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$AlCl_3$-Catalyzed Intermolecular Annulation of Thiol-Derivatives and Alkynes via 1,2-S-Migration at Room Temperature: Construction of 6-Substituted Benzo[*b*]thiophenes

E. Ramesh, Tirumaleswararao Guntreddi and Akhila K. Sahoo*

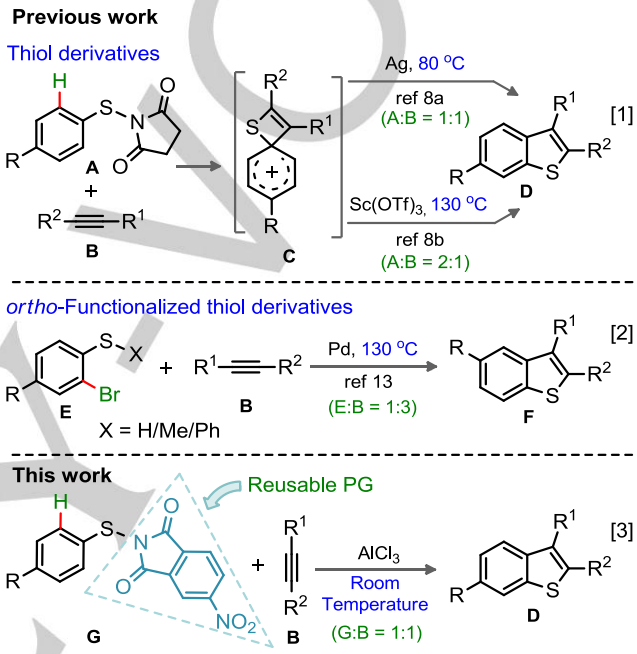
Dedicated to Prof. S. Chandrasekharan, IISc-Bangalore on the occasion of his 71st Birthday.

Abstract: A novel $AlCl_3$-catalyzed intermolecular oxidative annulation of N-arylthio phthalimide derivatives with alkynes is showcased at room temperature. The annulation involves oxidative cleavage of the S–N bond and the occurrence of 1,2-S-migration, which eventually allows the construction of diverse arrays of π-conjugated 6-substituted 2,3-diaryl benzo[*b*]thiophene derivatives.

Introduction

Development of novel synthetic methods for the efficient construction of benzo[*b*]thiophene analogues always draws significant attention; since the synthetic potential of benzo[*b*]thiophene heterocyclic compounds is truly reflected witnessing its presence in natural products,[1] drug candidates,[2] and π-extended materials.[3] Of course, enormous effort has gone crafting sustainable synthetic tools for the fabrication of benzo[*b*]thiophene core especially from the pre-functionalized thiol derivatives.[4] By contrast, the intermolecular annulation of readily accessible non-functionalized thiol-motifs and alkynes provides a straightforward handle to peripherally decorated benzo[*b*]thiophene skeleton, although the method is exceedingly important but poorly explored.[5] The use of ubiquitous *ortho*-C-H bond in thiol-derivatives not only broadens the scope of the annulation process but also allows the step and atom-efficient construction of benzo[*b*]thiophenes. Eventually, this annulation technique is synthetically viable between thiophenols and the activated alkynes (Michael acceptor); which involves an electrophilic/radical mode of cyclization.[6] Whereas the annulation of thiophenols with unactivated alkynes remains challenging; perhaps thiols are prone to undergo dimerization, hydrothiolation to alkynes, and catalyst poisoning. Moreover, annulation of *meta*-substituted thiophenols with alkynes invariably affects the reaction dynamics (on the basis of the steric and electronic nature of the substituent) forming two regioisomeric products. As a result, direct synthesis of 6-substituted benzo[*b*]thiophenes through oxidative annulation of thiophenol-derivatives and alkynes draws significant attention.

The direct construction of 2,3-diarylbenzo[*b*]thiophenes is still challenging; as most of the protocols employ trivial functional group manipulation of benzo[*b*]thiophene periphery and cyclization of highly functionalized *ortho*-π-tethered thiols, or *ortho*-halo thiol scaffolds in the presence of an activator or transition-metal catalysis.[4] One such interesting report for the synthesis of 6-substituted 2,3-diarylbenzo[*b*]thiophene involves an intramolecular cyclization of *para*-substituted arylthiovinyl sulfonic ester to a vinyl cation formation, a 1,2-sulfur migration from the thiete/Wheland intermediate (**C**), and finally aromatization.[7,8] Nonetheless, a Ni-catalyzed decarbonylative annulation of thiophthalic anhydride with alkynes directly provides 2,3-diarylbenzo[*b*]thiophenes.[9]



Scheme 1. Direct Strategy towards 2,3-Diarylbenzo[*b*]thiophenes

The redox-neutral strategy for the TM-catalyzed annulation of an oxidizable directing group (having O–N, N–N, N–O, and S–N bonds) enabled arenes with alkynes surfaces an efficient strategy to construct benzannulated heterocyclic compounds.[8, 10] Interestingly, N-arylthio succinimides and N-arylthio phthalimides have fruitfully been used for the functionalization of olefins[11] and alkynes[8] as well as a sulfenylating agent for the arylthiolation of arenes.[12]

We have recently revealed Ag-catalyzed direct oxidative cyclization between *para*-substituted N-arylthio succinimides and unactivated diaryl bearing alkynes for the selective synthesis of 6-substituted benzo[*b*]thiophene (Eq 1, Scheme 1).[8a] This transformation involves oxidative cleavage of S–N bond, 1,2-sulfur migration, and annulation via radical path; equimolar

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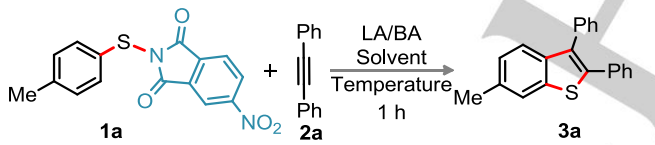
amount of both the reaction partners are smoothly reacted at 80 ºC (Eq 1, Scheme 1).[8a] Later, Glorius and co-workers demonstrated the synthesis of 6-substituted 2,3-diarylbenzo[*b*]thiophene from $Sc(OTf)_3$-mediated annulation of *para*-substituted N-arylthio succinimides (2.0 equiv) and alkynes (1.0 equiv) at 130 °C; the reaction involves vinyl-cation intermediate followed by cyclization, 1,2-S-migration, and aromatization (Eq 1, Scheme 1).[8b] Very recently, Chatani group showed Pd-catalyzed annulation between *ortho*-bromo-thiols (1.0 equiv) and alkynes (3.0 equiv) to furnish 2,3-disubstituted benzo[*b*]thiophenes at 130 ºC (Eq 2, Scheme 1).[13] The requirement of more equivalents of reaction partners and elevated temperature are essential to accomplish the intermolecular annulation of thiophenol derivatives with unactivated alkynes yielding the desired benzo[*b*]thiophenes, which eventually limits the synthetic potential of the strategy. These shortcomings inspired us to unravel an effective modified synthetic technique for $AlCl_3$-catalyzed annulation of *para*-substituted N-arylthio phthalimides (1.0 equiv) with diaryl alkynes (1.0 equiv) for the selective synthesis of 6-substituted 2,3-diarylbenzo[*b*]thiophene (Eq 3, Scheme 1). Interestingly, the reaction smoothly ensued at room temperature (RT) isolating the desired benzo[*b*]thiophene product along with the recovery of the phthalimide, which can be further reused.

