Mechanistic Insight from Lewis Acid-Dependent Selectivity and Reversible Haloboration, as Harnessed for Boron-Based Electrophilic Cyclization Reactions

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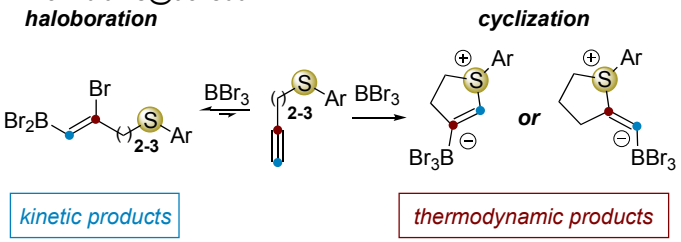


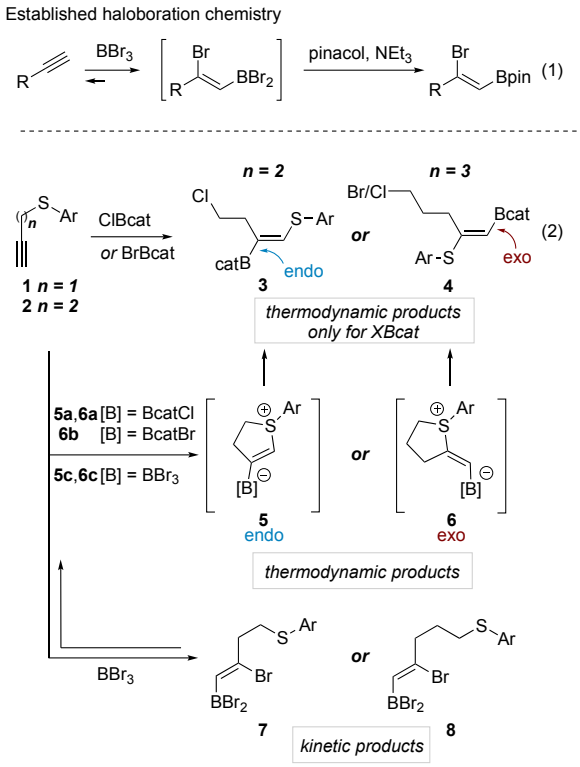
ABSTRACT: Different reaction selectivity occurs with the Lewis acids *B*-chlorocatecholborane (ClBcat), *B*-bromocatecholborane (BrBcat), and BBr_3, either favoring alkyne haloboration, electrophilic cyclization of a tethered nucleophilic sulfur onto the alkyne, or group transfer of the nucleophile. This reaction selectivity also depends on the chain length of the tethered nucleophile, revealing a subtle interplay of relative kinetics and thermodynamics. In all cases, BBr_3 reacts readily with alkynes to form haloborated products; however, this process is reversible, and this reversibility can be harnessed to ultimately access regio- and stereodefined cyclic sulfonium zwitterions via the slower, but thermodynamically favored, electrophilic cyclization pathway. Reversibility was noted by following the reaction by NMR spectroscopy, and by characterizing the kinetic and thermodynamic products by a combination of 2D NMR spectroscopy and single-crystal X-ray diffraction. The "mixed" reagent bromocatechol borane (BrBcat) displayed reactivity between ClBcat and BBr_3, producing bromoboration in some cases and electrophilic cyclization in others. With this enhanced understanding of the reaction dynamics, it becomes possible to use boron Lewis acids in a predictable manner in cases where haloboration is the kinetic product, but in which the reversibility of this reaction maintains access to eventual alternative reactivity leading to desired building blocks in organic synthesis.

Introduction

Haloboration reactions of alkynes using boron trihalides[1,2] or organoboron halides[3,4] are widely used in the synthesis of trisubstituted alkenes (eq 1).[5] The formed alkenes have predicable regio- and stereochemistry[6] and can serve as reagents in a wide array of reactions.[7,8] Studies comparing the reactivity of BBr_3 and BCl_3 with alkynes revealed a delicate balance between Lewis acidity, product mixture, and haloboration reversibility,[9] and that the reversibility can be used specifically to drive desired product outcome.[10] Calculations later provided a plausible relative scale for the reversibility.[11] Boronium ions have been used to haloborate internal alkynes,[12] because such internal alkyne reactions are sluggish relative to their terminal alkyne counterparts[11]. Detailed studies of the reversibility of haloboration with a range of substrates, including terminal and internal alkynes, as well as with substrates capable of competing reactivity, have been limited. Here, the reactivity of three boron-based Lewis acids is compared in detail. Conditions for reversibility of haloboration with both terminal and internal alkynes are established and it is shown that this reversibility can be harnessed to direct reactivity toward electrophilic-cyclization–group-transfer pathways that generate alkyne sulfides (Scheme 1).

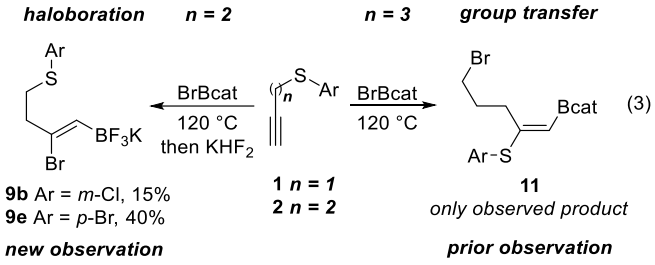
Recently, we reported the reaction of alkynes **1** and **2** with *B*-chlorocatecholborane (ClBcat). This reaction produced haloboration product only for long methylene chains ($n > 4$ CH_2) but for short methylene chains ($n = 2$ or 3 CH_2) instead formed the SAr group transfer products **3** and **4**, resulting from electrophilic cyclization followed by ring opening with the chloride nucleophile (Scheme 1, eq 2).[13]

Scheme 1. Haloboration of Alkynes Is Reversible and Is Harnessed to Cyclic Form Sulfonium Zwitterions



Results and Discussion

Studies here springboarded from an initial observation with a different but related Lewis acid: A chain-length effect was again observed with *B*-bromocatecholborane (BrBcat); however, in this case, the reaction with 2-methylene alkyne formed significant amounts of haloboration product **9**, but as we had previously reported, the 3-methylene alkyne had formed the group transfer product **10**[13] (eq 3).

