Supporting Information

for

Synthesis of dibenzosuberenone-based novel polycyclic \(\pi\)-conjugated dihydropyridazines, pyridazines and pyrroles

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Experimental procedures, copies of \(^1\)H NMR, \(^{13}\)C NMR, and HRMS(Q-TOF) spectra
Experimental

General

The one and two dimensional $^1$H and $^{13}$C NMR spectra were recorded on a Varian-400 or a Bruker-400 spectrometer in CDCl$_3$, CD$_3$CN, and DMSO-$d_6$ using tetramethylsilane as the internal reference. All spectra were recorded at 25 °C and coupling constants ($J$ values) are given in Hz. Chemical shifts are given in parts per million (ppm). Abbreviations used to define the multiplicities are as follows: s = singlet; d = doublet; dd = doublet of doublets; m = multiplet. Mass spectra were recorded on an Agilent Technologies 6530 Accurate-Mass Q-TOF–LC/MS spectrometer. Absorption spectrometry was performed using a Perkin Elmer Lambda 35 spectrophotometer. Steady-state fluorescence measurements were conducted using a Shimadzu RF-5301PC spectrofluorometer. Stock solutions of 3c-f and 3k ($1 \times 10^{-3}$ M) were prepared in acetonitrile. The concentration of 3c–f and 3k for all spectroscopy measurement was kept at 5 µM by diluting the stock solution. The reactions under microwave irradiation were carried out in a 300W CEM Discover microwave reactor.

General procedure A: Invers-Diels–Alder cycloaddition reactions between dibenzosuberenone (1) and tetrazine derivatives

Dibenzosuberenone (1) or p-quinone metide 11 and tetrazine 2 were dissolved in toluene in an ACE pressure tube. The reaction mixture was head and stirred. At the end of the reaction, the red color of tetrazine disappeared. The mixture was cooled to rt and some of the solvent was evaporated under reduced pressure. The precipitated product was purified by crystallization or silica gel column chromatography to give dihydropyridazines.

General procedure B: Oxidation with PIFA

To a solution of 3, 13 or 15 in 20 mL of CH$_2$Cl$_2$ was added PIFA and this was stirred at room temperature for 1 h to overnight. The solvent was evaporated, and the crude product was purified by column chromatography and crystallization to give corresponding oxidized products 4, 14 and 16.

General procedure C: Ring contraction of pyridazines to pyrroles

Zinc dust was added to a solution of pyridazine 4a,b and 13a,b in 10 mL of glacial acetic acid and the reaction was stirred. At the end of the reaction, mixture was filtered through Celite®, the filtrate was neutralized with the addition of saturated aqueous NaHCO$_3$, and extracted with EtOAc (2 × 25). The combined organic layer was dried over Na$_2$SO$_4$ and evaporated under vacuo. The obtained solid was purified by column
1,4-Di(pyridin-4-yl)-2,4a-dihydro-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (3c)

The reaction was performed according to the general procedure A with 1 (1.0 g, 4.85 mmol) and tetrazine 2c (575 mg, 2.43 mmol) in 3 mL toluene at 125 °C for 16 h. The precipitated product was filtered, washed with EtO and recrystallized from n-hexane/CH₂Cl₂ (1:9) to give 3c as yellow crystals (yield 1.93 g, 96%). Mp: 294-296 °C. ^1H-NMR (400 M Hz, CDCl₃): δ= 8.60 (d, J = 5.8 Hz, 2H), 8.57-8.52 (m, 3H), 8.28 (bs, NH, 1H), 7.98 (dd, J = 7.0 Hz, J = 1.4 Hz, 1H), 7.61 (d, J = 5.9 Hz, 2H), 7.44-7.33 (m, 3H), 7.20-7.13 (m, 3H), 6.86 (d, J = 7.5 Hz, 2H), 5.15 (s, 1H). ^13C-NMR (100 M Hz, CDCl₃): δ= 193.4, 150.8, 150.4, 142.9, 141.9, 138.41, 137.37, 137.3, 137.1, 135.6, 132.7, 132.5, 132.2, 132.0, 131.9, 131.6, 127.71, 127.65, 124.0, 123.95, 120.2, 106.1, 40.9. HRMS (Q-TOF): m/z [M + H]^+ calcd for C₂₇H₁₉N₄O: 415.1559, found: 415.1549.

1,4-Bis(3,5-dimethyl-1H-pyrazol-1-yl)-2,4a-dihydro-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (3d).

The reaction was performed according to the general procedure A with 1 (1.14 g, 5.55 mmol) and tetrazine 2d (1.0 g, 3.70 mmol) in 2 mL toluene at 120 °C for 48 h. The product was purified by column chromatography (SiO₂, n-hexane/EtOAc (4:1) to give 3d as an orange solid (yield 1.44 g, 87%). Mp: 228-230 °C. ^1H-NMR (400 M Hz, CDCl₃): δ= 8.46 (d, J = 7.9 Hz, 1H), 7.84 (bs, NH, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 7.4 Hz, 1H), 7.28-7.23 (m, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.68 (d, J = 7.7 Hz, 1H), 5.90 (s, 1H), 5.75 (s, 1H), 5.72 (s, 1H), 2.61 (s, 3H), 2.27 (s, 3H), 2.08 (s, 3H), 1.12 (s, 3H). ^13C-NMR (100 M Hz, CDCl₃): δ= 194.2, 151.3, 149.7, 142.5, 141.8, 138.4, 137.6, 137.5, 137.4, 136.2, 132.9, 132.2, 131.6, 131.3, 129.8, 129.2, 127.2, 127.0, 123.4, 109.4, 107.8, 100.5, 42.6, 14.8, 13.8, 13.7, 10.4. HRMS (Q-TOF): m/z [M + H]^+ calcd for C₂₇H₂₆N₁₅O: 449.2090, found: 449.2085.

