Tetrahedron 67 (2011) 1002–1010

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthetic scope, computational chemistry and mechanism of a base induced 5-*endo* cyclization of benzyl alkynyl sulfides

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ARTICLE INFO

Article history:
Received 13 September 2010
Received in revised form 29 November 2010
Accepted 30 November 2010
Available online 7 December 2010

Keywords:
Cyclization
Computational chemistry
Tautomerism
Dihydrothiophenes
Carbanions

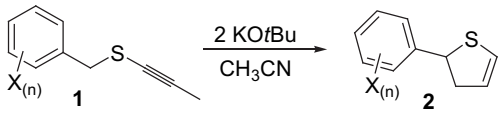
ABSTRACT

We present an experimental and computational study of the reaction of aryl substituted benzyl 1-alkynyl sulfides with potassium alkoxide in acetonitrile, which produces 2-aryl 2,3-dihydrothiophenes in poor to good yields. The cyclization is most efficient with electron withdrawing groups on the aromatic ring. Evidence indicates there is rapid exchange of protons and tautomerism of the alkynyl unit prior to cyclization. Theoretical calculations were also conducted to help rationalize the base induced 5-*endo* cyclization of benzyl 1-propynyl sulfide (**1a**). The potential energy surface was calculated for the formation of 2,3-dihydrothiophene in a reaction of benzyl 1-propynyl sulfide (**1a**) with potassium methoxide. Geometries were optimized with CAM-B3LYP/6-311+G(d,p) in acetonitrile with the CPCM solvent model. It is significant that the benzyl propa-1,2-dien-1-yl sulfane (**6**) possessed a lower benzylic proton affinity than the benzyl prop-2-yn-1-yl sulfane (**8**) thus favoring the base induced reaction of the former. From benzyl(propa-1,2-dien-1-yl sulfane (**6**), 2,3-dihydrothiophene can be formed via a conjugate base that undergoes 5-*endo-trig* cyclization followed by a protonation step.

1. Introduction

2,3-Dihydrothiophenes are useful synthetic precursors for many compounds including thiophenes,[1] thionucleoside derivatives,[2] and penicillin mimics.[3] Synthetic routes to 2,3-dihydrothiophenes are varied and numerous,[1f,4] with based-induced cyclizations playing an important role. Under basic conditions, starting substrates usually require the presence of electron withdrawing or other functionality to facilitate condensation chemistry or to directly participate in the cyclization.[5] Some cyclizations that make use of transition metals to target dihydrothiophenes[6] do not require such strong directing functionality.[6a] A radical based cyclization free of strong electron withdrawing groups provided mixtures of 2,3 and 2,5-dihydrothiophenes.[7]

In 2000, the Schwan group reported chemistry that created 2,3-dihydrothiophenes (**2**) by way of a *tert*-butoxide induced 5-*endo* cyclization of 2-substituted arylmethyl alkynyl sulfides (**1**), Eq. (1).[8] That reaction was thought to involve benzylic deprotonation and cyclization at the terminal carbon of the propynyl chain, even though the starting material did not possess unsaturation in the terminal carbon, nor held any other skeletal functionality to bring about carbon–carbon bond formation. Although there was no ostensible need for strong electron withdrawing groups or other reactive functionality in the substrates, there nevertheless was a requirement for an electron withdrawing group on the aryl ring. In the communication, some mechanistic data were offered, but some intriguing uncertainties remained.[8] How was it that the cyclization occurred most efficiently when the starting material did not have unsaturation at the propynyl terminus? Which tautomeric form of the 3-carbon unit is accepting the electron density? We now report that a broader selection of arylmethyl alkynyl sulfides succumbs to the cyclization and we offer some mechanistic and computational evidence concerning the mode of cyclization of the substrates.



(1)

2. Results and discussion

2.1. Scope of the reaction

The requisite starting materials (**1**) were accessible by adaption of benzylic halides or alcohols. The alcohols were converted to thiocyanates under Mitsunobu conditions, whereas the halides were

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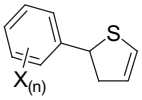
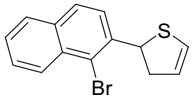
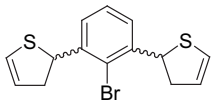
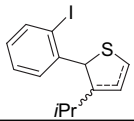
doi:10.1016/j.tet.2010.11.104

converted to thiocyanates or thiotosylates by direct substitution with appropriate sulfur reagent.[9] The $ArCH_2S–X$ reagents were then treated with an acetylide to bring forth the benzyl alkynyl sulfides.[10] Full synthetic procedures are in the Supplementary data.

In the communication,[8] many optimized reaction parameters were reported including solvent and substrate concentration. It was subsequently learned that KO^{t}Bu is preferred over sodium or lithium *tert*-butoxide. Thus, treating the starting sulfides **1** with 2 equiv of KO^{t}Bu in acetonitrile at various temperatures for 24 h affords a dihydrothiophene (**2**) with the aryl group at the 2-position and the double bond at the 4-position, Eq. (1).

The products and yields are outlined in Table 1. The products were identified through standard spectroscopic characterization. Particularly diagnostic are the five sets of non-aryl resonances in the ^{1}H NMR spectrum, each of which represents one proton from the dihydrothiophene ring. The ^{1}H NMR spectra consistently exhibit a ddd near 6.2 ppm, a dt near 5.6 ppm, a dd near 5.3 ppm, a ddt near 3.3 ppm, and a dddd near 2.9 ppm. The ^{1}H–^{1}H coupling constants of products match those of related heterocycles.[5c,11] The initial notion that a 2-substituted aryl group is required for cyclization[8] was found to be invalid, as the results show that electron withdrawing groups at other aryl position promote the reaction.

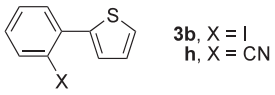
Table 1
Cyclization data for benzyl 1-alkynyl sulfides

#	Product	Temp (°C)[a]	Yield[b]
			
2a	X=2-H	Reflux	28[c,d]
b	X=2-I	0	75
c	X=2-Br	0	74
d	X=2-Cl	0	74
e	X=2-Me	Reflux	0
f	X=2-Ph	Reflux[e]	41[c,d]
g	X=2-F	Reflux	45
h	X=2-CN	Reflux	64
i	X=3-I	rt	68
j	X=4-I	rt	45
k	X=3-CF_3	Reflux	59
l	X=2-SPh	Reflux	66
m	X=2-S(O)Ph	Reflux	45[f]
n	X=2-$S(O)_2$Ph	Reflux	68
o	X=2,5-$(OMe)_2$	reflux	44[c,d]
p	X=3,5-$(OMe)_2$	Reflux	54[c]
q	X=3-NO_2	Reflux	0
r	X=2-NO_2	Reflux	0
s		0	72
t		60[f,g]	47
u		0	69[h]

[a] Reaction temperature. Compounds **1** were stirred for 24 h unless otherwise indicated.
[b] Yield is of isolated material unless otherwise indicated.
[c] Yield based on consumed starting material.
[d] Product could not be separated from starting material. Product was assigned based in the characteristic ^{1}H NMR peaks.
[e] Refluxed for 8 h.
[f] Mixture of diastereomers (1:1).
[g] Refluxed for 6 h.
[h] Ratio of isomers based on double bond position: 2,3/2,5=1/1.7.

The presence of the nitro groups prevented the reaction and starting material was fully recoverable in the 2-nitro case (**1r**), whereas full decomposition occurred in the 3-nitro case (**1q**). Replacing the aryl groups with heteroaryl groups prevented the reaction. Specifically, 2-bromothien-3-ylmethyl 1-propynyl sulfide, 2-furfuryl 1-propynyl sulfide, and 2-fluoro-4-iodopyrid-3-yl 1-propynyl sulfide did not cyclize. Also, positioning an iodine group at the *peri* position did not prompt cyclization of 8-iodonaphthalen-1-ylmethyl 1-propynyl sulfide.