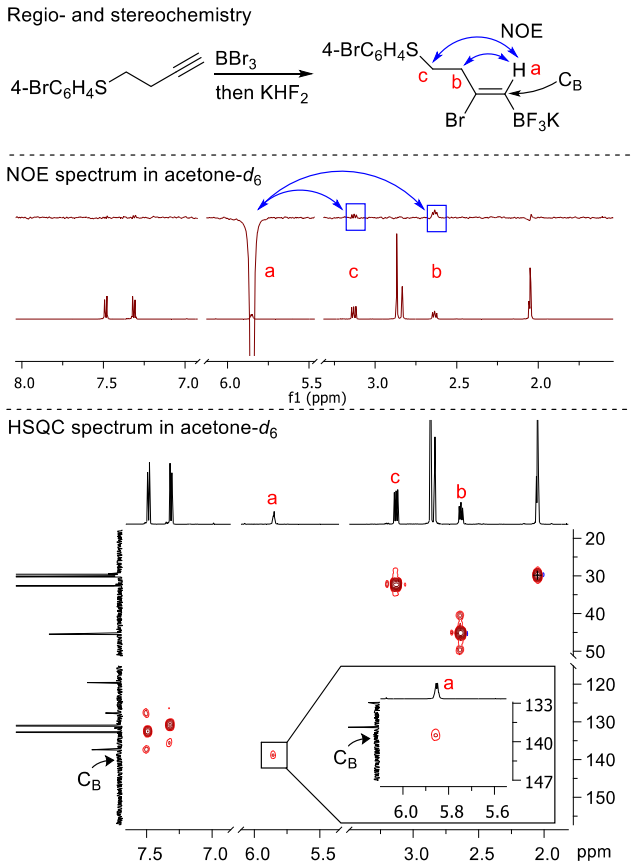


These examples served as an indicator for a delicate balance between ring size of intermediates and Lewis acids. This balance is corroborated by the comparison of 2-methylene group transfer product **3** and 3-methylene group transfer product **4** as opposite regioisomers. While alkene **3** is the product of endo cyclization, alkene **4** is the product of exo cyclization, indicating dependency on the ring size of the intermediate the reaction proceeds through (eq 2). This regiochemistry is consistent with a reaction mechanism guided by the ring size of the formed electrophilic cyclization intermediates, based on the alkyl chain length. Electrophilic cyclization intermediates **5** and **6** are formed by intramolecular nucleophilic attack of sulfur, similar to Larock-type cyclizations using boron electrophiles.[13–18] Alkyne-activation/cyclization to form intermediates **5** and **6** was determined as the rate-determining step.[13] Thus, we envisioned that a stronger Lewis acid[17,19] should accelerate formation of intermediates **5** and **6** and allow isolation of these zwitterions[20–22].

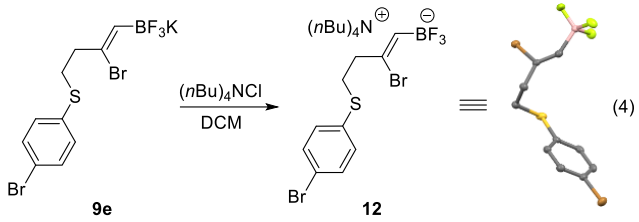
To test this hypothesis and to investigate the effect of a stronger Lewis acid on the overall reaction outcome, substrates **1** and **2** were reacted with BBr_3. Upon addition, a rapid exothermic reaction was observed. Treatment of the solution by KHF_2 to enhance product stability, and initial in situ NMR analysis showed formation of haloboration products of type **9.**

Due to the significant similarity of haloboration product compared to group transfer product by 1D ^{1}H NMR spectroscopy, and identical mass spectrometry data, HSQC, HMBC and NOE NMR experiments were key to product characterization. These methods also allowed for regio- and stereochemical assignment of products **9**. The NOE and HSQC NMR spectra of **9e** are shown in Scheme 2. These spectra data revealed that the boron was attached to the same carbon (indicated as C_B) as the terminal alkene proton (indicated as H_a), as can be seen by the cross peak of the alkene proton with a broadened carbon signal due to C–B splitting and quadrupolar line broadening (I_{11B} = 3/2). To verify the stereochemistry of the alkene, proton NOE experiments were conducted. The resulting data showed that the alkyl chain (with methylene protons *b* and *c*) was cis to the vinyl proton *a* (Scheme 2).

Scheme 2. NMR Spectroscopic Determination of Regio- and Stereochemistry



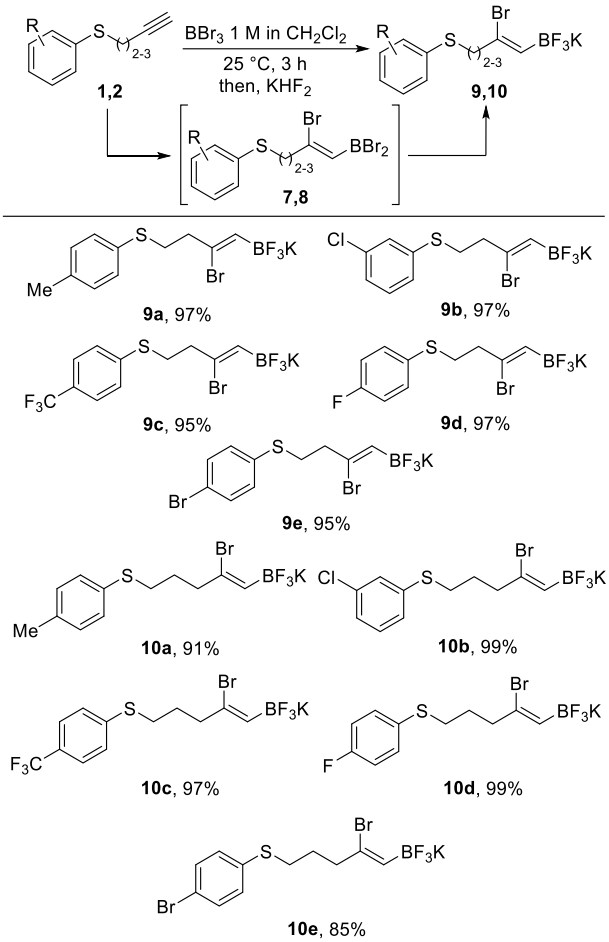
Additionally, long-range coupling HMBC spectroscopy (see SI) assisted in distinguishing between a hypothetical syn thioboration reaction without cyclization (not shown) and a bromoboration, by revealing coupling between aryl protons and carbon *c*, consistent with bromoboration structure **9**. Salt metathesis of **9e** with tetrabutylammoniumchloride enabled crystallization of the tetrabutylammonium analogue **12** suitable for X-ray crystallographic analysis, which further confirmed that haloboration had occurred under these conditions (eq 4; counter cation omitted for clarity).



(4)

With unisolated material characterized as haloboration products with BBr_3, attention next turned to product isolation (Table 1). Many attempts at isolating the bromoalkene–BBr_2 intermediates **7** and **8** directly were unsuccessful, and transesterification to conventional boronic esters like pinacol[6] in our hands resulted in significant amounts (>10%) of reversal to alkyne starting material, providing additional hints at bromoboration reversibility. In situ treatment with KHF_2, however, allowed isolation of the haloboration products as BF_3K salts, both for the 2-methylene bromoalkenes **9** and 3-methylene bromoalkenes **10**.

Table 1. Substrate Scope of Haloboration Products, Isolated as BF_3K Salts



After establishing that the reaction of terminal alkynes **1** and **2** at ambient temperature with BBr_3 in the presence intramolecular sulfur nucleophiles does not result in electrophilic cyclization but rather in rapid bromoboration, other reaction conditions to achieve electrophilic cyclization were explored. The possibility of bromoboration as the kinetic product, but electrophilic cyclization as the thermodynamic product, was next considered (Figure 1). Specifically, higher temperatures might reverse the reaction to starting materials and access alternative electrophilic cyclization products **13**.

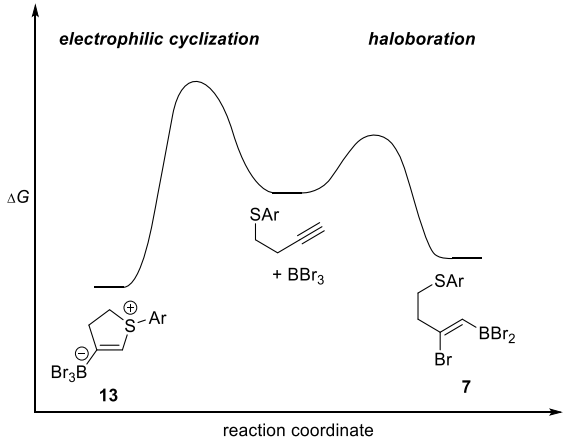
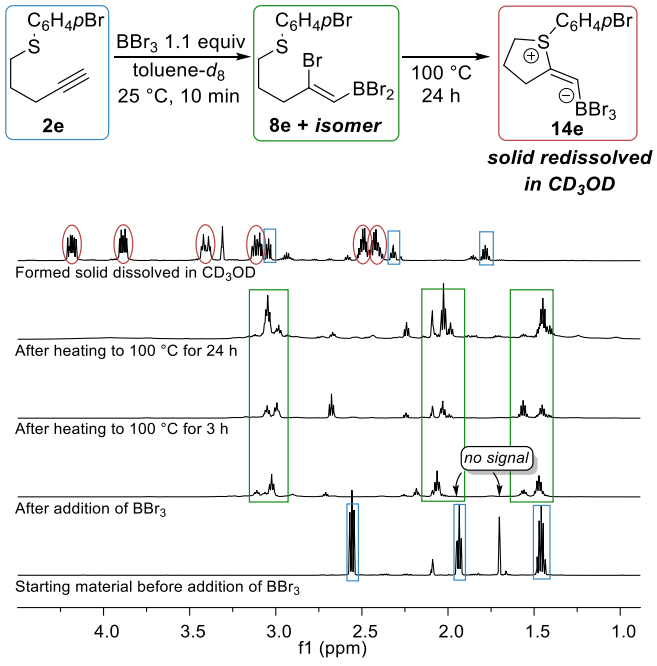


