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Supported copper triflate as an efficient catalytic system for the synthesis of highly functionalized 2-naphthol Mannich bases under solvent free condition

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ABSTRACT

Various heterogeneous catalysts (Lewis acid) have been prepared and screened for the synthesis of Betti bases in an attempt to reduce the environmental hazards associated with the conventional homogeneous Lewis acid system. And we found especially $Cu(OTf)_2{\cdot}SiO_2$ catalyzes the three-component coupling of aldehyde, 2-naphthol, and alicyclic amine to generate Betti base with high efficiency under neat conditions without additional co-catalyst or additive in air. The reaction is not sensitive to water and occurs smoothly in water as well.

The Mannich reaction is a classic method for the synthesis of many natural substances, pharmacophore and one of the most important methods in organic synthesis for providing carbon–carbon bond formation and its products are of considerable importance in industry.[1a] However, recently chemists are more interested to synthesize the Mannich product using one-pot multicomponent with environmentally friendly approach that maximizes the utility of known multicomponent reactions.[1b,c] One-pot multicomponent reactions have gained significant importance and attracted much attention on progress in synthesis of complex building blocks.[2a] These reactions are single step one-pot transformations proceeding through more than two subsequent reactions in which the product of the first is a substrate for the second. During the past few decades, many one-pot multi-component reactions have been reported for the making of new carbon–carbon, carbon–hetero atom, and hetero–hetero atom bonds.[2b–d] Especially, the ability of these unified multicomponent reactions that provide poly-functionalized heterocyclic scaffolds in single operation and in stereospecific manner is of great importance in organic synthesis and make them useful in medicinal chemistry.[3a,b] Recent development of solvent-free multicomponent reactions has attracted increasing interest from chemists. In this initiative, aided with the recent development of new strategies, the chemists have been showing more concern toward minimizing the environmental pollution caused by solvents and developing eco-compatible synthetic procedures.[4a,b]

One of the important reactions in the field of multicomponent synthesis is the Betti reaction which was discovered at the beginning of the 20th century by Mario Betti. Mario Betti was a distinguished Italian chemist, he has discovered the synthesis of 1-(α-aminoalkyl)-2-naphthols from a simple and straightforward condensation between 2-naphthol, aryl aldehydes, and ammonia, or amines, the formed product called Betti base.[5a,b] Initially Betti had concluded that the reaction proceeded via the nucleophilic attack of 2-naphthol carbon on imine produced from benzaldehyde and aniline. Later he proved that 2-naphthol should be a good carbon nucleophile toward the imine.[6]

The synthesis of 2-naphthol Mannich bases from this one of the modified Mannich reactions gives versatile synthetic building blocks which have a wide range of application such as useful precursor for the preparation of many nitrogen-containing pharmacophores and key intermediate for many multistep organic synthesis.[7a,b] Some of the 2-naphthol Mannich bases and related molecules are well reported as biologically active ingredients, medicaments.[7c] Moreover, we are also interested to emphasize on the recent reported patents which proved that this 2-naphthol Mannich bases (Fig. 1) are biologically multipurpose precursors, which can be useful in treatment of many infectious diseases such as Giardiasis and also showed their effectiveness in treatment of body pain as an analgesic drug.[7d,e] Besides, compounds of this type were reported in the literature as good potent oxytocic nature.[7h] Furthermore, Betti bases were used as ligands in the enantioselective addition of diethylzinc to aromatic aldehydes and showed highly efficient asymmetric induction in this addition.[7f] Also it has been proved that the (*S*)-Betti base is an excellent chiral

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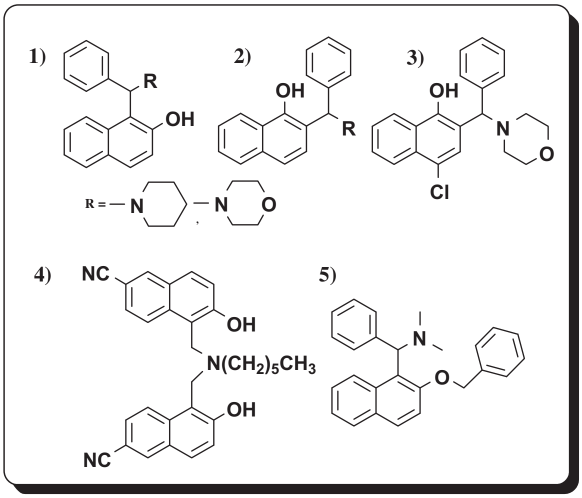


Figure 1. Biologically active reported Betti bases and their related structure.

auxiliary for the synthesis of enantiopure (2*S*,6*R*)-dihydropinidine and (2*S*,6*R*)-isosolenopsins.[7g] Due to multi applicability in biology as well as in chemistry, this adventitious moiety encourages us to develop an efficient route for their synthesis.

