Electronic Supplementary Information

M^{2+}, Ln^{3+}-Catalyzed Synthesis of [1,2,4]Triazine Core via Intramolecular C-H/N-H Functionalization and C-N Bond Formation (M = Mn, Zn, Cd; Ln = Dy, Tb)

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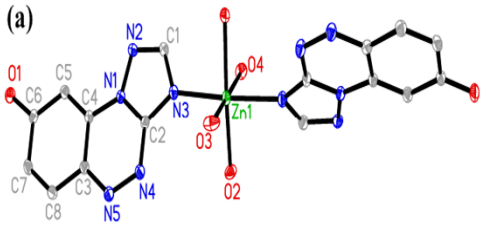
Experimental

Materials and Physical Measurements. All the commercial reagents and solvents were used without further purification unless otherwise stated. IR spectra were recorded as pressed KBr pellets on a Bruker Tensor 27 spectrophotometer. Elemental analyses were carried out using a Perkin-Elmer analyzer model 240. Luminescence spectra were recorded with an F-4500 fluorescence spectrophotometer. ^{1}H NMR spectra were recorded on a 400 MHz Digital NMR Spectrometer. Fluorescent Imaging experiments were conducted with Nikon 55i Fluorescent Microscope.

X-ray crystallography and data collection: The crystals were filtered from the solution and immediately coated with hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and placed in a Bruker Smart APEX(II) area detector using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 296(2) K. The structures were solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full–matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).[1] Hydrogen atoms were added theoretically and were riding on their parent atoms. Crystallographic data for **1-5**. **1**: $C_{32}H_{26}N_{20}O_7$, *Mr* = 802.73, monoclinic, space group *C2/c*, *a* = 26.008(3) Å, *b* = 6.8360(8) Å, *c* = 22.709(3) Å, *β* = 123.384(2)°, *V* = 3371.3(7) Å^3, *Z* = 4, *Dc* = 1.582 g· cm^{-3}, *F(000)* = 1656, *μ* = 0.119 cm^{-1}, R_1 = 0.0432, wR_2 = 0.1266. **2**: $C_{16}H_{16}MnN_{10}O_6$, *Mr* = 499.33, monoclinic, space group *C2/c*, *a* = 19.315(4) Å, *b* = 8.0880(16) Å, *c* = 11.970(2) Å, *β* = 94.203(9)°, *V* = 3371.3(7) Å^3, *Z* = 4, *Dc* = 1.778 g·cm^{-3}, *F(000)* = 1020, *μ* = 0.773

cm^{-1},R_1 = 0.0280, wR_2 = 0.0670. **3**: $C_{16}H_{16}ZnN_{10}O_6$, *Mr* = 509.78, monoclinic, space group *C2/c*, *a* = 19.020(3) Å, *b* = 8.0801(12) Å, *c* = 11.9530(17) Å, β = 94.235(8)°, *V* = 1832.0(5) $Å^3$, *Z* = 4, *Dc* = 1.848 $g{\cdot}cm^{-3}$, *F(000)* = 1040, μ = 1.407 cm^{-1}, R_1 = 0.0251, wR_2 = 0.0639. **4**: $C_{16}H_{16}CdN_{10}O_6$, *Mr* = 556.80, monoclinic, space group *C2/c*, *a* = 19.4542(7) Å, *b* = 8.1626(3) Å, *c* = 12.0696(5) Å, β = 94.203(2)°, *V* =1911.46(13) $Å^3$, *Z* = 4, *Dc* = 1.935$g{\cdot}cm^{-3}$, *F(000)* = 1112, μ = 1.206 cm^{-1},R_1 = 0.0202, wR_2 = 0.0671. **5**: $C_{18}H_{16}N_{10}O_3$, *Mr* = 420.41, monoclinic, space group *P21/n*, *a* = 6.8792(11) Å, *b* = 20.841(3) Å, *c* = 13.359(3) Å, β = 103.471(12)°, *V* = 1862.5(5) $Å^3$, *Z* = 4, *Dc* = 1.499 $g{\cdot}cm^{-3}$, *F(000)* = 872.0, μ = 0.110 cm^{-1}, R_1 = 0.0549, wR_2 = 0.1391. Crystallographic Data Centre under reference numbers 940757 for **1**, CCDC 940758 for **2**, 940759 for **3**, 940760 for **4**, 979363 for **5**. The data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: t44 1223336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).



