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In(OTf)$_3$-catalyzed intramolecular hydroarylation of α-phenylallyl β-ketosulfones – synthesis of sulfonyl 1-benzosuberones and 1-tetralones†

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In(OTf)$_3$-catalyzed intramolecular hydroarylation of α-phenylallyl β-ketosulfones provides sulfonyl 1-benzosuberones and 1-tetralones in moderate to good yields in refluxing $(CH_2Cl)_2$ under open-vessel and easy-operation reaction conditions. A plausible mechanism is proposed and discussed. This highly regioselective protocol provides an atom-economic ring-closure route.

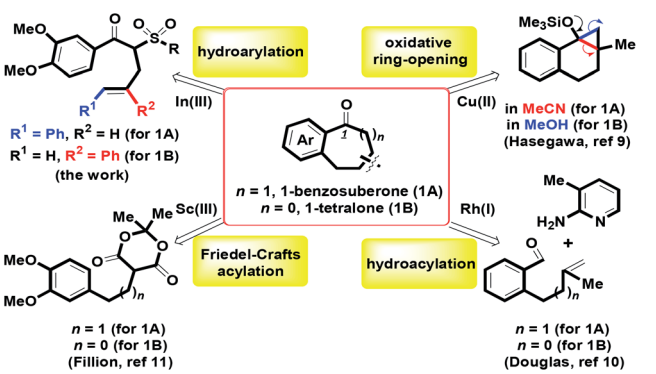
Introduction

Substituted benzocycles with a medium ring (six and seven-membered rings) commonly serve as core structures in many potential bioactive molecules,[1,2] natural products[3,4] and versatile synthetic blocks.[5,6] According to our recent reports, efficient synthesis of diverse tetralins and benzosuberans has been investigated *via* $BF_3 \cdot OEt_2$ mediated stereocontrolled formal (4 + 2) and (5 + 2) cycloaddition of 4-alkenols with veratrol.[7] For heterocyclic ring frameworks, we also provided a one-pot route for benzofused six- and seven-membered oxacycles by *m*CPBA-mediated intramolecular oxidative annulation of *ortho*-crotyl or cinnamyl arylaldehydes.[8] On the basis of previous experience, herein, the major works were focused on the preparation of 1-benzosuberone **1A** and 1-tetralone **1B** using the same synthetic route. By transition metal-catalyzed and Brønsted acid-promoted intramolecular benzannulation, a considerable number of attempts have been developed to prepare the skeletons of 1-benzosuberone and 1-tetralone *via* a kind of synthetic method.[9–11] For example, by the involvement of different solvents (MeCN and MeOH), Hasegawa and co-workers demonstrated that $Cu(BF_4)_2$-catalyzed regioselective oxidative ring-opening of benzofused bicyclic cyclopropyl silyl ethers provided two benzofused ring systems of **1A** and **1B** (Scheme 1).[9] Douglas *et al.* investigated whether the *ortho*-side arm length of benzaldehyde could regulate the hydroacylation of homoallyl ($n = 1$) or *o*-allyl ($n = 0$) with 2-aminopyridine to generate **1A** and **1B** in the presence of rhodium(I) catalysts.[10] By controlling the Sc(III) complex as the Lewis acid, the Fillion group explored efficient Friedel–Crafts acylation of α-arylpropyl and α-arylethyl Meldrum's acid derivatives for the formation of **1A** and **1B**.[11]

In spite of these attractive advancements, we envisioned that further investigation of a novel and efficient synthetic method for the formation of **1A** and **1B** was still highly desired. Herein, we present an In(OTf)$_3$-mediated synthesis of 1-tetralone and 1-benzosuberone *via* one-pot intramolecular hydroarylation of α-phenylallyl β-ketosulfones in refluxing $(CH_2Cl)_2$ *via* one carbon–carbon bond formation. For the hydroarylation of arenes with multiple bonds, different transition metals-catalyzed reactions become one of the most widely used strategies for diversified carbocycles and heterocycles.[12] These major metals include iridium,[13] cobalt,[14] platinum,[15] ruthenium,[16] bismuth,[17] gold,[18] rhodium,[19] zinc[20] and indium.[21] Other recent Brønsted and Lewis acid-mediated routes for atom-economic hydroarylation reactions have been thoroughly investigated.[22]

Results and discussion

On the basis of our previous reports,[23] starting substrates **4** were easily prepared *via* a three-step route, including (1) $CuBr_2$-



Scheme 1 Intramolecular routes of 1-benzosuberone **1A** and 1-tetralone **1B**.

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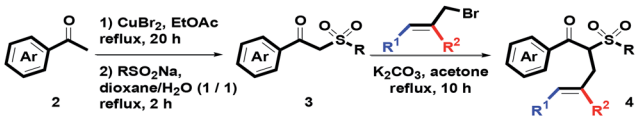
† Electronic supplementary information (ESI) available: Scanned photocopies of NMR spectral data for all compounds and X-ray analysis data of compounds **5a**, **5b**, **6a** and **10c**. CCDC 1915762, 1915763, 1915765 and 1915767. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra01962c

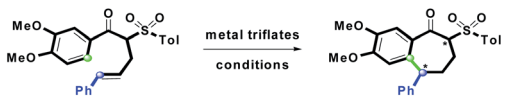


Scheme 2 Synthetic route of starting materials **4**.

mediated α-bromination of oxygenated acetophenones **2** in refluxing EtOAc for 20 h, (2) nucleophilic substitution of the resulting α-bromoacetophenone with RSO_2Na in a co-solvent of dioxane and water (v/v = 1/1) at reflux for 2 h and (3) α-phenylallylation of the corresponding β-ketosulfones **3** in the presence of K_2CO_3 in boiling acetone for 10 h, as shown in Scheme 2.

Among our researches on metal triflate-promoted synthetic applications of carbocyclic and heterocyclic skeletons,[24,25] especially, the synthesis of substituted pyridazines was accomplished by the $In(OTf)_3$-mediated cyclocondensation of α-propargyl β-ketosulfone with N_2H_4.[24] With the previous synthetic experience in mind, herein, the Lewis acid $In(OTf)_3$ was preferred to examine the hydroarylation of α-phenylallyl β-ketosulfone. The initial study (Table 1) was commenced with the treatment of 3,4-dimethoxyacetophenone (**4a**, Ar = 3,4-$(MeO)_2C_6H_3$, R = Tol, R^1 = Ph, R^2 = H, 1.0 mmol) in $(CH_2Cl)_2$ (20 mL) at 25 °C for 20 h using catalytic amounts of $In(OTf)_3$ (10 mol%). However, no desired **5a** was detected, and the starting material **1a** was recovered in a 90% yield (entry 1). By elevating the reaction temperature to reflux (25 → 84 °C), the yield of **5a** was increased to 91% (entry 2).

Table 1 Benzannulation conditions[a]

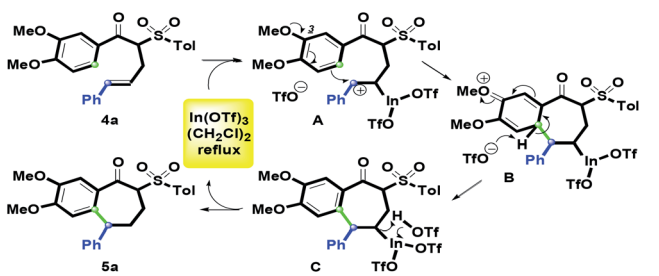


Entry	Metal triflates	Temp.	Solvent	Time	5a[b] (%)
1	$In(OTf)_3$ (10)	25	$(CH_2Cl)_2$	20	—[c]
2	**$In(OTf)_3$ (10)**	**84**	**$(CH_2Cl)_2$**	**20**	**91**
3	$In(OTf)_3$ (5)	84	$(CH_2Cl)_2$	20	41
4	$In(OTf)_3$ (15)	84	$(CH_2Cl)_2$	20	80
5	$In(OTf)_3$ (20)	84	$(CH_2Cl)_2$	20	63
6	$In(OTf)_3$ (10)	101	$MeNO_2$	20	55
7	$In(OTf)_3$ (10)	77	CCl_4	20	61
8	$In(OTf)_3$ (10)	153	DMF	20	—[d]
9	$In(OTf)_3$ (10)	84	$(CH_2Cl)_2$	15	75
10	$In(OTf)_3$ (10)	84	$(CH_2Cl)_2$	30	82
11	$Sn(OTf)_2$ (10)	84	$(CH_2Cl)_2$	20	—[c]
12	$Tm(OTf)_3$ (10)	84	$(CH_2Cl)_2$	20	—[c]
13	$Sc(OTf)_3$ (10)	84	$(CH_2Cl)_2$	20	47
14	$Ga(OTf)_3$ (10)	84	$(CH_2Cl)_2$	20	56
15	$Sc(OTf)_3$ (10)	84	$(CH_2Cl)_2$	15	30
16	AgOTf (10)	84	$(CH_2Cl)_2$	30	72
17	$Cu(OTf)_2$ (10)	84	$(CH_2Cl)_2$	20	78
18	$Fe(OTf)_3$ (10)	84	$(CH_2Cl)_2$	20	86
19	$Bi(OTf)_3$ (10)	84	$(CH_2Cl)_2$	20	84
20	$Fe(OTf)_3$ (10)	84	$(CH_2Cl)_2$	30	70

[a] The reactions were run on a 1.0 mmol scale with **4a**, metal triflate (mol%), temp. (°C), solvent (20 mL), time (h). [b] Isolated yields. [c] No reaction. [d] Complex products.

After adjusting the catalytic amounts of $In(OTf)_3$ from 10 to 5, 15 and 20 mol%, however, no better yields of **5a** were observed (entries 3–5). This meant that 10 mol% amounts of $In(OTf)_3$ were appropriate to trigger the reaction completely. Solvent screening was performed next. It was found that the reaction had low yields (55% and 61%) in $MeNO_2$ and CCl_4, respectively (entries 6 and 7), while no desired product was detected in DMF (entry 8). By changing the reaction time (20 → 15 and 30 h), the yields decreased to 75% and 82% (entries 9 and 10). From these observations, several commercially available metal triflates were examined next including: $Sn(OTf)_2$, $Tm(OTf)_3$, AgOTf, $Cu(OTf)_2$, $Sc(OTf)_3$, $Ga(OTf)_3$, $Fe(OTf)_3$ and $Bi(OTf)_3$. However, no isolation of the desired **5a** was observed and only **4a** was recovered under $Sn(OTf)_2$ or $Tm(OTf)_3$-mediated reaction (entries 11 and 12). After changing metal triflate to $Sc(OTf)_3$ or $Ga(OTf)_3$, better reactivity (47%, 56%) was observed (entries 13 and 14). To compare with $In(OTf)_3$ and $Sc(OTf)_3$, a diminished time (15 h) showed that $Sc(OTf)_3$ couldn't improve the yield (30%, entries 9 and 15). Subsequently, by replacing metal triflates with AgOTf or $Cu(OTf)_2$, **5a** could be isolated in 72% and 78% yields (entries 16 and 17). Furthermore, $Fe(OTf)_3$ and $Bi(OTf)_3$ provided similar yields for $In(OTf)_3$ (entries 18 and 19). In comparison with $In(OTf)_3$ and $Fe(OTf)_3$, an elongated time (30 h) described that $Fe(OTf)_3$ couldn't obtain better yield (70%, entries 10 and 20). From the results, we concluded that $In(OTf)_3$ was a key promoter affecting the benzannulation of α-cinnamyl β-ketosulfone **4a**. On the basis of ^{1}H-NMR spectra, the ratios of diastereomer **5a** were determined as an approximate ratio of 2/1 (for *trans*/*cis*) in entries 1–18. The configuration of major isomer of **5a** has to be found out as far as there is a ratio 2/1 of two isomers and one can be isolated from another by crystallization. The stereochemical structure of one isomer **5a** with α,δ-*trans*-configurated centers was determined by single-crystal X-ray analysis.[26]

