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One-Pot Access to 4-Aryl-2-arylacetoxynaphthalenes via Benzannulation of Oxygenated Arylacetic Acids and Alkyl Aryl Ketones

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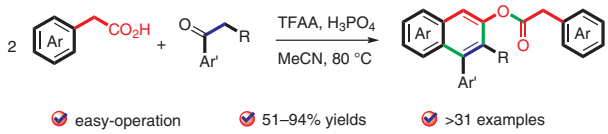

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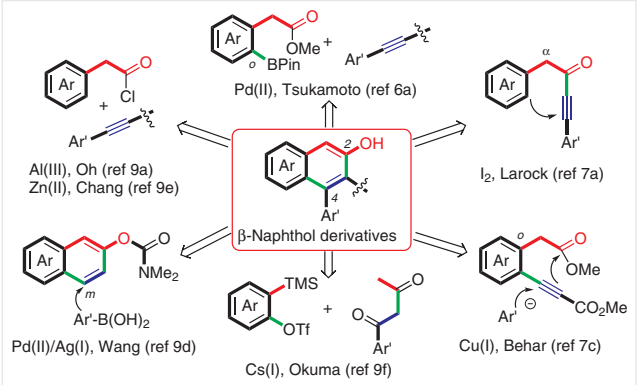
Abstract Trifluoroacetic anhydride mediated one-pot intermolecular formal (4+2) benzannulation of oxygenated arylacetic acids with alkyl aryl ketones provides 4-aryl-2-arylacetoxynaphthalenes in moderate to good yields in the presence of H_3PO_4 in an open-vessel in a straightforward procedure. A plausible mechanism is proposed and discussed. This protocol provides a highly effective ring-closure via two carbon–carbon (C–C) and one carbon–oxygen (C–O) bond-formation events.

Key words trifluoroacetic anhydride, benzannulation, arylacetic acids, 4-aryl-2-arylacetoxynaphthalenes, easy operation

Substituted naphthalenes[1] can be utilized as potential bioactive precursors,[2] unique natural products,[3] versatile synthetic blocks or ligands[4] and functionalized materials.[5] Among these, the synthetic development of β-naphthols has been attracting considerable attention. Traditionally, the construction of functionalized β-naphthols involves three major routes: (1) transition-metal-catalyzed tandem benzannulation,[6] (2) electrophilic or nucleophilic cyclocondensation[7] and (3) photo-promoted annulation.[8] Other routes for the formation of substituted β-naphthols have recently been investigated extensively.[9] For the preparation of 4-aryl-substituted β-naphthol derivatives, the diverse range of routes can be divided into three general pathways. These include an intermolecular formal (4+2) benzannulation of *o*-boronate arylacetate or arylacetyl chloride with alkyne,[6a,9a,9e] an intermolecular formal (4+2) benzannulation of benzyne with aroylacetone,[9f] an intramolecular ring-closure of α-aryl alkynone[7a] or *o*-acetyl arylpropiolate[7c] and a direct intermolecular *meta*-arylation of *O*-β-naphthyl carbamate with arylboronic acid,[9d] as shown in Scheme 1. In spite of these advances, some problems remain, such as multi-step routes, complex catalytic conditions, lack of broad substrate generality and the requirement for pre-functionalized fragments. Therefore, the development of a one-pot, efficient and straightforward synthetic method to access substituted β-naphthol derivatives is still highly desired.



Scheme 1 Routes to 4-aryl-substituted β-naphthol derivatives

We recently explored the synthetic application of oxygenated arylacetic acids to establish a polyoxygenated pentacyclic benzo[*g*]chrysene (BgC) framework using metal triflate promoted domino Friedel–Crafts acylation followed by photoinduced Scholl annulation strategies (Scheme 2, eq. 1).[10] In another approach, TFAA-mediated synthesis of 1-aryl isochroman-3-ones was developed by using an intermolecular (4+2) annulation of oxygenated arylacetic acids with arylaldehydes (Scheme 2, eq. 2).[11] Continuing our research on oxygenated arylacetic acids,[10,11] herein, we present a TFAA-mediated preparation of an oxygenated *O*-β-naphthyl ester skeleton by a one-pot reaction of oxygenated arylacetic acids with alkyl aryl ketones in the presence of

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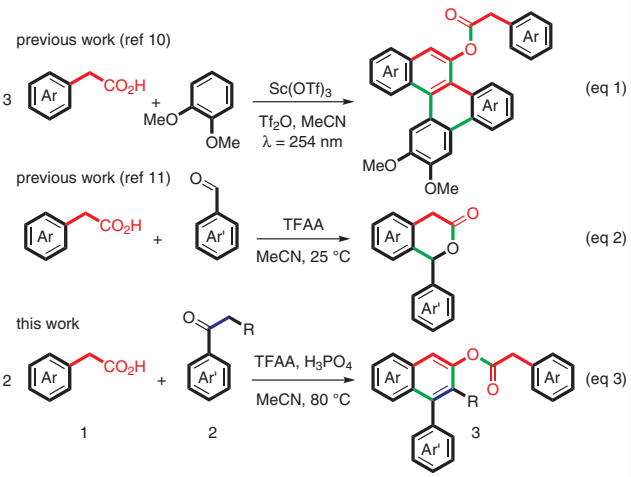
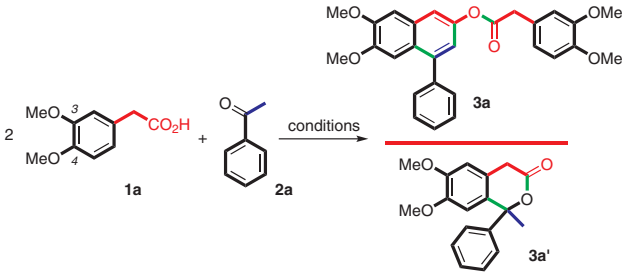
H_3PO_4 via two carbon–carbon (C–C) and one carbon–oxygen (C–O) bond formation events (green marks), as shown in Scheme 2, eq. 3.



Scheme 2 Our synthetic applications of arylacetic acids

The initial study commenced with treatment of homoveratric acid (**1a**, Ar = 3,4-$(MeO)_2C_6H_3$, 0.5 mmol) and acetophenone (**2a**, Ar′ = Ph, R = H, 1.0 mmol) in MeCN (20 mL) at room temperature (25 °C) for 10 hours using a combination of TFAA and H_3PO_4 (1.1 equiv) (Table 1). However, no desired **3a** was detected, and the benzo-fused δ-lactone **3a′** was obtained in 87% yield (entry 1).[11] When the reaction time was extended to 20 hours, the yield of **3a** increased to 17% along with a 68% yield of **3a′** (entry 2). By elevating the reaction temperature from 25 to 80 °C (r.t. to reflux) and reducing the reaction time (10 to 5 h), the yield of **3a** increased to 35% (entry 3). By extending the reaction time (5 to 10, 20 and 30 h), the yields increased to 61, 80, and 73%, respectively (entries 4–6). From the results, we established that the application of reflux temperature (80 °C) and extended reaction time (20 h) could increase the yield of **3a**. Subsequently, the number of equivalents of the combination of TFAA and H_3PO_4 was examined. After changing the number of equivalents of TFAA and H_3PO_4 from 1.1 to 0.5, 1.5 and 2.0, however, no better yields of **3a** were observed. This showed that when insufficient amounts of TFAA and H_3PO_4 were present, the reaction was not triggered completely (entry 7). Furthermore, the use of excess amounts of TFAA and H_3PO_4 provided slightly lower yields (79% and 75%, entries 8 and 9). Solvent screening was then performed. It was found that the reaction gave poorer yields (42% and 25%) in $CHCl_3$ and $MeNO_2$, respectively (entries 10 and 11), and no desired product was detected in DMF (entry 12). When TFAA was changed to Ac_2O or Tf_2O, different results were observed: No reaction was detected due to the poorer reactivity of Ac_2O (entry 13), and only 32% yield of **3a** was produced with the more reactive Tf_2O (entry 14). By replacing H_3PO_4 with HOAc, **3a** was isolated in a 62% yield (entry 15). For H_2SO_4, only unknown products were detected (40%, entry 16).

