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Synthesis of Trisubstituted Vinyl Sulfides via Oxidative Thiolation Initiated Cascade Reaction of Alkynoates with Thiols

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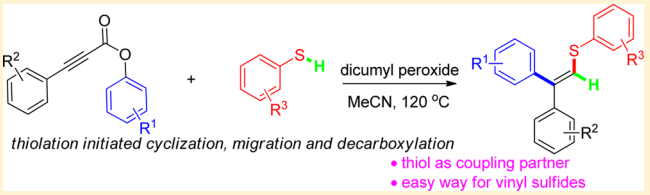
Supporting Information

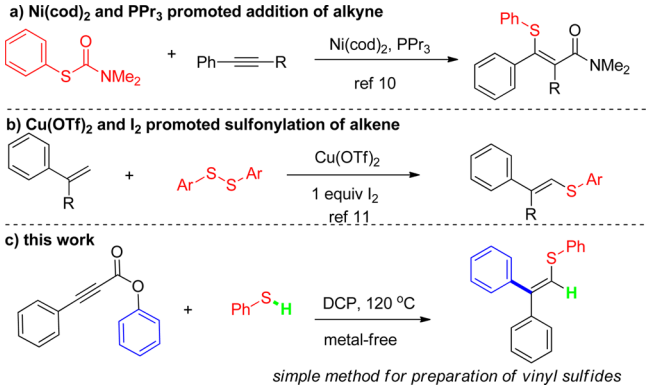
ABSTRACT: A thiolation initiated cascade reaction of aryl alkynoates has been developed with thiol as a coupling partner. This radical process has been demonstrated to proceed through S−H bond cleavage, thiolation of alkynoate, aryl migration, and decarboxylation. This reaction tolerates a wide scope of substrates resulting in good chemical yields, which provides an easy and practical strategy for preparation of trisubstituted vinyl sulfides.



Chemistry of sulfur has a profound effect on our daily lives, and the areas include energy, industry, food, healthcare, and so on.[1] Among the organosulfur compounds, vinyl sulfide takes up an important part, which widely exists in many natural products and biologically active molecules.[2] Vinyl sulfides are also versatile building blocks in organic synthesis and total synthesis of natural products.[3] For example, they can be used for Michael addition acceptors for preparation of benzylthiocrellidone[4] and Diels−Alder cycloaddition substrates for the total synthesis of (−)-β-selinene.[5] In the past decade, varieties of approaches have been developed as the preparation of substituted vinyl sulfides.[6,7] The mostly reported synthetic methods focused on metal-catalyzed cross-coupling reaction of vinyl halides with thiols,[8] and addition of thiols to the triple bond of alkynes.[9] In 2015, Kurahashi and Matsubara group described a nickel-catalyzed synthetic method for tetrasubstituted vinyl sulfides by reaction of internal alkynes with thiocarbamates as sulfur precursors.[10] Recently, Zhang group developed a copper and iodine-mediated C−H oxidative sulfonylation of olefins with diaryl disulfides for the synthesis of vinyl thioether (Scheme 1b).[11] These approaches usually need transition-metal catalysts or stoichiometric additives for the transformations. So, the development of new, conceptually different methods for more practical preparation of vinyl sulfides remains a significant challenge.

Aryl alkynoate representing an attractive intermediate, which could construct substituted coumarin derivatives by intramolecular cyclization reaction.[12] Also, alkynoates could undergo transition-metal catalyzed oxidative *ipso*-cyclization reaction to afford azaspiro[4.5]trienones derivatives.[13] Alkynoates have also been developed to react with ketene silyl acetals via [2+2]-cycloaddition affording functionalized cyclobutenediones.[14] Very recently, cascade migration and decarboxylation reaction of alkynoate represents a new trend for this intermediate, which affords alkyl, ether, benzyl and iodo substituted alkenes as products.[15]

Scheme 1. Synthesis of Vinyl Sulfides



Since the substituted alkenes could be easily prepared from the cascade reaction of aryl alkynoates, we envision that the vinyl sulfides could be obtained from the reaction of alkynoates with suitable sulfur precursor. Herein, we would like to report an easy and efficient method for the preparation of vinyl sulfides by the reaction of alkynoate with thiol[16] as sulfur precursor under metal-free condition (Scheme 1c). To the best of our knowledge, oxidative thiolation initiating aryl migration and decarboxylation of aryl alkynoates, has never been reported. Furthermore, this method provides a new strategy for the preparation of vinyl sulfides with readily available aryl alkynoates as starting materials without use of any metal-catalyst.

