RSC Advances

(revised)

Jan 8, 2016

Supporting information

A New Detection Mechanism Involving Keto-Enol Tautomerization: Selective Fluorescence Detection of Al(III) by Dehydration of Secondary Alcohols in Mixed DMSO/Aqueous Media

Madhubabu Alaparthi, Kadarkaraisamy Mariappan, Eric Dufek, Mariah Hoffman and Andrew G. Sykes

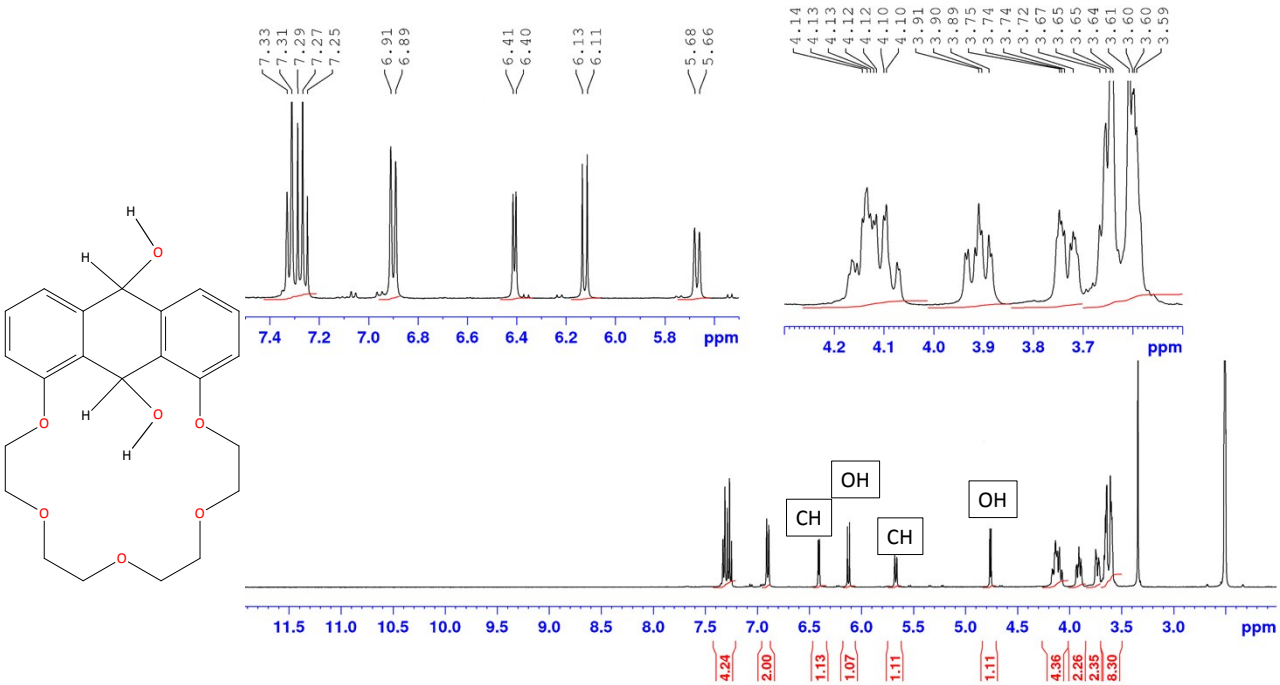


Figure S 1: ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

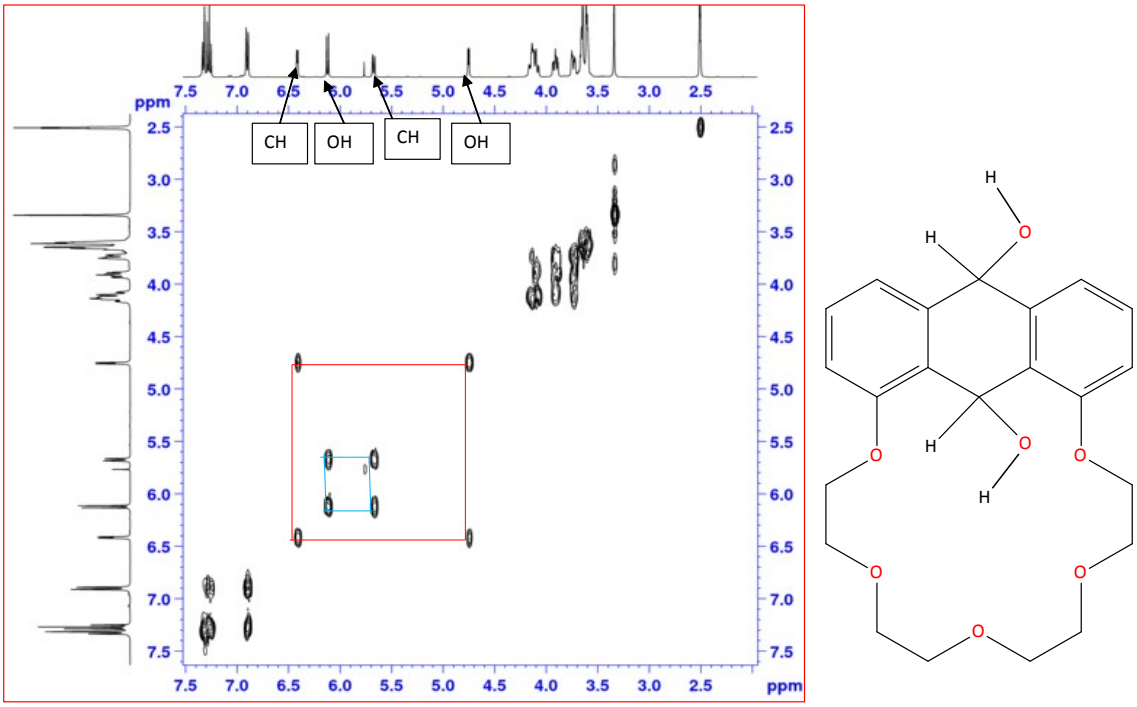


Figure S2: COSY spectrum of compound **2** in DMSO-d_6.

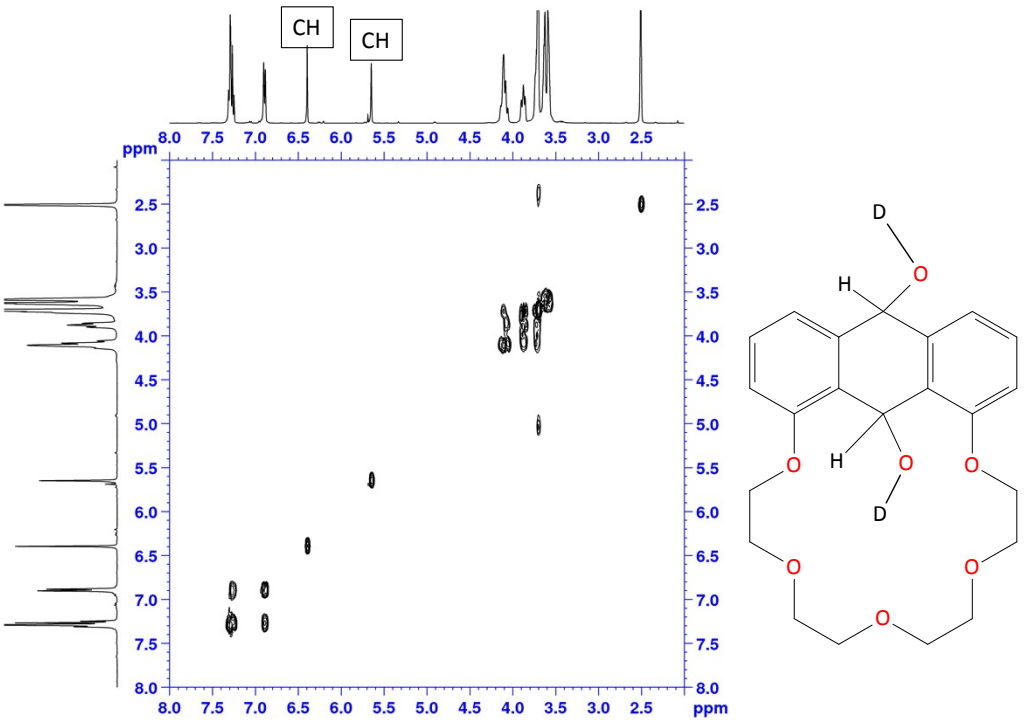


Figure S3: COSY spectrum of compound **2** in DMSO-d_6 D_2O exchange.

