Electronic supplementary information (ESI)

Table 1S Selected bond lengths, Å, and angles, °, for **1a** and **1b**

1a			
O(1)–C(5)	1.370(2)	O(2)–C(6)	1.373(2)
C(1)–C(2)	1.467(2)	C(5)–C(6)	1.414(2)
C(2)–C(3)	1.386(2)	C(6)–C(7)	1.382(2)
C(3)–C(4)	1.396(2)	C(2)–C(7)	1.415(2)
C(4)–C(5)	1.383(2)	C(1)–C(1A)	1.338(3)
C(1A)–C(1)–C(2)	127.8(2)	O(1)–C(5)–C(6)	115.9(1)
O(1)–C(5)–C(4)	124.9(1)	O(2)–C(6)–C(5)	114.9(1)
O(2)–C(6)–C(7)	125.1(1)	O(1)…O(2)	2.591

1b			
O(1)–C(5)	1.372(2)	O(1)–C(1)	1.445(2)
O(2)–C(6)	1.369(2)	O(2)–C(17)	1.443(2)
C(1)–C(2)	1.475(2)	C(5)–C(6)	1.418(2)
C(2)–C(3)	1.397(3)	C(6)–C(7)	1.391(2)
C(3)–C(4)	1.396(2)	C(2)–C(7)	1.410(3)
C(4)–C(5)	1.382(3)	C(1)–C(1A)	1.328(4)
C(5)–O(1)–C(8)	117.00(14)	C(6)–O(2)–C(17)	116.77(13)
C(15)–O(3)–C(16)	112.16(13)	C(13)–O(4)–C(14)	113.00(15)
C(11)–O(5)–C(12)	112.50(15)	C(9)–O(6)–C(10)	112.48(15)
O(1)–C(5)–C(4)	125.19(16)	O(1)–C(5)–C(6)	115.08(16)
O(2)–C(6)–C(5)	115.59(15)	O(2)–C(6)–C(7)	125.27(16)
C(1)–C(2)–C(3)	122.83(17)	C(2)–C(3)–C(4)	120.87(18)
C(3)-C(4)–C(5)	120.63(18)	C(4)–C(5)–C(6)	119.72(16)
C(5)–C(6)–C(7)	119.13(17)	C(2)–C(7)–C(6)	121.44(18)
C(3)–C(2)–C(7)	118.21(16)	C(1)–C(2)–C(7)	118.96(17)
C(1A)–C(1)–C(2)	127.2(2)	O(1)…O(2)	2.591

Table 2S Solution and solid-state ^{13}C NMR data for **1b**, **2b** and complexes [**1b** · **2b**], [(**1b**)$_2$ · **2b**]

	δ_C, ppm										
	C-1	C-2	C-5	C-6	C-3	C-4	CH=CH	C-α	C-α'	C-β	C-γ,δ,ε
1b (solution) [a]	131.26	109.75	112.61	120.02	148.72	148.23	127.00	68.26	68.15	69.32, 69.35	70.46, 70.57
[**1b** · **2b**] (solution) [a]	132.36	109.97	113.14	120.84	147.05	146.35	127.79	68.43	67.91	69.65, 69.51	70.92, 70.69, 70.32, 70.13, 70.04, 69.87
Δδ [b]	*1.10*	*0.22*	*0.53*	*0.82*	*–1.67*	*–1.88*	*0.79*	*0.17*	*0.24*	*0.16÷0.3 3*	*-0.70÷0.46*
[(**1b**)$_2$ · **2b**] (solution) [a]	131.75	109.06	112.65	120.75	147.15	146.77	127.17	68.26	67.81	69.46, 69.34	70.62, 70.51, 70.14, 70.11, 70.03
Δδ [b]	*0.49*	*-0.69*	*0.04*	*0.73*	*–1.57*	*–1.46*	*0.17*	*0.00*	*–0.34*	*-0.01÷0.14*	*-0.54÷0.16*
1b (solid) [c]	128.8	114.3 [f]	113.4 [f]	114.8 [f]	149.6	147.5	125.4	69.3, 70.8, 72.5			
Δδ' [d]	*2.5*	*–4.6*	*–0.8*	*5.2*	*–0.9*	*0.7*	*1.6*	*–4.4÷1.3*			
[(**1b**)$_2$ · **2b**] (solid) [c]	126.5 [e]		112.7 [e]		146.6 [e]		126.5 [e]	70.1			
Δδ [b]	*–2.3*	*–1.6*	*–0.7*	*–2.1*	*–3.0*	*–0.9*	*1.1*	*–2.4÷0.8*			

