Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 4733

Bsi(OTf)$_3$-mediated tandem annulation of 1-aryl isochroman-3-ones with oxygenated arenes: one-pot synthesis of polyoxygenated homotriptycenes†

Meng-Yang Chang, *[a,b] Chun-Yi Lin,[a] Shin-Mei Chen[a] and Yu-Ting Hsiao[a]

Received 30th March 2021,
Accepted 4th May 2021

DOI: 10.1039/d1ob00606a

rsc.li/obc

Bi(OTf)$_3$ (bismuth triflate)-mediated one-pot tandem annulation of oxygenated 1-aryl isochroman-3-ones with oxygenated arenes provides polyoxygenated homotriptycenes in moderate to good yields in $MeNO_2$ at reflux (101 °C) for 10 h under an air atmosphere and easy-operational conditions *via* intermolecular and intramolecular Friedel–Crafts type procedures. A plausible mechanism is proposed and discussed. This protocol provides a highly effective ring-closure *via* three carbon–carbon (C–C) bond formations.

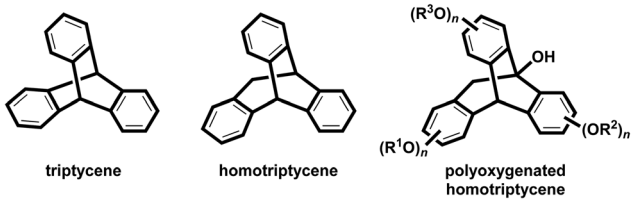
Introduction

The family of triptycene that contains a rigid three-pronged framework can be utilized as versatile molecular motors, unique electro- and photochemical sensitizers, potential bioactive molecules and functionalized Fréchet-type dendrimers.[1] Owing to these important synthetic applications in constructing diversified structures, many attempts to prepare the triptycene derivatives have been reported.[2] Compared with these members, however, there are few reports on the synthesis of substituted homotriptycene (tribenzobicyclo[3.2.2]nonatriene), as shown in Scheme 1.[3–7]

In 1970, Cristol and Pennelle described the first synthesized homotriptycenes *via* a Wagner-type ring enlargement of 1-aminomethyltriptycenes.[3] By the thermal dehydrogenation of anellated dibenzohomobarrelenes, Szeimies *et al.* also reported the second synthetic route.[4] Later, Saito *et al.* explored an alternative method using an intermolecular cycloaddition of strained benzocyclopropene with anthracene.[5] In spite of these advancements, some problems exist in the abovementioned papers, such as multi-step routes, complicated reaction conditions, the lack of broad substrate generality, and prefunctionalized fragments. A three-step route for the formation of substituted homotriptycenes has been thoroughly investigated by Cao *et al.*, including (i) benzylation of 10*H*-anthracen-9-one, (ii) the reduction of the resulting 10-benzylanthracen-9-one, and (iii) the intramolecular ring-closure of the corresponding 10-benzylanthracen-9-ol in the presence of Brønsted acid.[6] By $TiCl_4$-mediated [4 + 3] cycloaddition of 1-arylcyclopropane and anthracene, Ivanova *et al.* developed a method for preparing thieno-fused homotriptycenes.[7] Therefore, further investigation of a one-pot, efficient and easy-operational synthetic method for substituted homotriptycene is still highly desired.

Results and discussion

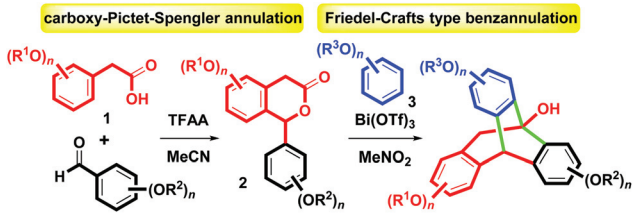
We recently explored the synthetic application of oxygenated arylacetic acid **1** for one-pot synthesis, and established the 1-aryl isochroman-3-one **2** *via* a trifluoroacetic anhydride (TFAA) promoted carboxy-Pictet–Spengler annulation in MeCN (Scheme 2).[8] For the preparation of the skeleton of 1-aryl isochroman-3-one, many efforts using elegant synthetic routes



Scheme 1 Structures of triptycene, homotriptycene and polyoxygenated homotriptycene.

[a]*Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan. E-mail: mychang@kmu.edu.tw*
[b]*Department of Medical Research, Kaohsiung Medical University Hospital, Kaohsiung 807, Taiwan*

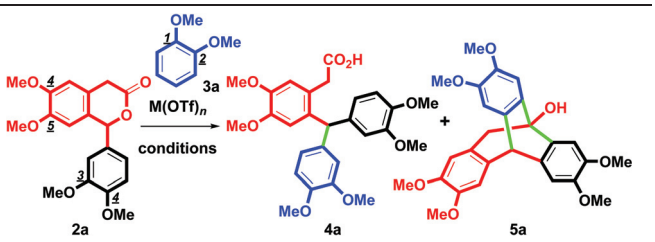
†Electronic supplementary information (ESI) available: Scanned photocopies of NMR spectral data for all compounds and X-ray analysis data of **5a** and **5w-2** were supported. CCDC 1938168–1938169. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ob00606a



Scheme 2 Our route of polyoxygenated homotriptycene.

have also been well-documented due to its specific chemoselectivity and diversified bioactivity. In continuation of the research on $Bi(OTf)_3$-promoted diversified reactions,[9,10] we present a $Bi(OTf)_3$-mediated synthesis of polyoxygenated homotriptycene by a one-pot tandem Friedel–Crafts type tandem annulation of 1-aryl isochroman-3-one **2** with oxygenated arene **3** in $MeNO_2$ *via* three carbon–carbon (C–C) bond formations (green marks). In Table 1, the initial study commenced with the treatment of **2a** ($(R^1O)_n$ = 4,5-$(MeO)_2$, $(R^2O)_n$ = 3,4-$(MeO)_2$, 1.0 mmol) and veratrole (**3a**, $(R^3O)_n$ = 1,2-$(MeO)_2$, 1.1 mmol) in $MeNO_2$ (20 mL) for 5 h in the presence of Bi $(OTf)_3$ (30 mol%).

Table 1 Annulation conditions[a]



Entry	$M(OTf)_n$	Solvent	Temp	Time	4a[b] %	5a[b] %
1[c]	$Bi(OTf)_3$ (30)	$MeNO_2$	25	5	51	—[d]
2	$Bi(OTf)_3$ (30)	$MeNO_2$	25	10	92	—[d]
3	$Bi(OTf)_3$ (30)	$MeNO_2$	70	5	48	40
4	$Bi(OTf)_3$ (30)	$MeNO_2$	70	10	15	78
5	$Bi(OTf)_3$ (30)	$MeNO_2$	101	5	20	70
6	$Bi(OTf)_3$ (30)	$MeNO_2$	101	10	Trace	88
7	$Bi(OTf)_3$ (30)	$MeNO_2$	101	15	Trace	82
8	$Bi(OTf)_3$ (40)	$MeNO_2$	101	10	Trace	85
9	$Bi(OTf)_3$ (20)	$MeNO_2$	101	10	12	78
10	$In(OTf)_3$ (30)	$MeNO_2$	101	10	10	78
11	$Fe(OTf)_3$ (30)	$MeNO_2$	101	10	12	78
12	$Sc(OTf)_3$ (30)	$MeNO_2$	101	10	20	69
13	$Ga(OTf)_3$ (30)	$MeNO_2$	101	10	29	60
14	$Cu(OTf)_2$ (30)	$MeNO_2$	101	10	42	47
15	$Sn(OTf)_2$ (30)	$MeNO_2$	101	10	45	42
16	$Hg(OTf)_2$ (30)	$MeNO_2$	101	10	50	42
17[c]	AgOTf (30)	$MeNO_2$	101	10	13	—[d]
18	$Bi(OTf)_3$ (30)	$(CHCl)_2$	84	10	79	—[d]
19	$Bi(OTf)_3$ (30)	MeCN	82	10	76	—[d]
20	$Bi(OTf)_3$ (30)	DMF	153	10	—[e]	—[e]
21[f]	$Bi(OTf)_3$ (30)	$MeNO_2$	101	10	Trace	88
22	$Bi(OTf)_3$ (30)	$MeNO_2$[g]	101	10	Trace	85

[a] The reactions were run on a 1.0 mmol scale with **2a**, **3a** (1.1 equiv.), $M(OTf)_n$ (mol%), temp (°C), solvent (20 mL), time (h). [b] Isolated yields. [c] **2a** (for entry 1, 38%; for entry 17, 58%) was recovered. [d] No detection. [e] Complex products. [f] Under a nitrogen atmosphere. [g] Dry $MeNO_2$.