On the basis of the experimental results, a plausible mechanism for the formation of **5a** is illustrated in Scheme 3. Initially, **4a** reacts with $In(OTf)_3$ to get benzylic carbocation **A** with an $In(OTf)_2$ arm. Then, the methoxy group on the C-3 position of the aryl ring promotes intramolecular electrophilic annulation to yield **B** *via* one carbon–carbon bond (green) formation. Next, the *in situ* generated triflate anion



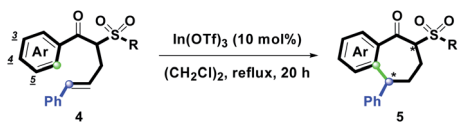
Scheme 3 Plausible mechanism.

deprotonates the proton of **B** to give **C** under the dehydrogenative aromatization process. Furthermore, **5a** is afforded by complexation of $In(OTf)_2$ moiety on **C** and the resulting TfOH. Subsequently, $In(OTf)_3$ could be regenerated for the next catalytic cycle. For the conversion from **C** to **5a**, Nishizawa *et al.* reported similar results for the $Hg(OTf)_2$-promoted the synthesis of vinyl-containing tetralins.[27]

To study the substrate scope and limitation of this route, we applied the optimal conditions established (Table 1, entry 2) to investigate $In(OTf)_3$ mediated intramolecular ring-closure of **4a–4n**. As shown in Table 2, 1-benzosuberones **5a–5l** were obtained in a yield range of 84–95% except for **5m** and **5n**. By use of the oxygenated aryl group (Ar = 3,4-$(MeO)_2C_6H_3$, 3,4-$CH_2O_2C_6H_3$, 3,4,5-$(MeO)_3C_6H_2$, and 3-$MeOC_6H_4$), the R substituents with aliphatic groups, and electron-donating, electron-neutral, electron-withdrawing aromatic groups were well-tolerated (entries 1–12). The diastereomeric ratios of (dr) **5a–5l** were determined as an approximate range of 5/1–1/1 based on the ^{1}H-NMR spectrum. On the other hand, when the R group was chosen as Tol and the Ar group was changed from oxygenated arenes to heterocyclic arenes, entries 13 and 14 showed that 2-thienyl and 2-furyl groups could not obtain the desired **5m** and **5n** and only complex products were observed. These complex cycloadducts with different stereoisomers could result from intramolecular Diels–Alder cycloaddition of 2-thienyl or 2-furyl and the phenylallyl group.

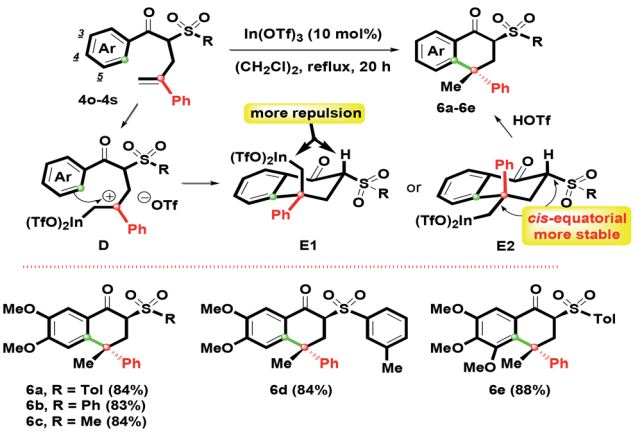
With the results in hand, adjusting the α-substituent of β-ketosulfones **3** from a cinnamyl to 2-phenylallyl group was the next aim, as shown in Scheme 4. By controlling the Ar group as the oxygenated substituents (3,4-$(MeO)_2C_6H_3$ and 3,4,5-$(MeO)_3C_6H_2$), **4o–4s** with different sulfonyl groups were easily

Table 2 Synthesis of **5a–5n**[a]



Entry	**4**, Ar=, R=	**5**[b] (%, dr)
1	**4a**, 3,4-$(MeO)_2C_6H_3$, Tol	**5a**, 91, 2/1
2	**4b**, 3,4-$(MeO)_2C_6H_3$, Ph	**5b**, 90, 4/1
3	**4c**, 3,4-$(MeO)_2C_6H_3$, 4-FC_6H_4	**5c**, 86, 5/1
4	**4d**, 3,4-$(MeO)_2C_6H_3$, 4-$MeOC_6H_4$	**5d**, 89, 1/1
5	**4e**, 3,4-$(MeO)_2C_6H_3$, 4-*n*BuC_6H_4	**5e**, 87, 1/1
6	**4f**, 3,4-$(MeO)_2C_6H_3$, Me	**5f**, 90, 3/1
7	**4g**, 3,4-$(MeO)_2C_6H_3$, *n*Bu	**5g**, 94, 1/1
8	**4h**, 3,4-$CH_2O_2C_6H_3$, Tol	**5h**, 93, 1/1
9	**4i**, 3,4,5-$(MeO)_3C_6H_2$, Tol	**5i**, 90, 3/1
10	**4j**, 3,4,5-$(MeO)_3C_6H_2$, Ph	**5j**, 95, 3/1
11	**4k**, 3,4,5-$(MeO)_3C_6H_2$, Me	**5k**, 92, 3/1
12	**4l**, 3-$MeOC_6H_4$, Tol	**5l**, 84, 1/1
13	**4m**, 2-Thienyl, Tol	**5m**, —[c]
14	**4n**, 2-Furyl, Tol	**5n**, —[c]

[a] The reactions were run on a 1.0 mmol scale with **4**, $In(OTf)_3$ (10 mol%), reflux (84 °C), $(CH_2Cl)_2$ (20 mL), 20 h. [b] Isolated yields (ratio: *trans*/*cis*). [c] Unknown and unidentified complex products.

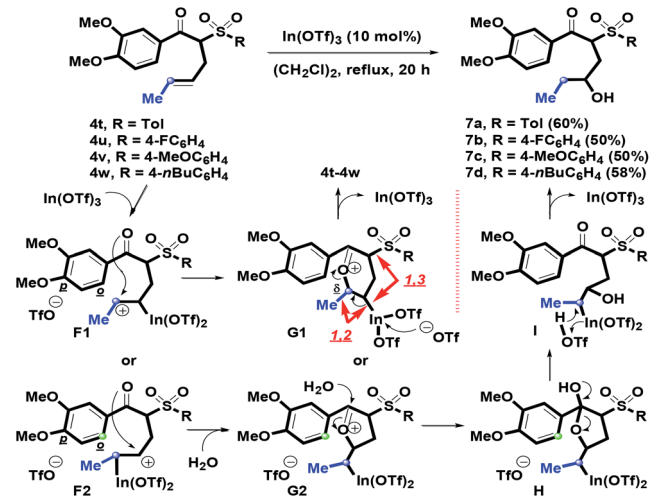


Scheme 4 Synthesis of **6a–6e**.

prepared in good yields by the K_2CO_3-mediated α-phenylallylation of β-ketosulfones with 2-phenylallyl bromide in boiling acetone for 10 h (see ESI†). According to the above conditions, 1-tetralones **6a–6e** were obtained in 83–88% yields *via* the $In(OTf)_3$ mediated intramolecular ring-closure of **4o–4s**. Compared with the formation of **5a–5l**, interestingly, **6a–6e** were generated in the sole isomer.

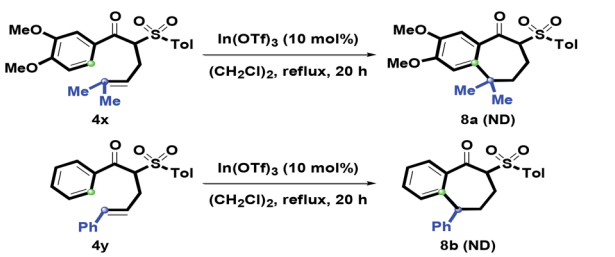
By the complexation of **4o–4s** and $In(OTf)_3$, the benzylic carbocation **D** initially formed with a primary $In(OTf)_2$ arm could generate two possible chair-like conformations **E1** and **E2**. For the relative configuration of **E1** and **E2**, the quaternary stereochemical center was the only difference. **E1** possessed more repulsion since the hydrogen and the primary $In(OTf)_2$ arm were orientated as a *cis*-configuration. Compared with **E1**, the primary $In(OTf)_2$ arm and sulfonyl group in **E2** were preferred for arranging as a equatorial position (*cis*-form) due to its higher stability and lower steric hindrance that was revealed. Then, by the participation of TfOH, **6a–6e** were afforded by complexation of $In(OTf)_2$ moiety on **E2**. This route provided highly effective regio- and stereocontrolled intramolecular hydroarylation to construct two stereochemical centers. The stereochemical structure of **6a** with the α,γ-configurated centers was determined by single-crystal X-ray crystallography.[26] On the basis of our observations, we found that the chair-like intermediate with a six-membered ring (for 1-tetralone skeleton) could trigger the generation of one isomer easier than the seven-membered ring intermediate (for 1-benzosuberone skeleton) *via* intramolecular electrophilic annulation.

In the next stage, we switched the α-substituent of β-ketosulfones **3** from aromatic phenylallyl groups into an aliphatic methylallyl (crotyl) group to examine intramolecular annulation. By the K_2CO_3-mediated α-crotylation of β-ketosulfones **3**, **4t–4w** with a mixture of *E*- and *Z*-form isomers were provided in modest to good (76–80%) yields. In particular, **7a–7d** were isolated as the major regioisomers, and the hydrated products displaced the predicted benzofused bicycles (Scheme 5). Firstly, **F1** or **F2** containing a secondary carbocation was generated *via* the $In(OTf)_3$-complexation of an α-alkenyl motif on **4t–4w**. Then, the lone-pair of oxygen atoms on a *para*-methoxy group could force the carbonyl group to stabilize the secondary carbocation



Scheme 5 Synthesis of 7a–7d.

and provide the oxonium cation **G1** or **G2** with a five or six-membered ring under intramolecular annulation. Compared with the formation of 1-benzosuberone (derived from **A** with a stable benzylic carbocation), however, the methoxy group on the arene ring of **F1** or **F2** could not initiate the intramolecular *o*-carbon addition process because the seven- or six-membered ring rather than the six (for **F1**) or five- (for **F2**) membered ring was undesirable for cyclizing. For the relative configuration of **G1**, 1,3-repulsion between the sulfonyl group and the indium side arm and 1,2-repulsion between the methyl group and the indium side arm were generated such that an *in situ* formed triflate anion mediating the reversed pathway may occur. Next, by participation of H_2O (from $(CH_2Cl)_2$ solvent),[28] transformation from **G2** to **H** could be achieved by the intermolecular addition of H_2O on the oxocarbenium ion of **G2**. After ring-opening of tetrahydrofuran ring on **H**, **I** was generated. You and coworkers have demonstrated the phenomenon to the formation of 2,2-disubstituted 2,3-dihydrofurans.[29a] For the $In(OTf)_3$-mediated intermolecular Michael addition of enone with H_2O or alcohols, Loh *et al.* reported similar results for preparing γ-hydroxy or alkoxyketones.[29b] Following the triflic acid-promoted deindiumation of **H**, the removal of $In(OTf)_3$ afforded **7a–7d** (50–60%). From the above results, we understood that R^1 (phenyl or methyl) was a key substituent that controlled intramolecular benzannulation.

