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N-Heterocyclic carbene as a Brønsted base catalyst for the amination of naphthol derivatives and alcoholysis of glutaric anhydrides

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ABSTRACT

A non-covalent Brønsted-basic *N*-heterocyclic carbene catalyzed (NHC) Friedel-Crafts type amination of naphthol derivatives using dialkyl azodicarboxylates as the aminating source and alcoholysis of various glutaric anhydrides using alcohol as pronucleophile is presented. Both of these reactions are performed in the presence of either commercially available free-carbene catalyst or in situ-generated carbene catalyst. Friedel-Crafts type amination reaction is an example of a hydroxy group facilitated amination reaction. Both reactions proceed via in situ activations of –OH group by the carbene catalyst through hydrogen bonding interaction and furnish the relevant products in moderate to excellent yields.

Organocatalysts usually the small organic molecules have been generally used to bring out various synthetic transformations that are exceptional. Besides, they are broadly employed to develop complementary reactions that are catalyzed by metal-catalysts [1]. In recent years, *N*-heterocyclic carbenes (NHCs) have been widely used as organocatalysts to construct various C–C and C–heteroatom bonds in organic synthesis [2]. Owing to the Lewis basic propensity of NHC, they are predominantly exploited as the nucleophilic catalyst. In general, the activation of starting precursors by NHC takes place through various modes of activation, in which the carbene catalyst and the functional group present on the substrate play a crucial role. Most of the Lewis base catalysis by NHC involves a reversible covalent-interaction between the carbene catalyst and the substrate [2,3]. In contrast, the substrate activation via non-covalent interaction by Brønsted basic NHC is less documented, although, NHCs are known for their characteristic Brønsted basic property [4].

In 2002, the application of NHC as a Brønsted base catalyst for transesterification reaction was showcased independently by Nolan [4a] as well as Waymouth and Hedrick [4b]. Later, Movassaghi and co-workers [4c] described amidation of esters mediated by NHC catalyst, and their NMR studies supported the activation of alcohol pronucleophile by NHC via hydrogen bonding interaction between an alcohol and carbene catalyst. Of late, Scheidt et al., reported NHC-catalyzed conjugate addition of alcohols to conjugate acceptors [4e]. Apart from this, various intra- and inter-molecular Michael addition reactions were realized through non-covalent activation of different pronucleophiles using a catalytic amount of NHC [4f–m].

Conventionally, aromatic amines are produced by reduction of nitroaromatics and cross-coupling reaction between aromatic halides and amines [5]. Direct amination of electron-rich arenes was first reported by Deils and Back [6a], and then, catalytic synthesis of the same was narrated in the presence of several metal-catalysts [6,7]. Jørgenson's group depicted the direct amination of naphthol derivatives using cinchona-alkaloid derived catalyst [7a,b]. Despite these developments, evolving new prospects for the synthesis of various aromatic amines via direct amination method is highly desirable. In this context, we envisioned the direct amination of 2-naphthol derivatives employing NHC as the catalyst by capitalizing on characteristic Brønsted basic nature of free carbenes.

We began the optimization study by choosing 2-naphthol **1a** as a precursor and di-*tert*-butyl azodicarboxylate (D^tBuAD, 2 equiv) **2a** as an aminating source. In the beginning, the catalytic use of commercially available free carbene catalysts such as IMes (1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, **A**) and IPr (1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene, **B**) in CH_2Cl_2 rendered the desired product **3aa** in 87% and 88% yields respectively (Scheme 1a). Also, we probed the role of carbene catalyst in the activation of **1a** toward Friedel-Crafts type amination reaction through ^1H NMR experiment. Mixing of 1:1 mixture of **1a** and IMes (**A**) in C_6D_6 (0.05 M at rt) resulted in the considerable downfield shift for the hydroxyl proton of **1a** (Scheme 1b), which reveals the pres-

