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Palladium-Catalyzed Arylation of Polar Organometallics Mediated by 9-Methoxy-9-Borabicyclo[3.3.1]nonane: Suzuki Reactions of Extended Scope

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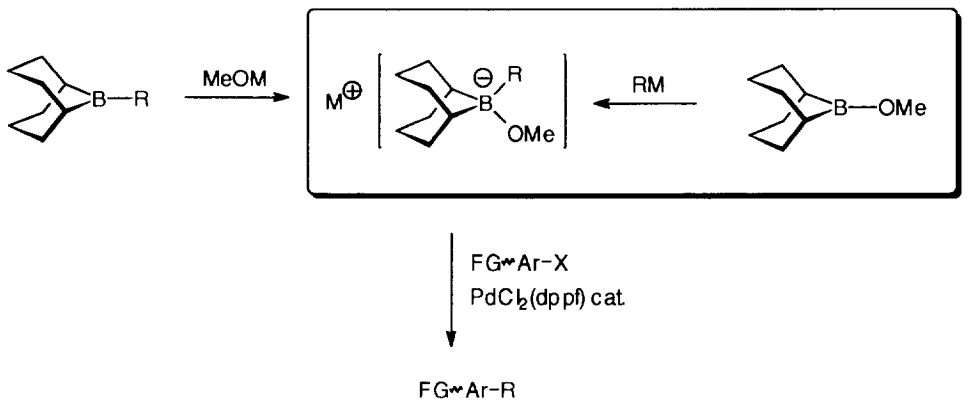
Abstract: An alternative way for performing Suzuki reactions is presented. The necessary borate which is the actual nucleophile in these palladium catalyzed C-C-bond formations is prepared from 9-methoxy-9-borabicyclo[3.3.1]nonane (9-OMe-9-BBN) and a polar organometallic reagent RM, and not as usually from a borane and a base. This approach allows cross couplings of aryl halides with e.g. alkynyl-, methyl-, or $TMSCH_2$-groups, which were beyond the scope of the conventional Suzuki reaction. The method is highly chemoselective and turned out to be compatible with aldehyde-, amide-, ketone-, ester- and cyano functions as well as with basic nitrogen atoms in the substrates. It was applied to the synthesis of the acetylenic natural products junipal (**9a**) and eutypine methyl ether (**10**). Since ^{11}B NMR studies revealed that the 9-OMe-9-BBN only serves as a shuttle for delivering the RM reagent but remains unchanged during the course of the reaction, it has been possible to device the first Suzuki-type reaction sub-stoichiometric in boron. This "catalytic" protocol was used to prepare compound **8** which is highly valuable for its chemoluminescence properties.

INTRODUCTION

In recent years the Suzuki reaction has gained particular attention and has found numerous applications to the synthesis of natural and non-natural products.[1] In its original form, it consists in the palladium-catalyzed cross-coupling of an aryl- or alkenyl halide (or triflate) with a boronic acid or boronate in the presence of a base (commonly aqueous NaOH, K_3PO_4, Na_2CO_3 etc).[2,3] An excellent compatibility with an array of functional groups in both reactants is one of the most prominent features of this process. Suzuki's subsequent discovery that 9-alkyl or 9-alkenyl-9-BBN derivatives, which are easily accessible by hydroboration of alkenes or alkynes, can be used instead of boronic acids has further increased the preparative scope of this transformation.[4]

From mechanistic studies it is likely that the respective boron reagent first reacts with the base to the corresponding borate, which serves as the actual nucleophile.[5] It transfers its organic ligand to the aryl (or alkenyl)-PdX species formed by insertion of the Pd(0) into the C-X bond ($X = -I > -Br > -SO_2CF_3 >> -Cl$)[1] of the substrate. The resulting diorganopalladium species undergoes a reductive elimination which leads to the desired product and regenerates the catalyst. We envisaged an alternative approach to cross-coupling reactions of this type: rather than forming the necessary borate from a borane and a base, we prepared it from 9-methoxy-9-borabicyclo[3.3.1]nonane (9-OMe-9-BBN) and a polar organometallic reagent RM (Scheme 1).[6]



Scheme 1. Two complementary ways for performing Suzuki reactions; FG = functional group

This concept bears the chance to transfer those entities R onto functionalized aryl(alkenyl) halides which are beyond the scope of traditional Suzuki reactions such as alkynyl-, $TMSCH_2$- or methyl groups. Urged by a preliminary publication of *Soderquist et al.*,[7] who recently reported a similar approach for cross-couplings of alkynes, we now disclose our first results along these lines.

