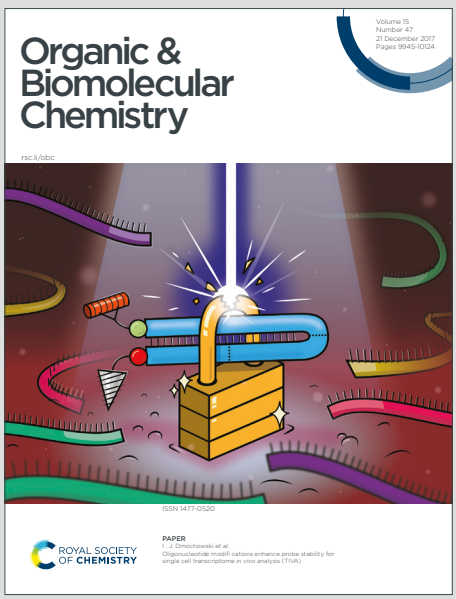
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: K. Chakrabarti, K. Dutta and S. Kundu, *Org. Biomol. Chem.*, 2020, DOI: 10.1039/D0OB01303J.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/obc

View Article Online
DOI: 10.1039/D0OB01303J

ARTICLE

Synthesis of N-Methylated Amines from Acyl Azides using Methanol

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Kaushik Chakrabarti,[a] Kuheli Dutta[a] and Sabuj Kundu[a]*

Transformation of acyl azide derivatives to N-methylamines is developed using methanol as C1 source following one-pot Curtius rearrangement and borrowing hydrogen methodology. Following this protocol various functionalised N-methylated amines were synthesized using (NNN)Ru(II) complex from carboxylic acids *via* acyl azide intermediate. Several kinetic studies and DFT calculations were carried out to support the mechanism and also to find out the role of the Ru(II) complex and base in this transformation.

Introduction

Development of different bond forming strategies which promote atom economy and utilizes renewable resources recently received considerable attention from scientific community.[1-3] Thus, for the efficient organic synthesis, development of more improved catalytic systems become highly desirable. Carboxylic acids are commonly available carbon framework from natural and synthetic resources with versatile structural diversity.[4, 5] Carboxylic acids act as an important synthons for various transformations among them decarbonylative cross-coupling is immersed as a powerful synthetic strategy for the formation of carbon-carbon and carbon-heteroatom bonds.[6-11]

Atom economic construction of C-N bond represent a crucial step for the synthesis of industrially relevant molecules.[12-14] In this context, N-methylated amines play a significant role in the synthesis of various pharmaceuticals, agrochemicals, dyes, and surfactants.[15-17] Commonly used methylating reagents like methyl iodide, diazomethane, formaldehyde, dimethyl sulphate, etc. create severe hazardous environmental impacts. Hence, development of greener and a relatively cheaper methylating reagents is highly desirable and for this purpose methanol is an attractive alternative.[18]

Recently, various fascinating protocols were developed for the sustainable transformation organic functional groups such as amine, nitro, nitrile, azide etc. to the corresponding N-methylated amines by utilizing methanol as a methylating agent.[18-34] Notably, all these functional groups are considered as surrogate of amines hence, converting them to the respective N-methylated amines is relatively straightforward. However, direct transformation of carboxylic acids to amines is challenging due to their opposite reactivity and polarity and it require several steps. In this context, development of new mythologies for the synthesis of N-methylated amines from carboxylic acid using methanol is very much fascinating. To the best of our knowledge conversion of carboxylic acids to N-methylated amines following the borrowing hydrogen principle is not explored yet (Fig. **1**).

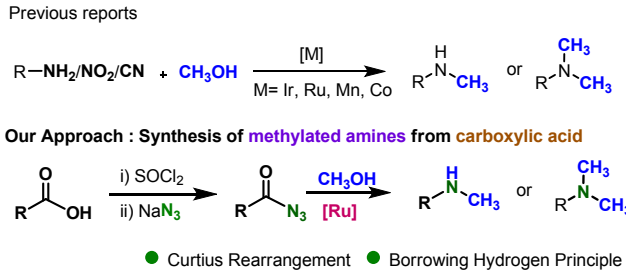


Fig. 1 Synthesis of N-methylated amines.

