



## MAIN AND BY-PROCESSES AT 1-(2-NITROARYL)-1H-BENZOTRIAZOLE REDUCTION

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**Keywords:** reduction, condensation, alkylation, 1-(2-aminoaryl)-1H-benzotriazoles, azoxybenzene, alkylamines

**Abstract.** The paper investigates the HCl concentration impact on the main and by-processes during the reduction of 1-(2-nitroaryl)-1H-benzotriazole by tin (II) chloride in acidic aqueous-alcoholic medium. The authors have observed the formation of azoxy compounds in addition to the target amino derivative at low HCl content in the reaction mass. The use of 36% hydrochloric acid causes the alkylation of the formed amino compound with alcohol as a solvent.

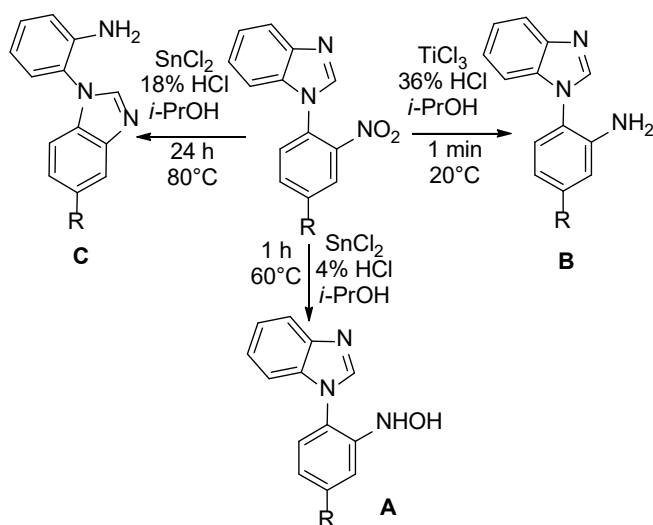
### For citation:

Begunov, R.S., Savina, L.I. & Khlopotinin, A.I. (2024) Main and by-processes at 1-(2-nitroaryl)-1H-benzotriazole reduction, *From Chemistry Towards Technology Step-By-Step*, 5(1), pp. 107-113 [online] Available at: <http://chemintech.ru/index.php/tor/issue/view/2024-5-1>

### Introduction

We have previously studied the reduction of 1-(2-nitroaryl)-1H-benzimidazole [1-3]. We found that, depending on the reaction conditions, the formation of several products is possible: hydroxylamino derivative (A), target amino compound (B), and its isomerization product (C). The regioselectivity of the reduction was most strongly influenced by the HCl content in the reaction mass.

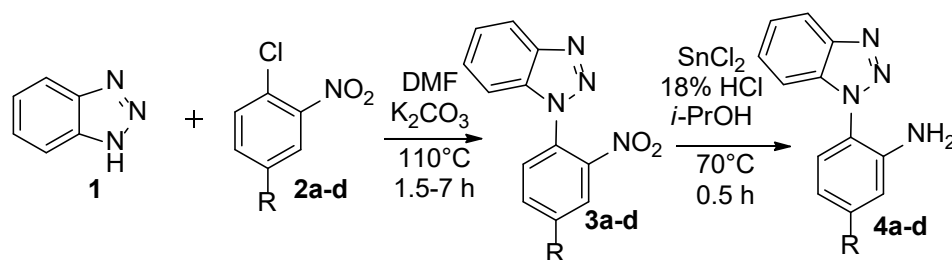
Further, we studied the impact of this factor on the 1(2-nitroaryl)-1H-benzotriazoles reduction. The choice of these substrates is due to resulting N-(aminoaryl)benzotriazole derivatives are widely used in drug development [4-7]. Also, isomerization process can be expected to occur during the reduction.





