Supporting Information

Synthesis of Dibenzo[a,d]cycloheptanoids via Aryne Insertion into 2-Arylidene-1,3-indandiones

Nagaraju Payili, a,b Santhosh Reddy Rekula, a Anjaiah Aitha, a V.V.S.R.N. Anji Karun Mutha, a
Challa Gangu Naidu, b Satyanarayana Yennam*, a

a Chemistry Services, GVK Biosciences Pvt. Ltd., Survey Nos: 125 (part) & 126, IDA Mallapur, Hyderabad -500076, Telangana, India

b Vignan’s Foundation for Science, Technology and Research (Deemed to be University) (VFSTRU), Vadlamudi, Guntur -522213, Andhra Pradesh, India.
**General Information:**

All the chemicals were commercially available and procured from companies like Aldrich, Spectrochem (India), S. D. Fine (India), and Avra (India) and have been carried forward without further purification. Solvents used in the present study are dried before prior use whenever required. Precoated TLC silica gel plates (Kieselgel 60 F254, Merck) were used for monitoring reactions. Purification was performed by column chromatography using silica gel (particle size 60-120 mesh, Merck). Melting points were determined in open capillary tubes on cintex melting point apparatus and are uncorrected. IR (KBr) spectra were recorded on a Perkin-Elmer FT/IR-4000 using ATR ($\nu_{max}$, in cm$^{-1}$) in the frequency range of 600-4000 cm$^{-1}$. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ on a Bruker DRX-400 & 500 (400 & 500 MHz FT NMR). Chemical shifts are presented in $\delta$ ppm employing TMS as internal reference. Splitting patterns were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra (HRMS) were recorded with an Agilent Technologies 6510 Q-TOF spectrometer.

**General experimental procedure for 3a-o:**

To a stirred solution of 2-benzylidene-1H-indene-1,3(2H)-dione (0.200 g, 8.57 mmol) in dry ACN (10 mL) was added 18-crown-6-ether (0.564 g, 2.13 mmol), potassium fluoride (0.247 g, 4258.0 mmol) under argon atmosphere and to this stirring solution was added appropriate aryl silyl triflate at room temperature. Then the reaction mixture was stirred at rt till the completion of reaction (monitored by TLC (5% EtOAc /pet ether)). The reaction mixture was diluted with EtOAc (20 mL) and water (20 mL), separated organic layer and then aq.layer was extracted with EtOAc (2×10 mL). The combined organic layers were washed with brine solution (20 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude reaction mixture was purified by column chromatography using hexanes/ethyl acetate (9:1 v/v) as eluent gave the compound 3a-o.
(E)-11-benzylidene-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3a): Yellow solid (97 mg, 74% yield, m.p. 166 - 170 °C); IR (film) ν_{max} 3015, 2997, 2350, 1662, 1268, 752 cm^{-1}; 1H NMR (400 MHz, CDCl₃): δ = 8.38 - 8.35 (m, 1H), 7.95 - 7.93 (m, 1H), 7.73 - 7.68 (m, 3H), 7.54 (s, 1H), 7.41 (t, J = 6.0 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.20 - 7.13 (m, 4H), 7.03 (d, J = 7.2 Hz, 2H); 13C NMR (101 MHz, CDCl₃): δ = 197.4, 190.0, 141.3, 140.8, 140.4, 134.1, 133.6, 133.1, 132.7, 131.6, 131.2, 130.5, 130.4, 130.1, 129.5, 128.9, 128.7, 128.3, 128.0; ESI-HRMS: calcd. for C_{22}H_{15}O_{2}+ (M+H)^+ 311.1072, found 311.1071.

(E)-11-(4-methylbenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3b): Yellow solid (77 mg, 56% yield, m.p. 129-131 °C); IR (film) ν_{max} 3018, 3000, 1666, 1589, 1269, 755 cm^{-1}; 1H NMR (400 MHz, CDCl₃): δ = 8.37-8.35 (m, 1H), 7.93 - 7.91 (m, 1H), 7.73-7.68 (m, 3H), 7.53 (s, 1H), 7.42 (dt, J = 7.2 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.24 - 7.21 (m, 1H), 6.97 - 6.91 (m, 4H), 2.27 (s, 3H); 13C NMR (101 MHz, CDCl₃): δ = 197.6, 190.0, 141.6, 140.9, 140.5, 136.6, 133.5, 133.3, 132.9, 132.7, 131.6, 131.2, 130.8, 130.5, 130.3, 129.4, 129.3, 128.8, 128.6, 127.9, 21.3; ESI-HRMS: calcd. for C_{23}H_{17}O_{2}+ (M+H)^+ 325.1229, found 325.1223.