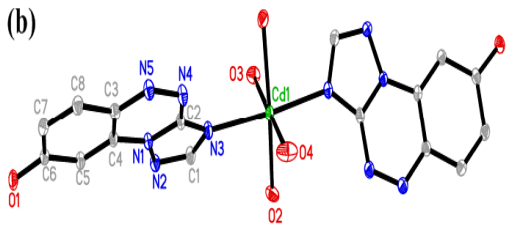


Figure S1. (a), (b) The atomic labeling diagram of **3**, **4**, respectively. All H atoms have been omitted for clarity.

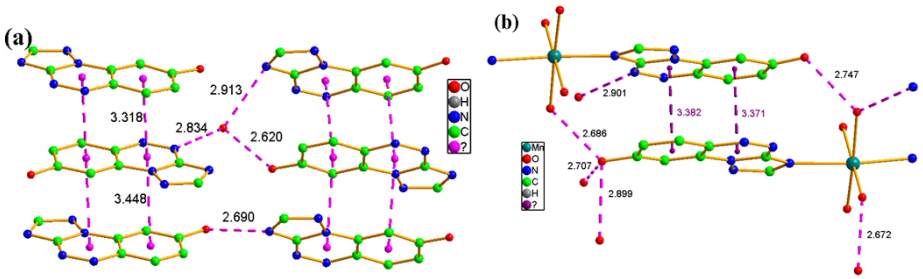


Figure S2. The supramolecular structure packed by π-π stacking, O–H···O and O–H···N hydrogen-bonding interaction in **1**(a) and **2**(b).

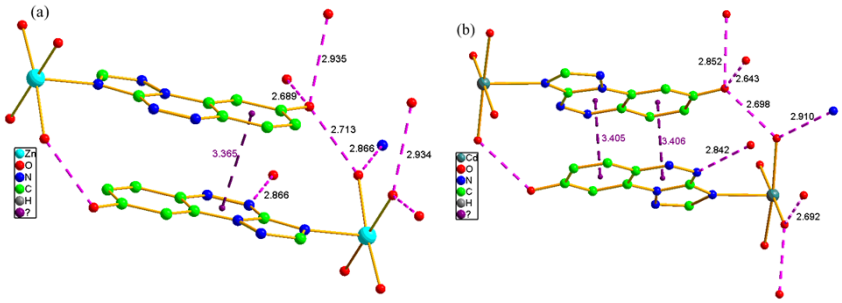


Figure S3. (a), (b) The supramolecular structure packed by π-π stacking, O–H···O and O–H···N hydrogen-bonding interaction in **3** and **4**, respectively.

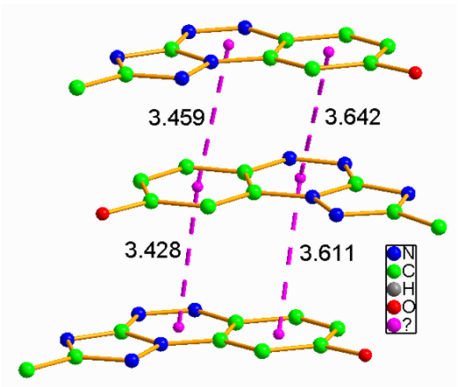
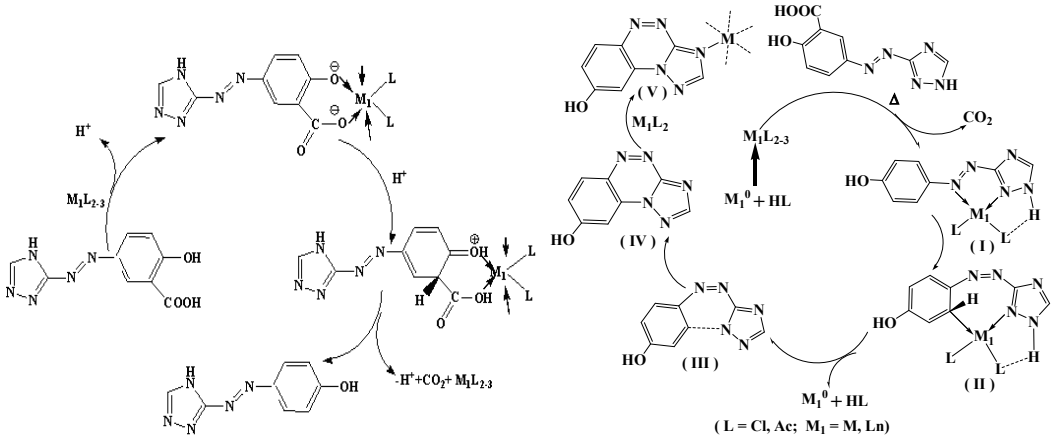


