Supporting Information

Synthesis

The synthesis of reference chromophore 1 and its extension 3 is outlined in Scheme 1. The synthetic approach to compound 11 was reported previously.\textsuperscript{[1]} 2,9-Diaminodibenzosuberone was prepared in two steps according to literature.\textsuperscript{[2]} Conversion of both amino groups into bromo substituents by a modified Sandmeyer reaction using copper(II)bromide and tert-butyl nitrite in acetonitrile\textsuperscript{[3]} was followed by the reduction of the carbonyl group with NaBH\textsubscript{4} in trifluoroacetic acid\textsuperscript{[4]} to yield compound 12.\textsuperscript{[5]}

Compound 22 was synthesised by a palladium catalysed Buchwald-Hartwig amination\textsuperscript{[6-10]} of 12 and di-p-anisylamine (15). Target compounds 1 and 3 were prepared under the same conditions by reaction of 11 with 4-iodotoluene or 22, respectively.

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {11};
\node (2) at (2,0) {22};
\node (3) at (4,0) {12};
\node (11) at (0,2) {i) \text{CuBr}_2, \text{tBuONO, MeCN}};
\node (12) at (0,4) {i) \text{CuBr}_2, \text{tBuONO, MeCN, NaBH}_4, \text{TFA}};
\node (4) at (2,2) {4-iodotoluene};
\node (5) at (4,2) {NaBH\textsubscript{4}, TFA};
\node (6) at (3,1) {11};
\node (7) at (5,1) {12};
\node (8) at (1,0) {1};
\node (9) at (3,0) {3};
\node (10) at (1,-2) {11};
\node (11) at (3,-2) {12};
\node (12) at (5,-2) {22};
\draw [->] (1) -- (11);
\draw [->] (2) -- (12);
\draw [->] (3) -- (5);
\end{tikzpicture}
\end{center}

\textbf{Scheme 1:} Synthesis of compounds 1 and 3. i) \text{Pd}_2(\text{dba})_3 \text{CHCl}_3, \text{P}\text{tBu}_3, \text{NaO}\text{tBu}, \text{toluene.}

The syntheses developed for compounds 4 – 10 are given in Scheme 2. First, the starting compound 9(10H)-acridone was protected by MEM chloride.\textsuperscript{[11]} After addition of 5-bromo-2-lithio-1,3-dimethylbenzene the protecting group was removed by sequential
addition of HCl and K$_2$CO$_3$ to yield the aromatic compound 13 in acceptable yields (42 %) compared to similar reactions reported in literature.$^{[12-15]}$ The diarylamine 14 was synthesised by a palladium catalysed aryl-$N$-coupling of 13 and 4-chloroaniline. Formation of compound 2 was finally accomplished in the same way as chromophore 3.

Scheme 2: Synthesis of compounds 2 and 4 – 10. i) Pd$_2$(dba)$_3$·CHCl$_3$, P$i$Bu$_3$, NaO$i$Bu, toluene.
Compounds 15, 16 and 20 are commercially available and were used without further purification. The synthesis of 18 is reported elsewhere. The precursor 17 is accessible by a palladium catalysed amination of 22 and 4-methylaniline. Using this palladium catalysed Buchwald-Hartwig amination, the Wurster’s Blue derivative 19 was obtained by reaction of (4-bromophenyl)dimethylaniline with p-anisidine. Following a procedure published by Kikugawa et al., we synthesised 21 in an one-step-reaction using commercially available 3,6-dibromo-9H-carbazole as the starting material. A direct methoxide displacement of bromo was achieved by using MeONa and CuI in DMF. All intermediates 22 – 28 were prepared by palladium catalysed aminations of 12 and the corresponding donor fragments 15 – 21. Finally, these key precursors were again coupled by Pd catalysis with 14 to obtain the desired target compounds 4 – 10.

Experimental Section

All chemicals were of standard quality and were used without further purification. All reactions under inert-gas conditions (nitrogen, dried with Sicapent from Merck, oxygen was removed by copper oxide catalyst R3-11 from BASF) were performed in flame-dried Schlenk tubes. If necessary, the solvents were purified and dried by standard procedures and kept under an inert-gas atmosphere. Flash-column chromatography was carried out using silica gel (32 – 63 µm) from MP Biomedicals. For column chromatography neutral alumina with activity V (63 – 200 µm) from Macherey-Nagel was used.

Melting points are uncorrected and were determined by using a Tottoli melting point apparatus from Büchi. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 FT spectrometer and a Bruker AVANCE 600 DMX FT spectrometer, respectively, at 25 °C. Mass spectra were recorded on a Finnigan MAT 90 spectrometer and on a Bruker Daltonic micrOTOF focus (ESI), respectively.

Microwave reactions were carried out in a µCHEMIST from MLS using a 50 ml 3-necked round-bottom flask (open system). The temperature of the reaction was measured directly with a fibre optic sensor.

General procedure for the palladium catalysed amination of aryl halides (GP)

A solution of the aryl halide, the aryl amine, Pd₂(dba)₃·CHCl₃, sodium tert-butoxide, P(Bu)₃ (0.33 M solution in hexane) in dry toluene was stirred under a nitrogen atmosphere at the given temperature for the given time. The mixture was diluted with dichloromethane and washed twice with a saturated Na₂S₂O₃ solution in water. The solvent was removed under reduced pressure and the crude product was purified by (flash-)column chromatography.
**Synthesis of precursors**

**2,9-Dibromodibenzosuberone** \([226946-20-9]\)

2,9-Diaminodibenzosuberone (1.85 g; 7.77 mmol) in dry acetonitrile (34 ml) was added to a solution of copper-(II)-bromide (4.55 g; 19.5 mmol) and tert-butyl nitrite (2.48 ml; 20.9 mmol) in dry acetonitrile (26 ml). The resulting suspension was stirred for 10 h at RT and subsequently heated for 2 h under reflux. After the addition of hydrochloric acid (40 ml of a 20 % solution) the solution was extracted with diethyl ether (4 x 40 ml). The combined organic layers were washed with hydrochloric acid and dried over magnesium sulphate. The solvent was removed in vacuo. The residue was purified by flash-column chromatography (CH\(_2\)Cl\(_2\) : PE = 1:4) which afforded 1.96 g (5.35 mmol, 69 %) of a colourless solid. M.p. 143 °C; \(^1\)H-NMR (400.1 MHz; \([\text{D}_1]\)chloroform): \(\delta = 8.13\) (d, \(4J_{HH} = 2.3\) Hz, 2H); 7.56 (dd, \(3J_{HH} = 8.2\) Hz, \(4J_{HH} = 2.2\) Hz, 2H); 7.12 (d, \(3J_{HH} = 8.1\) Hz, 2H); 3.14 (s, 4H); \(^{13}\)C-NMR (100.6 MHz; \([\text{D}_1]\)chloroform): \(\delta = 192.5\) (quart.); 140.8 (quart.); 139.6 (quart.); 135.6 (tert.); 133.6 (tert.); 131.3 (tert.); 120.9 (quart.); 34.4 (sec.). HRMS (70 eV, EI): \(m/z\) calcd for \([M^+\cdot] = \text{C}_{15}\text{H}_{10}\text{Br}_2\text{O}^+\): 363.90929; found: 363.90926 (\(\Delta = 0.08\) ppm).

**Compound 12**

Sodium borohydride (9.26 g; 245 mmol) was suspended under an inert gas atmosphere at 0 °C in trifluoroacetic acid (292 ml). A solution of 2,9-dibromodibenzosuberone (6.36 g; 17.4 mmol) in dichloromethane (130 ml) was added carefully at RT and was stirred for 12 h. An additional amount of sodium borohydride (4.49 g; 119 mmol) was added and the solution was stirred for further 2 h. The solution was hydrolysed with water (100 ml) and extracted with dichloromethane (3 x 80 ml). The combined organic layers were washed with water and dried over magnesium sulphate. The crude product was purified by flash-column chromatography (PE) to obtain 12 (5.50 g; 15.6 mmol; 90 %) as a colourless solid. M.p. 90 – 91 °C; \(^1\)H-NMR (400.1 MHz; \([\text{D}_6]\)acetone): \(\delta = 7.44\) (d, \(4J_{HH} = 2.1\) Hz, 2H); 7.29 (dd, \(3J_{HH} = 8.2\) Hz, \(4J_{HH} = 2.1\) Hz, 2H); 7.09 (d, \(3J_{HH} = 8.2\) Hz, 2H); 4.15 (s, 2H); 3.14 (s, 4H). \(^{13}\)C-NMR (100.6 MHz; \([\text{D}_6]\)acetone): \(\delta = 142.2\) (quart.); 139.5 (quart.); 132.6 (tert.); 132.5 (tert.); 130.6 (tert.); 120.0 (quart.); 40.0 (sec.); 32.3 (sec.). HRMS (70 eV, EI): \(m/z\) calcd for \([M^+] = \text{C}_{15}\text{H}_{12}\text{Br}_2\text{O}^+\): 349.93002; found: 349.93015 (\(\Delta = 0.37\) ppm).

