Supporting Information
for:

Pyridyl β-Ketoenols, Pyrazoles and Their Zinc Complexes: Synthesis, Photophysical Properties, and DNA Binding

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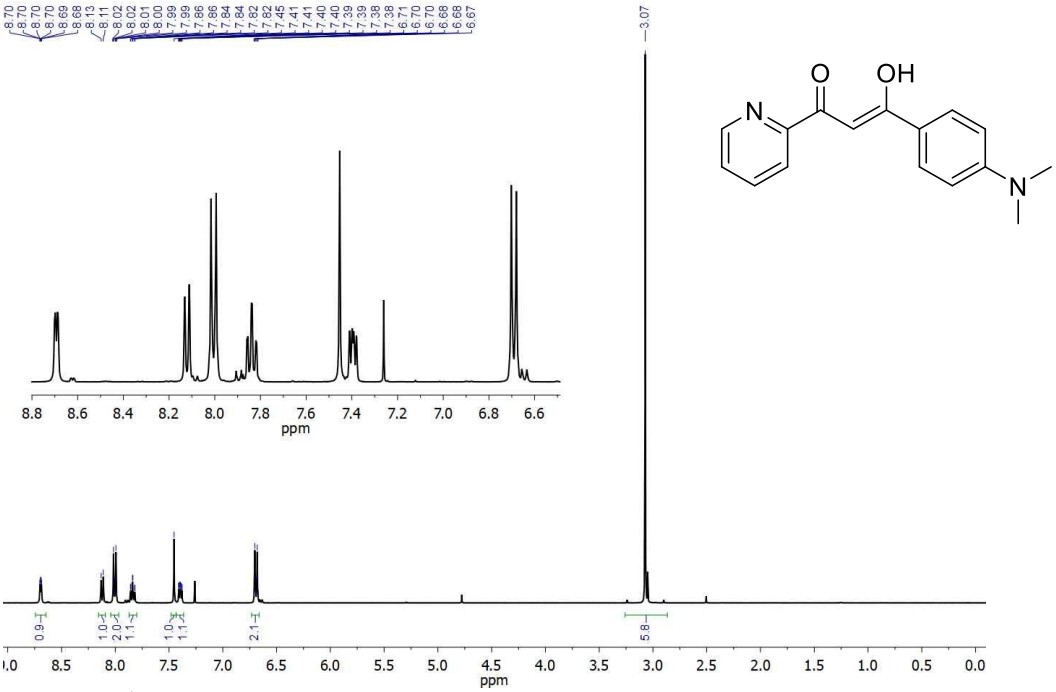

Figure S1. ^{1}H NMR spectrum (400 MHz, Chloroform-*d*, 298 K) of **L1**. δ 8.71 – 8.68 (m, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.84 (td, *J* = 7.7, 1.6 Hz, 1H), 7.45 (s, 1H), 7.39 (ddd, *J* = 7.6, 4.6, 1.2 Hz, 1H), 6.71 – 6.67 (m, 2H), 3.07 (s, 6H).

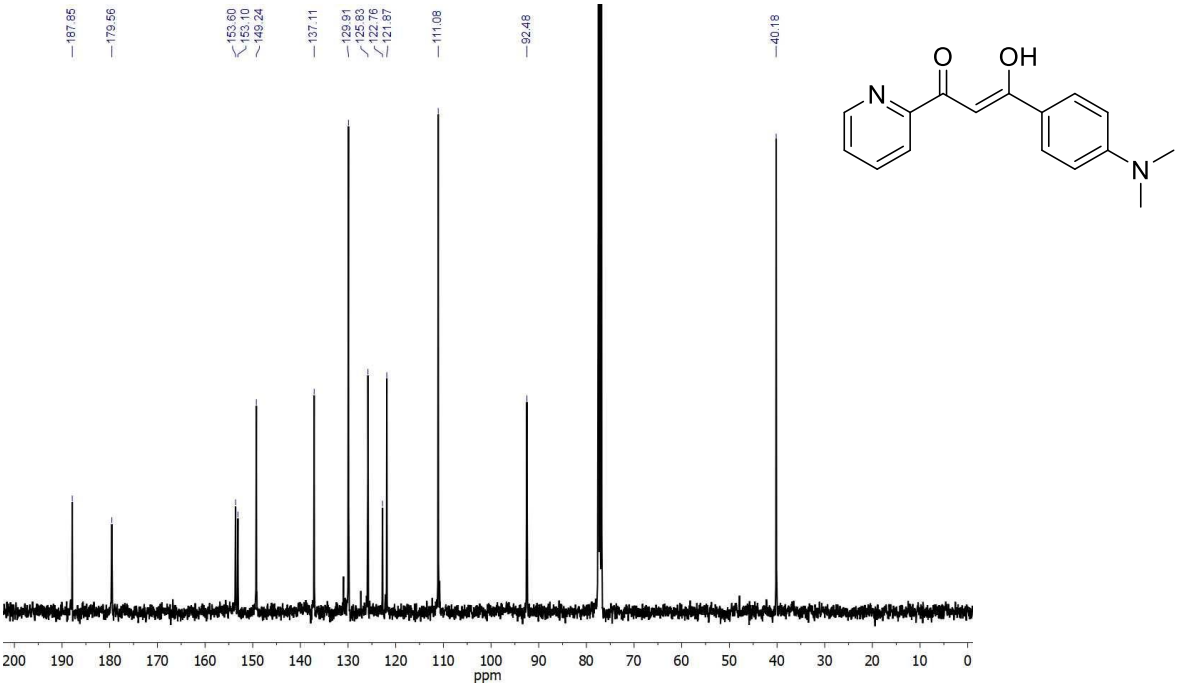

Figure S2. ^{13}C{^{1}H} NMR spectrum (101 MHz, Chloroform-*d*, 298 K) of **L1**. δ 187.85, 179.56, 153.60, 153.10, 149.24, 137.11, 129.91, 125.83, 122.76, 121.87, 111.08, 92.48, 40.18.

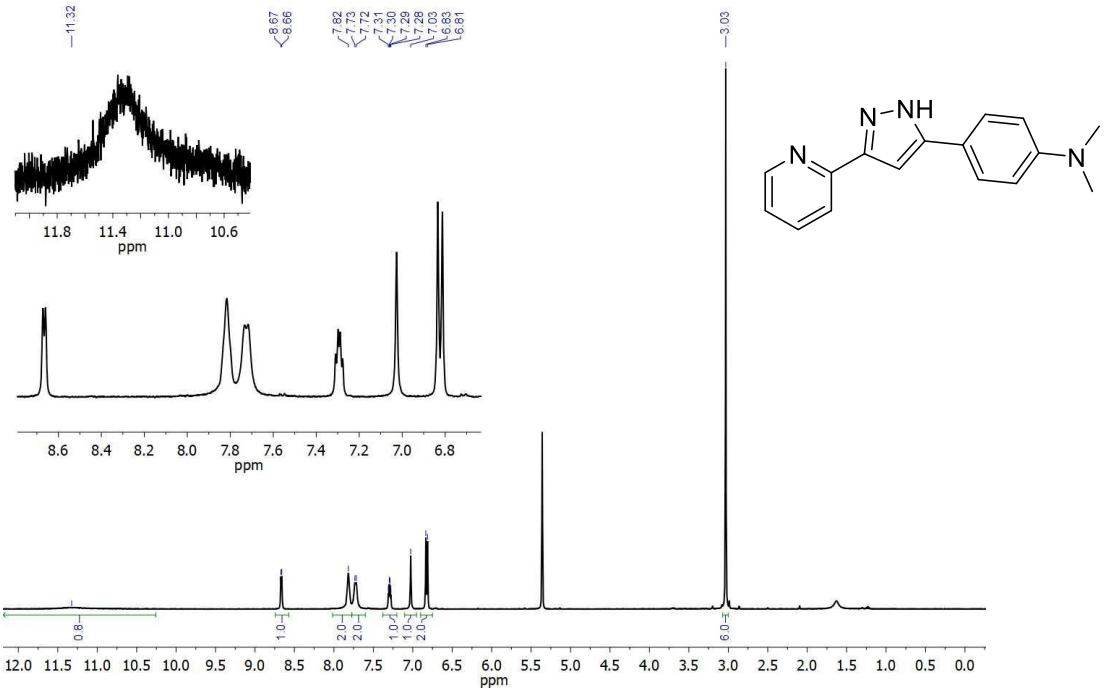

Figure S3. [1]H NMR spectrum (400 MHz, Methylene Chloride-d_2, 298 K) of **L2**. δ 11.32 (s, 1H), 8.67 (d, *J* = 4.7 Hz, 1H), 7.82 (m, 2H), 7.72 (d, *J* = 6.9 Hz, 2H), 7.38 – 7.20 (m, 1H), 7.03 (s, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.03 (s, 6H).