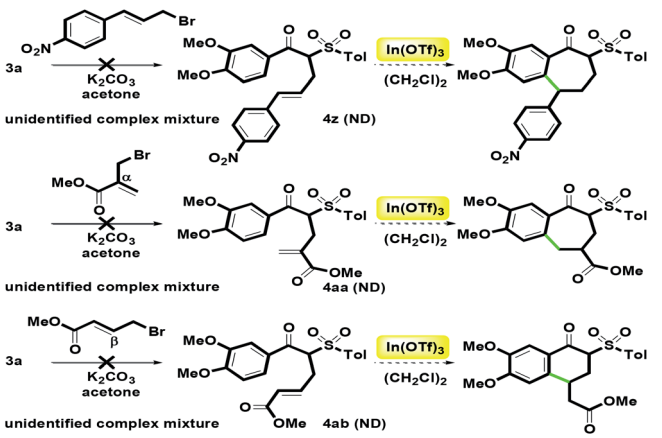


Scheme 6 Reaction of 4x–4y.

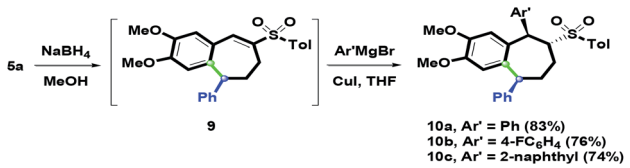
After examining the one-pot synthetic route, **4x** with an α-prenyl group was also examined (Scheme 6). In particular, treatment of **4x** with $In(OTf)_3$ afforded a complex dehydrated mixture *via* the formation of tertiary carbocation, and no desired product **8a** was detected. Adjusting the oxygenated Ar ring to a simple phenyl ring was also tested, however, no isolation of **8b** was observed under the above reaction conditions. After increasing the amount of $In(OTf)_3$ to 50 mol%, there was no generation of **8b**. On the basis of this phenomenon, we understood that the oxygenated group on Ar was the key factor in causing the formation of 1-benzosuberone *via* intramolecular benzannulation.

For other substituents at alkenyl moiety, we examined three commercially available allyl bromides, including (4-nitrophenyl)allyl bromide, α-bromomethyl methyl acrylate and β-bromomethyl methyl acrylate (Scheme 7). When the alkylation reaction of **3a** was treated with the three bromides in the presence of K_2CO_3, unidentified complex mixture were detected. Many attempts to desired products **4z**, **4aa** and **4ab** failed. Based on the results, we found that alkenyl moiety was not suitable to the two kinds of acrylate groups and the electron-withdrawing 4-nitrophenyl group. Therefore, we had no enough amounts of α-alkenyl β-ketosulfones **4z–4ab** to examine the $In(OTf)_3$-catalyzed intramolecular hydroarylation. Although the overall substrate scope is limited, the present route can provide the aromatic group (two kinds of phenylallyl) and the aliphatic group (crotyl) in the alkenyl moiety.

As the synthetic application of the $In(OTf)_3$-mediated intramolecular ring-closure, **5a** was chosen as the starting substrate to investigate synthetic applications (Scheme 8). When **5a** was treated with $NaBH_4$ in MeOH, the cyclic vinyl sulfone **9** was generated *via* a one-pot reduction and the spontaneous dehydration process. The dehydration process of the resulting β-hydroxysulfone could be spontaneous due to the acidic proton alfa to sulfone fragment. Furthermore, conjugated addition of **9** was studied. By choosing the Ar′ group as the aryl substituents (phenyl, 4-fluorophenyl and 2-naphthyl), **10a–10c** with the 1,5-*syn*-diaryl group were afforded in 83%, 76% and 74% yields, respectively, *via* Michael addition Ar′ copper species to vinyl



Scheme 7 Unsuccessful synthesis of 4z–4aa.



Scheme 8 Synthesis of **10a–10c**.

sulfones with Ar′MgBr and CuI. The stereochemical structure of **10c** was determined by single-crystal X-ray crystallography.[26] The results showed that the two aryl groups were orientated as *syn*-face. One possible reason is that the generated sandwich interaction for the aromatic (Ar)–copper–aromatic (Ar′) could control the introduction face of the Ar′ group. After the protonation of α-carbanion, three stereochemical centers were installed as the *trans–trans* conformation.

Conclusion

In summary, we have, herein, developed an $In(OTf)_3$-promoted facile and efficient one-pot synthesis of sulfonyl 1-benzosuberones and 1-tetralones *via* intramolecular hydroarylation of α-phenylallyl β-ketosulfones in refluxing $(CH_2Cl)_2$ in moderate to good yields under open-vessel and easy-operational reaction conditions. This highly regioselective protocol provides an atom-economic ring-closure route *via* one carbon–carbon bond formation. We have also discussed the related plausible reaction mechanisms. Further investigations regarding the synthetic application of metal triflates will be conducted and published in due course.

Experimental

General

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

A representative synthetic procedure of skeleton 3

$CuBr_2$ (450 mg, 2.0 mmol) was added to a solution of commercial available acetophenones (1.0 mmol) in EtOAc (30 mL) at 25 °C. The reaction mixture was stirred at reflux for 10 h. Then, the reaction mixture was cooled to 25 °C, filtered, neutralized with saturated $NaHCO_{3(aq)}$ (30 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Without further purification, substituted sodium sulfinate (2.1 mmol) was added to the resulting substituted α-bromoacetocephenones in a cosolvent of dioxane and water (20 mL, v/v = 1/1) at 25 °C. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to 25 °C and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded **3**. For the starting substrates **3**, these materials were known compounds and the analytical data are consistent with those in our previous reports.[23a,b]

A representative synthetic procedure of skeleton 4

K_2CO_3 (400 mg, 2.9 mmol) was added to a solution of **3** (1.0 mmol) in acetone (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Bromides (1.05 mmol) were added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 10 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 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 = 8/1–2/1) afforded **4**.

1-(3,4-Dimethoxyphenyl)-5-phenyl-2-(toluene-4-sulfonyl) pent-4-en-1-one (4a). **4a** was synthesized according to general synthetic procedure from **3a** (334 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 92% (414 mg); colorless solid; mp = 128–129 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1586; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 2H), 7.62 (dd, J = 2.0, 8.4 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.24–7.14 (m, 5H), 6.88 (d, J = 8.8 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 5.91 (dt, J = 7.2, 15.6 Hz, 1H), 5.13 (dd, J = 4.0, 10.8 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.03–2.96 (m, 1H), 2.95–2.88 (m, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.0, 154.3, 149.1, 145.4, 136.6, 133.9, 133.3, 130.3, 129.8 (2x), 129.5 (2x), 128.4 (2x), 127.6, 126.2 (2x), 124.6, 123.3, 110.7, 110.0, 69.2, 56.1, 56.0, 31.9, 21.7.

2-Benzenesulfonyl-1-(3,4-dimethoxyphenyl)-5-phenylpent-4-en-1-one (4b). **4b** was synthesized according to general synthetic procedure from **3b** (320 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 90% (393 mg); colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{25}O_5S$ 437.1423, found 437.1429; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.80 (m, 2H), 7.67–7.63 (m, 1H), 7.61 (dd, J = 2.0, 8.4 Hz, 1H), 7.55–7.50 (m, 2H), 7.46 (d, J = 2.0 Hz, 1H), 7.23–7.13 (m, 5H), 6.86 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 5.92 (dt, J = 7.6, 16.0 Hz, 1H), 5.17 (dd, J = 4.0, 10.4 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.05–2.92 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.8, 154.2, 149.1, 136.5, 136.4, 134.2, 133.9, 130.1, 129.7 (2x), 128.8 (2x), 128.4 (2x), 127.5, 126.1 (2x), 124.5, 123.2, 110.6, 110.0, 69.1, 56.1, 55.9, 31.7.

1-(3,4-Dimethoxyphenyl)-2-(4-fluorobenzenesulfonyl)-5-phenylpent-4-en-1-one (4c). 4c was synthesized according to general synthetic procedure from **3c** (338 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 86% (391 mg); colorless solid; mp = 133–134 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{24}FO_5S$ 455.1329, found 455.1324; ^1H NMR (400 MHz, $CDCl_3$): δ 7.84–7.79 (m, 2H), 7.60 (dd, J = 2.0, 8.4 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.22–7.13 (m, 7H), 6.85 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H), 5.92 (dt, J = 7.6, 15.6 Hz, 1H), 5.19 (dd, J = 4.0, 10.4 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.04–2.87 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.9, 166.1 (d, J = 255.4 Hz), 154.3, 149.1, 136.3, 134.0, 132.7 (d, J = 9.9 Hz, 2C), 132.2, 129.9, 128.4 (2x), 127.5, 126.0 (2x), 124.5, 122.9, 116.1 (d, J = 22.7 Hz, 2x), 110.4, 110.0, 69.0, 56.0, 55.8, 31.8.

1-(3,4-Dimethoxyphenyl)-2-(4-methoxybenzenesulfonyl)-5-phenylpent-4-en-1-one (4d). 4d was synthesized according to general synthetic procedure from **3d** (350 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 90% (420 mg); colorless solid; mp = 149–150 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_6S$ 467.1528, found 467.1525; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 9.2 Hz, 2H), 7.62 (dd, J = 2.0, 8.4 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.24–7.14 (m, 5H), 6.98 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 5.92 (dt, J = 7.2, 15.6 Hz, 1H), 5.13 (dd, J = 4.0, 10.4 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 3.03–2.87 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.2, 164.2, 154.2, 149.1, 136.6, 133.8, 132.0 (2x), 130.3, 128.4 (2x), 127.7, 127.5, 126.1 (2x), 124.6, 123.4, 114.1 (2x), 110.6, 110.0, 69.2, 56.1, 55.9, 55.6, 31.9.

2-(4-*n*-Butylbenzenesulfonyl)-1-(3,4-dimethoxyphenyl)-5-phenylpent-4-en-1-one (4e). 4e was synthesized according to general synthetic procedure from **3e** (376 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 83% (409 mg); colorless liquid; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{33}O_5S$ 493.2049, found 493.2052; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.58 (dd, J = 2.0, 8.4 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.22–7.12 (m, 5H), 6.82 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 5.93 (dt, J = 7.2, 15.6 Hz, 1H), 5.17 (dd, J = 4.8, 9.6 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.01–2.97 (m, 2H), 2.65 (t, J = 7.6 Hz, 2H), 1.61–1.54 (m, 2H), 1.37–1.24 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.8, 154.0, 150.0, 148.9, 136.4, 133.7 (2x), 133.6, 130.1, 129.6 (2x), 128.8, 128.3 (2x), 127.4, 126.0 (2x), 124.4, 123.3, 110.4, 109.9, 68.9, 56.0, 55.8, 35.5, 32.9, 31.5, 22.1, 13.7.

