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Synthesis of benzofused cyclobutaoxepanones *via* intramolecular annulation of *o*-cinnamyl chalcones†

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Intramolecular stereoselective annulation of *o*-cinnamyloxy chalcones provides two kinds of tricyclic benzofused cyclobutaoxepanones *via* the synthesized routes of DABCO/NBS (1,4-diazabicyclo[2.2.2]octane/*N*-bromosuccinimide)-mediated Baylis–Hillman type cyclization or low-pressure mercury (LP Hg) lamp-promoted photocontrolled [2 + 2] cycloaddition. Diversified reaction conditions have been investigated for one-pot facile, high-yield transformation.

Introduction

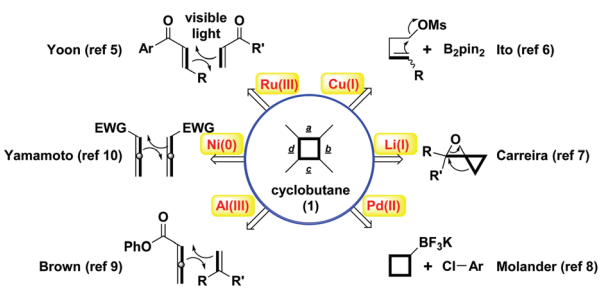
In organic fields, synthetic efforts toward the high ring-strain,[1–4] rigid skeleton of cyclobutanes have largely been focused on photoinitiated [2 + 2] cycloaddition (a + c sides),[5] intramolecular S_N2 cyclization of homoallylic mesylates (b side),[6] ring-expansion of cyclopropyl derivatives (d side),[7] and direct Suzuki–Miyaura coupling of BF_3K-containing cyclobutanes with haloarenes,[8] Lewis acid-mediated cycloaddition of allenes and allenoates (a + c sides),[9] metal-catalyzed [2 + 2] annulation of electron-deficient allenes (a + c sides),[10] and other elegant synthetic routes (Scheme 1).[11]

The cyclobutane unit can be found as a basic structural element in a wide range of naturally occurring compounds in bacteria, fungi, plants, and marine invertebrates. The molecules containing four-membered ring(s) represent potential biological properties, such as ivabradine,[12] iobucavir,[13] sceptrin,[14] hippolachnin A,[15] and piperarborenine B.[16] Compared with these previous synthetic routes, most showed photo-triggered [2 + 2] cycloaddition and metal-promoted [2 + 2] annulation in the formation of cyclobutane derivatives. However, there are few studies on non-photo and metal-free synthetic works. In spite of these prominent advancements, some problems exist, such as complicated catalytic conditions, lack of broad substrate generality, and prefunctionalized fragments. As a result of the recent findings, an easily controlled, inexpensive, open-vessel, and high-yield route in the preparation of functionalized cyclobutyl-conjugated molecules is still highly desired. Herein, we present the organoamine-mediated one-pot synthesis of tricyclic benzofused cyclobutaoxepanones *via* the DABCO/NBS-mediated Baylis–Hillman type intramolecular (2 + 2) stepwise annulation of *o*-cinnamyloxy chalcone under refluxing CCl_4 conditions (Scheme 2).

In fact, to the best of our knowledge, no cyclobutyl-fused ring on a core structure of benzoxepanone has been reported. Benzoxepanone moiety plays a key role in naturally occurring products[17] and bioactive molecules.[18] Therefore, a number of attempts to synthesize the skeletons of benzoxepanones have been reported *via* various prepared protocols.[19]

Results and discussion

Continuing our synthetic research on synthetic applications on substituted *o*-hydroxy-2-acetophenones for the generation of diversified benzannulated molecules (*e.g.*, benzofuran-3-ones, chroman-4-ones, aurones, flavones),[20] a convenient route for preparing benzofused cyclobutaoxepanones was explored next.



Scheme 1 Synthetic routes of cyclobutane core.

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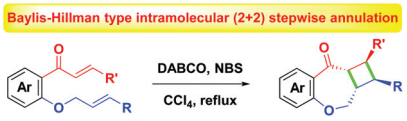
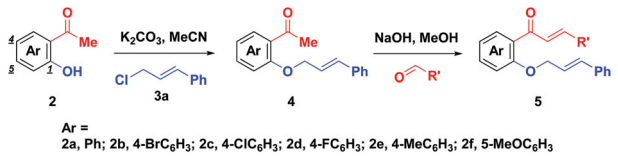


Scheme 2 Our synthetic route of benzofused cyclobutaoxepanones.

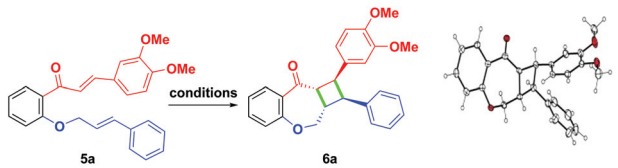
The required starting materials, *o*-cinnamyloxy chalcones **5**, were easily prepared from two-step synthetic routes, including the (1) *O*-allylation of substituted *o*-hydroxyacetophenones **2** with cinnamyl chloride (**3a**) in the presence of K_2CO_3, (2) followed by Claisen–Schmidt condensation of the resulting *o*-allyloxy acetophenones **4** with diversified arylaldehydes under the alkali-mediated conditions (Scheme 3).

The study commenced with the treatment of model substrates **5a** (Ar = Ph, R = Ph, R′ = 3,4-$(MeO)_2C_6H_3$, 1.0 mmol) and the combination of DABCO (0.6 equiv.) and NBS (0.6 equiv.) in CCl_4 (10 mL) at 25 °C for 10 h (Table 1, entry 1). By the reaction conditions it can be seen that only trace amounts (~3%) of **6a** were detected. After elongating the time from 10 to 15 and 20 h, similar results were observed (entries 2 and 3). Next, elevating the temperature to reflux (77 °C) and controlling the time at 10, 15, and 20 h, the yields of **6a** were increased to 75%, 90% and 88%, respectively (entries 4–6). From the results, we found that temperature is an important factor that affects the formation of **6a**. Then, by controlling the temperature and time as 77 °C and 15 h, the equivalents of DABCO and NBS were screened. In entry 7, we found that catalytic amounts (0.3 equiv.) of DABCO could provide **6a** in a 25% yield along with 55% of unknown products. By use of the stoichiometric amounts (1.1 equiv.) of DABCO, **6a** was isolated in an 85% yield (entry 8). From the phenomenon, we understood that 0.6 equivalents of DABCO was an appropriate amount for intramolecular annulation reaction.



Scheme 3 Synthesis of **5**.

Table 1 Reaction conditions[a]



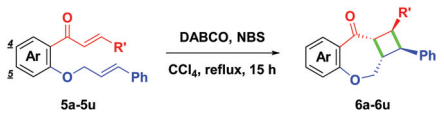
Entry	Base/NBS (equiv.)	Temp. (°C)	Time (h)	**6a**[b], %
1	DABCO (0.6)/NBS (0.6)	25	10	Trace
2	DABCO (0.6)/NBS (0.6)	25	15	Trace
3	DABCO (0.6)/NBS (0.6)	25	20	Trace
4	DABCO (0.6)/NBS (0.6)	77	10	75
5	DABCO (0.6)/NBS (0.6)	77	15	90
6	DABCO (0.6)/NBS (0.6)	77	20	88
7	DABCO (0.3)/NBS (0.6)	77	15	25[c]
8	DABCO (1.1)/NBS (0.6)	77	15	85
9	DABCO (0.6)/NBS (0.3)	77	15	77
10	DABCO (0.6)/NBS (1.1)	77	15	48[c]
11	DBU (0.6)/NBS (0.6)	77	15	—[d]
12	DMAP (0.6)/NBS (0.6)	77	15	65
13	BPY (0.6)/NBS (0.6)	77	15	60
14[e]	DABCO (0.6)/NBS (0.6)	82	15	36
15[f]	DABCO (0.6)/NBS (0.6)	84	15	81
16[g]	DABCO (0.6)/NBS (0.6)	85	15	70

[a] The reactions were run on a 1.0 mmol scale with **5a**, CCl_4 (10 mL). [b] Isolated yields. [c] Unknown mixture was isolated (for entry 7, 55%; entry 10, 40%). [d] **5a** (65%) was recovered. [e] MeCN. [f] $(CH_2Cl)_2$. [g] Glyme.

On the other hand, the equivalent of NBS was checked. Entry 9 showed that no better yield (77%) was detected when decreasing the amounts of NBS (0.3 equiv.). Although 0.3 equivalent of NBS could promote the stepwise (2 + 2) annulation completely, the isolated yield of **6a** was lower than 0.6 equivalents of NBS. In particular, the stoichiometric amounts (1.1 equiv.) of NBS initiated a multi-bromination of electron-rich arenes such that low yields (48%) of **6a** were isolated along with a major complex mixture (40%, entry 10). To obtain better yields, we wanted to change DABCO to other di-nitrogen atom-containing organoamines. When using DBU (0.6 equiv.), the desired **6a** could not be generated due to NBS reacting with the amidine moiety of DBU (entry 11), and only **5a** was recovered. By changing the base to DMAP (an aromatic amine), however, **6a** was produced in a 65% yield (entry 12). 2,2′-Bipyridine (BPY) also provided similar yields (60%) compared with DMAP (entry 13). Furthermore, three solvents with temperatures near boiling points (82–85 °C) were tested. Entries 14–16 show that MeCN, $(CH_2Cl)_2$ and glyme didn't obtain better yields (36% 81% and 70%) than CCl_4 (90%). From the above observations, we conclude that DABCO/NBS/CCl_4 is an optimal combination for synthesizing **6a** *via* a stepwise Baylis–Hillman type (2 + 2) annulation. The stereochemistry of **6a** was determined as a monoclinic crystal system and $P2_1/c$ space group by single-crystal X-ray analysis.[21]

To study the scope and limitations of this route, substituted *o*-cinnamyloxy acetophenones **5a–5u** were reacted with a combination of DABCO (0.6 equiv.) and NBS (0.6 equiv.) to afford diversified tricyclic benzofused cyclobutaoxepanones **6a–6u** under refluxing CCl_4 (77 °C/15 h) conditions, as shown in Table 2. With optimal conditions established (Table 1, entry 5), we found that this route allowed direct stepwise (2 + 2) annulation in good to excellent yields (86%–98%). Among entries 1–21, efficient formation of **6a–6u** showed that two aryl substituents (**5**, Ar and R′) did not affect the yields. After careful purification on a column chromatography, we found that skeleton **6** was isolated as the sole isomer, while no other diastereomers were observed on the basis of the analysis of NMR spectrum. Furthermore, the molecular structure of **6d** with the relative configuration of a cyclobutane ring was determined by single-crystal X-ray analysis.[21] For the electronic nature of the aryl substituent (Ar) of **5**, not only haloaryl

Table 2 Synthesis of **6a–6u** [a]



Entry	**5a–5u**, Ar=, R′=	**6a–6u** [b], %
1	**5a**, Ph, 3,4-$(MeO)_2C_6H_3$	**6a**, 90
2	**5b**, 4-BrC_6H_3, 3,4-$(MeO)_2C_6H_3$	**6b**, 94
3	**5c**, 4-ClC_6H_3, 3,4-$(MeO)_2C_6H_3$	**6c**, 93
4	**5d**, 4-FC_6H_3, 3,4-$(MeO)_2C_6H_3$	**6d**, 98
5	**5e**, 4-MeC_6H_3, 3,4-$(MeO)_2C_6H_3$	**6e**, 94
6	**5f**, 5-$MeOC_6H_3$, 3,4-$(MeO)_2C_6H_3$	**6f**, 90
7	**5g**, Ph, 3,4-$CH_2O_2C_6H_3$	**6g**, 90
8	**5h**, Ph, 3,4,5-$(MeO)_3C_6H_2$	**6h**, 94
9	**5i**, Ph, 3-$MeOC_6H_4$	**6i**, 90
10	**5j**, Ph, 4-$MeOC_6H_4$	**6j**, 90
11	**5k**, Ph, 2,3,4-$(MeO)_3C_6H_2$	**6k**, 90
12	**5l**, Ph, 2-HOC_6H_4	**6l**, 89
13	**5m**, Ph, 2,4-$(MeO)_2C_6H_3$	**6m**, 88
14	**5n**, Ph, 4-$NO_2C_6H_4$	**6n**, 86
15	**5o**, Ph, 4-PhC_6H_4	**6o**, 89
16	**5p**, Ph, 3,4-$Cl_2C_6H_3$	**6p**, 92
17	**5q**, Ph, 2-naphthyl	**6q**, 94
18	**5r**, Ph, 2-furyl	**6r**, 93
19	**5s**, Ph, 2-thienyl	**6s**, 95
20	**5t**, Ph, 2-FC_6H_4	**6t**, 87
21	**5u**, Ph, 4-pyridyl	**6u**, 87

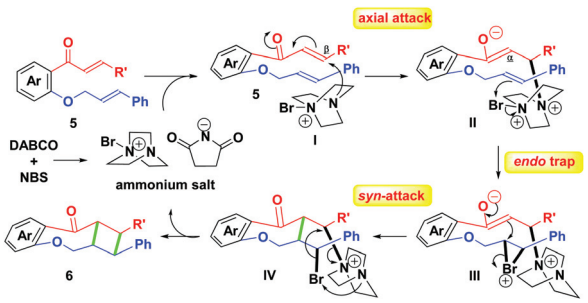
[a] The reactions were run on a 1.0 mmol scale with **5a–5u**, DABCO (70 mg, 0.6 mmol), NBS (107 mg, 0.6 mmol), CCl_4 (10 mL), reflux (77 °C), 15 h. [b] Isolated yields.