(E)-11-(4-fluorobenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3c): Yellow solid (103 mg, 74% yield, m.p. 134-138 °C); IR (film) ν_{max} 3008, 2922, 1663, 1588, 1269, 755 cm^{-1}; 1H NMR (500 MHz, CDCl₃): δ = 8.36-8.35 (m, 1H), 7.95 - 7.93 (m, 1H), 7.47 (s, 1H), 7.45 (dt, J = 10.0, 7.5 Hz, 1H), 7.34 (dt, J = 7.5, 10 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 6.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H); 13C NMR (126 MHz, CDCl₃): δ = 197.3, 189.9, 141.5, 140.8, 140.3, 139.7, 134.9, 133.7, 133.0, 132.8, 132.6, 131.8, 131.3, 130.6, 130.3, 130.09 (d, 1J C-F = 220.7 Hz), 129.5, 128.9, 128.6, 128.2; ESI-HRMS: calcd. for C_{22}H_{14}FO_{2}+ (M+H)^+ 329.0978, found 329.0984.

(E)-11-(4-chlorobenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3d): Yellow solid (114 mg, 78% yield, m.p. 100-104 °C); IR (film) ν_{max} 3010, 2921, 2323, 1588, 1268,
755 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.37 - 8.35$ (m, 1H), 7.95 - 7.93 (m, 1H), 7.74 - 7.69 (m, 3H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.35 (t, $J = 8.5$ Hz, 1H), 7.30 (dd, $J = 8.5$, 7.5 Hz, 2H), 7.17 (d, $J = 7.2$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 197.4$, 189.9, 141.8, 140.9, 139.9, 137.6, 133.8, 133.7, 132.9, 131.9, 131.7, 130.9, 129.6, 129.1, 128.3, 95.4; ESI-HRMS: calcd. for C$_{22}$H$_{14}$IO$_2$+ (M+H)$^+$ 437.0038, found 437.0033.

(E)-11-(4-(trifluoromethyl)benzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3g): Yellow solid (115 mg, 72% yield, m.p. 148-152°C); IR (film) $\nu$$_{max}$ 3006, 2924, 1666, 1588, 1325, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.38 - 8.35$ (m, 1H), 7.98 - 7.96 (m, 95.4; ESI-HRMS: calcd. for C$_{22}$H$_{14}$IO$_2$+ (M+H)$^+$ 437.0038, found 437.0033.

(E)-11-(4-(trifluoromethyl)benzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3g): Yellow solid (115 mg, 72% yield, m.p. 148-152°C); IR (film) $\nu$$_{max}$ 3006, 2924, 1666, 1588, 1325, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.38 - 8.35$ (m, 1H), 7.98 - 7.96 (m,
1H), 7.76 - 7.69 (m, 3H), 7.50 (s, 1H), 7.46 - 7.38 (m, 3H), 7.34 (dt, J = 8.0, 6.5 Hz, 1H), 7.12 (d, J = 8.8 Hz, 3H); 13C NMR (101 MHz, CDCl3): δ = 197.0, 189.9, 143.3, 140.7, 140.2, 138.9, 137.7, 133.8, 132.9, 132.8, 131.9, 130.5, 130.4, 130.3, 130.1, 129.7, 129.2, 128.9, 128.3, 125.3, 125.2, 123.7 (d, 1J C-CF3 = 269.9 Hz); ESI-HRMS: calcd. for C23H14F3O2+ (M+H)+ 379.0946, found 379.0944.

(E)-11-(3-(trifluoromethyl)benzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3h): Yellow solid (113 mg, 71% yield, m.p. 126-131 °C); IR (film) ʋmax 2990, 1663, 1588, 1269, 755 cm⁻¹; 1H NMR (500 MHz, CDCl3): δ = 8.28-8.26 (m, 1H), 8.17 - 8.15 (m, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.77 - 7.75 (m, 2H), 7.64 - 7.61 (t, J = 7.0 Hz, 1H), 7.54 - 7.50 (m, 4H), 7.49 - 7.38 (m, 2H), 6.73 (s, 1H) ; 13C NMR (126 MHz, CDCl3): δ = 193.8, 193.6, 144.9, 138.5, 137.2, 135.7, 135.3, 134.3, 133.7, 133.6, 133.4, 133.0, 131.8, 131.0, 130.8, 129.4, 129.3, 129.0, 127.8, 125.5, 125.1 124.88 (d, 1J C-CF3 = 270.0 Hz); HR-MS m/z 379.0940 (M+H+). ESI-HRMS: calcd. for C23H14F3O2+ (M+H)+ 379.0940, found 379.0940.

