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Synthesis of *N*-benzothiazol-2-yl-amides by Pd-catalyzed C(sp^2)–H functionalization

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ABSTRACT

A catalytic synthesis of *N*-benzothiazol-2-yl-amides from 1-acyl-3-(phenyl)thioureas was achieved in the presence of a palladium catalyst through the C(sp^2)–H functionalization/C–S bond formation. This synthetic methodology can produce various *N*-benzothiazol-2-yl-amides in high yields with good functional group tolerance.

1. Introduction

The benzothiazole moiety is an important scaffold due to its widespread occurrence in bioactive natural products, pharmaceuticals, organic optoelectronic materials, and ligands for phosphorescent complexes [1–4]. In particular, substituted *N*-benzothiazol-2-yl-amides are an important class of heterocyclic compounds that exhibit a wide range of biological properties [5–9] such as ubiquitin ligase inhibition [5], antitumor [6], antirotavirus infections [7], modulating the adenosine receptor [8,9], and the nuclear hormone receptor [9]. For example, the *N*-benzothiazol-2-yl-cyclohexanecarboxamide, as a new anticancer drug, was selected as one of the most promising screening hit compounds (Fig. 1) [6]. The acylation reaction from 2-aminobenzothiazole, one of the classical methods for the preparation of these molecules [5,6], is known for the limited diversity of the commercially available starting materials. Furthermore, the preparation of 2-aminobenzothiazole also required the use of the toxic bromine.

The past several years have witnessed the great progress in the development of the C–S bond formation promoted by transition metals, which can provide more efficient, practical, and straightforward approaches to valuable sulfur-containing compounds [10,11]. However, these methods have been mainly focused on the "traditional" cross-coupling reactions of ArX (X = Cl, Br, I, OTf, and $B(OH)_2$) and sulfides [12–39]. To achieve greener and more atom-economic C–S bond formations, transition metal-catalyzed direct oxidative cross-coupling of C–H bonds and sulfides would be ideal [40–47].

In our previous work, we have shown that *N*-benzothiazol-2-yl-amides can be synthesized smoothly by Cu-catalyzed intramolecular cyclization of various substituted 1-acyl-3-(2-bromophenyl)thioureas [48]. This method can provide more diversiform *N*-benzothiazol-2-yl-amides through the carbon-heteroatom formation under relatively mild conditions and avoid the use of the toxic bromine. However, the drawback of this procedure is the limited diversity of the commercially available starting materials due to the use of substituted ortho-haloarylamines. In order to further extend the diversity of *N*-benzothiazol-2-yl-amides, we have recently demonstrated an efficient intramolecular cyclization of substituted 1-acetyl-3-(2-phenyl)thiourea catalyzed by iron through C–H functionalization [49]. This method can provide more diversiform *N*-benzothiazol-2-yl-amides under relatively mild conditions. However, the purification of the target compounds is

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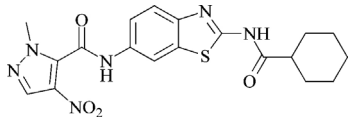


Fig. 1. Structure of Sankyo investigational new drugs.

challenging using the column chromatography or recrystallization, since it is inescapable to obtain 1-acetyl-3-phenylurea whose polarity is similar to that of 1-acetyl-3-(2-phenyl)thiourea. Recently, Doi's group [46] reported a Pd-catalyzed synthesis of 2-substituted benzothiazoles via a C–H Functionalization reaction. Therefore, we envisioned that Pd-catalyzed cyclization of 1-acyl-3-(2-phenyl)thiourea **1** would represent a viable method for the formation and purification of substituted *N*-benzothiazol-2-yl-amides **2** (Scheme 1).

2. Experimental

All reagents were commercially available and used as supplied. Dimethyl sulfoxide (DMSO) was dried and distilled from calcium hydride. *N*,*N*-Dimethylformamide (DMF), toluene, DME and CH_3CN were dried prior to use using standard methods. Unless otherwise stated, analytical grade solvents and commercially available reagents were used as received. Thin layer chromatography (TLC) employed glass 0.20 mm silica gel plates. Flash chromatography columns were packed with 200–300 mesh silica gel.

All new compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The IR spectra were run on a Nicolete spectrometer (KBr). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCEIII 400 MHz spectrometer. The chemical shifts (δ) were given in parts per million relative to an internal standard tetramethylsilane. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion (M^+). Melting points were determined on a Perkin-Elmer differential scanning calorimeter and the thermometer was uncorrected.