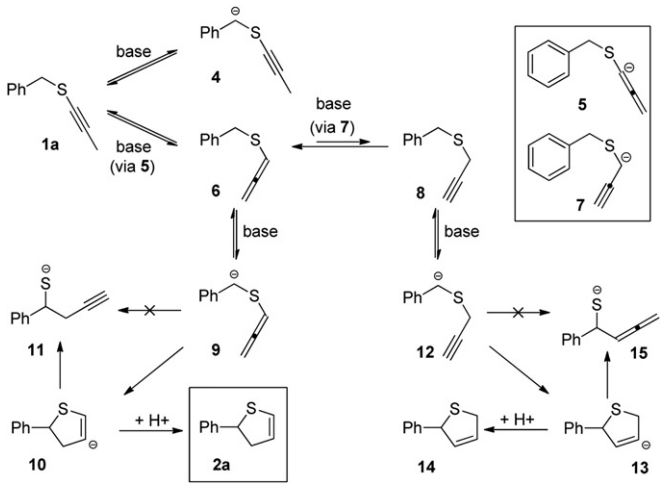
A selection of dihydrothiophenes has been shown to be oxidizable to thiophenes.[1c,e–g,12] Accordingly, we have achieved the successful conversion of heterocycles **2b** and **2h** into thiophenes **3b** and **3h** in 73 and 81% yields, respectively, with DDQ[1e] in $CHCl_3$. Moreover the additional functionality on the aryl unit provides a reactive feature for further adaption toward compounds and polymers with useful electronic properties.[13]



The cyclization represents a rare instance where C–C bond formation occurs without the need for functionality directly participating in condensation or other reactive chemistry. Apparently, after deprotonation, the unsaturation of the 3-carbon substituent on sulfur is sufficient to activate ring closure.

2.2. Mechanism and computations

Theoretical calculations have been conducted to help rationalize the base induced 5-*endo* cyclization of benzyl 1-alkynyl sulfides, which led us to the mechanistic proposal in Scheme 1, slightly modified from that reported in the original communication of 2000.[8] Model system **1a** was used to mimic the core of benzyl alkynyl sulfides bearing substituents on the aryl ring. Because it was impractical to compute the reaction with the potassium *tert*-butoxide base, the potential energy surface was calculated for the formation of 2,3-dihydrothiophene **2a** in a reaction of **1a** with potassium methoxide. Geometries were optimized with CAM-B3LYP/6-311+G(d,p)[14–16] in acetonitrile with the CPCM solvent model.[17]



Scheme 1.

The calculated structures are shown in Fig. 1 where K^+–π interactions are found for all structures. It is interesting to note that π-cation interactions are influenced less by inductive effects and more by through-space effects between the metal ion and substituents on

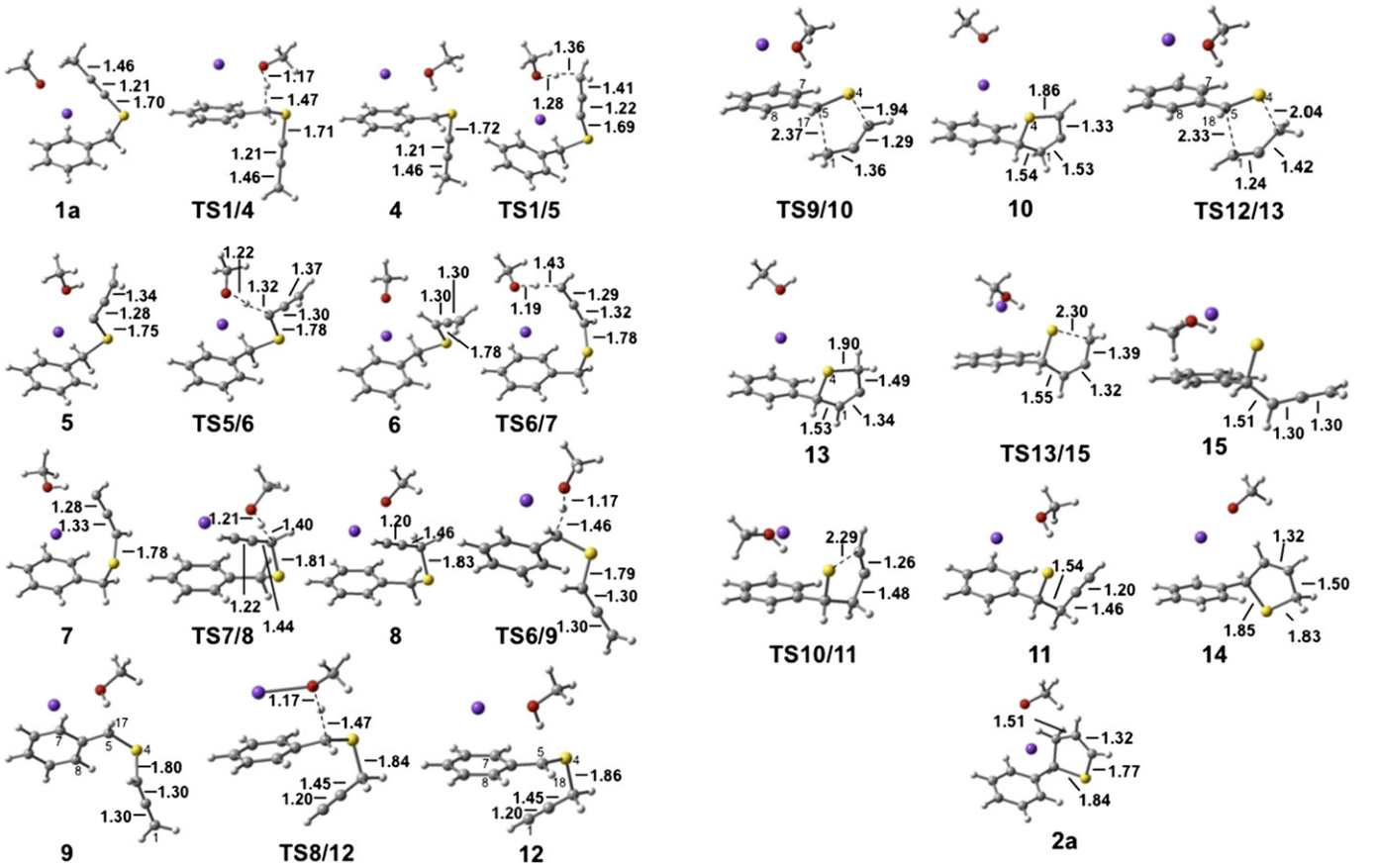


Fig. 1. Optimized CPMC-CAM-B3LYP/6-311+G(d,p) geometries for the KOMe-induced cyclization of **1a**. Calculations were carried out in acetonitrile. K^+, KOMe, and MeOH molecules were modeled explicitly. Bolded numbers aligned near the structures are bond distances in Å. Unbolded numbers on some of the structures are the atom numbers referred to in Table 2.

the aromatic rings,[18] and that the nitro substituent causes the ring to have a very weak π-cation interaction. Because of the complexity of the PES for the parent system **1a**, a computational examination of substituent effects was beyond the scope of our study.

The energetic features of the reaction are shown in Fig. 2. From Fig. 2A it is clear that allenyl species **6** plays a key role in the cyclization process to 2,3-dihydrothiophene **2a** because it is stabilized compared to **8**.

The formation of **4** from **1a** is a 'dead end' and did not convert to cyclic products. Allene **6** is formed in a two-step process from **1a** via intermediate **5**. A transition state for the loss of a benzylic proton from **6** has an activation barrier of 7.9 kcal/mol (Fig. 2B). Upon formation of deprotonated allene **9**, it can undergo a unimolecular 5-*endo*-*trig* cyclization yielding anion **10**, followed by protonation to form **2a**. While the thia-Wittig rearrangement has been elucidated yielding **11** (Fig. 2C), the experimental data suggest a rapid protonation of **10** and the formation of **2a**. An alternative mechanism involves the conversion of deprotonated alkyne **12** via a 5-*endo*-*dig* cyclization to give **13** followed by protonation to form **14**; however, the path to **12** is higher in energy.

Control experiments were performed in order to provide further understanding of the reaction mechanism. When the reaction was performed in CD_3CN, the products possessed essentially full deuteration at the non-aryl carbons, a result consistent with significant solvent intervention. Indeed, deuterium exchange experiments showed that methyl hydrogens of thioethers **1a**,**b**,**i**,**j** each exchanged with half-lives of ca. 25 s at −10 °C, whereas benzyl hydrogen exchange was faster, completing in <25 s at the same temperature. The onset of product was scaled to be substantially longer at the same temperature. Related experiments reaffirmed that the preferred tautomeric state of the 3-carbon unit was the 1-propynyl form as propargyl or allenyl tautomers were never observed by ^1H NMR of the cyclization mixture contents. Such an observation is fully consistent with past literature that indicates the conjugated form is the more thermodynamically stable.[19] Similarly, the computed protonation–deprotonation equilibria, which involve **1a**, **4-8** show relatively low activation energies of 0.4–8.2 kcal/mol and provide an explanation of how proton or deuterium can be incorporated in all C–H sites except on the phenyl ring.

