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Construction of Sulfonyl Oxabenzo[3.3.1]bicyclic Core via Cyclocondensation of β-Ketosulfones and *o*-Formyl Allylbenzenes

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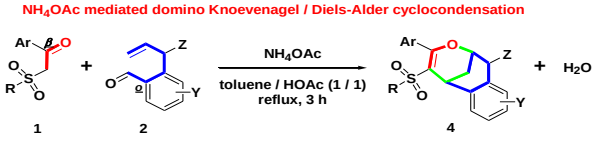
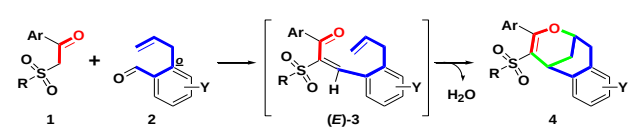


ABSTRACT: NH_4OAc mediated domino Knoevenagel/Diels-Alder cyclocondensation of β-ketosulfones **1** and *o*-formyl allylbenzenes **2** provides sulfonyl oxabenzo[3.3.1]bicyclic core **4** in a cosolvent of toluene and HOAc (v/v =1/1) at reflux for 3 h. The intermediate **3** contains a chalcone motif. The uses of various ammonium salts and solvent systems are investigated for facile and efficient transformation. The plausible mechanisms have been proposed and the DFT calculations have been included.

Introduction

Recently, we developed a one-pot easy-operational route for the synthesis of diversified carbocyclic or heterocyclic benzofused frameworks by functionalization of β-ketosulfones (α-sulfonyl ketones, **1**)[1] or *o*-formyl allylbenzenes (*o*-allyl benzaldehydes, **2**) building blocks under a series of domino benzannulation processes.[2] With receiving significant results, we wanted to investigate the possibility of the construction of novel core systems by the combination of two scaffolds via a single-step domino transformation. The domino reaction can reduce human effort, avoid reagent waste, combine multiple reactions, and save reaction time and cost.[3] In accordance with the powerful route, Knoevenagel condensation of active α-methylene compounds (for β-ketosulfones **1**) with carbonyl compounds (for *o*-formyl allylbenzenes **2**) in the presence of ammonium salts has been reported.[4,5] In particular, due to carbonyl compounds associating with an *o*-allyl arm such that the resulting intermediate (*E*)-**3** has a chalcone motif we can proceed with further intramolecular annulation to provide the unexpected bridged skeleton **4** with the oxabenzo[3.3.1]bicyclic core under single vessel conditions via a sequential intramolecular Diels-Alder cycloaddition (Scheme 1).

Scheme 1. Combination of β-Ketosulfones and *o*-Formyl Allylbenzenes



However, Knoevenagel condensations have been associated with Diels-Alder cycloadditions, Michael additions, and/or ene reactions for the preparation of highly multi-functionalized heterocycles.[6-7] Although developed synthetic protocols have been extensively explored for diversified skeletons, most 1,3-dicarbonyl compounds of the reported molecules were focused on β-ketoesters, β-diketones, and β-diesters. Among the present scaffolds derived from domino Knoevenagel condensation and the Diels-Alder cycloaddition route, a core structure having other β-carbonyl synthons is relatively rare, especially those with a sulfonyl substituent (Y = RSO_2).[8] Herein, we describe a highly effective synthesis of the bridged benzofused heterocyclic core system **4** bearing a rigid conformer of (*E*)-β-oxyvinyl sulfone with an electronic "push-pull" characteristic by a domino cyclocondensation route from readily available β-ketosulfones **1** and *o*-formyl allylbenzenes **2**, as shown in Scheme 2.

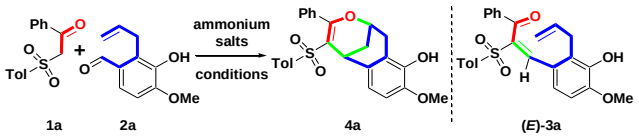
Scheme 2. Cyclocondensation Route of **4**

Results and Discussion

The initial study commenced with the treatment of model substrates **1a** (Ar = Ph, R = Tol, 0.5 mmol) and **2a** (Y = 1-HO-3-MeO, $Z^1 = Z^2$ = H, 0.5 mmol) with stoichiometric amounts of NH_4OAc (1.0 and 2.0 equivalents) in toluene at room temperature for 3 h as shown in Table 1. However, two conditions were unsuccessful (entries 1-2). When the reaction tempera-

ture was increased to reflux, 56 % and 42% yields of **4a** were provided under Dean-Stark distillation conditions, respectively (entries 3-4). With the results in hand, by controlling 1.0 equivalent of NH_4OAc at reflux temperature (111 °C), elongating reaction times (3 → 5 and 10 h, entries 5-6) did not provide better yields. Uncyclized **3a** was isolated in a range of 16%-24% yields under a boiling toluene condition. However, when HOAc was added to the reaction mixture, the isolated yield of **4a** was increased to 90% (entry 7). The result shows that this domino reaction proceeded well in the presence of HOAc. Using a cosolvent of toluene and HOAc (v/v, 1/1, 10 mL), we surveyed the effect of ammonium salts in constructing a bridged core structure, such as Et_4NOAc, Et_4NCl, $n Bu_4NF$, NH_4F, and NH_4I. However, none of them obtained higher yields of **4a** than NH_4OAc. Elongating the alkyl chains (NH_4OAc → Et_4NOAc), the yield of **4a** was decreased (68%, entry 8). Furthermore, after adjusting the anion from acetate to halide, no desired products were produced (entries 9-12). Next, other reactions (dioxane and xylene) were examined; however, the isolated yields were similar (72% and 79%) (entries 13-14). In entries 15-16, the concentrated (4 mL) and diluted (20 mL) solutions of toluene and HOAc produced lower yields (82% and 70%) than entry 7 (90%). From these observations, we conclude that NH_4OAc (1.0 equiv) provides optimal conditions (refluxing toluene/HOAc, 3 h) for one-pot cyclocondensation.

Table 1. Reaction Conditions[a]



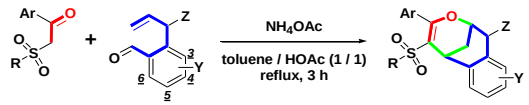
1a 2a 4a (*E*)-3a

entry	ammonium salts (equiv)	solvent	temp (°C)	time (h)	**4a** (%)[b]
1	NH_4OAc (1.0)	toluene	25	3	—[c]
2	NH_4OAc (2.0)	toluene	25	3	—[c]
3	NH_4OAc (1.0)	toluene	111	3	56[d]
4	NH_4OAc (1.0)	toluene	111	3	42[d]
5	NH_4OAc (1.0)	toluene	111	5	55[d]
6	NH_4OAc (1.0)	toluene	111	10	50[d]
7	NH_4OAc (1.0)	toluene/HOAc	118	3	90
8	Et_4NOAc (1.0)	toluene/HOAc	118	3	68
9	Et_4NCl (1.0)	toluene/HOAc	118	3	—[c]
10	$n Bu_4NF$ (1.0)	toluene/HOAc	118	3	—[c]
11	NH_4F (1.0)	toluene/HOAc	118	3	—[c]
12	NH_4I (1.0)	toluene/HOAc	118	3	—[c]
13	NH_4OAc (1.0)	dioxane/HOAc	118	3	72[e]
14	NH_4OAc (1.0)	xylene/HOAc	145	3	79[f]
15	NH_4OAc (1.0)	toluene/HOAc	118	3	82[g]
16	NH_4OAc (1.0)	toluene/HOAc	118	3	70[h]

[a]The reactions were run on a 0.5 mmol scale with **1a**, **2a** (1.0 equiv), solvents (10 mL). [b]Isolated yields. [c]No reaction. [d]**3a** was isolated in a range of 16%-24% yields. [e]10% of **3a** was isolated. [f]Complex mixture was isolated (~8%). [g]4 mL of toluene/HOAc (v/v = 1/1). [h]20 mL of toluene/HOAc (v/v = 1/1).