2.1. General procedure for the synthesis of 1-acyl-3-arylthioureas [49,50]

To a 25 mL round-bottom flask equipped with a magnetic stirring bar was added acyl chloride (10 mmol), NH_4SCN (15 mmol) and CH_2Cl_2 (20 mL), followed by PEG-400 (0.1 mmol). The mixture was stirred for approximately 3 h at room temperature. Aromatic amine (10 mmol) was added to the mixture and stirred for another 2 h at room temperature. The solvent was removed under reduced pressure to give the resulting residue as a solid, which was washed with water three times, to give the crude product. The analytical samples were obtained by recrystallization from C_2H_5OH in good yields (88–98%).

2.2. General procedure for the synthesis of N-benzothiazol-2-yl-amides by a Pd-catalysed C(sp^2)–H functionalization reaction

A round-bottom flask equipped with a stirring bar was charged with 1-acyl-3-arylthioureas (1 mmol), $PdCl_2$ (10 mol%), CuI (20 mol%), Cs_2CO_3 (2 equiv.), and L-proline (20 mol%) in 5 mL of DMSO. The mixture was stirred at 100 °C for the indicated time in Table 2. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatography (acetone/petroleum ether = 1:4) to yield the desired product **2**.

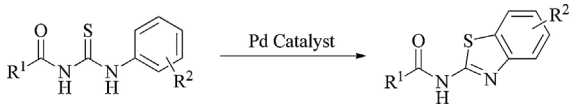
N-(4-Ethylbenzo[d]thiazol-2-yl)acetamide (**2f**): A gray solid (80% yield); mp: 264–268 °C; IR (cm^{-1}): 3169.9, 2990.1, 2359.9, 1661.1, 1550.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.67 (dd, 1H, J = 6.3, 2.9 Hz), 7.27 (dd, 2H, J = 4.4, 1.9 Hz), 3.04 (q, 2H, J = 7.6 Hz), 2.28 (s, 3H), 1.34 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.64(s), 156.91 (s), 146.45 (s), 136.81 (s), 131.98 (s), 125.25 (s), 124.22 (s), 118.92 (s), 25.36 (s), 23.51 (s), 14.79 (s); HRMS calcd. for $C_{11}H_{12}N_2OS$ $[M]^+$: 220.0670; found 20.0678.

N-(6-Fluorobenzo[d]thiazol-2-yl)acetamide (**2 g**): A white solid (94% yield); mp: 224–231 °C; IR (cm^{-1}): 3207.8, 3071.0, 2983.9, 2360.4, 1689.2; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, 1H, J = 8.9, 4.6 Hz), 7.53 (dd, 1H, J = 8.0, 2.5 Hz), 7.19 (td, 1H, J = 8.9, 2.6 Hz), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.33 (s), 160.93 (s), 158.50 (s), 121.30 (d, J = 9.1 Hz), 114.75 (s), 108.09 (s), 107.82 (s), 23.46 (s); HRMS calcd. for $C_9H_7FN_2OS$ $[M]^+$: 210.0263; found 210.0256.

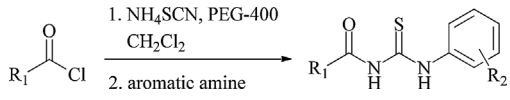
3. Results and discussion

While not commercially available, benzothioureas are stable and easily synthesized [50,51] from inexpensive starting materials in high yields on a multigram scale. Following Scheme 2, the synthesis of benzothioureas can be achieved in a straightforward manner starting from inexpensive aryl acid chloride and arylamines. Aryl acid chloride was treated with ammonium sulfocyanide in the presence of PEG-400 in CH_2Cl_2, followed by the addition of arylamines, to obtain 1-arylacyl-3-phenylthiourea in good to excellent yields. This intermediate can be used directly without further purifications.

In a preliminary experiment, we investigated the intramolecular C–S bond formation of 1-acetyl-3-phenylthiourea utilizing $PdCl_2$ (20%) and a mild base (K_2CO_3, 2 equiv.) in DMSO for 20 h at 100 °C (Table 1, entry 1). However, the reaction almost failed to take place. Subsequently, we screened several metal salts as co-catalysts, including $AlCl_3$, $CuCl_2$, $Cu(OAc)_2$, $CoCl_2$, $NiCl_2$, $FeCl_3$, CuI, and CuCl, and found that the addition of CuI considerably enhanced this reaction (Table 1, entries 2–8). However, the desired yield was still not obtained. Surprisingly, when Doi's condition was used, the yield was still very low (42%) (Table 1, entry 9). Generally, the choice of the ligands is important for the reaction catalyzed by the metal, which prompted us to explore the effect of several bidentate ligands. We carried out the reaction of 1-acetyl-3-phenylthiourea by screening these ligands, such as 1,10-phenanthroline, β-keto esters, β-diketones, and L-proline. (Table 1, entries 10–13), and we were pleased to find that the use of these ligands can notably improve the yield of the product under the same conditions, and that L-proline proved to be the best among an array of ligands tested (Table 1, entry 14). When the amount of CuI and $PdCl_2$ was decreased to 20 mol% and 10 mol%, respectively, the catalytic activity was maintained (Table 1, entry 14). Furthermore, we also investigated other bases (Cs_2CO_3 and K_3PO_4) (Table 1, entries 15–16), solvents (DMF, DME, and toluene) (Table 1, entries 17–19) and reaction time (Table 1, entries 20–21). When only CuI was used in