Figure S4. The π-π stacking interaction in **5**.



(1) decarboxylation (2)Wacker-type cyclization

Scheme S1 Proposed catalytic cyclization containing decarboxylation(1) and Wacker-type cyclization (2) using 5-azo-(1,2,4-triazolyl) salicylic acid as model reaction substrate.

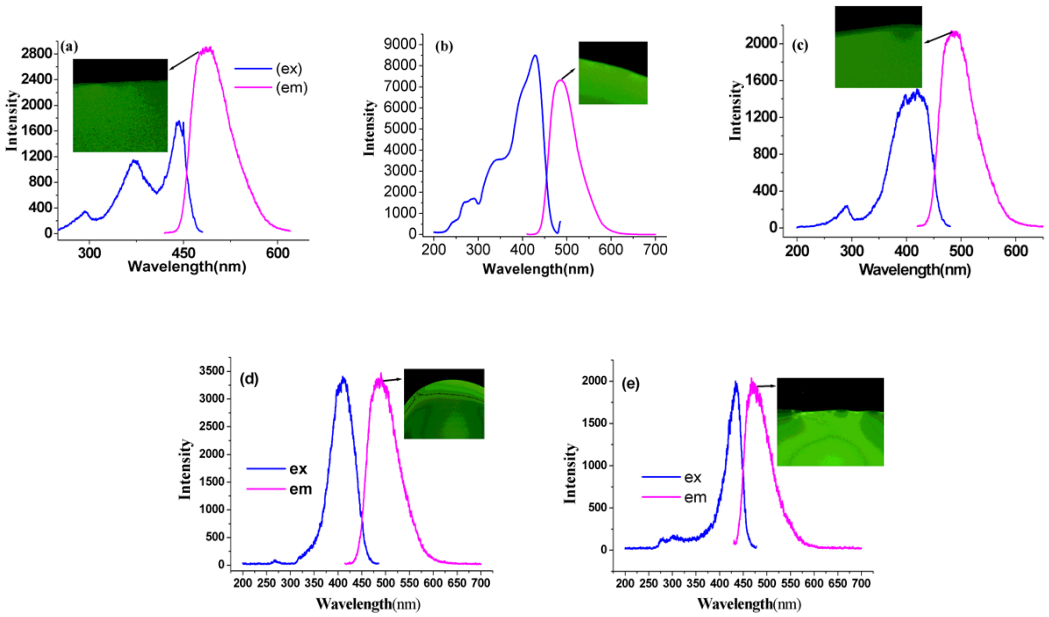
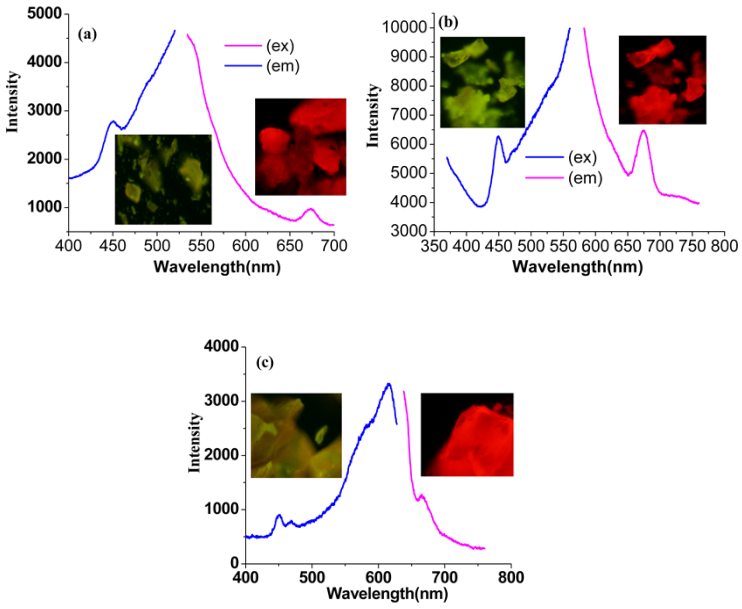