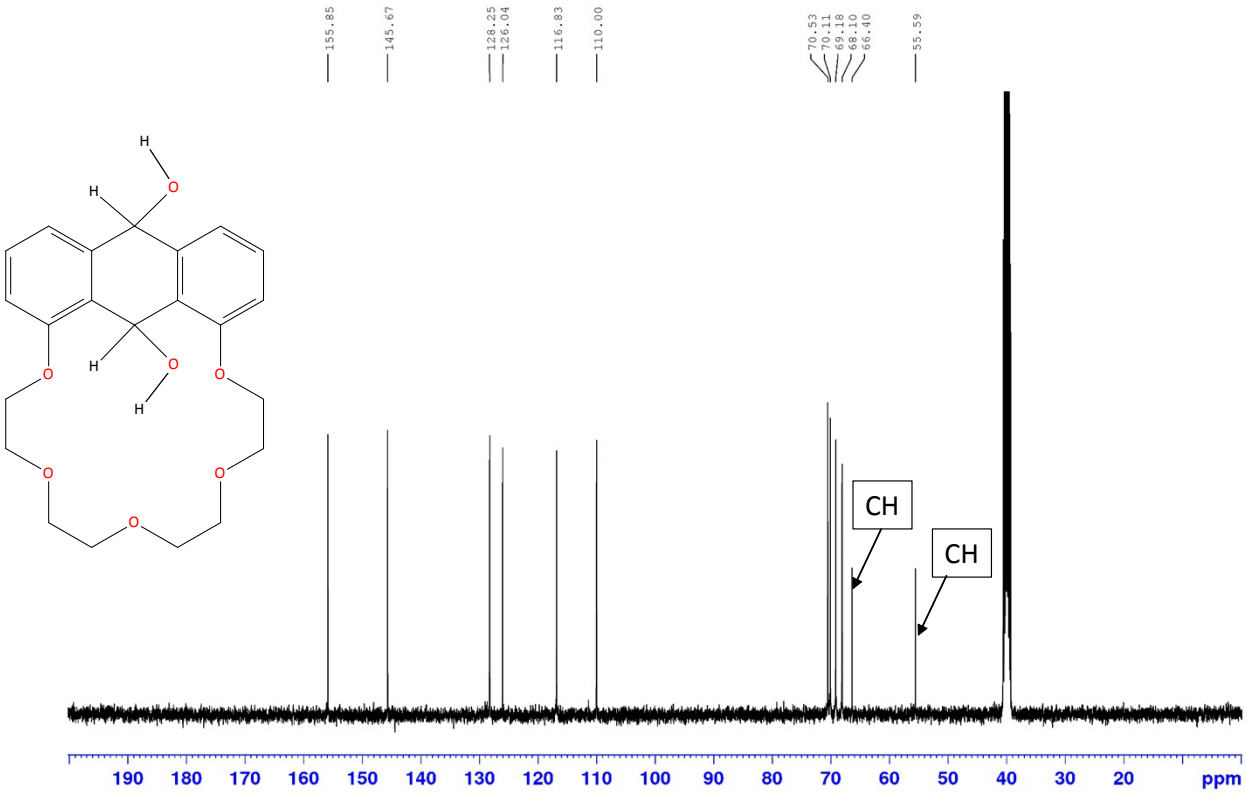


Figure S4: ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

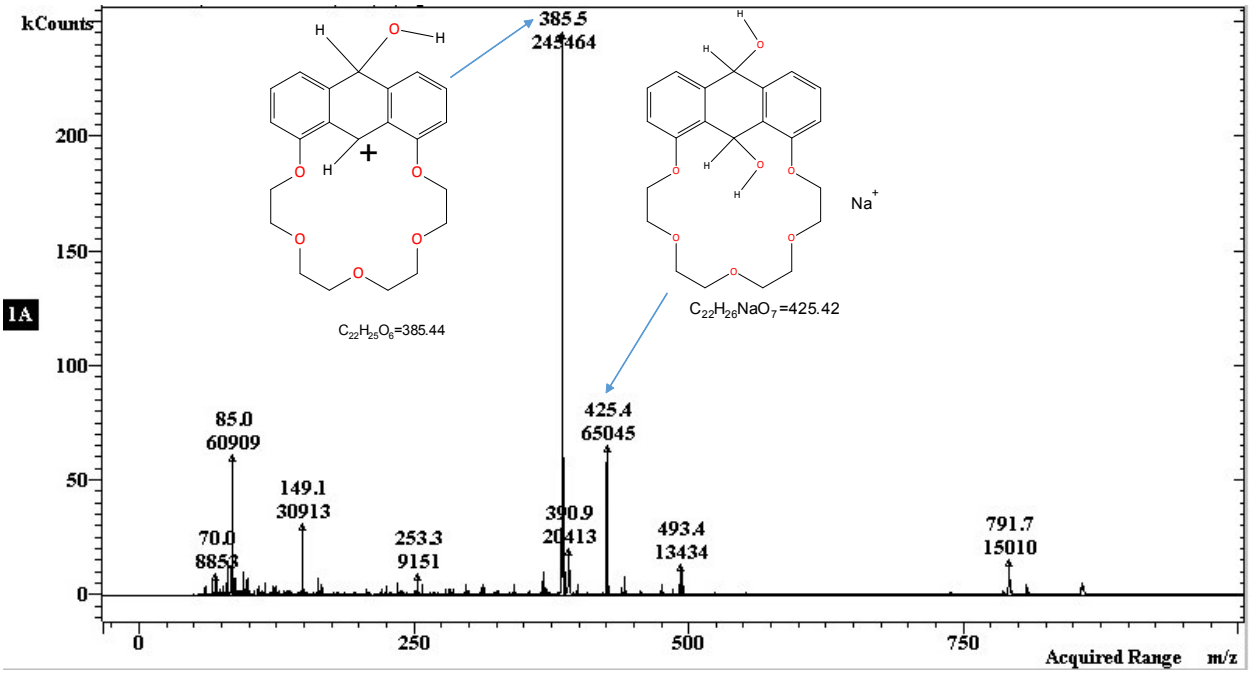


Figure S5: ESI-MS spectrum of compound **2**.

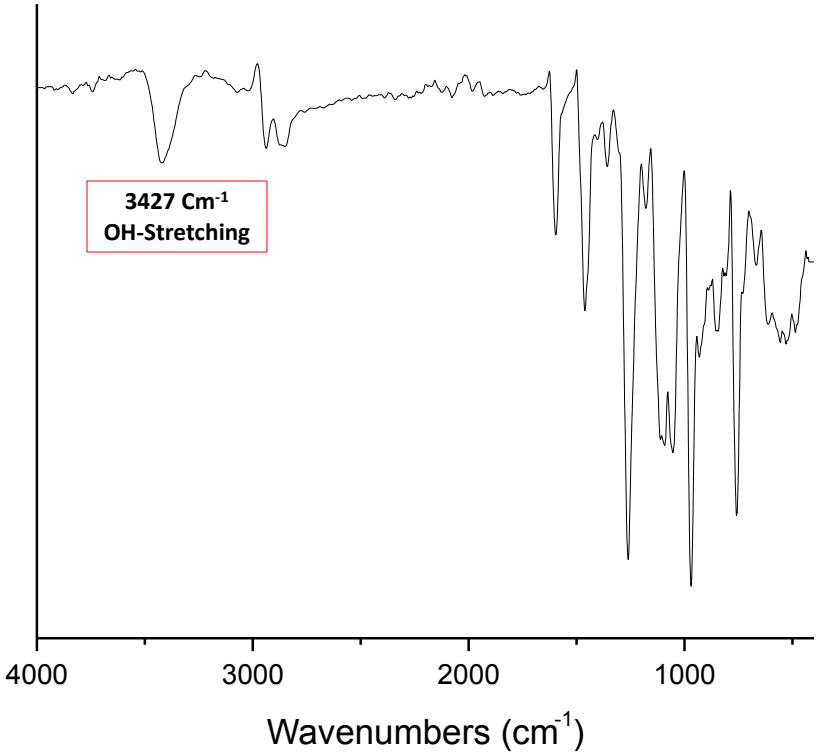


Figure S6: IR spectrum of compound **2**.