However, no desired **5a** was detected, and **4a** was isolated at a 51% yield along with a 38% yield of the starting material **2a** (entry 1). By elongating the time from 5 to 10 h, the yield of **4a** was increased to 92% (entry 2), and **5a** was not obtained. With the results in hand, the reaction temperature was adjusted to 70 °C. After 5 and 10 h, **5a** was generated at 40% and 78% yields, and **4a** was isolated at 48% and 15% yields (entries 3 and 4). The two ratios of **5a** and **4a** are nearly 1 : 1 and 5 : 1. By elongating the time (10 h) and elevating the temperature (70 °C), the yield of **5a** was increased. To improve the yield of **5a**, the temperature was adjusted to reflux (101 °C) next.

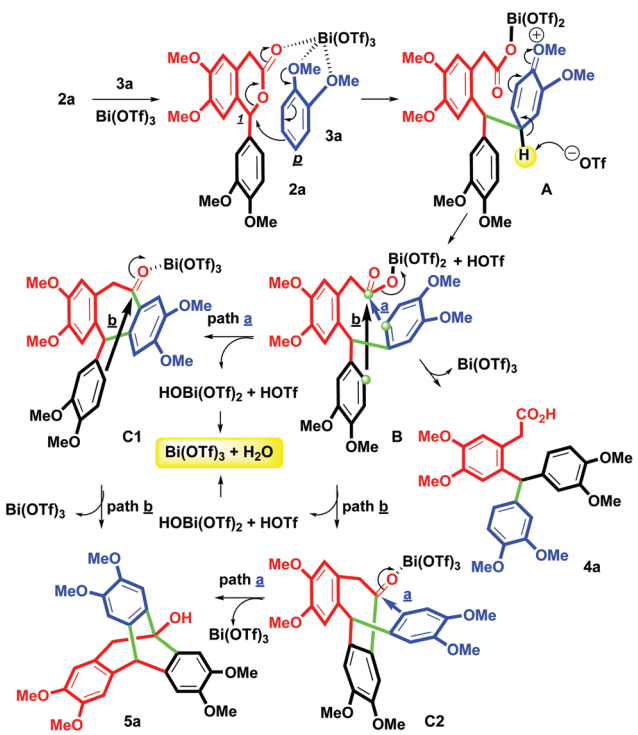
On the basis of 5 and 10 h conditions (entries 5 and 6), we found that 10 h provided a better yield (88%) than 5 h (70%) in the formation of **5a**. However, after 5 h and 10 h, the remaining amounts of **4a** were 20% and traces, respectively. In order to consume **4a**, the time was elongated further to 15 h (entry 7). Although **4a** was formed in trace amounts, **5a** was obtained at slightly lower yields (82%). From the results, we envisioned that the reflux temperature (101 °C) and an appropriate elongated time (10 h) could increase the yield of **5a**. Based on the reaction conditions, catalytic amounts of Bi $(OTf)_3$ were examined. After controlling the amounts from 30 to 40 mol%, however, no better yields (85%) of **5a** were observed (entry 8). By diminishing the amounts of $Bi(OTf)_3$ (30 → 20 mol%), the isolated yield was decreased to 78% (entry 9). Compared with 30 mol% amounts (entry 6), entries 8 and 9 showed that there were excess (40%) and insufficient (20%) amounts of $Bi(OTf)_3$, so that the reaction could not be triggered completely. Subsequently, the use of various commercially available metal triflates was investigated for the formation of **5a** (entries 10–17). These screened catalysts, which included catalytic amounts (30 mol%) of $In(OTf)_3$, $Fe(OTf)_3$, $Sc(OTf)_3$, $Ga(OTf)_3$, $Cu(OTf)_2$, $Sn(OTf)_2$, $Hg(OTf)_2$ and AgOTf, provided different yield ratios of **5a** and **4a**, respectively. Entries 10–13 showed that the trivalent metal complex provided **5a** as a major product for different distributed ratios of **5a** and **4a** (8 : 1–2 : 1), and similar yield ratios of **5a** and **4a** (~1 : 1) were shown in entries 14–16 by the use of a bivalent metal complex. In entry 17, interestingly, AgOTf only provided a 13% yield of **4a** and recovered 58% of **2a**. However, no desired **5a** was detected. From these experimental results, we thus found that different valent metal triflates provided different results for the distributing ratios of **5a** and **4a**.

On the basis of the refluxing $MeNO_2$ and the elongated time (10 h) (entries 6–17), a reasonable explanation could be that the bismuth ion was tighter to chelate with oxygenated substituents between carbonyl and methoxy groups than mono-, di- or other tri-valent metal ions. Thus, it was easier to generate bridged skeleton **5a** than **4a** with a carboxyl arm *via* the tandem Friedel–Crafts arylation processes. With these results in hand, we found that 30 mol% of $Bi(OTf)_3$ was the most reactive and used catalyst compared to other metal triflates derivatives. Solvent screening was performed next, during which $(CH_2Cl)_2$ and MeCN provided only **4a** at 79% and 76% yields, respectively, while no desired **5a** was detected (entries 18 and 19). Entry 20 showed that DMF provided

complex products because refluxing DMF forced the decomposition of $Bi(OTf)_3$. Under nitrogen atmosphere, **5a** was obtained in an 88% yield (entry 21). The results meant that air atmosphere (entry 6) and nitrogen atmosphere (entry 21) provided same yield. By use of dry $MeNO_2$, the yield of **5a** was produced in an 85% yield (entry 22). For entries 21 and 22, we understood that oxygen and water did not affect the overall reaction process. The structure of **5a** was determined by single-crystal X-ray analysis.[11]

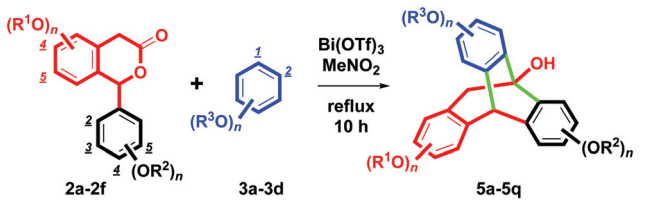
On the basis of our experimental results, a plausible Friedel–Crafts type tandem annulation mechanism for the formation of **4a** and **5a** is illustrated in Scheme 3. Initially, **2a** reacted with $Bi(OTf)_3$-chelated veratrole **3a** to obtain **A** *via* the involvement of the carbonyl group on **2a**. Then, the methoxy group of **3a** promoted an intermolecular *para*-carbon of the electron-rich benzene ring to conjugate into the C1-position of **3a**. After the ring-opening of isochroman-3-one ring, first, a new carbon–carbon bond was formed (green). Following this, the releasing triflate anion-mediated deprotonation of **A** led to **B** and triflic acid by the dehydrogenative aromatization procedure. Under a refluxing $MeNO_2$/10 h condition, the bismuth-chelated carboxylate on **B** could be installed by two kinds of routes. One was the direct protonation of bismuth-chelated carboxylate on **B** to achieve **4a** (a minor route). Another was intramolecular Friedel–Crafts type arylation between the bismuth-chelated carboxylate and two oxygenated arenes. With the *para*-methoxy groups on the electron-rich arene promoting a twice intramolecular ring-closure, **5a** could be generated by paths a → b (for **C1**) and b → a (for **C2**), respectively for two new carbon–carbon bond formations (green). Subsequently, Bi $(OTf)_3$ hydrate was regenerated by forming *in situ* $HOBi(OTf)_2$ and HOTf. From the possible mechanism, we found that the combination of $Bi(OTf)_3$ could efficiently organize a continuous sequence of one intermolecular Friedel–Crafts type substitution and two intramolecular ring-closures.

