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1. Experimental procedure and characterization data

General information. All commercial reagents were used without purification. NMR spectra were recorded using a Bruker Avance III spectrometer in CDCl₃ (¹H: 400.13 MHz; ¹³C: 100.61 MHz; ¹⁹F: 376.50 MHz); chemical shifts are reported as parts per million (δ =, ppm). The residual solvent peak (CHCl₃) was used as internal standard: 7.26 for ¹H and 77.16 ppm for ¹³C. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet/doublets of doublets. Coupling constants, *J*, are reported in Hz. Mass spectrum were recorded using a Bruker microTOF spectrometer (ionization by electrospray, positive ions detection). Melting points were determined in open capillary tubes on a Stuart SMP50 Automatic Melting Point Apparatus. Analytical thin-layer chromatography was carried out on UV-254 silica gel plates using appropriate eluents. Compounds were visualized with short-wavelength UV light. Column chromatography was performed with a flash purification system IsoleraTM Prime (Biotage[®]) using silica gel Merk grade 60 (0.040–0.063 mm) 230–400 mesh (gradient elution with *n*-hexane-acetone). HPLC was performed using an ECS28P00 instrument and YMC-Pack SIL-06 (250×20 mm) column. Diazo compounds **1** were synthesized according to previously described procedures.^{1,2}

General procedure for the catalytic decomposition of DAS 1 in DCM. Diazo compound 1 (0.5 or 1.0 mmol) was dissolved in dry DCM (1.8 or 3.6 mL) followed by addition of the catalyst solution (2.5 mM Rh₂(esp)₂ in DCM, 200 or 400 μ L, 0.1 mol %). The reaction mixture was stirred at ambient temperature for 0.5–1 hour (controlled by TLC). The reaction mixture was diluted with *n*-hexane (2 mL) and the resulting solution was subjected to column chromatography on silica gel, eluent cyclohexane–acetone (gradient from 10 to 50% of acetone) to afford dimer 2 and/or indene 3. In some cases, additional purification by HPLC was performed.

(8bR/S, 12bR/S, 15aS/R, 15bS/R) - 2, 14 - Diphenyl - 14, 15b - dihydro - 1H - dibenzo[2, 3:4, 5] azuleno[1, 8a - 1, 12b - 1, 12

c:7,8-*c*']dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2a): prepared according to the general procedure from diazo compound 1a (0.5 mmol). Yield: 97 mg (74%). Eluent – cyclohexane–acetone (from 0 to 25% of acetone). White solid; m.p. >250 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 4H), 7.38 (m, 1H), 7.34 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 7.20 – 7.16 (m, 2H), 6.98 (m, 2H), 6.76 (m, 1H), 5.31 (s, 1H), 4.76 (s, 1H), 3.71 (d, *J* = 1.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 173.9, 172.9, 166.9, 139.8, 139.3, 139.0, 136.4, 135.5, 131.4, 131.2, 130.5, 130.0, 129.4, 129.2, 129.12, 129.11, 128.9, 128.9, 128.7, 127.9, 127.7, 126.6, 126.4, 125.5, 72.3, 55.4, 53.0, 46.8. HRMS (ESI), *m*/*z* calcd for C₃₄H₂₂N₂NaO₄ [M+Na]⁺ 545.1472 found 545.1478.

Additionally, the experiment with diluting the reaction mixture 10 times (0.5 mmol in 18 mL) was performed. In this case, the content of indene increased, and it was isolated using column chromatography.

2-Phenylindeno[1,2-*c***]pyrrole-1,3(2***H***,8***H***)-dione (3a): yield: 19 mg (15%). Eluent – cyclohexane– acetone (from 10 to 50% of acetone). White solid; 163.2 – 165.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.83 (m, 1H), 7.70 – 7.58 (m, 1H), 7.55 – 7.46 (m, 4H), 7.41 (m, 3H), 3.87 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.6, 164.5, 151.3, 148.9, 148.2, 134.4, 132.1, 129.1, 129.0, 127.9, 127.7, 126.6, 125.5, 123.0, 33.6. HRMS (ESI),** *m/z* **calcd for C₁₇H₁₂NO₂ [M+H]⁺ 262.0863 found 262.0865.**

