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Transition-Metal-Free Synthesis of Borylated Thiophenes via Formal Thioboration

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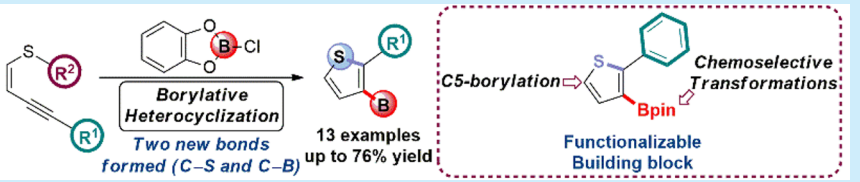
Supporting Information



ABSTRACT: A simple, regiocontrolled, and transition-metal-free approach to access exclusively 3-borylated thiophene derivatives is reported. The commercially available *B*-chlorocatecholborane reagent (ClBcat) acts as a carbophilic Lewis acid to activate the alkyne in readily synthesized (*Z*)-organylthioenyne substrates. This boron-induced activation initiates the formal thioboration and subsequent sulfur dealkylation, leading to the formation of 3-borylated thiophenes in good yields. The resulting borylated thiophenes are isolable as boronic esters (Bpin) and boronamides (Bdan). These borylated products are amenable to diverse downstream functionalization reactions, i.e., C−C bond formation through cross-coupling, azidation, bromination, and C−H activation.

Borylated heteroaromatic rings are key building blocks for accessing several derivatizations,[1−8] especially for the rapid generation of carbon−carbon bonds in preparation of bioactive molecules.[9−11] Among these heteroarenes, thiophene[12−18] rings bearing boron groups have found widespread applications in the synthesis of pharmaceutical drugs,[19] such as Bruton's tyrosine kinase (BTK) inhibitor **1** and as fungicide agrochemical[20] Penthiopyrad **2**. Furthermore, the combination of thiophene and boron units has displayed promising photophysical and redox properties[21,22] in the development of organic materials. Dithienoborepine (DTB) derivatives **3** have been introduced as functionalizable polycyclic π-electron systems (Figure 1).[23]

The installment of a boron functionality as a transient group into heteroarenes has been extensively explored, and several methods have been developed[24−27] such as Miyaura borylation,[28] sequential lithiation/borylation,[29] or C−H borylation.[30,31] However, these methods require the use of transition-metal catalysts, lack regioselectivity, and/or are incompatible with specific substrates, i.e., those possessing multiple halides or additional heterocyclic rings.

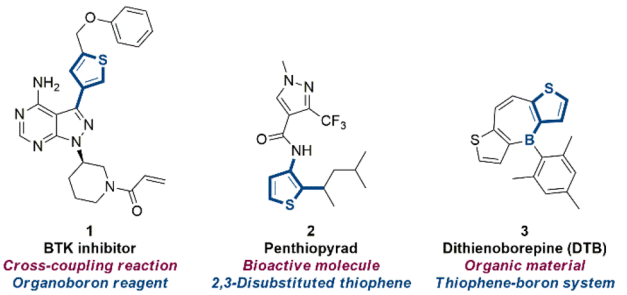


Figure 1. Synthetic importance of thiophene building blocks.

Aside from the established procedures requiring the use of halide-containing thiophenes[32] as precursors, the regioselective borylation of thiophenes has remained limited to iridium-catalyzed C−H borylation methods. Borylation at the α-position of the thiophene has been reported to be straightforward[33] due to the high acidity of the C−H bonds at that position; however, the current available strategies to incorporate a boron group at the 3- and 4-positions in a regioselective way have been restricted by the use of nonremovable directing groups such as aldimines and thiophene analogues presubstituted at the 2- and 5-positions[34] preventing the functionalization of the heterocycle in an efficient manner.

In a similar approach, the prior generation of a silica-supported iridium complex allowed Sawamura to perform an ester-directed borylation[35] (Scheme 1a). It is noteworthy that, to date, this is the only method leading to 3-borylated thiophenes with at least one unsubstituted α-position in one synthetic step. An additional technique described by Smith has led to the boron-containing thiophenes through a sequential iridium-catalyzed diborylation/monodeborylation route based on the higher reactivity of the 2- and 5-positions for selective iridium-catalyzed deborylation[36] (Scheme 1b). This strategy required the use of iridium catalysts over both steps of the procedure.

