Advanced Synthesis & Catalysis

Accepted Article

Title: Palladium-Catalyzed Regioselective Three-Component Cascade Bisthiolation of Terminal Alkynes

Authors: Huanfeng Jiang, Jianxiao Li, Can Li, Lu Ouyang, Chunsheng Li, Shaorong Yang, and Wanqing Wu

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701417

Link to VoR: http://dx.doi.org/10.1002/adsc.201701417

10.1002/adsc.201701417

FULL PAPER

DOI: 10.1002/adsc.200((will be filled in by the editorial sttaff**))**

Palladium-Catalyzed Regioselective Three-Component Cascade Bisthiolation of Terminal Alkynes

Jianxiao Li,[a] Can Li,[a] Lu Ouyang,[a] Chunsheng Li,[a] Shaorong Yang,[a] Wanqing Wu [a,*] and Huanfeng Jiang [a,*]

[a] Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China.
Fax: (+86) 20-87112906; E-mail: jianghf@scut.edu.cn;cewuwq@scut.edu.cn

Received: ((will be filled in by the editorial staff))

Abstract: An efficient and novel NHC(N-heterocyclic carbene)-palladium-catalyzed three-component cascade bisthiolation of terminal alkynes, K_2S (potassium sulfide) and diaryliodonium salts for the assembly of functionalized (*Z*)-1,2-bis(arylthio)alkene derivatives has been accomplished for the first time. This unique observation features a broad substrate scope, excellent functional-group tolerance, and high regioselectivity. Especially, an arylthiolate anion from diaryliodonium salts and potassium sulfide was proposed as the key intermediate in the catalytic cycle.

Keywords: NHC-Palladium; bisthiolation; terminal alkynes; (*Z*)-1,2-bis(arylthio)alkene derivatives

Introduction

Transition metal-catalyzed difunctionalization of alkynes are proven to be a straightforward and flexible approach to prepare synthetically valuable polyfunctionalized alkene derivatives in contemporary organic synthesis.[1] Particularly, terminal alkynes represent one of the most abundant and valuable building blocks, and have been extensively investigated and practiced in both academic and industrial settings.[2] In this regard, many remarkable approaches have been typically accomplished via transition-metal species catalyzed addition of alkynes with two elements of the *p*-block in one step.[3] However, most of these excellent strategies required functionalized precursors, reducing their versatility and simplicity. Arguably, cascade carbometalation process through the addition of carbon nucleophiles to alkynes is widely explored.[4] Nevertheless, the substrate scope is limited to activated aryl alkynes. More importantly, radical-mediated multicomponent cascade difunctionalization of alkynes is particularly appealing, and allowing the rapid assembly of molecular complexity.[5] Despite the significance, all of these elegant developments suffer from certain limitations, such as stringent reaction conditions, limited substrate scopes and/or regio- and stereoselectivity issues, which lower the synthetic efficiency and generality. Therefore, the development of an efficient and novel channel for the difunctionalization of alkynes from readily available starting materials is appealing, and extremely challenging.

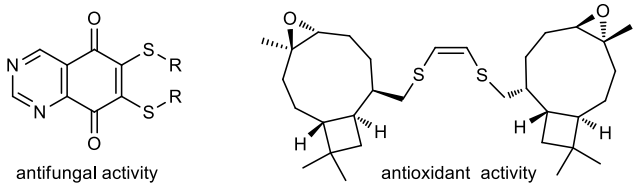
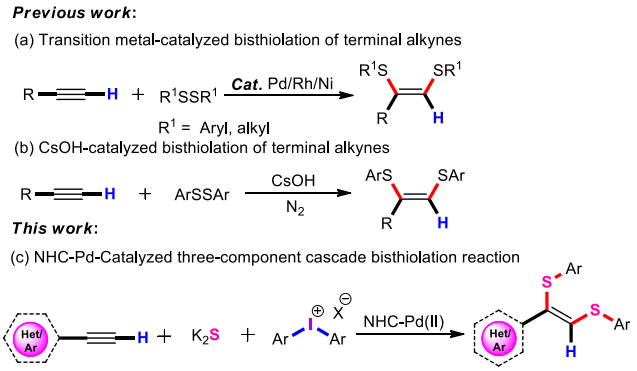


Figure 1. Examples of bioactive compounds containing bisthiolated alkenes scaffolds

In addition, (Z)-1,2-bisthiolated alkenes often serve as convenient intermediates in organic synthesis and materials chemistry,[6] as well as applications in the pharmaceutical and biologically active molecules[7] (Figure 1). Consequently, many representative methods have been well developed for constructing these scaffolds. Generically, all these elegant synthetic methodologies fall primarily into two categories. Undoubtedly, transition metal-catalyzed approaches have been established in the construction of these important structural frameworks in a step-economical and environmentally benign manners (Scheme 1a). Metal complexes of palladium,[8] rhodium,[9] and nickel[10] have been identified as extremely efficient catalysts for these transformations. For instance, Ananikov and co-workers discovered an elegant method for the synthesis of diverse (Z)-1,2-bis (arylthio)alkenes *via* palladium-catalyzed addition of disulfides to alkynes under solvent free conditions.[8b] After that, Ananikov and Beletskaya also developed an unprecedented Ni- and Pd-catalyzed bisthiolation of terminal alkynes for the preparation of (Z)-bis(alkylthio)alkenes with excellent stereoselectivity and high yields.[10] Moreover, Cai and co-workers described a palladium-catalyzed bisthiolation of diaryl disulfideswith terminal alkynes in room temperature ionic liquids.[8d] Alternatively, Xu and Yang disclosed a CsOH-

catalyzed addition of diaryl disulfides with terminal alkynes to construct (Z)-1,2-bis(arylthio)alkene derivatives under a nitrogen atmosphere (Scheme 1b).[11] Although the Pd-NHC complex catalyzed hydrothiolation of alkynes has been well established by Ananikov in 2015,[12] no unequivocal evidence for the Pd-NHC complex catalyzed bisthiolation of terminal alkynes has been reported so far. Recently, we have also successfully developed several protocols for the synthesis of structurally diverse sulfur-containing compounds from readily available starting materials.[13] Very recently, we reported a straightforward and highly effective NHC-palladium-catalyzed cascade annulation/alkynylation of 2-alkynylanilines with terminal alkynes to afford free (NH)-3-alkynylindole derivatives in ionic liquids.[14] Inspired by the aforementioned background and our long-standing interest in Pd-catalyzed functionalization of alkynes,[15] herein we demonstrate the first example of the NHC-palladium-catalyzed three-component cascade bisthiolation of unactivated terminal alkynes (Scheme 1c).

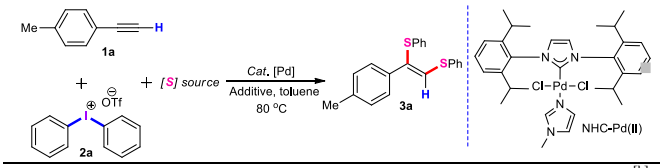


Scheme 1. Representative methods for the synthesis of (Z)-1,2-bis(arylthio)alkenes

Results and Discussion

For the initial screening and optimization of the reaction conditions, sodium sulfide, 1-ethynyl-4-methylbenzene (**1a**) and diphenyliodonium salt (**2a**) were chosen as the model substrates, and the results are summarized in Table 1. Initially, various palladium catalysts were examined, and NHC-Pd(II) was found to be the most effective catalysts (Table 1, entries 1-11). Subsequently, different inorganic sulfur sources were screened including K_2S, S_8, $Na_2S_2O_3$ and thiourea, and K_2S was the most effective inorganic sulfur source for this transformation (Table 1, entries 12-15). Delightfully, the yield increased greatly to 62% when $[C_2OHmim]Cl$ was added as the additive (Table 1, entry 20). Other additives, including $^nBu_4NCl$, $^nBu_4NBr$, [Bmim]Cl, $[Bmim]BF_4$ and $[C_2O_2mim]Cl$ were less effective than $[C_2OHmim]Cl$ (Table 1, entries 12, 16-19). Gratifyingly, when activated 4Å molecular sieves (MS) was added to the mixture, the desired product **3a** was detected in 86% yield by GC-MS (Table 1, entry 21). It is noted that, when the reaction was performed with only 3 mol % dosages of NHC-Pd(II) catalyst, the desired product **3a** was still detected in 86% yield (Table 1, entry 22). The addition of phosphorus ligands to the reaction led to a much diminished yield (Table 1, entries 24, 25). The efficiency of the reaction was dramatically decreased when conducted under open air (Table 1, entry 26). Further investigation establishes that NHC-Pd(II) catalyst, and $[C_2OHmim]Cl$ are both required for the current reaction (Table 1, entries 27, 28). When PhSH was employed as a thiolating reagent in this transformation, however, only a trace amount of the desired product **3a** was detected by GC-MS (Table 1, entry 29).

Table 1. Optimization of the reaction conditions [a]



Entry	Catalyst	[*S*]	Additive	Yield/% [b]
1	$Pd(PPh_3)_4$	Na_2S	nBu_4NCl	N.D.
2	$Pd_2(dba)_3$	Na_2S	nBu_4NCl	N.D.
3	Pd/C	Na_2S	nBu_4NCl	N.D.
4	$Pd(OAc)_2$	Na_2S	nBu_4NCl	trace
5	$Pd(TFA)_2$	Na_2S	nBu_4NCl	trace
6	$PdCl_2$	Na_2S	nBu_4NCl	8
7	$Pd(MeCN)_2Cl_2$	Na_2S	nBu_4NCl	11
8	$Pd(PhCN)_2Cl_2$	Na_2S	nBu_4NCl	17
9	$Pd(PPh_3)_2Cl_2$	Na_2S	nBu_4NCl	trace
10	$Pd(Py)_2Cl_2$	Na_2S	nBu_4NCl	21
11	NHC-Pd(II)	Na_2S	nBu_4NCl	35
12	NHC-Pd(II)	K_2S	nBu_4NCl	49
13	NHC-Pd(II)	S_8	nBu_4NCl	N.D.
14	NHC-Pd(II)	$Na_2S_2O_3$	nBu_4NCl	N.D.
15	NHC-Pd(II)	$(NH_2)_2CS$	nBu_4NCl	N.D.
16	NHC-Pd(II)	K_2S	nBu_4NBr	34
17	NHC-Pd(II)	K_2S	[Bmim]Cl	53
18	NHC-Pd(II)	K_2S	$[Bmim]BF_4$	16
19	NHC-Pd(II)	K_2S	$[C_2O_2mim]Cl$	28
20	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	62
21[c]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	86 (80)
22[d]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	86
23[e]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	83
24[f]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	45
25[g]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	56
26[h]	NHC-Pd(II)	K_2S	$[C_2OHmim]Cl$	trace
27[c]	-	K_2S	$[C_2OHmim]Cl$	N.D.
28[c]	NHC-Pd(II)	K_2S	-	69
29[c]	NHC-Pd(II)	PhSH	$[C_2OHmim]Cl$	trace

[a] Reactions were performed with **1a** (0.10 mmol), [***S***] (0.22 mmol), **2a** (0.30 mmol), catalyst (5 mol %), additive (2 equiv), solvent (1 mL) under N_2 atomosphere for 12 h. [Bmim]Cl: 1-butyl-3-methylimidazolium chloride. $[Bmim]BF_4$: 1-butyl-3-methylimidazolium tetrafluoroborate. $[C_2O_2mim]Cl$: 1-carboxymethyl-3-methylimidazolium chloride. $[C_2OHmim]Cl$: 1-hydroxyethyl-3-methylimidazolium chloride.

