

LiHMDS-Promoted Palladium or Iron-Catalyzed ipso-**Defluoroborylation of Aryl Fluorides**

Xianghu Zhao, Mingsheng Wu, Yisen Liu, and Song Cao*

Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (ECUST), Shanghai 200237, China

S Supporting Information

ABSTRACT: A novel and efficient method for the synthesis of arylboronic acid pinacol esters via a palladium- or ironcatalyzed cross-coupling reaction of aryl fluorides with bis(pinacolato)diboron (B₂pin₂) in the presence of LiHMDS was developed. The Pd-catalyzed defluoroborylation of fluoroarenes is compatible with a variety of functional groups such as primary and secondary amine, ketone, trifluoromethyl, alkoxy, and boryl. Remarkably, no external ligand is required for enhanced conversion efficiency.

rylboronate esters are indispensable and versatile reagents A in organic synthesis due to their broad availability, high stability, and ease of handling.¹ They have found wide applications in carbon-carbon bond formations, especially in palladium-catalyzed Suzuki-Miyaura cross-coupling reactions. Therefore, the efficient synthesis of arylboronate esters continues to attract considerable attention from synthetic chemists.³ To date, numerous methods have been developed for the synthesis of arylboronate esters.⁴ Among the various methodologies reported, the transition-metal-catalyzed borylation of aryl halides or triflates with bis(pinacolato)diboron $(B_2 pin_2)$ is probably the most common and efficient synthetic access to aryl boronic esters.⁵ Typically, aryl iodides, bromides, and even aryl chlorides could serve as effective coupling partners in transition-metal-catalyzed borylation reactions,⁶ whereas unreactive aryl fluorides are seldom used as coupling partners due to the inertness of the aryl-F bond toward oxidative addition to transition-metal complexes.

The activation and functionalization of the strong carbonfluorine bond have gained growing interest during the past two decades since they provide an alternative method for synthesis of structurally diverse molecules from fluoroorganic compounds.⁸ The transition-metal-catalyzed borylation of the C-F bond in polyfluorinated alkenes and arenes has become a hot topic in organic chemistry.⁹ For example, the group of Zhang reported an ortho-selective C-F bond borylation of polyfluoroarenes using $[Rh(cod)_2]BF_4$ as catalyst (Scheme 1a).¹⁰ In 2015, Martin et al. described the first Ni-catalyzed borylation of monofluoroarenes with B_2nep_2 via C-F activation and C-B bond formation (Scheme 1b).¹¹ Almost at the same time, Niwa and Hosoya developed a Ni-catalyzed defluoroborylation of monofluoroarenes with B₂pin₂ with the assistance of CuI (Scheme 1c).¹² Two years later, the same group reported Cucatalyzed ipso-borylation of polyfluoroarenes which enabled the synthesis of di- and triborylated arenes from di- and trifluoroarenes (Scheme 1d).¹³ In 2016, Radius, Marder, and



Scheme 1. C-F Bond Borylation of Fluoroarenes

$Ar^{F}-F + B_{2}pin_{2} \xrightarrow{[Rh(cod)_{2}]BF_{4} (5 \text{ mol } \%)}{KOAc, 80 \text{ °C}, 12 \text{ h}} Ar^{F}-Bpin$	(<i>a</i>) Zhang, 2015
ArF + B ₂ nep ₂ Ni(cod) ₂ (5 mol %), PCy ₃ (20 mol %) ArBnep NaOPh, THF, 110 °C, 12 h ArBnep	(<i>b</i>) Martin, 2015
ArF + B ₂ pin ₂ → Ni(cod) ₂ (10 mol %) PCy ₃ (50 mol %), CsF, toluene → Cul (20 mol %), 80 °C, 24 h → ArBpin	(c) Niwa and Hosoya, 2015
$Ar^{F}-F + B_{2}pin_{2} \xrightarrow{CuCl(PCy_{3})_{2} (5-60 \text{ mol } \%)}{CsF, \text{ toluene, 80 °C, 24 h}} Ar^{F}-Bpin$	(d) Niwa and Hosoya, 2017
$Ar^{F}\text{-}\textbf{F} + B_{2}pin_{2} \xrightarrow{\text{Ni(IMes)}_{2} (10 \text{ mol } \%)} \text{NMe}_{4}F/\text{CsF}, 80 \ ^{\circ}\text{C}, 15 \text{ h}} \xrightarrow{\text{Ar}^{F}\text{-}\textbf{Bpin}}$	(e) Marder and Radius, 2016
ArF + B ₂ pin ₂ Pd ₂ dba ₃ (2 mol %), LiHMDS, toluene, 80 °C, 12 or FeCl ₂ (20 mol %), LiHMDS, 110 °C, 12 h toluene:HMPA = 2:1	h → Ar Bpin (f) <i>This work</i>