(8b*R*/*S*,12b*R*/*S*,15a*S*/*R*,15b*S*/*R*)-2,14-Bis(4-methoxyphenyl)-14,15b-dihydro-1*H*-dibenzo[2,3:4,5]azuleno[1,8*a-c*:7,8*-c*′]dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2b): prepared according to the general procedure from diazo compound 1b (0.5 mmol). Yield: 106 mg (73%). Eluent – cyclohexane– acetone (from 10 to 50% of acetone). White solid, m.p. 195.7 – 196.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.51 – 7.42 (m, 3H), 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 (m 1H), 7.11 – 7.07 (m, 2H), 6.96 – 6.92 (m, 2H), 6.91 – 6.87 (m, 2H), 6.84 – 6.80 (m, 2H), 6.75 (m, 1H), 5.29 (s, 1H), 4.73 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.67 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 174.2, 173.2, 167.2, 159.8, 159.6, 139.9, 139.3, 139.0, 136.4, 135.2, 130.4, 130.1, 129.42, 129.37, 129.2, 129.1, 127.88, 127.85, 127.67, 127.61, 125.5, 124.0, 123.9, 114.4, 114.2, 72.1, 55.52, 55.48, 55.3, 52.9, 46.7. HRMS (ESI), *m*/*z* calcd for C₃₆H₂₆N₂NaO₆ [M+Na]⁺ 605.1683 found 605.1691.

(8bR/S,12bR/S,15aS/R,15bS/R)-2,14-Bis(4-(trifluoromethyl)phenyl)-14,15b-dihydro-1H-dibenzo-

[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2*c*): prepared according to the general procedure from diazo compound 1*c* (0.5 mmol). Yield: 121 mg (74%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid; m. p. 198.2 – 199.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 2.0 Hz, 1H), 7.74 – 7.64 (m, 3H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.44 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.31 (s, 1H), 4.79 (s, 1H), 3.76 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.3, 173.3, 172.7, 166.2, 139.6, 138.8, 138.7, 136.5, 136.1, 134.4 (q, *J* = 1.2 Hz), 134.2 (q, *J* = 1.1 Hz), 131.0 (q, *J* = 14.6 Hz), 130.7 (q, *J* = 14.6 Hz), 130.6, 129.8, 129.5, 129.44, 129.4, 129.2, 127.9, 127.8, 126.6, 126.46 (s), 126.2 (q, *J* = 3.7 Hz), 126.0 (q, *J* = 3.7 Hz), 125.4, 124.8 (q, *J* = 272.7 Hz), 122.1 (q, *J* = 273.7 Hz), 72.4, 55.3, 52.9, 46.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.85, -62.88. HRMS (ESI), *m/z* calcd for C₃₆H₂₀F₆N₂NaO₄ [M+Na]⁺ 681.1219 found 681.1225.

(8bR/S,12bR/S,15aS/R,15bS/R)-2,14-Di-p-tolyl-14,15b-dihydro-1H-dibenzo[2,3:4,5]azuleno[1,8a-

c:7,8-*c* ']dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2d): prepared according to the general procedure from diazo compound 1d (1 mmol). Yield: 173 mg (63%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid; m.p. 177.2 – 178.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 2.0 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.49 – 7.42 (m, 3H), 7.38 (t, J = 7.6 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.25 (m, 3H), 7.12 (m, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.86 (d, J = 8.3 Hz, 2H), 6.75 (d, J = 7.6 Hz, 1H), 5.29 (s, 1H), 4.74 (s, 1H), 3.68 (d, J = 2.0 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 174.1, 173.0, 167.0, 139.9, 139.4, 139.1, 139.0, 138.8, 136.4, 135.3, 130.4, 130.2, 129.8, 129.6, 129.43, 129.37, 129.2, 129.1, 128.8, 128.7, 127.9, 127.6, 126.4, 126.2, 125.5, 72.2, 55.4, 53.0, 46.8, 21.3, 21.2. HRMS (ESI), *m/z* calcd for C₃₆H₂₇N₂O₄ [M+H]⁺ 551.1965 found 551.1969.

(8bR/S,12bR/S,15aS/R,15bS/R)-2,14-Bis(4-fluorophenyl)-14,15b-dihydro-1H-dibenzo[2,3:4,5]-

azuleno[1,8*a-c*:7,8*-c'*]**dipyrrole-1,3,13,15**(2*H*,12*bH*,14*H*)-**tetraone** (2e): prepared according to the general procedure from diazo compound 1e (1 mmol). Yield: 211 mg (86%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid, m.p. 160.1 – 160.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.50 – 7.43 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 1H), 7.14 – 7.11 (m, 4H), 6.97 (m, 4H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.29 (s, 1H), 4.75 (s, 1H), 3.71 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 173.8, 173.0, 166.7, 163.6 (d, *J* = 250.5 Hz), 161.2 (d, *J* = 250.5 Hz), 139.7, 139.0, 138.9, 136.2, 135.9, 130.5, 129.7, 129.6, 129.5, 129.3 (d, *J* = 6.2 Hz), 128.5, 128.4, 128.3 (d, *J* = 8.8 Hz), 127.9, 127.7, 127.2 (d, *J* = 3.3 Hz), 127.1 (d, *J* = 3.2 Hz), 125.5, 116.33 (s), 116.2 (d, *J* = 22.8 Hz), 115.9 (d, *J* = 250.5 Hz), 72.3, 55.3, 52.9, 46.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.5, -111.8. HRMS (ESI), *m*/*z* calcd for C₃₄H₂₀F₂N₂NaO₄ [M+Na]⁺ 581.1283 found 581.1292.

