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Ethynyl sulfides as participants in cascade cycloaromatizations

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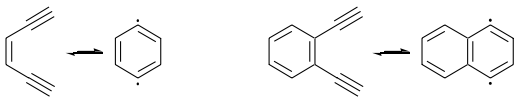
To Robert H. Grubbs for his many contributions to chemistry and his receipt of the Tetrahedron Prize

Abstract—Isomerization of soluble precursor compounds to produce fused-ring systems is an attractive approach for preparing conjugated polymers and oligomers. Cycloaromatization chemistry has previously been explored in this capacity employing reactions based on the Bergman cyclization. Using ethynyl sulfides with a terminal *o*-diethynylbenzene unit, an alternative strategy is demonstrated that offers selectivity advantages in the kinetically controlled radical cyclizations. The products are acene-fused thiophenes in which the diethynylsulfide acts as a relay for the diradical produced in a Bergman cyclization.

1. Introduction

Some of the most interesting properties of conjugated materials arise from molecules with high degrees of planarity and/or ring fusion. However, these structural features are often associated with poor solubility, hampering purification and application of these materials. A common strategy to avoid this problem is to add substituents, such as alkyl chains, that promote solubility.[1] The electronic properties of the compound in the solid state can be altered dramatically by such a perturbation because substituents often radically affect crystal packing. Alternative strategies that circumvent this concern employ soluble precursor routes such as Diels–Alder adducts[2–4] or silyl substituents on aromatic rings[5,6] during synthesis, purification, and sometimes deposition. Less well explored is the approach of producing conjugated materials by isomerization of a suitable precursor.[7–11] With this objective in mind, we explored cycloaromatization routes for the production of fused, conjugated molecules.

Cascade variants of the Bergman cyclization, a unique isomerization of an enediyne to a 1,4-didehydroarene[12,13] (Scheme 1), are a particularly intriguing route to conjugated oligomers and polymers and have attracted the attention of several groups.[8,9,14,15] The precursors are *cis*-substituted polyenynes or *ortho*-substituted arylene ethynylenes with generally good solubility, raising the expectation that fused



Scheme 1. Examples of the Bergman cyclization.

conjugated materials can be obtained from thermal isomerization either in solution or the solid state. The first examples of this approach concentrated on hydrocarbon systems. For example, Grubbs and Kratz constructed a precursor for a zipper reaction with the potential to lead to decorated graphite ribbons (Fig. 1).[8] However, differential scanning calorimetry indicated that a somewhat less exothermic reaction occurred than is expected for full aromatization. A related approach was pursued by Youngs and co-workers employing a cyclyne[16] (dehydrobenzoannulene with no alkenyl ring carbons) precursor with the potential to terminate the radical production intramolecularly to form a cyclic graphite ribbon (Fig. 1).[9] Neither of these approaches was reported to exclusively produce the desired cascade products.

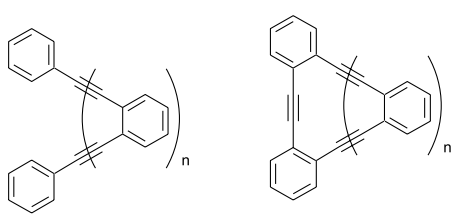


Figure 1. Oligomeric *ortho*-substituted arylene ethynylenes prepared by Grubbs (left)[8] and Youngs (right).[9] These compounds are potential precursors to fused acenes through a Bergman multicyclization.

