (10), 75 (4), 51 (4).

*4.2.20. 8-(2,5-Dimethyl-1H-pyrrol-1-yl)quinoline (**22**).*[14l] Yield 80%. Orange solid, mp 120–121 °C. TLC (20% ethyl acetate/hexane) R_f 0.22; ^1H NMR (400 MHz, $CDCl_3$) δ 8.97–8.96 (m, 1H), 8.23 (dd, 1H, *J*=8.3, 2.0 Hz), 7.93–7.90 (m, 1H), 7.64–7.63 (m, 2H), 7.43 (dd, 1H, *J*=8.3, 2.0 Hz), 6.02 (s, 2H), 1.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 145.4, 136.8, 135.9, 129.8, 129.7, 129.1, 128.4, 125.9, 121.6, 105.5, 12.8; IR (KBr) 3091, 3068, 2975, 1595, 1497, 1400 cm^{-1}; GC–MS *m/z* (rel intensity) 222 (M^+, 100), 207 (84), 180 (9), 155 (6), 129 (33), 103 (11), 77 (6), 51 (4).

*4.2.21. 2,5-Dimethyl-1-(naphthalen-4-yl)-1H-pyrrole (**23**).*[14b] Yield 96%. Pale yellow solid, mp 109–110 °C (lit.[14b] mp 120–122 °C). TLC (20% ethyl acetate/hexane) R_f 0.60; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J*=8.0 Hz), 7.57–7.49 (m, 2H), 7.44–7.42 (m, 2H), 7.13 (d, 1H, *J*=8.3 Hz), 6.01 (s, 2H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 134.2, 131.9, 129.8, 128.5, 128.0, 127.2, 126.5, 126.2, 125.4, 123.3, 105.4, 12.5; IR (KBr) 3101, 3062, 2980, 2929, 1594, 1409 cm^{-1};

GC–MS *m*/*z* (rel intensity) 221 (M^+, 100), 204 (32), 180 (3), 165 (11), 127 (16), 102 (9), 77 (5), 51 (3).

*4.2.22. 1-Phenyl-1,4-pentanedione (**24**).*[14f] Yield 75%. White liquid. TLC (20% ethyl acetate/hexane) R_f 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, J=7.1 Hz), 7.58–7.54 (m, 1H), 7.46 (t, 2H, J=7.6 Hz), 3.28 (t, 2H, J=6.3 Hz), 2.89 (t, 2H, J=6.3 Hz), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 198.5, 136.6, 133.1, 128.5, 127.9, 36.9, 32.4, 30.0; IR (KBr) 3422, 3061, 2914, 1702, 1686, 1597, 1448, 1358, 1211 cm^{-1}; GC–MS *m*/*z* (rel intensity) 176 (M^+, 5), 161 (21), 133 (12), 105 (100), 77 (43), 51 (12).

*4.2.23. 2-Methyl-1,5-diphenyl-1H-pyrrole (**25**).*[14g] Yield 86%. Pale yellow solid, mp 71–72 °C. TLC (20% ethyl acetate/hexane) R_f 0.51; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 3H), 7.16–7.10 (m, 5H), 7.06–7.05 (m, 2H), 6.35 (d, 1H, J=3.4 Hz), 6.09 (d, 1H, J=3.4 Hz), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 134.1, 133.5, 131.7, 128.9, 128.4, 127.9, 127.7, 127.3, 125.6, 108.6, 107.5, 13.3; IR (KBr) 3107, 3064, 2924, 1596, 1495, 1398 cm^{-1}; GC–MS *m*/*z* (rel intensity) 233 (M^+, 100), 217 (9), 191 (9), 115 (14), 77 (14), 51 (8).

