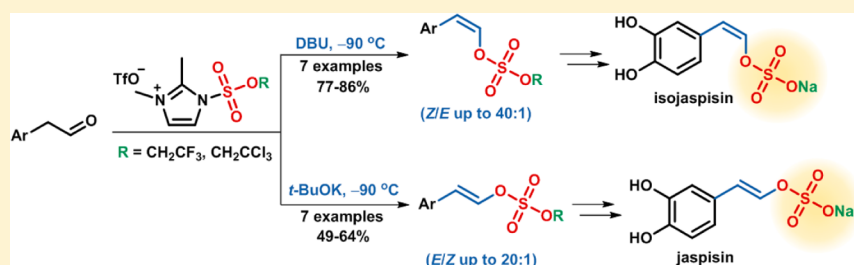


(E)- and (Z)-Stereodefined Enol Sulfate Esters Derived from α -Aryl Aldehydes: Stereocomplementary Synthesis of Styryl Sulfate Natural Products

Shuai Yu, Feng Li, and Sanghee Kim*¹

College of Pharmacy, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea

S Supporting Information



ABSTRACT: A method for the stereoselective formation of enol sulfate esters from α -aryl aldehydes is described. This method involved the stereocontrolled enolization of a carbonyl group with DBU or *t*-BuOK followed by trapping with a reactive sulfuryl imidazolium salt, providing the corresponding styryl enol sulfate esters in good to excellent yields and stereoselectivities. This method was applied to the first total synthesis of the enol sulfate natural products in a stereocomplementary manner.

Enol sulfate is an unusual functional group found in several natural products (Figure 1).¹ This functional group is also

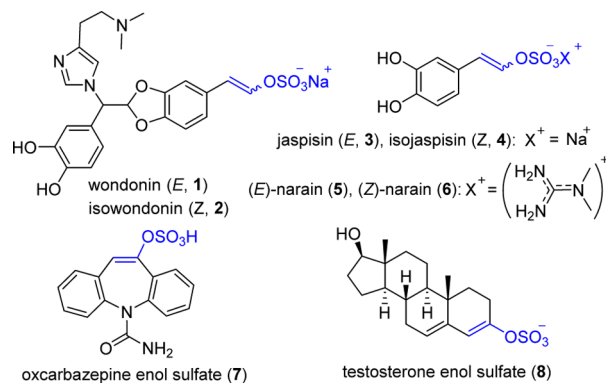


Figure 1. Structures of representative natural products and metabolites containing an enol sulfate moiety.

found in some metabolites of endogenous or exogenous substances, such as oxcarbazepine² and testosterone.³ Because sulfation is an important pathway for the conjugative metabolism of many chemicals, obtaining the structure of sulfated metabolites is useful in metabolism studies conducted at all stages of drug development.⁴ The sulfation of aliphatic and phenolic hydroxyl groups can be easily achieved by several conventional methods,⁵ including the employment of sulfur trioxide complexes. However, only a few synthetic methods for the preparation of enol sulfate have been reported. The reported methods for the formation of enol sulfate involve an

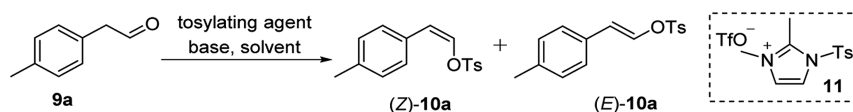
elimination reaction of a β -chloro *O*-sulfated substrate^{1e,6c} and a regioselective proton abstraction of a cyclic sulfate.^{6a,b} These elimination methods often suffer from low yields and force the introduction of enol sulfate in late stages of the synthesis because of the instabilities and high polarities of enol sulfates. Thus, the application of these methods in multistep syntheses might accompany difficulties, including the careful and intensive manipulation of other functional groups or protecting groups.

During our research on the total synthesis of natural products containing an enol sulfate group, we developed a method to synthesize (*Z*)-enol sulfate ester and briefly reported some results as a part of the total synthesis of isowondonin (2).⁷ Herein, we report the details on of the (*Z*)- and (*E*)-stereoselective formation of enol sulfate esters and disclose the scope of this method. In addition, we show the first total synthesis of jaspisin (3), isojaspisin (4), and (*Z*)-narain (6) utilizing this method.

We focused on the stereoselective formation of enol sulfates from α -aryl aldehyde substrates with the aim of the total synthesis of styryl sulfate natural products. Our strategy involved the *in situ* trapping of an enolate or enol intermediate with a suitable sulfating agent to form an enol sulfate in a protected form and removal of a protecting group. Indeed, the enolate trapping approach has been broadly employed in the enol sulfonation for the formation of enol sulfonates, such as vinyl (enol) tosylates or triflates.^{8,9} However, the stereoselective

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Table 1. Optimization of the Reaction Conditions^a

entry	tosylating agent (equiv)	base (equiv)	additive (equiv)	solvent	T	time	yield (%) ^b	Z/E ^c
1	TsCl (2)	DBU (1.5)		THF	rt	15 h	0	
2	Ts ₂ O (2)	DBU (1.5)		THF	rt	15 h	0	
3	Ts ₂ O (2)	LDA (1.5)		THF	-78 °C to rt	2 h	0	
4	11 (2)	DBU (1.5)		THF	rt	10 min	88	1.7:1
5	11 (2)	DBU (1.5)		THF	-90 °C	10 min	86	7.2:1
6	11 (2)	DBN (1.5)		THF	-90 °C	10 min	75	4:1
7	11 (2)	MTBD ^d (1.5)		THF	-90 °C	10 min	61	5.2:1
8	11 (2)	TEA (1.5)		THF	-90 °C	1 h	0	
9	11 (2)	DBU (1.5)		Et ₂ O	-90 °C	10 min	73	4:1
10	11 (2)	DBU (1.5)		CH ₂ Cl ₂	-90 °C	10 min	81	2:1
11	11 (2)	DBU (1.5)		THF-MeCN ^e	-90 °C	10 min	88	9:1
12	11 (2)	DBU (1.5)	<i>t</i> -BuOH (0.1)	THF	-90 °C	10 min	65	1.3:1
13	11 (1.2)	<i>t</i> -BuOK (1.5)		THF	-90 °C	10 min	90	1:9
14	11 (1.2)	<i>t</i> -BuOLi (1.5)		THF	-90 °C	10 min	52	1:4
15	11 (1.2)	<i>t</i> -BuONa (1.5)		THF	-90 °C	10 min	38	1:3

^aReactions were run with **9a** (0.22 mmol) at a substrate concentration of 0.05 M. ^bIsolated yield. ^cDetermined by ¹H NMR. ^dMTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. ^e1:1 v/v.

enol sulfonation was limited to carbonyl substrates with additional β -carbonyl groups or α -alkoxy groups, which affected the stereoselectivity of the reaction through chelation control.⁹ Because of the lack of such controlling functional groups on the α -aryl carbonyl substrates, a competent method to stereoselectively generate both geometric enolate isomers has yet to emerge.¹⁰

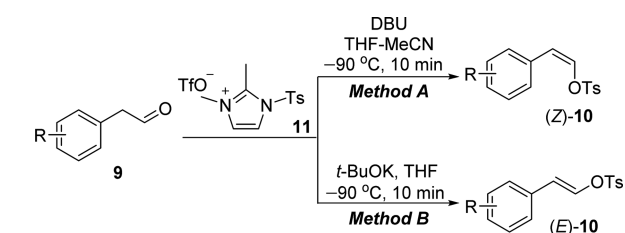
Given that the kinetic or thermodynamic factors in the enolization reaction significantly affected the stereochemical outcome,¹¹ it was envisioned that a judicious choice of reaction conditions would lead to the formation of (*E*)- and (*Z*)-enol sulfates in a stereocomplementary manner. To this end, the reaction conditions were studied using α -aryl aldehyde **9a** as a model substrate. In our initial studies, enol tosylation was investigated first before enol sulfation because enol tosylates are generally more stable than the corresponding sulfates, thus allowing us to more readily identify the stereoselective reaction conditions for the enol sulfation. In addition, the stereoselective enol tosylation is also valuable because stereofixed enol tosylates are useful metal-catalyzed cross-coupling partners.¹²