Figure S5. (a)-(e) The photoluminescent spectra of the aqueous solution of **2-6**, respectively. Insert is fluorescent images under blue light excitation.



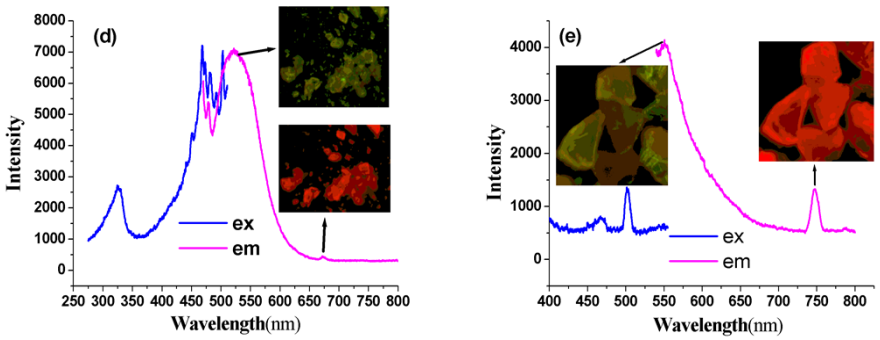


Figure S6. (a)-(e) The photoluminescent spectra of crystal phase of **2-6**, respectively. Insert is green-yellow imaging and red imaging taken by the fluorescence microscopy under blue and green light excitation.

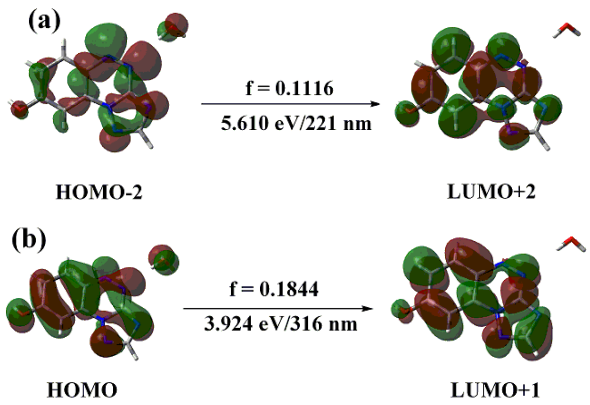
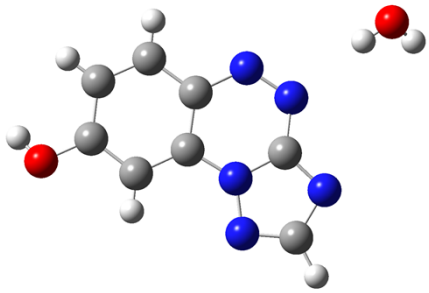


Figure S7 TD-DFT calculated state energy diagrams: (a), (b) for enol isomer in **1**.