1-(3,4-Dimethoxyphenyl)-2-methanesulfonyl-5-phenylpent-4-en-1-one (4f). 4f was synthesized according to general synthetic procedure from **3f** (258 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 84% (314 mg); colorless solid; mp = 154–155 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{23}O_5S$ 375.1266, found 375.1271; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J = 2.0, 8.4 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.26–7.17 (m, 5H), 6.90 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.00 (dt, J = 7.2, 15.6 Hz, 1H), 4.95 (dd, J = 4.0, 10.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.22–3.08 (m, 2H), 3.00 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.4, 154.7, 149.3, 136.3, 134.3, 129.7, 128.5 (2x), 127.8, 126.2 (2x), 124.8, 122.8, 110.6, 110.2, 68.2, 56.2, 55.9, 37.6, 32.4.

2-(*n*-Butane-1-sulfonyl)-1-(3,4-dimethoxyphenyl)-5-phenylpent-4-en-1-one (4g). 4g was synthesized according to general synthetic procedure from **3g** (300 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 90% (375 mg); colorless liquid; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{29}O_5S$ 417.1736, found 417.1743; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, J = 2.0, 8.4 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.23–7.14 (m, 5H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 15.6 Hz, 1H), 5.99 (dt, J = 7.2, 15.6 Hz, 1H), 5.03 (dd, J = 4.0, 10.8 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.24–3.14 (m, 2H), 3.11–3.04 (m, 2H), 1.86–1.77 (m, 2H), 1.48–1.39 (m, 2H), 0.92 (t, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.1, 154.4, 149.1, 136.2, 133.9, 129.7, 128.3 (2x), 127.5, 126.0 (2x), 124.7, 123.0, 110.5, 110.0, 68.1, 55.9, 55.7, 49.2, 31.8, 22.2, 21.6, 13.4.

1-Benzo[1,3]dioxol-5-yl-5-phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4h). 4h was synthesized according to general synthetic procedure from **3h** (318 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 92% (399 mg); colorless solid; mp = 180–182 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_5S$ 435.1266, found 435.1270; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 2.0, 8.4 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 7.34 (d, J = 8.8 Hz, 2H), 7.28–7.14 (m, 5H), 6.84 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.04 (d, J = 1.2 Hz, 1H), 6.03 (d, J = 1.6 Hz, 1H), 5.92 (dt, J = 7.2, 15.6 Hz, 1H), 5.07 (dd, J = 4.0, 10.4 Hz, 1H), 3.01–2.87 (m, 2H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.6, 152.7, 148.4, 145.4, 136.5, 134.0, 133.2, 132.0, 129.8 (2x), 129.5 (2x), 128.4 (2x), 127.5, 126.3, 126.1 (2x), 123.2, 108.5, 108.0, 102.1, 69.4, 31.8, 21.7.

5-Phenyl-2-(toluene-4-sulfonyl)-1-(3,4,5-trimethoxyphenyl)pent-4-en-1-one (4i). 4i was synthesized according to general synthetic procedure from **3i** (364 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 90% (432 mg); colorless solid; mp = 98–100 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{29}O_6S$ 481.1685, found 481.1681; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.24–7.15 (m, 5H), 7.19 (s, 2H), 6.42 (d, J = 16.0 Hz, 1H), 5.92 (dt, J = 7.6, 16.0 Hz, 1H), 5.12 (dd, J = 4.0, 10.4 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 6H), 3.07–2.89 (m, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.6, 152.9, 145.5, 143.5, 136.4, 134.1 (2x), 133.2, 132.1, 129.8 (2x), 129.5 (2x), 128.4 (2x), 127.6, 126.1 (2x), 123.1, 106.7 (2x), 69.7, 60.9, 56.2 (2x), 31.9, 21.6.

2-Benzenesulfonyl-5-phenyl-1-(3,4,5-trimethoxyphenyl)pent-4-en-1-one (4j). 4j was synthesized according to general synthetic procedure from **3j** (350 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 88% (410 mg); colorless liquid; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_6S$ 467.1528, found 467.1534; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.80 (m, 2H), 7.70–7.65 (m, 1H), 7.56–7.52 (m, 2H), 7.25–7.18 (m, 5H), 7.16 (s, 2H), 6.42 (d, J = 15.6 Hz, 1H), 5.92 (dt, J = 7.2, 15.6 Hz, 1H), 5.14 (dd, J = 4.0, 10.8 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 6H), 3.08–2.90 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.5, 153.0 (2x), 143.5, 136.4, 136.2, 134.3, 134.2, 132.0, 129.8 (2x),

128.9 (2x), 128.5 (2x), 127.7, 126.1 (2x), 123.0, 106.7 (2x), 69.6, 60.9, 56.3 (2x), 31.9.

2-Methanesulfonyl-5-phenyl-1-(3,4,5-trimethoxyphenyl)pent-4-en-1-one (4k). **4k** was synthesized according to general synthetic procedure from **3k** (288 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 87% (352 mg); colorless solid; mp = 134–136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{25}O_6S$ 405.1372, found 405.1378; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 2H), 7.22–7.13 (m, 5H), 6.47 (d, J = 16.0 Hz, 1H), 5.99 (dt, J = 7.2, 15.6 Hz, 1H), 5.04 (dd, J = 5.2, 9.2 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 6H), 3.13–3.09 (m, 2H), 2.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.0, 152.8 (2x), 143.6, 136.0, 134.1, 131.4, 128.3 (2x), 127.6, 125.9 (2x), 122.5, 106.5 (2x), 68.2, 60.6, 56.0 (2x), 37.5, 32.3.

1-(3-Methoxyphenyl)-5-phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4l). **4l** was synthesized according to general synthetic procedure from **3l** (304 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 84% (353 mg); colorless solid; mp = 119–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}O_4S$ 421.1474, found 421.1478; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.53 (dt, J = 0.8, 7.6 Hz, 1H), 7.43 (t, J = 1.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.24–7.16 (m, 5H), 7.11 (ddd, J = 0.8, 2.8, 8.4 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H), 5.94 (dt, J = 6.8, 16.0 Hz, 1H), 5.20 (dd, J = 4.4, 10.0 Hz, 1H), 3.80 (s, 3H), 3.07–2.93 (m, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.8, 159.7, 145.4, 138.3, 136.4, 134.0, 133.4, 129.7 (2x), 129.6, 129.5 (2x), 128.3 (2x), 127.5, 126.1 (2x), 123.0, 121.7, 120.5, 112.9, 69.6, 55.3, 31.7, 21.5.

5-Phenyl-1-thiophen-2-yl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4m). **4m** was synthesized according to general synthetic procedure from **3m** (280 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 87% (345 mg); colorless solid; mp = 110–112 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{21}O_3S_2$ 397.0932, found 397.0936; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 1.2, 4.0 Hz, 1H), 7.72–7.67 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.25–7.16 (m, 5H), 7.12 (dd, J = 4.0, 4.8 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 5.95 (dt, J = 7.2, 15.6 Hz, 1H), 4.90 (dd, J = 4.0, 10.8 Hz, 1H), 3.04–2.88 (m, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 183.8, 145.6, 144.3, 136.5, 136.1, 134.5, 134.2, 133.1, 129.8 (2x), 129.6 (2x), 128.6, 128.5 (2x), 127.6, 126.2 (2x), 123.1, 71.7, 31.3, 21.7.

1-Furan-2-yl-5-phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4n). **4n** was synthesized according to general synthetic procedure from **3n** (264 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 85% (323 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{21}O_4S$ 381.1161, found 381.1165; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 0.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 0.8, 3.6 Hz, 1H), 7.25–7.16 (m, 5H), 6.40 (dd, J = 1.6, 3.6 Hz, 1H), 6.42 (d, J = 15.6 Hz, 1H), 5.94 (dt, J = 7.2, 15.6 Hz, 1H), 4.97 (dd, J = 4.4, 10.8 Hz, 1H), 3.01–2.87 (m, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.5, 152.7, 147.9, 145.5, 136.5, 134.1, 133.4, 129.7 (2x), 129.6 (2x), 128.4 (2x), 127.6, 126.2 (2x), 123.0, 119.9, 113.1, 70.2, 30.7, 21.7.

1-(3,4-Dimethoxyphenyl)-4-phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4o). **4o** was synthesized according to general synthetic procedure from **3a** (334 mg, 1.0 mmol) and 2-phenylallyl bromide (205 mg, 1.05 mmol); yield = 84% (378 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1583; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.32–7.16 (m, 9H), 6.71 (d, J = 8.4 Hz, 1H), 5.16 (s, 1H), 5.12 (dd, J = 2.4, 11.6 Hz, 1H), 4.96 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.43 (d, J = 14.0 Hz, 1H), 3.16 (dd, J = 11.6, 14.0 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.1, 153.9, 148.8, 145.2, 142.4, 138.8, 133.5, 130.3, 129.7 (2x), 129.4 (2x), 128.5 (2x), 127.9, 126.1 (2x), 123.9, 116.1, 110.3, 109.8, 67.6, 56.0, 55.7, 34.1, 21.6.

2-Benzenesulfonyl-1-(3,4-dimethoxyphenyl)4-phenylpent-4-en-1-one (4p). **4p** was synthesized according to general synthetic procedure from **3b** (320 mg, 1.0 mmol) and 2-phenylallyl bromide (205 mg, 1.05 mmol); yield = 85% (371 mg); colorless solid; mp = 127–129 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}O_5S$ 437.1423, found 437.1428; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82–7.80 (m, 2H), 7.67–7.63 (m, 1H), 7.54–7.50 (m, 2H), 7.29–7.26 (m, 3H), 7.23–7.20 (m, 3H), 7.15 (dd, J = 1.6, 8.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 5.17 (s, 1H), 5.13 (dd, J = 2.4, 11.2 Hz, 1H), 4.98 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.45 (d, J = 13.6 Hz, 1H), 3.18 (dd, J = 11.2, 13.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.0, 154.0, 148.9, 142.3, 138.8, 136.5, 134.2, 130.3, 129.7 (2x), 128.8 (2x), 128.6 (2x), 128.0, 126.2 (2x), 123.9, 116.3, 110.3, 109.8, 67.6, 55.0, 55.8, 34.1.

1-(3,4-Dimethoxyphenyl)-2-methanesulfonyl-4-phenylpent-4-en-1-one (4q). **4q** was synthesized according to general synthetic procedure from **3f** (258 mg, 1.0 mmol) and 2-phenylallyl bromide (205 mg, 1.05 mmol); yield = 84% (314 mg); colorless solid; mp = 114–115 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{23}O_5S$ 375.1266, found 375.1269; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.26 (m, 6H), 7.20 (dd, J = 2.0, 8.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 5.24 (s, 1H), 5.09 (s, 1H), 4.93 (dd, J = 2.4, 11.6 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.56 (dd, J = 1.6, 13.6 Hz, 1H), 3.36 (dd, J = 11.6, 13.6 Hz, 1H), 3.01 (d, J = 0.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.5, 154.4, 149.0, 142.3, 138.4, 129.8, 128.7 (2x), 128.2, 126.3 (2x), 124.4, 116.5, 110.3, 110.0, 66.7, 56.1, 55.8, 37.6, 35.0.