In the condensed phase, our computations did not find a transition state(s) for the isomerization of **2a** to **14**. Additional control experiments on **2b** in CD_3CN, revealed minimal incorporation of D into the material. The 2,3-dihydro isomer (**2b**) is not amenable to migration of the double bond because its exchange is quite slow. We did not probe the equilibrium between **2b** and **14b** due to this slow exchange. The rate of H/D exchange of the starting material is substantially more rapid. It can be noted that re-exposure of **14u** (2,5-dihydro isomer of **2u**) to the reaction conditions causes the **2u**/**14u** isomer ratio to be re-established. However, **2u** does not exchange when re-exposed to the reaction conditions in CD_3CN. Attempts to prepare **14a** in order to study its exchange and isomerization behavior were not successful.

The reaction is most certainly a base mediated cyclization onto the terminus of the three carbon unit. The experimental exchange and computational data suggest that the propynyl/allenyl/propargyl equilibrium is dynamic, with the propynyl as the most populated entity (Fig. 2A). From Fig. 2, it is evident that formation of allenyl species is favored to the propargyl species and accounts for the path to 2,3-dihydrothiophene product in acetonitrile. 2,3-

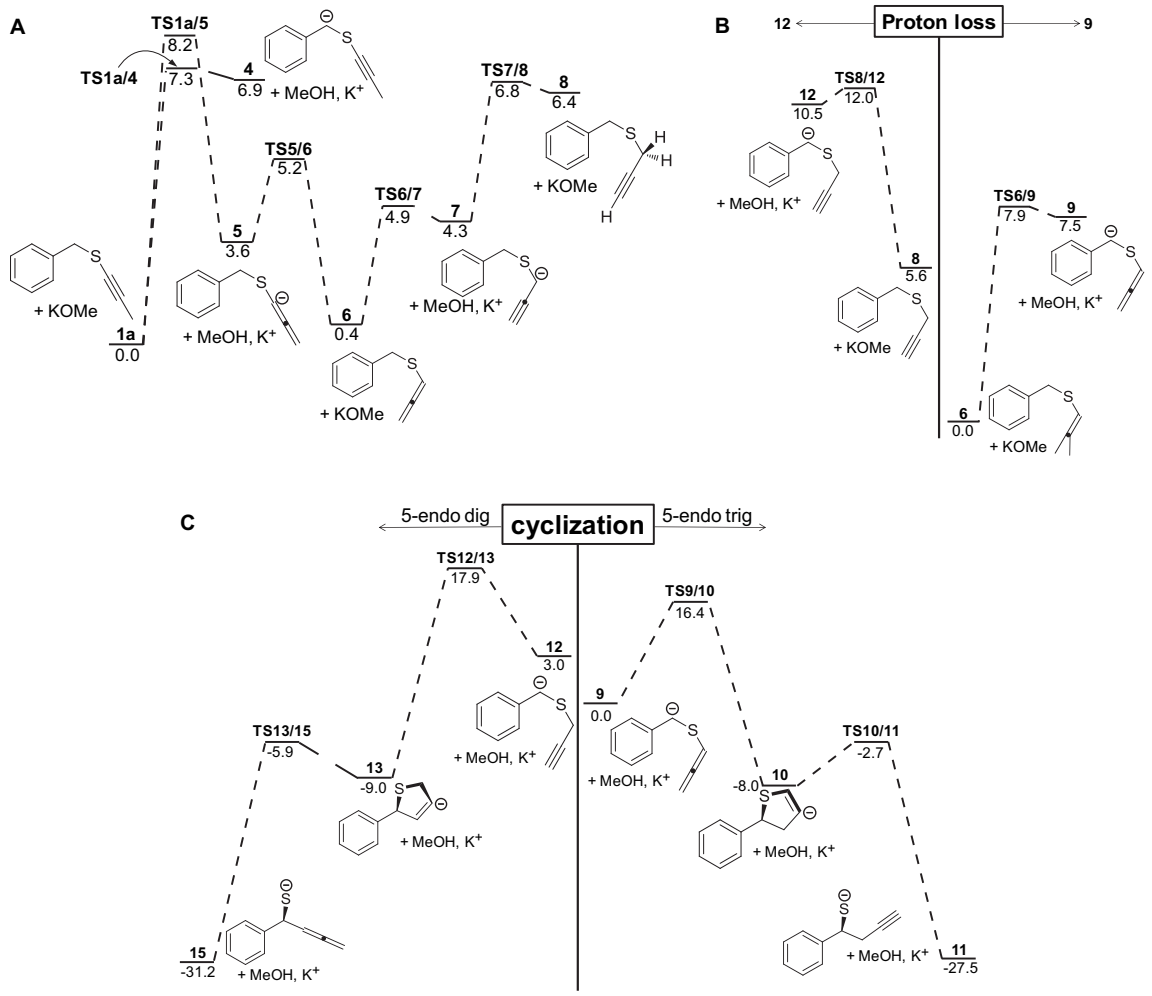


Fig. 2. A–C. CPCM-CAM-B3LYP/6-311+G(d,p) optimized potential energy surface in kcal/mol including thermal corrections for enthalpy (273.15 K). KOMe, K^+, and MeOH molecules were modeled explicitly. Transition states were confirmed by intrinsic reaction coordinate (IRC) calculations.

dihydrothiophene **2a** and 2,5-dihydrothiophene **14** are essentially isoenergetic. The relative energies of these two dihydrothiophene products were calculated to be within 2.8 kcal/mol of each other (Table S1). A change in the solvent or benzyl alkynyl sulfide structure may shift the reaction to propargyl species and the path to 2,5-dihydrothiophene product. The more rapid exchange at the benzylic site suggests that benzylic anions are available to attack the terminus of the 3-carbon unit when unsaturation is available (see Fig. 2C).

While there is ongoing interest in assessing *endo* versus *exo* cyclization preferences for single species,[20] we were not able to locate literature analyses of competitive *endo* cyclizations of equilibrating species. Given our findings, the chemistry at hand does not present a true competition, nevertheless our determination of transition state energies and parameters permit a comparison of two different but closely related entities. The simplicity of the system may serve as a model for other fundamental cyclizations affording five-membered rings.

Baldwin's rules suggest the 5-*endo-dig* cyclization should be allowed, and the 5-*endo-trig* should not.[21] However, the 5-*endo-trig* example in the current paper is allene-based with a geometry very close to the alkyne tautomer and was not specifically addressed by Baldwin.[22] As such, the cyclization tendencies of this comparison are difficult to distinguish without the assistance of computational chemistry.

The transitions states **TS9**/**10** and **TS12**/**13** differ only by a few kcal/mol. Furthermore, many of the calculated parameters are quite similar in the two transition states. For instance, the degrees of rehybridization of the benzylic carbon in the transitions states, as measured by changing dihedral angles, are essentially indistinguishable. However, the transition state differences worth noting relate to C-C bond formation, C(3)-S bond lengthening and the bending of the three carbon unit (Table 2).

Transition state **TS9**/**10** exhibits C–C bond forming at 2.37 Å, C(3)–S bond lengthening of 0.13 Å and a bend of the allene unit to 134°. As a comparison, **TS12**/**13** has closer C–C contacts at 2.33 Å, extra lengthening of C(3)–S (0.21 Å) and a lesser degree of bending at the sp. hybridized carbon (137°). Clearly, **TS12**/**13** calls upon and benefits from the extra lengthening of the C(3)–S bond and there is less inclination to bend at the allenyl/propynyl central carbon. Both of these features permit advanced C–C bond formation in the transition state. The **TS9**/**10** transition state is achieved with more bending at the allenyl carbon but with less developed C–C bond formation and does not require as much C(3)–S bond lengthening.

The data suggest the allene is more receptive to cyclization than the propynyl unit, as it demonstrates a greater propensity to bend during the cyclization. It is possible that such behavior would also come into play with other 5-*endo-dig*/*trig* cyclizations, such as with systems absent of sulfur or any other atom that could accommodate electron density.

