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One-pot generation of benzynes from 2-aminophenylboronates *via* a Rh(II)-catalyzed N–H amination/oxidation/elimination cascade process†

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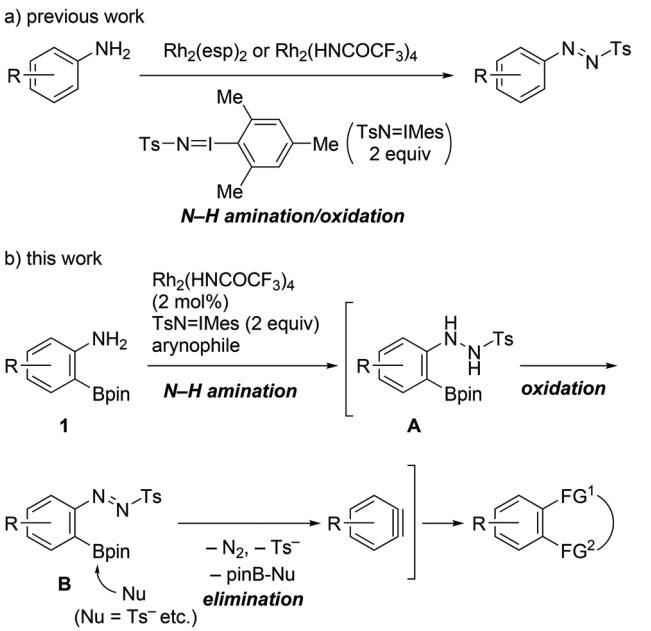
This article describes the first application of 2-aminophenylboronates as precursors for benzynes. Utilizing $Rh_2(HNCOCF_3)_4$ as the catalyst, Rh(II)-nitrene-mediated N–H amination of the starting material triggered a cascade of oxidation/elimination processes resulting in the generation of benzynes, thus providing suitable conditions for a one-pot cycloaddition with azides or furans. The transformation proceeded under acid-, base-, and fluoride-free conditions, below ambient temperature, and was applicable to a range of substrates containing glycoside and nucleoside moieties, as well as silyl-functional groups.

Introduction

Benzynes are unique reactive intermediates that participate in the simultaneous creation of two bonds, including C–C, C–H, or C–X (X = heteroatom) bonds, on adjacent aromatic carbons *via* a cycloaddition reaction or the sequential addition of a nucleophile and an electrophile.[1] With a view to further enhancing the synthetic utility of these reactive species, significant efforts have been devoted to developing efficient benzyne precursors.[2–6] Among the known precursors, 2-trimethylsilylphenyl triflates, which generate benzynes on treatment with fluoride salts, have been widely used. The advantages of using these compounds include availability, stability, and mild reaction conditions.[2–4] Aside from phenol derivatives, aniline derivatives comprise a more classical class of benzyne precursors such as 1-aminobenzotriazole, 1,2,3-benzothiadiazole 1,1-dioxide, and diazonium salts derived from anthranilic acids.[5] However, with the exception of anthranilic acids, the aforementioned precursors are not currently commonly used. Following early examples and some notable advancements in the area of aryne chemistry, also referred to as its renaissance, the development of novel aniline-based precursors has been stagnated over the last few decades.[6]

As part of the research on the transformation of anilines using the Rh(II)-nitrene species,[7,8] we recently reported the catalytic single-step synthesis of *N*-aryl-*N*′-tosyldiazenes from primary anilines.[8a] In the presence of dirhodium(II) complexes as the catalysts and 2 equiv. of (tosylimino)-2,4,6-trimethylphenyliodinane (TsN=IMes), anilines underwent N–H amination by Rh(II)-nitrene followed by oxidation to provide the products in one pot (Scheme 1a). Although tosyldiazenes dis-



Scheme 1 (a) Rh(II)-Catalyzed synthesis of *N*-aryl-*N*′-tosyldiazene. (b) Utilization of 2-aminophenylboronates as benzyne precursors through a Rh(II)-catalyzed N–H amination/oxidation/elimination cascade process.

