JOC The Journal of Organic Chemistry

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Iodine-Catalyzed Methylthiolative Annulation of 2-Alkynyl Biaryls with DMSO: A Metal-Free Approach to 9-Sulfenylphenanthrenes

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Cite This: J. Org. Chem. 2021, 86, 7881−7890 Read Online

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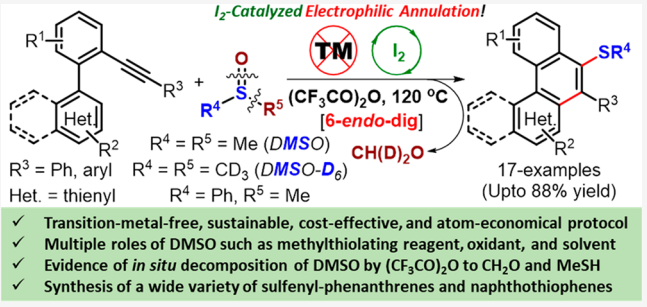
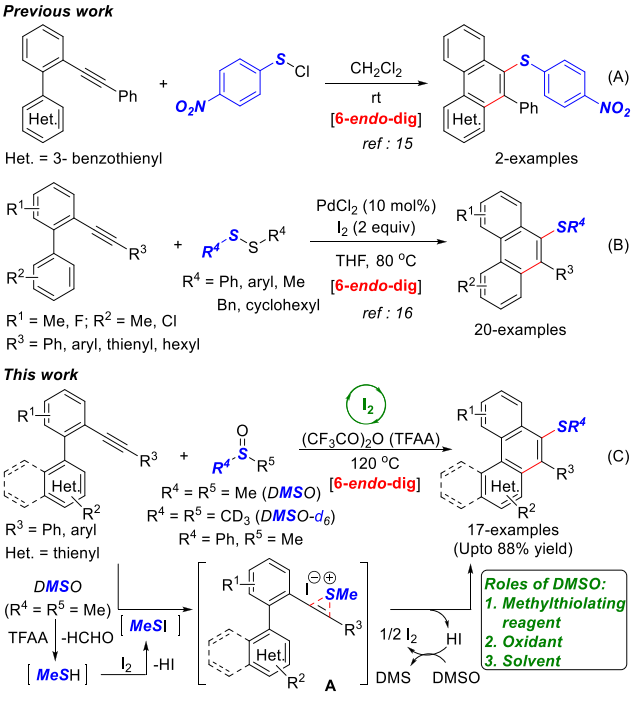
ABSTRACT: An iodine-catalyzed sustainable, cost-effective, and atom-economic synthetic methodology is developed to synthesize a wide variety of valuable sulfenylphenanthrenes and polycyclic heteroaromatics in moderate to high yield through electrophilic thiolative annulation of 2-alkynyl biaryls (6-*endo*-*dig* cyclization) using methyl sulfoxides such as dimethyl sulfoxide (DMSO) as the sulfur source under transition-metal-free conditions. The transformation requires only iodine in a catalytic amount and trifluoroacetic anhydride. Notably, DMSO played multiple roles such as methylthiolating reagent, oxidant, and solvent in this reaction.



Phenanthrenes, one of the important classes of polycyclic aromatic hydrocarbons, are ubiquitous in numerous biologically active compounds including natural products[1] and exhibit a broad spectrum of biological activities such as antiviral,[2] antimicrobial,[3] anticancer,[4] antitumor,[5] and anti-HIV[6] activity. Moreover, phenanthrene derivatives also exhibit interesting electronic[7] and optical[8] properties and are utilized in various useful materials, such as organic field-effect transistors[9] and solar cells.[10] Consequently, several synthetic strategies have been developed so far for the synthesis of phenanthrenes.[11,12] Among them, two synthetic strategies, i.e., transition-metal (TM) (Pd, Ir, Rh, and Fe)-catalyzed or visible-light photocatalyzed [4 + 2]-benzannulation of 2-functionalized 1,1′-biaryls with alkynes[13] and transition-metal (Pt, Au, Ga, Ir, Ru, Fe, and Sn)-catalyzed/mediated intramolecular carbocyclization or electrophilic annulation of 2-alkynyl biaryls (6-*endo*-*dig* cyclization) are widely employed, perhaps because of their high atom-economical feature and the requirement of relatively less prefunctionalized starting materials.[14] Despite significant advancement, the above-mentioned synthetic methods suffer from at least one of the following severe limitations, such as the requirement of (a) expensive and toxic transition-metal salts or complexes in catalytic or (sub)stoichiometric amounts, (b) expensive and hazardous ligand and reagents, (c) harsh or critical reaction conditions, and (d) limited substrate scope. In 2005, Larock et al. disclosed a transition-metal-free, electrophilic 6-*endo*-*dig* cyclization of 2-alkynyl biaryls with ICl, *N*-bromosuccinimide (NBS), and *p*-$O_2NC_6H_4SCl$ to synthesize 9-halo (I and Br)- and 9-(4-nitrophenyl)sulfenylphenanthrenes, respectively (Scheme 1 A).[15]

However, the requirement of a highly electrophilic arylsulfenyl chloride, *p*-$O_2NC_6H_4SCl$, and its commercial

Scheme 1. General Synthetic Strategies to 9-Sulfenylphenanthrenes



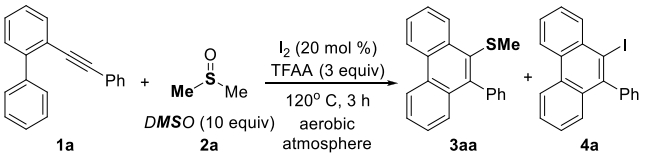
Received: April 14, 2021
Published: May 24, 2021

https://doi.org/10.1021/acs.joc.1c00861
J. Org. Chem. 2021, 86, 7881−7890

nonavailability eventually limited this method's scope to access 9-sulfenylphenanthrenes. In 2014, Qian and Zhang et al. reported a Pd-catalyzed general synthetic strategy for synthesizing 9-sulfenylphenanthrenes through electrophilic annulation of 2-alkynyl biaryls with diphenyl disulfides in the presence of 2 equiv of iodine (Scheme 1 B).[16] Despite broad substrate scope to access 9-sulfenylphenanthrenes, this method also suffered from several limitations such as the requirement of expensive, toxic, and rare transition-metal (Pd) catalysts in substoichiometric amounts (10 mol %), super stoichiometric (2 equiv) iodine, and relatively lower atom-economy of the reaction as only 0.5 equiv of the disulfide was utilized in the reaction. Herein, we designed and developed a TM-free, sustainable, cost-effective, and atom-economical synthetic strategy for the methylthiolative or phenylthiolative annulation of 2-alkynyl biaryls by using inexpensive and commercially available methyl sulfoxides such as DMSO as the source of thiomethyl group (−SMe), iodine (I_2) as the catalyst, and TFAA as a reagent to synthesize a wide variety of 9-sulfenylphenanthrenes and polycyclic heteroaromatics, i.e., naphthothiophenes (Scheme 1 C). We hypothesized that in the presence of iodine an electrophilic species, i.e., methyl sufenyl iodide (MeSI), could be generated through the *in situ* decomposition of DMSO by an electrophilic reagent such as TFAA into formaldehyde and thiomethanol.[16,17] Subsequently, the electrophilic methylthiolative annulation of 2-alkynyl biaryls with MeSI would furnish the desired product, 9-sulfenylphenanthrenes, via the formation of intermediate **A**.[16] During the reaction, HI is formed, which will be oxidized by DMSO under the reaction conditions to regenerate iodine in the catalytic cycle.[18] The unique feature of this protocol is the cost-effective, atom-economic, and sustainable synthetic approach to a wide variety of 9-sulfenylphenanthrenes and polycyclic heteroaromatics from readily available 2-alkynyl biaryls and DMSO, which played multiple roles such as methylthiolating reagent, oxidant, and solvent in the reaction. In recent times, DMSO has been utilized as the source of a thiomethyl (−SMe) group in developing a few transition-metal-catalyzed C−H methylthiolation reactions[19] and radical coupling reactions under TM-free conditions.[20]

