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Straightforward Synthesis of *N*-Methyl-4-(pin)B-2(3*H*)-benzothiazol-2-one: A Promising Cross-Coupling Reagent

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Abstract: Cyclo-condensation of *N*-methyl-2-bromoaniline with chlorocarbonylsulfenyl chloride (CCSC) promoted by $PhNMe_2$ and $AlCl_3$, afforded *N*-methyl-2-bromo-2(3*H*)-benzothiazol-2-one in good yield. Miyaura–Ishiyama cross-coupling of this brominated 2(3*H*)-benzothiazol-2-one with bis(pinacolato)diborone [$(pin)_2B_2$] produced a novel *N*-methyl-4-(pin)B-2(3*H*)-benzothiazol-2-one (**3**) using $(pin)_2B_2$ in the presence of the $PdCl_2(PPh_3)_2$ catalyst. The obtained 4-(pin)B compound is regarded as a new entry for the library of Suzuki–Miyaura cross-coupling reactions.

Keywords: heterocycles; benzothiazol-2-ones; cyclo-condensation; chlorocarbonylsulfenyl chloride; *S*,*N*-containing heterocycles; 4-substituted *N*-methyl-2-bromo-2(3*H*)-benzothiazol-2-ones; cross-coupling reagent; Suzuki–Miyaura cross-coupling; Miyaura–Ishiyama cross-coupling

1. Introduction

N-Substituted 2(3*H*)-benzothiazol-2-ones (**1**) are well-investigated *S*,*N*-containing heterocycles that are incorporated into various pharmaceuticals and agrochemicals [1] (Figure 1). Representative studies of **1** include the following: (1) tiaramide as a characteristic and useful anti-allergic drug [2]; (2) benazoline as a useful selective herbicide [3]; (3) chlobenthiazone as a potent agrochemical fungicide [4,5]; and (4) natural mevashuntin as a unique metabolite of an hydroxymethylglutaryl-CoA (HMG-CoA) reductase inhibitor [6] and as an efficient target for total synthesis [7]. Other notable pharmaceuticals have also been reported [8–11].

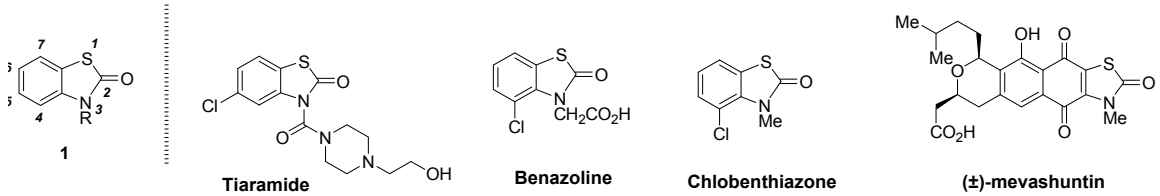


Figure 1. Representative biologically active compounds containing the *N*-substituted 2(3*H*)-benzothiazol-2-one structure.

Compared with simple unsubstituted, 6-chlorinated, and 5-acyl (or alkyl)-substituted *N*-alkyl-2(3*H*)-benzothiazol-2-ones, the synthesis of more inaccessible 4-substituted analogues is quite limited due to the three stereocongested contiguous substituents on the 4,8,9-positions. To the best of our knowledge, only three compounds containing the 4-substituted *N*-alkyl-2(3*H*)-benzothiazol-2-one structure have been reported: benazoline [3], chlobenthiazone [4,5], and mevashuntin [6] (Figure 1).

Among several synthetic approaches, one of the most straightforward forms of synthesis of *N*-alkyl-2(3*H*)-benzothiazol-2-ones utilizes cyclo-condensation of *N*-alkylaniline with chlorocarbonylsulfenyl chloride (ClC=OSCl, abbreviated CCSC) (**2**) [12], a unique commercially available bifunctional electrophilic reagent (Figure 2). The preparation of **2** on a >100 g scale was disclosed in the patent by the Bayer group [12]. Zumack and Kühle addressed the notable chemistry of CCSC (**2**) in their impressive review [13]; **2** serves as a key building blocks for various *S*,*N*-containing heterocyclic compounds. In connection with our studies utilizing **2** for the synthesis of *S*,*N*-containing heterocycles with a -COS- linkage, we reported on the synthesis of: (1) *N*-alkyl-2(3*H*)-benzothiazol-2-ones from *N*-alkylanilines [14]; (2) *N*-chloromethyl-2(3*H*)-benzothiazol-2-ones from *N*-aryltriazines [15]; (3) three *S*,*N*-heterocyclic compounds utilizing α-methoxycarbonylsulfenylation of ketones and aldehydes [16]; and (4) 1,3,4-(3*H*,6*H*)-thiadiazin-2-ones and 3(2*H*)-(*N*,*N*-dimethylamino)thiazolones from hydrazones [17].