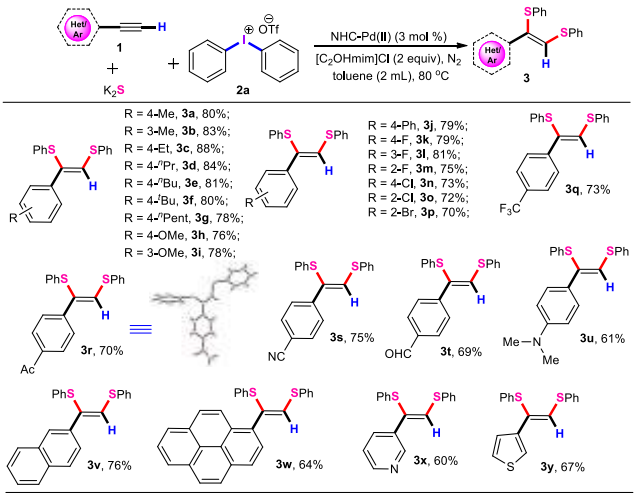
[b] Determined by GC using dodecane as the internal standard. N. D. = not detected.

[c] 50 mg 4Å MS was used

[d] 3 mol % NHC-Pd(II) was used

[e] At 100 °C.
[f] 10 mol % PPh_3 was added
[g] 10 mol % PCy_3 was added
[h] under air

Table 2. Substrate scope of aryl-substituted terminal alkynes [a]

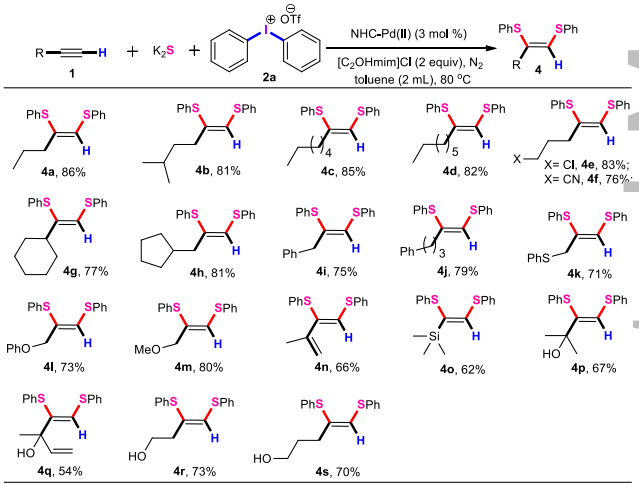


[a] Reaction conditions: **1** (0.20 mmol), K_2S (2.2 equiv), **2a** (3.0 equiv), NHC-Pd (3 mol %), 100 mg 4Å MS, [C_2OHmim]Cl (2 equiv) and toluene (2 mL) at 80 °C for 12 h. Yields referred to isolated yield.

Representative results are summarized in Table 2. Gratifyingly, both electron-donating and electron-withdrawing substituents on the phenyl ring were well accommodated, delivering the desired products in moderate to high yields. Aryl alkynes bearing with halogens, including F (**3k-3m**), Cl (**3n**, **3o**), and Br (**3p**), were all well tolerated, which offers the possibility for further derivatizations by transition metal-catalyzed coupling reactions. Moreover, aryl alkynes bearing moderate to strong electron-withdrawing groups, such as trifluoromethyl, acetyl and cyano groups were also successfully proceed with the current cascade reactions (**3q-3s**). Notably, aryl alkynes containing aldehyde group was amenable to this transformation, and furnished product **3t** in 69% yield. Prominently, *N*, *N*-dimethyl substituted alkyne (**1u**) was also smoothly transformed into the desired product **3u** in 61% yield. Additionally, 2-ethynylnaphthalene (**1v**) and 1-ethynylpyrene (**1w**) also worked well, providing the corresponding products **3v** and **3w** in 76% and 64% yields, respectively. Remarkably, the heteroaryl alkynes, such as 3-ethynylpyridine (**1x**) and 3-ethynylthiophene (**1y**), were also accommodated, furnishing the corresponding products **3x** and **3y** in 60% and 67% yields, respectively. Characterization of **3r** by X-ray crystallography unambiguously confirmed a *cis* configuration of the two sulphur moieties.[16] The configuration of **3i** was also determined by NOESY analysis (see Supporting Information).

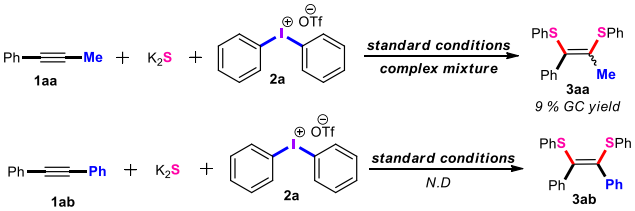
Subsequently, for further demonstrating the synthetic utility of this protocol, various structurally diverse aliphatic terminal alkynes were explored as well to examine their substrate scope, and the representative results are summarized in Table 3. Gratifyingly, linear chain alkynes (1-pentyne, 5-methyl-1-hexyne, 1-octyne and 1-nonyne), and 5-substituted 1-pentynes were compatible with the reaction conditions, affording the corresponding products in good yields (**4a-4f**). Interestingly, the substrates containing five- or six-membered-ring-substituted aliphatic alkynes also performed well under the optimized conditions (**4g** and **4h**). Importantly, alkyne substrates with thiophenyl, phenoxyl, and methoxyl groups the propargylic position engaged in this reaction uneventfully, and provided the desired products **4k**, **4l**, and **4m** in 71%, 73% and 80% yields, respectively. Particularly noteworthy was the functional group tolerance of this protocol, such as vinyl, TMS and hydroxyl were all perfectly accommodated, albeit with a slightly lower yield (**4n-4q**). Encouragingly, substrates containing free hydroxyl of linear chain alkynes participated in this protocol nicely without any deleterious effects on the reaction efficiency, thus offering the desired products **4r** and **4s** in 73% and 70% yields, respectively. The configuration of **4e** and **4i** were determined by NOESY analysis (see Supporting Information).

Table 3. Substrate scope of alkyl-substituted terminal alkynes [a]



[a] Reaction conditions: **1** (0.20 mmol), K_2S (2.2 equiv), **2a** (3.0 equiv), NHC-Pd (3 mol %), 100 mg 4Å MS, [C_2OHmim]Cl (2 equiv) and toluene (2 mL) at 80 °C for 12 h. Yields referred to isolated yield.

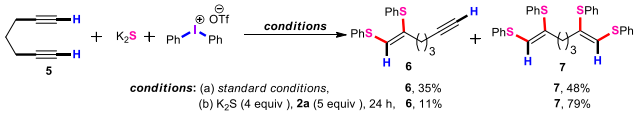
Scheme 2. Investigation of cascade bisthiolation of internal alkynes



Furthermore, the different kinds of internal alkynes were then investigated under the optimized reaction conditions. For instance, When prop-1-yn-1-

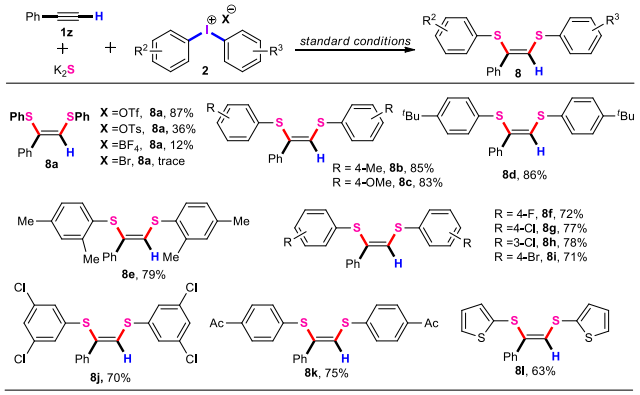
ylbenzene (**1aa**) was subjected to the standard reaction conditions, only a complex mixture was detected in 9% yield by GC-MS. We have also tested the 1,2-diphenylethyne (**1ab**) under the optimized reaction conditions. Unfortunately, no desired **3ab** was detected by GC-MS.[17]

Scheme 3. Cascade bisthiolation of hepta-1,6-diyne



Additionally, the practicality of the current procedure was further proved by investigation of the cascade bisthiolation of hepta-1,6-diyne (**5**), which provided the desired products **6** and **7** in comparable yields under the standard conditions (Scheme 3). Delightfully, increasing loadings of K_2S (4 equiv) and **2a** (5 equiv), the corresponding products **6** and **7** were isolated in 11% and 79% yields, respectively.

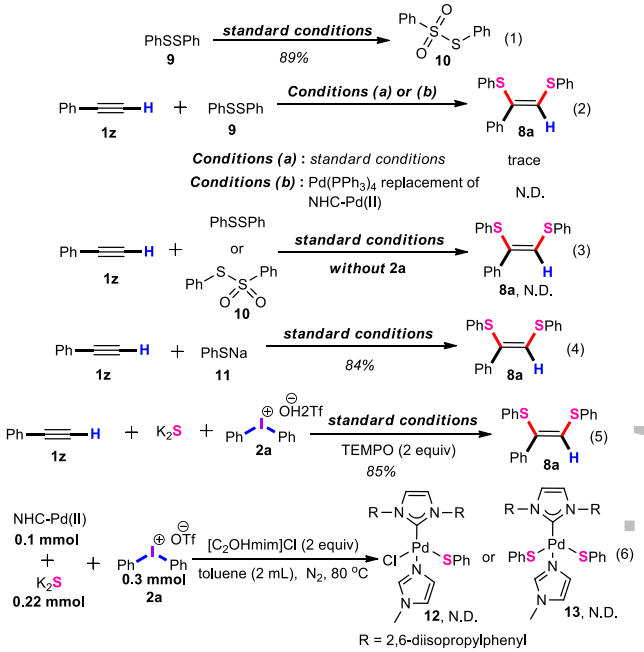
Table 4. Substrate scope of diaryliodonium salts [a]



[a] Reaction conditions: **1z** (0.20 mmol), K_2S (2.2 equiv), **2** (3.0 equiv), NHC-Pd (3 mol %), 100 mg 4Å MS, [C_2OHmim]Cl (2 equiv) and toluene (2 mL) at 80 °C for 12 h. Yields referred to isolated yield.

