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Reactivity of 5-(Alkynyl)dibenzothiophenium Salts:
Synthesis of Diynes, Vinyl Sulfones, and PhenanthrenesKevin Kafuta,^[a] Christian J. Rugen,^[a] Tobias Heilmann,^[a] Tianshu Liu,^[a] Christopher Golz,^[a] and Manuel Alcarazo*^[a]

In memory of Klaus Hafner.

The reactivity of 5-(alkynyl)dibenzothiophenium salts **1** is explored in the presence of different nucleophiles, dienes, and under photochemical conditions. Reaction with lithium acetylides affords diynes in moderate yields; while depending on the substitution pattern, the reaction with sulfinates delivers either the alkyne transfer products, alkynyl sulfones, or β -(sulfonium) vinyl sulfones through addition to the C–C triple bond. Similar behavior is observed when tosylamines are used as nucleophiles. Salts of general formula **1** also react with dienes to

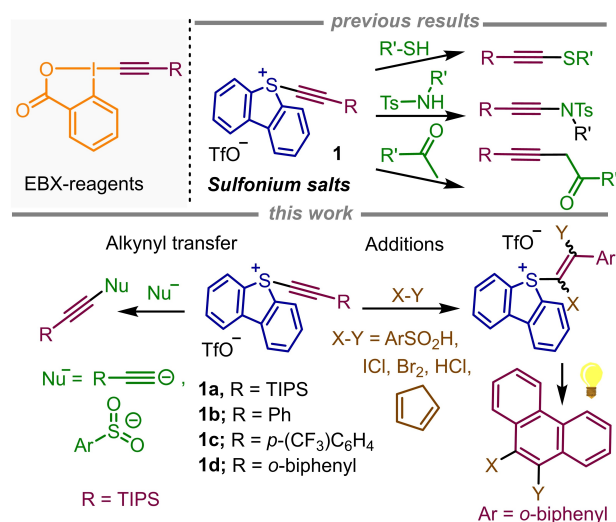
render the corresponding Diels-Alder cycloadducts. The vinyl sulfonium salts obtained by these routes further react with nucleophiles through a Michael addition, dibenzothiophene elimination sequence. Alternatively, they also engage in photo-induced radical cyclizations to produce substituted phenanthrenes. Attempts to use this specific addition/radical cyclization sequence for the construction of the 6a,7-dehydroaporphine skeleton present in several families of alkaloids are also described.

Introduction

Since their first preparation in the mid-1960s, the chemistry of alkynyl-substituted iodonium(III) salts has been well established.^[1] These species are known to serve as efficient alkynyl transfer reagents when reacting with nucleophiles, which make them convenient electrophilic acetylene synthons.^[2,3] Initial examples of that reactivity were published by Beringer,^[4] and Ochiai,^[5] their use in organic synthesis has been later popularized by Zhdankin,^[6] Ochiai himself,^[7] Stang^[8] and Waser^[9] using alkynylbenziodoxolones. Additionally, alkynyl-substituted iodonium(III) salts are known precursors of vinyl iodonium salts either via Michael type nucleophilic additions,^[10] or [4+2] cycloaddition reactions occurring at the C–C triple bond.^[11] The use of these I(III) derivatives however, is not always free of inconveniences. Specifically, some of these I(III) compounds are thermally unstable and show strong exothermic decompositions on heating.^[12]

Having this shortcoming in mind, we recently developed 5-alkynyl(dibenzothiophenium) salts **1**, which depict an improved safety profile and also efficiently serve as $[R-C\equiv C]^+$ synthons for

the metal-free alkylation of thiols, sulfonamides and activated methylene groups.^[13] Herein, we further study the reactivity of this family of compounds in two directions. Initially, the transfer of the alkyne moiety to additional nucleophiles such as acetylides or sulfonates is evaluated; diynes, triynes and alkynylsulfones are obtained from these reactions. Secondly, the addition of acids and halogens to the C–C triple bond of **1** or the Diels-Alder cycloaddition between the same alkyne moiety and dienes are presented. Finally, some further reactivity of the S-vinyl sulfonium salts thus obtained is described as well (Scheme 1); specifically, the photocatalyzed generation of vinyl radicals. Following this addition/radical generation/cyclization sequence, a series of phenanthrene derivatives have been



Scheme 1. From iodine to sulfur. General reactivity and synthetic applications of 5-(alkynyl)dibenzothiophenium salts.

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obtained from **1d**. Our attempts to use this strategy for the preparation of the 6a,7-dehydroaporphine skeleton are also reported; however, the yields obtained are rather poor.

Results and Discussion

Reaction of 5-(alkynyl) dibenzothiophenium salts with lithiated alkynes. Building upon the work of Stang, who was able to couple alkynyl iodonium tosylates with alkynylcopper(I) reagents to obtain asymmetric diacetylenes,^[14] we submitted **1a** to the reaction with terminal alkynes in the presence of a stoichiometric amount of lithium hexamethyldisilazane (LiHMDS). Gratifyingly, deprotonated alkynes proved to react with **1a** yielding the corresponding diynes in moderate to good yields. In all cases, however, the formation of homocoupling products in different amounts was detected, being the proportion of the diynes in the mixture strongly dependent on the substrate used. Moreover, altering the ratio of either the sulfonium salt or the alkyne, or replacing LiHMDS with *n*-butyllithium is detrimental, and causes the formation of increased amounts of homocoupling products. Suppressing the homocoupling however, is possible to a certain extension by addition of CuCN (1.0 equiv.) to the reaction mixture, which in situ generates dialkynylcuprates.^[14] For example, the yield of diyne **2b** was improved from 28% to 52% using this modification of the protocol.

The scope of the transformation is shown in Figure 1. Unfortunately, we have not been able to establish a relation between the electronic nature of the substrates and the amount of homocoupling product formed. For example, both electron-poor *p*-(CF₃)-phenylacetylene and electron-rich *p*-(OMe)-phenylacetylene performed poorly (38% and 28% yield, respectively), while *p*-(I)-phenylacetylene delivered the desired diyne in a respectable 71% yield. As expected, when the nucleophile used is already a 1,3-diyne the corresponding TIPS-capped triynes **2m–p** are delivered in moderate to good yields. The connectivity of **2f** and **2j** has been confirmed by X-ray crystallography (see the Supporting Information).

Our previous studies on the reaction of nucleophiles with isotope labelled **1a** makes us believe that the deprotonated alkyne most probably reacts via attack at the α -position of the alkyne, following elimination of the dibenzothiophene unit and concomitant regeneration of the triple bond (Figure 1).^[13b]

Reaction of 5-(alkynyl) dibenzothiophenium salts with sodium sulfonates and sulfonic acids. Exposure of **1a** to the sodium salt of (hetero)aryl or alkyl sulfonates in DCM:MeOH (1:1) cleanly resulted in the formation of alkynyl sulfones **3a–h** in moderate to excellent yields. With high probability, this reaction proceeds via attack of the sulfinate at the α -position of the alkyne as well, following elimination of dibenzothiophene and regeneration of the triple bond (Figure 2). Considering the product outcome, sulfonium salt **1a** behaves as its I(III)-analogues even if the operating reaction mechanism is not necessarily identical.^[16]

In marked contrast to the transformation just described, the reaction of sodium sulfonates with alkynyl sulfonium salt **1b**,

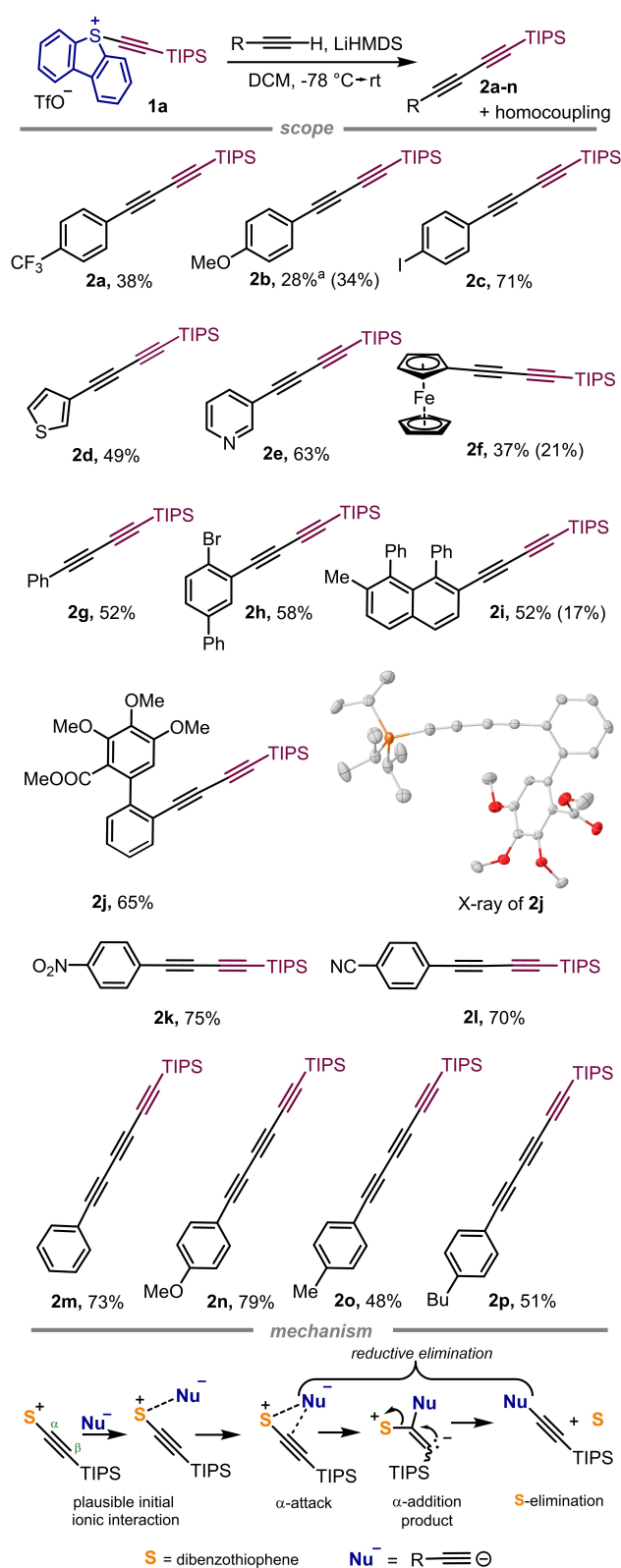


Figure 1. Substrate scope of the coupling of 5-(alkynyl) sulfonium salts with lithiated alkynes. All reagents were used in stoichiometric amounts and all reactions were quenched after 15 min. Yields are of the isolated asymmetric di- and triynes, in parenthesis the yields of the isolated homocoupling products.^[a] The yield of **2b** was improved to 52% when 1.0 equiv. of CuCN was added to the reaction mixture under otherwise identical conditions. X-ray structure of **2j**, ellipsoids shown at 50% probability and hydrogen atoms omitted for clarity.^[15]

