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Facile acid-catalyzed condensation of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone with phenols, methoxyaromatic systems and enols

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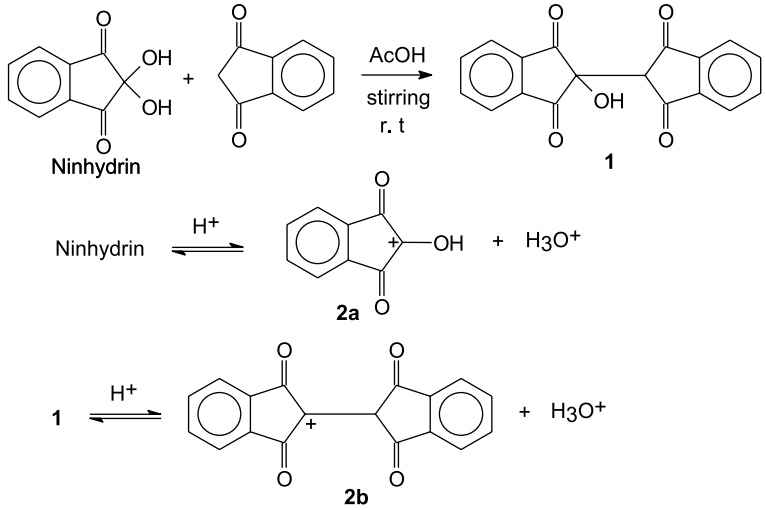
Abstract—Various phenols, methoxy aromatic compounds, 3- and 4-hydroxycoumarins and enols smoothly condense with 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone **1** in an acid medium producing 2-aryl/alkyl-2,2′-biindan-1,1′,3,3′-tetrones in high yields. The adducts of resorcinol, 1,3,5-trihydroxybenzene and α- and β-naphthols of **1** preferably remain in the intramolecular hemi-ketal form, confirmed by X-ray diffraction studies. On the other hand *para* and *meta* substituted phenols condense with **1** in an acid medium to produce 6 or 7 substituted 2′,4-spiro(1′,3′-indanedion)-indeno[3,2-*b*]chromenes in good yields.

1. Introduction

The mechanistic details of the formation of Ruhemann's Purple from the reaction of ninhydrin with amino acids is not fully understood, but it is accepted that the formation of 2,2′-dihydroxy-2,2′-biindan-1,1′,3,3′-tetrone, popularly known as hydrindantin, is a critical step in the whole process.[1] Although hydrindantin is structurally similar to ninhydrin, the instability of the former in acid medium prevents the study of its electrophilic chemistry towards various phenols and enolic substrates.[1d,2] On the other hand, the partially reduced derivative of hydrindantin, viz., 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone **1** (Scheme 1), which can be easily generated by the acid catalyzed condensation of ninhydrin with 1,3-indanedione,[3] is found to be quite stable in acid medium and therefore creates an



Scheme 1.

Keywords: 2-Hydroxy-2,2′-biindan-1,1′,3,3′-tetrone; Phenols; Enols; Electrophilic addition; Chromenes.
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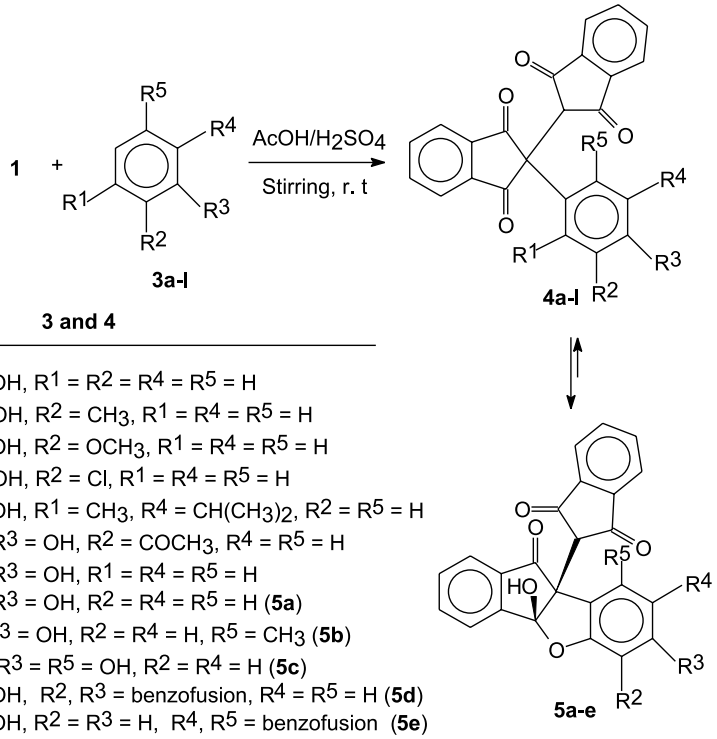
Table 1. Preparation of 2-aryl 2,2′-biindan-1,1′,3,3′-tetrones and chromenes by condensation of phenols with **1** in acid medium

Entry	Substrates	Products	Reaction time (h)	Yields (%)[a]	Mp (°C)[b]
Scheme 2					
1	Phenol	**4a**	6.0	73	272–273
2	*o*-Cresol	**4b**	5.0	69	248–250
3	Guaiacol	**4c**	5.0	62	243–245
4	*o*-Chlorophenol	**4d**	7.0	72	236–237
5	Thymol	**4e**	5.0	68	228–230
6	2,6-Dihydroxyacetophenone	**4f**	4.0	70	320–322
7	Catechol	**4g**	24.0	55	264–265
8	Resorcinol	**5a**	24.0	65	256–258
9	Orcinol	**5b**	24.0	60	268–269
10	1,3,5-Trihydroxybenzene	**5c**	20.0	61	280–281
11	α-Naphthol	**5d**	3.5	70	264–265
12	β-Naphthol	**5e**	3.5	72	255–256
Scheme 3					
13	*p*-Cresol	**9a**	5.0	82	285–286
14	*m*-Cresol	**9b**	6.0	73	254–255
15	*p*-Methoxyphenol	**9c**	6.0	68	298–299
16	*p*-Chlorophenol	**9d**	6.0	72	276–278
17	*p*-Bromophenol	**9e**	8.0	76	304–306
18	*m*-Iodophenol	**9f**	8.0	65	330–332
19	*p*-Chloro-*m*-cresol	**9g**	5.0	70	321–322
20	Ethyl *p*-hydroxybenzoate	**9h**	30.0	62	225–226
21	Methyl *p*-hydroxybenzoate	**9i**	32.0	65	258–259

[a] Yields refer to pure isolated products.
[b] Mps are uncorrected.

opportunity to study its electrophilic chemistry towards phenols, enols and aromatic substrates.

