IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 6 Issue 4, April 2019
ISSN (Online) 2348 – 7968
www.ijiset.com

Montmorillonite K-10 Supported $La(OTf)_3$: An Efficient Catalyst for the Synthesis of 1,2-Disubstituted Benzimidazoles

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Abstract

A series of 1,2-disubstituted benzimidazoles has been synthesized by an efficient methodology that utilizes the 5 mol% of montmorillonite K-10 supported Lanthanum triflate catalyst to promote the reaction of benzimidazoles with *o*-phenylenediamine to undergo nucleophilic addition reaction followed by cyclization that were reacted at 90°C for a period of 4h under conventional heating conditions. Conceptually, the layered silicates present in montmorillonite K-10 facilitates the binding of its Al^{+3} and Si^{+4} cations with triflate moiety of Lanthanum triflate to promote the reaction of benzimidazoles with *o*-phenylenediamine to form 1,2-disubstituted benzimidazoles. The combined effect of Montmorillonite K-10's Bronsted acidity and Lanthanum triflate's Lewis acidity intensifies its combined catalytic action compared to their individual effects. Mild reaction conditions, operational simplicity, use of cost-effective & reusable catalyst, high products yields and short reaction times are the assets of this new and environmentally benign reaction protocol.

Keywords: *1,2-Disubstituted benzimidazoles, substituted benzaldehydes,* o*-phenylenediamine, montmorillonite K-10, Lanthanum triflate.*

1. Introduction

The 1,2-disubstituted benzimidazole scaffold is identified as a potential medicinal agents that efficiently works for therapeutic applications like anticancer,[1] antioxidant,[2] anti-inflammatory,[3] antiviral,[4] obesity,[5] antimicrobial,[6] HSV-1,[7] HIV,[8] influenza,[9] and hypertension.[10] These 1,2-disubstituted benzimidazoles were established as commercial pharamaceutical agents[11] like agonist of γ-aminobutyric acid A receptor (GABAA),[12] anti-hypertensive telmisartan[13] and hepatitis C virus NS5B polymerase inhibitors.[14] Owing to the potential biological interest in 1,2-disubstituted benzimidazole family, a number of synthetic strategies have been developed for their synthesis. This fact prompted many chemists to work more in this field to synthesize various disubstituted benzimidazoles by using different types of conventional organic acids, Lewis acids, Bronsted acids, solid acid catalysts, catalytic amount of transition metals, nano-catalysts, ionic liquids and polymer supported catalysts such as trifluoroacetic acid,[15] SBA-15-supported poly(4-styrenesulfonyl-(perfluorobutylsulfonyl) imide),[16] $Bi(OTf)_3$,[17] nano copper(0)-stabilized on alumina,[18] nano-structured pyrophosphate ($Na_2CaP_2O_7$),[19] dodecylbenzenesulfonic acid (DBSA),[20] silica coated γ-Fe_2O_3 nanoparticles supported on 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$,[21] $NaHSO_3$,[22] alumina-sulfuric acid,[23] L-proline,[24] KIT-6 mesoporous silica-coated magnetite nanoparticles,[25] ZnO nanoparticles,[26] 1-heptanesulfonic acid sodium salt,[27] 1,4-diazabicyclo [2.2.2] octanium diacetate,[28] catalytic Ruthenium,[29] $Bi(OTf)_3$,[30] $Ce(NO_3)_3.6H_2O$,[31] lewis acidic ionic liquids of crown ether complex cations,[32] niobic acid,[33] amino glucose-functionalized silica-coated $NiFe_2O_4$ nanoparticles,[34] phosphine manganese(I) complex,[35] UiO-66-NH-SO_3H,[36] ytterbium loaded mesoporous silica nanoparticles[37] and Bimetallic Cu-Mn B spinel oxide.[38] All these accomplished methods are noteworthy and includes various types of conditions and techniques like neat synthesis,[15] aqueous medium,[17-22] grinding,[25] ball-milling technique,[26] solvent-free synthesis[33,34] and ultrasound assisted synthesis.[36]