**Compound 13**

Sodium hydride (1.10 g of a 60% suspension in an oil; 27.5 mmol) was added under an inert gas atmosphere to a solution of 9(10H)-acridone (2.00 g; 10.2 mmol) in DMF (200 ml) which
was stirred for 30 minutes at RT. The solution was cooled to 0 °C and 2-
methoxyethoxymethyl chloride (1.50 ml; 13.1 mmol) was added carefully. The mixture was
stirred for 30 minutes at 0 °C and for 2 h at RT. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (400 ml). The mixture was washed with a saturated NaCl solution (3 x 250 ml) and dried over magnesium sulphate. Subsequently the solvent was removed under reduced pressure. The crude product was purified by column chromatography (CH$_2$Cl$_2$ : PE = 1:1) to obtain N-(2-methoxyethoxy-methyl)-9-acridone (2.54 g; 8.97 mmol; 88 %) as a light yellow solid.

M.p. 181 °C; $^1$H-NMR (400.1 MHz; [D$_1$]chloroform): $\delta = 8.52$ (m, 2H); 7.75 – 7.68 (-, 4H); 7.32 (m, 2H); 5.81 (s, 2H); 3.86 (m, 2H); 3.64 (m, 2H); 3.44 (s, 3H).

A solution of $n$-BuLi (3.10 ml of a 1.55 M solution in hexane; 4.81 mmol) was added drop by drop to a solution of 4-bromo-1-iodo-2,6-dimethylbenzene (1.50 g; 4.82 mmol) in THF (40 ml) at –78 °C which was then stirred for 3 h. This solution was transferred via cannula to a solution of N-(2-methoxyethoxymethyl)-9-acridone (845 mg; 2.98 mmol) in THF (50 ml), which was cooled down to –78 °C and stirred for further 2 h. The solution was stirred for 10 h at RT, diluted hydrochloric acid was added, followed by the addition of a solution of potassium carbonate in water. The solution was extracted with dichloromethane (3 x 200 ml) and the combined organic layers were dried over magnesium sulphate. The solvent was removed under reduced pressure. Purification of the crude product was achieved by flash-column chromatography (CH$_2$Cl$_2$) to yield 13 (732 mg; 2.02 mmol; 42 %) as a yellow solid.

M.p. 194 °C; $^1$H-NMR (400.1 MHz; [D$_6$]acetone): $\delta = 8.26$ (ddd, $^3$J$_{HH} = 8.8$ Hz, $^4$J$_{HH} = 0.9$ Hz, $^5$J$_{HH} = 0.9$ Hz, 2H); 7.79 (ddd, $^3$J$_{HH} = 8.8$ Hz, $^3$J$_{HH} = 5.6$ Hz, $^4$J$_{HH} = 2.3$ Hz, 2H); 7.41 –7.34 (-, 6H); 1.72 (s, 6H); $^1$H$^{13}$C-NMR (100.6 MHz; [D$_6$]acetone): $\delta = 149.4$ (quart.); 145.2 (quart.); 139.7 (quart.); 134.6 (quart.); 130.8 (tett.); 130.5 (tett.); 130.4 (tett.); 126.6 (tett.); 125.9 (tett.); 125.0 (quart.); 122.5 (quart.); 19.9 (prim.).

HRMS (70 eV, EI): m/z calcd for [M$^+$] = C$_{21}$H$_{16}$BrN$^+$: 361.04606; found: 361.04619 ($\Delta = 0.36$ ppm).

**Compound 14**

Following GP: Compound 13 (120 mg; 331 $\mu$mol), 4-chloroaniline (57.2 mg; 448 $\mu$mol), Pd$_2$(dba)$_3$·CHCl$_3$ (4.68 mg; 4.52 $\mu$mol), P(t-Bu)$_3$ (24.0 $\mu$l; 7.92 $\mu$mol), sodium tert-butoxide (43.1 mg; 448 $\mu$mol), toluene (2 ml); 20 h at 100 °C, flash-column chromatography (CH$_2$Cl$_2$ → CH$_2$Cl$_2$ : EtOAc = 40:1); Yield: 124 mg (303 $\mu$mol; 92 %) of a yellow solid.

M.p. 267 °C; $^1$H-NMR (400.1 MHz; [D$_6$]acetone): $\delta = 8.25$ (m, 2H); 7.78 (ddd, $^3$J$_{HH} = 8.8$ Hz, $^3$J$_{HH} = 6.5$ Hz, $^4$J$_{HH} = 1.5$ Hz, 2H); 7.59 (ddd, $^3$J$_{HH} = 8.7$ Hz, $^4$J$_{HH} = 1.1$ Hz, $^5$J$_{HH} = 0.5$ Hz, 2H); 7.45 (ddd, $^3$J$_{HH} = 8.7$ Hz, $^3$J$_{HH} = 6.5$ Hz, $^4$J$_{HH} = 1.2$ Hz, 2H); 7.29 (AA', 2H); 7.17 (BB', 2H);
7.00 (s, 2H); 5.95 (s, 1H); 1.70 (s, 6H); \( \{^1H\}^{13}C\)-NMR (100.6 MHz; [D\(_2\)]dichloromethane): \( \delta = 149.5 \) (quart.); 146.9 (quart.); 143.2 (quart.); 142.3 (quart.); 138.5 (quart.); 130.4 (tert.); 130.2 (tert.); 129.6 (tert.); 128.3 (quart.); 126.5 (tert.); 126.2 (tert.); 125.8 (quart.); 119.6 (tert.); 117.0 (tert.); 20.3 (prim.).

HRMS (70 eV, EI): \( m/z \) calcd for [M\(^+\)] = C\(_{27}\)H\(_{21}\)ClN\(_2\): 408.13878; found: 408.13889 (\( \Delta = 0.27 \) ppm).

**Compound 17**

Following GP: Compound 15 (280 mg; 560 \( \mu \)mol), \( p \)-toluidine, (120 mg; 1.12 mmol), Pd\(_2\)(dba)_3·CHCl\(_3\) (5.91 mg; 5.71 \( \mu \)mol), P(t-Bu)_3 (30.4 \( \mu l \); 10.0 \( \mu \)mol), sodium tert-butoxide (699 \( \mu \)mol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 75 °C; holding time: 30 min at 75 °C); flash-column chromatography (CH\(_2\)Cl\(_2\) : PE = 2:1); Yield: 230 mg (437 \( \mu \)mol; 78 %) of a colourless solid.

M.p. 70 °C; \( ^1H\)-NMR (400.1 MHz; [D\(_6\)]acetone): \( \delta = 7.40 – 6.93 \) (-, 11H); 6.88 – 6.83 (-, 6H); 6.77 (d, 4\( J_{HH} = 2.3 \) Hz, 1H); 6.66 (dd, 3\( J_{HH} = 8.2 \) Hz, 4\( J_{HH} = 2.5 \) Hz, 1H); 3.90 (s, 2H); 3.77 (s, 6H); 3.06 (-, 4H); 2.23 (s, 3H); \( \{^1H\}^{13}C\)-NMR (150.9 MHz; [D\(_6\)]acetone): \( \delta = 156.6 \) (quart.); 147.7 (quart.); 143.1 (quart.); 142.5 (quart.); 142.3 (quart.); 140.8 (quart.); 140.7 (quart.); 133.0 (quart.); 131.4 (quart.); 131.08 (tert.); 131.06 (tert.); 130.4 (tert.); 129.8 (quart.); 126.8 (tert.); 122.8 (tert.); 120.6 (tert.); 118.4 (tert.); 115.95 (tert.); 115.89 (tert.); 115.5 (tert.); 55.7 (prim.); 41.6 (sec.); 32.8 (sec.); 32.6 (sec.); 20.6 (prim.).

