CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc
Europe

DOI: 10.1002/chem.201301899

Cyclisation versus 1,1-Carboboration: Reactions of $B(C_6F_5)_3$ with Propargyl Amides

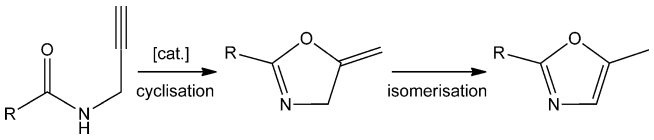
Rebecca L. Melen,[a] Max M. Hansmann,[a, b] Alan J. Lough,[a] A. Stephen K. Hashmi,[b] and Douglas W. Stephan*[a]

Abstract: A series of propargyl amides were prepared and their reactions with the Lewis acidic compound $B(C_6F_5)_3$ were investigated. These reactions were shown to afford novel heterocycles under mild conditions. The reaction of a variety of *N*-substituted propargyl amides with $B(C_6F_5)_3$ led to an intramolecular oxo-boration cyclisation reaction, which afforded the 5-alkylidene-4,5-dihydrooxazolium borate species. Secondary propargyl amides gave oxazoles in $B(C_6F_5)_3$ mediated (catalytic) cyclisation reactions. In the special case of disubstitution adjacent to the nitrogen atom, 1,1-carboboration is favoured as a result of the increased steric hindrance (1,3-allylic strain) in the 5-alkylidene-4,5-dihydrooxazolium borate species.

Keywords: 1,1-carboboration · alkynes · boron · cyclization · oxazoles · propargyl amides

Introduction

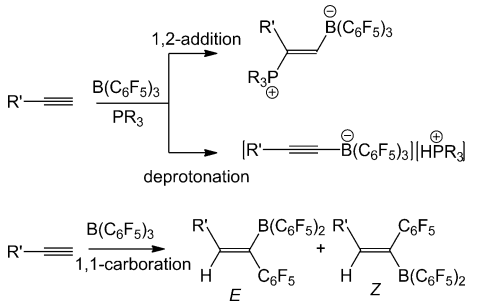
The cyclisation reactions of propargyl amides to the corresponding methylene-oxazolines and oxazoles (Scheme 1)



Scheme 1. Cyclisation of propargyl amides to oxazoles via methylene-oxazolines.

offer synthetic routes to heterocycles that occur in many natural products, drug and pharmaceutical molecules.[1] In particular these molecular fragments are found in anti-bacterials, herpes simplex virus type 1 (HSV-1) inhibitors, serine threonine phosphate inhibitors, antitumor agents and antifungal agents.[1c, 2] Additionally, oxazolines and oxazoles are important intermediates and reagents in organic synthesis, can be used as ligands[3] and act as protecting groups.[4] Such cyclisations are typically effected by transition-metal catalysts incorporating the coinage metals and platinum group elements, namely palladium,[5] silver[6] and gold.[7]

Boron-based reagents incorporating alkyl, vinyl and alkynyl boranes or borates are well established and important in a variety of organic transformations[8] including cross-coupling or transition-metal-catalysed addition reactions. More recently, the unveiling of frustrated Lewis pair (FLP)[9] reactivity has furthered the utility of B-reagents in stoichiometric and catalytic synthetic chemistry. Among the numerous small-molecule activation[10] reactions explored in FLP chemistry to date, the interaction of FLPs with alkynes[11] has been shown to proceed either to give 1,2-addition products or effect deprotonation of terminal alkynes affording salts of the form $[R_3PH][R{-}C{\equiv}C{-}B(C_6F_5)_3]$ (Scheme 2).[11] In general, more basic donors favoured the latter pathway, and thus use of amine donors in these FLP reactions with alkynes typically gave deprotonation except in the case of intramolecular ring closures.[12] In related chemistry, strongly electrophilic boron reagents have also been shown to react with alkynes on their own, yielding 1,1-carboboration product mixtures of *E* and *Z* isomers of vinyl boranes (Scheme 2).[13]



Scheme 2. Reactivity of FLPs and $B(C_6F_5)_3$ with terminal alkynes.

[a] Dr. R. L. Melen,[+] M. M. Hansmann,[+] Dr. A. J. Lough,[++] Prof. Dr. D. W. Stephan
Department of Chemistry, University of Toronto
80 St. George Street, Toronto, ON, M5S 3H6 (Canada)
E-mail: dstephan@chem.utoronto.ca

[b] M. M. Hansmann,[+] Prof. Dr. A. S. K. Hashmi
Organisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

[+] These authors equally contributed to this paper.

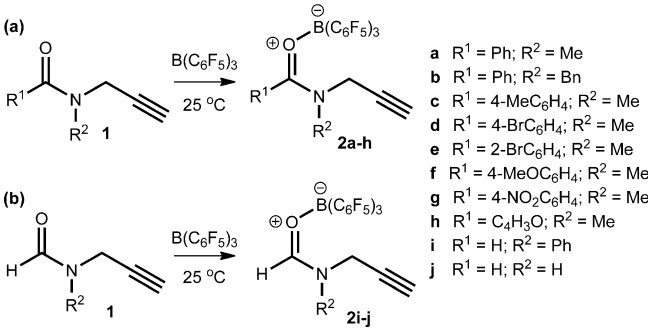
[++] Crystallographic investigation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301899.

The only metal-free method to induce cyclisations yielding oxazolines and oxazoles requires the use of harshly basic conditions.[1c, 2a,c,14] Given the reactivity of electrophilic boranes with alkynes, we were prompted to probe the reaction with propargyl amides. Herein, we describe $B(C_6F_5)_3$-promoted cyclisation reactions of propargyl amides under mild conditions, which afford a broad range of dihydrooxazolium borate species. Further work demonstrates the impact of steric effects, indicating that congestion can prompt catalysis or promote an alternative reaction pathway involving 1,1-carboboration.

Results and Discussion

N-Substituted propargyl amides are ideal starting materials to probe the reactivity of amide and alkyne functionalities with the Lewis acid $B(C_6F_5)_3$. These starting materials are also incapable of aromatisation to the corresponding oxazole and are readily accessible in high yields by the reaction of the corresponding propargyl amine with an acyl chloride in the presence of a base using known procedures.[7,16–22] Thus, the 1:1 reaction of $B(C_6F_5)_3$ with a series of *N*-substituted propargyl amides and formamides bearing a variety of functional groups on the benzene ring was monitored in situ by multinuclear NMR (^1H, ^{11}B and ^{19}F) spectroscopy (Scheme 3).



Scheme 3. Reaction of $B(C_6F_5)_3$ with various a) propargyl amides and b) propargyl formamides.

In all cases the first species detected was the expected adduct afforded by coordination of the Lewis basic amide to the Lewis acidic $B(C_6F_5)_3$. This boron–oxygen coordination was reflected in the ^{11}B NMR spectra by the presence of a broad peak around $\delta = 0$ ppm. In the case of the reaction of *N*-methyl-*N*-(prop-2-yn-1-yl)toluamide (**1c**) with $B(C_6F_5)_3$ in [D_8]toluene, colourless needle-shaped crystals of **2c** were obtained in 83% yield after 4 h at 45 °C. Similarly, the reaction of *N*-phenyl-*N*-(prop-2-yn-1-yl)formamide (**1i**) with $B(C_6F_5)_3$ afforded colourless crystals of the adduct **2i** after four days at 45 °C. In both of these cases, the structures of the products were confirmed by X-ray diffraction (Figure 1).

Subsequent heating of the 1:1 reaction mixtures of $B(C_6F_5)_3$ with *N*-substituted propargyl amides resulted in

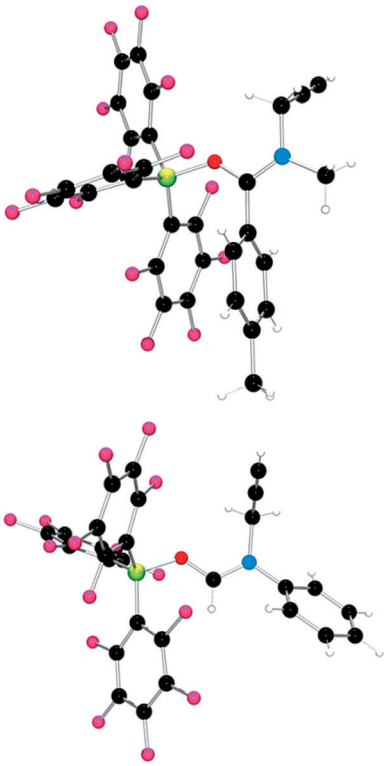


Figure 1. POV-ray depictions of the molecular structure of **2c** (top) and **2i** (bottom).

the emergence of a very sharp singlet at $\delta \approx -16$ ppm in the ^{11}B NMR spectrum and the disappearance of the peak at $\delta = 0$ ppm (Figure 2). This was attributed to the formation of a B–C bond, based on similar chemical shifts previously reported by Stephan and Erker et al.[12] The products formed in these reactions were found to be the 5-alkylidene-4,5-dihydrooxazolium borates **3a**–**h** (Scheme 4). These assignments were confirmed both spectroscopically and by X-ray crystallography (Figure 3). These products are formed by a 5-*exo*-oxo-boration cyclisation reaction (Scheme 4). In all cases these reactions showed exclusive Markovnikov and *Z*-selectivity. The formation of these products infers an equi-

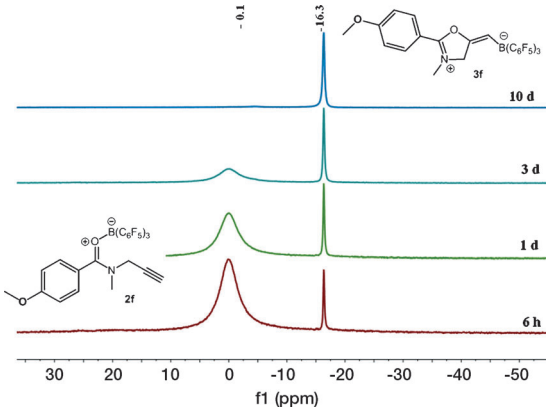
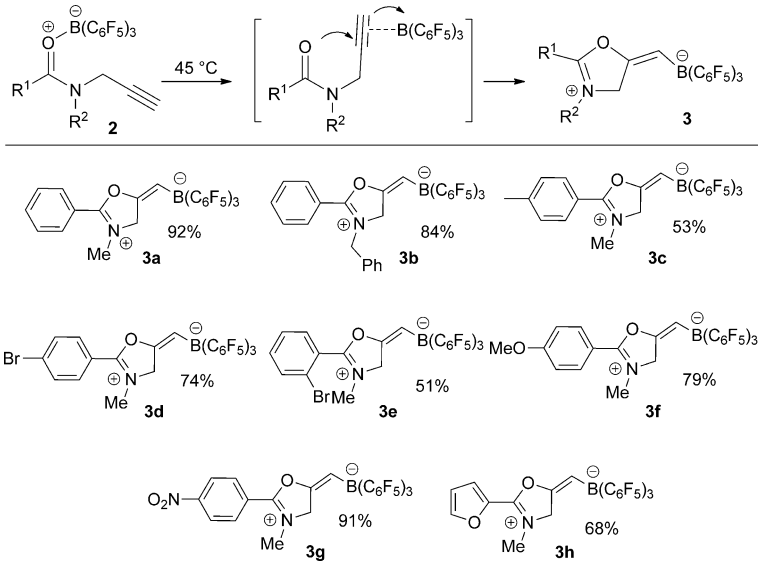


Figure 2. In situ ^{11}B NMR spectra at various time intervals of the reaction of **1f** with $B(C_6F_5)_3$ in [D_8]toluene at 45 °C.



Scheme 4. Cyclised products from the reactions of propargyl amides with $B(C_6F_5)_3$, isolated yields are indicated.

