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A C–H Functionalization Protocol for the Direct Synthesis of Benzobisthiazole Derivatives

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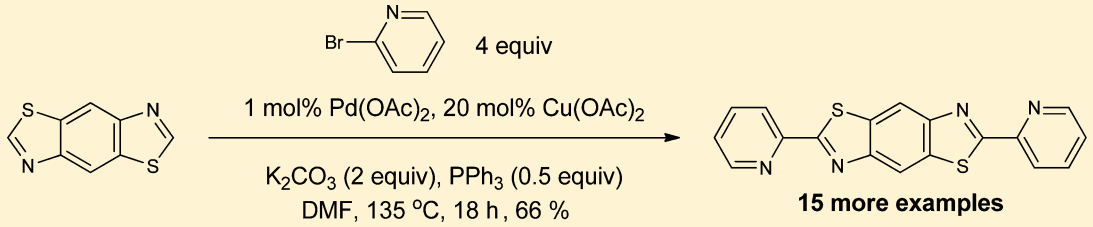
Supporting Information



ABSTRACT: Benzobisthiazole and thiazolothiazole derivatives are useful components in a variety of organic electronics devices resulting from their absorption, electroluminescence, and charge-transport properties. A convenient synthesis of these molecules via palladium/copper cocatalyzed C–H bond functionalization is described. Reaction conditions were optimized in a bromobenzene/benzobisthiazole system that allowed for the one-pot functionalization of both thioimidate positions of benzobisthiazole. The extension of this methodology to the synthesis of cruciform architectures and the functionalization of thiazolothiazole is also described.

The development of new solution-processable small molecule and polymeric organic semiconductors for use in printed devices, including organic field effect transistors (OFETs), organic photovoltaic cells (OPVs), and organic light-emitting diodes (OLEDs), continues to be an important research goal.[1−6] In particular, the development of stable, electron-transport materials with high charge-carrier mobilities is of importance for OFETs and OPVs.[7−9] Efforts to improve the performance of electron-transport materials have stimulated interest in developing robust methods for the incorporation of heterocycles with relatively high electron affinities (often referred to as "electron poor") into these materials.

Benzo[1,2-*d*;4,5-*d*′]bisthiazole (hereafter referred to as benzobisthiazole) is one such electron-poor heterocycle, and recent reports describe the self-assembly and charge-transport properties of small molecules built around this core (e.g., **1** and **2**, Figure 1),[10] as well as the use of benzobisthiazole-based donor–acceptor copolymers (e.g., **3**) in OPVs and highly stable OFETs.[11−14] In all cases, the construction of these materials requires either *de novo* synthesis of a prefunctionalized benzobisthiazole precursor or functionalization of each conjugated unit, followed by traditional Suzuki or Stille cross-coupling.

Related benzobisoxazole cruciform structures have also been used for surface modification in molecular electronics and as fluorophores in novel sensor chemistry.[15−19] Again, the synthesis of these materials requires prefunctionalization of the individual building blocks.

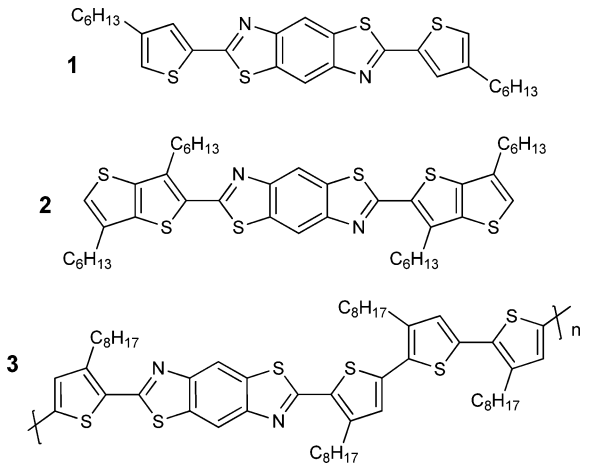


Figure 1. Structures of benzothiazole-based compounds investigated for use in printed organic electronic devices.

