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A Photocatalytic C(sp)–B Bond Formation Employing SOMOphilic Alkynyl Sulfones and Nucleophilic Boryl Radicals

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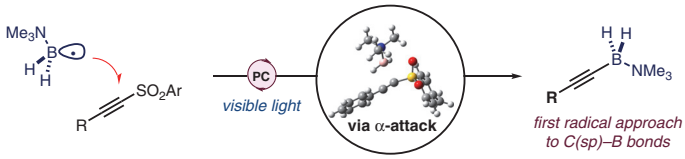

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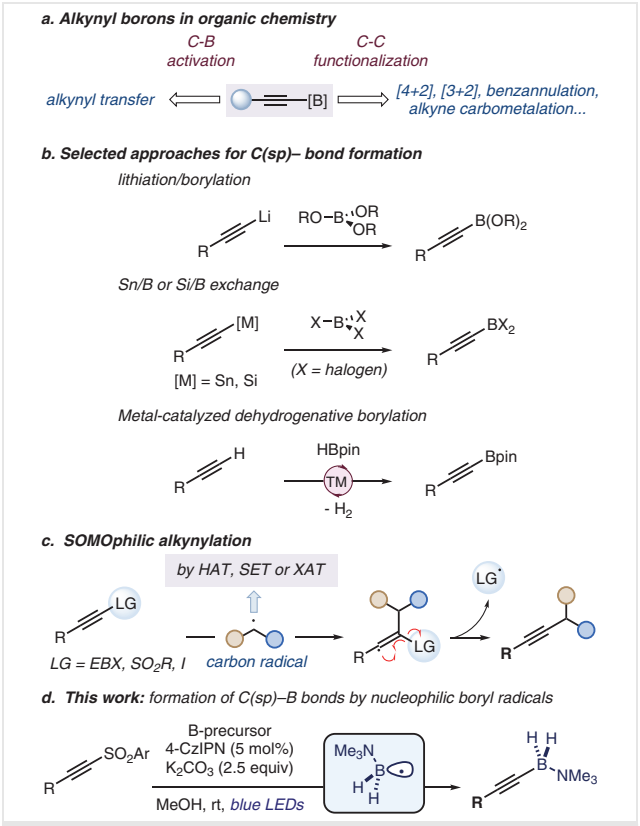
Abstract Alkynylboron compounds are important scaffolds with broad applicability in organic synthesis. In contrast to polar or metal-catalyzed processes, here a radical approach is employed for the addition of nucleophilic boryl radicals to electrophilic SOMOphiles for the construction of the C(sp)–B bond. The reaction renders the corresponding alkynylated amine boranes with broad functional group compatibility. In addition, theoretical studies have been carried out by means of DFT to understand the reactivity and selectivity of the addition process.

Key words boryl radical, photoredox, SOMOphile, alkynylation, organoborons

Boron-containing compounds are privileged building blocks in synthetic chemistry with broad applications in academia and industry.[1] This integral relevance arises from the ability of carbon–boron bonds to be easily converted into C–C, C–O, and C–N via cross-coupling reactions like the Nobel prize-winning Suzuki–Miyaura reaction, or the Chan–Lam process.[1] Indeed, almost 40% of all the transformations used by the pharmaceutical sector for the construction of C–C bonds involve the use of organoboron partners[2] and the Suzuki–Miyaura cross-coupling is overall the 5th most used reaction in pharma.[2b]

A particular family of interesting borylated compounds are alkynylborons.[3] The most direct application of these entities pertains to the direct alkynylation of electrophilic species by activation of the C(sp)–B bond (Scheme 1a).[4] They have been also used for cycloaddition and benzannulation reactions[5] where the alkyne motif behaves as a reactive π-system, enabling the access to (hetero)aromatics with site-selectivity orthogonal to typical direct borylation methods.[6] Additionally, the alkyne unit can be also functionalized by means of carbometalation approaches to obtain stereodefined multisubstituted olefins.[7]



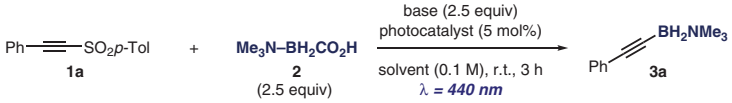
Scheme 1 a) Importance of alkynylborons in organic chemistry; b) Selected methods for the formation of C(sp)–B bonds; c) Trapping of carbon radicals with SOMOphiles for alkynylation reactions. EBX: Ethynylbenziodoxolone; d) This work: application of the SOMOphilic alkynylation concept employing nucleophilic boryl radicals.

In contrast to the research of sp^3- and sp^2-containing C–B bonds, the development of methods for C(sp)–B bond formation has been comparatively less explored, mainly due to the competing reactivity of the C(sp)–H bond of terminal alkynes versus the borylation of the C≡C bond.

Traditionally, compounds with C(sp)–B bond have been prepared by using the approach developed by Brown in the 70's by lithiation/borylation of terminal alkynes (Scheme 1b).[8] However, this approach requires the use of strong bases (e.g., ^{n}BuLi) to form the reactive lithium acetylide. Other polar approaches consist of the transmetalation between nucleophilic sources of alkynes, such as alkynylstannanes[9] or alkynylsilanes[10] with haloborons (Scheme 1b). In recent years, the use of transition metals has been more widely employed harnessing the potentially high catalytic turnover exerted by these systems. Several examples have been described using dehydrogenative processes with Ir,[11] Ag,[12] Zn,[13] Cu,[14] Mg,[15] and Fe,[16] enabling the access to stable alkynyl-Bpin (pin = pinacolate) products where the boron atom behaves as a Lewis acid (Scheme 1b). Organocatalytic methods are also known, but they are less explored and require the post-functionalization of the boron unit.[17]

Under this scenario, an alternative, yet missing approach, would be the use of radicals to promote the formation of the C(sp)–B bond. However, this is especially challenging since C(sp)–centered radicals are not stable. In contrast, extensive research has been developed in recent years for the exploration of boryl radicals as a new way of introducing this functionality,[18] including the addition to aromatics,[19] π-deficient olefins,[20] and styrenes.[21] Additionally,

