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Selective Suzuki–Miyaura Monocouplings with Symmetrical Dibromoarenes and Aryl Ditriflates for the One-Pot Synthesis of Unsymmetrical Triaryls

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The various parameters that would permit selective Suzuki–Miyaura monocouplings of symmetrical dihaloarenes were studied. High selectivity and efficiency can be obtained for a broad range of substrates by using operationally simple conditions and widely available reagents. The 38 different examples described provide a valuable toolbox for the rapid access to unsymmetrical triaryls, as illustrated by the preparation of diarylpyridine **8**, terphenyl **9**, and diarylpyrrole **10**.

Introduction

Polyaromatic sequences are widely found in a large variety of organic compounds of both biological and physical interest. As a consequence, many procedures have been developed for their preparation. Metal-catalyzed cross-coupling reactions[1] and, most prominently, the Suzuki–Miyaura reaction[2] probably constitute the most efficient strategies to construct these scaffolds through C–C bond formation. However, the construction of an unsymmetrical triaryl requires a certain degree of discrimination between the various reactive sites. The use of two different halides or pseudohalides allows such a differentiation but often requires tedious stepwise protocols for the preparation of the starting material.[3] An alternative lies in the synthesis of a substrate bearing identical halides with different steric and/or electronic environments.[4] A simpler approach would be to use more readily available symmetrical dihaloarenes and to perform a selective monocoupling to ensure the desymmetrization of the starting material. The resulting halodiarene would then constitute a versatile platform for subsequent functionalization. Despite its apparent simplicity, only a handful of studies have been fully devoted to this strategy. In 2005, Uozumi reported that such a monoarylation of dibromoarenes could be achieved by using an amphiphilic supported palladium(II) complex and an excess of triphenylphosphine,[5] but Sherburn showed that diarylation was the preferred outcome for diiodoarenes, whereas monoarylation of dibromoarenes could be achieved by using them in excess.[6] More recently, Hu also described that the use of an excess of triphenylphosphine could efficiently favor the formation of monoarylated compounds from dibromoarenes (though this is mainly limited to *ortho*-disubstituted compounds, for which steric interactions already tend to favor the formation of a monoarylated adduct).[7] McNulty conducted a similar study on dichlorobenzenes,[8] and the Langer group developed various sets of conditions for the selective coupling of polyhalogenated substrates.[9] We have previously shown that, as electron-rich arylboronic acids react faster than their electron-poor counterparts, selective monoarylations (with indole boronic acid)[10] and one-pot simultaneous dicouplings to yield unsymmetrical adducts could be performed.[11] This latter approach can be extremely valuable for accessing biologically interesting targets such as lamellarin A4 and G,[12] ningalin B,[13] and their analogs (Figure 1).[14]

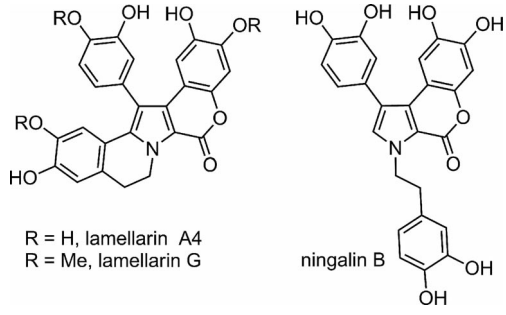

Figure 1. Natural marine triaryl compounds.

However, our one-pot procedure is somewhat limited by the necessity that each reactant has different electron density, and studies by other groups also have some limitations in terms of scope and practicality.[5,7] Indeed, a widely applicable and general strategy for this purpose is still needed by the synthetic community. In this context, we sought to study the monocoupling of various symmetrical aryl dibromides and ditriflates with a representative panel of boron derivatives to develop an efficient and operationally simple protocol that could eventually be amenable to one-pot desymmetrizing difunctionalization procedures. An ex-

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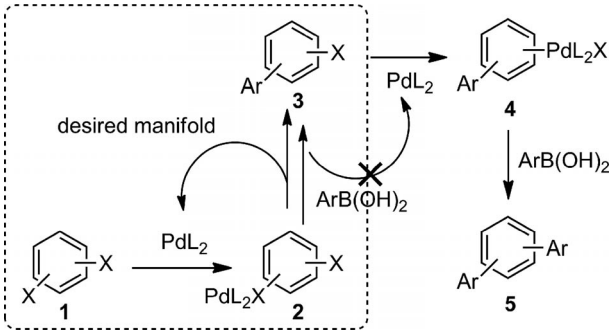
amination of the mechanism of the Suzuki–Miyaura cross-coupling reveals that a certain control over the oxidative addition is required to favor the monocoupling. Indeed, oxidative addition of the 14-electron Pd^0 complex to one of the two C–X bonds of dihalo compound **1** would give rise to complex **2** (Scheme 1). After a ligand exchange between X and a hydroxide ion, transmetallation with the boronic acid[15] followed by reductive elimination would then deliver the desired halodiaryl **3**. At this stage, the 14-electron Pd^0 species is regenerated and can either react with **1**, which is the desired manifold, or react with **3** to generate complex **4** and, thereafter, the unwanted symmetrical triaryl **5**.

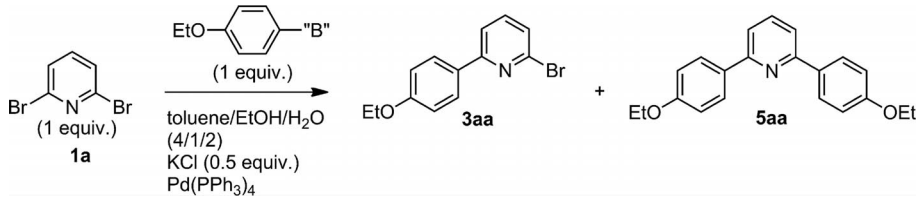


Scheme 1. Mono- vs. dicoupling.

Results and Discussion

In theory, the initial dihalo compound **1** should be slightly more reactive than the resulting monohaloarene **3** toward the oxidative addition and, thus, any factor that would render this step rate-determining would increase the chance of a selective monocoupling pathway. In addition to the properties of the dihaloarene, three parameters appeared as potentially critical and relatively flexible: the temperature, the nature of the boron species,[16] and the Pd/ligand ratio.[7] We started our study by reacting 1 equiv. of 2,6-dibromopyridine (**1a**) with 1 equiv. of *p*-ethoxyphenylboronic acid as benchmark compounds in toluene/EtOH/H_2O (4:1:2) in the presence of 8 equiv. of base (Na_2CO_3), 50 mol-% of KCl, and 0.5 mol-% of $Pd(PPh_3)_4$ (Table 1, Entry 1).[17] Tetrakis(triphenylphosphine)palladium(0) was chosen because this catalyst is widely available, quite robust, and also slowly generates the 14-electron species. Under these conditions, the monoarylated adduct **3aa** was the major product, but a significant amount of unwanted diarylpyridine **5aa** was also observed. Under the same conditions, the corresponding potassium trifluoroborate gave better results in terms of selectivity (Table 1, Entry 2). We then decided to use a slightly higher amount of catalyst but in conjunction with a twofold excess of triphenylphosphine. Thus, at a Pd/L ratio of 1:6, the amount of active 14-electron Pd^0 complex available would be lower and the oxidative addition to the more reactive dibromopyridine **1a** would be favored.[18] In this case, the boronic acid and the trifluoroborate exhibited identical reactivity and selectivity, but the 87:13 ratio observed was not entirely satisfactory (Table 1, Entries 3 and 4). We then lowered the temperature to r.t., which proved detrimental to the reactivity, as full conversion was only obtained after two days, but the selectivity was increased to 95:5 (Table 1, Entries 5 and 6). When boronic esters [both pinacol (pin) and neopentyl glycol (neopent)] were used, the selectivity was complete, but the

Table 1. Monocoupling optimization.



Entry	"B"	Pd [mol-%]	PPh_3 [mol-%]	Temp. [°C]	Na_2CO_3 [equiv.]	*t*	Conv.[a] [%]	**3/5**[a]	Yield[b] [%]
1	$B(OH)_2$	0.5	0	100	8	1.5 h	100	67:33	–
2	BF_3K	0.5	0	100	8	1.5 h	100	90:10	–
3	$B(OH)_2$	3	6	100	8	2.5 h	100	87:13	–
4	BF_3K	3	6	100	8	2.5 h	100	87:13	–
5	$B(OH)_2$	3	6	r.t.	8	2 d	100	95:5	–
6	BF_3K	3	6	r.t.	8	2 d	100	95:5	–
7	B(pin)	3	6	r.t.	8	2 d	13	100:0	–
8	B(neopent)	3	6	r.t.	8	2 d	21	100:0	–
9	$B(OH)_2$	3	6	40	8	6 h	100	91:9	–
10	BF_3K	3	6	40	8	6 h	100	95:5	–
11	B(pin)	3	6	40	8	6 h	<50	95:5	–
12	B(neopent)	3	6	40	8	6 h	<50	91:9	–
13	$B(OH)_2$	3	6	40	4	6 h	100	91:9	70
14	BF_3K	3	6	40	4	6 h	100	95:5	85
15	B(pin)	3	6	40	4	6 h	<50	95:5	42
16	B(neopent)	3	6	40	4	6 h	<50	95:5	51

[a] Determined by ^1H NMR analysis of the crude product mixtures. [b] Isolated yields.

conversion was extremely low even after 2 d (Table 1, Entries 7 and 8). To find a balance between reactivity and selectivity, the temperature was increased to 40 °C. Total reaction was now observed after 6 h, except for the boronic esters, and the selectivity remained excellent (Table 1, Entries 9–12) for all compounds. Finally, with only 4 equiv. of base (Table 1, Entries 13–16), both conversion and selectivity remained virtually unchanged, but the best yield of isolated monocoupled product was obtained with the trifluoroborate (85%; Table 1, Entry 14).