In order to simplify the synthesis of benzobisthiazole-based materials and potentially facilitate the tuning of their optical and electronic properties, we conducted a study examining recently developed thiazole C–H functionalization chemistry for the direct synthesis of symmetrically end-capped benzobisthiazoles.[20−22]

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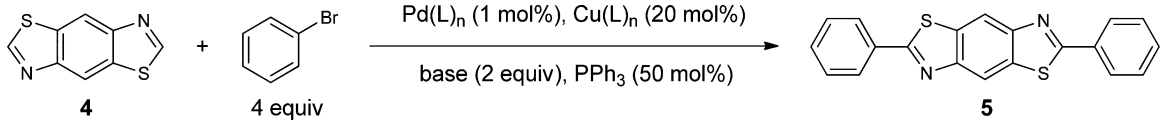
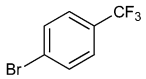
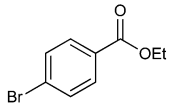
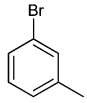
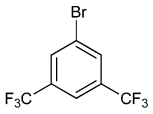
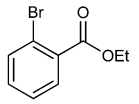
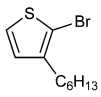
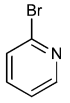
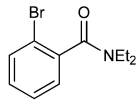
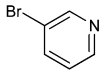
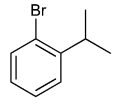
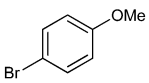
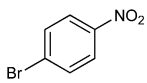
Table 1. Optimization of Benzobisthiazole Cross-Coupling with Bromobenzene



entry	$Pd(L)_n$	$Cu(L)_n$	solvent	base	temp (°C)	time (h)	conversion (%)[a]
1[b]	PXPd	CuI-xantphos	toluene	Cs_2CO_3	100	6.5	8
2	$Pd(OAc)_2$	$Cu(OAc)_2$	toluene	K_2CO_3	110	5.5	61
3	$Pd(OAc)_2$	$Cu(OAc)_2$	dioxane	K_2CO_3	100	5.5	23
4	$Pd(OAc)_2$	$Cu(OAc)_2$	xylenes	K_2CO_3	135	5.5	71
5	$Pd(OAc)_2$	$Cu(OAc)_2$	DMA	K_2CO_3	135	5.5	72
6	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	135	5.5	72
7	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	115	3.5	25
8	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	100	3.5	11
9[c]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	115	7.5	97
10[d]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	115	3.5	93
11[e]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	K_2CO_3	115	0.5	95

[a]Conversion is based on GC analysis using anthracene as an internal standard. [b]0.25 mol % PXPd (dichlorobis(chloro-di-*tert*-butylphosphine)palladium), 1 mol % CuI-xantphos, 2.5 equiv of Cs_2CO_3 were used, and no PPh_3 was added. [c]50 mol % $Cu(OAc)_2$ and 1.25 equiv of PPh_3. [d]75 mol % $Cu(OAc)_2$, 1.88 equiv of PPh_3. [e]1.0 equiv of $Cu(OAc)_2$, 2.5 equiv of PPh_3.

Table 2. Substrate Scope of Cu/Pd Cocatalyzed Cross-Coupling of Aryl Halides with Benzobisthiazole[a]

entry	ArBr	Yield A(%)	Yield B(%)	entry	ArBr	Yield A(%)	Yield B(%)	entry	ArBr	Yield A(%)	Yield B(%)
1		72	--	6		77	--	11		52	--
2		81	--	7		72	--	12		37	--
3		43	--	8		66	7	13		15	--
4		49	--	9		58	23	14		54	--
5		38	--	10		--	51				

[a]All yields are isolated.

In our initial experiments, application of Huang and co-workers' conditions for benzothiazole C−H functionalization to benzobisthiazole (**4**) provided the difunctionalized product **5** in only 8% conversion after 6.5 h (Table 1, entry 1).[20] The $Pd(OAc)_2/Cu(OAc)_2/PPh_3$ conditions reported by Huang et al. provided 61% conversion to **5** after 5.5 h.[21] Therefore, these conditions were used as the basis for further optimization (Table 1, entry 2). Entries 2−6 demonstrate the effect of solvent on the efficiency of conversion. Solvents that allowed the reaction to be carried out at higher temperature (xylenes, DMF, and DMA) all produced similarly high conversions (71−72%, entries 4−6, respectively). Lower boiling solvents gave lower conversions, with toluene delivering product **5** in 61% conversion and reactions run in dioxane only reaching 23%. In

