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$CuBr_2$-Mediated One-Pot Synthesis of Sulfonyl 9-Fluorenylidenes

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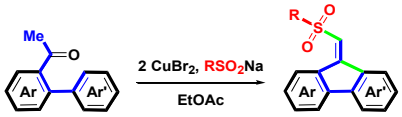


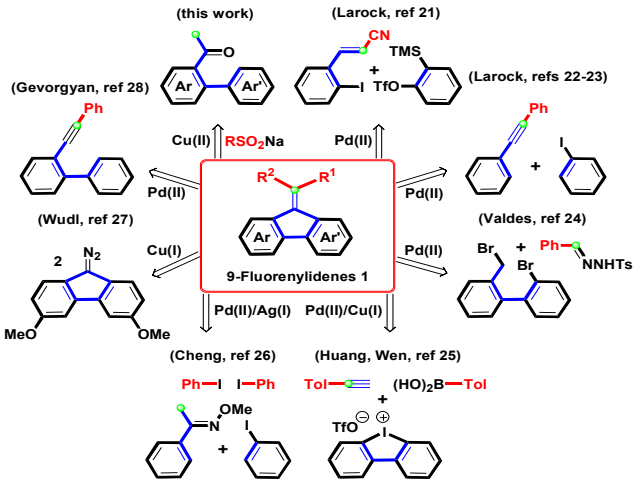
ABSTRACT: In this article, a high-yield method for the synthesis of sulfonyl 9-fluorenylidenes is described, which consists of a one-pot straightforward three-step synthetic route including (i) $CuBr_2$-mediated α-bromination of *o*-arylacetophenone, (ii) sequential nucleophilic substitution of the resulting α-bromo *o*-arylacetophenone with sodium sulfinate (RSO_2Na) and (iii) $CuBr_2$-mediated intramolecular Friedel-Crafts cyclizative dehydration. A plausible mechanism is proposed and discussed. This protocol provides a highly effective regio- and stereoselective annulation via formation of one carbon-carbon (C-C) bond and one carbon-sulfur (C-S) bond.

Introduction

The core skeleton of geminal diarylethylene is present in many pharmacophores, including tamoxifen, bexarotene and ratanhine.[1-11] Among these 1,1-diarylethylene derivatives, however, the tricyclic 9-fluorenylidene system (also known as methylidenefluorene) exhibits key functionalized properties in advanced material chemistry.[12-19] Due to their potential applications, the development of a one-pot facile transition metal-promoted synthetic route to access these motifs has attracted significant attention, and many development attempts have been reported. The conventional synthetic route towards substituted alkylidene or benzylidene fluorenes is based on Knoevenagel condensation of fluorene with aliphatic and aromatic aldehydes.[20] Recently, the palladium complex promoting pioneering methods have been explored as a main strategy, as shown in Scheme 1.[21-28] Other routes for the formation of substituted 9-fluorenylidenes **1** have been investigated.[29]

For example, Larock and coworkers reported palladium-catalyzed (3+2) annulation of *in situ* formed arynes and o-halostyrenes.[21] This group also developed a $Pd(OAc)_2$ mediated domino reaction of iodoarenes and arylacetylenes.[22-23] Paraja and Valdés demonstrated a $Pd_2(dba)_3$ catalyzed autotandem cross-coupling of *N*-tosylhydrazones and biphenyl bromides.[24] Huang and Wen explored the Pd(II)/Cu(I) mediated cascade multi-component reaction (MCR) of cyclic iodoniums, alkynes and boronic acids.[25] Cheng *et al.* described a Pd(II)/Ag(I) catalyzed multiple C-H bond functionalization of oximes and excess aryl iodides.[26] The Wudl group reported a Cu(I) catalyzed self-dimerization of 9-diazofluorenes.[27] Gevorgyan *et al.* studied the Pd(II) catalyzed C-H activation route to construct a methylidenefluorene framework.[28] In spite of these advancements, some problems exist, such as multi-step routes, complicated catalytic conditions, and lack of broad substrate generality and prefunctionalized fragments.

Scheme 1. Synthetic Routes of 9-Fluorenylidenes **1**

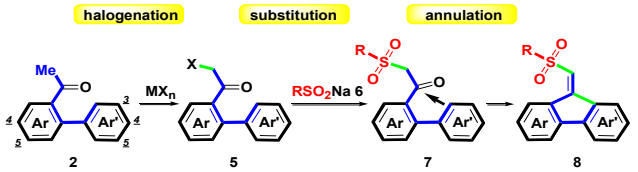


Therefore, further investigation of efficient synthetic methods for functionalized 9-fluorenylidenes is still highly desired. In fact, to the best of our knowledge, no vinyl sulfonyl-conjugated substituent on the core structure of 9-fluorenylidenes **1** has been reported to this point.[30] Owing to the specific chemoselectivity, multi-functionalized physical properties and diversified bioactivity, the introduction of the vinyl sulfonyl moiety to a key core skeleton has long held an important position in synthetic organic chemistry, materials science and pharmaceutical fields.

Results and Discussion

Continuing our research on the synthetic applications of β-sulfonyl styrenes,[31] we present a one-pot three-step method for sulfonyl 9-fluorenylidenes **8** via metal halide (MX_n)-mediated α-halogenation of *o*-arylacetophenones **2** (derived from cross-coupling of *o*-bromoacetophenones **3** with arylboronic acids **4**), sodium sulfinates (RSO_2Na) **6**-mediated substitution of the formed α-bromo *o*-arylacetophenones **5**, followed by intramolecular Friedel-Crafts-type dehydrative annulation of the resulting α-sulfonyl biarylketones **7** (Scheme 2).

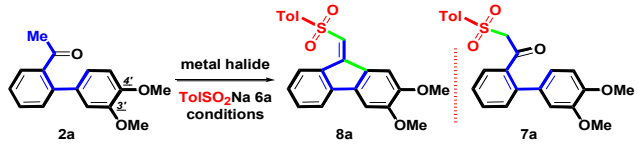
Scheme 2. Our Route to Sulfonyl 9-Fluorenylidenes **8**



2a, Ar = Ph, Ar' = 3,4-$(MeO)_2C_6H_3$
2b, Ar = Ph, Ar' = 3,4,5-$(MeO)_3C_6H_2$
2c, Ar = Ph, Ar' = 3-$MeOC_6H_4$
2d, Ar = 5-FC_6H_3, Ar' = 3,4-$(MeO)_2C_6H_3$
2e, Ar = 5-FC_6H_3, Ar' = 3,4,5-$(MeO)_3C_6H_2$
2f, Ar = 5-FC_6H_3, Ar' = 3-$MeOC_6H_4$
2g, Ar = 4,5-$(MeO)_2C_6H_2$, Ar' = 3,4-$(MeO)_2C_6H_3$
2h, Ar = 4,5-$(MeO)_2C_6H_2$, Ar' = 3,4,5-$(MeO)_3C_6H_2$
2i, Ar = 4,5-$(MeO)_2C_6H_2$, Ar' = 3-$MeOC_6H_4$
2j, Ar = 2-thienyl, Ar' = 3,4-$(MeO)_2C_6H_3$
2k, Ar = 2-thienyl, Ar' = 3,4,5-$(MeO)_3C_6H_2$
2l, Ar = 2-thienyl, Ar' = 3-$MeOC_6H_4$

6a, R = Tol; **6b**, R = Me; **6c**, R = 4-FC_6H_4; **6d**, R = 4-$MeOC_6H_4$

Table 1. Reaction Conditions[a]



entry	MX_n (equiv)	solvent (mL)	temp (°C)	time (h)	%[b]
1	$CuBr_2$ (2)	EtOAc (30)	60	10	80
2	$CuCl_2$ (2)	EtOAc (30)	60	10	15[c]
3	CuF_2 (2)	EtOAc (30)	60	10	—[d]
4	$ZnBr_2$ (2)	EtOAc (30)	60	10	—[d]
5	$NiBr_2$ (2)	EtOAc (30)	60	10	—[d]
6	$BiBr_3$ (2)	EtOAc (30)	60	10	—[d]
7	$InBr_3$ (2)	EtOAc (30)	60	10	—[d]
8	$FeBr_3$ (2)	EtOAc (30)	60	10	—[d]
9	$CuBr_2$ (2.5)	EtOAc (30)	60	10	74
10	$CuBr_2$ (1)	EtOAc (30)	60	10	38
11	$CuBr_2$ (0.5)	EtOAc (30)	60	10	12[c]
12	$CuBr_2$ (2)	EtOAc (15)	60	10	89
13	$CuBr_2$ (2)	EtOAc (10)	60	10	85
14	$CuBr_2$ (2)	$CHCl_3$ (15)	60	10	—[d]
15	$CuBr_2$ (2)	Toluene (15)	60	10	—[d]
16	$CuBr_2$ (2)	$MeNO_2$ (15)	60	10	—[e]
17	$CuBr_2$ (2)	DMF (15)	60	10	—[e]
18	$CuBr_2$ (2)	EtOAc (15)	77	10	78
19	$CuBr_2$ (2)	EtOAc (15)	25	10	15[f]
20	$CuBr_2$ (2)	EtOAc (15)	60	15	92
21	$CuBr_2$ (2)	EtOAc (15)	60	30	89

[a]The reactions were run on a 1.0 mmol scale with **2a**, metal halides (0.5-2.5 equiv), then **6a** (196 mg, 1.1 equiv). [b]Isolated yields. [c]**2a** was recovered (entry 2, 75%; entry 11, 68%). [d]No reaction. [e]Complex and unknown mixture. [f]**7**a (48%) was isolated.

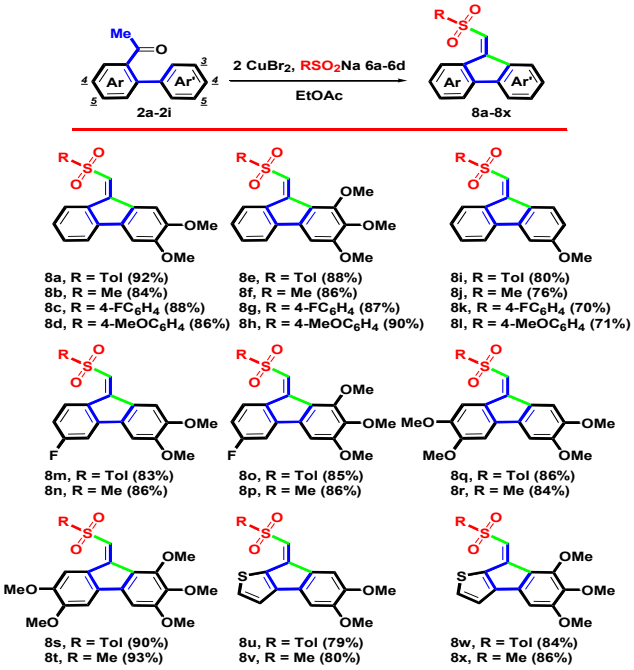
Compared with reports on transition metal mediated reactions, we initially chose commercially available copper halides as the promoters to screen optimal reaction conditions. On the basis of our previous copper-mediated synthetic work,[32] this study examined the formation of **8a**, commencing with $CuBr_2$ (2 equiv)-mediated treatment of model substrates **2a** (Ar = Ph, Ar' = 3,4-$(MeO)_2C_6H_3$, 1 mmol) and **6a** (R = Tol, 1.1 equiv) in EtOAc (30 mL) at 60 °C for 10 h (Table 1, entry 1). **8a** was isolated with 80% yield. In entry 2, $CuCl_2$ provided only 15% yield of **8a**, along with the major recovery of starting material **2a** (75%). With the use of CuF_2, no detection of **8a** was observed, and the starting material **2a** was recovered (entry 3). By controlling the halide as the bromide, five metal bromides were examined next (entries 4-8). From the results, we understood that $CuBr_2$ was a better promoter in the initial α-halogenation step than $CuCl_2$ or CuF_2.

