Research Article

***N*-tert-Butoxycarbonylation of Structurally Diverse Amines and Sulfamides under Water-Mediated Catalyst-Free Conditions**

**Zinelaabine Cheraïet, Souad Ouarna, Sihem Hessainia,
Malika Berredjem, and Nour-Eddine Aouf**

*LCOA, Bioorganic Chemistry Group, Chemistry Department, Sciences Faculty, Badji Mokhtar-Annaba University,
P.O. Box. 12, 23000 Annaba, Algeria*

Correspondence should be addressed to Nour-Eddine Aouf, noureddineaouf@yahoo.fr

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A simple, efficient, and eco-friendly protocol for the *N*-Boc protection of the amine moiety in a variety of compounds with di-*tert*-butyl dicarbonate under water-acetone catalyst-free conditions is described. The corresponding monocarbamate is obtained in excellent yields on short reaction times. No competitive side reactions such as isocyanate urea and O-Boc were observed. This method represents a reasonable alternative to the previous reported protection procedures.

1. Introduction

The protection of a functional group can be essential in the chemistry of poly functionalised molecules, when a reaction has to be carried out in a part of the compounds without the rest perturbing of the molecule. The development of simple and eco-friendly methods for the protection and deprotection of functional group continues to be a significant tool in synthetic chemistry of polyfunctional molecules [1, 2].

Nitrogen protection continues to attract a great deal of attention in a wide range of chemical fields, such as peptides, nucleosides, heterocyclic compounds, and other natural products. The protection of amines with *tert*-butoxycarbonyl (Boc) group is a widely used reaction in organic synthesis because of its inertness toward catalytic hydrogenolysis and resistance toward hydrolysis under most basic conditions and nucleophilic reagents [3]. *N*-Boc deprotection is generally achieved under mild acidic conditions such as trifluoroacetic acid (TFA), aqueous phosphoric acid in THF [4], or Lewis acid [5]. The deprotection can be carried out with montmorillonite K.10 clay [6], silica gel at low pressure [7], and by thermolytic cleavage although at high temperature [8, 9].

The *tert*-butoxycarbonyl (Boc) is easily introduced using commercially available di-*tert*-butyldicarbonate (*tert*-BuOCO)₂O under standard basic conditions. Various reagents and methods have been developed in the last years for the *N*-*tert*-butoxycarbonylation of amines. Most are carried out in the presence of an organic or inorganic base. Amines are converted to *N*-*tert*-Boc derivatives by reaction with di-*tert*-butyldicarbonate (Boc)₂O in the presence of: 4-(dimethylamino)-1-*tert*-butylcarbonylpyridinium DMAP [10], 4-(dimethylamino)-1-*tert*-butylcarbonyl pyridinium chloride [11] or tetrafluoroborate in aq NaOH [12], *tert*-butyl-2-pyridyl carbonate in the presence of K₂CO₃ in H₂O-DMF [13] or *tert*-butyl 1-chloroethyl carbonate in presence of K₂CO₃ in H₂O-THF [14], 2-*tert*-butoxycarbonyloxyimino-2-phenylacetoneitrile in the presence of Et₃N in H₂O-dioxane [15]. However, these protocols have various drawbacks as long times, preparation of *tert*-butoxycarbonylation reagents, and requirement of auxiliary substances.

The base-catalyzed reactions are often associated with the formation of isocyanate [16], urea [10], and *N*, *N*-di-Boc derivatives [17]. Moreover, the high toxicity of DMAP and reagents derived from it limits their use [18].

TABLE 1: *N*-Boc protection of amines derivative^a.

Entry	Substrate	Product	Time (min)	Yield* (%)
1			5	93
2			7	94
3			10	90
4			8	95
5			8	97
6			12	90
7			8	92
8			5	95

* All reactions conducted with 1 mmol of substrate in 1 mL of water : acetone 9.5 : 0.5.

* Isolation yield after purification.