co-workers disclosed a Ni(IMes)2-catalyzed C-F bond borylation of polyfluoroarenes using B₂pin₂ as the boron source (Scheme 1e).¹⁴ Although these reported methods for the defluoroborylation of fluoroarenes are efficient and versatile, these methodologies still suffer from one or more limitations, such as the use of additional ligand, limited substrate scope, and high catalyst loadings. Therefore, there is plenty of room for the exploration of a new catalytic system that can display broad substrate scope and high functional group compatibility.

Palladium-catalyzed cross-coupling reactions have emerged as a tremendously valuable synthetic tool in organic synthesis and pharmaceutical chemistry because a palladium catalyst exhibits powerful catalytic ability.² Particularly, various palladiumcatalyzed methods have emerged for the transformation of aryl iodides, bromides, chlorides, and triflates to the corresponding pinacol boronate esters.^{5b,c,6a,c} However, no examples of defluoroborylation of fluoroarenes to arylboronate esters using

Received: July 17, 2018

palladium catalysts have been reported so far. Considering the fact that palladium-catalyzed borylation of aryl halides methods offer a higher degree of functional group tolerance, we envisaged that defluoroborylation of unactivated fluoroarenes might be feasible under palladium catalysis. In this letter, we reported a novel and efficient method for the synthesis arylboronic acid pinacol esters via Pd- or Fe-catalyzed borylation of fluoroarenes with B₂pin₂ in the presence of LiHMDS (Scheme 1f).

We began our studies using the borylation of 4-fluoro-1,1'biphenyl (1a) with B_2pin_2 as the model reaction to optimize the reaction conditions (Table 1). Initially, different Pd catalysts

 Table 1. Optimization of the Reaction Conditions^a

Ph	F + B ₂ pin ₂	catalyst, base, solv 80 ºC, 12 h, Ar	Vent Ph	Bpin
	1a 2			3a
entry	catalyst (x mol %)	base (x equiv)	solvent	yield (%) ^b
1	none	LiHMDS (2.5)	THF	0
2	$Pd(PPh_3)_4(5)$	LiHMDS (2.5)	THF	15
3	$Pd(OAc)_2(5)$	LiHMDS (2.5)	THF	25
4	$PdCl_{2}(5)$	LiHMDS (2.5)	THF	35
5	$Pd_2dba_3(5)$	LiHMDS (2.5)	THF	41
6	$Pd_2dba_3(5)$	CsF (2.5)	THF	0
7	$Pd_2dba_3(5)$	LiOtBu (2.5)	THF	0
8	$Pd_2dba_3(5)$	NaOPh (2.5)	THF	0
9	$Pd_2dba_3(5)$	NaHMDS (2.5)	THF	2
10	$Pd_2dba_3(5)$	KHMDS (2.5)	THF	12
11	$Pd_2dba_3(5)$	LDA (2.5)	THF	20
12	$Pd_2dba_3(5)$	<i>t</i> BuLi (2.5)	THF	0
13	$Pd_2dba_3(5)$	LiHMDS (2.5)	CH ₃ CN	0
14	$Pd_2dba_3(5)$	LiHMDS (2.5)	DMF	0
15	$Pd_2dba_3(5)$	LiHMDS (2.5)	MTBE	12
16	$Pd_2dba_3(5)$	LiHMDS (2.5)	dioxane	27
17	$Pd_2dba_3(5)$	LiHMDS (2.5)	toluene	85
18	$Pd_2dba_3(2)$	LiHMDS (2.5)	toluene	84
19	$Pd_{2}dba_{3}$ (0.5)	LiHMDS (2.5)	toluene	18
20	$Pd_2dba_3(2)$	LiHMDS (2.0)	toluene	95
21	$Pd_2dba_3(2)$	LiHMDS (1.5)	toluene	80
-	_	(->	,	-> -