We commenced our investigation of methylthiolative annulation of 2-(phenylethynyl)-1,1′-biphenyl **1a** with 10 equiv DMSO **2a** using iodine and TFAA at 120 °C under an aerobic atmosphere. To our delight, when the reaction was conducted using 20 mol % of I_2 and 3 equiv of TFAA for 3 h, 91% of the desired product, methyl(10-phenylphenanthren-9-yl)sulfane **3aa** was formed along with a trace amount of 9-iodo-10-phenylphenanthrene **4a** (entry 1, Table 1). However, only 50% **3aa** was formed using 10 mol % of I_2 (entry 2, Table 1). When 20 mol % of tetrabutylammonium iodide (TBAI) was used instead of I_2, 65% of **3aa** was formed (entry 3, Table 1). Among various electrophilic reagents such as TFAA, acetic anhydride, CF_3SO_2Cl, and p-$NO_2C_6H_4SO_2Cl$, TFAA was found to be the best (entries 5−7 vs entry 1, Table 1). The use of 3 equiv of TFAA was found optimum for the reaction (entries 4 and 8 vs entry 1, Table 1). Lowering of reaction temperature from 120 °C had a negative impact on the reaction outcome; no product was formed at room temperature (entries 9 and 10 vs entry 1, Table 1). Lowering the stoichiometry of DMSO also negatively impacted the reaction outcome (entry 11, vs entry 1, Table 1). The use of inorganic and organic bases such as Na_2CO_3, K_3PO_4, and Et_3N also harmed the reaction's outcome (entries 12−14, Table 1). The

Table 1. Optimization of the Reaction Conditions[a]



entry	variation in conditions from scheme	yield[b] (%) 3aa	4aa
1.	none	91	trace
2.	10 mol % of I_2	50	trace
3.	20 mol % of TBAI was used instead of I_2	65	trace
4.	4 equiv of TFAA was used	90	8
5.	4 equiv of Ac_2O was used instead of TFAA	0	0
6.	4 equiv of CF_3SO_2Cl was used instead of TFAA	60	
7.	4 equiv of p-$NO_2C_6H_4SO_2Cl$ was used instead of TFAA	20	trace
8.	2 equiv of TFAA was used	55	trace
9.	reaction was conducted at 100 °C	30	trace
10.	reaction was conducted at room temperature (25 °C)	0	0
11.	5 equiv of DMSO was used	40	0
12.	3 equiv of Na_2CO_3 was used	7	trace
13.	3 equiv of K_3PO_4 was used	trace	trace
14.	3 equiv of Et_3N was used	trace	trace
15.	reaction was conducted without I_2 (blank experiment)	0	0
16.	reaction was conducted without TFAA (blank experiment)	0	0
17.	reaction was conducted under Ar atmosphere	trace	trace
18.	**reaction was conducted for 1.5 h** (conditions A)	**91**	**trace**
19.	reaction was conducted in toluene (0.4 M) using 2 equiv of DMSO for 22 h	60	trace
20.	**reaction was conducted in toluene (0.4 M) using 3 equiv of DMSO for 22 h** (conditions B)	**92**	**trace**
21.	reaction was conducted in m-xylene (0.4 M) using 3 equiv of DMSO for 22 h	60	15
22.	reaction was conducted in DMF (0.4 M) using 3 equiv of DMSO for 22 h	trace	trace

[a]All of the reactions were conducted on a 0.1 mmol scale. [b]Yield of the products was determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

blank experiments revealed the essential roles of iodine and TFAA in this reaction (entries 15 and 16, Table 1). Notably, a trace amount of **3aa** was formed when the reaction was conducted under an argon atmosphere (entry 17, Table 1). Thus, heating the reaction mixture of **1a** with 10 equiv of DMSO **2a** in the presence of 20 mol % I_2 and 3 equiv of TFAA at 120 °C under aerobic atmosphere for 1.5 h (conditions A) was found as the optimum conditions to furnish **3aa** in 91% yield (entry 18, Table 1).

To decrease the methyl sulfoxide loading, which would be useful for the reactions with other methyl sulfoxides, particularly the ones with a high melting point, we conducted several experiments using another solvent and DMSO. Among various solvents such as toluene, m-xylene, and DMF, toluene was found to be the best (entries 19−22, Table 1), and by using the same, the stoichiometry of DMSO could be lowered to 3 equiv. The reaction of **1a** with 3 equiv of **2a** in the presence of 20 mol % I_2 and 3 equiv of TFAA in toluene (0.4 M) at 120 °C under aerobic atmosphere (conditions B) furnished **3aa** in 92% yield (entry 20, Table 1). The full optimization table (Table S1) is given in the Supporting Information (SI).

https://doi.org/10.1021/acs.joc.1c00861
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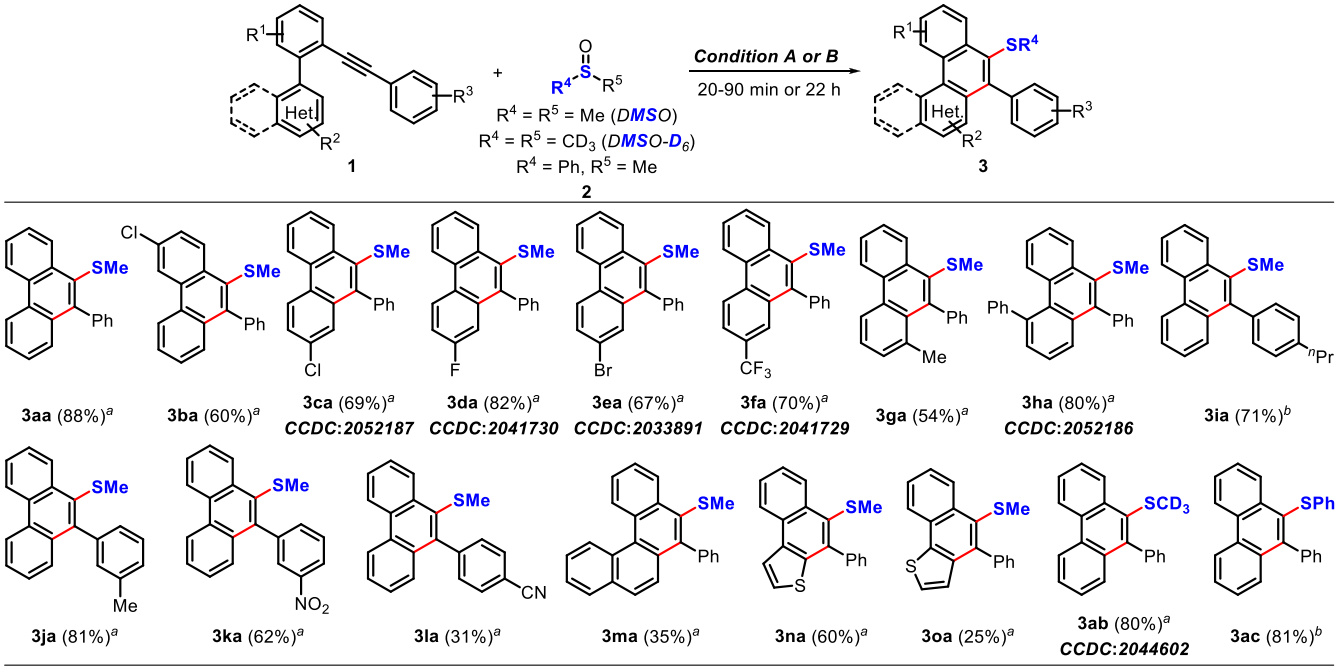
Scheme 2. Substrate Scope[a−c]



[a]Reaction conditions A: **1** (0.5 mmol), **2** (10 equiv), I_2 (20 mol %), TFAA (3 equiv), 120 °C. [b]Reaction conditions B: **1** (0.5 mmol), **2** (3 equiv), I_2 (20 mol %), TFAA (3 equiv), toluene (0.4 M), 120 °C. [c]Yield of product was reported in parentheses.