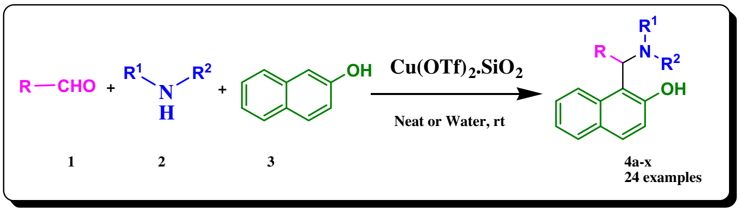
The usage of heterogeneous metal Lewis catalyst instead of traditional homogeneous metal Lewis and Brønsted acid catalysts, could possess a more environmentally friendly alternative. Moreover the use of metal heterogeneous catalysts under solvent-free conditions is becoming very popular as it has many advantages, such as faster rate of reaction, reduced hazardous solvent pollution, reusability, air/water compatibility, low cost, and remarkable ability to suppress side reactions in acid sensitive substrates that make them valuable and advantageous catalyst in synthetic processes. Copper triflate ($Cu(OTf)_2$), is less sensitive to air and moisture. The presence of triflates (OTf) has advantages of being water tolerant and less sensitive toward atmospheric exposure than halide Lewis acids. The supported copper triflate has various advantages due to its low toxicity, low price, ease of handling, reusability, and experimental simplicity. The supported $Cu(OTf)_2{\cdot}SiO_2$ catalyst exhibited both Lewis and Brønsted acidic surfaces due to the presence of residual moisture within $Cu(OTf)_2$, as well as the surface silanol groups of the silica, and the methanol used as solvent in the catalyst preparation.[8a] Sage et al. reported that $Cu(OTf)_2{\cdot}SiO_2$ is an efficient catalyst for cationic polymerization of styrene as compared to traditional vinyl polymerization catalyzed by homogeneous Lewis acid catalyst. Faster reaction rate and higher molecular weight polymers were observed compared to the homogeneous catalyst.[8a] Also the supported copper triflate as an adventitious catalytic system for the thioacetalization of carbonyl compounds under solvent free condition has been reported.[8b]

In continuation of our ongoing effort to the development of newer environmentally benign methodology for the synthesis of useful precursor in the field of biology, industry, and key intermediate for the multistep synthesis,[9a–d] we decided to investigate the efficiency of supported metal Lewis acid catalyst for the synthesis of biologically active Betti products. So herein we wish to report the multicomponent reaction for the synthesis of 1-(α-aminoalkyl)-2-naphthols from 2-naphthol, aldehyde, and alicyclic amine using $Cu(OTf)_2{\cdot}SiO_2$ as reusable catalyst at room temperature to 40 °C under neat condition in quantitative yield (Scheme 1). After series of studies we achieved excellent yields in very short duration at milder condition. It has been demonstrated that solvent-free reaction condition is an efficient technique for various organic reactions. Due to high concentration of the reactant leads to significant decrease in reaction time, increased yields, and easier workup procedure. Our studies indicated that this reaction proceeds with a catalytic amount of catalyst with short reaction time, and easy workup procedure is the one of the advantages of this protocol.

In the light of previously reported literature survey for the synthesis of this interesting moiety, there are very few reports available using different Lewis acid, Brønsted acid surfactant, and neutral and efficient non-ionic surfactant catalyst.[10a–d] Homogeneous Lewis acids are most commonly used catalysts for the fast and efficient catalytic system in the synthesis of verity of organic transformation. In addition, separation of the Lewis acid from the reaction products produces a large volume of acidic waste due to the water-quenching step needed to neutralize the acid. Hence we focused our initial investigation to find out a best heterogeneous catalytic system for this precious one-pot multicomponent Betti reaction. In our literature survey, the usage of silica supported metal Lewis acid as catalyst in the synthesis of 1-(α-aminoalkyl)-2-naphthols is unprecedented.