(E)-11-(3,4-difluorobenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3i): Yellow solid (101 mg, 68% yield, m.p. 138-142°C); IR (film) ʋmax 2923, 1665, 1588, 1273, 755 cm⁻¹; 1H NMR (500 MHz, CDCl3): δ = 8.36 - 8.35 (m, 1H), 7.95 - 7.93 (m, 1H), 7.75 - 7.70 (m, 3H), 7.46 (dt, J = 8.0 Hz, 1H), 7.39 - 7.36 (m, 2H), 7.18 (d, J = 8.0 Hz, 1H), 6.97 - 6.95 (m, 1H), 6.80 - 6.77 (m, 2H); 13C NMR (126 MHz, CDCl3): δ = 197.1, 189.8, 151.49 (d, 1J C-F = 240.0 Hz), 149.80 (d, 1J C-F = 240.0 Hz), 141.9, 140.8, 138.5, 133.8, 132.9, 131.9, 131.1, 130.6, 130.4, 130.1, 129.6, 129.2, 128.3, 126.9, 118.5, 117.4; ESI-HRMS: calcd. for C22H13F2O2+ (M+H)+ 347.0884, found 347.0881.

(E)-11-(3,5-dichlorobenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3j): Yellow solid (124 mg, 77% yield, m.p. 136-139°C); IR (film) ʋmax 2995, 1666, 1433, 1269, 754 cm⁻¹; 1H NMR (500 MHz, CDCl3): δ = 8.35 - 8.31 (m, 2H), 7.97 - 7.95 (m, 1H), 7.81 - 7.80 (m, 2H), 7.72 - 7.70 (m, 1H), 7.48 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.34 (s,
1H), 7.19 (s, 1H), 7.16 (d, J = 7.5 Hz, 1H), 6.85 (s, 1H); $^{13}$C NMR (126MHz,CDCl$_3$): δ = 196.7, 189.6, 143.6, 140.5, 140.2, 137.7, 137.0, 134.9, 134.1, 133.9, 133.5, 132.9, 131.9, 130.5, 130.1, 129.7, 129.4, 128.8, 128.1, 127.2; ESI-HRMS: calcd. for C$_{23}$H$_9$Cl$_2$O$_2$+ (M+H)$^+$ 379.0293, found 379.0276.

(E)-11-(2-(trifluoromethyl)benzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3k): Yellow solid (110 mg, 70% yield, m.p. 125-129 °C); IR (film) $\nu$ max 2922, 1660, 1585, 1304, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ = 8.38 - 8.36 (m, 1H), 7.97 - 7.95 (m, 1H), 7.86 (brs, 1H), 7.74 - 7.70 (m, 2H), 7.67 (t, J = 6.5 Hz, 2H), 7.34 - 7.21 (m, 2H), 7.20 - 7.15 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ = 197.5, 189.4, 143.9, 141.2, 140.2, 138.2, 133.7, 133.6, 133.5, 132.9, 131.6, 131.2, 131.1, 130.6, 129.7, 129.5, 128.7, 128.2, 127.8, 125.9, 125.2, 124.1 (d, $^1J$ C-CF$_3$ = 270.2 Hz), 122.9, 120.8; HR-MS m/z 379.0949 (M+H$^+$). ESI-HRMS: calcd. for C$_{23}$H$_{13}$Cl$_2$O$_2$+ (M+H)$^+$ 379.0946, found 379.0949.

(E)-11-benzylidene-2,3-dimethyl-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3l): Yellow solid (103 mg, 72% yield, m.p. 136–140 °C); IR (film) $\nu$ max 2921, 1658, 1584, 1259, 755 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ = 8.35 - 8.33 (m, 1H), 7.96 - 7.95 (m, 1H), 7.69 - 7.65 (m, 2H), 7.51 (s, 1H), 7.45 (s, 1H), 7.21 - 7.14 (m, 3H), 7.06 (d, J = 8.5 Hz, 2H), 6.98 (s, 1H), 2.30 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ = 197.1, 190.6, 141.2, 140.9, 140.3, 140.2, 138.3, 137.7, 134.3, 133.3, 132.6, 131.3, 130.5, 130.1, 129.5, 129.2, 128.9, 128.6, 128.2, 19.5, 19.4; HR-MS m/z 339.1380 (M+H$^+$). ESI-HRMS: calcd. for C$_{21}$H$_{19}$O$_2$+ (M+H)$^+$ 339.1385, found 339.1380.