(bromo, chloro) groups but also electron-neutral (methyl), electron-withdrawing (fluoro), and electron-donating (methoxy) groups were appropriate. For the R′ substituent, electron-releasing mono-, di-, tri oxygenated groups, the electron-withdrawing nitro group, dichloro, bicyclic 2-naphthyl, and heterocyclic groups (2-furyl, 2-thienyl, 2-pyridyl) were well tolerated.

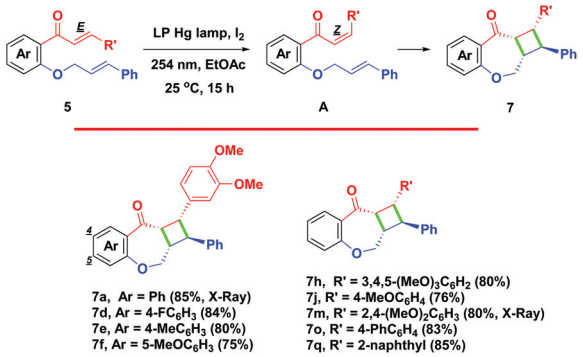
On the basis of our experimental results, a plausible mechanism for the stereoselective formation of skeleton **6** is illustrated in Scheme 4. Initially, the bromo-exchange reaction between DABCO and NBS provides a bromo ammonium succinimide complex. Upon a pseudo-axial intermolecular Michael addition, the tertiary amino group on the *in situ* formed intermediate **I** attacks in the β-position of skeleton **5** to lead to intermediate **II**. On the basis of the Baylis–Hillman-type pathway, the olefinic group of the styryl moiety on intermediate **II** could trap the bromo atom to release the tertiary amino group again from the *endo*-face. Following, α-carbanion attacks the *in situ* generated bromonium ion on intermediate **III** to give intermediate **IV** with a core of benzofused oxepanone. For synthetic applications on DABCO-Br complex (ammonium bromide salt), Xie *et al.* have reported similar phenomenon for highly asymmetric bromocyclization of tryptophol.[22] Finally, by the intramolecular nitrogen atom-promoted debromination, sequential removal of DABCO skeleton furnishes the transformation from intermediate **IV** to skeleton **6**. The resulting tricyclic structural framework of skeleton **6** possessed four contiguous *cis–trans–cis–trans* stereocenters on the cyclobutane ring.

Based on the results, photo-initiated intramolecular [2 + 2] cycloaddition of **5** with two olefinic arms was examined next, as shown in Scheme 5. First, treatment of model substrate **5a** (0.3 mmol) with the radiation of a low-pressure mercury lamp (LP Hg, λ = 254 nm, hard UV) provided sole **7a** in an 85% yield in the presence of iodine (10 mol%) for 15 h at 25 °C. Based on single-crystal X-ray diagram of **7a**,[21] the exact structure of **7a** could be determined. In particular, four contiguous stereocenters of the cyclobutane ring on **7a** possessed a *cis–cis–cis–trans* configuration. The reason for this is that the olefinic isomerization from (*E*)-**5a** to (*Z*)-**A** was initiated first. Then, the concerted [2 + 2] cycloaddition of **A** to **7a** was accomplished. Compared with the combination of DABCO/NBS, the alternative photolytic route provides complementary results in the construction of cyclobutane with four stereogenic centers. Furthermore, controlling the R′ = 3,4-$(MeO)_2C_6H_3$ group, **5d–5f** with different Ar group (4-FC_6H_3, 4-MeC_6H_3 and 5-$MeOC_6H_3$) produced **7d–7f** in 84%, 80%, and 75% yields, respectively. On the other way, by adjusting the Ar substituent as the Ph group, five R′ groups (*e.g.* 3,4,5-$(MeO)_3C_6H_2$, 4-$MeOC_6H_4$, 2,4-$(MeO)_2C_6H_3$, 4-PhC_6H_4 and 2-naphthyl) provided **7h**, **7j**, **7m**, **7o**, and **7q** in a range of 76%–85% yields.

To investigate the substrate scope, **5v–5y** with a styryloxy group were examined. According to the above synthetic route of **5a–5u** with a cinnamyoxy group, the starting materials **5v–5y** (R′ = 3,4-$(MeO)_2C_6H_3$, 4-$NO_2C_6H_4$, 2-naphthyl, 2-thienyl) were easily prepared from a two-step route (*O*-styrylation and



Scheme 4 Plausible mechanism.

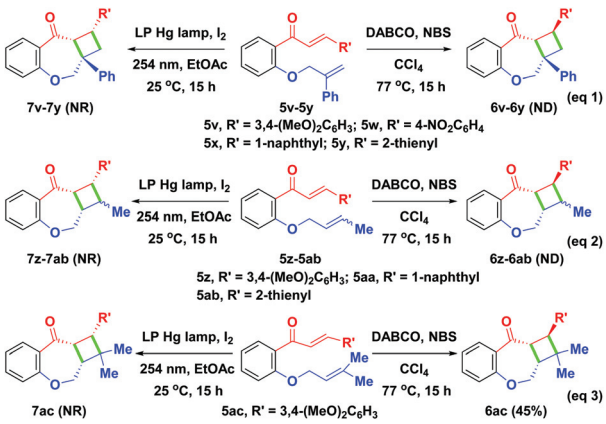


Scheme 5 Photo-triggered [2 + 2] cycloaddition of **5**.

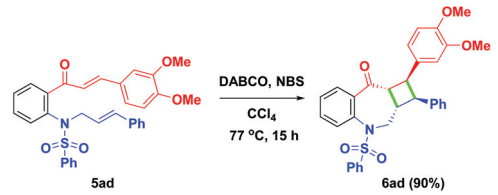
Claisen–Schmidt condensation). However, attempts to afford **6v–6y** failed since the steric hindrance of the Ph group inhibited intramolecular annulation between the carbanion and bromonium ion on intermediate **III** under the DABCO/NBS-mediated condition, and major bromo-containing products were separated among the product mixture (Scheme 6, eqn (1)). In particular, the photolytic reaction of **5v–5y** could not produce **7v–7y**. Only starting materials were recovered. Compared with the Ph group of the cinnamyloxy arm, we believed that the Ph group of the styryloxy arm could stabilize an *in situ* formed tertiary radical such that the reactivity was low. The steric hindrance of the Ph group could play another important role in affecting the formation of the cyclobutane ring.

Then, by changing the cinnamyloxy to a crotyloxy group, DABCO/NBS-mediated reactions of **5z-5ab** were checked. When the reaction of **5z-5ab** was treated with a combination of DABCO/NBS, however, a bromo-containing mixture displaced the desired **6z-6ab** (Scheme 6, eqn (2)). Compared with the cinnamyl group, we thought that the olefinic moiety of the crotyl group could exhibit higher reactivity to react with NBS for the formation of a brominium ion of intermediate **III** such that the intramolecular ring-closure would become complex. For photo-triggered annulation of **5z-5ab**, still no reactions were observed. The results were similar to those for **5v–5y**. From the results, we understand that homolytic bond cleavage of the crotyl group (an aliphatic substituent) was not easier to initiate than the cinnamyl group (an aromatic substituent) since the methyl group could not stabilize the formed radical species such that [2 + 2] cycloaddition was blocked. As shown in Scheme 6 and eqn (3), **5ac** with a prenyloxy arm was checked. Under DABCO/NBS conditions especially, **6ac** could be obtained in a 45% yield along with a 30% yield of an unknown bromo-containing mixture. Although the isolated yield of **6ac** was low, a geminal dimethyl-conjugated cyclobutane ring was formed. But, even using radiation of **5ac** with an LP Hg lamp, **7ac** was still not detected.

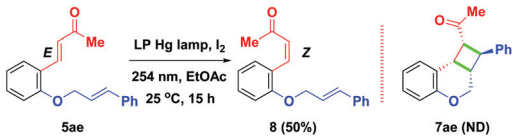
Based on the above-mentioned DABCO/NBS conditions, by changing the mode substrate **5a** with the *o*-cinnamyoxy group



Scheme 6 Reactions of **5v-5ac**.



Scheme 7 Synthesis of **6ad**.



Scheme 8 Synthesis of **7ae**.

to **5ad** with the *o*-cinnamylamino group, **6ad** was isolated in a 90% yield (Scheme 7). To date, no reports have documented the synthesis of the novel tricyclic cyclobutyl-fused benzoazepinone skeleton. On the other hand, two groups (2- and 4-positions) on the chalcone skeleton were exchanged to extend the photolytic applications. The starting material, **5ae**, was prepared from Claisen–Schmidt condensation of *o*-cinnamyloxy benzaldehyde with acetone, as shown in Scheme 8. Interestingly, after photolytic radiation of **5ae**, only 50% of **8** was obtained *via* the olefinic (*E*)- and (*Z*)-isomerization along with the recovery of 23% of **5ae**. The expected **7ae** with the tricyclic cyclobutyl-fused chromane skeleton was not detected.

In summary, we have developed a DABCO/NBS-controlled synthesis of tricyclic benzofused cyclobutaoxepanones *via* intramolecular stereoselective Baylis–Hillman type annulation of *o*-cinnamyloxy chalcones under refluxing CCl_4 reaction conditions in good to excellent yields. Also, a low-pressure mercury lamp-promoted photocontrolled intramolecular [2 + 2] cycloaddition of *o*-cinnamyloxy chalcones has been investigated. The process provides a one-pot pathway of two carbon–carbon bond formations. The uses of various organoamines and solvents are investigated for facile and efficient transformation. Related plausible mechanisms have been proposed. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic applications of *o*-cinnamyloxy chalcones will be conducted and published in due course.

Experimental

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. The heating mantle is used to provide a stable heat source. 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).

For the starting substituted *o*-hydroxyacetophenones **2a–2h**, allylic halides **3a–3d** and arylaldehydes, these reagents were obtained from commercial sources and used without further purification.

A representative synthetic procedure of skeleton 4 is as follows

K_2CO_3 (300 mg, 2.2 mmol) was added to a solution of *o*-hydroxyacetophenones **2a–2f**, *o*-*N*-phenylsulfonyl aminoacetophenone **2g** or *o*-hydroxybenzaldehyde **2h** (1.0 mmol) in MeCN (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Halides (1.1 mmol, for cinnamyl chloride **3a**, 170 mg; for styryl bromide **3b**, 220 mg; for crotyl bromide **3c**, 100 mg; for prenyl chloride **3d**, 115 mg) in MeCN (10 mL) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 20 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 = 20/1–10/1) afforded skeleton **4**.

1-[2-(3-Phenylallyloxy)phenyl]ethanone (4a). Yield = 95% (239 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{17}O_2$ 253.1229, found 253.1238, err (ppm): −3.67; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 2.0, 7.6 Hz, 1H), 7.48–7.42 (m, 3H), 7.37–7.33 (m, 2H), 7.31–7.27 (m, 1H), 7.04–7.00 (m, 2H), 6.76 (d, J = 16.0 Hz, 1H), 6.44 (dt, J = 5.6, 16.0 Hz, 1H), 4.81 (dd, J = 1.6, 6.0 Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 157.9, 136.1, 133.6, 133.5, 130.4, 128.70, 128.65 (2×), 128.1, 126.6 (2×), 123.6, 120.8, 112.9, 69.3, 32.0.

1-[5-Bromo-2-(3-phenylallyloxy)phenyl]ethanone (4b). Yield = 94% (310 mg); colorless solid; mp = 85–87 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{16}BrO_2$ 331.0334, found 331.0339, err (ppm): −1.51; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 2.4 Hz, 1H), 7.52 (dd, J = 2.8, 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.37–7.33 (m, 2H), 7.31–7.27 (m, 1H), 6.90 (d, J = 8.8 Hz, 1H), 6.75 (d, J = 16.0 Hz, 1H), 6.40 (dt, J = 6.0, 16.0 Hz, 1H), 4.78 (dd, J = 1.2, 6.0 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 156.9, 135.93, 135.87, 134.0, 132.9, 130.0, 128.6 (2×), 128.2, 126.7 (2×), 123.0, 114.8, 113.3, 69.6, 31.9.

