**General methods:** Unless otherwise noted, all reagents were used as received from commercial sources. All air and moisture sensitive reactions were conducted under a nitrogen or argon atmosphere in flame-dried or oven-dried glassware with magnetic stirring. Acetonitrile was dried using CaH$_2$, distilled and stored over 3Å molecular sieves prior to use. Tetrahydrofuran (THF) was dried over Na, benzophenone and distilled prior to use. Reactions were monitored by thin-layer chromatography (carried out on silica plates silica gel 60 F254, Merck) using UV-light, iodine and p-anisaldehyde for visualization. Column chromatography was carried out using silica gel (60-120 mesh or 100-200 mesh) packed in glass columns. Technical grade ethyl acetate and petroleum ether used for column chromatography were distilled prior to use. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ as solvent on 300 MHz or 400 MHz or 500 MHz spectrometer at ambient temperature. The coupling constant $J$ is given in Hz. The chemical shifts ($\delta$) are reported in ppm on scale downfield from TMS and using the residual solvent peak in CDCl$_3$ (H: $\delta = 7.26$ and C: $\delta = 77.0$ ppm) or TMS ($\delta = 0.0$) as internal standard and signal patterns are indicated as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, qd = quartet of doublet, m = multiplet, br = broad. IR spectra were recorded on a PerkinElmer spectrum 400 Infrared spectrophotometer and are reported as cm$^{-1}$. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

**Experimental procedures and analytical data:**

**A. General procedure for the annulation of benzyne with 1,3-diketones:**

In an oven dried round-bottom flask was taken anhydrous CsF (0.25 mmol, 2.5 eq) and to this was added a solution of 1,3-diketone (0.1 mmol, 1.0 eq) in anhydrous acetonitrile (1 mL), followed by aryne precursor silyl aryl triflate (0.125 mmol, 1.25 eq) in anhydrous acetonitrile (1 mL) and the reaction mixture was heated at 60-80 °C for 1-2 h. The progress of the reaction was monitored by TLC, after completion of the reaction, cooled to room temperature, diluted with H$_2$O (5 mL) and extracted with ethyl acetate (3x10 mL). The combined organic extract was washed with brine (10 mL) and dried over Na$_2$SO$_4$, volatiles were removed under reduced pressure to obtain crude compound which was purified by silica gel flash column chromatography to give benzannulated carbocyclic compounds.

**7,7-Dimethyl-7,8-dihydrobenzo[8]annulene-5,9(6H,10H)-dione (9a):**
By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9a as white solid (17.5 mg, 82%); mp: 79-80 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 8.16 (dd, J = 7.8, 1.5 Hz, 1H), 7.50 (td, \(J = 7.3, 1.5\) Hz, 1H), 7.42 (td, \(J = 7.8, 1.4\) Hz, 1H), 7.19 (d, \(J = 7.5\) Hz, 1H), 4.02 (s, 2H), 2.97 (s, 2H), 2.38 (s, 2H), 1.08 (s, 6H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): δ 207.6, 199.5, 137.6, 135.4, 133.3, 132.4, 131.2, 128.0, 54.9, 52.7, 51.1, 32.5, 29.5 (2C); IR (neat): \(\nu_{\text{max}}\) 1703, 1666, 1596, 1468, 1284, 1206, 767 cm\textsuperscript{-1}; HRMS (ESIMS) calcd for C\textsubscript{14}H\textsubscript{17}O\textsubscript{2} [M+H]\textsuperscript{+}: m/z 217.1223; found: 217.1232.