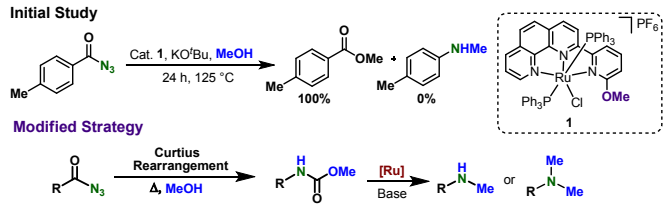
Amine group can be introduced in place of carboxylate group by following various celebrated rearrangement strategies such as Schmidt, Hofmann, Curtius and Lossen reactions.[35, 36] Additionally, direct conversion of carboxylic acids to amines by using ammonia was reported by Rauch *et al*. using CuO as catalyst at 220 °C .[37] However, all these protocols are not effective towards the synthesis of functionalised *di*- and *tri*-substituted amines. In literature, for converting carboxylate derivatives to *di* and *tri*-substituted amines, decarbonylative cross-coupling with substituted amines are known with elimination of CO_2 or CO.[38-41] However, synthesis of functionalized methylated amines by cross-coupling of carboxylate derivatives with volatile methylamines or other methylating agents are extremely rare and challenging. Acyl azides have been traditionally used as an aminating synthons following the Curtius rearrangement.[42] In this rearrangement, initially acyl azide is converted to an isocyanate molecule

[a] K. Chakrabarti, K. Dutta, Dr. S. Kundu
Department of Chemistry; Indian Institute of Technology Kanpur, Kanpur 208016, India. Email: sabuj@iitk.ac.in.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

under mild reaction conditions. Subsequently, by using appropriate nucleophiles such as water, alcohols or amines, isocyanate can be transformed to versatile range of functionalized amines, urethanes and ureas.[43, 44] Thus, for the synthesis of N-methylated amines from carboxylic acids via utilization of acyl azides as amine surrogate and methanol as C_1 source is fascinating which motivated us to explore this strategy (Fig. **1**).

Results and discussion

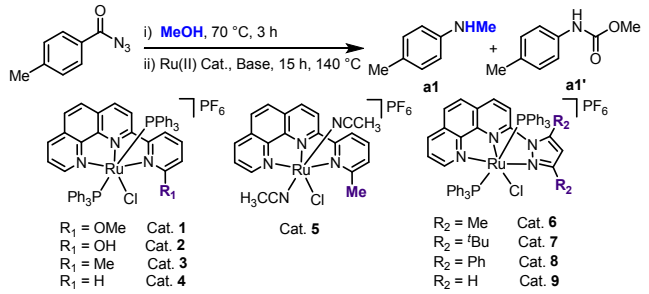
Initially, using thionyl chloride and sodium azide, 4-methylbenzoic acid was converted to 4-methylbenzoylazide[45] and it was selected as a model substrate. At first this acyl azides was heated in methanol in presence of phen-py based ruthenium complex **1**[46] and KO^{t}Bu (1 equiv.). However, in presence of strong base and nucleophilic solvent methanol, it furnished only methyl 4-methylbenzoate (Scheme **1**).



Scheme 1 Modification of the strategy.

To avoid the formation of methyl 4-methylbenzoate from 4-methylbenzoylazide, this strategy was modified. Firstly, the Curtius rearrangement was carried out by heating 4-methylbenzoylazide at 70 °C for 3 h in methanol in absence of base and Ru-catalyst, which produced methyl *p*-tolylcarbamate (**a1'**) quantitatively (Scheme **1**).

Table 1. Optimization for the transformation of 4-methylbenzoylazide to N, 4-dimethylaniline[a]

