Tetrahedron 75 (2019) 164–171

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Magnesium promoted autocatalytic dehydrogenation of amine borane complexes: A reliable, non-cryogenic, scalable access to boronic acids

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ARTICLE INFO

Article history:
Received 5 October 2018
Received in revised form
13 November 2018
Accepted 15 November 2018
Available online 28 November 2018

Keywords:
Borane
Boronic acids
Dehydrogenation
Tandem reaction
Magnesium

ABSTRACT

Owing to the unusual reactivity of dialkylamine-borane complexes, a methodology was developed to simply access boronic acids. The intrinsic instability of magnesium aminoborohydride was tweaked into a tandem dehydrogenation borylation sequence. Proceeding *via* an autocatalytic cycle, amineborane dehydrogenation was induced by a variety of Grignard reagents. Overall, addition of the organomagnesium species onto specially designed dialkylamine-borane complexes led to a variety of boronic acids in high yields. In addition, the reaction can be performed under Barbier conditions, on a large scale.

1. Introduction

Amine borane complexes have been of major interest, mostly for hydrogen storage purpose, as they are susceptible to undergo reversible dehydrogenation [1]. Ammonia borane and methylamineborane for example have a very high H_2 per mole content and lead the fierce competition for being of the key material used for hydrogen chemical storage [2,3]. In synthesis, their use is mostly related to the reducing ability of the Boron–Hydrogen bond [4], which usually requires activation to enhance the electrophilicity of the boron center [5]. Most common amine borane complexes are air and moisture stable [6] and easily prepared from the parent amine and any source of borane; in most cases borane dimethyl sulfide or borane-THF. Upon dehydrogenation, they form aminoboranes which display interesting properties as reducing agents. They also have been used for creating carbon boron bond using organometallic catalysis, mostly palladium based [7–12], but also with metallocene [13,14] or in the absence of any transition metal [15], owing to the high reactivity of diazonium salts. Recently, it has been shown that upon addition of Grignard to aminoboranes, and more specifically to diisopropylaminoborane, it was possible to selectively prepare boronic acids [16], borinic acids and the corresponding borinates [17], isolated under the form of dimethylaminoethanol or 8-hydroxyquinoline complexes. During this study, the unique properties of the arylaminoborohydride were related to the instability of the magnesium borohydrides [18] as compared to the lithium analogs (also known under the acronym of LAB) [19,20] and allowed a fine control of the number of substituent around the boron center without hampering yields. Hence, we envisioned taking advantages of the intrinsic instability of these magnesium aminoborohydrides to generate the trivalent aminoboranes required for the synthesis of boronic acids and propose a new synthesis of boronic acids based on a tandem dehydrogenation – addition sequence.

2. Results and discussion

Our study started with diisopropylamine borane (DIPAB, **1a**) and dicyclohexylamine borane (DICAB **1b**), for which the corresponding aminoboranes are well characterized and exist as monomers in solution [21]. Deprotonation with butyllithium of these amineborane complexes occurs on the nitrogen leading to the lithium aminoborohydride LAB, largely used by Singaram et al. as reducing agent or precursor of aminoborane by reaction with TMSCl [19,20]. In our case, the addition of phenylmagnesium bromide to the DIPAB **1a** in a 1:1 ratio quantitatively led to the magnesium

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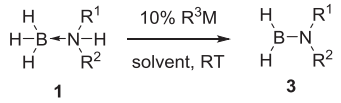
https://doi.org/10.1016/j.tet.2018.11.036
0040-4020/

dialkylaminoborohydride **Mg-2a** (scheme 1a). As expected, in THF at room temperature, this compound was fairly unstable, and the reaction mixture composition evolved rapidly to lead after 5 h solely to the corresponding diisopropylaminoborane **3a** (scheme 1a). Reaction is favored by the elimination of the magnesium hydride [17] but still too slow for practical application in a tandem process. In the aim of improving these processes kinetics, we thought about different ways of favoring hydride abstraction.

Thanks to the basicity of borohydride, addition of a mild acid, such as diisopropylammonium sulfate, led to the formation of the expected aminoborane. However, diisopropylamine resulting from the deprotonation of the ammonium, promoted the rearrangement around the boron center with the formation of bis(diisopropylamino)borane **4a** and borane under the form of DIPAB **1a** (scheme 1b). Providentially, DIPAB **1a** was acidic enough to react with the magnesium diisopropylaminoborohydride **Mg-2a**, leading to the diisopropylaminoborane **3a**, hydrogen and regenerating diisopropylaminoborohydride **Mg-2a** (scheme 1c). In this last reaction, the product being also a reactant, the reaction can be defined as autocatalytic [22].

Hence, we designed a preparation of aminoborane which would occur through autocatalytic dehydrogenation of dialkylamine borane **1** induced by a substoichiometric amount of Grignard reagent (Table 1). We optimized briefly the quantity, nature of the Grignard reagent, and solvent by adding 5% of organometallic reagent to a solution of amine borane complex. The conversion was followed by measurement of hydrogen evolvement, and product nature was confirmed by ^{1}H and ^{11}B NMR when conversion was above 5%. Using 10% of ethylmagnesium bromide in toluene, 5 h are required to achieve a complete conversion (Table 1, entry 1). Lowering the amount of organometallic to 5% or 1% led to a sluggish reaction. Reaction on DIPAB is equally effective, with a complete conversion in 5 h (Table 1, entry 2). Other amine borane complexes have been evaluated. Dimethylamine borane and morpholine borane (Table 1, entry 3 and 4) are unreactive under these conditions. Despite being secondary alkylamine boranes the corresponding aminoboranes are not monomeric in solution, which may displace the reaction equilibrium of the autocatalytic dehydrogenation. This was corroborated by the unreactivity of primary amine borane, such as *tert*-butylamine borane, benzylamineborane, hexylamine borane, cyclohexylamine borane, methylamine borane or ammonia borane. Other organometallic reagents were evaluated; *i*PrMgCl is as effective as EtMgBr (Table 1, entries 5). Even *n*BuLi, despite the stability of LAB, can promote auto dehydrogenation albeit in a sluggish manner (Table 1, entry 6). The intermediate reactivity of *i*PrMgCl.LiCl underlines the importance of the cation used for this reaction, as 38% conversion is obtained after 5 h

Table 1
Grignard induced dehydrogenation of amineboranes.

