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Selective Suzuki-Miyaura Mono-Couplings with Symmetrical Dibromoarenes and Arylditriflates for One-pot Synthesis of Unsymmetrical Triaryls.

Corinne Minard, Carole Palacio, Kevin Cariou, Robert H. Dodd*

Keywords: Suzuki-Miyaura, selective coupling, potassium trifluoroborates, triaryls

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

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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, building an unsymmetrical triaryl requires a certain degree of discrimination between the various reacting sites. The use of two different halides or pseudo-halides 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 having different steric and/or electronic environments.[4] A simpler approach would be to use symmetrical di-haloarenes, which are more readily available, and to perform a selective mono-coupling in order 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 using an amphiphilic supported palladium (II) complex and an excess of triphenylphosphine[5] but Sherburn showed that diarylation was the preferred outcome for diiodoarenes, while monoarylation of dibromoarenes could be achieved when 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 starting from dibromoarenes (though mainly limited to ortho disubstituted compounds, where steric interactions already tend to favor the formation of a mono-arylated adduct).[7] McNulty conducted a similar study on dichlorobenzenes,[8] while the Langer group developed various sets of conditions for selective coupling on polyhalogenated substrates.[9] In our case, we have previously shown that, since electron-rich arylboronic acids react faster than their electron-poor counterparts, selective monoarylations (with indole boronic acid)[10] and one-pot simultaneous dicouplings yielding 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] or ningalin B[13] (Figure 1), and their analogs.[14]

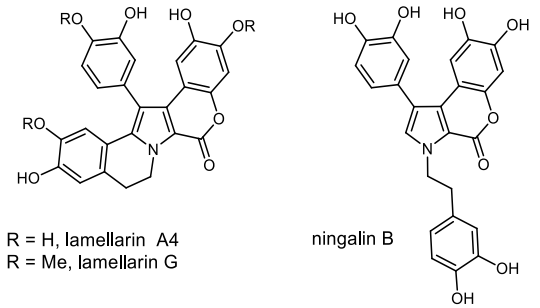
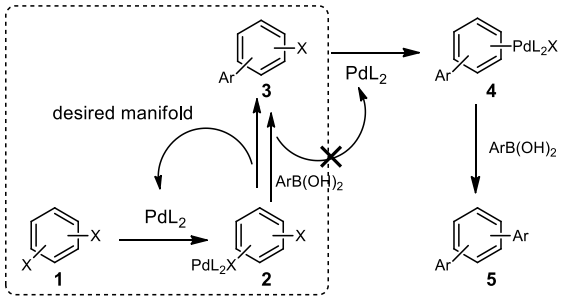


Figure 1. Triaryl Marine Natural Products.

However, our one-pot procedure is somewhat limited by the necessity of having different electron densities for each reactant, while 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 in need for the synthetic community. In this context, we sought to study the mono-coupling of various symmetrical aryl-dibromides and -ditriflates with a representative panel of boron derivatives in order to develop an efficient and operationally simple protocol that could eventually be amenable to one-pot desymmetrizing-difunctionalization procedures. When looking into the mechanism of the Suzuki-Miyaura cross-coupling it appears that in order to favor the mono-coupling a certain control over the oxidative addition is required. 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, transmetallation with the boronic acid[15] followed by reductive elimination would then deliver the desired halo-diaryl **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**.

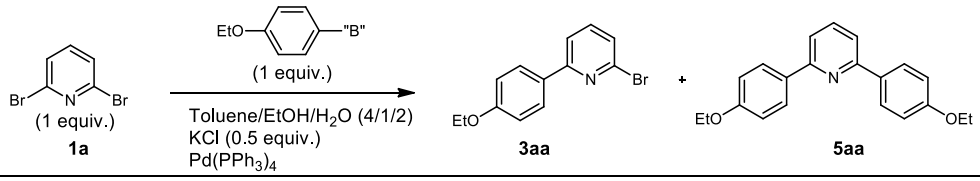


Scheme 1. Mono- vs. di-coupling.

Results and Discussion

In theory, the initial dihalo compound **1** should be slightly more reactive than the resulting mono-haloarene **3** toward the oxidative addition and thus any factor that would render this step rate-determining would increase the chance of a selective mono-coupling pathway. Besides 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] As benchmark compounds we started our study by reacting 1 equivalent of 2,6-dibromopyridine **1a** with 1 equivalent of *p*-ethoxyphenylboronic acid in a 4/1/2 mixture of toluene/EtOH/H_2O in the presence of 8 equivalents 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 quite slow in generating the 14-electron species. Under these conditions, monoarylated adduct **3aa** was the major compound formed but a significant amount of unwanted diarylpyridine **5aa** was also observed. Using the corresponding potassium trifluoroborate under the same conditions gave better results in terms of selectivity (entry 2). We then decided to use a slightly higher amount of catalyst but in conjunction with a two-fold excess of triphenylphosphine. Thus, by bringing the Pd:L ratio to 1:6 the amount of active 14-electron Pd(0) complex available would be lower and the oxidative addition into 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 (entries 3, 4). We then lowered the temperature to rt, which proved detrimental to the reactivity, since full conversion was only obtained after 2 days, but the selectivity was increased to 95/5 (entries 5, 6). When boronic esters (both pinacol and neopentylglycol) were used the selectivity was complete but the conversion extremely low, even after 2 days (entries 7, 8). In order to find a balance between reactivity and selectivity the temperature was raised to 40 °C. Total reaction was now observed after 6 h, except for the boronic esters, and the selectivity remained excellent (entries 9-12) for all compounds. Finally, using only 4 equivalents of base (entries 13-16), both conversion and selectivities remained virtually unchanged, but the best yield of isolated mono-coupled product was obtained when using the trifluoroborate (85%, entry 14).

Table 1. Mono-coupling Optimization.



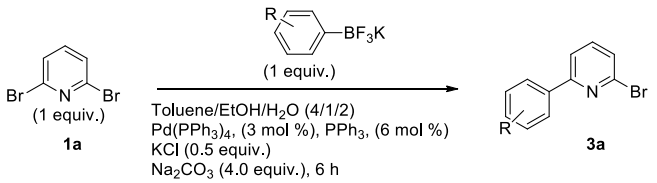
entry	"B"	Pd (mol %)	PPh_3 (mol %)	Temp.	Na_2CO_3 (equiv.)	t.	Conv.[a]	**3/5**[a]	yield[b]
1	$B(OH)_2$	0.5	0	100 °C	8	1.5 h	100%	67/33	-
2	**BF_3K**	0.5	0	100 °C	8	1.5 h	100%	90/10	-
3	$B(OH)_2$	**3**	**6**	100 °C	8	2.5 h	100%	87/13	-
4	BF_3K	3	6	100 °C	8	2.5 h	100%	87/13	-
5	$B(OH)_2$	3	6	**rt**	8	2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

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

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

Having determined the optimal conditions for this mono-coupling, we next varied the substituents on the trifluoroborate partner. *Para*-substituted compounds were first used so that only electronic rather than steric effects would be at play (Table 2, entries 1-4). Substituents with limited electronic effect such as methyl and fluorine reacted smoothly to afford the desired bromo diaryl with 69% and 70% yields. On the other hand, electron-withdrawing groups such as nitro and trifluoromethyl gave lower yields, which could not be improved by increasing the temperature in order to compensate for their lower reactivity. It is also important to note that, in the latter case, the difference of reactivity for the oxidative addition step between the starting dibromoarene and the mono-coupled product is lowered because of the electron-withdrawing nature of the newly introduced moiety, thus potentially disfavoring a selective process. *Meta*-methoxyphenyl trifluoroborate reacted poorly at 40 °C but raising the temperature to 70 °C and diminishing the reaction time allowed isolation of 62% of the desired compound (entry 5). The case of *ortho*-substituted boron reagents was expected to be problematic as steric effects are now at play. Indeed, only modest yields of mono-coupled product were obtained when reacting *o*-F, *o*-OMe and *o*-OBn phenyltrifluoroborates at 40 °C (34%-53%, entries 6-8).

