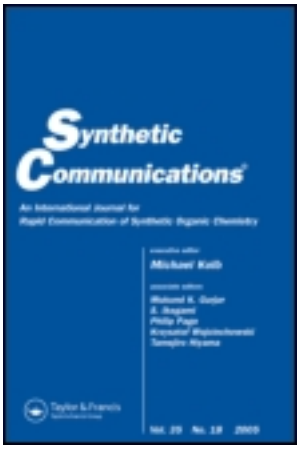

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PREPARATION OF TRIETHYLAMMONIUM TETRA-ARYLBORATES (TEATABs): COUPLING PARTNERS FOR THE SUZUKI REACTION

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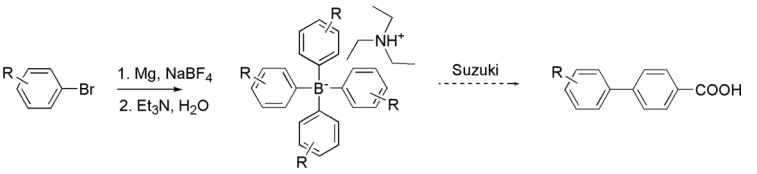
GRAPHICAL ABSTRACT



Abstract *Six triethylammonium tetra-arylborates (TEATABs) were synthesized via a convenient reproducible procedure and characterized by spectroscopic methods (^{1}H, ^{13}C, ^{11}B NMR and electrospray ionization–high-resolution mass spectrometry). The compounds could be stored at ambient temperature and were useful as reactants in the Suzuki reaction in aqueous conditions when using commercially available catalysts.*

Keywords Carboxybiphenyls; organoboron reagents; Suzuki reaction; tetra-arylborates

INTRODUCTION

Traditionally tetra-arylborates have been utilized for precipitation of different cations from water.[1–7] In addition, these compounds have been tested as chemical sensors,[8] as counter anions in ionic liquids,[9] in rhodium-catalyzed addition reactions,[10,11] and also in palladium-catalyzed reactions.[12–17] However, in most cases only the commercially available Ph_4BNa has been reported, and other substituted tetra-arylborates have not been studied.

The preparation of tetra-arylborates involves halogen–metal exchange and subsequent reaction with different boron reagents.[1–4,7,9,18–21] Although methods for the preparation of several tetra-arylborates have been reported, there is still a

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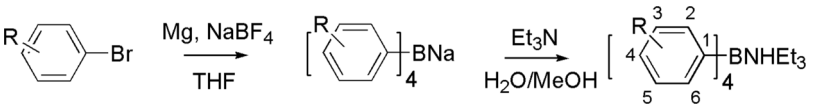
need for a more convenient procedure for differently substituted tetra-arylborates. In this work, we describe a reliable method for the preparation of these types of compounds. Six different tetra-arylborates were synthesized by utilizing triethylammonium as a counter ion. When tetra-arylborates were isolated and purified as Et_3NH^+ salts, the procedures were easy and convenient. In addition, the triethylammonium tetra-arylborates (TEATABs) were found to be suitable coupling partners for the Suzuki reaction.

RESULTS AND DISCUSSION

Tetra-arylborates have recently been prepared using a wide variety of methods.[1–4,8,18,20] So far, the isolation and purification of substituted tetra-arylborates have been problematic, and many operations are required. An advantage of our method is that formed Grignard reagent reacts in situ with $NaBF_4$, and transfer of the sensitive Grignard reagent solution from flask to flask can be omitted. The solubility of TEATABs in alcohol and water is less than corresponding sodium salts. To take advantage of this property, cation exchange was performed, and TEATABs were isolated in pure form by filtration. For most purposes, this crude product is pure enough for further use. This method is suitable for all prepared TEATABs regardless of substituent, and the preparation can be performed at gram scale (Table 1).

The solubility was tested in different solvent systems, which have been commonly utilized in the Suzuki reaction [dimethylformamide (DMF), DMF/H_2O (2:1), acetone, acetone/H_2O (3:2), toluene, toluene/EtOH (1:1), EtOH, EtOH/H_2O (1:1), and H_2O]. The Suzuki reactions with Ph_4BNa are normally performed at 0.1–0.4 M concentrations,[12–14,22] and therefore solubility was tested at concentrations between 0.1 and 1 M. Ph_4BNa was found highly soluble (0.6–1 M) in all tested solvents except toluene. Solubility of TEATAB **1** was low (<0.1 M) in these solvents.

Table 1. Preparation of TEATABs



Compound	Substituent R	Yield (%)[a]
1	H	75[b]
2	4-Cl	81
3	3-Cl	86
4	3,5-di-Cl	44
5	4-OMe	53
6	4- 	50

[a]Isolated yield after recrystallization. No attempts was made to find the best recrystallization solvents.

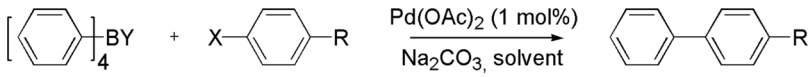
[b]Preparation started from commercially available Ph_4BNa, and only cation exchange was used.