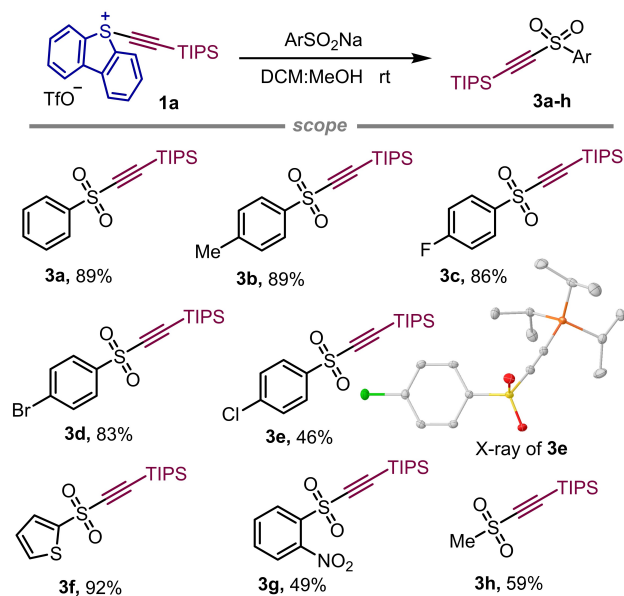
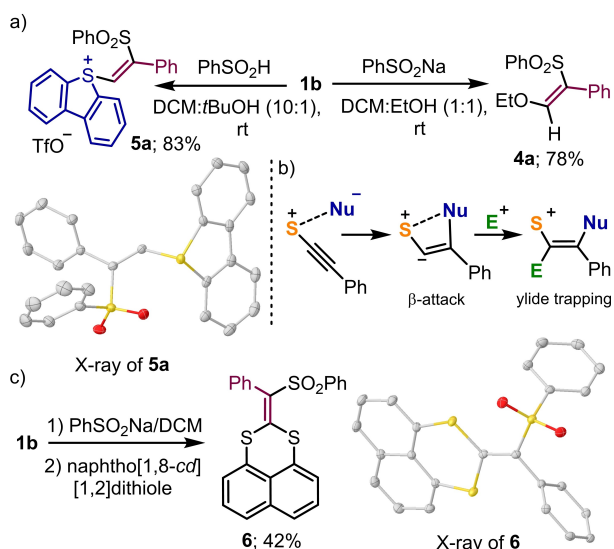


Figure 2. Substrate scope of the coupling of S-(alkynyl) sulfonium salts with sodium sulfonates. Yields are of the isolated products. X-ray structure of **3e**; ellipsoids shown at 50% probability and hydrogen atoms are omitted for clarity.^[15]

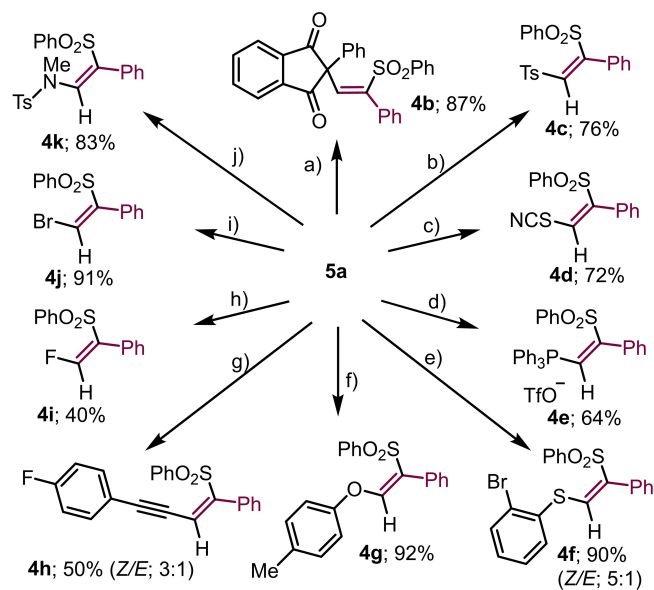
which has a terminal Ph group at the alkyne moiety, does not deliver alkynyl sulfones but β -ethoxy-(*Z*)-vinylsulfone **4a** (Scheme 2a). This different reactivity mode has been already described for selenonium and iodonium salts and reveals the preference of alkynyl sulfonium salts to suffer the attack of the nucleophile at the alkyne β -position when steric factors do allow it.^[17] Moreover, when **1b** was made react with benzenesulfonic acid in DCM:*t*-BuOH, (10:1) the (*Z*)- β -sulfonylalkenylsul-



Scheme 2. Synthesis of (*Z*)- β -sulfonylalkenylsulfonium salt **5a** and plausible mechanism for its formation. X-ray structures of **5a** and **6**; ellipsoids shown at 50% probability, anion in **5a** and hydrogen atoms removed for clarity.^[15]

fonium salt **5a** is cleanly isolated. This shows that in the absence of an appropriate nucleophile able to attack the vinyl sulfonium intermediate, the reaction stops after the initial addition to the C–C triple bond. The absolute stereocontrol of the addition reaction towards the *Z*-olefin might be considered a hint of the assisting role of the sulfonium moiety as directing group for the attack of the incoming nucleophile (Scheme 2b). Moreover, the intermediate ylide can be trapped with electrophiles other than a proton. For example, when the reaction of **1b** and sodium benzenesulfinate is carried out in the presence of excess of naphtho[1,8-*cd*][1,2]dithiole without protic solvent, then 2-methylenenaphtho[1,8-*de*][1,3]dithiine **6** is obtained (Scheme 2c). The formation of this product can be explained *via* a sequence starting with the β -attack of the sulfonate to **1b**, trapping of the ylidic intermediate by the disulfide, intramolecular Michael addition of the *in situ* generated sulfide moiety to the vinyl sulfonium fragment and final elimination of dibenzothiophene.

The reactivity of salt **5a** has been further examined; a set of ten different reactions involving nucleophiles of diverse nature that include C-, S-, N-, P-, O- and halogen-based ones, are shown in Scheme 3. Given the excellent leaving group properties of the dibenzothiophene unit, all nucleophiles tested are able to smoothly react with **5a** and replace this moiety affording the desired β -substituted vinyl sulfone with moderate to excellent yields. The substitution reaction takes place with retention of the *Z*-configuration of the olefin in most of the cases, as could be confirmed either by NOE experiments or comparison with literature.^[17a] This is remarkable since the

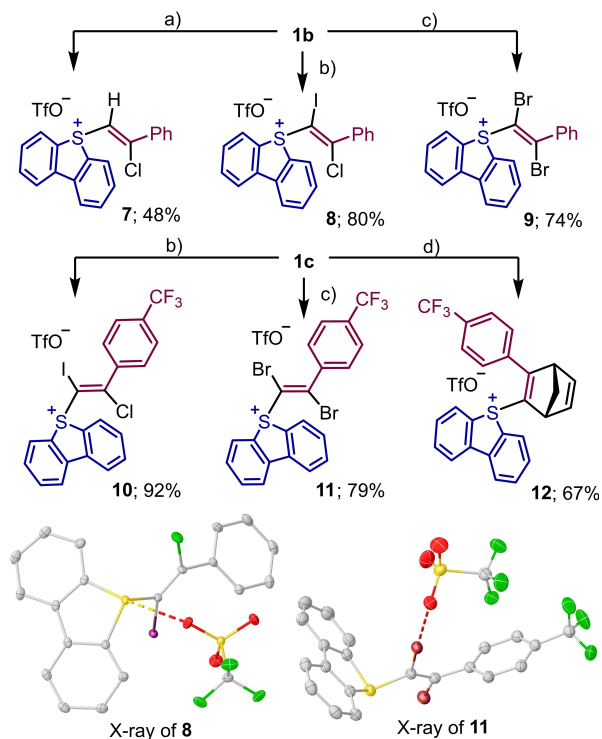


Scheme 3. Synthesis and reactivity (*Z*)- β -sulfonylalkenylsulfonium salt **5a**; a) 1,3-diketone (1.0 equiv.), Cs_2CO_3 (1.0 equiv.), CH_2Cl_2 , rt, 12 h; b) TsNa (1.0 equiv.), CH_2Cl_2 :*t*-BuOH (1:1), rt, 12 h; c) NaSCN (1.1 equiv.), CH_2Cl_2 /*t*-BuOH (1:1), rt, 12 h; d) PPh_3 (1.2 equiv.), CH_2Cl_2 , rt, 12 h; e) *o*-Br-thiophenol (1.0 equiv.), Cs_2CO_3 , CH_2Cl_2 , rt, 12 h; f) *p*-cresol (1.0 equiv.), Cs_2CO_3 (1.0 equiv.), CH_2Cl_2 , rt, 12 h; g) LiHMDS (1.0 equiv.), *p*-F-(C_6H_4)– $\text{C}\equiv\text{CH}$ (1.0 equiv.), CH_2Cl_2 , rt, 12 h; h) KF (1.2 equiv.), CH_2Cl_2 :*t*-BuOH (1:1), rt, 12 h; i) Bu_4NBr (1.0 equiv.), CH_2Cl_2 , rt, 12 h; j) MeNHTs (1.2 equiv.), Cs_2CO_3 (1.2 equiv.), CH_2Cl_2 , rt, 12 h.

Z- products obtained are often the thermodynamically less stable ones. Olefin isomerization could only be detected for compounds **4f** and **4h** and even in these cases it occurred in moderate extent (Scheme 3). A direct attack of the nucleophile to the sulfonium moiety in **5a**, followed by reductive coupling between the nucleophile and the vinyl moiety provides a feasible explanation for this stereochemical outcome; however, a Michael-type addition of the nucleophile to the α -carbon of the vinyl moiety followed by elimination of dibenzothiophene cannot be completely excluded, in particular for those cases where some isomerization is detected.