Figure 1. Energy diagram depicting reversible kinetic product haloboration (right) and thermodynamic product electrophilic cyclization (left).

To test this hypothesis, an NMR spectroscopy experiment with alkyne **2e** was conducted. The experiment revealed initial haloboration at room temperature to form **8e**, as expected (Scheme 3). Upon heating to 100 °C, however, significant formation of an unknown solid occurred in combination with formation of a second set of peaks from soluble material, assigned as isomerization of **8e** given the peak similarities (possibly from B/Br cis to B/Br trans). Decanting the solution and dissolving the precipitated solid in methanol-d_4 revealed the characteristic six diastereotopic aliphatic proton signals by ^{1}H NMR spectroscopy as expected for cyclic sulfonium zwitterion **14e**, the product of electrophilic cyclization. These experiments established successful reversibility of the kinetic haloboration pathway at elevated temperature and access to the thermodynamically favored electrophilic cyclization products.

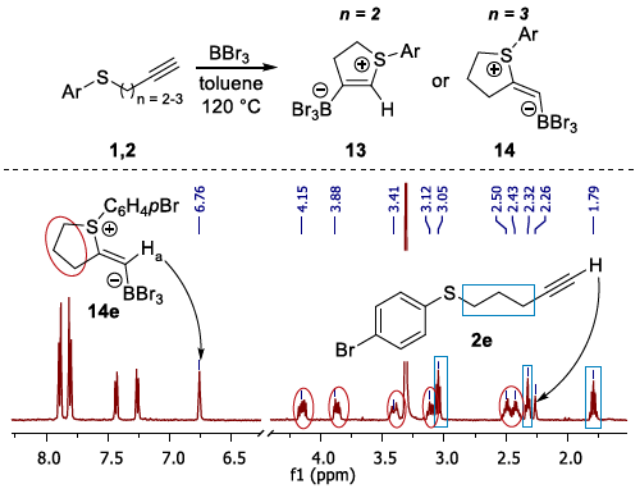
Scheme 3. ^{1}H NMR Spectra, Showing Initial Haloboration (bottom) and then Progression to Sulfonium Zwitterion in the Same Reaction Sample (top)



This reactivity pattern also occurred with alkyne **1e** (n = 2), which when reacted with BBr_3 and heated to 120 °C for 48 h in toluene, produced solid consistent with electrophilic cyclization to the (less soluble) zwitterion (Scheme 4). Attention next turned to isolation and characterization of the sulfonium zwitterions. For both reactions using **1e** and **2e** as substrates, the formed precipitate was isolated by filtration and washed with *n*-pentane, presumably yielding solid zwitterions **13e** and **14e** as colorless powders. Characterization of these compounds by NMR spectroscopy and HRMS, however, proved difficult. Solubility in nonpolar solvents was extremely poor and most polar solvents decomposed the compounds, likely because of their Lewis basicity, which competed for coordination at boron. The conjugated system of sulfur-through-carbon-to-boron may explain the high propensity for reversal to starting materials when oxygen-containing Lewis bases were introduced as solvents. The oxygen plausibly exchanges with bromide and coordinates to boron, reducing its Lewis acidity and therefore lowering the electron-accepting ability of the boron–carbon-π-system unit, resulting in simultaneous cleavage of the C–S and C–B bonds, reforming the alkyne.

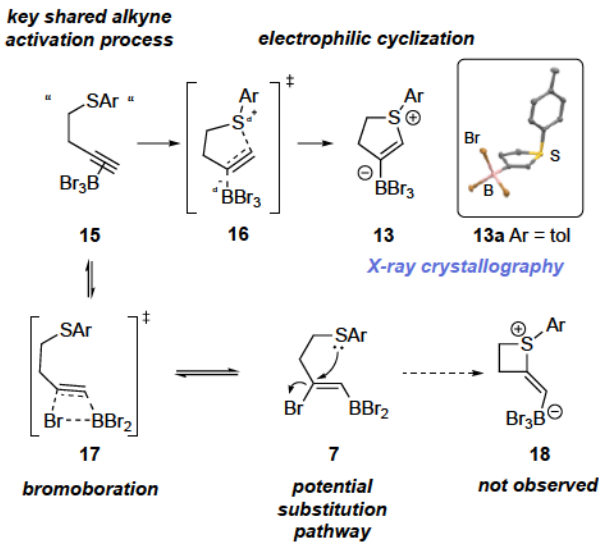
For example, methanol-d_4 dissolved the powder presumed to be pure compound **14e** but also resulted in competitive and eventually complete reversal to starting material **2e** (Scheme 4). A quickly acquired NMR spectrum nonetheless allowed for identification of the characteristic six diastereotopic alkyl protons with multiplets at 2.43, 2.50, 3.12, 3.41, 3.88 and 4.15 ppm, and an alkene signal at 6.76 ppm, indicating formation of cyclic sulfonium zwitterion **14e**. All remaining signals in the spectrum belonged to alkyne starting material with the characteristic terminal alkyne signal at 2.26 ppm. ^{1}H–^{13}C HSQC revealed coupling between alkene proton H_a and an invisible carbon signal due to coupling to boron which led to the assignment as the exo product with boron and terminal alkene proton on the same carbon. This outcome correlated with the stereoselectivity previously found for the group transfer reaction with ClBcat and 3-methylene alkynes.[13] (Regioselectivity of zwitterions **13** was ultimately shown to match the structure drawn in Scheme 4 by single-crystal X-ray crystallography of zwitterion **13a**, vide infra, Scheme 5.)

Scheme 4. Synthesis of Cyclic Sulfonium Zwitterions and ^{1}H NMR Spectrum Showing Reversion to Starting Material