Next, we explored the scope of 2-(arylethynyl)-1,1′-biaryls for the methythiolative annulation reaction with DMSO under conditions A or B (Scheme-2). Various electron-withdrawing and -donating group substituted 2-(phenylethynyl)-1,1′-biaryls participated in the reaction with DMSO smoothly under conditions A to furnish 10-phenyl-9-sulfenylphenanthrenes (**3ba**−**3ha**) in moderate to high yield. Notably, various halogens (Br, Cl, and F) were found intact in the various positions of phenanthrenes, which could further be utilized for the products' synthetic diversification via cross-coupling reaction. Moreover, electron-donating and -withdrawing group substituted 2-(arylethynyl)-1,1′-biphenyls also underwent methythiolative annulation reaction with DMSO under conditions A or B to furnish 10-aryl-9-sulfenylphenantheres (**3ia**−**3la**) in moderate to high yield except 2-(4-cyanophenylethynyl)-1,1′-biphenyl, which furnished the corresponding product, 4-(10-(methylthio)phenanthren-9-yl)benzonitrile (**3la**) in 31% yield. When 1-(2-(phenylethynyl)phenyl)-naphthalene was subjected to reaction with DMSO under conditions A, 6-phenyl-5-sulfenyl benzo[*c*]phenanthrene **3ma** was formed in low yield (35%). The 2-heteroaryl-substituted phenylethynylbenzenes also participated in the reaction with DMSO to furnish the corresponding polycyclic heteroaromatics such as naphthothiophenes (**3na** and **3oa**).

Significantly, the methylthiolative annulation was found to be highly regioselective since only one regioisomer, 5-(methylthio)-4-phenylnaphtho[2,1-*b*]thiophene **3na** was formed from 3-(2-(phenylethynyl)phenyl)thiophene **1n**, which also supported the electrophilic annulation reaction. The reaction of 2-(phenylethynyl)-1,1′-biphenyl **1a** with DMSO-d_6 **2b** under conditions A furnished (methyl-d_3)(10-phenylphenanthren-9-yl)sulfane **3ab** in 80% yield, which further supported that the source of the thiomethyl group is DMSO. When methyl phenyl sulfoxide **2c** was subjected to reaction with **1a** under conditions B, 81% of phenyl(10-phenylphenanthren-9-yl)sulfane **3ac** was formed. The structures of **3ca**, **3da**, **3ea**, **3fa**, **3ha**, and **3ab** were confirmed by X-ray crystallographic structure determination (see Figures S1−S6 and Table S2). In all of the reactions, the corresponding 9-iodophenanthrene was formed as the sole side product in 2−15% yield. In the reactions which produced the desired product in moderate yield, the corresponding starting material, i.e., 2-alkynyl biaryl, was also recovered.

To shed light on the reaction mechanism, we carried out few reactions, as outlined in Scheme 3. The reaction of **1a** with diphenyl sulfoxide did not furnish **3ac** (Scheme 3 A), which revealed the requirement of methyl sulfoxides to synthesize 9-sulfenylphenanthrenes from 2-alkynyl biaryls. A couple of radical quenching experiments of the model reaction in between **1a** and DMSO **2a** in the presence of a radical quencher such as galvinoxyl (Scheme 3 B) and butylated hydroxytoluene (BHT) (Scheme 3 C) were conducted, and **3aa** was formed in 91% and 89% yield, respectively, revealing the noninvolvement of free-radicals in the reaction. To prove the *in situ* decomposition of DMSO to MeSH and HCHO by TFAA, we probed a reaction for the *in situ* detection of formaldehyde, as outlined in Scheme 3D. The nucleophilic addition of the enolate of 2-phenylacetophenone (**5**) to the *in situ* formed formaldehyde from DMSO and TFAA furnished 3-hydroxy-1,2-diphenylpropan-1-one in 60% yield. When the mixture of DMSO and TFAA was treated with I_2 and stirred at room temperature for a while, MeSI was formed *in situ*, as evident by the LC−MS analysis (base peak at m/z = 174) of the reaction mixture (Figure S7). After 30 min, when **1a** was added to the reaction mixture and it was heated at 120 °C for 1.5 h, **3aa** was produced in 82% yield (Scheme 3E), which supported the fact that the intermediate MeSI is the active electrophilic species for the methylthiolative annulation of 2-alkynyl biaryls.

https://doi.org/10.1021/acs.joc.1c00861
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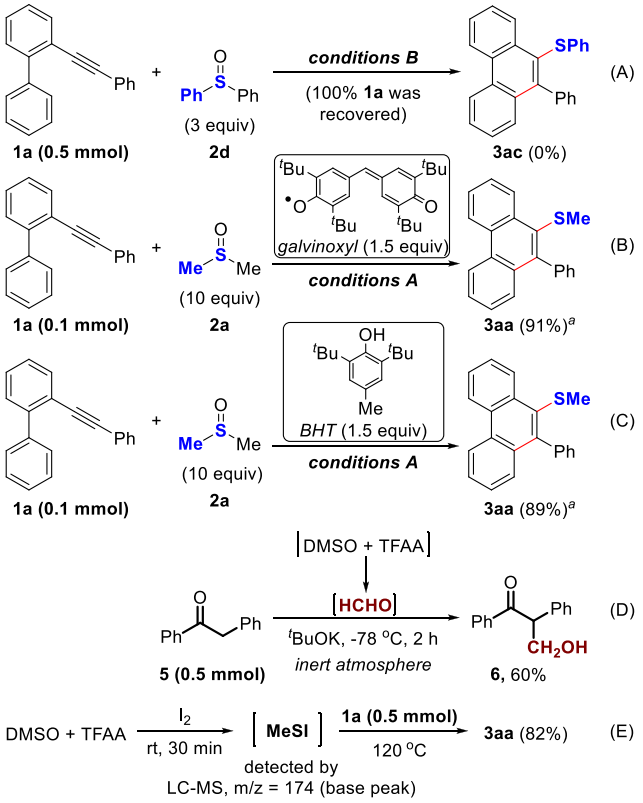
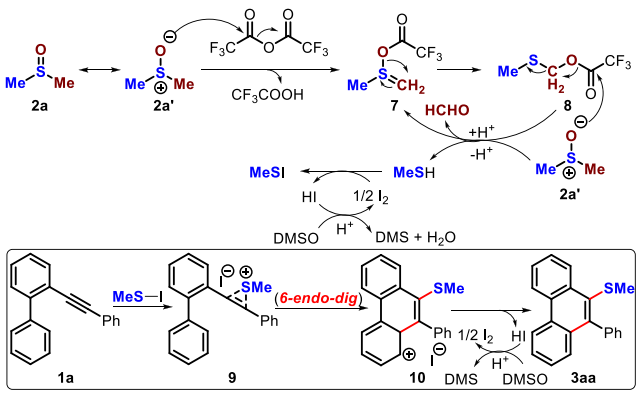
Scheme 3. Mechanistic Studies[a]



[a]Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard.

Based on the mechanistic studies and the previous literature reports,[16] we proposed a plausible mechanism for the methylthiolative annulation reaction of 2-alkynyl biaryls with DMSO as outlined in Scheme 4. Nucleophilic acyl substitution

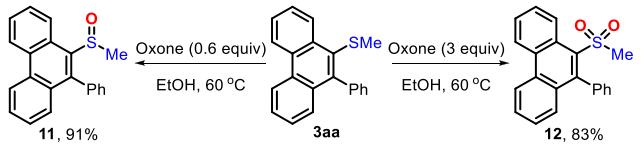
Scheme 4. Plausible Reaction Mechanism



of TFAA by DMSO followed by deprotonation produced a sulfur ylide **7** along with the formation of trifluoroacetic acid (TFA). A rearrangement of the ylide (**7**) through the intramolecular migration of the trifluoroacetate group from the *S*-center to the more electrophilic *C*-center furnished **8**. Next, *in situ* generated acid (TFA)-catalyzed nucleophilic acyl substitution of **8** by another DMSO molecule (**2a′**) reproduced the sulfur ylide **7** along with the formation of MeSH and HCHO through C−O and C−S bond cleavage. The *in situ* formed MeSH then immediately reacted with iodine to form the active electrophilic species, MeSI, along with the formation of HI. Finally, the electrophilic annulation of **1a** (6-*endo*-dig cyclization) with MeSI furnished **3aa** along with the formation of HI again, which was finally oxidized by DMSO under acidic conditions to regenerate iodine in the catalytic cycle.[18]

The synthetic diversification of the product, 10-phenyl-9-sulfenylphenanthrene **3aa** was demonstrated through sustainable and selective oxidation reactions using oxone as the oxidant to the corresponding sulfoxide and sulfone (Scheme 5). When **3aa** was heated with 0.6 equiv of oxone in ethanol at

Scheme 5. Synthetic Diversification of Sythesized Product, 10-Phenyl-9-sulfenylphenanthrene 3aa[a]



[a]Reactions were performed on a 0.3 mmol scale.

60 °C, 91% of the corresponding sulfoxide **11** was formed selectively.[21] However, when 3 equiv of oxone was used in ethanol, 83% of the corresponding sulfone **12** was formed (see the optimization of the reaction conditions to synthesize **12** selectively in Table S3).