SCHEME 1

The protection can also be affected with mild acidic conditions. There are examples of other modified methods for *ter*-butoxycarbonylation of amines with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [19], Amberlyst 15 [20], Guanidine hydrochloride [21], $\text{Zn}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ [22], ZrCl_4 [23], LiClO_4 [24], $\text{Cu}(\text{BF}_4)_2$ [25], sulfonic acid functionalized silica [26], and $\text{HClO}_4\text{-SiO}_2$ [27].

More recently, Akbari et al. reported an efficient protocol for the *N*-protection of various structurally amines using protic 1, 2, 3, 3-*tetra*-methyguanidinium acetate as recyclable catalyst under solvent free condition at room temperature [28]. Many of these methods suffer from disadvantages such high acidity, expensive reagents, and using more excess. Excessive amounts of catalysts, high temperature and slow rate reaction. Chankeshwara and Chakraborti [29] reported the catalyst-free chemoselective *N-tert*-butyloxycarbonylation of amines in water. This method is not reproducible because the limited solubility of $(\text{Boc})_2\text{O}$ in water under ambient conditions.

In recent years, much attention has been focused on searching greener or environmentally friendly chemical process. Water is the main solvent for life processes, and there is growing interest in using it as green solvent for organic transformations [30, 31]. However, reports about using water as a catalyst to promote organic reactions are very limited. Compared to conventional solvents water is preferred for organic reaction because it displays unparalleled and unique properties. Moreover, it is cheap, nontoxic, non-explosive, and environmentally acceptable [32, 33]. Thus, the

use of water instead of organic solvents has gained much importance in the development of sustainable protection in generally chemistry.

In this paper, we report efficient and eco-friendly protocol for chemoselective *N-tert*-butyloxycarbonylation of various structurally amines in water-related system under ambient conditions in the absence of any acid/base-catalyst.

2. Results and Discussion

In our quest of a “greener” approach toward *N*-Boc protection, we have carried out a series of experiments using commercially available di-*tert*-butyldicarbonate (*tert*-BuOCO)₂O and various structurally amines and water as solvent (Scheme 1). The *N-tert*-butyloxycarbonylation of various amines (Table 1) was carried out in distilled water with a minimum of acetone at room temperature and atmospheric pressure in the absence of any catalyst (Scheme 1).

The reactions were completed after 8–12 min, affording Boc protected amines in good and excellent yields (Table 1) and short time. In each case, only the mono *N*-Boc protected product was found. No isocyanate or urea formation was detected (by NMR of crude products).

The critical amount of water required was found to be 1 mL/mmol of amine and the minimum of the acetone for the solubility of $(\text{Boc})_2\text{O}$. The products were isolated by filtration (for solid products) or extraction with CH_2Cl_2 (for liquid products).

SCHEME 2

SCHEME 3

The chemoselectivity was further demonstrated in the case of *p*-aminophenol (entry 5) that did not form oxazolidinone.

To explore the scope and limitations of this reaction and view of the importance of peptide synthesis, we investigated the Boc-protection of various aminoesters derivatives of (Leu, Ala, Val, Leu, and Phe) (Table 2, entries 9–13).

All *N*-Boc-protected aminoesters were prepared from the corresponding starting from aminoacids after esterification and protection by reacting with $(\text{Boc})_2\text{O}$ in water at room temperature (Scheme 2).

As can be seen (Table 2, entries 9–13), the *N*-Boc protection process was quite satisfactory because it could be quantitatively converted to its *N*-Boc esters of α -amino acids.

It was quite interesting to observe the *N*-Boc protection of many of the substrates gave optically pure *N*-Boc derivatives (as determined by optical rotation and comparison with literature values).

As can be seen from results in Table 2, the isolated yield of 9a–13a were in the range of 92–96%, the reaction could be completed in 5 min and 12 min.

Encouraged by these experimental results, we extended our studies to series carboxylsulfamides aminoester derivatives (Scheme 3, Table 3).