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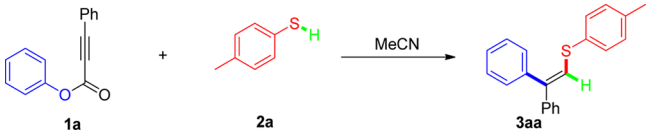
Based on the previous reports and our experience on the reactions of alkynoates,[15] phenyl alkynoate **1a** and 4-methylbenzenethiol **2a** were chosen as the model substrates for this thiolation initiated reaction. The reaction was carried out in acetonitrile at 120 °C with the use of additive. In the presence of TBAI, the reaction could happen, and afforded the corresponding vinyl sulfides in only 10% chemical yield (entry 1, Table 1). To our delight, application of molecular iodine as additive (entry 2) could increase the chemical yield to 40%. To further optimize the reaction condition, several oxidants, including DTBP (entry 3), TBHP (entry 4), DCP (entry 5), BPO (entry 6), and TBPB (entry 7), were tried in the reaction. The reaction could proceed smoothly when it was carried out in the presence of oxidant DCP, and the highest yield was found (57%, entry 7). Then, the amount of oxidant DCP was examined (entries 8−12). We found that the use of 1.0 equiv of DCP is the best choice, resulting in 79% yield (entry 10). Continuing the search for optimized conditions we found that the loading amount of 4-methylbenzenethiol **2a** shows obvious effect on the reaction efficiency. The results from entries 13−15 clearly disclose that 2.0 equiv of 4-methylbenzenethiol **2a** is the best loading. The attempts to improve the yield by varying reaction time (entry 16) or temperature (entry 17) were not successful, which suggests 120 °C and 24 h might be the optimized conditions. Finally, the addition of metal-catalysts, $Cu(OAc)_2$ and $FeCl_3$ (20 mol%), did not result any improvement on the reaction (entries 18 and 19).

Table 1. Optimization of the Reaction Conditions[a]

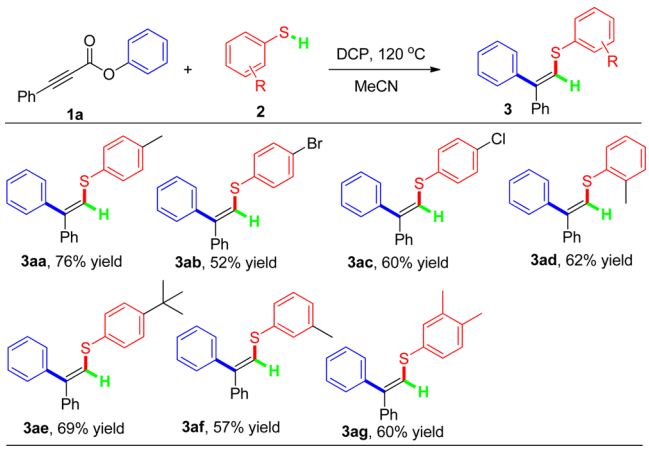


entry	additive	oxidant (equiv)	2a (equiv)	temp (°C)	yield (%)[b]
1	TBAI[c]		2	120	10
2	I_2[c]		2	120	40
3		DTBP (3.0)[d]	2	120	48
4		TBHP (3.0)[e]	2	120	23
5		DCP (3.0)[f]	2	120	57
6		BPO (3.0)[g]	2	120	14
7		TBPB (3.0)[h]	2	120	17
8		DCP (0.2)	2	120	44
9		DCP (0.5)	2	120	68
10		DCP (1.0)	2	120	79
11		DCP (1.5)	2	120	75
12		DCP (2.0)	2	120	58
13		DCP (1.0)	1	120	67
14		DCP (1.0)	1.2	120	60
15		DCP (1.0)	1.5	120	62
16		DCP (1.0)	2	120	71[i]
17		DCP (1.0)	2	100	33
18	$Cu(OAc)_2$[c]		2	120	trace
19	$FeCl_3$[c]		2	120	28

[a]Reaction conditions: **1a** and **2a** in CH_3CN (2 mL), 24 h. [b]NMR yield, CH_2Br_2 as an internal standard. [c]20 mol% amount was used. [d]DTBP: di-*tert*-butyl peroxide. [e]TBHP: *tert*-butyl hydroperoxide 70% aqueous solution. [f]DCP: dicumyl peroxide. [g]BPO: benzoyl peroxide. [h]TBPB: *tert*-butyl peroxybenzoate. [i]12 h.

