




Nickel-catalysed decarbonylative borylation of aryl fluorides†

Zhenhua Wang,^a Xiu Wang^a and Yasushi Nishihara *^b

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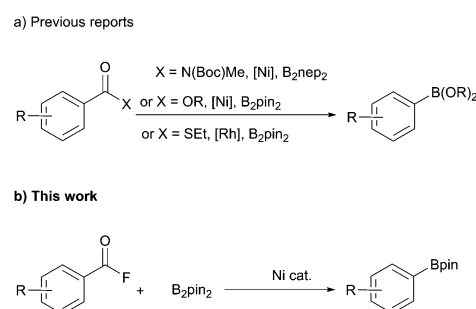
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The first Ni(cod)₂/PPh₃ catalyst system has been established for decarbonylative borylation of aryl fluorides with bis(pinacolato)-diboron. A wide range of functional groups in the substrates were well tolerated. The ease of access of the starting aryl fluorides indicates that these results might become an alternative to the existing decarbonylation events.

Arylboronic acids and arylboronates are versatile synthetic reagents in synthetic organic chemistry.¹ These compounds are conventionally synthesized by organolithium or magnesium compounds, which are not compatible with functional groups.² The further development of transition-metal-catalysed borylation reactions has allowed the synthesis of arylboronates from numerous aryl iodides, bromides, chlorides, or triflates.³ In recent years, much effort has been devoted to the synthesis of arylboronates *via* C–X (X = H,⁴ halogen,⁵ SR,⁶ OR,⁷ CN,⁸ or NR₂⁹) bond activation.

Taking into account the growing concerns on the environmental and sustainable events of our society, carboxylic acid as an aromatic feedstock alternative is in high demand. In particular, facile diversification of carboxylic acids into organoboron compounds shows high value.¹⁰ As such, several attempts have succeeded in the transformation of carboxylic acid derivatives such as amides,^{11,12} esters,^{13–15} thioesters,^{16,17} and chloride¹⁸ into the corresponding arylboronates in a decarbonylative manner (Scheme 1a). Very recently, the decarboxylative borylation of aliphatic and aromatic *N*-hydroxyphthalimide esters, derived from the corresponding carboxylic acids, were also disclosed.¹⁹

On the other hand, aryl fluorides easily prepared from the corresponding carboxylic acids,²⁰ arguably one of the simplest and most atom-economical derivatives in the aryl acid series,



Scheme 1 Decarbonylative borylation of carboxylic acid derivatives.

have received considerably less attention, presumably due to their low reactivity. In some cases, however, aryl fluorides were found to be a cross-coupling partner with organozinc,²¹ -silicon,²² and -boron²³ nucleophiles to generate various ketones without decarbonylation. Recently, Ogiwara and Sakai reported palladium-catalysed reduction of sp² and sp³ acid fluorides in a retentive or decarbonylative manner.²⁴ This report suggested that the retentive or decarbonylative pathway could be controlled by the ligands employed. Encouraged by the decarbonylative C–C bond formation, namely, trifluoromethylation of acid fluorides under a [(cinnamyl)PdCl]₂/xantphos catalytic system,²⁵ we also disclosed decarbonylative alkylation of aryl fluorides catalysed by Ni(cod)₂/DPPE.²⁶ To the best of our knowledge, however, the decarbonylative borylation of acid fluorides has been virtually unexplored.²⁷ Herein we report our results on the utilization of aryl fluorides as the electrophilic component in a nickel-catalysed decarbonylative borylation reaction (Scheme 1b).

Our initial studies involved the evaluation of various ligands and bases in the borylation reaction of benzoyl fluoride (**1a**) with bis(pinacolato)diboron (**2a**, (B₂pin₂)) catalysed by Ni(cod)₂ (Tables S1–S4, ESI†). To our delight, 33% of desired product **3a** was obtained when a stable and inexpensive ligand PPh₃ was employed. Extensive screening of the reaction conditions (see the ESI†) revealed that a mixture of 10 mol% of Ni(cod)₂, 30 mol% of PPh₃, 2.5 equiv. of KF, and 2.0 equiv. of NaCl as the additive

^a Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

^b Research Institute for Interdisciplinary Science, Okayama University,

3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan.