## Main body

We synthesized 1-(2-nitroaryl)-1*H*-benzotriazoles by the interaction of 1*H*-benzotriazole (**1**) with 1-chloro-2-nitroarenes **2a-d** at DMFA in the presence of  $K_2CO_3$ . According to [8, 9], the reaction of  $S_NAr$  **1** with 2,4-dinitrofluorobenzene under these conditions at 95 °C resulted in the formation of two products: 1- and 2-substituted benzotriazoles in the ratio of 3 : 1. However, only trace amounts of 2-(2-nitroaryl)-2*H*-benzotriazole occur in the reaction mass during the 1st reaction with nitrochloro derivatives at 110 °C. The yield of nitro compounds **3a-d** was 89–94% after recrystallization in isopropanol.

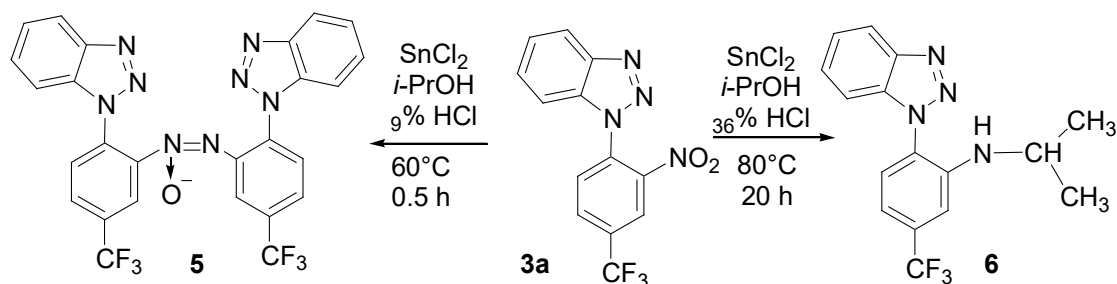


where R = a)  $CF_3$ , b) CN, c)  $COOEt$ , d) Cl

We performed the reduction of 1-(2-nitroaryl)-1*H*-benzotriazoles **3a-d** with tin (II) chloride in acidic aqueous-alcoholic medium. The use of this reducing system enables the efficient preparation of various aminoarenes [10, 11].

We have used isopropanol as a solvent for dissolving N-(2-nitroaryl)benzotriazoles under heating. The use of acetic acid was undesirable due to difficulties with product separation. Other proton solvents did not dissolve all nitro compounds. We added a solution of  $SnCl_2$  in 9-, 18-, or 36% HCl to the resulting solution of nitrosubstrate **3** at 70 °C. Substance **3a** was chosen as a model compound.

A condensation by-process of intermediately formed nitroso- and hydroxylamino derivatives occurred during the reduction of **3a** in a mixture of *i*-PrOH and 9% HCl. A compound with T.melt. 241–246 °C was isolated from the reaction mixture with  $m/z$   $[M]^+$  568 Da. Two sets of 7 aromatic proton signals from two N-arylbenzotriazole fragments of the molecule occur in the  $^1H$  NMR spectrum. The proton signals of one N-aryl substituent were shifted relative to the other one to a weaker field. It is characteristic for aromatic azoxy compounds [12, 13]. There were 26 signals of C atoms in the  $^{13}C$  NMR spectrum. Moreover, the signals of four carbon atoms of  $(C-CF_3)_2$  had the form of a quartet. Based on the data, the isolated substance was identified as 1,2-bis[2-(1*H*-benzotriazol-1-yl)-5-(trifluoromethyl)phenyl]diazene oxide (**5**).





The use of 36% hydrochloric acid contributed to the by-product of amino group alkylation with alcohol. Figure 1 shows the  $^1\text{H}$  NMR spectrum of 1-{2-[(propan-2-yl)amino]-4-(trifluoromethyl)phenyl}-1*H*-benzotriazole (**6**). The NH-, CH-, and  $\text{CH}_3$ -group protons signals occur in the  $^1\text{H}$  NMR spectrum of this compound, appearing in the structure during the nucleophilic substitution of the OH-group by amine. The amount of alkylation product increased with increasing reaction time and temperature up to 80 °C.

