Synthesis, characterisation and antibacterial activity of novel Ga(III) polypyridyl catecholate complexes

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Supporting Information

[Ga(bipy)$_2$(2,3-DHBA$_{-2H}$)](NO$_3$).H$_2$O (1)

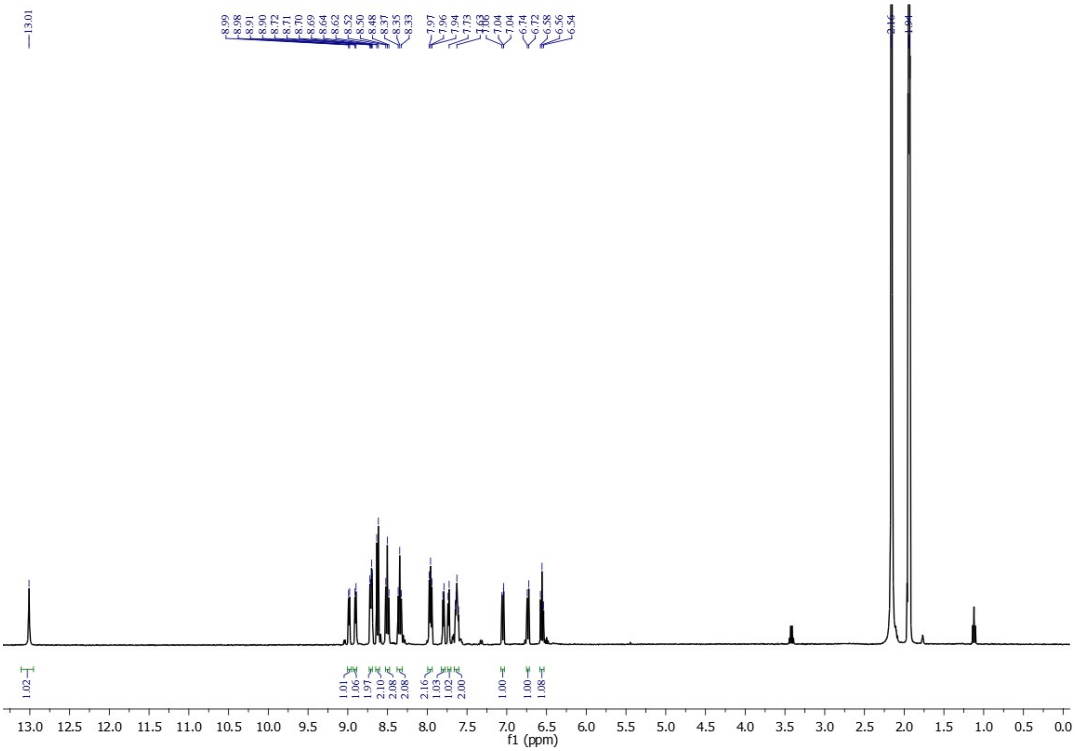


Figure S1. ^{1}H NMR spectrum of **1** (in CD$_3$CN).

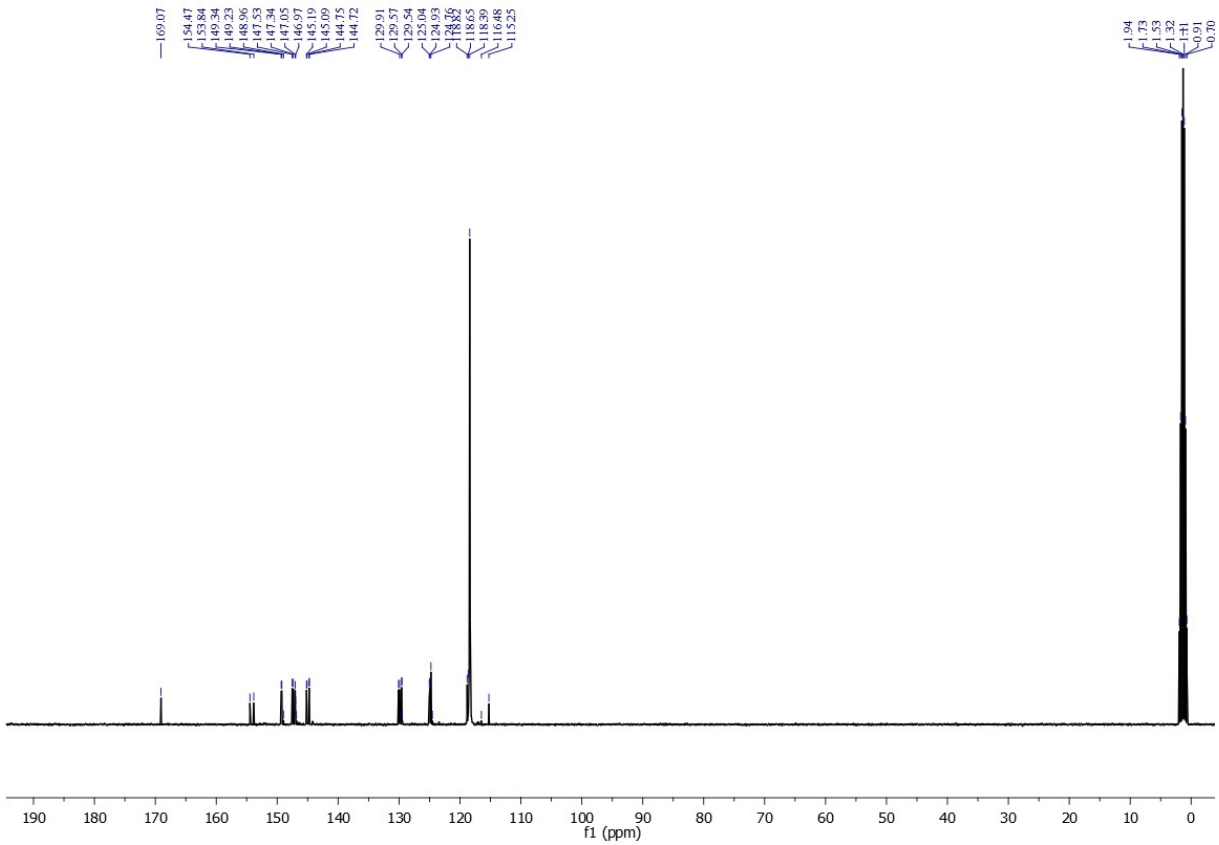


Figure S2. ^{13}C NMR spectrum of **1** (in CD_3CN).

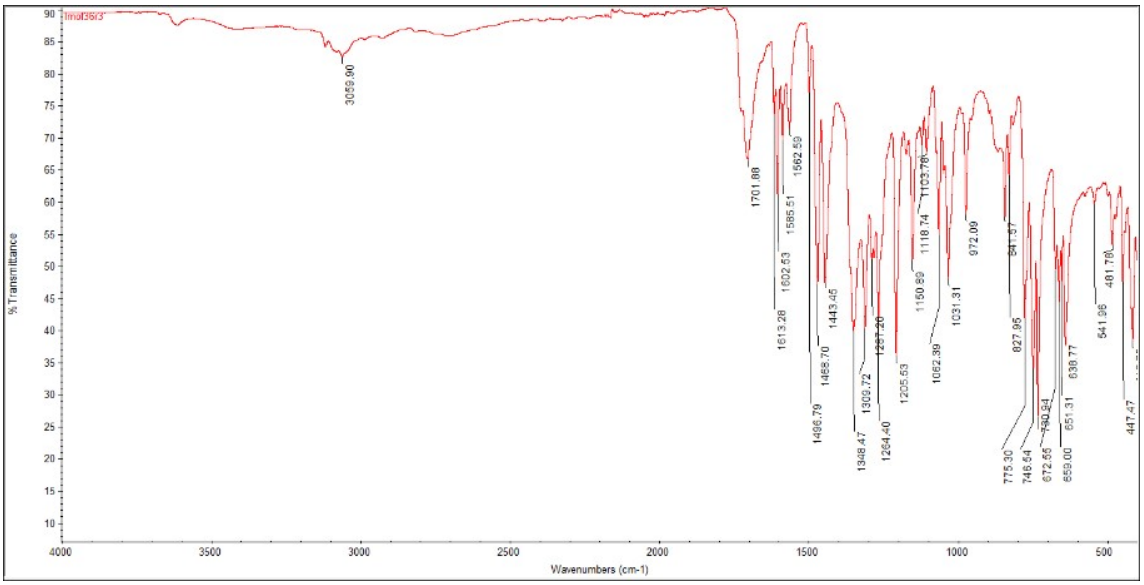


Figure S3. IR spectrum of **1**.

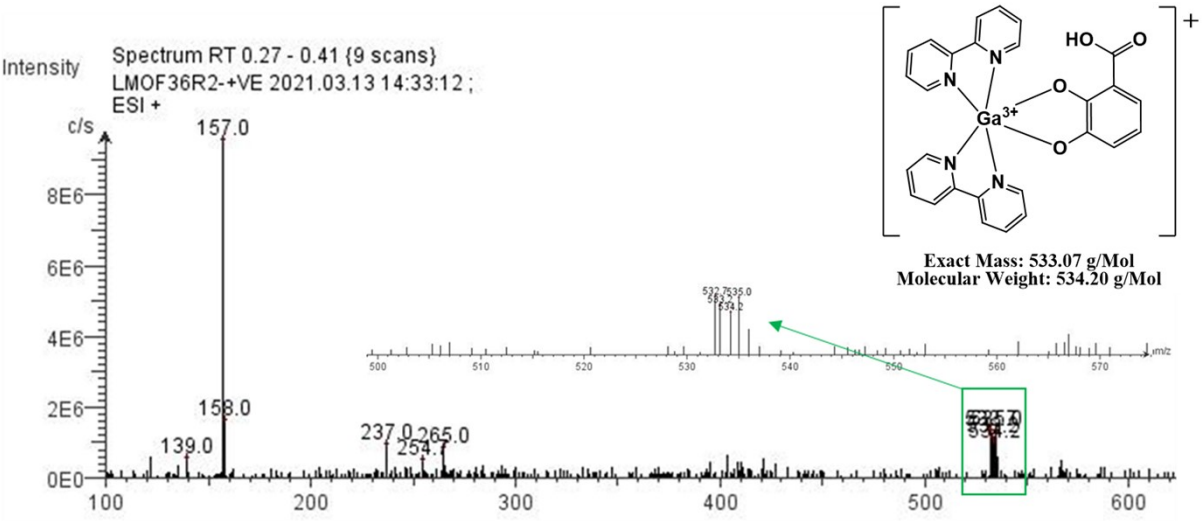
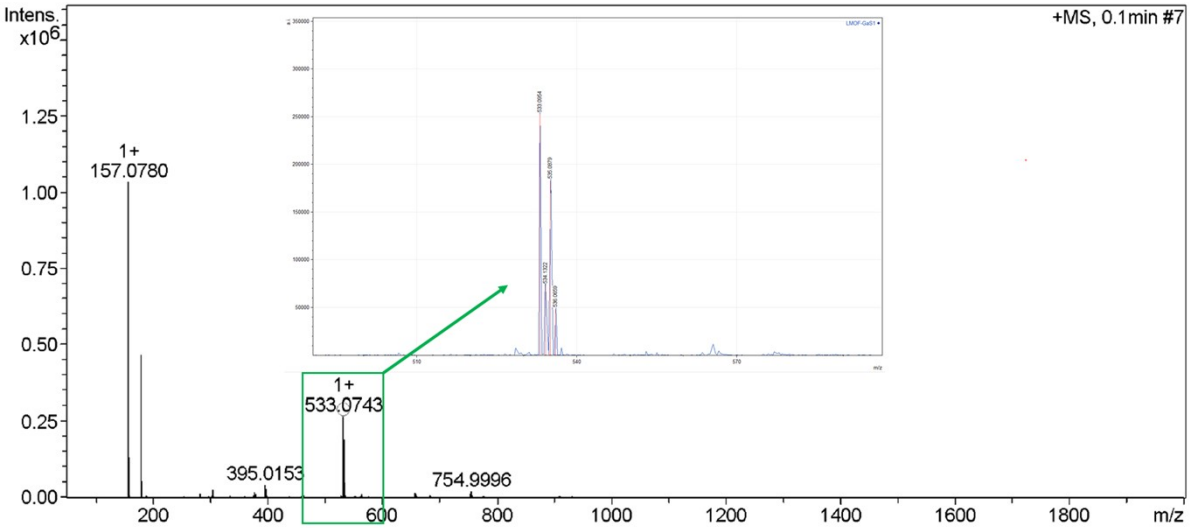


Figure S4. ESI mass spectrum of **1** (positive mode).