Keywords: Bergman cyclization; Cycloaromatization; Cascade; Enediyne; Thiophene; Ethynyl sulfide; Diradical; Conjugated materials.
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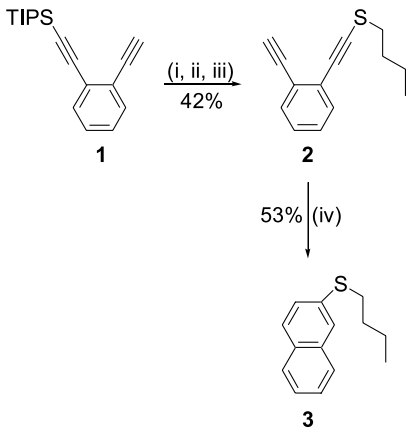
The failure of these synthetic routes to efficiently yield polyacenes can be traced to the tendency of five-membered cyclizations to proceed competitively with the desired six-membered ring formation. Model studies have shown, both experimentally[17] and theoretically,[18] that five-membered ring formation is favored over cyclization to produce six-membered rings. However, we hypothesized that if instead of the Bergman cyclization a five-membered ring cycloaromatization is employed, the competing four-membered ring cyclization would be much less favorable than the desired pathway. We have recently described the first five-membered ring cycloaromatization[19] involving the photochemical conversion of diethynyl sulfides to thiophenes through the presumed intermediacy of a thiophene-2,5-diyl. Although the reaction does not proceed well under thermal conditions the prospect of using a Bergman cyclization to trigger the five-membered ring cycloaromatization by a cascade reaction is an intriguing route to fused conjugated oligothiophenes.[20]

2. Approach

The Bergman cyclization of compounds with substituted ethynyl groups has been studied extensively.[21–24] In many cases the barrier for thermal reaction is substantially increased as a result of steric hindrance in the transition state. However, halogens and some other substituents lower the barrier for thermal reaction. Chlorine or bromine atoms on both triple bonds lower the temperatures required for cyclization and result in yields of 90 and 85%, respectively.[25] Surprisingly, little or no data exists for other chalcogenide-substituted ethynyl groups taking part in a Bergman cyclization. For example, attempts at the cycloaromatization of enediynyl ethyl ethers leads to retro-ene reactions to form enyne ketenes which further undergo the Moore cyclization.[26] Data have not been reported for sulfur, selenium, or tellurium.

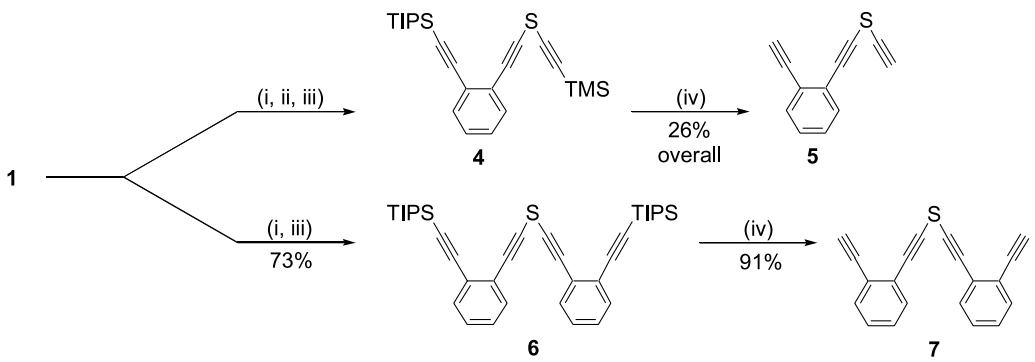
One aspect of concern, in the case of sulfur, is the potential for loss of the heteroatom from the 1,4-didehydroarene to produce an *o*-aryne radical. Accordingly, our initial investigation led us to determine the effect of sulfur on the Bergman cyclization for a simple model ethynyl sulfide: butyl *o*-diethynylbenzene sulfide **2**. The synthesis of this compound in protected form was achieved by treating mono TIPS-protected *o*-diethynylbenzene (**1**)[27] with excess butyllithium followed by quenching with SCl_2 (Scheme 2). One



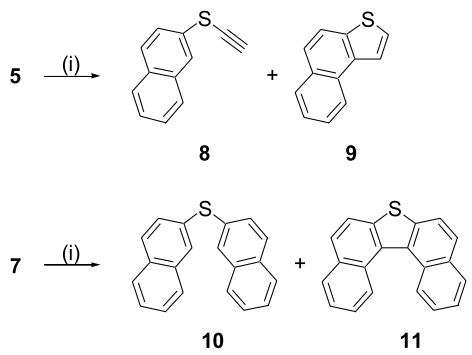
Scheme 2. Reagents and conditions: (i) BuLi, ether, −78 °C; (ii) SCl_2, ether, −78 °C; (iii) TBAF, THF, EtOH; (iv) benzene, CHD, 200 °C, 4 h.