Table 2
Selected computation data for cyclizations[a]

	9		**12**	
Original bond lengths of key atoms	C(2)–C(1)	1.30	C(2)–C(1)	1.20
	C(3)–C(2)	1.30	C(3)–C(2)	1.45
	S(4)–C(3)	1.80	S(4)–C(3)	1.86
Original indication of planarity of anion	C(7)–C(6)–C(5)–H(17)	−164.7	C(7)–C(6)–C(5)–H(18)	−171.3
	C(8)–C(6)–C(5)–H(17)	20.00	C(8)–C(6)–C(5)–H(18)	14.3
3-C Bond angle	C(1)–C(2)–C(3)	178.6	C(1)–C(2)–C(3)	179.6
	TS9/10		**TS12/13**	
Bond lengths of key bonds	C(2)–C(1)	1.36	C(2)–C(1)	1.24
	C(3)–C(2)	1.29	C(3)–C(2)	1.42
	S(4)–C(3)	1.94	S(4)–C(3)	2.04
Bond forming distance	C(5)–C(1)	2.37	C(5)–C(1)	2.33
3-C Bond angle	C(1)–C(2)–C(3)	133.8	C(1)–C(2)–C(3)	137.0
Rehybridization dihedral angles	C(7)–C(6)–C(5)–H(17)	173.5	C(7)–C(6)–C(5)–H(18)	173.0
	C(8)–C(6)–C(5)–H(17)	−8.33	C(8)–C(6)–C(5)–H(18)	−8.2
	10		**13**	
Bond lengths of key atoms	C(1)–C(2)	1.52	C(2)–C(1)	1.34
	C(2)–C(3)	1.33	C(3)–C(2)	1.49
	C(3)–S(4)	1.86	S(4)–C(3)	1.90
3-C Bond angle	C(3)–C(2)–C(1)	109.5	C(3)–C(2)–C(1)	112.4

[a] The numbering scheme is shown in Fig. 1. Bond distances in Å. Bond angles and dihedral angles in degrees.

3. Conclusions

A simple base-induced transition metal free 5-*endo* cyclization of benzyl 1-alkynyl sulfides (**1**) proceeds without the need for activating of electron withdrawing substituents directly attached to skeletal carbons. The 2,3-dihydrothiophene products (**2**) can be readily forwarded to 2-aryl thiophenes. Computational chemistry was performed to assist in the understanding of mechanism of cyclization and establish, which allenyl/propargyl tautomer is likely involved in the cyclization.

It is significant that the allenyl species **6**, formed in a stepwise path via **5**, is more stable than the propargyl species **8**. The weaker benzylic proton affinity of **6** than **8** favors the base induced reaction of **6**. From allenyl species **6**, 2,3-dihydrothiophene **2a** can be formed in three steps, including base **9**, which undergoes a 5-*endo-trig* cyclization to **10**.

4. Experimental

4.1. General

Melting points were determined using a MEL-TEMP melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Bomem FTIR spectrometer either neat or in a solution cell (CH_2Cl_2 or $CDCl_3$). NMR spectra for ^1H and ^{13}C NMR were recorded on a Bruker spectrometer at 400 and 100.6 MHz in $CDCl_3$ solution and are reported in parts per million δ (ppm) relative to tetramethylsilane internal standard or $CDCl_3$ at 7.26 ppm. Elemental analyses were performed by MHW labs of Phoenix, AZ. Mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry, McMaster University or the WATSPEC Mass Spectrometry Facility at the University of Waterloo. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium and benzophenone. Methylene chloride was freshly distilled from calcium hydride. Acetonitrile was distilled from calcium hydride and stored over 4 Å molecular sieves under an N_2 atmosphere. Potassium *tert*-butoxide was stored in a vial in a desiccator with anhydrous $CaSO_4$. All air and water sensitive reagents were transferred using oven-dried nitrogen-purged glass syringes. Flash chromatography was performed on new mesh Type 60 Å silica gel. Analytical thin-layer chromatography (TLC) was performed using 0.25 mm Merck Kieselgel 60 F_{254} glass-backed plates.

4.2. Computational methods

Density Functional Theory (DFT) calculations were conducted using the Gaussian 09 suite of programs.[15] The CAM-B3LYP method corrected for the long-range deficiencies of B3LYP and provided results close to coupled cluster calculations.[23] Condensed phase calculations for acetonitrile were carried out with the conductor-like polarizable continuum model (CPCM) of Cossi and coworkers[17] with the smoothing formalism that Karplus and York developed.[14e] The solute molecular cavity was specified using the Bondi radii values.[24] The computed values include thermal (273.15 K) corrections for enthalpy. Transition states were confirmed by examining the negative eigenvalue of the hessian matrix and by intrinsic reaction coordinate (IRC) calculations. GaussView 5 was used for the visualization of the molecules and the vibrational modes.[16]

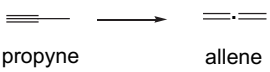
There are some shortcomings with the B3LYP functional.[25] For example, medium and long-range electron correlation errors are common.[26] The CAM-B3LYP functional was selected because of its good performance in calculations of electronic polarizabilities, as well as long-range exchange interactions by a Coulomb attenuating method, and medium-range interactions with an error fitting function.[14d,27]

Table 3 shows that the CAM-B3LYP calculation predicts greater stability of propyne versus allene, which is opposite to that found by experimental, and M05-2X and CCSD(T) methods.[29–31] The relative energetics of MP4,[19b] CCSD(T), and CAM-B3LYP calculations are quite similar to each other for methyl prop-1-yn-1-yl sulfane and methyl propa-1,2-dien-1-yl sulfane. However, our CAM-B3LYP calculations are not expected to have greater accuracy than ~4 kcal/mol. The average errors of B3LYP in thermochemistry calculations were ~3.6 kcal/mol (from a database of 177 reactions).[28]

4.3. General procedure for the cyclization of benzyl propynyl sulfides

In a flame-dried rbf is placed the benzyl propynyl sulfide (1 equiv) in dry CH_3CN (1 mL per 5 mg of substrate). In a second flask is placed KO^{t}Bu (2.0 equiv) in dry CH_3CN (1 mL per 5 mg of substrate). The solution of the substrate is added to the KO^{t}Bu solution via syringe and the reaction is stirred at rt or reflux for 24 h. Upon completion of the reaction, de-ionized water (DI) H_2O is

Table 3
Relative energies of propyne and allene, and of methyl prop-1-yn-1-yl sulfane and methyl propa-1,2-dien-1-yl sulfane

Method	*E* (kcal/mol)	Ref.
 propyne allene		
Experimental	−1.4	29
CCSD(T)/cc-pVQZ//MP2/cc-pVTZ	−1.4	30
M05-2X/6-311+G(2df,2p)	−1.2	31
CAM-B3LYP/6-311+G(d,p)	0.8	This work
 methyl prop-1-yn-1-yl sulfane methyl propa-1,2-dien-1-yl sulfane		
MP4/6-31+G(d)//RHF/6-31+G(d)	1.3	19b
IEFPCM-MP4/6-31+G(d)//PCM-RHF/6-31+G(d)	1.8	19b
CAM-B3LYP/6-311+G(d,p)	3.4	This work
CPCM-CAM-B3LYP/6-311+G(d,p)	2.6	This work
CCSD(T)/cc-pVQZ//MP2/cc-pVTZ	1.3	This work
CPCM-CCSD(T)/cc-pVQZ//CPCM-MP2/cc-pVTZ	0.6	This work

added and the layers separated. The aqueous layer is extracted with EtOAc (3×). The organics are combined, washed with DI H_2O (1×), satd aq NaCl (1×), dried over $MgSO_4$, and concentrated. See Table 1 for additional detail.

*4.3.1. 2-Phenyl-2,3-dihydrothiophene (**2a**).* The reaction of benzyl 1-propynyl sulfide **1a** (337 mg, 2.08 mmol) with KO^{t}Bu (467 mg, 4.16 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2a** (57.8 mg; 17%) and recovered starting material (132 mg) after flash chromatography. The yield based on recovered starting material was 28%. Spectral data were obtained as a mixture of the two compounds. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.41 (d, J=7.4 Hz, 1H, Ar H), 7.30–7.33 (m, 2H, Ar H), 7.23–7.26 (m, 2H, Ar H), 6.23 (dt, J=6.0 and 2.4 Hz, 1H, vinyl H), 5.59 (dt, J=6.0 and 2.4 Hz, 1H, vinyl H), 4.91 (dd, J=9.6 and 7.3 Hz, 1H, CH), 3.20 (ddt, J=16.5, 9.6, and 2.4 Hz, 1H, CH_2), 2.93 (ddt, J=16.5, 7.3, and 2.4 Hz, 1H, CH_2). Partial ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 128.6, 127.4, 127.0, 125.6, 120.5, 52.7, 43.9.