The typical enol tosylation results are shown in Table 1. When TsCl or Ts₂O were employed as a tosylating agent, the enol tosylation reaction was not successful even in the presence of a very strong base, such as LDA (entries 1–3). A survey of the literature disclosed that sulfonyl imidazolium triflates are superior sulfonating agents in comparison with sulfonyl chlorides for the sulfonation of hydroxyl groups or amino groups.¹³ Accordingly, we prepared and tested the tosyl imidazolium salt **11** as a new sulfonating agent. As shown in Table 1 (entry 4), the treatment of α -aryl aldehyde **9a** with the more-reactive sulfonyl imidazolium salt **11** in the presence of DBU in THF at room temperature afforded the desired enol tosylate **10a** in high yield (88%) with a *Z/E* ratio of 1.7:1. Lowering the temperature to -90 °C increased the selectivity of the reaction to 7.2:1 in favor of the *Z* isomer (entry 5). The selectivity decreased when other strong amine bases were employed (entries 6–7). Using a relatively mild base such as TEA failed to produce the enol tosylate (entry 8). To improve

the stereoselectivity, we proceeded to screen the solvent system (entries 9–11), which established THF-MeCN as the most-effective solvent system to afford the product in a *Z/E* ratio of 9:1 in high yield (entry 11).

Preliminary attempts to achieve *E*-selective enol tosylation commenced by adding a proton source to the *Z*-selective enol tosylation conditions. We hypothesized that the *Z*-enolate formed with DBU would be reprotonated by the proton source more rapidly than it would be trapped by the tosylating agent, which would eventually lead to a thermodynamic equilibrium and afford the thermodynamically favored *E*-enolate. Thus, we added a catalytic amount (0.1 equiv) of a proton source to the reaction conditions of entry 5 to test the effect of the extra proton in the stereoselectivity of the product. This trial (entry 12) did not reverse the *Z* selectivity of the reaction, but significantly decreased the *Z/E* ratio of the product to 1.3:1 by increasing the proportion of *E*-enol tosylate. Encouraged by this result, we attempted to replace DBU with a bulky alkoxide base, which can act as a proton source after proton abstraction from the substrate. After trials, we found that *t*-BuOK in THF at -90 °C selectively afforded *E*-enol tosylate (1:9) in high yield (entry 13). When *t*-BuONa or *t*-BuOLi was used as a base, the *E*-isomer was obtained as a major product, but the stereoselectivity and yield were much lower (entry 14 and 15).

Table 2 shows the substrate scope of the reactions under the conditions of entries 11 and 13 in Table 1. Some remarkable features are seen: (i) All α -aryl aldehyde substrates examined produced enol tosylates in good to excellent yields and stereoselectivities. (ii) Substrates bearing electron-withdrawing groups showed higher selectivities than those bearing electron-donating or electron-neutral groups (entries 1, 4, and 7 vs 2, 3, and 6). (iii) Substrates bearing an *ortho*-substituted group provided the corresponding enol sulfonates with higher selectivity than those with a *para*- or *meta*-substituent (entry 4 vs 1 and 5). The latter two features suggested that the electronegativity and position of the substituent on the aromatic ring of the substrate significantly affect the stereoselectivity of the reaction.

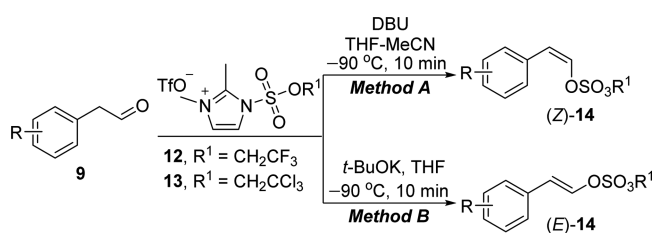
Table 2. Scope of the Enol Tosylation^a

entry	substrate	method	product	yield (%) ^b	Z/E ^c
1		A	(Z)-10b	87	23:1
		B	(E)-10b	85	1:14
2		A	(Z)-10c	88	7:1
		B	(E)-10c	91	1:10
3		A	(Z)-10d	90	20:1
		B	(E)-10d	87	1:20
4		A	(Z)-10e	86	50:1
		B	(E)-10e	82	1:50
5		A	(Z)-10f	81	23:1
		B	(E)-10f	85	1:16
6		A	(Z)-10g	90	8:1
		B	(E)-10g	92	1:8
7		A	(Z)-10h	85	10:1
		B	(E)-10h	73	1:13

^aMethod A: DBU (1.5 equiv), **11** (2.0 equiv), and THF-MeCN (1:1, v/v) (0.05 M) at $-90\text{ }^{\circ}\text{C}$. Method B: *t*-BuOK (1.5 equiv), **11** (1.2 equiv), and THF (0.05 M) at $-90\text{ }^{\circ}\text{C}$. ^bIsolated yield. ^cDetermined by ¹H NMR.

After establishing the optimal conditions for the stereoselective enol tosylation, we returned to our primary interest of enol sulfation. For a masking group for the sulfate, we chose 2,2,2-trifluoroethyl (TFE) and 2,2,2-trichloroethyl (TCE) groups because sulfate esters with these groups have proven to be sufficiently stable under a variety of conditions¹⁴ and can be readily converted back to the sulfates.¹⁵ Thus, the known sulfonyl imidazolium salts **12**^{15b} and **13**¹⁶ (Table 3) were employed as replacements of the tosyl imidazolium salt **11**. Under the same reaction conditions of the selective enol tosylation, imidazolium salts **12** and **13** successfully convert the α -aryl aldehyde **9** into the corresponding enol sulfate esters **14** in good yields and stereoselectivities. However, less-reactive TFEOSO₂Cl and TCEOSO₂Cl failed to convert the α -aryl aldehydes into the enol sulfate esters, similar to the enol tosylation reaction. Even the reagent combination of TFEOSO₂Cl and *N*-methylimidazole did not yield the product (see Table S1 in the Supporting Information).

Table 3 shows the results of the present stereocomplementary enol sulfation of α -aryl aldehydes. The substrates bearing electron-withdrawing or *ortho*-substituted groups provided the corresponding enol sulfate esters with high Z/E- or E/Z-selectivity (entries 2, 3, and 4), whereas substrates bearing electron-neutral, electron-donating, or *para*/*meta*-substituted groups afforded the corresponding enol sulfate esters with decreased selectivities (entries 1, 5, 6, and 7). These

Table 3. Scope of the Enol Sulfation^a

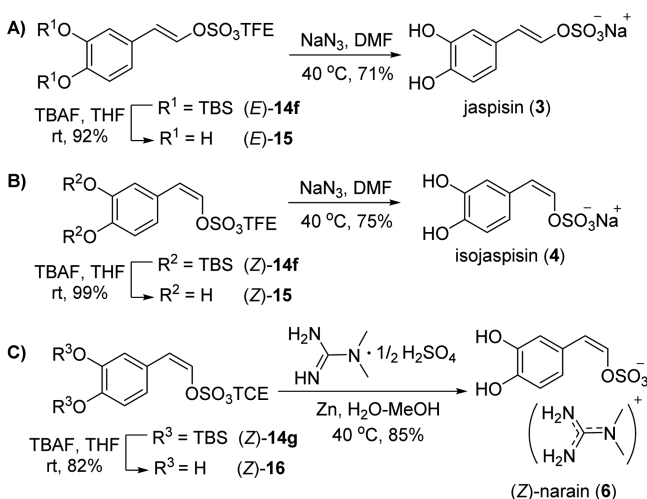
entry	substrate	sulfating agent	method	product	yield (%) ^b	Z/E ^c
1		12	A	(Z)-14a	80	10:1
			B	(E)-14a	60	1:8
2		12	A	(Z)-14b	80	12:1
			B	(E)-14b	51	1:20
3		12	A	(Z)-14c	82	40:1
			B	(E)-14c	53	1:11
4		12	A	(Z)-14d	76	20:1
			B	(E)-14d	46	1:16
5		12	A	(Z)-14e	77	7:1
			B	(E)-14e	64	1:8
6		12	A	(Z)-14f	86	6:1
			B	(E)-14f	55	1:12
7		13	A	(Z)-14g	83	5:1
			B	(E)-14g	49	1:10

^aMethod A: DBU (1.5 equiv), sulfating agent (2.0 equiv), and THF-MeCN (1:1, v/v) (0.05 M) at $-90\text{ }^{\circ}\text{C}$. Method B: *t*-BuOK (1.5 equiv), sulfating agent (1.2 equiv), and THF (0.05 M) at $-90\text{ }^{\circ}\text{C}$. ^bIsolated yield. ^cDetermined by ¹H NMR.

results are consistent with those of the enol tosylation. Compared to the (*E*)-enol tosylation (Table 2), the (*E*)-enol sulfation resulted in lower yields of the isolated products, which may be attributed to the lower stabilities of enol sulfates.