With the preliminary results above, various diaryliodonium salts were explored as well to examine their substrate scope, and the representative results are summarized in Table 4. As anticipated, diphenyliodonium triflate was a suitable substrate for this transformation, giving rise to the corresponding product **8a** in 87% yield. Unfortunately, when the anions of tosylate ($^-$OTs), tetrafluoroborate (BF_4^-) and bromide (Br^-) were investigated, the yield decreased dramatically. These results described above suggested that the nature of the anion of diaryliodonium salts markedly affected the overall reaction efficiency. Substrates possessing alkyl groups such as Me and ^{t}Bu performed marginally better, and the desired products were obtained in good yields. Moreover, the substrates containing various halo-substituents (**2f**-**2j**) could also undergo cascade bisthiolation to generate the corresponding products **8f**-**8j** in 71-78% yields. Remarkably, heteroaryl diaryliodonium salt **2l** was also well tolerated and afforded the desired product **8l** in 63% yield.

Scheme 4. Control experiments

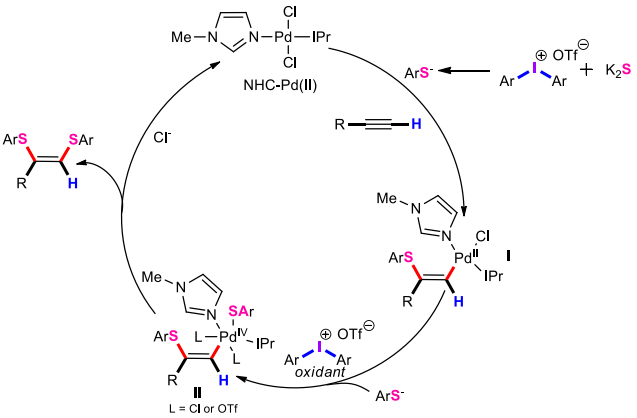


To gain mechanistic insights, several control experiments were conducted (Scheme 4). As mentioned previously, oxidation of 1,2-diphenyldisulfane (**9**) gave the thiosulfonate (**10**) in 89% yield (eq 1).[18] When treated with ethynylbenzene (**1z**) with 1,2-diphenyldisulfane (**9**), only a trace amount of the desired product **8a** was detected. Furthermore, in the presence of diaryliodonium salts and without base additives, the Pd(0)-catalyzed addition of alkynes with two elements of the *p*-block (ArSSAr) also been excluded (eq 2).[3] Subsequently, in the absence of **2a**, the formation of **8a** was completely inhibited (eq 3). All of these results described above suggested that 1,2-diphenyldisulfane (**9**) and thiosulfonate (**10**) might be not involved in the reaction. When sodium thiophenolate (**11**) was employed to react with ethynylbenzene under the standard conditions, the desired product **8a** was obtained in 84% GC yield (eq 4). Thus, this control reaction suggests that *in situ* generated PhS^- might be the key intermediate in this chemical process. When 2 equiv of radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to this reaction, the desired product **8a** was also detected in 85% GC yield (eq 5). This observation demonstrated that the reaction might not proceed by a free radical pathway. Finally, when NHC-Pd(II) (0.1 mmol) was employed to react with K_2S (0.22 mmol) and diphenyliodonium salt (**2a**, 0.3 mmol), however, no desired products Pd-NHC complex **12** or Pd-NHC complex **13** was detected by HRMS (eq 6). This observation demonstrated that the alkyne insertion into Pd-S bond was not involved in this reaction.

On the basis of the current results and previous reports, a plausible mechanism for this cascade transformation is depicted in Scheme 5. Initially, arylthiolate anion from diaryliodonium salts and potassium sulfide was formed.[19] Subsequently, the vinylpalladium intermediate **I** was formed by *cis*-

nucleopalladation of the terminal alkyne.[20] Then, the Pd^{IV} intermediate **II** was generated under oxidative conditions.[21] Finally, a reductive elimination produced the target products and the active catalyst species Pd^{II} to complete the catalytic cycle.[22] Despite all this, we still cannot be absolutely ruled out the alkynes insertion into Pd-S bond process, which have been demonstrated by Ananikov.[23]

Scheme 5. Proposed mechanism



Conclusion

In conclusion, we have successfully accomplished an efficient and novel strategy for the straightforward assembly of functionalized (*Z*)-1,2-bis(arylthio)alkenes derivatives *via* palladium-catalyzed three-component cascade bisthiolation of terminal alkynes, K_2S and diaryliodonium salts. This observation features a broad substrate scope, excellent functional-group tolerance, and high regioselectivity. Notably, this unique bisthiolation procedure used easily available, stable and odourless safe sulfur salt as ideal thiolating reagent, and shows potential capabilities to construct complex molecules in synthetic and pharmaceutical chemistry.

Experimental Section

All reagents and catalysts were purchased as analytical reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ or Acetone-d_6 as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. GC analyses were performed on a GC-7900 chromatograph with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer at an ionization voltage of 70 eV and equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were recorded in KBr disks with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

Representative procedure for preparation of (*Z*)-1,2-bis(arylthio)alkenes: A mixture of NHC-Pd(II) (3 mol %), K_2S (2.2 equiv), $[C_2OHmim]Cl$ (2.0 equiv), 4 Å MS (100 mg), and toluene (2 mL) was added to an Schlenk tube equipped with a stir-bar. A balloon filled with N_2 was connected to the Schlenk tube via the side tube and purged 3 times. Then, terminal alkynes (0.2 mmol), and diaryliodonium salts (3.0 equiv) were quickly added to the tube under N_2 atmosphere and stirred at 80 °C for 12 h. After the reaction was finished, the N_2 gas was released carefully and the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired products.

(*Z*)-(1-(*p*-Tolyl)ethene-1,2-diyl)bis(phenylsulfane) (3a) [24] **:** Yield: 80% (53.4 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 12.8, 7.6 Hz, 4H), 7.33 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.20 (s, 1H), 7.16 (t, J = 7.2 Hz, 2H), 7.07 (d, J = 7.6 Hz, 1H), 7.03 (d, J = 7.67 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 135.46, 134.96, 131.9, 130.5, 129.5, 129.3, 129.2, 128.9, 128.2, 127.5, 126.7, 125.8, 115.1, 21.1ppm; ν_{max}(KBr)/cm^{-1} 3057, 2919, 1578, 1475, 1438, 1022, 739; MS (EI) m/z 115, 167, 210, 225, 319, 334; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaS_2$, $[M+Na]^+$: 357.0742, found 357.0744.

(*Z*)-(1-(*m*-Tolyl)ethene-1,2-diyl)bis(phenylsulfane) (3b): Yield: 83% (55.4 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.39 - 7.27 (m, 5H), 7.25 (d, J = 8.0 Hz, 3H), 7.17 (t, J = 7.6 Hz, 2H), 7.10 (dt, J = 14.4, 7.6 Hz, 2H), 7.00 (d, J = 7.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.0, 136.5, 135.3, 134.9, 130.6, 129.4, 129.3, 128.9, 128.5, 128.3, 128.2, 127.6, 127.4, 125.9, 124.0, 21.5 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2920, 1580, 1475, 1438, 1087, 737; MS (EI) m/z 115, 167, 210, 225, 300, 334; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaS_2$, $[M+Na]^+$: 357.0742, found 357.0740.

(*Z*)-(1-(4-Ethylphenyl)ethene-1,2-diyl)bis(phenylsulfane) (3c): Yield: 88% (61.2 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.31 - 7.21 (m, 4H), 7.18 (t, J = 7.2 Hz, 2H), 7.07 (d, J = 7.6 Hz, 3H), 2.58 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.3, 135.8, 135.4, 135.0, 130.5, 130.4, 129.3, 128.9, 128.1, 127.9, 127.5, 126.7, 125.8, 28.5, 15.4 ppm; ν_{max}(KBr)/cm^{-1} 3064, 2923, 1648, 1576, 1471, 1269, 747; MS (EI) m/z 77, 115, 167, 239, 319, 348; HRMS-ESI (m/z): calcd for $C_{22}H_{20}NaS_2$, $[M+Na]^+$: 371.0899, found 371.0901.

(*Z*)-(1-(4-Propylphenyl)ethene-1,2-diyl) bis (phenylsulfane) (3d): Yield: 84% (60.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 - 7.44 (m, 4H), 7.38 - 7.32 (m, 2H), 7.31 - 7.28 (m, 1H), 7.24 (dd, J = 6.0, 2.0 Hz, 2H), 7.22 (s, 1H), 7.21 - 7.15 (m, 2H), 7.11 - 7.02 (m, 3H), 2.56 - 2.48 (m, 2H), 1.59 (dt, J = 14.8, 7.2 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 136.3, 135.6, 135.4, 135.0, 130.5, 129.4, 129.3, 128.9, 128.5, 128.1, 127.5, 126.6, 125.8, 37.6, 24.4, 13.8 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2924, 1642, 1579, 1474, 1082, 738; MS (EI) m/z 133, 193, 253, 277, 324, 362; HRMS-ESI (m/z): calcd for calcd for $C_{23}H_{22}NaS_2$, $[M+Na]^+$: 385.1055, found 385.1052.

(*Z*)-(1-(4-Butylphenyl)ethene-1,2-diyl)bis(phenylsulfane) (3e): Yield: 81% (61.0 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 8.0 Hz, 4H), 7.39 (dd, J = 8.0, 6.6 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.31 - 7.27 (m, 3H), 7.22 (dd, J = 8.4, 6.8 Hz, 2H), 7.16 - 7.06 (m, 3H) 2.62 - 2.53 (m, 2H), 1.58 (dq, J = 12.8, 7.6 Hz, 2H), 1.35 (dd, J = 15.0, 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.3, 135.6, 135.4, 135.0, 130.5, 129.4, 129.3, 128.9, 128.5, 128.1, 127.5, 126.6, 125.8, 35.3, 33.4, 22.3, 13.9 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2922, 1640,

1580, 1473, 1266, 751; MS (EI) m/z 115, 178, 207, 267, 319, 355, 376; HRMS-ESI (m/z): calcd for $C_{24}H_{24}NaS_2$, $[M+Na]^+$: 399.1212, found 399.1211.

(*Z*)-(1-(4-(*tert*-Butyl)phenyl)ethene-1,2-diyl)bis (phenylsulfane) (3f)[25]**:** Yield: 80% (60.2 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 8.8 Hz, 4H), 7.34 (t, J = 7.2 Hz, 2H), 7.27 (dd, J = 9.2, 6.6 Hz, 6H), 7.19 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 136.4, 136.1, 135.4, 135.1, 130.5, 129.3, 128.9, 128.9, 127.8, 127.5, 126.3, 125.7, 125.4, 34.6, 31.3 ppm; ν_{max}(KBr)/cm^{-1} 3064, 2960, 1578, 1539, 1473, 1269, 1085, 741; MS (EI) m/z 115, 167, 211, 251, 319, 376; HRMS-ESI (m/z): calcd for $C_{24}H_{24}NaS_2$, $[M+Na]^+$: 399.1212, found 399.1210.