Table 1 Reaction Development and Optimization Studies



Entry	Photocatalyst	Solvent	Base	Conversion of **1a** (%)[a]	Yield (%)[b] of **3a**
1	4-CzIPN	organic aprotic solvent[c]	Cs_2CO_3	>98	–
2	4-CzIPN	MeOH	Cs_2CO_3	>98	34
3	*fac*-Ir(ppy)$_3$	MeOH	Cs_2CO_3	>98	3
4	[Ir(dF(CF$_3$))$_2$(bpy)]PF$_6$	MeOH	Cs_2CO_3	>98	16
5	[Ir(dF(Me)ppy)$_2$(dtbbpy)]PF$_6$	MeOH	Cs_2CO_3	>98	13
6	Ir[*p*-F(*t*-Bu)-ppy]$_3$	MeOH	Cs_2CO_3	>98	10
7	Ir[(dF(OMe)ppy)$_2$(5,5′-dCF$_3$bpy)]PF$_6$	MeOH	Cs_2CO_3	>98	14
8	4-CzIPN	*t*BuOH	Cs_2CO_3	>98	12
9	4-CzIPN	*i*PrOH	Cs_2CO_3	>98	21
10	4-CzIPN	EtOH	Cs_2CO_3	>98	29
11	4-CzIPN	isoamyl alcohol	Cs_2CO_3	>98	19
12	4-CzIPN	MeOH	pyridine, lutidine, Et$_3$N, DABCO, TMG, ^{t}Bu-TMG	>98	–
13	4-CzIPN	MeOH	KOAc	>98	36
14	4-CzIPN	MeOH	K_3PO_4	>98	40
15	4-CzIPN	MeOH	$CsHCO_3$	>98	48
16	4-CzIPN	MeOH	Na_2CO_3	>98	37
17	4-CzIPN	MeOH	K_2CO_3	>98	61
18	–	MeOH	K_2CO_3	26	–
19	4-CzIPN	MeOH	–	51	–
20[d]	4-CzIPN	MeOH	K_2CO_3	>98	–
21[e]	4-CzIPN	MeOH	K_2CO_3	>98	43
22[f]	4-CzIPN	MeOH	K_2CO_3	>98	60

[a] Determined by ^{1}H NMR spectroscopy of the reaction crude.
[b] Isolated yield.
[c] Including CH_2Cl_2, THF, toluene, $PhCF_3$, EtOAc, acetone, DMF, and cyclohexane.
[d] No irradiation.
[e] Reaction run using 1.5 equiv. of **2**.
[f] Reaction run for 16 h.

they are known to undergo easy addition to C≡C bonds, leading to the *anti*-hydroboration[22] of these structural platforms, therefore posing additional hurdles to the construction of C(sp)–B bonds. Nevertheless, the utilization of boryl radicals for the formation of alkynylborons is an unmet challenge in the literature.

In order to develop such a method through a radical strategy, we focused on the concept of SOMOphilic alkynylation.[23] This strategy exploits electrophilic alkynes bearing a leaving group attached at the acetylenic carbon that favors the α-addition of open-shell, radical species. This renders the alkynylated product after homolytic extrusion of the leaving group (Scheme 1c). Typical SOMOphilic acetylenes are alkynyl sulfones, EBX- and iodo-containing alkynes, which have been employed in combination with different sources of carbon radicals (e.g., alkyl NHPI esters, Katritzky salts or alkyl halides among others).[23] Since this reactivity is enhanced by the presence of nucleophilic radicals, we decided to explore the use of amine-ligated boryl radicals ($R_3N–BH_2^{\bullet}$) owing to their increased nucleophilicity in comparison with other ligated boryl radicals, such as *N*-heterocyclic carbenes or pyridines.[24]

Herein we report the application of boryl radicals as borylating species of SOMOphilic acetylenes as a new way to form organoboron compounds (Scheme 1d). The method exploits, for the first time, a photoredox strategy employing aminocarboxylic acids under visible light, rendering the corresponding borylated products, which are stable at room temperature and isolable by typical chromatographic methods. Additionally, we include mechanistic studies by means of theoretical calculations to understand the regioselectivity during the addition of the boryl radical to the SOMOphile, and the plausible reaction mechanism.

Reaction Development and Optimization

At the outset we decided to use the aminocarboxylic acid **2**, recently developed by the Leonori group[25] as a way of forming the desired boryl radical (see Table 1). This species can be deprotonated by bases (pK_a ~8),[26] followed by SET (E_{ox} = +0.38 V vs SCE in CH_3CN)[25] with an excited photocatalyst to form the corresponding boryl radical and CO_2. As a SOMOphile we decided to use the alkynyl sulfone **1a**, which can be accessed in one step from the corresponding terminal alkyne using non-toxic reagents.[27] Unfortunately, we did not observe any borylation product between **1a** and **2** using 4-CzIPN and Cs_2CO_3 in the presence of different aprotic organic solvents, including CH_2Cl_2, THF, toluene, $PhCF_3$, EtOAc, acetone, DMF, and cyclohexane (Table 1, entry 1, for additional details see the Supporting Information). The use of protic solvents such as MeOH led to full conversion of the starting material **1a** with formation of the desired alkynyl borane **3a** in 34% yield (entry 2). Therefore, we decided to study other potential photocatalysts, but none of them enabled to increase the yield for the formation of **3a** (entries 3–7). Then, we explored other protic solvents such as ^{t}BuOH, ^{i}PrOH, EtOH, and isoamyl alcohol, leading to lower yields (entries 8–11). Finally, we decided to use different bases. The addition of organic bases such as pyridine, 2,6-lutidine, Et_3N, DABCO, TMG, or ^{t}Bu-TMG led to complete conversion of the alkynyl sulfone **1a** but inhibited the formation of the alkynyl borane **3a** (entry 12, for additional details see the Supporting Information). Inorganic bases such as KOAc, K_3PO_4, $CsHCO_3$, or Na_2CO_3 were more effective (entries 13–16). Delightfully, the use of K_2CO_3 led to a 61% yield of **3a** after 3 hours (entry 17). Control experiments demonstrated that both photocatalyst and base were necessary for the reaction (entries 18 and 19, respectively), and that light irradiation was required to promote the process (entry 20). The use of less amount of the $Me_3N–BH_2CO_2H$ reagent led to a lower yield of 43% (entry 21), while running the reaction for prolonged times did not affect the reaction outcome suggesting that once **3a** is formed, it remains stable under the reaction conditions (entry 22).