9. Calculations

9.1 Cartesian coordinates and total energies of enol isomer of **1**

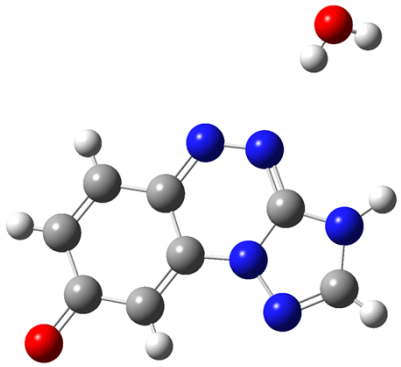


B3LYP 6-31g (d) E = -733.067300783 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.800900	5.095100	12.789100
2	1	0	-4.328700	4.766700	13.396700
3	7	0	-5.130300	4.687900	8.041000
4	7	0	-5.653600	5.889900	7.688900
5	7	0	-5.225700	4.623200	5.848500
6	7	0	-4.053888	2.813961	6.938524
7	7	0	-3.791028	2.312954	8.123041
8	6	0	-5.685700	5.786000	6.368200
9	6	0	-4.873300	3.936200	6.935000
10	6	0	-4.253300	2.941500	9.298000
11	6	0	-4.832000	4.231500	9.301300

12	6	0	-5.049100	4.956800	10.464600
13	1	0	-5.453500	5.794200	10.442400
14	6	0	-4.640800	4.384600	11.660900
15	6	0	-4.061800	3.090600	11.686500
16	1	0	-3.807900	2.717300	12.499800
17	6	0	-3.871500	2.384400	10.531700
18	1	0	-3.490600	1.536700	10.561900
19	8	0	-3.123900	0.846300	4.740500
20	1	0	-3.319000	1.373400	5.368200
21	1	0	-2.928800	1.373400	4.112900
22	1	0	-6.068306	6.569996	5.748634

9.2 Cartesian coordinates and total energies of keto isomer of **1**



B3LYP 6-31g (d), E =-733.023543943 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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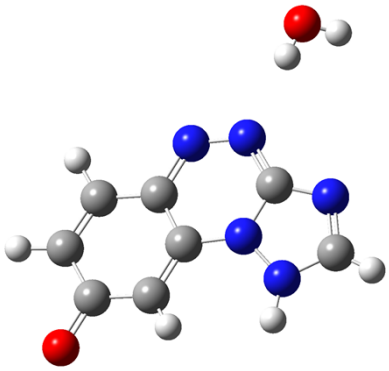
2	7	0	-5.130300	4.687900	8.041000
3	7	0	-5.653600	5.889900	7.688900
4	7	0	-5.225700	4.623200	5.848500
5	7	0	-4.318000	2.691300	6.979200
6	7	0	-4.008500	2.215500	8.148600
7	6	0	-5.685700	5.786000	6.368200
8	1	0	-6.007600	6.472300	5.828900
9	6	0	-4.873300	3.936200	6.935000
10	6	0	-4.253300	2.941500	9.298000
11	6	0	-4.832000	4.231500	9.301300
12	6	0	-5.049100	4.956800	10.464600
13	1	0	-5.453500	5.794200	10.442400

14	6	0	-4.640800	4.384600	11.660900
15	6	0	-4.061800	3.090600	11.686500
16	1	0	-3.807900	2.717300	12.499800
17	6	0	-3.871500	2.384400	10.531700
18	1	0	-3.490600	1.536700	10.561900
19	8	0	-3.123900	0.846300	4.740500
20	1	0	-3.319000	1.373400	5.368200
21	1	0	-2.928800	1.373400	4.112900
22	1	0	-5.165425	4.348449	4.888876

9.3 Cartesian coordinates and total energies of another keto isomer of **1**



B3LYP 6-31g (d), E = -733.035929942 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-4.845970	5.086713	12.787053
2	7	0	-5.132583	4.699333	8.035538
3	7	0	-5.400714	5.959187	7.690100
4	7	0	-4.986188	4.766722	5.908045
5	7	0	-4.318000	2.691300	6.979200
6	7	0	-4.008500	2.215500	8.148600
7	6	0	-5.374499	5.976888	6.365308
8	1	0	-5.562707	6.704566	5.817097
9	6	0	-4.877769	3.964196	6.906790
10	6	0	-4.253300	2.941500	9.298000
11	6	0	-4.832000	4.231500	9.301300
12	6	0	-5.049100	4.956800	10.464600

