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Oxidative nucleophilic substitution: transformation of alkylboronic derivatives

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ABSTRACT

An efficient amidation reaction is described in this paper. Potassium alkyltrifluoroborate salts can be transforming to amides from nitriles in the presence of copper acetate and boron trifluoride. An extension of this reaction allowed the formation of amines, ethers, and C–C bond.

1. Introduction

The amide function is one of the most widespread in nature. Often prepared from an amine and a carboxylic acid, a large choice of peptide coupling methods is described in the literature.[1] Among these classical approaches, the Ritter reaction appears as an alternative for the amide synthesis from alcohols or alkenes.[2] However, this reaction was performed in presence of Lewis acid[3] ($AlCl_3$, $SnCl_4$, $Bi(OTf)_3$, $BF_3{\cdot}OEt_2$, boric acid, etc.) or Brønsted acid[4] (concentrated H_2SO_4, triflic acid, formic acid or AcOH) at elevated temperatures. Many efforts were realized during the last decade to develop milder conditions. For example, Cossy and co-workers reported an iron-catalyzed Ritter reaction, which provided amides from benzylic alcohols.[5] Very recently, an iodine-catalyzed reaction allows amide formation from nitriles.[6] However, the scope of the reaction is limited by the requirement of high temperatures (>100 °C).

Another classical approach for the C–N bond formation is the Ullmann condensation, which was intensively studied to synthesize biaryl amine or biaryl ether from halide.[7] Since, Chan, Lam, and Evans have shown that boronic derivatives appear as excellent partners for the C–N bond formation.[8] The formation of C(aryl)–O, C(aryl)–N, C(aryl)–S bond is performed from reaction between boronic acids and a phenol, aniline or thiophenol, respectively, in presence of copper species.[9] In 2003, Batey and co-workers developed the C(aryl)–N bond formation by reaction of a potassium aryltrifluoroborate salts with an aniline or an amide mediated by copper species.[10] In this modified-Ullmann condensation potassium aryltrifluoroborate salts are generally used in excess compared to aniline. However these different studies indicate that boronic derivatives could be used as precursor for amide synthesis. Potassium trifluoroborate salts are stable to air, water[11] and a variety of reaction conditions.[12] They can be easily prepared from the corresponding boronic ester or acid. These crystalline derivatives are easy to handle and can efficiently substitute the corresponding boronic acids.[13] In our laboratory, we were interested in developing a suitable method for the formation of C–N bond with alkylboronic derivatives and a nitrogen source. To this end, we have combined the works of Chan, Lam and Batey with the Ritter reaction to develop a new method of amidation.[14] Herein we report a broader study of this mild and efficient Ritter-type amidation of alkylboronic derivatives with nitriles, proceeding at room temperature. The mechanistic study drove us to synthesize ethers, amines, and C–C bond.

2. Results and discussion

In order to reach optimized conditions, potassium 1-phenylethyltrifluoroborate **1** was considered with benzonitrile (Scheme 1) in the presence of copper acetate and $BF_3{\cdot}OEt_2$.

The evaluation of different Lewis acids showed that the highest yield of amidation was reached in the presence of boron trifluoride (48% in diethyl ether). The formation of the desired product was not observed with other Lewis acids ($TiCl_4$, $AlCl_3$, $ZnCl_2$, $ZrCl_4$, $CeCl_3$, and $B(Oi\text{-}Pr)_3$). Likewise, the expected amide was not formed when

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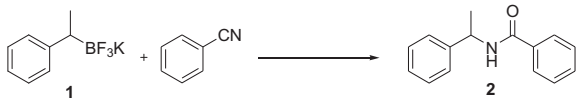
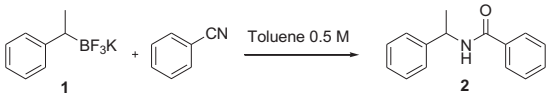


Scheme 1. Amidation of potassium alkyltrifluoroborate salts.

the reaction was carried out without Lewis acid (Table 1, entry 1). Moreover, in absence of copper acetate, boron trifluoride alone does not lead to amide formation (Table 1, entry 2). As a consequence, each reagent is necessary for the C–N bond formation. The amount of each reagent was then studied for optimal reactivity (Table 1). Nevertheless, reducing the amount of copper decreased considerably the yield (Table 1, entries 3–6). However the ratio $Cu(OAc)_2/BF_3{\cdot}OEt_2$ seems very important. When the reaction was realized with benzonitrile as solvent the reaction time was considerably reduced. Indeed, the conversion was complete in 10 min to afford the corresponding amide, which was detected by GC in 70% yield (Table 1, entry 1). To pursue the optimization condition of this reaction, the nature of the metal was studied.

Table 1
Determination of optimized conditions

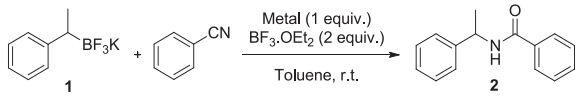


Entry	Benzonitrile mol %	$Cu(OAc)_2$ mol %	$BF_3{\cdot}OEt_2$ mol %	Yield[a] (%)
1	1000	100	—	0
2	1000	—	200	0
3	1000	10	20	25
4	1000	50	100	42
5	1000	10	200	15
6	1000	50	200	35
7	1000	100	200	70 (1 h)
8	Solvent 0.5 M	100	200	70 (10 min)[b]

[a] GC yield, internal standard heptadecane.
[b] Reaction was performed without toluene.