Scheme 1. Pd-catalyzed cyclization of 1-acyl-3-(2-aryl)thiourea by C–H functionalizations directly without further purification.



Scheme 2. The synthesis of 1-acyl-3-arylthioureas.

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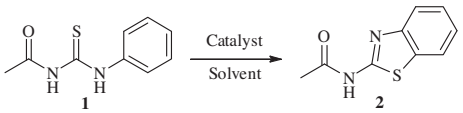
Table 1
Intramolecular cyclization of 1-acetyl-3-phenylthiourea: optimization of the catalytic condition.



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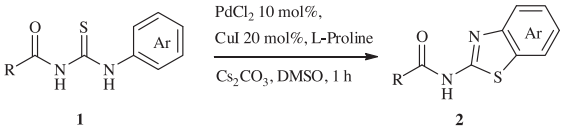
Entry	Cat.	Cocatalyst	Base (2 equiv.)	Ligand	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	$PdCl_2$ (20 mol%)	–	K_2CO_3	–	DMSO	100	20	0
2	$PdCl_2$ (20 mol%)	$CuCl_2$ (50 mol%)	K_2CO_3	–	DMSO	100	20	12
3	$PdCl_2$ (20 mol%)	$Cu(OAc)_2$ (50 mol%)	K_2CO_3	–	DMSO	100	20	48
4	$PdCl_2$ (20 mol%)	$CoCl_2$ (50 mol%)	K_2CO_3	–	DMSO	100	20	25
5	$PdCl_2$ (20 mol%)	$NiCl_2$ (50 mol%)	K_2CO_3	–	DMSO	100	20	30
6	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	–	DMSO	100	20	65
7	$PdCl_2$ (20 mol%)	CuCl (50 mol%)	K_2CO_3	–	DMSO	100	20	19
8	$PdCl_2$ (20 mol%)	$AlCl_3$ (50 mol%)	K_2CO_3	–	DMSO	100	20	Trace
9	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	–	DMSO/NMP	120	2	42
10	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	1,10-Phenanthroline	DMSO	100	15	74
11	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	β-Diketone	DMSO	100	15	83
12	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	β-Keto ester	DMSO	100	15	70
13	$PdCl_2$ (20 mol%)	CuI (50 mol%)	K_2CO_3	L-Proline	DMSO	100	15	90
14	$PdCl_2$ (10 mol%)	CuI (20 mol%)	K_2CO_3	L-Proline	DMSO	100	15	89
15	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	DMSO	100	15	97
16	$PdCl_2$ (10 mol%)	CuI (20 mol%)	K_3PO_4	L-Proline	DMSO	100	15	86
17	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	DMF	100	15	75
18	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	DME	100	15	43
19	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	Toluene	100	15	Trace
20[c]	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	DMSO	100	10	97
21	$PdCl_2$ (10 mol%)	CuI (20 mol%)	Cs_2CO_3	L-Proline	DMSO	100	8	96
22	–	CuI (20 mol%)	Cs_2CO_3	L-Proline	DMSO	100	16	0

Q4 [a] Yield of isolated product from reaction on a 1 mmol scale.

Table 2
The synthesis of *N*-benzothiazol-2-yl-amides.[a]



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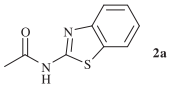
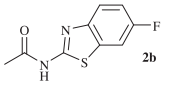
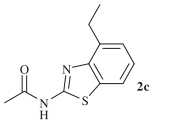
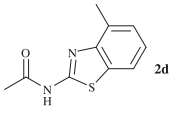
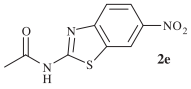
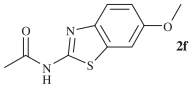
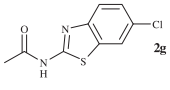
Entry	R	Ar	Product	Time (h)	Yield (%)[b]
1	CH_3	C_6H_5	 2a	8	96
2	CH_3	4-FC_6H_4	 2b	9	94
3	CH_3	2-$C_2H_5C_6H_4$	 2c	10	92
4	CH_3	2-$CH_3C_6H_4$	 2d	10	93
5	CH_3	4-$NO_2C_6H_4$	 2e	8	96
6	CH_3	4-$MeOC_6H_4$	 2f	8	98
7	CH_3	4-ClC_6H_4	 2g	9	95