equivalent of alkyllithium generates the acetylide and the remainder reacts with SCl_2 to attach a butyl chain. Treatment of this product with tetrabutylammonium fluoride (TBAF) leads to precursor **2**. Gratifyingly, the cyclization of this compound, effected by heating at 200 °C in benzene with 6 M 1,4-cyclohexadiene (CHD) as trapping agent, proceeded smoothly to afford 2-naphthyl butyl sulfide (**3**) in 53% yield. Competition experiments between **2** and *o*-diethynylbenzene[28] indicate that the presence of the sulfur atom increases the barrier to cyclization as evidenced by the decreased conversion of **2** relative to *o*-diethynylbenzene.[29] These observations are in agreement with computational predictions for an enediyne bearing an SH group attached to the triple bond.[24]

Having demonstrated the compatibility of ethynyl sulfides with the Bergman cyclization, the first cascade reaction was attempted. The precursor **4** was synthesized via deprotonation of a mixture of **1** and excess trimethylsilylacetylene using butyllithium followed by quenching with SCl_2 (Scheme 3). Deprotection with TBAF (Scheme 3) yielded *o*-diethynylbenzene ethynyl sulfide **5**. This compound, like many hydrogen-terminated ethynyl sulfides, is particularly prone to decomposition upon exposure to heat and light. Heating **5** to 200 °C for 4 h in the presence of CHD (0.10–10.5 M in benzene) afforded a mixture of naphthalenes (Scheme 4). Surprisingly, the major compound was not the expected naphtho[2,1-*b*]thiophene (**9**), but rather ethynyl 2-naphthyl sulfide (**8**). This indicates that cyclization of the initially formed arene radical onto the triple bond is not fast



Scheme 3. Reagents and conditions: (i) BuLi, ether, −78 °C; (ii) trimethylsilylacetylene; (iii) SCl_2, ether, −78 °C; (iv) TBAF, THF, EtOH.



Scheme 4. Reagents and conditions: (i) benzene, CHD, 200 °C, 4 h.

compared to intermolecular trapping by CHD under these conditions. Although decreasing the concentration of trapping agent led to the expected shift in product ratio towards the thiophene product (**9**), **8** was always the overwhelmingly preferred isomer. Increasing the yield of **9** by using much lower concentrations of CHD was not successful as a result of the tendency of polymerization to compete with small molecule production.[30] Indeed a challenge with **2** and related substrates is the poor thermal stability of the free ethynyl sulfide as evidenced by rapid darkening of the pure substances at room temperature.

In order to circumvent the stability problems associated with free ethynyl sulfides, a cyclization precursor was employed lacking this reactive functionality. The cascade cyclization of bis(*o*-diethynylbenzene)sulfide **7**[31] was expected to afford dinaphtho[2,1-*b*:1′,2′-*d*]thiophene (**11**) through an initial 1,4-diradical followed by cyclization onto the ethynyl sulfide and subsequent naphthalene ring formation (Scheme 4). This last step might also be expected to proceed with five-membered ring formation to create a terminal benzofulvene which would presumably further react under the conditions employed.[17] Performing experiments on **7** under the same conditions as **5** led to the cascade product **11** which was obtained in 10% yield with 0.8 M CHD after heating to 200 °C for 4 h. The yield of **11** is remarkable considering the fact that there is substantial steric interaction between hydrogens in the 'bay region' of this compound.[32] In contrast to **5**, cyclization onto the ethynyl sulfide competes more equally with intermolecular trapping as evidenced by the 11% yield of bis(2-naphthyl)-sulfide (**10**) under these conditions. Although product **10** is expected to arise from independent cyclization and trapping of each *o*-diethynylbenzene unit, cascade reaction is a more energetically viable approach to **11** in order to avoid invoking a tetraradical intermediate. At lower concentrations of CHD, formation of **11** is favored over that of **10**. However, once the concentration of CHD is greater than ~0.6 M, **10** is trapped preferentially (Tables 1 and 2).