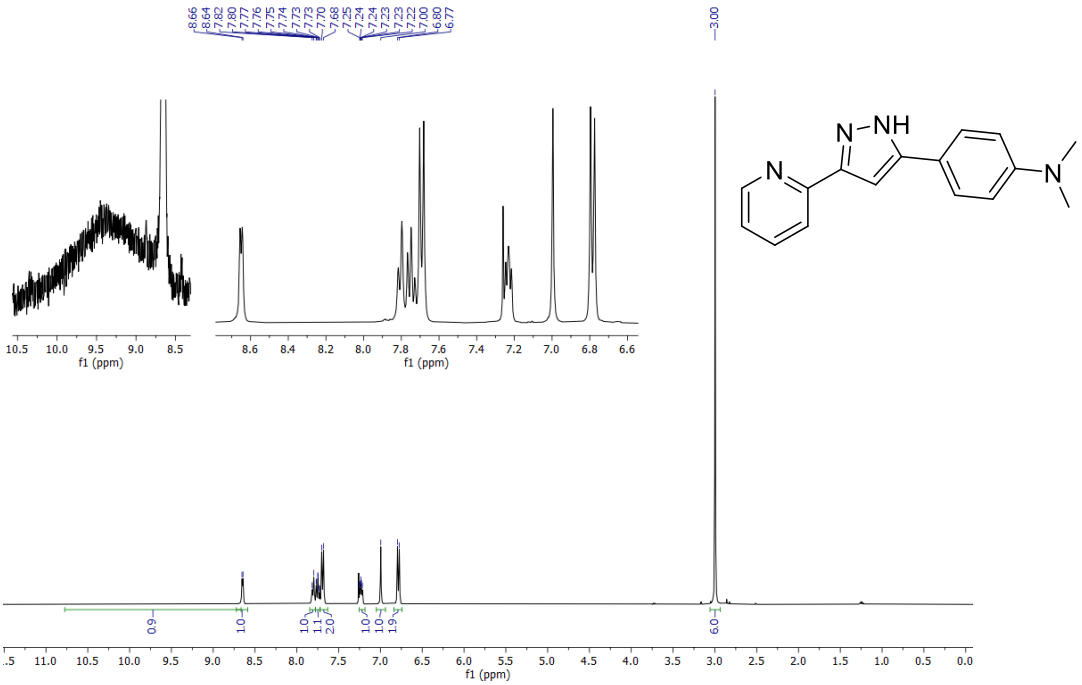

Figure S3b. [1]H NMR spectrum (400 MHz, Chloroform-*d*, 298 K) of **L2**. δ 9.37 (bs, 1H), 8.65 (d, *J* = 4.9 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.75 (td, *J* = 7.6, 1.7 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.00 (s, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.00 (s, 6H).

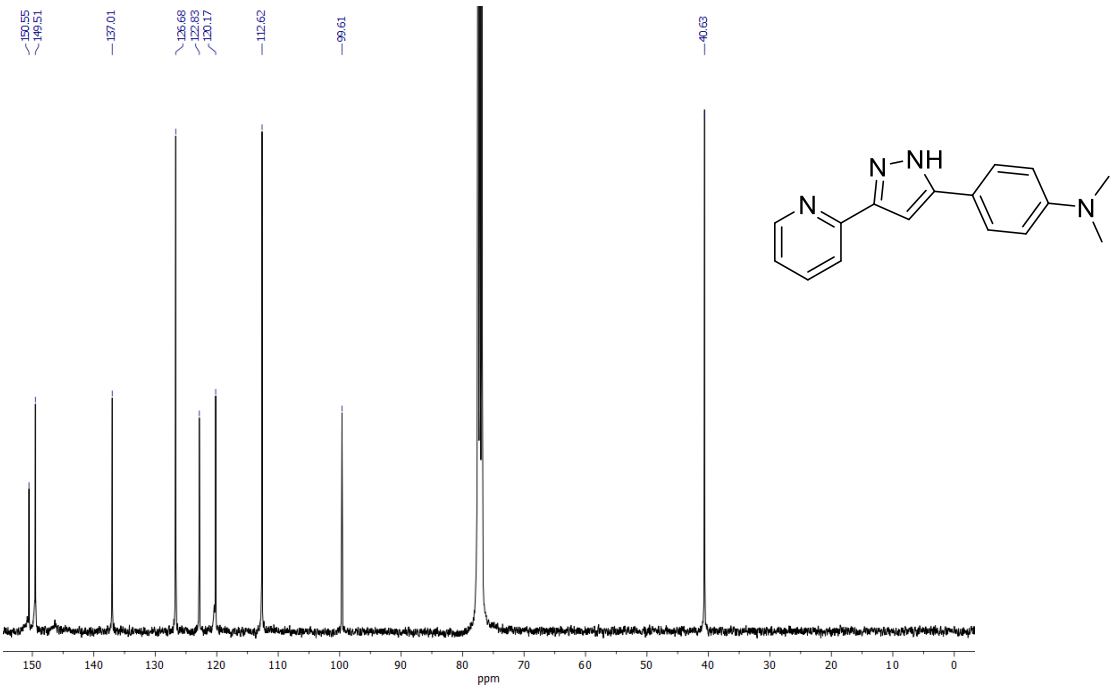

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Chloroform-*d*, 298 K) of **L2**. δ 150.55, 149.51, 137.01, 126.68, 122.83, 120.17, 112.62, 99.61, 40.63.

