



# A versatile way for the synthesis of monomethylamines by reduction of *N*-substituted carbonylimidazoles with the NaBH<sub>4</sub>/I<sub>2</sub> system

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## Full Research Paper

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## Abstract

An economical and versatile protocol for the one-pot synthesis of monomethylamines by reduction of *N*-substituted carbonylimidazoles with NaBH<sub>4</sub>/I<sub>2</sub> in THF at reflux temperature is described. This method used no special catalyst and various monomethylamines can be easily obtained in moderate to good yields from a wide range of raw materials including amines (primary amines and secondary amines), carboxylic acids and isocyanates. Besides, an interesting reduction selectivity was observed. Exploration of the reaction process shows that it undergoes a two-step pathway via a formamide intermediate and the reduction of the formamide intermediate to monomethylamine as the rate-determining step. This work can contribute significantly expanding the applications of *N*-substituted carbonylimidazoles.

## Introduction

*N*-Methylamines are widely found in natural products, fine chemicals, agrochemicals, pharmaceuticals and dyes [1-4]. Traditional methods for the preparation of *N*-methylamines involve the direct methylation of amines by using methyl halides [5-7], dimethyl sulfate [8], diazomethane [9], methyl triflate [10,11] or dimethyl carbonate [12-15] as the methylation reagents and the reductive amination reactions by using formaldehyde or paraformaldehyde as the “indirect” alkylation reagents [16-19]. Recently, a variety of promising methylating agents or C1 sources such as formic acid [20,21], methanol [22-

31] and carbon dioxide (CO<sub>2</sub>) [32-39] have been developed for the *N*-methylation of amines. However, these *N*-alkylation methods often require the employment of expensive catalysts, and the *N*-alkylation of primary amines generally does not stop with monomethylation as expected and inevitably provides a mixture of multiple methylated products because of the competing overalkylation reactions [14,16-43].

In order to obtain pure monomethylation product, the conventional method is to introduce alkyl formate, formacyl, methy-

lene or their equivalents to amines, followed by reduction to give monomethylamines [44–51]. Protection/methylation/deprotection strategies have also been developed for the preparation of monomethylation objects, which are particularly suitable for peptide chemistry since protecting groups are often required in peptide synthesis [52,53]. These multistep reaction methods are conducive to avoid overmethylation products.

Although procedures for the synthesis of monomethylamines have been developed over the past years, the starting materials are mainly restricted regarding amines, in addition, expensive reagents or catalysts are usually required, which limit their applications to some extent. *N*-Substituted carbonylimidazoles, as important members of the carbonylimidazole family [54,55], are highly attractive intermediates with suitable stability for isolation or storage, and various good methods for their preparation have been developed by employing different starting materials such as amines [56–58], isocyanates [59–61] and carboxylic acids [62]. Since the carbonyl carbon atom of the carbonylimidazole moiety is easily attacked by a nucleophile the imidazole group readily dissociates. The *N*-substituted carbonylimidazoles have favorable reactivity and can be widely used in the synthesis of various valuable products such as ureas [63–70], carbamates [66,71–74], thiocarbamates [66], and cyanoforamides [75]. However, all of these works are primarily focused on the substitution reaction of *N*-substituted carbonylimidazoles. In our previous work, we conveniently prepared formamides by reducing *N*-substituted carbonylimidazoles with NaBH<sub>4</sub> [62] (Scheme 1). The reaction mechanism shows that the H<sup>−</sup> ion acted as a nucleophile to attack the carbonyl carbon to cause the imidazolium ion to leave without reducing the carbonyl group. Although this work expands the application of *N*-substituted carbonylimidazoles, the reaction can still be regarded as a substitution reaction, which is attributed to the weak reducibility of NaBH<sub>4</sub>.

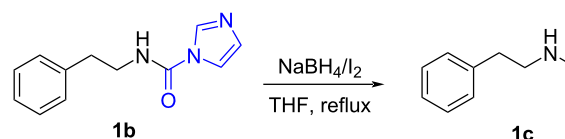
In this work, our goal is to reduce the carbonyl group in *N*-substituted carbonylimidazoles. The inexpensive NaBH<sub>4</sub>/I<sub>2</sub> system has great attraction because it is more reductive due to

the generation of highly reactive BH<sub>3</sub>–THF by adding iodine to NaBH<sub>4</sub> in THF [76–78] and the reaction conditions are not significantly changed compared to our previous preparation of formamide. With this reduction system, we achieved a one-step conversion from *N*-substituted carbonylimidazoles to methylamines. This interesting work will help to synthesize pure monomethylamines from a wide range of raw materials including amines, carboxylic acids and isocyanates under mild and safe reaction conditions.

