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Copper-Catalyzed Regiodivergent Borylation of Fluorinated Alkynes and Palladium-Catalyzed Regiospecific Suzuki-Miyaura cross-coupling

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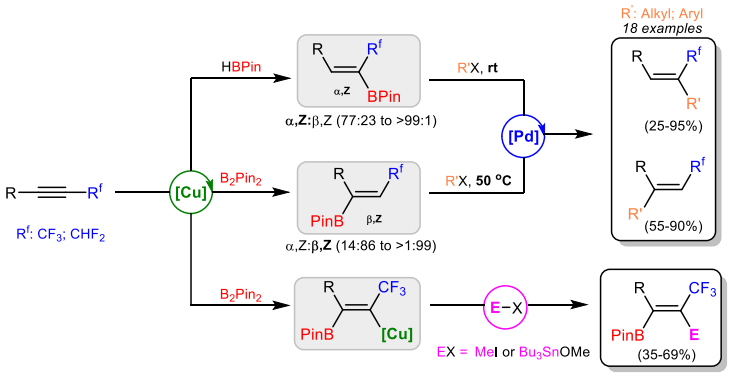
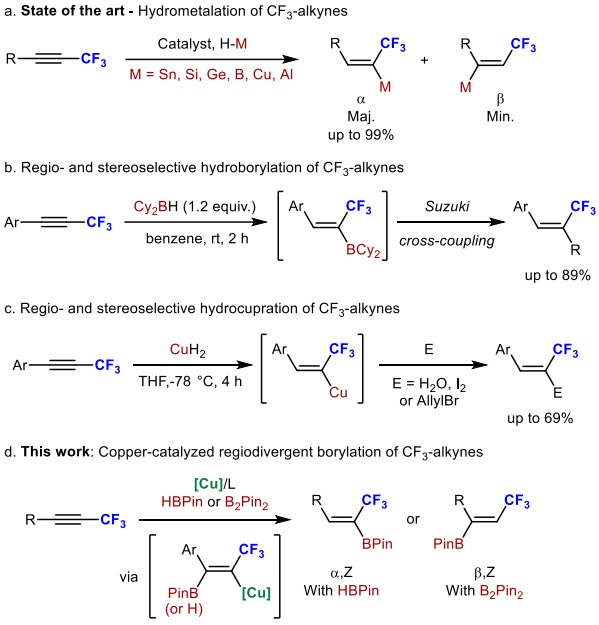


Abstract Alkenylboranes are key intermediates in modern organic synthesis, and they are usually obtained by borylation of alkynes. We report herein a highly regio- and stereoselective syntheses of α,*Z*- and β,*Z*-trifluoromethylated-alkenylboranes via copper-catalyzed borylation reactions. Further functionalization by palladium-catalyzed Suzuki-Miyaura cross-coupling have been developed and interestingly a drastic difference of reactivity between α- and β-borylated isomers has been identified.

Key words Borylation, fluorine, alkyne, copper, regiodivergent

Nowadays, the synthesis of fluorinated molecules is essential in drug discovery and crop science, with roughly 20% of the marketed drugs being fluoro-pharmaceuticals and more than 50% of agrochemicals containing at least a fluorine atom. [1] It is well established that the incorporation of fluorine or fluorinated motifs into organic molecules will modify the physicochemical properties such as lipophilicity and bioavailability for instance ; they are used as bioisosters and therefore enhance biological activities.[2] Hydrometallation reactions are key transformations in modern organic synthesis to control the stereoselectivity depending on the reaction conditions and the concomitant installation of a metal or metalloid for further functionalizations.[3] Several reports about the hydrometallation of R^f-alkynes are known in the literature such as hydrostannylation, hydrosilylation, hydrogermylation, hydroboration, hydrocupration or hydroalumination (Scheme 1,a-c).[4] Surprisingly, in all these methods the major product is formed with introduction of the metal/metalloid (M) on the C-α to the CF_3 (Scheme 1), while metalation is reversed with biased substrates such as R^f-ynoates where the metal is mainly introduced on the C-β to the R^f moiety because of reversed polarization.[5]