The preparation of sulfamides amino-esters derivatives (14–19) was performed in four steps starting from amino acids (Gly, Ala, Val, Leu, and Phe) and chlorosulfonyl isocyanate (CSI) and *tert*-butanol after four steps: esterification-sulfamoylation, carbamoylation, and deprotection previously described [34].

The *N*-Boc protection reaction was studied using compounds 14–18 as substrates in the same conditions. 1.0 mmol was treated with $(\text{Boc})_2\text{O}$ 260 mg, 1 mmol in water : acetone at room temperature (Table 3, entries 14–18). The reaction was monitored by TLC. In most of cases, the desired product was obtained in good at excellent yields (Scheme 3).

The reaction preserves stereochemical integrity of amino esters derivatives. The reactions were rapid with most of

the sulfamides studied (5–10 min) and were compatible with diverse sulfamides.

The propriety of this method can be formative of the application in the organic synthesis and particularly in peptide synthesis.

To explore the scope and limitations of this reaction, we extended our study the *N*-protection of cyclosulfamides (Scheme 4).

The synthesis of the cyclosulfamides (entries 19–23) was achieved starting from CSI, and amino acids (Gly, Ala, Val, Leu, and Phe) according a general procedure previously described [34]. The derivatization of amino acids allowed the introduction of an alkyl group on C-4 well-defined configuration.

The cyclosulfamides (Table 4, entries 19–23) were tested under the same conditions of present protocol. The reaction is monitored by TLC, which indicates complete disappearance of (19–23) within 8 min at room temperature and atmospheric pressure, to afford the corresponding *N*-protected cyclosulfamides (19a–23a) with excellent yields.

N-Boc chiral cyclosulfamides entry (19–23) gave optically *N*-*t*-Boc derivatives (as determined by optical rotation and HPLC). In all cases, the *N*-protected cyclosulfamides (19a–23a) were less polar than his precursor (TLC).

To explore the mechanism of these processes, we assume that hydrogen bond formation between water and the carbonyl oxygen atom of $(\text{Boc})_2\text{O}$ causes electrophilic activation of the carbonyl group which make more susceptible to nucleophilic attack. Intramolecular nucleophilic attack by the nitrogen atom on the carbonyl carbon activated followed by release of CO_2 , *t*-BuOH, H_2O and forms the carbamate (Scheme 5).

The structures of all the compounds were unambiguously confirmed by usual spectroscopic methods. For the final derivatives, the different NMR spectra showed a signal of NH proton and appearance of signal corresponding to the *tert*-butyl protons. These compounds exhibited characteristic absorption in the IR spectrum with the absorption at $1702\text{--}1712\text{ cm}^{-1}$ ($\text{C}=\text{O}$).

SCHEME 4

TABLE 2: *N*-Boc protection of aminoesters^a.

Entry	Substrate	Product	Time (min)	Yield* (%)
9			5	96
10			10	94
11			8	92
12			10	95
13			5	95

^a All reactions conducted with 1 mmol of substrate in 1 mL of water: acetone 95:5.

* Isolation yield after purification.

SCHEME 5: Electrophilic activation of $\text{Boc}_2(\text{O})$ during water-mediated catalyzed the *N*-Boc formation from amines.

3. Conclusions

In summary, we have developed a novel and efficient route for water-mediated *N*-*tert*-butoxycarbonylation of amines at room temperature. The absence of acid/base and the use of water makes present procedure environmentally friendly. We are exploring the protection of various diverse amines

with other protecting groups applications and will report the finding in due course.

4. Experimental Section

All commercial chemicals and solvents were without further purification. All reactions were carried out under inert argon atmosphere. Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded in a 250 MHz Brücker spectrometer. Microanalysis was performed in the microanalysis laboratory of ENSCM (Montpellier). Chemical shifts are reported in δ units (ppm) with TMS as reference. All coupling constants *J* are reported in Hertz. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and combination of these signals. Electron Ionisation mass spectra (30 eV) were recorded in positive or negative mode on a Water MicroMass ZQ. High-resolution mass spectra were measured on a Jeol SX102 mass spectrometer and recorded in FAB positive mode. All reactions were monitored by TLC on silica Merck 60 F254 precoated aluminium plates and were developed by spraying with ninhydrin solution. Optical rotations were measured on a JUSCO DIP-370 digital polarimeter. Columns

TABLE 3: *N*-Boc protection of linear carboxysulfamides^a.