## Results and Discussion

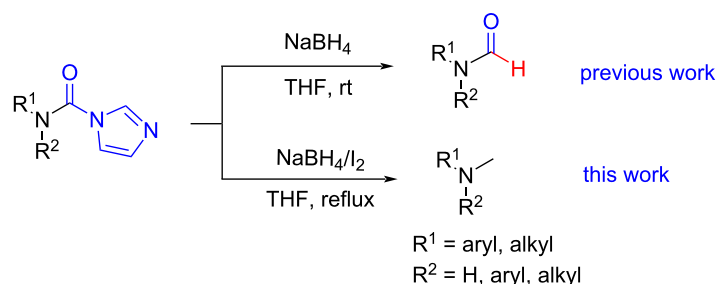
Initially, *N*-phenethyl-1*H*-imidazole-1-carboxamide (**1b**) was chosen as a model substrate to react with 3.0 equiv of NaBH<sub>4</sub> and 1.0 equiv of I<sub>2</sub> in THF at reflux temperature, as expected, the carbonylimidazole moiety was successfully converted into a methyl group and the target monomethylamine (**1c**) was obtained in 70% yield after 6 h (Table 1, entry 1). When the amount of NaBH<sub>4</sub> was increased from 3.0 equiv to 4.0 equiv and 5.0 equiv, the reaction time was shortened from 6 h to 4 h

**Table 1:** Optimization of the reaction conditions.<sup>a</sup>



Entry	NaBH <sub>4</sub> (equiv)	I <sub>2</sub> (equiv)	Time (h) <sup>b</sup>	Yield (%) <sup>c</sup>
1	3.0	1.0	6	70
2	4.0	1.0	4	72
3	5.0	1.0	1	74
4	6.0	1.0	0.9	75
5	5.0	0.5	6	trace <sup>d</sup>
6	5.0	1.5	1	73

<sup>a</sup>The reactions were carried out with **1b** (1.0 equiv, 2 mmol), NaBH<sub>4</sub>, I<sub>2</sub>, THF (25 mL) under reflux temperature. <sup>b</sup>The reaction was monitored by TLC. <sup>c</sup>Isolated yield was based on **1b**. <sup>d</sup>The isolated yield of **1c** and *N*-(phenethyl)formamide was 1% (trace) and 62%, respectively.



**Scheme 1:** The synthesis of formamides and monomethylamines.

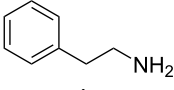
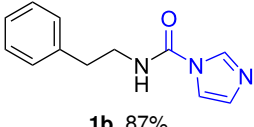
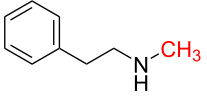
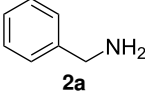
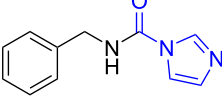
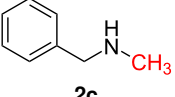
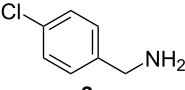
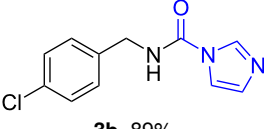
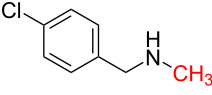
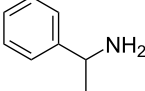
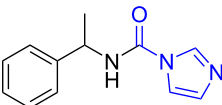
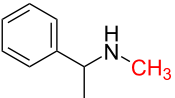
and 1 h, respectively. When further increasing the amount of NaBH<sub>4</sub> to 6.0 equiv, only a slight decrease of the reaction time was observed. In addition, the yield of **1c** showed few changes with the increase of the amount of NaBH<sub>4</sub> from 3.0 equiv to 6.0 equiv. Obviously, 5.0 equiv of NaBH<sub>4</sub> was optimal to perform the reaction. Since I<sub>2</sub> was used to improve the reducibility of NaBH<sub>4</sub>, we next investigated the effect of the amount of I<sub>2</sub> on the reaction. The use of 0.5 equiv of I<sub>2</sub> in the presence of 5.0 equiv of NaBH<sub>4</sub> afforded after 6 h only traces of methylamine but 62% of *N*-(phenethyl)formamide (Table 1, entry 5). Increasing the amount of I<sub>2</sub> from 1.0 equiv to 1.5 equiv (Table 1, entry 6) did not significantly accelerated the reaction. All the above described results might indicate that an assembly of 1.0 equiv of I<sub>2</sub> and 5.0 equiv of NaBH<sub>4</sub> was sufficient to complete the reaction in one hour.

With the optimized reaction conditions in hand, we investigated the synthesis of other *N*-methylamines from various *N*-substituted carbonylimidazoles (Table 2). As a proof of the versatility and applicability of the proposed method, *N*-substituted carbonylimidazoles were prepared from amines (**1b–14b**)