1-[5-Chloro-2-(3-phenylallyloxy)phenyl]ethanone (4c). Yield = 90% (257 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{16}ClO_2$ 287.0839, found 287.0846, err (ppm): −2.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 2.8 Hz, 1H), 7.44–7.27 (m, 6H), 6.93 (d, J = 8.8 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.40 (dt, J = 6.0, 16.0 Hz, 1H), 4.75 (dd, J = 1.2, 6.0 Hz, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 156.3, 135.8, 133.8, 132.9, 129.9, 129.4, 128.5 (2×), 128.1, 126.5 (2×), 125.9, 122.9, 114.3, 69.5, 31.8.

1-[5-Fluoro-2-(3-phenylallyloxy)phenyl]ethanone (4d). Yield = 90% (243 mg); colorless solid; mp = 77–79 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{16}FNO_2$ 271.1134, found 271.1128, err (ppm): 2.21; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, J = 3.2, 8.8 Hz, 1H), 7.44–7.27 (m, 5H), 7.18–7.13 (m, 1H), 6.97 (dd, J = 4.4, 9.2 Hz, 1H), 6.75 (d, J = 16.0 Hz, 1H), 6.42 (dt, J = 6.0, 16.0 Hz, 1H), 4.78 (dd, J = 1.2, 6.0 Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8 (d, J = 238.8 Hz), 154.2, 136.0, 134.1, 133.8, 128.7 (2×), 128.2, 126.61 (2×), 126.59 (d, J = 3.0 Hz), 123.3, 120.0 (d, J = 23.5 Hz), 116.5 (d, J = 23.5 Hz), 114.4 (d, J = 6.9 Hz), 70.0, 31.9.

1-[5-Methyl-2-(3-phenylallyloxy)phenyl]ethanone (4e). Yield = 93% (247 mg); colorless solid; mp = 59–60 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{18}H_{19}O_2$ 267.1385, found 267.1380, err (ppm): 1.87; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 2.4 Hz, 1H), 7.43–7.41 (m, 2H), 7.37–7.33 (m, 2H), 7.30–7.24 (m, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.43 (dt, J = 6.0, 16.0 Hz, 1H), 4.78 (dd, J = 1.2, 6.0 Hz, 2H), 2.67 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 156.0, 136.2, 134.1, 133.4, 130.6, 130.2, 128.6 (2×), 128.4, 128.1, 126.6 (2×), 123.9, 113.0, 69.4, 32.0, 20.2.

1-[4-Methoxy-2-(3-phenylallyloxy)phenyl]ethanone (4f). Yield = 96% (271 mg); colorless solid; mp = 79–81 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{18}H_{19}O_3$ 283.1334, found 283.1329, err (ppm): 1.77; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.8 Hz, 1H), 7.44–7.41 (m, 2H), 7.42–7.33 (m, 2H), 7.31–7.26 (m, 1H), 6.76 (d, J = 16.0 Hz, 1H), 6.54 (dd, J = 2.0, 8.4 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.43 (dt, J = 6.0, 16.0 Hz, 1H), 4.78 (dd, J = 1.2, 6.0 Hz, 2H), 3.85 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 164.3, 160.0, 136.1, 133.7, 132.7, 128.6 (2×), 128.1, 126.6 (2×), 123.4, 121.4, 105.3, 99.4, 69.3, 55.5, 32.1.

1-[2-(2-Phenylallyloxy)phenyl]ethanone (4g). Yield = 93% (234 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{17}O_2$ 253.1229, found 253.1238, err (ppm): −3.56; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 1.6, 7.6 Hz, 1H), 7.49–7.44 (m, 3H), 7.39–7.32 (m, 3H), 7.04–6.99 (m, 2H), 5.62 (s, 1H), 5.47 (d, J = 0.8 Hz, 1H), 5.02 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 157.8, 142.9, 138.1, 133.5, 130.5, 128.5 (3×), 128.2, 126.1 (2×), 120.9, 115.7, 112.6, 70.5, 31.7.

1-(2-But-2-enyloxyphenyl)ethanone (4h). Two isomers (*E*/*Z* = 5/1); yield = 89% (169 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{12}H_{15}O_2$ 191.1072, found 191.1080, err (ppm): −4.19; for major *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, J = 2.0, 8.0 Hz, 1H), 7.24 (dt, J = 2.0, 8.4 Hz, 1H), 6.81–6.75 (m, 2H), 5.73–5.66 (m, 1H), 5.60–5.53 (m, 1H), 4.35 (dd, J = 1.2, 5.6 Hz, 2H), 2.46 (s, 3H), 1.59 (dd, J = 1.2, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 157.6, 133.0, 130.0, 129.7, 128.4, 125.0, 119.9, 112.3, 68.6, 31.4, 17.2.

1-[2-(3-Methylbut-2-enyloxy)phenyl]ethanone (4i). Yield = 85% (173 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for

$C_{13}H_{17}O_2$ 205.1229, found 205.1238, err (ppm): −4.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, J = 1.6, 8.0 Hz, 1H), 7.45–7.41 (m, 1H), 6.99–6.94 (m, 2H), 5.52–5.48 (m, 1H), 4.61 (d, J = 6.8 Hz, 2H), 2.62 (s, 3H), 1.80 (d, J = 1.2 Hz, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 158.3, 138.3, 133.5, 130.3, 128.6, 120.4, 119.2, 112.7, 65.3, 32.0, 25.7, 18.2.

***N*-(2-Acetylphenyl)-*N*-(3-phenylallyl)benzenesulfonamide (4j).** Yield = 60% (235 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{23}H_{22}NO_3S$ 392.1320, found 392.1326, err (ppm): −1.53; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.57 (m, 4H), 7.48–7.44 (m, 2H), 7.38–7.19 (m, 7H), 6.76 (dd, J = 1.2, 7.6 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 6.8, 16.0 Hz, 1H), 4.60 (br s, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.4, 141.5, 138.1, 136.2, 136.0, 134.6, 132.8, 131.1, 129.0, 128.9, 128.8 (2×), 128.4 (2×), 128.3, 127.9, 127.7 (2×), 126.3 (2×), 123.3, 54.2, 30.1.

2-(3-Phenylallyloxy)benzaldehyde (4k). Yield = 68% (162 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{16}H_{15}O_2$ 239.1072, found 239.1080, err (ppm): −3.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.6 (s, 1H), 7.80 (dd, J = 2.0, 8.0 Hz, 1H), 7.55 (dd, J = 1.6, 8.4 Hz, 1H), 7.45–7.43 (m, 2H), 7.38–7.34 (m, 2H), 7.31–7.27 (m, 1H), 7.06–7.2 (m, 2H), 6.77 (d, J = 16.4 Hz, 1H), 6.42 (dt, J = 2.0, 16.0 Hz, 1H), 4.79 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 160.8, 135.9, 135.7, 133.3, 128.5 (2×), 128.2, 128.0, 126.4 (2×), 124.9, 123.2, 120.7, 112.7, 68.9.

A representative synthetic procedure of skeleton 5 is as follows

Sodium hydroxide (NaOH, 100 mg, 2.5 mmol) was added to a solution of **4** (1.0 mmol) in MeOH (10 mL) at 25 °C. A solution of substituted arylaldehydes (1.0 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 (monitored by TLC). The solvent was concentrated under reduced pressure. The residue was diluted with water (10 mL) and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 20/1–6/1) afforded skeleton **5**.

3-(3,4-Dimethoxyphenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5a). Yield = 80% (320 mg); colorless solid; mp = 131–133 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1763, err (ppm): −2.49; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J = 2.0, 7.6 Hz, 1H), 7.63 (d, J = 15.6 Hz, 1H), 7.46–7.41 (m, 1H), 7.43 (d, J = 15.6 Hz, 1H), 7.26–7.17 (m, 5H), 7.13 (dd, J = 2.0, 8.4 Hz, 1H), 7.05 (dt, J = 1.2, 7.6 Hz, 1H), 7.04 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.37 (dt, J = 5.6, 16.4 Hz, 1H), 4.74 (dd, J = 1.6, 5.6 Hz, 2H), 3.82 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 157.0, 150.9, 148.9, 142.8, 135.9, 132.7, 132.7, 130.5, 129.4, 128.3 (2×), 127.8, 127.7, 126.3 (2×), 125.2, 123.4, 122.4, 120.9, 112.8, 110.9, 110.1, 68.9, 55.7, 55.5.

1-[5-Bromo-2-(3-phenylallyloxy)phenyl]-3-(3,4-dimethoxyphenyl)propenone (5b). Yield = 84% (402 mg); colorless solid; mp = 146–148 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}BrO_4$ 479.0858, found 479.0866, err (ppm): −1.67; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 15.6 Hz, 1H), 7.50 (dd, J = 2.4, 8.8 Hz, 1H), 7.35 (d, J = 15.6 Hz, 1H), 7.26–7.17 (m, 5H), 7.11 (dd, J = 1.6, 8.4 Hz, 1H), 7.02 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 16.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.33 (dt, J = 5.6, 16.0 Hz, 1H), 4.70 (d, J = 4.8 Hz, 2H), 3.82 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 156.1, 151.1, 149.0, 143.8, 135.8, 135.1, 133.2, 133.0, 131.0, 128.4 (2×), 127.9, 127.6, 126.4 (2×), 124.5, 122.9, 122.6, 114.7, 113.4, 111.0, 110.3, 69.3, 55.8, 55.5.

1-[5-Chloro-2-(3-phenylallyloxy)phenyl]-3-(3,4-dimethoxyphenyl)propenone (5c). Yield = 86% (373 mg); colorless solid; mp = 128–130 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}ClO_4$ 435.1363, found 435.1370, err (ppm): −1.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 2.8 Hz, 1H), 7.61 (d, J = 15.6 Hz, 1H), 7.41 (dd, J = 2.8, 8.8 Hz, 1H), 7.35 (d, J = 16.0 Hz, 1H), 7.28–7.22 (m, 5H), 7.15 (dd, J = 2.0, 8.4 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 1H), 6.72 (d, J = 16.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.37 (dt, J = 5.2, 16.0 Hz, 1H), 4.76 (dd, J = 1.6, 6.0 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 155.7, 151.3, 149.1, 144.0, 136.0, 133.3, 132.3, 130.9, 130.2, 128.6 (2×), 128.1, 127.8, 126.5 (2×), 126.4, 124.7, 123.1, 122.8, 114.5, 111.1, 110.3, 69.6, 55.9, 55.7.

3-(3,4-Dimethoxyphenyl)-1-[5-fluoro-2-(3-phenylallyloxy)phenyl]propenone (5d). Yield = 83% (347 mg); colorless solid; mp = 123–125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}FO_4$ 419.1659, found 419.1653, err (ppm): 1.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 15.6 Hz, 1H), 7.42 (dd, J = 3.2, 8.8 Hz, 1H), 7.41 (d, J = 15.6 Hz, 1H), 7.28–7.22 (m, 5H), 7.18 (dd, J = 3.2, 8.4 Hz, 1H), 7.16 (dd, J = 2.4, 8.4 Hz, 1H), 7.05 (d, J = 2.0 Hz, 1H), 7.00 (dd, J = 4.0, 8.8 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.38 (dt, J = 5.6, 16.0 Hz, 1H), 4.75 (dd, J = 1.6, 5.6 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 157.1 (d, J = 239.6 Hz), 153.4 (d, J = 1.6 Hz), 151.2, 149.1, 143.9, 136.0, 133.2, 130.8 (d, J = 6.1 Hz), 128.5 (2×), 128.0, 127.8, 126.5 (2×), 124.7, 123.4, 122.8, 119.1 (d, J = 23.5 Hz), 117.0 (d, J = 23.5 Hz), 114.7 (d, J = 7.6 Hz), 111.1, 110.3, 70.1, 55.9, 55.7.

3-(3,4-Dimethoxyphenyl)-1-[5-methyl-2-(3-phenylallyloxy)phenyl]propenone (5e). Yield = 73% (302 mg); colorless solid; mp = 114–116 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_4$ 415.1909, found 415.1915, err (ppm): −1.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 16.0 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 16.0 Hz, 1H), 7.27–7.18 (m, 6H), 7.15 (dd, J = 1.6, 8.4 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 16.4 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.38 (dt, J = 5.2, 16.0 Hz, 1H), 4.74 (dd, J = 1.6, 5.6 Hz, 2H), 3.85 (s, 3H), 3.73 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 155.1, 150.9, 149.0, 142.8, 136.1, 133.3, 132.7, 130.9, 130.5, 129.4, 128.4 (2×), 128.0, 127.8, 126.4 (2×), 125.4, 123.7, 122.5, 113.1, 111.0, 110.2, 69.3, 55.8, 55.6, 20.3.

3-(3,4-Dimethoxyphenyl)-1-[4-methoxy-2-(3-phenylallyloxy)phenyl]propenone (5f). Yield = 84% (361 mg); colorless solid; mp = 132–133 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found

431.1851, err (ppm): 1.86; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 15.6 Hz, 1H), 7.26–7.20 (m, 5H), 7.13 (dd, J = 2.0, 8.4 Hz, 1H), 7.03 (d, J = 1.6 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 6.58 (d, J = 8.8 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.40 (dt, J = 5.2, 15.6 Hz, 1H), 4.73 (dd, J = 1.2, 5.6 Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9, 164.0, 159.3, 150.6, 148.9, 141.7, 136.0, 133.1, 133.0, 128.4 (2×), 128.2, 127.9, 126.4 (2×), 125.5, 123.2, 122.4, 122.0, 111.0, 110.4, 105.6, 99.5, 69.1, 55.8, 55.5, 55.4.