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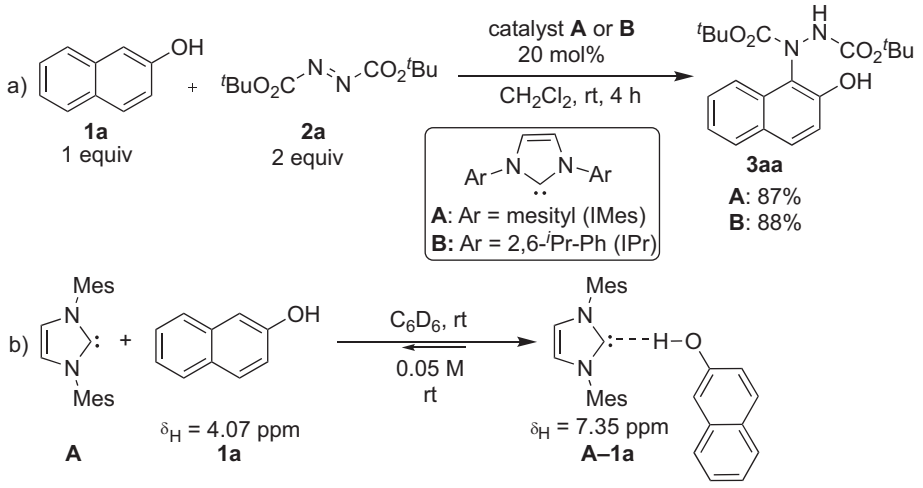
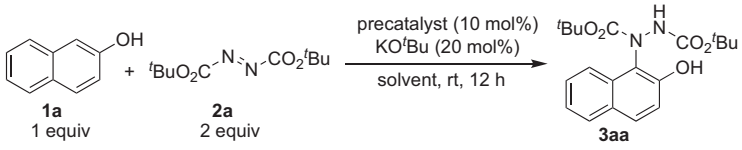


Scheme 1. a) Friedel-Crafts type amination of 2-naphthol mediated by free carbene catalyst. b) Activation of 2-naphthol via carbene-2-naphthol complex (A-1a).

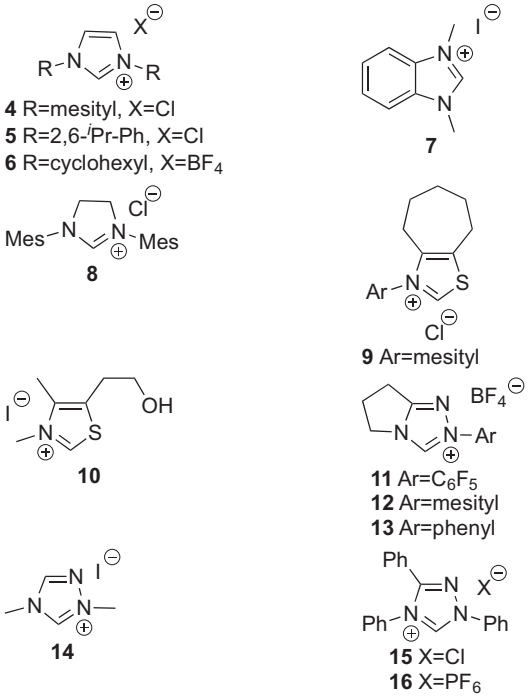
ence of hydrogen bonding interaction between **1a** and **A**, and this scrutiny is in good accordance with the analogous study described by Movassaghi's group [4c].

Based on these promising findings, we envisaged optimizing the reaction conditions using in situ-generated carbene catalyst from NHC precatalyst and base as it has a more practical advantage

Table 1
Optimization of Reaction conditions.



entry	precatalyst	solvent	yield (%)[a]
1	**4**	CH_2Cl_2	35
2	**5**	CH_2Cl_2	57
3	**6**	CH_2Cl_2	52
4	**7**	CH_2Cl_2	40
5	**8**	CH_2Cl_2	63
6	**9**	CH_2Cl_2	57
7	**10**	CH_2Cl_2	71
8	**11**	CH_2Cl_2	44
9	**12**	CH_2Cl_2	64
10	**13**	CH_2Cl_2	55
11	**14**	CH_2Cl_2	72
12	**15**	CH_2Cl_2	67
13	**16**	CH_2Cl_2	80
14	**16**	THF	71
15	**16**	Et_2O	88
16	**16**	CH_3CN	85
17	**16**	DMF	62
18	**16**	toluene	94
19	**16**	$CHCl_3$	96[b]
20	**16**	$CHCl_3$	75[b,c]
21	–	$CHCl_3$	14[d]



[a] Isolated yield.
[b] 4 h reaction time.
[c] 8 mol% of KO^{t}Bu.
[d] In the absence of precatalyst and base.