(*Z*)-(1-(4-Pentylphenyl)ethene-1,2-diyl)bis (phenylsulfane) (3g): Yield: 78% (60.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 8.2 Hz, 4H), 7.38 (dd, J = 8.0, 6.4 Hz, 2H), 7.33 (d, J = 7.2 Hz, 1H), 7.28 (t, J = 4.0 Hz, 3H), 7.22 (t, J = 7.6 Hz, 2H), 7.11 (dd, J = 14.2, 7.6 Hz, 3H), 2.61 - 2.51 (m, 2H), 1.63 - 1.56 (m, 2H), 1.37 - 1.29 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.3, 135.6, 135.4, 135.0, 130.5, 129.4, 129.3, 128.9, 128.5, 128.1, 127.5, 126.6, 125.8, 35.5, 31.5, 31.0, 22.5, 14.0 ppm; ν_{max}(KBr)/cm^{-1} 3064, 2922, 1581, 1476, 1257, 1143, 738; MS (EI) m/z 115, 167, 211, 281, 319, 355, 390; HRMS-ESI (m/z): calcd for $C_{25}H_{26}NaS_2$, $[M+Na]^+$: 413.1368, found 413.1363.

(*Z*)-(1-(4-Methoxyphenyl)ethene-1,2-diyl)bis (phenylsulfane) (3h)[24]**:** Yield: 76% (53.4 mg) as a yellow solid; mp = 53.6 - 54.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 - 7.45 (m, 4H), 7.38 - 7.32 (m, 2H), 7.31 - 7.27 (m, 1H), 7.23 (dd, J = 6.8, 1.6 Hz, 2H), 7.20 - 7.14 (m, 2H), 7.12 - 7.05 (m, 2H), 6.80 - 6.74 (m, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 135.5, 134.9, 133.9, 131.5, 130.4, 129.5, 129.3, 128.9, 128.3, 128.1, 127.4, 125.9, 113.8, 55.3 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2986, 1600, 1501, 1429, 1260, 747; MS (EI) m/z 109, 165, 226, 281, 350; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaOS_2$, $[M+Na]^+$: 373.0691, found 373.0691.

(*Z*)-(1-(3-Methoxyphenyl)ethene-1,2-diyl)bis (phenylsulfane) (3i): Yield: 78% (54.6 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.30 (d, J = 7.0 Hz, 1H), 7.25 (d, J = 7.7 Hz, 3H), 7.20 - 7.13 (m, 4H), 7.12 - 7.05 (m, 2H), 6.73 (dd, J = 7.2, 4.4 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 140.3, 136.8, 135.2, 134.8, 130.6, 129.4, 129.3, 129.1, 128.9, 128.3, 127.6, 126.0, 119.3, 113.1, 112.6, 55.3 ppm; ν_{max}(KBr)/cm^{-1} 3058, 2980, 1580, 1474, 1263, 751; MS (EI) m/z 77, 109, 165, 226, 241, 319, 350; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaOS_2$, $[M+Na]^+$: 373.0691, found 373.0688.

(*Z*)-(1-([1,1'-Biphenyl]-4-yl)ethene-1,2-diyl)bis (phenylsulfane) (3j): Yield: 79% (62.6 mg) as a green solid; mp = 135.1 - 136.4 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.57 - 7.45 (m, 6H), 7.38 (dd, J = 13.6, 6.4 Hz, 4H), 7.34 - 7.27 (m, 5H), 7.19 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 140.3, 137.8, 136.9, 135.3, 134.8, 133.0, 130.7, 129.4, 129.0, 128.8, 128.2, 127.7, 127.4, 127.1, 127.0, 126.9, 126.0 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2924, 1651, 1580, 1480, 1440, 741; MS (EI) m/z 133, 191, 253, 281, 321, 396; HRMS-ESI (m/z): calcd for $C_{26}H_{20}NaS_2$, $[M+Na]^+$: 419.0899, found 419.0896.

(*Z*)-(1-(4-Fluorophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3k)[25]**:** Yield: 79% (53.4 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 - 7.46 (m, 4H), 7.36 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.17 (dd, J = 14.8, 7.0 Hz, 3H), 7.09 (t, J = 7.0 Hz, 1H), 6.91 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 247.5 Hz), 136.0 (d, J = 1.2 Hz), 135.1, 134.9 (d, J = 3.3 Hz), 134.4, 130.7, 129.4, 128.9, 128.6, 128.5, 128.4, 127.7, 126.2, 115.3 (d, J = 21.7 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 1584, 1542, 1499, 740; MS (EI) m/z 77, 109, 165, 229, 338; HRMS-ESI (m/z): calcd for $C_{20}H_{15}FNaS_2$, $[M+Na]^+$: 361.0491, found 361.0489.

(*Z*)-(1-(3-Fluorophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3l): Yield: 81% (54.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.48 (m, 2H), 7.40 - 7.31 (m, 4H), 7.30 - 7.27 (m, 2H), 7.21 (ddt, J = 12.4, 8.0, 3.2 Hz, 5H), 7.11 (dt, J = 9.2, 4.2 Hz, 1H), 6.87 (td, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 245.7 Hz), 141.1 (d, J = 7.7 Hz), 138.3, 134.9, 134.3, 132.0, 130.8, 129.4, 129.0, 128.3, 127.8, 126.2, 122.4 (d, J = 2.6 Hz), 115.1, 114.4 (d, J = 21.5 Hz), 113.6 (d, J = 22.9 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3065, 2922, 1581, 1538, 1476, 1434, 738; MS (EI) m/z 108, 152, 165, 196, 229, 338; HRMS-ESI (m/z): calcd for $C_{20}H_{15}FNaS_2$, $[M+Na]^+$: 361.0491, found 361.0489.

(*Z*)-(1-(2-Fluorophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3m): Yield: 75% (50.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 13.2, 5.6 Hz, 2H), 7.39 - 7.31 (m, 8H), 7.30 - 7.27 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.14 - 7.07 (m, 1H), 6.98 (dd, J = 13.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, J = 248.4 Hz), 140.0 (d, J = 7.6 Hz), 137.2 (d, J = 10.8 Hz), 133.9, 133.7, 130.5 (d, J = 2.4 Hz), 130.2, 129.3, 128.9, 128.7, 128.7, 128.6, 128.5, 127.5, 126.3, 115.8 (d, J = 23.0 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 1545, 1479, 1438, 746; MS (EI) m/z 65, 77, 109, 165, 229, 281, 338; HRMS-ESI (m/z): calcd for $C_{20}H_{15}FNaS_2$, $[M+Na]^+$: 361.0491, found 361.0488.

(*Z*)-(1-(4-Chlorophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3n): Yield: 73% (51.6 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (ddd, J = 8.8, 7.6, 1.6 Hz, 3H), 7.37 - 7.28 (m, 5H), 7.24 - 7.15 (m, 6H), 7.14 - 7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.2, 135.0, 134.3, 133.9, 133.7, 133.4, 130.8, 129.4, 129.0, 128.6, 128.5, 128.0, 126.2 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 1578, 1536, 1479, 739; MS (EI) m/z 109, 165 210, 245, 354; HRMS-ESI (m/z): calcd for $C_{20}H_{15}ClNaS_2$, $[M+Na]^+$: 377.0196, found 377.0198.

(*Z*)-(1-(2-Chlorophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3o): Yield: 72% (50.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 2H), 7.40 - 7.30 (m, 5H), 7.27 (d, J = 7.2 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.11 (d, J = 7.2 Hz, 1H), 7.09 - 7.04 (m, 2H), 6.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.1, 135.2, 133.4, 133.0, 131.2, 130.6, 130.1, 129.9, 129.2, 128.7, 128.7, 128.5, 127.3, 126.9, 126.4 ppm; ν_{max}(KBr)/cm^{-1} 3059, 2921, 1576, 1471, 1433, 745; MS (EI) m/z 65, 109, 165, 210, 245, 319, 354; HRMS-ESI (m/z): calcd for $C_{20}H_{15}ClNaS_2$, $[M+Na]^+$: 377.0196, found 377.0198.

(*Z*)-(1-(2-Bromophenyl)ethene-1,2-diyl)bis (phenylsulfane) (3p): Yield: 70% (55.8 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.38 - 7.31 (m, 5H), 7.27 (d, J = 7.6 Hz, 1H), 7.14 (dt, J = 12.2, 7.2 Hz, 4H), 6.99 (t, J = 7.6 Hz, 1H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 135.5, 135.2, 133.2, 133.1, 131.3, 131.2, 130.5, 130.2, 129.2, 128.9, 128.7, 127.3, 127.0, 126.9, 123.3 ppm; ν_{max}(KBr)/cm^{-1} 3059, 2922, 1576, 1471, 1434, 747; MS (EI) m/z 96, 165, 207, 281, 319, 398; HRMS-ESI (m/z): calcd for $C_{20}H_{15}BrNaS_2$, $[M+Na]^+$: 420.9691, found 420.9688.

(*Z*)-(1-(4-(Trifluoromethyl)phenyl)ethene-1,2-diyl)bis (phenylsulfane) (3q): Yield: 73% (56.6 mg) as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.50 (dd, J = 12.8, 8.0 Hz, 4H), 7.42 - 7.31 (m, 4H), 7.32 (d, J = 7.2 Hz, 1H), 7.23 - 7.16 (m, 3H), 7.11 (t, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.2 (q, J = 10.6 Hz), 134.1 (q, J = 256.3 Hz), 130.9, 129.5, 129.1,

128.7, 128.6, 128.5, 128.3, 128.1, 126.8, 126.3, 125.4 (q, *J* = 3.8 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3060, 2926, 1580, 1478, 1436, 1324, 1120, 741; MS (EI) m/z 109, 210, 239, 279, 388; HRMS-ESI (m/z): calcd for $C_{21}H_{15}F_3NaS_2$, $[M+Na]^+$: 411.0459, found 411.0455.

(*Z*)-1-(4-(1,2-Bis(phenylthio)vinyl)phenyl)ethanone (3r): Yield: 70% (50.6 mg) as a yellow solid; mp = 127.3 - 128.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.47 - 7.35 (m, 4H), 7.28 (d, *J* = 4.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 143.1, 140.0, 135.9, 134.7, 134.2, 130.9, 129.4, 129.0, 128.6, 128.3, 128.0, 127.8, 126.7, 126.2, 26.6 ppm; ν_{max}(KBr)/cm^{-1} 3059, 2923, 1683, 1596, 1478, 1436, 1264, 740; MS (EI) m/z 86, 117, 161, 207, 246, 321, 362; HRMS-ESI (m/z): calcd for $C_{22}H_{18}NaOS_2$, $[M+Na]^+$: 385.0691, found 385.0687.

(*Z*)-4-(1,2-Bis(phenylthio)vinyl)benzonitrile (3s): Yield: 75% (51.8 mg) as a yellow solid; mp = 84.2 - 85.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 6.4 Hz, 4H), 7.41 - 7.33 (m, 5H), 7.24 - 7.15 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.0, 141.3, 132.3, 132.2, 131.5, 131.1, 129.8, 129.5, 129.2, 128.4, 127.1, 118.1, 114.4, 108.0 ppm; ν_{max}(KBr)/cm^{-1} 3059, 2923, 2226, 1579, 1476, 1438, 740; MS (EI) m/z 103, 133, 167, 207, 236, 281, 345; HRMS-ESI (m/z): calcd for $C_{21}H_{15}NaS_2$, $[M+Na]^+$: 368.0538, found 368.0544.