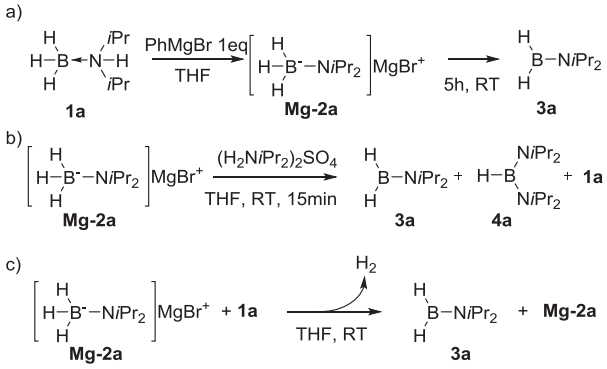


Entry	R^1	R^2	R^3M	solvent	time[a]	Conv.[b]
1	Cy	Cy	EtMgBr	toluene	5 h	>95%
2	*i*Pr	*i*Pr	EtMgBr	toluene	5 h	>95%
3	Me	Me	EtMgBr	toluene	5 h	7%
4	$-(CH_2)_2O(CH_2)_2-$		EtMgBr	toluene	5 h	<1%
5	Cy	Cy	*i*PrMgCl	toluene	5 h	>95%
6	Cy	Cy	*n*BuLi	toluene	48 h	50%
7	Cy	Cy	*i*PrMgCl.LiCl	toluene	5 h	38%
8	Cy	Cy	*i*PrMgCl.LiCl[c]	toluene	5 h	>95%
9	Cy	Cy	$ZnEt_2$	toluene	5 h	4%
10	Cy	Cy	EtMgBr	THF	1 h	20%
11	*i*Pr	*i*Pr	EtMgBr	THF	1 h	20%
12	Me	Me	EtMgBr	THF	19 h	21%[d]
13	Cy	Cy	PhMgBr	THF	5 min	>95%
14	*i*Pr	*i*Pr	PhMgBr	THF	4 min	>95%

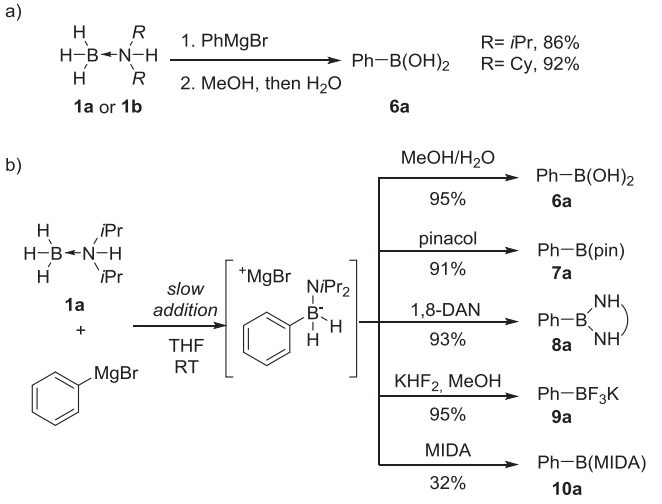
[a] Time for reaching maximum conversion.
[b] Conversion evaluated using H_2 volume evolvement.
[c] 15% of R^3M was used d 14% after 1 h, 17% after 5 h.

(Table 1, entry 7) which can be improved to 95% when 15% of the organometallic is used (Table 1, entry 8). Diethylzinc is ineffective (Table 1, entries 9). Observing the difference in reactivity depending on solvent in which organometallics were commercialized (solution in THF, Et_2O or hexane) prompted us to evaluate other solvents. Surprisingly, THF turned out to diminish the reactivity with EtMgBr with a maximal conversion of 20% (Table 1, entries 10–12 vs entries 1–3), but led to very efficient reactions using phenylmagnesium bromide (Table 1, entries 13–14). This reaction is consistent with alkaline earth silylamides catalyzed dehydrogenation of amine borane [23].

The success of this approach was translated into the direct addition of Grignard reagent onto amine borane complexes. Indeed, upon addition of phenyl magnesium bromide to a THF solution of DICAB (Scheme 2a), the reaction is complete after 1 h at room temperature and led almost quantitatively to the phenylboronic



Scheme 1. Preparation of diisopropylaminoborane **3a** *via* deprotonation using PhMgBr.



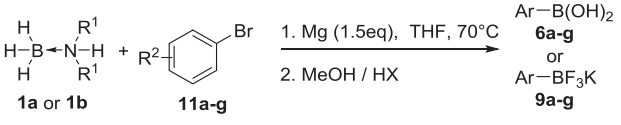
Scheme 2. Preparation of various boron derivatives *via* autocatalytic dehydrogenation-addition sequence.

acid **6a** after hydrolysis in a MeOH/H_2O mixture. The same reaction performed using DIPAB led to the same product in a good 86% yield (Scheme 2a). A slow addition of phenylmagnesium bromide allowed improving this yield up to 95% (Scheme 2b). Under Barbier conditions, using DIPAB and PhBr **5a**, yield was equally good. In both case the initial presence of a minimal amount of Grignard is allowing for a more efficient dehydrogenation limiting the competing direct deprotonation of the amine borane complex unproductively consuming the nucleophilic Grignard. Corroborating dehydrogenation results, only bulky amine borane complexes were found suitable for this tandem reaction. If reaction on DIPAB and DICAB led to $PhBF_3K$ after treatment with KHF_2 in MeOH [24], in 95 and 96% yield respectively, the same reaction performed with *tert*-butylamine borane, morpholine borane or dimethyl borane were less efficient and products were isolated only in 42%, 15% and 5% yield respectively. Reaction with triethylamine borane led to no conversion.