To study the scope and limitations of this approach, **1** and **2** were reacted with NH_4OAc to afford diversified **4**, as shown in Table 2. With optimal conditions established (Table 1, entry 7), we found that this route allowed a direct dehydration/[4+2] annulation under mild conditions in moderate to good yields (73%-90%). Among entries 1~20, the efficient formation of **4a**-**4t** showed that these substituents (for **1a**-**1n**, Ar and R; for **2a**-**2f**, Y and Z) did not affect the yield changes. For the electronic nature of aryl substituents (Ar) of **1**, not only electron-neutral but also electron-withdrawing and electron-donating groups were appropriate. For sulfonyl substituents (R) of **1**, both aliphatic (Me and *n*Bu) and aromatic groups were well-tolerated. Different oxygenated groups (Y) and olefinic groups (Z) on **2** were also suitable to form core structures **4**. For the overall domino Knoevenagel/Diels-Alder cyclocondensation process, we envisioned that the electronic effect played a very important facor for affecting the construction of oxabenzo[3.3.1]bicyclic core because a stronger electron-donating group (Y = 3-OH and 4-MeO) could increase the reactivity of allylbenzaldehyde skeleton such that the intramolecular Diels-Alder cycloaddition was triggered easily. Furthermore, the relative stereochemical structures of **4a**, **4b**, **4p** and **4s** were determined by single-crystal X-ray crystallography.[9]

Table 2. Synthesis of **4**[a]



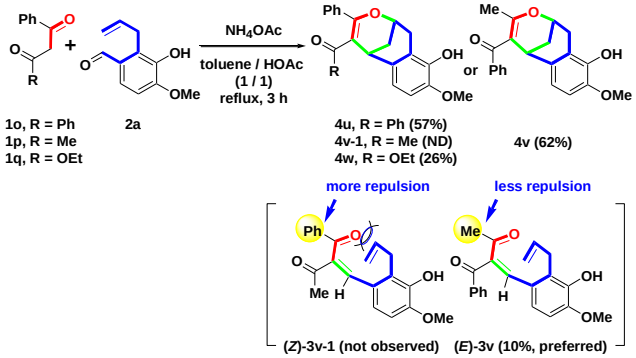
1 2 4

entry	**1**, Ar =, R =	**2**, Y =, Z =	**4**, (%)[b]
1	**1a**, Ph, Tol	**2a**, 3-HO-4-MeO, H	**4a**, 90
2	**1b**, 4-FC_6H_4, Tol	**2a**, 3-HO-4-MeO, H	**4b**, 83
3	**1c**, Tol, Tol	**2a**, 3-HO-4-MeO, H	**4c**, 84
4	**1d**, 4-$MeOC_6H_4$, Tol	**2a**, 3-HO-4-MeO, H	**4d**, 83
5	**1e**, 4-$CF_3C_6H_4$, Tol	**2a**, 3-HO-4-MeO, H	**4e**, 86
6	**1f**, 4-$NO_2C_6H_4$, Tol	**2a**, 3-HO-4-MeO, H	**4f**, 83
7	**1g**, 4-PhC_6H_4, Tol	**2a**, 3-HO-4-MeO, H	**4g**, 82
8	**1h**, 2-naphthyl, Tol	**2a**, 3-HO-4-MeO, H	**4h**, 84
9	**1i**, 3,4-$Cl_2C_6H_3$, Tol	**2a**, 3-HO-4-MeO, H	**4i**, 80
10	**1j**, Ph, Ph	**2a**, 3-HO-4-MeO, H	**4j**, 87
11	**1k**, Ph, 4-FC_6H_4	**2a**, 3-HO-4-MeO, H	**4k**, 83
12	**1l**, Ph, 4-$MeOC_6H_4$	**2a**, 3-HO-4-MeO, H	**4l**, 87
13	**1m**, Ph, Me	**2a**, 3-HO-4-MeO, H	**4m**, 73
14	**1n**, Ph, *n*Bu	**2a**, 3-HO-4-MeO, H	**4n**, 76
15	**1a**, Ph, Tol	**2b**, 3,4-$(MeO)_2$, H	**4o**, 86
16	**1c**, Tol, Tol	**2b**, 3,4-$(MeO)_2$, H	**4p**, 89
17	**1a**, Ph, Tol	**2c**, 3-*n*BuO-4-MeO, H	**4q**, 84
18	**1a**, Ph, Tol	**2d**, 3-*c*C_5H_9O-4-MeO, H	**4r**, 88
19	**1a**, Ph, Tol	**2e**, 3,4-$(MeO)_2$, Me	**4s**, 80
20	**1a**, Ph, Tol	**2f**, 3-HO, H	**4t**, 78

[a]The reactions were run on a 0.5 mmol scale with **1**, **2** (1.0 equiv), NH_4OAc (1.0 equiv), toluene/HOAc (v/v = 8/2, 10 mL), 3 h, reflux. [b]Isolated yields.

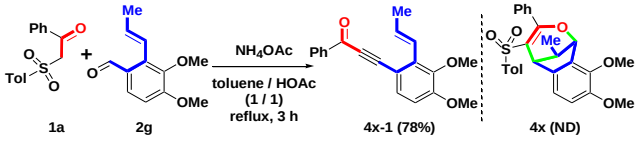
As an extension of the one-pot route, cyclocondensations of β-diketones **1o**-**1p** with **2a** were investigated next (Scheme 3). Treatment of **1o** (R = Ph) with **2a** provided sole **4u** in a 57% yield. However, reaction of unsymmetrical **1p** (R = Me) with **2a** produced only one isomer **4v** (62%) along with one uncyclized **3v** (10%) due to less repulsion between acetyl and *o*-allylaryl groups on **3v**. Another pair of **4v-1** and **3v-1** was not detected. By the steric effect, **3v** was genrated as (*E*)-configuration and was cyclized to **4v** becuase phenylketone was a bulkier group than methylketone. For the phenomenon of steric hindrance, our experimental results were also similar to Swenson and Zhang reports.[8b] The related configuration was confirmed through ^{1}H NMR spectrum analysis. The methyl group of **4v-1** (a α-methyl ketone signal) should exhibit one singlet at nearly δ 2.40-2.70. However, in the methyl group of **4v** (a vinylic signal) one singlet appeared at δ 1.58. From the two positions of two methyl group signals, we concluded that the predicted structure of **4v** was reasonable. For the β-ketoester **1q**, only a 26% yield of **4w** was generated since the ester group was unstable under refluxing acidic conditions.

