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Room-Temperature Ligand-Free Pd/C-Catalyzed C−S Bond Formation: Synthesis of 2-Substituted Benzothiazoles

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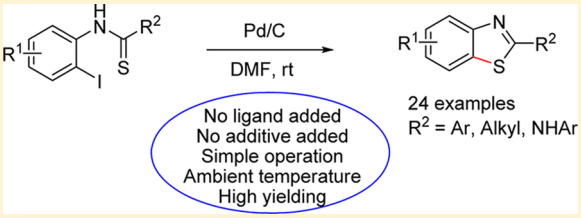
Supporting Information

ABSTRACT: The synthesis of 2-substituted benzothiazoles has been achieved via cyclization of *o*-iodothiobenzanilide derivatives using Pd/C as the catalyst at room temperature. The protocol is ligand-free, additive-free, and high-yielding and involves very mild conditions.

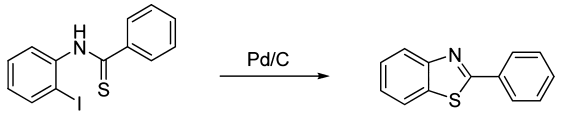


While many efficient and versatile methods have been developed for the formation of C−S bonds catalyzed by organometallics, transition-metal-catalyzed C−S bond formation reactions remain underdeveloped compared with methods for the formation of C−C, C−O, and C−N bonds, presumably because sulfur is known to poison metal catalysts.[1] Among all of the metal catalysts used in C−S bond formation reactions, palladium is one of the most widely used transition metals. Palladium on carbon, usually used as a hydrogenation and hydrogenolysis catalyst, has also been used as a heterogeneous catalyst in many coupling reactions.[2] Pd/C has many advantages over homogeneous palladium catalysts, such as easy separation and recovery, considerably less heavy-metal contamination of the products, wide commercial availability, and relatively low cost. However, the applications of Pd/C or other solid-supported palladium catalysts in C−S bond formation reactions are scarce.[3]

2-Substituted benzothiazoles are an important class of heterocyclic compounds because of their broad biological and pharmaceutical properties.[4] They are typically prepared via condensation of *o*-aminothiophenol or 2-haloaniline with carbonyl-containing compounds or equivalents;[5] oxidative intramolecular cyclization of thiobenzanilide;[6] transition-metal-catalyzed direct C−H functionalization/cyclization of thiobenzanilides;[7] transition-metal-catalyzed cyclization of *o*-halothiobenzanilides,[5m,8] *o*-haloarylthioureas,[8b,9] or *o*-halobenzanilides with various sulfur sources;[8c,10] and other methods.[8b,11] Nonetheless, the approaches suffer from limitations such as limited starting materials, the use of stoichiometric or excess amounts of oxidant, more than one type of metal, or harsh reaction conditions. A highly efficient and mild protocol for the synthesis of benzothiazoles would be of great interest to synthetic chemists. We present here a heterogeneous Pd/C-catalyzed C−S bond formation method for the preparation of 2-substituted benzothiazoles through cyclization of *o*-iodothiobenzanilides at room temperature without the addition of any ligands and additives.

During our study of new synthetic methods for the preparation of 2-substituted benzothiazoles,[7b] it was discovered that *o*-iodothiobenzanilide (**1a**) underwent cyclization to afford 2-phenylbenzothiazole (**2a**) in 87% yield with Pd/C catalyst at room temperature in methanol (Table 1, entry 1). Compared with many other transition-metal-catalyzed reactions, this reaction system was very simple because no ligand or additives were required. A quick survey of solvents showed that DMF gave the best result, as **2a** was formed in 98% yield after 12 h at room temperature in DMF (Table 1, entry 4). Meanwhile, the starting material was not fully consumed when CH_3CN or CH_2Cl_2 was used as the solvent, and the product **2a** was formed in 32% or 26% yield, respectively, after 24 h (Table 1, entries 2 and 3). Investigation of the catalyst loading showed that 2 mol % Pd/C was required. The yield was reduced to

Table 1. Optimization of the Reaction Conditions



1a **2a**

Entry	Catalyst Loading (mol %)	Solvent	Temp.	Time (h)	HPLC Yield
1	2	MeOH	rt	24	87
2	2	CH_3CN	rt	24	32
3	2	CH_2Cl_2	rt	24	26
4	2	DMF	rt	12	98
5	1	DMF	rt	12	57
6	0.5	DMF	rt	12	39
7	2	DMF	50 °C	12	96
8	1	DMF	50 °C	12	53
9	0.5	DMF	50 °C	12	24

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57% or 39% when 1 or 0.5 mol % Pd/C was used, respectively (Table 1, entries 5 and 6). Attempts to raise the reaction temperature to reduce the catalyst loading were not successful either (Table 1, entries 7−9).

