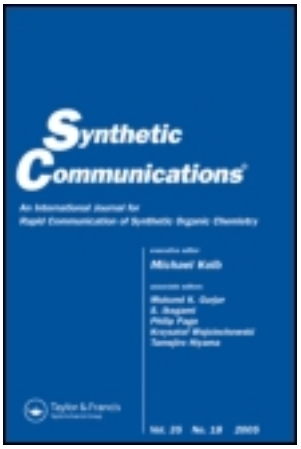

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Paal-Knorr Pyrrole Synthesis Using Recyclable Amberlite IR 120 Acidic Resin: A Green Approach

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Accepted author version posted online: 17 Nov 2011.Version of record first published: 25 Jan 2012.

To cite this article: Aarti Devi , Shallu , M. L. Sharma & Jasvinder Singh (2012): Paal-Knorr Pyrrole Synthesis Using Recyclable Amberlite IR 120 Acidic Resin: A Green Approach, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:10, 1480-1488

To link to this article: http://dx.doi.org/10.1080/00397911.2010.540766

Synthetic Communications®, 42: 1480–1488, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.540766

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PAAL–KNORR PYRROLE SYNTHESIS USING RECYCLABLE AMBERLITE IR 120 ACIDIC RESIN: A GREEN APPROACH

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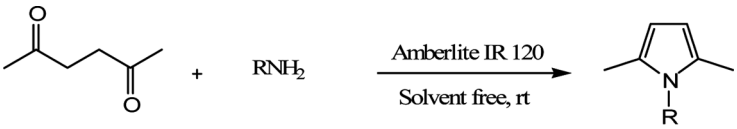
GRAPHICAL ABSTRACT



R = alky, aryl, heteroaromatic or polyaryl group.

Abstract *Amberlite IR 120 acidic resin, a polymer matrix, has been demonstrated as a catalyst for Paal-Knorr condensation of 2,5-hexadione with primary amines under solvent-free conditions. This is an efficient, mild, and green methodology for N-substituted pyrrole derivatives.*

Keywords Amberlite IR 120; Paal–Knorr condensation; pyrrole; solvent free

INTRODUCTION

Pyrroles are an important class of heterocyclic compounds with different biological activities.[1] Many members of this family are used as antimalarial, anti-inflammatory, anti-asthmatic, antibacterial, antihypertensive, and tyrosine kinase inhibiting agents,[2] for example, lipitor[3] (cholesterol-lowering drug) and amtolmetin[4] (anti-inflammatory agent). Functionalized pyrroles are abundant in nature, forming characteristic subunits of haeme, chlorophyll, bile pigments, and vitamin B_{12}.[5] Despite their importance from pharmacological, industrial, and synthetic points of view, relatively few methods for their preparation have been reported.[6] Of the current methods, such as Hantzsch,[7] Knorr,[8] and aza-Wittig[9] reactions, Paal–Knorr[10] has experienced a rekindled interest from synthetic perspectives because it is simple and straightforward. Various catalysts reported for Paal–Knorr reaction, such as $Ti(OiPr)_4$.[11] Al_2O_3,[12] $Bi(NO_3)_3$,[13] $Bi(OTf)_3$,[14] $Sc(OTf)_3$,[15] montmorillonite-KSF,[16] sulfamic acid,[17a] $CoCl_2$,[17b] Indium (III)[17c]

Received August 23, 2010.
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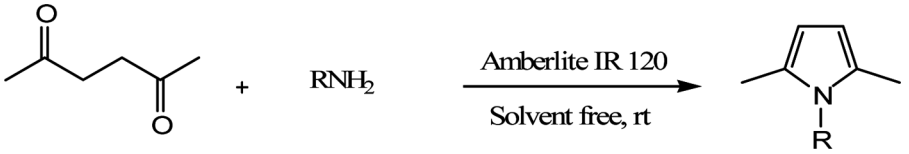


Scheme 1. Paal–Knorr pyrrole condensation. R = alkyl, aryl, heteroaromatic or polyaryl group.