The enol sulfate esters (*E*)-14f, (*Z*)-14f, and (*Z*)-14g (Table 3) were utilized for the first total synthesis of the jaspisin family of natural products (Figure 1).^{1a-c} Jaspisins and narains differ in their counterions, and they are comprised of a pair of geometric isomers. As shown in Scheme 1A, removal of the TBS groups in (*E*)-14f using TBAF furnished catechol (*E*)-15, which upon treatment with NaN₃ in DMF to remove the TFE group, afforded jaspisin (**3**) in good overall yield (65%). The synthesis of isoaspisin **4** was achieved from the (*Z*)-enol sulfate ester **14f** in 74% overall yield using the same sequence of reactions as applied to the synthesis of jaspisin (**3**) (Scheme 1B). Narains are *N,N*-dimethylguanidinium styryl sulfates. Our initial attempts to exchange the sodium ion of the jaspisins with an *N,N*-dimethylguanidinium ion for the formation of the narains were not successful because the jaspisins easily decomposed under the ion-exchange conditions. Thus, we relied on an enol sulfate substrate with a TCE group that is generally removed with Zn/NH₄HCO₂ in polar protic solvent to give a sulfate as an ammonium salt.^{15a} We anticipated that the replacement of NH₄HCO₂ with an *N,N*-dimethylguanidinium salt in the cleavage of the TCE-sulfate ester would afford a sulfate product as an *N,N*-dimethylguanidinium salt. With this modification, we were able to obtain (*Z*)-narain (**6**) in good

Scheme 1. Synthesis of Jaspispin (3), Isojaspispin (4), and (Z)-Narain (6)



overall yield from (Z)-14g in two steps involving the cleavage of TCE ester group with Zn and *N,N*-dimethylguanidine sulfate in H₂O/MeOH at 40 °C (Scheme 1C). The spectroscopic data for synthesized 3, 4, and 6 were identical to natural jaspispin, isojaspispin, and (Z)-narain, respectively (see Table S2–S4 in the Supporting Information).

In conclusion, we developed an efficient method for the stereoselective preparation of enol sulfate esters from α -aryl aldehydes. The reaction utilizes the strategy of in situ trapping of an enolate with a reactive sulfonyl imidazolium salt. To achieve a high stereoselectivity for the enolization, we examined several bases and found that DBU afforded the (Z)-isomer as the major product, while *t*-BuOK favored the formation of the (E)-isomer. A variety of α -aryl aldehydes were tested under the optimized conditions and produced enol sulfates in good to excellent yields with moderate to high (Z)- or (E)-selectivities. TFE- and TCE-enol sulfate esters were readily converted to enol sulfates. Application of this method was demonstrated in a concise total synthesis of the styryl sulfate natural products jaspispin (3), isojaspispin (4), and (Z)-narain (6).

EXPERIMENTAL SECTION

General Procedures. All chemicals were of reagent grade and were used as received. All reactions were performed under dry nitrogen using distilled, dry solvents. The reactions were monitored by TLC (Merck, Silica gel 60 F₂₅₄). Flash column chromatography was performed on silica gel (230–400 mesh). The ¹H NMR (300, 400, 500, 600, or 800 MHz) and ¹³C NMR (75, 100, 125, 150, or 200 MHz) spectra were recorded. Chemical shifts (δ) are reported in ppm relative to the nondeuterated solvent as an internal reference; coupling constants (*J*) are given in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The ¹H NMR spectra are presented as follows: chemical shift (multiplicity, coupling constant, integration). Melting points were measured using a Buchi B-540 melting point apparatus without correction. The IR spectra were measured on a Fourier-transform infrared spectrometer. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) or quadrupole time-of-flight (Q-TOF).

1,2-Dimethyl-3-tosylimidazolium Triflate (11). This compound was prepared using reference to a literature procedure.¹³ 2-Methylimidazole (10 g, 0.12 mol) was suspended in dry CH₂Cl₂ (40 mL) and cooled to 0 °C. *p*-Tosyl chloride (22 g, 0.12 mol) in CH₂Cl₂ (40 mL) was added over 15 min. Then, the reaction mixture was

stirred at room temperature for 1 h. The organic layer was concentrated, and the crude product was recrystallized from EtOAc-hexane to give white crystals (26 g). To a solution of the obtained white crystals (26 g) in dry Et₂O (200 mL), methyltriflate (10.5 mL, 93.11 mmol) was added over 15 min via a syringe at 0 °C. A white precipitate rapidly appeared during the addition. The reaction mixture was stirred for 1 h, suction filtered, washed with dry ether, and dried under vacuum. The desired tosyl imidazolium salt 11 (40 g, 85% for two steps) was obtained as a white powder; mp 91–92 °C; ¹H NMR (300 MHz, CD₃CN) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 2H), 3.63 (s, 3H), 2.65 (s, 3H), 2.43 (s, 3H); ¹³C NMR (75 MHz, CD₃CN) δ 150.4, 132.1, 124.4, 120.5, 118.3, 36.6, 22.0, 12.1; IR (neat) ν_{\max} 3117, 1610, 1223, 1153, 1025, 782, 681 (cm⁻¹); HRMS (FAB): calcd. for C₁₂H₁₅N₂O₂S [M]⁺ 251.0854, found 251.0858.

4-(2-Hydroxyethyl)-1,2-phenylene Dibenzoate. This compound was prepared using reference to a literature procedure.¹⁷ To a solution of 2-(3,4-dihydroxyphenyl)ethyl alcohol (154 mg, 1.0 mmol) in CH₂Cl₂ (10 mL), benzoyl disulfide (548 mg, 2.0 mmol), Et₃N (0.55 mL, 4 mmol), and DMAP (48 mg, 0.4 mmol) were added at room temperature. The mixture was stirred at room temperature for 15 h. Then, the mixture was diluted with H₂O and extracted with EtOAc. The organic layer was dried over MgSO₄ and concentrated in vacuo. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 1:1) to afford the product (148 mg, 41%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.6 Hz, 4H), 7.51 (td, *J* = 1.8 Hz, 7.5 Hz, 2H), 7.37–7.27 (m, 5H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 1.9 Hz, 8.3 Hz, 1H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.90 (t, *J* = 6.5 Hz, 2H), 1.80 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 142.4, 140.9, 137.8, 133.7, 133.6, 130.1, 128.8, 128.7, 128.5, 128.4, 127.3, 124.0, 123.4, 63.3, 38.6; IR (neat) ν_{\max} 3450, 1736, 1502, 1450, 1241, 1110, 1051, 1021, 699 (cm⁻¹); HRMS (FAB): calcd. for C₂₂H₁₉O₅ [M+H]⁺ 363.1232, found 363.1233.

4-(2-Oxoethyl)-1,2-phenylene Dibenzoate (9h). Dess-Martin periodinane (177 g, 0.42 mmol) was added to a solution of 4-(2-hydroxyethyl)-1,2-phenylene dibenzoate (137 mg, 0.38 mmol) in CH₂Cl₂ (4 mL). The reaction mixture was stirred at room temperature for 1 h. After the starting materials disappeared by monitoring with TLC, water was added. Then, the resulting mixture was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo. Flash column chromatography (silica gel, hexane/EtOAc, 3:1) afforded 9h (100 mg, 73%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 4H), 8.04 (d, *J* = 8.0 Hz, 4H), 7.52 (td, *J* = 0.8 Hz, 7.5 Hz, 2H), 7.39–7.33 (m, 5H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 1.9 Hz, 8.2 Hz, 1H), 3.73 (d, *J* = 1.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.5, 164.1, 164.0, 142.7, 141.8, 133.7, 133.6, 130.6, 130.1, 128.5, 128.4, 127.7, 124.7, 123.9, 49.6; IR (neat) ν_{\max} 1736, 1598, 1503, 1240, 1110, 1051, 1021, 753, 699 (cm⁻¹); HRMS (FAB): calcd. for C₂₂H₁₇O₅ [M+H]⁺ 361.1076, found 361.1081.