Upon addition of PhMgBr, the resulting aminoarylborohydride can undergo different solvolytic workups (Scheme 2b). As previously mentioned, the addition of an aqueous solution of methanol led to the formation of the boronic acid **6a**. Addition of methanol followed by transesterification with a diol, typically pinacol, leads to the boronic ester, in our case the pinacol boronate **7a** in 91% yield. The same reaction with 1,8-diaminonaphthalene (1,8-DAN) yielded Suginome's diaminoarylborane **8a** in 93% yield. A methanolic solution of KHF_2 produced the aryltrifluoroborate **9a** in 95% yield, but the formation of the MIDA ester was less efficient and product **10a** was isolated only in 32% yield. Overall, this method seems compatible with most of the known chemistry of aminoarylborane.

As Barbier conditions were found to work equally well, the reaction scope was then explored using this method. Adding more than 1.5 equivalent of amine borane complex only led to a more complex purification procedure; 1 equivalent was not sufficient to avoid the formation of some borinic acid (less than 5%). As such, using 1.25 eq of amine borane complex, 1.5 eq of Mg, arylbromides are converted into the corresponding boronic acids in high yields (Table 2). Substitution of aromatic moiety with alkyl groups such as methyl (Entries 2–4, 6) or butyl (Entries 5, 9) did not affect yields. Methoxy groups (entries 7 and 8) or trifluoromethyl (entry 12) and fluoro (entry 13) led to the boronic acids in 91%, 90% and 82% yield respectively. Naphthyl groups are tolerated regardless of the bromine position (Entries 10 and 11) and gave the corresponding 2-naphtyl and 1-naphthyl boronic acid in 80% and 82% yield respectively. Overall the reaction is efficient using either DIPAB (Entries 1–7) or DICAB (entries 8–13). Fluorinating workup led to aryltrifluoroborate **9** (Entries 1–6), aqueous workup led to boronic acids **6** (Entries 7–14) without major changes in yield and purities. A limitation was observed when 4-nitrobromobenzene was used. Despite our tries and even though no bromoarene was remaining in the reaction mixture, the product was not observed and the amine borane complex was left unreacted. It confirms the reaction scope limitation to functional groups resistant to organometallics. But more importantly, it stresses out the strong dependence of the autocatalytic dehydrogenation kinetics to the nature of the Grignard.

Table 2
Dehydrogenation-borylation sequence under Barbier conditions.



Entry	Amine Borane	Ar	HX	Product	Yield[a]
1	DIPAB **1a**	Ph	KHF_2	**9a**	95%
2	DIPAB **1a**	2-MeC_6H_4	KHF_2	**9b**	96%
3	DIPAB **1a**	3-MeC_6H_4	KHF_2	**9c**	89%
4	DIPAB **1a**	4-MeC_6H_4	KHF_2	**9d**	96%
5	DIPAB **1a**	4-*n*BuC_6H_4	KHF_2	**9e**	85%
6	DIPAB **1a**	3,4-$Me_2C_6H_3$	KHF_2	**9f**	91%
7	DIPAB **1a**	4-$MeOC_6H_4$	H_2O	**6g**	98%
8	DICAB **1b**	4-$MeOC_6H_4$	H_2O	**6g**	91%
9	DICAB **1b**	4-*n*BuC_6H_4	H_2O	**6e**	99%
10	DICAB **1b**	2-Naphth	H_2O	**6h**	80%
11	DICAB **1b**	1-Naphth	H_2O	**6i**	82%[b]
12	DICAB **1b**	4-$CF_3C_6H_4$	H_2O	**6j**	90%
13	DICAB **1b**	4-FC_6H_4	H_2O	**6k**	82%
14	DICAB **1b**	4-$NO_2C_6H_4$	H_2O	**6l**	0%

[a] Isolated yield after recrystallization in H_2O (**6**) or acetone/Et_2O (**9**).
[b] Isolated yield after recrystallization EtOH/H_2O 1/9.

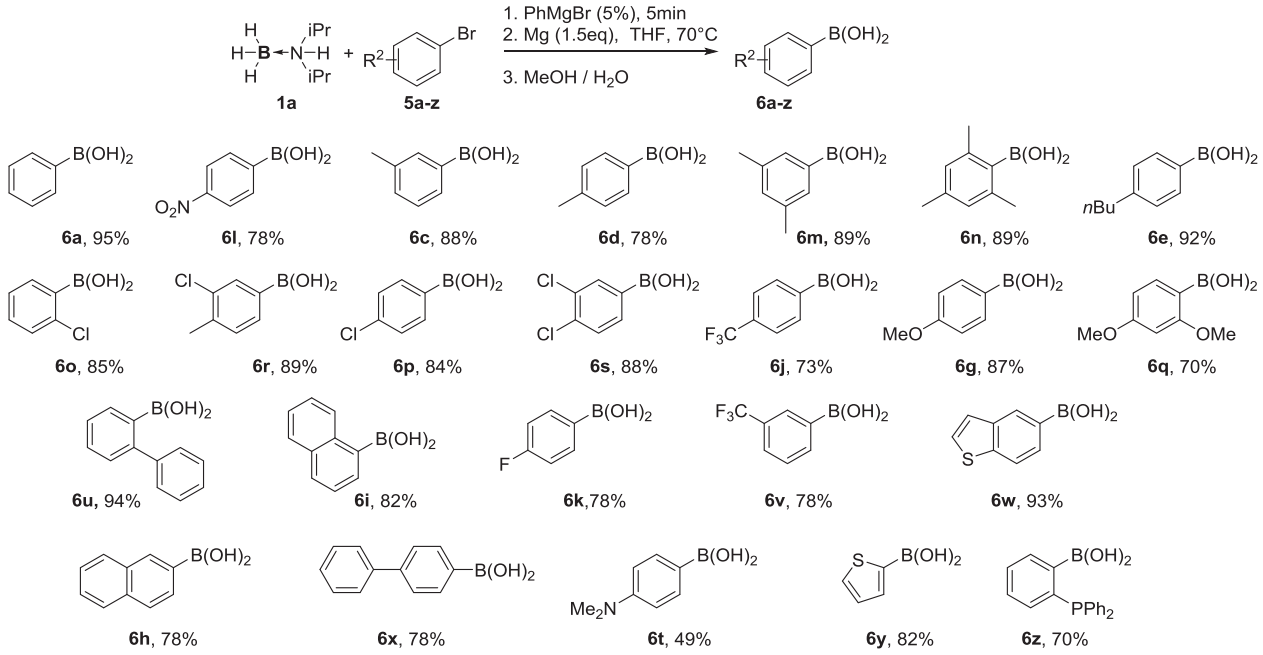
To avoid side reactions due to a putative slow dehydrogenation, we used a two steps process with the addition of 5% of PhMgBr on amine borane **1a** or **1b** during 5 min followed by the addition of Mg and ArBr (Scheme 3). In that case, dehydrogenation occurs irrespectively from the bromoarene nature. Indeed, reaction is now equally effective on simple bromobenzene but compatible with the presence of nitro group as 4-nitrophenylboronic acid was isolated in 78% yield after recrystallization in Et_2O. The alkyl substituted bromobenzenes are well tolerated leading to the corresponding boronic acids in 78–92% yield.