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order to assess the importance of the reaction temperature relative to solvent polarity, a series of reactions were conducted in DMF (entries 6−8). Decreasing the temperature from 135 to 115 to 100 °C dramatically decreased the conversions from 72% to 25% to 11% (Table 1, entries 6−8). We note that increasing the amount of $Cu(OAc)_2$ from 20 to 50 mol % at 115 °C caused conversion to increase from 25% to 97% in 7.5 h (Table 1, entries 7 and 9). Further increasing the $Cu(OAc)_2$ loading to 100 mol % facilitated 95% conversion in just 30 min (Table 1, entry 11). These observations are consistent with a reaction mechanism in which copper insertion into the thiazole C−H bond is rate-limiting.[23]

Our optimization studies led us to adopt two sets of conditions for further consideration. In cases where both reagents and products are robust and large-scale preparation is required, the extended reaction time at 135 °C with 20 mol % copper would be preferred (Table 1, entry 6). However, in cases where either the starting materials or the products are sensitive, increased copper loading allows for milder reaction conditions (lower temperature, reduced reaction time, Table 1, entry 11).

With these considerations in mind, we examined the influence of substitution on the reaction outcome using lower catalyst loading (Table 2). The electron-neutral aryl halides bromobenzene and 3-bromotoluene (Table 2, entries 1 and 2) afforded the desired difunctionalized products in good isolated yields at 71% and 81%, respectively. However, more electron-rich aryl halides tended to result in reduced yields. *p*-Bromoanisole (Table 2, entry 5) gave just 38% of the desired product, while 2-bromothiophene and 2-bromo-3-hexylthiophene provided 49% and 43% of the desired products, respectively (Table 2, entries 4 and 3). In these cases, the lower yields may be due to the very electron-rich nature of the thiophenes, or competing palladium catalyzed thiophene polymerization, a known process, may be consuming the starting material.[24,25] In contrast, electron-poor aryl halides tended to perform well in the direct arylation. The electron-poor aryl halide *p*-trifluoromethylbromobenzene gave 77% of the desired product, while 1-bromo-3,5-bis(trifluoromethyl)-benzene gave the desired difunctionalized product in 72% yield. These data suggest that this methodology may provide a robust route for accessing electron-poor materials with the potential to act as electron-transport materials. For example, both 2- and 3-bromo-substituted pyridines were well-tolerated in these reactions (Table 2, entries 8 and 9). These coupling partners can often prove problematic because of their coordination to metal centers under similar conditions.[26] Although the difunctionalized product was still the major component in the reaction mixture (66% and 58%, respectively), the mono-functionalized product was also observed in each case. Our hypothesis is that, due to decreased solubility, the mono-functionalized product precipitated from the reaction mixture and was, therefore, not fully converted to the difunctionalized product. This hypothesis was supported by the reaction with *p*-bromonitrobenzene in which the very insoluble monofunctionalized product was the only product observed (51%, entry 10).

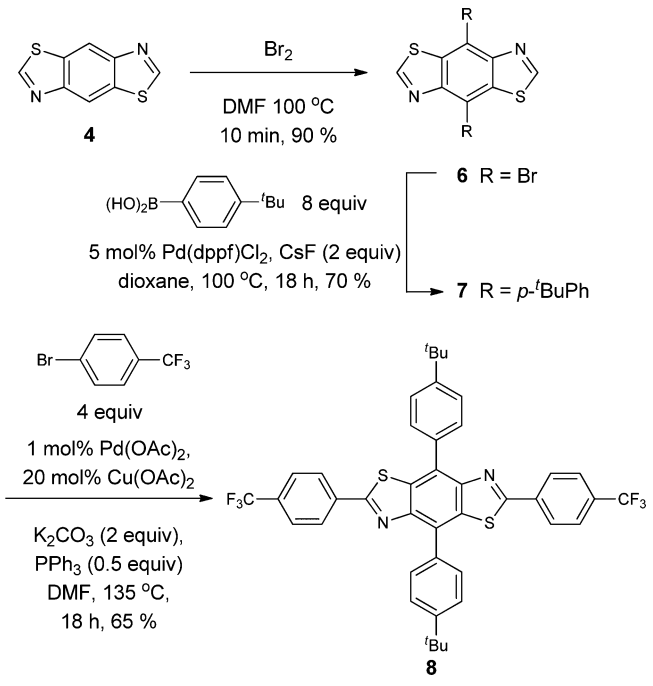
To construct electron-poor materials with extended conjugation, we attempted to couple benzobisthiazole with *N*,*N*′-bis(*n*-octyl)-2-bromonaphthalenediimide (not shown). Despite simple electron-poor aryl bromides and heterocyclic aryl bromides having been successfully coupled, we were unable to obtain any product using either set of conditions that were established during reaction optimization: either low copper loading and high temperature or high loading of copper and lower temperature.

