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The Facile and Direct Formylation of Organoboron Aromatic Compounds with Benzodithiolylium Tetrafluoroborate

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Organoboron compounds can be used to effect a direct formylation in the absence of transition metals. We report that the direct reaction between boronic derivatives and benzodithiolylium tetrafluoroborate, a commercially available carbenium ionic compound, is possible and provides access to many interesting compounds without the use of transition metals. The direct reaction of the carbenium ion with boronic derivatives results in the formation of substituted arylcarbenium ions, a number of which can be further utilized in materials chemistry or for the direct transformation into other compounds. In addition to the rich chameleonic chemical nature of the benzodithiol intermediate, such species can also undergo a metallation reaction and subsequent treatment with a wide range of electrophiles to access a variety of functional groups (aldehyde, ketone, acid, and alkyl groups).

Introduction

The transition-metal-catalyzed addition of organoboron compounds to electrophilic C=X double bonds (X = N, O, and C) has traditionally been one of the most important methods for the construction of C–C bonds.[1] Aryl and alkenyltrifluoroborates as well as trialkoxyborates have been used in the absence of transition metals,[2] whereas arylboronic acids and arylboronates are commonly used in the presence of Lewis base additives.[3] The formation of boron ate complexes and their successive reaction with carbon electrophiles such as iminium ions, Michael acceptors, and stabilized carbocations have been recently explored.[4] To quantify the nucleophilicity of arylboron compounds and further explore the scope and limitations of organoboron reagents in transition-metal-free carbon–carbon bond forming reactions, Mayr and Knochel have recently applied the benzhydrylium methodology to create a nucleophilicity scale for these compounds.[5] Their results have confirmed that the experimentally determined nucleophilicity values of organoboron compounds are between those of organolithium and organosilicon compounds. A particularly interesting feature of this study was the establishment of new nucleophilicity parameters to design transition-metal-free C–C bond forming reactions. Using the rule of thumb for nucleophile-electrophile combinations,[6] a reaction between an electrophile (E) and a suitable nucleophile (N) may take a place at room temperature when E-N > –5 (for s_N = 1 and 1 M concentration of both reagents to afford a 50% conversion after 24 h at 20 °C). On the basis of the measured range of the nucleophilicity parameters for organoboron reagents, Mayr highlighted the possible scope of organoboron compounds in new, reasonably tolerant, and functional-group-compatible organic transformations, which avoided the use of transition metals.[7]

Recently, we explored the reactivity of commercially available and stable 1,3-benzodithiolylium tetrafluoroborate (**1**)[8] in organocatalytic reactions.[9] The benzodithiolyl group introduced by an organocatalytic strategy is chameleonic in nature and can be used to generate its anionic or cationic equivalent. It can also be easily removed by Raney nickel or transformed into a carbonyl or acid group. By introducing the benzodithiolyl group in an organocatalytic fashion and the successive treatment with Raney nickel, a formal stereoselective α-methyl alkylation of aldehydes was achieved, and this strategy was successfully applied to the total syntheses of natural products.[10] With the favorable stability and reactivity of the benzodithiolyl group, we asked ourselves whether **1** could be used in the formylation of organoboron reagents, that is, in a direct reaction realized without any transition metal. The resulting substrates are potentially useful intermediates, which could then allow the direct transformation of boron reagents into other compounds. In this report, we describe a full account of our findings.

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Results and Discussion

Although transition-metal-free carbon–carbon bond forming reactions between organoboronates as the nucleophilic partner and a stabilized carbenium ion are not well established in the literature, they are potentially of great interest to industry and academia. The Mayr scale[11] and its relations provide a basis to combine an element of systematic rational design with the chemical intuition that has guided previous efforts in this area of organic synthesis (see Figure 1). The activation of the BF_3K group is sufficient for the organocatalytic Friedel–Crafts alkylation of α,β-unsaturated iminium ions ($-10 < E < -5$, E = electrophilicity according to Mayr[6b]), as described by MacMillan.[12] With a wide range of nucleophilic boronate compounds from which to choose and a quantitative correlation to govern their reactivity in hand, the problem remains to select a suitably versatile electrophilic partner.

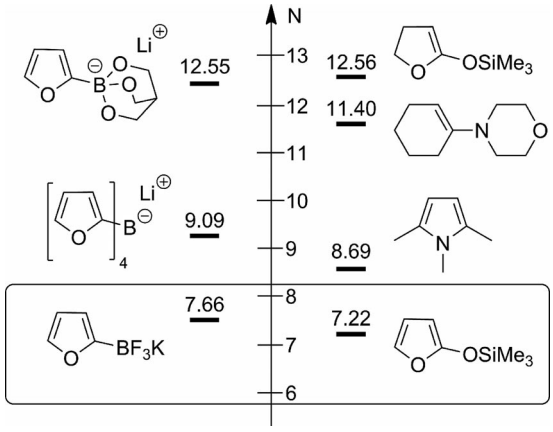
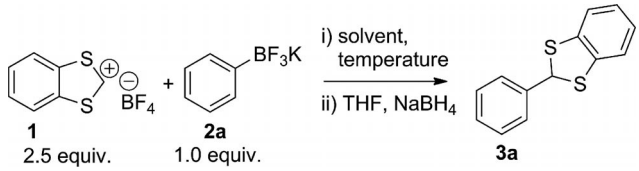


Figure 1. The nucleophilicity of boronic derivatives according to Mayr scale rationalization.

