

SUPPLEMENTARY MATERIAL

Table S1. Observed first-order rate constants, k'_{obsd} , for formation of the 1,3-dimethoxy adduct **4b-Me** in methanol. ^a

pH ^b	[MeO ⁻], mol dm ⁻³	k'_{obsd} , s ⁻¹
11.72	1.10×10^{-5}	9.09
12.02	2.19×10^{-5}	13.36
12.18	3.16×10^{-5}	17.60
12.26	3.80×10^{-5}	16.20
12.45	5.89×10^{-5}	20.20
12.68	1.00×10^{-4}	31.80
12.75	1.18×10^{-4}	32.50
12.89	1.62×10^{-4}	50.20
13.04	2.29×10^{-4}	68.40

(a) T = 20 °C, I = 0.01 mol dm⁻³; (b) pH = pK_s + log[MeO⁻] + log γ_± = 16.68 + log[MeO⁻]
with pK_s = 16.86 at 20°C. ^{33,36}

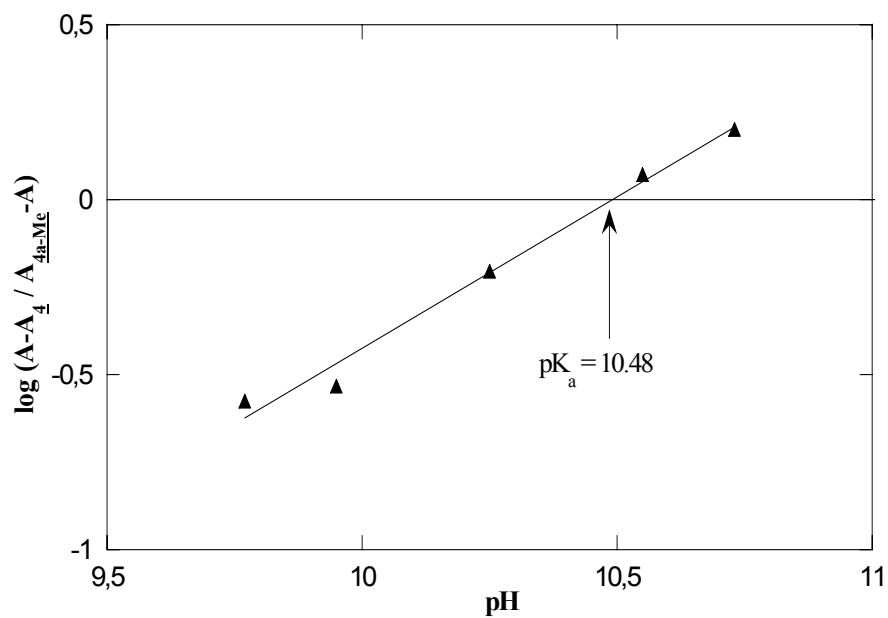


Figure S1. Effect of pH on the ionization ratio of **4** into the stable 1,1-adduct **4a-Me** at T = 20 °C in methanol.

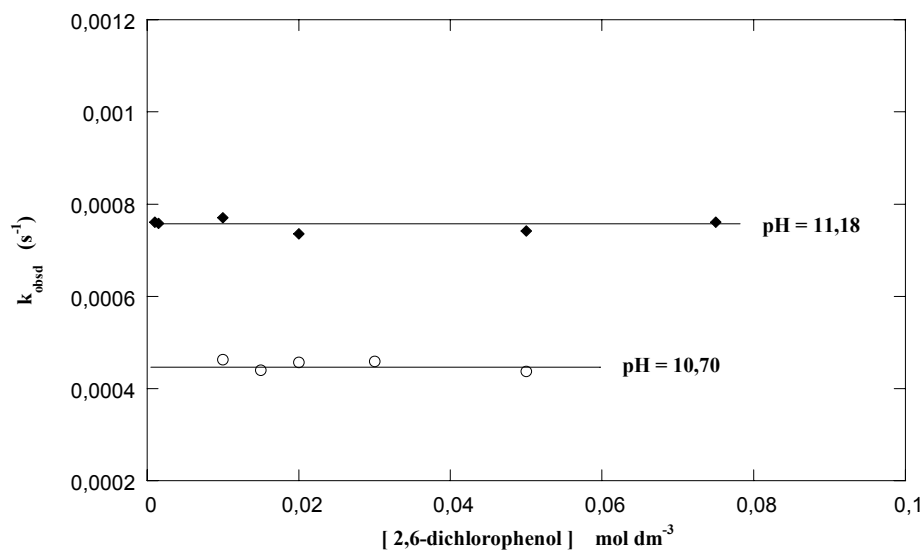


Figure S2. Plots showing the lack of dependence of the observed first-order rate constant k'_{obsd} for formation of the 1,1-adduct **4a-Me** on the 2,6-dichlorophenol buffer concentration at pH = 10.70 and pH = 11.18. (T = 20 °C in methanol).

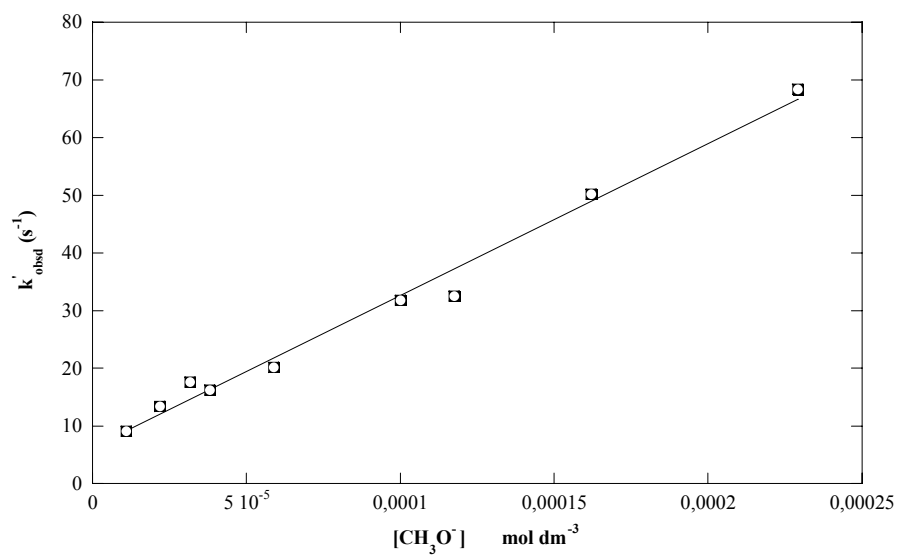


Figure S3. Influence of the MeO⁻ concentration on the observed first-order rate constant k'_{obsd} for formation of the 1,3-dimethoxy adduct **4b-Me** at pH \geq 10.7 and T = 20 °C in methanol.