ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

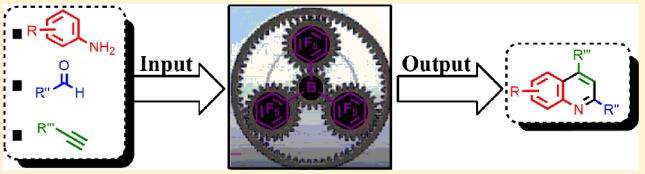
Mechanistic Insights into the $B(C_6F_5)_3$-Initiated Aldehyde–Aniline–Alkyne Reaction To Form Substituted Quinolines

Valerio Fasano, James E. Radcliffe, and Michael J. Ingleson*

School of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

Supporting Information

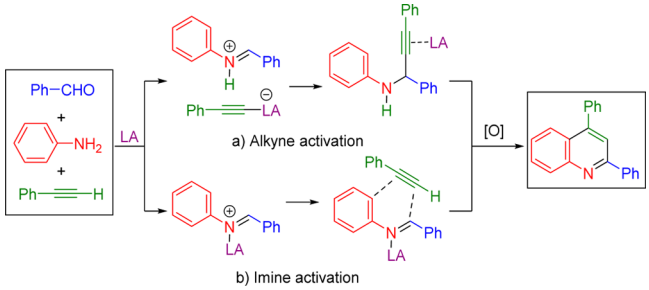
ABSTRACT: A substoichiometric quantity of the Lewis acid $B(C_6F_5)_3$ is sufficient to initiate the aldehyde–amine–alkyne reaction, in a one-pot methodology that enables the synthesis of a range of functionalized quinolines. Optimization studies revealed that key requirements for the high-yielding tricomponent reaction initiated by $B(C_6F_5)_3$ at raised temperatures include an excess of the *in situ* generated imine (which acts as a hydrogen acceptor) and an alkyne substituent able to stabilize positive charge buildup during the cyclization. Mechanistic experiments revealed that under these conditions $B(C_6F_5)_3$ is acting as a Lewis acid-assisted Brønsted acid, with $H_2O–B(C_6F_5)_3$ being the key species enabling catalytic quinoline formation. This was indicated by deuterium labeling studies and the observation that the cyclization of *N*-(3-phenylpropargyl)aniline using $B(C_6F_5)_3$ under anhydrous conditions afforded the zwitterion [(*N*-H-3-$B(C_6F_5)_3$-4-Ph-quinolinium], which does not undergo protodeboronation to release $B(C_6F_5)_3$ and the quinoline product under a range of conditions. Finally, a brief substrate scope exploration demonstrated that this is an operationally simple and effective methodology for the production of functionalized quinolines.



Quinolines are ubiquitous in natural products, pharmaceutically active compounds, ligands, and functional materials.[1] Over the past two centuries, multiple routes to quinolines have been developed since the first synthesis by Skraup,[2] including the Doebner–Von Miller,[3] Combes,[4] Conrad–Limpach,[5] Friedlander,[6] and Pfitzinger syntheses.[7] Although these methods are effective, they often require prefunctionalization of the starting materials, and regioselectivity issues can arise when using 1,3-dielectrophiles. Multicomponent reactions (MCRs), in which three or more compounds are mixed together in a single step, are efficient methods to rapidly furnish complex products.[8] The MCR approach has been applied to quinoline syntheses via the aldehyde–aniline–alkyne reaction (also referred to as the A^3 reaction). In this an imine, produced *in situ*, undergoes nucleophilic attack by an alkyne to yield a propargylamine.[9] The *N*-aryl propargylamine then reacts further, forming a quinoline motif upon cyclization/oxidation (Scheme 1).

The first application of the A^3 reaction for quinoline synthesis used catalytic CuCl,[10] and since then, multiple examples have been reported using a range of transition metal or lanthanide catalysts (generally proposed to form metal acetylide nucleophiles during the catalytic cycle, Scheme 1a).[11] A different pathway proceeds with Brønsted and certain Lewis acids, which instead activate the imine to nucleophilic attack by the alkyne, in a variant of the Povarov reaction (Scheme 1b).[12] In the past decade, the Lewis acid $B(C_6F_5)_3$ has attracted attention as a metal-free alternative to transition metal catalysis, with one major focus being the functionalization of alkynes.[13] On the basis of previous work using $B(C_6F_5)_3$ we were interested in determining if $B(C_6F_5)_3$ was a viable catalyst for the A^3 reaction. Specific literature relevant to this study

Scheme 1. Pathways for the A^3 Reaction[a]



[a]LA = Lewis acid.

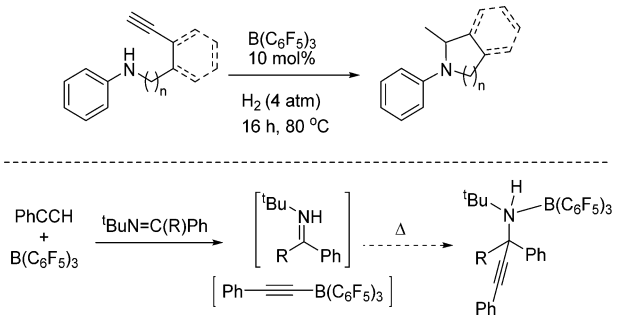
reported that $B(C_6F_5)_3$ activates alkynes toward cyclization to form complex aromatic carbo- or boracyclic compounds (e.g., dibenzopentalene and benzoborolate).[14] Similarly, intramolecular hydroaminations[15] and oxoborations[16] of terminal alkynes have been reported using stoichiometric $B(C_6F_5)_3$, allowing the synthesis of N- and O-heterocyclic aromatic compounds. The possibility of cyclizing alkynes with catalytic $B(C_6F_5)_3$ has also been investigated as reported for 1,5-enynes[17] or anilines with a pendent alkyne (Scheme 2, top).[16]

Furthermore, in previous work, Stephan and co-workers have reported that the frustrated Lewis pair (FLP) system *N*-benzylidene *tert*-butylimine/$B(C_6F_5)_3$ was able to activate phenylacetylene, yielding the iminium alkynylborate (Scheme 2, bottom).[18] Interestingly, upon heating the reaction, the

Received: March 6, 2017

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX–XXX

Scheme 2. (Top) Intramolecular Hydroamination of Terminal Alkynes with Catalytic $B(C_6F_5)_3$; (Bottom) Propargyl Amine Formation Using $B(C_6F_5)_3$