To study the scope of this route (Table 2), treatment of different multi-oxygenated 1-aryl isochroman-3-ones **2a–2f** (R^1O = dimethoxy, dioxymethylene; R^2O = dimethoxy, dioxymethylene, trimethoxy) with oxygenated arenes **3a–d** (R^3O = dimethoxy, dioxymethylene, di-*n*-butoxy, di-*n*-octoxy) was reacted with catalytic amounts (30 mol%) of $Bi(OTf)_3$ to give polyoxygenated homotriptycenes **5a–5q** based on optimal conditions. By controlling the R^1, R^2, and R^3 substituents on three arenes as the dioxygenated or trioxygenated groups, **5a–5q** were isolated at good to excellent yields (86%–96%, entries 1–17). After elongating the carbon chain (R^3O) from methoxy (CH_3O) to *n*-butoxy (C_4H_9O) or *n*-octoxy ($C_8H_{17}O$) on the arene group of **3**, the isolated yields were similar. The results show that the different aromatic groups were well-tolerated. In particular, for the reaction of **3a** with **2g** having a 3-methoxy (R^2 = 3-MeO), the desired **5r** was isolated at a 60% yield along with a 30% yield of **5r–1** (Scheme 4, eqn (1)). The reason behind the action is that the electron-donating efficiency of the mono-C3-methoxyphenyl group was weaker than the dimethoxyphenyl group such that non-bridged tricyclic dibenzosuberone skeletons could be generated as minor products during intramolecular Friedel–Crafts type procedure. Furthermore, Bi



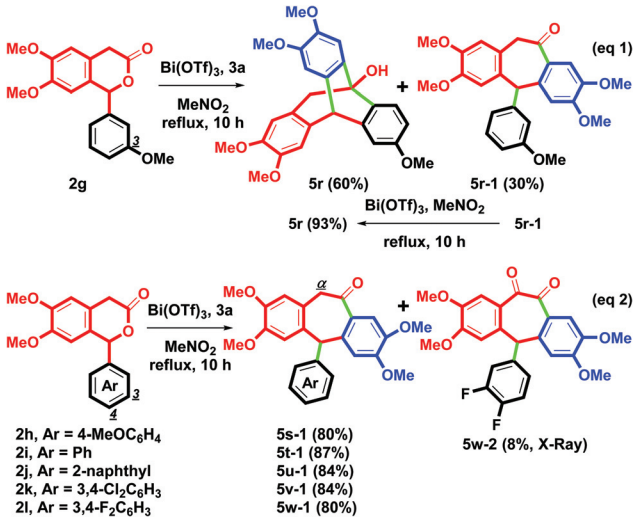
Scheme 3 Plausible mechanism.

Table 2 Synthesis of **5a–5q**[a]



Entry	2, $(R^1O)_n$ =, $(R^2O)_n$ =	3, $(R^3O)_n$ =	5[b], %
1	**2a**, 4,5-$(MeO)_2$, 3,4-$(MeO)_2$	**3a**, 1,2-$(MeO)_2$	**5a**, 88
2	**2a**, 4,5-$(MeO)_2$, 3,4-$(MeO)_2$	**3b**, 1,2-CH_2O_2	**5b**, 89
3	**2a**, 4,5-$(MeO)_2$, 3,4-$(MeO)_2$	**3c**, 1,2-(nBuO)$_2$	**5c**, 87
4	**2a**, 4,5-$(MeO)_2$, 3,4-$(MeO)_2$	**3d**, 1,2-(nOctO)$_2$	**5d**, 90
5	**2b**, 4,5-$(MeO)_2$, 3,4,5-$(MeO)_3$	**3d**, 1,2-(nOctO)$_2$	**5e**, 94
6	**2b**, 4,5-$(MeO)_2$, 3,4,5-$(MeO)_3$	**3c**, 1,2-(nBuO)$_2$	**5f**, 90
7	**2c**, 4,5-$(MeO)_2$, 3,4-CH_2O_2	**3b**, 1,2-CH_2O_2	**5g**, 92
8	**2d**, 4,5-CH_2O_2, 3,4,5-$(MeO)_3$	**3d**, 1,2-(nOctO)$_2$	**5h**, 92
9	**2e**, 4,5-CH_2O_2, 3,4-$(MeO)_2$	**3c**, 1,2-(nBuO)$_2$	**5i**, 90
10	**2b**, 4,5-$(MeO)_2$, 3,4,5-$(MeO)_3$	**3a**, 1,2-$(MeO)_2$	**5j**, 96
11	**2b**, 4,5-$(MeO)_2$, 3,4,5-$(MeO)_3$	**3b**, 1,2-CH_2O_2	**5k**, 90
12	**2d**, 4,5-CH_2O_2, 3,4,5-$(MeO)_3$	**3c**, 1,2-(nBuO)$_2$	**5l**, 89
13	**2e**, 4,5-CH_2O_2, 3,4-$(MeO)_2$	**3a**, 1,2-$(MeO)_2$	**5m**, 90
14	**2e**, 4,5-CH_2O_2, 3,4-$(MeO)_2$	**3b**, 1,2-CH_2O_2	**5n**, 86
15	**2d**, 4,5-CH_2O_2, 3,4,5-$(MeO)_3$	**3a**, 1,2-$(MeO)_2$	**5o**, 90
16	**2f**, 4,5-CH_2O_2, 3,4-CH_2O_2	**3b**, 1,2-CH_2O_2	**5p**, 94
17	**2f**, 4,5-CH_2O_2, 3,4-CH_2O_2	**3c**, 1,2-(nBuO)$_2$	**5q**, 89

[a] The reactions were run on a 1.0 mmol scale with **2**, **3** (1.1 equiv.), Bi $(OTf)_3$ (200 mg, 30 mol%), reflux (101 °C), $MeNO_2$ (20 mL), 10 h. [b] Isolated yields.

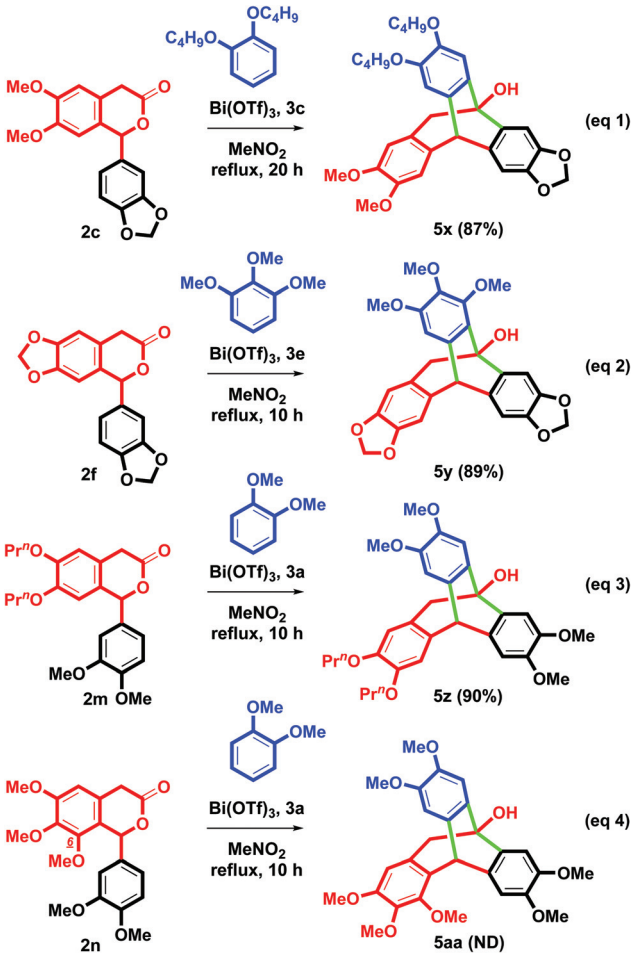


Scheme 4 Synthesis of **5r**, **5r-1**–**5w-1** and **5w-2**.

$(OTf)_3$-mediated annulation of **5r–1** provided **5r** in a 93% yield under the extending time (10 h) conditions. The extending time could trigger the conversion from **5r–1** to **5r** completely. From the above results, we found that all arenes on **2** and **3** required the dioxygenated groups to construct a rigid core skeleton of homotriptycene.