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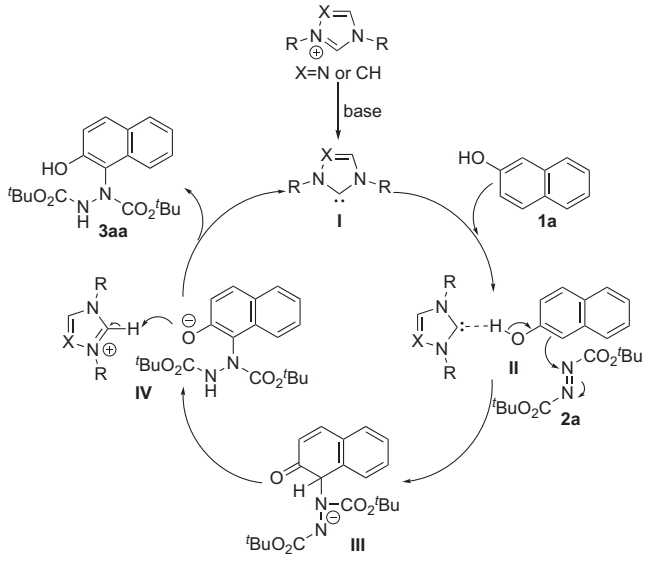
and also lucrative. On the basis of this hypothesis, the use of various imidazolium pre-catalysts (**4** to **7**) together with KO^{t}Bu (20 mol%) afforded the anticipated amination product **3aa** in moderate yields (entries 1–4, Table 1). Furthermore, NHC pre-catalysts such as imidazolinium (**8**), thiazolium (**9** and **10**) and triazolium (**11** to **15**) were less efficient and delivered **3aa** in considerable yields (entries 5–12). Satisfyingly, the aminated 2-naphthol **3aa** was obtained in 80% yield when the triazolium pre-catalyst **16** was engaged as the catalyst (entry 13), which is presumably due to the increased acidity of triazolium precatalysts than other pre-catalysts, wherein the in situ produced conjugate acid of the catalytic species could act as proton source (see Scheme 2) [3l]. Several bases were screened for the amination of 2-naphthol derivatives in the presence of **16**, among them KO^{t}Bu furnished the desired product in excellent yield (*see ESI for the base screenings*). Remarkably, the amination reaction proceeded well when $CHCl_3$ was used as a solvent in the presence of pre-catalyst **16** and furnished the requisite product in excellent yield (96% yield, entry 19). To ensure the complete utilization of base during in situ-generation of active carbene catalyst, 10 mol% of pre-catalyst **16** and 8 mol% of KO^{t}Bu was employed, and the expected product **3aa** was obtained in 75% yield (entry 20) [9].

With the optimized reaction conditions in hand, we went on to scrutinize the scope of various naphthol derivatives and dialkyl azodicarboxylates. A series of di-alkyl azodicarboxylates such as di-*tert*-butyl azodicarboxylate (D^{t}BuAD, **2a**) diethyl azodicarboxylate (DEAD, **2b**), diisopropyl azodicarboxylate (DIAD, **2c**) and dibenzyl azodicarboxylate (**2d**) reacted with **1a** to afford the corresponding aminated products (entries **3ab-ad**, Table 2) in good yields. Similarly, excellent yields were obtained in the case of 2-naphthol bearing an aryl substituent (**1b**) (Table 2, entries **3ba-bd**). Whereas, an electron- donating group (such as a methoxy group) on the 2-naphthol (**1c**) ring resulted in the formation of analogous aminated product in appreciable yields (entries **3ca-cd**). Besides, the direct amination reaction proceeded well for the substrate bearing bromo-substituent at 3- and 6-position (**1d** and **1e**) and offered the concomitant products in better yields (entries **3da** and **3ea-ed**, Table 2). Electron-withdrawing groups such as cyano, ester, amide, and ketone at the various position of the naphthol ring (**1f-1j**) reacted smoothly and delivered the requisite products in moderate to excellent yields (entries **3fa-3ja**), however, 2-naphthol bearing nitro substituent at the *peri*-position failed to undergo amination reaction presumably due to strong electron-withdrawing nature of nitro group which makes 8-nitro-2-naphthol less nucleophilic towards amination reaction. Additionally, 2-naphthol holding an allylic ether functionality at 7-position handed the desired product in moderate yield (56%, entry **3ka**). Interestingly, substituents at the *peri*-position of 2-naphthol (**1l** and **1m**) with D^{t}BuAD (**2a**) furnished the desired products **3la** and **3ma** in 74% and 68% yields, respectively. Next, we explored 2-naphthol derivative encompassing a hetero-atom on its ring (**1n**) for the amination reaction, and the corresponding target products were obtained in moderate to good yields (entries **3na-3nd**). Ultimately, the efficacy of the reaction was tested with hydroxycoumarin (**1o**) with **2a** as an aminating source, and the corresponding aminated product was attained in high yield (93%, entry **3oa**).