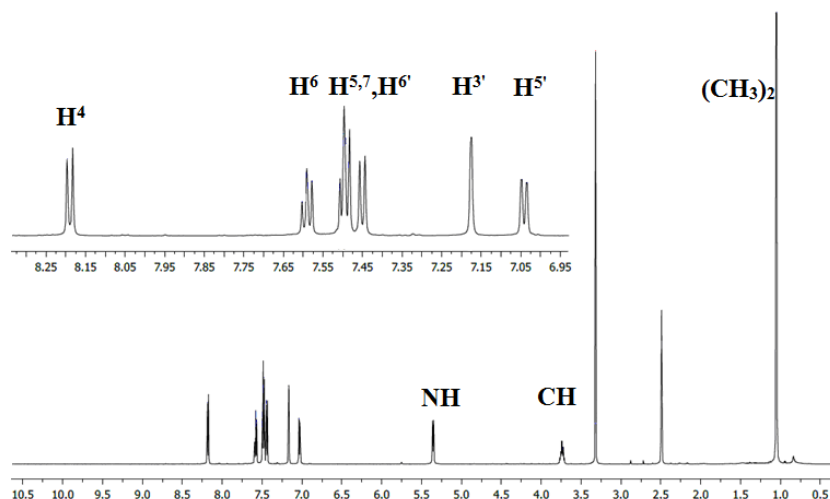


Fig. 1.  $^1\text{H}$  NMR spectrum of 1-{2-[(propan-2-yl)amino]-4-(trifluoromethyl)phenyl}-1*H*-benzotriazole (**6**)

Individually, amino compounds **4** were obtained using 18% HCl. The yield of amines **4** was 94–98%. The isomerization products of *N*-(2-aminoaryl)benzotriazoles were not observed at different HCl content in the reaction mass, as it was observed in the reduction of *N*-(2-nitroaryl)benzimidazoles with  $\text{SnCl}_2$  in acidic water-alcohol medium.

The structure of benzotriazoles **4** was proved by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy and high-resolution mass spectrometry. A complete assignment of proton signals was given by  $^1\text{H}$ - $^1\text{H}$  NMR spectroscopy. Figure 2 shows the  $^1\text{H}$  NMR spectrum of compound **4a**.

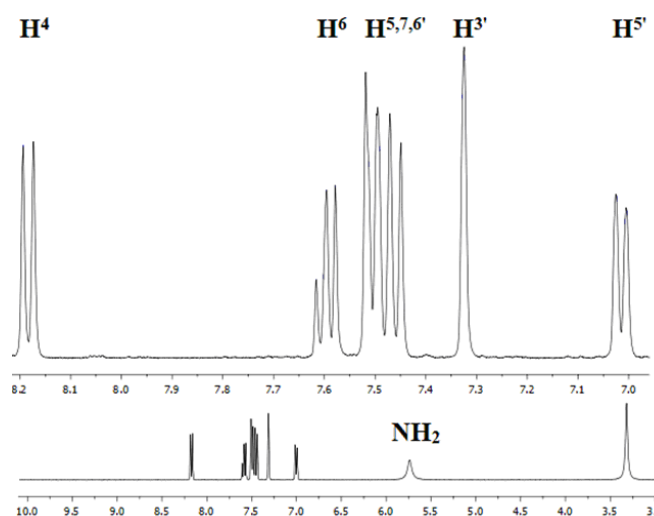


Fig. 2.  $^1\text{H}$  NMR spectrum of 1-[2-amino-4-(trifluoromethyl)phenyl]-1*H*-benzotriazole (**4a**)

Signal of two amino group protons at 5.53 ppm.; they have the form of a broad singlet. Also, 7 signals of aromatic protons occur in the  $^1\text{H}$  NMR spectrum of **4a**, appearing



in the spectrum in the interval 7.01-8.18 ppm. The absorption bands of the N-phenyl fragment protons were significantly shifted to the strong field region: H<sup>3</sup> at 1.75 ppm., H<sup>5</sup> at 1.8 ppm. and least of all H<sup>6</sup> at 1.35 ppm. compared to the corresponding nitro compound. The signal of H<sup>5</sup> para-relative to the amino group has the form of a duplicated doublet. It released in the strongest field of the spectrum. The signal of H<sup>4</sup> of the benzotriazole cycle, strongly deshielded by the nitrogen atom of the triazole ring, occurred at 8.18 ppm. in the weakest field. The same patterns of location and type of proton signals in <sup>1</sup>H NMR spectra were observed for other N-(2-aminoaryl)benzotriazoles.