Recently, we have reported borylative heterocyclizations[37−45] to access heteroaryl boronic ester analogues in a

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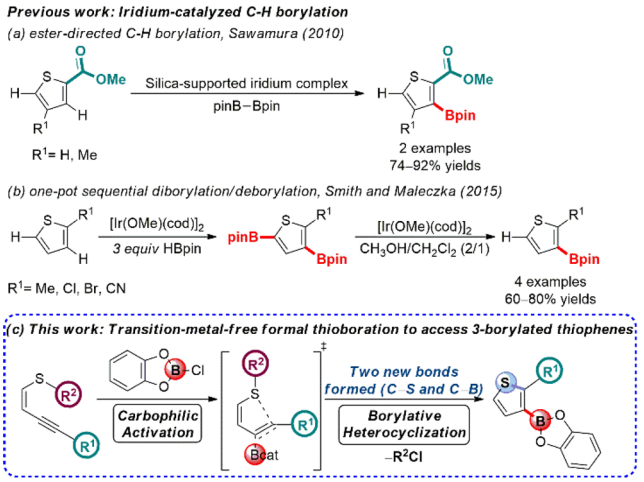
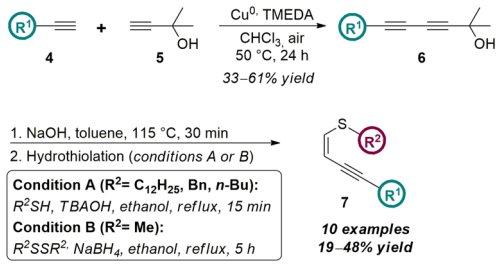
Scheme 1. Current Strategies for the Borylation of Thiophenes



regiocontrolled manner through carbophilic activation of C−C π bonds[46−52] by using the commercially available *B*-chlorocatecholborane (ClBcat) via a cyclization−dealkylation sequence. This strategy enabled construction of borylated 5- and 6-membered heteroaromatic rings that were primed for accessing the rich downstream functionalization chemistry of boron, including cross-coupling reactions. We now report an extension of this strategy to the transition-metal-free synthesis of borylated thiophenes via formal thioboration (Scheme 1c). This reaction exclusively produces the 3-borylated regioisomer, in complement to alternative borylation strategies, and does not require a transition metal.

(*Z*)-Organylthioenyne analogues are efficient starting materials due to their straightforward preparation from readily available alkynes. A sequential route involving a copper-catalyzed heterocoupling[53] of alkynes **4** with 2-methylbut-3-yn-2-ol **5** followed by cleavage under basic conditions[54] of the buta-1,3-diyne derivatives **6** and subsequent hydrothiolation[55−57] allowed access to monosubstituted (*Z*)-organylthioenynes **7** in moderate-to-good yields (Scheme 2). This procedure was applied to the majority of the substrates.

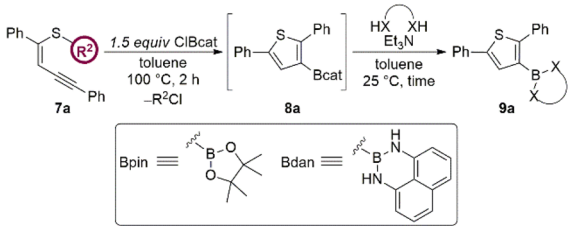
Scheme 2. Synthesis of (*Z*)-Organylthioenyne Substrates



Our initial investigation was performed with disubstituted **7a** as a model substrate due to ease of the reaction analysis by ^{1}H NMR spectroscopy (synthesized via Cu-catalyzed homocoupling of phenylacetylene followed by hydrothiolation; see Supporting Information (SI) for reaction conditions). This investigation permitted identification of 1.5 equiv of ClBcat reagent as optimal to complete the conversion to **8a** after 2 h in toluene at 100 °C. Two types of boron interconversions were explored in order to facilitate the isolation of the resulting borylated thiophene **9**. Boronic esters (Bpin)[58] were chosen for the potential direct derivatization of the boron group, and boronamides (Bdan)[59] were incorporated as masked boron groups to allow us the option of functionalizing the thiophene ring prior to boron-mediated transformations.