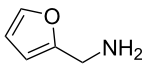
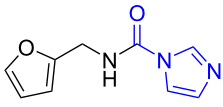
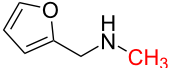
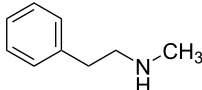
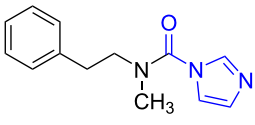
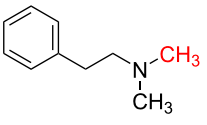
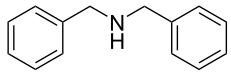
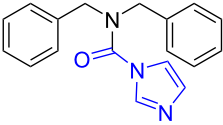
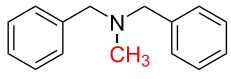
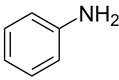
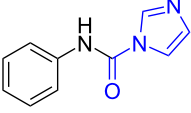
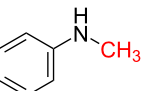
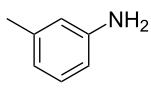
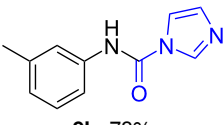
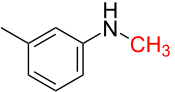
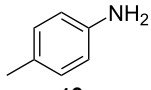
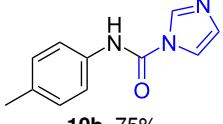
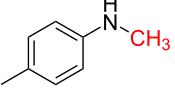
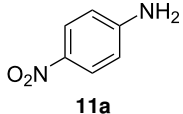
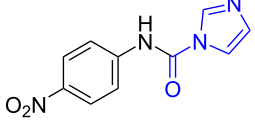
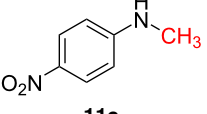
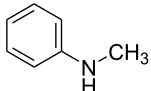
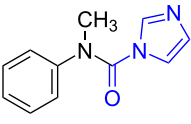

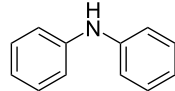
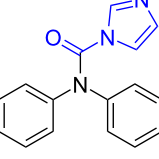
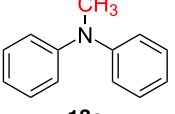
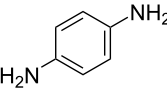
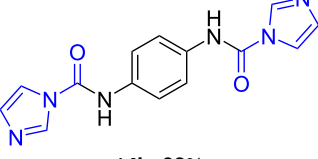
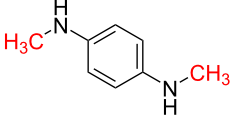
[56–58,62,64], isocyanates (**15b–17b**) [59–61], and carboxylic acids (**18b–20b**) [62], respectively (for detailed experimental procedures, see Supporting Information File 1). All types of these *N*-substituted carbonylimidazoles reacted smoothly with NaBH<sub>4</sub>/I<sub>2</sub> to provide the corresponding *N*-methylamines in satisfactory yields.

The impact of different substituents on the reaction were well investigated. As shown in Table 2, the alkyl substituents (R) in the *N*-alkyl carbonylimidazoles had a weak influence on the reaction (Table 2, entries 1–7, 18, and 19). Whether the *N*-alkyl carbonylimidazoles bear one substituent (e.g., **1b–5b**, **15b**, **18b**, **19b**) or two substituents (e.g., **6b** and **7b**), the reaction proceeded well, affording the desired product in 60–83% yields. Note that the reaction time of **7b** (2 h) was obviously longer than that of **1b–6b** (1 h), **18b** (1 h) and **19b** (1 h), possibly because the steric hindrance of the two benzyl groups on **7b** slowed the reaction. Encouraged by the above mentioned results, we then tested *N*-aryl carbonylimidazoles in the reaction. To our delight, *N*-aryl carbonylimidazoles with either electron-donating (**9b** and **10b**) or electron-withdrawing groups

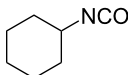
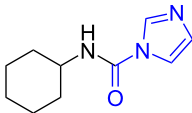
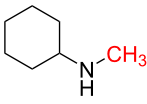
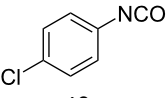
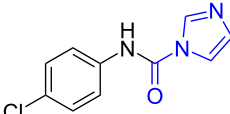
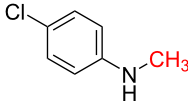
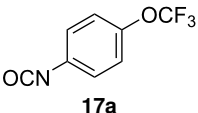
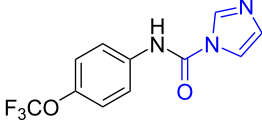
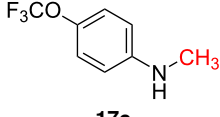
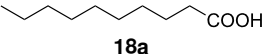
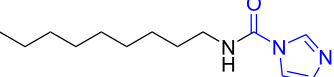
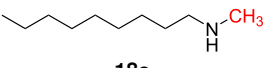
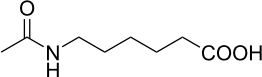
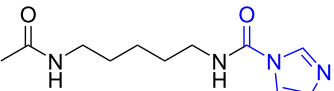
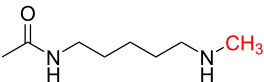
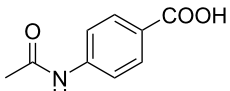
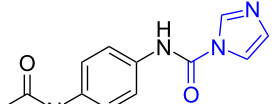
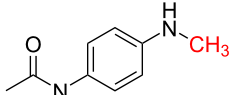
**Table 2:** Synthesis of monomethylamines from amines, carboxylic acids and isocyanates.<sup>a</sup>