ESI pos. (high resolution): calcd for [M\(^+\)] = C\(_{36}\)H\(_{34}\)N\(_2\)O\(_2\): 526.26148; found: 526.26053 (\( \Delta = 1.80 \) ppm).

**Compound 19** [54480-44-3]

Following GP: 4-bromo-\( N,N \)-dimethylaniline (2.00 g; 10.0 mmol), \( p \)-anisidine (1.60 g; 13.0 mmol), Pd\(_2\)(dba)_3·CHCl\(_3\) (275 mg; 266 \( \mu \)mol), P(t-Bu)_3 (1.42 ml; 469 \( \mu \)mol), sodium tert-butoxide (699 \( \mu \)mol), toluene (60 ml); 3 d at 80 °C; column chromatography (PE → PE : CH\(_2\)Cl\(_2\) = 20:1); Yield: 881 mg (3.64 mmol; 36 %) of a dark yellow oil.

\( ^1H\)-NMR (400.1 MHz; [D\(_6\)]acetone): \( \delta = 6.95 \) (AA', 2H); 6.90 (AA',2H); 6.72 (BB', 2H); 3.72 (s, 3H); 2.85 (s, 6H).

**Compound 21** [57103-01-2]

Sodium (1.70 g; 73.9 mmol) was dissolved in dry methanol (20 ml) and 3,6-dibromocarbazole (1.20 g; 3.69 mmol), copper-(I)-iodide (2.96 g; 15.5 mmol) and dry DMF (40 ml) were added and heated under reflux for 3 h. After ethyl acetate (160 ml) was added, the mixture was filtered over celite and washed with brine (3 x 75 ml). The solvent was removed under reduced pressure. The crude product was purified by flash-column
chromatography (CH₂Cl₂ : PE = 1:1) to yield 21 (750 mg; 3.30 mmol; 89 %) as a colourless solid.

M.p. 113 – 114 °C; ¹H-NMR (400.1 MHz; [D₆]acetone): δ = 9.89 (s, 1H); 7.64 (d, JHH = 2.4 Hz; 2H); 7.37 (m, 2H); 7.00 (dd, JHH = 8.7 Hz, JHH = 2.5 Hz, 2H); 3.87 (s, 6H); ¹³C-NMR (100.6 MHz; [D₆]acetone): δ = 154.4 (quat.); 136.6 (quat.); 124.4 (quat.); 115.9 (tert.); 112.5 (tert.); 103.5 (tert.); 56.1 (prim.).

HRMS (70 eV, EI): m/z calcd for [M⁺] = C₁₄H₁₃NO₂⁺: 227.09408; found: 227.09399 (Δ = 0.40 ppm).

**Compound 22**

Following GP: Compound 12 (312 mg; 886 µmol), di(4-methoxyphenyl)amine (204 mg; 890 µmol), Pd₂(db₃)₃·CHCl₃ (11.5 mg; 11.1 µmol), P(t-Bu)₃ (50.0 µl; 16.5 µmol), sodium tert-butoxide (106 mg; 1.10 mmol), toluene (7 ml); 60 h at 35 °C; column chromatography (PE : CH₂Cl₂ = 9:1); Yield: 156 mg (312 µmol; 35 %) of a colourless solid.

M.p. 112 °C; ¹H-NMR (400.1 MHz; [D₆]acetone): δ = 7.38 (d, JHH = 2.1 Hz, 1H); 7.28 (dd, JHH = 8.1 Hz, JHH = 2.1 Hz, 1H); 7.09 (d, JHH = 8.2 Hz, 1H); 6.96 (AA', 4H); 6.95 (d, JHH = 5.7 Hz, 1H); 6.86 (BB', 4H); 6.80 (d, JHH = 2.4 Hz); 6.66 (dd, JHH = 8.2 Hz, JHH = 2.5 Hz, 1H); 4.00 (s, 2H); 3.78 (s, 6H); 3.15 – 3.05 (-, 4H);

¹³C-NMR (100.6 MHz; [D₆]acetone): δ = 156.8 (quat.); 147.9 (quat.); 142.7 (quat.); 142.2 (quat.); 140.0 (quat.); 139.8 (quat.); 132.4 (quat.); 132.4 (tert.); 132.3 (tert.); 131.2 (tert.); 130.2 (tert.); 127.0 (tert.); 122.7 (tert.); 120.7 (tert.); 119.7 (quat.); 115.5 (quat.); 55.7 (prim.); 41.5 (sec.); 32.7 (sec.); 32.1 (sec.).

HRMS (70 eV, EI): m/z calcd for [M⁺] = C₂₉H₂₈BrNO₂⁺: 499.11414; found: 499.11399 (Δ = 0.26 ppm).

**Compound A**

Compound A was obtained as a secondary product within the synthesis of 22. Yield: 134 mg (207 µmol; 47 %) of a colourless solid.

M.p. 124 °C; ¹H-NMR (400.1 MHz; [D₆]acetone): δ = 6.97 – 6.92 (-, 10H); 6.84 (BB', 8H); 6.72 (d, JHH = 2.4 Hz, 2H); 6.66 (dd, JHH = 8.2 Hz, JHH = 2.5 Hz, 2H); 3.83 (s, 2H); 3.77 (s, 12H); 3.06 (s, 4H); ¹³C-NMR (100.6 MHz; [D₆]acetone): δ = 156.7 (quat.); 147.7 (quat.); 142.2 (quat.); 140.7 (quat.); 132.8 (quat.); 131.1 (tert.); 126.9 (tert.); 122.7 (tert.); 120.4 (tert.); 115.5 (tert.); 55.7 (prim.); 41.5 (sec.); 32.7 (sec.).

HRMS (70 eV, EI): m/z calcd for [M⁺] = C₄₃H₄₀N₂O₄⁺: 648.29826; found: 648.29844 (Δ = 0.28 ppm).
**Compound 23**

Following GP: Compound 12 (300 mg; 852 µmol), di-(4-methylphenyl)amine (168 mg; 852 µmol), Pd$_2$(dba)$_3$·CHCl$_3$ (11.0 mg; 10.6 µmol), P(t-Bu)$_3$ (47.9 µl; 15.8 µmol), sodium tert-butoxide (102 mg; 1.06 mmol), toluene (4 ml); 20 h at 100 °C; column chromatography (PE : CH$_2$Cl$_2$ = 5:1); Yield: 68.0 mg (145 µmol; 17 %) of a colourless solid.

M.p. 67 °C; $^1$H-NMR (400.1 MHz; [D$_6$]acetone): $\delta$ = 7.39 (d, $^4$J$_{HH}$ = 2.0 Hz, 1H); 7.29 (dd, $^3$J$_{HH}$ = 8.0 Hz, $^4$J$_{HH}$ = 2.1 Hz, 1H); 7.09 (d, $^3$J$_{HH}$ = 8.2 Hz, 1H); 7.06 (AA', 4H); 7.00 (d, $^3$J$_{HH}$ = 8.2 Hz, $^4$J$_{HH}$ = 2.1 Hz, 1H); 6.90 (d, $^4$J$_{HH}$ = 2.3 Hz, 1H); 6.88 (BB', 4H); 6.76 (dd, $^3$J$_{HH}$ = 8.2 Hz, $^4$J$_{HH}$ = 2.4 Hz, 1H); 4.02 (s, 2H); 3.19 – 3.07 (-, 4H); 2.27 (s, 6H);

$^{13}$C-NMR (100.6 MHz; [D$_6$]acetone): $\delta =$ 147.2 (quart.); 146.6 (quart.); 142.7 (quart.); 140.2 (quart.); 139.7 (quart.); 133.9 (quart.); 132.8 (quart.); 132.4 (tert.); 132.3 (tert.); 131.4 (tert.); 130.7 (tert.); 124.9 (tert.); 124.8 (tert.); 119.7 (quart.); 40.5 (sec.); 32.6 (sec.); 32.2 (sec.); 20.8 (prim.).