(8b*R*/*S*,12b*R*/*S*,15a*S*/*R*,15b*S*/*R*)-2,14-Dibenzyl-14,15b-dihydro-1*H*-dibenzo[2,3:4,5]azuleno[1,8*ac*:7,8-*c*']dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2*f*): prepared according to the general procedure from diazo compound 1*f* (1 mmol). Yield: 187 mg (68%). White solid, m.p. 232.0–234.0 °C. Eluent – cyclohexane–acetone (from 10 to 50% of acetone). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 1.9 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.43 – 7.38 (m, 2H), 7.32 (m, 7H), 7.21 (m, 5H), 7.03 (m, 2H), 6.70 (m, 1H), 5.10 (s, 1H), 4.59 (s, 1H), 4.28 (dd, *J* = 49.6, 14.3 Hz, 2H), 4.06 (dd, *J* = 14.1, 12.2 Hz, 2H), 3.36 (d, *J* = 1.9 Hz, 1H). NMR data is in accordance with previously reported.³

(8bS/R,12bR/S,15aS/R,15bS/R)-7,11-Dimethyl-2,14-diphenyl-14,15b-dihydro-1H-dibenzo-

[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2h): prepared according to the general procedure from diazo compound 1h (1.0 mmol). Yield: 253 mg (93%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid; m.p. >250 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.52 (s, 1H), 7.44 – 7.38 (m, 3H), 7.34 – 7.30 (m, 4H), 7.29 (m, 1H), 7.20 – 7.14 (m, 4H), 7.03 – 6.97 (m, 2H), 6.59 (s, 1H), 5.23 (s, 1H), 4.71 (s, 1H), 3.68 (d, *J* = 2.0 Hz, 1H), 2.46 (s, 3H), 2.28 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 174.2, 173.1, 167.0, 139.9, 139.24, 139.23, 139.21, 136.8, 135.8, 133.6, 131.5, 131.3, 130.5, 130.4, 130.1, 129.09, 129.06, 128.88, 128.80, 128.6, 128.2, 127.6, 126.6, 126.4, 125.8, 72.4, 55.3, 52.6, 46.9, 21.7, 21.4. HRMS (ESI), *m/z* calcd for C₃₆H₂₇N₂O4 [M+H]⁺ 551.1965 found 551.1968.

(8bS/R,12bR/S,15aS/R,15bS/R)-2,14-Diphenyl-7,11-bis(trifluoromethyl)-14,15b-dihydro-1H-

dibenzo[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2i): prepared according to the general procedure from diazo compound 1i (0.5 mmol). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). Additionally purified by HPLC (eluent – *n*-hexane – ethyl acetate, from 10 to 30% of ethyl acetate). Yield: 30 mg (18%). Amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.40 – 7.31 (m, 4H), 7.18 – 7.12 (m, 2H), 7.01 – 6.95 (m, 3H), 5.39 (s, 1H), 4.87 (s, 1H), 3.73 (d, *J* = 2.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 175.9, 172.9, 172.2, 166.2, 142.8, 140.1, 139.9, 138.9, 133.6, 132.4 (q, *J* = 33.0 Hz), 131.8, 131.3 (q, *J* = 32.9 Hz), 131.1, 130.8, 129.22, 129.17, 129.1, 128.3, 126.70 (q, *J* = 3.3 Hz), 126.4, 126.2, 125.8 (q, *J* = 3.6 Hz), 125.0 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 273.4 Hz), 123.0 (q, *J* = 3.6 Hz), 122.4 (q, *J* = 273.4 Hz), 72.2, 55.0, 52.7, 46.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.4, -62.9. HRMS (ESI), *m*/z calcd for C₃₆H₂₀F₆N₂NaO₄ [M+Na]⁺ 681.1220 found 681.1218.

(8bS/R,12bR/S,15aS/R,15bS/R)-5,9-Difluoro-2,14-diphenyl-14,15b-dihydro-1*H*-dibenzo[2,3:4,5]azuleno[1,8*a*-*c*:7,8-*c*']dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2j): prepared according to the general procedure from diazo compound 1j (1.0 mmol). Yield: 167 mg (60%). Eluent – cyclohexane– acetone (from 10 to 50% of acetone). White solid, m.p. >250 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (t, J = 2.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 7.36 – 7.29 (m, 4H), 7.21 – 7.12 (m, 4H), 6.98 (m, 2H), 6.58 (m, 1H), 5.40 (s, 1H), 4.80 (s, 1H), 3.76 (d, J = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.0, 173.2, 172.5, 166.2, 161.3 (d, J = 165.0 Hz), 159.3 (d, J = 164.7 Hz), 141.7 (d, J = 4.8 Hz), 138.3, 131.9 (d, J = 7.3 Hz), 131.2, 131.0, 130.97, 130.89, 129.2, 129.03, 129.01, 128.9, 128.8 (d, J = 6.2 Hz), 126.7 (d, J = 17.7 Hz), 126.5, 126.3, 124.3 (d, J = 2.8 Hz), 123.8 (d, J = 14.4 Hz), 121.4 (d, J = 3.7 Hz), 116.2 (d, J = 19.7 Hz), 115.4 (d, J = 21.5 Hz), 72.2, 55.4, 50.0, 46.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.0, -113.2. HRMS (ESI), m/z calcd for C₃₄H₂₀F₂N₂NaO₄ [M+Na]⁺ 581.1283 found 581.1280.