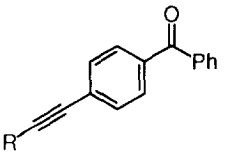
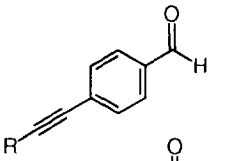
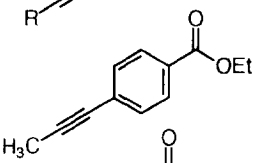
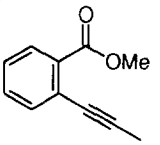
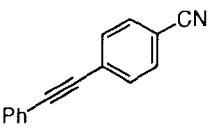
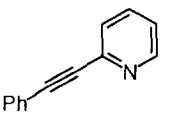
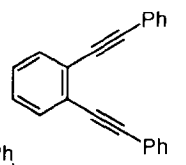
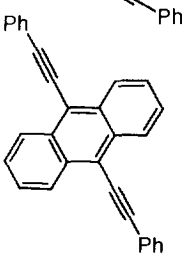
RESULTS AND DISCUSSION

Addition of phenylethynyl potassium to a solution of 9-OMe-9-BBN in THF at ambient temperature results in the instantaneous and quantitative formation of the corresponding borate complex as evident from the ^{11}B NMR spectrum of the mixture. Addition of $PdCl_2(dppf)$ or $Pd(PPh_4)_4$ (3 mol%) and 4-bromobenzophenone followed by gentle heating of the resulting red-brown solution leads to essentially quantitative formation of the coupling product **1a**. The conversion can easily be observed by the precipitation of KBr and can be quantitatively monitored by ^{11}B NMR spectroscopy.

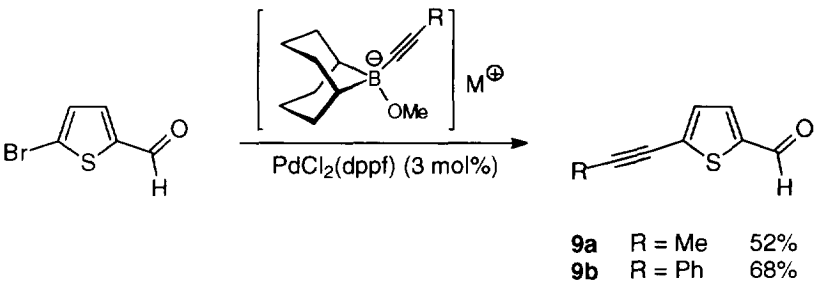
Table 1 summarizes the preparative results obtained for cross couplings of alkynyl metals with some representative aryl halides. From the compiled data it is evident, that alkynyl potassium, -sodium and -lithium reagents are equally suitable as starting materials and can be chosen just upon criteria of availability. More importantly, the reaction turned out to be compatible with a variety of sensitive functionalities including aldehyde-, ketone-, ester- and nitrile groups. Entry 8 shows that basic heteroatoms in the starting materials do not compete with the organometallic reagent for the Lewis-acidic boron center of 9-OMe-9-BBN and therefore do not pose any problems.

This new cross-coupling reaction of alkynyl groups with aryl halides has been applied to the formation of some acetylenic natural products. Thus, junipal (**9a**, R = Me), a metabolite isolated from *Daedalea juniperina* Murr., as well as its phenyl analogue **9b** (R = Ph) were obtained in reasonable yields in one step each from commercial 5-bromo-2-formylthiophene (Scheme 2).[8] Again the aldehyde function in the substrate was nicely compatible with the reaction conditions.

