

Selectfluor 介导的高效高选择性地脱除叔丁氧羰基方法研究

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摘要 商品化的 selectfluor[即 1-氯甲基-4-氟-1,4-重氮化二环 2.2.2 辛烷双(四氟硼酸)盐]具有不吸潮的特性, 是一种被应用得最为广泛的氟代试剂。因此, 发现并理解其新的反应特性对于应用该试剂具有非常重要的意义。本工作报道了 selectfluor 可以用于选择性脱除双保护氨基上的一个叔丁氧羰基保护基。该方法具有条件温和、操作简单、化学选择性好等特点。跟其他方法相比, 该脱保护方法有一定的应用价值, 被成功应用于一系列氨基酸衍生物的脱保护, 在医药上合成有潜在用途的嘌呤衍生物。以氘代乙腈为溶剂的核磁反应实验解释了为什么该反应需要等物质的量的 selectfluor 试剂。

关键词 selectfluor; 叔丁氧羰基; 脱保护; 选择性; 合成

Efficient and Chemoselective Deprotection of *N*-*t*-Butyloxycarbonyl Group Mediated by SelectfluorZeng, Yijie^a Duan, Yue^a Zhao, Hui^{*,b} Hu, Xiangguo^{*,a}^(a) National Engineering Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022)^(b) Anhui Engineering Technology Research Center for Extraction and Isolation of Active Components, Anhui Academy of Applied Technology, Hefei 230031)

Abstract Selectfluor, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2] octane bis(tetrafluoroborate), is among the most popular fluorinating reagents owing to its commercial availability and non-hygroscopic property. The discovery and understanding of new reactivities of selectfluor are thus important for reaction design and optimization when this popular reagent is employed. It has been found that selectfluor could selectively remove Boc group from doubly protected amines in acetonitrile. This deprotection could be of interest when compared to other reported methods, not only because selectfluor is a solid and easy-to-handle, but also because the reaction is mild, operationally simple and chemoselective. The potential usefulness of this method is demonstrated by the deprotection of a series of protected amino acids and a one-step synthesis of pharmaceutically important purine derivative. The NMR experiments conducted in CD₃CN explain why stoichiometric amount of selectfluor is needed for a successful reaction.

Keywords selectfluor; *t*-butyloxycarbonyl; deprotection; selectivity; synthesis

Selectfluor, (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate)), is among the most popular electrophilic fluorinating reagents owing to its commercial availability and non-hygroscopic property.^[1] At the same time, the relatively weak N—F bond (homolytic bond dissociation energy: 254.9 kJ/mol in CH₃CN) also renders it as a powerful radical fluorine source in the presence of photocatalysts or transition-metal catalysts.^[2] Furthermore, it can also be used as an oxidant owing to its

strong oxidative property.^[3] The discovery and understanding of new reactivities of selectfluor are thus important for reaction design and optimization when this popular reagent is employed.

The *t*-butyloxycarbonyl (Boc) group is one of the most commonly used protective group of amine in organic synthesis, because of the ease of incorporation and removal of this group when necessary, as well as its chemical orthogonality with other common amine protecting groups such as

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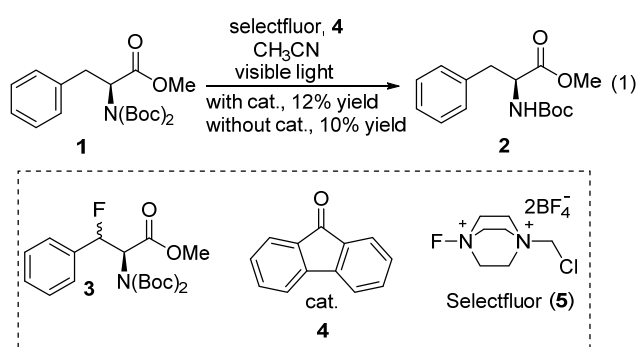
国家自然科学基金(No. 21502076)、江西省自然科学基金(No. 20161BAB213068)、合肥市百人计划及江西省杰出青年基金(No. 20171BCB23039)资助项目。

carboxybenzyl (Cbz) and fluorenylmethoxycarbonyl (Fmoc). Although it is common to protect an amine group with mono-Boc group, double protection of amine with *N,N*-di-Boc or *N,N*-Boc, carbamate group is necessary under various circumstances. For example, di-Boc protected amines are frequently used as convenient phthalimide equivalents in Mitsunobu and Gabriel reactions.^[4] Double protection of amine with Boc is also required to resist strong oxidation conditions.^[5] The selective deprotection of Boc group from doubly protected amine is hence desirable. Although the deprotection of Boc protecting group is well documented,^[4] only a few methods are suitable for the selective removal of Boc group from a doubly protected amine.^[6]

Herein, we report a new mode of reactivity of selectfluor. We demonstrate for the first time that selectfluor can selectively remove Boc group from di-protected amines in acetonitrile under mild conditions in a chemoselective fashion.

