RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2023, **13**, 9231

Solvent-controlled amidation of acid chlorides at room temperature: new route to access aromatic primary amides and imides amenable for late-stage functionalization†

Chandrasekaran Sivaraj and Thirumanavelan Gandhi *

Received 19th January 2023
Accepted 6th March 2023

DOI: 10.1039/d3ra00403a

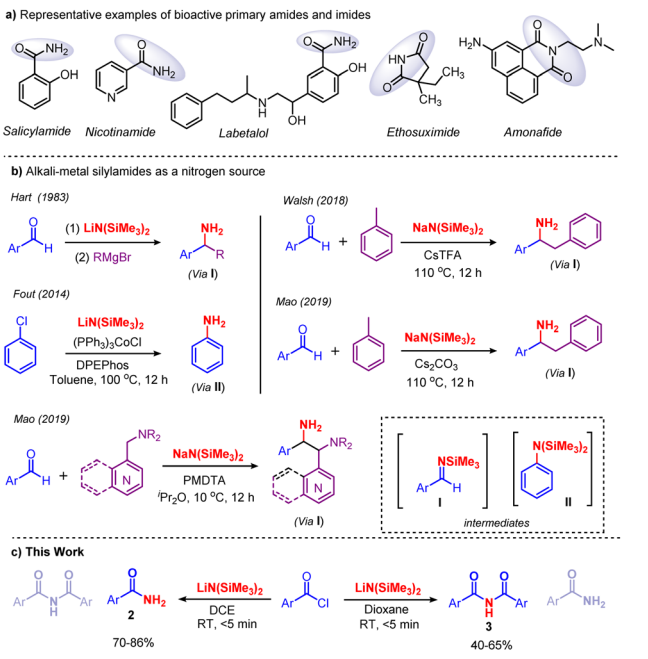
rsc.li/rsc-advances

Herein, we report a solvent-controlled highly selective amidation and imidation of aroyl chlorides using an alkali-metal silyl-amide reagent (LiHMDS), which serves as a nitrogen source at room temperature. A unique feature of this method lies in the sequential silyl amidation of aryol chlorides and nitrogen–silicon bond cleavage of the corresponding *N*,*N*-bis(trimethylsilyl)benzamide in a one-pot method in a very short reaction time. This effective strategy was extended to late-stage functionalization.

Introduction

Amides and imides are vital and appealing functionalities that are ubiquitous in biology, pharmaceutical intermediates, natural products, and materials science.[1] They are bestowed with remarkable properties which substantiate their existence in engineering plastics, lubricants, fertilizers, detergents, agrochemicals, proteins, *etc.*[2,3] In particular, primary benzamides are found in various drugs, such as salicylamide, nicotinamide, labetalol, frovatriptan, niraparib, lenvatinib, ethosuximide and amonafide (Scheme 1a). Therefore, tremendous efforts have been made to develop synthetic methods for the preparation of primary amides. Classically, primary amides are accessed using carboxylic acid derivatives,[4] aldehydes,[5] alcohols,[6,7] nitriles,[8] and oximes.[9–11] Later, various nonclassical strategies, such as oxidative-amidation,[12] hydroamination[13] and C–N coupling reactions,[14] were developed. Very recently, new methodologies for the synthesis of primary amides were established. Mechanochemical, transamidation, ring-opening selective cleavage and direct amidation were developed by Menéndez,[15] Lee,[16] Lin[17] and Chen,[18] respectively.

Traditionally, imides are prepared *via* two routes: (i) acylation of amides with acyl chlorides, carboxylic esters, and anhydrides,[19] and (ii) a Mumm rearrangement of isoimides.[20] However, both of these methods suffer from limited substrate scope; furthermore, Mumm rearrangement demands pre-functionalization and results in moderate yields.[21] Recently, considerable effort has been devoted to the synthesis of imides, and in this regard several methods have been developed, such as the metal-catalyzed carbonylation of amides,[22] the oxidation of amides,[23] and the oxidative decarboxylation of amino acids,[24] among others.[25–33] Recently, the Liang group reported the synthesis of imides by the chemoselective acylation of *N*-acyl-glutarimides with *N*-acylpyrroles and aryl esters under transition-metal-free conditions.[21] However, the reported imide synthesis displays certain drawbacks in terms of corrosive precursors, prefunctionalized substrates, specialized reagents, and excessive oxidants; besides, they are time-consuming with a limited substrate scope. The development of greener and

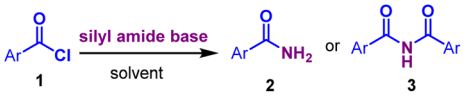


Scheme 1 Metal-silylamides as a nitrogen source.

Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India. E-mail: velan.g@vit.ac.in

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3ra00403a

Table 1 Optimization of the reaction conditions

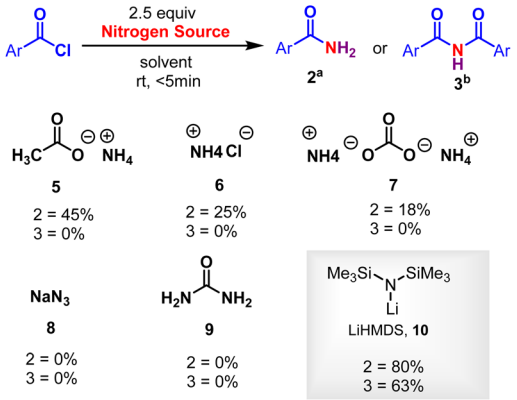


Entry	Nitrogen source	Solvent	Yield (%) 2	3
1	**LiHMDS in THF**	**DCE**	**80**	**10**
2	LiHMDS in toluene	DCE	0	0
3	NaHMDS in THF	DCE	60	5
4	KHMDS in toluene	DCE	0	0
5	LiHMDS in THF	$CHCl_3$	10	0
6	LiHMDS in THF	TFE	5	0
7	LiHMDS in THF	DCM	4	45
8	**LiHMDS in THF**	**Dioxane**	**10**	**63**
9	LiHMDS in THF	DMF	0	38
10	LiHMDS in THF	THF	0	35
11	LiHMDS in THF	Et_2O	0	30
12	LiHMDS in THF	CH_3CN	0	25
13	LiHMDS in THF	Toluene	0	23
14	LiHMDS in THF	Acetone	0	10
15	LiHMDS in THF	DMSO	0	6
16	LiHMDS in THF	EtOAc	0	4
17	LiHMDS in THF	EtOH	0	0
18	LiHMDS in THF	MeOH	0	0

more practical methods for the synthesis of primary amides and imides remains in demand. Our group has a long-standing interest in Brønsted base [$MN(SiMe_3)_2$, M = Li, Na and K] promoted organic transformations, especially the cleavage of C–C and C–O bonds in *C*-acyl imidazolium salts and esters, respectively.[34] Recently, we have shown that $KN(SiMe_3)_2$ promotes the acylation of weakly acidic C–H bonds in toluene derivatives.[35] Along these lines, in 1983 Hart and co-workers reported for the first time that [$MN(SiMe_3)_2$, M = Li, Na and K] acts as a base and nitrogen source in converting aryl aldehydes to aryl amines. Likewise, Fout, Walsh, and Mao used [$MN(SiMe_3)_2$, M = Li, Na and K] as a nitrogen source for amination reactions (Scheme 1b).[36] To the best of our knowledge, the usage of [$MN(SiMe_3)_2$, M = Li, Na and K] as a nitrogen source for amination reactions at ambient temperature in a short reaction time is unknown. Herein, we report the solvent controlled metal-free, additive-free amidation and imidation of acid chlorides using $LiN(SiMe_3)_2$ as a nitrogen source in a very short reaction time at ambient temperature (Scheme 1c).

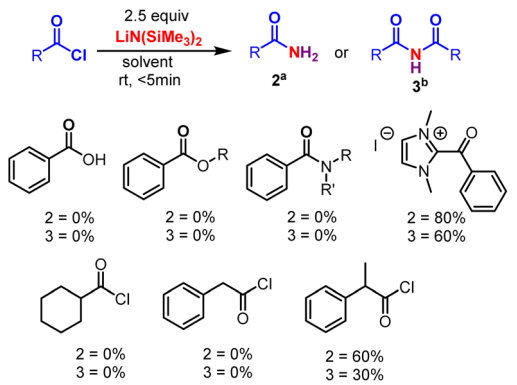
Results and discussion

Initially, the metal-free amidation of aroyl chlorides with $LiN(SiMe_3)_2$ (in THF) was investigated. The reaction of 1.0 equiv. benzoyl chloride **1** with 2.5 equiv. $LiN(SiMe_3)_2$ at room temperature in DCE for 5 min resulted in the formation of the benzamide **2a** in 80% yield. An increment in $LiN(SiMe_3)_2$ (from 2.5 to 3.0 equiv.) reduced the yield of **2**, while decreasing it (from 2.5 to 1.0 equiv.) resulted in the appearance of unidentifiable products (without hampering the reaction progression). In the