(*Z*)-4-(1,2-Bis(phenylthio)vinyl)benzaldehyde (3t): Yield: 69% (48.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.73 (q, *J* = 8.4 Hz, 4H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.46 (s, 1H), 7.43 - 7.34 (m, 3H), 7.20 (dd, *J* = 14.8, 7.6 Hz, 4H), 7.11 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 144.5, 140.9, 135.2, 134.6, 134.1, 131.0, 129.9, 129.5, 129.1, 128.3, 128.1, 127.6, 127.1, 126.3 ppm; ν_{max}(KBr)/cm^{-1} 3345, 3057, 2921, 1694, 1594, 1531, 1475, 748; MS (EI) m/z 109, 178, 207, 239, 281, 348; HRMS-ESI (m/z): calcd for $C_{21}H_{16}NaOS_2$, $[M+Na]^+$: 371.0535, found 371.0538.

(*Z*)-4-(1,2-Bis(phenylthio)vinyl)-*N*,*N*-dimethylaniline (3u): Yield: 61% (44.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 6.8 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 3H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.10 - 7.03 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 2H), 2.90 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 135.9, 135.4, 131.6, 130.2, 130.1, 129.2, 128.9, 128.0, 127.7, 127.1, 126.9, 125.6, 112.1, 40.4 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2919, 1603, 1514, 1440, 1356, 1167, 741; MS (EI) m/z 109, 144, 210, 239, 254, 327, 363; HRMS-ESI (m/z): calcd for $C_{22}H_{22}NS_2$, $[M+H]^+$: 364.1188, found 364.1193.

(*Z*)-(1-(Naphthalen-2-yl)ethene-1,2-diyl)bis (phenylsulfane) (3v): Yield: 76% (56.2 mg) as a white solid; mp = 100.5 - 101.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.80 - 7.71 (m, 2H), 7.70 (d, *J* = 10.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 9.2, 5.2 Hz, 3H), 7.35 (d, *J* = 8.0 Hz, 3H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.05 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.2, 135.3, 134.8, 133.4, 132.8, 130.7, 130.0, 129.4, 129.2, 129.0, 128.3, 128.1, 127.7, 127.6, 126.3, 126.1, 125.9, 125.9, 124.6 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2922, 1632, 1582, 1475, 1439, 743; MS (EI) m/z 109, 152, 228, 261, 326, 370; HRMS-ESI (m/z): calcd for $C_{24}H_{18}NaS_2$, $[M+Na]^+$: 393.0742, found 393.0745.

(*Z*)-(1-(Pyren-1-yl)ethene-1,2-diyl)bis(phenylsulfane) (3w): Yield: 64% (56.8 mg) as a white solid; mp = 126.4 - 127.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.2 Hz, 1H), 8.08 (dt, *J* = 12.4, 7.2 Hz, 4H), 7.97 - 7.88 (m, 5H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 10.4 Hz, 2H), 6.96 - 6.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.5, 133.1, 131.7, 131.3, 130.9, 130.0, 129.3, 128.6, 127.7, 127.6, 127.5, 127.3, 127.3, 127.2, 126.1, 125.3, 125.1, 124.8, 124.3 ppm; ν_{max}(KBr)/cm^{-1} 3046, 2922, 1582, 1475, 1438, 750; MS (EI) m/z 110, 165, 207, 281, 334, 400, 444; HRMS-ESI (m/z): calcd for $C_{30}H_{20}NaS_2$, $[M+Na]^+$: 467.0899, found 467.0901.

(*Z*)-3-(1,2-Bis(phenylthio)vinyl)pyridine (3x): Yield: 60% (38.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.40 (d, *J* = 4.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.16 - 7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 147.8, 138.4, 134.6, 134.1, 133.7, 130.8, 129.4, 129.2, 129.1, 128.8, 127.9, 126.5, 126.2, 123.2 ppm; ν_{max}(KBr)/cm^{-1} 3057, 2923, 1578, 1540, 1476, 1408, 741; MS (EI) m/z 96, 133, 191, 207, 249, 281, 321; HRMS-ESI (m/z): calcd for $C_{19}H_{16}NS_2$, $[M+H]^+$: 322.0719, found 322.0724.

(*Z*)-3-(1,2-Bis(phenylthio)vinyl)thiophene (3y)[25]**:** Yield: 67% (43.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.40 - 7.32 (m, 3H), 7.29 (t, *J* = 9.2 Hz, 4H), 7.24 - 7.16 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 136.1, 135.2, 134.9, 130.7, 129.3, 129.0, 127.9, 127.6, 126.1, 125.9, 125.4, 124.2, 122.2 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2921, 1648, 1576, 1473, 1437, 737; MS (EI) m/z 65, 109, 184, 217, 260, 326; HRMS-ESI (m/z): calcd for $C_{18}H_{14}NaS_3$, $[M+Na]^+$: 349.0150, found 349.0149.

(*Z*)-Pent-1-ene-1,2-diylbis(phenylsulfane) (4a)[25]**:** Yield: 86% (49.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 5.6 Hz, 2H), 7.25 - 7.19 (m, 2H), 6.57 (s, 1H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.58 - 1.47 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.0, 130.5, 129.8, 129.5, 129.1, 128.9, 128.7, 126.9, 126.8, 39.2, 21.8, 13.4 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2958, 2926, 1579, 1475, 1267, 1023, 746; MS (EI) m/z 65, 91, 109, 135, 147, 167, 286; HRMS-ESI (m/z). calcd for $C_{17}H_{18}NaS_2$, $[M+Na]^+$: 309.0742, found 309.0739.

(*Z*)-(5-Methylhex-1-ene-1,2-diyl)bis(phenylsulfane) (4b): Yield: 81% (50.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.25 - 7.20 (m, 2H), 6.55 (s, 1H), 2.30 - 2.20 (m, 2H), 1.46 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.39 (dd, *J* = 14.8, 7.0 Hz, 2H), 0.80 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.9, 133.9, 130.7, 129.7, 129.1, 129.0, 128.7, 126.9, 126.8, 37.9, 35.1, 27.4, 22.4 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2953, 1579, 1473, 1438, 1264, 1022, 743; MS (EI) m/z 77, 91, 115, 147, 167, 258, 314; HRMS-ESI (m/z): calcd for $C_{19}H_{22}NaS_2$, $[M+Na]^+$: 337.1055, found 337.1057.

(*Z*)-Oct-1-ene-1,2-diylbis(phenylsulfane) (4c): Yield: 85% (55.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 13.6, 7.6 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.25 - 7.17 (m, 2H), 6.56 (s, 1H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.48 (dd, *J* = 14.0, 6.8 Hz, 2H), 1.29 - 1.18 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.5, 133.9, 130.5, 129.7, 129.1, 129.1, 128.9, 126.9, 126.8, 37.1, 31.5, 28.5, 28.5, 22.6, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3066, 2926, 1580, 1476, 1441, 1266, 1022, 741; MS (EI) m/z 67, 91, 109, 135, 167, 199, 328; HRMS-ESI (m/z): calcd for $C_{20}H_{24}NaS_2$, $[M+Na]^+$: 351.1212, found 351.1213.

(*Z*)-Non-1-ene-1,2-diylbis(phenylsulfane) (4d): Yield: 82% (56.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 9.2, 5.6 Hz, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.25 - 7.19 (m, 2H), 6.56 (s, 1H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.55 - 1.45 (m, 2H), 1.28 - 1.17 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 134.5, 133.9, 130.5, 129.7, 129.1, 129.0, 128.9, 126.9, 126.8, 37.1, 31.8, 29.0, 28.8, 28.6, 22.6, 14.1 ppm; ν_{max}(KBr)/cm^{-1} 3063, 2926, 1580, 1475, 1439, 1265, 1023, 743; MS (EI) m/z 91,

109, 135, 147, 199, 277, 342; HRMS-ESI (m/z): calcd for $C_{21}H_{26}NaS_2$, $[M+Na]^+$: 365.1368, found 365.1367.

(*Z*)-(5-Chloropent-1-ene-1,2-diyl)bis(phenylsulfane) (4e): Yield: 83% (53.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 3H), 7.34 - 7.27 (m, 4H), 7.24 (t, J = 4.8 Hz, 1H), 6.67 (s, 1H), 3.48 (t, J = 6.4 Hz, 2H), 2.42 (t, J = 7.2 Hz, 2H), 1.95 (p, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.3, 131.5, 131.5, 130.6, 130.0, 129.2, 129.1, 127.1, 127.0, 44.0, 33.8, 31.0 ppm; ν_{max}(KBr)/cm^{-1} 3063, 2923, 1579, 1476, 1439, 1275, 1023, 743; MS (EI) m/z 65, 109, 147, 167, 285, 320; HRMS-ESI (m/z): calcd for $C_{17}H_{17}ClNaS_2$, $[M+Na]^+$: 343.0352, found 343.0347.

(*Z*)-5,6-Bis(phenylthio)hex-5-enenitrile (4f): Yield: 76% (47.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2H), 7.40 - 7.32 (m, 5H), 7.31 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 6.70 (s, 1H), 2.41 (t, J = 7.2 Hz, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.83 (p, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.9, 132.7, 130.6, 130.2, 130.2, 129.3, 129.2, 127.4, 127.3, 35.3, 24.0, 16.1 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 2245, 1576, 1473, 1436, 1266, 1081, 746; MS (EI) m/z 65, 91, 109, 147, 167, 247, 311; HRMS-ESI (m/z): calcd for $C_{18}H_{17}NNaS_2$, $[M+Na]^+$: 334.0695, found 334.0692.

(*Z*)-(1-Cyclohexylethene-1,2-diyl)bis(phenylsulfane) (4g): Yield: 77% (50.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 4.0 Hz, 3H), 7.28 (d, J = 7.6 Hz, 3H), 7.25 (d, J = 6.8 Hz, 1H), 7.17 (t, J = 6.8 Hz, 1H), 6.73 (s, 1H), 2.13 (t, J = 11.2 Hz, 1H), 1.93 (d, J = 12.4 Hz, 2H), 1.73 (d, J = 11.2 Hz, 2H), 1.28 (dd, J = 15.6, 7.6 Hz, 3H), 1.15 (dd, J = 15.6, 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.1, 133.9, 132.1, 130.3, 129.1, 128.9, 128.5, 127.0, 125.9, 46.2, 32.9, 26.5, 26.1 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2925, 1579, 1476, 1440, 1267, 1078, 743; MS (EI) m/z 79, 91, 109, 135, 167, 217, 326; HRMS-ESI (m/z): calcd for $C_{20}H_{22}NaS_2$, $[M+Na]^+$: 349.1055, found 349.1057.