1-(3,4-Dimethoxyphenyl)-4-phenyl-2-(toluene-3-sulfonyl)pent-4-en-1-one (4r). **4r** was synthesized according to general synthetic procedure from **3o** (334 mg, 1.0 mmol) and 2-phenylallyl bromide (205 mg, 1.05 mmol); yield = 80% (360 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1584; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60–7.58 (m, 2H), 7.42–7.35 (m, 2H), 7.27–7.24 (m, 3H), 7.22–7.18 (m, 3H), 7.13 (dd, J = 2.0, 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 5.16 (s, 1H), 5.10 (dd, J = 2.4, 11.2 Hz, 1H), 4.98 (s, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.43 (d, J = 14.0 Hz, 1H), 3.22 (dd, J = 11.6, 14.0 Hz, 1H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 189.8, 153.8, 148.7, 142.4, 139.0, 138.7, 136.5, 134.8, 130.2, 129.7, 128.6, 128.5 (2x), 127.9, 126.6, 126.1 (2x), 123.8, 116.2, 110.1, 109.8, 67.5, 55.9, 55.7, 33.8, 21.1.

4-Phenyl-2-(toluene-4-sulfonyl)-1-(3,4,5-trimethoxyphenyl) pent-4-en-1-one (4s). **4s** was synthesized according to general synthetic procedure from **3i** (364 mg, 1.0 mmol) and 2-phenyl-allyl bromide (205 mg, 1.05 mmol); yield = 83% (399 mg); colorless solid; mp = 118–121 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{29}O_6S$ 481.1685, found 481.1680; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.4 Hz, 2H), 7.26–7.18 (m, 7H), 6.73 (s, 2H), 5.14 (s, 1H), 5.10 (dd, J = 2.4, 11.6 Hz, 1H), 4.94 (s, 1H), 3.81 (s, 3H), 3.62 (s, 6H), 3.46 (d, J = 13.2 Hz, 1H), 3.11 (dd, J = 11.6, 13.6 Hz, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.7, 152.5 (2x), 145.2, 142.9, 141.8, 138.3, 133.3, 132.0, 129.4 (2x), 129.3 (2x), 128.4 (2x), 127.8, 125.9 (2x), 116.2, 105.7 (2x), 67.6, 60.5, 55.7 (2x), 34.0, 21.3.

1-(3,4-Dimethoxyphenyl)-2-(toluene-4-sulfonyl)hex-4-en-1-one (4t). **4t** was synthesized according to general synthetic procedure from **3a** (334 mg, 1.0 mmol) and crotyl bromide (141 mg, 1.05 mmol); two isomers (ratio: *trans*/*cis* = 8/1); yield = 80% (311 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{25}O_5S$ 389.1423, found 389.1428; for major product: ^1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.56 (m, 3H), 7.46 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 1H), 5.49–5.41 (m, 1H), 5.19–5.11 (m, 1H), 5.01 (dd, J = 4.0, 10.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 2.82–2.64 (m, 2H), 2.41 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.1, 154.1, 149.0, 145.2, 133.4, 130.4, 129.7 (2x), 129.6, 129.4 (2x), 124.5, 124.4, 110.6, 110.0, 69.3, 56.1, 55.9, 31.4, 21.6, 17.8.

1-(3,4-Dimethoxyphenyl)-2-(4-fluorobenzenesulfonyl)hex-4-en-1-one (4u). **4u** was synthesized according to general synthetic procedure from **3c** (338 mg, 1.0 mmol) and crotyl bromide (141 mg, 1.05 mmol); two isomers (ratio: *trans*/*cis* = 6/1); yield = 82% (322 mg); colorless solid; mp = 110–112 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{22}FO_5S$ 393.1172, found 393.1178; ^1H NMR (400 MHz, $CDCl_3$): δ 7.83–7.73 (m, 2H), 7.56 (dd, J = 2.0, 8.8 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.19–7.08 (m, 2H), 6.86 (d, J = 8.4 Hz, 1H), 5.48–5.39 (m, 1H), 5.17–5.06 (m, 1H), 5.03 (dd, J = 3.2, 10.4 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.79–2.59 (m, 2H), 1.46 (dd, J = 1.2, 6.4 Hz, 3H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.0, 166.0 (d, J = 255.5 Hz), 154.2, 149.1, 132.6 (d, J = 9.9 Hz, 2x), 132.3 (d, J = 3.0 Hz), 130.1, 129.8, 124.4, 124.0, 116.0 (d, J = 22.0 Hz, 2x), 110.4, 110.0, 69.1, 56.0, 55.8, 31.4, 17.7.

1-(3,4-Dimethoxyphenyl)-2-(4-methoxybenzenesulfonyl)hex-4-en-1-one (4v). **4v** was synthesized according to general synthetic procedure from **3d** (350 mg, 1.0 mmol) and crotyl bromide (141 mg, 1.05 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 78% (315 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{25}O_6S$ 405.1372, found 405.1377; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72–7.65 (m, 2H), 7.61–7.56 (m, 1H), 7.46–7.44 (m, 1H), 6.97–6.93 (m, 2H), 6.88–6.86 (m, 1H), 5.49–5.41 (m, 1H), 5.19–5.10 (m, 1H), 5.01 (dd, J = 3.2, 10.4 Hz, 1H), 3.934 (s, 9/4H), 3.928 (s, 3/4H), 3.91 (s, 9/4H), 3.90 (s, 3/4H), 3.85 (s, 3/4H), 3.84 (s, 9/4H), 2.80–2.62 (m, 2H), 1.54 (dd, J = 0.8, 6.8 Hz, 3/4H), 1.48 (d, J = 6.4 Hz, 9/4H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.3, 164.0, 154.0, 149.0, 131.9 (2x), 130.4, 129.6, 128.2, 124.41, 124.40, 113.9 (2x), 110.5, 110.0, 69.3, 56.1, 55.9, 55.6, 31.4, 17.8.

2-(4-*n*-Butylbenzenesulfonyl)-1-(3,4-dimethoxyphenyl)hex-4-en-1-one (4w). **4w** was synthesized according to general synthetic procedure from **3e** (376 mg, 1.0 mmol) and crotyl bromide (141 mg, 1.05 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 76% (327 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{31}O_5S$ 431.1892, found 431.1896; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.64 (m, 2H), 7.58–7.53 (m, 1H), 7.46–7.44 (m, 1H), 7.31–7.26 (m, 2H), 6.88–6.85 (m, 1H), 5.49–5.42 (m, 1H), 5.20–5.12 (m, 1H), 5.03–4.98 (m, 1H), 3.94 (s, 9/4H), 3.93 (s, 3/4H), 3.92 (s, 9/4H), 3.91 (s, 3/4H), 2.84–2.70 (m, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.62–1.56 (m, 2H), 1.49 (dt, J = 1.2, 6.4 Hz, 3H), 1.37–1.28 (m, 2H), 0.92 (d, J = 7.2 Hz, 3H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.2, 154.1, 150.0, 149.1, 133.7, 130.4, 129.8 (2x), 128.8 (2x), 128.3, 124.5, 124.4, 110.6, 109.9, 69.3, 56.1, 55.9, 35.6, 33.0, 31.3, 22.2, 17.8, 13.8.

1-(3,4-Dimethoxyphenyl)-5-methyl-2-(toluene-4-sulfonyl)hex-4-en-1-one (4x). **4x** was synthesized according to general synthetic procedure from **3a** (334 mg, 1.0 mmol) and prenyl bromide (155 mg, 1.05 mmol); yield = 74% (298 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{27}O_5S$ 403.1579, found 403.1584; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 2H), 7.54 (dd, J = 2.0, 8.4 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.4 Hz, 1H), 4.96 (dd, J = 4.8, 9.6 Hz, 1H), 4.85–4.81 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.74–2.69 (m, 2H), 2.37 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.4, 153.9, 148.9, 145.0, 136.0, 133.6, 130.3, 129.5 (2x), 129.3 (2x), 124.3, 117.5, 110.4, 109.9, 69.1, 56.0, 55.8, 27.1, 24.4, 21.5, 17.6.

1,5-Diphenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (4y).[30] **4y** was synthesized according to general synthetic procedure from **3p** (274 mg, 1.0 mmol) and cinnamyl bromide (205 mg, 1.05 mmol); yield = 88% (343 mg); colorless solid; mp = 112–113 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{23}O_3S$ 391.1368, found 391.1374; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96–7.94 (m, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.60–7.55 (m, 1H), 7.46–7.43 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.24–7.15 (m, 5H), 6.41 (d, J = 16.0 Hz, 1H), 5.93 (dt, J = 7.2, 15.6 Hz, 1H), 5.21 (dd, J = 4.0, 10.4 Hz, 1H), 3.06–2.92 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 145.5, 137.0, 136.4, 134.0, 133.9, 133.2, 129.7 (2x), 129.5 (2x), 129.0 (2x), 128.7 (2x), 128.4 (2x), 127.5, 126.1 (2x), 123.1, 69.5, 31.7, 21.6.

A representative synthetic procedure of skeletons 5–7

$In(OTf)_3$ (6 mg, 0.01 mmol) was added to a solution of **4** (1.0 mmol) in $(CH_2Cl)_2$ (20 mL) at 25 °C. The reaction mixture was stirred at reflux (84 °C) for 20 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1–2/1) afforded **5–7**.

2,3-Dimethoxy-9-phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetra hydrobenzocyclohepten-5-one (5a). **5a** was synthesized

according to general synthetic procedure from **4a** (450 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 2/1); yield = 91% (410 mg); colorless solid; mp = 176–178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1587; for major product, ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 8.0 Hz, 2H), 7.27–7.20 (m, 5H), 7.17 (s, 1H), 7.00 (d, J = 7.2 Hz, 2H), 6.56 (s, 1H), 4.53 (dd, J = 2.4, 7.2 Hz, 1H), 4.39 (dd, J = 6.8, 10.4 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 2.65–2.60 (m, 1H), 2.42 (s, 3H), 2.30–2.17 (m, 2H), 2.04–1.96 (m, 1H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.4, 152.0, 147.6, 144.5, 141.8, 137.0, 135.0, 131.0, 129.3 (2x), 128.8 (2x), 128.6 (2x), 127.3 (2x), 126.5, 113.7, 111.6, 73.2, 55.8 (2x), 48.7, 29.6, 22.2, 21.4. Single-crystal X-ray diagram: crystal of compound **5a** was grown by slow diffusion of EtOAc into a solution of compound **5a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, a = 8.6479(4) Å, b = 11.7181(6) Å, c = 12.4402(7) Å, V = 1137.93(10) Å^3, Z = 2, d_{calcd} = 1.315 g cm^{-3}, $F(000)$ = 476, 2θ range = 1.802–26.452°, R indices (all data) R_1 = 0.0662, wR_2 = 0.1132.