3-Benzo[1,3]dioxol-5-yl-1-[2-(3-phenylallyloxy)phenyl]propenone (5g). Yield = 87% (334 mg); colorless solid; mp = 99–101 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{21}O_4$ 385.1440, found 385.1432, err (ppm): 2.08; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (dd, J = 2.0, 7.6 Hz, 1H), 7.61 (d, J = 15.6 Hz, 1H), 7.44 (dt, J = 2.0, 8.0 Hz, 1H), 7.39 (d, J = 15.6 Hz, 1H), 7.26–7.18 (m, 5H), 7.06–6.98 (m, 4H), 6.69 (d, J = 16.0 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.34 (dt, J = 5.6, 16.4 Hz, 1H), 6.85 (s, 2H), 4.71 (dd, J = 1.2, 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.9, 157.1, 149.3, 148.1, 142.2, 136.0, 132.8, 132.6, 130.5, 129.4, 129.3, 128.2 (2×), 127.6, 126.3 (2×), 125.3, 124.6, 123.3, 120.9, 112.8, 108.3, 106.5, 104.2, 68.8.

1-[2-(3-Phenylallyloxy)phenyl]-3-(3,4,5-trimethoxyphenyl)propenone (5h). Yield = 80% (344 mg); colorless solid; mp = 92–94 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1863, err (ppm): −0.93; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, J = 2.0, 7.6 Hz, 1H), 7.59 (d, J = 15.6 Hz, 1H), 7.47 (dt, J = 2.0, 8.0 Hz, 1H), 7.42 (d, J = 15.6 Hz, 1H), 7.26–7.18 (m, 5H), 7.09–7.04 (m, 2H), 6.80 (s, 2H), 6.73 (d, J = 16.4 Hz, 1H), 6.37 (dt, J = 5.6, 16.4 Hz, 1H), 4.80 (dd, J = 1.6, 5.6 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 157.1, 153.3 (2×), 143.0, 140.1, 136.0, 132.9, 132.5, 130.6, 130.5, 129.7, 128.5 (2×), 127.9, 126.6, 126.3 (2×), 123.5, 121.1, 112.9, 105.5 (2×), 69.0, 60.9, 55.9 (2×).

3-(3-Methoxyphenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5i). Yield = 84% (311 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1654, err (ppm): −1.89; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 1.6, 7.6 Hz, 1H), 7.69 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 15.6 Hz, 1H), 7.48 (dt, J = 2.0, 8.0 Hz, 1H), 7.28–7.02 (m, 10H), 6.89 (dt, J = 2.0, 8.4 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 5.6, 16.4 Hz, 1H), 4.76 (dd, J = 1.6, 5.6 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 159.7, 157.2, 142.4, 136.3, 136.0, 133.0, 132.8, 130.6, 129.7, 129.2, 128.3 (2×), 127.7, 127.4, 126.3 (2×), 123.3, 120.9, 120.7, 115.9, 113.2, 112.8, 68.9, 54.9.

3-(4-Methoxyphenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5j). Yield = 85% (315 mg); colorless solid; mp = 115–117 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1642, err (ppm): 1.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, J = 2.0, 7.6 Hz, 1H), 7.66 (d, J = 16.0 Hz, 1H), 7.52–7.44 (m, 4H), 7.29–7.22 (m, 5H), 7.07 (dt, J = 0.8, 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.77–6.72 (m, 3H), 6.41 (dt, J = 5.6, 16.0 Hz, 1H), 4.78 (dd, J = 1.6, 5.6 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 161.3, 157.3, 142.6, 136.1, 133.1, 132.8, 130.7, 130.0 (2×), 129.6, 128.5 (2×), 127.83, 127.75 (2×), 126.5, 125.1, 123.6, 121.0, 114.2 (2×), 112.9, 69.1, 55.2.

1-[2-(3-Phenylallyloxy)phenyl]-3-(2,3,4-trimethoxyphenyl)propenone (5k). Yield = 79% (340 mg); colorless solid; mp = 89–91 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1864, err (ppm): −1.16; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 16.0 Hz, 1H), 7.73 (dd, J = 1.6, 7.6 Hz, 1H), 7.54 (d, J = 16.0 Hz, 1H), 7.44 (dt, J = 1.6, 7.6 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.26–7.20 (m, 5H), 7.04 (dt, J = 0.8, 7.6 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.40 (dt, J = 5.2, 15.6 Hz, 1H), 6.33 (d, J = 8.8 Hz, 1H), 4.75 (dd, J = 1.2, 5.6 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 157.2, 155.3, 153.5, 142.1, 137.5, 136.1, 132.9, 132.8, 130.6, 129.6, 128.4 (2×), 127.7, 126.4 (2×), 126.2, 123.6, 122.9, 122.0, 120.9, 112.8, 107.5, 69.0, 61.4, 60.7, 55.8.

3-(2-Hydroxyphenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5l). Yield = 74% (263 mg); colorless solid; mp = 150–152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{21}O_3$ 357.1491, found 357.1498, err (ppm): −1.96; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 16.0 Hz, 1H), 7.71 (dd, J = 1.6, 8.0 Hz, 1H), 7.68 (d, J = 16.0 Hz, 1H), 7.51–7.45 (m, 2H), 7.31–7.20 (m, 5H), 7.18 (dt, J = 1.6, 8.4 Hz, 1H), 7.08–7.01 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.46 (br s, 1H), 6.40 (dt, J = 1.6, 16.0 Hz, 1H), 4.80 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 157.4, 155.4, 138.6 (2×), 136.2, 133.1, 133.0, 131.4, 130.8, 129.6, 129.2, 128.6 (2×), 127.9, 126.5 (2×), 123.7, 122.4, 121.1, 120.9, 116.5, 113.1, 69.3.

3-(2,4-Dimethoxyphenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5m). Yield = 82% (328 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1760, err (ppm): −1.74; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 16.0 Hz, 1H), 7.71 (dd, J = 2.0, 7.6 Hz, 1H), 7.53 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.44 (dt, J = 2.0, 7.6 Hz, 1H), 7.26–7.22 (m, 5H), 7.05 (dt, J = 0.8, 7.6 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.74 (dt, J = 1.2, 16.0 Hz, 1H), 6.42–6.36 (m, 2H), 6.26 (dd, J = 2.0, 8.4 Hz, 1H), 4.76 (dd, J = 1.2, 5.6 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 162.7, 160.0, 157.1, 138.3, 136.2, 132.6, 132.5, 130.5, 130.1, 130.0, 128.4 (2×), 127.7, 126.4 (2×), 125.3, 123.7, 120.9, 117.1, 112.9, 105.1, 98.3, 69.0, 55.29, 55.27.

3-(4-Nitrophenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5n). Yield = 78% (300 mg); colorless solid; mp = 173–175 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{20}NO_4$ 386.1392, found 386.1399, err (ppm): −1.81; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.8 Hz, 2H), 7.81 (dd, J = 2.0, 8.0 Hz, 1H), 7.73 (d, J = 16.0 Hz, 1H), 7.65 (d, J = 16.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.53 (dt, J = 1.6, 8.0 Hz, 1H), 7.30–7.25 (m, 5H), 7.10 (dt, J = 1.2, 8.4 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.76 (dt, J = 1.2, 16.0 Hz, 1H), 6.43 (dt, J = 5.6, 16.0 Hz, 1H), 4.81 (dd, J = 1.6, 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 157.9, 148.1, 141.4, 138.5, 135.8, 134.2, 134.0, 131.2, 131.1, 128.7 (2×), 128.6 (2×), 128.5 (2×), 126.4 (2×), 124.0 (2×), 123.1, 121.3, 112.9, 69.3.

3-Biphenyl-4-yl-1-[2-(3-phenylallyloxy)phenyl]propenone (5o). Yield = 80% (333 mg); colorless solid; mp = 138–140 °C (recrys-

tallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{30}H_{25}O_2$ 417.1855, found 417.1850, err (ppm): 1.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, J = 2.0, 7.6 Hz, 1H), 7.76 (d, J = 15.6 Hz, 1H), 7.66 (d, J = 16.0 Hz, 1H), 7.64–7.46 (m, 9H), 7.41–7.37 (m, 1H), 7.28–7.22 (m, 5H), 7.10 (dt, J = 1.2, 8.4 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.78 (dt, J = 1.2, 16.0 Hz, 1H), 6.44 (dt, J = 5.6, 16.0 Hz, 1H), 4.80 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 157.5, 142.7, 142.0, 140.1, 136.1, 134.1, 133.3, 133.2, 130.8, 129.3, 128.81 (3×), 128.77 (2×), 128.5 (2×), 127.9, 127.7, 127.4 (2×), 127.2, 126.9 (2×), 126.5 (2×), 123.5, 121.1, 69.1.

3-(3,4-Dichlorophenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5p). Yield = 80% (326 mg); colorless solid; mp = 244–246 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{19}Cl_2O_2$ 409.0762, found 409.0768, err (ppm): −1.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 2.0, 7.6 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.51 (s, 1H), 7.52–7.48 (m, 2H), 7.34 (dd, J = 1.6, 8.4 Hz, 1H), 7.33–7.23 (m, 5H), 7.21 (d, J = 8.4 Hz, 1H), 7.08 (dt, J = 0.8, 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.7 (d, J = 16.0 Hz, 1H), 6.39 (dt, J = 5.6, 16.0 Hz, 1H), 4.80 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 157.6, 139.3, 135.9, 135.3, 133.8, 133.59, 133.56, 133.1, 130.9, 130.8, 129.9, 129.0, 128.9, 128.6 (2×), 128.1, 126.9, 126.5 (2×), 123.2, 121.2, 113.0, 69.2.

3-Naphthalen-2-yl-1-[2-(3-phenylallyloxy)phenyl]propenone (5q). Yield = 84% (328 mg); colorless solid; mp = 129–131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{28}H_{23}O_2$ 391.1698, found 391.1706, err (ppm): −2.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.79–7.67 (m, 5H), 7.60 (d, J = 8.4 Hz, 1H), 7.52–7.44 (m, 3H), 7.21–7.05 (m, 7H), 6.75 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 5.6, 16.0 Hz, 1H), 4.81 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 157.4, 142.7, 136.1, 134.2, 133.3, 133.2, 133.1, 132.7, 130.8, 130.3, 129.4, 128.7, 128.5, 128.4 (2×), 127.9, 127.7, 127.5, 127.0, 126.53, 126.47 (2×), 123.7, 123.5, 121.1, 113.0, 69.2.

3-Furan-2-yl-1-[2-(3-phenylallyloxy)phenyl]propenone (5r). Yield = 78% (257 mg); colorless solid; mp = 84–86 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{19}O_3$ 331.1334, found 331.1342, err (ppm): −2.42; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 2.0, 7.6 Hz, 1H), 7.51 (d, J = 1.2 Hz, 2H), 7.45 (dt, J = 1.6, 8.4 Hz, 1H), 7.30–7.22 (m, 6H), 7.05 (dt, J = 0.8, 8.4 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.77 (dt, J = 1.6, 16.0 Hz, 1H), 6.64 (dd, J = 2.8, 3.6 Hz, 1H), 6.43–6.37 (m, 2H), 4.76 (d, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 157.3, 151.5, 144.5, 136.2, 132.9, 132.5, 130.5, 129.2, 128.7, 128.3 (2×), 127.6, 126.3 (2×), 124.7, 123.5, 120.9, 115.4, 112.9, 112.3, 68.9.

1-[2-(3-Phenylallyloxy)phenyl]-3-thiophen-2-ylpropenone (5s). Yield = 73% (253 mg); colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{19}O_2S$ 347.1106, found 347.1110, err (ppm): −1.15; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 15.6 Hz, 1H), 7.74 (dd, J = 2.0, 8.0 Hz, 1H), 7.48 (dt, J = 2.0, 8.4 Hz, 1H), 7.41 (d, J = 15.6 Hz, 1H), 7.29–7.24 (m, 7H), 7.09–6.99 (m, 3H), 6.75 (dt, J = 1.6, 16.0 Hz, 1H), 6.42 (dd, J = 5.6, 16.0 Hz, 1H), 4.79 (dd, J = 1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 157.3, 140.6, 136.2, 135.0, 133.1, 133.0, 131.3, 130.7, 129.2, 128.4 (2×), 128.3, 128.1, 127.8, 126.5 (2×), 126.3, 123.5, 121.0, 112.9, 69.1.