Table 1 Annulation Conditions[a]



Entry	Anhydride/acid (equiv)	Temp (°C)	Solvent	Time (h)	**3a** (%)[b]
1	TFAA/H_3PO_4 (1.1:1.1)	25	MeCN	10	–[c]
2	TFAA/H_3PO_4 (1.1:1.1)	25	MeCN	20	17[c]
3	TFAA/H_3PO_4 (1.1:1.1)	80	MeCN	5	35[c]
4	TFAA/H_3PO_4 (1.1:1.1)	80	MeCN	10	61[c]
5	TFAA/H_3PO_4 (1.1:1.1)	80	MeCN	20	80
6	TFAA/H_3PO_4 (1.1:1.1)	80	MeCN	30	73
7	TFAA/H_3PO_4 (0.5:0.5)	80	MeCN	20	38[c]
8	TFAA/H_3PO_4 (1.5:1.5)	80	MeCN	20	79
9	TFAA/H_3PO_4 (2.0:2.0)	80	MeCN	20	75
10	TFAA/H_3PO_4 (1.1:1.1)	61	$CHCl_3$	20	42[c]
11	TFAA/H_3PO_4 (1.1:1.1)	80	$MeNO_2$	20	25[c]
12	TFAA/H_3PO_4 (1.1:1.1)	80	DMF	20	–[d]
13	Ac_2O/H_3PO_4 (1.1:1.1)	80	MeCN	20	–[e]
14	Tf_2O/H_3PO_4 (1.1:1.1)	80	MeCN	20	32[d]
15	TFAA/AcOH (1.1:1.1)	80	MeCN	20	62
16	TFAA/H_2SO_4 (1.1:1.1)	80	MeCN	20	–[d]

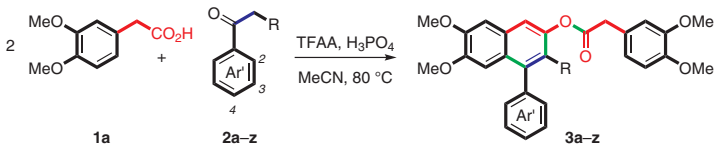
[a] The reactions were performed on a 1.0 mmol scale with **1a**, **2a** (0.5 equiv), temp (°C), solvent (20 mL), time (h).
[b] Isolated yield.
[c] Compound **3a′** was isolated (entry 1, 87%; entry 2, 68%; entry 3, 35%; entry 4, 10%; entry 7, 30%; entry 10, 34%; entry 11, 50%).
[d] Complex unknown products (entry 12, 75%; entry 14, 30%; entry 16, 40%).
[e] No reaction.

To study the scope of this approach, the reaction of **1a** with a range of alkyl aryl ketones **2a–z** was examined with the combination of TFAA and H_3PO_4 to give 4-aryl-2-arylacetoxynaphthalenes **3a–x**. The products were obtained in a range of 51–94% under the optimal conditions established (Table 1, entry 5), as shown in Table 2. By fixing the methyl group (R = H, entries 1–17) for the reaction of **2a–q** with **1a**, stronger electron-withdrawing (Ar′ = 4-F, 4-CF_3, 4-NO_2) aryl groups provided rather lower yields (62, 60, and 51%; entries 2, 5, and 6) than other electron-donating and electron-neutral groups. Changing the R group from H to Me, Et and Ph, entries 18–21 showed that **3r–u** produced 60–81%

yields. Since Ar′ has a heterocyclic ring (entries 22–25), 2-furyl, 3-bromo-2-thienyl and 2-thienyl groups provided similar yields (74%, 76%, 80%), but no reaction was observed for Ar′ = 2-pyridyl group because the nitrogen atom trapped the proton such that the one-pot reaction was inhibited (entry 25). Furthermore, when the Ar′ group was changed to *n*-propyl (an aliphatic group), no desired product **3z** was isolated (entry 26); this result may stem from a cross self-aldol reaction of 2-pentanone (**2z**) replacing the desired one-pot reaction. From the results, we found that Ar′ with oxygenated groups provided better yields than other substituents. A possible reason for this is that the oxygenated group on arene (Ar′) played a key factor in promoting the tandem benzannulation process.

On the basis of our experimental results, a plausible mechanism for the formation of **3a** is illustrated in Scheme 3. Initially, **1a** reacts with protonated TFAA (generated in situ from protonation of TFAA with H_3PO_4) to form **A** and TFA. By the involvement of **2a**, the carbonyl group of **2a** attacks the anhydride motif on **A** to give **B**. Following this, the methoxy group on the 3-position of electron-rich arene promotes an intramolecular ring-closure to yield **C** with a δ-lactone ring. Then, **C** is converted into **3a′** via a dehydro-

Table 2 Synthesis of **3a–z**[a]

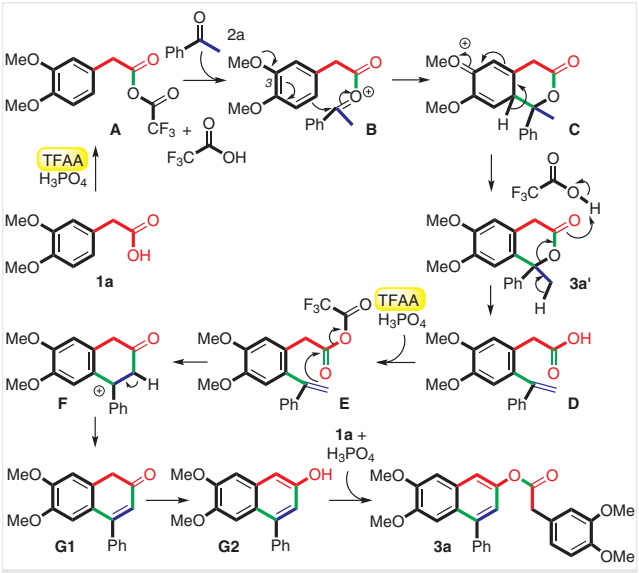


1a 2a–z 3a–z

Entry	2	R	Ar′	3	Yield (%)[b]
1	**2a**	H	Ph	**3a**	80
2	**2b**	H	4-FC_6H_4	**3b**	62
3	**2c**	H	4-MeC_6H_4	**3c**	76
4	**2d**	H	4-$MeOC_6H_4$	**3d**	92
5	**2e**	H	4-$F_3CC_6H_4$	**3e**	60
6	**2f**	H	4-$O_2NC_6H_4$	**3f**	51
7	**2g**	H	4-PhC_6H_4	**3g**	70
8	**2h**	H	2-naphthyl	**3h**	72
9	**2i**	H	3-$MeOC_6H_4$	**3i**	86
10	**2j**	H	2-BrC_6H_4	**3j**	80
11	**2k**	H	2,5-$(MeO)_2C_6H_3$	**3k**	86
12	**2l**	H	4-ClC_6H_4	**3l**	80
13	**2m**	H	3,4-$Cl_2C_6H_3$	**3m**	68
14	**2n**	H	3,4-$(MeO)_2C_6H_3$	**3n**	92
15	**2o**	H	3,4-$CH_2O_2C_6H_3$	**3o**	92
16	**2p**	H	2,4-$(MeO)_2C_6H_3$	**3p**	90
17	**2q**	H	3,4,5-$(MeO)_3C_6H_2$	**3q**	94
18	**2r**	Me	Ph	**3r**	81
19	**2s**	Et	Ph	**3s**	78
20	**2t**	Ph	Ph	**3t**	63
21	**2u**	Ph	4-FC_6H_4	**3u**	60
22	**2v**	H	2-furyl	**3v**	74
23	**2w**	H	3-Br-2-thienyl	**3w**	76
24	**2x**	H	2-thienyl	**3x**	80
25	**2y**	H	2-pyridyl	**3y**	–[c]
26	**2z**	H	*n*Pr	**3z**	–[c]

[a] The reactions were performed using a 1.0 mmol scale with **1a**, **2a–z** (0.5 equiv), reflux (80 °C), MeCN (20 mL), 20 h.
[b] Isolated yield.
[c] No reaction.

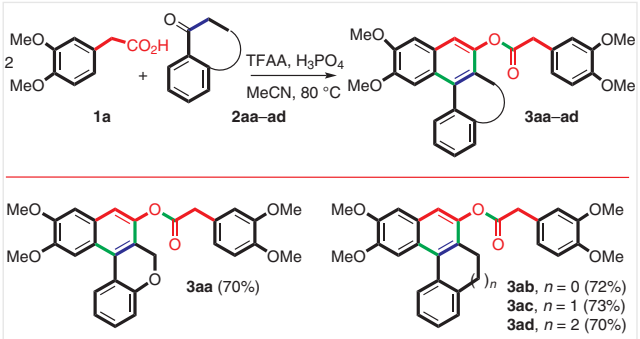
genative aromatization. After β-elimination of protonated **3a′** to give **D**, ring-opening of the benzo-fused δ-lactone occurs. Subsequently, by treatment of **D** with the repeated protonated TFAA, **E** is generated. Intramolecular cyclization of **E** affords **F** with a dibenzylic tertiary carbocation. Next, deprotonation of **F** and tautomerization of **G1** furnishes the construction of **G2** with a β-naphthol skeleton. Finally, **3a** is formed via intramolecular esterification of **G2** with a second equivalent of **1a**.