Our recent interest in cross-coupling reactions, directed towards medicinal and process chemistry, [18–22], led us to investigate a concise synthesis of novel 4-(pinacolato)borane (pin)B derivative **3** derived from *N*-methyl-4-bromo-2(3*H*)-benzothiazol-2-one (**5**), which could serve as a convenient substrate for Suzuki–Miyaura cross-coupling reactions (Figure 2). A literature survey using SciFinder® revealed that a 6-(pin)B analogue was reported as the synthetic intermediate for: (1) inhibitors of matrix metalloproteinases (MMPs) and the production of tumor necrosis factor α (TNF α) [23]; (2) treatment of inflammatory respiratory diseases [24]; (3) modulators of aldosterone synthase and/or 11-β hydroxylase [25]; and (4) inhibitors of IKKβ (IκB Kinase-β) kinase [26]. Taking this background into account, we planned the synthesis of the less accessible and novel 4-(pinB) regioisomer **3**.

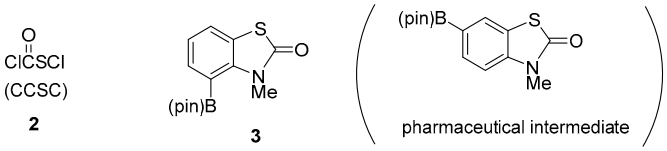
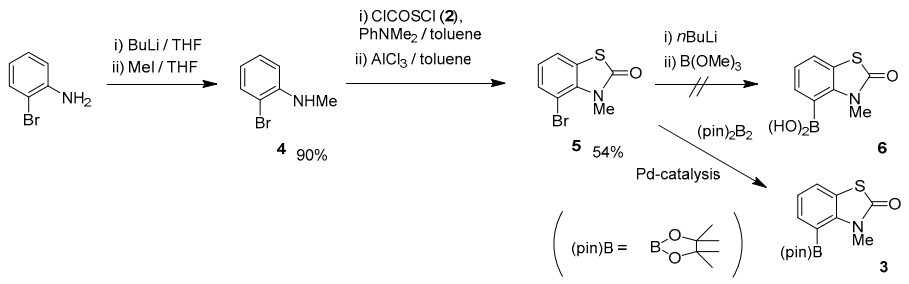


Figure 2. Chlorocarbonylsulfenyl chloride (CCSC) (**2**) and 4-*N*-methyl-4-(pin)B-2(3*H*)-benzothiazol-2-one derivative **3**.

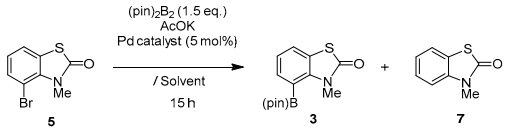
Scheme 1 shows the synthetic route for target compound **3**. Monomethylation of 2-bromoaniline gave *N*-methyl-2-bromoaniline (**4**) in 90% yield using the method of Barluenga and coworkers [27]. Cyclo-condensation of **4** using CCSC (**2**)/$PhNMe_2$-combined reagents, followed by the treatment with $AlCl_3$, afforded *N*-methyl-4-bromo-2(3*H*)-benzothiazol-2-one (**5**) in 54% yield. To prepare the boronic acid derivative we initially examined the lithiation of **5** using *n*-BuLi or *t*-BuMgCl at −78 °C, followed by treatment with $B(OMe)_3$. The reaction was sluggish, however, and only gave trace amounts of boronic acid derivative **6**. Thus, we turned our attention to investigating the more neutral Miyaura–Ishiyama protocol using bis(pinacolato)diborone [$(pin)_2B_2$] [28] to obtain 4-(pinacolato)borane [(pin)B] derivative **3**.