Table 1. Palladium-catalyzed arylations of alkynyl metal reagents mediated by 9-OMe-9-BBN.[a]

Entry	Substrate	RM	Product			Yield(%)
1	4-bromobenzophenone	PhC≡CK		**1a**	R = Ph	89
2		MeC≡CNa		**b**	R = Me	89
3	4-bromobenzaldehyde	MeC≡CNa		**2a**	R = Me	67
4		PhC≡CK		**b**	R = Ph	77
5	ethyl 4-bromobenzoate	MeC≡CNa		**3**		86
6	methyl 2-bromobenzoate	MeC≡CNa		**4**		87
7	4-bromobenzonitrile	PhC≡CK		**5**		93
8	2-bromopyridine	PhC≡CK		**6**		82
9	1,2-dibromobenzene	PhC≡CK		**7**		87
10	9,10-dibromoanthracene	PhC≡CK		**8**		85[b]
11	9,10-dibromoanthracene	PhC≡CLi				84[b]

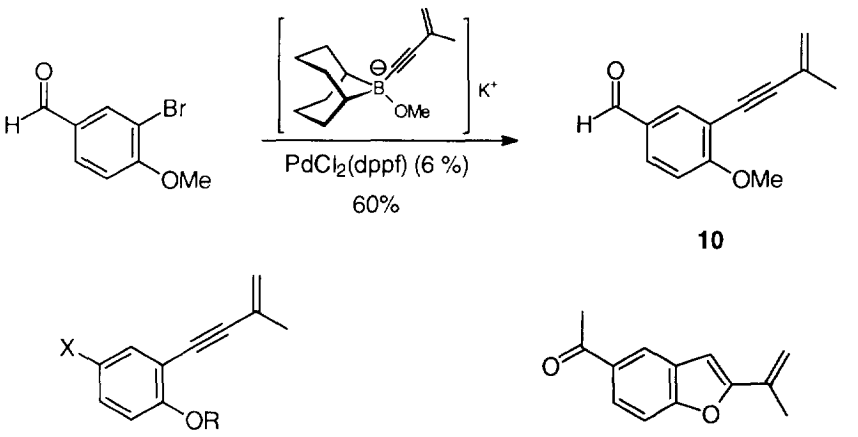
[a] Reaction conditions: ArBr (1 equiv.), 9-OMe-9-BBN (1.2 equiv.), RM (1.2 equiv.), $PdCl_2$(dppf) (3 mol%), THF, reflux unless stated otherwise. [b] with 6 mol% of $PdCl_2$(dppf).



9a R = Me 52%
9b R = Ph 68%

Scheme 2. One-pot synthesis of junipal **9a** and its analogue **9b** from a commercially available substrate

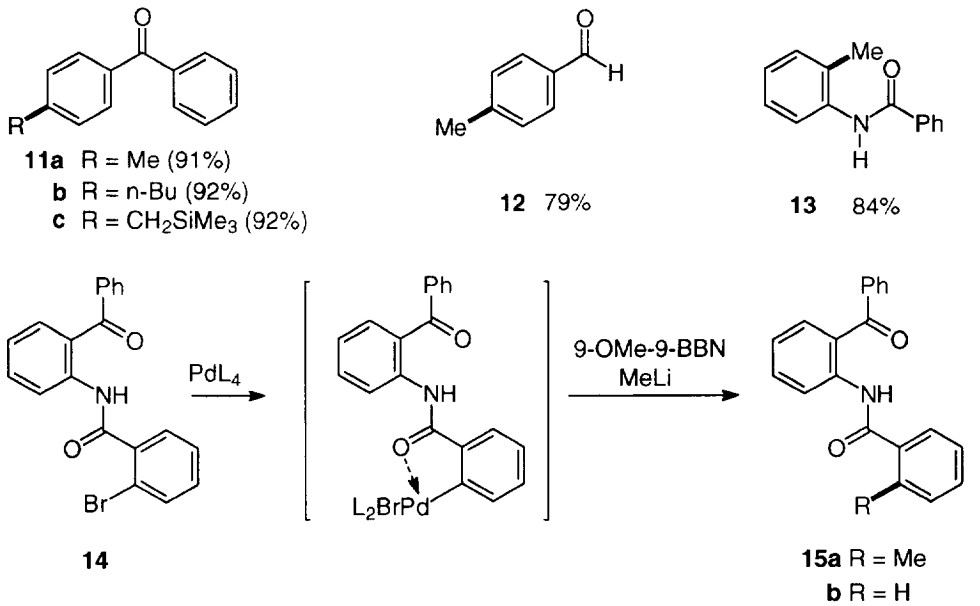
Likewise, reaction of commercially available 3-bromo-4-methoxybenzaldehyde with the borate derived from 3-methyl-3-buten-1-ynyl potassium and 9-OMe-9-BBN in the presence of catalytic amounts of Pd(0) afforded eutypine methyl ether **10** in 60% yield (Scheme 3). This compound is a pathogenic fungal metabolite of *Eutypa lata* which is responsible for severe dieback of vineyards in Europe; moreover **10** is a known intermediate for the synthesis of dehydrotremetone, a toxic principle of *Eupatorium urticaefolium*.[9] These applications together with the examples reported by *Soderquist*[7] clearly demonstrate that this 9-OMe-9-BBN-mediated procedure denotes the desired extension of the Suzuki reaction to alkynes. In all cases the yields obtained favorably compare with those of the best current alternatives for performing cross couplings of sp-sp^2 carbon atoms.[10]