**9-Methyl-6,7-dihydro-5H-benzo[7]annulene-5,8(9H)-dione (9b):**

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9b a pale yellow solid (14.0 mg, 75%). mp: 65-66 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.82 (dd, \(J = 7.6, 1.4\) Hz, 1H), 7.54 (td, \(J = 7.6, 1.5\) Hz, 1H), 7.39 (t, \(J = 7.5\) Hz, 1H), 7.29 (d, \(J = 7.9\) Hz, 1H), 4.34 (q, \(J = 6.9\) Hz, 1H), 3.18-3.10 (m, 1H), 3.05-2.99 (m, 1H), 2.74-2.71 (m, 2H), 1.52 (d, \(J = 6.9\) Hz, 3H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ 208.0, 202.7, 137.6, 137.2, 133.1, 129.7, 127.8, 126.0, 48.0, 39.0, 35.7, 13.1; IR (neat): \(\nu_{\text{max}}\) 1716, 1676, 1596, 1453, 1286, 1216, 1102, 934, 771 cm\textsuperscript{-1}; HRMS (ESIMS) calcd for C\textsubscript{12}H\textsubscript{13}O\textsubscript{2} [M+H]\textsuperscript{+}: m/z 189.0910; found: 189.0920.

**9-Allyl-6,7-dihydro-5H-benzo[7]annulene-5,8(9H)-dione (9c):**

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9c as a yellow liquid (14.8 mg, 69%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.81 (dd, \(J = 7.7, 1.5\) Hz, 1H), 7.52 (td, \(J = 7.6, 1.5\) Hz, 1H), 7.39 (td, \(J = 7.6, 1.0\) Hz, 1H), 7.23 (d, \(J = 7.8\) Hz, 1H), 5.79-5.68 (m, 1H), 5.10-5.00 (m, 2H), 4.20 (t, \(J = 7.3\) Hz, 1H), 3.17-2.89 (m, 3H), 2.80-2.58 (m, 3H); \textsuperscript{13}C NMR (100 MHz,
9-Methyl-6,7-dihydro-5H-cyclohepta[4,5]benzo[1,2-d][1,3]dioxole-5,8(9H)-dione (9d):

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9d as semi-solid (18.0 mg, 79%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.36 (s, 1H), 6.75 (s, 1H), 6.04–6.02 (m, 2H), 4.37 (q, $J = 6.7$ Hz, 1H), 3.18–3.11 (m, 1H), 3.03–2.98 (m, 1H), 2.71–2.69 (m, 2H), 1.47 (d, $J = 6.7$ Hz, 3H);

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 207.7, 200.1, 152.1, 147.2, 134.2, 131.3, 109.5, 106.1, 102.0, 46.9, 39.1, 35.4, 13.1; IR (neat): $\nu_{\text{max}}$ 1715, 1662, 1465, 1361, 1271, 1249, 1035, 772 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{13}$H$_{13}$O$_4$ [M+H]$^+$: m/z 233.0808; found: 233.0813.

2,4-Dimethoxy-9-methyl-6,7-dihydro-5H-benz[7]annulene-5,8(9H)-dione (9e):

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:5 ethyl acetate/hexanes) to yield 9e as semi-solid (17.5 mg, 71%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.43 (d, $J = 2.1$ Hz, 1H), 6.34 (d, $J = 2.1$ Hz, 1H), 3.92 (q, $J = 6.9$ Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.93–2.90 (m, 2H), 2.81–2.75 (m, 2H), 2.68–2.62 (m, 1H), 1.43 (d, $J = 6.9$ Hz, 3H);

$^{13}$C NMR (125 MHz, CDCl$_3$): δ 208.5, 202.9, 162.7, 159.0, 140.3, 120.3, 103.2, 97.6, 56.0, 55.3, 48.6, 40.0, 36.7, 13.1; IR (neat): $\nu_{\text{max}}$ 1715, 1683, 1599, 1459, 1327, 1203, 1159, 772 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{14}$H$_{16}$O$_4$Na [M+Na]$^+$: m/z 271.0941; found: 271.0951.

10-Methyl-7,8-dihydrobenzo[8]annulene-5,9(6H,10H)-dione (9f):

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9f as semi solid (13.5 mg, 72%).

$^1$H NMR (300 MHz, CDCl$_3$): δ 7.47–7.41 (m, 1H), 7.36–7.30 (m, 2H), 7.28–7.23 (m,
1H), 4.02 (q, J = 6.8 Hz, 1H), 3.03-2.95 (m, 2H), 2.62-2.57 (m, 2H), 2.09-1.81 (m, 2H), 1.45 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 209.8, 209.0, 140.9, 135.3, 130.8, 127.7, 127.2, 126.0, 48.5, 45.0, 43.7, 21.3, 15.7; IR (neat): $\nu_{\text{max}}$ 1702, 1652, 1597, 1449, 1278, 756 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{13}$H$_{15}$O$_2$ [M+H]$^+$: m/z 203.1067; found: 203.1072.