With the optimized conditions in hand, we then explored the substrate scope of the current cascade reaction of phenyl alkynoates **1a** with varieties of thiols (Scheme 2). As shown in Scheme 2, the reaction proceeded smoothly for a wide range of thiols to give the corresponding vinyl sulfides with 52−76% chemical yields. The substituents on the aromatic ring of thiols, including methyl, chloro, bormo, and *t*-butyl, could all be well tolerated. Gratifyingly, the presence of *t*-butyl functionality on the aromatic ring caused no effect on the reaction, and the reaction occurred quite cleanly giving the expected product **3ae** in 69% yield. It was also noticeable that the presence of substituents in the different positions on the aromatic ring was perfectly tolerated regardless the *ortho*-, *meta*-, *para*-position (**3aa**, **3ad**, **3af**). Thiol with disubstituted aromatic ring (**2g**) was also good substrate for this reaction, which could be transferred into the corresponding product (**3ag**) in 60% yield. Arylthiols with electron-withdrawing groups (CF_3, NO_2) were found to give the products, but that they were not sufficiently stable to be fully characterized.

Scheme 2. Substrate Scope of Thiols[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), DCP (0.2 mmol), **2** (0.4 mmol), with acetonitrile (2.0 mL) as solvent at 120 °C for 24 h. [b]Isolated yield.

With these results in hand, we then focused on exploring the scope of alkynoates (Scheme 3). As shown in Scheme 3, starting compounds containing various electron-withdrawing substituents on the aromatic ring are more affordable. These substrates reacted quite easily with 4-methylbenzenethiol **2a** and gave the expected products **3ea**, **3fa**, and **3ja** in higher isolated yields comparing with the results from substrates with electron-donating groups (**3ba**, **3da**). Of particular interest was the reaction of alkynoate **1c** bearing two substituent groups on the aromatic ring and this substrate could be easily converted into the desired product **3ca** in 62% yield. Then, we were interested to investigate the regioselectivity of this reaction by using the substrates with different substituted aromatic rings on ester group and alkynyl moiety. All these examined alkynoates could work very well in this reaction, affording the corresponding product **3ka-na** with up to 80% chemical yield. However, these reactions showed almost no regioselectivity and the two regio-isomers were obtained in the ratio of about 1:1 determined by ^1H NMR.

As the final goal in this study, we were interested to know the reactivity of thiol comparing to disulfide, as disulfide has been widely used as sulfur radical precursor.[17] The reaction of alkynoate **1a** was carried out under the standard condition with the use of thiol and disulfide as coupling partners (Scheme 4).

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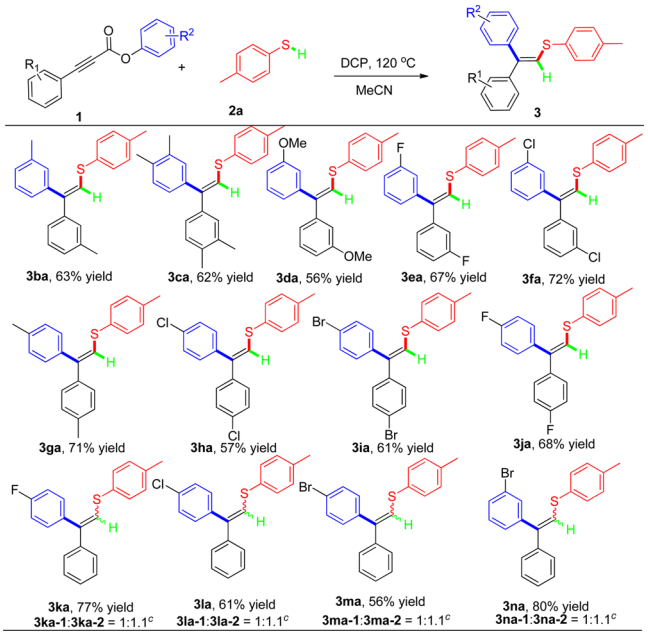
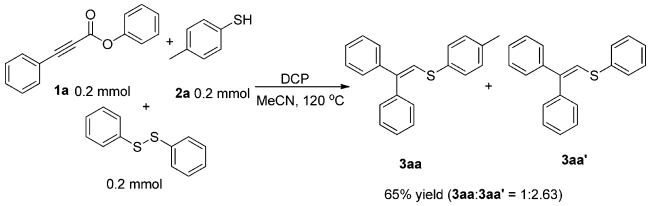
Scheme 3. Reaction Scope of Aryl Alkynoates[a,b]



[a]Reaction conditions: **1** (0.2 mmol), DCP (0.2 mmol), **2a** (0.4 mmol), with acetonitrile (2.0 mL) as solvent at 120 °C for 24 h. [b]Isolated yield. [c]Regioselectivity determined by ^{1}H NMR.