With the optimized reaction conditions identified, we started to investigate the scope and functional group compatibility of this heterogeneous Pd/C-catalyzed cyclization reaction (Table 2). The results showed that the reaction is quite general. In some cases, higher catalyst loadings were necessary to accelerate sluggish reactions. Substitutions such as methyl, fluoro, and chloro groups at the para position of the *o*-iodoaniline did not affect the reaction. The corresponding benzothiazoles were obtained in isolated yields of 83%, 84%, and 94%, respectively (entries 2−4). Substitution on the other phenyl ring also had little impact on the reaction. Both strong electron-withdrawing and electron-donating groups were tolerated (71% for *p*-methoxy, 80% for *o*-methoxy, 91% for *p*-chloro, and 75% for *p*-cyano; entries 5−8). When both phenyl rings were substituted, the cyclization reactions proceeded well (entries 9−13). A heterocyclic compound was also a suitable substrate, as compound **2n**, in which the phenyl ring was replaced by pyridyl, was obtained in 78% isolated yield under the standard conditions. Attemps to extend the reaction to other *o*-halothiobenzanilides failed. No reaction occurred under the standard reaction conditions using *o*-bromothiobenzanilide or *o*-chlorothiobenzanilide as the substrate. Only a trace amount of the desired cyclization product was observed at elevated temperature.

Compared with the synthesis of 2-arylbenzothiazoles, synthetic methods for 2-alkylbenzothiazoles have been much less reported. To our delight, the reactions of substrates bearing alkyl groups also proceeded well, giving the corresponding 2-alkylbenzothiazoles (Table 3). Substrates with a primary alkyl group, such as methyl, propyl, pentyl, and neopentyl, gave isolated yields of 80%, 82%, 86%, and 80%, respectively (entries 1−4). Methyl substitution required a higher catalyst loading and a longer reaction time. The reaction was not affected by steric bulkiness of the substituents. Cyclopropyl and cyclopentyl groups afforded the corresponding products in 79% and 88% yield, respectively (entries 5 and 6). Tertiary alkyl groups (*tert*-butyl and adamantyl) gave yields of 79% and 91%, respectively (entries 7 and 8). When the alkyl group was substituted with functional groups, such as carbamate in compound **1w**, the cyclization occurred without problems (81% yield; entry 9). Since thioamide **1w** was prepared from glycine, it could be envisioned that a series of benzothiazoles with amino functionality on the C-2 alkyl substituent could be prepared starting from other amino acids. The substituents were not limited to alkyl groups, as 2-(2-phenylvinyl)-benzothiazole was obtained in 86% yield under the standard conditions (entry 10).

The Pd/C-catalyzed cyclization reaction is not limited to the synthesis of 2-aryl- and 2-alkyl-substituted benzothiazoles. We also tested the protocol on *o*-iodoarylthiourea **1y**. The reaction worked with a Pd/C catalyst loading of 20 mol %. The desired 2-amino-substituted product **2y** was obtained in 60% isolated yield at room temperature after 24 h. (Scheme 1)

As aryl iodide is reduced by Pd/C under a hydrogen atmosphere, we were curious to see whether compound **1a** would be reduced as usual or still undergo cyclization under a hydrogen atmosphere. It turned out that the cyclized product **2a** was formed in 92% HPLC yield as the only product. On the contrary, only reduction occurred when *o*-iodobenzanilide **3** was subjected to the same conditions (Scheme 2). These results indicate that the sulfur atom plays a key role in directing the reaction pathway.

A plausible reaction pathway is proposed in Scheme 3. It is believed that the reaction is likely initiated by coordination of the sulfur atom to Pd/C,[9a] leading to the formation of complex **5**. Subsequent formation of six-membered palladacycle **6** followed by reductive elimination would then afford the 2-substituted benzothiazole **2a** and regenerate Pd/C.

In summary, we have developed a synthesis of 2-substituted benzothiazoles via cyclization of *o*-iodothiobenzanilides. A C−S bond is formed through the transformation. The reaction uses inexpensive, readily available Pd/C as the catalyst without the addition of a ligand or additive. It works well under very mild conditions. The method can be used for the synthesis of 2-aryl-, 2-alkyl-, and 2-aminobenzothiazoles. It is complementary to the existing protocols for the synthesis of 2-substituted benzothiazoles.