6-Benzenesulfonyl-2,3-dimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5b). **5b** was synthesized according to general synthetic procedure from **4b** (436 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 4/1); yield = 90% (393 mg); colorless solid; mp = 183–184 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}O_5S$ 437.1423, found 437.1428; for major product: ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.72 (m, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 7.30–7.24 (m, 3H), 7.20 (s, 1H), 7.03–7.01 (m, 2H), 6.58 (s, 1H), 4.55 (dd, J = 2.4, 7.2 Hz, 1H), 4.44 (dd, J = 6.8, 10.4 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 2.49–2.43 (m, 1H), 2.31–2.17 (m, 2H), 2.05–1.97 (m, 1H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.3, 152.1, 147.7, 141.7, 138.1, 137.1, 133.8, 133.6, 128.9 (2x), 128.8 (4x), 127.5 (2x), 126.7, 113.8, 111.7, 73.1, 56.0 (2x), 48.7, 29.7, 22.3. Single-crystal X-ray diagram: crystal of compound **5b** was grown by slow diffusion of EtOAc into a solution of compound **5b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 12.2830(19) Å, b = 19.038(4) Å, c = 9.2274(14) Å, V = 2059.2(6) Å^3, Z = 4, d_{calcd} = 1.408 g cm^{-3}, $F(000)$ = 920, 2θ range = 1.737–26.458°, R indices (all data) R_1 = 0.0745, wR_2 = 0.1146.

6-(4-Fluorobenzenesulfonyl)-2,3-dimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5c). **5c** was synthesized according to general synthetic procedure from **4c** (454 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 5/1); yield = 86% (391 mg); colorless solid; mp = 205–206 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{24}FO_5S$ 455.1329, found 455.1332; for major product: ^1H NMR (400 MHz, $CDCl_3$): δ 7.81–7.76 (m, 2H), 7.30–7.21 (m, 4H), 7.16–7.09 (m, 2H), 7.05–7.03 (m, 2H), 6.59 (s, 1H), 4.58 (d, J = 5.2 Hz, 1H), 4.41 (dd, J = 7.2, 10.4 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 2.55–2.48 (m, 1H), 2.29–2.13 (m, 2H), 2.08–1.99 (m, 1H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.1, 165.7 (d, J = 254.7 Hz), 152.3, 147.8, 141.5, 137.3, 134.1, 132.0 (d, J = 9.8 Hz, 2x), 130.9, 128.9 (2x), 127.5 (2x), 126.8, 116.1 (d, J = 22.7 Hz, 2x), 113.8, 111.7, 73.0, 56.0 (2x), 48.5, 29.6, 22.3.

2,3-Dimethoxy-6-(4-methoxybenzenesulfonyl)-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5d). **5d** was synthesized according to general synthetic procedure from **4d** (466 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 1/1); yield = 89% (415 mg); colorless solid; mp = 158–160 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_6S$ 467.1528, found 467.1532; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 9.2 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.35–7.11 (m, 6H), 7.01 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 9.2 Hz, 1H), 6.56 (s, 1/2H), 6.11 (s, 1/2H), 4.54 (dd, J = 4.4, 6.8 Hz, 1/2H), 4.43 (dd, J = 6.8, 11.6 Hz, 1/2H), 4.38 (dd, J = 4.8, 12.0 Hz, 1/2H), 4.06 (dd, J = 4.0, 6.8 Hz, 1/2H), 3.89 (s, 3/2H), 3.86 (s, 3/2H), 3.84 (s, 3/2H), 3.83 (s, 3/2H), 3.78 (s, 3/2H), 3.51 (s, 3/2H), 2.68–2.02 (m, 1/2H), 2.46–2.39 (m, 1/2H), 2.32–1.97 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 195.7 (1/2x), 194.6 (1/2x), 163.8 (1/2x), 163.6 (1/2x), 152.0 (1/2x), 151.5 (1/2x), 147.6 (1/2x), 147.3 (1/2x), 143.2 (1/2x), 141.8 (1/2x), 138.0 (1/2x), 137.0 (1/2x), 131.9, 131.2 (2x), 131.1 (1/2x), 130.9 (1/2x), 129.9 (1/2x), 129.4 (1/2x), 128.71, 128.68, 128.5, 127.4, 127.0 (1/2x), 126.6 (1/2x), 113.92 (1/2x), 113.89 (1/2x), 113.7 (1/2x), 112.0 (1/2x), 111.6 (1/2x), 110.8 (1/2x), 73.4 (1/2x), 73.1 (1/2x), 55.9, 55.57, 55.55 (1/2x), 55.47 (1/2x), 48.8 (1/2x), 47.0 (1/2x) 32.2 (1/2x), 29.7 (1/2x), 23.1 (1/2x), 22.3 (1/2x).

6-(4-*n*-Butylbenzenesulfonyl)-2,3-dimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5e). **5e** was synthesized according to general synthetic procedure from **4e** (492 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 1/1); yield = 87% (428 mg); colorless solid; mp = 185–187 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{33}O_5S$ 493.2049, found 493.2056; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.37–7.72 (m, 7H), 7.20 (d, J = 8.8 Hz, 1/2H), 7.19–7.12 (m, 1/2H), 7.06 (s, 1/2H), 7.01 (d, J = 7.6 Hz, 1/2H), 6.57 (s, 1/2H), 6.11 (s. 1/2H), 4.54 (dd, J = 4.4, 6.8 Hz, 1/2H), 4.45 (dd, J = 6.8, 11.6 Hz, 1/2H), 4.40 (dd, J = 4.8, 12.0 Hz, 1/2H), 4.09 (dd, J = 4.0, 6.8 Hz, 1/2H), 3.89 (s, 3/2H), 3.82 (s, 3/2H), 3.79 (s, 3/2H), 3.52 (s, 3/2H), 2.69 (t, J = 7.6 Hz, 1H), 2.65 (t, J = 7.6 Hz, 1H), 2.45–2.41 (m, 1/2H), 2.30–2.11 (m, 2H), 2.02–1.95 (m, 1/2H), 1.65–1.55 (m, 2H), 1.39–1.30 (m, 2H), 0.92 (t, J = 7.6 Hz, 3/2H), 0.91 (t, J = 7.2 Hz, 3/2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 195.6 (1/2x), 194.4 (1/2x), 152.0 (1/2x), 151.6 (1/2x), 149.6 (1/2x), 149.4 (1/2x), 147.6 (1/2x), 147.3 (1/2x), 143.1 (1/2x), 141.8 (1/2x), 137.9 (1/2x), 137.0 (1/2x), 135.8 (1/2x), 135.2 (1/2x), 131.1 (1/2x), 130.8 (1/2x), 129.6, 128.9, 128.8, 128.72 (2x), 128.67, 128.5, 127.4, 127.1 (1/2x), 126.6 (1/2x), 113.7 (1/2x), 112.0 (1/2x), 111.6 (1/2x), 110.8 (1/2x), 73.1 (1/2x), 73.0 (1/2x), 55.9, 55.5, 48.7 (1/2x), 47.0 (1/2x), 35.51 (1/2x), 35.45 (1/2x), 33.0, 32.1 (1/2x) 29.7 (1/2x), 22.8 (1/2x), 22.3 (1/2x), 22.2 (1/2x), 22.1 (1/2x), 13.8. Single-crystal X-ray diagram: crystal of compound **5e** was grown by slow diffusion of EtOAc into a solution of compound **5e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 12.2830(19) Å, b = 19.038(4) Å, c = 9.2274(14) Å, V = 2059.2(6) Å^3, Z = 4, d_{calcd} = 1.408 g cm^{-3}, $F(000)$ = 920, 2θ range = 1.737–26.458°, R indices (all data) R_1 = 0.0745, wR_2 = 0.1146.

6-Methanesulfonyl-2,3-dimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5f). 5f was synthesized according to general synthetic procedure from **4f** (374 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 90% (337 mg); colorless solid; mp = 187–188 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{23}O_5S$ 375.1266, found 375.1269; for major product, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.28 (m, 3H), 7.26–7.19 (m, 2H), 7.25 (s, 1H), 6.17 (s, 1H), 4.19–4.14 (m, 2H), 3.90 (s, 3H), 3.57 (s, 3H), 3.31 (s, 3H), 2.81–2.73 (m, 1H), 2.37–2.32 (m, 2H), 2.14–2.04 (m, 1H); for major product, $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.1, 152.3, 147.6, 142.3, 137.7, 130.5, 128.9 (2x), 128.6 (2x), 127.3, 111.8, 111.2, 71.5, 56.1, 55.7, 46.7, 41.8, 31.4, 21.3.

6-(*n*-Butane-1-sulfonyl)-2,3-dimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5g). 5g was synthesized according to general synthetic procedure from **4g** (416 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 1/1); yield = 94% (391 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{29}O_5S$ 417.1736, found 417.1740; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.18 (m, 5H), 7.06 (d, J = 7.6 Hz, 1H), 6.56 (s, 1/2H), 6.12 (s, 1/2H), 4.63–4.60 (m, 1/2H), 4.17–4.11 (m, 3/2H), 3.88 (s, 3/2H), 3.84 (s, 3/2H), 3.77 (s, 3/2H), 3.58–3.51 (m, 1/2H), 3.53 (s, 3/2H), 3.44–3.37 (m, 1/2H), 3.26–3.19 (m, 1/2H), 3.09–3.02 (m, 1/2H), 2.75–2.68 (m, 1/2H), 2.50–2.42 (m, 1/2H), 2.36–2.20 (m, 2H), 2.11–2.01 (m, 1/2H), 1.91–1.81 (m, 2H), 1.68–1.60 (m, 1/2H), 1.59–1.45 (m, 1H), 1.41–1.30 (m, 1H), 0.96 (t, J = 7.2 Hz, 3/2H), 0.88 (t, J = 7.2 Hz, 3/2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.7 (1/2x), 196.0 (1/2x), 152.3 (1/2x), 152.1 (1/2x), 147.7 (1/2x), 147.4 (1/2x), 141.9 (1/2x), 141.8 (1/2x), 137.1 (1/2x), 136.8 (1/2x), 130.7 (1/2x), 130.4 (1/2x), 128.7, 128.6, 128.5, 127.5, 127.1 (1/2x), 126.6 (1/2x), 113.4 (1/2x), 111.6 (1/2x), 111.2 (1/2x), 110.9 (1/2x), 69.9 (1/2x), 69.5 (1/2x), 55.8, 55.4, 53.5 (1/2x), 52.3 (1/2x), 48.2 (1/2x), 46.1 (1/2x), 30.7 (1/2x), 29.4 (1/2x), 23.3 (1/2x), 23.2 (1/2x), 21.6 (1/2x), 21.5 (1/2x), 20.8 (1/2x), 20.2 (1/2x), 13.4 (1/2x), 13.3 (1/2x).

9-Phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-1,3-dioxacyclohepta[f]inden-5-one (5h). 5h was synthesized according to general synthetic procedure from **4h** (435 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 1/1); yield = 93% (404 mg); colorless liquid; 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 7.88 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.38–7.11 (m, 5H), 7.14 (d, J = 8.4 Hz, 1H), 7.04 (s, 1/2H), 7.02 (d, J = 7.6 Hz, 1H), 6.92 (s, 1/2H), 6.52 (s, 1/2H), 6.11 (s, 1/2H), 5.99 (s, 1H), 5.91 (d, J = 1.2 Hz, 1/2H), 5.89 (d, J = 1.6 Hz, 1/2H), 4.52 (t, J = 6.0 Hz, 1/2H), 4.40–4.31 (m, 1H), 4.02 (t, J = 8.4 Hz, 1/2H), 2.72–2.65 (m, 1/2H), 2.46 (s, 3/2H), 2.43 (s, 3/2H), 2.33–2.20 (m, 5/2H), 2.19–2.04 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 196.4 (1/2x), 195.0 (1/2x), 151.0 (1/2x), 150.7 (1/2x), 146.8 (1/2x), 146.4 (1/2x), 144.9 (1/2x), 144.8 (1/2x), 142.4 (1/2x), 142.2 (1/2x), 139.1 (1/2x), 138.7 (1/2x), 135.7 (1/2x), 135.2 (1/2x), 132.7 (1/2x), 132.5 (1/2x), 129.52, 129.50, 129.46, 128.93, 128.86, 128.7, 128.5, 127.6, 127.2 (1/2x), 126.7 (1/2x), 111.0 (1/2x), 109.0 (1/2x), 108.9 (1/2x), 108.0 (1/2x), 101.9 (1/2x), 101.7 (1/2x), 73.9 (1/2x), 72.7 (1/2x), 49.4 (1/2x), 46.8 (1/2x), 31.3 (1/2x), 29.8 (1/2x), 22.5 (1/2x), 22.0 (1/2x), 21.64 (1/2x), 21.60 (1/2x).