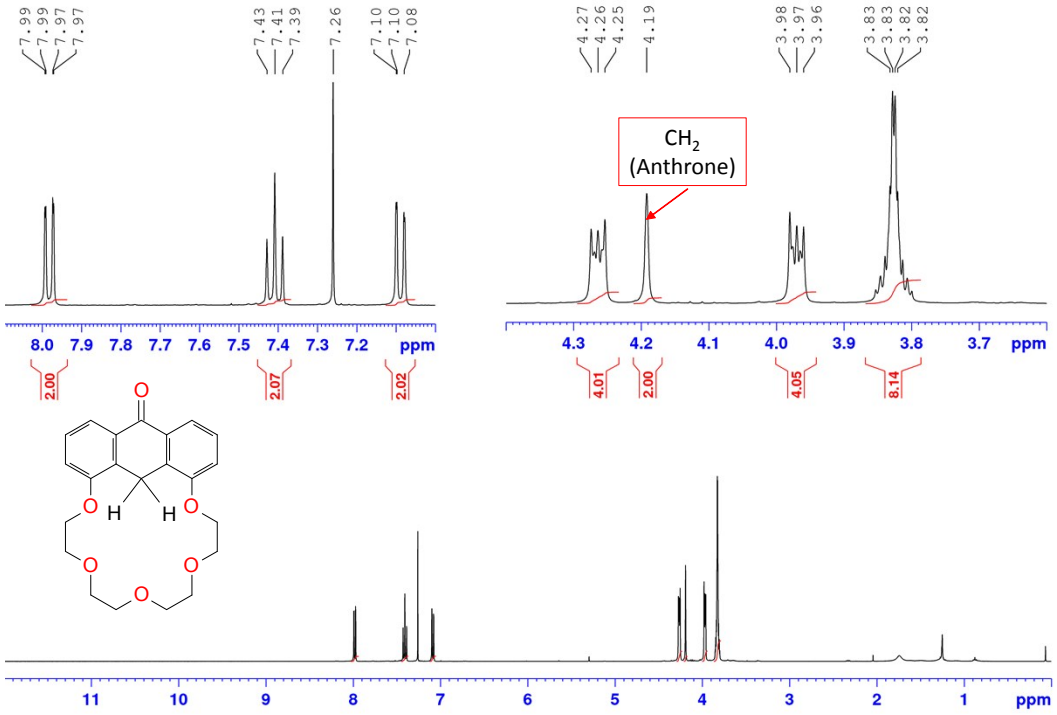


Figure S7: ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

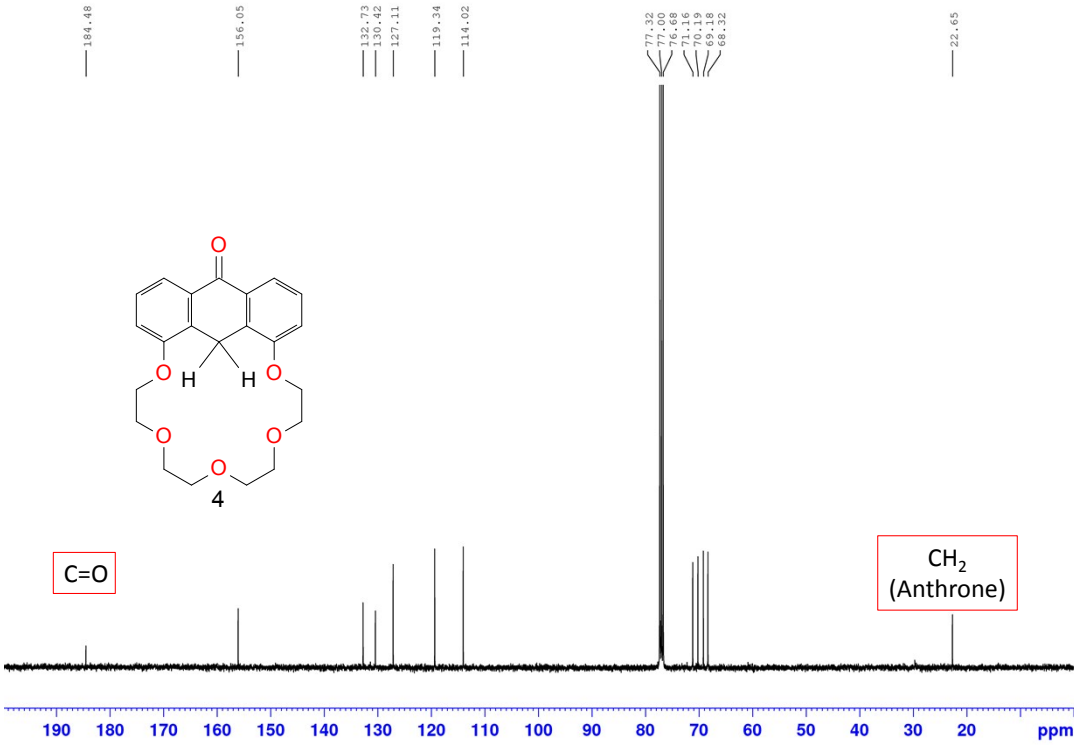


Figure S8: ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

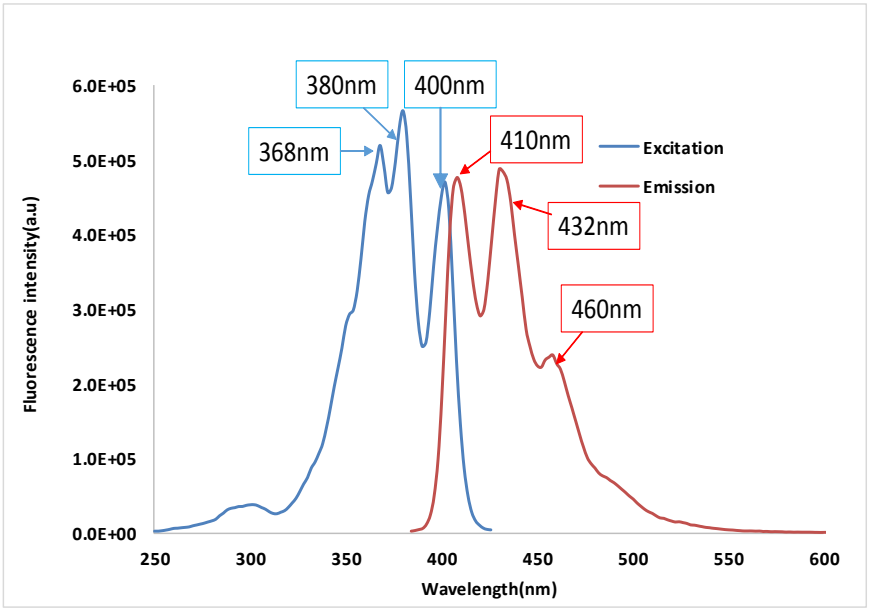


Figure S9: Excitation and Emission spectrum of 3.0 mL of 100um compound **2** in DMSO + pH = 7 buffer (10%). λex = 365 nm.

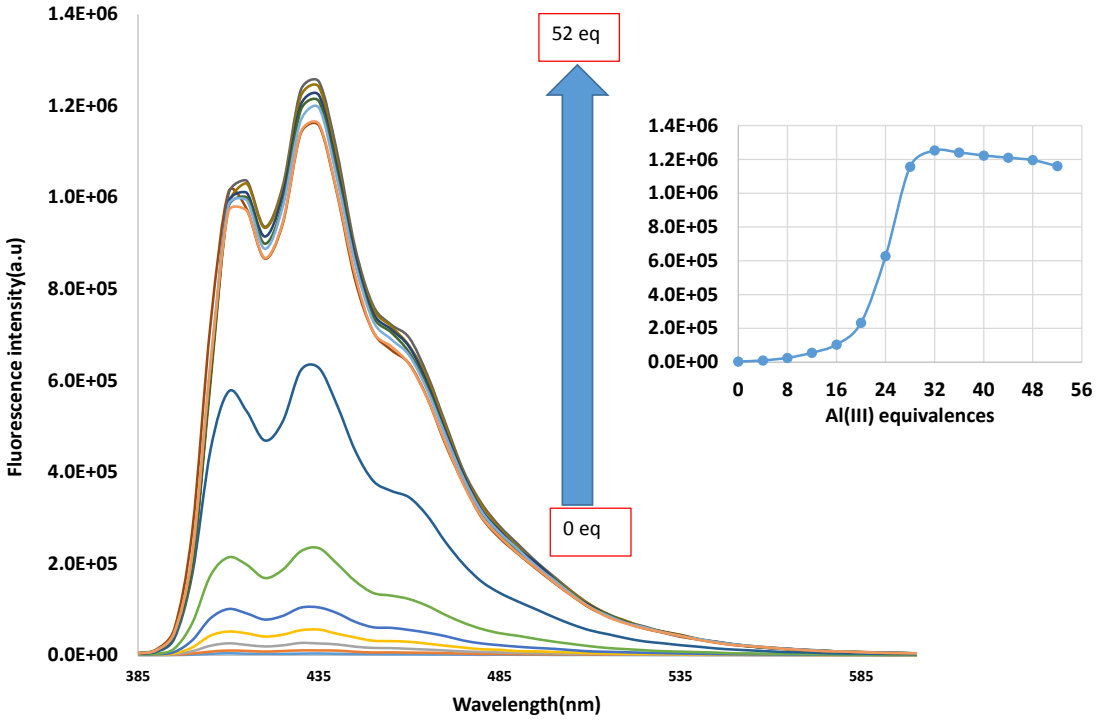


Figure S10: Fluorescence spectrum of 10^{-4} M compound **2** in DMSO (90%) + pH = 7 buffer (10%) with added 10 - 130 uL of $1.2x10^{-1}$ M Al(III) $(ClO_4)_3$ in water (0-52eq). λex = 365 nm.