Scheme 3. Synthesis of **4u**, **4v**, **3v** and **4w**



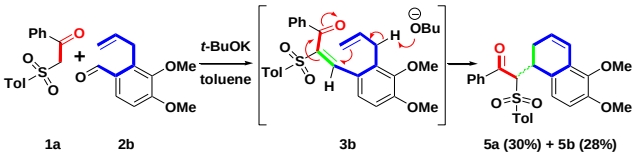
As shown in Scheme 4, by changing 2-allyl to 2-vinyl group, a one-pot domino reaction was studied. Using a boiling NaOH methanolic solution, olefin migration of **2b** was furnished to **2g**.[10] In particular, when **1a** was reacted with **2g** by the above conditions, only a 78% yield of ynone **4x-1** was generated and the predicted oxabenzo[3.2.1]bicyclic core **4x** was not produced via the NH_4OAc mediated domino Knoevenagel condensation and dehydrosulfonylation under refluxing conditions.[11]

Scheme 4. Synthesis of **4x-1**



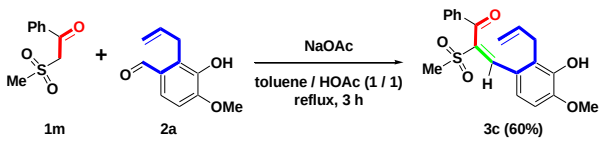
After changing NH_4OAc to *t*-BuOK, no desired bridged skeleton **4** was observed. Unexpectedly, a pair of isomers, **5a** and **5b**, with a dihydronaphthalene skeleton was isolated in 30% and 28% yields, respectively via a *t*-BuOK promoted reaction of **1a** with **2b** in refluxing toluene for 3 h (Scheme 5).[12] The initial event should show that **3b** was formed by Knoevenagel condensation of **1a** with **2a**. After deprotonation of the benzylic proton on **3b** by the *t*-butoxide ion, two isomers, **5a** and **5b** were obtained in a ratio of 1:1 via an intramolecular tandem deprotonation/olefin migration/Michael addition sequence.

Scheme 5. Synthesis of **5a**-**5b**



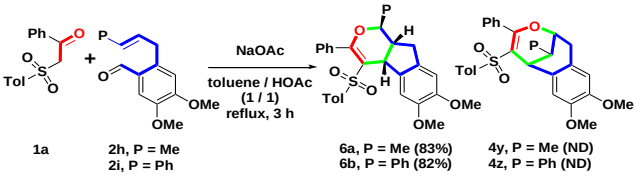
Furthermore, when NaOAc was chosen as the base for a one-pot reaction of **1m** with **2a**, the chalcone skeleton **3c** was isolated in a 60% yield along with two starting materials **1m** and **2a**, and trace amounts of **4m** (Scheme 6). The results showed that **3c** was produced as the major product in the presence of the buffer solution of the NaOAc/HOAc system. The structure of **3c** was determined by single-crystal X-ray crystallography.[9]

Scheme 6. Synthesis of **3c**



In contrast, the domino reaction of **1a** with **2h** (P = Me) or **2i** (P = Ph) provided the tricyclic *cis*-fused **6a** and **6b** via a highly regioselective process in 83% and 82% yields, respectively under NH_4OAc mediated conditions (Scheme 7). The structural frameworks of **6a** and **6b** were determined by single-crystal X-ray crystallography.[9] The results are in agreement with Tietze reports.[13]

Scheme 7. Synthesis of **6a**-**6b**



Density functional theory (DFT) calculations were performed to provide the rationale behind the different reaction behavior induced by the terminal substitution on the dienophile moiety (P group). The endo- and exo-cycloaddition of **1a** with **2a** (P = H), with **2h** (P = Me), and with **2i** (P = Ph) starting from the corresponding benzylidene intermediates were calculated (Figure 1). The results show that the endo-cycloaddition product (i.e., bridged product) is thermodynamically more stable than the exo-cycloaddition product (i.e., tricyclic fused product) for all three systems. However, from a kinetic point of view, the reaction **1a** + **2a** favors endo-cycloaddition path whereas the reactions **1a** + **2h** and **1a** + **2i** favor exo-cycloaddition path. In other words, the observed

Figure 2. The optimized geometries of the transition states and the frontier molecular orbitals of diene and dienophile moieties. The red wave line indicates the bond at which the molecule is divided into diene and dienophile moieties.

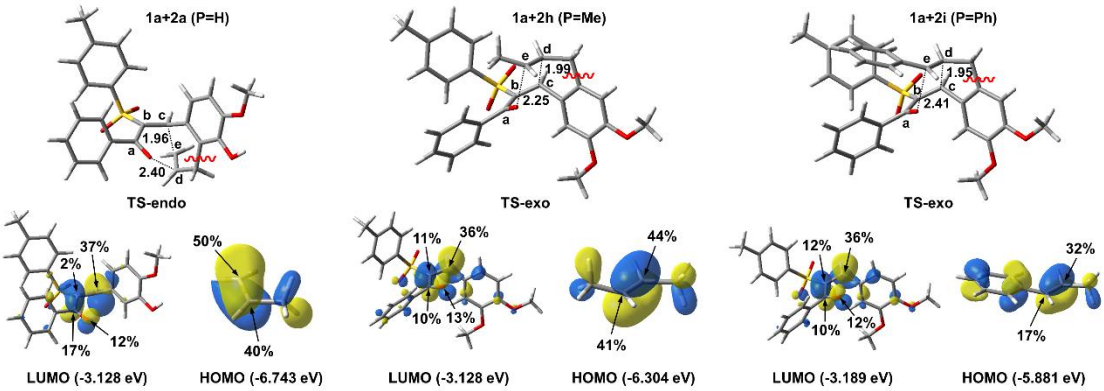
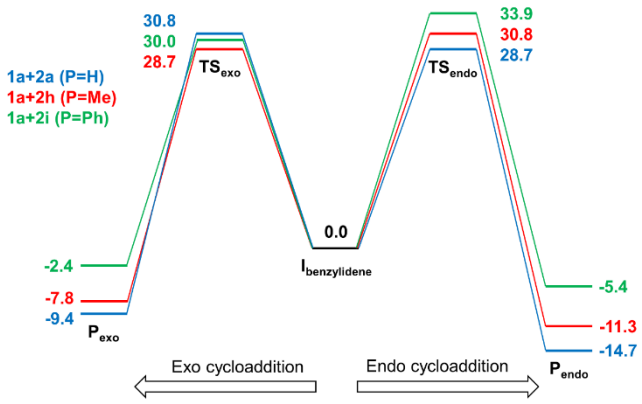
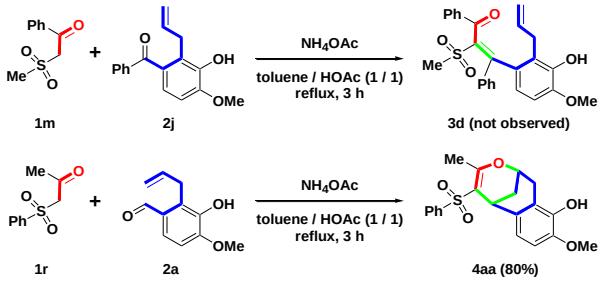


Figure 1. DFT calculated free energy profile. The unit is kcal/mol.



regioselectivity is a consequence of kinetic control. Molecular orbital analysis reveals that the cycloaddition reaction is conducted through the interaction between the LUMO of diene and the HOMO of dienophile, namely the electron flow is from dienophile to diene. The energy gap between the HOMO of diene and the LUMO of dienophile is relatively large and, therefore, the role of the corresponding interaction in the cycloaddition reaction is excluded. The LUMO of diene moiety and the HOMO of dienophile moiety fixed at the transition state geometry are depicted in Figure 2. It can be seen that the LUMO of diene always has the largest distribution on C_c atom (36-37%). In contrast, the HOMO distribution of dienophile is affected by the terminal substitution. Without substitution (P = H), the terminal C_e atom possesses a larger HOMO coefficient (50%). As a consequence, the relative orientation between diene and dienophile at the transition state **TS_{endo}** maximizes the orbital overlap through the $C_c \cdots C_e$ interaction. On the contrary, the introduction of electron donating groups at terminal C_e pushes the HOMO distribution towards the C_d atom, leading to a larger HOMO coefficient on the C_d atom (44% for P = Me and 32% for P = Ph). Under this circumstance, the optimal orbital overlap between the LUMO of diene and the HOMO of dienophile occurs at the transition state **TS_{exo}** ($C_c \cdots C_d$ interaction) rather than at **TS_{endo}**. These computational results suggest that the substitution at the terminal carbon of dienophile moiety (P group) is a key factor for the product distribution.