9-Oxo-4a,9-dihydro-2H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarboxamide (3e)

The reaction was performed according to the general procedure A with 1 (1.0 g, 4.85 mmol) and tetrazine 2e (163 mg, 0.97 mmol) at 100 °C for overnight (solvent free). The product was filtered, washed with Et₂O and recrystallized from n-hexane/CH₂Cl₂ (1:9) to give 3e as green crystals (yield 292 mg, 95%). Mp: 282-283 °C decomposition. ^1H-NMR (400 M Hz, DMSO-d₆): δ= 10.79 (bs, 1H, NH), 8.35 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.69-7.63 (m, 2H), 7.60 (s, 1H), 7.58-7.45 (m, 4H), 7.38 (s, 1H), 7.35 (d, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 4.99 (s, 1H). ^13C-NMR (100 M Hz, DMSO-d₆): δ= 192.8, 165.5, 164.7, 138.6, 138.4, 138.1, 136.2, 132.5, 132.2, 131.2, 131.0, 130.4, 130.0, 129.7, 127.5, 126.7, 123.2, 105.2, 36.6. HRMS (Q-TOF): m/z [M + H]^+ calcd for C₁₉H₁₅N₄O₃: 347.1144, found: 347.1137.
9-Oxo-4a,9-dihydro-2H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarbonitrile (3f)

The reaction was performed according to the general procedure A with 1 (500 mg, 2.42 mmol) and tetrazine 2f (160 mg, 1.21 mmol) in 5 mL toluene at 100 °C for 2 h. The precipitated product was filtrated, washed with Et₂O and recrystallized from n-hexane/CH₂Cl₂ (1:9) to give 3f as green crystals (yield 1.31g, 87%). Mp: 245-246 ˚C.

1H-NMR (400 M Hz, CDCl₃): δ= 8.53 (dd, J = 7.1 Hz, J = 1.5 Hz, 1H), 8.39 (bs, 1H, NH), 7.88 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.1 Hz, 1H), 7.73-7.64 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 4.94 (s, 1H).

13C-NMR (100 M Hz, CDCl₃): δ= 192.1, 138.4, 137.2, 133.9, 133.23, 133.18, 132.9, 132.3, 131.2, 129.3, 129.0, 123.6, 122.45, 115.4, 114.5, 112.6, 107.8, 41.9. HRMS (Q-TOF): m/z [M + H]+ calcd for C₁₉H₁₁N₄O: 311.0933, found: 311.0931.

Reaction of Dibenzosuberenone (1) with 3,6-dichloro-1,2,4,5-tetrazine (2k).

The reaction was performed according to the general procedure A with 1 (1.14 g, 5.55 mmol) and tetrazine 2k (0.56 g, 3.70 mmol) in 10 mL toluene at 120 °C for 48 h. The crude reaction products was purified by column chromatography on silica gel (10% EtOAc/n-hexane).

1. Fraction: 1,4-Dichloro-2,4a-dihydro-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (3k). Yellow solid (yield 164 mg, 27%). Mp: 223-224 ˚C. 1H-NMR (400 M Hz, CDCl₃): δ=8.49 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 7.87 (dd, J = 7.6 Hz, J = 1.3 Hz, 1H), 7.83 (dd, J = 7.7 Hz, J = 1.0 Hz, 1H), 7.57 (dt, J = 7.6 Hz, J = 1.5 Hz, 1H), 7.53 (dt, J = 7.7 Hz, J = 1.3 Hz, 1H), 7.48 (dt, J = 8.0 Hz, J = 1.3 Hz, 1H), 7.41 (s, 1H, NH), 7.40 (dt, J = 7.6 Hz, J = 1.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 4.90 (s, 1H). 13C-NMR (100 M Hz, CDCl₃): δ=192.9, 138.4, 136.3, 136.0, 135.5, 134.4, 132.7, 132.5, 131.9, 131.8, 130.2, 128.1, 127.9, 124.7, 123.1, 102.8, 50.0. HRMS (Q-TOF): m/z [M + H]+ calcd for C₁₇H₁₁Cl₂N₂O: 329.0248, found: 329.0248.

2. Fraction: 1,4-Dichloro-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (4k). Colorless solid (yield 199 mg, 33%). Mp: 257-258 °C. 1H-NMR (400 M Hz, CDCl₃): δ=7.96-7.90 (m, 2H), 7.63-7.56 (m, 6H). 13C-NMR (100 M Hz, CDCl₃): δ=196.1, 155.8, 146.2, 135.9, 131.42, 131.39, 130.0, 127.3, 126.0. HRMS (Q-TOF): m/z [M + H]+ calcd for C₁₇H₉Cl₂N₂O: 327.0092, found: 327.0088.

Reaction of dibenzosuberenone (1) with 3,6-dibromo-1,2,4,5-tetrazine (3l).

The reaction was performed according to the general procedure A with 1 (1.0 g, 4.85 mmol) and tetrazine 2l (235 mg, 0.98 mmol) at 100 °C for overnight (solvent free). The crude reaction products was purified by recrystallization from CH₂Cl₂/n-Hexane (9:1). Pyridazine 4l was obtained by first crystallization. Then recrystallization of the residue afforded diboromo 5l.
1. Fraction: 1,4-Dibromo-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (4l). Colorless solid (yield 186 mg, 46%). Mp: 300–301 °C. 1H-NMR (400 M Hz, CDCl₃): δ=7.98-7.92 (m, 2H), 7.61-7.53 (m, 6H). 13C-NMR (100 M Hz, CDCl₃): δ=196.0, 149.8, 146.1, 137.4, 131.7, 131.4, 129.9, 128.8, 125.8. HRMS (Q-TOF): m/z [M + H]+ calcd for C₁₇H₁₇Br₂N₂O: 416.9061, found: 416.9045.

