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Synthesis of potassium and tetra *n*-butylammonium 2-substituted-1,3-dithianotrifluoroborate salts and addition to chiral cyclic *N*-acyliminium ions

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ABSTRACT

The synthesis of potassium 2-substituted-1,3-dithianotrifluoroborate salts and tetra-*n*-butyl ammonium derivatives is described. The reaction proceeds under mild reaction conditions and the corresponding products were obtained in moderate to good yields. The reactivity of these compounds in reactions with chiral cyclic *N*-acyliminium ions was evaluated.

1. Introduction

Carbon–carbon bond formation is a major focus of research in organic synthesis. Tools for making such bonds are indispensable for the construction of complex molecules and intense efforts are continuously directed toward developing novel and selective bond forming reactions. In the recent years, organoboron compounds have become one of the most popular organometallic reagents in the carbon–carbon bond formation chemistry.[1] The great applicability (in place of other organometallic reagents) is due to some features of the organoboron compounds; e.g., (1) compatibility with many functional groups; (2) availability of reagents via hydroboration and transmetallation; (3) low toxicity; (4) their ultimate degradation into the environmentally friendly boric acid and in addition (5) the handling and removal of boron-containing byproducts is easier when compared to other organometallic reagents.

The organoboron compounds more used are boronic acids and boronate esters, but these compounds have some drawbacks, among them we can mention the low stability, very high price of some reagents, and high sensitivity to air and moisture. To solve the problems those organoboron have been replaced by organotrifluoroborate salts.[2] These latter reagents are very stable to air and moisture, crystalline solids, easily prepared from inexpensive materials, and these compounds show a greater nucleophilicity compared with their boronic acids or boronate esters analogs.[2]

In 1965, Corey and Seebach introduced the use of 1,3-dithianes as important umpolung linchpins in organic synthesis.[3] This tactic for over 40 years has become a mainstay for the union of both simple and complex fragments.[4]

Among the most important features of these compounds is their stability under both acidic and basic conditions[5] and their potential utility in organic synthesis as acyl carbanion equivalents in carbon–carbon bond forming reactions.[3,6] A wide range of electrophiles, including alkyl halides, aldehydes, and epoxides, react smoothly with the derived acylanion equivalents.[7]

To the best of our knowledge only three papers in the literature describe the reaction of 2-lithio-1,3-dithianes with trialkylboranes[8] (R_3B) and trimethyl borates ($(RO)_3B$).[9]

N-Acyliminium ions[10] are very important in organic synthesis since they are reactive intermediates involved in the synthesis of many compounds with interesting biological properties. Nucleophilic additions to *N*-acyliminium ions constitute an important method to provide α-functionalized amino compounds and for the preparation of alkaloids and many other biologically active nitrogen heterocycles.[11]

2. Results and discussion

In connection with our research interest on the preparation and reactivity of potassium organotrifluoroborate salts, and their use as intermediates in organic synthesis,[9,11m,12] we wish to report here a general procedure to access various air-stable and storable potassium 2-organo-1,3-dithianotrifluoroborate salts readily available from the corresponding 1,3-dithiane reagents (Scheme 1).

We initially focused our attention on the optimization of the reaction conditions for the synthesis of the potassium 2-organo-1,3-dithianotrifluoroborate salts starting from the 2-methyl-1,3-dithiane **1a** (Table 1).

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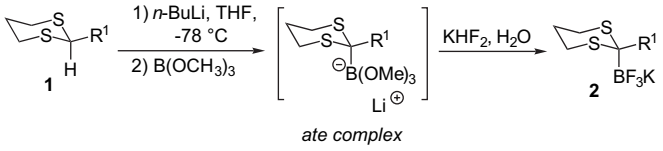


Scheme 1.

In a first test, the deprotonation of the corresponding 1,3-dithiane **1a** with 1.0 equiv of *n*-BuLi at −78 °C in THF was followed by reaction of the lithium salt intermediate with 1.2 equiv of $B(OCH_3)_3$. The transmetallation reaction was performed at −30 °C for 1 h and then 1 h at room temperature. The resulting 'ate complex' (Scheme 1), which could be detected as a singlet at δ 5.49 ppm in the ^{11}B NMR spectra, was reacted with saturated aqueous solution of KHF_2 at −20 °C for 1 h and then at room temperature for 1 h to afford the desired potassium 2-methyl-1,3-dithianotrifluoroborate salt **2a** in only 21% isolated yield (Table 1, entry 1).

A variety of reaction conditions were tested as shown in Table 1. Among the tested solvent systems, the use of THF and 1.0 equiv of HMPA as additive provided the best result and the desired product was yielded in 79% (Table 1, entry 5). The use of *t*-BuLi instead of *n*-BuLi did not increase the yield, and when the reaction was carried out in hexane in presence of TMEDA (1.0 equiv) no product was obtained (Table 1, entry 8).

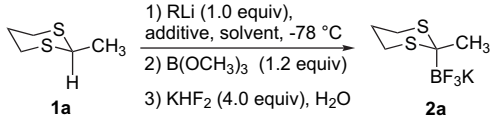
These optimized conditions were subsequently applied to the different 1,3-dithianes **1b**–**k** as outlined in Table 2. The reaction proceeded with satisfactory to good yields in most cases for alkyl, alkenyl, alkynyl, and silyl 1,3-dithianes (Table 2, entries 1–7). Despite the use of a fluorine source, 2-trimethylsilyl group remains intact (Table 2, entry 4).

However, much to our surprise, under these conditions the reaction proceeded in low yields when we used 2-aryl or 2-heteroaryl-1,3-dithianes, probably due to the less nucleophilic 2-lithium-2-aryl-1,3-dithiane intermediate in comparison to his aliphatic analog.

To improve the yields, different boron sources were examined (Table 3). The use of $BH_3{\cdot}S(CH_3)_2$ and $BF_3{\cdot}OEt_2$ provided the best results (Table 3, entries 4 and 5). Between these two options, we decided to use $BF_3{\cdot}OEt_2$, because it is less expensive and most environmentally friendly. Using this protocol, the corresponding products were obtained in moderated yields (Table 2, entries 8–11).

Although K^+ salts have been synthetically useful, they are insoluble in some organic media, and require polar solvents such as acetonitrile, acetone, methanol or water at elevated temperatures for dissolution.

Table 1
Search for the best reactions conditions



Entry	R–Li	Solvent	Additive	Yield[a] (%)
1	*n*-BuLi	THF	—	21
2	*n*-BuLi	THF	TMEDA	25
3	*n*-BuLi	THF	12-Crown-4	28
4	*n*-BuLi	THF	DMPU	37
5	*n*-BuLi	THF	HMPA	79
6	*n*-BuLi	Et_2O	—	7
7	*n*-BuLi	DME	—	10
8	*n*-BuLi	Hexane	TMEDA	n.r.
9	*t*-BuLi	THF	—	19

[a] Isolated yield after recrystallization from diethyl ether.

This problem can be solved by a simple counterion exchange reaction.[13] Therefore, the potassium 2-organo-1,3-dithianotrifluoroborates **2a**–**k** were submitted to a counterion exchange protocol with tetra-*n*-butylammonium hydroxide (TBAOH) affording the TBA derivatives **3a**–**k** (Table 2). As shown in Table 2, the products **3a**–**k** were obtained in very high yields (90–97%). In all cases further purification was unnecessary.

