Karaj branch

Journal of Applied Chemical Research
jacr.kiau.ac.in

Journal of Applied Chemical Research, 12, 3, 31-41 (2018)

Application of Nicotinic Acid Functionalized Chlorosulfonic Acid as a Green Catalyst for the Synthesis of Bis(2-methyl-1*H*-indole) Derivatives

Syedeh Fatemeh Hosseinzadeh, Masoud Mokhtary*

Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran

(Received 07 Sep. 2017; Final version received 11 Dec. 2017)

Abstract

3-Carboxy-1-sulfopyridin-1-ium chloride ($[CPySO_3H]^+Cl^-$) as a novel ionic organocatalyst for the condensation of aldehydes and 2-methylindole to synthesize bis(2-methyl-1*H*-indole) derivatives in acetonitrile at room temperature has been developed. Some tetrakis (2-methyl-1*H*-indole) derivatives have also been synthesized by the reaction of 2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde and 2-methylindole or indole in the presence of chlorosulfonic acid immobilized on nicotinic acid ($[CPySO_3H]^+Cl^-$) at room temperature. All products formed in excellent yields over short reaction times under mild and environmentally friendly conditions. This methodology offers significant improvements for the synthesis of bis(2-methyl-1*H*-indole) derivatives with regard to the yield of products, simplicity in operation and reusability of the catalyst.

***Keywords**: Bis(2-methyl-1H-indole), Chlorosulfonic acid, 3-Carboxy-1-sulfopyridin-1-ium, Tetrakis (2-methyl-1H-indole), Nicotinic acid.*

**Corresponding author:* *Masoud Mokhtary, Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran. E-mail: mmokhtary@iaurasht.ac.ir.*

Introduction

As part of in progress developments in green synthetic strategies, the design of organic reactions under room temperature is an area of current interest due to the most effective way to save energy. Indole is widely distributed in the natural environment and can be produced by a variety of bacteria. As an intercellular signal molecule, indole regulates various aspects of bacterial physiology, including spore formation, plasmid stability, resistance to drugs, biofilm formation, and virulence [1]. The amino acid tryptophan is an indole derivative and the precursor of the neurotransmitter serotonin [2]. Many drugs contain the indole ring as their core structures. For example: fluvastatin sodium (Lescol) **I** is an HMG-CoA reductase inhibitor. In addition, sumatriptan succinate (Imitrex) **II**, a serotonin receptor (5-HTIBID) agonist, is used to treat migraines. Also, naratnptan (Naramig) **III** is an indole-containing anti-migraine drug on the market. Furthermore, delavirdine (Rescriptor) **IV** is a novel HIV-1 reverse transcriptase inhibitor for HIV-positive individuals and zafirlukast (Accolate) **V** is an antiasthma drug (Figure 1) [3].