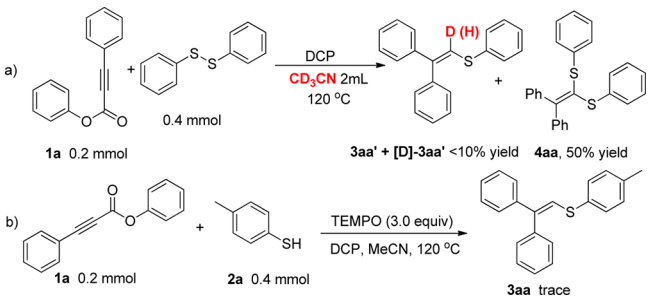
The reaction afforded the desired products **3aa** and **3aa′** with the ratio of 1:2.63, which indicates disulfide is slightly more active for the current reaction.

Scheme 4. Reaction with the Use of Thiol and Disulfide as Coupling Partners



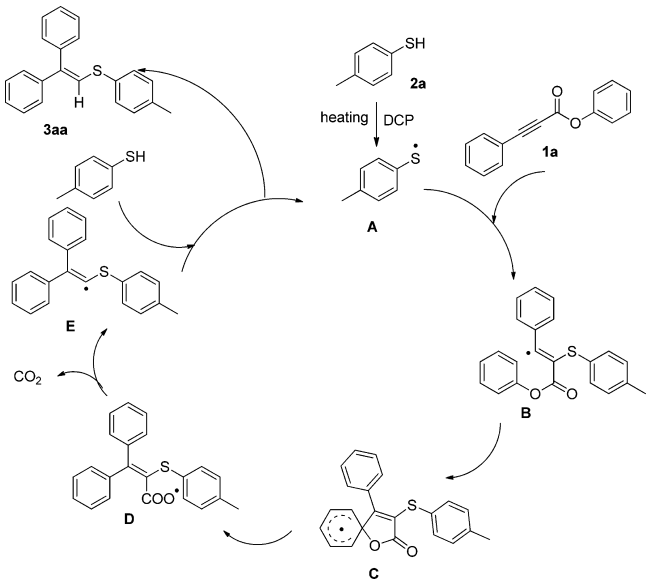
To elucidate the experimental results and propose the mechanism for this reaction, two control experiments were carried out. First, one reaction with disulfides as sulfur precursor in D-acetonitrile was performed (Scheme 5a), to investigate where the acetylenic hydrogen in the product vinyl sulfide comes from. The reaction afforded **4aa** as main product along with trace number of **3aa′** and [**D**]-**3aa′**. This result indicates that the hydrogen atom came from S−H of thiol. Then, a control intermediate-trapping experiment with the addition of the radical-trapping reagents 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was carried out (Scheme 5b). The formation of desired product **3aa** was suppressed, and the result indicates that the transformation may proceed via a radical course.

Scheme 5. Control Experiments



On the basis of the experiment results above and the literature reports,[15] a possible mechanism of this thiolation initiated cascade radical reaction is proposed in Scheme 6.

Scheme 6. Proposal Mechanism



Initially, the aryl sulfur radical **A** generates from 4-methylbenzenethiol **2a** via S−H bond cleavage under heating with the aid of oxidant DCP.[16b,c] Then, intermediate **A** couples with alkynoate **1a** to give intermediate **B**. Subsequently, the intermediate **B** proceeds through intramolecular spirocyclization to afford the spiro intermediate **C**, which undergoes the aryl migration via cleavage of C−O bond to give the carboxyl radical **D**.[12h] Subsequent decarboxylation of carboxyl radical **D** generates intermediate **E** with the release of CO_2. Finally, the intermediate alkene radical **E** reacts with 4-methylbenzenethiol **2a** to afford the final vinyl sulfide product **3aa** along with the generation of aryl sulfur radical **A** for the next cycle.