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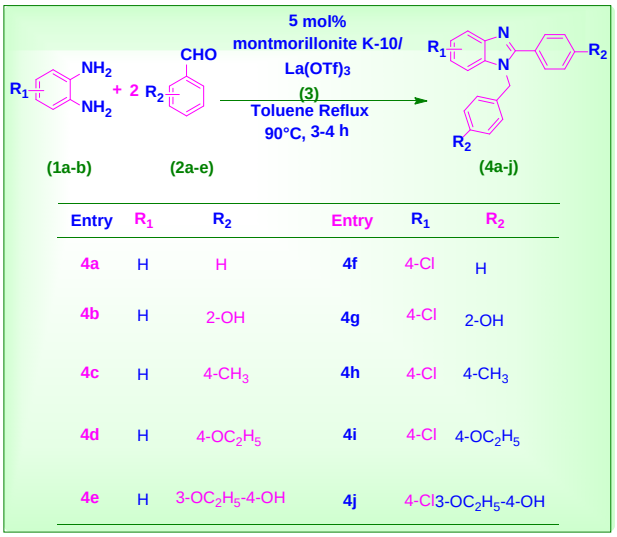
On the other hand, the use of solid acid catalysts has been more prioritized in organic synthesis rather than other catalysts as they having many advantages like easy recyclability, non-toxicity and operational simplicity. Our interest on the catalytic applications of montmorillonite K-10 supported La(OTf)$_3$ catalyzed organic transformations, we have investigated and succeeded in the synthesis of 1,2-disubstitued benzimidazoles by using montmorillonite K-10 supported La(OTf)$_3$ as a potential media for facilitating the reaction of various phenylene diamines and aldehydes and developed it as a methodology. In recent years, montmorillonite K-10 supported metal triflates have emerged as a powerful catalyst and used in many useful organic transformations under mild reaction conditions. Moreover, it is inexpensive, easy to handle, thermally stable, non-toxic and recyclable. To the best of our knowledge there are no reports on the synthesis of 1,2-disubstitued benzimidazole derivatives by using montmorillonite K-10 supported La(OTf)$_3$ as a catalyst.

2. Experimental

2.1 General

The solvents & reagents were procured from Sigma-Aldrich & Lancaster and were used for the reaction & purification purposes. Solvents used for the reactions were purified by double distillation processes in the laboratory itself. Conventional heating reactions were performed on Remi magnetic stirrer cum heater by refluxion followed by condensation setup. Melting points of the purified products were determined in open capillaries using Guna melting point apparatus. The IR spectra were recorded on Bruker FT-IR spectrometer equipped with single reflection sampling module and the absorptions were reported in wavenumbers (cm^{-1}). Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker 500MHZ NMR spectrometer operating at 500MHZ for ^{1}H NMR, 125MHZ for ^{13}C NMR by recording in $CDCl_3$ and referenced to TMS (^{1}H and ^{13}C). Mass spectra were recorded on a JEOL GCMATE II GC-MS spectrophotometer at SAIF, IIT Chennai. Elemental analysis for C, H, N elements was performed on a Thermo Finnigan Instrument. All solvents used for chromatographic, spectroscopic and other physical studies were reagent grade and used in the study. For optimizing the experimental parameters synthesis of 1-benzyl-2-phenyl-1H-benzo[d]imidazole (**4a**) from *o*-phenylenediamine (**1a**) and benzaldehyde (**2a**) along with 5 mol% of montmorillonite K-10 supported La(OTf)$_3$ (**3**) catalyst has been taken as a model reaction.