Various reports established that the C-2 position of ninhydrin is reactive to nitrogen-, sulfur-, oxygen-, and carbon-based nucleophiles.[4] Acid catalysed condensation of ninhydrin with various phenols, enols and aromatic substrates has been studied extensively.[5–10] In all these cases the protonation of the hydroxy group of ninhydrin is followed by elimination of water to produce the C-2 carbocation **2a** (Scheme 1) which then undergoes nucleophilic attack from various phenols, enols and aromatic substrates.[9] Likewise **1** can potentially generate a C-2 carbocation **2b** (Scheme 1) in acid medium. So far no efforts have been made to examine the electrophilic chemistry of **1** towards various substrates. In this paper we have carried out an extensive study to explore the electrophilic chemistry of **1**.



Scheme 2.

2. Results and discussion

In the present study it has been noted that 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone **1** like ninhydrin, condenses with various phenols (Table 1, entries 1–5), polyhydroxy benzenes (entries 6–10) as well as α- and β-naphthols (entries 11 and 12). This is done simply by stirring in a solution of acetic acid and few drops of conc. H_2SO_4 at room temperature for a period varying from 2.5 to 24 h to produce the adducts 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **4** in high yield (Scheme 2). In general, **1** is found to be slightly less reactive than ninhydin in acid medium[5] because the carbocation **2b** generated from **1** is comparatively less stable and more sterically crowded than that of the oxonium ion **2a** derived from ninhydrin (Scheme 1).[9a] As a result, **1** needs a few drops of conc. H_2SO_4 as catalyst in the reaction, and longer reaction time for adduct formation. The electrophilic attack to phenols generally takes place at the *para* position with respect to the hydroxy groups, producing the adducts 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **4a–e**. ^1H and ^{13}C NMR spectra for most of the adducts **4a–e** display a symmetrical pattern for two 1,3-dioxoindane moieties indicating tetraketo structures with a plane of symmetry.

In the case of substrates like resorcinol, orcinol, 1,3,5-trihydroxybenzene as well as α- and β-naphthols the electrophilic attack of carbocation **2b** takes place at the *ortho* position with respect to the hydroxy groups. ^1H and ^{13}C NMR spectra of these adducts **4h–l** show an unsymmetrical structure formation. This observation indicates that they preferably remain in the intramolecular hemi-ketal form **5** (Scheme 2). Further X-ray studies of the adducts **5c** and **5e** derived by the condensation of **1** with 1,3,5-trihydroxybenzene and β-naphthol, respectively, confirm the hemi-ketal structures with the *cis* geometry of the vicinal –OH and 1,3-indanedionyl moiety at the bridgehead of the bicyclo[3.3.0] system (Figs. 1 and 2).[11] In the case of catechol, the newly formed C–C bond does not have any *ortho* hydroxy group for the formation of a hemi-ketal, and as a result it produces a symmetrical adduct **4g**. 2,6-Dihydroxyacetophenone (entry 6) also undergoes the reaction as with other polyhydroxy benzenes (entries 7–10) to produce adduct **4f**, in contrast to the earlier

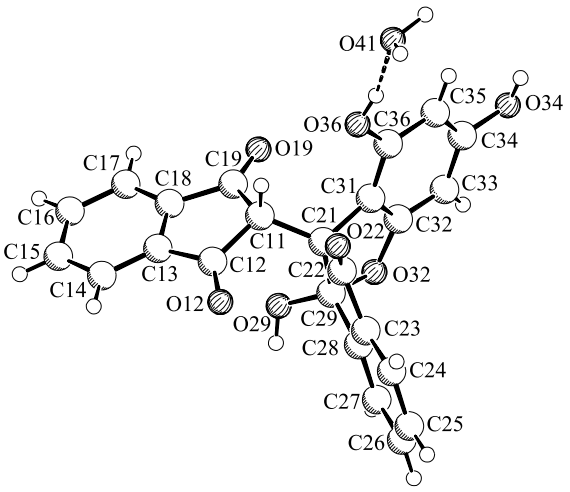


Figure 1. X-ray crystal structure of hemi-ketal **5c**.

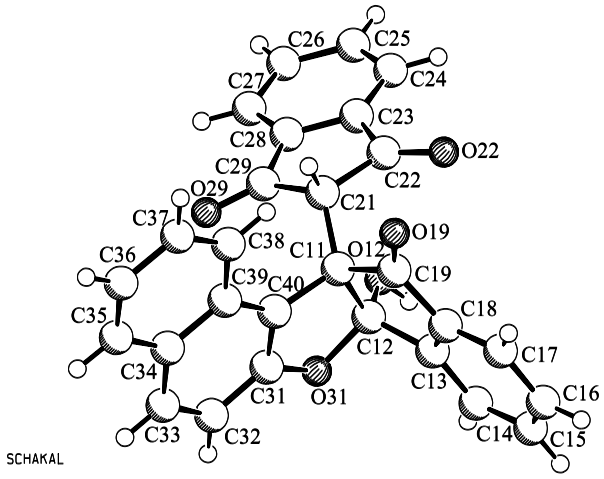


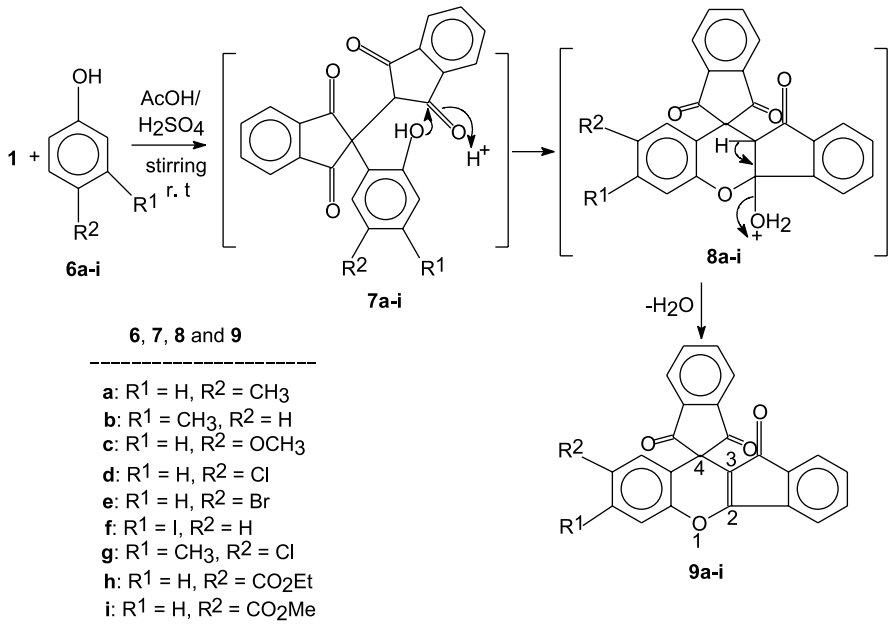
Figure 2. X-ray crystal structure of hemi-ketal **5e**.

report[7a] that the acid catalyzed condensation with ninhydrin generally fails if an electron-withdrawing group like $–NO_2$, –CHO, $–CO_2Et$ etc. is attached to the benzene ring of the phenolic substrate **3**. It is found by NMR study that in spite of having an *ortho* hydroxy group with respect to the newly formed C–C bond in the adduct **4f**, hemi-ketal formation does not occur, probably due to the electron-withdrawing effect of the acetyl group.