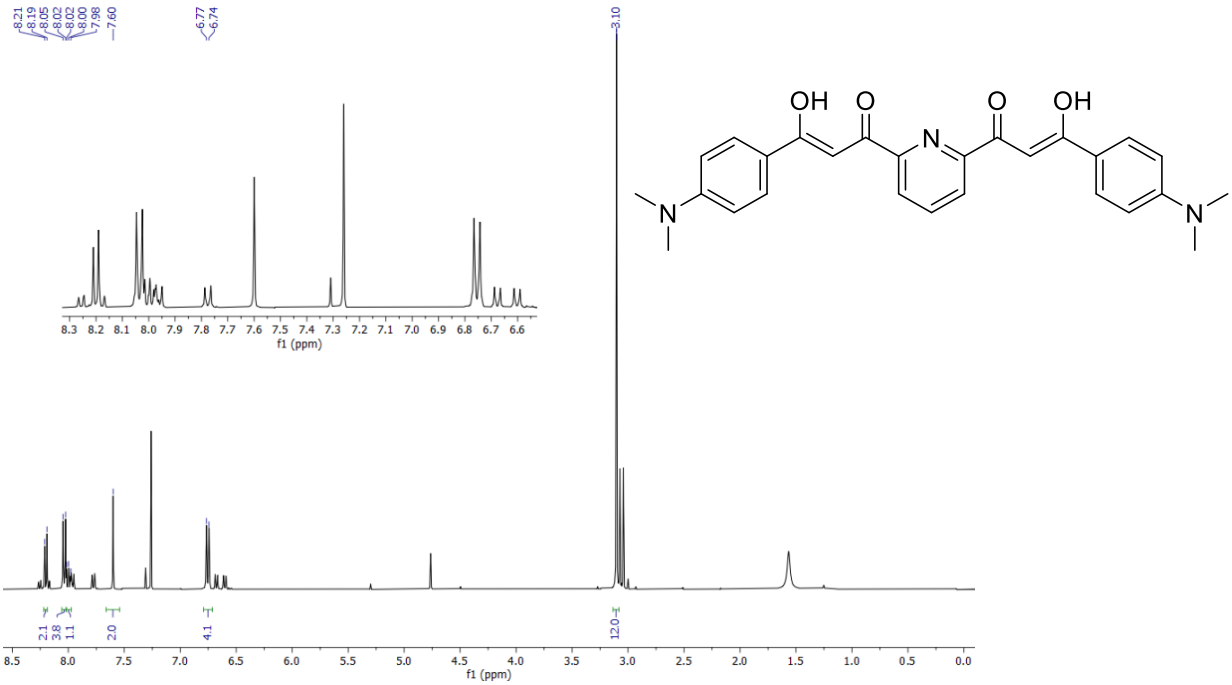

Figure S5. ^{1}H NMR spectrum (400 MHz, Chloroform-*d*, 298 K) of **L3**. δ 8.20 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 4H), 8.00 (t, *J* = 7.8 Hz, 1H) 7.60 (s, 2H), 6.75 (d, *J* = 9.2 Hz, 4H), 3.10 (s, 12H). Major tautomer (enol-enol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.98 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 9.1 Hz, 2H), 7.31 (s, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 9.1 Hz, 2H), 4.76 (s, 2H), 3.07 (s, 6H), 3.04 (s, 6H). Minor tautomer (keto-enol)

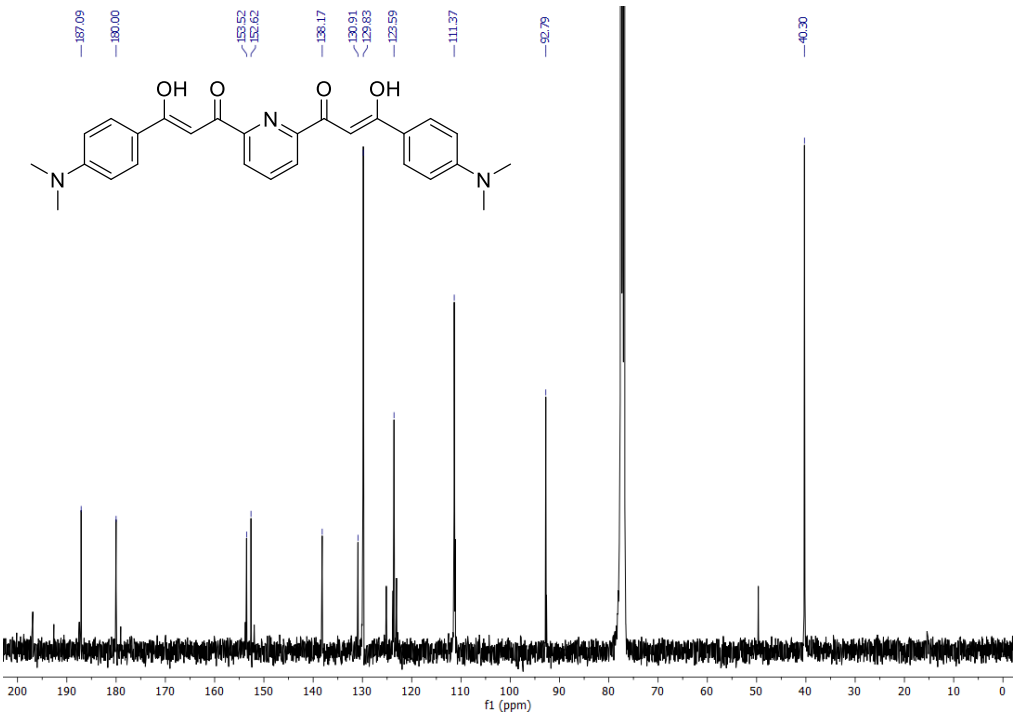

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Chloroform-*d*, 298 K) of **L3**. δ 187.09, 180.00, 153.52, 152.62, 138.17, 130.91, 129.83, 123.59, 111.37, 92.79, 40.30.

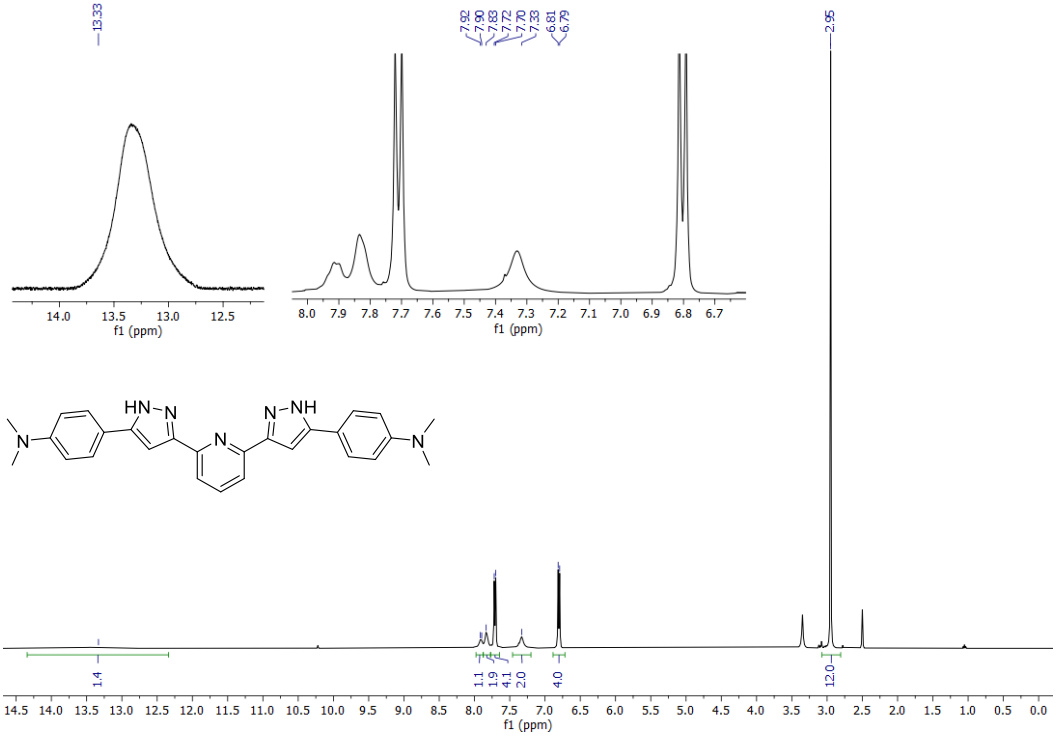

Figure S7. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **L4**. δ 13.33 (bs, 2H), 7.91 (t, *J* = 6.8 Hz, 1H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 4H), 7.33 (s, 2H), 6.80 (d, *J* = 8.5 Hz, 4H), 2.95 (s, 12H).

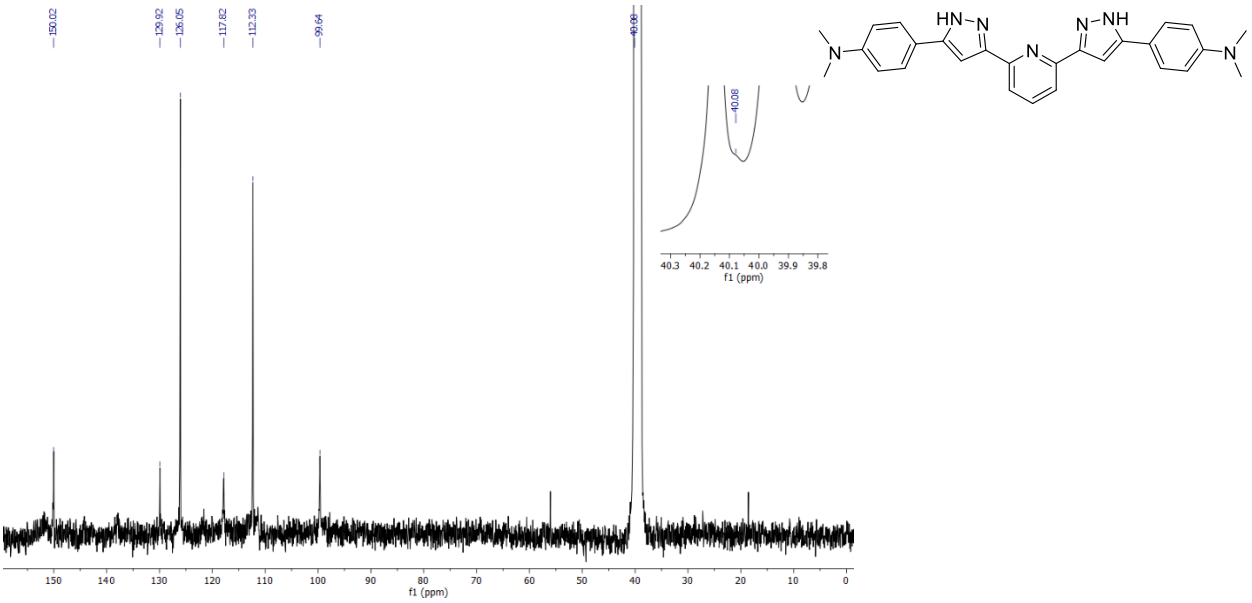

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **L4**. δ 150.02, 129.92, 126.05, 117.82, 112.33, 99.64, 40.08. *Peaks at 18.6 and 56.0 ppm trace ethanol.

