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Substituted 5,6,11,12-Tetradehydrodibenzo[*a*,*e*]cyclooctenes: Syntheses, Properties, and DFT Studies of Substituted Sondheimer–Wong Diynes

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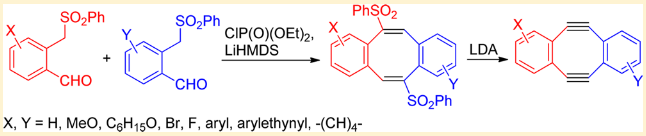
Supporting Information

ABSTRACT: Highly strained cyclic acetylenes 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctenes (Sondheimer–Wong diynes) having various substituents on their benzene rings were synthesized successfully by one-pot treatment of the corresponding formyl sulfones with diethyl chlorophosphate/lithium hexamethyldisilazide (LiHMDS) and then lithium diisopropylamide (LDA). When mixtures of two types of formyl sulfones bearing different substituents were subjected to this protocol, the unsymmetrically substituted Sondheimer–Wong diynes could be synthesized in a stepwise manner by isolation of the heterocoupled vinyl sulfone intermediates followed by their treatment with LDA. The UV–vis absorption spectra and cyclic voltammograms of the substituted Sondheimer–Wong diynes were recorded. The electronic effect of substituents on the diynes was investigated in their click reactions and nucleophilic and electrophilic additions.



X, Y = H, MeO, $C_6H_{15}O$, Br, F, aryl, arylethynyl, -$(CH)_4$-

■ INTRODUCTION

Aryl alkynes have attracted great attention because they have rigid arrays bearing expanded π systems[1] and thus can serve as organic optoelectronic materials such as dyes for photoelectron conversion devices,[2] light-emitting materials for electroluminescence (EL),[3] and organic semiconductor materials.[4] Aryl alkynes undergo a variety of transformations in organic synthesis to give newly formed expanded π systems. Addition of nucleophiles or electrophiles to the triple bond gives vinyl units,[5] and Diels–Alder reactions of aryl alkynes with cyclopentadienone followed by elimination of carbon monoxide furnish benzene units.[6] Terminal acetylenes undergo Sonogashira coupling with aryl halides to provide aryl alkynes bearing more expanded π systems.[7] A cyclic aryl alkyne, 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (Sondheimer–Wong diyne, **2a**)[8] (Figure 1), exhibits high reactivity because of its inherent strain energy (ca. 15 kcal/mol per triple bond).[9] For instance, when **2a** is treated with an alkyl or aryl azide, the desired click reaction of **2a** with the azide proceeds without Cu catalyst to give the corresponding triazole (Scheme 1).[10] Sondheimer–Wong diyne **2a** serves as a precursor of the 16-π-electron antiaromatic compound dibenzopentalene, and nucleophilic addition of alkyllithium[11] or electrophilic addition of dihalogene[12] to **2a** provides dibenzopentalene skeletons through accompanying transannulation. Despite such synthetic availability, only a few synthetic methods for **2a** have been reported. In 1974, Wong and Sondheimer succeeded in the first synthesis of **2a** by bromination of dibenzo[*a*,*e*]cyclooctene followed by *t*-BuOK-promoted dehydrobromination (36% yield over two steps).[8a] Using the same procedure, Wong succeeded in the syntheses of the dinaphtho derivative **2i** and the benzonaphtho derivative **2ai** and in their Diels–Alder cyclizations.[8e] In 2002, Wudl and co-workers reported a more efficient synthesis of **2a** using α,α'-dibromo-*o*-xylene as the starting compound.[8c] In this route, the synthesis of a precursor of **2a**, dibenzo[*a*,*e*]cyclooctene, could be carried out on a large scale (>50 g) to achieve a yield of 58% over three steps: Li-promoted dimeric cyclization of α,α'-dibromo-*o*-xylene (80%), NBS bromination (>90%), and *t*-BuOK-promoted dehydrobromination (80%). The following two-step transformation of dibenzo[*a*,*e*]cyclooctene to **2a** was also dramatically improved in comparison with that of Sondheimer's original procedure (36% yield (75% × 48%)) and proceeded in 87% yield. Wudl and co-workers achieved another practical synthesis of **2a** from commercially available dibenzosuberenone.[8c] This process involves ring expansion of dibenzosuberenone with trimethylsilyldiazomethane (70% yield), conversion to the triflate (60%), bromination of the olefin moiety, and *t*-BuOK-promoted dehydrobromination (98% yield over two steps). In 2002, we realized a one-pot synthesis of **2a** by taking advantage of a double elimination protocol starting from formylbenzyl sulfone **1a** (Scheme 2).[8b] In our synthesis, when a THF solution of **1a** and diethyl chlorophosphate was treated with LiHMDS and LDA successively, **2a** was obtained in 61% yield after column chromatography on silica gel. Although our protocol involves a

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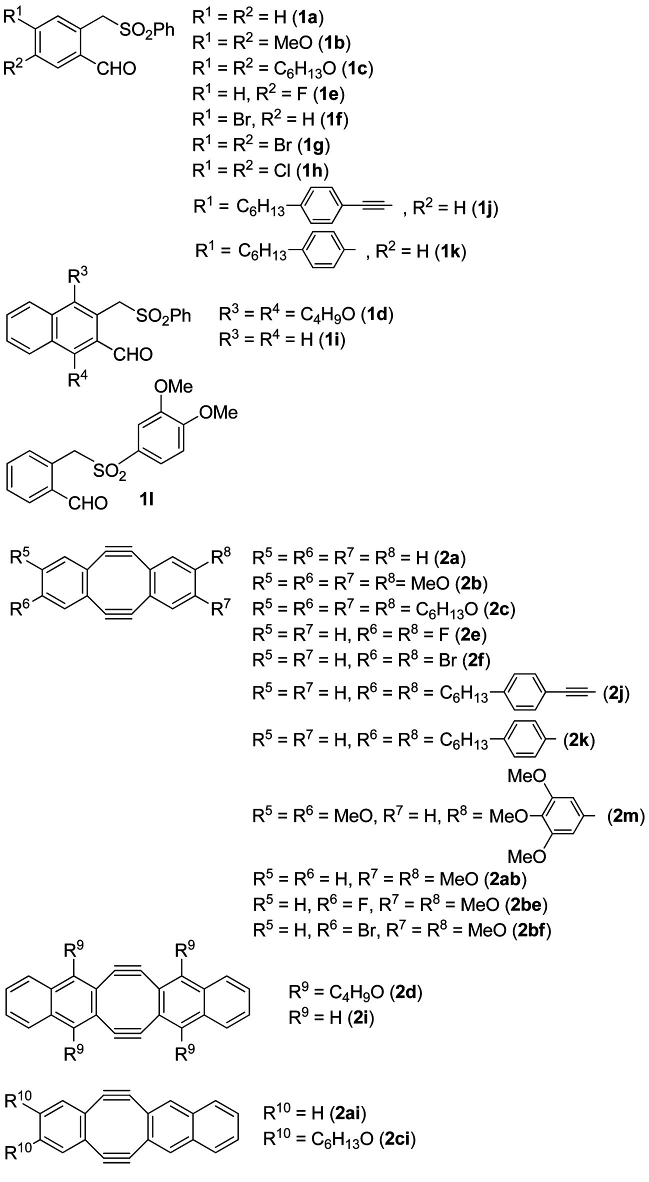
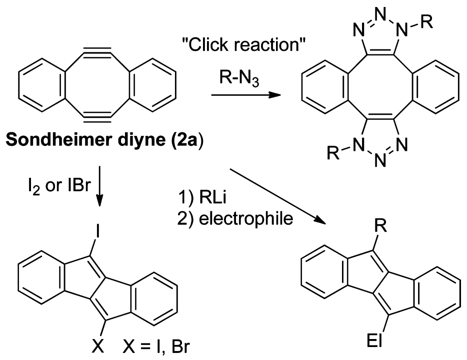
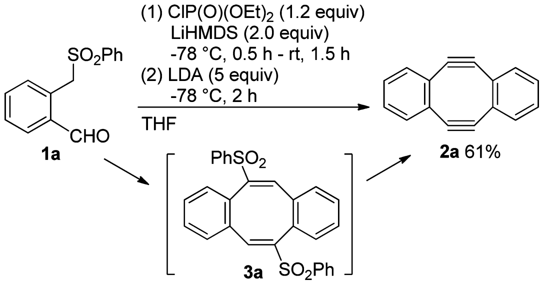


Figure 1. Structures of sulfones **1** and cyclic diynes **2**.

Scheme 1. Transformation of 2a to a Ditriazole and Pentalenes



Scheme 2. One-Pot Synthesis of Sondheimer Diyne 2a



number of reactions such as deprotonation of benzyl sulfone **1a**, intermolecular and intramolecular Wittig−Horner-type olefinations to provide cyclic vinyl sulfone **3a**, and elimination of sulfinic acid from **3a**, all of these reactions proceed in a one-pot manner.[13,14] Thus, practical synthetic processes to afford **2a** were realized, but syntheses of substituted derivatives except for **2i** and **2ai** still had not been achieved (Figure 1).[8e] In order to expand cyclic diyne chemistry and develop new π systems such as pentalenes and triazoles, we applied our double elimination protocol to the synthesis of substituted cyclic diynes **2b**−**2ci** (Figure 1). We describe herein the preparation of substituted formyl sulfones **1b**−**l** and their transformation to substituted cyclic diynes **2b**−**2ci** by means of our double elimination protocol.

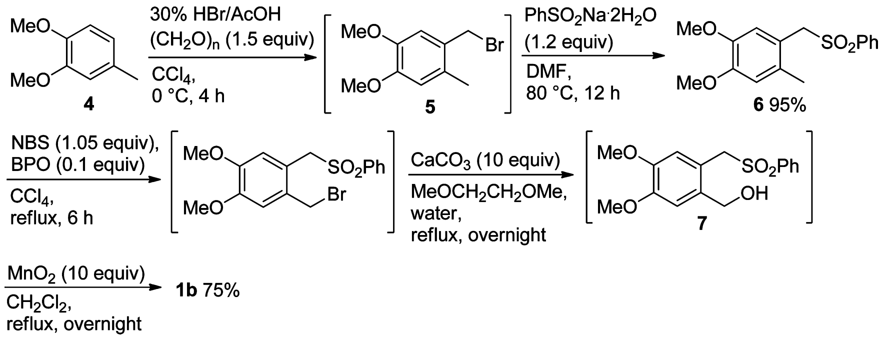
■ RESULTS AND DISCUSSION

First, synthetic routes for substituted formyl sulfones **1b**−**l** were developed. Dimethoxy-substitued formyl sulfone **1b** was prepared from commercially available 3,4-dimethoxytoluene (**4**), as shown in Scheme 3. When **4** was treated with paraformaldehyde in the presence of HBr and AcOH, bromomethylation proceeded regioselectively to give **5**, and treatment of **5** with $PhSO_2Na$ in DMF provided benzyl sulfone **6** in 95% yield over two steps. Sulfone **6** was transformed to hydroxybenzyl sulfone **7** through bromination (NBS, BPO) and nucleophilic hydroxylation ($CaCO_3$, water). Oxidation of the resulting benzyl alcohol **7** with MnO_2 gave the desired dimethoxyformylbenzyl sulfone **1b** in 75% yield over three steps. Other formyl sulfones **1c**−**i** were prepared by similar procedures. Bromoformylbenzyl sulfone **1f** was transformed to 4-hexylphenylethynyl derivative **1j** and 4-hexylphenyl-substituted derivative **1k** by Sonogashira[7] and Suzuki−Miyaura coupling,[15] respectively.

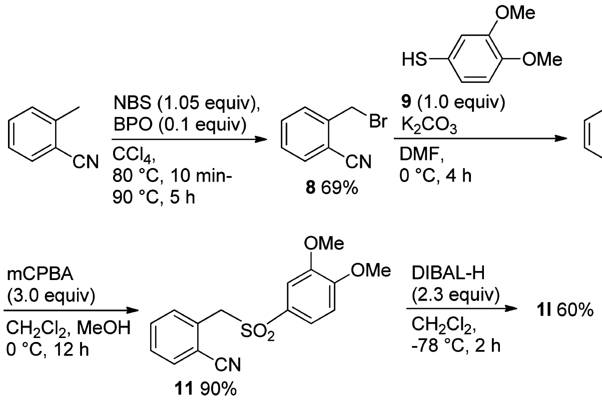
Sulfone **1l** bearing a 3,4-dimethoxyphenylsulfonyl group was synthesized as shown in Scheme 4. Treatment of *o*-tolunitrile with NBS and BPO gave bromide **8** in 69% yield. Nucleophilic substitution of bromide **8** with **9** in the presence of K_2CO_3 provided benzyl phenyl sulfide **10** in 98% yield. Subjection of **10** to *m*CPBA oxidation of the sulfide moiety followed by DIBAL-H reduction of the cyano group in the resulting sulfone **11** afforded **1l** (90% × 60%).

Having these substituted formyl sulfones in hand, we attempted to transform them to the corresponding cyclic acetylenes by invoking the double elimination protocol (Scheme 5). When LiHMDS and LDA were added successively to a THF solution of **1b** and diethyl chlorophosphate, tetramethoxy-substituted cyclic acetylene **2b** was obtained in 57% yield after purification by column chromatography on silica gel. A stepwise procedure for **2b** proceeded smoothly as well to afford a similar result: 51% yield for two steps (58% × 88%). Cyclic acetylene **2b** is a yellow powdery compound that has poor solubility in any organic solvents. Surprisingly, **2b** is remarkably stable and could be kept at rt in the air for over 6 months.[16] Subjection of bis(hexyloxy)-substituted formyl sulfone **1c** to the one-pot double elimination protocol provided

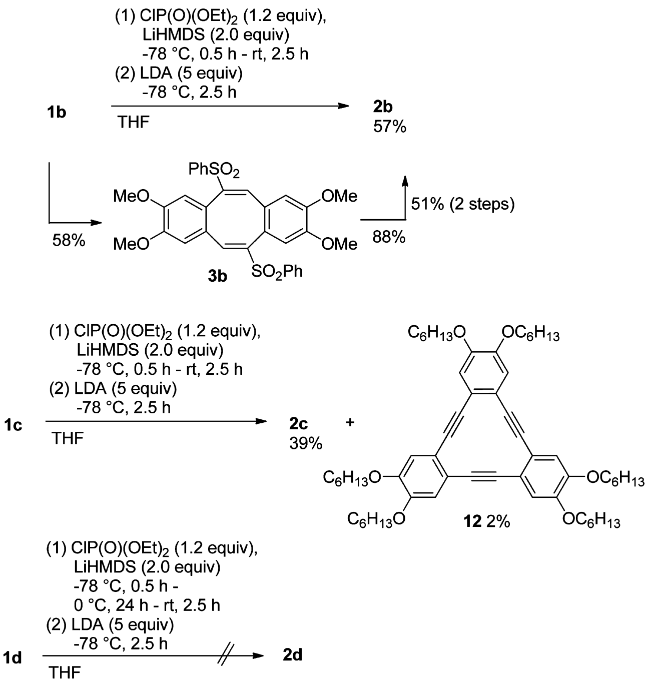
Scheme 3. Synthesis of Sulfone 1b



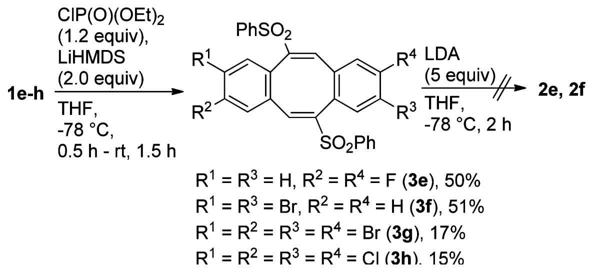
Scheme 4. Synthesis of Sulfone 11



Scheme 5. Synthesis of Cyclic Diynes 2b and 2c



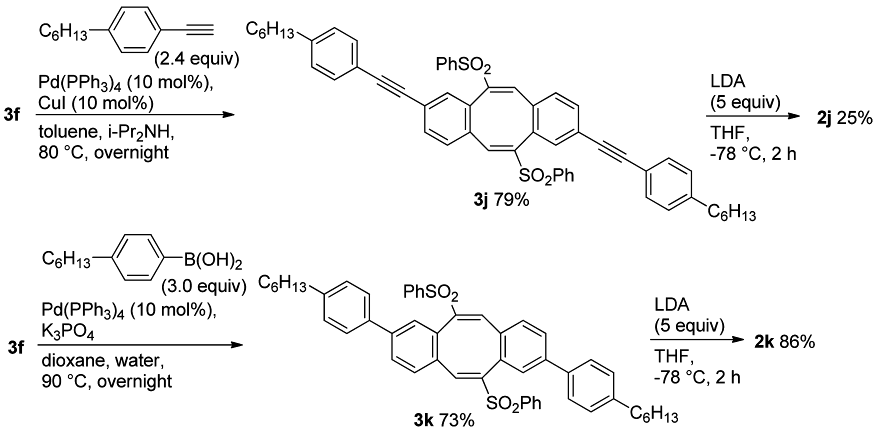
Scheme 6. Synthesis of Cyclic Vinyl Sulfones 3e−h



2c and **12** in 39% and 2% yield, respectively. Tetra(hexyloxy)-substituted cyclic acetylene **2c** exhibited higher solubility than **2b** because of the longer alkyl chains of **2c**. When bis(butoxy)-substituted sulfone **1d** was used, the cyclization proceeded sluggishly, and **2d** was not obtained.