We have reported on other highly enantioselective α-alkylations of aldehydes that have resulted from a carbenium ion,[13] but benzodithiolylium **1** has a number of particularly striking applications in the rapidly evolving field of organocatalysis.[9,10] The stability of **1** along with the possibility of the benzodithiol to undergo a metallation followed by treatment with an alkylating agent and then with Raney Nickel for the simple elimination of this group prompted us to investigate the reactivity of **1** with a range of organoboron reagents. As the electrophilicity of **1** falls in a range (i.e., $-4 < E < -3$), we examined its reactivity in the presence of a number of functionalized aryltrifluoroborate salts. From inspection of the Mayr nucleophilicity parameters that are published for organoboron reagents,[5] the aryltrifluoroborate salts exhibit moderate nucleophilicity (see Figure 1). However, the more nucleophilic boron ate complexes were not suitable for the carbenium ion, as the alcohol that is in equilibrium with the ate complex is presumed to intercept the carbenium ion. The desired compounds were obtained after the reduction of the carbenium ion intermediate by treatment with $NaBH_4$ (see Scheme 1). Because of the easy access to compound **1**, the procedure to optimize this reaction was conducted with 2.5 equiv. of this electrophile. The results for the process of screening the solvent are shown in Table 1. Using acetonitrile resulted in a significantly higher conversion in comparison to the other solvents tested, for example, dichloroethane (DCE), toluene, and dioxane. No trace amounts of the product were identified when *N*,*N*-dimethylformamide (DMF) was used. In addition, the conversion in each of the examined solvents did not increase as the reaction temperature was raised above 80 °C, and, as such, 80 °C was selected as the optimum reaction temperature.



Scheme 1. Direct formylation of **1** with boronic derivative **2a** (THF = tetrahydrofuran).

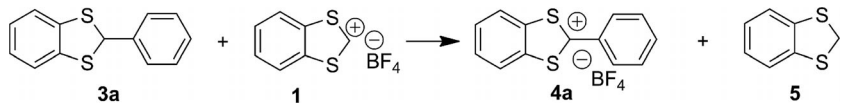
Table 1. Reaction conditions for the direct formylation of **2a** with electrophilic reagent **1**.[a]

Entry	*T* [h]	Solvent	Temp. [°C]	% Yield[b]
1	16	DCE	r.t.	60
2	48	DMF	r.t.	0
3	24	THF	r.t.	10
4	24	dioxane	r.t.	17
5	16	toluene	r.t.	50
6	16	CH_3CN	r.t.	73
7[c]	10	CH_3CN	80	74

[a] The reaction was conducted under nitrogen atmosphere for the indicated time. [b] Isolated yields after a fast chromatographic purification on neutral Al_2O_3. [c] The ^1H NMR spectrum of the crude reaction mixture showed almost complete conversion in CH_3CN.

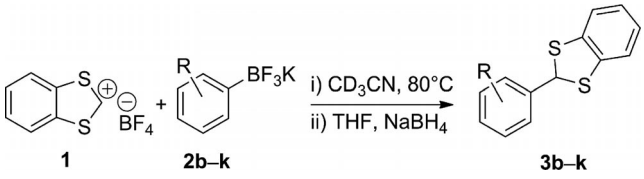
This reaction was effective at room temperature, but longer reaction times were necessary to achieve a satisfactory conversion. The chemical properties of CH_3CN are not thought to affect reaction rate. In fact, Mayr has observed only minor changes in the rate of the reaction when sp^2-hybridized trivalent boron compounds were employed in CH_3CN compared to CH_2Cl_2, thereby excluding the possibility that acetonitrile coordinates to the sp^2-hybridized boron center. The number of equivalents of **1** was important to drive the reaction toward the desired product.

It is well known that carbenium ions can be obtained by a hydride shift.[14] As soon as the aryl benzodithiol **3a** was obtained, the product was transformed into the corresponding cationic compound **4a** (see Scheme 2). To drive the reaction toward the formation of the more stabilized cation **4a**, which is stable in air and isolatable by filtration, almost 2.5 equiv. of **1** were necessary. To isolate the compound in its neutral form, the crude reaction mixture underwent a reduction reaction by treatment with $NaBH_4$ to afford desired **3a** in high yields. The isolation of a number of products proved to be challenging because of their tendency to form stabilized cations. Fortunately, preparative TLC on neutral Al_2O_3 resulted in only minor decomposition (formation of the carbenium ion by a hydride shift).



Scheme 2. Formation of the most stable cationic compounds by hydride shift.

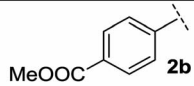
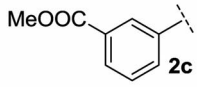
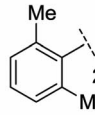
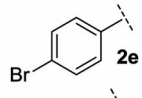
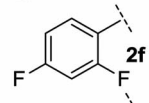
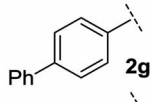
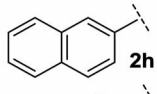
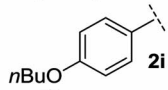
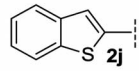
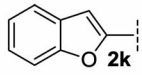
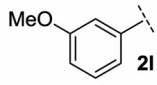
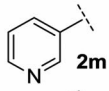
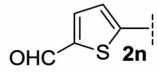
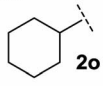
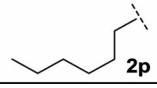
The case of the reaction with aryltrifluoroborate **2a**, which demonstrated a successful conversion into the corresponding coupled product in good yield, was extended to other aryltrifluoroborates (see Scheme 3 and Table 2). All the trifluoroborate salts were prepared from commercially available boronic acid through a simple procedure described by Molander.[15] Aryltrifluoroborates with electron-donating groups (i.e., **2g**–**2i**) on the aromatic ring resulted in both better conversions into the coupled products and better yields of the isolated products in comparison to those with electron-withdrawing groups (i.e., **2b** and **2c**). An explanation for this is the increased nucleophilicity of the organic residue in the case of an activated ring system that contained electron-donating groups as opposed to a relatively deactivated ring that contained electron-withdrawing groups. This reaction was also tolerant of halide functionalities on the aromatic ring. Both **2e** and **2f** underwent the coupling reaction with a high conversion, but only **3e** was successfully isolated as a pure product. Strongly electron-deficient aromatic substrates (i.e., pyridine, formylthiophenes, etc.)[16] were unreactive under the reaction conditions. The products were purified by preparative TLC on neutral Al_2O_3.