3-(2-Fluorophenyl)-1-[2-(3-phenylallyloxy)phenyl]propenone (5t). Yield = 72% (258 mg); colorless solid; mp = 73–74 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{20}FO_2$ 359.1447, found 359.1456, err (ppm): −2.51; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 16.0 Hz, 1H), 7.80 (dd, J = 1.6, 7.6 Hz, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.55 (dt, J = 1.6, 7.6 Hz, 1H), 7.47 (dt, J = 2.0, 7.6 Hz, 1H), 7.28–7.22 (m, 6H), 7.07 (dt, J = 0.8, 7.6 Hz, 1H), 7.05–7.02 (m, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.91 (dt, J = 1.2, 7.6 Hz, 1H), 6.73 (dt, J = 1.2, 16.0 Hz, 1H), 6.39 (dt, J = 5.6, 16.0 Hz, 1H), 4.73 (dd, J = 1.2, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 161.3 (d, J = 252.5 Hz), 157.4, 135.9, 134.4 (d, J = 3.0 Hz), 133.2, 133.0, 131.2 (d, J = 8.3 Hz), 130.6, 129.2 (d, J = 6.1 Hz), 128.79 (d, J = 2.3 Hz), 128.75, 128.3 (2×), 127.7, 126.3 (2×), 124.2 (d, J = 3.0 Hz), 123.2, 122.9 (d, J = 11.4 Hz), 120.8, 115.8 (d, J = 22.0 Hz), 112.7, 68.9.

1-[2-(3-Phenylallyloxy)phenyl]-3-pyridin-3-ylpropenone (5u). Yield = 73% (249 mg); colorless solid; mp = 106–108 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{23}H_{20}NO_2$ 342.1494, found 342.1501, err (ppm): −2.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, J = 2.0 Hz, 1H), 8.48 (d, J = 1.6, 4.8 Hz, 1H), 7.79 (dt, J = 2.0, 8.0 Hz, 1H), 7.74 (dd, J = 2.0, 7.6 Hz, 1H), 7.62 (d, J = 0.8 Hz, 2H), 7.47 (dt, J = 2.0, 8.4 Hz, 1H), 7.26–7.23 (m, 5H), 7.07–6.98 (m, 3H), 6.71 (d, J = 16.0 Hz, 1H), 6.37 (dt, J = 1.6, 16.0 Hz, 1H), 4.76 (dd, J = 1.2, 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 157.5, 150.6, 150.1, 138.1, 135.8, 133.7, 133.5, 133.3, 130.8, 130.7, 129.0, 128.8, 128.5 (2×), 127.9, 126.3 (2×), 123.5, 123.2, 121.1, 112.9, 69.1.

3-(3,4-Dimethoxyphenyl)-1-[2-(2-phenylallyloxy)phenyl]propenone (5v). Yield = 84% (336 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1758, err (ppm): −1.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 1.6, 7.6 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 7.44–7.36 (m, 3H), 7.27 (d, J = 15.6 Hz, 1H), 7.26–7.21 (m, 3H), 7.04–6.99 (m, 4H), 6.78 (d, J = 8.8 Hz, 1H), 5.51 (s, 1H), 5.47 (d, J = 1.2 Hz, 1H), 4.92 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 156.7, 150.8, 148.8, 142.9, 142.3, 137.8, 132.5, 130.2, 129.6, 128.2 (2×), 127.8, 127.7, 125.6 (2×), 124.8, 122.7, 120.9, 114.4, 112.8, 110.8, 109.9, 70.0, 55.6, 55.5.

3-(4-Nitrophenyl)-1-[2-(2-phenylallyloxy)phenyl]propenone (5w). Yield = 82% (316 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{20}NO_4$ 386.1392, found 386.1388, err (ppm): 1.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.8 Hz, 2H), 7.76 (dd, J = 2.0, 8.0 Hz, 1H), 7.58–7.39 (m, 7H), 7.33–7.28 (m, 3H), 7.12 (d, J = 7.6 Hz, 1H), 7.09 (dt, J = 1.2, 8.0 Hz, 1H), 5.64 (s, 1H), 5.47 (d, J = 0.8 Hz, 1H), 5.02 (d, J = 0.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 157.6, 148.1, 142.2, 141.4, 138.8, 138.0, 137.5, 133.9, 131.2, 130.5, 128.7 (2×), 128.6 (2×), 128.3, 125.7 (2×), 123.9 (2×), 121.4, 115.9, 112.8, 70.6.

3-Naphthalen-1-yl-1-[2-(2-phenylallyloxy)phenyl]propenone (5x). Yield = 84% (328 mg); colorless solid; mp = 123–125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{28}H_{23}O_2$ 391.1698, found 391.1694, err (ppm): 1.02; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 15.6 Hz, 1H), 8.23 (dd, J

= 1.6, 7.6 Hz, 1H), 7.90–7.88 (m, 2H), 7.82 (dd, J = 1.6, 7.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.59–7.49 (m, 4H), 7.44–7.41 (m, 3H), 7.27–7.21 (m, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 5.58 (s, 1H), 5.51 (d, J = 0.8 Hz, 1H), 5.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 157.2, 142.3, 139.2, 137.7, 133.5, 133.0, 132.2, 131.6, 130.7, 130.2, 129.6, 129.2, 128.5, 128.3 (2×), 127.9, 126.6, 126.0, 125.7 (2×), 125.3, 124.9, 123.4, 121.1, 115.2, 112.8, 70.4.

1-[2-(2-Phenylallyloxy)phenyl]-3-thiophen-2-ylpropenone (5y). Yield = 80% (277 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{19}O_2S$ 347.1106, found 347.1115, err (ppm): −2.59; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 15.2 Hz, 1H), 7.71 (dd, J = 2.0, 8.0 Hz, 1H), 7.50–7.43 (m, 3H), 7.35–7.26 (m, 5H), 7.19 (dd, J = 0.4, 3.2 Hz, 1H), 7.09–7.02 (m, 3H), 5.60 (s, 1H), 5.53 (d, J = 1.2 Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 157.0, 142.2, 140.3, 137.8, 135.1, 132.8, 131.1, 130.4, 129.3, 128.4, 128.3 (2×), 128.0, 127.9, 125.8, 125.7 (2×), 121.0, 114.8, 112.9, 70.1.

1-(2-But-2-enyloxyphenyl)-3-(3,4-dimethoxyphenyl)propenone (5z). Two isomers (E/Z = 5/1); yield = 75% (254 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{21}H_{23}O_4$ 339.1596, found 339.1603, err (ppm): −2.06; for major E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 1.6, 7.6 Hz, 1H), 7.56 (d, J = 15.6 Hz, 1H), 7.41 (dt, J = 0.8, 7.6 Hz, 1H), 7.32 (d, J = 15.6 Hz, 1H), 7.14 (dd, J = 2.8, 7.6 Hz, 1H), 7.09 (d, J = 2.0 Hz, 1H), 7.00 (dt, J = 0.8, 7.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 5.85–5.78 (m, 1H), 5.70–5.63 (m, 1H), 4.53 (dt, J = 1.2, 5.6 Hz, 2H), 3.89 (s, 6H), 1.64 (dd, J = 1.6, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 157.2, 151.0, 149.0, 142.9, 132.6, 130.3, 129.9, 128.1, 125.4, 125.3, 125.1, 122.8, 120.7, 113.0, 111.0, 109.9, 69.1, 55.8, 55.7, 17.7.

1-(2-But-2-enyloxyphenyl)-3-naphthalen-1-ylpropenone (5aa). Two isomers (E/Z = 5/1); yield = 76% (249 mg); colorless solid; mp = 77–79 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{23}H_{21}O_2$ 329.1542, found 329.1551, err (ppm): −2.73; for major E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 16.0 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.87–7.82 (m, 4H), 7.64 (d, J = 15.6 Hz, 1H), 7.56–7.43 (m, 4H), 7.07 (dt, J = 0.8, 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.87–5.79 (m, 1H), 5.75–5.65 (m, 1H), 4.50 (dt, J = 1.2, 5.6 Hz, 2H), 1.64 (dd, J = 1.2, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 157.4, 138.5, 133.4, 133.0, 132.9, 132.2, 131.5, 130.5, 130.2, 130.11, 130.08, 129.5, 128.4, 126.4, 125.8, 125.2, 124.7, 123.2, 120.6, 112.7, 68.9, 17.5.

1-(2-But-2-enyloxyphenyl)-3-thiophen-2-ylpropenone (5ab). Two isomers (E/Z = 4/1); yield = 79% (224 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{17}H_{17}O_2S$ 285.0949, found 285.0940, err (ppm): 3.16; for major E-isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 15.6 Hz, 1H), 7.69–7.67 (m, 1H), 7.41–7.32 (m, 3H), 7.24–7.33 (m, 1H), 7.01–6.95 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 5.88–5.79 (m, 1H), 5.70–5.66 (m, 1H), 4.50 (d, J = 5.6 Hz, 2H), 1.67 (dd, J = 1.2, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 157.3, 140.5, 134.6, 132.9, 131.1, 130.40, 130.37, 130.2, 128.1, 127.9, 126.1, 125.2, 120.5, 112.7, 69.0, 17.6.

3-(3,4-Dimethoxyphenyl)-1-[2-(3-methylbut-2-enyloxy)phenyl] propenone (5ac). Yield = 80% (282 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{25}O_4$ 353.1753, found 353.1761, err (ppm): −2.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, J = 1.6, 7.6 Hz, 1H), 7.55 (d, J = 15.6 Hz, 1H), 7.42 (dt, J = 1.6, 7.6 Hz, 1H), 7.34 (d, J = 16.0 Hz, 1H), 7.14 (ddd, J = 0.4, 2.0, 8.4 Hz, 1H), 7.09 (d, J = 2.0 Hz, 1H), 7.02 (dt, J = 1.2, 7.6 Hz, 1H), 6.98 (dd, J = 0.8, 8.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 5.48–5.44 (m, 1H), 4.59 (d, J = 6.4 Hz, 2H), 3.898 (s, 3H), 3.896 (s, 3H), 1.71 (d, J = 0.8 Hz, 3H), 1.69 (d, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 157.4, 151.0, 149.0, 142.9, 138.0, 132.6, 130.4, 129.7, 128.2, 125.3, 122.7, 120.7, 119.3, 113.1, 111.0, 110.1, 65.6, 55.9, 55.8, 25.6, 18.2.

***N*-{2-[3-(3,4-Dimethoxyphenyl)acryloyl]phenyl}-*N*-(3-phenylallyl) benzenesulfonamide (5ad).** Yield = 83% (447 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{32}H_{30}NO_5S$ 540.1845, found 540.1854, err (ppm): −1.67; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.75 (m, 2H), 7.60–7.58 (m, 1H), 7.52–7.36 (m, 6H), 7.27–7.11 (m, 8H), 7.03–7.00 (m, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 6.19 (dt, J = 7.2, 16.0 Hz, 1H), 4.41 (dd, J = 0.8, 6.4 Hz, 2H), 3.912 (s, 3H), 3.905 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.3, 151.4, 149.2, 145.4, 141.5, 139.5, 137.0, 136.2, 134.5, 132.8, 130.8, 130.2, 129.6, 128.9 (2×), 128.4 (2×), 128.3, 128.0 (2×), 127.8, 127.7, 126.5 (2×), 124.1, 123.7, 123.4, 111.0, 110.1, 55.93, 55.91, 55.2.

4-[2-(3-Phenylallyloxy)phenyl]but-3-en-2-one (5ae). Sodium hydroxide (NaOH, 100 mg, 2.5 mmol) was added to a solution of **4k** (240 mg, 1.0 mmol) in a co-solvent of acetone (10 mL) and MeOH (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 20 h (monitored by TLC). The solvent was concentrated under reduced pressure. The residue was diluted with water (10 mL) and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 20/1–6/1) afforded compound **5ae**. Yield = 84% (234 mg); colorless solid; mp = 85–87 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1391, err (ppm): −2.15; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 16.4 Hz, 1H), 7.58 (dd, J = 1.6, 7.6 Hz, 1H), 7.44–7.41 (m, 2H), 7.38–7.33 (m, 3H), 7.30–7.26 (m, 1H), 7.01–6.97 (m, 2H), 6.79 (d, J = 16.4 Hz, 1H), 6.76 (d, J = 16.4 Hz, 1H), 6.44 (dt, J = 5.6, 16.0 Hz, 1H), 4.79 (dd, J = 1.2, 5.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 157.2, 138.6, 136.1, 133.1, 131.7, 128.6 (2×), 128.2, 128.0, 127.7, 126.5 (2×), 123.8, 123.6, 121.0, 112.6, 69.0, 27.1.

A representative synthetic procedure of skeleton 6 is as follows

NBS (107 mg, 0.6 mmol) was added to a solution of **5** (1.0 mmol) in CCl_4 (10 mL) at 25 °C. Then, DABCO (70 mg, 0.6 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred under an air atmosphere (open-vessel condition) at reflux (77 °C) for 15 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with 2 N $HCl_{(aq)}$ (10 mL) and the mixture was 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 = 15/1–5/1) afforded skeleton **6**.