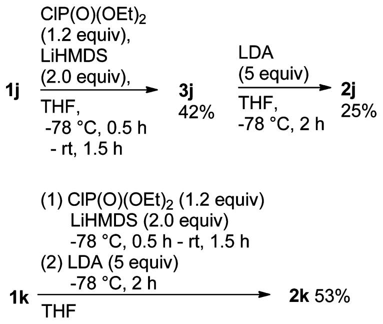
When halogen-substituted formyl sulfones **1e−h** were treated with diethyl chlorophosphate (1.2 equiv) and LiHMDS (2.0 equiv) in THF, the corresponding dihalogen-substituted cyclic vinyl sulfones **3e** and **3f** were obtained in moderate yields (50% and 51%, respectively) while tetrahalogen-substituted derivatives **3g** and **3h** were obtained only in poor yields (17% and 15%, respectively) (Scheme 6). Subjection of **3e** and **3f** to LDA-promoted elimination resulted in the formation of a mixture of unidentified byproducts. These results indicated that the halogen-substituted cyclic acetylenes were difficult to synthesize from **1e−h** by invoking the double elimination protocol. Therefore, we attempted to transform the bromo substituents in **3f** to other functional groups before elimination of sulfinic acid. As shown in Scheme 7, cyclic vinyl sulfone **3f** served well as a building block for the syntheses of phenylethynyl- and phenyl-substituted cyclic acetylenes **2j** and **2k**, respectively. Bis(4-hexylphenylethynyl)- and bis(4-hexylphenyl)-substituted cyclic vinyl sulfones **3j** and **3k** were produced from **3f** by Sonogashira[7] and Suzuki−Miyaura coupling[15] in 79% and 73% yield, respectively, and treatment of **3j** and **3k** with 5 equiv of LDA gave the desired bis(4-hexylphenylethynyl)- and bis(4-hexylphenyl)-substituted cyclic

Scheme 7. Syntheses of Cyclic Diynes **2j** and **2k**



acetylenes **2j** and **2k**, respectively. These cyclic acetylenes **2j** and **2k** could also be synthesized from bis(4-hexylphenylethynyl)- and bis(4-hexylphenyl)-substituted formyl sulfones **1j** and **1k**, respectively, by invoking the double elimination protocol (Scheme 8).

Scheme 8. Syntheses of Cyclic Diynes **2j** and **2k** from **1j** and **1k**



We previously reported that the high polarity of the sulfonyl group enables easy isolation of diarylethenyl sulfone intermediates and that sequential treatment of the diarylethenyl sulfones with LDA gives the desired diarylethynes, which are otherwise difficult to separate from hydrocarbon byproducts.[17] We applied this polarity-assisted separation technology[18] to the synthesis of unsymmetrically substituted cyclic acetylenes. When a 1:1 mixture of **1a** and **1b** was treated with diethyl chlorophosphate (1.2 equiv) and LiHMDS (2.0 equiv) in THF, three cyclic vinyl sulfones **3a**, **3b**, and **3ab** were obtained (Scheme 9). Because these three sulfones exhibit different polarities in TLC in accordance with number of methoxy substituents (R_f = 0.55 for **3a**, 0.30 for **3ab**, and 0.16 for **3b** (EtOAc/CH_2Cl_2/hexane, 1:2:4)), these sulfones could be isolated by column chromatography on silica gel in pure form in yields of 21% for **3a**, 19% for **3ab**, and 15% for **3b**. LDA-promoted elimination of sulfinic acid from **3ab** proceeded smoothly to furnish the desired unsymmetrically substituted cyclic acetylene **2ab** in 86% yield (16% over two steps). This stepwise synthesis of unsymmetrically substituted cyclic acetylenes could be applied to the syntheses of other derivatives, including **2be** (15% (17% × 86%)), **2bf** (8% (11% × 76%)), and **2ci** (25% (28% × 91%)). In sharp contrast to these examples, when a mixture of **1b** and **1h** was subjected to the same cyclization, the desired cyclic ethenyl sulfone **3bh** was not obtained, and the homocyclized ethenyl sulfones **3b** and **3h** were obtained as the sole products.

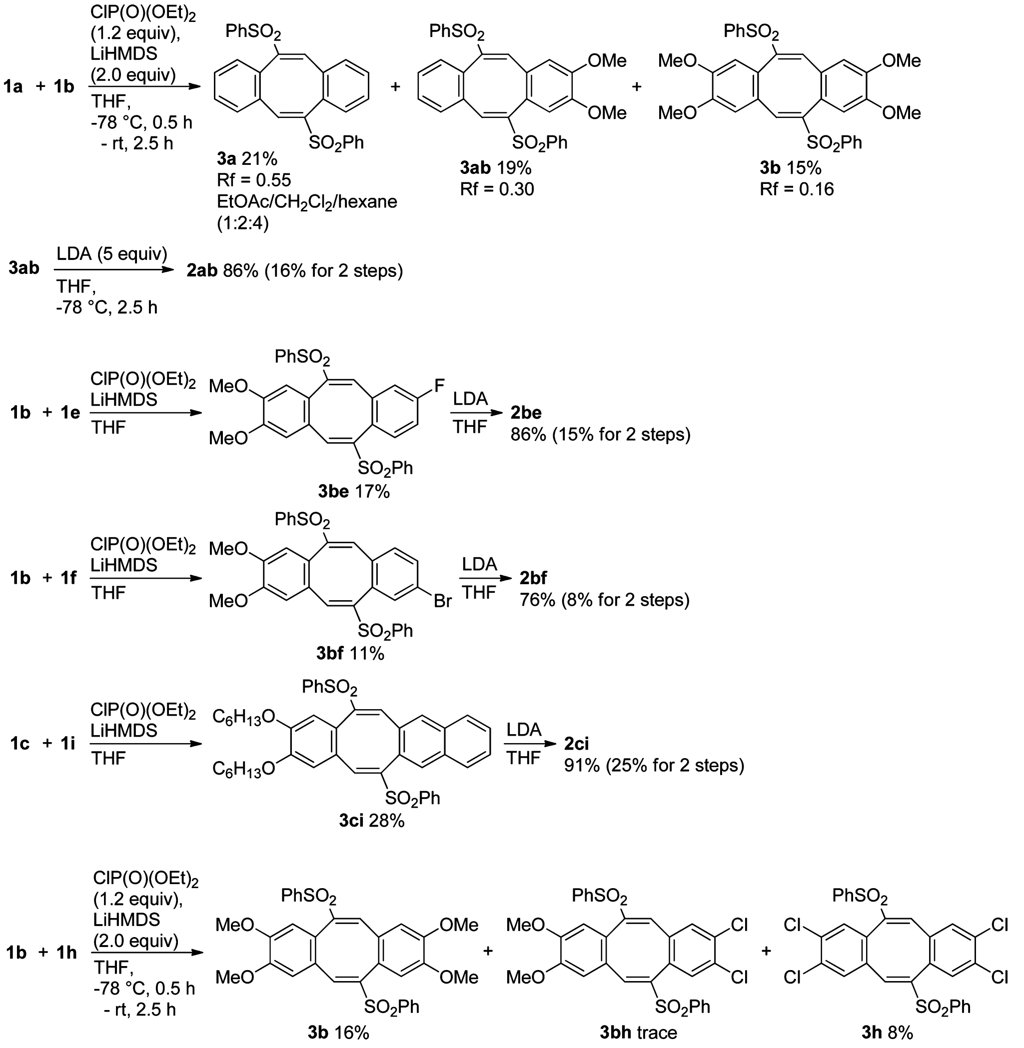
The bromo- and dimethoxy-substituted cyclic vinyl sulfone **3bf** obtained from the reaction between **1b** and **1f** could be used as a building block for the synthesis of aryl-substituted derivative **2m** (Scheme 10). Suzuki–Miyaura coupling of **3bf** with 3,4,5-trimethoxyphenylboronic acid gave **3m** quantitatively, and the following LDA-promoted elimination of sulfinic acid in **3m** afforded the desired 3,4,5-trimethoxyphenyl-substituted derivative **2m**.

We found that for synthesis of derivative **2ai**, 3,4-dimethoxyphenyl sulfone **1l** served well. In this synthesis, the polar methoxy groups of **1l** enabled easy isolation of the cyclic vinyl sulfone **3il** from the homocyclization products **3i** and **3l** (Scheme 11). Subsequent treatment of **3il** with LDA provided the target cyclic acetylene **2ai** in 86% yield (20% yield over two steps). Although a stepwise synthesis of **2ai** invoking Wittig olefination and bromination/dehydrobromination was reported in 1990, the isolation of **2ai** was not achieved, and **2ai** was used for the following Diels–Alder reaction in an impure form.[8e] In sharp contrast to that report, our synthesis (polarity-assisted purification of **3il**/LDA-promoted elimination of sulfinic acid) enabled easy isolation of **2ai** in pure form using conventional column chromatography on silica gel.

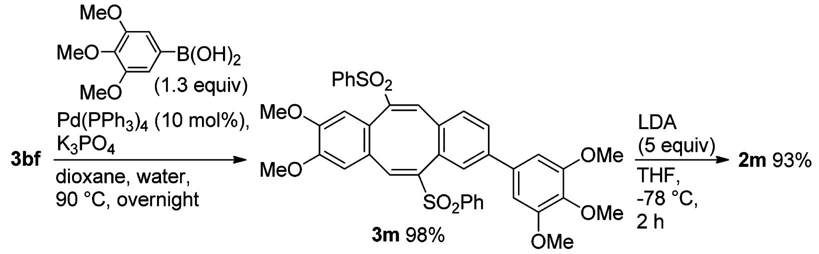
Table 1 presents a summary of the chemical shifts of the acetylenic carbons in the cyclic diyne moieties of **2** together with chemical shifts calculated at the B3LYP/6-31G(d) level. All of the acetylenic carbons in the cyclic diyne moieties of **2** were observed at chemical shifts downfield from 103 ppm, and these results are rather consistent with the calculated chemical shifts. In contrast to this, the signals for the acetylenic carbons of the phenylethynyl groups attached to the cyclic diyne core in **2j** were observed at 87.6 and 92.1 ppm. When nucleus-independent chemical shifts (NICS(1)) were calculated for **2**, all of the cyclic diyne moieties of **2** showed positive values (Table 1).[19] Almost all of the NICS(1) values were larger than 5.0 ppm, but in cyclic diynes having efficiently expanded π systems such as phenylethynyl (**2j**) and naphtho (**2ai**, **2ci**) moieties, smaller NICS(1) values were observed: 4.84 ppm for **2j**, 3.31 for **2ai**, and 3.23 ppm for **2ci**.

Table 2 presents a summary of strain energies of the synthesized cyclic diynes **2** calculated at the PM3 level, and Table 3 shows the same summary for compounds **2d**, **2e**, and **2f** that could not be synthesized by the double elimination protocol. All of the substituted cyclic diynes **2** show similar values of strain energy. This result indicates that the syntheses

Scheme 9. Syntheses of Cyclic Diynes 2ab, 2be, 2bf, and 2ci



Scheme 10. Synthesis of Cyclic Diyne 2m



of **2d**, **2e**, and **2f** invoking the double elimination protocol were retarded not because of larger strain energies but for other reasons. In the synthesis of **2d**, the bulkiness of the butoxy groups attached in the vicinity of the reaction site probably prevents the intermolecular and/or intramolecular approach of the sulfonylmethyl anion to the formyl group.[20] In the syntheses of cyclic diynes **2e** and **2f**, because of the rather low energies of their LUMOs (−2.16 eV for **2e** and −2.38 eV for **2f**; Table 3), they undergo nucleophilic addition of basic species to form the unidentified byproducts.[21,22]

In order to get further insight into the substituent effects on the physical properties of **2**, UV−vis absorption and photoluminescence spectra and cyclic voltammograms were recorded for **2**. The UV−vis absorption spectra of cyclic acetylenes **2a**, **2b**, **2c**, **2j**, **2k**, **2m**, **2ab**, **2be**, **2ai**, and **2ci** were recorded in CH_2Cl_2 and are shown in Figure 2, and the spectral data are summarized in Table 4 along with the corresponding results of TD-DFT calculations (B3LYP/6-31G(d)).

Cyclic acetylene **2a** exhibited a sharp absorption at 272 nm, and the alkoxy-substituted derivatives **2b**, **2c**, **2ab**, and **2be** underwent bathochromic shifts in accordance with the numbers of methoxy groups on the benzene rings: tetramethoxy, λ_{max} = 287 nm (**2b**), 289 nm (**2c**); dimethoxy, λ_{max} = 283 nm (**2ab**), 282 nm (**2be**). For **2m** with a 3,4,5-trimethoxyphenyl group attached on the benzene ring, a large bathochromic shift was observed, indicating efficient expansion of the π system in the newly formed biphenyl unit. More efficient expansion of the π system was observed in bis(phenylethynyl)- and diphenyl-

Scheme 11. Synthesis of Cyclic Diyne 2ai

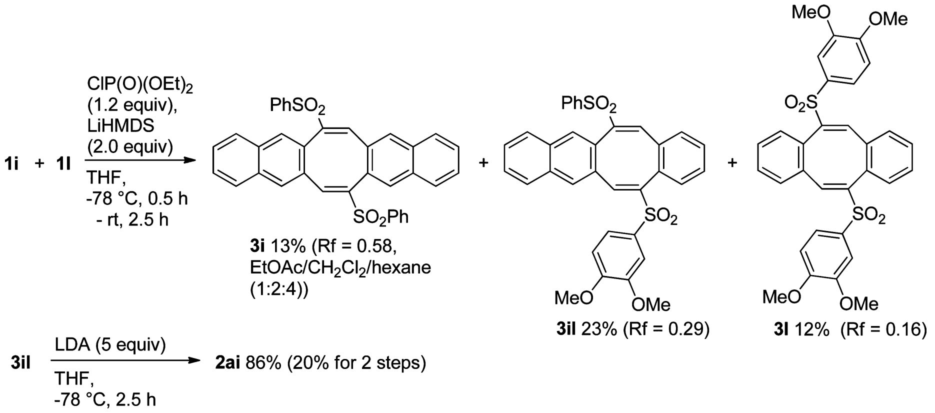


Table 1. Recorded[a] and Calculated[b] Chemical Shifts of Acetylenic Carbons and NICS(1) Values for Cyclic Diynes 2[b] (All Values in ppm)

	2a	2b	2c[c]	2j[d]	2k[d]
^{13}C NMR[e]	109.3 (106.8)	108.6 (105.9)	108.5 (105.9)	109.7 (106.9)	109.6 (107.0)
				110.0 (108.1)	109.7 (107.4)
				87.6	
				92.1	
NICS(1)	5.33	5.12	5.12	4.84	5.10

	2m	2ab	2be	2ai	2ci[c]
^{13}C NMR[e]	103.7 (105.9)	108.8 (106.2)	107.3 (105.1)	109.3 (106.5)	109.0(106.0)
	103.7 (106.7)	109.1 (106.7)	108.0 (105.5)	109.6 (107.4)	109.5 (107.3)
	108.5 (106.7)		108.7 (106.1)		
	108.8 (106.9)		110.7 (107.8)		
NICS(1)	5.08	5.24	5.12	3.31	3.23

[a] Recorded in $CDCl_3$. [b] The structures of **2** were optimized, and their chemical shifts and NICS(1) values were calculated at the B3LYP/6-31G level. [c] Calculations were performed on methoxy derivatives. [d] Calculations were performed on methyl derivatives. [e] Calculated chemical shifts are shown in parentheses.

