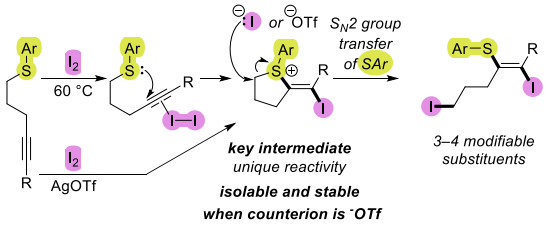
Iodination–Group-Transfer Reactions to Generate Trisubstituted Iodoalkenes with Regio- and Stereochemical Control

Joseph A. Kaplan and Suzanne A. Blum*

Department of Chemistry
University of California, Irvine
Irvine, CA 92697, United States

Supporting Information Placeholder



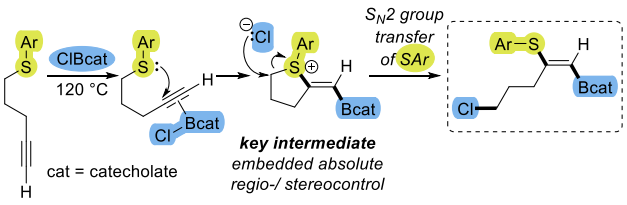
ABSTRACT: The regio- and stereodefined synthesis of trisubstituted alkenes remains a significant synthetic challenge. Herein, a method is developed for producing regio- and stereodefined trisubstituted iodoalkenes by diverting intermediates from an iodination–electrophilic-cyclization mechanism. Specifically, cyclized sulfonium ion-pair intermediates are diverted to alkenes by ring-opening with nucleophilic iodide. Alternatively, scavenging of the iodide by AgOTf prevents ring-opening, enabling isolation of the sulfonium ion-pair intermediate. Isolation of the ion pair enables access to complementary reactivity, including ring-opening by alternative nucleophiles (i.e., amines), yielding trisubstituted acyclic alkenes and an example acyclic tetrasubstituted alkene. X-ray crystallographic determination of reaction intermediates and products confirm the initial electrophilic-cyclization step sets the stereo- and regiochemistry of the product. The products serve as synthetic building blocks by readily participating in downstream functionalization reactions, including oxidation, palladium-catalyzed cross-coupling, and nucleophilic displacement.

Introduction

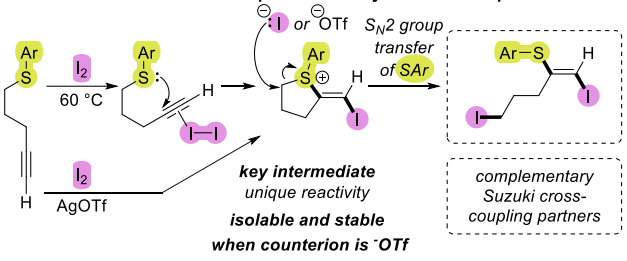
Trisubstituted alkenes play a central role in imparting desirable properties to pharmaceuticals,[1,2] natural products,[3] and organic materials.[4] Furthermore, these alkenes serve as potent synthetic intermediates, especially in cases where the regio- and stereochemical information in the starting alkene is transferred to the resulting products.[5–7] As such, methods for producing trisubstituted alkenes with regio- and stereochemical control are crucial. However, generating regio- and stereodefined trisubstituted alkenes remains a significant synthetic challenge.[8–13]

Herein, a known class of electrophilic-cyclization reactions[14–20] is mechanistically modified by intercepting the cyclized intermediates via nucleophilic ring opening with simultaneous group transfer,[21,22] in order to produce trisubstituted alkenes with regio- and stereochemical control. This ring-opening of the cyclized intermediate provides a mechanistic alternative to (i.e., "interruption of"[23]) the well-established "Larock-type" pathway of electrophilic-cyclization dealkylation.[14–21] In previous work, the first example of this electrophilic-cyclization–group-transfer was demonstrated with boron as the electrophile, generating trisubstituted borylated alkenes with regio- and stereocontrol (Scheme 1a).[22] The term "group transfer" in this context refers to the transfer of the SAr group to a different carbon during the reaction. We hypothesized that the mechanistic concept may be applicable to a broader range of electrophiles. Now, investigating additional electrophiles has led to the discovery of an iodination–group-transfer reaction that produces trisubstituted iodoalkenes with regio- and stereochemical control (Scheme 1b).

a. Previous work: Borylative Electrophilic Heterocyclization/Group-Transfer



b. This work: Iodination Electrophilic Heterocyclization/Group-Transfer



Scheme 1. Group transfer reactions.

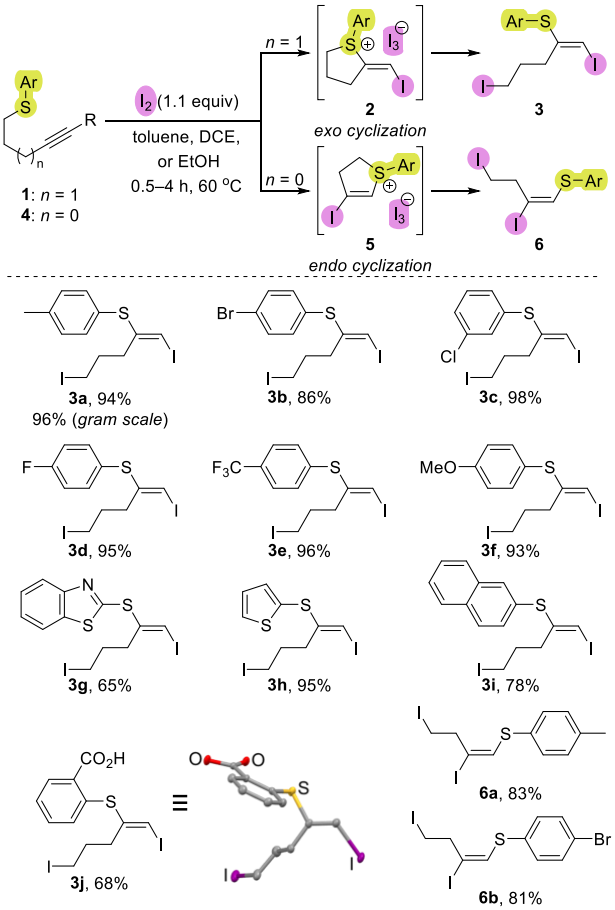
These iodinated products provide complementary reactivity in metal-catalyzed cross-coupling reactions (by acting as oxidative addition partners) to the aforementioned borylated alkenes (which act as transmetallation partners). Additionally, isolation of the key ion-pair intermediate led to mechanistic insight and accessed reactivity not available to the final group-transfer product. Iodine as a reagent is also amenable to synthesis on scale.[24,25]

In one synthetic step, this iodination–group-transfer reaction produces an alkenyl iodide, an alkyl iodide, and an alkenyl sulfide, valuable building blocks for synthesis (Scheme 1b). Alkenyl sulfides are present in antibacterials,[1,2,26,27] or alternatively participate in cross-coupling reactions through C–S cleavage.[28,29] Iodoalkenes are amenable to a suite of functionalization reactions, including cross-coupling reactions.[30–34]

Results and Discussion

Studies examined the iodination–group-transfer reaction on starting materials with two different chain lengths separating the nucleophilic sulfur from the alkyne: a three-methylene chain (**1**) and a two-methylene chain (**4**) (Scheme 2). Starting material **1** was obtained in one step from a substitution reaction of 5-chloro-1-pentyne with the corresponding thiol nucleophile in good yields. Starting material **4** was similarly obtained from 4-bromo-1-butyne or 1-hydroxy-3-heptyne. High yields of iodination–group transfer products **3** and **6** were achieved at 60 °C in 0.5–4 h in toluene, ethanol, or dichloroethane. Full conversion of starting materials was achieved with a slight excess (1.1 equiv) of I_2.

The substrate scope is shown in Scheme 2, with product alkenes generated in moderate-to-excellent yields (65–98%), including on the gram scale (**3a**; 96%). The reaction was compatible with a range of aryl and heteroaryl groups on sulfur; *S*-alkyl groups were expressly avoided to intentionally deviate from traditional Larock-type demethylation/dealkylation pathways. Diiodinated product **3e** (96%) is noteworthy due to its high yields when compared to otherwise similar group transfer reactions attempted with ClBcat, which were lower yielding, presumably due to decomposition of material at the high heat required for the boron-based reaction (120 °C).[22] Product **3g** (65%) is notable as benzothiazoles are desirable functionalities in pharmaceuticals.[35] Product **3j** (68%) shows that the reaction is compatible with acidic functional groups. The relatively lower isolated yield of **3j** was accounted for by decomposition during recrystallization, plausibly caused by reversion to the reaction intermediate and alkyne starting material.



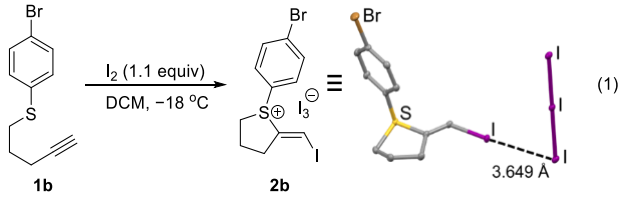
Scheme 2. Overall group-transfer reaction and substrate scope, yielding diiodides **3** and **6**. X-ray crystal structure of **3j**, with thermal ellipsoids shown at 50% probability (C, gray; I, purple; O, red; S, yellow).

X-ray crystallographic characterization showed that the regiochemistry and stereochemistry of **3j** are consistent with the two-step mechanism of cyclization–ring-opening with concurrent sulfur-group-transfer as shown in Scheme 2. Similar regiochemical outcomes were previously observed with boron electrophiles.[22]

To further investigate the mechanism of this reaction, substrate **1b** was subjected to otherwise identical reaction conditions but at reduced temperature, −18 °C, in DCM (eq 1). Under these conditions, magenta crystals formed. This brightly colored and insoluble material was plausibly a reaction intermediate, given the comparatively high solubility and lack of color of corresponding product **3b**. Single-crystal X-ray diffraction revealed sulfonium triiodide salt **2b**. This crystal structure provided further evidence of proposed cyclized intermediates of class **2** and supported that the stereo- and regiochemistry of the reaction is dictated by the stereo- and regiochemistry of the cyclized sulfonium intermediate; no yield was obtained for **2b**, as single crystal was used for identification (thermal ellipsoids shown at 50% probability). A previously characterized "frozen" boron zwitterion[22] provided structural analogy to likely reaction intermediates; however, intermediate **2b** is plausibly directly along the reaction coordinate for the electrophilic-cyclization–group-transfer reaction, providing previously missing mechanistic support for this class of reactions.