Scheme 3. Reaction of **1** with different boronic derivatives.

The facile formation of the cation by a hydride shift can be advantageously used for the preparation of new hydridic reagents for organocatalytic reductions.[14] The *ipso* Friedel–Crafts electrophilic aromatic substitution mechanism is presumed to be the prevalent reaction pathway in this class of reactions. Mayr et al. reported that changing the counterion in the reaction of a number of borates with a benzhydrylium cation did not result in a significant change in the rate of the reaction.[5] This indicates a rate-determining carbon–carbon bond forming step in which the carbon–boron bond is not yet fully broken, which is a result fully consistent with the Friedel–Crafts S_EAr mechanism. However, electron-rich aromatic compounds can also undergo a direct reaction with **1**.[8b] In fact, when *p*-methoxybenzene was treated with **1** in CH_3CN, satisfactory yields of the Friedel–Crafts product were achieved (70%). However, less activated substrates such as toluene or xylenes were unreactive. The facility of a direct reaction is determined by the position of the arene compounds on the Mayr scale. For the moderately activated substrates presented in Table 2, the

Table 2. Addition of the benzodithiolylium **1** to electron-rich and electron-poor aryltrifluoroborates.

Entry[a]	R'BF_3K	Product	Conv. (% yield)[b]
1		**3b**	45 (30)
2		**3c**	52 (32)
3		**3d**	68 (40)
4		**3e**	68 (33)
5		**3f**	64[c]
6		**3g**	85 (70)
7		**3h**	100 (72)
8		**3i**	87 (67)
9		**3j**	98 (30)
10		**3k**	99 (84)
11		**3l**	99 (58)[d]
12		**3m**	[e]
13		**3n**	[e]
14		**3o**	[e]
15		**3p**	[f]

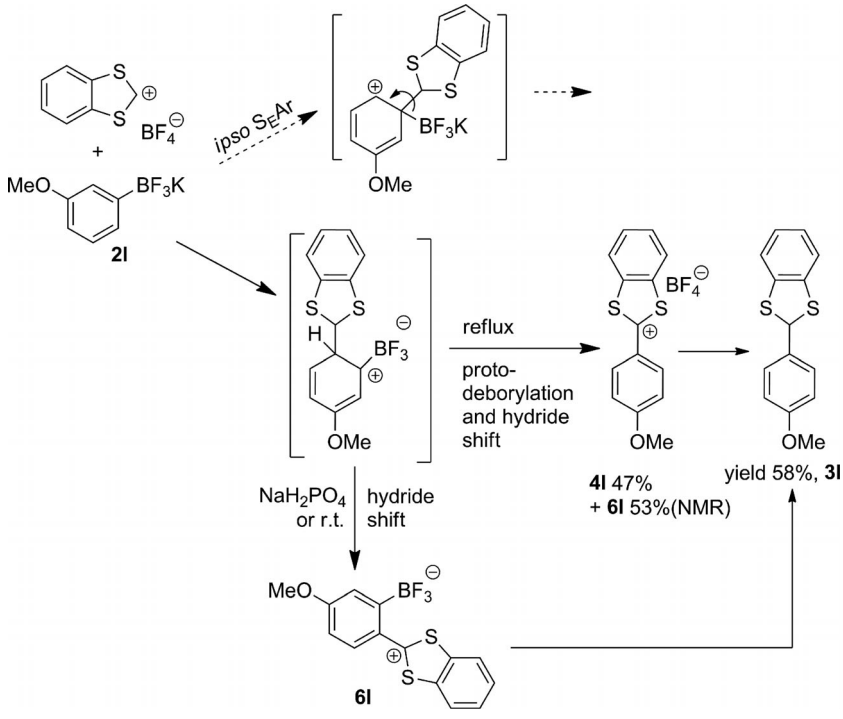
[a] All the reactions were conducted in CD_3CN. [b] Conversion was determined by ^1H NMR analysis of the crude reaction mixture in CD_3CN. The isolated yield after chromatographic purification on neutral Al_2O_3 is reported in parenthesis. [c] Product was obtained as inseparable mixture with benzodithiol **5**. [d] Product obtained was *para* substituted. [e] No reaction. [f] Trace amounts of the desired compound was determined by GC–MS analysis.

Friedel–Crafts type reaction was not possible. In addition, we examined the possibility of a competition between the activating effect of the BF_3K on the aromatic ring and the *ipso* activation by the trifluoroborate. Substitution at the CH-position of a heterocycle and aromatic ring can be faster that *ipso* substitution. Mayr recently reported[17] that the BF_3K group activates the position attached to boron by a factor of 10^3–10^4, whereas adjacent CH-positions are activated by a factor of 10^5–10^6. In fact, when we submitted the potassium 3-methoxyphenyltrifluoroborate salt (**2l**, *meta* substituted) to **1** under the optimized reaction conditions, the reaction led to the isolation of the corresponding *para*-substituted compound **3l** (see Scheme 4).