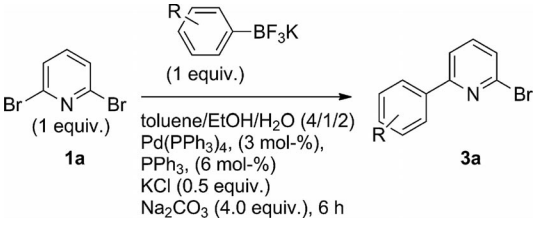
Here, the nature of the boron function plays an important role as, in our hands, potassium trifluoroborates were more conducive to higher yields. Although their advantages are now well established,[19] their robustness is crucial for selective monocouplings, as an excess of boron derivative (which could be counterproductive) is not necessary to attain high yields.

Having determined the optimal conditions for this monocoupling, we next varied the substituents of the trifluoroborate partner. We first used *para*-substituted compounds so that only electronic rather than steric effects would be at play (Table 2, Entries 1–4). Substituents with limited electronic effects such as methyl and fluoride reacted smoothly to afford the desired bromodiaryls in 69 and 70% yield. On the other hand, electron-withdrawing groups such as nitro and trifluoromethyl gave lower yields, which could not be improved by increasing the temperature to compensate for their lower reactivity. In the latter case, it is also important to note that the difference of reactivity for the oxidative addition step between the starting dibromoarene and the monocoupled product is lowered because of the electron-withdrawing nature of the newly introduced moiety; thus, the selective process is potentially disfavored. (*m*-Methoxyphenyl)trifluoroborate reacted poorly at 40 °C, but an increased temperature of 70 °C and a shorter reaction time allowed isolation of 62% of the desired compound (Table 2, Entry 5). *ortho*-Substituted boron reagents were expected to be problematic as steric effects would now be at play. Indeed, only modest yields of monocoupled product were obtained with *o*-F, *o*-OMe, and *o*-OBn phenyltrifluoroborates at 40 °C (34–53%; Table 2, Entries 6–8).

Nevertheless, an increased temperature of 70 °C allowed the steric hindrance to be overcome and led to satisfactory yields (54–70%). In this case, the loss of selectivity that could be expected at a higher reaction temperature was tempered by the addition of more triphenylphosphine and shorter reaction times. Finally, (3,4-dimethoxyphenyl)trifluoroborate was tested (Table 2, Entry 9). Although the yield was moderate at 40 °C (47%), an increased temperature of 70 °C only proved detrimental; the main issue is that the high reactivity of this compound tends to favor dicoupling.

The next step was to test these conditions with a wider range of symmetrical dibromoarenes and -heteroarenes as the electronic properties of the trifluoroborate partner were varied. First, 3,5-dibromopyridine (**1b**) was treated with 4-OEt-, 4-CH_3- and 4-NO_2-$C_6H_4BF_3K$, and the results were quite similar to those obtained with 2,6-dibromopyridine and gave moderate-to-good yields of the desired bromodiarenes (64–76%; Table 3, Entries 1–3). With *m*- (**1c**; Table 3, Entries 4–6) and *p*-dibromobenzene (**1d**; Table 3, Entries 7–9), the same trend was observed: borates substituted with

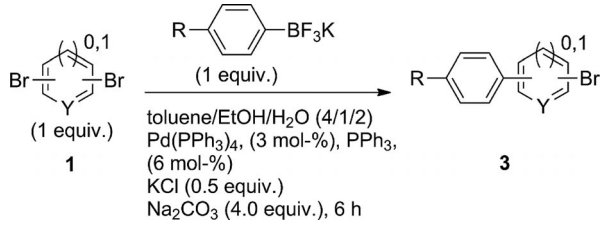
Table 2. Monocoupling of 2,6-dibromopyridine.



Entry	R	3	Temp. [°C]	Yield [%]	Temp. [°C]	Yield[a] [%]
1	4-CH_3	**3ab**	40	69	–	–
2	4-F	**3ad**	40	70	–	–
3	4-NO_2	**3ac**	40	63	100	55
4	4-CF_3	**3ae**	40	45	70	22[b]
5	3-OMe	**3af**	40	38	70	62[c]
6	2-F	**3ag**	40	44	70	54[b]
7	2-OMe	**3ah**	40	34	70	70[c]
8	2-OBn	**3ai**	40	53	70	65[b]
9	3,4-OMe	**3aj**	40	47	70	34[d]

[a] Isolated yields. [b] 4 h reaction time, 12 mol-% PPh_3. [c] 4 h reaction time. [d] 4 h reaction time, a 7:3 ratio for **3aj/5aj** was determined by analysis of the crude product by ^{1}H NMR spectroscopy.

Table 3. Monocoupling of various symmetrical dibromoarenes.



Entry	Dibromoarene	R	3	Temp. [°C]	Yield[a] [%]
1	3,5-dibromopyridine (**1b**)	OEt	**3ba**	40	76
2	**1b**	CH_3	**3bb**	40	76
3	**1b**	NO_2	**3bc**	40	64
4	1,3-dibromobenzene (**1c**)	OEt	**3ca**	40	82
5	**1c**	CH_3	**3cb**	40	77
6	**1c**	NO_2	**3cc**	40	47
7	1,4-dibromobenzene (**1d**)	OEt	**3da**	40	76
8	**1d**	CH_3	**3db**	40	73
9	**1d**	NO_2	**3dc**	40	55
10	1,2-dibromobenzene (**1e**)	OEt	**3ea**	70	49
11	**1e**	CH_3	**3eb**	70	49[b]
12	**1e**	NO_2	**3ec**	70	33
13	**1e**	OEt	**3ea**	100	74
14	**1e**	CH_3	**3eb**	100	40
15	**1e**	NO_2	**3ec**	100	49
16	2,5-dibromothiophene (**1f**)	OEt	**3fa**	70	53[c]
17	**1f**	CH_3	**3fb**	70	45[c]
18	**1f**	F	**3fd**	70	45

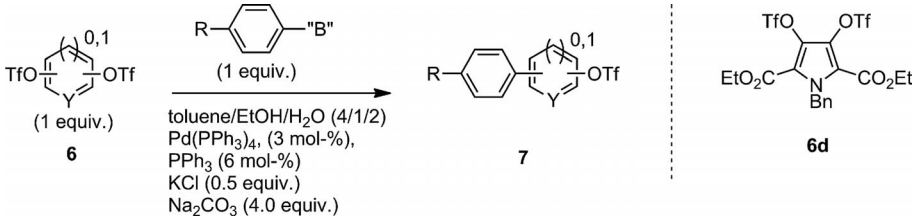
[a] Isolated yields. [b] Conversion as determined by analysis of the ^{1}H NMR spectrum: 49% of **3**, 39% of **1**, and 12% of the dicoupled product. [c] 1.5 equiv. of $ArBF_3K$.

electron-donating groups (EDGs) gave yields above 70% (Table 3, Entries 4–5 and 7–8), whereas borates substituted with electron-withdrawing groups (EWGs) led to the desired compound with yields of ca. 50% (Table 3, Entries 6 and 9). In these latter cases, a significant amount of dicoupling product was also observed. Owing to the limited electronic differentiation between the dibromo starting material and the monoarylated adduct, the product distribution tends to be roughly statistical (i.e., a 1:2:1 distribution for **1**/**3**/**5**).

For *o*-dibromobenzene (**1e**), the steric interactions, which could favor a selective monocoupling,[7] mostly proved detrimental as the reaction mixture had to be heated to 70 °C to reach moderate yields (Table 3, Entries 10–12). An increased reaction temperature of 100 °C was necessary to produce yields comparable to those obtained with **1c** and **1d**, except in the case of the tolylboronate, for which purification of the desired compound proved challenging (Table 3, Entries 13–15). Finally, 2,5-dibromothiophene (**1f**) was also tested in this reaction and, despite extensive optimization trials, only low-to-moderate yields could be attained even when an excess of the boron reagent was used (Table 3, Entries 16–18).