N,N,N′,N′-tetrachlorobenzene-1,3-disulfonamide, and N,N′-diiodo-N,N′-1,2-ethanediylbis(p-toluenesulfonamide)[17d] are associated with one or other of these drawbacks: poor yield, harsh reaction conditions, tedious workup leading to toxic-metal-containing waste, requirement for inert atmosphere or high temperature, use of stoichiometric or expensive reagents, destruction of catalyst, and use of toxic solvents such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF). Therefore, the search continues for a better catalyst for the synthesis of pyrroles in terms of operational simplicity, reusability, economic viability, and greater selectivity.

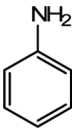
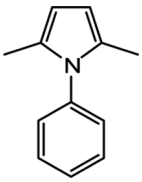
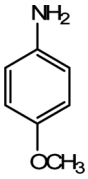
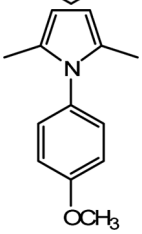
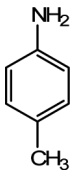
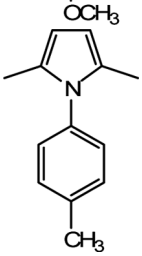
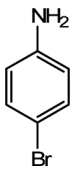
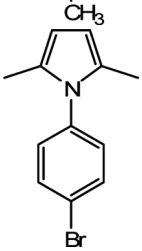
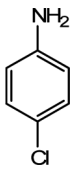
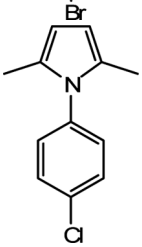
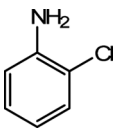
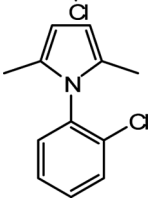
The development of new catalytic methods without use of any metal catalyst or toxic solvents, with efficient recycling of catalyst, and avoiding stringent reaction conditions is a *conditio sine quo non* in chemical research for economically and environmentally attractive processes worldwide. One such method in organic synthesis is the use of reagents and catalysts that are bound to a polymer matrix insoluble in the reaction media, so that they can be recycled.[18a] Use of styryl resin (D001) has been reported in literature.[18b] Amberlite IR 120 acidic resin is polystyrene divinylbenzene polymer with supported $-SO_3H$ functional group. Here, this resin has been used as an efficient, cost-effective, and recyclable heterogeneous catalyst for Paal-Knorr pyrrole synthesis under solvent-free conditions.

RESULTS AND DISCUSSION

Recently, the use of solid acids as heterogeneous catalysts has received tremendous interest in organic synthesis[19] because these can be easily separated from the reaction mixture by simple filtration and can be reused with or without activation, making the process economically more viable. During the past few years, amberlite IR 120 acidic resin has emerged as a substitute for conventional acidic catalysts in various organic reactions such as alcohol oxidation,[20] α-amino phosphonates synthesis,[21] glycosyl dihydropyridones synthesis,[22] and synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazole.[23] In continuation of our work on environmentally friendly synthetic strategies,[24] we herein report a facile method of pyrrole synthesis by condensation of 1,4-diketones with primary amines in the presence of amberlite IR 120 acidic resin.