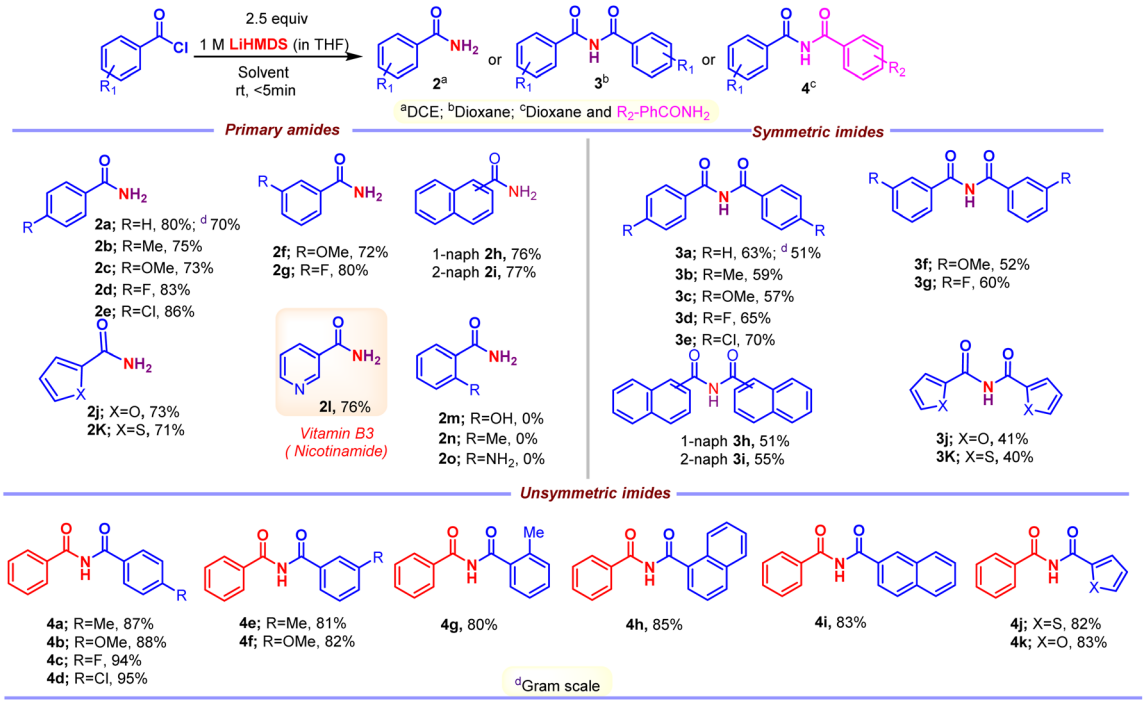


Scheme 2 Other nitrogen sources. Reaction conditions were as follows: aroyl chloride 1 (0.2 mmol), LiHMDS (2.5 equiv.), [a]DCE (3 mL) and [b]dioxane (3 mL), RT, <5 min.

absence of $LiN(SiMe_3)_2$ (in THF) no product was observed, suggesting that $LiN(SiMe_3)_2$ promotes the process. Other silyl amides like NaHMDS (in THF) and KHMDS (in Toluene) were tried. No reaction was observed in case of KHMDS in toluene (Table 1, entry 4), whereas reduction in the yield of **2** was observed when NaHMDS in THF was used (Table 1, entry 3). We next tested various nitrogen sources (ammonium salts, azide and urea). Among these, ammonium salts gave the desired primary amides, whereas LiHMDS were the best (Scheme 2). The relative importance of various solvents on the reaction, such as $CHCl_3$, TFE, DCM, dioxane, DMF, THF, diethyl ether, acetonitrile, toluene, acetone, DMSO, ethyl acetate, ethanol and methanol, was examined (Table 1, entries 5–18). Among these, halogenated solvents showed a trace amount of **2** (Table 1, entries 5–7), and, surprisingly, non-halogenated solvents showed the formation of imide **3** devoid of **2** (Table 1, entries 9–18). Thus, dioxane was found to the best solvent to give **3** in a higher yield (63%) (Table 1, entry 8). This investigation reveals that the solvents play a crucial role in the formation of **2** and **3**. Furthermore, various acyl sources, such as acids, esters, amides, *C*-acyl imidazolium salts, aliphatic acid chlorides,



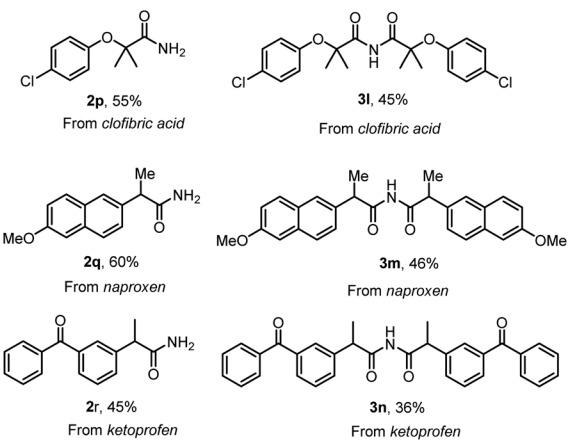
Scheme 3 Other acyl sources. Reaction conditions were as follows: aroyl chloride 1 (0.2 mmol), LiHMDS (2.5 equiv.), [a]DCE (3 mL) and [b]dioxane (3 mL), RT, <5 min.