In order to test the potential use of the 2-organo-1,3-dithianotrifluoroborate salts as transfer of acyl group in the stereoselective synthesis of functionalized *N*-heterocycles via *N*-acyliminium ions, we performed the reaction of the 5-acetoxy-2-pyrrolidinone with various 2-organo-1,3-dithianotrifluoroborate salts, following the methodology recently developed by us.[11m] For this purpose, the *N*-benzyl-3,4,5-triacetoxy-2-pyrrolidinone **4** was treated with $BF_3{\cdot}Et_2O$ (4.0 equiv) in CH_2Cl_2 at −78 °C for 1 h to ensure in situ formation of the corresponding *N*-acyliminium ion. Next, potassium 1,3-dithianotrifluoroborate (1.2 equiv) was added and the reaction was allowed to warm to room temperature and stirred for 6 h and these results were summarized in Table 4.

The reaction proceeded with moderate to good yields and in good levels of diastereoselection in most cases. However, to our surprise no product was obtained when 2-aryl-1,3-dithianes were employed. We believe that the low reactivity of the compounds containing aryl groups was attributed to poor nucleophilicity of the carbon bonded to boron.

In order to demonstrate the efficiency of our methodology we carried out the reaction of 2-lithium-1,3-dithiane with *N*-acyliminium ion mediated by $BF_3{\cdot}OEt_2$. For this purpose, the 2-pyrrolidinone **4** was treated with $BF_3{\cdot}Et_2O$ (4.0 equiv) in CH_2Cl_2 at −78 °C for 1 h[11m] followed by addition of 2-lithium-1,3-dithiane[3b] and stirring at room temperature for 6 h. For our surprise, the compound **5b** was obtained in only 23% isolated yield in an 80:20 diastereoisomeric ratio in favor to the *anti*-isomer.

The stereochemistry of the newly created stereogenic center of **5b** was determined by ^1H NMR analysis of the crude mixture. The cis relative stereochemistry of the major product was established after analysis of the multiplicity and vicinal coupling constant of the hydrogen attached to the α-nitrogen (H-5) and then was extended to the other related compounds.

For the analogous 2-pyrrolidinones the vicinal coupling constant $^3J_{(H5-H4)}$ for the *syn*-isomer shows smaller value than the *anti*-isomer. These chemical correlations are in agreement with the major isomer obtained by us and the relative stereochemistry of the major isomer was assigned as being *syn*.[11m,14]

The compound **5b** (in a 70:30 mixture of *syn*/*anti* diastereomers) was submitted to thioketal hydrolysis using Dess–Martin periodinane (DMP) in $CH_3CN/CH_2Cl_2/H_2O$ according to methodology recently described by Panek and co-workers[15] (Scheme 2). By use of this protocol, the respective aldehyde was obtained in 78% yield.

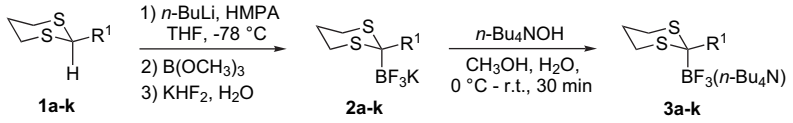
The crystal structure of potassium (1,3-dithian-2-yl)-2-*n*-butyl trifluoroborate salt is a representative for this class of compounds (Fig. 1). The compound **2e** was carefully recrystallized from dry methanol to afford the desired crystal.

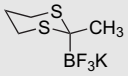
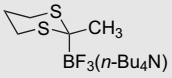
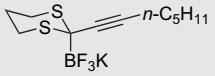
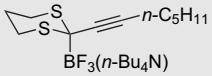
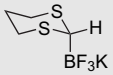
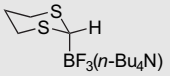
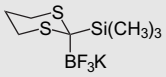
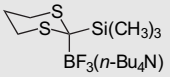
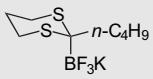
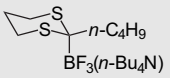
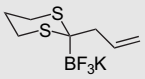
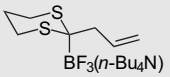
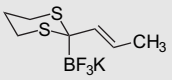
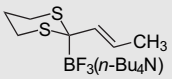
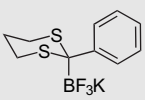
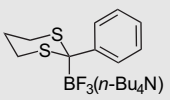
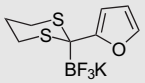
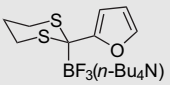
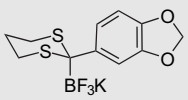
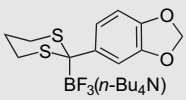
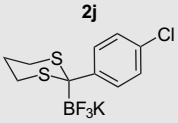
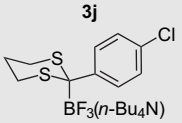
The compound crystallizes as discrete K^+ and $C_8H_{15}BF_3S_2^-$ moieties. The closest distance between a cation and an anion is K F_1 2.638(2) Å, which is between K and F_1. Each K^+ is surrounded by four anions making close contacts with four F atoms with distances ranging between 2.638(2) and 2.793(2) Å. There is a C–H···F intermolecular short contact: C6···F_{1i}=3.580(4), H6B···F_{1i}=2.67 Å, C6–H6B···F_{1i}=157° (i=1−x, 1−y, 1−z).

3. Conclusion

In summary, we have described the first synthesis of potassium- and tetra-*n*-butylammonium-2-organo-1,3-dithianotrifluoroborate

Table 2
Synthesis of potassium 2-substituted-1,3-dithianotrifluoroborate salts **2a**–**k** and their tetra-*n*-butyl ammonium derivatives **3a**–**k**

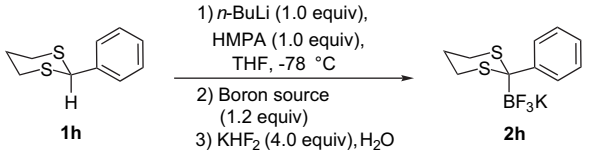


Entry	R^1	Product (**2a**–**k**)	Yield (%)	Product (**3a**–**k**)	Yield[c] (%)
1	CH_3	 **2a**	79[a]	 **3a**	92
2	n-$C_5H_{11}C{\equiv}C$	 **2b**	63[a]	 **3b**	90
3	H	 **2c**	83[a]	 **3c**	91
4	$Si(CH_3)_3$	 **2d**	75[a]	 **3d**	97
5	n-C_4H_9	 **2e**	58[a]	 **3e**	91
6	$H_2C{=}CHCH_2$	 **2f**	67[a]	 **3f**	95
7	(E)-$CH_3(H)C{=}CH$	 **2g**	41[a]	 **3g**	91
8	C_6H_5	 **2h**	13[a] 45[b]	 **3h**	95
9	2-furyl	 **2i**	8[a] 33[b]	 **3i**	97
10	3,4-$(CH_2)O_2C_6H_3$	 **2j**	11[a] 48[b]	 **3j**	91
11	4-Cl–C_6H_4	 **2k**	9[a] 37[b]	 **3k**	93

[a] Condition A: (i) *n*-BuLi (1.0 equiv), HMPA (1.0 equiv), THF, −78 °C, 1 h; (ii) $B(OMe)_3$ (1.2 equiv), −30 °C for 1 h, then 1 h at rt; (iii) KHF_2 (4.0 equiv), H_2O, −20 °C, 1 h then 1 h at rt.
[b] Condition B: (i) *n*-BuLi (1.0 equiv), HMPA (1.0 equiv), THF, −78 °C, 1 h. (ii) $BF_3{\cdot}OEt_2$ (1.2 equiv), −30 °C, 1 h, then 1 h at rt; (iii) KHF_2 (4.0 equiv), H_2O, −20 °C for 1 h and then 1 h at rt.
[c] Isolated yield after extraction.

