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NBS-mediated cyclization of *trans*-cinnamic alcohols

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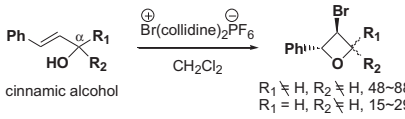
ABSTRACT

An efficient and straightforward three-step synthetic route toward 2,4-disubstituted-3-bromooxetanes **5** with the trans–trans contiguous stereogenic centers is developed from functionalized chalcones **3** via $NaBH_4$-mediated reduction of chalcones **3**, followed by NBS-mediated electrophilic cyclization of the resulting *trans*-cinnamic alcohols **4** in good yield. Skeleton **3** is prepared by Claisen–Schmidt condensation of substituted arylaldehydes **1** and aryl methyl ketones or *tert*-butyl methyl ketones **2**. The synthetic route obtained high yields, and the total reaction procedure took only one day. The substituent effect of skeleton **3**, various reaction conditions, and plausible mechanism were well-investigated.

1. Introduction

Halodecarboxylation of functionalized cinnamic acids (α,β-unsaturated carboxylic acids) is a useful methodology in the organic field for preparing diversified β-halostyrenes (vinyl halides).[1,2] There are many protocols and reagents reported for the bromodecarboxylation of cinnamic acids;[2] however, the modified Hunsdiecker reaction is the most popular approach among the existing methods.[3] In comparison with reports in the related studies on the bromination of cinnamic acids, few reports focus on the bromination of cinnamic alcohols. In a previous work, Rousseau and coworkers found that the bromination of cinnamyl alcohols (prepared from addition of lithium phenylacetylide to carbonyl compounds, followed by reduction of the resulting alkyne) in CH_2Cl_2 in the presence of bis(collidine)bromide(I) hexafluorophosphate ($Br^+(collidine)_2PF_6^-$) yielded 3-bromooxetanes; they suggested that cinnamyl tertiary alcohols possessing a *gem*-disubstituted group could provide better yields by the *endo-trig* electrophilic cyclization via carbocationic intermediate. But, secondary alcohols led mainly to degradation; oxetanes were only obtained in low yields.[4] It was also observed that no β-bromostyrene was isolated from the brominative cyclization of cinnamyl alcohols. Further screening of reaction substrates revealed that bromination of cinnamyl secondary alcohols with α-substituent was insufficient to produce the moderate yields of the oxetane skeleton; however, the formation of poor yields of the corresponding oxetanes was observed and the major complicated polymers were isolated under the reaction conditions, as shown in Scheme 1.



Scheme 1. Rousseau's bromocyclization of cinnamic alcohols.

To continue our recent investigation of the Claisen–Schmidt condensation for the preparation of oxygenated and benzannulated rigid molecules (e.g., benzo[*g*]indazoles, azahomoisotwistanes),[5] a facile, stereochemical, high-yield, easy-operation route for NBS-mediated synthesis of 2,4-disubstituted-3-bromooxetanes was studied next.

2. Results and discussion

To initiate the synthetic work, chalcone **3a** was prepared via Claisen–Schmidt condensation of 4-methoxybenzaldehyde (**1a**) with acetophenone (**2a**) in a qualitative yield under an aqueous alkaline methanolic solution, as shown in Scheme 2. In an attempt to develop a practical method of oxetane skeleton **5**, an $NaBH_4$-mediated reduction of compound **3a** followed by the *N*-bromosuccinimide (NBS)-mediated intramolecular electrophilic cyclization of the resulting *trans*-cinnamic alcohol **4a** provided the sole 2,4-diphenyloxetane **5a** in a 78% yield. We found that product **5a** possessed the stereochemical trans–trans orientation at the contiguous chiral center of the C_2–C_3–C_4 position.

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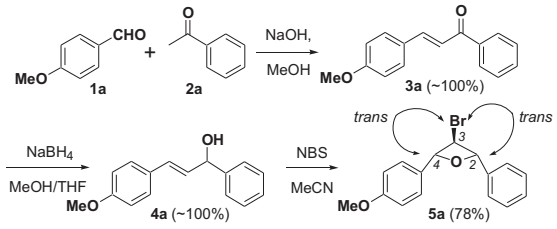
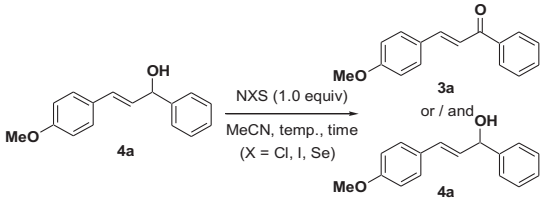


Scheme 2. Synthesis of compound **5a**.

After compound **4a** was treated with 1.0 equiv of *N*-chlorosuccinimide (NCS) in MeCN, we found that the compound **4a** recovery was complete at 0 °C for 1 h, as shown in Table 1. By the elevated reaction temperature (0 °C, rt, reflux) and time (1 h, 4 h), no reaction and an unknown mixture were observed (entries 1–4). In the reaction of compound **4a** with *N*-iodosuccinimide (NIS), only compound **3a** was isolated under different conditions (entries 5 and 6). A similar phenomenon was also shown in entries 7 and 8 via the *N*-selenosuccinimide (NSeS)-mediated oxidation of compound **4a**. From the experimental results, we found that no desired oxetane skeleton was formed. For the distribution of products, three events can be summarized: (1) NCS exhibited a poorer chloronium ion source for the electrophilic cyclization of cinnamic alcohol **4a**; (2) the NIS-mediated oxidative ability regarding the reaction of cinnamic alcohol **4a** was stronger than that of NSeS; and (3) the oxidation reaction of cinnamic alcohol **4a** with NIS and NSeS was preferred to proceed, in comparison with the electrophilic cyclization.