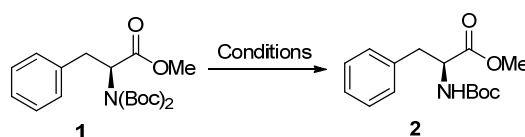
1 Results and discussion

As a continuing interest in stereoselectively fluorinated compounds,^[7] recently we conducted the photo-catalyzed benzylic fluorination developed by Chen and co-workers,^[8] using di-Boc protected phenyl alanine **1** as the substrate. To our surprise, no desired product **3** was observed after 24 h, but the Boc deprotected compound **2** was obtained instead in low yield (Eq. 1). We quickly realized the potential of selectfluor for the selective removal of a Boc group, and set out for further investigation.



Initially, We chose compound **1** for the optimization of reaction condition. When 1 equiv. of selectfluor reagent in acetonitrile was used, 50 °C was needed to get a full conversion and the desired product **2** was obtained in 85% yield (Table 1, Entry 2). Increasing the temperature gave lower yield possibly due to the deprotection of the two Boc groups on compound **1** (Entry 3). Varying the amount of selectfluor showed that the highest yield was obtained when 1 equiv. of selectfluor was employed (Entries 4~6). Solvents screening showed that acetonitrile was the best choice for this transformation. Thus, the optimized conditions are as follows: substrates (0.25 mmol), selectfluor (1.0 equiv.), and CH₃CN (5 mL), stirring for 10 h at 50 °C.

Table 1 Optimization of the reaction condition for the deprotection of *N*-Boc group^a



Entry	Selectfluor/equiv.	Solvent	<i>t</i> /°C	Yield/%
1	1.0	CH ₃ CN	40	76
2	1.0	CH₃CN	50	85
3	1.0	CH ₃ CN	70	77
4	0.5	CH ₃ CN	50	60
5	0.8	CH ₃ CN	50	78
6	2.0	CH ₃ CN	50	85
7	1.0	THF	50	trace
8	1.0	EtOAc	50	trace
9	1.0	CHCl ₃	50	trace
10	1.0	CH ₂ Cl ₂	50	trace
11	1.0	MeOH	50	13
12	1.0	DMSO	50	23
13	1.0	DMF	50	Trace

^a All of the reactions were carried out on 0.25 mmol scale for 10 h.

With the optimized condition in hand, we next proceeded to test of the substrate scope. As shown in Table 2, deprotection of the Boc group from di-Boc protected phenylalanine **1** proceeded well to furnish the corresponding mono *N*-Boc products **2** in good yield (Table 2, Entry 1). Other carbamates protected phenylalanines **6**, **8** and **10** were also viable substrates. In these cases, the *N*-Boc group was removed selectively in high yields, leaving the *N*-Cbz, *N*-CO₂Me and *N*-CO₂Et groups intact (Entries 2~4). It is interesting to note that this condition only deprotected *N*-Boc from the *N,N*-carbamate, Boc-protected substrates. *N,N*-Ts, Boc- and *N,N*-Ac, Boc-protected substrates **12**, **14** were stable under the reaction conditions (Entries 5, 6). This interesting selectivity is obviously different from the previous methods and may be useful for the design of chemoselective reactions.^[6c,6e] The reaction condition is suitable for the deprotection of other protected amino acids, and compounds **16**, **18**, **20**, **22**, **24**, **26**, **28**, **30** and **32** all underwent the deprotection smoothly to afford the desired products in good yields (Entries 7~15). It is noteworthy that the deprotection took place without affecting the chiral center of the α -amino acids tested. The comparison experiments showed that deprotected amino acids with one chiral center such as **2**, **7**, **9**, **11** have identical specific rotation to the samples obtained from the free phenylalanine through selective protection,^[9] and the ¹H NMR of crude products **25** and **33** also indicated no detectable epimerization. Although *O*-Boc is generally believed to be much more labile than its *N*-counterpart, *N*-Boc group can be removed selectively under this condition (Entry 16). Other common protecting groups for hydroxyl, such as benzoyl (Bz) and *tert*-butyloxycarbonyl (TBS), were quite compatible with the reaction conditions (Entries 17, 18). The relative low yield of TBS-substrates might be due to the