Substrate Scope

Having found optimal conditions for the borylation reaction, we further explored the substrate scope of the process (Scheme 2).

Plain alkyl groups could be introduced at the aromatic unit at *ortho*-, *meta*-, and *para*-positions. This was exemplified by the synthesis of alkylated products **3b**, **3c**, and **3d**, respectively, with medium to good yields. These examples showcase the tolerance of the method to benzylic positions, which could be activated by hydrogen atom transfer (HAT). Next, we studied the effect of electronically different aromatics. Electron-rich substituents such as *p*-OMe (**3e**) were tolerated, albeit the reaction yield was slightly lower (33%) and required more reaction time (5 h), likely because of the lower electrophilicity of the acetylenic unit. Contrarily, electron-poor substituents such as *p*-CO_2Me and *p*-CF_3 (**3f** and **3g**, respectively) reacted well. Remarkably, we did not observe boryl radical-mediated defluorination of the CF_3 group in the latter case.[28] Then, we explored π-extended systems like 1-naphthyl (**3h**) and *p*-Ph (**3i**) rendering the desired borylated products in 56% and 68% yield, respectively. Subsequently, we studied the tolerance of the method to the presence of halides, obtaining the corresponding products with *p*-Cl (**3j**) and *m*-F (**3k**) in good yields. Importantly, the formation of **3k** highlights the applicability of the method to incorporate fluorinated aromatic scaffolds, since boryl radicals are known to undergo addition to these entities.[19] We expanded the scope to electron-rich heteroaromatics (**3l**) and non-aromatic alkynes (**3m**), forming the desired products in 69% and 52% yield, respectively. Finally, we could apply these conditions for the access to borylated complex substrates such as ethynyl estradiol derivative **3n** in 24% yield. Despite the low yield obtained, this ex-

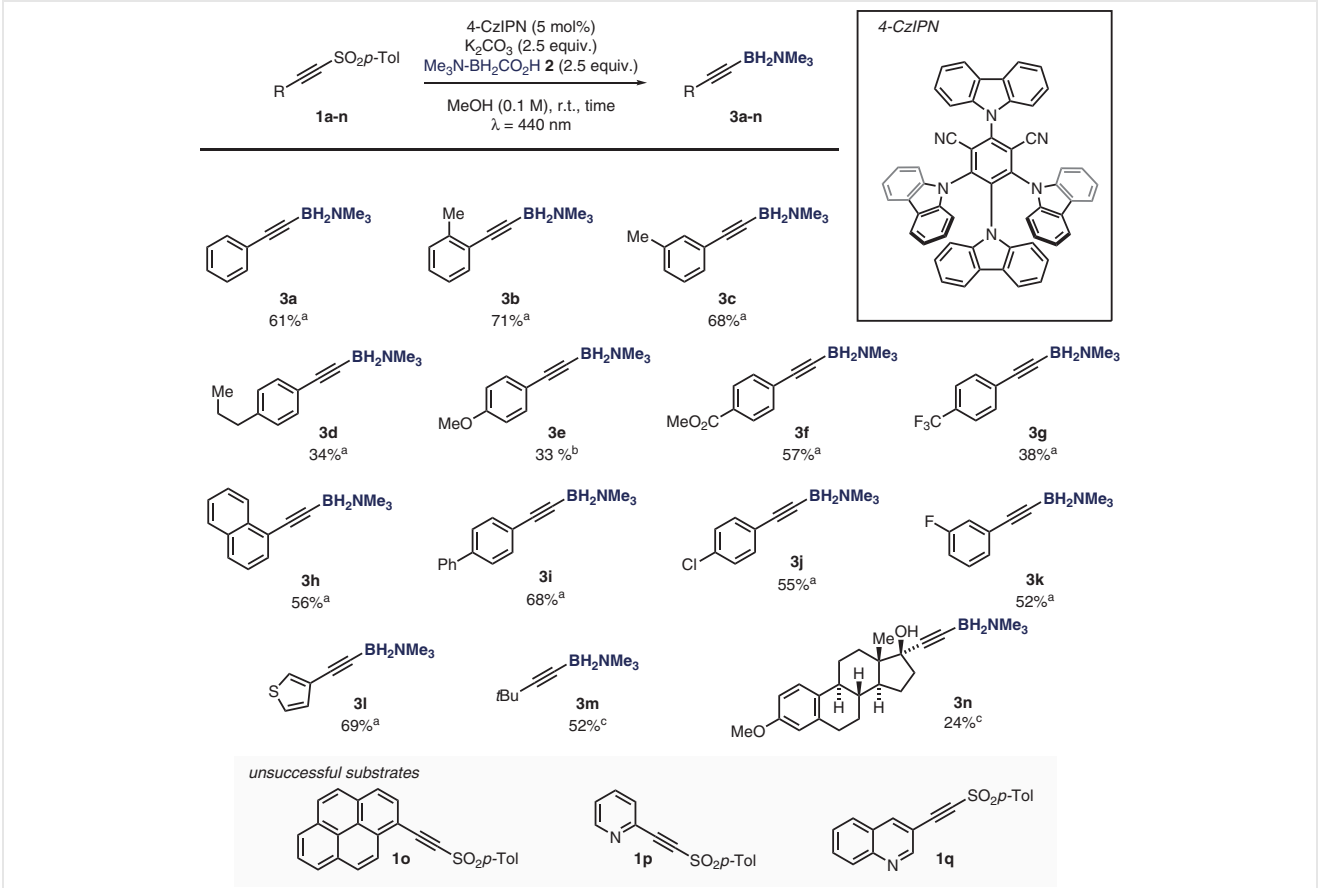
ample showcases the applicability of the method to complex substrates. Importantly, we did not detect the product from hydroboration of the triple bond in any case. Unfortunately, we could not apply the method for the borylation of challenging π-systems such as pyrene (**1o**), or π-deficient heteroaromatics such as pyridine (**1p**) or quinoline (**1q**). In these cases, we observed full decomposition of the starting material, but we could not isolate any by-product (Scheme 2, bottom part).