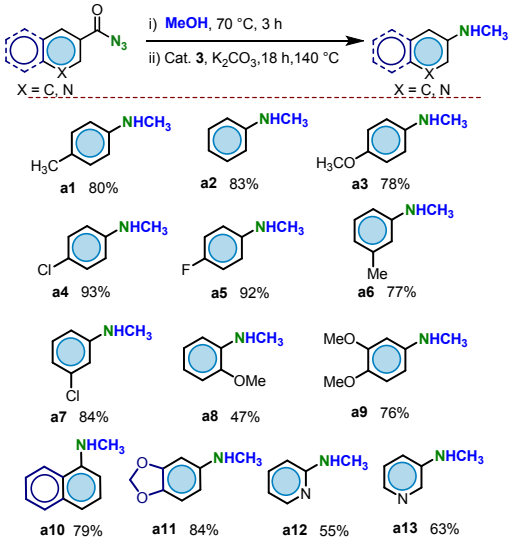


Entry	Catalyst (2 mol%)	Base (equiv.)	Yield of a1 (%)	Yield of a1' (%)
1	1	KO^{t}Bu (1.0)	46	50
2	2	KO^{t}Bu (1.0)	27	68
3	**3**	KO^{t}Bu (1.0)	52	46
4	4	KO^{t}Bu (1.0)	28	70
5	5	KO^{t}Bu (1.0)	26	73
6	6	KO^{t}Bu (1.0)	47	50
7	7	KO^{t}Bu (1.0)	38	59
8	8	KO^{t}Bu (1.0)	30	68
9	9	KO^{t}Bu (1.0)	36	61
10	$RuCl_2(PPh_3)_3$	KO^{t}Bu (1.0)	23	73
11	$RuHCl(CO)(PPh_3)_3$	KO^{t}Bu (1.0)	26	71
12	3	KOH (1.0)	68	30
13	3	NaOH (1.0)	17	78
14	3	K_2CO_3 (1.0)	82	12
15	3	Na_2CO_3 (1.0)	16	81
16	3	Cs_2CO_3 (1.0)	77	13
17	3	NaOMe (1.0)	30	66
18	3	NaO^{t}Bu (1.0)	25	74
19[b]	3	K_2CO_3 (1.0)	**88**	9
20	3	K_2CO_3 (0.5)	45	53
21	3	K_2CO_3 (0.75)	72	16
22	3	K_2CO_3 (1.25)	85	13
23	3	K_2CO_3 (1. 5)	86	8

[a]Reaction conditions: 4-methylbenzoylazide (0.372 mmol), Ru(II) Cat. (2 mol%), base (X equiv.), methanol (1.5 mL), 15 h, 140 °C (oil bath temperature). ^{1}H NMR yield (1,3,5-trimethoxybenzene was used as internal standard). [b]18 h heating.

Next, in the same pot Ru-catalyst and base were added and heated for the N-methylation reaction. Following this one-pot two step methodology, various Ru-complexes[20, 21, 47] were screened using KO^{t}Bu as a base and methanol as a methylating agent (Table **1**, entries **1-9**). Ru(II) precursors like $RuCl_2(PPh_3)_3$ and $Ru(H)(Cl)(CO)(PPh_3)_3$ were also tested, which showed less reactivity compared to the complex **3** (Table **1**, entries **10-11**). Among all the Ru(II) complexes screened in this reaction, complex **3** delivered the highest yield of N,4-dimethylaniline (Table **1**, entry **3**). After screening the catalysts, different bases were tested in presence of complex **3** in which K_2CO_3 (1.0 equiv.) presented the best yield (82%) of N, 4-dimethylaniline within 15 h (Table **1**, entries **12-23**). Finally, complex **3** with 1.0 equiv. K_2CO_3 within 18 h furnished 88% yield of the desired product (Table **1**, entry **19**).

Table 2. Scope of N-methylation of aryl acyl azides[a]



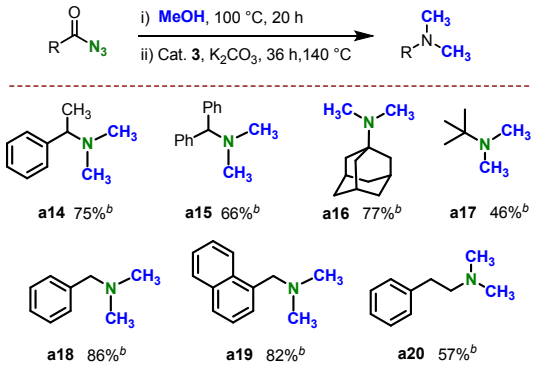
[a]Reaction conditions: azide (1 mmol), Cat. **3** (2 mol%), K_2CO_3 (1 mmol), methanol (3.0 mL), 18 h, 140 °C (oil bath temperature). Isolated yields.

DOI: 10.1039/D0OB01731

After optimization of the reaction conditions, this protocol was applied on variety of acyl azides which was synthesized from corresponding acids to evaluate the scope of this methodology. Different *ortho*, *para*- and *meta*- substituted aryl acyl azides bearing both electron donating and electron withdrawing substituents furnished the final methylated amines with good to excellent isolated yields (Table **2**, entries **a1**-**a9**). Then, the scope of the reaction was further expanded by converting naphthyl and benzodioxole acyl azides to N-methylated amines successfully (Table **2**, entries **a10**-**a11**). Interestingly, heteroatom containing 2-pyridyl and 3-pyridyl acyl azides were selectively furnished the corresponding N-methylated amines (Table **2**, entries **a12**-**a13**).

Afterward, the reactivity of benzyl and alkyl acyl azides were tested which provided the dimethylated product in presence of 3 mol% cat. **3** after 36 h (Table **3**, entries **a14**-**a17**). Notably, with these substrates 20 h heating at 100 °C was required for the Curtius rearrangement step. Additionally, in this reaction conditions, 2-phenylacetyl azide, 2-(naphthalen-1-yl)acetyl azide and 3-phenylpropanoyl azide provided the N,N-dimethylated amines in good to moderate yields (Table **3**, entries **a18**-**a20**).