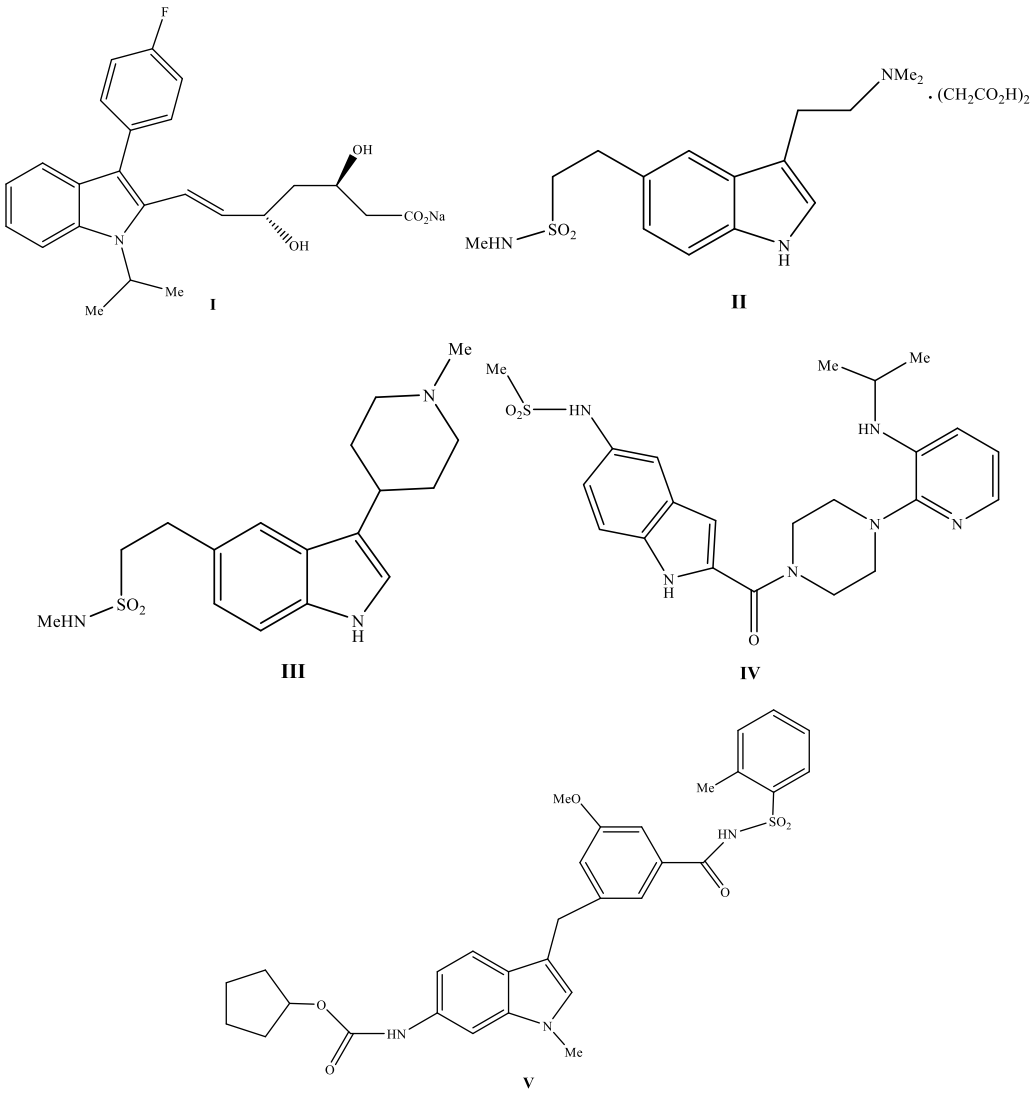
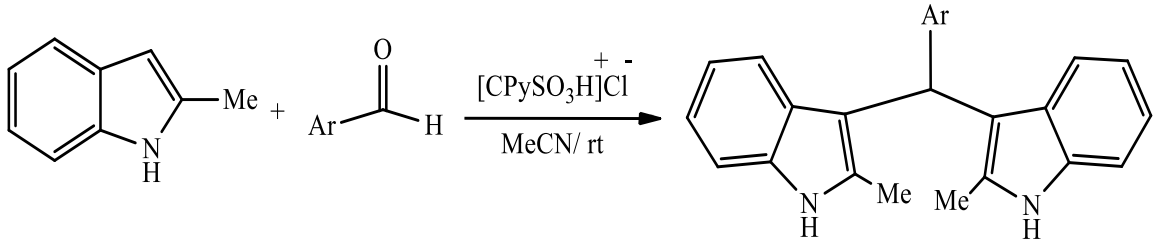


Figure 1. Drugs contain the indole-ring as their core structures.

Bis(indolyl)alkane derivatives have been the subject of considerable levels of interest because of their numerous applications in pharmaceutical and biological research, where they have been reported to show antitumor [4], antihyperlipidemic [5], and anticancer [6] activity. Therefore, the synthesis of bis(indolyl)alkanes under mild and environmentally friendly conditions is attractive.

Usually, bis(indolyl)alkanes were prepared using the three-component reaction of indole derivatives and aldehydes or ketones. Due to a variety of applications of bis(indolyl)alkanes, several methods have been developed for their synthesis. PVSA [7], Nafion-H [8], ($[Et_3NSO_3H]Cl$ [9], squaric acid [10], Indion Ina 225H resin [11], *p*-sulfonic acid calix[4]arene [12], I_2 [13], $[P(4\text{-VPH})ClO_4]$ [14], Tamarind fruit juice [15], $ZnCl_2$/urea [16], benzoic acid/H_2O [17], 4-H_3SPA [18], and nanomaterials [19–27] have been utilized for the synthesis of bis(indolyl)alkanes. Development of novel synthetic procedures based on green chemistry processes is increasingly of interest in organic synthesis because of economic and environmental concerns. Following our interest in the design of new green catalyst in multi-component reactions [28-30], herein, 3-carboxy-1-sulfopyridin-1-ium chloride ($[CPySO_3H]^+Cl^-$) has been successfully applied to perform the reaction of aldehydes, and 2-methylindole in acetonitrile at room temperature to synthesize bis(2-methyl-1*H*-indole) derivatives. The products formed in excellent yields over short reaction times under mild and environmentally friendly conditions (Scheme 1).