However, no reactions occurred on $ZnBr_2$, $NiBr_2$, $BiBr_3$, $InBr_3$ or $FeBr_3$, respectively. To increase the yield of **8a**, the equivalency of $CuBr_2$ was adjusted from 2.0 to 2.5, 1.0 or 0.5, but the isolated yields could not be enhanced (entries 9-11). In particular, by diminishing the solvent volume (30 → 15 or 10), the yield of **8a** was increased to 89% (entry 12) and 85% (entry 13), respectively. This meant that the condensed reaction system could trigger the initial α-bromination. However, when the reaction solvent was changed from EtOAc to $CHCl_3$, toluene, $MeNO_2$ or DMF, no higher yields were accomplished (entries 14-17). No reactions were detected for $CHCl_3$ and toluene. $MeNO_2$ or DMF provided a complex unknown mixture. In entry 18, by elevating the reaction temperature from a warming (60 °C) to boiling (77 °C) temperature, the yield was decreased to 78%. Interestingly, when the reaction temperature was decreased to room temperature (25 °C), the desired **8a** was afforded in only 15% yield, along with a major 48% yield of **7a** (entry 19). Subsequently, elongated time (10 h → 15 or 30 h) did improve the yields to 92% and 89%, respectively (entries 20-21). An excellent conversion from **2a** to **8a** was achieved in 15 h. From these observations, we concluded that 2 equivalents of $CuBr_2$ provided optimal conditions (60 °C, 15 h) in the presence of $TolSO_2Na$ **6a** for a one-pot intramolecular annulation procedure. The expeditious synthetic route sets up the skeleton of sulfonyl 9-fluorenylidenes via formation of one C-C bond and one C-S bond under mild conditions.

To study the substrate scope and limitation of this one-pot route, **2a-2i** and **6a-6d** were reacted under optimal $CuBr_2$-mediated reaction conditions to afford diversified **8a-8x**, as shown in Scheme 3. With optimal conditions established (Table 1, entry 20), we found that this route allowed a direct intramolecular Friedel-Crafts annulation under easy-operational and open-vessel conditions in moderate to excellent yields. Controlling the Ar group as a phenyl group (for **2a-2c**, Ar = Ph), the formation of **8a-8l** showed that different oxygenated mono-, di- or tri-substituents (3-MeO, 3,4-$(MeO)_2$, 3,4,5-$(MeO)_3$) on the aromatic ring (Ar') provided yields in the range of 70%-92% in the presence of RSO_2Na **6a-6d** (R = Tol, Me, 4-FC_6H_4, 4-$MeOC_6H_4$). From the yield distribution, we found that di- and tri-methoxy groups produced better yields than the mono-methoxy group because di- and tri-oxygenated groups provided more electron density in the Ar' ring such that the arene ring could attack the benzylic carbonyl group more easily to obtain better yields. For the four sulfonyl

substituents (R) of **6**, aliphatic, electron-withdrawing and electron-donating aromatic groups were well-tolerated. With this idea in mind, the Ar' ring was chosen for di- and tri-methoxy groups to investigate the following reactions.

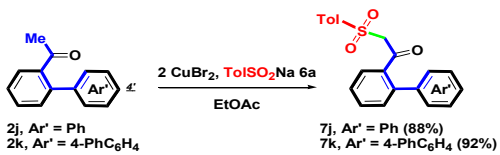
Scheme 3. Synthesis of **8a-8x**[a-b]



[a]The reactions were run on a 1.0 mmol scale with **2a-2i**, **6a-6d** (1.1 equiv), $CuBr_2$ (450 mg, 2.0 mmol), and EtOAc (15 mL) for 15 h at 60 °C. [b]Isolated yields.

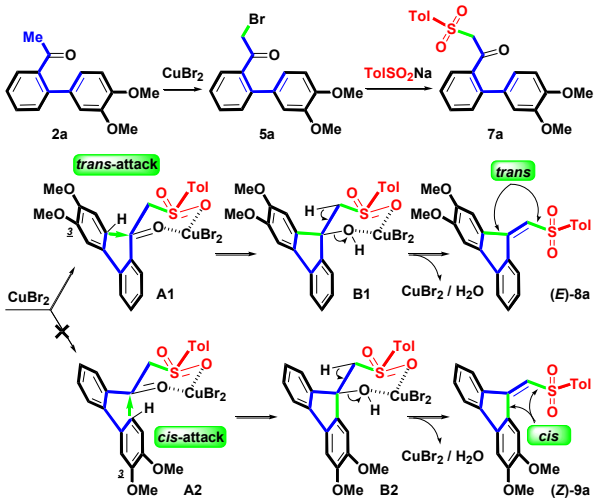
On the other hand, when the Ar group was changed from an electron-neutral phenyl group to electron-withdrawing 5-fluorophenyl (for **2d-2e**) and electron-donating 4,5-dimethoxyphenyl groups (for **2f-2g**), **8m-8t** showed that the different substituents (Ar and R) did not affect the yield changes (83%-93%) in the presence of **6a-6b**. For the electronic nature of the Ar substituent, not only the electron-neutral groups but also the electron-withdrawing groups and electron-donating groups, were suitable. Then, for the heterocyclic 2-thienyl group (for **2h-2i**), **8u-8x** were isolated in 79%-86% yields. Furthermore, the structures of **8b-8c**, **8e**, **8h**, **8s-8t** and **8v** were determined by single-crystal X-ray analysis.[33] Surprisingly, all of the crystal structures showed that the sulfonyl group was oriented to the same face of the Ar group. From the literature, we found that polymethoxy-substituted fluorenes with strong dependence on the optical properties have been reported as highly reversible electrochromic materials.[34]

Scheme 4. Synthesis of **7j-k**



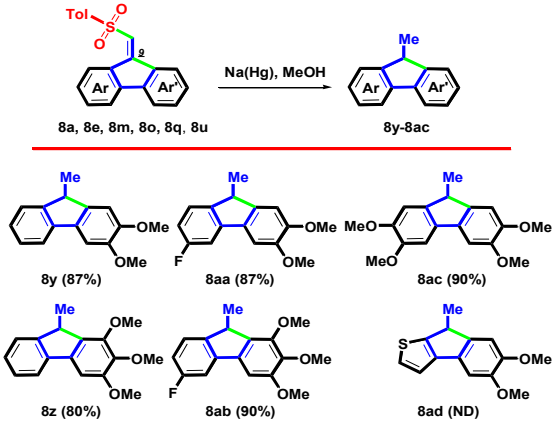
With the above results in hand, the Ar' group with non-oxygenated phenyl groups was examined next (Scheme 4). Controlling Ar = Ph and R = Tol, we adjusted the Ar' group to the phenyl or biphenyl groups (for **2j-2k**). However, no desired tricyclic skeleton of sulfonyl 9-fluorenylidenes **8** was obtained, and only α-sulfonyl biarylketones **7j-7k** were produced in high yields (88% and 92%) under the α-bromination and sulfonyl substitution processes.

Scheme 5. Plausible Mechanism



On the basis of the experimental results, a plausible mechanism for the formation of **8a** is illustrated in Scheme 5. First, one equivalent of $CuBr_2$-mediated α-bromination of **2a** followed by $TolSO_2Na$-mediated nucleophilic substitution of the bromide in the resulting **5a** yields **7a**. Then, another equivalent of $CuBr_2$ chelates the carbonyl and sulfonyl groups on **7a**, yielding **A1** and **A2** via a six-membered ring intermediate. From the intramolecular addition face of the dimethoxyphenyl group, **A1** is preferred for generation over **A2** because it possesses a *trans*-configured orientation with less steric hindrance. On the basis of the formed conformation of **A1**, the electron-donating methoxy (3-MeO) group could trigger the *para*-carbon of the phenyl group to stereoselectively attack the carbonyl site to produce **B1** via copper-mediated intramolecular Friedel-Crafts addition. By the *anti*-deprotonated removal (E2 process) of the copper-chelated hydroxyl group on **B1**, **8a** was provided, along with the release of $CuBr_2$ and H_2O.[32] Two new-forming bonds (green marks) on **8a** could be orientated in *trans*-configuration via formation of carbon-carbon bond and carbon-sulfur bond. In the pathway of **A2**, however, intramolecular 3-methoxy-promoted *cis*-addition faces bulkier repulsion than **A1** such that the (*Z*)-**9a** stereoisomer could not be generated from **B1**. The DFT calculations were carried out for the intermediates proposed in Scheme 5. The results showed that the *cis*-**A2** was about 7 kcal/mol higher than the *trans*-**A1**, supporting the proposed mechanism (Figure S1, see Supporting Information). However, the two stereoisomers of product (*E*)-**8a** and (*Z*)-**9a** were almost isoenergetic with the latter being slightly lower in energy than the former by 0.8 kcal/mol (Figure S1). This theoretical prediction implies that although the stereoisomer (*Z*)-**9a** could not be generated by the synthetic route, it should be produced from photoisomerization of (*E*)-**8a**. For the formation of a fluorene skeleton, the reaction mechanism not only explains the stereospecific *trans*-orientation between sulfonyl and Ar' groups but also demonstrates **8a** as the (*E*)-isomer. We envision that $CuBr_2$ efficiently controlled the formation of the copper-chelated intermediate and increased the yield in generation of **8a**.

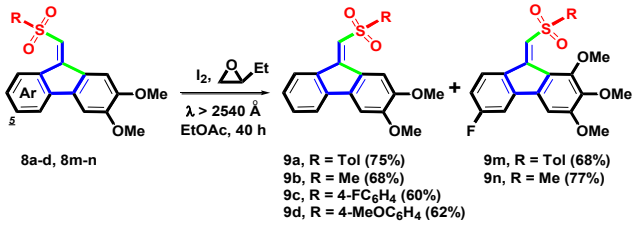
Scheme 6. Synthesis of **8y-8ac**[a-b]



[a]The reactions were run on a 1.0 mmol scale with **8a**, **8e**, **8m**, **8o**, **8q** and **8u**, Na(Hg) (300 mg), and MeOH (15 mL) for 1 h at 25 °C. [b]Isolated yields.