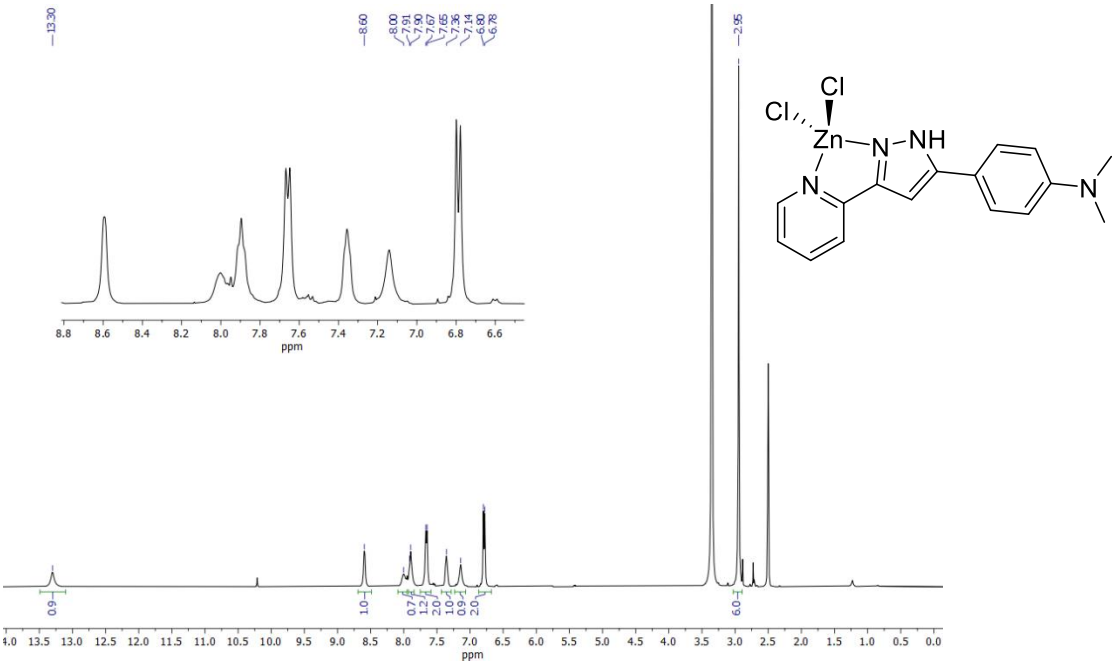

Figure S9. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **L2-Zn**. δ 13.30 (s, 1H), 8.60 (bs, 1H), 8.00 (m, 1H), 7.90 (t, J = 6.3 Hz, 1H), 7.66 (d, J = 8.8 Hz, 2H), 7.36 (dd, J = 6.3 Hz, 5.2 Hz, 1H), 7.14 (s, 1H), 6.79 (d, J = 8.8 Hz, 2H), 2.95 (s, 6H).

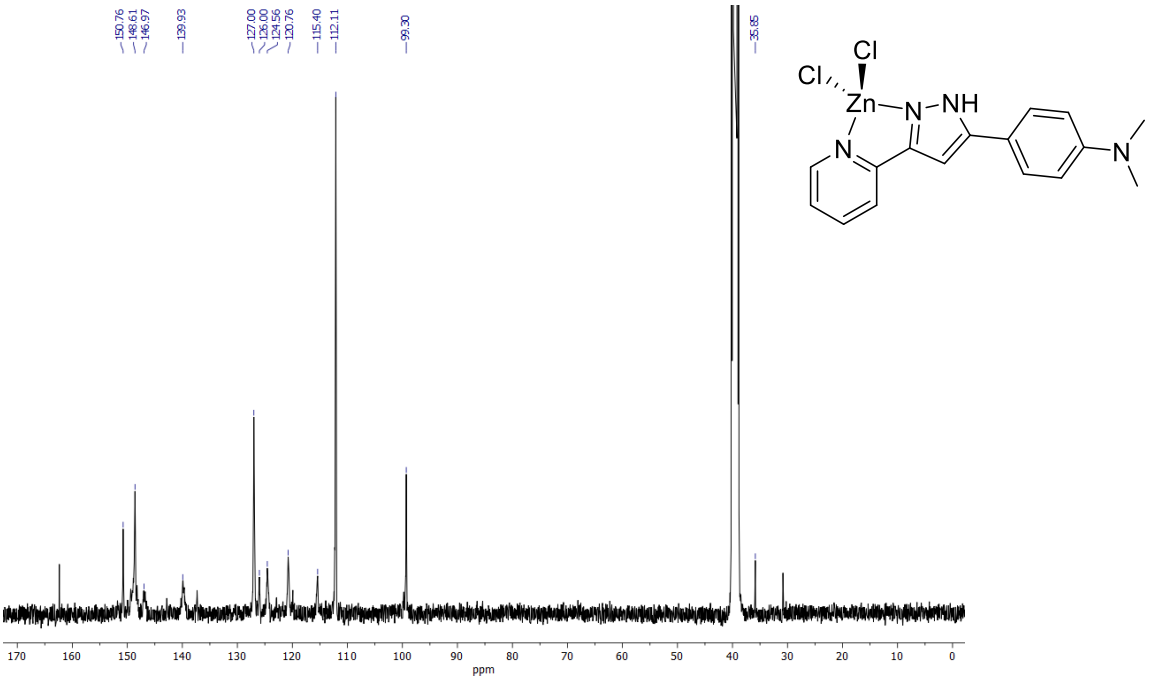

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **L2-Zn**. δ 150.76, 148.61, 146.97, 139.93, 127.00, 126.00, 124.56, 120.76, 115.40, 112.11, 99.30, 35.85. Trace DMF observed at 30.82 and 162.36 ppm.