**7,7-Dimethyl-7,8-dihydrocycloocta[4,5]benzo[1,2-d][1,3]dioxole-5,9(6H,10H)-dione (9g):**

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 9g as a pale yellow solid (20.5 mg, 79%). mp: 130-131 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.67 (s, 1H), 6.61 (s, 1H), 6.05 (s, 2H), 3.93 (s, 2H), 2.93 (s, 2H), 2.40 (s, 2H), 1.06 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 207.7, 197.3, 151.7, 147.8, 132.2, 132.1, 111.8, 110.5, 102.1, 54.7, 52.7, 51.0, 32.5, 29.5 (2C); IR (neat): $\nu_{\text{max}}$ 1701, 1656, 1486, 1372, 1274, 1038 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{15}$H$_{16}$O$_4$Na [M+Na]$^+$: m/z 283.0941; found: 283.0963.

**5H-Dibenzo[a,d][7]annulene-5,10(11H)-dione (11a):**

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 11a as red coloured solid (17.0 mg, 77%); mp: 70-71 °C; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.17-8.14 (m, 1H), 8.06-8.03 (m, 1H), 7.72-7.64 (m, 3H), 7.50-7.45 (m, 1H), 7.39-7.33 (m, 2H), 4.26 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 195.4, 194.3, 140.5, 134.9, 134.9, 133.3, 133.1, 132.4, 130.3, 129.3, 129.2, 129.0, 128.9, 127.9, 50.3; IR (neat): $\nu_{\text{max}}$ 1792, 1690, 1590, 1283, 1087, 911, 768 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{15}$H$_{10}$O$_2$Na [M+Na]$^+$: m/z 245.0573; found: 245.0557.

**5H-Benzo[4',5']cyclohepta[1',2':4,5]benzo[1,2-d][1,3]dioxole-5,10(11H)-dione (11b):**

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 11b as brown solid (18.0 mg, 69%). Mp: 82-83 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.20-8.18 (m, 1H), 8.01-7.98 (m, 1H),
7.71-7.64 (m, 2H), 7.16 (s, 1H), 6.76 (s, 1H), 6.02 (s, 2H), 4.16 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 194.7, 193.4, 151.0, 147.5, 137.3, 135.2, 134.3, 133.2, 133.0, 130.6, 129.1, 125.1, 109.4, 109.0, 102.0, 49.9; IR (neat): $\nu_{\text{max}}$ 1690, 1670, 1483, 1288, 1267, 1038, 758 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{16}$H$_{10}$O$_4$Na [M+Na]$^+$: m/z 289.0471; found: 289.0445.

**11-Phenyl-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (11c):**

![11c](image)

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 11c as a pale yellow solid (21.5 mg, 73%); mp:141-142 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.07 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.94 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.77 (dd, $J$ = 8.1, 1.5 Hz, 1H), 7.63 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.60-7.53 (m, 2H), 7.50-7.46 (m, 2H), 7.17-7.10 (m, 3H), 6.88-6.85 (m, 2H), 5.49 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 196.4, 194.03, 140.9, 137.8, 136.3, 133.8, 133.4, 132.7, 132.3, 132.2, 130.4, 130.3, 130.2, 129.7, 128.7, 128.6, 127.7, 127.3, 66.3; IR (neat): $\nu_{\text{max}}$ 1683, 1672, 1587, 1286, 1218, 770 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{21}$H$_{15}$O$_2$ [M+H]$^+$: m/z 299.1067; found: 299.1093.