*4.2.24. 1-(2-Ethylphenyl)-2-methyl-5-phenyl-1H-pyrrole (**26**).* Yield 86%. Yellow liquid. TLC (20% ethyl acetate/hexane) R_f 0.69; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.16 (m, 4H), 7.04–6.94 (m, 5H), 6.33 (d, 1H, J=3.4 Hz), 6.03 (d, 1H, J=3.4 Hz), 2.09–1.95 (m, 2H), 1.92 (s, 3H), 0.83 (t, 3H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.9, 134.1, 133.6, 131.6, 129.4, 129.0, 128.5, 127.9, 126.9, 126.3, 125.5, 107.9, 107.1, 23.3, 13.4, 12.9; IR (KBr) 3101, 3067, 2970, 2934, 1515, 1494, 1394 cm^{-1}; GC–MS *m*/*z* (rel intensity) 261 (M^+, 100), 246 (80), 230 (20), 184 (15), 115 (12), 77 (8); Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.30; H, 7.51; N, 5.73.

*4.2.25. 2-Methyl-5-phenyl-1-o-tolyl-1H-pyrrole (**27**).*[14m] Yield 94%. Yellow solid, mp 60–61 °C. TLC (20% ethyl acetate/hexane) R_f 0.67; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 3H), 7.20–7.18 (m, 1H), 7.10–7.04 (m, 5H), 6.39 (d, 1H, J=3.4 Hz), 6.10 (d, 1H, J=3.4 Hz), 1.99 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.9, 133.9, 133.6, 131.2, 130.8, 129.3, 128.3, 127.9, 126.9, 126.5, 125.6, 107.9, 107.2, 17.3, 12.8; IR (KBr) 3070, 3029, 2920, 1601, 1514, 1497, 1394 cm^{-1}; GC–MS *m*/*z* (rel intensity) 247 (M^+, 100), 232 (48), 170 (13), 115 (16), 91 (10), 65 (8).

*4.2.26. 2-Methyl-5-phenyl-1-m-tolyl-1H-pyrrole (**28**).* Yield 94%. Yellow solid, mp 72–73 °C. TLC (20% ethyl acetate/hexane) R_f 0.72; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.21 (m, 1H), 7.13–7.11 (m, 3H), 7.07–7.06 (m, 3H), 6.97–6.94 (m, 2H), 6.34 (d, 1H, J=3.4 Hz), 6.08 (d, 1H, J=3.4 Hz), 2.31 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.8, 134.1, 133.5, 131.7, 128.9, 128.6, 128.1, 127.9, 127.6, 125.51, 125.52, 108.5, 107.3, 21.3, 13.3; IR (KBr) 3095, 3036, 2920, 1603, 1516, 1491, 1395 cm^{-1}; GC–MS *m*/*z* (rel intensity) 247 (M^+, 100), 230 (9), 191 (8), 115 (11), 91 (7), 65 (5); Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 86.90; H, 7.02; N, 5.19.

*4.2.27. 2-Methyl-5-phenyl-1-p-tolyl-1H-pyrrole (**29**).*[14m] Yield 93%. Pale yellow solid, mp 73–74 °C. TLC (20% ethyl acetate/hexane) R_f 0.73; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.12 (m, 4H), 7.06–7.04 (m, 5H), 6.34 (d, 1H, J=3.4 Hz), 6.07 (d, 1H, J=3.4 Hz), 2.36 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.7, 134.1, 133.6, 131.7, 129.5, 128.1, 127.9, 127.7, 125.5, 108.4, 107.3, 21.1, 13.3; IR (KBr) 3034, 2922, 1601, 1516, 1445, 1398 cm^{-1}; GC–MS *m*/*z* (rel intensity) 247 (M^+, 100), 191 (13), 129 (9), 115 (12), 91 (9), 65 (10).

*4.2.28. 1-(4-Isopropylphenyl)-2-methyl-5-phenyl-1H-pyrrole (**30**).* Yield 85%. White solid, mp 78–79 °C. TLC (20% ethyl acetate/hexane) R_f 0.68; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 2H, J=8.3 Hz), 7.05–7.04 (m, 2H), 6.99–6.97 (m, 5H), 6.27 (d, 1H, J=3.4 Hz), 6.00 (d, 1H, J=3.4 Hz), 2.90–2.80 (m, 1H), 2.06 (s, 3H), 1.18 (d, 6H, J=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 136.9, 134.1, 133.6, 131.8, 128.1, 127.8, 127.7, 126.8, 125.5, 108.4, 107.2, 33.7, 23.9, 13.3; IR (KBr) 3036, 2961, 2926, 1512, 1456, 1396 cm^{-1}; GC–MS *m*/*z* (rel intensity) 275 (M^+, 100), 260 (15), 232 (10), 191 (10), 115 (9); Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.25; H, 7.83; N, 4.87.