Moreover, the nature of the substitutionally labile R^2 attached to the sulfur atom of **7a** was studied. The use of a dodecyl group attached to the sulfur atom led to **8a** and the corresponding boronic acid pinacol ester **9a**-*Bpin* after S_N2 dealkylation by chloride, but the chromatographic purification did not afford pure product due to coelution with the byproduct 1-chlorododecane (Table 1, entry 1). The

Table 1. Effect of the Sulfur Substituents[a]



entry	R^2	time[b]	boron group	yield (%)[c]
1	$C_{12}H_{25}$	2 h	Bpin	–[d]
2	Bn	2 h	Bpin	0
3	*n*-Bu	2 h	Bpin	40
4	*n*-Bu	16 h	Bdan	45
5	**Me**	**2 h**	**Bpin**	**69**
6	Me	16 h	Bdan	56
7	Me	2 h	Bpin	53[e]

[a]See SI for details. [b]Reaction time for the boron-interconversion step. [c]Yield of isolated product. [d]Coelution with 1-chlorododecane. [e]1 equiv of 1-bromobutane was used as additive.

introduction of a benzyl group did not deliver the expected product **9a**, but gave a trisubstituted thiophene with no boron group[60] (Table 1, entry 2). The isolation of **9a** was possible by R^2 = *n*-Bu leading to the Bpin and Bdan derivatives in moderate yields as an initial result (Table 1, entries 3−4). Finally, the replacement of *n*-Bu by a methyl group as an R^2 substitution enabled the improvement of the yield of **9a**-*Bpin* to 69% and **9a**-*Bdan* to 56% (Table 1, entries 5 and 6). This difference in yield may have been caused by noninnocence of the 1-chloroalkane byproducts generated during the dealkylation step; the 1-chlorobutane (bp 77−78 °C, from R^2 = *n*-Bu) remained in solution for the boron-interconversion step, but the chloromethane (bp −24 °C, from R^2 = Me) evaporated prior to the isolation procedure. A higher halide analogue 1-bromobutane (bp 100−104 °C) was selected as an additive in order to examine the potential influence of these dealkylation products. A decrease in yield was observed for the synthesis of **9a**-*Bpin* in the presence of 1-bromobutane (added to the reaction, Table 1, entry 7) and supported the noninnocent role of the byproducts from the sulfur dealkylation.

We then focused on the robustness of this methodology with different substitutions as well as its tolerance toward relevant functional groups for further derivatizations. A substrate scope was initiated starting from diversely substituted (*Z*)-organylthioenyne derivatives **7** with R^2 = methyl. The technique was applied to the monosubstituted substrate **7b** and gave the envisioned borylated thiophene **9b** with no group attached at the 5-position in 73% yield for the Bpin product and 49% for

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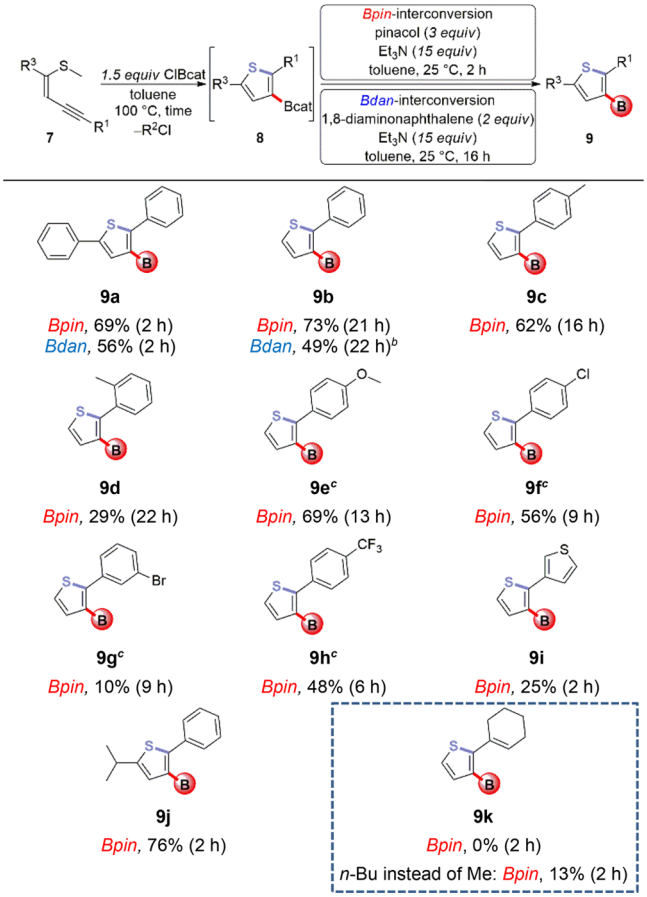
the Bdan analogue (Scheme 3). It is interesting to mention that the reaction time leading to the nonisolated boronic ester