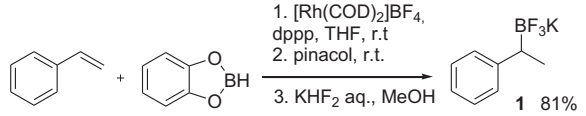
Based on results obtained in Table 2 the nature of the metallic species is important since a lower yield was observed when reactions were performed with iron acetate (Table 2, entry 4), manganese acetate (Table 2, entry 8) or cobalt acetate (Table 2, entry 9). Moreover the nature of the ligand seems to have an influence on the amide formation. Indeed less than 10% of desired product was obtained with chloride or acetylacetonate ligand (Table 2, entries 1, 2, 5, 6). When the expected transformation did not occur, the formation of 1-phenylethanol was identified. Best conditions were defined as following: $Cu(OAc)_2$ 1 equiv, $BF_3{\cdot}OEt_2$ 2 equiv, in 0.5 M of toluene with 10 equiv of nitrile. In order to study the scope and the limitation of this reaction, different potassium trifluoroborates salts were prepared according to the literature. More precisely, the preparation of compound **1** was realized as described by Crudden (Scheme 2).[15]

Table 2
Screening of different metals



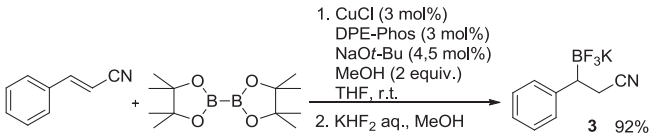
Entry	Metal[a]	Yield[b] (%)
1	$FeCl_2$	3
2	$FeCl_3$	—
3	$Fe(acac)_3$	12
4	$Fe(OAc)_2$	36
5	CuCl	11
6	$CuCl_2$	4
7	$Cu(OAc)_2$	70
8	$Mn(OAc)_2$	38
9	$Co(OAc)_2$	26
10	$Co(acac)_3$	—
11	$Ni(acac)_3$	19

[a] Conditions: potassium trifluoroborate salt (0.5 mmol), benzonitrile (5 mmol), metal (0.5 mmol), $BF_3{\cdot}OEt_2$ (1 mmol), toluene (1 mL), rt, 15 h.
[b] GC yield, internal standard heptadecane.



Scheme 2. Preparation of potassium 1-phenylethyltrifluoroborate.

In the case of cinnamic substrates, the boronic derivatives were prepared by the copper-catalyzed addition of bis(pinacolato) diboron on the conjugated double bond (Scheme 3).[16]



Scheme 3. Synthesis of compound **3**.

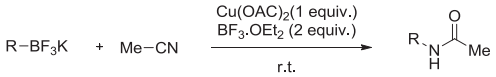
Finally, the Vedejs conditions[17] were applied on the commercial sources of boron derivatives to prepare potassium organotrifluoroborate salts **5**–**10**.

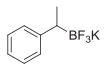
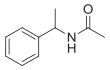
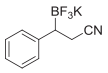
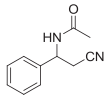
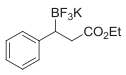
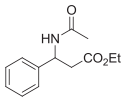
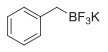
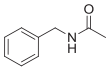
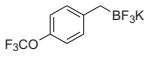
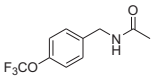
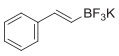
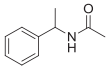
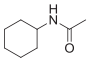
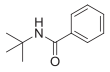
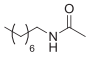
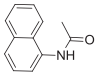
The optimized conditions for amidation were applied on the different homemade potassium organotrifluoroborate salts (Table 3). Acetonitrile was employed as nitrile source and solvent.

These conditions were efficient especially for *N*-(1-phenylethyl) acetamide **12**, which was isolated in 75% yield after 10 min of reaction (Table 3, entry 1).

Different benzylic trifluoroborate salts were studied and the corresponding amides were formed in 51–66% yields (Table 3, entries 2–5). In these conditions, trifluoroborate salts **2** and **3** were oxidized and afforded alcohols as by-products. In these particular cases, the purification was difficult because amides and alcohols exhibit similar retention factor values. For compound **3**, different conditions were tested in order to check the formation of the four membered-ring lactam, unfortunately this product was never detected. Primary benzylic potassium trifuoroborate salts afforded the expected amide with good isolated yield (Table 3 entries 4 and 5). Surprisingly, treatment of potassium *E*-vinyltrifluoroborate **7** with copper acetate and $BF_3{\cdot}OEt_2$ in acetonitrile gives the unexpected *N*-(1-phenylethyl)acetamide in 80% yield (Table 4, entry 6). The formation of this product is not in agreement with our mechanistic hypothesis. However, the monitoring of this reaction by GC–MS shows the formation of styrene during the reaction. This compound was then converted into amide by classical Ritter mechanism, due to the presence of an excess on $BF_3{\cdot}OEt_2$ in the reaction media. The formation of this product could be explained by the addition of nitrile on benzylic position following by the reduction of the C–B bond. Secondary alkylboronic derivatives seem to be less reactive since desired amide was isolated in 70% yield after 86 h of reaction (Table 3, entry 7). *tert*-Butyltrifluoroborate potassium salt treated in presence of benzonitrile leads to the corresponding amide **18** in 56% yields. The reactivity decreases considerably with primary alkylboronic derivatives. Indeed, potassium octyltrifluoroborate was reduced in alkane and expected amide was not observed (Table 3, entry 8). The same observation was done with potassium aryltrifluoroborate salts, the reduction of starting material was the only reaction (Table 3, entry 9).