Scheme 1. Synthesis of bis(2-methyl-1*H*-indole) derivatives catalyzed by $[CPySO_3H]^+Cl^-$.

Experimental

General

High-purity chemical reagents were purchased from the Merck Chemical Company. Melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ on a Bruker Advance DRX-400 MHz instrument spectrometer using TMS as internal standard. Fourier transform infrared (FT-IR) spectra were performed in the transmission mode (Shimadzu, SP-1100, P-UV-Com instrument) on powder samples that were ground with KBr and compressed into a pellet. The thermal stability was determined by thermogravimetric analysis (TGA, Mettler Toledo). The TGA thermograms were recorded at a heating rate of 10 °C/min in the temperature ranging from the room temperature to 600 °C in an

inert atmosphere. Elemental analyses were done on a Carlo-Erba EA1110CNNO-S analyzer and agreed with the calculated values.

Preparation of the catalyst

To a solution of nicotinic acid (10 mmol) in 25 ml CH_2Cl_2, a solution of chlorosulfonic acid (10 mmol) in CH_2Cl_2 (15 ml) was added dropwise and the mixture stirred for 2 h at room temperature. The resulting powder was filtered and washed with CH_2Cl_2 (2×10 ml) and dried in a vacuum desiccator to give $[CPySO_3H]^+Cl^-$ as a white stable powder.

General procedure for the synthesis of bis(indolyl)methanes

To a mixture of 2-methylindole (2 mmol), aldehyde (1 mmol), acetonitrile (3 mL) as a solvent, $[CPySO_3H]^+Cl^-$ (0.1 mmol) was added and the mixture stirred magnetically at room temperature. After complete conversion, as indicated by TLC (hexane/ethyl acetate 4:1), the reaction mixture was cooled to room temperature. The precipitate was filtered and dried under vacuum. The product was purified by recrystallization in ethanol 96%.

Synthesis of 2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde

To a mixture of 2-hydroxy benzaldehyde (10 mmol), 1,4-dibromobutane (5 mmol), NaOH (10 mmol) was added and the mixture stirred magnetically in ethanol at reflux conditions. After 24h, the reaction mixture was cooled to room temperature. The precipitate was filtered and dried under vacuum. The product was purified by recrystallization in ethanol.

Synthesis of tetrakis (2-methyl-1H-indole) derivatives

To a mixture of 2-methylindole or indole (4 mmol), 2,2'-(butane-1,4-diylbis(oxy))- dibenzaldehyde (1 mmol), acetonitrile (5 mL) as a solvent, $[CPySO_3H]^+Cl^-$ (0.1 mmol) was added and the mixture stirred magnetically at room temperature. After complete conversion, as indicated by TLC (hexane/ethyl acetate 4:1), the reaction mixture was cooled to room temperature. The precipitate was filtered and dried under vacuum. The product was purified by recrystallization in ethanol 96%.

Spectral data of the new products

3-carboxy-1-sulfopyridin-1-ium chloride $[CPySO_3H]^+Cl^-$

White powder, yield = 94%; FT-IR (KBr): $\bar{\nu}$ = 3157 (O-H stretch), 1731 (C=O stretch), 1631 (C=N stretch), 1621, 1533 (aromatic C=C stretch), 1176, 1107, (SO_2 asymmetric and symmetric stretch)

cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 8.06 (dd, J = 6, 5.6 Hz, 1H), 8.82 (dt, J = 8, 1.6 Hz, 1H), 9.05 (dd, J = 5.6, 1.6 Hz, 1H), 9.27 (d, J = 1.6 Hz, 1H), 11.74 (sbr, 2H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.0, 147.5, 145.2, 144.4, 129.7 127.2 ppm. Anal. Calcd. (%) for $C_6H_6NSO_5Cl$: C, 30.07; H, 2.52, N, 5.85. Found: C, 30.13; H, 2.64, N, 5.89.

2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde

White powder, yield = 90%; FT-IR (KBr): $\bar{\nu}$ = 2950 (aromatic C-H stretch), 2880 (aliphatic C-H stretch), 2758 (aldehyde C-H stretch), 1674 (C=O stretch), 1598, 1485 (aromatic C=C stretch), 1456, 1386, 1288, 1244, 1191 (C-O stretch), 1161, 1103, 1047, 1008, 975, 846, 815, 754 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.99-2.04 (m, 4H), 4.22-4.24 (m, 4H), 7.05 (t, J =7.2, 2H),7.23 (d, J = 8.4, 2H), 7.63-7.70 (m, 4H), 10.39 (2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.71, 68.39, 113.92, 121.02, 124.65, 128.10, 189.60 ppm.