Table 2. Strain Energies[a] of Cyclic Diynes 2 (in kcal/mol)

2a	2b	2c[b]	2j[c]	2k[c]	2m	2ab	2be	2ai	2ci[b]
33.9	33.7	33.7	33.9	33.9	33.1	33.8	33.8	32.7	32.6

[a] The structures of **2** were optimized, and their strain energies were calculated at the PM3 level. [b] Calculations were performed on methoxy derivatives. [c] Calculations were performed on methyl derivatives.

Table 3. Strain Energies (in kcal/mol)[a] and HOMO/LUMO Levels (in eV)[b] of Cyclic Diynes 2d, 2e, and 2f

	2d[c]	2e	2f
strain energy	30.0	33.9	33.9
E_{LUMO}	−1.62	−2.16	−2.38
E_{HOMO}	−4.99	−5.62	−5.76

[a] The structures of the cyclic diynes were optimized, and their strain energies were calculated at the PM3 level. [b] The structures of the cyclic diynes were optimized, and then their HOMO and LUMO energy levels were calculated at the B3LYP/6-31G(d) level. [c] Calculations were performed on the methoxy derivative.

substituted derivatives **2j** and **2k**, which exhibited their largest absorption bands at 341 and 312 nm with absorption ends at 355 and 335 nm, respectively. For benzonaphtho derivatives **2ai** and **2ci**, large red shifts of the absorption bands were observed: $\Delta\lambda_{max}$ (relative to λ_{max} of **2a**) = 29 nm for **2ai** and 42 nm for **2ci**. Between these benzonaphtho derivatives **2ai** and **2ci**, the substitution with alkoxy groups led to a bathochromic shift: λ_{max} = 301 nm for **2ai** versus 314 nm for **2ci**. All of the λ_{max} values recorded for cyclic acetylenes **2** showed considerable agreement with the simulation results.

When compounds **2** in CH_2Cl_2 were irradiated with UV light, the benzonaphtho derivatives **2ai** and **2ci** exhibited blue emission, but the other compounds **2** did not. The emissions of **2ai** and **2ci** were observed at 463 and 515 nm, respectively, and their photoluminescence quantum yields were 0.01 (Figure 3). TD-DFT calculations demonstrated that the HOMO−LUMO transitions in the benzonaphtho derivatives **2ai** and **2ci** were allowed, resulting in photoluminescence: the oscillator strengths for the $S_0 \rightarrow S_1$ transitions (f_1) were 0.0008 (65 → 66) at 436 nm for **2ai** and 0.0029 (121 → 122) at 445 nm for **2ci** (Table 4). In contrast, the HOMO−LUMO transitions in cyclic acetylenes **2a**, **2b**, **2c**, **2j**, **2k**, **2ab**, and **2be** were prohibited ($f_1 \leq 0.0004$), resulting in the nonfluorescent properties. Despite a large oscillator strength (f_1 = 0.0199), **2m** did not exhibit fluorescence because of nonemissive relaxation ascribable to flexible rotation along the C−C bond between the phenyl and cyclic diyne moieties.[23,24]

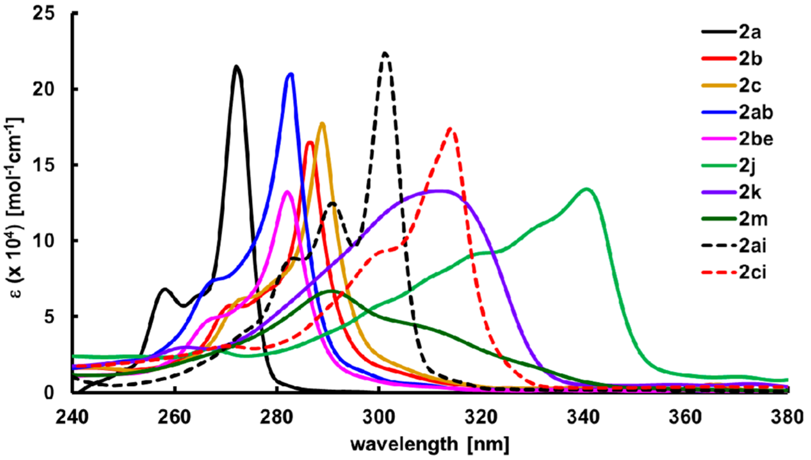


Figure 2. UV−vis absorption spectra (1.0×10^{-6} M in CH_2Cl_2 for **2a** and **2ai**, 1.0×10^{-4} M in CH_2Cl_2 for the others.).

Table 4. Summary of UV−Vis Absorption Data for Cyclic Diynes 2 and Calculated Largest λ_{max} Values, HOMO−LUMO Transition Wavelengths, and Oscillator Strengths

	2a	2b	2c	2j	2k	2m	2ab	2be	2ai	2ci
exptl λ_{max} (ε)[a]	272 (2.1)	287 (1.6)	289 (1.8)	341 (1.3)	312 (1.3)	291 (0.7)	283 (2.1)	282 (1.3)	301 (2.2)	314 (1.7)
calcd λ_{max} (f)[b]	273 (1.13)	284 (1.15)	287 (1.76)	368 (2.92)	324 (2.01)	298 (1.30)	280 (0.74)	283 (0.78)	301 (1.69)	308 (2.07)
calcd $\lambda_{H\rightarrow L}$ (f)[b]	466 (0.0)	484 (0.0)	485 (0.2)	517 (0.0)	491 (0.1)	489 (19.9)	476 (0.4)	478 (0.3)	436 (0.8)	445 (2.9)

[a] Spectra were recorded at room temperature in CH_2Cl_2 (1.0×10^{-6} M for **2a** and **2ai**, 1.0×10^{-4} M for the others). λ_{max} is the maximum wavelength for the largest absorption peak in nm. The molar absorptivities ε are in units of 10^5 M^{-1} cm^{-1}. [b] Calculations were performed at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. λ_{max} is the maximum wavelength for the largest absorption peak in nm, $\lambda_{H\rightarrow L}$ is the wavelength of the HOMO → LUMO transition in nm, and f is the oscillator strength ($\times 10^{-3}$).

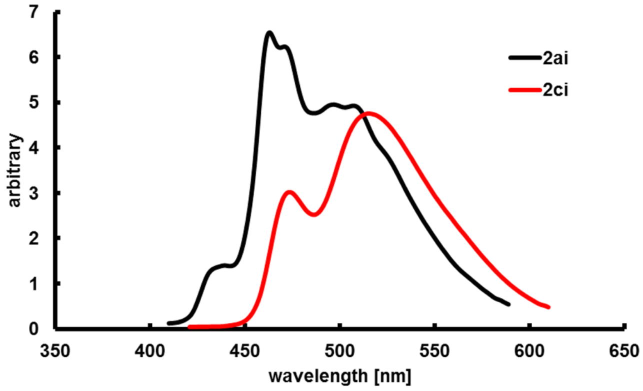


Figure 3. Photoluminescence spectra of **2ai** and **2ci** in CH_2Cl_2 (1.0×10^{-6} M).

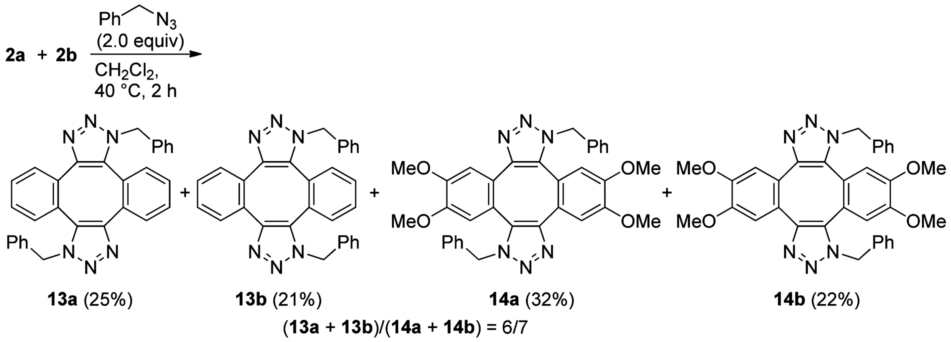
The electrochemical properties of **2** were measured by cyclic voltammetry in CH_2Cl_2, and Table 5 summarizes all of the half-wave potentials recorded in reference to Fc/Fc^+ and the HOMO and LUMO levels calculated by DFT (B3LYP/6-31G(d)). All of the cyclic acetylenes **2** underwent smooth oxidation, and the half-wave potentials were observed in the range between +1.10 and +0.41 V, while **2j** exhibited irreversible oxidation. Cyclic acetylene **2a** showed an oxidation peak at +1.10 V, and at this potential **2a** underwent two-electron oxidation to provide the 14-π-electron aromatic dication species **2a**$^{2+}$.[25] Substitution of the benzene rings with electron-donating alkoxy groups provided smaller oxidation potentials in accordance with the numbers of alkoxy groups: +1.10 V for **2a**, +0.71 V for **2be** (two MeO−, F−), +0.65 V for **2ab** (two MeO−), +0.44 for **2b** (four MeO−), and +0.41 V for **2c** (four $C_6H_{13}O$−). The similar substituent effect was shown in the benzonaphtho motif series **2ai** and **2ci**. Bis(hexyloxy)-substituted cyclic acetylene **2ci** underwent facile electrochemical oxidation in comparison to **2ai**: +0.58 V for **2ci** and +1.06 V for **2ai**. DFT calculations (B3LYP/6-31G(d)) performed on **2** demonstrated that alkoxy substituents on the benzene moieties afford higher HOMO levels, resulting in the easy electrochemical oxidation of **2**. The expansion of the π system in **2j**, **2k**, and **2m** facilitated their smooth oxidation, but for **2j** only an irreversible oxidation profile was recorded, indicating the instability of the corresponding cationic species derived from **2j**. Although no reduction potential was observed

Table 5. Reduction and Oxidation Potentials (in V vs Fc/Fc^+)[a] and Calculated LUMO and HOMO Levels (in eV) for 2[b]

	2a	2b	2c	2j	2k	2m	2ab	2be	2ai	2ci
$E_{1/2}^{red}$	−	−	−	−1.97	−2.16	−	−	−	−	−
E_{LUMO}	−1.95	−1.83	−1.74	−2.22	−1.97	−1.88	−1.89	−1.99	−1.86	−1.76
$E_{1/2}^{ox}$	+1.10	+0.44	+0.41	irrev.	+0.92	+0.65	+0.65	+0.71	+1.06	+0.58
E_{HOMO}	−5.44	−5.17	−5.07	−5.20	−5.22	−5.15	−5.29	−5.38	−5.49	−5.31

[a] The reduction and oxidation potentials were measured under the following conditions: in CH_2Cl_2 (1.0×10^{-4} M, 100 mV/s scan rate, 0.1 M Bu_4NPF_6) using a glassy carbon working electrode, a Pt counter electrode, and a Ag/Ag^+ reference electrode (0.01 M $AgNO_3$ and 0.1 M tetrabutylammonium perchlorate in acetonitrile) in 0.1 M $LiClO_4$/acetonitrile. [b] Calculations were performed at the B3LYP/6-31G(d) level.

Scheme 12. Competitive Click Reaction of 2a and 2b

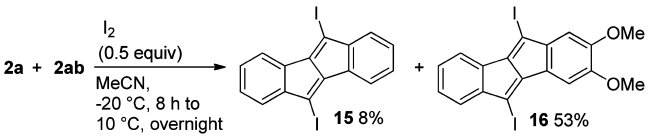


for **2a**, phenylethynyl- and phenyl-substituted derivatives **2j** and **2k** underwent smooth reduction at −1.97 and −2.16 V, respectively. The DFT calculations indicated that the expansion of the π system in **2j** and **2k** resulted in lower LUMO levels, facilitating easy electrochemical reduction.

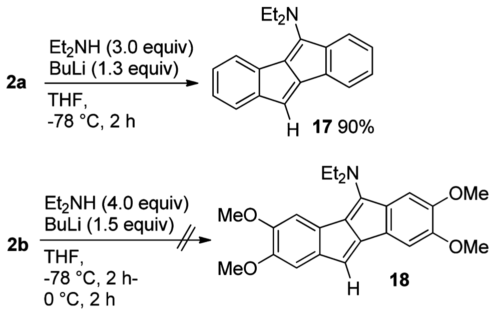
Finally, we carried out several transformations of ethyne moieties in **2** in order to evaluate the electronic effect of methoxy groups on the benzene rings. When a CH_2Cl_2 solution of **2a**, **2b**, and benzyl azide in 1:1:2 ratio was heated at 40 °C for 3 h, the expected click reaction proceeded smoothly to form **13a** (25%), **13b** (21%), **14a** (32%), and **14b** (22%) (Scheme 12).[10a] The ratio of the ditriazoles derived from **2a** and **2b** was 6:7, and tetramethoxy-substituted derivative **2b** showed a slightly higher reactivity in comparison with **2a**. Kinetic studies demonstrated that the second-order rate constants for the click reactions of **2a** and **2b** with benzyl azide in methanol at 25 °C were $k = 0.063$ and $0.14\ \mathrm{M^{-1}\ s^{-1}}$, respectively.[26] These results are consistent with the higher reactivity of **2b** as observed in the competitive reaction.

We reported syntheses of dibenzopentalenes through the addition of an electrophile or nucleophile to the acetylene moiety of **2a** followed by transannulation.[11,12] Competitive iodination of **2a** and **2ab** afforded dibenzopentalene **16** preferentially (8% yield for **15**, 53% yield for **16**) (Scheme 13). The selective formation of **16** as observed in this competitive reaction could be attributed to the electron-donating effect of the methoxy groups, which led to a higher HOMO level of **2ab** to promote addition of I^+ to the acetylene moiety: E_{HOMO} (B3LYP/6-31G(d)) = −5.44 eV for **2a** and −5.29 eV for **2ab**. In nucleophilic addition of lithium diethylamide to **2a**, the expected reaction proceeded smoothly to afford **17** in 90% yield (Scheme 14). In sharp contrast to this, the same nucleophilic addition of lithium amide to **2b** did not occur even at higher reaction temperature (0 °C, 2 h), and **18** was not observed; this was the case because the high LUMO level of **2b** disturbed the addition of lithium amide to the acetylene moiety: E_{LUMO} (B3LYP/6-31G(d)) = −1.95 eV for **2a** and −1.83 eV for **2b**.