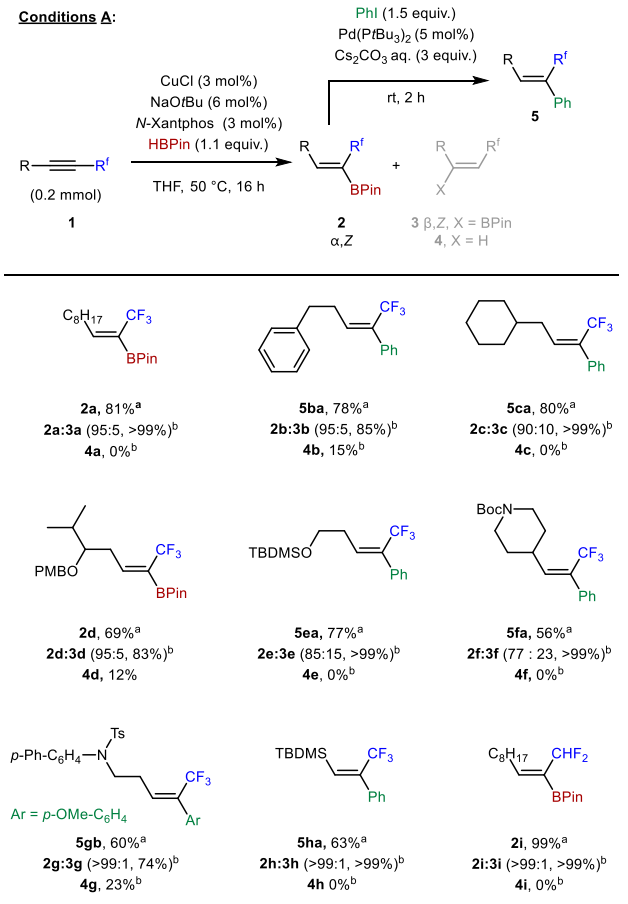


Scheme 1: Hydrometallation of CF_3-alkynes

Few years ago, we reported an efficient method for the synthesis and the use of CF_3-alkynes **1** in regioselective hydrostannylation, germylation and silylation reactions. [4i-j,6] The regioselectivity of the hydrometallation was mainly controlled by the polarization of the alkyne toward the CF_3 moiety either under palladium-catalyzed or radical conditions. More recently, we identified that less polarized alkynes such as ynamides were suitable substrates to perform palladium-catalyzed regiodivergent hydrogermylation and hydrostannylation reactions, where the regioselectivity of the metalation was controlled by the electronic and steric effects of the phosphorus ligands.[7] Unfortunately, such strategy is not applicable to CF_3-alkynes **1**, however we capitalized herein on the polarization of **1** and the high regioselectivity of the metalation on the C-α to the CF_3 to propose highly selective copper-catalyzed regiodivergent borylation

