Supporting Information

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Preparation of compound 3: In a dry two-neck flask equipped with a reflux condenser under an argon atmosphere was placed a solution of triflate 5 (214 mg, 0.488 mmol, 2.1 equiv.) in THF (5 mL). A suspension of dichlorobis(triphenyl-phosphine)palladium (19 mg, 0.003 mmol, 0.1 equiv.) in THF (2 mL), a solution of diboronate 4 (89 mg, 0.234 mmol, 1 equiv.) in THF (5 mL), a 2 M Na₂CO₃ aqueous solution (4.8 mL) and 8 mL of THF were successively added. After heating at reflux for 3 hours, water (30 mL) was added. The aqueous phase was extracted with CH₂Cl₂ (3 x 20 mL), then the combined organic phases were dried over MgSO₄, filtered and concentrated under vacuo. Upon addition of diethyl ether, a yellow-green powder precipitated. Silica gel chromatography (6:4 hexane / ethyl acetate) then afforded compound 3 (104 mg, 63%) as a yellow solid. M. p. 236-237°C; ¹H NMR (300 MHz, CDCl₃): δ = 3.63, 3.80 (two s, 3 H each, C(O)C=C-OCH₃), 3.86, 3.87 (two s, 3 H each, Ar-OCH₃), 3.90, 3.92 (two s, 3 H each, COOCH₃), 6.95, 6.98 (two d, J = 8.5 Hz, 2 H each, H-10' and H-10''), 7.54-7.63 (m, 2 H, H-2 and H-3), 7.67 (broad d, J = 8.5 Hz, 1 H, H-6), 7.68, 7.73 (two d, J = 8.5 Hz, 2 H each, H-9' and H-9''), 7.90 (s, 1 H, H-8), 7.97 (broad d, J = 7.1 Hz, 1 H, H-4), 7.98
(d, J = 8.5 Hz, 1 H, H-5); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 52.6 (2C, two CH$_3$O), 55.2 (2C, two CH$_3$O), 60.6 (CH$_3$O), 61.5 (CH$_3$O), 103.4, 106.5 (C-3’ and C-3’’), 114.1 (2C, C-10’ and C-10’’), 116.9 (2C, C-6’ and C-6’’), 123.2 (2C, C-1 and C-7), 125.9, 126.5 (C-8’ and C-8’’), 127.3, 127.5, 128.7, 129.3, 130.1, 131.3, 133.1 (C-2, C-3, C-4, C-4a, C-5, C-6, C-8, C-8a), 130.6, 130.7 (C-9’ and C-9’’), 139.4, 139.5 (C-5’ and C-5’’), 160.3 (2C, C-11’ and C-11’’), 163.0, 164.0 (C-4’ and C-4’’), 166.8 (2C, C-7’ and C-7’’), 168.0 (2C, C-2’ and C-2’’); elemental analysis calcd (%) for C$_{40}$H$_{32}$O$_{12}$: C 68.18, H 4.58; found: C 68.03, H 4.83; IR (KBr pellet): $\nu_{\text{max}}$ = 1040, 1512, 1599, 1629, 1731, 1770, 2949, 3001 cm$^{-1}$.