E-mail: ynishih@okayama-u.ac.jp

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at 140 °C for 24 h in a mixed solvent system, toluene and octane (v/v = 2/1), provided the best result, affording **3a** in 83% yield (Table 1, entry 1). Other air-stable Ni(II) salts other than Ni(cod)₂ resulted in a lower yield of **3a** (entries 2 and 3). Palladium catalysts such as Pd(OAc)₂ and Pd(dba)₂ were inefficient (entries 4 and 5). Although [Rh(OH)(cod)]₂ was reported to be efficient in decarbonylative borylation of aromatic thioesters,¹⁶ it showed moderate reactivity (entry 6). Replacement of PPh₃ with other monodentate phosphine ligands under identical reaction conditions decreased the yield (entries 7–9). Interestingly, the yield of **3a** was increased in the order of CsF < NaF < KF (Table S4, ESI[†]), suggesting that a counteranion is important to some extent.²⁸ A similar tendency was observed in the additives; NaCl and KCl afforded good yields, while LiCl, CsCl and TBAC (tetrabutylammonium chloride) gave poor results (entries 10–13). This revealed that suitable counteranions may play a vital role in this transformation. These results are associated with recent publications that demonstrate the important role of counteranions in C–O bond activation in reactions of aryl ethers.²⁹ When no NaCl was added, the yield was slightly decreased to 67% (entry 14). No desired product was detected in the absence of Ni(cod)₂ or PPh₃ in the decarbonylative borylation process (entries 15 and 16). The KF additive was found to be essential to proceed the reaction (entry 17), suggesting that an external activator of B₂pin₂ is required. When we applied certain conditions to the analogous benzoyl chloride at 140 °C (entry 18) and even at room temperature, 50 °C, or 80 °C, no decarbonylative borylation product was detected. It is indicated that a fluoride moiety plays a crucial role and conversion of benzoyl fluoride

in situ into benzoyl chloride in the presence of NaCl can be ruled out during this transformation.

With the optimized conditions in hand, the generality of the reaction was subsequently investigated (Table 2). A wide range of electronically and sterically diverse aryl fluorides with bis(pinacolato)diboron (**2a**) were smoothly converted into the corresponding arylboronates. Aryl fluorides bearing electron-donating alkyl and alkoxy groups in the *para*-position afforded arylboronates **3b–3f** in 50–82% yields. High chemoselectivity of this decarbonylative borylation was demonstrated by the synthesis of **3i** bearing the ester functionality unreacted. This result suggests that this methodology is complementary to the decarbonylative borylation of aromatic esters.^{13–15} Moreover, the introduction of electron-withdrawing groups onto benzoyl fluoride led to a slight decrease in the yields of products **3k** and **3l**. Reaction of benzoyl fluoride with *ortho*-substituents under the identical reaction conditions proceeds smoothly to yield **3n–3p**. Naphthyl (**3q** and **3r**), anthracenyl (**3s**), and biphenyl (**3g**, **3m**, and **3t**)-containing arylboronates were successfully obtained in good to high yields. On the other hand, although the decarbonylative borylation using vinyl and benzyl precursors have been elucidated, no traces of the desired products **3** were detected.

To evaluate the utility of this decarbonylative borylation reaction, reactions of a series of diborons have been carried out (Table 3). Using bis(hexylene glycolato)diboron (**2b**) and bis(neopentyl glycolato)diboron (**2c**, B₂nep₂) instead of **2a** with benzoyl fluoride (**1a**) gave the corresponding arylboronates **4b** and **4c** in 54% and 55% yields, respectively. The reaction of

Table 1 Optimization of the reaction conditions^a

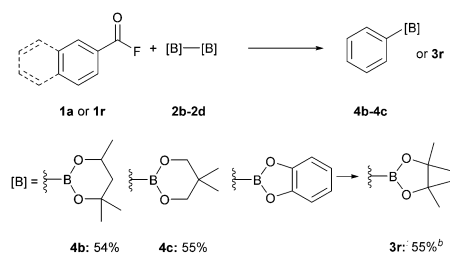
Entry	Deviation from standard conditions	Yield ^b (%)
1	None	85 (83) ^c
2	NiCl ₂ instead of Ni(cod) ₂	52
3	Ni(OAc) ₂ ·4H ₂ O instead of Ni(cod) ₂	4
4	Pd(OAc) ₂ instead of Ni(cod) ₂	16
5	Pd(dba) ₂ instead of Ni(cod) ₂	23
6	[Rh(OH)(cod)] ₂ instead of Ni(cod) ₂	50
7	PCy ₃ instead of PPh ₃	16
8	P(OPh) ₃ instead of PPh ₃	46
9	P ⁿ Bu ₃ instead of PPh ₃	71
10	LiCl instead of NaCl	5
11	KCl instead of NaCl	79
12	CsCl instead of NaCl	23
13	TBAC instead of NaCl	25
14	Without NaCl	67
15	Without Ni(cod) ₂	0
16	Without PPh ₃	0
17	Without KF	< 1
18	Benzoyl chloride instead of 1a	0

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. ^b Determined by GC analysis. ^c An isolated yield is shown in parentheses.