13	1	0	-5.453500	5.794200	10.442400
14	6	0	-4.640800	4.384600	11.660900
15	6	0	-4.110803	3.069823	11.704941
16	6	0	-3.871500	2.384400	10.531700
17	8	0	-3.123900	0.846300	4.740500
18	1	0	-3.319000	1.373400	5.368200
19	1	0	-2.928800	1.373400	4.112900
20	1	0	-5.651640	6.722435	8.285489
21	1	0	-3.944762	2.591950	12.647792
22	1	0	-3.516859	1.376239	10.584057

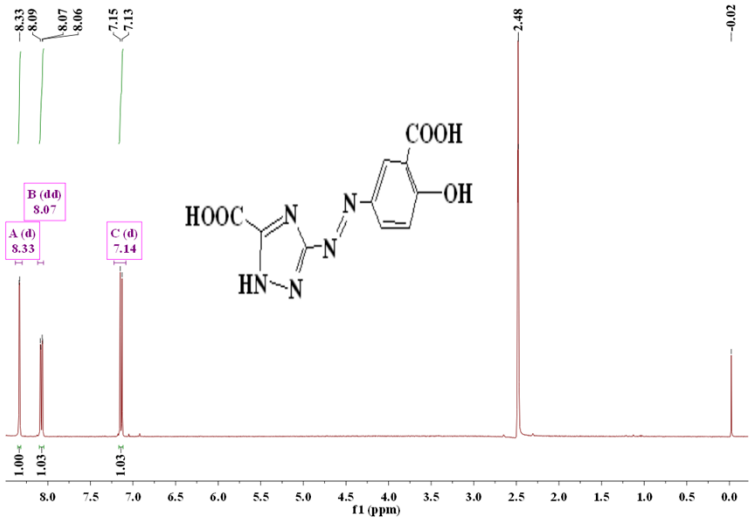


Figure S8. ^{1}H NMR Spectra recorded in DMSO (δ, ppm) of 5-azo-(3-carboxyl-1,2,4-triazolyl) salicylic acid.

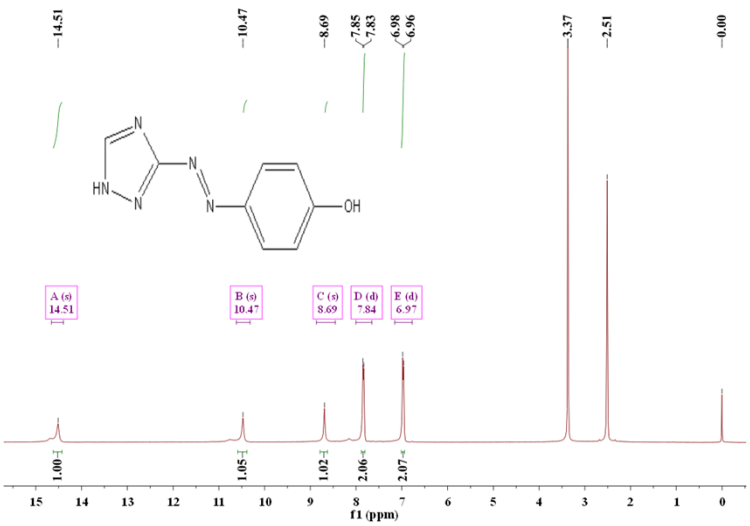


Figure S9. [1]H NMR Spectra recorded in DMSO (δ, ppm) of 4-azo-(1,2,4-triazolyl) phenol.

