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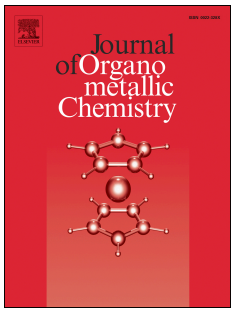

Base free Suzuki acylation reactions of sodium (aryl trihydroxyborate) salts: A novel synthesis of substituted aryl ketones

Siphamandla Sithebe, Patience Molefe

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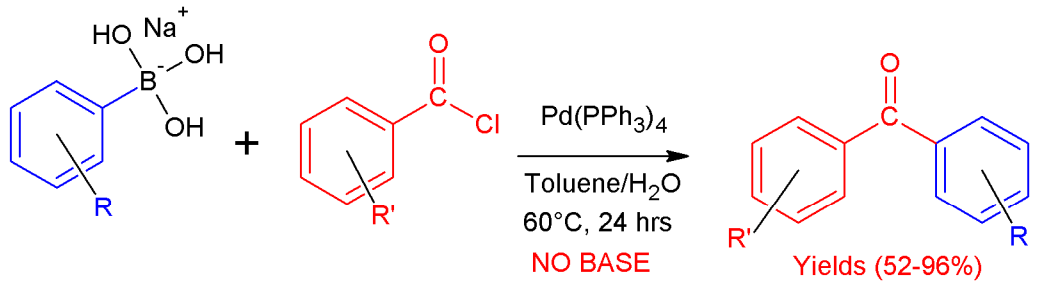

Yields (52-96%)

25 examples

R = *p*-CF_3, *p*-OMe, *p*-SMe, H, *p*-Me

R' = *o*-F, *p*-NO_2, *p*-Me, *p*-OMe, *m*-F, *p*-Cl, *p*-Br, H, *p*-OH, *p*-NH_2

BASE FREE SUZUKI ACYLATION REACTIONS OF SODIUM (ARYL TRIHYDROXYBORATE) SALTS: A NOVEL SYNTHESIS OF SUBSTITUTED ARYL KETONES.

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The first simple and efficient base free $Pd(PPh_3)_4$ catalysed synthesis of substituted aryl ketones from acyl chlorides and easily accessible sodium aryl trihydroxyborate salts in aqueous toluene is reported. The reaction conditions appeared versatile and tolerable to a variety of functional groups including, CF_3, OMe, SMe, Br, NO_2, F, OH and NH_2 furnishing 25 examples of substituted aryl ketones in isolated yields of up to 96% in 24 hours. Beside the high purity, the ease and convenience of the isolation compared to boronic acids, sodium aryl trihydroxyborate salts could be used subsequently without the addition of excess amount of an activator and are more user-friendly in terms of the use of accurate reaction stoichiometry.

Keywords

Base free, Suzuki-Miyaura acylation, substituted ketones, sodium aryl trihydroxyborate salts, aromatic acyl chlorides.

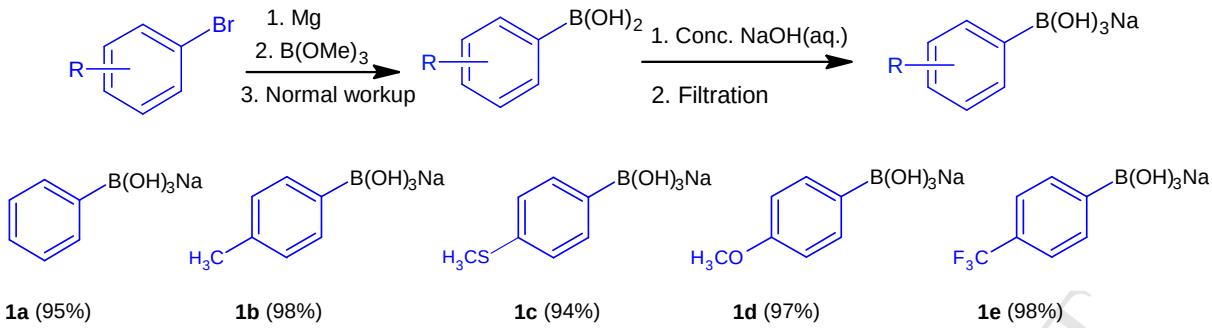
Introduction

The development of synthetic procedures capable of introducing acyl functionalities have proven fruitful and are of great tool to construct a number of carbonyl organic compounds including carboxylic esters, thioesters, amides, ketones to name but a few [1]. Substituted aromatic ketones are particularly important building blocks present in many natural products and biologically active pharmaceutical compounds such as sulisobenzone [2a], (*S)*-ketoprofen [1c] and Safalcone [2b] and are also important reaction intermediate in organic synthesis [3]. Traditional approaches to aromatic ketones including, various oxidation processes [4], Friedel-Crafts acylation [5] and the use of organometallic reagents as nucleophiles [6]. These methods, however, entails limitations and drawbacks such as harsh reaction conditions, poor regioselectivity and functional group compatibility [7]. Alternative methods, such as carbonylative cross-coupling reaction of aryl halides with aryl boronic acids, under carbon monoxide atmosphere, have appeared with improved regioselectivity and functional group compatibility and have emerged as attractive protocols for the preparation of aromatic ketones [8]. On the other hand, palladium-catalysed acylative Suzuki cross-coupling of carboxylic acids derivatives with boronic acids and boronate esters, in the presence of at least two equivalence of a base, have become a method of choice for the synthesis of ketones particularly because the starting materials are readily available, non-toxic, stable towards moisture and easy to handle [9]. Great advancements have been witnessed in acylative Suzuki coupling reaction in terms of acyl sources since the use of acyl chlorides as acylating agents pioneered by Bumagin et al [10]. A variety of acyl donors have been wildly explored including carboxylic anhydrides [11a], carboxylic acids [9], thiol esters [11b], and very recently amides [11c, 11d]. Even though there is a great progress/development in acyl sources, aryl boronic acids are still overwhelmingly dominating as aryl sources in

acylative Suzuki coupling reactions. Only a few other aryl sources have been reported in acylative Suzuki coupling of carboxylic acid derivatives including aryl boronate [12], diarylborinic acids and sodium tetraarylboronates [9, 11d]. Thus, the necessity to develop other aryl sources is evident. Cammidge *et al*. established that aryltrihydroxyborate salts could be coupled smoothly with aryl halides in the Suzuki-Miyaura cross-coupling reaction thus expanding the scope of aryl sources [13a]. The suitability of aryltrihydroxyborate salts as efficient nucleophiles was further supported by Molander *et al* [13b]. Given that these activated boron species, sodium (aryltrihydroxyborate) salts, could be used directly without the need of additional base and are more stable and more reactive than aryl boronic acids [13], we rationalise that it should be more logic to couple sodium (aryltrihydroxyborate) salts with acyl chlorides thus enriching acylative Suzuki cross-coupling reactions with respect to arylating agents. To the best of our knowledge, there are no reports describing base free Suzuki acylation reaction of sodium (aryltrihydroxyborate) salts with acyl chlorides to synthesise substituted diaryl ketones. Herein, we report on the first practical and efficient base free $Pd(PPh_3)_4$ catalysed acylative Suzuki coupling reactions of sodium (aryltrihydroxyborate) salts with acyl chlorides in aqueous toluene.