Despite the starting stoichiometry of 1.1 equiv of I_2-to-**1b**, the I_3^- counterion of **2b** suggests an alternative kinetic order with dependence on 2 equivalents of I_2. This intermediate

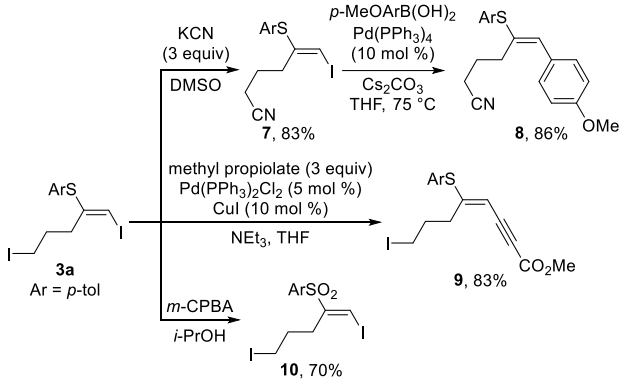
suggests that I_2 might catalyze the reaction by stabilizing I^- in solution to form **2b**, a process also observed with bromination of alkenes and alkynes with Br_2.[36,37] With 3.649 Å, the distance between the alkenyl iodine and the closest iodine on I_3^- is less than the combined van der Waals radii of two iodine atoms, indicating an intermolecular interaction. This structure thus plausibly shows the residual interaction of stabilization of the iodide during electrophilic attack by the second equivalent of I_2, similar to that attributed to bromonium and Br_3^- in the crystal structure of a bromination intermediate.[37]



(1)

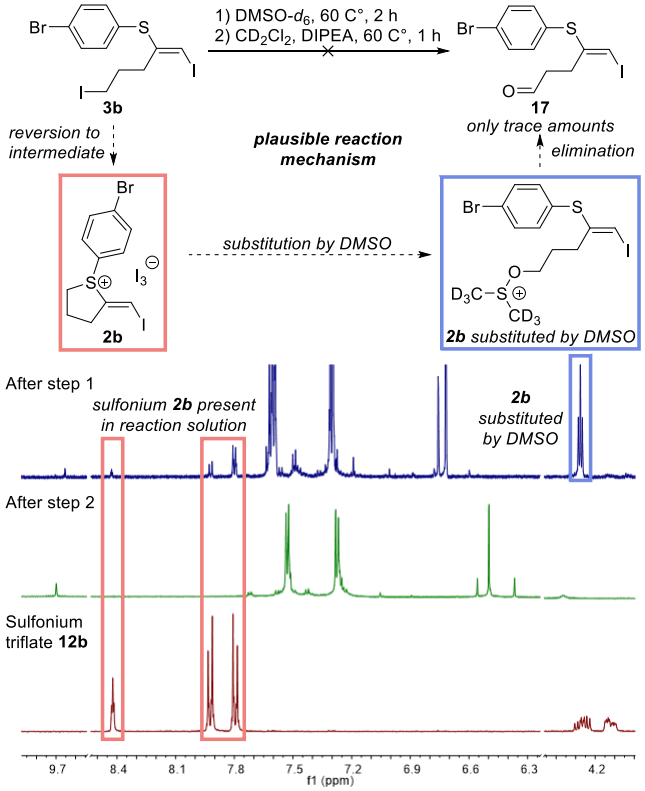
Compared to the previously reported borylative-group-transfer reaction,[22] the iodine group-transfer reaction completes more rapidly and at a lower temperature, reflecting similar trends when comparing boron and iodine in traditional ("Larock-type") electrophilic-cyclization demethylation reactions. For example, an electrophilic-cyclization–demethylation reaction with I_2 to generate 3-iodobenzothiophenes from I_2 proceeded at room temperature in 10 min.[38] In contrast, a cyclization reaction to form the analogous 3-borylated benzothiophenes with ClBcat required a heightened temperature of 100 °C and 4 h.[39] When compared to these two prior demethylation examples, the group-transfer reactions described previously with boron[22] and here with I_2 required a higher temperature (120 °C or 60 °C, respectively) and a longer reaction time (24+ h or 0.5–4 h, respectively), reflective of a slower rate-determining step (plausibly ring opening).

The amenability of the product diiodides towards downstream reactions was next showcased (Scheme 3). Compound **3a** underwent a substitution reaction with cyanide, producing **7** (83%); further Suzuki cross-coupling of **7** with methoxyphenylboronic acid formed **8** (86%). Sonogashira cross-coupling of **3a** formed conjugated enyne **9** (83%). Oxidation of sulfur gave *α*,*β*-unsaturated sulfone **10** (70%).



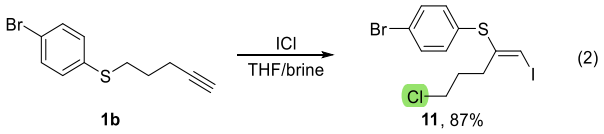
Scheme 3. Downstream functionalization reactions demonstrating synthetic utility of group-transfer-derived **3a**.

In another downstream functionalization attempt, alkyl iodide **3b** was subjected to Kornblum oxidation conditions to yield aldehyde **17** (Scheme 4). Initial attempts were unnsuccessful. However, analysis of these unsucessful reaction mixtures by ^{1}H NMR spectroscopy produced an increased understanding which lead to a change in approach: Subjecting **3b** to plausible Korblum oxidation conditions and monitoring by ^{1}H NMR spectroscopy indicated that trace aldehyde **17** was indeed formed. While it was possible that this trace **17** formed via reaction of **3b** through the indended substitution of the alkyl iodide by DMSO, followed by elimination, closer examination of the spectra suggested an intriguing alternative mechanism. ^{1}H NMR spectroscopy indicated that sulfonium intermediate **2b**, distinguishable by its distinctive downfield triplet, was produced after 2 h in DMSO at 60 °C by reversion/recyclization of **3b**. Compound **2b** was subsequently consumed after addition of Hünig's base. These observations suggest that desired aldehyde **17** may form faster by nuclophilic attack of DMSO on the stronger electrophile **2b** than the originally envisioned attack on **3b**. This alternative mechanism is shown with dotted arrows in Scheme 4. This proposed higher reactivity of the intermediate suggested a strategy for successful oxidation, namely, to directly oxidize isolated intermediate **2** instead of attempting to proceed through **3.** This strategy was ultimately successfully implemented by direct reaction of isolated sulfonium ion pair **12b** with DMSO to yielded aldehyde **17** (75%) under otherwise identical reaction conditions (vida infra, Scheme 6).



Scheme 4. Kornblum oxidation reaction conditions with diiodide **3b** and ^{1}H NMR spectra of the reaction solution.

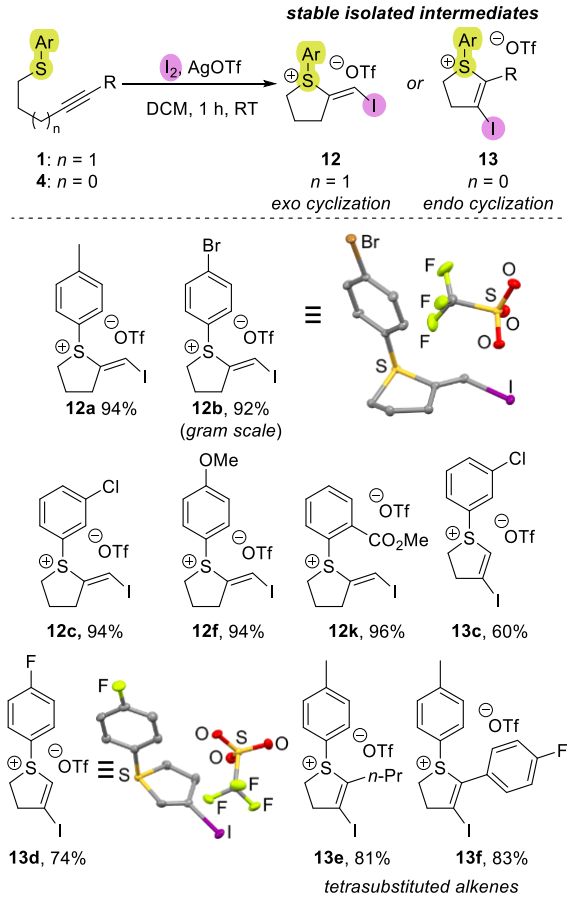
The electrophile iodine monochloride (ICl) functions as a successful alternative to I_2, generating chloroiodoalkene **11** (87%) from alkyne **1b** (eq 2). This electrophile is established to participate in other electrophilic cyclization reactions.[40]



(2)

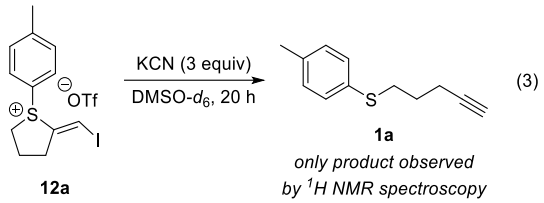
Given the intriguing complementary reactivity suggested by observation of sulfonium ion intermediate **2** by ^{1}H NMR

spectroscopy in Scheme 4, experiments next focused on isolation of a suite of sulfonium ion pair intermediates **12** and **13** to enable closer examination of their structure and distinct reactivity**.** Compounds **12** and **13** were reliably isolated upon addition of silver(I) triflate to scavenge the I^- nucleophile and prevent ring opening (Scheme 5). Crystal structures of sulfonium triflates **12b** and **13d** confirmed the identity of this class of ion pairs. The trans stereochemistry of the sulfur and iodide demonstrated anti addition to the alkyne, regardless of chain length. These crystal structures provided evidence that regiochemistry of the intermediate is dictated by the chain length of the starting substrate, with the 2-methylene chain resulting in 5-endo cyclization and the 3-methylene chain resulting in 5-exo cyclization. A longer chain substrate (*n* = 2) was briefly examined and found to give predominantly analogous cyclization on the basis of ^{1}H NMR spectroscopic analysis of the crude reaction mixture, which showed the characteristic diastereotopic signals arising from the ring hydrogens (see SI). These sulfonium regio- and stereochemistries match known electrophilic cyclizations of analogous alkynyl sulfides with iodine that occur without group transfer.[18]



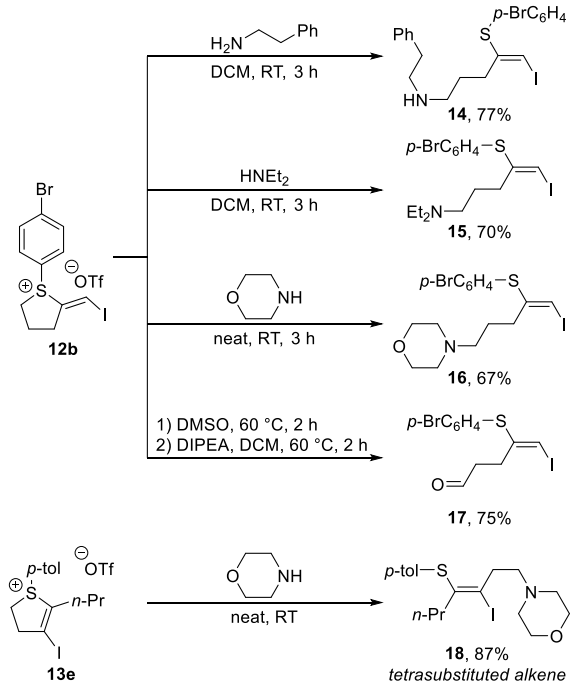
Scheme 5. Cyclized sulfonium triflate ion pair isolation, through a AgOTf scavenging route. X-ray crystal structures **12b** and **13d** with thermal ellipsoids shown at 50% probability (C, gray; Br, orange; F, lime green; I, purple; O, red; S, yellow).

The reactivity of sulfonium triflates **12** were next investigated in detail, and indeed found to be complementary to those of diiodies **3**. For example, as shown previously in Scheme 3, group-transfer product **3a** yielded nitrile **8** upon subsitution with cyanide. However, analogus treatment of sulfonium triflate **12a** with cyanide under otherwise identical conditions resulted only in cycloreversion to alkyne **1a** (eq 3). This outcome is somewhat surprising given the apparent higher electrophilicity of the +S–C bond in sulfonium **12** compared to the neutral C–I bond in **3** when exhibited through preferential reactivity of **12** toward nucleophilic attack by DMSO (Scheme 6). Instead, the reversion to starting alkyne **1a** suggests that nucleophilic cyanide may attack the iodine of the C–I bond rather than the carbon of the S–C bond, causing elimination. Nucleophilic attack of iodine rather than carbon is somewhat unexpected; however, such attack may resemble that of iodine in carbon tetraiodide in Appel[41] and Corey-Fuchs[42] reactions, which experiences nucleophilic attack, or of organoiodides in lithium–halogen exchange which can have character of this attack[43].