1,2,3-Trimethoxy-9-phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5i). 5i was synthesized according to general synthetic procedure from **4i** (480 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 90% (432 mg); colorless solid; mp = 182–183 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{29}O_6S$ 481.1685, found 481.1692; for major product, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 2H), 7.25–7.14 (m, 5H), 7.03 (s, 1H), 7.00 (d, J = 7.6 Hz, 2H), 4.86 (dd, J = 2.4, 7.6 Hz, 1H), 4.43 (dd, J = 7.2, 10.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.51 (s, 3H), 2.41 (s, 3H), 2.46–2.36 (m, 1H), 2.18–2.07 (m, 2H), 1.96–1.90 (m, 1H); for major product, $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 195.1, 152.3, 151.8, 145.6, 144.6, 141.8, 134.9, 134.2, 129.9, 129.4 (2x), 129.0 (2x), 128.5 (2x), 127.1 (2x), 126.4, 107.7, 73.1, 60.7, 60.6, 56.0, 42.0, 29.8, 22.6, 21.5.

6-Benzenesulfonyl-1,2,3-trimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5j). 5j was synthesized according to general synthetic procedure from **4j** (466 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 95% (443 mg); colorless solid; mp = 138–139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_6S$ 467.1528, found 467.1523; for major product, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 2H), 7.59–7.55 (m, 1H), 7.46–7.42 (m, 2H), 7.23–7.13 (m, 3H), 7.04 (s, 1H), 7.00 (d, J = 7.6 Hz, 2H), 4.87 (dd, J = 2.4, 7.6 Hz, 1H), 4.46 (dd, J = 7.2, 10.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.52 (s, 3H), 2.45–2.38 (m, 1H), 2.17–2.09 (m, 2H), 1.93–1.85 (m, 1H); for major product, $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.7, 152.4, 151.8, 145.7, 140.5, 137.9, 134.1, 133.6, 129.9, 128.9 (2x), 128.8 (2x), 128.5 (2x), 127.0 (2x), 126.4, 107.7, 72.8, 60.7, 60.6, 56.0, 41.8, 29.7, 22.5.

6-Methanesulfonyl-1,2,3-trimethoxy-9-phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5k). 5k was synthesized according to general synthetic procedure from **4k** (404 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 3/1); yield = 92% (372 mg); colorless solid; mp = 163–164 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{25}O_6S$ 405.1372, found 405.1375; for major product, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.19 (m, 3H), 7.10–7.08 (m, 2H), 7.09 (s, 1H), 4.96 (dd, J = 2.4, 7.6 Hz, 1H), 4.24 (dd, J = 6.4, 11.6 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.55 (s, 3H), 3.03 (s, 3H), 2.58–2.52 (m, 1H), 2.28–2.18 (m, 2H), 2.12–2.05 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 196.3, 152.5, 151.9, 146.0, 141.3, 134.0, 130.0, 128.7 (2x), 127.1 (2x), 126.7, 107.7, 71.8, 60.8, 60.7, 56.0, 41.5, 39.8, 29.8, 22.1.

3-Methoxy-9-phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one (5l). 5l was synthesized according to general synthetic procedure from **4l** (420 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 1/1); yield = 84% (353 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}O_4S$ 421.1474, found 421.1478; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.38–6.91 (m, 9H), 6.80 (dd, J = 2.8, 8.8 Hz, 1/2H), 6.60 (d, J = 8.8 Hz, 1/2H), 4.54 (dd, J = 4.4, 6.8 Hz, 1/2H), 4.41 (dd, J = 6.8, 11.6 Hz, 1/2H), 4.38 (dd, J = 4.8, 12.0 Hz, 1/2H), 4.04 (t, J = 6.8 Hz, 1/2H), 3.82 (s, 3/2H), 3.75 (s, 3/2H), 2.67–2.62 (m, 1/2H), 2.46 (s, 3/2H), 2.43 (s, 3/2H), 2.35–2.17 (m, 5/2H), 2.15–2.06 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$): δ 197.9 (1/2x), 196.6 (1/2x), 158.2 (1/2x), 158.1 (1/2x), 144.9 (1/2x), 144.8 (1/2x), 142.8 (1/2x), 142.5 (1/2x), 139.61 (1/2x), 139.57 (1/2x), 135.4 (1/2x), 135.1 (1/2x), 134.5 (1/2x), 134.2 (1/2x), 132.9 (1/2x), 130.2 (1/2x), 129.54, 129.49 (2x), 128.9, 128.7, 128.6, 128.5, 127.6, 126.9 (1/2x), 126.5 (1/2x), 119.2 (1/2x) 118.2 (1/2x), 112.7 (1/2x), 111.8 (1/2x), 73.8 (1/2x), 72.9 (1/2x), 55.39 (1/2x), 55.37 (1/2x), 48.3 (1/2x), 46.5 (1/2x), 31.8 (1/2x), 29.8 (1/2x), 22.9 (1/2x), 22.5 (1/2x), 21.61 (1/2x), 21.56 (1/2x).

6,7-Dimethoxy-4-methyl-4-phenyl-2-(toluene-4-sulfonyl)-3,4-dihydro-2*H*-naphthalen-1-one (6a). 6a was synthesized according to general synthetic procedure from **4o** (450 mg, 1.0 mmol); yield = 84% (378 mg); colorless solid; mp = 129–131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1583; ^1H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2H), 7.49 (s, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.27–7.18 (m, 3H), 6.94–6.91 (m, 2H), 6.81 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.80 (dd, J = 4.4, 13.6 Hz, 1H), 3.07 (dd, J = 4.4, 13.2 Hz, 1H), 2.70 (dd, J = 13.2, 13.6 Hz, 1H), 2.41 (s, 3H), 1.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.7, 154.5, 148.4, 145.2, 144.6, 143.5, 136.5, 129.4 (2x), 129.3 (2x), 128.7 (2x), 127.0, 126.6 (2x), 125.7, 109.1, 108.8, 66.9, 56.1, 56.0, 42.4, 38.2, 30.1, 21.6. 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 $P2_1/c$, a = 17.4857(9) Å, b = 9.6877(5) Å, c = 17.1467(9) Å, V = 2547.4(2) Å^3, Z = 4, d_{calcd} = 1.175 g cm^{-3}, $F(000)$ = 952, 2θ range = 2.376–26.419°, R indices (all data) R_1 = 0.0524, wR_2 = 0.1009.

2-Benzenesulfonyl-6,7-dimethoxy-4-methyl-4-phenyl-3,4-dihydro-2*H*-naphthalen-1-one (6b). 6b was synthesized according to general synthetic procedure from **4p** (436 mg, 1.0 mmol); yield = 83% (362 mg); colorless solid; mp = 136–138 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{25}O_5S$ 437.1423, found 437.1430; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, 2H), 7.64–7.59 (m, 1H), 7.55–7.50 (m, 2H), 7.49 (s, 1H), 7.28–7.19 (m, 3H), 6.94–6.92 (m, 2H), 6.82 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.83 (dd, J = 4.4, 14.0 Hz, 1H), 3.08 (dd, J = 4.4, 13.2 Hz, 1H), 2.72 (dd, J = 13.2, 14.0 Hz, 1H), 1.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.6, 154.6, 148.5, 145.2, 143.5, 139.5, 133.6, 129.3 (2x), 128.7 (4x), 127.0, 126.6 (2x), 125.7, 109.1, 108.9, 66.9, 56.2, 56.0, 42.4, 38.2, 30.2.

2-Methanesulfonyl-6,7-dimethoxy-4-methyl-4-phenyl-3,4-dihydro-2*H*-naphthalen-1-one (6c). 6c was synthesized according to general synthetic procedure from **4q** (374 mg, 1.0 mmol); yield = 84% (314 mg); colorless solid; mp = 155–156 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{23}O_5S$ 375.1266, found 375.1275; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.28–7.18 (m, 3H), 6.95–6.92 (m, 2H), 6.86 (s, 1H), 3.954 (s, 3H), 3.948 (s, 3H), 3.57 (dd, J = 4.4, 13.6 Hz, 1H), 3.23 (s, 3H), 2.99 (dd, J = 4.4, 13.2 Hz, 1H), 2.68 (dd, J = 13.2, 13.6 Hz, 1H), 1.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.4, 154.9, 148.6, 145.3, 143.9, 128.7 (2x), 127.0, 126.5 (2x), 125.5, 109.2, 108.9, 65.3, 56.2, 56.0, 43.1, 41.9, 35.8, 30.0.

6,7-Dimethoxy-4-methyl-4-phenyl-2-(toluene-3-sulfonyl)-3,4-dihydro-2*H*-naphthalen-1-one (6d). 6d was synthesized according to general synthetic procedure from **4r** (450 mg, 1.0 mmol); yield = 84% (378 mg); colorless solid; mp = 175–176 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{27}O_5S$ 451.1579, found 451.1586; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.71 (m, 2H), 7.50 (s, 1H), 7.41–7.40 (m, 2H), 7.27–7.19 (m, 3H), 6.94–6.91 (m, 2H), 6.82 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.83 (dd, J = 4.0, 13.6 Hz, 1H), 3.05 (dd, J = 4.0, 12.8 Hz, 1H), 2.71 (dd, J = 13.6, 13.6 Hz, 1H), 2.41 (s, 3H), 1.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.6, 154.5, 148.5, 145.2, 143.4, 139.4, 138.9, 134.4, 129.3, 128.7 (2x), 128.6, 127.0, 126.6 (2x), 126.4, 125.8, 109.1, 108.9, 66.7, 56.1, 56.0, 42.4, 38.2, 30.2, 21.3.

5,6,7-Trimethoxy-4-methyl-4-phenyl-2-(toluene-4-sulfonyl)-3,4-dihydro-2*H*-naphthalen-1-one (6e). 6e was synthesized according to general synthetic procedure from **4s** (480 mg, 1.0 mmol); yield = 88% (423 mg); colorless solid; mp = 245–247 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{29}O_6S$ 481.1685, found 481.1689; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.32–7.26 (m, 3H), 7.29 (s, 1H), 7.20–7.17 (m, 2H), 4.36 (dd, J = 6.0, 12.8 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.86 (s, 3H), 2.68–2.60 (m, 2H), 2.44 (s, 3H), 1.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.2, 152.9, 151.0, 150.3, 148.6, 144.8, 137.8, 136.1, 129.6 (2x), 129.4 (4x), 128.3 (2x), 126.1, 125.7, 104.7, 66.6, 60.5, 59.1, 55.9, 42.0, 41.0, 22.2, 21.7.