Table 3
Reactivity of organotrifluoroborate salts

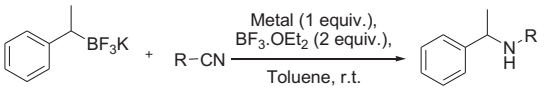


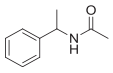
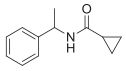
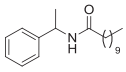
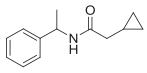
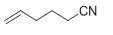
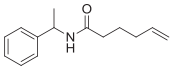
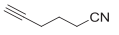
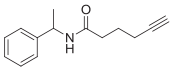
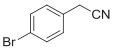
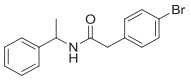
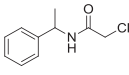
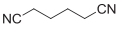
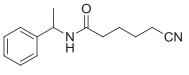
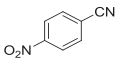
Entry	Substrates		Products		Isolated yield[a] (%)
1		**1**		**12**	75
2		**3**		**13**	(51)[b]
3		**4**		**14**	(66)[b]
4		**5**		**15**	61
5		**6**		**16**	66
6		**7**		**12**	80
7		**8**		**17**	70[c]
8		**9**		**18**	56
9		**10**		**19**	—
10		**11**		**20**	—

[a] Conditions: potassium trifluoroborate salt (1 mmol), acetonitrile (2 mL), $Cu(OAc)_2$ (1 mmol), $BF_3{\cdot}OEt_2$ (2 mmol), rt, 15 h.
[b] GC–MS yield.
[c] 86 h of reaction.

Later, different nitriles were engaged in this amide formation reaction with potassium 1-phenylethyltrifluoroborate **1**. As some nitriles studied were solids, the reaction was carried out in the presence of toluene as solvent. A series of primary alkylnitriles were tested and were found to be efficient partners for amide bond formation. The expected amides were isolated in good yields from 75 to 93%, in 1 h at room temperature (Table 4, entries 1–4). However, when the alkyl chain possesses a terminal alkene or alkyne, the isolated yields were lower and reached only 36 and 56%, respectively (Table 4, entries 5 and 6). In the latter case, no by-products from homo-coupling of alkyne were observed thus explaining the moderate yield. In the case of 4-bromoacetonitrile, the expected product **26** (Table 4, entry 7) was not detected, the only formed product comes from the reduction of the C–Br bond. Dinitrile substrates were also considered. If no reaction occurred with malonitrile, glutaronitrile afforded only the monoamide **27** with a moderate yield of 57%. Substituted aromatic nitriles were also studied and the presence of electron-withdrawing group or electron-donating group gave similar results (Table 4, entries 10–12). Moreover, in the case of 4-nitrobenzonitrile (Table 4, entry 10) a GC analysis revealed the formation 2,3-diphenylbutane

Table 4
Reactivity of different nitriles



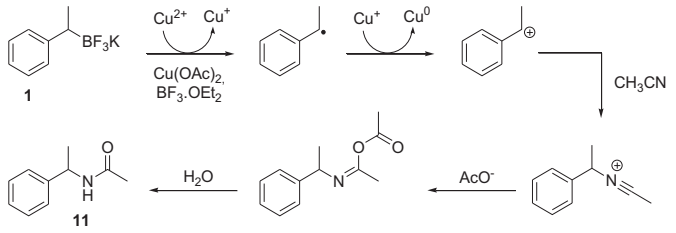
Entry	Substrates	Products		Isolated yield[a] (%)
1	H_3C–CN		**12**	75[b]
2			**21**	85[b]
3			**22**	93[b]
4			**23**	70[b]
5			**24**	36
6			**25**	56
7			**26**	—
8			**27**	—
9			**28**	57
10			**29**	51
11			**30**	53
12			**31**	53
13			**32**	57

[a] Conditions: potassium trifluoroborate salt (1 mmol), nitrile (10 mmol), $Cu(OAc)_2$ (1 mmol), $BF_3{\cdot}OEt_2$ (2 mmol), toluene (2 mL), rt15 h.
[b] 1 h of reaction.

(dimer) in a 1:1 ratio with expected amide. Finally, the amidation in the presence of cinnamonitrile was performed in 57% yield.

Based on the results summarized in the different tables, we were able to propose a mechanism (Scheme 4). While, in the literature, oxidative processes of boronic derivatives in presence of transition metal involve a radical intermediate,[18] these different results let us supposed that the mechanism can be compared to the Ritter reaction with the formation of a carbocation.