Table 1
Reaction conditions of compound **4a**[a,b]

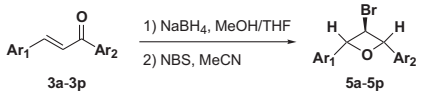


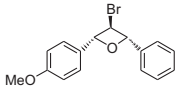
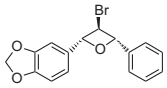
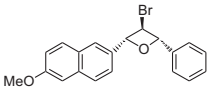
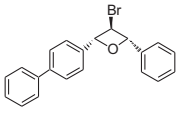
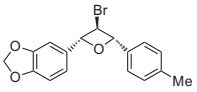
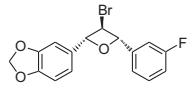
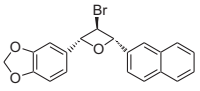
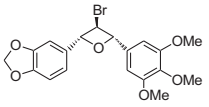
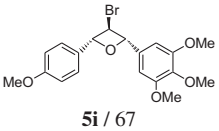
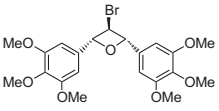
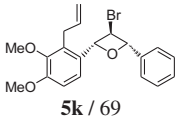
Entry	NXS	Temp	Time (h)	Yield (%)		
				4a	**3a**	Complex mixture
1	NCS	0 °C	1	~100[c]	—	—
2	NCS	0 °C	4	~100[c]	—	—
3	NCS	rt	4	95	—	—
4	NCS	Reflux	4	—	—	95[d]
5	NIS	0 °C	1	—	90	—
6	NIS	Reflux	1	—	82	—
7	NSeS	0 °C	1	15	77	—
8	NSeS	rt	4	—	90	—

[a] The reactions were run on a 1.0 mmol scale with compound **4a**.
[b] The product ratios were determined by ^{1}H NMR analysis.
[c] The starting material **4a** was recovered in quantitative yields.
[d] The unknown mixture was obtained with different amounts.

Changing two aryl substituents (Ar_1 and Ar_2) of skeleton **3**, the skeleton of different 2,4-diaryl-1-bromooxetanes **5a**–**p** was isolated via the abovementioned protocol (see Table 2). Diversified chalcone skeleton **3** provided quantitative yields via Claisen–Schmidt condensations of arylaldehydes **1** and aryl methyl ketones **2**. We observed that the equivalent of NaOH (2.5 equiv) and the reaction time (6 h) would be the key factors for the optimal reaction conditions. Next, quantitative yields of skeleton **4** were derived via an $NaBH_4$-mediated reduction of skeleton **3**. Without further purification, NBS-mediated bromination of crude skeleton **4** was examined. With the facile and high-yield procedure, the reaction of skeleton **4** with NBS provided skeleton **5** with 60–78% yields in MeCN at 0 °C for 1 h (see entries 1–16). The structure of compound **5k** was constructed using single-crystal X-ray analysis.[6] The overall three-step synthetic procedure is a straightforward, efficient, and high-yield route to prepare compounds **5a**–**p**, and involves (1) one purification (by column chromatography), (2) short reaction time (1 day), and (3) two quantitative-yield reactions.

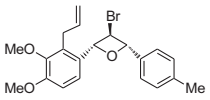
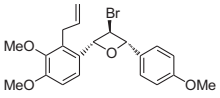
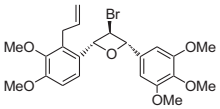
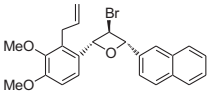
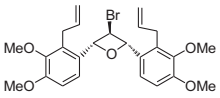
Table 2
Synthesis of compounds **5a**–**p**[a]



Entry	Products **5**/Yield (%)[b]
1	 **5a** / 78
2	 **5b** / 76
3	 **5c** / 69
4	 **5d** / 70
5	 **5e** / 72
6	 **5f** / 70
7	 **5g** / 68
8	 **5h** / 65
9	 **5i** / 67
10	 **5j** / 62
11	 **5k** / 69

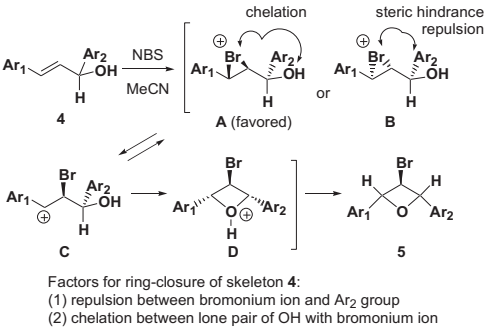
(*continued on next page*)

Table 2 (*continued*)

Entry	Products **5**/Yield (%)[b]
12	 **5l** / 72
13	 **5m** / 67
14	 **5n** / 60
15	 **5o** / 62
16	 **5p** / 66

[a] For the best two-step reaction conditions: compounds **3a**–**p** (1.0 mmol), $NaBH_4$ (70 mg, 2.0 mmol), MeOH/THF (v/v=1/1, 10 mL), rt, 1 h, and NBS (178 mg, 1.0 mmol), 0 °C, 1 h.
[b] Compounds **5a**–**p** was >95% pure as determined by ^1H NMR analysis.