*4.2.29. 2-Methyl-5-phenyl-1-(2-propylphenyl)-1H-pyrrole (**31**).* Yield 97%. Orange liquid. TLC (20% ethyl acetate/hexane) R_f 0.81; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 4H), 7.04–6.99 (m, 5H), 6.35 (d, 1H, J=3.5 Hz), 6.05 (d, 1H, J=3.5 Hz), 2.11–2.04 (m, 1H), 1.96–1.91 (m, 4H), 1.33–1.12 (m, 2H), 0.68 (t, 3H, J=7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 138.1, 134.1, 133.6, 131.6, 129.7, 129.6, 128.3, 127.9, 126.9, 126.3, 125.5, 107.9, 107.1, 32.4, 22.1, 14.0, 12.9; IR (KBr) 3070, 3033, 2960, 2933, 1602, 1514, 1491, 1394 cm^{-1}; GC–MS *m*/*z* (rel intensity) 275 (M^+, 100), 260 (81), 230 (27), 198 (12), 129 (11), 115 (16), 91 (9), 77 (9), 51 (6); Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 86.74; H, 8.09; N, 4.89.

*4.2.30. 1-(4-Methoxyphenyl)-2-methyl-5-phenyl-1H-pyrrole (**32**).*[14n] Yield 92%. White solid, mp 89–90 °C. TLC (20% ethyl acetate/hexane) R_f 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05–7.04 (m, 2H), 7.00–6.99 (m, 5H), 6.79 (d, 2H, J=8.8 Hz), 6.26 (d, 1H, J=3.4 Hz), 5.99 (d, 1H, J=3.4 Hz), 3.73 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 134.2, 133.6, 132.2, 131.9, 129.4, 127.9, 127.7, 125.5, 114.1, 108.3, 107.1, 55.4, 13.2; IR (KBr) 3069, 3002, 2937, 2835, 1601, 1514, 1445, 1247 cm^{-1}; GC–MS *m*/*z* (rel intensity) 263 (M^+, 100), 248 (20), 207 (23), 115 (9), 77 (4).

*4.2.31. 1-(3-Methoxyphenyl)-2-methyl-5-phenyl-1H-pyrrole (**33**).*[14n] Yield 98%. Yellow solid, mp 77–78 °C. TLC (20% ethyl acetate/hexane) R_f 0.64; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, 1H, J=8.0 Hz), 7.08–6.97 (m, 5H), 6.80–6.77 (m, 1H), 6.68 (dt, 1H, J=8.0, 1.5 Hz), 6.61 (t, 1H, J=1.5 Hz), 6.27 (d, 1H, J=3.4 Hz), 6.01 (d, 1H, J=3.4 Hz), 3.62 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 140.4, 134.1, 133.5, 131.6, 129.5, 127.9, 127.6, 125.6, 120.8, 114.1, 113.2, 108.6, 107.4, 55.3, 13.3; IR (KBr) 3066, 2921, 2835, 1601, 1514, 1489, 1223 cm^{-1}; GC–MS *m*/*z* (rel intensity) 263 (M^+, 100), 218 (8), 115 (9), 77 (6).

*4.2.32. 1-(2-Methoxyphenyl)-2-methyl-5-phenyl-1H-pyrrole (**34**).*[14n] Yield 94%. Yellow solid, mp 68–69 °C. TLC (20% ethyl acetate/hexane) R_f 0.64; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 1H), 7.03–7.00 (m, 6H), 6.86–6.83 (m, 2H), 6.28 (d, 1H, J=3.4 Hz), 6.02 (d, 1H, J=3.4 Hz), 3.59 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 134.5, 133.8, 132.0, 130.3, 129.2, 128.1, 127.8, 125.6, 120.6, 111.9, 107.94, 107.93, 106.9, 55.5, 12.6; IR (KBr) 3069, 2922, 1601, 1506, 1460, 1024 cm^{-1}; GC–MS *m*/*z* (rel intensity) 263 (M^+, 100), 248 (27), 232 (13), 217 (11), 115 (13), 77 (8), 51 (5).