*4.3.2. 2-(2-Iodophenyl)-2,3-dihydrothiophene (**2b**).* The reaction of 2-iodobenzyl propynyl sulfide (**1b**) (194 mg, 0.674 mmol) with KO^{t}Bu (180 mg, 1.35 mmol) yielded 2,3-dihydrothiophene **2b** (180 mg; 75%) as a yellow liquid after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.84 (dd, J=7.7 and 1.1 Hz, 1H, Ar H), 7.61 (dd, J=7.7 and 1.6 Hz, 1H, Ar H), 7.33 (dt, J=7.7 and 1.1 Hz, 1H Ar H), 6.94 (dt, J=7.7 and 1.6 Hz, 1H, Ar H), 6.25 (ddd, J=6.0, 2.6 and 1.7 Hz, 1H, vinyl H), 5.63 (dt, J=6.0 and 2.8 Hz, 1H, vinyl H), 5.13 (dd, J=9.7 and 5.0 Hz, 1H, CH), 3.27 (ddt, J=16.8, 9.7, and 2.8 Hz, 1H CH_2), 2.83 (dddd, J=16.8, 5.0, 2.8, and 1.7 Hz, 1H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 145.6, 139.4, 128.9, 128.7, 127.5, 125.4, 120.4, 99.9, 56.0, 42.9. IR (neat, cm^{-1}) 3060, 2937, 2894, 2844, 1583, 1563, 1463, 1436, 1012. EIMS, m/z (%): 288 (7, M^+), 161 (37), 128 (100), 127 (23), 116 (17), 115 (39), 89 (19), 85 (18), 77 (32), 63 (25), 62 (15), 51 (32), 50 (28), 45 (31). HREIMS: Calcd for $C_{10}H_9SI$: 287.9470. Found: 287.9457.

*4.3.3. 2-(2-Bromophenyl)-2,3-dihydrothiophene (**2c**).* The reaction of 2-bromobenzyl propynyl sulfide (**1c**) (209 mg, 0.867 mmol) with KO^{t}Bu (195 mg, 1.73 mmol) in acetonitrile yielded 2,3-dihyrothiophene **2c** (154 mg; 74%) as a yellow liquid after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.62 (dd, J=7.7 and 1.6 Hz, 1H, Ar H), 7.55 (dd, J=7.7 and 1.2 Hz, 1H, Ar H), 7.29 (dt, J=7.7 and 1.2 Hz, 1H, Ar H), 7.11 (dt, J=7.7 and 1.6 Hz, 1H, Ar H), 6.24 (ddd, J=6.0, 2.6 and 1.7 Hz, 1H, vinyl H), 5.61 (dt, J=6.0 and 2.9 Hz, vinyl H), 5.27 (dd, J=9.7 and 4.9 Hz, 1H, CH), 3.27 (ddt, J=16.8, 9.7 and 2.6 Hz, 1H, CH_2), 2.86 (dddd, J=16.8, 4.9, 2.9 and 1.7 Hz, 1H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 142.5, 132.7, 128.7, 128.1, 127.9, 125.4, 123.3, 120.4, 50.8, 42.3. IR (neat, cm^{-1}) 3062, 2938, 2896, 2842, 1588, 1567, 1467, 1440, 1265, 1025. EIMS, m/z (%): 242 (20, M^+ for ^{81}Br), 240 (21, M^+ for ^{79}Br), 161 (37), 128 (100), 116 (18), 115 (24), 84 (22), 51 (15), 49 (23), 47 (16), 45 (29). Anal. Calcd for $C_{10}H_9BrS$: C, 49.81; H, 3.76. Found: C, 49.79; H, 3.88.

*4.3.4. 2-(2-Chlorophenyl)-2,3-dihydrothiophene (**2d**).* The reaction of 2-chlorobenzyl propynyl sulfide (**1d**) (231 mg, 1.18 mmol) with KO^{t}Bu (264 mg, 2.35 mmol) in acetonitrile yielded 2,3-dihydrothiophene **2d** (171 mg; 74%) as a yellow liquid after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.62 (dd, J=7.6 and 1.7 Hz, 1H, Ar H), 7.36 (dd, J=7.6 and 1.4 Hz, 1H, Ar H), 7.25 (dt, 7.6 and 1.4 Hz, 1H, Ar H), 7.19 (dt, J=7.6 and 1.7 Hz, 1H, Ar H), 6.24 (ddd, J=6.0, 2.6 and 1.8 Hz, 1H, vinyl H), 5.60 (dt, J=6.0 and 3.0 Hz, 1H, vinyl H), 5.31 (dd, J=9.7 and 5.1 Hz, 1H, CH), 3.26 (ddt, J=16.7, 9.7 and 2.6 Hz, 1H, CH_2), 2.87 (dddd, J=16.7, 5.1, 3.0 and 1.8 Hz, 1H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 140.8, 132.7, 129.4, 128.4, 127.9, 127.2, 125.4, 120.4, 48.1, 42.2. IR (neat, cm^{-1}) 3070, 2939, 2896, 2842, 1472, 1444, 1051, 1037. EIMS, m/z (%): 196 (7, M^+ for ^{37}Cl), 194 (7, M^+ for ^{35}Cl), 86 (31), 84 (46), 58 (22), 51 (20), 49 (72), 47 (15), 43 (100), 42 (15). HREIMS: calcd for $C_{10}H_9ClS$: 196.0113. Found: 196.0101.

*4.3.5. 2-(2-Phenylphenyl)-2,3-dihydrothiophene (**2f**).* The reaction of 2-phenylbenzyl propynyl sulfide (**1f**) (157 mg, 0.659 mmol) with KO^{t}Bu (148 mg, 1.32 mmol) in refluxing acetonitrile yielded a mixture of 2,3-dihydrothiophene **2f** (38.6 mg; 25%) and recovered starting material (63.2 mg) after flash chromatography. The yield based on recovered starting material was 41%. Spectral data obtained as a mixture of dihydrothiophene **2f** and benzyl propynyl sulfide **1f**. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.51–7.17 (m, 9H, Ar H's), 6.18 (dt, J=4.6 and 2.0 Hz, 1H, vinyl H), 5.51 (dt, J=4.6 and 3.1 Hz, vinyl H), 4.97 (dd, J=9.5 and 7.3 Hz, 1H, CH), 3.06–2.93 (m, 2H, CH_2).

*4.3.6. 2-(2-Fluorophenyl)-2,3-dihydrothiophene (**2g**).* The reaction of 2-fluorobenzyl propynyl sulfide (**1g**) (204 mg, 1.13 mmol) with KO^{t}Bu (255 mg, 2.27 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2g** (92 mg; 45%) as a yellow liquid after flash

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.56 (dt, J=7.7 and 1.7 Hz, 1H), 7.26–7.20 (m, 1H), 7.12 (t, J=7.7 Hz, 1H), 7.02 (ddd, J=10.3, 8.2, and 1.1 Hz, 1H), 6.42 (ddd (app. dt), J=6.1, 2.3, and 2.3 Hz, 1H), 5.60 (dt, J=6.1 and 2.8 Hz, 1H), 5.20 (dd, J=9.7 and 6.1 Hz), 3.22 (dddd (apparent ddt), J=16.6, 9.7 and 2.6 Hz, 1H), 2.90 (dddd (apparent ddt), J=16.6, 6.1, 2.6, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 159.6 (d, $J_{13C-19F}$=246.3), 130.4 (d, $J_{13C-19F}$=13.5 Hz), 128.7 (d, $J_{13C-19F}$=8.2 Hz), 128.2 (d, $J_{13C-19F}$=3.3 Hz), 125.3, 124.3 (d, $J_{13C-19F}$=3.3 Hz), 120.4, 115.2 (d, $J_{13C-19F}$=22.1 Hz), 44.2 (d, $J_{13C-19F}$=2.8 Hz), 42.5. IR ($CDCl_3$, cm^{-1}): 3066, 3044, 2932, 2892, 2840, 1717, 1614, 1585, 1488, 1456, 1278, 1264, 1230, 1173, 1094, 1035, 1006, 832, 805. CIMS, m/z (%): 181.0 (24, $(M+H)^+$), 180.0 (100, M^+), 179.0 (15, $(M-H)^+$), 147.1 (40), 146.1 (14), 49.0 (22). Anal. Calcd for $C_{10}H_9SF$: C, 66.64%, H: 5.03%. Found: C, 66.41%; H, 5.13%.