3. Conclusions

Ethynyl sulfides are compatible with the Bergman cyclization as demonstrated by reactions in which one, two or three rings are formed through cycloaromatization. As demonstrated in the synthesis of dinaphthylthiophene, conjugated compounds can be produced by this route. The potential to extend these studies to longer oligoethynylsulfides[33] suggests a promising entry to fused conjugated materials including higher thienoacenes.[20]

Table 1. Yields and relative ratios of products **8** and **9** from the cyclization of **5** at 200 °C

[CHD] (M)	Yield **8** (%)	Yield **9** (%)	**8/9**
0.1	3.9	1.0	3.7
0.2	8.2	1.9	4.4
0.4	11	2.3	4.7
0.6	14	2.0	6.9
0.8	16	2.1	7.4
1	18	1.9	9.5
2	18	1.3	14
4	18	0.68	27
8	12	0.67	18
10.5	9.4	0.52	18

Table 2. Yields and relative ratios of products **10** and **11** from the cyclization of **7** at 200 °C

[CHD] (M)	Yield **10** (%)	Yield **11** (%)	**10/11**
0.1	0.96	3.2	0.30
0.2	1.9	5.1	0.38
0.4	3.6	7.2	0.50
0.6	7.4	8.6	0.86
0.8	11	9.9	1.2
1	13	9.0	1.5
2	22	9.2	2.4
4	33	8.1	4.1
8	38	4.5	8.4
10.5	41	3.4	12

4. Experimental

4.1. General

Cycloaromatizations employed solutions of the cyclization precursors (3.5 mM) in benzene with CHD. Aliquots (0.5 mL) of the stock solutions were degassed with three freeze/pump/thaw cycles and sealed in glass tubes under vacuum. Reactions were performed in a Parr Reactor, containing benzene to balance the internal pressure of the tubes, equipped with a 4835 control unit. Yields were measured by gas chromatography employing *m*-terphenyl as an internal standard on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector. Product identity was confirmed by GC–MS using a ThermoQuest Trace GC equipped with a Finnigan Polaris/GCQ Plus Ion Trap MS by comparison of retention times and mass fragmentation patterns to those of authentic samples prepared by independent routes (vide infra). ^{1}H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm. Infrared absorption spectra were collected on a Nicolet Avatar 360 IR spectrometer. Elemental analysis and high-resolution mass spectrometry data were provided by the University of Michigan Analytical Laboratory. Ether and THF were dried by passage through activated alumina. CHD was filtered through silica gel prior to use. All other reagents were used as received. All reactions were conducted under nitrogen atmosphere. Compounds **1**,[27] **3**,[34] **9**,[35] **10**,[36] and **11**[35] were synthesized as described in the literature.

4.1.1. Butyl *o*-diethynylbenzene sulfide 2. A solution of **1** (382 mg, 1.35 mmol) in ether (30 mL) was cooled to −78 °C. BuLi (1.6 M in hexanes, 9.50 mL, 15.2 mmol) was added dropwise and allowed to stir for 1 h. A solution of SCl_2 (0.440 mL, 6.93 mmol) in ether (10 mL) cooled to 0 °C was added dropwise via cannula. The mixture was allowed to stir for 1 h and then warmed over 2 h. Quenching with water (75 mL) was followed by extraction with hexanes (3×50 mL). The organic layers were combined, washed with brine (2×150 mL), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (hexanes) yielded 2 with the triple bond protected as the ethynyl triisopropylsilyl group (241 mg of a pale yellow oil, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.43 (m, 1H), 7.41–7.37 (m, 1H), 7.25–7.17 (m, 2H), 2.82 (t, J=7.3 Hz, 2H), 1.78 (tt, J=7.4, 7.4 Hz, 2H), 1.48 (qt, J=7.4, 7.3 Hz, 2H), 1.16 (s, 21H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.62, 131.85, 127.93, 127.38, 126.37, 125.53, 105.33, 94.85, 91.59, 84.19, 35.59, 31.39, 21.38, 18.64, 13.51, 11.26; GC–MS (EI) *m*/*z* (% relative intensity) 370 (42, M^+), 327 (100), 303 (8), 285 (10), 271 (8), 257 (16), 247 (19), 229 (41), 219 (28), 201 (52), 195 (28), 181 (33), 167 (14), 141 (14); IR (film) 3060, 2958, 2941, 2891, 2864, 2160, 1475, 1464, 1440, 1382, 1365, 1272, 1232, 1203, 1159, 1099, 1072, 1016, 995, 946, 918, 883, 814, 756, 677, 665, 636 cm^{-1}. Anal. Calcd for $C_{23}H_{34}SSi$: C, 74.53; H, 9.35. Found: C, 74.11; H, 9.11.