**11-Phenyl-5H-benzo[4',5']cyclohepta[1',2':4,5]benzo[1,2-d][1,3]dioxole-5,10(11H)-dione (11d):**

![11d](image)

By following the general procedure A the titled compound was prepared and purified by column chromatography (1:10 ethyl acetate/hexanes) to yield 11d as semi-solid (22.0 mg, 65%); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.00 (dd, $J$ = 7.6, 1.4 Hz, 1H), 7.96 (dd, $J$ = 7.9, 1.2 Hz, 1H), 7.62 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.53 (td, $J$ = 7.6, 1.4 Hz, 1H), 7.28 (s, 1H), 7.17-7.09 (m, 3H), 6.90-6.88 (m, 3H), 6.09 (d, $J$ = 1.4 Hz, 1H), 6.07 (d, $J$ = 1.4 Hz, 1H), 5.36 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 196.6, 194.03, 140.9, 137.8, 136.3, 133.8, 133.4, 132.7, 132.3, 132.2, 130.4, 130.3, 130.2, 129.7, 128.7, 128.6, 127.7, 127.3, 66.3; IR (neat): $\nu_{\text{max}}$ 1683, 1672, 1587, 1286, 1218, 770 cm$^{-1}$; HRMS (ESIMS) calcd for C$_{21}$H$_{15}$O$_2$ [M+H]$^+$: m/z 299.1067; found: 299.1093.
\( \nu_{\text{max}} 1682, 1664, 1587, 1502, 1290, 1253, 1038, 758 \text{ cm}^{-1} \); HRMS (ESIMS) calcd for C\textsubscript{22}H\textsubscript{15}O\textsubscript{4} [M+H]\textsuperscript{+}: m/z 343.0965; found: 343.0988.

**11-Allyl-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (11e):**

\[
\begin{align*}
\text{By following the general procedure A the titled compound was prepared and purified by} \\
\text{column chromatography (1:10 ethyl acetate/hexanes) to yield 11e a pale yellow solid (17.5} \\
\text{mg, 67\%); mp: 81-82 °C; }^1\text{H NMR (500 MHz, CDCl}_3): \delta 8.20-8.16 (m, 1H), 8.00-7.96 (m,} \\
\text{1H), 7.71-7.67 (m, 3H), 7.49 (t, }J = 7.6 \text{ Hz, 1H}), 7.37 (t, }J = 7.6 \text{ Hz, 1H}), 7.34 (d, }J = 7.6 \text{ Hz,} \\
\text{1H), 5.71-5.63 (m, 1H), 4.98-4.92 (m, 2H), 4.39 (m, 1H), 2.94-2.88 (m, 1H), 2.73-2.67 (m,} \\
\text{1H); }^{13}\text{C NMR (125 MHz, CDCl}_3): \delta 197.0, 195.2, 140.1, 136.8, 134.6, 134.2, 133.6, 133.3,} \\
\text{132.9, 132.3, 129.8, 129.7, 129.5, 127.9, 127.4, 117.6, 158.7, 35.9; IR (neat): }\nu_{\text{max}} 1691,} \\
\text{1658, 1289, 926, 770 cm}^{-1}; \text{ HRMS (ESIMS) calcd for C}_{18}H_{15}O_2 [M+H]^+: m/z 263.1067;} \\
\text{found: 263.1078.}
\end{align*}
\]