Interestingly it was observed that *para* or *meta* substituted phenols **6a–i** such as *p*-cresol, *m*-cresol, *p*-methoxyphenol, *p*-bromophenol, *m*-iodophenol etc. condense with **1** in acid medium to furnish 6 or 7 substituted 2′,4-spiro(1′,3′-indanedion)-indeno[3,2-*b*]chromenes[12] **9a–i** as yellow precipitates in fairly good yields (Table 1, Scheme 3). In these reactions initially the arylated intermediates 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **7a–i** are formed by the nucleophilic attack of phenols **6a–i** to the carbocation **2b** in the acetic acid and conc. H_2SO_4 mixture (Scheme 3). Subsequently, the arylated intermediates **7a–i** undergo an intramolecular nucleophilic attack by the phenolic hydroxy group to either of the carbonyl groups at $C_{1'}$ or $C_{3'}$, followed by dehydration to furnish chromenes **9a–i**. The *para* or *meta* substituted phenols **6a–i** are required for the reaction which ensure the initial formation of adducts only *ortho* to the phenolic hydroxy group. The intermediates **7a–i** and **8a–i** were not isolated. Ethyl and methyl *p*-hydroxy benzoates **6h,i** are found to take a longer time for chromene formation than the phenols **6a–g** due to the electron-withdrawing effect of the ethyl and methyl carboxylate groups (Table 1).

All the chromenes **9a–i** were thoroughly characterized by ^1H and ^{13}C NMR studies and confirmed for **9a** by two dimensional ^{13}C–^1H correlation studies. The solid state structure of **9b** was determined by single crystal X-ray diffraction study. The result is shown in Figure 3.

It has also been observed that various methoxy aromatic systems such as anisole, veratrole, 1,3-dimethoxy-, 1,4-dimethoxy- and 1,2,3-trimethoxybenzene (Table 2, entries 22–26) react with **1** in acetic acid and few drops of conc. H_2SO_4 at room temperature to furnish the adduct 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **10a–e** in high yields



Scheme 3.

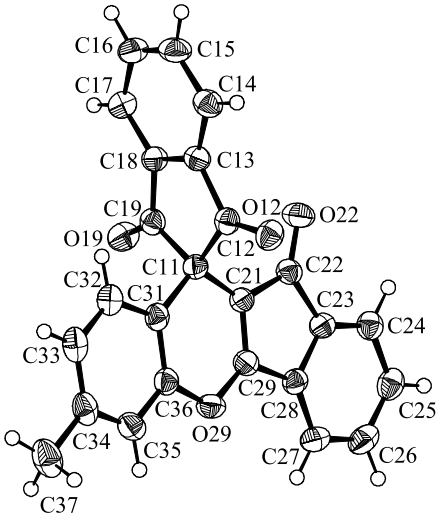
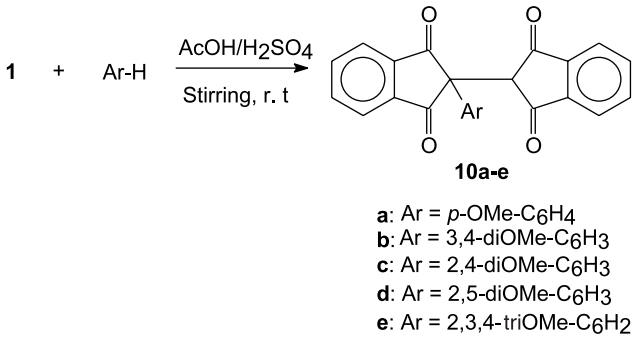


Figure 3. Diamond-plot of chromene **9b** with thermal ellipsoids (50% probability) and atom numbering scheme.



Scheme 4.

(Scheme 4). In the case of anisole, the preferred electrophilic attack is at the *para* position with respect to the methoxy group. ^{1}H and ^{13}C NMR spectra of the adducts **10a–e** indicate the formation of symmetrical tetrone structures. X-ray structure of the adduct **10e** derived from **1** and 1,2,3-trimethoxybenzene shows the preferred conformation of the molecule in the solid state (Fig. 4).[11]

Table 2. Preparation of 2-aryl/alkyl 2,2′-biindan-1,1′,3,3′-tetrones by condensation of methoxy aromatic systems and enols with **1** in acid medium

Entry	Substrates	Products	Reaction time (hr)	Yields (%)[a]	Mp (°C)[b]
Scheme 4					
22	Anisole	**10a**	3.0	75	239–240
23	1,2-Dimethoxybenzene	**10b**	4.0	72	225–226
24	1,3-Dimethoxybenzene	**10c**	2.5	75	230–231
25	1,4-Dimethoxybenzene	**10d**	4.0	70	217–218
26	1,2,3-Trimethoxybenzene	**10e**	4.5	67	221–222
Scheme 5					
27	4-Hydroxycoumarin	**11a**	4.0	68	296–298
28	3-Hydroxycoumarin	**11b**	4.0	65	259–260
29	1,3-Indanedione	**11c**	5.0	62	Ref.[13]
30	1,3-Cyclohexadione	**11d**	4.5	60	288–290

[a] Yields refer to pure isolated products.
[b] Mps are uncorrected.

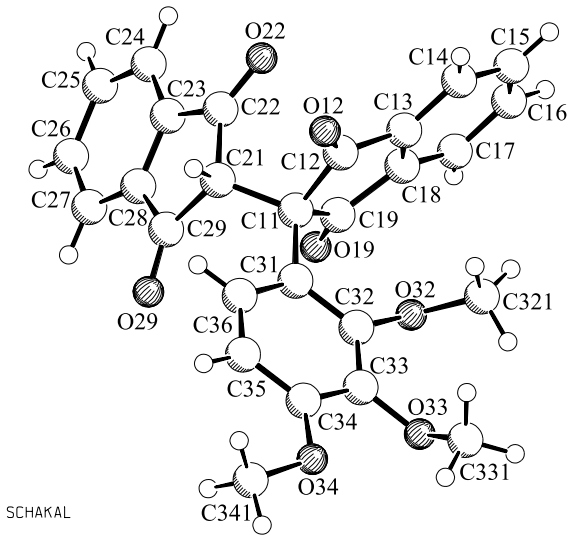
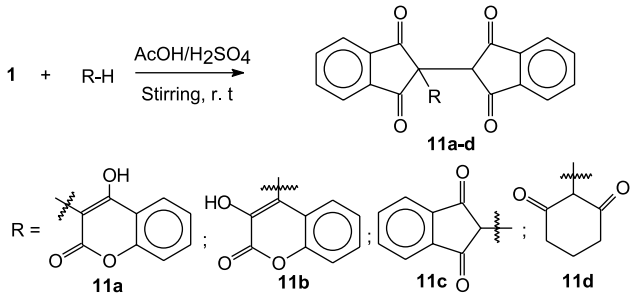


Figure 4. X-ray crystal structure of **10e**.