"Reaction conditions: 1a (0.1 mmol), B_2pin_2 (0.15 mmol), solvent (1.0 mL), 80 °C, 12 h, Ar. ^bYields determined by GC analysis and based on 1a.

were examined. Among the tested Pd catalysts, Pd₂dba₃ proved to be more suitable for the reaction (entries 2-5). As anticipated, no borylated product was observed in the absence of a Pd catalyst (entry 1). Generally, the borylation reaction could be achieved by using CsF, NaOPh and MOtBu (M = Na, K, Li) as bases.^{4a,6c,7a} However, alkaline metal hexamethyldisilazide (MHMDS, M = Na, K, Li) is scarcely used as bases or additives in borylation reactions.¹⁵ The only successful example of a borylation reaction of this type involved the Pd-catalyzed ipso-borylation of aryl sulfides with B₂pin₂ using lithium hexamethyldisilazide (LiHMDS or LiN(SiMe₃)₂) as activator.¹⁶ Subsequently, the influence of the base on the reaction was examined (entries 5-12). The results indicate that LiHMDS was uniquely effective for the transformation, affording the expected product 3a in 41% yield (entry 5), whereas the use of other bases, such as NaHMDS, KHMDS, and LDA, resulted in poor yields. Moreover, no reaction took place with CsF, NaOPh, LiOtBu, and tBuLi, recovering the starting fluoroarene 1a.

Next, a brief screening of the solvents was carried out (entries 5 and 13–17), and it revealed that toluene had a pronounced

effect on the reaction and the yield of **3a** could be dramatically increased to 85%. We were delighted to find that decreasing the amount of Pd₂dba₃ from 5 mol % to 2 mol % would also furnish **3a** in good yield (entry 18). Further decreasing the amount of Pd₂dba₃ to 0.5 mol % led to a remarkable decrease in the yield (entry 19). Finally, the effect of amount of LiHMDS on the reaction was also studied (entries 5 and 20–21). The highest yield (95%) of the borylation product **3a** was achieved when 2.0 equiv of LiHMDS were used.

With the optimized conditions in hand (Table 1, entry 20), we next examined the scope of the Pd-catalyzed borylation of various fluoroarenes with B_2pin_2 (2) (Scheme 2). In most cases,





^aReaction conditions: 1 (0.5 mmol), 2 (0.75 mmol), Pd_2dba_3 (0.01 mmol), LiHMDS (1.0 mmol), toluene (2.5 mL), 80 °C, 12 h, Ar. Isolated yields. ^b1w = 4,4'-difluoro-1,1'-biphenyl, 1w' = 4-chloro-4'-fluoro-1,1'-biphenyl, 1w'' = 4-bromo-4'-fluoro-1,1'-biphenyl, 3w = 3w' = 3w''.