Scheme 3. Regioselective Synthesis of 3-Borylated Thiophenes[a]



[a]Yields of the isolated product are quoted as an average over at least two experiments. [b]Reaction on 1.4 mmol scale. [c]Formation of **8** was performed at 120 °C.

8b (18 h) was longer than that for **8a** (2 h) as observed by ^{1}H NMR spectroscopy in our preliminary study. The incorporation of a methyl group at the *para*-position of the phenyl in the starting material **7c** led to generation of product **9c** in 69% yield. In contrast, ortho analogue **7d** afforded **9d** in 29% yield, showing the effects of sterics around the reactive alkyne. The formal thioboration proceeded in good yields with substrates containing electron-donating groups; **9e** was synthesized in 69% yield. Halides were tolerated as represented with the chlorinated **9f** (56%) and lower-yielding brominated **9g** (10%) derivatives but required a higher reaction temperature to complete the initial borylative heterocyclization to **8f,g**. Such halide substitutions provided the potential for orthogonal X/B reactivity on the resulting thiophenes.

It was also possible to synthesize borylated heterocycle **9h** with electron-withdrawing groups such as the trifluoromethyl attached to the aryl component, but in lower yield. The procedure allowed unique access to the *mono*-borylated dithiophene product **9i**, an interesting building block for the synthesis of oligothiophenes[61] in 25% yield with complete regioselectivity. Product **9i** would not be a candidate for synthesis via alternative, previously published methods due to the presence of three competing unsubstituted and more reactive C−H bonds.

This approach afforded the multiply substituted thiophene **9j** in 76% yield, combining an arene group, an aliphatic chain, and a boronic ester without using transition-metal-mediated transformations. While aryl and heteroaryl groups were able to undergo formal thioboration and boron interconversion in good yields, the introduction of a cycloalkenyl effected the borylative heterocyclization and **9k** was not obtained from **7k** with R^2 = Me. Nevertheless, the use of (*Z*)-organylthioenyne **7k-Bu** bearing a *n*-butyl group allowed the access to **9k** in low yield, showing the effect of the substituent R^2 on the accessibility of the product **9**.

Next, the diverse utility of borylated heterocycles **9** was showcased through a range of regiocontrolled functionalizations that aimed to generate important building blocks for possible late-stage modifications (Figure 2). The formation of

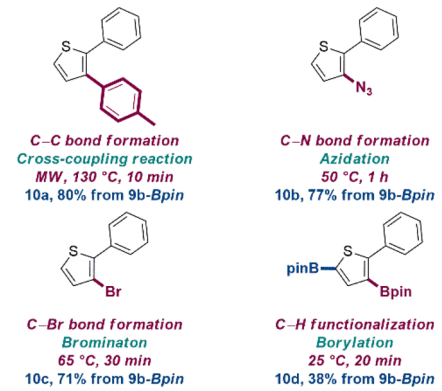


Figure 2. Functionalization of borylated thiophenes **9**.