Results and Discussion

To begin our investigation, we first synthesised different sodium (aryl trihydroxyborates) from cheap and easily accessible aryl halides following previously reported methods.[13] The corresponding aryl halide was reacted with magnesium turnings to produce Grignard reagents which were subsequently quenched with trimethoxyborate solution followed by the addition of concentrated NaOH(aq) (**Scheme 1**).[13]

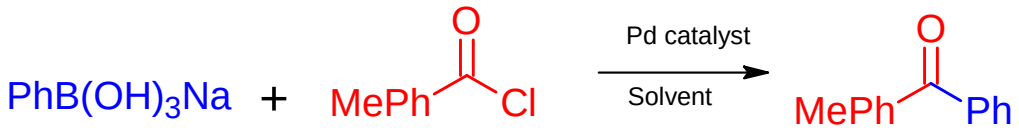


1a (95%) **1b** (98%) **1c** (94%) **1d** (97%) **1e** (98%)

Scheme 1. Preparation of sodium aryl trihydroxyborate salts.

To investigate the suitability of our method in the synthesis of ketones, we initially studied the reaction between sodium (phenyltrihydroxyborate) (**1a**) with toluoyl chloride (**2a**) under different reaction conditions as a model reaction (**Scheme 2**). The results of this investigation into determining the optimal reaction conditions for the palladium-catalysed base free Suzuki acylation reactions are summarised in Table 1. The cross-coupling reaction of **1a** with **2a,** in the absence of a catalyst, resulted in no product formation and only the starting materials were detected (Table 1, entry 1). The combination of palladium chloride with monodentate as well as bindentate phosphine ligands, for example, $PdCl_2/PPh_3$ and $PdCl_2$/dppf gave **3a** in low yields (Table 1, entry 2 and 3). The addition of water slightly improved the yield of **3a** to 48% (Table 1, entry 4) probably because of the solubility of **1a** in aqueous toluene. Other palladium (II) species afforded the desired product **3a** with unsatisfactory yields (Table 1, entries 5-8). A sharp increase in the yield (79%) of product **3a** was observed when $Pd(PPh_3)_4$ was used as a catalyst in aqueous acetone (Table 1, entry 9).

Table 1: Initial optimisation of reaction conditions. [a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Yield (%)[b]
1	—	Toluene (r.t.)	0
2	$PdCl_2/PPh_3$	Toluene (r.t)	27
3	$PdCl_2$/dppf	Toluene (r.t)	19
4	$PdCl_2$/dppf	Toluene/H_2O (r.t)	48
5	$Pd(PPh_3)_2Cl_2$/ PPh_3	Toluene/H_2O (r.t)	51
6	$Pd(OAc)_2$/dppf	Toluene/H_2O (r.t)	31
7	$Pd(COD)_2Cl_2$/ PPh_3	Toluene/H_2O (r.t.)	Trace
8	$Pd(PPh_3)_2Cl_2$/dppf	Toluene/H_2O (60 °C)	55
9	$Pd(PPh_3)_4$	Acetone/H_2O (60 °C)	79
10	$Ni(dppf)_2$/dppf	Toluene/H_2O (60 °C)	23
11	$Ni(acac)_2/PPh_3$	Toluene/H_2O (60 °C)	Trace
12	$Pd(PPh_3)_4$	Toluene/H_2O (r.t.)	71
13	**$Pd(PPh_3)_4$**	**Toluene/H_2O (60 °C)**	**88**
14	$Pd(PPh_3)_4$	THF/ H_2O (60)	67
15	$Pd(PPh_3)_4$	Toluene/H_2O (100 °C)	52[C]

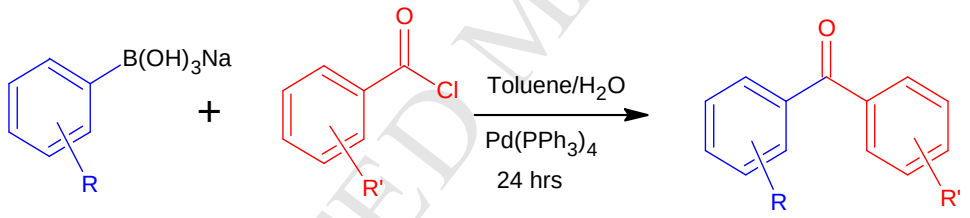
[a] Reaction conditions: **1a** (1 mmol), **2a** (1.1 mmol), Pd catalyst (0.01 mmol), ligand (0.02 mmol), toluene (2 mL), 0.5 mL (water), 24 hours. [b] Isolated yields after column and radial chromatography. [C] Microwave reactor was used, 100 W, 100Psi, Closed vessel, 10 minutes.

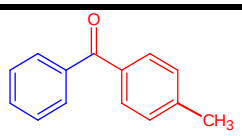
Given that nickel-based catalysts are increasingly becoming popular in cross-coupling reactions [14], we performed the optimisation experiments in the presence of $Ni(dppf)_2$/dppf and $Ni(acac)_2/PPh_3$ catalysts. Unfortunately, both catalysts afforded

3a in poor yields (Table 1, entries 10 and 11). The best result was observed using $Pd(PPh_3)_4$ catalyst in aqueous toluene at 60 °C (Table 1, entry 13). Increasing temperature above 60°C only furnished **3a** in a yield of 52% and promoted the formation of homo-coupling by-products (Table 1, entry 15).

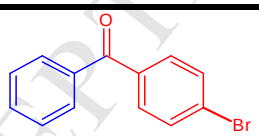
With the optimised reaction conditions in hand (Table 1, entry 13), the scope and limitations of the current investigation was explored using a diverse range of acyl chlorides and sodium (aryl trihydroxyborate) salts bearing electron-donating and/or electron-withdrawing substituents and the results are summarised in Table 2.