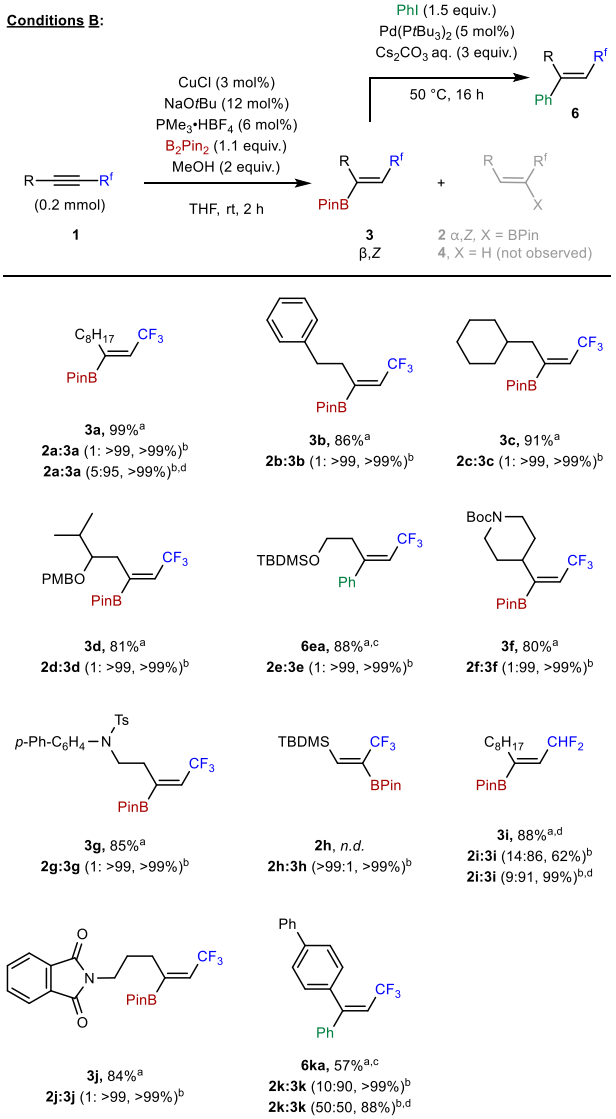
reactions of CF_3-alkynes (Scheme 1d). The strategy relies on hydrocupration and borylcupration key steps, with HBpin or B_2Pin_2 respectively, with regioselective introduction of the copper on the C-α to the CF_3 in both cases.[8] Thermal selective palladium-catalyzed Suzuki-Miyaura cross-coupling was then developed with α- or β-borylated products.

After a short screening of reaction parameters with CF_3-decyne **1a** (see supporting information for details), we optimized two sets of conditions for the regioselective introduction of pinacolborane (BPin) on the C-α or C-β to the CF_3. In condition A,[9] using CuCl (3 mol%), *N*-XantPhos (3 mol%), NaO*t*-Bu (6 mol%) and HBPin (1.1 equiv.) after 16 h at 50 °C in THF, we obtained a 95:5 **2a**:**3a** ratio with 81% isolated yield for **2a**. In condition B,[10] using CuCl (3 mol%), PMe_3•HBF_4 (6 mol%), NaO*t*-Bu (12 mol%), B_2Pin_2 (1.1 equiv.) and MeOH (2 equiv.) after 3 h at 20 °C in THF, we obtained a 1:>99 **2a**:**3a** ratio with 99% isolated yield for **3a**. Unfortunately, use of the same ligand for both conditions A and B led to lower regioselectivity, but still with a clear α:β dichotomy by using HBpin or B_2Pin_2. Noteworthy, we confirmed that no reaction takes place without catalyst, while a 50:50 **2a**:**3a** ratio was obtained in the absence of phosphorous ligand with a very low conversion. With the optimized conditions in hands, we investigated the scope and limitations with conditions A and B. In conditions A (Scheme 2), we noticed that the borylation step is moisture sensitive leading occasionally to the formation of reduced product **4**. In some cases, the α-borylated products **2**



Scheme 2: Regioselective α-borylation of R^f-alkynes. [a] Isolated yield. [b] Ratio **2**:**3** and NMR yield determined by ^{19}F and ^1H NMR with $PhCF_3$ as internal standard.