Electron rich or electron poor substituted bromoarenes reacted equally well. Dimethylamino group are well tolerated, but 4-$Me_2NC_6H_4B(OH)_2$ was isolated only in 49% yield, most of the product being lost during recrystallization due to its high solubility in water. It is corroborated by the good yield obtained using 3-$Me_2NC_6H_4Br$ which was recrystallized in 93% yield. The preparation of chloride substituted boronic acid remained very efficient under Barbier conditions. Regardless of the position of the chlorine substituent, the corresponding arylboronic acids were isolated in 84–89% yield. Polyaromatics or heteroaromatics reacted equally well. The only limitation of this reaction seemed to be the generation of the Grignard and its stability under the reaction conditions. However preliminary studies have shown that the reaction is relatively fast and could be extended to less stable organometallics using flow systems. In addition, after dehydrogenation of DIPAB or DICAB, the addition of ArLi or ArMgBr is equally effective and a combined used of PhMgBr for dehydrogenation and *n*BuLi for metal halide exchange turned out as efficient as the Barbier process.

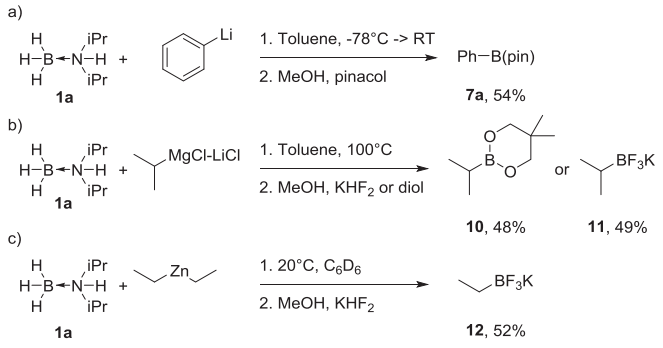
Finally, the reaction was expanded to the use of other organometallic reagents (Scheme 4). Phenyllithium, as expected owing to poor dehydrogenation abilities, led to the product in a mere 54% yield (Scheme 4a). *i*PrMgCl-LiCl was promoting also dehydrogenation but less efficiently; hence, neopentylglycol isopropylborate **10** was isolated in 48% yield after reaction at 100 °C, and this reactivity was corroborated isolating the corresponding trifluoroborate salt **11** in 49% yield (Scheme 4b). Even though diethylzinc failed to promote dehydrogenation of DIPAB, the reaction in a 1/1 ratio was surprisingly more efficient, and potassium ethyltrifluoroborate **12** was isolated in 52% yield (Scheme 4c).

3. Conclusion

We found that boronic acids could be obtained very simply and directly by reaction between an arylbromide and a dialkylamine borane complex in the presence of magnesium. Arylboronic acids are mostly synthesized by addition below −60 °C [25] of an aryllithium or arylmagnesium halide to a trialkoxyborane [26–28] followed by a hydrolysis typically using aqueous HCl. Particular advantages of this new chemistry include (1) the simplicity of the



Scheme 3. Boronic acid synthesis *via* PhMgBr promoted dehydrogenation - Barbier borylation sequence.



Scheme 4. Extension to other organometallics.

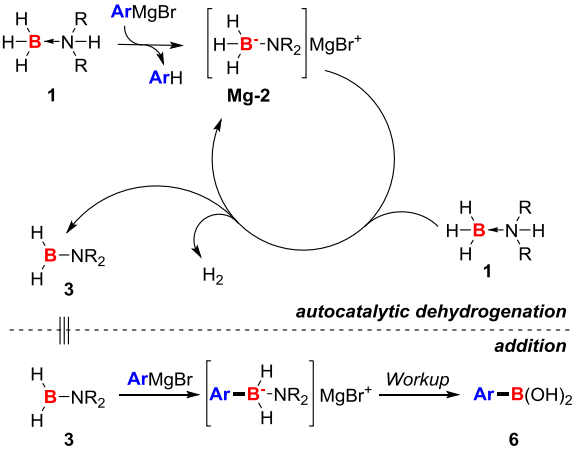
procedure, which basically consists into refluxing three reagents (ArBr, Mg and DIPAB or DICAB) in THF (2) the absence of cryogenic condition to obtain the boronic acid still in the absence of borinic acid (3) the robustness of the reaction which can often be performed open air without major loss in yield, (4) the extension into a one pot dehydrogenation-borylation procedure when the *in situ* formed Grignard is not reactive in dehydrogenation, (5) both DIPAB and DICAB are air and moisture stable, DICAB being a crystalline white solid which can be prepared on 100 g scale in the laboratory from $NaBH_4$ and dicyclohexylamine (See ESI) and (6) the feasibility on larger scale in the laboratory with standard equipment. The synthesis of 1-naphthylboronic acid has for example been performed on a 10 g scale in 82% yield using DIPAB. Large scale operation implied that specific attention had to be taken during dehydrogenation as hydrogen evolves rapidly. It required good temperature control and gas exhaust to avoid possible reaction runaway. It is noteworthy that DIPAB and DICAB are both currently commercially available from Sigma Aldrich (DICAB [131765-96-3] catalogue no. 900348, DIPAB [55124-35-1] catalogue no. 900347).