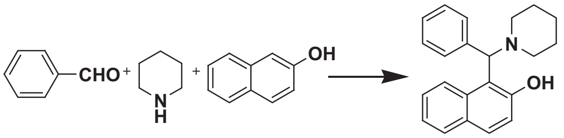
Initially, in search of best catalytic system for this one-pot synthesis, optimization of various reaction parameters like different metal Lewis acid catalysts, temperature, and solvent was carried out (Table 1). In order to establish the real effectiveness of the catalyst for the synthesis of Betti base, a test reaction was performed without catalyst using 2-naphthol, benzaldehyde, and piperidine at room temperature in air. It was found that only a trace amount of product was obtained in the absence of catalyst even after 12 h (Table 1, entry 2). Even though we increased temperature up to 100 °C for this catalyst free reaction, there was no appreciable improvement in yield (Table 1, entry 2). In search of effective, eco-friendly, and efficient reusable catalytic system for this reaction, same test reaction was performed with different supported metal Lewis acid catalysts such as Cu–Sn (200 mesh, 100 mg), $Cu(OTf)_2{\cdot}SiO_2$, $Zn(OTf)_2{\cdot}SiO_2$, $TiO_2{\cdot}SiO_2$, $BF_3{\cdot}SiO_2$, and $ZnCl_2{\cdot}SiO_2$ (Table 1). To study the role of SiO_2, reaction was tested with SiO_2 (100 mg) only, and we observed comparable good yield as compared to catalysts free reaction (Table 1, entry 4). Among all screened catalysts $Cu(OTf)_2{\cdot}SiO_2$ gave the best result in view of yield and reaction time (Table 1, entry 5). In contrast $TiO_2{\cdot}SiO_2$, $BF_3{\cdot}SiO_2$, and $ZnCl_2{\cdot}SiO_2$ did not afford the desired product in good yields. Careful analysis of screened supported Lewis acid catalyst, shows that silica supported metal triflate such as $Cu(OTf)_2{\cdot}SiO_2$ and $Zn(OTf)_2{\cdot}SiO_2$ were effective than other silica supported metal Lewis acid catalyst, but promising results were obtained with silica supported copper triflate catalyst in lesser time with better yield.

Once we found $Cu(OTf)_2{\cdot}SiO_2$ as best catalyst for this reaction, temperature and solvent optimization was done. We screened var-



Scheme 1. Supported copper triflate catalyzed synthesis of Betti base.

Table 1
Screening of various types of heterogeneous catalysts and solvents for the synthesis of compound **4a**.[a]



Entry	Catalyst (10 mol %)	Solvent	Temp (°C)	Time (h)	Yield[b]
1	–	Toluene	rt	12	Trace
2	–	Toluene	100	12	⩽30
3	Cu–Sn (200 mesh, 100 mg)	Toluene	rt	12	52
4	SiO_2	Toluene	100	12	62
5	$Cu(OTf)_2\cdot SiO_2$	Toluene	rt	12	78
6	$Zn(OTf)_2\cdot SiO_2$	Toluene	rt	12	74
7	$TiO_2\cdot SiO_2$	Toluene	rt	12	54
8	$BF_3\cdot SiO_2$	Toluene	rt	12	37
9	$ZnCl_2\cdot SiO_2$	Toluene	rt	12	56
10	$Cu(OTf)_2\cdot SiO_2$	THF	rt	12	53
11	$Cu(OTf)_2\cdot SiO_2$	CH_3CN	rt	12	73
12	$Cu(OTf)_2\cdot SiO_2$	Water	rt	7	81
13	$Cu(OTf)_2\cdot SiO_2$	Ethanol	rt	12	56
14	$Cu(OTf)_2\cdot SiO_2$	Toluene	80	12	82
15	$Cu(OTf)_2\cdot SiO_2$	Neat	rt	1	84
16	$Cu(OTf)_2\cdot SiO_2$	Neat	40	0.75	92
17	$Cu(OTf)_2\cdot SiO_2$	Neat	60	1	93
18	$Cu(OTf)_2\cdot SiO_2$ (05 mol %)	Neat	40	2	69
19	$Cu(OTf)_2\cdot SiO_2$ (20 mol %)	Neat	40	1	93

[a] Reactions and conditions: benzaldehyde (0.6 mmol), piperidine (0.5 mmol), 2-naphthol (0.5 mmol) at room temperature.