a carbon−carbon bond was achieved by a Suzuki cross-coupling reaction between **9b**-*Bpin* and 4-iodotoluene under microwave conditions to give **10a** in 80% yield. The conversion of the boronic ester group of **9b**-*Bpin* into an amine surrogate azide was conducted via a copper-catalyzed azidation with $TMSN_3$ and CuCl leading to **10b** in 77% yield.[62] The interconversion into a brominated derivative **10c** was performed with a stoichiometric amount of $CuBr_2$ in 71% yield.[63] The derivatization of the 5-position was also explored and resulted in the direct α-borylation of **9b**-*Bpin* with HBpin under iridium catalysis at room temperature to afford **10d** in 38% yield (Figure 2; see SI for reaction conditions). This demonstrated ability to derivatize through both C−H activation and cross-coupling strategies makes these building blocks potential partners in the synthesis of hexaarylbenzenes (HABs).[64,65]

In conclusion, we have reported a simple method to access 3-borylated thiophene derivatives via formal thioboration. Substrates are readily available, no transition-metal catalyst is required, and the borylative heterocyclization/dealkylation sequence proceeds with the commercially available reagent ClBcat. Borylated thiophene products with one of the α-positions unsubstituted were synthesized to emphasize the exclusive formation of one regioisomer without a directing group, in contrast to previous iridium-catalyzed methods to borylated thiophenes. These reactions proceed via a different mechanism and distinct bond disconnections, creating a complementary synthetic toolkit for generating this important heterocyclic product class. Moreover, a study of potential

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downstream applications of **9** has been conducted and has shown the versatility of this method toward various functionalization reactions. This methodology thus represents a unique approach to synthesize 3-borylated thiophenes without transition metals, and the range of potential applications provides additional research opportunities for the regiocontrolled and rapid synthesis of novel thiophene-based products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02727.