Indeed, we believe that the combination of boron trifluoride and copper acetate generates an oxidative complex, able to reverse the polarity of the C–B bond and form a carbocation, which react subsequently with the nucleophilic nitrogen atom of the nitriles. The corresponding amide is obtained after hydrolysis of the latter

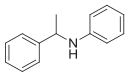
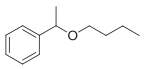
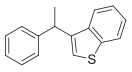
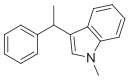
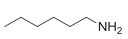
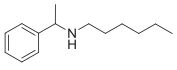
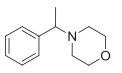
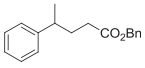
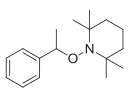


Scheme 4. Proposed mechanism for Ritter-type amidation.

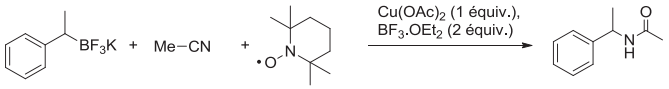
intermediate. We suppose that boron trifluoride removed acetate ligand to form a 'naked' copper II species, although the formation of a difluoroborane species can currently not be excluded.[17,19] Thus, this activated metal would be more reactive for redox reaction and generate copper metal. The formation of metallic copper is observed in the end of each effective reaction. Moreover, 1 equiv of copper II is necessary to reach high yields. In fact, when 0.5 equiv are used the yield do not exceed 42%. Furthermore, the formation of the carbocation intermediate is supported by the fact that the reaction did not occur with aryltrifluoroborate salts. Indeed, formation of carbocation on aryl is much disfavored.

From the proposed mechanism, other nucleophiles were engaged with compound **1** in the presence of copper acetate and boron trifluoride. Results are detailed in Table 5. Amines from aniline were prepared with a good yield of 86% (Table 5, entry 1). In the presence of 1-butanol the corresponding ether was isolated in 40% yield (Table 5, entry 2). Alkylation of benzo[*b*]thiophene should be performed in these conditions. However, in order to decrease the formation of by-products, which come from benzothiophene, only 2 equiv of this reagent were utilized in this case. When *N*-methylindole was used, the corresponding product was formed in a moderate yield. Finally, azides can be prepared by this methodology. From both trimethylsilylazide and sodium azide, good conversions can be reached. Surprisingly, when alkylamine were used as substrates, the desired products **38** and **39** were not obtained. When benzyl acrylate and TEMPO were used as nucleophile, the formation of the expected products was not observed. Moreover an experiment, where acetonitrile and TEMPO were in competition was carried on and only amide formation was observed (Scheme 5). These examples reinforce our hypothetical mechanism on the cationic character of this transformation.

Table 5
Reactivity of different nucleophiles

Entry	Substrates	Products		Yield[a] (%)
1			**33**	86
2			**34**	40
3			**35**	61[b]
4			**36**	35[c,d]
5	$TMSN_3$		**36**	83[c]
6	NaN_3		**37**	85[c]
7			**38**	—
8			**39**	—
9			**40**	—
10			**41**	—

[a] Conditions: potassium trifluoroborate salt (1 mmol), Nucleophile (10 equiv), $Cu(OAc)_2$ (1 mmol), $BF_3{\cdot}OEt_2$ (2 mmol), rt15 h.
[b] Only 2 equiv of benzothiophene were used for this reaction.
[c] Determined by GC–MS.
[d] Only 2 equiv of *N*-methylindole were used for this reaction.



Scheme 5. Determination of a radical intermediate.

3. Conclusion

As a conclusion, we have developed an efficient reaction in mild conditions for amidation of potassium alkyltrifluoroborate salts from nitriles and mediated by copper acetate and boron trifluoride. This transformation was realized at room temperature without the need of adding ligand for the copper. We supposed that the mechanism involves an oxidative nucleophilic substitution. The possible formation of a benzylic carbocation intermediate gives new possibility for the functionalization of boronic derivatives.

4. Experimental section

4.1. General

NMR spectra were recorded on either a Bruker DRX 300 operating at 300 MHz and 75 MHz for ^1H and ^{13}C acquisitions, respectively, or a Bruker DRX 400 operating at 400 MHz, 100 MHz, and 376 MHz for ^1H, ^{13}C, and ^{19}F acquisitions, respectively. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard. Data as reported as follows: s=singlet, d=doublet, t=triplet, q=quadruplet, m=multiplet, and br=broad, coupling constant in hertz, integration. High-resolution mass spectra were obtained on ThermoFinnigan MAT 95 XL spectrometers. Melting points are recorded on melting point apparatus Stuart SMT 10.

Copper acetate, boron trifluoride etherate (ca. 48% BF_3), nitriles and commercially available boronic derivatives (1-naphthalenb oronic acid, 1-octylboronic acid, cyclohexylboronic acid, *trans*-2-phenylvinylboronic acid, potassium benzyltrifluoroborate, 4-(trifluoromethoxy)benzylboronic acid pinacol ester) were purchased from Acros or Aldrich and used as received.