Removal of the TIPS group from the above sulfide (153 mg, 0.411 mmol) was achieved by stirring in THF (2.5 mL) with TBAF (1.0 M in THF, 0.81 mL, 0.81 mmol) and EtOH (0.05 mL) until starting material was consumed as indicated by TLC analysis. The mixture was added to water (10 mL) and extracted with hexanes (3×10 mL). The organic layers were combined, washed with brine (2×30 mL), and dried over anhydrous Na_2SO_4. Flash chromatography (9:1, hexanes/CH_2Cl_2), yielded **2** as a pale yellow oil (88.2 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.46 (m, 1H), 7.40–7.37 (m, 1H), 7.29–7.25 (m, 1H), 7.24–7.20 (m, 1H), 3.27 (s, 1H), 2.83 (t, J=7.3 Hz, 2H), 1.85 (tt, J=7.4, 7.4 Hz, 2H), 1.49 (qt, J=7.5, 7.4 Hz, 2H) 0.96 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.58, 131.20, 128.53, 127.32, 126.73, 123.86, 91.55, 84.71, 80.72, 80.69, 35.63, 31.29, 21.38, 15.53; GC–MS (EI) *m*/*z* (% relative intensity) 214 (51, M^+), 184 (9), 158 (100), 114 (33); IR (film) 3300, 3286, 3061, 2958, 2929, 2872, 2168, 2108, 1475, 1438, 1379, 1255, 1225, 1159, 1095, 1036, 935, 916, 874, 756, 650 cm^{-1}. HRMS-EI (*m*/*z*): M^+ calcd for $C_{14}H_{14}S$, 214.0816; found, 214.0822.

4.1.2. Triyne 4. A solution of **1** (694.1 mg, 2.46 mmol) in ether (80 mL) was cooled to −78 °C. BuLi (2.5 M in hexanes, 9.65 mL, 24.1 mmol) was added dropwise followed by slow addition of trimethylsilylacetylene (3.10 mL, 22.4 mmol). After stirring 2 h, a solution of SCl_2 (0.770 mL, 12.1 mmol) in ether (30 mL) cooled to 0 °C was added dropwise via cannula. The mixture was allowed to stir for 2 h and then warmed over 2 h. Quenching with water (150 mL) was followed by extraction with hexanes (3×100 mL). The organic layers were combined, washed with brine (2×150 mL), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (hexanes) yielded **4** (567 mg, 56%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.29–7.23 (m, 2H), 1.16 (s, 21H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.45, 132.38, 128.60, 127.96, 126.47, 125.10, 104.69, 103.24, 95.75, 93.82, 86.03, 75.34, 18.64, 11.22, −0.46; GC–MS (EI) *m*/*z* (% relative intensity) 410 (1.3, M^+) 367 (34), 325 (75), 299 (50), 283 (100), 251 (61), 235 (85), 223 (41), 219 (31), 209 (31), 195 (36), 191 (15), 165 (13), 149 (7), 115 (6); IR (film) 3063, 2958, 2943, 2891, 2866, 2160, 2104, 1475, 1464, 1441, 1383, 1365, 1252, 1234, 1203, 1159, 1099, 1072, 1037, 1016, 995, 949, 920, 871, 845, 812, 758, 700, 677, 665, 635 cm^{-1}. Anal. Calcd for $C_{24}H_{34}SSi_2$: C, 70.18; H, 8.34. Found: C, 69.92; H, 8.21.