2-(3,4-Dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6a). Yield = 90% (72 mg); colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1758, err (ppm): −1.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (dd, J = 1.6, 7.6 Hz, 1H), 7.43 (dt, J = 1.6, 8.0 Hz, 1H), 7.17–7.13 (m, 2H), 7.10–7.05 (m, 3H), 7.01–6.98 (m, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.60 (dd, J = 1.6, 8.4 Hz, 1H), 6.30 (d, J = 1.6 Hz, 1H), 4.53–4.51 (m, 1H), 4.49 (d, J = 3.6 Hz, 1H), 4.32 (dd, J = 8.8, 12.4 Hz, 1H), 3.99 (dd, J = 1.2, 6.0 Hz, 1H), 3.94 (dd, J = 7.6, 10.0 Hz, 1H), 3.76 (s, 3H), 3.73–3.65 (m, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 160.4, 148.3, 147.2, 139.3, 133.5, 131.7, 130.9, 128.1 (2×), 127.8 (2×), 126.3, 126.2, 121.9, 119.8, 119.6, 111.7, 110.5, 74.8, 55.7, 55.5, 53.6, 45.0, 43.4, 43.1. 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 = 17.962(3) Å, b = 10.2398(15) Å, c = 11.0654(16) Å, V = 2030.8(5) Å^3, Z = 4, d_{calcd} = 1.310 g cm^{-3}, F(000) = 848, 2θ range 2.273–26.665°, R indices (all data) $R1$ = 0.0878, w$R2$ = 0.2262.

5-Bromo-2-(3,4-dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6b). Yield = 94% (90 mg); colorless solid; mp = 145–147 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}BrO_4$ 479.0858, found 479.0863, err (ppm): −1.04; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 2.8 Hz, 1H), 7.50 (dd, J = 2.4, 8.8 Hz, 1H), 7.17–7.06 (m, 3H), 6.99–6.97 (m, 3H), 6.63 (d, J = 8.4 Hz, 1H), 6.58 (dd, J = 2.0, 8.4 Hz, 1H), 6.28 (d, J = 1.6 Hz, 1H), 4.52–4.46 (m, 2H), 4.29 (dd, J = 8.8, 12.4 Hz, 1H), 3.99–3.87 (m, 2H), 3.76 (s, 3H), 3.71–3.62 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 159.5, 148.3, 147.3, 139.1, 136.2, 133.2, 131.4, 128.2 (2×), 127.8 (2×), 127.7, 126.5, 121.9, 119.6, 114.4, 111.7, 110.6, 75.1, 55.7, 55.6, 53.6, 45.0, 43.4, 42.9.

5-Chloro-2-(3,4-dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6c). Yield = 93% (81 mg); colorless solid; mp = 154–156 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}ClO_4$ 435.1363, found 435.1370, err (ppm): −1.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 2.8 Hz, 1H), 7.37 (dd, J = 2.4, 8.8 Hz, 1H), 7.17–7.07 (m, 3H), 7.04 (d, J = 8.8 Hz, 1H), 6.99–6.97 (m, 2H), 6.63 (d, J = 8.4 Hz, 1H), 6.58 (dd, J = 1.6, 8.0 Hz, 1H), 6.28 (d, J = 2.0 Hz, 1H), 4.52–4.47 (m, 2H), 4.30 (dd, J = 8.8, 12.4 Hz, 1H), 3.99–3.87 (m, 2H), 3.76 (s, 3H), 3.71–3.63 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 159.0, 148.3, 147.3, 139.1, 133.3, 131.5, 130.1, 128.2 (2×), 127.8 (3×), 127.2, 126.4, 121.6, 119.6, 111.7, 110.6, 75.1, 55.7, 55.6, 53.6, 45.0, 43.4, 42.9.

2-(3,4-Dimethoxyphenyl)-5-fluoro-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6d). Yield = 98% (82 mg); colorless solid; mp = 146–148 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}FO_4$ 419.1659, found 419.1653, err (ppm): 1.43; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, J = 3.2, 9.2 Hz, 1H), 7.17–7.05 (m, 5H), 7.05–6.98 (m, 2H), 6.63 (d, J = 8.4 Hz, 1H), 6.59 (dd, J = 1.6, 8.4 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 4.51–4.45 (m, 2H), 4.30 (dd, J = 4.4, 12.4 Hz, 1H), 4.00 (ddd, J = 1.2, 6.4, 10.8 Hz, 1H), 3.94 (dd, J = 6.4, 10.0 Hz, 1H), 3.76 (s, 3H), 3.69–3.61 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 157.5 (d, J = 240.3 Hz), 156.8 (d, J = 1.4 Hz), 148.3, 147.3, 139.2, 131.5, 128.1 (2×), 127.8 (2×), 126.9 (d, J = 6.0 Hz), 126.4, 121.6 (d, J = 7.6 Hz), 120.8 (d, J = 24.3 Hz), 119.6, 116.1 (d, J = 24.3 Hz), 111.7, 110.5, 75.2, 55.7, 55.5, 53.5, 45.1, 43.5, 43.0. Single-crystal X-Ray diagram: crystal of compound **6d** was grown by slow diffusion of EtOAc into a solution of compound **6d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $C2/c$, a = 27.5645 (11) Å, b = 7.0521(3) Å, c = 22.8442(10) Å, V = 4038.4(3) Å^3, Z = 8, d_{calcd} = 1.376 g cm^{-3}, F(000) = 1760, 2θ range 1.625–26.487°, R indices (all data) $R1$ = 0.0412, w$R2$ = 0.0881.

2-(3,4-Dimethoxyphenyl)-5-methyl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6e). Yield = 94% (78 mg); colorless solid; mp = 108–110 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_4$ 415.1909, found 415.1916, err (ppm): −1.69; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 2.0 Hz, 1H), 7.24 (dd, J = 2.4, 8.4 Hz, 1H), 7.18–7.04 (m, 3H), 7.01–6.98 (m, 3H), 6.63 (d, J = 8.4 Hz, 1H), 6.58 (dd, J = 2.0, 8.4 Hz, 1H), 6.30 (d, J = 1.6 Hz, 1H), 4.50 (dd, J = 6.4, 10.0 Hz, 1H), 4.45 (dd, J = 4.0, 12.4 Hz, 1H), 4.30 (dd, J = 8.8, 12.4 Hz, 1H), 4.01–3.91 (m, 2H), 3.76 (s, 3H), 3.67–3.62 (m, 1H), 3.58 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 158.5, 148.3, 147.2, 139.5, 134.5, 131.9, 131.4, 130.7, 128.1 (3×), 127.9 (2×), 126.3, 119.8, 119.6, 111.7, 110.5, 74.8, 55.7, 55.6, 53.7, 45.1, 43.5, 43.2, 20.3.

2-(3,4-Dimethoxyphenyl)-6-methoxy-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6f). Yield = 90% (77 mg); colorless solid; mp = 136–138 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1865, err (ppm): −1.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.8 Hz, 1H), 7.16–7.13 (m, 2H), 7.09–7.06 (m, 1H), 7.01–6.99 (m, 2H), 6.64 (d, J = 9.2 Hz, 1H), 6.63 (d, J = 8.8 Hz, 1H), 6.61 (br s, 1H), 6.60–6.57 (m, 1H), 6.29 (d, J = 1.6 Hz, 1H), 4.49–4.44 (m, 2H), 4.35 (dd, J = 8.0, 12.4 Hz, 1H), 3.99–3.91 (m, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 3.61–3.52 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 164.0, 162.7, 148.2, 147.1, 139.5, 132.8, 131.9, 128.1 (2×), 127.9 (2×), 126.3, 119.59, 119.56, 111.6, 110.5, 109.7, 103.6, 75.1, 55.7, 55.5 (2×), 53.4, 45.2, 43.9, 42.7.

2-Benzo[1,3]dioxol-5-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6g). Yield = 90% (69 mg); colorless solid; mp = 133–135 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{21}O_4$ 385.1440, found 385.1446, err (ppm): −1.56; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 1.6, 7.6 Hz, 1H), 7.43 (dt, J = 2.0, 8.4 Hz, 1H), 7.19–7.15 (m, 2H), 7.11–7.04 (m, 3H), 7.01–6.99 (m, 2H), 6.55 (d, J = 8.0 Hz, 1H), 6.47 (dd, J = 1.2, 8.0 Hz, 1H), 6.44 (d, J = 1.6 Hz, 1H), 5.80 (d, J = 1.6 Hz, 1H), 5.79 (d, J = 1.6 Hz, 1H), 4.52–4.48 (m, 2H), 4.30 (dd, J = 8.8, 12.0 Hz,

1H), 3.97–3.88 (m, 2H), 3.72–3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 160.4, 147.3, 145.7, 139.1, 133.5, 133.1, 130.9, 128.1 (2×), 127.8 (2×), 126.3, 126.2, 121.9, 121.0, 119.8, 108.4, 107.7, 100.7, 74.8, 53.7, 45.0, 43.6, 43.1.

1-Phenyl-2-(3,4,5-trimethoxyphenyl)-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6h). Yield = 94% (81 mg); colorless solid; mp = 134–136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1865, err (ppm): −1.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 2.0, 8.0 Hz, 1H), 7.43 (dt, J = 1.6, 8.0 Hz, 1H), 7.19–7.15 (m, 2H), 7.11–7.05 (m, 3H), 7.02–7.00 (m, 2H), 6.12 (s, 2H), 4.52–4.48 (m, 2H), 4.32 (dd, J = 8.8, 12.4 Hz, 1H), 3.99–3.93 (m, 2H), 3.70 (s, 3H), 3.70–3.67 (m, 1H), 3.62 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 160.4, 152.6 (2×), 139.2, 134.9, 133.6, 130.9 (2×), 128.1 (2×), 127.8 (2×), 126.4, 126.1, 121.9, 119.9, 105.3 (2×), 74.7, 60.7, 55.9 (2×), 53.7, 44.9, 43.9, 42.9.

2-(3-Methoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6i). Yield = 90% (67 mg); colorless solid; mp = 113–115 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1652, err (ppm): −1.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 1.6, 8.0 Hz, 1H), 7.43 (dt, J = 1.6, 8.4 Hz, 1H), 7.17–6.99 (m, 8H), 6.61–6.56 (m, 2H), 6.48 (t, J = 2.0 Hz, 1H), 4.57 (dd, J = 6.0, 10.0 Hz, 1H), 4.51 (dd, J = 4.0, 12.4 Hz, 1H), 4.31 (dd, J = 9.2, 12.4 Hz, 1H), 4.03 (ddd, J = 0.8, 6.0, 10.4 Hz, 1H), 3.96 (dd, J = 7.6, 10.4 Hz, 1H), 3.75–3.65 (m, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 160.4, 159.2, 140.8, 139.2, 133.5, 130.9, 128.9, 128.0 (2×), 127.8 (2×), 126.31, 126.27, 121.9, 120.3, 119.8, 113.7, 111.8, 74.8, 55.0, 53.3, 45.0, 43.7, 43.3.

2-(4-Methoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6j). Yield = 90% (67 mg); colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1653, err (ppm): −1.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 1.6, 8.0 Hz, 1H), 7.43 (dt, J = 1.6, 8.4 Hz, 1H), 7.16–7.04 (m, 5H), 6.99–6.97 (m, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 4.53 (dd, J = 7.6, 11.6 Hz, 1H), 4.51 (dd, J = 4.0, 7.6 Hz, 1H), 4.30 (dd, J = 9.2, 12.4 Hz, 1H), 3.97 (ddd, J = 0.8, 6.0, 10.8 Hz, 1H), 3.92 (dd, J = 8.0, 10.4 Hz, 1H), 3.75–3.68 (m, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 160.4, 157.8, 139.3, 133.5, 131.3, 130.9, 128.9 (2×), 128.0 (2×), 127.8 (2×), 126.3, 126.2, 121.9, 119.8, 113.4 (2×), 74.9, 55.1, 53.7, 45.0, 43.2, 43.1.

1-Phenyl-2-(2,3,4-trimethoxyphenyl)-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6k). Yield = 90% (77 mg); colorless solid; mp = 149–151 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1866, err (ppm): −1.62; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 1.6, 8.0 Hz, 1H), 7.42 (dt, J = 1.6, 8.4 Hz, 1H), 7.12–7.00 (m, 7H), 6.78 (d, J = 8.4 Hz, 1H), 6.46 (d, J = 8.8 Hz, 1H), 4.73 (dd, J = 6.8, 10.0 Hz, 1H), 4.47 (dd, J = 3.6, 12.4 Hz, 1H), 4.35 (dd, J = 8.8, 12.4 Hz, 1H), 4.04 (ddd, J = 0.8, 6.8, 10.0 Hz, 1H), 3.92–3.85 (m, 2H), 3.74 (s, 3H), 3.64 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 160.3, 152.2, 151.5, 141.6, 139.7, 133.4, 130.9, 127.8 (2×), 127.6 (2×), 126.2, 126.0, 124.9, 121.7, 121.6, 119.8, 106.1, 74.7, 60.3, 60.2, 55.7, 52.2, 45.0, 43.4, 39.0.