*4.3.7. 2-(2-Cyanophenyl)-2,3-dihydrothiophene (**2h**).* The reaction of 2-cyanobenzyl propynyl sulfide (**1h**) (239 mg, 1.27 mmol) with KO^{t}Bu (286 mg, 2.55 mmol) in acetonitrile yielded 2,3-dihydrothiophene **2h**[7a] (153 mg, 64%) as a white solid (mp 83–84.5 °C) after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.75 (d, J=8.0Hz, 1H), 7.63–7.54 (m, 2H), 7.34 (t, J=7.6 Hz, 1H), 6.24 (ddd apparent dt, J=6.0 and 2.1 Hz, 1H), 5.58 (dt, J=6.0 and 2.7 Hz, 1H), 5.26 (dd, J=9.9 and 5.5 Hz, 1H), 3.34 (ddt, J=16.8, 9.9, and 2.5 Hz, 1H), 2.87 (dddd (apparent ddt), J=16.8, 5.5, and 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 147.5, 133.4, 132.7, 127.7, 127.6, 125.4, 120.1, 117.5, 111.0, 49.2, 43.5. IR (CH_2Cl_2, cm^{-1}): 3018, 2843, 2226, 1599, 1482, 1449, 1212, 1166, 1041, 1003. CIMS, m/z (%): 188.1 (27, $(M+H)^+$), 187.0 (56, M^+), 186.0 (100, $(M-H)^+$), 154.1 (21). Anal. Calcd for $C_{11}H_9SN$: C, 70.55%, H: 4.84%. Found: C, 70.53%; H, 5.04%.

*4.3.8. 2-(3-Iodophenyl)-2,3-dihydrothiophene (**2i**).* The reaction of 3-iodobenzyl propynyl sulfide (**1i**) (591 mg, 2.05 mmol) with KO^{t}Bu (460 mg, 4.10 mmol) in acetonitrile yielded 2,3-dihydrothiophene **2i** (402 mg, 68%) as a yellow oil after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.92 (s, 1H), 7.75 (d, J=7.9 Hz, 1H), 7.53 (d, J=7.9 Hz, 1H), 7.22 (t, J=7.9 Hz, 1H), 6.40 (ddd (apparent dt), J=6.1 and 2.2 Hz, 1H), 5.74 (dt, J=6.1 and 2.7 Hz, 1H), 4.96 (dd, J=9.7 and 6.7 Hz, 1H), 3.37 (ddt, J=16.6, 9.7, and 2.2 Hz, 1H), 3.05 (dddd (apparent ddt), J=16.6, 6.7, and 2.7 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 145.9, 136.4, 135.9, 130.3, 126.3, 125.5, 120.3, 94.4, 51.7, 43.8. IR (neat, cm^{-1}): 3052, 2925, 2836, 1714, 1587, 1563, 1471, 1421, 1263, 1193, 1065, 994, 882, 781. CIMS, m/z (%): 305 (70, $(M+NH_3)^+$), 289 (14, $(M+H)^+$), 161 (6), 128 (7). Anal. Calcd for $C_{10}H_9SI$: C, 41.68%; H, 3.15%. Found: C, 41.48%; H, 3.25%.

*4.3.9. 2-(4-Iodophenyl)-2,3-dihydrothiophene (**2j**).* The reaction of 4-iodobenzyl propynyl sulfide (**1j**) (556 mg, 1.93 mmol) with KO^{t}Bu (433 mg, 3.86 mmol) in acetonitrile yielded 2,3-dihydrothiophene **2j** (250 mg, 45%) as a yellow oil after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.80 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 6.40 (ddd (apparent dt), J=6.1 and 2.0 Hz, 1H), 5.74 (dt, J=6.1 and 2.7 Hz, 1H), 4.99 (dd, J=9.7 and 6.7 Hz, 1H), 3.36 (ddt, J=16.6, 9.7, and 2.4 Hz, 1H), 3.03 (dddd (apparent ddt), J=16.6, 6.7, and 2.4 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 143.3, 137.6, 128.9, 125.5, 120.3, 92.6, 51.9, 43.8. IR (neat, cm^{-1}): 3054, 3019, 2927, 2854, 1900, 1713, 1584, 1564, 1484, 1434, 1400, 1277, 1259, 1102, 1005, 943, 911, 857, 818, 780. EIMS, m/z (%): 288 (78, M^+), 161 (8), 128 (100), 115 (30). HREIMS Calcd for $C_{10}H_9SI$: 287.9466. Found: 287.9470.

*4.3.10. 3-(Trifluoromethyl)phenyl-2,3-dihydrothiophene (**2k**).* The reaction of 3-(trifluoromethyl)benzyl propynyl sulfide (**1k**) (218 mg, 0.95 mmol) with KO^{t}Bu (213 mg, 1.89 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2k** (122 mg, 59%) as a yellow oil after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.65 (s, 1H), 7.59 (d, J=7.7 Hz, 1H), 7.51 (d, J=7.7 Hz, 1H), 7.43 (t, J=7.7 Hz, 1H), 6.24 (ddd (apparent dt), J=6.1 and 2.2 Hz, 1H), 5.59 (dt, J=6.1 and 2.8 Hz, 1H), 4.91 (dd, J=9.7 and 6.5 Hz, 1H), 3.24 (ddt, J=16.6, 9.7, and 2.6 Hz, 1H), 2.91 (dddd, J=16.6, 6.5, 2.8, and 2.2 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 144.6, 130.8(q, $J_{13C-19F}$=32.3 Hz), 130.4, 129.1, 125.5, 124.2, 124.0 (q, $J_{13C-19F}$=272.1 Hz), 123.8, 120.3, 51.8, 43.9. IR (neat, cm^{-1}): 3066, 2930, 1716, 1613, 1596, 1492, 1450, 1329, 1261, 1166, 1125, 1098, 1073, 1002, 902, 804, 739, 702. CIMS m/z (%): 231 (10, $(M+H)^+$), 230 (59, M^+), 197 (12), 177 (16), 86 (24), 84 (38), 51 (35), 49 (100), 47 (17), 30 (22). HRCIMS: calcd for $C_{11}H_9F_3S$: 230.0377. Found: 230.0372.

*4.3.11. 2-(Phenylthio)phenyl-2,3-dihydrothiophene (**2l**).* The reaction of 2-(phenylthio)benzyl propynyl sulfide (**1l**) (210 mg, 0.77 mmol) with KO^{t}Bu (172 mg, 1.53 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2l** (137 mg, 66%) as a yellow oil after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.72 (dd, J=7.9, 1Hz, 1H), 7.38–7.14 (m, 8H), 6.21 (ddd, J=6.1, 2.2, and 2.0 Hz, 1H), 5.56 (dt, J=6.1 and 2.7 Hz, 1H), 5.50 (dd, J=9.9 and 5.6 Hz, 1H), 3.13 (ddt, J=16.8, 9.9, and 2.7 Hz, 1H), 2.82 (dddd, J=16.8, 5.0, 2.7, and 2.0 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 145.7, 136.5, 134.0, 132.1, 129.4, 129.1, 128.9, 128.0, 127.7, 126.4, 125.5, 120.3, 48.6, 43.0. IR ($CDCl_3$, cm^{-1}): 3057, 3016, 2926, 2839, 1717, 1581, 1476, 1466, 1439, 1328, 1301, 1277, 1194, 1158, 1083, 1068, 1057, 1038, 1024, 1000, 738. CIMS, m/z (%): 271 (97, $(M+H)^+$), 270 (100, M^+), 242 (27), 223 (20), 215 (17), 214 (25), 197 (29), 193 (75), 161 (48), 160 (30), 147 (17), 128 (33), 115 (16). Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07%; H, 5.22%. Found: C, 70.92%; H, 5.30%.