Table 2 Decarbonylative borylation of aryl fluorides^{a,b}

1a-1v	2a	3a-3v
R = H (3a): 83%	3q : 82%	3r : 68%
<i>p</i> -Me (3b): 65%		
<i>p</i> - ⁿ Bu (3c): 82%		
<i>p</i> -OMe (3d): 60%		
<i>p</i> -O ⁿ Bu (3e): 68%		
<i>p</i> -OBn (3f): 50%		
<i>p</i> -Ph (3g): 87%		
<i>p</i> -NMe ₂ (3h): 60%	3s : 55%	3t : 71%
<i>p</i> -CO ₂ Me (3i): 64%		
<i>p</i> -COPh (3j): 71%		
<i>p</i> -CN (3k): 45%		
<i>p</i> -CF ₃ (3l): 56%		
<i>m</i> -Ph (3m): 60%		
<i>o</i> -Me (3n): 38% (55%) ^b	3u : 50%	3v : 75%
<i>o</i> -Ph (3o): 78%		
<i>o</i> -CF ₃ (3p): 49% (62%) ^b		

^a Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. ^b Ni(cod)₂ (0.06 mmol), PPh₃ (0.18 mmol).

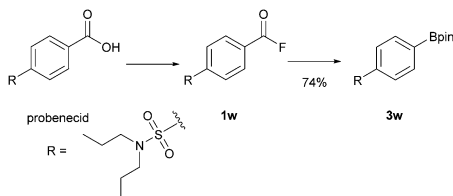
Table 3 Elucidation of other diborons^{a,b}

^a Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h. ^b **1r** (0.2 mmol), **2d** (0.4 mmol), then pinacol (4 equiv.) and NEt₃ (0.5 mL) at room temperature for 1 h.

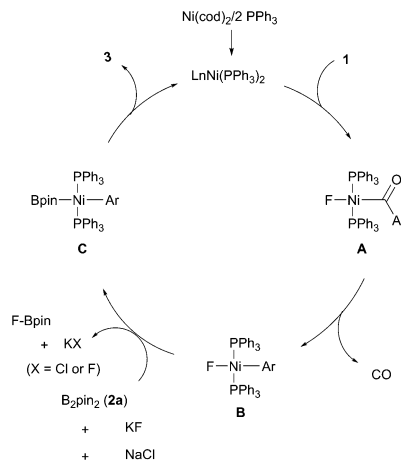
2-naphthoyl fluoride (**1r**) with bis(catecholato)diboron (**2d**, B₂cat₂), followed by the replacement with pinacol also yielded **3r** in 55% yield.

This nickel-catalysed decarbonylative borylation was also viable with complex molecular precursors bearing functional groups. For example, a carboxylic acid-containing drug, probenecid,³⁰ primarily used to treat gout and hyperuricemia, could be subjected to the two-step fluorination/decarbonylative borylation sequences. After fluorination of probenecid by conventional methods,^{20c} aroyl fluoride **1w** was smoothly converted into the target arylboronate **3w** in 74% yield (Scheme 2), whereas the attempt to elucidate the one-pot synthesis of arylboronates without isolation of aroyl fluorides was found to be unsuccessful. To our delight, this decarbonylative borylation is applicable to a large-scale synthesis. The 10-mmol scale experiment provided 1.19 g of **3a** in 58% yield.