Experimental procedures, characterization data, ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Duret, G.; Quinlan, R.; Bisseret, P.; Blanchard, N. *Chem. Sci.* **2015**, *6*, 5366−5382.
(2) Xu, L.; Zhang, S.; Li, P. *Chem. Soc. Rev.* **2015**, *44*, 8848−8858.
(3) Li, J.; Grillo, A. S.; Burke, M. D. *Acc. Chem. Res.* **2015**, *48*, 2297−2307.
(4) Crudden, C. M.; Ziebenhaus, C.; Rygus, J. P. G.; Ghozati, K.; Unsworth, P. J.; Nambo, M.; Voth, S.; Hutchinson, M.; Laberge, V. S.; Maekawa, Y.; Imao, D. *Nat. Commun.* **2016**, *7*, 11065−11071.
(5) Close, A. J.; Kemmitt, P.; Mark Roe, S.; Spencer, J. *Org. Biomol. Chem.* **2016**, *14*, 6751−6756.
(6) Rygus, J. P. G.; Crudden, C. M. *J. Am. Chem. Soc.* **2017**, *139*, 18124−18137.
(7) Li, J.; Ballmer, S. G.; Gillis, E. P.; Fujii, S.; Schmidt, M. J.; Palazzolo, A. M. E.; Lehmann, J. W.; Morehouse, G. F.; Burke, M. D. *Science* **2015**, *347*, 1221−1226.
(8) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*; Wiley-VCH Verlag: 2006.
(9) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.
(10) Lennox, A. J. J.; Lloyd-Jones, G. C. *Isr. J. Chem.* **2010**, *50*, 664−674.
(11) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412−443.
(12) Gabriele, B.; Mancuso, R.; Veltri, L.; Maltese, V.; Salerno, G. *J. Org. Chem.* **2012**, *77*, 9905−9909.
(13) Zhang, G.; Yi, H.; Chen, H.; Bian, C.; Liu, C.; Lei, A. *Org. Lett.* **2014**, *16*, 6156−6159.
(14) Reddy, C. R.; Valleti, R. R.; Reddy, M. D. *J. Org. Chem.* **2013**, *78*, 6495−6502.
(15) Kurandina, D.; Gevorgyan, V. *Org. Lett.* **2016**, *18*, 1804−1807.
(16) Santana, A. S.; Carvalho, D. B.; Cassemiro, N. S.; Viana, L. H.; Hurtado, G. R.; Amaral, M. S.; Kassab, N. M.; Guerrero, P. G.; Barbosa, S. L.; Dabdoub, M. J.; Baroni, A. C. M. *Tetrahedron Lett.* **2014**, *55*, 52−55.
(17) Mancuso, R.; Gabriele, B. *Molecules* **2014**, *19*, 15687−15719.
(18) Gabriele, B.; Mancuso, R.; Salerno, G.; Larock, R. C. *J. Org. Chem.* **2012**, *77*, 7640−7645.
(19) Meng, K.; Jiancun, Z.; Yonggang, W.; Yong, T.; Qing-cong, L.; Jun, W.; Zhonghui, W. WO 2017/133630, 2017.
(20) Devendar, P.; Yang, G. F. *Top. Curr. Chem.* **2017**, *375*, 375−382.
(21) Lepeltier, M.; Lukoyanova, O.; Jacobson, A.; Jeeva, S.; Perepichka, D. F. *Chem. Commun.* **2010**, *46*, 7007−7009.
(22) Ren, Y.; Jäkle, F. *Dalt. Trans.* **2016**, *45*, 13996−14007.
(23) Levine, D. R.; Siegler, M. A.; Tovar, J. D. *J. Am. Chem. Soc.* **2014**, *136*, 7132−7139.
(24) Molander, G. A.; Trice, S. L. J.; Dreher, S. D. *J. Am. Chem. Soc.* **2010**, *132*, 17701−17703.
(25) Molander, G. A.; Trice, S. L. J.; Kennedy, S. M.; Dreher, S. D.; Tudge, M. T. *J. Am. Chem. Soc.* **2012**, *134*, 11667−11673.
(26) Zhang, L.; Jiao, L. *J. Am. Chem. Soc.* **2017**, *139*, 607−610.
(27) Candish, L.; Teders, M.; Glorius, F. *J. Am. Chem. Soc.* **2017**, *139*, 7440−7443.
(28) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508−7510.
(29) Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 5394−5397.
(30) Larsen, M. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 4287−4299.
(31) Ros, A.; Fernández, R.; Lassaletta, J. M. *Chem. Soc. Rev.* **2014**, *43*, 3229−3243.
(32) Borowska, E.; Durka, K.; Luliński, S.; Serwatowski, J.; Woźniak, K. *Eur. J. Org. Chem.* **2012**, *2012*, 2208−2218.
(33) Chotana, G. A.; Kallepalli, V. A.; Maleczka, R. E.; Smith, M. R. *Tetrahedron* **2008**, *64*, 6103−6114.
(34) Sasaki, I.; Ikeda, T.; Amou, T.; Taguchi, J.; Ito, H.; Ishiyama, T. *Synlett* **2016**, *27*, 1582−1586.
(35) Kawamorita, S.; Ohmiya, H.; Sawamura, M. *J. Org. Chem.* **2010**, *75*, 3855−3858.
(36) Kallepalli, V. A.; Gore, K. A.; Shi, F.; Sanchez, L.; Chotana, G. A.; Miller, S. L.; Maleczka, R. E.; Smith, M. R. *J. Org. Chem.* **2015**, *80*, 8341−8353.
(37) Hirner, J. J.; Faizi, D. J.; Blum, S. A. *J. Am. Chem. Soc.* **2014**, *136*, 4740−4745.
(38) Chong, E.; Blum, S. A. *J. Am. Chem. Soc.* **2015**, *137*, 10144−10147.
(39) Johnson, J. S.; Chong, E.; Tu, K. N.; Blum, S. A. *Organometallics* **2016**, *35*, 655−662.
(40) Tu, K. N.; Hirner, J. J.; Blum, S. A. *Org. Lett.* **2016**, *18*, 480−483.
(41) Faizi, D. J.; Issaian, A.; Davis, A. J.; Blum, S. A. *J. Am. Chem. Soc.* **2016**, *138*, 2126−2129.
(42) Faizi, D. J.; Davis, A. J.; Meany, F. B.; Blum, S. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 14286−14290.
(43) Issaian, A.; Faizi, D. J.; Bailey, J. O.; Mayer, P.; Berionni, G.; Singleton, D. A.; Blum, S. A. *J. Org. Chem.* **2017**, *82*, 8165−8178.
(44) Issaian, A.; Tu, K. N.; Blum, S. A. *Acc. Chem. Res.* **2017**, *50*, 2598−2609.
(45) Tu, K. N.; Gao, C.; Blum, S. A. *J. Org. Chem.* **2018**, *83*, 11204−11217.
(46) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem. - Eur. J.* **2010**, *16*, 3005−3008.
(47) Melen, R. L.; Hansmann, M. M.; Lough, A. J.; Hashmi, A. S. K.; Stephan, D. W. *Chem. - Eur. J.* **2013**, *19*, 11928−11938.
(48) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. *J. Am. Chem. Soc.* **2014**, *136*, 777−782.
(49) Wilkins, L. C.; Hamilton, H. B.; Kariuki, B. M.; Hashmi, A. S. K.; Hansmann, M. M.; Melen, R. L. *Dalt. Trans.* **2016**, *45*, 5929−5932.
(50) Soltani, Y.; Wilkins, L. C.; Melen, R. L. *Angew. Chem., Int. Ed.* **2017**, *56*, 11995−11999.