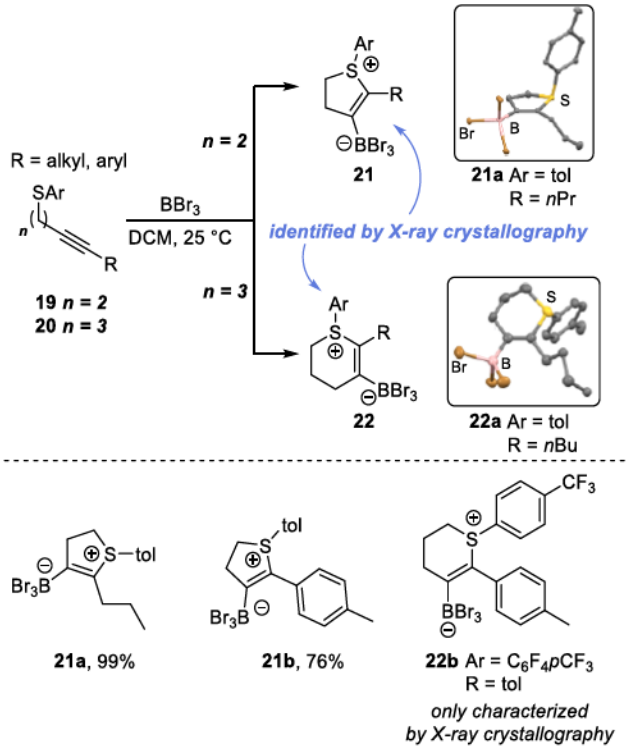
Typically, haloboration reactions regioselectively form the alkene with boron on the terminal carbon,[6] similar to that demonstrated with these substrates in Table 1. The 2-methylene substrates **1** also provided a suitable basis to disfavor the mechanistic possibility of a theoretical in-plane S_N2-type substitution reaction (Scheme 5).[23,24] An in-plane intramolecular S_N2-type substitution[23,24] of bromoalkene **7** would result in the exo 4-membered sulfonium product **18**, which was not observed. Therefore, alkynes **1** are likely to proceed through transition state **16**, in which boron is at the carbon from endo cyclization. Consistent with this regiochemical outcome was the structure of zwitterion **13a** as characterized by X-ray crystallography.

Scheme 5. Observed Regiochemistry Verifying the Mechanism; X-Ray Crystal Structure, with thermal ellipsoids shown at 50% probability (C, gray; Br, brown; B, pink; S, yellow)



Haloboration products derived from internal alkynes are established to be higher in energy[11] relative to their respective starting materials.[12] Drawing from this prior work, we envisioned that internal alkynes would therefore disfavor haloboration as a kinetic product, perhaps allowing for formation of cyclization products derived from internal alkynes to be formed as both the kinetic and thermodynamic product (contrary to the behavior of terminal alkynes)(Scheme 6). Indeed, both 2-methylene and 3-methylene *internal* alkynes underwent cyclization to form sulfonium zwitterions at 25 °C. Zwitterion **21a** was thermally stable when heated to 80 °C in $CDCl_3$ for 4 d. These tetrasubstituted alkenes crystallized from the reaction mixtures, which allowed for representative X-ray structural determination for compounds **21a** (99%), **22a** and **22b**, with the structure of solid **21b** (76%) assigned by analogy.

Scheme 6. Cyclization of Internal Alkynes; Thermal Ellipsoids Shown at 50% Probability (C, gray; Br, brown; B, pink; S, yellow)



Zwitterions **21a** and **21b** dissolved slightly in CD_2Cl_2, which allowed analysis by NMR spectroscopy. However, ^{1}H NMR spectroscopy of the crystalline solid of **22a** in CD_2Cl_2 revealed an almost 1:1 ratio of two sets of proton signals, potentially due to equilibration between 5- and 6-membered rings in solution. This equilibration seems plausible given that **22a** is the only compound characterized as a 6-membered ring in the solid state, suggesting that an alternative 5-membered ring analog (similar to other substrates) may be close in energy. In contrast to the observation for zwitterion **22a**, *n* = 2 compounds **21a** and **21b** only show endo cyclization to the 5-membered rings and show no evidence of equilibration to the 4-membered rings. These observations with internal alkynes are consistent with those described in Scheme 5 for terminal alkynes wherein 5-membered ring **13a** is formed, but 4-membered ring **18** is not observed. Together these data show that ring size determines regiochemical outcome.

Conclusion

Alkyne sulfides provided a platform to investigate haloboration reactions and competing electrophilic

cyclization reactions. At low temperatures, these compounds reacted selectively with BBr_3 to form haloboration products which were isolated as BF_3K salts. Heating these bromoboration products resulted in reversibility, such that bromoborated compounds could be used to generate cyclic sulfonium zwitterions. NMR spectroscopic analysis of reaction mixtures and X-ray structural analysis of the zwitterions revealed that the formation of sulfonium zwitterions is guided by a combination of Lewis acidity of the boron reagent, the tether length of the nucleophile, and electronic effects of the alkyne. Specifically, the higher the Lewis acidity of the boron reagent, the more prone the reaction is toward kinetic haloboration, eventually overcoming chain length as a determining factor, but not overcoming electronic effects that disfavor haloboration of internal alkynes. These data broaden the understanding of the interplay of boron Lewis acidity with reaction selectivity, and may allow for new approaches to implement the reversibility of haloboration in organic synthesis.

Experimental Section

General Methods

Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments (spectra in SI).

General Procedure A: Synthesis of Alkyne Thioether Substrates 1 and 2. Modifying a known procedure,[13] the arylthiol substrate (2.0 g), DMF (40 mL), and a stir bar were added into a 250 mL round bottom flask at ambient temperature. The flask was capped with a rubber septum, and fitted with a needle as a nitrogen inlet. In order to add solid K_2CO_3 (5 equiv), the needle was removed, the cap was briefly popped off, and the solid added. The cap and needle were replaced. After 5 min, the appropriate alkyne halide was added neat using a syringe. The reaction was heated to 65 °C in an oil bath, and stirred 12–16 h. After this time substantial solid (presumably salt) was visible in the flask. The mixture was diluted with diethyl ether (100 mL) and extracted with deionized water (2 × 100 mL). The resulting water extracts were back extracted with diethyl ether (1 × 50 mL). The combined ethereal extracts were dried over Na_2SO_4, decanted, concentrated under reduced pressure to give a crude thioether that was then subjected to further purification via column chromatography (100% hexanes, or hexanes–Et_2O, 0–2% gradient) to yield the analytically pure alkyne thioether. ^{1}H NMR spectra for these compounds matched those published previously.[13]

1-(5-Chloropent-1-yn-1-yl)-4-methylbenzene (**SI-1**). In a glovebox, copper(I)iodide (9.6 mg, 0.050 mmol, 0.041 equiv), dichlorobis(triphenylphosphine)palladium(II) (17.2 mg, 24.5 µmol, 0.020 equiv) and triphenylphosphine (13.4 mg, 51.1 µmol, 0.042 equiv) were dissolved in THF (0.5 mL). 1-Iodo-4-methylbenzene (300.1 mg, 1.376 mmol, 1.1 equiv) was dissolved in THF (0.2 mL). Both solutions were poured into a glass bomb. Under nitrogen atmosphere, 5-chloropent-1-yne (0.13 g, 0.13 mL, 1.2 mmol, 1.0 equiv) and nondried triethylamine (12 mL) were poured in the bomb. The reaction mixture was heated at 60 °C for 18 h. During that time, the reaction was monitored periodically by TLC (100% hexanes, UV) until the starting material was fully consumed. After the reaction mixture was cooled to ambient temperature, the mixture was quenched with saturated NH_4Cl solution (1 × 10 mL) and washed with DI water (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, and filtered via gravity filtration through glass wool. The filtrate was concentrated in vacuo. The crude product was purified via silica gel flash column chromatography with an elution gradient of 100% hexanes to 20% ethyl acetate–hexanes. Product-containing fractions were combined and concentrated in vacuo to yield alkyne (**SI-1**) as a colorless oil (160.7 mg, 67%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.60 (t, *J* = 6.7 Hz, 2H), 2.34 (s, 3H), 2.05 (quint, *J* = 6.5 Hz, 2H). This spectrum is in agreement with previously reported spectral data.[25]