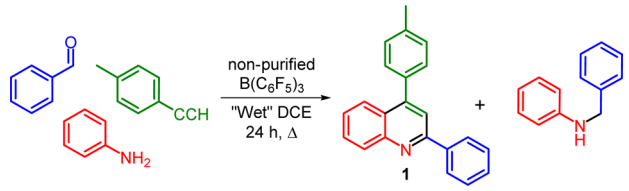
authors observed NMR spectra consistent with acetylide transfer to the iminium cation, but isolation of any propargylamines was unsuccessful. On the basis of the above precedence, it is feasible that the Lewis acid $B(C_6F_5)_3$ could be employed as catalyst to accomplish the A^3 reaction due to its ability to activate both alkyne (acetylide formation) and imine (via nitrogen coordination) and initiate cyclization of substituted alkynes.[13e] Furthermore, $B(C_6F_5)_3$ can be tolerant of water and anilines/imines (at raised temperatures); thus the imine can be formed *in situ* (producing an equivalent of H_2O), which is necessary for the A^3 reaction.[19] However, because strong Brønsted acids also can catalyze the A^3 reaction, H_2O–$B(C_6F_5)_3$ is also a potential initiator, as it has a similar pK_a to HCl (in MeCN),[20] and this Brønsted acid has been used recently by Maron et al. to catalyze a number of conversions.[21] Herein we report the $B(C_6F_5)_3$-initiated A^3 reaction for the synthesis of substituted quinolines and our mechanistic investigations to identify the key initiator.

RESULTS AND DISCUSSION

Our investigation started by assessing the feasibility of $B(C_6F_5)_3$ to initiate the formation of quinolines, specifically, adding 1 equiv of *p*-tolylacetylene to *N*-benzylidene aniline (generated *in situ* from the condensation of 1 equiv of benzaldehyde and 1.2 equiv of aniline), in the presence of 20 mol % $B(C_6F_5)_3$, using 1,2-dichloroethane (DCE) as solvent (Table 1). The reaction was performed under ambient conditions, without any purification of starting materials, catalyst, or solvent. Upon heating at 80 °C for 24 h, full imine consumption was observed, but no propargylamine was detected. Instead, the two major products formed in a 1:1 ratio (by ^{1}H NMR spectroscopy) were 4-tolyl-2-phenylquinoline **1** and *N*-benzylaniline (entry 1). The use of other solvents (e.g., MeCN or toluene) under otherwise identical conditions led to lower conversions to **1**.

While quinoline **1** resulted from the desired three-component reaction, *N*-benzylaniline derives from the reduction of the parent imine, presumably via a transfer hydrogenation process where the imine acts as a hydrogen acceptor in the oxidation step to form the quinoline as previously observed.[22] This prompted us to increase the amount of both benzaldehyde and aniline (entries 2–4), which improved the quinoline yield significantly (63%, entry 3) up to a certain loading, beyond which no further improvement was observed. In previous work, raised temperatures proved essential for protonation of the inactive $[HOB(C_6F_5)_3]^-$ to enable a critical concentration of $B(C_6F_5)_3$ to form post H_2O dissociation;[19] therefore the reaction was performed at higher temperatures

Table 1. A^3 Reaction Initiated by $B(C_6F_5)_3$[a]



entry	PhCHO (equiv)	$PhNH_2$ (equiv)	$B(C_6F_5)_3$ (mol %)	temp (°C)[a]	yield **1** (%)[b]
1	1	1.2	20	80	33
2	2	2.2	20	80	52
3	3	3.2	20	80	63
4	5	5.2	20	80	63
5	3	3.2	20	90	70
6	3	3.2	20	100	73 (70)
7	3	3.2	20	110	69
8	3	3.2	20	120	66
9[c]	3	3.2	20	100	65
10[d]	3	3.2	20	100	72
11	3	3.2	10	100	65
12	3	3.2	0	100	<5

[a]Reactions run in sealed tubes under ambient atmosphere (1 equiv of alkyne used in each reaction). [b]Conversion relative to the alkyne and calculated by ^{1}H NMR spectroscopy versus cyclohexane as an internal standard (in parentheses = isolated yield). [c]Reaction in PhCl. [d]Reaction in *o*-dichlorobenzene.

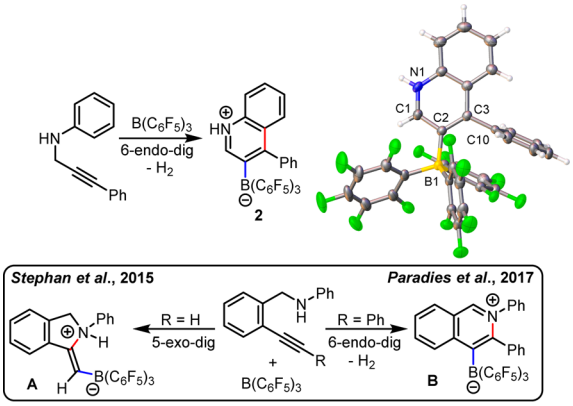
(entries 5–8). The reaction performed at 100 °C proved optimal, affording the desired quinoline **1** in 73% NMR yield and 70% isolated yield, a notable outcome for the three-component A^3 reaction (entry 6). The optimized conditions gave similar outcomes in other halogenated solvents such as chloro- or 1,2-dichlorobenzene (entries 9 and 10). Finally, reducing the $B(C_6F_5)_3$ loading to 10 mol % resulted in a slightly lower conversion, while in the absence of $B(C_6F_5)_3$ the reaction was unsuccessful (entries 11 and 12, respectively).

To assess the feasibility of a mechanism involving *N*-(3-phenylpropargyl)aniline formation and subsequent $B(C_6F_5)_3$-initiated cyclization/oxidation, *N*-(3-phenylpropargyl)aniline was combined with an equimolar amount of $B(C_6F_5)_3$ in wet DCE. On mixing, the initial boron species formed was $[HOB(C_6F_5)_3]^-$ (by ^{11}B and ^{19}F NMR spectroscopy) from deprotonation of H_2O–$B(C_6F_5)_3$ by the aniline as previously reported.[19] However, upon heating to 100 °C for 1 h, the zwitterion **2** was produced as the major product (Scheme 3). No significant quantity of reduction byproducts (e.g., di- or tetrahydroquinolines) was observed by ^{1}H NMR spectroscopy, consistent with the evolution of gas observed. This indicates that H_2 is produced as the major byproduct from oxidation to form **2**. The ^{11}B NMR spectrum of the zwitterion **2** showed a sharp peak at −14 ppm, while 15 inequivalent signals were observed in the ^{19}F NMR spectrum due to the hindered rotation in this 3,4-disubstituted quinoline.