Results and Discussion

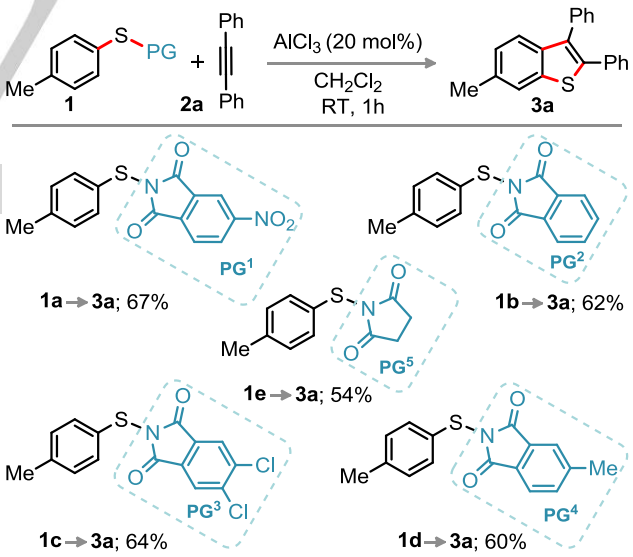
The synthesis of 6-substituted 2,3-diarylbenzo[*b*]thiophene from N-arylthio succinimide and alkyne in the presence of Ag-catalysis at an elevated temperature inspired us to investigate the identical transformation of the N-arylthio phthalimide compounds under the influence of acid catalyst at an ambient conditions. To begin with, the reaction of N-(thio-*p*-tolyl)-4-nitrophthalimide (**1a**) with 1,2-diphenyl acetylene (**2a**) was experimented in the presence of Brønsted and/or Lewis acid catalyst at room temperature. The reaction optimization details are shown in Table 1. Pleasingly, the reaction in the presence of TFA in dichloromethane (DCM) at RT led to 6-methyl-2,3-diphenyl benzothiophene (**3a**) in 24% yield with 1,2-migration of S-moiety (entry 1, Table 1). Motivated with this initial result, various Brønsted acids camphorsulfonic acid (CSA), TfOH, MsOH, and AcOH were screened in order to obtain enhanced amount of **3a**. Even a trace of **3a** was not detected, when the reaction was conducted in the presence of CSA and AcOH (entries 2 & 3); while the use of TfOH or MsOH marginally promoted the reaction (entries 4 and 5). By contrast, Lewis acid $ZnCl_2$ mediated reaction of **1a** and **2a** produced 10% **3a** (entry 6) To our delight, enhanced yield of **3a** (78%) was achieved, when the reaction was performed in presence of $AlCl_3$ at RT (entry 7); interestingly, complete consumption of **1a** was observed with the isolation of 92% protecting group (4-nitrophthalimide; PG^1) (entry 7). However, the same reaction in 0.5 mmol scale provided 67% of **3a** (entry 7). Other Lewis acid catalysts $FeCl_3$ and $BF_3{\cdot}OEt_2$ were found moderate (entries 8 and 9). Among the screening of various solvents, CH_2Cl_2 (DCM) was found facile, while 1,4-dioxane was ineffective (entries 10–12). The use of acid-catalyst is therefore indispensible, as no product was detected in the absence of Lewis acid catalyst (entry 13). The reaction in presence of radical quencher TEMPO (1.0 equiv) / BHT (1.0 equiv) did not affect the reaction outcome (entries 14 & 15), precluding the possible involvement of radical intermediate in this reaction.

Table 1. Optimization of Reaction Conditions[a]



entry	LA/BA (20 mol %)	Solvent (0.5 mL)	Temperature (°C)	yield (%)[b]
1	TFA	CH_2Cl_2	RT	24
2	CSA	CH_2Cl_2	RT	NR
3	AcOH	CH_2Cl_2	RT	NR
4	TfOH	CH_2Cl_2	RT	18
5	MsOH	CH_2Cl_2	RT	15
6	$ZnCl_2$	CH_2Cl_2	RT	10
7	$AlCl_3$	CH_2Cl_2	RT	78 (67[c])
8	$FeCl_3$	CH_2Cl_2	RT	52
9	$BF_3.OEt_2$	CH_2Cl_2	RT	40
10	$AlCl_3$	$ClCH_2CH_2Cl$	RT	61
11	$AlCl_3$	Dioxane	RT	NR
12	$AlCl_3$	CH_3CN	RT	54
13	–	CH_2Cl_2	RT	NR
14	$AlCl_3$	CH_2Cl_2	RT	71[d]
15	$AlCl_3$	CH_2Cl_2	RT	52[e]
16	$AlCl_3$	CH_2Cl_2	RT	65[f,c]
17	$AlCl_3$	CH_2Cl_2	RT	52[g,c]
18	$AlCl_3$	CH_2Cl_2	50	68[c]
19	$AlCl_3$	CH_2Cl_2	10	29[c]

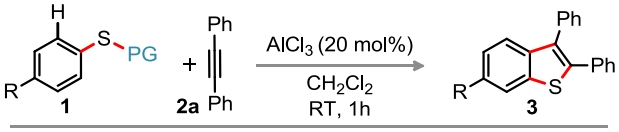
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol). [b]Conversion based on crude ^1H NMR of starting material. [c]**1a** (0.5 mmol), CH_2Cl_2 (2.0 mL), isolated yields. [d]TEMPO (0.1 mmol). [e]BHT (0.1 mmol), [f]$AlCl_3$ (25 mol%), [g]$AlCl_3$ (10 mol%). NR = no reaction.

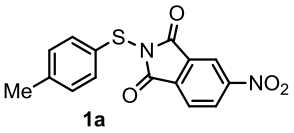
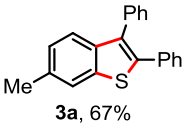
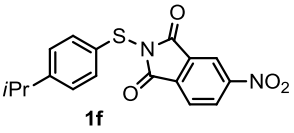
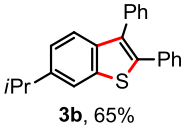
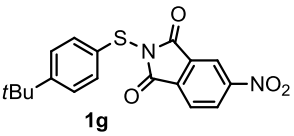
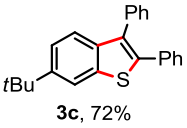
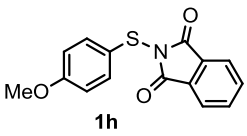
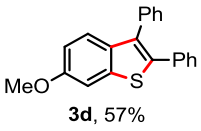
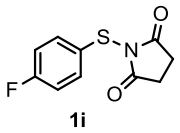
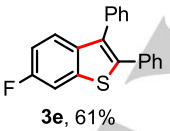
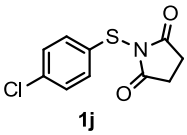
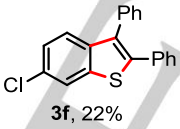
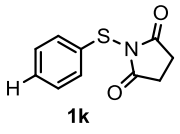
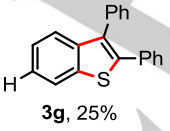
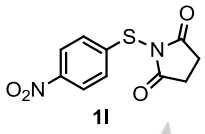
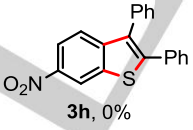


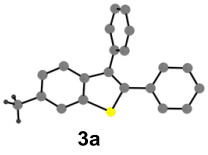
Scheme 2. Synthesis of 6-Methyl-2,3-diphenylbenzo[*b*]thiophenes.[a,b] [a]Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL) at RT, 1 h. [b]Isolated yields.