Scheme 3 Plausible mechanism

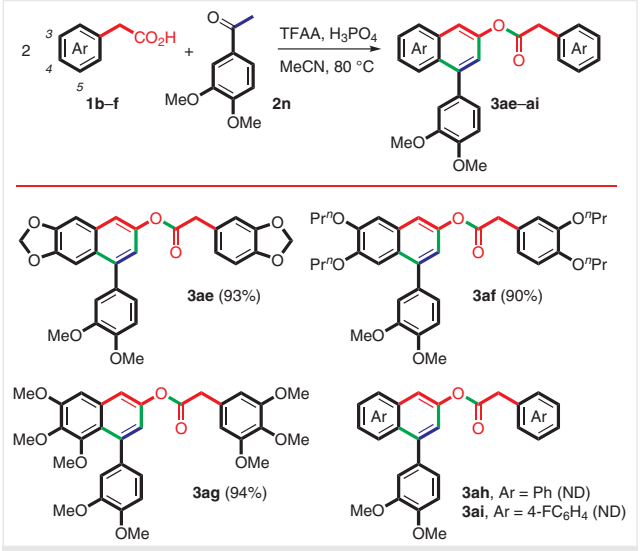
From the possible mechanism, we found that the combination of TFAA and H_3PO_4 could facilitate a continuous sequence of intermolecular Friedel–Crafts type reactions and intramolecular ring-closures efficiently. Comparing the reaction systems described in our previous report (TFAA, 25 °C, 10 h)[11] and the present work (TFAA, H_3PO_4, 80 °C, 20 h), we concluded that the addition of H_3PO_4, the extension of reaction time (10 to 20 h), and the elevation of the reaction temperature (25 to 80 °C) led to more complete formation of the arylacetoxynaphthalene skeleton than TFAA alone, based the plausible reaction pathways (see Scheme 5).

As an extension of TFAA/H_3PO_4-mediated intermolecular (4+2) annulations of homoveratric acid **1a** with alkyl aryl ketones **2a–z**, four cyclic benzoketones **2aa–ad** were studied (Scheme 4). Under the conditions described above, benzopyrone **2aa** produced **3aa** in 77% yield, and other benzocycles (*n* = 1–3, indanone **2ab**, tetralone **2ac** and benzosuberone **2ad**) provided 72%, 73% and 70% yields, respectively. The results show that the ring-size did not affect the isolated yields. The molecular structures of **3t** and **3ab** were determined by single-crystal X-ray crystallography.[12]



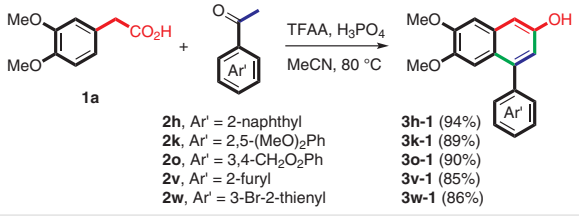
Scheme 4 Synthesis of **3aa–ad**

With these results in hand, five arylacetic acids **1b–f** were then screened (Scheme 5). By using 3,4-dimethoxyacetophenone (**2n**) as a two-carbon synthon, 3,4-methylenedioxyphenylacetic acid (**1b**) generated **3ae** in excellent yield (93%) under similar conditions. Changing the 3,4-dioxygenated group to a di-*n*-propyloxy group (for **1c**), produced an isolated yield of **3af** of 90%. Compound **1d**, with a 3,4,5-trimethoxy group, also afforded a high yield (94%) for the formation of **3ag** with eight methoxy groups. One plausible reason to account for the high yields observed with these substrates is that the electron-donating methoxy group on arene (for Ar) could provide a driving force to facilitate the intramolecular ring-closure leading to the formation of the β-naphthol skeleton. However, when phenylacetic acid (**1e**) was treated under TFAA/H_3PO_4-mediated reaction conditions, no desired **3ah** with a naphthalene skeleton was observed due to the lack of an electron-rich substituent on the Ar ring to trigger the reaction process. For **1f**, with an electron-withdrawing 4-fluorophenyl group, no desired product **3ai** was obtained.



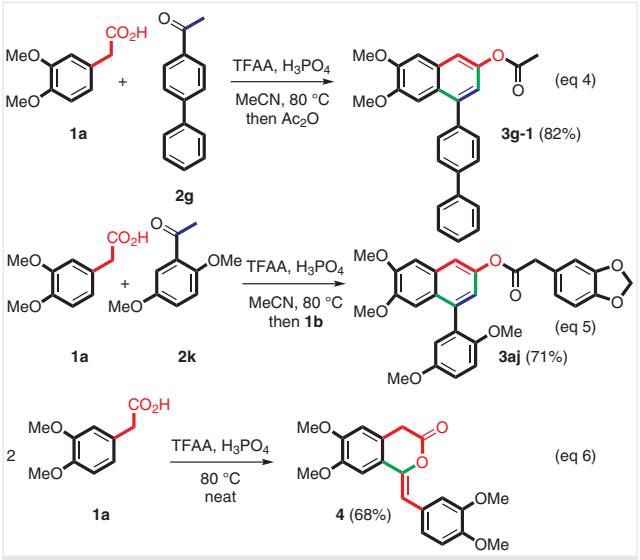
Scheme 5 Reaction of **1b–f** with **2n**

After examining the one-pot synthetic route, a study using equimolar amounts of model substrates **1a** and **2h**, **2k**, **2o**, **2v** or **2w** was also explored (Scheme 6). Similarly, treatment of **1a** (1 equiv) with **2h**, **2k**, **2o**, **2v** or **2w** (1 equiv) afforded β-naphthols **3h-1**, **3k-1**, **3o-1**, **3v-1** or **3w-1** in 94, 89, 90, 85 and 86% yields, respectively, in the presence of TFAA and H_3PO_4. The results also demonstrated the formation of intermediate **G2** as a plausible reaction mechanism. Therefore, using equimolar amounts of the two starting materials could lead to high yields of products. On the basis of the reaction conditions, the replacement of the side chain was examined, and acetylation was studied (Scheme 7, eq. 4). After the one-pot reaction of **1a** with **2g** provided a β-naphthol skeleton, further esterification of β-naphthol formed in situ with the addition of excess amounts Ac_2O afforded **3g-1**, with an acetate arm, in 82% yield. The results showed that the 2-acyloxy group was installed into the β-naphthol skeleton efficiently by a stepwise addition of an anhydride reagent. Furthermore, under similar conditions, **3aj** was obtained in 71% yield in a one-pot intermolecular formal (4+2) benzannulation of **1a** and **2k**, and sequential esterification of the resulting β-naphthol with **1b** (eq. 5). Compared with the formation of **3a**, the results showed that the sequence of addition of arylacetic acids **1a** and **1b** could determine the regioselectivity of the generation of **3aj**. On the other hand, by the involvement of TFAA and H_3PO_4, two equivalents of **1a** were combined to provide **4**, with the benzylidene benzolactone skeleton, under neat conditions via the cyclodimerization procedure (eq. 6).[13] The molecular structures of **3g-1** and **4** were confirmed by single-crystal X-ray analysis.[12]



Scheme 6 Synthesis of **3h-1**, **3k-1**, **3o-1**, **3v-1** and **3w-1**

In summary, we have herein explored the use of a combination of TFAA and H_3PO_4 to promote a facile and efficient one-pot synthesis of 4-aryl-2-arylacetoxynaphthalenes via intermolecular formal (4+2) benzannulation of oxygenated arylacetic acids with alkyl aryl ketones. The reaction is operationally straightforward and proceeds in MeCN at reflux in moderate to good yields under open-vessel conditions. To our knowledge, there have been no reports on the use of alkyl aryl ketones as a two-carbon synthon in the formation of substituted naphthalenes. The process provides a cascade pathway of carbon–carbon followed by carbon–oxygen bond formation events. We have also discussed related plausible reaction mechanisms. Further investigations regarding the synthetic application of arylacetic acids are under way in our laboratory.