(*Z*)-(3-Cyclopentylprop-1-ene-1,2-diyl)bis (phenylsulfane) (4h): Yield: 81% (52.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.39 (m, 2H), 7.38 - 7.33 (m, 4H), 7.32 - 7.28 (m, 3H), 7.25 - 7.21 (m, 1H), 7.20 - 7.16 (m, 1H), 6.58 (s, 1H), 2.24 (d, J = 7.2 Hz, 2H), 2.14 (dp, J = 15.2, 7.6 Hz, 1H), 1.70 (td, J = 11.2, 5.4 Hz, 2H), 1.58 (dd, J = 9.2, 4.8 Hz, 2H), 1.50 (ddd, J = 8.4, 6.4, 4.0 Hz, 1H), 1.14 - 1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 134.0, 133.8, 130.3, 129.9, 129.7, 129.1, 128.9, 126.9, 126.7, 43.5, 38.6, 32.2, 25.1 ppm; ν_{max}(KBr)/cm^{-1} 3064, 2946, 1580, 1476, 1439, 1266, 1077, 743; MS (EI) m/z 91, 115, 147, 167, 199, 258, 326; HRMS-ESI (m/z): calcd for $C_{20}H_{22}NaS_2$, $[M+Na]^+$: 349.1055, found 349.1057.

(*Z*)-(3-Phenylprop-1-ene-1,2-diyl)bis(phenylsulfane) (4i): Yield: 75% (50.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 6.4 Hz, 4H), 7.29 (dd, J = 15.6, 8.0 Hz, 6H), 7.24 - 7.17 (m, 3H), 7.10 (d, J = 7.2 Hz, 2H), 6.54 (s, 1H), 3.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.7, 133.4, 133.2, 131.1, 130.9, 129.6, 129.2, 129.1, 129.0, 128.4, 127.1, 126.9, 126.6, 43.2 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2920, 1579, 1477, 1439, 1265, 1075, 746; MS (EI) m/z 91, 115, 167, 223, 281, 334; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaS_2$, $[M+Na]^+$: 357.0742, found 357.0743.

(*Z*)-(5-Phenylpent-1-ene-1,2-diyl)bis(phenylsulfane) (4j): Yield: 79% (57.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.38 - 7.29 (m, 6H), 7.23 (dd, J = 11.6, 6.0 Hz, 4H), 7.15 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.56 (s, 1H), 2.54 (t, J = 7.6 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 1.89 - 1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 135.8, 133.7, 133.7, 130.7, 129.9, 129.7, 129.2, 129.0, 128.4, 128.3, 127.0, 126.9, 125.8, 36.6, 35.0, 30.1 ppm; ν_{max}(KBr)/cm^{-1} 3062, 2928, 1579, 1476, 1441, 1267, 1082, 744; MS (EI) m/z 91, 147, 207, 253, 328, 362; HRMS-ESI (m/z): calcd for $C_{23}H_{22}NaS_2$, $[M+Na]^+$: 385.1055, found 385.1059.

(*Z*)-Prop-1-ene-1,2,3-triyltris(phenylsulfane) (4k): Yield: 71% (52.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.35 - 7.28 (m, 6H), 7.24 (dd, J = 9.6, 6.0 Hz, 5H), 7.16 (d, J = 7.2 Hz, 2H), 6.70 (s, 1H), 3.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.3, 133.2, 131.2, 130.8, 129.9, 129.2, 129.1, 129.0, 128.9, 127.4, 127.2, 127.1, 126.9, 41.4 ppm; ν_{max}(KBr)/cm^{-1} 3059, 2921, 1573, 1472, 1434, 1266, 1072, 743; MS (EI) m/z 91, 109, 123, 147, 179, 257, 366; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaS_3$, $[M+Na]^+$: 389.0463, found 389.0462.

(*Z*)-(3-Phenoxyprop-1-ene-1,2-diyl)bis(phenylsulfane) (4l): Yield: 73% (51.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.31 (dd, J = 7.6, 6.0 Hz, 4H), 7.27 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.10 (s, 1H), 6.94 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 4.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 135.5, 135.0, 133.2, 130.2, 130.2, 129.5, 129.3, 129.2, 127.3, 127.1, 125.7, 121.3, 115.0, 70.2 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2922, 1586, 1484, 1230, 1023, 747; MS (EI) m/z 91, 123, 147, 179, 257, 316, 350; HRMS-ESI (m/z): calcd for $C_{21}H_{18}NaOS_2$, $[M+Na]^+$: 373.0691, found 373.0693.

(*Z*)-(3-Methoxyprop-1-ene-1,2-diyl)bis(phenylsulfane) (4m): Yield: 80% (46.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.37 - 7.28 (m, 5H), 7.24-7.20 (m, 1H), 6.98 (s, 1H), 3.95 (s, 2H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.6, 133.4, 130.4, 130.1, 129.2, 129.1, 127.4, 127.2, 126.9, 74.6, 58.1 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 1577, 1473, 1440, 1268, 1112, 749; MS (EI) m/z 69, 109, 147, 177, 243, 288; HRMS-ESI (m/z): calcd for $C_{16}H_{16}NaOS_2$, $[M+Na]^+$: 311.0535, found 311.0531.

(*Z*)-(3-Methylbuta-1,3-diene-1,2-diyl)bis(phenylsulfane) (4n): Yield: 66% (37.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.2 Hz, 2H), 7.39 - 7.28 (m, 3H), 7.25 - 7.19 (m, 4H), 7.18 - 7.10 (m, 2H), 5.51 (s, 1H), 4.98 (s, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.7, 135.7, 135.3, 130.6, 129.5, 129.3, 128.9, 127.6, 127.3, 125.6, 115.6, 20.9 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2925, 1669, 1580, 1477, 1439, 1268, 1019, 746; MS (EI) m/z 65, 91, 109, 142, 175, 207, 251, 284; HRMS-ESI (m/z): calcd for $C_{17}H_{16}NaOS_2$, $[M+Na]^+$: 307.0586, found 307.0590.

(*Z*)-(1,2-Bis(phenylthio)vinyl)trimethylsilane (4o): Yield: 62% (39.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.35 - 7.27 (m, 5H), 7.23 - 7.19 (m, 3H), 7.18 (d, J = 7.2 Hz, 1H), 0.01 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 134.9, 134.8, 132.0, 130.4, 129.8, 129.6, 129.6, 129.5, 128.7, 0.00 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2923, 1580, 1510, 1476, 1265, 926, 749; MS (EI) m/z 91, 109, 167, 186, 262, 316; HRMS-ESI (m/z): calcd for $C_{17}H_{20}NaOS_2Si$, $[M+Na]^+$: 339.0668, found 339.0666.

(*Z*)-2-Methyl-3,4-bis(phenylthio)but-3-en-2-ol (4p)[26]: Yield: 67% (40.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 2H), 7.35 (dd, J = 9.6, 5.6 Hz, 6H), 7.34 - 7.28 (m, 2H), 7.16 (t, J = 7.2 Hz, 1H), 2.17 (s, 1H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.0, 134.9, 134.9, 130.7, 129.2, 129.1, 127.6, 127.0, 125.7, 75.1, 29.4 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2924, 1576, 1476, 1441, 1286, 1022, 750; MS (EI) m/z 59, 91, 134, 177, 207, 287, 302; HRMS-ESI (m/z): calcd for $C_{17}H_{18}NaOS_2$, $[M+Na]^+$: 325.0691, found 325.0690.

(Z)-3-Methyl-1,2-bis(phenylthio)penta-1,4-dien-3-ol (4q): Yield: 54% (33.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.0 Hz, 2H), 7.37 - 7.33 (m, 4H), 7.32 - 7.28 (m, 4H), 7.16 (t, J = 7.2 Hz, 1H), 6.02 (dd, J = 17.2, 10.6 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.13 (d,

J = 10.6 Hz, 1H), 2.41 (s, 1H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 139.1, 134.9, 134.8, 133.0, 130.7, 129.3, 129.0, 127.6, 127.3, 125.8, 113.7, 27.1 ppm; ν_{max}(KBr)/cm^{-1} 3456, 3060, 2926, 1669, 1579, 1477, 1440, 1322, 1022, 741; MS (EI) m/z 77, 110, 134, 187, 243, 296, 314; HRMS-ESI (m/z): calcd for $C_{18}H_{18}NaOS_2$, $[M+Na]^+$: 337.0691, found 337.0693.

(*Z*)-3,4-Bis(phenylthio)but-3-en-1-ol (4r): Yield: 73% (42.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.36 - 7.27 (m, 5H), 7.24 - 7.19 (m, 1H), 6.72 (s, 1H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 1.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.4, 133.0, 130.4, 130.1, 129.2, 129.2, 129.1, 127.2, 127.1, 60.9, 40.1 ppm; ν_{max}(KBr)/cm^{-1} 3387, 3060, 2928, 1579, 1476, 1438, 1027, 743; MS (EI) m/z 77, 91, 128, 147, 207, 288; HRMS-ESI (m/z): calcd for $C_{16}H_{16}NaOS_2$, $[M+Na]^+$: 311.0535, found 311.0533.

(*Z*)-4,5-Bis(phenylthio)pent-4-en-1-ol (4s): Yield: 70% (42.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 17.6, 8.0 Hz, 4H), 7.25 - 7.19 (m, 2H), 6.63 (s, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.82 - 1.71 (m, 2H), 1.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 133.5, 132.9, 130.5, 130.4, 129.9, 129.2, 129.1, 127.0, 126.9, 61.8, 33.3, 31.5 ppm; ν_{max}(KBr)/cm^{-1} 3354, 2932, 1580, 1476, 1439, 1026, 743; MS (EI) m/z 91, 109, 167, 207, 277, 302; HRMS-ESI (m/z): calcd for $C_{17}H_{18}NaOS_2$, $[M+Na]^+$: 325.0691, found 325.0692.

(*Z*)-Hept-1-en-6-yne-1,2-diylbis(phenylsulfane) (6)[27]**:** Yield: 35% (21.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.39 - 7.31 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.67 (s, 1H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.18 (td, *J* = 6.8, 2.2 Hz, 2H), 1.93 (s, 1H), 1.75 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 133.5, 132.6, 130.6, 130.6, 129.9, 129.2, 129.1, 127.0, 126.9, 83.8, 68.9, 35.7, 27.1, 17.4 ppm; ν_{max}(KBr)/cm^{-1} 3297, 3062, 2931, 1579, 1476, 1438, 1262, 1084, 745; MS (EI) m/z 65, 77, 91, 109, 147, 173, 201, 277, 310; HRMS-ESI (m/z): calcd for $C_{19}H_{18}NaS_2$, $[M+Na]^+$: 333.0742, found 333.0747.