Thus, we have studied the impact of temperature, reaction time, and HCl concentration on the selectivity of 1-(2-nitroaryl)-1*H*-benzotriazole reduction by tin (II) chloride in acidic aqueous-alcoholic medium. We found the possibility of by-processes of intermediate products condensation of incomplete reduction of the nitro group and alkylation of the formed amino compound in addition to the synthesis of the target amino compound.

### Experimental part

We determined the melting points on a PolyTherm A apparatus at a heating rate of 3 °C/min and did not adjust. We recorded NMR spectra on a Bruker DRX-400 for DMSO-*d*<sub>6</sub> solutions. The remaining solvent proton signals in <sup>1</sup>H NMR (δ 2.50 ppm) were used as the reference for the chemical shift counts. Mass spectra were recorded on a FINNIGAN MAT INCOS 50 instrument, electron flux energy 70 eV.

#### Synthesis procedure of 1-(2-nitroaryl)-1*H*-benzotriazoles **3a-d**.

We heated the reaction mixture containing 2 g (0.017 mol) of benzotriazole **1**, 3.5 g (0.026 mol) of anhydrous K<sub>2</sub>CO<sub>3</sub> and 0.017 mol of *ortho*-nitrohalogenarene **2a-d** to 110 °C and stirred for 1.5 h for the synthesis of **3a, b**, 2 h for **3c** and 7 h for **3d**. We cooled it and poured it into the water, filtered the residue off, then washed it several times with water and dried it. It was recrystallized in isopropanol.

**1-(2-nitro-4-(trifluoromethyl)phenyl)-1*H*-benzotriazole (3a)**. Yield is 93%. T.melt. is 133–136 °C. NMR spectrum <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm., *J*/Hz): 7.61 (td, 1H, H<sup>5</sup>, *J* 8.3, 1.0 Hz), 7.77 (td, 1H, H<sup>6</sup>, *J* 8.3, 1.0 Hz), 7.85 (d, 1H, H<sup>7</sup>, *J* 8.4 Hz), 8.28 (d, 1H, H<sup>4</sup>, *J* 8.4 Hz), 8.40 (d, 1H, H<sup>6</sup>, *J* 8.8 Hz), 8.81 (dd, 1H, H<sup>5</sup>, *J* 8.8, 2.5 Hz), 9.07 (d, 1H, H<sup>3</sup>, *J* 2.6 Hz). HRMS: *m/z* calculated C<sub>13</sub>H<sub>7</sub>F<sub>3</sub>N<sub>4</sub>O<sub>2</sub> 309.2196 [M+H]<sup>+</sup>, found 309.2191.

**1-(4-cyano-2-nitrophenyl)-1*H*-benzotriazole (3b)**. Yield is 94%. T.melt. is 221–223 °C. NMR spectrum <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm., *J*/Hz): 7.61 (td, 1H, H<sup>5</sup>, *J* 8.3, 1.5 Hz), 7.73 (td, 1H, H<sup>6</sup>, *J* 8.3, 1.2 Hz), 7.83 (d, 1H, H<sup>7</sup>, *J* 8.4 Hz), 8.25 (d, 1H, H<sup>4</sup>, *J* 8.3 Hz), 8.35 (d, 1H, H<sup>6</sup>, *J* 8.5 Hz), 8.54 (dd, 1H, H<sup>5</sup>, *J* 8.3, 1.5 Hz), 8.96 (d, 1H, H<sup>3</sup>, *J* 1.8 Hz). HRMS: *m/z* calculated C<sub>13</sub>H<sub>7</sub>N<sub>5</sub>O<sub>2</sub> 266.2320 [M+H]<sup>+</sup>, found 266.2315.