Overall the mechanistic implications of magnesium aminoborohydride instability have been turned into a practical method for accessing boronic acids (Scheme 5). However it also has fundamental consequences in many aspects, especially considering that the dehydrogenation of amine borane could be promoted by PhMgBr leading to an autocatalytic reaction. Investigations are under way to extend this reactivity in the domain of hydrogen storage or for other synthetic applications.

4. Experimental section

4.1. Generalities

THF was dried over sodium/benzophenone and freshly distilled before use. Toluene was dried over calcium hydride and freshly distilled before use. Methanol was dried over magnesium/iodine and freshly distillated before use. All those process were done under argon atmosphere. All commercially available reagents were use directly as received unless specified. Dicyclohexylamine and



Scheme 5. Mechanism of tandem autocatalytic dehydrogenation addition of arylmagnesium bromides to aminoborane complexes.

diisopropylamine were dried over calcium hydride and distilled before use. All laboratory glassware was dried in oven and cooled under vacuum before use. Analytical thin layer chromatography (TLC) was carried out using 0.25 mm silica plates purchased from Merck. Eluted plates were visualized using KMnO4 solution. Silica gel chromatography was performed using 230–400 mesh silica gel purchased from Merck.

NMR were recorded on Bruker Avance 300, Advance 400 or Advance 600 spectrometer. ^{1}H Chemical shifts (δ) are given in ppm relative to tetramethylsilane (external standard). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, m = multiplet, t = triplet, q = quadruplet, sx = sextuplet, h = heptuplet, bs = broad singlet. ^{13}C NMR chemical shifts (δ) are given in ppm relative to tetramethylsilane (external standard). ^{11}B NMR chemical shifts (δ) are given in ppm relative to $BF_3.OEt_2$ (external standard). ^{19}F NMR chemical shifts (δ) are given in ppm relative to $BF_3.OEt_2$ (external standard). GC-MS analyses were performed on an Agilent 7890A equipped with a J&W Scientific DB-1701 capillary column, an Agilent 5975C triple axis detector (EI) using the following method: 50 °C for 5 min then 10 °C/min until 220 °C.

Diisopropylamine borane complex DIPAB (1a) To a stirred solution of di*iso*propylamine (70.6 mL, 0.5 mol) and $NaBH_4$ (30 g, 0.79 mol) in THF (500 mL) was added at 0 °C over a period of 45 min sulfuric acid (16 mL, 0.3 mol). The mixture was allowed to warm to room temperature and stirred for 3 h. The crude was concentrated under vacuum and the residue was triturated in CH_2Cl_2, and then filtrated to eliminate all solid residues. The filtrate was washed with water (4 × 100 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give the amine-borane complex as colorless oil which solidified upon cooling (51.8 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.72–2.90 (m, 2H), 1.91 (q, $J_{H\text{-}B}$ = 91 Hz, 3H), 1.05 (d, J = 6.6 Hz, 6H), 0.96 (d, J = 6.6 Hz, 6H). ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −20.4 (q, $J_{H\text{-}B}$ = 91 Hz).

Dicyclohexylamine borane complex DICAB (1b) A 3000 mL three-necked round bottomed flask equipped with a mechanical stirrer, a thermometer and a dropping funnel was charged with anhydrous THF (1500 mL, purchased from Aldrich, used directly without purification) and $NaBH_4$ (56.75 g, 1.5 mol purchased from Aldrich, used directly without purification) The heterogeneous mixture was vigorously agitated using a mechanical stirrer and cooled with an ice/salt bath (Ice (5 kg) and salt (1.5 kg) were used to keep an external temperature of −13 °C and an internal temperature of −5 °C during all the process. A dropping funnel was charged with 40 mL of H_2SO_4 (0.75 mol). The H_2SO_4 solution was added dropwise maintaining the internal temperature below −5 °C (1h30). A Cy_2NH (73 mL, 1 mol, purchased from Alfa Aesar, used directly without purification) solution in THF (100 mL) was added dropwise maintaining the temperature below 0 °C (3h30). The mixture was vigorously agitated during 20 h at room temperature. The mixture was filtrated over fritted funnel and the resulting solid was triturated with THF (3 × 400 mL). THF filtrate was concentrated under reduced pressure and recrystallized from THF/pentane to yield 178 g of white crystals (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.96 (s, 1H), 2.89–2.75 (m, 2H), 1.95–1.48 (m, 13H), 1.36–1.01 (m, 7H). ^{11}B NMR (128 MHz, $CDCl_3$): δ (ppm) −20.32 (q).

4.2. General procedures

4.2.1. Addition under Barbier conditions (procedure A)

A solution in THF (4 mL) of DIPAB (863 mg, 7.5 mmol), Mg (182 mg, 7.5 mmol) and arylbromide (5 mmol) was stirred at 70 °C until no starting arylbromide remains (TLC).

4.2.2. PhMgBr dehydrogenation followed by the addition under Barbier conditions (procedure B)

To a solution in THF (4 mL) of DIPAB (863 mg, 7.5 mmol) and Mg (182 mg, 7.5 mmol) were added a PhMgBr 1M THF solution (375 μL, 375 μmol) at room temperature. After 10 min, 30 mL of anhydrous THF were added followed by the arylbromide (5 mmol).

4.2.3. Work up for potassium aryltrifluoroborates (procedure C)

The reaction mixture was cooled down to 0 °C and quenched slowly with 7 mL of MeOH. After 1 h, volatile were removed under reduced pressure and the resulting solid was dissolved in MeOH. An aqueous solution of KHF_2 (4.5 eq, 10 mL) was added at room temperature. After 1 h at room temperature, volatiles were removed under reduced pressure; the solid was extracted with anhydrous acetone and the resulting powder was recrystallized from acetone/Et_2O or acetone/pentane.