Table 2: Base free Palladium-Catalysed acylation reactions of sodium (aryltrihydroxyborate) salts with acyl chlorides.[a]

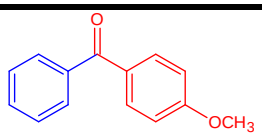




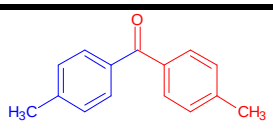
3a (88%)



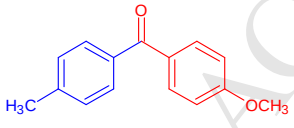
3b (74%)



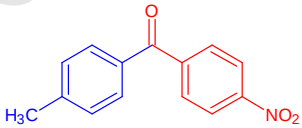
3c (79%)



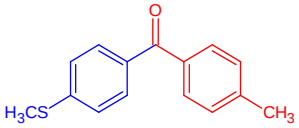
3d (94%)



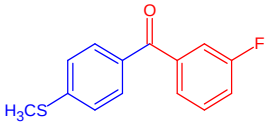
3e (86%)



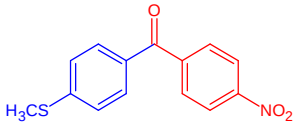
3f (67%)



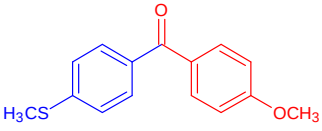
3g (74%)



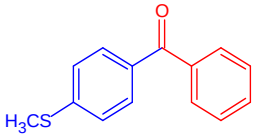
3h (86%)



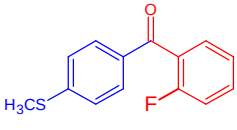
3i (69%)



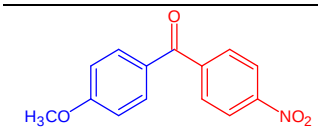
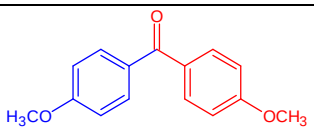
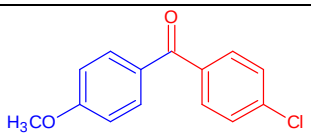
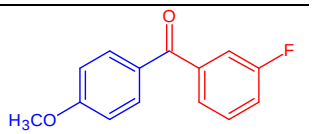
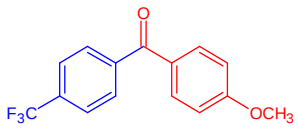
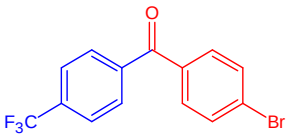
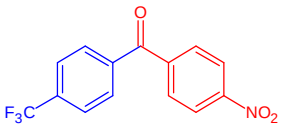
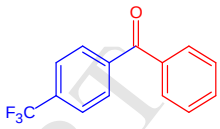
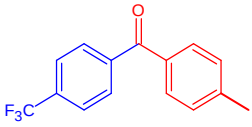
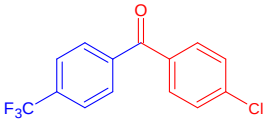
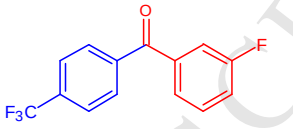
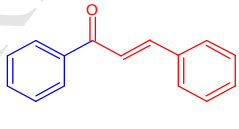
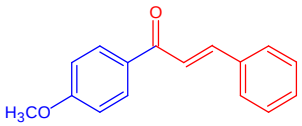
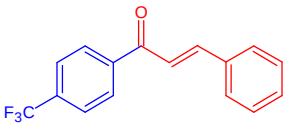
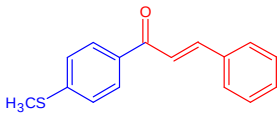
3j (94%)



3k (89%)



3l (51%)

			
3m (64%)	**3n** (93%)	**3o** (90%)	**3p** (73%)
			
3q (82%)	**3r** (91%)	**3s** (70%)	**3t** (86%)
			
3u (81%)	**3v** (89%)	**3w** (94%)	**3aa** (0%)
			
3bb (0%)	**3cc** (0%)	**3dd** (0%)	**3ee** (0%)

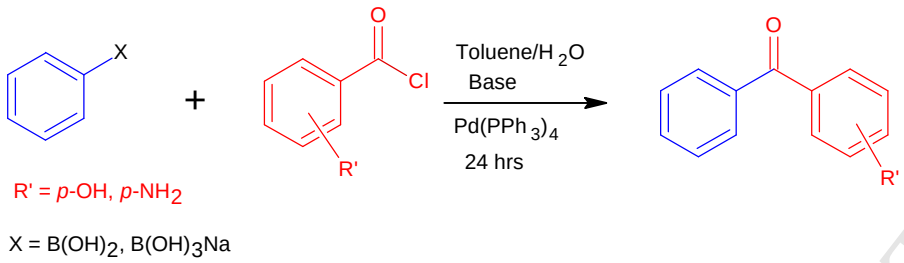
[a] Reaction conditions: Acyl chloride (1.1 mmol), sodium aryl trihydrxyboronate (1.0 mmol), $Pd(PPh_3)_4$ (0.01 mmol), toluene (2.0 mL) and water (0.5 mL). All reaction were conducted under an argon atmosphere to avoid premature oxidation of $Pd(PPh_3)_4$ at 60 °C, 24 hours. All yields were isolated using column and/or radial chromatography.

Sodium (phenyltrihydroxyborate) (**1a**) reacted efficiently with acyl chlorides bearing electron-donating as well as electron-withdrawing substituents, giving substituted ketones **3a-3c** in moderate to good yields (Table 2). Similar, the acylation reactions of sodium (4-methylphenyltrihydroxyborate) (**1b**) with different acyl chlorides proceeded smoothly affording ketones **3d** and **3e** in 94% and 86%, respectively. In general, the acylative cross-coupling reactions of all sodium (aryl trihydroxyborate salts) with 4-nitrobenzoyl chloride provides the desired ketones (**3f**, **3i**, **3m** and **3s**) in lower yields compared to other acyl chlorides probably due to competitive hydrolysis

reactions. Sodium (4-(methylthio)phenyltrihydroxyborate) (**1c**) underwent efficient acylation reactions with several acid chlorides leading to functionalised ketones **3g**-**3k** in 74-94%. As expectedly, the cross-coupling reaction of sodium (4-(methythio)phenyltrihydroxyborate) (**1c**) with 2-substituted acyl chloride gave a poor 51% yield (Table 1, **3l**), presumably because of *ortho*-steric hindrance. The trihydroxyborate reagent bearing an electron rich methoxy group (**1d**) also reacted smoothly with the acyl chlorides to afford the corresponding products (**3m-3p**) in good to excellent yields (64-93%). The acylation reactions of sodium (4-(trifluoromethyl)phenylborate) (**1e**) with different nucleophiles were mostly favoured giving the coupled-products in yields greater than 70% (Table 2). For example, substrate **1e** coupled favourably with electrophiles bearing moderate electron-withdrawing substituents (Br, F and Cl) generating the expected diaryl ketones **3r**, **3v** and **3w** in 91%, 89% and 94% isolated yields, respectively. To further investigate the scope and limitations of this reaction, we examined the reaction of cinnamoyl chloride with trihydroxyboronate nucleophiles (**1a-1e**), however, there were no products formed (Table 2, **3aa, 3bb, 3cc** and **3dd**) and only the starting materials were detected along with the hydrolysis product (cinnamic acid). Further investigations into finding optimal reaction conditions for alkyl and alkenyl acyl chlorides with trihydroxyborate reagents are currently underway in our laboratory.