Entry	Substrate	Product	Time (min)	Yield* (%)
14			5	56
15			10	94
16			10	90
17			15	97
18			6	92

^a All reactions conducted with 1 mmol of substrate in 10 mL of water : acetone 9.5 : 0.5.

* Isolated yield after purification.

TABLE 4: *N*-Boc protection of cyclosulfamides^a.

Entry	Substrate	Product	time (min)	Yield* (%)
19			3	90
20			5	96
21			9	95
22			8	93
23			6	90

^a All reactions conducted with 1 mmol of substrate in 10 mL of Water : acetone 9.5 : 0.5.

* Isolated yield after purification.

chromatographies were performed on Merck silica gel (230–400 mesh). Compounds 1–9 are available commercially N2-Boc-4-alkyle-N5-benzyl-1,2,5thiadiazolidine 1,1-dioxide (1–5).

The synthesis of the compounds, starting from (CSI) chlorosulfonyl isocyanate *tert*-butyl alcohol and methyl esters of amino acids (glycine, L-alanine, L-leucine, and L-phenylalanine) has been previously reported [34].

***N*-Boc Protection: General Procedure.** In a 50 mL round flask with 9.5 mL of distilled water and 0.5 mL acetone, 1 mmol of amine was added, the mixture was stirred at room temperature for the few minutes.

Dichloromethane was added (5 mL), and the mixture was stirred. Progress of the reaction is monitored by TLC, which indicates complete disappearance of precursors amines. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuum. The residue was purified by column chromatography on silica gel with (CH₂Cl₂/MeOH, 9:1) to afford the *N*-Boc amines derivatives in high yields.

The synthesis of the compounds 14–23 has been previously reported for our research group [35, 36].

(*S*)-Methyl 2-((*N*-(*Tert*-Butoxycarbonyl)Sulfamoyl)Amino)-3-Methylbutanoate **16a**. (Yield 92%); $R_f = 0.72$ (CH₂Cl₂-MeOH, 9:1), (mp 89–90°C), $[\alpha]_D = +2.5$ ($c = 1$, EtOH), (KBr) ν , cm⁻¹: 1752 and 1697 (C=O), 1352 and 1158 (SO₂); 3332, 3258 and 3274 (NH), 2964 (CH). ¹H NMR (CDCl₃): δ 7.20 (s, H, NH-Boc), 5.75 (d, $J = 8.3$ Hz, 1H, NH), 3.90 and 3.95 (dd, $J = 4.8$ and $J' = 4.8$ Hz, 1H, C*H); 3.78 (s, 3H, OCH₃); 2.20 (m, 1H, 3H, CH *i*Pr); 0.90 and 1.10 (2d, $J = 6.8$ Hz, 6H, 2CH₃), 1.45 (s, 9H, *t*-Bu). ¹³C NMR spectrum (125 MHz, CDCl₃): δ , ppm (J , Hz): 19.70, 20.00, 27.56, 30.30, 56.70, 62.20, 84.34, 153.56, 175.60.

Mass Spectrum (ESI⁺, 30 eV), m/z (I_{rel} , %): 311 [M+H]⁺ (100). Found, %: C, 34.42; H, 6.71; N, 13.12. C₆H₁₄N₂O₂S. Calculated, %: C, 34.28; H, 6.66; N, 13.33.