4.2.4. Work up for arylboronic acid (procedure D)

The reaction mixture was cooled down to 0 °C and quenched slowly with 7 mL of MeOH. After 1 h, volatile were removed under reduced pressure and the resulting solid was dissolved in 1N HCl/MeOH (7/3). After 1 h at room temperature, 100 mL of AcOEt were added, the organic phase was washed with 1N HCl (30 mL) and brine (3 × 30 mL). Organic phases were concentrated under reduced pressure yielding a solid which was recrystallized from H_2O.

4.3. Characterization

All compounds have been characterized and compared with authentic samples, available commercially or through the palladium catalyzed borylation [7,13,14,21]

4.3.1. Phenylboronic acid [98-80-6] **6a** [29]

532 mg of phenylboronic acid was obtained as a white solid starting from 785 mg of bromobenzene following procedures B and D (88%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.95–7.85 (m, 2H), 7.45–7.30 (m, 3H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 29.0. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 137.5, 134.5, 130.5, 128.5.

4.3.2. B-(3-Methylphenyl)boronic acid [17933-03-8] **6c** [30]

595 mg of *B*-(3-methylphenyl)boronic acid was obtained as a white solid starting from 860 mg of 3-methylbromobenzene following procedures B and D (88%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.70–7.67 (m, 2H), 7.25–7.23 (dd, J = 9 Hz 2H), 7.08 (bs, 2H), 2.33 (s, 3H, CH_3). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.1. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 134.7, 131.1, 130.8, 127.3, 20.5.

4.3.3. B-(4-Methylphenyl)boronic acid [5720-05-8] **6d** [14]

528 mg of *B*-(4-methylphenyl)boronic acid was obtained as a white solid starting from 860 mg of 4-methylbromobenzene following procedures B and D (78%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.75 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 7.5 Hz, 2H), 2.29 (s, 3H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 29.5. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 138.5, 136.1, 126.4, 21.9.

4.3.4. B-(4-Butylphenyl)boronic acid [145240-28-4] **6e** [31]

819 mg of *B*-(4-butylphenyl)boronic acid was obtained as a white solid starting from 1.066 g of 4- *n*-butylbromobenzene following procedures B and D (92%), following procedure A and D with DICAB (yield 99%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.81–7.79 (d, J = 6 Hz, 2H), 7.21–7.19 (d, J = 6 Hz, 1H), 7.06 (s, 2H), 2.63 (t, J = 7.5 Hz, 2H), 1.61 (q, J = 9 Hz 2H), 1.35 (sx, J = 6 Hz 2H), 0.93 (t, J = 7.5 Hz, 3H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.0.

^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 144.9, 134.2, 127.5, 35.4, 33.5, 22.1, 13.3.

4.3.5. B-(4-methoxyphenyl)boronic acid [5720-07-0] **6g** *[29]*

663 mg of *B*-(4-methoxyphenyl)boronic acid was obtained as a white solid starting from 941 mg of 4-methoxybromobenzene following procedures B and D (87%); following procedure A and D (yield 98%) ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.85–7.82 (dd, J = 3, 6 Hz, 2H), 6.96 (s, 2H), 6.93–6.91 (dd, J = 1.5, 3 Hz, 2H), 3.82 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 28.9. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 161.7, 135.8, 112.9, 54.4.

4.3.6. B-2-Naphthalenylboronic acid [32316-92-0] **6h** *[32]*

670 mg of (Naphthalen-2-yl)boronic acid was obtained as a white solid starting from 1.04 g of 2-bromonaphtalene following procedures B and D (78%); following procedure A and D with DICAB (yield 80%). ^{1}H NMR (300 MHz DMSO-d_6): δ (ppm) 8.56 (s, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.04 (m, 1H), 7.99–7.85 (m, 2H), 7.60–7.45 (m, 2H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 29.3. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 134.3, 134.2, 133.0, 130.9, 128.7, 128.0, 127.0, 126.5, 125.9.

4.3.7. B-1-Naphthalenylboronic acid [13922-41-3] **6i** *[28]*

10.3 g of (Naphthalen-1-yl)boronic acid was obtained as a white solid starting from 15.52 g of 1-bromonaphtalene following procedures B and D (80%); following procedure A and D with DICAB (yield 82%).^{1}H NMR (300 MHz acetone-d_6): δ (ppm) 8.62–8.59 (m, 1H), 7.94–7.87 (m, 3H), 7.50–7.45 (m, 3H), 7.44 (s, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 30.3. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 135.6, 129.7, 128.8, 128.2, 125.5, 125.2, 149.9.

4.3.8. B-(4-Trifluoromethylphenyl)boronic acid [128796-39-4] **6j** *[33]*

696 mg of *B*-(4-Trifluoromethylphenyl)boronic acid was obtained as a white solid starting from 1.125 g of 4-trifluoromethylbromobenzene following procedures B and D (73%); following procedure A and D with DICAB (yield 90%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 8.09–8.06 (d, J = 9 Hz, 2H), 7.71–7.69 (d, J = 9 Hz 2H), 7.57 (br s, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 28.4. ^{19}F NMR (282 MHz, DMSO-d_6) δ −61.3.

4.3.9. B-(4-Fluorophenyl)boronic acid [1765-93-1] **6k** *[34]*

607 mg of *B*-(4-fluorophenyl)boronic acid was obtained as a white solid starting from 880 mg of 4-fluoro-bromobenzene following procedure B and D (73%); following procedures A and D with DICAB (yield 82%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.05 (s, 2H), 7.88–7.83 (dd, J = 9, 6 Hz, 2H), 7.17–7.11 (t, J = 9 Hz, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 22.16. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 163.6 (d, J = 263 Hz), 136.1 (d, J = 64.3 Hz), 114.3 (d, J = 19.6 Hz). ^{19}F NMR (282 MHz, DMSO-d_6) δ −111.9.