### 2-Methyl-8H-dibenzo[3,4:6,7]cyclohepta[1,2-b]furan-8-one (12):

\[
\begin{align*}
\text{To a stirred solution of allyl compound 11e (30.0 mg, 0.114 mmol) in DMF (2 mL) and H}_2\text{O} \\
\text{(0.5 mL) under the atmosphere of O}_2 \text{ (balloon pressure) was added PdCl}_2 \text{ (5.3 mg, 0.03} \\
\text{mmol) and CuCl (3.0 mg, 0.03 mmol), the reaction was stirred for 2 h. After the completion} \\
\text{of reaction (by TLC), the mixture was filtered through a pad of celite and washed with} \\
\text{diethyl ether (2 x 15 mL). The ethereal layer was washed with cold water (2 x 5 mL) and} \\
\text{dried over Na}_2\text{SO}_4, \text{volatiles were removed in rota vapour to give crude compound, which} \\
\text{was used for next reaction without any further purification. To a stirred solution of above} \\
\text{prepared compound (30.0 mg, crude) in benzene (3.0 mL) was added catalytic amount of p-} \\
\text{TSA (3.0 mg) and refluxed for 2 h. After completion of the reaction solvent was removed in} \\
\text{rota vapour and the crude mixture was purified by column chromatography (1:10 ethyl} \\
\text{acetate/hexanes) to yield 12 a pale yellow solid (22.0 mg, 74\%); mp: 102-103 °C; }^1\text{H NMR} \\
\text{(500 MHz, CDCl}_3): \delta 8.11 (dd, }J = 7.9, 1.2 \text{ Hz, 1H), 8.09 (dd, }J = 8.1, 1.2 \text{ Hz, 1H), 8.06 (d, }J \\
\end{align*}
\]
= 8.1 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.63 (m, 2H), 7.47 (t, J = 7.9 Hz, 2H), 6.63 (s, 1H), 2.48 (s, 3H); 13C NMR (125 MHz, CDCl3): δ 194.3, 153.0, 147.5, 137.8, 135.9, 132.0, 131.9, 130.5, 130.2, 130.0, 128.0, 127.9, 127.6, 126.2, 123.8, 123.7, 106.7, 13.7; IR (neat): v_max 1637, 1598, 1312, 1271, 1153, 926, 756 cm⁻¹; HRMS (ESIMS) calcd for C18H12O2Na[M+Na]⁺: m/z 283.0730; found: 283.0744.

3-Bromo-1,4-dimethoxynaphthalen-2-yl acetate (16):

To a stirred solution of bis(acetoxy)iodobenzene (BAIB) (1.9 g, 5.85 mmol) in anhydrous CH2Cl2 (40.0 mL) at 0 °C was added trimethylsilyl bromide (TMSBr) (1.55 mL, 11.7 mmol) and the mixture was stirred for 30 min at the same temperature. To this 1,4-dimethoxynaphthalene 14 (1.0 g, 5.32 mmol) in 15.0 mL CH2Cl2 was added dropwise. The resulting orange colour reaction mixture was stirred at 0 °C, after TLC indicated the complete consumption of starting material an additional bis(acetoxy)iodobenzene (BAIB) (3.8 g, 11.7 mmol) was added to the reaction in one portion. The reaction mixture was stirred for 20 min at 0 °C and quenched by adding saturated hypo solution (50.0 mL). Layers were separated and the aqueous layer was extracted with CH2Cl2 (2 x 50 mL). The combined organic extract was dried over Na2SO4, the solvent was removed in vacuo to afford the crude product which was purified by silica gel column chromatography (1:9 ethyl acetate/hexane) to give known compound 16 (1.35 g, 78%) as pale yellow solid. mp: 129-130 °C (lit:1:130-131 °C); 1H NMR (300 MHz, CDCl3): δ 8.14-8.08 (m, 2H), 7.60-7.52 (m, 2H), 4.00 (s, 3H), 3.95 (s, 3H), 2.46 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 168.3, 150.6, 144.6, 137.6, 128.0, 127.3, 127.0, 126.8, 122.5, 122.3, 109.4, 62.0, 61.7, 20.7; IR (neat): v_max 2936, 1776, 1360, 1189, 1084, 1016 cm⁻¹; HRMS (ESIMS) calcd for C14H13BrO4Na [M+Na]⁺: m/z 346.9889; found: 346.9885.

3-Bromo-1,4-dimethoxynaphthalen-2-ol (17):

To a stirred solution of compound 16 (1.25 g, 3.89 mmol) in MeOH (25 mL) at 0 °C was added K2CO3 (0.79 g, 5.76 mmol) and stirred at the same temperature, after completion of the reaction indicated by TLC (1 h) MeOH was removed and the crude reaction mixture was
diluted with EtOAc (50 mL) and washed with H₂O (30 mL) and brine solution (20 mL). The organic layer was dried over Na₂SO₄ and volatiles were removed to give compound 17 as a pale yellow solid (0.99 g, 91%). This was utilized for next reaction without any further purification. mp: 114-115 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.05 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 6.04 (s, 1H), 4.00 (s, 3H), 3.98 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 150.7, 142.7, 137.0, 127.5, 127.0, 124.4, 123.5, 122.4, 120.9, 105.5, 61.6 (2C); IR (neat): νmax 3434, 2938, 1585, 1457, 1362, 1271, 1080, 767 cm⁻¹; HRMS (ESIMS) calcd for C₁₂H₁₁BrO₃Na [M+Na]⁺: m/z 304.9784; found: 304.9798.