2.2 Montmorillonite K-10/ La(OTf)$_3$ catalyzed synthesis of 4a-j



Entry	R_1	R_2	Entry	R_1	R_2
4a	H	H	4f	4-Cl	H
4b	H	2-OH	4g	4-Cl	2-OH
4c	H	4-CH_3	4h	4-Cl	4-CH_3
4d	H	4-OC_2H_5	4i	4-Cl	4-OC_2H_5
4e	H	3-OC_2H_5-4-OH	4j	4-Cl	3-OC_2H_5-4-OH

Scheme 1: Montmorillonite K-10 supported La(OTf)$_3$ catalyzed synthesis of 1,2-disubstituted benzimidazoles

A mixture of *o*-phenylenediamine (**1a**) and benzaldehyde (**2a**) in 1:2 molar ration was taken in toluene along with 5 mol% of montmorillonite K-10 supported La(OTf)$_3$ (**3**) catalyst and refluxed at 90°C for a period of 4h on a conventional heating stirrer for completion of the reaction (**Scheme 1**). After completion of reaction as indicated by thin layer chromatography (TLC) the reaction mixture was cooled and poured in to ice cold water. The obtained solid product was filtered and washed with water and purified by column chromatography on silica gel as absorbent with ethyl acetate & hexane (1:2) as an eluent to get pure product **4a** with 94% of yield (mp: 133-135°C). Montmorillonite K-10 supported La(OTf)$_3$ was recovered by filtration and reused for four consecutive runs. Same procedure was adopted for the synthesis of remaining title compounds (**4b-j**). The comparable reactivity of substrates has been assessed based on the obtained yields of their corresponding products and reaction times consumed for their accomplishment. In such, the reactivity of *o*-phenylenediamine **(1a)** is higher than 4-chloro phenylenediamine **(1b)** with respect to the aldehydes **(2a-e)** that were used for the synthesis of title compounds **(4a-e)**, whereas the reactivity of aldehydes were observed in the order of **2c** (4-CH_3) > **2b** (2-OH) > **2a** (H) > **2d** (4-OC_2H_5) > **2e** (3-OC_2H_5-4-OH) depending on the nature of substituents present on them. Title compounds **(4a-j)** were characterized by their physical, spectral and elemental analysis datum and have been provided in the following sections.

2.3 Spectral & elemental characterization data of 4a-j

1-benzyl-2-phenyl-1H-benzo[d]imidazole ***(4a):*** Yield: 94%; White yellow solid; mp: 133-135; IR (ZnSe): υ 3230 (NH) 2923 (Ar, C-H), 1437 (C=N), 1360 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 5.42 (s, 2H), 7.09 (d, 2H Ar), 7.12-7.47 (m, 6H), 7.63 (d, 2H), 7.89 (d, 2H), 8.08 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 47.5, 110.4, 114.9, 119.2, 121.4, 122.4, 123.3,123.9, 127.6, 127.8, 128.1, 128.7, 130.1, 130.7, 136.4, 136.8, 142.1, 154.3, 158.4, 160.7; LCMS (ESI): m/z 284 (M^+). Anal. Calcd for $C_{20}H_{16}N_2$ (%): C, 84.48; H, 5.67; N, 9.53; Found: C, 83.58; H, 5.61; N, 9.42.

2-(1-(2-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol ***(4b):*** Yield: 92%; Yellow solid; mp: 144-146; IR (ZnSe): υ 3328 (OH), 3236 (NH) 2921 (Ar, C-H), 1466 (C=N), 1333 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 5.68 (s, 2H), 7.23- 7.33 (m, 6H), 7.55-7.59, (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.9, 114.6, 115.3, 119.4, 121.2, 122.4, 123.5, 123.8, 127.3, 128.4, 128.8, 129.2, 129.7, 130.3, 136.2, 143.5, 147.7, 151.6, 153.7, 158.6; LCMS (ESI): m/z 316 (M^+). Anal. Calcd for $C_{20}H_{16}N_2O_2$ (%): C, 75.93; H, 5.10; N, 8.86; Found: C, 75.12; H, 5.04; N, 8.76.

1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole ***(4c):*** Yield: 93%; White solid; mp: 131-133; IR (ZnSe): υ 3235 (NH) 2922 (Ar, C-H), 1428 (C=N), 1368 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 2.14 (s, 6H), 5.36 (s, 2H), 6.95-6.94 (d, 2H) 7.05-7.31 (m, 4H), 7.83 (d, 2H), 7.88 (d, 2H),7.95 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.1, 20.3, 51.5, 113.3, 125.5, 125.7, 126.6, 126.5, 127.4, 127.5, 128.8, 128.6, 129.3, 129.1, 130.6, 131.4, 131.6, 138.4, 139.7, 148.4, 149.7, 151.6; LCMS (ESI): m/z 312 (M^+). Anal. Calcd for $C_{22}H_{20}N_2$ (%): C, 84.58; H, 6.45; N, 8.97; Found: C, 83.68; H, 6.38; N, 8.87.