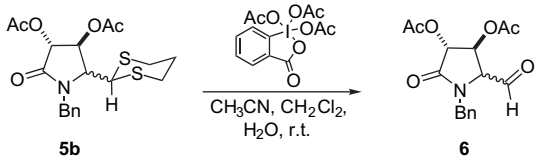
salts and this work represents an expansion in the chemistry of organotrifluoroborate salts. These compounds were obtained in moderate to good yields under very mild reaction conditions. We demonstrated that the obtained potassium 1,3-dithianotrifluoroborates salts have interesting synthetic properties as transfer of acyl group to *N*-acyliminium ions. Studies of the reactivity of these compounds in other kind of reactions are ongoing in our lab and will be reported in due course.

Table 3
Improved reaction conditions for aromatic derivatives



Entry	Boron source	Yield[a] (%)
1	$B(OCH_3)_3$	13
2	$B(O\text{-}i\text{-}Pr)_3$	15
3	$B(n\text{-}Bu)_4$	n.r.
4	$BH_3{\cdot}S(CH_3)_2$	44
5	$BF_3{\cdot}Et_2O$	45

[a] Isolated yield after recrystallization from diethyl ether.



Scheme 2.

4. Experimental

4.1. General

All air-sensitive and/or water-sensitive reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions. Standard syringe techniques were applied for transfer of dry solvents and some air-sensitive reagents and were introduced into reaction vessels through a rubber septum. The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light, 5% vanillin in 10% H_2SO_4 and heat as developing agents. Merck silica gel (particle size 0.040–0.063 mm) was used for flash chromatography. THF was distilled from sodium–benzophenone before use. CH_2Cl_2 was distilled from P_2O_5 and stored over MS 4 Å under atmosphere of dry nitrogen. NMR spectra were recorded with Bruker DPX 300 (300 MHz) instrument using DMSO-d_6, CD_3OD or $CDCl_3$ as solvent and calibrated using tetramethylsilane as internal standard. Chemical shifts are reported in δ ppm relative to $(CH_3)_4Si$ for ^1H and DMSO-d_6, CD_3OD or $CDCl_3$ for ^{13}C NMR. The ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). The ^{11}B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ (0.0 ppm), with a negative sign indicating an upfield shift. Coupling constants (J) are reported in hertz. Ratios of mixtures of diastereoisomers were determined by peak integration in the ^1H NMR spectra of the crude product. Infrared (IR) spectra were obtained from CH_3OH or $CHCl_3$ solutions, using a Varian 3100 FT-IR spectrophotometer and wavelengths are reported in cm^{-1}. Mass spectra (MS) were measured on a Shimadzu GCMS-QP5050A mass spectrometer. The HRMS spectra were measured on a Bruker Daltonics Micro TOF (direct inlet probe).

4.2. General procedure for the synthesis of potassium 2-substituted-1,3-dithianotrifluoroborate salts

A solution of 2-methyl-1,3-dithiane (1.34 g, 10 mmol, 1.0 equiv) in 20 mL of dry THF was cooled to −78 °C under nitrogen. *n*-BuLi (7.33 mL, 1.5 M in hexane, 10 mmol, 1.0 equiv) and HMPA (1.8 mL, 10 mmol, 1.0 equiv) were added dropwise, and the solution was stirred for 1 h at this temperature. $B(OCH_3)_3$ (12 mmol, 1.2 equiv) was then added dropwise at −78 °C. The solution was stirred at −30 °C for 1 h and at room temperature for another 1 h after which a saturated aqueous solution of potassium hydrogen difluoride (3.12 g, 40 mmol, 4.0 equiv) was added to the vigorously stirred solution. The resulting mixture was allowed to stir for 1 h at −20 °C, after which it was allowed to warm to room temperature for 1 h.

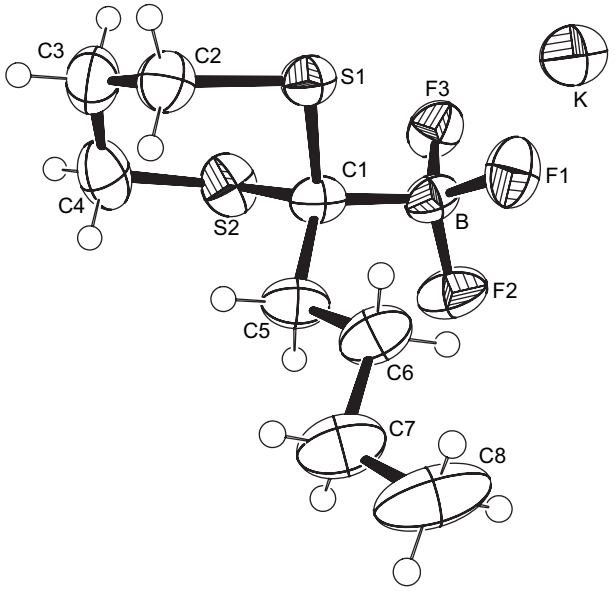
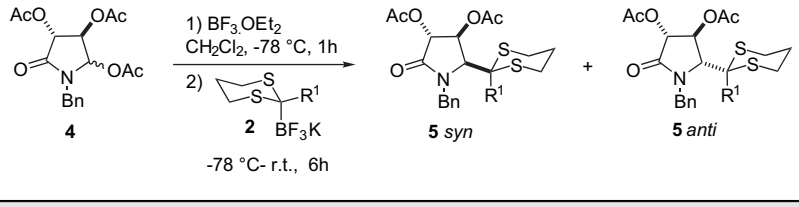


Figure 1. ORTEP depiction of the crystal structure of **2e**; $C_8H_{15}{\cdot}BF_3KS_2$, Mw=378.31, $P2_1/a$, a=10.218(1), b=10.2843(7), c=12.628(1) Å; β=108.835(4)°, R_{obs}=0.0553 for 2818 reflections and 136 refined parameters. C.C.D.C. number 686771.

Table 4
5-Substituted 2-pyrrolidinones **5a–e**



Entry	R^1	Product	Yield (%)	*syn*/*anti* Ratio[a]
1	CH_3	**5a**	68	80:20
2	H	**5b**	54	70:30
3	$n\text{-}C_4H_9$	**5c**	42	90:10
4	Me_3Si	**5d**	63	70:30
5	$H_2C{=}CHCH_2$	**5e**	51	90:10

[a] Ratios determined by ^1H NMR (300 MHz) integration of the hydrogen attached to the α-nitrogen carbon on the crude reaction mixture.

After this time, the solvent was removed under reduced pressure, and the resulting white solid was dried under high vacuum for 3 h to remove all water. The solid was then washed with hot acetone. The resulting organic solution was filtered, and the solvent was removed to afford a fluffy white solid. This solid was then dissolved in hot acetone and precipitated with diethyl ether, after which the solution was cooled to −20 °C to complete precipitation of the solid. The product **2a** was collected as a white crystalline solid (1.72 g, 79%).