(8bS/R,12bR/S,15aS/R,15bS/R)-2,14-Dibenzyl-7,11-difluoro-14,15b-dihydro-1*H*-dibenzo[2,3:4,5]azuleno[1,8*a*-*c*:7,8-*c'*]dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2k) and (3'E,4Z,4'Z)-4,4'-(hydrazine-1,2-diylidene)bis(1-benzyl-3-((*E*)-4-fluorobenzylidene)-pyrrolidine-2,5-dione) (4k): prepared according to the general procedure from diazo compound 1g (1.0 mmol). As a result of the reaction, bisazine 4k precipitate was obtained, which was additionally purified by recrystallization from hot methanol. Solution with dimer 2k and other soluble impurities was subjected to column chromatography on silica gel, eluent cyclohexane–acetone (gradient from 10 to 50% of acetone).

Compound 2k: Yield: 123 mg (42%) White solid, m.p. 237.1 – 239.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 2.0 Hz, 1H), 7.37 – 7.33 (m, 3H), 7.32 – 7.30 (m, 4H), 7.27 – 7.21 (m, 4H), 7.17 (m, 2H), 7.08 (m, 2H), 7.03 (m, 1H), 6.43 (m, 1H), 5.02 (s, 1H), 4.57 (s, 1H), 4.32 (d, J = 14.1 Hz, 1H), 4.22 (d, J = 14.3 Hz, 1H), 4.08 (d, J = 14.3 Hz, 1H), 4.02 (d, J = 14.1 Hz, 1H), 3.34 (d, J = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.4, 174.1, 172.3, 167.3, 164.2 (d, J = 250.4 Hz), 161.7 (d, J = 253.5 Hz), 141.7 (d, J = 6.2 Hz), 141.3 (d, J = 8.8 Hz), 135.5, 134.9, 134.6 (d, J = 2.8 Hz), 133.4, 132.5, 132.4 (d, J = 2.5 Hz), 132.3, 130.0 (d, J = 0.7 Hz), 129.0, 128.9, 128.6 (d, J = 3.5 Hz), 128.5, 128.0, 127.9, 117.0 (d, J = 13.4 Hz), 116.8 (d, J = 12.0 Hz), 114.6 (d, J = 21.8 Hz), 112.7 (d, J = 23.3 Hz), 71.5, 55.4 (d, J = 1.9 Hz), 52.0, 46.0, 42.2, 42.0. ¹⁹F NMR (376 MHz, CDCl₃) δ -108.5, -111.2. HRMS (ESI), m/z calcd for C₃₆H₂₄F₂N₂NaO₄ [M+Na]⁺ 609.1596 found 609.1600.

Compound 4k: Yield: 56 mg (18%). Yellow solid, m.p. 245.2 – 247.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.38 (m, 4H), 7.93 (s, 2H), 7.43 (m, 4H), 7.35 (m, 6H), 7.09 (m, 4H), 4.83 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 165.0 (d, *J* = 256.3 Hz), 160.8, 141.0, 136.0 (d, *J* = 9.0 Hz), 135.2, 134.0, 129.5 (d, *J* = 3.0 Hz), 129.0, 128.8, 128.3, 118.5 (d, *J* = 2.2 Hz), 116.0 (d, *J* = 21.8 Hz), 42.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -105.8. HRMS (ESI), *m/z* calcd for C₃₆H₂₄F₂N₂NaO₄ [M+Na]⁺ 637.1658 found 637.1661.