Scheme 13. Competitive Electrophilic Addition in 2a versus 2ab



Scheme 14. Nucleophilic Addition of Lithium Diethylamide to 2a



■ SUMMARY

A series of substituted cyclic diynes were successfully synthesized from formylbenzyl sulfones by means of a double elimination protocol. Tetra- and dihalogen-substituted derivatives were not obtained using this protocol because they underwent decomposition under the basic reaction conditions. When a mixture of two types of formylbenzyl sulfones with different substituents were subjected to a stepwise double elimination protocol, the desired unsymmetrically substituted cyclic diynes were synthesized through isolation of the corresponding cyclic vinyl sulfone intermediate and LDA-promoted elimination of sulfinic acid. All of the substituted cyclic diynes showed similar strain energies (ca. 33 kcal/mol) irrespective of their substituents. In the UV−vis absorption spectra, substitution with alkoxy groups and expansion of the π system by phenylethynyl or phenyl groups induced bathochromic shifts of λ_{max}. Benzonaphtho derivatives also exhibited a bathochromic shift in comparison with dibenzo derivatives. It is noteworthy that upon UV irradiation the benzonaphtho derivatives exhibited emission in CH_2Cl_2, although the fluorescence quantum yields were indeed low ($\Phi_F = 0.01$). Although the cyclic diynes facilely underwent electrochemical oxidation, they did not undergo reduction. In the electrophilic addition of iodine to the cyclic diynes to form dibenzopentalenes, electron-donating methoxy substituents enhanced the addition of iodine. In the click reaction with azide, the same accelerating effect of the methoxy groups was observed. In contrast to these, methoxy groups disturbed the nucleophilic addition of lithium amide to the cyclic diyne.

■ EXPERIMENTAL SECTION

General Remarks. *Materials: General Procedures.* The reactions were carried out under an atmosphere of argon or nitrogen with freshly distilled solvents, unless otherwise noted. Dry tetrahydrofuran

(THF), dry Et_2O, and dry dichloromethane were purchased. Diisopropylamine, MeOH, CCl_4, hexamethylphosphoric triamide (HMPA), and dioxane were distilled from CaH_2, and toluene was distilled from sodium. A hexane solution of BuLi was purchased and titrated before use. Silica gel was used for column chromatography. The other materials were purchased from common commercial sources and used without additional purification.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on 300 or 500 MHz and 75 or 125 MHz spectrometers, respectively, in $CDCl_3$ and calibrated with tetramethylsilane (TMS) as an internal reference. For high-resolution mass spectral analyses, MALDI-TOF mass spectrometry was used. UV−vis absorption and emission spectra were measured under argon. For kinetic studies, the absorbance spectra (UV) were measured with a spectrophotometer using a quartz cuvette (10 mm light path) while the temperature was kept at 25 °C by an air-cooled-type Peltier thermostated cell holder. Absolute phtoluminescence quantum yields were measured using an integrating sphere system. CV was performed at 25 °C under argon.

Syntheses. *Synthesis of **1a**. (i). Synthesis of 1-Cyano-2-(phenylsulfonylmethyl)benzene.*[8b] A 100 mL flask was charged with 2-methylbenzonitrile (1.35 g, 10.0 mmol), *N*-bromosuccinimide (NBS) (1.87 g, 10.5 mmol), benzoyl peroxide (BPO) (242.0 g, 1.0 mmol), and CCl_4 (20.0 mL). After the mixture had been stirred at 80 °C for 5 min and at 90 °C for 5 h, it was allowed to cool to room temperature and filtered. The filtrate was washed with $NaHCO_3$(aq), dried over $MgSO_4$, and filtered, and the solvents were evaporated in vacuo. A mixture of the crude product, benzenesulfinic acid sodium salt dihydrate (2.4 g, 12.0 mmol), and DMF (20.0 mL) was stirred at 80 °C overnight, and the reaction mixture was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was subjected to recrystallization from CH_2Cl_2/hexane to give 1-cyano-2-(phenylsulfonylmethyl)benzene (2.15 g, 78%) in a pure form. Colorless needles; mp 157−160 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.57 (s, 2H), 7.27−7.57 (m, 4H), 7.62−7.73 (m, 5H).

*(ii). Synthesis of **1a**.*[8b] A 100 mL flask was charged with 1-cyano-2-(phenylsulfonylmethyl)benzene (1.29 g, 5.0 mmol) and CH_2Cl_2 (15 mL), and DIBAL-H (1.0 M in hexane, 11.5 mL, 11.5 mmol) was added at −78 °C. After the mixture had been stirred at this temperature for 2 h, aqueous NH_4Cl was poured into the mixture. After the usual workup with 1 M HCl and CH_2Cl_2, the solvents were evaporated in vacuo, and the residue was subjected to filtration through a thin pad (silica gel; CH_2Cl_2) and recrystallization from CH_2Cl_2/hexane to give **1a** (1.01 g, 78%) in a pure form. Colorless needles; mp 143−145 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 5.03 (s, 2H), 7.43−7.48 (m, 3H), 7.55−7.63 (m, 3H), 7.69−7.75 (m, 3H), 9.83 (s, 1H).

*Synthesis of **1b**. (i). Synthesis of **6**.* A suspension of **4** (4.5 g, 30.0 mmol), and paraformaldehyde (1.35 g, 45.0 mmol) in dry CCl_4 (50.0 mL) was cooled to 0 °C under N_2. To this suspension was added dropwise a solution of HBr/AcOH (33%, 12.0 mL) during the course of 3−5 min, and the resulting mixture was stirred for 4 h at 0 °C. Then the resulting mixture was poured into cold water (100.0 mL), and the organic layer was separated, washed with 5% $NaHCO_3$(aq), and dried over anhydrous $MgSO_4$. Evaporation of the solvents in vacuo afforded a white solid. To this crude product were added benzenesulfinic acid sodium salt dihydrate (7.20 g, 36.0 mmol) and DMF (50.0 mL). After the mixture had been stirred at 80 °C overnight, the reaction mixture was cooled to rt. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was purified by chromatography (EtOAc/hexane, 1:4) to give **6** (8.73 g, 95%) in a pure form. White powder; mp 158−160 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.65 (s, 3H), 3.84 (s, 3H), 4.31 (s, 2H), 6.41 (s, 1H), 6.61 (s, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 18.8, 55.6, 59.6, 113.1 (d), 114.2 (d), 117.8, 128.7, 128.8, 130.8, 133.5, 138.0, 146.5, 148.8; HRMS (MALDI-TOF) 329.0795 (M + Na^+), calcd for $C_{16}H_{18}O_4SNa$ 329.0823.

*(ii). Synthesis of **1b**.* To a suspension of **6** (1.84 g, 6.0 mmol) in CCl_4 (55.0 mL) under N_2 were added NBS (1.12 g, 6.3 mmol) and BPO (145.2 mg, 0.6 mmol) quickly at 90 °C, and then the resulting mixture was heated at 100 °C. After it had been stirred at this temperature for 6 h, the reaction mixture was cooled to rt. After the usual workup with CH_2Cl_2/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated, and the residue was used for the next step. To this crude product were added $CaCO_3$ (6.0 g, 60.0 mmol), $MeOCH_2CH_2OMe$ (20.0 mL), and H_2O (20.0 mL). After the resulting mixture had been heated at 120 °C overnight, it was cooled to rt, and the remaining $CaCO_3$ was neutralized with dilute HCl(aq) solution. After the usual workup with CH_2Cl_2/H_2O, the solvents were evaporated in vacuo, and the residue was used for the next step. To crude product **7** were added MnO_2 (5.22 g, 60.0 mmol) and CH_2Cl_2 (20.0 mL). After the resulting mixture had been heated at 50 °C overnight, it was allowed to cool to rt and filtered, and the filtrate was dried in vacuo. The residue was purified by chromatography (EtOAc/hexane, 1:1) to give **1b** (1.44 g, 75%) in a pure form. Pale-yellow powder; mp 145−147 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.95 (s, 3H), 4.91 (s, 2H), 6.79 (s, 1H), 7.24 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 9.78 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.9 (q), 56.1 (q), 57.0 (t), 113.6 (d), 115.3 (d), 123.4, 127.8, 128.4, 128.8, 133.7, 137.6, 149.2, 152.7, 189.4; HRMS (MALDI-TOF) 320.0737 (M^+), calcd for $C_{16}H_{16}O_5S$ 320.0718.

*Synthesis of **1c**. (i). Synthesis of 1,2-Bis(hexyloxy)-4-methylbenzene.* A flask under N_2 was charged with 4-methylbenzene-1,2-diol (2.48 g, 20.0 mmol), 1-bromohexane (9.9 g, 60.0 mmol), K_2CO_3 (8.29 g, 60.0 mmol), KI (332.0 mg, 2.0 mmol), and EtOH (30.0 mL). After the resulting mixture had been stirred at refluxing temperature for 30 h, it was allowed to cool to room temperature, and the remaining K_2CO_3 was neutralized with dilute HCl(aq) solution. After the usual workup with CH_2Cl_2/H_2O, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (CH_2Cl_2/hexane, 1:8) to give 1,2-bis(hexyloxy)-4-methylbenzene (5.56 g, 95%) in a pure form. Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87−0.90 (m, 6H), 1.30−1.34 (m, 8H), 1.46−1.47 (m, 4H), 1.76−1.83 (m, 4H), 2.27 (s, 3H), 3.93−3.97 (m, 4H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.70 (s, 1H), 6.77 (d, *J* = 8.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 25.7, 29.27, 29.31, 31.6, 69.0, 69.5, 114.2, 114.9 (d), 120.9 (d), 130.5, 146.8, 149.0; HRMS (MALDI-TOF) 292.2395 (M^+), calcd for $C_{19}H_{32}O_2$ 292.2402.

(ii). Synthesis of 1,2-Bis(hexyloxy)-4-methyl-5-(phenylsulfonylmethyl)benzene. The synthesis of 1,2-bis(hexyloxy)-4-methyl-5-(phenylsulfonylmethyl)benzene was carried out according to the procedure described above for **6**. Purification: chromatography (EtOAc/hexane, 1:6). Yield: 8.49 g, 95%. White powder; mp 58−60 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.86−0.91 (m, 6H), 1.28−1.33 (m, 8H), 1.43−1.46 (m, 4H), 1.72−1.81 (m, 4H), 1.99 (s, 3H), 3.75 (t, *J* = 6.8 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 4.28 (s, 2H), 6.46 (s, 1H), 6.59 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 13.8, 18.6, 18.7, 22.4, 25.5, 28.95, 28.98, 31.4, 59.6, 68.8, 69.0, 115.3 (d), 116.7 (d), 117.9, 128.6, 128.7, 130.8, 133.4, 138.1, 146.6, 149.1; HRMS (MALDI-TOF) 469.2391 (M + Na^+), calcd for $C_{26}H_{38}O_4SNa$ 469.2389.

(iii). Synthesis of 1,2-Bis(hexyloxy)-4-hydroxymethyl-5-(phenylsulfonylmethyl)benzene. To a suspension of 1,2-bis(hexyloxy)-4-methyl-5-(phenylsulfonylmethyl)benzene (4.47 g, 10.0 mmol) in CCl_4 (30.0 mL) were added NBS (1.87 g, 10.5 mmol) and BPO (0.24 g, 1.0 mmol) quickly at 90 °C, and then the resulting mixture was heated at 100 °C. After the mixture had been stirred at this temperature for 6 h, it was cooled to room temperature. After the usual workup with CH_2Cl_2/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated, and the residue used for the next step. To the crude product were added $CaCO_3$ (10.0 g, 100.0 mmol), $MeOCH_2CH_2OMe$ (30.0 mL), and H_2O (30.0 mL), and the resulting mixture was heated at 120 °C overnight. The remaining $CaCO_3$ was neutralized with dilute HCl(aq) solution. After the usual workup with CH_2Cl_2/water, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:2) to give 1,2-bis(hexyloxy)-4-hydroxymethyl-5-

(phenylsulfonylmethyl)benzene (3.70 g, 80%) in a pure form. White powder; mp 66−67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89−0.91 (m, 6H), 1.33−1.45 (m, 12H), 1.69−1.73 (m, 2H), 1.78−1.83 (m, 2H), 3.15 (s, br, 1H), 3.65 (t, J = 6.7 Hz, 2H), 3.98 (t, J = 6.5 Hz, 2H), 4.43 (s, 2H), 4.51 (s, 2H), 6.27 (s, 1H), 6.91 (s, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.63 (t, J = 7.0 Hz, 1H), 7.71 (d, J = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.60, 25.64, 29.0, 29.1, 31.5, 31.6, 59.5, 62.7, 68.98, 69.04, 115.0, 116.9, 117.6, 128.8, 129.1, 133.88, 133.94, 137.9, 148.1, 149.6; HRMS (MALDI-TOF) 485.2357 ($M + Na^+$), calcd for $C_{26}H_{38}O_5SNa$ 485.2338.

*(iv). Synthesis of **1c**.* A flask was charged with 1,2-bis(hexyloxy)-4-hydroxymethyl-5-(phenylsulfonylmethyl)benzene (2.78 g, 6.0 mmol), MnO_2 (5.22 g, 60.0 mmol), and CH_2Cl_2 (20.0 mL). After the resulting mixture had been heated at 50 °C overnight, it was cooled to room temperature and filtered. The filtrate was dried in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:3) to give **1c** (2.52 g, 91%) in a pure form. White powder; mp 96−97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90−0.94 (m, 6H), 1.34−1.37 (m, 8H), 1.47−1.49 (m, 4H), 1.81−1.87 (m, 4H), 4.00 (t, J = 6.7 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 4.90 (s, 2H), 6.79 (s, 1H), 7.20 (s, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.67 (d, J = 7.3 Hz, 2H), 9.67 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 25.5, 25.6, 28.8, 28.9, 31.4, 31.5, 57.2, 69.18, 69.21, 116.1 (d), 116.6 (d), 123.2, 127.5, 128.7, 128.8, 133.8, 137.8, 149.1, 153.1, 189.7; HRMS (MALDI-TOF) 460.2289 (M^+), calcd for $C_{26}H_{36}O_5S$ 460.2283.

*Synthesis of **1d**. (i). Synthesis of 1,4-Dibutoxy-2-methylnaphthalene.* A flask was charged with 1,4-diacetoxy-2-methylnaphthalene (2.58 g, 10.0 mmol), NaH (1.06 mg, 44.0 mmol), BuI (7.36 g, 40.0 mmol), HMPA (7.88 g, 44.0 mmol), and THF (30.0 mL) under N_2. After the resulting mixture had been heated at 80 °C for 48 h, it was cooled to room temperature. After the usual workup with CH_2Cl_2/H_2O, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (CH_2Cl_2/hexane, 1:3) to give 1,4-dibutoxy-2-methylnaphthalene (2.64 g, 92%) in a pure form. White powder; mp 36−37 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00−1.04 (m, 6H), 1.56−1.65 (m, 4H), 1.85−1.91 (m, 4H), 2.42 (s, 3H), 3.88 (t, J = 6.7 Hz, 1H), 4.06 (t, J = 6.5 Hz, 1H), 6.58 (s, 1H), 7.39 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.0 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 8.22 (d, J = 8.6 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 14.1, 16.4, 16.5, 19.5, 31.4, 32.6, 67.9, 73.6, 107.5 (d), 121.5, 122.2, 124.3, 125.3, 125.7, 126.2, 128.9, 145.8, 150.8; HRMS (MALDI-TOF) 286.1935 (M^+), calcd for $C_{19}H_{26}O_2$ 286.1933.

(ii). Synthesis of 1,4-Dibutoxy-2-methyl-3-(phenylsulfonylmethyl)naphthalene. The synthesis of 1,4-dibutoxy-2-methyl-3-(phenylsulfonylmethyl)naphthalene was carried out according to the procedure described above for **6**. Purification: chromatography (EtOAc/hexane, 1:8). Yield: 11.2 g, 85%. White powder; mp 51−53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3H), 1.04 (t, J = 7.6 Hz, 3H), 1.40−1.45 (m, 2H), 1.60−1.69 (m, 4H), 1.88−1.94 (m, 2H), 2.49 (s, 3H), 3.74 (t, J = 6.4 Hz, 2H), 3.90 (t, J = 6.8 Hz, 2H), 7.34−7.41 (m, 3H), 7.49 (dd, J = 1.3 Hz, J = 8.3 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.38, 13.42, 13.9, 14.0, 19.2, 19.4, 32.4 (d), 55.6, 73.9, 74.6, 118.0, 122.4, 122.6, 125.4, 126.7, 127.2, 128.5, 129.4, 133.4, 138.9, 149.4, 151.4; HRMS (MALDI-TOF) 440.2032 (M^+), calcd for $C_{26}H_{32}O_4S$ 440.2021.