Scheme 3. One-pot formation of eutypine methyl ether **10** from a commercially available substrate.

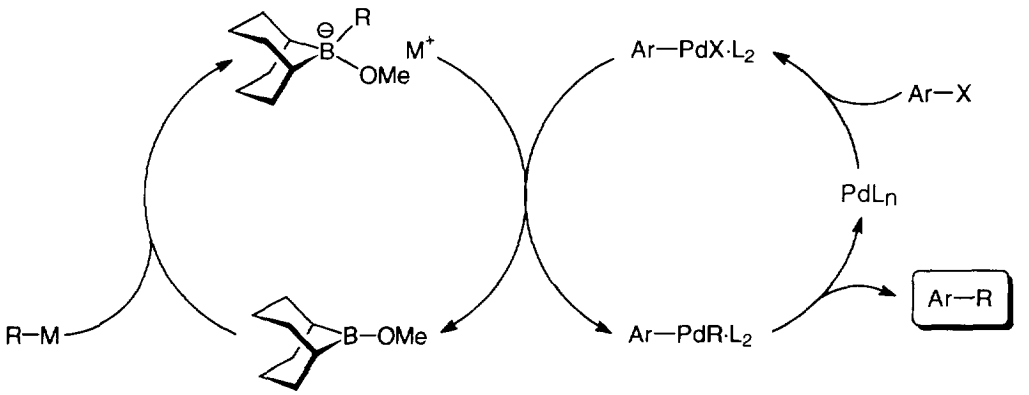
Polar organometallic reagents other than alkali metal acetylides can also be cross coupled with haloarenes. For example, methyllithium, *n*-butyllithium and trimethylsilylmethyllithium in the presence of 9-OMe-9-BBN and catalytic amounts of Pd(0) reacted chemo- and regioselectively with different substituted aryl bromides at the site of the halo atom without damaging proximate aldehyde-, keto- or amide groups (Scheme 4); compounds **11a-c**, **12** and **13** were thus obtained in excellent yields. Not only is the transfer of a methyl- or a trimethylsilylmethyl group obviously beyond the scope of the classical Suzuki protocol which relies upon the hydroboration of alkenes,[4] but this new procedure also favorably compares with existing methodologies for cross coupling of organolithium compounds with aryl halides due to its excellent compatibility with other electrophilic functionalities which do not resist to RLi.[11,12] Moreover, it avoids any toxic reagents and might therefore be appropriate for applications to pharmaceutically relevant targets. In this regard it may rival the well established Stille coupling[10i,11c] based on the use of organotin compounds as nucleophiles, which shows a similar scope and selectivity profile. Bromide **14** reacted slowly, most likely due to ligation of the amide carbonyl group onto the organopalladium intermediate, and simple reduction of the C-Br bond coincided with the methyl group transfer in this particular case.

It should be mentioned however, that the choice of the organometallic precursor is crucial. While *e.g.* MeLi reacted smoothly, the corresponding MeMgCl did not. ^{11}B NMR spectroscopy revealed that in this latter case the intermediate borate with a $MgCl^+$ counterion formed from 9-OMe-9-BBN and the Grignard reagent is too unstable.[13] Another limitation was observed in the attempted transfer of bulky substituents: in line with previous observations that the Suzuki reaction is sensitive to steric hindrance,[1] the use of *tert*-butyllithium as nucleophile did not lead to the desired coupling products but the starting material was recovered unchanged even after extended periods of time.[14]



Scheme 4. Cross-couplings of polar organometallics with functionalized aryl bromides mediated by 9-OMe-9-BBN. The newly formed bond is highlighted.