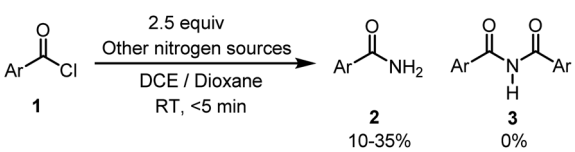
Scheme 4 Synthesis of primary amides, symmetric and unsymmetric imides. Reaction conditions were as follows: aroyl chloride 1 (0.2 mmol), LiHMDS (2.5 equiv.), DCE (3 mL) and dioxane (3 mL), RT, <5 min.

aromatic side chain carboxyl chlorides and α-substituted aromatic side chain carboxyl chlorides were examined (Scheme 3). Among these *C*-acyl imidazolium salts and α-substituted aromatic side chain carboxyl chlorides gave products **2** and **3**, which reveals that this protocol is a substrate selective reaction.

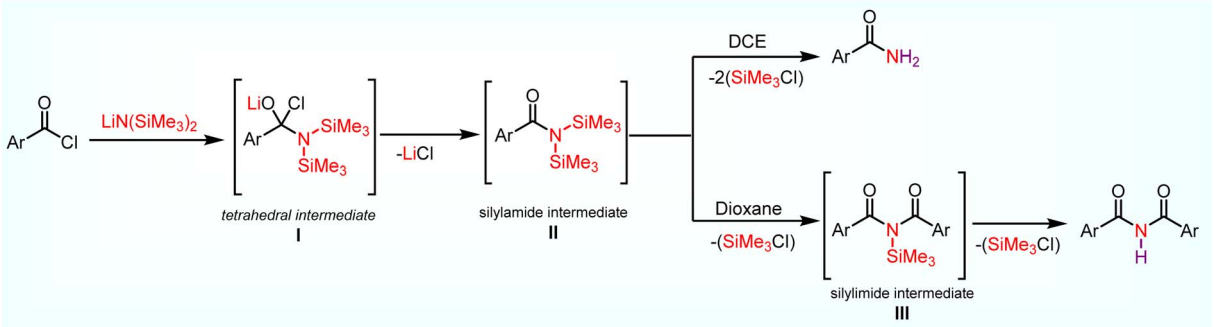
With the optimized conditions in hand, the substrate scope was first surveyed for the reaction of primary amides and symmetric imides (Scheme 4). Various examples of acid chlorides were subjected to the synthesis of corresponding products. The substrates with electron-withdrawing groups, **2d**, **2e**, **2g**, **3d**, **3e** and **3g**, were well tolerated compared with that to electron-releasing groups, **2b**, **2c**, **2f**, **3b**, **3c** and **3f**, in amidation and imidation reactions. Importantly, the amidation reaction does not progress with substrates possessing *ortho* substituents, **2m–2o**. Successively, our intent was to explore unsymmetrical imides **4** (Scheme 4) by adopting this approach. The reaction of acid chloride **1** with primary amide **2a** in the presence LiHMDS in dioxane at room temperature afforded unsymmetrical imides **4**. There were no significant changes in yield with respect to electron-releasing or electron-withdrawing groups, **4a–4g**. Additionally, poly- and heterocyclic substrates were compatible to give amides **2h–2k**, symmetric imides **3h–3k**, and unsymmetric imides **4h–4k** in moderate to good yields. This protocol could be extended to the synthesis of drug nicotinamide **2l** from its corresponding acid chloride. Scale-up experiments were performed in order to put forth the practicality of the solvent-controlled amidation and imidation methodology by using aroyl chloride (1 g, 7.14 mmol) as a test molecule under the optimized reaction conditions. As can be clearly seen from Scheme 4, the isolated yields of **2a** (70% yield) and **3a** (51%) are



Scheme 5 Late-stage functionalization of drugs. Reaction conditions were as follows: acid chloride 1 (0.2 mmol), LiHMDS (2.5 equiv.), DCE (3 mL) and dioxane (3 mL), RT, <5 min.



Scheme 6 Control experiment. Reaction conditions were as follows: acid chloride 1 (0.2 mmol), LiHMDS (2.5 equiv.), DCE (3 mL) and dioxane (3 mL), RT, <5 min.



Scheme 7 Plausible mechanistic pathways.

quite satisfactory. Late-stage functionalization strategies are currently receiving great interest in both the drug discovery and chemical biology, and in this regard, solvent controlled amidation and imidation studies were carried out on three different drug molecules, clofibric acids **2p** and **3l**, naproxens **2q** and **3m**, and ketoprofens **2r** and **3n** (Scheme 5).

Further, to understand this methodology, a control experiment was carried out (Scheme 6). Precursor **1** reacted with other nitrogen sources (ammonium salts, azide and urea) under the optimal reaction conditions resulted in the formation of **2**, and no **3** was formed. From this result, it is deciphered that non-silylamide nitrogen sources preferentially gave primary amides **2** whereas silylamide ones move forward to give **3** by reacting with aroyl chloride.

Based on the above studies and literature report, a plausible mechanism for the formation of primary amides and imides is depicted in Scheme 7. Initially, nucleophilic addition of the nitrogen in $LiN(SiMe_3)_2$ to the electrophilic carbonyl carbon of **1** forms a tetrahedral intermediate **I**. Then, **I** proceeds to form a key silylamide intermediate **II** [21] ($ArC(=O)N(SiMe_3)_2$) *via* LiCl elimination. Intermediate **II** can proceed through two different pathways based on the chosen solvent. In the presence of DCE (polar solvent), the chlorine atom in DCE coordinates with silicon in silyl amide intermediate **II**, which helps to cleave both nitrogen–silicon bonds simultaneously in silyl amide intermediate **II** instead of one more acid chloride to deliver amide **2** during the acidic work up. In the case of dioxane (non-polar solvents), the cleavage of the nitrogen–silicon bond in silyl amide intermediate **II** is difficult due to less solubility.[37] Further, one more acid chloride is required to cleave the nitrogen–silicon bond in silyl amide intermediate **II** to form a new intermediate **III**, which leads to symmetric imides **3** during acidic work up.

Conclusions

In summary, we developed a straightforward and efficient synthetic methodology for the synthesis of primary amides, symmetric and unsymmetric imides. Both the amidation (34 examples) and the late-stage functionalization of drugs (7 examples) worked smoothly with the yields ranging from 50 to 70%. The major advantages of the presented methodology over the existing ones are that (i) there is no need for the external amine source and oxidant, (ii) it does not require any metal catalyst, (iii) it enables the selective synthesis of primary amides and imides in high yields, (iv) it allows the derivatization of drug molecules, (v) it uses safe solvents at room temperature, and (vi) the reaction completes in a very short time, thus avoiding harsh conditions. Therefore, we think that this solvent-controlled amidation and imidation protocol will create a new perspective for the synthesis of primary amides/imides and related drug molecules.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The Department of Science and Technology-SERB, India (CRG/2021/001143) and the Seed grant-SG20210167, Vellore Institute of Technology, Vellore, are gratefully acknowledged.

Notes and references

1 (*a*) A. Greenberg, C. M. Breneman and J. F. Liebman, *The amide linkage: selected structural aspects in chemistry, biochemistry, and materials science*, WileyInterscience, 2000; (*b*) G. Benz, *Synthesis of amides and related compounds: comprehensive organic synthesis*, Pergamon, 1991.

2 (*a*) J. M. Humphrey and A. R. Chamberlin, Chemical synthesis of natural product peptides: coupling methods for the incorporation of noncoded amino acids into peptides, *Chem. Rev.*, 1997, **97**, 2243–2266; (*b*) M. K. Hargreaves, J. G. Pritchard and H. R. Dave, Cyclic carboxylic monoimides, *Chem. Rev.*, 1970, **70**, 439–469.

3 (*a*) L. Mei and Y. Bing, A simple synthesis of salicylamide and 2,5-diphenylpyrazine, *Res. Chem. Intermed.*, 2015, **41**, 3491–3496; (*b*) A. Tahara, A. Matsuyama-Yokono and M. Shibasaki, Effects of antidiabetic drugs in high-fat diet and streptozotocin- nicotinamide-induced type 2 diabetic mice, *Eur. J. Pharmacol.*, 2011, **655**, 108–116.

4 (*a*) Q. Song, Q. Feng and K. Yang, Synthesis of primary Amides *via* Copper-Catalyzed Aerobic Decarboxylative ammoxidation of Phenylacetic Acids and α-

Hydroxyphenylacetic acids with Ammonia in water, *Org. Lett.*, 2014, **16**, 624–627; (*b*) A. R. Chhatwal, H. V. Lomax, A. J. Blacker, J. M. J. Williams and P. Marcé, Direct synthesis of amides from nonactivated carboxylic acids using urea as nitrogen source and $Mg(NO_3)_2$ or imidazole as catalysts, *Chem. Sci.*, 2020, **11**, 5808–5818.

5 (*a*) Y. Wang, W. Guo, A. L. Guan, S. Liu and Z. J. Yao, Half-Sandwich Iridium Complexes Based on β-Ketoamino Ligands: Preparation, Structure, and Catalytic Activity in Amide Synthesis, *Inorg. Chem.*, 2021, **60**, 11514–11520; (*b*) J. M. Concellón, H. Rodríguez-Solla, C. Concellón, C. Simal and N. Alvaredo, Sequential synthesis of (*E*)-α,β-unsaturated primary amides with complete stereoselectivity, *J. Org. Chem.*, 2010, **75**, 3451–3453; (*c*) S. C. Ghosh, Copper-catalyzed oxidative amidation of aldehydes with amine salts: synthesis of primary, secondary, and tertiary amides, *J. Org. Chem.*, 2012, **77**, 8007–8015.

6 K. Yamaguchi, H. Kobayashi, T. Oishi and N. Mizuno, Heterogeneously Catalyzed Synthesis of Primary Amides Directly from Primary Alcohols and Aqueous Ammonia, *Angew. Chem., Int. Ed.*, 2012, **51**, 544–547.

7 K. Yamaguchi, H. Kobayashi, Y. Wang, T. Oishi, Y. Ogasawara and N. Mizuno, Green oxidative synthesis of primary amides from primary alco-hols or aldehydes catalyzed by a cryptomelane-type manganese oxide-based octahedral molecular sieve, OMS-2, *Catal. Sci. Technol.*, 2013, **3**, 318–327.

8 X. Fan, W. Deng, Z. Liu and Z. Yao, Half-Sandwich Iridium Complexes for the One-Pot Synthesis of Amides: Preparation, Structure, and Diverse Catalytic Activity, *Inorg. Chem.*, 2020, **59**, 16582–16590.

9 R. García-Álvarez, A. E. Díaz-Álvarez, J. Borge, P. Crochet and V. Cadierno, Ruthenium-catalyzed rearrangement of aldoximes to primary amides in water, *Organometallics*, 2012, **31**, 6482–6490.

10 P. J. González-Liste, V. Cadierno and S. E. García-Garrido, Catalytic Rearrangement of Aldoximes to Primary Amides in Envi-ronmentally Friendly Media under Thermal and Microwave Heat-ing: Another Application of the Bis(allyl)-Ruthenium (IV) Dimer $[\{RuCl(\mu\text{-}Cl)\ (\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$, *ACS Sustain. Chem. Eng.*, 2015, **3**, 3004–3011.

11 J. Bosson, N. Marion and S. P. Nolan, Au/Ag-Cocatalyzed Aldoximes to Amides Rearrangement under Solvent- and Acid-Free Conditions, *J. Org. Chem.*, 2010, **75**, 1197–1202.

12 (*a*) J. Gao and G.-W. Wang, Direct oxidative amidation of aldehydes with anilines under mechanical milling conditions, *J. Org. Chem.*, 2008, **73**, 2955–2958; (*b*) S. C. Ghosh, J. S. Ngiam, A. M. Seayad, D. T. Tuan, C. L. Chai and A. Chen, Copper-catalyzed oxidative amidation of aldehydes with amine salts: synthesis of primary, secondary, and tertiary amides, *J. Org. Chem.*, 2012, **77**, 8007–8015.

13 (*a*) Y. Uenoyama, T. Fukuyama, O. Nobuta, H. Matsubara and I. Ryu, Alkyne carbonylation by radicals: Tin-radical-catalyzed synthesis of alpha-methylene amides from 1-alkynes, carbon monoxide, and amines, *Angew. Chem., Int. Ed.*, 2005, **44**, 1075–1078; (*b*) W.-K. Chan, C.-M. Ho, M.-K. Wong and C.-M. Che, Oxidative amide synthesis and *N*-terminal α-amino group ligation of peptides in aqueous medium, *J. Am. Chem. Soc.*, 2006, **128**, 14796–14797.

14 G. Meng, S. Shi and M. Szostak, Cross-coupling of amides by N–C bond activation, *Synlett*, 2016, **27**, 2530–2540.

15 J. Gómez-Carpintero, J. D. Sánchez, J. F. González and J. C. Menéndez, Mechanochemical Synthesis of Primary Amides, *J. Org. Chem.*, 2021, **86**, 14232–14237.

16 J. Chen, Y. Xia and S. Lee, Transamidation for the Synthesis of Primary Amides at Room Temperature, *Org. Lett.*, 2020, **22**, 3504–3508.

17 K. Govindan and W. Y. Lin, Ring Opening/Site Selective Cleavage in N-Acyl Glutarimide to Synthesize Primary Amides, *Org. Lett.*, 2021, **23**, 1600–1605.

18 Y. Guo, R. Wang, J. Kang, Y. Ma, C. Xu, J. Li and X. Chen, Efficient synthesis of primary and secondary amides via reacting esters with alkali metal amidoboranes, *Nat. Commun.*, 2021, **12**, 1–9.

19 (*a*) A. Giovannini, D. Savoia and A. Umani-Ronchi, Organometallic ring-opening reactions of *N*-acyl and *N*-alkoxycarbonyl lactams. Synthesis of cyclic imines, *J. Org. Chem.*, 1989, **54**, 228–233; (*b*) M. B. Andrus and R. F. Keyes, Synthesis of mixed acyclic imides using pentafluorophenyl esters, *Tetrahedron Lett.*, 1998, **39**, 5465–5468.

20 (*a*) J. P. Schwarz, Preparation of acyclic isoimides and their rearrangement rates to imides, *J. Org. Chem.*, 1972, **37**, 2906–2908; (*b*) K. Brady and A. F. Hegarty, The isoimide–imide rearrangement, *J. Chem. Soc., Perkin Trans. 1*, 1980, **2**, 121–126.

21 J. Li, J. Yao, L. Chen, D. Zou, P. J. Walsh and G. Liang, Chemoselective acylation of: N-acylglutarimides with N-acylpyrroles and aryl esters under transition-metal-free conditions, *Org. Chem. Front.*, 2021, **8**, 6344–6349.

22 (*a*) A. Schnyder and A. F. Indolese, Synthesis of unsymmetrical aroyl acyl imides by aminocarbonyla-tion of aryl bromides, *J. Org. Chem.*, 2002, **67**, 594–597; (*b*) L. Ran, Z. H. Ren, Y. Y. Wang and Z. H. Guan, Palladium-Catalyzed Aminocarbonylation of Aryl Iodides with Amides and N-alkyl Anilines, *Chem.–Asian J.*, 2014, **9**, 577–583; (*c*) H. Li, K. Dong, H. Neumann and M. Beller, Palladium-Catalyzed Hydroamidocarbonylation of Olefins to Imides, *Angew. Chem., Int. Ed.*, 2015, **127**, 10377–10381; (*d*) Y. Li, K. Dong, F. Zhu, Z. Wang and X. F. Wu, Copper-Catalyzed Carbonylative Coupling of Cycloalkanes and Amides, *Angew. Chem., Int. Ed.*, 2016, **55**, 7227–7230.

23 (*a*) L. Xu, S. Zhang and M. L. Trudell, Novel chromium (VI) catalyzed oxidation of *N*-alkylamides to imides with periodic acid, *Chem. Commun.*, 2004, **14**, 1668–1669; (*b*) K. C. Nicolaou and C. J. Mathison, Synthesis of Imides, N-Acyl Vinylogous Carbamates and Ureas, and Nitriles by Oxidation of Amides and Amines with Dess–Martin Periodinane, *Angew. Chem., Int. Ed.*, 2005, **117**, 6146–6151; (*c*) J. Sperry, The oxidation of amides to imides: a powerful synthetic trans-formation, *Synthesis*, 2011, **2011**, 3569–3580; (*d*) H. Yu, Y. Chen and Y. Zhang, TBHP/

TEMPO-Mediated Oxidative Synthesis of Imides from Amides, *Chin. J. Chem.*, 2015, **33**, 531–534.

24 (*a*) A. Itoh, T. Kodama, S. Inagaki and Y. Masaki, New synthetic method of imides through oxidative photodecarboxylation reaction of *N*-protected α-amino acids with FSM-16, *Chem. Lett.*, 2000, **29**, 542–543; (*b*) W. Huang, M. Wang and H. Yue, Conversion of *N*-acyl amino acids into imides via oxidative decarboxylation induced by Ag^{+}/Cu^{2+}/$S_2O_8^{2-}$ in water, *Synthesis*, 2008, 1342–1344.

25 X. Ye, C. Xie, Y. Pan, L. Han and T. Xie, Copper-Catalyzed Synthesis of α-Amino Imides from Tertiary Amines: Ugi-Type Three-Component Assemblies Involving Direct Functionalization of sp^3 C–Hs Adjacent to Nitrogen Atoms, *Org. Lett.*, 2010, **12**, 4240–4243.

26 T. Tomizawa, K. Orimoto, T. Niwa and M. Nakada, Preparation of imides via the palladium-catalyzed coupling reac-tion of organoborons with methyl *N*-[methoxy(methylthio)methylene]carbamate as a one-carbon elongation reaction, *Org. Lett.*, 2012, **14**, 6294–6297.