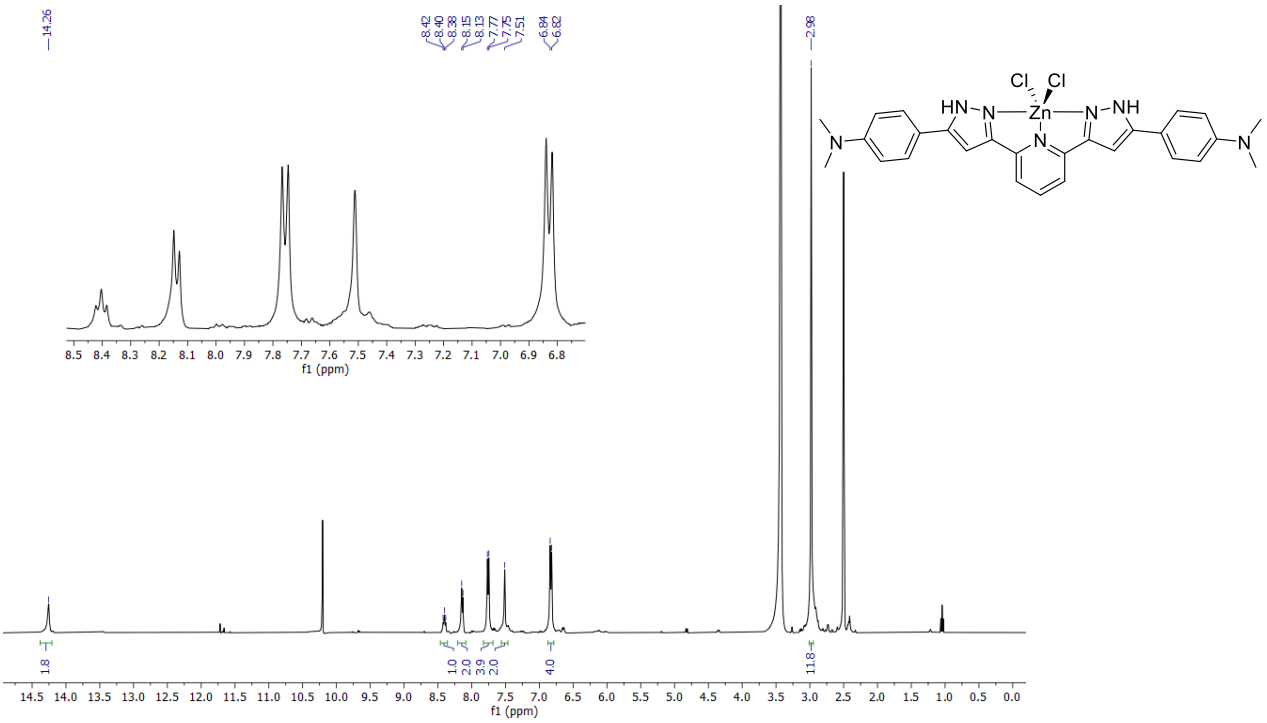

Figure S11. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **L4-Zn**. δ 14.26 (bs, 1H), 8.40 (t, J = 7.8 Hz, 1H), 8.14 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 8.4 Hz, 4H), 7.51 (s, 2H), 6.83 (d, J = 8.6 Hz, 4H), 2.98 (s, 12H).

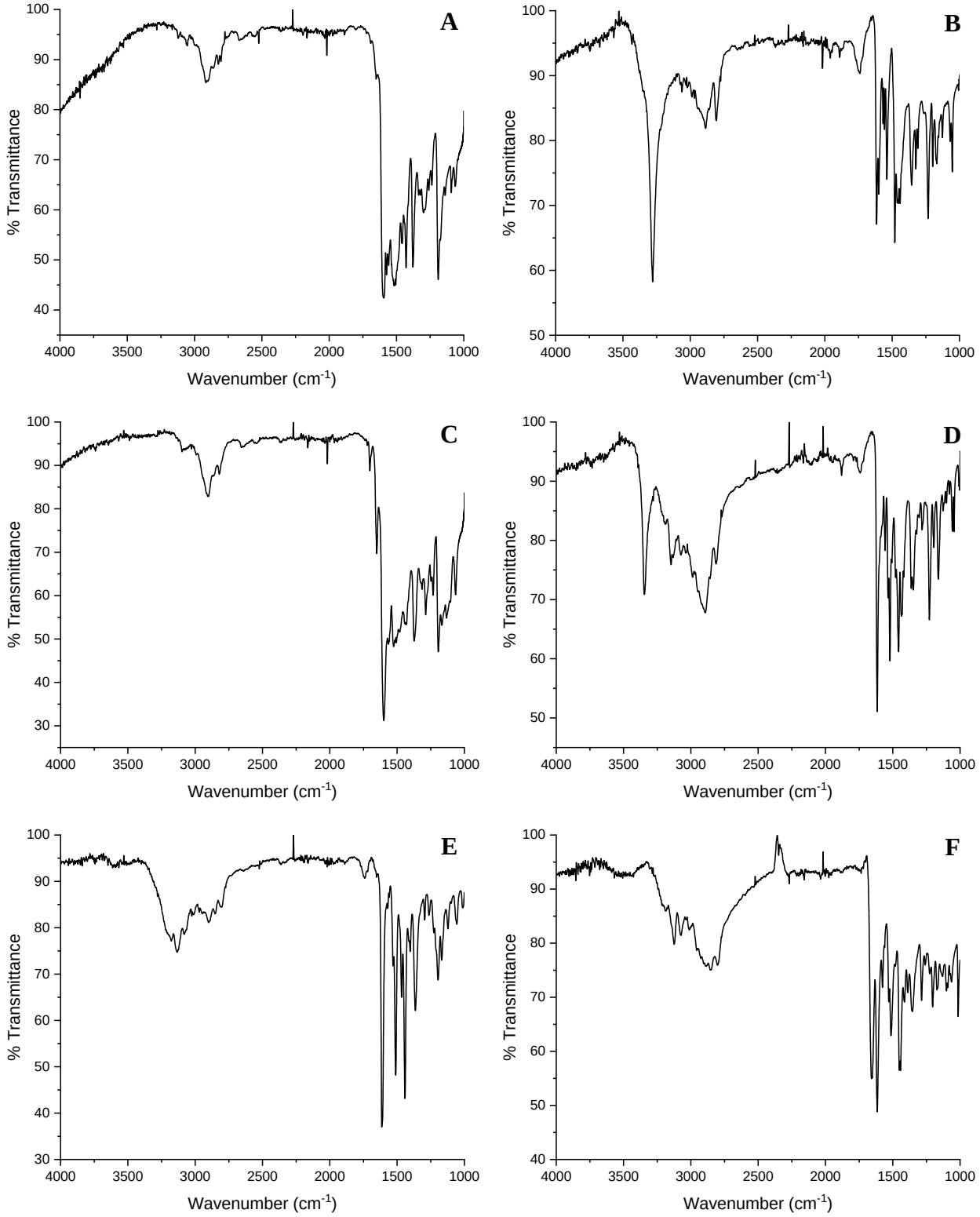

Figure S12. Infrared spectra of **L1** (A), **L2** (B), **L3** (C), **L4** (D), **L2-Zn** (E), and **L4-Zn** (F) taken by ATR method.