1-(4-ethoxybenzyl)-2-(4-ethoxyphenyl)-1H-benzo[d]imidazole ***(4d):*** Yield: 91%; White solid; mp: 157-159; IR (ZnSe): υ 3229 (NH) 2928 (Ar, C-H), 1428 (C=N), 1365 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 1.12-1.56 (m, 6H), 3.98-4.47 (m, 4H), 6.88-6.92 (m, 4H), 7.21- 7.33 (m, 4H), 7.55-7.58 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 14.4, 47.9, 63.5, 114.7, 115.1, 119.6, 121.5, 122.3, 123.2, 123.7, 127.5, 128.4, 128.6, 129.3, 129.7, 130.4, 136.6, 143.5, 147.3, 151.3, 153.8, 158.6, 160.5; LCMS (ESI): m/z 372 (M^+). Anal. Calcd for $C_{24}H_{24}N_2O_2$ (%): C, 77.39; H, 6.50; N, 7.52; Found: C, 76.51; H, 6.43; N, 7.42.

2-ethoxy-4-(1-(3-ethoxy-4-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol ***(4e):*** Yield: 92%; Pale yellow solid; mp: 145-147; IR (ZnSe): υ 3342 (OH), 3287 (NH) 2978 (Ar, C-H), 1448 (C=N), 1369 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 1.42-1.48 (t, 6H), 4.12-4.22 (q, 4H), 5.38 (s, 2H), 6.85-6.92 (d, 4H), 7.06-7.20 (m, 6H), 7.46 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.3, 15.9, 68.3, 68.7, 112.3, 113.5, 115.6, 116.8, 117.3, 118.1, 119.8, 123.7, 127.0, 127.4, 128.1, 128.9, 137.6, 137.5, 138.2, 139.4, 148.3, 148.7, 149.2, 151.7; LCMS (ESI): m/z 404 (M^+). Anal. Calcd for $C_{24}H_{24}N_2O_4$ (%): C, 71.27; H, 5.98; N, 6.93; Found: C, 70.51; H, 5.91; N, 6.85.

1-benzyl-5-chloro-2-phenyl-1H-benzo[d]imidazole ***(4f):*** Yield: 90%; Pale yellow solid; mp: 148-150; IR (ZnSe): υ 3245 (NH) 2933 (Ar, C-H), 1445 (C=N), 1355 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 5.50 (s, 2H), 6.99-7.11 (d, 2H), 7.12-7.62 (m, 6H), 7.63-7.76 (d, 2H), 7.86 (s, 1H), 7.92-8.02 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 48.3, 113.3, 115.2, 116.8, 124.6, 124.8, 125.2, 125.6, 126.1, 127.4, 127.8, 128.2, 128.4, 129.3, 129.7, 138.3, 138.6, 139.5, 139.7, 151.3; LCMS (ESI): m/z 318.5 (M^+). Anal. Calcd for $C_{20}H_{15}ClN_2$ (%): C, 75.35; H, 4.74; N, 8.79; Found: C, 77.45; H, 4.68; N, 8.69.

2-(5-chloro-1-(2-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)phenol ***(4g):*** Yield: 89%; Yellow solid; mp: 149-151; IR (ZnSe): υ 3332 (OH), 3239 (NH) 2925 (Ar, C-H), 1469 (C=N), 1333 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 5.64 (s, 2H) 7.28-7.12 (m, 7H), 7.60-7.52 (m, 3H), 8.36 (s, 1H), 9.61 (s, 1H), 9.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.5, 114.8, 114.6, 115.3, 117.4, 118.2, 120.4, 121.5, 121.3, 124.4, 127.3, 128.2, 129.6, 130.4, 131.8, 140.4, 140.6, 152.4, 153.6, 154.5; LCMS (ESI): m/z 350.5 (M^+). Anal. Calcd for $C_{20}H_{15}ClN_2O_2$ (%): C, 68.48; H, 4.31; N, 7.99; Found: C, 67.75; H, 4.26; N, 7.90.

