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Synthesis of 2-fluoromethylbenzimidazoles, 2-fluoromethyl benzothiazoles and 2-fluoromethylimidazo [4,5-*b*] pyridines using $(Ph_3P)_2PdCl_2$ catalyst

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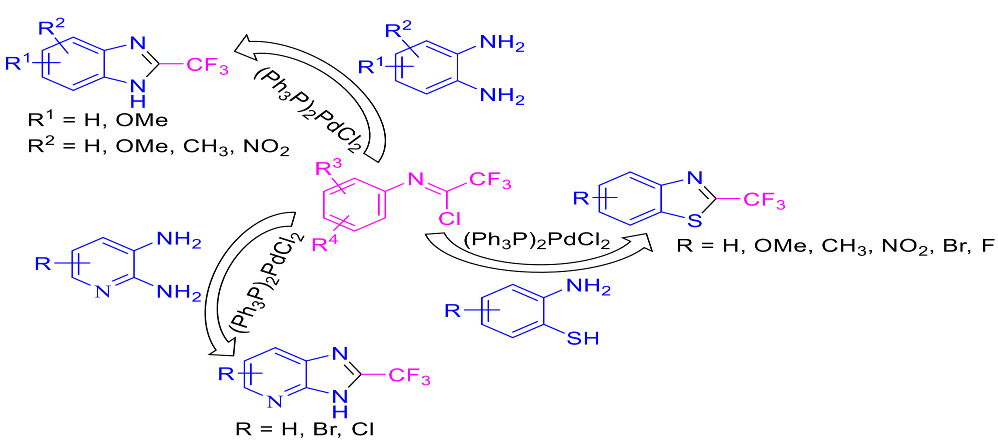
Abstract

An efficient one-pot method for the synthesis of 2-fluoromethylbenzimidazoles, 2-fluoromethylbenzothiazoles and 2-fluoromethylimidazo[4,5-*b*]pyridines by the treatment of the of 2,2,2-trifluoro-*N*-arylacetimidoyl chlorides with 1,2-phenylenediamines, 2-aminothiophenols and 2,3-diaminopyridines using $(Ph_3P)_2PdCl_2$ as the single catalyst in dry THF is demonstrated. The reaction occurs via Pd-catalyzed C-Cl bond/C-N bond formation in high yields with good function group diversity. Very simple purification and $(Ph3P)_2PdCl_2$ as the single catalyst without adding any other additives or oxidants are as advantage of this method.



Keywords: Palladium, N-aryl-2,2,2-trifluoroacetimidoyl chlorides, 2-trifluoromethylbenzimidazoles, 2-trifluoromethylbenzothiazoles, 2-fluoromethylimidazo[4,5-*b*]pyridine.

Introduction

Five-membered heterocyclic rings, such as benzothiazoles, and benzimidazoles has been found in natural products, and widely used in synthesis of pharmaceutical and agrochemical compounds.[1,2,3] These compounds have been extensively studied for their biological and therapeutic activities, such as a cathepsin S inhibitor[4], a HIV reverse transcriptase inhibitor[5], an anticancer agent[6], and an orexin-1 receptor antagonist.[7] 2-Fluoroalkylated benzimidazoles have been used in the synthesis of pharmaceutical drugs and agricultural chemicals due to the potency to modify physiochemical effects, bioavailability, and linking abilities in comparison with their 2-alkylbenzimidazoles.[8-11]

Synthesis of 2-fluoroalkylbenzimidazole derivatives has gained attention in the literature in recent years. Several synthetic methods have been used for preparation of these compounds: condensation of 1,2-phenylenediamines and reductive cyclization of 1,2-nitroanilines with fluorinated organic acids, [12-14] the reaction of PIDA(phenyliodine(III) diacetate) with N-arylbromodifluoro (or trifluoro)acetamidines [15,16] and trifluoromethylation of benzimidazoles via C-H oxidation reactions [17] are some of the most important of these.