In order to determine if palladium coordination with the *ortho* amide or steric inhibition was detrimental to the reaction with *N*,*N*′-bis(*n*-octyl)-2-bromonaphthalenediimide, we examined a series of simple model compounds (Table 2, entries 11−14). We observed that an ester in the *para* position was well-tolerated (52% yield, entry 11); however, when the ester was in the *ortho* position, the yield dropped to 37%. An amide in the *ortho* position decreased the yield to 15% (Table 2, entry 13), which is consistent with coordination to the palladium being detrimental to the reaction since the amide is the stronger coordinating group. From these two data points, we could not rule out *ortho* substitution itself preventing cross-coupling with the naphthalenediimide substrate, so we also examined the noncoordinating 1-bromo-2-isopropylbenzene in the reaction. The yield of this reaction was 54% (Table 2, entry 14); significantly lower than other alkyl substituted bromobenzenes like 3-bromotoluene, which gave 81% of the desired product. This indicates that both *ortho* substitution and proximity of a group able to coordinate inhibit the reaction, and as such, we did not pursue the naphthalenediimide further.

Having established the reactivity profile of the C−H bond functionalization reaction, we sought to expand this methodology to the synthesis of cruciform architectures, an important structural motif in sensors and optoelectronics.[19,27] We were able to directly brominate the 4- and 8-positions of benzobisthiazole using Br_2 in DMF (**6**, 90% yield, Scheme 1). These electrophilic bromination conditions gave exclusively the 4,8-bromination and no functionalization at the 2- or 6-positions.

Differentiating the 4,8- and 2,6-positions allowed for the Suzuki cross-coupling to efficiently elaborate the 4,8-axis (**7**, Scheme 1). The strict requirement for a copper cocatalyst in the thiazole C−H functionalization reaction prevents any competing reaction at the thioimidate positions during Suzuki

Scheme 1. Cruciform Synthesis from Benzobisthiazole



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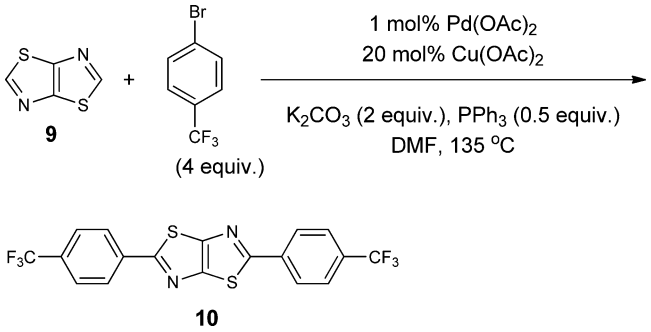
cross-coupling. Subsequent dual C−H arylation under our established conditions completes the synthesis of the cruciform structure (**8**) in just three steps from the parent benzobisthiazole.

In addition to the benzobisthiazole systems, we were also interested in thiazolothiazole systems.[28−30] Because of the similarities between thiazolothiazoles and benzobisthiazoles, we were confident that our methodology would be effective with thiazolothiazole (**9**) as an alternative coupling partner and would streamline the synthesis of these molecules. The coupling of **9** with *p*-trifluoromethylbromobenzene proceeded well, affording the desired product **10** in 65% yield (Scheme 2).

Scheme 2. Thiazolothiazole Cross-Coupling with *p*-Trifluoromethylbromobenzene



Herein, we have described a simple and general methodology to access densely functionalized benzobisthiazole materials in one step. This methodology has the potential to impact the materials and organic electronic communities due to the electron-poor nature of the products making them useful in the development of organic field effect transistors, organic photovoltaic cells, and organic light-emitting diodes.

EXPERIMENTAL SECTION

General Method A for the Synthesis of Substituted Benzobisthiazoles. Benzobisthiazole (192 mg, 1.0 mmol), ArBr (4.0 mmol, 4 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (36 mg, 0.20 mmol, 20 mol %), K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv), and PPh_3 (131 mg, 0.5 mmol, 0.5 equiv) were combined in an oven-dried flask and purged with nitrogen. DMF (3 mL) was added, and the reaction was heated to 135 °C until the starting material was consumed, as indicated by TLC analysis. The reaction mixture was filtered, the filtrate was washed with water (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The organic layers were combined, washed with aqueous copper sulfate and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The title compounds were purified by flash chromatography on silica gel.