In aqueous ethanol, however, the solubility difference between Ph_4BNa and TEATAB **1** was remarkable. Also, the solubility of substituted TEATAB **2** was examined in toluene, toluene/EtOH (1:1), EtOH, and EtOH/water (1:1). The compound was soluble in toluene/EtOH (1:1) (0.6 M) and EtOH (0.9 M), unlike TEATAB **1**, but it was practically insoluble in EtOH/water (1:1) (<0.1 M). TEATAB **1**, was not soluble in the examined solvents at concentrations where the Suzuki reaction is normally performed, except for acetone/H_2O (0.3 M) and DMF/water (0.2 M). Solubility of TEATAB **2** was greater than solubility of TEATAB **1**, but both were practically insoluble in water.

These compounds offer a good alternative to known and routinely used organoboron compounds for transition-metal-catalyzed reactions. Also, boronic acids, boronate esters, and organotrifluoroborates have been prepared using halogen–metal exchange and subsequent reaction with boron reagents.[23] In general, boronic acids and organotrifluoroborates react fast and in good yields under coupling conditions. However, the determination of the precise stoichiometry of boronic acids in the reaction is difficult because of their ability to form dimers and trimers during storage. Potassium organotrifluoroborates have the same benefits as TEATABs. Both of them are stable and easily prepared and purified. However, highly corrosive and poisonous reagents such as KF, KHF_2, or HF are needed in the preparation of organotrifluoroborates.[24]

After the successful preparation of TEATABs, the utility of these novel salts in the Suzuki reaction was explored. Both Na^+ and Et_3NH^+ salts were examined in parallel. The reactivity of TEATAB **1** and commercially available sodium tetraphenylborate (Ph_4BNa) were compared utilizing the same reaction as Bumagin and Bykov.[14] The reactivity of TEATAB **1** was similar or slightly better than that of the corresponding sodium salt (Table 2, entries 1–8). When water was used as a

Table 2. Suzuki reaction using TEATAB **1** and Ph_4BY[a]



Entry	Halide X/R	Solvent	Borate Y	Temp. (°C)	Time (h)	Yield (%)	Literature yield[14]
1	I/-NO_2	H_2O	Na^+	100	2	71	96
2	I/-NO_2	H_2O	Et_3NH^+	100	2	79	
3	I/-NO_2	H_2O	Na^+	25	24	75	50
4	I/-NO_2	H_2O	Et_3NH^+	25	24	14	
5	I/-NO_2	Acetone/H_2O (3:2)	Na^+	25	10	98	98
6	I/-NO_2	Acetone/H_2O (3:2)	Et_3NH^+	25	10	98	
7	I/-NO_2	DMF/H_2O (2:1)	Na^+	25	10	76	81
8	I/-NO_2	DMF/H_2O (2:1)	Et_3NH^+	25	10	86	
9	Br/-OMe	Acetone/H_2O (3:2)	Na^+	25	2	72[b]	
10	Br/-OMe	Acetone/H_2O (3:2)	Et_3NH^+	25	2	72[b]	

[a]Reaction conditions: tetra-arylborate (0.27 mmol), 4-iodonitrobenzene (1 mmol), $Pd(OAc)_2$ (1 mol%), Na_2CO_3 (1 mmol), and solvent (5.3 ml).

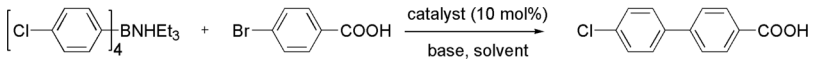
[b]10 mol% of catalyst was used.

solvent and the reaction was performed at room temperature (entries 3 and 4), the sodium salt produced a greater yield than TEATAB **1**. This is due to the higher solubility of Ph_4BNa in water. On the other hand, when the reaction was performed at 100 °C (entries 1 and 2), the yields were almost equal. According to these experiments, we concluded that acetone/H_2O was the best solvent system (entries 5 and 6) for the reaction. To further explore the compatibility of TEATABs in the Suzuki reaction, these substrates were subjected to the reaction with an electron-rich halide (entries 9 and 10). The reaction was rapid and completed at room temperature regardless of the cation. In addition, the yields were comparable to those reactions where trifluoroborates were utilized as coupling partners.[23]

Previous reports have focused on unsubstituted tetra-arylborates (Ph_4BX) as reactants in the Suzuki coupling.[12–15] Only one example where substituted tetra-arylborates have been used as reactants can be found in the literature.[17] When the chlorinated TEATAB **2** was used as the reactant, a dramatic difference in reactivity was noticed. Surprisingly, no reaction could be observed between TEATAB **2** and 4-iodonitrobenzene in acetone/water at room temperature, unlike TEATAB **1** (Table 2, entry 6). When the reaction was performed at 85 °C for 18 h, 69% of the desired product was obtained. The reaction was repeated by using 4-bromoanisole as the halide. Also in this case, external heating was needed, and 4-methoxy-4′-chlorobiphenyl was obtained in 62% yield.