(Z)-4-Methylstyryl 4-Methylbenzenesulfonate [(Z)-10a]. A solution of 9a (54 mg, 0.39 mmol) in THF-MeCN (v/v 1:1) (6.8 mL) was cooled to –90 °C (cooling bath using liquid nitrogen and MeOH), and then, DBU (0.089 mL, 0.59 mmol) was added to the solution. The reaction mixture was stirred at –90 °C for 5 min. Then, tosylating agent 11 (318 mg, 0.79 mmol) in 1 mL THF-MeCN (v/v 1:1) was added. The resulting mixture was stirred at –90 °C for 10 min, diluted with water and extracted with EtOAc. The organic layer was dried over MgSO₄ and concentrated in vacuo. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1) to afford the product (101 mg, 88%, Z/E = 9:1 mixture from ¹H NMR). The pure (Z)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid; mp 105–106 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.1 Hz, 16.6 Hz, 4H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 6.8 Hz, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.4, 137.8, 133.4, 132.6, 129.8, 129.6, 129.1, 129.0, 127.8, 115.7, 21.6, 21.2; IR (neat) ν_{\max} 1651, 1592, 1513, 1362, 1175, 1091, 996, 885, 814, 721, 675 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₃S [M]⁺ 288.0820, found 288.0818.

In an analogous manner, (*Z*)-enol tosylates **10b–10h** and (*Z*)-enol sulfates **14a–14g** were obtained from the corresponding α -aryl aldehydes **9a–9i**.

(Z)-4-Fluorostyryl 4-Methylbenzenesulfonate [(Z)-10b]. Compound (*Z*)-**10b** (68 mg, 87%, *Z/E* = 23:1) was obtained from **9b** (37 mg, 0.27 mmol), DBU (0.06 mL, 0.40 mmol) and **11** (214 mg, 0.53 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 48–49 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.39 (q, *J* = 4.7 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 6.8 Hz, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 163.7, 160.5, 145.5, 133.8, 132.5, 130.9, 130.8, 129.9, 128.6, 127.9, 115.5, 115.2, 114.7, 21.6; IR (neat) ν_{\max} 1658, 1594, 1508, 1366, 1226, 1176, 1003, 888, 832, 817, 724, 675 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0566.

(Z)-4-Methoxystyryl 4-Methylbenzenesulfonate [(Z)-10c]. Compound (*Z*)-**10c** (67 mg, 88%, *Z/E* = 7:1) was obtained from **9c** (37 mg, 0.25 mmol), DBU (0.055 mL, 0.37 mmol), and **11** (197 mg, 0.49 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid; mp 79–80 °C; ¹H NMR (800 MHz, CDCl₃) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 6.8 Hz, 1H), 5.66 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 2.39 (s, 3H); ¹³C NMR (200 MHz, CDCl₃) δ 159.2, 145.3, 132.6, 130.5, 129.9, 127.8, 125.2, 115.4, 113.7, 55.2, 21.6; IR (neat) ν_{\max} 1605, 1512, 1361, 1306, 1260, 1174, 1036, 992, 884, 813, 736 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₄S [M]⁺ 304.0769, found 304.0765.

(Z)-2-Methylstyryl 4-Methylbenzenesulfonate [(Z)-10d]. Compound (*Z*)-**10d** (58 mg, 90%, *Z/E* = 20:1) was obtained from **9d** (30 mg, 0.22 mmol), DBU (0.05 mL, 0.33 mmol), and **11** (178 mg, 0.44 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (800 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.12–7.08 (m, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 5.91 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H), 2.12 (s, 3H); ¹³C NMR (200 MHz, CDCl₃) δ 145.2, 135.9, 134.3, 132.4, 130.9, 129.8, 129.7, 129.4, 127.9, 127.8, 125.7, 114.8, 21.6, 19.8; IR (neat) ν_{\max} 1651, 1596, 1485, 1459, 1368, 1175, 1093, 1003, 882, 813, 735, 674 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₃S [M]⁺ 288.0820, found 288.0816.

(Z)-2-Fluorostyryl 4-Methylbenzenesulfonate [(Z)-10e]. Compound (*Z*)-**10e** (67 mg, 86%, *Z/E* = 50:1) was obtained from **9e** (37 mg, 0.27 mmol), DBU (0.06 mL, 0.40 mmol) and **11** (214 mg, 0.53 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 49–50 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.73 (td, *J* = 1.6 Hz, 7.7 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.22–7.16 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.95 (td, *J* = 0.9 Hz, 9.4 Hz, 1H), 6.68 (d, *J* = 6.9 Hz, 1H), 5.98 (d, *J* = 6.9 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.3, 157.9, 145.6, 135.5, 135.4, 132.4, 130.4, 129.9, 129.5, 129.4, 127.9, 124.0, 123.9, 120.4, 120.3, 115.2, 114.9, 107.4, 107.3, 21.6; IR (neat) ν_{\max} 1658, 1597, 1485, 1453, 1369, 1247, 1219, 1174, 1010, 879, 741, 672 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0568.

(Z)-3-Fluorostyryl 4-Methylbenzenesulfonate [(Z)-10f]. Compound (*Z*)-**10f** (62 mg, 81%, *Z/E* = 23:1) was obtained from **9f** (36 mg, 0.26 mmol), DBU (0.058 mL, 0.39 mmol) and **11** (208 mg, 0.52 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid. mp 52–53 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.23–7.19 (m, 1H), 7.15–7.11 (m, 2H), 6.90 (td, *J* = 4.1 Hz, 11.4 Hz, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 5.69 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.3, 145.6, 135.0, 134.5, 134.4, 132.4, 129.9, 129.8, 129.7, 127.8, 124.8, 115.7, 115.5, 114.8, 114.6, 114.5, 21.6; IR (neat) ν_{\max} 1656, 1581, 1483, 1442, 1370, 1234, 1176, 1093, 1013, 944, 854, 787, 725, 674 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0573.

(Z)-3,4-Bis(benzyloxy)styryl 4-Methylbenzenesulfonate [(Z)-10g]. Compound (*Z*)-**10g** (92 mg, 90%, *Z/E* = 8:1) was obtained from **9g** (71 mg, 0.21 mmol), DBU (0.048 mL, 0.32 mmol), and **11** (170 mg, 0.42 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.42 (dd, *J* = 7.3 Hz, 17.5 Hz, 4H), 7.35 (q, *J* = 7.3 Hz, 4H), 7.30–7.25 (m, 4H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.89 (dd, *J* = 1.8 Hz, 8.4 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.50 (d, *J* = 6.8 Hz, 1H), 5.59 (d, *J* = 6.8 Hz, 1H), 5.14 (s, 2H), 5.08 (s, 2H), 2.36 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.6, 148.4, 145.4, 137.0, 132.7, 132.6, 129.8, 128.4, 127.8, 127.7, 127.4, 126.1, 122.9, 115.4, 115.3, 114.3, 71.0, 70.9, 21.6; IR (neat) ν_{\max} 1598, 1510, 1453, 1368, 1264, 1175, 1136, 1003, 854, 809, 731, 693 (cm⁻¹); HRMS (FAB): calcd. for C₂₉H₂₆O₅S [M]⁺ 486.1501, found 486.1495.