Table 3. Scope of N-methylation of benzyl and alkyl acyl azides[a]



[a]Reaction conditions: acyl azide (1 mmol), Cat. **3** (3 mol%), K_2CO_3 (1 mmol), methanol (3.0 mL), 36 h, 140 °C (oil bath temperature). Isolated yields.

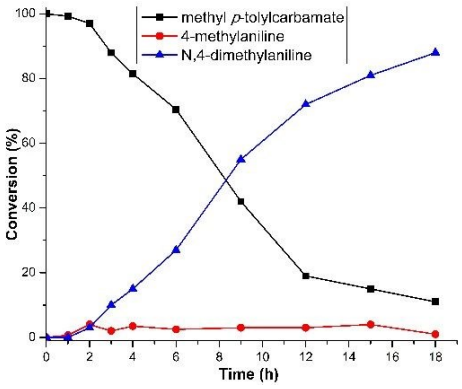


Fig. 2 Time dependent product distribution studies of methyl *p*-tolylcarbamate to N, 4-dimethylaniline.

To get insight of the reaction mechanism, time dependent product distribution was monitored during the transformation of methyl *p*-tolylcarbamate to N-methylated amines (Fig. **2**). In this reaction, concentration of methyl *p*-tolylcarbamate was decreased gradually and concentration of N, 4-dimethylaniline increased steadily. Notably, during the whole course of the reaction concentration of 4-methylaniline was remained very low (Fig. **2**). This suggested that the probably the rate of conversion of methyl *p*-tolylcarbamate to 4-methylaniline was relatively slower than the conversion of 4-methylaniline to N, 4-dimethylaniline.

As time course analysis of the reaction suggested that the conversion of methyl *p*-tolylcarbamate to 4-methylaniline was slower than the methylation of 4-methylaniline; thus, further mechanistic studies were carried to investigate the conversion of methyl *p*-tolylcarbamate to 4-methylaniline (Fig. **3A**). For this purpose, two parallel control experiments were conducted for the conversion of methyl *p*-tolylcarbamate to 4-methylaniline, one in presence of only K_2CO_3 and other with catalyst **3** and K_2CO_3. Notably, rate of conversion of methyl *p*-tolylcarbamate was similar under both these conditions. This experiment suggested that the Ru complex had no role in the transformation of methyl *p*-tolylcarbamate to 4-methylaniline (Fig. **3A**).

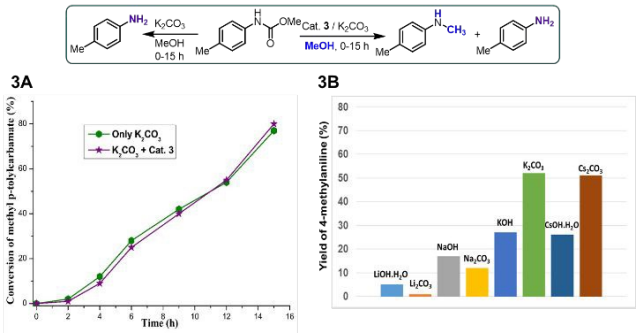
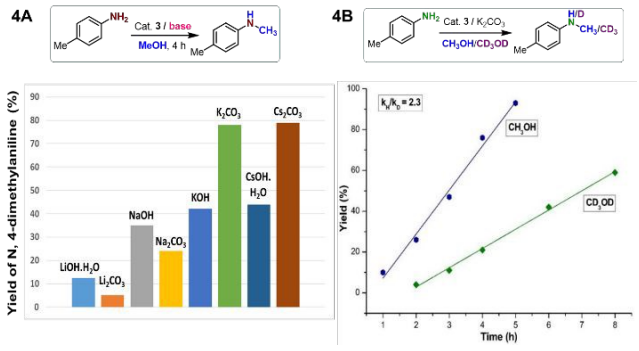


Fig. 3 3A) Investigation of the role of K_2CO_3 and Cat. **3** in the transformation of carbamate ester to 4-methylaniline; 3B) Effect of counter cation of bases in the transformation of carbamate ester to 4-methylaniline without Cat. **3**.

After that, several experiments were conducted to understand the effect of hydroxide and carbonate bases for the conversion of methyl *p*-tolylcarbamate to 4-methylaniline (Fig. **3B**). It was found that for lithium and sodium counter cation containing hydroxide bases exhibited better performance than their corresponding carbonate bases. Whereas, with the bigger potassium and caesium counter cation, reverse trend was observed (Fig. **3B**). The reactivity difference of carbonate and hydroxide bases in this transformation is not clear to us at this moment.