Scheme 7 Synthesis of **3g-1**, **3aj**, and **4**

All reagents and solvents were obtained from commercial sources and used without further purification. The starting substrates **1** and **2** were purchased commercially and were used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. A heating mantle was used to provide a stable heat source. Products in organic solvents were dried with anhydrous magnesium sulfate ($MgSO_4$) before concentration in vacuo. Melting points were determined with an SMP3 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with 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 Finnigan/Thermo Quest MAT 95XL mass spectrometer. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

Synthesis of 3a′, 3a–x and 3aa–ag; General Procedure

Trifluoroacetic anhydride (TFAA, 230 mg, 1.1 mmol) and phosphoric acid (H_3PO_4, 110 mg, 1.1 mmol) were added to a solution of oxygenated arylacetic acids **1a–d** (1.0 mmol) in MeCN (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min. Ketone **2a–x** or **2aa–ad** (0.5 mmol) in MeCN (5 mL) was added to the reaction mixture at 25 °C, and the reaction mixture was stirred at reflux (80 °C) for 20 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 the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10:1 to 1:1) afforded compounds **3a′**, **3a–x** and **3aa–ag**.

6,7-Dimethoxy-1-methyl-1-phenylisochroman-3-one (3a′)[11]

For Table 1, entry 1.

Yield: 87% (130 mg); colorless solid; mp 159–161 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.19 (m, 3 H), 7.15–7.13 (m, 2 H), 6.98 (s, 1 H), 6.65 (s, 1 H), 3.92 (s, 3 H), 3.86 (s, 3 H), 3.44 (d, *J* = 18.4 Hz, 1 H), 3.07 (dd, *J* = 0.8, 18.4 Hz, 1 H), 2.00 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 171.0, 149.2, 147.9, 143.3, 130.1, 128.3 (2C), 127.8, 125.2 (2C), 123.0, 110.4, 108.5, 85.9, 56.2, 55.9, 36.2, 29.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}O_4$: 299.1283; found: 299.1288.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-dimethoxy-4-phenylnaphthalen-2-yl Ester (3a)

Yield: 80% (183 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.39 (m, 5 H), 7.40 (d, *J* = 2.4 Hz, 1 H), 7.17 (s, 1 H), 7.11 (s, 1 H), 7.00 (d, *J* = 2.4 Hz, 1 H), 6.97–6.94 (m, 2 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 2 H), 3.79 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 149.9, 149.3, 149.0, 148.3, 146.8, 140.4, 140.2, 130.2, 129.7 (2×), 128.4 (2×), 127.5, 125.9, 125.3, 121.5, 119.9, 116.7, 112.4, 111.3, 106.5, 104.8, 55.91 (2×), 55.87, 55.7, 41.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{27}O_6$: 459.1808; found: 459.1806.

(3,4-Dimethoxyphenyl)acetic Acid 4-(4-Fluorophenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3b)

Yield: 62% (148 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2 H), 7.40 (d, *J* = 2.4 Hz, 1 H), 7.20–7.14 (m, 2 H), 7.11 (s, 1 H), 7.08 (s, 1 H), 6.98 (d, *J* = 2.4 Hz, 1 H), 6.97–6.94 (m, 2 H), 6.87 (d, *J* = 9.2 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 2 H), 3.80 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 162.3 (d, *J* = 245.6 Hz), 150.0, 149.4, 149.0, 148.4, 146.8, 139.2, 136.1 (d, *J* = 3.8 Hz), 131.2 (d, *J* = 7.5 Hz, 2×), 130.1, 125.9, 125.4, 121.5, 119.9, 116.9, 115.4 (d, *J* = 21.3 Hz, 2×), 112.4, 111.3, 106.5, 104.5, 55.89 (2×), 55.86, 55.7, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{26}FO_6$: 477.1714; found: 477.1715.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-*p*-tolylnaphthalen-2-yl Ester (3c)

Yield: 76% (179 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.37 (m, 3 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 7.21 (s, 1 H), 7.10 (s, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 6.97–6.94 (m, 2 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 2 H), 3.80 (s, 3 H), 2.44 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 149.9, 149.2, 149.0, 148.3, 146.9, 140.4, 137.23, 137.21, 130.2, 129.5 (2×), 129.1 (2×), 126.0, 125.4, 121.5, 119.8, 116.5, 112.4, 111.3, 106.4, 104.9, 55.90 (2×), 55.85, 55.7, 41.1, 21.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{29}O_6$: 473.1964; found: 473.1963.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-(4-methoxyphenyl)naphthalen-2-yl Ester (3d)

Yield: 92% (225 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.8 Hz, 2 H), 7.37 (d, *J* = 2.4 Hz, 1 H), 7.19 (s, 1 H), 7.10 (s, 1 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.98–6.94 (m, 3 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 3.98 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.84 (s, 2 H), 3.81 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 159.0, 149.9, 149.2, 149.0, 148.3, 146.8, 140.1, 152.5, 130.7 (2×), 130.1, 125.9, 125.5, 121.5, 119.8, 116.4, 113.8 (2×), 112.4, 111.3, 106.4, 104.9, 55.9 (2×), 55.8, 55.7, 55.3, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{29}O_7$: 489.1913; found: 489.1920.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-(4-trifluoromethylphenyl)naphthalen-2-yl Ester (3e)

Yield: 60% (158 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.44 (d, *J* = 2.0 Hz, 1 H), 7.12 (s, 1 H), 7.06 (s, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 6.96 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.94 (s, 1 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.85 (s, 2 H), 3.80 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.1, 149.7, 148.4, 146.7, 143.9, 138.7, 130.2, 130.12 (q, *J* = 37.9 Hz), 130.05 (2×), 130.0, 125.8, 125.4 (q, *J* = 3.8 Hz, 2×), 125.0, 123.7 (q, *J* = 270.6 Hz), 121.5, 120.0, 117.5, 112.4, 111.3, 106.6, 104.2, 55.9 (2×), 55.82, 55.76, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{26}F_3O_6$: 527.1682; found: 527.1683.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-(4-nitrophenyl)naphthalen-2-yl Ester (3f)

Yield: 51% (128 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.8 Hz, 2 H), 7.67 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 2.4 Hz, 1 H), 7.13 (s, 1 H), 7.011 (d, *J* = 2.4 Hz, 1 H), 7.006 (s, 1 H), 6.96 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.94 (s, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 4.00 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.85 (s, 2 H), 3.80 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.3, 149.9, 149.1, 148.4, 147.3, 147.1, 146.7, 137.7, 130.6 (2×), 130.3, 125.7, 124.7, 123.8 (2×), 121.6, 120.0, 118.1, 112.4, 111.3, 106.7, 103.8, 55.9, 55.8, 41.0, 22.7, 14.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{26}NO_8$: 504.1659; found: 504.1658.

(3,4-Dimethoxyphenyl)acetic acid 4-biphenyl-4-yl-6,7-dimethoxynaphthalen-2-yl ester (3g)

Yield: 70% (187 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.69 (m, 4 H), 7.58 (d, *J* = 8.4 Hz, 2 H), 7.52–7.47 (m, 2 H), 7.42 (d, *J* = 2.0 Hz, 1 H), 7.41–7.37 (m, 1 H), 7.26 (s, 1 H), 7.13 (s, 1 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 6.98–6.95 (m, 2 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 4.00 (s, 3 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.85 (s, 2 H), 3.83 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.0, 149.4, 149.0, 148.3, 146.9, 140.6, 140.3, 140.0, 139.2, 130.2, 130.1 (2×), 128.9 (2×), 127.5, 127.1 (2×), 127.0 (2×), 125.9, 125.3, 121.5, 119.9, 116.8, 112.4, 111.3, 106.5, 104.8, 55.89 (2×), 55.86, 55.8, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{31}O_6$: 535.2121; found: 535.2123.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy[1,2′]binaphthalenyl-3-yl Ester (3h)

Yield: 72% (183 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 0.8 Hz, 1 H), 7.94–7.88 (m, 3 H), 7.63 (dd, *J* = 2.0, 8.4 Hz, 1 H), 7.57–7.53 (m, 2 H), 7.44 (d, *J* = 2.4 Hz, 1 H), 7.20 (s, 1 H), 7.14 (s, 1 H), 7.11 (d, *J* = 2.4 Hz, 1 H), 6.98–6.95 (m, 2 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 4.00 (s, 3 H), 3.90 (s, 3 H), 3.88 (s, 3 H), 3.86 (s, 2 H), 3.74 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 150.0, 149.4, 149.0, 148.3, 146.9, 140.3, 137.8, 133.5, 132.7, 130.2, 128.5, 128.1, 127.9, 127.8, 127.7, 126.4, 126.2, 125.9, 125.5, 121.5, 120.2, 116.9, 112.4, 111.3, 106.5, 104.8, 55.9 (3×), 55.7, 41.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{29}O_6$: 509.1964; found: 509.1963.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-(3-methoxyphenyl)naphthalen-2-yl Ester (3i)

Yield: 86% (210 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 2 H), 7.20 (s, 1 H), 7.10 (s, 1 H), 7.08–6.95 (m, 6 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 6 H), 3.80 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 159.6, 150.0, 149.3, 149.1, 148.4, 146.8, 140.3, 130.2, 129.4, 125.9, 125.3, 124.4, 122.1, 121.5, 119.7, 116.8, 115.1, 113.3, 112.4, 111.3, 106.4, 104.9, 55.91 (2×), 55.87, 55.7, 55.3, 41.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{29}O_7$: 489.1913; found: 489.1919.