**1-(2-nitro-4-(ethoxycarbonyl)phenyl)-1*H*-benzotriazole (3b)**. Yield is 91%. T.melt. 115–119 °C. NMR spectrum <sup>1</sup>H (DMSO-*d*<sub>6</sub>, δ, ppm., *J*/Hz): 1.39 (m, 3H, CH<sub>3</sub>), 4.45 (m, 2H, CH<sub>2</sub>), 7.58 (td, 1H, H<sup>5</sup>, *J* 8.3, 1.0 Hz), 7.72 (td, 1H, H<sup>6</sup>, *J* 8.3, 1.0 Hz), 7.81 (d, 1H, H<sup>7</sup>, *J* 8.2 Hz), 8.24 (m, 2H, H<sup>4,6</sup>), 8.49 (dd, 1H, H<sup>5</sup>, *J* 8.5, 1.5 Hz), 8.72 (d, 1H, H<sup>3</sup>, *J* 1.8 Hz). HRMS: *m/z* calculated C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub> 313.2850 [M+H]<sup>+</sup>, found 313.2845.



**1-(2-nitro-4-chlorophenyl)-1H-benzotriazole (3a).** Yield is 89%. T.melt. is 118–121 °C. NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J/\text{Hz}$ ): 7.58 (td, 1H,  $\text{H}^5$ ,  $J$  8.3, 1.0 Hz), 7.69 (td, 1H,  $\text{H}^6$ ,  $J$  8.3, 1.0 Hz), 7.76 (d, 1H,  $\text{H}^7$ ,  $J$  8.2 Hz), 8.14 (m, 2H,  $\text{H}^{4,5}$ ), 8.25 (d, 1H,  $\text{H}^6$ ,  $J$  8.5 Hz), 8.51 (d, 1H,  $\text{H}^3$ ,  $J$  1.8 Hz). HRMS:  $m/z$  calculated  $\text{C}_{12}\text{H}_7\text{N}_4\text{O}_2\text{Cl}$  275.6650  $[\text{M}+\text{H}]^+$ , found 275.6632.

**Synthesis procedure of 1-(2-aminoaryl)-1H-benzotriazoles (4a-d).**

We added a solution of 0.034 mol  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 50 ml of 18% HCl to a solution of 0.011 mol **3a-g** in 50 ml *i*-PrOH at 70 °C under stirring. We evaporated the *i*-PrOH after 0.5 h. Then we cooled the reaction mass, treated with  $\text{NH}_4\text{OH}$  to  $\text{pH} = 8$ , and extracted with hot chloroform ( $\Sigma = 250$  ml). We obtained amino compounds **4a-d** after distillation with chloroform.

**1-(2-amino-4-(trifluoromethyl)phenyl)-1H-benzotriazole (4a).** Yield is 98%. T.melt. is 136–139 °C. NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J/\text{Hz}$ ): 5.75 (s, 2H,  $\text{NH}_2$ ), 7.01 (dd, 1H,  $\text{H}^5$ ,  $J = 1.8$ ,  $J = 8.2$ ); 7.32 (d, 1H,  $\text{H}^3$ ,  $J = 1.7$ ); 7.46 (d, 1H,  $\text{H}^6$ ,  $J = 8.3$ ); 7.49–7.53 (m, 2H,  $\text{H}^{5,7}$ ); 7.56 (t, 1H,  $\text{H}^6$ ,  $J = 9.4$ ); 8.18 (d, 1H,  $\text{H}^4$ ,  $J = 8.1$ ). NMR spectrum  $^{13}\text{C}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): 111.4, 112.5 (qu,  $J = 4$ ), 113.44, 120.4, 123.3, 124.7 (qu,  $J = 271$ ), 125.0, 129.0, 129.3, 131.7 (qu,  $J = 31$ ), 133.7, 145.5, 145.9. HRMS:  $m/z$  calculated  $\text{C}_{13}\text{H}_{10}\text{F}_3\text{N}_4$  279.2400  $[\text{M}+\text{H}]^+$ , found 279.2398.