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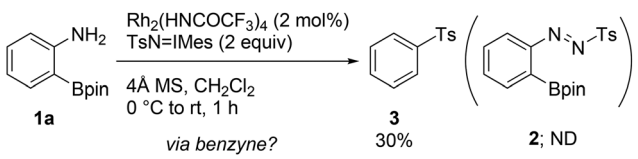
†Electronic supplementary information (ESI) available: Experimental procedures, compound characterization data, and copies of NMR spectra for all new compounds. See DOI: 10.1039/c9qo01115c

played higher stability than diazonium salts, their C–N bonds were readily transformed into C–C bonds *via* the Suzuki–Miyaura or Sonogashira coupling.[9] Thus, we successfully validated the compounds as safer surrogate of diazonium salts for C–N bond transformation.

In this context, we herein report the utilization of 2-aminophenylboronates as novel benzyne precursors through the combined use of $Rh_2(HNCOCF_3)_4$ and TsN=IMes (Scheme 1b). Under the described conditions, the Rh(II)-nitrene-mediated N–H amination of the starting materials triggered a cascade of oxidation/elimination processes resulting in the generation of benzynes, thus providing suitable conditions for a one-pot cycloaddition with azides or furans.

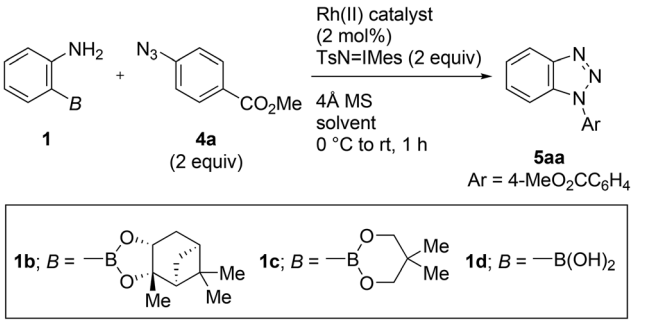
Results and discussion

During the course of our previous study (Scheme 1a),[8a] we found that the reaction of a commercially available 2-aminophenylboronic acid pinacol ester (**1a**) under $Rh_2(HNCOCF_3)_4$ catalysis unexpectedly provided phenyl *p*-tolyl sulfone (**3**) in 30% yield, instead of tosyldiazene **2** (Scheme 2). This result, including simultaneous transformation of the neighboring C–N and C–B bonds, strongly indicated the generation of the benzyne intermediate from **1a** *in situ*. On the basis of this hypothesis, we subsequently attempted to trap benzyne with an arynophile, methyl 4-azidobenzoate (**4a**). As expected, the reaction in the presence of **4a** (2 equiv.), and under otherwise identical conditions, led to the formation of cycloadduct **5aa** in 57% yield (Table 1, entry 1). Therefore, 2-aminophenylboronate undeniably functioned as a benzyne precursor under the described conditions. Virtually the same result was obtained using the inverse ratio of the precursor and the arynophile (entry 2, **1a** : **4a** = 1.5 : 1). Changing the solvent from CH_2Cl_2 to MeCN had little impact on the product yields, whereas toluene and benzotrifluoride led to a slight drop in the obtained yields (entries 3–5). The influence of iminoiodinane was also investigated (entry 6).[10] In contrast to previous work, no significant difference was observed between TsN=IMes and TsN=IPh. Utilizing $Rh_2(HNCOCF_3)_4$ as the catalyst was remarkably effective for the transformation, particularly in comparison to the commonly used Rh(II) catalysts such as $Rh_2(OAc)_4$ and $Rh_2(esp)_2$ (entry 1 *vs.* entries 7 and 8). A review of the starting boronates indicated that pinanediolate **1b** provided a comparable outcome to pinacolate **1a**, whereas less bulky neopentylglycolate **1c** and unprotected boronic acid **1d** resulted in a noticeable drop in the yields (entries 1, 9–11).



Scheme 2 Unexpected transformation of 2-aminophenylboronate **1a** under Rh(II)-catalyzed amination conditions. pin = pinacolato.