In contrast to the chemoselectivity shown in eq 3, sulfonium triflate **12b** was readily substituted[44] by phenethylamine, diethylamine, or morpholine via ring opening, yielding amines **14**, **15**, and **16**, respectively, in decent yields (68–77%; Scheme 6). As mentioned previously, sulfonium **12b** yielded aldehyde **17** through Kornblum oxidation (75%).

Tetrasubstituted alkene **18** was accessible through isolated ion pair **13e** by ring opening with morpholine (87%); as hinted by their lack of representation in the substrate scope in Scheme 2, internal alkynes did not proceed to give stable diiodide tetrasubstituted alkene analogs of **3** or **6**, apparently because of reversion back to and/or thermodynamic preference for alkynes **1** or **4,** or intermediates **2** or **5**. Thus, mechanistic understanding and the isolation of plausible reaction intermediates enabled access to complementary downstream reactivity.



Scheme 6. Downstream functionalization of isolated ion pairs **12b** and **13e**.

Conclusions

The mechanistic pattern of electrophilic-cyclization–group transfer was developed and demonstrated beyond boron, opening the door to a broader use of electrophiles. By extending the mechanistic concept to reactions with I_2, alkenyl iodides are produced, providing complementary cross-coupling partners to those available from boron. Isolation of the cyclized intermediate bolsters evidence of two-step cyclization–group-transfer mechanism and the regio- and stereochemistry it imparts to the iodoalkene after ring-opening. The reaction intermediate and their isolable analogues are amenable to complementary downstream functionalization, including Kornblum oxidation and amination. This electrophilic-cyclization–group-transfer reaction provides a mechanistically complementary method to synthesize tri- and tetrasubstituted alkenes with regio- and stereochemical control, which may allow new routes for drug discovery and materials synthesis.

Experimental Section

Synthesis of Alkynyl Sulfide Substrates 1 and 4. Substrates were synthesized according to known procedures,[22,45] except for substrates **1g**, **1h**, and **1j** which were synthesized using similar conditions to each other, and substrate **4f** which was synthesized by a Sonogashira coupling of **1a** and 1-fluoro-4-iodobenzene:

*Pent-4-yn-1-yl(p-tolyl)sulfane (**1a**)* was prepared according to a literature procedure[22] in 84% yield on 1.5 g scale from 4-methylbenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.27 (d, J = 8.4 Hz, 2H), 7.10 (d, 7.8 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.35–2.33 (m, 5H), 1.97 (t, J = 2.4 Hz, 1H), 1.82 (quint, J = 7.2 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*(4-bromophenyl)(pent-4-yn-1-yl)sulfane (**1b**)* was prepared according to a literature procedure[22] in 91% yield on 1.9 g scale from 4-bromobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.40 (d, 2H), 7.21 (d, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.34 (m, 2H), 1.98 (m, 1H), 1.83(tt, *J* = 7.0 Hz, *J* = 7.0 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*(3-chlorophenyl)(pent-4-yn-1-yl)sulfane (**1c**)* was prepared according to a literature procedure[22] in 85% yield on 0.5 g scale from 3-chlorobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31 (m, 1H), 7.20 (m, 2H), 7.14 (m, 1H), 3.05 (t, J = 7.2 Hz, 2H), 2.36 (td, J = 10.3 Hz, J = 2.7 Hz, 2H), 2.00 (t, J = 2.6 Hz, 1H), 1.86 (tt, J = 7.0 Hz, J = 7.0 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*(4-fluorophenyl)(pent-4-yn-1-yl)sulfane (**1d**)* was prepared according to a literature procedure[22] in 96% yield on 0.5 g scale from 4-bromobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.36 (m, 2H), 7.00 (m, 2H), 2.98 (t, J = 7.2 Hz, 2H), 2.34 (td, J = 10.3 Hz, J = 2.6 Hz, 2H), 1.98 (t, J = 2.6 Hz, 1H), 1.83(tt, J = 7.0 Hz, J = 7.0 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*Pent-4-yn-1-yl(4-(trifluoromethyl)phenyl)sulfane (**1e**)* was prepared according to a literature procedure[22] in 58% yield on 0.5 g scale from 4-(trifluoromethyl)benzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.51 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 3.10 (t, J = 7.2 Hz, 2H), 2.37 (td, J = 10.2 Hz, J = 2.6 Hz, 2H), 2.01 (t, J = 2.6 Hz, 1H), 1.89 (tt, J = 7.0 Hz, J = 7.0 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*(4-methoxyphenyl)(pent-4-yn-1-yl)sulfane (**1f**)* was prepared according to a literature procedure[22] in 88% yield on 0.5 g scale from 4-methoxybenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.36 (m, 2H), 6.85 (m, 2H), 3.80 (s, 3H), 2.92 (t, J = 7.1 Hz, 2H), 2.33 (td, J = 6.9 Hz, J = 2.6 Hz, 2H), 1.96 (t, J = 2.6 Hz, 1H), 1.78 (tt, J = 7.1 Hz, J = 7.1 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*2-(pent-4-yn-1-ylthio)benzo[d]thiazole (**1g**)*. To a 50 mL round bottom flask equipped with a stir bar was added benzo[*d*]thiazole-2(3*H*)-thione (0.50 g, 3.0 mmol, 1.0 equiv), K_2CO_3 (0.61 g, 4.4 mmol, 1.5 equiv), and acetone (9 mL). While stirring this mixture, 5-chloropent-1-yne (0.30 g, 0.31 mL, 2.9 mmol, 1.0 equiv) was added dropwise. The glass joint of an air condenser equipped with a finned aluminum jacket was fitted with a PTFE O-ring, and the air condenser was inserted into the neck of the round bottom flask. The top of the condenser was capped with a septum equipped with an outlet needle. Then, the reaction mixture was heated to reflux and stirred for 18 h. After the reaction mixture was cooled to ambient temperature, the mixture was vacuum filtered through a Buchner funnel with cellulose paper, and the solids were washed with acetone (20 mL). The filtrate was then concentrated in vacuo to give the crude oil. The oil was dissolved in DCM (20 mL) and washed with DI water (20 mL). The aqueous layer was then extracted with DCM (2 × 20 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 material was purified via normal phase column chromatography (0–20% EtOAc in hexanes) to afford alkyne **1g** as a clear, colorless oil (0.60 g, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (m, 1H), 7.75 (m, 1H), 7.42 (m, 1H), 7.30 (m, 1H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.41 (m, 2H), 2.08 (m, 2H), 2.01 (t, *J* = 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 166.7, 153.3, 135.3, 126.2, 124.4, 121.7, 121.1, 83.0, 69.6, 32.4, 28.1, 17.6. (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{12}H_{11}NS_2$ 233.0333, found 233.0331.

*2-(pent-4-yn-1-ylthio)thiophene (**1h**)*. To a 50 mL round bottom flask equipped with a stir bar was added thiophene-2-thiol (0.29 g, 2.5 mmol, 1.0 equiv), K_2CO_3 (0.52 g, 3.8 mmol, 1.5 equiv), and acetone (5 mL). While stirring this mixture, 5-chloropent-1-yne (0.31 g, 0.32 mL, 3.0 mmol, 1.2 equiv) was added dropwise. The glass joint of an air condenser equipped with a finned aluminum jacket was fitted with a PTFE O-ring and the air condenser was inserted into the neck of the round bottom flask. The top of the condenser was capped with a septum equipped with an outlet needle. The reaction mixture was heated to reflux and stirred for 21 h. After the reaction mixture was cooled to ambient temperature, the mixture was vacuum filtered through a Buchner funnel with cellulose paper, and the solids were washed with acetone (20 mL). The filtrate was then concentrated in vacuo to give the crude oil. The filtrate was concentrated in vacuo. The crude material was purified via normal phase column chromatography (0–20% DCM in hexanes) to afford alkyne **1h** as a clear, colorless oil (0.34 g, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.12 (m, 1H), 6.97 (m, 1H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.34 (m, 2H), 1.96 (t, *J* = 2.7, 1H), 1.82 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 134.2, 133.9, 129.5, 127.7, 83.4, 69.2, 37.7, 28.0, 17.2. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_9H_{10}S_2$ 182.0224, found 182.0218.

*Naphthalen-2-yl(pent-4-yn-1-yl)sulfane (**1i**)* was prepared according to a literature procedure[22] in 58% yield on 0.5 g scale from naphthalene-2-thiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.77 (m, 4H), 7.47 (m, 1H), 7.43 (m, 2H), 3.92 (s, 3H), 3.15 (t, J = 7.2 Hz, 2H), 2.38 (td, J = 6.9 Hz, J = 2.6 Hz, 2H), 2.00

(t, J = 2.6 Hz, 1H), 1.95 (tt, J = 7.0 Hz, J = 7.0 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*2-(pent-4-yn-1-ylthio)benzoic acid (**1j**)*. To a 50 mL round bottom flask equipped with a stir bar was added 2-mercaptobenzoi acid (0.39 g, 2.5 mmol, 1.0 equiv), K_2CO_3 (0.86 g, 6.3 mmol, 2.5 equiv), and acetone (5 mL). While stirring this mixture, 5-chloropent-1-yne (0.31 g, 0.32 mL, 3.0 mmol, 1.2 equiv) was added dropwise. The glass joint of an air condenser equipped with a finned aluminum jacket was fitted with a PTFE O-ring, and the air condenser was inserted into the neck of the round bottom flask. The top of the condenser was capped with a septum equipped with an outlet needle. The reaction mixture was heated to reflux and stirred for 20 h. After the reaction mixture was cooled to ambient temperature, the mixture was vacuum filtered through a Buchner funnel with cellulose paper, and the solids were washed with acetone (20 mL). The filtrate was then concentrated in vacuo to give the crude oil. The oil was dissolved in DCM (30 mL) and the solution was washed with 1 M HCl (20 mL). The aqueous layer was then extracted with DCM (2 × 30 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 material was purified via normal phase column chromatography (20–60% EtOAc in hexanes) to afford alkyne **1j** as a colorless powder (0.51 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 2H), 7.50 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.21 (m, 1H), 3.08 (t, *J* = 7.4 Hz, 2H), 2.41 (m, 2H), 2.02 (m, 1H), 1.96 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 170.9, 142.4, 133.4, 132.8, 126.6, 126.0, 124.3, 83.2, 69.5, 31.0, 27.1, 18.1. HRMS (ESI-TOF) *m*/*z* $[M-H]^-$ calcd for $C_{12}H_{12}O_2S$ 219.0477, found 219.0480.

*Methyl 2-(pent-4-yn-1-ylthio)benzoate (**1k**)* was prepared according to a literature procedure[22] in 79% yield on 0.5 g scale from 2-mercaptobenzoate. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.96 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.45 (m, 1H), 7.37 (m, 1H), 7.16 (m, 1H), 3.92 (s, 3H), 3.06 (t, J = 7.3 Hz, 2H), 2.40 (td, J = 10.2 Hz, J = 2.6 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.95 (tt, J = 7.1 Hz, J = 7.1 Hz, 2H). This spectrum is in agreement with previously reported spectral data.

*But-3-yn-1-yl(p-tolyl)sulfane (**4a**)* was prepared according to a literature procedure[45] in 91% yield on 4.0 g scale from 4-methylbenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 2.46 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H), 2.03 (s, 1H). This spectrum is in agreement with previously reported spectral data.