*4.2.33. 1-(4-Fluorophenyl)-2-methyl-5-phenyl-1H-pyrrole (**35**).*[14o] Yield 80%. Yellow solid, mp 99–100 °C. TLC (20% ethyl acetate/hexane) R_f 0.63; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–7.02 (m, 4H), 6.98–6.96 (m, 5H), 6.26 (d, 1H, J=3.4 Hz), 6.01 (d, 1H, J=3.4 Hz), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, J=247.5 Hz), 135.4 (d, J=2.9 Hz), 134.3, 133.3, 131.7, 129.9 (d, J=8.7 Hz), 127.9 (d, J=21.1 Hz), 125.8, 116.0, 115.8, 108.7, 107.6, 13.2; IR (KBr) 3109, 3070, 2921, 1509, 1396, 1219 cm^{-1}; GC–MS *m*/*z* (rel intensity) 251 (M^+, 100), 235 (8), 209 (10), 115 (12), 95 (10), 75 (7).

*4.2.34. 1-(4-Chlorophenyl)-2-methyl-5-phenyl-1H-pyrrole (**36**).*[14p] Yield 83%. Yellow solid, mp 102–103 °C (lit.[14p] mp 105–106 °C). TLC (20% ethyl acetate/hexane) R_f 0.70; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.18–7.14 (m, 2H), 7.12–7.03 (m, 5H), 6.34 (d, 1H, J=3.4 Hz), 6.09 (d, 1H, J=3.4 Hz), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 134.2, 133.2, 133.1, 131.5, 129.6,

129.2, 128.1, 127.8, 125.9, 108.9, 107.9, 13.3; IR (KBr) 3068, 3030, 2924, 1516, 1496, 1396 cm^{-1}; GC–MS *m/z* (rel intensity) 267 (M^+, 100), 231 (18), 191 (23), 129 (10), 115 (13), 77 (10), 51 (5).

*4.2.35. 1-(4-Bromophenyl)-2-methyl-5-phenyl-1H-pyrrole (**37**).*[14p] Yield 81%. Yellow solid, mp 119–120 °C (lit.[14p] mp 125–126 °C). TLC (20% ethyl acetate/hexane) R_f 0.60; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 2H, *J*=8.5 Hz), 7.10–7.07 (m, 2H), 7.04–7.01 (m, 1H), 6.97–6.94 (m, 4H), 6.26 (d, 1H, *J*=3.4 Hz), 6.02 (d, 1H, *J*=3.4 Hz), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 134.1, 133.1, 132.1, 131.5, 129.9, 128.1, 127.8, 125.9, 121.1, 109.0, 107.9, 13.3; IR (KBr) 3059, 3034, 2972, 2920, 1516, 1491, 1396 cm^{-1}; GC–MS *m/z* (rel intensity) 313 (M^++2, 100), 311 (M^+, 100), 230 (29), 191 (23), 129 (10), 108 (17), 76 (8).

*4.2.36. 1-(4-Iodophenyl)-2-methyl-5-phenyl-1H-pyrrole (**38**).*[14p] Yield 84%. Yellow solid, mp 128–129 °C (lit.[14p] mp 139–140 °C). TLC (20% ethyl acetate/hexane) R_f 0.65; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 2H, *J*=8.5 Hz), 7.11–7.07 (m, 2H), 7.03–7.01 (m, 1H), 6.98–6.96 (m, 2H), 6.81 (d, 2H, *J*=8.5 Hz), 6.26 (d, 1H, *J*=3.4 Hz), 6.01 (d, 1H, *J*=3.4 Hz), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.1, 134.1, 133.1, 131.5, 130.2, 128.1, 127.8, 125.9, 109.1, 107.9, 92.5, 13.3; IR (KBr) 3067, 2972, 2922, 1508, 1497, 1319 cm^{-1}; GC–MS *m/z* (rel intensity) 359 (M^+, 100), 230 (15), 191 (10), 109 (8), 76 (6).