(*S*)-Methyl 2-((*N*-(*Tert*-Butoxycarbonyl)Sulfamoyl)Amino)-4-Methylpentanoate **17a**. (Yield 95%); $R_f = 0.67$ (CH₂Cl₂-MeOH, 9:1), (mp 67–68°C), $[\alpha]_D = -14.5$ ($c = 1$, MeOH), (KBr) ν , cm⁻¹: 1751 and 1698 (C=O), 1358 and 1162 (SO₂); 3310 and 3251 (NH), 2987 (CH). ¹H NMR spectrum (250 MHz, CDCl₃): δ , ppm (J , Hz): 7.25 (s, H, NH-Boc), 5.20 (s, 1H, NH exch), 4.25 (t, $J = 7.4$, 1H, C*H); 3.66 (s, 3H, OCH₃); 1.85 (m, 1H, *i*Pr), 1.55 (m, 2H, CH₂ β); 1.48 (s, 9H, *t*-Bu), 0.93 and 0.75 (2d, $J = 2.9$, 6H, 2CH₃). ¹³C NMR spectrum (125 MHz, CDCl₃): δ , ppm (J , Hz): 21.32, 22.73, 24.38, 27.52, 41.40, 52.77, 54.74, 84.54, 152, 20, 174.79.

Mass Spectrum (ESI⁺, 30 eV), m/z (I_{rel} , %): 325 [M+H]⁺, (100).

Found, %: C, 37.46; H, 7.13; N, 12.54. C₇H₁₆N₂O₂S. Calculated, %: 37.50; H, 7.14; N, 12.50.

(*S*)-Methyl 2-((*N*-(*Tert*-Butoxycarbonyl)Sulfamoyl)Amino)-3-Phenylpropanoate **18a**. (Yield 95%); $R_f = 0.68$ (CH₂Cl₂-MeOH, 9:1), (mp 131–132°C), $[\alpha]_D = +12$ ($c = 1$, MeOH), IR (KBr, ν cm⁻¹): 1745 and 1702 (C=O), 1338 and 1152 (SO₂);

3312, 3245, 3482, (NH). ¹H NMR spectrum (250 MHz, CDCl₃): δ , ppm (J , Hz): 7.25 (s, H, NH-Boc), 7.25 (m, 5H, Ar-H), 7.10 (s, H, NH-Boc), 5.60 (d, 1H, $J = 8.8$ Hz, NH), 4.90 (s, 2H, NH₂), 4.40 (dt, $J = 5.5$ Hz and $J' = 8.8$ Hz, 1H, C*H); 3.65 (s, 3H, OCH₃); 3.00 and 3.20 (2dd, (ABX system) ¹ $J = 5.7$, ² $J = 7.00$ and $J_{gem} = 13.8$, 2H, CH₂), 1.45 (s, 9H, *t*-Bu). ¹³C NMR spectrum (125 MHz, CDCl₃): δ , ppm (J , Hz): 27.45, 39.50, 52.50, 58.60, 84, 67, 127.70, 129.80, 129.90, 137.30, 150.00, 173.50. Mass Spectrum (ESI⁺, 30 eV), m/z (I_{rel} , %): 359 [M+H]⁺ (100). Anal. Calcd for C₁₀H₁₄N₂O₂S; C, 46.51; H, 5.42; N, 10.85. Found; C, 46.49; H, 5.39; N, 10.80.

(*R*)-*Tert*-Butyl 5-Benzyl-4-Isopropyl-1,2,5-thiadiazolidine-2-Carboxylate 1,1-Dioxide **21a**. (Yield 96%); $R_f = 0.72$ (CH₂Cl₂-MeOH, 95-5); (mp 82–84°C), $[\alpha]_D = +5$ ($c = 1$, EtOH). (KBr) ν , cm⁻¹: 3331 and 3314 (NH); 1345 and 1165 (SO₂), 1708 (CO). ¹H NMR spectrum (250 MHz, CDCl₃): δ , ppm (J , Hz): 7.40 (m, 5H, ArH); 4.35 (d, $J = 13.8$ Hz, 1H, CH₂-Ph); 3.95 (d, $J = 13.8$ Hz, 1H, CH₂-Ph); 3.40 (m, 3H, *CH and CH₂); 2.8 (m, 1H, CH *i*Pr); 1.58 (s, 9H, *t*-Bu), 0.90 and 1.00 (2d, $J = 6.7$ Hz, 6 H, 2CH₃). ¹³C NMR spectrum (125 MHz, CDCl₃): δ , ppm (J , Hz): 166.65, 139.2, 128.3, 129.4, 12.5, 84, 52, 51.2, 50.6, 32.3, 27, 42, 23.5, 19.4, 18.2.