*(4-bromophenyl)(but-3-yn-1-yl)sulfane (**4b**)* was prepared according to a literature procedure[22] in 72% yield on a 0.9 g scale from 4-bromobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (d, J = 7.2 Hz, 2 H), 7.23 (d, J = 7.8 Hz, 2H), 3.05 (t, J = 7.2 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 2.05 (d, 1.2 Hz, 1H). This spectrum is in agreement with previously reported spectral data.

*But-3-yn-1-yl(3-chlorophenyl)sulfane (**4c**)* was prepared according to a literature procedure[22] in 72% yield on a 0.7 g scale from 3-chlorobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.34 (s, 1H), 7.23–7.17 (m, 3H), 3.09 (t, J = 7.4 Hz; 2H), 2.51 (td, J = 7.4, 2.4 Hz, 2H), 2.06 (t, J = 2.4 Hz, 1H). This spectrum is in agreement with previously reported spectral data.

*But-3-yn-1-yl(4-fluorophenyl)sulfane (**4d**)* was prepared according to a literature procedure[22] in 72% yield on a 0.6 g scale from 4-fluorobenzenethiol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41–7.38 (m, 2H), 7.03–6.99 (m, 2H), 3.00 (t, J = 7.2 Hz, 2H), 2.44 (td, J = 7.8, 3.0 Hz, 2H), 2.03 (t, J = 3.0 Hz, 1H). This spectrum is in agreement with previously reported spectral data.

*Hept-3-yn-1-yl(p-tolyl)sulfane (**4e**)* was prepared according to a literature procedure[22] in 55% yield on a 0.5 g scale over two steps from 4-methylbenzenethiol and hept-3-yn-1-ol. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.30 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 3.01 (t, J = 7.6 Hz, 2H), 2.47–2.44 (m, 2H), 2.33 (s, 3H), 2.15–2.13 (m, 2H), 1.55–1.49 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H). This spectrum is in agreement with previously reported spectral data.

*(4-(4-fluorophenyl)but-3-yn-1-yl)(p-tolyl)sulfane (**4f**)*. To a 25 mL round bottom flask equipped with stir bar was added $Pd(PPh_3)_2Cl_2$ (122 mg, 0.174 mmol, 5.0 mol %) and copper(I) iodide (66.2 mg, 0.347 mmol, 10. mol %). This flask was sealed with a rubber septum then evacuated and filled with N_2 3×. In a 25 mL conical flask sealed with a rubber septum, NEt_3 was sparged with N_2 for 1 h. The sparged NEt_3 was then transferred to the round bottom flask by syringe. The resulting solution was stirred while 1-fluoro-4-iodobenzene (0.60 mL, 5.2 mmol, 1.5 equiv) was added slowly through the septum by syringe. The resulting solution was stirred at ambient temperature for 5 min. Terminal alkyne **4a** (0.61 g, 3.5 mmol, 1.0 equiv) was then added slowly through the septum by syringe. The solution was left to stir for 21 h. The reaction solution was then diluted with DI water (20 mL) and extracted with EtOAc (3 x 20 mL). The organic layers were combined and washed with saturated NH_4Cl solution (20 mL) and brine (20 mL). The organic layer was then dried over Na_2SO_4 and filtered via gravity filtration through glass wool. The filtrate was then concentrated in vacuo. The crude material was then purified by normal-phase column chromatography (10% DCM in pentanes) to afford substrate **4f** as a white solid (0.63 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.32 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.97 (m, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 162.3 (d, *J* = 248.6 Hz), 137.0, 133.6 (d, *J* = 8.2 Hz), 131.7, 131.1, 129.9, 119.7 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 22.0 Hz), 87.8, 87.8, 80.8, 33.9, 21.2, 20.6. ^{19}F NMR (564 MHz, $CDCl_3$) δ −111.8. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{17}H_{15}FS$ 270.0879, found 270.0878.

Procedure A. Preparation of Iodoalkenes 3. To a 1 dram vial equipped with a stir bar was added substrate **1** (0.250 mmol, 1.00 equiv), iodine (69.8 mg, 0.275 mmol, 1.10 equiv), and toluene (0.5 mL). The reaction mixture was then stirred vigorously on a heating block set to 60 °C. After 30 min, the reaction mixture was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was dissolved in DCM (5 mL) and washed with saturated $Na_2S_2O_3$ solution. The aqueous layer was extracted with DCM (3 × 5 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 to yield **3**.

*(E)-(1,5-diiodopent-1-en-2-yl)(p-tolyl)sulfane (**3a**)*. Prepared according to Procedure A with no modifications to yield iodoalkene **3a** as a brown oil (104 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.16 (m, 2H), 6.03 (s, 1H), 3.21 (t, *J* = 7.1 Hz, 2H), 2.46 (m, 2H), 2.36 (s, 3H), 2.12 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.3, 139.0, 133.5, 130.4, 128.4, 75.3, 38.4, 31.8, 21.4, 5.2. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}I_2S$ 443.8906, found 443.8924.

*Gram scale synthesis of **3a**:* To a 50 mL round bottom flask equipped with a stir bar was added substrate **1a** (1.01 g, 5.31 mmol, 1.00 equiv), iodine (1.48 g, 5.84 mmol, 1.10 equiv), and toluene (11 mL). The round bottom flask was sealed with a rubber septum. The reaction mixture was then stirred vigorously on a heating block set to 60 °C. After 30 min, the reaction mixture was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was washed with saturated $Na_2S_2O_3$ solution (50 mL). The aqueous layer was extracted with DCM (3 × 30 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 to yield iodoalkene **3a** as a brown oil (2.25 g, 96%).

*(E)-(4-bromophenyl)(1,5-diiodopent-1-en-2-yl)sulfane (**3b**)*. Prepared according to Procedure A except that the reaction mixture was stirred and heated for 2 h rather than 30 min. The crude material was purified by normal-phase column chromatography (silica, 100% hexanes) to afford iodoalkene **3b** as a colorless oil (110 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.23 (m, 2H), 6.31 (s, 1H), 3.20 (t, *J* = 7.0 Hz, 2H), 2.47 (m, 2H), 2.10 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 141.9, 133.9, 132.7, 131.8, 122.7, 79.1, 38.3, 31.6, 5.0. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}BrI_2S$ 507.7854, found 507.7852.

*(E)-(3-chlorophenyl)(1,5-diiodopent-1-en-2-yl)sulfane (**3c**)*. Prepared according to Procedure A with no modifications to yield iodoalkene **3c** as a yellow oil (104 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.28 (m, 2H), 7.24 (m, 1H), 6.44 (s, 1H), 3.20 (t, *J* = 6.99 Hz, 2H), 2.47 (m, 2H), 2.10 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 141.5, 135.2, 134.9, 131.5, 130.6, 129.9, 128.4, 80.7, 38.3, 31.6, 5.0. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}ClI_2S$ 463.8360, found 463.8377.

*(E)-(1,5-diiodopent-1-en-2-yl)(4-fluorophenyl)sulfane (**3d**)*. Prepared according to Procedure A with no modifications to yield iodoalkene **3d** as a colorless oil (107 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.07 (m, 2H), 6.09 (s, 1H), 3.21 (t, *J* = 7.0 Hz, 2H), 2.46 (m, 2H), 2.11 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.7 Hz), 143.0, 135.4 (d, *J* = 8.4 Hz), 127.2 (d, *J* = 3.5 Hz), 116.8 (d, *J* = 22.0 Hz), 76.1, 38.3, 31.6, 5.1. ^{19}F NMR (564 MHz, $CDCl_3$) δ −112.0. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{11}H_{11}FI_2S$ 447.8655, found 447.8670.

*(E)-(1,5-diiodopent-1-en-2-yl)(4-(trifluoromethyl)phenyl)sulfane (**3e**)*. Prepared according to Procedure A with no modifications to yield iodoalkene **3e** as a colorless solid (119 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 6.65 (s, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.51 (m, 2H), 2.10 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 140.6, 138.7, 130.6, 129.6 (q, *J* = 33.0 Hz), 126.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 271.8 Hz), 83.6, 38.3, 31.5, 4.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ −62.7. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{12}H_{11}F_3I_2S$ 497.8623, found 497.8625.

*(E)-(1,5-diiodopent-1-en-2-yl)(4-methoxyphenyl)sulfane (**3f**)*. Prepared according to Procedure A with no modifications to yield iodoalkene **3f** as a colorless oil (107 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 2H), 6.89 (m, 2H), 5.82 (s, 1H), 3.82 (s, 3H), 3.22 (t, *J* = 7.1 Hz, 2H), 2.45 (m, 2H), 2.12 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 160.5, 144.1, 136.0, 122.0, 115.3, 71.9, 55.5, 38.4, 31.8, 5.3. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{12}H_{14}I_2OS$ 459.8855, found 459.8856.

*(E)-2-((1,5-diiodopent-1-en-2-yl)thio)benzo[d]thiazole (**3g**)*. A 1 dram vial was charged with substrate **1g** (58.3 mg, 0.250 mmol, 1.00 equiv). A separate 1 dram vial was charged with iodine (69.8 mg, 0.275 mmol, 1.10 equiv) and toluene (0.5 mL). The resulting homogeneous solution from the iodine-containing vial was then added to the vial containing the alkyne. The vial was equipped with a stir bar, sealed with a cap, and stirred at ambient temperature for 24 h. The resulting reaction mixture was washed with saturated $Na_2S_2O_3$ solution (1 × 10 mL), then washed with DI water (1 × 10 mL), and brine (1 × 10 mL). The aqueous layers were combined and extracted with DCM (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 material was purified via normal-phase column chromatography (silica, 0–5% EtOAc in hexanes) to afford iodoalkene **3g** as a yellow oil (79 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 3.21 (t, *J* = 6.9 Hz, 1H), 2.77 (m, 2H), 2.16 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) (reaction rerun and spectrum retaken at higher concentration to find all peaks) δ 164.5, 153.8,138.3,136.1, 126.6, 125.2, 122.6, 121.2, 90.7, 39.2, 31.4, 4.8. HRMS (ESI-TOF) *m*/*z* $[M+H]^+$ calcd for $C_{12}H_{12}I_2NS_2$ 487.8501, found 487.8501.

*(E)-2-((1,5-diiodopent-1-en-2-yl)thio)thiophene (**3h**)*. Prepared according to Procedure A, with the modification that the crude oil was then purified by normal-phase column chromatography (silica, 100% hexanes) to afford iodoalkene **3h** as a colorless oil (104 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (m, 2H), 6.89 (m, 2H), 6.01 (s, 1H), 3.22 (t, *J* = 7.0 Hz, 2H), 2.46 (m, 2H), 2.12 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 143.8, 136.7, 132.1, 129.4, 128.2, 74.0, 38.0, 31.6, 5.1. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_9H_{10}I_2S_2$ 435.8314, found 435.8323.

*(E)-(1,5-diiodopent-1-en-2-yl)(naphthalen-2-yl)sulfane (**3i**)*. A 1 dram vial was charged with substrate **1i** (56.6 mg, 0.250 mmol, 1.00 equiv). A separate 1 dram vial was charged with iodine (69.8 mg, 0.275 mmol, 1.10 equiv) and toluene (0.5 mL). The resulting homogeneous solution from the iodine-containing vial was then added to the vial containing the alkyne. The vial was equipped with a stir bar, sealed with a cap, and heated to 60 °C for 30 min. After cooling to ambient temperature, the reaction mixture was washed with saturated $Na_2S_2O_3$ solution (1 × 10 mL), DI water (1 × 10 mL), and brine (1 × 10 mL). The aqueous layers were combined and extracted with DCM (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 material was purified by normal-phase column chromatography (silica, 100% hexanes) to afford iodoalkene **3i** as a white solid (94 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 (m, 3H), 7.53 (m, 2H), 7.43 (m, 1H), 6.24 (s, 1H), 3.21 (t, *J* = 7.1 Hz, 2H), 2.52 (m, 2H), 2.15 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 142.6, 133.9, 132.9, 132.1, 129.7, 129.5, 129.3, 128.0, 127.8, 127.0, 127.0, 77.6, 38.5, 31.7, 5.1. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{15}H_{14}I_2S$ 479.8906, found 479.8887.