*4.3.12. 2-(Phenylsulfinyl)phenyl-2,3-dihydrothiophene (**2m**).* The reaction of 2-(phenylsulfinyl)benzyl propynyl sulfide (**1m**) (119 mg, 0.41 mmol) with KO^{t}Bu (93.5 mg, 0.83 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2m** (528 mg, 45%) as a white solid and a 1:1 mixture of diastereomers after flash chromatography on silica gel (20–40% hexanes eluent). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers), δ: 7.95–7.93 (m, 1H), 7.86–7.84 (m, 1H), 7.73–7.71 (m, 2H), 7.60–7.56 (m, 2H), 7.50–7.45 (m, 5H), 6.17 (ddt, J=8.4, 5.9, and 2.2 Hz 1H), 5.57 (dt, J=5.9 and 2.8 Hz, 0.5H), 5.42 (ddt (apparent dt), J=8.4 and 2.3 Hz, 0.5H), 5.31–5.28 (m, 0.5H), 3.25 (ddt, J=16.8, 10.0, and 2.6 Hz, 0.5H), 2.94 (dddd, J=16.8, 5.7, 3.2, and 2.5 Hz, 0.5H), 2.80 (ddt, J=16.8, 10.0, and 2.6 Hz, 0.5H), 2.51 (dddd, J=16.8, 5.7, 3.2, 2.5, 0.5H). ^{13}C NMR (100.6 MHz, $CDCl_3$, mixture of isomers), δ: 144.9, 144.6, 142.7, 142.5, 141.8, 132.1, 132.0, 131.3, 131.2, 129.4, 129.0, 128.7, 128.6, 128.4, 127.7, 126.0, 125.5, 125.3, 125.2, 125.0, 120.4, 119.6, 46.3, 46.0, 44.0, 43.7. IR ($CDCl_3$, cm^{-1}): 3057, 2927, 2839, 1582, 1472, 1442, 1328, 1306, 1279, 1260, 1191, 1159, 1122, 1083, 1035, 998, 960, 918, 850. CIMS, m/z (%): 288.1 (3, $(M+H)^+$), 287 (19, M^+), 242 (22), 235 (11), 233 (19), 217 (12), 200 (24), 199 (21), 197 (45), 194 (13), 193 (100), 192 (23), 191 (57), 184 (12), 162 (10), 161 (68), 160 (57), 159 (18), 147 (40), 134 (15), 128 (65), 116 (14), 115 (39). HRCIMS: calcd for $C_{16}H_{15}S_2O$: 287.0564. Found: 287.0563.

*4.3.13. 2-(Phenylsulfonyl)phenyl-2,3-dihydrothiophene (**2n**).* The reaction of 2-(phenylsulfonyl)benzyl propynyl sulfide (**1n**) (207 mg, 0.69 mmol) with KO^{t}Bu (154 mg, 1.37 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2n** (141 mg, 68%) as a yellow solid after flash chromatography on silica gel (mp 109–113 °C). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.17 (dd, J=8.0 and 1.2 Hz, 1H), 7.87–7.82 (m, 3H), 7.62–7.51 (m, 4H), 7.44 (dt, J=8.0 and 1.2 Hz, 1H), 6.12 (ddd, J=6.0, 2.0, and 2.0 Hz, 1H), 5.66 (dd, J=10.3 and 5.0 Hz, 1H), 5.46 (ddd (apparent dt), J=6.0 and 2.7 Hz, 1H), 3.09 (ddt, J=17.1, 10.3, 2.7), 2.69 (dddd, J=17.1, 5.0, 2.7, and 2.0 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 144.7, 141.6, 137.0, 134.5, 133.3, 129.6, 129.3, 128.9, 127.6, 127.4, 125.3, 119.9, 45.7, 44.4. IR ($CDCl_3$, cm^{-1}): 3072, 2935, 2846, 2686, 1590, 1571, 1470, 1447, 1315, 1156, 1126, 1091, 1058. CIMS m/z (%): 303 (67, $(M+H)^+$), 302 (21, M^+), 238 (32), 237 (19), 233 (11), 214 (16), 192 (17), 191 (100), 166 (16), 165 (11), 161 (19), 160 (61), 129 (12), 128 (41), 125 (16), 116 (15), 115 (37), 91 (25), 78 (17), 77 (25). HRCIMS: calcd for $C_{16}H_{15}O_2S_2$: 303.0513. Found: 303.0530.

*4.3.14. 2,5-Dimethoxyphenyl-2,3-dihydrothiophene (**2o**).* The reaction of 2,5-dimethoxybenzyl propynyl sulfide (**1o**) (300 mg,

1.35 mmol) with KO^{t}Bu (304 mg, 2.71 mmol) in refluxing acetonitrile yielded a mixture of 2,3-dihydrothiophene **2o** (81 mg; 27%) and recovered starting material (115 mg) after flash chromatography. The yield based on recovered starting material was 44%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.09 (d, J=2.9 Hz, 1H, Ar H), 6.73–6.80 (m, 2H, Ar H), 6.21 (ddd, J=6.0, 2.6, and 1.8 Hz, 1H, vinyl H), 5.60 (dt, J=6.0 and 2.9 Hz, 1H, vinyl H), 5.24 (dd, J=9.6 and 5.6 Hz, 1H, CH), 3.81 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.15 (ddt, J=16.6, 9.6 and 2.6 Hz, 1H, CH_2), 2.87 (dddd, J=16.6, 5.6, 2.9 and 1.8 Hz, 1H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 148.5, 125.4, 122.7, 120.7, 113.6, 113.2, 112.2, 111.4, 56.1, 55.7, 45.1, 41.7. IR (neat, cm^{-1}) 3004, 2941, 2910, 2837, 1499, 1220, 1048. GC/MS, m/z (%): 222 (100, M$^+$), 189 (69), 174 (45), 158 (24), 146 (9), 115 (8), 91 (9), 45 (10).

*4.3.15. 3,5-Dimethoxyphenyl-2,3-dihydrothiophene (**2p**).* The reaction of 3,5-dimethoxy benzyl propynyl sulfide (**1p**) (270 mg, 1.22 mmol) with KO^{t}Bu (275 mg, 2.45 mmol) in refluxing acetonitrile yielded 2,3-dihydrothiophene **2p** (113 mg, 42%) as a colorless oil after flash chromatography on silica gel. The yield based on recovered starting material was 54%. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.57 (d, J=2.3 Hz, 2H), 6.36 (t, J=2.3 Hz, 1H), 6.21 (dt, J=6.1 and 2.2 Hz, 1H), 5.57 (dt, J=6.1 and 3.0 Hz, 1H), 4.84 (dd, J=9.6 and 7.3 Hz, 1H), 3.78 (s, 6H), 3.17 (ddt, J=16.6, 9.6, and 2.7 Hz, 1H), 2.92 (dddd, J=16.6, 7.3, 2.7, and 2.2 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 168.2, 160.8, 145.7, 125.5, 120.6, 105.0(2), 99.2(2), 55.3, 52.9, 43.7. IR ($CDCl_3$, cm^{-1}): 3073, 3008, 2960, 2940, 2840, 1607, 1596, 1469, 1431, 1350, 1205, 1196, 1157, 1067, 940, 927, 848, 836. CIMS, m/z (%): 223 (40, (M+H)$^+$), 222 (51, M$^+$), 189 (100), 174 (19), 158 (10). HRCIMS: calcd for $C_{12}H_{14}O_2S$: 222.0715. Found: 222.0715.

*4.3.16. 2-(1-Bromonaphth-2-yl)-2,3-dihydrothiophene (**2s**).* The reaction of 1-bromonaphth-2-yl propynyl sulfide (**1s**) (209 mg, 0.716 mmol) with KO^{t}Bu (161 mg, 1.43 mmol) yielded 2,3-dihydrothiophene **2s** (150 mg; 72%) as a yellow liquid after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 8.33 (d, J=8.5 Hz, 1H, Ar H), 7.79 (m, 3H, Ar H), 7.59 (m, 1H, Ar H), 7.50 (m, 1H, Ar H), 6.30 (ddd, J=6.0, 2.5, and 1.9 Hz, 1H, vinyl H), 5.70 (dd, J=10.0 and 5.2 Hz, 1H, CH), 5.65 (dt, J=6.0 and 2.8 Hz, 1H, vinyl H), 3.38 (ddt, J=16.9, 10.0 and 2.5 Hz, 1H, CH_2), 2.95 (dddd, J=16.9, 5.2, 2.8 and 1.9 Hz, 1H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 140.7, 133.8, 132.5, 128.3, 128.0, 127.8, 127.5, 126.4, 125.7, 125.3, 122.5, 120.5, 51.6, 43.0. IR (neat, cm^{-1}) 3060, 2933, 2901, 2844, 1502, 1330, 1259, 818. EIMS, m/z (%): 292 (12, M$^+$ for ^{81}Br), 290 (12, M$^+$ for ^{79}Br), 211 (39), 179 (15), 178 (100), 165 (19). Anal. Calcd for $C_{14}H_{11}BrS$: C, 57.74; H, 3.81. Found: C, 57.90; H, 4.00.