*3,3'-((3-chlorophenyl)methylene)bis(2-methyl-1H-indole) (**3c**)*

White solid, FT-IR (KBr): $\bar{\nu}$ = 3398 (NH stretch), 3047 (aromatic C-H stretch), 2916 (aliphatic C-H stretch), 1458 (aromatic C=C stretch), 744 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 6H, $2CH_3$), 6.23 (s, 1H, CH), 6.85 (td, 2H, J = 7.2, 1.2Hz), 6.97 (d, 2H, J = 8Hz), 7.04 (td, 2H, J = 7.2, 1.2 Hz), 7.16 (td, 1H, J = 12.8, 1.2 Hz), 7.19 (td, 1H, J = 7.6,1.6 Hz), 7.27-7.31 (m, 3H), 7.41 (dd, 1H, J = 7.6, 1.2 Hz), 7.76 (s, 2H, NH) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12.26, 37.37, 110.00, 112.01, 118.97, 119.18, 120.67, 126.46, 127.61, 129.03, 129.51, 131.04, 131.98, 134.59, 135.00, 141.38 ppm. Anal. Calcd. (%) for $C_{25}H_{21}N_2Cl$: C, 78.01; H, 5.50, N, 7.28. Found: C, 77.96; H, 5.44, N, 7.19.

*3,3'-((3-bromophenyl)methylene)bis(2-methyl-1H-indole) (**3f**)*

White solid, FT-IR (KBr): $\bar{\nu}$ = 3396 (NH stretch),3047 (aromatic C-H stretch),2914,2852 (aliphatic C-H stretch), 1456 (aromatic C=C stretch), 744 (aromatic C-H out of plane bending) cm^{-1}; ^1H NMR (400 MHz,$CDCl_3$): δ = 2.10 (s, 6H, $2CH_3$), 6.23 (s, 1H, CH), 6.86 (td, 2H, J = 7.2Hz,1.2 Hz), 6.88 (d, 2H, J = 6 Hz), 7.05 (td, 2H, J = 7.2, 0.8 Hz), 7.12 (td, 1H, J = 7.6, 1.6 Hz),7.27 (td, 2H, J = 9.6, 1.6 Hz), 7.29-7.31 (m, 2H), 7.42 (dd, 1H, J = 7.6, 1.2 Hz), 7.75 (s, 2H, NH) ppm; ^{13}C NMR: δ = 12.25, 37.37, 110.01, 112.01, 118.97, 119.18, 120.67, 126.46, 127.62, 129.03, 129.52, 131.04, 131.99, 134.59, 135.00, 141.38 ppm. Anal. Calcd. (%) for $C_{25}H_{21}N_2Br$: C, 69.94; H, 4.93, N, 6.52. Found: C, 70.03; H, 5.04, N, 6.45.

*1,4-bis(2-(di(1H-indol-3-yl)methyl)phenoxy)butane (**3k**)*

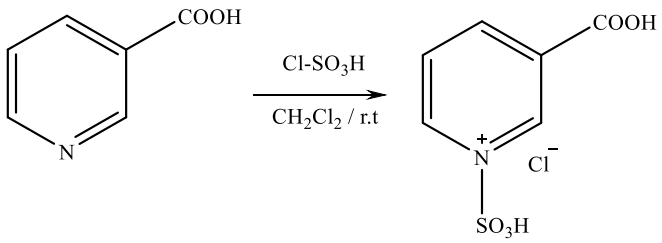
White solid, yield = 91%; m.p = 158-160 °C; FT-IR (KBr): $\bar{\nu}$ = 3404 (NH stretch), 3055 (aromatic C-H stretch), 2929, 2860 (aliphatic C-H stretch), 1454 (aromatic C=C stretch), 744 (aromatic C-H out of plane bending), 1238 (C-O stretch) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.61 (sbr, 4H), 3.69 (sbr, 4H), 6.21 (s, 2H), 6.75-6.85 (m, 12H), 6.99 (td, 4H, *J* = 8 Hz, 0.8Hz), 7.10-7.14 (m, 4H), 7.23 (d, 4H),7.34 (d, 4H), 10.77 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.60, 32.10, 67.08, 111.85, 112.15, 118.31, 118.57, 119.28, 120.37, 121.24, 123.90, 124.07, 127.18, 127.21, 127.40, 129.38, 133.53, 136.84, 137.00, 156.11 ppm. Anal. Calcd. (%) for $C_{50}H_{42}N_4O_2$: C, 82.16; H, 5.79, N, 7.67. Found: C, 82.06; H, 5.76, N, 7.59.