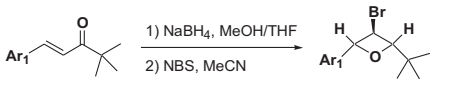
The possible mechanism for the formation of skeleton **5** is described in Scheme 3. The initial event can be considered the preferred formation of intermediate **A** with the bromonium ions by the possible intramolecular chelation between the bromonium ions and the hydroxyl group. Intermediate **B** could not be generated easily due to the possible repulsion at the same face between the aryl group of skeleton **4** and the involvement of the bromo group. During the equilibrium of intermediates **A** and **C**, the oxygen lone pair promoted ring-opening of the bromonium ion on intermediate **A**, followed by an intramolecular ring-closure of intermediate **C**. After a proton exchange of intermediate **D**, skeleton **5** with the 3-bromo group was produced.



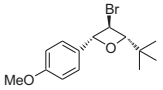
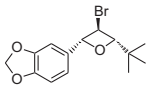
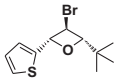
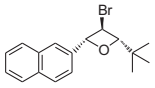
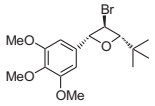
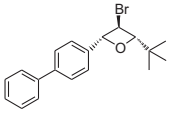
Scheme 3. The possible reaction mechanism of skeleton **5**.

To further examine synthetic route, Ar_2 group (skeleton **3**) was changed to *tert*-butyl group. Compounds **5q**–**v** were isolated in excellent 88%–94% yields by the above conditions (see Table 3). But, while changing the aromatic group (Ar_1 or Ar_2) from the phenyl to 4-trifluoromethylphenyl (4-CF_3Ph) and 4-nitrophenyl (4-NO_2Ph) group or nitrogen-containing heterocyclic groups (3-indole, 2-quinoline, 2-pyrrole, 4-pyridine) on the chalcone skeleton, attempts at establishing the desired oxetane skeleton failed under the above two-step conditions. Comparing the shown yields in Tables 2 and 3, we believed that the Ar_1 functionality of these substrates should be electron-rich (bearing the electron-donating group) or easy to delocalization (naphthalenyl or bis-phenyl group) for the benzylic cation, and favored the attack of inner hydroxyl from the less hindrance face. Therefore, it is easy to unstandard that the stability (life time) of planar benzylic carbocation generated during the reaction is crucial to achieve such stereoselectivity (via steric interactions).

Table 3
Synthesis of compounds **5q**–**v**[a]

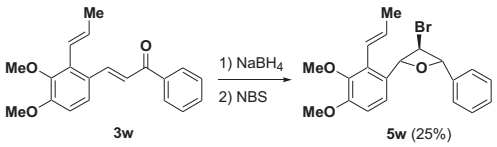


3q-3v 5q-5v

Entry	Products **5**/Yield (%)[b]
1	 **5q** / 92
2	 **5r** / 91
3	 **5s** / 92
4	 **5t** / 88
5	 **5u** / 94
6	 **5v** / 90

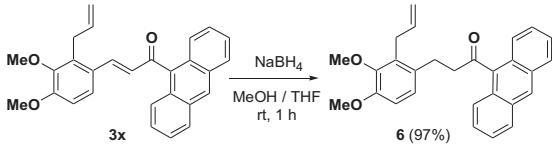
[a] For the best two-step reaction conditions: compounds **3q**–**v** (1.0 mmol), $NaBH_4$ (70 mg, 2.0 mmol), MeOH/THF (v/v=1/1, 10 mL), rt, 1 h, and NBS (178 mg, 1.0 mmol), 0 °C, 1 h.
[b] The isolated products **5q**–**v** were >95% pure as determined by ^1H NMR analysis.

After reducing compound **3w** with 1.0 equiv of $NaBH_4$ at rt for 1 h, the NBS-mediated cyclization of the resulting alcohol obtained compound **5w** in only 25% yield (see Scheme 4). We thought both of the internal olefins competed with the bromonium ion to form major unknown products.

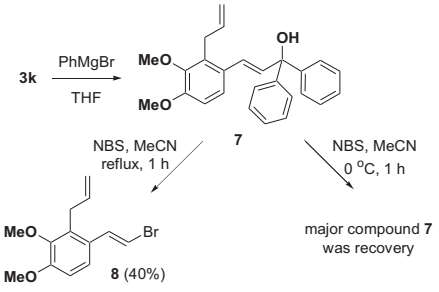


Scheme 4. Reaction of compound **3w**.

When compound **3x** (Ar_2=9-anthracenyl group) was treated with 1.0 equiv of $NaBH_4$ at rt for 1 h, the olefinic motif of compound **6** was regioselectively reduced with a 97% yield in the co-solvent of MeOH and THF (see Scheme 5). The conjugation loss should be the major reason to yield compound **6** because reduction to chalcone **6** involved less conjugation loss than reduction to the alcohol. When the reaction substrate was changed to tertiary cinnamic alcohol **7** (generated from the Grignard addition of compound **3k** with phenylmagnesium bromide in THF), the NBS-mediated intramolecular electrophilic cyclization of compound **7** provided the recovery of the starting material at 0 °C for 1 h. By increasing the reaction temperature, compound **8** was detected in refluxing MeCN in 40% yield, as shown in Scheme 6.



Scheme 5. Reaction of compound **3x**.



Scheme 6. NBS-mediated reaction of compound **7**.