To conclude, thiol as a new radical coupling partner has been developed for the cascade reaction of aryl alkynoates under metal-free condition. This radical process has been demonstrated to proceed through S−H bond cleavage, thiolation of alkynoate, aryl migration, and decarboxylation. This reaction was carried out under simple condition and tolerated a wide range of aryl alkynoates and thiols substrate, to give vinyl sulfide with good chemical yields. Furthermore, the current reaction provides a new and efficient access to vinyl sulfides.

EXPERIMENTAL SECTION

General Procedure for the Cascade Radical Reaction of Aryl Alkynoates. A sealable reaction tube equipped with a magnetic stirrer bar was charged with phenyl 3-phenylpropiolate **1a** (44.4 mg, 0.2 mmol), DCP (dicumyl peroxide, 0.2 mmol, 54 mg), 4-methylbenzenethiol **2a** (49.6 mg, 0.4 mmol), and acetonitrile (2.0 mL). The rubber septum was then replaced by a Teflon−coated screw cap, and the reaction vessel placed in an oil bath at 120 °C. After stirring the

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mixture at this temperature for 24 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water, dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (elute: hexane) to afford the corresponding product **3aa** in 76% yield.

*(2,2-Diphenylvinyl)(p-tolyl)sulfane (**3aa**).*[18] White solid. mp 86−88 °C. Yield: 45.9 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.39 (m, 2H), 7.38−7.31 (m, 5H), 7.30−7.20 (m, 5H), 7.14 (d, J = 7.9 Hz, 2H), 6.82 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.2, 139.3, 137.0, 132.8, 130.1, 129.9, 129.8, 128.4, 128.3, 127.8, 127.2, 125.3, 21.1. IR (Attenuated total reflection, cm^{-1}): 1583, 1490, 1441, 1333, 1265, 1094, 1073, 1030, 941, 904. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{18}S$] 302.1129, found 302.1131.

*(4-Bromophenyl)(2,2-diphenylvinyl)sulfane (**3ab**).* White solid. mp 90−92 °C. Yield: 38.2 mg (52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.32 (m, 4H), 7.31−7.28 (m, 1H), 7.28−7.24 (m, 2H), 7.23−7.15 (m, 7H), 6.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 141.2, 139.0, 135.8, 132.2, 130.9, 129.7, 128.5, 128.4, 128.0, 127.6, 127.3, 123.0, 120.7. IR (Attenuated total reflection, cm^{-1}): 1471, 1441, 1090, 1083, 1001, 811, 769. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{20}H_{15}{}^{79}BrS$] 366.0078, found 366.0070.

*(4-Chlorophenyl)(2,2-diphenylvinyl)sulfane (**3ac**).* Yellow oil. Yield: 38.6 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.39 (m, 2H), 7.38−7.32 (m, 5H), 7.30−7.23 (m, 7H), 6.77 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.3, 139.0, 135.1, 132.8, 130.7, 129.7, 129.3, 128.5, 128.4, 128.0, 127.5, 127.3, 123.2. IR (Attenuated total reflection, cm^{-1}): 1587, 1475, 1388, 1091, 984, 939, 823. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{20}H_{15}{}^{35}ClS$] 322.0583, found 322.0587.

*(2,2-Diphenylvinyl)(o-tolyl)sulfane (**3ad**).* Yellow oil. Yield: 37.4 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.46 (m, 1H), 7.45−7.41 (m, 1H), 7.41−7.38 (m, 2H), 7.37−7.34 (m, 1H), 7.30−7.13 (m, 9H), 6.74 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 141.4, 139.3, 138.3, 135.7, 130.4, 130.3, 129.8, 128.4, 128.3, 127.8, 127.3, 127.2, 127.1, 126.7, 124.3, 20.7. IR (Attenuated total reflection, cm^{-1}): 1379, 1087, 1046, 880, 589, 579. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{18}S$] 302.1129, found 302.1134.

*(4-(tert-Butyl)phenyl)(2,2-diphenylvinyl)sulfane (**3ae**).* Light yellow oil. Yield: 47.5 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.32 (m, 9H), 7.29−7.21 (m, 5H), 6.85 (s, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.6, 140.2, 139.3, 132.9, 129.8, 129.8, 128.4, 128.3, 127.8, 127.2, 126.2, 125.2, 34.6, 31.3. IR (Attenuated total reflection, cm^{-1}): 1490, 1441, 1393, 1336, 1266, 1119, 1071, 1013. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{24}H_{24}S$] 344.1599, found 344.1592.