(E)-2,3-dimethyl-11-(4-methylbenzylidene)-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3m): Yellow solid (97 mg, 65% yield, m.p. 138–142 °C); IR (film) $\nu$ max 2924, 1614, 1450, 1031, 614 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ = 8.35 - 8.33 (m, 1H), 7.94 - 7.93 (m, 1H), 7.67 - 7.65 (m, 2H), 7.50 (s, 1H), 7.44 (s, 1H), 7.01 (s, 1H), 6.96 (s, 4H), 2.31 (s, 3H), 2.23 (s, 3H).
2.28 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 197.3, 190.5, 141.1, 140.5, 140.4, 139.8, 139.3, 138.3, 137.6, 133.3, 133.1, 132.5, 131.4, 130.5, 130.2, 129.4, 129.2, 129.1, 128.8, 128.7, 21.3, 19.6, 19.4; ESI-HRMS: calcd. for C$_{25}$H$_{21}$O$_2$+ (M+H)$^+$ 353.1542, found 353.1553.

(E)-11-benzylidene-3-fluoro-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione & (E)-11-benzylidene-2-fluoro-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3n & 3n’): Yellow solid (97 mg, 72% yield, m.p. 152-156 °C); IR (film) $\nu$ max 3436, 2921, 1661, 1588, 1250, 755 cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 8.26-8.24 (m, 1H), 7.93 - 7.84 (m, 3H), 7.57 -7.54 (m, 2H), 7.38 – 7.24 (m, 5H), 7.06 -7.04 (m, 2H); $^{13}$C NMR (126 MHz, DMSO-$d_6$): $\delta$ = 195.6, 188.8, 188.5, 163.0, 162.92, 162.91, 162.8, 162.0 (d, $^1$J C-F = 245.7 Hz), 160.9, 142.3, 142.2, 141.4, 140.8, 139.5, 139.3, 139.2, 134.3, 133.6, 133.5, 133.4, 132.9, 132.8, 132.7, 130.1, 129.8, 129.5, 129.3, 128.6, 128.3, 126.9, 119.3, 119.2, 116.8, 116.6, 114.7, 114.5; LC-MS m/z 329.34 (M+H$^+$).

(E)-11-benzylidene-4-methoxy-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (3p): Yellow solid (103 mg, 73% yield, m.p. 186-190 °C); IR (film) $\nu$ max 3517, 2933, 1672, 1575, 1266, 747 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.28 (d, $J$ = 8.8 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 1H), 7.69 -7.63 (m, 2H), 7.54 (s, 5H), 7.25 -7.14 (m, 6H), 6.89 (d, $J$ = 8.4 Hz, 1H), 6.75 (d, $J$ = 7.6 Hz, 1H), 3.89 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 196.7, 189.8, 156.2, 143.2, 141.4, 140.4, 134.2, 133.7, 132.6, 132.0, 131.9, 131.7, 130.3, 130.1, 129.9, 128.9, 128.5, 128.3, 127.9, 122.2, 111.0, 56.0; LC-MS m/z 341.1827 (M+H$^+$).

General experimental procedure for 4a-f:

To a stirred solution of 2-benzylidene-1H-indene-1,3(2H)-dione (0.200 g, 8.57 mmol) in dry ACN (10 mL) was added cesium fluoride (0.389 g, 25.640 mmol), then added appropriate aryl silyl triflate and the reaction was stirred at same temperature for 6 h, TLC analysis (5% EtoAc /pet ether) showed completion of the reaction. The reaction mixture was
diluted with EtOAc (20 mL) and water (20 mL), separated organic layer and then aq.layer was extracted with EtOAc (2×10 mL). The combined organic layers were washed with brine solution (20 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude reaction mixture was purified by column chromatography using hexanes/ethyl acetate (9:1 v/v) as eluent gave the compounds 4a, 4b, 4e & 4f- 4f’.

**Benzo[f]tetraphene-9,14-dione (4a):** Yellow solid (55 mg, 42% yield, m.p. 129–133 °C); IR (film) νₘₐₓ 2919, 1659, 1580, 1294, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 9.39 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.22 (t, J = 7.4 Hz, 1H), 7.83 - 7.74 (m, 3H); ¹³C NMR (101 MHz, CDCl₃):  δ = 187.0, 134.1, 133.6, 133.4, 132.8, 129.8, 129.5, 128.3, 127.3, 126.3, 122.7; HR-MS m/z 309.0921 (M+H⁺). ESI-HRMS: calcd. for C₂₂H₁₃O₂⁺ (M+H)⁺ 309.0916, found 309.0921. [Note:The compound-4a is a symmetrical molecule and its corresponding ¹H NMR spectrum indicated half integral protons only i.e-6 protons instead of 12 protons].