1,4-Dimethoxy-3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (13):

The mixture of bromonapthol 17 (0.90 g, 2.20 mmol) and hexamethyldisilazide (HMDS) (0.92 mL, 4.40 mmol) were combined in THF (15.0 mL) and heated to 75 °C and maintained for 4 h. The reaction was cooled to room temperature and volatiles were removed under vacuum. The resulting crude compound was directly used for next step. The crude compound was taken up in THF (30.0 mL) and cooled to −80 °C, n-Butyllithium (1.51 mL of 1.6 M in hexane, 2.42 mmol) was added slowly and stirred for 15 min, to this triflic anhydride (0.44 mL, 2.64 mmol) was added drop wise at −80 °C. The reaction was quenched by the addition of saturated aqueous sodium bicarbonate solution (10.0 mL) and subsequently warmed to room temperature, diluted with H₂O (20.0 mL) and ethyl acetate (30.0 mL). Layers were separated and aqueous layer was extracted with ethyl acetate (2 x 30 mL), the combined organic extract was washed with brine (25 mL), concentrated under vacuum and purified by flash chromatography (5:95 ethyl acetate/hexanes) to yield 13 as semi-solid (0.97 g, 75%); ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.13 (m, 1H), 8.08-8.06 (m, 1H), 7.62-7.54 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 0.49 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 159.5, 143.9, 142.2, 129.9, 128.1, 127.7, 127.0, 123.6, 123.0, 122.8, 120.4, 118.8 (q, J = 320 Hz), 117.2, 64.0, 62.5, 1.3; IR (neat): νmax 2955, 1609, 1565, 1411, 1213, 1141, 1052, 961, 842, 769 cm⁻¹; HRMS (ESIMS) calcd for C₁₆H₁₉F₃O₅SiNa [M+Na]⁺: m/z 431.0567; found: 431.0562.

In an oven dried round-bottom flask was taken anhydrous CsF (0.38 g, 2.45 mmol, 2.5 eq) and to this was added a solution of 1,3-indandione 10a (0.143 g, 0.98 mmol, 1.0 eq) in anhydrous acetonitrile (10 mL). Followed by, aryne precursor silyl napthyl triflate 13 (0.5 g, 1.22 mmol, 1.25 eq) in anhydrous acetonitrile (10 mL) was added and the reaction mixture was heated at 75-80 °C for 1.5 h. The reaction was cooled to room temperature, diluted with H2O (20.0 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic extract was washed with brine (20 mL) and dried over Na2SO4, volatiles were removed in rota vapour to obtain crude compound which was purified by silica gel flash column chromatography (1:9 ethyl acetate/hexanes) to give benzannulated cyclic compound 15 as a light yellow solid (0.253 g, 78%); mp: 120-122 °C (lit:121.5-122.5 °C); 1H NMR (300 MHz, CDCl3): δ 8.15-8.10 (m, 3H), 7.98 (d, J = 7.4 Hz, 1H), 7.73-7.51 (m, 4H), 4.40 (s, 2H), 4.02 (s, 3H), 4.00 (s, 3H); 13C NMR (75 MHz, CDCl3): δ 195.8, 193.5, 150.6, 149.6, 141.4, 133.6, 133.0, 132.5, 130.7, 130.2, 129.1, 129.0, 128.8, 128.1, 126.9, 123.6, 122.7, 116.7, 64.6, 63.3, 42.8; IR (neat): υ_{max} 1686, 1590, 1354, 1284, 1049, 770 cm⁻¹; HRMS (ESI) calcd for C21H16O4Na [M+Na]⁺: m/z 355.0941; found: 355.0946.