HRMS (70 eV, EI): m/z calcd for [M+H$^+$] = C$_{29}$H$_{26}$BrN$^+$: 467.12431; found: 467.12224 ($\Delta$ = 2.07 ppm).

**Compound 24**

Following GP: Compound 17 (480 mg; 911 µmol), 12 (3.00 g; 8.52 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (9.61 mg; 9.28 µmol), P(t-Bu)$_3$ (49.5 µl; 16.3 µmol), sodium tert-butoxide (109 mg; 1.13 mmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 75 °C; holding time: 30 min at 75 °C); flash-column chromatography (CH$_2$Cl$_2$ : PE = 1:2); Yield: 210 mg (263 µmol; 29 %) of a colourless solid.

M.p. 138 – 140 °C; $^1$H-NMR (400.1 MHz; [D$_6$]acetone): $\delta$ = 7.37 (d, $^4$J$_{HH}$ = 2.0 Hz, 1H); 7.28 (dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 2.0 Hz, 1H); 7.15 – 6.89 (-, 11H); 6.88 – 6.77 (-, 7H); 6.75 – 6.68 (-, 3H); 6.66 (dd, $^3$J$_{HH}$ = 8.2 Hz, $^4$J$_{HH}$ = 2.4 Hz, 1H); 3.97 (s, 2H); 3.82 (s, 2H); 3.75 (s, 6H); 3.18 – 3.04 (-, 8H); 2.26 (s, 3H);

$^{13}$C-NMR (150.9 MHz; [D$_6$]acetone): $\delta =$ 156.6 (quart.); 147.8 (quart.); 146.8 (quart.); 146.4 (quart.); 142.7 (quart.); 142.2 (quart.); 140.9 (quart.); 140.7 (quart.); 140.1 (quart.); 139.8 (quart.); 134.4 (quart.); 133.8 (quart.); 132.8 (quart.); 132.31 (quart.); 132.28 (tert.); 131.4 (tert.); 131.3 (tert.); 131.0 (tert.); 130.7 (tert.); 130.6 (tert.); 130.2 (tert.); 126.9 (tert.); 126.8 (tert.); 125.0 (tert.); 123.0 (tert.); 122.8 (tert.); 122.7 (tert.); 122.6 (tert.); 120.4 (tert.); 119.7 (quart.); 115.4 (tert.); 55.7 (prim.); 41.2 (sec.); 40.4 (sec.); 32.8 (sec.); 32.53 (sec.); 52.49 (sec.); 32.2 (sec.); 20.8 (prim.).

ESI pos. (high resolution): calcd for [M+H$^+$] = C$_{51}$H$_{46}$BrN$_2$O$_2$$^+$: 797.27372; found: 797.27368 ($\Delta$ = 0.04 ppm).

**Compound 25**

Following GP: Compound 18 (218 mg, 427 µmol), 12 (300 mg, 852 µmol), Pd$_2$(dba)$_3$·CHCl$_3$ (6.00 mg; 5.80 µmol), P(t-Bu)$_3$ (24.0 µl; 7.92 µmol), sodium tert-butoxide (51.0 mg; 531
µmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 75 °C; holding time: 20 min at 75 °C); flash-column chromatography (CH₂Cl₂ : PE = 1:1); Yield: 103 mg (132 µmol; 31 %) of a yellow solid.

M.p. 139 – 141 °C; ¹H-NMR (400.1 MHz; [D₆]acetone): δ = 7.41 (m, 1H); 7.33 – 7.26 (s, 5H); 7.16 – 7.06 (s, 8H); 7.02 – 6.91 (s, 3H); 6.90 – 6.84 (s, 3H); 6.78 (BB', 2H); 4.07 (s, 2H); 3.80 (s, 6H); 3.17 – 3.13 (s, 4H); 2.31 (s, 3H); ¹³C-NMR (150.9 MHz; [D₆]acetone): δ = 157.7 (quart.); 149.8 (quart.); 148.9 (quart.); 146.1 (quart.); 145.5 (quart.); 142.6 (quart.); 140.9 (quart.); 140.6 (quart.); 139.7 (quart.); 135.4 (quart.); 134.3 (quart.); 133.0 (tert.); 133.0 (tert.); 132.4 (tert.); 132.3 (tert.); 131.7 (tert.); 131.0 (tert.); 128.3 (tert.); 126.4 (tert.); 126.2 (tert.); 124.3 (tert.); 122.0 (tert.); 119.7 (quart.); 119.4 (tert.); 116.7 (quart.); 115.8 (tert.); 114.9 (quart.); 89.7 (quart.); 89.0 (quart.); 55.7 (prim.); 40.3 (sec.); 32.5 (sec.); 20.8 (prim.).

ESI pos. (high resolution): calcd for [M⁺] = C₅₀H₄₁BrN₂O₂⁺: 780.23459; found: 780.23283 (Δ = 2.26 ppm).

Compound 26
Following GP: Compound 19 (250 mg; 1.03 mmol), 12 (1.20 g; 3.41 mmol), Pd₂(db[a]₃·CHCl₃ (14.5 mg; 14.0 µmol), P(t-Bu)₃ (57.9 µl; 19.1 µmol), sodium tert-butoxide (123 mg; 1.28 mmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 100 °C; holding time: 1 h at 100 °C); flash-column chromatography (CH₂Cl₂); Yield: 244 mg (475 µmol; 46 %) of a yellow oil.

¹H-NMR (400.1 MHz; [D₆]acetone): δ = 7.38 (d, 4J₃H = 2.0 Hz, 1H); 7.28 (dd, 3J₄H = 8.1 Hz, 4J₃H = 2.1 Hz, 1H); 7.08 (d, 3J₃H = 8.1 Hz, 1H); 6.99 – 6.88 (s, 5H); 6.84 (BB', 2H); 6.79 – 6.60 (s, 2H); 3.98 (s, 2H); 3.77 (s, 3H); 3.16 – 3.01 (s, 4H); 2.91 (s, 6H); 13C-NMR (150.9 MHz; [D₆]acetone): δ = 156.3 (quart.); 148.42 (quart.); 148.40 (quart.); 148.1 (quart.); 142.7 (quart.); 142.3 (quart.); 139.7 (quart.); 138.3 (quart.); 132.3 (tert.); 132.2 (tert.); 131.5 (quart.); 130.9 (tert.); 130.0 (tert.); 127.4 (tert.); 126.4 (tert.); 121.7 (tert.); 119.8 (tert.); 119.6 (quart.); 115.3 (tert.); 114.4 (tert.); 55.6 (prim.); 40.9 (prim.); 40.6 (sec.); 32.7 (sec.); 32.0 (sec.).

HRMS (70 eV, EI): m/z calcd for [M⁺] = C₃₀H₂₉BrN₂O⁺: 512.14578; found: 512.14527 (Δ = 1.00 ppm).

Compound 27
Following GP: Compound 12 (200 mg; 568 µmol), phenothiazine (102 mg; 512 µmol), Pd₂(db[a]₃·CHCl₃ (16.7 mg; 16.1 µmol), P(t-Bu)₃ (71.0 µl; 23.4 µmol), sodium tert-butoxide (136 mg; 1.42 mmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 45 °C; holding time: 40 min at 45 °C); flash-column chromatography (CH₂Cl₂ : PE = 1:7); Yield: 81.0 mg (172 µmol; 34 %) of a colourless solid.
M.p. 218 – 220 °C; \(^1\)H-NMR (400.1 MHz; \([D_6]\)acetone): \(\delta = 7.47\) (d, \(^4\)J\text{HH} = 2.0 Hz, 1H); 7.44 (d, \(^3\)J\text{HH} = 8.0 Hz, 1H); 7.33 (dd, \(^3\)J\text{HH} = 8.1 Hz, \(^4\)J\text{HH} = 2.1 Hz, 1H); 7.30 (d, \(^4\)J\text{HH} = 2.3 Hz, 1H); 7.22 (dd, \(^3\)J\text{HH} = 8.0 Hz, \(^4\)J\text{HH} = 2.3 Hz, 1H); 7.16 (d, \(^3\)J\text{HH} = 8.2 Hz, 1H); 7.02 (dd, \(^3\)J\text{HH} = 7.3 Hz, \(^4\)J\text{HH} = 1.83 Hz, 2H); 6.90 – 6.78 (-, 4H); 6.22 (dd, \(^3\)J\text{HH} = 8.0 Hz, \(^4\)J\text{HH} = 2.3 Hz, 1H); 4.26 (s, 2H); 3.34 – 3.20 (-, 4H); \(^1\)H-NMR (100.6 MHz; \([D_6]\)acetone): \(\delta = 145.3\) (quart.); 142.5 (quart.); 142.3 (quart.); 139.7 (quart.); 139.5 (quart.); 133.0 (tert.); 132.4 (tert.); 127.9 (tert.); 127.4 (tert.); 124.3 (tert.); 120.8 (quart.); 120.0 (quart.); 117.0 (tert.); 40.3 (sec.); 32.7 (sec.); 32.2 (sec.);
ESI pos. (high resolution): calcd for \([M^+\cdot\text{D}_6]^+\) = C\(_{27}\)H\(_{20}\)BrNS\(_2\)·\([D_6]\): 469.04943; found: 469.04998 (\(\Delta = 1.17\) ppm).