*(2,2-Diphenylvinyl)(m-tolyl)sulfane (**3af**).* Yellow oil. Yield: 34.4 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.39 (m, 2H), 7.38−7.32 (m, 3H), 7.31−7.18 (m, 8H), 7.08−7.02 (m, 1H), 6.86 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.8, 139.3, 139.0, 136.2, 130.2, 129.8, 129.0, 128.4, 128.3, 127.8, 127.7, 127.3, 127.2, 126.7, 124.4, 21.4. IR (Attenuated total reflection, cm^{-1}): 1592, 1494, 1441, 940, 770, 753. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{18}S$] 302.1129, found 302.1130.

*(3,4-Dimethylphenyl)(2,2-diphenylvinyl)sulfane (**3ag**).* Colorless oil. Yield: 38.2 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.33 (m, 5H), 7.30−7.16 (m, 7H), 7.09 (d, J = 7.8 Hz, 1H), 6.83 (s, 1H), 2.24 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 139.9, 139.3, 137.7, 135.8, 133.0, 131.4, 130.4, 129.8, 128.4, 128.3, 127.8, 127.7, 127.2, 127.2, 125.6, 19.8, 19.5. IR (Attenuated total reflection, cm^{-1}): 1597, 1494, 1442, 905, 811, 727, 697. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{22}H_{20}S$] 316.1286, found 316.1281.

*(2,2-Di-m-tolylvinyl)(p-tolyl)sulfane (**3ba**).* Yellow oil. Yield: 41.6 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.27 (m, 3H), 7.20−7.10 (m, 6H), 7.08−7.00 (m, 3H), 6.78 (s, 1H), 2.37 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 140.5, 139.3, 138.0, 137.9, 136.9, 133.0, 130.3, 130.1, 129.9, 128.5, 128.2, 128.2, 128.0, 127.8, 126.9, 124.9, 124.4, 21.6, 21.5, 21.1. IR (Attenuated total reflection, cm^{-1}): 1601, 1490, 1092, 1017, 840, 804, 779, 758, 714. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{23}H_{22}S$] 330.1442, found 330.1439.

*(2,2-Bis(3,4-dimethylphenyl)vinyl)(p-tolyl)sulfane (**3ca**).* Colorless oil. Yield: 44.4 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (m, 2H), 7.17 (d, J = 8.2 Hz, 1H), 7.15−7.07 (m, 4H), 7.05−7.00 (m, 2H), 6.97 (dd, J = 7.8, 2.0 Hz, 1H), 6.70 (s, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 139.5, 136.9, 136.7, 136.5, 136.4, 136.1, 135.7, 133.3, 130.8, 129.9, 129.8, 129.6, 129.5, 128.4, 127.3, 124.8, 123.3, 21.1, 19.9, 19.9, 19.7, 19.5. IR (Attenuated total reflection, cm^{-1}): 1491, 1447, 1264, 1091, 1017, 890, 803, 736. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{25}H_{26}S$] 358.1755, found 358.1764.

*(2,2-Bis(3-methoxyphenyl)vinyl)(p-tolyl)sulfane (**3da**).* Colorless oil. Yield: 40.6 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 3H), 7.23−7.10 (m, 3H), 6.99−6.73 (m, 7H), 3.81 (s, 3H), 3.75 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 159.5, 142.8, 140.5, 139.5, 137.1, 132.8, 130.2, 129.9, 129.4, 129.2, 125.8, 122.2, 119.8, 115.1, 113.5, 113.1, 112.3, 55.3, 55.3, 21.1. IR (Attenuated total reflection, cm^{-1}): 1381, 1088, 1045, 879, 585. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{23}H_{22}O_2S$] 362.1341, found 362.1347.

*(2,2-Bis(3-fluorophenyl)vinyl)(p-tolyl)sulfane (**3ea**).* Colorless oil. Yield: 45.3 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.31 (m, 3H), 7.26−7.19 (m, 1H), 7.19−7.11 (m, 3H), 7.10−7.02 (m, 2H), 7.01−6.84 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 ($^1J_{CF}$ = 247.4 Hz), 143.2, 143.1, 140.8, 140.8, 137.6, 137.1, 137.0, 137.0, 132.0, 130.6, 130.2 ($^3J_{CF}$ = 9.0 Hz), 129.8, 129.8, 128.2, 125.5 ($^4J_{CF}$ = 3.0 Hz), 122.7, 122.7, 116.8 ($^2J_{CF}$ = 21.2 Hz), 115.1, 114.8, 114.2, 114.0, 114.0, 113.8, 21.1. IR (Attenuated total reflection, cm^{-1}): 1429, 1379, 1088, 1045, 879, 806, 769. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{16}F_2S$] 338.0941, found 338.0939.