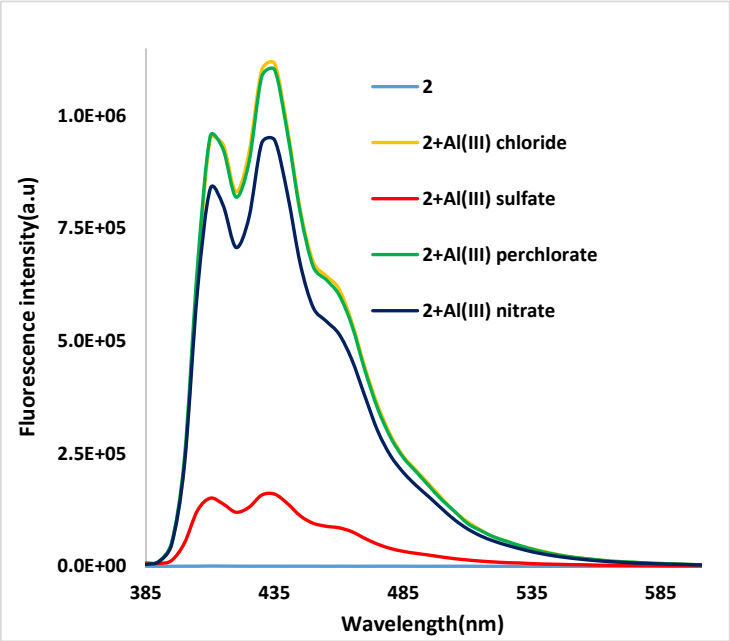


Figure S11: Fluorescence spectrum of 3.0 mL of 100uM compound **2** in DMSO + pH = 7 buffer (10%) with added 30 eq of $1.2x10^{-1}$ M Al(III) salts (Chloride, perchlorate, nitrate, sulfate) in water λex = 365nm.

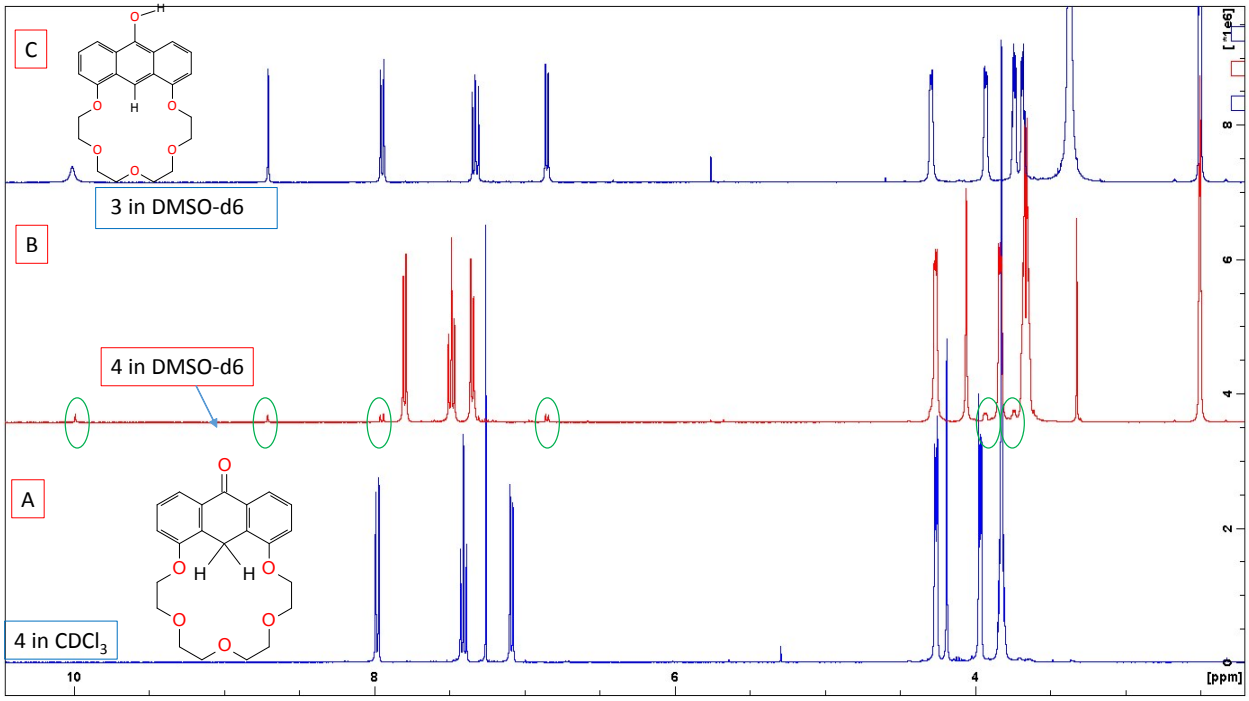


Figure S12: (A) ^{1}H NMR spectrum of compound **4** in $CDCl_3$, (B) ^{1}H NMR spectrum of compound **4** in DMSO-d_6 and (C) ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

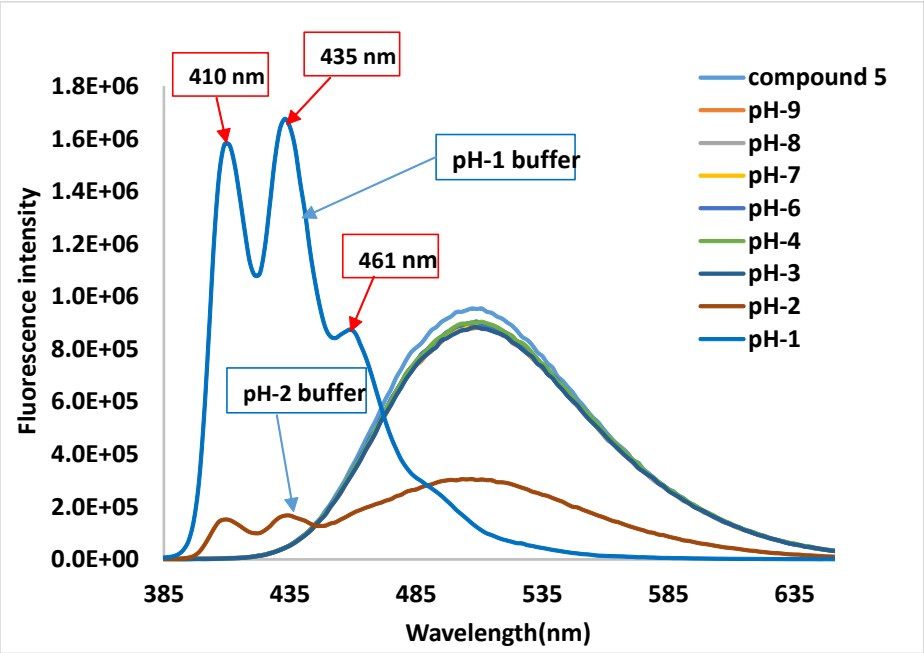


Figure S13: Fluorescence spectrum of 3.0 mL of 100uM compound **5** in CH_3CN with added 50ul of pH = 1 buffer. λex = 365 nm.

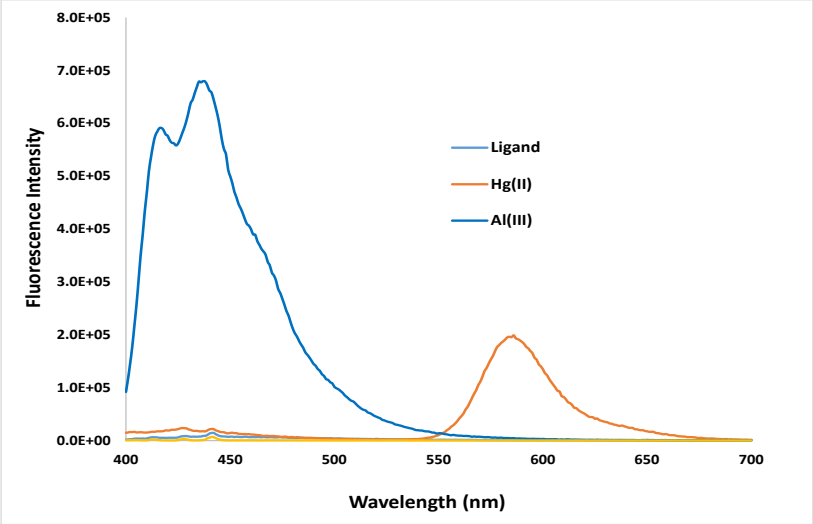


Figure S14: Emission spectra of $4.0x10^{-5}$ M **7** in CH_3CN with 5.0 equivalents of added Al(III) or Hg(II). λ_{ex} = 390 nm.