To demonstrate the true benefit of the base free acylative Suzuki-Miyaura cross coupling protocol, we synthesised aryl ketones bearing base sensitive hydroxyl and amino functionalities which are rather difficult to synthesis following the traditional Suzuki-Miyaura cross-coupling reaction (**Table 3**).[26,27].

Table 3: Synthesis of base senstivite diaryl ketones.[a]



R' = *p*-OH, *p*-NH_2

X = $B(OH)_2$, $B(OH)_3Na$

Entry	R'	nucleophile	Base	Yield (%)
1	OH	$PhB(OH)_2$	NaOH	trace
2	NH_2	$PhB(OH)_2$	NaOH	trace
3	OH	$PhB(OH)_2$	K_2CO_3	8
4	NH_2	$PhB(OH)_2$	K_2CO_3	trace
5	OH	$PhB(OH)_3Na$	–	64
6	NH_2	$PhB(OH)_3Na$	–	57

[a] Reaction conditions: Acyl chloride (1.1 mmol), nucleophile (1.0 mmol), $Pd(PPh_3)_4$ (0.01 mmol), toluene (2.0 mL) and water (0.5 mL). All reaction were conducted under an argon atmosphere to avoid premature oxidation of $Pd(PPh_3)_4$ at 60 °C, 24 hours. All yields were isolated using column and/or radial chromatography.

The cross coupling reaction of phenyl boronic acid with either 4-aminobenzoylchloride or 4-hydroxybenzoylchloride, in the presence of a base (NaOH or K_2CO_3), afforded the desired products (4-aminobenzophenone or 4-hydroxybenzophenone) in only trace amounts (Table 3, entries 1-4). The poor yields might be attributed to a base catalysed formation of the side products due to the competative side reaction between an amino or the hydroxyl functionality with the acyl chloride. The application of a base free acylation using trihydroxyborate salt as a nucleophile afforded the desired products with improved yields of 64 and 57 % (Table 3, entries 5 and 6).

The main motivation behind the isolation and subsequent application of sodium (aryltrihydroxyborate) salts was to investigate whether these pure, free-flowing powder can be coupled with acyl chlorides in the Suzuki acylation reactions without the addition of excess amount of a base. Gratifyingly, it became apparent that these salts are excellent coupling partners in the Suzuki acylation reactions with aromatic acyl chlorides. As anticipated, the nucleophiles do not require base activation step as evident with no requirement of a base which is a great advantage for the synthesis of ketones bearing base sensitive functional groups. In addition, sodium (aryl trihydroxyborate salts) are pure thus eliminating the formation of inseparable mixtures of boronic acids and boronic acid anhydrides making it convenient to calculate the correct reaction stoichiometry [13].

Conclusion

We have developed the first base-free Suzuki acylation reactions of easily isolated free flowing sodium (aryl trihydroxyborate salts) with different aromatic acyl chlorides in aqueous toluene. The catalytic system appeared versatile and general, tolerating a variety of functional groups such as OH, NH_2, NO_2, OMe, SMe CF_3, F, Cl and Br whilst furnishing the coupled-products with isolated yields of up to 96% isolated yields in 24 hours. Sodium (aryltrihydroxyborate) salts are therefore excellent coupling partners for the synthesis of ketones under neutral Suzuki-acylative reaction conditions developed.

Experimental

General consideration:

Commercially available reagents were used without further purification. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376.2 MHz) spectra were recorded as solution in the specified deuterated solvents and are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard. ^{11}B NMR spectra

were referenced to $BF_3 \cdot OEt_2$ (external, neat, with capillary tube of acetone-*d*6 for the deuterium lock). Purifications of the products were performed by flash-column chromatography and centrifugal preparative thin-layer chromatography (chromatotron) on Fluka silica gel 60 cat No. 70–230 mesh (0.063–0.2 mm) and Merk silica gel cat. No. 1.07749, respectively.

General procedure for the synthesis of sodium aryl trihydroxyborate salts.

Aryl halide (8.20 mmol), Mg (398.0 mg, 16.40 mmol) and dry THF (50.0 mL) were placed in a 100 mL round-bottomed flask equipped with a Dean and Stark Apparatus, magnetic stirrer bar and reflux condenser. The mixture was stirred at room temperature until Grignard reagent has formed completely (minimum 30 minutes) and eventually cooled to –78 °C. Trimethyl borate solution (1.83 mL, 16.40 mmol) was added dropwise at –78 °C and the mixture was stirred overnight. THF was removed under reduced pressure leaving a white precipitate which was dissolved in refluxing toluene (30.0 mL) followed by the addition of concentrated NaOH solution until no further precipitation occurred. The precipitate was filtered under vacuum, dried in an oven and used without further purification[13a].

Sodium (phenyltrihydroxyborate) (1a): Following the general procedure [13a], compound **1a** was obtained as cream white powder (95%): ^{1}H NMR (400 MHz, D_2O) δ_H: 7.16-7.21 (m, 1H), 7.25-7.30 (m, 2H), 7.53 (d, *J* = 6.79 Hz, 2H) . ^{13}C{1H} NMR (100 MHz, D_2O) δ_C: (C-B is not observed) 125.7, 127.3, 131.3, 167.7. ^{11}B NMR (128 MHz, D_2O) δ_B: 3.1 ppm (s). Anal. calcd. for $C_6H_8NaBO_3$: C, 44.50, H, 4.98 Found C, 44.45, H, 4.92.

Sodium (4-methylphenyltrihydroxyborate) (1b): Following the general procedure[13a], compound **1b** was obtained as cream white powder (98%): ^{1}H NMR (400 MHz, D_2O) δ_H: 2.28 (s, 3H), 7.14 (d, *J*= 7.44 Hz, 2H), 7.45 (d, *J* = 7.73 Hz, 2H). ^{13}C{1H} NMR (100 MHz, D_2O) δ_C: (C-B is not observed) 20.2, 127.9, 131.5,

135.4, 168.0. ^{11}B NMR (128 MHz, D_2O) δ_B: 3.2 ppm (s). Anal. calcd. for $C_7H_{10}NaBO_3$: C,47.78, H, 5.72 Found C, 44.71, H, 5.68.