*(E)-2-((1,5-diiodopent-1-en-2-yl)thio)benzoic acid (**3j**)*. To a 1 dram vial equipped with a stir bar was added substrate **1j** (55.1 mg, 0.250 mmol, 1.00 equiv), iodine (69.8 mg, 0.275 mmol, 1.10 equiv), and ethanol (0.5 mL). The mixture was then stirred vigorously on a heating block set to 60 °C. After 4 h, the reaction mixture was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was dissolved in DCM (5 mL) and washed

with saturated $NaHS_2O_3$ solution then 1 M HCl. The aqueous layers were combined and extracted with DCM (2 × 5 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 to give a crude solid. The crude solid was recrystallized in ethanol and DI water to yield iodoalkene **3j** as colorless crystals (80.2 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (m, 1H), 7.51 (m, 1H), 7.28 (m, 1H), 7.21 (m, 1H), 7.01 (s, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.56 (m, 2H), 2.10 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.6, 140.8, 140.5, 133.5, 132.6, 128.2, 126.7, 125.6, 89.4, 38.7, 31.6, 5.4. Accurate mass was attempted but could not be obtained for this compound, possibly due to loss of iodide during mass analysis.

Formation of Crystals of 3j for Single-Crystal X-Ray Analysis. Product **3j** was prepared as described above without purification by recrystallization. The crude material was dissolved in hot ethanol. The vial was left at ambient temperature for 3 d. The formed crystals were then submitted to the X-ray crystallography facility for characterization.

*(E)-(2,4-diiodobut-1-en-1-yl)(p-tolyl)sulfane (**6a**)*. To a 1 dram vial equipped with a stir bar was added substrate **4a** (35.3 mg, 0.200 mmol, 1.0 equiv), iodine (55.8 mg, 0.220 mmol, 1.1 equiv), and 1,2-dichloroethane (0.5 mL). The mixture was then stirred vigorously on a heating block set to 60 °C. After 2 h, the reaction mixture was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was dissolved in DCM (1 mL) and washed with saturated $Na_2S_2O_3$ solution. The aqueous layer was extracted with DCM (2 × 5 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 to give crude material. The crude material was purified by normal-phase column chromatography (silica, 100% hexanes) to yield iodoalkene **6a** as a colorless oil (71.4 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.15 (m, 2H), 6.93 (s, 1H), 3.15 (t, *J* = 7.0 Hz, 2H), 3.15 (t, *J* = 7.1 Hz, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.8, 134.3, 130.7, 130.4, 130.2, 96.6, 43.2, 21.2, 2.9. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{11}H_{12}I_2S$ 429.8749, found 429.8768.

*(E)-(4-bromophenyl)(2,4-diiodobut-1-en-1-yl)sulfane (**6b**)*. To a 1 dram vial equipped with a stir bar was added substrate **4b** (35.3 mg, 0.200 mmol, 1.0 equiv), iodine (55.8 mg, 0.220 mmol, 1.1 equiv), and toluene (0.5 mL). The mixture was then stirred vigorously on a heating block set to 60 °C. After 3 h, the reaction mixture was removed from the heating block and allowed to cool to ambient temperature. The reaction mixture was washed with saturated $Na_2S_2O_3$ solution. The aqueous layer was extracted with DCM (3 × 5 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 to give crude material. The crude material was purified by normal-phase column chromatography (silica, 100% hexanes) to yield iodoalkene **6b** as a colorless oil (80.5 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.23 (m, 2H), 6.92 (s, 1H), 3.31 (t, *J* = 7.0 Hz, 2H), 3.16 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 133.6, 132.5, 132.3, 131.1, 121.5, 99.8, 43.0, 3.0. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{10}H_9BrI_2S$ 493.7698, found 493.7689.

Formation of Crystal 2b In Situ. *(E)-1-(4-bromophenyl)-2-(iodomethylene)tetrahydro-1H-thiophen-1-ium triiodide (**2b**)*. To a 1 dram vial was added substrate **1b** (63.8 mg, 0.250 mmol, 1.00 equiv), iodine (69.8 mg, 0.275 mmol, 1.10 equiv), and DCM (0.5 mL). The mixture was then left in the freezer at −18 °C. After 2 d, a crystalline solid was observed in the reaction mixture. After 11 d, a sample of the solid and mother liquor was transferred to a separate 1 dram vial and covered in crystallization oil. This vial with crystals and oil was immediately brought to the X-ray crystallography facility for characterization.

*(E)-6-iodo-5-(p-tolylthio)hex-5-enenitrile (**7**)*. A 1 dram vial equipped with a stir bar was charged with potassium cyanide (48.8 mg, 0.750 mmol, 3.00 equiv), followed by a solution of alkyl iodide **3a** (111 mg, 0.250 mmol, 1.00 equiv) dissolved in DMSO (2 mL). The reaction mixture was allowed to stir for 22 h at ambient temperature. The reaction mixture was washed with 0.33 M NaOH (15 mL). The aqueous layer was extracted with hexanes (3 × 10 mL). The organic layers were combined and filtered via gravity filtration through glass wool. The filtrate was concentrated in vacuo. The crude material was purified by normal-phase column chromatography (silica, 0-30% EtOAc in hexanes) to yield **7** as a colorless oil (70.8 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.10 (s, 1H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 1.96 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 142.8, 139.2, 133.4, 130.5, 128.1, 119.4, 76.1, 36.1, 23.7, 21.4, 16.6. HRMS (CI-TOF) *m*/*z* $[M]^+$ calcd for $C_{13}H_{14}INS$ 342.9892, found 342.9908.

*(E)-6-(4-methoxyphenyl)-5-(p-tolylthio)hex-5-enenitrile (**8**)*. In a glove box under N_2 atmosphere, a 25 mL bomb containing a stir bar was charged with cesium carbonate (195 mg, 0.600 mmol, 3.00 equiv), $Pd(PPh_3)_4$ (23.1 mg, 20.0 μmol, 10.0 mol %), iodoalkene **7** (68.6 mg, 0.200 mmol, 1.00 equiv), (4-methoxyphenyl)boronic acid (42.5 mg, 0.250 mmol, 1.40 equiv), and THF (2 mL). The bomb was closed with a screw cap and brought out of the glove box. DI water (0.10 mL, 5.5 mmol, 31 equiv) was sparged with N_2 and was then added to the bomb under N_2 flow. The reaction mixture was heated to 75 °C and stirred for 19 h. The solution was then diluted in EtOAc (10 mL) and washed with DI water (10 mL). The aqueous layer was then extracted with EtOAc (2 × 10 mL). The organic layers were then combined, dried over Na_2SO_4, and filtered via gravity filtration through glass wool. The filtrate was concentrated in vacuo. The crude material was purified by normal phase HPLC (0–30% EtOAc in hexanes) to afford alkene **8** as a brown oil (55.8 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.16 (m, 4H), 6.88 (m, 2H), 6.70 (s, 1H), 3.81 (s, 3H), 2.54 (m, 2H), 2.35 (s, 3H), 2.28 (t, *J* = 7.3 Hz, 2H), 1.96 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 158.9, 137.9, 135.3, 132.6, 132.3, 130.2, 130.0, 129.8, 129.2, 119.5, 114.1, 55.4, 30.3, 12.5, 21.3, 16.7. HRMS (ESI-TOF) *m/z* [M+Na]+ calcd for $C_{20}H_{21}NOSNa$ 346.1241, found 346.1239.

*Methyl (E)-8-iodo-5-(p-tolylthio)oct-4-en-2-ynoate (**9**)*. In a glovebox under N_2 atmosphere a 20 mL scintillation vial equipped with stir bar was charged with iodoalkene **3a** (55.5 mg, 0.125 mmol, 1.00 equiv), copper(I) iodide (2.38 mg, 12.5 μmol, 10.0 mol %), and $Pd(PPh_3)_2Cl_2$ (4.39 mL, 6.25 μmol, 5.00 mol %) which was dissolved in NEt_3 (2 mL). After stirring this mixture for 15 min, a solution of methyl propiolate (31.5 mg, 0.375 mmol, 3.00 equiv) in THF (0.5 mL) was added slowly dropwise. The mixture was then stirred for 2.5 h at ambient temperature. The reaction mixture was then diluted with EtOAc (10 mL) and washed with saturated NH_4Cl solution (5 mL) and DI water (5 mL). The combined aqueous layers were extracted with EtOAc (1 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and filtered via gravity filtration through glass wool. The filtrate was concentrated to a crude material. The crude material was

purified by normal-phase column chromatography (silica, 0–10% EtOAc in hexanes) to yield enyne **9** as a yellow oil (41.4 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.92 (s, 1H), 3.75 (s, 3H), 3.25 (t, *J* = 7.1 Hz, 2H), 2.69 (m, 2H), 2.39 (s, 3H), 2.20 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.2, 154.8, 140.6, 135.5, 130.8, 125.7, 99.1, 85.8, 84.5, 52.7, 35.5, 33.1, 21.5, 4.7. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{16}H_{17}IO_2S$ 401.0072, found 401.0073.

*(E)-1-((1,5-diiodopent-1-en-2-yl)sulfonyl)-4-methylbenzene. (**10**)*. A 1 dram vial equipped with a stir bar was charged with *m*-CPBA (79.9 mg, 54 % Wt, 0.25 mmol, 2.5 equiv) and isopropanol (1 mL) and the solution was stirred in an ice bath at 0 °C. A separate 1 dram vial was charged with thioalkene **3a** (44.4 mg, 0.100 mmol, 1 equiv) dissolved in DCM (0.2 mL). The DCM solution was then added to the isopropanol solution dropwise. The vial containing the reaction solution was capped and allowed to stir at 0 °C for 1 h. The reaction solution was then diluted with EtOAc (5 mL) and washed with 1 M NaOH and saturated $Na_2S_2O_3$ solution. The combined aqueous layers were extracted with EtOAc (2 × 5 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 and washed through a celite plug with DCM. This wash step left behind a white solid that is plausibly *m*-chlorobenzoic acid. The DCM wash was then concentrated in vacuo and purified by column chromatography (silica, 0–20% EtOAc in hexanes) to yield *α,β*-unsaturated sulfone **10** (33.3 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.76 (m, 2H), 7.36 (m, 2H), 3.16 (t, *J* = 6.6 Hz, 2H), 2.46 (m, 2H), 2.46 (s, 3H), 1.97 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.3, 145.3, 135.2, 130.3, 128.6, 97.5, 33.9, 30.8, 21.9, 5.4. HRMS (ESI-TOF) *m*/*z* [M+Na]$^+$ calcd for $C_{12}H_{14}I_2O_2S$ 498.8702, found 498.8682.