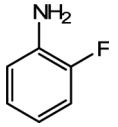
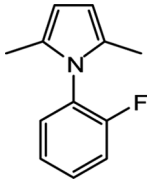
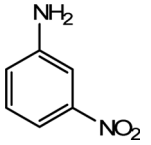
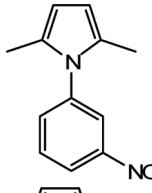
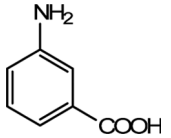
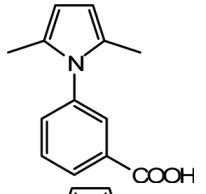
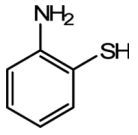
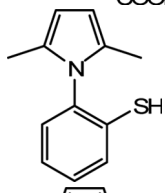
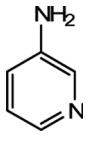
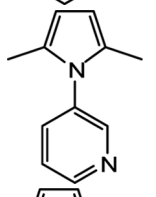
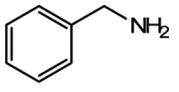
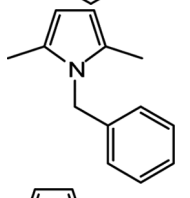
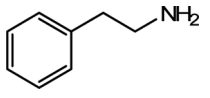
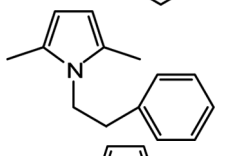
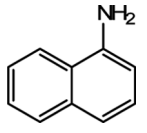
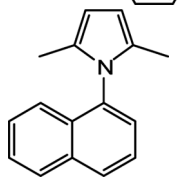
In conventional systems, an excess of amine usually has to be used to promote condensation. From a recent atom-economical standpoint, the use of equimolar substrates is strongly required. Thus, initially we treated aniline with nearly equimolar 2,5-hexadione to obtain exclusive product N-phenyl-2,5-dimethylpyrrole in 99% yield after 18 min. Under microwave irradiation, we get 98% yield for the reaction in 12 min, but all the reported reactions were carried out at room temperature to minimize energy consumption, which is one of the principles of green chemistry. The results obtained with various amines are shown in Table 1. It is clear from

Table 1. Paal–Knorr pyrrole synthesis using amberlite IR 120

No.	Amine	Product	Time (min)	Mp (°C)	Yield (%)
1			18	—	96
2			20	60–61	92
3			20	45–46	99
4			30	75–76	93
5			28	56–57	91
6			32	—	70

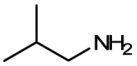
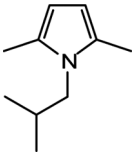
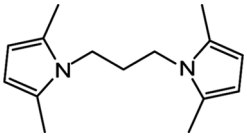
(*Continued*)

Table 1. Continued

No.	Amine	Product	Time (min)	Mp (°C)	Yield (%)
7			30	—	99
8			36	84–85	98
9			30	145–146	97
10			36	—	98
11			48	—	93
12			16	47–48	99
13			14	—	99
14			40	120–121	99

(*Continued*)

Table 1. Continued

No.	Amine	Product	Time (min)	Mp (°C)	Yield (%)
15			6	—	99
16			5	—	99

Note. All the compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectra and verified by comparison with literature/authentic samples.

the Table 1 that the reactions proceed very well in both aliphatic and aromatic amines. Less nucleophilic aromatic amines require longer times for completion of reaction compared to more nucleophilic aliphatic amines. A structure–activity relationship study in aromatic amines shows that aromatic amines with electron-donating groups react faster to aromatic amines with electron-withdrawing groups. The substitution pattern on the aromatic ring makes a large impact on reactivity as shown by 2, 3, and 4-nitro anilines, where 2-nitro aniline did not react at all, 4-nitro aniline gives 30% yield, and 3-nitro aniline gives 98% yield of product. Similarly, 4-amino benzoic acid did not react at all, but 3-aminobenzoic acid gives corresponding pyrrole in 97% yield. Sterically very hindered 2-amminoacetophenone and 2-aminothiophenone did not yield any product. Heteroaromatic 3-amino pyridine reacted excellently to give corresponding pyrrole in 92% yield. With 1,3-diaminopropane, bispyrrole was obtained in 99% yield. It is gratifying that the present methodology is compatible with various functionalities such as methoxy, nitro, -SH, and halo groups.