Scheme 8. Reaction of **1m** with **2j** and synthesis of **4aa**



After adjusting aldehyde group to ketone group, a one-pot domino reaction was examined (Scheme 8). However, when **1m** was treated with **2j**, no condensed product **3d** was detected under similar conditions. Ever after elongating the time to 30 h, no reactions were observed. The results show that the carbonyl motif of ketone **2j** possessed poor reactivity for **1m** such that the Knoevenagel condensation could not be triggered. For the present optimal cyclocondensation condition, the *o*-allyl benzoketone substrate was the limitation. Furthermore, after exchanging the methyl group (R, methanesulfonyl) and the phenyl (Ar, phenylketone) group on β-arylketo alkylsulfone **1m**, **1r** with the benzenesulfonyl group and the methylketone group was examined. By the one-pot reaction of **1r** and **2a**, **4aa** was produced in an 80% yield. From the results, we understand that β-alkylketo arenesulfone is well-applied to domino Knoevenagel/Diels-Alder cyclocondensation.

In summary, we have developed a NH_4OAc promoted one-pot route for the synthesis of sulfonyl oxabenzo[3.3.1]bicyclic core **4** by a domino Knoevenagel condensation/Diels-Alder cycloaddition of β-ketosulfones **1** and *o*-formyl allylbenzenes **2** in a cosolvent of toluene and HOAc (v/v =1/1) at reflux for 3 h in moderate to good yields. Chalcones **3** were the key intermediates. The one-pot process provides a series of multifunctionalized **4** via a cascade pathway of one C-C and two C-C bond formations. The structures of the key products were confirmed by X-ray crystallography. The plausible mechanisms have been proposed and the density functional theory (DFT) calculations have been included. Further investigations regarding the synthetic application of β-ketosulfones **1** and *o*-formyl allylbenzenes **2** will be conducted and published in due course.

Experimental Section

General. All 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. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^{1}H 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 mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

*A representative synthetic procedure of skeleton **2** is as follows*: Sodium sulfinates (RSO_2Na, 6.0 mmol) was added to a solution of substituted 2-bromoacetophenones (5.0 mmol) in a cosolvent of 1,4-dioxane and water (20 mL, v/v = 1:1) at rt. The reaction mixture was stirred at reflux for 6 h. The reaction mixture was cooled to rt, concentrated, and partitioned with CH2Cl2 (3 x 30 mL) and water (30 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude β-ketosulfones under reduced pressure. Crude β-ketosulfones **2** were recrystallized from EtOAc in nearly quantitative yields. β-Ketosulfones **2** are known compounds and the analytical data are consistent with those in previous literature.[14]

*A representative synthetic procedure of skeleton **4** is as follows:* NH_4OAc (39 mg, 0.5 mmol) was added to a solution of **1** (0.5 mmol) in a cosolvent of toluene and HOAc (v/v = 1/1, 10 mL) at rt. The reaction mixture was stirred at rt for 10 min under Dean-Stark distillation apparatus. **2** (0.5 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 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 = 8/1~4/1) afforded **4**.

*5-Methoxy-11-phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (**4a**)*. Yield = 90% (202 mg); Colorless solid; mp = 201-203 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{25}O_5S$ 449.1423, found 449.1424; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.17-7.13 (m, 2H), 7.05-7.03 (m, 2H), 6.88 (s, 4H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.77 (s, 1H), 5.09-5.06 (m, 1H), 4.43-4.41 (m, 1H), 3.90 (s, 3H), 3.18 (dd, *J* = 5.2, 19.6 Hz, 1H) 3.10 (d, *J* = 19.6 Hz, 1H), 2.26 (s, 3H), 2.19-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 144.7, 143.4, 142.3, 134.0, 133.6, 133.1, 129.6 (2x), 129.1, 128.6 (2x), 127.3 (2x), 126.8 (2x), 120.1, 119.3, 117.9, 108.4, 70.7, 56.1, 32.6, 30.4, 27.7, 21.3. Single-crystal X-Ray diagram: crystal of compound **4a** was grown by slow diffusion of EtOAc into a solution of compound **4a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 10.3973(5) Å , *b* = 11.4451(5) Å , *c* = 18.3533(9) Å , *V* = 2161.19(18) Å^3, *Z* = 4, d_{calcd} = 1.378 g/cm^3, *F*(000) = 944, 2θ range 2.103~26.408°, R indices (all data) R1 = 0.0382, wR2 = 0.0879.

*3-(2-Allyl-3-hydroxy-4-methoxyphenyl)-1-phenyl-2-(toluene-4-sulfonyl)propenone (**3a**)*. For Table 1, entry 3: Yield = 16% (37 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{25}O_5S$ 449.1423, found 449.1430; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.79-7.76 (m, 4H), 7.45-7.41 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28-7.25 (m, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 6.02-5.92 (m, 1H), 5.73 (br s, 1H), 5.16 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.10 (dq, *J* = 1.6, 17.2 Hz, 1H), 3.74 (s, 3H), 3.63 (d, *J* = 5.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.7, 148.2, 144.5, 143.5, 140.2, 138.8, 137.3, 135.8, 135.3, 133.9, 129.7 (4x), 128.6 (2x), 128.4 (2x), 125.5, 124.5, 122.0, 116.0, 108.1, 55.8, 30.4, 21.6.

*11-(4-Fluorophenyl)-5-methoxy-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (**4b**)*. Yield = 83% (193 mg); Colorless solid; mp = 176-178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{24}FO_5S$ 467.1329, found 467.1332; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.0 Hz, 1H), 7.06-7.01 (m, 2H), 6.93-6.88 (m, 4H), 6.87-6.81 (m, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.79 (br s, 1H), 5.09-5.06 (m, 1H), 4.41-4.40 (m, 1H), 3.90 (s, 3H), 3.18 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.08 (d, *J* = 19.2 Hz, 1H), 2.28 (s, 3H), 2.22-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, *J* = 247.9 Hz), 160.7, 144.7, 143.4, 142.5, 139.9, 132.9, 131.8 (d, *J* = 8.3 Hz, 2x), 129.6 (d, *J* = 3.8 Hz), 128.7 (2x), 126.7 (2x), 120.1, 119.7, 117.8, 114.3 (d, *J* = 21.2 Hz, 2x), 108.4, 70.8, 56.1, 32.6, 30.4, 27.7, 21.3. Single-crystal X-Ray diagram: crystal of compound **4b** was grown by slow diffusion of EtOAc into a solution of compound **4b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 2/c, *a* = 24.9437(14) Å , *b* = 8.7955(5) Å , *c* = 11.5489(6) Å , *V* = 2526.1(2) Å^3, *Z* = 2, d_{calcd} = 1.338 g/cm^3, *F*(000) = 1060, 2θ range 0.819~26.408°, R indices (all data) R1 = 0.0444, wR2 = 0.1185.