The zwitterion **2** was isolated in 45% yield by crystallization from DCM/pentane. The solid-state structure (Scheme 3, right) confirmed the formulation as **2**, which contains all trigonal planar carbons and nitrogen in the quinoline motif. Steric crowding was indicated by the C3-phenyl ring being almost orthogonal to the quinoline moiety (dihedral angles ~85°) along with large C3–C2–B1 (126.8(2)°) and C2–C3–C10 (123.1(2)°) angles. The formation of **2** is notable, as in the absence of the phenyl alkyne substituent no cyclization was

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX–XXX

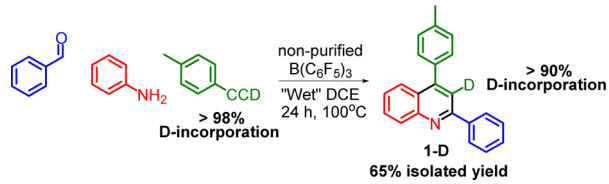
Scheme 3. *Elemento*-boration of *N*-(3-Phenylpropargyl)aniline with $B(C_6F_5)_3$: (Right) Solid-State Structure of 2, Thermal Ellipsoids at the 50% Probability Level (a Cocrystallized Molecule of DCM Is Omitted for Clarity); (Inset) Disparate Outcomes Reported by Stephan, Paradies, and Co-workers on the Cyclization of Terminal- and Phenyl-Substituted Alkynes



observed by Stephan and co-workers on reacting $B(C_6F_5)_3$ with *N*-propargylaniline.[15b] This highlights the essential stabilizing effect the phenyl provides to a vinyl cation-type intermediate. Furthermore, the formation of **2** indicates that the 6-endo-dig cyclization is favored over 5-exo-dig; in contrast many examples of the latter are reported for the cyclization of propargylamides[16] or for the inter- and intramolecular hydroamination of terminal alkynes with $B(C_6F_5)_3$.[15] Once again, the alkynyl phenyl group plays a key role in favoring the formation of the vinyl cation that leads to the 6-endo-dig cyclization over that leading to 5-exo-dig cyclization. An analogous observation has been recently reported by Paradies and colleagues in the cyclization/dehydrogenation of benzyl amino alkyne with stoichiometric $B(C_6F_5)_3$ (Scheme 3, inset).[15c]

Notably, prolonged heating did not result in subsequent conversion of **2** to free $B(C_6F_5)_3$ and quinoline. Furthermore, **2** proved stable to protodeboronation with exogenous acid (e.g., stable to $HNTf_2$ addition) or bases, even on prolonged heating (e.g., refluxing in neat AcOH). This indicates that the catalytic reaction to form **1** does not proceed via *N*-propargylaniline cyclization initiated by $B(C_6F_5)_3$. This was confirmed by the reaction of 0.2 equiv of unpurified $B(C_6F_5)_3$ in "wet" 1,2-dichloroethane with 1 equiv of *N*-(3-phenylpropargyl)aniline with heating at 100 °C for 1 h, leading to formation of **2** as a minor product, but even after prolonged heating (24 h) significant *N*-(3-phenylpropargyl)aniline remained unreacted. This latter reaction also indicates that an alternative mechanism involving *N*-(phenylpropargyl)aniline cyclization on activation by a Brønsted acid (e.g., $H_2O{-}B(C_6F_5)_3$) instead of $B(C_6F_5)_3$ also was not proceeding. To confirm this using the conditions/reagents that lead to **1**, labeling experiments using a deuterated alkyne were performed (Scheme 4). Using the optimized reaction conditions (entry 6), replacing *p*-tolylacetylene with 1-deuterium-*p*-tolylacetylene (>98% D-incorporation), a comparable yield of quinoline **1** was obtained. Importantly, the isolated quinoline showed >90% deuterium incorporation at position 3. This outcome is incompatible with the formation of *N*-(1,3-diphenylpropargyl)aniline as an intermediate, as cyclization of this species by a Brønsted acid will produce a low level of deuterium incorporation due to the large excess of H_2O

Scheme 4. Deuterium Labeling Experiment[a]

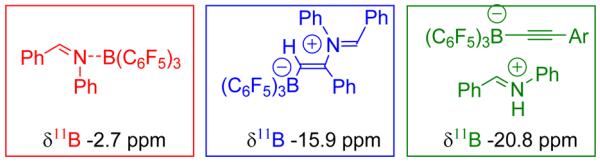


[a]Identical reaction conditions to Table 1, entry 6.

present in nonpurified DCE and derived from the imine formation. Therefore, based on these experiments a mechanism proceeding by acetylide transfer and an *N*-propargylaniline intermediate is disfavored.

An alternative possible mechanism is imine activation by an electrophile with the iminium species then reacting directly with the terminal alkyne. To probe this, the reaction between *N*-benzylidene aniline and *p*-tolylacetylene (3:1 equiv) was explored in the presence of purified $B(C_6F_5)_3$ (20 mol %) in dichloromethane (DCM) (at 60 °C) or in DCE (at 100 °C) under anhydrous conditions. In both cases upon heating for 24 h, quinoline **1** was a minor product, with the imine-borane adduct and the iminium alkynylborate salt observed *in situ* as major species (by ^{11}B and ^{19}F NMR spectroscopy). The reaction was repeated using an equimolar mixture of imine/alkyne/$B(C_6F_5)_3$ under anhydrous conditions. Upon mixing, $^{11}B/^{19}F$ NMR analysis revealed that the main species formed at room temperature were the imine-borane adduct (^{11}B NMR broad peak at −2.7 ppm), the iminium alkynylborate (^{11}B NMR at −20.8 ppm), and the 1,2-addition product (^{11}B NMR at −15.9 ppm, Scheme 5). After prolonged stirring (20 h at 25

Scheme 5. ^{11}B NMR δ of Imine-Borane Adduct (Red), the 1,2-Addition Product (Blue), and the Iminium Alkynylborate (Green), Obtained from an Equimolar Mixture of *N*-Benzylidene Aniline, *p*-Tolylacetylene, and $B(C_6F_5)_3$



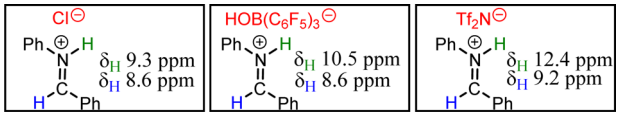
°C), the imine-borane adduct and the iminium alkynylborate were the two major boron species (by $^{11}B/^{19}F$ NMR spectroscopy), with 4-tolyl-2-phenylquinoline **1** and 4-tolyl-2-phenyl-1,2-dihydroquinoline observed as minor products by ^1H NMR and GC-MS analysis.