5-chloro-1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole ***(4h):*** Yield: 91%; Pale yellow solid; mp: 138-140; IR (ZnSe): υ 3217 (NH) 2954 (Ar, C-H), 1433 (C=N), 1365 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 2.44 (s, 6H), 5.68 (s, 2H), 7.85-7.95 (m, 3H), 7.96-8.03 (m, 4H), 8.21-8.34 (m, 2H), 8.44-8.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 20.8, 51.7, 113.4, 114.3, 114.5, 114.7, 115.6, 115.8, 116.4, 117.3, 125.3, 125.6, 126.1, 126.5, 127.3, 127.6, 128.9, 128.7, 138.7, 139.5, 151.6; LCMS (ESI): m/z 346.5 (M^+). Anal. Calcd for $C_{22}H_{19}ClN_2$ (%): C, 76.18; H, 5.52; N, 8.08; Found: C, 75.37; H, 5.46; N, 7.99.

5-chloro-1-(4-ethoxybenzyl)-2-(4-ethoxyphenyl)-1H-benzo[d]imidazole ***(4i):*** Yield: 93%; Yellow solid; mp: 142-144; IR (ZnSe): υ 3234 (NH) 2932 (Ar, C-H), 1426 (C=N), 1366 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 1.28-1.34 (t, 6H), 3.98-4.07 (q, 4H), 5.79 (s, 2H), 6.85-6.98 (m, 3H), 7.12-7.15 (m, 3H), 7.91-7.98 (m, 3H), 8.32 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 52.4, 64.5, 114.4, 114.6, 115.3, 116.5, 122.4, 124.3, 128.6, 129.4, 129.8, 129.7, 140.5, 140.8, 153.4, 156.6, 159.5; LCMS (ESI): m/z 406.5 (M^+). Anal. Calcd for $C_{24}H_{23}ClN_2O_2$ (%): C, 70.84; H, 5.70; N, 6.88; Found: C, 70.09; H, 5.63; N, 6.80.

4-(5-chloro-1-(3-ethoxy-4-hydroxybenzyl)-1H-benzo[d]imidazol-2-yl)-2-ethoxyphenol ***(4j):*** Yield: 92%; Brown solid; mp: 153-155; IR (ZnSe): υ 3345 (OH), 3288 (NH) 2975 (Ar, C-H), 1443 (C=N), 1369 (C-N) cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 1.42-1.44 (t, 6H), 4.13-4.19 (q, 4H), 5.79 (s, 2H), 6.54-6.62 (m, 3H), 7.00-7.12 (m, 3H), 7.55-7.68 (m, 2H), 8.36 (m, 1H), 9.83 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.6, 52.8, 64.5, 110.6, 112.7, 115.4, 115.7, 116.1, 116.8, 122.3, 123.7, 124.4, 129.5, 128.8, 140.6, 145.8, 148.4, 149.2, 153.6; LCMS (ESI): m/z 438.5 (M^+). Anal. Calcd for $C_{24}H_{23}ClN_2O_4$ (%): C, 65.68; H, 5.28; N, 6.38; Found: C, 64.98; H, 5.22; N, 6.31.

3. Results & Discussion

The experimental parameters like selection of catalyst, optimized catalyst concentration and effective reaction operating temperature that are needed to accomplish the products in good yields along with the reusability of the catalyst were optimized by taking synthesis of **4a** as a model reaction.