Because of this diminished reactivity of substituted TEATABs, a revision of reaction conditions was necessary to get greater conversion and shorter reaction times. The reaction between TEATAB **2** and 4-bromobenzoic acid was chosen as a model reaction (Table 3). In the context of an ongoing synthetic project in our group, we were interested in the preparation of carboxy-functionalized biaryls.[25] In addition, 4-bromobenzoic acid has been widely utilized in the Suzuki reaction previously.[12–15] At first, $Pd(OAc)_2$ was used as the catalyst, and different solvents

Table 3. Effect of the base and the catalyst on the Suzuki reaction in different solvents[a]



Entry	Catalyst	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)
1	$Pd(OAc)_2$	Acetone/H_2O (3:2)	Na_2CO_3	rt	2	50
2	$Pd(OAc)_2$	Acetone/H_2O (3:2)	Na_2CO_3	85	18	60
3	$Pd(OAc)_2$	DMF/H_2O (2:1)	Na_2CO_3	85	48	74
4	$Pd(OAc)_2$	EtOH/H_2O (1:1)	Na_2CO_3	85	18	55
5	Pd/C	Acetone/H_2O (3:2)	Na_2CO_3	85	18	26
6	Pd/C	EtOH/H_2O (1:1)	Na_2CO_3	85	18	40
7	$Pd(PPh_3)_4$	Acetone/H_2O (3:2)	Na_2CO_3	85	4	86[b]
8	$Pd(PPh_3)_4$	EtOH/H_2O (1:1)	Na_2CO_3	85	2	97[b]
9	$Pd(PPh_3)_4$	EtOH/H_2O (1:1)	NaOH	85	18	61[b]
10	$Pd(PPh_3)_4$	EtOH/H_2O (1:1)	Et_3N	85	18	44[b]

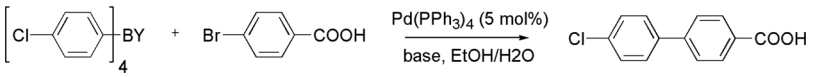
[a]Reaction conditions: TEATAB **1** (0.068 mmol), 4-bromobenzoic acid (0.25 mmol), base (0.5 mmol), and solvent (1 ml).

[b]Same results were also obtained when 5 mol% catalyst was used.

were tested (Table 3, entries 1–4). DMF/H_2O (entry 3) was found to be a slightly better solvent system than acetone/H_2O, but an extended reaction time was needed to obtain a good yield. The previously reported catalyst, Pd/C,[13] was also tested, but only poor yields were obtained (entries 5 and 6). The ligandless catalyst system was replaced by the commonly used $Pd(PPh_3)_4$ system, and reactions were performed in acetone/water and ethanol/water solvent mixtures. Complete conversion and excellent yields were obtained after 2 h in ethanol/water and after 4 h in acetone/water (Table 3, entries 7 and 8). The choice of base plays an important role in the Suzuki reaction[26,27] and therefore sodium carbonate, sodium hydroxide, and triethylamine were tested (entries 8–10). Sodium carbonate proved to be the best base, under these reaction conditions (entry 8). When NaOH was used as a base, the yield of the product was reduced (entry 9). Et_3N was also less effective as a base (entry 10). In summary, entry 8 gave the best results, taking into account the reaction time (2 h) and yield (97%).

There is a reason to assume that cation exchange takes place in the reaction media.[13] To prove this hypothesis, TEATAB **1** (1 equiv, 0.24 mmol) was placed in a test tube with EtOH/H_2O (1:1) (2.4 ml) and Na_2CO_3 (aq.) (6.7 equiv). The mixture was heated to 80 °C and kept at that temperature for 2 h. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated to dryness. An NMR sample was prepared, and only sodium tetra-arylborate could be observed. This experiment clearly shows that cation exchange takes place under these reaction conditions. To examine the influence of cation exchange on reactivity, TEATAB **2** and the corresponding sodium salt were subjected to the Suzuki reaction. Triethylamine and sodium carbonate were used as bases, and the yields were compared (Table 4). With both tetra-arylborates, the best results were obtained when both Na^+ and Et_3NH^+ were present in the reaction media (Table 4, entries 2 and 3). The best result was obtained when Et_3NH^+ was used as a counter ion and Na_2CO_3 as a base (Table 4, entry 3). When triethylamine was used as a base, the yield was lower (Table 4, entry 2). This behavior can be explained by the fact that triethylamine has been reported to be a far less efficient base in the Suzuki reaction.[28] The main reason for this base effect is not only the basicity of the anion but also the contribution of the cation, because metal cations accelerate the formation of palladium–boron complexes.[28] Organic amine bases have been reported to have a

Table 4. Effect of use of different bases and cations (Y) of the tetra-arylborate[a]