In conclusion, we have developed an iodine-catalyzed sustainable, cost-effective, and atom-economic synthetic methodology for the methylthiolative annulation of 2-alkynyl biaryls with DMSO to synthesize a wide variety of sulfenylphenanthrenes and polycyclic heteroaromatics, i.e., naphthothiophenes (15 new molecules) in moderate to good yields under transition-metal-free, aerobic, and simple reaction conditions. The mechanistic studies revealed that the reaction proceeded through the *in situ* decomposition of DMSO by TFAA to formaldehyde and MeSH, facilitated under the *in situ* formed acid catalytic conditions. Notably, DMSO played multiple roles in the methylthiolative annulation reaction, such as the methylthiolating reagent, oxidant, and solvent. The synthetic utility of the synthesized product, 10-phenyl-9-sulfenylphenanthrene **3aa**, was demonstrated by preparing other new but potential molecules, 9-(methylsulfinyl)-10-phenylphenanthrene and 9-(methylsulfonyl)-10-phenylphenanthrene through selective and sustainable oxidation of **3aa** by using oxone. To the best of our knowledge, this is the first report of iodine catalyzed methylthiolative annulation reaction using DMSO as the sulfur source. We believe this cost-effective, sustainable, atom-economic, and simple strategy will be further explored in synthesizing various potential classes of organic molecules.

EXPERIMENTAL SECTION

General Experimental Information. All reagents and solvents including DMSO were purchased from Sigma-Aldrich and TCI chemical companies. Flash column chromatography was performed using silica gel (100−200 mesh). The starting materials such as 2-(phenylethynyl)-1,1′-biaryls and products such as 9-sulfenylphenanthrenes and naphthothiophenes were characterized by ^{1}H, ^{13}C, and ^{19}F NMR. NMR spectra were recorded on a Bruker 400 MHz instrument (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 376 MHz for ^{19}F NMR). Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra can be

https://doi.org/10.1021/acs.joc.1c00861
J. Org. Chem. 2021, 86, 7881−7890

found in the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm) and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.00 ppm) and all were obtained with ^{1}H decoupling. Coupling constants are reported in hertz. Reactions were monitored by thin layer chromatography (TLC) and ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. Mass spectral data of unknown compounds were obtained from BITS-Pilani, Pilani Campus, India, on a high resolution mass spectrometer, HRMS (6545 Q-TOF LC/MS, Agilent). Melting points of unknown compounds were recorded on a KRUSS Optronic M3000 apparatus. The solvent system used for crystallization was the mixture of dichloromethane and hexane (2:1). The crystals were grown by the slow evaporation of the solvent from the solution. The single-crystal XRD data collection and data reduction were performed using CrysAlis PRO on a single-crystal Rigaku Oxford XtaLab Pro diffractometer.

*General Experimental Procedure for the Synthesis of 2-(Phenylethynyl)-1,1′-biaryls (**1a** and **1b**). Representative Experimental Procedure for the Synthesis of 5-Chloro-2-(phenylethynyl)-1,1′-biphenyl (**1b**).* **Step 1**:[22] 4-Chloro-2-iodoaniline (2.54 g, 10 mmol, 1 equiv), phenyl boronic acid (0.403 g, 10 mmol), $Pd(PPh_3)_4$ (0.578 g, 0.5 mmol), K_2CO_3 (8.3 g, 60 mmol), and solvent (320 mL, PhMe/H_2O/EtOH = 4.4:1:1) were taken in a 250 mL round-bottom flask (RBF). The reaction mixture was refluxed in an oil bath, and the progress of the reaction was monitored by TLC until the completion of the reaction. The mixture was cooled to room temperature and extracted with ethyl acetate (30 × 3 mL) three times. The combined organic layer was further washed with brine (30 mL) and subsequently dried over anhydrous Na_2SO_4. Finally, the solvent was evaporated under reduced pressure to obtain the crude product which was purified by flash column chromatography on silica gel to afford 4-chloro-[1,1′-biphenyl]-2-amine (1.98 g, 9.7 mmol) in 97% yield.

The product was characterized by ^{1}H and ^{13}C NMR spectroscopy, and the corresponding analytical data is given, which also matched with the reported literature:[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.34 (m, 5H), 7.13−7.08 (m, 2H), 6.72−6.67 (m, 1H), 3.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.13, 138.26, 129.95, 128.94, 128.89, 128.15, 127.64, 123.10, 116.63.

Step 2:[22] 4-Chloro-[1,1′-biphenyl]-2-amine (1.6 g, 8 mmol, 1 equiv) was added to a solution of aqueous HCl (4.16 mL in 13 mL of H_2O), cooled to 0 °C, and added gradually to an aqueous solution of $NaNO_2$(0.672 g in 13.28 mL H_2O) and KI (2 g in 13.28 mL H_2O) at 0 °C. The reaction mixture was stirred for 10−15 min at 0 °C, and further stirring was continued at room temperature for 12 h. After the completion of the reaction, saturated $Na_2S_2O_3$ solution was added. The crude reaction mixture was extracted with ethyl acetate (30 × 3 mL), washed with water (30 × 2 mL) twice, and purified through silica gel coloumn chromatography to provide 5-chloro-2-iodo-1,1′-biphenyl (1.58 g, 5 mmol) in 64% yield.

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy which matched with the reported literature.[22]

Step 3:[23] 5-Chloro-2-iodo-1,1′-biphenyl (1.58 g, 5 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.07 g, 0.2 mmol), CuI (0.038 g, 0.2 mmol), and Et_3N (13 mL) were added in a flame-dried two neck RBF under N_2 atmosphere in a standard Schlenk line process and stirred for 5 min at room temperature. Then phenylacetylene (659 μL, 6 mmol, 1.2 equiv) was added to the reaction mixture under nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature. After the completion of the reaction, the solvent was evaporated under reduced pressure. The crude reaction mixture was diluted with ethyl acetate (30 mL) and washed with water three times (3 × 10 mL). The crude product was purified through silica gel column chromatography to provide 2-chloro-5-(phenylethynyl)-1,1′-biphenyl **1b** (1.275 g, 4.4 mmol) in 88.5% yield.

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy which matched with the reported literature.[23]

1a was also synthesized from commercially available [1,1′-biphenyl]-2-amine by following **steps 2** and **3** as mentioned above and characterized by ^{1}H and ^{13}C NMR spectroscopy. The analytical data of **1a** matched with the reported literature.[23]

*General Experimental Procedure for the Synthesis of 2-(Phenylethynyl)-1,1′-biaryls (**1c**−**1k** and **1m**−**1o**). Reperesentative Experimental Procedure for the Synthesis of 4′-Chloro-2-(phenylethynyl)-1,1′-biphenyl (**1c**).* **Step 1**:[24] 2-Iodoaniline (2.19 g, 10 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.4 mmol), CuI (0.076 g, 0.4 mmol), and Et_3N (26 mL) were taken in a flame-dried two-neck RBF in a standard Schlenk-line process under N_2 atmosphere, and the solution was stirred at room temperature for 5 min. Phenylacetylene (1318 μL, 12 mmol, 1.2 equiv) was added to the RBF, and the reaction mixture was stirred for 3 h at room temperature. After the completion of the reaction, the solvent was evaporated. The crude reaction mixture was diluted with ethyl acetate (100 mL) and washed with water three times (3 × 10 mL). The crude product was purified through silica gel column chromatography to provide 2-(phenylethynyl)aniline (1.62 g, 8.4 mmol) in 84% yield as yellow solid.

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[24]

Step 2:[25] 2-(Phenylethynyl)aniline (1.55 g, 8 mmol) was added to a solution of *p*-TsOH·H_2O (4.57 g, 24 mmol) dissolved in MeCN (48 mL). The resulting suspension of ammonium salt was cooled to 0 °C and was added gradually to a solution of $NaNO_2$ (1.11 g, 16 mmol) and KI (3.32 g, 20 mmol) in water (4.8 mL). The reaction mixture was stirred for 10−15 min at 0 °C. After completion of the reaction, saturated $NaHCO_3$ and $Na_2S_2O_3$ solution were added. The crude reaction mixture was extracted with ethyl acetate (100 mL), washed with water (30 × 3 mL) three times, and purified through silica gel coloumn chromatography to provide 1-iodo-2-(phenylethynyl)-benzene in 50% yield as yellow liquid.