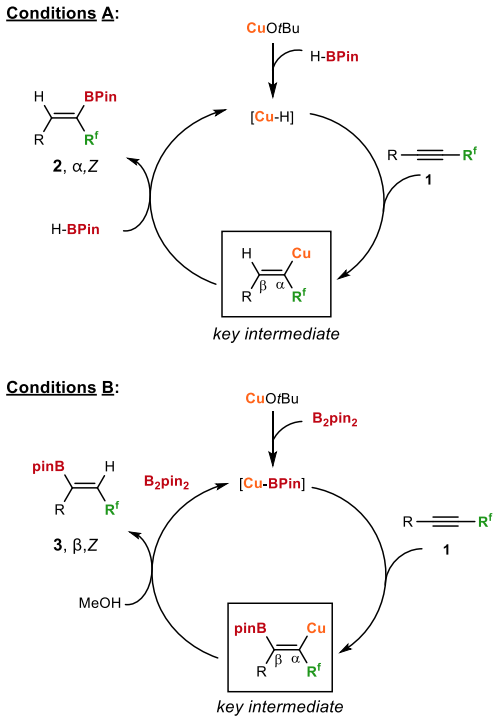
were poorly stable over purification, so we engaged the crude mixture in direct Suzuki-Miyaura cross coupling at room temperature and isolated corresponding α-arylated products **5** in good yields. Since previous reports mainly investigated aromatic substrates,[4] we mainly explored aliphatic substrates which gave mostly high selectivity ranging from 77:23 to >99:1 α,*Z*:β,*Z*. Protected alcohols (**1d-e**) or amines (**1f-g**) are well tolerated, as well as silyl groups (**1h**). Interestingly, the reaction is also compatible with the replacement of the CF_3 by a CF_2H (**1i**) delivering α,*Z* product **2i** in excellent 99% yield. An aromatic alkyne substrate was also evaluated leading to a low 55:45 α,*Z*:β,*Z* selectivity (**5ka**:**6ka**), with a significant amount of protodeborylation product **4**.[11] Conditions B (Scheme 3) were much more robust and excellent selectivities (up to >99:1) were obtained with formation of β,*Z* isomer (**3a-j**).



Scheme 3: Regioselective β-borylation of R^f-alkynes. [a] Isolated yield. [b] Ratio **2**:**3** and NMR yield determined by ^{19}F and ^1H NMR with $PhCF_3$ as internal standard. [c] Obtained after cross-coupling reaction with PhI (1.5 equiv.), Pd(P*t*Bu$_3$)$_2$ (5 mol%), Cs_2CO_3 aq. (3 equiv.), 50 °C. [d] Phox (6 mol%) was used as ligand.

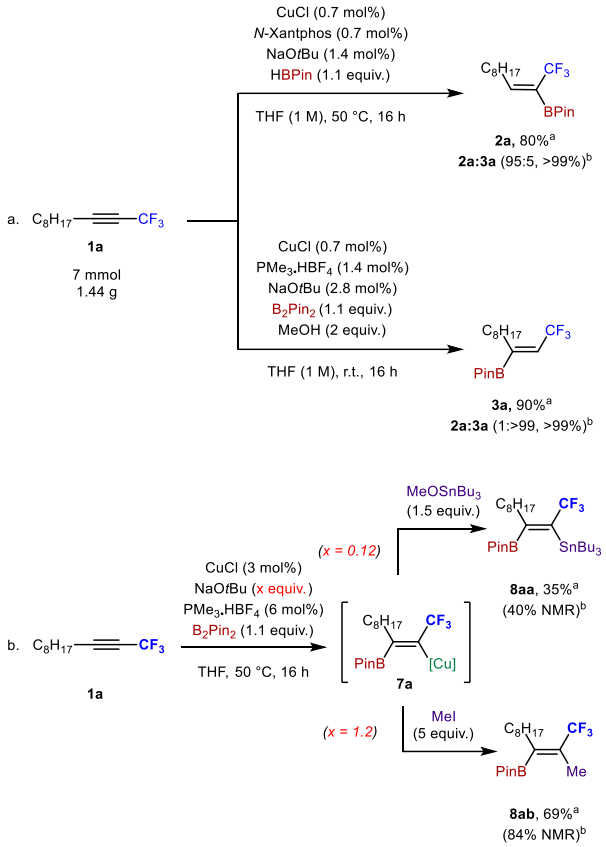
The β-arylated product **6** can be easily prepared following a similar two steps sequence, such as for **6ea** obtained in 88% over two steps. Surprisingly, reaction with silylated alkyne **1h** did not yield adduct **3h**, but only isomer **2h** was formed instead in