[b] Isolated yields.

Table 2
The reuse of $Cu(OTf)_2\cdot SiO_2$ in the synthesis of compound **4a**

Entry	Reaction cycle	Yield[a]
1	Ist (fresh run)	92
2	IInd cycle	88
3	IIIrd cycle	81

[a] Isolated yield.

ious solvents, such as toluene, EtOH, CH_3CN, water and THF at room temperature. Among the tested different organic solvents only toluene and acetonitrile were found to give moderate yields. It is worthy of note, that when we performed the reaction in aqueous media, reaction was completed with good yield as compared to conventional organic solvents (Table 1, entry 12).

It is observed that under solvent condition, it required longer times (7–12 h) to afford comparable yields. A similar model reaction was carried out using 10 mol % of $Cu(OTf)_2\cdot SiO_2$ at room temperature without solvent. It was observed that reaction proceeded in an efficient manner in few minutes with increased yield (84%) under solvent free condition at room temperature (Table 1, entry 15). Practically due to high concentration of reactant, rate of reaction was faster in neat condition. When we found solvent free condition gives better yield in lesser time, we decided to study the effect of temperature on the rate of reaction with different temperature optimization. Surprisingly, the best result was obtained by using 10 mol % $Cu(OTf)_2\cdot SiO_2$ at room temperature in 1 h (84%), affording a high yield of 92% in 45 min at 40 °C under neat condition.

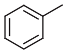
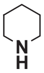
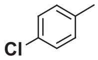
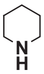
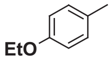
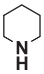
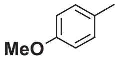
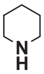
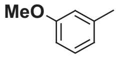
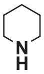
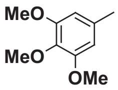
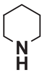
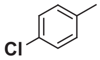
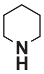
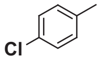
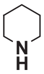
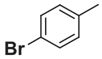
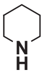
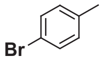
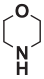
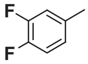
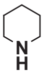
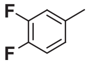
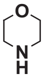
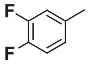
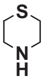
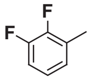
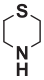
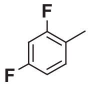
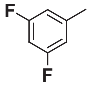
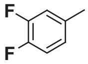
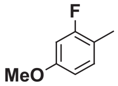
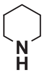
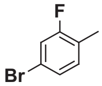
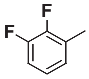
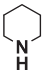
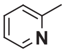
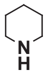
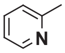
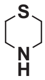
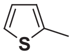
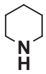
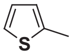
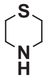
Once found the best catalyst and solvent condition, we studied the effect of varying amount of $Cu(OTf)_2\cdot SiO_2$ catalyst for this one-pot multicomponent system. In order to evaluate the appropriate catalyst loading, a model reaction was carried out using 5 and 20 mol % of $Cu(OTf)_2\cdot SiO_2$ at 40 °C without solvent (Table 1, entries 18 and 19). It was found that 10 mol % of catalyst shows maximum yield in minimum time. A larger loading amount of the catalyst (20 mol %) neither increases the yield nor shortens the conversion time. So, 10 mol % of catalyst was found to be the optimal quantity and sufficient to push the reaction forward. It was found that instead of 1.0 equiv aldehyde the use of 1.2 equiv of aldehyde provides a better yield. A few examples of supported Cu species have been reported as efficient catalyst in organic transformation and reusability was ascertained with minimal losses of Cu.[11a,b] This prompted us to study the reusability of the $Cu(OTf)_2\cdot SiO_2$ catalyst for at least two more cycles. Accordingly, after the first fresh run with 92% yield, the catalyst was recovered by dissolving reaction mixture in hot ethanol and catalyst was removed by filtration. The recovered catalyst was dried under vacuum at 60 °C for 12 h and tested up to two more reaction cycles. Recycling and reuse of the catalyst showed minimal decreases in yields. The product **4a** was obtained in 92%, 88%, and 81% yields after successive cycles. (Table 2, entries 1–3), thus proving the catalyst's reusability. Careful analysis of Table 2 shows that there is no significant loss of catalytic activity of this supported catalyst, thus proving that the catalyst shows very less leaching of copper during the course of reaction in the solution. The stability and recovery of this supported catalyst has also been proved by Sage et al.[8a]