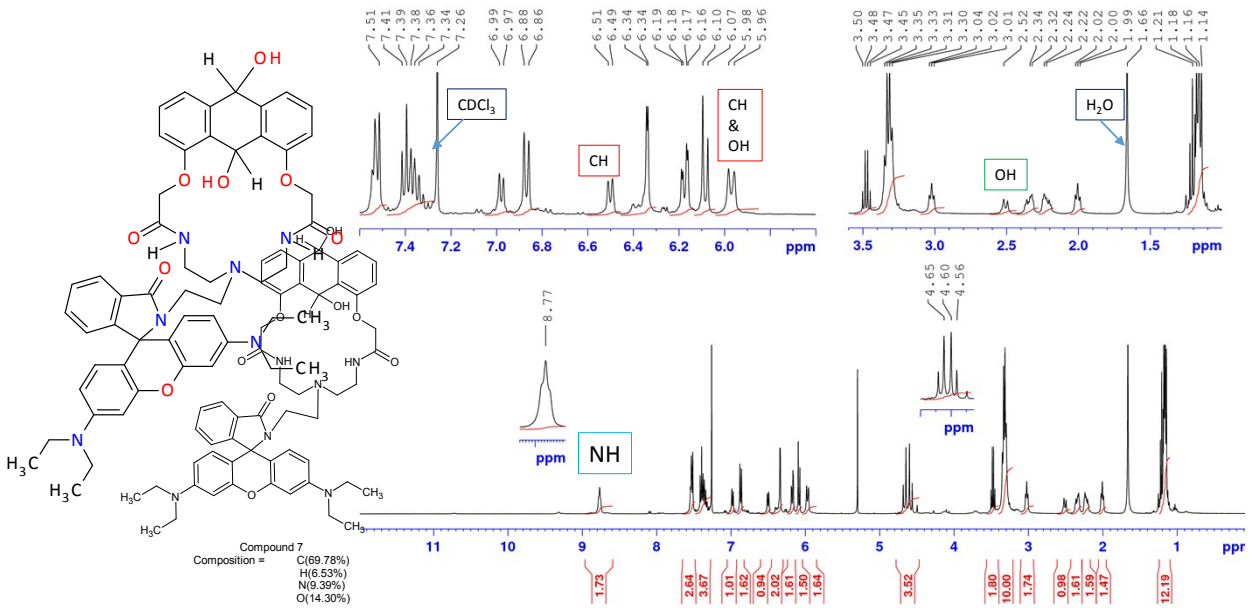


Figure S15: ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

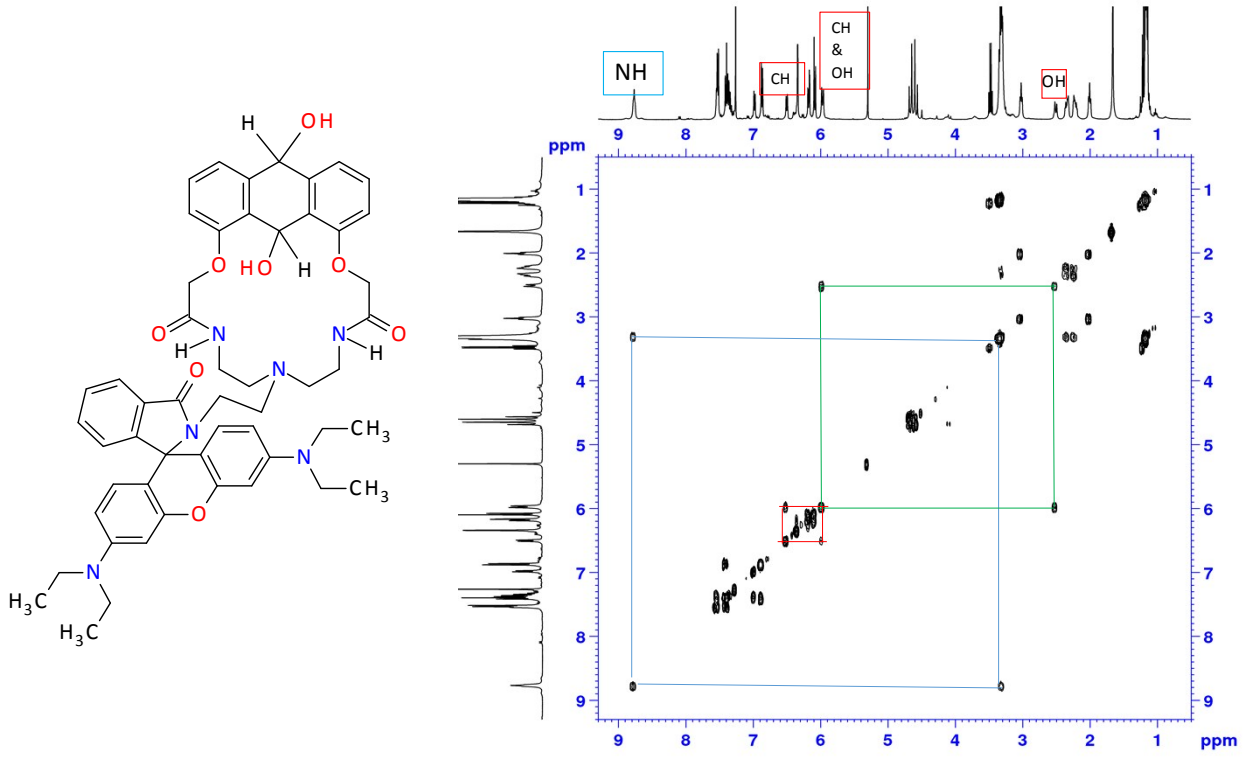


Figure S16: COSY spectrum of compound **7** in $CDCl_3$.

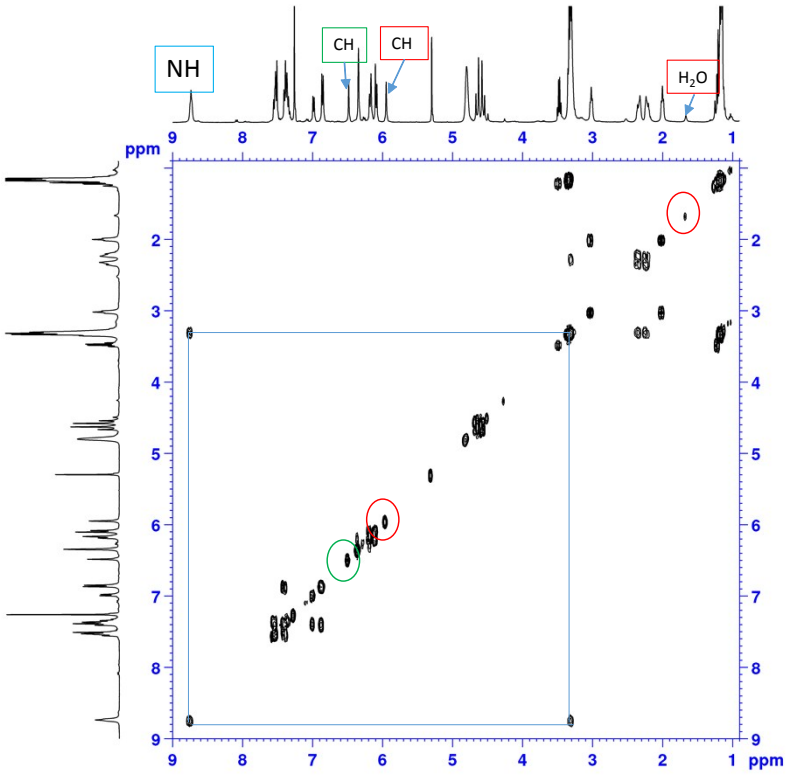


Figure S17: COSY spectrum of compound **7** in $CDCl_3$ D_2O exchange.