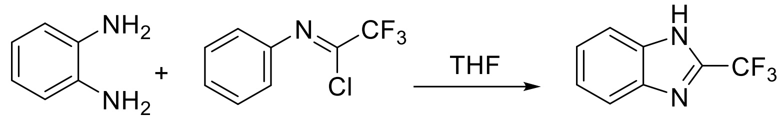
Trifluoromethylation has been studied extensively owing to the interesting effects of the heterocyclic compounds contain trifluoromethyl group and corresponding fluorinated organic compounds in the fields of medicinal chemistry, agrochemical [18,19] and substance.[20] Progress and efficient use of the trifluoromethyl group for the synthetic scaffold would be interesting for the synthesis of many trifluoromethylated organic compounds. Trifluoroacetimidoyl chlorides are examples of some of the hopeful framework, which have been newly used for the synthesis of nitrogen-contain trifluoromethylated heterocycles[21-23]. In this investigation, trifluoroacetimidoyl chlorides are prepared by refluxing a mixture of trifluoracetic acid and a primary aryl amine in carbon tetrachloride using triethylamine and triphenylphosphine.[24,25] Then these intermediates have been used for the synthesis of 2-trifluoromethylbenzimidazoles, 2-trifluoromethylimidazopyridine, and 2-trifluoromethylbenzothiazoles in one step.

Continuing our program on the synthesis of trifluoromethylated compounds and novel procedures for preparation of heterocyclic compounds contain trifluoromethyl group [26,27], herein we wish to report the expanded scope and a new procedure for preparation of 2-trifluoromethylbenzimidazoles, 2-trifluoromethylbenzothiazoles, and 2-trifluoromethylimidazopyridines using reaction of the trifluoromethylimidoyl chlorides with 1,2-phenylenediamines, 2-aminothiophenols and 2,3-diaminopyridines, respectively, using $(Ph_3P)_2PdCl_2$ as the sole catalyst.

Results and Discussion

The reaction conditions were optimized using the reaction of 2,2,2-trifluoro-*N*-phenylacetimidoyl chloride **2a** and 1,2 phenylenediamine **1a** as a model. We investigated the effect of $(Ph_3P)_2PdCl_2$ (mol%) and temperature on the reaction in THF as solvent. Both at room temperature and refluxing in absence of $(Ph_3P)_2PdCl_2$ no product was observed after 4 and 2 days, respectively (Table 1, entry 1 and 2, respectively). When the reaction was conducted with $(Ph_3P)_2PdCl_2$ (5 mol %, and 10 mol %) as a catalyst, at room temperature in THF after 18 h 2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole **3a** was obtained in 15 % yield (Table 1, entry 3 and 4). In order to increase the yield, the reaction was carried out under reflux conditions and 2-(trifluoromethyl)-1*H*-benzo[d]imidazole **3a** was obtained in 92 and 90 % yields after 15 h in the presence of 5 mol % and 10 mol % of catalyst, respectively (Table 1, entry 5 and 6).

Table 1. Optimization of conditions reaction for synthesis of compounds **3**

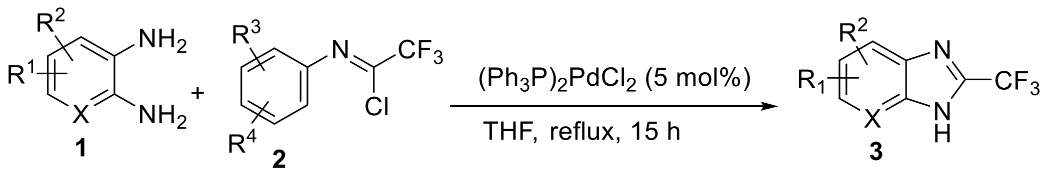


1a **2a** **3a**

Entry	Catalyst (mol%)	Temperature	Time	Yield (%)
1	-	r.t	4 d	no product
2	-	reflux	2 d	no product
3	$(Ph_3P)_2PdCl_2$ (5)	r.t	18 h	15
4	$(Ph_3P)_2PdCl_2$ (10)	r.t	18 h	15
5	$(Ph_3P)_2PdCl_2$ (5)	reflux	15 h	92
6	$(Ph_3P)_2PdCl_2$ (10)	reflux	15 h	90