(3,4-Dimethoxyphenyl)acetic acid 4-(2-bromophenyl)-6,7-dimethoxynaphthalen-2-yl ester (3j)

Yield: 80% (214 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.46 (d, *J* = 2.4 Hz, 1 H), 7.42 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.38 (dt, *J* = 2.0, 8.8 Hz, 1 H), 7.30 (dt, *J* = 2.4, 8.0 Hz, 1 H), 7.11 (s, 1 H), 6.97 (d, *J* = 2.4 Hz, 1 H), 6.96–6.93 (m, 2 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 6.68 (s, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.88 (s, 3 H), 3.84 (s, 2 H), 3.75 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 150.0, 149.4, 149.0, 148.3, 146.6, 140.6, 139.0, 132.8, 131.8, 129.7, 129.3, 127.3, 125.9, 125.3, 123.9, 121.5, 120.0, 117.3, 112.4, 111.3, 106.4, 104.6, 55.9 (2×), 55.8, 55.7, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{26}BrO_6$: 537.0913; found: 537.0919.

(3,4-Dimethoxyphenyl)acetic Acid 4-(2,5-Dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3k)

Yield: 86% (223 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 2.4 Hz, 1 H), 7.09 (s, 1 H), 7.01 (d, *J* = 2.4 Hz, 1 H), 6.95–6.84 (m, 7 H), 3.97 (s, 3 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 3.83 (s, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.63 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 153.5, 151.0, 149.8, 149.0, 148.9, 148.2, 146.7, 136.9, 129.6 (2×), 125.9, 125.7, 121.4, 120.1, 117.1, 116.8, 114.0, 112.33, 112.27, 111.2, 106.2, 105.1, 56.1, 55.8 (2×), 55.7, 55.6, 55.5, 40.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{31}O_8$: 519.2019; found: 519.2023.

(3,4-Dimethoxyphenyl)acetic Acid 4-(4-Chlorophenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3l)

Yield: 80% (197 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 5 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 6.97–6.94 (m, 3 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 2 H), 3.80 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.0, 149.5, 149.0, 148.4, 146.8, 139.0, 138.6, 133.6, 131.0 (2×), 130.2, 128.7 (2×), 125.9, 125.2, 121.5, 119.9, 117.1, 112.4, 111.3, 106.5, 104.4, 55.90 (2×), 55.88, 55.7, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{26}ClO_6$: 493.1418; found: 493.1420.

(3,4-Dimethoxyphenyl)acetic Acid 4-(3,4-Dichlorophenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3m)

Yield: 68% (179 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 2.0 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.42 (d, *J* = 2.4 Hz, 1 H), 7.33 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.11 (s, 1 H), 7.05 (s, 1 H), 6.97 (d, *J* = 2.4 Hz, 1 H), 6.95 (d, *J* = 7.6 Hz, 1 H), 6.94 (s, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 3.99 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.84 (s, 2 H), 3.82 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 150.1, 149.7, 149.1, 148.4, 146.7, 140.2, 137.6, 132.7, 131.8, 131.5, 130.4, 130.2, 129.0, 125.8, 124.9, 121.5, 119.9, 117.6, 112.4, 111.3, 106.6, 104.0, 55.9 (3×), 55.8, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}Cl_2O_6$: 527.1028; found: 527.1030.

(3,4-Dimethoxyphenyl)acetic Acid 4-(3,4-Dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3n)

Yield: 92% (238 mg); colorless solid; mp 157–159 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 2.4 Hz, 1 H), 7.21 (s, 1 H), 7.10 (s, 1 H), 7.05–6.93 (m, 6 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 3.882 (s, 3 H), 3.875 (s, 3 H), 3.84 (s, 2 H), 3.80 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 149.8, 149.2, 149.0, 148.6, 148.4, 148.3, 146.7, 140.2, 132.8, 130.1, 125.9, 125.4, 121.9, 121.5, 119.7, 116.5, 112.9, 112.4, 111.2, 111.1, 106.4, 104.8, 55.90, 55.86, 55.82 (2×), 55.79, 55.6, 40.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{31}O_8$: 519.2019; found: 519.2025.

(3,4-Dimethoxyphenyl)acetic Acid 4-Benzo[1,3]dioxol-5-yl-6,7-dimethoxynaphthalen-2-yl Ester (3o)

Yield: 92% (231 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 2.4 Hz, 1 H), 7.20 (s, 1 H), 7.09 (s, 1 H), 6.97–6.90 (m, 6 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.03 (s, 2 H), 3.98 (s, 3 H), 3.90 (s, 3 H), 3.88 (s, 3 H), 3.832 (s, 3 H), 3.826 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 149.9, 149.2, 149.0, 148.3, 147.6, 147.0, 146.7, 139.9, 134.0, 130.1, 125.9, 125.4, 123.1, 121.5, 119.8, 116.6, 112.4, 111.2, 110.1, 108.2, 106.4, 104.7, 101.1, 55.83 (2×), 55.79, 55.7, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{27}O_8$: 503.1706; found: 503.1708.

(3,4-Dimethoxyphenyl)acetic Acid 4-(2,4-Dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3p)

Yield: 90% (233 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 2.4 Hz, 1 H), 7.21 (d, *J* = 9.2 Hz, 1 H), 7.08 (s, 1 H), 6.98 (d, *J* = 2.4 Hz, 1 H), 6.95–6.93 (m, 2 H), 6.86–6.84 (m, 2 H), 6.61–6.58 (m, 2 H), 3.97 (s, 3 H), 3.90 (s, 3 H), 3.881 (s, 3 H), 3.878 (s, 3 H), 3.83 (s, 2 H), 3.77 (s, 3 H), 3.68 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 160.7, 157.8, 149.7, 148.93, 148.90, 148.2, 146.8, 136.9, 132.1, 129.6, 126.2, 126.0, 121.5, 121.4, 120.4, 116.5, 112.4, 111.2, 106.2, 105.3, 104.3, 98.7, 55.81 (2×), 55.75, 55.6, 55.4, 55.3, 41.0.

HRMS (ESI-TOF): *m*/*z*: [M + H]$^+$ calcd for $C_{30}H_{31}O_8$: 519.2019; found: 519.2016.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-(3,4,5-trimethoxyphenyl)naphthalen-2-yl Ester (3q)

Yield: 94% (258 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 2.4 Hz, 1 H), 7.23 (s, 1 H), 7.11 (s, 1 H), 7.01 (d, *J* = 2.4 Hz, 1 H), 6.96–6.95 (m, 2 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 6.70 (s, 2 H), 3.99 (s, 3 H), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.86 (s, 6 H), 3.85 (s, 2 H), 3.82 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 153.1 (2×), 150.0, 149.3, 149.0, 148.3, 146.7, 140.3, 137.4, 135.7, 130.2, 125.9, 125.3, 121.5, 119.6, 116.8, 112.4, 111.3, 106.8 (2×), 106.5, 104.8, 61.0, 56.2 (2×), 55.89 (2×), 55.87, 55.8, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{33}O_9$: 549.2125; found: 549.2126.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-3-methyl-4-phenylnaphthalen-2-yl Ester (3r)

Yield: 81% (191 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 2 H), 7.44–7.40 (m, 1 H), 7.36 (s, 1 H), 7.26–7.23 (m, 2 H), 7.05 (s, 1 H), 6.99–6.96 (m, 2 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 6.61 (s, 1 H), 3.96 (s, 3 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.87 (s, 2 H), 3.66 (s, 3 H), 1.86 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 149.3, 149.0, 148.3, 146.6, 139.4, 139.1, 129.9 (2×), 129.5 (2×), 127.8, 127.2, 126.9, 126.0, 125.3, 121.6 (2×), 117.1, 112.4, 111.2, 105.9, 105.3, 55.87, 55.85, 55.8, 55.4, 41.1, 14.2.