For optimizing the recyclability of the catalyst, experiments were performed over aniline and 2,5-hexadione. Fresh catalyst gave a yield of 96%, and when the same catalyst was repeatedly used up to six times under similar conditions, the yields were 96, 96, 96, 95, 96, and 95% respectively. Thus, the catalyst was recycled and reused for six times with slight degradation on each step but without any loss of activity of undegraded resin.

CONCLUSION

In conclusion, we have demonstrated a mild, efficient, and environmentally friendly approach to the synthesis of substituted pyrroles using amberlite IR 120 acidic resin as heterogeneous catalyst. Significant features of this strategy include operational simplicity, solvent-free conditions, good yields, no side products, no requirement for extra source of energy such as microwave or ultrasound, and tolerance of various functionalities.

EXPERIMENTAL

NMR spectra were recorded on a Jeol AL 300-MHz Fourier transform (FT) NMR instrument. Mass spectra were recorded on a Q-TOF Micro (Waters) mass spectrometer. Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer IR spectrophotometer. All solvents and reagents were purchased from Aldrich with high quality and were used without any further purification. All yields refer to isolated products.

Typical Procedure

A mixture of 2,5-hexadione (570 mg, 5 mmol), aniline (558 mg, 6 mmol), and amberlite IR 120 (200 mg) was stirred at room temperature under solvent-free conditions for 18 min. After completion of reaction, as monitered by thin-layer chromatography (TLC), the reaction mixture was diluted with diethyl ether and filtered to recover the catalyst. The ether layer was washed with saturated sodium bicarbonate solution and brine solution, dried (anhydrous Na_2SO_4), and concentrated in vacuo. The residue was purified by silica-gel column chromatography (eluting with 20% ethyl acetate in hexane) to afford pure product N-phenyl-2,5-dimethylpyrrole (846 mg) in 99% yield. The recovered catalyst was washed with 5% diluted HCl and dried prior to reuse. The IR spectrum of the recovered catalyst was identical to that of the commercially available catalyst, which was reused for further reactions (six times) without loss of activity. All the compounds are known and were identified by comparison with those of the authentic samples.

Product Characterization Data[17]

2,5-Dimethyl-1-phenyl-1H-pyrrole (Entry 1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 6H), 5.80 (s, 2H), 7.17 (m, 2H), 7.42 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.86, 103.81, 125.66, 126.29, 126.56, 126.86, 136.98.

1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole (Entry 2). Mp 60–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 6H), 3.84 (s, 3H), 5.77 (s, 2H), 6.94 (d, 2H), 7.23 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.40, 52.58, 103.00, 111.53, 125.91, 126.61, 129.32, 156.21.

2,5-Dimethyl-1-p-tolyl-1H-pyrrole (Entry 3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 6H), 2.40 (s, 3H), 5.81 (s, 2H), 7.07 (d, 2H), 7.22 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.56, 18.67, 103.21, 125.55, 125.98, 127.21, 134.05, 134.69.

1-(4-Bromophenyl)-2,5-dimethyl-1H-pyrrole (Entry 4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 6H), 5.78 (s, 2H), 7.06 (d, 2H), 7.55 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.90, 104.46, 119.32, 125.90, 127.71, 130.07, 136.06.

1-(4-Chlorophenyl)-2,5-dimethyl-1H-pyrrole (Entry 5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 6H), 5.83 (s, 2H), 7.09 (d, 2H), 7.37 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.85, 104.32, 126.14, 127.15, 127.41, 131.34.

1-(2-Chlorophenyl)-2,5-dimethyl-1H-pyrrole (Entry 6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 6H), 5.83 (d, 2H), 7.25 (m, 1H), 7.34 (m, 2H), 7.50

(m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.35, 103.87, 116.78, 125.35, 126.02, 127.32, 128.53, 131.84, 140.95.

2,5-Dimethyl-1-(2-fluorophenyl)-1H-pyrrole (Entry 7). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 6H), 5.98 (d, 2H), 7.32 (m, 3H), 7.47 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.25, 104.05, 116.23, 122.23, 124.63, 126.66, 127.52, 128.45, 157.91.