Herein, we propose a plausible mechanism for an NHC-promoted Friedel-Crafts type amination of 2-naphthol derivatives based on the literature precedence (Scheme 2) [4]. At the outset, the hydrogen bonding interaction between free-carbene catalyst (**I**) and 2-naphthol (**1a**) activates the **1a** for nucleophilic attack (as shown in step **II**), which then, undergoes Friedel-Crafts type amination reaction with **2a** to form the intermediate **III**. Next, intramolecular-proton exchange, followed by protonation of resultant oxy-anion by triazolium precatalyst produces the target product **3aa** and regenerates the active free-carbene (**I**) in the catalytic cycle (step **IV**).



Scheme 2. Plausible mechanistic pathway.

NHC-promoted alcoholysis of glutaric anhydrides

Then, we envisaged an alcoholysis of glutaric anhydrides using alcohols as pronucleophile by embracing Brønsted basic activation of alcohol by a carbene catalyst demonstrated by Scheidt's group [4e]. The ensuing hemiesters (having chemically two distinctive carbonyl groups) are important synthetic intermediate for several bioactive molecules. Various metal catalysts and cinchona-alkaloid based catalysts were previously known to mediate asymmetric desymmetrization of *meso*-anhydrides [8].

To validate our speculation, a model reaction was performed in the presence of a commercially available free-carbene catalyst such as **A** (IMes, 10 mol%) using 3-phenylglutaric anhydride (**4a**) as a precursor, MeOH (**5a**, 10 equiv) as the pronucleophile in toluene. Gratifyingly, the desired hemiester (**6aa**) was obtained in good yield (Scheme 3a). Next, we endeavoured the same reaction by exercising carbene catalyst which is in situ generated from NHC precatalyst (**4**) and DBU, and as expected the desired hemiester was obtained in excellent yields (Scheme 3b) [10].

With these findings in hand, further alcoholysis experiments were performed using various glutaric anhydrides. As summarized in Table 3, methanolytic desymmetrization of phenyl glutaric anhydride (**4a**) furnished the desired hemiester in excellent yield (entry **6aa**, Table 3). Increasing the carbon chain of the alcohol scaffold such EtOH (**5b**), 2-propanol (**5c**), allylic alcohol (**5d**), and propargyl alcohol (**5e**) resulted in slight deterioration of the product yields, surmising that steric factor and acidity of the alcohols may be the possible reasons (entries **6ab-6ae**, Table 3) [4b]. Then, we investigated the alcoholysis of glutaric anhydride bearing substituent at the para position of the phenyl ring, for instance, 3-(4-fluorophenyl)glutaric anhydride (**4b**) on methanolysis afforded the corresponding hemiester in good yield (Table 3, entry **6ba**). Next, we explored a methanolysis of unsymmetrical cyclic anhydride like phenylsuccinic anhydride (**4c**), and in this case, the hemiester was isolated as the sole product, presumably due to steric hindrance exerted by the phenyl group (entry **6ca**, Table 3). In addition, preliminary investigations on asymmetric version of this reaction were performed in the presence of