With these results in hand, desulfonylative reduction of sulfonyl 9-fluorenylidene was examined, as shown in Scheme 6.[35] Controlling the sulfonyl as the tosyl group, treatment of **8a**, **8e**, **8m**, **8o** and **8q** with freshly prepared sodium amalgam (Na(Hg)) provided 9-methylfluorenes **8y-8ac** in a range of 80%-90% yields under the standard conditions via a tandem 1,4-reduction followed by desulfonylation reaction.[36-37] In particular, over-reduced products replaced the predicted methylidenefluorenes. A possible reason for this could be that the 9-carbon on a dibenzylic position could provide a more reactive site for the one-pot domino reduction procedure. The structures of **8y**, **8aa** and **8ac** were determined by single-crystal X-ray analysis.[33] However, attempts to afford **8ad** failed due to Na(Hg)-mediated decomposition of the thienyl ring on **8u**.

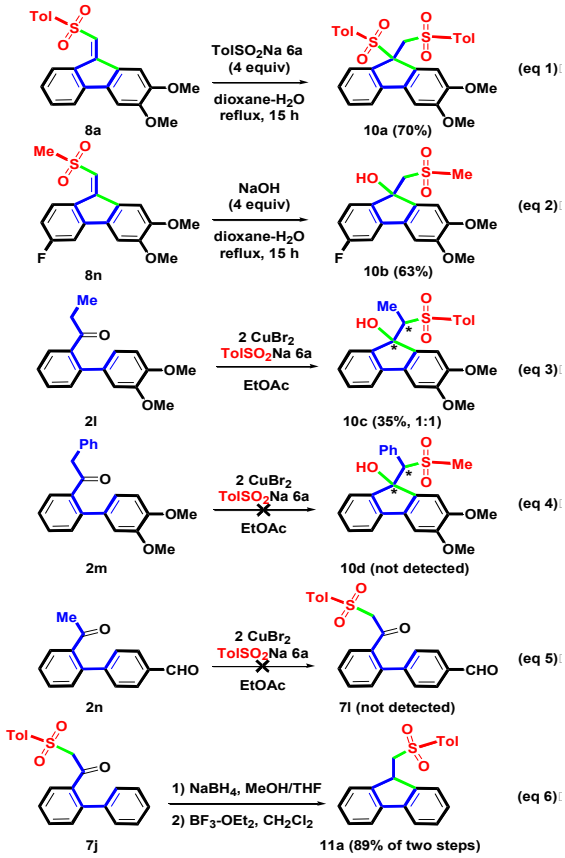
Scheme 7. Synthesis of **9a-9d** and **9m-9n**



Encouraged by the above results, the formation of **9a** was examined next, as shown in Scheme 7.[38-39] Under photolytic irradiation conditions (λ > 2540 Å, EtOAc, 25 °C), iodine-mediated olefin isomerization from (*E*)-**8a** to (*Z*)-**9a** was achieved directly in 75% yield during 40 h in the presence of excess amounts of 1,2-epoxybutane.[40] The transformation was monitored by a TLC plate. By the protocol, **9b-9d** were achieved successfully from **8b-8d** (Ar = Ph) in 68%, 60% and 62% yields. For photolytic isomerization of **8m-8n** with the electron-withdrawing group (Ar = 5-FC_6H_3), **9m-9n** were obtained in 68% and 77% yields, respectively. The structures of **9a** and **9c** were determined by single-crystal X-ray analysis.[33] These results showed that the photolytic irradiation could enable *E*/*Z*-isomerization of sulfonyl fluorenylidenes to proceed well.

As an extension of one-pot annulations, the synthetic applications of **8a** or **8n** with excess nucleophiles $TolSO_2Na$ or NaOH were investigated next (Scheme 8). Treatment of **8a** with **6a** (4 equiv) provided solely **10a** with the bis-sulfonyl group in 70% yield in a cosolvent of dioxane and water (v/v = 2/1) via the intermolecular conjugate addition on the quaternary carbon center (eq 1). As shown in eq 2, by changing $TolSO_2Na$ to NaOH, **10b** was produced in 63% yield, along with a trace mixture of *E*-**8n** and Z-**9n** isomers by a hydroxyl group mediated Michael addition under similar conditions. The structure of **10a** was determined by single-crystal X-ray analysis.[33] From two 1,4-conjugated reactions, we understood that bulkier tosyl and smaller hydroxyl nucleophiles were reactive for introducing the β-substituent of sulfonyl fluorenylidenes under refluxing conditions.

Scheme 8. Synthesis of **10a-10c** and **11a**

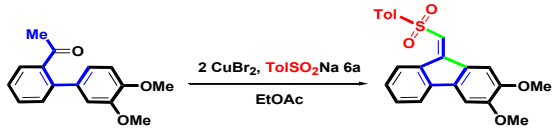


$CuBr_2$-mediated reaction of **2l** (an ethyl group) with $TolSO_2Na$ **6a** was examined next. Surprisingly, no isolation of the sulfonyl fluorenylidene skeleton was detected, and only **10c** with a β-hydroxy sulfone was isolated in 35% yield (eq 3). On the basis of ^{1}H-NMR spectra, the ratio of diastereomer **10c** was determined as an approximate ratio of 1/1 (see Supporting Information). When changing the ethyl group (for **2l**) to the benzyl group (for **2m**), treatment of **2m** with **6a** provided only a complex and unidentified mixture under the abovementioned $CuBr_2$-mediated reaction conditions (eq 4). We believe that bulkier methyl and phenyl groups provided steric strain, inhibiting the formation of the sulfonyl fluorenylidene skeleton. Unexpectedly, when **2n** containing an electron-withdrawing 4-formyl group was reacted with the combination of $CuBr_2$ and $TolSO_2Na$ **6a** (eq 5), the desired **7l** was not detected within the resulting unknown complex mixture. One possible reason should be that $CuBr_2$ activated the aldehyde group such that **6a**

could react with the corresponding bromide intermediates to generate complex results. Following, **7j** was chosen as the model substrate to construct tricyclic non-oxygenated sulfonyl fluorene **11a** (eq 6). Reduction of **7j** with $NaBH_4$ provided the β-hydroxysulfone intermediate. Involvement of $BF_3{\cdot}OEt_2$, intramolecular Friedel-Crafts annulation of the resulting β-hydroxysulfone obtained **11a** in 89% yield. By use of a two-step synthetic route, a non-oxygenated sulfonyl fluorene was also produced. Compared with the abovementioned $CuBr_2$-mediated route (Scheme 4), this present method exhibited complementary function.

Furthermore, a gram-scale synthesis of **8a** was shown in Scheme 9. When the reaction scale for $CuBr_2$-mediated one-pot annulation of **2a** and $TolSO_2Na$ **6a** increased to 3.9 mmol (1.0 g) and 4.5 mmol (800 mg), **8a** was isolated in 82% (1.25 g) yield in EtOAc at 60 °C. Although the yield (82%) was slightly lower than that of the 1.0 mmol scale (92%), the route could provide a gram-scale synthesis for sulfonyl 9-fluorenylidene.

Scheme 9. Gram-Scale Synthesis of **8a**



2a (1.0 g, 3.9 mmol) 8a (82%, 1.25 g)

In summary, we developed a $CuBr_2$-mediated one-pot regio- and stereoselective synthesis of sulfonyl 9-fluorenylidenes **8** via a straightforward three-step route, including α-bromination of *o*-arylacetophenones **2**, substitution of the resulting α-bromo *o*-arylacetophenones **5** with RSO_2Na **6** and Friedel-Crafts-type annulation of α-sulfonyl *o*-arylacetophenones **7**. The substrate scope and limitations are investigated for facile and efficient transformation via formation of one carbon-carbon bond and one carbon-sulfur bond. Related plausible mechanisms have been proposed. Photolytic *E/Z*-isomerization and a conjugated addition have been discussed. Up to a dozen structures of the products were confirmed by X-ray crystallography. Further investigations regarding the copper-mediated synthetic works will be conducted and published in due course.

Experimental Section

General. All catalysts (metal salts), reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. The heating mantle is used to provide a stable heat source. Products in organic solvents were dried with anhydrous magnesium sulfate ($MgSO_4$) before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High-resolution mass spectra (HRMS) were measured with a double focusing mass spectrometer by ESI using a hybrid ion-trap. X-ray crystal structures were determined with a diffractometer (CAD4, Kappa CCD).

The starting reagents were obtained from commercial sources and used without further purification, including (1) *o*-bromoacetophenones **3a-3f** (for **3a**, 1-(2-bromophenyl)ethanone; **3b**, 1-(2-bromo-4-fluorophenyl)ethanone; **3c**, 1-(2-bromo-4,5-dimethoxyphenyl)ethanone; **3d**, 1-(3-bromothiophen-2-yl)ethanone; **3e**, 1-(2-bromophenyl)propan-1-one; **3f**, 1-(2-bromophenyl)-2-phenylethanone), (2) arylboronic acids **4a-4f** (for **4a**, 3,4-dimethoxyphenylboronic acid; **4b**, 3,4,5-trimethoxyphenylboronic acid; **4c**, 3-methoxyphenylboronic acid; **4d**, phenylboronic acid; **4e**, 4-biphenylboronic acid; **4f**, 4-formylphenylboronic acid), and (3) sodium sulfinates RSO_2Na **6a-6d** (for **6a**, R = Tol; **6b**, R = Me; **6c**, R = 4-FC_6H_4; **6d**, R = 4-$MeOC_6H_4$).

*General synthetic procedure of compounds **2a-2n** is as follows:* Commercial available arylboronic acids **4a-4f** (5.0 mmol), $Pd(OAc)_2$ (180 mg, 20 mol %), PPh_3 (263 mg, 1.0 mmol) and Na_2CO_3 (420 mg, 4.0 mmol) were added stepwise to a solution of commercial available *o*-bromoacetophenones **3a-3f** (4.0 mmol) in EtOH (15 mL) at 25 °C. The reaction mixture was stirred at reflux for 8 h (the reaction was traced by TLC). The reaction mixture was cooled to 25 °C, concentrated, and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-2/1) afforded compounds **2a-2n**.

*1-(3',4'-Dimethoxybiphenyl-2-yl)ethanone (**2a**).* **2a** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 78% (800 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{16}NaO_3$ 279.0997, found 279.0992; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 2H), 7.37-7.32 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 6.84 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 1.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.2, 148.9, 148.8, 140.9, 140.0, 133.1, 130.4, 129.8, 127.5, 127.0, 121.2, 111.8, 111.2, 55.78, 55.76, 30.2.

*1-(3',4',5'-Trimethoxybiphenyl-2-yl)ethanone (**2b**).* **2b** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4b** (1060 mg, 5.0 mmol); Yield = 76% (870 mg); Colorless solid; mp = 82-83 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{18}NaO_4$ 309.1103, found 309.1100; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 7.41-7.37 (m, 2H), 6.54 (s, 2H), 3.88 (s, 3H), 3.84 (s, 6H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.2, 153.3 (2x), 141.0, 140.2, 137.8, 136.2, 130.5, 129.7, 127.6, 127.5, 106.0 (2x), 60.9, 56.1 (2x), 30.4.

*1-(3'-Methoxybiphenyl-2-yl)ethanone (**2c**).* **2c** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4c** (760 mg, 5.0 mmol); Yield = 80% (724 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{14}NaO_4$ 249.0892, found 249.0888; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 1H), 7.49 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.43-7.38 (m, 2H), 7.33 (dt, *J* = 0.4, 7.6 Hz, 1H), 6.95-6.89 (m, 3H), 3.83 (s, 3H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 204.9, 159.7, 142.1, 140.9, 140.3, 130.6, 130.0, 129.7, 127.7, 127.5, 121.4, 114.3, 113.5, 55.2, 30.4.