Reaction of 5-(alkynyl) dibenzothiophenium salts with halogens and dienes. The straightforward addition of sulfonic acids to **1b** made us believe that β -halovinyl sulfonium salts and α,β -dihalovinyl sulfonium salts might also be accessed, respectively, via addition of HX or X₂ (X=halogen) to the corresponding 5-(alkynyl)dibenzothiophenium salts **1**. These reactions actually work efficiently, and the desired mono- and dihalogenated products **7–11** have been obtained in good to excellent yields (Scheme 4). The atom connectivity of compounds **8** and **11** has been subsequently confirmed by X-ray analysis.

The formation of **7**, **8** and **10** is diastereo- and regioselective and probably follows the mechanism already described in Scheme 2b. The synthetic potential of these products is obvious if one considers the known differences in reactivity of alkenyl chlorides, bromides, iodides, and sulfonium salts.^[18] Interest-



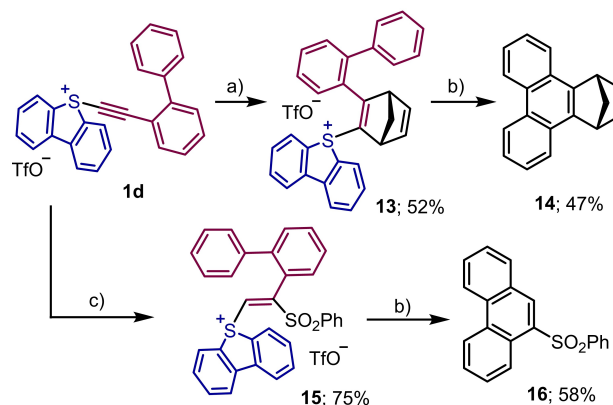
Scheme 4. Additions to the triple bond of **1b–c**; a) 2 M HCl in Et₂O (1.5 equiv.), CH₂Cl₂, rt, 12 h; b) ICl (1.2 equiv.), CH₂Cl₂, rt, 12 h; c) Br₂ 1.0 (equiv.), CH₂Cl₂, rt, 12 h; d) cyclopentadiene (5.0 equiv.), CH₃CN, 100 °C, μ W, 2 h. X-ray structures of **8** and **11**; hydrogen atoms removed for clarity and ellipsoids shown at 50% probability.^[15]

ingly, alkynyl sulfonium salts also undergo smoothly Diels-Alder cycloaddition with cyclopentadiene to deliver the corresponding bicyclic cyclohexadiene **12** in good yield. This reactivity is again parallel to that already observed for alkynyl-substituted hypervalent I(III) reagents.^[19]

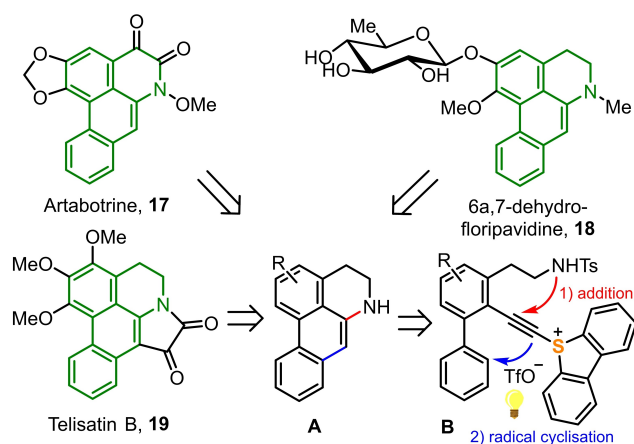
Additionally, having in mind the ability of sulfonium salts to generate organic radicals *via* mesolytic S–C bond cleavage after accepting one electron, we set up to study whether appropriately designed alkenyl-substituted sulfonium salts could be used for the assembly of phenanthrene skeletons *via* radical induced cyclization.^[20] Hence, we prepared **13** and **15** from **1d** following the methods herein reported, and submitted these products to photochemically induced one electron reduction using very similar reaction conditions to those recently developed by Procter and coworkers for the coupling between the exo-aryl group of dibenzothiophenium salts and non-functionalized (hetero)arenes^[21]. To our delight, the proposed transformation took place smoothly and the expected phenanthrenes **14** and **16** were obtained, albeit with moderate yields (Scheme 5).^[22]

Synthesis of the 6a,7-dihydroaporphine scaffold. Finally, we decided to explore whether the just described addition/cyclisation protocol would be useful for the synthesis of the 6a,7-dihydroaporphine core **A**, a tetracyclic amine which constitutes the skeleton of dozens of alkaloids such as for example Artabotrine (**17**),^[23] (–)-6a,7-dehydrofloripavidine (**18**),^[24] or Telisatin B (**19**),^[25] among others.^[26] We envisaged that if access to sulfonium salts of general formula **B** could be provided, then, intramolecular hydroamination of the triple bond followed by cyclization of the photochemically generated vinyl radical should deliver the desired tetracycle (Scheme 6).

In order to evaluate the feasibility of the synthetic strategy just presented, known tosylamide **20** was chosen as appropriate starting material. Regioselective bromination and subsequent iodination of this compound following a protocol already described for similar substrates affords compound **21**.^[27] Sonogahira reaction with TIPS-protected acetylene selectively delivered the corresponding alkyne **22**, which was subsequently



Scheme 5. Phenanthrene syntheses *via* photochemical methods; a) cyclopentadiene (5.0 equiv.), CH₃CN, μ W, 100 °C, 3 h; b) Cs₂CO₃ (1.1 equiv.), [Ru(bpy)₃]Cl₂·6 H₂O (2 mol%), CH₃CN, Blue LED (28 W), rt, 16 h; c) PhSO₂H (2.0 equiv.), CH₂Cl₂/*t*-BuOH (8:1), rt, 12 h.

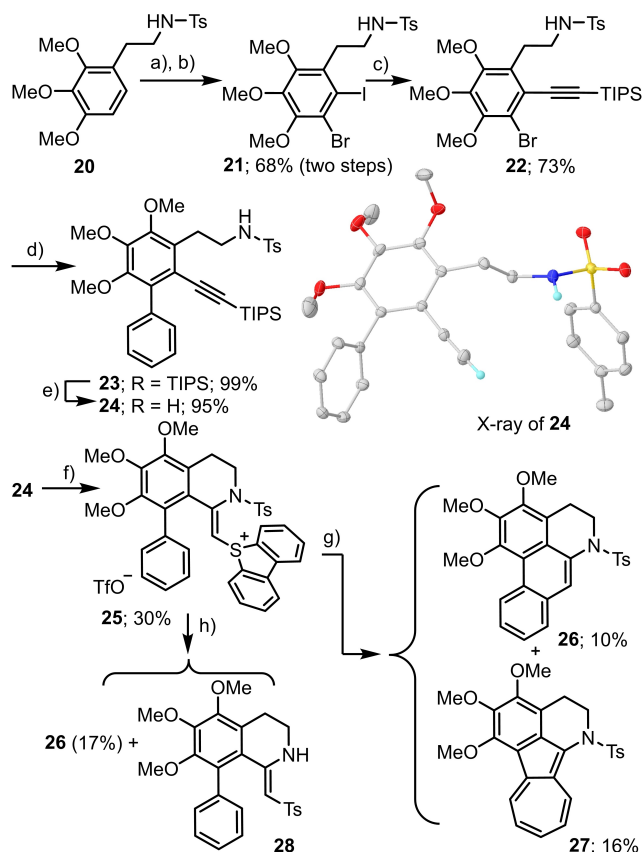


Scheme 6. Synthetic strategy for the synthesis of the 6a,7-dihydroaporphine scaffold.

cross-coupled with phenylboronic acid to produce biphenyl derivative **23**. Unfortunately, all attempts to install the sulfonium moiety directly in **23** were unsuccessful probably due to the steric demand of the TIPS group. For this reason, **23** was treated with TBAF to afford the terminal acetylene **24** in excellent yield as a crystalline material. The atom connectivity of this product was established by X-ray crystallography (Scheme 7). Treatment of **24** with activated dibenzothiophene S-oxide finally afforded a sulfonium salt, which is not the expected alkynyl substituted one but already the result of the intramolecular addition of the sulfonamide moiety to the alkyne fragment **25** (Scheme 7). The stage was then set for the key photocyclization, which occurred under the optimized conditions already identified for the preparation of **14** and **16**. Unfortunately, though the desired *N*-tosyl dihydroaporphine **26** could be obtained from that experiment, the isolated yield is rather poor. In fact, the main product identified from the mixture is azulene **27**; a structure that has been proposed to derive from the insertion of an in situ generated vinyl carbene into the proximal C–C bond of the adjacent phenyl rest.^[28] Treatment of **25** with strong bases such as KH does not solve the selectivity problem. In fact, complex reaction mixtures are obtained from which **26** is again isolated in low yields. From a crystal formed from the crude reaction mixture, we could also identify **28** as side product by X-ray diffraction; however, we were not able to isolate an analytically pure sample of that enamine.

Conclusion

We have further evaluated the reactivity of 5-(alkynyl) dibenzothiophenium salts, which are easily prepared from the reaction of dibenzothiophene S-oxide with TMS-capped or even free alkynes. While TIPS-substituted salts react with nucleophiles transferring the alkyne moiety; aryl substituted salts preferentially suffer addition reactions to the C–C triple bond to deliver 5-vinyl sulfonium species. The further transformation of these



Scheme 7. Studies towards the synthesis of the 6a,7-dihydroaporphine scaffold; a) NBS, 60 °C, 16 h; b) NIS, TFA, CH₃CN, μW 110 °C, 16 h.; c) TIPS-acetylene, Pd(PPh₃)₂Cl₂, CuI, NEt₃, THF, μW 90 °C, 60 h.; d) PhB(OH)₂, Pd(PPh₃)₂Cl₂, Na₂CO₃, DME/H₂O, μW 120 °C, 26 h.; e) TBAF, THF, rt, 2 h.; f) dibenzothiophene S-oxide, Tf₂O, CH₂Cl₂, –50 °C → –20 °C, 16 h.; g) [Ru-(bipy)₃]₂·6H₂O (3 mol%), blue LEDs, Cs₂CO₃ (1.4 equiv.), CH₃CN; h) KH (3.0 equiv.), KOf-Bu (10 mol%). X-ray of **24** drawn at 50% probability level; only amide and ethynyl protons shown.^[15]

initial adducts into *Z*-configured vinyl sulfones and phenanthrenes is also described herein. Considering the multitude of products that might be gained following these protocols, we do believe that the chemistry of 5-alkynyl sulfonium salts shows a vast synthetic potential, which is still under study in our laboratory.

Experimental Section

General experimental details: All reactions were carried out using pre-dried glassware under nitrogen atmosphere unless otherwise stated. Dry and degassed solvents (THF, dichloromethane, toluene, *n*-pentane, diethyl ether) were obtained with the MBraun Solvent Purification System (MB-SPS-800) or by distillation over appropriate drying agents and stored under nitrogen atmosphere. Flash chromatography was performed either on Merck 60 (40–63 μm) or Macherey-Nagel 60 (40–63 μm) silica gel. Thin-layer chromatography (TLC) analyses were performed using polygram SIL G/UV254 from Macherey-Nagel and visualized by UV irradiation and/or phosphomolybdic acid, KMnO₄ or *p*-anisaldehyde dip. All commercially available products (Acros Organics, ABCR, Alfa Aesar, Sigma

Aldrich, Fluorochem, TCl) were used as received. Compounds **1a**, **1b** and **1c** were synthesized according to known procedures.^[13]

General procedure for the synthesis of compounds 2a–2p

The corresponding 1-alkyne or 1,3 diene (0.2 mmol, 1.0 equiv.) was dissolved in anhydrous DCM (2 mL, 0.1 M) under inert atmosphere and LiHMDS (0.2 mL of a 1 M solution in THF, 0.2 mmol, 1.0 equiv.) was added at -78°C under stirring. The reaction mixture was allowed to warm up to 0°C and stirred for additional 5 min. Successively, it was cooled back to -78°C , and **1a** (103 mg, 0.2 mmol, 1.0 equiv.) was added in one portion. Then, the reaction mixture was allowed to warm up to r.t. and stirred for an additional 10 min. Finally, the reaction was quenched with water and extracted with EtOAc ($3\times 5\text{ mL}$). The desired products were obtained after purification by column chromatography using pentane as eluent. As representative example the spectroscopic characterization of **2e** is listed: $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 8.73$ (s, 1H), 8.56 (d, $J = 4.2$ Hz, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.29–7.22 (m, 1H), 1.11 (s, 21H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): $\delta = 153.5$, 149.3, 139.6, 123.1, 119.2, 89.9, 89.0, 78.0, 72.2, 18.7, 11.4 ppm. IR (neat): $\tilde{\nu} = 2940$, 2862, 2204, 2106, 1462, 1404, 996, 882, 659, 602 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{25}\text{NSi}^+$ [$M+H$] $^+$: 283.1751; found: 283.1750. See the SI for the characterization of all other dienes and trienes.

General procedure for the synthesis of compounds 3a–3h

Sulfonium salt **1a** (103 mg, 0.2 mmol, 1.0 equiv.) and the corresponding sulfinat (0.24 mmol, 1.2 equiv.) were dissolved in DCM:MeOH 1:1 (5 mL), and the reaction mixture was stirred for 30 min at r.t. Upon completion of the reaction (monitoring via TLC), pentane (5 mL) was added, and the reaction mixture was transferred directly to a pre-wetted (hexane) silica column and eluted with the same solvent to afford the desired products. As representative example the spectroscopic characterization of **3g** is listed: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.33$ –8.26 (m, 1H), 7.99–7.92 (m, 1H), 7.87–7.79 (m, 2H), 1.20–1.06 (m, 21H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 148.3$, 135.4, 135.2, 133.1, 131.0, 125.5, 102.6, 99.3, 18.5, 11.1 ppm. IR (ATR): $\tilde{\nu} = 2948$, 2867, 2360, 2340, 2124, 1542, 1336, 1159, 803, 575 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{NO}_4\text{SSi}^+$ [$M+H$] $^+$: 368.1346; found: 368.1342. See the SI for the characterization of all other alkylnyl sulfones.

(Z)-2-Phenyl-2-[2-phenyl-2-(phenylsulfonyl)vinyl]-1H-indene-1,3(2H)-dione 4b: A mixture of **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv.) and 1,3-indandione (29.2 mg, 0.2 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at room temperature for 12 h and then directly transferred to a pre-wetted column (hexane). Pure **4b** (80.8 mg, 173.9 μmol , 87%) was obtained as an orange oil by column chromatography (gradient hexanes \rightarrow hexanes:EtOAc 4:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.90$ (s, 1H), 7.53 (t, $J = 7.2$ Hz, 2H), 7.49–7.45 (m, 2H), 7.45–7.29 (m, 12H), 7.27–7.23 (m, 2H), 7.16 (d, $J = 7.2$ Hz, 1H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 192.8$, 168.2, 150.7, 139.1, 138.4, 133.51, 133.45, 130.8, 130.6, 130.6, 129.6, 129.6 (2 overlapped ^{13}C signals), 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.5, 122.8, 119.4, 116.9 ppm. IR (neat): $\tilde{\nu} = 3725$, 3626, 1715, 1378, 1308, 1204, 1146, 1082, 689, 646 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{20}\text{NaO}_4\text{S}^+$ [$M+Na$] $^+$: 487.0975; found: 487.0975.

(Z)-1-Methyl-4-[[2-phenyl-2-(phenylsulfonyl)vinyl]sulfonyl]benzene 4c: Compound **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.) and sodium *p*-tolylsulfinate (35.6 mg, 0.2 mmol, 1.0 equiv.) were dissolved in CH_2Cl_2 /*t*-BuOH 1:1 (2 mL) and the reaction mixture was stirred at room temperature for 12 h. Pure **4c** (60.6 mg, 0.152 mmol, 76%) was obtained as a colorless oil by column

chromatography (gradient hexanes \rightarrow hexanes:EtOAc 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.98$ (d, $J = 8.3$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.47–7.32 (m, 5H), 7.29–7.24 (m, 2H), 7.22–7.18 (m, 2H), 6.87 (s, 1H), 2.47 (s, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 151.9$, 145.3, 141.4, 138.6, 138.4, 134.4, 132.7, 130.4, 129.9, 129.8, 129.4, 129.1, 128.6, 128.5, 21.9 ppm. IR (neat): $\tilde{\nu} = 3060$, 3011, 1595, 1325, 1148, 1079, 907, 726, 670, 563 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{O}_4\text{S}_2^+$ [$M+H$] $^+$: 399.0719; found: 399.0704.

(Z)-[(1-Phenyl-2-thiocyanatovinyl)sulfonyl]benzene 4d: Salt **5a** (115.3 mg, 0.2 mmol, 1 equiv.) was added in one portion to a stirred solution of NaSCN (19.5 mg, 0.24 mmol, 1.2 equiv.) in a mixture of CH_2Cl_2 (1 mL) and *t*-BuOH (1 mL). The reaction mixture was stirred at r.t. for 12 h. Column chromatography (gradient hexanes \rightarrow hexanes:EtOAc 4:1) of the reaction mixture thus obtained afforded pure **4d** (43.4 mg, 0.144 mmol, 72%) as a white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.65$ (dd, $J = 8.4$, 1.2 Hz, 2H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.47–7.42 (m, 2H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.22–7.18 (m, 2H), 6.99 (s, 1H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 142.5$, 138.1, 134.6, 131.7, 131.2, 130.2, 129.5, 129.4, 128.8, 128.1, 111.9 ppm. IR (neat): $\tilde{\nu} = 3030$, 1737, 1367, 1306, 1210, 1146, 1084, 753, 684, 651 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{11}\text{NNaO}_2\text{S}_2^+$ [$M+Na$] $^+$: 324.0123; found: 324.0122.

(Z)-Triphenyl[2-phenyl-2-(phenylsulfonyl)vinyl]phosphonium trifluoromethanesulfonate 4e: A Schlenk flask equipped with a stirring bar was charged with **5a** (115.3 mg, 0.2 mmol, 1 equiv.) and Ph_3P (63 mg, 0.24 mmol, 1.2 equiv.). Both reactants were dissolved in CH_2Cl_2 (2 mL) and the reaction mixture was stirred at room temperature for 12 h. After this the solvent was evaporated and diethyl ether (10 mL) was added to precipitate the salt, which was filtered off, washed once more with diethyl ether (10 mL) and dried in vacuo. Salt **4e** (83.8 mg, 0.128 mmol, 64%) was obtained as a white solid. $^1\text{H NMR}$ (400 MHz, CD_3CN): $\delta = 8.54$ (d, $J = 8.6$ Hz, 2H), 8.31 (d, $J = 7.9$ Hz, 2H), 7.98 (t, $J = 7.7$ Hz, 2H), 7.95–7.88 (m, 5H), 7.87–7.82 (m, 2H), 7.77 (d, $J = 7.5$ Hz, 3H), 7.64–7.59 (m, 3H), 7.46–7.38 (m, 2H), 7.31 (d, $J = 4.6$ Hz, 4H), 6.85 (s, 1H) ppm. $^{31}\text{P NMR}$ (162 MHz, CD_3CN): $\delta = 16$ ppm. $^{13}\text{C NMR}$ (101 MHz, CD_3CN): $\delta = 166.5$, (d, $^2J_{\text{P-C}} = 3.6$ Hz), 157.3, 141.0, 136.8, 135.8, 135.7 (d, $^4J_{\text{P-C}} = 3.2$ Hz), 135.0 (d, $^1J_{\text{P-C}} = 10.8$ Hz), 134.6 (d, $^4J_{\text{P-C}} = 10.7$ Hz), 132.9, 132.4, 131.7, 131.3 (d, $^1J_{\text{P-C}} = 13.3$ Hz), 131.0 (d, $^2J_{\text{P-C}} = 13.5$ Hz), 130.8, 130.2, 130.2, 129.7 (d, $^2J_{\text{P-C}} = 13.7$ Hz), 129.6 (d, $^1J_{\text{P-C}} = 14.0$ Hz), 127.9, 125.3, 122.1 (q, $^1J_{\text{C-F}} = 321$ Hz), 122.0 (d, $^1J_{\text{P-C}} = 93.7$ Hz), 121.3 ppm. IR (ATR): $\tilde{\nu} = 3730$, 3628, 2266, 1648, 1255, 1148, 1029, 686, 636, 515 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{32}\text{H}_{26}\text{O}_2\text{PS}^+$ [$M-\text{OTf}$] $^+$: 505.1386; found: 505.1385.

(E/Z)-2-Bromophenyl[2-phenyl-2-(phenylsulfonyl)vinyl] sulfane 4f: A suspension of **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv.) and 2-bromobenzenethiol (37.8 mg, 0.2 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was stirred at r.t. for 12 h and then directly transferred to a pre-wetted chromatography column (hexanes). Pure **4f** (77.6 mg, 179.8 μmol , 90%) was obtained as a white solid (mixture of *Z/E* isomers (5:1)) after column chromatography (gradient hexanes \rightarrow hexanes:EtOAc 1:1). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.85$ (dd, $J = 8.4$, 1.2 Hz, 2H), 7.67–7.61 (dt $J = 1.4$, 8.0 Hz, 2H), 7.59–7.52 (m, 1H), 7.47–7.42 (m, 2H), 7.41–7.26 (m, 4H), 7.26–7.19 (m, 3H), 6.98 (s, 1H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 144.7$, 140.4, 136.3, 135.7, 134.4, 134.3, 134.0, 133.6, 130.6, 130.3, 130.0, 129.0, 128.8, 128.44, 128.39, 127.8 ppm. IR (ATR): $\tilde{\nu} = 3728$, 3626, 1737, 1557, 1447, 1306, 1146, 1084, 753, 664 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{S}_2^+$ [$M+H$] $^+$: 430.9770; found: 430.9769.

(Z)-1-Methyl-4-[[2-phenyl-2-(phenylsulfonyl)vinyl]oxy]benzene 4g: A suspension of **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv.) and *p*-cresol (21.6 mg, 0.2 mmol, 1.0 equiv.) was stirred in CH_2Cl_2 (2 mL) at r.t. for 12 h. Then, the solvents were evaporated, and the residue was charged into a pre-

wetted chromatography column (hexanes). Pure **4g** (64.5 mg, 0.184 mmol, 92%) was obtained as a white solid by column chromatography (gradient hexanes→hexanes:EtOAc 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.98 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.61–7.56 (m, 1H), 7.52–7.46 (m, 2H), 7.43–7.36 (m, 5H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.90 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 2.31 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 154.4, 150.3, 142.5, 134.9, 133.1, 131.3, 131.0, 130.4, 129.0, 128.8, 128.5, 128.1, 125.9, 117.2, 20.8 ppm. IR (ATR): $\tilde{\nu}$ = 3080, 2923, 1632, 1600, 1504, 1224, 1141, 726, 686, 574 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₁H₁₈NaO₃S⁺ [*M* + Na]⁺: 373.0869; found: 373.0863.

(*Z*)-[2-Fluoro-1-(phenylsulfonyl)vinyl]benzene **4i**: **5a** (115.3 mg, 0.2 mmol, 1 equiv.) was added in one portion to a solution of KF (13.9 mg, 0.24 mmol, 1.2 equiv.) in CH₂Cl₂ (1 mL) and *t*-BuOH (1 mL). The reaction mixture was stirred for 12 h at r. t. Then, the solvents were evaporated, and the residue was charged into a pre-wetted chromatography column (hexanes). Pure product **4i** (21.0 mg, 80 μmol, 40%) was obtained as a white solid by column chromatography (gradient hexanes→hexanes:EtOAc 4:1). ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29–7.25 (m, 2H), 6.83 (d, *J* = 78.5 Hz, 1H) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -101.96 (d, *J* = 78.6 Hz) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 152.8 (d, ¹*J*_{C-F} = 292.7 Hz), 140.8, 133.9, 131.0 (d, ²*J*_{C-F} = 3.2 Hz), 130.2, 130.2, 129.9, 129.2, 128.7, 128.1 (d, ³*J*_{C-F} = 1.1 Hz) ppm. IR (neat): $\tilde{\nu}$ = 3728, 3628, 1648, 1325, 1180, 1135, 1079, 732, 667, 553 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₄H₁₂FO₂S⁺ [*M* + H]⁺: 263.0537; found: 263.0538.

(*Z*)-[2-Bromo-1-(phenylsulfonyl)vinyl]benzene **4j**: Salt **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.) and NEt₃Br (64.5 mg, 0.2 mmol, 1.0 equiv.) were dissolved in CH₂Cl₂ (2 mL). The reaction mixture was stirred at room temperature for 12 h and then directly transferred to a pre-wetted column (hexanes). Analytically pure **4j** (58.8 mg, 181.9 μmol, 91%) was obtained as a colorless oil by column chromatography (gradient hexanes→hexanes:EtOAc 8:2). ¹H NMR (400 MHz, CDCl₃): δ = 7.84–7.79 (m, 2H), 7.60 (ddt, *J* = 7.9, 7.0, 1.2 Hz, 1H), 7.49–7.44 (m, 2H), 7.41–7.36 (m, 1H), 7.34–7.29 (m, 2H), 7.25–7.21 (m, 2H), 7.01 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 147.7, 139.8, 134.2, 133.9, 130.0, 129.7, 129.0, 129.0 (2 overlapped ¹³C signals), 128.4, 117.4 ppm. IR (neat): $\tilde{\nu}$ = 1576, 1445, 1319, 1146, 1082, 836, 718, 686, 533, 512 cm⁻¹. HRMS (ESI) *m/z* calcd for C₁₄H₁₁BrNaO₂S⁺ [*M* + Na]⁺: 344.9555; found: 344.9553.

(*Z*)-*N*,4-dimethyl-*N*-[2-phenyl-2-(phenylsulfonyl)vinyl]benzene sulfonamide **4k**: A suspension of **5a** (115.3 mg, 0.2 mmol, 1.0 equiv.), Cs₂CO₃ (78.2 mg, 0.24 mmol, 1.2 equiv.) and *N*,4-dimethyl benzene-sulfonamide (44.5 mg, 0.24 mmol, 1.2 equiv.) in CH₂Cl₂ (2 mL) was stirred at r.t. for 12 h. and then directly transferred to a pre-wetted column (hexanes). Compound **4k** (71.0 mg 0.166 mmol, 83%) was obtained as an off-white solid after purification by column chromatography (gradient hexanes→hexanes:EtOAc 1:1). ¹H NMR (400 MHz, CDCl₃): δ = 8.38 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.56–7.47 (m, 3H), 7.40–7.33 (m, 4H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H), 2.46 (s, 3H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 145.3, 139.8, 136.7, 134.2, 133.0, 132.5, 130.4, 129.5, 129.3, 128.8, 128.3, 128.0, 127.5, 122.2, 34.8, 21.8 ppm. IR (ATR): $\tilde{\nu}$ = 1630, 1357, 1287, 1170, 1141, 1082, 978, 943, 688, 545 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₂H₂₂NNaO₄S₂⁺ [*M* + Na]⁺: 450.0804; found: 450.0794.

(*Z*)-5-[2-Phenyl-2-(phenylsulfonyl)vinyl]-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate **5a**: A Schlenk flask was equipped with a stirring bar and charged with **1b** (1.01 g, 2.32 mmol, 1.0 equiv.) and phenylsulfonic acid (330 mg, 2.32 mmol, 1.0 equiv.). The reactants were dissolved in a mixture of DCM (10 mL) and *t*-BuOH (1 mL) and the reaction mixture was stirred at room temperature for 12 h. After this, the solvents were evapo-

rated, and diethyl ether (2×40 mL) was added to wash the salt, which was finally dried in vacuo. Product **5a** was obtained as a beige solid (1.113 g, 1.93 mmol, 83%); *m.p.*: 184–185 °C. ¹H NMR (400 MHz, CD₃CN) δ = 8.52 (d, *J* = 8.2 Hz, 2H), 8.31 (d, *J* = 7.8 Hz, 2H), 7.98 (t, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.87–7.83 (m, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64–7.59 (m, 2H), 7.43 (t, *J* = 8.7 Hz, 1H), 7.34–7.29 (m, 4H), 6.84 (s, 1H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 157.5, 141.1, 136.9, 136.3, 135.8, 132.9, 132.5, 131.7, 130.9, 130.6, 130.30, 130.28, 129.8, 129.6, 127.9, 125.4, 122.1 (q, ¹*J*_{C-F} = 321 Hz) ppm. IR (ATR): $\tilde{\nu}$ = 2360, 2337, 1447, 1309, 1253, 1224, 1148, 1028, 759, 635 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₆H₁₉O₂S₂⁺ [*M*–OTf]⁺: 427.0821; found: 427.0821.

2-[Phenyl(phenylsulfonyl)methylene]naphtho[1,8-*de*][1,3] dithiine **6**: **1b** (87.0 mg, 0.20 mmol, 1.0 equiv.), naphtho[1,8-*cd*][1,2]dithioline (76.1 mg, 0.4 mmol, 2.0 equiv.), 15-C-5 (100.1 mg, 90 μL, 0.45 mmol, 2.25 equiv.) and sodium phenylsulfinate (49.2 mg, 0.3 mmol, 1.5 equiv.) were dissolved in DCM (3 mL) and the mixture stirred at r.t. under nitrogen overnight. Then, the solvents were evaporated and the residue charged into a pre-wetted silica column (hexanes). Pure **6** (36.3 mg, 83.9 μmol, 42%) was obtained as a white solid after column chromatography (gradient hexanes→hexanes:EtOAc 8:2). ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.61–7.55 (m, 2H), 7.50 (d, *J* = 6.2 Hz, 1H), 7.48–7.35 (m, 6H), 7.30–7.26 (m, 1H), 7.10 (dd, *J* = 11.3, 7.2 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 143.3, 140.7, 134.3, 133.5, 133.1, 131.8, 130.8, 129.6, 128.9, 128.8, 128.3, 128.2, 128.1, 127.5, 127.4, 126.7, 126.4, 124.1, 123.3, 122.7 ppm. IR (ATR): $\tilde{\nu}$ = 1557, 1506, 1314, 1207, 1146, 1082, 684, 667, 651, 577 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₄H₁₇O₂S₃⁺ [*M* + H]⁺: 433.0385; found: 433.0388.