(iii). Synthesis of 1,4-Dibutoxy-2-hydroxymethyl-3-(phenylsulfonylmethyl)naphthalene. The synthesis of 1,4-dibutoxy-2-hydroxymethyl-3-(phenylsulfonylmethyl)naphthalene was carried out according to the procedure described above for 1,2-bis(hexyloxy)-4-hydroxymethyl-5-(phenylsulfonylmethyl)benzene. Purification: chromatography (EtOAc/hexane, 1:3). Yield: 2.19 g, 80%. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H), 1.06 (t, J = 7.6 Hz, 3H), 1.39−1.46 (m, 2H), 1.61−1.69 (m, 4H), 1.94−2.00 (m, 2H), 3.36 (s, 1H), 3.74 (t, J = 6.1 Hz, 2H), 4.14 (t, J = 6.4 Hz, 2H), 4.82 (s, 2H), 5.01 (s, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.1 Hz, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.6 Hz, 1H), 8.11 (t, J = 8.6 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 14.1, 19.2, 19.4, 32.3, 32.5, 55.0, 57.4, 74.7, 76.5, 116.9, 122.7, 123.1, 126.5, 127.0, 128.1, 128.6, 128.7, 129.6, 129.7, 133.7, 138.3, 151.4, 151.7; HRMS (MALDI-TOF) 456.1988 (M^+), calcd for $C_{26}H_{32}O_5S$ 456.1970.

*(iv). Synthesis of **1d**.* The synthesis of **1d** was carried out according to the procedure described above for **1c**. Purification: chromatography (EtOAc/hexane, 1:3). Yield: 2.62 g, 96%. White powder; mp 94−95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00−1.05 (m, 6H), 1.50−1.64 (m, 4H), 1.80−1.86 (m, 2H), 1.90−1.96 (m, 2H), 3.98 (t, J = 6.4 Hz, 2H), 4.09 (t, J = 6.7 Hz, 2H), 5.30 (s, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.58−7.68 (m, 3H), 7.75 (d, J = 7.3 Hz, 2H), 7.98 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 10.51 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 13.9, 14.0, 19.3, 32.2, 32.3, 52.3, 75.6, 78.8, 114,9, 123.4, 123.5, 124.6, 127.8, 128.5, 128.7, 129.2, 129.4, 131.4, 133.4, 139.5, 152.5, 159.1, 192.1; HRMS (MALDI-TOF) 454.1812 (M^+), calcd for $C_{26}H_{30}O_5S$ 454.1814.

*Synthesis of **1e**. (i). Synthesis of 2-Cyano-4-fluoro-1-(phenylsulfonylmethyl)benzene.* The synthesis of 2-cyano-4-fluoro-1-(phenylsulfonylmethyl)benzene was carried out according to the procedure described above for 1-cyano-2-(phenylsulfonylmethyl)-benzene. Purification: recrystallization from CH_2Cl_2/hexane. Yield: 1.87 g, 68%. Pale-yellow powder; mp 157−159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.55 (s, 2H), 7.27 (dd, J = 2.8 Hz, J = 8.0 Hz, 1H), 7.35 (dt, J = 2.8 Hz, J = 8.0 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.58−7.61 (m, 1H), 7.67−7.73 (m, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −91.42 (s, 1F); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 59.5 (t), 115.4 (d), 115.6 (d, J_{C-F} = 9.3 Hz), 119.5 (dd, J = 5.9 Hz, J_{C-F} = 25.1 Hz), 120.6 (dd, J = 3.3 Hz, J_{C-F} = 21.4 Hz), 127.7 (d, J_{C-F} = 4.2 Hz), 128.5, 129.3, 134.2 (d, J_{C-F} = 7.7 Hz), 134.3, 137.1, 161.9 (d, J_{C-F} = 252.7 Hz); HRMS (MALDI-TOF) 298.0343 ($M + Na^+$), calcd for $C_{14}H_{10}FNNaO_2S$ 298.0314.

*(ii). Synthesis of **1e**.* The synthesis of **1e** was carried out according to the procedure described above for **1a**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4). Yield: 723.6 mg, 52%. White powder; mp 138−140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (s, 2H), 7.23−7.30 (m, 1H), 7.34−7.39 (m, 1H), 7.44−7.50 (m, 3H), 7.60−7.69 (m, 3H), 9.84 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −94.03 (s, 1F); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 56.9 (t), 119.6 (d, J_{C-F} = 22.3 Hz), 120.6 (d, J_{C-F} = 21.4 Hz), 124.7 (d, J_{C-F} = 3.4 Hz), 128.4, 128.9, 134.0, 135.6 (d, J_{C-F} = 7.8 Hz), 136.4 (d, J = 1.2 Hz, J_{C-F} = 5.9 Hz), 137.7, 162.9 (d, J_{C-F} = 251.7 Hz), 190.0 (d); HRMS (MALDI-TOF) 301.0331 ($M + Na^+$), calcd for $C_{14}H_{11}FO_3SNa$ 301.0311.

*Synthesis of **1f**. (i). Synthesis of Methyl 4-Bromo-2-methylbenzoate.*[27] To a suspension of 4-bromo-2-methylbenzoic acid (10.75 g, 50.0 mmol) and MeOH (60.0 mL) was added dropwise $SOCl_2$ (11.90 g, 100.0 mmol) during the course of 10−15 min at 0 °C, and the resulting mixture was heated at refluxing temperature overnight and then cooled to room temperature. After the usual workup with CH_2Cl_2/H_2O and brine, evaporation of the solvents in vacuo afforded methyl 4-bromo-2-methylbenzoate (11.45 g, 100%) in a pure form. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.57 (s, 3H), 3.88 (s, 3H), 7.36 (d, J = 8.5 Hz, 1H), 7.40 (s, 1H), 7.77 (d, J = 8.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 21.5 (d), 51.9 (d), 126.6, 128.2, 128.8 (d), 132.1, 134.4 (d), 142.4, 167.1.

(ii). Synthesis of Methyl 4-Bromo-2-(phenylsulfonylmethyl)-benzoate. A 100 mL flask was charged with methyl 4-bromo-2-methylbenzoate (4.58 g, 20.0 mmol), NBS (3.74 g, 21.0 mmol), BPO (484.0 mg, 2.0 mmol), and CCl_4 (50.0 mL). After the mixture had been stirred at 80 °C for 10 min and at 90 °C overnight, it was allowed to cool to room temperature and filtered. The filtrate was washed with $NaHCO_3$(aq), dried over $MgSO_4$, and filtered. The solvents were evaporated in vacuo. To the crude product were added benzenesulfinic acid sodium salt dihydrate (4.80 g, 24.0 mmol) and DMF (40.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was subjected to recrystallization from CH_2Cl_2/hexane to give methyl 4-bromo-2-(phenylsulfonylmethyl)benzoate (5.24 g, 71%). Pale-yellow powder; mp 105−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 3H), 5.02 (s, 2H), 7.44 (d, J = 1.9 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.55 (dd, J = 1.9 Hz, J = 8.3 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.66 (d, J = 7.0 Hz,

2H), 7.76 (d, *J* = 8.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 52.3 (d), 58.6, 126.6, 128.6, 128.9, 129.4, 131.1, 132.0, 132.3, 133.8, 136.1 (d), 138.0, 166.4; HRMS (MALDI-TOF) 367.9725 (M^+), calcd for $C_{15}H_{13}BrO_4S$ 367.9718.

(iii). Synthesis of 4-Bromo-1-hydroxymethyl-2-(phenylsulfonylmethyl)benzene. To a solution of methyl 4-bromo-2-(phenylsulfonylmethyl)benzoate (2.95 g, 8.0 mmol) in CH_2Cl_2 (16.0 mL) was added slowly DIBAL-H (1.0 M in hexane, 20.8 mL, 20.8 mmol) at 0 °C, and the resulting mixture was stirred at room temperature overnight. After the mixture had been cooled to 0 °C, aqueous NH_4Cl was poured into the mixture. After the usual workup with 1 N HCl and CH_2Cl_2, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:2) to give 4-bromo-1-hydroxymethyl-2-(phenylsulfonylmethyl)benzene (2.59 g, 95%) in a pure form. White powder; mp 131−133 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.80 (t, *J* = 6.1 Hz, 1H), 4.47 (s, 2H), 4.61 (d, *J* = 6.1 Hz, 2H), 6.99 (d, *J* = 1.6 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.47 (dd, *J* = 1.5 Hz, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 59.2 (t), 62.5 (t), 121.6, 128.1, 128.6, 129.3, 131.8 (d), 132.5 (d), 134.3, 135.1 (d), 137.5, 139.9; HRMS (MALDI-TOF) 339.9748 (M^+), calcd for $C_{14}H_{13}BrO_3S$ 339.9769.

(iv). Synthesis of ***1f****.* The synthesis of **1f** was carried out according to the procedure described above for **1c**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4). Yield: 1.95 g, 96%. White powder; mp 143−145 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.97 (s, 2H), 7.46−7.54 (m, 3H), 7.59−7.66 (m, 2H), 7.69−7.73 (m, 3H), 9.83 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.1, 128.56, 128.60, 129.0, 130.6, 132.7, 133.3, 134.0, 135.3, 136.6, 137.9, 190.9; HRMS (MALDI-TOF) 360.9523 (M + Na^+), calcd for $C_{14}H_{11}BrO_3SNa$ 360.9510.

Synthesis of ***1g****.* To a solution of 1,2-dibromo-4,5-dimethylbenzene (5.28 g, 20.0 mmol) in CCl_4 (40.0 mL) were added NBS (3.74 g, 21.0 mmol) and BPO (484.0 mg, 2.0 mmol). After the mixture had been stirred at 90 °C overnight, it was cooled to room temperature and filtered. The filtrate was washed with $NaHCO_3$(aq), dried over $MgSO_4$, and filtered. The combined organic layers were evaporated, and the residue was subjected to chromatography (hexane to hexane/CH_2Cl_2, 6:1) to give 1,2-dibromo-4,5-bis(bromomethyl)benzene (5.90 g, ca. 70%). A 100 mL flask was charged with the crude product (5.90 g, ca. 14.0 mmol), benzenesulfinic acid sodium salt dihydrate (2.33 g, 11.7 mmol), and DMF (20.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:6) to give 1,2-dibromo-4-bromomethyl-5-(phenylsulfonylmethyl)benzene (2.32 g, ca. 41%). A 100 mL flask was charged with the crude product (2.32 g, ca. 4.8 mmol), KOAc (1.41 g, 14.4 mmol), and DMF (8.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo. To the crude product 4-acetoxymethyl-1,2-dibromo-5-(phenylsulfonylmethyl)benzene were added KOH (1.62 g, 28.8 mmol), H_2O (10.0 mL), and acetone (5.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvent was evaporated in vacuo. To the crude product 1,2-dibromo-4-hydroxymethyl-5-(phenylsulfonylmethyl)benzene were added MnO_2 (4.17 g, 48.0 mmol) and CH_2Cl_2 (20 mL). After the resulting mixture had been heated at 50 °C overnight, it was cooled to room temperature and filtered. The filtrate was dried in vacuo, and the residue was subjected to chromatography (EtOAc/CH_2Cl_2/hexane, 2:1:9) to give **1g** (1.02 g, 51%) in a pure form. White powder; mp 177−179 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 4.89 (s, 2H), 7.53 (t, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 2H), 7.97 (s, 1H), 9.78 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.7, 126.5, 128.6, 128.8, 129.2, 131.3, 134.2, 134.5, 137.8, 138.3, 138.5 (d), 189.5; HRMS (MALDI-TOF) 416.8816 (M + H^+), calcd for $C_{14}H_{11}Br_2O_3S$ 416.8796.

Synthesis of ***1h****. (i). Synthesis of 1,2-Dichloro-4,5-bis(hydroxymethyl)benzene.*[28] To a suspension of 4,5-dichlorophthalic acid (2.35 g, 10.0 mmol) in THF (30.0 mL) was added BH_3·THF (1.0 M in THF, 26.0 mL, 26.0 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 24 h. The resulting mixture was cooled to 0 °C and quenched with a 1:1 mixture of THF and water (40.0 mL). K_2CO_3 powder was added until the aqueous and organic layers separated. The two layers were separated, and the aqueous layer was extracted with THF (50.0 mL × 2). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was dried in vacuo to give 1,2-dichloro-4,5-bis(hydroxymethyl)benzene (1.97 g, 95%), and the crude product was used in the next step without further purification. White powder; ^1H NMR (500 MHz, $CDCl_3$) δ 2.59 (s, 2H), 4.70 (s, 4H), 7.48 (s, 2H).

(ii). Synthesis of 1,2-Bis(bromomethyl)-4,5-dichlorobenzene.[29] To a suspension of 1,2-dichloro-4,5-bis(hydroxymethyl)benzene (1.97 g, 9.5 mmol) in Et_2O (20.0 mL) was added PBr_3 (6.17 g, 22.8 mmol) over 3 min at 0 °C. The resulting mixture was stirred for 12 h at room temperature, and then the mixture was poured into ice/water. The organic layer was separated, washed with brine, and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the residue was subjected to chromatography (CH_2Cl_2/hexane, 1:8) to give 1,2-bis(bromomethyl)-4,5-dichlorobenzene (2.81 g, 89%) in a pure form. White powder; ^1H NMR (500 MHz, $CDCl_3$) δ 4.54 (s, 4H), 7.45 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 28.0 (t), 132.6 (d), 133.0, 136.3.

(iii). Synthesis of 4-Bromomethyl-1,2-dichloro-5-(phenylsulfonylmethyl)benzene. A 100 mL flask was charged with 1,2-bis(bromomethyl)-4,5-dichlorobenzene (3.99 g, 12.0 mmol), benzenesulfinic acid sodium salt dihydrate (2.00 g, 10.0 mmol), and DMF (25.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:6) to give 4-bromomethyl-1,2-dichloro-5-(phenylsulfonylmethyl)benzene (2.09 g, 53%) in a pure form. White powder; mp 168−169 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 4.45 (s, 2H), 4.48 (s, 2H), 7.03 (s, 1H), 7.47 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.69−7.73 (m, 1H), 7.76−7.78 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 29.5, 58.7, 127.0, 128.5, 129.4, 132.4, 132.9, 133.5, 134.4, 134.5, 137.6, 137.9; HRMS (MALDI-TOF) 391.9020 (M^+), calcd for $C_{14}H_{11}BrCl_2O_2S$ 391.9040.

(iv). Synthesis of ***1h****.* A 100 mL flask was charged with 4-bromomethyl-1,2-dichloro-5-(phenylsulfonylmethyl)benzene (4.73 g, 12.0 mmol), KOAc (3.53 g, 36.0 mmol), and DMF (20.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo. To the crude product 4-acetoxymethyl-1,2-dichloro-5-(phenylsulfonylmethyl)benzene were added KOH (4.04 g, 72.0 mmol), water (30.0 mL), and acetone (10.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo. To the crude product 1,2-dichloro-4-hydroxymethyl-5-(phenylsulfonylmethyl)benzene were added MnO_2 (10.4 g, 120.0 mmol) and CH_2Cl_2 (60 mL). After the resulting mixture had been heated at 50 °C overnight, it was cooled to room temperature and filtered. The filtrate was dried in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:3) to give **1h** (3.00 g, 76%) in a pure form. White powder; mp 158−160 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 4.92 (s, 2H), 7.50−7.55 (m, 3H), 7.63−7.69 (m, 1H), 7.73−7.76 (m, 2H), 7.84 (s, 1H), 9.79 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.6, 128.4, 128.5, 129.2, 134.0, 134.2, 134.3, 135.2, 135.4 (d), 137.8, 138.3, 189.3 (d); HRMS (MALDI-TOF) 327.9722 (M^+), calcd for $C_{14}H_{10}Cl_2O_3S$ 327.9728.