*1-(5-Fluoro-3',4'-dimethoxybiphenyl-2-yl)ethanone (**2d**).* **2d** was synthesized according to general synthetic procedure from

3b (864 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 74% (811 mg); Colorless solid; mp = 84-86 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}FNaO_3$ 297.0903, found 297.0900; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 1H), 7.09-7.04 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 1.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.8, 163.6 (d, *J* = 250.2 Hz), 149.4, 149.1, 143.1 (d, *J* = 8.4 Hz), 137.1 (d, *J* = 3.1 Hz), 132.2, 130.4 (d, *J* = 9.1 Hz), 121.2, 116.7 (d, *J* = 22.0 Hz), 114.1 (d, *J* = 21.3 Hz), 111.7, 111.3, 56.0, 55.9, 30.3.

*1-(5-Fluoro-3',4',5'-trimethoxybiphenyl-2-yl)ethanone (**2e**).* **2e** was synthesized according to general synthetic procedure from **3b** (864 mg, 4.0 mmol) and **4b** (1060 mg, 5.0 mmol); Yield = 78% (949 mg); Colorless solid; mp = 78-79 °C (recrystallized from hexanes and EtOAc); HHRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{17}FNaO_4$ 327.1009, found 327.1005; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 1H), 7.10-7.05 (m, 2H), 6.51 (s, 2H), 3.88 (s, 3H), 3.85 (s, 6H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.7, 163.5 (d, *J* = 250.9 Hz), 153.4 (2x), 143.1 (d, *J* = 8.3 Hz), 138.2, 137.1 (d, *J* = 2.2 Hz), 135.1 (d, *J* = 1.6 Hz), 130.3 (d, *J* = 9.1 Hz), 116.6 (d, *J* = 22.9 Hz), 114.4 (d, *J* = 22.0 Hz), 105.9 (2x), 61.0, 56.2 (2x), 30.3.

*1-(4,5,3',4'-Tetramethoxybiphenyl-2-yl)ethanone (**2f**).* **2f** was synthesized according to general synthetic procedure from **3c** (1032 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 80% (1.01 g); Colorless solid; mp = 150-151 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{20}NaO_5$ 339.1208, found 339.1204; ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.81 (s, 1H), 3.93 (s, 6H), 3.92 (s, 3H), 3.88 (s, 3H), 1.94 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.5, 150.8, 148.92, 148.88, 148.0, 135.1, 133.6, 132.7, 121.3, 112.7, 112.2, 111.20, 111.17, 56.06, 56.04, 55.95, 55.9, 30.3.

*1-(4,5,3',4',5'-Pentamethoxybiphenyl-2-yl)ethanone (**2g**).* **2g** was synthesized according to general synthetic procedure from **3c** (1032 mg, 4.0 mmol) and **4b** (1060 mg, 5.0 mmol); Yield = 81% (1.12 g); Colorless solid; mp = 105-106 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{22}NaO_6$ 369.1314, found 369.1308; ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.82 (s, 1H), 6.51 (s, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H), 3.85 (s, 6H), 1.98 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.5, 153.6, 153.2 (2x), 150.8, 148.1, 136.6, 135.2, 132.6, 112.5, 111.1, 106.2 (2x), 61.0, 56.2, 56.1, 56.0, 55.9, 30.2. Single-crystal X-Ray diagram: crystal of compound **2g** was grown by slow diffusion of EtOAc into a solution of compound **2g** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 10.0533(5) Å, *b* = 10.1641(6) Å, *c* = 10.8552(6) Å, *V* = 890.53(9) Å^3, *Z* = 2, d_{calcd} = 1.292 g/cm^3, *F*(000) = 368, 2*θ* range 2.112~26.398°, R indices (all data) R1 = 0.0516, wR2 = 0.1126.

*1-[3-(3,4-Dimethoxyphenyl)thiophen-2-yl]ethanone (**2h**).* **2h** was synthesized according to general synthetic procedure from **3d** (816 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 76% (797 mg); Colorless solid; mp = 110-111 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{14}NaO_3S$ 285.0561, found 285.0558; ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 5.2 Hz, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 6.85 (br s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.8, 148.8, 148.3, 146.3, 139.2, 131.7, 130.6, 128.4, 121.4, 112.1, 110.7, 55.6, 55.5, 28.8.

*1-[3-(3,4,5-Trimethoxyphenyl)thiophen-2-yl]ethanone (**2i**).* **2i** was synthesized according to general synthetic procedure from **3d** (816 mg, 4.0 mmol) and **4b** (1060 mg, 5.0 mmol); Yield = 75% (876 mg); Colorless solid; mp = 131-132 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{16}NaO_4S$ 315.0667, found 315.0664; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 5.2 Hz, 1H), 6.99 (d, *J* = 5.2 Hz, 1H), 6.54 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.8, 152.8 (2x), 146.3, 139.5, 137.8, 131.6, 131.5, 130.8, 106.2 (2x), 60.6, 55.9 (2x), 28.8.

*1-Biphenyl-2-ylethanone (**2j**).* **2j** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4d** (610 mg, 5.0 mmol); Yield = 81% (635 mg); Colorless oil; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{12}NaO$ 219.0786, found 219.0780; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.50 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.45-7.33 (m, 7H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 204.7, 140.8, 140.6, 140.4, 130.6, 130.1, 128.7 (2x), 128.6 (2x), 127.77, 127.76, 127.3, 30.3.

*1-[1,1';4',1"]Terphenyl-2-ylethanone (**2k**).* **2k** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4e** (990 mg, 5.0 mmol); Yield = 80% (870 mg); Colorless solid; mp = 93-94 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{16}NaO$ 295.1099, found 295.1096; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70-7.65 (m, 4H), 7.60-7.36 (m, 9H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 204.9, 140.8, 140.7, 140.3, 140.1, 139.6, 130.7, 130.2, 129.3 (2x), 128.8 (2x), 127.9, 127.53, 127.47 (2x), 127.3 (2x), 127.0, 30.5.

*1-(3',4'-Dimethoxybiphenyl-2-yl)propan-1-one (**2l**).* **2l** was synthesized according to general synthetic procedure from **3e** (848 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 75% (810 mg); Colorless oil; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{18}NaO_3$ 293.1154, found 293.1150; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.35 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 2.0, 8.4 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 2.26 (q, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.3, 148.9, 148.8, 141.1, 139.5, 133.2, 130.2, 129.8, 127.4, 127.1, 121.1, 111.8, 111.2, 55.9 (2x), 36.1, 8.6.

*1-(3',4'-Dimethoxybiphenyl-2-yl)-2-phenylethanone (**2m**).* **2m** was synthesized according to general synthetic procedure from **3f** (1096 mg, 4.0 mmol) and **4a** (910 mg, 5.0 mmol); Yield = 70% (930 mg); Colorless oil; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}NaO_3$ 355.1310, found 355.1318; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.34 (m, 4H), 7.23-7.15 (m, 3H), 66.96-6.85 (m, 5H), 3.94 (s, 3H), 3.81 (s, 3H), 3.57 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.5, 149.1, 148.9, 140.6, 139.6, 134.1, 133.0, 130.4, 129.8, 129.4 (2x), 128.2 (2x), 127.9, 127.1, 126.6, 121.2, 112.0, 111.4, 55.9, 55.8, 49.4.

*2'-Acetylbiphenyl-4-carbaldehyde (**2n**).* **2n** was synthesized according to general synthetic procedure from **3a** (792 mg, 4.0 mmol) and **4f** (750 mg, 5.0 mmol); Yield = 58% (520 mg);

Colorless oil; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{12}NaO_2$ 247.0735, found 247.0728; ^1H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.56 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.51-7.48 (m, 1H), 7.39 (dd, *J* = 1.2, 7.6 Hz, 1H), 2.15 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.3, 191.7, 147.2, 140.2, 139.4, 135.5, 131.0, 130.3, 129.9 (2x), 129.5 (2x), 128.3 (2x), 30.3.

*General synthetic procedure of compounds **7a**, **7j-7k** and **8a-8x** is as follows:* $CuBr_2$ (450 mg, 2.0 mmol) was added to a solution of *o*-arylacetophenones **2a-n** (1.0 mmol) in EtOAc (15 mL) at 25 °C. The reaction mixture was stirred at 60 °C for 15 min. Then, RSO_2Na **6a-d** (1.1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 60 °C for 15 h (for **7a**, 25 °C, 15 h). The reaction mixture was cooled to 25 °C, neutralized with saturated $NaHCO_{3(aq)}$ (30 mL), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-2/1) afforded compounds **7a**, **7j**-**7k** and **8a**-**8x**.

*1-(3',4'-Dimethoxybiphenyl-2-yl)-2-(toluene-4-sulfonyl)ethanone (**7a**).* **7a** was synthesized according to general synthetic procedure from **2a** (256 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); For Table 1, entry 19 (25 °C, 10 h); Yield = 48% (197 mg); Colorless solid; mp = 165-167 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{22}NaO_5S$ 433.1086, found 433.1079; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.47 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.40 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.35 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.75-6.73 (m, 2H), 3.942 (s, 2H), 3.936 (s, 3H), 3.86 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.7, 149.5, 145.0, 140.5, 139.0, 136.0, 132.2, 131.8, 129.9, 129.6 (2x), 129.5, 129.2, 128.4 (2x), 127.4, 121.6, 111.8, 111.5, 66.4, 56.0 (2x), 21.7. Single-crystal X-Ray diagram: crystal of compound **7a** was grown by slow diffusion of EtOAc into a solution of compound **7a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 7.9278(10) Å, *b* = 8.4094(10) Å, *c* = 15.9103(19) Å, *V* = 1001.5(2) Å^3, *Z* = 2, d_{calcd} = 1.361 g/cm^3, *F*(000) = 432, 2*θ* range 1.312~26.461°, R indices (all data) R1 = 0.0397, wR2 = 0.0951.

*1-Biphenyl-2-yl-2-(toluene-4-sulfonyl)ethanone (**7j**).* **7j** was synthesized according to general synthetic procedure from **2j** (196 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 88% (308 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{18}NaO_3S$ 373.0874, found 373.0870; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 4H), 7.43-7.39 (m, 4H), 7.34 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.27-7.25 (m, 2H), 7.21-7.19 (m, 2H), 3.91 (s, 2H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.3, 145.0, 140.6, 139.6, 138.9, 135.9, 131.8, 130.0, 129.6 (2x), 129.3, 129.1 (2x), 128.9 (2x), 128.6, 128.4 (2x), 127.7, 66.4, 21.6.

*1-[1,1';4',1"]Terphenyl-2-yl-2-(toluene-4-sulfonyl)ethanone (**7k**).* **7k** was synthesized according to general synthetic procedure from **2k** (272 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 90% (383 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{22}NaO_3S$ 449.1187, found 449.1182; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 4H), 7.58-7.38 (m, 9H), 7.30-7.23 (m, 4H), 4.01 (s, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.4, 145.0, 141.4, 140.2, 139.9, 138.9, 138.4, 135.9, 131.9, 130.1, 129.6 (2x), 129.40 (2x), 129.36, 128.9 (2x), 128.4 (2x), 127.82, 127.78 (2x), 127.7, 127.1 (2x), 66.5, 21.6.