Attempted Kornblum Oxidation of 3b with DMSO. A 1 dram vial was charged with product **3b** (10 mg, 20 μmol, 1 equiv) followed by DMSO-d_6 (0.5 mL). The solution was transferred to an NMR tube. The NMR tube was capped and inserted into an aluminum heating block set to 60 °C. After 2 h, the NMR tube was cooled to ambient temperature and the reaction solution was analyzed by ^{1}H NMR spectroscopy. After analysis, the solution was transferred to a 1 dram vial equipped with a stir bar. A separate 1 dram vial was charged with DIPEA (13 mg, 0.10 mmol, 5 equiv) and CD_2Cl_2 (0.5 mL). The CD_2Cl_2 solution was then added dropwise to the DMSO-d_6 solution while stirring. The combined solution was then stirred at 60 °C for 1 h. The resulting solution was then transferred in full to an NMR tube and analyzed by ^{1}H NMR spectroscopy.

*(E)-(4-bromophenyl)(5-chloro-1-iodopent-1-en-2-yl)sulfane (**11**)*. A 1 dram vial was charged with substrate **1b** (63.8 mg, 0.250 mmol, 1 equiv) and THF (0.5 mL). A separate 1 dram vial was charged with ICl (40.6 mg, 13.1 μL, 250 μmol, 1 equiv) and brine (0.5 mL). The resulting homogeneous solution from the ICl and brine was then added to the vial containing the alkyne. The vial was equipped with a stir bar, sealed with a cap, and allowed to stir at ambient temperature for 4 h. The reaction mixture was washed with saturated $Na_2S_2O_3$ solution (1 × 10 mL), DI water (1 × 10 mL), and brine (1 × 10 mL). The aqueous layers were combined and extracted with DCM (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 material was purified by normal-phase column chromatography (silica, 0–5% EtOAc in hexanes) to afford iodoalkene **11** as a yellow oil (91 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.24 (m, 2H), 6.30 (s, 1H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.52 (m, 2H), 2.04 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 133.9, 132.7, 131.8, 122.7, 78.9, 44.1, 34.8, 30.6. HRMS (CI-TOF) *m*/*z* [M]$^+$ calcd for $C_{11}H_{11}BrClIS$ 415.8498, found 415.8513.

Procedure B. Preparation of Sulfonium Triflates 12 and 13. A 1 dram vial was charged with substrate **1** or **4** (0.250 mmol, 1 equiv) and DCM (1.0 mL). A separate 1 dram vial equipped with a stir bar was charged with iodine (63.5 mg, 0.250 mmol, 1 equiv) and AgOTf (64.2 mg, 0.250 mmol, 1 equiv). The DCM solution of substrate **1** was then transferred into the iodine–AgOTf vial. The vial was sealed with a plastic screw cap and covered with aluminum foil to block out light. The reaction mixture was then stirred at ambient temperature for 1 h. The reaction mixture was then diluted with 10 mL Et_2O and filtered through a celite plug. This filtrate was discarded, and the plug containing residual solids was then washed with acetonitrile (10 mL). The acetonitrile filtrate was concentrated in vacuo.

*(E)-2-(iodomethylene)-1-(p-tolyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**12a**)*. Prepared according to Procedure B with no further purification to yield sulfonium triflate **12a** as a yellow solid (109 mg, 94%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.94 (t, *J* = 2.6 Hz, 1H), 7.59 (m, 2H), 7.50 (m, 2H), 4.14 (m, 1H), 3.90 (m, 1H), 3.14 (m, 1H), 2.85 (m, 1H), 2.50 (m, 1H), 2.44 (s, 3H), 2.37 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN) δ 146.6, 141.4, 132.6, 130.5, 124.1, 95.4, 53.0, 38.3, 26.5, 21.5. ^{19}F NMR (564 MHz, CD_3CN) δ −79.33. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{12}H_{14}IS$ 316.9861, found 316.9858.

*(E)-1-(4-bromophenyl)-2-(iodomethylene)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**12b**)*. A 50 mL round bottom flask equipped with a stir bar was charged with iodine (995 mg, 3.92 mmol, 1 equiv), AgOTf (1.01 g, 3.92 mmol, 1 equiv), and DCM (10 mL). This mixture was stirred in an ice bath for 5 min to precool before addition of substrate. Separately, a 20 mL scintillation vial was charged with substrate **1a** (1.00 g, 3.92 mmol, 1 equiv) and DCM (10 mL). The solution of **1a** was then added slowly to the round bottom flask in the ice bath while stirring. The round bottom flask was capped with a glass stopper, and the mixture was stirred at 0 °C for 1 h. The mixture was then diluted with Et_2O (40 mL) and filtered through a celite plug. The celite plug was then washed with Et_2O (60 mL). The combined filtrate was discarded. The celite plug containing the residual solids was then washed with acetonitrile (70 mL). The acetonitrile filtrate was concentrated in vacuo to afford sulfonium triflate **12b** as a yellow solid (1.92 g, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (t, *J* = 2.5 Hz, 1H), 7.91 (m, 2H), 7.80 (m, 2H), 4.24 (m, 1H), 4.13 (m, 1H), 3.08 (m, 1H) 2.74 (m, 1H), 2.47 (m, 1H), 2.18 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 140.4, 133.5, 131.1, 127.1, 127.1, 97.3, 51.2, 37.0, 25.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ −77.73. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{11}H_{11}BrIS$ 380.8810, found 380.8793.

Formation of Crystals of 12b for Single-Crystal X-Ray Analysis. A 1 dram vial was charged with product **12b** (ca. 50 mg). Acetonitrile was added slowly until the solid was completely dissolved. Et_2O was then layered on top of the acetonitrile solution. The resulting mixture was left at ambient temperature for 5 d. The formed crystals were left in the mother liquor and brought to the X-ray crystallography facility for characterization.

*(E)-1-(3-chlorophenyl)-2-(iodomethylene)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**12c**)*. Prepared

according to Procedure B with no modification to yield sulfonium triflate **12c** as a colorless solid (114 mg, 94%). ^{1}H NMR (400 MHz, CD_3CN) δ 8.09 (t, *J* = 2.6 Hz, 1H), 7.75 (m, 2H), 7.65 (m, 2H), 4.18 (m, 1H), 4.01 (m, 1H), 3.15 (m, 1H) 2.84 (m, 1H), 2.52 (m, 1H), 2.33 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN) δ 140.1, 137.2, 135.0, 129.9, 129.0, 129.0, 97.3, 53.2, 38.2, 26.6. ^{19}F NMR (376 MHz, CD_3CN) δ −79.32. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{11}H_{11}ClIS$ 336.9315, found 336.9305.

*(E)-2-(iodomethylene)-1-(4-methoxyphenyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**12f**)*. Prepared according to Procedure B with no modification to yield sulfonium triflate **12f** as a brown solid (113 mg, 94%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.84 (t, *J* = 2.6 Hz, 1H), 7.64 (m, 2H), 7.19 (m, 2H), 4.14 (m, 1H), 3.89 (s, 3H), 3.84 (m, 1H), 3.13 (m, 1H), 2.86 (m, 1H), 2.48 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ 165.2, 142.4, 133.2, 117.5 ,117.4, 94.4, 56.9, 53.1, 38.2, 26.3. ^{19}F NMR (376 MHz, CD_3CN) δ −79.31. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{12}H_{14}IOS$ 332.9810, found 332.9809.

*(E)-2-(iodomethylene)-1-(2-(methoxycarbonyl)phenyl)tetrahydro-1H-thiophen-1-ium trifluoromethanesulfonate (**12k**)*. Prepared according to Procedure B with no modification to yield sulfonium triflate **12k** as a yellow solid (122 mg, 96%). ^{1}H NMR (400 MHz, CD_3CN) δ 8.33 (m, 1H), 8.09 (t, *J* = 2.5 Hz, 1H), 7.89 (m, 2H), 7.62 (m, 1H), 4.26 (m, 1H), 4.01 (s, 3H), 3.89 (m, 1H), 3.15 (m, 1H), 2.92 (m, 1H), 2.46 (m, 1H), 2.13 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ 167.2, 138.9, 136.0, 134.7, 133.9, 131.1, 129.9, 128.5, 99.0, 54.5, 54.2, 38.9, 25.9. ^{19}F NMR 376 MHz, CD_3CN) δ −79.33. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]+ calcd for $C_{13}H_{14}IO_2S$ 360.9759, found 360.9758.

*1-(3-chlorophenyl)-4-iodo-2,3-dihydro-1H-thiophen-1-ium trifluoromethanesulfonate (**13c**)*. Prepared according to Procedure B with no modification to yield sulfonium triflate **13c** as a yellow solid (70.5 mg, 60%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.77 (m, 2H), 7.68 (m, 2H), 6.80 (t, *J* = 2.0 Hz, 1H), 4.27 (m, 1H), 3.80–3.61 (m, 2H), 3.44 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN) δ 137.0, 135.7, 133.2, 130.7, 129.8, 128.9, 120.3, 115.7, 48.8, 47.4. ^{19}F NMR (376 MHz, CD_3CN) δ −79.25. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{10}H_9ClIS$ 322.9158, found 322.9147.

*1-(4-fluorophenyl)-4-iodo-2,3-dihydro-1H-thiophen-1-ium trifluoromethanesulfonate (**13d**)*. Prepared according to Procedure B with no modification to yield sulfonium triflate **13d** as a brown crystalline solid (84.3 mg, 74%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.80 (t, *J* = 2.6 Hz, 1H), 7.43 (m, 2H), 6.79 (t, *J* = 2.0 Hz, 1H), 4.24 (m, 1H), 3.74–3.61 (m, 2H), 3.44 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_3CN) δ 167.3 (d, *J* = 255.9 Hz), 134.4 (d, *J* = 10.1 Hz), 122.4 (d, *J* = 3.0 Hz), 121.1, 119.3 (d, J = 23.6 Hz), 114.7, 48.8, 47.3. ^{19}F NMR (376 MHz, CD_3CN) δ −79.26, −103.98. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{10}H_9FIS$ 306.9454, found 306.9451.

Formation of Crystals of 13d for Single-Crystal X-Ray Analysis. A portion of the solid (ca. 20 mg) was charged into a 1 dram vial and dissolved in MeOH (ca. 0.5 mL). This vial was left uncapped. After 3 d, the solvent had evaporated, leaving behind crystals. These crystals were submitted to the X-ray crystallography facility for analysis.

*4-iodo-5-propyl-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium trifluoromethanesulfonate (**13e**)*. A 1 dram vial was charged with substrate **4e** (75 mg, 0.34 mmol, 1 equiv). A separate 1 dram vial equipped with a stir bar was charged with iodine (87 mg, 0.250 mmol, 1 equiv), AgOTf (88 mg, 0.250 mmol, 1 equiv), and DCM (1.5 mL). The DCM solution of substrate **1** was then transferred into the iodine–AgOTf vial. The vial was sealed with a plastic screw cap and covered with aluminum foil. The reaction mixture was stirred at ambient temperature for 1 h. The reaction mixture was then filtered through celite and rinsed through with DCM (10 mL). The filtrate was washed with saturated $Na_2S_2O_3$ solution (1 × 1 mL) and DI water (1 × 5 mL). The combined aqueous layers were extracted with DCM (2 × 5 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 and purified by normal-phase column chromatography (0–100% [10% MeOH in DCM] in hexanes) to afford sulfonium triflate **13e** as a yellow oil (138 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 4.63 (m, 1H), 3.85 (m, 1H), 3.71 (m, 1H), 3.57 (m, 1H), 2.67 (m, 1H), 2.47 (s, 3H), 2.15 (m, 1H), 1.50 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.1, 132.8, 132.4, 130.5, 121.1, 108.0, 47.3, 46.3, 33.2, 21.9, 21.0, 13.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ −78.15. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{14}H_{18}IS$ 345.0174, found 345.0168.