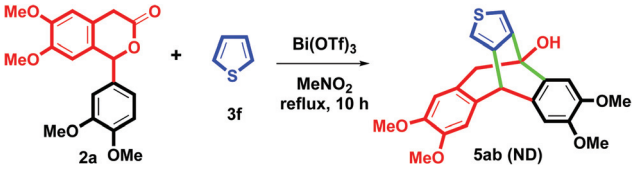
To demonstrate the plausibility, an extension of the Bi $(OTf)_3$-mediated tandem annulation on treatment of **2h–2l** with **3a** was examined next (Scheme 4, eqn (2)). When the Ar group was exchanged from the *o*-dioxygenated aryl group to other aryl groups (Ar = 4-$MeOC_6H_4$, phenyl, 2-naphthyl, 3,4-$Cl_2C_6H_3$ and 3,4-$F_2C_6H_3$), however, only tricyclic dibenzosuberones **5s-1–5w-1** were provided at a range of 80%–87% yields. The results show that the dioxygenated group on the Ar group was a very important factor in promoting the formation of a bicyclic tribenzobicyclo[3.2.2]core. Interestingly, **5w-2** with a cyclic dibenzodione could be obtained at a trace amount (8% yield) since the 3,4-difluorophenyl group-mediated the autoxidation of the α-position on **5w-1** under an air atmosphere condition. The structure of **5w-2** was determined by single-crystal X-ray analysis.[11]

With the results in hand, a $Bi(OTf)_3$-mediated combination of **2c** and **3c** was screened next (Scheme 5). By controlling the optimal reaction time (10 h), however, the desired **5x** was isolated at only a 60% yield along with a non-separated mixture of acid **4x** and ketone **5x-1** (30% yield). In order to increase the yield, we found that elongating the reaction time to 20 h could enhance the yield of **5x** to 87% (eqn (1)). By the involvement of 1,2,3-trimethoxybenzene (**3e**), treatment of **2f** with **3e** produced **5y** at an 89% yield under optimal reaction conditions (eqn (2)). On the basis of the mentioned conditions, **5z** with two *n*-propyl arms could be obtained at a 90% yield *via* $Bi(OTf)_3$-mediated tandem annulation of **2m** and **3a** (eqn (3)). For the **2n** with three methoxy groups (for R^1), surprisingly, attempts to afford the desired **5aa** failed due to the steric hindrance of the C6-methoxy group that inhibited the annulation (eqn (4)).

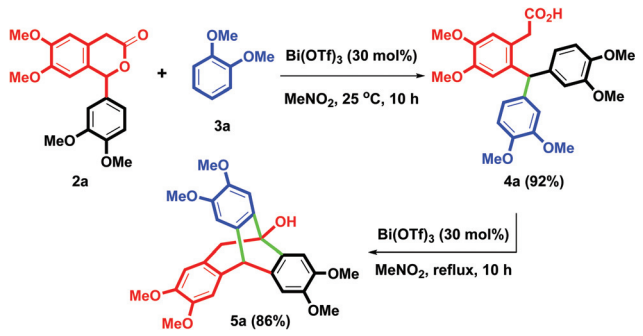


Scheme 5 Synthesis of **5x–5z**.

To understand the electronic influence of heteroaromatics on **3**, thiophene (**3f**) was examined under the above optimal reaction conditions, as shown in Scheme 6. However, $Bi(OTf)_3$-mediated tandem annulation of **2a** with **3f** provided only the starting material **2a** in a 70% yield and unidentified and complex unknown mixture (~15%). The desired bridged **5ab** could not be isolated. Next, by changing heteroaromatics from thiophene (**3f**) to indole (**3g**) and pyrrole (**3h**), the expected **4ao** could not obtained and only starting material **2a** was recovered (73% and 68%). Under the standard reaction conditions, these results were similar. From this phenomenon, we understood that oxygenated group on **3** could enrich the electron density of the aromatic ring easily than heteroaromatics **3f–3h**.



Scheme 6 Reactions of **2a** with **3f**.



Scheme 7 Stepwise control experiment.

Although substrate **3** was limited to serve as the oxygenated aryl group, the route still provided a novel and efficient synthesis of the polyoxygenated homotriptycenes skeleton.

To understand the reaction procedure, stepwise control experiments were performed, as shown in Scheme 7. Initially, $Bi(OTf)_3$ (30 mol%)-mediated Friedel–Crafts alkylation of **2a** and **3a** produced **4a** in a 92% yield at 25 °C for 10 h (Table 1, entry 2) *via* the lactone ring-opening pathway. With **4a** in hand, the formation of **5a** was studied. By using catalytic amounts (30 mol%) of $Bi(OTf)_3$, **4a** was converted to **5a** in an 86% yield after heating at reflux (101 °C) for 10 h. Compared with the one-pot process (Table 1, entry 6, 88% yield), the stepwise two-step route provided a lower total yield of **5a** (81%). The two-step experiments could exhibit that $Bi(OTf)_3$ is an optimal catalyst to promote the overall reaction procedure efficiently.

In summary, we have herein developed a combination of $Bi(OTf)_3$-promoted facile, air atmosphere, and easy-operational synthesis of polyoxygenated homotriptycenes *via* intermolecular tandem annulation of oxygenated 1-aryl isochroman-3-ones with oxygenated arenes in $MeNO_2$ at reflux for 10 h in good yields. As far as we know, there have been no reports on the use of $Bi(OTf)_3$ serving as the catalyst in the formation of a substituted tribenzobicyclo[3.2.2]core system. The Friedel–Crafts type process provides a cascade pathway of three carbon–carbon bond formations. We have also discussed the related plausible reaction mechanisms. Further investigations regarding the metal triflates-mediated synthetic application 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 air 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. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a 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 substrates arylacetic acids and aldehydes, these materials were purchased commercially and were used without further purification.

A representative synthetic procedure of compounds 2a–2m is as follows[8]

Trifluoroacetic anhydride (TFAA, 210 mg, 1.0 mmol) was added to a solution of arylacetic acids **1** (1.0 mmol) in MeCN (8 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Aldehydes (1.0 mmol) in MeCN (2 mL) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 10 h. The solvent of reaction mixture 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 = 15/1–1/1) afforded compounds **2a–2m**. For the starting compounds **2a–2m**, the general synthetic procedure has been described in our previous report.[8]

A representative synthetic procedure of compounds 4a and 5a–5r, 5r-1–5w-1, 5w-2, 5x–5z is as follows

$Bi(OTf)_3$ (200 mg, 0.3 mmol) was added to a solution of **2** (1.0 mmol) in $MeNO_2$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. **3** (1.1 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux (101 °C) for 10 h under an air atmosphere condition. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded compounds **4a** and **5a–5r**, **5r-1–5w-1**, **5w-2**, **5x–5z**.

{2-[Bis-(3,4-dimethoxyphenyl)methyl]-4,5-dimethoxyphenyl} acetic acid (4a)

In Table 1, entry 6, Yield = 5% (24 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{31}O_8$ 483.2019, found 483.2026; ^1H NMR (400 MHz, $CDCl_3$): δ 9.60 (br s, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.73 (s, 2H), 6.63 (d, J = 2.0 Hz, 2H), 6.50 (dd, J = 2.0, 8.4 Hz, 2H), 6.41 (s, 1H), 5.58 (s, 1H), 3.84 (s, 3H), 3.81 (s, 6H), 3.70 (s, 6H), 3.60 (s, 3H), 3.53 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 177.8, 148.6 (2×), 147.7, 147.3 (2×), 147.1, 135.7 (2×), 135.4, 124.1, 121.2 (2×), 113.8, 113.3, 112.5 (2×), 110.6 (2×), 55.7, 55.6, 55.58 (2×), 55.56 (2×), 51.5, 37.8.