3.1 Optimization of the catalyst

Synthesis of 1-benzyl-2-phenyl-1*H*-benzo[d]imidazole **(4a)** has been taken as a model reaction to optimize the effective catalyst and investigated the efficacy of some Lewis acid catalysts, Bronsted acid catalysts and solid catalysts (**Table 1**). In such we have investigated the activity of Lewis acid catalysts like Bismuth triflate [$Bi(OTf)_3$], Lanthanum triflate [$La(OTf)_3$] and Ytterbium triflate [$Yb(OTf)_3$], Bronsted acids like *p*-Toluenesulfonic acid [PTSA] and [2-(Sulfooxy)ethyl]sulfamic acid [SESA], Bronsted acid cum ionic liquid 1-Methylimidazolium triflouroacetate [[Hmim]TFA], solid supported catalysts like Amberlite IR-120, Alumina-sulfuric acid [Al_2O_3-SO_3H], mesoporous Santa Barbara Amorphous supported with poly(4-styrenesulfonyl-(perfluorobutylsulfonyl)imide) [SBA-15/ PSPI], ZnO nanoparticles [ZnO-NP] and Montmorillonite K-10 and Montmorillonite K-10 supported Lanthanum triflate [Montmorillonite K-10/ $La(OTf)_3$]. All the reactions were performed in toluene solvent with 10mol% of catalyst concentrations and the operating temperatures to accomplish 4a in high yield of corresponding catalysts were presented in **Table 1**. The yields of compound **4a** with Montmorillonite K-10/ $La(OTf)_3$ catalyst is quite higher (94%) compared to others and hence we have considered this as a cost-effective, eco-friendly catalyst engaged with simple operating procedures and proceed further for optimizing other parameters for this methodological protocol.

Table 1: Optimization of catalyst source for the synthesis of 4a

S.No.	*Catalyst*	*Temperature (ºC)*	*Time (h)*	*Yield (%)*
1	$Bi(OTf)_3$	90	8	83
2	$La(OTf)_3$	90	8	85
3	$Yb(OTf)_3$	90	9	88
4	PTSA	90	6	82
5	SESA	85	7	86
6	[Hmim]TFA	80	5	91
7	Amberlite IR-120	80	8	88
8	Al_2O_3-SO_3H	85	9	89
9	SBA-15/ PSPI	85	6	75
10	ZnO-NP	85	5	82
11	Montmorillonite K-10	90	7	78
12	Montmorillonite K-10/ $La(OTf)_3$	90	4	94

3.2 Optimization of catalyst concentration

Synthesis of 1-benzyl-2-phenyl-1*H*-benzo[*d*]imidazole, **4a** by loading of 1:2 ration of substrates along with various concentrations of Montmorillonite K-10/ $La(OTf)_3$ catalyst (**3**) operated at uniform conditions of reaction have accomplished it in 83, 90, 94, 94, 94% yields respectively. It is noticed that 5mol% of Montmorillonite K-10/ $La(OTf)_3$ catalyst concentration is effective one in accomplishing **4a** in 94% yield and higher catalyst concentrations have not shown any effect (**Table 2**). The higher concentrations of catalyst (7.5% & 10.0%) were identified as ineffective compared to 5.0% due to the fact that these catalyst molecules will interfere more in the solvent system and hence it will retards the reactivity of the substrates and disturbs the interacted catalyst molecules and substrates. Hence the higher percentages of the catalyst has not shown any progressive effect on enhancement of the product yields.

Table 2: Catalyst concentration optimization studies of 4a

S.No.	*Catalyst (mol%)*	*Time (h)*	*Yield (%)*
1	1.0	6	83
2	2.5	5	90
3	5.0	4	94

4	7.5	4	94
5	10.0	4	94

3.3 Optimization of catalyst concentration

Synthesis of **4a** has performed at different temperatures in the range of 60-90ºC with 5ºC interval and have accomplished the product in 60, 62, 64, 75, 84, 90 & 94% yields (**Table 3**). From the results we have identified the effective temperature (90ºC) has produced the product **4a** with 94% yield and there is no progress in the percentage of yield beyond 90ºC and the yield remained unaltered. Here the percentage of yield was considered into account only for the products that were purified from their crude ones by column chromatography technique.