*4.3.17. 2,6-Bis(2,3-dihydro-5-thienyl)-2-bromobenzene (**2t**).* The reaction of 2,6-bis(1-propynylthio)-2-bromobenzene (**1t**) (201 mg, 0.616 mmol) with KO^{t}Bu (277 mg, 2.47 mmol) yielded 2,3-dihydrothiophene **2t** (93.4 mg; 47%) as yellow liquid after flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.51 (d, J=7.5 Hz, 2H, Ar H), 7.26 (t, J=7.5 Hz, 1H, Ar H), 6.22 (m, 2H, vinyl H's), 5.61 (m, 2H, vinyl H's), 5.34 (dt, J=9.5 and 3.9 Hz, 2H, CH), 3.26 (m, 2H, CH_2), 2.85 (m, 2H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 143.1, 143.0, 128.6, 127.8, 127.8, 127.0, 126.8, 125.5, 125.3, 120.6, 120.4, 51.6, 51.5, 42.3, 42.2. IR (neat, cm^{-1}) 3072, 2933, 2896, 2843, 1415, 1021, 792.

*4.3.18. 2-(2-Iodophenyl)-3-propyl-2,3-dihydrothiophenes (**2u**) and 2-(2-iodophenyl)-3-propyl-2,5-dihydrothiophene (**2u′**).* The reaction of 2-iodobenzyl hexynyl sulfide (**1u**) (453 mg, 1.37 mmol) with KO^{t}Bu (308 mg, 2.75 mmol) in acetonitrile at rt yielded 2,3-dihydrothiophenes **2u** (69 mg; 15%) and 2,5-dihydrothiophene **14u** (302 mg; 67%) as a yellow liquids after two flash chromatographies. Data for *cis*-**2u**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.82 (dd, J=7.7 and 1.2 Hz, 1H, Ar H), 7.74 (dd, J=7.7 and 1.6 Hz, 1H, Ar H), 7.38 (dt, J=7.7 and 1.2 Hz, 1H, Ar H), 6.95 (dt, J=7.7 and 1.6 Hz, 1H, Ar H), 6.29 (dd, J=6.2 and 1.7 Hz, 1H, vinyl H), 5.68 (dd, J=6.2 and 2.8 Hz, 1H, vinyl H), 5.35 (d, J=8.8 Hz, 1H, CH), 3.38 (m, 1H, CH), 1.55 (m, 2H, CH_2), 1.30–1.05 (m, 2H, CH_2), 0.78 (t, J=7.2 Hz, 3H, CH_3). Data for *trans*-**2u**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.83 (dd, J=7.8 and 1.1 Hz, 1H, Ar H), 7.54 (dd, J=7.8 and 1.6 Hz, 1H, Ar H), 7.32 (dt, J=7.8 and 1.1 Hz, 1H, Ar H), 6.93 (dt, J=7.8 and 1.6 Hz, 1H, Ar H), 6.19 (dd, J=6.0 and 1.3 Hz, 1H, vinyl H), 5.65 (dd, J=6.0 and 2.9 Hz, 1H, vinyl H), 4.73 (d, J=4.0 Hz, 1H, CH), 3.14 (m, 1H, CH), 1.63 (m, 2H, CH_2), 1.42 (sextet, J=7.4 Hz, 2H, CH_2), 0.93 (t, J=7.4 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 146.1, 139.3, 128.8, 127.9, 125.1, 124.4, 100.0, 61.2, 55.9, 36.2, 20.6, 14.2. IR (neat, cm^{-1}) 3047, 2959, 2930, 2873, 1463, 1010, 911. EIMS, m/z (%): 330 (56, M$^+$), 287 (100), 160 (56), 128 (19), 115 (34). Data for **14u**: ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.80 (dd, J=7.7 and 1.1 Hz, 1H, Ar H), 7.34 (dt, J=7.7 and 1.1 Hz, 1H, Ar H), 7.26 (dd, J=7.7 and 1.8 Hz, 1H, Ar H), 6.92 (ddd, J=7.7, 7.5, and 1.8 Hz, 1H, Ar H), 5.80 (d, J=1.0 Hz, 1H, CH), 5.50 (d, J=5.1 Hz, 1H, vinyl H), 3.89 (m, 1H, CH_2), 3.77 (d (br), J=14.3 Hz, 1H, CH_2), 2.01–1.93 (m, 1H, CH_2), 1.88–1.81 (m, 1H, CH_2), 1.58–1.35 (m, 2H, CH_2), 0.88 (t, J=7.3 Hz, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 146.0, 145.4, 139.2, 129.0, 129.0, 128.7, 124.2, 100.6, 63.8, 37.7, 31.6, 21.2, 13.9. IR (neat, cm^{-1}) 3058, 2962, 2933, 2875, 2850, 1584, 1563, 1463, 1436, 1011, 832, 792. Anal. Calcd for $C_{13}H_{15}IS$: C, 47.28; H, 4.58. Found: C, 47.15; H, 4.46.

4.4. General procedure for the oxidation of 2-aryl-2,3-dihydrothiophenes

To a solution of DDQ (1.6 equiv) was added a solution of the dihydrothiophene (1.0 equiv) in $CHCl_3$. The reaction is stirred at rt for 24 h. Upon completion of the reaction, the solution is filtered and diluted with CH_2Cl_2 and washed with DI H_2O (4×). The organic solution is then washed with satd aq NaCl (1×), dried over $MgSO_4$, and concentrated.

*4.4.1. Oxidation of dihydrothiophene **2b**.* To a solution of **2b** (205 mg, 0.71 mmol, 1.0 equiv) in $CHCl_3$ (15 mL) was added DDQ (258 mg, 1.14 mmol, 1.6 equiv) and the reaction was stirred for 24 h. Workup as indicated and flash chromatography on silica gel (100% hexane eluent) provided thiophene **3b** (149 mg, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.98 (dd, J=7.9 and 0.8 Hz, 1H), 7.45 (dd, J=7.4 and 1.8 Hz, 1H), 7.39 (m, 2H), 7.21 (dd, J=3.6 and 1.1 Hz, 1H), 7.12 (dd, J=5.1 and 3.6 Hz, 1H), 7.02 (dt, J=7.4 and 1.8 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 144.9, 139.9, 139.4, 131.3, 129.4, 128.1, 127.6, 126.8, 125.9, 99.6. IR (neat, cm^{-1}): 3146, 3119, 2915, 2848, 1723, 1680, 1594, 1501, 1435, 1408, 1375, 1243, 1212, 1151, 1131, 1071, 1011, 937, 886, 809, 739. CIMS, m/z (%): 287 ((M+H)+, 30), 286 (M+, 39), 161 (100), 160 (19). Anal. Calcd for $C_{10}H_7SI$: C, 41.98%; H, 2.47%. Found: C, 41.79%; H, 2.60%.

*4.4.2. Oxidation of dihydrothiophene **2h**.* To a solution of **2h** (120 mg, 0.64 mmol, 1.0 equiv) in $CHCl_3$ (15 mL) was added DDQ (233 mg, 1.03 mmol, 1.6 equiv) and the reaction was stirred for 24 h. Workup as indicated and flash chromatography on silica gel (5–10% EtOAc/hexane eluent) provided thiophene **3h**[32] (96.3 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.72 (dd, J=8.0 and 1.0 Hz, 1H), 7.63 (dd, J=3.7 and 1.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.42 (dd, J=5.1 and 1.0 Hz, 1H), 7.37 (t, J=6.1 and 1.6 Hz, 1H), 7.14 (dd, J=5.1 and 3.7 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 139.3, 137.4, 134.2, 132.9, 129.6, 128.1, 127.5 (2), 127.2, 118.8, 109.9. IR (neat, cm^{-1}): 3108, 3074, 2224, 1595, 1565, 1528, 1482, 1444, 1354, 1277, 1247, 1213, 1189, 1166, 1107, 1042, 962, 853, 836, 761.

Acknowledgements

The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute

of General Medical Sciences or the National Institutes of Health. Computational support was provided by the Graduate Center computational facility and the City University of New York's High Performance Computing Research Center. ÁC and AG thank the National Institutes of Health (SC1 GM093830) for support. ALS thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support. LKM also thanks NSERC for a Postgraduate scholarship.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.11.104. These data include MOL files and InChiKeys of the most important compounds described in this article.

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