(5-(p-Tolyl)pent-4-yn-1-yl)(4-(trifluoromethyl)phenyl)sulfane (3b) (**20b**). In a 10 mL round bottom flask, 4-(trifluoromethyl)benzenethiol (**SI-1**) (79.2 mg, 60.0 µL, 445 µmol, 1 equiv) was diluted in acetone (1 mL). K_2CO_3 (92.6 mg, 670 µmol, 1.51 equiv) was added to the flask. Under stirring condition, 1-(5-chloropent-1-yn-1-yl)-4-methylbenzene (93.9 mg, 487 µmol, 1.10 equiv) was added dropwise. The glass joints of an air condenser equipped with a finned aluminum jacket were greased and the air condenser was inserted into the round bottom flask. The top of the condenser was capped with a septum. An outlet needle was inserted into the septum. The reaction mixture was heated to reflux and stirred for five d. During that time the reaction was monitored periodically by TLC (100% hexanes, UV) until the starting material was fully consumed. After the reaction mixture was cooled to ambient temperature, the mixture was washed with DI water (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and filtered via gravity filtration through glass wool. The filtrate was concentrated in vacuo. The crude product was purified via silica gel flash column chromatography with an elution gradient of 100% hexanes to 20% ethyl acetate:hexanes. Product-containing fractions were combined and concentrated in vacuo to yield alkyne **20b** as a pale-yellow solid (99.9 mg, 67%). ^{1}H NMR (tol-d_8, 600 MHz): δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6,94 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 1.99 (s, 3H), 1.60 (quint, *J* = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (tol-d_8, 151 MHz): δ 142.7 (d, J_{C-F} = 1.5 Hz), 138.0, 131.9, 129.4, 127.5, 127.0 (q, J_{C-F} = 33 Hz), 125.8 (q, J_{C-F} = 3.7 Hz), 125.0 (q, J_{C-F} = 270 Hz), 121.3, 88.1, 82.5, 31.2, 28.1, 21.2, 18.7. ^{19}F NMR (tol-d_8, 565 MHz): δ −62.0 (s). HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for for $C_{19}H_{17}F_3S$ 334.1003, found 334.1007.

General Procedure B: Synthesis of Trifluoroborates 9 and 10 Employing BBr_3. In an oven-dried 20 mL glass vial, a stirbar was added, as was a solution of the thioether (1 equiv, on mmol scale detailed below) in DCM (3 mL). This solution was cooled in an ice-bath. The vial was capped with a rubber septum and fitted with a needle as a nitrogen inlet, and a second needle as a nitrogen outlet. The solution was cooled in an ice bath. A solution of BBr_3 (3.0 equiv, 1.0 M in DCM) was added. After addition of the BBr_3, the cold bath was removed, and the reaction was allowed to warm to ambient temperature. After 2 h, solid KHF_2 (10 equiv) was added to the solution and the solution was vigorously stirred for 30 min. ***Caution: deionized water was added very slowly drop-wise to the mixture and a highly exothermic reaction ensued! Waiting for reaction effervescence to stop between each drop is recommended.*** Once the reaction no-longer effervesced, as seen by lack of bubbles and no further heat generation, deionized water (5 mL) was

added to the vial. The vial was capped and then shaken. The resulting suspension was then placed in a −20 °C freezer for 2 h to settle. After 2 h, the mixture was removed from the freezer, allowed to thaw, and then the product was collected via vacuum filtration (PTFE, from a Williamson Microscale Kit). The filter cake was washed successively with hexanes (25 mL), deionized water (100 mL), cold diethyl ether (25 mL); alternatively, due to apparent higher solubility in ether, compounds containing fluoro- and trifluoromethyl substituents were washed with hexanes (25 mL), deionized water (100 mL) and cold diethyl ether (5 mL). The solids were scraped from the filter, and transferred to a glass watch glass or beaker to dry at ambient temperature and pressure for 12–16 h. *Note: the filtration flask was charged with KOH (25 mL, 2.0 M) prior to filtration to neutralize any HF in the filtrate to avoid glass etching.*

Potassium(Z)-(2-bromo-4-(p-tolylthio)but-1-en-1-yl)trifluoroborate (**9a**). Performing General Procedure B employing thioether **4a** (254.9 mg, 1.446 mmol, 1.00 equiv), BBr_3 (4.34 mL, 4.34 mmol, 3.00 equiv) and KHF_2 (1.13 g, 14.5 mmol, 10.0 equiv) to yield 509 mg (97%) of **9a** as a white solid. MPt. > 260 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ 7.29–7.26 (m, 2H), 7.15–7.13 (m, 2H), 5.83 (m, 1H), 3.08–3.05 (m, 2H), 2.62–2.59 (m, 2H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 137.1, 137.0, 134.3, 134.2, 130.99, 130.98, 130.82, 130.77, 46.4, 46.3, 33.9, 30.8, 21.39, 21.38. ^{11}B NMR (192 MHz, acetone-d_6): δ 1.8 (quartet, *J* = 53 Hz). ^{19}F NMR (565 MHz, acetone-d_6): δ −139.0 (multiplet). HRMS (ES-TOF) *m*/*z* $[M+K]^+$ calcd for $C_{11}H_{12}BBrF_3K_2S$ 402.9144, found 402.9156.

Potassium(Z)-(2-bromo-4-((3-chlorophenyl)thio)but-1-en-1-yl)trifluoroborate (**9b**). Compound **9b** was synthesized by two different methods, one of these methods employed BBr_3 as the Lewis acid and the second method employed BrBcat. Both electrophiles produced the same final product. **Method 1:** Performing General procedure B employing thioether **1b** (256.0 mg, 1.302 mmol, 1.00 equiv), BBr_3 (3.90 mL, 3.90 mmol, 3.00 equiv) and KHF_2 (1.021 g, 13.07 mmol, 10.04 equiv) to yield 489.1 mg (97%) of **9b** as a white solid. **Method 2:** In a glovebox, under an atmosphere of nitrogen, a 20 mL vial was charged with a stirbar and thioether **1b** (246.9 mg, 1.26 mmol, 1.00 equiv) was dissolved in 5 mL of dry toluene and solid BrBcat (909.1 mg, 3.77 mmol, 3.00 equiv.) was added to the mixture and allowed to reflux for 48 h. The solution was allowed to cool to ambient temperature and solid KHF_2 (994.1 mg, 12.7 mmol, 10.1 equiv) was added to the mixture and stirred for an additional 30 min, then deionized water was slowly added until the reaction stopped effervescing heat and gas bubbles. The solid was collected via vacuum filtration, then washed with hexanes (25 mL), deionized water (50 mL) and ether (25 mL). The resulting off-white solid could then be washed with a minimum amount of dichloromethane to remove a tannish-brown impurity to yield 72.2 mg (15%) of **9b** as a white solid. MPt. > 260 °C. ^{1}H NMR (700 MHz, acetone-d_6): δ 7.38 (t, *J* = 1.4 Hz, 1 H), 7.34 (dd, *J* = 7.7, 15.4 Hz, 1 H), 7.30 (dt, *J* = 1.4 Hz, 8.4 Hz), 7.19 (ddd, *J* = 1.4, 2.1, 7.7 Hz, 1H), 5.87 (quartet, *J* = 3.5 Hz, 1H), 3.19–3.15 (m, 2H), 2.63–2.68 (m, 2H). ^{13}C{^{1}H} NMR (175 MHz, acetone-d_6): δ 141.2, 135.8, 131.9, 128.7, 127.8, 126.9, 46.1, 32.9. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.5 (quartet, *J* = 53 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −139.0 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{10}H_9BBrClF_3K_2S$ $[M+K]^+$ 422.8616, found 422.8612.