*2,3-Dimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8a**).* **8a** was synthesized according to general synthetic procedure from **2a** (256 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 92% (361 mg); Red solid; mp = 189-190 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{20}NaO_4S$ 415.0980, found 415.0974; ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.40 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.35-7.31 (m, 3H), 7.21 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.00 (s, 1H), 6.974 (s, 1H), 6.967 (s, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.5, 149.1, 146.0, 144.5, 142.8, 139.0, 134.9, 133.6, 131.4, 129.9 (2x), 129.5, 127.2 (2x), 127.1 (2x), 122.2, 118.7, 104.8, 102.8, 56.2, 56.1, 21.6.

*9-Methanesulfonylmethylene-2,3-dimethoxy-9H-fluorene (**8b**).* **8b** was synthesized according to general synthetic procedure from **2a** (256 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 84% (265 mg); Red solid; mp = 82-83 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{16}NaO_4S$ 339.0667, found 339.0662; ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.37 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.23 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.04 (s, 1H), 7.03 (s, 1H), 6.95 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 3.23 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.8, 149.4, 147.6, 143.0, 135.0, 133.4, 131.7, 129.5, 129.1, 127.4, 121.4, 119.1, 104.8, 102.9, 56.3, 56.2, 43.4. Single-crystal X-Ray diagram: crystal of compound **8b** was grown by slow diffusion of EtOAc into a solution of compound **8b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 8.5546(2) Å, *b* = 9.0687(2) Å, *c* = 9.9760(2) Å, *V* = 740.46(3) Å^3, *Z* = 2, d_{calcd} = 1.419 g/cm^3, *F*(000) = 332, 2*θ* range 2.254~26.410°, R indices (all data) R1 = 0.0348, wR2 = 0.0860.

*9-(4-Fluorobenzenesulfonylmethylene)-2,3-dimethoxy-9H-fluorene (**8c**).* **8c** was synthesized according to general synthetic procedure from **2a** (256 mg, 1.0 mmol) and **6c** (200 mg, 1.1 mmol); Yield = 88% (348 mg); Red solid; mp = 171-172 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{17}FNaO_4S$ 419.0729, found 419.0725; ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 7.6 Hz, 1H), 8.09-8.05 (m, 2H), 7.39 (dd, *J* = 0.8, 7.6 Hz, 1H), 7.34 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.23-7.17 (m, 3H), 6.98 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 3.95 (s, 3H), 3.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.6 (d, *J* = 254.0 Hz), 152.6, 149.2, 146.6, 142.8, 137.9 (d, *J* = 3.8 Hz), 134.9, 133.4, 131.5, 129.9 (d, *J* = 9.9 Hz, 2x), 129.7, 129.3, 127.2, 121.4, 118.8, 116.5 (d, *J* = 22.8 Hz, 2x), 104.9, 102.8, 56.2, 56.1. Single-crystal X-Ray diagram: crystal of compound **8c** was grown by slow diffusion of EtOAc into a solution of compound **8c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 9.0626(2) Å, *b* = 9.7391(2) Å, *c* = 11.0422(2) Å, *V* = 897.30(3) Å^3, *Z* = 2,

d_{calcd} = 1.467 g/cm^3, F(000) = 412, 2θ range 1.995~26.441^o, R indices (all data) R1 = 0.0429, wR2 = 0.1040.

*2,3-Dimethoxy-9-(4-methoxybenzenesulfonylmethylene)-9H-fluorene (**8d**).* **8d** was synthesized according to general synthetic procedure from **2a** (256 mg, 1.0 mmol) and **6d** (213 mg, 1.1 mmol); Yield = 86% (351 mg); Red solid; mp = 168-169 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{23}H_{20}NaO_5S$ 431.0929, found 431.0922; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.33 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.21 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.00 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.970 (s, 1H), 6.965 (s, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.6, 152.4, 149.1, 145.4, 142.7, 134.8, 133.6, 133.5, 121.3, 129.9, 129.43 (2x), 129.37, 127.1, 122.6, 118.7, 114.4 (2x), 104.8, 102.7, 56.2, 56.1, 55.6.

*1,2,3-Trimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8e**).* **8e** was synthesized according to general synthetic procedure from **2b** (286 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 88% (371 mg); Red solid; mp = 148-149 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{22}NaO_5S$ 445.1086, found 445.1078; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.89 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.35-7.30 (m, 3H), 7.24 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.89 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.83 (s, 3H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 152.2, 144.9, 144.2, 141.8, 141.7, 139.2, 137.5, 134.0, 130.8, 129.7 (2x), 129.1, 127.6, 126.9 (2x), 126.0, 121.1, 119.0, 99.2, 61.0, 60.2, 56.2, 21.5. Single-crystal X-Ray diagram: crystal of compound **8e** was grown by slow diffusion of EtOAc into a solution of compound **8e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 9.4622(6) Å, *b* = 9.7507(6) Å, *c* = 13.1691(10) Å, *V* = 1022.78(12) Å^3, *Z* = 2, d_{calcd} = 1.372 g/cm^3, *F*(000) = 444, 2θ range 1.636~26.507^o, R indices (all data) R1 = 0.0724, wR2 = 0.1696.

*9-Methanesulfonylmethylene-1,2,3-trimethoxy-9H-fluorene (**8f**).* **8f** was synthesized according to general synthetic procedure from **2b** (286 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 86% (298 mg); Red gum; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{18}H_{18}NaO_5S$ 369.0773, found 369.0768; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.49 (dd, *J* = 0.4, 7.6 Hz, 1H), 7.35 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.25 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.90 (s, 1H), 4.03 (s, 3H), 3.95 (s, 3H), 3.85 (s, 3H), 3.19 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 152.4, 146.2, 141.9, 141.6, 137.4, 133.8, 131.0, 128.7, 127.8, 125.0, 120.6, 119.3, 99.2, 61.0, 60.3, 56.2, 43.2.

*9-(4-Fluorobenzenesulfonylmethylene)-1,2,3-trimethoxy-9H-fluorene (**8g**).* **8g** was synthesized according to general synthetic procedure from **2b** (286 mg, 1.0 mmol) and **6c** (200 mg, 1.1 mmol); Yield = 87% (371 mg); Red solid; mp = 127-128 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{23}H_{19}FNaO_5S$ 449.0835, found 449.0827; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.09-8.05 (m, 2H), 7.86 (s, 1H), 7.47 (dd, *J* = 0.4, 7.6 Hz, 1H), 7.35 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.26 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.23-7.19 (m, 2H), 6.90 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.4 (d, *J* = 253.9 Hz), 156.8, 152.3, 145.6, 141.9, 141.7, 138.3 (d, *J* = 3.8 Hz), 137.6, 133.9, 131.0, 129.8 (d, *J* = 9.8 Hz, 2x), 129.1, 127.7, 125.3, 120.9, 119.2, 116.4 (d, *J* = 22.7 Hz, 2x), 99.3, 61.0, 60.2, 56.2.

*1,2,3-Trimethoxy-9-(4-methoxybenzenesulfonylmethylene)-9H-fluorene (**8h**).* **8h** was synthesized according to general synthetic procedure from **2b** (286 mg, 1.0 mmol) and **6d** (213 mg, 1.1 mmol); Yield = 90% (394 mg); Red solid; mp = 133-134 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{24}H_{22}NaO_6S$ 461.1035, found 461.1028; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.88 (s, 1H), 7.48 (dd, *J* = 0.4, 7.6 Hz, 1H), 7.35 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.27 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.90 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.4 (2x), 156.6, 152.3, 144.5, 141.84, 141.75, 137.5, 134.1, 133.9, 130.8, 129.2 (2x), 127.7, 126.5, 121.2, 119.0, 114.3 (2x), 99.2, 61.1, 60.2, 56.2, 55.6. Single-crystal X-Ray diagram: crystal of compound **8h** was grown by slow diffusion of EtOAc into a solution of compound **8h** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 12.1394(8) Å, *b* = 12.8311(9) Å, *c* = 16.4085(12) Å, *V* = 2401.3(3) Å^3, *Z* = 4, d_{calcd} = 1.213 g/cm^3, *F*(000) = 920, 2θ range 1.315~26.466^o, R indices (all data) R1 = 0.1030, wR2 = 0.1813.

*3-Methoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8i**).* **8i** was synthesized according to general synthetic procedure from **2c** (226 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 80% (290 mg); Red solid; mp = 161-162 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{22}H_{18}NaO_3S$ 385.0874, found 385.0871; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.99 (s, 1H), 6.82 (dd, *J* = 2.8, 8.8 Hz, 1H), 3.91 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.8, 145.2, 145.1, 144.5, 140.4, 139.0, 138.9, 131.5, 131.0, 129.9 (2x), 127.8, 127.1 (2x), 126.0, 121.4, 121.2, 119.9, 113.0, 106.0, 55.6, 21.6.

*9-Methanesulfonylmethylene-3-methoxy-9H-fluorene (**8j**).* **8j** was synthesized according to general synthetic procedure from **2c** (226 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 76% (217 mg); Red solid; mp = 171-172 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{16}H_{14}NaO_3S$ 309.0561, found 309.0557; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.82 (dd, *J* = 2.4, 8.8 Hz, 1H), 3.92 (s, 3H), 3.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.0, 146.7, 145.4, 140.4, 138.5, 131.4, 131.1, 128.1, 125.7, 121.5, 120.2, 120.0, 113.1, 106.3, 55.6, 43.2.

*9-(4-Fluorobenzenesulfonylmethylene)-3-methoxy-9H-fluorene (**8k**).* **8k** was synthesized according to general synthetic procedure from **2c** (226 mg, 1.0 mmol) and **6c** (200 mg, 1.1 mmol); Yield = 70% (256 mg); Red gum; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{15}FNaO_3S$ 389.0624, found 389.0619; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.8 Hz, 1H), 8.08-8.05 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.48

(d, J = 7.6 Hz, 1H), 7.38 (dt, J = 0.8, 7.6 Hz, 1H), 7.25-7.19 (m, 3H), 7.09 (d, J = 2.8 Hz, 1H), 6.96 (s, 1H), 6.81 (dd, J = 2.8, 8.8 Hz, 1H), 3.91 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.7 (d, J = 254.0 Hz), 163.0, 145.8, 145.3, 140.4, 138.8 (d, J = 3.8 Hz), 138.0, 131.5, 131.3, 129.9 (d, J = 9.9 Hz, 2x), 128.0, 125.8, 121.5, 120.4, 120.0, 116.6 (d, J = 22.7 Hz, 2x), 113.0, 106.2, 55.6.

*3-Methoxy-9-(4-methoxybenzenesulfonylmethylene)-9H-fluorene (**8l**)*. **8l** was synthesized according to general synthetic procedure from **2c** (226 mg, 1.0 mmol) and **6d** (213 mg, 1.1 mmol); Yield = 71% (268 mg); Red gum; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}NaO_4S$ 401.0824, found 401.0817; ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 9.2 Hz, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.36 (dt, J = 1.2, 7.6 Hz, 1H), 7.21 (dt, J = 1.2, 7.6 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 7.01-6.97 (m, 3H), 6.82 (dd, J = 2.4, 8.8 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.6, 162.8, 145.1, 144.6, 140.3, 138.9, 133.6, 131.5, 131.0, 129.4, 129.3, 127.8, 126.0, 121.6, 121.4, 119.9, 114.5 (2x), 113.0, 106.0, 55.7, 55.6.