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
533.074335	1	C27H20GaN4O4	533.073480	-0.9	-1.6	20.5	ok	even	13.6

Figure S5. HR-MS ESI mass spectrum of **1** (positive mode).

[Ga(bipy)$_2$(3,4-DHBA$_{-2H}$)](NO$_3$).H$_2$O (2)

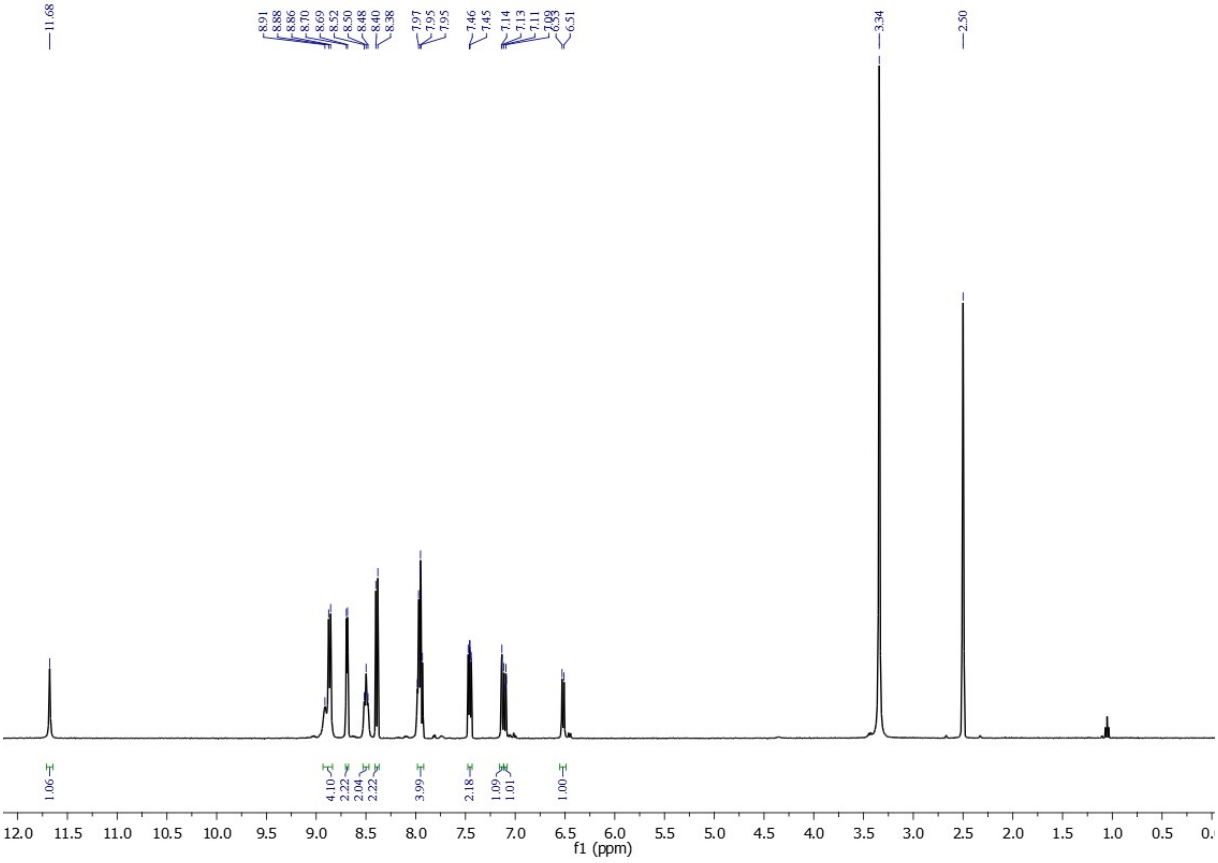


Figure S6. ^{1}H NMR spectrum of **2** (in DMSO-*d*^{6}).

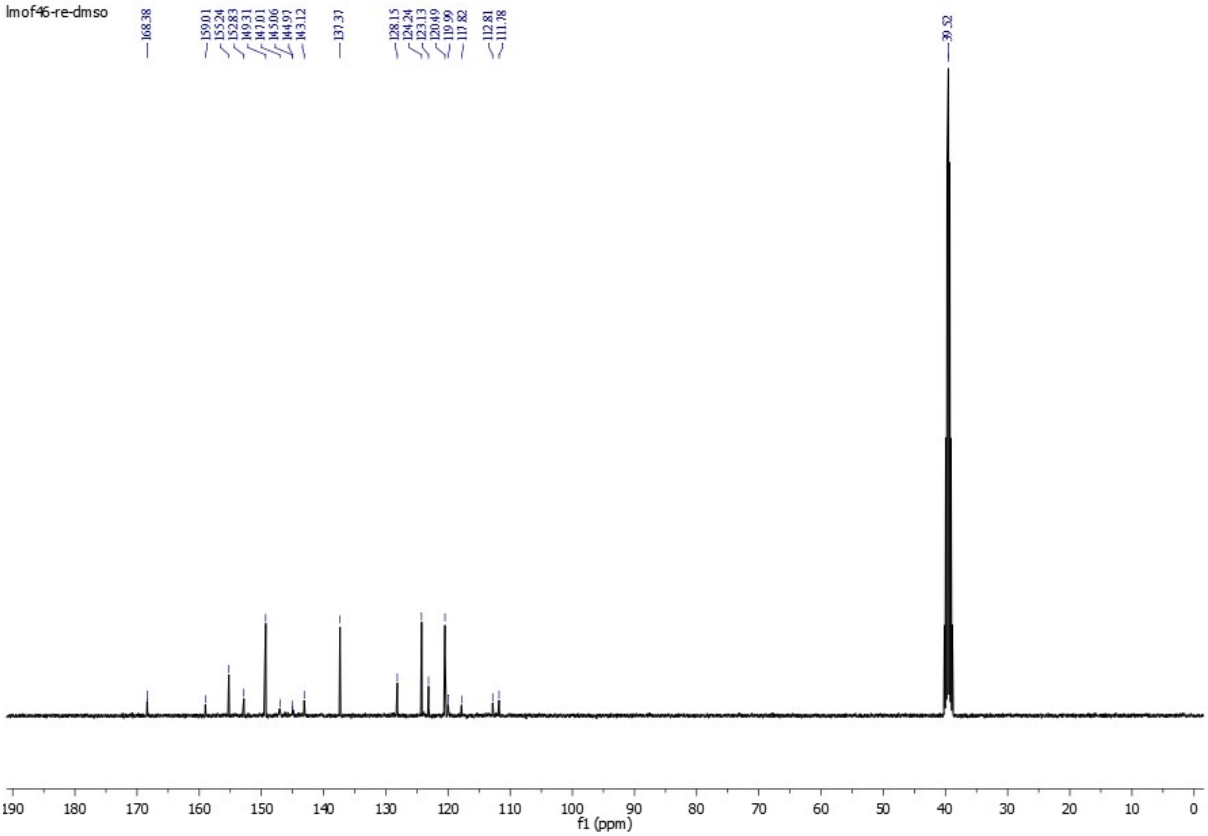


Figure S7. ^{13}C NMR spectrum of **2** (in DMSO-d^6).

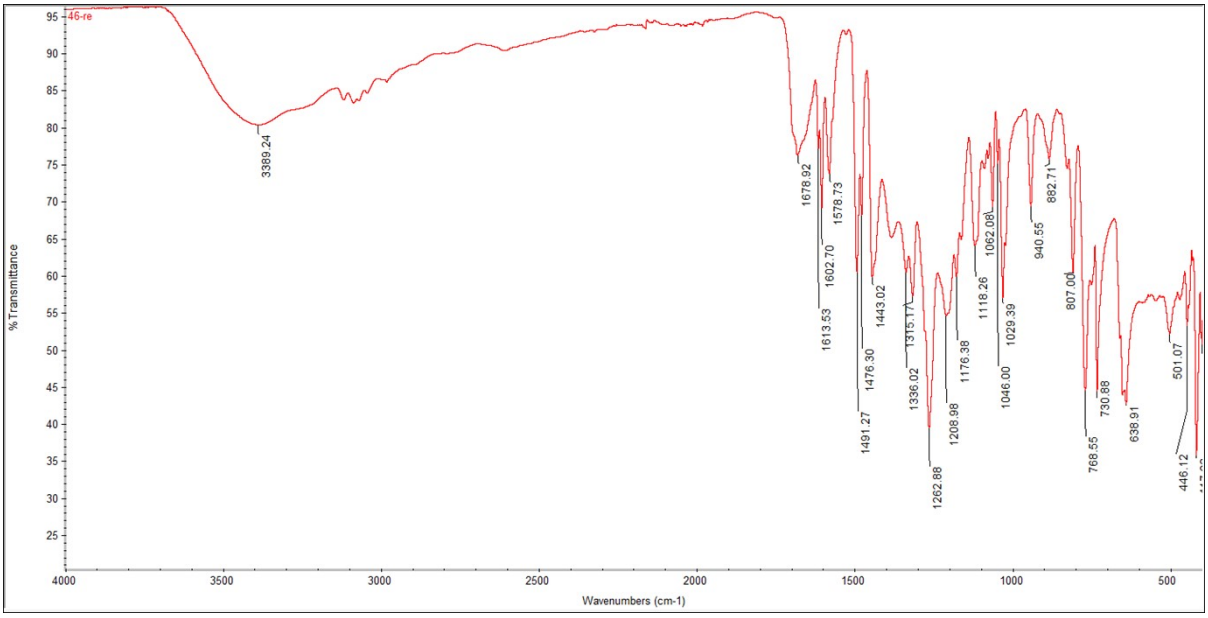


Figure S8. IR spectrum of **2**.