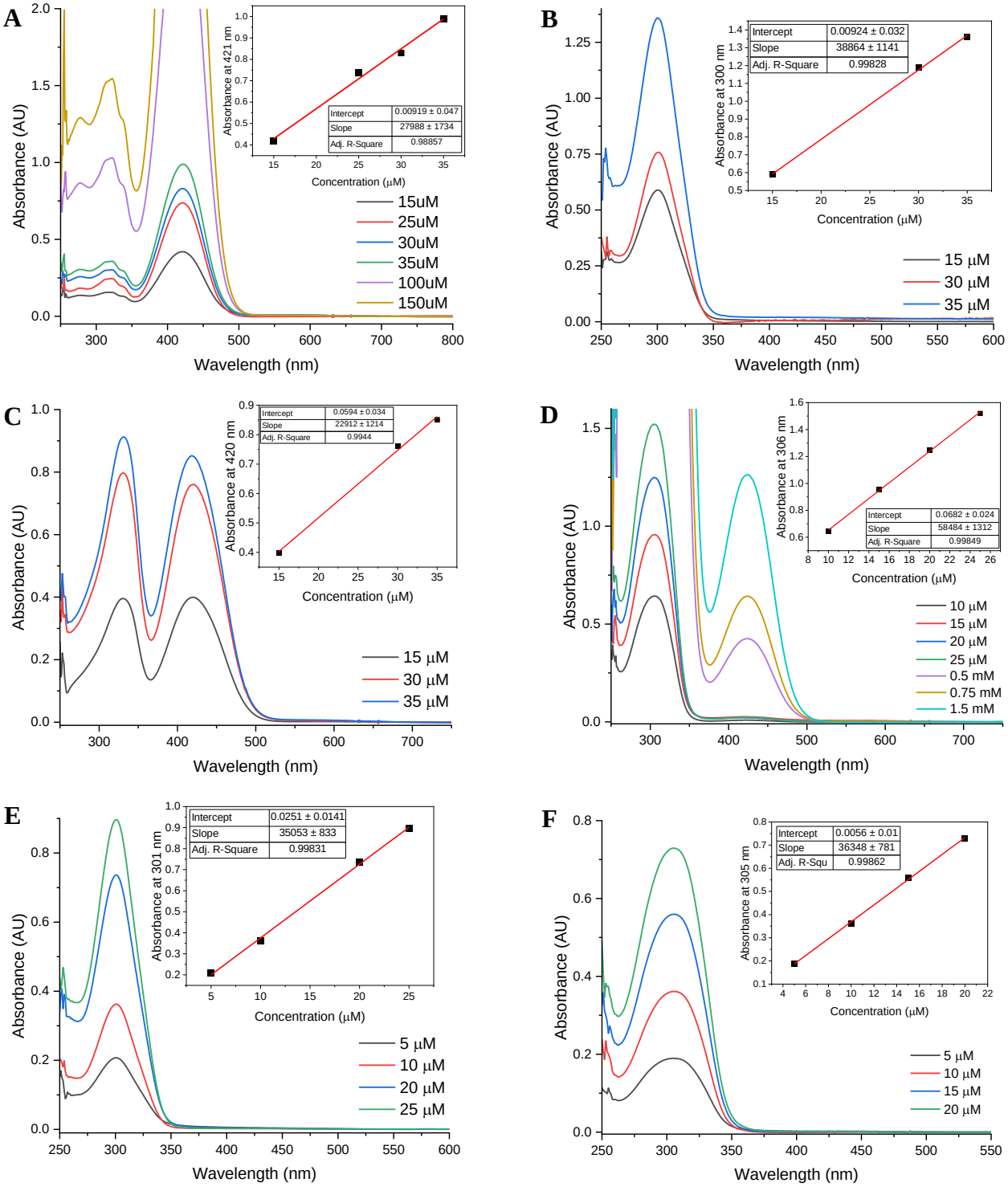

Figure S13. UV-visible absorbance overlay and Beer's Law plots for **L1** (A), **L2** (B), **L3** (C), **L4** (D), **L2-Zn** (E), and **L4-Zn** (F).

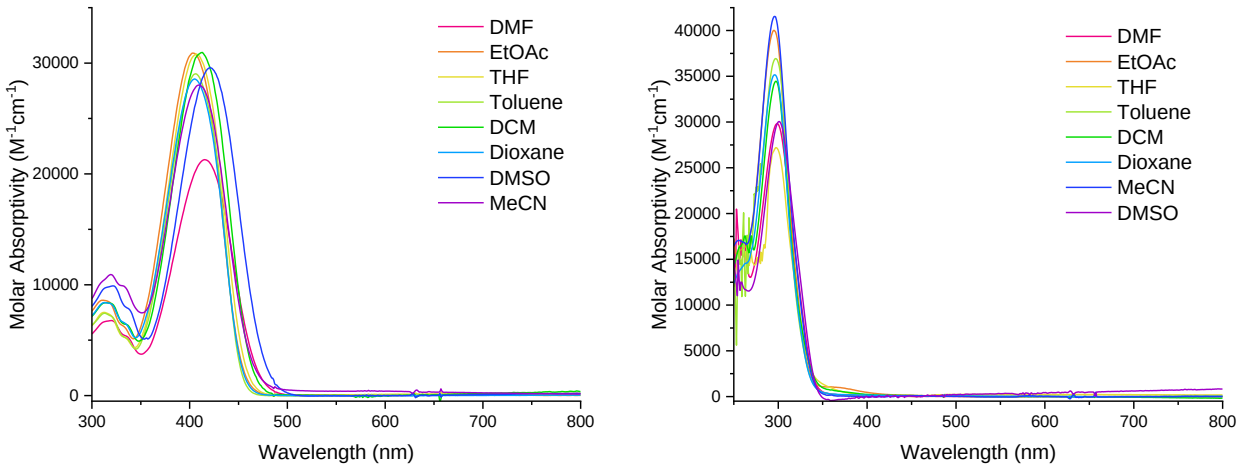

Figure S14. UV-visible absorbance spectra overlay of **L1** (left) and **L2** (right) in various solvents taken at 0.025 mM at 298K.

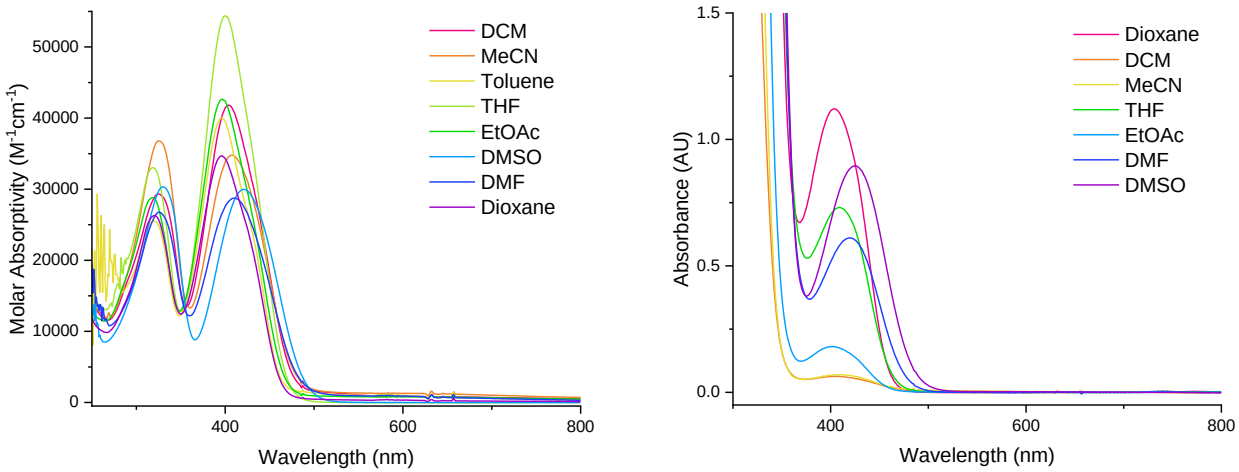

Figure S15. UV-visible absorbance spectra overlay of **L3** (left) in various solvents taken at 0.025 mM at 298 K. UV-visible absorbance spectra overlay of **L4** (right) in various solvents taken at 298 K. Due to limited solubility in other solvents, molar absorptivities were not calculated outside of DMSO, but presented to display the low energy transition at ~400 nm is always observed.

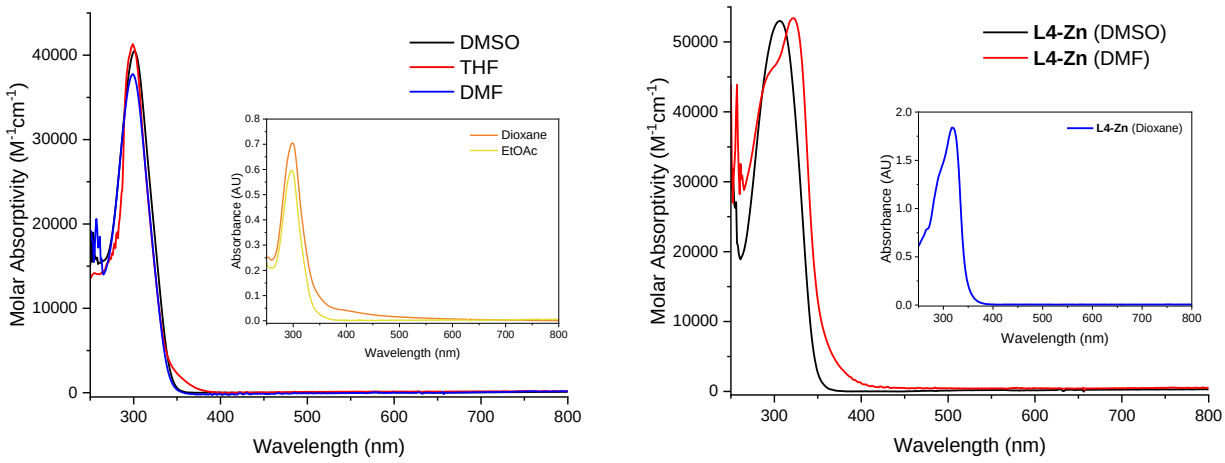

Figure S16. UV-visible absorbance spectra overlay of **L2-Zn** (left) and **L4-Zn** (right) in various solvents taken at 0.025 mM at 298K. Molar absorptivities were not calculated for dioxane or ethyl acetate due to limited solubility, but presented to display the absorbance at ~300 nm is always observed for each complex.