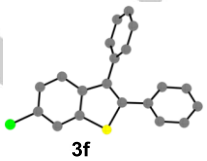
The reaction outcome was not largely affected, when $AlCl_3$ (25/10 mol%) was employed (entries16 and 17). Conducting the

Table 2. Synthesis of 2,3-Diphenylbenzo[*b*]thiophenes: Substrate Scope I.[a,b]



Entry	Substrate	Product
1	 **1a**	 **3a**, 67%
2	 **1f**	 **3b**, 65%
3	 **1g**	 **3c**, 72%
4	 **1h**	 **3d**, 57%
5	 **1i**	 **3e**, 61%
6	 **1j**	 **3f**, 22%
7	 **1k**	 **3g**, 25%
8	 **1l**	 **3h**, 0%


3a


3f

[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL) at RT for 1 h. [b]Isolated yields.

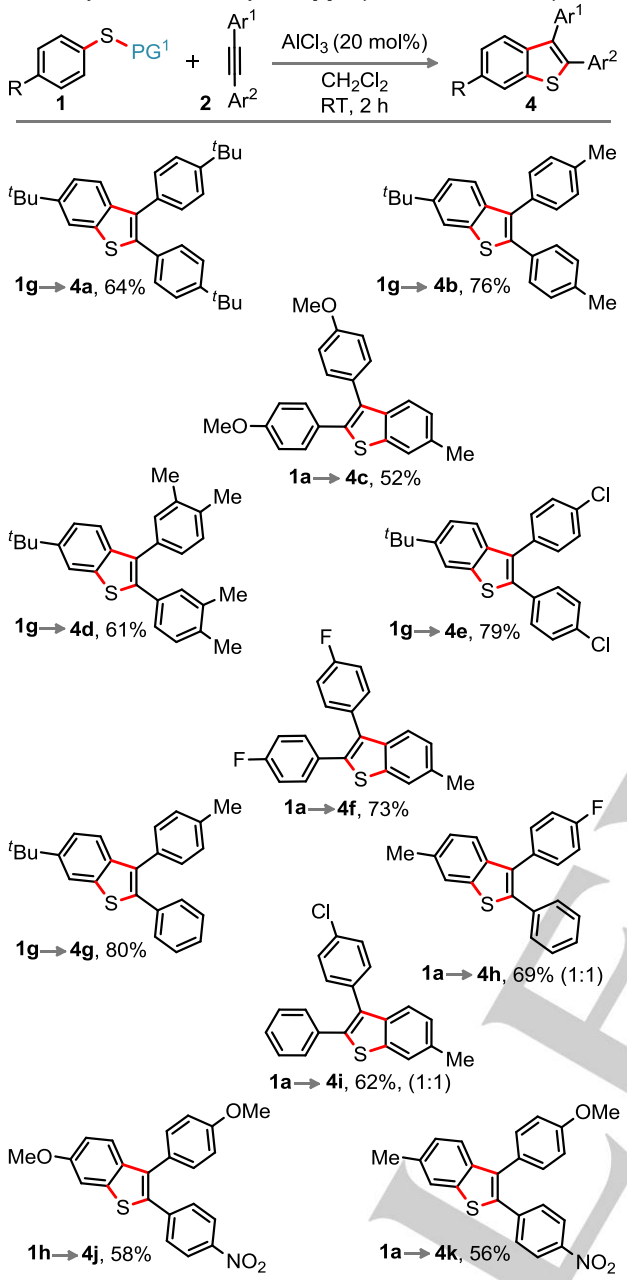
experiment at 50 °C did not improve the product yield (entry 18); moreover, the reaction at 10 °C was inefficient (entry 19).

The synthesis of benzothiophene **3a** from **1a** with 4-nitrophthalimide S–N protecting group and **2a** under the $AlCl_3$ at RT (shown in entry 7, Table 1) provoked us probing the identical annulations of various phthalimide/succinimide bearing 4-methyl thiophenol derivatives with **2a** (Scheme 2). The S–N protected 4-methyl-thiophenol compounds having electron-deficient phthalimide moiety (4-NO_2; **1a** and 4,5-di-Cl; **1c**) underwent annulation with **2a** more effectively than the electron-neutral **1b** and electron-rich phthalimide (4-Me; **1d**) derivatives. The succinimide bearing thiol **1e** is equally effective, providing 54% of **3a**. As the electron-deficient phthalimide moiety enhances polarizability of S–N bond, which in turn is responsible for deliberating the better reaction outcome. Thus, formation of **3a** is effectively sensed from the 4-nitrophthalimide S–N protecting group containing **1a**.

The optimized condition [**1a** (0.5 mmol, 1.0 equiv), **2a** (0.5 mmol, 1.0 equiv), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL), RT, 1 h] was next examined to probe the scope and limitations for the synthesis of benzothiophene derivatives through direct annulation of N-(arylthio)-phthalimide/-succinimide derivatives **1** with **2a**. The results were summarized in Table 2. The 4-NO_2-phthalimide bearing electron-rich thiophenol derivatives successfully underwent annulation with **2a** to afford the desired benzothiophene products **3a**–**3c** in good yields (entries 1–3). The corresponding 4-NO_2-phthalimide bearing 4-OMe thiol compound was found unstable; pleasingly, annulation of phthalimide containing 4-OMe thiophenol **1h** with **2a** led to **3d** (57%) (entry 4). Repeated attempts to isolate the phthalimide enabled halo (F, Cl) containing thiol derivatives were failed. By contrast, the stable N-(halo-arylthio)-succinimides **1i** and **1j** were reacted with **2a** to construct **3e** (61%) and **3f** (22%), respectively (entries 5 and 6). The chloro group is amenable to further synthetic manipulations. As such, the annulations proceed through 1,2-S-migration to provide the desired 6-substituted benzo[*b*]thiophene derivatives. Structure of **3a** and **3f** was further elucidated by the X-ray crystallographic analysis (Table 2). Likewise, 2,3-diphenyl benzo[*b*]thiophene (**3g**) was accessed from N-(phenylthio)-succinimide **1k** (entry 7). Disappointingly, the *p*-NO_2-substituted thiol derivative **1l** did not provide the desired product **3h**; a consequence of strong electron withdrawing (NO_2) group of arenes, which eventually affects the effective generation of sulfonium species and the electrophilic ipso-attack of arene motifs to the in-situ generated vinylic-cation.

We next explored scrutinizing the annulation of various unactivated diaryl alkynes **2** with **1a/1g** (Table 3). The reaction of electron donating *p*-*t*-Bu containing thiol derivative **1g** with *p*-*t*-Bu (**2b**) or *p*-Me (**2c)** substituted diaryl alkynes under the standard conditions delivered the corresponding 6-*t*-Bu containing 2,3-diarylbenzothiophenes **4a** (64%) and **4b** (76%). Pleasingly, electron-rich alkyne having *p*-OMe aryl moiety **2d** reacted with *p*-Me substituted thiol derivative **1a** to afford 52% of **4c**; this reaction was previously not successful under the Ag-catalyzed conditions.[8a] Likewise, annulation of **1g** with *m*,*p*-di-methyl substituted 1,2-diaryl acetylene (**2e**) furnished **4d** in moderate yield. The products **4e** and **4f** were constructed through the annulation of *p*-Cl (**2f**) and *p*-F (**2g**) substituted 1,2-diaryl acetylenes with **1g** and **1a**, respectively (Table 3). The annulation of **1a/1g** with the unsymmetrical alkynes was next examined. In general, the reaction with unsymmetrical alkynes produces mixture of two regioisomeric