(Z)-4-(2-(Tosyloxy)vinyl)-1,2-phenylene Dibenzoate [(Z)-10h]. Compound (*Z*)-**10h** (38 mg, 85%, *Z/E* = 10:1) was obtained from **9h** (32 mg, 0.088 mmol), DBU (0.02 mL, 0.13 mmol), and **11** (70 mg, 0.17 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (500 MHz, CDCl₃) δ 8.03 (dd, *J* = 7.2 Hz, 12.3 Hz, 4H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.52 (q, *J* = 7.2 Hz, 2H), 7.41–7.33 (m, 6H), 7.28 (dd, *J* = 2.7 Hz, 8.3 Hz, 3H), 6.67 (d, *J* = 6.8 Hz, 1H), 5.74 (d, *J* = 6.8 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.1, 145.6, 142.2, 141.9, 134.9, 133.6, 132.3, 131.3, 130.1, 130.0, 128.6, 128.4, 127.9, 127.4, 124.0, 123.3, 114.4, 21.6; IR (neat) ν_{\max} 1740, 1655, 1597, 1501, 1372, 1241, 1175, 1111, 1051, 1011, 867, 812, 667 (cm⁻¹); HRMS (FAB): calcd. for C₂₉H₂₂O₇S [M]⁺ 514.1086, found 514.1090.

(Z)-4-Methylstyryl (2,2,2-Trifluoroethyl) Sulfate [(Z)-14a]. Compound (*Z*)-**14a** (53 mg, 80%, *Z/E* = 10:1) was obtained from **9a** (30 mg, 0.22 mmol), DBU (0.05 mL, 0.33 mmol), and **12** (183 mg, 0.45 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 42–43 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 6.3 Hz, 1H), 5.95 (d, *J* = 6.9 Hz, 1H), 4.43 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.8, 133.5, 129.4, 129.2, 128.6, 122.3, 117.4, 67.2 (q, 1C, *J*_{CF} = 154.3 Hz), 21.2; IR (neat) ν_{\max} 1409, 1285, 1171, 1038, 984, 907, 820, 729, 658 (cm⁻¹); HRMS (FAB): calcd. for C₁₁H₁₁F₃O₄S [M]⁺ 296.0330, found 296.0334.

(Z)-4-Fluorostyryl (2,2,2-Trifluoroethyl) Sulfate [(Z)-14b]. Compound (*Z*)-**14b** (52 mg, 80%, *Z/E* = 12:1) was obtained from **9b** (30 mg, 0.22 mmol), DBU (0.05 mL, 0.33 mmol), and **12** (183 mg, 0.45 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (500 MHz, CDCl₃) δ 7.48 (q, *J* = 4.7 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 6.6 Hz, 1H), 5.94 (d, *J* = 6.6 Hz, 1H), 4.47 (q, *J* = 7.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 164.2, 160.9, 133.9, 133.8, 131.2, 131.1, 128.4, 128.3, 127.6, 123.0, 120.8, 119.3, 116.1, 115.9, 115.6, 67.3 (q, 1C, *J*_{CF} = 154.5 Hz); IR (neat) ν_{\max} 1604, 1510, 1413, 1282, 1172, 1041, 993, 960, 901, 835, 675 (cm⁻¹); HRMS (FAB): calcd. for C₁₀H₈F₄O₄S [M]⁺ 300.0079, found 300.0078.

(Z)-2-Methylstyryl (2,2,2-Trifluoroethyl) Sulfate [(Z)-14c]. Compound (*Z*)-**14c** (109 mg, 82%, *Z/E* = 40:1) was obtained from **9d** (60 mg, 0.45 mmol), DBU (0.1 mL, 0.67 mmol), and **12** (367 mg, 0.90 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.48 (m, 1H), 7.23–7.19 (m, 3H), 6.71 (d, *J* = 6.5 Hz, 1H), 6.21 (d, *J* = 6.5 Hz, 1H), 4.21 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 136.5, 134.6, 130.3, 130.0, 129.3, 128.6, 126.0, 123.0, 119.4, 116.6, 67.0 (q, 1C, *J*_{CF} = 154.0 Hz), 19.8; IR (neat) ν_{\max} 1418, 1282, 1170, 1041, 988, 961, 897, 829, 768, 674 (cm⁻¹); HRMS (FAB): calcd. for C₁₁H₁₁F₃O₄S [M]⁺ 296.0330, found 296.0332.

(*Z*)-3-Fluorostyryl (2,2,2-Trifluoroethyl) Sulfate [(*Z*)-14d]. Compound (*Z*)-14d (98 mg, 76%, *Z/E* = 20:1) was obtained from **9f** (60 mg, 0.43 mmol), DBU (0.097 mL, 0.65 mmol), and **12** (354 mg, 0.87 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (800 MHz, CDCl₃) δ 7.34 (td, *J* = 6.0 Hz, 8.0 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.22 (td, *J* = 1.9 Hz, 9.9 Hz, 1H), 7.02 (td, *J* = 2.5 Hz, 8.4 Hz, 1H), 6.70 (d, *J* = 6.6 Hz, 1H), 5.94 (d, *J* = 6.6 Hz, 1H), 4.49 (q, *J* = 7.7 Hz, 2H); ¹³C NMR (200 MHz, CDCl₃) δ 163.3, 162.1, 134.9, 133.4, 133.3, 130.3, 130.2, 125.1, 121.8, 120.5, 116.0, 115.9, 115.7, 67.4 (q, 1C, *J*_{CF} = 154.0 Hz); IR (neat) *v*_{max} 1583, 1425, 1282, 1171, 1041, 1003, 868, 787, 676 (cm⁻¹); HRMS (FAB): calcd. for C₁₀H₈F₄O₃S [M]⁺ 300.0079, found 300.0072.

(*Z*)-3,4-Bis(benzyloxy)styryl (2,2,2-Trifluoroethyl) Sulfate [(*Z*)-14e]. Compound (*Z*)-14e (46 mg, 77%, *Z/E* = 7:1) was obtained from **9g** (40 mg, 0.12 mmol), DBU (0.027 mL, 0.18 mmol), and **12** (101 mg, 0.25 mmol). The pure (*Z*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (500 MHz, CDCl₃) δ 7.44–7.41 (m, 4H), 7.36 (q, *J* = 3.8 Hz, 4H), 7.29 (t, *J* = 11.0 Hz, 2H), 7.14 (d, *J* = 1.9 Hz, 1H), 6.97 (dd, *J* = 1.9 Hz, 8.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 6.6 Hz, 1H), 5.82 (d, *J* = 6.6 Hz, 1H), 5.18 (s, 4H), 4.27 (q, *J* = 7.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 149.3, 148.5, 136.9, 136.8, 132.8, 128.5, 127.9, 127.8, 127.1, 124.7, 123.3, 116.9, 115.5, 114.3, 71.0, 70.9, 67.5 (q, 1C, *J*_{CF} = 154.5 Hz); IR (neat) *v*_{max} 1602, 1512, 1419, 1266, 1200, 1170, 995, 854, 808, 732, 694 (cm⁻¹); HRMS (FAB): calcd. for C₂₄H₂₁F₃O₆S [M]⁺ 494.1011, found 494.1002.

The characterization data and spectra of compound (*Z*)-14f and (*Z*)-15 were reported in our previous report.⁷

(*Z*)-3,4-Bis(*tert*-butyldimethylsilyloxy)styryl (2,2,2-Trichloroethyl) Sulfate [(*Z*)-14g]. Compound (*Z*)-14g (78 mg, 83%, *Z/E* = 5:1) was obtained as a colorless oil from **9i** (60 mg, 0.16 mmol), DBU (0.035 mL, 0.24 mmol), and **13** (146 mg, 0.32 mmol); ¹H NMR (600 MHz, CDCl₃) δ 7.11 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 2.0 Hz, 8.5 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 5.82 (q, *J* = 6.8 Hz, 1H), 4.66 (s, 2H), 0.98 (s, 9H), 0.96 (s, 9H), 0.21 (s, 6H), 0.19 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 147.6, 146.9, 132.9, 125.0, 123.1, 121.8, 121.0, 116.8, 80.1, 25.9, 25.8, 18.4, -4.0, -4.1; IR (neat) *v*_{max} 2950, 1503, 1411, 1275, 1250, 1001, 827, 769 (cm⁻¹); HRMS (FAB): calcd. for C₂₂H₃₈Cl₃O₆SSi₂ [M+H]⁺ 591.0993, found 591.1011.