Table 2. Mono-coupling on 2,6-dibromopyridine.



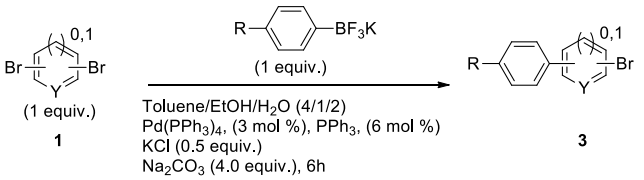
entry	R	3	Temp.	yield	Temp.	yield [a]
1	4-CH_3	**3ab**	40 °C	69%		
2	4-F	**3ad**	40 °C	70%		
3	4-NO_2	**3ac**	40 °C	63%	100 °C	55%
4	4-CF_3	**3ae**	40 °C	45%	70 °C	22%[b]
5	3-OMe	**3af**	40 °C	38%	70 °C	62%[c]
6	2-F	**3ag**	40 °C	44%	70 °C	54%[b]
7	2-OMe	**3ah**	40 °C	34%	70 °C	70%[c]
8	2-OBn	**3ai**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

Nevertheless, increasing the temperature to 70 °C allowed the steric hindrance to be overcome leading to satisfactory yields (54 %-70 %). In this case, the loss of selectivity that could be expected at a higher reaction temperature was tempered by adding more triphenylphosphine and shortening the reaction time. Finally, 3,4-dimethoxyphenyl trifluoroborate was tested (entry 9). While the yield was moderate at 40 °C (47 %), increasing the temperature to 70 °C only proved detrimental, the main issue being that the high reactivity of this compound tends to favor dicoupling.

The next step was to test these conditions on a wider range of symmetrical dibromo-arenes and -heteroarenes while still varying the electronic properties of the trifluoroborate partner. First, 3,5-dibromopyridine **1b** was reacted 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, giving moderate to good yields of the desired bromodiarene (64%-76%, Table 3, entries 1-3). When switching to *meta*- and *para*-dibromobenzenes (**1c**, entries 4-6 and **1d**, 7-9), the same trend was observed with EDG-substituted borates giving yields above 70% (entries 4-5,7-8), while EWG-substituted borates led to the desired compound with yields around 50% (entries 6,9). In these latter cases, a significant amount of di-coupling product was also observed. Because of the limited electronic differentiation between the dibromo starting material and the mono-arylated adduct, the product distribution tends to be roughly statistical (*ie* a 1:2:1 distribution for **1**:**3**:**5**, respectively).

Table 3. Mono-coupling on various symmetrical dibromoarenes.



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

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

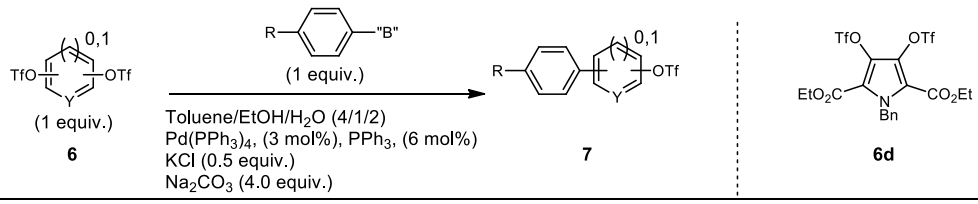
For *ortho*-dibromobenzene **1e** the steric interactions, which could favor a selective monocoupling,[7] mostly proved detrimental as the reaction mixture had to be heated to 70 °C in order to reach moderate yields (entries 10-12). Increasing the reaction temperature to 100 °C was necessary to produce 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 (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 (entries 16-18).

In order to further broaden the scope of this study we then turned our attention to various arene ditriflates which, for the most part, can 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. Running the reaction (using 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%, entry 2). However, while the *p*-tolyltrifluoroborate gave a satisfactory yield of 69% (entry 5) the *para*-nitro derivative only led to a complex mixture (entry 6). Resorcinol ditriflate **6b** exhibited a lower reactivity which could readily be enhanced by heating at 70 °C and prolonging the reaction time to 20 h to provide the *p*-OEt and *p*-Me products with good yields (entries 7,8).Even the *p*-NO_2 product was obtained with a satisfying 57% yield under these conditions (entry 9). In the case of the catechol ditriflate **6c** the same trend was observed even at 70 °C but the yields were lower, probably because of the unfavorable steric interactions (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 calculated by NMR for both *p*-OEt and *p*-Me compounds, but both products proved quite sensitive to chromatographic purification (entries 13,14). For *p*-nitrobenzenetrifluoroborate, the desired monocoupled adduct could only be isolated with a modest 31% yield (entry 15). Because of the electron-withdrawing nature of the group introduced, the mono-coupled product was quite reactive as evidenced by the isolation of 34% of the di-coupled adduct, while 27% of the unreacted starting material was also recovered.