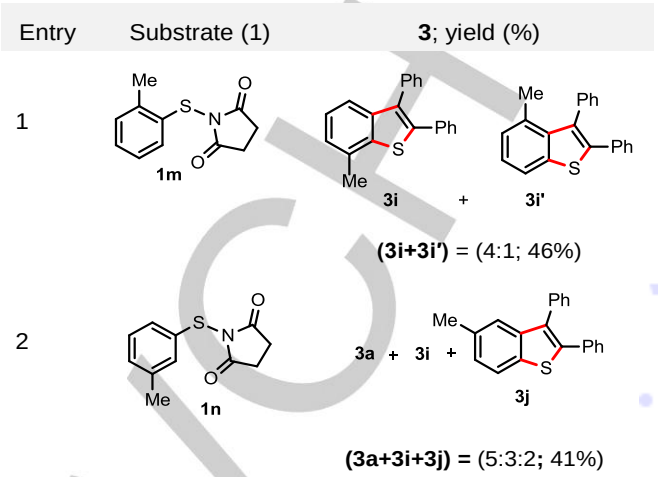
Table 3. Synthesis of 2,3-Diarylbenzo[*b*]thiophenes: Substrate Scope II. [a,b]



[a]Reaction conditions: **1a/1g** (0.5 mmol), **2** (0.5 mmol), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL) at RT for 2 h. [b]Isolated yields.

products. Surprisingly, product **4g** (single regioisomer) was formed from the unsymmetrical diaryl alkyne **2h** with **1g** under the optimized conditions (Table 3). Probably, the electronic perturbation of arene motifs affects the delivery of single product **4g**. Likewise, annulation of **1a** with halo group substituted unsymmetrical diaryl alkynes **2i** or **2j** produced inseparable mixture of two regioisomers **4h** or **4i** (1:1) in good yields (Table 3). Gratifyingly, annulation of EWG-*p*-NO_2/EDG-*p*-OMe bearing unsymmetrical alkyne **2k** with **1h/1a** exclusively furnished the corresponding benzo[*b*]thiophene **4j** and **4k**, respectively, as single regioisomer (Table 3); a consequence from the electronic perturbation of arene motifs.

Table 4. Reaction of *ortho* and *meta*-Substituted N-Arylthio Succinimides with 2a. [a,b]

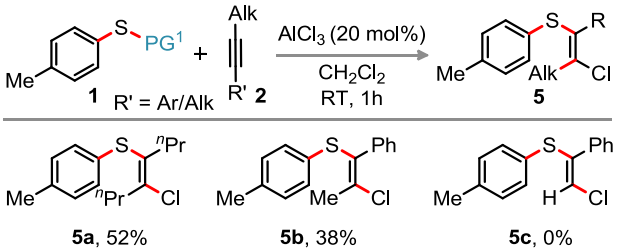


[a]Reaction conditions: **1** (0.5 mmol), **3a** (0.5 mmol), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL) at RT for 1 h. [b]mixture of products.

We next explored examining the annulation of *ortho/meta* substituted thiol of N-arylthio succinimide derivatives and the results were summarized in Table 4. Interestingly, the annulation of N-(thio-*o*-tolyl)-succinamide (**1m**) with **2a** provided inseparable mixture of two different products [with 1,2-S-migration **3i'** and S-retention **3i** in 1:4 ratio] (entry 1, Table 4).[8a] Not surprisingly, cyclization of N-(thio-*m*-tolyl)-succinimide (**1n**) with **2a** also furnished inseparable mixture of three benzothiophene products with the S-retention (**3a**), 1,2-S-migration (**3i**) and 1,2′-S-migration (**3j**) in overall 48% yield (entry 2, Table 4).

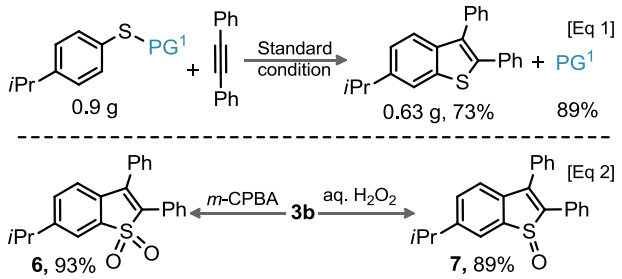
We next studied the annulation of the challenging alkyl-bearing alkynes (Table 5). To our surprise, the reaction of **1a** with 1,2-dialkyl/aryl-alkyl acetylenes under the optimized conditions results chloro-thiolation of alkyne providing β-chloroalkenyl sulfides **5a** (52%) and **5b** (38%) (Table 5); [14] probably quenching of the less stable alkyl-substituted vinyl cation, obtained in situ via the attack of alkyne to the activated sulfonium species, with the chloride ion is favored over the electrophilic ipso substitution by the arene motif. Disappointingly, repeated attempts for the annulation of terminal alkyne (i.e. phenyl acetylene) with **1a** failed under the oxidative conditions.

Table 5. Reaction of **1a** with alkyl substituted alkynes.[a,b]



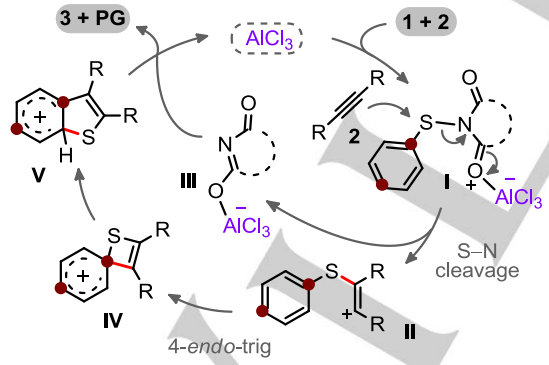
[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), $AlCl_3$ (20 mol %), CH_2Cl_2 (2.0 mL) at RT for 2 h. [b]Isolated yields.

The robustness of the catalytic conditions is successfully tested performing the annulation of **1f** (0.9 g) with **2a** (0.47 g) at RT to provide **3b** (630 mg) in 73% yield, offering opportunity for reaction scalability. The isolation of 4-nitrophthalimide (451 mg, 89%) truly demonstrates the atom-efficient protocol of the current transformation (Eq 1, Scheme 3). As expected, independent oxidation of **3b** with *m*-CPBA and aq. H_2O_2 delivered the corresponding sulfone (**6**, 93%) and sulfoxide (**7**, 89%), respectively (Eq 2, Scheme 3).



Scheme 3. Synthetic Elaboration of Benzothiophene.

To rationalize the observed results, a tentative mechanism of the current annulation is proposed in Scheme 4. Corroborated with the insightful theoretical supporting data resulted from Glorius and co-workers for benzothiophene synthesis,[8b] we formally believe that the reaction begins with the coordination of $AlCl_3$ to the phthalimide moiety of **1**, which eventually triggers the polarization of S–N bond and generates the electrophilic thiophenol intermediate **I**.[8b] Next, the nucleophilic attack of the alkyne to **I** then produce the vinyl cation species **II** with the release of Al-enabled phthalimide derivative **III**.[8b] Then intramolecular electrophilic 4-*endo*-trig spirocyclization of the proximal *ipso*-carbon with the vinyl cation **II** rapidly forms the unstable spirocyclohexadienyl arenium-intermediate **IV**.[8] The



Scheme 4. Plausible Mechanism

ring expansion of species **IV** through 1,2-S-migration produces the intermediate **V**.[10] Finally, deprotonation-aromatization of **V** affords final product **3**. The protonation of **III** generates phthalimide-derivative, liberating $AlCl_3$ for the next cycle.

Conclusions

In conclusion, we have successfully demonstrated a modified direct annulation method of N-arylthio phthalimide derivatives with unactivated alkynes to access the challenging π–conjugated 6-substituted 2,3-diaryl benzo[*b*]thiophenes. The reaction is successfully performed at room temperature in the presence of inexpensive $AlCl_3$ and is efficient. The reaction is scalable with the isolation of phthalimide moiety, which makes the current process practicable. The identical reaction with dialkyl alkynes provides β-chloroalkenyl sulfides. The synthetic utility of the current method for the construction of π–extended and V-shaped benzothiophene analogues are being actively pursued in our laboratory.