2,5-Dimethyl-1-(3-nitrophenyl)-1H-pyrrole (Entry 8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 6H), 5.84 (d, 2H), 7.56 (d, 1H), 7.68 (t, 1H), 8.07 (s, 1H), 8.24 (d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.49, 104.84, 120.65, 125.66, 126.13, 127.28, 131.60, 137.81, 146.18.

3-(2,5-Dimethyl-pyrrol-l-yl)benzoic Acid (Entry 9). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 6H), 5.71 (d, 2H), 7.76 (m, 2H), 8.25 (m, 2H), 12.21 (bs, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.51, 105.83, 120.32, 125.17, 126.23, 128.19, 130.26, 132.61, 139.52, 166.34.

2-(2,5-Dimethyl-pyrrol-l-yl)benzenethiol (Entry 10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.80 (s, 3H), 1.95 (s, 3H), 2.76 (bs, 1H), 5.87 (d, 2H), 7.09 (m, 2H), 7.28 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.25, 10.44, 104.43, 116.34, 123.83, 125.69, 125.96, 129.19, 129.32, 145.63.

3-(2,5-Dimethyl-pyrrol-l-yl)pyridine (Entry 11). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 6H), 5.83 (d, 2H), 7.40 (m, 1H), 7.55 (m, 1H), 8.50 (d, 1H), 8.62 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.13, 107.13, 123.40, 128.40, 135.28, 135.73, 148.66, 149.53. EIMS (70 eV) m/z 172.1 [M^+], 171.1, 156.1.

1-Benzyl-2,5-dimethyl-1H-pyrrole (Entry 12). Mp 43–44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 6H), 5.11 (s, 2H), 5.77 (s, 2H), 6.81 (m, 2H), 7.23 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.48, 44.65, 103.82, 123.59, 125.95, 126.92, 128.64, 136.66.

2,5-Dimethyl-1-phenethyl-1H-pyrrole (Entry 13). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 6H), 2.85 (t, 2H, $J = 7.50$ Hz), 3.91 (t, 2H, $J = 7.50$ Hz), 5.74 (s, 2H), 7.03 (m, 2H), 7.25 (m, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.21, 35.46, 43.02, 103.25, 124.43, 124.80, 126.40, 126.66, 136.31.

2,5-Dimethyl-1-(naphthalene-1-yl)-1H-pyrrole (Entry 14). Mp 120–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83 (s, 6H), 5.90 (s, 2H), 7.20 (m, 1H), 7.51 (m, 4H), 7.58 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.58, 103.82, 107.39, 116.80, 121.40, 122.52, 125.93, 126.45, 129.97, 132.14, 133.96.

2,5-Dimethyl-1-(2-methylpropyl)-1H-pyrrole (Entry 15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (d, 6H, $J = 6.60$ Hz), 2.17 (m, 1H), 2.36 (s, 6H), 3.67 (d, 2H, $J = 6.60$ Hz), 5.85 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 11.33, 18.47, 28.39, 49.02, 104.09, 125.27.

1,3-Bis-(2,5-dimethyl-pyrrol-1-yl)propane (Entry 16). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (m, 2H), 2.13 (s, 12H), 3.71 (t, 4H), 5.67 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.09, 10.37, 30.38, 40.06, 103.27, 103.96, 123.88, 124.33.

ACKNOWLEDGMENT

The authors are very grateful to the University Grants Commission India (UGC) for financial assistance.