*4.2.1. Potassium (1,3-dithian-2-yl)-2-methyl trifluoroborate (**2a**)*

Mp=241 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.91–3.00 (m, 2H), 2.56–2.63 (m, 2H), 1.83–2.01 (m, 2H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 30.7, 27.7, 25.1 (2C), 24.6; ^{19}F NMR (282 MHz, DMSO-d_6) δ −152.79 (q, J=50.5 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 4.67 (q, J=50.3 Hz). Anal. Calcd for $C_5H_9BF_3KS_2$: C, 25.01; H, 3.78. Found: C, 25.05; H, 3.66. LRMS m/z: 279 (M+K); IR (CH_3OH solution, cm^{-1}): 2978, 2907, 1411, 1241, 1049, 946.

*4.2.2. Potassium (1,3-dithian-2-yl)-2-(hept-1-ynyl) trifluoroborate (**2b**)*

Mp=261 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.00–3.07 (m, 1H), 2.78 (t, J=5.4 Hz, 2H), 2.35 (t, J=8.0 Hz, 1H), 1.79–1.88 (m, 2H), 1.45–1.67 (m, 1H), 1.09–1.32 (m, 5H), 0.91 (t, J=8.0 Hz, 2H), 0.82 (t, J=8.0 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 55.8, 44.6, 31.4, 27.9, 26.6, 25.9, 25.8 (2C), 24.8, 14.8, 14.5; ^{19}F NMR (282 MHz, DMSO-d_6) δ −151.55 (q, J=53.4 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 2.58 (q, J=51.0 Hz). Anal. Calcd for $C_{11}H_{17}BF_3KS_2$: C, 41.25; H, 5.35. Found: C, 40.94; H, 5.06. LRMS m/z: 359 (M+K); IR (CH_3OH solution, cm^{-1}): 2989, 2907, 2119, 1411, 1243, 1041, 935.

*4.2.3. Potassium (1,3-dithian-2-yl) trifluoroborate (**2c**)*

Mp=237 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.26 (t, J=3.0 Hz, 1H), 2.72–2.82 (m, 2H), 2.60 (dt, J=12.0, 3.0 Hz, 2H), 1.99–2.08 (m, 1H), 1.76–1.89 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 31.8, 31.6 (2C), 28.2; ^{19}F NMR (282 MHz, DMSO-d_6) δ −148.31 (q, J=50.7 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ −1.18 (q, J=50.8 Hz). Anal. Calcd for $C_4H_7BF_3KS_2$: C, 21.25; H, 3.12. Found: C, 21.28; H, 2.83. LRMS m/z: 265 (M+K); IR (CH_3OH solution, cm^{-1}): 2925, 2911, 1417, 1043, 909.

*4.2.4. Potassium (1,3-dithian-2-yl)-2-(trimethylsilyl) trifluoroborate (**2d**)*

Mp=283 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.11–3.23 (m, 2H), 2.21–2.78 (m, 2H), 1.70–1.89 (m, 2H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 27.4, 27.1 (2C), −1.4; ^{19}F NMR (282 MHz, DMSO-d_6) δ −136.78 (q, J=50.8 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 5.92 (q, J=49.3 Hz). Anal. Calcd for $C_7H_{15}BF_3KS_2Si$: C, 28.18; H, 5.07. Found: C, 28.09; H, 4.98. LRMS m/z: 337 (M+K); IR (CH_3OH solution, cm^{-1}): 2986, 2911, 1417, 1239, 1044, 944.

*4.2.5. Potassium (1,3-dithian-2-yl)-2-n-butyl trifluoroborate (**2e**)*

Mp=252 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.66–2.71 (m, 2H), 2.31–2.38 (m, 2H), 1.79–1.84 (m, 3H), 1.59–1.72 (m, 1H), 1.31–1.42 (m, 2H), 1.19 (sext, J=7.5 Hz, 2H), 0.83 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 35.9, 28.6, 26.3, 23.3 (2C), 23.1, 14.3; ^{19}F NMR (282 MHz, DMSO-d_6) δ −153.13 (q, J=53.5 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 4.10 (q, J=57.6 Hz). Anal. Calcd for $C_8H_{15}BF_3KS_2$: C, 34.04; H, 5.36. Found: C, 33.92; H, 5.16. LRMS m/z: 321 (M+K); IR (CH_3OH solution, cm^{-1}): 2987, 2912, 1419, 1238, 1043, 945.

*4.2.6. Potassium (1,3-dithian-2-yl)-2-allyl trifluoroborate (**2f**)*

Mp=225 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.89–6.03 (m, 1H), 4.88 (d, J=17.3 Hz, 1H), 4.76 (d, J=8.6 Hz, 1H), 2.65–2.78 (m, 4H), 2.32–2.40 (m, 2H), 1.82–1.86 (m, 1H); 1.72–1.74 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 139.0, 112.7, 40.7, 26.0, 23.2 (2C); ^{19}F NMR (282 MHz, DMSO-d_6) δ −152.59 (q, J=50.7 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 4.20 (q, J=56.2 Hz). Anal. Calcd for $C_7H_{11}BF_3KS_2$: C, 31.58; H, 4.17. Found: C, 31.47; H, 4.03. LRMS m/z: 305 (M+K); IR (CH_3OH solution, cm^{-1}): 2986, 2911, 1618, 1418, 1238, 1044, 944.

*4.2.7. Potassium (1,3-dithian-2-yl)-(E)-2-(prop-1-enyl) trifluoroborate (**2g**)*

Mp=259 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.90 (d, J=10.8 Hz, 1H), 2.56–2.83 (m, 4H), 1.90–2.12 (m, 2H), 1.51–1.60 (m, 1H), 0.76 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 149.0, 115.1, 31.0, 30.1, 26.3, 16.7; ^{19}F NMR (282 MHz, DMSO-d_6) δ −152.41 (q, J=52.5 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 4.31 (q, J=56.8 Hz). Anal. Calcd for $C_7H_{11}BF_3KS_2$: C, 31.58; H, 4.17. Found: C, 31.29; H, 3.85. LRMS m/z: 305 (M+K); IR (CH_3OH solution, cm^{-1}): 2981, 2915, 1639, 1420, 1239, 1047, 931.

*4.2.8. Potassium (1,3-dithian-2-yl)-2-phenyl trifluoroborate (**2h**)*

Mp=277 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.92–7.18 (m, 5H), 2.38–2.52 (m, 2H), 2.03–2.25 (m, 2H), 1.54 (t, J=6.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.3, 129.9 (2C), 127.3 (2C), 123.5, 27.8, 26.4, 25.3 (2C); ^{19}F NMR (282 MHz, DMSO-d_6) δ −149.59 (q, J=47.9 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 3.07 (q, J=47.6 Hz). Anal. Calcd for $C_{10}H_{11}BF_3KS_2$: C, 39.74; H, 3.67. Found: C, 39.55; H, 3.52. LRMS m/z: 341 (M+K); IR (CH_3OH solution, cm^{-1}): 2982, 2910, 2347, 1415, 1046, 944.

*4.2.9. Potassium (1,3-dithian-2-yl)-2-(2-furanyl) trifluoroborate (**2i**)*

Mp=271 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.43 (s, 1H), 6.31 (s, 1H), 6.14 (s, 1H), 2.67–2.77 (m, 2H), 2.31–2.38 (m, 2H), 1.82–1.93 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.6, 140.4, 110.4, 106.7, 26.4, 26.0 (2C); ^{19}F NMR (282 MHz, DMSO-d_6) δ −150.50 (q, J=49.3 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 3.51 (q, J=48.7 Hz). Anal. Calcd for $C_8H_9BF_3KOS_2$: C, 32.88; H, 3.10. Found: C, 32.73; H, 2.89. LRMS m/z: 331 (M+K); IR (CH_3OH solution, cm^{-1}): 2975, 2907, 1647, 1373, 1069, 904.