2. Fraction: 10,11-dibromo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (5l). Colorless solid (yield 107 mg, 30%). Mp 204-206 °C. 1H-NMR (400 M Hz, CDCl₃): δ=7.09 (dd, J = 7.9 Hz, J = 1.5 Hz, 2H), 7.57 (dt, J = 7.3 Hz, J = 1.5 Hz, 2H), 7.50 (dt, J = 7.9 Hz, J = 1.5 Hz, 2H), 7.41 (d, J = 7.3 Hz, J = 1.5 Hz, 2H), 5.80 (s, 2H). 13C-NMR (100 M Hz, CDCl₃): δ=122.3, 130.5, 129.0, 129.0, 126.1, 125.0, 123.2. HRMS (Q-TOF): m/z [M + H]+ calcd for C₁₅H₁₁Br₂O: 364.9177, found: 364.9165.

Dimethyl 9-oxo-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarboxylate (4a)

The reaction was performed according to the general procedure B with 3a (1 g, 2.66 mmol) and PIFA (1.14 g, 2.66 mmol) at room temperature °C for 1 h. The product was purified by gradient chromatography (Al₂O₃, hexane then CH₂Cl₂/EtOAc (1:1)) and recrystallization from CH₃COOH to give 4a as a colorless crystal (945 mg, 95% yield). mp = 224-225 °C. 1H-NMR (400 M Hz, CDCl₃): δ= 7.76-7.72 (m, 2H), 7.66-7.55 (m, 6H), 3.80 (s 6H). 13C-NMR (100 M Hz, CDCl₃): δ= 195.3, 165.8, 154.9, 145.1, 133.2, 131.3, 131.1, 128.9, 128.5, 127.3. HRMS (Q-TOF): m/z [M + H]+ calcd. for C₂₁H₁₅N₂O₅: 375.0981, found: 375.0974.

1,4-Di(pyridin-2-yl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (4b)

The reaction was performed according to the general procedure B with 3b (1 g, 2.41 mmol) and PIFA (1.04 g, 2.41 mmol) at room temperature °C for 1 h. The product was purified by gradient chromatography (Al₂O₃, hexane then MeOH/EtOAc (1:4)) and recrystallization from MeOH/diethyl ether (9:1) to give 4b as a colorless crystal (896 mg, 90% yield). Mp = 248 °C (decomposition). 1H-NMR (400 M Hz, CDCl₃): δ= 8.49 (bd, J = 4.7 Hz, 2H), 7.73 (dt, J = 7.7 Hz, J = 1.7 Hz, 2H), 7.67-7.62 (m, 4H), 7.37 (dt, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.27 (m, 2H), 7.05 (dt, J = 7.7 Hz, J = 1.3 Hz, 2H), 6.98 (bd, J = 7.8 Hz, 2H). 13C-NMR (100 M Hz, CDCl₃): δ= 196.8, 158.8, 156.4, 149.3, 146.0, 136.5, 133.9, 131.7, 130.2, 129.53, 129.46, 126.2, 125.0, 123.2. HRMS (Q-TOF): m/z [M + H]+ calcd. for C₂₇H₁₇N₄O: 413.1402, found: 413.1392.

1,4-Di(pyridin-4-yl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-one (4c)

The reaction was performed according to the general procedure B with 3c (1.0 g, 2.41 mmol) and PIFA (1.56 g, 3.62 mmol) at room temperature °C for overnight. The product was purified by column chromatography (SiO₂, n-hexane/EtOAc (3:7)) and recrystallization from MeOH/diethyl ether (9:1) to give 4c as a colorless crystal (866 mg, 87% yield). Mp > 300 °C. 1H-NMR (400 MHz, DMSO-d₆): δ= 8.59 (d, J = 4.7 Hz, 2H), 7.92 (dd, J = 7.9 Hz, J = 1.5 Hz, 2H), 7.67 (dt, J = 7.7 Hz, J = 1.5 Hz, 2H), 7.55 (m, 2H), 7.27 (m, 2H), 7.05 (dt, J = 7.7 Hz, J = 1.3 Hz, 2H), 6.98 (bd, J = 7.8 Hz, 2H). 13C-NMR (100 M Hz, CDCl₃): δ= 196.8, 158.8, 156.4, 149.3, 146.0, 136.5, 133.9, 131.7, 130.2, 129.53, 129.46, 126.2, 125.0, 123.2. HRMS (Q-TOF): m/z [M + H]+ calcd. for C₂₇H₁₇N₄O: 413.1402, found: 413.1392.
1,4-Bis(3,5-dimethyl-1H-pyrazol-1-yl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyrazidin-9-one (4d)

The reaction was performed according to the general procedure B with 3d (500 mg, 1.11 mmol) and PIFA (575 mg, 1.34 mmol) at room temperature for 4 h. The product was purified by column chromatography (SiO$_2$, n-hexane/EtOAc (7:3)) and recrystallization from CH$_2$Cl$_2$/n-hexane (9:1) to give 4d as a white crystal (453 mg, 91% yield). mp = 315-317 °C (decomposed). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.60 (d, $J = 7.6$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 7.9$ Hz, 2H), 5.92 (s, 2H), 2.17 (s, 6H), 2.00 (s, 6H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 195.9, 153.9, 151.1, 146.0, 141.8, 133.9, 130.4, 130.4, 129.0, 127.9, 126.4, 107.7, 13.6, 11.4. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{27}$H$_{23}$N$_6$O: 447.1933, found: 447.1924.