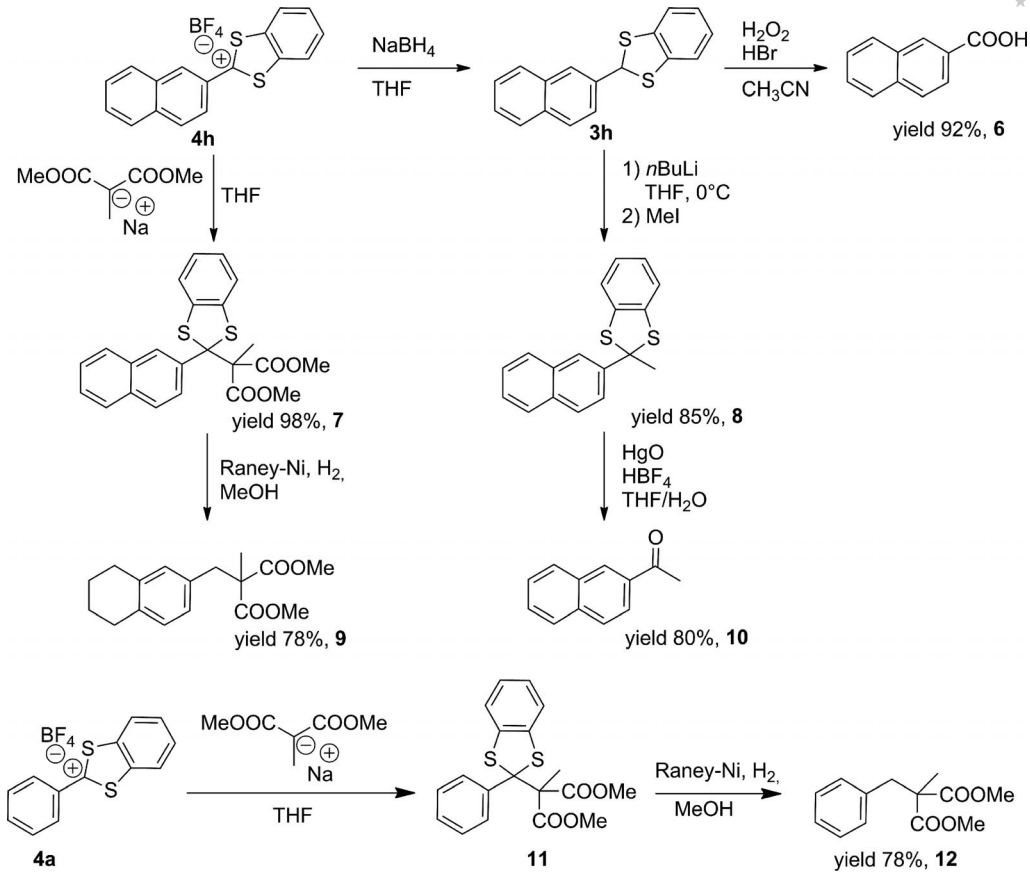
The activating effects of the BF_3K group on the vicinal and more remote positions of indole, furan, benzofuran, and thiophenes were also investigated by Mayr.[17] By selecting an electrophile as a reference compound, a quantitative structure–activity relationship showed that BF_3K enhanced the nucleophilic reactivity of the C-3 position of indole less when it was located at C-3 (*ipso*) than when it was located at another position, such as the vicinal C-2 or the remote C-5 position. Similarly in furans, the nucleophilic reactivity of the heterocycle was enhanced more when the BF_3K group was located in a remote position than when it was located at the *ipso* position. Therefore, the *ipso* activation of the BF_3K is less than its activation at a vicinal or remote position. In almost all the examples examined in Table 2, the vicinal or remote position of the aromatic compound was less activated compared to the *ipso* position. When **2l** was considered, the competition of *ipso* versus vicinal substitution was observed. Mayr reported that the proto-deborylation, which is promoted by the Friedel–Crafts mechanism, can be effectively eliminated by amine scavengers to trap the proton that is released during the electrophilic attachment. In fact, when **2l** was treated with **1** in the presence of NaH_2PO_4 or at room temperature, compound **6l** was characterized by ^1H NMR spectroscopy.[18]

The versatility and synthetically utility of the benzodithiol group is illustrated in the Scheme 5, where all the transformations investigated occurred in high yields. The benzodithiol group can be easily alkylated by an electrophile following its treatment with *n*BuLi. Therefore, aromatic ketones can be easily obtained starting from an aryltrifluoroborate. The benzodithiol group can also be oxidized to the corresponding carboxylic acid.

The benzodithiol is not only the masked form of a corresponding aldehyde, ketone, or acid, but it is also possible to eliminate the group by hydrogenation, which provides access to alkyl aryl compounds. The direct obtainment of a carbenium ion in the reaction can be advantageously used for the successive addition of nucleophiles. This transformation can be accomplished through a one-pot, two-step procedure. The electrophilicity of intermediate cations such as **4a** or **4h** is not very high. This limited capacity to behave as a powerful electrophile restricts the range of nucleophiles that can be used to intercept these arylbenzodithiolylium cations.[19] In fact, on the upper end of Mayr's scale, enamines appear as strong nucleophiles, and their reaction with appropriate electrophiles demonstrate rate constants in the diffusion-controlled region. Two separate, but direct, reactions of electrophilic compound **3a** with two such enamines, 1-morpholinocyclohexene and 1-morpholinocyclopentene, did not result in any further coupling product as determined by ^1H NMR analysis after 17 h. Only very reac-



Scheme 4. Reactions of electron-rich boronic acid derivative.



Scheme 5. Multistep reaction sequences utilizing the chameleonic benzodithiol group.

tive nucleophiles, positioned at or below 18 on the Mayr scale[7] could be used for a reaction to be obeserved. In fact, when the anion of dimethyl 2-methylmalonate (prepared by addition of NaH in THF) was added to compound **4h**, we isolated the desired adduct **7** in high yield. Interestingly, the treatment of **7** with Raney-Ni resulted in the elimination of the benzodithiol moiety and the reduction of the less substituted benzene ring. When the reaction was repeated with compound **11**, the elimination of the benzodithiol group occurred without this side reaction.