*4.2.10. Potassium (1,3-dithian-2-yl)-2-(3,4-methylenedioxy-phenyl) trifluoroborate (**2j**)*

Mp=268 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.24 (s, 1H), 7.19 (d, J=8.2 Hz, 1H), 6.63 (d, J=8.2 Hz, 1H), 5.82 (s, 2H), 2.34–2.44 (m, 2H), 2.15–2.20 (m, 2H), 1.62–1.72 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.9, 143.8, 140.5, 122.8, 110.6, 107.0, 100.7, 26.4, 25.3 (2C); ^{19}F NMR (282 MHz, DMSO-d_6) δ −148.90 (q, J=49.7 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 3.25 (q, J=53.4 Hz). Anal. Calcd for $C_{11}H_{11}BF_3KO_2S_2$: C, 38.16; H, 3.20. Found: C, 38.09; H, 3.11. LRMS m/z: 385 (M+K); IR (CH_3OH solution, cm^{-1}): 2989, 2923, 1419, 1230, 1045, 946.

*4.2.11. Potassium (1,3-dithian-2-yl)-2-(4-chloro-phenyl) trifluoroborate (**2k**)*

Mp=287 °C (decomp.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.81 (d, J=8.4 Hz, 2H), 7.24 (d, J=8.4 Hz, 2H), 2.27–2.52 (m, 4H), 1.69–1.81 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 145.4, 131.3 (2C), 127.8, 126.6 (2C), 25.8, 24.8 (2C); ^{19}F NMR (282 MHz, DMSO-d_6) δ −149.64 (q, J=54.8 Hz); ^{11}B NMR (96 MHz, DMSO-d_6) δ 3.39 (q, J=52.5 Hz). Anal. Calcd for $C_{10}H_{10}BClF_3KS_2$: C, 35.67; H, 2.99. Found: C, 35.59; H, 2.79. LRMS m/z: 375 (M+K); IR (CH_3OH solution, cm^{-1}): 2974, 2903, 1657, 1393, 1067, 880.

4.3. General procedure for preparation of tetra-*n*-butyl-ammonium 2-substituted-1,3-dithianotrifluoroborates salts (3)

A solution of potassium (1,3-dithian-2-yl)-2-methyl trifluoroborate **2a** (0.24 g, 1 mmol) in MeOH (3 mL) and water (3 mL)

was cooled to 0 °C and a solution of *n*-Bu_4NOH (0.74 mL, 1.50 M, 1.1 mmol) was slowly added over 5 min. The reaction was warmed to room temperature and stirred for 30 min. The reaction mixture was diluted with CH_2Cl_2 (10 mL), the layers separated, and the aqueous phase further extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo to afford 0.40 g of a colorless oil (92%, **3a**).

4.3.1. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-methyl trifluoroborate (**3a**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.22 (t, J=8.0 Hz, 8H), 2.89–2.98 (m, 2H), 2.63 (dt, J=13.6, 3.5 Hz, 2H), 1.86–1.95 (m, 2H), 1.69 (s, 3H), 1.48–1.60 (m, 8H), 1.40 (sext, J=8.0 Hz, 8H), 0.97 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.4 (4C), 29.6, 26.8, 24.5, 23.9 (4C), 19.6 (C), 13.6 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.13 (q, J=53.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.17 (q, J=51.9 Hz). Anal. Calcd for $C_{21}H_{45}BF_3NS_2$: C, 56.87; H, 10.23; N, 3.16. Found: C, 56.63; H, 9.94; N, 2.98. LRMS *m*/*z*: 201 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2979, 2902, 1428, 1043, 930.

4.3.2. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(hept-1-ynyl) trifluoroborate (**3b**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.26 (t, J=8.0 Hz, 8H), 2.79–2.83 (m, 2H), 2.41–2.54 (m, 4H), 1.84 (t, J=8.0 Hz, 2H), 1.55–1.65 (m, 8H), 1.44 (sext, J=8.0 Hz, 8H), 1.21–1.31 (m, 6H), 0.97 (t, J=8.0 Hz, 12H), 0.85 (t, J=8.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.6 (4C), 56.4, 45.3, 32.1, 28.6, 27.2, 26.5, 26.3 (2C), 25.4, 14.8, 14.6, 23.7 (4C), 19.6 (4C), 13.7 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −155.19 (q, J=61.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.20 (q, J=55.7 Hz). Anal. Calcd for $C_{27}H_{53}BF_3NS_2$: C, 61.93; H, 10.20; N, 2.67. Found: C, 61.64; H, 10.01; N, 2.46. LRMS *m*/*z*: 281 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2961, 2912, 1428, 1047, 934.

4.3.3. Tetra-n-butylammonium (1,3-dithian-2-yl) trifluoroborate (**3c**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.47 (s, 1H), 3.16 (t, J=8.0 Hz, 8H), 2.66–2.76 (m, 2H), 2.56 (dt, J=13.6, 3.5 Hz, 2H), 1.82–2.01 (m, 2H), 1.49–1.59 (m, 8H), 1.37 (sext, J=8.0 Hz, 8H), 0.92 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.3 (4C), 31.0 (2C), 27.2, 23.9 (4C), 19.6 (4C), 13.6 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −151.18 (q, J=54.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.50 (q, J=55.6 Hz). Anal. Calcd for $C_{20}H_{43}BF_3NS_2$: C, 55.93; H, 10.09; N, 3.26. Found: C, 55.73; H, 9.82; N, 3.05. LRMS *m*/*z*: 187 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2978, 2900, 1429, 1041, 920.

4.3.4. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(trimethylsilyl) trifluoroborate (**3d**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.24 (t, J=8.0 Hz, 8H), 2.74–2.86 (m, 2H), 2.33 (dt, J=13.6, 3.5 Hz, 2H), 1.80–2.05 (m, 2H), 1.56–1.66 (m, 8H), 1.42 (sext, J=8.0 Hz, 8H), 0.95 (t, J=8.0 Hz, 12H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.3 (4C), 30.8, 27.1, 26.4, 23.8 (4C), 19.5 (4C), 13.5 (4C), −1.75 (3C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −155.30 (q, J=61.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.12 (q, J=54.8 Hz). Anal. Calcd for $C_{23}H_{51}BF_3NS_2Si$: C, 55.06; H, 10.25; N, 2.79. Found: C, 54.77; H, 10.03; N, 2.65. LRMS *m*/*z*: 259 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2982, 2909, 1427, 1045, 936.

4.3.5. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(n-butyl) trifluoroborate (**3e**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (t, J=8.0 Hz, 8H), 2.85–2.94 (m, 2H), 2.62 (dt, J=13.6, 3.5 Hz, 2H), 1.92–2.06 (m, 4H), 1.54–1.68 (m, 10H), 1.45 (sext, J=8.0 Hz, 8H), 1.27–1.36 (m, 2H), 1.01 (t, J=8.0 Hz, 12H), 0.95 (t, J=8.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.5 (4C), 36.6, 28.9, 26.6, 24.3, 23.9, 23.7 (4C), 19.6 (4C), 14.3, 13.6 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −157.59 (q, J=62.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.03 (q, J=54.5 Hz). Anal. Calcd for $C_{24}H_{51}BF_3NS_2$: C, 59.36; H, 10.59; N, 2.88. Found: C, 59.11; H, 10.28; N, 2.67. LRMS *m*/*z*: 243 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2980, 2911, 1429, 1046, 935.