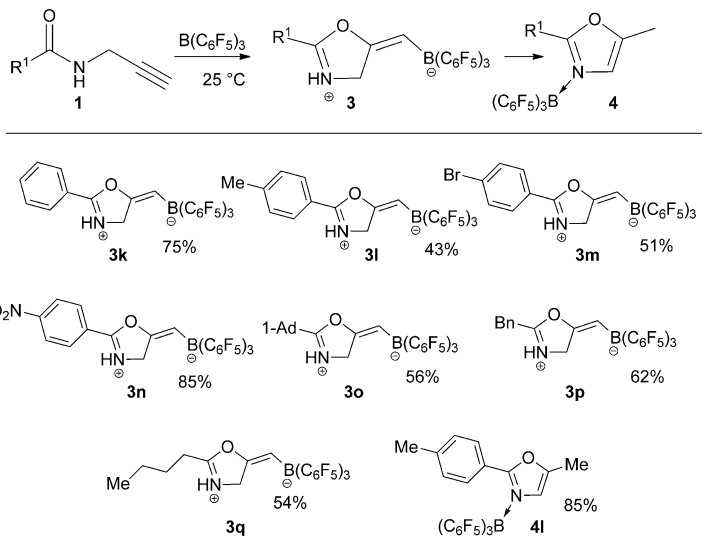
librium involving borane interaction with the alkyne followed by nucleophilic attack of the activated alkyne by the carbonyl–oxygen atom. The *Z*-configured products are consistent with this view, as a concerted oxo-boration cyclisation mechanism would be expected to give an *E*-configured olefinic fragment. In the case of **3b**, **3d**, **3e**, **3g** and **3h** single-crystal X-ray crystallography confirmed the nature of the zwitterionic dihydrooxazolium borate products (Figure 3). The metric parameters of the essentially planar dihydrooxazolium rings were very similar.

Although these reactions are relatively slow at room temperature, they were accelerated upon heating to 45 °C or by performing the reaction in polar solvents such as CD_2Cl_2 or [D_8]THF. Nonetheless, [D_8]toluene is the preferred solvent as the reactions proceeded more cleanly; use of polar solvents or temperatures above 45 °C resulted in minor by-products such as those arising from the 1,1-carboboration pathway suggested by ^{19}F NMR spectroscopy (vide infra).

The rate of these reactions appeared empirically to be dependent upon the nature of the substituent on the aromatic ring and followed the order *p*-NO_2 > *p*-H > *p*-OMe. This suggests that electron-withdrawing substituents (which decrease the basicity of the amide-oxygen atom), promote dissociation of the Lewis acid in the rate-determining step, allowing the Lewis acid to activate the alkyne thus affording cyclisation (Scheme 4). This view is further supported by the observation that attempts to effect the cyclisation of **2i** or **2j** proved unsuccessful, even upon heating to 45 °C for two days. The lack of reactivity of **2i** and **2j** is attributable to the stronger B–O bond, which disfavours dissociation. In addition, the generation of a cationic charge on the N=C–O moiety from cyclisation would also disfavour cyclisation. In the cases of **1a**–**h** the aromatic substituent at R^1 stabilises the benzylic cationic charge by conjugation.

Variation in the Lewis acid was also investigated. Reaction of **1c** with BPh_3, $(C_6F_5)_2BCl$, Mes_2BF, 9-BBNCl, HB-$(C_6F_5)_2$ as well as the isoelectronic heavier group 13 Lewis acid $Al(C_6F_5)_3$ were probed. In these cases, either no reaction occurred or the results proved inconclusive as a variety of products was obtained as evidenced by NMR spectroscopy.

The reactions of N–H-substituted propargyl amides with $B(C_6F_5)_3$ were also explored. These reactions initially afforded the 5-alkylidene-4,5-dihydrooxazolium borate species **3k**–**3q**, which were isolated (Scheme 5). The yields based on in situ NMR spectroscopy are all consistently high, but the isolated yields in some cases were lowered as a result



Scheme 5. Products from substrates with N-H substituted propargyl amides; isolated yields are indicated.

of incomplete crystallisation. In the case of **3o** and **3p**, these products were crystallographically characterised (Figure 4). In comparison to the cyclisation experiments with the *N*-substituted propargyl amides, the N–H compounds formed more rapidly and consequently could be prepared at room temperature. It is noteworthy that related derivatives can be prepared by using transition-metal catalysts.[5–7] In these cases, the N–H proton migrates to the vinyl fragment, affording oxazoles. In the case of gold catalysts, this has been shown to proceed by anti-oxyauration followed by proto-deauration to afford the 5-alkylidene-4,5-dihydrooxazole and subsequent isomerisation to produce the oxazole.[7] It is also interesting to highlight that in the case of the transition metals it is a challenging task to capture the corresponding vinyl-transition-metal compounds. For example,

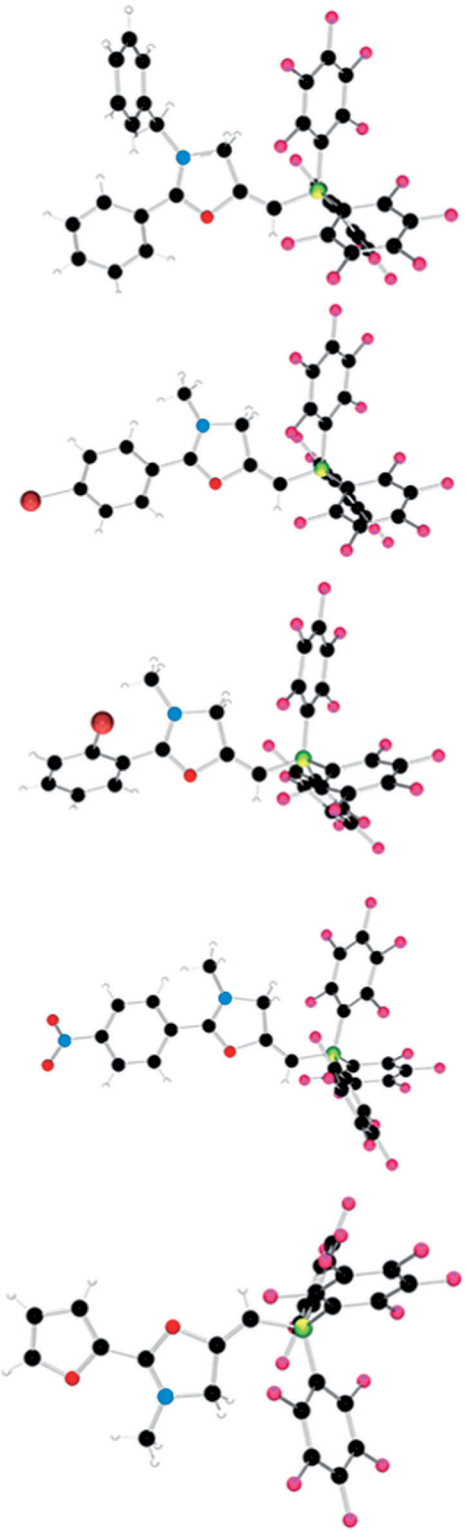


Figure 3. POV-ray depictions of the molecular structure of **3b**, **3d**, **3e**, **3g** and **3h** (from top to bottom).

fast protodeauration of the C–Au bond can only be suppressed by addition of an external sterically bulky base.[7e] In contrast, for the formation of the present species, the C–B bonds in the vinyl boron products **3** are much less

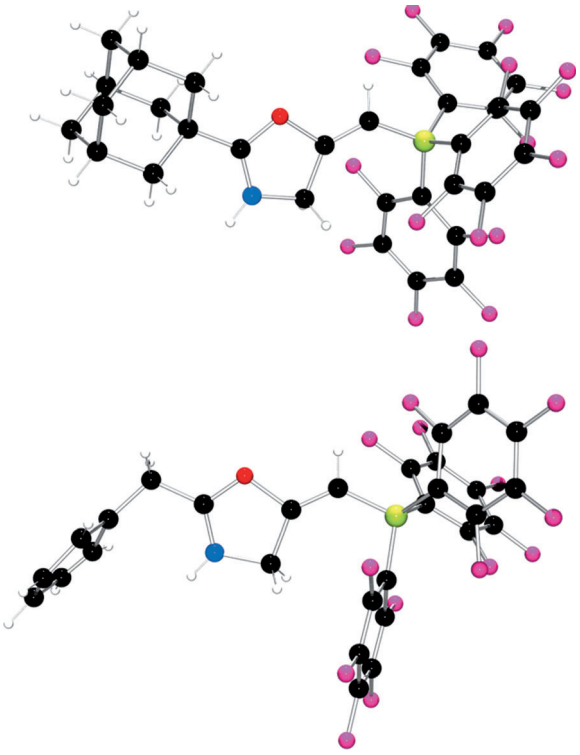


Figure 4. POV-ray depictions of the molecular structure of **3o** (top) and **3p** (bottom).

prone towards protonation and thus these may be of interest for use in organic synthesis.

The corresponding reaction of 4-methyl-*N*-(prop-2-yn-1-yl)benzamide **1l** with $B(C_6F_5)_3$ was followed by in situ ^1H, ^{11}B and ^{19}F NMR spectroscopy. At room temperature, the ^{11}B NMR data in [D_8]toluene initially showed a peak at $\delta = 0.6$ ppm after 6 h due to the Lewis acid/base adduct **2l**, which subsequently isomerised to give the cyclised product **3l**, as revealed by a new resonance at $\delta = -16.3$ ppm (ca. 60 % conversion). Performing the reaction at higher temperatures (45 °C) resulted in the formation of a new species (**4l**) (Scheme 5), which gave a signal at $\delta = -6.8$ ppm in the ^{11}B NMR spectrum. ^1H, ^{11}B and ^{19}F NMR spectroscopy suggested the formulation of **4l** as the borane adduct of the corresponding oxazole (Scheme 5). This assignment was confirmed by the independent synthesis of the oxazole **5l**[7] and the combination with $B(C_6F_5)_3$, which yielded the adduct with identical NMR spectral parameters to **4l**. Subsequently, the formulation of **4l** was further confirmed by an X-ray crystallographic study (Figure 5). In related reactions, heating the compounds **3k**, **3m** and **3n** to 60 °C in [D_8]THF, afforded the analogous borane adducts of the corresponding oxazoles **4k**, **4m** and **4n** in high yield, as observed by ^1H, ^{11}B and ^{19}F NMR spectroscopy.[15] This demonstrates that migration of the proton from nitrogen to effect protonation of the C–B bond prompts formation of the aromatic oxazole.

Efforts to exploit this chemistry for the catalytic synthesis of oxazoles were unsuccessful, inferring that the N→B

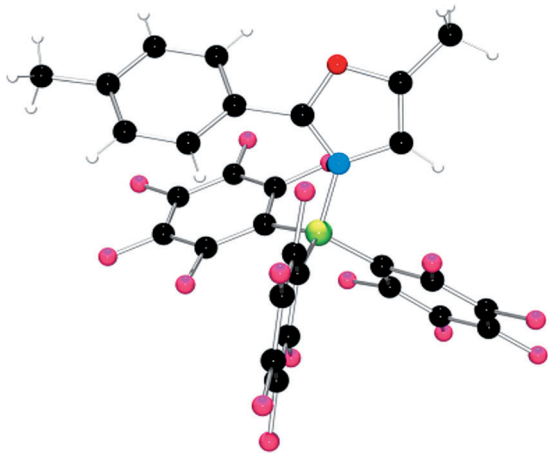


Figure 5. POV-ray depictions of the molecular structure of **4l**.