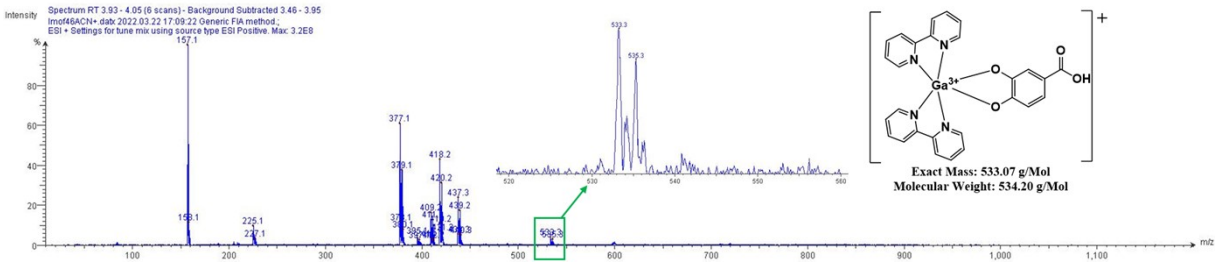


Figure S9. ESI mass spectrum of **2** (in positive mode).

$[Ga(bipy)_2(3,4,5\text{-}THBA_{-2H})](NO_3).H_2O$ (3)

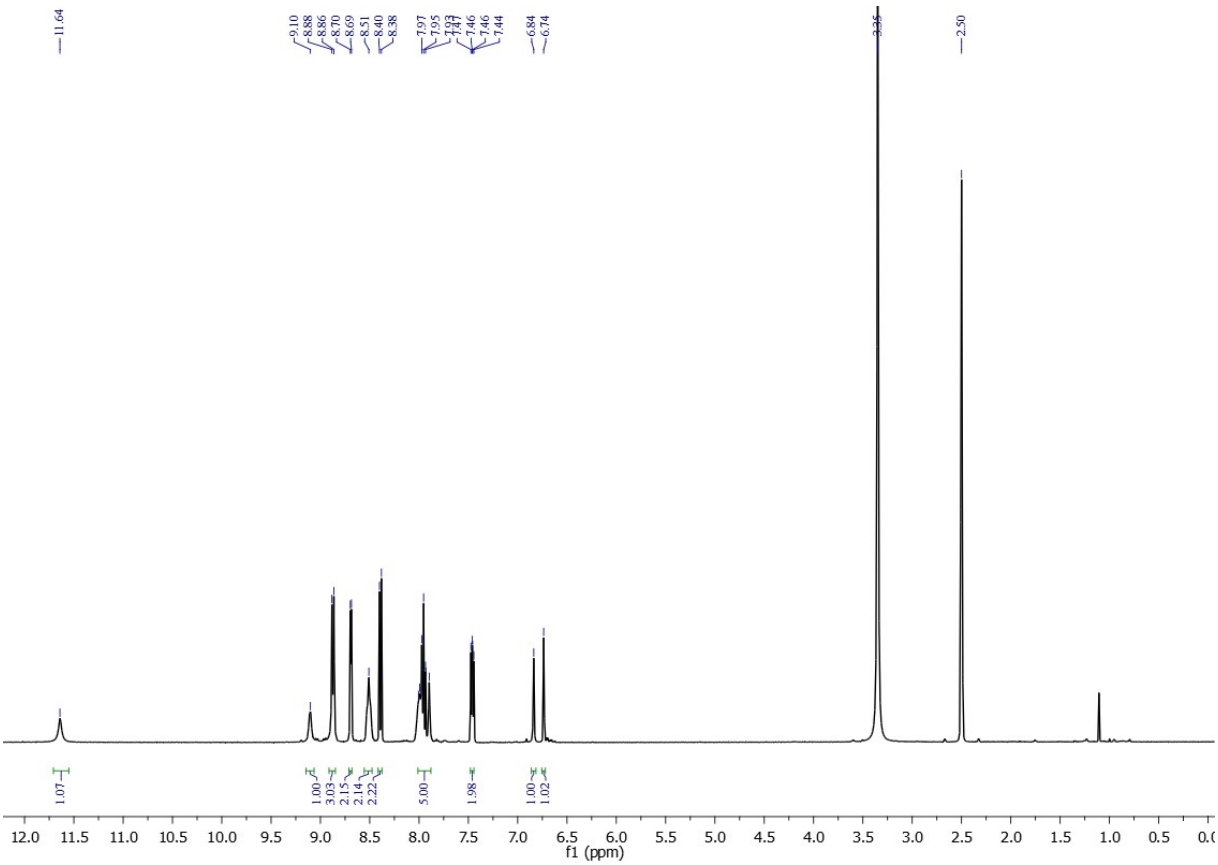


Figure S10. ^{1}H Figure S5. ^{13}H NMR spectrum of **3** (in DMSO-*d*^{6}).

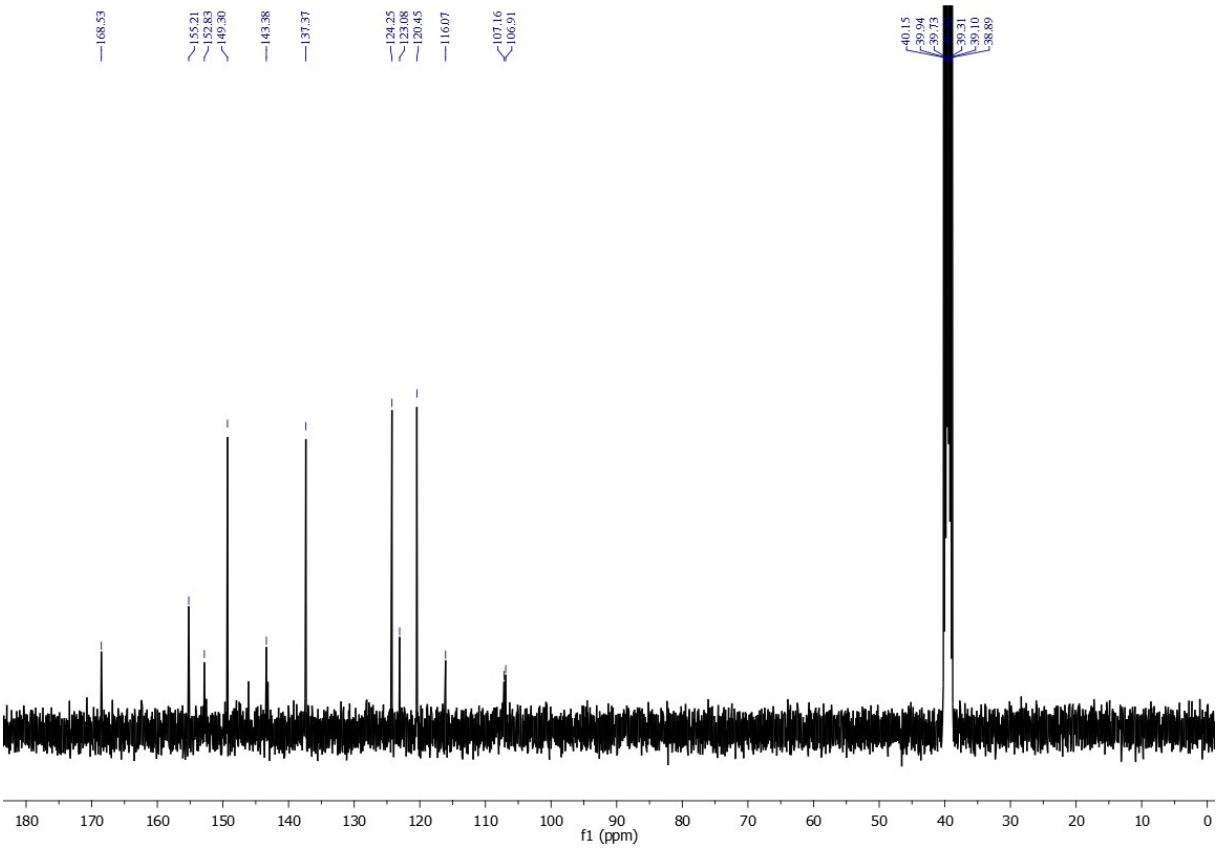


Figure S11. ^{13}C NMR spectrum of **3** (in DMSO-d^6).

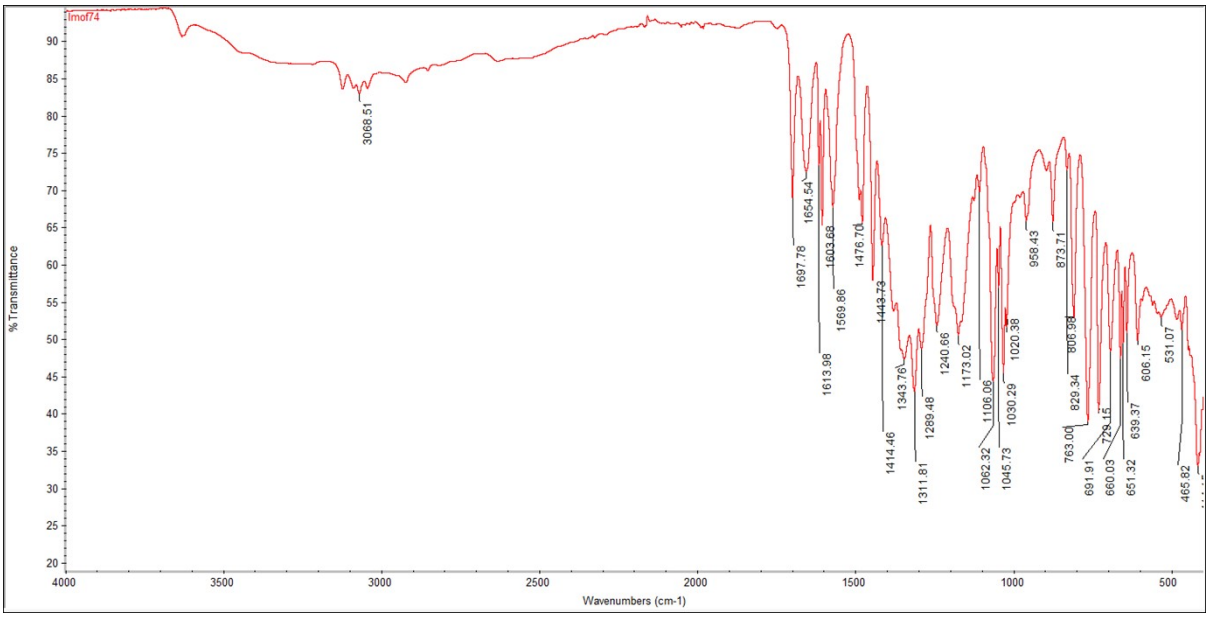


Figure S12. IR spectrum of **3**.

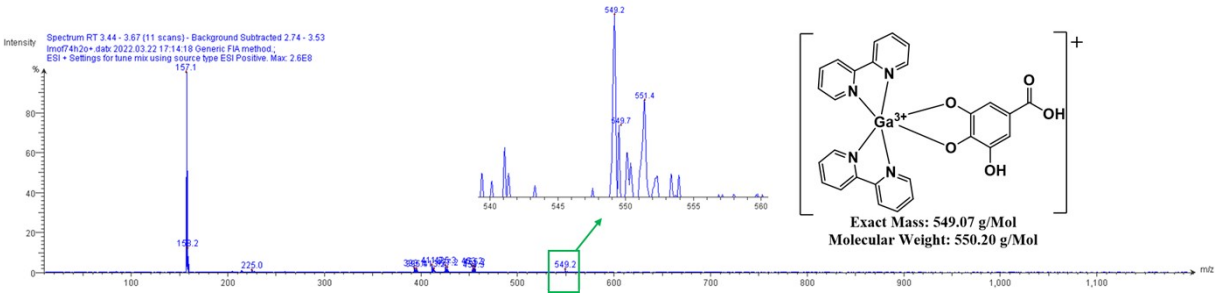


Figure S13. ESI mass spectrum of **3** (in positive mode).