(8bS/R,12bR/S,15aS/R,15bS/R)-2,14-Dicyclopropyl-7,11-difluoro-14,15b-dihydro-1H-dibenzo-

[2,3:4,5]azuleno[1,8*a-c*:7,8*-c*']dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2l): prepared according to the general procedure from diazo compound 1l (0.86 mmol). Yield: 89 mg (43%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid; m.p. >250 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.37 (m, 2H), 7.17 (m, 2H), 7.07 – 6.99 (m, 1H), 6.40 (m, 1H), 5.02

(s, 1H), 4.46 (s, 1H), 3.30 (d, J = 2.0 Hz, 1H), 2.75 – 2.69 (m, 1H), 2.47 (m, 1H), 1.10 – 1.04 (m, 1H), 1.00 (m, 3H), 0.95 – 0.84 (m, 3H), 0.69 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 177.9, 175.3, 174.3, 168.5, 163.47 (d, J = 246.9 Hz), 161.5 (d, J = 248.2 Hz), 142.4 (d, J = 8.7 Hz), 135.5, 133.3, 133.2 (d, J = 3.1 Hz), 132.6, 130.6, 130.0 (d, J = 9.0 Hz), 116.9, 116.7 (d, J = 6.1 Hz), 116.5, 114.6 (d, J = 21.4 Hz), 112.1 (d, J = 22.9 Hz), 71.2, 54.6, 51.9, 45.5, 22.4, 22.2, 5.2, 5.0, 4.9, 4.78. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.3, -112.3. HRMS (ESI), *m*/*z* calcd for C₂₈H₂₀F₂N₂NaO₄ [M+Na]⁺ 509.1283 found 509.1294.

(8bS/R,12bR/S,15aS/R,15bS/R)-7,11-Dichloro-2,14-diisobutyl-14,15b-dihydro-1H-dibenzo-

[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2m): prepared according to the general procedure from diazo compound 1m (1.0 mmol). Yield: 143 mg (52%). Eluent – cyclohexane–acetone (from 10 to 50% of acetone). White solid; m.p. 198.9 – 200.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.68 (s, 1H), 7.44 (m, 1H), 7.34 (m, 2H), 7.18 (m, 1H), 6.66 (s, 1H), 5.07 (s, 1H), 4.55 (s, 1H), 3.41 (d, *J* = 2.0 Hz, 1H), 3.39 – 3.31 (m, 2H), 3.23 (m, 1H), 3.09 (m, 1H), 1.99 (m, 1H), 1.77 (m, 1H), 0.91 (d, *J* = 2.3 Hz, 3H), 0.89 (d, *J* = 2.3 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H), 0.57 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 177.2, 174.7, 173.4, 167.8, 141.6, 140.5, 137.4, 135.4, 135.4, 134.9, 132.9, 131.7, 130.6, 129.7, 129.5, 128.6, 127.9, 125.8, 71.2, 55.3, 52.5, 46.3, 46.0, 45.9, 27.3, 26.8, 20.1, 19.9, 19.6, 19.5. HRMS (ESI), *m*/z calcd for C₃₀H₂₉Cl₂N₂O₄ [M+H]⁺ 551.1499 found 551.1497.

(8bR/S,12bR/S,15aS/R,15bS/R)-6,10-Dimethoxy-2,14-diphenyl-14,15b-dihydro-1H-dibenzo-

[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12*bH*,14*H*)-tetraone (2n): prepared according to the general procedure from diazo compound 1n (0.5 mmol). After column chromatography (eluent – cyclohexane–acetone (from 10% to 50% of acetone) two fractions were obtained: a mixture of two regioisomeric indenes (ratio 1.8:1.0, yield 82 mg (56%)) and contaminated dimer 2n. Pure compound 2n was obtained by HPLC (eluent – DCM–methanol (from 0% to 10% of methanol). Yield: 18 mg (12%). Amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 2.0 Hz, 1H), 7.59 (m, 1H), 7.42 (m, 3H), 7.31 (m, 3H), 7.19 – 7.14 (m, 2H), 7.02 – 6.96 (m, 4H), 6.80 (m, 2H), 6.74 (m, 1H), 5.17 (s, 1H), 4.65 (s, 1H), 3.84 (s, 6H), 3.70 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 174.3, 173.0, 166.9, 160.6, 158.9, 141.7, 137.4, 135.4, 131.4, 131.3, 131.2, 130.74, 130.68, 130.5, 129.1, 128.93, 128.90, 128.7, 126.6, 126.4, 126.2, 115.9, 115.7, 114.5, 112.4, 72.4, 55.6, 55.5, 54.6, 52.5, 46.9. HRMS (ESI), *m*/*z* calcd for C₃₆H₂₆N₂NaO₆ [M+Na]⁺ 605.1683 found 605.1680.

2-(2-Chlorophenyl)indeno[1,2-*c*]**pyrrole-1,3(2***H***,8***H***)-dione (30):** prepared according to the general procedure from diazo compound **10** (1.0 mmol). Yield: 105 mg (35%). Eluent – cyclohexane–acetone

(from 10 to 50% of acetone). White solid; m.p. 197.7 – 199.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (m, 1H), 7.70 – 7.65 (m, 1H), 7.58 (m, 1H), 7.53 – 7.46 (m, 2H), 7.46 – 7.40 (m, 2H), 7.41 – 7.34 (m, 1H), 3.93 (d, *J* = 24.6 Hz, 1H), 3.85 (d, *J* = 24.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 163.9, 151.7, 149.2, 148.2, 134.4, 133.7, 131.1, 130.5, 130.4, 129.9, 129.1, 127.9, 127.7, 125.5, 123.1, 33.7. HRMS (ESI), *m*/*z* calcd for C₁₇H₁₀ClNNaO₂ [M+Na]⁺ 318.0292 found 318.0288.