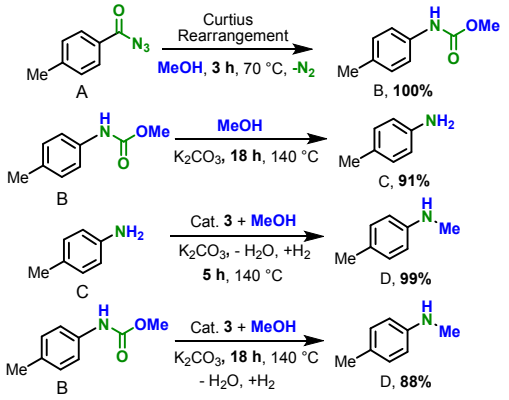


View Article Online
DOI: 10.1039/D0OB01303J

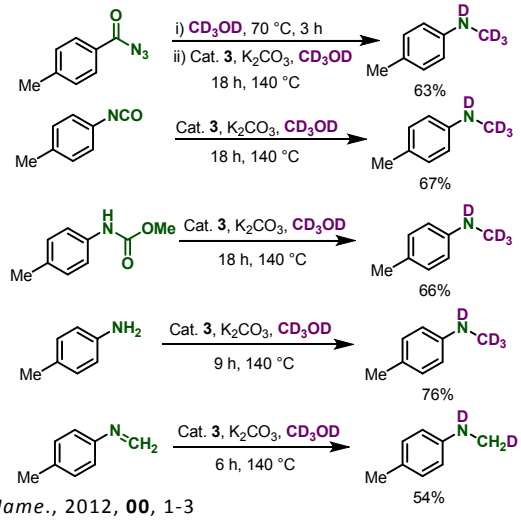
Fig. 4 4A) Effect of counter cation of bases in N-methylation of 4-methylaniline; 4B) KIE in N-methylation of 4-methylaniline catalysed by complex **3**.

Base played a key role in metal catalyzed N-methylation reactions using methanol.[20, 21, 48] Therefore, the effect of different carbonate and hydroxide bases were investigated in the N-methylation reaction catalyzed by complex **3** (Fig. **4A**). Notably, with these bases, similar trend was observed as mentioned with transformation of carbamate ester (Fig. **3B**) and among the carbonate and hydroxide bases reactivity increased in the order of size of the counter cation Li<Na<K~Cs (Fig. **4A**). This study suggested that both in the transformation of carbamate ester to amine and in N-methylation of amine step, counter cation of bases have crucial role. Methanol dehydrogenation is one of the vital step in N-methylation reaction. To understand the importance of the methanol dehydrogenation step, KIE study was performed for the N-methylation of 4-methylaniline using CH_3OH and CD_3OD in presence of Cat. **3** which revealed that k_H/k_D for this reaction is **2.3** (Fig. **4B**). These results indicated that the C-H bond breaking of methanol is kinetically important in this transformation.

To understand this multistep reaction more clearly, each crucial steps of the transformation of acyl azide to N-methylamines was studied more carefully (Scheme **2**). These control experiments as well as time frame analysis of the reactions clearly suggested that conversion of methyl-*p*-tolylcarbamate (**B**) to 4-methylaniline (**C**) was much slower than the Curtius rearrangement and methylation steps (Scheme **2**).



Scheme 2. Control experiments.



Scheme 3. Experiments with methanol-d_4.

For further illustration about the mechanism of this study, kinetic experiments with methanol-d_4 were performed (Scheme **3**). 4-Methylbenzoylazide was converted to D_4-N, 4-dimethylaniline (63%) under optimized conditions (Scheme **3**). The other intermediates such as 4-methylphenylisocyanate, methyl-*p*-tolylcarbamate, 4-methylaniline and 4-methyl-N-methyleneaniline were also furnished the corresponding deuterium incorporated methylamines by using methanol-d_4 (Scheme **3**). These experiments idicated potential involvement of these intermediates in this transformation and methanol acted as the C1 source as well as the hydrogen donor.