Synthesis of ***1i****. (i). Synthesis of 2,3-Bis(hydroxymethyl)-naphthalene.*[28] To a suspension of $LiAlH_4$ (759.1 mg, 20.0 mmol) in THF (40.0 mL) was added naphthalene-2,3-dicarboxylic anhydride (1.98 g, 10.0 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h and then carefully quenched with water and 3 N HCl aqueous solution. The mixture was extracted with a mixed solvent of THF/$CHCl_3$ (1:2). The organic phase was washed with water, saturated $NaHCO_3$, and brine and then dried over $MgSO_4$. Evaporation of the solvents in vacuo provided 2,3-bis(hydroxymethyl)-

naphthalene (1.88 g, quantitative). Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90 (s, 2H), 4.92 (s, 4H), 7.50–7.52 (m, 2H), 7.84 (s, 4H). The ^{13}C NMR spectrum could not be recorded because of poor solubility.

(ii). Synthesis of 2,3-Bis(bromomethyl)naphthalene.[30] The synthesis of 2,3-bis(bromomethyl)naphthalene was carried out according to the reported procedure for 1,2-bis(bromomethyl)-4,5-dichlorobenzene. Purification: chromatography (CH_2Cl_2/hexane, 1:8). Yield: 2.57 g, 86%. White powder; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (s, 4H), 7.48–7.51 (m, 2H), 7.77–7.80 (m, 2H), 7.84 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 31.1, 127.2, 127.7, 130.8, 133.2, 133.7.

(iii). Synthesis of 2-Hydroxymethyl-3-(phenylsulfonylmethyl)naphthalene. A 100 mL flask was charged with 2,3-bis(bromomethyl)naphthalene (3.77 g, 12.0 mmol), benzenesulfinic acid sodium salt dihydrate (2.00 g, 10.0 mmol), and DMF (30.0 mL). After the mixture had been stirred at 80 °C overnight, it was cooled to room temperature. After the usual workup with water and EtOAc, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4) to give 2-bromomethyl-3-(phenylsulfonylmethyl)naphthalene (2.25 g, ca. 60%). To the crude product were added $CaCO_3$ (6.00 g, 60.0 mmol), $MeOCH_2CH_2OMe$ (30.0 mL), and H_2O (30.0 mL), and the resulting mixture was heated at reflux overnight and then cooled to room temperature. The mixture was neutralized with dilute HCl(aq) solution. After the usual workup with CH_2Cl_2/H_2O, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/hexane, 1:1) to give 2-hydroxymethyl-3-(phenylsulfonylmethyl)naphthalene (1.56 g, 83%) in a pure form. White powder; mp 143–145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (t, J = 6.1 Hz, 1H), 4.71 (s, 2H), 4.82 (d, J = 6.1 Hz, 2H), 7.44–7.53 (m, 5H), 7.64–7.68 (m, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.83 (t, J = 7.9 Hz, 1H), 7.88 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 59.6, 63.6, 123.9, 126.6, 127.0, 127.5, 127.6, 128.6, 129.1, 132.4, 132.56, 132.60, 133.2, 133.9, 137.4, 137.8; HRMS (MALDI-TOF) 312.0827 (M^+), calcd for $C_{18}H_{16}O_3S$ 312.0820.

*(iv). Synthesis of **1i**.* The synthesis of **1i** was carried out according to the procedure described above for **1c**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:1:2) and then reprecipitation from EtOAc/hexane. Yield: 1.68 g, 90%. White powder; mp 194–196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.21 (s, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.57–7.64 (m, 2H), 7.67–7.71 (m, 3H), 7.87–7.88 (m, 2H), 7.98 (d, J = 8.0 Hz, 1H), 8.20 (s, 1H), 9.91 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 57.8 (t), 123.5, 127.9, 128.0, 128.7, 128.8, 129.0, 129.9, 132.1, 132.2, 133.7, 134.1, 134.7, 138.4, 138.9 (d), 192.4; HRMS (MALDI-TOF) 333.0577 (M + Na^+), calcd for $C_{18}H_{14}O_3SNa$ 333.0561.

*Synthesis of **1j**.* A flask was charged with **1f** (1.70 g, 5.0 mmol), 1-ethynyl-4-hexylbenzene (1.21 g, 6.0 mmol), $Pd(PPh_3)_4$ (288.9 mg, 0.25 mmol), CuI (47.6 mg, 0.25 mmol), diisopropylamine (3.0 mL), and toluene (20.0 mL), and the mixture was stirred under nitrogen at 80 °C overnight. After the usual workup with EtOAc/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (EtOAc/hexane, 1:5 to 1:4) to give **1j** (1.89 g, 85% yield) in a pure form. White powder; mp 102–104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87–0.90 (m, 3H), 1.30–1.36 (m, 6H), 1.59–1.65 (m, 2H), 2.63 (t, J = 8.0 Hz, 2H), 5.00 (s, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.45–7.48 (m, 4H), 7.56 (s, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.64–7.73 (m, 4H), 9.79 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 28.8, 31.1, 31.6, 35.9 (t), 57.3 (t), 87.2, 94.7, 119.2, 128.5, 128.6, 128.8, 129.0, 129.2, 131.7 (d), 132.0, 133.3, 133.8, 134.2, 136.5 (d), 138.0, 144.5, 191.0 (d); HRMS (MALDI-TOF) 444.1776 (M^+), calcd for $C_{28}H_{28}O_3S$ 444.1759.

*Synthesis of **1k**.* A flask was charged with 4-hexylphenylboronic acid (1.34 g, 6.5 mmol), **1f** (1.70 g, 5.0 mmol), $Pd(PPh_3)_4$ (288.9 mg, 0.25 mmol), dioxane (15.0 mL), and a solution of K_3PO_4 (1.48 g, 7.0 mmol) in H_2O (3.0 mL), and the mixture was stirred under nitrogen at 90 °C overnight. After the usual workup with EtOAc/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (hexane/EtOAc, 1:4) to give **1k** (1.93 g, 92%) in a pure form. White powder; mp 109–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86–0.91 (m, 3H), 1.24–1.36 (m, 6H), 1.61–1.67 (m, 2H), 2.65 (t, J = 8.0 Hz, 2H), 5.07 (s, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.42–7.48 (m, 4H), 7.58 (s, 1H), 7.70–7.77 (m, 5H), 9.85 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 28.9, 31.2, 31.6, 35.5 (t), 57.7 (t), 127.1 (d), 127.3, 128.6, 128.8, 129.0 (d), 129.2, 132.1 (d), 132.9, 133.7, 134.9, 135.7, 138.1, 143.9, 146.0, 191.5; HRMS (MALDI-TOF) 420.1782 (M^+), calcd for $C_{26}H_{28}O_3S$ 420.1759.

*Synthesis of **1l**. (i). Synthesis of **10**.* A flask was charged with **8** (1.96 g, 10.0 mmol) and K_2CO_3 (1.52 g, 11.0 mmol) in DMF (15.0 mL). Then **9** (1.70 g, 10.0 mmol) was added under N_2 at 0 °C, and the resulting mixture was stirred at this temperature for 4 h. After water (30.0 mL) and EtOAc (30 mL) had been added, the organic layer was separated, washed with brine three times, and dried over $MgSO_4$. The solvents were evaporated under reduced pressure, and the residue was subjected to chromatography (EtOAc/hexane, 1:3) to give **10** (2.80 g, 98%) in a pure form. Pale-yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.85 (s, 3H), 4.16 (s, 2H), 6.75 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.94 (dd, J = 2.0 Hz, J = 8.2 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.30 (dt, J = 1.3 Hz, J = 7.7 Hz, 1H), 7.45 (dt, J = 1.3 Hz, J = 7.5 Hz, 1H), 7.58 (dd, J = 1.1 Hz, J = 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 39.5, 55.86 (d), 55.89 (d), 111.4 (d), 112.6, 116.9 (d), 117.5, 124.2, 126.9 (d), 127.5 (d), 130.1 (d), 132.5 (d), 132.8 (d), 142.2, 148.8, 149.4; HRMS (MALDI-TOF) 285.0795 (M^+), calcd for $C_{16}H_{15}NO_2S$ 285.0823.

*(ii). Synthesis of **11**.* To a solution of **10** (2.85 g, 10.0 mmol) in CH_2Cl_2 (15.0 mL) was added a solution of *m*-CPBA (5.16 g, 30.0 mmol) in CH_3OH (15.0 mL) at 0 °C, and the mixture was stirred at this temperature overnight. After the resulting mixture had been poured into H_2O, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine. The solvents were evaporated under reduced pressure, and the residue was subjected to chromatography (EtOAc/hexane, 1:2, then EtOAc/hexane/MeOH, 2:6:1) to give **11** (2.86 g, 90%) in a pure form. White powder; mp 141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.95 (s, 3H), 4.58 (s, 2H), 6.91 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 3.7 Hz, 1H), 7.34 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H), 7.43–7.48 (m, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.63–7.66 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 56.0 (q), 56.2 (q), 60.7 (t), 110.5, 110.6, 114.3, 116.6, 122.9 (d), 128.7, 129.1 (d), 132.0, 132.1, 132.7, 132.8, 149.0, 153.7; HRMS (MALDI-TOF) 317.0721 (M^+), calcd for $C_{16}H_{15}NO_4S$ 317.0722.

*(iii). Synthesis of **1l**.* The synthesis of **1l** was carried out according to the procedure described above for **1a**. Purification: chromatography (EtOAc/hexane, 1:1). Yield: 961.1 mg, 60%. White powder; mp 146–148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.91 (s, 3H), 5.02 (s, 2H), 6.88 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 2.2 Hz, 1H), 7.30 (dd, J = 2.1 Hz, J = 8.3 Hz, 1H), 7.39–7.40 (m, 1H), 7.54–7.59 (m, 2H), 7.75–7.77 (m, 1H), 9.88 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.8 (q), 55.9 (q), 57.6 (t), 110.1 (d), 110.5 (d), 122.5 (d), 129.08, 129.14, 129.3, 133.2, 133.5 (d), 133.7, 134.4, 148.4, 153.1, 191.7; HRMS (MALDI-TOF) 320.0715 (M^+), calcd for $C_{16}H_{16}O_5S$ 320.0718.

*Synthesis of **2a**[8b] (One-Pot Manner).* A 100 mL flask was charged with **1a** (520.6 mg, 2.0 mmol), ClP(O)(OEt)$_2$ (0.34 mL, 2.4 mmol), and THF (40 mL), and LiHMDS (1.0 M in THF, 4.0 mL, 4.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min and then at room temperature for 1.5 h, LDA (1.0 M in THF/hexane, 10.0 mL, 10.0 mmol) was added at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and aqueous NH_4Cl was poured into the mixture. After the usual workup with water and AcOEt, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (CH_2Cl_2/hexane, 2:3) to give **2a** (110.0 mg, 55%) in a pure form. Yellow powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73–6.76 (m, 4H), 6.92–6.95 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 109.3, 126.9, 129.0, 132.8.

*Synthesis of **2b** (One-Pot Manner).* The synthesis of **2b** was carried out according to the procedure described above for **2a**. Purification: chromatography (CH_2Cl_2). Yield: 182.6 mg, 57%. Yellow powder; mp

205 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 12H), 6.26 (s, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.9 (d), 108.6, 111.0 (d), 125.9, 148.7; HRMS (MALDI-TOF) 320.1039 (M^+), calcd for $C_{20}H_{16}O_4$ 320.1049.

*Synthesis of **2b** (Stepwise Manner).* A 100 mL flask was charged with **1b** (1.28 g, 4.0 mmol), $ClP(O)(OEt)_2$ (0.68 mL, 4.8 mmol), and THF (60.0 mL), and LiHMDS (1.0 M in THF, 8.0 mL, 8.0 mmol) was added at −78 °C. The mixture was stirred at −78 °C for 30 min and then at room temperature for 2.5 h, and aqueous NH_4Cl solution was poured into the mixture. After the usual workup with water and AcOEt, the solvents were evaporated in vacuo, and the residue was subjected to chromatography ($EtOAc/CH_2Cl_2$/hexane, 1:1:2) to give **3b** (701.4 mg, 58%) in a pure form. To a THF (4.0 mL) solution of **3b** (604.7 mg, 1.0 mmol) was added LDA (1.0 M in THF/hexane, 5.0 mL, 5.0 mmol) slowly at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and aqueous NH_4Cl was poured into the mixture. After the usual workup with water and CH_2Cl_2, the solvents were evaporated in vacuo, and the residue was subjected to reprecipitation from EtOAc/hexane to give **2b** (281.9 mg, 88%) in a pure form. Pale-yellow powder; mp 227−229 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 6H), 3.83 (s, 6H), 6.45 (s, 2H), 7.03 (s, 2H), 7.31 (s, 2H), 7.42−7.51 (m, 8H), 7.62−7.65 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.8 (d), 55.9 (d), 109.3 (d), 113.1 (d), 121.4, 128.0, 128.7, 128.9, 133.7, 139.0 (d), 139.2, 144.1, 148.7, 149.7; HRMS (MALDI-TOF) 604.1253 (M^+), calcd for $C_{32}H_{28}O_8S_2$ 604.1226.

*Synthesis of **2c**.* The synthesis of **2c** was carried out according to the procedure described above for **2a**. Purification: chromatography (CH_2Cl_2/hexane, 1:2, then CH_2Cl_2/hexane, 1:1). Yields: **2c** (234.3 mg, 39%); **12** (9.6 mg, 1.6%).

Data for **2c**: Yellow powder; mp 141−143 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.0 Hz, 12H), 1.21−1.26 (m, 16H), 1.31−1.37 (m, 8H), 1.64−1.69 (m, 8H), 3.79 (t, *J* = 6.8 Hz, 8H), 6.17 (s, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 25.5, 29.0, 31.5, 69.2, 108.5, 113.3 (d), 125.7, 148.7; HRMS (MALDI-TOF) 600.4180 (M^+), calcd for $C_{40}H_{56}O_4$ 600.4179.

Data for **12**: Yellow powder; mp 122−124 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88−0.92 (m, 18H), 1.33−1.37 (m, 24H), 1.43−1.47 (m, 12H), 1.78−1.83 (m, 12H), 3.96 (t, *J* = 6.8 Hz, 12H), 6.72 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 25.6, 29.0, 31.5, 68.9, 91.8, 115.5 (d), 119.6, 149.0; HRMS (MALDI-TOF) 900.6270 (M^+), calcd for $C_{60}H_{84}O_6$ 900.6268.

*Attempted Synthesis of **2d**.* A 100 mL flask was charged with **1d** (909.2 mg, 2.0 mmol), $ClP(O)(OEt)_2$ (0.34 mL, 2.4 mmol), and THF (40.0 mL), and LiHMDS (1.0 M in THF, 4.0 mL, 4.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min, at 0 °C for 24 h, and then at room temperature for 24 h, LDA (1.0 M in THF/hexane, 10.0 mL, 10.0 mmol) was added at −78 °C. After the reaction mixture was stirred at this temperature for 3 h, TLC analysis indicated only a trace amount of **2d** was formed.

*Synthesis of **2j**.* To a THF (4.0 mL) solution of **3j** (255.9 mg, 0.30 mmol) was added LDA (1.0 M in THF/hexane, 1.5 mL, 1.5 mmol) slowly at −78 °C. The reaction mixture was stirred at this temperature for 2 h, and H_2O (20 mL) was poured into the mixture. After the usual workup with water and CH_2Cl_2, the solvents were evaporated in vacuo, and the residue was subjected to a short chromatography (CH_2Cl_2) and then reprecipitation from CH_2Cl_2/hexane to give **2j** (42.7 mg, 25%) in a pure form. Yellow powder; mp 186 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 0.87−0.89 (m, 6H), 1.30−1.34 (m, 12H), 1.57−1.62 (m, 4H), 2.61 (t, *J* = 7.6 Hz, 4H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 1.5 Hz, 2H), 7.09 (dd, *J* = 2.4 Hz, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 4H), 7.40 (d, *J* = 8.3 Hz, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 31.2, 31.7, 35.9, 87.6, 92.1, 109.7, 110.0, 119.7, 124.6, 126.8 (d), 128.5 (d), 129.7 (d), 131.6 (d), 131.8, 132.2 (d), 133.0, 144.0; HRMS (MALDI-TOF) 568.3111 (M^+), calcd for $C_{44}H_{40}$ 568.3130.