excellent 99% NMR yield and regioselectivity, probably because of the very hindered TBDMS group which makes the β-position poorly accessible. The regioselectivity drops a little bit with CF_2H (**3i**) in classical conditions, but it rises a bit more up to 9:91 **2i**:**3i** by replacing PMe_3 by Phox ligand. With aromatic substrates (**1k**), the BPin adducts **3** were not very robust, and a slight decrease in selectivity was observed up to 10:90 **2k**:**3k**, but the corresponding cross-coupling product **6ka** was obtained in 57% yield over two steps. In that case replacing the PMe_3 by Phox ligand was detrimental and gave a 50:50 mixture of α:β isomers. Based on previous reports,[8] we can propose the following mechanisms (Scheme 4): In both conditions, the first step is the formation of the copper active species Cu-H and Cu-BPin (condition A and B, respectively). The key intermediates are resulted from the *cis* addition of these last species to the alkyne with in both cases selective introduction of the copper on the carbon adjacent to the CF_3 (C-α). In condition A, a transmetallation with HBPin delivers compound **2** with concomitant regeneration of the active Cu-H species. In condition B, an alcoholysis with methanol generates compound **3** and Cu-BPin is regenerated by reaction of Cu-OMe with B_2Pin_2.



Scheme 4: Proposed mechanisms for the regiodivergent borylation of CF_3-alkyne.

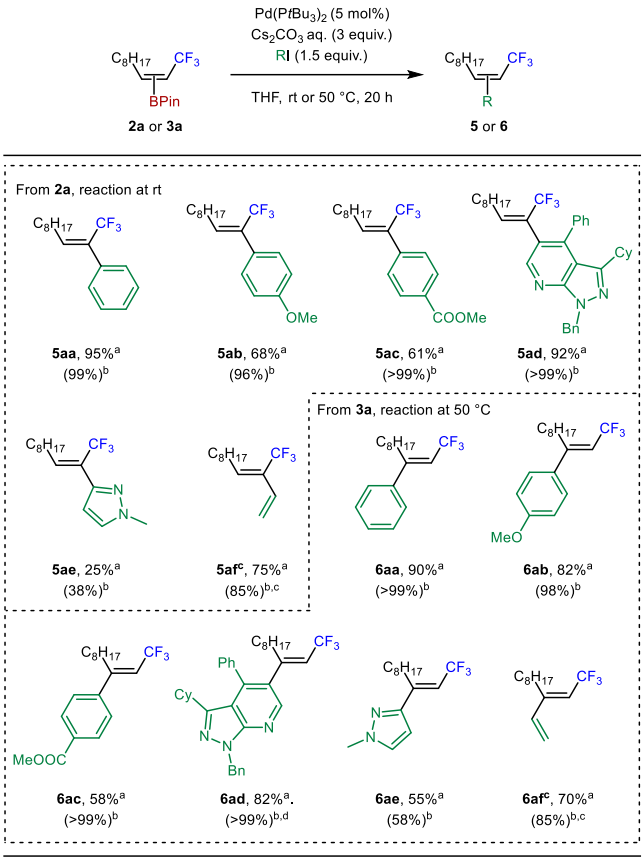
Both conditions A and B were then scaled up on gram-scale (Scheme 5,a) and the catalyst loading was even decreased to 0.7 mol% of copper without noticeable changes in term of regioselectivity and yield. We then tried to capitalize on the formation of a vinyl-copper intermediate **7** (in conditions B) and we envisaged to trap this intermediate with electrophile to generate a tetra-substituted fluorinated alkene **8** (Scheme 5,b). Thus, by replacing the methanol as proton source (condition B) by electrophiles such as $MeOSnBu_3$ or MeI, we obtained products **8aa** and **8ab** in 35% and 69% yields, respectively.[12-13]



Scheme 5: Gram scale regiodivergent borylation of CF_3-alkynes and trapping of the vinylcopper intermediate with electrophiles. [a] Isolated yield. [b] Ratio **2a**:**3a** and NMR yield determined by ^{19}F and ^{1}H NMR with $PhCF_3$ as internal standard.