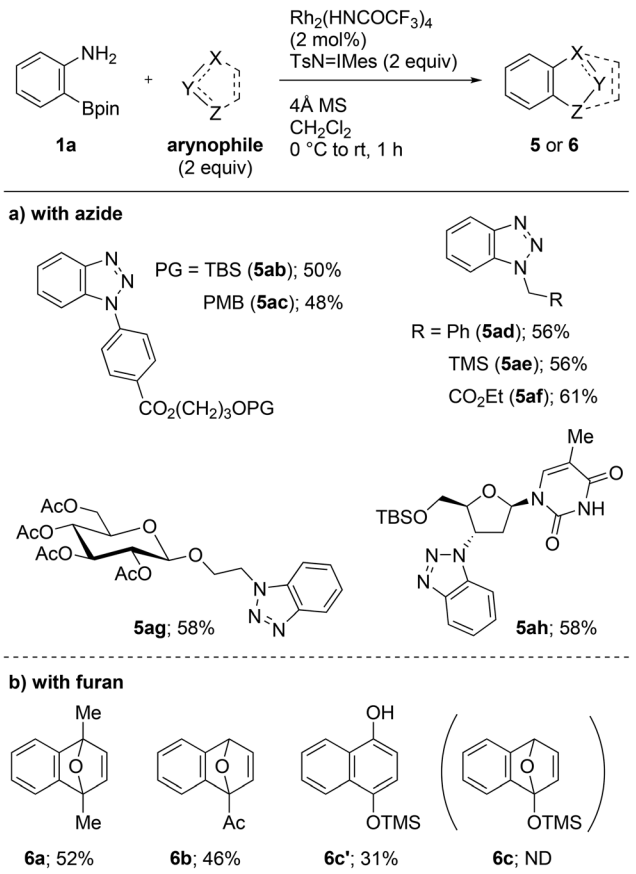
Table 1 Dirhodium(II)-catalyzed cycloaddition of 2-aminophenylboronates **1** with methyl 4-azidobenzoate (**4a**)[a]



Entry	Aniline	Rh(II)-Catalyst	Solvent	Yield[b] (%)
1	**1a**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	57
2[c]	**1a**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	58
3[d]	**1a**	$Rh_2(HNCOCF_3)_4$	MeCN	57
4	**1a**	$Rh_2(HNCOCF_3)_4$	Toluene	41
5	**1a**	$Rh_2(HNCOCF_3)_4$	$CF_3C_6H_5$	51
6[e]	**1a**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	53
7	**1a**	$Rh_2(OAc)_4$	CH_2Cl_2	17
8	**1a**	$Rh_2(esp)_2$	CH_2Cl_2	33
9	**1b**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	58
10	**1c**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	12
11	**1d**	$Rh_2(HNCOCF_3)_4$	CH_2Cl_2	12

[a] Reaction conditions: **1** (0.10 mmol), **4a** (0.20 mmol), Rh(II) catalyst (0.002 mmol, 2 mol%), iminoiodinane (0.20 mmol), and 4 Å MS (powder, 40 mg) in the indicated solvent (1.0 mL). [b] Isolated yield. [c] **1a** : **4a** : TsN=IMes = 1.5 : 1.0 : 3.0. [d] 3 Å MS was used. [e] TsN=IPh was used. Ts = tosyl. esp = α,α,α,α-tetramethyl-1,3-benzenedipropanoate.