**1-(2-Amino-4-cyanophenyl)-1H-benzotriazole (4b).** Yield is 97%. T.melt. is 154–156 °C. NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J/\text{Hz}$ ): 5.78 (s, 2H,  $\text{NH}_2$ ), 7.12 (dd, 1H,  $\text{H}^5$ ,  $J = 1.8$ ,  $J = 8.1$ ); 7.34 (d, 1H,  $\text{H}^3$ ,  $J = 1.8$ ); 7.45 (d, 1H,  $\text{H}^6$ ,  $J = 8.2$ ); 7.47–7.51 (m, 2H,  $\text{H}^{5,7}$ ); 7.59 (t, 1H,  $\text{H}^6$ ,  $J = 9.2$ ); 8.19 (d, 1H,  $\text{H}^4$ ,  $J = 8.2$ ). NMR spectrum  $^{13}\text{C}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): 111.13, 113.98, 119.42, 120.24, 124.37, 125.21, 129.11, 129.46, 133.62, 145.53, 145.97. HRMS:  $m/z$  calculated  $\text{C}_{13}\text{H}_{10}\text{N}_5$  236.2516  $[\text{M}+\text{H}]^+$ , found 236.2518.

**1-(2-Amino-4-ethoxycarbonylphenyl)-1H-benzotriazole (4c).** Yield is 95%. T.melt. 132–136 °C. NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J/\text{Hz}$ ): 1.34 (m, 3H,  $\text{CH}_3$ ), 4.35 (m, 2H,  $\text{CH}_2$ ), 5.62 (s, 2H,  $\text{NH}_2$ ), 7.29 (dd, 1H,  $\text{H}^5$ ,  $J = 1.9$ ,  $J = 8.2$ ), 7.37 (d, 1H,  $\text{H}^6$ ,  $J = 8.2$ ), 7.48 (m, 2H,  $\text{H}^{5,7}$ ), 7.59 (t, 1H,  $\text{H}^6$ ,  $J = 8.4$ ), 7.65 (d, 1H,  $\text{H}^3$ ,  $J = 1.7$ ), 8.17 (d, 1H,  $\text{H}^4$ ,  $J = 8.2$ ). NMR spectrum  $^{13}\text{C}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): 14.69, 61.51, 111.52, 117.19, 117.98, 120.26, 124.31, 125.02, 128.32, 128.84, 132.48, 133.61, 144.79, 145.97, 166.27. HRMS:  $m/z$  calculated  $\text{C}_{15}\text{H}_{15}\text{N}_4\text{O}$  267.3053  $[\text{M}+\text{H}]^+$ , found 267.3051.

**1-(2-Amino-4-chlorophenyl)-1H-benzotriazole (4d).** Yield is 94%. T. melt. is 154–156 °C. NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J/\text{Hz}$ ): 5.53 (s, 2H,  $\text{NH}_2$ ), 6.73 (dd, 1H,  $\text{H}^5$ ,  $J = 1.7$ ,  $J = 8.1$ ); 7.03 (d, 1H,  $\text{H}^3$ ,  $J = 1.7$ ); 7.24 (d, 1H,  $\text{H}^6$ ,  $J = 8.1$ ); 7.46 (m, 2H,  $\text{H}^{5,7}$ ); 7.57 (t, 1H,  $\text{H}^6$ ,  $J = 9.3$ ); 8.16 (d, 1H,  $\text{H}^4$ ,  $J = 8.2$ ). NMR spectrum  $^{13}\text{C}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): 111.29, 116.11, 116.29, 119.62, 120.21, 124.78, 128.81, 129.76, 133.98, 135.67, 145.79, 146.43. HRMS:  $m/z$  calculated  $\text{C}_{12}\text{H}_{10}\text{ClN}_4$  245.6871  $[\text{M}+\text{H}]^+$ , found 245.6873.

**Synthesis procedure of 1,2-bis[2-(1H-benzotriazol-1-yl)-5-(trifluoromethyl)phenyl] diazene oxide (5)**

We performed the reduction similarly to the above-described procedure for the amino compounds synthesis. We used 9% hydrochloric acid instead of 18% hydrochloric acid. We heated the dry product mixture obtained after distillation of chloroform in DMFA. The azoxy compound was precipitated on cooling. Yield is 17%. T.melt. is 241–246 °C.