Sodium (4-methylthiophenyltrihydroxyborate) (1c): Following the general procedure[13a], compound **1c** was obtained as white powder (94%): ^{1}H NMR (400 MHz, D_2O) δ_H: 2.47 (s, 3H), 7.25 (d, *J* = 8.20 Hz, 2H), 7.52 (d, *J* = 8.27 Hz, 2H) . ^{13}C{1H} NMR (100 MHz, D_2O) δ_C: (C-B is not observed) 15.1, 125.9, 132.2, 133.7, 165.0. ^{11}B NMR (128 MHz, D_2O) δ_B: 3.8 ppm (s). Anal. calcd. for $C_7H_{10}NaBO_3S$: C,40.42, H, 4.84, S, 7.69 Found C, 40.39, H, 4.80, S, 7.79.

Sodium (4-methoxyphenyltrihydroxyborate) (1d): Following the general procedure[13a], compound **1d** was obtained as white powder (97%): ^{1}H NMR (400 MHz, D_2O) δ_H: 3.80 (s, 3H), 6.91 (d, *J* = 8.56 Hz, 2H), 7.49 (d, *J* = 8.56 Hz, 2H). ^{13}C {1H} NMR (100 MHz, D_2O) δ_C: (C-B is not observed) 55.2, 112.8, 132.6, 157.0, 167.6. ^{11}B NMR (128 MHz, D_2O) δ_B: 3.4 ppm (s). Anal. calcd. for $C_7H_{10}NaBO_4$: C, 43.79, H, 5.25 Found C, 43.71, H, 5.22.

Sodium (4-trifluoromethylphenyltrihydroxyborate) (1e): Following the general procedure[13a], compound **1e** was obtained as white powder (98%): ^{1}H NMR (400 MHz, D_2O) δ_H:7.56 (d, *J* = 7.99 Hz, 2H), 7.68 (d, *J* = 7.67 Hz, 2H). ^{13}C{1H} NMR (100 MHz, D_2O) δ_C: (C-B is not observed) 126.3, 126.4, 126.9 (q, $^1J_{CF}$ = 33 Hz), 168.0. F{^{1}H} NMR (376.2 MHz, D_2O): δ_F -63.6 (s). ^{11}B NMR (128 MHz, D_2O) δ_B: 2.5 ppm (s). Anal. calcd. for $C_7H_7NaBO_3$: C, 36.53, H, 3.07 Found C, 36.46, H, 3.03.

General procedure for the Suzuki-Miyaura acylation reactions.

The corresponding borate salt (1 mmol), $Pd(PPh_3)_4$ (0.01 mmol, 11.56 mg), degassed toluene (2.0 mL), degassed water (0.50 mL) were place in a 50 mL round-bottomed flask with a magnetic stirrer bar and a rubber septum. The content of the flask was kept under argon while acyl chloride (1.10 mmol), dissolved in degassed toluene (1.0 mL), was added dropwise *via* a syringe and the flask was heated to 60 °C on the oil bath. After 24 hours, the reaction mixture was filtered and solvent removed under *vacue.* The resulting residue was dissolved in DCM and was purified using flash-

column chromatography or centrifugal preparative thin-layer chromatography (chromatotron) using Hexane: Ethyl acetate (9:1) as an eluent.

Phenyl(*p*-tolyl)methanone(3a) [9]**:** Following the general procedure, compound **3a** was obtained as white crystalline solid (88%): (400 MHz, $CDCl_3$) δ_H: 7.45–7.51 (m, 2H), 7.56–7.61 (m, 1H), 7.78–7.82 (m, 2H). ^{13}C {1H} NMR (100. MHz, $CDCl_3$) δ_C: 128.3, 130.1, 132.4, 137.6, and 196.75. MS (EI), *m/z* (%): 39 (5), 51 (10), 65 (11), 77 (22), 91 (30), 105 (30), 119 (100), 196 [M^+] (60).

(4-Bromophenyl)(phenyl)methanone (3b)[16]**:** Following the general procedure, compound **3b** was obtained as crystalline solid (74%): ^1H NMR (400 MHz, $CDCl_3$): 7.48-754 (m, 2 H), 7.60-7.73 (m, 5H), 7.78-7.82 (m, 2 H).^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ_C: 127.5, 128.4, 129.9, 131.5, 131.6, 132.6, 136.3, 137.2 and 195.6. MS (EI), *m/z* (%): 51 (12), 77 (42), 105 (100), 152 (10), 183 (25), 260 [M^+] (50).

(4-Methoxyphenyl)(phenyl) methanone (3c)[11d]**:** Following the general procedure, compound **3c** was obtained as white crystalline solid (79%): (400 MHz, $CDCl_3$) δ_H: 3.87 (s, 3H), 6.95–6.98 (m, 2H), 7.46 (t, 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.74–7.76 (m, 2H), 7.81–7.84 (m, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 55.5, 113.5, 128.1, 129.7, 130.2, 131.8, 132.5, 138.3, 163.2 and 195.5 MS (EI), *m/z* (%): 50 (8), 77 (25), 105 (25), 151 (100), 228 [M^+] (58).

Bis(*p*-tolyl)methanone (3d)[11d]**:** Following the general procedure, compound **3d** was obtained as white powder (94%) : (400 MHz, $CDCl_3$) δ_H: 2.46 (s, 3H), 7.30 (d, *J* = 8.01 Hz, 4H), 7.73 (d, *J* = 8.05 Hz, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 21.6, 128.9, 130.1, 135.2, 142.9 and 196.2. MS (EI), *m/z* (%): 39 (4), 65 (15), 91 (31), 119 (100), 195 (10), 210 [M^+] (31).

(4-Methoxyphenyl)(*p*-tolyl)methanone (3e)[11c]**:** Following the general procedure, compound **3e** was obtained as white solid (86%): ^1H NMR (400 MHz, $CDCl_3$) δ_H: 2.44 (s, 3H), 3.94 (s, 3H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H). ^{13}C {1H} NMR (100. MHz, $CDCl_3$) δ_C: 21.6, 55.4, 113.5, 128.8, 130.0, 130.5, 132.4, 135.5, 142.6, 163.0 and 195.3. MS (EI), *m/z* (%): 65 (8), 77 (15), 91 (21), 107 (9), 119 (25), 135 (100), 211 (13), 226 [M^+] (50).

(4-Nitrophenyl)(*p*-tolyl)methanone (3f) [17]**:** Following the general procedure, compound **3f** was obtained as white solid (67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 2.51 (s, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 2H), 8.46 (d, *J* = 8.0 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 21.7, 123.4, 129.3, 130.3, 130.5, 133.6, 143.3, 144.5, 149.7 and 194.5. MS (EI), *m/z* (%): 39 (9), 50 (9), 65 (17), 76 (10), 91 (39), 104 (5), 119 (100), 241 [M^+] (20).