EXPERIMENTAL SECTION

General Information. All of the reactions were carried out under a N_2 atmosphere using predried glassware. Thiobenzanilides were synthesized according to literature methods. Other chemicals, including Pd/C and anhydrous DMF, were obtained from commercial sources and used without further purification. Column chromatography was performed on silica gel (300−400 mesh) using technical-grade EtOAc and petroleum ether. NMR spectra were recorded in $CDCl_3$ on 300 and 400 MHz spectrometers. ^{1}H NMR chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0 ppm) or residual $CHCl_3$ (7.26 ppm). ^{13}C NMR chemical shifts are reported relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. High-resolution mass spectra were measured on a high-resolution TOF instrument with electrospray ionization. Melting points are uncorrected. IR data (ν_{max}) are reported in reciprocal centimeters and were collected on an FT-IR spectrophotometer. The structures of compounds **2a**−**h** were confirmed by comparison of data to those in ref 7e.

General Procedure. To a solution of *o*-iodothiobenzanilide **1** (0.5 mmol) in DMF (5 mL) was added 10% Pd/C (2 mol % unless otherwise specified). The reaction mixture was stirred at room temperature under a N_2 atmosphere. After completion of the reaction as monitored by TLC, the reaction mixture was diluted with EtOAc (10 mL) and filtered through a Celite pad to remove Pd/C. To the filtrate was added H_2O (15 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. Flash silica gel column chromatography rinsed with petroleum ether/ethyl acetate afforded the desired benzothiazole product **2**.

*2-Phenylbenzothiazole (**2a**).* The general procedure was followed using *N*-(2-iodophenyl)benzothioamide (169.5 mg, 0.5 mmol). Purification by column chromatography yielded **2a** (93.8 mg, 89%) as a white solid. R_f = 0.35 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.11 (m, 3H), 7.89 (d, J = 7.9 Hz, 1H), 7.49−7.52 (m, 4H), 7.38 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 154.0, 135.0, 133.5, 130.9, 128.9, 127.4, 126.2, 125.1, 123.1, 121.5.

*6-Methyl-2-phenylbenzothiazole (**2b**).* The general procedure was followed using *N*-(2-iodo-4-methylphenyl)benzothioamide (176.6 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2b** (93.3 mg, 83%) as a white solid. R_f = 0.30 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 3.9, Hz, 2H), 7.96 (d, J = 8.3 Hz, 1H), 7.68 (s, 1H), 7.48−7.49 (m, 3H), 7.30 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 152.2, 135.3, 135.2, 133.7, 130.7, 128.9, 127.9, 127.4, 122.7, 121.3, 21.5.

*6-Fluoro-2-phenylbenzothiazole (**2c**).* The general procedure was followed using *N*-(4-fluoro-2-iodophenyl)benzothioamide (178 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by

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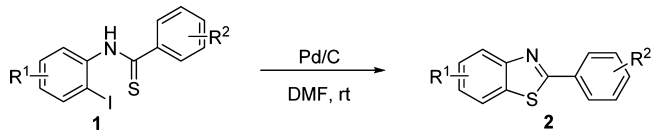
Table 2. Synthesis of 2-Arylbenzothiazoles[a]



1 2

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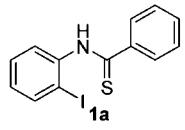
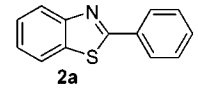
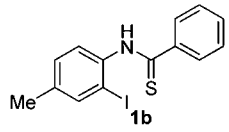
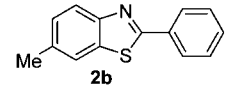
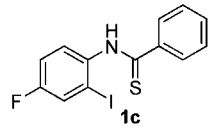
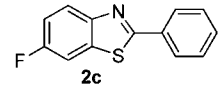
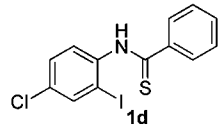
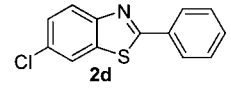
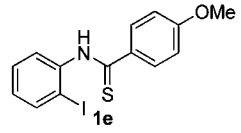
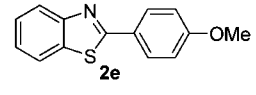
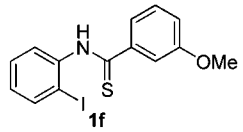
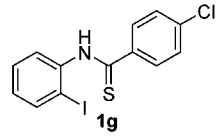
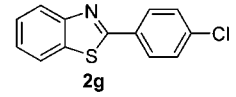
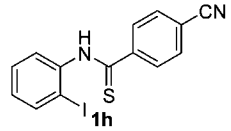
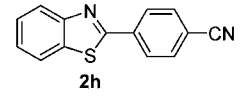
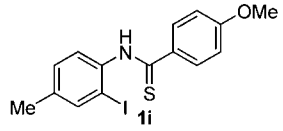
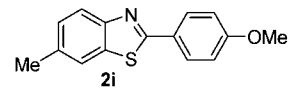
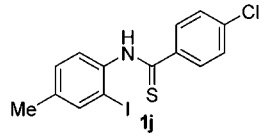
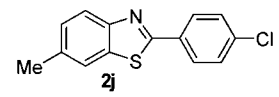
1	 1a	 2a	12	89
2	 1b	 2b	36	83[c]
3	 1c	 2c	6	84[c]
4	 1d	 2d	6	94
5	 1e	 2e	6	71[c]
6	 1f	 2f	24	80
7	 1g	 2g	6	91
8	 1h	 2h	12	75[c]
9	 1i	 2i	24	90[c]
10	 1j	 2j	6	71