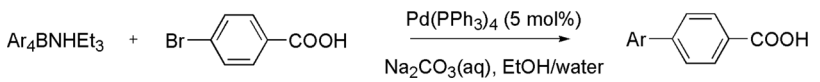
Entry	Y	Base	Yield (%)
1	Na^+	Na_2CO_3	50
2	Na^+	Et_3N	68
3	Et_3NH^+	Na_2CO_3	97
4	Et_3NH^+	Et_3N	44

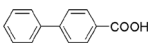
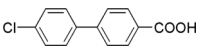
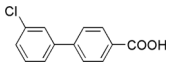
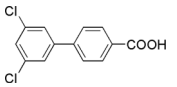
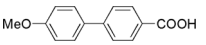
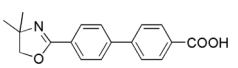
[a]Reaction conditions: tetra-arylborate (0.068 mmol), 4-bromobenzoic acid (0.25 mmol), base (0.5 mmol), and EtOH/H_2O (1 ml).

co-operative role in the coupling reaction.[29] These results indicate that the presence of triethylamine increases the reactivity, but the reaction also needs the smaller cation Na^+ for greater conversion. The reaction mechanism is more complicated also because free carboxylic acid could play an active role in this reaction. It has been reported that carboxylic acid and amine groups attach to the tetracoordinated boron by replacement of two phenyl groups.[30] As a conclusion, both amines and carboxylic acids can play an active role in the Suzuki reaction. Currently, the co-operative role of carboxy- and amino- functionalities in the Suzuki reaction is under further investigation in our laboratory.

Finally the differentially substituted TEATABs **1**–**6** were subjected to the reaction conditions according to Table 3, entry 8. The results are collected in Table 5. Monochloro-substituted TEATABs **2** and **3** furnished the coupling products in good to excellent yields (entries 2 and 3). However, when the TEATAB was adorned with two chloro-substituents, the desired biphenyl was not obtained. This effect of the extension of electron-withdrawing properties indicates that electron-donating substituents would make the TEATABs more reactive. Accordingly, 4-methoxy-4′-carboxybiphenyl was obtained in 95% yield (entry 5). Another electron-withdrawing group containing TEATAB **6** (entry 6) was tested, but it was totally unreactive under these reaction conditions. One explanation could be the interaction of the oxazoline group with the Pd catalyst.

Table 5. Suzuki reaction between TEATABs **1**–**6** and 4-bromobenzoic acid[a]



Entry	Ar_4BNHEt_3	Product	Yield (%)
1	**1**		90
2	**2**		97
3	**3**		73[b]
4	**4**		Traces[b,c]
5	**5**		95
6	**6**		—[d]

[a]Reaction conditions: TEATAB (0.18 mmol), 4-bromobenzoic acid (0.60 mmol), $Pd(PPh_3)_4$ (0.030 mmol, 5 mol%), Na_2CO_3(aq) (1.19 mmol), and $EtOH/H_2O$ (1:1) (0.5 ml) at 85 °C, 2 h.

[b]Reaction time was 18 h.

[c]NMR analysis indicated that traces of desired compound were formed as well as many side products. Isolation was not attempted.

[d]After 48 h, the product was not observed.

The mechanism of this reaction has not been fully explored. In the proposed mechanism, the oxidative addition is followed by the coupling of one aryl group of Ar_4BNa.[13] The generated Ar_3B, $Ar_2B(OH)$, and $ArB(OH)_2$ take part in the presence of base in the next catalytic cycles. This means that the first catalytic cycle takes place in the absence of base.[31] However, in the case of trifluoroborate salts, no reaction was observed when the reaction was performed without a base,[24b] suggesting that one or more fluorine groups must be replaced by hydroxyl groups to form a new type of tetracoordinated species [for example, $ArBF_2(OH)^-$]. This kind of replacement cannot take place when TEATABs are used because otherwise quantitative yields could not be obtained. Braga et al. have proposed that palladium and boron are connected to each other via an oxygen bridge during the transmetallation step.[32] The structure of this intermediate in the transmetallation step of the reactions of tetra-arylborates is unknown. Further mechanistic studies are ongoing in our laboratory.

In conclusion, substituted TEATABs were prepared using convenient and reproducible methods, and their properties in the Suzuki reaction were investigated. TEATABs could be obtained as stable solids and are easier to prepare and purify than their corresponding Na^+ salts. In addition, the reactivity of TEATABs in the Suzuki reaction is comparable and even better. Moreover, TEATABs are new and interesting orgonoboron reagents, which offer good atom economy in cross-coupling reactions. The large reactivity difference between TEATAB **1** and TEATAB **2** shows that substituents in the aromatic rings have considerable effect in the tetracoordinated boron. Electron-withdrawing substituents were found to reduce the yield. Also, the counter cation and steric hindrance appears to have an effect on the reactivity. Further mechanistic studies need to be performed before any further conclusions can be made.