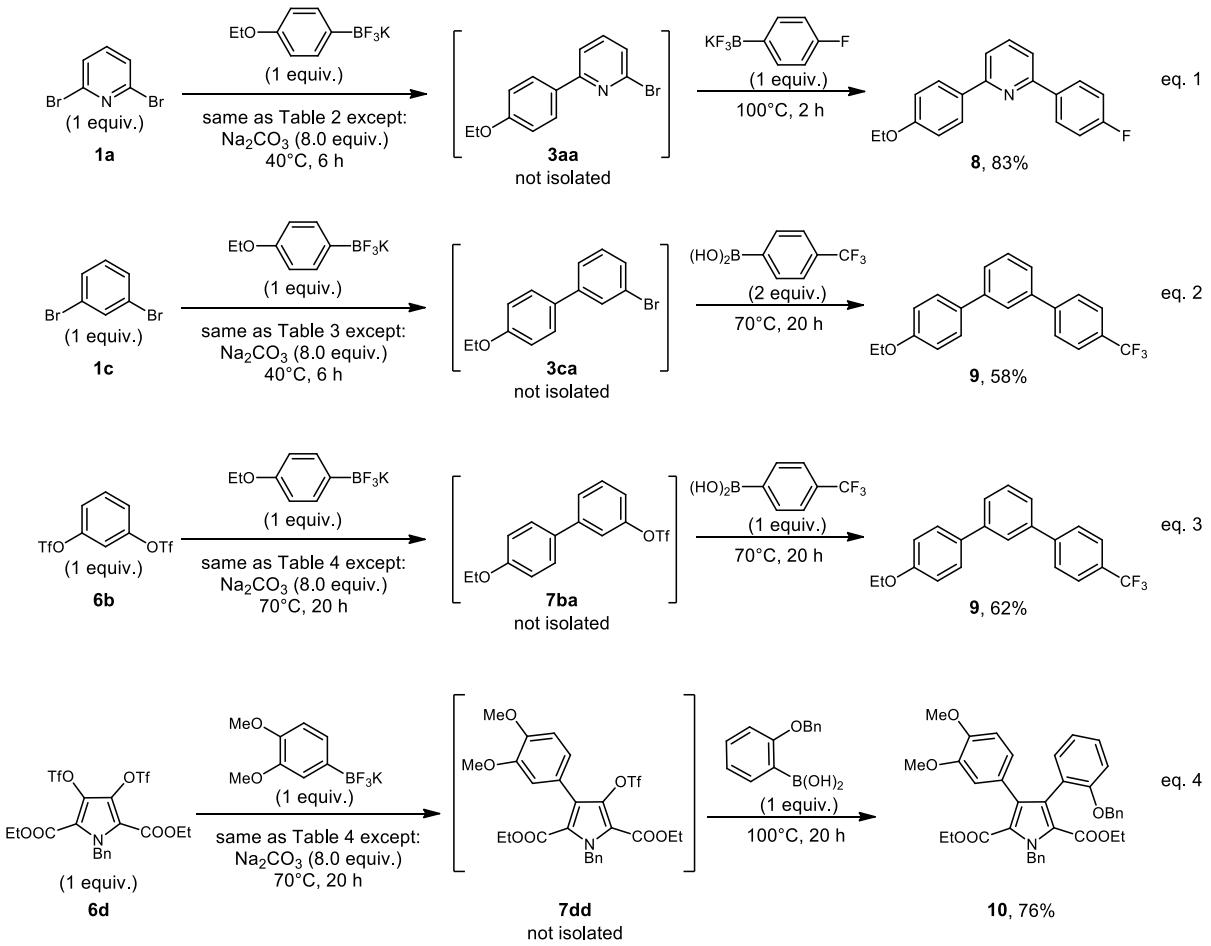
The usefulness of the mono-coupling strategy and the robustness of our conditions were ascertained by accomplishing one-pot desymmetrizing double Suzuki-Miyaura couplings to give the desired triaryl derivatives.[20] The optimized mono-coupling conditions were first applied to dibromopyridine **1a** with *p*-ethoxyphenyl potassium trifluoroborate, only doubling the amount of base introduced, to give arylpyridine **3aa** that was not isolated. After the requisite 6 h, *p*-fluorophenyl potassium trifluoroborate was added and the reaction mixture was heated at 100 °C for 2h. This method allowed the isolation of the unsymmetrical diarylpyridine **8** with an excellent 83% yield (Scheme 2, eq.1). A similar procedure was then applied to 1,3-dibromobenzene **1c** (eq. 2) and resorcinol ditriflate **6b** (eq. 3), using *p*-ethoxyphenyl potassium trifluoroborate (under the optimized conditions described in: Table 3-entry 4, for **1c** and Table 4-entry 7, for **6b**) followed by *p*-trifluoromethylphenylboronic acid. The corresponding terphenyl **9** was obtained in both cases with 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** using first 3,4-dimethoxyphenyl potassium trifluoroborate (under the optimized conditions described in Table 4 entry 13) followed by *o*-benzyloxyphenylboronic acid to give diarylpyrrole **10** with a 76% isolated yield (eq. 4).

Table 4. Mono-coupling 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	Pyrrole **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] Complex mixture. [c] Conversion as determined by analysis of the ^{1}H NMR: 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.

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 also because isolation of the unstable intermediate mono-triflate is avoided, thus allowing the target compound to be obtained with an excellent yield.

Conclusions

Overall, we have shown that selective mono Suzuki-Miyaura cross-coupling can be accomplished on a wide range of symmetrical dihaloarenes using 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 requiring 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 run 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. The moiety bearing the electron-withdrawing substituent should thus be incorporated in a second coupling, as the lower reactivity of these compounds can then be compensated by using harsher conditions. Finally, while this selective mono-coupling can grant access to many valuable synthons for further transformations, it also offers opportunities for a second Suzuki-Miyaura cross-coupling to rapidly access triaryl scaffolds. This was showcased by performing highly efficient desymmetrizing one-pot double Suzuki-Miyaura reactions on dibromopyridine **1a**, 1,3-dibromobenzene **1c**, resorcinol ditriflate **6b** and pyrroleditriflate **6d**. Further efforts in this direction, including the preparation and evaluation of libraries of biologically relevant compounds, are currently underway in our laboratory and will be reported in due course.

Experimental Section

General Methods: Melting points were measured in capillary tubes on a Büchi B-540 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on Bruker spectrometers: Avance 300 MHz (QNP - ^{13}C, ^{31}P, ^{19}F - probe or Dual ^{13}C probe) and Avance 500 MHz (BB0 - ATM probe or BBI - ATM probe). Carbon NMR (^{13}C) spectra were recorded at 125 or 75 MHz, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. NMR experiments were carried out in deuterochloroform ($CDCl_3$), chemical shifts (δ) are reported in parts per million (ppm) with reference to $CDCl_3$ (^{1}H: 7.24; ^{13}C: 77.23). The following abbreviations are used for the proton spectra multiplicities: s: singlet, bs: broad 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 a LCT (Micromass) instrument using electrospray ionization (ES), or from a Time of Flight

analyzer (ESI-MS) for the high resolution mass spectra (HRMS). APPI spectra were obtained with an Agilent 1290 Infinity SFC instrument using a Q-ToF 6540 analyser and APPI ionization. Analytical thin-layer chromatography was performed on silica gel 60 F_{254} on aluminum plates (Merck) and visualized under a UVP Mineralight UVLS-28 lamp (254 nm) and with ninhydrin and *p*-anisaldehyde stains. Preparative thin-layer chromatography was performed on silica gel 60 F_{254} (Merck, 0.5 mm). Flash chromatography was conducted on Merck silica gel 60 (40-63 µm) at medium pressure (300 mbar) or on CombiFlash apparatus (Serlabo Technologies), using standard settings. For Suzuki-Miyaura couplings, solvents were always freshly degassed with argon. Organic extracts were dried over 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 following literature procedures. Pyrrole derivatives were also synthesized according to literature procedures.[14a]

General Procedure A, Suzuki-Miyaura Monocouplings: The aryldibromide (or arylditriflate, 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 in a sealing 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, respectively) was injected *via* syringe. The septum was replaced by a screwcap, the tube was sealed and the reaction mixture was stirred at the appropriate temperature (40°C-100°C) for 6-20 h. The resulting mixture was then cooled to RT, extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting crude material was performed by flash silica gel chromatography or preparative TLC using the appropriate solvent system.

General Procedure B, Suzuki-Miyaura One-pot Double Couplings: The aryldibromide (or arylditriflate, 1 equiv.), the first boron derivative (1 equiv.), sodium carbonate (8 equiv.), potassium chloride (0.5 equiv.) and triphenylphosphine (6 mol%) were successively introduced in a sealing 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, respectively) was injected via syringe. The septum was replaced by a screwcap, the tube was sealed and the reaction mixture was stirred at the appropriate temperature (40 °C-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 °C-100 °C) for an additional 6-20 h. The resulting mixture was then cooled to rt, extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting crude material was performed by flash silica gel chromatography or preparative TLC using the appropriate solvent system.