the defluoroborylation reaction proceeded smoothly to give the corresponding borylation products 3 in moderate to good yields under the optimal conditions. Generally, fluoroarenes bearing electron-neutral (1b), weak (such as 1d, 1f, and 1h) or strong electron-donating groups (1c) gave the desired products in higher yields than substrates bearing electron-withdrawing groups (1k). However, the fluoroarenes having strong electron-withdrawing groups such as NO2 and CN (e.g., 1fluoro-4-nitrobenzene and 4-fluorobenzonitrile) were unfavorable for the reaction and gave complex mixtures. Notably, fluoroacetophenones (1k and 1l) are suitable substrates for this transformation, leaving the keto group intact. Unfortunately, substrates containing ester and amide groups (e.g., ethyl 4fluorobenzoate and N-(4-fluorophenyl)acetamide) could not work well and only small amounts of borylated products were detected (GC-MS, ~30%). Importantly, when ortho-, meta-, or

para-fluoroanilines were used as the substrates, the reactions proceeded efficiently to furnish the borylation products in high yields (GC-MS, above 80%). Although the reaction itself proceeded well, borylated anilines are not very stable, only paraand meta-borylated anilines (3m and 3n) could be isolated in moderate yields. The ortho-borylated aniline was presumably lost in the workup procedure. In addition, secondary anilines are compatible with this new Pd-based catalytic system (30). The position of the substituent on the benzene ring of fluoroarenes has an obvious influence on the yield of the desired product. For example, fluoroarenes possessing a phenyl group in the paraposition afforded the expected product in excellent yield (3a), whereas the shift of the phenyl group to the meta- or orthopositions gave reduced reaction yields (3f and 3g). However, when difluorobenzene or 1,2,3,4,5-pentafluorobenzene were used as substrates, only small or trace amounts of borylated products were detected and no diborylated products were observed.

It was reported that fluoroarenes with an extended π conjugated system exhibited high reactivity in Ni or Cucatalyzed defluoroborylation reaction.¹¹ Thus, Niwa, Hosoya, and Martin have extensively investigated borylation of fluorobiaryls.^{11–13} For comparison purposes, we also applied this Pd-catalyzed borylation to a variety of substituted 4fluorobiaryls. The results indicate that both electron-rich and -poor biaryl fluorides could be efficiently transformed to the desired products in moderate to high yields. Functional groups such as amino, methoxy, dioxole, tert-butyl, trifluoromethyl, boryl, and fluoro groups were compatible with the borylation process. The tolerance of amino and existing boryl groups was particularly useful, which offers an opportunity for further synthetic transformation. Compared to fluoroarenes, fluorobiaryls had no obvious impact on the reaction efficiency. Finally, when 4-chloro- or 4-bromo-4'-fluoro-1,1'-biphenyl were used as coupling partners, the borylation reaction took place selectively at the C-Cl or C-Br bond in preference to the C-F bond and the C–F bond remained intact (3w = 3w' = 3w''). The results suggest that aryl bromides and aryl chlorides are also suitable for this Pd-catalyzed borylation reaction system.

Gratifyingly, the procedure could be scaled up to a gram scale (1j, 7.0 mmol). Without further optimization, the borylation of 1j could produce the desired arylboronate product 3j in moderate yield with 1.0 mol % of catalyst loading (Scheme 3).

Scheme 3. Borylation of 1-Fluoronaphthalene on a 7.0 mmol Scale



According to our experimental results and the reported literature studies, 2b,16 a plausible reaction mechanism for Pdcatalyzed defluoroborylation of fluoroarenes is proposed in Scheme 4. Initially, one of the boron atoms of the B₂pin₂ is coordinated to strong base LiN(SiMe₃)₂ to give the Lewis adduct of sp²-sp³ diborane compound I.¹⁷ The B–B bond of diborane compound could be activated and then cleaved heterolytically. The oxidative addition of the C–F bond in fluoroarenes at Pd(0) complex gives LArPd(II)F adduct III. Subsequently, transmetalation of III with intermediate I results the formation of LArPd(II)Bpin IV and intermediate II. Finally,





reductive elimination from the Pd complex **IV** furnishes the desired arylboronic esters along with the regeneration of the active catalytic species Pd(0) to close the catalytic cycle. In addition, the resulting intermediate **II** may readily dissociate into fluoroborane (FBpin) and LiN(TMS)₂ which seem to be unstable under the reaction conditions and convert into pinBN(TMS)₂ and LiF because of the strong Li–F interaction.¹⁸ Furthermore, a considerable amount of byproduct pinBN(TMS)₂ could be detected by GC-MS. It should be mentioned that when replacing LiHMDS with NaHMDS or performing the reaction at room temperature, only small or trace amounts of pinBN(TMS)₂ could be observed.