4- and 3-Hydroxycoumarins (Table 2, entries 27 and 28) behave like enolic compounds and react with **1** in AcOH/H_2SO_4 to produce adducts **11a** and **11b** when stirred for about 4 h at room temperature (Scheme 5). 1,3-Indanedione and 1,3-cyclohexadione, which preferably remain in enolic form, also react with **1** to furnish the products **11c** and **11d**, respectively. The biologically active trisindanedione **11c** was also synthesized previously from ninhydrin.[13] The adducts **11a–d** display somewhat symmetrical ^1H and ^{13}C NMR spectra for the two 1,3-dioxoindane parts, and thus prefer to remain in the tetraketo form in contrast to adducts



Scheme 5.

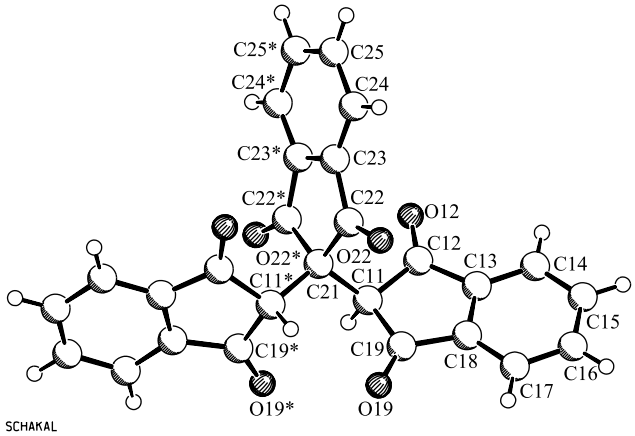


Figure 5. X-ray crystal structure of trisindanedione **11c**.

4h–l which stay mainly in the hemi-ketal form **5a–e** (Scheme 2). X-ray study of the adduct **11c** derived from **1** and 1,3-indanedione shows a structure with a C_2 axis of symmetry (Fig. 5).[11]

In summary, efficient routes to 2-aryl/alkyl-2,2′-biindan-1,1′,3,3′-tetrones and some hemi-ketals of the bicyclo-[3.3.0]octano system have been derived through facile condensation of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone with hydroxy- and methoxy aromatic systems as well as with enols under acid catalysis. The study has also led to the development of a new and facile method for the preparation of 6 or 7 substituted 2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromenes from readily available ninhydrin.

3. Experimental

Melting points were determined in open capillary tubes. IR spectra were examined in KBr disc on a Perkin–Elmer-782 spectrophotometer. Proton magnetic resonance spectra (^1H NMR) and carbon magnetic resonance spectra (^{13}C NMR) were recorded on Bruker AM 300L (300 MHz) or a Bruker DRX-500 (500 MHz) spectrometers in the solvents indicated. Chromatography was performed on Merck silica gel 60. TLC analyses were run on Merck silica gel (60F-254) plates (0.25 mm), precoated with a fluorescent indicator.

3.1. Preparation of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone 1

The substrate 1,3-indanedione (0.61 g, 4.2 mmol) was added to a solution of ninhydrin (0.25 g, 1.4 mmol) in acetic acid (10 mL). The mixture was stirred at room temperature for 2 h. The white solid product **1** was filtered out and washed thoroughly with acetic acid and then with water. The product **1** was purified by silica-gel column chromatography using $CHCl_3$ as the eluent (yield ~87%).

3.1.1. 2-Hydroxy-2,2′-biindan-1,1′,3,3′-tetrone 1. White solid, mp 189–191 °C, IR (KBr): (cm^{-1}) 3428, 1704, 1586, 1264; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.02–7.83 (8H, m), 5.46 (1H, s), 3.97 (1H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.3 (2C), 196.2 (2C), 142.2 (2C), 141.2 (2C), 136.6 (d, 2C), 136.3 (d, 2C), 124.3 (d, 2C), 123.6 (d, 2C), 76.3, 53.4 (d). Anal. Calcd for $C_{18}H_{10}O_5$: C, 70.59; H, 3.29. Found: C, 70.64; H, 3.35%.

3.2. General procedure for preparation of 2-aryl/alkyl-2,2′-biindan-1,1′,3,3′-tetrones (entries 1–30)

A mixture of 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone **1** (0.43 g, 1.4 mmol) in acetic acid (8 mL) was warmed to make a clear solution. The appropriate substrates such as phenols (**3** and **6**), methoxybenzenes (Ar-H), enols (R-H) etc. (4.2 mmol) and 0.5–1.0 mL conc. H_2SO_4 were then added (for catechol, resorcinol, orcinol and 1,3,5-trihydroxybenzene addition of H_2SO_4 is not necessary) at room temperature and stirred for a certain period (Tables 1 and 2). The solid products were filtered out and washed thoroughly with acetic acid and then with water. The products were purified by silica-gel column chromatography using ethyl

acetate and pet-ether as eluent. The resulting solids were further purified by crystallization from $CHCl_3$/pet-ether.

3.2.1. 2-(4-Hydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4a. White solid, mp 272–273 °C, IR (KBr): (cm^{-1}) 3482, 1702, 1588, 1263, 771; ^1H NMR (300.13 MHz, acetone-d_6) δ: 8.68 (1H, br. s), 7.99–7.85 (8H, m), 7.21 (2H, d, J=8.8 Hz), 6.82 (2H, d, J=8.8 Hz), 4.56 (1H, s); ^{13}C NMR (75.47 MHz, acetone-d_6) δ: 199.0 (2C), 197.6 (2C), 158.3, 143.2 (2C), 142.5 (2C), 137.1 (d, 2C), 136.6 (d, 2C), 129.8 (d, 2C), 125.1, 124.5 (d, 2C), 123.6 (d, 2C), 116.5 (d, 2C), 65.1, 56.4 (d). Anal. Calcd for $C_{24}H_{14}O_5$: C, 75.39; H, 3.69. Found: C, 75.45; H, 3.74%.

3.2.2. 2-(3-Methyl-4-hydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4b. White solid, mp 248–250 °C, IR (KBr): (cm^{-1}) 3292, 1705, 1592, 1264, 757; ^1H NMR (300.13 MHz, acetone-d_6) δ: 8.55 (1H, s), 7.98–7.83 (8H, m), 7.13 (1H, d, J=2.2 Hz), 6.98 (1H, dd, J=8.6, 2.2 Hz), 6.77 (1H, d, J=8.6 Hz), 4.55 (1H, s), 2.08 (3H, s); ^{13}C NMR (75.47 MHz, acetone-d_6) δ: 199.0 (2C), 197.6 (2C), 156.4, 143.2 (2C), 142.5 (2C), 137.1 (d, 2C), 136.6 (d, 2C), 131.0 (d), 127.2 (d), 125.6, 125.1, 124.5 (d, 2C), 123.6 (d, 2C), 115.9 (d), 64.2, 56.5 (d), 16.4 (q). Anal. Calcd for $C_{25}H_{16}O_5$: C, 75.75; H, 4.07. Found: C, 75.81; H, 4.14%.