3. Conclusion

In summary, we have successfully presented an efficient and straightforward three-step synthetic route for the stereochemical synthesis of 2,4-disubstituted-3-bromooxetanes **5a**–**w** with the trans–trans orientation via NaOH-mediated Claisen–Schmidt condensation, $NaBH_4$-mediated reduction, and NBS-mediated electrophilic cyclization. The synthetic route obtained high yields from the three-step route, and the total reaction procedure took only 1 day. The substituent effect of skeleton **3**, various NXS-mediated reaction conditions, and plausible mechanism were well-investigated. Further investigation regarding enantioselective bromocyclization[7] of cinnamic alcohol analogues will be conducted and published in due course.

4. Experimental section

4.1. General

All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried over anhydrous $MgSO_4$ 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 200/400 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). Elemental analyses were carried out with Heraeus Vario III-NCSH, Heraeus CHN-OS-Rapid Analyzer or Elementar Vario EL III.

4.2. A representative synthetic procedure of skeleton 3 is as follows

NaOH (160 mg, 4.0 mmol) was added to a solution of substituted benzaldehydes **1** (2.0 mmol) in MeOH (20 mL) at rt. Then aryl methyl ketones **2a**–**p** (2.05 mmol) or *tert*-butyl methyl ketones **2q**–**v** (2.05 mmol) was added to the reaction mixture. The reaction mixture was stirred at reflux for 6 h. The reaction mixture was concentrated to yield the residue. The residue was extracted with EtOAc (3×30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude skeleton **3** with quantitative yields. Without further purification, reduction of crude skeleton **3** was treated with $NaBH_4$ in the next step. Synthesis of skeleton **3** is a known protocol and the related analytical data are consistent with those in the literature.[5a,b]

A representative data of (*E*)-3-(3,4-*dimethoxy*-2-((*E*)-*prop*-1-*enyl*)*phenyl*)-1-*phenylprop*-2-*en*-1-*one* (**3w**). Yield=~100% (615 mg); HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_3$ 309.1491, found 309.1493; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J=15.6 Hz, 1H), 8.01–7.98 (m, 2H), 7.58–7.54 (m, 1H), 7.51–7.47 (m, 3H), 7.33 (d, J=15.6 Hz, 1H), 6.86 (d, J=8.4 Hz, 1H), 6.59 (dq, J=1.6, 16.0 Hz, 1H), 5.87 (dq, J=6.4, 16.0 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 1.96 (dd, J=1.6, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.82, 154.05, 146.51, 144.72, 138.44, 134.97, 134.52, 132.40, 128.46 (3×), 128.37 (2×), 126.92, 123.64, 123.57, 121.33, 60.20, 55.79, 19.31; Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.12; H, 6.65. Single-crystal X-ray diagram: crystal of compound **3w** was grown by slow diffusion of EtOAc into a solution of compound **3w** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group *Pbca*, a=7.3376(7) Å, b=11.2660(10) Å, c=38.619(4) Å, V=3192.5(5) Å^3, Z=8, d_{calcd}=1.283 g/cm^3, $F(000)$=1312, 2θ range 1.05–26.40°, R indices (all data) $R1$=0.0485, $wR2$=0.1115.

4.3. A representative synthetic procedure of skeleton 5 is as follows

$NaBH_4$ (70 mg, 2.0 mmol) was slowly added to a solution of the resulting skeleton **3** (1.0 mmol) in the co-solvent of MeOH (5 mL) and THF (5 mL) at rt. The reaction mixture was stirred at rt for 1 h. Saturated $NaHCO_{3(aq)}$ (5 mL) was added to the reaction mixture and the solvent was concentrated. 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. Without further purification, NBS (178 mg, 1.0 mmol) was added to a solution of the resulting crude skeleton **4** in MeCN (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. Saturated $NaHCO_{3(aq)}$ (5 mL) was added to the reaction mixture and the solvent was concentrated. 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=10/1 to 6/1) afforded skeleton **5**.

*4.3.1. 3-Bromo-2-(4-methoxyphenyl)-4-phenyloxetane (**5a**).* Yield=78% (248 mg); Colorless solid; mp=53–54 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{16}BrO_2$ 319.0334, found 319.0339; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.54 (m, 2H), 7.49–7.37 (m, 5H), 6.98–6.95 (m, 2H), 5.81 (d, *J*=7.6 Hz, 1H), 5.76 (d, *J*=7.6 Hz, 1H), 4.45 (t, *J*=7.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.25, 139.25, 131.03, 128.83, 128.73 (2×), 127.60 (2×), 125.54 (2×), 114.11 (2×), 87.00, 86.51, 55.32, 50.28.

*4.3.2. 5-(3-Bromo-4-phenyloxetan-2-yl)benzo[1,3]dioxole (**5b**).* Yield=76% (252 mg); Colorless solid; mp=73–74 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{14}BrO_3$ 333.0126, found 333.01267; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.47–7.37 (m, 3H), 7.04 (d, *J*=2.0 Hz, 1H), 6.99 (ddd, *J*=0.4, 2.0, 8.0 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 6.00–5.99 (m, 2H), 5.79 (d, *J*=7.6 Hz, 1H), 5.71 (dd, *J*=0.8, 7.2 Hz, 1H), 4.41 (t, *J*=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.20, 148.07, 139.06, 132.87, 128.87, 128.75 (2×), 125.52 (2×), 119.89, 108.38, 106.35, 101.27, 87.00, 86.53, 50.21.