2-(2-Hydroxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6l). Yield = 89% (63 mg); colorless solid; mp = 164–166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{21}O_3$ 357.1491, found 357.1498, err (ppm): −1.96; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 8.13 (dd, J = 2.0, 8.4 Hz, 1H), 7.60 (dt, J = 2.0, 8.0 Hz, 1H), 7.31–7.16 (m, 9H), 7.01 (dd, J = 0.8, 8.0 Hz, 1H), 6.89 (dt, J = 0.8, 8.4 Hz, 1H), 4.40 (d, J = 8.8 Hz, 2H), 3.98 (t, J = 9.6 Hz, 1H), 3.81 (t, J = 9.6 Hz, 1H), 3.42 (dd, J = 9.2, 11.2 Hz, 1H), 2.69 (dt, J = 8.8, 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 159.7, 155.1, 140.9, 136.5, 130.0, 128.74, 128.70 (2×), 128.6, 127.1, 126.6 (2×), 126.5, 126.2, 125.0, 124.7, 119.9, 117.6, 73.6, 53.5, 45.7, 43.2, 40.3.

2-(2,4-Dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6m). Yield = 88% (70 mg); colorless solid; mp = 150–152 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1761, err (ppm): −1.99; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 2.0, 8.0 Hz, 1H), 7.42 (dt, J = 1.6, 8.0 Hz, 1H), 7.11–7.07 (m, 4H), 7.05–6.98 (m, 4H), 6.31 (dd, J = 2.4, 8.0 Hz, 1H), 6.08 (d, J = 2.4 Hz, 1H), 4.60 (dd, J = 7.6, 10.0 Hz, 1H), 4.42–4.40 (m, 2H), 4.19–4.14 (m, 1H), 3.91 (dd, J = 6.0, 10.0 Hz, 1H), 3.69 (s, 3H), 3.51–3.46 (m, 1H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 160.4, 159.4, 157.8, 140.4, 133.5, 131.1, 127.8 (2×), 127.6, 127.5 (2×), 126.3, 126.0, 121.8, 120.02, 119.97, 103.1, 98.0, 74.7, 55.2, 54.6, 52.0, 45.2, 43.8, 39.8.

2-(4-Nitrophenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6n). Yield = 86% (66 mg); colorless solid; mp = 176–178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{20}NO_4$ 386.1392, found 386.1396, err (ppm): −1.03; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.8 Hz, 2H), 7.77 (dd, J = 2.0, 8.0 Hz, 1H), 7.45 (dt, J = 1.6, 8.0 Hz, 1H), 7.17–7.06 (m, 7H), 6.98–6.96 (m, 2H), 4.67 (dd, J = 6.4, 10.0 Hz, 1H), 4.52 (dd, J = 4.0, 12.4 Hz, 1H), 4.34 (dd, J = 9.2, 12.4 Hz, 1H), 4.08 (ddd, J = 1.2, 6.4, 10.4 Hz, 1H), 4.02 (dd, J = 6.8, 10.4 Hz, 1H), 3.75–3.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0, 160.5, 147.2, 146.2, 138.3, 133.9, 130.9, 128.7 (2×), 128.4 (2×), 127.7 (2×), 126.9 (2×), 125.8, 123.1, 122.1, 120.0, 74.6, 52.9, 45.1, 43.8, 43.0.

2-Biphenyl-4-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6o). Yield = 89% (74 mg); colorless solid; mp = 195–197 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{30}H_{25}O_2$ 417.1855, found 417.1859, err (ppm): −0.96; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 2.0, 8.0 Hz, 1H), 7.50–7.26 (m, 8H), 7.17–7.01 (m, 9H), 4.64 (dd, J = 6.0, 10.0 Hz, 1H), 4.54 (dd, J = 4.0, 12.4 Hz, 1H), 4.34 (dd, J = 9.2, 12.4 Hz, 1H), 4.07 (ddd, J = 0.8, 6.0, 10.4 Hz, 1H), 4.00 (dd, J = 7.6, 10.0 Hz, 1H), 3.79–3.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 160.4, 140.7, 139.2, 138.7, 138.3, 133.5, 130.9, 128.6 (2×), 128.4 (2×), 128.1 (2×), 127.8 (2×), 127.0, 126.8 (2×), 126.5 (2×), 126.33, 126.25, 121.9, 119.8, 74.8, 53.4, 45.0, 43.5, 43.3.

2-(3,4-Dichlorophenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6p). Yield = 92% (75 mg); colorless solid; mp = 114–116 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{19}Cl_2O_2$ 409.0762, found 409.0768, err (ppm): −1.47; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 2.0, 8.0 Hz, 1H), 7.44 (dt, J = 1.6, 8.0 Hz, 1H), 7.20–7.05 (m, 7H), 6.99–6.96 (m, 2H), 6.75 (dd, J = 2.0, 8.0 Hz, 1H), 4.54–4.49 (m, 2H), 4.31 (dd, J = 9.2, 12.4 Hz, 1H), 3.97–3.93 (m, 2H), 3.74–3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 160.4, 139.6, 138.4, 133.7, 131.9, 130.9, 130.0, 129.83, 129.78, 128.4 (2×), 127.7 (2×), 127.4, 126.8, 126.0, 122.0, 119.9, 74.7, 53.1, 44.8, 43.0, 42.9.

2-Naphthalen-2-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6q). Yield = 94% (73 mg); colorless solid; mp = 139–141 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{28}H_{23}O_2$ 391.1698, found 391.1690, err (ppm): 2.05; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, J = 2.0, 8.0 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.56 (br s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.48–7.35 (m, 3H), 7.14–7.07 (m, 4H), 7.03–6.97 (m, 4H), 4.77 (dd, J = 6.0, 10.0 Hz, 1H), 4.55 (dd, J = 4.0, 12.4 Hz, 1H), 4.37 (dd, J = 9.2, 12.4 Hz, 1H), 4.19 (ddd, J = 0.8, 6.0, 10.4 Hz, 1H), 4.06 (dd, J = 7.2, 10.0 Hz, 1H), 3.83–3.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 160.5, 139.2, 136.8, 133.5, 133.1, 131.9, 130.9, 128.1 (2×), 127.8 (2×), 127.6, 127.4 (2×), 126.7, 126.31, 126.27, 126.0, 125.7, 125.3, 121.9, 119.9, 74.8, 53.3, 45.0, 43.9, 43.5.

2-Furan-2-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6r). Yield = 93% (61 mg); colorless solid; mp = 118–120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{19}O_3$ 331.1334, found 331.1340, err (ppm): −1.81; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, J = 2.0, 8.0 Hz, 1H), 7.42 (dt, J = 1.6, 8.0 Hz, 1H), 7.22–7.12 (m, 5H), 7.08–7.04 (m, 3H), 6.12 (dt, J = 1.6, 3.2 Hz, 1H), 5.95 (dd, J = 0.8, 2.8 Hz, 1H), 4.60 (dd, J = 4.0, 10.0 Hz, 1H), 4.57 (dd, J = 4.0, 12.0 Hz, 1H), 4.12 (t, J = 12.0 Hz, 1H), 4.06–3.98 (m, 1H), 3.91 (ddd, J = 0.8, 4.0, 10.4 Hz, 1H), 3.78 (t, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 160.5, 153.3, 141.5, 138.8, 133.3, 130.6, 128.0 (2×), 127.2 (2×), 126.5, 126.4, 121.7, 119.7, 110.0, 107.3, 74.9, 52.1, 44.6, 43.2, 37.5.

1-Phenyl-2-thiophen-2-yl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6s). Yield = 95% (66 mg); colorless solid; mp = 142–144 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{19}O_2S$ 347.1106, found 347.1110, err (ppm): −1.15; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J = 1.6, 7.6 Hz, 1H), 7.44 (dt, J = 2.0, 8.4 Hz, 1H), 7.23–7.12 (m, 3H), 7.11–7.05 (m, 4H), 6.98 (dt, J = 1.2, 5.2 Hz, 1H), 6.77 (dd, J = 3.2, 5.2 Hz, 1H), 6.67 (dt, J = 1.2, 3.2 Hz, 1H), 4.83–4.80 (m, 1H), 4.58–4.54 (m, 1H), 4.23–4.18 (m, 1H), 3.94–3.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 160.5, 142.7, 138.4, 133.5, 130.7, 128.0 (2×), 127.6 (2×), 126.6, 126.4, 126.3, 125.0, 123.9, 121.8, 119.8, 74.8, 55.2, 45.4, 42.6, 34.5.

2-(2-Fluorophenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6t). Yield = 87% (62 mg); colorless solid; mp = 148–150 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{24}H_{20}FO_2$ 359.1447, found 359.1452, err (ppm): −1.39; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 1.6, 7.6 Hz, 1H), 7.45 (dt, J = 1.6, 8.4 Hz, 1H), 7.17–6.92 (m, 10H), 6.73 (dt, J = 1.2, 8.0 Hz, 1H), 4.78 (dd, J = 7.2, 10.0 Hz, 1H), 4.49 (dd, J = 3.6, 12.4 Hz, 1H), 4.39 (dd, J = 4.8, 12.4 Hz, 1H), 4.16 (ddd, J = 0.8, 7.2, 10.4 Hz, 1H), 3.99 (dd, J = 6.4, 10.0 Hz, 1H), 3.70–3.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 160.5 (d, J = 244.1 Hz), 160.4, 139.1, 133.6, 131.0, 128.2 (d, J = 4.5 Hz), 128.0 (d, J = 8.4 Hz), 127.9 (2×), 127.6 (2×), 126.4, 126.3 (d, J = 15.1 Hz), 126.1, 123.6 (d, J = 3.1 Hz), 121.9, 120.0, 114.8 (d, J = 22.0 Hz), 74.6, 51.6, 44.9, 43.2, 38.8.

1-Phenyl-2-pyridin-3-yl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6u). Yield = 87% (59 mg); colorless solid; mp = 151–153 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{23}H_{20}NO_2$ 342.1494, found 342.1487, err (ppm): 2.05; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 2.4 Hz, 1H), 8.26 (dd, J = 1.6, 8.8 Hz, 1H), 7.74 (dd, J = 2.0, 8.0 Hz, 1H), 7.44 (dt, J = 2.0, 8.4 Hz, 1H), 7.24 (dt, J = 2.0, 8.0 Hz, 1H), 7.16–7.04 (m, 5H), 7.00–6.95 (m, 3H), 4.60 (dd, J = 6.0, 10.0 Hz, 1H), 4.54 (dd, J = 4.0, 12.0 Hz, 1H), 4.30 (dd, J = 10.0, 12.0 Hz, 1H), 4.01–3.96 (m, 2H), 3.82–3.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 160.4, 149.6, 147.5, 138.2, 135.2, 134.6, 133.7, 130.8, 128.3 (2×), 127.7 (2×), 126.6, 126.0, 122.7, 121.9, 119.9, 74.7, 52.6, 44.7, 42.8, 41.4.

2-(3,4-Dimethoxyphenyl)-1,1-dimethyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6ac). Yield = 45% (32 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{22}H_{25}O_4$ 353.1753, found 353.1761, err (ppm): −2.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, J = 2.0, 8.0 Hz, 1H), 7.40 (dt, J = 1.6, 8.4 Hz, 1H),7.05 (d, J = 8.0 Hz, 1H), 7.02 (dt, J = 0.8, 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.70 (dd, J = 2.0, 8.4 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 4.54 (dd, J = 2.8, 12.8 Hz, 1H), 4.32 (dd, J = 2.8, 12.4 Hz, 1H), 3.97 (t, J = 10.0 Hz, 1H), 3.86 (s, 3H), 3.85 (dd, J = 9.6, 12.4 Hz, 1H), 3.84 (s, 3H), 2.61–2.56 (m, 1H), 1.35 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 160.2, 148.7, 147.6, 133.7, 132.3, 131.2, 125.9, 121.8, 120.3, 119.0, 111.0, 110.7, 72.4, 55.9, 55.8, 50.8, 50.6, 46.8, 40.0, 25.4, 24.5.

8-Benzenesulfonyl-2-(3,4-dimethoxyphenyl)-1-phenyl-1,2,2a,8,9,9a-hexahydro-8-azabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (6ad). Yield = 90% (97 mg); colorless solid; mp = 180–181 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{32}H_{30}NO_5S$ 540.1845, found 540.1850, err (ppm): −0.93; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J = 1.6, 7.6 Hz, 1H), 7.84–7.79 (m, 3H), 7.60–7.56 (m, 1H), 7.51–7.47 (m, 3H), 7.31 (dt, J = 1.2, 8.0 Hz, 1H), 7.17–7.13 (m, 2H), 7.13–7.07 (m, 1H), 6.91 (d, J = 7.2 Hz, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.40 (dd, J = 2.0, 8.4 Hz, 1H), 6.26 (d, J = 2.0 Hz, 1H), 4.69 (dd, J = 5.2, 14.4 Hz, 1H), 4.49 (dd, J = 2.8, 9.2 Hz, 1H), 4.16–4.07 (m, 1H), 3.80 (s, 3H), 3.65 (t, J = 9.6 Hz, 1H), 3.56 (s, 3H), 3.42 (dd, J = 12.4, 14.8 Hz, 1H), 3.06 (dd, J = 2.4, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 148.3, 147.4, 140.9, 140.7, 138.6, 133.1, 132.8, 132.5, 131.2, 131.0, 129.4 (2×), 128.1 (2×), 127.4 (2×), 126.7 (2×), 126.3, 126.2, 125.6, 119.4, 113.0, 110.4, 56.0, 55.73, 55.69, 51.5, 46.0, 42.6, 42.0.