Heteroaromatic electron-poor substrates were also investigated under the optimal reaction conditions. In general, they did not perform as well as the other substrates reported in Table 2. Neither 3-pyridinyl trifluoroborate **2m** nor 5-formylthiophene trifluoroborate **2n** underwent a successful coupling reaction. Other trifluoroborate salts were investigated as well. Potassium (phenylethenyl)trifluoroborate was treated with 1,3-benzodithiolylium tetrafluoroborate, but no trace of the reaction product was observed after 48 h at 80 °C. Unsaturated adducts such as the vinyl trifluoroborate salt were unreactive. We also examined cyclohexyl trifluoroborate **2o** and hexyl trifluoroborates **2p**. With the latter, there were trace amounts of the desired adduct that were observed by GC–MS analysis, but we were unable to isolate it as decomposition occurred during chromatography.

Conclusions

In summary, by taking advantage of the results from the kinetic and synthetic studies described by Mayr, we were able to design a simple and effective procedure for the direct formylation of aryltetrafluoroborate salts. The advantage of introducing the benzodithiol group stems from its chameleonic chemical nature, as this group can be used for further transformations. The cationic aryl benzodithiolylium compounds, accessible through a direct reaction of **1**, are potentially of use in materials science. We are currently expanding the limitation of this chemistry by studying related reactions that involve a variety of boronic derivatives and suitable carbenium ion precursors.

Experimental Section

General Methods: The ^{1}H NMR spectroscopic data were recorded with Varian Gemini 200 and Varian MR 400 spectrometers. Chemical shifts are reported in ppm relative to TMS with the residual solvent resonance as the internal standard (chloroform, δ = 7.27 ppm). Data are reported in the order of chemical shift, multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad singlet (br. s), and multiplet (m)], and coupling constants (Hz). The ^{13}C NMR spectroscopic data were recorded with Varian Gemini 200 and Varian MR 400 spectrometers. Chemical shifts are reported in ppm relative to TMS with the solvent as the internal standard

(deuterochloroform, δ = 77.0 ppm). LC–electrospray ionization mass spectra were obtained with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was performed with 240–400 mesh silica gel. Melting points were measured with a Bibby Stuart Scientific Melting Point Apparatus SMP 3. Reactions were carried out under inert gas and anhydrous conditions. Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and used without further purification.

General Procedure for the Preparation of Potassium Aryl and Heteroaryl Trifluoroborates: To a solution of boronic acid (1 equiv.) in MeOH (3.5 M solution) under nitrogen was added KHF_2 (3 equiv.) in one portion at 0 °C. To this suspension was added H_2O dropwise at 0 °C. The ice-water bath was removed, and the reaction was stirred at room temperature for 1 h. The mixture was then concentrated and dried overnight in vacuo. The desired product was then extracted from the crude solid with acetone (2 × 5 mL) and sonication and then further extracted with hot acetone (2 × 5 mL). The collected extracts were then concentrated, and the residue was redissolved in a minimal amount of acetone (5 mL). The addition of ether (5 mL) encouraged precipitation of the product. The collected product was isolated by filtration and dried in vacuo.

Potassium 2,4-Difluorophenyltrifluoroborate (2f): The general procedure was used with 2,4-difluorophenylboronic acid (200 mg, 1.266 mmol) and KHF_2 (290 mg, 3.723 mmol). The reaction was completed in 1 h. Acetone (5 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (2 mL). The addition of hexane (4 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure product (267 mg, 1.212 mmol, 96% yield) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]-acetone): δ = 6.48 (td, J = 9.8, 2.4 Hz, 1 H), 6.59 (td, J = 8.5, 2.3 Hz,1 H), 7.35 (q, J = 7.8 Hz, 1 H) ppm. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –99.58, –111.17 (q, J = 8.3 Hz), –134.21 (q, J = 45.6 Hz) ppm.

Potassium 4-Biphenyltrifluoroborate (2g): The general procedure was used with 4-biphenylboronic acid (100 mg, 0.505 mmol) and KHF_2 (315 mg, 4.039 mmol). The reaction was completed in 2 h. Acetone (5 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (2 mL). The addition of ether (10 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure product (108 mg, 0.414 mmol, 82% yield) as a white solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.27–7.33 (m, 1 H), 7.39–7.49 (m, 4 H), 7.52 (d, J = 7.7 Hz, 2 H),7.61–7.66 (m, 2 H) ppm. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –138.7 ppm.

Potassium Naphthalene-2-trifluoroborate (2h): The general procedure was used with naphthalene-2-boronic acid (200 mg, 1.163 mmol) and KHF_2 (272 mg, 3.489 mmol). The reaction was completed in 10 min. Acetone (3 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (2 mL). The addition of hexane (3 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure product (253 mg, 1.08 mmol, 93% yield) as a white solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.32–7.42 (m, 2 H), 7.62–7.71 (m, 2 H), 7.75–7.83 (m, 2 H), 7.92 (s, 1 H) ppm. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –129.9 ppm.

Preparation of Potassium Benzo[*b*]thien-2-yltrifluoroborate (2j): The general procedure was used with benzo[*b*]thien-2-ylboronic acid (100 mg, 0.562 mmol) and KHF_2 (131.5 mg, 1.686 mmol). The reaction was completed in 30 min. Acetone (5 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (2 mL). The addition of ether (10 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure product (94 mg, 0.393 mmol, 70% yield) as an off-white solid. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.09 (m, 1 H), 7.12–7.20 (m, 2 H), 7.63 (dt, J = 7.8, 1.0 Hz, 1 H), 7.74 (m, 1 H) ppm. ^{19}F NMR (377 MHz, CD_3CN): δ = –138.36 ppm.

Potassium 3-Methoxyphenyltrifluoroborate (2l): The general procedure was used with 3-methoxyphenylboronic acid (200 mg, 1.316 mmol) and KHF_2 (821 mg, 10.526 mmol). Relative to the general procedure, this corresponds to an increase from 3 to 8 equiv. in the amount of KHF_2. The reaction was completed in 2 h. Acetone (5 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (3 mL). The addition of ether (5 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure product (248 mg, 1.200 mmol, 91% yield) as a white solid. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –142.85 ppm.