Once the effective catalytic amount of the catalyst was proven, we extended our study to investigate generality and efficiency of developed protocol using $Cu(OTf)_2\cdot SiO_2$ (10 mol %) under solvent-free condition at 40 °C with 2-naphthol, functionalized aromatic aldehydes, and different alicyclic amines to prepare a series of substituted aminobenzylnaphthols (Table 3). Various aromatic aldehydes with different substituents at ortho, meta, or *para*-positions show equal ease toward the product formation in high yields. The obtained results were shown in Table 3. Careful analysis of Table 3 reveals that the reactions were compatible with various functionalized aldehydes and secondary amines using this catalytic system. In contrast, aromatic aldehydes having groups like Cl, F, Br, and MeO showed better reactivity and the reactions were completed in shorter time. Heteroaryl aldehydes like nicotinaldehyde and thiophene-2-carbaldehyde afforded the desired product in quantitative yields. We eventually achieved excellent yields in very short duration at milder condition. Surprisingly best yield was obtained with alicyclic amines like morpholine and thiomorpholine as compared to piperidine and pyrrolidine.

The reported as well as synthesized novel compounds were further characterized by their spectral properties (^1H, ^{13}C NMR, and HRMS). Moreover, single crystal X-ray diffraction analysis was done for compounds **4a** and ORTEP diagram of the compound **4a** is shown in Figure 2. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL)[12a] was used for structure solution and full matrix least squares refinement on F^2. [12b] The single-crystal X-ray analysis of **4a** clearly indicates that C11 has '**R**' relative configuration. The naphthol ring is almost planar which is at an angle of 72.75° with respect to the benzene ring shown in Figure 3 and molecular packing diagram provided as Figure 4 (Figs. 3 and 4 given as Supplementary data).

In conclusion, the main advantages of this present methodology are the simple work-up, easy recovery of catalyst, no need for anhydrous condition, no base, or any additional activator required, and the residue was crystallized from ethanol to give the pure product without further purification. A possible mechanism of this one pot reaction is expected on the basis of reported literature.[6] It is assumed that, after formation of iminium ion from benzaldehyde and secondary amines followed by the nucleophilic attack of 2-naphthol carbon on iminium carbon, subsequent shifting of hydrogen atom leads to the formation of 1-(α-aminoalkyl)-2-naphthols (Scheme 2). A variety of silica supported Lewis acid cat-

Table 3
Synthesis of diversified aminoalkyl naphthol derivatives via Scheme 1[a]

Entry	R	Amine	Time (h)	Yield[b]
4a			0.75	92
4b			1	95
4c			2.5	82
4d			1.16	90
4e			1	88
4f			2	94
4g			0.66	91
4h			0.75	95
4i			3	87
4j			1.33	90
4k			0.83	85
4l			1.16	88
4m			0.83	93
4n			0.5	92
4o			0.75	84
4p			0.33	94
4q			1.16	90
4r			2	88
4s			0.5	86
4t			1.33	90
4u			0.5	72
4v			1.18	80
4w			0.75	74
4x			0.66	83

[a] Reactions and conditions: benzaldehyde (0.6 mmol), piperidine (0.5 mmol), 2-naphthol (0.5 mmol), and 10 mol % $Cu(OTf)_2{\cdot}SiO_2$ at 40 °C under neat condition.

[b] Products were isolated by recrystallization from ethanol except products **4c**, **4e**, **4f**, and **4g** purified using column chromatography.