The product was characterized by the ^{1}H NMR spectroscopy and matched with the reported literature.[25]

Step-3:[26] 1-Iodo-2-(phenylethynyl)benzene (0.913 g, 3 mmol), phenyl boronic acid (0.403 g, 3.3 mmol), $Pd(PPh_3)_4$ (0.174 g, 0.15 mmol), K_2CO_3 (2.5 g, 18 mmol), and solvent (96 mL, PhMe/H_2O/EtOH = 4.4:1:1) were added subsequently in a 250 mL round-buttom flask. The resulting mixture was refluxed in an oil bath, and the progress of the reaction was monitored by thin layer chromatography up to completion. The mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain the crude product, which was purified by flash column chromatography on silica gel to afford 4′-chloro-2-(phenylethynyl)-1,1′-biphenyl **1c** (0.704 g, 2.1 mmol) in 70% yield.

The product **1c** was characterized by ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[26]

The other starting materials **1d**,[26] **1e**, **1f**,[26] **1g**,[26] **1h**,[29] **1m**,[26] **1n**, and **1o** were also synthesized by following the above-mentioned protocol and characterized fully by ^{1}H and ^{13}C NMR spectroscopy.

*Reperesentative Experimental Procedure for the Synthesis of 2-(m-Tolylethynyl)-1,1′-biphenyl (**1j**).* **Step 1**:[27] [1,1′-Biphenyl]-2-amine (1.70 g, 10 mmol) was taken to aqueous HCl (5.2 mL, H_2O 16.6 mL) solution. The reaction mixture was cooled to 0−5 °C. After 5 min, aqueous $NaNO_2$ solution (0.84 g in 16.6 mL H_2O) was added dropwise at 0−5 °C. The resulting solution turned yellow after the addition of aqueous KI solution (2.50 g in 16.6 mL H_2O). The reaction mixture was stirred vigorously for 18 h. After the completion of the reaction, the solution was quenched by the addition of aqueous $Na_2S_2O_3$ solution. The resulting solution was extracted with ethyl acetate (30 × 3 mL) and washed with water (30 mL). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain the crude product which was purified by flash column chromatography on silica gel to afford 2-iodo-1,1′-biphenyl (2.38 g, 8.5 mmol) in 85% yield.

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy which matched with the reported literature.[27]

Step 2:[28] In a RBF, $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol) and CuI (0.028 g, 0.15 mmol) were added to a solution of 2-iodo-1,1′-biphenyl (2.80 g, 3 mmol) in Et_3N (9 mL) under nitrogen

https://doi.org/10.1021/acs.joc.1c00861
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atmosphere in a standard Schlenk-line process. The reaction mixture was stirred for 5 min. Then 1-ethynyl-3-methylbenzene (465 μL, 3.6 mmol, 1.2 equiv) was added to the RBF. The resulting mixture was then heated in an oil bath under nitrogen atmosphere at 70 °C for 18 h. The reaction mixture was allowed to cool to room temperature. Then the solvent was evaporated under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 30 mL). The combined organic layer was washed with water three times (3 × 30 mL) and concentrated under reduced pressure to obtain the crude product which was purified by column chromatography through silica gel to afford 2-(*m*-tolylethynyl)-1,1′-biphenyl **1j** (0.52 g, 1.94 mmol) in 63% yield.

The product **1j** was characterized by ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[28]

The other starting materials **1i** and **1k** were also synthesized by following the above-mentioned protocol and characterized fully by ^{1}H and ^{13}C NMR spectroscopy.

*Experimental Procedure for the Synthesis of 4-([1,1′-Biphenyl]-2-ylethynyl)benzonitrile (**1l**).* **Step-1**:[29] $PdCl_2(PPh_3)_2$ (0.14 g, 0.4 mmol) and CuI (0.076 g, 0.4 mmol) were added to a solution of 2-iodo-1,1′-biphenyl (2.80 g, 10 mmol) in Et_3N (26 mL) under nitrogen atmosphere in a standard Schlenk-line process. The reaction mixture was stirred for 5 min. Then trimethylsilylacetylene (1709 μL, 12 mmol, 1.2 equiv) was added to the RBF. The resulting mixture was heated in an oil bath under nitrogen atmosphere at 70 °C for 18 h. The mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 30 mL). The combined organic layer was washed with brine (30 mL) and concentrated under reduced pressure. The crude product was purified by column chromatography through silica gel to afford the corresponding product, ([1,1′-biphenyl]-2-ylethynyl)trimethylsilane (1.0464 g, 4.2 mmol) in 42% yield.

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[29]

Step 2:[30] K_2CO_3 (1.104 g, 8 mmol) was added into the solution of ([1,1′-biphenyl]-2-ylethynyl)trimethylsilane (1.001 g, 4 mmol) dissolved in MeOH (8.37 mL). The reaction mixture was stirred for 3 h at room temperature. After the completion of the reaction, solvent was evaporated under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 30 mL). The combined organic layer was washed with brine (30 mL) and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain pure 2-ethynyl-1,1′-biphenyl in 99% yield (0.704 g, 3.95 mmol).

The product was characterized by the ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[30]

Step-3:[14e] To a solution of 4-bromobenzonitrile (231 μL, 2 mmol, 1 equiv) in Et_3N (20 mL) and DMF (6 mL) were added $PdCl_2(PPh_3)_2$ (0.070 g, 0.1 mmol) and CuI (0.019 g, 0.1 mmol) under nitrogen atmosphere in a standard Schlenk-line process. The reaction mixture was stirred for 5 min under N_2 atmosphere. Then, 2-ethynyl-1,1′-biphenyl (337 μL, 2 mmol, 1 equiv) was added to the reaction mixture. The resulting mixture was then heated in an oil bath under nitrogen atmosphere at 70 °C for 18 h. The mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 30 mL). The combined organic layer was washed with brine solution (30 mL) and concentrated under reduced pressure. The crude product was purified by flash column chromatography through silica gel to afford the product 4-([1,1′-biphenyl]-2-ylethynyl)benzonitrile **1l** (0.2 g, 0.72 mmol) in 36% yield.

The product was characterized by ^{1}H and ^{13}C NMR spectroscopy, which matched with the reported literature.[14e]

General Experimental Procedure for the Synthesis of 10-Aryl-9-sulfenylphenanthrenes or Naphthothiophenes (3aa−3oa and 3ab−3ac). *Conditions A.* To a solution of 2-(phenylethynyl)-1,1′:2′,1″-terphenyl **1h** (0.165 g, 0.5 mmol, 1 equiv) in DMSO **2a** (0.36 mL, 5 mmol, 1.4 M) was added I_2 (0.0254 g, 0.1 mmol) in a flame-dried RBF. Then TFAA (0.212 mL, 1.5 mmol) was added to the RBF, and the reaction mixture was stirred in an oil bath at 120 °C under aerobic atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the resulting solution was extracted with ethyl acetate three times (3 × 10 mL), and the combined organic layer was washed with water (3 × 10 mL). The solvent was evaporated under reduced pressure to afford the crude product which was purified by flash column chromatography through silica gel to afford the product, (4,10-diphenylphenanthren-9-yl)(methyl)sulfane **3ha** (0.151 g, 0.401 mmol) in 80% yield.

Conditions B. To a solution of 2-(phenylethynyl)-1,1′-biphenyl **1a** (0.127 g, 0.5 mmol, 1 equiv) and (methylsulfinyl)benzene **2c** (0.21 g, 1.5 mmol, 3 equiv) in toluene (1.25 mL, 0.4 M) was added I_2 (0.0254 g, 0.1 mmol) in a flame-dried RBF. Then TFAA (0.212 mL, 1.5 mmol) was added to the RBF, and the reaction mixture was stirred in an oil bath at 120 °C under aerobic atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the resulting solution was extracted with ethyl acetate three times (3 × 10 mL). The combined organic layer was washed with water (3 × 10 mL) and evaporated under reduced pressure. The crude product was purified by flash column chromatography through silica gel to afford pure phenyl(10-phenylphenanthren-9-yl)sulfane **3ac** (0.147 g, 0.405 mmol) in 81% yield.