General Method B for the Synthesis of Substituted Benzobisthiazoles. Benzobisthiazole (192 mg, 1.0 mmol), ArBr (4.0 mmol, 4 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), $Cu(OAc)_2$ (36 mg, 0.20 mmol, 20 mol %), K_2CO_3 (276 mg, 2.0 mmol, 2.0 equiv), and PPh_3 (131 mg, 0.5 mmol, 0.5 equiv) were combined in an oven-dried flask and purged with nitrogen. DMF (3 mL) was added, and the reaction was heated to 135 °C until the starting material was consumed, as indicated by TLC analysis. The reaction mixture was filtered, and the filter cake was washed with water (20 mL). The solid was dried under vacuum to give the title compound.

2,6-Diphenylbenzobisthiazole (5, Table 2, entry 1). General method A with bromobenzene (628 mg, 4.0 mmol) provided after chromatography (R_f = 0.2; 15% hexanes in EtOAc) the title compound as an amorphous yellow powder (244 mg, 71%). Its spectroscopic data were in good agreement with the literature.[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (s, 2H), 8.01−8.13 (m, 4H), 7.51−7.52 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.2, 152.4, 134.7, 133.7, 131.5, 129.3, 127.0, 115.7. HRMS (+APCI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{13}N_2S_2$ 345.0516; Found 345.0514.

2,6-Di-*m*-tolylbenzobisthiazole (Table 2, entry 2). General method B with 1-bromo-3-methylbenzene (684 mg, 4.0 mmol) provided the title compound as an amorphous yellow powder (301 mg, 81%). Its spectroscopic data were in good agreement with the literature.[32] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 (s, 2H), 7.95 (s, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 6H). HRMS (+APCI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2S_2$ 373.0828; Found 373.0825. IR (thin film, cm^{-1}) ν = 3358, 1624, 1560, 1395, 1308.

2,6-Bis(3-hexylthiophen-2-yl)benzobisthiazole (Table 2, entry 3). General method A with 2-bromo-3-hexylthiophene (988 mg, 4.0 mmol) provided after chromatography (R_f = 0.4; 10% hexanes in EtOAc) the title compound as an amorphous pale green powder (225 mg, 43%). Its spectroscopic data were in good agreement with the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (s, 2H), 7.41 (d, *J* = 5.1, 2H), 7.01 (d, *J* = 5.1, 2H), 3.06 (t, *J* = 7.8, 4H), 1.73 (p, *J* = 7.0, 4H), 1.46 (p, *J* = 7.0, 4H), 1.36−1.29 (m, 8H), 0.89 (t, *J* = 7.0, 6H).

2,6-Di(thiophen-2-yl)benzobisthiazole (Table 2, entry 4). General method A with 2-bromothiophene (652 mg, 4.0 mmol) provided after chromatography (R_f = 0.2; 10% hexanes in EtOAc) the title compound as an amorphous pale green powder (173 mg, 49%). Its spectroscopic data were in good agreement with the literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 2H), 8.01 (d, *J* = 3.1, 2H), 7.59 (d, *J* = 3.1, 2H), 7.25 (m, 2H).

2,6-Bis(4-methoxyphenyl)benzobisthiazole (Table 2, entry 5). General method A with 1-bromo-4-methoxybenzene (748 mg, 4.0 mmol) provided after chromatography (R_f = 0.1; 10% hexanes in EtOAc) the title compound as an amorphous green powder (153 mg, 38%). Its spectroscopic data were in good agreement with the literature.[34] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (s, 2H), 8.06 (d, *J* = 8.6, 4H), 7.02 (d, *J* = 8.6, 4H), 3.89 (s, 6H).

2,6-Bis(4-(trifluoromethyl)phenyl)benzobisthiazole (Table 2, entry 6). General method B with 1-bromo-4-(trifluoromethyl)-benzene (896 mg, 4.0 mmol) provided the title compound as an amorphous pale green powder (370 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.62 (s, 2H), 8.24 (d, *J* = 8.2 Hz, 4 H), 7.78 (d, *J* = 8.2 Hz, 4 H). ^{13}C NMR (75 MHz, solid-state) δ = 170.2, 156.3, 155.4, 137.7, 136.7, 129.4, 127.2, 119.0, 118.1. HRMS (+APCI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{11}N_2F_6S_2$ 481.0262; Found 481.0273. IR (thin film, cm^{-1}) ν = 1568, 1408, 1323, 1170, 1131.