**3-Methylbenzo[f]tetraphene-9,14-dione (4b):** Yellow solid (73 mg, 54% yield, m.p. 155–159 °C); IR (film) νₘₐₓ 3029, 1700, 1589, 1359, 1247, 953 cm⁻¹ ; ¹H NMR (500 MHz, CDCl₃): δ = 9.38 (d, J = 8.0, 1H), 9.26 (d, J = 9.0 Hz, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.31 (s, 1H), 8.21 - 8.19 (m, 2H), 7.80 - 7.72 (m, 4H), 7.58 (d, J = 8.5 Hz, 1H) 2.65 (s, 3H); ¹³C NMR (126 MHz, CDCl₃):  δ = 187.2, 186.9, 139.9, 134.2, 134.1, 133.6, 133.5, 133.5, 133.0, 132.8, 131.8, 130.1, 129.7, 129.6, 129.3, 128.2, 127.5, 126.3, 126.2, 125.2, 122.7, 122.5, 22.2; ESI-HRMS: calcd. for C₂₃H₁₅O₂⁺ (M+H)⁺ 323.1072, found 323.1090.

**3-Methoxybenzo[f]tetraphene-9,14-dione (4e):** Yellow solid (80 mg, 56% yield, m.p. 165–169 °C); IR (film) νₘₐₓ 3010, 2922, 1658, 1604, 1269, 754 cm⁻¹ ; ¹H NMR (500 MHz, CDCl₃): δ = 9.38 (dd, J = 7.5 Hz, 1H), 9.26 (d, J = 9.5 Hz, 1H), 8.57 (d, J = 9.5 Hz,1H), 8.18 - 8.14 (m, 2H), 7.99 (d, J = 7.5 Hz, 1H), 7.77 - 7.69 (m, 4H), 7.31 (dd, J = 9.50 Hz, 1H) 4.04 (s, 3H); ¹³C NMR (126 MHz, CDCl₃):  δ = 187.3, 186.7, 160.4, 135.6, 134.2, 134.0, 133.5,
2-Methylbenzo[f]tetraphene-9,14-dione & 3-Methylbenzo[f]tetraphene-9,14-dione (4f & 4f’): Yellow solid (84 mg, 62% yield, m.p. 136–140 °C); IR (film) νmax 3434, 2920, 1660, 1591, 1271, 755 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 9.32 (dd, J = 8.5 Hz, 2H), 9.21 (d, J = 9.0 Hz, 1H), 9.12 (s, 1H), 8.65 (dd, J = 8.0 Hz, 2H), 8.55 (d, J = 8.5 Hz, 1H), 8.44 (s, 1H), 8.17-8.16 (m, 4H), 7.75 - 7.67 (m, 8H), 7.57 (dd, J = 8.0 Hz, 2H), 7.62 (s, 3H), 2.61 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ = 187.1, 187.08, 187.02, 186.9, 139.8, 138.2, 134.1, 134.06, 133.5, 133.4, 133.0, 132.7, 132.6, 132.4, 131.7, 131.2, 130.0, 129.7, 129.6, 129.4, 129.2, 129.1, 128.1, 127.8, 127.4, 127.3, 126.9, 126.2, 126.2, 125.1, 122.6, 122.5, 22.1, 22.0. LC-MS m/z 323.36 (M+H⁺).  

5H-Dibenzo[a,d][7]annulene-5,10(11H)-dione (7): Yellow oil (203 mg, 75% yield); ¹H NMR (400 MHz, CDCl₃): δ = 8.17 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.72 - 7.65 (m, 3H), 7.48 (t, J = 7.2 Hz, 1H), 7.36 (m, 1H), 4.26 (s, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 195.7, 194.6, 140.7, 137.9, 135.1, 133.5, 133.3, 132.6, 130.5, 129.5, 129.4, 129.2, 129.1, 128.1, 50.5; MS (ES⁺): m/z 223.14 [M+H⁺^+]  

11-Benzyl-5H-dibenzo[a,d][7]annulene-5,10(11H)-dione (9): Yellow solid (120 mg, 68% yield, m.p. 87–91 °C); IR (film) νmax 3010, 2923, 1709, 1449, 1249, 673 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.86 - 7.84 (m, 2H), 7.70 - 7.68 (m, 2H), 7.53 (d, J = 9.2 Hz, 2H), 7.34 (t, J = 6.8 Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.10 (d, J = 6.8 Hz, 2H), 7.07 - 6.99 (m, 3H), 3.61 (s, 2H); ¹³C NMR (126 MHz, CDCl₃): δ = 201.2, 142.2, 137.0, 135.6, 135.5, 133.6, 132.9, 132.4, 130.4, 129.8, 128.9, 128.7, 128.4, 128.0, 127.8, 126.9, 126.8, 123.3, 63.9, 41.9; ESI-HRMS: calcd. for C₂₂H₁₇O₂⁺ (M+H⁺) 313.1229, found 313.1236.
Spectra:
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:
C: 0-22 H: 0-15 O: 0-2