HRMS (ESI): *m*/*z* [M+1]$^+$ calcd for $C_{29}H_{29}O_6$: 473.1964; found: 473.1968.

(3,4-Dimethoxyphenyl)acetic Acid 3-Ethyl-6,7-dimethoxy-4-phenylnaphthalen-2-yl Ester (3s)

Yield: 78% (190 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 3 H), 7.38 (s, 1 H), 7.26–7.24 (m, 2 H), 7.05 (s, 1 H), 6.99–6.96 (m, 2 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 6.52 (s, 1 H), 3.96 (s, 3 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.87 (s, 2 H), 3.64 (s, 3 H), 2.25 (q, *J* = 7.6 Hz, 2 H), 0.82 (t, *J* = 7.6 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 149.3, 149.0, 148.9, 148.3, 146.2, 139.1, 138.8, 131.3, 129.9 (2×), 128.3 (2×), 127.8, 127.3, 127.1, 126.0, 121.7, 117.8, 112.5, 111.3, 105.9, 105.6, 55.91, 55.88, 55.8, 55.4, 41.4, 21.7, 14.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{31}O_6$: 487.2121; found: 487.2124.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-3,4-diphenylnaphthalen-2-yl Ester (3t)

Yield: 63% (168 mg); colorless solid; mp 119–120 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1 H), 7.25–7.18 (m, 3 H), 7.13 (s, 1 H), 7.12–7.10 (m, 2 H), 7.13–7.10 (m, 3 H), 7.02–6.98 (m, 2 H), 6.83 (s, 1 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 6.61–6.58 (m, 2 H), 4.00 (s, 3 H), 3.87 (s, 3 H), 3.81 (s, 3 H), 3.70 (s, 3 H), 3.44 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 149.9, 149.3, 148.7, 148.1, 145.3, 139.2, 138.6, 136.5, 131.6, 130.8 (2×), 130.6 (2×), 129.1, 127.7 (2×), 127.1 (2×), 126.73, 126.71, 126.3, 125.6, 121.5, 117.7, 112.3, 111.0, 105.9, 105.7, 55.9, 55.8, 55.7, 55.5, 40.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{31}O_6$: 535.2121; found: 535.2122.

Single-crystal X-ray diagram: a crystal of compound **3t** was grown by slow diffusion of EtOAc into a solution of compound **3t** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 9.9310(3) Å, *b* = 6.8766(2) Å, *c* = 40.3543(11) Å, *V* = 2751.16(14) Å^3, *Z* = 4, d_{calcd} = 1.291 g/cm^3, *F*(000) = 1128, 2θ range 2.022–26.378°, R indices (all data) R1 = 0.0892, wR2 = 0.2254; CCDC 1910997.[12]

(3,4-Dimethoxyphenyl)acetic Acid 4-(4-Fluorophenyl)-6,7-dimethoxy-3-phenylnaphthalen-2-yl Ester (3u)

Yield: 60% (166 mg); colorless solid; mp 180–181 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1 H), 7.13 (s, 1 H), 7.10–7.05 (m, 5 H), 6.99–6.90 (m, 4 H), 6.78 (s, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.60–6.57 (m, 2 H), 4.00 (s, 3 H), 3.87 (s, 3 H), 3.81 (s, 3 H), 3.72 (s, 3 H), 3.44 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 161.6 (d, *J* = 244.1 Hz), 150.0, 149.4, 148.7, 148.1, 145.3, 138.1, 136.3, 134.5 (d, *J* = 3.8 Hz), 132.4 (d, *J* = 8.4 Hz, 2×), 131.9, 130.5 (2×), 129.1, 127.3 (2×), 126.7, 126.4, 125.5, 121.5, 118.0, 114.8 (d, *J* = 21.2 Hz, 2×), 112.3, 111.1, 106.0, 105.4, 55.9, 55.8, 55.7, 55.6, 40.4.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{30}FO_6$: 553.2027; found: 553.2022.

(3,4-Dimethoxyphenyl)acetic Acid 4-Furan-2-yl-6,7-dimethoxynaphthalen-2-yl Ester (3v)

Yield: 74% (166 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1 H), 7.60 (dd, *J* = 1.2, 2.0 Hz, 1 H), 7.38 (d, *J* = 2.4 Hz, 1 H), 7.31 (d, *J* = 2.4 Hz, 1 H), 7.08 (s, 1 H), 6.97–6.95 (m, 2 H), 6.88 (d, *J* = 8.8 Hz, 1 H), 6.72 (d, *J* = 3.2 Hz, 1 H), 6.58 (dd, *J* = 2.0, 3.2 Hz, 1 H), 3.99 (s, 3 H), 3.97 (s, 3 H), 3.92 (s, 3 H), 3.90 (s, 3 H), 3.85 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.5, 152.9, 149.9, 149.8, 149.1, 148.4, 146.8, 142.4, 130.5, 128.6, 125.9, 124.1, 121.6, 118.7, 117.7, 112.4, 111.5, 111.3, 109.2, 106.6, 104.5, 55.9 (2×), 55.83, 55.78, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{25}O_7$: 449.1600; found: 449.1602.

(3,4-Dimethoxyphenyl)acetic Acid 4-(3-Bromothiophen-2-yl)-6,7-dimethoxynaphthalen-2-yl Ester (3w)

Yield: 76% (206 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 2.4 Hz, 1 H), 7.41 (d, *J* = 5.2 Hz, 1 H), 7.13 (s, 1 H), 7.12 (d, *J* = 5.2 Hz, 1 H), 7.10 (s, 1 H), 7.01 (s, 1 H), 6.96–6.93 (m, 2 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 3.98 (s, 3 H), 3.90 (s, 3 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.84 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 150.1, 149.7, 148.9, 148.3, 146.2, 135.9, 130.6, 129.9, 129.8, 126.4, 125.74, 125.69, 122.0, 121.5, 118.5, 112.3, 111.2, 110.7, 106.3, 104.9, 55.8 (3×), 57.7, 40.9.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{24}BrO_6S$: 543.0477; found: 543.0481.

(3,4-Dimethoxyphenyl)acetic Acid 6,7-Dimethoxy-4-thiophen-2-ylnaphthalen-2-yl Ester (3x)

Yield: 80% (186 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1 H), 7.42 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.40 (d, *J* = 2.4 Hz, 1 H), 7.25 (dd, *J* = 1.2, 3.6 Hz, 1 H), 7.16 (dd, *J* = 3.2, 5.2 Hz, 1 H), 7.15 (d, *J* = 2.4 Hz, 1 H), 7.01 (s, 1 H), 6.97–6.94 (m, 2 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 3.99 (s, 3 H), 3.91 (s, 3 H), 3.889 (s, 3 H), 3.885 (s, 3 H), 3.84 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.4, 150.0, 149.6, 149.0, 148.3, 146.5, 141.3, 132.5, 130.2, 127.3, 127.2, 125.9, 125.8, 125.6, 121.5, 120.8, 117.5, 112.4, 111.3, 106.5, 104.7, 55.9 (2×), 55.84, 55.75, 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{25}O_6S$: 465.1372; found: 465.1378.

(3,4-Dimethoxyphenyl)acetic Acid 10,11-Dimethoxy-6*H*-5-oxa-benzo[*c*]phenanthren-7-yl Ester (3aa)

Yield: 70% (170 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.88 (s, 1 H), 7.37 (s, 1 H), 7.30 (dt, *J* = 1.6, 7.6 Hz, 1 H), 7.18–7.13 (m, 2 H), 7.08 (s, 1 H), 6.99–6.92 (m, 2 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 4.81 (s, 2 H), 4.00 (s, 3 H), 3.98 (s, 3 H), 3.92 (s, 3 H), 3.91 (s, 3 H), 3.86 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.1, 156.5, 149.9, 149.6, 149.2, 148.5, 142.6, 130.3, 128.9, 127.6, 127.1, 125.6, 124.9, 124.2, 123.0, 121.8, 121.6, 117.9, 117.5, 112.3, 111.4, 106.9, 104.5, 64.4, 55.94, 55.93, 55.8 (2×), 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{27}O_7$: 487.1757; found: 487.1762.