4.3.6. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-allyl trifluoroborate (**3f**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.15–6.28 (m, 1H), 5.02 (d, J=16.8 Hz, 1H), 4.93 (d, J=10.0 Hz, 1H), 3.26 (t, J=8.0 Hz, 8H), 2.86–2.94 (m, 3H), 2.63 (dt, J=13.6, 3.5 Hz, 3H), 1.93–1.96 (m, 2H), 1.58–1.69 (m, 8H), 1.39–1.51 (m, 8H), 1.01 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 112.7, 58.5 (4C), 40.7, 28.9, 26.6, 24.3, 23.7 (4C), 19.6 (4C), 13.6 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −158.50 (q, J=62.0 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.13 (q, J=55.5 Hz). Anal. Calcd for $C_{23}H_{47}BF_3NS_2$: C, 58.93; H, 10.09; N, 2.98. Found: C, 58.64; H, 9.80; N, 2.79. LRMS *m*/*z*: 227 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2981, 2918, 1428, 1047, 936.

4.3.7. Tetra-n-butylammonium (1,3-dithian-2-yl)-(E)-2-(prop-1-enyl) trifluoroborate (**3g**)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (d, J=10.8 Hz, 1H), 3.26 (t, J=8.0 Hz, 8H), 2.63–2.83 (m, 4H), 1.90–2.12 (m, 2H), 1.58–1.69 (m, 8H), 1.39–1.51 (m, 8H), 1.01 (t, J=8.0 Hz, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 115.2, 58.5 (4C), 31.1, 30.2, 26.6, 23.7 (4C), 19.6 (4C), 16.8, 13.6 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −156.30 (q, J=62.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.15 (q, J=55.6 Hz). Anal. Calcd for $C_{23}H_{47}BF_3NS_2$: C, 58.93; H, 10.09; N, 2.98. Found: C, 58.67; H, 9.86; N, 2.83. LRMS *m*/*z*: 227 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2982, 2911, 1428, 1047, 936.

4.3.8. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-phenyl trifluoroborate (**3h**)

Mp=109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J=8.0 Hz, 2H), 7.30 (t, J=8.0 Hz, 2H), 7.05 (t, J=8.0 Hz, 1H), 3.11 (t, J=8.0 Hz, 8H), 2.68–2.76 (m, 2H), 2.36 (dt, J=13.6, 3.5 Hz, 2H), 1.81–2.06 (m, 2H), 1.50–1.61 (m, 8H), 1.37–1.46 (m, 8H), 0.99 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4, 129.9 (2C), 127.5 (2C), 123.6, 58.4 (4C), 29.8, 27.1, 26.5, 23.8 (4C), 19.5 (4C), 13.5 (4C), ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.70 (q, J=60.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.09 (q, J=55.8 Hz). Anal. Calcd for $C_{26}H_{47}BF_3NS_2$: C, 61.76; H, 9.37; N, 2.77. Found: C, 61.50; H, 9.11; N, 2.64. LRMS *m*/*z*: 263 (M−TBA$^+$), IR ($CHCl_3$ solution, cm^{-1}): 2983, 2927, 1425, 1056, 939.

4.3.9. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(2-furanyl) trifluoroborate (**3i**)

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.40 (s, 1H), 6.32 (s, 1H), 3.20 (t, J=8.0 Hz, 8H), 2.92–3.01 (m, 2H), 2.44 (dt, J=13.6, 3.5 Hz, 2H), 1.97–2.05 (m, 2H), 1.55–1.65 (m, 8H), 1.37–1.49 (m, 8H), 1.00 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 140.5, 110.5, 106.8, 58.4 (4C), 30.6, 27.2, 26.5, 23.7 (4C), 19.6 (4C), 13.4 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −154.50 (q, J=60.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.23 (q, J=55.8 Hz). Anal. Calcd for $C_{24}H_{45}BF_3NOS_2$: C, 58.17; H, 9.15; N, 2.83. Found: C, 57.90; H, 8.86; N, 2.67. LRMS *m*/*z*: 253 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2989, 2929, 1426, 1059, 947.

4.3.10. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(3,4-methylenedioxy-phenyl) trifluoroborate (**3j**)

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.21 (d, J=8.2 Hz, 1H), 6.71 (d, J=8.2 Hz, 1H), 5.89 (s, 2H), 3.25 (t, J=8.0 Hz, 8H), 2.95–3.04 (m, 2H), 2.51 (dt, J=13.6, 3.5 Hz, 2H), 1.99–2.07 (m, 2H), 1.57–1.69 (m, 8H), 1.38–1.50 (m, 8H), 1.02 (t, J=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 143.9, 140.6, 122.9, 110.7, 107.1, 100.7, 58.4 (4C), 30.7, 27.3, 26.6, 23.8 (4C), 19.7 (4C), 13.5 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −153.60 (q, J=60.8 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.21 (q, J=54.8 Hz). Anal. Calcd for $C_{27}H_{47}BF_3NO_2S_2$: C, 59.00; H, 8.62; N, 2.55. Found: C, 58.72; H, 8.33; N, 2.43. LRMS

m/*z*: 307 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2945, 2926, 1423, 1059, 949.

4.3.11. Tetra-n-butylammonium (1,3-dithian-2-yl)-2-(4-chloro-phenyl) trifluoroborate (**3k**)

Mp=127 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J*=8.5 Hz, 2H), 7.18 (d, *J*=8.5 Hz, 2H), 3.07 (t, *J*=8.0 Hz, 8H), 2.62–2.70 (m, 2H), 2.34 (dt, *J*=13.6, 3.5 Hz, 2H), 1.75–2.02 (m, 2H), 1.48–1.56 (m, 8H), 1.34–1.44 (m, 8H), 0.97 (t, *J*=8.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 131.4 (2C), 127.9, 126.7 (2C), 58.4 (4C), 26.0, 25.8, 24.8 (2C), 23.8 (4C), 19.5 (4C), 13.5 (4C); ^{19}F NMR (282 MHz, $CDCl_3$) δ −155.70 (q, *J*=61.5 Hz); ^{11}B NMR (96 MHz, $CDCl_3$) δ 4.02 (q, *J*=54.8 Hz). Anal. Calcd for $C_{26}H_{46}BF_3NClS_2$: C, 57.83; H, 8.59; N, 2.59. Found: C, 57.54; H, 8.25; N, 2.41. LRMS *m*/*z*: 297 (M−TBA$^+$); IR ($CHCl_3$ solution, cm^{-1}): 2985, 2923, 1429, 1049, 944.