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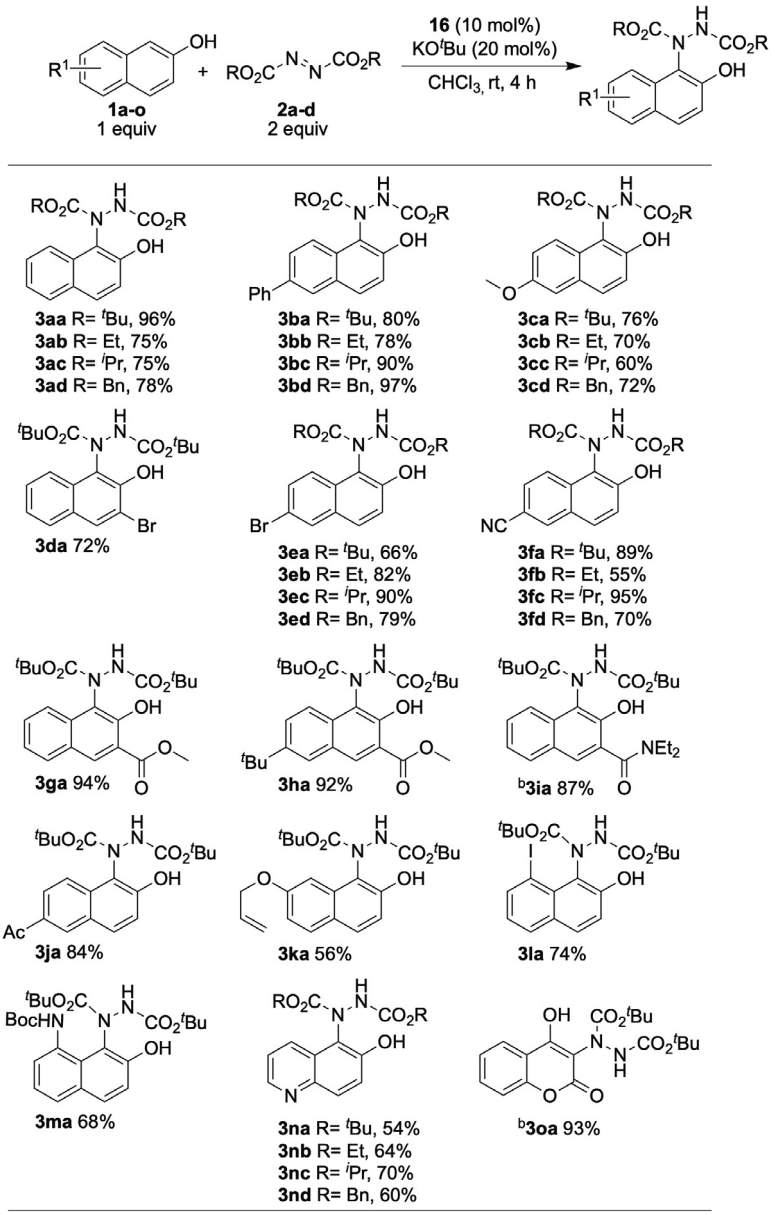
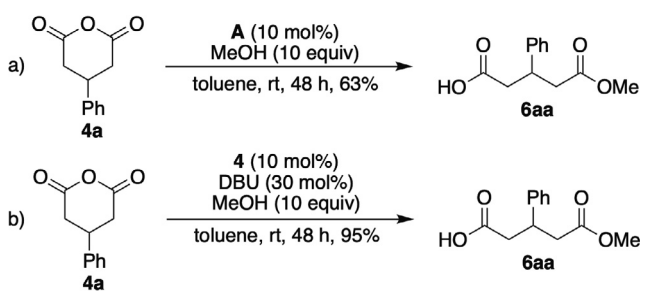
Table 2
NHC-catalyzed amination of naphthol derivatives.[a]



[a]Isolated yield. [b]$CHCl_3$:DMF (9:1).



Scheme 3. a) Free carbene-catalyzed alcoholysis of 3-phenylglutaric anhydride, b) alcoholysis of phenylglutaric anhydride mediated by in situ-generated carbene catalyst.

10 mol% of chiral NHC precatalysts such as **17** or **18** and 8 mol% of a base such as DBU at −20 °C delivered **6aa** in 65% and 94% yield respectively with 0% ee (Scheme 4A and 4B). Besides, engagement of proton-shuttling strategy [4m,n] which proceeds through an assembled transition state for the methanolysis of phenylglutaric anhydrides rendered **6aa** as a racemic mixture in 69% yield (Scheme 4C). Based on the literature precedence and also by our observations, we contemplate that either lack of rigid transition state or reversibility of the reaction may be the possible reason for the absence of asymmetric induction [4e,f]. Additionally, if the deprotonation step for in situ generations of carbene catalyst from precatalyst and a base is reversible, then the reaction could possibly be promoted by the base rather than NHC, which eventually will result in a racemic product [10].