2,3,7,8,15,16-Hexamethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5a)

Yield = 88% (408 mg); Colorless solid; mp >250 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{29}O_7$ 465.1913, found 465.1923; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 2H), 6.89 (s, 2H), 6.81 (s, 1H), 6.39 (s, 1H), 4.60 (s, 1H), 3.91 (s, 3H), 3.872 (s, 6H), 3.871 (s, 6H), 3.71 (s, 3H), 3.20 (s, 2H), 2.66 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8 (2×), 147.6 (2×), 146.8, 134.9 (2×), 134.2 (3×), 132.7, 125.6, 115.0, 110.9, 108.6 (2×), 105.9 (2×), 73.8, 56.2 (2×), 56.11 (2×), 56.07, 55.8, 53.3, 43.9. Single-crystal X-Ray diagram: crystal of compound **5a** was grown by slow diffusion of EtOAc into a solution of compound **5a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group *Pna*21, a = 15.2055 (18) Å, b = 17.986(2) Å, c = 8.4082(11) Å, V = 2299.5(5) Å^3, Z = 4, d_{calcd} = 1.342 g cm^{-3}, F(000) = 984, 2θ range 1.754–26.510°, R indices (all data) R_1 = 0.1004, wR_2 = 0.1476.

7,8,16,17-Tetramethoxy-5,10-dihydro-11*H*-5,11-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-11-ol (5b)

Yield = 89% (399 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_7$ 449.1600, found 449.1603; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.24 (s, 1H), 6.88 (s, 1H), 6.83 (s, 1H), 6.78 (s, 1H), 6.38 (s, 1H), 5.89 (d, J = 1.2 Hz, 1H), 5.87 (d, J = 1.2 Hz, 1H), 4.57 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.87 (s, 3H), 3.71 (s, 3H), 3.17 (d, J = 2.0 Hz, 2H), 2.60 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.82, 147.76, 147.7, 146.8, 146.4, 146.2, 136.6, 135.6, 134.7, 133.9, 132.5, 125.6, 115.0, 110.8, 108.6, 105.9, 105.8, 103.3, 100.9, 74.0, 56.2, 56.1 (2×), 55.8, 53.5, 43.8.

7,8-Di-*n*-butoxy-2,3,15,16-tetramethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5c)

Yield = 87% (477 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{41}O_7$ 549.2852, found 549.2856; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 2H), 6.89 (s, 1H), 6.88 (s, 1H), 6.80 (s, 1H), 6.38 (s, 1H), 4.57 (s, 1H), 4.00–3.97 (m, 4H), 3.90 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H), 3.20 (s, 2H), 2.77 (br s, 1H), 1.80–1.71 (m, 4H), 1.53–1.42 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.9 (2×), 147.7, 147.6, 147.5, 146.7, 135.1, 135.0, 134.5, 134.3, 132.8, 125.7, 115.0, 111.2, 110.8, 108.8, 108.5, 106.0, 73.7, 69.5, 69.3, 56.10, 56.06, 56.0, 55.8, 53.2, 43.9, 31.4 (2×), 19.2, 19.1, 13.8 (2×).

2,3,7,8-Tetramethoxy-15,16-bis(*n*-octyloxy)-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5d)

Yield = 90% (594 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{41}H_{57}O_7$ 661.4104, found 661.4115; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 7.27 (s, 1H), 6.88 (s, 2H), 6.80 (s, 1H), 6.39 (s, 1H), 4.57 (s, 1H), 4.01–3.94 (m, 4H), 3.91 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.71 (s, 3H), 3.19 (s, 2H), 2.54 (br s, 1H), 1.82–1.75 (m, 4H), 1.46–1.40 (m, 4H), 1.33–1.26 (m, 16H), 0.88 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.0 (2×), 147.8, 147.7, 147.6, 146.8, 135.1, 135.0, 134.5, 134.3, 132.8, 125.7, 115.0, 111.2, 110.9, 108.7, 108.6, 105.9, 73.9, 69.9, 69.6, 56.2, 56.12, 56.08, 55.8, 53.2, 43.9, 31.8 (2×), 29.4 (2×), 29.34 (2×), 29.27 (2×), 26.0 (2×), 22.6 (2×), 14.1 (2×).

2,3,7,8,9-Pentamethoxy-15,16-bis(*n*-octyloxy)-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5e)

Yield = 94% (649 mg); Colorless solid; mp = 125–127 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{42}H_{59}O_8$ 691.4210, found 691.4215; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 6.84 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 6.72 (s, 1H), 6.42 (s, 1H), 4.53 (s, 1H), 4.05 (s, 3H), 4.02 (dt, J = 1.2, 6.8 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.32 (d, J = 16.4 Hz, 1H), 3.25 (d, J = 16.4 Hz, 1H), 1.83–1.74 (m, 4H), 1.46–1.40 (m, 4H), 1.32–1.27 (m, 16H), 0.88 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.0, 150.3, 148.3, 147.8, 147.7, 146.8, 140.4, 138.7, 135.4, 132.5, 132.4, 126.6, 124.9, 114.8, 110.9, 110.8, 109.3, 105.6, 74.5, 69.7, 69.4, 62.1, 60.8, 56.1, 56.0, 55.8, 54.2, 47.0, 31.8 (2×), 29.4 (2×), 29.33 (2×), 29.25 (2×), 26.0 (2×), 22.6 (2×), 14.1 (2×).

15,16-Di-*n*-butoxy-2,3,7,8,9-pentamethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5f)

Yield = 90% (520 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{34}H_{43}O_8$ 579.2958, found 579.2962; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 6.85 (s, 1H), 6.78 (s, 1H), 6.732 (s, 1H), 6.730 (s, 1H), 6.42 (s, 1H), 4.54 (s, 1H), 4.07 (t, J = 6.4 Hz, 2H), 4.06 (s, 3H), 3.98 (t, J = 6.8 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.33 (d, J = 16.4 Hz, 1H), 3.25 (d, J = 16.4 Hz, 1H), 1.82–1.73 (m, 4H), 1.53–1.43 (m, 4H), 0.960 (t, J = 7.2 Hz, 3H), 0.955 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.0, 150.2, 148.2, 147.8, 147.6, 146.8, 140.4, 138.7, 135.4, 132.5, 132.3, 126.5, 124.8, 114.7, 110.81, 110.77, 109.3, 105.5, 74.5, 69.4, 69.1, 62.1, 60.8, 56.1, 56.0, 55.8, 54.2, 47.0, 31.39, 31.37, 19.2 (2×), 13.8 (2×).

17,18-Dimethoxy-5,11-([1,2]benzenomethano)anthra[2,3-*d*:6,7-*d*′]bis([1,3]dioxole)-11(5*H*)-ol (5g)

Yield = 92% (398 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{21}O_7$ 433.1287, found 433.1295; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 2H), 6.82 (s, 2H), 6.75 (s, 1H), 6.38 (s, 1H), 5.90 (d, J = 1.2 Hz, 2H), 5.87 (d, J = 1.2 Hz, 2H), 4.54 (s, 1H), 3.89 (s, 3H), 3.71 (s, 3H), 3.14 (s, 2H), 2.49 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8, 146.9, 146.5 (2×), 146.2 (2×), 136.4 (2×), 135.3 (2×), 132.3, 125.5, 114.8, 110.6, 105.8 (2×), 103.3 (2×), 101.0 (2×), 74.1, 56.2, 55.9, 53.7, 43.8.

7,8,9-Trimethoxy-16,17-bis(*n*-octyloxy)-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5h)

Yield = 92% (620 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{41}H_{55}O_8$ 675.3897, found 675.3905; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 6.81 (s, 1H), 6.77 (s, 1H), 6.70 (s, 2H), 6.39 (s, 1H), 5.82 (s, 2H), 4.51 (s, 1H), 4.05 (s, 3H), 4.04 (t, J = 6.8 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 3.80 (s,

3H), 3.28 (d, J = 16.4 Hz, 1H), 3.21 (d, J = 16.4 Hz, 1H), 1.83–1.75 (m, 4H), 1.49–1.40 (m, 4H), 1.38–1.26 (m, 16H), 0.90–0.86 (m, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 150.2, 148.2, 147.7, 146.4, 145.4, 140.4, 138.5, 135.3, 133.2, 132.2, 127.9, 124.8, 111.6, 110.7, 109.2, 107.6, 105.5, 100.8, 74.4, 69.7, 69.4, 62.2, 60.9, 56.0, 54.4, 47.6, 31.8 (2×), 29.4 (4×), 29.3 (2×), 26.0 (2×), 22.6 (2×), 14.1 (2×).