*6-Fluoro-2,3-dimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8m**)*. **8m** was synthesized according to general synthetic procedure from **2d** (274 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 83% (340 mg); Red solid; mp = 197-198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{19}FNaO_4S$ 433.0886, found 433.0884; ^1H NMR (400 MHz, $CDCl_3$): δ 8.68-8.64 (m, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.07 (dd, J = 1.6, 8.0 Hz, 1H), 6.95 (s, 1H), 6.95-6.92 (m, 1H), 6.92 (s, 1H), 6.85 (dt, J = 2.0, 8.8 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.1 (d, J = 250.2 Hz), 152.5, 149.6, 145.7 (d, J = 9.1 Hz), 144.7, 144.6, 138.8, 133.5, 131.3 (d, J = 9.9 Hz), 130.9, 129.9 (2x), 129.4, 127.2 (2x), 121.9 (d, J = 1.5 Hz), 113.3 (d, J = 22.0 Hz), 106.5 (d, J = 23.5 Hz), 104.7, 102.9, 56.24, 56.20, 21.6.

*6-Fluoro-9-methanesulfonylmethylene-2,3-dimethoxy-9H-fluorene (**8n**)*. **8n** was synthesized according to general synthetic procedure from **2d** (274 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 86% (287 mg); Red solid; mp = 241-242 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{15}FNaO_4S$ 357.0573, found 357.0570; ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, J = 4.8, 8.4 Hz, 1H), 7.14 (dd, J = 2.4, 8.4 Hz, 1H), 7.04 (s, 1H), 7.01 (s, 1H), 6.92 (s, 1H), 6.89 (dt, J = 2.4, 8.4 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 3.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.3 (d, J = 251.7 Hz), 152.8, 149.9, 146.3, 146.0 (d, J = 9.1 Hz), 133.6, 130.9 (d, J = 9.8 Hz), 130.5, 129.3, 121.0 (d, J = 1.5 Hz), 113.6 (d, J = 22.8 Hz), 107.0 (d, J = 23.5 Hz), 104.7, 103.1, 56.3 (2x), 43.5.

*6-Fluoro-1,2,3-trimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8o**)*. **8o** was synthesized according to general synthetic procedure from **2e** (304 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 85% (374 mg); Red solid; mp = 170-171 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{21}FNaO_5S$ 463.0991, found 463.0985; ^1H NMR (400 MHz, $CDCl_3$): δ 8.72 (dd, J = 5.2, 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.85 (s, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.15 (dd, J = 2.4, 8.4 Hz, 1H), 6.93 (dt, J = 2.8, 8.8 Hz, 1H), 6.86 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.84 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.8 (d, J = 250.2 Hz), 156.7, 152.3, 144.7 (d, J = 9.9 Hz), 144.4, 143.7, 142.3, 139.2, 136.3, 131.1 (d, J = 9.8 Hz), 130.0 (d, J = 3.0 Hz), 129.9 (2x), 127.1 (2x), 125.9 (d, J = 2.3 Hz), 122.1, 114.1 (d, J = 21.9 Hz), 106.7 (d, J = 24.2 Hz), 99.5, 61.1, 60.3, 56.3, 21.6.

*6-Fluoro-9-methanesulfonylmethylene-1,2,3-trimethoxy-9H-fluorene (**8p**)*. **8p** was synthesized according to general synthetic procedure from **2e** (304 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 86% (313 mg); Red solid; mp = 141-142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{17}FNaO_5S$ 387.0678, found 387.0676; ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, J = 5.2, 8.4 Hz, 1H), 7.80 (s, 1H), 7.19 (dd, J = 2.8, 8.0 Hz, 1H), 6.95 (dt, J = 2.8, 8.8 Hz, 1H), 6.88 (s, 1H), 4.06 (s, 3H), 3.98 (s, 3H), 3.88 (s, 3H), 3.20 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.9 (d, J = 250.9 Hz), 156.9, 152.4, 145.0, 144.8, 142.3, 136.3, 131.7 (d, J = 9.9 Hz), 129.9 (d, J = 3.0 Hz), 124.7 (d, J = 2.3 Hz), 122.7, 114.3 (d, J = 22.0 Hz), 107.0 (d, J = 23.5 Hz), 99.5, 61.1, 60.5, 56.4, 43.5.

*2,3,6,7-Tetramethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8q**)*. **8q** was synthesized according to general synthetic procedure from **2f** (316 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 86% (389 mg); Red solid; mp = 206-207 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{24}NaO_6S$ 475.1191, found 475.1184; ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.90 (s, 3H), 6.80 (s, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 151.9, 148.2, 147.7, 146.2, 144.5, 139.1, 137.4, 134.9, 130.3, 129.9 (2x), 126.8 (2x), 125.9, 120.0, 113.2, 105.1, 102.3, 102.1, 56.20, 56.17, 56.1, 56.0, 21.6.

*9-Methanesulfonylmethylene-2,3,6,7-tetramethoxy-9H-fluorene (**8r**)*. **8r** was synthesized according to general synthetic procedure from **2f** (316 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 84% (316 mg); Red solid; mp = 242-243 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{19}H_{20}NaO_6S$ 399.0878, found 399.0872; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 6.93 (s, 1H), 6.91 (s, 1H), 6.90 (s, 1H), 6.77 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 3.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.3, 152.1, 148.3, 147.9, 147.4, 137.6, 134.9, 129.9, 125.6, 119.1, 112.7, 105.0, 102.4, 102.3, 56.2 (2x), 56.11, 56.07, 43.4.

*1,2,3,6,7-Pentamethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**8s**)*. **8s** was synthesized according to general synthetic procedure from **2g** (346 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 90% (434 mg); Red solid; mp = 203-204 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{26}H_{26}NaO_7S$ 505.1297, found 505.1291; ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.77 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.77 (s, 1H), 3.98 (s, 3H), 3.954 (s, 3H), 3.947 (s, 3H), 3.93 (s, 3H), 3.82 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 156.4 (2x), 152.3, 151.6, 148.4, 145.4, 144.2, 141.0, 139.5, 137.7, 136.3, 129.8 (2x), 126.8 (2x), 124.1, 121.4, 112.8, 102.1, 98.7, 61.1, 60.3, 56.3, 56.2, 56.1, 21.6. Single-crystal X-Ray diagram: crystal of compound **8s** was grown by slow diffusion of EtOAc into a solution of compound **8s** in CH_2Cl_2 to yield colorless prisms. The compound

crystallizes in the monoclinic crystal system, space group P 21/n, a = 8.1007(8) Å, b = 25.249(3) Å, c = 11.9527(11) Å, V = 2367.4(4) Å^3, Z = 4, d_{calcd} = 1.354 g/cm^3, F(000) = 1016, 2θ range 1.613~26.403°, R indices (all data) R1 = 0.0418, wR2 = 0.0867.

*9-Methanesulfonylmethylene-1,2,3,6,7-pentamethoxy-9H-fluorene (**8t**).* **8t** was synthesized according to general synthetic procedure from **2g** (346 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 93% (378 mg); Red solid; mp = 176-177 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_7S$ 429.0984, found 429.0976; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.68 (s, 1H), 6.96 (s, 1H), 6.78 (s, 1H), 4.02 (s, 3H), 3.98 (s, 3H), 3.96 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 3.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.6, 152.3, 151.8, 148.5, 146.3, 140.9, 137.6, 136.4, 126.5, 123.1, 120.9, 112.3, 102.3, 98.7, 61.0, 60.4, 56.3, 56.12, 56.06, 43.3. Single-crystal X-Ray diagram: crystal of compound **8t** was grown by slow diffusion of EtOAc into a solution of compound **8t** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 19.3636(3) Å, b = 13.1724(2) Å, c = 14.6482(3) Å, V = 3709.69(11) Å^3, Z = 8, d_{calcd} = 1.455 g/cm^3, F(000) = 1712, 2θ range 1.874~26.394°, R indices (all data) R1 = 0.0395, wR2 = 0.0921.

*5,6-Dimethoxy-8-(toluene-4-sulfonylmethylene)-8H-1-thiacyclopenta[a]indene (**8u**).* **8u** was synthesized according to general synthetic procedure from **2h** (262 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 79% (314 mg); Red solid; mp = 184-185 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{21}H_{18}NaO_4S_2$ 421.0544, found 421.0537; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 4.8 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 5.2 Hz, 1H), 6.95 (s, 1H), 6.86 (s, 1H), 6.65 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.9, 151.6, 147.5, 144.9, 141.6, 138.6, 137.5, 133.1, 132.9, 131.6, 130.0 (2x), 127.2 (2x), 118.3, 117.4, 106.6, 103.5, 56.3, 56.2, 21.7.

*8-Methanesulfonylmethylene-5,6-dimethoxy-8H-1-thiacyclopenta[a]indene (**8v**).* **8v** was synthesized according to general synthetic procedure from **2h** (262 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 80% (258 mg); Red solid; mp = 205-206 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{15}H_{14}NaO_4S_2$ 345.0233, found 345.0227; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 4.8 Hz, 1H), 7.04 (d, J = 4.8 Hz, 1H), 7.02 (s, 1H), 6.86 (s, 1H), 6.69 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.15 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 151.8, 147.6, 143.5, 137.7 (2x), 132.7, 131.7, 118.4, 116.2, 106.6, 103.9, 56.4, 56.2, 43.2. Single-crystal X-Ray diagram: crystal of compound **8v** was grown by slow diffusion of EtOAc into a solution of compound **8v** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, a = 8.6178(7) Å, b = 9.0183(7) Å, c = 9.6399(8) Å, V = 713.24(10) Å^3, Z = 2, d_{calcd} = 1.501 g/cm^3, F(000) = 336, 2θ range 2.213~26.392°, R indices (all data) R1 = 0.0360, wR2 = 0.0824.

*5,6,7-Trimethoxy-8-(toluene-4-sulfonylmethylene)-8H-1-thiacyclopenta[a]indene (**8w**).* **8w** was synthesized according to general synthetic procedure from **2i** (292 mg, 1.0 mmol) and **6a** (196 mg, 1.1 mmol); Yield = 84% (360 mg); Red solid; mp = 135-136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{22}H_{20}NaO_5S_2$ 451.0650, found 451.0643; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 4.8 Hz, 1H), 7.48 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 5.2 Hz, 1H), 6.70 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.80 (s, 3H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.1, 152.4, 151.6, 144.5, 140.7, 140.5, 138.9, 136.8, 134.3, 134.1, 129.8 (2x), 127.0 (2x), 123.7, 121.2, 118.1, 100.2, 61.1, 60.4, 56.3, 21.6.