Experimental Section

General Experimental: All the reactions were performed in an oven-dried Schlenk flask/pressure tubes under an argon atmosphere. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh or 230-400 Mesh silica gel eluting with hexane and ethyl acetate mixture. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber.

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded based on the resonating frequencies as follows: (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) and (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz) having the solvent resonance as internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Few cases tetramethylsilane (TMS) at 0.00 ppm was used as reference standard. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in (Hz), and integration. Data for ^{13}C NMR, ^{19}F NMR were reported in terms of chemical shift (ppm). IR spectra were reported in cm^{-1}. High resolution mass spectra were obtained in ESI mode. LC-MS spectra were obtained with ionization voltage of 70ev; data was reported in the form of *m/z* (intensity relative to base peak = 100). Elemental (C, H N) analysis were carried out using FLASH EA 1112 analyzer. Melting points were determined by electro-thermal heating and are uncorrected.

Materials: Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Following the standerd procedures, the solvents were dried and stored over molecular sieves under inert gas (nitrogen, argon) atmosphere. Diphenyl acetylene (**2a**), 4-octyne(**2l**), 1-Phenylpropyne(**2m**), TFA, CSA, TfOH, MsOH, AcOH, $AlCl_3$, $FeCl_3$, and $BF_3.OEt_2$ were purchased, and used as received Analytical and spectral data of all the known compounds are exactly matching with the reported values.

General Procedure for the Perparation of Symmetrical Diaryl Alkynes (2b–g):[15] To a mixture of $PdCl_2(PPh_3)_2$ (6.0 mol %), CuI (10 mol %) and aryl iodide (1.0 mmol) in benzene (5.0 mL) was added DBU (6.0 mmol) followed by trimetyhylsilyl acetylene (0.5 mmol) and de-ionized water (40 mol %) under an argon atmosphere at RT. The resulting mixture was heated at 80 °C for 18 h in the absence of light. Upon completion, the reaction mixture was cooled to RT and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine and dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate. Analytical and spectral data of these compounds are exactly matching with the reported values.

General Procedure for the Perparation of Unsymmetrical Diaryl Alkynes (2h–k):[16] To a mixture of $PdCl_2(PPh_3)_2$ (2.0 mol %), CuI (4.0

mol %) and aryl iodide (1.0 mmol) in THF (5.0 mL) was added Et_3N (3.0 mmol) followed by aryl/alkyl bearing acetylenes (1.0 mmol) under an argon atmosphere at RT. The resulting mixture was heated at 60 °C for 16 h in the absence of light. Upon completion, the reaction mixture was cooled to RT and diluted with diethyl ether. The organic layer was washed with water, 10% HCl (2 × 5.0 mL), and brine and dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate. Analytical and spectral data of these compounds are exactly matching with the reported values.

General Procedure for the Preparation of N-Arylthio Phthalimide (1): [17] To a solution of thiophenols (**1′,** 1.0 equiv) and Et_3N (0.1 equiv) in CH_2Cl_2 (5.0 mL for 2.0 mmol) was added SO_2Cl_2 (1.0 equiv) drop wise under an argon atmosphere at 0 °C. After stirring for 15 min, the mixture was warmed to RT and stirred for 30 min and then cooled to 0 °C. The resulting solution was transferred via cannula to a solution of phthalimide (1.0 equiv) and Et_3N (0.1 equiv) in CH_2Cl_2 (5.0 mL for 2.0 mmol) at 0 °C, and the mixture was warmed to RT over 1 h. The resulting mixture diluted with water and extracted with CH_2Cl_2 (2 × 10 mL, for 1.0 mmol). The combined extracts were washed with brine. The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate (5:1). Analytical and spectral data of compounds **1b, 1h** are exactly matching with the reported values.

5-Nitro-2-(*p*-tolylthio)isoindoline-1,3-dione (1a): 1a (1.3 g, 51%), yellow solid. mp = 164–165 °C; R_f = 0.50 (8:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 1.6 Hz, 1H), 8.61 (dd, J = 8.2 & 1.8 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.5, 151.9, 141.2, 136.3, 133.7, 133.3, 130.3, 130.2, 129.6, 125.2, 119.2, 21.3; IR (KBr) ν_{max} 2915, 1735, 1539, 1278, 1064, 717 cm^{-1}; HRMS (ESI) for $C_{15}H_{14}N_3O_4S$ (M+NH_4)$^+$: calcd. 332.0700, found 332.0705.

5,6-Dichloro-2-(*p*-tolylthio)isoindoline-1,3-dione (1c): 1c (0.92 g, 59%), colorless solid. mp = 162–163 °C; R_f = 0.77 (8:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 140.9, 139.7, 133.3, 131.0, 130.7, 130.1, 125.9, 21.3; IR (KBr) ν_{max} 1733, 1315, 1069, 734 cm^{-1}; HRMS (ESI) for $C_{15}H_{13}Cl_2N_2O_2S$ (M+NH_4)$^+$: calcd. 355.0069, found 355.0073.

5-Methyl-2-(*p*-tolylthio)isoindoline-1,3-dione (1d): 1d (1.08 g, 61%), pale yellow solid. mp = 175–176 °C; R_f = 0.54 (8:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 1H), 7.72–7.63 (m, 1H), 7.59–7.49 (m, 3H), 7.11 (d, J = 7.6 Hz, 2H), 2.49 (s, 3H) 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 167.8, 146.0,140.0, 135.1, 134.8, 132.3, 131.5, 129.9, 129.4, 124.3, 123.8, 22.0, 21.2 ; IR (KBr) ν_{max} 3488, 1729, 1275, 1049, 734 cm^{-1}; HRMS (ESI) for $C_{16}H_{13}NNaO_2S$ (M+Na)$^+$: calcd. 306.0559, found 306.0567.

2-((4-*iso*-Propylphenyl)thio)isoindoline-1,3-dione (1f): 1f (1.14 g, 62%), yellow solid. mp = 138–139 °C; R_f = 0.61 (8:2 hexane/EtOAc); 1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 2.0 Hz, 1H), 8.62 (dd, J = 8.0 & 2.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 2.92–2.81 (m, 1H), 1.20 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 165.6, 151.95, 151.88, 136.3, 133.9, 133.3, 130.6, 129.6, 127.6, 125.2, 119.2, 33.9, 23.6; IR (KBr) ν_{max} 2930, 2359, 1735, 1541, 1276, 716 cm^{-1}; HRMS (ESI) for $C_{17}H_{15}N_2O_4S$ (M+H)$^+$: calcd. 343.0747, found 343.0748.

2-((4-(*tert*-Butyl)phenyl)thio)-5-nitroisoindoline-1,3-dione (1g): 1g (1.16 g, 54%), yellow solid. mp = 166–167 °C; R_f = 0.59 (8:2 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl^3$) δ 8.70 (d, J = 1.6 Hz, 1H), 8.62 (dd, J = 8.0 & 2.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 165.6, 154.2, 151.9, 136.3, 133.5, 133.4, 130.3, 129.6, 126.6, 125.2, 119.3, 34.8, 31.0; IR (KBr) ν_{max} 2962, 2868, 1737, 1540, 1277, 1062, 716 cm^{-1}; MS (EI) m/z (%) 355 (M^+–1, 100); Anal. Calcd. for $C_{18}H_{16}N_2O_4S$: C, 60.66; H, 4.53; N, 7.86; Found: C, 60.72; H, 4.49; N, 7.81.

General Procedure for Preparation of N-Arylthio Succinimide (1):[10a] To a solution of N-chlorosuccinimide (NCS) (1.0 equiv) in CH_2Cl_2 (5.0 mL for 2.0 mmol) was added thiophenols (**1′,** 1.0 equiv) and Et_3N (1.0 equiv) drop wise under an argon atmosphere at 0 °C. The resulting mixture was stirred for 12 h at RT. After completion, the reaction mixture was quenched with saturated aqueous NH_4Cl solution. The organic layer was separated; the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL, for 1.0 mmol). The combined extracts were washed with brine. The organic layer was dried over Na_2SO_4. Solvent was filtered and evaporated under reduced pressure. The crude residue was purified using column chromatography on silica gel using hexane/ethyl acetate (4:1). Following this procedure, the N–thioaryl succinamides **1e** and **1i–n** were prepared. Analytical and spectral data of these compounds are exactly matching with the reported values.

General Procedure for Annulation, Synthesis of Benzo[*b*]thiophenes: The N-arylthio succinimide/phthalimide (**1,** 0.5 mmol) and 1,2-diarylalkyne (**2**, 0.5 mmol) were taken in a Schlenk tube. Subsequently, $AlCl_3$ (14 mg, 20 mol %) was introduced into the flask in a Glove box. Solvent 1,1-dichloromethane (2.0 mL) was added to the mixture and the resulting mixture was stirred at RT for 1–2 h. Upon completion, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered over a small pad of Celite. Solvent was evaporated under the reduced pressure and the crude residue was purified through silica gel column chromatography using n-hexane eluent to give the desired product **3/4**.

6-Methyl-2,3-diphenylbenzo[*b*]thiophene (3a):[8a] **3a** (101 mg, 67%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.46–7.34 (m, 8H), 7.29–7.26 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.7, 138.3, 135.7, 134.5, 134.4, 133.0, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 126.1, 123.0, 121.9, 21.5.

6-*iso*-Propyl-2,3-diphenylbenzo[*b*]thiophene (3b):[8a] **3b** (107 mg, 65%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.41–7.29 (m, 8H), 7.24–7.19 (m, 3H), 3.08–2.97 (m, 1H) 1.32 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl3) δ 145.7, 139.1, 138.6, 135.7, 134.4, 133.0, 131.6, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 123.8, 123.1, 119.2, 34.2, 24.2.

6-*tert*-Butyl-2,3-diphenylbenzo[*b*]thiophene (3c):[8a] **3c** (124 mg, 72%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.49–7.37 (m, 8H), 7.31–7.27 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 139.0, 138.8, 138.6, 135.7, 134.4, 132.9, 130.4, 129.6, 128.6, 128.3, 127.5, 127.3, 122.8, 122.7, 118.2, 34.9, 31.5.

6-Methoxy-2,3-diphenylbenzo[*b*]thiophene (3d):[8a] **3d** (90 mg, 57%), pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.8 Hz, 1H), 7.41–7.27 (m, 8H), 7.24–7.20 (m, 3H), 6.95 (dd, J = 9.0 & 2.2 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 140.1, 136.8, 135.7, 135.0, 134.4, 132.8, 130.3, 129.4, 128.6, 128.3, 127.4, 127.3, 124.0, 114.4, 104.5, 55.6.

6-Fluoro-2,3-diphenylbenzo[*b*]thiophene (3e): [8a] **3e** (93 mg, 61%), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.48 (m, 2H), 7.41–7.34 (m, 3H), 7.32–7.27 (m, 4H), 7.25–7.20 (m, 3H), 7.06 (td, J = 8.8 & 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (d, J = 246 Hz), 139.6 (d, J = 10 Hz), 139.0 (d, J = 3 Hz), 137.4, 135.2, 133.9, 132.7, 130.3, 129.5, 128.7, 128.4, 127.8, 127.5, 124.4 (d, J = 9 Hz), 113.3 (d, J = 24 Hz), 108.1 (d, J = 25 Hz).

6-Chloro-2,3-diphenylbenzo[*b*]thiophene (3f):[8a] 3f (36 mg, 22%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 1.6 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.41–7.37 (m, 3H), 7.31–7.27 (m, 5H), 7.25–7.23 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ140.0, 139.7, 139.4, 135.0, 133.8, 132.8, 130.5, 130.3, 129.5, 128.7, 128.4, 127.9, 127.6, 125.2, 124.2, 121.6.

2,3-Diphenylbenzo[*b*]thiophene (3g):[8a] 3g (36 mg, 25%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.85 (m, 1H), 7.62–7.57 (m, 1H), 7.40–7.28 (m, 9H), 7.26–7.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ140.9, 139.5, 138.8, 135.5, 134.2, 133.2, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.3, 122.0.

7-Methyl-2,3-diphenylbenzo[*b*]thiophene (3i) and 4-Methyl-2,3-diphenylbenzo[*b*]thiophene (3i'):[8a] Inseparable mixture of **3i/3i'** (4:1) (69 mg, 46%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.47–7.17 (m, 19H), 7.06 (d, J = 7.2 Hz, 1H), 2.62 (s, 1H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 139.6, 139.2, 138.9, 138.5, 138.2, 135.8, 134.52, 134.47, 134.45, 134.37, 133.9, 131.6, 131.1, 130.4, 129.6, 128.6, 128.3, 128.1, 127.9, 127.6, 127.4, 127.35, 127.30, 127.1, 124.9, 124.8, 124.1, 121.0, 120.0, 21.5, 20.2.
Ratio of the both regioisomers **3i**:**3i'** was determined based on the characteristic Me-^{1}H proton integretion. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H for **3i/3i'**: δ = 1.98 (s, 3H, 78%, major)/2.62 (s, 3H, 22%, minor).

6-Methyl-2,3-diphenylbenzo[*b*]thiophene (3a), 5-Methyl-2,3-diphenylbenzo[*b*]thiophene (3j) and 7-Methyl-2,3-diphenylbenzo[*b*]thiophene (3i):[8a] The reaction between 1-(*m*-tolylthio)pyrrolidine-2,5-dione **1m** and **2a** under the optimization conditions provided inseparable mixture of **3a**, **3i**, and **3j** (5:3:2) (61 mg, 41%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 10.0, 5.0 Hz, 2H), 7.67 (bs, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.42–7.29 (m, 19H), 7.27–7.14 (m, 12H), 7.06 (d, J = 7.2 Hz, 1H), [2.49 (s, 3H), 2.41 (s, 1H), 1.98 (s, 2H)]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.7, 139.6, 139.2, 139.1, 138.7, 138.5, 138.3, 138.2, 136.0, 135.7, 134.51, 134.47, 134.45, 134.37, 134.2, 133.0, 132.9, 131.1, 130.44, 130.38, 129.6, 129.55, 129.52, 128.62, 128.59, 128.3, 128.1, 127.9, 127.6, 127.5, 127.4, 127.35, 127.27, 127.1, 126.2, 126.1, 124.1, 123.2, 123.0, 121.9, 121.7, 121.1, 120.0, 21.54 (**3i**), 21.50 (**3a**).
Ratio of the three regioisomers **3a**:**3i**:**3j** was determined based on the characteristic Me-^{1}H proton integration. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H for **3a/3i/3j**: δ= 2.49 (s, 3H, 48%, major)/ 1.98 (s, 3H, 30%, minor)/ 2.41 (s, 3H, 22%, minor). The Me peak appeared at 2.49 and 1.98 is matching with the previously observed compound **3a** and **3i**, respectively.