Suzuki Reactions Sub-Stoichiometric in Boron. 9-OMe-9-BBN only serves as a shuttle for delivering the polar organometallic reagent via the corresponding borate complex but remains unchanged during the course of the reaction. This is evident from ^{11}B NMR spectroscopy where its signal at $\delta \approx +56$ ppm reappears and gains intensity at the expense of the borate as the reaction proceeds. Therefore it might be possible to run the same transformations with only *sub-stoichiometric* amounts of 9-OMe-9-BBN (Scheme 5).



Scheme 5. Suzuki cross coupling reactions sub-stoichiometric in 9-OMe-9-BBN

In fact, when phenylethynyl potassium was added in portions to a refluxing suspension of 9,10-dibromoanthracene, $PdCl_2(dppf)$ (6 mol%) and 9-OMe-9-BBN (30 mol%) a clean conversion took place with formation of **8** in 69% isolated yield. This compound is highly valuable for chemoluminescence research.[15] The yield could be further improved to 78% when a solution of phenylethynyl lithium in THF was slowly dropped into the mixture of 9,10-dibromoanthracene, the palladium catalyst and 9-OMe-9-BBN (20 mol%). This latter result achieved with only 10 mol% boron per newly formed C-C-bond compares well with the 84-85% of **8** obtained using a stoichiometric amount of the respective preformed borate (Table 1, entries 10 and 11). Control experiments without any 9-OMe-9-BBN failed due to an incompatibility of the catalyst with the alkynyl metals. This clearly features the essential role of 9-OMe-9-BBN for maintaining the catalytic cycle. Our new procedure may therefore outline a way to render Suzuki coupling reactions catalytic in both palladium and boron, which may be relevant for applications on a larger scale. Further studies on this and related aspects are in progress.

EXPERIMENTAL

General. All reactions were carried out under Ar using Schlenk-techniques unless stated otherwise. NMR: Spectra were recorded on a Bruker WH 400 or an AC 200 spectrometer at 400.1 or 200.1 MHz (^1H) and 100.6 or 50.3 MHz (^{13}C), respectively, in $CDCl_3$ (Aldrich) unless stated otherwise. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The multiplicity in the ^{13}C NMR spectra refers to the geminal protons (DEPT). MS: Varian CH-5 (70eV). IR: Nicolet FT-7199. Melting points: Gallenkamp apparatus (uncorrected). 9-OMe-9-BBN was prepared from $[9\text{-H-9-BBN}]_2$ and MeOH according to a literature

procedure.[6] The palladium catalysts and the halo arenes were purchased from Aldrich Chemical Co. and used as received, substrate **14** was prepared as described previously.[16] Flash chromatography: Merck silica gel 60 (230-400 mesh) using hexane/ethyl acetate in various proportions as eluent. The THF used was dried by distillation over Mg-anthracene and was transferred under Ar.

Representative procedure for the cross coupling of polar organometallics RM with aryl halides mediated by 9-OMe-9-BBN: 9,10-Bis(phenylethynyl)anthracene (8). To a suspension of phenylethynyl potassium (992 mg, 7.1 mmol) in THF (60 mL) was added 9-OMe-9-BBN (1.08 g, 7.1 mmol) with stirring under Ar. After a few minutes a colorless and clear solution of the corresponding borate had formed to which $PdCl_2$(dppf) (155 mg, 6 mol%) and 9,10-dibromoanthracene (1.075 g, 3.2 mmol) were added successively. After refluxing the red-brown mixture for 1 h, the solvent together with residual 9-OMe-9-BBN was pumped off *in vacuo* (10^{-3} Torr). The remaining solid was suspended in CH_2Cl_2 (60 mL); filtration of the insoluble residues and evaporation of the filtrate gave crude **8** (≈ 1.2 g, quant.) which was essentially pure in GC. Recrystallization from hexane/ethyl acetate (20°C → -78°C) afforded **8** as bright red-orange crystals (1.03 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 3.2, 6.8, 4H), 7.78 (dd, J = 1.6, 8, 4H), 7.64 (dd, J = 3.2, 6.4, 4H), 7.40-7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (s), 131.7 (d), 128.7 (d), 128.6 (d), 127.3 (d), 126.8 (d), 123.4 (s), 118.5 (s), 102.4 (s), 86.5 (s); MS: *m/z* (rel. intensity): 378 (100, M^+), 376 (9), 374 (8), 300 (4), 189 (18).