*8-Methanesulfonylmethylene-5,6,7-trimethoxy-8H-1-thiacyclopenta[a]indene (**8x**).* **8x** was synthesized according to general synthetic procedure from **2i** (292 mg, 1.0 mmol) and **6b** (112 mg, 1.1 mmol); Yield = 86% (303 mg); Red solid; mp = 112-114 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{16}NaO_5S_2$ 375.0337, found 375.0333; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 4.8 Hz, 1H), 7.46 (s, 1H), 7.08 (d, J = 4.8 Hz, 1H), 6.72 (s, 1H), 4.04 (s, 3H), 3.94 (s, 3H), 3.84 (s, 3H), 3.14 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.3, 152.6, 151.8, 142.4, 140.5, 137.0, 134.1, 134.0, 123.1, 120.3, 118.3, 100.3, 61.1, 60.5, 56.3, 43.0.

*General synthetic procedure of compounds **8y-8ac** is as follows:* Freshly prepared Na(Hg) (300 mg) was added to a solution of **8a**, **8c**, **8m**, **8o**, **8q** (1.0 mmol) in MeOH (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 1 h. The reaction mixture was filtrated and concentrated. The crude products was diluted with saturated $NaHCO_{3(aq)}$ (10 mL), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-2/1) afforded compounds **8y**-**8ac**.

*2,3-Dimethoxy-9-methyl-9H-fluorene (**8y**).* **8y** was synthesized according to general synthetic procedure from **8a** (392 mg, 1.0 mmol); Yield = 87% (209 mg); White solid; mp = 130-132 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{16}H_{16}NaO_2$ 263.1048, found 263.1045; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.27 (s, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.05 (s, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.86 (q, J = 7.6 Hz, 1H), 1.51 (d, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.0, 149.9, 148.7, 141.5, 140.8, 132.8, 126.8, 125.6, 123.7, 118.7, 107.2, 102.9, 56.09, 56.08, 42.2, 18.3. Single-crystal X-Ray diagram: crystal of compound **8y** was grown by slow diffusion of EtOAc into a solution of compound **8y** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, a = 10.592(4) Å, b = 10.873(5) Å, c = 11.134(4) Å, V = 1249.1(9) Å^3, Z = 2, d_{calcd} = 1.278 g/cm^3, F(000) = 512, 2θ range 1.866~26.602°, R indices (all data) R1 = 0.1193, wR2 = 0.2436.

*1,2,3-Trimethoxy-9-methyl-9H-fluorene (**8z**).* **8z** was synthesized according to general synthetic procedure from **8c** (396 mg, 1.0 mmol); Yield = 80% (216 mg); Colorless gum; HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{17}H_{18}NaO_3$ 293.1154, found 293.1150; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 7.2 Hz, 1H), 7.48 (dd, J = 0.8, 7.6 Hz, 1H), 7.35 (dt, J = 1.2, 8.0 Hz, 1H), 7.29 (dt, J = 1.2, 7.6 Hz, 1H), 7.08 (s, 1H), 4.05 (q, J = 7.2 Hz, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 3.94 (s, 3H), 1.57 (d, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ 153.8, 150.8, 149.5, 141.5, 140.3, 136.3, 132.9, 126.7, 126.4, 123.8, 119.2, 99.0, 61.0, 60.6, 56.2, 41.3, 17.5.

*6-Fluoro-2,3-dimethoxy-9-methyl-9H-fluorene (**8aa**)*. **8aa** was synthesized according to general synthetic procedure from **8m** (410 mg, 1.0 mmol); Yield = 87% (225 mg); White solid; mp = 129-131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{15}FNaO_2$ 281.0954, found 281.0951; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 4.8, 8.0 Hz, 1H), 7.29 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.19 (s, 1H), 7.02 (s, 1H), 6.92 (dt, *J* = 2.4, 8.0 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.80 (q, *J* = 7.2 Hz, 1H), 1.47 (d, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 241.0 Hz), 149.4, 148.8, 144.3 (d, *J* = 2.3 Hz), 142.7 (d, *J* = 9.1 Hz), 142.6, 132.0 (d, *J* = 3.0 Hz), 124.5 (d, *J* = 9.1 Hz), 122.1 (d, *J* = 22.8 Hz), 107.1, 105.8 (d, *J* = 22.7 Hz), 103.0, 56.12, 56.09, 41.7, 18.3. Single-crystal X-Ray diagram: crystal of compound **8aa** was grown by slow diffusion of EtOAc into a solution of compound **8aa** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 11.0688(9) Å, *b* = 14.9195(13) Å, *c* = 7.8135(7) Å, *V* = 1263.71(19) Å^3, *Z* = 4, d_{calcd} = 1.358 g/cm^3, *F*(000) = 544, 2*θ* range 1.879~26.477°, R indices (all data) R1 = 0.0362, wR2 = 0.0852.

*6-Fluoro-1,2,3-trimethoxy-9-methyl-9H-fluorene (**8ab**)*. **8ab** was synthesized according to general synthetic procedure from **8o** (440 mg, 1.0 mmol); Yield = 90% (259 mg); White solid; mp = 86-88 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{17}FNaO_3$ 311.1059, found 311.1052; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 4.8, 8.0 Hz, 1H), 7.30 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.00 (s, 1H), 6.94 (dt, *J* = 2.4, 8.4 Hz, 1H), 4.02 (s, 3H), 3.95 (q, *J* = 7.2 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 1.52 (d, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4 (d, *J* = 241.0 Hz), 153.8, 150.6, 144.7 (d, *J* = 2.3 Hz), 142.1 (d, *J* = 9.1 Hz), 141.8, 135.2 (d, *J* = 3.1 Hz), 133.8, 124.5 (d, *J* = 9.1 Hz), 122.9 (d, *J* = 22.7 Hz), 106.1 (d, *J* = 22.8 Hz), 99.0, 60.8, 60.4, 56.0, 40.6, 17.4.

*2,3,6,7-Tetramethoxy-9-methyl-9H-fluorene (**8ac**)*. **8ac** was synthesized according to general synthetic procedure from **8q** (452 mg, 1.0 mmol); Yield = 90% (270 mg); White solid; mp = 173-175 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{20}NaO_4$ 323.1259, found 323.1253; ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 2H), 7.01 (s, 2H), 3.99 (s, 6H), 3.94 (s, 6H), 3.78 (q, *J* = 7.6 Hz, 1H), 1.47 (d, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.7 (2x), 148.0 (2x), 141.5 (2x), 133.2 (2x), 107.5 (2x), 102.3 (2x), 56.19 (2x), 56.16 (2x), 42.1, 18.5. Single-crystal X-Ray diagram: crystal of compound **8ac** was grown by slow diffusion of EtOAc into a solution of compound **8ac** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P m n 21, *a* = 14.7692(17) Å, *b* = 10.2619(12) Å, *c* = 5.9666(6) Å, *V* = 904.30(17) Å^3, *Z* = 2, d_{calcd} = 1.415 g/cm^3, *F*(000) = 404, 2*θ* range 1.985~26.640°, R indices (all data) R1 = 0.0304, wR2 = 0.0795.

*General synthetic procedure of compounds **9a-9d** and **9m-9n** is as follows:* **8a-8d** and **8m-8n** (0.3 mmol) and iodine (100 mg, 0.4 mmol) was dissolved in EtOAc (30 mL) at 25 °C. Then, 1,2-epoxybutane (440 mg, 6.0 mmol) was added to the reaction mixture and the reaction mixture was irradiated under a nitrogen atmosphere with a lamp (λ > 2540 Å), using a Pyrex glass filter at 25 °C for 40 h. The reaction mixture was washed with saturated $Na_2S_2O_{3(aq)}$ (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-4/1) afforded compounds **9a-9d** and **9m-9n**.

*2,3-Dimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**9a**)*. **9a** was synthesized according to general synthetic procedure from **8a** (118 mg, 0.3 mmol); Yield = 75% (294 mg); Red solid; mp = 176-177 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{20}NaO_4S$ 415.0980, found 415.0976; ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.34-7.29 (m, 3H), 7.12 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.04 (s, 1H), 6.98 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.3, 148.7, 145.7, 144.6, 140.9, 138.9, 138.2, 137.5, 131.1, 129.9 (2x), 126.9 (2x), 126.6, 125.9, 121.4, 121.2, 118.9, 113.0, 102.6, 56.2, 56.1, 21.6. Single-crystal X-Ray diagram: crystal of compound **9a** was grown by slow diffusion of EtOAc into a solution of compound **9a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 2/c, *a* = 8.3017(5) Å, *b* = 10.3840(6) Å, *c* = 21.3810(12) Å, *V* = 1838.22(19) Å^3, *Z* = 4, d_{calcd} = 1.418 g/cm^3, *F*(000) = 824, 2*θ* range 1.910~26.462°, R indices (all data) R1 = 0.0385, wR2 = 0.0891.

*9-Methanesulfonylmethylene-2,3-dimethoxy-9H-fluorene (**9b**)*. **9b** was synthesized according to general synthetic procedure from **8b** (95 mg, 0.3 mmol); Yield = 68% (215 mg); Red solid; mp = 178-179 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{16}NaO_4S$ 339.0667, found 339.0663; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.15 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.04 (s, 1H), 6.94 (s, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.4, 148.8, 147.0, 140.9, 137.8, 137.6, 131.3, 126.8, 125.5, 121.2, 120.4, 118.9, 112.4, 102.8, 56.11, 56.06, 43.3.

*9-(4-Fluorobenzenesulfonylmethylene)-2,3-dimethoxy-9H-fluorene (**9c**)*. **9c** was synthesized according to general synthetic procedure from **8c** (119 mg, 0.3 mmol); Yield = 60% (238 mg); Red solid; mp = 218-219 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{17}FNaO_4S$ 419.0729, found 419.0722; ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.07-8.03 (m, 2H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.23-7.18 (m, 2H), 7.11 (dt, *J* = 0.8, 8.4 Hz, 1H), 7.03 (s, 1H), 6.92 (s, 1H), 3.99 (s, 3H), 3.96 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.6 (d, *J* = 254.7 Hz), 152.5, 148.7, 146.2, 140.9, 138.1, 137.9 (d, *J* = 3.0 Hz), 137.6, 131.2, 129.7 (d, *J* = 9.1 Hz, 2x), 126.7, 125.6, 121.2, 120.6, 118.9, 116.6 (d, *J* = 22.0 Hz, 2x), 112.9, 102.7, 56.1, 56.0. Single-crystal X-Ray diagram: crystal of compound **9c** was grown by slow diffusion of EtOAc into a solution of compound **9c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 2/c, *a* = 8.3081(3) Å, *b* = 10.2495(3) Å, *c* = 20.9221(7) Å, *V* = 1775.85(10) Å^3, *Z* = 4, d_{calcd} = 1.483 g/cm^3, *F*(000) = 824, 2*θ* range 1.953~26.448°, R indices (all data) R1 = 0.0397, wR2 = 0.0951.

*2,3-Dimethoxy-9-(4-methoxybenzenesulfonylmethylene)-9H-fluorene (**9d**)*. **9d** was synthesized according to general synthetic procedure from **8d** (122 mg, 0.3 mmol); Yield = 62% (253 mg); Red solid; mp = 183-184 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{20}NaO_5S$ 431.0929, found 431.0921; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.10 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.03 (s, 1H), 6.98 (d, *J* = 9.2 Hz, 2H), 6.96 (s, 1H), 3.980 (s, 3H), 3.976 (s, 3H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.6, 152.2, 148.7, 145.1, 140.8, 138.2, 137.4, 133.4, 131.0, 129.1 (2x), 126.5, 125.8, 121.8, 121.1, 118.8, 114.4 (2x), 112.9, 102.5, 56.1, 56.0, 55.6.