*4-bis(2-(bis(2-methyl-1H-indol-3-yl)methyl)phenoxy)butane (**3l**)*

White solid, yield = 96%; m.p = 172-175 °C; FT-IR (KBr): $\bar{\nu}$ = 3404 (NH stretch), 3053 (aromatic C-H stretch), 2921, 2873 (aliphatic C-H stretch), 1456 (aromatic C=C stretch), 742 (aromatic C-H out of plane bending), 1240 (C-O stretch) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.58 (sbr, 4H), 2.01 (s, 12H), 3.36-3.38 (m, 4H), 6.00 (s, 2H), 6.62-6.68 (m, 6H), 6.75 (t, 6H, *J* = 8 Hz), 6.87 (t, 4H, *J* = 1.2 Hz), 6.91 (d, 2H, *J* = 0.8 Hz), 7.15-7.22 (m, 6H), 10.67 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.20, 19.05, 24.40, 33.28, 65.58, 110.70, 111.57, 112.41, 112.44, 118.30, 118.61, 119.82, 119.90, 127.66, 129.05, 129.73, 132.07, 132.62, 135.44, 156.98 ppm. Anal. Calcd. (%) for $C_{54}H_{50}N_4O_2$: C, 30.07; H, 2.52, N, 5.85. Found: C, 30.13; H, 2.64, N, 5.89.

Results and discussion

In this study, $[CPySO_3H]^+Cl^-$ is obtained by simple reaction of chlorosulfonic acid with the nicotinic acid (Scheme 2). The structure of the $[CPySO_3H]^+Cl^-$ was identified by FT-IR, ^1H NMR, ^{13}C NMR and elemental analysis. The corresponding spectral data are reported in the Experimental section.



Scheme 2. Preparation of $[CPySO_3H]^+Cl^-$.

Characterization of the SO_3H group present on the catalyst was performed by recording the Fourier transform infrared spectroscopy. The O–H stretching near 3157 cm^{-1}, the C=O stretching at 1731 cm^{-1}, the C=N stretching at 1631 cm^{-1}, the C=C stretching at 1621 and 1533 cm^{-1}, the SO_2 asymmetric and symmetric stretching was observed at 1176 and 1107 cm^{-1} respectively. These results provided the evidences that chlorosulfonic acid was successfully attached to the nicotinic acid. The thermal behavior of $[CPySO_3H]^+Cl^-$ was also studied by thermal gravimetric analysis (Figure 2). The thermal gravimetric analysis of the catalyst showed a decreasing peak at temperature around 300–375 °C which can be related to the loss of the sulfonic and carboxylic acid groups. The thermal analysis data showed that the catalyst is stable to 250 °C.