2-(5-Chloro-2-methoxyphenyl)indeno[1,2-*c***]pyrrole-1,3(***2H***,8***H***)-dione (3p):** prepared according to the general procedure from diazo compound **1p** (1.0 mmol). Yield: 111 mg (34%). Eluent – cyclohexane– acetone (from 10 to 50% of acetone). White solid; m.p. 184.5 – 185.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (m, 1H), 7.68 – 7.64 (m, 1H), 7.48 (m, 2H), 7.40 (m, 1H), 7.28 (s, 1H), 6.98 (m, 1H), 3.90 (d, *J* = 24.1 Hz, 1H), 3.83 (d, *J* = 24.1 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.4, 164.3, 154.6, 151.7, 149.3, 148.2, 134.5, 130.5, 130.3, 128.9, 127.8, 125.5, 125.4, 123.0, 121.6, 113.0, 56.2, 33.6. HRMS (ESI), *m/z* calcd for C₁₈H₁₂ClNNaO₃ [M+Na]⁺ 348.0398 found 348.0400.

Ethyl 2-(1,3-dioxoindeno[1,2-*c*]pyrrol-2(1*H*,3*H*,8*H*)-yl)benzoate (3q): prepared according to the general procedure from diazo compound 1q (1.0 mmol). Yield: 180 mg (54%). Eluent – cyclohexane– acetone (from 10 to 50% of acetone). White solid; m.p. 158.6 – 160.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (m, 1H), 7.93 – 7.88 (m, 1H), 7.68 (m, 2H), 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 7.40 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.89 (br.s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 165.1, 164.8, 151.8, 149.4, 148.2, 134.5, 133.1, 131.8, 131.7, 130.7, 128.9, 128.7, 127.8, 125.5, 123.0, 61.3, 33.6, 14.1. HRMS (ESI), *m*/*z* calcd for C₂₀H₁₅NNaO₄ [M+Na]⁺ 356.0893 found 356.0891.

(8bR/S,12bR/S,15aS/R,15bS/R)-5,9-Dimethyl-2,14-diphenyl-14,15b-dihydro-1*H*-dibenzo[2,3:4,5]azuleno[1,8*a-c*:7,8*-c'*]dipyrrole-1,3,13,15(2*H*,12b*H*,14*H*)-tetraone (2r), 7-methyl-2-phenylindeno-[1,2*-c*]pyrrole-1,3(2*H*,8*H*)-dione (3r) and compound 5: prepared according to the general procedure from diazo compound 1r (1.0 mmol). After column chromatography pure indene 3r and the mixture of dimers 2r and 5 (129 mg, ratio 1.0:0.3) were obtained. Individual compounds 2r and 5 were isolated by HPLC (eluent – *n*-hexane–ethyl acetate (from 10% to 30% of ethyl acetate)).

Compound 2r: Yield: 85 mg (31%). Amorphous solid. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, J = 1.9 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.31 (m, 2H), 7.26 (m, 1H), 7.23 (m, 1H), 7.18 (m, 3H), 7.12 (m, 1H), 6.97 (m, 2H), 6.41 (m, 1H), 5.20 (s, 1H), 4.70 (s, 1H), 3.71 (d, J = 1.9 Hz, 1H), 2.49 (s, 3H), 2.05 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 174.1, 173.0, 167.0, 139.3, 139.2, 138.6, 137.1, 136.7, 134.7, 133.3, 131.4, 131.2, 130.5, 130.1, 129.9, 129.4, 129.1,

129.0, 128.9, 128.8, 128.7, 126.6, 126.5, 126.4, 122.7, 72.1, 55.3, 51.8, 46.7, 19.9, 19.2. HRMS (ESI), *m/z* calcd for C₃₆H₂₇N₂O₄ [M+H]⁺ 551.1965 found 551.1969

Compound 3r: Yield: 83 mg (30%). Yellow solid, m.p. 183.5 – 185.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 7.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.38 (m, 4H), 7.29 (d, J = 7.1 Hz, 1H), 3.73 (s, 2H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.7, 164.7, 151.6, 148.5, 146.9, 134.9, 134.0, 132.1, 130.2, 129.1, 128.2, 127.6, 126.5, 120.6, 32.5, 18.8. HRMS (ESI), m/z calcd for C₁₈H₁₄NO₂ [M+H]⁺ 276.1019 found 276.1020

Compound 5: Yield: 22 mg (8%). White solid; m.p. 238.6 – 240.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.42 (m, 4H), 7.40 – 7.34 (m, 4H), 7.30 – 7.27 (m, 4H), 7.25 (d, *J* = 7.6 Hz, 2H), 5.88 (s, 2H), 4.19 (s, 2H), 2.42 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 175.3, 174.5, 141.1, 139.8, 133.9, 131.4, 130.5, 129.3, 129.0, 128.7, 126.2, 123.7, 55.5, 52.9, 52.2, 19.9. HRMS (ESI), *m/z* calcd for C₃₆H₂₆N₂NaO₄ [M+Na]⁺ 573.1785 found 573.1785.