NMR spectrum  $^1\text{H}$  (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J$ /Hz): 7.48-7.61 (m, 7 H), 7.66 (d, 1H,  $J = 1.7$ ), 7.78 (dd, 1H,  $J = 1.9$ ,  $J = 9.2$ ), 7.91 (d, 1H,  $J = 9.1$ ), 7.96 (dd, 1H,  $J = 1.9$ ,  $J = 9.2$ ), 8.03 (d, 1H,  $J = 9.1$ ), 8.17 (d, 2H,  $J = 9.2$ ). NMR spectrum  $^{13}\text{C}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): 110.7, 111.6, 120.7, 123.9, 125.5, 125.7, 125.9, 128.6, 129.8, 129.8, 129.9, 130.4, 130.6, 130.9, 133.9, 134.2, 134.4, 134.9, 135.2, 135.9, 139.7, 144.9, 146.2. HRMS:  $m/z$  calculated  $\text{C}_{26}\text{H}_{15}\text{F}_6\text{N}_8\text{O}$  569.4401  $[\text{M}+\text{H}]^+$ , found 569.3989

### Synthesis procedure of 1-{2-[(propan-2-yl)amino]-4-(trifluoromethyl)phenyl}-1H-benzotriazole (6).

We performed the reduction similarly to the above-described procedure for the synthesis of amino compounds. We used 36% hydrochloric acid instead of 18% hydrochloric acid. We separated the dry mixture of products obtained after distillation of chloroform by TLC. The eluents were ethyl acetate: hexane = 7 : 1.  $R_f = 0.294$ . Yield is 11%. T.melt. is 102–107 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm.,  $J$ /Hz): 1.06 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ,  $J = 6.3$ ), 3.76 (dsept, 1H,  $\text{CH}(\text{CH}_3)_2$ ,  $J = 8.1$ ,  $J = 6.3$ ), 5.37 (d, 1H, NH,  $J = 8.1$ ), 7.04 (dd, 1H,  $\text{H}^5$ ,  $J = 1.9$ ,  $J = 8.1$ ), 7.18 (d, 1H,  $\text{H}^3$ ,  $J = 1.9$ ), 7.45 (d, 1H,  $\text{H}^6$ ,  $J = 8.1$ ), 7.47–7.53 (m, 2H,  $\text{H}^5$ ,  $\text{H}^7$ ), 7.59 (ddd, 1H,  $\text{H}^6$ ,  $J = 1.0$ ,  $J = 6.9$ ,  $J = 8.2$ ), 8.19 (d, 1H,  $\text{H}^4$ ,  $J = 8.5$ ).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm.): 21.8 ( $\text{CH}(\text{CH}_3)_2$ ), 43.3 ( $\text{CH}(\text{CH}_3)_2$ ), 108.6 (k,  $\text{C}^3$ ,  $J = 3.9$  Hz), 110.8 ( $\text{C}^7$ ), 111.5 (k,  $\text{C}^5$ ,  $J = 3.9$ ), 119.6 ( $\text{C}^4$ ), 123.9 (k,  $\text{C}^1$ ,  $J = 1.4$  Hz), 124.1 (k,  $\text{CF}_3$ ,  $J = 272.6$ ), 124.4 ( $\text{C}^5$ ), 128.2 ( $\text{C}^6$ ), 128.7 ( $\text{C}^6$ ), 131.3 (k,  $\text{C}^4$ ,  $J = 31.6$  Hz), 133.1 ( $\text{C}^{7a}$ ), 143.2 ( $\text{C}^2$ ), 145.3 ( $\text{C}^{3a}$ ). NMR spectrum  $^{19}\text{F}$  (DMSO- $d_6$ ,  $\delta$ , ppm.): - 62.27. HRMS:  $m/z$  calculated  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{N}_4$  321.1329  $[\text{M}+\text{H}]^+$ , found 321.1323

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*Received 14.02.2024*

*Approved after reviewing 28.02.2024*

*Accepted 12.03.2024*