To collect more information, we carried out DFT calculation for the N-methylation of 4-methylaniline catalyzed by the complex **3** (Fig. **5**). This process was divided into three steps: (a) dehydrogenation of methanol, (b) imine formation and (c) hydrogenation of the C=N bond. First, base assisted activation of complex **3** in presence of methanol generated the intermediate **I1**. Next, dissociation of PPh_3 from **I1** produced the intermediate **I2**. The intermediate **I2** followed a concerted four-membered cyclic transition state (β-hydrogen elimination step) **TS1** (21.61 kcal/mol) to dehydrogenate methanol and formed Ru-H intermediate **I3** (Fig. **5**). The formaldehyde molecule generated in this dehydrogenation step subsequently reacted with the amine to give the corresponding imine molecule. Next, hydrogenation of imine occurred by Ru-H through another transition state **TS2** (27.81 kcal/mol) with the activation barrier of 3.32 kcal/mol (Figure **5**). Finally, from the intermediate **I5**, **I2** and N-methylamine product were formed through methanolysis. From the DFT calculation, it was observed that N-methylene imine hydrogenation step (**TS2**) required over all higher energy barrier than the β-hydrogen elimination step (**TS1**).

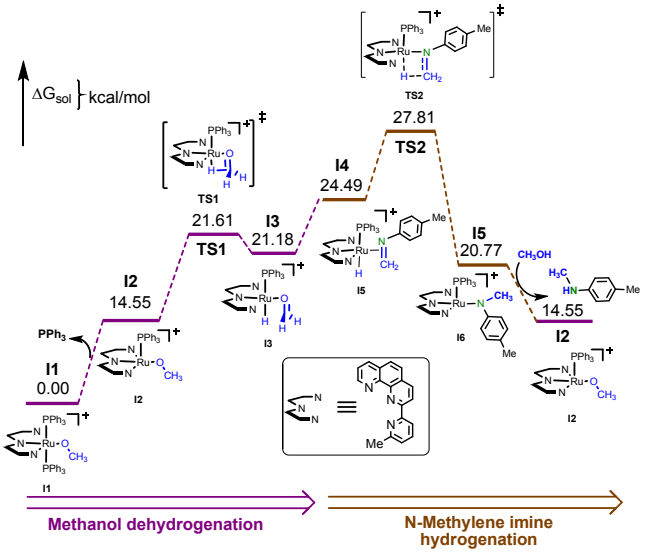
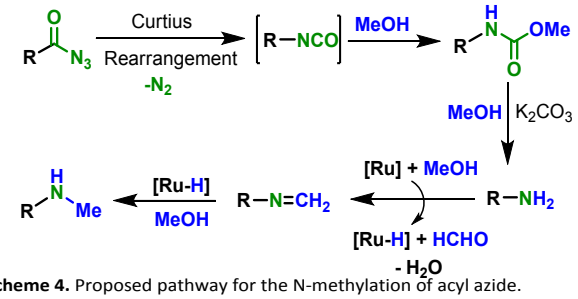


Fig. 5 Calculated Gibbs free energies (kcal/mol) for the formation of N, 4-dimethylaniline from 4-methylaniline using methanol (Hybrid functional, M06-2X was used with the LANL2DZ basis set for Ru and 6-31G** basis set for *non*-metal elements).

Based on the several control experiments and kinetic studies, the schematic pathway for the formation of N-methylated amine from acyl azide using methanol was proposed (Scheme **4**). Initially, following the Curtius rearrangement, acyl azide was converted to carbamate ester. Next, base mediated transformation generated the amine derivative from carbamate ester (Scheme **4**). Subsequently, methanol dehydrogenation by the catalyst **3** would generated formaldehyde and the [Ru-H] species. This formaldehyde reacted with the amine to give the corresponding imine (Scheme **4**). Finally, the imine was hydrogenated by the [Ru-H] to form the N-methylated amine product (Scheme **4**).



Scheme 4. Proposed pathway for the N-methylation of acyl azide.

Conclusions

In conclusion, transformation of various acyl azides to the corresponding N-methyl amines was developed by combining one-pot Curtius rearrangement and BH methodology. Interestingly, following this protocol varieties of aryl, benzyl and aliphatic carboxylic acids were successfully converted to methylated amines via acyl azide intermediate catalyzed by a simple (NNN)Ru(II) complex. Control experiments suggested that the Ru(II) complex had no role in transformation of carbamate ester to amine and this step was slower than the N-methylation step. Additionally, the counter cation of base has vital role in both transformation of carbamate ester to amine and in N-methylation of amine steps. Kinetic isotope effect study indicated that methanol dehydrogenation is one of the kinetically important step. Finally, DFT calculation was carried out for further understanding of this transformation. To the best of our knowledge, for the first time N-methylated amines were synthesized from carboxylic acids via acyl azide intermediates instead of common amine synthons.