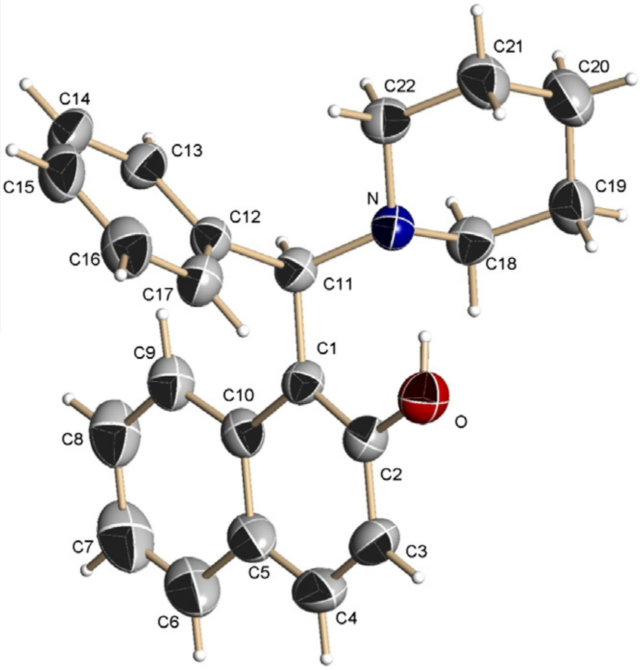
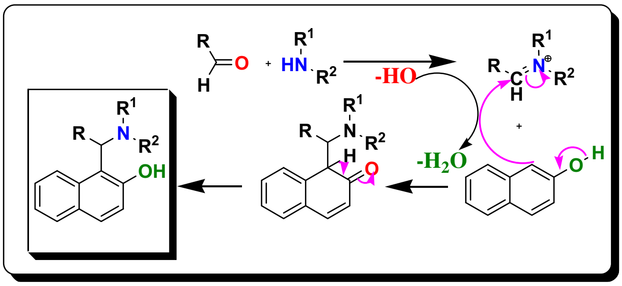


Figure 2. ORTEP of compound **4a**. Ellipsoids are drawn at 50% probability.



Scheme 2. A possible mechanism for the synthesis of 1-(α-aminoalkyl)-2-naphthols.

alysts, viz., $Cu(OTf)_2{\cdot}SiO_2$, $Zn(OTf)_2{\cdot}SiO_2$, $TiO_2{\cdot}SiO_2$, $BF_3{\cdot}SiO_2$, and $ZnCl_2{\cdot}SiO_2$, were applied for the multi-component one-pot synthesis of Betti bases by a modified Mannich condensation. The use of 10 mol % $Cu(OTf)_2{\cdot}SiO_2$ at rt to 40 °C was found to be a simple and straightforward protocol for the synthesis of polyfunctionalized Betti bases using three-components, *viz*., substituted benzaldehydes, alicyclic amine, and 2-naphthol.

Acknowledgment

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Supplementary data

General chemicals and experimental procedure are given in reference section.[13–15] All new compounds are well characterized by their spectral properties (^1H and ^{13}C NMR and HRMS) and copies of NMR spectra were provided as Supplementary data. All crystallographic parameters and data of compound **4a** are provided. The complete set of structural parameters for compound **4a** (CCDC No.874639) in CIF format is available as an Electronic Supplementary Publication from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/conts/retrieving.html.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.022.

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13. General: Chemicals were purchased from Aldrich and Alfa aesar Chemical Companies. NMR spectra were recorded in ppm in $CDCl_3$ on a Jeol JNM ECP 400 NMR instrument using TMS as internal standard. HR-MS were recorded on Jeol JMS-700 mass spectrometer. Melting points are taken in open capillaries and are uncorrected; Electrothermal-9100 (Japan) instrument was used to determine the melting point of the compounds.
14. *Preparation of supported copper triflate:* A supported $Cu(OTf)_2$ catalyst were prepared by adopting the literature precedent Sage et al.[8a] Copper trifluoromethanesulfonate (0.18 g, 0.5 mmol) was added to methanol (50 ml) in a 100-ml 3-neck round bottom flask equipped with a reflux condenser and a magnetic stirrer bar. The silica (230–400 mesh, 5 g, pretreated at 600 °C for 18 h) was added and the resulting slurry was stirred at room temperature under N_2 atmosphere for 2.5 h. The solvent was then evaporated in vacuo at 80 °C for 1 h. The resulting solid product obtained was light blue depending on the loading.
15. *Typical procedure for the 1-(α-aminoalkyl)-2-naphthol derivatives:* A mixture of 2-naphthol (1.0 equiv), amine (1.0 equiv), and aldehyde (1.2 equiv) was stirred at room temperature to 40 °C without any solvent in the presence of 10 mol % of catalyst for certain period as indicated in Table 3. After completion of reaction indicated by TLC, the reaction mixture was dissolved in hot ethanol and the catalyst was recovered by filtration and product was recrystallized from ethanol. ^1H and ^{13}C NMR data of the known compounds were in good agreement with those in the literature. All new compounds were completely characterized by their analytical and spectral data. Spectroscopic data for new compounds are given and scan spectra were provided as Supplementary data.