2. Crystallographic data for compounds 2a and 5

X-ray Single Crystal analysis was performed on Rigaku XtaLAB Synergy-S diffractometer with monochromated CuKα radiation. Crystal growth was performed by slow evaporation of solution in *n*-hexane/acetone mixture (1:1) at 5 °C. The crystal was kept at 100 K during data collection. Using Olex2⁴, the structures were solved with the SHELXT⁵ structure solution program using Intrinsic Phasing and refined with the SHELXL^{6,7} refinement package using Least Squares minimization. CCDC 2155454 (**2a**) and CCDC 2144354 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.

Table S1. Crystal data and ORTEP representation for 2a (2155454)		
Empirical Formula	$C_{34}H_{22}N_2O_4$	
Formula weight	522.53	
Temperature, K	100.15	
Crystal system	monoclinic	
Space group	P2 ₁	
a/Å	9.64990(10)	
b/Å	13.35850(10)	
c/Å	9.85390(10)	
α/°	90	
β/°	91.5160(10)	
γ/°	90	
Volume/Å ³	1269.80(2)	
Z	2	
$\rho_{calc}g/cm^3$	1.367	
μ/mm ⁻¹	0.730	
F(000)	544.0	
Crystal size/mm ³	$0.12 \times 0.12 \times 0.1$	
Radiation	$CuK\alpha (\lambda = 1.54184)$	
20 range for data collection/°	8.978 to 160.002	
Index ranges	$-12 \le h \le 11, -16 \le k \le 16, -12 \le l \le 12$	
Reflections collected	18324	
Independent reflections	5274 [$R_{int} = 0.0329, R_{sigma} = 0.0279$]	
Data/restraints/parameters	5274/1/361	
Goodness-of-fit on F ²	1.065	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0305, wR_2 = 0.0765$	
Final R indexes [all data]	$R_1 = 0.0310, wR_2 = 0.0770$	
Largest diff. peak/hole / e Å ⁻³	0.15/-0.20	



Figure S1. ORTEP representation of compound **2a** (thermal ellipsoids are shown at 50% probability)

Table S2. Crystal data and ORTEP representation for 5 (2144354)		
Empirical Formula	$C_{36}H_{26}N_2O_4$	
Formula weight	550.61	
Temperature, K	100(2)	
Crystal system	monoclinic	
Space group	I 2/a	
a/Å	13.9998(2)	
b/Å	13.5871(2)	
c/Å	17.2134(3)	
α/°	90	
β/°	108.553(2)	
γ/°	90	
Volume/Å ³	3104.11(9)	
Z	4	
ρ _{calc} g/cm ³	1.302	
μ/mm ⁻¹	0.695	
F(000)	1280	
Crystal size/mm ³	0.18 imes 0.16 imes 0.08	
Radiation	$CuK\alpha (\lambda = 1.54184)$	
20 range for data collection/°	4.2360 to 79.3520	
Index ranges	$-17 \le h \le 17, -10 \le k \le 17, -21 \le l \le 21$	
Reflections collected	11804	
Independent reflections	$3271 [R_{int} = 0.0405, R_{sigma} = 0.0370]$	
Data/restraints/parameters	3271/0/211	
Goodness-of-fit on F ²	1.074	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0370, wR_2 = 0.0942$	
Final R indexes [all data]	$R_1 = 0.0405, wR_2 = 0.0968$	
Largest diff. peak/hole / e Å ⁻³	0.283/-0.216	



Figure S2. ORTEP representation of compound **5** (thermal ellipsoids are shown at 50% probability)