All other products were obtained analogeously. Their analytical data are compiled below. The coupling reactions can be conveniently surveyed by means of ^{11}B NMR spectroscopy as described in the text. Diagnostic shifts for the boron intermediates involved are summarized in Table 2.

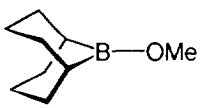
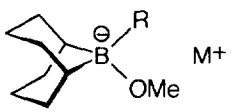
4-(Phenylethynyl)benzophenone (1a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.79 (d, 4H), 7.54-7.63 (m, 5H), 7.47 (t, 2H), 7.34-7.38 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.8 (s), 137.4 (s), 136.7 (s), 132.4 (d), 131.7 (d), 131.3 (d), 130.0 (d), 129.9 (d), 128.7 (d), 128.4 (d), 128.3 (d), 127.5 (s), 122.7 (s), 92.4(s), 88.6 (s). MS: *m/z* (rel. intensity): 282 (100, M^+), 205 (81), 176 (27), 151 (13), 127 (8), 105 (27), 77 (26).

4-(1-Propyn-1-yl)benzophenone (1b). IR (cm^{-1}): 2250, 2210, 1650; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76 (t, 4H), 7.43-7.62 (m, 5H), 2.09 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 195.9 (s), 137.5 (s), 136.1 (s), 132.3 (d), 131.3 (d), 129.9 (d), 129.8 (d), 128.4 (d), 128.2 (d), 89.4 (s), 79.3 (s), 4.40 (q). MS: *m/z* (rel. intensity): 220 (87, M^+), 143 (100), 115 (28), 105 (29), 77 (24).

4-(1-Propyn-1-yl)benzaldehyde (2a). IR (cm^{-1}): 2260, 2220, 1700; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.98 (s, 1H, -CHO), 7.80 and 7.52 (AB, 4H, J = 7.5), 2.09 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.5 (s), 135.0 (s), 132.0 (d), 129.5 (d), 127.9 (s), 90.6 (s), 79.2 (s), 4.5 (q). MS: *m/z* (rel. intensity): 144 (100, M^+), 143 (52), 115 (40), 63 (10).

4-(Phenylethynyl)benzaldehyde (2b). IR (cm^{-1}): 2220, 1700, 1600; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.99 (s, 1H, -CHO), 7.84 and 7.65 (AB, 4H), 7.51-7.58 (m, 2H), 7.35-7.39 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.3 (s), 135.3 (s), 132.0 (d), 131.7 (d), 129.5 (d), 128.9 (d), 128.4 (d), 122.4 (s), 93.4 (s), 88.5 (s). MS: *m/z* (rel. intensity): 206 (100, M^+), 205 (52), 176 (30), 151 (13), 88 (7).

Table 2. Diagnostic ^{11}B NMR shifts of the boron species involved. The spectra were taken from aliquots of the crude reaction mixtures in THF with $BF_3 \cdot Et_2O$ as external standard (Bruker AC 200 spectrometer, 64 MHz).

Boron compound	R	M^+	δ (^{11}B NMR)
	---	---	+ 56.4
	R = C≡CPh	K^+	- 4.5
	R = C≡CPh	Li^+	- 3.6
	R = C≡CMe	Na^+	- 4.6
	R = C≡CC(CH_2)Me	K^+	- 4.7
	R = n-Bu	Li^+	- 0.4
	R = Me	Li^+	- 1.4
	R = CH_2SiMe_3	Li^+	+ 0.1

Ethyl 4-(1-propyn-1-yl)benzoate (3). IR (cm^{-1}): 2260, 2220, 1720, 1610; ^1H NMR (200 MHz, $CDCl_3$) δ 7.95 (d, 2H), 7.42 (d, 2H), 4.35 (q, 2H), 2.05 (s, 3H), 1.37 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (s), 131.2 (d), 129.2 (d), 129.1 (s), 128.6 (s), 89.1 (s), 79.2 (s), 60.9 (t), 14.2 (q), 4.3 (q). MS: *m/z* (rel. intensity): 188 (51, M^+), 160 (16), 143 (100), 115 (41), 89 (10), 63 (9).