(*E*)-4-Methylstyryl 4-Methylbenzenesulfonate [(*E*)-10a]. A solution of **9a** (30 mg, 0.22 mmol) in THF (3.4 mL) was cooled to -90 °C (cooling bath using liquid nitrogen and MeOH), and then, *t*-BuOK in THF (1.0 M, 0.33 mL, 0.33 mmol) was added to the solution. The reaction mixture was stirred at -90 °C for 5 min. Then, tosylating agent **11** (107 mg, 0.26 mmol) in 1 mL THF was added. The resulting mixture was stirred at -90 °C for 10 min, and diluted with water and extracted with EtOAc. The organic layer was dried over MgSO₄ and concentrated in vacuo. The crude product was purified using column chromatography on silica gel (hexane/EtOAc, 15:1) to afford the product (57 mg, 88%, *Z/E* = 1:9 mixture from ¹H NMR). The pure (*E*)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid; mp 98–99 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.11–7.06 (m, 4H), 7.02 (d, *J* = 12.3 Hz, 1H), 6.25 (d, *J* = 12.3 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 145.3, 138.1, 135.5, 132.5, 129.9, 129.8, 129.4, 128.0, 126.3, 120.7, 21.6, 21.1; IR (neat) *v*_{max} 1651, 1592, 1513, 1363, 1174, 997, 884, 814, 720, 674 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₃S [M]⁺ 288.0820, found 288.0826.

In an analogous manner, (*E*)-enol tosylates **10b**–**10h** and (*E*)-enol sulfates **14a**–**14g** were obtained from the corresponding α -aryl aldehydes **9a**–**9i**.

(*E*)-4-Fluorostyryl 4-Methylbenzenesulfonate [(*E*)-10b]. Compound (*E*)-10b (72 mg, 85%, *Z/E* = 1:14) was obtained from **9b** (40 mg, 0.29 mmol), *t*-BuOK in THF (1.0 M, 0.43 mL, 0.43 mmol),

and **11** (140 mg, 0.35 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 57–58 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 5.3 Hz, 8.7 Hz, 2H), 7.00–6.93 (m, 3H), 6.27 (d, *J* = 12.3 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.3, 145.5, 135.9, 132.4, 129.9, 128.8, 128.0, 127.9, 119.5, 115.8, 115.6, 21.6; IR (neat) *v*_{max} 1654, 1596, 1505, 1371, 1224, 1176, 1043, 921, 874, 816, 742, 660 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0572.

(*E*)-4-Methoxystyryl 4-Methylbenzenesulfonate [(*E*)-10c]. Compound (*E*)-10c (61 mg, 91%, *Z/E* = 1:10) was obtained from **9c** (33 mg, 0.22 mmol), *t*-BuOK in THF (1.0 M, 0.33 mL, 0.33 mmol), and **11** (107 mg, 0.26 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from EtOAc-hexane as a white crystalline solid; mp 85–86 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 12.4 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 12.3 Hz, 1H), 3.76 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 145.3, 134.6, 132.4, 129.9, 128.0, 127.6, 125.1, 120.5, 114.1, 55.2, 21.6; IR (neat) *v*_{max} 1603, 1509, 1368, 1247, 1173, 1029, 953, 880, 815, 741 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₄S [M]⁺ 304.0769, found 304.0779.

(*E*)-2-Methylstyryl 4-Methylbenzenesulfonate [(*E*)-10d]. Compound (*E*)-10d (65 mg, 87%, *Z/E* = 1:20) was obtained from **9d** (35 mg, 0.26 mmol), *t*-BuOK in THF (1.0 M, 0.39 mL, 0.39 mmol), and **11** (125 mg, 0.31 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (800 MHz, CDCl₃) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.17–7.15 (m, 1H), 7.11 (t, *J* = 7.0 Hz, 2H), 6.88 (d, *J* = 12.2 Hz, 1H), 6.47 (d, *J* = 12.2 Hz, 1H), 2.44 (s, 3H), 2.16 (s, 3H); ¹³C NMR (200 MHz, CDCl₃) δ 145.4, 136.5, 135.9, 132.4, 131.5, 130.4, 129.9, 128.2, 128.1, 126.2, 125.9, 119.2, 21.6, 19.7; IR (neat) *v*_{max} 1647, 1596, 1371, 1176, 1037, 925, 877, 804, 739, 664 (cm⁻¹); HRMS (FAB): calcd. for C₁₆H₁₆O₃S [M]⁺ 288.0820, found 288.0818.

(*E*)-2-Fluorostyryl 4-Methylbenzenesulfonate [(*E*)-10e]. Compound (*E*)-10e (76 mg, 82%, *Z/E* = 1:50) was obtained from **9e** (44 mg, 0.32 mmol), *t*-BuOK in THF (1.0 M, 0.48 mL, 0.48 mmol) and **11** (153 mg, 0.38 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 45–46 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.23–7.16 (m, 3H), 7.06–6.98 (m, 2H), 6.33 (d, *J* = 12.4 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.7, 158.4, 145.5, 138.5, 138.4, 132.4, 129.9, 129.4, 129.3, 128.5, 128.4, 128.0, 124.3, 124.2, 120.7, 120.5, 115.9, 115.7, 114.1, 21.7; IR (neat) *v*_{max} 1652, 1487, 1459, 1371, 1177, 1045, 947, 881, 810, 749, 664 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0573.

(*E*)-3-Fluorostyryl 4-Methylbenzenesulfonate [(*E*)-10f]. Compound (*E*)-10f (62 mg, 85%, *Z/E* = 1:16) was obtained from **9f** (35 mg, 0.25 mmol), *t*-BuOK in THF (1.0 M, 0.38 mL, 0.38 mmol) and **11** (122 mg, 0.30 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid; mp 53–54 °C; ¹H NMR (800 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.23 (q, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 12.3 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.93–6.89 (m, 2H), 6.27 (d, *J* = 12.3 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (200 MHz, CDCl₃) δ 163.5, 162.3, 145.6, 137.1, 135.0, 134.9, 132.3, 130.3, 130.2, 130.0, 128.0, 122.2, 122.1, 119.3, 119.2, 115.0, 114.8, 113.1, 112.9, 21.6; IR (neat) *v*_{max} 1652, 1584, 1491, 1435, 1346, 1240, 1169, 1030, 811, 776, 738, 687 (cm⁻¹); HRMS (FAB): calcd. for C₁₅H₁₃FO₃S [M]⁺ 292.0569, found 292.0560.

(*E*)-3,4-Bis(benzyloxy)styryl 4-Methylbenzenesulfonate [(*E*)-10g]. Compound (*E*)-10g (94 mg, 92%, *Z/E* = 1:8) was obtained from **9g** (70 mg, 0.21 mmol), *t*-BuOK in THF (1.0 M, 0.32 mL, 0.32 mmol), and **11** (101 mg, 0.25 mmol). The pure (*E*)-isomer was obtained by recrystallization in the freezer from Et₂O-hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* =

8.3 Hz, 2H), 7.43–7.29 (m, 12H), 6.89 (d, $J = 12.3$ Hz, 1H), 6.82–6.79 (m, 2H), 6.71 (dd, $J = 1.8$ Hz, 8.3 Hz, 1H), 6.18 (d, $J = 12.3$ Hz, 1H), 5.12 (s, 2H), 5.11 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.2, 149.0, 145.3, 137.0, 135.0, 132.5, 129.9, 128.5, 128.0, 127.9, 127.8, 127.3, 127.2, 126.2, 120.5, 120.3, 115.0, 113.0, 71.5, 71.2, 21.6; IR (neat) ν_{max} 1597, 1510, 1371, 1256, 1175, 1045, 810, 731, 664 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{29}\text{H}_{26}\text{O}_5\text{S}$ $[\text{M}]^+$ 486.1501, found 486.1509.