Potassium(Z)-(2-bromo-4-((4-(trifluoromethyl)phenyl)thio)but-1-en-1-yl)trifluoroborate (**9c**). Performing General Procedure B employing thioether **1c** (248 mg, 1.08 mmol, 1.00 equiv), BBr_3 (3.24 mL, 3.24 mmol, 3.00 equiv) and KHF_2 (852.0 mg, 10.91 mmol, 10.1 equiv) to yield 426.1 mg (95%) **9c** as a white solid. MPt. > 260 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 5.89 (quartet, *J* = 3.6 Hz, 1H), 3.25–3.21 (m, 2H), 2.71–2.68 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 144.6 (quartet, J = 1.5 Hz), 128.4, 128.0, 127.8, 127.75, 127.71, 127.6, 127.3, 126.9 (quartet, *J* = 3.9 Hz), 126.8, 125.0, 45.6, 31.9, 30.8. ^{11}B NMR (192 MHz, acetone-d_6): δ 1.4 (quartet, *J* = 49 Hz). ^{19}F NMR (565 MHz, acetone-d_6): δ −62.8, −139.1. HRMS (ES-TOF) *m*/*z* calcd for $C_{11}H_9BBrF_6K_2S$ $[M+K]^+$ 453.8916, found 453.8914.

Potassium(Z)-(2-bromo-4-((4-fluorophenyl)thio)but-1-en-1-yl)trifluoroborate (**9d**). Performing General Procedure B employing thioether **1d** (251 mg, 1.39 mmol, 1.00 equiv), BBr_3 (4.17 mL, 4.17 mmol, 3.00 equiv) and KHF_2 (1.085 g, 13.9 mmol, 10.0 equiv) to yield 495 mg (97%) **9d** as a white solid. MPt. > 260 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.47–7.42 (m, 2H), 7.14–7.08 (m, 2H), 5.83 (quartet, *J* = 3.5 Hz, 1H), 3.10–3.06 (m, 2H), 2.17–2.58 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 163.4, 161.5, 160.4, 132.83, 132.80, 132.7, 132.6, 116.8, 116.7, 45.8, 34.0. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.51 (quartet, *J* = 60 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −118.0, −139.2 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{10}H_9BBrF_4K_2S$ $[M+K]^+$ 404.8914, found 404.8916.

Potassium(Z)-(2-bromo-4-((4-bromophenyl)thio)but-1-en-1-yl)trifluoroborate (**9e**). Compound **9e** was synthesized by two different methods, one of these methods employed BBr_3 as the Lewis acid and the second method employed BrBcat. Both electrophiles produced the same final product. **Method 1:** Performing General Procedure B employing thioether **1e** (270.3 mg, 1.121 mmol, 1.00 equiv), BBr_3 (3.36 mL, 3.36 mmol, 3.00 equiv) and KHF_2 (877.0 mg, 11.23 mmol, 10.0 equiv) to yield 456.0 mg (95%) **9e** as a white solid. **Method 2:** In a glovebox, under an atmosphere of nitrogen, a 20 mL vial was charged with a stirbar and thioether **1e** (159.2 mg, 0.660 mmol, 1.00 equiv) was dissolved in 5 mL of dry toluene and solid BrBcat (400.1 mg, 2.01 mmol, 3.05 equiv) was added to the mixture and allowed to reflux for 48 h. The solution was allowed to cool to ambient temperature and solid KHF_2 (522.0 mg, 6.68 mmol, 10.1 equiv) was added to the mixture and stirred for an additional 30 min, then deionized water was slowly added until the reaction stopped effervescing heat and gas bubbles. The solid was collected via vacuum filtration, then washed with hexanes (25 mL), deionized water (50 mL) and diethyl ether (25 mL). The resulting off-white solid was then washed with a minimum amount of dichloromethane to remove a tannish-brown impurity to yield 112.9 mg (40%) **9e** as a white solid. MPt. > 260 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.51–7.46 (m, 2H), 7.34–7.29 (m, 2H), 5.86 (quartet, *J* = 3.5 Hz, 1H), 3.15–3.11 (m, 2H), 2.65–2.63 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 137.5, 132.8, 131.1, 119.6, 45.6, 32.7. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.4 (quartet, *J* = 51 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −139.2 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{10}H_9BBr_2F_3KS$ $[M+K]^+$ 463.8147, found 463.8157.

Potassium(Z)-(2-bromo-5-(p-tolylthio)pent-1-en-1-yl)trifluoroborate (**10a**). Performing General Procedure B employing thioether **2a** (243 mg, 1.28 mmol, 1.00 equiv),

BBr_3 (3.83 mL, 3.83 mmol, 3.00 equiv) and KHF_2 (1.013 g, 13.0 mmol, 10.1 equiv) to yield 437.5 mg (91%) **10a** as a white solid. MPt. = 160 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.26 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 5.80 (quartet, *J* = 4.2 Hz, 1H), 2.93–2.89 (m, 2H), 2.49 (t, *J* = 7 Hz, 2H), 1.82 (quint, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 136.9, 134.3, 131.1, 131.0, 130.9, 130.8, 129.9 (quartet, *J* = 4.5 Hz), 45.0, 33.4, 29.1, 21.4. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.6 (quartet, *J* = 56 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −139.0 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{12}H_{14}BBrF_3K_2S$ [M+K]$^+$; 414.9321, expt. 414.9317.

Potassium(Z)-(2-bromo-5-((3-chlorophenyl)thio)pent-1-en-1-yl)trifluoroborate (**10b**). Performing General Procedure B employing thioether **2b** (259.4 mg, 1.230 mmol, 1.00 equiv), BBr_3 (3.70 mL, 3.70 mmol, 3.01 equiv) and KHF_2 (962.4 mg, 12.32 mmol, 10.0 equiv) to yield 475.1 mg (99%) **10b** as a white solid. MPt. > 260 °C. ^{1}H NMR (700 MHz, acetone-d_6): δ 7.35 (t, *J* = 1.4 Hz, 1H), 7.31 (dd, *J* = 7.7, 15.4 Hz, 1H), 7.29 (dt, *J* = 1.4, 7.7 Hz, 1H), 7.18 (ddd, *J* = 1.4, 2.1, 7.7 Hz, 1H), 5.83 (quartet, *J* = 3.5 Hz, 1H), 3.03–3.00 (m, 2H), 2.51 (t, *J* = 7 Hz, 2H), 1.87 (quint, *J* = 7 Hz, 2H). ^{13}C{^{1}H} NMR (175 MHz, acetone-d_6): δ 141.1, 135.6, 131.7, 129.3, 128.6, 127.6, 126.6, 45.1, 32.2, 28.8. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.5 (quartet, *J* = 67 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −139.0 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{11}H_{11}BBrClF_3K_2S$ [M+K]$^+$ 436.8752, found 436.8753.

Potassium(Z)-(2-bromo-5-((4-(trifluoromethyl)phenyl)thio)pent-1-en-1-yl)trifluoroborate (**10c**). Performing General Procedure B employing thioether **2c** (267.1 mg, 1.09 mmol, 1.00 equiv), BBr_3 (3.28 mL, 3.28 mmol, 3.01 equiv) and KHF_2 (857.3 mg, 10.98 mmol, 10.1 equiv) to yield 401.6 mg (97%) **10c** as a white solid. MPt. > 260 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ 7.61 (d, *J* = 8 Hz, 2H), 7.51 (d, *J* = 8 Hz, 2H), 5.86–5.80 (m, 1H), 3.07 (t, *J* = 7 Hz, 2 H), 2.53 (t, *J* = 7 Hz, 2H), 1.91 (quint, *J* = 7 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 144.7, 129.6 (multiplet), 128.6, 128.4, 127.6 (quartet, *J* = 33 Hz), 126.9 (quartet, *J* = 4.5 Hz), 126.8, 125.0, 123.2, 45.0, 31.3, 30.8, 28.7. ^{11}B NMR (192 MHz, acetone-d_6): δ 1.4 (quartet, *J* = 54 Hz). ^{19}F NMR (565 MHz, acetone-d_6): δ −62.8, −139.0 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{12}H_{11}BBrF_6K_2S$ [M+K]$^+$ 470.9018, found 470.9010.