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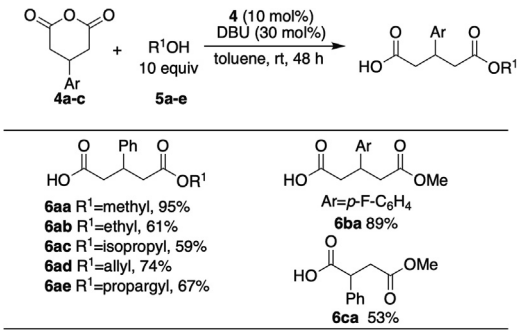
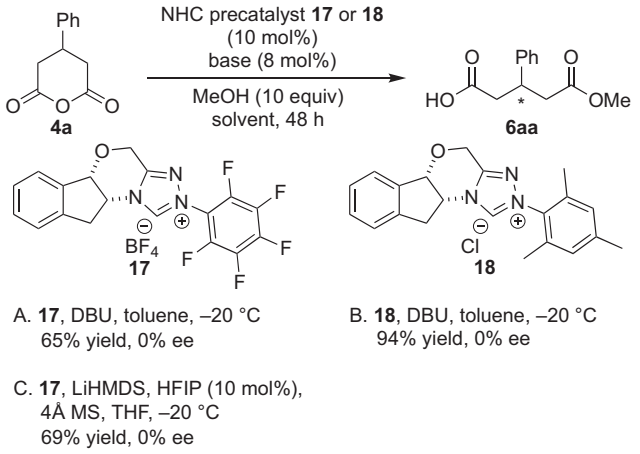
Table 3
N-Heterocyclic carbene-catalyzed alcojolysis of glutaric anhydrides.[a]

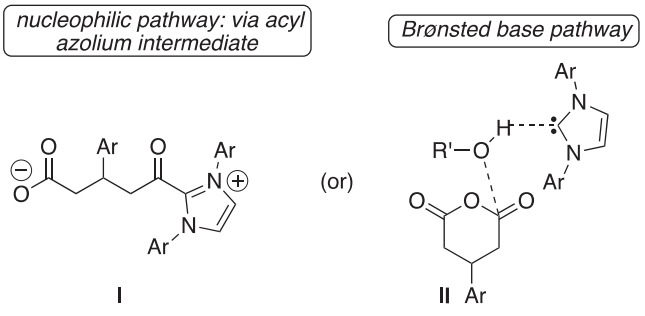


[a]Isolated yield.



Scheme 4. Asymmetric methanolytic desymmetrization of phenylglutaric anhydride.

Herein, we speculate two possible pathways for NHC-mediated alcoholysis of glutaric anhydrides. 1) NHC as a nucleophilic catalyst can form acyl azolium intermediate with glutaric anhydride via nucleophilic ring-opening reaction [3j]. Then, nucleophilic attack by the alcohol on the acyl azolium intermediate delivers the desired hemiester and also regenerates the catalyst in the catalytic cycle. Conversely, 2) NHC as a Brønsted base activates the alcohol through a non-covalent hydrogen-bonding interaction [4]. Thus, activated alcohol further undergoes an alcoholytic ring-opening reaction on the glutaric anhydride to furnish the requisite hemiester (Scheme 5).



Scheme 5. Plausible mechanism for NHC-mediated alcoholysis of glutaric anhydrides.

In conclusion, we have documented a non-covalent Brønsted basic *N*-heterocyclic carbene enabled Friedel-Crafts type amination of 2-naphthol derivatives using various dialkyl azodicarboxylates as an aminating source. Subsequently, we probed the alcoholysis of glutaric anhydrides to hemiesters using *N*-heterocyclic carbene as a non-covalent Brønsted basic catalyst. We showcased that both the methodologies work well in the presence of commercially available free-carbene catalyst, which clearly backs the Brønsted basic role of NHC in these reactions, and also, the same reactions were demonstrated by deploying in situ-generated carbene catalyst. Future scope in this direction includes development of an asymmetric version of the direct amination reaction of naphthols using chiral NHC catalyst.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.151131.