These results suggest the formation of the imine-borane Lewis adduct is not the dominant pathway leading to **1** due to the disparity observed in the degree of conversion to **1** performing the reaction with catalytic $B(C_6F_5)_3$ under "wet" conditions (as in the A^3 reaction) versus that under anhydrous conditions (isolated imine and alkyne with no Brønsted acid present). This prompted us to search for an alternative electrophile for imine activation. The $H_2O{-}B(C_6F_5)_3$ adduct has been previously utilized as a Brønsted acid catalyst,[21] and we envisaged that the principal imine activation pathway could be by protonation of the imine. To test this hypothesis, the optimized reaction (aldehyde/aniline:alkyne, 3:3.2:1) was repeated under "wet" conditions in DCE replacing $B(C_6F_5)_3$

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX−XXX

with 20 mol % HCl, a Brønsted acid with comparable pK_a to $H_2O{-}B(C_6F_5)_3$ (pK_a = 8.5 and 8.4, respectively, in MeCN).[20] However, upon heating this reaction mixture at 100 °C for 24 h, minimal quinoline **1** was formed using HCl as catalyst. While initially surprising we surmised that despite the similar pK_a values in MeCN, in DCE and with aniline/imine bases the degree of association between the protonated imine and chloride or $[HOB(C_6F_5)_3]^-$ counteranions would be significantly different. The degree of association between iminium cations and the anion has been previously documented to affect significantly the electrophilicity of the iminium cation.[23] This is supported by the observation that the *N*-H proton of *N*-benzylidene anilinium is shifted 1.2 ppm further downfield when the chloride counterion was replaced by $[HOB(C_6F_5)_3]^-$, indicating a weaker association between the iminium cation and $[HOB(C_6F_5)_3]$ anion (Scheme 6).

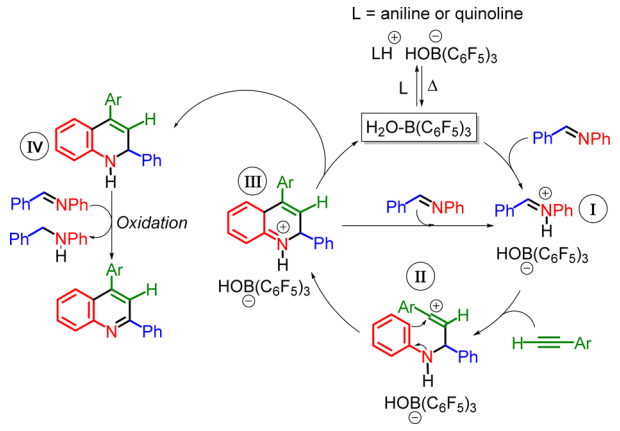
Scheme 6. ^{1}H NMR δ of *N*-Benzylidene Anilium Salts



Seeking a Brønsted acid that will lead to a more activated iminium cation (than the Cl congener), $HNTf_2$ was investigated, as it is reported to be almost a factor of 10^8 more Brønsted acidic than $H_2O{-}B(C_6F_5)_3$, albeit in MeCN (pK_a $HNTf_2$ = 0.3 in MeCN).[24] *N*-Benzylidene aniline was protonated with 1 equiv of $HNTf_2$ in DCE, which led to an *N*-H resonance shifted further downfield to 12.4 ppm. This chemical shift suggests a more electrophilic iminium cation is formed, and therefore the A^3 reaction was repeated using 20 mol % of $HNTf_2$. This led to the desired quinoline **1** being obtained in 75% NMR yield under identical conditions to that using $B(C_6F_5)_3$ (entry 6, Table 1), confirming that a Brønsted acid-initiated process is feasible provided a sufficiently weakly coordinating anion is utilized.[12d] Based on these observations feasible key processes occurring *in situ* in the tricomponent reaction are summarized in Scheme 7.

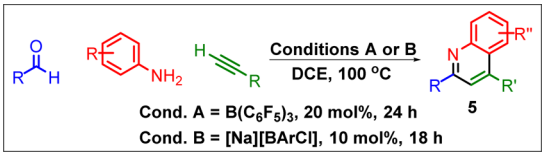
As reported in our previous work,[19] $H_2O{-}B(C_6F_5)_3$ is reversibly deprotonated by the weakly Brønsted basic anilines. At raised temperatures, enough $H_2O{-}B(C_6F_5)_3$ is available to protonate the imine (or the aniline is close enough in basicity to the imine for proton transfer to occur directly). $[HOB(C_6F_5)_3]^-$ is then a suitably weakly coordinating anion to allow the iminium cation (**I**) to be sufficiently electrophilic to undergo nucleophilic attack by the alkyne. The generated vinyl cation intermediate **II**, stabilized by the phenyl substituent, is then trapped by nucleophilic attack by the *ortho*-carbon of the aniline, yielding the dihydroquinolinium species **III**. The latter releases a proton (possibly by protonating the anion $[HOB(C_6F_5)_3]^-$ or directly protonating another molecule of imine) and forming **IV** (or tautomers thereof). Oxidation of the dehydroquinoline furnishes the final quinoline, with an equivalent of imine acting as a hydrogen acceptor. This transfer hydrogenation could be catalyzed by $B(C_6F_5)_3$, as reported in previous studies.[22]

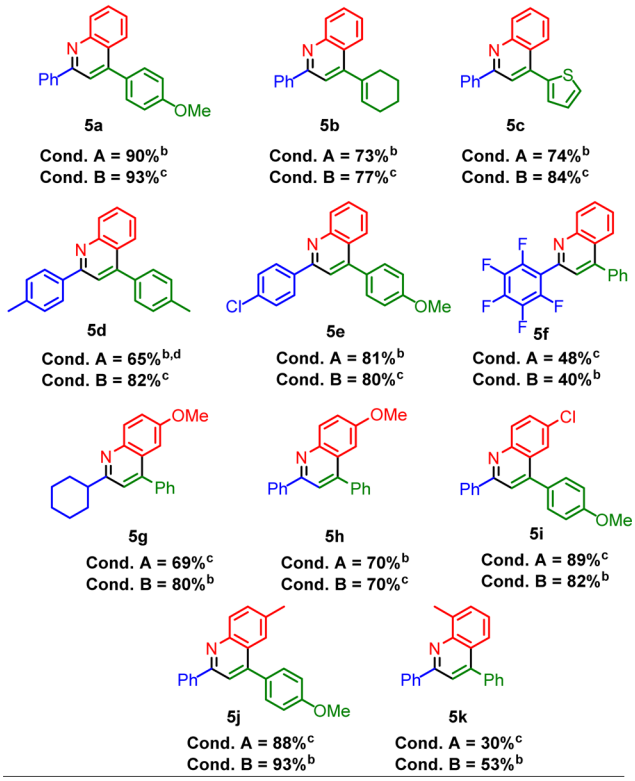
Scheme 7. Proposed A^3 Reaction Pathway Initiated by $H_2O{-}B(C_6F_5)_3$