(1*Z*,6*Z*)-Hepta-1,6-diene-1,2,6,7-tetrayltetrakis (phenylsulfane) (7)[8b]**:** Yield: 79% (83.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.35 (m, 4H), 7.34 - 7.29 (m, 7H), 7.27 (d, *J* = 8.0 Hz, 4H), 7.24 (t, *J* = 5.6 Hz, 3H), 7.19 (ddd, *J* = 7.2, 3.6, 1.2 Hz, 2H), 6.50 (s, 2H), 2.18 (t, *J* = 7.2 Hz, 4H), 1.76 - 1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7 (2C), 133.6 (2C), 133.2 (2C), 130.6 (2C), 130.1 (2C), 129.9 (2C), 129.2 (2C), 129.0 (2C), 127.0 (2C), 126.9 (2C), 36.1 (2C), 27.3 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2926, 1578, 1476, 1438, 1266, 1023, 745; HRMS-ESI (m/z): calcd for $C_{31}H_{28}NaS_4$, $[M+Na]^+$: 551.0966, found 551.0971.

(*Z*)-(1-Phenylethene-1,2-diyl)bis(phenylsulfane) (8a)[25]**:** Yield: 87% (55.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.33 - 7.28 (m, 5H), 7.23 (dd, *J* = 10.2, 5.6 Hz, 3H), 7.12 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 136.5, 135.3, 134.7, 130.6, 129.4, 129.3, 128.9, 128.4, 128.3, 127.7, 127.6, 126.8, 125.9 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2922, 1579, 1537, 1475, 1438, 738; MS (EI) m/z 77, 109, 178, 211, 277, 320; HRMS-ESI (m/z): calcd for $C_{20}H_{16}NaS_2$, $[M+Na]^+$: 343.0586, found 343.0582.

(*Z*)-(1-Phenylethene-1,2-diyl)bis(*p*-tolylsulfane) (8b)[25]**:** Yield: 85% (59.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.27 (m, 2H), 7.24 - 7.13 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.94 (s), 137.8, 136.9, 135.8, 131.8, 131.1, 131.0, 130.0, 129.7, 129.2, 128.6, 128.4, 127.5, 126.8, 21.2, 21.0 ppm; ν_{max}(KBr)/cm^{-1} 3056, 2921, 1539, 1489, 1441, 1267, 1087, 753; MS (EI) m/z 123, 165, 210, 225, 281, 348; HRMS-ESI (m/z): calcd for $C_{22}H_{20}NaS_2$, $[M+Na]^+$: 371.0899, found 371.0900.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-methoxyphenyl) sulfane) (8c)[25]**:** Yield: 83% (63.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 13.6, 8.2 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.00 (s, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 158.5, 138.8, 136.5, 133.3, 131.2, 129.8, 128.3, 127.4, 126.9, 125.9, 125.2, 114.9, 114.5, 55.4, 55.2 ppm; ν_{max}(KBr)/cm^{-1} 3058, 2923, 1585, 1486, 1448, 1239, 1025, 817; MS (EI) m/z 96, 139, 165, 241, 281, 334, 380; HRMS-ESI (m/z): calcd for $C_{22}H_{20}NaO_2S_2$, $[M+Na]^+$: 403.0797, found 403.0796.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-(*tert*-butyl)phenyl) sulfane) (8d): Yield: 86% (74.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 4.8 Hz, 3H), 7.22 (d, *J* = 4.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 4H), 1.33 (s, 9H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 148.9, 139.1, 137.8, 131.8, 131.3, 130.8, 128.5, 128.4, 127.7, 127.4, 126.7, 126.4, 126.0, 34.6, 34.4, 31.3, 31.2 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2959, 1591, 1539, 1489, 1267, 1117, 754; MS (EI) m/z 121, 151, 207, 268, 338, 387, 432; HRMS-ESI (m/z): calcd for $C_{28}H_{32}NaS_2$, $[M+Na]^+$: 455.1838, found 455.1845.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((2,4-dimethylphenyl) sulfane) (8e): Yield: 79% (59.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.03 - 6.97 (m, 2H), 6.91 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 6H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 139.0, 138.3, 137.3, 136.2, 135.9, 132.4, 131.5, 131.2, 130.9, 130.0, 129.5, 129.0, 128.3, 127.6, 127.4, 127.1, 126.8, 21.1, 20.9, 20.8, 20.3 ppm; ν_{max}(KBr)/cm^{-1} 3048, 2920, 1598, 1478, 1443, 1232, 1052, 812; MS (EI) m/z 91, 137, 165, 224, 310, 376; HRMS-ESI (m/z): calcd for $C_{24}H_{24}NaS_2$, $[M+Na]^+$: 399.1212, found 399.1215.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-fluorophenyl) sulfane) (8f): Yield: 72% (51.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 6.8 Hz, 4H), 7.25 - 7.16 (m, 5H), 7.11 - 7.02 (m, 3H), 6.88 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 248.3 Hz), 161.6 (d, *J* = 246.1 Hz), 138.4, 135.9, 133.1 (d, *J* = 8.2 Hz), 130.9 (d, *J* = 8.0 Hz), 130.2, 130.1 (d, *J* = 3.6 Hz), 129.5 (d, *J* = 3.3 Hz), 128.5, 127.8, 126.9, 116.5 (d, *J* = 22.0 Hz), 116.0 (d, *J* = 22.1 Hz) ppm; ν_{max}(KBr)/cm^{-1} 3062, 2922, 1587, 1485, 1443, 1225, 822; MS (EI) m/z 127, 165, 196, 294, 356; HRMS-ESI (m/z): calcd for $C_{20}H_{14}F_2NaS_2$, $[M+Na]^+$: 379.0397, found 379.0398.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-chlorophenyl) sulfane) (8g): Yield: 77% (59.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 12.8, 7.2 Hz, 3H), 7.18 - 7.07 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.8, 133.9, 133.5, 133.1, 132.0, 131.9, 129.9, 129.7, 129.5, 129.1, 128.6, 128.0, 126.8 ppm; ν_{max}(KBr)/cm^{-1} 3060, 2924, 1539, 1473, 1440, 752; MS (EI) m/z 108, 165, 245, 310, 338, 388; HRMS-ESI (m/z): calcd for $C_{20}H_{14}Cl_2NaS_2$, $[M+Na]^+$: 410.9806, found 410.9802.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((3-chlorophenyl) sulfane) (8h): Yield: 78% (60.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 6.4 Hz, 3H), 7.32 (dd, *J* = 16.0, 6.4 Hz, 4H), 7.25 - 7.17 (m, 4H), 7.13 (t, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.8, 134.6, 133.7, 132.6, 131.4, 131.0, 130.3, 129.5, 129.1, 128.7, 128.6, 128.5, 128.3, 128.0, 126.7, 126.4, 125.9 ppm; ν_{max}(KBr)/cm^{-1} 3061, 2923, 1535, 1471, 1438, 745; MS (EI) m/z 65, 109, 167, 208, 244, 279,

388; HRMS-ESI (m/z): calcd for $C_{20}H_{14}Cl_2NaS_2$, $[M+Na]^+$: 410.9806, found 410.9810.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-bromophenyl) sulfane) (8i): Yield: 71% (67.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 4.8 Hz, 1H), 7.25 - 7.21 (m, 2H), 7.19 - 7.06 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 135.8, 133.9, 133.5, 133.1, 132.0, 131.9, 129.9, 129.7, 129.5, 129.1, 128.6, 128.0, 126.8 ppm; ν_{max}(KBr)/cm^{-1} 3036, 2928, 1656, 1549, 1473, 1416, 750; MS (EI) m/z 96, 167, 208, 398, 476; HRMS-ESI (m/z): calcd for $C_{20}H_{14}Br_2NaS_2$, $[M+Na]^+$: 498.8796, found 498.8793.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((3,5-dichlorophenyl) sulfane) (8j): Yield: 70% (63.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.2 Hz, 2H), 7.38 - 7.27 (m, 6H), 7.19 (s, 1H), 7.11 - 7.02 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.7, 135.7, 135.3, 135.1, 130.2, 128.8, 128.6, 128.1, 127.9, 126.8, 126.3, 125.9 ppm; ν_{max}(KBr)/cm^{-1} 3072, 2924, 1560, 1486, 1408, 753; MS (EI) m/z 102, 134, 165, 208, 244, 278, 335, 388, 456; HRMS-ESI (m/z): calcd for $C_{20}H_{12}Cl_4NaS_2$, $[M+Na]^+$: 478.9027, found 478.9024.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((4-acetylphenyl) sulfane) (8k): Yield: 75% (60.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.2 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.39 (s, 1H), 7.33 - 7.27 (m, 3H), 7.25 - 7.19 (m, 2H), 2.59 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 197.0, 141.5, 141.4, 138.1, 135.7, 134.9, 134.5, 130.2, 129.2, 128.9, 128.9, 128.8, 128.4, 127.1, 126.7, 26.6, 26.5 ppm; ν_{max}(KBr)/cm^{-1} 3057, 2923, 1680, 1586, 1486, 1435, 1261, 1093, 757; MS (EI) m/z 96, 139, 207, 281, 331, 380, 404; HRMS-ESI (m/z): calcd for $C_{24}H_{20}NaO_2S_2$, $[M+Na]^+$: 427.0797, found 427.0803.

(*Z*)-(1-Phenylethene-1,2-diyl)bis((2-thiopheneyl)sulfane) (8l): Yield: 63% (41.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 5.2 Hz, 1H), 7.22 (dd, J = 13.4, 5.6 Hz, 4H), 7.17 (d, J = 5.6 Hz, 1H), 7.07 (d, J = 3.6 Hz, 1H), 7.00 (dd, J = 5.2, 3.6 Hz, 1H), 6.81 (dd, J = 5.2, 3.6 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.7, 133.7, 133.0, 132.6, 131.8, 131.5, 130.0, 129.1, 128.3, 127.9, 127.8, 127.4, 127.2 ppm; ν_{max}(KBr)/cm^{-1} 3066, 2923, 1545, 1441, 1402, 750; MS (EI) m/z 71, 115, 184, 217, 277, 332; HRMS-ESI (m/z): calcd for $C_{16}H_{12}NaS_4$, $[M+Na]^+$: 354.9714, found 354.9711.

Supporting Information

Copies of the ^{1}H NMR and ^{13}C NMR spectra for all compounds are available in the supporting Information.

Acknowledgements

This work was supported by the financial support from the National Key Research and Development Program of China (2016YFA0602900), the National Natural Science Foundation of China (21502055, 21490572 and 21420102003), and the Fundamental Research Funds for the Central Universities (2015ZM150 and 2015ZY001).

References

[1] For selected reviews, a) B. Godoi, R. F. Schumacher, G. Zeni, *Chem. Rev*. **2011**, *111*, 2937-2980; b) Y. Shimizu, M. Kanai, *Tetrahedron Lett*. **2014**, *55***,** 3727-3737; c) B. M. Trost, C.-J. Li, Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations. Wiley-VCH, Weinheim, **2014**; d) R. Chinchilla, C. Najerá, *Chem. Rev*. **2014**, *114*, 1783-1826; e) V. P. Boyarskiy, D. S. Ryabukhin, N. A. Bokach, A. V. Vasilyev, *Chem. Rev*. **2016**, *116*, 5894-5986; f) A. Defert, D. B. Werz, *Chem. Eur. J*. **2016**, *22*, 16718-16732.