Table 3: Reaction temperature optimization studies

S.No.	Temperature (°C)	Time (h)	Yield (%)
1	60	4	60
2	65	4	62
3	70	4	64
4	75	2	75
5	80	3	84
6	85	3	90
7	90	4	94

3.4 Reusability of the catalyst

Catalyst reusability has been checked with the synthesis of **4a** operated under optimized conditions for articulating the cost-effectiveness of this protocol. The catalyst after the reaction was filtered off and thoroughly washed with hot ethanol for 2-3 times and dried in vacuum oven over a period of 5-6h and reused in the reaction for synthesis of **4a**. This practice has been continued till accomplishing the product **4a** in good yields. The reusability of the catalyst and its corresponding yields were presented in **Fig. 1**. Product **4a** has obtained in 94, 94, 93, 90, 85, 80 & 73% yields in 7 cycles, where the effective reusability of the catalyst has been limited only up to four cycles beyond that the yields were comparatively low.

Fig. 1 Reusability of the catalyst

4a has obtained in 94, 94, 93, 90, 85, 80 & 73% yields in 7 cycles, where the effective reusability of the catalyst has been limited only up to four cycles beyond theat the yields were comparatively low o pronounce it as a cost-effective methodology.

3.5 Mechanistic action of Montmorillonite K-10 supported La(OTf)$_3$ catalyst

Montmorillonite K-10 clay material with general formula $Al_2Si_4O_{10}(OH)_2.nH_2O$ exists in the form of layered silicates and is useful to support the catalysts and reagents to easily participate in organic synthesis. Mainly montmorillonite K-10 promotes the condensation reactions, addition reactions and protection reactions of carbonyls in organic synthesis. Here the Al^{+3} and Si^{+4} cations are easily binds with the triflate groups of the La(OTf)$_3$ and exists as a combined catalyst to participate in organic reactions. Here Montmorillonite K-10 is a Bronsted acid and La(OTf)$_3$ is a Lewis acid and hence the combined action of the Montmorillonite K-10 supported La(OTf)$_3$ catalyst will be more compared to their individual effects. Hence, this will show more intense catalytic action in heterogeneous catalysis as it is also advantageous with its low cost and eco-friendliness. The plausible reaction mechanism involving the catalyst has been schematically explained in **Fig. 2**.

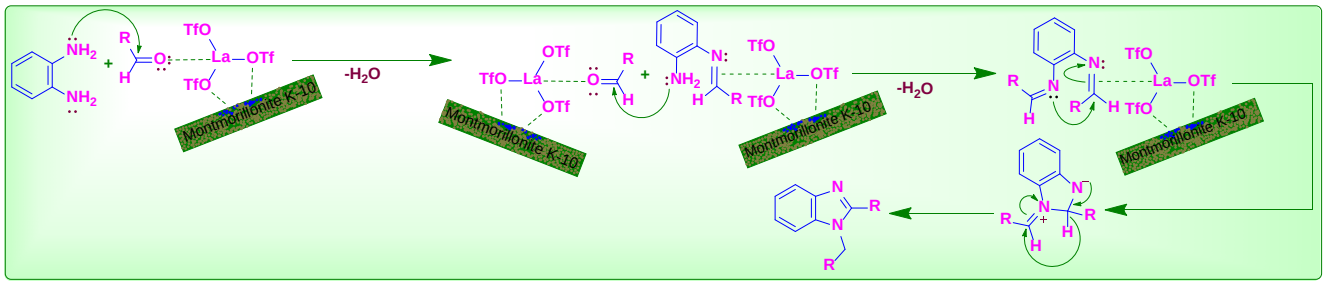


Fig. 2 Plausible mechanism for montmorillonite K-10/ $La(OTf)_3$ mediated synthesis of 1,2-disubstituted benzimidazoles

4. Conclusions

Montmorillonite K-10 supported Lanthanum triflate has successfully used for the first time to synthesize 1,2-disubstituted benzimidazoles. The driving force of this cost-effective and eco-friendly methodology is binding of Al^{+3} and Si^{+4} cations with triflate groups that will creates more positive charge on La^{+3} ions. Then these La^{+3} ions easily interact with aldehydes to promote the reaction with *o*-phenylenediamine *via* nucleophilic addition and cyclization steps to form the product in high yields.

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