With the optimized conditions in hand, we then investigated the cycloaddition using a range of azides (Scheme 3a). All the aryl and alkyl azides that were examined gave cycloadducts **5ab–ah** in 48–61% yield. It is notable that the trialkylsilyl and the enolizable carbonyl groups remained unaffected during the transformation (**5ab**, **5ae**, **5af**, **5ag**, and **5ah**). These results indicate that the novel methodology is orthogonal to the conventional fluoride- or strong base-mediated approaches in terms of functional group tolerance. The present protocol was also applicable to complex azides, associated with biomolecules including glycoside and nucleoside moieties. The reaction with 2-azidoethyl β-D-glucopyranoside proceeded without anomerization and resulted in the formation of **5ag** in 58% yield. The late-stage functionalization of *O*-(*tert*-butyldimethylsilyl) (TBS) protected zidovudine, an azide-containing anti-HIV nucleoside used in the clinic, was achieved, and cycloadduct **5ah** was obtained in 58% yield. Aside from the cycloaddition with azides, the reactions with furans, including 2,5-dimethylfuran and 2-acetylfuran, gave cycloadduct **6a** and **6b** in 52% and 46% yields, respectively (Scheme 3b). Utilizing 2-trimethylsilyloxyfuran led to the formation of 1-naphthol **6c′** in 31% yield *via* the ring opening of cycloadduct **6c**.[11] Unfortunately, reactions with other arynophiles such as 2,5-diphenylisobenzofuran, anthracene, nitrone, and β-ketoester failed to provide the expected cycloadducts.[12] However, the reason is currently unclear.



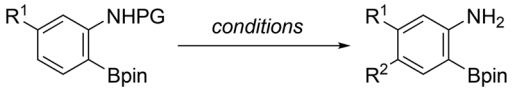
Scheme 3 $Rh_2(HNCOCF_3)_4$-catalyzed cycloadditions of 2-aminophenylboronate **1a** with azides or furans. TBS = *tert*-butyldimethylsilyl. PMB = *para*-methoxybenzyl. TMS = trimethylsilyl.

Our attention next turned to the preparation of functionalized 2-aminophenylboronates (Table 2). Although the Miyaura borylation of 2-haloaniline derivatives or the corresponding nitrobenzenes provides reliable access to the described compounds,[13,14] the post-functionalization of 2-aminophenylboronate would have the advantage of a rapid and divergent conversion to a series of precursors. The brominated precursor **1e** was prepared from **1a** by treatment with *N*-bromosuccinimide (NBS) (entry 1). A gold-catalyzed C–H insertion of phenyldiazoacetate into the *N*-Boc-protected aniline **1a′** proceeded at the *para* position of the amino group, albeit in low yield,[15] and the desired benzyne precursor **1f** was obtained after removal of the Boc group by treatment with trifluoroacetic acid (TFA) (entry 2). A methoxycarbonyl-substituted precursor **1g** was readily available from the corresponding commercially available starting materials such as 2-aminophenylboronic acid or the more inexpensive 2-nitrophenylboronic acid (see ESI†). Reduction of **1g** with DIBAL-H, followed by protection with the TBS group gave benzyl silyl ether **1h** (entry 3).[16]

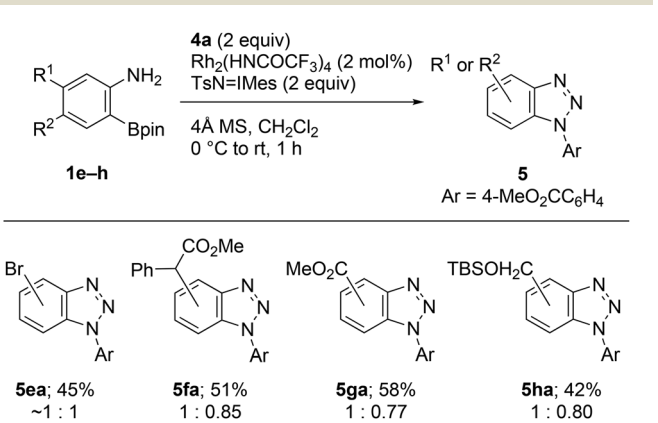
Similarly to **1a**, all the synthesized precursors **1e–h** uneventfully generated substituted benzyne species under identical conditions, and cycloadducts **5ea–ha** were obtained as mixture of the regioisomers (Scheme 4).