Computational Studies

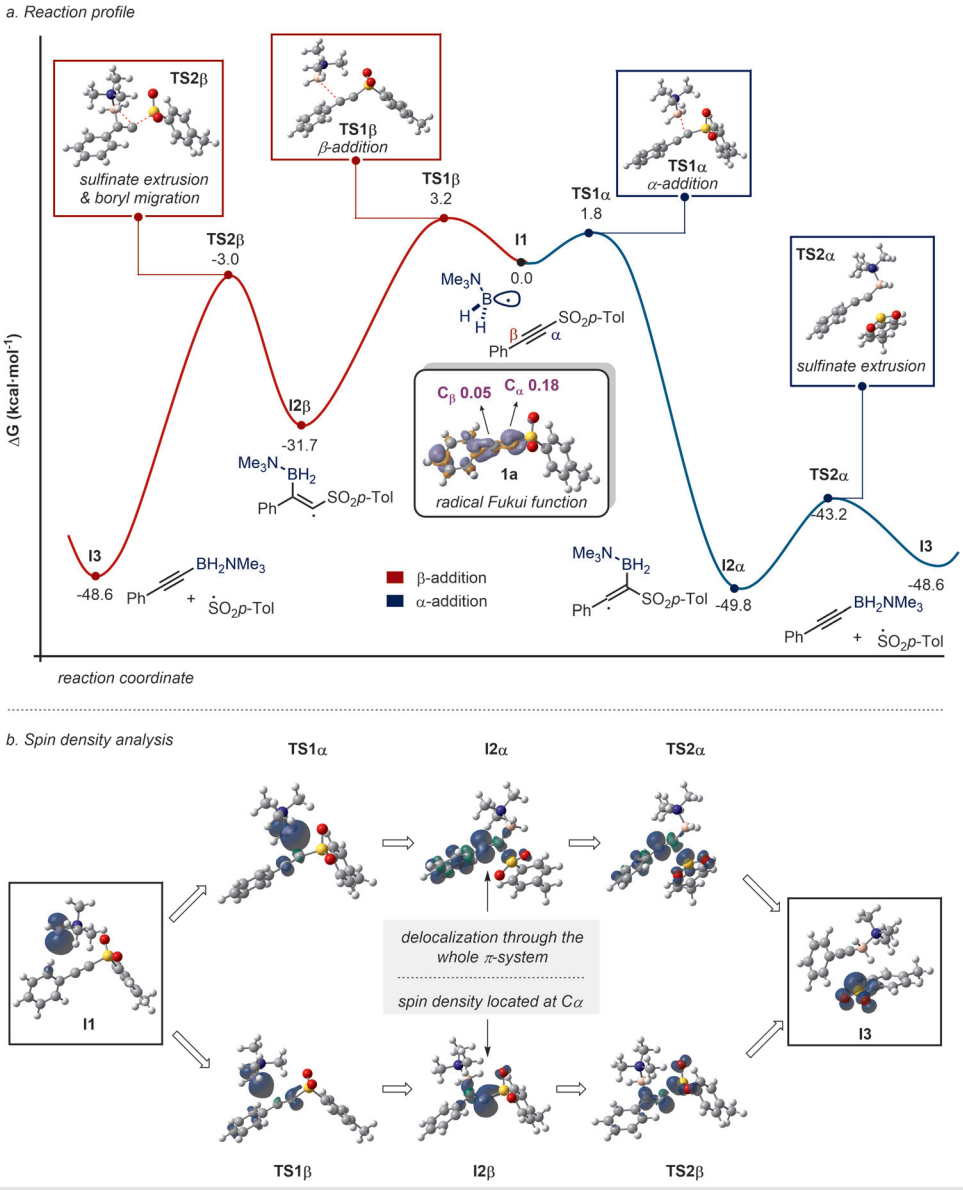
Then, we decided to study the plausible mechanism for this new borylation reaction. Generally, for carbon radical additions to SOMOphilic species, there are two mechanistic possibilities postulated in the literature:[23] (1) the first one is the *ipso*-addition of the radical with respect to the sulfonyl group (α-pathway). This mechanism would lead to a conjugated radical at the β-position, which may suffer sulfinate extrusion to render the final product and the *p*-TolSO$_2$ radical. Alternatively, (2) the radical may add to the β-position of the alkyne through a Michael-type process, to form an sp^2-hybrized alkenyl radical α to the sulfonyl group. In this mechanism, the excision of the C–S bond to extrude the sulfinate radical would generate a carbene-type species, from which migration of the R group takes place to form the alkynylation product.

In order to shed light on this aspect, we carried out DFT calculations (Scheme 3). For this study, we considered the model substrate **1a** (R = Ph) and the Me$_3$N–BH$_2$ radical formed after SET-induced decarboxylation comparing both α-(blue pathway) and β-additions (red pathway) (Scheme 3a). We found that the α-addition ($\Delta G^{\neq}$ = 1.8 kcal mol^{-1}) is slightly more favorable than the β-addition ($\Delta G^{\neq}$ = 3.2 kcal mol^{-1}). This result is in good agreement with the reactivity predicted by the corresponding Fukui function,[29] which showed that the C$_\alpha$ position is more susceptible to a radical attack (C$_\alpha$ 0.18 vs C$_\beta$ 0.05).