(3,4-Dimethoxyphenyl)acetic Acid 2,3-Dimethoxy-7*H*-benzo[*c*]-fluoren-6-yl Ester (3ab)

Yield: 72% (169 mg); colorless solid; mp 164–166 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.4 Hz, 1 H), 7.94 (s, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.40 (s, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.16 (s, 1 H), 7.04–7.02 (m, 2 H), 6.92 (d, *J* = 8.8 Hz, 1 H), 4.12 (s, 3 H), 4.00 (s, 3 H), 3.94 (s, 3 H), 3.93 (s, 3 H), 3.91 (s, 2 H), 3.69 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.1, 149.7, 149.12, 149.08, 148.5, 144.4, 143.8, 142.3, 137.4, 133.3, 130.1, 126.8, 126.1, 125.8, 125.0, 123.4, 122.3, 121.7, 116.9, 112.5, 111.4, 107.3, 102.9, 56.0 (2×), 55.9, 55.8, 41.2, 34.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{27}O_6$: 471.1808; found: 471.1813.

Single-crystal X-ray structure: Crystals of compound **3ab** were grown by slow diffusion of EtOAc into a solution of compound **3ab** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group C 2/c, *a* = 23.7585(9) Å, *b* = 15.1466(6) Å, *c* = 14.5717(6) Å, *V* = 4676.2(3) Å^3, *Z* = 8, d_{calcd} = 1.337 g/cm^3, *F*(000) = 1984, 2θ range 1.653–26.413°, R indices (all data) R1 = 0.0354, wR2 = 0.0894; CCDC 1910998.[12]

(3,4-Dimethoxyphenyl)acetic Acid 2,3-Dimethoxy-7,8-dihydro-benzo[*c*]phenanthren-6-yl Ester (3ac)

Yield: 73% (177 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.6 Hz, 1 H), 7.88 (s, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.32–7.25 (m, 3 H), 7.07 (s, 1 H), 7.00–6.97 (m, 2 H), 6.89 (d, *J* = 8.8 Hz, 1 H), 3.99 (s, 3 H), 3.95 (s, 3 H), 3.910 (s, 3 H), 3.907 (s, 3 H), 3.87 (s, 2 H), 2.73–2.69 (m, 2 H), 2.56–2.52 (m, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 149.4, 149.2, 149.0, 148.4, 144.9, 139.5, 134.1, 132.7, 129.4, 128.9, 127.9 (2×), 127.1, 126.0, 124.0, 121.6 (2×), 117.3, 112.4, 111.3, 106.6, 105.1, 55.9 (2×), 55.78, 55.77, 41.0, 28.9, 23.1.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{29}O_6$: 485.1964; found: 485.1963.

(3,4-Dimethoxyphenyl)acetic Acid 2,3-Dimethoxy-8,9-dihydro-7*H*-benzo[6,7]cyclohepta[1,2-*a*]naphthalen-6-yl Ester (3ad)

Yield: 70% (174 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.47 (m, 1 H), 7.37–7.29 (m, 5 H), 7.07 (s, 1 H), 7.00–6.98 (m, 2 H), 6.87 (d, *J* = 8.8 Hz, 1 H), 3.98 (s, 3 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.87 (s, 2 H), 3.80 (s, 3 H), 2.53–2.48 (m, 2 H), 2.42–2.34 (m, 1 H), 1.94–1.89 (m, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.9, 149.3, 149.2, 149.0, 148.4, 145.2, 140.9, 137.8, 137.1, 129.9, 128.9, 128.6, 128.1, 127.8, 126.1, 125.6, 125.3, 121.6, 117.4, 112.3, 111.3, 106.2, 104.9, 55.91, 55.89, 55.8, 55.6, 41.2, 32.3, 30.9, 23.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{31}O_6$: 499.2121; found: 499.2126.

Benzo[1,3]dioxol-5-yl-acetic Acid 8-(3,4-Dimethoxyphenyl)naphtho[2,3-*d*][1,3]dioxol-6-yl Ester (3ae)

Yield: 93% (226 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 2.0 Hz, 1 H), 7.17 (s, 1 H), 7.10 (s, 1 H), 6.70 (d, *J* = 2.4 Hz, 1 H), 6.97–6.95 (m, 3 H), 6.91 (d, *J* = 1.6 Hz, 1 H), 6.84 (d, *J* = 1.6, 7.6 Hz, 1 H), 6.80 (d, *J* = 7.6 Hz, 1 H), 6.00 (s, 2 H), 5.96 (s, 2 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 3.80 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.3, 148.7, 148.5, 148.0, 147.9, 147.8, 146.9, 146.8, 140.7, 132.8, 131.4, 127.0, 126.9, 122.5, 122.0, 119.9, 117.3, 113.0, 111.0, 109.7, 108.4, 103.9, 102.5, 101.2, 101.1, 55.9 (2×), 41.0.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{23}O_8$: 487.1393; found: 487.1396.

(3,4-Dipropoxyphenyl)acetic Acid 4-(3,4-Dimethoxyphenyl)-6,7-dipropoxynaphthalen-2-yl Ester (3af)

Yield: 90% (284 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 2.4 Hz, 1 H), 7.20 (s, 1 H), 7.09 (s, 1 H), 7.04–6.96 (m, 5 H), 6.92 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 3.99 (t, *J* = 6.4 Hz, 4 H), 3.96 (s, 3 H), 3.88 (s, 3 H), 3.85 (t, *J* = 6.4 Hz, 2 H), 3.81 (s, 2 H), 1.94–1.81 (m, 8 H), 1.10–0.99 (m, 12 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.6, 149.9, 149.20, 149.19, 148.6, 148.5, 148.4, 146.7, 140.0, 133.0, 130.2, 126.1, 125.5, 122.0, 121.7, 119.5, 116.4, 115.0, 114.0, 113.0, 111.1, 107.9, 106.6, 70.81, 70.77, 70.3, 70.2, 55.94, 55.93, 41.0, 22.6 (2×), 22.4, 22.3, 10.5 (4×).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{38}H_{47}O_8$: 631.3271; found: 631.3278.

(3,4,5-Trimethoxyphenyl)acetic Acid 4-(3,4-Dimethoxyphenyl)-5,6,7-trimethoxynaphthalen-2-yl Ester (3ag)

Yield: 94% (272 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 2.4 Hz, 1 H), 6.95 (s, 1 H), 6.92–6.86 (m, 3 H), 6.91 (s, 1 H), 6.61 (s, 2 H), 3.95 (s, 3 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 3.86 (s, 6 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.29 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.0, 153.3, 153.2 (3×), 149.7, 147.5, 147.2, 147.0, 142.1, 139.8, 137.2, 136.1, 132.3, 128.8, 121.9, 120.6, 117.0, 112.8, 109.7, 106.3 (2×), 102.9, 61.0, 60.73, 60.70, 56.0 (2×), 55.81, 55.77, 55.7, 41.5.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{32}H_{35}O_{10}$: 579.2230; found: 579.2236.

Synthesis of 3h-1, 3k-1, 3o-1, 3v-1 and 3w-1; General Procedure

Trifluoroacetic anhydride (TFAA, 230 mg, 1.1 mmol) and phosphoric acid (H_3PO_4, 110 mg, 1.1 mmol) were added to a solution of homoveratric acid (**1a**, 98 mg, 0.5 mmol) in MeCN (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min. Ketone **2h**, **2k**, **2o**, **2v** or **2w** (0.5 mmol) in MeCN (5 mL) was added to the reaction mixture at 25 °C and the reaction mixture was stirred at reflux (80 °C) for 20 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 = 10:1 to 1:1) afforded compounds **3h-1**, **3k-1**, **3o-1**, **3v-1** and **3w-1**.

6,7-Dimethoxy[1,2′]binaphthalenyl-3-ol (3h-1)

Yield: 94% (155 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.90 (m, 3 H), 7.85–7.82 (m, 1 H), 7.60 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.56–7.51 (m, 2 H), 7.18 (s, 1 H), 7.12 (d, *J* = 2.4 Hz, 1 H), 7.03 (d, *J* = 2.4 Hz, 1 H), 7.03 (s, 1 H), 5.99 (br s, 1 H), 3.97 (s, 3 H), 3.73 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.0, 149.8, 147.7, 140.5, 138.1, 133.4, 132.5, 131.1, 128.3, 128.0, 127.9, 127.70, 127.66, 126.3, 126.1, 122.3, 117.0, 108.7, 105.6, 105.1, 55.7, 55.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{19}O_3$: 331.1334; found: 331.1339.

4-(2,5-Dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-ol (3k-1)

Yield: 89% (151 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 2.8 Hz, 1 H), 6.96–6.93 (m, 3 H), 6.90 (d, *J* = 2.8 Hz, 1 H), 6.88 (dd, *J* = 1.2, 2.8 Hz, 1 H), 6.82 (s, 1 H), 4.80 (br s, 1 H), 3.94 (s, 3 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.65 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 153.5, 151.9, 151.1, 149.8, 147.5, 137.1, 130.6, 130.2, 122.6, 117.2, 117.0, 113.9, 112.4, 108.8, 105.43, 105.39, 56.2, 55.73, 55.69, 55.6.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{21}O_5$: 341.1389; found: 341.1396.