Iron is one of the most abundant metals in nature. Consequently, iron has attracted considerable attention in the field of cross-coupling reactions. Compared to the expensive palladium and relatively toxic nickel catalysts, iron catalysts are inexpensive, readily available, and environmentally friendly.¹¹ Although various iron-catalyzed borylations of alkyl, allyl, and aryl halides have been realized,²⁰ the borylation of fluoroarenes with Fe catalysts remains unexplored. Encouraged by the above results obtained from the borylation of fluoroarenes with Pd catalyst, we turned our attention to the iron-catalyzed crosscoupling reaction of fluoroarenes with B2pin2. After careful screening of iron catalysts, solvents, and reaction temperatures, we found that the borylation of fluoroarenes could proceed smoothly in the presence of 20 mol % FeCl₂ and 3.2 equiv of LiHMDS using toluene and HMPA as the solvent (2:1 in volume) at 110 °C for 12 h. Subsequently, we applied the optimized conditions to a variety of fluoroarenes and biaryl fluorides (Scheme 5). It was found that only biaryl fluorides proceeded well, affording the borylation products in moderate to good yields, whereas fluoroarenes without a π -conjugated system such as 1b-1e gave the expected products in poor yields (\sim 20%, GC). The scope of this Fe-catalyzed borylation reaction was still limited, and the reaction efficiency was relatively low. However, considering ready availability, low cost, high earth abundance, and nontoxicity of the iron catalyst, this new Fe-catalyzed borylation might be an alternative method for the synthesis of arylboronate esters from biaryl fluorides.

In summary, we have developed a novel and efficient method for the synthesis of arylboronate esters via Pd- or Fe-catalyzed cross-coupling reaction of aryl fluorides with bis(pinacolato)diboron (B_2pin_2) in the presence of LiHMDS without any additional ligand. In comparison with the earlier Ni- and Cucatalyzed defluoroborylation, the newly developed Pd-catalyzed reaction systems can tolerate primary and secondary amine and ketone groups. Notably, the Pd-catalyzed reaction could be performed on a gram scale with lower catalyst loading. Importantly, LiHMDS plays a particularly key role in the transformation, which might be attributed to the strong Li–F

Scheme 5. Fe-Catalyzed Defluoroborylation of Biaryl Fluorides^{*a*}



^{*a*}Reaction conditions: 1 (0.2 mmol), 2 (0.56 mmol), $FeCl_2$ (0.04 mmol), LiHMDS (0.64 mmol), toluene/HMPA = 0.8 mL/0.4 mL, 110 °C, 12 h, Ar. Isolated yields. ^{*b*}20 mol % TMEDA ($N_iN_iN'_iN'_i$ tetramethylethylene diamine) was added, 0.5 h.

interaction. Despite the low catalytic activity of the Fe catalyst for borylation, it is much cheaper and more easily available than Ni- and Pd-based catalysts. Therefore, we anticipate that the current protocol may provide a scalable, cost-effective, and complementary method of accessing valuable arylboronate esters from various fluoroarenes and biaryl fluorides.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02228.

Experimental details and spectral data for all products (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: scao@ecust.edu.cn

ORCID 💿

Song Cao: 0000-0002-3231-6136 Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (Grant Nos. 21472043 and 21272070).