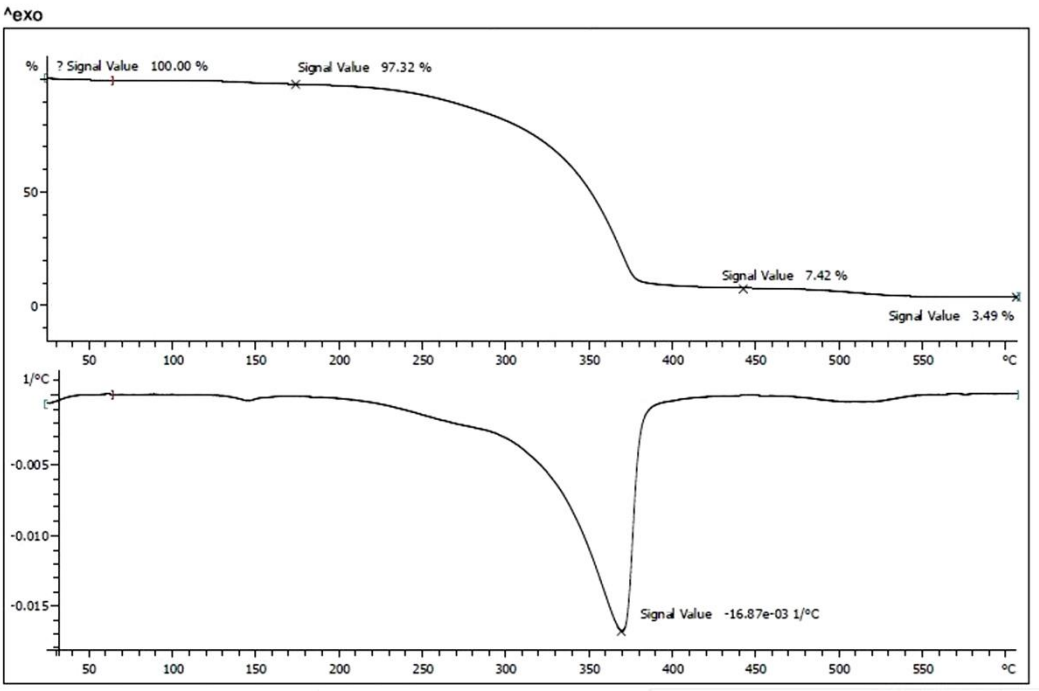
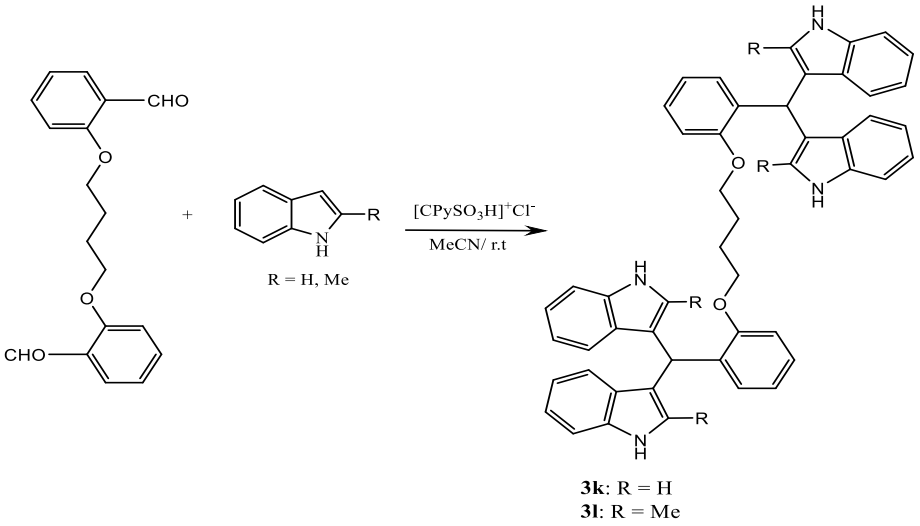


Figure 2. The thermal gravimetric analysis diagram of $[CPySO_3H]^+Cl^-$.

In order to optimize the reaction conditions and get the best catalytic activity, the reaction of 4-chlorobenzaldehyde and 2-methylindole were examined as a model reaction in the several solvents such as n-hexane, ethylacetoacetate, acetonitrile, methanol, ethanol and solvent-free conditions. The model reaction was also carried out using L-proline, nicotinic acid, and 3-carboxy-1-sulfopyridin-1-ium chloride ($[CPySO_3H]^+Cl^-$). In this study, it was observed that $[CPySO_3H]^+Cl^-$ (10 mol %) in acetonitrile at room temperature is more efficient with respect to reaction time and the yield of the desired product. After optimizing the catalyst amount, a diversity of bis(2-methyl-1*H*-indole) derivatives were synthesized using $[CPySO_3H]^+Cl^-$ in excellent yields (Table 1, entries 1-10). The reactions worked well with all benzaldehydes with electron-donating or

electron-withdrawing substituent. Furthermore, $[CPySO_3H]^+Cl^-$ has been successfully applied to perform the reaction of 2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde, and indole or 2-methylindole in acetonitrile at room temperature to provide new tetrakis (2-methyl-1*H*-indole) derivatives in excellent yields (Scheme 3).



Scheme 3. Synthesis of tetrakis (2-methyl-1*H*-indole) derivatives catalyzed by $[CPySO_3H]^+Cl^-$.

Table 1. Synthesis of bis(indolyl)methanes[a].