3.2.3. 2-(3-Methoxy-4-hydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4c. White solid, mp 243–245 °C, IR (KBr): (cm^{-1}) 3528, 1709, 1515, 1263; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.99–7.96 (2H, m), 7.90–7.87 (2H, m), 7.85–7.79 (4H, m), 7.03 (1H, d, J=1.7 Hz), 6.88–6.81 (2H, m), 5.66 (1H, s), 4.21 (1H, s), 3.89 (3H, s). Anal. Calcd for $C_{25}H_{16}O_6$: C, 72.81; H, 3.91. Found: C, 72.90; H, 3.85%.

3.2.4. 2-(3-Chloro-4-hydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4d. White solid, mp 236–237 °C, IR (KBr): (cm^{-1}) 3221, 1704, 1589, 1266, 761; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.00–7.96 (2H, m), 7.90–7.79 (6H, m), 7.42 (1H, d, J=2.3 Hz), 7.27 (1H, dd, J=8.7, 2.3 Hz), 6.99 (1H, d, J=8.7 Hz), 5.69 (1H, s), 4.18 (1H, s). Anal. Calcd for $C_{24}H_{13}O_5Cl$: C, 69.15; H, 3.14; Cl, 8.52. Found: C, 69.23; H, 3.21; Cl, 8.61%.

3.2.5. 2-(2-Methyl-4-hydroxy-5-isopropylphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4e. Light yellow solid, mp 228–230 °C, IR (KBr): (cm^{-1}) 3310, 1703, 1590, 1259, 758; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.99–7.96 (2H, m), 7.91–7.86 (2H, m), 7.85–7.78 (5H, m), 6.84 (1H, s), 6.53 (1H, s), 4.65 (1H, s), 3.02–2.98 (1H, m), 2.53 (3H, s), 1.05 (6H, d, J=11.1 Hz); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 198.5 (2C), 197.0 (2C), 152.3, 142.3 (4C), 137.2, 135.6 (d, 2C), 135.4 (d, 2C), 132.0, 128.1, 123.8 (d, 2C), 123.2 (d, 2C), 120.0, 66.0, 54.6 (d), 27.2 (d), 22.3 (q, 2C), 22.1 (q). Anal. Calcd for $C_{28}H_{22}O_5$: C, 76.70; H, 5.06. Found: C, 76.78; H, 5.13%.

3.2.6. 2-(2,4-Dihydroxy-3-acetylphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4f. White solid, mp 320–322 °C, IR (KBr): (cm^{-1}) 3283, 1713, 1638, 1274, 1219; ^1H NMR (300.13 MHz, acetone-d_6) δ: 7.99–7.66 (8H, m), 7.58 (1H, d, J=8.4 Hz), 6.57 (1H, d, J=8.4 Hz), 4.52 (1H, s), 2.59 (3H, s); ^{13}C NMR (125 MHz, acetone-d_6): 204.5, 198.0, 197.1, 165.0, 143.6, 142.1, 137.0, 136.4, 136.2, 132.9, 131.9, 125.5, 124.3, 123.5, 111.2, 65.0, 55.3, 32.3. Anal. Calcd for $C_{26}H_{16}O_7$: C, 70.91; H, 3.66. Found: C, 70.85; H, 3.73%.

3.2.7. 2-(3,4-Dihydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4g. Light greenish solid, mp 264–265 °C, IR (KBr): (cm^{-1}) 3429, 1702, 1589, 1264, 1194, 769; ^1H NMR (500 MHz, acetone-d_6) δ: 7.99–7.86 (8H, m), 6.92 (1H, d, J=2.1 Hz), 6.76 (1H, d, J=8.3 Hz), 6.67 (1H, dd, J=8.3, 2.1 Hz), 4.49 (1H, s). Anal. Calcd for $C_{24}H_{14}O_6$: C, 72.36; H, 3.54. Found: C, 72.43; H, 3.61%.

3.2.8. 2-(2,4-Dihydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4h (remains as hemiketal 5a). White solid, mp 256–258 °C, IR (KBr): (cm^{-1}) 3293, 1709, 1603, 1267, 1136, 767; ^1H NMR (500 MHz, acetone-d_6) δ:8.40 (1H, s), 7.87–7.76 (7H, m), 7.64–7.61 (1H, m), 7.41 (1H, s), 7.27 (1H, d, J=8.3 Hz), 6.50 (1H, dd, J=8.3, 2.1 Hz), 6.21 (1H, d, J=2.1 Hz), 4.40 (1H, s); ^{13}C NMR (125 MHz, acetone-d_6) δ: 198.3, 197.6, 196.5, 160.1, 158.4, 150.7, 143.1, 141.8, 136.0, 135.9, 135.4, 135.2, 130.9, 125.4, 124.2, 123.7, 122.8, 122.7, 116.0, 113.3, 109.3, 97.6, 65.4, 55.0. Anal.Calcd for $C_{24}H_{14}O_6$: C, 72.36; H, 3.54. Found: C, 72. 45; H, 3.64%.

3.2.9. 2-(2,4-Dihydroxy-6-methylphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4i (remains as hemiketal 5b). White solid, mp 268–269 °C, IR (KBr): (cm^{-1}) 3429, 1704, 1587, 1265, 1214; ^1H NMR (500 MHz, acetone-d_6) δ: 8.27 (1H, s), 7.85–7.74 (7H, m), 7.64–7.62 (1H, m), 7.33 (1H, s), 6.30 (1H, d, J=1.5 Hz), 6.03 (1H, d, J=1.9 Hz), 4.67 (1H, s), 2.58 (3H, s). Anal. Calcd for $C_{25}H_{16}O_6$: C, 72.81; H, 3.91. Found: C, 72.93; H, 4.01%.

3.2.10. 2-(2,4,6-Trihydroxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4j (remains as hemiketal 5c). White solid, mp 280–281 °C, IR (KBr): (cm^{-1}) 3445, 3325, 1710, 1620, 1465, 1269, 1132; ^1H NMR (300.13 MHz, acetone-d_6) δ: 8.39 (1H, s), 8.05 (1H, s), 7.89–7.80 (8H, m), 7.47 (1H, s), 6.01 (1H, d, J=1.8 Hz), 5.78 (1H, d, J=1.8 Hz), 4.67 (1H, s). Anal. Calcd for $C_{24}H_{14}O_7$: C, 69.56; H, 3.41. Found: C, 69.62; H, 3.50%.

3.2.11. 2-(1-Hydroxynaphthyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4k (remains as hemiketal 5d). Light yellow solid, mp 264–265 °C, IR (KBr): (cm^{-1}) 3401, 1704, 1590, 1256, 774; ^1H NMR (300.13 MHz, DMSO-d_6) δ: 8.85 (1H, d, J=6.3 Hz), 8.51 (1H, d, J=8.1 Hz), 8.22 (1H, d, J=8.1 Hz), 8.15–7.79 (4H, m), 7.56–7.30 (4H, m), 6.94 (1H, dd, J=7.9, 1.5 Hz), 6.84 (1H, d, J=7.8 Hz), 6.73–6.69 (1H, m), 5.55 (1H, s); ^{13}C NMR (75.47 MHz, DMSO-d_6) δ: 198.3, 198.0, 197.3, 154.5, 154.0, 141.5, 141.2, 137.6, 137.1, 136.6, 133.8, 129.7, 127.2, 126.6, 126.3, 125.3, 124.7, 124.4, 123.6, 123.5, 121.0, 120.4, 108.2, 108.1, 107.9, 66.8, 63.7, 55.5. Anal. Calcd for $C_{28}H_{16}O_5$: C, 77.77; H, 3.73. Found: C, 77.83; H, 3.65%.