*4.2.37. 1-(3-Fluorophenyl)-2-methyl-5-phenyl-1H-pyrrole (**39**).* Yield 86%. White solid, mp 75–76 °C. TLC (20% ethyl acetate/hexane) R_f 0.76; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.18 (m, 2H), 7.04–6.98 (m, 5H), 6.87–6.80 (m, 2H), 6.27 (d, 1H, *J*=3.4 Hz), 6.02 (d, 1H, *J*=3.4 Hz), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J*=247.9 Hz), 140.9 (d, *J*=9.5 Hz), 134.2, 133.2, 131.57, 130.0, 129.9, 128.0, 127.7, 125.9, 124.4 (d, *J*=3.3 Hz), 115.9 (d, *J*=22.3 Hz), 114.5 (d, *J*=21.1 Hz), 109.0, 107.9, 107.89, 13.3; IR (KBr) 3072, 3036, 2923, 1593, 1516, 1491, 1394 cm^{-1}; GC–MS *m/z* (rel intensity) 251 (M^+, 100), 235 (9), 209 (7), 115 (11), 95 (9), 75 (5); Anal. Calcd for $C_{17}H_{14}FN$: C, 81.25; H, 5.62; N, 5.57. Found: C, 80.57; H, 5.97; N, 5.57.

*4.2.38. 1-(2-Fluorophenyl)-2-methyl-5-phenyl-1H-pyrrole (**40**).*[14g] Yield 83%. Yellow solid, mp 88–89 °C. TLC (20% ethyl acetate/hexane) R_f 0.68; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (m, 1H), 7.10–7.00 (m, 8H), 6.29 (d, 1H, *J*=3.4 Hz), 6.04 (d, 1H, *J*=3.4 Hz), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, *J*=250.3 Hz), 134.7, 133.2, 132.1, 130.8, 129.6, 129.5, 128.0, 127.4 (d, *J*=9.1 Hz), 127.3 (d, *J*=21.9 Hz), 125.9, 124.4 (d, *J*=4.1 Hz), 116.5 (d, *J*=20.3 Hz), 108.8, 107.7, 107.67, 12.5; IR (KBr) 3101, 3065, 2922, 1506, 1456, 1396 cm^{-1}; GC–MS *m/z* (rel intensity) 251 (M^+, 100), 230 (7), 115 (11), 75 (9), 51 (5).

*4.2.39. 4-(2-Methyl-5-phenyl-1H-pyrrol-1-yl)benzonitrile (**41**).* Yield 75%. White solid, mp 113–114 °C. TLC (20% ethyl acetate/hexane) R_f 0.54; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 2H, *J*=8.6 Hz), 7.16 (d, 2H, *J*=8.6 Hz), 7.11–7.03 (m, 3H), 6.93–6.92 (m, 2H), 6.28 (d, 1H, *J*=3.4 Hz), 6.05 (d, 1H, *J*=3.4 Hz), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.2, 132.9, 132.8, 131.3, 129.0, 128.2, 127.9, 126.2, 118.2, 110.9, 109.9, 108.8, 13.4; IR (KBr) 3091, 3070, 2922, 2229, 1603, 1506, 1394 cm^{-1}; GC–MS *m/z* (rel intensity) 258 (M^+, 100), 242 (8), 115 (14), 102 (12), 51 (5); Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 82.84; H, 5.25; N, 9.96.