Entry	Substrate	Carbamoylimidazole	Time (h) <sup>b</sup>	Product	Yield (%) <sup>c</sup>
	$  \begin{array}{c}  \text{R}^1\text{R}^2\text{NH} \\  \text{R}^1\text{NCO} \\  \text{R}^1\text{COOH} \\  \mathbf{a} \\  \text{R}^1 = \text{aryl, alkyl} \\  \text{R}^2 = \text{H, aryl, alkyl}  \end{array}  \xrightarrow{[56-62]}  \begin{array}{c}  \text{R}^1 \\    \\  \text{N} \\    \\  \text{C=O} \\    \\  \text{Imidazole} \\  \mathbf{b}  \end{array}  \xrightarrow[\text{THF, reflux}]{\text{NaBH}_4/\text{I}_2}  \begin{array}{c}  \text{R}^1 \\    \\  \text{N-CH}_3 \\    \\  \text{R}^2 \\  \mathbf{c}  \end{array}  $				
1			1		74
2			1		67
3			1		67
4			1		65

**Table 2:** Synthesis of monomethylamines from amines, carboxylic acids and isocyanates.<sup>a</sup> (continued)

5	 <b>5a</b>	 <b>5b, 87%</b>	1	 <b>5c</b>	70
6	 <b>1c</b>	 <b>6b, 88%</b>	1	 <b>6c</b>	83
7	 <b>7a</b>	 <b>7b, 85%</b>	2	 <b>7c</b>	60
8	 <b>8a</b>	 <b>8b, 70%</b>	4	 <b>8c</b>	72
9	 <b>9a</b>	 <b>9b, 78%</b>	4	 <b>9c</b>	85
10	 <b>10a</b>	 <b>10b, 75%</b>	4	 <b>10c</b>	80
11	 <b>11a</b>	 <b>11b, 55%</b>	4	 <b>11c</b>	70
12	 <b>8c</b>	 <b>12b, 89%</b>	4	 <b>12c</b>	71
13	 <b>13a</b>	 <b>13b, 57%</b>	6	 <b>13c</b>	67
14 <sup>d</sup>	 <b>14a</b>	 <b>14b, 83%</b>	10	 <b>14c</b>	70

**Table 2:** Synthesis of monomethylamines from amines, carboxylic acids and isocyanates.<sup>a</sup> (continued)

15			1		74
16			4		74
17			4		72
18			1		77
19			1		65
20			4		68

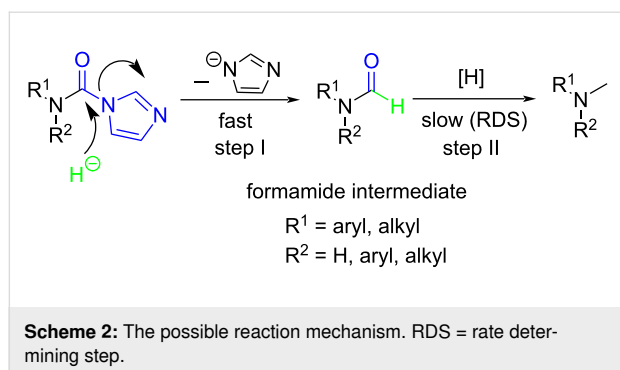
<sup>a</sup>The reactions were carried out with carbonylimidazole (1.0 equiv, 2 mmol), NaBH<sub>4</sub> (5.0 equiv, 10.0 mmol), I<sub>2</sub> (1.0 equiv, 2 mmol) and THF (25 mL) under reflux. <sup>b</sup>Monitored by TLC. <sup>c</sup>Isolated yield was based on carbonylimidazole. <sup>d</sup>10.0 equiv of NaBH<sub>4</sub> and 2 equiv of I<sub>2</sub> was used.

(**11b**, **16b** and **17b**) on the aryl rings were all transformed, affording the expected products in 70–85% yields. *N*-Aryl carbonylimidazoles with two substituents, such as **12b** (R<sup>1</sup> = methyl, R<sup>2</sup> = phenyl) and **13b** (R<sup>1</sup> = phenyl, R<sup>2</sup> = phenyl), were also amenable to this protocol, giving the corresponding products **12c** and **13c** in 71% and 67% yield, respectively. Furthermore, by using 2.0 equiv of I<sub>2</sub> and 10.0 equiv of NaBH<sub>4</sub>, the substrate **14b** with two *N*-substituted carbonylimidazole moieties could also undergo this reaction and provided the desired product **14c** in moderate yield (70%). Additionally, our protocol was applicable to prepare *N,N*-dimethylamines by step-by-step methylation. Employing the monomethylated products **1c** and **8c**, *N,N*-dimethylamine **6c** and **12c** can be obtained, respectively, via repeating our synthesis procedure.

In order to understand the reduction selectivity of the method, the substrates bearing acetamide groups (**19b** and **20b**) were

tested in the reaction. To our pleasure, both aliphatic and aromatic amides reacted smoothly and provided the expected products in satisfactory yields, with the acetyl groups being unaffected. This suggested that the *N*-acetyl groups in *N*-substituted carbonylimidazoles were well tolerated during the reduction, and our method showed interesting reduction selectivity.

To gain some preliminary insight into the reaction process, two representative intermediates for the synthesis of aliphatic methylamine **1c** and aromatic methylamine **8c** had been isolated and identified as corresponding formamides (see Supporting Information File 1). Furthermore, by following the reaction with TLC, we found that the reaction time (hours) from the formamide intermediate to the corresponding methylamine product was much longer than the time (minutes) from the *N*-substituted carbonylimidazole to the formamide. This indicated that the reaction might undergo a two-step pathway via the formamide intermediate (Scheme 2).



In the first step (step I), *N*-substituted carbonylimidazole was rapidly converted into the formamide intermediate by the attack of a hydrogen anion as we had reported before [62]. Subsequently, the carbonyl group of the formamide intermediate was reduced to furnish the desired *N*-methylamine in the second step (step II) [79–81]. Step II proceeded much slower than step I, so it could be treated as rate-determining step (RDS). The required longer reaction time for *N*-aryl carbonylimidazoles (over 4 h) than that for *N*-alkyl carbonylimidazoles (about 1 h) can be well explained by the two-step mechanism. In step I, the *N*-aryl carbonylimidazoles might react much faster than *N*-alkyl carbonylimidazoles, because the stronger conjugation system of the resulting *N*-aromatic formamides made them more stable and easier to generate. However, these more stable *N*-aryl formamide intermediates were less reactive and directly slowed the reaction in step II, which resulted in a longer reaction time of the *N*-aryl carbonylimidazoles in the whole reaction.

The substrate **13b**, bearing two phenyl rings, which not only had a large steric hindrance like **7b**, but also had a strong conjugation system, took much longer time (6 h) to complete the reaction.

As shown by the reaction mechanism, the methyl group was converted from the carbonylimidazole moiety by full reduction and therefore no competing overalkylation reactions occurred.

Although the *N*-methylamine could be prepared from carboxylic acid or amine by our method, the methyl source was remarkably different (Scheme S1, Supporting Information File 1). For amines, the carbon source of the methyl group is from the carbonyl group of the carbonylimidazole; while for carboxylic acids, the carbon source is the carboxyl group. When carboxylic acids were used, the carboxyl moiety was first converted to an isocyanate via Curtius rearrangement [82–85], then reacted with imidazole to form the carbonylimidazole, and eventually reduced to the methyl moiety. In the whole process, no extra carbon was introduced.

## Conclusion

In conclusion, we have developed an economical and versatile protocol for the one-pot synthesis of monomethylamines by reduction of *N*-substituted carbonylimidazoles with the NaBH<sub>4</sub>/I<sub>2</sub> system. This work further extends the application of *N*-substituted carbonylimidazoles. By employing inexpensive and commercially available reagents, a variety of aliphatic and aromatic monomethylamines were obtained in moderate to good yields from a broad substrate scope including not only amines (both primary amines and secondary amines) but also carboxylic acids or isocyanates. The acetamide group was well tolerated in our reduction, implying our method showed interesting reduction selectivity.

## Supporting Information

### Supporting Information File 1

Experimental part.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-18-104-S1.pdf>]

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## References

- Paul, B.; Shee, S.; Chakrabarti, K.; Kundu, S. *ChemSusChem* **2017**, *10*, 2370–2374. doi:10.1002/cssc.201700503
- Davis, D. A.; Hamilton, A.; Yang, J.; Cremer, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martínez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. *Nature* **2009**, *459*, 68–72. doi:10.1038/nature07970
- Seayad, A.; Ahmed, M.; Klein, H.; Jackstell, R.; Gross, T.; Beller, M. *Science* **2002**, *297*, 1676–1678. doi:10.1126/science.1074801
- Salvatore, R. N.; Yoon, C. H.; Jung, K. W. *Tetrahedron* **2001**, *57*, 7785–7811. doi:10.1016/s0040-4020(01)00722-0
- Olsen, R. K. *J. Org. Chem.* **1970**, *35*, 1912–1915. doi:10.1021/jo00831a042
- Schreiber, S. L.; Anthony, N. J.; Dorsey, B. D.; Hawley, R. C. *Tetrahedron Lett.* **1988**, *29*, 6577–6580. doi:10.1016/s0040-4039(00)82401-6
- Vedejs, E.; Kongkittigam, C. *J. Org. Chem.* **2001**, *66*, 7355–7364. doi:10.1021/jo0104882

8. Prashad, M.; Har, D.; Hu, B.; Kim, H.-Y.; Repic, O.; Blacklock, T. J. *Org. Lett.* **2003**, *5*, 125–128. doi:10.1021/ol0268440
9. Leggio, A.; Alò, D.; Belsito, E. L.; Di Gioia, M. L.; Romio, E.; Siciliano, C.; Liguori, A. *J. Pept. Sci.* **2015**, *21*, 644–650. doi:10.1002/psc.2777
10. Lebleu, T.; Ma, X.; Maddaluno, J.; Legros, J. *Chem. Commun.* **2014**, *50*, 1836–1838. doi:10.1039/c3cc48997c
11. Kano, T.; Tanaka, Y.; Maruoka, K. *Tetrahedron* **2007**, *63*, 8658–8664. doi:10.1016/j.tet.2007.03.179
12. Selva, M.; Tundo, P.; Perosa, A. *J. Org. Chem.* **2002**, *67*, 9238–9247. doi:10.1021/jo026057g
13. Zheng, J.; Darcel, C.; Sortais, J.-B. *Chem. Commun.* **2014**, *50*, 14229–14232. doi:10.1039/c4cc05517a
14. Cabrero-Antonino, J. R.; Adam, R.; Junge, K.; Beller, M. *Catal. Sci. Technol.* **2016**, *6*, 7956–7966. doi:10.1039/c6cy01401a
15. Seo, H.; Bédard, A.-C.; Chen, W. P.; Hicklin, R. W.; Alabugin, A.; Jamison, T. F. *Tetrahedron* **2018**, *74*, 3124–3128. doi:10.1016/j.tet.2017.11.068
16. Borch, R. F.; Hassid, A. I. *J. Org. Chem.* **1972**, *37*, 1673–1674. doi:10.1021/jo00975a049
17. Alinezhad, H.; Tajbakhsh, M.; Salehian, F.; Fazli, K. *Synth. Commun.* **2010**, *40*, 2415–2420. doi:10.1080/00397910903249606
18. Ge, X.; Luo, C.; Qian, C.; Yu, Z.; Chen, X. *RSC Adv.* **2014**, *4*, 43195–43203. doi:10.1039/c4ra04414b
19. Petricci, E.; Santillo, R.; Castagnolo, D.; Cini, E.; Taddei, M. *Adv. Synth. Catal.* **2018**, *360*, 2560–2565. doi:10.1002/adsc.201701619
20. Savourey, S.; Lefèvre, G.; Berthet, J.-C.; Cantat, T. *Chem. Commun.* **2014**, *50*, 14033–14036. doi:10.1039/c4cc05908e
21. Sorribes, I.; Junge, K.; Beller, M. *Chem. – Eur. J.* **2014**, *20*, 7878–7883. doi:10.1002/chem.201402124
22. Zhang, L.; Zhang, Y.; Deng, Y.; Shi, F. *RSC Adv.* **2015**, *5*, 14514–14521. doi:10.1039/c4ra13848a
23. Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J.-B. *J. Catal.* **2017**, *347*, 57–62. doi:10.1016/j.jcat.2017.01.004
24. Neumann, J.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M. *Chem. – Eur. J.* **2017**, *23*, 5410–5413. doi:10.1002/chem.201605218
25. Dang, T. T.; Ramalingam, B.; Seayad, A. M. *ACS Catal.* **2015**, *5*, 4082–4088. doi:10.1021/acscatal.5b00606
26. Liang, R.; Li, S.; Wang, R.; Lu, L.; Li, F. *Org. Lett.* **2017**, *19*, 5790–5793. doi:10.1021/acs.orglett.7b02723
27. Choi, G.; Hong, S. H. *Angew. Chem., Int. Ed.* **2018**, *57*, 6166–6170. doi:10.1002/anie.201801524
28. Maji, M.; Chakrabarti, K.; Paul, B.; Roy, B. C.; Kundu, S. *Adv. Synth. Catal.* **2018**, *360*, 722–729. doi:10.1002/adsc.201701117
29. Jiang, L.; Zhang, X.; Wang, Y.; Guo, F.; Hou, Z. *Asian J. Org. Chem.* **2021**, *10*, 2165–2169. doi:10.1002/ajoc.202100339
30. Wang, J.; Qiang, W.; Ye, S.; Zhu, L.; Liu, X.; Loh, T.-P. *Catal. Sci. Technol.* **2021**, *11*, 3364–3375. doi:10.1039/d0cy02442b
31. Paul, B.; Maji, M.; Panja, D.; Kundu, S. *Asian J. Org. Chem.* **2022**, *11*, e202100678. doi:10.1002/ajoc.202100678
32. Jacquet, O.; Frogneux, X.; Das Neves Gomes, C.; Cantat, T. *Chem. Sci.* **2013**, *4*, 2127–2131. doi:10.1039/c3sc22240c
33. Li, Y.; Fang, X.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 9568–9571. doi:10.1002/anie.201301349
34. Yang, Z.; Yu, B.; Zhang, H.; Zhao, Y.; Ji, G.; Ma, Z.; Gao, X.; Liu, Z. *Green Chem.* **2015**, *17*, 4189–4193. doi:10.1039/c5gc01386k
35. Niu, H.; Lu, L.; Shi, R.; Chiang, C.-W.; Lei, A. *Chem. Commun.* **2017**, *53*, 1148–1151. doi:10.1039/c6cc09072a