REFERENCES

1. (a) Lainton, J.; Hoffman, J. W.; Martin, B. R.; Compton, D. R. 1-Alkyl-3-(1-naphthoyl)-pyrroles: A new class of cannabinoid. *Tetrahedron Lett.* **1995**, *36*, 1401–1403; (b) Rango, R.; Marshal, G. R.; Di Santo, R.; Costi, R.; Rompei, S.; Artico, M. Antimycobacterial pyrroles: Synthesis, anti-*Micobacterium* tuberculosis activity, and QSAR studies. *Bioorg. Med. Chem.* **2008**, *8*, 1423–1432.
2. Manning, A. R.; Devis, D. J. Targetting JNK for therapeutic benefit: From junk to gold? *Nat. Rev., Drug Discov.* **2003**, *2*, 554–565.
3. Roth, B. D. Preparation of *trans*-6-[(cabamoylpyrrolyl)alkyl]-4-hydroxypyranones as hypocholesterolemics. *Chem. Abstr.* **1987**, *107*, 198087.
4. Anzalone, S. Use of amtolmetin guacil as an anti-Inflammatory agent, which also inhibits gastric secretion. *Chem. Abstr.* **1997**, *126*, 139884.
5. De Leo, C. Y.; Ganem, B. A new approach to porphobilinogen and its analogues. *Tetrahedron* **1997**, *53*, 7731–7752.
6. Gilchrist, T. L. Synthesis of aromatic heterocycles. *J. Chem. Soc., Perkin Trans. 1* **1998**, 615–628.
7. (a) Hantzsch, A. Pyrrole synthesis. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 1474; (b) Trautwein, A. W.; Submuth, R. D.; Jung, G. Hanzsch pyrrole synthesis on solid support. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2381–2384.
8. (a) Knorr, L. Synthesis of pyrroles. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1635; (b) Alberola, A.; Ortega, A. G.; Sadaba, M. L.; Sanudo, C. Versatility of weinreb amides in the knorr pyrrole synthesis. *Tetrahedron* **1999**, *55*, 6555–6566.
9. (a) Alonso, C.; Aparicio, D.; Rubiales, G.; de los Santos, J. M. The aza-Wittig reaction: An efficient tool for the construction of carbon–nitrogen double bonds. *Tetrahedron* **2007**, *63*, 523–575; (b) Freifeld, I.; Shojaei, H.; Langer, P. Synthesis of 2-alkylidenepyrrolidines and pyrroles by condensation of 1,3-dicarbonyl dianions with α-azidoketones and subsequent intramolecular staudinger-aza-wittig reaction. *J. Org. Chem.* **2006**, *71*, 4965–4968.
10. (a) Jones, R. A.; Been, R. G. P. *The Chemistry of Pyrroles*; Academic Press: New York, 1977; p. 3; (b) Chiu, P. K.; Sammes, M. P. The synthesis and chemistry of azolenins, part 18: Preparation of 3-ethoxycarbonyl-3-pyrrole via paal–knorr reaction, and sigmatropic rearrangements involving competitive ester migrations C-2, C-4, and N. *Tetrahedron* **1990**, 46, 3439–3456.
11. Yu, S. X.; Quesne, P. W. Metabolites, 3: Total synthesis of (±) funebral, a rotationally restricted pyrrole alkaloid, using a novel paal–Knorr reaction. *Tetrahedron Lett.* **1995**, *36*, 6205–6208.
12. Ballini, R.; Barboni, L.; Bosica, G.; Petrini, M. 2, 5-Dialkylfurans and nitroalkanes as source of 2,3,5-trialkylpyrroles. *Synlett* **2000**, *11*, 391–393.
13. Banik, B. K.; Renteria, M.; Dasgupta, S. K. A straightforward highly efficient paal–Knorr synthesis of pyrroles. *Tetrahedron Lett.* **2005**, *46*, 2643–2645.
14. Yadav, J. S.; Reddy, B. V.; Eashwaraiah, B.; Gupta, M. K. $Bi(OTf)_3$/[bmim]BF_4 as novel and reusable catalytic system for the synthesis of furan, pyrrole, and thiophene derivatives. *Tetrahedron Lett.* **2004**, *45*, 5873–5876.
15. Chen, J.; Wu, H.; Zheng, Z.; Jin, C.; Zhang, X.; Su, W. An approach to the Paal–Knorr pyrroles synthesis catalyzed by $Sc(OTf)_3$ under solvent-free conditions. *Tetrahedron Lett.* **2006**, *47*, 5383–5387.