*4.2.40. 3-(2-Methyl-5-phenyl-1H-pyrrol-1-yl)benzonitrile (**42**).* Yield 85%. White solid, mp 105–106 °C. TLC (20% ethyl acetate/hexane) R_f 0.46; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J*=7.8 Hz), 7.38 (t, 2H, *J*=7.8 Hz), 7.28 (d, 1H, *J*=8.0 Hz), 7.09–7.04 (m, 3H), 6.92 (d, 2H, *J*=9.0 Hz), 6.27 (d, 1H, *J*=3.4 Hz), 6.04 (d, 1H, *J*=3.4 Hz), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 134.3, 133.0, 132.7, 131.6, 131.3, 130.8, 129.9, 128.2, 127.9, 126.2, 117.8, 113.1, 109.6, 108.5, 13.3; IR (KBr) 3099, 3066, 2922, 2231, 1508, 1495, 1393 cm^{-1}; GC–MS *m/z* (rel intensity) 258 (M^+, 100), 183 (14), 128 (15), 115 (10), 102 (12), 77 (7), 51 (6); Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.48; H, 5.53; N, 10.65.

*4.2.41. 2-(2-Methyl-5-phenyl-1H-pyrrol-1-yl)benzonitrile (**43**).* Yield 60%. White solid, mp 98–99 °C. TLC (20% ethyl acetate/hexane) R_f 0.40; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, 1H, *J*=7.6, 1.2 Hz), 7.52 (td, 1H, *J*=7.8, 1.5 Hz), 7.38–7.35 (m, 1H), 7.22 (d, 1H, *J*=8.0 Hz), 7.09–6.97 (m, 5H), 6.31 (d, 1H, *J*=3.4 Hz), 6.08 (d, 1H, *J*=3.4 Hz), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 135.0, 133.4, 133.3, 132.8, 131.7, 130.4, 128.3, 128.1, 127.8, 126.1, 115.9, 113.5, 109.7, 108.7, 12.8; IR (KBr) 3070, 3034, 2922, 2229, 1516, 1456, 1394 cm^{-1}; GC–MS *m/z* (rel intensity) 258 (M^+, 100), 183 (14), 128 (15), 115 (10), 102 (12), 77 (7), 51 (6); Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.69; H, 5.57; N, 10.82.

*4.2.42. 8-(-2-Methyl-5-phenyl-1H-pyrrol-1-yl)quinoline (**44**).* Yield 77%. White solid, mp 111–112 °C. TLC (20% ethyl acetate/hexane) R_f 0.30; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90–8.89 (m, 1H), 8.11 (dd, 1H, *J*=8.3, 1.7 Hz), 7.75 (dd, 1H, *J*=7.3, 2.2 Hz), 7.40–7.32 (m, 3H), 6.88 (s, 5H), 6.38 (d, 1H, *J*=3.4 Hz), 6.13 (d, 1H, *J*=3.4 Hz), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 151.3, 151.27, 145.4, 137.2, 135.9, 135.4, 133.9, 133.2, 130.2, 128.9, 128.2, 127.7, 127.4, 125.9, 125.4, 121.6, 108.6, 107.3, 12.9; IR (KBr) 3055, 2976, 2920, 1599, 1516, 1499, 1402 cm^{-1}; GC–MS *m/z* (rel intensity) 284 (M^+, 100), 269 (15), 241 (8), 156 (11), 129 (17); Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.63; H, 5.84; N, 9.99.

*4.2.43. 2-Methyl-1-(naphthalene-4-yl)-5-phenyl-1H-pyrrole (**45**).*[14g] Yield 90%. Green liquid, mp 108–109 °C. TLC (20% ethyl acetate/hexane) R_f 0.70; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, 2H, *J*=6.6 Hz), 7.42–7.33 (m, 3H), 7.29–7.26 (m, 2H), 6.94–6.85 (m, 5H), 6.40 (d, 1H, *J*=3.4 Hz), 6.11 (d, 1H, *J*=3.4 Hz), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.3, 134.0, 133.5, 132.9, 131.9, 128.5, 128.1, 127.8, 127.2, 127.1, 126.9, 126.4, 125.6, 125.3, 123.4, 108.3, 107.2, 12.7; IR (KBr) 3057, 2922, 2854, 1599, 1508, 1408 cm^{-1}; GC–MS *m/z* (rel intensity) 283 (M^+, 100), 241 (7), 165 (8), 127 (12).

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References and notes

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