[Ga(phen)$_2$(2,3DHBA$_{-2H}$)](NO$_3$).H$_2$O (4)

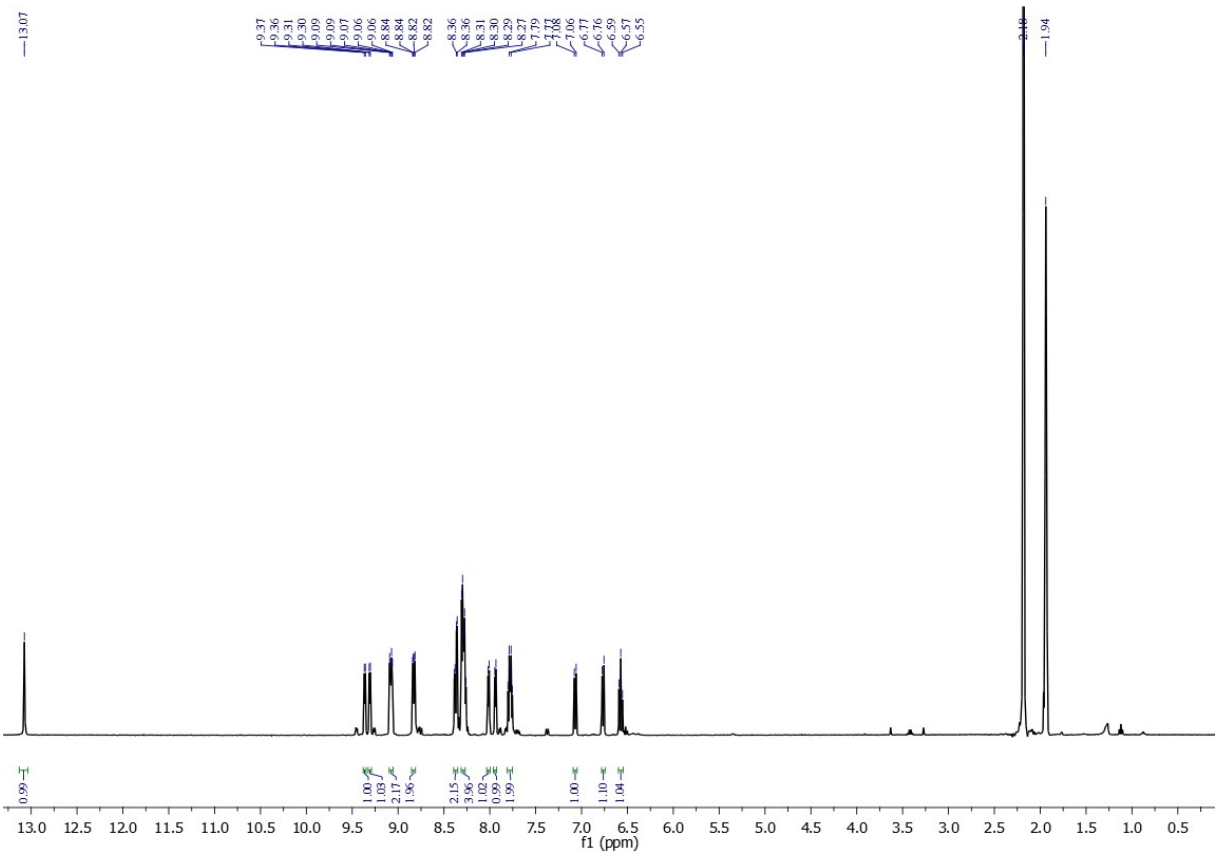


Figure S14. ^{1}H NMR spectrum of **4** (in CD_3CN).

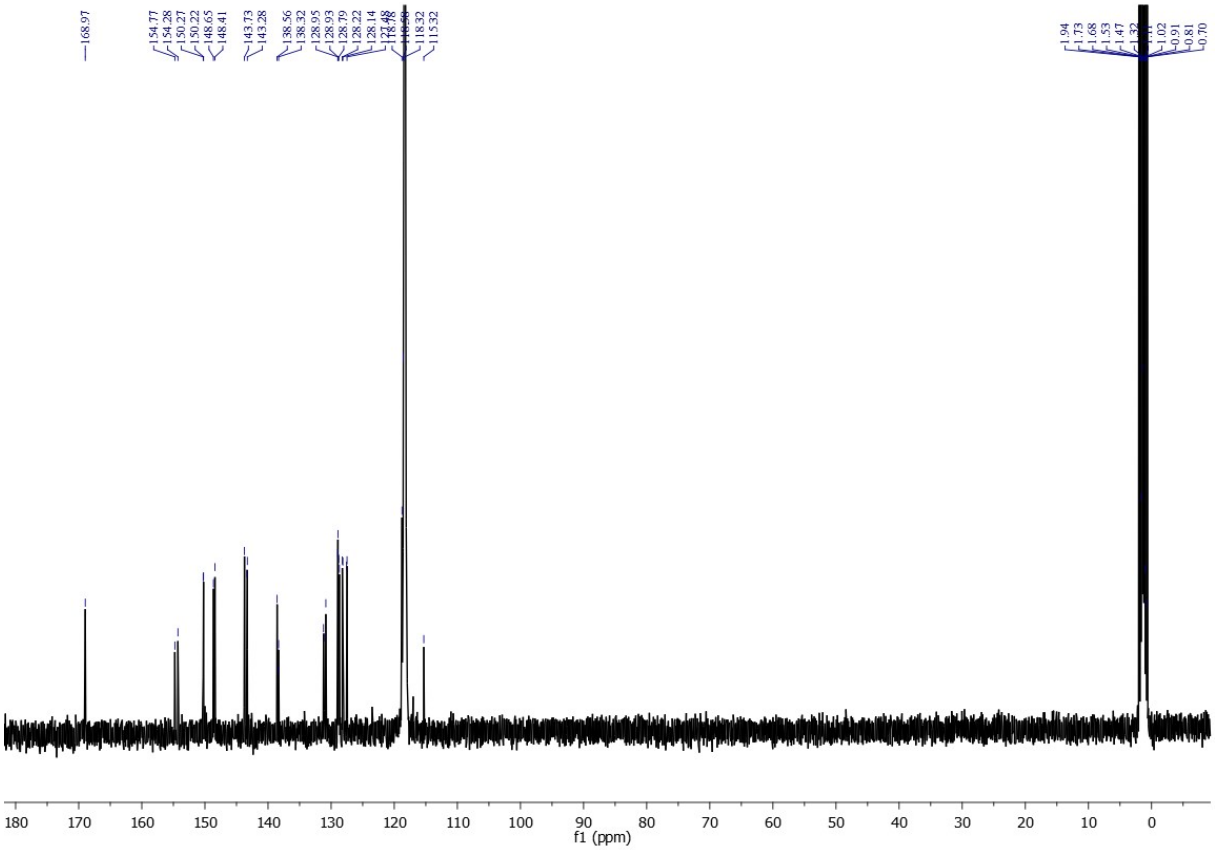


Figure S15. ^{13}C NMR spectrum of **4** (in CD_3CN).

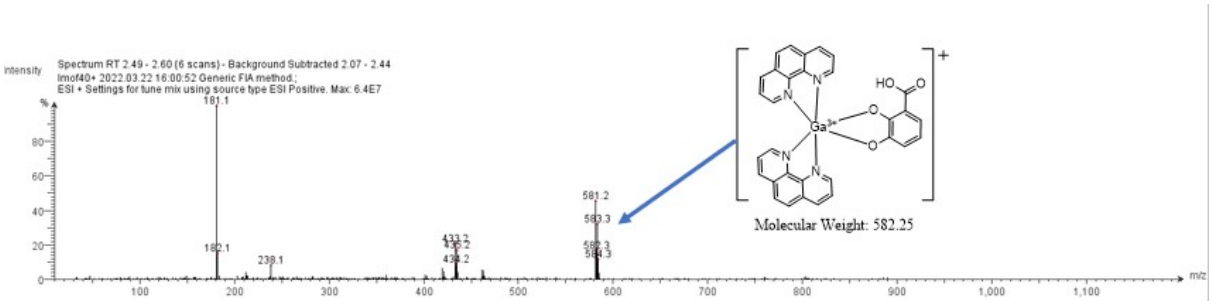


Figure S16. ESI mass spectrum of **4** (in positive mode).

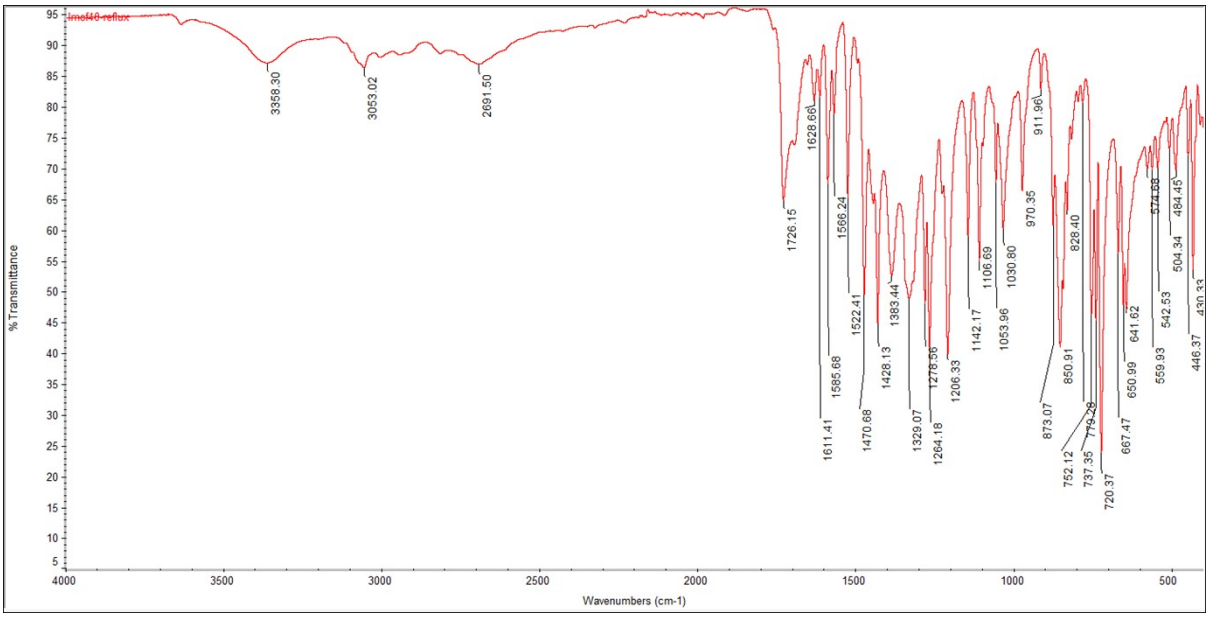


Figure S17. IR spectrum of **4**.