\textit{Compound 28}
Following GP: Compound 21 (675 mg; 2.97 mmol), 12 (4.96 g; 14.1 mmol), Pd\(_2\)(dba)_3·CHCl\(_3\) (34.8 mg; 33.6 \(\mu\)mol), P(t-Bu)_3 (179 \(\mu\)l; 59.1 \(\mu\)mol), sodium tert-butoxide (395 mg; 4.11 mmol), toluene (20 ml); heated in a microwave oven (gradient of heating: 10 min RT to 80 °C; holding time: 1 h at 80 °C); flash-column chromatography (CH\(_2\)Cl\(_2\) : PE = 1:2); Yield: 478 mg (959 \(\mu\)mol; 32 %) of a light yellow solid.
M.p. 99 °C; \(^1\)H-NMR (400.1 MHz; \([D_6]\)acetone): \(\delta = 7.74\) (d, \(^4\)J\text{HH} = 2.5 Hz, 2H); 7.49 – 7.36 (-, 3H); 7.36 – 7.31 (-, 2H); 7.29 (d, \(^3\)J\text{HH} = 9.0 Hz, 2H); 7.15 (d, \(^3\)J\text{HH} = 8.1 Hz, 1H); 7.02 (dd, \(^3\)J\text{HH} = 9.0 Hz, \(^4\)J\text{HH} = 2.5 Hz, 2H); 4.28 (s, 2H); 3.90 (s, 6H); 3.34 – 3.20 (-, 4H); \(\{{^1\text{H}}\}^{13}\text{C-NMR}\) (150.9 MHz; \([D_6]\)acetone): \(\delta = 155.2\) (quart.); 141.9 (quart.); 140.2 (quart.); 139.9 (quart.); 139.1 (quart.); 137.1 (quart.); 136.7 (quart.); 132.1 (tert.); 130.3 (tert.); 129.8 (tert.); 127.61 (tert.); 127.59 (tert.); 127.0 (tert.); 125.3 (quart.); 124.6 (quart.); 116.0 (tert.); 111.5 (tert.); 103.8 (tert.); 56.2 (prim.); 40.9 (sec.); 32.9 (sec.); 32.8 (sec.);
ESI pos. (high resolution): calcd for \([M^+\cdot\text{D}_6]^+\) = C\(_{29}\)H\(_{24}\)BrNO\(_2\)·\([D_6]\): 497.09849; found: 497.09897 (\(\Delta = 0.95\) ppm).

\textit{Synthesis of reference chromophores}

\textit{Chromophore 1}
Following GP: Compound 11 (152 mg; 399 \(\mu\)mol), 4-iodotoluene (176 mg; 807 \(\mu\)mol), Pd\(_2\)(dba)_3·CHCl\(_3\) (22.4 mg; 21.6 \(\mu\)mol), P(t-Bu)_3 (102 \(\mu\)l; 33.7 \(\mu\)mol), sodium tert-butoxide (97.0 mg; 1.01 mmol), toluene (5 ml); 24 h at 45 °C; flash-column chromatography (CH\(_2\)Cl\(_2\) : EtOAc = 30:1); Yield: 143 mg (304 \(\mu\)mol; 76 %) of a yellow solid.
M.p. 247 °C; \(^1\)H-NMR (400.1 MHz; \([D_6]\)acetone): \(\delta = 8.22\) (dd, \(^3\)J\text{HH} = 8.6 Hz, \(^4\)J\text{HH} = 1.0 Hz, \(^5\)J\text{HH} = 1.0 Hz, 2H); 7.86 (dd, \(^3\)J\text{HH} = 8.6 Hz, \(^4\)J\text{HH} = 1.3 Hz, \(^5\)J\text{HH} = 0.7 Hz, 2H); 7.83 (dd, \(^3\)J\text{HH} = 220 °C; \(^1\)H-NMR (400.1 MHz; \([D_6]\)acetone): \(\delta = 7.47\) (d, \(^4\)J\text{HH} = 2.0 Hz, 1H); 7.44 (d, \(^3\)J\text{HH} = 8.0 Hz, 1H); 7.33 (dd, \(^3\)J\text{HH} = 8.1 Hz, \(^4\)J\text{HH} = 2.1 Hz, 1H); 7.30 (d, \(^4\)J\text{HH} = 2.3 Hz, 1H); 7.22 (dd, \(^3\)J\text{HH} = 8.0 Hz, \(^4\)J\text{HH} = 2.3 Hz, 1H); 7.16 (d, \(^3\)J\text{HH} = 8.2 Hz, 1H); 7.02 (dd, \(^3\)J\text{HH} = 7.3 Hz, \(^4\)J\text{HH} = 1.83 Hz, 2H); 6.90 – 6.78 (-, 4H); 6.22 (dd, \(^3\)J\text{HH} = 8.0 Hz, \(^4\)J\text{HH} = 2.3 Hz, 1H); 4.26 (s, 2H); 3.34 – 3.20 (-, 4H); \(^1\)H-NMR (100.6 MHz; \([D_6]\)acetone): \(\delta = 145.3\) (quart.); 142.5 (quart.); 142.3 (quart.); 139.7 (quart.); 139.5 (quart.); 133.0 (tert.); 132.4 (tert.); 132.3 (tert.); 132.0 (tert.); 130.5 (tert.); 130.0 (tert.); 127.9 (tert.); 127.4 (tert.); 123.4 (tert.); 120.8 (quart.); 120.0 (quart.); 117.0 (tert.); 40.3 (sec.); 32.7 (sec.); 32.2 (sec.);
ESI pos. (high resolution): calcd for \([M^+\cdot\text{D}_6]^+\) = C\(_{29}\)H\(_{24}\)BrNO\(_2\)·\([D_6]\): 497.09849; found: 497.09897 (\(\Delta = 0.95\) ppm).
= 8.7 Hz, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.4$ Hz, 2H); 7.54 (ddd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.2$ Hz, 2H); 7.41 (AA', 2H); 7.36 (AA', 2H); 7.30 (BB', 2H); 7.26 (AA', 2H); 7.22 (BB', 2H); 7.19 (BB', 2H); 2.36 (s, 3H). $^1$H$^{13}$C-NMR (100.6 MHz; [D$_6$]acetone): $\delta = 149.3$ (quart.); 148.2 (quart.); 147.4 (quart.); 146.9 (quart.); 144.9 (quart.); 139.4 (quart.); 130.7 (tert.); 130.2 (tert.); 129.7 (tert.); 129.6 (quart.); 127.9 (quart.); 127.3 (tert.); 126.0 (tert.); 125.8 (tert.); 125.7 (quart.); 125.5 (tert.); 122.7 (prim.).

HRMS (70 eV, EI): $m/z$ calcd for [M$^{+}$] = C$_{32}$H$_{23}$ClN$_2$·+: 470.15443; found: 470.15489 ($\Delta = 0.98$ ppm).

Chromophore 2
Following GP: Compound 14 (100 mg; 245 $\mu$mol), 4-iodotoluene (65.4 mg; 300 $\mu$mol), Pd$_2$(dba)$_3$·CHCl$_3$ (3.47 mg; 3.35 $\mu$mol), P(t-Bu)$_3$ (17.8 $\mu$l; 5.87 $\mu$mol), sodium tert-butoxide (31.9 mg; 332 $\mu$mol), toluene (4 ml); 18 h at 95 °C; flash-column chromatography (CH$_2$Cl$_2$ : EtOAc = 40:1); Yield : 110 mg (220 $\mu$mol; 90 %) of a yellow solid.