*1 mmol Scale Detailed Experimental Procedure for the Synthesis of (4,10-Diphenylphenanthren-9-yl)(methyl)sulfane **3ha** under Conditions A.* To a solution of 2-(phenylethynyl)-1,1′:2′,1″-terphenyl **1h** (0.33 g, 1 mmol, 1 equiv) in DMSO **2a** (0.72 mL, 10 mmol, 1.4 M) was added I_2 (0.0508 g, 0.2 mmol) in a flame-dried RBF. Then TFAA (0.424 mL, 3 mmol) was added to the RBF, and the reaction mixture was stirred in an oil bath at 120 °C under aerobic atmosphere. The progress of the reaction was monitored by TLC. After completion of the reaction, the resulting solution was extracted with ethyl acetate three times (3 × 10 mL), and the combined organic layer was washed with water (3 × 10 mL). The solvent was evaporated under reduced pressure to afford the crude product which was purified by flash column chromatography through silica gel to afford the product, (4,10-diphenylphenanthren-9-yl)(methyl)sulfane **3ha** (0.324 g, 0.74 mmol) in 74.5% yield.

*Experimental Procedure for the Synthesis of 9-(Methylsulfinyl)-10-phenylphenanthrene **11**.*[21] Oxone (0.0553 g, 0.18 mmol) was added to the solution of methyl(10-phenylphenanthren-9-yl)sulfane **3aa** (0.0901 g, 0.3 mmol) dissolved in ethanol (1.5 mL). The reaction mixture was stirred in an oil bath at 60 °C. The progress of the reaction was monitored by TLC. After the completion of the reaction the solvent was evaporated under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 10 mL). The combined organic layer was washed with water (3 × 10 mL) and evaporated under reduced pressure. The crude product was purified by flash column chromatography through silica gel to afford the 9-(methylsulfinyl)-10-phenylphenanthrene **11** in (0.0862 g, 0.273 mmol) in 91% yield.

*Experimental Procedure for the Synthesis of 9-(Methylsulfonyl)-10-phenylphenanthrene **12**.*[21] Oxone (0.553 g, 1.8 mmol) was added to the solution of methyl(10-phenylphenanthren-9-yl)sulfane (0.91 g, 0.3 mmol) dissolved in ethanol (1.5 mL). The reaction mixture was stirred in an oil bath at 60 °C. The progress of the reaction was monitored by TLC until completion. After the completion of the reaction the solvent was evaporated under reduced pressure. The crude reaction mixture was extracted with ethyl acetate three times (3 × 10 mL). The combined organic layer was washed with water (3 × 10 mL) and evaporated under reduced pressure. The crude product was purified by flash column chromatography through silica gel to afford the 9-(methylsulfonyl)-10-phenylphenanthrene 12 in (0.083g, 0.25 mmol) 83% yield.

*4′-Bromo-2-(phenylethynyl)-1,1′-biphenyl (**1e**).* White solid (2 mmol scale, 0.34 g, 51%); eluent hexane; mp = 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.4 Hz, 1H), 7.58 (q, J = 8.7 Hz, 4H), 7.44−7.29 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.5, 139.4, 133.0, 131.3, 131.0, 129.3, 128.6, 128.32, 128.28, 127.4, 123.2, 121.8, 121.5, 92.6, 88.9 (overlapping peak present); HRMS (ESI), m/z calcd for $C_{20}H_{13}Br$ [M]: 332.0201; found: 332.0203.

https://doi.org/10.1021/acs.joc.1c00861
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*2-((4-Propylphenyl)ethynyl)-1,1′-biphenyl (**1i**).* Yellow viscous liquid (2 mmol scale, 0.312 g, 52.6%); eluent hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.58 (m, 3H), 7.48−7.28 (m, 6H), 7.25−7.23 (m, 2H), 7.09 (d, J = 8.2 Hz, 2H), 2.59−2.53 (t, 2H), 1.61 (m, J = 7.5 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 143.0, 140.6, 132.8, 131.2, 129.4, 128.4, 128.3, 127.8, 127.4, 127.0, 121.8, 120.6, 92.5, 88.7, 37.9, 24.3, 13.7 (overlapping peaks present); HRMS (ESI), m/z calcd for $C_{23}H_{20}$ [M]: 296.1565; found: 296.1508.

*2-((3-Nitrophenyl)ethynyl)-1,1′-biphenyl (**1k**).* Yellow solid (2 mmol scale, 0.297 g, 49.7%); eluent hexane/EtOAc (16:1, v/v); mp = 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21−8.14 (m, 1H), 8.11 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.70−7.65 (m, 3H), 7.60−7.56 (m, 1H), 7.52 (m, 2H), 7.49−7.45 (m, 3H), 7.44−7.35 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.0, 144.3, 140.2, 136.7, 132.8, 129.5, 129.23, 129.15, 127.9, 127.7, 127.1, 126.0, 125.1, 122.6, 120.5, 92.0, 89.6 (overlapping peak present). Anal Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.75; H, 4.18; N, 5.08.

*3-(2-(Phenylethynyl)phenyl)thiophene (**1n**).* Colorless liquid (2 mmol scale, 0.397, 76.2%); eluent hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 2.9 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 5.0 Hz, 1H), 7.51 (d, J = 7.1 Hz, 1H), 7.47−7.43 (m, 2H), 7.42−7.37 (m, 2H), 7.37−7.28 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.0, 138.2, 133.2, 131.4, 129.0, 128.7, 128.6, 128.3, 128.2, 126.9, 124.7, 123.6, 123.4, 121.1, 92.6, 89.6. Anal. Calcd for $C_{18}H_{12}S$: C, 83.04; H, 4.65; S, 12.31; found C, 83.25; H, 4.78; S, 12.01.

*2-(2-(Phenylethynyl)phenyl)thiophene (**1o**).* Colorless liquid (2 mmol scale, 0.373 g, 71.6%); eluent hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (ddd, J = 8.9, 8.0, 1.6 Hz, 3H), 7.54−7.49 (m, 2H), 7.36 (ddd, J = 6.5, 5.8, 1.2 Hz, 5H), 7.29 (td, J = 7.6, 1.3 Hz, 1H), 7.14 (dd, J = 5.1, 3.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.6, 136.0, 133.7, 131.4, 129.0, 128.6, 128.3, 127.14, 127.05, 126.8, 125.9, 123.4, 120.6, 93.7, 89.5 (Overlapping peak present); HRMS (ESI) m/z: calcd for $C_{18}H_{12}S$ [M]: 260.0660; found: 260.0607.

*Methyl(10-phenylphenanthren-9-yl)sulfane (**3aa**).*[16] White solid (0.5 mmol scale, 0.132 g, 88%); eluent hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 7.5, 1.9 Hz, 1H), 8.81−8.74 (m, 2H), 7.78−7.70 (m, 2H), 7.66 (m, 1H), 7.58−7.50 (m, 3H), 7.49−7.41 (m, 2H), 7.36 (dd, J = 7.9, 1.6 Hz, 2H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.2, 140.8, 132.1, 132.0, 131.6, 130.8, 130.5, 129.9, 128.4, 128.1, 127.7, 127.4, 127.3, 127.1, 126.9, 126.6, 123.0, 122.5, 20.0.

*(6-Chloro-10-phenylphenanthren-9-yl)(methyl)sulfane (**3ba**).* Yellow Solid (0.5 mmol scale, 0.101 g, 60.3%); eluent hexane; mp = 92−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 8.9 Hz, 1H), 8.73 (d, J = 2.1 Hz, 1H), 8.64 (d, J = 8.3 Hz, 1H), 7.71−7.64 (m, 2H), 7.58−7.43 (m, 5H), 7.35 (dd, J = 7.7, 1.6 Hz, 2H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.5, 140.4, 133.1, 132.5, 131.9, 131.2, 130.4, 129.8, 129.5, 129.4, 128.5, 128.1, 127.8, 127.4, 127.2, 122.6, 122.5, 20.0; HRMS (ESI) m/z: calcd for $C_{21}H_{15}ClS$ [M]: 334.0583; found: 334.0567.

*(2-Chloro-10-phenylphenanthren-9-yl)(methyl)sulfane (**3ca**).* Off white crystalline solid (0.5 mmol scale, 0.116 g, 69%); eluent hexane; mp = 185−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, J = 7.6, 2.0 Hz, 1H), 8.73−8.68 (d, J = 8.9 Hz, 1H), 8.66 (d, J = 8.9 Hz, 1H), 7.80−7.69 (m, 2H), 7.62−7.49 (m, 4H), 7.39 (d, J = 2.2 Hz, 1H), 7.32 (dd, J = 7.8, 1.6 Hz, 2H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.2, 140.0, 133.3, 132.7, 131.9, 130.3, 129.8, 128.9, 128.3, 127.9, 127.7, 127.6, 127.4, 127.2, 124.2, 122.9, 20.0; Anal. Calcd for $C_{21}H_{15}ClS$: C, 75.32; H, 4.52; S, 9.57. Found: C, 75.43; H, 4.55; S, 8.84. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2052187).