(E)-4-(2-(Tosyloxy)vinyl)-1,2-phenylene Dibenzoate [(E)-10h]. Compound (E)-10h (32 mg, 73%, $Z/E = 1:13$) was obtained from 9h (31 mg, 0.086 mmol), *t*-BuOK in THF (1.0 M, 0.13 mL, 0.13 mmol), and 11 (41 mg, 0.10 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ^1H NMR (400 MHz, CDCl_3) δ 8.03–8.00 (m, 4H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.54–7.50 (m, 2H), 7.37–7.31 (m, 6H), 7.29 (s, 1H), 7.23 (d, $J = 2.0$ Hz, 1H), 7.18 (dd, $J = 2.0$ Hz, 8.4 Hz, 1H), 7.08 (d, $J = 12.4$ Hz, 1H), 6.31 (d, $J = 12.3$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 164.0, 145.6, 142.7, 142.2, 137.1, 133.7, 132.2, 131.7, 130.1, 130.0, 128.5, 128.4, 128.0, 124.7, 123.9, 121.3, 119.1, 21.6; IR (neat) ν_{max} 1739, 1597, 1504, 1451, 1375, 1240, 1176, 1047, 841, 746, 701, 662 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{29}\text{H}_{22}\text{O}_7\text{S}$ $[\text{M}]^+$ 514.1086, found 514.1097.

(E)-4-Methylstyryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14a]. Compound (E)-14a (39 mg, 60%, $Z/E = 1:8$) was obtained from 9a (30 mg, 0.22 mmol), *t*-BuOK in THF (1.0 M, 0.33 mL, 0.33 mmol), and 12 (109 mg, 0.26 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid; mp 45–46 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 12.2$ Hz, 1H), 6.57 (d, $J = 12.2$ Hz, 1H), 4.58 (q, $J = 7.6$ Hz, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 135.7, 129.6, 128.5, 126.6, 122.7, 121.8, 120.0, 67.1 (q, 1C, $J_{\text{CF}} = 154.5$ Hz), 21.2; IR (neat) ν_{max} 1414, 1281, 1170, 1026, 893, 831, 790, 661 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$ $[\text{M}]^+$ 296.0330, found 296.0324.

(E)-4-Fluorostyryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14b]. Compound (E)-14b (64 mg, 51%, $Z/E = 1:20$) was obtained from 9b (60 mg, 0.43 mmol), *t*-BuOK in THF (1.0 M, 0.65 mL, 0.65 mmol), and 12 (212 mg, 0.52 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ^1H NMR (500 MHz, CDCl_3) δ 7.27 (q, $J = 4.0$ Hz, 2H), 7.04–7.01 (m, 3H), 6.57 (d, $J = 12.3$ Hz, 1H), 4.59 (q, $J = 7.7$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.5, 161.3, 136.1, 128.4, 128.3, 127.6, 123.2, 120.7, 119.5, 116.2, 115.9, 67.3 (q, 1C, $J_{\text{CF}} = 154.5$ Hz); IR (neat) ν_{max} 1603, 1510, 1413, 1282, 1173, 1026, 961, 894, 840, 763 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{10}\text{H}_8\text{F}_4\text{O}_4\text{S}$ $[\text{M}]^+$ 300.0079, found 300.0081.

(E)-2-Methylstyryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14c]. Compound (E)-14c (78 mg, 53%, $Z/E = 1:11$) was obtained from 9d (67 mg, 0.50 mmol), *t*-BuOK in THF (1.0 M, 0.75 mL, 0.75 mmol), and 12 (244 mg, 0.60 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 6.8$ Hz, 1H), 7.18–7.15 (m, 2H), 6.94 (d, $J = 12.1$ Hz, 1H), 6.80 (d, $J = 12.1$ Hz, 1H), 4.60 (q, $J = 7.7$ Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.7, 136.2, 130.6, 130.4, 128.8, 126.4, 126.2, 120.1, 67.3 (q, 1C, $J_{\text{CF}} = 154.5$ Hz), 19.7; IR (neat) ν_{max} 1416, 1282, 1169, 1020, 891, 834, 748, 661 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_4\text{S}$ $[\text{M}]^+$ 296.0330, found 296.0337.

(E)-3-Fluorostyryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14d]. Compound (E)-14d (31 mg, 46%, $Z/E = 1:16$) was obtained from 9f (32 mg, 0.23 mmol), *t*-BuOK in THF (1.0 M, 0.35 mL, 0.35 mmol), and 12 (113 mg, 0.27 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.27 (m, 1H), 7.11 (d, $J = 12.3$ Hz, 1H), 7.07 (d, $J = 9.0$ Hz, 2H), 7.02–

6.98 (m, 2H), 6.56 (d, $J = 12.3$ Hz, 1H), 4.59 (q, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 161.7, 137.2, 133.8, 133.7, 130.6, 130.5, 122.5, 120.5, 119.9, 115.8, 115.6, 113.5, 113.3, 67.4 (q, 1C, $J_{\text{CF}} = 154.3$ Hz); IR (neat) ν_{max} 1586, 1420, 1282, 1170, 1025, 961, 865, 781, 683 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{10}\text{H}_8\text{F}_4\text{O}_4\text{S}$ $[\text{M}]^+$ 300.0079, found 300.0076.

(E)-3,4-Bis(benzyloxy)styryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14e]. Compound (E)-14e (57 mg, 64%, $Z/E = 1:8$) was obtained from 9g (60 mg, 0.18 mmol), *t*-BuOK in THF (1.0 M, 0.27 mL, 0.27 mmol), and 12 (88 mg, 0.22 mmol). The pure (E)-isomer was obtained by recrystallization in the freezer from Et_2O -hexane as a white crystalline solid. The crystalline solid melted to give a colorless oil when warmed up to room temperature; ^1H NMR (800 MHz, CDCl_3) δ 7.42 (dd, $J = 7.3$ Hz, 17.7 Hz, 4H), 7.35 (q, $J = 7.8$ Hz, 4H), 7.30 (q, $J = 7.3$ Hz, 2H), 6.93 (d, $J = 12.1$ Hz, 1H), 6.88–6.86 (m, 2H), 6.82 (dd, $J = 1.9$ Hz, 8.3 Hz, 1H), 6.49 (d, $J = 12.1$ Hz, 1H), 5.15 (s, 2H), 5.14 (s, 2H), 4.57 (q, $J = 7.7$ Hz, 2H); ^{13}C NMR (200 MHz, CDCl_3) δ 149.6, 149.1, 136.8, 135.2, 128.5, 128.0, 127.9, 127.3, 127.2, 124.7, 121.7, 120.7, 114.8, 113.1, 71.4, 71.1, 67.2 (q, 1C, $J_{\text{CF}} = 153.5$ Hz); IR (neat) ν_{max} 1512, 1417, 1280, 1168, 1018, 868, 733, 695 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{24}\text{H}_{21}\text{F}_3\text{O}_6\text{S}$ $[\text{M}]^+$ 494.1011, found 494.1009.

(E)-3,4-Bis((tert-butyl)dimethylsilyloxy)styryl (2,2,2-Trifluoroethyl) Sulfate [(E)-14f]. Compound (E)-14f (39 mg, 55%, $Z/E = 1:12$) was obtained as a colorless oil from 9i (50 mg, 0.13 mmol), *t*-BuOK in THF (1.0 M, 0.20 mL, 0.20 mmol) and 12 (63 mg, 0.16 mmol); ^1H NMR (600 MHz, CDCl_3) δ 6.92 (d, $J = 12.4$ Hz, 1H), 6.77 (s, 2H), 6.74 (s, 1H), 6.48 (d, $J = 12.4$ Hz, 1H), 4.57 (q, $J = 7.6$ Hz, 2H), 0.97 (s, 9H), 0.96 (s, 9H), 0.19 (s, 6H), 0.18 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.9, 147.2, 135.0, 124.7, 121.9, 121.4, 120.1, 119.5, 67.3 (q, 1C, $J_{\text{CF}} = 154.5$ Hz), 25.9, 25.8, 18.5, 18.4, –4.0, –4.1; IR (neat) ν_{max} 2936, 2864, 1513, 1423, 1298, 1205, 835 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{22}\text{H}_{38}\text{F}_3\text{O}_6\text{SSi}_2$ $[\text{M}+\text{H}]^+$ 543.1880, found 543.1876.