	δ_C, ppm								
	C-2	C-6	C-4	C-3	C-5	CH=CH	CH_2N	CH_2NH_3	CH_2
2b (solution) [a]	145.49	145.49	152.05	126.81	126.81	134.65	58.62	36.99, 36.90 [g]	28.69
[**1b** · **2b**] (solution) [a]	144.68	144.68	151.67	126.45	126.45	134.35	58.50	36.20, 36.10 [g]	29.67
Δδ [b]	*–0.81*	*–0.81*	*–0.38*	*–0.36*	*–0.36*	*–0.30*	*–0.12*	*–0.80*	*0.98*
[(**1b**)$_2$ · **2b**] (solution) [a]	143.89	143.89	151.01	125.71	125.71	133.91	58.63	36.33, 36.23 [g]	30.02
Δδ [b]	*–1.60*	*–1.60*	*–1.04*	*–1.10*	*–1.10*	*–0.74*	*0.01*	*–0.67*	*1.33*
2b (solid) [c]	145.0	148.0	150.0	127.9	122.1	133.1	59.9	39.6	28.6
Δδ' [d]	*0.5*	*–2.5*	*2.1*	*–1.1*	*4.7*	*1.6*	*–1.3*	*–2.7*	*0.1*
[(**1b**)$_2$ · **2b**] (solid) [c]		146.6 [e]			126.5 [e]	131.6 [e]	58.6	36.6	30.0
Δδ [b]	*1.6*	*–1.4*	*–3.4*	*–1.4*	*4.4*	*–1.5*	*–1.3*	*–3.0*	*1.4*

[a] In CD_3CN/D_2O solutions (95/5, v/v) at a concentration of 0.023 M, 25°C. [b] Δδ = δ(complex) – δ(single component), ppm. [c] At ambient temperature. [d] Δδ = δ(solution) – δ(solid), ppm. [e] Strongly broadened and markedly overlapped signals difficult for assignment. [f] Interchangeable signals.

Table 3S Crystal data, X-ray experiment details, and structure solution and refinement parameters for **1a,b**

Compound	**1a**	**1b**
Empirical formula	$C_{18}H_{20}O_4$	$C_{34}H_{48}O_{12}$
Formula weight	300.34	648.72
Colour, habit	Colorless, plate	Colorless, plate
Crystal size [mm]	0.36 × 0.24 × 0.10	0.60 × 0.40 × 0.02
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions:		
a [Å]	8.9484(5)	42.778(2)
b [Å]	6.7152(3)	9.0073(3)
c [Å]	12.4323(7)	8.6096(3)
β [°]	92.500(3)	95.988(2)
Volume [$Å^3$]	746.35(7)	3299.3(2)
Z	2	4
Density (calcd.) [g cm^{-3}]	1.336	1.306
Absorption coeff. [mm^{-1}]	0.094	0.098
F(000)	320	1392
Diffractometer	Bruker SMART–6	Bruker SMART–6
Temperature [K]	120.0(2)	100.0(2)
θ range for data collection	2.28 to 23.26	2.31 to 26.00
Radiation λ [Å]	Graphite-monochromated Mo-K_α (0.71073)	Graphite-monochromated Mo-K_α (0.71073)
Reflections collected	2775	8379
Index ranges	$-8 \le h \le 9$, $-7 \le k \le 7$, $-13 \le l \le 12$	$-43 \le h \le 52$, $-11 \le k \le 11$, $-10 \le l \le 10$
Independent reflections	1064 [R(int) = 0.0278]	2900 [R(int) = 0.0661]
Absorption correction	SADABS	SADABS
Min. / Max. transmission	0.9671 and 0.9907	0.8887 and 0.9855
Data/restraints/parameters	1064/ 0 / 141	2900 / 0 / 305
Goodness-of-fit on F^2	1.008	1.011
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0844$	$R_1 = 0.0410$, $wR_2 = 0.0807$
R indices (all data)	$R_1 = 0.0448$, $wR_2 = 0.0892$	$R_1 = 0.0751$, $wR_2 = 0.0906$
Extinction coefficient	0.007(3)	0.0009(2)
Largest diff. peak and hole [e $Å^{-3}$]	0.168 / -0.149	0.188 / -0.188