Entry	Aryl	Product	Time (min)	Yield (%)[b]	Mp °C [Lit.]
1	C_6H_5	**3a**	12	96	242-243 241-244[18]
2	4-Cl-C_6H_4	**3b**	12	97	232-234 235-237[18]
3	3-Cl-C_6H_4	**3c**	12	94	194-196
4	2-Cl-C_6H_4	**3d**	12	90	220-222 223-225[18]
5	4-NO_2-C_6H_4	**3e**	10	98	239-241 238-240[18]
6	3-Br-C_6H_4	**3f**	12	97	190-192
7	4-MeO-C_6H_4	**3g**	18	94	194-196 194-195[18]
8	3-MeO-C_6H_4	**3h**	20	92	235-237 176-177[18]
9	4-Me-C_6H_4	**3i**	20	93	175-176 176-177[18]
10	C_6H_4	**3j**	15	97[c]	281-283 283-284[15]

[a]Reaction and conditions: aromatic aldehydes (1 mmol), 2-methylindole (2 mmol), and $[CPySO_3H]^+Cl^-$ (0.1 mmol) in CH_3CN (3 mL).

[b]All yields refer to isolated products.
[c]Reaction and conditions: Terephthalaldehyde (1 mmol), 2-methylindole (4 mmol), and $[CPySO_3H]^+Cl^-$ (0.1 mmol) in CH_3CN (5 mL).

In order to examine the efficiency of the present method for the synthesis of bis(2-methyl-1*H*-indole) derivatives, compound **3a** was compared with some of those reported in the literature (Table 2). As one can see, our results show a very good comparison with previously reported data when all terms, including yields, reaction times, and reaction conditions are taken into account.

Table 2. Comparison of $[PVPP\text{-}SO_3H]^+Cl^-$ with some other catalysts for synthesis of **3a**.

Entry	Catalyst	Reaction conditions	Time	Yield (%)	Ref.
1	PVSA	EtOH/ r.t.	2 h	91	[7]
2	$[Et_3NSO_3H]Cl$	r.t.	15 min	79	[9]
3	*p*-Sulfonic acid calix[4]arene	H_2O/ 80 °C	18 min	90	[12]
4	$P(4\text{-}VPH)ClO_4$	r.t./ grinding	8 min	87	[14]
5	Tamarind Juice	H_2O/ 80 °C	2 h	85	[15]
6	$ZnCl_2$/urea	60 °C	12 min	93	[16]
7	Benzoic acid	H_2O/ 80 °C	15 h	83	[17]
8	$4\text{-}H_3SPA$	H_2O/ r.t.	15 min	89	[18]
9	-	r.t.	3 days	69	[31]
10	$[CPySO_3H]^+Cl^-$	CH_3CN/ r.t.	12 min	96	This work

To check the reusability of the catalyst, it was employed the synthesis of 3,3'-((4-chlorophenyl)methylene)bis(2-methyl-1*H*-indole) **3b** by reaction of 4-Cl-benzaldehyde (1mmol) and 2-methylindole (2 mmol) five cycles under the optimum conditions. The catalyst powder was recovered after evaporation of the solvent and washed with dichloromethane (2 × 10 ml). Afterward, according to the amount of catalyst the required amount of fresh 4-Cl-benzaldehyde and 2-methyl-indole were added. The results showed that the catalyst can be reused five consecutive times without significant loss of its catalytic activity (Table 3).

Table 3. The recycling of $[CPySO_3H]^+Cl^-$ for the preparation of product **3b**[a].

Run	1	2	3	4	5
Yield (%)	97	95	93	91	90

[a]Reaction and conditions: 4-Cl-benzaldehyde (1 mmol), 2-methyl-indole (1 mmol), and $[CPySO_3H]^+Cl^-$ (0.1 mol%).

Conclusion

We have developed a simple, clean, efficient and one-pot procedure for the synthesis of bis(2-methyl-1*H*-indole) derivatives and some tetrakis (2-methyl-1*H*-indole) derivatives by the three-component reaction of aromatic aldehyde, or 2,2'-(butane-1,4-diylbis(oxy))dibenzaldehyde and 2-methylindole using 3-carboxy-1-sulfopyridin-1-ium chloride ($[CPySO_3H]^+Cl^-$) as a new ionic organocatalyst at room temperature.

Acknowledgements

Financial support by Rasht Branch, Islamic Azad University Grant No. 4.5830 is gratefully acknowledged.

References

[1] J.H. Lee, J. Lee, *FEMS Microbiol. Rev.*, 34, 426 (2010).

[2] D.L. Nelson, M.M. Cox, *Lehninger* Principles of Biochemistry (4th ed.), New York: W.H. Freeman (2005).

[3] J.J. Li, *Heterocyclic Chemistry in Drug Discovery*, John Wiley & Sons, Inc., Hoboken, New Jersey (2013).

[4] P. Diana, A. Carbone, P. Barraja, A. Martorana, O. Gia, L. DallaVia, G. Cirrincione, *Bioorg. Med. Chem. Lett.*, 17, 6134 (2007).