References

[1] (a) S. Bertelsen, K.A. Jørgensen, Chem. Soc. Rev. 38 (2009) 2178;
(b) F. Giacalo, M. Gruttadauria, P. Agrigento, R. Noto, Chem. Soc. Rev. 41 (2012) 2406;
(c) J. Alemá, S. Cabrera, Chem. Soc. Rev. 42 (2013) 774;
(d) C.M.R. Volla, I. Atodirese, M. Rueping, Chem. Rev. 114 (2014) 2390;
(e) A. Borissov, T.Q. Davies, S.R. Ellis, T.A. Fleming, M.S.W. Richardson, D.J. Dixon, Chem. Soc. Rev. 45 (2016) 5474.
[2] (a) D. Enders, O. Niemeier, A. Henseler, Chem. Rev. 107 (2007) 5606;
(b) N. Marion, S. Díez-Gonzµlez, S.P. Nolan, Angew. Chem. Int. Ed. 46 (2007) 2988;
(c) V. Nair, R.S. Menon, A.T. Biju, C.R. Sinu, R.R. Paul, A. Jose, V. Sreekumar, Chem. Soc. Rev. 40 (2011) 5336;
(d) A.T. Biju, N. Kuhl, F. Glorius, Acc. Chem. Res. 44 (2011) 1182;
(e) X. Bugaut, F. Glorius, Chem. Soc. Rev. 41 (2012) 3511;
(f) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, Chem. Soc. Rev. 42 (2013) 2142;
(g) S.J. Ryan, L. Candish, D.W. Lupton, Chem. Soc. Rev. 42 (2013) 4906;
(h) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature 510 (2014) 486.
[3] (a) A. Chan, K.A. Scheidt, J. Am. Chem. Soc. 128 (2006) 4558;
(b) Q. Liu, S. Perreault, T. Rovis, J. Am. Chem. Soc. 130 (2008) 14066;
(c) A.T. Biju, N.E. Wurz, F. Glorius, J. Am. Chem. Soc. 132 (2010) 5970;
(d) C.G. Goodman, J.S. Johnson, J. Am. Chem. Soc. 136 (2014) 14698;
(e) S.S. Sohn, E.L. Rosen, J.W. Bode, J. Am. Chem. Soc. 126 (2004) 14370;
(f) C. Guo, B. Sahoo, C.G. Daniliuc, F. Glorius, J. Am. Chem. Soc. 136 (2014) 17402;
(g) N.T. Reynolds, J.R.D. Alaniz, T. Rovis, J. Am. Chem. Soc. 126 (2004) 9518;
(h) Q. Ni, H. Zhang, A. Grossmann, C.C.J. Loh, C. Merkens, D. Enders, Angew. Chem. Int. Ed. 52 (2013) 13562;
(i) J. Kaeobamrung, M.C. Kozlowski, J.W. Bode, Proc. Natl. Acad. Sci. USA 107 (2010) 20661;
(j) F.C. Eric, W.N. Gregory, M. Matthew, M. Andreas, L.H. James, J. Am. Chem. Soc. 124 (2002) 914;
(k) N. Stefan, P.D. Andrew, Polym. Int. 65 (2016) 16, and references cited therein;
(l) S.S. Sohn, J.W. Bode, Org. Lett. 7 (2005) 3873.
[4] (a) G.A. Grasa, R.M. Kissling, S.P. Nolan, Org. Lett. 4 (2002) 3583;
(b) G.W. Nyce, J.A. Lamboy, E.F. Connor, R.M. Waymouth, J.L. Hedrick, Org. Lett. 4 (2002) 3587;
(c) M. Movassaghi, M.A. Schmidt, Org. Lett. 7 (2005) 2453;
(d) M.A. Schmidt, P. Müller, M. Movassaghi, Tetrahedron Lett. 49 (2008) 4316;
(e) E.M. Phillips, M. Riedrich, K.A. Scheidt, J. Am. Chem. Soc. 132 (2010) 13179;
(f) P. Arde, R.V. Anand, RSC Adv. 6 (2016) 77111;
(g) Q. Kang, Y. Zhang, Org. Biomol. Chem. 9 (2011) 6715;
(h) M. Fèvre, M. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, Chem. Soc. Rev. 42 (2013) 2142, and references cited therein;
(i) H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail, J.L. Hedrick, Macromolecules 48 (2015) 3153, and references cited therein;

(j) S. Santra, A. Porey, J. Guin, J. Asian, Org. Chem. 7 (2018) 477;
(k) T. Boddaert, Y. Coquerel, J. Rodriguez, Chem. Eur. J. 17 (2011) 2266;
(l) G. Singh, P. Goswami, R.V. Anand, Org. Biomol. Chem. 16 (2018) 384;
(m) J. Chen, Y. Huang, Nat. Commun. 5 (2014) 3437;
(n) L. Wang, J. Chen, Y. Huang, Angew. Chem. Int. Ed. 54 (2015) 15414.