Mass Spectrum (ESI⁺, 30 eV), m/z (I_{rel} , %): 355. [M+H]⁺ (72), 91 [Bn]⁺ (80).

Anal. For C₁₂H₁₈N₂O₂S Calcd: C, 56.69; H, 7.08; N, 11.02. found: C, 56.67; H, 7.14; N, 10.95.

(*R*)-*Tert*-Butyl 4,5-Dibenzyl-1,2,5-thiadiazolidine-2-Carboxylate 1,1-Dioxide **23a**. (Yield = 93%); $R_f = 0.52$ (CH₂Cl₂); (mp 97–98°C), $[\alpha]_D = -23^\circ$ ($c = 1$, EtOH). (KBr) ν , cm⁻¹: 3269 (NH); 1338 and 1172 (SO₂). ¹H NMR spectrum (250 MHz, CDCl₃): δ , ppm (J , Hz): 7.52 (m, 10H, ArH); 4.40 (m, 1H, CH_{asy}); 4.10 (d, $J = 13.6$, 1H, CH₂-Ph); 4.35 (d, $J = 13.6$, 1H, CH₂-Ph); 2.90 (m, 2H, CH₂); 3.50 and 3.20 (2dd, $J = 18.3$, ¹ $J = 4.7$ and ² $J = 7.3$, Hz, 2H, CH₂-Ph), 1.45 (s, 9H, *t*-Bu). ¹³C NMR spectrum (125 MHz, CDCl₃): δ , ppm (J , Hz): 138.7, 137.3, 129.2, 128.3, 127.5, 127.1, 125.5, 124.5, 57.3, 54.2, 52.1, 42.7.

Mass Spectrum (ESI⁺, 30 eV), m/z (I_{rel} , %): 303 [M+H]⁺ (100), 91 [Bn]⁺ (67).

Found, %: C, 63.51; H, 5.92; N, 9.29. C₁₆H₁₈N₂O₂S. Calculated, %: C, 63.57; H, 5.96; N, 9.27.

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References

- [1] T. W Greene and P. G. Wuts, *Protective Group in Organic Synthesis*, John Wiley, New York, NY, USA, 4rd edition, 2007.