4.4. General procedure for the synthesis of 5-(2-organo-1,3-dithianyl)-2-pyrrolidinones (5a–e)

4.4.1. (3R,4R)-3,4-Diacetoxy-5-(2-methyl-1,3-dithianyl)-1-benzyl-2-pyrrolidinone (**5a**)

To a solution of the 5-acetoxy-2-pyrrolidinone **4** (349 mg, 1.0 mmol) in CH_2Cl_2 (4.0 mL) at −78 °C under nitrogen atmosphere was added dropwise the $BF_3{\cdot}Et_2O$ (0.50 mL, 4.0 mmol, 4.0 equiv). The reaction mixture was kept 1 h at −78 °C when potassium (2-methyl-1,3-dithianyl) trifluoroborate (**2a**) (288 mg, 1.2 mmol, 1.2 equiv) was added in one portion. After 1 h at −78 °C, the reaction mixture was stirred 6 h at room temperature when it was quenched with saturated $NaHCO_3$ (10 mL). The mixture was diluted with CH_2Cl_2 (20 mL), and the organic phase was washed with 10% HCl (10 mL), saturated $NaHCO_3$ (10 mL), and dried over $MgSO_4$. Evaporation under reduced pressure, followed by column chromatography on silica gel (20% ethyl acetate in hexanes) afforded **5a** in an 80:20 *syn*/*anti* mixture as a yellow oil, in 68% yield (287 mg). Both isomers have nearly the same R_f values and they could not be separated by column chromatography. The *syn*/*anti* ratio was determined to be 80:20 by the ^1H NMR (300 MHz) analysis of the crude product. Major isomer: *syn* **5a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.27–7.34 (m, 5H), 5.39 (d, *J*=4.8 Hz, 1H), 5.35 (dd, *J*=4.8, 4.8 Hz, 1H), 5.11 (d, *J*=15.0 Hz, 1H), 4.20 (d, *J*=15.0 Hz, 1H), 4.15 (d, *J*=4.8 Hz, 1H), 2.87–2.95 (m, 2H), 2.52–2.69 (m, 2H), 2.16 (s, 3H), 2.05 (s, 3H), 1.95 (s, 3H), 1.82–1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 169.9, 167.0, 134.9, 128.9, 128.4, 128.2, 75.5, 73.8, 64.8, 54.6, 43.9, 31.6, 29.2, 27.8, 24.2, 20.8, 20.6; IR ($CHCl_3$ solution, cm^{-1}): 3021, 2937, 1755, 1721, 1451. GC/MS *m*/*z* (%): 423 (2) [M$^+$], 309 (10), 290 (24), 230 (28), 188 (63), 160 (13), 133 (17), 106 (15), 91 (100), 65 (11), 43 (45). HRMS (ESI, positive) *m*/*z* calcd for $C_{20}H_{25}NO_5S_2$: 424.1253 ([M+H]$^+$); found: 424.1241 ([M+H]$^+$). Minor isomer: *anti* **5a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.27–7.34 (m, 5H), 5.56 (d, *J*=8.0 Hz, 1H), 5.30 (dd, *J*=8.0, 8.0 Hz, 1H), 5.08 (d, *J*=15.0 Hz, 1H), 4.72 (d, *J*=8.0 Hz, 1H), 4.05 (d, *J*=15.0 Hz, 1H), 2.87–2.95 (m, 2H), 2.52–2.69 (m, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.94 (s, 3H), 1.82–1.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 169.7, 165.8, 134.4, 128.8, 128.3, 128.0, 75.4, 72.7, 64.0, 53.8, 43.7, 31.4, 29.0, 27.6, 24.0, 20.7, 20.5.

4.4.2. (3R,4R)-3,4-Diacetoxy-5-(1,3-dithianyl)-1-benzyl-2-pyrrolidinone (**5b**)

The product **5b** was prepared as described in the general procedure and was obtained in a 70:30 *syn*/*anti* mixture as a colorless oil in 54% yield (220 mg). Major isomer: *syn* **5b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.54 (m, 5H), 5.42 (d, *J*=4.9 Hz, 1H), 5.38 (dd, *J*=4.9, 4.9 Hz, 1H), 5.14 (d, *J*=15.0 Hz, 1H), 4.52 (dd, *J*=4.9, 4.3 Hz, 1H), 4.32 (d, *J*=15.0 Hz, 1H), 4.23 (d, *J*=4.3 Hz, 1H), 2.73–3.12 (m, 2H), 2.56–2.69 (m, 2H), 2.19 (s, 3H), 2.10 (s, 3H), 1.85–1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 168.5, 167.1, 134.7, 128.7, 128.5, 128.2, 75.4, 73.6, 64.3, 54.3, 43.7, 31.7, 29.7, 27.1, 20.6, 20.4; IR ($CHCl_3$ solution, cm^{-1}): 3020, 2933, 1759, 1725, 1457. GC/MS *m*/*z* (%): 409 (1) [M$^+$], 318 (15), 290 (35), 119 (12), 106 (21), 91 (100), 43 (78). HRMS (ESI, positive) *m*/*z* calcd for $C_{19}H_{23}NO_5S_2$: 410.1096 ([M+H]$^+$); found: 410.1141 ([M+H]$^+$). Minor isomer: *anti* **5b**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.54 (m, 5H), 5.58 (d, *J*=8.2 Hz, 1H), 5.32 (dd, *J*=8.2, 8.2 Hz, 1H), 5.05 (d, *J*=15.0 Hz, 1H), 4.55 (dd, *J*=8.2, 4.1 Hz, 1H), 4.35 (d, *J*=15.0 Hz, 1H), 4.27 (d, *J*=4.1 Hz, 1H), 2.73–3.12 (m, 2H), 2.56–2.69 (m, 2H), 1.85–1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 168.3, 166.9, 134.6, 128.6, 128.5, 128.3, 75.3, 73.5, 64.1, 54.2, 43.5, 31.4, 29.6, 27.0, 20.5, 20.3.

4.4.3. (3R,4R)-3,4-Diacetoxy-5-(2-n-butyl-1,3-dithianyl)-1-benzyl-2-pyrrolidinone (**5c**)

The product **5c** was prepared as described in the general procedure and was obtained in a 90:10 *syn*/*anti* mixture as a colorless oil in 42% yield (195 mg). Major isomer: *syn* **5c**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.29–7.46 (m, 5H), 5.41 (d, *J*=5.0 Hz, 1H), 5.33 (dd, *J*=5.0, 5.0 Hz, 1H), 5.08 (d, *J*=14.5 Hz, 1H), 4.16 (d, *J*=14.5 Hz, 1H), 4.06 (d, *J*=5.0 Hz, 1H), 2.88–2.96 (m, 2H), 2.50–2.65 (m, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 1.96 (t, *J*=7.1 Hz, 2H), 1.80–1.89 (m, 2H), 1.29–1.38 (m, 4H), 0.91 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.3, 168.5, 135.2, 128.8, 128.5, 128.3, 75.6, 73.7, 64.7, 54.5, 43.7, 31.5, 29.3, 27.9, 26.6, 24.2, 23.1, 20.8, 20.6, 14.6; IR ($CHCl_3$ solution, cm^{-1}): 3025, 2935, 1751, 1720, 1229. GC/MS *m*/*z* (%): 465 (2) [M$^+$], 375 (12), 332 (23), 290 (17), 175 (10), 106 (19), 91 (100), 43 (71). HRMS (ESI, positive) *m*/*z* calcd for $C_{23}H_{31}NO_5S_2$: 466.1722 ([M+H]$^+$); found: 466.1751 ([M+H]$^+$). Minor isomer: *anti* **5c**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.29–7.46 (m, 5H), 5.51 (d, *J*=8.2 Hz, 1H), 5.30 (dd, *J*=8.2, 8.2 Hz, 1H), 5.03 (d, *J*=14.8 Hz, 1H), 4.10 (d, *J*=14.8 Hz, 1H), 4.01 (d, *J*=8.2 Hz, 1H), 2.88–2.96 (m, 2H), 2.50–2.65 (m, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 1.96 (t, *J*=7.1 Hz, 2H), 1.80–1.89 (m, 2H), 1.29–1.38 (m, 4H), 0.91 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1, 168.4, 135.1, 128.8, 128.5, 128.3, 75.3, 73.5, 64.4, 54.2, 43.5, 31.4, 29.3, 27.9, 26.6, 24.2, 23.1, 20.8, 20.6, 14.6.