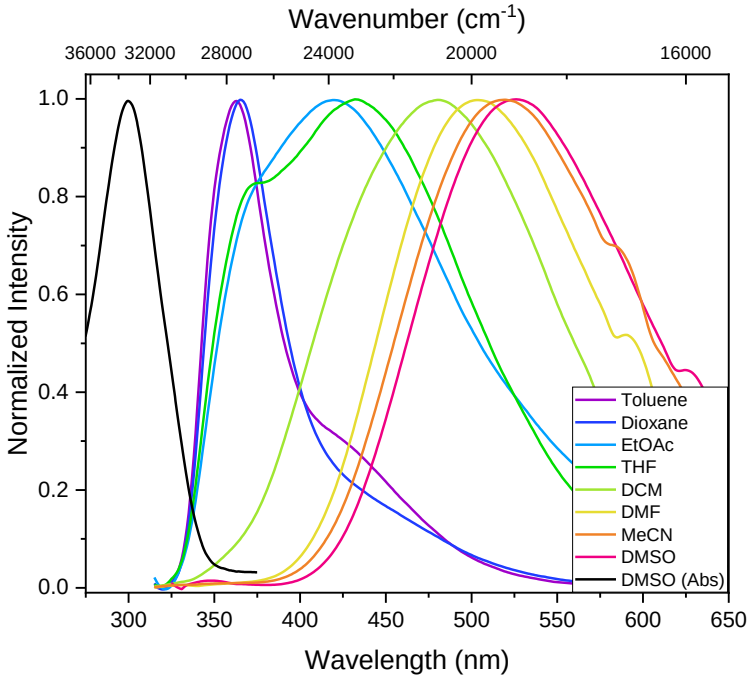

Figure S17. Emission spectra overlay of **L2** taken in various solvents at 298 K. The absorbance feature for **L2** in DMSO is shown in black for reference. Excitation was performed at the lowest energy absorbance maxima for each solvent (**Table S1**).

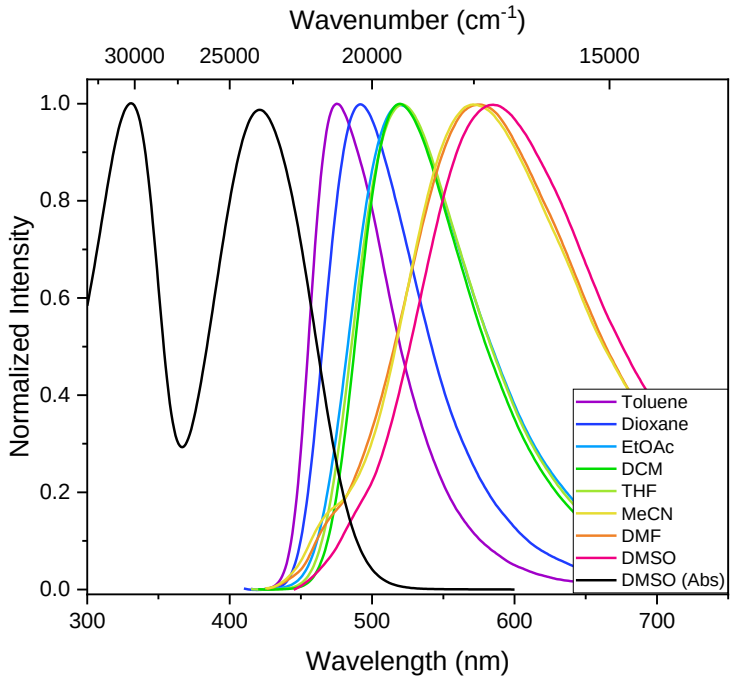

Figure S18. Emission spectra overlay of **L3** taken in various solvents at 298 K. The absorbance feature for **L3** in DMSO is shown in black for reference. Excitation was performed at the lowest energy absorbance maxima for each solvent (**Table S1**).

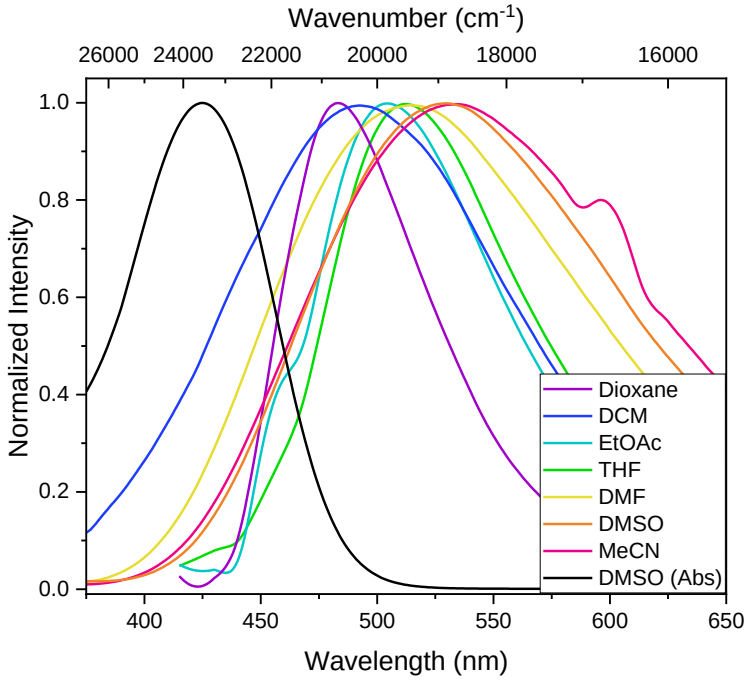

Figure S19. Emission spectra overlay of **L4** taken in various solvents at 298 K. The absorbance feature for **L4** in DMSO is shown in black for reference. Excitation was performed at the lowest energy absorbance maxima for each solvent (**Table S1**).

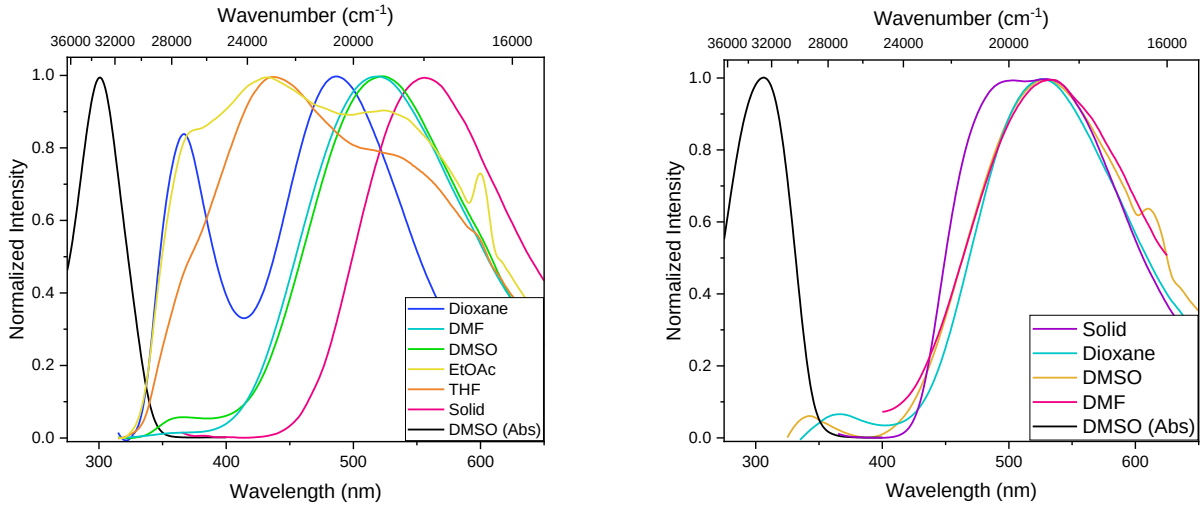

Figure S20. Emission spectra overlay of **L2-Zn** (left) and **L4-Zn** (right) in DMSO (red) and dioxane (blue) taken at 0.01 mM at 298K. The absorbance features for **L2-Zn** and **L4-Zn** in DMSO are shown in black for reference. Excitation was performed at the lowest energy absorbance maxima for each solvent (**Table S1**). Due to limited solubility in dioxane, complex **L2-Zn** was heated at 100 °C to fully dissolve, and showed partial thermal decay as supported by the peak observed at 367 nm coincident with free ligand **L2** in dioxane. Only the emission peak at 486 nm is attributed to **L2-Zn** in dioxane.