A plausible reaction pathway for this transformation is illustrated in Scheme 1b. The N–H amination of aniline **1** with Rh(II)-nitrene leads to the formation of *N*-aryl-*N′*-tosylhydrazine **A**, which on reacting with TsN=IMes is immediately oxidized into *N*-aryl-*N′*-tosyldiazene **B**.[8a] It is suspected that after activation of the boronate group with internal nucleophiles (*i.e.*, Ts^-, $TsNH_2$, *etc.*),[4d,f,17] elimination of the boronate and tosyldiazene moieties results in the one-pot generation of benzynes. To verify the proposed pathway, we then attempted to isolate the putative intermediate **A** or **B** utilizing the described conditions; however, all our efforts were unsuccessful. Instead, *N*-tosylhydrazine **8c** was prepared through an alternative synthetic pathway, which included electrophilic amination of 3-methoxyphenylboronate **7** with benzyl 2,2,2-trichloroethyl azodicarboxylate, followed by a three-step manipulation of the protecting groups (Scheme 5).[18,19] The cycloaddition of **8c** with azide **4a** was subsequently investigated. Treatment of the starting material with TsN=IMes resulted in the formation of the expected cycloadduct **9** in the presence or absence of the

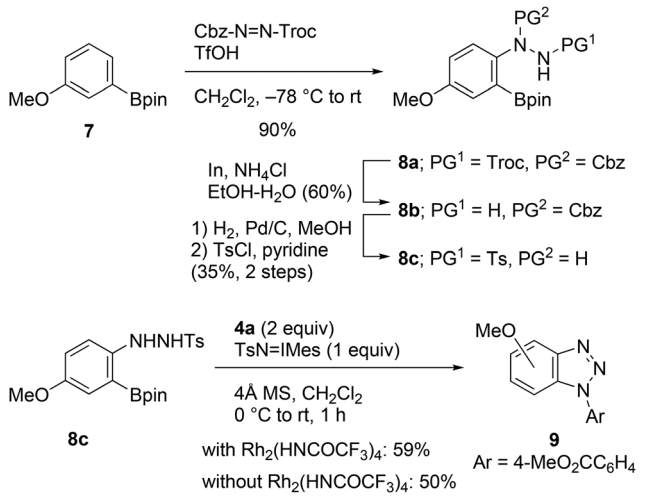
Table 2 Synthesis of functionalized 2-aminophenylboronates **1e–h**



Entry	Substrate	Conditions (yield)	Product
1	**1a** R^1 = H PG = H	NBS, NH_4OAc MeCN (95%)	**1e** R^1 = H R^2 = Br
2	**1a′** R^1 = H PG = Boc	(1) $Ph_3PAuNTf_2$ $PhCH(N_2)CO_2Me$ CH_2Cl_2 (28%) (2) TFA CH_2Cl_2 (46%)	**1f** R^1 = H R^2 = $CHPhCO_2Me$
3	**1g** R^1 = CO_2Me PG = H	(1) DIBAL-H, THF −40 °C (66%) (2) TBSCl, TBAB CH_2Cl_2 (47%)	**1h** R^1 = CH_2OTBS R^2 = H



Scheme 4 $Rh_2(HNCOCF_3)_4$-catalyzed cycloaddition of 2-aminophenylboronates **1e–h** with methyl 4-azidobenzoate (**4a**).



Scheme 5 Synthesis of *N*-aryl-*N*′-tosylhydrazine **8c** and cycloaddition with methyl 4-azidobenzoate (**4a**).

$Rh_2(HNCOCF_3)_4$ catalyst. Consequently, the reaction pathway presented in Scheme 1b was verified.