3.2.12. 2-(2-Hydroxynaphthyl)-2,2′-biindan-1,1′,3,3′-tetrone, 4l (remains as hemiketal 5e). White solid, mp 255–256 °C, IR (KBr): (cm^{-1}) 3263, 1704, 1593, 1270, 722; ^1H NMR (300.13 MHz, DMSO-d_6) δ: 8.82 (1H, br. s), 8.47 (1H, d, J=8.5 Hz), 7.89–7.70 (6H, m), 7.61–7.50 (4H, m), 7.34 (1H, t, J=7.8 Hz), 7.05 (1H, d, J=8.8 Hz), 5.10

(1H, s). Anal. Calcd for $C_{28}H_{16}O_5$: C, 77.77; H, 3.73. Found: C, 77.85; H, 3.64%.

3.2.13. 6-Methyl-2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromene, 9a. Yellow solid, mp 285–286 °C, IR (KBr): (cm^{-1}) 1711, 1649, 1396, 1252; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.16–8.13 (2H, m), 8.00–7.96 (2H, m), 7.41–7.25 (5H, m), 7.12 (1H, dd, $J=8.4$, 1.6 Hz), 6.40 (1H, d, $J=1.6$ Hz), 2.14 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 198.3 (2C), 190.5, 171.3, 149.1, 143.2 (2C), 136.8, 136.1 (d, 2C), 132.5 (d), 132.0, 130.7 (d), 130.5 (d), 127.6 (d), 124.2 (d, 2C), 123.3, 121.9 (d), 119.7, 118.9 (d), 118.6 (d), 105.7, 54.4, 20.6. Anal. Calcd for $C_{25}H_{14}O_4$: C, 79.36; H, 3.73. Found: C, 79.30; H, 3.69%.

3.2.14. 7-Methyl-2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromene, 9b. Yellow solid, mp 254–255 °C, IR (KBr): (cm^{-1}) 3438, 1709, 1650, 1389, 1243; ^1H NMR (300.13 MHz, acetone-d_6) δ: 8.16–8.15 (4H, m), 7.61–7.33 (5H, m), 6.99 (1H, d, $J=7.9$ Hz), 6.66 (1H, d, $J=7.9$ Hz). 2.36 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.8, 191.1, 171.8, 151.1, 143.5, 140.8, 137.2, 136.6, 133.0, 132.3, 131.2, 127.6, 127.4, 124.7, 122.3, 119.7, 119.3, 117.4, 106.1, 21.5. Anal. Calcd for $C_{25}H_{14}O_4$: C, 79.36; H 3.73. Found: C, 79.42; H, 3.81%.

3.2.15. 6-Methoxy-2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromene, 9c. Yellow solid, mp 298–299 °C, IR (KBr): (cm^{-1}) 3438, 1707, 1645, 1394, 1197; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.16–8.13 (2H, m), 7.99–7.97 (2H, m), 7.40–7.26 (5H, m), 6.87 (1H, dd, $J=9.0$, 2.9 Hz), 6.12 (1H, d, $J=2.9$ Hz), 3.63 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.6, 191.0, 171.9, 157.7, 145.5, 143.4, 137.1, 136.7, 133.0, 132.4, 131.2, 124.7, 122.3, 121.1, 120.1, 119.3, 114.9, 113.2, 106.0, 56.0. Anal. Calcd for $C_{25}H_{14}O_5$: C, 76.14; H, 3.58. Found: C, 76.25; H, 3.68%.

3.2.16. 6-Chloro-2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromene, 9d. Yellow solid, mp 276–278 °C, IR (KBr): (cm^{-1}) 1710, 1651, 1394, 1247; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.10–8.07 (2H, m), 7.95–7.91 (2H, m), 7.38–7.24 (6H, m), 6.53 (1H, d, $J=1.4$ Hz). Anal. Calcd for $C_{24}H_{11}O_4Cl$: C, 72.27; H, 2.78; Cl, 8.90. Found: C, 72.35, H, 2.86; Cl, 8.79%.

3.2.17. 6-Bromo-2′,4-spiro(1′, 3′-indanedion)-indeno-[3,2-*b*]chromene, 9e. Yellow solid, mp 304–306 °C, IR (KBr): (cm^{-1}) 3430, 1708, 1654, 1392, 1256; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.18–8.15 (2H, m), 8.03–7.99 (2H, m), 7.45–7.36 (5H, m), 7.27 (1H, apparent d, $J=8.1$ Hz), 6.74 (1H, d, $J=2.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.0, 190.7, 171.3, 150.6, 143.3, 137.0, 136.8, 133.3, 133.2, 132.1, 131.4, 130.6, 125.0, 122.6, 122.3, 120.9, 119.4, 119.3, 105.9, 54.6.

3.2.18. 7-Iodo-2′,4-spiro(1′,3′-indanedion)-indeno[3,2-*b*]-chromene, 9f. Yellow solid, mp 330–332 °C, IR (KBr): (cm^{-1}) 3436, 1710, 1651, 1383, 1251; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.16–8.13 (2H, m), 8.02–7.98 (2H, m), 7.77 (1H, d, $J=1.7$ Hz), 7.47–7.33 (5H, m), 6.37 (1H, d, $J=8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.9, 190.6, 171.2, 151.3, 143.1, 137.0, 136.5, 135.6, 133.3, 131.8, 131.4, 129.0, 128.1, 124.7, 122.4, 120.0, 119.4, 105.8, 94.2.

3.2.19. 6-Chloro-7-methyl-2′,4-spiro(1′, 3′-indanedion)-indeno[3,2-*b*]chromene, 9g. Yellow solid, mp 321–322 °C, IR (KBr): (cm^{-1}) 3438, 1707, 1647, 1377, 1245; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.10–8.07 (2H, m), 7.96–7.92 (2H, m), 7.39–7.21 (4H, m), 7.19 (1H, s), 6.52 (1H, s), 2.30 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.1, 190.7, 171.0, 149.5, 143.1, 138.8, 137.0, 136.7, 133.2, 132.0, 131.4, 127.6, 124.7, 124.6, 122.3, 121.2, 119.4, 119.0, 105.7, 20.3. Anal. Calcd for $C_{25}H_{13}O_4Cl$: C, 72.73; H, 3.17; Cl, 8.60. Found: C, 72.82; H, 3.26; Cl, 8.55%.