*5-(4-fluorophenyl)-4-iodo-1-(p-tolyl)-2,3-dihydro-1H-thiophen-1-ium trifluoromethanesulfonate (**13f**)*. A 1 dram vial was charged with substrate **4f** (67.6 mg, 0.250 mmol, 1 equiv). A separate 1 dram vial equipped with a stir bar was charged with iodine (63.5 mg, 0.250 mmol, 1 equiv), AgOTf (64.2 mg, 0.250 mmol, 1 equiv), and DCM (1.0 mL). The DCM solution of substrate **1** was then transferred into the iodine–AgOTf vial. The vial was sealed with a plastic screw cap and covered with aluminum foil. The reaction mixture was stirred at ambient temperature for 1 h. The reaction mixture was then diluted with 10 mL Et_2O and filtered through a celite plug. This filtrate was separated and the plug was then washed with acetonitrile (10 mL). The Et_2O filtrate was concentrated in vacuo and dissolved in DCM (5 mL). This solution was washed with saturated $Na_2S_2O_3$ solution (1 × 5 mL). The aqueous layer was extracted with DCM (2 × 5 mL). The DCM layers were combined, dried over Na_2SO_4, and filtered via gravity filtration through glass wool. This filtrate was combined with the acetonitrile filtrate and concentrated in vacuo to afford sulfonium triflate **13f** as a yellow solid (113 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.43 (m, 4H), 7.07 (m, 2H), 4.85 (m, 1H), 3.97–3.80 (m, 3H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.9 (d, *J* = 253.5 Hz), 147.1, 132.4, 132.1 (d, *J* = 8.9 Hz), 130.7, 130.5, 124.8 (d, *J* = 2.7 Hz), 121.4, 116.9 (d, *J* = 22.3 Hz), 108.6, 48.0, 47.3, 21.9. ^{19}F NMR (564 MHz, $CDCl_3$) δ −78.07, −106.81. HRMS (ESI-TOF) *m/z* [M−$^-$OTf]$^+$ calcd for $C_{17}H_{15}FIS$ 396.9923, found 396.9907.

Potassium Cyanide Substitution Comparison Experiment with Sulfonium Ion Pair. A 1 dram vial equipped with a stir bar was charged with potassium cyanide (12.2 mg, 0.188 mmol, 3 equiv), followed by a solution of sulfonium triflate **12a** (29.1 mg, 0.0625 mmol, 1 equiv) dissolved in DMSO-d_6 (0.5 mL). The reaction mixture was allowed to stir for 20 h at ambient temperature. The resulting solution was then transferred to an NMR tube and analyzed by ^{1}H NMR spectroscopy.

*(E)-4-((4-bromophenyl)thio)-5-iodo-N-phenethylpent-4-en-1-amine (**14**)*. A 1 dram vial equipped with a stir bar was charged with sulfonium triflate **13b** (66.4 mg, 0.125 mmol, 1 equiv). A separate 1 dram vial was charged with 2-phenylethan-1-amine (45.4 mg, 0.375 mmol, 3 equiv) and DCM (1 mL). The DCM solution was then added to the sulfonium triflate vial. The vial was capped and stirred at

ambient temperature for 3 h. The reaction solution was then diluted with DCM (5 mL) and washed with 1 M NaOH (10 mL). The aqueous layer was extracted with DCM (2 × 5 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 material was purified by normal-phase column chromatography (0–30% EtOAc in hexanes with 1% NEt_3) to afford amine **14** as a yellow oil (48.1 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.29 (m, 2H), 7.21 (m, 5H), 6.22 (s, 1H), 2.88 (t, *J* = 6.9 Hz, 2H), 2.82 (t, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 2.38 (m, 2H), 1.75 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 134.2, 140.1, 133.8, 132.6, 132.2, 128.9, 128.6, 126.3, 122.5, 78.2, 51.1, 48.8, 36.5, 35.1, 27.8. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{19}H_{22}BrINS$ 501.9701, found 501.9707. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{22}BrINS$ 453.9701, found 453.9713.

*(E)-4-((4-bromophenyl)thio)-N,N-diethyl-5-iodopent-4-en-1-amine (**15**)*. A 1 dram vial equipped with a stir bar was charged with sulfonium triflate **13b** (66.4 mg, 0.125 mmol, 1 equiv). A separate 1 dram vial was charged with diethylamine (27.4 mg, 0.375 mmol, 3 equiv) and DCM (1 mL). The DCM solution was then added to the sulfonium triflate vial. The vial was capped and stirred at ambient temperature for 3 h. The reaction solution was then diluted with DCM (5 mL) and washed with 1 M NaOH (5 mL). The aqueous layer was extracted with DCM (2 × 5 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 material was purified by normal-phase column chromatography (0–20% EtOAc in hexanes with 1% NEt_3) to afford amine **15** as a yellow oil (39.8 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.24 (m, 2H), 6.22 (s, 1H), 2.54 (q, *J* = 7.1 Hz, 4H), 2.46 (m. 2H), 2.37 (m, 2H), 1.75 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.5, 133.9, 132.6, 132.3, 122.5, 77.8, 52.1, 46.9, 35.5, 24.9, 11.8. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{22}BrINS$ 453.9701, found 453.9713.

*(E)-4-(4-((4-bromophenyl)thio)-5-iodopent-4-en-1-yl)morpholine (**16**)*. A 1 dram vial equipped with a stir bar was charged with sulfonium triflate **13b** (106 mg, 0.200 mmol, 1 equiv) was added morpholine (1.01 g, 1.00 mL, 11.6 mmol, 58 equiv). The reaction mixture was capped and stirred at ambient temperature for 3 h. The reaction solution was then diluted with Et_2O (5 mL) and washed with 1 M NaOH (5 mL). The aqueous layer was extracted with Et_2O (2 × 5 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 material was purified by normal-phase column chromatography (0–40% EtOAc in hexanes) to afford amine **16** as a brown oil (62.5 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.23 (m, 2H), 6.25 (s, 1H), 3.71 (br s, 4H), 2.54–2.39 (m, 6H), 2.38–2.31 (br s, 2H), 1.75(br s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 143.3, 133.7, 132.6, 132.2, 122.5, 78.2, 67.0, 57.9, 53.7, 35.1, 24.4. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{15}H_{20}BrINOS$ 467.9494, found 467.9495.

*(E)-4-((4-bromophenyl)thio)-5-iodopent-4-enal (**17**)*. A 1 dram vial equipped with a stir bar was charged with sulfonium triflate **13b** (53.1 mg, 0.100 mmol, 1 equiv) and DMSO (2.5 mL). The reaction vial was placed in a heating block and stirred at 60 °C for 2 h. A separate 1 dram vial was charged with DIPEA (64.6 mg, 0.500 mmol, 5 equiv) and DCM (2.5 mL). The DCM solution was added dropwise to the DMSO vial. The vial of combined solutions was then capped and stirred at 60 °C for 1 h. The reaction solution was allowed to cool to ambient temperature and quenched with 1 M HCl (10 mL). This mixture was extracted with hexanes (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 material was purified by normal-phase column chromatography (0–10% EtOAc in hexanes) to afford aldehyde **17** colorless oil (29.7 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.47 (m, 2H), 7.22 (m, 2H), 6.37 (s, 1H), 2.69 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 200.5, 141.6, 133.5, 132.8, 131.7, 122.7, 80.0, 41.6, 30.3. HRMS (CI-TOF) *m*/*z* [M]$^+$ calcd for $C_{11}H_{10}BrIOS$ 395.8680, found 395.8692.

*(E)-4-(3-iodo-4-(p-tolylthio)hept-3-en-1-yl)morpholine (**18**)*. A 1 dram vial equipped with a stir bar was charged with sulfonium triflate **14e** (105 mg, 0.212 mmol, 1 equiv) and morpholine (1.07 g, 1.06 mL, 12.3 mmol, 58 equiv). The reaction mixture was capped and stirred at ambient temperature for 2 h. The reaction solution was then mixed with hexanes (30 mL). The mixture was washed with 1 M NaOH (1 × 10 mL), DI water (2 × 10 mL), and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4 and filtered via gravity filtration through glass wool. The filtrate was concentrated in vacuo to afford amine **18** as a yellow oil (79.9 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.70 (t, *J* = 4.5 Hz, 4H), 3.17 (t, *J* = 7.4 Hz, 2H), 2.56 (d, *J* = 7.4 Hz, 2H), 2.51 (br s, 4H), 2.36–2.31 (m, 5H), 1.52 (m, 2H), 0.86 (t, *J* = 7.34 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.8, 137.0, 131.4, 130.4, 129.9, 107.3, 67.1, 58.0, 53.9, 43.4, 41.1, 21.3, 21.2, 13.6. HRMS (ESI-TOF) *m*/*z* [M+H]$^+$ calcd for $C_{18}H_{27}INOS$ 432.0858, found 432.0858.

ASSOCIATED CONTENT

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, experimental for investigation of an *n* = 2 substrate, single crystal X-ray structure information, NMR spectra

Accession Codes

CCDC 2279048-2279051 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, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Suzanne A. Blum - Department of Chemistry, University of California, Irvine, California 92697-2025, United States; https://orcid.org/0000-0002-8055-1405; blums@uci.edu

Author

Joseph A. Kaplan - Department of Chemistry, University of California, Irvine, California 92697-2025, United States; https://orcid.org/0000-0003-0837-8801

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REFERENCES

(1) Vardakas, K. Z.; Voulgaris, G. L.; Maliaros, A.; Samonis, G.; Falagas, M. E. Prolonged versus Short-Term Intravenous Infusion of Antipseudomonal β-Lactams for Patients with Sepsis: A Systematic Review and Meta-Analysis of Randomised Trials. *Lancet Infect. Dis.* **2018**, *18*, 108–120, DOI: 10.1016/S1473-3099(17)30615-1.

(2) Edwards, J. R. Meropenem: A Microbiological Overview. *J. Antimicrob. Chemother.* **1995**, *36*, 1–17, DOI: 10.1093/jac/36.suppl_A.1.

(3) Ludwiczuk, A.; Skalicka-Woźniak, K.; Georgiev, M. I. Terpenoids. In *Pharmacognosy*; Elsevier, 2017; pp 233–266, DOI: 10.1016/B978-0-12-802104-0.00011-1.

(4) Yan, C.; Barlow, S.; Wang, Z.; Yan, H.; Jen, A. K. Y.; Marder, S. R.; Zhan, X. Non-Fullerene Acceptors for Organic Solar Cells. *Nat. Rev. Mater.* **2018**, *3*, 1–19, DOI: 10.1038/natrevmats.2018.3.

(5) Plesniak, M. P.; Huang, H. M.; Procter, D. J. Radical Cascade Reactions Triggered by Single Electron Transfer. *Nat. Rev. Chem.* **2017**, *1*, 1–16, DOI: 10.1038/S41570-017-0077.

(6) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. The Diels-Alder Reaction in Total Synthesis. *Angew. Chem. Int. Ed.* **2002**, *41*, 1668–1698, DOI: 10.1002/1521-3773(20020517)41:10<1668::AID-ANIE1668>3.0.CO;2-Z.

(7) Yoder, R. A.; Johnston, J. N. A Case Study in Biomimetic Total Synthesis: Polyolefin Carbocyclizations to Terpenes and Steroids. *Chem. Rev.* **2005**, *105*, 4730–4756, DOI: 10.1021/cr040623l.

(8) Flynn, A. B.; Ogilvie, W. W. Stereocontrolled Synthesis of Tetrasubstituted Olefins. *Chem. Rev.* **2007**, *107*, 4698–4745, DOI: 10.1021/cr050051k.