7,8-Di-*n*-butoxy-16,17-dimethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5i)

Yield = 90% (479 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{37}O_7$ 533.2539, found 533.2543; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.27 (s, 1H), 6.863 (s, 1H), 6.856 (s, 1H), 6.79 (s, 1H), 6.35 (s, 1H), 5.80 (s, 2H), 4.54 (s, 1H), 4.01 (dt, J = 2.0, 6.8 Hz, 2H), 3.97 (dt, J = 1.6, 6.4 Hz, 2H), 3.95 (br s, 1H), 3.85 (s, 6H), 3.15 (br s, 2H), 1.80–1.72 (m, 4H), 1.52–1.43 (m, 4H), 0.96 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.99, 147.96, 147.7, 147.6, 146.2, 145.3, 135.0, 134.9, 134.2, 134.0, 133.7, 127.0, 111.7, 111.1, 108.7, 108.5, 107.7, 105.9, 100.7, 73.6, 69.5, 69.2, 56.1, 56.0, 53.3, 44.6, 31.39, 31.36, 19.2, 19.1, 13.8 (2×).

2,3,7,8,9,15,16-Heptamethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5j)

Yield = 96% (474 mg); White solid; mp = 196–198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{31}O_8$ 495.2019, found 495.2028; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 6.85 (s, 1H), 6.80 (s, 1H), 6.77 (s, 1H), 6.74 (s, 1H), 6.43 (s, 1H), 4.57 (s, 1H), 4.07 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.3.33 (d, J = 16.4 Hz, 1H), 3.26 (d, J = 16.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.0, 150.2, 147.8, 147.4, 146.8, 140.4, 138.6, 135.1, 132.4, 132.1, 126.5, 124.7 (2×), 114.7, 110.7, 107.9, 106.8, 105.5, 74.4, 62.1, 60.8, 56.1, 56.03 (2×), 56.01, 55.8, 54.2, 46.9.

7,8,15,16,17-Pentamethoxy-5,10-dihydro-11*H*-5,11-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-11-ol (5k)

Yield = 90% (430 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{27}O_8$ 479.1706, found 479.1715; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 1H), 6.79 (s, 1H), 6.77 (s, 1H), 6.73 (s, 1H), 6.72 (s, 1H), 6.42 (s, 1H), 5.89 (d, J = 1.6 Hz, 1H), 5.87 (d, J = 1.6 Hz, 1H), 4.55 (s, 1H), 4.05 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.31 (d, J = 16.4 Hz, 1H), 3.22 (d, J = 16.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 150.2, 147.9, 146.8, 146.5, 146.0, 140.4, 138.3, 136.8, 133.8, 132.0, 126.4, 124.6, 114.6, 110.6, 105.5, 105.1, 104.5, 100.8, 74.5, 62.2, 60.9, 56.1, 56.0, 55.8, 54.4, 46.9.

16,17-Di-*n*-butoxy-7,8,9-trimethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5l)

Yield = 89% (500 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{39}O_8$ 563.2645, found 563.2653; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 6.83 (s, 1H), 6.78 (s, 1H), 6.71 (s, 1H), 6.70 (s, 1H), 6.40 (s, 1H), 5.82 (s, 2H), 4.51 (s, 1H), 4.05 (s, 3H), 4.05 (t, J = 6.8 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.29 (d, J = 16.4 Hz, 1H), 3.22 (d, J = 16.8 Hz, 1H), 1.83–1.74 (m, 4H), 1.54–1.44 (m, 4H), 0.963 (t, J = 7.6 Hz, 3H), 0.961 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 150.2, 148.2, 147.7, 146.4, 145.4, 140.4, 138.5, 135.3, 133.2, 132.3, 127.9, 124.7, 111.6, 110.7, 109.2, 107.6, 105.5, 100.7, 74.3, 69.3, 69.1, 62.1, 60.8, 56.0, 54.3, 47.6, 31.4 (2×), 19.2 (2×), 13.8 (2×).

7,8,16,17-Tetramethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5m)

Yield = 90% (403 mg); White solid; mp = 220–222 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{25}O_7$ 449.1600, found 449.1607; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 2H), 6.87 (s, 2H), 6.81 (s, 1H), 6.36 (s, 1H), 5.80 (s, 2H), 4.57 (s, 1H), 3.858 (s, 6H), 3.855 (s, 6H), 3.16 (s, 2H), 2.78 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7 (2×), 147.6 (2×), 146.3, 145.4, 134.8 (2×), 133.9 (2×), 132.5, 126.9, 111.7, 108.5 (2×), 107.7, 105.8 (2×), 100.7, 73.6, 56.1 (2×), 56.0 (2×), 53.3, 44.5.

7,8-Dimethoxy-16,17-methylenedioxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5n)

Yield = 86% (372 mg); White solid; mp = 167–169 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{21}O_7$ 433.1287, found 433.1293; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 7.22 (s, 1H), 6.86 (s, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.35 (s, 1H), 5.89 (d, J = 1.2 Hz, 1H), 5.87 (d, J = 1.6 Hz, 1H), 5.81 (d, d = 2.0 Hz, 2H), 4.54 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.13 (s, 2H), 2.60 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.8, 147.7, 146.44, 146.37, 146.2, 145.5, 136.5, 135.3, 134.6, 133.8, 133.4, 126.9, 111.7, 108.5, 107.7, 105.8 (2×), 103.2, 100.9, 100.8, 73.8, 56.2, 56.0, 53.6, 44.5.

7,8,9,16,17-Pentamethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5o)

Yield = 90% (430 mg); White solid; mp = 214–216 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{27}O_8$ 479.1706, found 479.1712; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 6.84 (s, 1H), 6.81 (s, 1H), 6.75 (s, 1H), 6.73 (s, 1H), 6.40 (s, 1H), 5.81 (s, 2H), 4.56 (s, 1H), 4.06 (s, 3H), 3.93 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.30 (d, J = 16.8 Hz, 1H), 3.23 (d, J = 16.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.0, 150.1, 147.8, 147.4, 146.4, 145.4, 140.3, 138.3, 135.0, 133.0, 132.1, 127.7, 124.5, 111.5, 107.8, 107.5, 106.6, 105.4, 100.7, 74.2, 62.1, 60.8, 56.0, 55.92, 55.90, 54.2, 47.4.

7,8,16,17-Bis(methylenedioxy)-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5p)

Yield = 94% (391 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{17}O_7$ 417.0974, found 417.0982; ^1H NMR

(400 MHz, $CDCl_3$): δ 7.21 (s, 2H), 6.78 (s, 2H), 6.75 (s, 1H), 6.34 (s, 1H), 5.90 (d, J = 1.2 Hz, 2H), 5.87 (d, J = 1.2 Hz, 2H), 5.82 (s, 2H), 4.49 (s, 1H), 3.01 (s, 2H), 2.68 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.4 (3×), 146.2 (2×), 145.4, 136.3 (2×), 135.0 (2×), 133.2, 126.8, 111.6, 107.6, 105.7 (2×), 103.2 (2×), 100.9 (2×), 100.8, 73.9, 53.8, 44.3.

16,17-Di-*n*-butoxy-7,8-methylenedioxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5q)

Yield = 89% (459 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{33}O_7$ 517.2226, found 517.2231; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.22 (s, 1H), 6.85 (s, 1H), 6.79 (s, 1H), 6.76 (s, 1H), 6.36 (s, 1H), 5.90 (d, J = 1.6 Hz, 1H), 5.88 (d, J = 1.2 Hz, 1H), 5.81 (s, 2H), 4.50 (s, 1H), 4.01 (t, J = 6.4 Hz, 2H), 3.99 (br s, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.13 (s, 2H), 1.80–1.73 (m, 4H), 1.53–1.42 (m, 4H), 0.97 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.1, 146.4, 146.3, 146.2, 145.5, 136.6, 135.4, 134.8, 134.0, 133.6, 127.0, 125.1, 111.7, 111.1, 108.6, 107.7, 105.8, 103.2, 100.9, 100.8, 73.8, 69.6, 69.3, 53.6, 44.5, 31.5, 31.4, 19.2 (2×), 13.8 (2×).