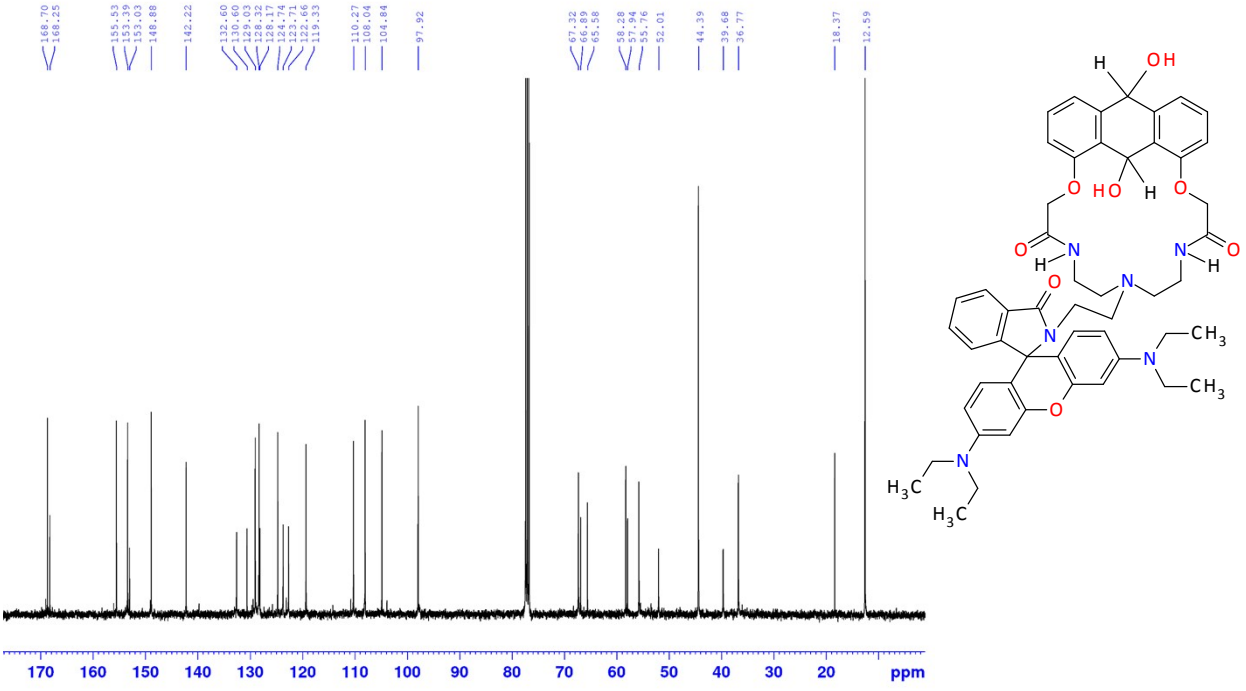


Figure S18: ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

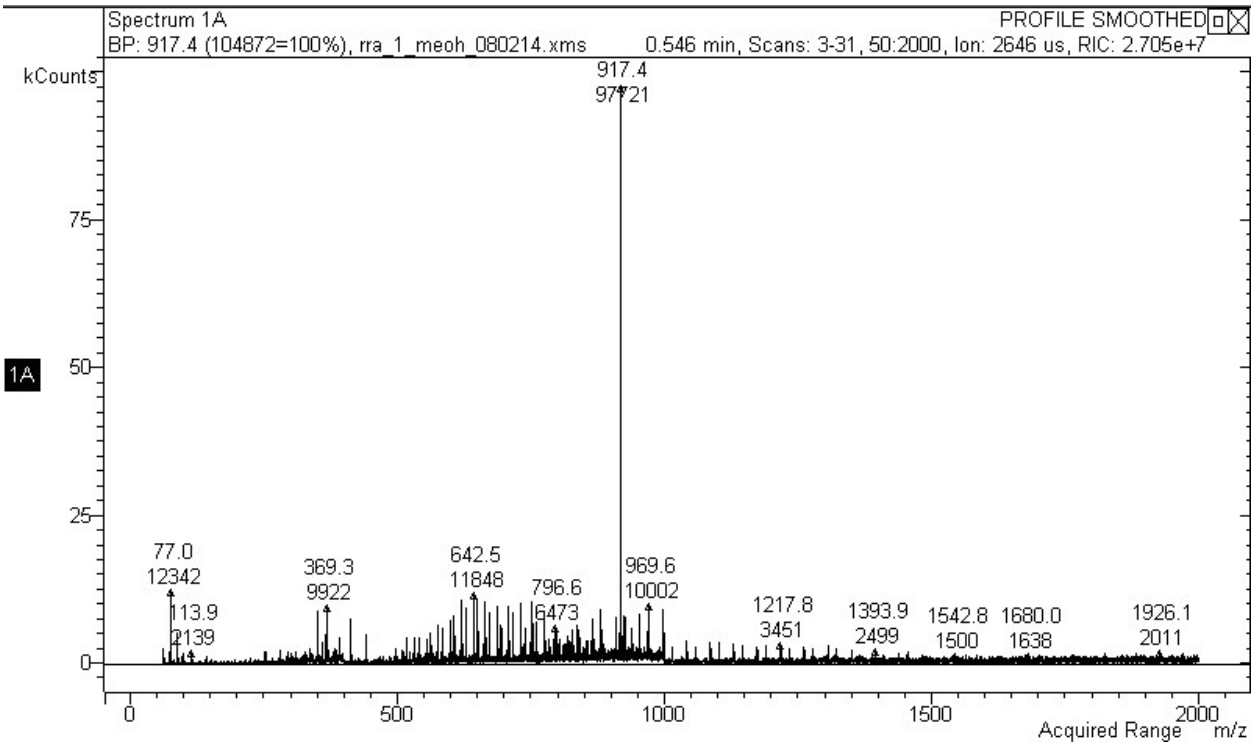


Figure S19: Mass spectrum of compound **7**.