Finally, we confirmed that α- and β-BPin olefins **2a** and **3a** could be easily engaged in classical Suzuki-Miyaura cross coupling (Scheme 6).[14] After a short optimization, we found that using a catalytic amount of $Pd(PtBu_3)_2$ and aqueous solution of cesium carbonate in THF was an efficient system to perform cross-coupling of both **2a** and **3a** with various aryl- and heteroaryliodides. Interestingly, both isomers react differently, α-BPin isomer (**2**) readily reacts at room temperature while at least 50 °C is needed to transform the β-BPin isomer (**3**) as confirmed by sequential regioselective cross-coupling from an equimolar mixture of **2a**:**3a** (see supporting information for details). Cross-coupling proved to be effective with electronically diverse aromatic adducts (**5aa-ac** and **6aa-ac**) in good to excellent yields. Heterocycles are also well tolerated (**5ad-ae** and **6ad-ae**). Noteworthy, introduction of 7-aza-indazole substrate in β position (**6ad**) requires to increase the reaction temperature up to 75 °C to reach a descent yield of 82%. Furthermore, the use of vinylbromide as coupling partner allowed the formation of dienes **5af** and **6af** in good yields. We propose that the difference of reactivity of **2a** and **3a** in cross-coupling reaction is mainly due to difference of electronic density of the carbon bearing the BPin in compounds **2** or **3**. Due to the high electron-withdrawing effect of CF_3 and BPin group, the C-α to the CF_3 in compound **2** is relatively electronically enriched and becomes a competent nucleophile. In contrast, the C-β to the CF_3 in compound **3** is rather electron depleted and thus a much weaker nucleophile for Suzuki–Miyaura cross-coupling, which means that the reaction

requires higher activation energy. Further studies are underway in our group to verify this hypothesis.



Scheme 6: Thermal selective palladium-catalyzed Suzuki-Miyaura cross-coupling. [a] Isolated yield. [b] NMR yield determined by ^{19}F and ^{1}H NMR with $PhCF_3$ as internal standard. [c] Vinylbromide was used as coupling partner. [d] Reaction performed at 75 °C.

In conclusion, we have developed an efficient regiodivergent copper-catalyzed borylation of polarized R^f-alkynes, thanks to regioselective hydrocupration and borylcupration key steps. We confirmed the possibility to scale-up the reactions on gram scale while decreasing the catalyst loading, and we proved that vinyl-copper intermediate could be trapped with electrophiles. Thermal selective palladium-catalyzed Suzuki-Miyaura cross-coupling was also developed to selectively functionalize α- or β-borylated olefins.

Funding Information

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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(9) General procedure condition A: In a dry Schlenk tube under nitrogen equipped with a magnetic stir bar were introduced CuCl (3 mol%, 0.6 mg, 0.006 mmol), NaOtBu (6 mol%, 1.15 mg, 0.012 mmol) and N-Xantphos (3 mol%, 3.3 mg, 0.006 mmol) in dry THF (2 mL). The reaction mixture was stirred for 30 min at room temperature. The reaction was cooled down to 0 °C and pinacolborane (1.1 equiv., 0.22 mmol, 28.2 mg) was added. The reaction mixture was stirred for 10 min, and the CF_3-alkyne **1** (1 equiv., 0.2 mmol) was then added to the solution at 0 °C. The mixture was stirred at 50 °C overnight. After completion of the reaction, the mixture was filtered through a plug of silica gel and washed with EtOAc. The solution was concentrated under reduced pressure and purified on silica gel column chromatography.
(*Z*)-4,4,5,5-Tetramethyl-2-(1,1,1-trifluoroundec-2-en-2-yl)-1,3,2-dioxaborolane 2a Prepared from 1,1,1-trifluoroundec-2-yne **1a** (41.2 mg, 0.2 mmol). The product was purified by silica gel column chromatography (petroleum ether/EtOAc 95:5) to afford **2a** (54 mg, 81 % yield) as a colorless oil. **^{1}H-NMR ($CDCl_3$, 500 MHz)**: δ (ppm) = 0.88 (t, *J* = 6.8 Hz, 3H), 1.26 - 1.33 (m, 22H), 1.42