4.3.10. B-(4-Nitrophenyl)boronic acid [24067-17-2] **6l** *[34]*

723 mg of *B*-(4-nitrophenyl)boronic acid was obtained as a white solid starting from 1.011 g of 4- nitro-bromobenzene following procedures B and D (78%). ^{1}H NMR (300 MHz DMSO-d_6): δ (ppm) 8.20–8.17 (d, J = 9 Hz, 2H), 8.04–8.01 (d, J = 9 Hz, 2H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 29.0. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 149.2, 135.7, 125.5.

4.3.11. B-(3,5-Dimethyphenyl)boronic acid [172975-69-8] **6m** *[34]*

130 mg of *B*-(3,5-dimethylphenyl)boronic acid was obtained as a white solid starting from 185 mg of 1-bromo-3,5-dimethylbenzene following procedures B and D (89%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.90 (bs, 2H, OH), 7.39–7.14 (s, 2H), 7.02 (s, 1H), 2.26 (s, 6H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 29.2. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 136.3, 132.3, 131.8, 21.4.

4.3.12. B-(2,4,6-Trimethylphenyl)boronic acid [5980-97-2] **6n** *[28]*

723 mg of *B*-(2,4,6-trimethylphenyl)boronic acid was obtained as a white solid starting from 995 mg of bromomesitylene following procedures B and D (83%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.05 (s, 2H), 6.73 (s, 2H), 2.22 (s, 6H), 2.19 (s, 3H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 31.39. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 138.9, 136.6, 126.8, 22.4, 21.2.

4.3.13. B-(2-Chlorophenyl)boronic acid [3900-89-8] **6o** *[35]*

664 mg of *B*-(2-chlorophenyl)boronic acid was obtained as a white solid starting from 1.01 g of 2-chloro-bromobenzene following procedures B and D (85%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.60–7.20 (m, 4H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 28.9 ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 134.9, 134.0, 130.7, 128.7, 126.0.

4.3.14. B-(4-chlorophenyl)boronic acid [5980-97-2] **6p** *[29]*

131 mg of *B*-(4-chlorophenyl)boronic acid was obtained as a white solid starting from 191 mg of 4-chloro-bromobenzene following procedures B and D (84%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.89–7.87 (dd, J = 6, 1.5 Hz, 2H), 7.42–7.38 (dt, J = 9, 3 Hz, 2H), 7.31 (s, 2H). ^{11}B NMR (96 MHz, DMSO-d_6): δ (ppm) 28.6. ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 135.9, 135.8, 127.6.

4.3.15. B-(2,4-Dimethoxyphenyl)boronic acid [133730-34-4] **6q** *[36]*

663 mg of *B*-(2,4-Dimethoxyphenyl)boronic acid was obtained as a white solid starting from 1.08 g of 2,4-dimethoxy-bromobenzene following procedures B and D (70%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.77–7.74 (dd, J = 3, 6 Hz, 1H), 7.21–7.15 (t, J = 9 Hz, 1H), 6.81 (s, 2H), 6.70–6.50 (m, 1H), 3.94 (s, 3H), 3.85 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.0. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 166.3, 163.6, 137.8, 106.0, 105.4, 97.4, 55.0, 54.6.

4.3.16. B- (3-Chloro-4-methylphenyl)boronic acid [175883-63-3] **6r** *[32]*

663 mg of *B*-(3-Chloro-4-methylphenyl)boronic acid was obtained as a white solid starting from 1.03 g of 4-bromo-3-chlorotoluene following procedures B and D (89%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.84 (s, 1H), 7.72–7.70 (d, J = 6 Hz, 1H), 7.33–7.31 (d, J = 6 Hz, 1H), 7.28 (s, 2H), 2.38 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 28.4. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 137.7, 136.9, 134.4, 132.6, 130.5, 19.2.

4.3.17. B-(3,4-Dichlorophenyl)boronic acid [151169-75-4] **6s** *[37]*

666 mg of *B*-(3,4-dichlorophenyl)boronic acid was obtained as a white solid starting from 1.13 g of 4-bromo-1,2-dichlorobenzene following procedures B and D (88%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.99 (d, J = 1.2 Hz, 1H), 7.82–7.79 (dd, J = 1.5, 8.1 Hz, 1H), 7.59–7.56 (d, J = 9 Hz, 1H), 7.51 (s, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 28.22. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 135.9, 133.9, 131.5, 131.3k, 129.9.

4.3.18. B-(4-(N,N-Dimethylamino)phenyl)boronic acid [28611-39-4] **6t** *[28]*

410 mg of *B*-(4-(*N*,*N*-Dimethylamino)phenyl)boronic acid was obtained as a white solid starting from 1.13 g of 4-(*N*,*N*-Dimethylamino)-bromobenzene following procedures B and D (49%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.75–7.72 (dd, J = 3, 6 Hz, 2H), 6.80 (s, 2H), 6.72–6.69 (dd, J = 3, 6 Hz, 2H), 2.97 (s, 6H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.0. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 135.4, 111.1, 39.3 (C_{quat} ipso to amino group not observed).

4.3.19. 2-Biphenylboronic acid [4688-76-0] ***6u*** *[28]*

713 mg of 2-Biphenylboronic acid was obtained as a white solid starting from 1.2 g of 2-bromobiphenyl following procedures B and D (94%). ^{1}H NMR (300 MHz acetone-d_6): δ (ppm) 7.75–7.60 (m, 2H), 7.55–7.30 (m, J = 7.5, 7H), 6.84 (s, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.1. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 145.5, 143.5, 133.0, 128.8, 128.7, 128.5, 128.2, 126.8, 126.1.

4.3.20. B-(3-Trifluoromethylphenylboronic acid [1423-26-3] ***6v*** *[38]*

148 mg of *B*-(3-Trifluoromethylphenyl)boronic acid was obtained as a white solid starting from 225 mg of 3-trifluoromethylbromobenzene following procedures B and D (78%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 8.09–8.06 (d, J = 9 Hz, 2H), 7.71–7.69 (d, J = 9 Hz 2H), 7.57 (bs, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 27.8. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 162.3 (q, J = 247 Hz), 126.32, 124.2, 123.9, 114.2 (q, J = 4.0 Hz), 113.9 (q, J = 3.9 Hz) ^{19}F NMR (282 MHz, DMSO-d_6) δ −61.0.