(4-Methylthiophenyl)(*p*-tolyl)methanone (3g)[18]**:** Following the general procedure, compound **3g** was obtained as pale yellow product (74%) : (400 MHz, $CDCl_3$) δ_H: 2.46 (s, 3H), 2.55 (s, 3H), 7.29-7.35 (m, 4H), 7.71 (d, *J* = 8.13 Hz, 2H), 7.75 (d, *J* = 8.18 Hz, 2H). ^{13}C{1H} NMR (100. MHz, $CDCl_3$) δ_C: 14.9, 21.6, 124.8, 126.2, 128.9, 129.5, 130.0, 130.5, 130.6, 134.0, 135.1, 142.9, 144.9, 145.5, 162.5 and 195.5. MS (EI), *m/z* (%): 65 (18), 91 (33), 119 (63), 151 (100), 195 (12), 242 [M^+] (80).

(4-Methythiophenyl)(3-fluorophenyl)methanone (3h) [19]**:** Following the general procedure, compound **3h** was obtained as white powder (86%) : (400 MHz, $CDCl_3$) δ_H: 2.57 (s, 3H), 7.27-7.36 (m, 3H), 7.44-7.54 (m, 2H), 7.53-7.58 (m, 1H), 7.76 (d, *J* = 8.5 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 14.8, 116.5 (d, *J* = 22 Hz), 119.1 (d, *J* = 22 Hz), 124.9, 125.5, 127.1 (d, *J* = 8 Hz), 129.9 (d, *J* = 8 Hz), 130.5, 133.0, 139.9 (d, *J* = 6.6 Hz), 145.9, 161.1 (d, *J* = 250 Hz), and 194.2. ^{19} F {^{1}H} NMR (376.2 MHz, $CDCl_3$): δ_F -111.4 (s).MS (EI), *m/z* (%): 95 (20), 123 (30), 151 (2), 151 (100), 246 [M^+] (68).

(4-Methythiophenyl)(4-nitrophenyl)methanone (3i)[17]**:** Following the general procedure, compound **3i** was obtained as yellow crystals (69%) : (400 MHz, $CDCl_3$) δ_H: 2.58 (s, 3H), 7.34 (d, *J* = 8.50 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 8.36 (d, *J* = 8.8 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$,) δ_C: 14.7, 123.5, 125.0, 130.4, 132.2, 143.3, 147.0, 149.7 and 193.7. MS (EI), *m/z* (%): 77 (67), 122 (12), 123 (45), 151 (100), 150 (45), 227 (89), 273 [M^+] (24).

(4-Methylthiophenyl)(4-methoxyphenyl)methanone (3j)[18]**:** Following the general procedure, compound **3i** was obtained as colourless crystals (94%) :(400 MHz, $CDCl_3$) δ_H: 2.56 (s, 3H), 3.91 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H). ^{13}C {1H} NMR (100 MHz,

$CDCl_3$) δ_C: 14.9, 55.4, 113.5, 124.9, 130.3, 132.3, 134.4, 144.4, 163.0, 194.6. MS (EI), *m/z* (%): MS (EI), *m/z* (%): 65 (18), 91 (33), 119 (63), 151 (100), 195 (12), 258 [M^+] (80).

(4-Methylthiophenyl)(phenyl)methanone (3k)[18]**:** Following the general procedure, compound **3k** was obtained as yellow crystalline solid (89%) : (400 MHz, $CDCl_3$) δ_H: 2.56 (s, 3H), 7.28–7.36 (m, 2H), 7.47–7.54 (m, 2H), 7.57-7.63 (m, 1H), 7.75-7.82 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 14.8, 124.8, 127.1, 128.2, 129.8, 130.6, 132.1, 133.7, 137.9, 145.3 and 195.7. MS (EI), *m/z* (%): 50 (8), 77 (25), 105 (25), 151 (100), 228 [M^+] (58).

(4-Methylthiophenyl)(2-fluorophenyl)methanone (3l)[20]**:** Following the general procedure, compound **3l** was obtained as colourless crystals (51%) :(400 MHz, $CDCl_3$) δ_H: 2.54 (s, 3H), 7.14-7.21 (m, 1H), 7.25-7.34 (m, 3H), 7.50-7.58 (m, 2H), 7.74-7.81 (m, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 14.7, 116.2 (d, *J* = 22 Hz), 124.2, 124.8, 127.2, 130.6 (d, *J* = 3 Hz), 132, 133.5, 146.6, 158.6, 161.1 (d, *J* = 250 Hz) and 192.3. ^{19} F{^{1}H} NMR (376.2 MHz, $CDCl_3$): δ_F -63.6 (s).MS (EI), *m/z* (%): 95 (20), 123 (25), 151 (25), 151 (100), 246 [M^+] (60).

(4-Methoxyphenyl)(4-nitrophenyl)methanone (3m)[18]**:** Following the general procedure, compound **3m** was obtained as colourless solid (64%) : (400 MHz, $CDCl_3$) δ_H: 3.93 (s, 3H), 7.02 (d, *J* = 8.76 Hz, 2H), 7.84 (d, *J* = 8.77 Hz, 2H), 7.90 (d, *J* = 8.50 Hz, 2H), 8.35 (d, *J* = 8.45 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 55.6, 114.0, 123.4, 128.9, 130.3, 132.6, 143.8, 149.5, 164.0, and 193.4 MS (EI), *m/z* (%): 77 (67), 122 (12), 92 (14), 123 (45), 151 (100), 150 (45), 227 (89), 257.2 [M^+] (45).

Bis(4-methoxyphenyl)methanone (3n)[18]**:** Following the general procedure, compound **3n** was obtained as colourless needles (93%) : (400 MHz, $CDCl_3$) δ_H: 3.91 (s, 6H), 6.99 (d, *J* = 8.77 Hz, 4H), 7.81 (d, *J* = 8.75 Hz, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 55.4, 113.4, 130.8, 132.2, 162.8, and 194.4. MS (EI), *m/z* (%): 77 (13), 122 (12), 92 (10), 107 (10), 135 (100), 211 (15), 242 [M^+] (30).

(4-Methoxyphenyl)(4-chlorophenyl)methanone (3o)[18]**:** Following the general procedure, compound **3o** was obtained as colourless solid (90%) : (400 MHz, $CDCl_3$) δ_H: 3.91 (s, 3H), 6.99 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 55.2, 113.7, 128.5, 129.8, 131.1, 132.4, 136.4, 138.2, 163.4, and 194.2. MS (EI), *m/z* (%): 77 (15), 92 (10),111 (15), 135 (100), 246 [M^+] (30).