- 1.48 (m, 2H), 2.35 - 2.41 (m, 2H), 6.79 (t, *J* = 7.6 Hz, 1H); **^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz):** δ (ppm) = 14.3, 22.8, 24.8, 28.8; 29.3, 29.5, 29.6, 30.5, 32.0, 84.2, 125.3 (q, *J* = 274.4 Hz), 128.5 (q, *J* = 32.2 Hz), 158.5 (q, *J* = 5.2 Hz); **^{19}F{^{1}H}-NMR ($CDCl_3$, 471 MHz):** - 56.2 (s, 3F); **^{11}B-NMR ($CDCl_3$, 160 MHz):** 29.1 (s, 1B); **IR spectrum (neat)** (cm^{-1}) = 2926, 2857, 1635, 1357, 1113, 983, 854, 704; **MS (ESI**): *m/z* calculated for $C_{17}H_{31}BF_3O_2^{+\bullet}$ $[M+H]^{+\bullet}$ 335.24, found 335.24.

(10) General procedure condition B: In a dry Schlenk tube under nitrogen equipped with a magnetic stir bar were introduced CuCl (3 mol%, 0.6 mg, 0.006 mmol), NaO*t*Bu (12 mol%, 2.4 mg, 0.024 mmol) and $PMe_3.HBF_4$ (6 mol%, 2.0 mg, 0.012 mmol) in dry THF (2 mL). The reaction mixture was stirred for 15 min at room temperature. The reaction is cooled down to 0 °C and bis(pinacolato)diboron (1.1 equiv., 0.22 mmol, 55.8 mg) was added to the solution. The reaction mixture was stirred for 10 min at 0 °C and then the CF_3-alkyne **1** (1 equiv., 0.2 mmol) was added, followed by MeOH (2 equiv., 0.4 mmol, 16.2 µL). The mixture was stirred at rt until full consumption of the alkyne. After completion of the reaction, the mixture was filtered through a plug of silica gel and washed with EtOAc. The solution was concentrated under reduced pressure and purified on silica gel column chromatography.

(*Z*)-4,4,5,5-Tetramethyl-2-(1,1,1-trifluoroundec-2-en-3-yl)-1,3,2-dioxaborolane 3a

Prepared from 1,1,1-trifluoroundec-2-yne **1a** (41.2 mg, 0.2 mmol). Isolated by silica gel column chromatography (PE/EtOAc 95:5) to afford **3a** (66 mg, 99 % yield) as a colorless oil. **^{1}H-NMR ($CDCl_3$, 500 MHz)**: δ (ppm) = 0.88 (t, *J* = 6.9 Hz, 3H), 1.23 - 1.31 (m, 22H), 1.35 - 1.41 (m, 2H), 2.31-2.35 (m, 2H), (q, *J* = 9.1 Hz, 1H); **^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz):** δ (ppm) = 14.3, 22.8, 24.8, 29.3, 29.5, 29.6, 29.7, 30.1, 32.0, 84.4, 123.2 (q, *J* = 273.8 Hz), 128.5 (q, *J* = 32.5 Hz), 158.5 (q, *J* = 5.0 Hz); **^{19}F{^{1}H}-NMR ($CDCl_3$, 471 MHz):):** δ (ppm) = **-** 58.3 (s, 3F); **^{11}B-NMR ($CDCl_3$, 160 MHz):** 30.1 (s, 1B); **IR spectrum (neat)** (cm^{-1}) = 2926, 1380 1339, 1263, 1111, 863, 690; **MS (ESI**): *m/z* calculated for $C_{17}H_{31}BF_3O_2^{+\bullet}$ $[M+H]^{+\bullet}$ 335.24, found 335.24.

(11) See supporting information for details.

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(14) General procedure for Suzuki-Miyaura cross-coupling: A dry Schlenk tube under nitrogen equipped with a magnetic stir bar was charged with boronic ester **2** or **3** (1 equiv., 0.2 mmol), $Pd(PtBu_3)_2$ (5 mol %, 5.1 mg), and aryl iodide (1.5 equiv., 1.5 mmol), THF (0.25 mL), Cs_2CO_3 (3 equiv., 0.6 mmol, 195.5 mg) and H_2O (60 µL). The mixture was then stirred at r.t. (with **2**) or 50 to 75 °C (with **3**) until full consumption of the boronic ester as followed by TLC and ^{19}F NMR. The mixture was quenched by addition of H_2O and extracted three times with EtOAc. Organic layers were washed with brine and dried with $MgSO_4$, filtered, concentrated under reduced pressure and purified by silica gel column chromatography delivering products **5** (from 2) or **6** (from 3).