Potassium(Z)-(2-bromo-5-((4-fluorophenyl)thio)pent-1-en-1-yl)trifluoroborate (**10d**). Performing General Procedure B employing thioether **2d** (243.6 mg, 1.21 mmol, 1.00 equiv), BBr_3 (3.62 mL, 3.62 mmol, 3.00 equiv) and KHF_2 (956.0 mg, 12.2 mmol, 10.1 equiv) to yield 460.4 mg (99%) **10d** as a white solid. MPt. > 260 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.45–7.40 (m, 2H), 7.13–7.07 (m, 2H), 5.80 (quartet, *J* = 3.5 Hz, 1H), 2.95–2.91 (m, 2H), 2.49 (t, *J* = 7 Hz, 2H), 1.82 (quint, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ 163.5, 162.0, 133.37, 133.5, 133.02, 132.97, 129.5 (multiplet), 117.2, 117.0, 45.0, 33.9, 29.0. ^{11}B NMR (160 MHz, acetone-d_6): δ 1.6 (quartet, *J* = 59 Hz). ^{19}F NMR (470 MHz, acetone-d_6): δ −118.2, −139.0. HRMS (ES-TOF) *m*/*z* calcd for $C_{11}H_{11}BBrF_4K_2S$ [M+K]$^+$ 417.9105, found 417.9106.

Potassium(Z)-(2-bromo-5-((4-bromophenyl)thio)pent-1-en-1-yl)trifluoroborate (**10e**). Performing General Procedure B employing thioether **2e** (256 mg, 1.00 mmol, 1.00 equiv), BBr_3 (2.00 mL, 2.00 mmol, 2.00 equiv) and KHF_2 (801.0 mg, 12.2 mmol, 10.1 equiv) to yield 377 mg (85%) **10e** as a white solid. ^{1}H NMR (600 MHz, acetone-d_6): δ 7.49–7.45 (m, 2H), 7.32–7.28 (m, 2H), 5.81 (quartet, *J* = 3.6 Hz, 1H), 2.99–2.96 (m, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.82 (quint, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 138.00, 137.99, 137.98, 133.1, 131.4, 129.5 (multiplet), 119.9, 119.84, 119.83, 32.5, 30.8, 28.8. ^{11}B NMR (192 MHz, acetone-d_6): δ 1.6 (quartet, *J* = 54 Hz). ^{19}F NMR (565 MHz, acetone-d_6): δ −138.9 (multiplet). HRMS (ES-TOF) *m*/*z* calcd for $C_{11}H_{11}BBr_2F_3K_2S$ [M+K]$^+$ 480.8249, found 480.8263.

Synthesis of alkene 11 to characterize chemoselectivity (group transfer). Alkene **11** was synthesized using a known procedure.[13] 2D spectra available in SI. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59–7.58 (m, 2H), 7.39–7.38 (m, 2H), 7.20–7.19 (m, 2H), 7.08–7.06 (m, 2H), 5.19 (s, 1H), 3.55 (t, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.32 (quint, *J* = 7.5 Hz, 2H).

Mechanistic Study of Reversibility. Alkyne **2e** (27.4 mg, 1.00 equiv, 107 µmol) was weighed into a dry J. Young tube and the NMR tube was transferred into the glovebox. Then, phenanthrene (3.83 mg, 21.5 µmol, 0.20 equiv) and dry toluene-d_8 (0.5 mL) were added, and the NMR tube was closed with a PTFE screw stopper. A starting ^{1}H NMR spectroscopic measurement was taken of the clear slight yellow solution.

The J. Young tube was taken into the glovebox and BBr_3 (120 µL, 1.0 M in DCM, 30. mg, 120 µmol, 1.1 equiv) solution was added at 25 °C. The solution turned orange–brown immediately. The mixture was left at 25 °C for 1 h after which another ^{1}H NMR spectroscopy measurement was taken. The sample was heated to 100 °C for 3 h during which lots of solid formed then left at 25 °C overnight. Then, another ^{1}H NMR spectroscopy measurement was taken, followed by heating the sample to 100 °C for 24 h after which the last ^{1}H NMR spectroscopy measurement was taken. All spectra were obtained at 600 MHz with solvent suppression for the DCM signal from the BBr_3 reagent. Unfortunately, phenanthrene as an intended internal standard appeared not completely inert under these conditions, as its signals started showing signs of decomposition.

(E)-tribromo((1-(4-bromophenyl)tetrahydro-2H-thiophen-1-ium-2-ylidene)methyl)borate (**14e**). In a dry glass bomb with a stir bar thioether **2e** (255 mg, 1.00 mmol, 1 equiv) was degassed and dissolved in toluene (10 mL). The yellow solution was cooled to 0 °C and BBr_3 (2.0 mL, 1.0 M in DCM, 500 mg, 2.0 mmol, 2.0 equiv) solution was added. Immediate precipitation of orange solid which slowly turned to brown oil at 0 °C was observed. Using a counter stream of nitrogen a reflux condenser was attached and the reaction mixture was stirred and heated to 120 °C for 46 h. The reaction mixture (grey solid in red/brown solution) was cooled to 25 °C and 5 mL dry $CHCl_3$ was added. The solid then was filtered, washed with 5 mL $CHCl_3$ and 2 × 5 mL hexanes followed by drying on high vacuum to yield **14e** as grey powder (278 mg, 550 µmol, 55%). The solid was poorly soluble in most solvents. Methanol allowed measurement of a ^{1}H NMR spectrum but also results in reversal to starting material **2e**. ^{1}H NMR (CD_3OD, 600 MHz): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 2.1 Hz, 1H), 4.18–4.12 (m, 1H), 3.89–3.84 (m, 1H), 3.43–3.37 (m, 1H), 3.19–3.08 (m, 1H), 2.53–2.38 (m, 2H). HRMS attempted, but the molecular ion was not found, possibly due to reversion of the product to starting alkyne under MS conditions.

Synthesis of 12 and 13a for Single-Crystal X-Ray Analysis. *Tetrabutylammonium(Z)-(4-bromo-2-((4-*

bromophenyl)thio)but-1-en-1-yl)trifluoroborate (**12**). Potassiumtrifluoroborate **9e** (100. mg, 234 µmol, 1 equiv) was dissolved in dry DCM (1 mL) in a 1 dram vial and tetrabutylammonium chloride (64.9 mg, 234 µmol, 1 equiv) was added and the vial was capped. The original solid slowly dissolved and the solution turned cloudy from precipitation of KCl. The vial was left at ambient temperature for the KCl to settle for 24 h. The solution above the settled solid was then decanted into another vial where it was left to slowly evaporate, yielding an oily solid. The oily residue was layered with Et_2O and left at 25 °C for 6 d which resulted in formation of colorless crystals. The crystals were analyzed by X-ray diffraction to reveal **12**. Analysis of the solid by NMR spectroscopy showed **12** with approximately 10% contamination with tetrabutylammonium fluoride and tetrafluoroborate.

Tribromo(1-(p-tolyl)-4,5-dihydro-1H-thiophen-1-ium-3-yl)borate (**13a**). In a dry glass bomb with a stir bar thioether **1a** (350 mg, 1.0 equiv, 2.0 mmol) was degassed and dissolved in toluene (4 mL). The yellow solution was cooled to 0 °C and BBr_3 (4.0 mL, 1.0 M in DCM, 4.0 mmol, 2.0 equiv) solution was added. Using a counter stream of N_2 a reflux condenser was attached and the reaction mixture was stirred and heated to 130 °C for 72 h. The reaction formed a red-brown oil with clear yellow solution above. All volatiles were removed on high vac and the flask was taken into the glovebox. The oil was then dissolved in 2 mL of DCM and 20 mL pentane was added to wash the product. The mixture remained a biphasic oil-liquid mixture. The pentane was left in the flask for impurities to diffuse into it. After 3 d the solution was decanted, the residual oil dissolved in 2 mL of DCM and 20 mL pentane was added. After 7 d colorless crystals formed from the oil which were analyzed by X-ray diffraction to reveal **13a**.