[2] For selected reviews, a) H. Kuniyasu, H. Kurosawa, *Chem. Eur. J*. **2002**, *8*, 2660-2665; b) T. Besset, T. Poisson, X. Pannecoucke, *Eur. J. Org. Chem*. **2015**, 2765-2789; c) H. Yoshida, *ACS Catal*. **2016**, *6*, 1799-1811.

[3] For selected reviews, a) I. Beletskaya, C. Moberg, *Chem. Rev*. **1999**, *99*, 3435-3462; b) I. Beletskaya, C. Moberg, *Chem. Rev*. **2006**, *106*, 2320-2354; c) M. Oestreich, E. Hartmann, M. Mewald, *Chem. Rev*. **2013**, *113*, 402-441. For selected examples, d) T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc*. **1993**, *115*, 7219-7225; e) M. Iwasaki, N. Topolovčan, H. Hu, Y. Nishimura, G. Gagnot, R. Nanakorn, R. Yuvacharaskul, K. Nakajima, Y. Nishihara, *Org. Lett*. **2016**, *18*, 1642-1645; f) M. B. Ansell, J. Spencer, O. Navarro, *ACS Catal*. **2016**, *6*, 2192-2196; g) B. Gao, H, Huang, *Adv.Synth. Catal*. **2016**, *358*,4075-4084.

[4] For selected reviews, a) A. Ding, H. Guo, Comprehensive Organic Synthesis, 2nd ed. Elsevier, Oxford, **2014**; b) D. Qian, J. Zhang, *Chem. Soc. Rev*. **2015**, *44*, 677-698; c) A. Düfert, D. B. Werz, *Chem. Eur. J*. **2016**, *22*, 16718-16732.

[5] For selected examples, a) Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang, A. Lei, *J. Am. Chem. Soc*. **2013**, *135*, 11481-11484; b) T. Xu, C. W. Cheung, X. Hu, *Angew. Chem. Int. Ed*. **2014**, *53*, 4910-4914; c) Z. Li, A. García-Domínguez, C. Nevado, *J. Am. Chem. Soc*. **2015**, *137*, 11610-11613; d) Y.-T. He, Q. Wang, L.-H. Li, X.-Y. Liu, P.-F. Xu, Y.-M. Liang, *Org. Lett*. **2015**, *17*, 5188-5191; e) Z. Li, A. García-Domínguez, C. Nevado, *Angew. Chem. Int. Ed*. **2016**, *55*, 6938-6941; f) W. Su, T.-J. Gong, Q. Zhang, Q. Zhang, B. Xiao, Y. Fu, *ACS Catal*. **2016**, *6*, 6417-6421.

[6] a) Z. Duan, Z. Wei, W. Xu, D. Zhu, *Tetrahedron Lett*. **2009**, *50*, 2597-2600; b) M. J. Koh, R. K. M. Khan, S. Torker, M. Yu, M. S. Mikus, A. H. Hoveyda, *Nature* **2015**, *517*, 181-186; c) B. F. Makume, M. C. Maumela, C. W. Holzapfel, J. T. Dixon, *Appl. Catal. A-Gen*. **2017**, *542*, 262-270.

[7] a) C.-K. Ryu, R.-E. Park, M.-Y. Ma, J.-H. Nho, *Bioorg. Med. Chem. Lett*. **2007**, *17*, 2577-2580; b) C.-K. Ryu, Y. H. Kim, H. A. Im, J. Y. Kim, J. H. Yoon, A. Kim, *Bioorg. Med. Chem. Lett*. **2012**, *22*, 500-503; c) Y. V. Gyrdymova, D. V. Sudarikov, O. G. Shevchenko, S. A. Rubtsova, P. A. Slepukhin, A. V. Kutchin, *Chem. Biodivers*. **2017**, *14*, e1700296.

[8] a) H. Kuniyasu, A. Ogawa, S.-I. Miyazaki, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc*. **1991**, *113*, 9796-9803; b) V. P. Ananikov, I. P. Beletskaya, *Org. Biomol. Chem*. **2004**, *2*, 284-287; c) V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, *Synlett* **2005**, *6*, 1015-

1017; d) M. Cai, Y. Wang, W. Hao, *Green Chem*. **2007**, *9*, 1180-1184.

[9] M. Arisawa, M. Yamaguchi, *Org. Lett*. **2001**, *3*, 763-764.

[10] V. P. Ananikov, K. A. Gayduk, I. P. Beletskaya, V. N. Khrustalev, M. Y. Antipin, *Chem. Eur. J*. **2008**, *14*, 2420-2434.

[11] K. B. Zou, X. H. Yin, W. Q. Liu, R. H. Qiu, R. X. Li, L. L. Shao, Y. H. Li, X. Hua Xu, R. H. Yang, *Synthetic Commun*. **2009**, *39*, 2464-2471.

[12] E. S. Degtyareva, J. V. Burykina, A. N. Fakhrutdinov, E. G. Gordeev, V. N. Khrustalev, V. P. Ananikov, *ACS Catal*. **2015**, *5*, 7208-7213.

[13] a) X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu, H. Jiang, *Angew. Chem. Int. Ed*. **2014**, *53*, 4205-4208; b) Y. Xu, X. Tang, W. Hu, W. Wu, H. Jiang, *Green Chem*. **2014**, *16*, 3720-3723; c) J. Li, C. Li, S. Yang, Y. An, W. Wu, H. Jiang, *J. Org. Chem*. **2016**, *81*, 2875-2887; d) J. Li, C. Li, S. Yang, Y. An, W. Wu, H. Jiang, *J. Org. Chem*. **2016**, *81*, 7771-7783; e) J. Li, Y. An, J. Li, S. Yang, W. Wu, H. Jiang, *Org. Chem. Front*. **2017**, *4*, 1590-1594.

[14] J. Li, C. Li, L. Ouyang, C. Li, W. Wu, H. Jiang, *Org. Biomol. Chem*. **2017**, *15*, 7898-7908.

[15] a) Y. Li, X. Liu, H. Jiang, B. Liu, Z. Chen, P. Zhou, *Angew. Chem. Int. Ed*. **2011**, *50*, 6341-6345; b) L. Huang, Q. Wang, X. Liu, H. Jiang, *Angew. Chem. Int. Ed*. **2012**, *51*, 5696-5700; c) J. Li, W. Yang, S. Yang, L. Huang, W. Wu, Y. Sun, H. Jiang, *Angew. Chem., Int. Ed*. **2014**, *53*, 7219-7222; d) J. Li, S. Yang, W. Wu, H. Jiang, *Chem. Commun*. **2014**, *50*, 1381-1383; e) J. Li, W. Hu, C. Li, S. Yang, W. Wu, H. Jiang, *Org. Chem. Front*. **2017**, *4*, 373-376. For review, f) W. Wu, H. Jiang, *Acc. Chem. Res*. **2014**, *47*, 2483-2504.

[16] CCDC 1551065 (**3r**) contains the supplementary crystallographic data for this paper.

[17] Compared with the terminal alkynes, 1,2-diphenylethyne (**1ab**) was relatively sluggish on the necleopalladation of alkynes, see: a) J. Huang, L. Zhou, H. Jiang, *Angew. Chem. Int. Ed.* **2006**, *45*, 1945-1949; b) J. Li, S. Yang, L. Huang, H. Chen, H. Jiang, *RSC Adv*. **2013**, *3*, 11529-11532.

[18] a) M. Abdo, S. Knapp, *J. Org. Chem*. **2012**, *77*, 3433-3438; b) Y. Zheng, F.-L. Qing, Y. Huang, X.-H. Xu, *Adv. Synth. Catal*. **2016**, *358*, 3477-3481; c) Y. Yang, S. Zhang, L. Tang, Y. Hu, Z. Zha, Z. Wang, *Green Chem*. **2016**, *18*, 2609-2613.

[19] a) C. Chen, Y. Xie, L. Chu, R.-W. Wang, X. Zhang, F.-L. Qing, *Angew. Chem. Int. Ed*. **2012**, *51*, 2492-2495; b) M. Wang, J. Wei, Q. Fan, X. Jiang, *Chem. Commun*. **2017**, *53*, 2918-2921.

[20] a) S. Ma, X. Lu, *J. Org. Chem*. **1993**, *58*, 1245-1250; b) G. Zhu, Z. Zhang, *J. Org. Chem*. **2005**, *70*, 3339-3341; c) H. Peng, G. Liu, *Org. Lett*. **2011**, *13*, 772-775.

[21] a) X. Tong, M. Beller, M. K. Tse, *J. Am. Chem. Soc*. **2007**, *129*, 4906-4907; b) S. Tang, P. Peng, S.-F. Pi, Y. Liang, N.-X. Wang, J.-H. Li, *Org. Lett*. **2008**, *10*, 1179-1182; c) A. J. Hickman, M. S. Sanford, *ACS Catal*. **2011**, *1*, 170-174; d) K. B. McMurtrey, J. M. Racowski, M. S. Sanford, *Org. Lett*. **2012**, *14*, 4094-4097. For review, e) G. Yin, X. Mu, G. Liu, *Acc. Chem. Res*. **2016**, *49*, 2413-2423.

[22] Aryl iodobenzene derivatives was observed by GC-MS analysis when the reaction was finished. This observation was compatible with the literature reference, K. Muñiz, C. H. Hövelmann, J. Streuff, *J. Am. Chem. Soc*. **2008**, *130*, 763-773.

[23] a) V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, V. N. Khrustalev, M. Y. Antipin, T. V. Timofeeva, *J. Am. Chem. Soc*. **2007**, *129*, 7252-7253; b) V. P. Ananikov, N. V. Orlov, S. S. Zalesskiy, I. P. Beletskaya, V. N Khrustalev, K. Morokuma, D. G. Musaev, *J. Am. Chem. Soc*. **2012**, *134*, 6637-6649.

[24] W.-S. Guo, Y.-C. Wang, Q. Dou, L.-R. Wen, M. Li, *Org. Chem. Front*. **2017**, *4*, 510-513.

[25] J. Chen, S. Chen, X. Xu, Z. Tang, C.-T. Au, R. Qiu, *J. Org. Chem*. **2016**, *81*, 3246-3255.

[26] A. V. Moro, C. W. Nogueira, N. B. V. Barbosa, P. H. Menezes, J. B. T. da Rocha, G. Zeni, *J. Org. Chem*. **2005**, *70*, 5257-5268.

[27] V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, *J. Organomet. Chem*. **2003**, *687*, 451-461.

10.1002/adsc.201701417

FULL PAPER

Palladium-Catalyzed Regioselective Three-Component Cascade Bisthiolation of Terminal Alkynes

Adv. Synth. Catal. **2017**,

Jianxiao Li,[a] Can Li,[a] Lu Ouyang,[a] Chunsheng Li,[a] Shaorong Yang,[a] Wanqing Wu [a,*] and Huanfeng Jiang [a,*]