*5-Methoxy-12-(toluene-4-sulfonyl)-11-p-tolyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (**4c**)*. Yield = 84% (194 mg); Colorless solid; mp = 152-154 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1578; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 1H), 6.99-6.89 (m, 8H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.86 (s, 1H), 5.07-5.04 (m, 1H), 4.40-4.38 (m, 1H), 3.87 (s, 3H), 3.16 (dd, *J* = 4.8, 19.2 Hz, 1H), 3.09 (d, *J* = 18.8 Hz, 1H), 2.32 (s, 3H), 2.28 (s, 3H), 2.16-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 144.6, 143.3, 142.2, 140.0, 139.1, 133.0, 130.7, 129.3 (2x), 128.4 (2x), 127.8 (2x), 126.7 (2x), 119.9, 118.7, 117.9, 108.3, 70.5, 56.0, 32.5, 30.4, 27.6, 21.2 (2x).

*5-Methoxy-11-(4-methoxyphenyl)-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (**4d**)*. Yield = 83% (198 mg); Colorless solid; mp = 158-160 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ for $C_{27}H_{27}O_6S$ 479.1528, found 479.1530; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.92-6.87 (m, 4H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.79 (s, 1H), 5.07-5.04 (m, 1H), 4.41-4.39 (m, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.17 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.08 (d, *J* = 19.2 Hz, 1H), 2.26 (s, 3H), 2.17-

2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 160.3, 144.6, 143.4, 142.2, 140.1, 133.2, 131.1 (2x), 128.5 (2x), 126.7 (2x), 125.9, 120.0, 119.0, 117.9, 112.6 (2x), 108.4, 70.6, 56.1, 55.2, 32.6, 30.5, 27.7, 21.3.

5-Methoxy-12-(toluene-4-sulfonyl)-11-(4-trifluoromethylphenyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4e)***. Yield = 86% (222 mg); Colorless solid; mp = 203-205 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{24}F_3O_5S$ 517.1297, found 517.1302; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 5.90 (s, 1H), 5.09 (s, 1H), 4.40 (s, 1H), 3.88 (s, 3H), 3.18 (dd, *J* = 5.2, 19.6 Hz, 1H), 3.11 (d, *J* = 19.6 Hz, 1H), 2.27 (s, 3H), 2.19-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 144.8, 143.5, 142.7, 139.5, 137.1, 132.5, 130.9 (q, *J* = 32.6 Hz), 130.0 (2x), 128.7 (2x), 126.7 (2x), 124.1 (q, *J* = 3.7 Hz, 2x), 123.7 (d, *J* = 270.7 Hz), 120.1, 119.9 (2x), 108.4, 71.0, 56.0, 32.6, 30.2, 27.5, 21.2.

5-Methoxy-11-(4-nitrophenyl)-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4f)***. Yield = 83% (205 mg); Colorless solid; mp = 204-206 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{24}NO_7S$ 494.1274, found 494.1277; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.82 (br s, 1H), 5.12-5.10 (m, 1H), 4.34-4.32 (m, 1H), 3.90 (s, 3H), 3.21-3.08 (m, 2H), 2.30 (s, 3H), 2.12 (t, *J* = 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 148.0, 144.8, 143.5, 143.2, 140.0, 139.5, 132.2, 130.8 (2x), 129.0 (2x), 126.7 (2x), 122.4 (2x), 120.2, 120.0, 117.6, 108.5, 71.3, 56.1, 32.6, 30.5, 27.5, 21.4.

11-Biphenyl-4-yl-5-methoxy-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4g)***. Yield = 82% (215 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{32}H_{29}O_5S$ 525.1736, found 525.1733; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.51-7.42 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 1.6, 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 4.49 (d, *J* = 1.6 Hz, 1H), 3.92 (s, 3H), 3.22 (dd, *J* = 4.8, 18.8 Hz, 1H), 3.15 (d, *J* = 18.8 Hz, 1H), 2.63-2.20 (m, 1H), 2.17 (s, 3H), 2.14-2.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 144.7, 143.4, 142.3, 139.9, 133.2, 133.1, 132.1, 130.8, 129.8 (2x), 128.4 (2x), 128.3 (2x), 127.5, 126.9, 126.8 (3x), 126.3, 126.0, 120.1, 119.8, 117.9, 108.4, 70.8, 56.1, 32.7, 30.4, 27.8, 21.2.

5-Methoxy-11-naphthalen-2-yl-12-(toluene-4-sulfonyl)-10-oxa-tricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4h)***. Yield = 84% (209 mg); Colorless solid; mp = 167-169 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{30}H_{27}O_5S$ 499.1579, found 499.1577; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.51-7.42 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 1.6, 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 1H), 5.13-5.11 (m, 1H), 4.49 (q, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 3.22 (dd, *J* = 5.2, 19.6 Hz, 1H), 3.15 (d, *J* = 19.2 Hz, 1H), 2.26-2.20 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 144.7, 143.5, 142.3, 139.9, 133.2, 133.1, 132.1, 130.8, 129.8, 128.4 (2x), 128.3, 127.5, 126.9, 126.81, 126.78 (2x), 126.3, 126.0, 120.1, 119.8, 118.0, 108.4, 70.8, 56.1, 32.7, 30.4, 27.8, 21.2.

11-(3,4-Dichlorophenyl)-5-methoxy-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4i)***. Yield = 80% (206 mg); Colorless solid; mp = 194-196 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{23}Cl_2O_5S$ 517.0643, found 517.0648; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 2.0, 8.4 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.81 (s, 1H), 5.09-5.07 (m, 1H), 4.40 (q, *J* = 1.6 Hz, 1H), 3.90 (s, 3H), 3.17 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.08 (d, *J* = 19.2 Hz, 1H), 2.31 (s, 3H), 2.13 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 144.8, 143.5, 143.1, 139.5, 133.5, 133.2, 132.5, 131.6, 131.1, 129.4, 129.3, 128.8 (2x), 126.8 (2x), 120.6, 120.0, 117.7, 108.5, 71.1, 56.1, 32.6, 30.3, 27.6, 21.3.

12-Benzenesulfonyl-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4j)***. Yield = 87% (189 mg); Colorless solid; mp = 210-212 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{25}H_{23}O_5S$ 435.1266, found 435.1269; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.15-6.98 (m, 8H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 5.10-5.08 (m, 1H), 4.45 (q, *J* = 2.8 Hz, 1H), 3.91 (s, 3H), 3.19 (dd, *J* = 5.6, 19.2 Hz, 1H), 3.10 (d, *J* = 19.2 Hz, 1H), 2.22-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 144.7, 143.5, 142.8, 133.4, 133.1, 131.6, 129.6 (2x), 129.2, 128.0 (2x), 127.3 (2x), 126.7 (2x), 120.1, 119.1, 117.9, 108.4, 70.8, 56.1, 32.6, 30.3, 27.7.

12-(4-Fluorobenzenesulfonyl)-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4k)***. Yield = 83% (188 mg); Colorless solid; mp = 181-183 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{25}H_{22}FO_5S$ 453.1172, found 453.1174; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18-7.15 (m, 2H), 7.04-7.02 (m, 2H), 6.94-6.90 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.74-6.69 (m, 2H), 5.82 (s, 1H), 5.11-5.09 (m, 1H), 4.45 (q, *J* = 3.2 Hz, 1H), 3.90 (s, 3H), 3.20 (dd, *J* = 5.6, 19.6 Hz, 1H), 3.10 (d, *J* = 19.6 Hz, 1H), 2.24-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (d, *J* = 252.4 Hz), 162.1, 144.7, 143.5, 138.8, 133.3, 133.0, 129.6 (2x), 129.4 (d, *J* = 9.1 Hz, 2x), 129.3, 127.4 (2x), 119.9, 119.3, 117.9, 115.0 (d, *J* = 22.0 Hz, 2x), 108.3, 70.8, 56.1, 32.6, 30.3, 27.7.