*4.3.3. 3-Bromo-2-(6-methoxynaphthalen-2-yl)-4-phenyloxetane (**5c**).* Yield=69% (254 mg); Colorless solid; mp=140–142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{18}BrO_2$ 369.0490, found 369.0491; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J*=8.8 Hz, 1H), 7.91 (d, *J*=1.2 Hz, 1H), 7.88 (d, *J*=8.8 Hz, 1H), 7.71 (dd, *J*=1.6, 8.8 Hz, 1H), 7.57–7.54 (m, 2H), 7.48–7.38 (m, 4H), 7.33 (d, *J*=9.2 Hz, 1H), 5.99 (d, *J*=7.2 Hz, 1H), 5.90 (d, *J*=7.2 Hz, 1H), 4.52 (t, *J*=7.2 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.27, 139.01, 134.94, 133.34, 129.37, 129.28, 129.02 (2×), 128.82 (2×), 127.15, 125.70 (2×), 125.21, 124.86, 114.11, 87.20, 86.83, 57.03, 49.83.

*4.3.4. 2-Biphenyl-4-yl-3-bromo-4-phenyloxetane (**5d**).* Yield=70% (255 mg); Colorless solid; mp=118–119 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{18}BrO$ 365.0541, found 365.0545; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.54 (m, 8H), 7.49–7.36 (m, 6H), 5.89 (t, *J*=7.6 Hz, 1H), 5.87 (d, *J*=7.6 Hz, 1H), 4.51 (t, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.93, 140.55, 139.08, 137.98, 128.95, 128.84 (2×), 128.77 (2×), 127.56, 127.51 (2×), 127.14 (2×), 126.20 (2×), 125.67 (2×), 87.00, 86.84, 50.04.

*4.3.5. 5-(3-Bromo-4-p-tolyloxetan-2-yl)benzo[1,3]dioxole (**5e**).* Yield=72% (249 mg); Colorless solid; mp=90–92 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{16}BrO_3$ 347.0283, found 347.02833; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J*=8.0 Hz, 2H), 7.26 (d, *J*=8.0 Hz, 2H), 7.07 (d, *J*=1.6 Hz, 1H), 7.01 (dd, *J*=1.6, 8.0 Hz, 1H), 6.86 (d, *J*=8.0 Hz, 1H), 6.00 (s, 2H), 5.76 (d, *J*=7.6 Hz, 1H), 5.70 (d, *J*=7.6 Hz, 1H), 4.42 (t, *J*=7.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.13, 148.03, 138.83, 136.02, 132.95, 129.38 (2×), 125.68 (2×), 119.84, 108.34, 106.32, 101.23, 86.78, 86.57, 50.36, 21.24.

*4.3.6. 5-[3-Bromo-4-(3-fluorophenyl)oxetan-2-yl]benzo[1,3]dioxole (**5f**).* Yield=70% (244 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{16}H_{13}BrFO_3$ 351.0032, found 351.0031; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.38 (m, 1H), 7.28–7.22 (m, 2H), 7.10–7.05 (m, 1H), 7.00–6.96 (m, 2H), 6.85 (d, *J*=8.0 Hz, 1H), 6.00 (s, 2H), 5.77 (d, *J*=7.2 Hz, 1H), 5.71 (d, *J*=7.2 Hz, 1H), 4.36 (t, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.02 (d, *J*=246.3 Hz), 148.32, 148.12, 141.69 (d, *J*=6.8 Hz), 132.53, 130.48 (d, *J*=8.1 Hz), 120.83 (d, *J*=3.1 Hz), 119.92, 115.72 (d, *J*=20.5 Hz), 112.35 (d, *J*=22.7 Hz), 108.43, 106.30, 101.33, 87.18, 85.63, 49.87.

*4.3.7. 5-(3-Bromo-4-naphthalen-2-yloxetan-2-yl)benzo[1,3]dioxole (**5g**).* Yield=68% (260 mg); Colorless solid; mp=120–122 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{16}BrO_3$ 383.0283, found 383.0288; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.94–7.87 (m, 3H), 7.62 (dd, *J*=1.6, 8.4 Hz, 1H), 7.56–7.51 (m, 2H), 7.09 (d, *J*=1.6 Hz, 1H), 7.03 (dd, *J*=1.6, 8.0 Hz, 1H), 6.87 (d, *J*=8.0 Hz, 1H), 6.00 (br s, 2H), 5.96 (d, *J*=7.2 Hz, 1H), 5.78 (d, *J*=7.2 Hz, 1H), 4.50 (t, *J*=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.23, 148.10, 136.42, 133.47, 133.06, 132.83, 128.80, 128.21, 127.80, 126.53, 126.49, 124.81, 122.77, 119.99, 108.41, 106.42, 101.30, 87.20, 86.64, 50.11.

*4.3.8. 5-[3-Bromo-4-(3,4,5-trimethoxyphenyl)oxetan-2-yl]benzo[1,3]dioxole (**5h**).* Yield=65% (274 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{19}H_{20}BrO_6$ 423.0443, found 423.0438; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20–7.01 (d, *J*=1.6 Hz, 1H), 6.97 (ddd, *J*=0.4, 1.6, 8.4 Hz, 1H), 6.83 (d, *J*=8.0 Hz, 1H), 6.71 (s, 2H), 5.98–5.97 (m, 2H), 5.70 (d, *J*=6.8 Hz, 1H), 5.68 (d, *J*=7.2 Hz, 1H), 4.38 (t, *J*=7.2 Hz, 1H), 3.89 (s, 6H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.55 (2×), 148.22, 148.09, 138.18, 134.78, 132.71, 119.85, 108.31, 106.23, 102.12 (2×), 101.27, 86.85, 86.45, 60.78, 56.11 (2×), 50.04.