The proposed mechanism of decarbonylative borylation of aroyl fluorides is shown in Scheme 3. Initially, oxidative addition of aroyl fluorides to Ni(0) generates the acyl-nickel(II) intermediate **A**.³¹⁻³³ Although our attempt to isolate **A** was unsuccessful, we found some clues for arylnickel species **B**. The reaction of Ni(cod)₂/2 PPh₃ with benzoyl fluoride in C₆D₆ at rt provided a characteristic broad singlet at -409.9 ppm in the ¹⁹F{¹H} NMR spectrum and a doublet at 15.1 ppm with a *J*_{P-F} of 44 Hz in the ³¹P{¹H} NMR spectrum even after 1 h. Considering the results obtained by Sanford,³³ the formed oxidative adduct Ni(COPh)-F(PCy₃)₂ caused decarbonylation to form Ni(Ph)F(PCy₃)₂ at room temperature within 10 min, in our case, the *in situ* generated Ni(COPh)F(PPh₃)₂ must be more unstable due to the weak coordination ability of PPh₃ than PCy₃. We thus concluded that



Scheme 2 Two-step borylation of probenecid.^a ^aReaction conditions: **1w** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)₂ (0.02 mmol), PPh₃ (0.06 mmol), KF (0.5 mmol), NaCl (0.4 mmol), toluene (0.66 mL), octane (0.33 mL), 140 °C, 24 h.



Scheme 3 Proposed mechanism.

the subsequent extrusion of carbon monoxide forming **B** could take place prior to transmetalation. Transmetalation between complex **B** and B₂pin₂ assisted by external KF (and NaCl) affords borylnickel(II) intermediate **C**. Finally, reductive elimination delivers the targeted arylboronates **3**, regenerating the Ni(0) species to complete a catalytic cycle.

In summary, we have developed the first decarbonylative borylation of aroyl fluorides with the assistance of an abundant and inexpensive metal Ni/PPh₃ catalytic system with B₂pin₂ as a coupling nucleophile, which is capable of producing various aromatic boronates. Importantly, this method realized that carboxylic acids can be converted into a wide array of arylboronates *via* aroyl fluorides. Currently, we are investigating the theoretical calculations to determine the reaction mechanism including a decarbonylation step, and other transition-metal-catalysed transformations of aroyl fluorides.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) A. Suzuki, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E. Negishi, Wiley-Interscience, New York, 2002, pp. 249-262; (b) N. Miyaura, *Top. Curr. Chem.*, 2002, **219**, 11; (c) A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6723.
- (a) D. G. Hall, *Boronic Acids*, Wiley, New York, 2005; (b) D. G. Hall, *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*, Wiley-VCH, Weinheim, 2005.
- (a) T. Ishiyama, M. Murata and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508; (b) T. Ishiyama, Y. Itoh, T. Kitano and N. Miyaura, *Tetrahedron Lett.*, 1997, **38**, 3447; (c) J. Takagi, K. Takahashi, T. Ishiyama and N. Miyaura, *J. Am. Chem. Soc.*, 2002, **124**, 8001; (d) K. L. Billingsley, T. E. Barder and S. L. Buchwald, *Angew. Chem.*,