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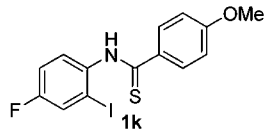
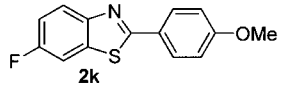
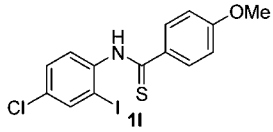
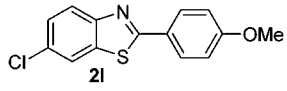
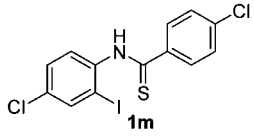
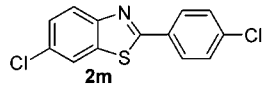
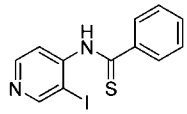
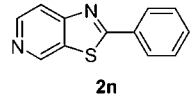
11	 1k	 2k	12	91[c]
12	 1l	 2l	6	80[c]
13	 1m	 2m	6	88
14	 1n	 2n	12	78[d]

[a]Reaction conditions: substrate **1** (0.5 mmol) and Pd/C (2 mol %) in DMF (5 mL) at room temperature, unless otherwise noted. [b]Isolated yields. [c]Pd/C (5 mol %). [d]Pd/C (10 mol %).

column chromatography yielded **2c** (96.3 mg, 84%) as a yellow solid. R_f = 0.40 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−8.04 (m, 3H), 7.56 (dd, J = 7.9, 1.8 Hz, 1H), 7.47−7.54 (m, 3H), 7.19−7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.68, 160.4 (d, J = 244.5 Hz), 150.67, 135.94 (d, J = 10.5 Hz), 133.24, 130.92, 128.96, 127.33, 124.03 (d, J = 9.8 Hz), 114.83 (d, J = 24.0 Hz), 107.72 (d, J = 27 Hz).

*6-Chloro-2-phenylbenzothiazole (**2d**).* The general procedure was followed using *N*-(4-chloro-2-iodophenyl)benzothioamide (186.8 mg, 0.5 mmol). Purification by column chromatography yielded **2d** (115 mg, 94%) as a pale-yellow solid. R_f = 0.35 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.06 (m, 2H), 7.96 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 1.6 Hz, 1H), 7.48−7.50 (m, 3H), 7.43 (dd, J = 8.7, 1.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 152.6, 136.1, 133.1, 131.1, 131.0, 129.0, 127.4, 127.0, 123.8, 121.1.

*2-(4-Methoxyphenyl)benzothiazole (**2e**).* The general procedure was followed using *N*-(2-iodophenyl)-4-methoxybenzothioamide (184.6 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2e** (85.5 mg, 71%) as a white solid. R_f = 0.15 (PE/EtOAc = 30:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00−8.03 (m, 3H), 7.84 (d, J = 7.3 Hz, 1H), 7.45 (t, J = 7.0 Hz, 1H), 7.33 (t, J = 7.0 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 161.8, 154.1, 134.8, 129.0, 126.3, 126.1, 124.7, 122.7, 121.4, 114.3, 55.3.

*2-(3-Methoxyphenyl)benzothiazole (**2f**).* The general procedure was followed using *N*-(2-iodophenyl)-3-methoxybenzothioamide (122 mg, 0.5 mmol). Purification by column chromatography yielded **2f** (96.4 mg, 80%) as a white solid. R_f = 0.25 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.63−7.68 (m, 2H), 7.97 (t, J = 7.6 Hz, 1H), 7.37−7.40 (m, 2H), 7.04 (d, J = 8.1 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 159.9, 153.9, 134.9, 134.7, 129.9, 126.2. 125.1, 123.1, 121.5, 120.1, 117.2, 111.9, 55.3.