[5] (a) R.C. Larock, Comprehensive Organic Transformations: a Guide to Functional Group Preparations, 2nd ed., Wiley-VCH, New York, 1999, pp. 823–827;
(b) G.V. Smith, F. Notheisz, Heterogeneous Catalysis in Organic Chemistry, Academic Press, New York, 1999, pp. 71–79;
(c) M. Kienle, S.R. Dubbaka, K. Brade, P. Knochel, Eur. J. Org. Chem. (2007) 4166;
(d) A. Ricci (Ed.), Modern Amination Methods, Wiley-VCH, Weinheim, 2000;
(e) A. Ricci (Ed.), Amino Group Chemistry, From Synthesis to the Life Sciences, Wiley-VCH, Weinheim, 2007.

[6] (a) O. Diels, I. Back, Chem. Ber. 54 (1921) 213;
(b) H. Mitchell, Y. Leblanc, J. Org. Chem. 59 (1994) 682;
(c) Y. Leblanc, N. Boudreault, J. Org. Chem. 60 (1995) 4268;
(d) W.J. Kinart, C.M. Kinart, J. Organomet. Chem. 665 (2003) 233;
(e) W.J. Kinart, C.M. Kinart, R. Oszczeda, Q.T. Tran, Catal. Lett. 103 (2005) 185;
(f) L. Gu, B.S. Neo, Y. Zhang, Org. Lett. 2011 (1872) 13;
(g) S.M. Inamdar, V.K. More, S.K. Mandal, Tetrahedron Lett. 54 (2013) 530;
(h) J.-H. Zhang, J.-H. Xu, D.-J. Cheng, C. Shi, X.-Y. Liu, B. Tan, Nat. Commun. 7 (2016) 10677;
(i) L. Jia, Q. Tang, M. Luo, X. Zeng, J. Org. Chem. 83 (2018) 5082;
(j) J.S. Yadav, B.V.S. Reddy, G. Veerendhar, R. Srinivasa Rao, K. Nagaiah, Chem. Lett. 31 (2002) 318;
(k) S. Bombek, R. Lenarsic, M. Kocevar, L. Saint-Jalmes, J.-R. Desmurs, S. Polanc, Chem. Commun. (2002) 1494.

[7] (a) S. Brandes, M. Bella, A. Kjærsgaard, K.A. Jørgensen, Angew. Chem. Int. Ed. 45 (2006) 1147;
(b) S. Brandes, B. Niess, M. Bella, A. Prieto, J. Overgaard, K.A. Jørgensen, Chem. Eur. J. 12 (2006) 6039;
(c) S.-G. Wang, Q. Yin, C.-X. Zhuo, S.-L. You, Angew. Chem. Int. Ed. 54 (2015) 647.

[8] (a) P. Gopinath, T. Watanabe, M. Shibasaki, Org. Lett. 14 (2012) 1358;
(b) A. Spivey, B. Andrews, Angew. Chem. Int. Ed. 40 (2001) 3131;
(c) J. Hiratake, Y. Yamamoto, J. Oda, J. Chem. Soc., Chem. Commun. (1985) 1717;
(d) R. Aitken, J. Gopal, Tetrahedron: Asymmetry 1 (1990) 517;
(e) C. Bolm, A. Gerlach, C.L. Dinter, Synlett (1999) 195;
(f) N. Chaubey, S.M. Date, S.K. Ghosh, Tetrahedron: Asymmetry 19 (2008) 2721;
(g) S. Park, E.H. Nam, H.B. Jang, J.S. Oh, S. Some, Y.S. Lee, C.E. Song, Adv. Synth. Catal. 352 (2010) 2211.

[9] As observed in the previous literature reports of NHC (as a Brønsted base catalyst)-mediated synthetic transformations [4c,f] the replacement of active free carbene catalyst (both commercially available IMes, and in situ generated carbene catalyst) with KO^{t}Bu (20 mol%) for the direct amination of 2-naphthol also furnished the corresponding product **3aa** in 94% yield.

[10] Similarly, the alcoholysis of phenylglutaric anhydride only in the presence of a base such as DBU rendered **6aa** in 49% yield.

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