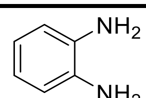
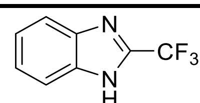
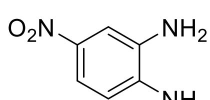
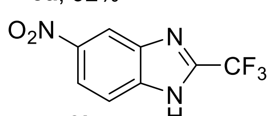
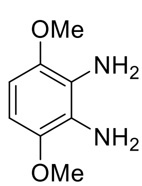
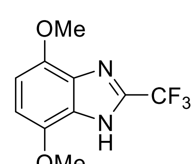
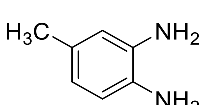
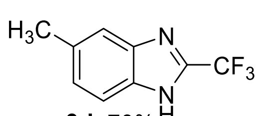
Various 2-trifluoromethylbenzimidazoles were prepared using this effective method (Table 2). In addition to 1,2-phenylenediamine, other derivatives containing electron-withdrawing and electron-donating substituents on the aromatic ring (entry 2, 3) were well tolerated, giving the 2-trifluoromethylbenzimidazoles and 2-trifluoromethylimidazopyridine **3a-g** in 70% to 92% yields.

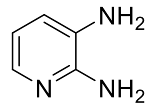
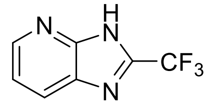
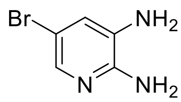
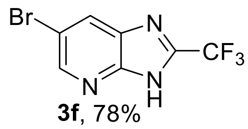
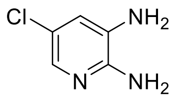
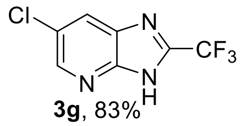
Table 2. Synthesis of 2-trifluoromethylbenzimidazoles and 2-trifluoromethylimidazopyridine **3a-g**



X = C, N

R^3 = H, CF_3; R^4 = H, CF_3, Me

Entry	Substrate	Product	Time(h)	M.P [b](°C)	M.P [a](°C)
1	 **1a**	 **3a**, 92%	15	205-207	200-202[28]
2	 **1b**	 **3b**, 89%	12	155-156	148-150[28]
3	 **1c**	 **3c**, 72%	12	212	213-215[29]
4	 **1d**	 **3d**, 70%	70	163	162-164[28]

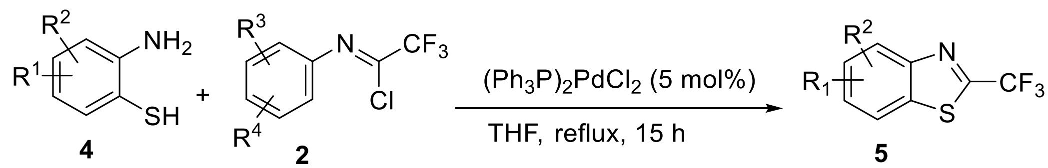
5	 **1e**	 **3e**, 81%	24	260	253-255[28]
6	 **1f**	 **3f**, 78%	18	290	292-294[28]
7	 **1g**	 **3g**, 83%	17	195	194-196[28]

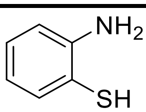
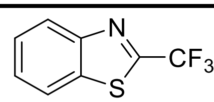
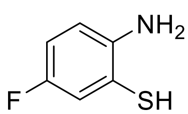
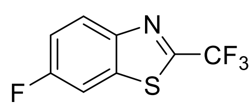
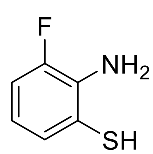
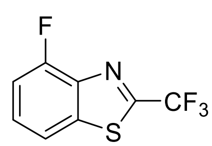
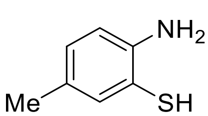
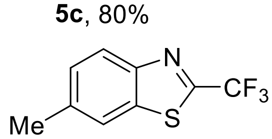
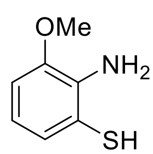
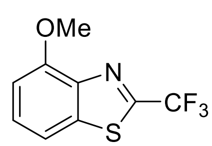
[a]Reaction conditions: 0.5 M diamine in trifluoroacetic acid, 70 C, 16 h[30]