M.p. 252 °C; $^1$H-NMR (400.1 MHz; [D$_6$]acetone): $\delta = 8.25$ (m, 2H); 7.85 (ddd, $^3J_{HH} = 8.8$ Hz, $^3J_{HH} = 6.4$ Hz, 2H); 7.61 (ddd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 1.5$ Hz, $^4J_{HH} = 0.7$ Hz, 2H); 7.55 (ddd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 6.4$ Hz, $^4J_{HH} = 1.2$ Hz, 2H); 7.33 (AA', 2H); 7.23 (AA', 2H); 7.19 – 7.13 (-, 4H); 7.03 (s, 2H); 2.35 (s, 3H); 1.65 (s, 6H); $^1$H$^{13}$C-NMR (100.6 MHz; [D$_2$]dichloromethane): $\delta = 149.5$ (quart.); 148.0 (quart.); 147.3 (quart.); 146.8 (quart.); 145.2 (quart.); 138.3 (quart.); 134.0 (quart.); 130.4 (tert.); 130.3 (tert.); 129.7 (quart.); 129.5 (tert.); 127.2 (quart.); 126.4 (tert.); 126.3 (tert.); 125.7 (tert.); 125.6 (quart.); 125.0 (tert.); 122.8 (tert.); 21.0 (prim.); 20.2 (prim.).

HRMS (70 eV, EI): $m/z$ calcd for [M$^{+}$] = C$_{34}$H$_{27}$ClN$_2$·+: 498.18577; found: 498.18580 ($\Delta = 0.08$ ppm).

Synthesis of cascades
Cascade 3
Following GP: Compound 11 (95.2 mg; 250 $\mu$mol), 15 (123 mg; 246 $\mu$mol), Pd$_2$(dba)$_3$·CHCl$_3$ (3.91 mg; 3.78 $\mu$mol), P(t-Bu)$_3$ (17.8 $\mu$l; 5.87 $\mu$mol), sodium tert-butoxide (32.1 mg; 334 $\mu$mol), toluene (4 ml); 16 h at 100 °C; column chromatography (PE → PE : CH$_2$Cl$_2$ = 2:1 → PE : CH$_2$Cl$_2$ = 1:1 → PE : CH$_2$Cl$_2$ = 1:2); Yield: 73.0 mg (91.2 $\mu$mol; 36 %) of a yellow solid.

M.p. 142 – 145 °C; $^1$H-NMR (600.1 MHz; [D$_2$]dichloromethane): $\delta = 8.22$ (m, 2H); 7.87 (m, 2H); 7.78 (ddd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.3$ Hz, 2H); 7.47 (ddd, $^3J_{HH} = 8.7$ Hz, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.2$ Hz, 2H); 7.34 – 7.20 (-, 7H); 7.15 (AA', 2H); 7.05 – 6.94 (-, 7H); 6.79 (BB', 4H); 6.75 (d, $^4J_{HH} = 2.4$ Hz, 1H); 6.70 (dd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.4$ Hz, 1H); 3.91 (s,
Cascade 4
Following GP: Compound 14 (95.0 mg; 232 µmol), 22 (115 mg; 230 µmol), Pd2(dba)3·CHCl3 (3.26 mg; 3.15 µmol), P(t-Bu)3 (16.7 µl; 5.51 µmol), sodium tert-butoxide (30.0 mg; 312 µmol), toluene (4 ml); 17 h at 100 °C; column chromatography (CH2Cl2 : PE = 1:1); Yield: 131 mg (158 µmol; 69 %) of a yellow solid.
M.p. 191 °C; 1H-NMR (400.1 MHz; [D2]dichloromethane): δ = 8.25 (m, 2H); 7.79 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.6 Hz, 4JHH = 1.5 Hz, 2H); 7.61 (ddd, 3JHH = 8.8 Hz, 4JHH = 1.2 Hz, 5JHH = 0.5 Hz, 2H); 7.47 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.5 Hz, 4JHH = 1.2 Hz, 2H); 7.25 (AA′, 2H); 7.14 – 7.07 (-, 3H); 7.03 – 6.92 (-, 9H); 6.79 (BB′, 4H); 6.75 (d, 4JHH = 2.2 Hz, 1H); 6.71 (dd, 3JHH = 8.1 Hz, 4JHH = 2.2 Hz, 1H); 3.91 (s, 2H); 3.75 (s, 6H); 3.19 – 3.08 (-, 4H); 1.62 (s, 6H); {1H}13C-NMR (100.6 MHz; [D2]dichloromethane): δ = 156.1 (quart.); 149.5 (quart.); 147.8 (quart.); 147.3 (quart.); 147.2 (quart.); 145.5 (quart.); 141.7 (quart.); 140.7 (quart.); 140.0 (quart.); 138.4 (quart.); 135.4 (quart.); 132.2 (quart.); 131.1 (tert.); 130.5 (tert.); 130.4 (tert.); 130.3 (tert.); 129.8 (tert.); 129.5 (tert.); 127.3 (quart.); 126.5 (quart.); 126.4 (tert.); 126.3 (tert.); 125.8 (tert.); 125.6 (quart.); 125.3 (tert.); 123.7 (quart.); 123.6 (tert.); 122.9 (tert.); 122.0 (tert.); 120.0 (tert.); 114.9 (tert.); 55.8 (prim.); 41.4 (sec.); 32.6 (sec.); 32.1 (sec.); 20.2 (prim.).
HRMS (70 eV, EI): m/z calcd for [M+] = C54H42ClN3O2·+: 799.29601; found: 799.29713 (Δ = 1.40 ppm).

Cascade 5
Following GP: Compound 14 (60.0 mg; 147 µmol), 23 (68.0 mg; 145 µmol), Pd2(dba)3·CHCl3 (2.06 mg; 1.99 µmol), P(t-Bu)3 (10.5 µl; 3.47 µmol), sodium tert-butoxide (18.9 mg; 197 µmol), toluene (3 ml); 20 h at 100 °C; flash-column chromatography (CH2Cl2 → CH2Cl2 : EtOAc = 40:1); Yield: 74.3 mg (93.3 µmol; 64 %) of a yellow solid.
M.p. 192 °C; 1H-NMR (400.1 MHz; [D2]dichloromethane): δ = 8.25 (m, 2H); 7.79 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.5 Hz, 4JHH = 1.4 Hz, 2H); 7.60 (m, 2H); 7.46 (ddd, 3JHH = 8.6 Hz, 3JHH = 6.5
Hz, $^4J_{HH} = 1.2$ Hz, 2H); 7.25 (AA', 2H); 7.15 – 7.08 (-, 3H); 7.03 (AA', 4H); 7.01 – 6.97 (-, 3H); 6.95 (s, 2H); 6.91 (BB', 4H); 6.84 (d, $^4J_{HH} = 2.3$ Hz, 1H); 6.79 (dd, $^3J_{HH} = 8.1$ Hz, $^4J_{HH} = 2.5$ Hz, 1H); 3.93 (s, 2H); 3.15 (s, 4H); 2.27 (s, 6H); 1.63 (s, 6H); $^{1}H$-$^{13}$C-NMR (150.9 MHz; [D$_2$]dichloromethane): $\delta$ = 149.5 (quart.); 147.8 (quart.); 147.1 (quart.); 146.7 (quart.); 146.6 (quart.); 145.9 (quart.); 145.5 (quart.); 140.6 (quart.); 140.1 (quart.); 138.3 (quart.); 135.3 (quart.); 133.5 (quart.); 132.5 (quart.); 131.1 (tert.); 130.6 (tert.); 130.4 (tert.); 130.3 (tert.); 130.1 (tert.); 129.8 (quart.); 129.5 (quart.); 127.3 (quart.); 126.4 (tert.); 126.3 (tert.); 125.7 (quart.); 125.6 (tert.); 125.3 (tert.); 124.5 (tert.); 124.0 (tert.); 123.6 (tert.); 122.9 (tert.); 122.0 (tert.); 41.2 (sec.); 32.5 (sec.); 32.2 (sec.); 20.8 (prim.); 20.2 (prim.).