[Ga(bipy)$_2$(CafA$_{-2H}$)](NO$_3$).H$_2$O (5)

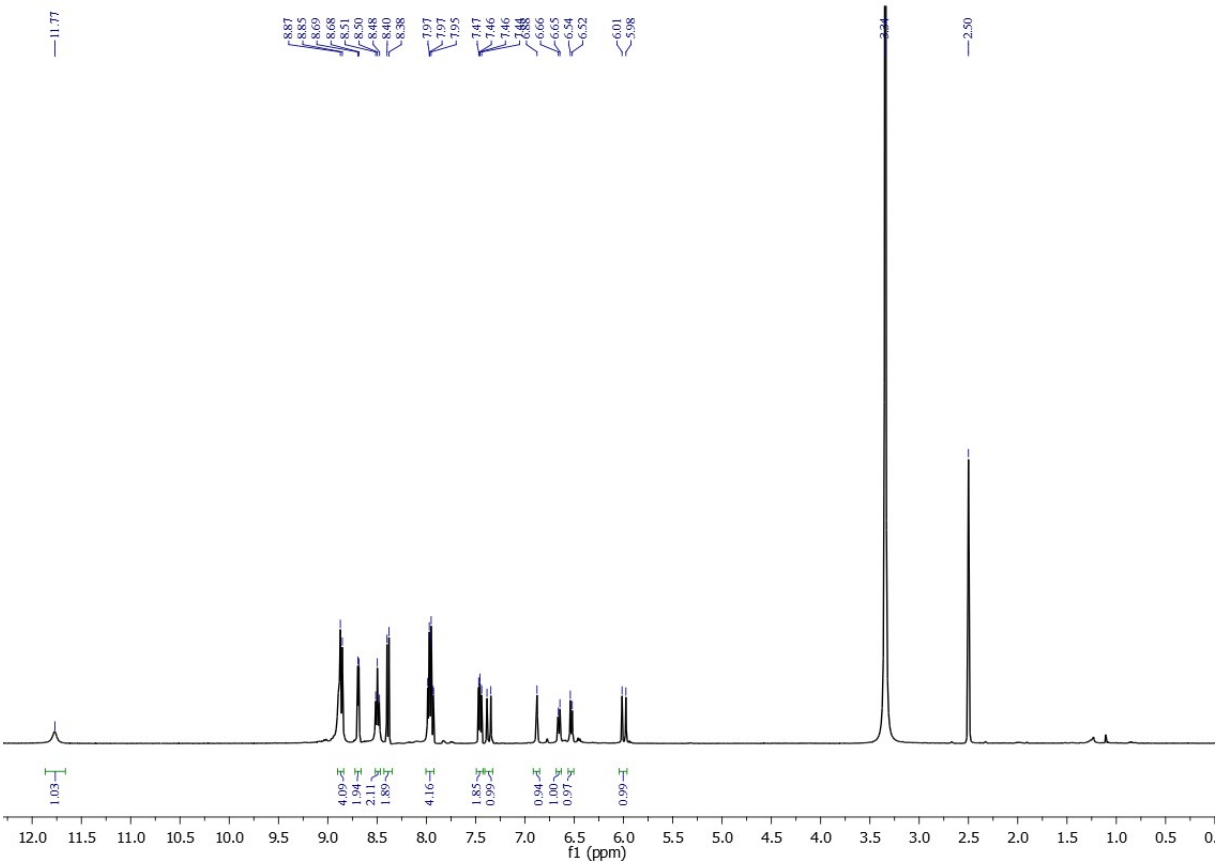


Figure S18. ^{1}H NMR spectrum of **5** (in DMSO-*d*^{6}).

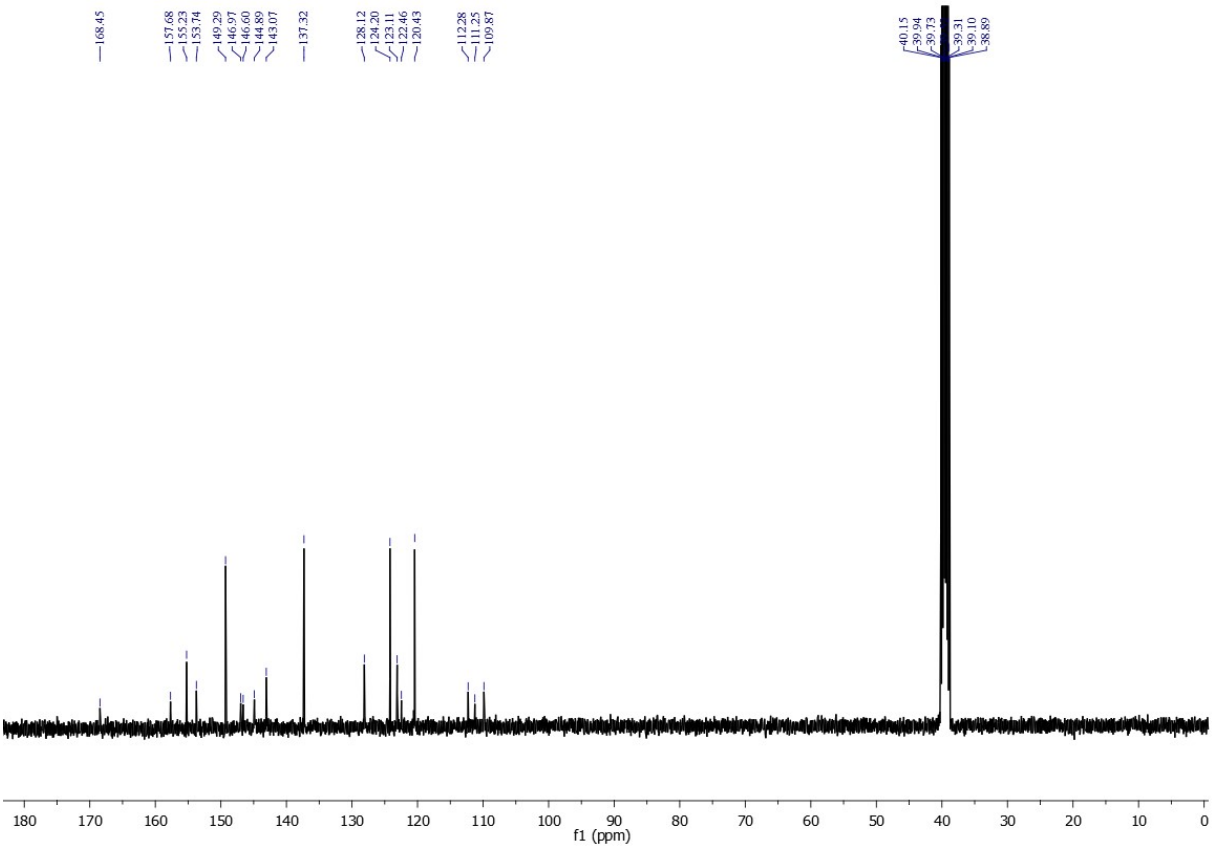


Figure S19. ^{13}C NMR spectrum of **5** (in DMSO-d^6).

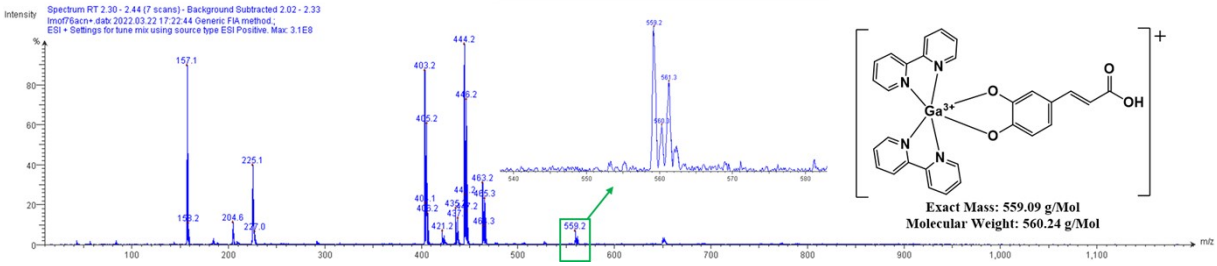


Figure S20. ESI mass spectrum of **5** (in positive mode).

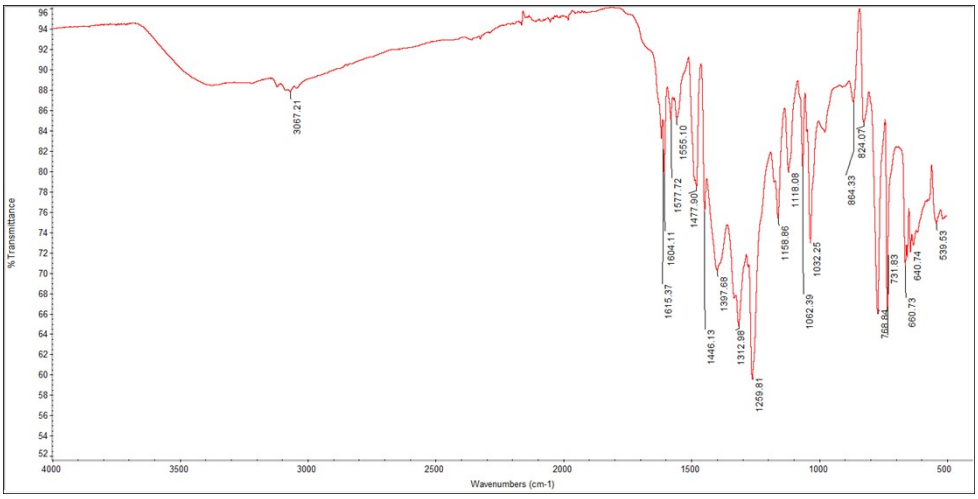


Figure S21. IR spectrum of **5.**

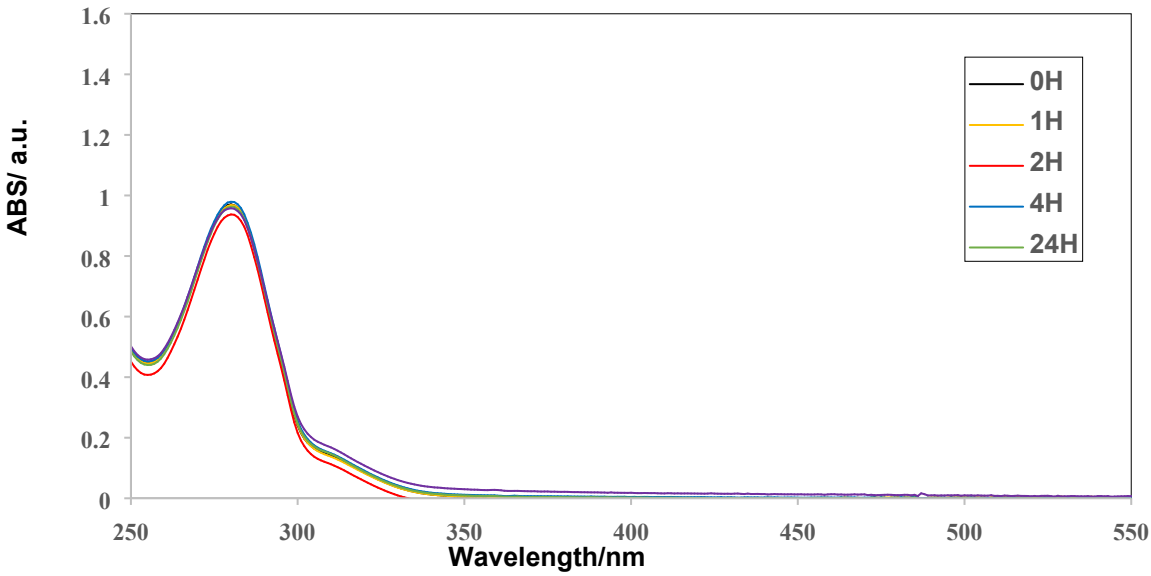
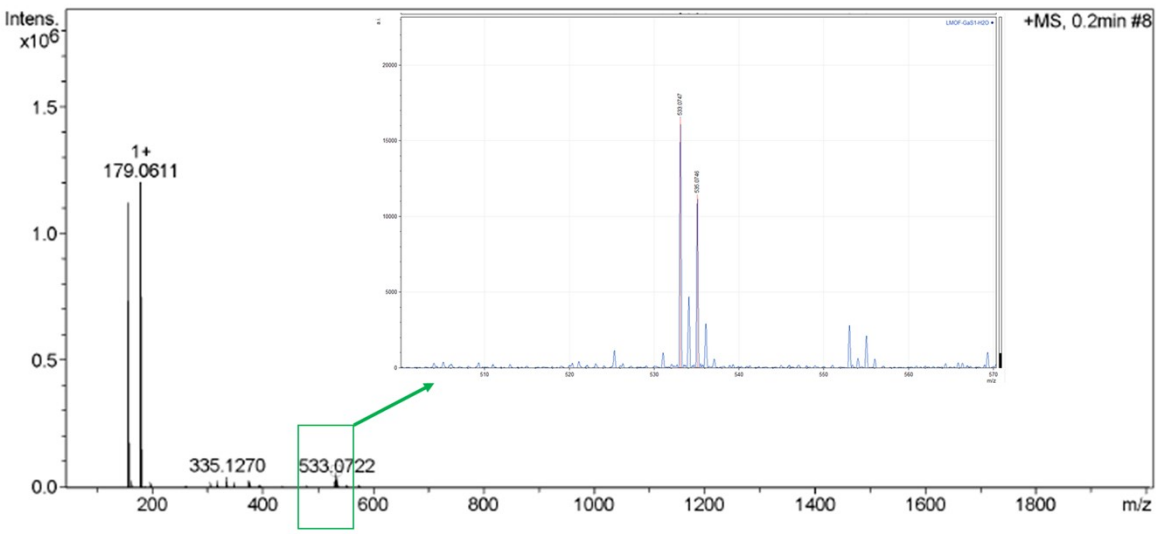


Figure S22. UV-Vis spectrum of **1** (50 µM) in water over the course of 24 h at 37°C.



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
533.072184	1	C27H20GaN4O4	533.073480	1.3	2.4	20.5	ok	even	14.3

Figure S23. HRMS spectrum of **1** after 24 h in water at 37°C.

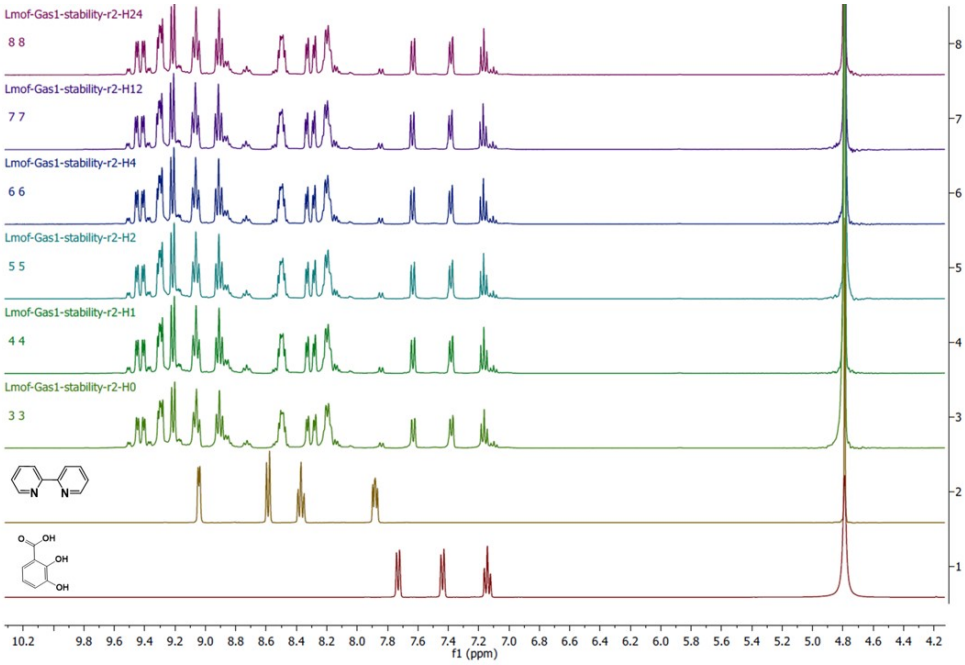


Figure S24. ^{1}H NMR study of **1** in D_2O:CD_3CN (50:50) over 24 h at 37 °C stacked with ^{1}H NMR sepctra of bipy and 2,3-DHBA in D_2O:CD_3CN (50:50).

Table S1. Crystal data and structure refinement for **1** to **4**.

Identification code	**1**	**2**	**3**	**4**
Empirical formula	$C_{28}H_{24}F_6GaN_4O_5P$	$C_{27}H_{20}F_6GaN_4O_4P$	$C_{27.2}H_{24.97}Cl_{0.5}F_3GaN_4O_{7.28}P_{0.5}$	$C_{32.5}H_{24.5}F_6GaN_4O_{4.75}P$
Formula weight	711.20	679.16	684.34	761.75
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	tetragonal	monoclinic
Space group	C2/c	$P2_1/c$	$I4_1/acd$	$P2_1/c$
a (Å)	24.412(2)	24.4395(7)	32.0378(10)	15.8706(9)
b (Å)	9.5067(8)	8.6262(3)	32.0378(10)	8.8591(5)
c (Å)	23.7787(19)	26.9096(7)	23.4142(11)	23.0866(12)
α (°)	90	90	90	90
β (°)	93.720(2)	110.5153(14)	90	109.0030(10)
γ (°)	90	90	90	90
Volume (Å^3)	5506.9(8)	5313.3(3)	24032.8(19)	3069.1(3)
Z	8	8	32	4
ρ_{calc} (g/cm^3)	1.716	1.698	1.513	1.649
μ (mm^{-1})	1.147	2.771	1.057	1.035
F(000)	2880.0	2736.0	11150.0	1542.0
Crystal size (mm^3)	0.34 × 0.09 × 0.05	0.226 × 0.136 × 0.032	0.197 × 0.168 × 0.13	0.284 × 0.117 × 0.072
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Reflections collected	30714	103969	109222	47191
Independent reflections	5725 R_{int} = 0.1300, R_{sigma} = 0.0839	10065 R_{int} = 0.0716, R_{sigma} = 0.0358	5574 R_{int} = 0.1062, R_{sigma} = 0.0300	7116 R_{int} = 0.0873, R_{sigma} = 0.0472
Data/restraints/parameters	5725/2/414	10065/1185/1057	5574/82/464	7116/228/535
Goodness-of-fit on F^2	1.015	1.056	1.073	1.068
Final R indexes [I≥2σ(I)]*	R_1 = 0.0319, wR_2 = 0.0824	R_1 = 0.0436, wR_2 = 0.0996	R_1 = 0.0339, wR_2 = 0.0829	R_1 = 0.0581, wR_2 = 0.1330
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0872	R_1 = 0.0672, wR_2 = 0.1127	R_1 = 0.0391, wR_2 = 0.0868	R_1 = 0.0876, wR_2 = 0.1465
Largest diff. peak/hole (e Å^{-3})	0.33/-0.19	0.44/-0.27	0.34/-0.24	1.13/-1.10

*$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

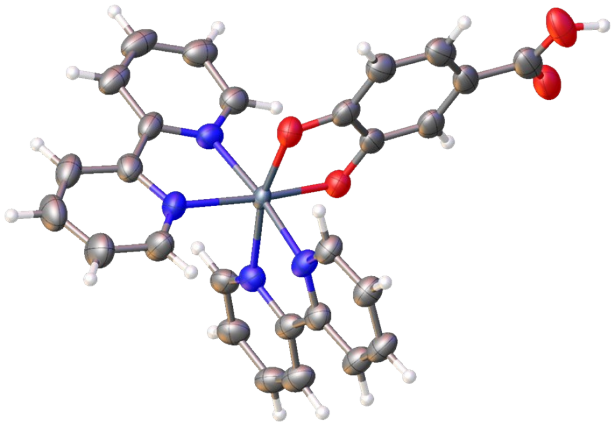


Fig. S25. Major occupied moiety (65% occupied) of one of the two independent cations in the asymmetric unit of **2** with displacement shown at 50% probability. See SI Fig S23 for the complete asymmetric unit of the PF_6 salt.

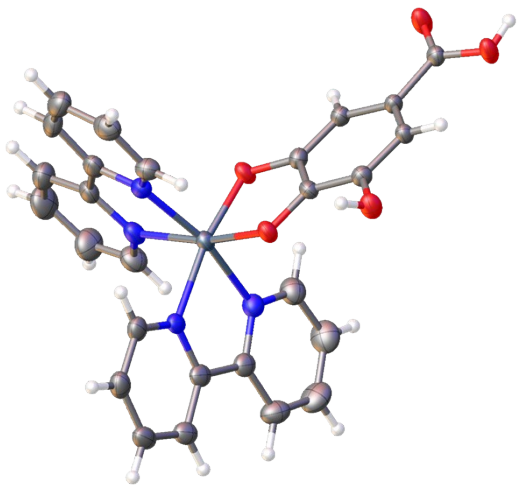


Fig. S26. Structure of the complex cation of **3** only with displacement shown at 50% probability. The salt is comprised of a mixed PF6/Cl anion with H2O and MeOH solvates which are not shown. See SI Fig S24 for the complete asymmetric unit of the mixed anion salt.

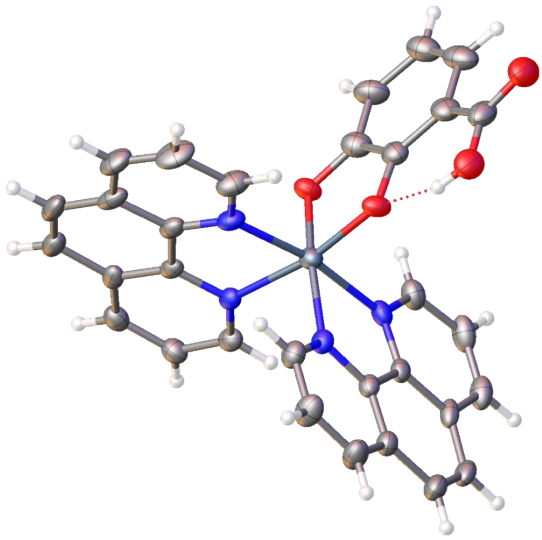


Fig. S27. Structure of complex cation of **4** with displacement shown at 50% probability. A PF_6 salt, solvated with partially occupied EtOH are not shown. See SI Fig S31 for the complete asymmetric unit.