Preparation of pulvinic compound 10: In a dry two-neck flask equipped with a reflux condenser under an argon atmosphere were placed triflate 5 (130 mg, 0.3 mmol, 1 equiv.), phenylboronic acid (40 mg, 0.34 mmol, 1.1 equiv.), potassium phosphate (95 mg, 0.45 mmol, 1.5 equiv.), tetrakis(triphenylphosphine)palladium (10 mg, 3 mol%) and dioxane (1.5 mL). After heating at reflux for 4 hours, the yellow suspension had turned brown. A saturated solution of NH$_4$Cl (10 mL) was added. The aqueous phase was extracted with diethyl ether (3 x 10 mL), then the combined organic phases were dried over MgSO$_4$, filtered and concentrated under vacuo. Silica gel chromatography (7:3 pentane / ethyl acetate) then afforded compound 10 (96 mg, 86%) as a yellow solid. M. p. 168°C, lit$^{[12]}$ 172-173°C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.78 (s, 3 H, C(O)C=C-OCH$_3$), 3.86 (s, 3 H, Ar-OCH$_3$), 3.92 (s, 3 H, COOCH$_3$), 6.95 (d, $J$ = 9.2 Hz, 2 H, H-10), 7.41-7.46 (m, 3 H, H-3’, H-4’), 7.52 (dd, $J$ = 7.3, 1.2 Hz, 2 H, H-2’), 7.67 (d, $J$ = 9.2 Hz, 2 H, H-9); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 52.9 (CH$_3$O), 55.5 (CH$_3$O), 61.4 (CH$_3$O), 108.0 (C-3), 114.5 (C-10), 116.5 (C-6), 123.6 (C-1’), 127.3, 128.6, 128.7, 129.0, 130.1 (C-2’, C-3’, C-4’, C-6, C-8), 131.0 (C-9), 140.2 (C-5), 160.7 (C-11), 163.0
(C-4), 167.4 (C-7), 168.0 (C-2); IR (KBr pellet): $\nu_{\text{max}} = 1597, 1622, 1725, 1768, 2934$ cm$^{-1}$.

Procedure for the ESI-MS speciation study of norbadione A dipotassium salt: Dipotassium salt of norbadione A was provided by Dr Melvyn Gill (Univ. of Melbourne, Australia) and repeatedly purified by chromatography on Sephadex LH-20, with methanol/acetone/water (95/3/2) as eluent. All solvents were HPLC grade. A $10^{-4}$ M stock solution of norbadione A dipotassium salt in methanol was prepared. Cesium chloride was introduced by addition of 10 to 60 $\mu$L of solutions of appropriate concentration into 1 mL of the stock solution. The mass spectrometric measurements were recorded in positive ion mode using a QuattroII triple-quadrupole spectrometer equipped with an ESI interface (Micromass, Manchester, UK). The cone voltage was set to 25 V and nitrogen operating at 300 L/h was employed as both the drying and nebulizing gas.

Neutral loss spectra discussed were the result of synchronised scans of MS1 and MS3 such as the spectra show the masses of all complexes that lost a fragment of specific mass into the radiofrequency-only collision cell containing argon collision gas at a nominal pressure of $2.10^{-3}$ mbar.

Calculation methods: Our method is based on the measurements of relative ion abundances and assumption was made that singly charged complexes containing the same ligand have close response factors. This assumption, which is not always justified, have already been discussed in the literature$^{[7]}$ and seems reasonable in the present case. For each amount of cesium added, relative peak intensities were measured and expressed in terms of $I_i = \alpha_i I_{100}$, where $I_{100}$ is the ionic current of the main peak. This main peak does not correspond to the same species throughout a speciation study. Assuming that the sum of all peak intensities in one spectrum corresponds to a total concentration of $10^{-4}$ M ligand, the concentration of each species can be determined. The free cesium equilibrium concentration is determined by: $[\text{Cs}^+]_{eq} = n \times 10^{-4}$ M $-$ ([1:1 complex] + 2 x [1:2 complex]), where $n =$ number of equivalents of CsCl added. The total ionic current of $[\text{MK}_2+\text{K}]^+$ and $[\text{MK}_2+\text{Na}]^+$ complexes versus concentration of $\text{MK}_2$ in methanol achieved a linear relationship for concentrations ranging from 2.0 x
$10^{-5}$ M to $1.8 \times 10^{-4}$ M. Thus, it would be possible to assess equilibrium concentrations with a sufficient reliability to justify the calculation of stability constants.

Assuming an equivalence between concentrations and thermodynamic activities, the following equation can be used to assess the stability constant $\beta$ of the complex of norbadione A dipotassium salt and one cesium cation.

$$\beta = \frac{(\text{MK}_2 \cdot \text{Cs}^+)}{(\text{MK}_2)(\text{Cs}^+)}$$