(9) Buttard, F.; Sharma, J.; Champagne, P. A. Recent Advances in the Stereoselective Synthesis of Acyclic All-Carbon Tetrasubstituted Alkenes. *Chem. Commun.* **2021**, *57*, 4071–4088, DOI: 10.1039/d1cc00596k.

(10) Ding, W.; Chai, J.; Wang, C.; Wu, J.; Yoshikai, N. Stereoselective Access to Highly Substituted Vinyl Ethers via *trans*-Difunctionalization of Alkynes with Alcohols and Iodine(III) Electrophile. *J. Am. Chem. Soc.* **2020**, *142*, 8619–8624, DOI: 10.1021/jacs.0c04140.

(11) Chai, J.; Ding, W.; Wang, C.; Ito, S.; Wu, J.; Yoshikai, N. Ritter-Type Iodo(III)Amidation of Unactivated Alkynes for the Stereoselective Synthesis of Multisubstituted Enamides. *Chem. Sci.* **2021**, *12*, 15128–15133, DOI: 10.1039/D1SC05240C.

(12) Zhou, P.; Pan, Y.; Tan, H.; Liu, W. I_2 –DMSO–H_2O: A Metal-Free Combination System for the Oxidative Addition of Alkynes to Access (*E*)-*α*-Iodo-*β*-Methylsulfonylalkenes. *J. Org. Chem.* **2019**, *84*, 15662–15668, DOI: 10.1021/acs.joc.9b02302.

(13) Suero, M. G.; Bayle, E. D.; Collins, B. S. L.; Gaunt, M. J. Copper-Catalyzed Electrophilic Carbofunctionalization of Alkynes to Highly Functionalized Tetrasubstituted Alkenes. *J. Am. Chem. Soc.* **2013**, *135*, 5332–5335, DOI: 10.1021/ja401840j.

(14) Godoi, B.; Schumacher, R. F.; Zeni, G. Synthesis of Heterocycles via Electrophilic Cyclization of Alkynes Containing Heteroatom. *Chem. Rev.* **2011**, *111*, 2937–2980, DOI: 10.1021/cr100214d.

(15) Nakamura, I.; Yamamoto, Y. Transition-Metal-Catalyzed Reactions in Heterocyclic Synthesis. *Chem. Rev.* **2004**, *104*, 2127–2198, DOI: 10.1021/cr020095i.

(16) Issaian, A.; Tu, K. N.; Blum, S. A. Boron-Heteroatom Addition Reactions via Borylative Heterocyclization: Oxyboration, Aminoboration, and Thioboration. *Acc. Chem. Res.* **2017**, *50*, 2598–2609, DOI: 10.1021/acs.accounts.7b00365.

(17) Zeni, G.; Larock, R. C. Synthesis of Heterocycles via Palladium-Catalyzed Oxidative Addition. *Chem. Rev.* **2006**, *106*, 4644–4680, DOI: 10.1021/cr0683966.

(18) Ren, X. F.; Turos, E.; Lake, C. H.; Churchill, M. R. Regiochemical and Stereochemical Studies on Halocyclization Reactions of Unsaturated Sulfides. *J. Org. Chem.* **1995**, *60*, 6468–6483, DOI: 10.1021/jo00125a038.

(19) Yata, T.; Kita, Y.; Nishimoto, Y.; Yasuda, M. Regioselective Synthesis of 5-Metalated 2-Pyrones by Intramolecular Oxymetalation of Carbonyl-Ene-Yne Compounds Using Indium Trihalide. *J. Org. Chem.* **2019**, *84*, 14330–14341, DOI: 10.1021/acs.joc.9b02186.

(20) Aggarwal, T.; Kumar, S.; Verma, A. K. Iodine-Mediated Synthesis of Heterocycles via Electrophilic Cyclization of Alkynes. *Org. Biomol. Chem.* **2016**, *14*, 7639–7653, DOI: 10.1039/C6OB01054G.

(21) Chen, Y.; Hee, S.; Liu, X.; Das, S.; Hong, D.; Leung, P.-H.; Li, Y.; Li, J.; Liu, J. ICl-Mediated Functional Group Interconversion from Methyl Homopropargyl Ether to *α*-Iodo-*γ*-Chloroketone. *J. Org. Chem.* **2022**, *87*, 15129–15138, DOI: 10.1021/acs.joc.2c01638.

(22) Kaplan, J. A.; Issaian, A.; Stang, M.; Gorial, D.; Blum, S. A. Repurposing π Electrophilic Cyclization/Dealkylation for Group Transfer. *Angew. Chem. Int. Ed.* **2021**, *60*, 25776–25780, DOI: 10.1002/anie.202112351.

(23) Trudel, V.; Tien, C.-H.; Trofimova, A.; Yudin, A. K. Interrupted Reactions in Chemical Synthesis. *Nat. Rev. Chem.* **2021**, *5*, 604–623, DOI: 10.1038/s41570-021-00304-2.

(24) Stumpf, A.; Cheng, Z. K.; Wong, B.; Reynolds, M.; Angelaud, R.; Girotti, J.; Deese, A.; Gu, C.; Gazzard, L. Development of an Expedient Process for the Multi-Kilogram Synthesis of Chk1 Inhibitor GDC-0425. *Org. Process Res. Dev.* **2015**, *19*, 661–672, DOI: 10.1021/acs.oprd.5b00105.

(25) Girardin, M.; Dolman, S. J.; Lauzon, S.; Ouellet, S. G.; Hughes, G.; Fernandez, P.; Zhou, G.; O'Shea, P. D. Development of a Practical Synthesis of Stearoyl-CoA Desaturase (SCD1) Inhibitor MK-8245. *Org. Process Res. Dev.* **2011**, *15*, 1073–1080, DOI: 10.1021/op200186d.

(26) Sader, H. S.; Johnson, D. M.; Jones, R. N. In Vitro Activities of the Novel Cephalosporin LB 11058 against Multidrug-Resistant Staphylococci and Streptococci. *Antimicrob. Agents Chemother.* **2004**, *48*, 53–62, DOI: 10.1128/AAC.48.1.53-62.2004.

(27) Ceruti, M.; Balliano, G.; Rocco, F.; Milla, P.; Arpicco, S.; Cattel, L.; Viola, F. Vinyl Sulfide Derivatives of

Truncated Oxidosqualene as Selective Inhibitors of Oxidosqualene and Squalene-Hopene Cyclases. *Lipids* **2001**, *36*, 629–636, DOI: 10.1007/s11745-001-0767-8.

(28) Itami, K.; Kamei, T.; Yoshida, J. Diversity-Oriented Synthesis of Tamoxifen-Type Tetrasubstituted Olefins. *J. Am. Chem. Soc.* **2003**, *125*, 14670–14671, DOI: 10.1021/ja037566i.

(29) Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. Nickel-Induced Conversion of Carbon-Sulphur into Carbon-Carbon Bonds. One-Step Transformations of Enol Sulphides into Olefins and Benzenethiol Derivatives into Alkylarenes and Biaryls. *J. Chem. Soc., Chem. Commun.* **1979**, *14*, 637–638, DOI: 10.1039/C39790000637.

(30) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483, DOI: 10.1021/cr00039a007.

(31) Stille, J. K. The Palladium-Catalyzed Cross-Coupling Reactions of Organotin Reagents with Organic Electrophiles. *Angew. Chem. Int. Ed.* **1986**, *25*, 508–524, DOI: 10.1002/anie.198605081.

(32) Doucet, H.; Hierso, J.-C. Palladium-Based Catalytic Systems for the Synthesis of Conjugated Enynes by Sonogashira Reactions and Related Alkynylations. *Angew. Chem. Int. Ed.* **2007**, *46*, 834–871, DOI: 10.1002/anie.200602761.

(33) Baba, S.; Negishi, E. A Novel Stereospecific Alkenyl-Alkenyl Cross-Coupling by a Palladium- or Nickel-Catalyzed Reaction of Alkenylalanes with Alkenyl Halides. *J. Am. Chem. Soc.* **1976**, *98*, 6729–6731, DOI: 10.1021/ja00437a067.

(34) Suzuki, A. Recent Advances in the Cross-Coupling Reactions of Organoboron Derivatives with Organic Electrophiles. *J. Organomet. Chem.* **1999**, *576*, 147–168, DOI: S0022-328X(98)01055-9.

(35) Law, C. S. W.; Yeong, K. Y. Current Trends of Benzothiazoles in Drug Discovery: A Patent Review (2015–2020). *Expert Opin. Ther. Pat.* **2022**, *32*, 299–315, DOI: 10.1080/13543776.2022.2026327.

(36) Bianchini, R.; Chiappe, C.; Lo Moro, G.; Lenoir, D.; Lemmen, P.; Goldberg, N. Spectroscopic and Theoretical Investigations of Electrophilic Bromination Reactions of Alkynes: The First Evidence for π Complexes as Reaction Intermediates. *Chem. - A Eur. J.* **1999**, *5*, 1570–1580, DOI: 10.1002/(SICI)1521-3765(19990503)5:5<1570::AID-CHEM1570>3.0.CO;2-A.

(37) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. The Question of Reversible Formation of Bromonium Ions during the Course of Electrophilic Bromination of Olefins. 2. The Crystal and Molecular Structure of the Bromonium Ion of Adamantylideneadamantane. *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508, DOI: 10.1021/ja00301a021.

(38) Larock, R. C.; Yue, D. Synthesis of Benzo[*b*]Thiophenes by Electrophilic Cyclization. *Tetrahedron Lett.* **2001**, *42*, 6011–6013, DOI: 10.1016/S0040-4039(01)01149-2.

(39) Faizi, D. J.; Davis, A. J.; Meany, F. B.; Blum, S. A. Catalyst-Free Formal Thioboration to Synthesize Borylated Benzothiophenes and Dihydrothiophenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 14286–14290, DOI: 10.1002/anie.201608090.

(40) Gabriele, B.; Mancuso, R.; Larock, R. Recent Advances in the Synthesis of Iodoheterocycles via Iodocyclization of Functionalized Alkynes. *Curr. Org. Chem.* **2013**, *18*, 341–358, DOI: 10.2174/1385272813179990034.

(41) Tsuji, T.; Takenaka, K. Facile 5'-Halogenation of Unprotected Nucleosides. *Nucleosides, Nucleotides and Nucleic Acids* **1987**, *6*, 575–580, DOI: 10.1080/07328318708069986.

(42) Gaviña, F.; Luis, S. V; Ferrer, P.; Costero, A. M.; Marco, J. A. 1,1-Di-Iodoalkenes from Aldehydes and Triphenylphosphine–Carbon Tetraiodide. *J. Chem. Soc., Chem. Commun.* **1985**, No. 5, 296–297, DOI: 10.1039/C39850000296.

(43) Bailey, W. F.; Patricia, J. J. The Mechanism of the Lithium - Halogen Interchange Reaction : A Review of the Literature. *J. Organomet. Chem.* **1988**, *352*, 1–46, DOI: 10.1016/0022-328X(88)83017-1.

(44) Holst, D. E.; Wang, D. J.; Kim, M. J.; Guzei, I. A.; Wickens, Z. K. Aziridine Synthesis by Coupling Amines and Alkenes via an Electrogenerated Dication. *Nature* **2021**, *596*, 74–79, DOI: 10.1038/s41586-021-03717-7.

(45) Capella, L.; Montevecchi, P. C.; Nanni, D. Tin Radical Addition to Alkynyl Sulfides: Reactivity of the Intermediate Thioalkyl-Substituted .Beta.-(Tributylstannyl)Vinyl Radicals. *J. Org. Chem.* **1994**, *59*, 3368–3374, DOI: 10.1021/jo00091a025.

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