*(2,2-Bis(3-chlorophenyl)vinyl)(p-tolyl)sulfane (**3fa**).* White solid. mp 120−122 °C. Yield: 53.2 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.30 (m, 5H), 7.29−7.12 (m, 6H), 7.10−7.01 (m, 1H), 6.85 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.4, 137.7, 136.7, 134.5, 134.4, 131.9, 130.6, 130.1, 129.9, 129.7, 129.6, 128.5, 128.2, 128.0, 127.3, 127.0, 125.2, 21.1. IR (Attenuated total reflection, cm^{-1}): 1559, 1465, 1402, 1077, 959, 837, 816, 801. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{16}{}^{35}Cl_2S$] 370.0350, found 370.0353.

*(2,2-Di-p-tolylvinyl)(p-tolyl)sulfane (**3ga**).* White solid. mp 119−121 °C. Yield: 46.9 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.30 (m, 2H), 7.27−7.19 (m, 4H), 7.16−7.10 (m, 4H), 7.07 (d, J = 8.1 Hz, 2H), 6.73 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 139.0, 137.5, 137.0, 136.8, 136.5, 133.2, 129.9, 129.9, 129.7, 129.1, 129.0, 127.2, 123.6, 21.4, 21.2, 21.1. IR (Attenuated total reflection, cm^{-1}): 1586, 1510, 1492, 1181, 1112, 829, 815. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{23}H_{22}S$] 330.1442, found 330.1441.

*(2,2-Bis(4-chlorophenyl)vinyl)(p-tolyl)sulfane (**3ha**).* White solid. mp 103−105 °C. Yield: 42.3 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dt, 2H), 7.33 (dt, 2H), 7.28 (dt, 2H), 7.25−7.21 (m, 2H), 7.18−7.10 (m, 4H), 6.80 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.5, 137.4, 137.2, 133.8, 133.2, 132.1, 131.2, 130.4, 130.1, 128.8, 128.6, 128.3, 126.9, 21.1. IR (Attenuated total reflection, cm^{-1}): 1485, 1393, 1088, 1014, 929, 810, 727. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{16}{}^{35}Cl_2S$] 370.0350, found 370.0355.

*(2,2-Bis(4-bromophenyl)vinyl)(p-tolyl)sulfane (**3ia**).* White solid. mp 131−133 °C. Yield: 55.9 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.40 (m, 2H), 7.38−7.36 (m, 2H), 7.32−7.24 (m, 2H), 7.21−7.19 (m, 2H), 7.18−7.12 (m, 2H), 7.06−7.04 (m, 2H), 6.81 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 137.6, 137.6, 137.4, 132.0, 131.8, 131.5, 131.5, 130.4, 130.1, 128.7, 127.1, 122.0, 121.4, 21.1. IR (Attenuated total reflection, cm^{-1}): 1488, 1392, 1067, 1011, 1006, 929, 807. HRMS (TOF MS EI$^+$) m/z calcd for [$C_{21}H_{16}{}^{79}Br_2S$] 457.9339, found 457.9340.

*(2,2-Bis(4-fluorophenyl)vinyl)(p-tolyl)sulfane (**3ja**).* White solid. mp 110−112 °C. Yield: 46.1 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.26 (m, 4H), 7.22−7.05 (m, 6H), 7.00−6.91 (m, 2H), 6.73 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 ($^1J_{CF}$ = 248.4 Hz), 138.1, 137.7, 137.7, 137.3, 136.6, 135.0, 135.0, 132.4, 131.6 ($^3J_{CF}$ = 8.0 Hz), 130.2, 130.0, 129.1, 128.8, 128.7, 127.9, 126.6, 126.5, 125.5,

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115.6 ($^2J_{CF}$ = 21.2 Hz), 21.1. IR (Attenuated total reflection, cm^{-1}): 1501, 1232, 1217, 1155, 844, 815, 784. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{21}H_{16}F_2S$] 338.0941, found 338.0937.