6-(*tert*-Butyl)-2,3-bis(4-(*tert*-butyl)phenyl)benzo[*b*]thiophene (4a) and 5-(*tert*-Butyl)-2,3-bis(4-(*tert*-butyl)phenyl)benzo[*b*]thiophene (4a'): The reaction between **1g** and **2b** under the optimization conditions provided inseparable mixture of **4a** and **4a'** (97:3) (146 mg, 64%), colorless crystalline solid. mp = 116–117 °C; R_f = 0.35 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (bd, J = 1.5 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 2H), 7.40 (dd, J = 8.5 & 2.0 Hz, 1H), 7.31–7.27 (m, 6H), 1.42 (s, 9H), 1.40 (s, 9H) 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 150.1, 147.7, 139.2, 138.7, 138.6, 132.8, 132.5, 131.6, 129.9, 128.9, 125.4, 125.2, 122.9, 122.5, 118.1, 34.9, 34.6, 34.5, 31.5, 31.4, 31.2; IR (KBr) ν_{max} 2961, 2867, 1462, 1363, 1265, 836 cm^{-1}; HRMS (ESI) for $C_{32}H_{39}S$ $(M+H)^+$: calcd. 455.2767, found 455.2765.

6-*tert*-Butyl-2,3-di-*p*-tolylbenzo[*b*]thiophene (4b):[8a] 4b (141 mg, 76%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.8 & 1.6 Hz, 1H), 7.24–7.17 (m, 6H), 7.04 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.30 (s, 3H) 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 138.9, 138.8, 138.7, 137.3, 136.8, 132.8, 132.5, 131.7, 130.2, 129.4, 129.3, 129.0, 122.9, 122.5, 118.1, 34.9, 31.5, 21.3, 21.2.

2,3-bis(4-Methoxyphenyl)-6-methylbenzo[*b*]thiophene (4c) and 2,3-bis(4-Methoxyphenyl)-5-methylbenzo[*b*]thiophene (4c'): The reaction between **1a** and **2d** under the optimization conditions provided inseparable mixture of **4c** and **4c'** (97:3) (94 mg, 52%), pale yellow solid. mp = 137–138 °C; R_f = 0.32 (19:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.24 (d, J = 8.5 Hz, 4H), 7.13 (dd, J = 8.0 & 1.0 Hz, 1H), 6.93 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 3.78 (s, 3H) 2.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 158.8, 139.1, 138.7, 137.8, 134.2, 131.8, 131.5, 130.6, 128.1, 127.0, 126.0, 122.8, 121.8, 114.1, 113.8, 55.21, 55.19, 21.5; IR (KBr) ν_{max} 2955, 2835, 1607, 1540, 1248, 811 cm^{-1}; HRMS (ESI) for $C_{23}H_{20}NaO_2S$ $(M+Na)^+$: calcd. 383.1076, found 383.1077.

6-(*tert*-Butyl)-2,3-bis(3,4-dimethylphenyl)benzo[*b*]thiophene (4d) and 5-(*tert*-Butyl)-2,3-bis(3,4-dimethylphenyl)benzo[*b*]thiophene (4d'): The reaction between **1g** and **2e** under the optimization conditions provided inseparable mixture of **4d** and **4d'** (87:13) (122 mg, 61%), colorless crystalline solid. mp = 141–142 °C; R_f = 0.30 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 1.6 Hz, 1H), 7.52 (d, J = 7.6 Hz 1H), 7.40 (dd, J = 8.6 & 1.8 Hz, 1H), 7.22–7.13 (m, 3H), 7.07–6.96 (m, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 139.1, 138.7, 138.6, 136.6, 136.4, 136.0, 135.4, 133.3, 132.5, 132.1, 131.3, 130.6, 129.8, 129.5, 127.8, 126.8, 122.8, 122.4, 118.1, 34.9, 31.5, 19.8, 19.7, 19.6, 19.5; IR (KBr) ν_{max} 2963, 2866, 1449, 1263, 821 cm^{-1}; HRMS (ESI) for $C_{28}H_{30}NaS$ $(M+Na)^+$: calcd. 421.1960, found 421.1960.

6-*tert*-Butyl-2,3-bis(4-chlorophenyl)benzo[*b*]thiophene (4e):[8a] 4e (162 mg, 79%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.87 (bs, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.44–7.36 (m, 3H), 7.26–7.21 (m 6H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ148.5, 139.0, 138.1, 137.8, 133.8, 133.5, 132.6, 132.0, 131.6, 130.7, 129.0, 128.7, 123.0, 122.6, 118.3, 35.0, 31.5.

2,3-bis(4-Fluorophenyl)-6-methylbenzo[*b*]thiophene (4f):[8a] 4f (123 mg, 73%), colorless crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.67 (bs, 1H), 7.43 (d, J = 6.4 Hz, 1H), 7.29–7.23 (m, 4H), 7.17 (dd, J = 6.4 & 0.8 Hz, 1H), 7.11–7.08 (m, 2H), 6.98–6.92 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.25 (d, J = 250 Hz), 162.16 (d, J = 248 Hz), 138.9, 138.5, 137.4, 134.8, 132.0 (d, J = 3 Hz), 131.3 (d, J = 4 Hz), 131.2 (d, J = 8 Hz), 130.3 (d, J = 3 Hz), 126.3, 122.8, 121.9, 115.7 (d, J = 21 Hz), 115.4 (d, J = 21 Hz), 21.5.

6-(*tert*-Butyl)-2-phenyl-3-(*p*-tolyl)benzo[*b*]thiophene (4g): 4g (142 mg, 80%), colorless crystalline solid. mp = 169–170 °C; R_f = 0.27 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.4 & 1.6 Hz, 1H), 7.35–7.29 (m, 2H), 7.25–7.15 (m, 7H), 2.38 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ147.9, 139.0, 138.7, 138.5, 136.9, 134.6, 132.9, 132.6, 130.2, 129.5, 129.3, 128.3, 127.4, 122.9, 122.6, 118.1, 34.9, 31.5, 21.3; IR (KBr) ν_{max} 2960, 2866, 1597, 1263, 866, 820 cm^{-1}; HRMS (ESI) for $C_{25}H_{25}S$ $(M+H)^+$: calcd. 357.1671, found 357.1670.

3-(4-Fluorophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (4h) and 2-(4-Fluorophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (4h'):[8a] Inseparable mixture of **4h** and **4h'** (1:1, 110 mg, 69%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.65 (bs, 1H), 7.48–7.34 (m 2H), 7.31–7.22 (m, 6H), 7.15 (dd, J = 8.6 & 1.0 Hz, 1H), 7.07 (t, J = 8.8 Hz, 1H), 6.91 (t, J = 8.8 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 248 Hz), 162.1 (d, J = 247 Hz), 139.1, 139.0, 138.6, 137.1, 135.4, 134.7, 134.2, 132.0 (d, J = 8 Hz), 131.8, 131.6, 131.2 (d, J = 8 Hz),130.3, 129.5, 128.7, 128.4, 127.6, 127.4, 126.2, 123.0, 122.7, 122.0, 121.96, 121.87, 115.6 (d, J = 22 Hz), 115.3 (d, J = 22 Hz), 21.5.

Both the regioisomeric products **4h** and **4h′** are indistinguishable by ^{1}H NMR, however, the ^{13}C NMR studies clearly reveals the formation of both regioisomers **4h** and **4h′**.