27 H. Aruri, U. Singh, S. Kumar, M. Kushwaha, A. P. Gupta, R. A. Vishwakarma and P. P. Singh, I_2/aqueous TBHP-catalyzed coupling of amides with methylarenes/aldehydes/alcohols: metal-free synthesis of imides, *Org. Lett.*, 2016, **18**, 3638–3641.

28 C. S. Digwal, U. Yadav, P. V. S. Ramya, S. Sana, B. Swain and A. Kamal, Vanadium-Catalyzed Oxidative C(CO)-C(CO) Bond Cleavage for C-N Bond Formation: One-Pot Domino Transformation of 1,2-Diketones and Amidines into Imides and Amides, *J. Org. Chem.*, 2017, **82**, 7332–7345.

29 Y. Shen, Q. Li, G. Xu and S. Cui, Coupling of Carboxylic Acids with Ynamides and Subsequent Rear-rangement for the Synthesis of Imides/Amides, *Org. Lett.*, 2018, **20**, 5194–5197.

30 S. Ghorai and D. Lee, Synthesis of Imides, Imidates, Amidines, and Amides by Intercept-ing the Aryne-Isocyanide Adduct with Weak Nucleophiles, *Org. Lett.*, 2019, **21**, 7390–7393.

31 T. Brandhofer, A. Gini, S. Stockerl, D. G. Piekarski and O. García Mancheño, Direct C–H Bond Imidation with Benzoyl Peroxide as a Mild Oxi-dant and a Reagent, *J. Org. Chem.*, 2019, **84**, 12992–13002.

32 J. L. Xu, H. Tian, J. H. Kang, W. X. Kang, W. Sun, R. Sun, Y. M. Li and M. Sun, Ag(I)-catalyzed addition of cyclopropenones and nitrones to ac-cess imides, *Org. Lett.*, 2020, **22**, 6739–6743.

33 T. Yao, T. Yao, B. Wang, D. He, X. Zhang, X. Li and R. Fang, Ligand-controlled palladium-catalyzed chemoselective multicomponent reaction of olefin-tethered aryl halides, isocyanides, and carboxylic acids: Diversified synthesis of imides, *Org. Lett.*, 2020, **22**, 6784–6789.

34 (*a*) S. Karthik, K. Muthuvel and T. Gandhi, Base-Promoted Amidation and Esterification of Imidazolium Salts *via* Acyl C–C bond Cleavage: Access to Aromatic Amides and Esters, *J. Org. Chem.*, 2018, **84**, 738–751; (*b*) K. Muthuvel, S. Karthik and T. Gandhi, DBU-Promoted α-Acylation of 2-Oxindoles through Acyl C–C Bond Cleavage: Imidazolium Salts as an Emerging Acylating Agent, *Asian J. Org. Chem.*, 2020, **9**, 769–772; (*c*) P. K. R. Panyam, R. Sreedharan and T. Gandhi, Synthesis of topologically constrained naphthalimide appended palladium (II) – *N*-heterocyclic carbene complexes-insights into additive controlled product selectivity, *Org. Biomol. Chem.*, 2020, **18**, 3843–3847.

35 R. Sreedharan, P. K. Pal, P. K. R. Panyam, U. D. Priyakumar and T. Gandhi, Synthesis of α-Aryl Ketones by Harnessing the Non-Innocence of Toluene and its Derivatives: Enhancing the Acidity of Methyl Arenes by a Brønsted Base and their Mechanistic Aspects, *Asian J. Org. Chem.*, 2022, **11**, 3–8.

36 (*a*) D. J. Hart, K. Kanai, D. G. Thomas and T. K. Yang, Preparation of primary amines and 2-azetidinones *via* *N*-Trimethylsilyl imines, *J. Org. Chem.*, 1983, **48**, 289–294; (*b*) Z. Wang, Z. Zheng, X. Xu, J. Mao and P. J. Walsh, One-pot aminobenzylation of aldehydes with toluenes, *Nat. Commun.*, 2018, **9**, 1–8; (*c*) H. Guan, X. Cao, P. J. Walsh and J. Mao, One-Pot Aminoalkylation of Aldehydes: Diastereoselective Synthesis of Vicinal Diamines with Azaarylmethylamines, *Org. Lett.*, 2019, **21**, 8679–8683; (*d*) G. Liu, P. J. Walsh and J. Mao, Alkaline-Metal-Catalyzed One-Pot Aminobenzylation of Aldehydes with Toluenes, *Org. Lett.*, 2019, **21**, 8514–8518.

37 J. R. Bowser, P. J. Williams and K. Kurz, Cleavage of silicon-nitrogen bonds by acid chlorides: an unusual synthetic route to amides, *J. Org. Chem.*, 1983, **48**, 4111–4113.