Scheme 1. Synthetic route for (pin)B derivative **3**.

As expected, compared with the preparation of 6-(pin)B isomer, the reaction of **5** gave poor results under the identical conditions [23] due to higher stereocongestion; a considerable reduction to form byproduct **7** was observed. To solve the problem, various Pd-catalysis conditions were screened and these results are listed in Table 1. The most standard method using a $PdCl_2$(dppf) catalyst under several conditions resulted in the formation of **3** in a maximum 30% yield with **7** (7–78%) as main product (entries 1–6). Pd catalysts bearing bisphosphine ligands such as $PdCl_2$(dppe), $PdCl_2$(dppb) gave unsatisfactory results (entries 7,8). The use of a $Pd_2(dba)_3$ catalyst resulted in no reaction. Gratifyingly, $PdCl_2(PPh_3)_2$ using cyclopentyl methyl ether (CPME) solvent furnished **5** in 51% isolated yield.

Table 1. Screening of Pd catalysts for Miyaura–Ishiyama cross-coupling.



Entry	Catalyst	Equivalent (AcOK)	Solvent	Temp./°C	Yield 3/% [a]	Yield 7/% [a]	Recovery 5/% [a]
1	$PdCl_2$(dppf)	1.5	MeOH	60	6	7	52
2		2.0	Toluene	110	7	44	0
3		3.0	DMSO		trace	30	0
4			1,4-dioxane	100	20	78	0
5		1.0			7	46	0
6		1.5			30	45	0
7	$PdCl_2$(dppe)				18	18	38
8	$PdCl_2$(dppb)			40	27	0	0
9	$Pd_2(dba)_3$				0	0	0
10	$PdCl_2(PPh_3)_2$				47	32	0
11			DME	80	20	13	24
12			MTBE	55	22	14	33
13			CPME	100	60 (51) [b]	15	0

[a] Determined by ^{1}H-NMR of the crude product using IS (ethylene carbonate). [b] Isolated.

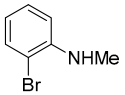
On the other hand, Miyaura–Ishiyama cross-coupling using chlobenthiazone instead for **5** with $(pin)_2B_2$ did not proceed due to lower reactivity of the chlorinated substrate.

2. Experimental Section

General

All reactions were carried out in oven-dried glassware under an argon atmosphere. Flash column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). TLC analysis was performed on 0.25 mm Silicagel Merck 60 F_{254} plates. Melting points were determined on a hot stage microscope apparatus (ATM-01, AS ONE, Osaka, Japan) and were uncorrected. NMR spectra were recorded on a JEOL DELTA 300 or JEOLRESONANCE ECX-500 spectrometer (JEOL, Tokyo, Japan), operating at 300 MHz or 500 MHz for ^{1}H-NMR, and at 75 MHz or 120 MHz for ^{13}C-NMR. Chemical shifts (δ ppm) in $CDCl_3$ were reported downfield from TMS (= 0) for ^{1}H-NMR. For ^{13}C-NMR, chemical shifts were reported relative to $CDCl_3$ (77.00 ppm) as an internal reference. IR Spectra were recorded on a JASCO FT/IR-5300 spectrophotometer (JASCO Corporation, Tokyo, Japan). Mass spectra were measured on a JEOL JMS-T100LC spectrometer (JEOL, Tokyo, Japan).

2-Bromo-N-methylaniline (**4**) [29]

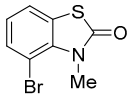


n-BuLi (1.60 M in hexane, 13.0 mL, 20.0 mmol) was added to a stirred solution of 2-bromoaniline (3.44 g, 20.0 mmol) in THF (20 mL) at −78 °C under an Ar atmosphere, followed by stirring at same

temperature for 15 min. MeI (1.3 mL, 20.0 mmol) was slowly added at that temperature and the mixture was allowed to warm to 20–25 °C. Stirring continued at same temperature for an additional 20 h. Water was added to the stirred mixture, which was extracted twice with ethyl acetate (AcOEt). The organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The resulting crude oil was purified by SiO_2 column chromatography (hexane/AcOEt = 10:1) to give the desired product (3.54 g, 90%).