3.2.20. 6-Carbethoxy-2′,4-spiro(1′, 3′-indanedion)-indeno[3,2-*b*]chromene, 9h. Yellow solid, mp 225–226 °C, IR (KBr): (cm^{-1}) 3437, 1712, 1652, 1392, 1258; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.17–8.15 (2H, m), 8.03 (1H, d, $J=1.8$ Hz), 8.01–7.99 (2H, m), 7.93 (1H, dd, $J=$ 8.6, 1.8 Hz), 7.44–7.34 (4H, m), 6.81 (1H, d, $J=8.6$ Hz), 4.26 (2H, q, $J=7.1$ Hz), 1.28 (3H, t, $J=7.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.2, 190.8, 171.3, 165.2, 154.4, 143.4, 136.9, 136.7, 133.2, 132.0, 131.6, 131.5, 130.0, 128.9, 124.9, 122.6, 120.6, 119.5, 119.3, 106.3, 61.7, 54.7, 14.6. Anal. Calcd for $C_{27}H_{16}O_6$: C, 74.31; H, 3.70. Found: C, 74.40; H, 3.81%.

3.2.21. 6-Carbomethoxy-2′,4-spiro(1′, 3′-indanedion)-indeno[3,2-*b*]chromene, 9i. Yellow solid, mp 258–259 °C, IR (KBr): (cm^{-1}) 3410, 1711, 1390, 1255; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 8.18–8.15 (2H, m), 8.04 (1H, d, $J=1.8$ Hz), 8.03–7.99 (2H, m), 7.47–7.34 (6H, m), 3.80 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.2, 190.7, 171.2, 165.7, 154.5, 143.4, 136.9, 136.7, 133.3, 131.9, 131.7, 131.5, 130.0, 128.5, 124.9, 122.6, 120.6, 119.5, 119.4, 106.3, 54.7, 52.7. Anal. Calcd for $C_{26}H_{14}O_6$: C, 73.93; H, 3.34. Found: C, 74.01; H, 3.41%.

3.2.22. 2-(4-Methoxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 10a. Light yellow solid, mp 239–240 °C, IR (KBr): (cm^{-1}) 1705, 1594, 1511, 1264, 762; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.95–7.80 (8H, m), 7.35 (2H, d, $J=8.2$ Hz), 6.88 (2H, d, $J=8.2$ Hz), 4.23 (1H, s), 3.77 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.9 (2C), 196.5 (2C), 159.8, 142.2 (2C), 141.6 (2C), 135.8 (d, 2C), 135.5 (d, 2C), 128.9 (d, 2C), 124.7, 123.9 (d, 2C), 123.2 (d, 2C), 114.4 (d, 2C), 63.1, 55.9 (q), 55.2 (d). Anal. Calcd for $C_{25}H_{16}O_5$: C, 75.75; H, 4.07. Found: C, 75.82; H, 4.13%.

3.2.23. 2-(3,4-Dimethoxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 10b. Light yellow solid, mp 225–226 °C, IR (KBr): (cm^{-1}) 1703, 1591, 1513, 1255, 764; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.98–7.78 (8H, m), 7.05 (1H, d, $J=2.1$ Hz), 6.89 (1H, dd, $J=8.5$, 2.1 Hz), 6.80 (1H, d, $J=$ 8.5 Hz), 4.23 (1H, s), 3.87 (3H, s), 3.76 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.8 (2C), 196.4 (2C), 149.6, 147.2, 142.2 (2C), 141.6 (2C), 135.8 (d, 2C), 135.5 (d, 2C), 125.0, 123.9 (d, 2C), 123.2 (d, 2C), 120.7 (d), 111.6 (d), 111.0 (d), 63.2, 56.2 (q), 56.0 (q), 55.9 (d). Anal. Calcd for $C_{26}H_{18}O_6$: C, 73.23; H, 4.25. Found: C, 73.31; H, 4.33%.

3.2.24. 2-(2,4-Dimethoxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 10c. Light yellow solid, mp 230–231 °C, IR

(KBr): (cm^{-1}) 1710, 1592, 1264, 791; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.94–7.75 (8H, m), 7.29 (1H, d, $J=8.7$ Hz), 6.54 (1H, dd, $J=8.7$, 2.2 Hz), 6.39 (1H, d, $J=2.2$ Hz), 4.67 (1H, s), 3.76 (3H, s), 3.52 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.5 (2C), 196.8 (2C), 160.9, 158.4, 142.2 (4C), 135.3 (d, 2C), 135.1 (d, 2C), 130.4 (d), 123.3 (d, 2C), 123.0 (d, 2C), 115.7, 106.2 (d), 100.5 (d), 62.1, 55.8 (q), 55.3 (q), 54.6 (d). Anal. Calcd for $C_{26}H_{18}O_6$: C, 73.23; H, 4.25. Found: C, 73.29; H, 4.31%.

3.2.25. 2-(2,5-Dimethoxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 10d. White solid, mp 217–218 °C, IR (KBr): (cm^{-1}) 1707, 1594, 1502, 1266, 1228, 759; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.96–7.77 (8H, m), 7.02 (1H, d, $J=2.1$ Hz), 6.85–6.78 (2H, m), 4.64 (1H, s), 3.77 (3H, s), 3.48 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.1 (2C), 196.5 (2C), 154.6, 151.7, 142.4 (2C), 142.3 (2C), 135.4 (d, 2C), 135.1 (d, 2C), 125.0, 123.4 (d, 2C), 123.2 (d, 2C), 116.0 (d), 115.2 (d), 114.6 (d), 61.2, 57.0 (q), 55.8 (q), 55.2 (d). Anal. Calcd for $C_{26}H_{18}O_6$: C, 73.23; H, 4.25. Found: C, 73.34; H, 4.36%.

3.2.26. 2-(2,3,4-Trimethoxyphenyl)-2,2′-biindan-1,1′,3,3′-tetrone, 10e. White solid, mp 221–222 °C, IR (KBr): (cm^{-1}) 1708, 1594, 1267, 784; ^1H NMR (300.13 MHz, $CDCl_3$) δ: 7.94–7.76 (8H, m), 7.25 (1H, d, $J=9.0$ Hz), 6.75 (1H, d, $J=9.0$ Hz), 4.48 (1H, s),3.84 (3H, s), 3.73 (3H, s), 3.51 (3H, s); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 197.1 (2C), 196.6 (2C), 153.9 (2C), 151.6, 142.3 (2C), 142.2 (2C), 135.4 (d, 2C), 135.1 (d, 2C), 123.8 (d), 123.4 (d, 2C), 123.1 (d, 2C),120.9, 108.1 (d), 61.8, 60.4 (q), 60.1 (q), 56.0 (q), 55.5 (d). Anal. Calcd for $C_{27}H_{20}O_7$: C, 71.05; H, 4.42. Found: C, 71.13; H, 4.51%.

3.2.27. 2-[3-(4-Hydroxy coumarin)]-2,2′-biindan-1,1′,3,3′-tetrone, 11a. White solid, mp 296–298 °C, IR (KBr): (cm^{-1}) 3190, 1739, 1696, 1273, 757; ^1H NMR (300.13 MHz, DMSO-d_6) δ: 7.91–7.80 (8H, m), 7.61 (1H, t, $J=8.5$ Hz), 7.52 (1H, d, $J=7.7$ Hz), 7.41 (1H, d, $J=8.4$ Hz), 7.27 (1H, t, $J=7.5$ Hz), 5.32 (1H, s); ^{13}C NMR (75.47 MHz, DMSO-d_6) δ: 197.4 (2C), 197.1 (2C), 162.4, 157.8, 154.6, 141.6 (4C), 135.5 (d, 4C), 133.5 (d), 124.5 (d), 124.2 (d), 122.8 (d, 2C), 122.5 (d, 2C), 116.8 (d), 111.6, 100.0, 64.2, 51.0 (d). Anal. Calcd for $C_{27}H_{14}O_7$: C, 72.00; H, 3.13. Found: C, 72.08; H, 3.21%.