Conclusions

In conclusion, we demonstrated that 2-aminophenylboronates can be used as novel benzyne precursors. In the presence of the dirhodium(II)-complex catalyst, Rh(II)-nitrene-mediated N–H amination of the precursors triggered a cascade of oxidation/elimination processes resulting in the generation of benzynes, thus providing the desired cycloadducts in one pot. The transformation proceeded under acid-, base-, and fluoride-free conditions, below ambient temperature, and was orthogonal to the conventional methods in terms of functional group tolerance. Consequently, this methodology was applicable to a range of substrates containing glycoside and nucleoside moieties, as well as silyl-functional groups. Further extension of this methodology to a range of (hetero)aryne precursors as well as further mechanistic evaluation are currently in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) P. M. Tadross and B. M. Stoltz, *Chem. Rev.*, 2012, **112**, 3550; (*b*) A. V. Dubrovskiy, N. A. Markina and R. C. Larock, *Org. Biomol. Chem.*, 2013, **11**, 191; (*c*) H. Yoshida, Nucleophilic Coupling with Arynes, in *Comprehensive Organic Synthesis*, ed. P. Knochel and G. A. Molander, Elsevier, Amsterdam, 2nd edn, 2014, vol. 4, p. 517; (*d*) A. E. Goetz, T. K. Shah and N. K. Garg, *Chem. Commun.*, 2015, **51**, 34; (*e*) S. Yoshida and T. Hosoya, *Chem. Lett.*, 2015, **44**, 1450; (*f*) F. M. Idiris and C. R. Jones, *Org. Biomol. Chem.*, 2017, **15**, 9044; (*g*) A. Yoshimura, A. Saito and V. V. Zhdankin, *Chem. – Eur. J.*, 2018, **24**, 15156; (*h*) H. Takikawa, A. Nishii, T. Sakai and K. Suzuki, *Chem. Soc. Rev.*, 2018, **47**, 8030.

2 (*a*) Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.*, 1983, 1211; (*b*) N. Furukawa, T. Shibutani and H. Fujihara, *Tetrahedron Lett.*, 1987, **28**, 2727; (*c*) T. Matsumoto, T. Hosoya, M. Katsuki and K. Suzuki, *Tetrahedron Lett.*, 1991, **32**, 6735; (*d*) T. Kitamura and M. Yamane, *J. Chem. Soc., Chem. Commun.*, 1995, 983.

3 (*a*) M. Uchiyama, T. Miyoshi, Y. Kajihara, T. Sakamoto, Y. Otani, T. Ohwada and Y. Kondo, *J. Am. Chem. Soc.*, 2002, **124**, 8514; (*b*) I. Sapountzis, W. Lin, M. Fischer and P. Knochel, *Angew. Chem., Int. Ed.*, 2004, **43**, 4364; (*c*) T. Hamura, T. Arisawa, T. Matsumoto and K. Suzuki, *Angew. Chem., Int. Ed.*, 2006, **45**, 6842; (*d*) H. S. Kim, S. Gowrisankar, E. S. Kim and J. N. Kim, *Tetrahedron Lett.*, 2008, **49**, 6569; (*e*) A. A. Cant, L. Roberts and M. F. Greaney, *Chem. Commun.*, 2010, **46**, 8671; (*f*) T. Ikawa, T. Nishiyama, T. Nosaki, A. Takagi and S. Akai, *Org. Lett.*, 2011, **13**, 1730; (*g*) S. Kovács, Á. I. Csincsi, T. Z. Nagy, S. Boros, G. Timári and Z. Novák, *Org. Lett.*, 2012, **14**, 2022; (*h*) T. Hamura, Y. Chuda, Y. Nakatsuji and K. Suzuki, *Angew. Chem., Int. Ed.*, 2012, **51**, 3368; (*i*) T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby and B. P. Woods, *Nature*, 2012, **490**, 208; (*j*) S. Yoshida, K. Uchida and T. Hosoya, *Chem. Lett.*, 2014, **43**, 116; (*k*) Q. Chen, H. Yu, Z. Xu, L. Lin, X. Jiang and R. Wang, *J. Org. Chem.*, 2015, **80**, 6890; (*l*) S. K. Sundalam, A. Nilova, T. L. Seidl and D. R. Stuart, *Angew. Chem., Int. Ed.*, 2016, **55**, 8431; (*m*) E. Gorobets, M. Parvez, D. J. Derksen and B. A. Keay, *Chem. – Eur. J.*, 2016, **22**, 8479; (*n*) M. Wang and Z. Huang, *Org. Biomol. Chem.*, 2016, **14**, 10185; (*o*) M. Mesgar and O. Daugulis, *Org. Lett.*, 2016, **18**, 3910; (*p*) T. Ikawa, S. Masuda, H. Nakajima and S. Akai, *J. Org. Chem.*, 2017, **82**, 4242; (*q*) J. Shi, H. Xu, D. Qiu, J. He and Y. Li, *J. Am. Chem. Soc.*, 2017, **139**, 623; (*r*) Y. Nishiyama, S. Kamada, S. Yoshida and T. Hosoya, *Chem. Lett.*, 2018, **47**, 1216; (*s*) K. Devaraj, F. J. L. Ingner, C. Sollert, P. J. Gates, A. Orthaber and L. T. Pilarski, *J. Org. Chem.*, 2019, **84**, 5863.