- Int. Ed.*, 2007, **46**, 5359; (e) G. A. Molander, S. L. J. Trice and S. D. Dreher, *J. Am. Chem. Soc.*, 2010, **132**, 17701.
- 4 (a) S. K. Bose, A. Deisenberger, A. Eichhorn, P. G. Steel, Z. Y. Lin and T. B. Marder, *Angew. Chem., Int. Ed.*, 2015, **54**, 11843; (b) H. L. Li, Y. Kuninobu and M. Kanai, *Angew. Chem., Int. Ed.*, 2017, **56**, 1495; (c) Q. Yin, H. F. T. Klare and M. Oestreich, *Angew. Chem., Int. Ed.*, 2017, **56**, 3712; (d) M. E. Hoque, R. Bisht, C. Haldar and B. Chattopadhyay, *J. Am. Chem. Soc.*, 2017, **139**, 7745; (e) W. N. Palmer, C. Zarate and P. J. Chirik, *J. Am. Chem. Soc.*, 2017, **139**, 2589; (f) G. H. Wang, L. Liu, H. Wang, Y. S. Ding, J. Zhou, S. Mao and P. F. Li, *J. Am. Chem. Soc.*, 2017, **139**, 91; (g) M. Murai, N. Nishinaka and K. Takai, *Angew. Chem., Int. Ed.*, 2018, **57**, 5843.
- 5 (a) C. T. Yang, Z. Q. Zhang, H. Tajuddin, C. C. Wu, J. Liang, J. H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder and L. Liu, *Angew. Chem., Int. Ed.*, 2012, **51**, 528; (b) T. Niwa, H. Ochiai, Y. Watanabe and T. Hosoya, *J. Am. Chem. Soc.*, 2015, **137**, 14313; (c) X. W. Liu, J. Echavarren, C. Zarate and R. Martin, *J. Am. Chem. Soc.*, 2015, **137**, 12470; (d) W. H. Guo, Q. Q. Min, J. W. Gu and X. G. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 9075; (e) J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. T. Du, T. B. Marder and U. Radius, *J. Am. Chem. Soc.*, 2016, **138**, 5250; (f) T. Niwa, H. Ochiai and T. Hosoya, *ACS Catal.*, 2017, **7**, 4535; (g) T. Yoshida, L. Iliès and E. Nakamura, *ACS Catal.*, 2017, **7**, 3199; (h) W. B. Liu, X. B. Yang, Y. Gao and C. J. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8621.
- 6 (a) Y. Uetake, T. Niwa and T. Hosoya, *Org. Lett.*, 2016, **18**, 2758; (b) M. Bhanuchandra, A. Baralle, S. Otsuka, K. Nogi, H. Yorimitsu and A. Osuka, *Org. Lett.*, 2016, **18**, 2966; (c) H. Saito, K. Nogi and H. Yorimitsu, *Synthesis*, 2017, 4769; (d) H. Minami, S. Otsuka, K. Nogi and H. Yorimitsu, *ACS Catal.*, 2018, **8**, 579.
- 7 (a) H. Kinuta, M. Tobisu and N. Chatani, *J. Am. Chem. Soc.*, 2015, **137**, 1593; (b) C. Zarate, R. Manzano and R. Martin, *J. Am. Chem. Soc.*, 2015, **137**, 6754; (c) K. Nakamura, M. Tobisu and N. Chatani, *Org. Lett.*, 2015, **17**, 6142; (d) M. Tobisu, J. Zhao, H. Kinuta, T. Furukawa, T. Igarashi and N. Chatani, *Adv. Synth. Catal.*, 2016, **358**, 2417.
- 8 (a) J. Zhang, X. Wang, H. Yu and J. Ye, *Synlett*, 2012, 1394; (b) M. Tobisu, K. Nakamura and N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 5587; (c) H. Zhang, S. Hagihara and K. Itami, *Chem. – Eur. J.*, 2015, **21**, 16796; (d) J. Hu, H. Sun, W. Cai, X. Pu, Y. Zhang and Z. Shi, *J. Org. Chem.*, 2016, **81**, 14.
- 9 M. Tobisu, K. Nakamura and N. Chatani, *J. Am. Chem. Soc.*, 2014, **136**, 5587.
- 10 During our submission of this manuscript, the palladium-catalysed decarbonylative borylation of carboxylic acids has been reported, see: C. Liu, C. Ji, X. Hong and M. Szostak, *Angew. Chem., Int. Ed.*, DOI: 10.1002/anie.201810145.
- 11 J. F. Hu, Y. Zhao, J. J. Liu, Y. M. Zhang and Z. Z. Shi, *Angew. Chem., Int. Ed.*, 2016, **55**, 8718.
- 12 S. C. Lee, L. Guo, H. Yue, H. H. Liao and M. Rueping, *Synlett*, 2017, 2594.
- 13 X. H. Pu, J. F. Hu, Y. Zhao and Z. Z. Shi, *ACS Catal.*, 2016, **6**, 6692.
- 14 L. Guo and M. Rueping, *Chem. – Eur. J.*, 2016, **22**, 16787.
- 15 L. Guo and M. Rueping, *Acc. Chem. Res.*, 2018, **51**, 1185.
- 16 H. Ochiai, Y. Uetake, T. Niwa and T. Hosoya, *Angew. Chem., Int. Ed.*, 2017, **56**, 2482.