GVK Bio sciences (pvt) Ltd
Analytical Research and Development
511707D1838-10 (0.343) AM [Cn,4, 21.00, Ar,5.0, 185.00, 1.00, LB S]; Sm (Mh, 5x0.00); Sb (1.40.00)
311.1071

Minimum:
Maximum:
Mass Calc. Mass mDa DPM DBE i-FTI Formula
311.1071 311.1072 -0.1 -0.3 15.5 8.8 c22 H15 O2

HRMS spectrum of 3a
Date of analysis: 03-Oct-2017 12:35:15
Instrument ID: ANL-MCL3 LCMS-001
1-TOF MS ES+
697

HMBC Spectrum of 3a
(CDCl3, 400MHz)


**C NMR Spectrum of 3b (CDCl₃, 101MHz)**

<table>
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<th>ppm</th>
<th>260</th>
<th>180</th>
<th>160</th>
<th>140</th>
<th>120</th>
<th>100</th>
<th>80</th>
<th>60</th>
<th>40</th>
<th>20</th>
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</table>

**Elemental Composition Report**

**Single Mass Analysis**

- Tolerance = 1000.0 PPM
- DBE: min = -1.5, max = 50.0
- Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 5 results within limits (up to 1 closest results for each mass)

Elements Used:
C: 0.23  H: 0.17  O: 0.2  I: 0.1

**GVK-MS-ESI**

5117071631-10 (0.344 AM, C₆H₄, 20.00, Ar, C₆H₄, 10.00, 185.09, 185.09, 185.09, 185.09, 185.09, 185.09, 185.09, 185.09, 185.09)

**GVK Bio Sciences Pvt Ltd**

Analytical Research and Development

Date of analysis: 03 Oct 2017

Institute name: EASL-ESI

1 TOF MS ES⁺ 3.0563

**Minimum:**

- Mass: 325.1223
- Calc. Mass: 325.1229
- mDa: 0.6
- PPM: 1.8
- DBE: 15.5
- 1-FIT: 14.7
- Formula: C₂₃H₁₇O₂
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.22  H: 0.14  O: 0.2  F: 0.1

HRMS Spectrum of 3c

Data: 03-Oct-2017 17:25:58
Instrument ID: ANL-MLC-3:LCMS-6311
1: TQF-MS ESI-

m/z

Minimum:

Maximum:

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  Formula

329.0984  329.0978  0.6  1.8  15.5  3872.3  C22 H14 O2 F
Elemental Composition Report

**Single Mass Analysis**

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

11 formula(e) evaluated with 8 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0.22  H: 0.14  O: 0.2  Cl: 0.1  I: 0.1

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**HRMS Spectrum of 3d**

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**Table: Mass Analysis**

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<td>37.0</td>
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Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected fillers: None

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.22  H: 0.14  O: 0.2  Br: 0.1

GVK NAC PAGE 94-4Br
GVK Bio sciences (pvt) Ltd
Analytical Research and Development

511707D1630-13 (0.336) AM (Cen2, 50.00, Ar, 5.0, 1.0, 15.0, 1.0, 1.0, 1.0, 1.0, 5.0, 1.0); Sm (Mn, 5x2.00); Sb (1x, 1.0, 1.0); Cm (0x, 1.0, 1.0)
369.0184

Minimum:
1000.0  1000.0  -1.5
Maximum:
Mass  Calc. Mass  mDa  PPM  DBE  1-FIT  Formula
389.0184  389.0177  0.7  1.8  15.5  98.9  C22 H14 O2 Br

13C NMR Spectrum of 3f
(CDCl3, 101MHz)

Reference Code: L114/KO13-ONK-NAC-PAGE-12
Software: eddy2
Archive directory:
Assign: 13C-NMR
Data created on: Jul 04 2017
Department: NATO
**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron lens
4 formula(s) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0.22  H: 0.14  O: 0.2  I: 0.1

**HRMS Spectrum of 3f**

Instruments ID: ANL-MC3-LCMS-001
1-TOF MS ES+
231

Minimum: 437.0033
Maximum: 437.0039

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<th>m/z</th>
<th>PPM</th>
<th>DBE</th>
<th>1-FIT</th>
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<td>437.0039</td>
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<td>15.5</td>
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$^1$H NMR Spectrum of 3g (CDCl$_3$, 400MHz)

$^{13}$C NMR Spectrum of 3g (CDCl$_3$, 101MHz)
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-29  H: 0-14  O: 0-2  F: 0-3