4 In recent years, 2-borylphenyl triflates have also emerged as efficient precursors for the generation of benzynes under various conditions, including treatment with transition metal catalysts, organolithium reagents, and fluoride salts. (*a*) M. Retbøll, A. J. Edwards, A. D. Rae, A. C. Willis,

M. A. Bennett and E. Wenger, *J. Am. Chem. Soc.*, 2002, **124**, 8348; (*b*) Y. Sumida, T. Kato and T. Hosoya, *Org. Lett.*, 2013, **15**, 2806; (*c*) J.-A. García-López and M. F. Greaney, *Org. Lett.*, 2014, **16**, 2338; (*d*) T. Ikawa, R. Yamamoto, A. Takagi, T. Ito, K. Shimizu, M. Goto, Y. Hamashima and S. Akai, *Adv. Synth. Catal.*, 2015, **357**, 2287; (*e*) Y. Sumida, T. Sumida, D. Hashizume and T. Hosoya, *Org. Lett.*, 2016, **29**, 5600; (*f*) A. Yoshimura, J. M. Fuchs, K. R. Middleton, A. V. Maskaev, G. T. Rohde, A. Saito, P. S. Postnikov, M. S. Yusubov, V. N. Nemykin and V. V. Zhdankin, *Chem. – Eur. J.*, 2017, **23**, 16738.

5 (*a*) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, 1963, **85**, 1549; (*b*) G. Wittig and R. W. Hoffmann, *Org. Synth.*, 1967, **47**, 4; (*c*) C. D. Campbell and C. W. Rees, *J. Chem. Soc. C*, 1969, 742; (*d*) C. Spiteri, C. Mason, F. Zhang, D. J. Ritson, P. Sharma, S. Keeling and J. E. Moses, *Org. Biomol. Chem.*, 2010, **8**, 2537; (*e*) W. Huang, Q. Gao and G.-J. Boons, *Chem. – Eur. J.*, 2015, **21**, 12920; (*f*) E. M. Serum, S. Selvakumar, N. Zimmermann and M. P. Sibi, *Green Chem.*, 2018, **20**, 1448.

6 A. W. Gann, J. W. Amoroso, V. J. Einck, W. P. Rice, J. J. Chambers and N. A. Schnarr, *Org. Lett.*, 2014, **16**, 2003.

7 Reviews on Rh(II)-nitrene, see; (*a*) P. Müller and C. Fruit, *Chem. Rev.*, 2003, **103**, 2905; (*b*) A. R. Dick and M. S. Sanford, *Tetrahedron*, 2006, **62**, 2439; (*c*) J. L. Roizen, M. E. Harvey and J. Du Bois, *Acc. Chem. Res.*, 2012, **45**, 911; (*d*) J. Buendia, G. Grelier and P. Dauban, *Adv. Organomet. Chem.*, 2015, **64**, 77; (*e*) B. Darses, R. Rodrigues, L. Neuville, M. Mazurais and P. Dauban, *Chem. Commun.*, 2017, **53**, 493.

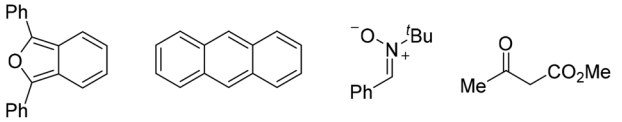
8 (*a*) M. Ito, A. Tanaka, K. Higuchi and S. Sugiyama, *Eur. J. Org. Chem.*, 2017, 1272; (*b*) M. Ito, T. Nakagawa, K. Higuchi and S. Sugiyama, *Org. Biomol. Chem.*, 2018, **16**, 6876.