Combining the mechanistic investigations allows the key requirements for the successful three-component reaction initiated by $B(C_6F_5)_3$ at raised temperatures in "wet" solvent to be defined as (i) sufficient excess *in situ* imine to act as hydrogen acceptor and (ii) a substituent adjacent to the C−C triple bond of the alkyne able to stabilize the vinyl cation intermediate. With the requirements for the A^3 reaction in hand, the scope of this process catalyzed by 20 mol % of nonpurified $B(C_6F_5)_3$ in "wet" DCE was explored (Table 2, condition A). The same substrate screening was also tested in

Table 2. A^3 Reaction Catalyzed by Triarylboranes[a]





[a]Reactions run in sealed tubes under ambient atmosphere (aldehyde/aniline/alkyne, 3:3.2:1). [b]Isolated yield. [c]^{1}H NMR yield using C_6H_{12} as standard. [d]48 h.

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX−XXX

the presence of catalytic $B(3,5\text{-}Cl_2\text{-}C_6H_3)_3$, synthesized *in situ* from the protodeboronation of sodium tetrakis(3,5-dichlorophenyl)borate (termed herein [Na][BArCl]), as previously reported (Table 2, conditions B).[25]

This scoping revealed that different functionalized alkynes were compatibile (**5a−c**), with *in situ* conversions and isolated yields generally good. Furthermore, the alkyne substituent is not limited to (hetero)aryl groups, as shown by **5b**. However, the importance of the cation stabilizing effect was highlighted when 1-octyne and *p*-trifluoromethylphenylacetylene were used as alkynes, with no desired quinolines observed in both cases. The formation of quinoline **5b** shows that the alkyne moiety reacts in preference to the vinyl moiety[26] and that the imine acts as hydrogen acceptor in preference over the C═C bond (benzylaniline was again observed as a byproduct). Functional groups on the benzaldehyde moiety were also tolerated (**5d−f**). The lower yield of quinoline **5f** derived from pentafluorobenzaldehyde could be due to the lower Brønsted basicity of the fluorinated imine, disfavoring protonation. Replacing benzaldehyde with cyclohexylcarboxyaldehyde was also possible, obtaining the desired quinoline **5g** in good yield. Finally, substitutions on the anilines component were also feasible (**5h−j**), although when 2-methylaniline was employed, lower yields were obtained (**5k**), possibly due to the increased steric bulk around the imine nitrogen increasing the barrier to nucleophilic attack by the alkyne.

In summary, $B(C_6F_5)_3$ is an effective initiator for the aldehyde−aniline−alkyne reaction at raised temperature to form quinolines. This is an operationally simple methodology where all the components are mixed at the start under ambient conditions and without the need for purification of solvent, borane, or reagents. Excess aldehyde and aniline has to be used since the imine acts as a hydrogen acceptor, facilitating the oxidation of the dihydroquinoline. Mechanistic insights revealed that the reaction does not proceed via alkyne activation by $B(C_6F_5)_3$. Instead imine protonation by $H_2O{-}B(C_6F_5)_3$ appears to be the main imine activation mode, although direct imine complexation to the borane may still be operative as a minor pathway. Finally, this study shows that the catalytic activity of $H_2O{-}B(C_6F_5)_3$ as a Brønsted acid has to be carefully assessed alongside that of $B(C_6F_5)_3$ when utilizing this borane in "wet" conditions; furthermore, despite their comparable pK_a values (in MeCN) the use of HCl as a test for Brønsted acid catalysis by $H_2O{-}B(C_6F_5)_3$ is not necessarily sufficient, as the different coordinating ability of Cl^- and $[HOB(C_6F_5)_3]^-$ can result in disparate outcomes in low-nucleophilicity media (e.g., dichloroethane).

EXPERIMENTAL SECTION

General Comments. Unless otherwise indicated, all manipulations were conducted under ambient conditions and all compounds and solvents were purchased from commercial sources and used as received. When required, commercial $B(C_6F_5)_3$ was dried by stirring a suspension in pentane with Et_3SiH (5 equiv for 1 equiv of borane) for 24 h at room temperature, followed by *in vacuo* solvent removal and subsequent sublimation. Solvents for column chromatography were of technical grade and used without further purification. Column chromatography was performed on silica gel (230−400 mesh). NMR spectra were recorded with a Bruker AV-400 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm relative to residual protio impurities and the deuterated solvent resonance, respectively, while ^2H, ^{11}B, and ^{19}F NMR spectra were referenced to external $Si(CD_3)_4$, $BF_3{\cdot}Et_2O$, and Cl_3CF, respectively. Coupling constants *J* are given in hertz (Hz). GC-MS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with a triple-axis detector. The column employed was an Agilent J&W HP-5 ms ((5%-phenyl)methylpolysiloxane) with the following dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 μm. Mass spectra were recorded on a Waters QTOF mass spectrometer. Purity was indicated by multinuclear NMR spectroscopy in organic solvents (in which the sample fully dissolved) and supported by MS or GC-MS analysis.