*Synthesis of **2k**.* The synthesis of **2k** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:2). Yield: 134.4 mg, 86%. Yellow powder; mp 156 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 0.87−0.92 (m, 6H), 1.28−1.36 (m, 12H), 1.59−1.65 (m, 4H), 2.62 (t, *J* = 8.0 Hz, 4H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 1.9 Hz, 2H), 7.14 (dd, *J* = 1.8 Hz, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 4H), 7.38 (d, *J* = 8.3 Hz, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 29.0, 31.4, 31.7, 35.6, 109.6, 109.7, 125.5 (d), 125.6, 126.6 (d), 127.0 (d), 127.1 (d), 128.9 (d), 131.0, 133.5, 136.6, 142.0, 143.1; HRMS (MALDI-TOF) 520.3115 (M^+), calcd for $C_{40}H_{40}$ 520.3130.

*Synthesis of **2k** from **1k** (One-Pot Manner).* The synthesis of **2k** was carried out according to the procedure described above for **2a**. Purification: chromatography (CH_2Cl_2/hexane, 1:2). Yield: 276.0 mg, 53%.

*Synthesis of **2ab**.* The synthesis of **2ab** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:1). Yield: 67.2 mg, 86%. Yellow powder; mp 129 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 6H), 6.32 (s, 2H), 6.63−6.65 (m, 2H), 6.85−6.86 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.9 (q), 108.8, 109.1, 111.1 (d), 125.6, 126.4, 128.7, 133.1, 148.9; HRMS (MALDI-TOF) 260.0866 (M^+), calcd for $C_{18}H_{12}O_2$ 260.0837.

*Synthesis of **2be**.* The synthesis of **2be** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:1). Yield: 71.8 mg, 86%. Yellow powder; mp 128 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 6H), 6.32 (s, 1H), 6.33 (s, 1H), 6.39 (dd, *J* = 2.5 Hz, *J* = 8.6 Hz, 1H); 6.54 (dt, *J* = 2.5 Hz, *J* = 8.3 Hz, 1H); 6.58−6.61 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.96 (d), 55.99 (d), 107.3 (d, J_{C-F} = 4.2 Hz), 108.0 (d, J_{C-F} = 1.6 Hz), 108.7 (d, J_{C-F} = 2.1 Hz), 110.7 (d, J_{C-F} = 1.0 Hz), 111.1 (d, *J* = 6.8 Hz), 111.4 (d, *J* = 6.7 Hz), 114.7 (td, *J* = 5.2 Hz, J_{C-F} = 22.2 Hz), 115.0 (dd, *J* = 7.0 Hz, J_{C-F} = 25.1 Hz), 124.9, 125.9, 127.4 (m), 129.1 (d, J_{C-F} = 4.2 Hz), 135.5 (d, J_{C-F} = 9.8 Hz), 149.0, 149.4, 162.6 (d, J_{C-F} = 249.7 Hz); HRMS (MALDI-TOF) 278.0771 (M^+), calcd for $C_{18}H_{11}FO_2$ 278.0743.

*Synthesis of **2bf**.* The synthesis of **2bf** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:1). Yield: 77.3 mg, 76%. Yellow powder; mp 120 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 6H), 6.32 (d, *J* = 2.2 Hz, 2H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 1.8 Hz, 1H), 6.99 (dd, *J* = 2.2 Hz, *J* = 8.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.0 (d), 107.3, 108.0, 110.2, 110.8, 111.2 (d), 111.3 (d), 122.5, 125.1, 125.5, 127.2 (d), 129.6 (d), 131.5 (d), 132.1, 135.1, 149.1, 149.3; HRMS (MALDI-TOF) 337.9928 (M^+), calcd for $C_{18}H_{11}BrO_2$ 337.9942.

*Synthesis of **2ci**.* The synthesis of **2ci** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:1). Yield: 123.0 mg, 91%. Yellow-green powder; mp 137−138 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88−0.91 (m, 6H), 1.29−1.34 (m, 8H), 1.40−1.46 (m, 4H), 1.73−1.79 (m, 4H), 3.90 (t, *J* = 6.8 Hz, 4H), 6.47 (s, 2H), 7.13 (s, 2H), 7.29−7.32 (m, 2H), 7.45−7.47 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 25.6, 29.0, 31.5, 69.2, 109.0, 109.5, 112.7, 112.8, 125.0, 125.8, 127.5, 128.1, 133.1, 149.3; HRMS (MALDI-TOF) 450.2560 (M^+), calcd for $C_{32}H_{34}O_2$ 450.2559.

*Synthesis of **2ai**.* The synthesis of **2ai** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:4). Yield: 64.6 mg, 86%. Yellow-green powder; mp 124 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 6.93−6.95 (m, 2H), 7.05−7.06 (m, 2H), 7.25−7.27 (m, 2H), 7.36−7.38 (m, 2H), 7.53−7.55 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 109.3, 109.6, 126.5 (d), 126.9 (d), 127.7, 127.8, 128.3, 128.9 (d), 132.2, 133.4; HRMS (MALDI-TOF) 250.0779 (M^+), calcd for $C_{20}H_{10}$ 250.0783.

*Synthesis of **2m**.* The synthesis of **2m** was carried out according to the procedure described above for **2j**. Purification: chromatography (CH_2Cl_2/hexane, 1:4). Yield: 118.9 mg, 93%. Yellow powder; mp 148 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 6H), 3.87 (s, 3H), 3.90 (s, 6H), 6.35 (d, *J* = 1.3 Hz, 1H), 6.64 (s, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 1.9 Hz, 1H), 7.05 (dd, *J* = 2.1 Hz, *J* = 7.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.96 (d), 55.99 (d), 56.2 (q), 60.9 (t), 103.6, 103.7, 108.8, 109.0, 109.6, 109.9, 111.2 (d), 125.25, 125.33, 125.4, 125.7, 126.6 (d), 127.0 (d), 131.8, 133.8, 135.3, 138.1, 141.7, 149.1 (d), 153.4; HRMS (MALDI-TOF) 426.1462 (M$^+$), calcd for $C_{27}H_{22}O_5$ 426.1467.

*Synthesis of **3e**.* A 100 mL flask was charged with **1e** (1.11 g, 4.0 mmol), $ClP(O)(OEt)_2$ (0.68 mL, 4.8 mmol), and THF (60.0 mL), and LiHMDS (1.0 M in THF, 8.0 mL, 8.0 mmol) was added at −78 °C. The mixture was stirred at −78 °C for 30 min and then at room temperature for 2.5 h, and aqueous NH_4Cl solution was poured into the mixture. After the usual workup with water and AcOEt, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4) to give **3e** (531.0 mg, 50%) in a pure form. White powder; mp 245−247 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (dd, J = 2.7 Hz, J = 8.6 Hz, 2H), 7.00 (dt, J = 2.8 Hz, J = 8.3 Hz, 2H), 7.27 (s, 2H), 7.43 (d, J = 8.0 Hz, 4H), 7.48−7.53 (m, 6H), 7.68 (t, J = 7.7 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −109.99 (s, 1F); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 114.0 (dd, J = 8.5 Hz, J_{C-F} = 22.5 Hz), 115.9 (dd, J = 9.1 Hz, J_{C-F} = 22.0 Hz), 124.6 (d, J_{C-F} = 3.5 Hz), 128.1, 129.1, 133.0 (d, J_{C-F} = 8.7 Hz), 134.2, 137.7 (d, J_{C-F} = 8.3 Hz), 137.8, 138.4, 144.9, 162.8 (d, J_{C-F} = 250.4 Hz); HRMS (MALDI-TOF) 543.0487 (M + Na$^+$), calcd for $C_{28}H_{18}F_2O_4S_2Na$ 543.0512.

*Synthesis of **3f**.* The synthesis of **3f** was carried out according to the procedure described above for **3e**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:7) and then reprecipitation from CH_2Cl_2/hexane. Yield: 642.4 mg, 51%. White powder; mp 276−277 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, J = 8.2 Hz, 2H), 7.31 (s, 2H), 7.44 (dd, J = 2.2 Hz, J = 8.2 Hz, 2H), 7.46−7.55 (m, 10H), 7.66−7.69 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 122.7, 128.2, 128.4 (d), 129.2, 130.6, 132.7 (d), 133.3 (d), 134.1, 134.2, 138.2, 138.4 (d), 144.2; HRMS (MALDI-TOF) 639.9020 (M$^+$), calcd for $C_{28}H_{18}Br_2O_4S_2$ 639.9013.

*Synthesis of **3g**.* The synthesis of **3g** was carried out according to the procedure described above for **3e**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:7) and then reprecipitation from CH_2Cl_2/hexane. Yield: 136.0 mg, 17%. White powder; mp 246 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.28 (s, 2H), 7.49−7.51 (m, 4H), 7.56 (t, J = 7.4 Hz, 4H), 7.59 (s, 2H), 7.69−7.72 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 125.7, 127.0, 128.3, 129.1, 129.4, 131.7 (d), 134.4, 135.2, 135.3 (d), 137.4 (d), 138.0, 144.6; HRMS (MALDI-TOF) 795.7248 (M$^+$), calcd for $C_{28}H_{16}Br_4O_4S_2$ 795.7224.

*Synthesis of **3h**.* The synthesis of **3h** was carried out according to the procedure described above for **3e**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:7) and then reprecipitation from CH_2Cl_2/hexane. Yield: 93.4 mg, 15%. Pale-yellow powder; mp 245−257 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 2H), 7.29 (s, 2H), 7.50 (d, J = 7.7 Hz, 6H), 7.55 (t, J = 7.3 Hz, 4H), 7.71 (t, J = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 128.3, 128.5, 128.7 (d), 129.4, 132.3 (d), 133.5, 134.5, 134.6, 137.5 (d), 138.1, 144.7; HRMS (MALDI-TOF) 642.9112 (M + Na$^+$), calcd for $C_{28}H_{16}Cl_4O_4S_2Na$ 642.9142.

*Synthesis of **3j** from **3f**.* A 100 mL flask was charged with 1-ethynyl-4-hexylbenzene (321.2 mg, 0.50 mmol), **3f** (223.6 mg, 0.12 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol), diisopropylamine (2.0 mL), and toluene (6.0 mL), and the mixture was stirred under nitrogen at 80 °C overnight. After the usual workup with CH_2Cl_2/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc, 6:1) to give **3j** (337.0 mg, 79%) in a pure form. Pale-yellow powder; mp 78−80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86−0.89 (m, 6H), 1.29−1.32 (m, 12H), 1.54−1.61 (m, 4H), 2.60 (t, J = 8.0 Hz, 4H), 6.96 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.6 Hz, 4H), 7.36−7.42 (m, 8H), 7.48−7.53 (m, 8H), 7.61 (d, J = 1.5 Hz, 2H), 7.65−7.69 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 31.2, 31.7, 35.9, 87.3, 91.9, 119.6, 124.2, 127.1 (d), 128.3 (d), 128.5 (d), 129.1 (d), 131.6 (d), 132.3 (d), 133.5, 134.0, 134.8, 138.59, 138.62, 138.7, 144.0, 144.8; HRMS (MALDI-TOF) 852.3328 (M$^+$), calcd for $C_{56}H_{52}O_4S_2$ 852.3307.

*Synthesis of **3j** from **1j**.* The synthesis of **3j** was carried out according to the procedure described above for **3e**. Purification: chromatography (EtOAc/hexane, 1:5). Yield: 716.6 mg, 42%.

*Synthesis of **3k**.* A flask was charged with 4-hexylphenylboronic acid (309.1 mg, 1.5 mmol), **3f** (321.2 mg, 0.50 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), dioxane (4.0 mL), and a solution of K_3PO_4 (318.4 mg, 1.5 mmol) in H_2O (1.0 mL), and the mixture was stirred under nitrogen at 90 °C overnight. After the usual workup with CH_2Cl_2/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was subjected to column chromatography on silica gel (hexane/EtOAc, 6:1) to give **3k** (293.9 mg, 73%) in a pure form. Pale-yellow powder; mp 72−74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85−0.88 (m, 6H), 1.29−1.30 (m, 12H), 1.58−1.61 (m, 4H), 2.61 (t, J = 7.9 Hz, 4H), 7.04 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 4H), 7.42−7.52 (m, 16H), 7.62−7.66 (m, 2H), 7.72 (d, J = 1.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 31.4, 31.7, 35.6, 126.8 (d), 127.5, 127.6 (d), 128.2, 128.9, 129.0, 129.4, 133.8, 134.0, 136.4, 138.96, 138.98, 139.05, 141.0, 143.0, 144.6; HRMS (MALDI-TOF) 827.3207 (M + Na$^+$), calcd for $C_{52}H_{52}O_4S_2Na$ 827.3205.

*Synthesis of **3ab**.* A 100 mL flask was charged with **1a** (260.3 mg, 1.0 mmol), **1b** (320.4 mg, 1.0 mmol), $ClP(O)(OEt)_2$ (0.34 mL, 2.4 mmol), and THF (40.0 mL), and LiHMDS (1.0 N in THF, 4.0 mL, 4.0 mmol) was added at −78 °C. After the mixture had been stirred at −78 °C for 30 min and then at room temperature for 2.5 h, aqueous NH_4Cl solution was poured into the mixture. After the usual workup with water and AcOEt, the solvents were evaporated in vacuo, and the residue was subjected to chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4) to give **3a** (101.8 mg, 21.0%), **3ab** (105.1 mg, 19.3%), and **3b** (87.8 mg, 14.5%) in a pure form.

Data for **3a**:[8b] Pale-yellow powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97−6.99 (m, 2H), 7.22−7.30 (m, 4H), 7.36−7.50 (m, 12H), 7.61−7.66 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 126.9, 128.0, 128.3, 128.8, 128.9, 129.3, 130.7, 133.8, 135.6, 138.79, 138.81, 144.6.

Data for **3ab**: White powder; mp 203−205 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 (s, 6H), 6.45 (s, 1H), 6.97−6.99 (m, 2H), 7.27−7.30 (m, 2H), 7.33 (s, 1H), 7.36 (s, 1H), 7.41−7.53 (m, 9H), 7.61−7.64 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.8 (d), 55.9 (d), 109.2 (d), 113.1 (d), 121.1, 127.0, 127.1, 128.0, 128.3 (d), 128.5, 129.0, 129.2, 129.3, 130.8 (d), 133.8, 135.9, 138.8 (d), 139.0, 139.1 (d), 144.4, 144.5, 148.7, 149.8; HRMS (MALDI-TOF) 567.0916 (M + Na$^+$), calcd for $C_{30}H_{24}O_6S_2Na$ 567.0912.

*Synthesis of **3be**.* The synthesis of **3be** was carried out according to the procedure described above for **3ab**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4). Yields: **3e** (52.1 mg, 10.0%); **3be** (95.1 mg, 16.9%); **3b** (70.1 mg, 11.6%).

Data for **3be**: White powder; mp 222−224 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.81 (s, 3H), 6.44 (s, 1H), 6.71 (dd, J = 2.5 Hz, J = 8.5 Hz, 1H), 6.96 (s, 1H), 7.00 (dt, J = 2.5 Hz, J = 8.5 Hz, 1H), 7.25 (s, 1H), 7.33 (s, 1H), 7.43−7.55 (m, 9H), 7.64−7.68 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.65 (s, 1F); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.85 (d), 55.93 (d), 109.2 (d), 112.9 (d), 114.0 (dd, J = 10.3 Hz, J_{C-F} = 22.2 Hz), 115.8 (dd, J = 11.1 Hz, J_{C-F} = 21.9 Hz), 120.8, 125.2 (d, J_{C-F} = 4.2 Hz), 128.0, 128.2, 129.0, 129.1, 133.0 (m), 133.9, 137.3 (d), 138.2 (d, J_{C-F} = 8.3 Hz), 138.6, 139.0, 139.5 (d), 143.6, 145.5, 148.8, 149.9, 162.8 (d, J_{C-F} = 252.2 Hz); HRMS (MALDI-TOF) 563.1005 (M + H$^+$), calcd for $C_{30}H_{24}FO_6S_2$ 563.0998.