4.1.3. *o*-Diethynylbenzene ethynyl sulfide 5. The compound was more conveniently prepared by the same method as **4** without isolation of the deprotected intermediates; **1** (609 mg, 2.16 mmol), trimethylsilylacetylene (2.62 mL, 18.9 mmol), BuLi (2.5 M in hexanes, 8.50 mL, 21.3 mmol), and SCl_2 (0.675 mL, 10.6 mmol). After removal of the trimethylsilyl group by stirring in ether (2.5 mL) and MeOH (2.5 mL) with K_2CO_3 (6 mg) until starting material was consumed as indicated by TLC analysis, the crude material was poured into water (10 mL) and extracted with hexanes (3×10 mL). The organic layers were combined, washed with brine (2×10 mL), and dried over anhydrous Na_2SO_4. The solvent and diethynylsulfide byproduct were removed by rotary evaporation. The triisopropylsilyl group was removed by dissolution of the crude material in THF (5 mL) and stirring with TBAF (8.4 mL, 8.4 mmol) and EtOH (0.20 mL) until all starting material was consumed as indicated by TLC analysis. The mixture was added to water (20 mL) and extracted with hexanes (3×20 mL). The organic layers were combined, and washed with brine (2×60 mL), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (9:1, hexanes/CH_2Cl_2) yielded **5** (103 mg, 26%) as an unstable yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.44 (m, 2H), 7.35–7.27 (m, 2H), 3.33 (s, 1H), 3.02 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.55, 131.93, 128.64, 128.49, 124.98, 124.71, 93.72, 84.13, 81.57, 81.46, 75.04, 67.50; IR (film) 3288, 3063, 2177, 2108, 2054, 1963, 1917, 1475, 1441, 1095, 1036, 953, 876, 758, 690, 656, 625 cm^{-1}. HRMS-EI (*m*/*z*): M^+ calcd for $C_{12}H_6S$, 182.0190; found, 182.0194.

4.1.4. Tetrayne 6. A solution of **1** (952.2 mg, 3.37 mmol) in ether (50 mL) was cooled to −78 °C. BuLi (1.6 M in hexanes, 2.10 mL, 3.36 mmol) was added dropwise and the reaction mixture allowed to stir for 2 h. A solution of SCl_2 (0.110 mL, 1.73 mmol) in ether (10 mL) cooled to 0 °C was added dropwise via cannula. The mixture was allowed to stir for 1 h and then warmed over 2 h. Quenching with water (100 mL) was followed by extraction with hexanes (3×100 mL). The organic layers were combined, washed with brine (2×150 mL), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (9:1, hexanes/CH_2Cl_2) yielded **6** (731 mg, 73%) as a viscous yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.44 (m, 4H), 7.26 (td, J=7.5, 2.1 Hz, 4H), 1.15 (s, 42H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.38, 132.06, 128.37, 127.87, 126.20, 125.10, 104.65, 95.68, 93.40, 75.82, 18.68, 11.31; MS (EI, 70 eV) *m*/*z* (% relative intensity) 594 (35, M^+) 551 (17), 509 (34), 467 (27), 425 (21), 321 (14), 239 (26), 157 (67), 115 (100); IR (film)

3061, 2956, 2943, 2891, 2864, 2160, 1558, 1475, 1464, 1441, 1383, 1365, 1275, 1234, 1203, 1159, 1097, 1072, 1036, 1016, 995, 949, 920, 883, 845, 812, 756, 677, 665, 636 cm^{-1}; HRMS-EI (*m*/*z*): M^+ calcd for $C_{38}H_{50}SSi_2$, 594.3172; found, 594.3157. Anal. Calcd for $C_{38}H_{50}SSi_2$: C, 76.60; H, 8.47. Found: C, 76.74; H, 8.37.