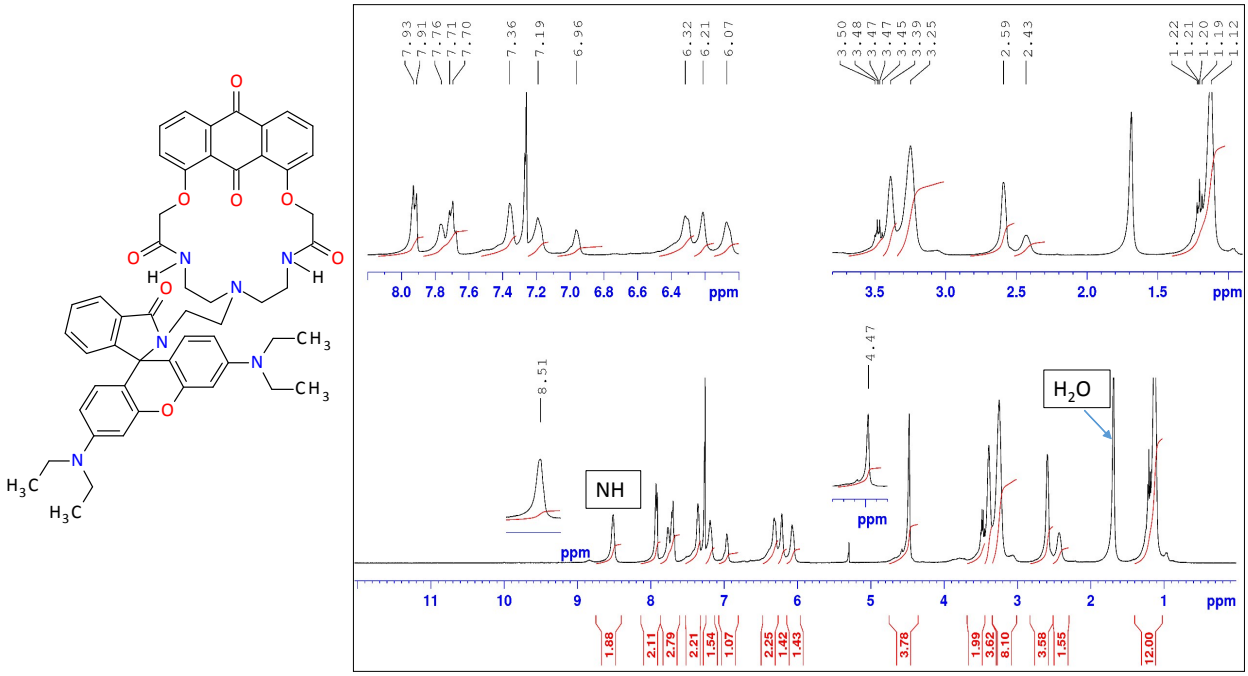


Figure S20: ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

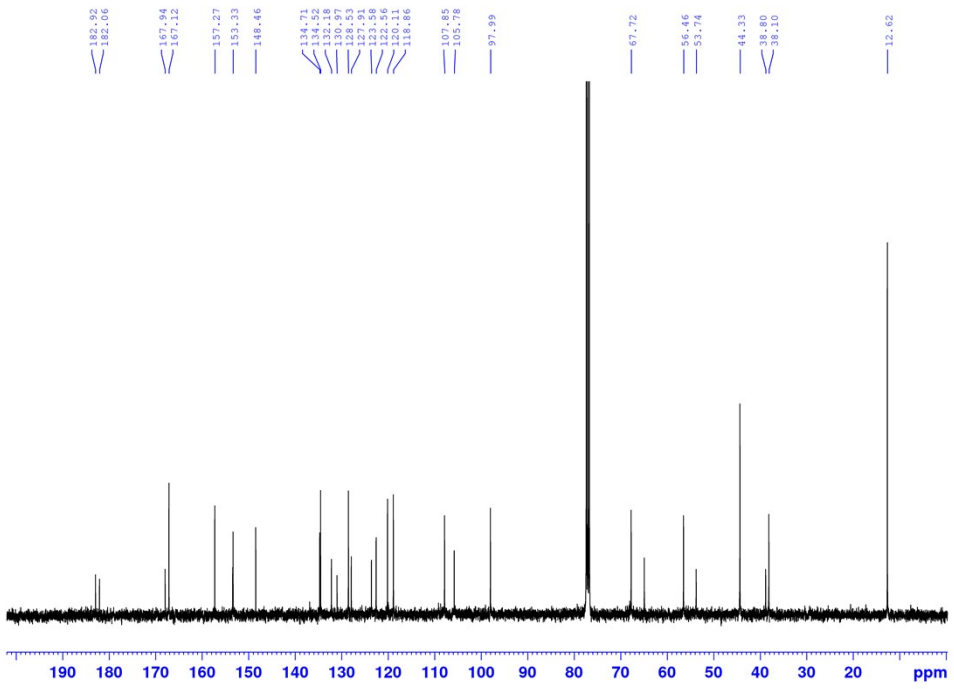


Figure S21: ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

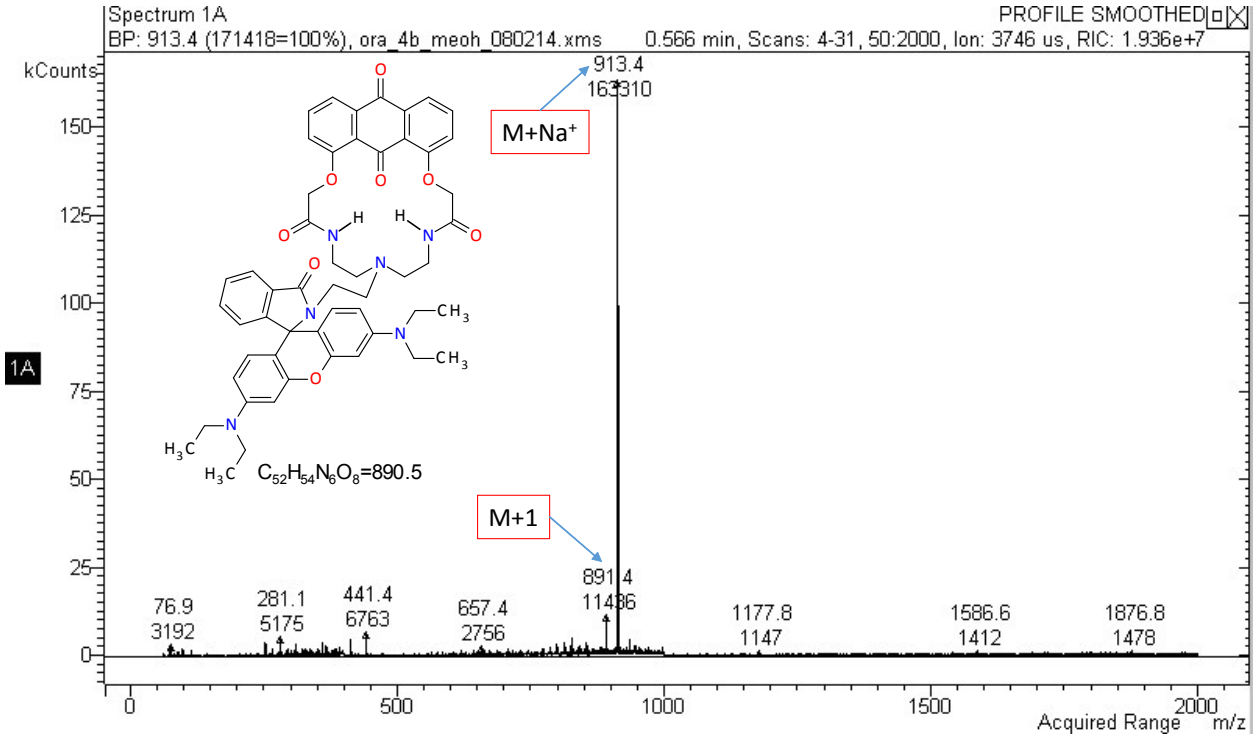
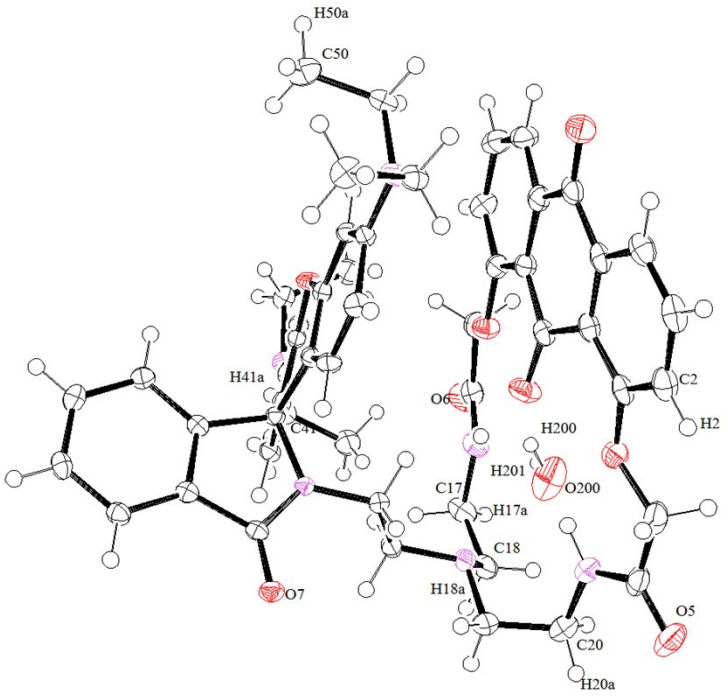


Figure S22: Mass spectrum of compound **6**.



Donor	Acceptor	Distance(A)
O200	O6	2.832(3)
O200	O5	2.770(3)
C2	O200	3.220(3)
C17	O200	3.487(3)
C18	O7	3.555(3)
C20	O5	2.757(3)
C41	O7	3.465(2)
C50	O7	3.462(3)

Figure S23: Thermal Ellipsoid diagram (30%) of compound **6** with one water molecule; hydrogen bond distances between donor and acceptor.

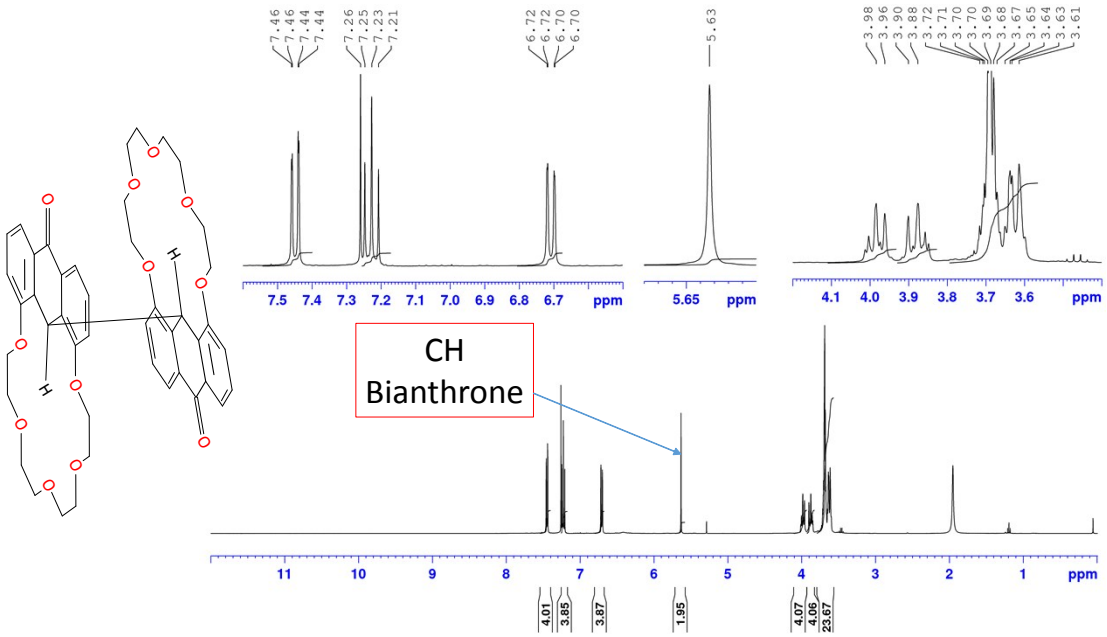


Figure S24: ^{1}H NMR spectrum of **11** in DMSO-d6.