*2-(4-Chlorophenyl)benzothiazole (**2g**).* The general procedure was followed using 4-chloro-*N*-(2-iodophenyl)benzothioamide (186.8 mg, 0.5 mmol). Purification by column chromatography yielded **2g** (111.5 mg, 91%) as a pale-yellow solid. R_f = 0.40 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 8.3 Hz, 2H), 7.91 (d, J = 7.9 Hz, 1H), 7.46−7.53 (m, 3H), 7.40 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 154.0, 137.0, 135.0, 132.0, 129.2, 128.6, 126.4, 125.4, 123.2, 121.6.

*2-(4-Cyanophenyl)benzothiazole (**2h**).* The general procedure was followed using 4-cyano-*N*-(2-iodophenyl)benzothioamide (182.1 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2h** (88.5 mg, 75%) as a white solid. R_f = 0.15 (PE/EtOAc = 30:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 8.09 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.1 Hz, 1H), 7.41 (t, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 153.9, 137.3, 135.2, 132.6, 127.7, 126.7, 126.0, 123.7, 121.7, 118.2, 113.9.

*2-(4-Methoxyphenyl)-6-methylbenzothiazole (**2i**).*[12] The general procedure was followed using *N*-(2-iodo-4-methylphenyl)-4-methoxybenzothioamide (191.6 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2i** (114.7 mg, 90%) as a white solid. R_f = 0.15 (PE/EtOAc = 30:1); mp = 177.7−179.0 °C (lit. 174−177 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.56 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 6.89 (d, J = 8.3 Hz, 2H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 161.7, 152.3, 135.0, 134.8, 128.9, 127.7, 126.5, 122.3, 121.3, 114.3, 55.4, 21.5; IR 2994, 2920, 2833, 2042, 1596, 1435, 1247, 962, 825, 563 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{15}H_{14}NOS$ 256.0796, found 256.0786.

*2-(4-Chlorophenyl)-6-methylbenzothiazole (**2j**).*[11b] The general procedure was followed using 4-chloro-*N*-(2-iodo-4-methylphenyl)-benzothioamide (193.9 mg, 0.5 mmol). Purification by column chromatography yielded **2j** (92.2 mg, 71%) as a pale-yellow solid. R_f = 0.35 (PE/EtOAc = 30:1); mp = 193.2−193.9 °C (lit. 136−138 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.3 Hz, 1H), 7.65 (s, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 152.1, 136.7, 135.6, 135.2, 132.2, 129.2, 128.5, 128.1, 122.7, 121.3; IR 2911, 2848, 1902, 1474, 1399, 1087, 965, 810, 688, 617, 563 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{11}ClNS$ 260.0301, found 260.0297.

*6-Fluoro-2-(4-methoxyphenyl)benzothiazole (**2k**).*[12] The general procedure was followed using *N*-(4-fluoro-2-iodophenyl)-4-methoxybenzothioamide (193.6 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2k** (117.8 mg, 91%) as a white solid. R_f = 0.20 (PE/EtOAc = 30:1);

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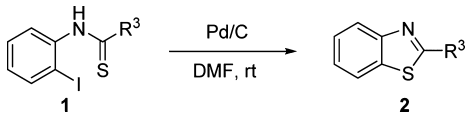
Table 3. Synthesis of 2-Alkylbenzothiazoles[a]



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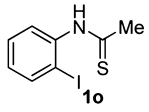
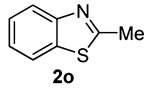
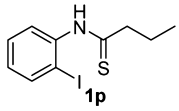
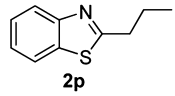
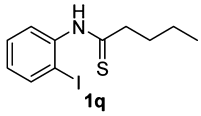
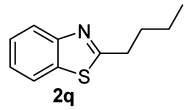
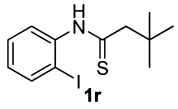
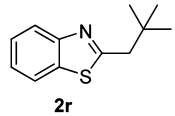
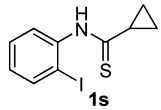
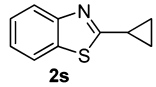
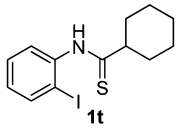
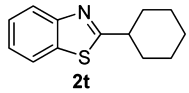
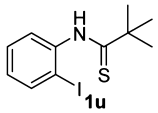
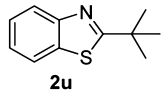
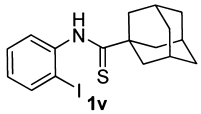
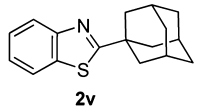
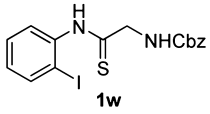
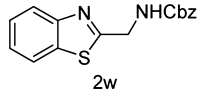
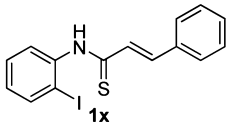
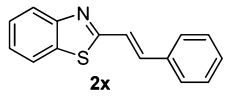
1	 1o	 2o	24	80[c]
2	 1p	 2p	6	82[d]
3	 1q	 2q	6	86[d]
4	 1r	 2r	6	80
5	 1s	 2s	6	79[d]
6	 1t	 2t	24	88
7	 1u	 2u	6	79
8	 1v	 2v	6	91
9	 1w	 2w	12	81
10	 1x	 2x	6	86