2-Bromo-6-(4-ethoxyphenyl)pyridine (3aa): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 4.06 (q, *J* = 6.9 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.31 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.51 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 114.8 (2CH), 118.3 (CH), 125.6 (CH), 128.5 (2CH), 130.2 (C), 139.1 (CH), 142.2 (C), 158.5 (C), 160.5 (C); IR (neat): ν = 2975, 2926, 1606, 1574, 1547, 1512, 1432, 1421, 1392, 1251, 1115, 1042, 790 cm^{-1}; HRMS (ESI): calc. for $C_{13}H_{13}{}^{79}BrNO_2$ [M+H] m/z 278.0102, found m/z 278.0173, calc. for $C_{13}H_{13}{}^{81}BrNO_2$ [M+H] m/z 280.0082, found m/z 280.0151.

2-Bromo-6-(*p*-tolyl)pyridine (3ab): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. After extraction, purification of the crude material by flash chromatography on silica gel (0% to 40% CH_2Cl_2 in heptane) afforded **3ab** as a white powder (34 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.63 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 118.1 (CH), 126.1 (CH), 127.1 (2CH), 129.7 (2CH), 135.1 (C), 139.1 (CH), 140.0 (C), 142.3 (C), 158.8 (C); IR (neat): ν = 3028, 2913, 2855, 1579, 1544, 1512, 1429, 1413, 1124, 790 cm^{-1}; HRMS (ESI): calc. for $C_{12}H_{11}{}^{79}BrN$ [M+H] m/z 247.9997, found m/z 248.0081, calc. for $C_{12}H_{11}{}^{81}BrN$ [M+H] m/z 249.9976, found m/z 250.0058.

2-Bromo-6-(4-nitrophenyl)pyridine (3ac): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 1H), 7.66 (dd, *J* = 7.7, 7.9 Hz, 1H), 7.75 (dd, *J* = 7.7, 0.9 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.0 (CH), 124.2 (2CH), 128.0 (2CH), 128.2 (CH), 139.5 (CH), 142.8 (C), 143.6 (C), 148.7 (C), 156.0 (C); IR (neat): ν = 3110, 3085, 2962, 1507, 1343, 1259, 1087, 1047, 1012, 790 cm^{-1}; HRMS (ESI): calc. for $C_{11}H_8{}^{79}BrN_2O_2$ [M+H] m/z 278.9691, found m/z 278.9787, calc. for $C_{11}H_8{}^{81}BrN_2O_2$ [M+H] m/z 280.9670, found m/z 280.9781.

2-Bromo-6-(4-fluorophenyl)pyridine (3ad): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-fluorophenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. After extraction, purification of the crude material using 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, 2H), 7.38 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.96 (dd, *J* = 8.8, 5.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.0 (d, *J* = 21.8 Hz, 2CH), 118.8 (CH), 126.5 (CH), 129.1 (d, *J* = 8.7 Hz, 2CH), 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); IR (neat): ν = 3079, 2924, 1596, 1578, 1547, 1508, 1428, 1414, 1386, 1227, 1124, 851, 790 cm^{-1}; HRMS (ESI): calc. for $C_{11}H_8{}^{79}BrFN$ [M+H] m/z 251.9746, found m/z 251.9834, calc. for $C_{11}H_8{}^{81}BrFN$ [M+H] m/z 253.9725, found m/z 253.9808.

2-Bromo-6-(4-(trifluoromethyl)phenyl)pyridine (3ae): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-trifluoromethanephenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. After extraction, purification of the crude material using 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, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.67-7.73 (m, 3H), 8.09 (d, *J* = 8.0 Hz, 2H); ^{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, 2CH), 127.5 (2CH), 127.6 (CH), 132.2 (q, *J* = 47.5 Hz, C), 138.3 (C), 139.4 (CH), 141.1 (C), 142.7 (C); IR (neat): ν = 3079, 2927, 1575, 1551, 1432, 1312, 1110, 1072, 848, 793, 747 cm^{-1}; HRMS (ESI): calc. for $C_{12}H_8{}^{79}BrF_3N$ [M+H] m/z 301.9714, found m/z 301.9814, calc. for $C_{12}H_8{}^{81}BrF_3N$ [M+H] m/z 303.9693, found m/z 303.9799.

2-Bromo-6-(3-methoxyphenyl)pyridine (3af): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 3-methoxyphenyltrifluoroborate (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 was stirred at 70 °C for 4 hours. After extraction, purification of the crude material using 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, 3H), 6.93-6.99 (m, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.45-7.58 (m, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H); ^{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); IR (neat): ν =3074, 2934, 2835, 1575, 1549, 1424, 1217, 1123, 1037, 790 cm^{-1}; HRMS (ESI): calc. for $C_{12}H_{11}{}^{79}BrNO_2$ [M+H] m/z 263.9946, found m/z 264.0012, calc. for $C_{12}H_{11}{}^{81}BrNO_2$ [M+H] m/z 265.9925, found m/z 266.0001.

2-Bromo-6-(2-fluorophenyl)pyridine (3ag): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 2-fluorophenyltrifluoroborate (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 was stirred at 70 °C for 4 hours. After extraction, purification of the crude material using 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, 1H), 7.23 (td, *J* = 7.9, 1.2 Hz, 1H), 7.31-7.39 (m, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.9 Hz, 1H), 8.01 (td, *J* = 7.9, 1.9 Hz, 1H); ^{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); IR (neat): ν = 3075, 2922, 1575, 1547, 1493, 1434, 1393, 1211, 1111, 802, 790 cm^{-1}; HRMS (ESI): calc. for $C_{11}H_8{}^{79}BrFN$ [M+H] m/z 251.9746, found m/z 251.9818, calc. for $C_{11}H_8{}^{81}BrFN$ [M+H] m/z 253.9725, found m/z 253.9798.

2-Bromo-6-(2-methoxyphenyl)pyridine (3ah): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 2-methoxyphenyltrifluoroborate (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 was stirred at 70 °C for 4 hours. After extraction, purification of the crude material using 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, 3H), 6.92 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.00 (td, *J* = 7.9, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.31 (td, *J* = 7.9, 1.9 Hz, 1H), 7.47 (t, *J* = 7.9, 1H), 7.78 (dd, *J* = 7.9, 1.2 Hz, 2H); ^{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). IR (neat): ν = 2936, 2837, 1573, 1427, 1239, 1124, 1032, 790 cm^{-1}; HRMS (ESI): calc. for $C_{12}H_{11}{}^{79}BrNO_2$ [M+H] m/z 263.9946, found m/z 264.0042, calc. for $C_{12}H_{11}{}^{81}BrNO_2$ [M+H] m/z 265.9925, found m/z 266.0013.

2-Bromo-6-(2-benzyloxyphenyl)pyridine (3ai): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 2-benzyloxyphenyltrifluoroborate (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 was stirred at 70 °C for 4 hours. After extraction, purification of the crude material using 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, 2H), 7.07 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.12 (td, *J* = 7.7, 1.1 Hz, 1H), 7.25-7.40 (m, 7H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.90 (dd, *J* = 7.7, 0.7 Hz, 1H); ^{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 (2CH), 128.1 (CH), 128.7 (2CH), 130.7 (CH), 131.7 (CH), 137.0 (C), 138.2 (CH), 141.6 (C), 156.4 (C), 157.2 (C); IR (neat): ν = 2923, 2854, 1600, 1573, 1428, 1391, 1127, 1007, 790 cm^{-1}; HRMS (ESI): calc. for $C_{18}H_{15}{}^{79}BrNO_2$ [M+H] m/z 340.0259, found m/z 340.0314, calc. for $C_{18}H_{15}{}^{81}BrNO_2$ [M+H] m/z 342.0296, found m/z 342.0238.

2-Bromo-6-(3,4-dimethoxyphenyl)pyridine (3aj): Prepared according to general procedure A by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 2,4-dimethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. After extraction, purification of the crude material using 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, 3H), 3.92 (s, 3H), 6.86 (d, *J* = 8.3 Hz, 1H), 7.27 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.40-7.50 (m, 2H), 7.52-7.57 (m, 2H); ^{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); IR (neat): ν = 3001, 2959, 2934, 2835, 1546, 1513, 1420, 1254, 1170, 1022, 790 cm^{-1}; HRMS (ESI): calc. for $C_{13}H_{13}{}^{79}BrNO_2$ [M+H] m/z 294.0051, found m/z 294.0130, calc. for $C_{13}H_{13}{}^{81}BrNO_2$ [M+H] m/z 296.0031, found m/z 296.0112.

3-Bromo-5-(4-ethoxyphenyl)pyridine (3ba): Prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 4.02 (q, *J* = 7.0 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.90-7.96 (m, 1H), 8.23-9.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.9 (CH_2), 115.4 (3CH), 128.5 (3CH), 128.7 (C), 136.6 (CH), 146.1 (C), 148.7 (C), 159.8 (C); IR (neat): ν = 2975, 2926, 1606, 1575, 1547, 1512, 1433, 1421, 1392, 1251, 1115, 1045, 790 cm^{-1}; HRMS (ESI): calc. for $C_{13}H_{13}{}^{79}BrNO$ [M+H] m/z 278.0102, found m/z 278.0120, calc. for $C_{13}H_{13}{}^{81}BrNO$ [M+H] m/z 280.0082, found m/z 280.0113.

3-Bromo-5-(4-methylphenyl)pyridine (3bb): Prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol),

with potassium 4-methylphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 7.27 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.97-7.98 (m, 1H), 8.61 (s, 1H), 8.72 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 121.1 (C), 127.2 (2CH), 130.1 (2CH), 133.6 (C), 136.8 (CH), 138.4 (C), 139.0 (C), 146.4 (CH), 149.2 (CH); IR (neat): ν = 3024, 2917, 2854, 1739, 1433, 1377, 1218, 1107, 1008, 825 cm^{-1}; HRMS (ESI): calc. for $C_{12}H_{11}{}^{79}BrN$ [M+H] m/z 247.9997, found m/z 248.0088, calc. for $C_{12}H_{11}{}^{81}BrN$ [M+H] m/z 249.9976, found m/z 250.0066.

3-Bromo-5-(4-nitrophenyl)pyridine (3bc): Prepared according to general procedure A by reacting 3,5-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 2H), 8.10 (t, J = 2.0 Hz, 1H), 8.34 (d, J = 8.8 Hz, 2H), 8.77 (dd, J = 15.7, 2.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.6 (C), 124.8 (2CH), 128.4 (2CH), 136.4 (C), 138.0 (CH), 142.5 (C), 145.9 (CH), 148.4 (C), 150.4 (CH); IR (neat): ν = 3109, 3085, 2963, 1511, 1343, 1259, 1089, 1047, 1015, 790 cm^{-1}; HRMS (ESI): calc. for $C_{11}H_8{}^{79}BrN_2O_2$ [M+H] m/z 278.9691, found m/z 278.9761, calc. for $C_{11}H_8{}^{81}BrN_2O_2$ [M+H] m/z 280.9670, found m/z 280.9768.

1-Bromo-3-(4-ethoxyphenyl)benzene (3ca): Prepared according to general procedure A by reacting 1,3-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 3.99 (q, J = 7.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 7.15-7.22 (m, 1H), 7.30-7.38 (m, 2H), 7.40 (d, J = 8.8 Hz, 2H), 7.61 (t, J = 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.7 (CH_2), 115.0 (2CH), 123.1 (C), 125.5 (CH), 128.3 (2CH), 129.7 (CH), 129.9 (CH), 130.4 (CH), 132.2 (C), 143.2 (C), 159.1 (C); IR (neat): ν = 2977, 2929, 1606, 1579, 1469, 1393, 1251, 1188, 1047, 790 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{13}{}^{79}BrO$ [M$^+$] m/z 276.0150, found m/z 276.0166, calc. for $C_{14}H_{13}{}^{81}BrO$ [M$^+$] m/z 278.0129, found m/z 278.0147.

1-Bromo-3-(4-methylphenyl)benzene (3cb): Prepared according to general procedure A by reacting 1,3-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.19-7.25 (m, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.39-7.44 (m, 3H), 7.45-7.49 (m, 1H), 7.69 (t, J = 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 123.1 (C), 125.7 (CH), 127.1 (2CH), 129.8 (2CH), 130.1 (CH), 130.2 (CH), 130.4 (CH), 137.0 (C), 138.0 (C), 143.5 (C); IR (neat): ν = 3032, 2857, 1555, 1467, 1450, 1030, 822, 790 cm^{-1}; HRMS (APPI): calc. for $C_{13}H_{11}{}^{79}Br$ [M$^+$] m/z 246.0044, found m/z 246.0032, calc. for $C_{13}H_{11}{}^{81}Br$ [M$^+$] m/z 248.0024, found m/z 248.0013.

1-Bromo-3-(4-nitrophenyl)benzene (3cc): Prepared according to general procedure A by reacting 1,3-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (dd, J = 7.9, 7.6 Hz, 1H), 7.49-7.59 (m, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.75 (t, J = 1.8 Hz, 1H), 8.29 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.5 (C), 124.4 (2CH), 126.2 (CH), 128.1 (2CH), 130.7 (CH), 130.9 (CH), 131.6 (C), 132.1 (CH), 141.1 (C), 146.2 (C); IR (neat): ν = 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): Prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3H), 4.06 (q, J = 7.0 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (CH_3), 63.6 (CH_2), 114.9 (2CH), 120.7 (C), 127.7 (C), 128.0 (2CH), 128.3 (2CH), 131.8 (2CH), 139.8 (C), 158.8 (C); IR (neat): ν = 2980, 2929, 1738, 1604, 1475, 1390, 1283, 1248, 1197, 1045, 815, 800 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{13}{}^{79}BrO$ [M$^+$] m/z 276.0150, found m/z 276.0134, calc. for $C_{14}H_{13}{}^{81}BrO$ [M$^+$] m/z 278.0129, found m/z 278.0115.

1-Bromo-4-(4-methylphenyl)benzene (3db): Prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.23 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 121.4 (C), 127.0 (2CH), 128.8 (2CH), 129.7 (C), 140.3 (C), 129.8 (2CH), 132.0 (2CH), 137.7 (C); IR (neat): ν = 3030, 2855, 1555, 1462, 1450, 1025, 821, 790 cm^{-1}; HRMS (APPI): calc. for $C_{13}H_{11}{}^{79}Br$ [M$^+$] m/z 246.0044, found m/z 246.0064, calc. for $C_{13}H_{11}{}^{81}Br$ [M$^+$] m/z 248.0024, found m/z 248.0044.

1-Bromo-4-(4-nitrophenyl)benzene (3dc): Prepared according to general procedure A by reacting 1,4-dibromobenzene (47 mg, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J =

8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.7 (C), 124.5 (2CH), 127.9 (2CH), 129.1 (2CH), 132.6 (2CH), 137.9 (C), 146.6 (C), 147.5 (C); IR (neat): ν = 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): Prepared according to general procedure A by reacting 1,2-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 100 °C for 6 hours. The reaction was stirred at 100 °C for 6 hours. After extraction, purification of the crude material by preparative TLC (10% EtOAc in heptane) afforded **3ea** as a white powder (41 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3H), 4.07 (q, J = 7.0 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 7.10-7.20 (m, 1H), 7.27-7.31 (m, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.7 (CH_2), 114.1 (2CH), 123.1 (C), 127.5 (CH), 128.6 (CH), 130.7 (2CH), 131.6 (CH), 133.3 (CH), 133.6 (C), 142.5 (C), 158.7 (C); IR (neat): ν = 2971, 2925, 1601, 1570, 1469, 1393, 1251, 1181, 1044, 790 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{13}{}^{78}BrO$ [M+] m/z 276.0150, found m/z 276.0135, calc. for $C_{14}H_{13}{}^{81}BrO$ [M+] m/z 278.0129, found m/z 278.0115.

1-Bromo-2-(4-methylphenyl)benzene (3eb): Prepared according to general procedure A by reacting 1,2-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 was stirred at 100 °C for 6 hours. 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, 3H), 7.17-7.24 (m, 1H), 7.27-7.30 (m, 1H), 7.31-7.41 (m, 4H), 7.69 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 122.9 (C), 127.5 (CH), 128.7 (CH), 128.9 (2CH), 129.5 (2CH), 131.5 (CH), 133.3 (CH), 137.6 (C), 138.4 (C), 142.8 (C); IR (neat): ν = 3029, 2847, 1551, 1459, 1450, 1025, 817, 790 cm^{-1}; HRMS (APPI): calc. for $C_{13}H_{11}{}^{78}Br$ [M+] m/z 246.0044, found m/z 246.0036, calc. for $C_{13}H_{11}{}^{81}Br$ [M+] m/z 248.0024, found m/z 248.0017.

1-Bromo-2-(4-nitrophenyl)benzene (3ec): Prepared according to general procedure A by reacting 1,2-dibromobenzene (24 µL, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 was stirred at 100 °C for 6 hours. 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, 2H), 7.40 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.69 (dd, (d, J = 8.0, 1.1 Hz, 1H), 8.28 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.0 (C), 123.3 (2CH), 127.7 (CH), 129.9 (CH), 130.5 (2CH), 130.9 (CH), 133.5 (CH), 140.4 (C), 147.5 (C), 153.5 (C); IR (neat): ν = 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): Prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 70 °C overnight. After extraction, purification of the crude material by flash chromatography on neutral alumina gel (2% 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, 3H), 4.03 (q, J = 7.0 Hz, 2H), 6.84-6.92 (m, 3H), 6.97 (d, J = 3.9 Hz, 1H), 7.40 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 110.3 (C), 115.2 (2CH), 122.3 (CH), 126.6 (C), 127.2 (2CH), 130.9 (CH), 146.1 (C), 159.1 (C); IR (neat): ν = 2997, 2896, 1618, 1400, 1254, 1164, 1015 cm^{-1}; HRMS (APPI): calc. for $C_{12}H_{11}{}^{79}BrOS$ [M$^+$] m/z 281.9714, found m/z 281.9732, calc. for $C_{12}H_{11}{}^{81}BrOS$ [M$^+$] m/z 283.9694, found m/z 283.9711.

2-Bromo-5-(4-methylphenyl)thiophene (3fb): Prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 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, 3H), 7.00 (bs, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 110.9 (C), 122.9 (CH), 125.7 (2CH), 129.9 (2CH), 130.9 (CH), 131.1 (C), 138.1 (C), 146.3 (C); IR (neat): ν = 2994, 1510, 1441, 1394, 1074, 1045 cm^{-1}; HRMS (APPI): calc. for $C_{11}H_9{}^{79}BrS$ [M$^+$] m/z 251.9608, found m/z 251.9637, calc. for $C_{11}H_9{}^{81}BrS$ [M$^+$] m/z 253.9598, found m/z 253.9616.

2-Bromo-5-(4-fluorophenyl)thiophene (3fd): Prepared according to general procedure A by reacting 2,5-dibromothiophene (23 µL, 0.2 mmol), with potassium 4-fluorophenyltrifluoroborate (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 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, 4H), 7.39-7.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.3 (C), 116.1 (d, J = 21.8 Hz, 2CH), 123.5 (CH), 127.4 (d, J = 8.1 Hz, 2CH), 130.0 (d, J = 3.2 Hz, C), 131.1 (CH), 145.0 (C), 162.5 (d, J = 246.5 Hz, C); IR (neat): □ = 3082, 1613, 1381, 1394, 1170, 1037, 865 cm^{-1}; HRMS (APPI): calc. for $C_{10}H_6{}^{79}BrFS$ [M$^+$] m/z 255.9358, found m/z 255.9386, calc. for $C_{10}H_6{}^{81}BrFS$ [M$^+$] m/z 257.9364, found m/z 257.9337.

1-Trifluoromethanesulfonyl-4-(4-ethoxyphenyl)-benzene (7aa): Prepared according to general procedure A by reacting 1,4-ditrifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 4.07 (q, J = 7.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 115.2 (2CH), 119.1 (q, J = 321.3 Hz, CF_3), 121.8 (2CH), 128.4 (2CH), 128.5 (2CH), 131.8 (C), 141.6 (C), 148.7 (C), 159.3 (C); IR (neat): ν = 2988, 2902, 1604, 1491, 1422, 1394, 1209, 1150, 1044, 817 cm^{-1}; HRMS (APPI): calc. for $C_{15}H_{13}F_3O_4S$ [M$^+$] m/z 346.0487, found m/z 346.0469.

1-Trifluoromethanesulfonyl-4-(4-methylphenyl)-benzene (7ab): Prepared according to general procedure A by reacting 1,4-ditrifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 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, 3H), 7.24-7.27 (m, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 118.9 (q, J = 321.0 Hz, CF_3), 121.6 (2CH), 127.0 (2CH), 128.6 (2CH), 129.7 (2CH), 136.4 (C), 138.0 (C), 141.6 (C), 148.7 (C); IR (neat): ν = 2930, 1493, 1425, 1190, 1050, 810 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{11}F_3O_3S$ [M+] m/z 316.0381, found m/z 316.0369.

1-Trifluoromethanesulfonyl-3-(4-ethoxyphenyl)-benzene (7ba): Prepared according to general procedure A by reacting 1,3-di trifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, J = 7.0 Hz, 3H), 4.07 (q, J = 7.0 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 7.18 (ddd, J = 8.0, 2.3, 1.0 Hz, 1H), 7.40-7.44 (m, 1H), 7.48 (d, J = 8.9 Hz, 2H), 7.44-7.49 (m, 1H), 7.52-7.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.8 (CH_2), 115.2 (2CH), 119.0 (q, J = 320.3 Hz, CF_3), 119.3 (CH), 119.6 (CH), 126.7 (CH), 128.4 (2CH), 130.6 (CH), 131.5 (C), 143.8 (C), 150.3 (C), 159.5 (C); IR (neat): ν = 2988, 2902, 1604, 1491, 1422, 1394, 1209, 1150, 1044, 817 cm^{-1}; HRMS (APPI): calc. for $C_{15}H_{13}F_3O_4S$ [M$^+$] m/z 346.0487, found m/z 346.0473.

1-Trifluoromethanesulfonyl-3-(4-methylphenyl)-benzene (7bb): Prepared according to general procedure A by reacting 1,3-ditrifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 7.09-7.16 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.32-7.46 (m, 4H) 7.46-7.54 (m, 1H). ^{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 (2CH), 130.0 (2CH), 130.6 (CH), 136.4 (C), 138.6 (C), 144.2 (C), 150.3 (C); IR (neat): ν = 2945, 2855, 1598, 1530, 1417, 1345, 1212, 1126 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{11}F_3O_3S$ [M+] m/z 316.0381, found m/z 316.0372.

1-Trifluoromethanesulfonyl-3-(4-nitrophenyl)benzene (7bc): Prepared according to general procedure A by reacting 1,3-di trifluoromethanesulfonylbenzene (75 mg, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30-7.40 (m, 1H), 7.50 (t, J = 1.9 Hz, 1H), 7.54-7.67 (m, 2H), 7.71 (d, J = 8.9 Hz, 2H), 8.32 (d, J = 8.9 Hz, 2H); ^{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 (2CH), 127.6 (CH), 128.3 (2CH), 131.3 (CH), 141.7 (C), 145.4 (C), 148.0 (C), 150.3 (C); IR (neat): ν = 2925, 2865, 1613, 1481, 1421, 1244, 1200, 1139, 1126 cm^{-1}; MS: no ionization could be observed for this compound.

1-Trifluoromethanesulfonyl-2-(4-ethoxyphenyl)-benzene (7ca): Prepared according to general procedure A by reacting 1,2-ditrifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (t, J = 7.0 Hz, 3H), 4.00 (q, J = 7.0 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 7.28-7.54 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 63.7 (CH_2), 114.7 (2CH), 118.6 (q, J = 321.2 Hz, CF_3), 122.3 (CH), 128.0 (C), 128.6 (CH), 128.7 (CH), 130.7 (2CH), 132.1 (CH), 135.5 (C), 147.1 (C), 159.3 (C); IR (neat): ν =2990, 2888, 1614, 1495, 1422, 1397, 1209, 1162, 1056, 877 cm^{-1}; HRMS (APPI): calc. for $C_{15}H_{13}F_3O_4S$ [M$^+$] m/z 346.0487, found m/z 346.0481.

1-Trifluoromethanesulfonyl-2-(4-methylphenyl)-benzene (7cb): Prepared according to general procedure A by reacting 1,2-ditrifluoromethanesulfonyl-benzene (75 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 7.18 (d, J = 7.5 Hz, 2H), 7.23-7.43 (m, 6H); ^{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 (4CH), 132.0 (CH), 132.7 (C), 135.6 (C), 138.2 (C), 146.9 (C); IR (neat): ν =2990, 2888, 1614, 1495, 1422, 1397, 1209, 1162, 1056, 877 cm^{-1}; HRMS (APPI): calc. for $C_{14}H_{11}F_3O_3S$ [M$^+$] m/z 316.0381, found m/z 316.0372.

1-Trifluoromethanesulfonyl-2-(4-nitrophenyl)benzene (7cc): Prepared according to general procedure A by reacting 1,2-di-trifluoromethanesulfonylbenzene (75 mg, 0.2 mmol), with potassium 4-nitrophenyltrifluoroborate (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 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.56 (m, 4H), 7.63 (d, J = 8.9 Hz, 2H), 8.31 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.3 (q, J = 321.0 Hz, CF_3), 122.7 (CH), 124.0 (2CH), 129.1 (CH), 130.6 (2CH), 130.7 (CH), 131.9 (CH), 133.6 (C), 142.4 (C), 146.6 (C), 147.9 (C); IR (neat): ν = 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-triflyl-pyrrole-2,5-carboxylate (7da): Prepared according to general procedure A by reacting pyrrole **6d** (120 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 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, 3H), 1.32 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2 Hz, 3H), 3.98-4.09 (m, 4H), 4.34 (q, J = 6.9 Hz, 2H), 6.08 (s, 2H), 6.88 (d, J = 8.7 Hz, 2H), 7.00

(d, J = 6.6 Hz, 2H), 7.16-7.31 (m, 5H); ^{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 (2CH), 118.0 (q, J = 317.0 Hz, CF_3), 118.3 (C), 121.9 (C), 123.3 (2C), 126.2 (2CH), 127.3 (CH), 128.4 (2CH), 131.5 (2CH), 136.1 (C), 137.7 (C), 158.9 (C), 159.1 (C), 160.6 (C); IR (neat): ν = 2983, 1721, 1556, 1425, 1286, 1243, 1185, 1135, 1022, 921, 829, 731 cm^{-1}; HRMS (ESI): m/z = 570.1433, calcd. for $[M+H]^+$ $C_{26}H_{27}F_3NO_8S$: 570.1409.

Diethyl-*N*-benzyl-3-(4-methylphenyl)-4-triflyl-pyrrole-2,5-carboxylate (7db): Prepared according to general procedure A by reacting pyrrole **6d** (120 mg, 0.2 mmol), with potassium 4-methylphenyltrifluoroborate (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 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, 3H), 1.27 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 3.96 (q, J = 7.2 Hz, 2H), 4.28 (q, J = 7.2 Hz, 2H), 6.02 (s, 2H), 6.95 (d, J = 6.9 Hz, 2H), 7.06-7.28 (m, 7H); ^{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 (2CH), 126.7 (C), 127.4 (CH), 128.5 (2CH), 128.6 (2CH), 130.1 (2CH), 136.0 (C), 137.7 (C), 137.8 (C), 159.1 (C), 160.6 (C); IR (neat): ν = 2963, 1718, 1424, 1289, 1220, 1187, 1133, 1021, 925, 820, 697 cm^{-1}; HRMS (ESI): m/z = 540.1299, calcd. for $[M+H]^+$ $C_{25}H_{25}F_3NO_7S$: 540.1304.

Diethyl-*N*-benzyl-3-(4-nitrophenyl)-4-triflyl-pyrrole-2,5-carboxylate (7dc): Prepared according to general procedure A by reacting pyrrole **6d** (60 mg, 0.1 mmol), with potassium 4-nitrophenyltrifluoroborate (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 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, 3H), 1.28 (t, J = 7.2 Hz, 3H), 3.98 (q, J = 7.2 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.08 (s, 2H), 6.96 (d, J = 6.9 Hz, 2H), 7.17-7.31 (m, 3H), 7.44 (d, J = 8.7 Hz, 2H), 8.19 (d, J = 8.7 Hz, 2H); ^{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 (2CH), 123.2 (C), 126.3 (2CH), 127.6 (CH), 128.7 (2CH), 131.4 (2CH), 135.4 (C), 137.1 (C), 137.2 (C), 147.5 (C), 158.9 (C), 159.8 (C); IR (neat): ν = 2919, 1726, 1524, 1421, 1348, 1276, 1216, 1187, 1133, 1018, 930, 853, 760 cm^{-1}; HRMS (ESI): m/z = 571.0973, calcd. for $[M+H]^+$ $C_{24}H_{22}F_3N_2O_9S$: 571.0998.

2-(4-Fluorophenyl)-6-(4-ethoxyphenyl)pyridine (8): Prepared according to general procedure B by reacting 2,6-dibromopyridine (46 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was first stirred at 40 °C for 6 h. Potassium 4-fluorophenyltrifluoroborate (40 mg, 0.2 mmol) was then added at rt and the mixture was heated at 100 °C during 2 h. After filtration on silica, chromatography of the crude reaction product on silica using 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, 3H), 4.02 (q, J = 7.1 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 7.09 (t, J = 8.1 Hz, 2H), 7.55-7.48 (m, 2H), 7.68 (t, J = 8.1 Hz, 1H), 8.00 (d, J = 8.9 Hz, 2H), 8.08-8.03 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (CH_3), 63.6 (CH_2), 114.6 (2CH), 115.5 (d, J = 21.2 Hz, 2CH), 117.5 (CH), 117.8 (CH), 128.2 (2CH), 128.7 (d, J = 8.3 Hz, 2CH), 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); IR (neat): ν = 2940, 1515, 1413, 1344, 701 cm^{-1}; HRMS (ESI): calc. for $C_{19}H_{17}FNO$ $[M+H]^+$ m/z 294.1289, found m/z 294.1301.

4-Ethoxy-4''-(trifluoromethyl)-1,1':3',1''-terphenyl (9): Prepared according to the general procedure B by reacting 1,3-dibromobenzene **1c** (24 µL, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was stirred at 40 °C for 6 hours. 4-trifluoromethylphenylboronic acid (76 mg, 0.4 mmol) was then added and the mixture was heated at 70 °C during 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 %).

Prepared according to the general procedure B by reacting 1,3-ditrifluoromethanesulfonylbenzene **6b** (75 mg, 0.2 mmol), with potassium 4-ethoxyphenyltrifluoroborate (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 was first stirred at 70 °C for 20 h. 4-Trifluoromethylphenylboronic acid (38 mg, 0.2 mmol) was then added and the mixture was heated at 70 °C during 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, 3H), 4.08 (q, J = 7.0 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.47-7.61 (m, 5H), 7.66-7.79 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (CH_3), 63.8 (CH_2), 115.1 (2CH), 124.5 (q, J = 271.8 Hz, CF_3), 125.8 (CH), 125.9 (q, J = 3.6 Hz, 2CH), 126.0 (CH), 126.8 (CH), 127.7 (2CH), 128.5 (2CH), 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); IR (neat): ν = 2987, 2926, 1605, 1516, 1475, 1328, 1252, 1170, 1129 cm^{-1}; HRMS (ESI): m/z = 425.2329, calcd. for $[M+2MeCN+H]^+$ $C_{25}H_{24}F_3N_2O$: 425.1841.

Diethyl-*N*-benzyl-3-(2-benzyloxyphenyl)-4-(3,4-dimethoxyphenyl)-pyrrole-2,5-carboxylate (10): Prepared according to general procedure B by reacting pyrrole **6d** (60 mg, 0.1 mmol), with potassium 3,4-dimethoxyphenyltrifluoroborate (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 was first stirred at 70 °C for 20 h. 2-Benzyloxyphenyboronic acid (27 mg, 0.12 mmol) was then added at rt and the mixture was heated at 100 °C during 20 h. After filtration on silica, chromatography of the crude reaction product on silica using 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, 3H), 0.83 (t, J = 6.8 Hz, 3H), 3.43 (s, 3H), 3.72 (s, 3H), 3.86 (q, J = 6.8 Hz, 2H), 3.94 (q, J = 6.8 Hz, 2H), 4.84 (s, 2H), 6.03 (s, 2H), 6.50 (s, 1H), 6.57 (s, 1H), 6.58 (s, 1H), 6.74 (d, J = 7.4 Hz, 2H), 6.90 (dd, J = 7.4, 1.2 Hz, 1H), 7.05-6.98 (m, 2H), 7.28-7.06 (m, 9H); ^{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 (2CH), 126.7 (2CH), 126.8 (CH), 127.2 (C), 127.5 (CH), 127.8 (C), 128.2 (CH), 128.4 (2CH), 128.5 (2CH), 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); IR (neat): ν = 2927, 2853, 1712, 1454, 1234, 1200, 1138, 1027, 731cm^{-1}; HRMS (ESI): calc. for $C_{38}H_{38}NO_7$ $[M+H]^+$ m/z 620.2643, found m/z 620.2660.

Supporting Information: Supporting Information contains copies of ^{1}H NMR and ^{13}C NMR spectra.

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[21] The corresponding *p*-methoxy terphenyl has been prepared using different procedures from non-commercial starting materials and in both cases the yields are under 50%: a) M.-Y. Chang, C.-K. Chan, S.-Y. Lin, M.-H. Wu *Tetrahedron* **2013**, *69*, 9616–9624; b) P. García-García, M. A. Fernández-Rodríguez, E. Aguilar *Angew. Chem.* **2009**, *121*, 5642–5645; *Angew. Chem. Int. Ed.* **2009**, *48*, 5534–5537.

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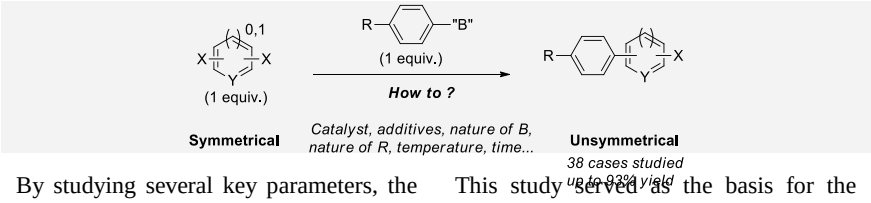
Entry for the Table of Contents

Layout 2:

Cross-Couplings



By studying several key parameters, the factors that allow achieving selective Suzuki-Miyaura mono-coupling on symmetrical dihaloarenes have been outlined. This study served as the basis for the efficient synthesis of unsymmetrical triaryls from symmetrical dibromoarenes and arylditriflates using a one-pot desymmetrizing double Suzuki-Miyaura coupling.

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Selective Suzuki-Miyaura Mono-Couplings with Symmetrical Dibromo-arenes and Arylditriflates for One-pot Synthesis of Unsymmetrical Triaryls.

Keywords: Suzuki-Miyaura, selective coupling, potassium trifluoroborates, triaryls