36. Cui, X.; Dai, X.; Zhang, Y.; Deng, Y.; Shi, F. *Chem. Sci.* **2014**, *5*, 649–655. doi:10.1039/c3sc52676c
37. Tamura, M.; Miura, A.; Gu, Y.; Nakagawa, Y.; Tomishige, K. *Chem. Lett.* **2017**, *46*, 1243–1246. doi:10.1246/cl.170419
38. Toyao, T.; Siddiki, S. M. A. H.; Morita, Y.; Kamachi, T.; Touchy, A. S.; Onodera, W.; Kon, K.; Furukawa, S.; Ariga, H.; Asakura, K.; Yoshizawa, K.; Shimizu, K.-i. *Chem. – Eur. J.* **2017**, *23*, 14848–14859. doi:10.1002/chem.201702801
39. Lin, S.; Liu, J.; Ma, L. *J. CO2 Util.* **2021**, *54*, 101759. doi:10.1016/j.jcou.2021.101759
40. Du, X.-L.; Tang, G.; Bao, H.-L.; Jiang, Z.; Zhong, X.-H.; Su, D. S.; Wang, J.-Q. *ChemSusChem* **2015**, *8*, 3489–3496. doi:10.1002/cssc.201500486
41. Santoro, O.; Lazreg, F.; Minenkov, Y.; Cavallo, L.; Cazin, C. S. J. *Dalton Trans.* **2015**, *44*, 18138–18144. doi:10.1039/c5dt03506f
42. Jiang, X.; Wang, C.; Wei, Y.; Xue, D.; Liu, Z.; Xiao, J. *Chem. – Eur. J.* **2014**, *20*, 58–63. doi:10.1002/chem.201303802
43. Goyal, V.; Naik, G.; Narani, A.; Natte, K.; Jagadeesh, R. V. *Tetrahedron* **2021**, *98*, 132414. doi:10.1016/j.tet.2021.132414
44. Paquette, L. A.; Tae, J. *J. Org. Chem.* **1998**, *63*, 2022–2030. doi:10.1021/jo9722921
45. Benoit, W. L.; Parvez, M.; Keay, B. A. *Tetrahedron: Asymmetry* **2009**, *20*, 69–77. doi:10.1016/j.tetasy.2008.12.027
46. Fuentes de Arriba, Á. L.; Seisdedos, D. G.; Simón, L.; Alcázar, V.; Raposo, C.; Morán, J. R. *J. Org. Chem.* **2010**, *75*, 8303–8306. doi:10.1021/jo101723v
47. Sun, N.; Wang, S.; Mo, W.; Hu, B.; Shen, Z.; Hu, X. *Tetrahedron* **2010**, *66*, 7142–7148. doi:10.1016/j.tet.2010.06.091
48. Barluenga, J.; Bayón, A. M.; Campos, P.; Asensio, G.; Gonzalez-Nuñez, E.; Molina, Y. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1631–1636. doi:10.1039/p19880001631
49. Crochet, R. A., Jr.; Blanton, C. D., Jr. *Synthesis* **1974**, 55–56. doi:10.1055/s-1974-23242
50. Zhang, J.; Chang, H.-M.; Kane, R. R. *Synlett* **2001**, 643–645. doi:10.1055/s-2001-13378
51. Blackburn, C.; LaMarche, M. J.; Brown, J.; Che, J. L.; Cullis, C. A.; Lai, S.; Maguire, M.; Marsilje, T.; Geddes, B.; Govek, E.; Kadambi, V.; Doherty, C.; Dayton, B.; Brodjjan, S.; Marsh, K. C.; Collins, C. A.; Kym, P. R. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2621–2627. doi:10.1016/j.bmcl.2006.02.044
52. Das, D.; Khan, H. P. A.; Shivahare, R.; Gupta, S.; Sarkar, J.; Siddiqui, M. I.; Ampapathi, R. S.; Chakraborty, T. K. *Org. Biomol. Chem.* **2017**, *15*, 3337–3352. doi:10.1039/c6ob02610a
53. Avula, K.; Mohapatra, D. K. *Tetrahedron Lett.* **2016**, *57*, 1715–1717. doi:10.1016/j.tetlet.2016.03.017
54. Heller, S. T.; Fu, T.; Sarpong, R. *Org. Lett.* **2012**, *14*, 1970–1973. doi:10.1021/ol300339q
55. Meng, G.; Szostak, R.; Szostak, M. *Org. Lett.* **2017**, *19*, 3596–3599. doi:10.1021/acs.orglett.7b01575
56. Rawling, T.; McDonagh, A. M.; Tattam, B.; Murray, M. *Tetrahedron* **2012**, *68*, 6065–6070. doi:10.1016/j.tet.2012.05.002
57. Velavan, A.; Sumathi, S.; Balasubramanian, K. K. *Org. Biomol. Chem.* **2012**, *10*, 6420–6431. doi:10.1039/c2ob25412c
58. McBurney, R. T.; Walton, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 7349–7354. doi:10.1021/ja402833w
59. Jöst, C.; Nitsche, C.; Scholz, T.; Roux, L.; Klein, C. D. *J. Med. Chem.* **2014**, *57*, 7590–7599. doi:10.1021/jm5006918
60. Ren, Y.; Rousseaux, S. A. L. *J. Org. Chem.* **2018**, *83*, 913–920. doi:10.1021/acs.joc.7b02905