3-(4-Chlorophenyl)-6-methyl-2-phenylbenzo[*b*]thiophene (4i) and 2-(4-Chlorophenyl)-6-methyl-3-phenylbenzo[*b*]thiophene (4i′):[8a] Inseparable mixture of **4i** and **4i′** (1:1, 104 mg, 62%), colorless crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65, (bs, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.43–7.34 (m, 3H), 7.31–7.23 (m, 4H), 7.20 (bd, J = 3.4 Hz, 2H), 7.18–7.13 (m, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ139.1, 139.0, 138.8, 138.6, 138.3, 136.8, 135.4, 134.8, 134.7, 134.13, 134.06, 133.51, 133.48, 133.2, 132.9, 131.7, 130.7, 130.3, 129.6, 128.9, 128.7, 128.5, 128.4, 127.7, 127.5, 126.3, 123.1, 122.7, 122.0, 121.9, 21.5.
Both the regioisomeric products **4i** and **4i′** are indistinguishable by ^{1}H NMR, however, the ^{13}C NMR studies clearly reveals the formation of both regioisomers **4i** and **4i′**.

6-Methoxy-3-(4-methoxyphenyl)-2-(4-nitrophenyl)benzo[*b*]thiophene (4j): 4j (113 mg, 58%), pale yellow solid. mp = 152–153 °C; R_f = 0.25 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.8 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.20–7.92 (m, 3H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ159.3, 158.3, 146.3, 141.4, 140.6, 135.3, 134.9, 133.2, 131.2, 129.6, 126.9, 124.7, 123.6, 115.0, 114.5, 104.4, 55.6, 55.2; IR (Neat) ν_{max} 2863, 1642, 1237, 728, 628 cm^{-1}; HRMS (ESI) for $C_{22}H_{17}NNaO_4S$ $(M+Na)^+$: calcd. 414.0770, found 414.0773.

3-(4-Methoxyphenyl)-6-methyl-2-(4-nitrophenyl)benzo[*b*]thiophene (4k): **4k** (105 mg, 56%), yellow solid. mp = 164–165 °C; R_f = 0.31 (49:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2H), 7.69 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.23–7.17 (m, 3H), 6.97 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ159.3, 146.5, 141.5, 139.4, 138.7, 135.7, 135.4, 134.8, 131.3, 129.9, 126.9, 126.6, 123.6, 122.0, 114.5, 55.3, 21.6; IR (Neat) ν_{max} 2923, 1579, 1237, 749, 632 cm^{-1}; HRMS (ESI) for $C_{22}H_{18}NO_3S$ $(M+H)^+$: calcd. 376.1002, found 376.1005.

(*E*)-4-Chloro-5-(*p*-tolylthio)-4-octene (5a):[14] The reaction between **1a** and 4-octyne (**2l**) under the optimization conditions provided **5a** (69 mg, 51%), colorless liquid. R_f = 0.4 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 2.35–2.28 (m, 5H), 1.69–1.48 (m, 4H), 0.93 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ138.6, 136.3, 131.5, 130.2, 129.7, 129.5, 38.9, 35.7, 21.3, 21.0, 13.5, 13.2; IR (Neat) ν_{max} 2823, 1523, 1247, 748, 612 cm^{-1}; HRMS (ESI) for $C_{15}H_{22}ClS$ $(M+H)^+$: calcd. 269.1125, found 269.1115.

(E)-1-Chloro-2-(*p*-tolylthio)-2-methylstyrene (5b):[14] The reaction between **1a** and 1-phenylpropyne (**2m**) under the optimization conditions provided **5b** (53 mg, 38%), colorless liquid. R_f = 0.34 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.2 Hz, 2H), 7.42–7.31 (m, 3H), 7.20 (d, J = 7.2 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 2.34 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ138.7, 137.2, 131.3, 131.0, 130.6, 129.8, 129.2, 128.6, 128.5, 128.0, 21.8, 21.1; IR (Neat) ν_{max} 2964, 1482, 1286, 762, 692 cm^{-1}; MS (EI) m/z (%) 274 (M^+, 100); Anal. Calcd. for $C_{16}H_{15}ClS$: C, 69.93; H, 5.50; N, 0.00; Found: C, 69.85; H, 5.56; N, 0.07.

Synthesis of 6-*iso*-Propyl-2,3-diphenylbenzo[*b*]thiophene 1,1-dioxide (6):[8a] To a solution of **3b** (1.0 mmol) in dry CH_2Cl_2 (10 mL) was added *m*-CPBA (2.0 mmol) under an argon atmosphere. The resulting mixture was stirred at RT overnight. Upon completion, solvent was evaporated and the crude material was purified by column chromatography eluting with hexane/EtOAc 95:5 to give the desired sulfone **6** (335 mg, 93%), colorless crystalline solid. mp = 226–227 °C; R_f = 0.42 (95:5 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.74 (s, 1H), 7.52–7.36 (m, 6H), 7.35–7.27 (m, 5H), 7.21 (d, J = 8.0 Hz, 1H), 3.07–2.98 (m, 1H), 1.30 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ151.9, 138.1, 136.7, 136.5, 131.6, 131.0, 130.8, 129.42, 129.36, 129.2, 129.1, 129.0, 128.6, 127.2, 124.1, 119.5, 34.2, 23.7; IR (Neat) ν_{max} 2963, 1479, 1297, 741, 698 cm^{-1}; HRMS (ESI) for $C_{23}H_{20}NaO_2S$ $(M+Na)^+$: calcd. 383.1076, found 383.1077.

Synthesis of 6-*iso*-Propyl-2,3-diphenylbenzo[*b*]thiophene 1-oxide (7):[18] To a solution of **3b** (1.0 mmol) in CH_2Cl_2 (5.0 mL) was added aq.H_2O_2 (5.0 mmol). The resulting mixture was stirred at RT overnight. Upon completion, the reaction mixture saturated with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. Solvent was evaporated and the crude material was purified by column chromatography eluting with hexane/EtOAc 90:10 to give **7** (306 mg, 89%), colorless crystalline solid. mp = 126–127 °C; R_f = 0.55 (85:15 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.81 (s, 1H), 7.61 (d, J = 8.4, Hz, 1H), 7.48–7.39 (m, 7H), 7.33–7.28 (m, 4H), 3.17-3.08 (m, 1H), 1.41 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ145.7, 139.1, 138.6, 135.7, 134.4, 133.0, 131.6, 130.4, 129.5, 128.6, 128.3, 127.5, 127.3, 123.8, 123.1, 119.2, 34.2, 24.2; IR (Neat) ν_{max} 2957, 2923, 1595, 1439, 1029, 694 cm^{-1}; HRMS (ESI) for $C_{23}H_{20}NaOS$ $(M+Na)^+$: calcd. 367.1127, found 367.1127.

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Keywords: Benzo[*b*]thiophene • Annulation • Lewis acid • unactivated alkynes • 1,2-S-Migration

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$AlCl_3$ Catalysis

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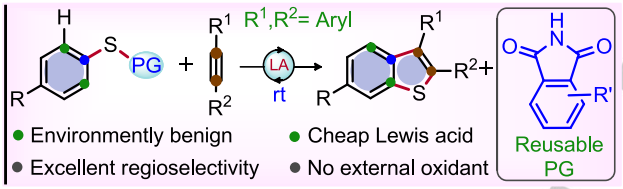
$AlCl_3$-Catalyzed Intermolecular Annulation of Thiol-Derivatives and Alkynes via 1,2-S-Migration at Room Temperature: Construction of 6-Substituted Benzo[b]thiophenes



A novel $AlCl_3$-catalyzed intermolecular oxidative annulation of N-arylthio phthalimide derivatives with alkynes is showcased at room temperature. The annulation involves oxidative cleavage of the S–N bond and the occurrence of 1,2-S-migration, which eventually allows the construction of diverse arrays of π-conjugated 6-substituted 2,3-diaryl benzo[b]thiophene derivatives.