4.1.5. Bis(*o*-diethynylbenzene)sulfide 7. Removal of the triisopropylsilyl group from **6** (405 mg, 0.681 mmol) was achieved by stirring in THF (10 mL) with TBAF (1.0 M in THF, 2.70 mL, 2.70 mmol) and EtOH (0.80 mL) until TLC analysis indicated complete consumption of **6**. The mixture was added to water (20 mL) and extracted with ether (3×20 mL). The organic layers were combined, washed with brine (2×60 mL), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (9:1, petroleum ether/CH_2Cl_2) yielded **7** (175 mg, 91%) as an unstable yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.52–7.46 (m, 4H), 7.33–7.27 (m, 4H), 3.33 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.81, 132.16, 128.76, 128.75, 125.50, 124.91, 93.41, 81.90, 81.82, 76.49; IR (KBr) 3286, 3059, 2168, 2112, 1446, 1439, 1332, 1275, 1252, 1203, 1194, 1165, 1095, 1038, 955, 870, 771, 762, 665, 650, 631, 575, 555, 532, 509, 463 cm^{-1}. HRMS-EI (*m*/*z*): M^+ calcd for $C_{20}H_{10}S$, 282.0503; found, 282.0509.

4.1.6. Ethynyl 2-naphthyl sulfide (8). A solution of 2-bromonaphthalene (531 mg, 2.56 mmol) in ether (20 mL) was cooled to 0 °C. *t*-BuLi (1.5 M in pentane, 3.40 mL, 5.44 mmol) was added dropwise and stirred five minutes. Trimethylsilylacetylene (0.175 mL, 1.27 mmol) was added slowly and stirred 30 min. SCl_2 (0.080 mL, 1.126 mmol) was added dropwise and stirred 1 h. After quenching with NH_4Cl (sat, 3 mL), the mixture was poured into water (40 mL) and extracted with hexanes (3×20 mL). The combined organic layers were washed with brine (2×60 mL) and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (hexanes) yielded 2-naphthyl trimethylsilylacetylene sulfide (37.5 mg, 15%) as an orange-yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90–7.88 (m, 1H), 7.84–7.80 (m, 2H), 7.78–7.75 (m, 1H), 7.52–7.44 (m, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.77, 132.09, 129.65, 128.97, 127.87, 127.15, 126.88, 126.03, 124.63, 124.09, 106.63, 90.21, −0.17; GC–MS (EI) *m*/*z* (% relative intensity) 256 (100, M^+), 243 (30), 241 (24), 225 (21), 165 (20), 127 (5), 115 (5), 75 (18); IR (film) 3057, 2958, 2926, 2899, 2852, 2096, 1626, 1587, 1502, 1452, 1410, 1342, 1250, 1132, 1070, 964, 951, 883, 843, 818, 760, 743, 700, 627 cm^{-1}.

Removal of the trimethylsilyl group from 2-naphthyl trimethylsilylacetylene sulfide (24.5 mg, 0.956 mmol) was achieved by stirring in ether (2 mL) and MeOH (2 mL) with K_2CO_3 (5 mg) until all starting material was consumed as indicated by TLC analysis. The mixture was poured into water (10 mL) and extracted with hexanes (3×10 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. (16.2 mg, 92%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.94–7.92 (m, 1H), 7.84–7.77 (m, 3H), 7.53–7.46 (m, 3H), 3.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.67, 132.08, 129.00, 128.69, 127.79, 127.11, 126.87, 126.11, 125.05, 124.28, 87.06, 71.06; GC–MS (EI) *m*/*z* (% relative intensity) 184 (100, M^+), 152 (51), 139 (25), 126 (11), 115 (8); IR (KBr) 3259, 3053, 2955, 2924, 2852, 2037, 1622, 1587, 1483, 1271, 1240, 1196, 1132, 1063, 960, 941, 891, 858, 812, 748, 714, 584, 563, 478, 467, 457 cm^{-1}. HRMS-EI (*m*/*z*): M^+ calcd for $C_{12}H_8S$, 184.0346; found, 184.0344.

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References and notes

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