61. Meng, H.; Sun, K.; Xu, Z.; Tian, L.; Wang, Y. *Eur. J. Org. Chem.* **2021**, 1768–1772. doi:10.1002/ejoc.202100113
62. Chen, Z.; Cao, Y.; Tian, Z.; Zhou, X.; Xu, W.; Yang, J.; Teng, H. *Tetrahedron Lett.* **2017**, *58*, 2166–2170. doi:10.1016/j.tetlet.2017.04.072
63. Peng, Z.; Wong, J. W.; Hansen, E. C.; Puchlopek-Dermenci, A. L. A.; Clarke, H. J. *Org. Lett.* **2014**, *16*, 860–863. doi:10.1021/ol403630g
64. Padiya, K. J.; Gavade, S.; Kardile, B.; Tiwari, M.; Bajare, S.; Mane, M.; Gaware, V.; Varghese, S.; Harel, D.; Kurhade, S. *Org. Lett.* **2012**, *14*, 2814–2817. doi:10.1021/ol301009d
65. de Greef, T. F. A.; Nieuwenhuizen, M. M. L.; Sijbesma, R. P.; Meijer, E. W. *J. Org. Chem.* **2010**, *75*, 598–610. doi:10.1021/jo902053t
66. Duspara, P. A.; Islam, M. S.; Lough, A. J.; Batey, R. A. *J. Org. Chem.* **2012**, *77*, 10362–10368. doi:10.1021/jo302084a
67. Wong, E. C. N.; Reekie, T. A.; Werry, E. L.; O'Brien-Brown, J.; Bowyer, S. L.; Kassiou, M. *Bioorg. Med. Chem. Lett.* **2017**, *27*, 2439–2442. doi:10.1016/j.bmcl.2017.04.005
68. Venter, J.; Perez, C.; van Otterlo, W. A. L.; Martínez, A.; Blackie, M. A. L. *Bioorg. Med. Chem. Lett.* **2019**, *29*, 1597–1600. doi:10.1016/j.bmcl.2019.04.049
69. Jones, C. D.; Simmons, H. T. D.; Horner, K. E.; Liu, K.; Thompson, R. L.; Steed, J. W. *Nat. Chem.* **2019**, *11*, 375–381. doi:10.1038/s41557-019-0222-0
70. Kondoh, A.; Ishikawa, S.; Terada, M. *J. Am. Chem. Soc.* **2020**, *142*, 3724–3728. doi:10.1021/jacs.9b13922
71. Rannard, S. P.; Davis, N. J.; Herbert, I. *Macromolecules* **2004**, *37*, 9418–9430. doi:10.1021/ma0489218
72. Griffin, R. J.; Evers, E.; Davison, R.; Gibson, A. E.; Layton, D.; Irwin, W. J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1205–1211. doi:10.1039/p19960001205
73. Alsarraf, J.; Petitpoisson, L.; Pichette, A. *Org. Lett.* **2021**, *23*, 6052–6056. doi:10.1021/acs.orglett.1c02116
74. Zhao, C.; Ye, Z.; Ma, Z.-x.; Wildman, S. A.; Blaszczyk, S. A.; Hu, L.; Guizei, I. A.; Tang, W. *Nat. Commun.* **2019**, *10*, 4015. doi:10.1038/s41467-019-11976-2
75. Nugent, J.; Campbell, S. G.; Vo, Y.; Schwartz, B. D. *Eur. J. Org. Chem.* **2017**, 5110–5118. doi:10.1002/ejoc.201700974
76. Prasad, A. S. B.; Kanth, J. V. B.; Periasamy, M. *Tetrahedron* **1992**, *48*, 4623–4628. doi:10.1016/s0040-4020(01)81236-9
77. Rodrigues, A.; Olivato, P. R.; Rittner, R. *Synthesis* **2005**, 2578–2582. doi:10.1055/s-2005-872101
78. Harish, V.; Periasamy, M. *Tetrahedron: Asymmetry* **2017**, *28*, 175–180. doi:10.1016/j.tetasy.2016.12.002
79. Abinet, E.; Martin, D.; Standfuss, S.; Kulinna, H.; Spaniol, T. P.; Okuda, J. *Chem. – Eur. J.* **2011**, *17*, 15014–15026. doi:10.1002/chem.201102145
80. Garnier-Amblard, E. C.; Mays, S. G.; Arrendale, R. F.; Baillie, M. T.; Bushnev, A. S.; Culver, D. G.; Evers, T. J.; Holt, J. J.; Howard, R. B.; Liebeskind, L. S.; Menaldino, D. S.; Natchus, M. G.; Petros, J. A.; Ramaraju, H.; Reddy, G. P.; Liotta, D. C. *ACS Med. Chem. Lett.* **2011**, *2*, 438–443. doi:10.1021/ml2000164
81. Nakagawa, Y.; Irie, K.; Yanagita, R. C.; Ohigashi, H.; Tsuda, K.-i.; Kashiwagi, K.; Saito, N. *J. Med. Chem.* **2006**, *49*, 2681–2688. doi:10.1021/jm050857c
82. Teng, H.; He, Y.; Wu, L.; Su, J.; Feng, X.; Qiu, G.; Liang, S.; Hu, X. *Synlett* **2006**, 877–880. doi:10.1055/s-2006-939044
83. Teng, H.; Zhang, Z.; Zhou, Y.; Chen, Z.; Chen, Q.; Liu, Y.; Xu, W. *RSC Adv.* **2015**, *5*, 71868–71872. doi:10.1039/c5ra10622b
84. Balci, M. *Synthesis* **2018**, *50*, 1373–1401. doi:10.1055/s-0036-1589527
85. Wang, L.; Qin, R.-Q.; Yan, H.-Y.; Ding, M.-U. *Synthesis* **2015**, 3522–3528. doi:10.1055/s-0034-1378874

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