Table 2 Test of the substrate scope

$$\text{R}^2\text{-N(R}^1\text{)-Boc} \xrightarrow[\text{CH}_3\text{CN, 50 } ^\circ\text{C, 24 h}]{\text{F-N}^+\text{-(pyrrolidine ring)-Cl} \cdot 2\text{BF}_4^-} \text{R}^2\text{-NH-R}^1$$

Entry	Substrate	Product	Yield/%	Entry	Substrate	Product	Yield/%
1			85	11			73
2			80	12			70
3			84	13			77
4			76	14			89
5			0	15			78
6			0	16			71
7			77	17			72
8			86	18			62
9			83	19			82
10			81	20			60

presence of small amount of fluoride ion (Entry 18). *N*-Boc could be also selectively removed from a benzyl amine substrate in good yield (Entry 19). Finally, this conditions could be used to prepare the mono-Boc protected purine **43** in one-step in 10 h. Previously, this pharmaceutically important compound needed to be prepared from **42** in two steps and 4 d.^[10] This experiment thus demonstrated the potential usefulness of this method.

As for the mechanism, we postulated that selectfluor may serve as a Lewis acid to effect the deprotection of Boc group owing to the F^+ nature of this reagent.^[6a–6e,11] Similar mechanism for the deprotection of doubly protected amino group with an iron catalyst has been reported previously.^[6c] The need of stoichiometric amount of selectfluor may be due to the decomposition of this reagent under the reaction conditions. This was supported by the NMR experiment of **1** in CD_3CN , in which significant amount of unidentified decomposed product (possibly **44**, two peaks at around δ 3.5~4.0) of selectfluor (two peaks at around δ 4.4 and 4.75) was visible in the 400 MHz 1H NMR spectra (Figure 1).

3 Conclusions

Based on the unexpected observation when conducting the Chen's procedure for the benzylic fluorination of **1**,^[8] It has been found for the first time that selectfluor could selectively remove a Boc group from doubly protected amines in acetonitrile. This deprotection could be of interest when compared to other reported methods,^[6a–6e] not only because selectfluor is a solid and easy-to-handle, but also because the reaction is mild, operationally simple and chemoselective. The potential usefulness of this method is demonstrated by the deprotection of a series of protected amino acids and a one-step synthesis of pharmaceutically important purine **43**. The NMR experiment conducted in CD_3CN explains why stoichiometric amount of selectfluor is needed for a successful reaction. In addition to providing a new method for deprotection, the reactivity of selectfluor demonstrated in this work should be valuable for reaction

design and optimization when this popular fluorinating reagent is employed.

4 Experimental section

4.1 General information

All reagents were used as received from commercial sources without further purification or prepared as described in the literature. All solvents were dried over 4 Å molecular sieves before use unless otherwise stated. Reactions were stirred using Teflon-coated magnetic stirring bars. Analytical thin layer chromatography (TLC) was performed with 0.20 mm silica gel 60 F plates with 254 nm fluorescent indicator. TLC plates were visualized by ultra-violet light or by treatment with a spray of Pancaldi reagent $[(NH_4)_6MoO_4, Ce(SO_4)_2, H_2SO_4, H_2O]$ or a solution 0.5% (*V/V*) ninhydrin in *n*-butanol. Chromatographic purification of products was carried out by flash column chromatography on silica gel (230~400 mesh). Melting points were determined using a WRX-4 visual melting point apparatus. Both melting points and boiling points are uncorrected. Infrared spectra were recorded on an IR Affinity-1. NMR spectra were measured in $CDCl_3$ (with TMS as internal standard) or D_2O or MeOD on a Bruker AV400 (1H at 400 MHz, ^{13}C at 100 MHz, ^{19}F at 376 MHz) magnetic resonance spectrometer. High-resolution mass spectra (HRMS) were recorded on a SYNAPT G2Si High Definition MS System. The HRMS were measured under ESI model (specified in the section of characterization data).