- [2] P. J. Kocienski, *Protecting Groups*, George Thieme, Stuttgart, Germany, 3rd edition, 2004.
- [3] C. Agami and F. Couty, "The reactivity of the *n*-boc protecting group: an underrated feature," *Tetrahedron*, vol. 58, no. 14, pp. 2701–2724, 2002.
- [4] B. Li, R. Bemish, R. A. Buzon et al., "Aqueous phosphoric acid as a mild reagent for deprotection of the *t*-butoxycarbonyl group," *Tetrahedron Letters*, vol. 44, no. 44, pp. 8113–8115, 2003.
- [5] D. S. Bose, K. K. Kumar, and A. V.N. Reddy, "A new protocol for selective deprotection of *N*-*tert*-butoxycarbonyl protective group (*t*-Boc) with $\text{Sn}(\text{OTf})_2$," *Synthetic Communications*, vol. 33, no. 3, pp. 445–450, 2003.
- [6] N. S. Shaikh, A. S. Gajare, V. H. Deshpande, and A. V. Bedekar, "A mild procedure for the clay catalyzed selective removal of the *tert*-butoxycarbonyl protecting group from aromatic amines," *Tetrahedron Letters*, vol. 41, no. 3, pp. 385–387, 2000.
- [7] T. Apelqvist and D. Wensbo, "Selective removal of the *n*-boc protective group using silica gel at low pressure," *Tetrahedron Letters*, vol. 37, no. 9, pp. 1471–1472, 1996.
- [8] V. H. Rawal, R. J. Jones, and M. P. Cava, "Photocyclization strategy for the synthesis of antitumor agent CC-1065: synthesis of dideoxy PDE-I and PDE-II. Synthesis of thiophene and furan analogues of dideoxy PDE-I and PDE-II," *Journal of Organic Chemistry*, vol. 52, no. 1, pp. 19–28, 1987.
- [9] K. Nadia, B. Malika, K. Nawel, B. MedYazid, R. Zine, and N.-E. Aouf, "Simple and efficient cleavage reaction of the Boc Group in heterocyclic compounds," *Journal of Heterocyclic Chemistry*, vol. 41, no. 1, pp. 57–60, 2004.
- [10] Y. Basel and A. Hassner, "Di-*tert*-butyl dicarbonate and 4-(dimethylamino)pyridine revisited. their reactions with amines and alcohols," *Journal of Organic Chemistry*, vol. 65, no. 20, pp. 6368–6380, 2000.
- [11] E. Guibé-Jampel and M. Wakselman, "A water-soluble agent for the *t*-butoxycarbonylation of amines," *Journal of the Chemical Society D*, no. 6, p. 267, 1971.
- [12] G. Le Corre, E. Guibé-Jampel, and M. Wakselman, "Groupements protecteurs benzyloxycarbonyles substitues alcalinobiles," *Tetrahedron*, vol. 34, no. 20, pp. 3105–3112, 1978.
- [13] S. Kim and J. Lee, "T-butyl 2-pyridyl carbonate: a useful reagent for *T*-butoxycarbonylation of amino acids," *Chemistry Letters*, vol. 13, no. 2, pp. 237–238, 1984.
- [14] G. Sennyei, G. Barcelo, and J. P. Senet, "Synthesis and use of dibenzylpyrocarbonate: preparation of dipeptide free *n*-benzyloxycarbonyl glycine," *Tetrahedron Letters*, vol. 27, no. 44, pp. 5375–5376, 1986.
- [15] M. Itoh, D. Hagiwara, and T. Kamiya, "A new *tert*-butyloxycarbonylating reagent, 2-*tert*-butyloxycarbonyloxymino-2-phenylacetone trile," *Tetrahedron Letters*, vol. 16, no. 49, pp. 4393–4394, 1975.
- [16] H. J. Knölker and T. Braxmeier, "Isocyanates—part 3. synthesis of carbamates by dmap-catalyzed reaction of amines with di-*tert*-butyldicarbonate and alcohols," *Tetrahedron Letters*, vol. 37, no. 33, pp. 5861–5864, 1996.
- [17] S. Darnbrough, M. Mervic, S. M. Condon, and C. J. Burns, "An improved synthesis of *N*-Boc protected aryl amines," *Synthetic Communications*, vol. 31, no. 21, pp. 3273–3280, 2001.
- [18] D. V. Sweet, *Registry of Toxic Effects of Chemical Substances 1985-86*, U.S. Government Printing Office, Washington, DC, USA, 1988.
- [19] A. Heydari, R. K. Shiroodi, H. Hamadi, M. Esfandyari, and M. Pourayoubi, "*N*-*tert*-butoxycarbonylation of amines using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as an efficient heterogeneous and recyclable catalyst," *Tetrahedron Letters*, vol. 48, no. 33, pp. 5865–5868, 2007.