*(2-(4-Fluorophenyl)-2-phenylvinyl)(p-tolyl)sulfane (**3ka**).* White solid. mp 89−91 °C. Yield: 49.2 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.39 (m, 1H), 7.37−7.31 (m, 4H), 7.30−7.16 (m, 4H), 7.16−7.03 (m, 3H), 6.99−6.92 (m, 1H), 6.80 (s, 0.45H), 6.74 (s, 0.49H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 ($^1J_{CF}$ = 248.4 Hz), 146.5, 141.4, 139.1, 139.1, 138.7, 137.8, 137.8, 137.2, 137.2, 136.6, 135.2, 135.1, 132.7, 132.5, 131.6, 131.6, 130.2, 130.2, 130.0, 130.0, 129.7, 129.1, 128.8, 128.8, 128.5, 128.4, 127.9, 127.9, 127.3, 127.1, 126.6, 126.5, 125.6, 125.2, 125.2, 115.5 ($^2J_{CF}$ = 21.2 Hz), 21.1. IR (Attenuated total reflection, cm^{-1}): 1599, 1505, 1491, 1220, 1156, 1017, 933. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{21}H_{17}FS$] 320.1035, found 320.1042.

*(2-(4-Chlorophenyl)-2-phenylvinyl)(p-tolyl)sulfane (**3la**).* White solid. mp 55−57 °C. Yield: 41.1 mg (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.27 (m, 7H), 7.26−7.18 (m, 3H), 7.18−7.11 (m, 3H), 6.81 (s, 0.43H), 6.80 (s, 0.47H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.0, 138.9, 138.8, 138.7, 137.7, 137.3, 137.3, 133.6, 132.97, 132.5, 132.4, 131.25, 130.3, 130.2, 130.0, 129.7, 128.7, 128.5, 128.5, 128.4, 128.4, 128.0, 127.4, 127.2, 126.2, 126.0, 21.1. IR (Attenuated total reflection, cm^{-1}): 1490, 1441, 1397, 1090, 1009, 945, 936, 806, 775. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{21}H_{17}{}^{35}ClS$] 336.0740, found 336.0738.

*(2-(4-Bromophenyl)-2-phenylvinyl)(p-tolyl)sulfane (**3ma**).* Light yellow solid. mp 70−72 °C. Yield: 42.6 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.51 (m, 1H), 7.43−7.31 (m, 6H), 7.26−7.19 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.11−7.06 (m, 1H), 6.81 (s, 0.47H), 6.81 (s, 0.52H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.5, 138.9, 138.7, 138.7, 138.2, 137.3, 137.3, 136.6, 132.5, 132.4, 131.6, 131.6, 131.4, 130.4, 130.2, 130.0, 129.7, 129.1, 128.7, 128.6, 128.4, 128.4, 128.0, 127.9, 127.4, 127.2, 126.6, 126.4, 126.0, 121.8, 121.1, 21.1. IR (Attenuated total reflection, cm^{-1}): 1491, 1442, 1090, 1045, 1010, 880, 804, 698. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{21}H_{17}BrS$] 380.0234, found 380.0236.

*(2-(3-Bromophenyl)-2-phenylvinyl)(p-tolyl)sulfane (**3na**).* Colorless oil. Yield: 60.8 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.39 (m, 2H), 7.39−7.18 (m, 8H), 7.18−7.09 (m, 3H), 6.83 (s, 0.44H), 6.82 (s, 0.50H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 141.4, 141.0, 138.6, 138.5, 138.2, 137.4, 137.3, 132.7, 132.4, 132.4, 130.8, 130.5, 130.3, 130.0, 130.0, 129.9, 129.8, 129.7, 128.6, 128.6, 128.5, 128.0, 127.4, 127.4, 127.1, 126.6, 125.8, 122.6, 122.6, 21.2. IR (Attenuated total reflection, cm^{-1}): 1559, 1491, 1442, 1399, 1091, 1072, 947. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{21}H_{17}BrS$] 380.0234, found 380.0243.

*(2,2-Diphenylethene-1,1-diyl)bis(phenylsulfane) (**4aa**).*[19] Yellow solid. mp 98−100 °C. Yield: 39.6 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.22 (m, 10H), 7.20−7.15 (m, 6H), 7.15−7.10 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 142.1, 134.8, 131.2, 129.5, 129.5, 128.4, 128.0, 127.7, 126.8. IR (Attenuated total reflection, cm^{-1}): 1578, 1473, 1438, 1077, 1022, 963, 837. HRMS (TOF MS EI$^+$) *m*/*z* calcd for [$C_{26}H_{20}S_2$] 396.1006, found 396.1015.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01770.

Full spectroscopic data for compounds **3** and **4aa** and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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