3. Biological data

Cell culture

A549 lung cancer cells and WI-26 VA4 lung epithelial-like cells were purchased from the ATCC. A549 cells were maintained in F12-K (Corning, NY, USA) supplemented with 10% fetal bovine serum (Fetal Bovine Serum, qualified, Australia; Gibco, Loughborough, UK), penicillin (100 UI mL⁻¹), streptomycin (100 μ g mL⁻¹), and GlutaMax (1.9 mM, Gibco, UK). WI-26 VA4 cells were maintained in Advanced MEM (Gibco, Loughborough, UK) supplemented with 5% fetal bovine serum (Fetal Bovine Serum, qualified, Australia, Gibco, UK), penicillin (100 UI mL⁻¹), streptomycin (100 μ g mL⁻¹), and GlutaMax (1.87 mM, Gibco, UK), penicillin (100 UI mL⁻¹), streptomycin (100 μ g mL⁻¹), and GlutaMax (1.87 mM, Gibco, Loughborough, UK). All cells line cultivation under a humidified atmosphere of 95% air/5% CO₂ at 37°C. Subconfluent monolayers, in the log growth phase, were harvested by a brief treatment with TrypLE Express solution (Gibco, Loughborough, UK) in phosphate buffered saline (PBS, Capricorn Scientific, Germany) and washed three times in serum-free PBS. The number of viable cells was determined by trypan blue exclusion.

MTT assay

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The effects of the synthesized compounds on cell viability were determined using the MTT colorimetric test. All examined cells were diluted with the growth medium to 3.5×10^4 cells per mL and the aliquots $(7 \times 10^3 \text{ cells per } 200 \ \mu\text{L})$ were placed in individual wells in 96-well plates (Eppendorf, Hamburg, Germany) and incubated for 24 h. The next day, the cells were treated with synthesized compounds separately in concentration 250.0 μ M concentration and diluted at various concentrations for determination of IC₅₀ and incubated for 72 h at 37 °C in 5% CO₂ atmosphere. Each compound was tested in triplicate. After incubation, the cells were treated with 40 μ L MTT solution (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, 5 mg mL⁻¹ in PBS) and incubated for 4 h. After additional 4-h incubation, the medium with MTT was removed and DMSO (150 μ L) was added to dissolve the formazan crystals. The plates were shaken for 10 min. The optical density of each well was determined at 560 nm using GloMax Multi+ (Promega, Madison, WI, USA) microplate reader. Each of the tested compounds was evaluated for cytotoxicity in three separate experiments. All stock solutions for biological evaluations were prepared via dissolving synthesized compounds in DMSO.

References

- 1. Chupakhin, E. G.; Kantin, G. P.; Dar'in, D. V.; Krasavin, M. Convenient preparation of (*E*)-3arylidene-4-diazopyrrolidine-2,5-diones in array format. *Mendeleev Commun.* **2021**, *31*, 36-38.
- Chupakhin, E.; Gecht, M.; Ivanov, A.; Kantin, G.; Dar'in, D.; Krasavin, M. (*E*)-3-Arylidene-4diazopyrrolidine-2,5-diones: Preparation and Use in Rh^{II}-Catalyzed X–H Insertion Reactions towards Novel, Medicinally Important Michael Acceptors. *Synthesis* 2021, *53*, 1292-1300.
- Vepreva, A.; Kantin, G.; Krasavin, M.; Dar'in. A General Way to Spiro-Annulated 2-Benzoxepines via Rh₂(esp)₂-catalyzed [5+2] Cycloaddition of Diazo Arylidene Succinimides to Ketones. *Synthesis* 2022. doi: 10.1055/s-0037-1610790.
- Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
- 5. Sheldrick, G. M. SHELXT-Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A* **2015**, A71, 3-8.
- 6. Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr. Sect. A 2008, 64, 112–122.
- Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr. Sect. C 2015, 71, 3–8.

2. Copies of ¹H, ¹³C NMR, ¹⁹F and NOESY NMR spectra





Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 3a



Copies of 1 H (400.13 MHz, CDCl₃) and 13 C{ 1 H} (100.61 MHz, CDCl₃) spectra of **2b**



Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2c

Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2c





Copies of 1 H (400.13 MHz, CDCl₃) and 13 C{ 1 H} (100.61 MHz, CDCl₃) spectra of 2d



Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2e



Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2e



Copies of 1 H (400.13 MHz, CDCl₃) and 13 C{ 1 H} (100.61 MHz, CDCl₃) spectra of **2h**



Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2i

Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2i





Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2j

Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2j





Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2k

Copies of 1H (400.13 MHz, CDCl₃) and $^{13}C\{^1H\}$ (100.61 MHz, CDCl₃) spectra of 4k

Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 4k

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2l

Copy of $^{19}F\{^1H\}$ (376.50 MHz, CDCl₃) spectrum of 2l

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2m

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2n

Copies of 1 H (400.13 MHz, CDCl₃) and 13 C{ 1 H} (100.61 MHz, CDCl₃) spectra of **30**

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 3p

Copies of 1H (400.13 MHz, CDCl₃) and $^{13}C\{^1H\}$ (100.61 MHz, CDCl₃) spectra of 3q

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 2r

Copies of ¹H (400.13 MHz, CDCl₃) and ¹³C{¹H} (100.61 MHz, CDCl₃) spectra of 3r

Copies of 1 H (400.13 MHz, CDCl₃) and 13 C{ 1 H} (100.61 MHz, CDCl₃) spectra of 5