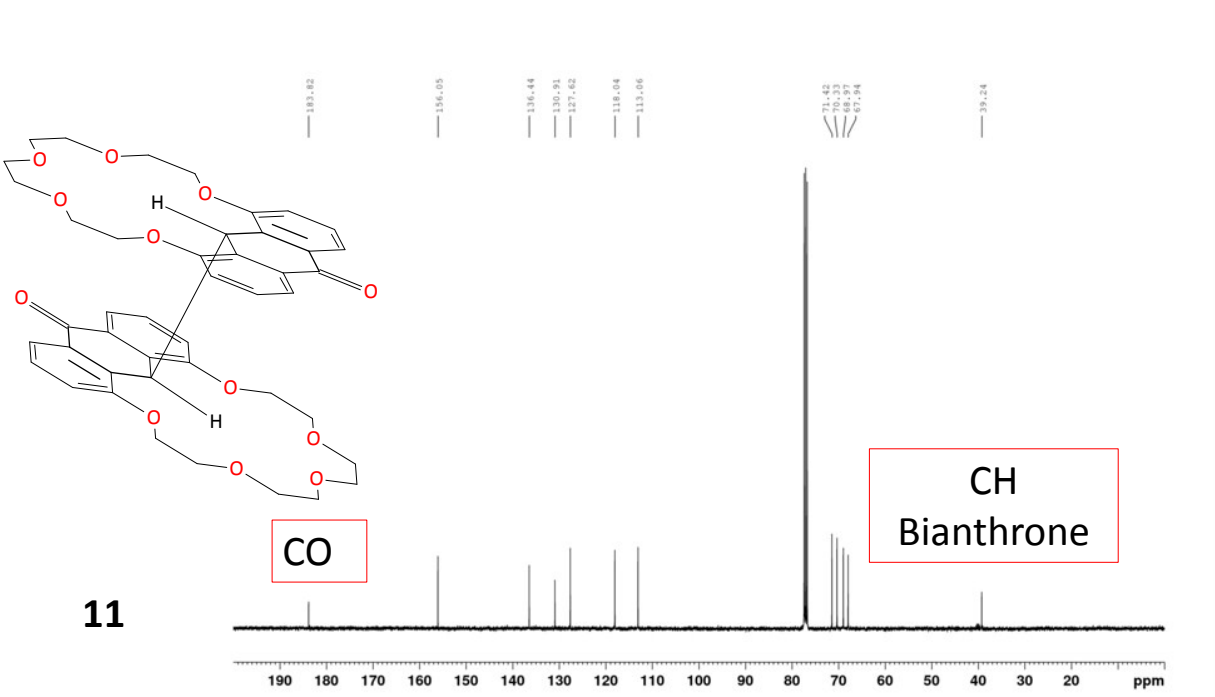


Figure S25: ^{13}C NMR spectrum of compound **11** in $CDCl_3$.

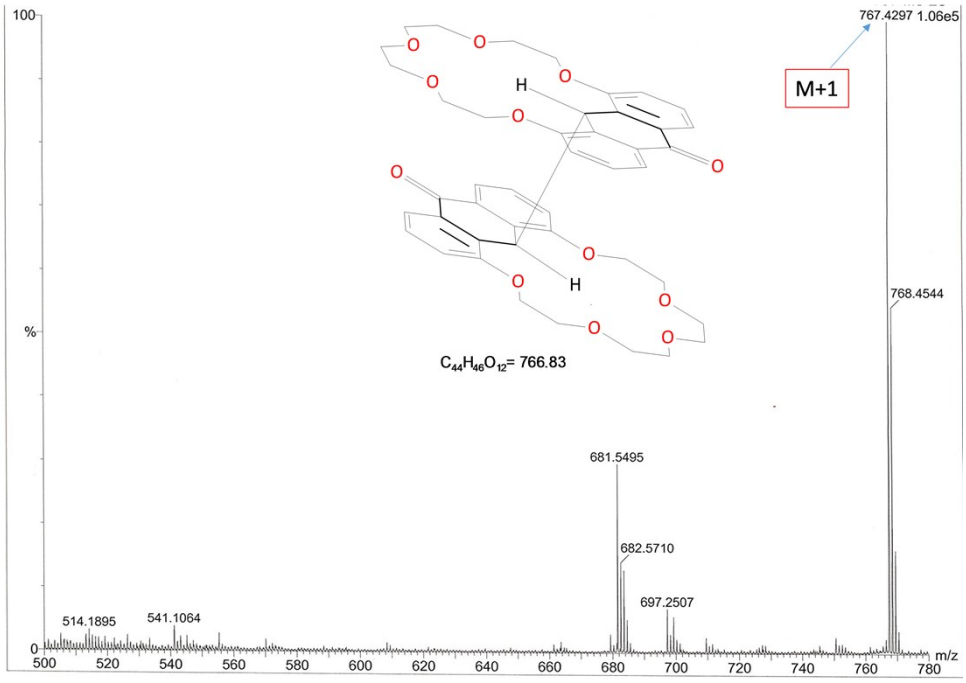


Figure S26: Mass spectroscopy of compound **11.**

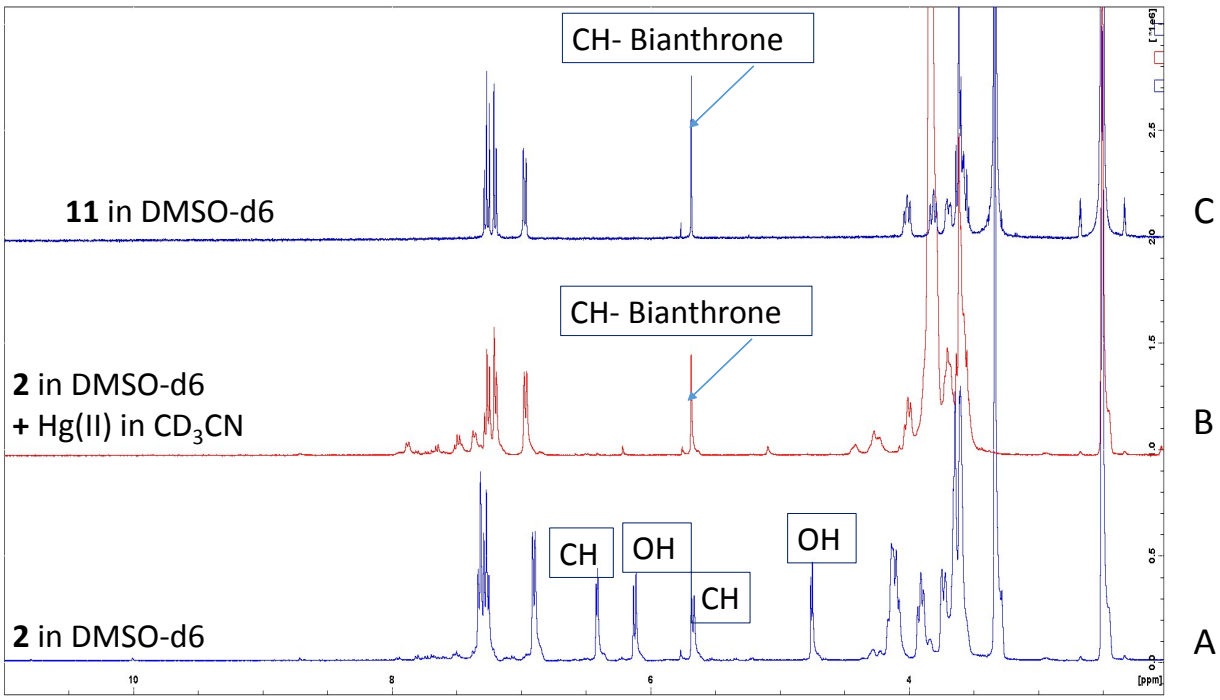


Figure S27: (A) ^{1}H NMR spectrum of **2** in DMSO-d6. (B) **2** in DMSO-d6 + Hg(II) in CD_3CN after 30 min. (C) **11** in DMSO-d6.

Table S1: Crystallographic data of compounds **2**, **4**, **6** and **11**.

	2	**4**	**6.H_2O**	**11**
Empirical formula	$C_{22}H_{26}O_7$	$C_{22}H_{24}O_6$	$C_{52}H_{54}N_6O_8$. H_2O	$C_{44}H_{46}O_{12}$
Formula weight	402.43	384.40	909.02	766.8
Wavelength	MoK_α 0.71073	MoK_α 0.71073	MoK_α 0.71073	MoK_α 0.71073
System	SMART APEII	SMART APEII	SMART APEXII	SMART APEXII
Temperature, K	100(2)	100(2)	100(2)	295(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	P21/n	P21/n	P21/c
a, Å	7.7175(6)	12.2726(5)	11.6503(6)	12.537(1)
b, Å	13.5383(11)	13.7003(6)	26.3127(13)	11.121(1)
c, Å	18.6624(15)	22.4713(10)	14.6567(7)	13.500(1)
α, °	90	90	90	90
β, °	90.12(1)	96.75(10)	96.09(10)	92.734(1)
γ, °	90	90	90	90
Volume, $Å^3$	1949.9(3)	3752.1(3)	4467.7(4)	1880.0(3)
Z	4	8	4	2
Density (calc)$g.cm^{-3}$	1.371	1.361	1.351	1.355
Absorb. coef. mm^{-1}	0.102	0.099	0.093	0.098
F(000)	1632	1632	1928	812
θ range	2.64-25.42	2.24-28.79	1.55-26.50	1.7- 25.5
Index ranges (h,k,l)	±9,±16,±23	±16;±18;±30	±14;-32+33;±18	±15;±13;±16
Independent reflections	4020	9382	9256	19077
Observed reflections	3843	7974	6993	3488
Max/Min trans.	0.903/0.970	0.991/0.995	0.987/0.993	0.976/0.995
Data/ restr./ param.	4220/0/270	9382/0/505	9256/2/620	3488/7/261
Goodness-of-fit	1.079	1.016	1.026	1.049
Final R indices[$I>2\sigma(I)$]	0.0401	0.0381	0.0451	0.0894
R indices (all data)	0.0412	0.0467	0.0664	0.1219
Peak/hole	0.468, -0.313	0.357, -0.266	0.362, -0.306	0.78/-0.74
CCDC #	1436743	1436744	1436745	1444688