DOI: 10.1021/acs.orglett.8b02727
Org. Lett. XXXX, XXX, XXX−XXX

(51) Lawson, J. R.; Melen, R. L. *Inorg. Chem.* **2017**, *56*, 8627−8643.
(52) Warner, A. J.; Churn, A.; McGough, J. S.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2017**, *56*, 354−358.
(53) Su, L.; Dong, J.; Liu, L.; Sun, M.; Qiu, R.; Zhou, Y.; Yin, S. F. *J. Am. Chem. Soc.* **2016**, *138*, 12348−12351.
(54) De Orbe, M. E.; Amenós, L.; Kirillova, M. S.; Wang, Y.; López-Carrillo, V.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2017**, *139*, 10302−10311.
(55) Dabdoub, M. J.; Dabdoub, V. B.; Lenardão, E. J.; Hurtado, G. R.; Barbosa, S. L.; Guerrero, P. G.; Nazário, C. E. D.; Viana, L. H.; Santana, A. S.; Baroni, A. C. M. *Synlett* **2009**, *2009*, 986−990.
(56) Santana, A. S.; Carvalho, D. B.; Casemiro, N. S.; Hurtado, G. R.; Viana, L. H.; Kassab, N. M.; Barbosa, S. L.; Marques, F. A.; Guerrero, P. G.; Baroni, A. C. M. *Tetrahedron Lett.* **2012**, *53*, 5733−5738.
(57) Kesharwani, T.; Giraudy, K. A.; Morgan, J. L.; Kornman, C.; Olaitan, A. D. *Tetrahedron Lett.* **2017**, *58*, 638−641.
(58) Sandford, C.; Aggarwal, V. K. *Chem. Commun.* **2017**, *53*, 5481−5494.
(59) Noguchi, H.; Hojo, K.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 758−759.
(60) Freeman, F.; Lu, H.; Zeng, Q.; Rodriguez, E. *J. Org. Chem.* **1994**, *59*, 4350−4354.
(61) Zhang, L.; Colella, N. S.; Cherniawski, B. P.; Mannsfeld, S. C. B.; Briseno, A. L. *ACS Appl. Mater. Interfaces* **2014**, *6*, 5327−5343.
(62) Li, Y.; Gao, L. X.; Han, F. S. *Chem. - Eur. J.* **2010**, *16*, 7969−7972.
(63) Thompson, A. L. S.; Kabalka, G. W.; Akula, M. R.; Huffman, J. W. *Synthesis* **2005**, *2005*, 547−550.
(64) Suzuki, S.; Segawa, Y.; Itami, K.; Yamaguchi, J. *Nat. Chem.* **2015**, *7*, 227−233.
(65) Suzuki, S.; Yamaguchi, J. *Chem. Commun.* **2017**, *53*, 1568−1582.

DOI: 10.1021/acs.orglett.8b02727
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