Potassium Pyridin-3-yltrifluoroborate (2m): The general procedure was used with 3-pyridylboronic acid (50 mg, 0.407 mmol) and KHF_2 (101 mg, 1.301 mmol). The reaction was completed in 10 min. Acetone (3 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (1 mL). The addition of hexane (3 mL) led to the precipitation of the product along with what was identified as the zwitterionic form of the salt – potassium pyridiniumtrifluoroborate. The product was filtered, collected, and dried in vacuo to afford the desired pure product (56 mg, 0.301 mmol, 74% yield) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 6.99 (m, 1 H), 7.69 (d, 1 H), 8.24 (m, 1 H), 8.61 (s, 1 H) ppm. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –142.93 ppm.

Potassium (5-Formyl-2-thienyl)trifluoroborate (2n): The general procedure was used with (5-formyl-2-thienyl)boronic acid (100 mg, 0.641 mmol) and KHF_2 (160 mg, 2.051 mmol). The reaction was completed in 30 min. Acetone (4 mL) was added to the crude solid, and the resulting mixture was sonicated and then filtered. This procedure was repeated (2×). The combined filtrates were concentrated in vacuo, and the crude solid was redissolved in a minimal amount of hot acetone (2 mL). The addition of ether (5 mL) led to the precipitation of the product, which was filtered, collected, and dried in vacuo to afford the desired pure yellow-brown product (101 mg, 0.462 mmol, 72% yield). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 7.09 (s, 1 H), 7.68 (s, 1 H), 9.81 (s, 1 H) ppm. ^{19}F NMR (377 MHz, [D$_6$]acetone): δ = –132.7 ppm.

Potassium (Phenylethenyl)trifluoroborate: A solution of phenylacetylene (300 mg, 2.94 mmol) in THF (5.88 mL) was cooled to –78 °C under nitrogen. *n*BuLi (2.5 M in hexane, 1.176 mL, 2.94 mmol, 1 equiv.) was added dropwise, and the solution was stirred for 1 h at this temperature. Trimethylborate (459 mg,

4.41 mmol, 1.5 equiv.) was then added dropwise at –78 °C. The solution was stirred at this temperature for 1 h, and a saturated aqueous solution of KHF_2 (1.376 g, 17.64 mmol, 6 equiv.) was added to the vigorously stirred solution. The resulting mixture was stirred at –20 °C for 1 h and then was warmed to room temperature for 1 h. The solvent was removed under reduced pressure, and the resulting white solid was dried under high vacuum for 2 h. The solid was then extracted with acetone (2 × 5 mL) and hot acetone (3 × 5 mL). The combined organic mixtures were filtered, and the solvent was removed to afford a fluffy white solid. This solid was then dissolved in hot acetone and precipitated with the addition of diethyl ether. The solution was cooled to –20 °C to complete the precipitation of the solid. The product was collected to afford potassium (phenylethenyl)trifluoroborate (330 mg, 1.59 mmol, 54% yield) as a white crystalline solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.31–7.22 (m, 2 H), 7.40–7.34 (m, 1 H) ppm. ^{19}F NMR (377 MHz, CD_3CN): δ = –135.17 ppm.

General Procedure for the Coupling of Potassium Organotrifluoroborates with 1,3-Benzodithiolylium Tetrafluoroborate: To a stirred solution of the potassium organotrifluoroborate (1 equiv.) in acetonitrile (1 mL) under nitrogen was added 1,3-benzodithiolylium tetrafluoroborate (**1**, 2.5 equiv.). The mixture was heated at 80 °C and then stirred overnight (16 h). The solvent was then removed under reduced pressure. THF (1 mL) was added to dissolve the resulting solid, and to the stirred mixture was added $NaBH_4$ (10 equiv.) over the course of 1 h at 0 °C. Water (5 mL) was added, and the mixture was then transferred to a separatory funnel. EtOAc was added, and the aqueous layer was thoroughly extracted with EtOAc (3 × 2.5 mL). The combined organic extracts were dried with Na_2SO_4 and then filtered. Removal of the solvent under reduced pressure and subsequent purification by preparative TLC (neutral-alumina) afforded the product.

2-Phenylbenzo[*d*][1,3]dithiole (3a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (s, 1 H), 7.06 (dd, *J* = 3.0, 5.8 Hz, 2 H), 7.21 (dd, *J* = 3.0, 5.8 Hz, 2 H), 7.29–7.37 (m, 3 H), 7.55 (dd, *J* = 2.0, 7.4 Hz, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 56.5 (1 C), 121.9 (2 C), 125.8 (2 C), 127.1 (2 C), 128.7 (2 C), 128.8 (1 C), 137.5 (2 C), 139.9 (1 C) ppm. HRMS: calcd. for $C_{13}H_{10}S_2$ 230.02239; found 230.02261.

Methyl 4-(Benzo[*d*][1,3]dithiol-2-yl)benzoate (3b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 6.13 (s, 1 H), 7.07 (dd, *J* = 3.0, 5.8 Hz, 2 H), 7.22 (dd, *J* = 3.0, 5.8 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.98 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 52.2 (1 C), 55.6 (1 C), 122.0 (2 C), 125.7 (1 C), 126.0 (2 C), 127.0 (2 C), 130.1 (2 C), 137.2 (2 C), 151.0 (1 C), 198.0 (1 C) ppm. HRMS: calcd. for $C_{15}H_{12}O_2S_2$ 288.02787; found 288.02809.