[a]Reaction conditions: substrate **1** (0.5 mmol) and Pd/C (2 mol %) in DMF (5 mL) at rt, unless otherwise noted. [b]Isolated yields. [c]Pd/C (10 mol %). [d]Pd/C (5 mol %).

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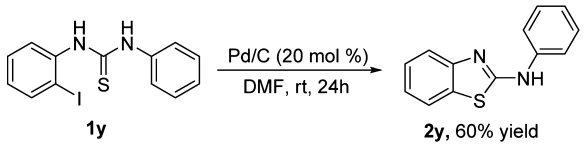
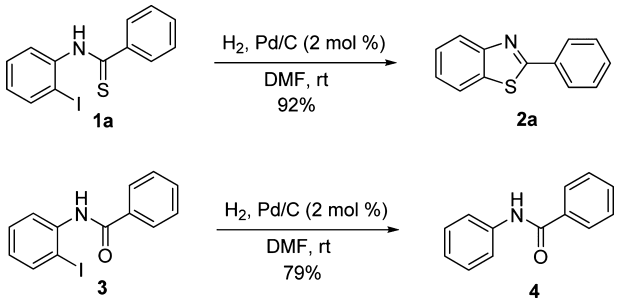
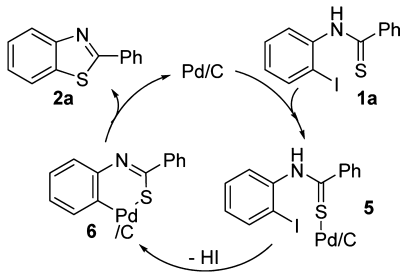
Scheme 1. Synthesis of 2-Aminobenzothiazole 2y



Scheme 2. Cyclization versus Hydrogenation



Scheme 3. Proposed Mechanism



mp = 132.9–133.7 °C (lit. 110–112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.97 (m, 3H), 7.51 (dd, J = 8.0, 1.9 Hz, 1H), 7.18 (td, J = 8.0, 2.0 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H); 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.50, 161.87, 160.2 (d, J = 244.0 Hz), 150.77, 135.74 (d, J = 11 Hz), 128.92, 126.08, 123.55 (d, J = 9 Hz), 114.64 (d, J = 24.0 Hz), 114.34, 107.70 (d, J = 27.0 Hz) 55.39; IR 3080, 2836, 2357, 1601, 1453, 1250, 968, 813, 697, 575 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{11}FNOS$ 260.0545, found 260.0534.

*6-Chloro-2-(4-methoxyphenyl)benzothiazole (**2l**).*[12] The general procedure was followed using *N*-(4-chloro-2-iodophenyl)-4-methoxybenzothioamide (201.9 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2l** (110 mg, 80%) as a pale-yellow solid. R_f = 0.20 (PE/EtOAc = 30:1); mp = 160.7–161.1 °C (lit. 134–137 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 2H), 7.90 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.7, 2.1 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 162.0, 152.7, 135.9, 130.5, 129.0, 126.9, 125.9, 123.4, 121.0, 114.4, 55.4. IR 3063, 2839, 2360, 1604, 1480, 1239, 1096, 965, 822, 694, 567 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{14}H_{11}ClNOS$ 276.0250, found 276.0234.

*6-Chloro-2-(4-chlorophenyl)benzothiazole (**2m**).* The general procedure was followed using 4-chloro-*N*-(4-chloro-2-iodophenyl)-benzothioamide (203.4 mg, 0.5 mmol). Purification by column chromatography yielded **2m** (123 mg, 88%) as a white solid. R_f = 0.40 (PE/EtOAc = 40:1); mp = 200.9–203.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.97 (m, 3H), 7.84 (s, 1H), 7.45–7.43 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 152.6, 137.3, 136.2, 131.7, 131.3, 129.3, 128.7, 127.3, 124.0, 121.2; IR 3083, 2357, 1893, 1593, 1471, 1396, 1298, 1087, 956, 816, 652, 563 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{13}H_8Cl_2NS$ 279.9755, found 279.9749.