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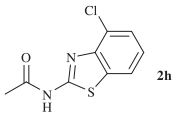
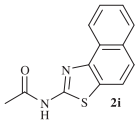
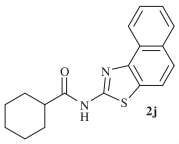
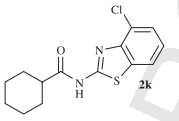
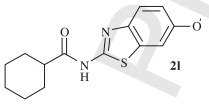
Table 2 (*Continued*)

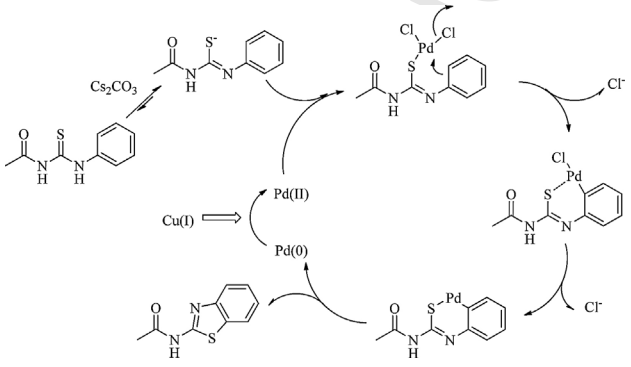
Entry	R	Ar	Product	Time (h)	Yield (%)[b]
8	CH_3	2-ClC_6H_4	 2h	12	88
9	CH_3	Naphthyl	 2i	12	96
10	Cyclohexyl	Naphthyl	 2j	12	93
11	Cyclohexyl	2-ClC_6H_4	 2k	10	91
12	Cyclohexyl	4-$MeOC_6H_4$	 2l	11	88

[a] Reaction conditions: **1** (1 mmol), $PdCl_2$ (10 mol%), CuI (20 mol%), Cs_2CO_3 (2 equiv.), and L-proline (20 mol%) in 5 mL of DMSO at 100 °C.
[b] All yields are isolated yields.

this cyclization, no reaction can take place (Table 1, entry 22). Thus, the optimized reaction conditions are as the follows: substrate (1 mmol), $PdCl_2$ (10 mol%), CuI (20 mol%), Cs_2CO_3 (2 equiv.), L-proline (20 mol%) in DMSO (4 mL) within 8 h at 100 °C.

In response to this encouraging result, we used a range of substituted 1-acetyl-3-(phenyl)thioureas to investigate the scope and limitation of this reaction. The corresponding products were obtained in excellent yields (88–98%). The results obtained under the optimized conditions are listed in Table 2. Initially, the substituents of phenyl were screened. The results demonstrate that little effect of the substituted groups on the benzene ring was observed for this transformation. Furthermore, substituents at different positions of the phenyl ring do not significantly affect the efficiency (Table 2, entries 1–8). It is noteworthy that the halosubstituted benzenes survived leading to halo-substituted products, which can be used for further transformations (Table 2, entries 2, 7, 8 and 11). In order to make the new Sankyo investigational drugs, the R group was selected as a cyclohexyl to give the corresponding products (Table 2, entries 10–12).

Although extensive studies on reaction mechanism have not yet been carried out, the proposed mechanism can be proposed according to the similar palladium-catalyzed processes [51] (Scheme 3). 1-Acetyl-3-(phenyl)thiourea was converted to the thioenolate in the presence of Cs_2CO_3. Pre-association of the sulphur atom in the thioenolate to $Pd(OAc)_2$ facilitates the *ortho*-palladation process with the concomitant release of chloride ion. The formation of the six-membered palladacycle and the subsequent reductive elimination leads to *N*-benzothiazol-2-yl-amide and Pd(0). The Pd(0) species are reoxidized to Pd(II) by CuI, thus completing the catalytic cycle.



Scheme 3. Postulated reaction mechanism.

4. Conclusion

In conclusion, we have achieved an efficient intramolecular cyclization of substituted 1-acetyl-3-(2-phenyl) thioureas catalyzed by palladium(II) catalysts through C(sp^2)–H functionalization. This method can provide more diversiform *N*-benzothiazol-2-yl-amides efficiently and quickly in high yields under relatively mild conditions. The combination of the generality with respect to the substrate scope and facile accessibility to the starting materials may generate numerous synthetic possibilities. Further mechanistic analysis of these reactions will be the subject of future work.

Acknowledgments

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