5-Methoxy-12-(4-methoxybenzenesulfonyl)-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol ***(4l)***. Yield = 87% (202 mg); Colorless solid; mp = 199-201 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{25}O_6S$ 465.1372, found 465.1372; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 2H), 7.17-7.13 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 8.8 Hz, 2H), 6.00 (br s, 1H), 5.04 (d, *J* = 1.6 Hz, 1H), 4.41 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.17 (dd, *J* = 5.2, 19.6 Hz, 1H), 3.08 (d, *J* = 19.2 Hz, 1H), 2.17-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 161.2, 144.5, 143.3, 134.4, 133.4, 132.9, 129.4 (2x), 128.9,

128.6 (2x), 127.1 (2x), 119.7, 119.3, 117.8, 113.0 (2x), 108.2, 70.4, 55.8, 55.2, 32.4, 30.2, 27.5.

12-Methanesulfonyl-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (***4m***). Yield = 73% (136 mg); Colorless solid; mp = 203-205 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{20}H_{21}O_5S$ 373.1110, found 373.1112; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.33 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.82 (br s, 1H), 5.15-5.12 (m, 1H), 4.35 (q, *J* = 3.2 Hz, 1H), 3.88 (s, 3H), 3.24 (dd, *J* = 5.2, 19.6 Hz, 1H), 3.16 (d, *J* = 19.2 Hz, 1H), 2.37 (s, 3H), 2.24 (dt, *J* = 3.2, 13.2 Hz, 1H), 2.13-2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 144.7, 143.6, 133.9, 133.2, 129.6, 129.2 (2x), 127.7 (2x), 119.0, 118.2, 117.8, 108.3, 70.7, 56.0, 45.0, 32.6, 30.3, 27.4.

12-(Butane-1-sulfonyl)-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (***4n***). Yield = 76% (157 mg); Colorless solid; mp = 156-158 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{23}H_{27}O_5S$ 415.1579, found 415.1580; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.33 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.79 (s, 1H), 5.15-5.12 (m, 1H), 4.31 (q, *J* = 3.2 Hz, 1H), 3.87 (s, 3H), 3.23 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.16 (d, *J* = 19.2 Hz, 1H), 2.41-2.34 (m, 1H), 2.29-2.20 (m, 2H), 2.13-2.09 (m, 1H), 1.29-1.19 (m, 2H), 1.11-1.02 (m, 2H), 0.66 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 144.7, 143.5, 133.8, 133.2, 129.7, 129.4 (2x), 127.7 (2x), 119.5, 117.9, 117.1, 108.3, 70.6, 56.0, 55.4, 32.6, 30.2, 27.5, 23.9, 21.2, 13.3.

5,6-Dimethoxy-11-phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene (***4o***). Yield = 86% (199 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1580; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 1H), 7.30-7.25 (m, 1H), 7.17-7.13 (m, 2H), 7.05-7.02 (m, 2H), 6.88 (s, 4H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.07-5.04 (m, 1H), 4.40 (q, *J* = 3.2 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.22 (dd, *J* = 5.2, 19.6 Hz, 1H), 3.13 (d, *J* = 19.6 Hz, 1H), 2.26 (s, 3H), 2.18-2.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 150.9, 146.9, 142.3, 139.9, 133.5, 132.7, 129.5 (2x), 129.1, 128.6 (2x), 127.2 (2x), 126.7 (2x), 125.6, 124.5, 119.2, 110.3, 70.8, 59.8, 55.7, 32.9, 30.4, 27.6, 21.2.

5,6-Dimethoxy-12-(toluene-4-sulfonyl)-11-p-tolyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene (***4p***). Yield = 89% (212 mg); Colorless solid; mp = 179-181 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{28}H_{29}O_5S$ 477.1736, found 477.1735; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 1H), 6.99-6.88 (m, 8H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.05-5.03 (m, 1H), 4.37-4.35 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.20 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.12 (d, *J* = 19.2 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.15-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 150.9, 146.9, 142.3, 140.1, 139.3, 132.8, 130.7, 129.4 (2x), 128.6 (2x), 127.9 (2x), 126.8 (2x), 125.7, 124.5, 118.8, 110.3, 70.7, 59.9, 55.8, 33.0, 30.5, 29.69, 21.33 (2x). Single-crystal X-Ray diagram: crystal of compound **4p** was grown by slow diffusion of EtOAc into a solution of compound **4p** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21, *a* = 11.0102(3) Å, *b* = 9.1251(2) Å, *c* = 11.4970(3) Å, *V* = 1154.80(5) Å^{3}, *Z* = 2, d_{calcd} = 1.371 g/cm^{3}, *F*(000) = 504, 2θ range 1.772~26.373^{o}, R indices (all data) R1 = 0.0359, wR2 = 0.0760.

6-Butoxy-5-methoxy-11-phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene (***4q***). Yield = 84% (212 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{30}H_{33}O_5S$ 505.2049, found 505.2047; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.17-7.13 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.87-6.81 (m, 5H), 5.06-5.04 (m, 1H), 4.41 (q, *J* = 1.6 Hz, 1H), 4.06-4.00 (m, 1H), 3.95-3.90 (m, 1H), 3.86 (s, 3H), 3.22 (dd, *J* = 5.2, 7.6 Hz, 1H), 3.15 (d, *J* = 19.2 Hz, 1H), 2.25 (s, 3H), 2.19-2.08 (m, 2H), 1.78-1.70 (m, 2H), 1.55-1.46 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 151.0, 146.2, 142.2, 139.9, 133.4, 132.7, 129.5 (2x), 129.1, 128.5 (2x), 127.2 (2x), 126.7 (2x), 125.7, 124.2, 119.3, 110.3, 72.0, 70.8, 55.8, 33.2, 32.4, 30.4, 27.6, 21.2, 19.2, 13.9.

6-Cyclopentyloxy-5-methoxy-11-phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene (***4r***). Yield = 88% (227 mg); Colorless solid; mp = 134-136 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{31}H_{33}O_5S$ 517.2049, found 517.2044; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 1H), 7.29-7.24 (m, 1H), 7.16-7.12 (m, 2H), 7.00-6.98 (m, 2H), 6.84-6.79 (m, 5H), 5.04-5.01 (m, 1H), 4.99-4.95 (m, 1H), 4.40 (q, *J* = 3.2 Hz, 1H), 3.85 (s, 3H), 3.18 (dd, *J* = 5.2, 19.2 Hz, 1H), 3.09 (d, *J* = 19.2 Hz, 1H), 2.24 (s, 3H), 2.20-2.07 (m, 2H), 1.84-1.69 (m, 6H), 1.65-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 150.8, 144.9, 142.1, 139.9, 133.4, 132.7, 129.5 (2x), 129.0, 128.4 (2x), 127.2 (2x), 126.6 (2x), 126.1, 123.8, 119.4, 110.4, 83.5, 70.8, 55.7, 33.6, 33.0, 32.7, 30.5, 27.6, 23.62, 23.56, 21.2.