4-Benzo[1,3]dioxol-5-yl-6,7-dimethoxynaphthalen-2-ol (3o-1)

Yield: 90% (146 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (s, 1 H), 7.04 (d, *J* = 2.4 Hz, 1 H), 7.00 (s, 1 H), 6.96–6.95 (m, 1 H), 6.93–6.92 (m, 2 H), 6.88 (d, *J* = 2.4 Hz, 1 H), 6.04 (s, 2 H), 5.20 (br s, 1 H), 3.98 (s, 3 H), 3.81 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 151.9, 149.9, 147.7, 147.6, 146.9, 140.3, 134.5, 131.1, 123.0, 122.4, 116.6, 110.1, 108.4, 108.3, 105.5, 105.1, 101.1, 55.8, 55.7.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}O_5$: 325.1076; found: 325.1072.

4-Furan-2-yl-6,7-dimethoxynaphthalen-2-ol (3v-1)

Yield: 85% (115 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 1 H), 7.60 (d, *J* = 1.2 Hz, 1 H), 7.22 (d, *J* = 2.4 Hz, 1 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 7.00 (s, 1 H), 6.71 (d, *J* = 3.2 Hz, 1 H), 6.58 (dd, *J* = 1.6, 3.2 Hz, 1 H), 5.00 (br s, 1 H), 3.99 (s, 3 H), 3.96 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 153.3, 151.8, 150.0, 148.2, 142.3, 131.4, 128.8, 121.2, 115.3, 111.4, 109.7, 108.9, 105.6, 104.8, 55.78, 55.75.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_4$: 271.0970; found: 271.0964.

4-(3-Bromothiophen-2-yl)-6,7-dimethoxynaphthalen-2-ol (3w-1)

Yield: 86% (157 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 5.2 Hz, 1 H), 7.14 (d, *J* = 2.8 Hz, 1 H), 7.12 (d, *J* = 5.2 Hz, 1 H), 7.02 (d, *J* = 2.8 Hz, 1 H), 7.00 (s, 1 H), 6.96 (s, 1 H), 5.60 (br s, 1 H), 3.97 (s, 3 H), 3.84 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 151.6, 150.1, 148.1, 136.5, 130.8, 130.6, 130.3, 126.2, 122.8, 118.8, 110.52, 110.49, 105.5, 105.3, 55.81, 55.75.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}BrO_3S$: 364.9847; found: 364.9853.

Acetic Acid 4-Biphenyl-4-yl-6,7-dimethoxynaphthalen-2-yl Ester (3g-1)

Trifluoroacetic anhydride (TFAA, 230 mg, 1.1 mmol) and phosphoric acid (H_3PO_4, 110 mg, 1.1 mmol) were added to a solution of homoveratric acid **1a** (98 mg, 0.5 mmol) in MeCN (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min, then ketone **2g** (98 mg, 0.5 mmol) in MeCN (5 mL) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux (80 °C) for 20 h, then cooled to 25 °C. Ac_2O (150 mg, 1.5 mmol) was added and the reaction mixture was stirred at reflux (80 °C) for 1 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 the crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10:1 to 1:1) afforded compound **3g-1**.

Yield: 82% (163 mg); colorless solid; mp 166–168 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.69 (m, 4 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.51–7.47 (m, 2 H), 7.45 (d, *J* = 2.4 Hz, 1 H), 7.41–7.37 (m, 1 H), 7.28 (s, 1 H), 7.15 (s, 1 H), 7.09 (d, *J* = 2.4 Hz, 1 H), 4.02 (s, 3 H), 3.83 (s, 3 H), 2.36 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 169.8, 150.0, 149.4, 146.8, 140.6, 140.3, 140.0, 139.2, 130.3, 130.1 (2×), 128.9 (2×), 127.4, 127.1 (2×), 127.1 (2×), 125.3, 120.1, 116.9, 106.5, 104.8, 55.9, 55.8, 21.2.

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{26}H_{23}O_4$: 399.1596; found: 399.1598.

Single-crystal X-ray structure: Crystals of compound **3g-1** were grown by slow diffusion of EtOAc into a solution of compound **3g-1** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a = 14.6778(7) Å, b = 9.3020(5) Å, c = 14.7948(8) Å, V = 2015.60(18) Å^3, Z = 4, d_{calcd} = 1.313 g/cm^3, F(000) = 840, 2θ range 1.893–26.428°, R indices (all data) R1 = 0.0438, wR2 = 0.0921; CCDC 1910999.[12]

Benzo[1,3]dioxol-5-yl-acetic Acid 4-(2,5-Dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl Ester (3aj)

Trifluoroacetic anhydride (TFAA, 230 mg, 1.1 mmol) and phosphoric acid (H_3PO_4, 110 mg, 1.1 mmol) were added to a solution of homoveratric acid **1a** (98 mg, 0.5 mmol) in MeCN (15 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 30 min, then ketone **2k** (90 mg, 0.5 mmol) in MeCN (5 mL) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux (80 °C) for 20 h, then cooled to 25 °C. Compound **1b** (90 mg, 0.5 mmol) was added and the reaction mixture was stirred at reflux (80 °C) for 1 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 = 10:1 to 1:1) afforded compound **3aj**.

Yield: 71% (178 mg); colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 2.4 Hz, 1 H), 7.09 (s, 1 H), 7.00 (d, J = 2.4 Hz, 1 H), 6.96 (s, 1 H), 6.95 (d, J = 2.4 Hz, 1 H), 6.91 (d, J = 1.6 Hz, 1 H), 6.89 (dd, J = 1.2, 2.4 Hz, 1 H), 6.86 (s, 1 H), 6.84 (d, J = 1.6 Hz, 1 H), 6.80 (d, J = 8.0 Hz, 1 H), 5.96 (s, 2 H), 3.98 (s, 3 H), 3.78 (s, 2 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.64 (s, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 170.2, 153.6, 151.2, 149.8, 149.1, 147.8, 146.9, 146.7, 137.0, 129.7, 129.6, 127.1, 125.8, 122.5, 120.1, 117.2, 116.8, 114.2, 112.4, 109.7, 108.4, 106.3, 105.2, 101.0, 56.2, 55.81, 55.77, 55.6, 41.1.

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{29}H_{27}O_8$: 503.1706; found: 507.1712.

1-(3,4-Dimethoxybenzylidene)-6,7-dimethoxyisochroman-3-one (4)

Trifluoroacetic anhydride (TFAA, 230 mg, 1.1 mmol) and phosphoric acid (H_3PO_4, 110 mg, 1.1 mmol) were added to a solution of homoveratric acid (**1a**, 196 mg, 1.0 mmol) at 25 °C. The reaction mixture was stirred at 120 °C for 20 h, then cooled to 25 °C. 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 = 10:1 to 1:1) afforded compound **4**.

Yield: 68% (121 mg); colorless solid; mp 159–160 °C (recrystallized from hexanes and EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 2.0 Hz, 1 H), 7.30 (dd, J = 2.0, 8.4 Hz, 1 H), 7.05 (s, 1 H), 6.88 (d, J = 8.4 Hz, 1 H), 6.61 (s, 1 H), 6.12 (s, 1 H), 3.96 (s, 3 H), 3.95 (s, 3 H), 3.911 (s, 3 H), 3.908 (s, 3 H), 3.81 (s, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.6, 150.3, 148.8, 148.7, 148.5, 145.4, 127.0, 122.7, 121.0, 120.8, 112.3, 111.0, 109.5, 107.8, 106.4, 56.2, 56.1, 55.8 (2×), 34.5.

HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{20}H_{21}O_6$: 357.1338; found: 357.1345.

Single-crystal X-ray structure: Crystals of compound **4** were grown by slow diffusion of EtOAc into a solution of compound **4** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P21/c, a = 14.7513(11) Å, b = 15.0932(10) Å, c = 7.8241(5) Å, V = 1702.9(2) Å^3, Z = 4, d_{calcd} = 1.390 g/cm^3, F(000) = 752, 2θ range 1.412–26.445°, R indices (all data) R1 = 0.0608, wR2 = 0.1163; CCDC 1911000.[12]

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690799. Included are scanned copies of NMR spectral data for all compounds and X-ray analysis data of **3t**, **3ab**, **3g-1** and **4**.

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