4.2. Synthesis of potassium trifluoroborate salts

*4.2.1. Potassium (1-phenylethyl)trifluoroborate [329976-80-9] (**1**).* In a 250 mL round-bottomed flask, under argon, $[Rh(cod)_2]BF_4$ (394 mg, 0.97 mmol) and dppb (481 mg, 1.17 mmol) were suspended in anhydrous and deoxygenated THF (75 mL). The suspension was stirred at room temperature until a homogeneous orange solution was obtained (10 min). Styrene (5.7 mL, 50.0 mmol)

was added to the reaction mixture and the resulting solution was stirred 10 min at room temperature. Then a solution of catecholborane (6.4 mL, 60.0 mmol) in 25 mL of THF was added dropwise. The reaction mixture was stirred overnight at room temperature. Pinacol (12.16 g, 102.90 mmol) was added rapidly in one batch, and the vessel was flushed with a vigorous flow of argon. The solution was stirred overnight at room temperature. The solvent was removed and the resulting crude was purified by flash chromatography (silica gel, cyclohexane/Et_2O: 95/5). To the solution of pinacol ester (40 mmol) in MeOH (100 mL) was added aqueous potassium hydrogen fluoride (50 mL, 4.5 M, 225 mmol). The resulting white slurry was stirred at room temperature for 30 min, concentrated in vacuo and dissolved in hot acetone. The mixture was filtered, the filtrate was concentrated in vacuo and the residue recrystallised from a minimal amount of ether, to afford 7.1 g (81% yield) of the corresponding potassium trifluoroborate salt as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.03 (m, 4H), 6.86 (m, 1H), 1.56 (br, 1H), 1.02 (d, J=9.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 152.2 (Cq), 127.6 (CH), 126.8 (CH), 122.3 (CH), 17.3 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −150.5. Mp (Et_2O) 206–207 °C.

*4.2.2. Potassium (3-ethoxy-3-oxo-1-phenylpropyl)trifluoroborate (**4**).* CuCl (30 mg, 0.3 mmol), NaO*t*-Bu (87 mg, 0.9 mmol), and DPEphos ligand (162 mg, 0.3 mmol) were placed in an oven-dried Schlenk tube and THF (8 mL) were added under argon. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (2.79 g, 11 mmol) and THF (6 mL) were added. The reaction mixture was stirred for 10 min and ethyl cinnamate (1.68 mL, 10 mmol) was added, followed by MeOH (1.62 mL, 40 mmol). The reaction tube was washed with THF (6 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The crude was purified by silica gel chromatography (cyclohexane/AcOEt: 95/5). To the solution of pinacol ester (1.0 g, 3.28 mmol) in MeOH (10 mL) was added aqueous potassium hydrogen fluoride (5 mL, 4.5 M, 22.5 mmol). The resulting white slurry was stirred at room temperature for 30 min, concentrated in vacuo and dissolved in hot acetone. The mixture was filtered, the filtrate was concentrated in vacuo and the residue recrystallised from a minimal amount of ether, to afford 0.73 mg (78% yield) of the corresponding potassium trifluoroborate salt as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.02 (m, 4H), 6.89 (m, 1H), 3.81 (q, J=7.0 Hz, 2H), 2.42 (m, 2H), 1.97 (br, 1H), 0.97 (t, J=7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 174.7 (Cq), 148.6 (Cq), 127.8 (2 CH), 126.8 (2 CH), 122.6 (CH), 58.6 (CH_2), 36.8 (CH_2), 14.1 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −143.5. Mp (Et_2O) 147–148 °C.

*4.2.3. Potassium (2-cyano-1-phenylethyl) trifluoroborate (**3**).* Using the same procedure, the title compound was isolated in 92% yield (1.61 g) ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.08 (m, 5H), 2.56 (m, 2H), 1.81 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 146.6 (Cq), 127.7 (2 CH), 127.2 (2 CH), 123.6 (CH), 122.5 (Cq), 19.1 (CH_2). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −144.3. Mp (Et_2O) 194–195 °C.

4.3. General procedure for preparation of potassium trifluoroborate salt

To a solution of boronic acid or pinacol ester (40 mmol) in methanol (100 mL) was added aqueous potassium hydrogen fluoride (50 mL, 4.5 M, 225 mmol). The resulting white slurry was stirred at room temperature for 30 min, concentrated in vacuo and dissolved in hot acetone. The mixture was filtered, the filtrate was concentrated in vacuo and the residue recrystallised from a minimal amount of ether, to afford the corresponding potassium trifluoroborate salt.

*4.3.1. Potassium (4-(trifluoromethoxy)benzyl)trifluoroborate [1201331-15-8] (**6**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.06 (d, J=8.3 Hz, 2H), 7.0 (d, J=8.3 Hz, 2H), 1.50 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 146.6 (Cq), 144.1 (Cq), 129.6 (2 CH), 120.6 (q, J_{C-F}=254.5 Hz, CF_3), 119.6 (2 CH). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −57.3 (CF_3), −137.5 (BF_3K). Mp (Et_2O) 173–175 °C (white solid).