5,6-Dimethoxy-8-methyl-11-phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene (***4s***). Yield = 80% (190 mg); Colorless solid; mp = 147-149 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{28}H_{29}O_5S$ 477.1736, found 477.1741; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.17-7.13 (m, 2H), 7.04-7.99 (m, 4H), 6.94-6.91 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.57 (dd, *J* = 2.0, 3.6 Hz, 1H), 4.37 (br s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.41 (q, *J* = 7.2 Hz, 1H), 2.40 (ddd, *J* = 0.8, 3.6, 12.8 Hz, 1H), 2.29 (s, 3H), 1.99-1.94 (m, 1H), 1.26 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 151.3, 147.9, 142.4, 140.1, 133.7, 131.2, 131.0, 129.4 (2x), 129.2, 128.7 (2x), 127.3 (2x), 126.8 (2x), 124.4, 119.5, 110.8, 77.8, 60.7, 55.7, 37.4, 31.0, 24.0, 21.4, 19.4. Single-crystal X-Ray diagram: crystal of compound **4s** was grown by slow diffusion of EtOAc into a solution of compound **4s** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 12.0995(7) Å, *b* = 11.0442(6) Å, *c* = 18.1654(10) Å, *V* = 2385.7(2) Å^{3}, *Z* = 4, d_{calcd} = 1.327 g/cm^{3}, *F*(000) = 1008, 2θ range 1.874~26.413^{o}, R indices (all data) R1 = 0.0503, wR2 = 0.1051.

11-Phenyl-12-(toluene-4-sulfonyl)-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (***4t***). Yield = 78% (163 mg); Colorless solid; mp = 157-158 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{25}H_{23}O_4S$ 419.1317, found 419.1315; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 3H), 7.17-7.13 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.04-7.02 (m, 2H), 6.90-6.85 (m, 3H),

6.87 (br s, 1H), 6.66 (dd, *J* = 0.8, 8.0 Hz, 1H), 5.10-5.08 (m, 1H), 4.47 (dd, *J* = 3.2, 4.8 Hz, 1H), 3.14 (dd, *J* = 5.6, 19.2 Hz, 1H), 3.05 (d, *J* = 19.2 Hz, 1H), 2.26 (s, 3H), 2.19-2.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 154.0, 142.4, 141.1, 139.8, 133.5, 129.6 (2x), 129.2, 128.7 (2x), 127.3 (2x), 126.83, 126.80 (2x), 121.5, 119.0, 118.4, 113.2, 71.0, 32.7, 30.8, 27.5, 21.3.

*(6-Hydroxy-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-12-yl)phenylmethanone (**4u**).* Yield = 57% (113 mg); Purple gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{23}O_4$ 399.1596, found 399.1562; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.15 (m, 2H), 7.10-6.90 (m, 8H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 5.85 (br s, 1H), 5.24-5.22 (m, 1H), 4.38 (dd, *J* = 1.2, 4.4 Hz, 1H), 3.78 (s, 3H), 3.39 (dd, *J* = 5.6, 19.2 Hz, 1H), 3.29 (d, *J* = 19.2 Hz, 1H), 2.25 (dt, *J* = 3.2, 12.8 Hz, 1H), 2.11 (dt, *J* = 2.0, 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 158.9, 144.3, 143.4, 140.0, 135.4, 134.6, 130.8, 129.4 (2x), 129.1, 128.8 (2x), 127.4 (2x), 127.3 (2x), 118.2, 117.7, 116.9, 108.3, 70.2, 55.9, 32.5, 32.3, 26.9.

*(6-Hydroxy-5-methoxy-11-methyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-12-yl)phenylmethanone (**4v**).* Yield = 62% (104 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{21}H_{21}O_4$ 337.1440, found 337.1442; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.31 (m, 5H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 5.76 (br s, 1H), 5.03-5.00 (m, 1H), 4.16 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 3.13 (d, *J* = 3.6 Hz, 2H), 2.12 (dt, *J* = 3.6, 12.8 Hz, 1H), 2.02 (dt, *J* = 1.6, 12.8 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 160.1, 144.2, 143.5, 141.6, 134.9, 131.3, 128.30 (2x), 128.27 (2x), 118.1, 117.9, 116.4, 108.4, 69.8, 56.0, 32.4, 31.3, 26.8, 20.8.

*2-(2-Allyl-3-hydroxy-4-methoxybenzylidene)-1-phenylbutane-1,3-dione (**3v**).* Yield = 10% (17 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{21}H_{21}O_4$ 337.1440, found 337.1446; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.84-7.81 (m, 2H), 7.50-7.45 (m, 1H), 7.36-7.32 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.03-5.93 (m, 1H), 5.74 (s, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.01 (dq, *J* = 1.6, 17.2 Hz, 1H), 3.77 (s, 3H), 3.60 (dt, *J* = 1.6, 6.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 195.8, 147.9, 143.5, 139.9, 139.1, 136.2, 135.7, 133.7, 129.1 (2x), 128.6 (2x), 125.9, 125.1, 121.9, 115.6, 108.3, 55.8, 30.4, 27.2.

*6-Hydroxy-5-methoxy-11-phenyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraene-12-carboxylic acid ethyl ester (**4w**).* Yield = 26% (48 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{22}H_{23}O_5$ 367.1546, found 367.1548; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 5.14-5.12 (m, 1H), 4.18-4.16 (m, 1H), 4.01-43.95 (m, 1H), 3.93-3.86 (m, 1H), 3.85 (s, 3H), 3.26 (dd, *J* = 5.6, 19.2 Hz, 1H), 3.15 (d, *J* = 19.6 Hz, 1H), 2.19-2.13 (m, 1H), 2.04-2.00 (m, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 161.6, 144.3, 143.3, 137.1, 134.9, 128.6, 128.3 (2x), 127.4 (2x), 118.34, 118.31, 108.2, 108.1, 70.2, 59.6, 55.9, 32.4, 30.4, 26.8, 13.5.

*3-(3,4-Dimethoxy-2-propenylphenyl)-1-phenylpropynone (**4x-1**).* Yield = 78% (119 mg); Colorless solid; mp = 97-99 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{19}O_3$ 307.1334, found 307.1335; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.61-7.57 (m, 1H), 7.52-7.48 (m, 2H), 7.01 (s, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.17 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 154.7, 151.0, 141.7, 139.8, 138.5, 136.8, 133.1, 129.5, 128.7 (2x), 128.6 (2x), 127.4, 122.9, 120.3, 108.1, 61.4, 55.9, 13.1.

*12-Benzenesulfonyl-5-methoxy-11-methyl-10-oxatricyclo[7.3.1.0^{2,7}]trideca-2,4,6,11-tetraen-6-ol (**4aa**).* Yield = 80% (149 mg); Colorless solid; mp = 204-205 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{20}H_{21}O_5S$ 373.1110, found 373.1112; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.47-7.43 (m, 1H), 7.38-7.33 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.56 (br s, 1H), 4.97-4.94 (m, 1H), 4.15 (br s, 1H), 3.82 (s, 3H), 3.11-2.99 (m, 2H), 2.03 (s, 3H), 1.99-1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 144.6, 143.6, 143.4, 132.9, 132.0, 128.6 (2x), 126.2 (2x), 119.4, 117.7, 114.9, 108.2, 70.2, 56.0, 32.3, 30.3, 27.5, 19.0.