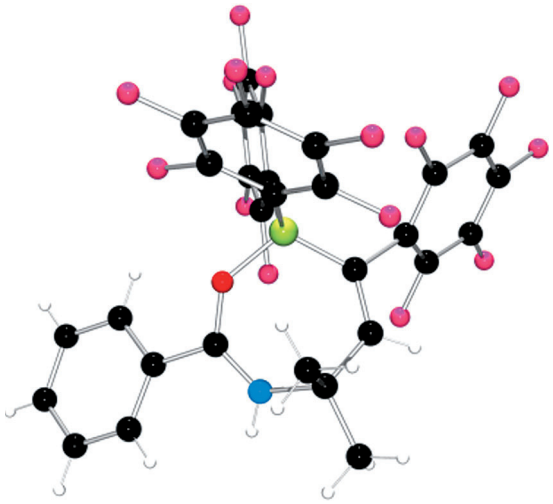
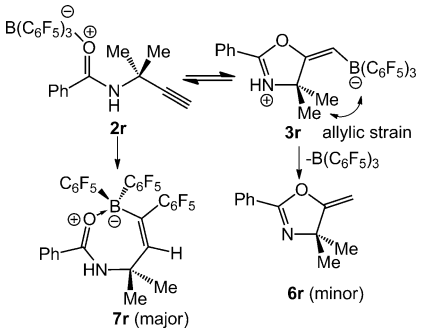


Figure 6. POV-ray depictions of the molecular structure of **7r**.

dative bond in the product is too strong to release $B(C_6F_5)_3$ precluding its role as a catalyst. To overcome this issue a derivative bearing a more bulky adamantyl substituent (**1o**) at R^1 was employed, as this should sterically frustrate the dative N→B bond in the borane–oxazole adduct. This proved to be a suitable strategy as **1o** is catalytically converted to the oxazole using 10 mol% $B(C_6F_5)_3$ in 83% yield after 10 days at 100 °C. While this is slow, this finding does demonstrate the concept that propargyl amides can be catalytically cyclised without the participation of a transition-metal catalyst.

It was further envisaged that the additional steric bulk of the propargyl amide **1r** would facilitate catalytic cyclisation. In this case the formation of the oxazole would not be possible but rather an alkylideneoxazoline (**6r**, Scheme 6) would



Scheme 6. Reactions pathways of **2r** affording **7r** and **6r**.

result. However, a new species (**7r**) is formed in high yield (Scheme 6). The nature of **7r** was confirmed unambiguously by X-ray crystallography to be the product of a 1,1-carboboration reaction (Figure 6), in which one of the B–C bonds of $B(C_6F_5)_3$ adds to the terminal carbon atom of the alkyne with concurrent migration of the terminal H to the β-carbon atom. Interestingly, this formation of **7r** is selective for the *Z*-product in which the amide-oxygen atom coordinates intramolecularly to the boron atom to give a seven-membered ring. This stands in stark contrast to previous studies where mixtures of *E* and *Z* isomers were observed even in the presence of intramolecular coordination.[13] Monitoring the reaction by NMR spectroscopy reveals the initial but transient formation of **3r**. However, this cyclisation is apparently reversible as this is consumed in the formation of the 1,1-carboboration product **7r**. This may result from increased steric hindrance from the *gem*-CMe_2 group and $B(C_6F_5)_3$ which lie *cis* to each other in the cyclised intermediate, leading to 1,3-allylic strain which disfavours the cyclisation event. Further evidence for the transient nature of **3r** is the observation of the minor byproduct, the alkylideneoxazoline **6r** by ^{1}H NMR spectroscopy (Scheme 6).

Conclusion

In conclusion, our study has demonstrated that Lewis acidic $B(C_6F_5)_3$ can promote the intramolecular cyclisations of a broad range of propargyl amides by an *anti* oxo-boration mechanism affording zwitterionic 5-alkylidene-4,5-dihydrooxazolium borate species. This reaction was shown to be highly *Z*-selective even in the presence of a variety of functional groups. Furthermore, reactions of the N–H propargyl amides also proceed via 5-alkylidene-4,5-dihydrooxazolium borate intermediates, undergoing rearrangement to form oxazoles in which $B(C_6F_5)_3$ is coordinated to the oxazole nitrogen atom. Bulky substituents such as an adamantyl group allow the reaction to become catalytic in $B(C_6F_5)_3$ due to the weakening of the dative N→B bond in the oxazole product. Disubstitution adjacent to the nitrogen atom of the propargyl amide prompts 1,1-carboboration as a result of 1,3-allylic strain in the cyclised product. The isolation of the vinyl boron derivatives in high yields suggests the possibility of further application in organic synthesis. It is this aspect that is the subject of on-going efforts.

Experimental Section

General considerations: With the exception of the synthesis of starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBRAUN) was used to manipulate solids including the storage starting materials, room temperature reactions, product recovery and sample preparation for analysis. Molecular sieves (4 Å) were dried at 120 °C for 24 h prior to use. All solvents (toluene, CH_2Cl_2, THF, pentane, hexane) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored over molecular sieves under a nitrogen atmosphere. Deuterated solvents were dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. *N*-Methyl-*N*-(prop-2-yn-1-yl)benzamide (**1a**),[7g] *N*-benzyl-*N*-(prop-2-yn-1-yl)benzamide (**1b**),[7g] 4-methoxy-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (**1f**),[16] *N*-methyl-*N*-(prop-2-yn-1-yl)furan-2-carboxamide (**1h**),[7f] *N*-phenyl-*N*-(prop-2-yn-1-yl)formamide (**1i**)[17] and 4-methyl-*N*-(prop-2-yn-1-yl)benzamide (**1l**)[7a] were prepared according to literature methods. *N*-(Prop-2-yn-1-yl)formamide (**1j**),[18] *N*-(prop-2-yn-1-yl)benzamide (**1k**),[7a] *N*-(prop-2-yn-1-yl)adamantane-1-carboxamide (**1o**)[7a] *N*-(2-*m*ethylbut-3-yn-2-yl)benzamide (**1r**),[5b, 19] 5-methyl-2-(*p*-tolyl)oxazole (**5l**)[20] 4-bromo-*N*-(prop-2-yn-1-yl)benzamide (**1m**),[21] 2-phenyl-*N*-(prop-2-yn-1-yl)acetamide (**1p**),[7f] *N*-(prop-2-yn-1-yl)pentanamide (**1r**)[22] and 4-nitro-*N*-(prop-2-yn-1-yl)benzamide (**3n**),[5d, 20] were synthesised previously. ^1H, ^{13}C ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance III, a Bruker Avance 500 or a Varian Mercury 400 spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $[D_8]$toluene, $[D_6]$benzene, $[D_8]$THF, $CDCl_3$ and CD_2Cl_2 as internal standards. NMR spectra were referenced to $CFCl_3$ (^{19}F) and $BF_3{\cdot}Et_2O/CDCl_3$ (^{11}B). All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). A Perkin–Elmer Analyser was used for carbon, hydrogen and nitrogen elemental analyses. High resolution mass spectrometry was performed in house employing DART or electrospray ionisation techniques in positive-ion mode. Mass spectral data were recorded on an AB/Sciex QStarXL mass spectrometer (ESI) or a JEOL AccuTOF model JMS-T1000 LC mass spectrometer (DART).

Synthesis of *N*-propargylcarboxamides: General procedure A: *N*-Propargylcarboxamides were prepared by a method similar to that previously reported for *N*-benzyl-*N*-(prop-2-yn-1-yl)benzamide. Triethylamine (1 equiv) and 4-dimethylaminopyridine (DMAP; 0.02 equiv) were added to a solution of propargyl amine (1.0 equiv) in CH_2Cl_2 (ca. 20 mL) and was stirred for 15 min. The solution was then cooled to 0 °C and the corresponding acyl chloride (1.0 equiv) was added dropwise. The resulting mixture was stirred at this temperature for 30 min and was allowed to warm to room temperature and was stirred for a further 3 h. After quenching the reaction with water, the aqueous layer was extracted with CH_2Cl_2 (2×). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and the solvent was removed under vacuum and the product purified by column chromatography or recrystallisation.

General procedure B: To a solution of amide (1.0 equiv) in THF was added NaH (1.2 equiv, 60% in mineral oil) at 0 °C. The solution was warmed up to room temperature, stirred for 1 h, cooled to 0 °C and propargyl bromide (1.2 equiv, 80% in toluene) added. The resulting mixture was stirred at this temperature for 30 min and was allowed to warm to room temperature and was stirred for a further 3 h. After quenching the reaction with brine, the aqueous layer was extracted with CH_2Cl_2 (2×). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and the solvent was removed under vacuum and the product purified by column chromatography or recrystallisation.

Synthesis of *N*-methyl-*N*-(prop-2-yn-1-yl)benzamide, 1a: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and benzoyl chloride (690 μL, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as a colourless oil (662 mg, 3.82 mmol, 76%) whose ^1H NMR spectra were comparable with those previously reported.[7g] $R_f = 0.43$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.53$–7.38 (m, 5H, Ph), 4.38 (s, br., 1H, CH_2 rotamer), 4.01 (s, br., 1H, CH_2 rotamer), 3.15 (s, br., 3H, CH_3 rotamer), 3.07 (s, br., 3H, CH_3 rotamer), 2.32 ppm (s, br., 1H, -C≡CH).

Synthesis of *N*-benzyl-*N*-(prop-2-yn-1-yl)benzamide, 1b: According to general procedure B, *N*-benzylbenzamide (1.0 g, 4.73 mmol), NaH (227 mg, 1.2 equiv, 60% in mineral oil), propargyl bromide (632 μL, 5.7 mmol, 1.2 equiv, 80% in toluene) were allowed to react in THF (30 mL). Column chromatography on SiO_2 (hexane/EtOAc, 9:1) afforded the product as a colourless oil (781 mg, 3.13 mmol, 66%) whose ^1H NMR spectra were comparable with those previously reported.[7g] $R_f = 0.49$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.64$–7.16 (m, 10H, Ar-H), 4.96 –4.60 (m, br., 2H CH_2 rotamer), 4.29 (s, br., 1H, CH_2 rotamer), 3.88 (s, br., 1H, CH_2 rotamer), 2.32 ppm (s, br., 1H, -C≡CH).

Synthesis of *N*-4-dimethyl-*N*-(prop-2-yn-1-yl)benzamide, 1c: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and *p*-toluoyl chloride (661 μL, 5.0 mmol) were allowed to reacted in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as an off-white solid (798 mg, 4.26 mmol, 85%). $R_f = 0.37$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.39$ (m, br., 2H, Ar-H), 7.21 (d, $^3J_{HH} = 7.8$ Hz, Ar-H), 4.41–3.94 (m, br., 2H, CH_2 rotamer), 3.10 (s, br., 3H, CH_3), 2.38 (s, 3H, CH_3), 2.30 ppm (s, br., 1H, -C≡CH); ^{13}C NMR (500 MHz $[D_8]$toluene, 298 K): $\delta = 170.8$ (s), 140.0 (s), 137.9 (s), 134.0 (s), 100.7 (s), 79.8 (s), 72.6 (s), 68.1 (s), 26.2 ppm (s); elemental analysis calcd (%) for $C_{12}H_{13}NO$: C 76.98, H 7.00, N 7.48; found: C 76.71, H 7.49, N 7.43; DART MS, *m/z*: 188.1 (calcd for $[M+H]^+$: 188.1).

Synthesis of 4-bromo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide, 1d: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and *p*-bromobenzoyl chloride (1.10 g, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as a white solid (840 mg, 3.33 mmol, 67%). $R_f = 0.26$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.56$ (m, 2H, Ar-H), 7.37 (s, br., Ar-H), 4.36 (s, br., 1H, CH_2 rotamer), 3.98 (s, br., 1H, CH_2 rotamer), 3.09 (s, br., CH_3), 2.32 ppm (s, br., 1H, -C≡CH); ^{13}C NMR (500 MHz, $[D_6]$benzene, 298 K): $\delta = 169.4$ (s), 135.1 (s), 131.7 (s), 129.3 (s), 124.2 (s), 78.9 (s), 72.6 ppm (s), the peaks due to the CH_2 and CH_3 groups could not be assigned presumably due to broadening of peaks due to rotation about the amide bond; elemental analysis calcd (%) for $C_{11}H_{10}NOBr$: C 52.41, H 4.00, N 5.57; found: C 52.29, H 3.84, N 5.50; DART MS, *m/z*: 252.0 (calcd for $[M+H]^+$: 252.0).

Synthesis of 2-bromo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide, 1e: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and 2-bromobenzoyl chloride (653 μL, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as an off-white solid (855 mg, 3.4 mmol, 68%). $R_f = 0.39$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $[D_8]$toluene, 298 K): $\delta = 7.59$–7.23 (m, 4H, Ar H), 4.42 and 3.89 (m, 2H, CH_2 rotamers), 3.20 and 2.92 (s, 3H, CH_3 rotamers), 2.28 ppm (m, 1H, -C≡CH); ^{13}C NMR (500 MHz $[D_8]$toluene, 298 K): $\delta = 167.8$ (s), 167.7 (s), 138.9 (s), 138.6 (s), 137.5 (s), 132.8 (s), 132.7 (s), 130.6 (s), 129.9 (s), 127.5 (s), 127.4 (s), 119.6 (s), 119.5 (s), 78.7 (s), 78.3 (s), 73.0 (s), 72.2 (s), 39.9 (s), 35.4(s), 34.4 (s), 31.5 ppm (s), two different rotamers; elemental analysis calcd (%) for $C_{11}H_{10}NOBr$: C 52.41, H 4.00, N 5.56; found: C 52.25, H 4.00, N 5.56; DART MS, *m/z*: 252.0 (calcd for $[M+H]^+$: 252.0).

Synthesis of 4-methoxy-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide, 1f: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and *p*-methoxybenzoyl chloride (677 μL, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as a colourless oil (724 mg, 3.56 mmol, 71%) whose ^1H NMR spectra were comparable with those previously reported.[16] $R_f = 0.30$ (hexane/EtOAc, 1:1); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 7.47$ (d, $^3J_{HH} = 8.4$ Hz, 2H, Ar-H), 6.91 (d, $^3J_{HH} = 8.4$ Hz, 2H, Ar-H), 4.20 (s,

br., 2H, CH_2), 3.83 (s, 3H, -OCH_3), 3.11 (s, 3H, CH_3), 2.31 ppm (s, 1H, -C≡CH).

Synthesis of *N*-methyl-4-nitro-*N*-(prop-2-yn-1-yl)benzamide, 1g: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and *p*-nitrobenzoyl chloride (928 mg, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as a slightly yellow solid (753 mg, 3.45 mmol, 69%). R_f=0.42 (hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.29 (d, $^3J_{HH}$=8.6 Hz, 2H, Ar-H), 7.67 (m, br., 2H, Ar-H), 4.40 (s, br., 1H, CH_2 rotamer), 3.94 (s, br., 1H, CH_2 rotamer), 3.19 and 3.13 (s, 3H, CH_3 rotamers), 2.40 and 2.31 ppm (s, 1H, -C≡CH rotamers); ^{13}C NMR (500 MHz, $CDCl_3$, 298 K): δ=169.0 (s), 148.6 (s), 141.7 (s), 128.3 (s), 128.1 (s), 77.9 (s, br.), 77.8 (s, br.), 73.9 (s), 72.9 (s), 41.5 (s), 36.6 (s), 33.1 ppm (s), extra peaks observed dure to different rotamers. Elemental analysis calcd (%) for $C_{11}H_{10}N_2O_3$: C 60.55, H 4.62, N 12.84; found: C 60.23, H 4.92, N 12.73; DART MS, *m*/*z*: 219.1 (calcd for $[M+H]^+$: 219.1).

Synthesis of *N*-methyl-*N*-(prop-2-yn-1-yl)furan-2-carboxamide, 1h: According to general procedure A, *N*-methylpropargyl amine (420 μL, 5.0 mmol), DMAP (12.2 mg), NEt_3 (690 μL, 5.0 mmol) and 2-furoyl chloride (493 μL, 5.0 mmol) were allowed to react in CH_2Cl_2 (15 mL). Column chromatography on SiO_2 (hexane/EtOAc, 8:1 to 3:2) afforded the product as a colourless liquid (575 mg, 3.5 mmol, 70%) whose ^{1}H NMR spectra were comparable with those previously reported.[7f] R_f=0.35 (hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=7.51 (m, 1H, furan H), 7.08 (d,1H, $^3J_{HH}$=3.5 Hz, furan H), 6.48 (dd, 1H, $^3J_{HH}$=3.5, 1.8 Hz, furan H), 4.36 (s, br., 2H, CH_2), 3.27 (s, br., 3H, CH_3), 2.28 ppm (s, 1H, -C≡CH).

Synthesis of *N*-phenyl-*N*-(prop-2-yn-1-yl)formamide, 1i: According to general procedure B, formanilide (969 mg, 8.0 mmol), NaH (640 mg, 2.0 equiv, 60% in mineral oil), propargyl bromide (980 μL, 8.8 mmol, 1.1 equiv, 80% in toluene) were allowed to react in THF (40 mL). Column chromatography on SiO_2 (hexane/EtOAc, 4:1) afforded the product as an orange oil (450 mg, 2.83 mmol, 35%) whose ^{1}H NMR spectra were comparable with those previously reported.[17] R_f=0.26 (hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.42 (s, 1H, aldehyde H), 7.44 (m, 2H, Ph-H), 7.35–7.29 (M, 3 h, Ph-H), 4.55 (d, 1H, $^4J_{HH}$=2.5 Hz, CH_2), 2.22 ppm (t, $^4J_{HH}$=2.5 Hz, -C≡CH).

Synthesis of 4-methyl-*N*-(prop-2-yn-1-yl)benzamide, 1l: According to general procedure A, propargyl amine (512 μL, 8.0 mmol), DMAP (12.2 mg), NEt_3 (1.10 mL, 8.0 mmol) and *p*-toluoyl chloride (1.06 mL, 8.0 mmol) were allowed to react in CH_2Cl_2 (25 mL). Recrystallisation from pentane/CH_2Cl_2 afforded the product as an off-white solid (980 mg, 5.66 mmol, 71%) whose ^{1}H NMR spectra were comparable with those previously reported.[7a] R_f=0.42 (hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=7.68 (d, $^3J_{HH}$=8.11 Hz, 2H, Ar-H), 7.24 ($^3J_{HH}$=8.1 Hz, 2H, Ar-H), 6.22 (m, br., 1H, NH), 4.25 (m, 2H, CH_2), 2.24 (s, 3H, CH_3), 2.28 ppm (t, $^4J_{HH}$=2.4 Hz, 1H, -C≡CH).

Synthesis of 2c: $B(C_6F_5)_3$ (51 mg, 0.1 mmol) was dissolved in [D_8]toluene (0.7 mL) and was added to the *N*,4-dimethyl-*N*-(prop-2-yn-1-yl)benzamide (19 mg, 0.1 mmol). The reaction mixture was left for 4 h at 45°C resulting in a blue solution and colourless crystals of the product (58 mg, 83%, 0.08 mmol). ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): δ=0.7 ppm (s, br.); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): δ=132.2 (s, br., 2F, *o*-F), 157.6 (m, 1F, *p*-F), 163.9 ppm (m, 2F, *m*-F).

Synthesis of 2i: $B(C_6F_5)_3$ (204 mg, 0.4 mmol) was dissolved in toluene (4 mL) and was added to *N*-phenyl-*N*-(prop-2-yn-1-yl)formamide (64 mg, 0.4 mmol). The reaction mixture was heated to 45°C for four days resulting in a red solution. Removal of the solvent in vacuo afforded an oil which was recrystallised from a hexane/THF solution to give the pure product as colourless crystals (131 mg, 0.20 mmol, 49%). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ=8.03 (s, 1H, aldehyde H), 7.58–7.53 (m, 3H, Ph-H), 7.39–7.34 (m, 2H, Ph-H), 4.81 (d, $^4J_{HH}$=2.5 Hz, CH_2), 0.86 ppm (s, br., 1H, -C≡CH); ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): δ=1.5 ppm (s); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ=1.4 ppm (s); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): δ=−134.6 (dd, 2F, J_{FF}=23.7, 8.7 Hz, *o*-F), −156.0 (t, 1F, J_{FF}=20.6 Hz, *p*-F), −163.5 ppm (m, 2F, *m*-F); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ=−134.7 (dd, 2F, J_{FF}=23.5, 8.3 Hz, *o*-F), −157.4 (t, 1F, J_{FF}=20.4 Hz, *p*-F), −164.3 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ=166.0 (s), 148.7 (m), 140.9 (m), 137.9 (m), 137.9 (s), 131.4 (s), 131.1 (s), 125.6 (s), 76.0 (s), 74.5 (s), 40.1 ppm (s); elemental analysis calcd (%) for $C_{28}H_9NOBF_{10}$: C 50.12; H 1.35; N 2.09; found: C 50.12, H 1.32; N 2.13; DART MS, *m*/*z*: 160.1 (calcd for $[M-B(C_6F_5)_3]^+$: 160.1), no peak assignable to the molecular ion was observed.

Synthesis of 3a: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (ca. 2 mL) and was added to *N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (69 mg, 0.4 mmol). The reaction mixture was heated to 45°C for four days without stirring giving a brown/blue solution and a large crop of small colourless crystals. The remaining solvent was decanted off to afford colourless crystals of the product which were washed with pentane (3×3 mL) and dried in vacuo to give pure **3a** (251 mg, 0.37 mmol, 92%). ^{1}H NMR (400 MHz, [D_8]THF, 298 K): δ=7.89 (m, 2H, *o*-H), 7.83 (tt, $^3J_{HH}$=7.6 Hz, $^4J_{HH}$=1.2 Hz, 1H, *p*-H), 7.69 (t, br., $^3J_{HH}$=7.8 Hz, 2H, *m*-H), 6.64 (s, br., 1H, C=CH), 4.36 (d, $^4J_{HH}$=2.6 Hz, 2H, CH_2), 3.52 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, [D_8]THF, 298 K): δ=−16.8 ppm (s); ^{19}F NMR (377 MHz, [D_8]THF, 298 K): δ=−132.9 (d, 2F, $^3J_{FF}$=22.1 Hz, *o*-F), −163.7 (t, 1F, J_{FF}=20.2 Hz, *p*-F), −167.3 ppm (m, br., 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF, 298 K): δ=170.5 (s), 149.4 (m, $^3J_{CF}$= 243.9 Hz), 143.5 (m, br.), 139.5 (m, $^3J_{CF}$=248.0 Hz), 137.7 (m, $^3J_{CF}$= 248.5 Hz), 136.6 (s), 131.3 (s), 130.4 (s), 121.5 (s), 55.1 (s), 36.5 ppm (s), the carbon atoms bonded to boron could not be observed above the baseline; DART MS, *m*/*z*: 786.1 (calcd for $[M+H]+$: 786.1), 174.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 174.1); elemental analysis calcd (%) for $C_{29}H_{11}NOBF_{15}$: C 50.83, H 1.62, 2.04; found: C 50.86, H 1.67, N 2.25.

Synthesis of 3b: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to *N*-benzyl-*N*-(prop-2-yn-1-yl)benzamide (100 mg, 0.4 mmol). The reaction mixture was heated to 45°C for four days without stirring. The solution was allowed to cool to 25°C and the solvent removed in vacuo to give an orange oil. The oil was recrystallised from the cooling of a hot hexane/CH_2Cl_2 solution (CH_2Cl_2 was added dropwise to a mixture of the crude product in hexane (ca. 1 mL) until all precipitates were dissolved) to afford colourless crystals of the product (257 mg, 84%, 0.34 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ= 7.82–7.78 (m, 3H, Ar-H), 7.63 (m, 2H, Ar-H), 4.45–7.37 (m, 3H, Ar-H), 7.05 (d, 2H, $^3J_{HH}$=7.8 Hz, Ar-H), 6.49 (s, br., C=C-H), 4.87 (s, 2H, CH_2), 3.93 ppm (d, 2H, $^4J_{HH}$=2.7 Hz); ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): δ=−16.4 ppm (s); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ= −17.0 ppm (s); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): δ=132.2 (d, 2F, J_{FF}=20.5 Hz, *o*-F), 160.7 (t, 1F, J_{FF}=20.6 Hz, *p*-F), 165.1 ppm (m, 2F, *m*-F); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ=133.2 (d, 2F, J_{FF}=22.7 Hz, *o*-F), 161.9 (t, 1F, J_{FF}=20.4 Hz, *p*-F), 166.1 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ=170.9 (s), 148.7 (m, $^1J_{CF}$=243 Hz), 142.1 (m), 139.0 (m, $^1J_{CF}$=246 Hz), 137.2 (m, $^1J_{CF}$=250 Hz), 137.1 (s), 130.8 (s), 130.7 (s), 130.4 (s), 130.4 (s), 130.2 (s), 128.4 (s), 119.8 (s), 51.3 (s), 53.6 ppm (s), the carbon atoms bonded to boron could not be observed above the baseline; DART MS, *m*/*z*: 762.1 (calcd for $[M+H]+$: 762.1), 250.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 250.1); elemental analysis calcd (%) for $C_{35}H_{15}NOBF_{15}$: C 55.22, H 1.99, 1.84; found: C 55.94, H 2.36, N 2.03.

Synthesis of 3c: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to *N*-4-dimethyl-*N*-(prop-2-yn-1-yl)benzamide (75 mg, 0.4 mmol). The reaction mixture was heated to 45°C for four days without stirring to give a deep blue solution. Cooling of the solution resulted in precipitation of the product as colourless needles. Addition of pentane (5 mL) to the suspension followed by removal of the liquid phase by pipette and subsequent drying in vacuo afforded the crude product, which was washed with pentane (2×3 mL) and dried under vacuum to give the pure product as a light grey solid (150 mg, 53%, 0.21 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ=7.73 (d, $^3J_{HH}$= 8.1 Hz, 2H, Ar-H), 7.49 (d, $^3J_{HH}$=8.1 Hz, 2H, Ar-H), 6.53 (s, br., 1H, C= CH), 4.34 (s, br., 2H, CH_2), 3.48 (s, 3H, CH_3), 2.51 ppm (s, 3H, CH_3); in situ ^{11}B NMR (128 MHz, [D_8]toluene, 298 K):δ= −16.4 ppm (s); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ=−16.8 ppm (s); in situ ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): δ=−132.1 (d, 2F, J_{FF}=21.4 Hz, *o*-F), −161.1 (t, 1F, J_{FF}=20.5 Hz, *p*-F), −165.3 ppm (m, 2F, *m*-F); ^{19}F NMR

(377 MHz, CD_2Cl_2, 298 K): $\delta = -133.1$ (d, 2F, $J_{FF} = 22.1$ Hz, *o*-F), −162.1 (m, 1F, *p*-F), −166.2 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 170.5$ (s), 149.4 (s), 148.8 (m, $^1J_{CF} = 240.1$ Hz), 141.7 (s, br.), 139.1 (m, $^1J_{CF} = 246.4$ Hz), 137.0 (m, $^1J_{CF} = 247.1$ Hz), 131.2 (s), 130.6 (s), 121.6 (q, br., $^1J_{CB} = 52.9$ Hz), 116.7 (s), 54.7 (s), 37.0 (s), 22.3 ppm (s), the carbon atoms bonded to boron in $B(C_6F_5)$ could not be observed above the baseline; elemental analysis calcd (%) for $C_{30}H_{13}NOBF_{15}$: C 51.53, H 1.87, N 2.00; found: C 52.59, H 2.96, N 2.25; DART MS, *m/z*: 700.1 (calcd for $[M+H]^+$: 700.1), 188.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 188.1).

Synthesis of 3d: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to *N*-benzyl-*N*-(prop-2-yn-1-yl)benzamide (69 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for four days without stirring giving a pale orange solution and a small amount of crystals. Cooling the solution to −35 °C afforded a large quantity of crystals. The solution was decanted off and the crystals washed with pentane (3× 2 mL) and the resulting colourless crystals were dried in vacuo to yield the pure product (227 mg, 74%, 0.30 mmol). ^1H NMR (400 MHz, $[D_8]$THF, 298 K): $\delta = 7.90$ (s, 4H, Ar-H), 6.44 (s, br., 1H, C=CH), 4.36 (d, $^4J_{HH} = 2.5$ Hz, CH_2), 3.51 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, $[D_8]$toluene, 298 K): $\delta = -16.4$ ppm (s); ^{11}B NMR (128 MHz, $[D_8]$THF, 298 K): $\delta = -16.7$ ppm (s); ^{19}F NMR (377 MHz, $[D_8]$THF, 298 K): $\delta = -132.8$ (d, 2F, $J_{FF} = 22.1$ Hz, *o*-F), −163.6 (t, 1F, $J_{FF} = 20.1$ Hz, *p*-F), −167.2 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]$THF, 298 K): $\delta = 170.0$ (s), 149.4 (m, $^1J_{CF} = 238$ Hz), 143.4 (s), 149.4 (m, $^1J_{CF} = 246$ Hz), 137.5 (m, $^1J_{CF} = 252$ Hz), 133.9 (s), 132.9 (s), 131.8 (s), 120.5 (s), 55.5 (s), 36.5 ppm (s), the carbon atoms bonded to boron could not be observed above the baseline; elemental analysis calcd (%) for $C_{29}H_{10}NOBF_{15}Br$: C 45.59, H 1.32, N 1.83; found: C 45.53, H 1.46, N 1.80; DART MS, *m/z*: 764.0 (calcd for $[M+H]+$: 764.0), 252.0 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 252.0).

Synthesis of 3e: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to 2-bromo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (100 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for four days without stirring to give a pale purple solution. Removal of the solvent to generate a saturated solution followed by layering with hexane afforded small colourless crystals of the product. The remaining solution was decanted off and the resulting solid washed with hexane (3×3 mL) and dried in vacuo to give the pure product (157 mg, 0.21 mmol, 51%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.86$–7.84 (m, 1H, Ar-H), 7.69–7.57 (m, 3H, Ar-H), 6.60 (s, br., 1H, -C=CH), 4.37 (d, $^4J_{HH} = 2.3$ Hz, 2H, CH_2), 3.26 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, $[D_8]$toluene, 298 K): $\delta = -16.4$ ppm (s); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): $\delta = -16.9$ (s); ^{19}F NMR (377 MHz, $[D_8]$toluene, 298 K): $\delta = -132.3$ (d, 2F, $J_{FF} = 21.8$ Hz, *o*-F), −160.8 (t, $^3J_{FF} = 20.9$ Hz, 1F, *p*-F), −165.1 ppm (m, br., 2F, *m*-F); ^{19}F NMR (377 MHz, $[D_8]$toluene, 298 K): $\delta = -133.1$ (d, 2F, $J_{FF} = 22.4$ Hz, *o*-F), −161.9 (t, $^3J_{FF} = 20.6$ Hz, 1F, *p*-F), −166.0 ppm (m, br., 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 171.4$ (s), 148.8 (m, $^1J_{CF} = 238$ Hz), 142.4 (m), 139.2 (m, $^1J_{CF} = 248$ Hz), 137.3 (m, $^1J_{CF} = 248$ Hz), 136.6 (s), 135.0 (s), 131.1 (s), 129.2 (s), 123.3 (q, $^1J_{BC}$ ca. 51 Hz), 122.0 (s), 121.8 (s), 36.6 ppm (s), the carbon atom bonded to boron in the C_6F_5 groups could not be observed; elemental analysis calcd (%) for $C_{29}H_{10}NOBF_{15}Br$: C 45.59, H 1.32, N 1.83; found: C 45.52, H 1.49, N 1.89; DART MS, *m/z*: 764.0 (calcd for $[M+H]^+$: 764.0), 252.0 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 252.0).

Synthesis of 3f: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (2 mL) and was added to 4-methoxy-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (81 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for four days without stirring giving a blue/purple solution. Layering of pentane (5 mL) on top of the solution afforded very small colourless crystals of the product. The remaining solution was decanted off and the solid washed with pentane (3×3 mL) and dried in vacuo to give the pure product (241 mg, 79%, 0.32 mmol).^1H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.84$ (d, $^3J_{HH} = 9.0$ Hz, 2H, Ar-H), 7.14 (d, $^3J_{HH} = 9.0$ Hz, 2H, Ar-H), 6.50 (s, br., 1H, -C=CH), 4.29 (d, br., $^4J_{HH} = 2.4$ Hz, 2H, CH_2), 3.94 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 0.3 equivalents of residual toluene solvent was also observed at 7.24 (m), 7.16 (m) and 2.34 ppm (s) ppm; ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): −16.9 ppm (s); ^{11}B NMR (128 MHz, $[D_8]$toluene, 298 K): $\delta = -16.3$ ppm (s); ^{19}F NMR (377 MHz, $[D_8]$toluene, 298 K): $\delta = -132.1$ (d, 2F, $J_{FF} = 21.5$ Hz, *o*-F), −161.1 (t, 1F, $J_{FF} = 20.6$ Hz, *p*-F), −165.3 (m, 2F, *m*-F); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -133.2$ (d, 2F, $J_{FF} = 22.2$ Hz, *o*-F), −162.1 (t, 1F, $J_{FF} = 20.3$ Hz, *p*-F), −166.2 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 169.5$ (s), 166.9 (s), 148.9 (m, $^1J_{CF} = 242$ Hz), 139.1 (m, $^1J_{CF} = 248$ Hz), 138.6 (s, toluene), 137.3 (m, $^1J_{CF} = 248$ Hz), 133.4 (s), 129.5 (s, toluene), 128.7 (s, toluene), 125.8 (s, toluene), 116.1 (s), 111.1 (s), 56.7 (s), 54.8 (s), 21.5 ppm (s, toluene), the signals due to the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{30}H_{13}NO_2BF_{15}\cdot 0.33$ toluene: C 52.06, H 2.12, N 1.88; found: C 52.56, H 2.38, N 2.71; DART MS, *m/z*: 716.1 (calcd for $[M+H]^+$: 716.1), 204.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 204.1).

Synthesis of 3g: $B(C_6F_5)_3$ (204 mg, 0.1 mmol) was dissolved in toluene (3 mL) and was added to the *N*-methyl-4-nitro-*N*-(prop-2-yn-1-yl)benzamide (87 mg, 0.4 mmol). The reaction mixture was left for two days at 45 °C resulting in a yellow solution and colourless crystals of the product. The solution was decanted off and the crystals washed with pentane (3× 2 mL) and the product dried in vacuo to afford the product as a pale yellow crystalline solid (266 mg, 91%, 0.36 mmol). ^1H NMR (400 MHz, $[D_8]$THF, 298 K): $\delta = 8.51$ (d, $^3J_{HH} = 9.0$ Hz, 2H, Ar-H), 8.22 (d, $^3J_{HH} = 9.0$ Hz, 2H, Ar-H), 6.48 (s, br., 1H, -C=CH), 4.43 (s, br., 2H, CH_2), 3.54 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, $[D_8]$THF, 298 K): $\delta = -16.9$ ppm (s); ^{19}F NMR (377 MHz, $[D_8]$THF, 298 K): $\delta = -133.0$ (t, $^3J_{FF} = 21.6$ Hz, 2F, *o*-F), −163.6 (t, $^3J_{FF} = 20.2$ Hz, 1F, *p*-F), −167.2 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]$THF, 298 K): $\delta = 169.5$ (s), 152.9 (s), 149.4 (m, $^1J_{CF} = 241$ Hz), 139.6 (m, $^1J_{CF} = 245$ Hz), 137.7 (m, $^1J_{CF} = 250$ Hz), 132.8 (s), 126.8 (s), 125.2 (s), 55.2 (s), 36.5 ppm (s), the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{29}H_{10}N_2O_3BF_{15}$: C 47.70, H 1.38, N 3.84; found: C 47.66, H 1.51, N 3.83; DART MS, *m/z*: 731.1 (calcd for $[M+H]^+$: 731.1), 219.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 219.1).

Synthesis of 3h: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to the *N*-methyl-*N*-(prop-2-yn-1-yl)furan-2-carboxamide (65 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for four days without stirring. The solution was allowed to cool to 25 °C causing the product to crash out of solution. The solid was redissolved by the addition of THF (ca. 0.5 mL). Slow evaporation of the solvent afforded colourless crystals of the product (184 mg, 68%, 0.27 mmol); ^1H NMR (400 MHz, $[D_8]$THF, 298 K): $\delta = 8.22$ (dd, $J = 1.7$ Hz, 0.78 Hz, 1H, furan H), 7.88 (dd, $J = 3.9$ Hz, 0.78 Hz, 1H, furan H), 6.94 (dd, $J = 3.9$ Hz, 1.71 Hz, 1H, furan H), 6.37 (s, br., alkene H), 4.26 (m, br., 2H, CH_2), 3.62 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, $[D_8]$toluene, 298 K): $\delta = -16.4$ ppm (s); ^{19}F NMR (377 MHz, $[D_8]$toluene, 298 K): $\delta = -132.1$ (d, 2F, $J_{FF} = 21.6$ Hz, *o*-F), −161.1 (t, 1F, $J_{FF} = 20.8$ Hz, *p*-F), −165.3 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]$THF, 298 K): $\delta = 159.1$ (s), 153.2 (s), 149.4 (m, $^1J_{CF} = 240$ Hz), 143.7 (m), 139.7 (m, $^1J_{CF} = 246$ Hz), 138.4 (s), 137.7 (m, $^1J_{CF} = 245$ Hz), 127.2 (s), 115.0 (s), 54.4 (s), 35.2 ppm (s), the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{30}H_{15}NPBF_{10}\cdot C_7H_8$: C 53.22, H 2.23, N 1.83; found: C 53.04, H 2.23, N 1.83; DART MS, *m/z*: 676.1 (calcd for $[M+H]^+$: 676.1), 164.1 (calcd for $[M-B(C_6F_5)_3]^+$: 164.1).

Synthesis of 3k: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (6 mL) and was added to *N*-(prop-2-yn-1-yl)benzamide **1k** (64 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for six days without stirring giving a yellow solution. Slow evaporation of the solent afforded small colourless crystals of **3k** which were washed with pentane (3× 3 mL) and dried in vacuo to afford the pure product (202 mg, 75%, 0.30 mmol). ^1H NMR (400 MHz, $[D_8]$THF, 298 K): $\delta = 11.72$ (s, br., 1H, NH), 8.04 (d, $^3J_{HH} = 7.5$ Hz, 2H, *o*-H), 7.87 (t, $^3J_{HH} = 7.5$ Hz, 1H, *p*-H), 7.68 (t, $^3J_{HH} = 7.5$ Hz, 2H, *m*-H), 7.20–7.06 (m, toluene), 6.51 (s, 1H, -C=CH), 4.24 (s, 2H, CH_2), 2.30 ppm (s, toluene); ^{11}B NMR (128 MHz, $[D_8]$THF, 298 K): $\delta = -16.7$ ppm (s); ^{19}F NMR (377 MHz, $[D_8]$THF, 298 K): $\delta = -132.8$ (d, 2F, $J_{FF} = 21.5$ Hz, *o*-F), −163.7 (t, 1F, $J_{FF} = 20.1$ Hz, *p*-F), −167.3 ppm (m, 2F, *m*-F); $^{13}C\{^1H\}$ NMR (100 MHz, $[D_8]$THF, 298 K): $\delta = 172.1$(s), 149.4 (m, $^1J_{CF} = 241$ Hz), 146.0 (m), 139.7 (m, $^1J_{CF} = 241$ Hz), 137.8 (s, toluene), 137.5 (m, $^1J_{CF} = 245$ Hz), 130.7 (s), 130.5 (s), 129.8 (s, toluene), 129.1 (s, toluene), 126.2 (s, toluene), 121.6 (s), 47.1 (s), 21.7 ppm (s, toluene), the signals due to the carbon atoms bonded to

boron could not be observed; elemental analysis calcd (%) for $C_{28}H_9NOBF_{15}$·0.5 toluene: C 52.75, H 1.83, N 1.95; found: C 53.14, H 2.00, N 1.95; ESI(+) MS, *m/z*: 671.1 (calcd for $[M]^+$: 671.1).

Synthesis of 3l, (method a): $B(C_6F_5)_3$ (51 mg, 0.1 mmol) was dissolved in [D_8]toluene (0.7 mL) and was added to 4-methyl-*N*-(prop-2-yn-1-yl)benzamide (17 mg, 0.1 mmol). The reaction mixture was left at room temperature for seven days without stirring to give a pale yellow solution resulting in the cyclised product in 45% yield by NMR spectroscopy. ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): $\delta = -16.4$ ppm (s); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): $\delta = -131.2$ (d, 2F, $J_{FF} = 22.7$ Hz, *o*-F), −161.3 (t, $^3J_{FF} = 20.8$ Hz, 1F, *p*-F), −165.3 ppm (m, br., 2F, *m*-F).

Synthesis of 3l, (method b): $B(C_6F_5)_3$ (200 mg, 0.4 mmol) was dissolved in toluene (4 mL) and was added to 4-methyl-*N*-(prop-2-yn-1-yl)benzamide (68 mg, 0.4 mmol). The reaction mixture was left at room temperature for seven days without stirring to give a pale yellow solution. Evaporation of the toluene solvent afforded small colourless crystals of the product. The remaining solvent was removed and the product washed with pentane (2×3 mL) and dried in vacuo to yield the pure product as a white solid (117 mg, 43%, 0.17 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): $\delta = 8.09$ (s, br.), 7.85 (d, $^3J_{HH} = 8.3$ Hz, 2H, Ar-H), 7.50 (d, $J = 8.3$ Hz, 2H, Ar-H), 6.65 (s, br., C=CH), 4.29 (s, br., 2H, CH_2), 2.53 (s, 3H, CH_3), ca. 0.5 equiv toluene was observed at 7.25 (m) and 7.16 ppm (m); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): −16.9 ppm (s); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -133.1$ (d, 2F, $J_{FF} = 22.0$ Hz, *o*-F), −162.0 (t, 1F, $J_{FF} = 20.1$ Hz, *p*-F), −166.1 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 171.8$ (s), 151.7 (s), 148.8 (m, $^1J_{CF} = 235$ Hz), 144.4 (m), 139.0 (m, $^1J_{CF} = 246$ Hz), 138.6 (s, tol), 137.3 (m, $^1J_{CF} = 246$ Hz), 131.7 (s), 130.1 (s), 129.5 (s, tol), 128.7 (s, tol), 125.8 (s, tol), 116.0 (s), 46.3 (s, br.), 22.7 (s), 21.7 ppm (s, tol), B-bound carbon atoms were not be observed; elemental analysis calcd (%) for $C_{29}H_{11}NOBF_{15}$·0.5 toluene: C 53.38, H 2.07, N 1.92; found: C 53.58, H 2.26, N 1.93; DART MS, *m/z*: 686.1 (calcd for $[M+H]^+$: 686.1), 174.1 (calcd for $[M-B(C_6F_5)_3]^+$: 174.1).

Synthesis of 4l, (method a): $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to 4-methyl-*N*-(prop-2-yn-1-yl)benzamide (69 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for four days without stirring. Slow evaporation of the toluene solvent afforded colourless crystals of the product (163 mg, 0.24 mmol, 60%). ^{1}H NMR (400 MHz, [D_8]toluene, 298 K): $\delta = 7.08$ (d, $^3J_{HH} = 8.1$ Hz, 2H, *o*-H), 6.83 (s, br., 1H, C-H oxazole), 6.56 (d, $^3J_{HH} = 8.1$ Hz, 2H, *m*-H), 1.86 (s, 3H, CH_3), 1.54 (s, 3H, CH_3); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): 7.30 (d, $^3J_{HH} = 8.3$ Hz, 2H, *o*-H), 7.13 (d, $^3J_{HH} = 8.1$ Hz, 2H, *m*-H), 7.10 (s, br., 1H, C-H oxazole), 2.48 (d, $^4J_{HH} = 1.0$ Hz, 3H, CH_3), 2.35 ppm (s, 3H, CH_3); ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): $\delta = -6.7$ ppm (s, br.); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): $\delta = -7.1$ ppm (s); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): $\delta = -129.5$ (s, br., 1F, *o*-F), −131.6 (s, br., 1F, *o*-F), −132.8 (s, br., 4F, *o*-F), −155.3 (t, $^3J_{FF} = 19.5$ Hz, 1F, *p*-F), −156.9 (t, $^3J_{FF} = 20.9$ Hz, 2F, *p*-F), −162.1 (t, br., $^3J_{FF} = 19.7$ Hz, 1F, *m*-F),-163.3 (t, br., $^3J_{FF} = 20.3$ Hz, 1F, *m*-F), −164.4 ppm (t, br., $^3J_{FF} = 20.9$ Hz, 4F, *m*-F) (the C_6F_5 groups are not equivalent); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): $\delta = -129.2$ (m, 1F, *o*-F), −132.7 (m, 1F, *o*-F), −133.2 (s, br., 4F, *o*-F), −157.1 (t, $^3J_{FF} = 19.3$ Hz, 1F, *p*-F), −158.1 (t, $^3J_{FF} = 20.3$ Hz, 2F, *p*-F), −163.5 (m, br., 1F, *m*-F),-163.9 (m, br., 1F, *m*-F), −165.3 ppm (m, 4F, *m*-F) (the C_6F_5 groups are not equivalent); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): $\delta = 164.1$ (s), 150.8 (s), 148.7 (m), 144.6 (s), 140.7 (m), 137.4 (m), 129.5 (s), 129.4 (s), 123.0 (s, br.), 121.0 (s), 21.7 (s), 11.4 ppm (s), the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{29}H_{11}NOBF_{15}$·0.5 toluene: C 52.99, H 2.08, N 1.93; found: C 52.83, H 2.35, N 1.90; DART MS, *m/z*: 174.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 174.1).

Synthesis of 4l, (method b): $B(C_6F_5)_3$ (51 mg, 0.1 mmol) was dissolved in toluene (2 mL) and was added to 5-methyl-2-(*p*-tolyl)oxazole (17 mg, 0.1 mmol). The reaction mixture was left for 1 h without stirring. Slow evaporation of the toluene solvent afforded colourless crystals of the product (51 mg, 0.07 mmol, 74%). ^{1}H NMR (400 MHz, [D_8]toluene, 298 K): $\delta = 7.08$ (d, $^3J_{HH} = 8.4$ Hz, 2H, *o*-H), 6.80 (m, br., 1H, C-H oxazole), 6.54 (d, $^3J_{HH} = 8.4$ Hz, 2H, *m*-H), 1.85 (s, 3H, CH_3), 1.51 ppm (s, br., 3H, CH_3); ^{19}F NMR (377 MHz, [D_8]toluene, 298 K): $\delta = -129.6$ (s, br., 1F, *o*-F), −131.6 (s, br., 1F, *o*-F), −132.8 (s, br., 4F, *o*-F), −155.1 (t, $^3J_{FF} = 19.5$ Hz, 1F, *p*-F), −156.8 (t, $^3J_{FF} = 20.9$ Hz, 2F, *p*-F), −162.0 (t, br., $^3J_{FF} = 19.7$ Hz, 1F, *m*-F),-163.2 (t, br., $^3J_{FF} = 20.3$ Hz, 1F, *m*-F), −164.4 ppm (t, br., $^3J_{FF} = 20.9$ Hz, 4F, *m*-F) (the C_6F_5 groups are not equivalent); ^{11}B NMR (128 MHz, [D_8]toluene, 298 K): $\delta = -6.8$ ppm (s, br.).

Synthesis of 3m: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (8 mL) and was added to 4-bromo-*N*-(prop-2-yn-1-yl)benzamide (95 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for six days without stirring giving a pale yellow solution. Evaporation of the solvent afforded small colourless needles of the product. Removal of the remaining solvent by pipette followed by washing with pentane (3×3 mL) and drying in vacuo afforded the pure product (154 mg, 51%, 0.21 mmol). ^{1}H NMR (400 MHz, [D_8]THF, 298 K): $\delta = 11.76$ (s, br., 1H, NH), 7.96–7.90 (m, 4H, Ar-H), 6.51 (s, 1H, -C=CH), 4.27 ppm (s, 2H, CH_2), residual toluene solvent was also observed; ^{11}B NMR (128 MHz, [D_8]THF, 298 K): $\delta = -16.7$ ppm (s); ^{19}F NMR (377 MHz, [D_8]THF, 298 K): $\delta = -132.8$ (d, 2F, $J_{FF} = 21.4$ Hz, *o*-F), −163.6 (t, 1F, $J_{FF} = 20.2$ Hz, *p*-F), −167.2 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF, 298 K): $\delta = 171.6$ (s), 149.3 (m, $^1J_{CF} = 241$ Hz), 146.0 (m), 139.5 (m, $^1J_{CF} = 245$ Hz), 138.6 (s, toluene), 137.8 (m, $^1J_{CF} = 243$ Hz), 134.2 (s), 133.1 (s), 131.9 (s), 129.8 (s, toluene), 129.1 (s, toluene), 126.2 (s, toluene), 120.7 (s), 47.3 (s), 21.6 ppm (s, toluene), the signals due to the carbon atoms bonded to boron could not be observed; Elemental analysis calcd (%) for $C_{28}H_8NOBF_{15}Br$·toluene: C 49.91, H 1.91, N 1.66; found: C 49.36, H 2.20, N 1.66; ESI+ MS, *m/z*: 749.0, 751.0 (calcd for $[M]^+$: 749.0, 751.0), 512.0 (calcd for $[(B(C_6F_5)_3)+H]^+$: 512.0).

Synthesis of 3n: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (8 mL) and was added to 4-nitro-*N*-(prop-2-yn-1-yl)benzamide (82 mg, 0.4 mmol) immediately giving a yellow solution and precipitate. The reaction mixture was heated to 45 °C for one day without stirring. Removal of the solvent by pipette followed by washing the remaining solid with pentane (3×3 mL) and drying in vacuo afforded the pure product (242 mg, 85%, 0.34 mmol). ^{1}H NMR (400 MHz, [D_8]THF, 298 K): $\delta = 8.52$ (d, $^3J_{HH} = 9.0$ Hz, 2H, *m*-H), 8.28 (d, $^3J_{HH} = 9.0$ Hz, 2H, *o*-H), 6.56 (s, 1H, -C=CH), 4.34 (s, 2H, CH_2), 2.31 ppm (s, 3H, CH_3), residual toluene solvent was also observed; ^{11}B NMR (128 MHz, [D_8]THF, 298 K): $\delta = -16.7$ ppm (s); ^{19}F NMR (377 MHz, [D_8]THF, 298 K): $\delta = -132.9$ (d, 2F, $J_{FF} = 21.5$ Hz, *o*-F), −163.5 (t, 1F, $J_{FF} = 20.2$ Hz, *p*-F), −167.2 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF, 298 K): $\delta = 171.1$ (s), 153.3 (s), 149.4 (m, $^1J_{CF} = 237$ Hz), 146.6 (m), 139.6 (m, $^1J_{CF} = 246$ Hz), 138.6 (s, toluene), 137.6 (m, $^1J_{CF} = 244$ Hz), 129.8 (s, toluene), 129.1 (s, toluene), 126.9 (s), 126.2 (s, toluene), 125.5 (s), 47.6 (s), 21.6 ppm (s, toluene), the signals due to the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{28}H_8N_2O_3BF_{15}$·toluene: C 52.07, H 1.87, N 3.47; found: C 51.90, H 2.13, N 3.50; DART MS, *m/z*: 757.0 (calcd for $[M+K]^+$: 757.0), 739.0 (calcd for $[M+Na]^+$: 739.0), 734.1 (calcd for $[M+NH_4]^+$: 734.1), 205.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 205.2).

Synthesis of 3o: $B(C_6F_5)_3$ (255 mg, 0.5 mmol) was dissolved in toluene (5 mL) and was added to *N*-(prop-2-yn-1-yl)adamantane-1-carboxamide (109 mg, 0.5 mmol) affording an orange solution. The reaction mixture was heated to 45 °C for 2 h to give colourless needles of the product (**3o**), which were washed with pentane (2×3 mL) and dried in vacuo (203 mg, 56%, 0.28 mmol). ^{1}H NMR (400 MHz, [D_8]THF, 298 K): $\delta = 11.16$ (s, br., 1H, NH), 6.40 (s, br., 1H, C=CH), 4.01 (d, $^4J_{HH} = 2.8$ Hz, 2H, CH_2), 2.09 (s, br., 3H, Ad), 2.00 (m, br., 6H, Ad), 1.80 ppm (m, br., 6H, Ad); ^{11}B NMR (128 MHz, [D_8]THF, 298 K): $\delta = -16.6$ ppm (s); ^{19}F NMR (377 MHz, [D_8]THF, 298 K): $\delta = -132.7$ (d, 2F, $J_{FF} = 21.5$ Hz, *o*-F), −163.5 (t, $^3J_{FF} = 29.9$ Hz, 1F, *p*-F), −167.2 ppm (m, br., 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, [D_8]THF, 298 K): $\delta = 183.9$ (s), 149.3 (m, $^1J_{CF} = 244$ Hz), 146.2 (m), 139.5 (m, $^1J_{CF} = 242$ Hz), 137.6 (m, $^1J_{CF} = 244$ Hz), 46.6 (s), 38.5 (s), 37.6 (s), 36.7 (s), 28.5 ppm (s), the carbon atoms bonded to boron could not be observed; elemental analysis calcd (%) for $C_{32}H_{19}NOBF_{15}$·0.5 toluene: C 54.99, H 3.00, N 1.92; found: C 54.52, H 3.34, N 1.83; DART MS, *m/z*: 730.1 (calcd for $[(M+H]^+$: 730.1), 218.2 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 174.1).

Synthesis of 3p: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (4 mL) and was added to 2-phenyl-*N*-(prop-2-yn-1-yl)acetamide (69 mg, 0.4 mmol). The reaction mixture was heated to 45 °C for six days without

stirring. Removal of the solvent in vacuo afforded an oil that could be recrystallised from toluene/pentane. Removal of the remaining solvent by pipette followed by washing with pentane (3×3 mL) and drying in vacuo afforded the pure product (170 mg, 62%, 0.25 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ=7.87 (s, br., 1H, NH), 7.48 (m, 3H, Ar-H), 7.30 (m, 3H, Ar-H), 6.56 (s, 1H, -C=CH), 4.10 (s, 4H, CH_2); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ=−17.0 ppm (s); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): −133.2 (d, 2F, J_{FF}=22.1 Hz, *o*-F), −161.9 (t, 1F, J_{FF}=19.6 Hz, *p*-F), −166.1 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ=179.6 (s), 148.7 (m, $^1J_{CF}$=240 Hz), 145.0 (m), 139.3 (m, $^1J_{CF}$=249 Hz), 137.1 (m, $^1J_{CF}$=251 Hz), 130.9 (s), 130.6 (s), 130.2 (s), 127.8 (s), 122.6 (m), 46.3 (s), 35.0 ppm (s), the signals due to the carbon atoms bonded to boron in the C_6F_5 rings could not be observed; elemental analysis calcd (%) for $C_{29}H_{11}NOBF_{15}$: C 50.83, H 1.62, N 2.04; found: C 49.36, H 1.86, N 2.00; DART MS, *m*/*z*: 724.0 (calcd for $[M+K]^+$: 724.0), 708.1 (calcd for $[M+Na]^+$: 708.1), 703.1 (calcd for $[M+NH_4]^+$: 703.1), 686.1 ppm (calcd for $[M+Na]^+$: 686.1).

Synthesis of 3q: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (4 mL) and was added to *N*-(prop-2-yn-1-yl)pentanamide (56 mg, 0.4 mmol). The reaction mixture was heated to 45°C for six days without stirring, resulting in a pale yellow/orange solution. Removal of the solvent in vacuo followed by recrystallisation from toluene/THF/pentane afforded colourless crystals of the product. Removal of the remaining solvent by pipette followed by washing with pentane (3×3 mL) and drying in vacuo afforded the pure product (142 mg, 54%, 0.22 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ=10.47 (s, br., 1H, NH), 6.47 (s, 1H, -C=CH), 4.07 (s, br., 4H, CH_2), 2.67 (t, $^3J_{HH}$=7.8 Hz, 2H, CH_2), 1.73 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 0.96 (t, $^3J_{HH}$=7.3 Hz, 3H, CH_3), one equivalent of THF was also observed at 3.69 and 1.89 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ=−16.9 (s); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): −133.2 (d, 2F, J_{FF}=22.5 Hz, *o*-F), −162.2 (t, 1F, J_{FF}=20.6 Hz, *p*-F), −166.3 ppm (m, 2F, *m*-F); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ=179.8 (s), 148.8 (m, $^1J_{CF}$=239 Hz), 144.8 (m), 139.1 (m, $^1J_{CF}$=248 Hz), 138.6 (s, toluene), 137.3 (m, $^1J_{CF}$=246 Hz), 129.6 (s, toluene), 128.7 (s, toluene), 125.8 (s, toluene), 121.0 (m), 68.7 (s, THF), 46.2 (s), 28.1 (s), 27.0 (s), 26.0 (s, THF), 22. (s), 21.7 (s, toluene), 13.6 ppm (s), the signals due to the carbon atoms bonded to boron in the C_6F_5 rings could not be observed; elemental analysis calcd (%) for $C_{26}H_{13}NOBF_{15}$.tol: C 51.72, H 3.33, N 1.84; found: C 49.82, H 2.93, N 1.94; ESI+ MS, *m*/*z*: 690.0 (calcd for $[M+K]^+$: 690.0), 669.1 (calcd for $[M+NH_4]^+$: 669.1).

Synthesis of 5-methyl-2-(*p*-tolyl)oxazole, 51: 4-Methyl-*N*-(prop-2-yn-1-yl)-benzamide (407 mg, 2.35 mmol) was dissolved in CH_2Cl_2 (8 mL) and 5 mol% $AuCl_3$ added (36 mg, 0.2 mmol, 0.05 equiv). The resulting solution was stirred at room temperature for 6 h. The crude product was purified by column chromatography (hexanes:EtOAc=9:1 to 4:1) to give the pure oxazole as a colourless liquid (290 mg, 1.67 mmol, 71%). R_f=0.34 (hexanes:EtOAc=4:1) whose NMR spectra were comparable to those reported previously.[7] ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=7.89 (d, $^3J_{HH}$=8.1 Hz, 2H, *o*-H), 7.24 (d, $^3J_{HH}$=8.1 Hz, 2H, *m*-H), 6.81 (s, br., 2H, C-H oxazole), 2.39 (s, 3H, CH_3), 2.38 ppm (s, br., 3H, CH_3); ^{1}H NMR (400 MHz, [D_8]toluene, 298 K): δ=7.89 (d, $^3J_{HH}$=8.2 Hz, 2H, *o*-H), 6.94 (d, $^3J_{HH}$=8.2 Hz, 2H, *m*-H), 6.64 (m, br., 2H, C-H oxazole), 2.04 (s, 3H, CH_3), 1.89 ppm (d, $^4J_{HH}$=1.2 Hz, 3H, CH_3).

Synthesis of 2-(adamantan-1-yl)-5-methyloxazole (5o): $B(C_6F_5)_3$ (25 mg, 0.05 mmol) was dissolved in toluene (10 mL) and was added to *N*-(prop-2-yn-1-yl)adamantane-1-carboxamide (109 mg, 0.5 mmol). The reaction mixture was heated to 100°C for 10 days without stirring. The product was purified by column chromatography (80:20 hexanes:EtOAc) to give the pure product as an off-white oil (90.6 mg, 0.42 mmol, 83%) whose ^{1}H and ^{13}C NMR shifts were comparable to those reported previously.[7b] R_f (hexanes:EtOAc=80:20)=0.33; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=6.58 (d, $^4J_{HH}$=1.2 Hz, 1H, oxazole -H), 2.27 (d, $^4J_{HH}$=1.2 Hz, 3H, CH_3), 2.06 (br. s, 3H, Ad-H), 2.01 (m, 6H, Ad-H), 1.76 ppm (br. s, 6H, Ad-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ=170.0 (s), 147.7 (s), 122.1 (s), 40.6 (s), 36.7 (s), 35.6 (s), 20.2 (s), 11.0 ppm (s).

Synthesis of 7r: $B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 mL) and was added to *N*-(2-methylbut-3-yn-2-yl)benzamide (75 mg, 0.4 mmol). The reaction mixture was heated to 45°C for four days without stirring. Removal of the solvent in vacuo afforded a yellow oil, which was recrystallised from the layering of a hot, saturated solution with pentane. The crystals were washed with pentane (3×3 mL) and dried in vacuo to afford the pure product (104 mg, 0.15 mmol, 37%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ=7.75 (m, $^3J_{HH}$=7.9 Hz, 2H, *o*-H), 7.73 (tt, $^3J_{HH}$=7.5 Hz, $^4J_{HH}$=1.2 Hz, 1H, *p*-H), 7.56 (m, 2H, *m*-H), 7.53 (s, br., 1H, NH), 6.14 (s, 1H, C=CH), 1.73 (s, 6H, CH_3); ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ=1.4 (s, br.); ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ=−132.5 (m, 4F, *o*-F $B(C_6F_5)_2$), −140.8 (m, 2F, *o*-F C_6F_5), −158.6 (t, $^3J_{FF}$=20 Hz, 2F, *p*-F $B(C_6F_5)_2$), −158.8 (t, $^3J_{FF}$=21 Hz, 1F, *p*-F C_6F_5), −164.6 (m, 2F, *m*-F C_6F_5), −165.1 ppm (m, 4F, *m*-F C_6F_5); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K) partial: δ=170.8 (s), 148.6 (m, $^1J_{CF}$=248 Hz), 144.5 (m, $^1J_{CF}$=248 Hz), 142.7 (s), 140.6 (m), 140.33 (m, $^1J_{CF}$=248 Hz), 138.9–138.3 (m), 136.8–136.5 (m), 135.6 (s), 130.4 (s), 130.1 (s), 128.6 (s), 59.6 (s), 59.6 ppm (s); elemental analysis calcd (%) for $C_{30}H_{13}NOBF_{15}$: C 51.53, H 1.87, N 2.00; found: C 51.35, H 2.17, N 2.05; DART MS, *m*/*z*: 700.1 (calcd for $[(M+H]^+$: 700.1), 188.1 (calcd for $[(M-B(C_6F_5)_3)+H]^+$: 188.1).

X-ray crystallography: Crystals were coated in paratone oil and mounted in a cryoloop. Data were collected on Nonius Kappa CCD or Bruker APEX2 X-ray diffractometers using graphite-monochromated $Mo_{K\alpha}$ radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryostream cooler for both initial indexing and full data collection. Data were collected by using Bruker APEX-2 software and processed using SAINT and an absorption correction applied using multi-scan within the APEX-2 program.[23] The structures were solved by direct methods within the SHELXTL package. All structures were refined against F^2 using the SHELXTL package.[24] Unit cell parameters and refinement statistics are presented in the Supporting Information.

CCDC-939515, CCDC-939516, CCDC-939517, CCDC-939518, CCDC-939519, CCDC-939520, CCDC-939521, CCDC-939522, CCDC-939523, CCDC-939524, CCDC-939525 and CCDC-939526 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

NSERC of Canada is thanked for financial support. D.W.S. is grateful for the award of a Canada Research Chair. M.M.H. is grateful to the Fonds der chemischen Industrie for a Chemiefonds scholarship and the Studienstiftung des deutschen Volkes. We would also like to acknowledge Professor Mark Lautens for support of M.M.H. at the University of Toronto.

[1] a) Y. Kato, N. Fusetani, S. Matsunaga, K. Hashimoto, S. Fujita, T. Furuya, *J. Am. Chem. Soc.* **1986**, *108*, 2780–2781; b) S. Carmeli, R. E. Moore, G. M. L. Patterson, T. H. Corbett, F. A. Valeriote, *J. Am. Chem. Soc.* **1990**, *112*, 8195–8197; c) G. Pattenden, *J. Heterocycl. Chem.* **1992**, *29*, 607–618; d) P. Brown, D. J. Best, N. J. P. Broom, R. Cassels, P. J. O'Hanlon, T. J. Mitchell, N. F. Osborne, J. M. Wilson, *J. Med. Chem.* **1997**, *40*, 2563–2570; e) D. K. Dalvie, A. S. Kalgutkar, S. C. Khojasteh-Bakht, R. S. Obach, J. P. O'Donnell, *Chem. Res. Toxicol.* **2002**, *15*, 269–299.

[2] a) R. Lakhan, B. Ternai, *Adv. Heterocycl. Chem.* **1974**, *17*, 99–211; b) S. Lang-Fugmann, *Methoden der Organischen Chemie* (Ed.: E. Schaumann), Houben-Weyl, Thieme, Stuttgart, Germany, **1993**; c) D. C. Palmer, S. Venkatraman, *The Chemistry of Heterocyclic Compounds, A Series of Monographs, Oxazoles: Synthesis Reactions and Spectroscopy, Part A* (Ed.: D. C. Palmer), Wiley, New York, **2003**.

[3] a) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo, K. Itoh, *Organometallics* **1989**, *8*, 846–848; b) H. Nishiyama, S.-B. Park, K. Itoh, *Tetrahedron: Asymmetry* **1992**, *3*, 1029–1034; c) A. Gissibl, M. G. Finn, O. Reiser, *Org. Lett.* **2005**, *7*, 2325–2328.

[4] H. Vorbrüggen, K. Krolikiewicz, *Tetrahedron* **1993**, *49*, 9353–9372.

[5] a) A. Arcadi, S. Cacchi, L. Cascia, G. Fabrizi, F. Marinelli, *Org. Lett.* **2001**, *3*, 2501–2504; b) A. Bacchi, M. Costa, B. Gabriele, G. Pelizzi, G. Salerno, *J. Org. Chem.* **2002**, *67*, 4450–4457; c) A. Bacchi, M. Costa, N. Della Ca, B. Gabriele, G. Salerno, S. Cassoni, *J. Org. Chem.* **2005**, *70*, 4971–4979; d) E. M. Beccalli, E. Borsini, G. Broggini, G. Palmisano, S. Sottocornola, *J. Org. Chem.* **2008**, *73*, 4746–4749; e) A. Saito, K. Iimura, Y. Hanzawa, *Tetrahedron Lett.* **2010**, *51*, 1471–1474; f) N. T. Patil, *ChemCatChem* **2011**, *3*, 1121–1125; g) N. T. Patil, R. D. Kavthe, V. S. Shinde, *Tetrahedron* **2012**, *68*, 8079–8146.

[6] M. Harmata, C. Huang, *Synlett* **2008**, 1399–1401.

[7] a) A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391–4394; b) M. D. Milton, Y. Inada, Y. Nishibayashi, S. Uemura, *Chem. Commun.* **2004**, 2712–2713; c) A. S. K. Hashmi, M. Rudolph, S. Schymura, J. Visus, W. Frey, *Eur. J. Org. Chem.* **2006**, 4905–4909; d) D. Aguilar, M. Contel, R. Navarro, T. Soler, E. P. Urriolabeitia, *J. Organomet. Chem.* **2009**, *694,* 486–493; e) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396–8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; f) J. P. Weyrauch, A. S. K. Hashmi, A. Schuster, T. Hengst, S. Schetter, A. Littmann, M. Rudolph, M. Hamzic, J. Visus, F. Rominger, W. Frey, J. W. Bats, *Chem. Eur. J.* **2010**, *16*, 956–963; g) A. S. K. Hashmi, L. Molinari, F. Rominger, T. Oeser, *Eur. J. Org. Chem.* **2011**, 2256–2264; h) A. S. K. Hashmi, A. M. Schuster, M. Schmuck, F. Rominger, *Eur. J. Org. Chem.* **2011**, 4595–4602; i) O. A. Egorova, H. Seo, Y. Kim, D. Moon, Y. M. Rhee, K. H. Ahn, *Angew. Chem.* **2011**, *123*, 11648–11652; *Angew. Chem. Int. Ed.* **2011**, *50*, 11446–11450.

[8] a) H. C. Brown, *Organic Synthesis via Boranes*, Wiley, New York, **1975**; b) B. M. Mikhailov, Y. N. Bubnov, *Organoboron Compounds in Organic Synthesis*, Harwood Academic, New York, **1984**; c) A. Pelter, K. Smith, H. C. Brown, *Borane Reagents*, Academic Press Limited, London, **1988**; d) D. G. Hall, *Boronic Acids*, 2.ed. Wiley-VCH, Weinheim, **2011**.

[9] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[10] For recent reviews see: a) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535–1539; b) D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136; c) D. W. Stephan, *Chem. Commun.* **2010**, *46*, 8526–8533; d) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; e) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746.

[11] a) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397; b) C. Jiang, O. Blacque, H. Berke, *Organometallics* **2010**, *29*, 125–133; c) C. M. Mömming, G. Kehr, B. Wibbeling, R. Fröhlich, B. Schirmer, S. Grimme, G. Erker, *Angew. Chem.* **2010**, *122*, 2464–2467; *Angew. Chem. Int. Ed.* **2010**, *49*, 2414–2427; d) C. Chen, F. Eweiner, B. Wibbeling, R. Fröhlich, S. Senda, Y. Ohki, K. Tatsumi, S. Grimme, G. Kehr, G. Erker, *Chem. Asian J.* **2010**, *5*, 2199–2208; e) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* **2010**, *29*, 6594–6607; f) D. Winkelhaus, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Dalton Trans.* **2012**, *41*, 9143–9150.

[12] T. Voss, C. Chen, G. Kehr, E. Nauha, G. Erker, D. W. Stephan, *Chem. Eur. J.* **2010**, *16*, 3005–3008.

[13] For 1,1-carboboration reactions see: a) C. Chen, G. Kehr, R. Fröhlich, G. Erker, *J. Am. Chem. Soc.* **2010**, *132*, 13594–13595; b) O. Ekkert, G. Kehr, R. Fröhlich, G. Erker, *J. Am. Chem. Soc.* **2011**, *133*, 4610–4616; c) C. Chen, T. Voss, R. Fröhlich, G. Kehr, G. Erker, *Org. Lett.* **2011**, *13*, 62–65; d) J. Möbus, Q. Bonnin, K. Ueda, R. Fröhlich, K. Itami, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2012**, *124*, 1990–1993; *Angew. Chem. Int. Ed.* **2012**, *51*, 1954–1957; e) G. Kehr, G. Erker, *Chem. Commun.* **2012**, *48*, 1839–1850, and references therein; f) C. Eller, G. Kehr, C. G. Daniliuc, R. Fröhlich, G. Erker, *Organometallics* **2013**, *32*, 384–386.

[14] For the use of electrophilic halogen reagents in the intramolecular cyclisation reactions of amides and alkynes, see: S. Mehta, T. Yao, R. C. Larock, *J. Org. Chem.* **2012**, *77*, 10938–10944; C. Schlemmer, L. Andernach, D. Schollmeyer, B. F. Straub, T. Opatz, *J. Org. Chem.* **2012**, *77*, 10118–10124.

[15] See also the Supporting Information.

[16] S. Punna, S. Meunier, M. G. Finn, *Org. Lett.* **2004**, *6*, 2777–2779.

[17] K. Jayaprakash, C. S. Venkatachalam, K. K. Balasubramanian, *Tetrahedron Lett.* **1999**, *40*, 6493–6496.

[18] C. L. Allen, B. N. Atkinson, J. M. J. Williams, *Angew. Chem.* **2012**, *124*, 1412–1415; *Angew. Chem. Int. Ed.* **2012**, *51*, 1383–1386.

[19] X. Meng, S. Kim, *Org. Biomol. Chem.* **2011**, *9*, 4429–4431.

[20] G. C. Senadi, W.-P. Hu, J.-S. Hsiao, J. K. Vandavasi, C.-Y. Chen, J.-J. Wang, *Org. Lett.* **2012**, *14*, 4478–4481.

[21] S. Yasuhara, M. Sasa, T. Kusakabe, H. Takayama, M. Kimura, T. Mochida, K. Kato, *Angew. Chem.* **2011**, *123*, 3998–4001; *Angew. Chem. Int. Ed.* **2011**, *50*, 3912–3915.

[22] J. Deng, J. Tabei, M. Shiotsuki, F. Sanda, T. Masuda, *Macromolecules* **2004**, *37*, 1891–1896.

[23] APEX2 and SAINT software; Bruker AXS Inc., Madison, Wisconsin, USA.

[24] SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA.

Received: May 16, 2013
Published online: August 6, 2013