2,3,7,8,16-Pentamethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5r)

Yield = 60% (261 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{27}O_6$ 435.1808, found 435.1816; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.4 Hz, 1H), 7.28 (s, 1H), 6.90 (d, J = 2.4 Hz, 1H), 6.89 (s, 1H), 6.81 (s, 1H), 6.76 (dd, J = 2.4, 8.4 Hz, 1H), 6.38 (s, 1H), 5.63 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.24 (d, J = 16.0 Hz, 1H), 3.17 (d, J = 16.0 Hz, 1H), 2.89 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.6, 147.8, 147.7, 147.5, 146.8, 123.0, 135.1, 135.0, 133.5, 132.2, 125.8, 122.6, 114.9, 111.0, 110.8, 110.7, 108.6, 105.9, 73.6, 56.04, 56.00 (2×), 55.7, 55.2, 53.8, 44.2.

2,3,7,8-Tetramethoxy-5-(3-methoxyphenyl)-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5r-1)

Yield = 30% (130 mg); White solid; mp = 203–205 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{27}O_6$ 435.1808, found 435.1804; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.83 (s, 1H), 6.74 (dd, J = 1.6, 8.0 Hz, 1H), 6.73 (s, 1H), 6.52 (d, J = 7.6 Hz, 1H), 6.48 (s, 1H), 5.19 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.94 (d, J = 14.8 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 3.68 (s, 3H), 3.43 (d, J = 14.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.9, 159.6, 152.6, 148.1, 148.1, 147.4, 143.7, 138.2, 134.3, 129.3, 127.1, 125.2, 119.7, 114.1, 113.99, 113.96, 113.9, 113.1, 110.9, 57.9, 56.2, 56.1, 56.02, 56.00, 55.1, 49.5.

2,3,7,8-Tetramethoxy-5-(4-methoxyphenyl)-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5s-1)

Yield = 80% (347 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{27}O_6$ 435.1808, found 435.1814; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 6.99 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.84 (s, 2H), 6.77–6.73 (m, 3H), 5.19 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.929 (s, 3H), 3.931 (d, J = 14.8 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.43 (d, J = 14.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.9, 158.2, 152.6, 148.01, 147.97, 147.4, 138.7, 134.6, 133.8, 128.1 (2×), 127.1, 125.1, 114.1, 113.9, 113.8, 113.7 (2×), 113.1, 57.3, 56.2, 56.1, 56.0 (2×), 55.2, 49.4.

2,3,7,8-Tetramethoxy-5-phenyl-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5t-1)

Yield = 87% (352 mg); White solid; mp = 207–209 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{25}O_5$ 405.1702, found 405.1712; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.23–7.16 (m, 3H), 7.01 (s, 1H), 6.95–6.93 (m, 2H), 6.85 (s, 1H), 6.72 (s, 1H), 5.25 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.87 (d, J = 14.8 Hz, 1H), 3.82 (s, 3H), 3.42 (d, J = 14.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.7, 152.5, 148.0, 147.9, 147.3, 141.7, 138.2, 134.3, 128.2 (2×), 127.03, 126.96 (2×), 126.4, 125.0, 113.94, 113.86 (2×), 113.0, 57.8, 56.0, 55.9, 55.8 (2×), 49.3.

2,3,7,8-Tetramethoxy-5-naphthalen-2-yl-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5u-1)

Yield = 84% (382 mg); White solid; mp = 199–201 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{29}H_{27}O_5$ 455.1859, found 455.1863; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.79–7.76 (m, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.65–7.62 (m, 1H), 7.45–7.40 (m, 2H), 7.30 (s, 1H), 7.15 (dd, J = 1.6, 8.8 Hz, 1H), 7.10 (s, 1H), 6.91 (s, 1H), 6.74 (s, 1H), 5.40 (s, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 3.97 (s, 3H), 3.94 (d, J = 15.2 Hz, 1H), 3.86 (s, 3H), 3.40 (d, J = 14.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.8, 152.7, 148.1, 147.4, 139.2, 138.2, 134.2, 133.0, 132.0, 128.1, 127.8, 127.4, 127.3, 126.3 (2×), 125.8, 125.6, 125.4, 125.3, 114.04, 113.99, 113.96, 113.2, 58.2, 56.2, 56.1, 56.00, 55.96, 49.4.

5-(3,4-Dichlorophenyl)-2,3,7,8-tetramethoxy-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5v-1)

Yield = 84% (397 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}Cl_2O_5$ 473.0923, found 473.0930; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 6.99 (dd, J = 1.2, 2.0 Hz, 1H), 6.97 (s, 1H), 6.79 (s, 1H), 6.76 (ddd, J = 1.2, 2.0, 8.4 Hz, 1H), 6.74 (s, 1H), 5.13 (s, 1H), 3.97 (s, 3H), 3.924 (s, 3H), 3.921 (s, 3H), 3.85 (s, 3H), 3.80 (d, J = 14.8 Hz, 1H), 3.46 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.2, 152.7, 148.3 (2×), 147.6, 142.5, 136.9, 133.2, 132.7, 130.7, 130.1, 129.0, 127.0, 126.5, 124.9, 114.2, 113.8, 113.7, 113.3, 57.1, 56.1 (2×), 56.0 (2×), 49.4.

5-(3,4-Difluorophenyl)-2,3,7,8-tetramethoxy-5,11-dihydrodibenzo[*a*,*d*]cyclohepten-10-one (5w-1)

Yield = 80% (352 mg); White solid; mp = 126–128 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{23}F_2O_5$ 441.1514, found 441.1517; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.01–6.94 (m, 1H), 6.96 (s, 1H), 6.80 (s, 1H), 6.75–6.70 (m, 1H), 6.73 (s, 1H), 6.64–6.61 (m, 1H), 5.14 (s, 1H), 3.96 (s, 3H), 3.903 (s, 3H), 3.899 (s, 3H), 3.83 (s, 3H), 3.79 (d, J = 14.8 Hz, 1H), 3.45 (d, J = 15.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.2, 152.7, 150.2 (dd, J = 12.1,

247.1 Hz), 148.9 (dd, J = 12.8, 246.3 Hz), 148.3, 148.2, 147.5, 139.2 (t, J = 3.8 Hz), 137.3, 133.4, 126.9, 124.9, 122.9 (dd, J = 3.8, 6.1 Hz), 116.9 (d, J = 16.7 Hz), 116.2 (d, J = 18.2 Hz), 114.1, 113.7 (2×), 113.2, 57.0, 56.0 (2×), 55.9 (2×), 49.3.

5-(3,4-Difluorophenyl)-2,3,7,8-tetramethoxy-5*H*-dibenzo[*a*,*d*]cycloheptene-10,11-dione (5w-2)

Yield = 8% (36 mg); White solid; mp = 238–240 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{21}F_2O_6$ 455.1306, found 455.1315; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 6.96 (s, 2H), 6.95–6.89 (m, 1H), 6.53–6.48 (m, 1H), 6.43–6.39 (m, 1H), 5.05 (s, 1H), 4.03 (s, 6H), 3.91 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.0 (2×), 153.0 (2×), 150.2 (dd, J = 12.9, 247.9 Hz), 149.0 (dd, J = 13.0, 247.9 Hz), 148.7 (2×), 142.6 (t, J = 3.8 Hz), 138.0 (2×), 127.5 (2×), 123.6 (dd, J = 3.0, 6.0 Hz), 117.2 (d, J = 17.4 Hz), 117.0 (d, J = 18.2 Hz), 114.8 (2×), 112.2 (2×), 56.6, 56.3 (2×), 56.2 (2×). Single-crystal X-Ray diagram: crystal of compound **5w-2** was grown by slow diffusion of EtOAc into a solution of compound **5w-2** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, a = 11.9481(8) Å, b = 15.6973(9) Å, c = 12.0408(7) Å, V = 2107.6(2) Å^3, Z = 4, d_{calcd} = 1.432 g cm^{-3}, $F(000)$ = 944, 2θ range 1.826–26.446°, R indices (all data) R_1 = 0.0725, wR_2 = 0.1061.