*6-Fluoro-2,3-dimethoxy-9-(toluene-4-sulfonylmethylene)-9H-fluorene (**9m**)*. **9m** was synthesized according to general synthetic procedure from **8m** (123 mg, 0.3 mmol); Yield = 68% (279 mg); Red solid; mp = 186-187 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{19}FNaO_4S$ 433.0886, found 433.0880; ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.92 (dd, *J* = 1.6, 8.4 Hz, 2H), 7.38-7.33 (m, 3H), 7.11 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.00 (s, 1H), 6.90 (s, 1H), 6.80 (dt, *J* = 2.4, 8.4 Hz, 1H), 3.993 (s, 3H), 3.990 (s, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.3 (d, *J* = 248.6 Hz), 152.3, 149.3, 145.7, 144.5, 143.4 (d, *J* = 9.1 Hz), 138.9, 136.0, 133.9 130.0 (2x), 127.0 (2x), 126.7, 122.7 (d, *J* = 9.9 Hz), 121.6 (d, *J* = 2.3 Hz), 113.1 (d, *J* = 23.5 Hz), 113.0, 106.7 (d, *J* = 23.5 Hz), 102.8, 56.2, 56.1, 21.6.

*6-Fluoro-9-methanesulfonylmethylene-2,3-dimethoxy-9H-fluorene (**9n**)*. **9n** was synthesized according to general synthetic procedure from **8n** (100 mg, 0.3 mmol); Yield = 77% (257 mg); Red solid; mp = 188-189 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{15}FNaO_4S$ 357.0573, found 357.0568; ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.44 (dd, *J* = 5.2, 8.8 Hz, 1H), 7.14 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.04 (s, 1H), 6.90 (s, 1H), 6.86 (dt, *J* = 2.4, 8.8 Hz, 1H), 4.01 (s, 3H), 3.96 (s, 3H), 3.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5 (d, *J* = 249.4 Hz), 152.5, 149.5, 146.0, 143.4 (d, *J* = 9.1 Hz), 136.2, 133.5, 126.4, 122.8 (d, *J* = 9.8 Hz), 120.5 (d, *J* = 11.5 Hz), 113.4 (d, *J* = 23.5 Hz), 112.5, 106.9 (d, *J* = 24.2 Hz), 103.0, 56.3, 56.2, 43.4.

*2,3-Dimethoxy-9-(toluene-4-sulfonyl)-9-(toluene-4-sulfonylmethyl)-9H-fluorene (**10a**)*. $TolSO_2Na$ (710 mg, 4.0 mmol) was added to a solution of **8a** (392 mg, 1.0 mmol) in a cosolvent of H_2O (5 mL) and dioxane (10 mL) at 25 °C. The reaction mixture was stirred at reflux for 15 h. The reaction mixture was cooled to 25 °C, and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1-1/1) afforded compound **10a**. Yield = 70% (384 mg); Red solid; mp = 197-198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{28}NaO_6S_2$ 571.1225, found 571.1221; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.28 (dt, *J* = 0.8, 8.4 Hz, 1H), 7.17-7.14 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.95 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.63 (d, *J* = 14.8 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 2.32 (s, 3H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0, 148.9, 144.5, 144.4, 141.9, 136.7, 136.6, 135.2, 129.8 (2x), 129.5, 129.1 (2x), 128.12, 128.06 (2x), 127.9 (3x), 126.5, 126.3, 118.7, 109.0, 102.2, 74.5, 56.1, 55.9, 54.3, 21.5, 21.4. Single-crystal X-Ray diagram: crystal of compound **10a** was grown by slow diffusion of EtOAc into a solution of compound **10a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 20.676(2) Å, *b* = 14.0649(14) Å, *c* = 9.2725(8) Å, *V* = 2637.9(4) $Å^3$, *Z* = 4, d_{calcd} = 1.381 g/cm^3, *F*(000) = 1152, 2*θ* range 1.007~26.485°, R indices (all data) R1 = 0.1252, wR2 = 0.2791.

*6-Fluoro-9-methanesulfonylmethyl-2,3-dimethoxy-9H-fluoren-9-ol (**10b**)*. NaOH (160 mg, 4.0 mmol) was added to a solution of **8n** (334 mg, 1.0 mmol) in a cosolvent of H_2O (5 mL) and dioxane (10 mL) at 25 °C. The reaction mixture was stirred at reflux for 15 h. The reaction mixture was cooled to 25 °C, and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1-1/1) afforded compound **10b**. Yield = 63% (222 mg); Red liquid; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{17}FNaO_5S$ 375.0678, found 375.0672; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 6.0, 8.8 Hz, 1H), 7.21 (dt, *J* = 2.8, 8.4 Hz, 1H), 7.10 (s, 1H), 7.04 (dd, *J* = 2.8, 8.8 Hz, 1H), 6.76 (s, 1H), 4.23 (dd, *J* = 0.8, 14.8 Hz, 1H), 3.99 (dd, *J* = 0.4, 14.8 Hz, 1H), 3.96 (br s, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 3.05 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.1, 164.5 (d, *J* = 254.7 Hz), 149.9, 148.8, 143.4 (d, *J* = 9.1 Hz), 134.3 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 9.8 Hz), 131.4, 119.0 (d, *J* = 21.9 Hz), 115.6, 115.5 (d, *J* = 22.0 Hz), 113.2, 112.4, 63.3, 56.3, 56.2, 42.0.

*2,3-Dimethoxy-9-[1-(toluene-4-sulfonyl)ethyl]-9H-fluoren-9-ol (**10c**)*. $CuBr_2$ (450 mg, 2.0 mmol) was added to a solution of **2l** (270 mg, 1.0 mmol) in EtOAc (15 mL) at 25 °C. The reaction mixture was stirred at 60 °C for 15 min. Then, $TolSO_2Na$ **6a** (196 mg, 1.1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 60 °C for 15 h. The reaction mixture was cooled to 25 °C, neutralized with saturated $NaHCO_{3(aq)}$ (30 mL), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-2/1) afforded compound **10c**. Two isomers; Ratio = 1:1; Yield = 35% (148 mg); White solid; mp = 150-153 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{24}NaO_5S$ 447.1242, found 447.1235; ^1H NMR (400 MHz, $CDCl_3$): δ 8.02-8.00 (m, 1H), 7.63 (s, 1/2H), 7.57 (s, 1/2H), 7.38-7.20 (m, 3H), 6.89 (s, 1/2H), 6.83 (s, 1/2H), 6.77-6.70 (m, 4H), 5.53-5.44 (m, 1H), 4.06 (s, 3/2H), 4.05 (s, 3/2H), 3.92 (s, 3/2H), 3.89 (s, 3/2H), 2.20 (d, *J* = 6.8 Hz, 3/2H), 2.16 (s, 3H), 2.07 (d, *J* = 6.8 Hz, 3/2H), 1.60 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.0 (1/2x), 150.8 (1/2x), 149.3 (1/2x), 149.0 (1/2x), 143.9 (1/2x), 143.8 (1/2x), 142.6 (1/2x), 141.5 (1/2x), 140.5 (1/2x), 138.0 (1/2x), 135.9 (1/2x), 134.7 (1/2x), 132.9 (1/2x), 132.2 (1/2x), 129.8 (1x), 129.7 (1/2x), 129.6 (1/2x), 129.3 (1x), 129.2 (1x), 127.93 (1x), 127.92 (1x), 127.0 (1/2x), 126.6 (1/2x), 126.4 (1/2x), 125.9 (1/2x), 118.9 (1/2x), 118.6 (1/2x), 110.0 (1/2x), 109.0 (1/2x), 102.4 (1/2x), 102.1 (1/2x), 80.0

(1/2x), 79.9 (1/2x), 56.4 (1x), 56.0 (1x), 47.9 (1/2x), 47.8 (1/2x), 23.6 (1/2x), 23.5 (1/2x), 21.4 (1x).

*9-(Toluene-4-sulfonylmethyl)-9H-fluorene (**11a**)*. $NaBH_4$ (50 mg, 1.3 mmol) was added to a stirred solution of **7j** (350 mg, 1.0 mmol) in a cosolvent of THF and MeOH (10 mL, v/v = 1/1) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min, and the solvent was concentrated. The residue was diluted with water (10 mL), and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Without further purification, $BF_3{\cdot}OEt_2$ (185 mg, 1.3 mmol) was added to the stirred solution of the resulting β-hydroxysulfone in CH_2Cl_2 (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min, and the solvent was concentrated. The residue was diluted with saturated $NaHCO_{3(aq)}$ (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to affoard crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 20/1~10/1) afforded compound **11a**. Yield = 89% (297 mg); White solid; mp = 138-139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{18}NaO_2S$ 357.0925, found 357.0920; ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.40-7.36 (m, 4H), 7.30 (dt, *J* = 1.2, 7.6 Hz, 2H), 4.48 (t, *J* = 5.6 Hz, 1H), 3.59 (d, *J* = 5.6 Hz, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 145.0 (2x), 144.8 (2x), 140.7, 136.6, 130.1 (2x), 128.1 (2x), 127.8 (2x), 127.5 (2x), 125.1 (2x), 119.9 (2x), 60.5, 41.4, 21.6.

*Gram-Scale Synthesis of Compound **8a***. $CuBr_2$ (1.79 g, 8.0 mmol) was added to a solution of **2a** (1.0 g, 3.9 mmol) in EtOAc (40 mL) at 25 °C. The reaction mixture was stirred at 60 °C for 15 min. Then, $TolSO_2Na$ **6a** (800 mg, 4.5 mmol) was added to the reaction mixture. The reaction mixture was stirred at 60 °C for 18 h. The reaction was monitored by TLC. The reaction mixture was cooled to 25 °C, neutralized with saturated $NaHCO_{3(aq)}$ (50 mL), and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1-2/1) afforded compound **8a** (82%, 1.25 g).

DFT calculation. The M06-2X-D3 method was employed for the present DFT calculations. The elements Cu and Br were described by the SDD basis sets with effective core potentials, whereas the remaining elements were described by 6-31G* basis sets. Geometry optimizations and vibrational frequency calculations were carried out in the gas phase. To obtain more accurate energies, a larger basis set 6-311+G** was used for the elements except Cu and Br in the following single-point-energy calculations. The solvent effect (solvent = EtOAc) was included in the energy calculations by using the SMD solvation model. The thermal correction to Gibbs free energy with zero-point vibrational energies was made at standard conditions of 1 atm and 298.15 K. The setting of ultrafine grids was adopted for numerical integrations. All the calculations were achieved by using the Gaussian 09 program.[41]

ASSOCIATED CONTENT

Supporting Information

Scanned photocopies of NMR spectral data for all compounds and X-ray analysis data of **2g**, **7a**, **8b-c**, **8e**, **8h**, **8s-t**, **8v**, **8y**, **8aa**, **8ac**, **9a**, **9c**, **10a**, DFT results and optimized coordinates. This information 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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