Synthesis of internal alkyne substrates 19 and 20. Substrates **19a** and **19b** were synthesized using a known procedure.[13]

p-Tolyl(4-(p-tolyl)but-3-yn-1-yl)sulfane (**19b**). In a dry round bottom flask under N_2 atmosphere with a stir bar and a septum, 1-iodo-4-methylbenzene (2.23 g, 10.2 mmol, 1.50 equiv), copper(I)iodide (130 mg, 683 µmol, 0.10 equiv) and dichlorobis(triphenylphosphine)palladium (239 mg, 0.05 equiv, 0.340 mmol) were dissolved in triethylamine (20.5 mL) that had been sparged with N_2 for 15 min. While stirring, but-3-yn-1-yl(*p*-tolyl)sulfane (1.20 g, 6.81 mmol, 1 equiv) was added dropwise to the yellow solution, which then turned dark brown. The reaction mixture was stirred for 19 h at 25 °C. The reaction mixture was quenched with 5 mL H_2O and the resulting solution was transferred to a 125 mL separatory funnel. The aqueous mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were then washed with sat. NH_4Cl solution (1 × 20 mL) and brine (1 × 20 mL), dried over Na_2SO_4 and filtered. The crude product was solid-loaded purified via silica gel flash column chromatography with an elution gradient of 100% hexanes to 20% ethyl acetate–hexanes. Product-containing fractions were combined and concentrated in vacuo to yield **19b** as colorless solid (1.24 g, 4.65 mmol, 68%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 6H). ^{13}C{^{1}H} ($CDCl_3$, 600 MHz): δ 140.0, 136.9, 131.8, 131.6, 131.1, 129.9, 129.1, 120.5, 87.7, 81.9, 33.9, 21.6, 21.2, 20.7. HRMS (ES-TOF) *m*/*z* [M+Na]$^+$ calcd for $C_9H_{10}SNa$ 289.1027, found 289.1029.

Synthesis of Sulfonium Zwitterion Compounds 21 and 22.

Tribromo(2-propyl-1-(p-tolyl)-4,5-dihydro-1H-thiophen-1-ium-3-yl)borate (**21a**). In the glovebox, hept-3-yn-1-yl(p-tolyl)sulfane (**19a**)(43.7 mg, 1.00 equiv, 0.200 mmol) was weighed into a J. Young tube and dissolved in CD_2Cl_2 (0.5 mL). Then, BBr_3 (0.20 mL, 1.0 M in DCM, 50mg, 0.20 mmol, 1.0 equiv) was added and the tube was capped. The solution turned yellow immediately and in situ ^{1}H NMR spectroscopy showed complete consumption of starting material. The reaction mixture was left at 25 °C for 18 h, then transferred into a 1 dram vial. The 1 dram vial was placed into a scintillation vial containing pentane for diffusion crystallization. The vial was capped and cooled to −36 °C. The clear colorless solution was left at −36 °C for 5 d, after which a substantial quantity of clear colorless crystals formed. The mixture was filtered and evaporation of the volatiles on a glass filter frit yielded **21a** as colorless crystals (93.6 mg, 99%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 3.91–3.77 (m, 3H), 3.49–3.43 (m, 1H), 3.34–3.29 (m, 1H), 2.47 (s, 3H), 2.14–2.08 (m, 1H), 1.62–1.50 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) δ 147.0, 132.7, 130.4, 129.7, 122.2, 45.1, 44.0, 31.4, 22.5, 22.0, 14.0. ^{11}B NMR (193 MHz, CD_2Cl_2) δ −10.8. HRMS attempted, but the molecular ion was not found, possibly due to reversion of the product to starting alkyne under MS conditions.

Tribromo(1,2-di-p-tolyl-4,5-dihydro-1H-thiophen-1-ium-3-yl)borate (**21b**). In the glovebox, *p*-tolyl(4-(p-tolyl)but-3-yn-1-yl)sulfane (**19b**) (90.0 mg, 338 µmol, 1.00 equiv) was weighed into a glass bomb and dissolved in DCM (2 mL). Then BBr_3 (1.0 mL, 1.0 M in DCM, 250 mg, 1.0 mmol, 3.0 equiv) was added. The exothermic reaction caused DCM to boil briefly. The clear colorless solution was left at room temperature for 28 d, after which a substantial quantity of clear, colorless crystals formed. The mixture was filtered and evaporation of the volatiles on a glass filter frit yielded **21b** as colorless crystals (132 mg, 76%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.32–4.26 (m, 1H), 4.19–4.13 (m, 1H), 4.04–3.98 (m, 1H), 3.47–3.43 (m, 1H), 2.44 (s, 3H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) δ 147.1, 140.4, 132.5, 131.1, 130.5, 129.1, 128.2, 122.3, 45.5, 43.9, 21.8, 21.5. ^{11}B NMR (193 MHz, CD_2Cl_2) δ −10.9. HRMS attempted, but the molecular ion was not found, possibly due to reversion of the product to starting alkyne under MS conditions.

Tribromo(2-butyl-1-(p-tolyl)-1,4,5,6-tetrahydrothiopyrylium-3-yl)borate (**22a**). In the glovebox, dissolved non-4-yn-1-yl(p-tolyl)sulfane (**20a**) (24.6 mg, 0.100 mmol, 1.00 equiv) in toluene (0.5 mL) in a 1 mL dram vial and added BBr_3 (25.1 mg, 100 µL, 1.0 M in DCM, 100 µmol, 1.0 equiv). The vial was capped and left at 25 °C which resulted in no crystallization. The vial was then cooled to −36 °C for 7 d. The resulting colorless crystals were analyzed X-ray diffraction. The mother liquor was decanted, the crystalline solid rinsed with pentane, filtered and dried on a glass filter frit to give tribromo(2-butyl-1-(p-tolyl)-1,4,5,6-tetrahydrothiopyrylium-3-yl)borate (44.1 mg). HRMS attempted, but the molecular ion was not found, possibly due to reversion of the product to starting alkyne under MS conditions. Solubility appears to be accompanied by chemical change as shown in an example set of ^{1}H and ^{11}B NMR spectra in the SI (pages S99 and S100).

Tribromo(2-(p-tolyl)-1-(4-(trifluoromethyl)phenyl)-1,4,5,6-tetrahydrothiopyrylium-3-yl)borate (**22b**). In the glove box, (5-(p-tolyl)pent-4-yn-1-yl)(4-(trifluoromethyl)phenyl)sulfane (**20b**) (33.3 mg, 0.10 mmol, 1.00 equiv) is dissolved in DCM (1 mL). To the vial, BBr_3 (100 µL, 1.0 M in DCM, 0.10 mmol, 1.0 equiv) was added dropwise. The reaction mixture was left at ambient temperature. After 1 d, the vial was placed in the freezer at −36 °C. After 5 d, the mother liquor was decanted and the crystalline residue dried on a glass filter frit to give **22b** as colorless crystals (37.0 mg). HRMS attempted, but the molecular ion was not found, possibly due to reversion of the product to starting alkyne under MS conditions.

ASSOCIATED CONTENT

Notes

The authors declare no competing financial interest.

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General considerations; single crystal X-ray structure information; NMR spectra (PDF)

FAIR data, including the primary NMR FID files for new compounds, two-dimensional spectroscopy for structure determination and NMR spectroscopy experiments (ZIP)
Accession Codes

CCDC 2283752**,** 2283753, 2283754, 2283755 and 2283756 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

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