EXPERIMENTAL

Solvents and reagents were purchased from Sigma-Aldrich or Merck. Tetrahydrofuran (THF) was dried over sodium and freshly distilled before use. Other solvents and reagents were used as received. Thin-layer chromatography (TLC) was performed on precoated (silica gel 60 F_{254}) aluminum plates, and visualization was performed by ultraviolet light. Silica gel 60, particle size 0.040–0.063 nm, was used for column chromatography. ^1H and ^{13}C NMR spectra were measured with a Varian Mercury 300 spectrometer at 300 and 75 MHz, respectively, using $CDCl_3$, acetone-d_6, or dimethylsulfoxide (DMSO-d_6) as solvents. Chemical shifts are reported in δ values (ppm) relative to TMS. ^{11}B NMR spectra were measured with a Bruker AV-600 spectrometer as c. 50 mg/ml solutions in acetone-d_6 at 192.66 MHz. BF_3-etherate was used as an external standard ($\delta = 0.0$ ppm). Melting points were determined with a Stuard 110 melting-point apparatus. High-resolution mass spectra (HMRS-ESI) were recorded using a MicroTOF-Q mass spectrometer. The syntheses of TEATABs **2**–**6** were carried out under an argon atmosphere. The Suzuki reactions were performed in sealed tubes.

Triethylammonium Tetraphenylborate (1)

Commercially available sodium tetraphenylborate (11 g, 32 mmol) was dissolved in 100 ml of MeOH/water (1:1), and 200 ml of a 2.5 wt% solution (aq.) of

triethylamine (1.5 equiv.) was added. During the addition, a white precipitate was formed. The precipitate was filtered, washed with water, and dried in a vacuum. White solid (10.14 g, 75% yield); mp 197–198 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.35–7.31 (m, 8H, H2/H6), 6.96–6.94 (m, 8H, H3/H5), 6.91–6.79 (t, 4H, $J = 7.9$ Hz, H4), 3.22 (q, 6H, $J = 7.3$ Hz, CH_2), 1.26 (t, 9H, $J = 7.3$ Hz, CH_3); ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 164.96 ($J_{BC} = 49.4$ Hz, C1), 136.93 ($J_{BC} = 1.4$ Hz, C2/C6), 125.99 ($J_{BC} = 2.8$ Hz, C3/C5), 122.26 ($J_{BC} < 1$ Hz, C4); 48.13 (CH_2), 9.39 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −6.514. ESI-HRMS m/z calcd. for $C_{36}H_{52}BN_2$: 523.4224; found 523.4226 $[M + Et_3NH]^+$.

Triethylammonium Tetra(4-chlorophenyl)borate (2)

Sodium tetrafluoroborate (0.982 g, 0.009 mol), Mg turnings (0.932 g, 0.038 mol), and a crystal of I_2 were suspended in THF (2 ml) in a reaction flask. One-fifth of a solution of 4-chlorobromobenzene (7.20 g, 0.038 mol) in dry THF (20 ml) was added dropwise to the reaction mixture. The reaction mixture was stirred with gently warming to initiate the reaction. The rest of the solution was then slowly added to maintain reflux for 1 h. The mixture was stirred overnight at room temperature and quenched by pouring it into 100 ml of $Na_2CO_3/NaOH/H_2O$ (4:1:200) solution with vigorous stirring. The aqueous solution was saturated with NaCl and extracted with ether (4 × 50 ml). The ether was removed in vacuo, and a yellow syrup was obtained. The residue was dissolved in H_2O/MeOH (1:1, 100 ml) and filtered through a pad of celite to obtain a clear solution. The solution was treated with 2.5 wt% Et_3N solution (aq.) (2.6 equiv., 100 ml). The crude product precipitated and was filtered by suction. The crude product was dissolved in acetone (10 ml), and the insoluble material was filtered off. Water was added dropwise to the clear solution with vigorous stirring until a white precipitate formed. After filtration, a white solid was obtained (4.08 g, 81% yield); mp 101–103 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.20–7.15 (m, 8H, H2/H6), 6.98 (d, 8H, $J = 8.5$ Hz, H3/H5), 3.44 (q, 6H, $J = 7.3$ Hz, CH_2), 1.30 (t, 9H, $J = 7.3$ Hz, CH_3);^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 161.78 ($J_{BC} = 49.6$ Hz, C1), 138.07 ($J_{BC} = 1.7$ Hz, C2/C6)), 128.54 ($J_{BC} < 1$ Hz, C4), 126.29 ($J_{BC} = 3.1$ Hz, C3/C5), 48.00 (CH_2), 9.48 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −7.426. ESI-HRMS m/z calcd. for $C_{30}H_{32}BNNaCl_4$: 580.1280; found 580.1284 $[M + Na]^+$.