(4-Methoxyphenyl)(3-fluorophenyl)methanone (3p)[21]**:** Following the general procedure, compound **3p** was obtained as colourless solid (73%) : (400 MHz, $CDCl_3$) δ_H: 3.92 (s, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.25-7.32 (m, 1H), 7.45-7.50 (m, 2H), 7.53-7.58 (m, 1H), 7.84 (d, *J* = 8.9 Hz, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$,) δ_C: 55.5, 113.7, 116.5 (d, *J* = 22.3 Hz), 118.8 (d, *J* = 22.0 Hz), 125.4 (d, *J* = 3.7 Hz), 129.9 (d, *J* = 8.8 Hz), 132.5, 140.4, 161.2, 163.5 and 194.0. ^{19} F {^{1}H} NMR (376.2 MHz, $CDCl_3$): δ_F -111.9 (s). MS (EI), *m/z* (%): 64 (2), 77 (12), 95 (10), 107 (9), 123 (5), 135 (100), 230 [M^+] (44).

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (3q)[22]**:** Following the general procedure, compound **3q** was obtained as white needle-like crystals (82%): (400 MHz, $CDCl_3$) δ_H: 3.93 (s, 3H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.82-7.90 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 55.5, 123.6 (d, J_{CF} = 271.0 Hz), 125.2 (q, *J* = 3,7 Hz), 129.4, 129.7, 133.6 (q, $^2J_{CF}$ = 33.2 Hz), 141.5, 163.7 and 194.2. ^{19} F{^{1}H} NMR (376.2 MHz, $CDCl_3$): δ_F -63.6 (s). MS (EI), *m/z* (%): 77 (11), 92 (12), 107 (12), 135 (100), 145 (9), 280 [M^+] (33).

(4-Bromophenyl)(4-(trifluoromethyl)phenyl)methanone (3r)[23]**:** Following the general procedure, compound **3r** was obtained as light brown powder (91%) : (400 MHz, $CDCl_3$) δ_H: 7.65-7.72 (m, 4H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H). ^{13}C {1H} NMR (100. MHz, $CDCl_3$) δ_C: 123.7 (d, *J* = 271.0 Hz), 125.4 (q, $^2J_{CF}$ = 3.0 Hz), 128.3, 130.0, 131.5, 131.9, 133.8, 134.1 (q, J_{CF} = 33.5 Hz), 135.4, 140.3 and 194.4. ^{19} F {^{1}H} NMR (376.2 MHz, $CDCl_3$): δ_F -63.0 (s). MS (EI), *m/z* (%): 50 (40), 75 (49), 95 (13), 125 (15), 155 (29), 173 (62), 183 (100), 330 [M^++1] (15).

(4-nitrophenyl)(4-(-trifluoromethyl)phenyl)methanone (3s)[24]**:** Following the general procedure, compound **3s** was obtained as light yellow solid (70%) : (400

MHz, $CDCl_3$) δ_H: 7.83 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 8.76 Hz, 2H), 8.39 (d, *J* = 8.77 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 123.8 (d, *J* = 274. Hz) 125.7 (q, J_{CF} = 3.2 Hz), 130.5 (d, *J* = 57.0 Hz), 134.7 (q, J_{CF} = 33.2 Hz) 139.3, 141.8, 150.2 and 193.6. $^{19}F\{^1H\}$ NMR (376.2 MHz, $CDCl_3$): δ_F -63.1 (s).MS (EI), *m/z* (%): 50 (40), 76 (13), 95 (7), 120 (5), 173 (100), 295 [M^+] (55).

(4-(trifluoromethyl)phenyl)methanone (3t)[11d]**:** Following the general procedure, compound **3t** was obtained as white powder (86%) : (400 MHz, $CDCl_3$) δ_H: 7.50-7.57 (m, 2H), 7.63-7.69 (m, 1H), 7.78 (d, *J* = 8.20 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 7.91 Hz, 2H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ_C: 123.8 (d, *J* = 271.7 Hz), 125.3 (dd, *J* = 7.2 Hz), 125.7 (q, $^2J_{CF}$ = 3.0 Hz), 128.5, 130.1, 133.2, 133.5, 133.9 (d, $^1J_{CF}$ = 33 Hz), 136.7, 140.7 and 195.5. $^{19}F\{^1H\}$ NMR (376.2 MHz, $CDCl_3$): δ_F -63.6 (s). MS (EI), *m/z* (%): 51 (10), 77 (38), 105 (100), 145 (29), 173 (31), 250 [M^+] (38).

(*p*-tolyl)(4-(trifluoromethyl)phenyl)methanone (3u)[9]**:** Following the general procedure, compound **3u** was obtained as colourless crystals (81%) : (400 MHz, $CDCl_3$) δ_H: 2.48 (s, 3H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.72-7.80 (m, 4H), 7.90 (d, *J* = 8.2 Hz, 2H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$) δ_C: 21.6, 123.8 (d, $^1J_{CF}$ = 271.0 Hz), 125.4 (q, $^2J_{CF}$ = 3.2 Hz), 129.2, 130.2 (d, *J* = 33.5 Hz), 130.3, 133.7 (d, $^1J_{CF}$ = 33.0 Hz), 134.1, 141.1, 144.0 and 195.2. $^{19}F\{^1H\}$ NMR (376.2 MHz, $CDCl_3$,):MS (EI), *m/z* (%): 65 (10), 91 (38), 119 (100), 145 (19), 264 [M^+] (38).

(4-Chlorophenyl)(4-(trifluoromethyl)phenyl)methanone (3v)[25]**:** Following the general procedure, compound **3v** was obtained as white needle-like crystals (89%) : (400 MHz, $CDCl_3$) δ_H: 7.31-7.39 (m, 1H), 7.44-7.50 (m, 1H), 7.71-7.77 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ_C: 53.4, 116.7 (d, J_{CF} = 22.0 Hz), 120.1 (d, J_{CF} = 22 Hz), 123.9 (d, J_{CF} = 270.0 Hz) 125.4 (q, J_{CF} = 3.0 Hz), 125.8 (d, J_{CF} = 3.0 Hz), 128.4, 128.5, 130.2 (d, J_{CF} = 8.0 Hz), 132.3, 132.5, 134 (q, J_{CF} = 33.0 Hz), 140.1 and 194.1. $^{19}F\{^1H\}$ NMR (376.2 MHz, $CDCl_3$): δ_F -62.9 (s) and -111.8 (s). MS (EI), *m/z* (%): 77 (11), 92 (12), 107 (12), 135 (100), 145 (9), 280 [M^+] (33).