Minimum:  -1.5
Maximum:  5.0  1000.0  50.0

Mass  Calc. Mass  mDa  DBE  1/717  Formula
379.0944  379.0946  -0.2  -0.5  15.5  26.8  C23 H14 O2 F3

Current Data Parameters

Sample: 51101550154

PROCNO: 1

P-2569-DU-GVK-E126410-6

1H NMR Spectrum of 3h (CDCl₃ 500MHz)
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
23 formulas evaluated with 16 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-23  H: 0-14  O: 0-2  F: 0-3  I: 0-1

HRMS Spectrum of 3h

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Page 1
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-22  H: 0-13  O: 0-2  F: 0-2

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GWK (Bio sciences Pvt Ltd)
Analytical Research and Development

HRMS Spectrum of 3j

Date of analysis 05-Oct-2017 13:23:33
Instrument ID: ANL-MCL-3-CLSMSS01
2: TOF MS ESI+

Minimum: -1.5
Maximum: 5.0  1000.0  50.0

Mass  Calc. Mass  mDa  PPM  DBE  1-FIT  Formula
347.0881  347.0884  -0.3  -0.9  15.5  5.9  C22 H13 O2 F2

1H NMR Spectrum of 3j
(CDCl3, 600MHz)

Current Data Parameter
NAME  1117046517
REMARK  1
PROC  1

F1 - Acquisition parameter
NAME  1117046517
TIME  12:19:04
PEAK  1159470.0195
PPM  1.0
ACQ  1
TR  65.000
TE  3.00 wu
SN  1
NEX  1
PREP  100.000000
MAT  0
TR1  0.000000
PW1  22.000000 wu
P1  1.00

F2 - Processing parameters
NAME  1117046517
REMARK  1
PROC  1

F3 - Other parameters
NAME  1117046517
REMARK  1
PROC  1

F4 - Instrument parameter
NAME  1117046517
REMARK  1
PROC  1
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM  /  DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
6 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:
C: 0.22  H: 0.13  O: 0.2  Cl: 0.2

GVK Bio sciences (pvt) Ltd
Analytical Research and Development
511707D1839k 12 (0.385) AM (Cer,4,20.00,Ar,5,0,195.07,1,60,LS 5); Sn (Ms, 5x2.00); Sb (1,40.00)
379.0270

Minimum: -1.5
Maximum:  5.0  1000.0  50.0

Mass  Calc. Mass  mDa  PPM  DBE  1-FIT  Formula
379.0276  379.0293 -1.7  -4.5  15.5  26.2  C22 H13 O2 Cl2
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
21 formula(e) evaluated with 14 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:
C: 0.23  H: 0.14  O: 0.2  F: 0.3  Br: 0.1

Date of analysis: 03-Oct-2017 16:41:20
Instrument ID: ANL MOL 3 LCMS 001
1: TOF MS ES+
3.87e3

Minimum: 1000.0  1000.0  -1.5
Maximum: 1000.0  1000.0  50.0

Mass  Calc. Mass  MDA  PPM  DBE  1-FIT  Formula
379.0949  379.0946  0.3  0.8  15.5  16.4  C23 H14 O2 F3

NMR Spectrum of 3I
(CDCl₃, 500MHz)
C NMR Spectrum of 3l (CDCl₃, 126MHz)

HRMS Spectrum of 3l

Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoleptotopic Mass, Odd and Even Electron Ions
1 formula(s) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:
C: 0-24  H: 0-19  O: 0-2

Calc. Mass  m/z  PPM  DBE  i-FIT  Formula
339.1380  339.1385  -0.5  -1.5  15.5  171.3  C24 H19 O2
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-25 H: 0-21 O: 0-2

HRMS Spectrum of 3m

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<td>353.1553</td>
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<td>3.1</td>
<td>15.5</td>
<td>0.6</td>
<td>C25 H21 O2</td>
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</table>

^1H NMR Spectrum of 3n+3n'
(CDC6, 400MHz)
NOE studies of 3n+3n' 
(CDC$_6$, 400MHz)

'H NMR Spectrum of 3n+3n' 
(DMSO, 500 MHz)
In order to confirm the position of the F group (on phenyl ring which shown as labelled with number) in compound-3o, NMR studies were conducted. From the NOESY study on compound-3o, when we irradiate C2 attached H1 at 7.44 ppm, no signal intensity was enhanced and also observed the absence of proton on adjacent carbon (C3). Hence this spatial correlation supporting that the F group is attached adjacent to the C3 carbon only.
Mass Spectrum of 3a:3n
**1H NMR Spectrum of 3p**