(*Z*)-5-(2-Chloro-2-phenylvinyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate **7**: Salt **1b** (102 mg, 235 μmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (2 mL), and HCl (0.18 mL, 2 M solution in Et₂O; 360 μmol, 1.53 equiv.) was added. After stirring the reaction overnight the solvent was removed and diethyl ether (2×10 mL) was added to wash the resulting oil. Salt **7** (53.1 mg, 112.7 μmol, 48%) was obtained as a white foam. ¹H NMR (400 MHz, CD₃CN): δ = 8.32 (d, *J* = 8.6 Hz, 2H), 8.27 (d, *J* = 8.1 Hz, 2H), 7.97 (t, *J* = 8.2 Hz, 2H), 7.79 (t, *J* = 7.2 Hz, 2H), 7.76–7.73 (m, 2H), 7.61–7.57 (m, 1H), 7.52–7.47 (m, 2H), 6.84 (s, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 156.4, 141.0, 135.6, 134.3, 134.0, 132.6, 130.7, 130.2, 129.3, 128.7, 125.4, 122.1 (q, ¹*J*_{C-F} = 322 Hz), 113.7 ppm. IR (ATR): $\tilde{\nu}$ = 1702, 1557, 1445, 1253, 1221, 1151, 1028, 924, 753, 635 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₀H₁₄ClS⁺ [*M*–OTf]⁺: 321.0499; found: 321.0494.

(*E*)-5-(2-Chloro-1-iodo-2-phenylvinyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate **8**: Iodine monochloride (45.8 mg, 282 μmol, 1.2 equiv.) was added to a solution of **1b** (102 mg, 235 μmol, 1.0 equiv.) in CH₂Cl₂ (2 mL) and the reaction mixture stirred at r.t. overnight. Subsequently, the solvent was removed under reduced pressure and the residue washed with diethyl ether (3×10 mL). Removal of the solvent using a filtration cannula afforded **8** as a white solid, which was dried in vacuum (112.2 mg, 0.188 mmol, 80%), *m.p.*: 255 °C (with decomposition). ¹H NMR (400 MHz, CD₃CN): δ = 8.32 (dd, *J* = 8.1, 1.5 Hz, 2H), 8.28 (dd, *J* = 8.1, 1.6 Hz, 2H), 8.07–8.02 (m, 2H), 7.87–7.81 (m, 2H), 7.62 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.59–7.51 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 155.5, 141.8, 139.1, 136.5, 132.9, 132.9 (overlapped ¹³C signals), 130.9, 130.0, 129.8, 129.6, 125.6, 122.1 (q, ¹*J*_{C-F} = 321 Hz), 84.0 ppm. IR (ATR): $\tilde{\nu}$ = 3086, 2360, 2268, 1253, 1221, 1156, 1025, 758, 673, 638 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₀H₁₃ClIS⁺ [*M*–OTf]⁺: 446.9466; found: 446.9466.

(*E*)-5-(1,2-Dibromo-2-phenylvinyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium trifluoromethanesulfonate **9**: Bromine (37.6 mg, 12 μL, 235 μmol, 1.0 equiv.) was added to a solution of **1b** (102 mg, 235 μmol, 1.0 equiv.) in CH₂Cl₂ (2 mL) and the reaction stirred at r.t. overnight.

Removal of the solvent under reduced pressure afforded a solid that was washed with Et₂O (3×10 mL) and dried in vacuum. Compound **9** (103.3 mg, 173.8 μmol, 74%) was obtained as a yellow solid. ¹H NMR (400 MHz, CD₃CN): δ = 8.38 (d, *J* = 8.1 Hz, 2H), 8.31 (d, *J* = 8.6 Hz, 2H), 8.01 (t, *J* = 7.7 Hz, 2H), 7.83 (t, *J* = 8.4 Hz, 2H), 7.58 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.54–7.47 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 144.4, 141.9, 138.7, 136.6, 132.8, 132.6, 129.9, 129.8, 129.5, 129.3, 125.6, 122.1 (q, ¹J_{C-F} = 322 Hz), 108.2 ppm. IR (ATR): $\tilde{\nu}$ = 1445, 1258, 1224, 1156, 1025, 758, 697, 670, 635, 518 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₀H₁₃Br₂S⁺ [*M*-OTf]⁺: 442.9099; found: 442.9100.

(E)-5-[2-Chloro-1-iodo-2-[4-(trifluoromethyl)phenyl]vinyl]-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate 10: Iodine monochloride (268 mg, 1.65 mmol, 1.1 equiv.) was added in one portion to a stirred solution of **1c** (754 mg, 1.5 mmol, 1.0 equiv.) in CH₂Cl₂ (10 mL) and the reaction mixture stirred at r.t. overnight. Removal of the solvent under reduced pressure causes solidification of a residue, which was washed with hexane (3×100 mL). After drying in vacuum, salt **10** (917 mg, 1.38 mmol, 92%) was obtained as a yellow solid. ¹H NMR [400 MHz, (CD₃)₂CO]: δ = 8.58 (d, *J* = 8.1 Hz, 2H), 8.54 (d, *J* = 7.8 Hz, 2H), 8.12 (t, *J* = 8.1 Hz, 2H), 7.93 (s, 6H) ppm. ¹⁹F NMR [377 MHz, (CD₃)₂CO]: δ = -63.6, -78.8 ppm. ¹³C NMR [101 MHz, (CD₃)₂CO]: δ = 152.3, 143.2 (q, ⁴J_{C-F} = 1.3 Hz), 141.9, 136.4, 132.8, 131.5, 130.9, 130.5, 130.0, 126.9 (q, ³J_{C-F} = 3.6 Hz), 125.6, 124.6 (q, ¹J_{C-F} = 272.6 Hz), 122.3 (q, ¹J_{C-F} = 322.3 Hz), 87.6 ppm. IR (ATR): $\tilde{\nu}$ = 3730, 3628, 1739, 1325, 1242, 1165, 1023, 670, 633, 512 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₁H₁₂ClF₃S⁺ [*M*-OTf]⁺: 514.9340; found: 514.9344.

(E)-5-[1,2-Dibromo-2-[4-(trifluoromethyl)phenyl]vinyl]-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate 11: Bromine (36.8 mg, 11.8 μL, 230 μmol, 1.0 equiv.) was added in one portion to a solution of salt **1c** (115.6 mg, 230 μmol, 1.0 equiv.) in CH₂Cl₂ (2 mL) and the reaction mixture thus obtained was stirred at room temperature for 1 h. Removal of the solvent under reduced pressure, afforded a solid, which was washed with Et₂O (3×10 mL) and pentane (10 mL). Salt **11** (120.3 mg, 181.6 μmol, 79%) was obtained as a white solid. ¹H NMR (400 MHz, CD₃CN): δ = 8.37 (d, *J* = 7.7 Hz, 2H), 8.31 (dd, *J* = 8.1, 0.9 Hz, 2H), 8.03 (td, *J* = 7.7, 1.0 Hz, 2H), 7.86–7.80 (m, 4H), 7.76–7.71 (m, 2H) ppm. ¹⁹F NMR (377 MHz, CD₃CN): δ = -63.7, 79.3 ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 142.5, 142.1, 142.1, 136.8, 133.3, 133.0, 130.2, 130.0, 129.1, 127.1 (q, ³J_{C-F} = 3.8 Hz, CF₃), 125.9, 125.7, 122.1 (q, ¹J_{C-F} = 321 Hz), 110.5 ppm. IR (ATR): $\tilde{\nu}$ = 3730, 1325, 1255, 1224, 1159, 1130, 1063, 1028, 761, 635 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₁H₁₂Br₂F₃S⁺ [*M*-OTf]⁺: 512.8953; found: 512.8964.

5-[3-[4-(Trifluoromethyl)phenyl]bicyclo[2.2.1]hepta-2,5-dien-2-yl]-5H-dibenzo[b,d]thiophen-5-ium trifluoromethane-sulfonate 12: Freshly distilled cyclopentadiene (168.2 μL, 132.2 mg, 2.0 mmol, 5 equiv.) was added to a solution of **1c** (200 mg, 0.40 mmol, 1.0 equiv.) in MeCN (2 mL), and the reaction mixture was heated to 100 °C for 2 h under microwave irradiation. Subsequently, the solvent was evaporated and the residue washed with *n*-hexane (2×20 mL). The solid thus obtained was dried in vacuum affording **12** (152.4 mg, 0.268 mmol, 67%, a mixture of rotamers) as a pale green solid. ¹H NMR (400 MHz, CD₃CN): δ = 8.38 (dd, *J* = 8.2, 4.0 Hz, 2H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.03–7.94 (m, 6H), 7.87–7.82 (m, 1H), 7.71–7.60 (m, 2H), 6.97–6.92 (m, 1H), 6.24–6.20 (m, 1H), 4.25 (s, 1H), 2.77 (s, 1H), 2.22–2.15 (m, 1H), 1.99–1.96 (m, 1H) ppm. ¹⁹F NMR (377 MHz, CD₃CN): δ = -63.3, -79.3 ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 178.7, 143.3, 141.3, 141.2, 140.9, 136.6 (q, ⁴J_{C-F} = 1.3 Hz), 135.6, 135.5, 132.9 (q, ²J_{C-F} = 32.8 Hz), 132.68, 131.9, 131.3, 129.8, 129.44, 129.42, 129.42 (2 overlapped ¹³C signals), 129.0, 127.4, 127.1 (q, ³J_{C-F} = 3.8 Hz), 126.0, 125.6, 125.1 (q, ¹J_{C-F} = 272.0 Hz), 122.1 (q, ¹J_{C-F} = 320.2 Hz), 71.6, 60.0, 52.2 ppm (19 ¹³C signals expected, 26 detected because of the hindered rotation of the DBT-unit). IR

(ATR): $\tilde{\nu}$ = 3091, 2950, 1710, 1325, 1258, 1159, 1121, 1068, 1028, 635 cm⁻¹. HRMS (ESI) *m/z* calcd for C₂₆H₁₈F₃S⁺ [*M*-OTf]⁺: 419.1076; found: 419.1079.