7-Hydroxy-1-(2-methylprop-1-en-1-yl)benzo[g]benzo[5,6]cyclohepta[1,2,3-cd]benzofuran-8,13-dione, radermachol (5):

To a stirred solution of tetracyclic diketone 15 (250.0 mg, 0.753 mmol) and 3-methylcrotonoyl chloride (0.185 mL, 1.665 mmol) in CH2Cl2 (25.0 mL) was added AlCl3 (222.0 mg, 1.665 mmol); the orange brown solution was refluxed at 55 °C for 2 h, followed by quenching with 50.0 mL of saturated NH4Cl solution. Two layers were separated; the aqueous layer was extracted with CH2Cl2 (4 x 50 mL). The CH2Cl2 extract was washed with H2O (2 x 25 mL) and brine (25.0 mL) and dried over Na2SO4. Removal of the solvent gave the crude product, which was purified by silica gel column chromatography to give acrylated compound (49.8 mg, 18%). To a solution of this sample (30.0 mg, 0.0725 mmol) in CDCl3
(1.0 mL) in a NMR tube was added Me$_3$SiI (78.0 µL, 0.362 mmol). The solution was kept at 25 °C for 27 h. The solution was treated with excess MeOH; removal of the solvent yielded the crude product (41.0 mg). This material and p-TsOH (4.0 mg) were dissolved in 20 mL of dry benzene. The solution was heated under reflux for 5 h in a Dean-Stark apparatus and evaporated to give crude compound. The product was purified by silica gel column chromatography (1:9 ethyl acetate/hexanes) to give radermachol (5) as a red coloured solid (28.7 mg, 65%); mp: 213-214 °C, (lit²:214.5-216.5); $^1$H NMR of **Radermachol (5)** (500 MHz, CDCl$_3$): δ 15.28 (s, 1H), 8.57-8.54 (m, 2H), 8.38-8.36 (m, 1H), 8.10 (d, $J = 8.2$ Hz, 1H), 7.80-7.74 (m, 3H), 7.54 (ddd, $J = 8.2$, 7.0, 1.0 Hz, 1H), 7.20 (m, 1H), 2.41 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR of **Radermachol (5)** (125 MHz, CDCl$_3$): δ 192.6, 185.7, 164.1, 160.8, 148.3, 141.5, 138.5, 135.8, 133.3, 132.5, 132.0, 131.5, 130.9, 125.9, 125.5, 124.8, 123.4, 119.6, 117.7, 117.5, 114.2, 107.7, 28.7, 21.9; IR (neat): $\nu_{max}$ 1630, 1605, 1536, 1503, 772 cm$^{-1}$; HRMS (ESI) calcd for C$_{24}$H$_{17}$O$_4$ [M+H]$^+$: m/z 369.1121; found: 369.1129.

**References:**

$^1$H NMR of 9b
CDCl$_3$, 500 MHz

$^{13}$C NMR of 9b
CDCl$_3$, 75 MHz
$$^{13}C\text{ NMR of } 9c$$

CDCl$_3$, 100 MHz

$$^{13}C\text{ NMR of } 9c$$

CDCl$_3$, 400 MHz
$^1$H NMR of 9f
CDCl$_3$, 300 MHz

$^{13}$C NMR of 9f
CDCl$_3$, 75 MHz
$^1$H NMR of 11b
CDCl$_3$, 400 MHz

$^{13}$C NMR of 11b
CDCl$_3$, 75 MHz
$^{1}$H NMR of 11c
CDCl$_3$, 500 MHz

$^{13}$C NMR of 11c
CDCl$_3$, 125 MHz
$\text{H NMR of 16 CDCl}_3, 300 \text{ MHz}$

$\text{C NMR of 16 CDCl}_3, 100 \text{ MHz}$
OD Me
OMe
Br
OH
1
H NMR of 17
CDCl₃, 300 MHz

13C NMR of 17
CDCl₃, 75 MHz
$^1$H NMR of 15
CDCl$_3$, 300 MHz

$^{13}$C NMR of 15
CDCl$_3$, 75 MHz
$^1$H NMR of Radermachol (5)
CDCl$_3$, 500 MHz

$^{13}$C NMR of Radermachol (5)
CDCl$_3$, 125 MHz