**NOE Studies of 3p**
In order to confirm the position of the OCH$_3$ group (on phenyl ring which shown as labelled with number) in compound-3p, NMR studies were conducted. From the NOESY study on compound-3p, when we irradiate C$_2$ attached OCH$_3$ at 3.89 ppm, the corresponding H$_1$ at 6.90 ppm respective signal intensity was enhanced and also observed the absence of H$_2$ signal intensity. Hence, this spatial correlation supporting that the OCH$_3$ group is attached adjacent to the C$_3$ which bearing H$_1$. 
LC Method Details

Method: GVK, 5 MIN
Mobile Phase A: 0.1% FA in Water
Mobile Phase B: 0.1% FA in ACN
Gradient % of B: 0', 0.3', 2.8', 8', 98', 4.5', 4.5', 45', 3.5', 0'
Flow: 0.6ml/min
Column: BEH C18, (2.1*50)mm, 1.7um,

Detector Type: PDA
Wavelength Range 1 (nm): 215

UV Chromatogram
RT: 0.00 - 4.97 min: 1G

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<td>3.07</td>
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<td>3.50</td>
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<td>3.54</td>
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Mass spectrum of 3p
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(s) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.22  H: 0.13  O: 0.2

Date of analysis: 31 Jan 2019
Instrument ID: ANL-MCDS11-LCMS-001
1: TOP MS Es+

Minimum:  
Maximum: 

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<td>16.5</td>
<td>132.1</td>
<td>C22 H13 O2</td>
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$^1$H NMR Spectrum of 4b (CDCl$_3$, 500MHz)

$^{13}$C NMR Spectrum of 4b (CDCl$_3$, 126MHz)
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron ions
1 formula(s) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:
C: 0.23  H: 0.15  O: 0.2

HRMS Spectrum of 4b

Minimum: 5.0  1000.0  50.0

Mass  Calc. Mass  mDa  PPM  DBE  1-FIT  Formula
323.1090  323.1072  1.0  5.6  16.5  6.0  C23 H15 O2

^1HNMR Spectrum of 4e
(CDCl3, 500 MHz)
Elemental Composition Report

Single Mass Analysis
Tolerance = 1000.0 PPM  /  DBE: min = -1.5, max = 50.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-23  H: 0-15  O: 0-3

Sample Information:

Date of analysis: 03-Oct-2017 12:25:58
Instrument ID: NLC-MCLC-001
T: TOF MS ES+
5.1663

Minimum:                  Maximum:                  Mass   Calc. Mass   mDa   PPM   DBE   i-FIT   Formula
339.1025 339.1021 0.4 1.2 16.5 9.8 C23 H15 O3
Sample Name : GVR-NAG-215
Vial Position : F1-B-01
Date of Analysis : 4/23/2019 10:20:50 AM
Injection Vol : 0.400 µl
Acq. Method : RND-FA-4.01
Instrument ID : ANL-MCL5-LCMS-001

Column : ACQUITY UPLC BEH C18 (50mmx2.1mm, 1.7µm)
Mobile Phase : A: 0.1% FA IN WATER; B: 0.1% FA IN ACN
Gradient : Time (min) / A:B: 0/3, 0.3/3, 2.3/98, 3.5/98, 4.0/3, 4.01/3
Flow Rate : 0.6 ml/min
Column Temp : 60°C

**LC Chromatogram of 4f**

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<th>Area (Area %)</th>
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<td>2</td>
<td>2.39</td>
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<td>3</td>
<td>2.66</td>
<td>970.522 (98.309)</td>
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Mass spectrum of 4f
$^1$H NMR Spectrum of 7 (CDCl$_3$, 400MHz)

$^{13}$C NMR Spectrum of 7 (CDCl$_3$, 101MHz)
GVK Biosciences (Pvt.) Ltd.
Analytical Research and Development

Data File: BG_511805A7541  Sample ID: GVKBIO-PhD-FS-ANT
Sample Type: Unknown  Vial: GC6
Instrument Name: N/A  Injection Volume(μl): 1.00
Operator: Thermo Scientific  Run Time(min): 5.52
INSTRUMENT ID: ANL-MCL5-LCMS-005  Acquisition Date: 05/09/18 07:11:10 PM

LC Method Details

Method : GVK_5.5MIN
Mobile Phase A : 0.1% FA in Water
Mobile Phase B : 0.1% FA in ACN
Gradient % of B : 0/3, 0/3/5, 1/8/98, 4.5/98, 4.51/3, 5/3/3
Flow Rate : 0.6ml/min
Column : BEH C18, (2.1*50mm), 1.7μm

Detector Type: PDA
Wavelength Range 1 (nm): 215.00000

UV Chromatogram

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LC Chromatogram of 7
H NMR Spectrum of 8
(CDCl₃, 400MHz)

LC Chromatogram of 8
Mass Spectrum of 8
Reference: