Supporting Information

Aggregation Induced Emission from a new Naphthyridine-ethynyl-Gold(I) Complex as a potential tool for sensing Guanosine Nucleotides in Aqueous Media

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NMR Spectra/Data

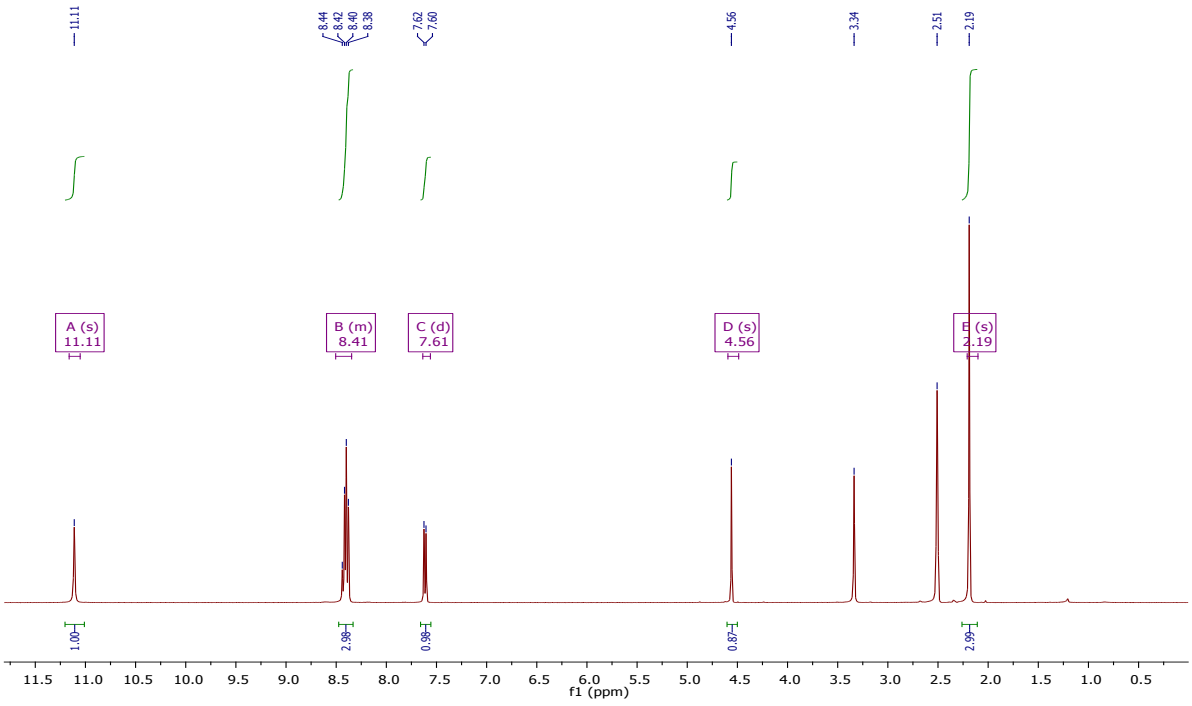


Figure S1. ^{1}H NMR spectrum of **2** in DMSO.

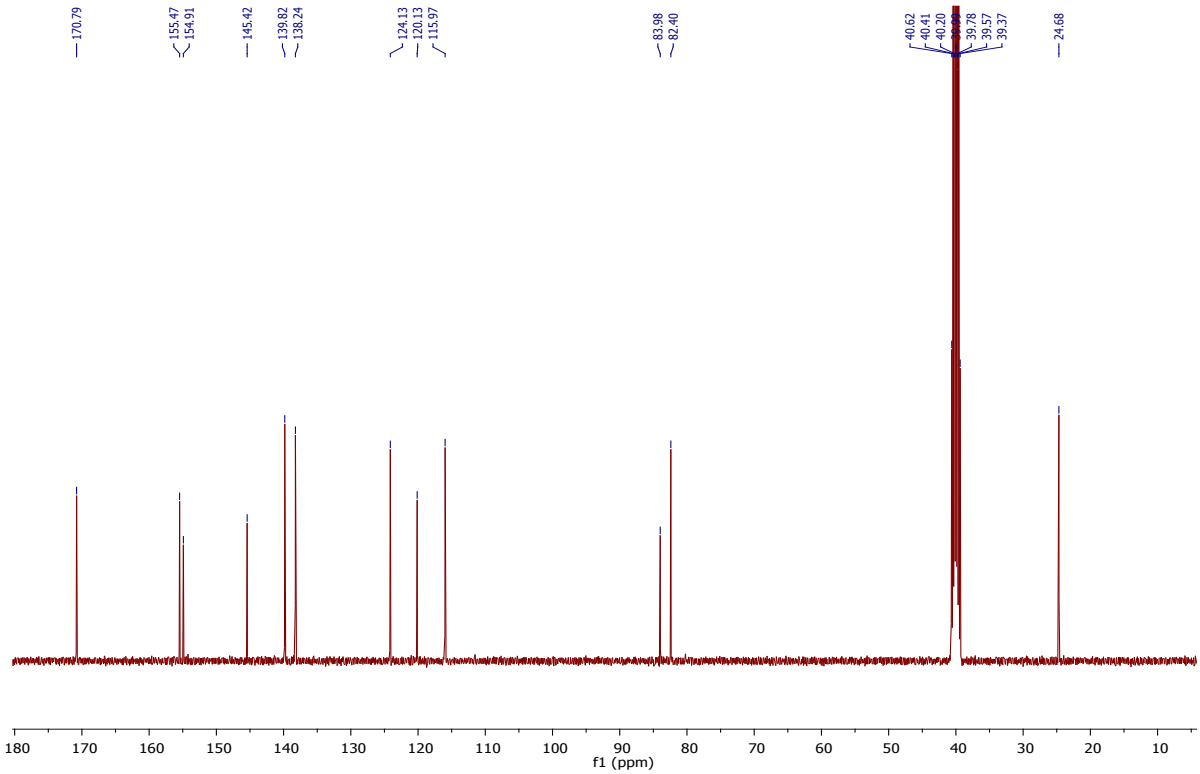


Figure S2. ^{13}C NMR spectrum of **2** in DMSO.

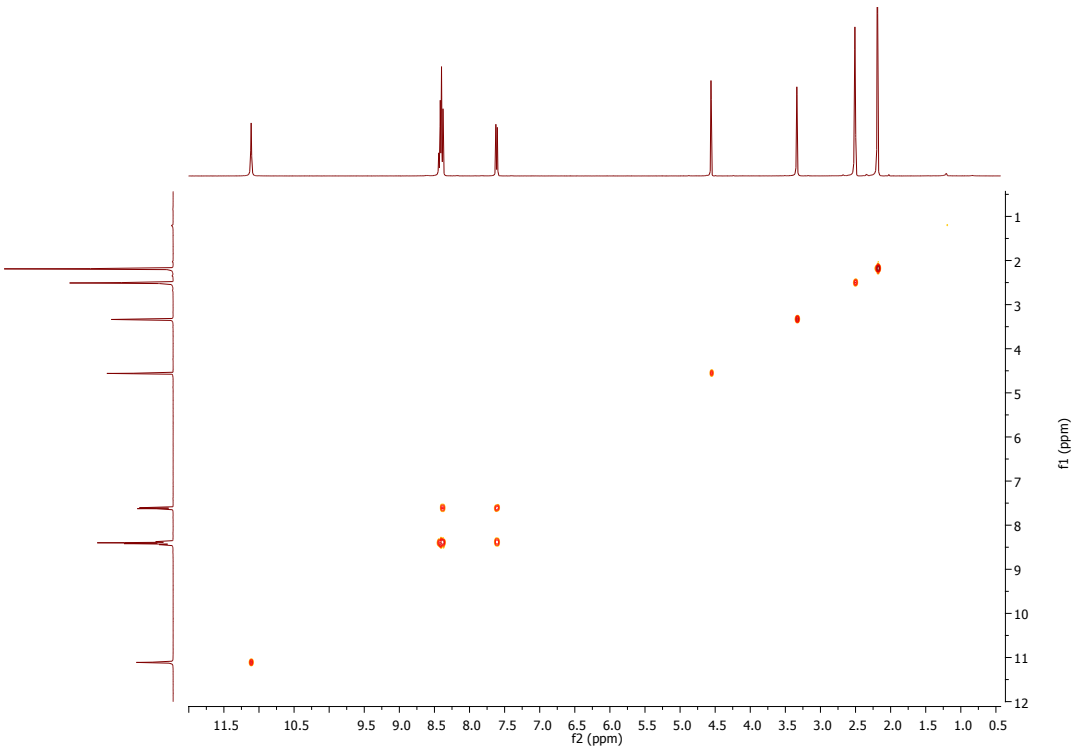


Figure S3. ^{1}H-^{1}H COSY NMR spectrum of **2** in DMSO.

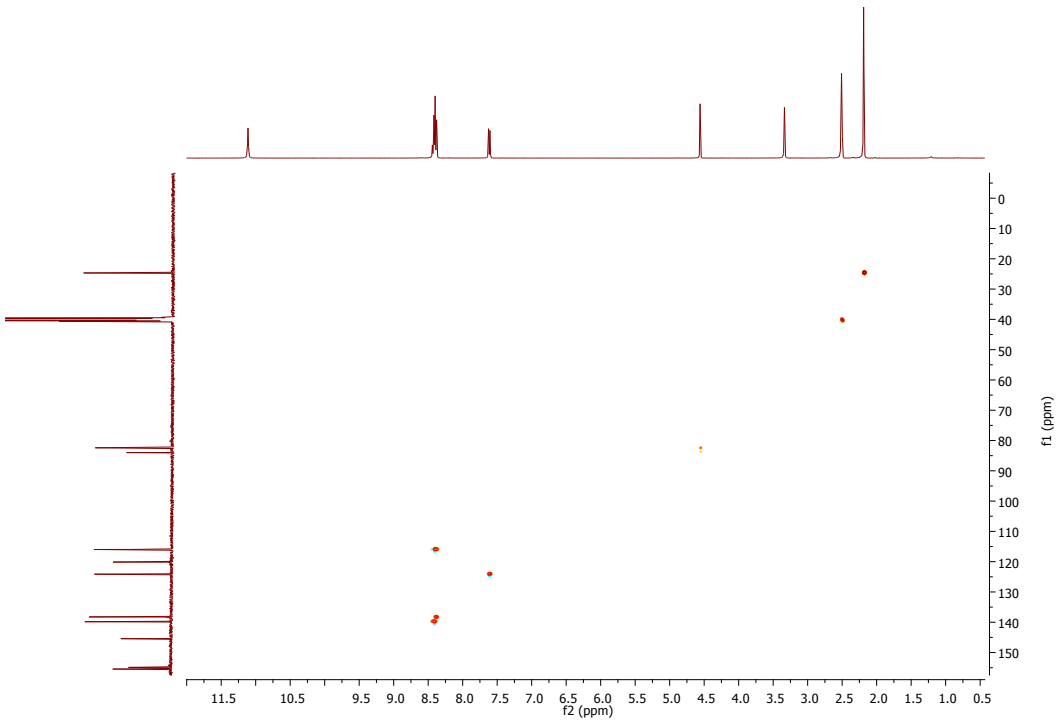


Figure S4. ^{1}H-^{13}C HSQC NMR spectrum of **2** in DMSO.

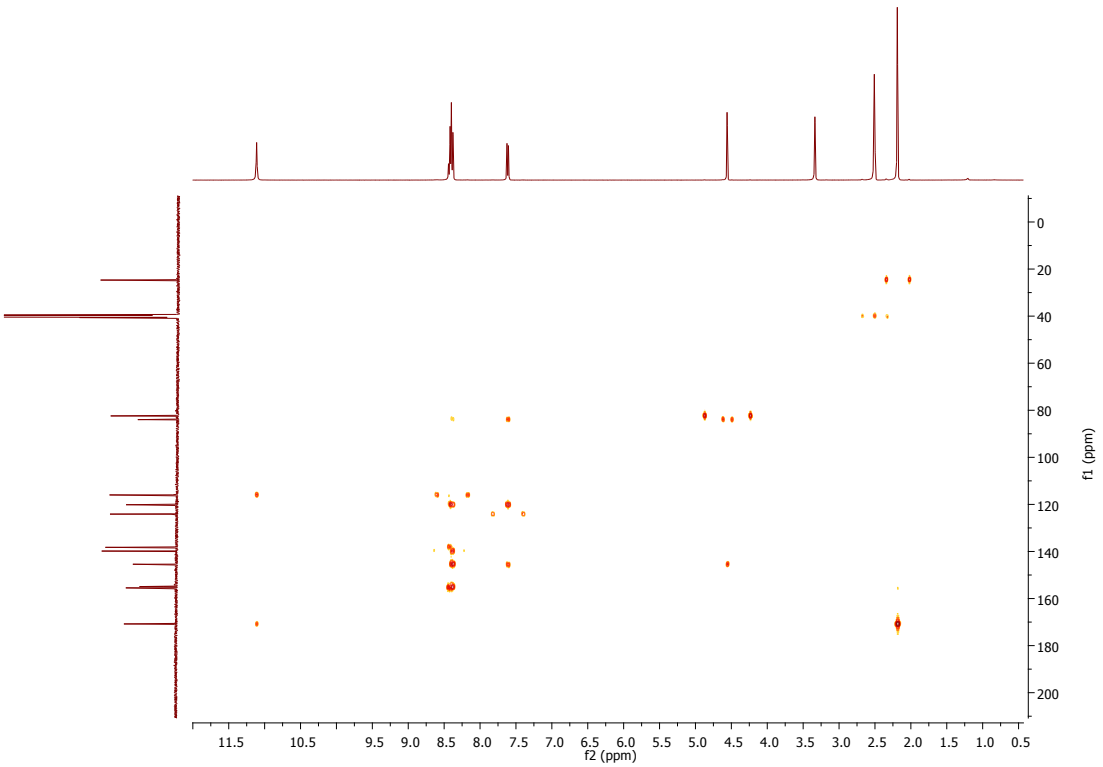
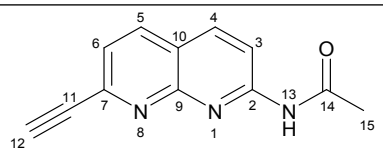


Figure S5. ^{1}H-^{13}CHMBC NMR spectrum of **2** in DMSO.

Table S1. NMR peak assignment for **2**.



Position	^{1}H	^{13}C
1	-	-
2	-	155.47*
3	8.44-8.38	115.97
4	8.44-8.38	139.82
5	8.44-8.38	138.24
6	7.61	124.13
7	-	145.42
8	-	-
9	-	154.91*
10	-	120.13
11	-	83.98
12	4.56	82.40
13	11.11	-
14	-	170.79
15	2.19	24.68

*These 13C signals are too close in chemical shifts for an unequivocal heteronuclear correlation.

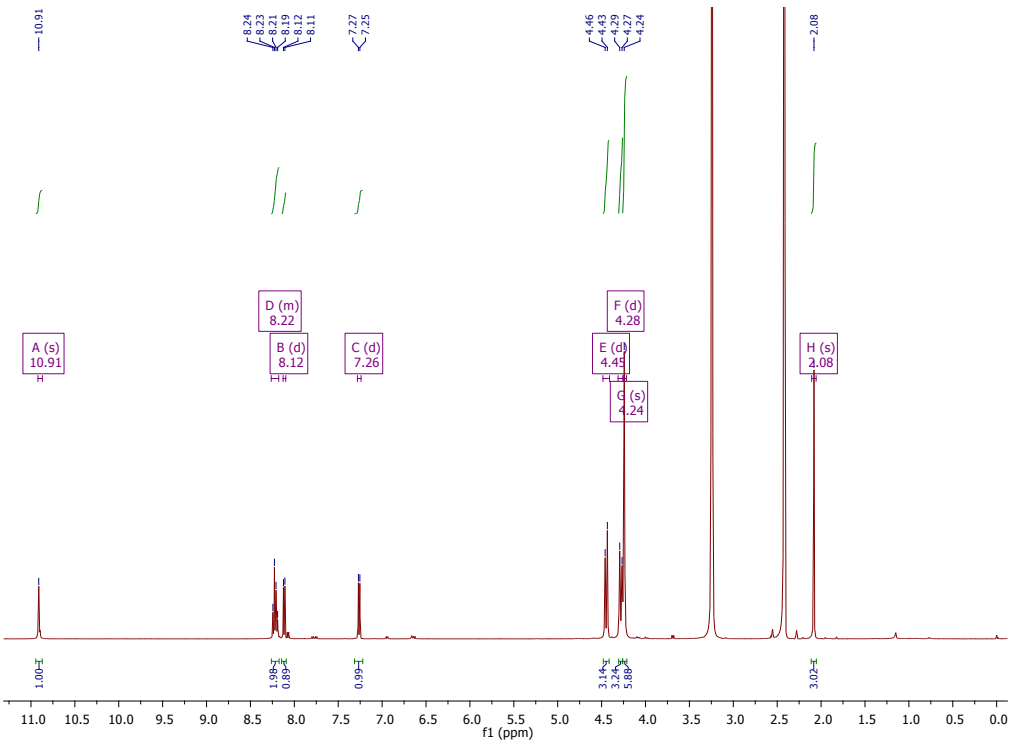


Figure S6. ^{1}H NMR spectrum of **3** in DMSO.

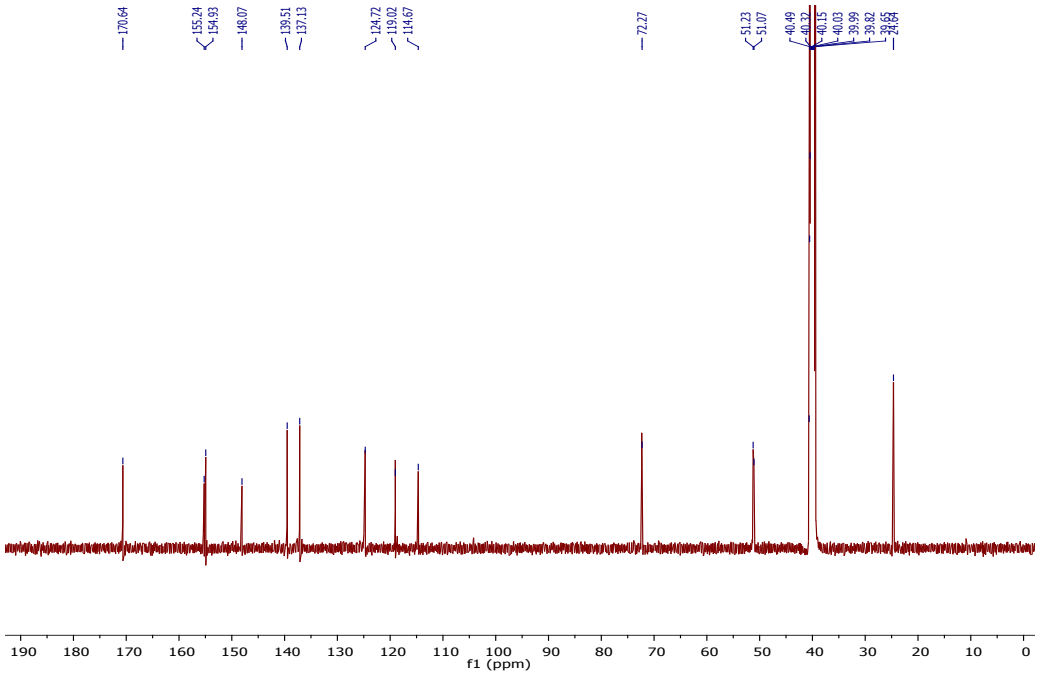


Figure S7. ^{13}C NMR spectrum of **3** in DMSO.

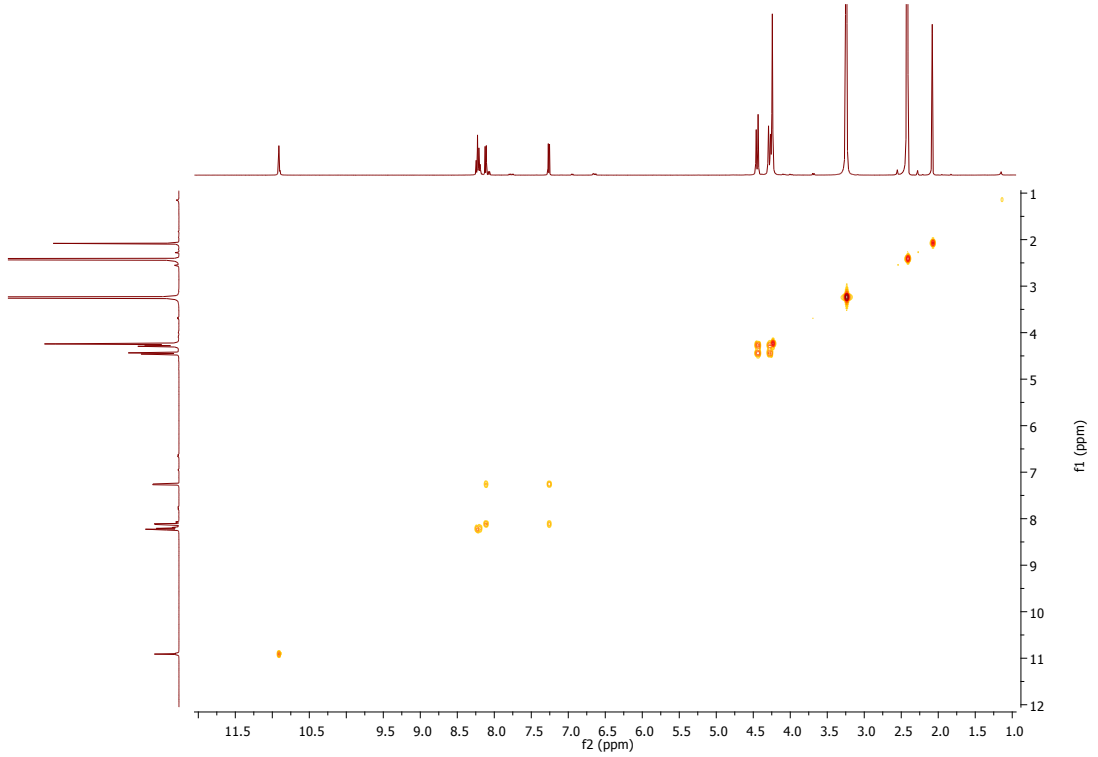


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of **3** in DMSO.

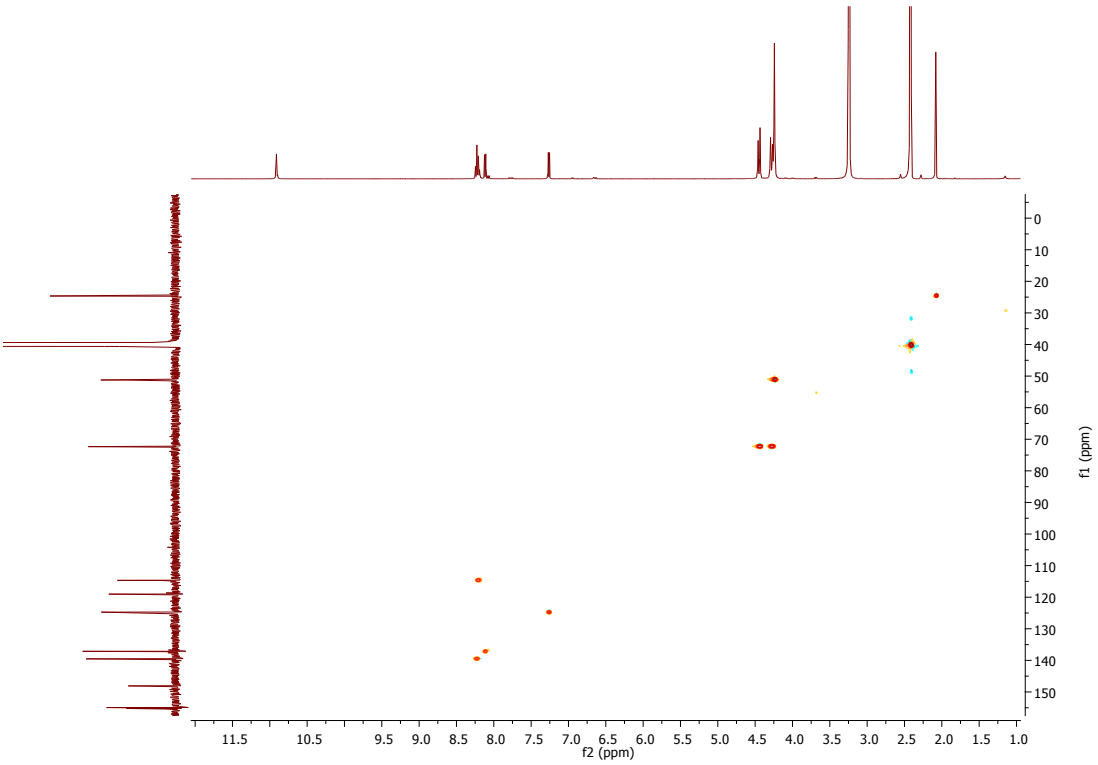


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of **3** in DMSO.

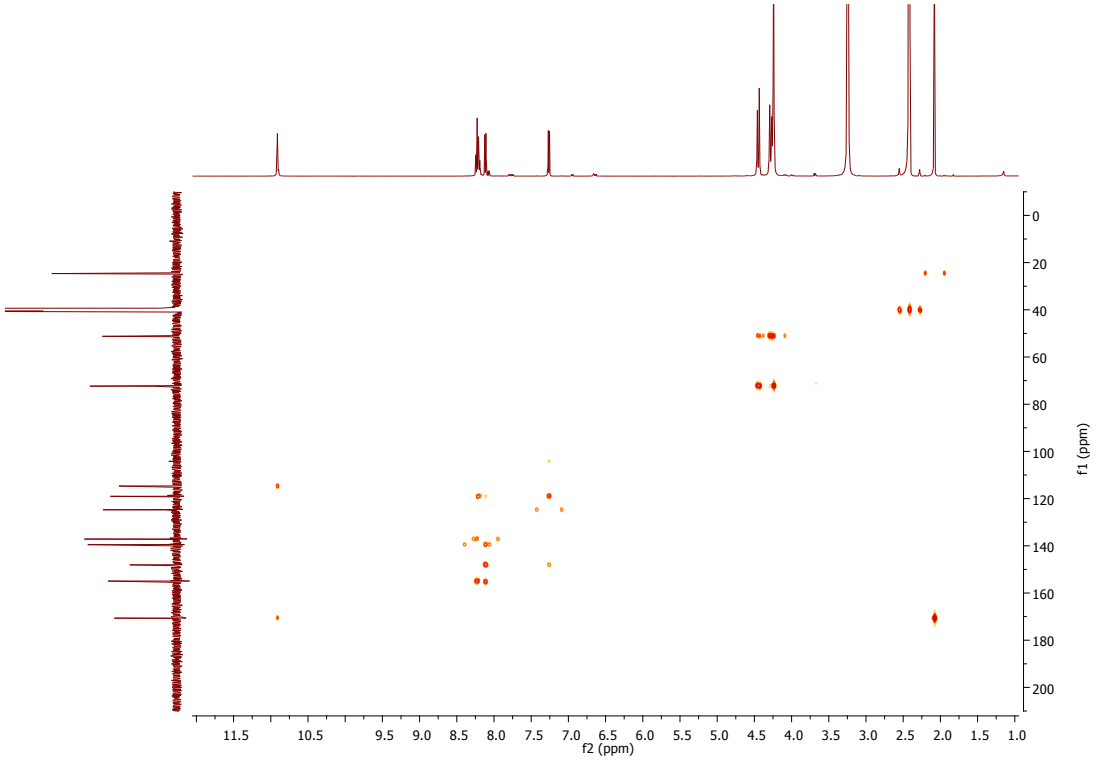


Figure S10. ^{1}H-^{13}C HMBC NMR spectrum of **3** in DMSO.

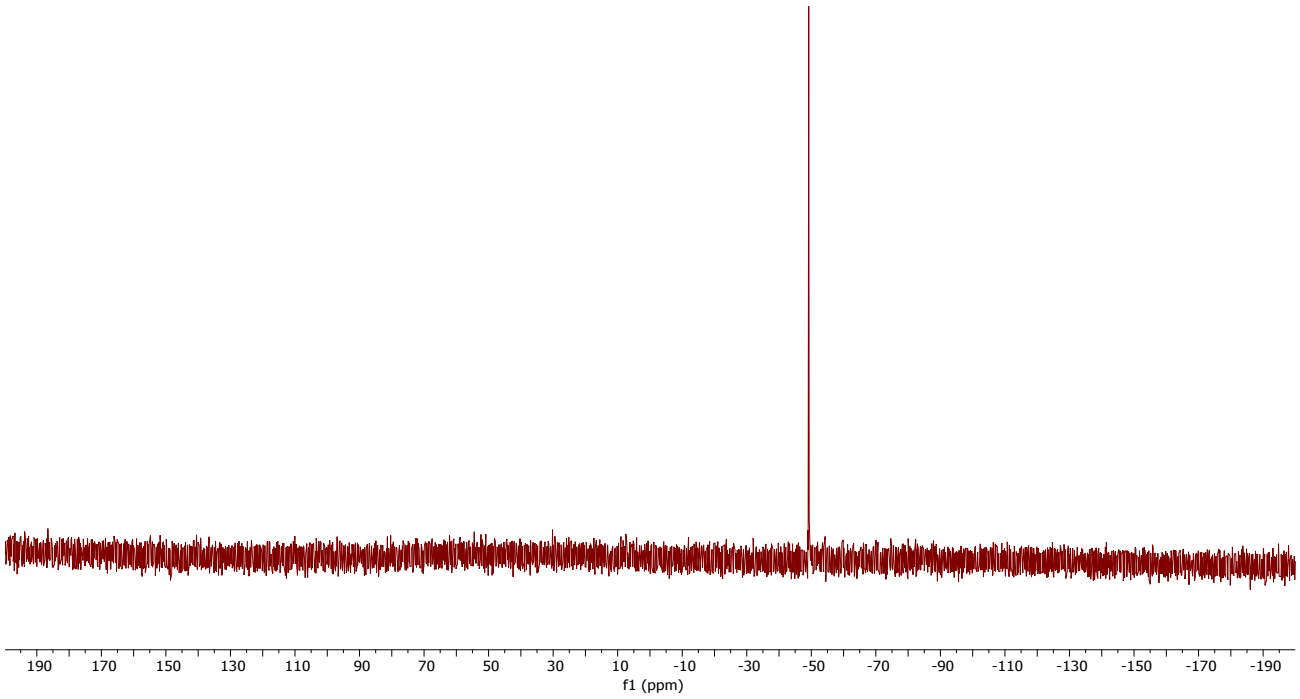
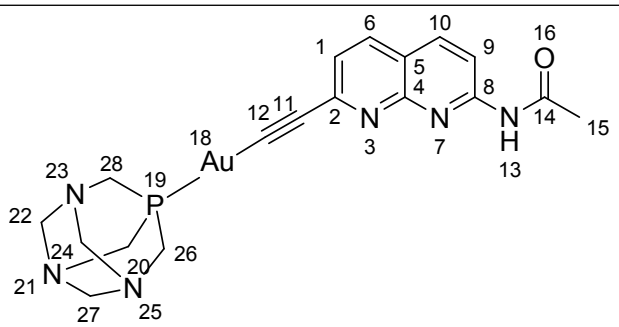


Figure S11. ^{31}P NMR spectrum of **3** in DMSO.

Table S2. NMR peak assignment for **3**.



Position	^{1}H	^{13}C
1	7.26	124.72
2	-	148.07
3	-	-
4	-	155.24
5	-	119.02
6	8.12	137.13
7	-	-
8	-	154.93
9	8.24-8.19	114.67
10	8.24-8.19	139.51
11	-	-*
12	-	-*
13	10.91	-
14	-	170.64
15	2.08	24.64
16	-	-
17	-	-
18	-	-
19	-	-
20	4.45/4.28**	72.27
21	-	-
22	4.24	51.23/51.07**
23	-	-
24	4.24	51.23/51.07**
25	-	-
26	4.45/4.28**	72.27
27	4.24	51.23/51.07**
28	4.45/4.28**	72.27

*These quaternary carbons were not observed, possibly due to (1) low relaxation times or (2) low sample concentration; **Unequivocal assignment of these signals was not possible on the acquired spectra.

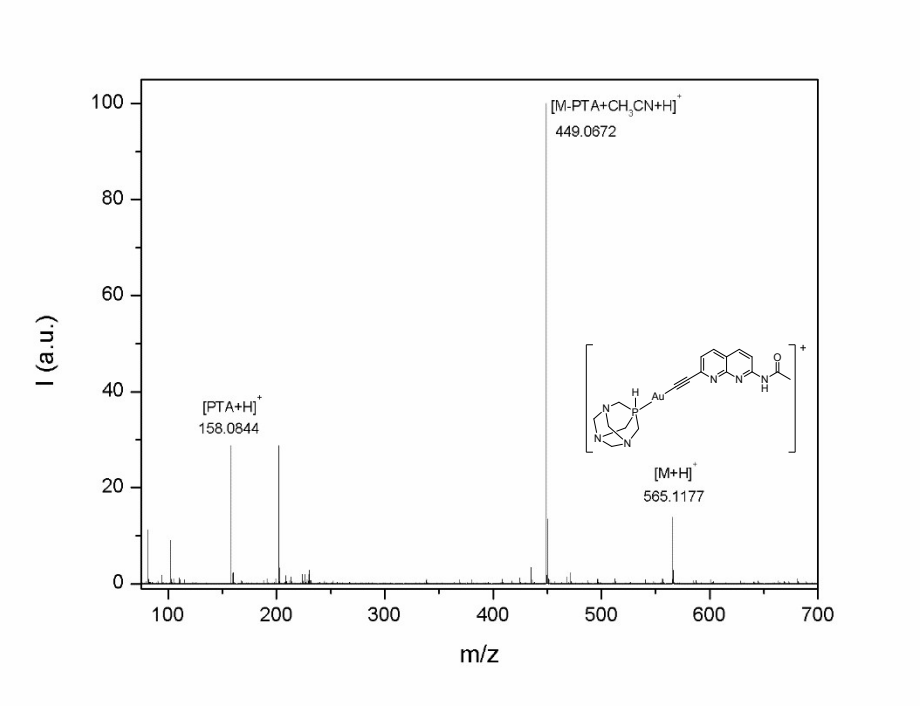


Figure S12. HR-MS spectrum of **3**.

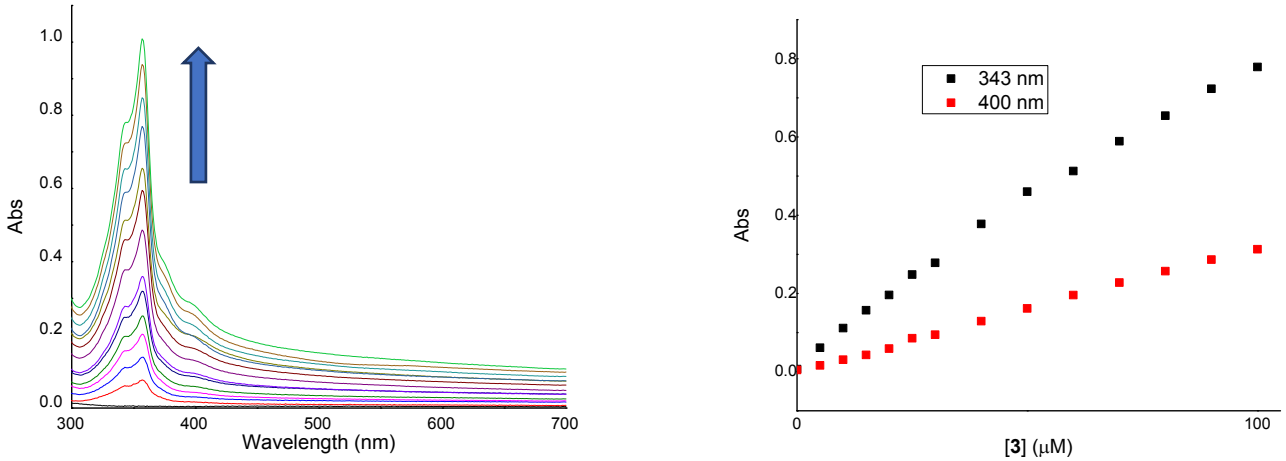


Figure S13. UV-Vis spectra at different concentrations of **3** in water (left); variations of absorbance at 343 nm and 400 nm at different concentrations of **3** (right).

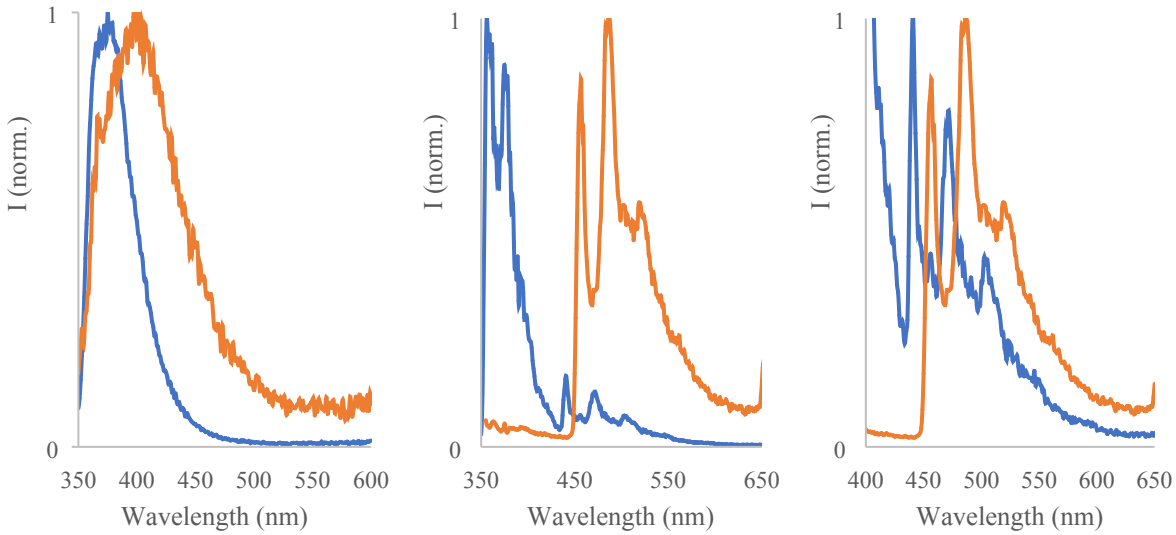


Figure S14. Left: Emission spectra of **2** (blue) and **3** (orange) in methanol at room temperature; Center: Normalized emission of **2** and **3** at 77K; Right: normalized spectra of **2** and **3** in the region between 400-650nm at 77K, for better comparison of the vibrational structure of the bands (λ_{exc} = 343 nm for all cases).

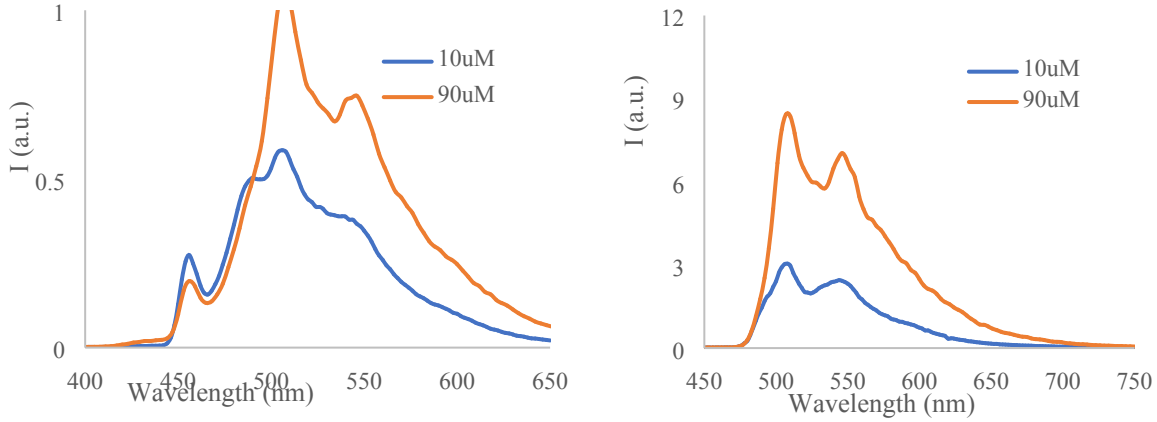


Figure S15. Emission spectra of 10 and 90 µM solutions of **3** at 77K in 10 mM HEPES buffer (pH 7.2), exciting at 343 nm (left) and 400 nm (right).

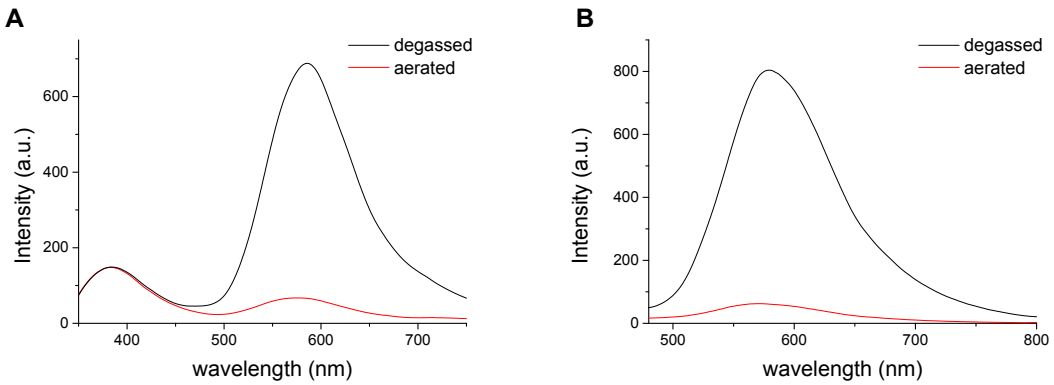


Figure S16. Steady-state emission spectra of a solid sample (powder) of **3** at room temperature in degassed (black line) and aerated (red line) conditions, exciting at (A) 320 nm and (B) 400 nm.

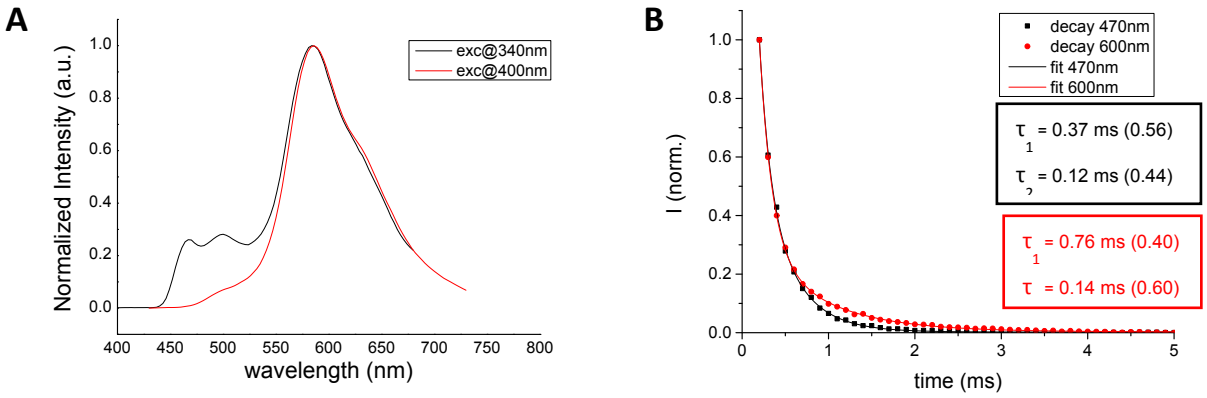


Figure S17. (A) Time-resolved emission spectra of **3** in solid state, exciting at 340 nm (black) and 400 nm (red). Delay = 0.2 ms; (B) decay profiles of the emission at 470 nm (black) and 600 nm (red). The contributions of each lifetime component are presented in brackets ($\tau_{average}$= 0.2 ms). Excitation wavelength was 320 nm.

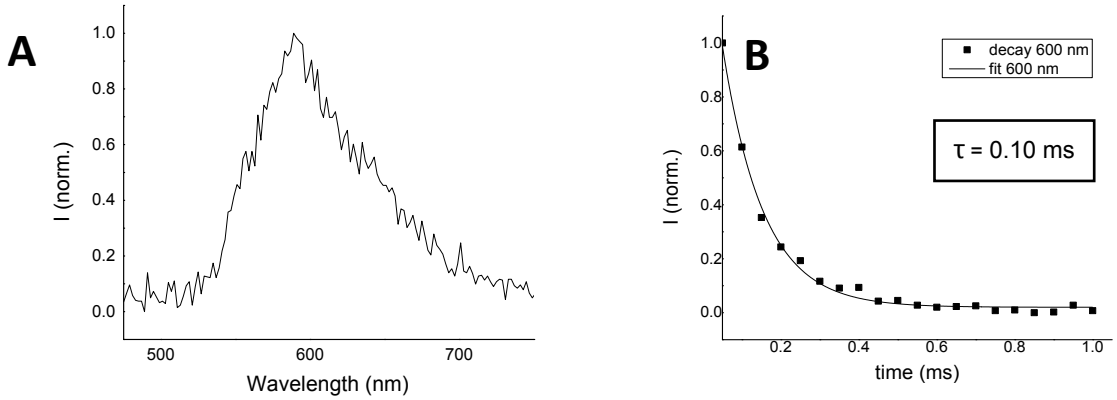


Figure S18. (A) Time-resolved emission spectra of **3** in 10mM HEPES buffer (pH7.2), $\lambda_{excitation}$ = 400 nm, delay = 0.2 ms. (B) Decay profile of the emission at 600 nm.

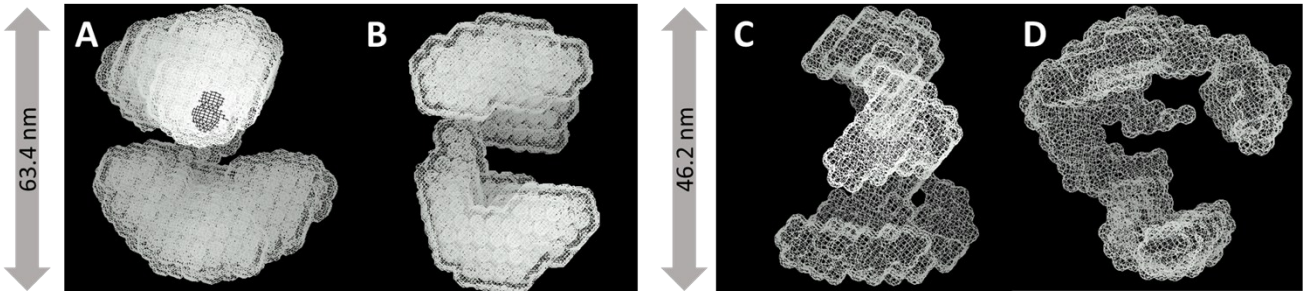


Figure S19. Low resolution structures obtained from SAXS measurements of **3** at 1 x 10^{-5} M in 100% DMSO (A and B) and 10% DMSO/ 90% H_2O mixture (C and D). The pairs A/B and C/D represent the same structure at two different views, shifted by 90º.

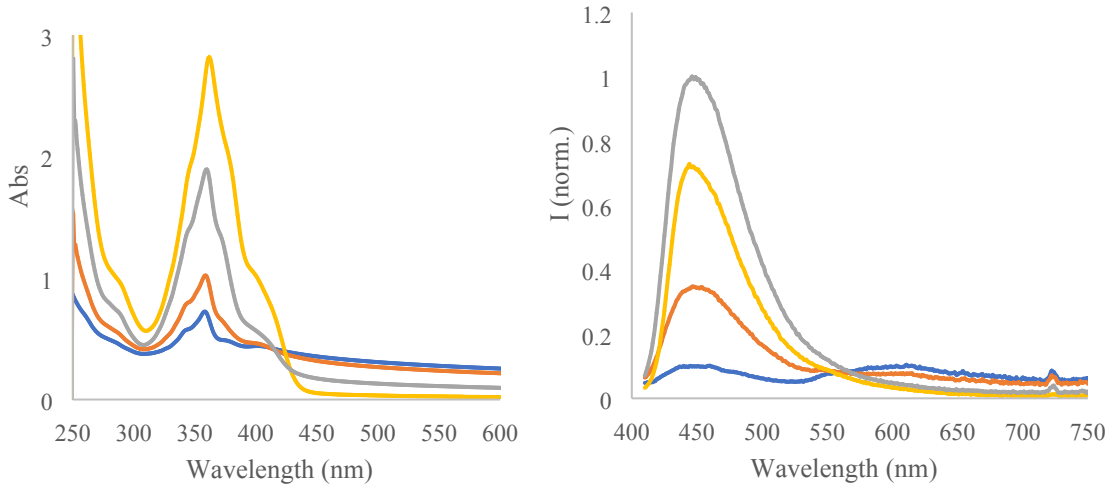


Figure 20. Absorption and emission (λ_{exc} = 410 nm) of **3** (60 µM) in different H_2O:DMSO mixtures: 100% water (blue), 90% water:10% DMSO (red), 75% water:25% DMSO (grey), and 50% water:50% DMSO (orange).

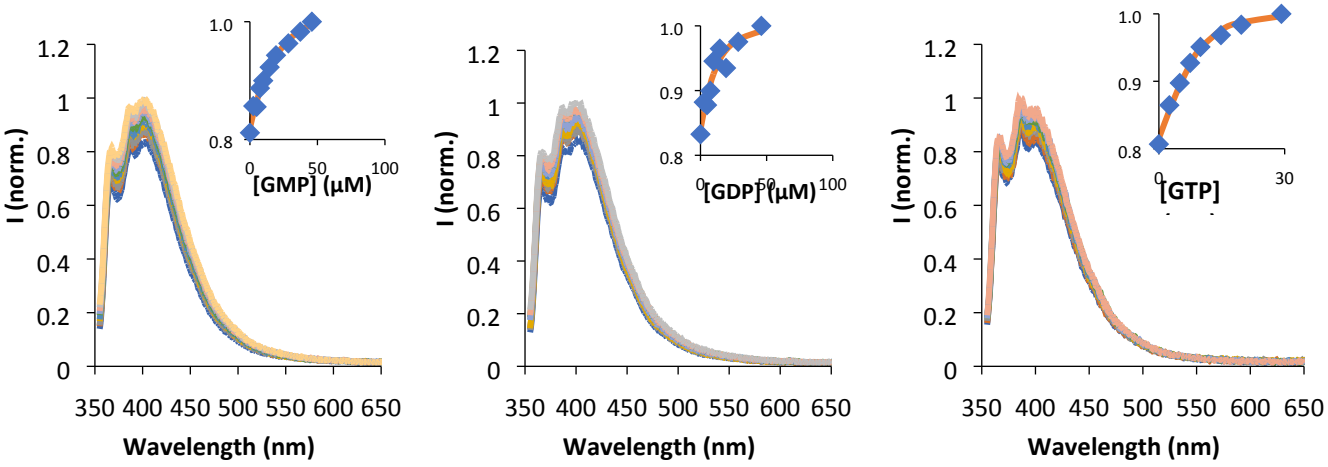


Figure S21. Emission spectra of **3** (10µM, in 10mM HEPES buffer at pH 7.2) in the presence of different amounts of Guanosine nucleotides, λ_{exc} = 343 nm. Insets show the trend of the normalized intensity versus concentration of respective Guanosine derivative.

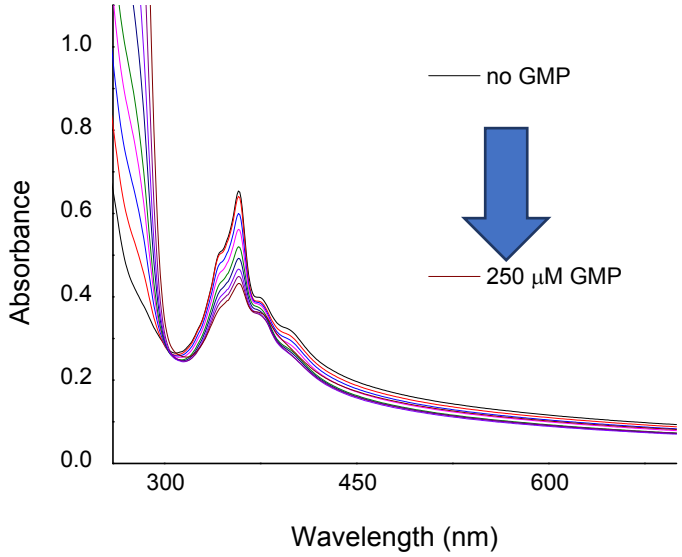


Figure S22. Variation of absorption of **3** (60 μM in 10 mM HEPES buffer at pH 7.2) in the presence of Guanosine 5'-monophosphate (GMP).

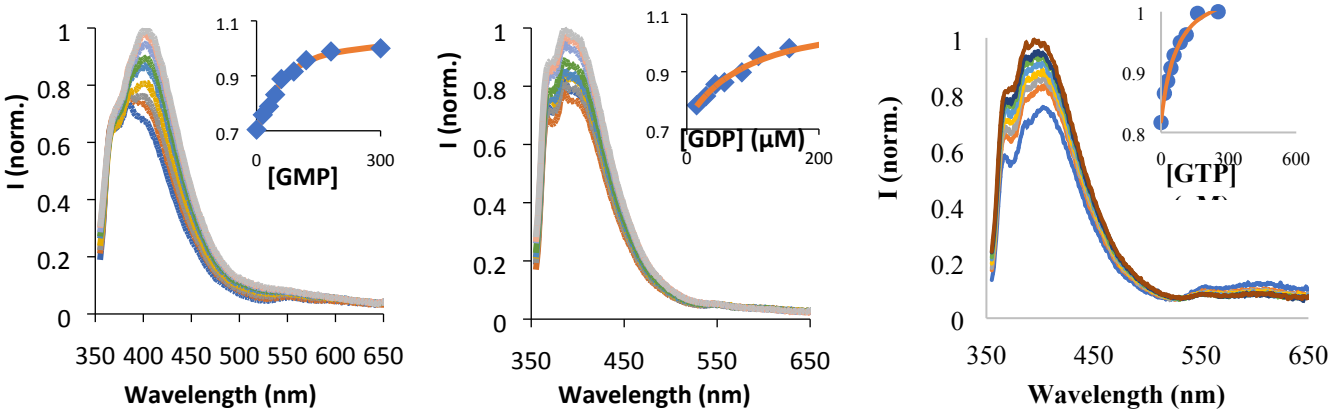


Figure S23. Emission spectra of **3** (60μM, in 10mM HEPES buffer at pH 7.2) in the presence of different amounts of Guanosine nucleotides, λ_{exc} = 343 nm. Insets show the trend of the normalized intensity versus concentration of respective Guanosine derivative.

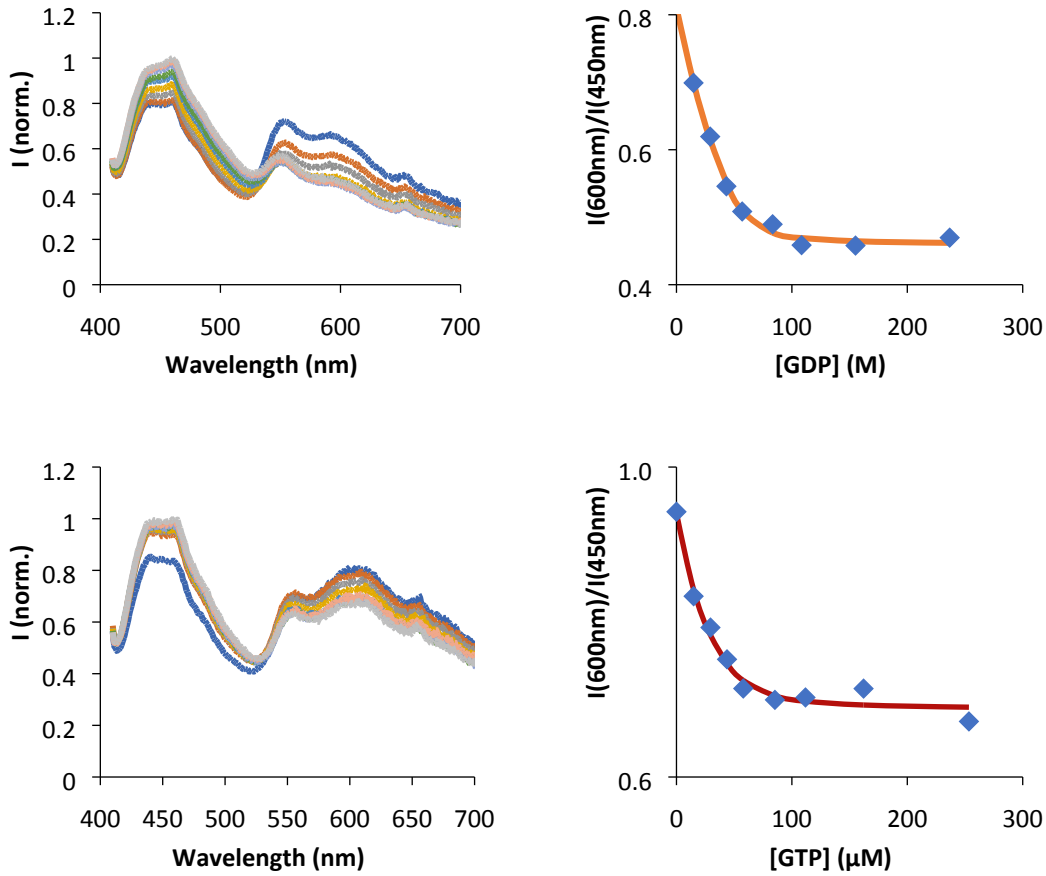


Figure S24. Emission spectra of **3** (60µM) in the presence of different amounts of GDP (left, top) and GTP (left, bottom). Respective insets of the ratio between the monomer and aggregates emission are shown on the right

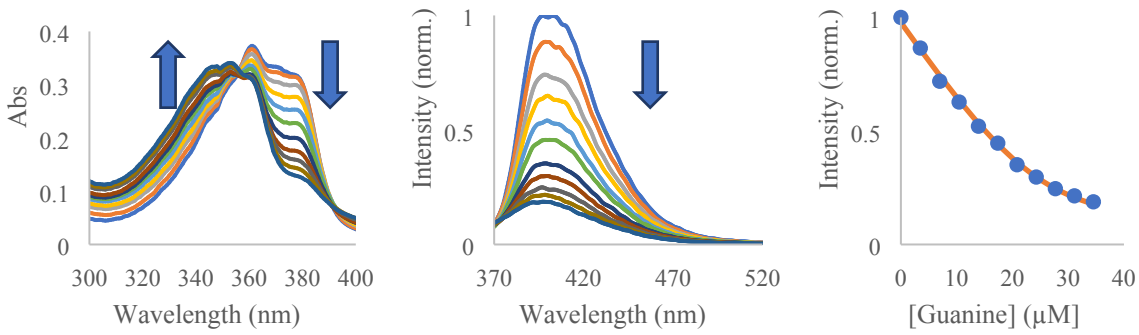


Figure S25. Absorption and emission (λ_{exc} = 372 nm) spectra of **2** in dichloromethane ($1x10^{-5}$ M), in the presence of increasing amounts of Guanine. The association constant was determined by fitting the experimental data to a 1:1 Henderson-Hasselbalch model using the Solver Add-In from Microsoft Excel, yielding a value of $4.2x10^{5}$ M^{-1}.

Table S3. Association constants for naphthyridine sensor systems towards Guanine derivatives reported in the literature.

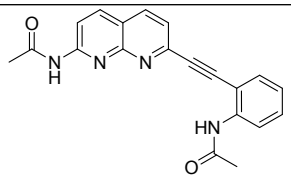
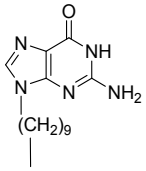
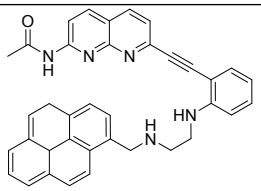
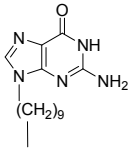
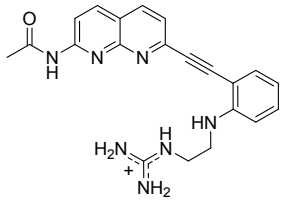
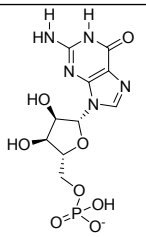
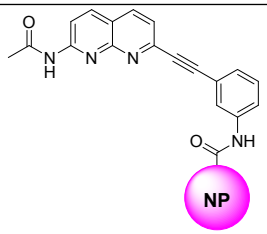
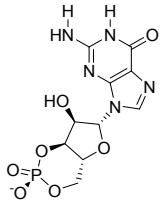
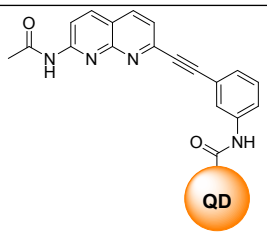
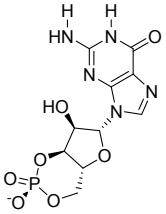
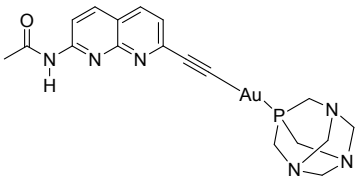
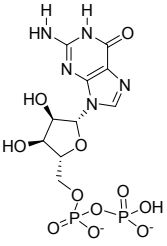
Sensor molecule	Analyte	K_{ass} (M^{-1})	Solvent	Reference
		9.1×10^4	CH_2Cl_2	13
		1.4×10^6	CH_2Cl_2	14
		1.6×10^4	water	14
		3.6×10^4	0.1M HEPES (pH7.4)	15
		3.1×10^5	0.1M HEPES (pH7.4)	16
		4.4×10^5	0.01M HEPES (pH7.4)	This work

Table S4. Crystal data and structure refinement for compound **2**.

Empirical formula	C12 H9 N3 O	
Formula weight	211.22	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 24.8320(8) Å	α= 90°.
	b = 7.2057(3) Å	β= 108.7530(10)°.
	c = 12.0342(4) Å	γ = 90°.
Volume	2038.99(13) $Å^3$	
Z	8	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	880	
Crystal size	0.200 x 0.100 x 0.100 mm^3	
Theta range for data collection	3.466 to 25.700°.	
Index ranges	-28<=h<=30, -8<=k<=8, -14<=l<=14	
Reflections collected	16950	
Independent reflections	1931 [R(int) = 0.0313]	
Completeness to theta = 25.242°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1931 / 0 / 150	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0959	
R indices (all data)	R1 = 0.0410, wR2 = 0.0986	
Largest diff. peak and hole	0.257 and -0.217 $e.Å^{-3}$	

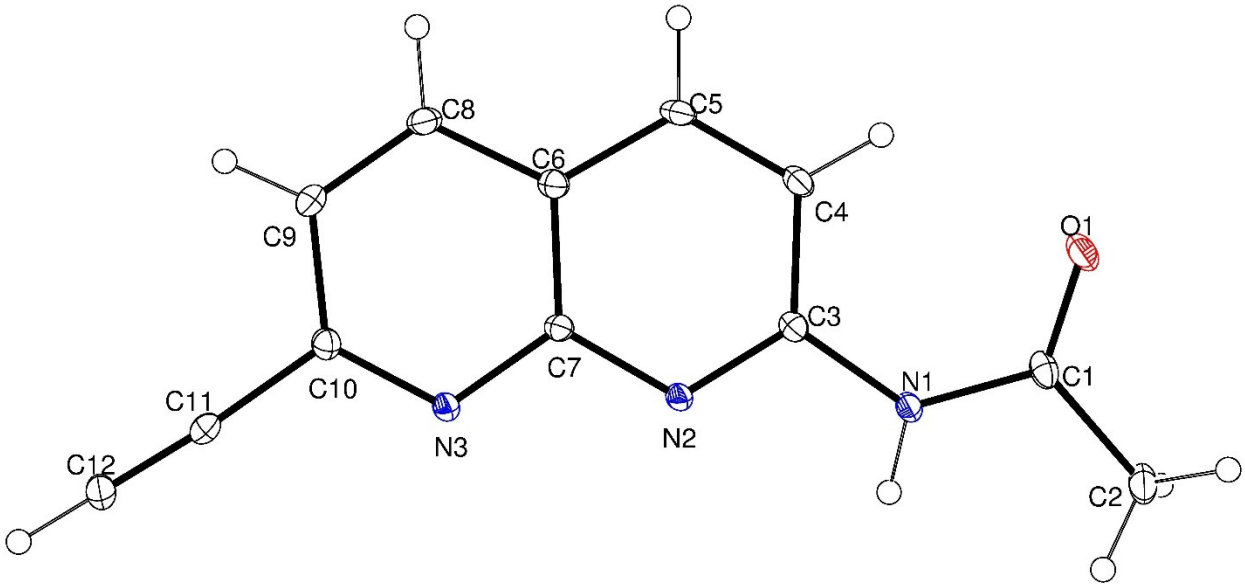


Fig. S26. ORTEP-3 diagram of compound **2**, using 30% probability level ellipsoids.

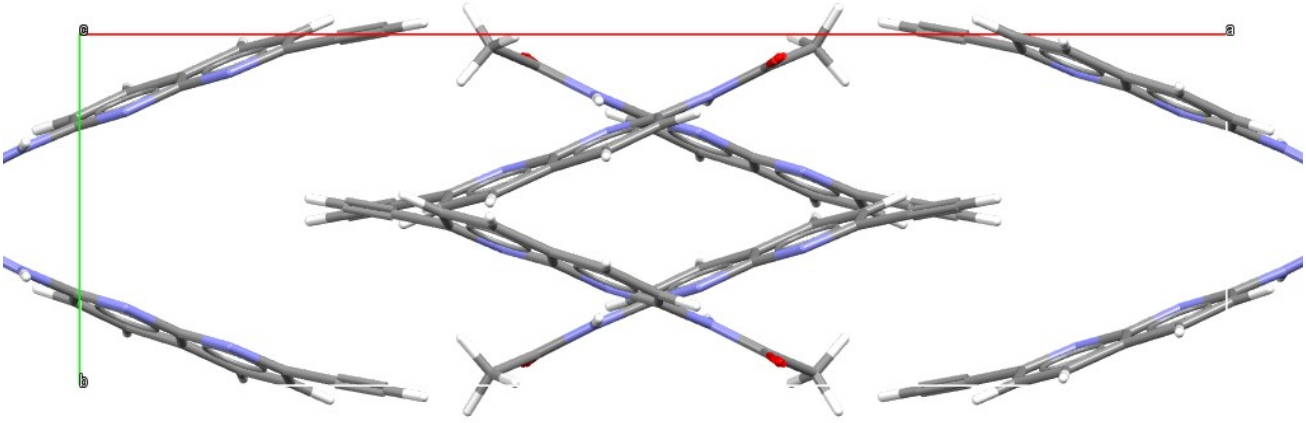


Fig. S27. MERCURY packing diagram viewed down the *c* axis.

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	9602(1)	2211(2)	1051(1)	14(1)
O(1)	11100(1)	4324(1)	659(1)	23(1)
C(8)	8604(1)	445(2)	-1725(1)	19(1)
N(3)	8693(1)	1098(2)	632(1)	15(1)
C(11)	7743(1)	114(2)	269(1)	18(1)
C(7)	9133(1)	1495(2)	234(1)	13(1)
N(1)	10510(1)	3271(2)	1640(1)	16(1)
C(6)	9108(1)	1195(2)	-943(1)	15(1)
C(4)	10058(1)	2408(2)	-445(1)	17(1)
C(5)	9591(1)	1684(2)	-1254(1)	18(1)
C(3)	10047(1)	2634(2)	725(1)	14(1)
C(10)	8221(1)	440(2)	-141(1)	16(1)
C(1)	11001(1)	4080(2)	1580(1)	18(1)
C(9)	8161(1)	77(2)	-1330(1)	19(1)
C(2)	11411(1)	4644(2)	2743(1)	23(1)
C(12)	7328(1)	-130(2)	534(1)	23(1)

Table S6. Bond lengths [Å] and angles [°] for compound **2**.

N(2)-C(3)	1.3205(15)	N(3)-C(7)-C(6)	122.74(11)
N(2)-C(7)	1.3620(16)	N(2)-C(7)-C(6)	122.19(11)
O(1)-C(1)	1.2235(16)	C(1)-N(1)-C(3)	128.36(11)
C(8)-C(9)	1.3596(18)	C(1)-N(1)-H(1)	118.7(9)
C(8)-C(6)	1.4089(18)	C(3)-N(1)-H(1)	112.9(9)
C(8)-H(8)	0.9300	C(8)-C(6)-C(5)	124.49(11)
N(3)-C(10)	1.3286(16)	C(8)-C(6)-C(7)	118.10(11)
N(3)-C(7)	1.3566(15)	C(5)-C(6)-C(7)	117.41(11)
C(11)-C(12)	1.1855(18)	C(5)-C(4)-C(3)	118.01(11)
C(11)-C(10)	1.4428(17)	C(5)-C(4)-H(4)	121.0
C(7)-C(6)	1.4139(17)	C(3)-C(4)-H(4)	121.0
N(1)-C(1)	1.3735(16)	C(4)-C(5)-C(6)	120.57(11)
N(1)-C(3)	1.3901(16)	C(4)-C(5)-H(5)	119.7
N(1)-H(1)	0.891(16)	C(6)-C(5)-H(5)	119.7
C(6)-C(5)	1.4117(17)	N(2)-C(3)-N(1)	113.52(10)
C(4)-C(5)	1.3557(18)	N(2)-C(3)-C(4)	123.35(11)
C(4)-C(3)	1.4270(17)	N(1)-C(3)-C(4)	123.10(11)
C(4)-H(4)	0.9300	N(3)-C(10)-C(9)	123.83(11)
C(5)-H(5)	0.9300	N(3)-C(10)-C(11)	117.17(11)
C(10)-C(9)	1.4140(18)	C(9)-C(10)-C(11)	118.99(11)
C(1)-C(2)	1.4982(18)	O(1)-C(1)-N(1)	123.34(12)
C(9)-H(9)	0.9300	O(1)-C(1)-C(2)	122.18(11)
C(2)-H(2A)	0.9600	N(1)-C(1)-C(2)	114.49(11)
C(2)-H(2B)	0.9600	C(8)-C(9)-C(10)	118.94(12)
C(2)-H(2C)	0.9600	C(8)-C(9)-H(9)	120.5
C(12)-H(12)	0.9300	C(10)-C(9)-H(9)	120.5
C(3)-N(2)-C(7)	118.44(10)	C(1)-C(2)-H(2A)	109.5
C(9)-C(8)-C(6)	119.12(11)	C(1)-C(2)-H(2B)	109.5
C(9)-C(8)-H(8)	120.4	H(2A)-C(2)-H(2B)	109.5
C(6)-C(8)-H(8)	120.4	C(1)-C(2)-H(2C)	109.5
C(10)-N(3)-C(7)	117.23(10)	H(2A)-C(2)-H(2C)	109.5
C(12)-C(11)-C(10)	175.71(13)	H(2B)-C(2)-H(2C)	109.5
N(3)-C(7)-N(2)	115.06(10)	C(11)-C(12)-H(12)	180.0

Table S7. Torsion angles [°] for compound **2**.

C(10)-N(3)-C(7)-N(2)	178.38(11)
C(10)-N(3)-C(7)-C(6)	-1.48(18)
C(3)-N(2)-C(7)-N(3)	-179.87(10)
C(3)-N(2)-C(7)-C(6)	-0.01(18)
C(9)-C(8)-C(6)-C(5)	-178.17(12)
C(9)-C(8)-C(6)-C(7)	1.34(19)
N(3)-C(7)-C(6)-C(8)	-0.26(19)
N(2)-C(7)-C(6)-C(8)	179.89(11)
N(3)-C(7)-C(6)-C(5)	179.28(11)
N(2)-C(7)-C(6)-C(5)	-0.57(18)
C(3)-C(4)-C(5)-C(6)	0.78(19)
C(8)-C(6)-C(5)-C(4)	179.65(12)
C(7)-C(6)-C(5)-C(4)	0.14(19)
C(7)-N(2)-C(3)-N(1)	-177.17(10)
C(7)-N(2)-C(3)-C(4)	1.03(18)
C(1)-N(1)-C(3)-N(2)	-169.36(12)
C(1)-N(1)-C(3)-C(4)	12.4(2)
C(5)-C(4)-C(3)-N(2)	-1.43(19)
C(5)-C(4)-C(3)-N(1)	176.59(12)
C(7)-N(3)-C(10)-C(9)	2.23(19)
C(7)-N(3)-C(10)-C(11)	-176.73(11)
C(3)-N(1)-C(1)-O(1)	-1.4(2)
C(3)-N(1)-C(1)-C(2)	178.74(12)
C(6)-C(8)-C(9)-C(10)	-0.68(19)
N(3)-C(10)-C(9)-C(8)	-1.2(2)
C(11)-C(10)-C(9)-C(8)	177.76(12)

Table S8. Hydrogen bonds for compound **2** [Å and °].

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
C4-H4	0.930	2.276	119.97	2.856	O1
N1-H1	0.891	2.097	170.85	2.980	N2 [-x+2, y, -z+1/

Table S9: XYZ coordinates and energies of adducts 6A and 6B models (kcal/mol)

6A (-6270.17)			
1.C	-7.861468	1.232261	0.131439
2.C	-11.559018	3.174104	-0.141281
3.C	-12.677393	2.367529	-0.172148
4.C	-12.500427	0.957529	-0.109039
5.N	-11.297241	0.370186	-0.021591
6.C	-7.862769	2.668720	0.077668
7.C	-9.062212	3.323399	-0.010897
8.C	-10.277456	2.589090	-0.048994
9.C	-10.183892	1.155638	0.009620
10.N	-8.990816	0.508779	0.098260
11.H	-11.651699	4.257752	-0.187283
12.H	-13.679991	2.777286	-0.242585
13.C	-13.646252	0.100321	-0.138896
14.H	-9.093995	4.410721	-0.053644
15.H	-6.913100	3.186319	0.107738
16.C	-14.626728	-0.607493	-0.165395
17.H	-15.491653	-1.232112	-0.187660
18.N	-6.692753	0.499088	0.220823
19.C	-5.371781	0.966793	0.282362
20.C	-4.347672	-0.146195	0.434262
21.O	-5.060949	2.154395	0.241251
22.H	-3.364743	0.249802	0.171814
23.H	-4.596089	-1.024186	-0.168767
24.H	-4.331171	-0.474814	1.482012
25.H	-6.810179	-0.539070	0.234685
26.N	-9.015048	-2.518943	0.124360
27.C	-10.178220	-3.264944	0.065738
28.N	-10.187063	-4.596705	0.019975
29.C	-8.947757	-5.132415	0.043877
30.C	-7.703754	-4.476128	0.109132
31.C	-7.698592	-3.046205	0.154017
32.N	-8.634525	-6.476388	0.009105
33.C	-7.241038	-6.571676	0.055854
34.N	-6.657130	-5.395735	0.115639
35.O	-6.723473	-2.271150	0.211657
36.N	-11.341985	-2.575150	0.067889
37.H	-9.073734	-1.484168	0.137318
38.H	-9.306026	-7.234043	-0.037848
39.H	-6.737946	-7.530882	0.041395
40.H	-12.196207	-3.105023	-0.030597
41.H	-11.358440	-1.546859	0.034660

6B (-6244.99)			
1.C	-7.958065	1.663219	0.212870
2.C	-11.719758	3.334714	-0.417584
3.C	-12.770198	2.448592	-0.482707
4.C	-12.506228	1.054630	-0.318989
5.N	-11.278261	0.560557	-0.122851
6.C	-8.031265	3.086880	0.118014
7.C	-9.258661	3.669853	-0.089006
8.C	-10.408101	2.846036	-0.202042
9.C	-10.225035	1.424064	-0.075013
10.N	-9.003695	0.862667	0.133423
11.H	-11.884941	4.405296	-0.526302
12.H	-13.790832	2.780173	-0.646573
13.C	-13.590207	0.122756	-0.358615
14.H	-9.358210	4.750011	-0.178006
15.H	-7.125365	3.684167	0.185788
16.C	-14.513247	-0.657299	-0.396017
17.H	-15.315809	-1.360158	-0.431915
18.N	-6.692508	1.073798	0.450427
19.C	-6.150806	-0.029902	-0.216963
20.C	-4.882783	-0.585857	0.417575
21.O	-6.649736	-0.510411	-1.224247
22.H	-5.128331	-1.569137	0.837203
23.H	-4.472966	0.044786	1.213523
24.H	-4.128534	-0.735426	-0.361064
25.H	-6.079094	1.566581	1.089588
26.N	-8.146014	-5.076912	0.010576
27.C	-7.861779	-3.781497	-0.369635
28.N	-8.719088	-2.793693	-0.246159
29.C	-9.904507	-3.171004	0.298164
30.C	-10.313376	-4.451603	0.718016
31.C	-9.391107	-5.551388	0.594133
32.N	-10.977836	-2.345057	0.530694
33.C	-11.977020	-3.142852	1.071812
34.N	-11.617258	-4.407580	1.202126
35.O	-9.493396	-6.738358	0.891388
36.N	-6.587279	-3.511957	-0.849455
37.H	-7.429844	-5.796502	-0.052216
38.H	-11.021770	-1.340195	0.302432
39.H	-12.940904	-2.731368	1.343497
40.H	-6.526546	-2.570867	-1.249053
41.H	-6.150734	-4.236014	-1.411244