9-Oxo-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarbonitrile (4f)

The reaction was performed according to the general procedure B with 3f ((500 mg, 1.61 mmol) and PIFA (693 mg, 1.61 mmol) at room temperature for overnight. The product was purified by column chromatography (SiO$_2$, n-hexane/EtOAc (4:1)) to give 4f as a white solid (392 mg, 79% yield). mp > 300 °C. $^1$H-NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.33 (d, $J = 7.0$ Hz, 2H), 7.91-7.82 (m, 4H), 7.77-7.72 (m, 2H). $^{13}$C-NMR (100 MHz, DMSO-$d_6$): $\delta$ = 193.7, 145.1, 140.0, 138.0, 132.8, 131.5, 130.8, 129.5, 128.7, 125.9. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{19}$H$_{13}$N$_4$O$_3$: 345.0988, found: 345.0979.

Caution: When working with nitrous gases a well ventilated fume hood is essential.

9-Oxo-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarboxamide (4e)

Nitrous gases, generated by adding conc. HCl (4.00 mL) to a solution of NaNO$_2$ (2.48 g) in water (6.00 mL), were bubbled at 0 °C through a solution of dihydropyridazine 3e (100 mg, 0.30 mmol) in CH$_2$Cl$_2$ (20.0 mL). The reaction mixture was stirred at the same temperature for 1 h. Excess gases and the some solvent were removed under reduced pressure. After the precipitated product was filtered and wash with CH$_2$Cl$_2$, pyridazine 4e (82.5 mg, 83%) was obtained as a white solid. mp > 300 °C. $^1$H-NMR (400 MHz, DMSO-$d_6$): $\delta$ = 8.36 (bs, NH, 2H), 7.95 (bs, NH, 2H), 7.89-7.85 (m, 2H), 7.69-7.57 (m, 6H). $^{13}$C-NMR (100 MHz, DMSO-$d_6$): $\delta$ = 196.0, 167.5, 157.4, 144.68, 131.73, 130.9, 130.8, 129.5, 128.7, 125.9. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{19}$H$_{13}$N$_4$O$_3$: 345.0988, found: 345.0979.
Dimethyl 8-oxo-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrole-1,3-dicarboxylate (10aa)

The reaction was performed according to the general procedure C with 4a (500 mg, 1.34 mmol) and Zinc dust (436.6 mg, 6.68 mmol) at room temperature °C for overnight. The product was purified by column chromatography (SiO₂, EtOAc/n-Hexane (1:4) and recrystallization from CH₂Cl₂ to give 10aa as a colorless crystal (369 mg, 82% yield). mp = 249-250 °C. ¹H-NMR (400 MHz, CDCl₃): δ= 10.11 (bs, NH, 1H), 7.80 (dd, J = 7.8 Hz, J = 1.1 Hz, 2H), 7.60 (dd, J = 7.5 Hz, J = 1.5 Hz, 2H), 7.49 (dt, J = 7.6 Hz, J = 1.6 Hz, 2H), 7.44 (dt, J = 7.5 Hz, J = 1.3 Hz, 2H), 3.86 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ= 199.7, 160.2, 143.0, 131.4, 129.6, 128.5, 128.3, 127.7, 126.3, 121.3, 52.1. HRMS (Q-TOF): m/z [M + H]⁺ calcd. for C₂₁H₁₈NO₅: 362.1028, found: 362.1028.

Dimethyl 8-hydroxy-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrole-1,3-dicarboxylate 10ab

The reaction was performed according to the general procedure C with 4a (500 mg, 1.34 mmol) and Zinc dust (873 mg, 13.36 mmol) at room temperature for overnight. The product was purified by column chromatography (SiO₂, EtOAc/n-Hexane (1:4) and recrystallization from CH₂Cl₂ to give 10aa as a colorless crystal (359 mg, 74% yield). mp = 245-246 °C. ¹H-NMR (400 MHz, CDCl₃): δ= 10.08 (bs, 1H, NH), 7.72 (bd, J = 7.8 Hz, 2H), 7.57 (dd, J = 7.6 Hz, J = 0.8 Hz, 2H), 7.37 (dt, J = 7.7 Hz, J = 1.0 Hz, 2H), 7.21 (dt, J = 7.5 Hz, J = 1.1 Hz, 2H), 5.45 (s, 1H), 3.84 (s, 6H), 2.25 (bs, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ= 160.7, 143.7, 130.9, 129.1, 128.4, 126.7, 125.5, 120.7, 120.0, 70.3, 52.0. HRMS (Q-TOF): m/z [M + H]⁺ calcd. for C₂₁H₁₈NO₅: 364.1185, found: 364.1171.

2,8-Dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8-ol (10ac)

A 10 mL round bottom microwave vial equipped with a stir bar was charged with pyrrole 10ab (200 mg 0.55 mmol), KOH (123.5 mg, 2.20 mmol) and 5 mL THF/CH₂OH/H₂O (2:2:1) solvent mixture. The vial was sealed and the reaction was irradiated (200W) in the microwave reactor at 150 °C for 2 h. The reaction mixture was extracted with EtOAc (2 × 25). The combined organic layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure to give 10ac as a brown solid (97mg, 70% yield). ¹H-NMR (400 MHz, DMSO-d₆): δ= 11.40 (s, NH, 1H), 7.70 (d, J = 7.4 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.30-7.13 (m, 6H), 5.96 (d, J = 3.9 Hz, 1H), 5.28 (bs, 1H). ¹³C-NMR (100 MHz, DMSO-d₆): δ= 142.4, 132.1, 127.27, 126.8, 126.2, 123.2, 122.6, 115.7, 69.8. HRMS (Q-TOF): m/z [M + Na]⁺ calcd. for C₁₇H₁₄NO: 270.0895, found: 270.0900.