Synthesis of 2. A J. Young NMR tube equipped with a DMSO-d_6 capillary was loaded with *N*-(3-phenylpropargyl)aniline (16 mg, 0.076 mmol, 1.00 equiv) and commercial $B(C_6F_5)_3$ (39 mg, 0.076 mmol, 1.00 equiv) in 1,2-dichloroethane (0.5 mL). After heating at 100 °C for 1 h, the main product detected by multinuclear NMR spectroscopy was the zwitterion quinolinium borate **2** (slight effervescence was seen upon opening the J. Young tube). The homogeneous reaction mixture was dried under reduced pressure, washed with hexane, and dried, obtaining the product **2** as a pale yellow solid (24 mg, 0.034 mmol, 45%). ^1H NMR (CD_2Cl_2, 400 MHz, 298 K): δ 11.93 (brs, 1H, NH), 8.85 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.94 (t, J = 8.1 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.7 Hz, 1H), 6.80−7.80 (brm, 3H), 5.70−6.60 (brs, 1H) ppm. ^1H NMR (CD_2Cl_2, 400 MHz, 243 K): δ 13.10 (brs, 1H, NH), 8.78 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.38−7.46 (m, 1H), 7.28−7.38 (m, 2H), 7.19 (d, J = 8.5 Hz, 1H), 6.99−7.10 (m, 1H), 5.89 (d, J = 7.2 Hz, 1H) ppm. ^{11}B NMR (CD_2Cl_2, 128 MHz, 298 K): δ −14.0 ppm. ^{19}F NMR (CD_2Cl_2, 376 MHz, 298 K): δ −126.2 (d, J = 24.2 Hz, 1F*o*), −127.5 (brs, 1F*o*), −129.3 (brs, 1F*o*), −132.0 (brs, 1F*o*), −132.5 (d, J = 21.5 Hz, 2F*o*), −160.1 (t, J = 20.1 Hz, 1F*p*), −161.9 (m, 2F*p*), −163.7 (t, J = 18.4 Hz, 1F*m*), −164.9 (bs, 1F*m*), −166.7 (m, 3F*m*), −167.9 (brs, 1F*m*) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, 298 K): δ 167.6, 148.1, 136.5, 135.3, 134.3, 131.1, 129.6, 129.1, 128.9, 128.5, 128.2, 119.1 ppm (C−B and C−F carbons were clearly resolved). MS: *m*/*z* calcd for $C_{33}H_{11}BF_{15}N$ 717.1, found ES^- 716.2 $[M - H^+]^-$, found ES^+ 550.1 $[M - (C6F5)^-]^+$. Accurate mass for $[M - H^+]^-$ 716.0672, found 716.0688.

General Procedure for the A^3 Reaction Initiated by $B(C_6F_5)_3$ or [Na][BArCl]. A J. Young NMR tube equipped with a DMSO-d_6 capillary was loaded with unpurified $B(C_6F_5)_3$ (0.2 equiv) or [Na][BArCl] (0.1 equiv) in nonpurified 1,2-dichloroethane, followed by the addition of aldehyde (3.0 equiv), aniline (3.2 equiv), and alkyne (1.0 equiv). After monitoring the initial reaction mixture by multinuclear NMR spectroscopy, the J. Young NMR tube was heated at 80 °C for 24 h. After cooling to room temperature, the system was monitored again by multinuclear NMR spectroscopy. The reaction mixture was then concentrated under reduced pressure, and the crude analyzed by GC-MS analysis and purified by flash column chromatography on silica gel.

*4-(4-Methoxyphenyl)-2-phenylquinoline (**5a**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (14 mg, 0.027 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.401 mmol, 3.00 equiv), aniline (39 μL, 0.431 mmol, 3.20 equiv), and 4-ethynylanisole (18 μL, 0.135 mmol, 1.00 equiv). After heating at 100 °C for 24 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 4-(4-methoxyphenyl)-2-phenylquinoline as a pale brown solid (38 mg, 0.122 mmol, 90%). R_f = 0.15. The NMR data were in agreement with those reported in the literature.[27]

*4-(Cyclohex-1-en-1-yl)-2-phenylquinoline (**5b**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (14 mg, 0.027 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.401 mmol, 3.00 equiv), aniline (39 μL, 0.431 mmol, 3.20 equiv), and 1-ethynylcyclohexene (16 μL, 0.135 mmol, 1.00 equiv). After heating at 100 °C for 24 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 4-(cyclohex-1-en-1-yl)-2-phenylquinoline as a pale yellow oil (28 mg, 0.098 mmol, 73%). R_f = 0.25. The NMR data were in agreement with those reported in the literature.[27]

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX−XXX

*2-Phenyl-4-(thiophen-2-yl)quinoline (**5c**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (15 mg, 0.029 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (45 μL, 0.438 mmol, 3.00 equiv), aniline (43 μL, 0.468 mmol, 3.20 equiv), and 3-ethynylthiophene (15 μL, 0.146 mmol, 1.00 equiv). After heating at 100 °C for 24 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 2-phenyl-4-(thiophen-2-yl)quinoline as a pale yellow solid (31 mg, 0.108 mmol, 74%). R_f = 0.20. The NMR data were in agreement with those reported in the literature.[27]

*2,4-Ditolylquinoline (**5d**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (14 mg, 0.026 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of 4-methylbenzaldehyde (47 μL, 0.390 mmol, 3.00 equiv), aniline (38 μL, 0.416 mmol, 3.20 equiv), and 4-ethynyltoluene (17 μL, 0.130 mmol, 1.00 equiv). After heating at 100 °C for 48 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 2,4-ditolylquinoline as a pale brown solid (26 mg, 0.084 mmol, 65%). R_f = 0.20. The NMR data were in agreement with those reported in the literature.[28]

*2-(4-Chlorophenyl)-4-(4-methoxyphenyl)quinoline (**5e**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (13 mg, 0.024 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of 4-chlorobenzaldehyde (52 mg, 0.359 mmol, 3.00 equiv), aniline (35 μL, 0.383 mmol, 3.20 equiv), and 4-ethynylanisole (16 μL, 0.120 mmol, 1.00 equiv). After heating at 100 °C for 24 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 2-(4-chlorophenyl)-4-(4-methoxyphenyl)quinoline as a pale yellow solid (33 mg, 0.097 mmol, 81%). R_f = 0.15. The NMR data were in agreement with those reported in the literature.[29]

*2-(Perfluorophenyl)-4-phenylquinoline (**5f**).* Following the general procedure, a J. Young NMR tube was loaded with [Na][BArCl] (8 mg, 0.013 mmol, 0.10 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of 2,3,4,5,6-pentafluorobenzaldehyde (50 μL, 0.401 mmol, 3.00 equiv), aniline (39 μL, 0.428 mmol, 3.20 equiv), and phenylacetylene (15 μL, 0.134 mmol, 1.00 equiv). After heating at 100 °C for 18 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 2-(perfluorophenyl)-4-phenylquinoline as a white solid (20 mg, 0.054 mmol, 40%). R_f = 0.15. The NMR data were in agreement with those reported in the literature.[30]

*2-Cyclohexyl-6-methoxy-4-phenylquinoline (**5g**).* Following the general procedure, a J. Young NMR tube was loaded with [Na][BArCl] (8 mg, 0.013 mmol, 0.10 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of cyclohexane carboxyaldehyde (50 μL, 0.401 mmol, 3.00 equiv), *p*-methoxyaniline (53 mg, 0.428 mmol, 3.20 equiv), and phenylacetylene (15 μL, 0.134 mmol, 1.00 equiv). After heating at 100 °C for 18 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 80:20), obtaining 2-cyclohexyl-6-methoxy-4-phenylquinoline as a pale gray solid (34 mg, 0.107 mmol, 80%). R_f = 0.50. The NMR data were in agreement with those reported in the literature.[31]