- [20] K. Shiva Kumar, J. Iqbal, and M. Pal, "Amberlyst-15: a mild, efficient and reusable heterogeneous catalyst for *N*-*tert*-butoxycarbonylation of amines," *Tetrahedron Letters*, vol. 44, no. 8113–8115, pp. 385–387, 2003.
- [21] F. Jahani, M. Tajbakhsh, H. Golchoubian, and S. Khaksar, "Guanidine hydrochloride as an organocatalyst for *N*-Boc protection of amino groups," *Tetrahedron Letters*, vol. 52, no. 12, pp. 1260–1264, 2011.
- [22] G. Bartoli, M. Bosco, A. Carlone, M. Locatelli, P. Melchiorre, and L. Sambri, "Asymmetric catalytic synthesis of enantiopure *N*-protected 1,2-amino alcohols," *Organic Letters*, vol. 6, no. 22, pp. 3973–3975, 2004.
- [23] G. V. M. Sharma, J. Janardhan Reddy, P. Sree Lakshmi, and P. Radha Krishna, "Rapid and facile lewis acid catalysed boc protection of amines," *Tetrahedron Letters*, vol. 45, no. 37, pp. 6963–6965, 2004.
- [24] A. Heydari and S. E. Hosseini, "Lithium perchlorate-catalyzed boc protection of amines and amine derivatives," *Advanced Synthesis and Catalysis*, vol. 347, no. 15, pp. 1929–1932, 2005.
- [25] S. V. Chankeshwara and A. K. Chakraborti, "Copper(ii) tetrafluoroborate as a novel and highly efficient catalyst for *N*-*tert*-butoxycarbonylation of amines under solvent-free conditions at room temperature," *Tetrahedron Letters*, vol. 47, no. 7, pp. 1087–1091, 2006.
- [26] B. Das, K. Venkateswarlu, M. Krishnaiah, and H. Holla, "A highly chemoselective boc protection of amines using sulfonic-acid-functionalized silica as an efficient heterogeneous recyclable catalyst," *Tetrahedron Letters*, vol. 47, no. 43, pp. 7551–7556, 2006.
- [27] A. K. Chakraborti and S. V. Chankeshwara, " $\text{HClO}_4\text{-SiO}_2$ as a new, highly efficient, inexpensive and reusable catalyst for *N*-*tert*-butoxycarbonylation of amines," *Organic and Biomolecular Chemistry*, vol. 4, no. 14, pp. 2769–2771, 2006.
- [28] J. Akbari, A. Heydari, L. Ma'mani, and S. Hassan Hosseini, "Protic ionic liquid [TMG][Ac] as an efficient, homogeneous and recyclable catalyst for BOC protection of amines," *Comptes Rendus Chimie*, vol. 13, no. 5, pp. 544–547, 2010.
- [29] S. V. Chankeshwara and A. K. Chakraborti, "Catalyst-free chemoselective *N*-*tert*-butyloxycarbonylation of amines in water," *Organic Letters*, vol. 8, no. 15, pp. 3259–3262, 2006.
- [30] P. A. Grieco, *Organic Synthesis in Water*, Blackie Academic and Professional, London, UK, 1998.
- [31] C.J. Li and T. H. Chang, *Organic Reactions in Aqueous Media*, Wiley, New York, NY, USA, 1997.
- [32] A. R. Katritzky, S. M. Allin, and M. Siskin, "Aqueous thermolysis: reactions of organic compounds with superheated water," *Accounts of Chemical Research*, vol. 29, no. 8, pp. 399–406, 1996.
- [33] J. Fraga-Dubreuil and M. Poliakoff, "Organic reactions in high-temperature and supercritical water," *Pure and Applied Chemistry*, vol. 78, no. 11, pp. 1971–1982, 2006.
- [34] N. Aouf, G. Dewynter, and J. L. Montero, "Synthesis and cyclization of carboxylsulfamides of amino acid derivatives," *Tetrahedron Letters*, vol. 32, no. 45, pp. 6545–6546, 1991.
- [35] Z. Regaïnia, M. Abdaoui, N. E. Aouf, G. Dewynter, and J. L. Montero, "Synthesis of 1,2,5-thiadiazolidines 1,1-dioxides (cyclosulfamides) starting from amino acids and chlorosulfonyl isocyanate," *Tetrahedron*, vol. 56, no. 3, pp. 381–387, 2000.

- [36] M. Berredjem, H. Djebbar, Z. Regainia et al., "Regiospecific synthesis and N-acylation of chiral 1,2,5-thiadiazolidines 1,1-dioxides," *Phosphorus, Sulfur and Silicon and the Related Elements*, vol. 178, no. 4, pp. 693–705, 2003.