1,3-Di(pyridin-2-yl)-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8-yl acetate (10ba)
The reaction was performed according to the general procedure C with 4b (500 mg, 1.21 mmol) and Zinc dust (1.59 g, 24.25 mmol) at 118 °C for 2 h. The product was crystallized from MeOH/diethyl ether (9:1) to give 10ba as a yellow crystal (409 mg, 76% yield). mp = 254-255 °C. 1H-NMR (400 MHz, CDCl₃): δ= 10.68 (bs, NH, 1H), 8.56 (bd, J = 4.7 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.38 (dt, J = 7.6 Hz, J = 1.7 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.23 (dt, J = 7.6 Hz, J = 1.0 Hz, 2H), 7.08-6.99 (m, 4H), 6.77 (s, 1H), 2.34 (s, 3H).

13C-NMR (100 MHz, CDCl₃): δ= 169.6, 150.4, 149.5, 139.8, 135.9, 130.1, 129.6, 128.4, 127.4, 126.5, 122.6, 121.4, 121.2, 121.1, 72.4, 21.3. HRMS (Q-TOF): m/z [M + H]⁺ calcd. for C₂₉H₂₂N₃O₂: 444.1712, found: 444.1702.

1,3-Di(pyridin-2-yl)-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8-ol (10bb)

To a solution of 10ba (500 mg, 1.13 mmol) in 10 mL of H₂O/EtOH (1:3) was added KOH (94.88 mg, 1.69 mmol) and stirred at room temperature for 4h. The reaction mixture was extracted with EtOAc (2 × 25). The combined organic layer was dried over Na₂SO₄ and evaporated under vacuo. The product was purified by column chromatography (SiO₂, EtOAc/n-Hexane (4:6) and recrystallization from CH₂Cl₂/n-hexane (9:1) to give 10bb as a yellow crystal (363 mg, 80% yield). mp = 273-274 °C. 1H-NMR (400 MHz, CDCl₃): δ= 10.76 (bs, NH, 1H), 8.62 (d, J = 4.6 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.50-7.30 (m, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.15-7.06 (m, 4H), 5.90 (s, 1H), 2.51 (s, 1H).

13C-NMR (100 MHz, CDCl₃): δ= 200.8, 150.6, 149.7, 142.5, 135.9, 131.4, 129.9, 129.4, 128.1, 127.5, 126.2, 123.2, 121.4(2C), 121.0, 70.7. HRMS (Q-TOF): m/z [M + H]⁺ calcd. for C₂₇H₂₀N₃O: 402.1606, found: 402.1605.

1,3-Di(pyridin-2-yl)dibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8(2H)-one (10bc)

To a solution of 10bb (500 mg, 1.25 mmol) in 10 mL of CH₂Cl₂ was added MnO₂ (1.08 g, 12.45 mmol) and stirred at room temperature for 3h. The solvent was evaporated under reduced pressure and the reaction mixture was filtered through Celite. The product was crystallized from MeOH/diethyl ether (9:1) to give 10ba as a yellow crystal (388 mg, 78% yield). mp = 244-245 °C. 1H-NMR (400 MHz, CDCl₃): δ= 10.50 (bs, NH, 1H), 8.64 (d, J = 4.6 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.41-7.30 (m, 6H), 7.15-7.09 (m, 2H). 13C-NMR (100 MHz, CDCl₃): δ= 200.8, 150.6, 149.7, 142.5, 135.9, 131.4, 130.4, 130.1, 130.0, 127.4, 127.3, 121.7, 121.4, 121.2. HRMS (Q-TOF): m/z [M + H]⁺ calcd. for C₂₇H₁₈N₃O: 402.1450, found: 402.1440.

Dimethyl 9-(4-hydroxyphenyl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarboxylate (13a)

The reaction was performed according to the general procedure A with 11 (500 mg, 1.77 mmol) and DET 2a (351 mg, 1.77 mmol) in 5 mL toluene at 80 °C for overnight.
The product was purified by column chromatography (SiO$_2$, n-hexane/EtOAc (1,5:8,5) to give 13a as a white solid (697 mg, 95% yield). mp = 270-271 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta=7.55-7.47$ (m, 4H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 2H), 6.68 (d, $J = 8.5$ Hz, 2H), 6.41 (d, $J = 8.5$ Hz, 2H), 5.37 (s, 1H), 4.92 (s, 1H), 3.85 (s, 6H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta=166.0, 154.0, 152.7, 147.5, 135.3, 130.9, 130.8, 130.1, 129.5, 129.3, 128.8, 127.0, 114.5, 56.3, 53.0$. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{27}$H$_{21}$N$_2$O$_5$: 453.1450, found: 453.1448.

4-(1,4-Di(pyridin-2-yl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-yl)phenol (13b)

The reaction was performed according to the general procedure A with 11 (500 mg, 1.77 mmol) and DPT 2b (841 mg, 1.77 mmol) in 5 mL toluene at 80 °C for 3 day. The mixture was cooled to room temperature and the precipitated product was filtrated, washed with Et$_2$O to give 13b as a white solid (808 mg, 93% yield). mp > 300 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta=8.61$ (d, $J = 4.6$ Hz, 2H), 7.82 (t, $J = 7.8$ Hz, 2H), 7.55 (d, $J = 7.5$ Hz, 2H), 7.46-7.39 (m, 2H), 7.37 (d, $J = 7.8$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 6.88 (t, $J = 7.6$ Hz, 2H), 6.83 (d, $J = 7.6$ Hz, 2H), 6.52 (d, $J = 8.4$ Hz, 2H), 5.53 (s, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta=158.6, 157.5, 156.8, 150.2, 149.5, 138.1, 138.0, 133.7, 132.1, 131.3, 130.8, 130.4, 126.8, 126.2, 124.9, 115.5, 57.9$. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{33}$H$_{23}$N$_4$O: 491.1872, found: 491.1872.

Dimethyl 9-(4-oxocyclohexa-2,5-dien-1-ylidene)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazine-1,4-dicarboxylate (14a)

The reaction was performed according to the general procedure B with 13a (500 mg, 1.11 mmol) and PIFA (570 mg,1.33 mmol) at room temperature for overnight. The product was purified by gradial chromatography (Al$_2$O$_3$, n-hexane then CH$_2$Cl$_2$/EtOAc (9:1)) and recrystallization from CH$_2$Cl$_2$/n-hexane (9:1) to give 14a as a yellow crystal (453 mg, 90% yield). mp = 253-254 °C. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta=7.59$ (t, $J = 7.5$ Hz, 2H), 7.54 (d, $J = 7.7$ Hz, 2H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.42-7.35 (m, 4H), 6.43 (d, $J = 10.0$ Hz, 2H), 3.89 (s, 6H).$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta=186.8, 165.9, 154.2, 151.6, 143.2, 136.4, 134.7, 130.8, 130.5, 129.7, 129.2, 129.2, 128.8, 128.0, 77.5, 77.2, 76.8, 53.5$. HRMS (Q-TOF): m/z [M + H]$^+$ calcd. for C$_{27}$H$_{19}$N$_2$O$_5$: 451.1294, found: 451.1283.

4-(1,4-Di(pyridin-2-yl)-9H-dibenzo[3,4:6,7]cyclohepta[1,2-d]pyridazin-9-ylidene)cyclohexa-2,5-dien-1-one (14b)

The reaction was performed according to the general procedure B with 13b (500 mg, 1.02 mmol) and PIFA (526 mg,1.22 mmol) at room temperature for overnight. The product was purified by gradial chromatography (Al$_2$O$_3$, n-hexane then EtOAc/MeOH (9:1)) and recrystallization from then MeOH/diethyl ether (9:1) to give 14b as a yellow
crystal (433 mg, 87% yield). mp = 272-273 °C. 1H-NMR (400 MHz, CDCl3): δ= 8.48 (d, J = 4.7 Hz, 2H), 7.79-7.74 (m, 4H), 7.64 (d, J = 10.1 Hz, 2H), 7.35-7.23 (m, 6H), 7.01-6.95 (m, 2H), 6.92 (d, J = 7.6 Hz, 2H), 6.51 (d, J = 10.1 Hz, 2H). 13C-NMR (100 MHz, CDCl3): δ= 187.0, 158.3, 156.3, 154.5, 149.3, 143.7(2C), 137.1, 136.5, 135.0, 131.4, 130.9, 130.10, 128.8, 127.3, 126.9, 124.9, 123.2. HRMS (Q-TOF): m/z [M + H]+ calcd. for C33H21N4O: 489.1715, found: 489.1700.

Dimethyl 8-(4-hydroxyphenyl)-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrole-1,3-dicarboxylate (15a)

The reaction was performed according to the general procedure C with 13a (500 mg, 1.1 mmol) and Zinc dust (722 mg, 11.1 mmol) at room temperature for overnight. The product was crystallized from MeOH/diethyl ether (9:1) to give 15a as a white crystal (301 mg, 62% yield). mp = 302-303 °C. 1H-NMR (400 MHz, Acetone-d6): δ = 10.86 (s, NH, 1H), 7.82 (s, OH, 1H), 7.63 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 6.36 (d, J = 8.5 Hz, 2H), 5.33 (s, 1H), 3.74 (s, 6H). 13C-NMR (100 MHz, Acetone-d6): δ = 161.1, 155.8, 144.9, 133.3, 133.0, 130.8, 129.9, 128.8, 128.5, 126.6, 120.9, 114.7, 57.7. HRMS (Q-TOF): m/z [M + H]+ calcd. for C27H22NO5: 440.1498, found: 440.1490.

4-(1,3-Di(pyridin-2-yl)-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8-yl)phenol (15b)

The reaction was performed according to the general procedure C with 13b (500 mg, 1.02 mmol) and Zinc dust (666 mg, 10.2 mmol) at room temperature for overnight. The product was crystallized from MeOH/diethyl ether (9:1) to give 15b as a brown crystal (278 mg, 57% yield). mp = 303-304 °C. 1H-NMR (400 MHz, CDCl3): δ = 10.15 (s, NH, 1H), 8.51 (d, J = 4.6 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 6.34 (d, J = 8.5 Hz, 2H), 5.32 (s, 1H), 3.74 (s, 6H). 13C-NMR (100 MHz, CDCl3): δ = 153.1, 150.8, 149.3, 143.2, 135.7, 134.1, 131.9, 131.5, 130.0, 127.7, 127.6, 127.4, 126.6, 123.6, 121.0, 120.6, 114.1, 57.6. HRMS (Q-TOF): m/z [M + H]+ calcd. for C33H24N3O: 478.1919, found: 478.1909.

Dimethyl 8-(4-oxocyclohexa-2,5-dien-1-ylidene)-2,8-dihydrodibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrole-1,3-dicarboxylate (16a)

The reaction was performed according to the general procedure B with 15a (500 mg, 1.02 mmol) and PIFA (526 mg, 1.22 mmol) at room temperature for overnight. The product was purified by gradial chromatography (Al2O3, n-hexane then CH2Cl2) and recrystallization from then CH2Cl2/n-hexane (9:1) to give 16a as a yellow crystal (444 mg, 89% yield). mp = 303-304 °C. 1H-NMR (400 MHz, CDCl3): δ = 9.98 (s, NH, 1H), 7.85-7.75 (m, 2H), 7.47 (d, J = 10.0 Hz, 2H), 7.44-7.36 (m, 4H), 7.37 (d, J = 10.0 Hz, 2H), 3.88 (s, 6H). 13C-NMR (100 MHz, CDCl3): δ = 187.3, 160.4,
158.2, 139.8, 137.8, 131.8, 129.0, 128.9, 128.8, 128.2, 127.7, 127.4, 120.7, 52.2. HRMS (Q-TOF): m/z [M + H]+ calcd. for C_{27}H_{20}NO_{5}: 438.1341, found: 438.1331.