*6-Methoxy-2,4-diphenylquinoline (**5h**).* Following the general procedure, a J. Young NMR tube was loaded with $B(C_6F_5)_3$ (14 mg, 0.027 mmol, 0.20 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.401 mmol, 3.00 equiv), *p*-methoxyaniline (53 mg, 0.428 mmol, 3.20 equiv), and phenylacetylene (15 μL, 0.134 mmol, 1.00 equiv). After heating at 100 °C for 24 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 6-methoxy-2,4-diphenylquinoline as a white solid (29 mg, 0.093 mmol, 70%). R_f = 0.20. The NMR data were in agreement with those reported in the literature.[27]

*6-Chloro-4-(4-methoxyphenyl)-2-phenylquinoline (**5i**).* Following the general procedure, a J. Young NMR tube was loaded with [Na][BArCl] (8 mg, 0.013 mmol, 0.10 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.401 mmol, 3.00 equiv), 4-chloroaniline (56 mg, 0.428 mmol, 3.20 equiv), and 4-ethynyltoluene (18 μL, 0.135 mmol, 1.00 equiv). After heating at 100 °C for 18 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 6-chloro-4-(4-methoxyphenyl)-2-phenylquinoline as a pale brown solid (38 mg, 0.110 mmol, 82%). R_f = 0.15. The data were in agreement with those reported in the literature.[32]

*4-(4-Methoxyphenyl)-6-methyl-2-phenylquinoline (**5j**).* Following the general procedure, a J. Young NMR tube was loaded with [Na][BArCl] (8 mg, 0.013 mmol, 0.10 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.404 mmol, 3.00 equiv), 4-methylaniline (47 mg, 0.431 mmol, 3.20 equiv), and 4-ethynylanisole (18 μL, 0.135 mmol, 1.00 equiv). After heating at 100 °C for 18 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 4-(4-methoxyphenyl)-6-methyl-2-phenylquinoline as a yellow solid (41 mg, 0.126 mmol, 93%). R_f = 0.10. The NMR data were in agreement with those reported in the literature.[33]

*8-Methyl-2,4-diphenylquinoline (**5k**).* Following the general procedure, a J. Young NMR tube was loaded with [Na][BArCl] (8 mg, 0.013 mmol, 0.10 equiv) in 1,2-dichloroethane (0.5 mL), followed by the addition of benzaldehyde (42 μL, 0.401 mmol, 3.00 equiv), 2-methylaniline (46 μL, 0.428 mmol, 3.20 equiv), and phenylacetylene (15 μL, 0.134 mmol, 1.00 equiv). After heating at 100 °C for 18 h, the reaction mixture was cooled to room temperature and then concentrated *in vacuo*. The crude was purified by flash chromatography (petr. ether/Et_2O, 95:5), obtaining 8-methyl-2,4-diphenylquinoline as a pale gray solid (21 mg, 0.071 mmol, 53%). R_f = 0.20. The NMR data were in agreement with those reported in the literature.[34]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00174.

Analytical data and crystallographic information (PDF)

Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: michael.ingleson@manchester.ac.uk.

ORCID

Michael J. Ingleson: 0000-0001-9975-8302

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was made possible by financial support from the EPSRC (EP/K03099X/1 and EP/M023346/1) and the Royal Society (for the award of a University Research Fellowship). Additional research data supporting this publication are available as Supporting Information accompanying this publication.

REFERENCES

(1) For uses of quinolines and derivatives see: (a) Michael, J. P. *Nat. Prod. Rep.* **2008**, *25*, 166−187. (b) Collin, G.; Höke, H. *Ullmann's encyclopedia of industrial chemistry* **2014**, *3*, 1145−1149 and references therein.

(2) Skraup, Z. H. *Ber. Dtsch. Chem. Ges.* **1880**, *13*, 2086−2089.

(3) Doebner, O.; Von Miller, W. *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 2812−2817.

(4) Combes, A. *Bull. Soc. Chim. Fr.* **1888**, *49*, 89.

(5) (a) Conrad, M.; Limpach, L. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 944. (b) Conrad, M.; Limpach, L. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 2990.

(6) Friedlander, P. *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 2572−2575.

(7) Pfitzinger, W. *J. Prakt. Chem.* **1886**, *33*, 100.

(8) D'Souza, D. M.; Müller, T. J. J. *Chem. Soc. Rev.* **2007**, *36*, 1095−1108.

(9) (a) Yoo, W.-J.; Zhao, L.; Li, C.-J. *Aldrichim. Acta* **2011**, *44*, 43−51. (b) Peshkov, V. A.; Pereshivkoa, O. P.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2012**, *41*, 3790−3807.

(10) Syeda, H. Z. S.; Halder, R.; Karla, S. S.; Das, J.; Iqbal, J. *Tetrahedron Lett.* **2002**, *43*, 6485−6488.

(11) For other examples of A^3 quinoline synthesis with metals see: (a) Meyet, C. E.; Larsen, C. H. *J. Org. Chem.* **2014**, *79*, 9835−9841. (b) Xiao, F.; Chen, Y.; Liu, Y.; Wang, J. *Tetrahedron* **2008**, *64*, 2755−2761. (c) Zhang, Y.; Li, P.; Wang, L. *J. Heterocyclic Chem.* **2011**, *48*, 153−157. (d) Cao, K.; Zhang, F.-M.; Tu, Y.-Q.; Zhuo, X.-T.; Fan, C.-A. *Chem. - Eur. J.* **2009**, *15*, 6332−6334. (e) Naidoo, S.; Jeena, V. *Heterocycles* **2016**, *92*, 1655−1664. (f) De Andrade, A.; Carvalho Dos Santos, G.; Da Silva-Filho, L. C. *J. Heterocyclic Chem.* **2015**, *52*, 273−277. (g) Tang, J.; Wang, L.; Mao, D.; Wang, W.; Zhang, L.; Wu, S.; Xie, Y. *Tetrahedron* **2011**, *67*, 8465−8469. (h) Sarode, P. B.; Bahekar, S. P.; Chandak, H. S. *Tetrahedron Lett.* **2016**, *57*, 5753−5756. (i) Zhang, X.; Liu, B.; Shu, X.; Gao, Y.; Lv, H.; Zhu, J. *J. Org. Chem.* **2012**, *77*, 501−510. (j) Kulkarni, A.; Török, B. *Green Chem.* **2010**, *12*, 875−878.