2,6-Bis(3,5-bis(trifluoromethyl)phenyl)benzobisthiazole (Table 2, entry 7). General method B with 1-bromo-3,5-bis-(trifluoromethyl)benzene (1172 mg, 4.0 mmol) provided the title compound as an amorphous yellow-green powder (443 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 2H), 8.56 (s, 4H), 8.02 (s, 2H). ^{13}C NMR (75 MHz, solid-state) δ = 162.6, 150.9, 134.1, 132.4, 131.3, 126.8, 122.4, 122.4, 117.1. HRMS (+APCI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_9N_2F_{12}S_2$ 617.0018; Found 617.0010. IR (thin film, cm^{-1}) ν = 3351, 1556, 1621, 1370, 1282, 1124.

2,6-Di(pyridin-2-yl)benzobisthiazole (Table 2, entry 8). General method A with 2-bromopyridine (632 mg, 4.0 mmol) provided after chromatography (R_f = 0.2; 1% DCM in EtOAc) the title compound as an amorphous yellow-green powder (228 mg, 66%). Its spectroscopic data were in good agreement with the literature.[35] ^{1}H NMR (400 MHz, DMSO-*d6*, 40 °C) δ = 8.88 (s, 2H), 8.74 (d, *J* = 3.9 Hz, 2H), 8.37 (d, *J* = 7.1 Hz, 2H), 8.05 (dd, *J* = 5.9, 2.0 Hz, 2 H), 7.60 (m, 2 H). ^{13}C NMR (75 MHz, solid-state) δ = 170.0, 152.4, 151.8, 146.6, 138.1, 135.8, 124.9, 121.8, 116.3. HRMS (+APCI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{11}N_4S_2$ 347.0420; Found 347.0417. IR (thin film, cm^{-1}) ν = 3349, 1559, 1453, 1397, 1315.

2,6-Di(pyridin-3-yl)benzobisthiazole (Table 2, entry 9). General method A with 3-bromopyridine (632 mg, 4.0 mmol) provided after chromatography (R_f = 0.2; 10% DCM in EtOAc) the title compound as an amorphous yellow-green powder (200 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.31 (s, 2H), 8.73 (d, *J* = 4.7 Hz, 2H), 8.64 (s, 2 H), 8.40 (d, *J* = 8.6 Hz, 2H), 7.46 (dd, *J* = 8.2, 5.9 Hz, 2

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H). ^{13}C NMR (75 MHz, solid-state) δ = 171.2, 162.9, 155.8, 150.2, 139.7, 137.7, 132.5, 124.5, 120.0. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{11}N_4S_2$ 347.0425; Found 347.0421. IR (thin film, cm^{-1}) ν = 3231, 1659, 1573, 1424, 1393, 1307.

2-(4-Nitrophenyl)benzobisthiazole (Table 2, entry 10). General method B with 1-bromo-4-nitrobenzene (804 mg, 4.0 mmol) provided the title compound as an amorphous yellow-green powder (159 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (s, 1H), 8.71 (d, J = 4.8 Hz, 1H), 8.69 (s, 1H), 8.64 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 7.88 (dt, J = 8.0, 2.0 Hz, 1 H), 7.42 (ddd, J = 7.6, 4.8, 1.2 Hz, 1 H). ^{13}C NMR (75 MHz, solid-state) δ = 167.29, 152.6, 154.5, 150.0, 140.0, 136.6, 134.2, 128.5, 126.0, 117.8. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{14}H_8N_3O_2S_2$ 314.0053; Found 314.0052. IR (thin film, cm^{-1}) ν = 3094, 1594, 1514, 1342, 1313.