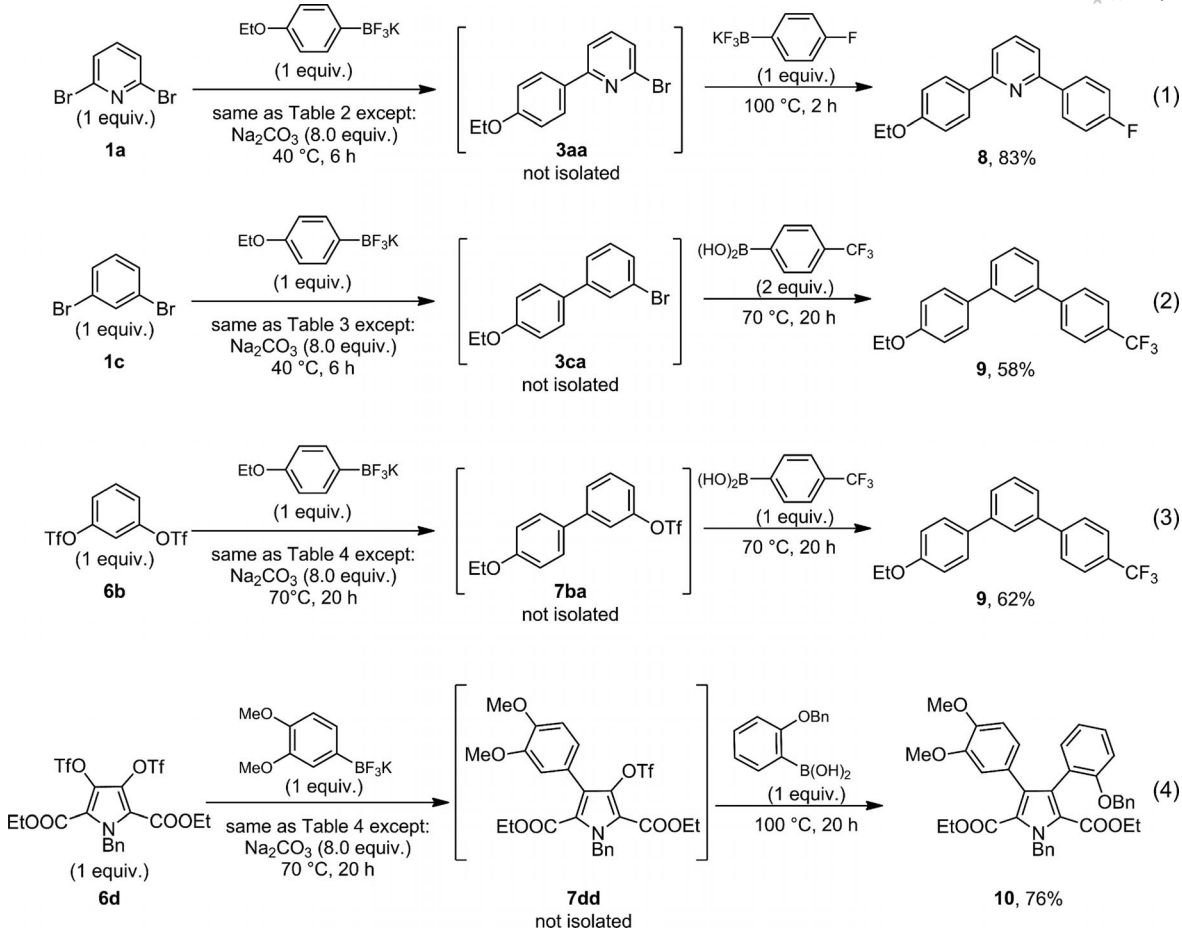
To further broaden the scope of this study, we then turned our attention to various arene ditriflates, which can generally be easily accessed from readily available diphenols and, therefore, constitute valuable synthons. We first wished to verify which boron function was the most suitable in this case. The reaction (with the same operating conditions as for the dibromoarenes) between the ditriflate **6a**, derived from hydroquinone, and different *para*-ethoxybenzeneboron derivatives (Table 4, Entries 1–4) clearly showed that the potassium trifluoroborate salt was again the optimal choice for a high-yielding mono-cross-coupling reaction (93%; Table 4, Entry 2). However, although the *p*-tolyltrifluoroborate gave a satisfactory yield of 69% (Table 4, Entry 5), the *p*-nitro derivative only led to a complex mixture (Table 4, Entry 6). Resorcinol ditriflate (**6b**) exhibited a lower reactivity, which could readily be enhanced at a higher temperature of 70 °C and a longer reaction time of 20 h to provide the *p*-OEt and *p*-Me products with good yields (Table 4, Entries 7 and 8). Even the *p*-NO_2 product was obtained with a satisfactory 57% yield under these conditions (Table 4, Entry 9). In the case of catechol ditriflate (**6c**), the same trend was observed even at 70 °C, but the yields were lower, probably because of the unfavorable steric interactions (Table 4, Entries 10–12). Finally, pyrrole **6d**, which constitutes a key starting material for lamellarin- and ningalin-like derivatives,[14] was submitted to the same reaction conditions. At 70 °C, excellent yields could be observed by NMR spectroscopy for both the *p*-OEt and the *p*-Me compound, but both products proved quite sensitive to chromatographic purification (Table 4, Entries 13 and 14). For (*p*-nitrophenyl)trifluoroborate, the desired monocoupled adduct could only be isolated in a modest 31% yield (Table 4, Entry 15). Owing to the electron-withdrawing nature of the group introduced, the monocoupled product was quite reactive as evidenced by the isolation of 34% of the dicoupled adduct, and 27% of the unreacted starting material was also recovered.

Table 4. Monocoupling optimization on ditriflates.



Entry	Arene ditriflate	B	R	7	Temp. [°C]	*t* [h]	Yield [%][a]
1	benzene-1,4-ditriflate (**6a**)	$B(OH)_2$	OEt	**7aa**	40	6	86
2	**6a**	BF_3K	OEt	**7aa**	40	6	93
3	**6a**	B(pin)	OEt	**7aa**	40	6	67
4	**6a**	B(neopent)	OEt	**7aa**	40	6	64
5	**6a**	BF_3K	CH_3	**7ab**	40	6	69
6	**6a**	BF_3K	NO_2	**7ac**	40	6	c.m.[b]
7	benzene-1,3-ditriflate (**6b**)	BF_3K	OEt	**7ba**	70	20	78
8	**6b**	BF_3K	CH_3	**7bb**	70	20	70
9	**6b**	BF_3K	NO_2	**7bc**	70	20	57
10	benzene-1,2-ditriflate (**6c**)	BF_3K	OEt	**7ca**	70	20	65
11	**6c**	BF_3K	CH_3	**7cb**	70	20	62
12	**6c**	BF_3K	NO_2	**7cc**	70	20	38
13	**6d**	BF_3K	OEt	**7da**	70	20	51 (75)[c]
14	**6d**	BF_3K	CH_3	**7db**	70	20	57 (75)[c]
15	**6d**	BF_3K	NO_2	**7dc**	70	20	31[d]

[a] Isolated yields. [b] c.m.: complex mixture. [c] Conversion as determined by ^1H NMR spectroscopy: 75% of **7**, 18% of **6**, and 7% of the dicoupled product. [d] 34% of the symmetrical dicoupled product and 27% of the starting material were isolated.



Scheme 2. One-pot synthesis of unsymmetrical triaryls.

The usefulness of the monocoupling strategy and the robustness of our conditions were ascertained by the accomplishment of one-pot desymmetrizing double Suzuki–Miyaura couplings to give the desired triaryl derivatives.[20] The optimized monocoupling conditions (with double the amount of base introduced) were first applied to dibromopyridine **1a** with potassium (*p*-ethoxyphenyl)trifluoroborate to give arylpyridine **3aa**, which was not isolated. After the requisite 6 h, potassium (*p*-fluorophenyl)trifluoroborate was added, and the reaction mixture was heated at 100 °C for 2 h. This method allowed the isolation of the unsymmetrical diarylpyridine **8** in an excellent 83% yield (Scheme 2, Equation 1). A similar procedure was then applied to 1,3-dibromobenzene **1c** (Scheme 2, Equation 2) and resorcinol ditriflate **6b** (Scheme 2, Equation 3) by using potassium (*p*-ethoxyphenyl)trifluoroborate (under the optimized conditions described in Table 3, Entry 4 for **1c** and Table 4, Entry 7 for **6b**) followed by (*p*-trifluoromethylphenyl)boronic acid. The corresponding terphenyl **9** was obtained in both cases in a satisfactory yield (58 and 62%, respectively), considering the lower reactivity of *p*-trifluoromethyl-substituted boron reagents.[21] Finally, this protocol was also implemented for pyrrole ditriflate **6d** by using potassium (3,4-dimethoxyphenyl)trifluoroborate (under the optimized conditions described in Table 4, Entry 13) followed by (*o*-benzyloxyphenyl)boronic acid to give diarylpyrrole **10** in a 76% isolated yield (Scheme 2, Equation 4).

This latter example is remarkable because it paves the way for the rapid construction of libraries of ningalin B analogs from a common platform and isolation of the unstable intermediate monotriflate is avoided; thus, the target compound can be obtained in an excellent yield.

Conclusions

We have shown that selective Suzuki–Miyaura monocross-coupling can be accomplished with a wide range of symmetrical dihaloarenes under operationally simple conditions. By adjusting several parameters such as the catalyst/ligand ratio and the temperature, the desired adducts can be obtained in good yields without elaborate ligands and/or catalyst systems or the use of an excess of the dihalo compound. A key feature that emerged from this study is that the most suitable substrates for selective coupling are the EDG-bearing arylboron derivatives. Indeed, the EDG has the doubly beneficial role of enhancing the first coupling, which can in turn be performed at a lower temperature, and of increasing the difference in reactivity between the dihaloarene and the resulting halodiaryl. This has an

impact on the order of the couplings if one wishes to introduce an EDG and an EWG on the same framework. Thus, the moiety bearing the electron-withdrawing substituent should be incorporated in a second coupling, as the lower reactivity of these compounds can then be compensated by using harsher conditions. Finally, although these selective monocouplings can grant access to many valuable synthons for further transformations, they also offer opportunities for a second Suzuki–Miyaura cross-coupling to rapidly access triaryl scaffolds. This was showcased by highly efficient desymmetrizing one-pot double Suzuki–Miyaura reactions of 2,6-dibromopyridine (**1a**), 1,3-dibromobenzene (**1c**), resorcinol ditriflate (**6b**), and 2,5-bis(ethoxycarbonyl)pyrrol-3,4-diol ditriflate (**6d**). Further efforts in this direction, including the preparation and evaluation of libraries of biologically relevant compounds, are underway in our laboratory and will be reported in due course.

Experimental Section

General Methods: Melting points were measured in capillary tubes with a Büchi B-540 apparatus. Infrared spectra were recorded with a Perkin–Elmer Spectrum BX FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with Bruker spectrometers: Avance 300 MHz (a QNP probe for ^{13}C, ^{31}P, ^{19}F or a dual ^{13}C probe) and Avance 500 MHz (BB0 ATM or BBI ATM probe). ^{13}C NMR spectra were recorded at 125 or 75 MHz by using a broadband-decoupled mode, and the multiplicities were obtained by using a JMOD or DEPT sequence. NMR experiments were performed in deuteriochloroform ($CDCl_3$), and chemical shifts (δ) are reported in parts per million (ppm) with reference to $CDCl_3$ (^{1}H: δ = 7.24 ppm; ^{13}C: δ = 77.23 ppm). The following abbreviations are used for the proton spectra multiplicities: s singlet, d doublet, t triplet, q quartet, hept heptuplet, m multiplet, br broad. Coupling constants (J) are reported in hertz [Hz]. Mass spectra were obtained either with an LCT (Micromass) instrument by electrospray ionization (ES) or from a time-of-flight analyzer (ESI-MS) for the high-resolution mass spectra (HRMS). Atmospheric pressure photoionization (APPI) spectra were obtained with an Agilent 1290 Infinity SFC instrument with a Q-ToF 6540 analyzer. Analytical thin-layer chromatography was performed with silica gel 60 F_{254} on aluminum plates (Merck), which were visualized under a UVP Mineralight UVLS-28 lamp (254 nm) and with ninhydrin and *p*-anisaldehyde stains. Preparative thin-layer chromatography was performed with silica gel 60 F_{254} (Merck, 0.5 mm). Flash chromatography was conducted with Merck silica gel 60 (40–63 μm) at medium pressure (300 mbar) or with a CombiFlash apparatus (Serlabo Technologies) with standard settings. For Suzuki–Miyaura couplings, solvents were always freshly degassed with argon. Organic extracts were dried with magnesium sulfate ($MgSO_4$). All reagents were obtained from commercial suppliers unless otherwise stated. All boronic acids were obtained from Frontier Scientific, and other boronic compounds (potassium organotrifluoroborates[19] and boronic esters)[22] were prepared by following literature procedures. Pyrrole derivatives were also synthesized according to literature procedures.[14a]

General Procedure A – Suzuki–Miyaura Monocouplings: The aryl dibromide (or aryl ditriflate, 1.0 equiv.), the boron derivative (1.0 equiv.), sodium carbonate (4.0 equiv.), potassium chloride (0.5 equiv.), and triphenylphosphine (6 mol-%) were successively introduced to a sealable tube. The tube was capped with a rubber septum and placed under an argon atmosphere. Tetrakis(triphenylphosphine)palladium(0) (3 mol-%) was then added, and a mixture of freshly degassed toluene/ethanol/water (4:1:2 v/v/v) was injected with a syringe. The septum was replaced by a screw cap, the tube was sealed, and the reaction mixture was stirred at the appropriate temperature (40–100 °C) for 6–20 h. The resulting mixture was then cooled to room temp., extracted with ethyl acetate, and washed with water. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting crude material was performed by flash silica gel chromatography or preparative TLC with an appropriate solvent system.

General Procedure B – Suzuki–Miyaura One-Pot Double Couplings: The aryl dibromide (or aryl ditriflate, 1 equiv.), the first boron derivative (1 equiv.), sodium carbonate (8 equiv.), potassium chloride (0.5 equiv.), and triphenylphosphine (6 mol-%) were successively introduced to a sealable tube. The tube was capped with a rubber septum and placed under an argon atmosphere. Tetrakis(triphenylphosphine)palladium(0) (3 mol-%) was then added, and a mixture of freshly degassed toluene/ethanol/water (4:1:2, v/v/v) was injected with a syringe. The septum was replaced by a screw cap, the tube was sealed, and the reaction mixture was stirred at the appropriate temperature (40–100 °C) for 6–20 h. The mixture was then cooled until reflux stopped, and the second boron derivative (1 equiv.) was then added. Again, the tube was sealed, and the reaction mixture was stirred at the appropriate temperature (40–100 °C) for an additional 6–20 h. The resulting mixture was then cooled to room temp., extracted with ethyl acetate, and washed with water. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting crude material was performed by flash silica gel chromatography or preparative TLC with an appropriate solvent system.

2-Bromo-6-(4-ethoxyphenyl)pyridine (3aa): Compound **3aa** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0 to 20% EtOAc in heptane) afforded **3aa** as a white powder (46 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (t, J = 6.9 Hz, 3 H), 4.06 (q, J = 6.9 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 7.31 (dd, J = 7.6, 1.0 Hz, 1 H), 7.51 (dd, J = 7.8, 7.6 Hz, 1 H), 7.58 (dd, J = 7.8, 1.0 Hz, 1 H), 7.91 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 114.8 (2 CH), 118.3 (CH), 125.6 (CH), 128.5 (2 CH), 130.2 (C), 139.1 (CH), 142.2 (C), 158.5 (C), 160.5 (C) ppm. IR (neat): $\tilde{\nu}$ = 2975, 2926, 1606, 1574, 1547, 1512, 1432, 1421, 1392, 1251, 1115, 1042, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{13}{}^{79}BrNO$ $[M + H]^+$ 278.0102; found 278.0173; calcd. for $C_{13}H_{13}{}^{81}BrNO$ $[M + H]^+$ 280.0082; found 280.0151.

2-Bromo-6-(*p*-tolyl)pyridine (3ab): Compound **3ab** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0 to 40% CH_2Cl_2 in hept-

ane) afforded **3ab** as a white powder (34 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.35 (dd, J = 7.6, 0.9 Hz, 1 H), 7.54 (dd, J = 7.7, 7.6 Hz, 1 H), 7.63 (dd, J = 7.7, 0.9 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 118.1 (CH), 126.1 (CH), 127.1 (2 CH), 129.7 (2 CH), 135.1 (C), 139.1 (CH), 140.0 (C), 142.3 (C), 158.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 3028, 2913, 2855, 1579, 1544, 1512, 1429, 1413, 1124, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{11}{}^{79}BrN$ [M + H]$^+$ 247.9997; found 248.0081; calcd. for $C_{12}H_{11}{}^{81}BrN$ [M + H]$^+$ 249.9976; found 250.0058.

2-Bromo-6-(4-nitrophenyl)pyridine (3ac): Compound **3ac** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0% to 20% EtOAc in heptane) afforded **3ac** as a yellow powder (35 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (dd, J = 7.9, 0.9 Hz, 1 H), 7.66 (dd, J = 7.7, 7.9 Hz, 1 H), 7.75 (dd, J = 7.7, 0.9 Hz, 1 H), 8.15 (d, J = 8.8 Hz, 2 H), 8.29 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.0 (CH), 124.2 (2 CH), 128.0 (2 CH), 128.2 (CH), 139.5 (CH), 142.8 (C), 143.6 (C), 148.7 (C), 156.0 (C) ppm. IR (neat): $\tilde{\nu}$ = 3110, 3085, 2962, 1507, 1343, 1259, 1087, 1047, 1012, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_8{}^{79}BrN_2O_2$ [M + H]$^+$ 278.9691; found 278.9787; calcd. for $C_{11}H_8{}^{81}BrN_2O_2$ [M + H]$^+$ 280.9670; found 280.9781.

2-Bromo-6-(4-fluorophenyl)pyridine (3ad): Compound **3ad** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-fluorophenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6.0 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3.0 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3ad** as a white powder (35 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (t, J = 8.8 Hz, 2 H), 7.38 (dd, J = 7.5, 1.1 Hz, 1 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.61 (dd, J = 7.5, 1.1 Hz, 1 H), 7.96 (dd, J = 8.8, 5.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.0 (d, J = 21.8 Hz, 2 CH), 118.8 (CH), 126.5 (CH), 129.1 (d, J = 8.7 Hz, 2 CH), 134.0 (d, J = 2.9 Hz, C), 139.3 (CH), 142.4 (C), 157.7 (C), 164.1 (d, J = 247.6 Hz, C) ppm. IR (neat): $\tilde{\nu}$ = 3079, 2924, 1596, 1578, 1547, 1508, 1428, 1414, 1386, 1227, 1124, 851, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_8{}^{79}BrFN$ [M + H]$^+$ 251.9746; found 251.9834; calcd. for $C_{11}H_8{}^{81}BrFN$ [M + H]$^+$ 253.9725; found 253.9808.

2-Bromo-6-[4-(trifluoromethyl)phenyl]pyridine (3ae): Compound **3ae** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-trifluoromethylphenyl)trifluoroborate (50 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (10% EtOAc in heptane) afforded **3ae** as a white powder (27 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dd, J = 7.7, 1.0 Hz, 1 H), 7.62 (t, J = 7.7 Hz, 1 H), 7.67–7.73 (m, 3 H), 8.09 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.6 (CH), 124.5 (q, J = 270.5 Hz, CF_3), 126.0 (q, J = 3.8 Hz, 2 CH), 127.5 (2 CH), 127.6 (CH), 132.2 (q, J = 47.5 Hz, C), 138.3 (C), 139.4 (CH), 141.1 (C), 142.7 (C) ppm. IR (neat): $\tilde{\nu}$ = 3079, 2927, 1575, 1551, 1432, 1312, 1110, 1072, 848, 793, 747 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_8{}^{79}BrF_3N$ [M + H]$^+$ 301.9714; found 301.9814; calcd. for $C_{12}H_8{}^{81}BrF_3N$ [M + H]$^+$ 303.9693; found 303.9799.

2-Bromo-6-(3-methoxyphenyl)pyridine (3af): Compound **3af** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (3-methoxyphenyl)trifluoroborate (43 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C for 4 h. After extraction, purification of the crude material by preparative TLC (30% CH_2Cl_2 in heptane) afforded **3af** as a white powder (32 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 6.93–6.99 (m, 1 H), 7.34 (d, J = 7.7 Hz, 1 H), 7.39 (d, J = 7.7 Hz, 1 H), 7.45–7.58 (m, 2 H), 7.58 (d, J = 7.7 Hz, 1 H), 7.65 (d, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6 (CH_3), 112.5 (CH), 115.8 (CH), 119.4 (CH), 119.6 (CH), 126.7 (CH), 130.0 (CH), 139.2 (CH), 139.3 (C), 142.3 (C), 158.6 (C), 160.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 3074, 2934, 2835, 1575, 1549, 1424, 1217, 1123, 1037, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{11}{}^{79}BrNO_2$ [M + H]$^+$ 263.9946; found 264.0012; calcd. for $C_{12}H_{11}{}^{81}BrNO_2$ [M + H]$^+$ 265.9925; found 266.0001.

2-Bromo-6-(2-fluorophenyl)pyridine (3ag): Compound **3ag** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (2-fluorophenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (6.0 mg, 12 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C for 4 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3ag** as a white powder (27 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (ddd, J = 11.6, 7.9, 1.2 Hz, 1 H), 7.23 (td, J = 7.9, 1.2 Hz, 1 H), 7.31–7.39 (m, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.57 (t, J = 7.9 Hz, 1 H), 7.76 (dd, J = 7.9, 1.9 Hz, 1 H), 8.01 (td, J = 7.9, 1.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.4 (d, J = 23.0 Hz, CH), 123.4 (d, J = 10.4 Hz, CH), 124.8 (d, J = 3.1 Hz, CH), 127.0 (CH), 131.3 (d, J = 12.1 Hz, CH), 131.4 (CH), 138.9 (CH), 142.1 (C), 154.3 (C), 154.5 (C), 160.7 (d, J = 251.1 Hz, C) ppm. IR (neat): $\tilde{\nu}$ = 3075, 2922, 1575, 1547, 1493, 1434, 1393, 1211, 1111, 802, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_8{}^{79}BrFN$ [M + H]$^+$ 251.9746; found 251.9818; calcd. for $C_{11}H_8{}^{81}BrFN$ [M + H]$^+$ 253.9725; found 253.9798.

2-Bromo-6-(2-methoxyphenyl)pyridine (3ah): Compound **3ah** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (2-methoxyphenyl)trifluoroborate (43 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C for 4 h. After extraction, purification of the crude material by preparative TLC (30% CH_2Cl_2 in heptane) afforded **3ah** as a white powder (37 mg, 70%). ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 6.92 (dd, J = 8.0, 0.7 Hz, 1 H), 7.00 (td, J = 7.9, 1.2 Hz, 1 H), 7.30 (dd, J = 8.0, 0.7 Hz, 1 H), 7.31 (td, J = 7.9, 1.9 Hz, 1 H), 7.47 (t, J = 7.9 Hz, 1 H), 7.78 (dd, J = 7.9, 1.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.8 (CH_3), 111.6 (CH), 121.37 (CH), 124.1 (CH), 126.1 (CH), 127.0 (C), 130.8 (CH), 131.6 (CH), 138.2 (CH), 141.6 (C), 146.9 (C), 157.2 (C) ppm. IR (neat): $\tilde{\nu}$ = 2936, 2837, 1573, 1427, 1239, 1124, 1032, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{11}{}^{79}BrNO$ [M + H]$^+$ 263.9946; found 264.0042; calcd. for $C_{12}H_{11}{}^{81}BrNO$ [M + H]$^+$ 265.9925; found 266.0013.

2-[2-(Benzyloxy)phenyl]-6-bromopyridine (3ai): Compound **3ai** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (2-benzyloxyphenyl)trifluoroborate (58 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 12 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C for 4 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3ai** as a white powder (44 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.12 (s, 2 H), 7.07 (dd, J = 8.3, 0.7 Hz, 1 H), 7.12 (td, J = 7.7, 1.1 Hz, 1 H), 7.25–7.40 (m, 7 H), 7.52 (t, J = 7.7 Hz, 1 H), 7.89 (dd, J = 7.7, 1.7 Hz, 1 H), 7.90 (dd, J = 7.7, 0.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.9 (CH_2), 113.3 (CH), 121.7 (CH), 124.2 (CH), 126.1 (CH), 126.7 (C), 127.3 (2 CH), 128.1 (CH), 128.7 (2 CH), 130.7 (CH), 131.7 (CH), 137.0 (C), 138.2 (CH), 141.6 (C), 156.4 (C), 157.2 (C) ppm. IR (neat): $\tilde{\nu}$ = 2923, 2854, 1600, 1573, 1428, 1391, 1127, 1007, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{15}{}^{79}BrNO$ [M + H]$^+$ 340.0259; found 340.0314; calcd. for $C_{18}H_{15}{}^{81}BrNO$ [M + H]$^+$ 342.0296; found 342.0238.

2-Bromo-6-(3,4-dimethoxyphenyl)pyridine (3aj): Compound **3aj** was prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (2,4-dimethoxyphenyl)trifluoroborate (49 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% EtOAc in heptane) afforded **3aj** as a white powder (28 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.92 (s, 3 H), 6.86 (d, J = 8.3 Hz, 1 H), 7.27 (dd, J = 7.7, 1.0 Hz, 1 H), 7.40–7.50 (m, 2 H), 7.52–7.57 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.2 (CH_3), 56.3 (CH_3), 110.2 (CH), 111.2 (CH), 118.5 (CH), 119.9 (CH) 125.8 (CH), 130.8 (C), 139.1 (CH), 142.2 (C), 149.5 (C), 150.7 (C), 158.4 (C) ppm. IR (neat): $\tilde{\nu}$ = 3001, 2959, 2934, 2835, 1546, 1513, 1420, 1254, 1170, 1022, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{13}{}^{79}BrNO_2$ [M + H]$^+$ 294.0051; found 294.0130; calcd. for $C_{13}H_{13}{}^{81}BrNO_2$ [M + H]$^+$ 296.0031; found 296.0112.

3-Bromo-5-(4-ethoxyphenyl)pyridine (3ba): Compound **3ba** was prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0 to 20% EtOAc in heptane) afforded **3ba** as a white powder (42 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.0 Hz, 3 H), 4.02 (q, J = 7.0 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.90–7.96 (m, 1 H), 8.23–9.07 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.9 (CH_2), 115.4 (3 CH), 128.5 (3 CH), 128.7 (C), 136.6 (CH), 146.1 (C), 148.7 (C), 159.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 2975, 2926, 1606, 1575, 1547, 1512, 1433, 1421, 1392, 1251, 1115, 1045, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{13}{}^{79}BrNO$ [M + H]$^+$ 278.0102; found 278.0120; calcd. for $C_{13}H_{13}{}^{81}BrNO$ [M + H]$^+$ 280.0082; found 280.0113.

3-Bromo-5-(4-methylphenyl)pyridine (3bb): Compound **3bb** was prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0 to 20% EtOAc in heptane) afforded **3bb** as a white powder (37 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.27 (d, J = 8.1 Hz, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.97–7.98 (m, 1 H), 8.61 (s, 1 H), 8.72 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 121.1 (C), 127.2 (2 CH), 130.1 (2 CH), 133.6 (C), 136.8 (CH), 138.4 (C), 139.0 (C), 146.4 (CH), 149.2 (CH) ppm. IR (neat): $\tilde{\nu}$ = 3024, 2917, 2854, 1739, 1433, 1377, 1218, 1107, 1008, 825 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{11}{}^{79}BrN$ [M + H]$^+$ 247.9997; found 248.0088; calcd. for $C_{12}H_{11}{}^{81}BrN$ [M + H]$^+$ 249.9976; found 250.0066.

3-Bromo-5-(4-nitrophenyl)pyridine (3bc): Compound **3bc** was prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by flash chromatography on silica gel (0% to 20% EtOAc in heptane) afforded **3bc** as a yellow powder (31 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.8 Hz, 2 H), 8.10 (t, J = 2.0 Hz, 1 H), 8.34 (d, J = 8.8 Hz, 2 H), 8.77 (dd, J = 15.7, 2.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.6 (C), 124.8 (2 CH), 128.4 (2 CH), 136.4 (C), 138.0 (CH), 142.5 (C), 145.9 (CH), 148.4 (C), 150.4 (CH) ppm. IR (neat): $\tilde{\nu}$ = 3109, 3085, 2963, 1511, 1343, 1259, 1089, 1047, 1015, 790 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_8{}^{79}BrN_2O_2$ [M + H]$^+$ 278.9691; found 278.9761; calcd. for $C_{11}H_8{}^{81}BrN_2O_2$ [M + H]$^+$ 280.9670; found 280.9768.

1-Bromo-3-(4-ethoxyphenyl)benzene (3ca): Compound **3ca** was prepared according to general procedure A by reacting 1,3-dibromobenzene (24 μL, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6.0 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3ca** as a white powder (45 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.0 Hz, 3 H), 3.99 (q, J = 7.0 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 7.15–7.22 (m, 1 H), 7.30–7.38 (m, 2 H), 7.40 (d, J = 8.8 Hz, 2 H), 7.61 (t, J = 1.9 Hz, 1 H) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.7 (CH_2), 115.0 (2 CH), 123.1 (C), 125.5 (CH), 128.3 (2 CH), 129.7 (CH), 129.9 (CH), 130.4 (CH), 132.2 (C), 143.2 (C), 159.1 (C) ppm. IR (neat): $\tilde{\nu}$ = 2977, 2929, 1606, 1579, 1469, 1393, 1251, 1188, 1047, 790 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{13}{}^{79}BrO$ $[M]^+$ 276.0150; found 276.0166; calcd. for $C_{14}H_{13}{}^{81}BrO$ $[M]^+$ 278.0129; found 278.0147.

1-Bromo-3-(4-methylphenyl)benzene (3cb): Compound **3cb** was prepared according to general procedure A by reacting 1,3-dibromobenzene (24 μL, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3cb** as a beige powder (38 mg, 77%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.19–7.25 (m, 2 H), 7.27 (d, J = 7.9 Hz, 1 H), 7.39–7.44 (m, 3 H), 7.45–7.49 (m, 1 H), 7.69 (t, J = 1.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 123.1 (C), 125.7 (CH), 127.1 (2 CH), 129.8 (2 CH), 130.1 (CH), 130.2 (CH), 130.4 (CH), 137.0 (C), 138.0 (C), 143.5 (C) ppm. IR (neat): $\tilde{\nu}$ = 3032, 2857, 1555, 1467, 1450, 1030, 822, 790 cm^{-1}. HRMS (APPI): calcd. for $C_{13}H_{11}{}^{79}Br$ $[M]^+$ 246.0044; found 246.0032; calcd. for $C_{13}H_{11}{}^{81}Br$ $[M]^+$ 248.0024; found 248.0013.

1-Bromo-3-(4-nitrophenyl)benzene (3cc): Compound **3cc** was prepared according to general procedure A by reacting 1,3-dibromobenzene (24 μL, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3cc** as a beige powder (26 mg, 47%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (dd, J = 7.9, 7.6 Hz, 1 H), 7.49–7.59 (m, 2 H), 7.69 (d, J = 8.8 Hz, 2 H), 7.75 (t, J = 1.8 Hz, 1 H), 8.29 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.5 (C), 124.4 (2 CH), 126.2 (CH), 128.1 (2 CH), 130.7 (CH), 130.9 (CH), 131.6 (C), 132.1 (CH), 141.1 (C), 146.2 (C) ppm. IR (neat): $\tilde{\nu}$ = 2988, 2901, 1511, 1406, 1394, 1343, 1242, 1074, 1056, 854 cm^{-1}. MS: no ionization could be observed for this compound.

1-Bromo-4-(4-ethoxyphenyl)benzene (3da): Compound **3da** was prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3da** as a white powder (42 mg, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3 H), 4.06 (q, J = 7.0 Hz, 2 H), 6.95 (d, J = 8.6 Hz, 2 H), 7.39 (d, J = 8.6 Hz, 2 H), 7.46 (d, J = 8.6 Hz, 2 H), 7.51 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (CH_3), 63.6 (CH_2), 114.9 (2 CH), 120.7 (C), 127.7 (C), 128.0 (2 CH), 128.3 (2 CH), 131.8 (2 CH), 139.8 (C), 158.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 2980, 2929, 1738, 1604, 1475, 1390, 1283, 1248, 1197, 1045, 815, 800 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{13}{}^{79}BrO$ $[M]^+$ 276.0150; found 276.0134; calcd. for $C_{14}H_{13}{}^{81}BrO$ $[M]^+$ 278.0129; found 278.0115.

1-Bromo-4-(4-methylphenyl)benzene (3db): Compound **3db** was prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3db** as a white powder (36 mg, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.23 (d, J = 8.2 Hz, 2 H), 7.42 (d, J = 8.6 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H), 7.52 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 121.4 (C), 127.0 (2 CH), 128.8 (2 CH), 129.7 (C), 140.3 (C), 129.8 (2 CH), 132.0 (2 CH), 137.7 (C) ppm. IR (neat): $\tilde{\nu}$ = 3030, 2855, 1555, 1462, 1450, 1025, 821, 790 cm^{-1}. HRMS (APPI): calcd. for $C_{13}H_{11}{}^{79}Br$ $[M]^+$ 246.0044; found 246.0064; calcd. for $C_{13}H_{11}{}^{81}Br$ $[M]^+$ 248.0024; found 248.0044.

1-Bromo-4-(4-nitrophenyl)benzene (3dc): Compound **3dc** was prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **3dc** as a beige powder (30 mg, 55%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.8 Hz, 2 H), 7.61 (d, J = 8.8 Hz, 2 H), 7.69 (d, J = 8.8 Hz, 2 H), 8.28 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.7 (C), 124.5 (2 CH), 127.9 (2 CH), 129.1 (2 CH), 132.6 (2 CH), 137.9 (C), 146.6 (C), 147.5 (C) ppm. IR (neat): $\tilde{\nu}$ = 2998, 2951, 1509, 1406, 1394, 1346, 1245, 1074, 1056, 871 cm^{-1}. MS: no ionization could be observed for this compound.

1-Bromo-2-(4-ethoxyphenyl)benzene (3ea): Compound **3ea** was prepared according to general procedure A by reacting 1,2-dibromobenzene (24 μL, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 100 °C for 6 h. After extraction, purification of the crude material by preparative TLC (10% EtOAc in heptane) afforded **3ea** as a white powder (41 mg, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3 H), 4.07 (q, J = 7.0 Hz, 2 H), 6.94 (d, J = 8.7 Hz, 2 H), 7.10–7.20 (m, 1 H), 7.27–7.31 (m, 2 H), 7.32 (d, J = 8.7 Hz, 2 H), 7.64 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.7 (CH_2), 114.1 (2 CH), 123.1 (C), 127.5 (CH), 128.6 (CH), 130.7 (2 CH), 131.6 (CH), 133.3 (CH), 133.6 (C), 142.5 (C), 158.7 (C) ppm. IR (neat): $\tilde{\nu}$ = 2971, 2925, 1601, 1570, 1469, 1393, 1251, 1181, 1044, 790 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{13}{}^{78}BrO$ $[M]^+$ 276.0150; found 276.0135; calcd. for $C_{14}H_{13}{}^{81}BrO$ $[M]^+$ 278.0129; found 278.0115.

1-Bromo-2-(4-methylphenyl)benzene (3eb): Compound **3eb** was prepared according to general procedure A by reacting 1,2-dibromobenzene (24 μL, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palla-

dium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 100 °C for 6 h. After extraction, purification of the crude material by preparative TLC (4% CH_2Cl_2 in heptane) afforded **3eb** as a white powder (20 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 7.17–7.24 (m, 1 H), 7.27–7.30 (m, 1 H), 7.31–7.41 (m, 4 H), 7.69 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 122.9 (C), 127.5 (CH), 128.7 (CH), 128.9 (2 CH), 129.5 (2 CH), 131.5 (CH), 133.3 (CH), 137.6 (C), 138.4 (C), 142.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 3029, 2847, 1551, 1459, 1450, 1025, 817, 790 cm^{-1}. HRMS (APPI): calcd. for $C_{13}H_{11}{}^{78}Br$ $[M]^+$ 246.0044; found 246.0036; calcd. for $C_{13}H_{11}{}^{81}Br$ $[M]^+$ 248.0024; found 248.0017.

1-Bromo-2-(4-nitrophenyl)benzene (3ec): Compound **3ec** was prepared according to general procedure A by reacting 1,2-dibromobenzene (24 µL, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 100 °C for 6 h. After extraction, purification of the crude material by preparative TLC (10% EtOAc in heptane) in heptane afforded **3ec** as a white powder (27 mg, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.34 (m, 2 H), 7.40 (ddd, J = 8.0, 6.8, 1.1 Hz, 1 H), 7.57 (d, J = 8.8 Hz, 2 H), 7.69 [dd, (d, J = 8.0, 1.1 Hz, 1 H)], 8.28 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.0 (C), 123.3 (2 CH), 127.7 (CH), 129.9 (CH), 130.5 (2 CH), 130.9 (CH), 133.5 (CH), 140.4 (C), 147.5 (C), 153.5 (C) ppm. IR (neat): $\tilde{\nu}$ = 2985, 2888, 1509, 1401, 1394, 1340, 1242, 1074, 1045, 844 cm^{-1}. MS: no ionization could be observed for this compound.

2-Bromo-5-(4-ethoxyphenyl)thiophene (3fa): Compound **3fa** was prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (69 mg, 0.3 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by flash chromatography on neutral alumina gel [2% methyl *tert*-butyl ether (MTBE) in heptane] afforded **3fa** as a white powder (30 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.0 Hz, 3 H), 4.03 (q, J = 7.0 Hz, 2 H), 6.84–6.92 (m, 3 H), 6.97 (d, J = 3.9 Hz, 1 H), 7.40 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 110.3 (C), 115.2 (2 CH), 122.3 (CH), 126.6 (C), 127.2 (2 CH), 130.9 (CH), 146.1 (C), 159.1 (C) ppm. IR (neat): $\tilde{\nu}$ = 2997, 2896, 1618, 1400, 1254, 1164, 1015 cm^{-1}. HRMS (APPI): calcd. for $C_{12}H_{11}{}^{79}BrOS$ $[M]^+$ 281.9714; found 281.9732; calcd. for $C_{12}H_{11}{}^{81}BrOS$ $[M]^+$ 283.9694; found 283.9711.

2-Bromo-5-(4-methylphenyl)thiophene (3fb): Compound **3fb** was prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (60 mg, 0.3 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (100% heptane) afforded **3fb** as a white powder (23 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.00 (br s, 2 H), 7.16 (d, J = 8.1 Hz, 2 H), 7.39 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 110.9 (C), 122.9 (CH), 125.7 (2 CH), 129.9 (2 CH), 130.9 (CH), 131.1 (C), 138.1 (C), 146.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 2994, 1510, 1441, 1394, 1074, 1045 cm^{-1}. HRMS (APPI): calcd. for $C_{11}H_9{}^{79}BrS$ $[M]^+$ 251.9608; found 251.9637; calcd. for $C_{11}H_9{}^{81}BrS$ $[M]^+$ 253.9598; found 253.9616.

2-Bromo-5-(4-fluorophenyl)thiophene (3fd): Compound **3fd** was prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol) with potassium (4-fluorophenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (2% MTBE in heptane) afforded **3fd** as a white powder (23 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89–7.19 (m, 4 H), 7.39–7.60 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.3 (C), 116.1 (d, J = 21.8 Hz, 2 CH), 123.5 (CH), 127.4 (d, J = 8.1 Hz, 2 CH), 130.0 (d, J = 3.2 Hz, C), 131.1 (CH), 145.0 (C), 162.5 (d, J = 246.5 Hz, C) ppm. IR (neat): $\tilde{\nu}$ = 3082, 1613, 1381, 1394, 1170, 1037, 865 cm^{-1}. HRMS (APPI): calcd. for $C_{10}H_6{}^{79}BrFS$ $[M]^+$ 255.9358; found 255.9386; calcd. for $C_{10}H_6{}^{81}BrFS$ $[M]^+$ 257.9364; found 257.9337.

4-(4-Ethoxyphenyl)phenyl Trifluoromethanesulfonate (7aa): Compound **7aa** was prepared according to general procedure A by reacting 1,4-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **7aa** as a white powder (64 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3 H), 4.07 (q, J = 7.0 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H), 7.29 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.9 Hz, 2 H), 7.58 (d, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 115.2 (2 CH), 119.1 (q, J = 321.3 Hz, CF_3), 121.8 (2 CH), 128.4 (2 CH), 128.5 (2 CH), 131.8 (C), 141.6 (C), 148.7 (C), 159.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 2988, 2902, 1604, 1491, 1422, 1394, 1209, 1150, 1044, 817 cm^{-1}. HRMS (APPI): calcd. for $C_{15}H_{13}F_3O_4S$ $[M]^+$ 346.0487; found 346.0469.

4-(4-Methylphenyl)phenyl Trifluoromethanesulfonate (7ab): Compound **7ab** was prepared according to general procedure A by reacting 1,4-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. After extraction, purification of the crude material by preparative TLC (0 to 20% CH_2Cl_2 in heptane) afforded **7ab** as a white powder (44 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 7.24–7.27 (m, 2 H), 7.34 (d, J = 8.8 Hz, 2 H), 7.47 (d, J = 8.2 Hz, 2 H), 7.64 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 118.9 (q, J = 321.0 Hz, CF_3), 121.6 (2 CH), 127.0 (2 CH), 128.6 (2 CH), 129.7 (2 CH), 136.4 (C), 138.0 (C), 141.6 (C), 148.7 (C) ppm. IR (neat): $\tilde{\nu}$ = 2930, 1493, 1425, 1190, 1050,

810 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{11}F_3O_3S$ $[M]^+$ 316.0381; found 316.0369.

3-(4-Ethoxyphenyl)phenyl Trifluoromethanesulfonate (7ba): Compound **7ba** was prepared according to general procedure A by reacting 1,3-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (0 to 20% CH_2Cl_2 in heptane) afforded **7ba** as a white powder (54 mg, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3 H), 4.07 (q, J = 7.0 Hz, 2 H), 6.97 (d, J = 8.9 Hz, 2 H), 7.18 (ddd, J = 8.0, 2.3, 1.0 Hz, 1 H), 7.40–7.44 (m, 1 H), 7.48 (d, J = 8.9 Hz, 2 H), 7.44–7.49 (m, 1 H), 7.52–7.58 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 115.2 (2 CH), 119.0 (q, J = 320.3 Hz, CF_3), 119.3 (CH), 119.6 (CH), 126.7 (CH), 128.4 (2 CH), 130.6 (CH), 131.5 (C), 143.8 (C), 150.3 (C), 159.5 (C) ppm. IR (neat): $\tilde{\nu}$ = 2988, 2902, 1604, 1491, 1422, 1394, 1209, 1150, 1044, 817 cm^{-1}. HRMS (APPI): calcd. for $C_{15}H_{13}F_3O_4S$ $[M]^+$ 346.0487; found 346.0473.

3-(4-Methylphenyl)phenyl Trifluoromethanesulfonate (7bb): Compound **7bb** was prepared according to general procedure A by reacting 1,3-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **7bb** as a white powder (44 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 7.09–7.16 (m, 1 H), 7.19 (d, J = 7.8 Hz, 2 H), 7.32–7.46 (m, 4 H) 7.46–7.54 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 119.0 (q, J = 318 Hz, CF_3), 119.7 (CH), 119.9 (CH), 127.0 (CH), 127.2 (2 CH), 130.0 (2 CH), 130.6 (CH), 136.4 (C), 138.6 (C), 144.2 (C), 150.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 2945, 2855, 1598, 1530, 1417, 1345, 1212, 1126 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{11}F_3O_3S$ $[M]^+$ 316.0381; found 316.0372.

3-(4-Nitrophenyl)phenyl Trifluoromethanesulfonate (7bc): Compound **7bc** was prepared according to general procedure A by reacting 1,3-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (20% CH_2Cl_2 in heptane) afforded **7bc** as a white powder (39 mg, 57%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.40 (m, 1 H), 7.50 (t, J = 1.9 Hz, 1 H), 7.54–7.67 (m, 2 H), 7.71 (d, J = 8.9 Hz, 2 H), 8.32 (d, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.0 (q, J = 319.4 Hz, CF_3), 120.6 (CH), 121.7 (CH), 124.6 (2 CH), 127.6 (CH), 128.3 (2 CH), 131.3 (CH), 141.7 (C), 145.4 (C), 148.0 (C), 150.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2865, 1613, 1481, 1421, 1244, 1200, 1139, 1126 cm^{-1}. MS: no ionization could be observed for this compound.

2-(4-Ethoxyphenyl)phenyl Trifluoromethanesulfonate (7ca): Compound **7ca** was prepared according to general procedure A by reacting 1,2-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (0 to 20% CH_2Cl_2 in heptane) afforded **7ca** as a white powder (45 mg, 65%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.0 Hz, 3 H), 4.00 (q, J = 7.0 Hz, 2 H), 6.89 (d, J = 8.8 Hz, 2 H), 7.28–7.54 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.7 (CH_2), 114.7 (2 CH), 118.6 (q, J = 321.2 Hz, CF_3), 122.3 (CH), 128.0 (C), 128.6 (CH), 128.7 (CH), 130.7 (2 CH), 132.1 (CH), 135.5 (C), 147.1 (C), 159.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 2990, 2888, 1614, 1495, 1422, 1397, 1209, 1162, 1056, 877 cm^{-1}. HRMS (APPI): calcd. for $C_{15}H_{13}F_3O_4S$ $[M]^+$ 346.0487; found 346.0481.

2-(4-Methylphenyl)phenyl Trifluoromethanesulfonate (7cb): Compound **7cb** was prepared according to general procedure A by reacting 1,2-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by flash column chromatography on silica gel (2% EtOAc in heptane) afforded **7cb** as a white powder (41 mg, 62%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 7.18 (d, J = 7.5 Hz, 2 H), 7.23–7.43 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 118.4 (q, J = 320.2 Hz, CF_3), 122.0 (CH), 128.5 (CH), 128.7 (CH), 129.2 (4 CH), 132.0 (CH), 132.7 (C), 135.6 (C), 138.2 (C), 146.9 (C) ppm. IR (neat): $\tilde{\nu}$ = 2990, 2888, 1614, 1495, 1422, 1397, 1209, 1162, 1056, 877 cm^{-1}. HRMS (APPI): calcd. for $C_{14}H_{11}F_3O_3S$ $[M]^+$ 316.0381; found 316.0372.

2-(4-Nitrophenyl)phenyl Trifluoromethanesulfonate (7cc): Compound **7cc** was prepared according to general procedure A by reacting 1,2-bis(trifluoromethylsulfonyloxy)benzene (75 mg, 0.2 mmol) with potassium (4-nitrophenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by preparative TLC (0 to 20% CH_2Cl_2 in heptane) afforded **7cc** as a white powder (25 mg, 38%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.56 (m, 4 H), 7.63 (d, J = 8.9 Hz, 2 H), 8.31 (d, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.3 (q, J = 321.0 Hz, CF_3), 122.7 (CH), 124.0 (2 CH), 129.1 (CH), 130.6 (2 CH), 130.7 (CH), 131.9 (CH), 133.6 (C), 142.4 (C), 146.6 (C), 147.9 (C) ppm. IR (neat): $\tilde{\nu}$ = 2922, 2871, 1613, 1487, 1415, 1249, 1212, 1143, 1128 cm^{-1}. MS: no ionization could be observed for this compound.

Diethyl *N*-Benzyl-3-(4-ethoxyphenyl)-4-(trifluoromethylsulfonyloxy)pyrrole-2,5-dicarboxylate (7da): Compound **7da** was prepared according to general procedure A by reacting pyrrole **6d** (120 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a

mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by flash column chromatography on neutral alumina gel (2% EtOAc in heptane) afforded **7da** as a white powder (58 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 6.9 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.41 (t, J = 7.2 Hz, 3 H), 3.98–4.09 (m, 4 H), 4.34 (q, J = 6.9 Hz, 2 H), 6.08 (s, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 6.6 Hz, 2 H), 7.16–7.31 (m, 5 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (CH_3), 13.9 (CH_3), 14.8 (CH_3), 49.8 (CH_2), 61.2 (CH_2), 61.7 (CH_2), 63.5 (CH_2), 113.9 (2 CH), 118.0 (q, J = 317.0 Hz, CF_3), 118.3 (C), 121.9 (C), 123.3 (2 C), 126.2 (2 CH), 127.3 (CH), 128.4 (2 CH), 131.5 (2 CH), 136.1 (C), 137.7 (C), 158.9 (C), 159.1 (C), 160.6 (C) ppm. IR (neat): $\tilde{\nu}$ = 2983, 1721, 1556, 1425, 1286, 1243, 1185, 1135, 1022, 921, 829, 731 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{27}F_3NO_8S[M + H]^+$ 570.1409; found 570.1433.

Diethyl *N*-Benzyl-3-(4-methylphenyl)-4-(trifluoromethylsulfonyloxy)pyrrole-2,5-dicarboxylate (7db): Compound **7db** was prepared according to general procedure A by reacting pyrrole **6d** (120 mg, 0.2 mmol) with potassium (4-methylphenyl)trifluoroborate (40 mg, 0.2 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by flash column chromatography on neutral alumina gel (30% CH_2Cl_2 in heptane) afforded **7db** as a white powder (62 mg, 57%). ^{1}H NMR (75 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.2 Hz, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 2.31 (s, 3 H), 3.96 (q, J = 7.2 Hz, 2 H), 4.28 (q, J = 7.2 Hz, 2 H), 6.02 (s, 2 H), 6.95 (d, J = 6.9 Hz, 2 H), 7.06–7.28 (m, 7 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH_3), 14.0 (CH_3), 21.3 (CH_3), 49.6 (CH_2), 61.3 (CH_2), 61.8 (CH_2), 118.0 (q, J = 318.0 Hz, CF_3), 118.3 (C), 123.4 (C), 123.5 (C), 126.2 (2 CH), 126.7 (C), 127.4 (CH), 128.5 (2 CH), 128.6 (2 CH), 130.1 (2 CH), 136.0 (C), 137.7 (C), 137.8 (C), 159.1 (C), 160.6 (C) ppm. IR (neat): $\tilde{\nu}$ = 2963, 1718, 1424, 1289, 1220, 1187, 1133, 1021, 925, 820, 697 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{25}F_3NO_7S$ $[M + H]^+$ 540.1304; found 540.1299.

Diethyl *N*-Benzyl-3-(4-nitrophenyl)-4-(trifluoromethylsulfonyloxy)-pyrrole-2,5-dicarboxylate (7dc): Compound **7dc** was prepared according to general procedure A by reacting pyrrole **6d** (60 mg, 0.1 mmol) with potassium (4-nitrophenyl)trifluoroborate (23 mg, 0.1 mmol), sodium carbonate (43 mg, 0.4 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (1.5 mg, 3 mol-%), and tetrakis(triphenylphosphine)palladium(0) (3.5 mg, 1.5 mol-%) in a mixture of degassed toluene/ethanol (0.70:0.20 mL) and degassed water (0.35 mL). The reaction mixture was stirred at 70 °C overnight. After extraction, purification of the crude material by flash column chromatography on silica gel (10% EtOAc in heptane) afforded **7dc** as a white powder (17 mg, 31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 3.98 (q, J = 7.2 Hz, 2 H), 4.30 (q, J = 7.2 Hz, 2 H), 6.08 (s, 2 H), 6.96 (d, J = 6.9 Hz, 2 H), 7.17–7.31 (m, 3 H), 7.44 (d, J = 8.7 Hz, 2 H), 8.19 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH_3), 13.9 (CH_3), 49.9 (CH_2), 61.7 (CH_2), 62.2 (CH_2), 117.9 (q, J = 319.5 Hz, CF_3), 119.1 (C), 121.2 (C), 123.0 (2 CH), 123.2 (C), 126.3 (2 CH), 127.6 (CH), 128.7 (2 CH), 131.4 (2 CH), 135.4 (C), 137.1 (C), 137.2 (C), 147.5 (C), 158.9 (C), 159.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 2919, 1726, 1524, 1421, 1348, 1276, 1216, 1187, 1133, 1018, 930, 853, 760 cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{22}F_3N_2O_9S$ $[M + H]^+$ 571.0998; found 571.0973.

2-(4-Fluorophenyl)-6-(4-ethoxyphenyl)pyridine (8): Compound **8** was prepared according to general procedure B by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (170 mg, 1.6 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was first stirred at 40 °C for 6 h. Potassium (4-fluorophenyl)trifluoroborate (40 mg, 0.2 mmol) was then added at room temp., and the mixture was heated at 100 °C for 2 h. After filtration through silica, chromatography of the crude reaction product on silica with 0 to 20% EtOAc in heptane afforded **8** (49.0 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (t, J = 7.1 Hz, 3 H), 4.02 (q, J = 7.1 Hz, 2 H), 6.92 (d, J = 8.9 Hz, 2 H), 7.09 (t, J = 8.1 Hz, 2 H), 7.55–7.48 (m, 2 H), 7.68 (t, J = 8.1 Hz, 1 H), 8.00 (d, J = 8.9 Hz, 2 H), 8.08–8.03 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (CH_3), 63.6 (CH_2), 114.6 (2 CH), 115.5 (d, J = 21.2 Hz, 2 CH), 117.5 (CH), 117.8 (CH), 128.2 (2 CH), 128.7 (d, J = 8.3 Hz, 2 CH), 131.8 (C), 135.8 (d, J = 2.8 Hz, C), 137.4 (CH), 155.6 (C), 156.6 (C), 159.9 (C), 163.5 (d, J = 246.5 Hz, C) ppm. IR (neat): $\tilde{\nu}$ = 2940, 1515, 1413, 1344, 701 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{17}FNO$ $[M + H]^+$ 294.1289; found 294.1301.

4-Ethoxy-4′′-(trifluoromethyl)-1,1′:3′,1′′-terphenyl (9): Compound **9** was prepared according to the general procedure B by reacting **1c** (24 μL, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (170 mg, 1.6 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was stirred at 40 °C for 6 h. (4-Trifluoromethylphenyl)boronic acid (76 mg, 0.4 mmol) was then added, and the mixture was heated at 70 °C for 20 h. After extraction, purification of the crude material by flash column chromatography on silica gel (2% CH_2Cl_2 in heptane) afforded **9** as a white powder (39 mg, 58%).

Compound **9** was also prepared according to the general procedure B by reacting **6b** (75 mg, 0.2 mmol) with potassium (4-ethoxyphenyl)trifluoroborate (46 mg, 0.2 mmol), sodium carbonate (170 mg, 1.6 mmol), potassium chloride (7 mg, 0.1 mmol), triphenylphosphine (3.0 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (7.0 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (1.40:0.35 mL) and degassed water (0.70 mL). The reaction mixture was first stirred at 70 °C for 20 h. (4-Trifluoromethylphenyl)boronic acid (38 mg, 0.2 mmol) was then added, and the mixture was heated at 70 °C or 20 h. After extraction, purification of the crude material by preparative TLC (2% CH_2Cl_2 in heptane) afforded **9** as a white powder (42 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3 H), 4.08 (q, J = 7.0 Hz, 2 H), 6.98 (d, J = 8.7 Hz, 2 H), 7.47–7.61 (m, 5 H), 7.66–7.79 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.8 (CH_2), 115.1 (2 CH), 124.5 (q, J = 271.8 Hz, CF_3), 125.8 (CH), 125.9 (q, J = 3.6 Hz, 2 CH), 126.0 (CH), 126.8 (CH), 127.7 (2 CH), 128.5 (2 CH), 129.6 (CH), 129.7 (q, J = 32.0 Hz, C), 133.4 (C), 140.5 (C), 141.9 (C), 145.0 (C), 159.0 (C) ppm. IR (neat): $\tilde{\nu}$ = 2987, 2926, 1605, 1516, 1475, 1328, 1252, 1170, 1129 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{24}F_3N_2O$ $[M + 2MeCN + H]^+$ 425.1841; found 425.2329.

Diethyl *N*-Benzyl-3-[2-benzyloxy)phenyl]-4-(3,4-dimethoxyphenyl)-pyrrole-2,5-dicarboxylate (10): Compound **10** was prepared according to general procedure B by reacting **6d** (60 mg, 0.1 mmol) with potassium (3,4-dimethoxyphenyl)trifluoroborate (25 mg,

0.1 mmol), sodium carbonate (85 mg, 0.8 mmol), potassium chloride (3.5 mg, 0.05 mmol), triphenylphosphine (1.5 mg, 6 mol-%), and tetrakis(triphenylphosphine)palladium(0) (3.5 mg, 3 mol-%) in a mixture of degassed toluene/ethanol (0.7:0.2 mL) and degassed water (0.35 mL). The reaction mixture was first stirred at 70 °C for 20 h. (2-Benzyloxyphenyl)boronic acid (27 mg, 0.12 mmol) was then added at room temp., and the mixture was heated to 100 °C for 20 h. After filtration through silica, chromatography of the crude reaction product on silica with 0 to 20% EtOAc in heptane afforded **10** as a white powder (47.0 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (t, J = 6.8 Hz, 3 H), 0.83 (t, J = 6.8 Hz, 3 H), 3.43 (s, 3 H), 3.72 (s, 3 H), 3.86 (q, J = 6.8 Hz, 2 H), 3.94 (q, J = 6.8 Hz, 2 H), 4.84 (s, 2 H), 6.03 (s, 2 H), 6.50 (s, 1 H), 6.57 (s, 1 H), 6.58 (s, 1 H), 6.74 (d, J = 7.4 Hz, 2 H), 6.90 (dd, J = 7.4, 1.2 Hz, 1 H), 7.05–6.98 (m, 2 H), 7.28–7.06 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3 (CH_3), 13.6 (CH_3), 49.6 (CH_2), 55.4 (CH_3), 55.7 (CH_3), 60.2 (CH_2), 60.6 (CH_2), 69.8 (CH_2), 109.9 (CH), 111.9 (CH), 113.5 (CH), 120.3 (CH), 122.6 (CH), 124.8 (C), 124.9 (C), 125.2 (C), 126.2 (2 CH), 126.7 (2 CH), 126.8 (CH), 127.2 (C), 127.5 (CH), 127.8 (C), 128.2 (CH), 128.4 (2 CH), 128.5 (2 CH), 131.2 (C), 132.0 (CH), 137.4 (C), 139.1 (C), 147.4 (C), 147.5 (C), 156.4 (C), 161.4 (C), 161.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 2927, 2853, 1712, 1454, 1234, 1200, 1138, 1027, 731 cm^{-1}. HRMS (ESI): calcd. for $C_{38}H_{38}NO_7$ $[M + H]^+$ 620.2643; found 620.2660.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra.

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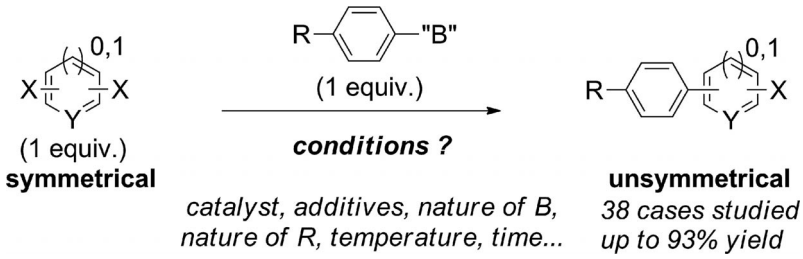
Cross-Coupling



Keywords: Synthetic methods / C–C coupling / Cross-coupling / Palladium

By studying several key parameters, the factors that allow selective Suzuki–Miyaura monocoupling of symmetrical dihaloarenes have been outlined. This study serves as the basis for the efficient synthesis of unsymmetrical triaryls from symmetrical dibromoarenes and aryl ditriflates by a one-pot desymmetrizing double Suzuki–Miyaura coupling.