Methyl 3-(Benzo[*d*][1,3]dithiol-2-yl)benzoate (3c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 6.21 (s, 1 H), 7.07 (dd, *J* = 3.3, 5.8 Hz, 2 H), 7.21 (dd, *J* = 3.3, 5.8 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.97 (d, *J* = 7.8 Hz, 1 H), 8.17 (s, 1 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 52.2 (1 C), 55.9 (1 C), 122.0 (2 C), 125.9 (2 C), 128.2 (1 C), 129.0 (1 C), 129.9 (1 C), 130.5 (1 C), 131.6 (1 C), 137.2 (2 C), 140.6 (1 C), 166.5 (1 C) ppm. HRMS: calcd. for $C_{15}H_{12}O_2S_2$ 288.02787; found 288.02765.

2-(2,6-Dimethylphenyl)benzo[*d*][1,3]dithiole (3d): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 6 H), 7.08–6.98 (m, 4 H), 7.09–7.21 (m, 3 H), 7.22–7.34 (m, 1 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 21.8 (2 C), 52.1 (1 C), 121.8 (2 C), 125.4 (2 C), 125.9 (1 C), 128.6 (2 C), 129.8 (2 C), 131.1 (1 C), 139.0 (2 C) ppm. HRMS: calcd. for $C_{15}H_{14}S_2$ 258.05369; found 258.05347.

2-(4-Bromophenyl)benzo[*d*][1,3]dithiole (3e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.09 (s, 1 H), 7.07 (dd, *J* = 3.2, 5.8 Hz, 2 H), 7.20 (dd, *J* = 3.2, 5.8 Hz, 2 H), 7.47–7.38 (m, 4 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$, 25 °C): δ = 139.3 (1 C), 137.1 (2 C), 131.8 (2 C), 128.7 (2 C), 125.9 (2 C), 125.6 (1 C), 122.0 (2 C), 55.6 (1 C) ppm. HRMS: calcd. for $C_{13}H_9BrS_2$ 307.93290; found 307.93312.

2-(2,4-Difluorophenyl)benzo[*d*][1,3]dithiole (3f): The compound was obtained as a inseparable mixture with the benzodithiole. Chromatographic purification was not possible in this as case. Many different eluent mixtures were used, but the compounds were not separable. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.26 (s, 1 H), 6.85–6.75 (m, 2 H), 7.73–7.64 (m, 1 H), 7.24 (dd, *J* = 3.3, 5.9 Hz, 2 H), 7.08 (dd, *J* = 3.3, 5.9 Hz, 2 H) ppm. HRMS: calcd. for $C_{13}H_8F_2S_2$ 266.00355; found 266.00333.

2-([1,1′-Biphenyl]-4-yl)benzo[*d*][1,3]dithiole (3g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.24 (s, 1 H), 7.08 (dd, *J* = 3.3, 5.8 Hz, 2 H), 7.23 (dd, *J* = 3.3, 5.8 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 7.3 Hz, 1 H), 7.52–7.59 (m, 4 H), 7.44 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 56.3 (1 C), 122.0 (2 C), 125.9 (2 C), 127.2 (2 C), 127.5 (4 C), 127.6 (1 C), 128.9 (2 C), 137.6 (2 C), 139.0 (1 C), 140.5 (1 C), 141.8 (1 C) ppm. HRMS: calcd. for $C_{19}H_{14}S_2$ 306.05369; found 306.05347.

2-(Naphthalen-2-yl)benzo[*d*][1,3]dithiole (3h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.37 (s, 1 H), 7.07 (dd, *J* = 3.3, 5.9 Hz, 2 H), 7.23 (dd, *J* = 3.3, 5.9 Hz, 2 H), 7.48 (dd, *J* = 3.3, 6.2 Hz, 2 H), 7.73 (d, *J* = 8.8 Hz, 1 H), 7.77–7.85 (m, 3 H), 7.89 (s, 1 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 56.8 (1 C), 122.0 (2 C), 124.9 (2 C), 125.9 (2 C), 126.5 (2 C), 127.7 (1 C), 128.1 (1 C), 129.0 (1 C), 132.5 (1 C), 133.4 (1 C), 137.1 (1 C), 137.6 (2 C) ppm. HRMS: calcd. for $C_{17}H_{12}S_2$ 280.03804; found 280.03822.

2-(4-Butoxyphenyl)benzo[*d*][1,3]dithiole (3i): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.67–1.79 (m, 2 H), 1.52–1.40 (m, 2 H), 3.93 (t, *J* = 6.5 Hz, 2 H), 6.22 (s, 1 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 7.03 (dd, *J* = 3.3, 5.7 Hz, 2 H), 7.17 (dd, *J* = 3.3, 5.7 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 13.8 (1 C), 19.2 (1 C), 31.2 (1 C), 56.6 (1 C), 67.7 (1 C), 114.6 (2 C), 121.9 (2 C), 125.7 (2 C), 128.4 (2 C), 131.1 (1 C), 137.7 (2 C), 159.5 (1 C) ppm. HRMS: calcd. for $C_{17}H_{18}OS_2$ 302.07991; found 302.08009.

2-(Benzo[*b*]thiophen-2-yl)benzo[*d*][1,3]dithiole (3j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.37 (s, 1 H), 7.13–7.40 (m, 2 H), 7.21–7.29 (m, 3 H), 7.28–7.33 (m, 2 H), 7.63–7.70 (m, 1 H), 7.70–7.77 (m, 1 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 52.2 (1 C), 122.3 (2 C), 122.4 (2 C), 123.8 (1 C), 124.5 (1 C), 124.9 (1 C), 125.8 (1 C), 126.0 (2 C), 136.7 (1 C), 138.8 (1 C), 139.8 (1 C), 145.3 (1 C) ppm. HRMS: calcd. for $C_{15}H_{10}S_3$ 285.99446; found 285.99439.