HRMS (70 eV, EI): $m/z$ calcd for [M$^+$] = C$_{56}$H$_{46}$ClN$_3$: 795.33748; found: 795.33828 ($\Delta = 1.40$ ppm).

Cascade 6

Following GP: Compound 14 (101 mg; 247 $\mu$mol), 24 (200 mg; 251 $\mu$mol), Pd$_2$(dba)$_3$-CHCl$_3$ (3.56 mg; 3.44 $\mu$mol), P(t-Bu)$_3$ (18.3 $\mu$l; 6.04 $\mu$mol), sodium tert-butoxide (32.8 mg; 341 $\mu$mol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 90 °C; holding time: 30 min at 90 °C); column chromatography (CH$_2$Cl$_2$ : PE = 1:2); Yield: 106 mg (94.2 $\mu$mol; 38 %) of a yellow solid.

M.p. 187 – 188 °C; $^1$H-NMR (400.1 MHz; [D$_2$]dichloromethane): $\delta$ = 8.25 (AA', 2H); 7.78 (ddd, $^3J_{HH} = 8.68$ Hz, $^3J_{HH} = 6.60$ Hz, $^4J_{HH} = 1.48$ Hz, 2H); 7.60 (AA', 2H); 7.46 (ddd, $^3J_{HH} = 8.62$ Hz, $^3J_{HH} = 6.54$ Hz, $^4J_{HH} = 1.17$ Hz, 2H); 7.24 (AA', 2H); 7.14 – 7.08 (-, 3H); 7.05 – 6.88 (-, 15H); 6.84 (d, $^4J_{HH} = 2.27$ Hz, 1H); 6.80 – 6.73 (-, 7H); 6.71 – 6.65 (-, 2H); 3.92 (s, 2H); 3.80 (s, 6H); 3.18 – 3.08 (-, 4H); 3.07 – 3.00 (-, 4H); 2.27 (s, 3H); 1.62 (s, 6); $^{1}H$-$^{13}$C-NMR (150.9 MHz; [D$_2$]dichloromethane): $\delta$ = 156.0 (quart.); 147.8 (quart.); 147.13 (quart.); 147.11 (quart.); 146.4 (quart.); 146.2 (quart.); 145.7 (quart.); 145.5 (quart.); 141.6 (quart.); 140.6 (quart.); 140.2 (quart.); 140.05 (quart.); 139.99 (quart.); 138.3 (quart.); 135.3 (quart.); 133.8 (quart.); 133.6 (quart.); 132.7 (quart.); 132.2 (quart.); 131.1 (tert.); 130.70 (tert.); 130.67 (tert.); 130.4 (tert.); 130.31 (quart.); 130.29 (quart.); 130.1 (tert.); 129.5 (tert.); 127.3 (quart.); 126.45 (tert.); 126.40 (tert.); 126.30 (tert.); 126.29 (tert.); 126.28 (tert.); 126.27 (tert.); 125.7 (tert.); 125.59 (quart.); 125.57 (quart.); 125.3 (tert.); 124.7 (tert.); 124.34 (tert.); 124.25 (tert.); 123.6 (tert.); 122.9 (tert.); 122.2 (tert.); 121.9 (tert.); 119.8 (tert.); 114.9 (tert.); 55.7 (prim.); 41.3 (sec.); 41.2 (sec.); 32.5 (sec.); 32.4 (sec.); 32.25 (sec.); 32.17 (sec.); 20.8 (prim.); 20.2 (prim.).

ESI pos. (high resolution): calcd for [M$^+$] = C$_{78}$H$_{65}$ClN$_4$O$_2$: 1124.47906; found: 1124.47791 ($\Delta = 1.02$ ppm).
Cascade 7
Following GP: Compound 14 (52.0 mg; 127 µmol), 25 (100 mg; 128 µmol), Pd₂(dba)₃·CHCl₃ (3.47 mg; 3.35 µmol), P(t-Bu)₃ (17.9 µl; 5.91 µmol), sodium tert-butoxide (16.7 mg; 174 µmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 90 °C; holding time: 1 h at 90 °C); column chromatography (CH₂Cl₂ : PE = 1:2); Yield: 96.0 mg (86.5 µmol; 68 %) of a yellow solid.

M.p. 188 – 190 °C; ¹H-NMR (400.1 MHz; [D₂]dichloromethane): δ = 8.24 (AA', 2H); 7.77 (ddd, ³JHH = 8.7 Hz, ³JHH = 6.5 Hz, ⁴JHH = 1.4 Hz, 2H); 7.60 (ddd, ³JHH = 8.7 Hz, ³JHH = 1.4 Hz, ⁵JHH = 0.7 Hz, 2H); 7.46 (ddd, ³JHH = 8.7 Hz, ³JHH = 6.5 Hz, ⁴JHH = 1.2 Hz, 2H); 7.29 – 7.21 (s, 6H); 7.13 – 7.04 (-, 10H); 7.04 – 6.94 (-, 6H); 6.93 – 6.83 (-, 8H); 6.79 (BB', 2H); 3.96 (s, 2H); 3.79 (s, 6H); 3.20 – 3.14 (-, 4H); 2.29 (s, 3H); 1.62 (s, 3H); ¹³C-NMR (150.9 MHz; [D₂]dichloromethane): δ = 156.9 (quart.); 149.5 (quart.); 149.0 (quart.); 148.2 (quart.); 147.8 (quart.); 147.1 (quart.); 146.6 (quart.); 145.55 (quart.); 145.54 (quart.); 144.9 (quart.); 140.50 (quart.); 140.48 (quart.); 140.4 (quart.); 138.4 (quart.); 135.2 (quart.); 135.0 (quart.); 133.9 (quart.); 132.39 (tert.); 132.36 (tert.); 131.1 (tert.); 130.9 (tert.); 130.4 (tert.); 130.32 (tert.); 130.27 (tert.); 129.9 (quart.); 129.5 (tert.); 127.5 (tert.); 127.3 (quart.); 126.4 (tert.); 126.3 (tert.); 125.68 (tert.); 125.54 (tert.); 125.3 (tert.); 123.6 (tert.); 123.5 (tert.); 122.9 (tert.); 121.7 (tert.); 119.3 (tert.); 116.1 (quart.); 115.1 (tert.); 114.4 (quart.); 89.2 (quart.); 88.5 (quart.); 55.8 (prim.); 41.2 (sec.); 32.4 (sec.); 32.3 (sec.); 20.9 (prim.); 20.2 (prim.).

ESI pos. (high resolution): calcd for [M⁺] = C₇₇H₆₁ClN₄O₂⁺: 1108.44776; found: 1108.44606 (∆ = 1.53 ppm).

Cascade 8
Following GP: Compound 14 (95.7 mg; 234 µmol), 26 (120 mg; 234 µmol), Pd₂(dba)₃·CHCl₃ (6.39 mg; 6.17 µmol), P(t-Bu)₃ (33.0 µl; 10.9 µmol), sodium tert-butoxide (30.8 mg; 320 µmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 90 °C; holding time: 1 h at 90 °C); flash-column chromatography (CH₂Cl₂ : EtOAc = 40:1); Yield: 103 mg (122 µmol; 52 %) of an orange solid.