- 17 T. Niwa, H. Ochiai, M. Isoda and T. Hosoya, *Chem. Lett.*, 2017, **46**, 1315.
- 18 C. A. Malapit, N. Ichiishi and M. S. Sanford, *Org. Lett.*, 2017, **19**, 4142.
- 19 (a) C. Li, J. Wang, L. M. Barton, S. Yu, M. Q. Tian, D. S. Peters, M. Kumar, A. W. Yu, K. A. Johnson, A. K. Chatterjee, M. Yan and P. S. Baran, *Science*, 2017, **356**, 1045; (b) L. Candish, M. Teders and F. Glorius, *J. Am. Chem. Soc.*, 2017, **139**, 7440; (c) D. Hu, L. Wang and P. Li, *Org. Lett.*, 2017, **19**, 2770; (d) A. Fawcett, J. Pradeilles, Y. H. Wang, T. Mutsuga, E. L. Myers and V. K. Aggarwal, *Science*, 2017, **357**, 283.
- 20 For selected papers for the synthesis of acid fluorides from the corresponding carboxylic acids, see: (a) L. A. Carpino and A. El-Faham, *J. Am. Chem. Soc.*, 1995, **117**, 5401; (b) A. El-Faham, *Chem. Lett.*, 1998, 671; (c) G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic and H. Cheng, *J. Org. Chem.*, 1999, **64**, 7048; (d) S. Grof, S. Laabs, A. Scherrmann, A. Sudau, N. Zhang and D. U. Nubbemeyer, *J. Prakt. Chem.*, 2000, **342**, 711; (e) C. Chen, C. T. Chien and C. H. Su, *J. Fluorine Chem.*, 2002, **115**, 75; (f) F. Beaulieu, L. P. Beauregard, G. Courchesne, M. Couturier, F. LaFlamme and A. L'Heureux, *Org. Lett.*, 2009, **11**, 5050; (g) J. M. White, A. R. Tunoori, B. J. Turunen and G. I. Georg, *J. Org. Chem.*, 2004, **69**, 2573; (h) C. O. Kangani and D. E. Kelley, *Tetrahedron Lett.*, 2005, **46**, 8917; (i) E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606; (j) T. Scattolin, K. Deckers and F. Schoenebeck, *Org. Lett.*, 2017, **19**, 5740.
- 21 Y. D. Zhang and T. Rovis, *J. Am. Chem. Soc.*, 2004, **126**, 15964.
- 22 Y. Ogiwara, Y. Maegawa, D. Sakino and N. Sakai, *Chem. Lett.*, 2016, **45**, 790.
- 23 Y. Ogiwara, D. Sakino, Y. Sakurai and N. Sakai, *Eur. J. Org. Chem.*, 2017, 4324.
- 24 Y. Ogiwara, Y. Sakurai, H. Hattori and N. Sakai, *Org. Lett.*, 2018, **20**, 4204.
- 25 S. T. Keaveney and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2018, **57**, 4073.
- 26 Y. Okuda, J. Xu, T. Ishida, C. Wang and Y. Nishihara, *ACS Omega*, 2018, **3**, 13129.
- 27 The Cu-catalysed boroacylation of allenes has been reported using aryl fluorides as electrophiles and B₂pin₂ as a nucleophile, see: A. Boreux, K. Indukuri, F. Gagosz and O. Riant, *ACS Catal.*, 2017, **7**, 8200.
- 28 Activation of B₂pin₂ with a fluoride ion, see: S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Mo, D. Qiu, M. S. Cheung, L. Dang, J. Wang, U. Radius, Z. Lin, C. Kleeborg and T. B. Marder, *Chem. – Eur. J.*, 2015, **21**, 7082.
- 29 (a) M. Tobisu, T. Takahira, T. Morioka and N. Chatani, *J. Am. Chem. Soc.*, 2016, **138**, 6711; (b) J. Cornella and R. Martin, *Org. Lett.*, 2013, **15**, 6298; (c) C. Zarate, M. Nakajima and R. Martin, *J. Am. Chem. Soc.*, 2017, **139**, 1191.
- 30 V. Morra, P. Davit, P. Capra, M. Vincenti, A. D. Stilo and F. Botrè, *J. Chromatogr. A*, 2006, **1135**, 219.
- 31 Oxidative addition of benzoyl fluoride to Ni(cod)₂/PET₃ has been reported, see: D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, 1977, **99**, 2501.
- 32 Synthesis of a palladium counterpart of complex A, Pd(COPh)F(PPh₃)₂, from Pd(COPh)I(PPh₃)₂ and AgF under sonication has been reported, see: V. V. Grushin, *Chem. – Eur. J.*, 2002, **8**, 1006.
- 33 During our submission of this manuscript, the isolation of the oxidative adduct Ni(COPh)F(PET₃)₂ and the decarbonylative complex Ni(Ph)F(PCy₃)₂ have been reported, see: C. A. Malapit, J. R. Bour, C. E. Brigham and M. S. Sanford, *Nature*, 2018, **563**, 100.