*4.3.9. 3-Bromo-2-(4-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)oxetane (**5i**).* Yield=67% (273 mg); Colorless solid; mp=64–66 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{22}BrO_5$ 409.0651, found 409.0658; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J*=8.8 Hz, 2H), 6.95 (d, *J*=8.8 Hz, 2H), 6.73 (s, 2H), 5.73 (d, *J*=7.6 Hz, 1H), 5.72 (d, *J*=7.2 Hz, 1H), 4.43 (t, *J*=7.2 Hz, 1H), 3.90 (s, 6H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.26 (2×), 153.57, 134.97 (2×), 130.86, 127.57 (2×), 114.11 (2×), 102.18 (2×), 86.86, 86.45, 60.81, 56.13 (2×), 55.29, 50.11.

*4.3.10. 3-Bromo-2,4-bis-(3,4,5-trimethoxyphenyl)oxetane (**5j**).* Yield=62% (290 mg); Colorless solid; mp=98–100 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{26}BrO_7$ 469.0862, found 469.0866; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (s, 4H), 5.73 (d, *J*=7.2 Hz, 2H), 4.41 (t, *J*=7.2 Hz, 1H), 3.88 (s, 12H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.59 (4×), 138.37 (2×), 134.65 (2×), 102.38 (4×), 86.87 (2×), 60.82 (2×), 56.09 (4×), 49.87.

*4.3.11. 2-(2-Allyl-3,4-dimethoxyphenyl)3-bromo-4-phenyloxetane (**5k**).* Yield=69% (268 mg); Colorless solid; mp=80–81 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{22}BrO_3$ 389.0752, found 389.0755; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H), 7.48 (d, *J*=8.4 Hz, 1H), 7.45–7.35 (m, 3H), 6.92 (d, *J*=8.8 Hz, 1H), 6.07–5.97 (m, 1H), 6.01 (d, *J*=7.2 Hz, 1H), 5.80 (d, *J*=7.2 Hz, 1H), 5.07 (dq, *J*=1.6, 10.0 Hz, 1H), 4.95 (dq, *J*=1.6, 17.2 Hz, 1H), 4.45 (t, *J*=7.2 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.60–3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.95, 147.22, 139.30, 136.66, 131.07, 130.81, 128.83, 128.71 (2×), 125.78 (2×), 121.92, 115.52, 110.54, 86.72, 83.74, 60.87, 55.68, 49.92, 30.15; Anal. Calcd for $C_{20}H_{21}BrO_3$: C, 61.71; H, 5.44. Found: C, 61.88; H, 5.61. Single-crystal X-ray diagram: crystal of compound **5k** was grown by slow diffusion of EtOAc into a solution of compound **5k** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group *P* 1 21/*c* 1, *a*=9.4758 (2) Å, *b*=24.6475(5) Å, *c*=15.2361(3) Å, *V*=3491.77(12) Å^3, *Z*=8, d_{calcd}=1.481 g/cm^3, *F*(000)=1600, 2θ range 2.14–26.40°, *R* indices (all data) *R*1=0.0437, *wR*2=0.0784.

*4.3.12. 2-(2-Allyl-3,4-dimethoxyphenyl)-3-bromo-4-p-tolyloxetane (**5l**).* Yield=72% (289 mg); Colorless viscous gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{24}BrO_3$ 403.0909, found 403.0906; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J*=8.4 Hz, 1H), 7.40 (d, *J*=8.0 Hz, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 6.92 (d, *J*=8.4 Hz, 1H), 6.07–5.97 (m, 1H), 5.99 (d,

J=7.2 Hz, 1H), 5.75 (d, J=7.2 Hz, 1H), 5.07 (dq, J=1.6, 10.0 Hz, 1H), 4.95 (dq, J=1.6, 17.2 Hz, 1H), 4.44 (t, J=7.2 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.60–3.56 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.90, 147.22, 138.81, 136.66, 136.26, 131.04, 130.92, 129.36 (2×), 125.96 (2×), 121.91, 115.49, 110.53, 86.77, 83.53, 60.85, 55.68, 50.08, 30.15, 21.26.

*4.3.13. 2-(2-Allyl-3,4-dimethoxyphenyl)-3-bromo-4-(4-methoxyphenyl) oxetane (**5m**).* Yield=67% (280 mg); Colorless solid; mp=75–77 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{24}BrO_4$ 419.0858, found 419.0862; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J=8.8 Hz, 1H), 7.45 (d, J=8.8 Hz, 2H), 6.95 (d, J=8.8 Hz, 2H), 6.93 (d, J=8.8 Hz, 1H), 6.08–5.98 (m, 1H), 5.98 (d, J=7.2 Hz, 1H), 5.72 (d, J=7.2 Hz, 1H), 5.08 (dq, J=1.6, 10.0 Hz, 1H), 4.96 (dq, J=1.6, 17.2 Hz, 1H), 4.46 (t, J=7.2 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.61–3.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.14, 152.83, 147.19, 136.60, 131.18, 130.96, 130.92, 127.68 (2×), 121.75, 115.43, 114.02 (2×), 110.47, 86.68, 83.25, 60.79, 55.62, 55.27, 50.11, 30.13.