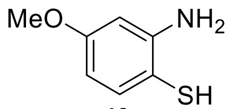
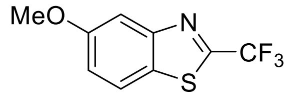
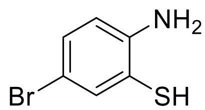
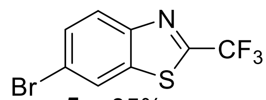
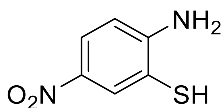
[b] Procedure B: 2,2,2-trifluoro-N-arylacetimidoyl chlorides with 1,2 phenylenediamine using $(Ph_3P)_2PdCl_2$ as the sole catalyst in dry THF

The generality of this procedure was examined by using various o-aminothiophenol derivatives **4a-h.** In all of the reactions corresponding 2-trifluoromethylbenzothiazole derivatives **5a-h** were produced in good yield (Table 3).

Table 3. Synthesis of 2-trifluoromethylbenzothiazoles **5a-h**



Entry	Substrate	Product	Time(h)	M.P[b] (˚C)	M.P[a](˚C)
1	 **4a**	 **5a**, 88%	10	68-70	74-78[31]
2	 **4b**	 **5b**, 83%	12	81	80[32]
3	 **4c**	 **5c**, 80%	11	52-54	54[32]
4	 **4d**	 **5d**, 83%	11	84-86	86[32]
5	 **4e**	 **5e**, 85%	15	78	80[32]

6	 **4f**	 **5f**, 84%	13	60	60[32]
7	 **4g**	 **5g**, 85%	14	96	96[31]
8	 **4h**	 **5h**, 87%	14	93	93[32]

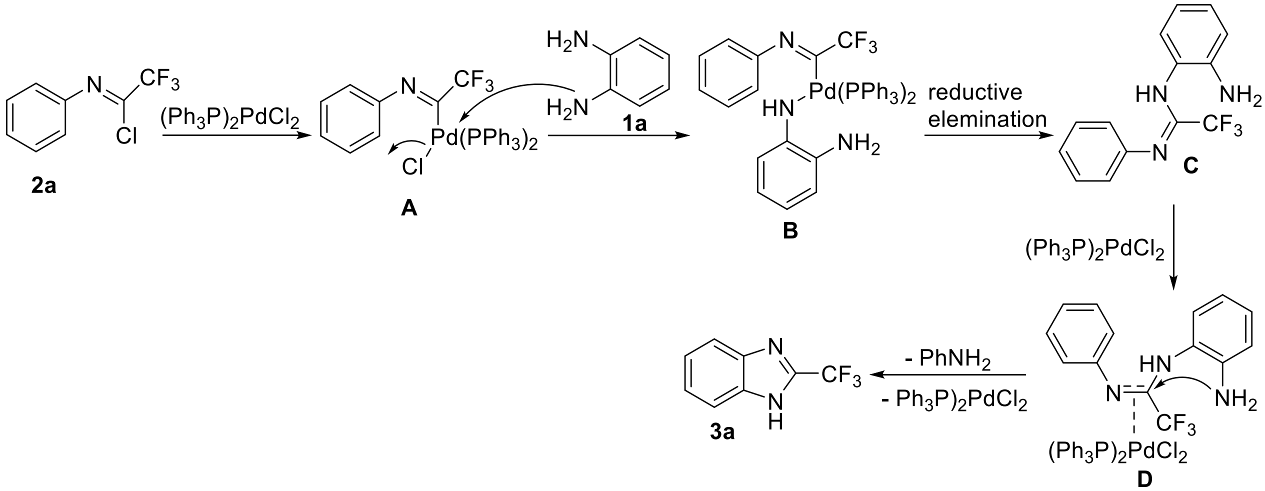
[a]Procedure A: trifluoromethyl imidoyl chloride with sodium hydrosulfide hydrate using $PdCl_2$ as the single catalyst in DMSO [30]

[b] Procedure B: 2,2,2-trifluoro-*N*-arylacetimidoyl chloride with 1,2-aminothiophenols using $(Ph_3P)_2PdCl_2$ as the sole catalyst in dry THF

Pd(II) complexes are generally electrophilic and air stable, and therefore connect to electron-rich systems, such as olefins, alkynes, and arenes. Given that the Pd(II) also increases effective methods of reactivity, the deficiency of Pd(II) study may initially seem surprising[25,28-32].