4.4.4. (3R,4R)-3,4-Diacetoxy-5-(2-trimethylsilyl-1,3-dithianyl)-1-benzyl-2-pyrrolidinone (**5d**)

The product **5d** was prepared as described in the general procedure and was obtained in a 70:30 *syn*/*anti* mixture as a colorless oil in 63% yield (303 mg). Major isomer: *syn* **5d**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.26–7.35 (m, 5H), 5.38 (d, *J*=4.7 Hz, 1H), 5.34 (dd, *J*=4.7, 4.7 Hz, 1H), 5.10 (d, *J*=15.2 Hz, 1H), 4.18 (d, *J*=15.2 Hz, 1H), 4.14 (d, *J*=4.7 Hz, 1H), 2.88–2.97 (m, 2H), 2.53–2.70 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 1.83–1.93 (m, 2H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.5, 167.3, 134.7, 128.6, 128.5, 128.1, 75.1, 73.3, 62.6, 51.8, 43.7, 31.5, 29.3, 27.5, 20.9, 20.5, 1.3; IR ($CHCl_3$ solution, cm^{-1}): 3021, 2937, 1750, 1724. GC/MS *m*/*z* (%): 481 (1) [M$^+$], 390 (21), 347 (15), 290 (24), 106 (13), 91 (100), 43 (75). HRMS (ESI, positive) *m*/*z* calcd for $C_{22}H_{31}NO_5S_2Si$: 482.1491 ([M+H]$^+$); found: 482.1536 ([M+H]$^+$). Minor isomer: *anti* **5d**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.26–7.35 (m, 5H), 5.55 (d, *J*=8.3 Hz, 1H), 5.29 (dd, *J*=8.3, 8.3 Hz, 1H), 5.07 (d, *J*=14.7 Hz, 1H), 4.14 (d, *J*=14.7 Hz, 1H), 4.03 (d, *J*=8.3 Hz, 1H), 2.86–2.93 (m, 2H), 2.51–2.68 (m, 2H), 2.14 (s, 3H), 2.06 (s, 3H), 1.83–1.93 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 169.4, 167.2, 134.6, 128.6, 128.5, 128.0, 74.8, 73.2, 62.5, 51.6, 43.6, 31.4, 29.3, 27.5, 20.8, 20.4, 1.3.

4.4.5. (3R,4R)-3,4-Diacetoxy-5-(2-allyl-1,3-dithianyl)-1-benzyl-2-pyrrolidinone (**5e**)

The product **5e** was prepared as described in the general procedure and was obtained in a 90:10 *syn*/*anti* mixture as a colorless oil in 51% yield (229 mg). Major isomer: *syn* **5e**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.35 (m, 5H), 5.73–5.91 (m, 1H), 5.40 (d, *J*=4.9 Hz, 1H), 5.30 (dd, *J*=17.3, 1.5 Hz, 1H), 5.26 (dd, *J*=4.9, 4.9 Hz, 1H), 5.22 (dd, *J*=10.0, 1.5 Hz), 5.10 (d, *J*=15.1 Hz, 1H), 4.23 (d, *J*=15.1 Hz, 1H), 4.12 (d, *J*=4.9 Hz, 1H), 2.87–2.95 (m, 2H), 2.75 (d, *J*=5.7 Hz, 2H),

2.51–2.68 (m, 2H), 2.15 (s, 3H), 2.09 (s, 3H), 1.83–1.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 169.8, 167.3, 135.3, 134.8, 128.8, 128.3, 128.2, 118.1, 75.3, 73.4, 63.8, 54.1, 43.9, 34.7, 29.2, 27.8, 24.2, 20.8, 20.6; IR ($CHCl_3$ solution, cm^{-1}): 3036, 2939, 1750, 1707. GC/MS *m*/*z* (%): 449 (2) [M^+], 408 (24), 358 (15), 290 (25), 159 (12), 91 (100), 43 (67), 41 (35). HRMS (ESI, positive) *m*/*z* calcd for $C_{22}H_{27}NO_5S_2$: 450.1409 ([M+H]$^+$); found: 450.1396 ([M+H]$^+$). Minor isomer: *anti* **5e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.35 (m, 5H), 5.73–5.91 (m, 1H), 5.51 (d, *J*=8.1 Hz), 5.30 (dd, *J*=17.3, 1.5 Hz, 1H), 5.15 (dd, *J*=8.1, 8.1 Hz, 1H), 5.22 (dd, *J*=10.0, 1.5 Hz), 5.05 (d, *J*=15.1 Hz, 1H), 4.19 (d, *J*=15.1 Hz, 1H), 4.08 (d, *J*=8.1 Hz, 1H), 2.87–2.95 (m, 2H), 2.75 (d, *J*=5.7 Hz, 2H), 2.51–2.68 (m, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 1.83–1.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 169.6, 167.1, 135.2, 134.5, 128.8, 128.2, 128.0, 118.1, 75.1, 73.3, 63.6, 54.0, 43.7, 34.5, 29.1, 27.8, 24.2, 20.7, 20.4.

4.5. Procedure for the thioketal hydrolysis of 5-(1,3-dithianyl)-2-pyrrolidinone 5b[15]

*4.5.1. (3R,4R)-3,4-Diacetoxy-5-formyl-1-benzyl-2-pyrrolidinone (**6**)*

To a solution of the compound **5b** (205 mg, 0.5 mmol) in 2.5 mL of 8:1:1 $CH_3CN/CH_2Cl_2/H_2O$ (0.2 M) was added 424 mg of Dess–Martin periodinane (1.0 mmol) in one portion. The reaction mixture was stirred at room temperature, exposed to air, for 2 h until complete consumption of starting material as observed by TLC. The reaction was quenched with 20 mL of 50% aqueous $NaHCO_3$. The layers were separated and the aqueous layer was extracted 3× into 50 mL of CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by flash chromatography (silica, 10% EtOAc/hexanes) affords the desired aldehyde **6** as a colorless oil in 78% yield (124 mg). Major isomer: *syn* **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (d, *J*=3.2 Hz, 1H), 7.21–7.43 (m, 5H), 5.48 (d, *J*=5.1 Hz, 1H), 5.21 (dd, *J*=5.1, 5.1 Hz, 1H), 5.10 (d, *J*=14.8 Hz, 1H), 4.72 (dd, *J*=5.1, 3.2 Hz, 1H), 4.42 (d, *J*=14.8 Hz, 1H), 2.15 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 170.3, 169.6, 167.5, 134.9, 128.8, 128.6, 128.3, 76.2, 74.1, 67.5, 45.2, 21.3, 21.1; IR ($CHCl_3$ solution, cm^{-1}): 3029, 2935, 2861, 2765, 1741, 1725, 1703. GC/MS *m*/*z* (%): 319 (2) [M^+], 276 (31), 228 (23), 91, (100), 43 (72). HRMS (ESI, positive) *m*/*z* calcd for $C_{16}H_{17}NO_6$: 320.1134 ([M+H]$^+$); found: 320.1201 ([M+H]$^+$).

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