4.2 General procedures for selective deprotection of Boc

To a stirred solution of corresponding amine (1 equiv.) in dry MeCN was added selectfluor (1 equiv.) in one portion. Then the mixture was stirred for 24 h at 50 °C, followed by quenching with ethyl acetate and water (*V*:*V*=1:1). The organic phase was washed with brine, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure after filtering. Then the crude product was purified by flash chromatography on silica gel(hexane/EtOAc) to give the

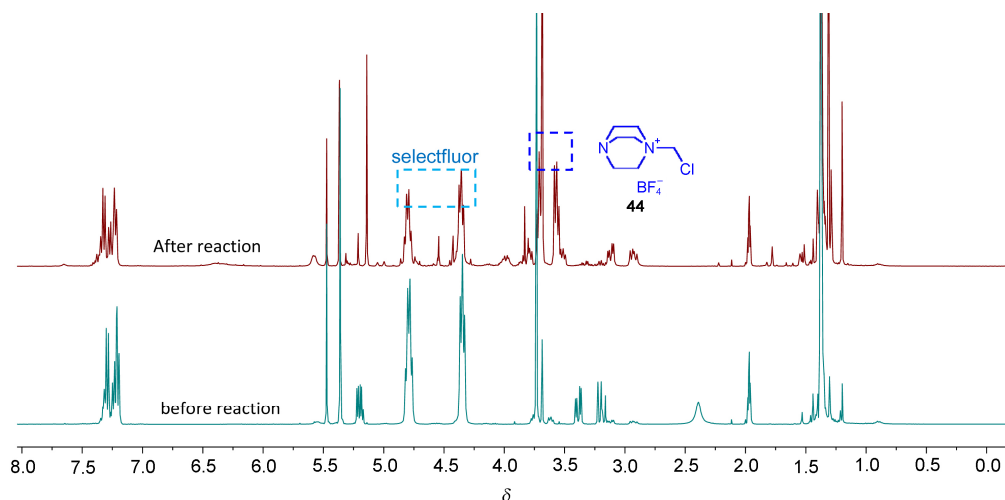


Figure 1 NMR study of deprotection of **1** with selectfluor in $CDCl_3$

deprotected compounds. The NMR data of compounds **2**, **7**, **9**, **11**, **17**, **19**, **21**, **23**, **25**, **27** are shown below. For the data of other compounds please see the Supporting Information.

(S)-Methyl 2-[(*tert*-butoxycarbonyl)amino]-3-phenylpropanoate (**2**): Colorless liquid. $[\alpha]_D^{25} + 40.8$ (c 1.0, CHCl₃) [lit.^[6b] $[\alpha]_D^{25} + 18.4$ (c 1.54, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.25~7.04 (m, 5H), 4.90 (d, *J*=7.29 Hz, 1H), 4.58~4.46 (m, 1H), 3.64 (s, 3H), 3.07~2.95 (m, 2H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.3, 154.0, 135.0, 128.3, 127.5, 126.0, 78.9, 53.4, 51.2, 37.3, 27.3.

(S)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-phenylpropanoate (**7**):^[12] Colorless liquid. $[\alpha]_D^{25} - 22.3$ (c 0.8, MeOH) [lit.^[13] $[\alpha]_D^{30} - 14.9$ (c 1.0, MeOH)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.34~7.26 (m, 10H), 5.22 (d, 1H), 5.09 (d, *J*=2.69 Hz, 2H), 4.66 (ddd, *J*=11.8, 5.9, 5.9 Hz, 1H), 3.72 (s, 3H), 3.17~3.03 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.0, 155.6, 129.3, 128.6, 128.5, 128.2, 128.1, 127.2, 67.0, 54.8, 52.4, 38.2.

(S)-Methyl 2-[(methoxycarbonyl)amino]-3-phenylpropanoate (**9**): Colorless liquid. $[\alpha]_D^{25} + 48.0$ (c 1.0, CHCl₃) [lit.^[14] $[\alpha]_D^{20} + 57.0$ (c 1.0, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.31~7.10 (m, 5H), 5.21 (d, *J*=7.34 Hz, 1H), 4.67~4.62 (m, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.15~3.04 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.1, 156.3, 135.8, 129.2, 128.6, 127.1, 54.8, 52.3, 52.2, 38.3.