Experimental

General Procedure for N-Methylation of Acyl Azides

A) Procedure for Aryl Acyl Azides

In a screw cap tube, acyl azide (1.0 mmol) and methanol (1.5 mL) were taken under argon atmosphere and heated at 70 °C in oil bath for 3 h. Then, it was cooled to room temperature and catalyst **3** (2 mol%), K_2CO_3 (1.0 mmol), methanol (1.5 mL) were added under inert condition and heated for specified time at 140 °C (oil bath temperature). After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated to dryness and subjected to ^{1}H NMR analysis for the calculation of the yield (1,3,5-trimethoxybenzene was used as internal standard). Finally, the pure methylated amines were isolated by column chromatography using silica gel and hexane-ethyl acetate or ethyl acetate-methanol as eluent.

View Article Online DOI: 10.1039/D0OB01303J

B) Procedure for Benzyl and Alkyl Acyl Azides

In a screw cap tube, acyl azide (1.0 mmol) and methanol (1.5 mL) were taken under argon atmosphere and heated at 100 °C in oil bath for 20 h. Then, it was cooled to room temperature and catalyst **3** (3 mol%), K_2CO_3 (1.0 mmol), methanol (1.5 mL) were added under inert condition and heated for specified time at 140 °C (oil bath temperature). After that, the reaction mixture was allowed to cool down at room temperature. The solvent was evaporated to dryness and subjected to ^{1}H NMR analysis for the calculation of the yield (1,3,5-trimethoxybenzene was used as internal standard). Finally, the pure methylated amines were isolated by column chromatography using silica gel and hexane-ethyl acetate or ethyl acetate-methanol as eluent.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the Department of Science and Technology, International Cooperation (INT/RUS/RFBR/P-326), India and the Science and Engineering Research Board (CRG/2018/000214), India for financial support. KC thanks UGC-India for fellowship. We also thank HPC IIT Kanpur for computational facilities.

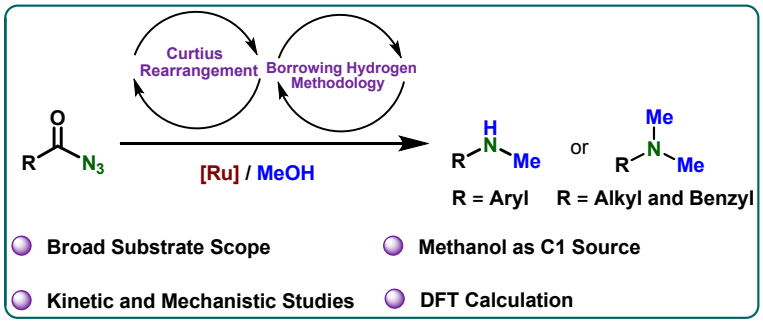
Notes and references

1. D. Seebach, *Angew. Chem. Int. Ed.*, 1990, **29**, 1320-1367.
2. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, England, 1998.
3. G. E. Dobereiner and R. H. Crabtree, *Chem. Rev.*, 2010, **110**, 681-703.
4. M. B. Smith, *Compendium of Organic Synthetic Methods*, John Wiley & Sons, Germany, 2014.
5. N. M. Rice, *Hydrometallurgy*, 1978, **3**, 111-133.
6. N. Rodríguez and L. J. Goossen, *Chem. Soc. Rev.*, 2011, **40**, 5030-5048.
7. P. Liu, G. Zhang and P. Sun, *Org. Biomol. Chem.*, 2016, **14**, 10763-10777.
8. T. Zhang, N.-X. Wang and Y. Xing, *J. Org. Chem.*, 2018, **83**, 7559-7565.
9. L. J. Gooßen, N. Rodríguez and K. Gooßen, *Angew. Chem. Int. Ed.*, 2008, **47**, 3100-3120.