9 (*a*) M. J. Evers, L. E. Christiaens, M. R. Guillaume and M. J. Renson, *J. Org. Chem.*, 1985, **50**, 1779; (*b*) J.-B. Liu, H. Yan, H.-X. Chen, Y. Luo, J. Weng and G. Lu, *Chem. Commun.*, 2013, **49**, 5268; (*c*) J.-B. Liu, F.-J. Chen, N. Liu and J. Hu, *RSC Adv.*, 2015, **5**, 45843; (*d*) S. Crespi, S. Protti and M. Fagnoni, *J. Org. Chem.*, 2016, **81**, 9612; (*e*) M. Malacarne, S. Protti and M. Fagnoni, *Adv. Synth. Catal.*, 2017, **359**, 3826; (*f*) Y. Xu, X. Yang and H. Fang, *J. Org. Chem.*, 2018, **83**, 12831; (*g*) L. Blank, M. Fagnoni, S. Protti and M. Rueping, *Synthesis*, 2019, **51**, 1243.

10 The use of other iminoiodinanes such as *p*NsN=IMes, 4-$ClC_6H_4SO_2N$=IMes, 4-$MeOC_6H_4SO_2N$=IMes did not improve product yield (36–51%).

11 M. Ballantine, M. L. Menard and W. Tam, *J. Org. Chem.*, 2009, **74**, 7570.

12 The structures of sluggish arynophiles are shown in below.



.

13 (*a*) P.-E. Broutin, I. Čerňa, M. Campaniello, F. Leroux and F. Colobert, *Org. Lett.*, 2004, **6**, 4419; (*b*) H. Fang, G. Kaur, J. Yan and B. Wang, *Tetrahedron Lett.*, 2005, **46**, 1671; (*c*) J. Lu, Z.-Z. Guan, J.-W. Gao and Z.-H. Zhang, *Appl. Organomet. Chem.*, 2011, **25**, 537; (*d*) H. Ji, L.-Y. Wu, J.-H. Cai, G.-R. Li, N.-N. Gan and Z.-H. Wang, *RSC Adv.*, 2018, **8**, 13643.

14 Recently, M. R. Smith III developed the NH_2-directed *ortho* C–H borylation using Ir catalyst. (*a*) S. M. Preshlock, D. L. Plattner, P. E. Maligres, S. W. Krska, R. E. Maleczka Jr. and M. R. Smith III, *Angew. Chem., Int. Ed.*, 2013, **52**, 12915; (*b*) M. R. Smith III, R. Bisht, C. Haldar, G. Pandey, J. E. Dannatt, B. Ghaffari, R. E. Maleczka Jr. and B. Chattopadhyay, *ACS Catal.*, 2018, **8**, 6216.

15 (*a*) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu and J. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 6904; (*b*) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan and X. Shi, *Angew. Chem., Int. Ed.*, 2014, **53**, 9817.

16 B. Sreedhar and V. S. Rawat, *J. Appl. Chem.*, 2012, **1**, 174. Silylation using conventional conditions (TBSCl/imidazole, TBSOTf/2,6-lutidine) did not give the desired outcome.

17 While the fate of boronate moiety is currently unclear, we considered that *p*-toluenesulfinate activated the boronate as *O*- or *S*-nucleophile. It is reported that boronates are even activated by water to generate benzynes from aryl(2-borylphenyl)iodonium salts (see ref. 4*f*). Similar to this, in our case, *p*-toluenesulfonamide can also be an activator.

18 (*a*) Y. Leblanc and N. Boudreault, *J. Org. Chem.*, 1995, **60**, 4268; (*b*) H. Mitchell and Y. Leblanc, *J. Org. Chem.*, 1994, **59**, 682.

19 T. Mineno, S.-R. Choi and M. A. Avery, *Synlett*, 2002, 883.