*4.3.2. Potassium trans-styryltrifluoroborate [201852-49-5] (**7**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.29 (d, J=7.3 Hz, 2H), 7.24 (m, 2H), 7.10 (t, J=7.2 Hz, 2H), 6.46 (d, J=18.1 Hz, 1H), 6.17 (dt, J=18.1, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 140.3 (Cq), 133.2 (CH), 133.1 (CH), 128.3 (2 CH), 125.9 (CH), 125.4 (2 CH). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −138.2. Mp (Et_2O) >250 °C (white solid).

*4.3.3. Potassium cyclohexyltrifluoroborate[446065-11-8] (**8**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 1.55 (m, 3H), 1.47 (m, 2H), 1.03 (m, 3H), 0.88 (m, 2H), −0.02 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 28.9 (2 CH_2), 28.4 (2 CH_2), 27.7 (CH_2). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −145.5 (white foamy solid).

*4.3.4. Potassium octyltrifluoroborate [329976-79-6] (**9**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 1.12 (m, 12H), 0.85 (q, J=6.9 Hz, 3H), −0.07 (t, J=8.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 33.24 (CH_2), 31.5 (CH_2), 29.5 (CH_2), 28.9 (CH_2), 25.7 (CH_2), 25.6 (CH_2), 22.2 (CH_2), 14.0 (CH_3). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −137.2. Mp (Et_2O) >250 °C (white solid).

*4.3.5. Potassium (1-naphthalene)trifluoroborate[166328-07-0] (**10**).* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 8.38 (m, 1H), 7.72 (m, 1H), 7.76 (m, 1H), 7.71 (m, 1H), 7.31 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 136.7 (Cq), 133.1 (Cq), 130.3 (Cq), 128.7 (CH), 128.6 (CH), 127.5 (CH), 125.4 (CH), 125.0 (CH), 124.0 (CH), 123.5 (CH). ^{19}F NMR (376 MHz, DMSO-d_6): δ (ppm): −135.5. Mp (Et_2O) >250 °C (white solid).

4.4. General procedure for amide synthesis

To a solution of copper (II) acetate (180 mg, 1 mmol) and potassium organotrifluoroborate (1 mmol) in toluene (2 mL) was added nitrile (10 mmol). Boron trifluoride (in solution in ether, ca. 48% BF_3) was then added. The reaction media was stirred 15 h at room temperature. The reaction media was poured in 10 mL of water and extracted with ethyl acetate (3×5 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$, filtered, and concentrated under reduce pressure. The crude was purified by chromatography on silica gel.

*4.4.1. N-(1-Phenylethyl)benzamide (**2**) [3480-59-9].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.76–7.78 (m, 2H), 7.28–7.75 (m, 8H), 6.36 (br, 1H), 5.34 (q, J=7.1 Hz, 1H), 1.60 (d, J=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 166.7 (Cq), 134.7 (Cq), 143.2 (Cq), 131.6 (CH), 128.9 (2 CH), 128.7 (2 CH), 127.6 (CH), 127.0 (2 CH), 126.4 (2 CH), 49.3 (CH), 21.8 (CH_3). HRMS EI: calculated for $[C_{15}H_{15}NO]^{+\bullet}$=225,1154, found=225,1146. Mp (MeOH) 122–123 °C (yellow solid).

*4.4.2. N-(1-Phenylethyl)acetamide (**12**) [36065-27-7].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.27–7.32 (m, 5H), 5.80 (br, 1H), 5.51 (q, J=7.1 Hz, 1H), 1.47 (d, J=7.1 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 170.4 (Cq), 137.6 (Cq), 128.8 (2 CH), 127.5 (CH), 126.3 (2 CH), 48.9 (CH), 27.0 (CH_3), 23.5 (CH_3).

*4.4.3. N-Benzylacetamide (**15**) [588-46-5].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 720–7.28 (m, 5H), 6.15 (br, 1H), 4.34 (d, J=5.7 Hz, 2H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 170.2 (Cq), 138.3 (Cq), 128.7 (2 CH), 127.8 (2 CH), 127.5 (CH), 43.7 (CH_2), 23.2

(CH_3). HRMS EI: calculated for $[C_9H_{11}NO]^{+\bullet}$=149.0841, found=149.0838. Mp (MeOH) 61–62 °C (white crystal).

*4.4.4. N-(4-(Trifluoromethoxy)benzyl)acetamide (**16**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.28 (d, *J*=8.6 Hz, 2H), 7.16 (d, *J*=8.6 Hz, 2H), 6.04 (br, 1H), 4.40 (d, *J*=5.8 Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 170.2 (Cq), 148.6 (Cq), 137.2 (Cq), 129.3 (2 CH), 121.3 (2 CH), 120.6 (q, J_{C-F}=254.5 Hz, CF_3), 43.0 (CH_2), 23.3 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −58.4. HRMS EI: calculated for $[C_{10}H_{10}F_3NO_2]^{+\bullet}$=233.0664, found=233.0663. Mp (MeOH) 122–123 °C (white crystal).