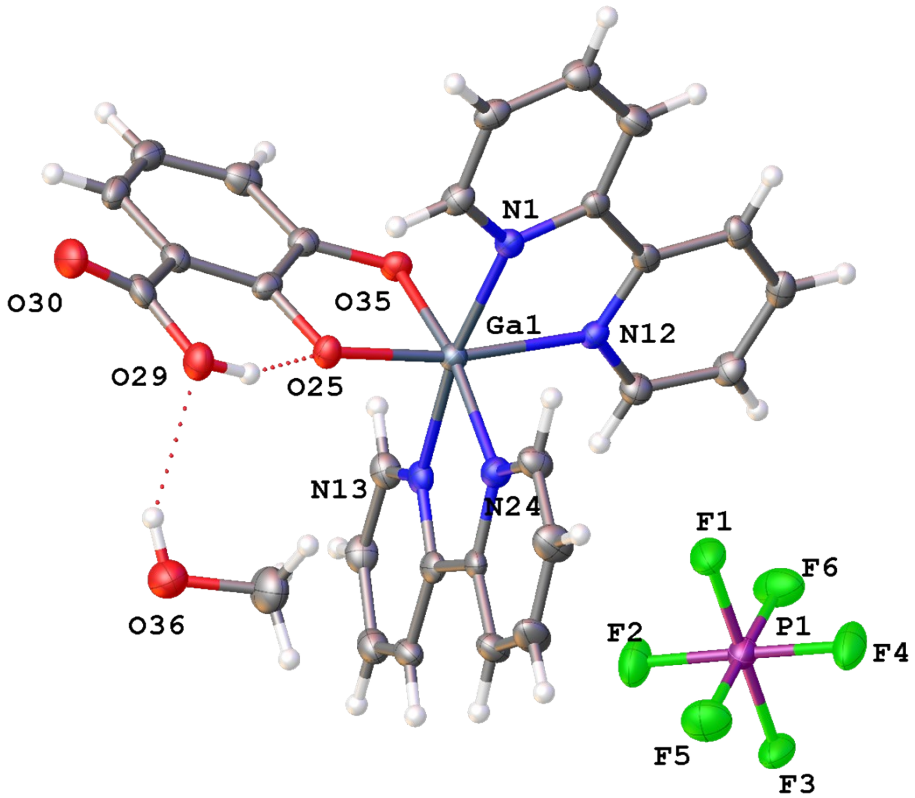
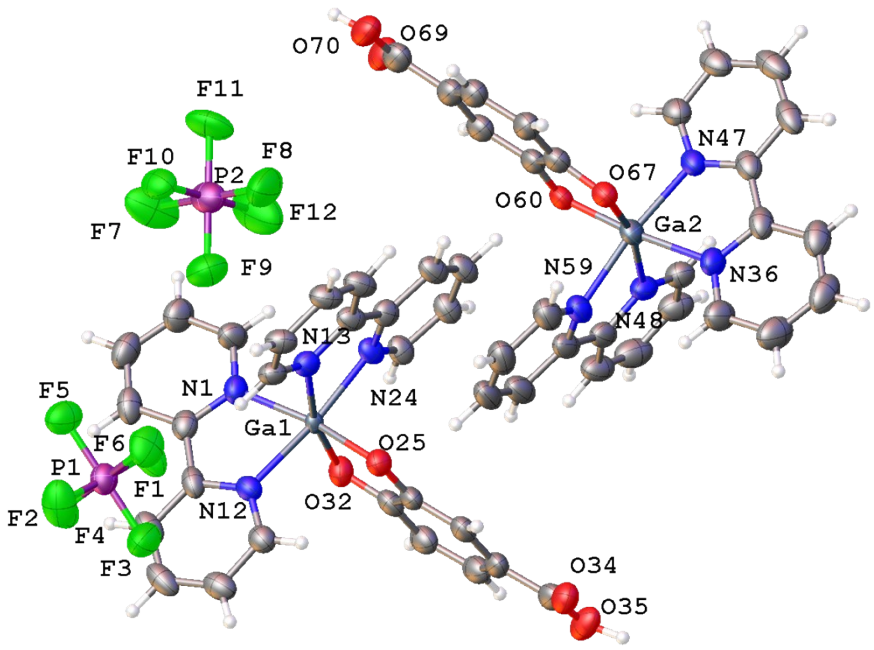
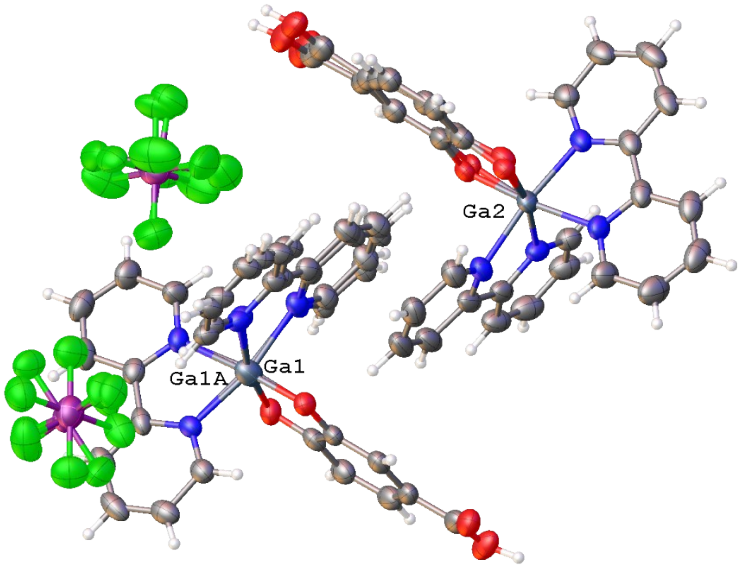


Fig. S28. Complete asymmetric unit of **1**, showing the PF_6 anion and methanol solvate with heteroatoms labelled only. Displacement shown at 50% probability.



A



B

Fig. S29. Complete asymmetric unit of **2** with displacement shown at 50% probability showing (A) the majority occupied moiety only with Ga/bipy 65% and 3,4-DHBA 52%; PF_6, P1: 83% and P2: 53% occupied with heteroatoms labelled only and (B) showing the complete disordered ion pairs.

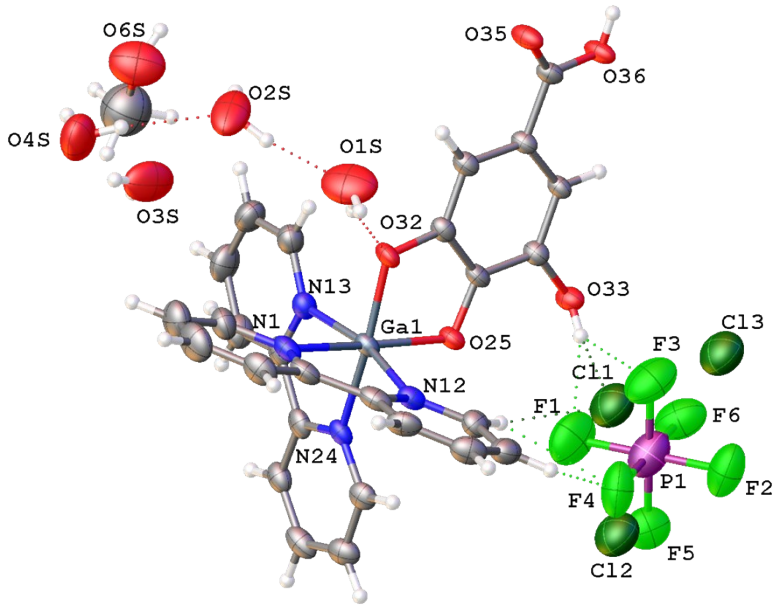


Fig. S30. **3** complete ion pair, showing the full asymmetric unit with mixed PF_6/Cl anion, water and methanol solvates. PF_6 anion is 50% occupied and water solvent molecules modelled over 4 locations (100:50:33:25%) with a partially occupied MeOH (20%). The residual Cl anion occupies three sites. Atomic displacement shown at 50% probability and heteroatoms labelled only.

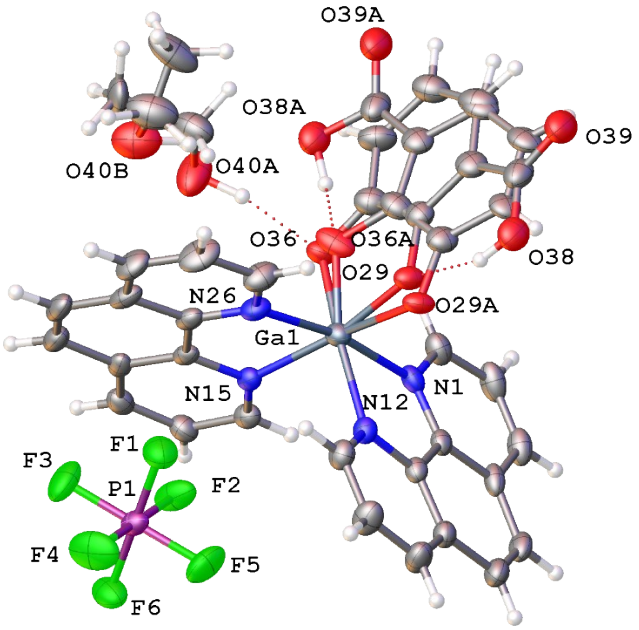


Fig. S31. Complete asymmetric unit of the ion pair in **4** showing the disorder in the 2,3-DHBA moiety (90:10% occupied). EtOH is 75% occupied over two locations (43:32%). Atomic displacement shown at 50% probability and heteroatoms labelled only.