However, one of the most important problems in development of application Pd(II) complexes in organic synthesis is the difficulty of reoxidizing Pd(0) → Pd(II). Recently oxidants such as O_2, $CuCl_2$, $Cu(OAc)_2$, benzoquinone, tert-butyl hydroperoxide (TBHP), MnO_2, and HNO_3 have been used for completing of the catalytic cycle to regenerate Pd(II). Surprisingly, when these oxidants were added to the reaction media has often intervened with the catalyst/ligand system (or the substrates themselves), and have resulted to problems in retaining chemo- or stereoselective processes[25,33-38]. A suggested reaction mechanism is provided in Scheme 1.

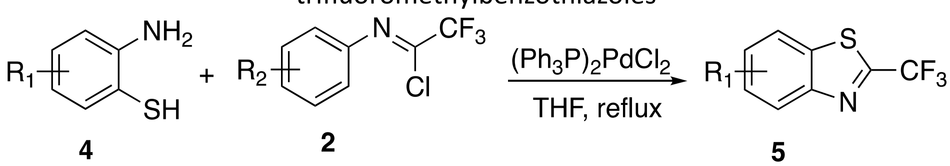
The first step is the insertion of the Pd(II) species to the C-Cl bond of imidoyl chloride to produce intermediate **A**. Subsequently, the amino nitrogen from the diamine attacks to the Pd-Cl bond, to generate the palladium complex intermediate **B**. Then the intermediate **B** by the reductive-elimination reaction Pd-complex gives *N*-(2-aminophenyl)-2,2,2-trifluoro-*N'*-phenylacetimidamide [23,39,40] which is activated by the Pd-catalyst to produce activated-complex **D**. Finally, an intermolecular nucleophilic attack on the C=N of **D** and then amine elimination from **D** produces 2-trifluoromethyl-1*H*-benzo[*d*]imidazole[36-38].

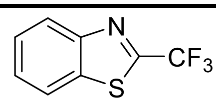
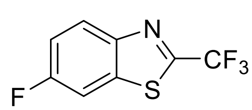
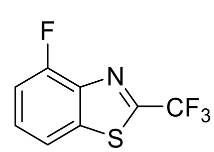
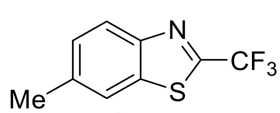
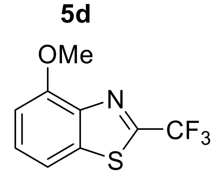


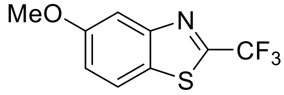
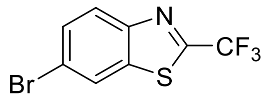
Scheme 1. A suggested mechanism for the synthesis of 2-trifluoromethyl-1*H*-benzo[d]imidazole

In order to illustrate the benefit of the present work in comparison with other reported results for synthesis of 2-trifluoromethylbenzothiazoles in the previously publications, we compared the results and reaction conditions of $(Ph_3P)_2PdCl_2$ with another procedure reported in the literature used in the synthesis of 2-trifluoromethylbenzothiazoles **5a-g** (Table 4).

Table 4. The comparison of yield other methods with $(Ph_3P)_2PdCl_2$ catalyst for synthesis of 2-trifluoromethylbenzothiazoles



Entry	Product	Procedure A[a] Yield (%)	Procedure B[b] Yield (%)
1	 **5a**	72	88
2	 **5b**	69	83
3	 **5c**	65	80
4	 **5d**	71	83
5	 **5e**	74	85

6	 **5f**	78	84
7	 **5g**	65	85

[a] Procedure A: trifluoromethylimidoyl chloride with sodium hydrosulfide hydrate using $PdCl_2$ as the single catalyst in DMSO [30]