3.2.28. 2-[4-(3-Hydroxy coumarin)]-2,2′-biindan-1,1′,3,3′-tetrone, 11b. White solid, mp 259–260 °C, IR (KBr): (cm^{-1}) 3289, 1713, 1274, 758; ^1H NMR (300.13 MHz, DMSO-d_6) δ: 9.43 (1H, s), 8.18 (1H, d, $J=7.6$ Hz), 7.90–7.76 (8H, m), 7.69–7.67 (1H, m), 7.49–7.36 (2H, m), 5.16 (1H, s); ^{13}C NMR (75.47 MHz, DMSO-d_6) δ: 196.6 (2C), 196.5 (2C), 153.1, 150.9, 148.9, 141.7 (2C), 141.0 (2C), 135.6 (d, 2C), 135.5 (d, 2C), 131.3 (d), 128.9 (d), 123.7 (d), 122.7 (d, 2C), 122.6 (d, 2C), 117.5, 116.5 (d), 113.1, 67.1, 53.0 (d). Anal. Calcd for $C_{27}H_{14}O_7$: C, 72.00; H, 3.13. Found: C, 72.10; H, 3.19%.

3.2.29. 2-(2,6-Dioxocyclohexanyl)-2,2′-biindan-1,1′,3,3′-tetrone, 11d. White solid, mp 288–290 °C, IR (KBr): (cm^{-1}) 3430, 1709, 1588, 1266; ^1H NMR (300.13 MHz, DMSO-d_6) δ: 9.00 (1H, s), 7.90–7.60 (8H, m), 4.65 (1H, s), 2.47–2.33 (6H, m). Anal. Calcd for $C_{24}H_{16}O_6$: C, 71.99; H, 4.03. Found: C, 72.12; H, 4.12%.

3.3. X-ray structure analyses.[11]

3.3.1. Compound 5c. Formula $C_{24}H_{14}O_7 \cdot H_2O$, $M=432.37$, colourless crystal $0.35\times0.30\times0.30$ mm^3, $a=15.516(1)$ Å, $b=8.764(1)$ Å, $c=15.268(1)$ Å, $\beta=104.49(1)°$, $V=2010.1(3)$ Å^3, $\rho_{calc}=1.429$ g cm^{-3}, $\mu=1.09$ cm^{-1}, empirical absorption correction ($0.963\leq T\leq0.968$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 11435 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.66$ Å^{-1}, 4745 independent ($R_{int}=0.036$) and 3691 observed reflections [$I\geq2\sigma(I)$], 298 refined parameters, $R=0.043$, $wR^2=0.102$, max. residual electron density 0.33 (-0.28) e Å^{-3}, hydrogens at water molecule from difference fourier calculations, other calculated and all refined as riding atoms.

3.3.2. Compound 5e. Formula $C_{28}H_{16}O_5 \cdot C_3H_6O$, $M=490.49$, colourless crystal $0.15\times0.10\times0.05$ mm^3, $a=8.525(1)$ Å, $b=17.239(1)$ Å, $c=16.290(1)$ Å, $\beta=93.92(1)°$, $V=2388.4(3)$ Å^3, $\rho_{calc}=1.364$ g cm^{-3}, $\mu=0.95$ cm^{-1}, empirical absorption correction ($0.986\leq T\leq0.995$), $Z=4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 15689 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.66$ Å^{-1}, 5689 independent ($R_{int}=0.059$) and 3234 observed reflections [$I\geq2\sigma(I)$], 337 refined parameters, $R=0.057$, $wR^2=0.112$, max. residual electron density 0.21 (-0.24) e Å^{-3}, hydrogens calculated and refined as riding atoms.

3.3.3. Compound 9b. Formula $C_{25}H_{14}O_4$, $M=378.36$, yellow crystal $0.20\times0.10\times0.06$ mm^3, $a=7.267(1)$ Å, $b=9.641(1)$ Å, $c=14.351(1)$ Å, $\alpha=103.85(1)°$, $\beta=101.49(1)°$, $\gamma=103.89(1)°$, $V=911.86(2)$ Å^3, $\rho_{calc}=1.378$ g cm^{-3}, $\mu=0.93$ cm^{-1}, empirical absorption correction ($0.982\leq T\leq0.994$), $Z=2$, triclinic, space group $P1$bar (No. 2), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 7847 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.62$ Å^{-1}, 3692 independent ($R_{int}=0.050$) and 2306 observed reflections [$I\geq2\sigma(I)$], 263 refined parameters, $R=0.052$, $wR^2=0.108$, max. residual electron density 0.23 (-0.22) e Å^{-3}, hydrogens calculated and refined as riding atoms.

3.3.4. Compound 10e. Formula $C_{27}H_{20}O_7$, $M=456.43$, colourless crystal $0.30\times0.30\times0.15$ mm^3, $a=7.689(1)$ Å, $b=22.698(1)$ Å, $c=12.166(1)$ Å, $\beta=95.31(1)°$, $V=2114.2(3)$ Å^3, $\rho_{calc}=1.434$ g cm^{-3}, $\mu=1.04$ cm^{-1}, no absorption correction ($0.969\leq T\leq0.985$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 8798 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.66$ Å^{-1}, 5003 independent ($R_{int}=0.026$) and 3888 observed reflections [$I\geq2\sigma(I)$], 310 refined parameters, $R=0.043$, $wR^2=0.108$, max. residual electron density 0.29 (-0.24) e Å^{-3}, hydrogens calculated and refined as riding atoms.

3.3.5. Compound 11c. Formula $C_{27}H_{14}O_6$, $M=434.38$, orange crystal $0.25\times0.20\times0.20$ mm^3, $a=12.511(1)$ Å, $b=10.591(1)$ Å, $c=15.533(1)$ Å, $\beta=95.39(1)°$, $V=2049.1(3)$ Å^3, $\rho_{calc}=1.408$ g cm^{-3}, $\mu=1.0$ cm^{-1}, empirical absorption correction ($0.975\leq T\leq0.980$), $Z=4$,

monoclinic, space group $C2/c$ (No. 15), $\lambda=0.71073$ Å, $T=198$ K, ω and ϕ scans, 6663 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]=0.66$ Å^{-1}, 2435 independent ($R_{\text{int}}=0.031$) and 2085 observed reflections [$I\geq 2\sigma(I)$], 150 refined parameters, $R=0.039$, $wR^2=0.094$, max. residual electron density 0.23 (-0.16) e Å^{-3}, hydrogens calculated and refined as riding atoms.

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