REFERENCES

(1) (a) Miyaura, N. In Metal-Catalyzed Cross-Coupling Reactions, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004. (b) Kotha, S.; Lahiri, K.; Kashinath, D. Tetrahedron 2002, 58, 9633. (c) Liu, Y.-Y.; Zhang, W.-B. Youji Huaxue 2016, 36, 2249. (d) Hu, J.; Gao, B.; Li, L.; Ni, C.; Hu, J. Org. Lett. 2015, 17, 3086. (e) Gu, L.-J.; Jin, C.; Zhang, H.-T. Chem. - Eur. J. 2015, 21, 8741. (f) Martin, R.; Buchwald, S. L. Acc. Chem. Res. 2008, 41, 1461.

(2) (a) Suzuki, A. Angew. Chem., Int. Ed. 2011, 50, 6722. (b) Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457. (c) Lennox, A. J.; Lloyd-Jones, G. C. Chem. Soc. Rev. 2014, 43, 412.

(3) (a) Furukawa, T.; Tobisu, M.; Chatani, N. J. Am. Chem. Soc. 2015, 137, 12211. (b) Chen, K.; Wang, L.; Meng, G.; Li, P. Synthesis 2017, 49, 4719. (c) Xu, Y.; Fang, H. Youji Huaxue 2018, 38, 738. (d) Yan, G.; Huang, D.; Wu, X. Adv. Synth. Catal. 2018, 360, 1040. (e) Xu, L.; Wang, G.; Zhang, S.; Wang, H.; Wang, L.; Liu, L.; Jiao, J.; Li, P. Tetrahedron 2017, 73, 7123.

(4) (a) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A.; Westcott, S. A.; Marder, T. B. *Chem. Rev.* **2016**, *116*, 9091. (b) Zhang, L.; Jiao, L. *J. Am. Chem. Soc.* **2017**, *139*, 607. (c) Hu, J.; Zhao, Y.; Liu, J.; Zhang, Y.; Shi, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 8718. (d) Uetake, Y.; Niwa, T.; Hosoya, T. Org. Lett. **2016**, *18*, 2758. (e) Li, H.-L.; Kuninobu, Y.; Kanai, M. Angew. Chem., Int. Ed. **2017**, *56*, 1495.

(5) (a) Kleeberg, C.; Dang, L.; Lin, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5350. (b) Ratniyom, J.; Dechnarong, N.; Yotphan, S.; Kiatisevi, S. *Eur. J. Org. Chem.* **2014**, *2014*, 1381. (c) Bej, A.; Srimani, D.; Sarkar, A. *Green Chem.* **2012**, *14*, 661. (d) Kubota, K.; Iwamoto, H.; Ito, H. *Org. Biomol. Chem.* **2017**, *15*, 285.

(6) (a) Littke, A. F.; Fu, G. C. Angew. Chem., Int. Ed. 2002, 41, 4176.
(b) Murata, M. Heterocycles 2012, 85, 1795. (c) Chow, W. K.; Yuen, O. Y.; Choy, P. Y.; So, C. M.; Lau, C. P.; Wong, W. T.; Kwong, F. Y. RSC Adv. 2013, 3, 12518.

(7) (a) Chen, W.; Bakewell, C.; Crimmin, M. Synthesis 2017, 49, 810.
(b) Teltewskoi, M.; Panetier, J. A.; Macgregor, S. A.; Braun, T. Angew. Chem., Int. Ed. 2010, 49, 3947. (c) Lindup, R. J.; Marder, T. B.; Perutz, R. N.; Whitwood, A. C. Chem. Commun. 2007, 3664. (d) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. J. Am. Chem. Soc. 2008, 130, 16069. (e) Bosque, R.; Clot, E.; Fantacci, S.; Maseras, F.; Eisenstein, O.; Perutz, R. N.; Renkema, K. B.; Caulton, K. G. J. Am. Chem. Soc. 1998, 120, 12634.

(8) (a) Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun, T. *Chem. Rev.*2015, 115, 931. (b) Zhang, X.; Cao, S. *Tetrahedron Lett.* 2017, 58, 375.
(c) Shen, Q.; Huang, Y.-G.; Liu, C.; Xiao, J.-C.; Chen, Q.-Y.; Guo, Y. J. *Fluorine Chem.* 2015, 179, 14. (d) Weaver, J.; Senaweera, S. *Tetrahedron* 2014, 70, 7413.