*Synthesis of **3bf**.* The synthesis of **3bf** was carried out according to the procedure described above for **3ab**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4). Yields: **3f** (131.7 mg, 20.5%); **3bf** (69.8 mg, 11.2%); **3b** (110.1 mg, 18.2%).

Data for **3bf**: Pale-yellow powder; mp 276−277 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.82 (s, 3H), 6.44 (s, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.97 (s, 1H), 7.29 (s, 1H), 7.32 (s, 1H), 7.42−7.53 (m, 9H), 7.60 (d, J = 2.1 Hz, 1H), 7.63−7.68 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.9 (d), 56.0 (d), 109.1 (d), 112.9 (d), 120.8, 122.5, 127.99, 128.04, 128.1, 128.4 (d), 129.0, 129.1, 131.3, 132.5 (d), 133.5 (d), 133.9, 134.0, 134.9, 137.7 (d), 138.7, 138.8, 139.8 (d), 143.3, 145.1, 148.9, 149.9; HRMS (MALDI-TOF) 622.0116 (M$^+$), calcd for $C_{30}H_{23}BrO_6S_2$ 622.0119.

*Synthesis of **3ci**.* The synthesis of **3ci** was carried out according to the procedure described above for **3ab**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:6:12). Yields: **3i** (84.8 mg, 14.5%); **3ci** (202.1 mg, 27.5%); **3c** (100.0 mg, 11.3%).

Data for **3i**: White powder; mp 290 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.48 (m, 12H), 7.50 (s, 2H), 7.62−7.66 (m, 4H), 7.68−7.73 (m, 4H), 7.93 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 125.8, 126.4 (d), 127.1, 127.6, 127.7, 128.3, 128.5, 129.0, 131.0, 131.9, 132.1, 132.6, 133.8, 138.8, 139.1 (d), 144.7; HRMS (MALDI-TOF) 585.1203 (M + H^+), calcd for $C_{36}H_{25}O_4S_2$ 585.1194.

Data for **3ci**: Pale-yellow foam; mp 66−68 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84−0.89 (m, 6H), 1.27−1.31 (m, 8H), 1.37−1.42 (m, 4H), 1.71−1.78 (m, 4H), 3.78−3.95 (m, 4H), 6.44 (s, 1H), 6.96 (s, 1H), 7.37−7.44 (m, 5H), 7.46−7.53 (m, 6H), 7.54 (s, 1H), 7.60−7.65 (m, 3H), 7.73 (d, J = 7.0 Hz, 1H), 7.79 (d, J = 7.0 Hz, 1H), 7.98 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 25.5, 28.9, 31.5, 68.8, 69.0, 110.7 (d), 114.5 (d), 120.6, 126.4, 126.5 (d), 127.1, 127.5, 127.6, 127.9, 128.1, 128.5, 128.88, 128.94, 131.0, 132.1, 132.4, 132.5, 133.68, 133.72, 138.4 (d), 138.8, 139.3, 139.6 (d), 143.9, 144.7, 148.7, 149.7; HRMS (MALDI-TOF) 757.2627 (M + Na^+), calcd for $C_{44}H_{46}O_6S_2Na$ 757.2634.

Data for **3c**: Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87−0.91 (m, 12H), 1.31−1.34 (m, 16H), 1.42−1.45 (m, 8H), 1.73−1.81 (m, 8H), 3.84−4.01 (m, 8H), 7.42−7.47 (m, 8H), 7.61 (t, J = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 13.9, 22.5, 25.6 (d), 28.9, 31.5 (d), 68.9 (m), 111.0 (d), 114.7 (d), 121.2, 127.9, 128.4, 128.8, 133.6, 139.0 (d), 139.3, 143.9, 148.7, 149.6; HRMS (MALDI-TOF) 884.4351 (M^+), calcd for $C_{52}H_{68}O_8S_2$ 884.4356.

*Attempted Synthesis of **3bh**.* The synthesis of **3bh** was carried out according to the procedure described above for **3ab**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:2:4). Yields: **3h** (52.9 mg, 8.5%); **3bh** (trace); **3b** (96.8 mg, 16%).

*Synthesis of **3il**.* The synthesis of **3il** was carried out according to the procedure described above for **3ab**. Purification: chromatography (EtOAc/CH_2Cl_2/hexane, 1:6:10, then EtOAc/CH_2Cl_2/hexane, 1:2:4, then EtOAc/CH_2Cl_2/hexane, 1:1:2). Yields: **3i** (76.0 mg, 13.1%); **3il** (135.1 mg, 22.7%); **3l** (70.0 mg, 11.6%).

Data for **3il**: White powder; mp 198−200 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 4.00 (s, 3H), 6.69 (d, J = 2.2 Hz, 1H), 7.00 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 6.7 Hz, 1H), 7.21−7.25 (m, 2H), 7.30 (dd, J = 2.1 Hz, J = 8.6 Hz, 1H), 7.41−7.51 (m, 9H), 7.57 (s, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.71 (t, J = 6.7 Hz, 2H), 7.83 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.0, 56.3 (d), 110.6 (d), 110.7 (d), 122.2 (d), 126.1, 126.6 (d), 126.8 (d), 127.1, 127.6, 128.3, 128.4, 128.95, 128.98 (d), 129.2, 129.3, 130.0, 130.65, 130.72, 132.0, 132.1, 132.6, 133.8, 135.7, 137.7 (d), 138.8, 139.0 (d), 144.6, 145.1, 148.8, 153.5; HRMS (MALDI-TOF) 617.1069 (M + Na^+), calcd for $C_{34}H_{26}O_6S_2Na$ 617.1068.

Data for **3l**: Pale-yellow powder; mp 189−191 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.67 (s, 6H), 3.98 (s, 6H), 6.71 (s, 2H), 6.98 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 7.7 Hz, 2H), 7.21−7.29 (m, 6H), 7.40−7.43 (m, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.0 (d), 56.3 (d), 110.6 (d), 122.2 (d), 127.0 (d), 128.0 (d), 129.1 (d), 129.5, 130.0, 130.4 (d), 135.9, 137.6 (d), 145.0, 148.7, 153.4; HRMS (MALDI-TOF) 627.1120 (M + Na^+), calcd for $C_{32}H_{28}O_8S_2Na$ 627.1123.

*Synthesis of **3m**.* A flask was charged with 3,4,5-trimethoxyphenylboronic acid (55.1 mg, 0.26 mmol), **3bf** (124.7 mg, 0.20 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol), dioxane (3.0 mL), and a solution of K_3PO_4 (59.4 mg, 0.28 mmol) in H_2O (1.0 mL), and the mixture was stirred under nitrogen at 90 °C overnight. After the usual workup with EtOAc/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (hexane/EtOAc, 1:1) to give **3m** (139.3 mg, 98% yield) in a pure form. White powder; mp 131−133 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H), 3.91 (s, 6H), 6.47 (s, 1H), 6.73 (s, 2H), 7.02 (s, 1H), 7.07 (d, J = 8.2 Hz, 1H), 7.38 (s, 1H), 7.41 (s, 1H), 7.44−7.53 (m, 9H), 7.65 (t, J = 7.1 Hz, 2H), 7.74 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.8 (d), 55.9 (d), 56.2 (q), 60.9 (t), 104.3 (d), 109.2 (d), 113.1 (d), 121.1, 127.46, 127.53, 127.6 (d), 128.0, 128.4, 128.9, 129.2 (d), 129.8, 133.8 (d), 134.6, 135.1, 138.2, 138.5, 138.6, 138.9, 139.2, 139.3, 139.4, 141.0, 144.2, 144.6, 148.7, 149.7, 153.5; HRMS (MALDI-TOF) 733.1523 (M + Na^+), calcd for $C_{39}H_{34}O_9S_2Na$ 733.1542.

Click Reaction of 2a with Benzyl Azide. To a solution of **2a** (40.0 mg, 0.2 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of benzyl azide (63.9 mg, 0.48 mmol) in CH_2Cl_2 (1.5 mL) at 40 °C. The mixture was stirred for 2 h at the same temperature and then concentrated under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH, 6:1) to give **13a** (57.8 mg, 61.9%) and **13b** (34.5 mg, 37.0%).

Data for **13a**:[10a] White powder; ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (d, J = 15.3 Hz, 2H), 5.50 (d, J = 15.3 Hz, 2H), 6.97−6.98 (m, 4H), 7.09 (d, J = 8.6 Hz, 2H), 7.26−7.38 (m, 6H), 7.40 (t, J = 7.9 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.71 (d, J = 7.0 Hz, 2H).

Data for **13b**:[10a] White powder; ^1H NMR (500 MHz, $CDCl_3$) δ 4.90 (d, J = 15.6 Hz, 2H), 5.31 (d, J = 15.3 Hz, 2H), 6.99−7.00 (m, 4H), 7.06−7.08 (m, 2H), 7.29−7.32 (m, 6H), 7.40−7.42 (m, 2H), 7.47−7.49 (m, 2H), 7.65−7.67 (m, 2H).

Click Reaction of 2b with Benzyl Azide. To a solution of **2b** (64.0 mg, 0.2 mmol) in CH_2Cl_2 (6.0 mL) was added a solution of benzyl azide (63.9 mg, 0.48 mmol) in CH_2Cl_2 (1.5 mL) at 40 °C. The mixture was stirred for 2 h at the same temperature and then concentrated under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2/hexane/EtOAc, 2:2:3) to give **14a** (69.2 mg, 59.0%) and **14b** (47.9 mg, 40.8%).

Data for **14a**: White powder; mp 143−145 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.39 (s, 6H), 3.95 (s, 6H), 5.16 (d, J = 15.9 Hz, 2H), 5.66 (d, J = 15.9 Hz, 2H), 6.39 (s, 2H), 7.13 (d, J = 7.7 Hz, 4H), 7.22 (s, 2H), 7.27−7.36 (m, 4H), 7.52−7.54 (m, 1H), 7.70−7.72 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 52.0, 55.3 (d), 56.0 (d), 112.3 (d), 113.3 (d), 118.1, 125.6, 126.6 (d), 128.1, 129.0 (d), 135.1, 136.1, 144.9, 149.1, 150.3; HRMS (MALDI-TOF) 586.2358 (M^+), calcd for $C_{34}H_{30}N_6O_4$ 586.2329.

Data for **14b**: White powder; mp 139−141 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.48 (s, 6H), 3.94 (s, 6H), 4.89 (d, J = 15.9 Hz, 2H), 5.45 (d, J = 15.9 Hz, 2H), 6.44 (s, 2H), 7.01−7.03 (m, 4H), 7.17 (s, 2H), 7.31−7.36 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 52.0, 55.6 (d), 56.0 (d), 112.7 (d), 112.8, 120.2, 123.6, 126.7 (d), 128.2 (d), 129.0 (d), 133.7, 136.0, 146.2, 149.6, 149.9; HRMS (MALDI-TOF) 586.2301 (M^+), calcd for $C_{34}H_{30}N_6O_4$ 586.2329.

Competitive Click Reaction of 2a and 2b with Benzyl Azide. To a solution of **2a** (40.0 mg, 0.2 mmol) and **2b** (64.0 mg, 0.2 mmol) in CH_2Cl_2 (10.0 mL) was added a solution of benzyl azide (53.3 mg, 0.4 mmol) in CH_2Cl_2 (1.5 mL) at 40 °C. The mixture was stirred for 2 h at the same temperature and then concentrated under reduced pressure. ^1H NMR analysis of the crude products suggested the formation of **13a** (23.3 mg, 25.0%), **13b** (19.7 mg, 21.0%), **14a** (37.5 mg, 32.0%), and **14b** (25.9 mg, 22.0%).

Competitive Iodination of 2a and 2ab. A solution of iodine (253.8 mg, 1.0 mmol) in CH_3CN (6.0 mL) was added to a solution of **2a** (200.0 mg, 1.0 mmol) and **2ab** (260.3 mg, 1.0 mmol) in CH_3CN (20.0 mL) at −20 °C under nitrogen, and the resulting mixture was stirred at −20 °C for 8 h and then at room temperature overnight. Saturated aqueous sodium hyposulfite was added to the reaction mixture. After the usual workup with water and CH_2Cl_2, the combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was subjected to chromatography (hexane to CH_2Cl_2) and reprecipitation from CH_3OH/CH_2Cl_2 to afford **15** (36.3 mg, 8%) and **16** (272.5 mg, 53%) in a pure form.

Data for **15**:[12] Brown powder; mp 199 °C (dec); ^1H NMR (500 MHz, $CDCl_3$) δ 6.84 (d, J = 7.4 Hz, 2H), 7.10 (t, J = 7.3 Hz, 2H), 7.07 (t, J = 7.3 Hz, 2H), 7.42 (d, J = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 94.4, 120.8 (d), 123.9 (d), 128.5 (d), 129.1 (d), 133.7, 150.0, 152.0.

Data for **16**: Dark-green powder; mp 200−202 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 6H), 6.36 (s, 1H), 6.71 (d, J = 7.0 Hz, 1H), 6.93−6.99 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.1 (q), 56.3 (q), 93.4, 93.9, 105.4 (d), 108.4, 120.1 (d), 123.6 (d), 126.4, 128.3, 128.5, 134.2, 143.4, 149.1, 149.6, 150.0,

151.2, 152.4; HRMS (MALDI-TOF) 513.8930 (M$^+$), calcd for $C_{18}H_{12}I_2O_2$ 513.8927.

Nucleophilic Addition of Diethylamide to 2a. A 25 mL flask was charged with diethylamine (109.7 mg, 1.5 mmol) and THF (3.0 mL). A hexane solution of BuLi (1.24 M, 0.65 mL, 0.52 mmol) was added dropwise at −78 °C. After the reaction mixture had been stirred at this temperature for 30 min, a solution of **2a** (100.0 mg, 0.50 mmol) in THF (1.5 mL) was added. After the reaction mixture had been stirred at this temperature for 2.0 h, water was poured into the mixture. After the usual workup with CH_2Cl_2/NH_4Cl(aq), the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was subjected to column chromatography on silica gel (CH_2Cl_2/hexane, 1:9) to give **17** (123.0 mg, 90%) in a pure form. Dark-brown powder; mp 106−108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (t, J = 7.0 Hz, 6H), 3.80 (q, J = 7.0 Hz, 4H), 6.40 (s, 1H), 6.83−6.91 (m, 3H), 7.00 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 9.5 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 14.3 (d), 46.4, 113.5 (d), 116.8, 120.4 (d), 121.3 (d), 122.6 (d), 123.2 (d), 123.5 (d), 124.2 (d), 126.4 (d), 128.5 (d), 133.5, 138.6, 143.6, 146.6, 147.3, 151.3; HRMS (MALDI-TOF) 273.1517 (M$^+$), calcd for $C_{20}H_{19}N$ 273.1517.

Attempted Nucleophilic Addition of Diethylamide to 2b. A 25 mL flask was charged with diethylamine (109.7 mg, 1.5 mmol) and THF (3.0 mL) under N_2. A hexane solution of BuLi (1.24 M, 0.65 mL, 0.52 mmol) was added dropwise at −78 °C. After the reaction mixture had been stirred at this temperature for 30 min, a solution of **2b** (160.1 mg, 0.50 mmol) in THF (10.0 mL) was added, and the resulting mixture was allowed to stir at this temperature for 2.0 h (TLC suggested that no reaction happened) and then 0 °C for 2.0 h (TLC suggested that decomposition of **2b** happened, and no desired product was formed).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Electrochemical measurement results; theoretical calculations such as TDDFT and strain energy; kinetic studies of the double-click reaction; and copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(24) Since the nonfluorescent property of **2m** is somewhat ambiguous, further investigations would be required.

(25) One- or two-electron oxidation could be distinguished by comparison of the semidifferential CV profiles in the oxidation of **2a** and ferrocene. See the Supporting Information for details.

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