1-(3,4-Dimethoxyphenyl)-4-hydroxy-2-(toluene-4-sulfonyl) hexan-1-one (7a). 7a was synthesized according to general synthetic procedure from **4t** (388 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 2/1); yield = 60% (244 mg); colorless liquid; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{27}O_6S$ 407.1528, found 407.1532; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69–7.61 (m, 3H), 7.49 (d, J = 2.0 Hz, 2/3H), 7.45 (dd, J = 2.0 Hz, 1/3H), 7.28 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2/3H), 6.87 (d, J = 8.8 Hz, 1/3H), 5.47 (dd, J = 2.8, 11.2 Hz, 2/3H), 5.25 (dd, J = 4.4, 8.4 Hz, 1/3H), 3.944 (s, 2H), 2.40–2.04 (m, 1H), 3.92 (s, 2H), 3.91 (s, 1H), 3.78–3.72 (m, 1/3H), 3.26 (br s, 2/3H), 2.42 (s, 3H), 2.37–2.20 (m, 2H), 1.52–1.36 (m, 2H), 1.43 (br s, 1H), 0.89 (t, J = 7.6 Hz, 1H), 0.86 (t, J = 7.2 Hz, 2H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 191.0, 154.2, 149.1, 145.1, 133.8, 130.4, 129.6 (2x), 129.5 (2x), 124.7, 110.6, 110.1, 69.9, 66.5, 56.1, 56.0, 35.1, 31.0, 21.6, 9.7.

1-(3,4-Dimethoxyphenyl)-2-(4-fluorobenzenesulfonyl)-4-hydroxyhexan-1-one (7b). 7b was synthesized according to general synthetic procedure from **4u** (392 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 2/1); yield = 50% (205 mg); colorless solid; mp = 87–89 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{20}H_{24}FO_6S$ 411.1278, found 411.1283; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.75 (m, 2H), 7.65 (dd, J = 2.0, 8.4 Hz, 2/3H), 7.60 (dd, J = 2.0, 8.4 Hz, 1/3H), 7.48 (d, J = 2.4 Hz, 2/3H), 7.44 (d, J = 2.4 Hz, 1/3H), 7.19–7.14 (m, 2H), 6.87 (d, J = 8.4 Hz, 2/3H), 6.76 (d, J = 8.4 Hz, 1/3H), 5.50 (dd, J = 2.4, 7.6 Hz, 2/3H), 5.27 (dd, J = 4.4, 8.4 Hz, 1/3H), 3.94 (s, 2H), 3.93 (s, 1H), 3.91 (s, 2H), 3.90 (s, 1H), 3.80–3.72 (m, 1/3H), 3.26–3.22 (m, 2/3H), 2.37–2.20 (m, 1H), 2.16–2.06 (m, 1H), 1.56 (br s, 1H), 1.51–1.35 (m, 2H), 0.88 (t, J = 7.6 Hz, 1H), 0.86 (t, J = 7.2 Hz, 2H); for major product: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 190.9, 166.0 (d, J = 255.4 Hz), 154.4, 154.1, 149.2, 132.5 (d, J =

9.9 Hz, 2x), 130.2, 124.7, 116.1 (d, J = 22.7 Hz, 2x), 110.5, 110.1, 69.8, 66.5, 56.2, 56.0, 35.2, 30.9, 9.6.

1-(3,4-Dimethoxyphenyl)-4-hydroxy-2-(4-methoxybenzene sulfonyl)hexan-1-one (7c). **7c** was synthesized according to general synthetic procedure from **4v** (404 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 2/1); yield = 50% (211 mg); colorless solid; mp = 95–97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{27}O_7S$ 423.1478, found 423.1488; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.64 (m, 8/3H), 7.61 (dd, J = 2.0, 8.4 Hz, 1/3H), 7.47 (d, J = 2.0 Hz, 2/3H), 7.44 (d, J = 2.0 Hz, 1/3H), 6.94–6.91 (m, 2H), 6.86 (d, J = 8.4 Hz, 2/3H), 6.85 (d, J = 8.4 Hz, 1/3H), 5.46 (dd, J = 3.2, 11.6 Hz, 2/3H), 5.25 (dd, J = 3.6, 8.4 Hz, 1/3H), 3.922 (s, 2H), 3.918 (s, 1H), 3.90 (s, 2H), 3.89 (s, 1H), 3.84 (s, 1H), 3.83 (s, 2H), 3.76–3.72 (br s, 1/3H), 3.25–3.22 (m, 2/3H), 2.35–2.22 (m, 1H), 2.16–2.02 (m, 1H), 1.66 (br s, 1H), 1.50–1.32 (m, 2H), 0.88 (t, J = 7.6 Hz, 1H), 0.85 (t, J = 7.2 Hz, 2H); for major product: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.2, 164.0, 154.1, 149.0, 131.7 (2x), 130.4, 128.2, 124.6, 114.0 (2x), 110.5, 110.1, 69.9, 66.5, 56.1, 55.9, 55.6, 35.1, 30.9, 9.6.

2-(4-*t*-Butylbenzenesulfonyl)-1-(3,4-dimethoxyphenyl)-4-hydroxyhexan-1-one (7d). **7d** was synthesized according to general synthetic procedure from **4w** (430 mg, 1.0 mmol); two isomers (ratio: *trans*/*cis* = 2/1); yield = 58% (260 mg); colorless liquid; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{33}O_6S$ 449.1998, found 449.2005; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.57 (dd, J = 2.0, 8.4 Hz, 1H), 7.45 (dd, J = 2.0, 8.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2/3H), 6.83 (d, J = 8.4 Hz, 1/3H), 5.47 (dd, J = 2.8, 7.6 Hz, 2/3H), 5.25 (dd, J = 4.4, 8.4 Hz, 1/3H), 3.93 (s, 2H), 7.92 (s, 1H), 3.91 (s, 2H), 3.89 (s, 1H), 3.77–3.75 (s, 1/3H), 3.29–3.24 (s, 2/3H), 2.64 (t, J = 7.6 Hz, 2H), 2.40–2.28 (m, 2/3H), 2.20–2.07 (m, 4/3H), 1.59–1.25 (m, 7H), 0.93–0.84 (m, 6H); for major product: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 191.0, 153.9, 149.9, 149.0, 134.1, 130.4, 129.6 (2x), 128.8 (2x), 124.5, 110.5, 110.0, 70.0, 66.4, 56.1, 55.9, 35.6, 34.9, 33.0, 31.0, 22.2, 13.8, 9.6.

A representative synthetic procedure of skeleton 10

$NaBH_4$ (68 mg, 2.0 mmol) was added to a solution of **5a** (225 mg, 0.5 mmol) in MeOH (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 3 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Without further purification, the freshly prepared arylmagnesium bromide (Ar′MgBr, 1.0 mmol) in THF (10 mL) was added to a solution of CuI (190 mg, 1.0 mmol) in THF (10 mL) at 25 °C. Then, a solution of the resulting vinyl sulfone (130 mg, 0.3 mmol) in THF (5 mL) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1–2/1) afforded **10**.

5-(4-Fluorophenyl)-2,3-dimethoxy-9-phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (10a). Yield = 83% (132 mg); colorless solid; mp = 214–215 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}FO_4S$ 531.2005, found 531.2011; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.41 (br s, 2H), 7.40 (br s, 2H), 7.33–7.28 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 7.05–7.01 (m, 2H), 6.87–6.83 (m, 2H), 6.25 (s, 1H), 5.99 (s, 1H), 5.25 (d, J = 9.2 Hz, 1H), 4.88 (dd, J = 6.4, 11.6 Hz, 1H), 3.90–3.86 (m, 1H), 3.54 (s, 3H), 3.48 (s, 3H), 2.63–2.53 (m, 2H), 2.34 (s, 3H), 2.04–1.96 (m, 1H), 1.56–1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, J = 244.9 Hz), 147.8, 146.8, 144.2, 142.5, 136.8, 136.5 (d, J = 3.0 Hz), 134.7, 130.7 (d, J = 8.4 Hz, 2x), 130.3, 129.3 (2x), 129.1 (2x), 128.4 (2x), 128.4 (2x), 126.7, 115.2 (d, J = 21.2 Hz, 2x), 111.9, 111.2, 65.9, 55.7, 55.7, 45.8, 44.0, 26.8, 24.4, 21.4.

2,3-Dimethoxy-9-phenyl-6-(toluene-4-sulfonyl)-5-*p*-tolyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (10b). Yield = 76% (120 mg); colorless solid; mp = 194–195 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{35}O_4S$ 527.2256, found 527.2263; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.30–7.20 (m, 5H), 7.14 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.2 Hz, 2H), 6.50 (s, 1H), 6.13 (s, 1H), 4.86 (d, J = 3.6 Hz, 1H), 3.88–3.83 (m, 1H), 3.77 (s, 3H), 3.75–3.71 (m, 1H), 3.56 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H), 2.26–2.21 (m, 1H), 2.05–1.97 (m, 1H), 1.83–1.74 (m, 1H), 1.41–1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 147.2, 144.7, 141.9, 139.6, 136.3, 134.6, 134.3, 129.7 (2x), 129.3 (2x), 129.13 (2x), 129.06, 128.3 (4x), 127.2 (2x), 126.7, 114.5, 111.3, 68.4, 55.8, 55.6, 47.0, 44.1, 28.9, 25.8, 21.6, 20.9.

2,3-Dimethoxy-5-naphthalen-2-yl-9-phenyl-6-(toluene-4-sulfonyl)-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (10c). Yield = 74% (125 mg); colorless solid; mp = 197–198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{35}O_4S$ 563.2256, found 563.2264; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.60–7.58 (m, 1H), 7.48–7.39 (m, 8H), 7.35 (s, 1H), 7.34–7.29 (m, 1H), 7.22 (d, J = 1.6, 8.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 6.11 (s, 1H), 5.37 (d, J = 9.2 Hz, 1H), 4.98 (dd, J = 6.8, 11.6 Hz, 1H), 4.13–4.06 (m, 1H), 3.55 (s, 3H), 3.37 (s, 3H), 2.77–2.73 (m, 1H), 2.70–2.60 (m, 1H), 2.11–2.03 (m, 1H), 1.84 (s, 3H), 1.67–1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 146.8, 144.0, 142.6, 137.7, 136.7, 134.8, 133.1, 132.1, 130.5, 129.2 (2x), 128.9 (2x), 128.3 (3x), 128.1 (2x), 128.0, 127.6, 127.4, 127.1, 126.7, 126.1, 125.8, 112.2, 111.2, 65.5, 55.8, 55.7, 46.9, 44.1, 26.9, 24.2, 20.9. Single-crystal X-ray diagram: crystal of compound **10c** was grown by slow diffusion of EtOAc into a solution of compound **10c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 15.699(4) Å, b = 7.434(2) Å, c = 24.908(8) Å, V = 2874.6(14) Å^3, Z = 4, d_{calcd} = 1.300 g cm^{-3}, $F(000)$ = 1192, 2θ range = 1.312–25.146°, R indices (all data) R_1 = 0.1166, wR_2 = 0.1989.

Conflicts of interest

There are no conflicts to declare.

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