(9) (a) Zhang, J.; Dai, W.; Liu, Q.; Cao, S. Org. Lett. 2017, 19, 3283.
(b) Sakaguchi, H.; Uetake, Y.; Ohashi, M.; Niwa, T.; Ogoshi, S.; Hosoya, T. J. Am. Chem. Soc. 2017, 139, 12855. (c) Kojima, R.; Kubota, K.; Ito, H. Chem. Commun. 2017, 53, 10688. (d) Tan, D.-H.; Lin, E.; Ji, W.-W.; Zeng, Y.-F.; Fan, W.-X.; Li, Q.; Gao, H.; Wang, H. Adv. Synth. Catal. 2018, 360, 1032. (e) Chen, K.; Cheung, M. S.; Lin, Z.; Li, P. Org. Chem. Front. 2016, 3, 875. (f) Mfuh, A. M.; Doyle, J. D.; Chhetri, B.; Arman, H. D.; Larionov, O. V. J. Am. Chem. Soc. 2016, 138, 2985. (g) Kalläne, S. I.; Teltewskoi, M.; Braun, T.; Braun, B. Organometallics 2015, 34, 1156.

(10) Guo, W.-H.; Min, Q.-Q.; Gu, J.-W.; Zhang, X. Angew. Chem., Int. Ed. 2015, 54, 9075.

(11) Liu, X.-W.; Echavarren, J.; Zarate, C.; Martin, R. J. Am. Chem. Soc. **2015**, 137, 12470.

(12) Niwa, T.; Ochiai, H.; Watanabe, Y.; Hosoya, T. J. Am. Chem. Soc. **2015**, 137, 14313.

(13) Niwa, T.; Ochiai, H.; Hosoya, T. ACS Catal. 2017, 7, 4535.

(14) Zhou, J.; Kuntze-Fechner, M. W.; Berthel, J. H. J.; Friedrich, A.; Du, Z.; Marder, T. B.; Radius, U. J. Am. Chem. Soc. **2016**, 138, 5250.

(15) (a) Yang, C.-T.; Zhang, Z.-Q.; Tajuddin, H.; Wu, C.-C.; Liang, J.; Liu, J.-H.; Fu, Y.; Czyzewska, M.; Steel, P.; Marder, T. B.; Liu, L. Angew. Chem., Int. Ed. **2012**, *51*, 528. (b) Wu, H.; Garcia, J. M.; Haeffner, F.; Radomkit, S.; Zhugralin, A. R.; Hoveyda, A. H. J. Am. Chem. Soc. **2015**, *137*, 10585.

(16) Bhanuchandra, M.; Baralle, A.; Otsuka, S.; Nogi, K.; Yorimitsu, H.; Osuka, A. *Org. Lett.* **2016**, *18*, 2966.

(17) (a) Dewhurst, R. D.; Neeve, E. C.; Braunschweig, H.; Marder, T. B. *Chem. Commun.* **2015**, *51*, 9594. (b) Pietsch, S.; Neeve, E. C.; Apperley, D. C.; Bertermann, R.; Mo, F.; Qiu, D.; Cheung, M. S.; Dang, L.; Wang, J.; Radius, U.; Lin, Z.; Kleeberg, C.; Marder, T. B. *Chem. - Eur. J.* **2015**, *21*, 7082.

- (19) (a) Bedford, R. B. Acc. Chem. Res. **2015**, 48, 1485. (b) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Chem. Rev. **2011**, 111, 1293.
- (20) (a) Bedford, R. B.; Brenner, P. B.; Carter, E.; Gallagher, T.; Murphy, D. M.; Pye, D. R. *Organometallics* **2014**, 33, 5940. (b) Yoshida, T.; Ilies, L.; Nakamura, E. ACS *Catal.* **2017**, *7*, 3199.