*(2-Fluoro-10-phenylphenanthren-9-yl)(methyl)sulfane (**3da**).* White crystalline solid (0.5 mmol scale, 0.130 g, 82%); eluent hexane; mp = 156−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (dd, J = 7.6, 1.9 Hz, 1H), 8.74−8.65 (m, 2H), 7.80−7.70 (m, 2H), 7.58−7.54 (m, 3H), 7.44−7.31 (m, 3H), 7.10 (dd, J = 10.8, 2.7 Hz, 1H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1 (d, $^1J_{C-F}$ = 245 Hz), 144.4, 144.3, 140.1, 133.4 (d, $^3J_{C-F}$ = 8.15 Hz), 133.1, 131.4, 130.4, 129.7, 128.2, 127.8, 127.5, 127.18, 127.15, 127.1, 124.8 (d, $^3J_{C-F}$ = 8.59 Hz), 122.7, 116.0 (d, $^2J_{C-F}$ = 23.63 Hz), 112.7, 19.9; Anal. Calcd for $C_{21}H_{15}FS$: C, 79.22; H, 4.75; S, 10.07. Found: C, 79.74; H, 4.32; S, 10.32. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2041730).

*(2-Bromo-10-phenylphenanthren-9-yl)(methyl)sulfane (**3ea**).* White crystalline solid (0.5 mmol scale, 0.127 g, 67%); eluent hexane; mp = 202−204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, J = 7.5, 1.9 Hz, 1H), 8.70 (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.9 Hz, 1H), 7.81−7.68 (m, 3H), 7.55 (dd, J = 6.8, 2.3 Hz, 4H), 7.32 (dd, J = 7.7, 1.7 Hz, 2H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 139.9, 133.6, 133.2, 131.9, 130.5, 130.2, 129.8, 129.2, 128.3, 127.8, 127.6, 127.2, 124.3, 122.8, 120.9, 20.0. Anal. Calcd for $C_{21}H_{15}BrS$: C, 66.50; H, 3.99; S, 8.45. Found: C, 66.66; H, 3.91; S, 7.86. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2033891).

*Methyl(10-phenyl-2-(trifluoromethyl)phenanthren-9-yl)sulfane (**3fa**).* Yellowish white crystalline solid (0.5 mmol scale, 0.128 g, 69.5%); eluent hexane; mp = 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 7.8 Hz, 1H), 8.84 (d, J = 8.9 Hz, 1H), 8.79 (d, J = 8.0 Hz, 1H), 7.86−7.76 (m, 3H), 7.73 (d, J = 6.7 Hz, 1H), 7.60−7.52 (m, 3H), 7.34 (d, J = 7.9 Hz, 2H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.9, 139.6, 133.5, 132.7, 132.5, 131.6, 130.0, 129.8, 129.6, 128.5, 128.3, 128.2, 127.9, 127.7, 127.3, 125.50, 125.46, 123.4, 122.9, 19.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.2. Anal. Calcd for $C_{22}H_{15}F_3S$: C, 71.72; H, 4.10; S, 8.70. Found: C, 71.48; H, 4.24; S, 8.10. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2041729).

*Methyl(4-methyl-10-phenylphenanthren-9-yl)sulfane (**3ga**).* White solid (0.5 mmol scale, 0.085 g, 54%); eluent hexane; mp = 75−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 8.1 Hz, 1H), 8.91 (d, J = 7.9 Hz, 1H), 7.79−7.75 (m, 1H), 7.73−7.69 (m, 1H), 7.57−7.53 (m, 4H), 7.37−7.53 (m, 4H), 3.19 (s, 3H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.5, 141.5, 134.8, 133.6, 132.8, 131.9, 131.7, 131.5, 130.8, 129.9, 128.0, 127.9, 127.4, 127.1, 126.9, 126.7, 125.6, 125.4, 27.2, 19.9; HRMS (ESI) m/z: calcd for $C_{22}H_{18}S$ [M]: 314.1129; found: 314.1133.

*(4,10-Diphenylphenanthren-9-yl)(methyl)sulfane (**3ha**).* White crystalline solid (0.5 mmol scale, 0.151 g, 80.3%); eluent hexane; mp = 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 7.3 Hz, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.59−7.37 (m, 14H), 7.14 (ddd, J = 8.5, 6.9, 1.4 Hz, 1H), 2.22 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.4, 145.0, 141.2, 140.1, 133.6, 132.9, 132.1, 131.4, 130.8, 130.0, 129.2, 129.1, 128.1, 127.9, 127.3, 127.09, 127.05, 126.8, 125.6, 124.7, 20.0. Anal. Calcd for $C_{27}H_{20}S$: C, 86.13; H, 5.35; S, 8.51. Found: C, 85.84; H, 5.43; S, 9.21. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2052186).

*Methyl(10-(4-propylphenyl)phenanthren-9-yl)sulfane (**3ia**).* Off-white crystalline solid (0.5 mmol scale, 0.121 g, 70.7%); eluent hexane; mp = 134−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 7.6, 1.9 Hz, 1H), 8.79 (dd, J = 7.7, 1.8 Hz, 1H), 8.76 (d, J = 8.6 Hz, 1H), 7.78−7.71 (m, 2H), 7.68−7.64 (m, 1H), 7.52−7.44 (m, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 2.4 Hz, 2H), 2.82−2.70 (m, 2H), 2.21 (s, 3H), 1.85−1.79 (m, 2H), 1.08 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.3, 141.6, 137.9, 129.7, 128.5, 128.1, 127.7, 127.4, 127.1, 126.7, 126.6, 122.9, 122.4, 38.0, 24.5, 20.0, 14.03; HRMS (ESI) m/z calcd for $C_{24}H_{22}S$ [M]: 342.1442; found: 342.1447.

*Methyl(10-(m-tolyl)phenanthren-9-yl)sulfane (**3ja**).* Yellowish white crystalline solid (0.5 mmol scale, 0.128 g, 81.4%); eluent hexane; mp = 205−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, J = 7.6, 1.9 Hz, 1H), 8.82−8.69 (m, 2H), 7.76−7.67 (m, 2H), 7.66−7.59 (m, 1H), 7.46−7.38 (m, 3H), 7.33−7.29 (m, 1H), 7.15 (d, J = 0.6 Hz, 2H), 2.46 (s, 3H), 2.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.4, 140.8, 137.6, 132.2, 132.0, 131.4, 130.8, 130.5, 128.5, 128.0, 127.9, 127.7, 127.4, 127.1, 126.9, 126.8, 126.6, 123.0, 122.4, 21.6, 20.1. Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77; S, 10.20. Found: C, 83.83; H, 6.17; S, 9.82.

*Methyl(10-(3-nitrophenyl)phenanthren-9-yl)sulfane (**3ka**).* Yellow viscous liquid (0.5 mmol scale, 0.107 g, 62%); eluent hexane/EtOAc (12:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, J = 6.4,

https://doi.org/10.1021/acs.joc.1c00861
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3.1 Hz, 1H), 8.81−8.77 (m, 2H), 8.39−8.36 (m, 1H), 8.25 (t, J = 1.7 Hz, 1H), 7.77 (dd, J = 6.3, 3.3 Hz, 2H), 7.73−7.67 (m, 3H), 7.51−7.46 (m, 2H), 7.30 (dd, J = 8.3, 0.9 Hz, 1H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.2, 142.6, 142.4, 136.3, 132.3, 131.6, 131.3, 131.0, 130.7, 129.1, 127.7, 127.6, 127.5, 127.0, 125.0, 123.1, 122.8, 122.4, 20.0; HRMS (ESI) m/z: calcd for $C_{21}H_{15}NO_2S$ [M]: 345.0823; found: 345.0796.