2-(Benzo[*b*]furan-2-yl)benzo[*d*][1,3]dithiole (3k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (s, 1 H), 6.78 (s, 1 H), 7.00–7.11 (m, 2 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 7.21–7.29 (m, 3 H), 7.39–7.50 (m, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 48.3 (1 C), 104.8 (1 C), 111.4 (1 C), 121.2 (1 C), 122.4 (2 C), 123.0 (1 C), 124.7 (1 C), 125.9 (2 C), 127.9 (1 C), 136.4 (2 C), 155.3 (1 C), 155.4 (1 C) ppm. HRMS: calcd. for $C_{15}H_{10}OS_2$ 270.01731; found 270.01715.

2-(4-Methoxyphenyl)benzo[*d*][1,3]dithiole (3l): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 6.23 (s, 1 H), 6.84 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 7.04 (dd, *J* = 3.2, 5.8 Hz, 2 H), 7.19 (dd, *J* = 3.2, 5.8 Hz, 2 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 55.3 (1 C), 56.5 (1 C), 114.0 (2 C), 121.8 (2 C), 125.7 (2 C), 128.4 (2 C), 131.5 (1 C), 137.7 (2 C), 159.9 (1 C) ppm. HRMS: calcd. for $C_{14}H_{12}OS_2$ 260.03296; found 260.03287.

Synthesis of 6: In a flask that was open to air was dissolved 2-(naphthalen-2-yl)benzo[*d*][1,3]dithiole (30 mg, 0.1 mmol, 1 equiv.) in CH_3CN (1.0 mL, 0.1 M solution). To this mixture was added H_2O_2 (70% solution, 0.57 mL, 0.4 mmol) followed by HBr (0.022 mL, 0.2 mmol, 2 equiv.) at room temperature. After 24 h, the reaction was quenched by the addition of a saturated solution of $NaHSO_3$ (1 mL) and a saturated solution of $NaHCO_3$ (5 mL). The aqueous phase was extracted with diethyl ether (2 × 5 mL). The aqueous phase was acidified with HCl (1 N solution, 5 mL) until the pH = 1 and was then extracted with ethyl acetate (2 × 5 mL). The combined organic phases were evaporated under reduced pressure to give the pure product (92% yield). Spectroscopic data were in agreement with the published data.[20]

Synthesis of 10: In a two-necked flask under nitrogen was dissolved 2-(naphthalen-2-yl)benzo[*d*][1,3]dithiole (30 mg, 0.1 mmol, 1 equiv.) in THF (1.0 mL, 0.1 M solution). *n*-Butyllithium (0.2 mmol, 2 equiv.) was added dropwise at 0 °C until the mixture was a persistent yellow color. The reaction mixture was stirred at 0 °C for 15 min, and then MeI (0.5 mmol, 0.5 equiv.) was added dropwise. The reaction was monitored by GC–MS and quenched by the addition of water. The mixture was extracted with diethyl ether (3 × 2 mL). The combined organic phases were evaporated under reduced pressure to give an oil. The crude product was dissolved in THF (1.0 mL), and the resulting solution was added to a suspension of HgO (0.8 mmol, 0.8 equiv.) in H_2O (1 mL) followed by the addition of HBF_4 (0.2 mL, 0.2 mL/mmol). After 15 h, $NaHCO_3$ was added until the solution was basic on the pH scale. The reaction mixture was filtered through Celite and washed with diethyl ether. The filtrate was extracted with diethyl ether (2 × 3 mL). The combined organic phases were evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica (cyclohexane/ethyl acetate, 95:5) provided the pure product (81% yield). Spectroscopic data were in agreement with the published data.[21]

General Procedure for the Synthesis of Malonates 9 and 12: Under nitrogen into a two-necked flask that contained NaH (20 mg, 0.5 mmol, 5 equiv.) was added THF (1 mL). Methyl dimethylmalonate (0.073 mL, 0.55 mmol, 5.5 equiv.) was subsequently added dropwise at 0 °C. After 20 min, the reaction mixture was added dropwise by cannula to a solution of 2-phenylbenzo[*d*][1,3]-dithiolylium tetrafluoroborate (**4a**, 77 mg, 0.1 mmol, 1 equiv.) in THF (0.5 mL, 0.05 M solution) under nitrogen. The reaction mixture was stirred at room temperature for 15 h and then was quenched by the addition of H_2O (2 mL). The mixture was extracted with diethyl ether (2 × 3 mL). The combined organic extracts were evaporated under reduced pressure, and the crude product was dissolved in MeOH (3 mL). To this solution was added Raney-Ni (slurry in water, 500 mg), and the mixture was stirred under H_2. After 48 h, the reaction mixture was filtered through Celite, which was washed with MeOH. The MeOH was evaporated, and H_2O/diethyl ether was added to the residue. The aqueous phase was extracted with diethyl ether (2 × 3 mL). The combined organic phases were evaporated under reduced pressure to give the crude product. Purification by flash chromatography on silica (cyclohexane/diethyl ether, 95:5) provided pure product **12** (78% yield). Spectroscopic data were in agreement with the published data.[22] Compound **9** was prepared according to same procedure to give pure product **9** (78% yield). Data for **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3 H), 1.72–1.81 (m, 4 H), 2.76–2.64 (m, 4 H), 3.15 (s, 2 H), 3.73 (s, 6 H), 6.75–6.82 (m, 2 H), 6.94 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100.76 MHz, $CDCl_3$): δ = 19.7 (1 C), 23.2 (2 C), 29.0 (1 C), 29.4 (1 C), 40.9 (1 C), 52.4 (2 C), 54.9 (1 C), 127.1 (1 C), 128.9 (1 C), 130.8 (1 C), 132.3 (1 C), 136.2 (1 C), 137.0 (1 C), 172.5 (2 C) ppm.

Supporting Information (see footnote on the first page of this article): Evidence of *ipso* substitution of compound **3j** and NMR spectra.

Acknowledgments

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