While both additions are exergonic and display low energy barriers, ruling out the reversible addition of the boryl radical to the alkyne, there is a much larger gap in the relative energies of the radical intermediates. In particular, the intermediate coming from the α-addition (**I2α**, –49.8 kcal·mol^{-1}) is *ca.* 20 kcal·mol^{-1} more stable than its β counterpart (**I2β**, –31.7 kcal·mol^{-1}). The analysis of the spin den-



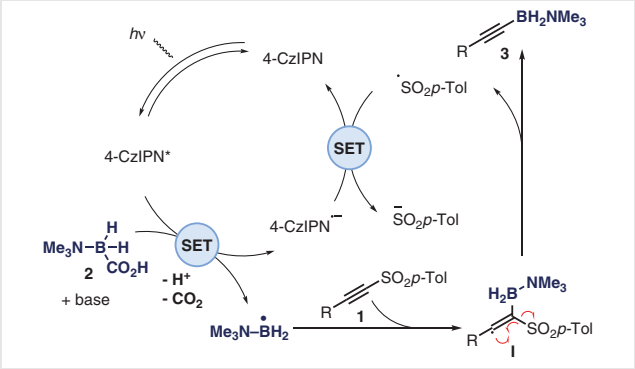
Scheme 2 Reaction scope for the radical borylation of alkynyl sulfones. [a] Reaction run for 3 h. [b] Reaction run for 5 h. [c] Reaction run for 16 h.



Scheme 3 Computational studies. a) Reaction profile for the addition of the boryl radical to **1a** at the α-(blue pathway) or β-position (red pathways); b) Evolution of spin density along the reaction pathway. The calculations were done at the UM06-2X/cc-pVTZ/SMD(MeOH)//UM06-2X/cc-pVDZ/gas level of theory.

sities of both structures revealed that this large energy difference can be related to the amount of delocalization of the unpaired electron (Scheme 3b). In **I2β**, this 'extra' electron is entirely localized at the C_α position. However, in **I2α**, due to the linear arrangement of the Ph–C=C moiety, the unpaired electron is delocalized over the whole π-conjugated system. All attempts to optimize a transition state that would lead from **I1** to the formation of the *Z*-isomer of **I2β** failed, always collapsing to the *E*-isomer.

Lastly, regarding the formation of **3a**, we found that the reaction from **I2α** is almost thermoneutral (ΔG_r = 1.2 kcal·mol^{-1}) and with a rather low activation barrier ($\Delta G^{\neq}$ = 6.6 kcal·mol^{-1}) (Scheme 3a). For **I2β** the reaction is clearly exergonic (ΔG_r = –16.9 kcal·mol^{-1}) but with a much larger barrier ($\Delta G^{\neq}$ = 28.7 kcal·mol^{-1}). Strikingly, and opposed to previous proposals,[23] IRC analysis showed that the conversion of **I2β** to **I3** takes place in a single step, with no detection of a carbene intermediate. The reaction follows a concerted but asynchronous pathway: first the C–S bond is cleaved, and migration of the boryl group occurs after-



Scheme 4 Tentative mechanistic proposal for the radical borylation of alkynyl sulfones

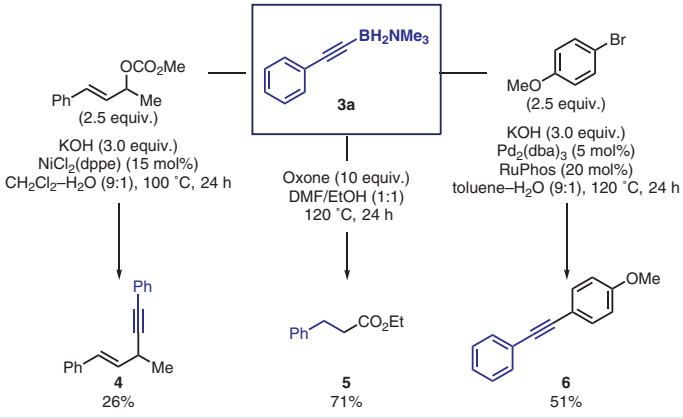
wards. All together, we propose that the reaction involves the α-addition of the boryl radical to sulfone followed by homolytic C–S cleavage, due to the low activation barriers and the higher stability of the radical intermediate. The same conclusions are obtained when the reaction profile for the formation of the alkyl-derivative **3m** was studied by DFT calculations (see the Supporting Information for details).

Therefore, a plausible catalytic cycle for the overall transformation is depicted in Scheme 4. First, the excited photocatalyst (E^*_{red} 4-CzIPN*/4-CzIPN$^{\bullet-}$ = + 1.35 V vs SCE in CH_3CN)[30] would oxidize the carboxylate anion from amino-carboxylic acid **2**, which is deprotonated in presence of the base (E_{ox} = +0.38 V vs SCE in CH_3CN).[25] After that, the extrusion of CO_2 would generate the nucleophilic boryl radical, which would then undergo α-addition to the SOMOphilic sulfone **1** to give the transient species **I**, where the radical is delocalized through the whole π-system. Following this, the elimination of the sulfinyl radical (*p*-TolSO$_2^{\bullet}$) would lead to the formation of the desired borylated product. Finally, the reduced radical anion from the photocatalyst (E_{red} 4-CzIPN/4-CzIPN$^{\bullet-}$ = –1.21 V vs SCE in CH_3CN)[30] would react with the sulfinate radical (E_{red} Ts$^{\bullet}$/Ts^{-} = –0.50 V vs SCE in CH_3CN)[31] by SET to recover the photocatalyst in the ground state and form the sulfinate anion, thereby closing the catalytic cycle.

Finally, we explored the potential synthetic applicability of the resulting alkynyl amine-boranes in preliminary experiments (Scheme 5). From these studies we concluded that the activation of the C(sp)–B bond enables the Tsuji–Trost-type alkynylation of allylic systems catalyzed by Ni (**4**), oxidation (**5**), and Suzuki–Miyaura cross-coupling (**6**).

In conclusion, we have developed the first method for the formation of C(sp)–B bonds by a photocatalytic radical approach. The key to the method lies in the use of Me_3N–BH_2CO_2H as a source of nucleophilic boryl radical, in combination with electrophilic alkynyl sulfones as SOMOphiles. The reaction renders the corresponding alkynylated amine-boranes with medium to good yields, which can be isolated by typical chromatographic methods and are stable under air. Additionally, we have determined the plausible regioselective outcome of the boryl radical attack onto the π-system through an α-addition pathway by means of DFT studies. Further photochemical studies and functionalization of the borylated products are currently ongoing in our group and will be reported in the future.

All chemicals were used directly without purification. All air and moisture sensitive reactions were carried out under N_2 atmosphere using standard Schlenk manifold technique. All solvents were bought from Acros with 99.8% purity. ^{1}H and ^{13}C NMR spectra were acquired at various field strengths as indicated and were referenced to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). ^{1}H NMR coupling constants are reported in hertz (Hz). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublet, etc.). ^{11}B NMR spectra were recorded and reported unreferenced. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI), positive electrospray (ESI) or at-



Scheme 5 Synthetic transformations

mospheric-pressure chemical ionization (APCI). Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in permanganate ($KMnO_4$) stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions.

Alkynyl sulfones were prepared according to known procedures and are known compounds.[27] $Me_3N–BH_2CO_2H$ was prepared according to reported procedure.[25]

In all boron containing compounds, the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus.[32]

C(sp)–B Borylation; General Procedure

An oven-dried 8 mL microwave vial equipped with a stirring bar was charged with the alkynyl sulfone **1** (0.1 mmol, 1.0 equiv.), 4-CzIPN (4 mg, 5 μmol, 5 mol%), K_2CO_3 (28 mg, 0.2 mmol, 2.0 equiv.), and the aminocarboxylic acid **2** (23 mg, 0.2 mmol, 2.0 equiv). The vial was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (3 ×). Anhyd and degassed MeOH (1.0 mL) was added. The vial was sealed with parafilm and was placed approximately 4 cm from blue LEDs (440 nm Kessil lamp). The blue LEDs were switched on with a fan and the contents of the vial were stirred at rt and the reaction followed by TLC analysis. Once the starting material was consumed, the tube was opened, and the solvent was evaporated. The resulting residue was purified by column chromatography on silica gel to give the product.

(Phenylethynyl)borane Trimethylamine Complex (3a)

Following the general procedure using 1-methyl-4-((phenylethynyl)sulfonyl)benzene (25.6 mg, 0.1 mmol, 1.0 equiv.) gave **3a** (10.6 mg, 61%) as a white solid; mp 110–112 °C; R_f = 0.51 [*n*-pentane/EtOAc (6:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 2 H), 7.25–7.18 (m, 3 H), 2.73 (s, 9 H), 2.16 (q, *J* = 98.7 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$). δ = 131.6, 128.1, 127.7, 126.9, 52.3, 29.9.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.64.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}BN$ $[M]^+$: 173.1376; found: 173.1374.

(*o*-Tolylethynyl)borane Trimethylamine Complex (3b)

Following the general procedure using 1-methyl-2-(tosylethynyl)benzene (27.0 mg, 0.1 mmol, 1.0 equiv.) gave **3b** (13.2 mg, 71%) as a yellowish oil; R_f = 0.50 [*n*-pentane/EtOAc (6:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.41 (dd, *J* = 7.4, 1.6 Hz, 1 H), 7.16 (d, *J* = 6.3 Hz, 1 H), 7.11 (td, *J* = 7.5, 1.6 Hz, 1 H), 7.08 (td, *J* = 7.4, 1.6 Hz, 1 H), 2.73 (s, 9 H), 2.46 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.4, 131.8, 129.2, 126.8, 125.4, 52.2, 21.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.45.

HRMS (ESI): *m*/*z* calcd $C_{12}H_{19}BN$ $[M – H]^+$: 188.1611; found: 188.1615.

(*m*-Tolylethynyl)borane Trimethylamine Complex (3c)

Following the general procedure using 1-methyl-3-(tosylethynyl)benzene (27.0 mg, 0.1 mmol, 1.0 equiv.) gave **3c** (12.7 mg, 68%) as an oil; R_f = 0.50 [*n*-pentane/EtOAc (6:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.29–7.20 (m, 2 H), 7.14 (t, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 7.7 Hz, 1 H), 2.72 (s, 7 H), 2.30 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.6, 132.2, 128.6, 128.0, 127.8, 52.2, 21.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.57.

HRMS (ESI): *m*/*z* calcd $C_{12}H_{19}BN$ $[M – H]^+$: 188.1611; found: 188.1612.

((4-Propylphenyl)ethynyl)borane Trimethylamine Complex (3d)

Following the general procedure using 1-methyl-4-(((4-propylphenyl)ethynyl)sulfonyl)benzene (29.8 mg, 0.1 mmol, 1.0 equiv.) gave **3d** (7.3 mg, 34%) as a white solid; mp 95–98 °C; R_f = 0.50 [*n*-hexane/EtOAc (4:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.1 Hz, 2 H), 7.06 (d, *J* = 8.1 Hz, 2 H), 2.71 (s, 9 H), 2.54 (t, *J* = 7.7 Hz, 2 H), 2.15 (q, *J* = 98.7 Hz, 2 H), 1.61 (hept, *J* = 7.4 Hz, 2 H), 0.92 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.5, 131.4, 128.3, 123.0, 52.2, 38.0, 24.5, 13.9.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.54 (t, *J* = 100.9 Hz).

HRMS (ESI): *m*/*z* calcd $C_{14}H_{21}BN$ $[M – H]^+$: 214.1767; found: 214.1764.

((4-Methoxyphenyl)ethynyl)borane Trimethylamine Complex (3e)

Following the general procedure using 1-methoxy-4-(tosylethynyl)benzene (28.6 mg, 0.1 mmol, 1.0 equiv.) gave **3e** (6.7 mg, 33%) as a white solid; R_f = 0.17 [*n*-hexane/EtOAc (7:3)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 8.7 Hz, 2 H), 3.77 (s, 3 H), 2.70 (s, 9 H), 2.13 (q, *J* = 102.5 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.7, 132.9, 118.3, 113.8, 55.4, 52.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.49 (t, *J* = 100.7 Hz).

HRMS (ESI): *m*/*z* calcd $C_{12}H_{17}BNO$ $[M – H]^+$: 202.1398; found: 202.1395.

Methyl 4-(Boraneylethynyl)benzoate Trimethylamine Complex (3f)

Following the general procedure using methyl 4-(tosylethynyl)benzoate (31.4 mg, 0.1 mmol, 1.0 equiv.) gave **3f** (13.2 mg, 57%) as a white solid; mp 102–106 °C; R_f = 0.51 [*n*-hexane/EtOAc (4:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.9 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3 H), 2.73 (s, 9 H), 2.16 (q, *J* = 99.5 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.1, 131.5, 130.8, 129.5, 128.3, 52.5, 52.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.65 (t, *J* = 101.4 Hz).

HRMS (ESI): *m*/*z* calcd $C_{13}H_{19}BNO_2$ $[M + H]^+$: 232.1503; found: 232.1500.

((4-(Trifluoromethyl)phenyl)ethynyl)borane Trimethylamine Complex (3g)

Following the general procedure using 1-methyl-4-(((4-(trifluoromethyl)phenyl)ethynyl)sulfonyl)benzene (32.4 mg, 0.1 mmol, 1.0 equiv.) gave **3g** (9.2 mg, 38%) as a yellowish oil; R_f = 0.48 [*n*-hexane/EtOAc (4:1)].

^1H NMR (600 MHz, $CDCl_3$): δ = 7.50 (s, 4 H), 2.73 (s, 9 H), 2.15 (q, *J* = 99.3 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.7, 125.2, 52.5.

^{19}F NMR (565 MHz, $CDCl_3$): δ = –62.6.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.69 (t, *J* = 101.3 Hz).

HRMS not found due to decomposition of material.

(Naphthalen-1-ylethynyl)borane Trimethylamine Complex (3h)

Following the general procedure using 1-(tosylethynyl)naphthalene (30.6 mg, 0.1 mmol, 1.0 equiv.) gave **3h** (12.5 mg, 56%) as an oil; R_f = 0.50 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.81 (d, *J* = 7.4 Hz, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.65 (dd, *J* = 7.1, 1.2 Hz, 1 H), 7.50 (dddd, *J* = 19.7, 8.1, 6.9, 1.4 Hz, 2 H), 7.38 (dd, *J* = 8.3, 7.1 Hz, 1 H), 2.79 (s, 9 H), 2.29 (dd, *J* = 198.5, 97.1 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 133.7, 133.4, 129.8, 128.2, 127.2, 126.9, 126.3, 126.1, 125.4, 123.7, 52.4.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.33 (t, *J* = 102.8 Hz).

HRMS (ESI): *m*/*z* calcd $C_{15}H_{19}BN$ [M – H]$^+$: 224.1611; found: 224.1615.

([1,1′-Biphenyl]-4-ylethynyl)borane Trimethylamine Complex (3i)

Following the general procedure using 4-(tosylethynyl)-1,1′-biphenyl (33.2 mg, 0.1 mmol, 1.0 equiv.) gave **3i** (16.9 mg, 68%) as a solid; mp 98–101 °C; R_f = 0.50 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.61–7.56 (m, 2 H), 7.50 (s, 4 H), 7.42 (t, *J* = 7.7 Hz, 2 H), 7.35–7.31 (m, 1 H), 2.74 (s, 9 H), 2.19 (q, *J* = 105.7 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.9, 139.6, 132.0, 128.9, 127.4, 127.1, 126.8, 124.9, 52.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.60.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}BNNa$ [M + Na]$^+$: 272.1581; found: 272.1577.

((4-Chlorophenyl)ethynyl)borane Trimethylamine Complex (3j)

Following the general procedure using 1-chloro-4-(tosylethynyl)benzene (29.0 mg, 0.1 mmol, 1.0 equiv.) gave **3j** (11.4 mg, 55%) as an oil; R_f = 0.52 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.1 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 2.72 (s, 9 H), 2.14 (dd, *J* = 200.9, 99.3 Hz, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 132.8, 132.7, 128.4, 124.4, 52.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.66 (t, *J* = 100.7 Hz).

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}BClN$ [M + H]$^+$: 208.1064; found: 208.1072.

((3-Fluorophenyl)ethynyl)borane Trimethylamine Complex (3k)

Following the general procedure using 1-fluoro-3-(tosylethynyl)benzene (27.5 mg, 0.1 mmol, 1.0 equiv.) gave **3k** (9.9 mg, 52%) as an oil; R_f = 0.46 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.23–7.16 (m, 2 H), 7.10 (d, *J* = 9.9 Hz, 1 H), 6.94–6.88 (m, 1 H), 2.72 (s, 9 H), 2.49–1.82 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 245.2 Hz), 129.6 (d, *J* = 8.5 Hz), 127.8 (d, *J* = 9.7 Hz), 127.4 (d, *J* = 3.0 Hz), 118.2 (d, *J* = 21.8 Hz), 114.1 (d, *J* = 21.2 Hz), 52.3.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.31 (t, *J* = 101.2 Hz).

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}BFN$ [M + H]$^+$: 192.1360; found: 192.1357.

(Thiophen-3-ylethynyl)borane Trimethylamine Complex (3l)

Following the general procedure using 3-(tosylethynyl)thiophene (26.2 mg, 0.1 mmol, 1.0 equiv.) gave **3l** (12.4 mg, 69%) as an oil; R_f = 0.46 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.19 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.09 (dd, *J* = 5.0, 1.2 Hz, 1 H), 2.70 (s, 9 H), 2.13 (d, *J* = 98.0 Hz, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 130.4, 126.7, 124.9, 124.6, 52.2.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.63.

HRMS (ESI): *m*/*z* calcd for $C_9H_{15}BNS$ [M + H]$^+$: 180.1018; found: 180.1023.

(3,3-Dimethylbut-1-yn-1-yl)borane Trimethylamine Complex (3m)

Following the general procedure using 1-((3,3-dimethylbut-1-yn-1-yl)sulfonyl)-4-methylbenzene (23.6 mg, 0.1 mmol, 1.0 equiv.) gave **3m** (8.0 mg, 52%) as an oil; R_f = 0.58 [*n*-pentane/EtOAc (6:1)].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.64 (s, 9 H), 1.96 (q, *J* = 99.2 Hz, 2 H), 1.24 (s, 9 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 52.0, 32.0, 28.2.

^{11}B NMR (193 MHz, $CDCl_3$): δ = –10.68 (t, *J* = 97.7 Hz).

HRMS (ESI): *m*/*z* calcd $C_9H_{19}BN$ [M – H]$^+$: 152.1605; found: 152.1602.

(8*R*,9*S*,13*S*,14*S*,17*R*)-17-Ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol)borane Trimethylamine Complex (3n)

Following the general procedure using the corresponding ethynyl estradiol derivative[33] **1n** (46 mg, 0.1 mmol, 1.0 equiv.) gave **3n** (9.2 mg, 24%) as an oil; R_f = 0.35 [*n*-pentane/EtOAc (4:1)].

1H NMR (600 MHz, $CDCl_3$): δ = 7.22 (d, *J* = 8.6 Hz, 1 H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1 H), 6.63 (d, *J* = 2.7 Hz, 1 H), 3.78 (s, 3 H), 2.88–2.82 (m, 2 H), 2.75 (s, 9 H), 2.40–2.33 (m, 1 H), 2.28 (ddd, *J* = 13.8, 9.7, 5.7 Hz, 1 H), 2.19 (td, *J* = 10.6, 9.7, 3.2 Hz, 1 H), 2.02 (dd, *J* = 10.9, 2.8 Hz, 1 H), 1.99 (dd, *J* = 10.9, 2.7 Hz, 1 H), 1.90–1.86 (m, 1 H), 1.83 (td, *J* = 13.1, 4.2 Hz, 1 H), 1.79–1.74 (m, 1 H), 1.74–1.69 (m, 1 H), 1.66–1.60 (m, 1 H), 1.48–1.37 (m, 4 H), 0.88 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.6, 138.1, 132.6, 126.5, 113.9, 111.7, 90.7, 85.7, 79.8, 65.4, 55.3, 49.8, 47.5, 43.9, 39.6, 39.1, 33.1, 31.7, 27.4, 26.6, 23.0, 13.0.

^{11}B NMR (192 MHz, $CDCl_3$): δ = –9.5 (br s).

HRMS (ESI): *m*/*z* calcd $C_{24}H_{37}BNO_2$ [M – H]$^+$: 382.2917; found: 382.2920.

Ni-Catalyzed Tsuji–Trost Reaction; General Procedure

An oven-dried 8 mL microwave vial equipped with a stirring bar was charged with the alkynyl amine-borane **3a** (17 mg, 0.1 mmol, 1.0 equiv.), $NiCl_2$(dppe) (8 mg, 15 µmol, 15 mol%), methyl (*E*)-(4-phenylbut-3-en-2-yl)carbonate (56 mg, 0.25 mmol, 2.5 equiv.), and KOH (17 mg, 0.3 mmol, 3.0 equiv.). The vial was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (3 ×). Anhyd and degassed 1,2-dichloroethane (0.90 mL) and H_2O (0.1 mL) were added and the mixture was allowed to stir at 100 °C in a preheated oil bath for 24 h. Then, the reaction was allowed to cool to r.t. and EtOAc (10 mL) was added. The organic phase was washed with H_2O (2 × 10 mL) and dried ($MgSO_4$). After removing the solvent in vacuo, the crude was further purified by column chromatography to give **4** as an oil (6 mg, 26%); R_f = 0.42 (*n*-pentane).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.21–7.46 (m, 10 H), 6.77 (d, *J* = 16.1 Hz, 1 H), 6.24 (dd, *J* = 6.5, 16.0 Hz, 1 H), 3.5 (m, 1 H), 1.45 (d, *J* = 7.4 Hz, 3 H).

The spectroscopic data are in accordance with the literature.[34]

Oxidation Reaction; General Procedure

Following a reported procedure,[35] an oven-dried 8 mL microwave vial equipped with a stirring bar was charged with the alkynyl amine-borane **3a** (17 mg, 0.1 mmol, 1.0 equiv.), Oxone (300 mg, 10 mmol, 10.0 equiv.), DMF (1.0 mL), and EtOH (1.0 mL). The vial was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl) and the mixture was allowed to stir at 120 °C in a preheated oil bath for 24 h. Then, the reaction was allowed to cool to rt and EtOAc (10 mL) was added. The organic phase was washed with H_2O (3 × 10 ml), brine (10 mL) and dried ($MgSO_4$). After removing the solvent in vacuo, the crude was further purified by column chromatography to give **5** as an oil (12.7 mg, 71%); R_f = 0.42 (*n*-pentane); R_f = 0.50 (*n*-pentane/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.35 (m, 2 H), 7.22–7.26 (m, 3 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 3.00 (t, *J* = 7.9 Hz, 2 H), 2.66 (t, *J* = 7.9 Hz, 2 H), 1.27 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 140.6, 128.5, 128.3, 126.3, 60.4, 36.0, 31.0, 14.2.

The spectroscopic data are in accordance with the literature.[36]

Suzuki–Miyaura Coupling; General Procedure

Adapted from a reported procedure:[25] A tube equipped with a stirring bar was charged with KOH (17 mg, 0.30 mmol, 3.0 equiv.), RuPhos (9.3 mg, 0.02 mmol, 20 mol%), $Pd_2(dba_3)$ (5 mg, 5 µmol, 5 mol%), the amine-borane **3a** (17 mg, 0.1 mmol, 1.0 equiv.), and 4-bromoanisole (47 mg, 0.25 mmol, 2.5 equiv.). The tube was capped with a Supelco aluminum crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (3 ×), then toluene–H_2O (0.8–0.2 mL; total 0.1 M) was added. The mixture was warmed to 120 °C and stirred for 24 h. The mixture was cooled to rt, diluted with brine (5 mL) and EtOAc (5 mL) and shaken vigorously. The layers were separated, and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The crude was purified by flash column chromatography on silica gel to give **6** as an oil (10.6 mg, 51%); R_f = 0.42 (*n*-pentane), R_f = 0.50 (*n*-pentane/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.44 (m, 4 H), 7.37–7.30 (m, 3 H), 6.87 (dt, *J* = 8.9, 2.7 Hz, 2 H), 3.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 133.1, 131.5, 128.3, 127.9, 123.6, 115.4, 114.0, 89.4, 88.1, 55.3.

The spectroscopic data are in accordance with the literature.[37]

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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