5-[3-([1,1'-Biphenyl]-2-yl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate 13: Freshly distilled cyclopentadiene (168.2 μL, 132.2 mg, 2.0 mmol, 5.0 equiv.) was added to a solution of **1d** (204 mg, 0.4 mmol, 1.0 equiv.) in MeCN (2 mL). The reaction mixture was heated at 100 °C for 3 h under microwave irradiation. Subsequently, the solvents were removed in vacuum and the solid thus obtained washed with Et₂O (3×30 mL). Compound **13** (119.9 mg, 207.9 μmol, 52%) was obtained as a brown solid. ¹H NMR (400 MHz, CD₃CN): δ = 8.29 (t, *J* = 9.4 Hz, 2H), 7.95–7.88 (m, 2H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.68–7.63 (m, 3H), 7.62–7.60 (m, 1H), 7.60–7.55 (m, 3H), 7.54–7.49 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.56–6.51 (m, 1H), 6.06–6.02 (m, 1H), 3.84–3.79 (m, 1H), 2.57–2.52 (m, 1H), 2.08–2.05 (m, 1H), 1.86–1.83 (m, 1H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 142.2, 141.7, 141.5, 141.1, 140.7, 135.4, 135.3, 132.5, 132.4, 132.1, 131.8, 131.7, 131.1, 130.0, 129.8, 129.6, 129.3, 129.2, 129.0, 128.8, 128.4, 128.0, 125.9, 125.5, 122.1 (q, ¹J_{C-F} = 322 Hz), 72.0, 61.2, 51.1 ppm. IR (ATR): $\tilde{\nu}$ = 3730, 3628, 3594, 1539, 1260, 1151, 1028, 755, 673, 651 cm⁻¹. HRMS (ESI) *m/z* calcd for C₃₁H₂₃S⁺ [*M*-OTf]⁺: 427.1515; found: 427.1518.

1,4-Dihydro-1,4-methanotriphenylene 14: A Schlenk flask equipped with a stirring bar was charged with **13** (115.3 mg, 0.2 mmol, 1.0 equiv.), Cs₂CO₃ (71.7 mg, 0.22 mmol, 1.1 equiv.) and [Ru(bipy)₃]Cl₂×6H₂O (3 mg, 4.0 μmol, 2.0 mol%), purged three times with nitrogen. After adding degassed MeCN (2 mL) the reaction mixture was exposed to blue LED light irradiation (28 W) at r.t. for 16 h. Subsequently, the solvents were evaporated and the residue charged into a pre-wetted silica column (hexanes). Pure **14** (22.8 mg, 94 μmol, 47%) was obtained after column chromatography (gradient hexanes→hexanes:CH₂Cl₂ 4:1) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (d, *J* = 8.1 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.66–7.56 (m, 4H), 7.02 (s, 2H), 4.63 (s, 2H), 2.55 (d, *J* = 6.6 Hz, 1H), 2.46 (d, *J* = 6.6 Hz, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 147.9, 143.8, 129.0, 128.7, 126.5, 125.3, 123.6, 123.5, 72.5, 49.2 ppm. IR (ATR): $\tilde{\nu}$ = 3060, 2980, 2928, 2862, 1506, 1298, 753, 720, 670, 660 cm⁻¹. HRMS (GCMS) *m/z* calcd for C₁₉H₁₄⁺ [*M*]⁺: 242.1090; found: 242.1090. Analytical data are identical to the previously reported ones.^[29]

(Z)-5-[2-([1,1'-Biphenyl]-2-yl)-2-(phenylsulfonyl)vinyl]-5H-dibenzo[b,d]thiophen-5-ium trifluoromethanesulfonate 15: A Schlenk flask was equipped with a stirring bar and charged with **1d** (944.5 mg, 1.85 mmol, 1.0 equiv.) and phenylsulfonic acid (526 mg, 3.70 mmol, 2.0 equiv.). Subsequently, CH₂Cl₂ (16 mL) and *t*-BuOH (2 mL) were added and the reaction mixture was stirred at r.t. overnight. After this, the solvents were evaporated to a minimal volume and Et₂O (50 mL) was added, which causes precipitation of crude **15**. The latter was filtered off, washed with Et₂O (30 mL) and dried in vacuo to afford **15** (905.6 mg, 138.7 μmol, 75%) as a pale yellow solid. ¹H NMR (400 MHz, CD₃CN): δ = 8.26 (d, *J* = 7.9 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.98–7.90 (m, 3H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.79–7.75 (m, 2H), 7.74–7.69 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.27–7.19 (m, 3H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.58 (d, *J* = 9.5 Hz, 2H), 6.52 (s, 1H) ppm. ¹³C NMR (101 MHz, CD₃CN): δ = 157.2, 143.8, 140.9, 139.8, 137.3, 136.2, 135.8, 132.9, 132.2, 131.9, 131.3, 130.9, 130.8, 130.6, 130.1, 129.9, 129.5, 129.2, 128.7, 128.6, 128.4, 125.4, 122.1 (q, ¹J_{C-F} = 321 Hz) ppm. IR (ATR): $\tilde{\nu}$ = 3735, 3626, 3064, 3014, 1445, 1255, 1148, 1025, 635 cm⁻¹. HRMS (ESI) *m/z* calcd for C₃₂H₂₃O₂S⁺ [*M*-OTf]⁺: 503.1134; found: 503.1137.

9-(Phenylsulfonyl)phenanthrene 16: A Schlenk flask was equipped with a stirring bar and charged with **15** (130.5 mg, 0.2 mmol, 1.0 equiv.), Cs₂CO₃ (71.7 mg, 0.22 mmol, 1.1 equiv.) and [Ru(bipy)₃]Cl₂×6H₂O (3 mg, 4.0 μmol, 2.0 mol%). Subsequently, CH₃CN (2 mL)

was added and the reaction mixture was exposed to blue LED light irradiation (28 W) at r.t. for 16 h. Subsequently, the solvents were evaporated and the residue charged into a pre-wetted silica column (hexanes). Pure **16** (36.9 mg, 115.8 μmol , 58%) was obtained by column chromatography (gradient hexanes→hexanes:EtOAc 4:1) as a pale-yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.92 (s, 1H), 8.74–8.67 (m, 2H), 8.63 (d, J = 9.0 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 7.3 Hz, 2H), 7.83 (t, J = 8.4 Hz, 1H), 7.73 (t, J = 7.1 Hz, 1H), 7.68 (t, J = 7.0 Hz, 1H), 7.62–7.58 (m, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ = 141.7, 134.3, 133.2, 133.1, 132.9, 131.4, 130.9, 130.2, 129.4, 129.2, 127.8, 127.7, 127.5, 127.5 (2 overlapped ^{13}C signals), 126.1, 125.5, 123.4, 122.9 ppm. IR (ATR): $\tilde{\nu}$ = 1447, 1322, 1151, 1082, 791, 753, 734, 686, 649, 566 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{NaO}_5\text{S}^+$ [$M + \text{Na}$] $^+$: 341.0607; found: 341.0608. Analytical data are identical to the previously reported ones.^[30]

***N*-(3-Bromo-2-iodo-4,5,6-trimethoxyphenethyl)-4-methylbenzenesulfonamide 21**: A solution of **20** (2.13 g, 5.83 mmol, 1.0 equiv.) and NBS (1.04 g, 5.84 mmol, 1.0 equiv.) in CCl_4 (20 mL) was stirred at 50 °C for 16 h in the dark. After cooling to rt, the reaction was quenched with water (25 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 \times 30 mL). The combined organic phases were washed with sat. aq. Na_2SO_3 (30 mL) and brine (30 mL), dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatography (hexane/EtOAc, 7:3) gave *N*-(5-bromo-2,3,4-trimethoxyphenethyl)-4-methylbenzenesulfonamide (2.31 g, 5.20 mmol, 89%) as an off-white solid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.67 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 6.88 (s, 1H), 4.61 (t, J = 5.9 Hz, 1H), 3.92–3.77 (m, 9H), 3.17 (q, J = 6.5 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.42 (s, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 151.6, 150.4, 147.5, 143.5, 137.1, 129.8, 128.3, 127.9, 127.2, 111.6, 61.1, 61.1, 61.1, 43.7, 30.3, 21.7 ppm. IR (ATR): $\tilde{\nu}$ = 2967, 2930, 2899, 2864, 2822, 1598, 1457, 1402, 1319, 1162, 1068, 1002, 807, 671, 554 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{BrNO}_5\text{S}^+$ [$M + \text{H}$] $^+$: 444.0475; found: 444.0477. To a solution of this compound (2.0 g, 4.50 mmol, 1.0 equiv.) in acetonitrile (19 mL) was added NIS (2.53 g, 11.25 mmol, 2.5 equiv.) and TFA (1.283 g, 0.86 mL, 11.25 mmol, 2.5 equiv.). The reaction mixture was stirred at 110 °C for 16 h under microwave irradiation. The reaction was quenched with sat. aq. Na_2SO_3 (50 mL) at rt, and the aqueous layer was extracted with DCM (3 \times 30 mL). The combined organic phases were washed with brine (40 mL), dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc, 9:1→3:1). Product **21** (1.94 g, 3.40 mmol, 76%) was obtained as a brownish oil. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.59 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.81 (t, J = 5.4 Hz, 1H), 3.93–3.81 (m, 9H), 3.19 (q, J = 6.4 Hz, 2H), 3.04 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 151.1, 150.7, 147.2, 143.4, 136.8, 132.5, 129.7, 127.0, 121.7, 101.6, 61.3, 61.0, 60.9, 42.3, 36.9, 21.7 ppm. IR (ATR): $\tilde{\nu}$ = 2936, 2861, 1735, 1458, 1398, 1386, 1325, 1154, 1094, 1046, 999, 813, 662, 548 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{BrNO}_5\text{S}^+$ [$M + \text{H}$] $^+$: 569.9441; found: 569.9444.

***N*-(3-Bromo-4,5,6-trimethoxy-2-[(triisopropylsilyl) ethynyl] phenethyl)-4-methylbenzenesulfonamide 22**: To a dry THF (11 mL) solution containing **21** (1.90 g, 3.33 mmol, 1.0 equiv.) and NEt_3 (4.6 mL), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (233 mg, 331.9 μmol , 10 mol%), CuI (126 mg, 0.662 mmol, 0.2 equiv.) and TIPS-acetylene (3.65 g, 4.49 mL, 20.0 mmol, 6.01 equiv.) were added, and the mixture was stirred at 90 °C for 60 h under microwave irradiation. The suspension thus obtained was filtered through a pad of silica gel and eluted with CH_2Cl_2 (60 mL). The filtrate was concentrated in vacuo and the residue purified by column chromatography (hexane/EtOAc, 10%→30%). Sulfonamide **22** (1.52 g, 2.43 mmol, 73%) was obtained as a colorless solid. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 7.51 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.75 (t, J = 5.2 Hz,

1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.24 (q, J = 6.1 Hz, 2H), 2.97 (t, J = 6.5 Hz, 2H), 2.38 (s, 3H), 1.12 (s, 21H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ = 151.2, 150.5, 147.8, 143.2, 136.5, 131.1, 129.5, 126.9, 121.2, 117.0, 102.5, 100.3, 61.2, 61.1, 61.0, 43.1, 28.8, 21.7, 18.8, 11.4 ppm. IR (ATR): $\tilde{\nu}$ = 2940, 2890, 2863, 2151, 1461, 1411, 1397, 1336, 1158, 1093, 1020, 812, 662, 549 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{43}\text{BrNO}_5\text{Si}^+$ [$M + \text{H}$] $^+$: 624.1809; found: 624.1802.