4-(1,3-Di(pyridin-2-yl)dibenzo[3,4:6,7]cyclohepta[1,2-c]pyrrol-8(2H)-ylidene)cyclohexa-2,5-dien-1-one (16b)

DDQ (238 mg, 1.05 mmol) and 15b (500 mg, 1.05 mmol) were dissolved in 20 mL CH_{2}Cl_{2} and stirred at room temperature for 30 min. The reaction mixture was washed with 20 mL of 5% NaHCO_{3} solution and H_{2}O (2x20 mL). The organic phase was dried over Na_{2}SO_{4} and the solvent was evaporated under reduced pressure to give 16b as a yellow solid (483 mg, 97% yield). mp > 300 °C. ^1H-NMR (400 MHz, CDCl_{3}): δ = 10.60 (s, NH, 1H), 8.62 (d, J = 4.7 Hz, 2H), 7.66–7.58 (m, 4H), 7.50 (dt, J = 7.8 Hz, J = 1.7 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.40-7.31 (m, 4H), 7.31-7.24 (m, 2H), 7.11 (dd, J = 6.4 Hz, J = 5.5 Hz, 2H), 6.43 (d, J = 10.1 Hz, 2H). ^13C-NMR (100 MHz, CDCl_{3}): δ = 187.3, 159.8, 150.5, 149.8, 139.3, 137.8, 136.0, 131.8, 130.7, 129.4, 129.2, 128.5, 128.4, 128.3, 127.2, 122.4, 121.7, 121.1. HRMS (Q-TOF): m/z [M + H]+ calcd. for C_{33}H_{22}N_{3}O: 476.1763, found: 476.1750.

Table 1. Some photophysical properties of cycloadducts 3c-3f and 3k.

| Compound | λ_{ems}/nm (λ_{exc}/nm) | λ_{abs}/nm | Stokes shift (nm) | Quantum yields (Φ_F) | ε (M^{-1}.cm^{-1}) |
|----------|------------------------|------------|-------------------|----------------------|-------------------|
| 3c       | 534 (400)              | 427        | 107               | 0.78                 | 5867              |
| 3d       | 539 (375)              | 408        | 131               | 0.60                 | 4987              |
| 3e       | 515 (360)              | 393        | 122               | 0.53                 | 3749              |
| 3f       | 487 (350)              | 378        | 109               | 0.28                 | 6044              |
| 3k       | 503 (350)              | 378        | 125               | 0.16                 | 5261              |
$^1$H NMR, $^{13}$C NMR, and HRMS Spectra:

**Fig. S1.** $^1$H-NMR spectrum of 3a (400 MHz, CDCl$_3$).
Fig. S2. $^{13}$C-NMR spectrum of 3a (100 MHz, CDCl$_3$).

Fig. S3. $^1$H-NMR spectrum of 3b (400 MHz, CDCl$_3$).
Fig. S4. $^{13}$C-NMR spectrum of 3b (100 MHz, CDCl$_3$).

Fig. S5. $^1$H-NMR spectrum of 3c (400 MHz, CDCl$_3$).
Fig. S6. $^{13}$C-NMR spectrum of 3c (100 MHz, CDCl$_3$).

Fig. S7. $^1$H-NMR spectrum of 3d (400 MHz, CDCl$_3$).
Fig. S8. $^{13}$C-NMR spectrum of 3d (100 MHz, CDCl$_3$).

Fig. S9. $^1$H-NMR spectrum of 3e (400 MHz, DMSO-$d_6$).
Fig. S10. $^{13}$C-NMR spectrum of 3e (100 MHz, DMSO-$d_6$).

Fig. S11. $^1$H-NMR spectrum of 3f (400 MHz, CDCl$_3$).
Fig. S12. $^{13}$C-NMR spectrum of 3f (100 MHz, CDCl$_3$).

Fig. S13. $^1$H-NMR spectrum of 3k (400 MHz, CDCl$_3$).
Fig. S14. $^{13}$C-NMR spectrum of 3k (100 MHz, CDCl$_3$).

Fig. S15. $^1$H-NMR spectrum of 4a (400 MHz, CDCl$_3$).
Fig. S16. $^{13}$C-NMR spectrum of 4a (100 MHz, CDCl$_3$).

Fig. S17. $^1$H-NMR spectrum of 4b (400 MHz, CDCl$_3$).
Fig. S18. $^{13}$C-NMR spectrum of 4b (100 MHz, CDCl$_3$).

Fig. S19. $^1$H-NMR spectrum of 4c (400 MHz, DMSO-d$_6$).
Fig. S20. $^{13}$C-NMR spectrum of 4c (100 MHz, DMSO-$d_6$).

Fig. S21. $^1$H-NMR spectrum of 4d (400 MHz, CDCl$_3$).
Fig. S22. $^{13}$C-NMR spectrum of 4d (100 MHz, CDCl$_3$).

Fig. S23. $^1$H-NMR spectrum of 4e (400 MHz, DMSO-$d_6$).
Fig. S24. $^{13}$C-NMR spectrum of 4e (100 MHz, DMSO-$d_6$).

Fig. S25. $^1$H-NMR spectrum of 4f (400 MHz, DMSO-$d_6$).
**Fig. S26.** $^{13}$C-NMR spectrum of 4f (100 MHz, DMSO-$d_6$).