Methyl 2-(1-propyn-1-yl)benzoate (4). ^1H NMR (200 MHz, $CDCl_3$) δ 7.88 (dd, 1H, J = 1.5, 7.6), 7.25-7.53 (m, 3H), 3.91 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (s), 133.9 (d), 131.5 (s), 131.3 (d), 129.8 (d), 126.9 (d), 124.3 (s), 91.2 (s), 78.1 (s), 51.8 (q), 4.4 (q); MS: *m/z* (rel. intensity): 174 (69, M^+), 159 (100), 143 (74), 115 (94), 103 (32), 89 (26), 65 (13), 63 (27).

4-(Phenylethynyl)benzonitrile (5). ^1H NMR (200 MHz, $CDCl_3$) δ 7.51-7.61 (m, 6H), 7.35-7.39 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.0 (d), 131.9 (d), 131.7 (d), 129.0 (s) 128.4 (d), 128.1 (s), 122.1 (s), 118.4 (s), 111.4 (s), 93.7 (s), 87.7 (s); MS: *m/z* (rel. intensity): 203 (100, M^+), 177 (4), 176 (6), 175 (4), 151 (3), 88 (4).

2-(Phenylethynyl)pyridine (6). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.60 (d, 1H, J ≈ 1), 7.58-7.65 (m, 3H), 7.49 (d, 1H), 7.34 (m, 3H), 7.17-7.22 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 149.8, 143.2, 135.9, 131.8, 128.8, 128.2, 126.9, 122.5, 122.0, 89.0, 88.5. MS: *m/z* (rel. intensity): 179 (100, M^+), 151 (9), 126 (7), 76 (11).

1,2-Bis(phenylethynyl)benzene (7). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51-7.60 (m, 6H), 7.25-7.38 (8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.8 (d), 131.6 (d), 128.4 (d), 128.3 (d), 128.0 (d), 125.8 (s), 123.3 (s), 93.6 (s), 88.3 (s). MS: *m/z* (rel. intensity): 278 (100, M^+), 276 (47), 274 (12), 138 (15).

2-Formyl-5-(1-propyn-1-yl)-thiophene (junipal) (9a). IR (cm^{-1}): 3300, 3290, 3080, 2920, 2840, 2805, 2230, 1665; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.82 (s, 1H, -CHO), 7.61 (d, 1H, J = 3.9), 7.14 (d, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3 (s), 142.8 (s), 136.0 (d), 133.9 (s), 131.7 (d), 95.8 (s), 72.7 (s), 4.8 (q). MS: *m/z* (rel. intensity): 150 (100, M^+), 149 (53), 121 (31), 77 (17).

2-Formyl-5-(phenylethynyl)-thiophene (9b). IR (cm^{-1}): 2200, 1670, 1490, 1440, 1225, 1050, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H,-CHO), 7.62 (d, 1H, J = 3.9), 7.49-7.53 (m, 2H), 7.32-7.37 (m, 3H), 7.27 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3 (s), 143.8 (s), 135.9 (d), 132.7 (s), 132.4 (d), 131.5 (d), 129.2 (d), 128.4 (d), 121.7 (s), 97.8 (s), 81.9 (s). MS: *m/z* (rel. intensity): 212 (100, M^+), 211 (51), 139 (34).

4-Methoxy-3-(3-methylbut-3-en-1-ynyl)benzaldehyde (10). ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.86 (s, 1H, -CHO), 7.93 (d, 1H), 7.81 (dd, 1H), 6.98 (d, 1H), 5.44 (m, 1H), 5.34 (m, 1H), 3.96 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 190.1, 164.2, 135.3, 131.5, 129.5, 126.6, 122.5, 113.5, 110.5, 95.7, 83.1, 56.2, 23.3; MS: *m/z* (rel. intensity): 200 (100, M^+), 185 (13), 159 (27), 135 (13), 128 (38), 115 (9), 63 (12).