4-Methyl-*N*-(2-{4,5,6-trimethoxy-2-[(triisopropylsilyl) ethynyl]-[1,1'-biphenyl]-3-yl}ethyl)-benzenesulfonamide 23: To a solution of **22** (1.42 g, 2.27 mmol, 1.0 equiv.) and phenylboronic acid (555 mg, 4.55 mmol, 2.0 equiv.) in DME (9.5 mL), Na_2CO_3 (1.21 g, 11.4 mmol, 5.0 equiv.) and water (3.4 mL) were added. Finally, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (160 mg, 228 μmol , 10 mol%) was added to the suspension and the reaction mixture was stirred at 120 °C for 26 h. under microwave irradiation. After cooling to rt, the mixture was acidified with aq. HCl (1 M) to pH = 1. The aqueous layer was extracted with EtOAc (3 \times 40 mL), the combined organic phases were washed with brine (50 mL), dried over MgSO_4 and concentrated under reduced pressure. Column chromatography (hexane/EtOAc, 10:1→3:1) yielded **23** (1.39 g, 2.24 mmol, 99%) as a colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.60 (d, J = 8.3 Hz, 2H), 7.38–7.24 (m, 5H), 7.20 (d, J = 7.9 Hz, 2H), 4.88 (t, J = 5.1 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.54 (s, 3H), 3.25 (q, J = 6.2 Hz, 2H), 3.02 (t, J = 6.5 Hz, 1H), 2.38 (s, 3H), 0.88 (s, 21H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ = 151.1, 150.5, 147.2, 143.0, 137.0, 136.5, 135.8, 130.2, 129.9, 129.5, 127.9, 127.3, 127.2, 119.0, 103.4, 98.6, 61.2, 61.1, 61.0, 43.5, 28.4, 21.6, 18.6, 11.2 ppm. IR (ATR): $\tilde{\nu}$ = 2939, 2889, 2863, 2146, 1460, 1416, 1405, 1333, 1158, 1090, 1048, 880, 813, 661, 549 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{35}\text{H}_{48}\text{NO}_5\text{Si}^+$ [$M + \text{H}$] $^+$: 622.3017; found: 622.3013.

***N*-(2-(2-ethynyl-4,5,6-trimethoxy-[1,1'-biphenyl]-3-yl)ethyl)-4-methylbenzenesulfonamide 24**: Under an atmosphere of nitrogen, a Schlenk flask was charged with **23** (126 mg, 202.6 μmol , 1.0 equiv.), and dry THF (2 mL) was added. A solution of TBAF (1 M in THF, 0.26 mL, 0.26 mmol, 1.3 equiv.) was added at 0 °C and the reaction mixture was stirred at rt for 2 h. The reaction was quenched with sat. aq. NH_4Cl (6 mL), and the aqueous phase was extracted with EtOAc (3 \times 15 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica (hexane/EtOAc, 20:1→3:1) to deliver **24** (89 mg, 0.19 mmol, 94%) as a colorless solid, m.p.: 154–155 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 7.66 (d, J = 8.3 Hz, 2H), 7.45–7.29 (m, 5H), 7.23 (d, J = 8.1 Hz, 2H), 4.83 (t, J = 5.4 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.53 (s, 3H), 3.25 (q, J = 6.7 Hz, 2H), 3.03–2.97 (m, 3H), 2.39 (s, 3H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ = 151.2, 150.5, 147.6, 143.1, 137.2, 136.2, 135.8, 130.4, 130.2, 129.6, 127.8, 127.6, 127.2, 117.5, 84.3, 80.5, 61.3, 61.0, 61.0, 43.4, 28.6, 21.7 ppm. IR (ATR): $\tilde{\nu}$ = 2936, 2871, 2836, 1460, 1415, 1404, 1327, 1155, 1103, 1020, 814, 705, 661, 548 cm^{-1} . HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_5\text{S}^+$ [$M + \text{H}$] $^+$: 466.1683; found: 466.1685.

Compound 25: In a Schlenk flask, dibenzothiophene-5-oxide (23.5 mg, 0.117 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (1 mL). Tf_2O (36.4 mg, 21.7 μL , 0.129 mmol, 1.10 equiv.) was added to the solution at –50 °C, and the red suspension obtained was stirred for 30 min at this temperature. Compound **24** (60.0 mg, 0.129 mmol, 1.1 equiv.) was added at –60 °C, and the reaction mixture was allowed to warm up to –20 °C overnight. The solvent was then removed in vacuo and the residue was washed with dry Et_2O (2 \times 2 mL) in an ultrasonic bath. Purification by column chromatography (CH_2Cl_2 /acetone, 9:1→1:1) delivered **25** (38.0 mg, 47.6 μmol , 41%) as a brown solid. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 8.33 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 7.9 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.79 (t, J = 7.6 Hz, 2H), 7.67 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.15–7.05 (m, 4H), 6.87 (t, J = 6.8 Hz, 1H), 4.49 (s, 1H), 3.91 (s, 3H), 3.87 (t, J = 6.5 Hz, 2H), 3.79 (s, 3H), 3.50 (s, 3H), 2.93 (t, J = 6.5 Hz, 2H), 2.44 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 151.4, 150.6, 150.2, 149.3, 146.1, 139.0, 135.4, 134.2, 133.3, 131.8, 130.5, 130.0, 129.9, 128.8, 128.6, 127.7, 127.6, 125.8, 123.6, 116.0, 61.3, 61.14, 61.11, 45.9, 21.9, 21.0 ppm (triflate-carbon not observed). IR (ATR): $\tilde{\nu}$ = 2939, 1597, 1448, 1402, 1332, 1257, 1232, 1156, 1028, 813, 751, 708, 635 cm⁻¹. HRMS (ESI): *m/z* calcd for C₃₈H₃₄NO₅S₂⁺ [M-OTf]⁺: 648.1873; found: 648.1874.

1,2,3-Trimethoxy-6-tosyl-5,6-dihydro-4H-dibenzo[de,g] quinoline 26 and 4,5,6-Trimethoxy-1-tosyl-2,3-dihydro-1H-azuleno[1,2,3-ij] isoquinoline 27: A flame-dried Schlenk flask was charged with **25** (34.9 mg, 43.7 μmol, 1.0 equiv.), Cs₂CO₃ (19.9 mg, 61.2 μmol, 1.4 equiv.) and [Ru(bpy)₃]Cl₂·6H₂O (0.97 mg, 1.3 μmol, 3 mol%). CH₃CN (1.0 mL) was added, and the solution was degassed with nitrogen for 5 min. The reaction mixture was irradiated with vigorous stirring at r.t. with blue LEDs (28 W) for 22 h. Subsequently, the solvent was removed in vacuo and the residue was purified by flash chromatography (hexane→hexane:EtOAc, 3:1) to give **26** (2.1 mg, 4.5 μmol, 10%) as a green solid and **27** (3.2 mg, 6.9 μmol, 16%) as a green-blue solid.

26: ¹H NMR (400 MHz, CDCl₃): δ = 9.53–9.47 (m, 1H), 8.00 (s, 1H), 7.90–7.84 (m, 1H), 7.64–7.54 (m, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 4.07 (t, *J* = 6.1 Hz, 2H), 4.02 (s, 3H), 3.96 (s, 3H), 3.79 (s, 3H), 2.81 (t, *J* = 6.1 Hz, 2H), 2.28 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 151.4, 149.2, 146.1, 143.6, 137.9, 131.8, 131.0, 129.5, 128.9, 128.4, 127.2, 127.1, 126.8, 126.7, 122.2 (2 overlapped ¹³C signals), 119.9, 61.3, 60.8, 60.5, 44.5, 22.3, 21.5 ppm. IR (ATR): $\tilde{\nu}$ = 2932, 2850, 1737, 1596, 1455, 1386, 1338, 1161, 1090, 1014, 721, 662, 567, 545 cm⁻¹. HRMS (ESI): *m/z* calcd for C₂₆H₂₆NO₅S⁺ [M+H]⁺: 464.1526; found: 464.1527.

27: ¹H NMR (600 MHz, CDCl₃): δ = 8.71 (dd, *J* = 8.6, 1.0 Hz, 1H), 8.37 (dt, *J* = 11.1, 0.9 Hz, 1H), 7.36–7.33 (m, 2H), 7.18 (ddt, *J* = 11.0, 8.4, 1.0 Hz, 1H), 7.02–7.00 (m, 2H), 6.99 (ddt, *J* = 11.1, 8.5, 0.8 Hz, 1H), 6.88 (ddd, *J* = 11.1, 8.4, 0.8 Hz, 1H), 4.15 (s, 3H), 4.00 (t, *J* = 5.9 Hz, 2H), 3.93 (s, 3H), 3.77 (s, 3H), 2.43 (t, *J* = 5.9 Hz, 2H), 2.28 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 151.4, 149.5, 143.8, 142.6, 138.4, 136.9, 135.8, 134.3, 132.8, 131.2, 130.1, 129.5, 127.5, 126.3, 124.0, 120.9, 115.0, 113.6, 61.7, 61.3, 60.7, 47.9, 21.6, 19.8. IR (ATR): $\tilde{\nu}$ = 2935, 2840, 1604, 1391, 1350, 1290, 1159, 1139, 1044, 1006, 708, 660, 543 cm⁻¹. HRMS (ESI): *m/z* calcd for C₂₆H₂₆NO₅S⁺ [M+H]⁺: 464.1531; found: 464.1526.

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Conflict of Interest

The authors declare no conflict of interest.

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