4-(10-(Methylthio)phenanthren-9-yl)benzonitrile (**3la**). Yellow solid (0.5 mmol scale, 0.051 g, 31.3%); eluent hexane/EtOAc (19:1, v/v); mp =155−157 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (dd, J = 7.5, 1.9 Hz, 1H), 8.81−8.74 (m, 2H), 7.78−7.70 (m, 2H), 7.66 (ddd, J = 8.3, 6.4, 1.9 Hz, 1H), 7.58−7.50 (m, 3H), 7.49−7.41 (m, 2H), 7.36 (dd, J = 7.9, 1.6 Hz, 2H), 2.20 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.8, 143.3, 132.0, 131.7, 131.6, 131.2, 131.0, 130.9, 130.6, 127.7, 127.6, 127.5, 127.4, 127.0, 123.1, 122.8, 120.0, 111.3, 20.0; HRMS (ESI) m/z: calcd for $C_{22}H_{15}NS$ [M]: 325.0925; found: 325.099.

Methyl(6-phenylbenzo[c]phenanthren-5-yl)sulfane (**3ma**). White solid (0.5 mmol scale, 0.062 g, 35.4%); eluent hexane; mp = 134−136 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (dd, J = 12.9, 8.2 Hz, 2H), 8.97 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.81−7.71 (m, 3H), 7.71−7.61 (m, 2H), 7.59−7.52 (m, 3H), 7.39 (dd, J = 8.4, 6.9 Hz, 3H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 140.8, 133.4, 133.1, 130.6, 130.3, 128.8, 128.7, 128.2, 128.1, 127.4 127.2, 127.0, 126.9, 126.4, 126.2, 126.1, 125.4, 20.1; HRMS (ESI) m/z: calcd for $C_{25}H_{18}S$ [M]: 350.1129; found: 350.1138.

5-(Methylthio)-4-phenylnaphtho[2,1-b]thiophene (**3na**). White solid (0.5 mmol scale, 0.092 g, 60%); eluent hexane; mp = 109−111 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.90−8.83 (m, 1H), 8.44−8.36 (m, 1H), 8.04 (d, J = 5.5 Hz, 1H), 7.71−7.65 (m, 2H), 7.60 (d, J = 5.4 Hz, 1H), 7.54−7.49 (m, 5H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.2, 140.7, 138.3, 138.0, 131.6, 129.7, 129.2, 129.1, 128.1, 128.0, 127.4, 126.8, 126.7, 125.9, 124.6, 124.3, 20.2; HRMS (ESI) m/z: calcd for $C_{19}H_{14}S_2$ [M]: 306.0537; found: 306.0494.

5-(Methylthio)-4-phenyl-3H-1λ^3-naphtho[1,2-b]thiophene (**3oa**). Colorless liquid (0.5 mmol scale, 0.038 g, 24.8%); eluent hexane; ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 7.7 Hz, 1H), 8.21 (d, J = 7.3 Hz, 1H), 7.65 (m, 2H), 7.55−7.47 (m, 3H), 7.44−7.37 (m, 3H), 6.99 (d, J = 5.4 Hz, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.2, 140.7, 138.3, 138.0, 131.6, 129.7, 129.2, 129.1, 128.1, 128.0, 127.4, 126.8, 126.7, 125.9, 124.6, 124.3, 20.2; HRMS (ESI) m/z: calcd for $C_{19}H_{14}S_2$ [M]: 306.0537; found: 306.0535.

(Methyl-d_3)(10-phenylphenanthren-9-yl)sulfane (**3ab**). White crystalline solid (0.5 mmol scale, 0.122 g, 80.4%); eluent hexane; mp =178−180 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 7.6 Hz, 1H), 8.82−8.76 (m, 2H), 7.82−7.72 (m, 2H), 7.70−7.66 (m, 1H), 7.63−7.44 (m, 5H), 7.40 (d, J = 6.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.2, 140.8, 132.1, 132.0, 130.7, 130.5, 129.9, 128.4, 128.0, 127.6, 127.4, 127.2, 127.1, 126.8, 126.6, 122.9, 122.4. Anal. Calcd for $C_{21}H_{13}D_3S$: C, 83.12; H, 6.31; S, 10.57. Found: C, 83.02; H, 6.55; S, 10.43. The assignment is supported by an X-ray crystallographic structure determination (CCDC 2044602).

Phenyl(10-phenylphenanthren-9-yl)sulfane (**3ac**).[16] Yellow solid (0.5 mmol scale, 0.147 g, 81.2%); eluent hexane; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (dd, J = 8.3, 3.9 Hz, 2H), 8.65 (d, J = 7.3 Hz, 1H), 7.76−7.67 (m, 2H), 7.60 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.54−7.49 (m, 2H), 7.47−7.40 (m, 3H), 7.29−7.26 (m, 2H), 7.16−6.98 (m, 3H), 6.93 (dd, J = 8.3, 1.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.8, 140.2, 139.0, 134.2, 132.3, 132.1, 131.1, 130.9, 130.0, 129.5, 128.73, 128.65, 128.5, 128.3, 128.1, 128.0, 127.63, 127.59, 127.4, 127.13, 127.06, 126.7, 126.4, 124.7, 122.8, 122.6 (overlapping peaks present).

3-Hydroxy-1,2-diphenylpropan-1-one (**6**).[31] White solid (0.5 mmol scale, 0.068 g, 60.1%); eluent hexane/EtOAc (10:1, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.4, 1.3 Hz, 2H), 7.40 (ddd, J = 6.8, 4.0, 1.3 Hz, 1H), 7.32−7.16 (m, 7H), 4.72 (dd, J = 8.4, 4.8 Hz, 1H), 4.20 (dd, J = 11.4, 8.4 Hz, 1H), 3.81 (dd, J = 11.4, 4.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 136.2, 136.1, 133.2, 129.2, 128.9, 128.5, 128.4, 127.6, 65.2, 56.4.

9-(Methylsulfinyl)-10-phenylphenanthrene (**11**). White solid (0.3 mmol scale, 0.0862 g, 91%); eluent hexane/EtOAc (4:1, v/v); mp = 183−185 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.55 (dd, J = 7.6, 2.0 Hz, 1H), 8.80 (d, J = 9.6 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H), 7.79−7.67 (m, 3H), 7.60−7.39 (m, 6H), 7.12 (d, J = 6.5 Hz, 1H), 3.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 136.8, 134.9, 131.4, 131.2, 130.6, 129.7, 129.6, 128.8, 128.7, 128.5, 128.1, 128.0, 127.4, 127.3, 127.0, 125.1, 123.4, 122.5, 38.7 (overlapping peaks present); HRMS (ESI) m/z: calcd for $C_{21}H_{16}OS$ [M]: 316.0922; found: 316.0893.

9-(Methylsulfonyl)-10-phenylphenanthrene (**12**). White solid (0.3 mmol scale, 0.083 g, 83%); eluent hexane/EtOAc (8:1, v/v); mp = 172−174 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (dd, J = 7.5, 2.2 Hz, 1H), 8.83 (dd, J = 7.5, 2.3 Hz, 1H), 8.76 (d, J = 8.3 Hz, 1H), 7.81−7.74 (m, 3H), 7.51 (ddd, J = 8.2, 5.4, 1.2 Hz, 4H), 7.42 (dd, J = 8.4, 1.0 Hz, 1H), 7.38−7.33 (m, 2H), 3.14 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.0, 137.9, 133.0, 132.0, 131.5, 131.1, 129.8, 129.6, 127.9, 127.82, 127.77, 127.6, 127.3, 126.8, 126.4, 123.3, 122.4, 46.0 (overlapping peaks present); HRMS (ESI) m/z: calcd for $C_{21}H_{16}O_2S$ [M]: 332.0871; found: 332.0781.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00861.

FAIR data including the primary NMR FID files for compounds **1a**−**1o**, **3aa-3oa**, **11** and **12** (ZIP)

Optimization of reaction conditions (full table), X-ray crystal structure and selected crystal data of **3ca**, **3da**, **3ea**, **3fa**, **3ha**, and **3ab**, optimization of reaction conditions for the synthesis of **11** and **12**, mass spectrum of *in-situ* generated MeSI, copies of ^1H and ^{13}C NMR spectra for all synthesized compounds (PDF)

Accession Codes

CCDC 2033891, 2041729−2041730, 2044602, and 2052186−2052187 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the Additional Competitive Research Grant (BITS/GAU/ACRG/2019/H602) of BITS-Pilani, Hyderabad campus, for this study. The NMR, SCXRD,

and LC-MS facilities at the Central Analytical Laboratory (CAL) of BITS-Pilani, Hyderabad campus, and the HRMS facility, funded by DST-FIST at BITS-Pilani, Pilani campus, are also gratefully acknowledged.

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https://doi.org/10.1021/acs.joc.1c00861
J. Org. Chem. 2021, 86, 7881−7890