(E)-3,4-Bis((tert-butyl)dimethylsilyloxy)styryl (2,2,2-Trichloroethyl) Sulfate [(E)-14g]. Compound (E)-14g (58 mg, 49%, $Z/E = 1:10$) was obtained as a colorless oil from 9i (75 mg, 0.20 mmol), *t*-BuOK in THF (1.0 M, 0.30 mL, 0.30 mmol) and 13 (109 mg, 0.24 mmol); ^1H NMR (600 MHz, CDCl_3) δ 6.98 (d, $J = 12.4$ Hz, 1H), 6.77 (s, 2H), 6.74 (s, 1H), 6.50 (d, $J = 12.4$ Hz, 1H), 4.77 (s, 2H), 0.97 (s, 9H), 0.96 (s, 9H), 0.18 (s, 6H), 0.17 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.8, 147.2, 135.1, 124.8, 121.7, 121.4, 120.1, 119.5, 92.3, 80.1, 25.8, 18.5, 18.4, –4.0, –4.1; IR (neat) ν_{max} 2930, 2857, 1509, 1421, 1252, 1126, 1003, 835, 778, 730 (cm^{-1}); HRMS (FAB): calcd. for $\text{C}_{22}\text{H}_{38}\text{Cl}_3\text{O}_6\text{SSi}_2$ $[\text{M}+\text{H}]^+$ 591.0993, found 591.1003.

(E)-3,4-Dihydroxystyryl (2,2,2-Trifluoroethyl) Sulfate [(E)-15]. The solution of tetra-*n*-butylammonium fluoride in THF (1.0 M, 0.36 mL, 0.36 mmol) was added to a solution of (E)-14f (100 mg, 0.18 mmol) in THF (1.8 mL). The reaction mixture was stirred at room temperature for 10 min. The resulting mixture was diluted with water and extracted with EtOAc. The organic layer was washed with brine, dried with MgSO_4 , filtered, and concentrated in vacuo. Flash column chromatography (silica gel, hexane/EtOAc, 2:1) afforded (E)-15 (53 mg, 92%) as a brown oil; ^1H NMR (CD_3OD , 500 MHz) δ 7.07 (d, $J = 12.1$ Hz, 1H), 6.82 (s, 1H), 6.72 (s, 2H), 6.57 (d, $J = 12.1$ Hz, 1H), 4.91 (q, $J = 8.1$ Hz, 2H); ^{13}C NMR (CD_3OD , 125 MHz) δ 148.3, 147.5, 136.7, 125.7, 124.7, 121.2, 117.4, 115.0, 69.3 (q, 1C, $J_{\text{CF}} = 151.3$ Hz); IR (neat) ν_{max} 2968, 1414, 1279, 1170, 996, 866, 815 (cm^{-1}); HRMS (FAB) calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_6\text{S}$ 314.0072 $[\text{M}]^+$, found 314.0079.

Jaspisin (3). To a solution of the (E)-15 (25 mg, 0.079 mmol) in DMF (0.8 mL), NaN_3 (10 mg, 0.16 mmol) was added. The mixture was stirred at 40 °C for 2 h. Then the solvent was evaporated, and the resulting residue was purified by Sephadex LH20 column chromatography (20% aqueous MeOH) to yield jaspisin (3) (14 mg, 71%) as obtained as a brown gum. ^1H NMR (800 MHz, D_2O) δ 7.02 (d, $J = 12.3$ Hz, 1H), 6.87 (d, $J = 1.6$ Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 6.77 (dd, $J = 1.6$ Hz, 8.2 Hz, 1H), 6.27 (d, $J = 12.3$ Hz, 1H); ^1H NMR (500 MHz, CD_3OD) δ 7.09 (d, $J = 12.5$ Hz, 1H), 6.75 (d, $J = 1.9$ Hz, 1H), 6.66 (d, $J = 8.1$ Hz, 1H), 6.61 (dd, $J = 1.9$ Hz, 8.1 Hz, 1H), 6.08 (d, $J = 12.5$ Hz, 1H); ^{13}C NMR (200 MHz, D_2O) δ 144.1, 143.7, 136.8, 126.7, 119.2, 117.2, 116.4, 113.4; ^{13}C NMR (125 MHz, CD_3OD) δ 147.2, 146.5, 139.6, 128.9, 119.9, 117.3, 116.7, 114.2; IR (neat) ν_{max}

3280, 1650, 1573, 1520, 1232, 1001, 890, 824, 735, 676 (cm⁻¹); HRMS (Q-TOF) calcd for C₈H₇O₆S 230.9969 [M-Na]⁻, found 230.9960.

Isojaspisin (4). This compound was synthesized from (Z)-14f (120 mg, 0.22 mmol) following the procedure for the synthesis of jaspisin (3). The crude product was purified by Sephadex LH20 column chromatography (20% aqueous MeOH) to yield isojaspisin (4) (41 mg, 74% for two steps) was obtained as a brown gum. ¹H NMR (400 MHz, D₂O) δ 7.21 (d, J = 1.8 Hz, 1H), 7.01 (dd, J = 1.8 Hz, 8.2 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.57 (d, J = 6.8 Hz, 1H), 5.68 (d, J = 6.8 Hz, 1H); ¹³C NMR (D₂O, 100 MHz) δ 143.9, 135.0, 128.7, 126.5, 122.0, 116.4, 116.2, 112.6; IR (neat) ν_{max} 3280, 1630, 1598, 1523, 1220, 1005, 890, 816, 734, 676 (cm⁻¹); HRMS (Q-TOF) calcd for C₈H₇O₆S 230.9969 [M-Na]⁻, found 230.9968.

(Z)-3,4-Dihydroxystyryl (2,2,2-Trichloroethyl) Sulfate [(Z)-16]. Compound (Z)-16 was synthesized from (Z)-14g (60 mg, 0.1 mmol) and the solution of tetra-*n*-butylammonium fluoride in THF (1.0 M, 0.2 mL, 0.2 mmol) following the procedure for the synthesis of (E)-15. The crude product was separated by silica gel column chromatography (hexane/EtOAc, 2:1) to afford (Z)-16 (29 mg, 82%) as a yellow gum. ¹H NMR (400 MHz, CD₃OD) δ 7.09 (d, J = 1.9 Hz, 1H), 6.86 (dd, J = 1.9 Hz, 8.3 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 6.5 Hz, 1H), 5.93 (d, J = 6.5 Hz, 1H), 4.86 (s, 2H); ¹³C NMR (75 MHz, CD₃OD) δ 148.1, 147.1, 134.4, 125.8, 123.9, 119.3, 118.0, 117.1, 82.1; IR (neat) ν_{max} 2875, 1369, 1240, 1096, 987, 854, 796 (cm⁻¹); HRMS (FAB): calcd. for C₁₀H₉Cl₃O₆S [M]⁺ 361.9185, found 361.9193.

(Z)-Narain (6). To a solution of the (Z)-16 (20 mg, 0.055 mmol) in MeOH (0.5 mL), zinc dust (25 mg, 0.38 mmol) was added. Then the *N,N*-dimethylguanidine sulfate (89 mg, 0.33 mmol) with H₂O (0.5 mL) was added. The mixture was stirred at 40 °C for 1 h. Then the solvent was evaporated, and the resulting residue was purified by Sephadex LH20 column chromatography (20% aqueous MeOH) to yield (Z)-narain (6) (15 mg, 85%) was obtained as a brown gum. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.79 (brs, 2H), 7.15 (brs, 4H), 7.05 (d, J = 1.6 Hz, 1H), 6.75 (dd, J = 1.5 Hz, 8.2 Hz, 1H), 6.63 (d, J = 8.1 Hz, 1H), 6.49 (d, J = 7.2 Hz, 1H), 5.15 (d, J = 7.2 Hz, 1H), 2.94 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 156.7, 144.6, 143.8, 137.4, 126.9, 119.9, 115.7, 115.1, 106.7, 37.7; IR (KBr) ν_{max} 3349, 3236, 1652, 1254, 1208 (cm⁻¹); HRMS (Q-TOF) calcd for C₈H₇O₆S 230.9969 [M-H]⁻, found 230.9957.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00868.

¹H and ¹³C NMR spectra for all compounds and NMR comparison of jaspisin, isojaspisin, and (Z)-narain with literature data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pennkim@snu.ac.kr.

ORCID

Sanghee Kim: 0000-0001-9125-9541

Notes

The authors declare no competing financial interest.

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