16. Banik, B. K.; Samajdar, S.; Banik, I. Simple synthesis of pyrroles. *J. Org. Chem.* **2004**, *69*, 213–216.
17. (a) De, S. K. Sulfamic acid as a novel, efficient, cost-effective, and reusable solid acid catalyst for the synthesis of pyrroles under solvent-free conditions. *Synth. Commun.* **2008**, *38*, 803–809; (b) De, S. K. Cobalt(II) chloride as a novel and efficient catalyst for the synthesis of 1,2,5-trisubstituted pyrroles under solvent free conditions. *Heteroatom Chem.* **2008**, *19*, 592–595; (c) Chen, J. X.; Liu, M. C.; Yang, X. L.; Ding, J. C.; Wu, H. Y. Indium(III)-catalyzed synthesis of N-substituted pyrroles under solvent-free conditions. *J. Braz. Chem. Soc.* **2008**, *19*, 877–883; (d) Ghorbani-Vaghei, R.; Veisi, H. One-pot synthesis of substituted pyrroles with N,N,N′,N′-tetrachlorobenzene-1,3-disulfonamide and N,N′-diiodo-N,N′-1,2-ethanediylbis(p-toluenesulfonamide) as novel catalytic reagents. *South Afr. J. Chem.* **2009**, *62*, 33–38.
18. (a) Hodge, P.; Sherrington, D. C. *Polymer-Supported Reactions in Organic Synthesis*. New York, John Willey & Sons: 1980; (b) Clark, J. H. Solid acids for green chemistry. *Acc. Chem. Res.* **2002**, *35*, 791–797; (c) Yuan, S. Z.; Liu, J.; Xu, L. A convenient synthesis of pyrroles catalyzed by acidic resin under solvent-free condition. *Chin. Chem. Lett.* **2010**, *21*, 664–668.
19. Bhati, N.; Sarma, K.; Goswami, A. Alcohol oxidation in ionic liquid with UHP and recyclable amberlite IR 120 acidic resin: A green approach. *Chem. Lett.* **2008**, *37*, 496–497.
20. Bhattacharya, A. K.; Rana, K. C. Amberlite IR 120–catalyzed three-component synthesis of α-amino phosphonates in one pot. *Tetrahedron Lett.* **2008**, *49*, 2598–2601.
21. Tiwari, V. K.; Tewari, N.; Katiyar, D.; Tripathi, R. P. One-pot amberlite IR 120–catalyzed synthesis of glycosyl dihydropyridones. *Manatsh. Chem.* **2007**, *138*, 1297–1302.
22. Sharma, S. D.; Konwar, D. Practical, ecofriendly, and chemoselective method for the synthesis of 2-aryl-1-arylmethyl-1H-benzimidazoles using amberlite IR 120 as a reusable heterogeneous catalyst in aqueous media. *Synth. Commun.* **2009**, *39*, 980–991.
23. (a) Singh, V.; Kaur, S.; Sapehiya, V.; Singh, J.; Kad, G. L. Microwave-accelerated preparation of [bmim]HSO_4 ionic liquid: An acid catalyst for improved synthesis of coumarines. *Catal. Commun.* **2005**, *6*, 57–60; (b) Gupta, N.; Sonu; Kad, G. L.; Singh, J. Acidic ionic liquid [bmim]HSO_4: An efficient catalyst for acetalization and thioacetalization of carbonyl compounds and their subsequent deprotection. *Catal. Commun.* **2007**, *8*, 1323–1328; (c) Gupta, N.; Kad, G. L.; Singh, J. Enhancing nucleophilicity in ionic liquid [bmim]HSO_4: A recyclable media and catalyst for the halogenation of alcohols. *J. Mol. Catal. A: Chemical* **2009**, *302*, 11–14.