(12) For A^3 quinoline as Povarov reaction variant see: (a) Das, B.; Jangili, P.; Kashanna, J.; Kumar, R. A. *Synthesis* **2011**, *20*, 3267−3270. (b) Li, X.; Mao, Z.; Wang, Y.; Chen, W.; Lin, X. *Tetrahedron* **2011**, *67*, 3858−3862. (c) Majumdar, K. C.; Ponra, S.; Ghosh, D.; Taher, A. *Synlett* **2011**, *1*, 104−110. (d) Zhang, X.; Xu, X.; Yu, L.; Zhao, Q. *Asian J. Org. Chem.* **2014**, *3*, 281−284.

(13) For recent reviews on FLP chemistry see: (a) Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 10018−10032. (b) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 6400−6441. (c) Stephan, D. W. *Acc. Chem. Res.* **2015**, *48*, 306−316. (d) Oestreich, M.; Hermeke, J.; Mohr, J. *Chem. Soc. Rev.* **2015**, *44*, 2202−2220. (e) *Topics in Current Chemistry: Frustrated Lewis Pairs I, II*; Erker, G.; Stephan, D. W., Eds.; Springer-Verlag: Berlin, Heidelberg, 2013.

(14) For recent reviews on applications of $B(C_6F_5)_3$ in the synthesis of heterocyclic and aromatic compounds see: (a) Melen, R. L. *Chem. Commun.* **2014**, *50*, 1161−1174. (b) Lawson, J. R.; Melen, R. L. *Inorg. Chem.*, ASAP article, DOI:10.1021/acs.inorgchem.6b02911 and references therein.

(15) For examples of hydroamination with $B(C_6F_5)_3$ see: (a) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem. - Eur. J.* **2010**, *16*, 3005−3008. (b) Mahdi, T.; Stephan, D. W. *Chem. - Eur. J.* **2015**, *21*, 11134−11142. (c) Tussing, S.; Ohland, M.; Wicker, G.; Flörke, U.; Paradies, J. *Dalton Trans.* **2017**, *46*, 1539−1545.

(16) For examples of oxoboration with $B(C_6F_5)_3$ see: (a) Melen, R. L.; Hansmann, M. M.; Lough, A. J.; Hashmi, A. S. K.; Stephan, D. W. *Chem. - Eur. J.* **2013**, *19*, 11928−11938. (b) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. *Chem. Commun.* **2014**, *50*, 7243−7245.

(17) Tamke, S.; Qu, Z.-W.; Sitte, N. A.; Flörke, U.; Grimme, S.; Paradies, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 4336−4339.

(18) Dureen, M. A.; Brown, C. C.; Stephan, D. W. *Organometallics* **2010**, *29*, 6594−6607.

(19) For the tolerance of $B(C_6F_5)_3$ to H_2O and anilines see: (a) Fasano, V.; Radcliffe, J. E.; Ingleson, M. J. *ACS Catal.* **2016**, *6*, 1793−1798. (b) Tiddens, M. R.; Klein Gebbink, R. J. M.; Otte, M. *Org. Lett.* **2016**, *18*, 3714−3717.

(20) Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581−10590.

(21) (a) Dryzhakov, M.; Hellal, M.; Wolf, E.; Falk, F. C.; Moran, J. *J. Am. Chem. Soc.* **2015**, *137*, 9555−9558. (b) Dryzhakov, M.; Moran, J. *ACS Catal.* **2016**, *6*, 3670−3673.

(22) For transfer hydrogenation using $B(C_6F_5)_3$ see: Farrell, J. M.; Heiden, Z. M.; Stephan, D. W. *Organometallics* **2011**, *30*, 4497−4500. (b) Chatterjee, I.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 1965−1968. (c) Chatterjee, I.; Qu, Z.-W.; Grimme, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 12158−12162. (d) Maier, A. F. G.; Tussing, S.; Schneider, T.; Flörke, U.; Qu, Z.-Q.; Grimme, S.; Paradies, J. *Angew. Chem., Int. Ed.* **2016**, *55*, 12219−12223. (e) Kojima, M.; Kanai, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 12224−12227.

(23) For spectroscopic studies on the degree of protonation of Schiff bases see: De Bicca Alencastro, R.; Badilescu, S.; Lussier, L. S.; Sandorfy, C.; Le Thanh, H.; Vocelle, D. *Int. J. Quantum Chem.* **1990**, *38*, 173−179. For different reaction outcomes due to H-bonding of the anion see Kaib, P. S.; List, B. *Synlett* **2016**, *27*, 156−158.

(24) Kutt, A.; Rodima, T.; Saame, J.; Raamat, E.; Maemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391−395.

(25) For [Na][BArCl] decomposition see: (a) Fasano, V.; Radcliffe, J. E.; Curless, L. D.; Ingleson, M. J. *Chem. - Eur. J.* **2017**, *23*, 187−193. (b) Fasano, V.; Ingleson, M. J. *Chem. - Eur. J.* **2017**, *23*, 2217−2224.

(26) To test the reactivity of alkenes as nucleophiles, a mixture of benzaldehyde, aniline, and styrene (3:3.2:1) was combined in DCE with 20 mol % of unpurified $B(C_6F_5)_3$; upon heating at 100 °C for 24 h, only 50% of styrene had reacted and the desired 2,4-diphenylquinoline was isolated in 8% yield.

(27) Cao, K.; Zhang, F.-M.; Tu, Y.-Q.; Zhuo, X.-T.; Fan, C.-A. *Chem. - Eur. J.* **2009**, *15*, 6332−6334.

(28) Liu, P.; Li, Y.; Wang, H.; Wang, Z.; Hu, X. *Tetrahedron Lett.* **2012**, *53*, 6654−6656.

(29) Adeloye, A. O.; Mphahlele, M. J. *J. Chem. Res.* **2014**, *38*, 254−259.

(30) Fan, S.; Yang, J.; Zhang, X. *Org. Lett.* **2011**, *13*, 4374−4377.

(31) Meyet, C. E.; Larsen, C. H. *J. Org. Chem.* **2014**, *79*, 9835−9841.

(32) Fan, X.; Zhang, X.; Zhang, Y. *Heteroat. Chem.* **2005**, *16*, 637−643.

(33) Jing, L.; Fang, L.; Yingzu, Z.; Xingge, M.; Xiaodong, J. *Org. Lett.* **2015**, *17*, 1409−1412.

(34) Zhang, Y.; Li, P.; Wang, L. *Journal of Heterocyclic Chemistry* **2011**, *48*, 153−157.

DOI: 10.1021/acs.organomet.7b00174
Organometallics XXXX, XXX, XXX−XXX