M.p. 193 °C; ¹H-NMR (400.1 MHz; [D₆]acetone): δ = 8.25 (m, 2H); 7.85 (ddd, ³JHH = 8.7 Hz, ³JHH = 6.4 Hz, ⁴JHH = 1.6 Hz, 2H); 7.62 – 7.56 (-, 2H); 7.53 (ddd, ³JHH = 8.6 Hz, ³JHH = 6.4 Hz, ⁴JHH = 1.2 Hz, 2H); 7.31 (AA', 2H); 7.18 – 7.08 (-, 4H); 7.05 – 6.89 (-, 8H); 6.82 (BB', 2H); 6.76 (m, 1H); 6.69 (BB', 2H); 6.65 (dd, ³JHH = 8.1 Hz, ⁴JHH = 2.5 Hz, 1H); 3.96 (s, 2H); 3.74 (s, 3H); 3.20 – 3.08 (-, 4H); 2.88 (s, 6H); 1.64 (s, 6H); ¹³C-NMR (150.9 MHz; [D₆]acetone): δ = 156.3 (quart.); 150.0 (quart.); 148.48 (quart.); 148.45 (quart.); 148.1 (quart.); 147.8 (quart.); 146.6 (quart.); 145.8 (quart.); 142.4 (quart.); 141.5 (quart.); 140.4 (quart.); 138.6 (quart.); 138.4 (quart.); 136.2 (quart.); 132.0 (quart.); 131.8 (tert.); 131.1 (tert.); 130.93 (tert.); 130.87
Cascade 9
Following GP: Compound 14 (200 mg, 489 µmol), 27 (242 mg, 514 µmol), Pd2(dba)3·CHCl3 (7.29 mg; 7.04 µmol), P(t-Bu)3 (37.5 µl; 12.4 µmol), sodium tert-butoxide (67.3 mg; 700 µmol), toluene (10 ml); heated in a microwave oven (gradient of heating: 10 min RT to 110 °C; holding time: 1 h at 110 °C); flash-column chromatography (CH2Cl2 : EtOAc = 60 : 1);
Yield: 335 mg (420 µmol; 86 %) of a yellow solid.
M.p. 212 °C; 1H-NMR (400.1 MHz; [D6]acetone): δ = 8.24 (m, 2H); 7.78 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.6 Hz, 4JHH = 1.5 Hz, 2H); 7.60 (m, 2H); 7.46 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.5 Hz, 4JHH = 1.2 Hz, 2H); 7.39 (m, 1H); 7.24 (AA', 2H); 7.21 – 7.15 (-, 3H); 7.11 (BB', 2H); 7.08 – 7.02 (-, 2H); 6.99 (dd, 3JHH = 7.4 Hz, 4JHH = 1.7 Hz, 2H); 6.95 (s, 2H); 6.85 – 6.74 (-, 4H); 6.25 (dd, 3JHH = 8.0 Hz, 4JHH = 1.3 Hz, 2H); 4.12 (s, 2H); 3.34 – 3.22 (-, 4H); 1.62 (s, 6H); 13C-NMR (100.6 MHz; [D6]acetone): δ = 149.8 (quart.); 147.8 (quart.); 147.1 (quart.); 146.6 (quart.); 145.7 (quart.); 144.8 (quart.); 142.0 (quart.); 140.3 (quart.); 138.9 (quart.); 138.4 (quart.); 135.1 (quart.); 132.2 (tert.); 131.3 (tert.); 131.1 (tert.); 130.3 (tert.); 129.9 (quart.); 129.6 (tert.); 129.3 (tert.); 127.4 (quart.); 127.2 (tert.); 126.9 (tert.); 126.4 (tert.); 126.3 (tert.); 125.8 (tert.); 125.5 (quart.); 125.3 (tert.); 123.8 (tert.); 123.0 (tert.); 122.7 (tert.); 120.5 (quart.); 116.4 (tert.); 41.2 (sec.); 32.8 (sec.); 32.2 (sec.); 20.2 (prim.).
ESI pos. (high resolution): calcd for [M+·] = C54H40ClN3S·+: 797.26260; found: 797.26366 (Δ = 1.33 ppm).

Cascade 10
Following GP: Compound 14 (114 mg; 279 µmol), 28 (155 mg; 311 µmol), Pd2(dba)3·CHCl3 (4.41 mg; 4.26 µmol), P(t-Bu)3 (22.7 µl; 7.49 µmol), sodium tert-butoxide (40.6 mg; 422 µmol), toluene (4 ml); 18 h at 100 °C; flash-column chromatography (CH2Cl2 : EtOAc = 40:1);
Yield: 157 mg (190 µmol; 68 %) of a yellow solid.
M.p. 187 °C; 1H-NMR (400.1 MHz; [D2]dichloromethane): δ = 8.23 (d, 3JHH = 8.7 Hz, 2H); 7.77 (ddd, 3JHH = 8.6 Hz, 3JHH = 6.7 Hz, 4JHH = 1.5 Hz, 2H); 7.61 – 7.57 (-, 2H); 7.55 (d, 4JHH = 2.5 Hz, 2H); 7.43 (ddd, 3JHH = 8.7 Hz, 3JHH = 6.6 Hz, 4JHH = 1.2 Hz, 2H); 7.40 – 7.33 (-, 3H); 7.31 (d, 3JHH = 8.8 Hz, 2H); 7.25 (AA', 2H); 7.17 (d, 3JHH = 8.2 Hz, 1H); 7.13 (BB', 2H); 7.09 – 7.03 (-, 2H); 7.00 (dd, 3JHH = 8.8 Hz, 4JHH = 2.5 Hz, 2H); 6.97 – 6.95 (-, 2H); 4.16 (s, 2H); 3.91 (s,
6H); 3.35 – 3.24 (s, 4H); 1.62 (s, 6H). \(^1H\)\(^{13}C\)-NMR (100.6 MHz; [D\(_2\)]dichloromethane): \(\delta = 154.4\) (quart.); 149.5 (quart.); 147.8 (quart.); 147.17 (quart.); 147.15 (quart.); 146.6 (quart.); 145.7 (quart.); 141.1 (quart.); 140.2 (quart.); 138.8 (quart.); 138.4 (quart.); 136.7 (quart.); 136.3 (quart.); 135.0 (quart.); 131.3 (tert.); 131.2 (tert.); 130.34 (tert.); 130.33 (tert.); 129.6 (tert.); 129.5 (tert.); 127.4 (quart.); 127.1 (tert.); 126.4 (tert.); 126.3 (tert.); 125.9 (tert.); 125.6 (quart.); 125.3 (tert.); 125.0 (quart.); 123.8 (tert.); 123.0 (tert.); 115.4 (tert.); 111.0 (tert.); 103.1 (tert.); 56.3 (prim.); 41.2 (sec.); 32.7 (sec.); 32.3 (sec.); 20.2 (prim.).

ESI pos. (high resolution): calcd for [M\(^+\)] = C\(_{56}\)H\(_{44}\)ClN\(_3\)O\(_2\)\(^+\): 825.31166; found: 825.31102 (\(\Delta = 0.78\) ppm).

References

[1] C. Lambert, J. Schelter, T. Fiebig, D. Mank, A. Trifonov, J. Am. Chem. Soc. 2005, 127, 10600-10610.
[2] W. S. Trahanovsky, J. L. Tunkel, J. C. Thoen, Y. Wang, J. Org. Chem. 1995, 60, 8407-8409.
[3] M. P. Doyle, B. Siegfried, J. F. Dellaria Jr., J. Org. Chem. 1977, 42, 2426-2431.
[4] G. W. Gribble, W. J. Kelly, S. E. Emery, Synthesis 1978, 10, 763-765.
[5] Because it turned out to be impossible to exchange selectively one bromine by one iodine atom in 12 we used 12 in a large excess in order to minimise the formation of symmetric substitution products.
[6] J. F. Hartwig, Synlett 1997, 4, 329-340.
[7] J. F. Hartwig, Angew. Chem., Int. Ed. Engl. 1998, 37, 2046-2067.
[8] M. Nishiyama, T. Yamamoto, Y. Koie, Tetrahedron Lett. 1998, 39, 617-620.
[9] J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, Acc. Chem. Res. 1998, 31, 805-818.
[10] T. Yamamoto, M. Nishiyama, Y. Koie, Tetrahedron Lett. 1998, 39, 2367-2370.
[11] T. Tanaka, T. Tasaki, Y. Aoyama, J. Am. Chem. Soc. 2002, 124, 12453-12462.
[12] T. Hasobe, S. Hattori, H. Kotani, K. Ohkubo, K. Hosomizu, H. Imahori, P. V. Kamat, S. Fukuzumi, Org. Lett. 2004, 6, 3103 - 3106.
[13] Although it is the common procedure to prepare phenylacridine derivatives by a Bernthsen reaction of diphenylamine and the adequately substituted benzoic acid, this reaction was not used to obtain compound 13 because this procedure gave low yields and involved time consuming purifications.
[14] A. Bernthsen, Chem. Ber. 1883, 16, 767-769.
[15] A. Bernthsen, Liebigs Ann. Chem. 1884, 224, 1-56.
[16] Y. Kikugawa, Y. Aoki, T. Sakamoto, J. Org. Chem. 2001, 66, 8612-8615.