4.3.21. 4-Biphenylboronic acid [5122-94-1] ***6x*** *[32]*

713 mg of 4-Biphenylboronic acid was obtained as a white solid starting from 1.20 g of 4-bromobiphenyl following procedures B and D (78%). ^{1}H NMR (300 MHz acetone-d_6): δ (ppm) 8.03–8.00 (d, J = 9 Hz, 2H), 7.71–7.66 (t, J = 7.5, 4H), 7.50–7.45 (t, J = 7.5, 2H), 7.40–7.35 (m, 1H), 7.29 (bs, 2H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 29.1. ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 142.6, 140.9, 134.8, 128.8, 127.5, 126.9, 126.0.

4.3.22. B-(2-thiophenyl)boronic acid [6165-68-0] ***6y*** *[32]*

105 mg of 2-thienylboronic acid was obtained as a pale yellow solid starting from 163 mg of 4-fluoro-2-bromothiophene following procedures B and D (82%). ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) 7.69 (d, J = 4.4 Hz, 2H), 7.32 (bs, 2H), 7.17 (dd, J = 4.5 Hz, J = 3.6 Hz, 1H). ^{11}B NMR (96 MHz, acetone-d_6): δ (ppm) 26.9 ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) 137.0, 132.7, 129.3.

4.3.23. B-(2-(diphenylphosphino)phenyl)boronic acid [1187936-76-0] ***6z*** *[39]*

Prepared from 2-bromotriphenylphosphine on a 5 mmol scale following procedures B and D (yield 70%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 8.12–8.03 (m, 4H), 7.87–7,81 (m, 3H), 7.77–7.69 (m, 4H), 7.63–7.56 (m, 1H), 7.53–7.44 (m, 1H), 7.41–7.33 (m, 1H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 32.0. ^{31}P NMR (122 MHz, acetone-d_6) δ (ppm) −13.3.

4.3.24. Potassium trifluoro(phenyl)borate [153766-81-5] ***9a*** *[40]*

Prepared from bromobenzene on a 5 mmol scale following procedures A and C (yield 95%) ^{1}H NMR (300 MHz, acetone-d_6) 7.47 (d, J = 6,6 Hz, 2H), 6.99–7.10 (m, 3H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 3,0 (q, J = 54 Hz).

4.3.25. Potassium (2-methylphenyl)trifluoroborate [274257-34-0] ***9b*** *[41]*

Prepared from 2-bromotoluene on a 5 mmol scale following procedures A and C (yield 96%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 7.47 (d, J = 6,8 Hz, 1H), 6.96–6.86 (m, 3H), 2.90 (s, 3H). NMR ^{13}C (75 MHz, acetone-d_6) 140.9, 131.8, 128.2, 125.2, 123.2, 21.2. ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 3.8 (q, J = 56 Hz).

4.3.26. Potassium (3-methylphenyl)trifluoroborate [850623-42-6] ***9c*** *[42]*

Prepared from 3-bromotoluene on a 5 mmol scale following procedures A and C (yield 89%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 7.37–7.21 (m, 2H), 6,99 (t, J = 7.3, 1H), 6.86 (d, J = 7.4, 1H), 2,23 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 3.8 (q, J = 53 Hz).

4.3.27. Potassium (4-methylphenyl)trifluoroborate [216434-82-1] ***9d*** *[40]*

Prepared from 4-bromotoluene on a 5 mmol scale following procedures A and C (yield 96%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 7.36 (d, J = 7.6 Hz, 2H), 6,92 (d, J = 7.6 Hz, 2H), 2.22 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 3.8 (q, J = 52 Hz).

4.3.28. Potassium (4-n-butylphenyl)trifluoroborate [1412414-09-5] ***9e*** *[42]*

Prepared from 4-butylbromobenzene on a 5 mmol scale following procedure A and C (yield 85%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 7,38 (d, J = 7.7 Hz, 2H), 6,93 (d, J = 7.5 Hz, 2H), 2.56–2.44 (m, 2H), 1.65–1.46 (m, 2H), 1.33 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 4,1 (q, J = 53 Hz).

4.3.29. Potassium (3,4-dimethylphenyl)trifluoroborate ***9f*** *[42]*

Prepared from 3,4-dimethylbromobenzene on a 5 mmol scale following procedures A and C (yield 91%) ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 7.27 (s, 1H), 7.22 (d, J = 7.3 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 2.18 (s, 3H), 2.17 (s, 3H). ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 3.9 (q, J = 43 Hz).

4.3.30. 5,5-Dimethyl-2-(1-methylethyl)- 1,3,2-dioxaborinane [61727-48-8] ***10*** *[43]*

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.55 (s, 4H), 0.91 (s, 13H); ^{11}B NMR (96 MHz, $CDCl_3$) δ (ppm) 30.7 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 71.9 (2C), 31.5, 21.7 (2C), 18.2 (2C).

4.3.31. Potassium trifluoroisopropylborate [1041642-13-0] ***11*** *[44]*

^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) 0.75 (d, 6H, J = 7.1 Hz), 0.48–0.25 (h, 1H, J = 7.1 Hz, CH); ^{11}B NMR (96 MHz, acetone-d_6) δ (ppm) 5.8 (q, $J_{B\text{-}F}$ = 56 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm) 18.9.

4.3.32. Potassium ethyltrifluoroborate [882871-21-8] ***12***

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 0.65 (t, 3H, J = 7.8 Hz, CH_3), −0.2–0 (m, 2H, CH_2); ^{11}B NMR (96 MHz, DMSO-d_6) δ (ppm) 5.03 (q, $J_{B\text{-}F}$ = 63 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 9.8.

Acknowledgment

We thank the CNRS and the “Ministere de l’Education Nationale et de la Recherche”, France for financial support.

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