16,17-Di-*n*-butoxy-7,8-dimethoxy-5,10-dihydro-11*H*-5,11-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-11-ol (5x)

Yield = 87% (463 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{37}O_7$ 533.2539, found 433.2546; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 1H), 7.24 (s, 1H), 6.88 (s, 1H), 6.82 (s, 1H), 6.77 (s, 1H), 6.38 (s, 1H), 6.89 (d, J = 1.6 Hz, 1H), 5.87 (d, J = 1.2 Hz, 1H), 4.54 (s, 1H), 4.00 (t, J = 6.4 Hz, 2H), 3.98 (t, J = 6.8 Hz, 2H), 3.90 (s, 3H), 3.72 (s, 3H), 3.16 (br d, J = 0.8 Hz, 2H), 2.55 (br s, 1H), 1.80–1.73 (m, 4H), 1.51–1.45 (m, 4H), 0.96 (t, J = 7.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.1, 148.0, 147.7, 146.8, 146.4, 146.1, 136.7, 135.7, 135.0, 134.2, 132.6, 125.7, 114.9, 111.2, 110.8, 108.7, 105.8, 103.3, 100.9, 73.9, 69.6, 69.3, 56.1, 55.8, 53.5, 43.9, 31.42, 31.40, 19.2 (2×), 13.8 (2×).

16,17-Methylenedioxy-7,8,9-trimethoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenobenzo[4′,5′]cyclohepta[1′,2′:4,5]benzo[1,2-*d*][1,3]dioxol-10-ol (5y)

Yield = 89% (411 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}O_8$ 463.1393, found 463.1399; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 6.77 (s, 2H), 6.71 (s, 1H), 6.69 (s, 1H), 6.40 (s, 1H), 5.90 (d, J = 1.2 Hz, 1H), 5.88 (d, J = 1.6 Hz, 1H), 5.82 (s, 2H), 4.52 (s, 1H), 4.05 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.28 (d, J = 16.8 Hz, 1H), 3.19 (d, J = 16.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.1, 150.1, 146.51, 146.48, 146.0, 145.48, 140.47, 138.1, 136.8, 133.5, 132.9, 127.8, 124.5, 111.5, 107.5, 105.5, 105.1, 104.4, 100.8 (2×), 74.4, 62.2, 60.9, 56.0, 54.5, 47.4.

7,8,15,16-Tetramethoxy-2,3-dipropoxy-5,11-dihydro-10*H*-5,10-[1,2]benzenodibenzo[*a*,*d*][7]annulen-10-ol (5z)

Yield = 90% (468 mg); Colorless gum; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{37}O_7$ 521.2539, found 521.2547; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 2H), 6.88 (s, 2H), 6.83 (s, 1H), 6.40 (s, 1H), 4.57 (s, 1H), 3.98 (t, J = 6.4 Hz, 2H), 3.87 (s, 6H), 3.86 (s, 6H), 3.78 (t, J = 6.8 Hz, 2H), 3.18 (s, 2H), 2.65 (br s, 1H), 1.85–1.79 (m, 2H), 1.75–1.69 (m, 2H), 1.03 (t, J = 7.6 Hz, 3H), 0.95 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.1, 147.7 (2×), 147.6 (2×), 147.0, 134.9 (2×), 134.3 (2×), 132.8, 126.0, 117.8, 114.1, 108.6 (2×), 105.9 (2×), 73.9, 71.4, 70.8, 56.2 (2×), 56.1 (2×), 53.2, 43.8, 22.7, 22.5, 10.5, 10.4.

Stepwise synthesis of compound 5a is as follows

$Bi(OTf)_3$ (200 mg, 0.3 mmol) was added to a solution of **2a** (344 mg, 1.0 mmol) in $MeNO_2$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min **3a** (152 mg, 1.1 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 10 h under an air atmosphere condition, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded compound **4a** (92%, 443 mg). Furthermore, $Bi(OTf)_3$ (200 mg, 0.3 mmol) was added to a solution of **4a** (482 mg, 1.0 mmol) in $MeNO_2$ (20 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was stirred at reflux (101 °C) for 10 h under an air atmosphere condition. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1–4/1) afforded compound **5a** (86%, 399 mg).

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors would like to thank the Ministry of Science and Technology of the Republic of China (Taiwan) for its financial support (MOST 109-2113-M-037-014-MY3).

Notes and references

1 C.-F. Chen and Y.-X. Ma, *Synthesis and reactions of triptycenes and their derivatives in Iptycenes Chemistry: From*

Synthesis to Applications, Springer, Berlin, Heidelberg, 2013, pp. 13–78.

2 Reviews on the synthetic applications on triptycenes, see: (*a*) T. R. Kelly, *Acc. Chem. Res.*, 2001, **34**, 514–522; (*b*) L. Zhao, Z. Li and T. Wirth, *Chem. Lett.*, 2010, **39**, 658–667.

3 S. J. Cristol and D. K. Pennelle, *J. Org. Chem.*, 1970, **35**, 2357–2361.

4 K. D. Baumgart, H. Harnish, U. S. Seebach and G. Szeimies, *Chem. Ber.*, 1985, **118**, 2883–2916.

5 K. Saito, K. Ito, K. Takahashi and S. Kagabu, *Org. Prep. Proced. Int.*, 1991, **23**, 196–197.

6 (*a*) H. Zhang, D. Cao, W. Liu, H. Jiang and H. Meier, *J. Org. Chem.*, 2011, **76**, 5531–5538; (*b*) W. Liu, D. Cao, C. Gao, Y. Jiang and H. Meier, *Sci. China, Ser. B: Chem.*, 2009, **52**, 1051–1056; (*c*) C. Gao, D. Cao, S. Xu and H. Meier, *J. Org. Chem.*, 2006, **71**, 3071–3076; (*d*) D. Cao, C. Gao and H. Meier, *Synlett*, 2005, 3166–3168.

7 O. A. Ivanova, E. M. Budynina, Y. K. Grishin, I. V. Trushkov and P. V. Verteletskii, *Eur. J. Org. Chem.*, 2008, 5329–5335.

8 M.-Y. Chang, S.-M. Chen and Y.-T. Hsiao, *J. Org. Chem.*, 2019, **84**, 11687–11698.

9 Recent examples on $Bi(OTf)_3$-mediated reactions, see: (*a*) Y. Gu, W. Huang, S. Chen and X. Wang, *Org. Lett.*, 2018, **20**, 4285–4289; (*b*) K.-X. Xie, Z.-P. Zhang and X. Li, *Org. Lett.*, 2017, **19**, 6708–6711; (*c*) T. Metz, J. Evans and L. M. Stanley, *Org. Lett.*, 2017, **19**, 3442–3445; (*d*) L. Lempenauer, E. Duñach and G. Lemière, *Org. Lett.*, 2016, **18**, 1326–1329; (*e*) P. Ondet, A. Joffrin, I. Diaf, G. Lemière and E. Duñach, *Org. Lett.*, 2015, **17**, 1002–1005; (*f*) B. C. Raju, K. V. Prasad, G. Saidachary and B. Sridhar, *Org. Lett.*, 2014, **16**, 420–423; (*g*) M. Murai, K. Origuchi and K. Takai, *Org. Lett.*, 2014, **16**, 3828–3831; (*h*) L.-J. Du, Y. Zhang, H.-Y. Zhang, G. Yin, X.-Y. Wang, J. Zhao and Y.-P. Han, *J. Org. Chem.*, 2020, **85**, 9863–9875; (*i*) Y.-P. Han, X.-S. Li, X.-Y. Zhu, M. Li, L. Zhou, X.-R. Song and Y.-M. Liang, *J. Org. Chem.*, 2017, **82**, 1697–1704.

10 $Bi(OTf)_3$-mediated reactions by the authors, see: (*a*) C.-K. Chan, Y.-L. Tsai and M.-Y. Chang, *Tetrahedron*, 2017, **73**, 3368–3376; (*b*) C.-K. Chan, N.-C. Hsueh, Y.-L. Tsai and M.-Y. Chang, *J. Org. Chem.*, 2017, **82**, 7077–7084; (*c*) M.-Y. Chang, Y.-C. Cheng and Y.-J. Lu, *Org. Lett.*, 2015, **17**, 1264–1267.

11 CCDC 1938168 (**5a**) and 1938169 (**5w-2**)† contain the supplementary crystallographic data for this paper.