[b] Procedure B: 2,2,2-trifluoro-N-arylacetimidoyl chloride with 1,2-aminothiophenols using $(Ph_3P)2PdCl_2$ as the sole catalyst in dry THF

Conclusions

We have illustrated a new and efficient procedure for synthesis of 2-trifluoromethylbenzimidazoles, 2-trifluoromethylbenzothiazoles, and 2-trifluoromethylimidazopyridines via Pd-catalyzed C-Cl bond using 2,2,2-trifluoro-*N*-arylacetimidoyl chlorides. In addition to its efficiency and simplicity, this single-step procedure displayed good functional group tolerance and used $(Ph_3P)_2PdCl_2$ as the single catalyst without adding any other additives or an oxidizing agent and provides good yields of trifluoromethylated compounds allowing very simple purification of products. Especially, $(Ph_3P)_2PdCl_2$ has been used as a new, mild, and effective catalyst and oxidant for the convenient synthesis of 2-trifluoromethylbenzothiazoles in good to excellent yields from the reaction of o-aminothiophenols with 2,2,2-trifluoro-*N*-phenylacetimidoyl chlorides in comparison to another methods.

Experimental Section

General. Trifluoroacetimidoyl chlorides were prepared by previously reported procedures. [24] All other chemicals used in this study were commercially available. Melting points were measured with a Barnstead electrothermal melting point apparatus. IR spectra (KBr, Neat) were measured on a Thermoscientific, Nicolet is 10 FT-IR spectrometer. Peaks are reported in wave numbers (cm^{-1}). All of the NMR spectra were recorded on a Bruker model DRX-500 AVANCE (^{1}H: 500, ^{13}C: 125, ^{19}F: 470 MHz) NMR spectrometer. Chemical shifts of ^{1}H and ^{13}C-NMR are reported in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard in DMSO-d_6 or $CDCl_3$ as a solvent and ^{19}F-NMR are reported in parts per million (ppm) from $CFCl_3$ as an internal standard in DMSO-d_6 or $CDCl_3$ as a solvent.

General procedure for preparation of compounds 3a-g, 5a-5g. A solution of the 2,2,2-trifluoro-*N*-arylacetimidoyl chloride (1 mmol) and bis(triphenylphosphine)- palladium (II)dichloride (5% mmol) in dry THF (5 ml) was stirred for 30 min at room temperature. Then diamine or aminothiol derivative (1 mmol) was added drop wise via a syringe, and the mixture was refluxed for 15 h under an N_2 atmosphere. The reaction mixture was filtered, and the solvent removed under reduced pressure. The obtained product was washed with n-hexane to give the crude product.

2-Trifluoromethyl-1*H*-benzo[d]imidazole (3a). 92%, mp 205-207 ˚C; IR (KBr) 3431, 2969, 1552, 1462 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ 13.90 (1H), 7.69 (2H), 7.34 (2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 140.03 (q, *J* 39.4 Hz), 140.0 (br), 134.5 (br), 124.03, 119.03 (q, *J* 270.3 Hz), 119.0 (br), 113.5 (br); ^{19}F-NMR ($CDCl_3$, 470 MHz) δ -63.15.

5-Methyl-2-trifluoromethyl-1*H*-benzo[*d*]imidazole (**3d**). 70%, mp 163 ˚C; IR (KBr) 3100, 2976, 1553, 1535 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ = 12.30 (1H), 7.56 (1H), 7.44 (2H), 2.40 (3H), ^{19}F-NMR ($CDCl_3$, 470 MHz) δ -63.01.

2-Trifluoromethyl-3*H*-imidazo[4,5-*b*]pyridine (3e). 81%, mp 260 ˚C; IR (KBr) 3460, 3071, 1586, 1500, 1461 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 500 MHz) δ 14.45 (1H), 8.51 (1H), 8.21 (1H), 7.40 (1H); ^{13}C- NMR (DMSO-d_6, 125 MHz) δ 149.8, 145.6, 142.3 (q, J_F 39.8 Hz), 131.8, 126.9, 119.4, 118.9 (q, J_F 269.3 Hz); ^{19}F-NMR ($CDCl_3$, 470 MHz) δ -76.10.

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