Diethyl 4,4′-(Benzobisthiazole-2,6-diyl)dibenzoate (Table 2, entry 11). General method A with ethyl 4-bromobenzoate (912 mg, 4.0 mmol) provided after chromatography (R_f = 0.4; 10% DCM in EtOAc) the title compound as an amorphous yellow-green powder (253 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 8.18 (bs, 8H), 4.41 (q, J = 7.4 Hz, 4 H), 1.42 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, solid-state) δ = 165.8, 163.6, 155.2, 152.2, 151.0, 135.5, 132.3, 130.6, 128.1, 122.4, 115.1, 62.9, 61.1, 17.0, 15.7, 14.2. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}N_2O_4S_2$ 489.0937; Found 489.0943. IR (thin film, cm^{-1}) ν = 1710, 1512, 1406, 1270.

Diethyl 2,2′-(Benzobisthiazole-2,6-diyl)dibenzoate (Table 2, entry 12). General method A with ethyl 2-bromobenzoate (912 mg, 4.0 mmol) provided after chromatography (R_f = 0.3; 20% DCM in EtOAc) the title compound as an amorphous yellow powder (180 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (s, 2H), 7.88 (dd, J = 7.0, 1.2 Hz, 2 H), 7.76 (dd, J = 7.0, 1.6 Hz, 2 H), 7.65−7.57 (m, 4 H), 4.25 (q, J = 7.0 Hz, 4 H), 1.09 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (75 MHz, solid-state) δ = 170.1, 165.7, 160.3, 155.2, 150.5, 132.3, 128.2, 116.4, 113.5, 61.9, 14.8. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}N_2O_4S_2$ 489.0937; Found 489.0942. IR (thin film, cm^{-1}) ν = 3367, 1626, 1594, 1550, 1392.

2,2′-(Benzobis(thiazole)-2,6-diyl)bis(*N*,*N*-diethylbenzamide) (Table 2, entry 13). General method A with 2-bromo-*N*,*N*-diethylbenzamide (1.02 g, 4.0 mmol) provided after chromatography (R_f = 0.2; 20% DCM in EtOAc) the title compound as an amorphous yellow powder (80 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 2 H), 7.95 (d, 2 H, J = 6.3), 7.53−7.50 (m, 4 H), 7.40−7.38 (m, 2 H), 3.91−3.80 (m, 2H), 3.41−3.30 (m, 2H), 3.21−3.10 (m, 4H), 1.32 (t, J = 7.0 Hz, 6 H), 0.97 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (75 MHz, solid-state) δ = 170.4, 167.7, 165.9, 160.2, 154.4, 153.0, 150.5, 139.0, 137.5, 134.7, 132.8, 130.1, 128.5, 125.8, 114.6, 44.2, 40.3, 14.5, 12.9. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{31}N_4O_2S_2$ 543.1883; Found 543.1885. IR (thin film, cm^{-1}) ν = 1631, 1427, 1310, 1221, 768.

2,6-Bis(2-isopropylphenyl)benzobisthiazole (Table 2, entry 14). General method B with 1-bromo-2-isopropylbenzene (796 mg, 4.0 mmol) provided the title compound as an amorphous yellow-green powder (229 mg, 54%). Its spectroscopic data were in good agreement with the literature.[32] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.70 (s, 2 H), 7.68−7.63 (m, 2 H), 7.53−7.44 (m, 6 H), 3.74 (m, 2 H), 1.30−1.23 (m, 12H).

4,8-Dibromobenzobisthiazole (6). Benzobisthiazole (100 mg, 0.53 mmol) and Br_2 (0.4 mL) were combined in anhydrous DMF (2 mL). The reaction vial was put in an oil bath preheated to 100 °C. After 10 min, the reaction mixture was cooled to room temperature and then poured into a saturated aqueous solution of $NaHSO_4$. An off-white solid precipitated out and was filtered off to give the title compound as an amorphous tan powder (183 mg, 90%). ^{1}H NMR (400 MHz, DMSO-*d*6) δ = 9.63 (s, 2H). ^{13}C NMR (75 MHz, solid-state) δ = 159.6, 148.1, 133.1, 113.5. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_8H_3Br_2N_2S_2$ 348.8098; Found 348.8099. IR (thin film, cm^{-1}) ν = 3392, 1649, 1471, 1417, 1389.