*4.4.5. N-(Cyclohexyl)acetamide (**17**) [1124-53-4].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 5.61 (br, 1H), 3.73 (m, 1H), 1.88–1.93 (m, 4H), 1.54–1.71 (m, 3H), 1.03–1.37 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 169.4 (Cq), 48.5 (CH), 33.3 (2 CH_2), 25.6 (CH_2), 24.9 (2 CH_2), 23.6 (CH_3). HRMS EI: calculated for $[C_8H_{15}NO]^{+\bullet}$=141.1154, found=141.1147. (white foamy solid).

*4.4.6. N-(1-Phenylethyl)cyclopropanecarboxamide (**21**) [78172-92-6].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.19–7.28 (m, 5H), 5.94 (br, 1H), 5.08 (q, *J*=7.0 Hz, 1H), 1.42 (d, *J*=7.0 Hz, 2H), 1.19 (m, 1H), 0.90 (m, 2H), 0.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 172.7 (Cq), 143.5 (Cq), 128.7 (2 CH), 127.4 (CH), 126.3 (2 CH), 48.9 (CH), 21.9 (CH), 14.9 (CH_3), 7.2 (2 CH_2). HRMS EI: calculated for $[C_{12}H_{15}NO]^{+\bullet}$: 189,1154, found=189.1148. Mp (MeOH) 89–91 °C (white crystal).

*4.4.7. N-(1-Phenylethyl)dodecanamide (**22**) [560090-64-4].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.24–7.36 (m, 5H), 5.65 (br, 1H), 5.14 (q, *J*=7.1 Hz, 1H), 2.16 (t, *J*=7.6 Hz, 2H), 1.48 (d, *J*=7.1 Hz, 3H), 1.24 (m, 18H), 0.88 (t, *J*=6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 172.3 (Cq), 143.4 (Cq), 128.8 (2 CH), 127.5 (CH), 126.3 (2 CH), 48.7 (CH), 37.1 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 29.6 (2 CH_2), 29.5 (2 CH_2), 29.4 (CH_2), 25.9 (CH_2), 22.8 (CH_2), 21.8 (CH_3), 14.5 (CH_3). HRMS EI: calculated for $[C_{20}H_{33}NO]^{+\bullet}$=303.2562, found=303.2562. Mp (MeOH) 180 °C degradation (yellow solid).

*4.4.8. 2-Cyclopropyl-N-(1-phenylethyl)acetamide (**23**) [1201331-51-2].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.20–7.27 (m, 5H), 6.15 (br, 1H), 5.11 (q, *J*=7.2 Hz, 1H), 2.09 (d, *J*=7.1 Hz, 2H), 1.43 (d, *J*=7.2 Hz, 3H), 0.92 (m, 1H), 0.55 (m, 2H), 0.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 171.6 (Cq), 143.4 (Cq), 128.8 (2 CH), 127.4 (CH), 126.2 (2 CH), 48.6 (CH), 41.6 (CH_2), 22.0 (CH), 7.2 (CH_3), 4.7 (2 CH_2). HRMS EI: calculated for $[C_{13}H_{17}NO]^{+\bullet}$=203.1310 found=203.1307. Mp (MeOH) 80–82 °C (white crystal).

*4.4.9. N-(1-Phenylethyl)hex-5-enamide (**24**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.18–7.29 (m, 5H), 5.95 (br, 1H), 5.70 (m, 1H), 5.10 (m, 1H), 4.91 (m, 2H), 2.09 (t, *J*=7.8 Hz, 2H), 1.97 (m, 2H), 1.66 (m, 2H), 1.40 (d, *J*=7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 172.0 (Cq), 143.4 (Cq), 137.9 (CH), 128.7 (2 CH), 127.3 (CH), 126.2 (2 CH), 115.3 (CH), 48.6 (CH), 35.9 (CH_2), 33.2 (CH_2), 24.8 (CH_2), 21.8 (CH_3). HRMS CI: calculated for $[C_{14}H_{19}NO+H]^+$=218.1539, found=218.1528 (yellow oil).

*4.4.10. N-(1-Phenylethyl)hex-5-ynamide (**25**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.23–7.33 (m, 5H), 6.12 (br, 1H), 5.09 (q, *J*=6.9 Hz, 1H), 2.29 (t, *J*=7.3 Hz, 2H), 2.22 (m, 2H), 1.95 (t, *J*=2.6 Hz, 1H), 1.66 (m, 2H), 1.44 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 171.4 (Cq), 143.3 (Cq), 128.6 (2 CH), 127.3 (CH), 126.1 (2 CH), 83.6 (CH), 69.3 (CH), 48.7 (CH_2), 35.1 (CH_2), 24.2 (CH_2), 21.9 (CH), 17.8 (CH_2). HRMS CI: calculated for $[C_{14}H_{17}NO+H]^+$=216.1383, found=216.1367 (yellow oil).

*4.4.11. 5-Cyano-N-(1-phenylethyl)pentanamide (**28**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.29–7.36 (m, 5H), 5.80 (br, 1H), 5.11 (q, *J*=6.8 Hz, 1H), 2.34 (t, *J*=6.8 Hz, 2H), 2.22 (t, *J*=6.8 Hz, 2H), 1.66–1.80 (m, 4H), 1.48 (d, *J*=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 171.0 (Cq), 143.2 (Cq), 128.8 (2 CH), 127.6 (CH), 126.2 (2 CH), 119.7 (Cq), 48.9 (CH), 35.6 (CH_2), 24.9 (CH_2), 24.7 (CH_2), 21.9 (CH_3), 17.1 (CH_2) (yellow oil).