*2-Phenylthiazolo[5,4-c]pyridine (**2n**).*[13] The general procedure was followed using *N*-(3-iodopyridin-4-yl)benzothioamide (51 mg, 0.15 mmol) and 10% Pd/C (0.015 mmol, 10 mol %) in DMF (1.5 mL). Purification by column chromatography yielded **2n** (24 mg, 78%) as a white solid. R_f = 0.28 (PE/EtOAc = 3:1); mp = 137.8–138.4 °C (lit. 135–136 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 0.7 Hz, 1H), 8.65 (d, J = 5.6 Hz, 1H), 8.13 (dd, J = 8.0, 1.5 Hz, 2H), 7.93 (dd, J = 5.6, 0.7 Hz, 1H), 7.59–7.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 158.8, 145.9, 144.2, 132.7, 132.1, 132.0, 129.2, 128.00, 117.4; IR 3036, 2363, 1578, 1474, 1405, 1230, 965, 843, 772, 688, 569 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{12}H_9N_2S$ 213.0490, found 213.0481.

*2-Methylbenzothiazole (**2o**).* The general procedure was followed using *N*-(2-iodophenyl)ethanethioamide (138.5 mg, 0.5 mmol) and 10% Pd/C (0.05 mmol, 10 mol %). Purification by column chromatography yielded **2o** (60 mg, 80%) as a colorless oil. R_f = 0.15 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 10.6 Hz, 1H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 153.3, 135.6, 125.9, 124.7, 122.2, 121.3, 20.1; IR 2922, 2848, 1715, 1462, 1256, 1012, 807, 739 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ C_8H_8NS 150.0377, found 150.0379.

*2-Propylbenzothiazole (**2p**).* The general procedure was followed using *N*-(2-iodophenyl)butanethioamide (152.5 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2p** (72.5 mg, 82%) as a colorless oil. R_f = 0.25 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 3.08 (t, J = 7.6 Hz, 2H), 1.86–1.95 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 153.1, 135.0, 125.7, 124.5, 122.3, 121.3, 36.1, 22.9, 13.6; IR 3066, 2967, 2872, 1524, 1435, 1307, 1152, 1063, 763, 724, 430 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{10}H_{12}NS$ 178.0690, found 178.0687.

*2-Butylbenzothiazole (**2q**).* The general procedure was followed using *N*-(2-iodophenyl)pentanethioamide (159.6 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2q** (73 mg, 86%) as a colorless oil. R_f = 0.25 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 3.11 (t, J = 7.6 Hz, 2H), 1.82–1.88 (m, 2H), 1.44–1.49 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 153.2, 135.0, 125.7, 124.5, 122.4, 121.4, 34.0, 31.7, 22.2, 13.7; IR 3066, 2961, 2857, 1521, 1432, 1075, 760, 727 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{11}H_{14}NS$ 192.0847, found 192.0841.

*2-Neopentylbenzothiazole (**2r**).*[14] The general procedure was followed using *N*-(2-iodophenyl)-3,3-dimethylbutanethioamide (166.5 mg, 0.5 mmol). Purification by column chromatography yielded **2r** (82 mg, 80%) as a pale-yellow solid. R_f = 0.30 (PE/EtOAc = 30:1); mp = 53.6–54.4 °C (lit. 54 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 3.01 (s, 2H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 153.2, 135.5, 125.7, 124.6, 122.6, 121.2, 47.9, 32.0, 29.6; IR 3051, 2952, 2360, 1509, 1438, 1239, 1102, 766, 650, 602 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{12}H_{16}NS$ 206.1003, found 206.0991.

*2-Cyclopropylbenzothiazole (**2s**).* The general procedure was followed using *N*-(2-iodophenyl)cyclopropanecarbothioamide (151.5 mg, 0.5 mmol) and 10% Pd/C (0.025 mmol, 5 mol %). Purification by column chromatography yielded **2s** (69 mg, 79%) as a colorless oil. R_f = 0.25 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 2.36–2.42 (m, 1H), 1.22 (d, J = 6.2 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 153.2, 134.0, 125.9, 124.2, 122.0, 121.3, 15.2, 11.6; IR 3066, 2926, 1724, 1515, 1435, 1242, 1111, 1048, 757, 724, 700 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{10}H_{10}NS$ 176.0534, found 176.0553.

*2-Cyclohexylbenzothiazole (**2t**).* The general procedure was followed using *N*-(2-iodophenyl)cyclohexanecarbothioamide (172.6 mg, 0.5 mmol). Purification by column chromatography yielded **2t** (95.5 mg, 88%) as a colorless oil. R_f = 0.25 (PE/EtOAc = 30:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 3.06–3.12 (m, 1H), 2.19 (d, J = 12.4 Hz, 2H), 1.87 (d, J = 12.8 Hz, 2H), 1.75 (d, J = 12.1 Hz, 1H), 1.59–1.68 (m, 2H), 1.39–1.48 (m, 2H), 1.25–1.35 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 153.0, 134.4, 125.7,

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124.4, 122.5, 121.4, 43.3, 33.2, 26.0, 25.7; IR 3063, 2926, 2851, 1515, 1435, 1248, 989, 751, 727, 430 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{13}H_{16}NS$ 218.1003, found 218.0993.