[5] K.V. Sashidhara, A. Kumar, M. Kumar, A. Srivastava, A. Puri, *Bioorg. Med. Chem. Lett*., 20 6504 (2010).

[6] A. Kamal, Y.V.V. Srikanth, M.J. Ramaiah, M.N.A. Khan, M.K. Reddy, M. Ashraf, A. Lavanya, S.N.C.V.L. Pushpavalli, Pal-Bhadra M. *Bioorg. Med. Chem. Lett*., 22, 571, (2012).

[7] S.S. Ekbote, K.M. Deshmukh, Z.S. Qureshi, B.M. Bhanage, *Green Chem. Lett. Rev.*, 4, 177 (2011).

[8] M. Kidwai, R. Chauhan, D. Bhatnagar, *Arabian J. Chem.*, 9, S2004 (2016).

[9] A. Zare, F. Bahrami, M. Merajoddin, M. Bandari, A. R. Moosavi-Zare, M.A. Zolfigol, A. Hasaninejad, M. Shekouhy, M.H. Beyzavi, V. Khakyzadeh, M. Mokhlesi, Z. Asgari, *Org. Prep. Proced. Int.*, 45, 211 (2013).

[10] N. Azizi, E. Gholibeghlo, Z. Manocheri, *Scientia Iranica C*, 19, 574 (2012).

[11] R. Surasani, D. Kalita, K.B. Chandrasekhar, *Green Chem. Lett. Rev*., 6, 113 (2013).

[12] S. M. Baghbanian, Y. Babajani, H. Tashakorian, S. Khaksar, M. Farhang, *C. R. Chimie*, 16, 129 (2013).

[13] K. V. Sashidhara, R. K. Modukuri, R. Sonkar, K. Bhaskara Rao, G. Bhatia, *Eur. J. Med. Chem.*, 68, 38 (2013).

[14] F. Shirini, S. Esmaeeli-Ranjbar, M. Seddighi, *Chin. J. Catal*., 35, 1017 (2014).

[15] R. Pal, *Indian J. Chem.*, 53B, 763 (2014).

[16] N. Seydi, H. Khabazzadeh, S. Saeednia, *Synth. React. Inorg. Met. Org. Nano Met. Chem.*, 45, 1501 (2015).

[17] A. K. Mallika, R. Pala, C. Guhaa, H. Mallik, *Green Chem. Lett. Rev*., 5, 321 **(**2012)

[18] H. Banari, H. Kiyani, A. Pourali, *Res. Chem. Intermed*., 43, 1635 (2017).

[19] K. Ghodrati, S.H. Hosseini, R. Mosaedi, C. Karami, F. Maleki, A. Farrokhi, Z. Hamidi, *Int. Nano Lett.*, 3, 13 (2013).

[20] R. Pegu, K.J. Majumdar, D.J. Talukdar, S. Pratihar, *RSC Adv*., 4, 3346 (2014).

[21] A. Shaabani, R. Afshari, S.E. Hooshmand, A.T. Tabatabaei, F. Hajishaabanha, *RSC Adv*., 6, 18113 (2016).

[22] D.A. Reddy, J. Choi, S. Lee, R. Ma, T.K. Kim, *RSC Adv*., 5, 67394 (2015).

[23] S. Sobhani, R. Jahanshahi, *New J. Chem*., 37, 1009 (2013).

[24] P.K. Chhattise, S.S. Arbuj, K.C. Mohite, S.V. Bhavsar, A.S. Horne, K.N. Handore, V.V. Chabukswar, *RSC Adv*., 4, 28623 (2014).

[25] H. Mahmoudi, A.A. Jafari, S. Saeedi, H. Firouzabadi, *RSC Adv*., 5, 3023 (2015).

[26] M. Kour, S. Paul, *New J. Chem*., 39, 6338 (2015).

[27] B. Sadeghi, F. Amiri-Tavasoli, A. Hassanabadi, *Synth. React. Inorg. Met. Org. Nano Met. Chem.*, 45, 1396 (2015).

[28] M. Mokhtary, S.A. Mirfarjood Langroudi, *Monatsh. Chem*., 145, 1489 (2014).

[29] M. Yosefzadeh, M. Mokhtary, *Iran J. Catal*., 6, 153 (2016).

[30] N. Azgomi, M. Mokhtary, *J. Mol. Catal. A: Chem*., 398, 58 (2015).

[31] K. L. Dhumaskar, S.G. Tilve, *Green Chem. Lett. Rev*., 5, 353 **(**2012).