10. M. Font, J. M. Quibell, G. J. P. Perry and I. Larrosa, *Chem. Commun.*, 2017, **53**, 5584-5597.
11. J. D. Weaver, A. Recio, A. J. Grenning and J. A. Tunge, *Chem. Rev.*, 2011, **111**, 1846-1913.
12. S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641.
13. R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit and N. Tongpenyai, *J. Chem. Soc., Chem. Commun.*, 1981, 611-612.
14. J. Bariwal and E. Van der Eycken, *Chem. Soc. Rev.*, 2013, **42**, 9283-9303.
15. A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410-1459.
16. H. C. Hailes, *Appl. Organomet. Chem.*, 2001, **15**, 315-315.
17. J. Leonard, A. J. Blacker, S. P. Marsden, M. F. Jones, K. R. Mulholland and R. Newton, *Org. Process Res. Dev.*, 2015, **19**, 1400-1410.
18. Y. Chen, *Chem. Eur. J.*, 2019, **25**, 3405-3439.
19. K. Natte, H. Neumann, M. Beller and R. V. Jagadeesh, *Angew. Chem. Int. Ed.*, 2017, **56**, 6384-6394.
20. K. Chakrabarti, A. Mishra, D. Panja, B. Paul and S. Kundu, *Green Chem.*, 2018, **20**, 3339-3345.
21. B. Paul, S. Shee, D. Panja, K. Chakrabarti and S. Kundu, *ACS Catal.*, 2018, **8**, 2890-2896.
22. J. Campos, L. S. Sharninghausen, M. G. Manas and R. H. Crabtree, *Inorg. Chem.*, 2015, **54**, 5079-5084.
23. T. T. Dang, B. Ramalingam and A. M. Seayad, *ACS Catal.*, 2015, **5**, 4082-4088.
24. Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao and Z. Liu, *Adv. Synth. Catal.*, 2017, **359**, 4278-4283.
25. K. Polidano, B. D. W. Allen, J. M. J. Williams and L. C. Morrill, *ACS Catal.*, 2018, **8**, 6440-6445.
26. A. Del Zotto, W. Baratta, M. Sandri, G. Verardo and P. Rigo, *Eur. J. Inorg. Chem.*, 2004, **2004**, 524-529.
27. O. Ogata, H. Nara, M. Fujiwhara, K. Matsumura and Y. Kayaki, *Org. Lett.*, 2018, **20**, 3866-3870.
28. S.-I. Murahashi, K. Kondo and T. Hakata, *Tetrahedron Lett.*, 1982, **23**, 229-232.
29. B. C. Roy, S. Debnath, K. Chakrabarti, B. Paul, M. Maji and S. Kundu, *Org. Chem. Front.*, 2018, **5**, 1008-1018.
30. B. Paul, S. Shee, K. Chakrabarti and S. Kundu, *ChemSusChem*, 2017, **10**, 2370-2374.
31. G. Choi and S. H. Hong, *Angew. Chem. Int. Ed.*, 2018, **57**, 6166-6170.
32. K. Natte, H. Neumann, R. V. Jagadeesh and M. Beller, *Nat. Commun.*, 2017, **8**, 1344.
33. V. N. Tsarev, Y. Morioka, J. Caner, Q. Wang, R. Ushimaru, A. Kudo, H. Naka and S. Saito, *Org. Lett.*, 2015, **17**, 2530-2533.
34. M. Maji, K. Chakrabarti, B. Paul, B. C. Roy and S. Kundu, *Adv. Synth. Catal.*, 2018, **360**, 722-729.
35. S. Lang and J. A. Murphy, *Chem. Soc. Rev.*, 2006, **35**, 146-156.
36. E. C. Franklin, *Chem. Rev.*, 1934, **14**, 219-250.
37. G. G. Arzoumanidis and F. C. Rauch, *J. Org. Chem.*, 1981, **46**, 3930-3932.
38. S. Arshadi, S. Ebrahimiasl, A. Hosseinian, A. Monfared and E. Vessally, *RSC Adv.*, 2019, **9**, 8964-8976.
39. C. A. Malapit, N. Ichiishi and M. S. Sanford, *Org. Lett.*, 2017, **19**, 4142-4145.
40. L. Guo and M. Rueping, *Acc. Chem. Res.*, 2018, **51**, 1185-1195.
41. Y. Jin and H. Fu, *Asian J. Org. Chem.*, 2017, **6**, 368-385.
42. T. L. Capson and C. D. Poulter, *Tetrahedron Lett.*, 1984, **25**, 3515-3518.
43. G. B. Bachman and J. E. Goldmacher, *J. Org. Chem.*, 1964, **29**, 2576-2579.
44. A. K. Ghosh, A. Sarkar and M. Brindisi, *Org. Biomol. Chem.*, 2018, **16**, 2006-2027.
45. M. Yoshida, K. Hishida, M. Minabe and K. Suzuki, *J. Org. Chem.*, 1980, **45**, 1783-1785.
46. B. Paul, K. Chakrabarti and S. Kundu, *Dalton Trans.*, 2016, **45**, 11162-11171.
47. K. Chakrabarti, B. Paul, M. Maji, B. C. Roy, S. Shee and S. Kundu, *Org. Biomol. Chem.*, 2016, **14**, 10988-10997.
48. A. Bagno, G. Scorrano and F. Terrier, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1017-1027.

View Article Online
DOI: 10.1039/D0OB01303J

Table of Content



Ru(II) complex catalysed direct transformation of acyl azides to N-methylamines was developed for the first time using methanol *via* one pot Curtius rearrangement and Borrowing Hydrogen methodology.