4-Methylbenzophenone (11a). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67-7.80 (m, 4H), 7.40-7.56 (m, 3H), 7.24 (d, 2H), 2.39 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.1 (s), 143.0 (s), 137.7 (s), 134.7 (s), 131.9 (d), 130.1 (d), 129.7 (d), 128.8 (d), 128.0 (d), 21.4 (q). MS: *m/z* (rel. intensity): 196 (57, M^+), 181 (9), 119 (100), 105 (29), 91 (29), 82 (11), 77 (25), 67 (13), 65 (14), 51 (10), 41 (11).

4-n-Butylbenzophenone (11b). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.70-7.82 (m, 4 H), 7.40-7.59 (m, 3H), 7.27 (d, 2H), 2.68 (t, 2H), 1.64 (tt, 2H), 1.37 (tq, 2H), 0.93(t, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.3 (s), 148.1 (s), 137.9 (s), 135.0 (s), 132.0 (d), 130.2 (d), 129.8 (d), 128.2 (d), 128.1 (d), 35.6 (t), 33.2 (t), 22.3 (t), 13.8 (q). MS: *m/z* (rel. intensity): 238 (47, M^+), 181 (14), 167 (15), 161 (100), 105 (31), 91 (13), 77 (13).

4-(Trimethylsilylmethyl)benzophenone (11c). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.71-7.83 (m, 4H), 7.45-7.60 (m, 3H), 7.11 (d, 2H, J = 8.4), 2.21 (s, 2H), 0.04 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.3, 146.6, 138.1, 133.3, 131.9, 130.4, 129.8, 128.1, 127.7, 27.9, -2.0; MS: *m/z* (rel. intensity): 268 (68, M^+), 253 (8), 178 (3), 90 (2), 73 (100).

p-Tolylaldehyde (**12**) was identified by comparison with an authentic sample.

N-(2-Methylphenyl)benzamide (13). IR (cm^{-1}): 3247, 3059, 1649, 1603, 1581, 1524, 1488, 1439, 1310, 1288, 910, 748, 715, 691, 600; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.87 (m, 4H), 7.39-7.57 (m, 3H), 7.05-7.26 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.7, 135.7, 134.9, 131.7, 130.5, 129.7, 128.7, 127.0, 126.7, 125.4, 123.4, 17.7; MS: *m/z* (rel. intensity): 211 (41, M^+), 105 (100), 77 (42).

The mixture of N-(2-benzoylphenyl)-2-methylbenzamide (**15a**) and N-(2-benzoylphenyl)benzamide (**15b**) obtained upon reaction of substrate **14** with MeLi/9-OMe-9-BBN according to the procedure described above could not be separated by flash chromatography. The products were unambiguously identified by GC/MS and by comparison with authentic samples.[16] Ratio **15a** : **15b** ≈ 2 : 1; Characteristic signals: ^{1}H NMR (200 MHz, $CDCl_3$) δ **15a**: 11.23 (br s, NH), 2.57 (s, -Me); **15b**: 12.0 (br s, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ **15a**: 199.6, 168.4, 20.1; **15b**: 200.2, 165.7.

Suzuki cross coupling reactions with sub-stoichiometric amounts of 9-OMe-9-BBN. Phenylethynyl lithium (3.3 mmol) was dissolved in THF (25 mL). Approximately 5 mL of this solution were added in one portion to a solution of 9-OMe-9-BBN (91 mg, 0.6 mmol) in THF (50 mL). 9,10-Dibromoanthracene (504 mg, 1.5 mmol) and $PdCl_2$(dppf) (73 mg, 0.09 mmol) were added and the mixture was refluxed for 45 min under Ar. The remaining solution of phenylethynyl lithium was then slowly dropped into the refluxing mixture over a period of 45 min and reflux was continued for 1 h. Standard work-up afforded product **8** (444 mg, 78%) which was identical in all respects to the sample described above.

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13. The ^{11}B NMR of the reaction mixture shows signals at δ + 56.4 ppm (9-OMe-9-BBN), +31.6 ppm and -19.4 ppm.

14. ^{11}B NMR indicates that the borate looses its MeO^- group leading to the formation of 9-*tert*-butyl-9-BBN (δ = 85.5 ppm) as the major component. 4-Bromobenzophenone was recovered in 73% yield together with a trace amount of benzophenone.

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