*2-(5,6-Dimethoxy-1,2-dihydronaphthalen-1-yl)-1-phenyl-2-(toluene-4-sulfonyl)ethanone (**5a**). and 2-(5,6-Dimethoxy-1,2-dihydronaphthalen-1-yl)-1-phenyl-2-(toluene-4-sulfonyl)ethanone (**5b**).* *t*-BuOK (225 mg, 2.0 mmol) was added to a solution of **1a** (137 mg, 0.5 mmol) in toluene (10 mL) at rt. The reaction mixture was stirred at rt for 10 min. **2b** (103 mg, 0.5 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 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 = 8/1~4/1) afforded **5a** and **5b**. For **5a**: Yield = 30% (69 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1577; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.32-7.28 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.97 (dd, *J* = 3.2, 9.6 Hz, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 6.24-6.20 (m, 1H), 5.46 (d, *J* = 10.4 Hz, 1H), 3.65 (s, 3H), 3.62 (s, 3H), 3.33-3.27 (m, 1H), 2.54-2.42 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.1, 152.0, 144.9, 144.8, 137.5, 135.4, 132.9, 129.6 (2x), 129.4 (2x), 127.9 (2x), 127.6 (2x), 127.5, 127.4, 125.4, 125.2, 121.9, 110.5, 69.0, 61.0, 55.6, 37.7, 26.3, 21.5. For **5b**: Yield = 28% (65 mg); Colorless gum; HRMS (ESI, M$^+$+1) calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1573; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.47-7.43 (m, 1H), 7.28-7.25 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 9.6 Hz, 1H), 5.71-5.66 (m, 1H), 5.29 (d, *J* = 6.0 Hz, 1H), 4.09-4.06 (m, 1H), 3.86 (s, 3H), 3.55 (s, 3H), 2.44-2.42 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 152.3, 144.5, 144.5, 137.3, 136.1, 133.5, 129.3 (2x), 129.2 (2x), 128.32 (2x), 128.25 (2x), 127.33, 127.27, 126.8, 124.9, 122.4, 110.9, 72.6, 60.9, 55.8, 37.2, 26.0, 21.5.

*3-(2-Allyl-3-hydroxy-4-methoxyphenyl)-2-methanesulfonyl-1-phenylpropenone (**3c**).* NaOAc (82 mg, 1.0 mmol) was add-

ed to a solution of **1m** (99 mg, 0.5 mmol) in toluene (10 mL) at rt. The reaction mixture was stirred at rt for 10 min. **2a** (96 mg, 0.5 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 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 = 8/1~4/1) afforded **3c**. Yield = 60% (112 mg); Colorless solid; mp = 156-158 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}O_5S$ 373.1110, found 373.1112; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.81 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.43 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 5.99-5.89 (m, 1H), 5.80 (br s, 1H), 5.13 (dd, *J* = 1.6, 10.0 Hz, 1H), 5.06 (dd, *J* = 1.6, 16.8 Hz, 1H), 3.74 (s, 3H), 3.59 (d, *J* = 6.0 Hz, 2H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 148.4, 143.6, 141.3, 137.4, 135.4, 135.1, 134.1, 129.7 (2x), 128.5 (2x), 125.5, 124.1, 122.1, 116.1, 108.1, 55.8, 43.6, 30.3. Single-crystal X-Ray diagram: crystal of compound **3c** was grown by slow diffusion of EtOAc into a solution of compound **3c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group C 2/c, *a* = 10.3098(6) Å, *b* = 19.1132(9) Å, *c* = 19.3897(10) Å, *V* = 3769.6(3) Å^3, *Z* = 8, d_{calcd}= 1.312 g/cm^3, *F*(000) = 1568, 2θ range 2.129~26.381^o, R indices (all data) R1 = 0.0446, wR2 = 0.0885.

*A representative synthetic procedure of skeleton **6** is as follows:* NH_4OAc (39 mg, 0.5 mmol) was added to a solution of **1a** (137 mg, 0.5 mmol) in co-solvent of toluene and HOAc (v/v = 1/1, 10 mL) at rt. The reaction mixture was stirred at rt for 10 min under Dean-Stark distillation apparatus. **2m-2n** (0.5 mmol) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 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 = 8/1~4/1) afforded **6**.

*6,7-Dimethoxy-1-methyl-3-phenyl-4-(toluene-4-sulfonyl)-1,4a,9,9a-tetrahydro-2-oxafluorene (**6a**).* Yield = 83% (198 mg); Colorless solid; mp = 210-212 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}O_5S$ 477.1736, found 477.1737; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.30-7.25 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.17-7.13 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 4.53 (d, *J* = 6.0 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.86-3.78 (m, 1H), 3.23 (dd, *J* = 6.8, 15.6 Hz, 1H), 2.73 (dd, *J* = 2.0, 15.6 Hz, 1H), 2.44-2.38 (m, 1H), 2.31 (s, 3H), 1.38 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 148.5, 148.4, 142.5, 140.2, 137.2, 133.9, 131.5, 129.5 (2x), 129.2, 128.7 (2x), 127.4 (2x), 126.9 (2x), 117.1, 109.8, 107.9, 73.3, 56.1, 56.0, 43.4, 42.7, 34.5, 21.4, 19.0. Single-crystal X-Ray diagram: crystal of compound **6a** was grown by slow diffusion of EtOAc into a solution of compound **6a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 9.2620(5) Å, *b* = 29.1519(15) Å, *c* = 10.0839(5) Å, *V* = 2719.9(2) Å^3, *Z* = 4, d_{calcd} = 1.371 g/cm^3, *F*(000) = 1176, 2θ range 1.397~26.722^o, R indices (all data) R1 = 0.0446, wR2 = 0.0895.

*6,7-Dimethoxy-1,3-diphenyl-4-(toluene-4-sulfonyl)-1,4a,9,9a-tetrahydro-2-oxafluorene (**6b**).* Yield = 82% (221 mg); Colorless solid; mp = 186-188 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{33}H_{31}O_5S$ 539.1892, found 539.1895; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.39-7.23 (m, 6H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.16-7.12 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.78 (s, 1H), 4.68 (d, *J* = 6.0 Hz, 1H), 4.61 (d, *J* = 10.0 Hz, 1H), 4.00 (s, 3H), 3.89 (s, 3H), 3.10 (dd, *J* = 6.4, 15.6 Hz, 1H), 2.83-2.78 (m, 1H), 2.56 (d, *J* = 15.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 148.54, 148.48, 142.6, 140.0, 138.3, 137.4, 133.5, 131.3, 129.4 (2x), 129.1, 128.71 (2x), 128.67, 128.5 (2x), 127.8 (2x), 127.3 (2x), 127.0 (2x), 117.5, 109.8, 108.1, 79.4, 56.1, 56.0, 43.5, 42.2, 33.9, 21.4. Single-crystal X-Ray diagram: crystal of compound **6b** was grown by slow diffusion of EtOAc into a solution of compound **6b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group C 2/c, *a* = 21.8205(14) Å, *b* = 11.6934(6) Å, *c* = 22.0291(15) Å, *V* = 5596.1(6) Å^3, *Z* = 8, d_{calcd} = 1.279 g/cm^3, *F*(000) = 2272, 2θ range 1.857~26.365^o, R indices (all data) R1 = 0.0455, wR2 = 0.1083.

DFT calculation: Geometry optimizations and frequency calculations were carried out by using B3LYP hybrid functional[15] in combination with 6-31+G(d) basis set. Empirical dispersion corrections were included in the calculations with Grimme's D3 method.[16] The optimized geometries have been confirmed to be local minima (all positive vibrational frequencies) or transition states (one imaginary vibrational frequency). Free energy corrections were performed at 1 atm and 384.15 K. All calculations were accomplished by Gaussian 09 program.[17]

ASSOCIATED CONTENT

Supporting Information

Scanned photocopies of NMR spectral data for all compounds, DFT theoretical calculations data and X-ray analysis data of **3c**, **4a**, **4b**, **4p**, **4s**, **6a**, and **6b**. 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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