**Fig. S27.** $^{1}$H-NMR spectrum of 4k (400 MHz, CDCl$_3$).
Fig. S28. $^{13}$C-NMR spectrum of 4k (100 MHz, CDCl$_3$).

Fig. S29. $^1$H-NMR spectrum of 4l (400 MHz, CDCl$_3$).
Fig. S30. $^{13}$C-NMR spectrum of 4I (100 MHz, CDCl$_3$).

Fig. S31. $^1$H-NMR spectrum of 5I (400 MHz, CDCl$_3$).
Fig. S32. $^{13}$C-NMR spectrum of 5l (100 MHz, CDCl$_3$).

Fig. S33. $^1$H-NMR spectrum of 10aa (400 MHz, CDCl$_3$).
Fig. S34. $^{13}$C-NMR spectrum of 10aa (100 MHz, CDCl₃).

Fig. S35. $^1$H-NMR spectrum of 10ab (400 MHz, CDCl₃).
Fig. S36. $^{13}$C-NMR spectrum of 10ab (100 MHz, CDCl$_3$).

Fig. S37. $^1$H-NMR spectrum of 10ac (400 MHz, DMSO-$d_6$).
Fig. S38. $^{13}$C-NMR spectrum of 10ac (100 MHz, DMSO-$d_6$).

Fig. S39. $^1$H-NMR spectrum of 10ba (400 MHz, CDCl$_3$).
Fig. S40. $^{13}$C-NMR spectrum of 10ba (100 MHz, CDCl$_3$).

Fig. S41. $^1$H-NMR spectrum of 10bb (400 MHz, CDCl$_3$).
Fig. S42. $^{13}$C-NMR spectrum of 10bb (100 MHz, CDCl$_3$).

Fig. S43. $^1$H-NMR spectrum of 10bc (400 MHz, CDCl$_3$).
Fig. S44. $^{13}$C-NMR spectrum of 10bc (100 MHz, CDCl$_3$).

Fig. S45. $^1$H-NMR spectrum of 13a (400 MHz, CDCl$_3$).
Fig. S46. $^{13}$C-NMR spectrum of 13a (100 MHz, CDCl$_3$).

Fig. S47. $^1$H-NMR spectrum of 13b (400 MHz, MeOD).
**Fig. S48.** $^{13}$C-NMR spectrum of 13b (100 MHz, MeOD).

**Fig. S49.** $^1$H-NMR spectrum of 14a (400 MHz, CDCl$_3$).
Fig. S50. $^{13}$C-NMR spectrum of 14a (100 MHz, CDCl₃).

Fig. S51. $^1$H-NMR spectrum of 14b (400 MHz, CDCl₃).
Fig. S52. $^{13}$C-NMR spectrum of 14b (100 MHz, CDCl$_3$).

Fig. S53. $^1$H-NMR spectrum of 15a (400 MHz, aceton-$d_6$).
**Fig. S54.** $^{13}$C-NMR spectrum of $15a$ (100 MHz, aceton-$d_6$).

**Fig. S55.** $^1$H-NMR spectrum of $15b$ (400 MHz, CDCl$_3$).
Fig. S56. $^{13}$C-NMR spectrum of 15b (100 MHz, CDCl₃).

Fig. S57. $^1$H-NMR spectrum of 16a (400 MHz, CDCl₃).
Fig. S58. $^{13}$C-NMR spectrum of 16a (100 MHz, CDCl$_3$).

Fig. S59. $^1$H-NMR spectrum of 16b (400 MHz, CDCl$_3$).
Fig. S60. $^{13}$C-NMR spectrum of 16b (100 MHz, CDCl$_3$).

Fig. S61. HRMS spectrum of 3a.
Fig. S62. HRMS spectrum of 3b.

![HRMS spectrum of 3b](image)

Fig. S63. HRMS spectrum of 3c.

![HRMS spectrum of 3c](image)

Fig. S64. HRMS spectrum of 3d.

![HRMS spectrum of 3d](image)

Fig. S65. HRMS spectrum of 3e.

![HRMS spectrum of 3e](image)
Fig. S66. HRMS spectrum of 3f.

Fig. S67. HRMS spectrum of 3k.

Fig. S68. HRMS spectrum of 4a.
Fig. S69. HRMS spectrum of 4b.

Fig. S70. HRMS spectrum of 4c.

Fig. S71. HRMS spectrum of 4d.
Fig. S72. HRMS spectrum of 4e.

Fig. S73. HRMS spectrum of 4f.

Fig. S74. HRMS spectrum of 4k.
Fig. S75. HRMS spectrum of 4l.

Fig. S76. HRMS spectrum of 5l.

Fig. S77. HRMS spectrum of 10aa.
Fig. S78. HRMS spectrum of 10ab.

Fig. S79. HRMS spectrum of 10ac.

Fig. S80. HRMS spectrum of 10ba.
Fig. S81. HRMS spectrum of 10bb.

Fig. S82. HRMS spectrum of 10bc.

Fig. S83. HRMS spectrum of 13a.
Fig. S84. HRMS spectrum of 13b.

### Peak List

| m/z       | z | Abund  |
|-----------|---|--------|
| 491.1872  | 1 | 9567481|
| 491.3647  | 1 | 254643.7|
| 492.1893  | 1 | 4344499.5|
| 492.3722  | 1 | 215148.05|
| 493.1926  | 1 | 840233.56|
| 494.1972  | 1 | 101482.65|
| 571.2254  | 1 | 184560.77|
| 580.1902  | 1 | 356810.16|
| 581.1944  | 1 | 145989.55|

Fig. S85. HRMS spectrum of 14a.
Fig. S86. HRMS spectrum of 14b.

Fig. S87. HRMS spectrum of 15a.

Fig. S88. HRMS spectrum of 15b.
Fig. S89. HRMS spectrum of 16a.

Fig. S90. HRMS spectrum of 16b.