(*Z*)-(1,1,1-Trifluoroundec-2-en-2-yl)benzene 5aa

Prepared from (*Z*)-4,4,5,5-tetramethyl-2-(1,1,1-trifluoroundec-2-en-2-yl)-1,3,2-dioxaborolane **2a** (0.15 mmol, 50.1 mg) and iodobenzene (1.5 equiv., 0.23 mmol, 25 µL). Purified by silica gel column chromatography (100% Cyclohexane) to afford **5aa** (40 mg, 95% yield) as a colorless oil. **^{1}H-NMR ($CDCl_3$, 500 MHz)**: δ (ppm) = 0.88 - 0.91 (m, 3H), 1.28 - 1.33 (m, 10H), 1.50 (quint., *J* = 7.3 Hz, 2H), 2.41 - 2.44 (qq, *J* = 7.4 Hz, *J* = 2.3 Hz, 2H), 6.03 (t, *J* = 7.7 Hz, 1H), 7.28 - 7.32 (m, 2H) 7.33 - 7.37 (m, 3H); **^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz):** δ (ppm) = 14.3, 22.8, 29.0 (q, *J* = 2.2 Hz), 29.3, 29.4, 29.5, 29.7, 32.0, 124.2 (q, *J* = 275.7 Hz), 128.1, 128.3 (2C), 131.6 (q, *J* = 29.6 Hz), 136.9 (q, *J* = 1.9 Hz), 142.6 (q, *J* = 3.2 Hz); **^{19}F-NMR ($CDCl_3$, 471 MHz):** - 57.1 (s, 3F); **IR spectrum (neat)** (cm^{-1}) = 2925, 2856, 1650, 1264, 1201, 1112, 759, 697; **HRMS (ESI**): *m/z* calculated for $C_{17}H_{23}F_3^{+\bullet}$ $[M]^{+\bullet}$ 284.1746, found 284.1741.

(*E*)-(1,1,1-Trifluoroundec-2-en-3-yl)benzene 6aa

Prepared from (*Z*)-4,4,5,5-tetramethyl-2-(1,1,1-trifluoroundec-2-en-3-yl)-1,3,2-dioxaborolane **3a** (0.15 mmol, 50 mg) and iodobenzene (1.5 equiv., 0.23 mmol, 25 µL). Purified by silica gel column chromatography (100% Cyclohexane) to afford **6aa** (38.2 mg, 90%) as a colorless oil. **^{1}H-NMR ($CDCl_3$, 500 MHz):** δ (ppm) = 0.86 (t, *J* = 7.0 Hz, 3H), 1.21 - 1.35 (m, 12H), 2.67 - 2.70 (m, 2H), 5.73 (q, *J* = 8.6 Hz, 1H), 7.34-7.39 (m, 5H); **^{13}C{^{1}H}-NMR ($CDCl_3$, 125 MHz):** δ (ppm) = 14.2, 22.8, 28.5, 29.2, 29.3, 29.6, 31.3, 31.9, 116.1 (q, *J* = 33.7 Hz), 123.8 (q, *J* = 271.0 Hz), 126.7, 128.7, 128.9, 140.2, 154.7 (q, *J* = 5.6 Hz); **^{19}F{^{1}H}-NMR ($CDCl_3$, 471 MHz):** δ (ppm) = - 56.5 (s, 3F); **IR spectrum (neat)** (cm-1) = 2626, 2856, 1650, 1263, 1110, 758, 696; **HRMS (ESI):** m/z calculated for $C_{17}H_{23}F_3^{+\bullet}$ $[M]^{+\bullet}$ 284.1746, found 284.1753.