4,8-Bis(4-(*tert*-butyl)phenyl)benzobisthiazole (7). Dibromobenzobisthiazole (400 mg, 1.14 mmol) was combined with (4-(*tert*-butyl)phenyl)boronic acid (203 mg, 1.14 mmol, 1 equiv), Pd(dppf)Cl_2 (41 mg, 0.057 mmol, 0.05 equiv), and CsF (347 mg, 2.28 mmol, 2 equiv) in anhydrous dioxane (26 mL). The mixture was refluxed, and additional portions of boronic acid (203 mg, 1.14 mmol) were added every 2 h until a total of 1626 mg (8 equiv) had been added. The reaction was refluxed for an additional 12 h for a total of 18 h. The reaction was cooled to room temperature; water was added to form an off-white precipitate. The solid was filtered and purified by flash chromatography on silica gel eluting with 5% EtOAc in hexanes (R_f = 0.6) to afford the title compound as an amorphous yellow powder (365 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (s, 2H), 7.78 (d, J = 8.4 Hz, 4H), 7.59 (d, J = 8.4 Hz, 4H), 1.40 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 151.7, 149.2, 135.3, 134.9, 129.6, 129.3, 126.0, 35.0, 31.6. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{29}N_2S_2$ 457.1769; Found 457.1773. IR (thin film, cm^{-1}) ν = 3026, 2950, 1450, 846.

4,8-Bis(4-(*tert*-butyl)phenyl)-2,6-bis(4-(trifluoromethyl)-phenyl)benzobis(thiazole) (8). 4,8-Bis(4-(*tert*-butyl)phenyl)-benzobisthiazole (190 mg, 0.42 mmol), 1-bromo-4-(trifluoromethyl)-benzene (375 mg, 0.23 mL, 1.66 mmol, 4 equiv), $Cu(OAc)_2$ (15 mg, 0.08 mmol, 0.20 equiv), K_2CO_3 (115 mg, 0.83 mmol, 2.0 equiv), and PPh_3 (54.6 mg, 0.21 mmol, 0.5 equiv) were combined in an oven dry flask and purged with nitrogen. $Pd(OAc)_2$ (0.93 mg, 0.0042 mmol, 0.01 equiv) was added as a solution in DMF (0.01 M, 0.42 mL). Additional DMF (1.6 mL) was added, and the reaction was heated to 115 °C until the reaction was complete by TLC (18 h). The reaction was cooled to room temperature, water was added, and a yellow solid precipitated. The solid was isolated by filtration and purified on a silica column (R_f = 0.4; 5% EtOAc in hexanes) to give the title compound as an amorphous yellow powder (180 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, J = 7.6 Hz, 4H), 7.93 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 7.6 Hz, 4H), 7.62 (d, J = 7.6 Hz, 4H), 1.45 (s, 18H). ^{13}C NMR (75 MHz, solid-state) δ = 166.3, 152.6, 149.6, 136.8, 134.9, 131.9, 130.4, 129.0, 126.6, 125.2, 35.5, 32.0. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{35}F_6N_2S_2$ 745.2140; Found 745.2150. IR (thin film, cm^{-1}) ν = 2962, 1320, 1126, 1067.

2,5-Bis(4-(trifluoromethyl)phenyl)thiazolothiazole (10). A round-bottom flask was charged with thiazolothiazole (20 mg, 0.14 mmol), 1-bromo-4-(trifluoromethyl)benzene (126 mg, 0.56 mmol, 4 equiv), $Cu(OAc)_2$ (5 mg, 0.028 mmol, 0.2 equiv), K_2CO_3 (38 mg, 0.28 mmol, 2.0 equiv), and PPh_3 (18 mg, 0.07 mmol, 0.5 equiv) and purged with nitrogen. $Pd(OAc)_2$ (0.3 mg, 0.0014 mmol, 0.01 equiv) was added as a solution in anhydrous DMF (0.01 M, 0.14 mL). Additional anhydrous DMF (0.85 mL) was then added, and the reaction was heated to 135 °C under an atmosphere of nitrogen. Once the reaction was complete (18 h), it was filtered and the solid was washed with DCM and water. The solid was dried under vacuum to afford the title compound as an amorphous brown powder (40 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, J = 8.4 Hz, 4 H), 7.74 (d, J = 8.4 Hz, 4 H). ^{13}C NMR (75 MHz, solid-state) δ = 168.3, 150.7, 137.1, 131.7, 125.8. HRMS (+APCI) m/z: $[M + H]^+$ Calcd for $C_{18}H_9N_2F_6S_2$ 431.0106; Found 431.0107. IR (thin film, cm^{-1}) ν = 3382, 1615, 1559, 1405, 1323, 1123, 1110.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all new compounds can be found in the Supporting Information. 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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