*4.3.14. 2-(2-Allyl-3,4-dimethoxyphenyl)-3-bromo-4-(3,4,5-trimethoxyphenyl)oxetane (**5n**).* Yield=60% (287 mg); Colorless viscous gum; HRMS (ESI, M^++1) calcd for $C_{23}H_{28}BrO_6$ 479.1069, found 479.1075; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J=8.8 Hz, 1H), 6.90 (d, J=8.8 Hz, 1H), 6.72 (s, 2H), 6.07–5.97 (m, 1H), 5.99 (d, J=7.2 Hz, 1H), 5.73 (d, J=7.2 Hz, 1H), 5.07 (dq, J=1.6, 10.0 Hz, 1H), 4.94 (dq, J=1.6, 17.2 Hz, 1H), 4.43 (t, J=7.2 Hz, 1H), 3.89 (s, 9H), 3.86 (s, 3H), 3.82 (s, 3H), 3.59–3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.56 (2×), 152.99, 147.29, 138.26, 136.63, 135.00, 131.17, 130.72, 121.78, 115.52, 110.44, 102.55 (2×), 86.74, 83.67, 60.86, 60.85, 56.18 (2×), 55.69, 49.84, 30.14.

*4.3.15. 2-(2-Allyl-3,4-dimethoxyphenyl)-3-bromo-4-(naphthalen-2-yl)oxetane (**5o**).* Yield=62% (272 mg); Colorless solid; mp=106–108 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{24}BrO_3$ 439.0909, found 439.0912; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.92–7.86 (m, 3H), 7.63 (dd, J=1.6, 8.8 Hz, 1H), 7.57–7.51 (m, 3H), 6.94 (d, J=8.8 Hz, 1H), 6.09 (d, J=7.2 Hz, 1H), 6.09–6.01 (m, 1H), 5.99 (d, J=7.2 Hz, 1H), 5.10 (dq, J=1.6, 10.0 Hz, 1H), 4.99 (dq, J=1.6, 17.2 Hz, 1H), 4.55 (t, J=7.2 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.64–3.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.96, 147.22, 136.67, 136.62, 133.45, 133.06, 131.11, 130.75, 128.71, 128.18, 127.78, 126.48, 126.45, 125.03, 123.02, 121.98, 115.53, 110.57, 86.79, 83.90, 60.85, 55.66, 49.79, 30.15.

*4.3.16. 2,4-Bis-(2-allyl-3,4-dimethoxyphenyl)-3-bromo-oxetane (**5p**).* Yield=66% (322 mg); Colorless solid; mp=131–133 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{25}H_{30}BrO_5$ 489.1277, found 489.1282; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J=8.4 Hz, 2H), 6.90 (d, J=8.4 Hz, 2H), 6.07–5.95 (m, 2H), 5.98 (d, J=7.2 Hz, 2H), 5.06 (dq, J=1.6, 10.0 Hz, 2H), 4.95 (dq, J=1.6, 17.2 Hz, 2H), 4.47 (t, J=7.2 Hz, 1H), 3.88 (s, 6H), 3.82 (s, 6H), 3.59–3.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.82 (2×), 147.13 (2×), 136.63 (2×), 131.14 (2×), 130.87 (2×), 122.01 (2×), 115.43 (2×), 110.42 (2×), 83.28 (2×), 60.78 (2×), 55.59 (2×), 49.78, 30.09 (2×).

*4.3.17. 3-Bromo-2-tert-butyl-4-(4-methoxyphenyl)oxetane (**5q**).* Yield=92% (274 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{14}H_{20}BrO_2$ 299.0647, found 299.0651; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J=8.8 Hz, 2H), 6.92 (d, J=8.8 Hz, 2H), 5.53 (d, J=7.6 Hz, 1H), 4.57 (d, J=7.6 Hz, 1H), 4.36 (t, J=7.6 Hz, 1H), 3.81 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.01, 131.17, 127.28 (2×), 114.00 (2×), 93.38, 86.13, 55.29, 43.63, 34.18, 24.45 (3×).

*4.3.18. 3-Bromo-2-tert-butyl-4-(3,4-methylenedioxyphenyl)oxetane (**5r**).* Yield=91% (284 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{14}H_{18}BrO_3$ 313.0439, found 313.0442; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, J=2.0 Hz, 1H), 6.89 (dd, J=2.0, 8.0 Hz, 1H), 6.80 (d, J=8.0 Hz, 1H), 5.97 (s, 2H), 5.49 (d, J=7.6 Hz, 1H), 4.56 (d, J=7.6 Hz, 1H), 4.33 (t, J=7.6 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.94 (2×), 133.04, 119.53, 108.31, 106.12, 101.18, 93.42, 86.13, 43.59, 34.16, 24.44 (3×).

*4.3.19. 3-Bromo-2-tert-butyl-4-thiophen-2-yloxetane (**5s**).* Yield=92% (252 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{11}H_{16}BrOS$ 275.0105, found 275.0108; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, J=1.2, 5.2 Hz, 1H), 7.13 (dd, J=1.2, 3.2 Hz, 1H), 7.01 (dd, J=3.2, 5.2 Hz, 1H), 5.77 (d, J=7.6 Hz, 1H), 4.56 (d, J=7.6 Hz, 1H), 4.48 (t, J=7.6 Hz, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.25, 126.92 (2×), 126.38, 93.16, 81.93, 44.31, 34.09, 24.29 (3×).

*4.3.20. 3-Bromo-2-tert-butyl-4-naphthalen-2-yloxetane (**5t**).* Yield=88% (280 mg); Colorless solid; mp=61–62 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{20}BrO$ 319.0698, found 319.0697; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (m, 4H), 7.56–7.50 (m, 3H), 5.82 (d, J=7.6 Hz, 1H), 4.70 (d, J=7.6 Hz, 1H), 4.44 (t, J=7.6 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.67, 133.36, 133.09, 128.58, 128.15, 127.77, 126.39, 126.30, 124.48, 122.72, 94.00, 86.20, 43.38, 34.20, 24.43 (3×).