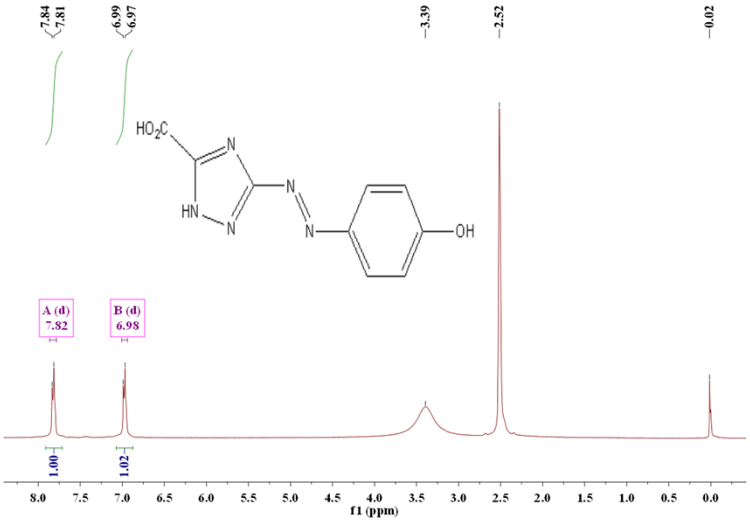


Figure S10. [1]H NMR Spectra recorded in DMSO (δ, ppm) of 4-azo-(3-carboxyl-1,2,4-triazolyl) phenol.

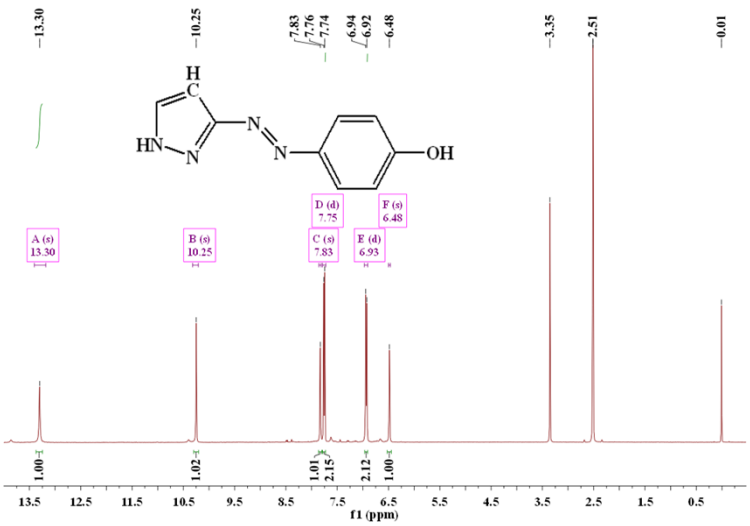


Figure S11. [1]H NMR Spectra recorded in DMSO (δ, ppm) of 4-azo-(1,2-pyrazolyl) phenol.

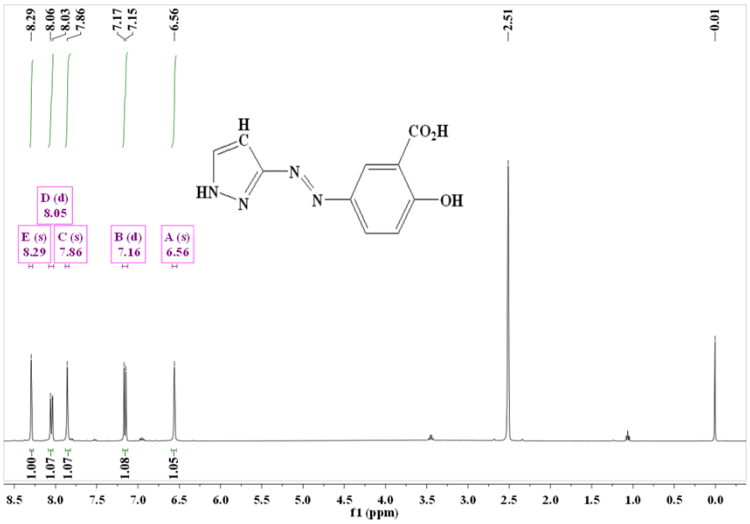


Figure S12. [1]H NMR Spectra recorded in DMSO (δ, ppm) of 5-azo-(1,2-pyrazolyl) salicylic acid.

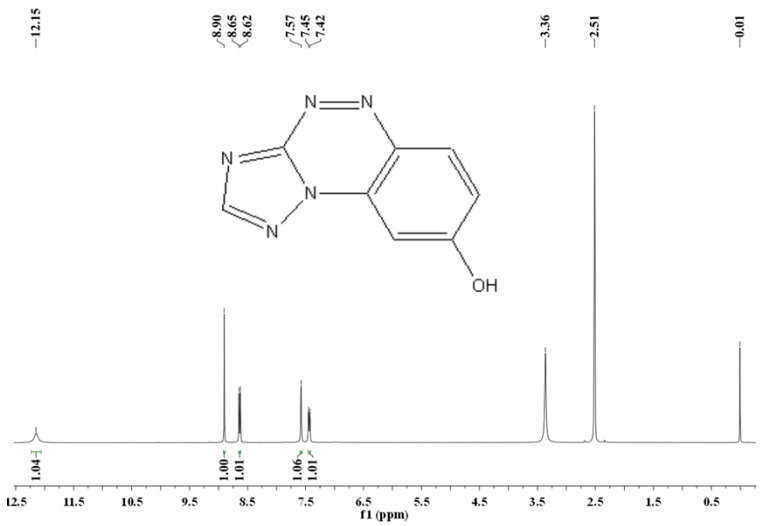


Figure S13. [1]H NMR Spectra recorded in DMSO (δ, ppm) of **1**.

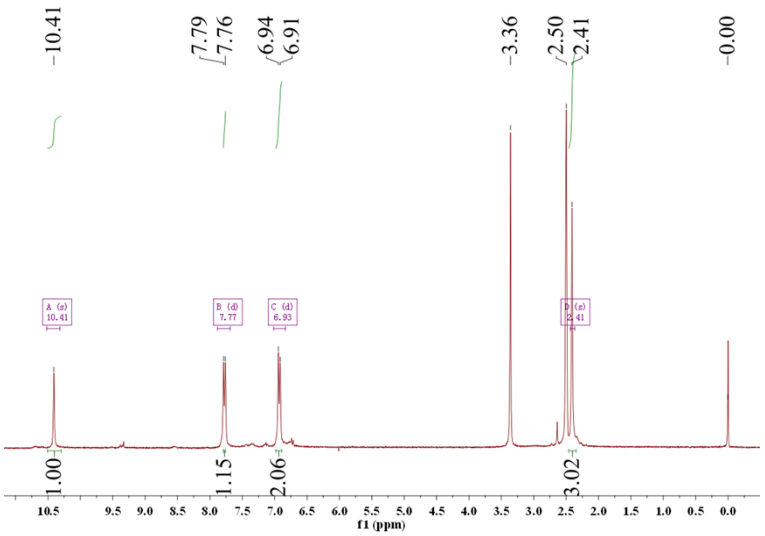


Figure S14. [1]H NMR Spectra recorded in DMSO (δ, ppm) of **5**.

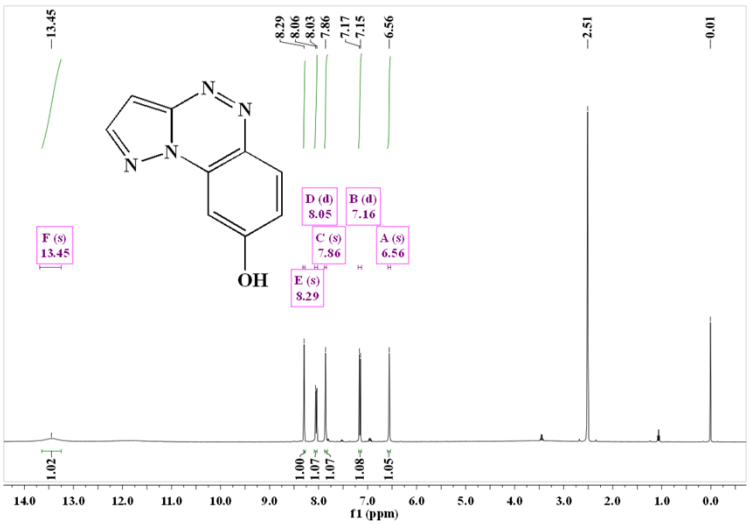


Figure S15. ^{1}H NMR Spectra recorded in DMSO (δ, ppm) of **6**.

References

[1] (a) Sheldrick, G. M. SHELXS-97, Program for solution of crystalstructures; University of Göttingen: Göttingen, Germany, 1997; (b) Sheldrick, G. M. SHELXL-97, Program for refinement of crystalstructures; University of Göttingen: Göttingen, Germany 1997.