*4.4.12. Methyl 4-((1-phenylethyl)carbamoyl) benzoate (**30**) [925136-89-6].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.09 (d, *J*=8.5 Hz, 2H), 7.82 (d, *J*=8.5 Hz, 2H), 7.35 (m, 5H), 6.34 (br, 1H), 5.35 (q, *J*=6.9 Hz, 1H), 3.94 (s, 3H), 1.64 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 166.4 (Cq), 165.8 (Cq), 142.9 (Cq), 138.6 (Cq), 132.9 (Cq), 129.9 (2 CH), 128.9 (2 CH), 127.8 (CH), 127.1 (2 CH), 126.4 (2 CH), 52.5 (CH), 49.6 (CH_3), 21.7 (CH_3). EIMS *m*/*z* (% relative abundance): 283 (38), 268 (12), 163 (100), 135 (15), 120 (11), 104 (28), 103 (12), 77 (10). Mp (MeOH) 150–151 °C (yellow crystal).

*4.4.13. 4-Methyl-N-(1-phenylethyl)benzamide(**31**) [17537-45-0].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.66 (d, *J*=8.1 Hz, 2H), 7.20–7.40 (m, 7H), 6.30 (br, 1H), 5.32 (q, *J*=7.1 Hz, 1H), 2.38 (s, 3H), 1.60 (d, *J*=7.1 Hz, 3H). HRMS ESI: calculated for $[C_{16}H_{17}NO+H]^+$=240.1388, found=240.1390 (white solid).

*4.4.14. N-(1-Phenylethyl)cinnamamide (**32**) [1004997-26-5].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.56 (d, *J*=15.6 Hz, 1H), 7.38 (m, 2H), 7.23–7.29 (m, 7H), 7.18 (m, 1H), 6.35 (d, *J*=15.6 Hz, 1H), 6.01 (br, 1H), 5.21 (q, *J*=7.2 Hz, 1H), 1.48 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 165.1 (Cq), 143.2 (Cq), 141.3 (Cq), 134.9 (CH), 129.7 (CH), 128.9 (2 CH), 128.8 (2 CH), 127.9 (2 CH), 127.5 (CH), 126.4 (2 CH), 120.8 (CH), 49.0 (CH), 21.7 (CH_3). Mp (MeOH) 136–137 °C (yellow crystal).

*4.4.15. N-(1-Phenylethyl)aniline (**33**) [779-54-4].* ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.40 (m, 2H), 7.36 (m, 2H), 7.26 (m, 1H), 7.13 (t, *J*=7.8 Hz, 1H), 6.69 (t, *J*=7.3 Hz, 1H), 6.55 (d, *J*=7.8 Hz, 2H), 4.53 (q, *J*=6.8 Hz, 1H), 1.55 (d, *J*=6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 147.4 (Cq), 145.3 (Cq), 129.2 (2 CH), 128.7 (2 CH), 127.0 (2 CH), 122.9 (CH), 117.4 (CH), 113.4 (2 CH), 53.6 (CH), 25.1 (CH_3). EIMS *m*/*z* (% relative abundance): 197 (41), 183 (13), 182 (100), 105 (53), 104 (15), 93 (35), 79 (10), 77 (26), 51 (12) (colorless oil).

*4.4.16. (1-Butoxyethyl)benzene (**34**) [4157-77-1].* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.19–7.27 (m, 5H), 4.32 (q, *J*=6.3 Hz, 1H), 3.23 (t, *J*=6.6 Hz, 2H), 1.47 (m, 2H), 1.36 (d, *J*=6.3 Hz, 3H), 1.28 (m, 2H), 0.82 (t, *J*=7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 144.5 (Cq), 128.5 (2 CH), 127.4 (CH), 126.2 (2 CH), 78.0 (CH), 68.6 (CH_2), 39.2 (CH_2), 24.3 (CH_3), 19.5 (CH_2), 14.0 (CH_3). EIMS *m*/*z* (% relative abundance): 163 (71), 107 (100), 106 (23), 105 (82), 103 (12), 79 (41), 77 (24), 51 (15), 43 (21), 41 (25).

*4.4.17. 3-(1-Phenylethyl)benzo[b]thiophene (**35**) [114838-47-0].* ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 7.94 (d, *J*=6.55 Hz, 1H), 7.63 (s, 1H), 7.61 (m, 1H), 7.26–7.35 (m, 6H), 7.14 (m, 1H), 4.48 (q, *J*=7.2 Hz, 1H), 1.66 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 145.5 (Cq), 140.2 (Cq), 139.9 (Cq), 138.2 (Cq), 128.4 (2 CH), 127.1 (2 CH), 126.1 (CH), 124.2 (CH), 123.8 (CH), 122.9 (CH), 122.3 (CH), 121.9 (CH), 38.5 (CH), 22.3 (CH_3). EIMS *m*/*z* (% relative abundance): 238 (43), 224 (17), 223 (100), 222 (20), 221 (24) 178 (11).

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References and notes

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