*4.3.21. 3-Bromo-2-tert-butyl-4-(3,4,5-trimethoxyphenyl)oxetane (**5u**).* Yield=94% (337 mg); Colorless solid; mp=83–84 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{24}BrO_4$ 359.0858, found 359.0863; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (s, 2H), 5.52 (d, J=7.6 Hz, 1H), 4.58 (d, J=7.6 Hz, 1H), 4.30 (t, J=7.6 Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.39 (2×), 137.96, 134.85, 102.07 (2×), 93.52, 86.06, 60.72, 55.99 (2×), 43.51, 34.13, 24.32 (3×).

*4.3.22. 2-Biphenyl-4-yl-3-bromo-4-tert-butyloxetane (**5v**).* Yield=90% (310 mg); Colorless solid; mp=87–88 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{19}H_{22}BrO$ 345.0854, found 345.0856; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.52–7.44 (m, 4H), 7.39–7.35 (m, 1H), 5.68 (d, J=7.6 Hz, 1H), 4.65 (d, J=7.6 Hz, 1H), 4.41 (t, J=7.6 Hz, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.59, 140.62, 138.17, 128.80 (2×), 127.47 (2×), 127.38 (2×), 127.11, 125.88 (2×), 93.82, 85.97, 43.44, 34.19, 24.43 (3×).

*4.3.23. 3-Bromo-2-(3,4-dimethoxy-2-propenylphenyl)-4-phenyloxetane (**5w**).* Yield=25% (97 mg); Colorless solid; mp=63–65 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{22}BrO_3$ 389.0752, found 389.0759; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 3H), 7.46–7.36 (m, 3H), 6.92 (d, J=8.4 Hz, 1H), 6.48 (dq, J=1.6, 16.0 Hz, 1H), 6.11 (dq, J=6.4, 16.0 Hz, 1H), 6.03 (d, J=7.2 Hz, 1H), 5.80 (d, J=7.2 Hz, 1H), 4.53 (t, J=7.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 1.98 (dd, J=1.6, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.81, 146.46, 139.39, 133.64, 132.15, 129.72, 128.72, 128.66 (2×), 125.65 (2×), 123.27, 122.49, 110.67, 86.50, 83.79, 60.07, 55.78, 50.14, 19.15.

4.4. 3-(2-Allyl-3,4-dimethoxyphenyl)-1-anthracen-9-yl-propan-1-one (6)

$NaBH_4$ (70 mg, 2.0 mmol) was slowly added to a solution of compound **3x** (2.0 mmol) in the co-solvent of MeOH (5 mL) and THF (5 mL) at rt. The reaction mixture was stirred at rt for 1 h. Saturated $NaHCO_{3(aq)}$ (5 mL) was added to the reaction mixture and the solvent was concentrated. 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=8/1 to 4/1) afforded compound **6**. Yield=97% (795 mg); Colorless viscous gum; HRMS (ESI, M^++1) calcd for $C_{28}H_{27}O_3$ 411.1960, found 411.0963; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.04–8.01 (m, 2H), 7.72–7.68 (m, 2H), 7.50–7.44 (m, 4H), 6.97 (d, J=8.4 Hz, 1H), 6.75 (d, J=8.4 Hz, 1H), 5.98 (m, 1H), 4.93 (dq, J=1.6, 10.4 Hz, 1H), 4.85 (dq, J=1.6, 17.2 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.47 (dt, J=1.6, 6.0 Hz, 2H), 3.33–3.29 (m, 2H), 3.20–3.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.61, 151.19, 137.07 (2×), 134.10 (2×), 132.20, 131.03, 128.77 (2×), 128.17 (2×), 127.20, 126.93, 126.67 (2×), 125.44 (2×), 124.57, 124.29 (2×), 115.02, 110.48, 60.76, 55.68, 47.70, 30.55, 26.27.

4.5. (*E*)-2-Allyl-1-(2-bromovinyl)-3,4-dimethoxybenzene (8)

A solution of phenylmagnesium bromide (1.0 M in THF, 1.5 mL, 1.5 mmol) was added to a stirred solution of compound **3k** (308 mg, 1.0 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at rt for 5 h. Water (5 mL) was added to the reaction mixture and the mixture was filtered through a short plug of Celite. The filtrate was concentrated under reduced pressure. The residue was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford different crude product under reduced pressure. Without further purification, NBS (178 mg, 1.0 mmol) was added to a solution of the resulting crude compound **7** in MeCN (5 mL) at rt. The reaction mixture was stirred at reflux for 1 h. Saturated $NaHCO_{3(aq)}$ (5 mL) was added to the reaction mixture and the solvent was concentrated. 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=10/1 to 6/1) afforded compound **8**. Yield=40% (113 mg); Colorless oil; HRMS (ESI, M^++1) calcd for $C_{13}H_{16}BrO_2$ 283.0334, found 283.0338; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J=13.6 Hz, 1H), 7.07 (d, J=8.4 Hz, 1H), 6.78 (d, J=8.4 Hz, 1H), 6.51 (d, J=14.0 Hz, 1H), 5.99–5.89 (m, 1H), 5.04 (dq, J=1.6, 10.4 Hz, 1H), 4.90 (dq, J=1.6, 17.2 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.47 (dt, J=1.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.80, 147.19, 136.29, 135.12, 131.05, 129.08, 121.91, 115.55, 110.50, 105.90, 60.90, 55.68, 30.40.

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Supplementary data

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6. CCDC 903763 (**5k**) and 903764 (**3w**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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