(3-Fluorophenyl)(4-(trifluoromethyl)phenyl)methanone (3w)[25]**:** Following the general procedure, compound **3w** was obtained as white needle-like crystals (94%) : (400 MHz, $CDCl_3$) δ_H: 7.51 (d, *J* = 8.5 Hz, 2H), 7.76-7.81 (m, 4H), 7.89 (m, 2H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ_C: 116.7 (d, J_{CF} = 22.9 Hz), 120.1 (d, *J* = 21.3 Hz) 125.4 (q, *J* = 11.8, 3.7 Hz) 125.8 (d, *J* = 2.9 Hz), 128.5, (d, *J* = 12.5 Hz), 130.1, 130.2 (d, *J* = 8.3 Hz), 131.5 (d, *J* = 3 Hz), 132.2 (d, *J* = 10.3 Hz), 138.8 (d, *J* = 7 Hz), 140.1, 162.2 (d, $^1J_{CF}$ = 248 Hz) and 194.2. MS (EI), *m/z* (%): 43 (11), 75 (21), 95 (8), 111 (25), 113 (9), 139 (100), 141 (40), 173 (30), 284 [M^+] (30).

(4-aminophenyl)phenyl-methanone:[26] Following the general procedure, the titled compound was obtained as yellow crystals (57%) :(400 MHz, $CDCl_3$) δ_H: 4.16 (br s, NH_2), 6.68 (d, *J* = 8.7 Hz, 2H), 7.44-7.51 (m, 2H), 7.52-7.58 (m, 1H), 7.70-7.78 (m, 4H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ_C: 113.6, 127.3, 128.1, 129.5, 131.4, 132.9, 138.9, 151.1 and 195.3. MS (EI), *m/z* (%): 39 (16), 50 (8), 51 (30), 63 (9), 65 (40), 79 (38), 92 (30), 105 (8), 120 (100), 197 [M^+] (55).

(4-hydroxyphenyl)phenyl-methanone: [27] Following the general procedure, the titled compound was obtained as cream white powder (64%) : (400 MHz, $CDCl_3$) δ_H: 4.16 (br s, NH_2), 6.98 (d, *J* = 8.7 Hz, 2H), 7.47-7.53 (m, 2H), 7.57-7.63 (m, 1H), 7.66 (s, 1H), 7.76-7.84 (m. 4H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ_C: 115.4, 128.3, 129.4,129.8, 132.2, 133.2, 138.0, 161.0 and 197.1. MS (EI), *m/z* (%): 39 (6), 41 (8), 63 (11), 77 (20), 85 (5), 93 (38), 92 (11), 105 (20), 121 (100), 198 [M^+] (55).

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Appendix. Supporting Information

Supporting Information File 1

Copies of ^1H,^{13} C and ^{11}B NMR of synthesised compounds are available.

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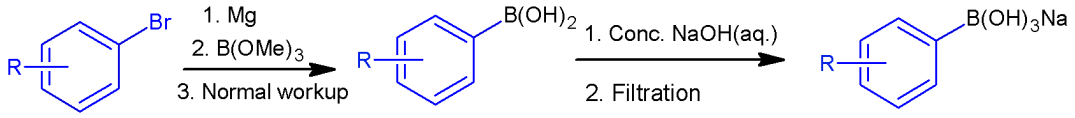

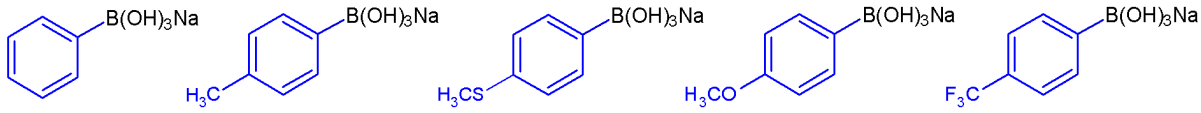

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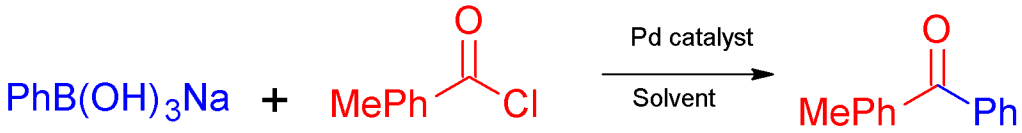

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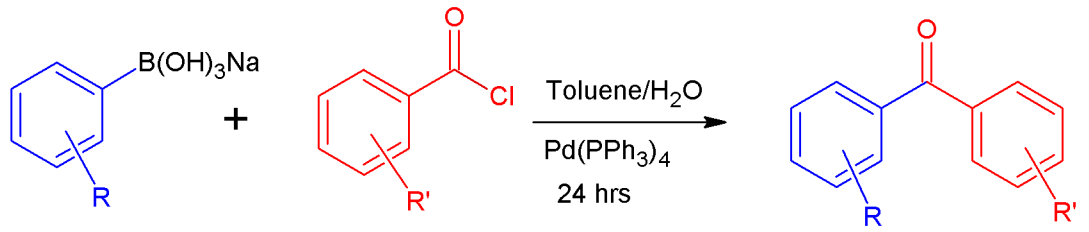

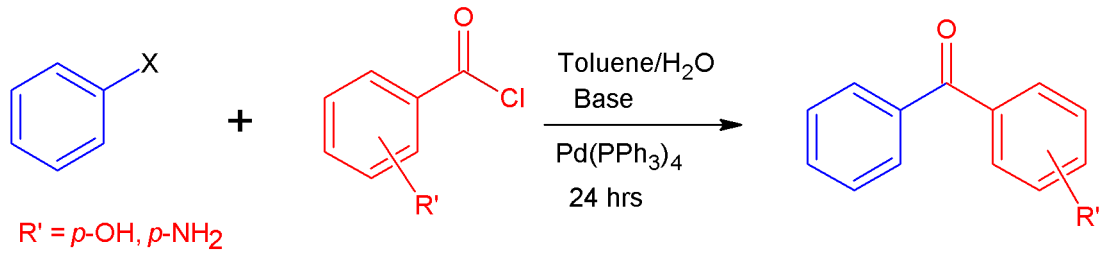

R' = *p*-OH, *p*-NH_2

X = $B(OH)_2$, $B(OH)_3Na$

- Base-free palladium-catalysed Suzuki acylation transformation of sodium (aryltrihydroxyborate) salts and aromatic acyl chlorides to substituted ketones.
- The desired substituted diarylketones were produced in isolated yields of up to 96% at 60 °C in aqueous toluene.
- Electrophiles bearing base sensitive functional groups were also accommodated in the developed procedure.
- The first acylation procedure to cross-couple ultra-stabilised sodium (aryltrihydroxyborate) salts as activated nucleophiles with aromatic acyl chlorides to prepare ketones.

.