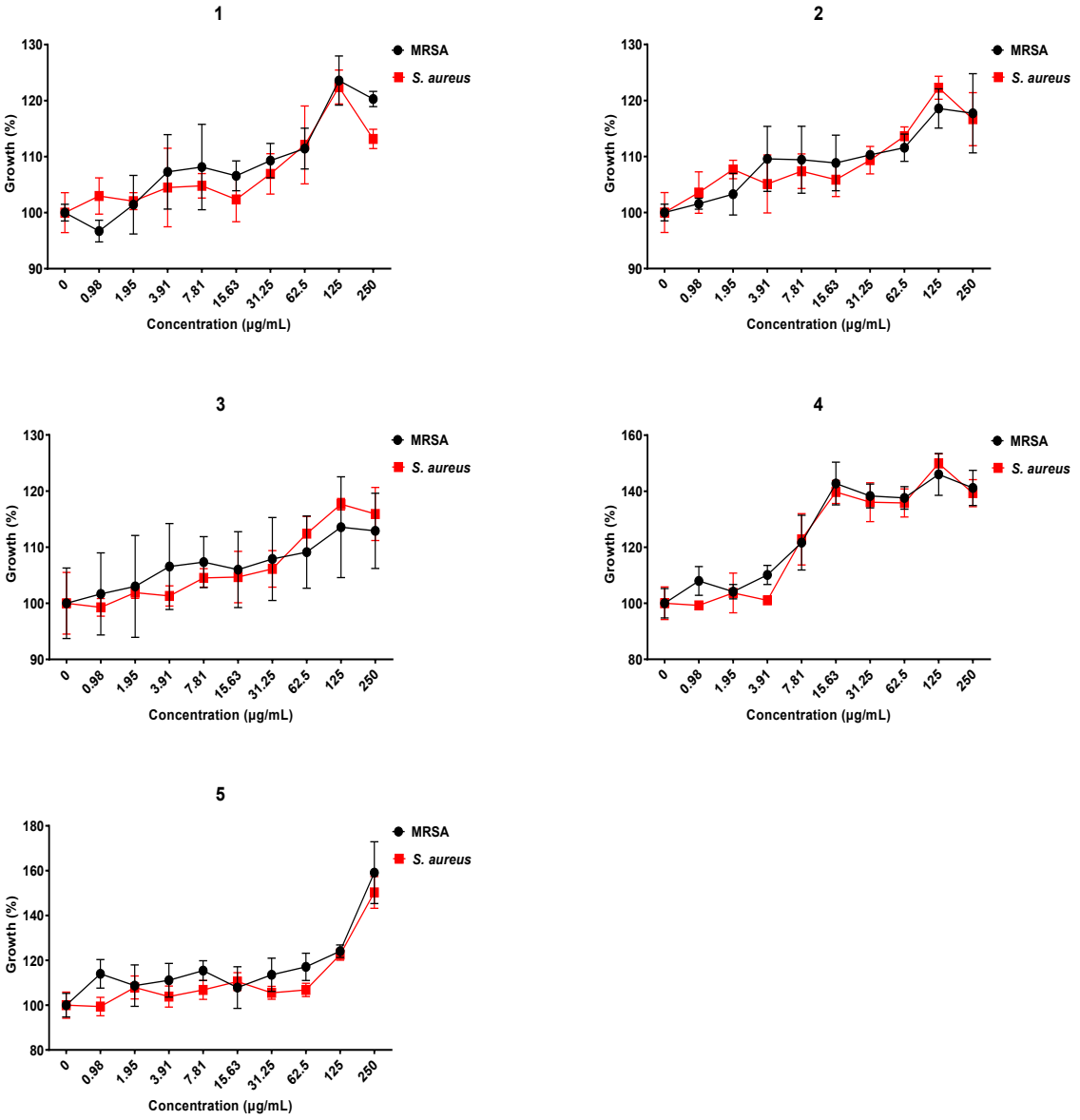


Figure S32. *in vitro* susceptibility assays for 1 to 5 against *S. Aureus* and MRSA. GraphPad Prism, n= 3.

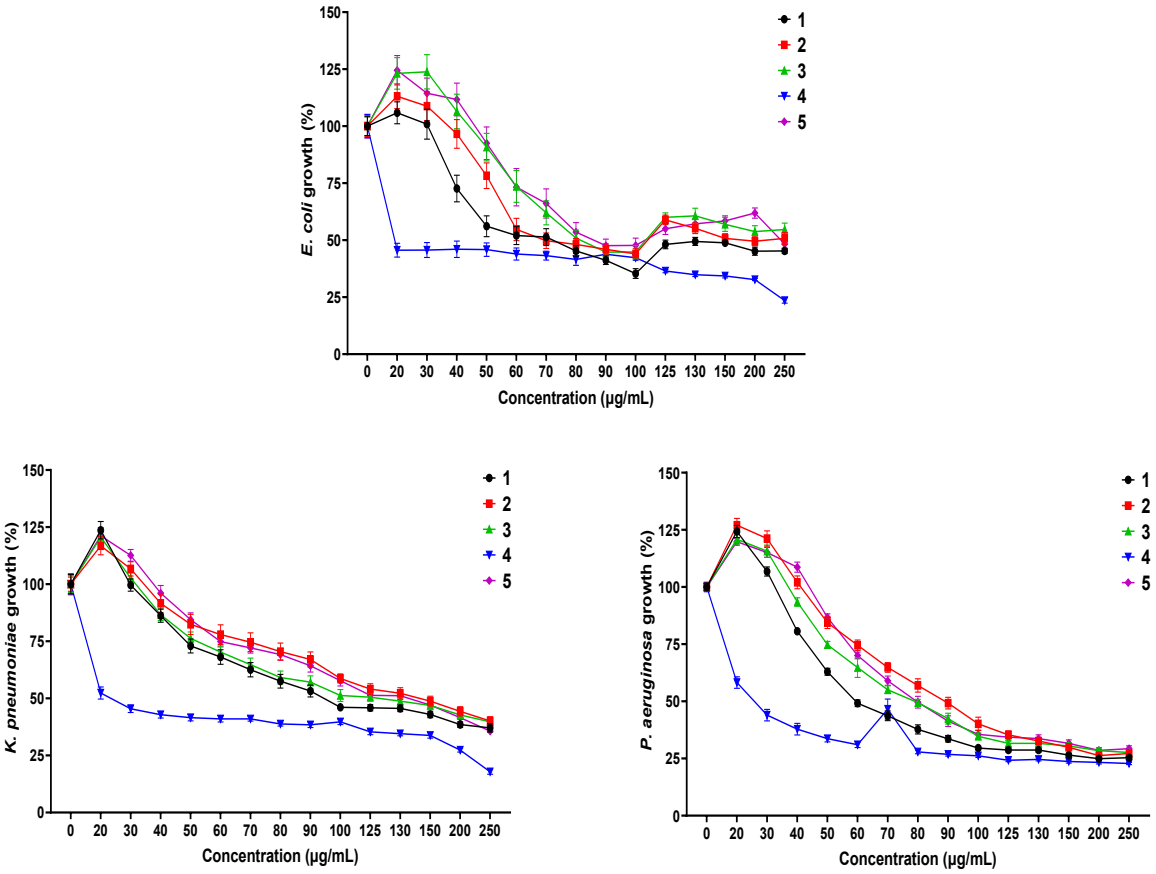


Figure S33. *in vitro* susceptibility assays for 1 to 5 against *E.coli, K. pneumoniae and P. aeruginosa*. GraphPad Prism, n= 3.

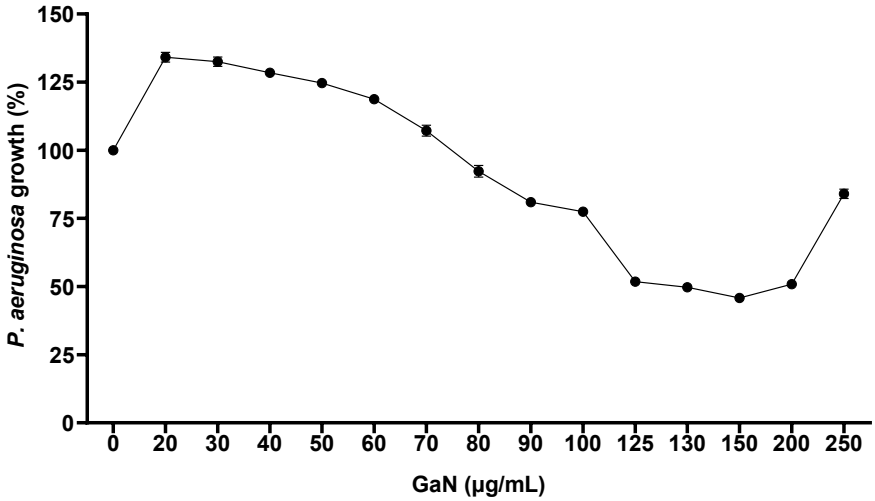


Figure S34. *in vitro* susceptibility assays for $Ga(NO_3)_3$ against *E.coli, K. pneumoniae and P. aeruginosa*. GraphPad Prism, n= 3.

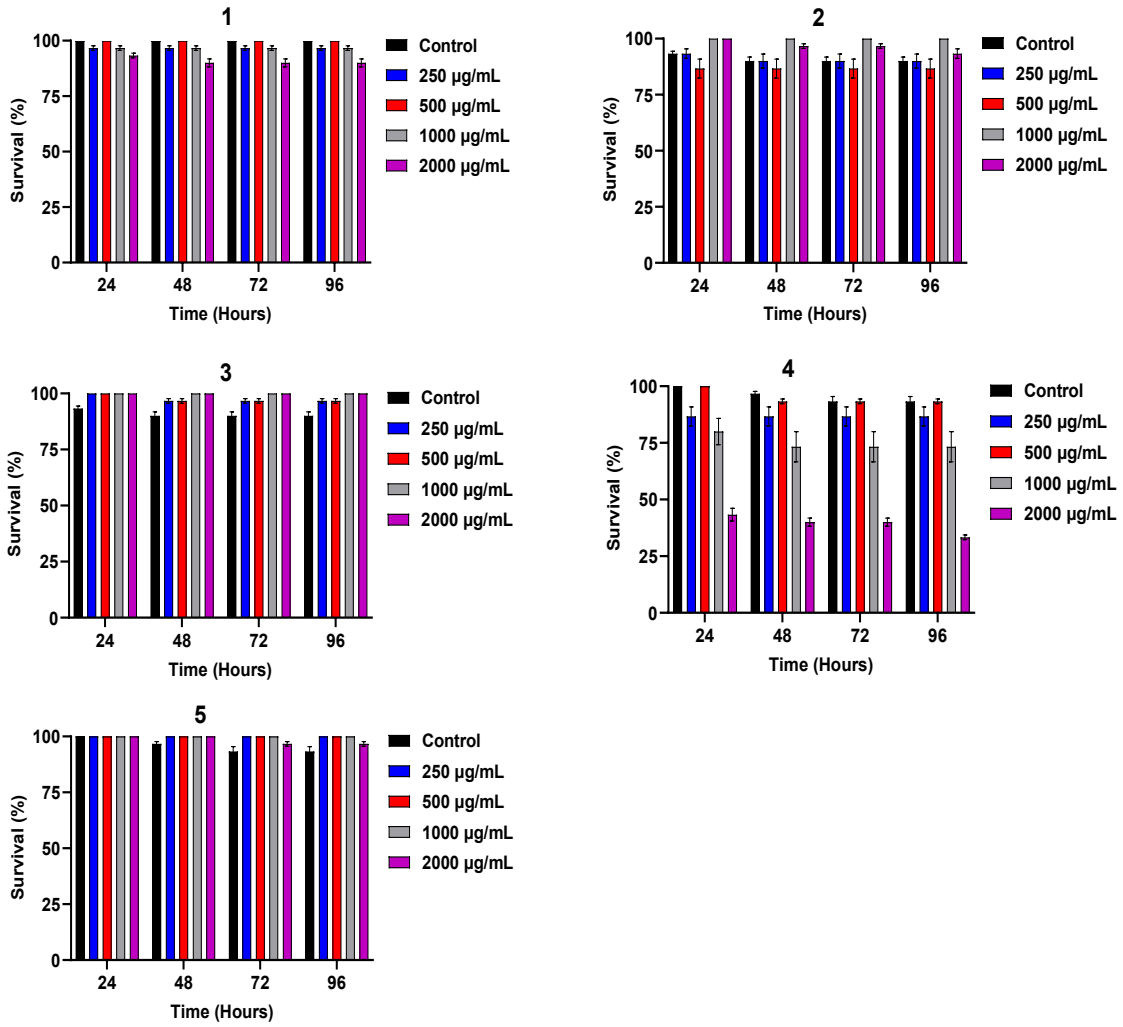


Figure S35. *in vivo toxicity* assays for 1 to 5 against *G. melonella*. GraphPad Prism, n= 3.