Yellow pale oil; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.89 (s, 3H), 4.34 (s, 1H), 6.56–6.59 (m, 1H), 6.61–6.63 (m, 1H), 7.19–7.22 (m, 1H), 7.40–7.42 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 30.53, 109.5, 110.6, 117.5, 128.5, 132.2, 145.9.

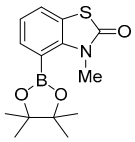
4-Bromo-3-methylbenzo[d]thiazol-2(3H)-one (**5**) [4,5]



Chlorocarbonylsulfenyl chloride (CCSC; **2**) (0.90 mL, 11.0 mmol) was added to a stirred solution of 2-bromo-*N*-methylaniline (1.86 g, 10.0 mmol) and *N*,*N*-dimethylaniline (1.33 g, 11.0 mmol) in toluene (10 mL) at 0–5 °C. Stirring continued at same temperature for 1 h under an Ar atmosphere. The reaction mixture was filtered through celite to remove HCl salt of *N*,*N*-dimethylaniline, and the filtrate was added to a stirred suspension of $AlCl_3$ (2.00 g, 15.0 mmol) in toluene (10 mL) at room temperature. The mixture was refluxed for 3 h. After cooling to room temperature, water was added to the stirred mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude product was purified by SiO_2 column chromatography (hexane/AcOEt = 10:1) to give the crude solid. Recrystallization from 2-propanol gave the desired product (1.31 g, 54%).

Colorless crystals; mp 130–132 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ =3.87 (s, 3H), 6.97–7.00 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 33.40, 104.0, 121.6, 123.7, 124.9, 132.4, 134.8, 170.0; IR (neat): ν_{max} = 1450, 1435, 1311, 1265, 1257, 1211, 1193, 1149, 1128, 1093, 1072 cm^{-1}; HRMS (ESI): *m*/*z* calcd. for C_8H_6BrNOS $[M + Na]^+$ 243.9432; found: 243.9405.

3-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(3H)-benzothiazolone (**3**)



Bis(pinacolato)diboron ($(pin)_2B_2$) (190 mg, 0.75 mmol), KOAc (74 mg, 0.75 mmol), and bis(triphenylpho sphine)palladium(II) dichloride (20 mg, 0.5 mmol) were successively added to a stirred suspension of 4-bromo-3-methylbenzothiazol-2-one **5** (122 mg, 0.50 mmol) in CPME at 20–25 °C under an N_2 atmosphere, and the mixture was stirred at 110 °C for 20 h. Water was added to the mixture, which was extracted twice with AcOEt. The combined organic phase was washed with water and brine, dried, and concentrated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 5:1), and washed with hexane to give the desired product (75 mg, 51%).

Colorless crystals; mp 98–100 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 12 H), 3.60 (s, 3H), 7.13–7.16 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.57 (d, 1H, *J* = 7.5 Hz) ; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.8, 32.1, 84.8, 122.4, 122.8, 124.6, 133.4, 141.1, 170.5.; IR (neat): ν_{max} = 1591, 1404, 1141, 1109, 1078, 1056, 1008, 960, 869, 846 cm^{-1}; HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{18}BNO_3S$, $[M + Na]^+$ 314.1001; found: 314.1000.

3. Conclusions

Straightforward synthesis of a novel 4-(pinacolato)borane [(pin)B] derivative of *N*-methyl-2(3*H*)-benzothiazol-2-one was performed through two key steps: (1) cyclo-condensation of *N*-methyl-2-bromoaniline with chlorocarbonylsulfenyl chloride (CCSC) to give *N*-methyl-2-bromo-2(3*H*)-benzothiazol-2-one; and (2) Miyaura–Ishiyama cross-coupling of this intermediate to produce 3-methyl-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2(3*H*)-benzothiazol-2-one.

Supplementary Materials: The following are available online at www.mdpi.com/1422-8599/2018/1/M976. All materials (substrates and reagents) in this work are commercially available at an inexpensive price. Copies of the ^{1}H, and ^{13}C-NMR spectra for compounds **3**, **4**, and **5** are available in the supplementary information.

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Author Contributions: S.I. contributed the overall syntheses. Y.T. prepared the whole manuscript. H.N. assisted in the references.

Conflicts of Interest: The authors declare no conflict of interest.

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