(S)-Methyl 2-[(ethoxycarbonyl)amino]-3-phenylpropanoate (**11**):^[15] Colorless liquid. $[\alpha]_D^{25} + 36.2$ (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ : 7.31~7.11 (m, 5H), 5.21 (s, 1H), 4.66~4.61 (m, 1H), 4.09 (dd, *J*=14.20, 7.20 Hz, 2H), 3.70 (s, 3H), 3.15~3.04 (m, 2H), 1.21 (t, *J*=7.20 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.2, 155.9, 135.9, 129.2, 128.6, 127.1, 61.2, 54.7, 52.3, 38.3, 14.5.

Methyl 2-[(*tert*-butoxycarbonyl)amino]acetate (**17**):^[16] Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ : 5.62 (t, *J*=5.81 Hz, 1H), 3.68 (s, *J*=5.81 Hz, 2H), 3.74 (s, 3H), 1.45 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 170.8, 155.8, 79.5, 51.8, 42.0, 28.1.

(S)-Methyl 2-[(*tert*-butoxycarbonyl)amino]propanoate (**19**): Colorless liquid. $[\alpha]_D^{25} - 5.2$ (c 1.0, CHCl₃) [lit.^[6b] $[\alpha]_D^{25} - 2.75$ (c 1.0, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 5.08 (s, 1H), 4.33 (p, *J*=7.4 Hz, 1H), 3.75 (s, 3H), 1.45 (s, 9H), 1.37 (d, *J*=7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 173.8, 155.1, 79.9, 52.3, 49.2, 28.3, 18.7.

(S)-Methyl 2-(((benzyloxy)carbonyl)amino)propanoate (**21**): Colorless liquid. $[\alpha]_D^{25} - 37.5$ (c 1.0, MeOH) [lit.^[17] $[\alpha]_D^{25} - 33.0$ (c 1.0, MeOH)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.41~7.27 (m, 5H), 5.24 (s, 1H), 5.04 (dd, *J*=14.22, 7.02 Hz, 1H), 3.65 (s, 3H), 1.52 (s, 3H), 1.46 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.2, 153.5, 151.1, 135.2, 128.5, 128.4, 128.3, 83.7, 68.8, 54.3, 52.2, 27.9, 15.6.

(S)-Methyl 2-[(*tert*-butoxycarbonyl)amino]-4-methylpentanoate (**23**):^[18] Pale yellow liquid. $[\alpha]_D^{25} - 7.3$ (c 1.0, CHCl₃) [lit.^[19] $[\alpha]_D^{25} - 4.21$ (c 1.56, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 5.23 (d, *J*=8.91 Hz, 1H), 4.34~4.29 (m, 1H), 3.73 (s, 3H), 1.76~1.66 (m, 1H), 1.62~1.44 (m, 2H), 1.44 (s, 9H), 0.95 (d, *J*=2.32 Hz, 3H), 0.94 (d, *J*=

2.32 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 173.8, 155.3, 79.4, 51.9, 41.5, 28.2, 24.6, 22.7, 21.7.

(2S,3S)-Methyl 2-[(*tert*-butoxycarbonyl)amino]-3-methylpentanoate (**25**): Colorless liquid. $[\alpha]_D^{25} + 18.3$ (c 1.0, CHCl₃) [lit.^[20] $[\alpha]_D^{25} + 16.6$ (c 3.7, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 5.07 (d, *J*=9.1 Hz, 1H), 4.27 (dd, *J*=9.1, 4.9 Hz, 1H), 3.73 (s, 3H), 1.96~1.72 (m, 1H), 1.45 (s, 9H), 1.28~1.05 (m, 1H), 0.95~0.98 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.9, 155.5, 79.8, 57.9, 52.0, 38.0, 28.3, 25.0, 15.5, 11.6.

(S)-Dimethyl 2-[(*tert*-butoxycarbonyl)amino]-pentanedioate (**27**):^[21] Colorless oil. $[\alpha]_D^{25} + 15.8$ (c 1.2, CHCl₃) [lit.^[20] $[\alpha]_D^{25} + 12.5$ (c 2.0, CHCl₃)]; ¹H NMR (400 MHz, CDCl₃) δ : 5.06 (d, *J*=7.74 Hz, 1H), 4.26 (s, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 2.41~2.27 (m, 2H), 2.20~2.06 (m, 1H), 1.95~1.82 (m, 1H), 1.37 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.2, 171.6, 154.3, 79.0, 51.8, 51.4, 50.8, 29.0, 27.3, 26.8.

Supporting Information General procedure for the synthesis of the substrates and ¹H NMR, ¹³C NMR spectra of products. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

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