A representative synthetic procedure of skeletons 7 and 8 is as follows

Iodine (8 mg, 0.03 mmol) was added to a solution of **5** (0.2 mmol) in degassed EtOAc (30 mL) at 25 °C. Then, 1,2-

epoxybutane (20 mg, 0.3 mmol) was added to the reaction mixture at 25 °C. By use of a Pyrex glass filter, the reaction mixture was irradiated under a nitrogen atmosphere with a LED lamp (λ > 2540 Å) at 25 °C for 15 h. The reaction mixture was washed with saturated $Na_2S_2O_{3(aq)}$ (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 = 20/1–8/1) afforded skeletons **7** and **8**.

2-(3,4-Dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7a). Yield = 85% (68 mg); colorless solid; mp = 155–157 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1759, err (ppm): −1.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 4H), 7.27–7.22 (m, 3H), 7.01 (dd, J = 1.2, 7.6 Hz, 1H), 6.87 (dt, J = 0.8, 8.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.67 (dd, J = 1.6, 8.4 Hz, 1H), 6.61 (d, J = 1.6 Hz, 1H), 4.46 (dd, J = 3.2, 12.8 Hz, 1H), 4.39 (dd, J = 8.4, 12.8 Hz, 1H), 4.22 (t, J = 9.6 Hz, 1H), 4.10 (t, J = 9.6 Hz, 1H), 4.04 (t, J = 9.6 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.26 (dt, J = 3.2, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 158.9, 148.5, 147.4, 142.4, 133.1, 131.6, 131.2, 128.7 (2×), 127.5, 126.8, 126.4 (2×), 121.4, 119.5, 119.2, 110.7, 110.4, 72.2, 55.8, 55.6, 54.4, 46.3, 42.9, 42.3. Single-crystal X-Ray diagram: crystal of compound **7a** was grown by slow diffusion of EtOAc into a solution of compound **7a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 13.8730(7) Å, b = 22.7202(12) Å, c = 6.3384(3) Å, V = 1974.10(17) Å^3, Z = 4, d_{calcd} = 1.347 g cm^{-3}, F(000) = 848, 2θ range 1.485–26.410°, R indices (all data) $R1$ = 0.0849, w$R2$ = 0.1787.

2-(3,4-Dimethoxyphenyl)-5-fluoro-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7d). Yield = 84% (70 mg); colorless solid; mp = 157–159 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{24}FO_4$ 419.1659, found 419.1668, err (ppm): −2.14; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.27–7.23 (m, 3H), 7.08–7.02 (m, 2H), 7.00–6.96 (m, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.66 (dd, J = 2.0, 8.0 Hz, 1H), 6.64 (d, J = 2.0 Hz, 1H), 4.44 (dd, J = 3.2, 12.4 Hz, 1H), 4.36 (d, J = 8.0, 12.4 Hz, 1H), 4.21 (t, J = 9.6 Hz, 1H), 4.11 (t, J = 9.6 Hz, 1H), 4.05 (t, J = 9.6 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.30–3.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 157.2 (d, J = 239.6 Hz), 155.3, 148.6, 147.6, 142.3, 131.4, 128.7 (2×), 128.2 (d, J = 6.1 Hz), 126.9, 126.4 (2×), 121.3 (d, J = 7.6 Hz), 120.6 (d, J = 23.5 Hz), 119.2, 116.2 (d, J = 24.3 Hz), 110.8, 110.6, 72.7, 55.8, 55.7, 54.2, 46.5, 43.1, 42.3.

2-(3,4-Dimethoxyphenyl)-5-methyl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7e). Yield = 80% (66 mg); colorless solid; mp = 154–156 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_4$ 415.1909, found 415.1918, err (ppm): −2.17; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.27–7.22 (m, 3H), 7.14 (dd, J = 2.8, 8.4 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 6.66 (dd, J = 2.0, 8.4 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 4.42 (dd, J = 3.2, 12.8 Hz, 1H), 4.36 (d, J = 8.0, 12.4 Hz, 1H), 4.22 (t, J = 9.6 Hz, 1H), 4.08 (t, J = 9.6 Hz, 1H), 4.03 (t, J = 9.6 Hz, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.27–3.20 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 156.9, 148.5, 147.5, 142.5, 134.1, 131.7, 131.0, 130.8, 128.7 (2×), 127.2, 126.7, 126.4 (2×), 119.4 (2×), 110.7, 110.5, 72.2, 55.8, 55.6, 54.5, 46.5, 42.9, 42.2, 20.1.

2-(3,4-Dimethoxyphenyl)-6-methoxy-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7f). Yield = 75% (65 mg); colorless solid; mp = 160–162 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1863, err (ppm): −0.93; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.8 Hz, 1H), 7.35–7.31 (m, 2H), 7.27–7.22 (m, 3H), 6.70 (d, J = 8.4 Hz, 1H), 6.66 (dd, J = 1.6, 8.0 Hz, 1H), 6.60 (d, J = 1.6 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.46 (dd, J = 2.4, 8.8 Hz, 1H), 4.47–4.38 (m, 2H), 4.28–4.23 (m, 1H), 4.09–4.01 (m, 2H), 3.814 (s, 3H), 3.808 (s, 3H), 3.71 (s, 3H), 3.22–3.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 163.8, 161.0, 148.4, 147.5, 142.7, 133.4, 131.6, 128.6 (2×), 126.7, 126.4 (2×), 121.1, 119.5, 110.7, 110.6, 109.4, 103.0, 72.2, 55.7, 55.6, 55.5, 54.4, 46.9, 42.8, 41.6.

1-Phenyl-2-(3,4,5-trimethoxyphenyl)-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7h). Yield = 80% (69 mg); colorless solid; mp = 170–172 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{27}H_{27}O_5$ 431.1859, found 431.1866, err (ppm): −1.62; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.23 (m, 7H), 7.01 (dd, J = 1.2, 8.4 Hz, 1H), 6.85 (dt, J = 1.2, 8.0 Hz, 1H), 6.27 (s, 2H), 4.47–4.39 (m, 2H), 4.29 (t, J = 10.0 Hz, 1H), 4.15 (t, J = 9.6 Hz, 1H), 4.06 (t, J = 10.0 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 6H), 3.27–3.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 158.6, 152.8 (2×), 142.5, 136.4, 134.8, 133.1, 131.3, 128.7 (2×), 127.5, 126.8, 126.3 (2×), 121.4, 119.4, 104.1 (2×), 71.8, 60.8, 55.9 (2×), 54.9, 46.7, 42.2, 41.8.

2-(4-Methoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7j). Yield = 76% (56 mg); colorless solid; mp = 152–154 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{25}H_{23}O_3$ 371.1647, found 371.1655, err (ppm): −2.16; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 4H), 7.27–7.21 (m, 3H), 7.06 (d, J = 8.4 Hz, 2H), 7.00 (dd, J = 0.8, 8.4 Hz, 1H), 6.88 (dt, J = 1.2, 8.0 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 4.50 (dd, J = 3.6, 12.8 Hz, 1H), 4.33 (dd, J = 9.6, 12.8 Hz, 1H), 4.14 (t, J = 10.0 Hz, 1H), 4.07 (t, J = 9.2 Hz, 1H), 4.02 (t, J = 9.2 Hz, 1H), 3.77 (s, 3H), 3.29 (dt, J = 3.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 159.1, 158.0, 142.3, 133.0, 131.2, 131.0, 128.7 (2×), 128.2 (2×), 127.6, 126.8, 126.5 (2×), 121.4, 119.4, 113.4 (2×), 72.6, 55.2, 53.9, 45.9, 43.5, 42.9.

2-(2,4-Dimethoxyphenyl)-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7m). Yield = 80% (64 mg); colorless solid; mp = 203–205 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{26}H_{25}O_4$ 401.1753, found 401.1745, err (ppm): 1.99; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.24 (m, 7H), 7.01–6.97 (m, 2H), 6.90 (dt, J = 0.8, 8.0 Hz, 1H), 6.41 (d, J = 2.4 Hz, 1H), 6.37 (dd, J = 2.4, 8.4 Hz, 1H), 4.54 (dd, J = 4.4, 12.8 Hz, 1H), 4.24 (dd, J = 10.4, 12.4 Hz, 1H), 4.08–4.03 (m, 3H), 3.78 (s, 3H), 3.74 (s, 3H), 3.37–3.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 159.39, 159.35,

158.1, 142.3, 132.5, 130.4, 128.6 (2×), 127.7, 126.9, 126.7, 126.6 (2×), 121.3, 120.7, 119.2, 103.4, 98.0, 73.4, 55.2, 55.1, 52.8, 44.4, 43.1, 41.6. Single-crystal X-Ray diagram: crystal of compound **7m** was grown by slow diffusion of EtOAc into a solution of compound **7m** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, a = 9.4174(5) Å, b = 10.5047(5) Å, c = 11.7070(6) Å, V = 1015.58(9) Å^3, Z = 2, d_{calcd} = 1.310 g cm^{-3}, F(000) = 424, 2θ range 1.866–26.432°, R indices (all data) $R1$ = 0.0443, w$R2$ = 0.0909.

2-Biphenyl-4-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7o). Yield = 83% (69 mg); colorless solid; mp = 140–142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{30}H_{25}O_2$ 417.1855, found 417.1848, err (ppm): 1.68; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.48–7.21 (m, 14H), 7.02–6.99 (m, 1H), 6.86 (dt, J = 0.8, 8.4 Hz, 1H), 4.53 (dd, J = 4.0, 12.8 Hz, 1H), 4.34 (dd, J = 10.0, 12.8 Hz, 1H), 4.21 (t, J = 9.6 Hz, 1H), 4.19–4.09 (m, 2H), 3.39–3.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 159.1, 142.1, 141.0, 139.0, 138.5, 133.0, 130.9, 128.7 (2×), 128.6 (2×), 127.5, 127.4 (2×), 127.0 (3×), 126.9, 126.7 (2×), 126.5 (2×), 121.4, 119.4, 72.7, 53.8, 46.0, 43.4, 43.2.

2-Naphthalen-2-yl-1-phenyl-2,2a,9,9a-tetrahydro-1*H*-8-oxabenzo[*a*]cyclobuta[*d*]cyclohepten-3-one (7q). Yield = 85% (66 mg); colorless solid; mp = 153–155 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^+ + 1) calcd for $C_{28}H_{23}O_2$ 391.1698, found 391.1705, err (ppm): −1.79; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 3.6, 6.0 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.66 (dd, J = 3.6, 6.0 Hz, 1H), 7.54 (br s, 1H), 7.42–7.38 (m, 2H), 7.36–7.23 (m, 8H), 7.01 (dd, J = 0.8, 8.4 Hz, 1H), 6.78 (dt, J = 1.2, 8.4 Hz, 1H), 4.57 (dd, J = 3.6, 12.4 Hz, 1H), 4.36 (dd, J = 9.6, 12.8 Hz, 1H), 4.31 (t, J = 9.6 Hz, 1H), 4.23 (t, J = 8.8 Hz, 1H), 4.18 (t, J = 8.8 Hz, 1H), 3.39 (dt, J = 3.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 159.2, 142.2, 137.0, 133.2, 133.0, 132.2, 130.9, 128.8 (2×), 127.7, 127.6, 127.5 (2×), 126.9, 126.5 (2×), 126.0, 125.8, 125.3, 125.1, 121.4, 119.4, 72.9, 53.8, 46.4, 43.4, 43.2.

4-[2-(3-Phenylallyloxy)phenyl]but-3-en-2-one (8). Yield = 50% (28 mg); colorless oil; HRMS (ESI, M^+ + 1) calcd for $C_{19}H_{19}O_2$ 279.1385, found 279.1391, err (ppm): −2.15; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.25 (m, 7H), 7.18 (d, J = 12.4 Hz, 1H), 6.97–6.94 (m, 2H), 6.72 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 5.6, 16.0 Hz, 1H), 6.20 (d, J = 12.4 Hz, 1H), 4.74 (dd, J = 1.2, 5.6 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 156.1, 136.3, 136.2, 133.1, 130.9, 130.5, 129.6, 128.6 (2×), 127.9, 126.5 (2×), 125.0, 124.1, 120.5, 112.0, 69.0, 30.3.

Conflicts of interest

There are no conflicts of interest to declare.

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