Triethylammonium Tetra(3-chlorophenyl)borate (3)

Compound **3** was prepared in a way similar to compound **2**. The crude product was recrystallized from methanol/water (1:1). White solid (4.33 g, 86% yield); mp 182–185 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.24–7.20 (m, 4H, H2 or H6), 7.18–7.13 (m, 4H, H2 or H6), 7.02 (t, 4H, $J = 7.6$ Hz, H5), 6.92–6.88 (m, 4H, H4), 3.42 (q, 6H, $J = 7.3$ Hz, CH_2), 1.38 (t, 9H, $J = 7.3$ Hz, CH_3). ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 165.86 ($J_{BC} = 49.4$ Hz, C1), 135.74 ($J_{BC} = 1.7$ Hz, C6), 134.85 ($J_{BC} = 1.3$ Hz, C2), 132.87 ($J_{BC} = 3.9$ Hz, C3), 128.19 ($J_{BC} = 3.1$ Hz, C5), 123.16 ($J_{BC} < 1$ Hz, C4), 48.14 (CH_2), 9.40 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −6.766. ESI-HRMS m/z calcd. for $C_{30}H_{32}BNNaCl_4$: 580.1280; found 580.1265 $[M + Na]^+$.

Triethylammonium Tetra(3,5-dichlorophenyl)borate (4)

Compound **4** was prepared in a way similar to compound **2**. The crude product was recrystallized from MeOH/water. White solid (2.68 g, 44% yield); mp 198–201 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.10–7.05 (12H, m, ArH), 3.47 (q, 6H, $J = 7.3$ Hz, CH_2), 1.41 (t, 9H, $J = 7.3$ Hz, CH_3). ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 165.45 ($J_{BC} = 49.4$ Hz, C1), 133.94 (C2/C6, overlap with peak 133.88), 133.88 (C3/C5, overlap with peak 133.94), 123.91 (C4), 48.17 (CH_2), 9.42 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −6.939. ESI-HRMS calcd. for $C_{30}H_{28}BNCl_8K$: 731.9460; found 731.9452 $[M + K]^+$.

Triethylammonium Tetra(4-methoxyphenyl)borate (5)

Sodium tetrafluoroborate (0.23 g, 0.002 mol) and Mg turnings (0.40 g, 0.017 mol) were placed in a reaction flask under argon. Dry THF (1 ml) and a crystal of I_2 crystal were added. A solution of 4-bromoanisole (3.12 g, 0.017 mol) in dry THF (10 ml) was added dropwise. Isolation and purification was performed by a procedure similar to that described previously. White solid (0.57 g, 53% yield); mp 106–109 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.22–7.18 (m, 8H, H2/H6), 6.55 (d, 8H, $J = 8.5$ Hz, C3/C5), 3.32 (q, 6H, $J = 7.3$ Hz, CH_2), 1.33 (t, 9H, $J = 7.3$ Hz, CH_3); ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 156.72 ($J_{BC} = 50.1$ Hz, C1), 156.23 ($J_{BC} < 1$ Hz, C4), 137.41 ($J_{BC} = 1.7$ Hz, C2/C6), 111.72 ($J_{BC} = 3.0$ Hz, C3/C5), 54.87 (OCH_3), 48.02 (CH_2), 9.40 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −7.667. ESI-HRMS calcd. for $C_{40}H_{60}BN_2O_4$: 643.4646; found 643.4650 $[M + Et_3NH]^+$.

Triethylammonium Tetra[4-(4,4-dimethyl)-4,5-dihydro-oxazoles)phenyl]borate (6)

Compound **6** was prepared in a way similar to compound **2**. The crude product was dissolved in THF/water (1:2) and filtered through celite. A solution of triethylamine (2.5 wt%, 2.6 equiv.) was added to the clear solution with vigorous stirring. The formed white precipitate was filtered, washed with toluene, and recrystallized from THF/H_2O. White solid (3.64 g, 50% yield); mp 247–248 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.60–7.57 (d, 8H, $J = 8.3$ Hz, H2/H6), 7.41–6.44 (m, 8H, H3/H5), 4.06 (s, 8H, CH_2O,), 1.32 [s, 24H, $(CH_3)_2C$], 2.47 (q, 6H, $J = 7.3$ Hz, CH_2), 0.92 (t, 9H, $J = 7.3$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 165.11 (O<u>C</u>=N), 135.88 (C1), 125.93 (C2/C6 and C3/C5), 121.0 (C4), 79.05 (OCH_2), 66.57 [$(CH_3)_2$<u>C</u>], 46.41 (CH_2), 28.26 [(<u>C</u>$H_3)_2C$], 8.83 (CH_3); ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −6.401. ESI-HRMS calcd. for $C_{44}H_{50}BN_4O_4$: 709.3925; found 709.3947 $[M\text{-}Et_3NH + 2H]^+$.

Sodium Tetra(4-chlorophenyl)borate[18]

The preparation was carried out using a published method.[18] ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm): 7.21–7.15 (m, 8H, H2/H6), 6.99 (d, 8H, $J = 6.42$ Hz, H3/H5). ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm): 162.53 ($J_{BC} = 49.6$ Hz, C1),

138.81 (J_{BC} = 1.7 Hz, C2/C6), 129.27 (J_{BC} < 1 Hz, C4), 127.02 (J_{BC} = 3.0 Hz, C3/C5). ^{11}B NMR (192.55 MHz, acetone-d_6) δ (ppm): −6.689.

General Procedure for the Suzuki Coupling: Preparation of 4′-Chlorobiphenyl-4-carboxylic Acid from TEATAB 2

TEATAB **2** (101 mg, 0.18 mmol), 4-bromobenzoic acid (115 mg, 0.60 mmol), $Pd(PPh_3)_4$ (35 mg, 0.030 mmol, 5 mol%), 2 M Na_2CO_3 (aq.) (595 µl, 1.19 mmol) and $EtOH/H_2O$ (1:1) (0.5 ml) were placed in a sealed tube. The reaction mixture was stirred at 85 °C for 18 h. The reaction was quenched by adding 3 M HCl (0.5 ml) and diluted with EtOAc (30 ml). The reaction mixture was filtered through celite and was washed with water (2 × 15 ml) and brine (1 × 15 ml). After drying (Na_2SO_4) and filtration, the solvents were removed by a rotary evaporator. The crude product was purified using column chromatography [eluent $CHCl_3$–MeOH (90:10)] or recrystallization (EtOAc/MeOH), and the desired compound was obtained as a white solid (135 mg, yield 97%).

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REFERENCES

1. Vandeberg, J. T.; Moore, C. E.; Cassaretto, F. P.; Posvic, H. Tetraarylborates, III: Preparation and reagent properties of sodium tetrakis(p-trifluoromethylphenyl)borate and sodium tetrakis(m-fluorophenyl)borate. *Anal. Chim. Acta* **1969**, *44*, 175–183.
2. Moore, C. E.; Cassaretto, F. P.; Posvic, H.; McLafferty, J. J. Tetraarylborates, II: Preparation and reagent properties of sodium tetrakis(p-fluorophenyl)borate, a selective reagent for cesium. *Anal. Chim. Acta* **1966**, *35*, 1–5.
3. Meisters, M.; Moore, C. E.; Cassaretto, F. P. Tetraarylborates, IV: Preparation and reagent properties of sodium tetrakis[m-(trifluoromethyl)phenyl]borate. *Anal. Chim. Acta* **1969**, *44*, 287–291.
4. Jarzembowski, F.; Cassaretto, F.; Posvic, H.; Moore, C. E. Tetraarylborates, VI: Preparation and reagent properties of sodium tetrakis(m-chlorophenyl)borate. *Anal. Chim. Acta* **1974**, *73*, 409–412.
5. Chao, S.; Moore, C. E. Studies in the tetraarylborates, part VII: The preparation and reagent properties of some new nitrogen heterocyclic tetraarylborates, especially sodium tetrakis(1-imidazolyl)borate, a novel gravimetric reagent for hydrogen ion. *Anal. Chim. Acta* **1978**, *100*, 457–467.
6. Hirishi, N.; Naoko, T.; Masaji, Y. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate: Highly lipophilic stable anionic agent for solvent-extraction of cations. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600–2604.
7. Pacey, G. E.; Moore, C. E. The synthesis and reagent properties of magnesium tetrakis(4-tert-butylphenyl)borate. *Talanta* **1981**, *28*, 688–690.

8. Alaviuhkola, T.; Bobacka, J.; Nissinen, M.; Rissanen, K.; Ivaska, A.; Pursiainen, J. Synthesis, characterization, and complexation of tetraarylborates with aromatic cations and their use in chemical sensors. *Chem. Eur. J.* **2005**, *11*, 2071–2080.
9. van den Broeke, J.; Stam, M.; Lutz, M.; Kooijman, H.; Spek, A.; Deelman, B.; van Koten, G. Designing ionic liquids: 1-Butyl-3-methylimidazolium cations with substituted tetraphenylborate counterions. *Eur. J. Inorg. Chem.* **2003**, 2798–2811.
10. Ueura, K.; Miyamura, S.; Satoh, T.; Miura, M. Rhodium-catalyzed addition of arylboron compounds to nitriles, ketones, and imines. *J. Organomet. Chem.* **2006**, *691*, 2821–2826.
11. Shintani, R.; Tsutsumi, Y.; Nagaosa, M.; Nishimura, T.; Hayashi, T. Sodium tetraarylborates as effecive nucleophiles in rhodium/diene-catalyzed 1,4-addition to β,β-disubstituted α, β-unsaturated ketones: Catalytic asymmetric construction of quaternary carbon stereocenters. *J. Am. Chem. Soc.* **2009**, *131*, 13588–13589.
12. Lu, G.; Franzen, R.; Yu, X. J.; Xu, Y. J. Synthesis of flurbiprofen via Suzuki reaction catalyzed by palladium charcoal in water. *Chin. Chem. Lett.* **2006**, *17*, 461–464.
13. Lu, G.; Franzen, R.; Zhang, Q.; Xu, Y. J. Palladium charcoal-catalyzed, ligandless Suzuki reaction by using tetraarylborates in water. *Tetrahedron Lett.* **2005**, *46*, 4255–4259.
14. Bumagin, N.; Bykov, V. Ligandless palladium-catalyzed reactions of arylboronic acids and sodium tetraphenylborate with aryl halides in aqueous media. *Tetrahedron* **1997**, *53*, 14437–14450.
15. Bykov, V. V.; Bumagin, N. A. Effective heterogeneous palladium catalysis of the reaction of organoboron compounds with aryl halides. *Russ. Chem. Bull.* **1997**, *46*, 1344–1346.
16. Leadbeater, N.; Marco, M. Transition-metal-free Suzuki-type coupling reactions: Scope and limitations of the methodology. *J. Org. Chem.* **2003**, *68*, 5660–5667.
17. Ciattini, P.; Morera, E.; Ortar, G. Palladium-catalyzed cross-coupling reactions of vinyl and aryl triflates with tetra-arylborates. *Tetrahedron Lett.* **1992**, *33*, 4815–4818.
18. Anulewicz-Ostrowska, R.; Klis, T.; Krajewski, D.; Lewandowski, B.; Serwatowski, J. Synthesis of some halogenated tetraarylborates. *Tetrahedron Lett.* **2003**, *44*, 7329–7331.
19. Murphy, S. T.; Yang, X.; Schuster, G. B. Cyanine borate salts that form penetrated ion pairs in benzene solution: Synthesis, properties, and structure. *J. Org. Chem.* **1995**, *60*, 2411–2422.
20. Yakelis, N.; Bergman, R. Safe preparation and purification of sodium tetrakis[(3,5-trifluoromethyl)phenylborate (NaBArF24): Reliable and sensitive analysis of water in solutions of fluorinated tetraarylborates. *Organometallics* **2005**, *24*, 3579–3581.
21. Yoo, A.; Moore, C. The synthesis of some lipophilic tetra-arylborates for use in membrane-electrode preparation. *Talanta* **1991**, *38*, 493–496.
22. Kuuloja, N.; Kylmälä, T.; Xu, Y. J.; Franzen, R. Synthesis of xenbucin using Suzuki reaction catalyzed by Pd/C in water. *Cent. Eur. J. Chem.* **2008**, *6*, 390–392.
23. Hall, D. *Boronic acid*; Wiley VCH: Weinheim, Germany, 2005, p. 28.
24. (a) Vedejs, E.; Chapman, R.; Fields, S.; Lin, S.; Schrimpf, M. Conversion of arylboronic acids into potassium aryltrifluoroborates—Convenient precursor of arylboron difluoride Lewis acids. *J. Org. Chem.* **1995**, *60*, 3020–3027; (b) Batey, R. A.; Quach, T. D. Synthesis and cross-coupling reaction of tetraalkylammonium organotrifluoronborate salts. *Tetrahedron Lett.* **2001**, *42*, 9099–9103.
25. Kylmala, T.; Kuuloja, N.; Xu, Y.; Rissanen, K.; Franzen, R. Synthesis of chlorinated biphenyls by Suzuki cross-coupling using diamine or diimine-palladium complexes. *Eur. J. Org. Chem.* **2008**, 4019–4024.
26. Kotha, S.; Lahiri, K.; Kashinath, D. Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis. *Tetrahedron* **2002**, *58*, 9633–9695.
27. Suzuki, A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576*, 147–168.
28. Cepanec, I. *Synthesis of Biaryls*; Elsevier: Zagreb, Croatia, 2004; p. 364.

29. McKinley, N.; O'Shea, D. Efficient synthesis of aryl vinyl ethers exploiting 2,4,6-trivinylcyclotriboroxane as a vinylboronic acid equivalent. *J. Org. Chem.* **2004**, *69*, 5087–5092.
30. Bessler, K.; Dourado, E.; Carvalho, M.; Lemos, S.; Ellena, J. An alternative method for the preparation of diphenylboron chelates: The crystal and molecular structures of (pyridine-2-acetyloximato)diphenylboron and (1-phenylazo-2-naphtholato)diphenylboron. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1935–1940.
31. During the preparation of this manuscript, utilization of NHC-boranes in the Suzuki reaction was reported. The mechanistical proposal was in accordance with Ref. 13. Monot, J.; Brahmi, M. M.; Ueng, S-H.; Robert, C.; Desage-El Murr, M.; Curran, D.; Malacria, M.; Fensterbank, L.; Lacote, E. *Org. Lett.* **2009**, *11*, 4914–4917.
32. Braga, A. A. C.; Morgon, N. H.; Ujaque, G.; Lledós, A.; Maseras, F. Computational study of the transmetallation process in the Suzuki–Miayra cross-coupling of aryls. *J. Organomet. Chem.* **2006**, *691*, 4459–4466.