*2-tert-Butylbenzothiazole (**2u**).* The general procedure was followed using *N*-(2-iodophenyl)-2,2-dimethylpropanethioamide (159.6 mg, 0.5 mmol). Purification by column chromatography yielded **2u** (75.4 mg, 79%) as a colorless oil. R_f = 0.35 (PE/EtOAc = 30:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 153.2, 134.9, 125.6, 124.4, 122.6, 121.4, 38.2, 30.7; IR 3063, 2961, 2926, 1679, 1509, 1435, 1361, 1256, 1048, 1007, 751, 727, 441 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{11}H_{14}NS$ 192.0847, found 192.0847.

*2-Adamantanebenzothiazole (**2v**).*[15] The general procedure was followed using *N*-(2-iodophenyl)adamantanethioamide (198.7 mg, 0.5 mmol). Purification by column chromatography yielded **2v** (122.4 mg, 91%) as a white solid. R_f = 0.33 (PE/EtOAc = 30:1); mp = 84.9−85.9 °C (lit. 103.5−104.5 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 2.14 (s, 9H), 1.81 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.0, 153.1, 134.3, 125.6, 124.2, 122.5, 121.4, 42.9, 40.0, 36.4, 28.5; IR 2899, 2842, 2366, 1510, 1438, 1001, 804, 754, 724, 676 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{17}H_{20}NS$ 270.1316, found 270.1299.

*Benzyl Benzothiazol-2-ylmethylcarbamate (**2w**).* The general procedure was followed using benzyl 2-(2-iodophenylamino)-2-thioxoethylcarbamate (106.5 mg, 0.25 mmol) and DMF (2.5 mL). Purification by column chromatography yielded **2w** (60 mg, 81%) as a white solid. R_f = 0.30 (PE/EtOAc = 3:1); mp = 118.4−119.7 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.36 (m, 6H), 5.88 (s, 1H), 5.16 (s, 2H), 4.78 (d, J = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.3, 152.9, 136.1, 135.0, 128.5, 128.2, 128.1, 126.1, 125.1, 122.8, 121.7, 67.2, 43.4. IR 3289, 3030, 2354, 1682, 1536, 1259, 962, 754, 697, 572 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{16}H_{15}N_2O_2S$ 299.0860, found 299.0849.

*2-Styrylbenzothiazole (**2x**).*[16] The general procedure was followed using (*E*)-*N*-(2-iodophenyl)-3-phenylprop-2-enethioamide (182.6 mg, 0.5 mmol). Purification by column chromatography yielded **2x** (101.9 mg, 86%) as a white solid. R_f = 0.20 (PE/EtOAc = 30:1); mp = 108.5−109.5 °C (lit. 106−108 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 6.6 Hz, 2H), 7.33−7.49 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 153.7, 137.5, 135.3, 134.2, 129.3, 128.8, 127.3, 126.2, 125.2, 122.8, 122.0, 121.4; IR 3054, 2363, 1628, 1477, 1447, 1319, 1188, 953, 745, 688, 664, 611, 548 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{15}H_{12}NS$ 238.0690, found 238.0679.

*N-Phenylbenzothiazol-2-ylamine (**2y**).*[17] The general procedure was followed using 1-(2-iodophenyl)-3-phenylthiourea (177 mg, 0.5 mmol) and 10% Pd/C (0.1 mmol, 20 mol %). Purification by column chromatography yielded **2w** (68 mg, 60%) as a white solid. R_f = 0.20 (PE/EtOAc = 10:1); mp = 163.8−164.2 °C (lit. 158−159 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.49−7.51 (m, 2H), 7.40 (t, J = 7.9 Hz, 2H), 7.32 (t, J = 7.1 Hz, 1H), 7.13−7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 151.2, 139.9, 129.7, 129.5, 126.1, 124.4, 122.3, 120.8, 120.4, 119.2; IR 3185, 2940, 2360, 1623, 1557, 1444, 1218, 920, 742, 668, 587 cm^{-1}; HRMS (ESI) calcd for $[M + H]^+$ $C_{13}H_{11}N_2S$ 227.0643, found 227.0628.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all products, IR spectra for compounds **2i**−**y**, and X-ray crystallographic data for compound **2k** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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