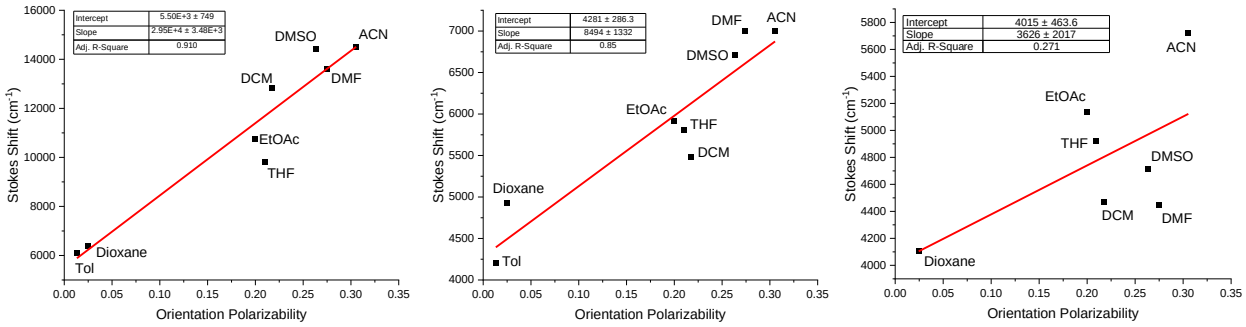

Figure S21. Lippert plots of **L2** (left, $R^2 = 0.91$), **L3** (center, $R^2 = 0.85$), and **L4** (right, $R^2 = 0.27$).

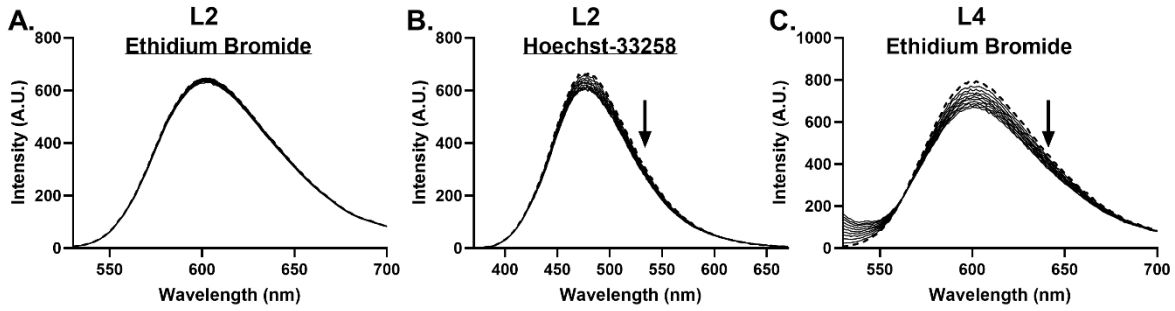

Figure S22. Fluorescence emission spectra of dye:DNA complexes in the competitive displacement assay with **L2** and **L4**. Ethidium bromide (5 µM) was incubated with ct-DNA (50 µM) in 10 mM MOPS, pH 7.2, prior to titration of **L2** (**A**) and **L4** (**C**). Experimental conditions were repeated with Hoechst-33258 (5 µM) (**B**). Arrows indicate the direction of spectral changes upon increasing additions of ligand.

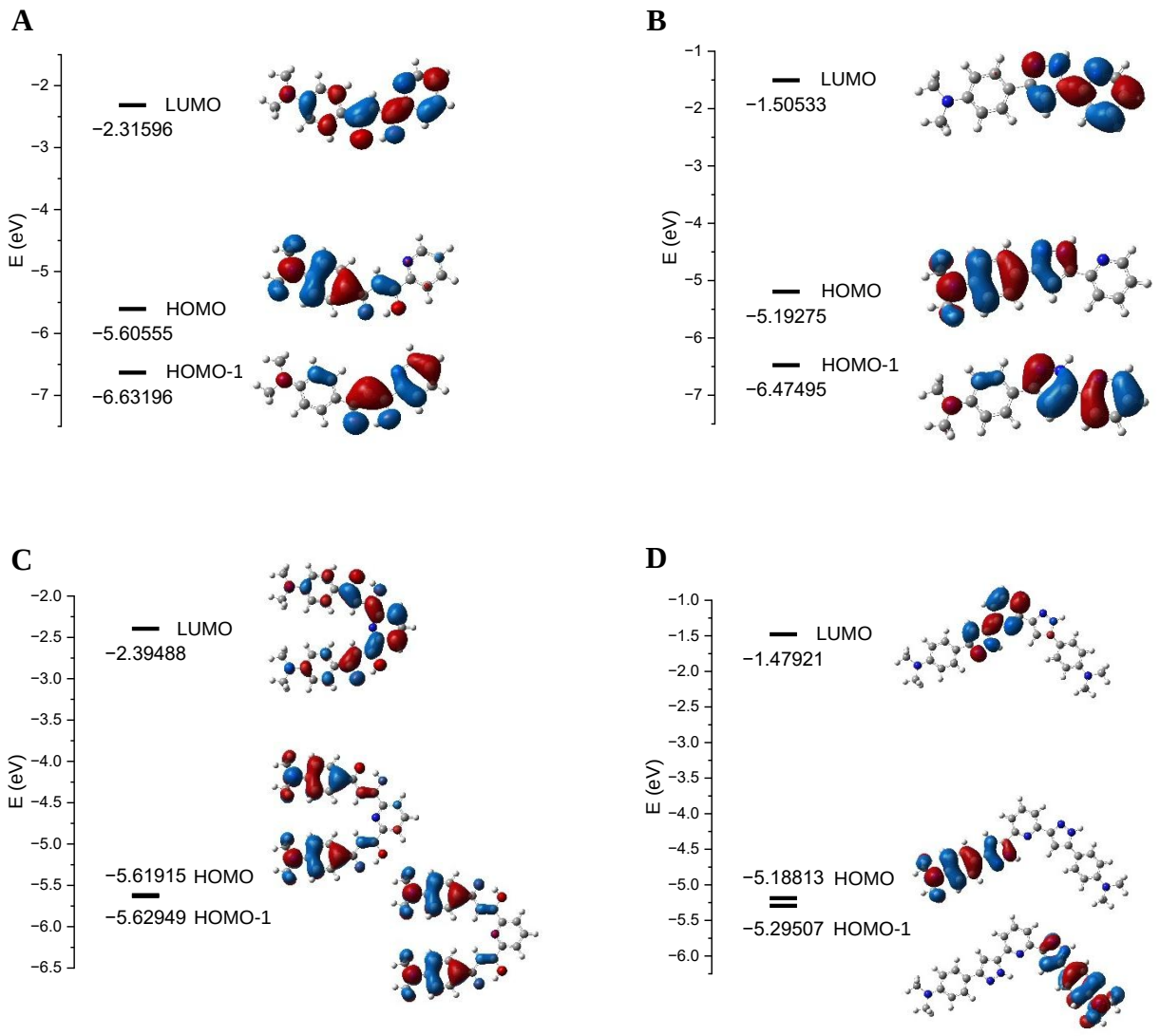

Figure S23. DFT-computed (B3LYP/6-311g*) Kohn-Sham frontier molecular orbitals for **L1** (A), **L2** (B), **L3** (C), and **L4** (D). Energies reported in electronvolts (eV).

Table S1. Fluorescence emission λ_{max} of investigated compounds in various solvents.[a]

Solvent	L1	L2	L3	L4	L2-Zn	L4-Zn
MeCN	551 (409)	519 (296)	571 (325, 408)	537 (409)	-	-
DCM	508 (413)	480 (297)	519 (325, 404)	519 (404)	-	-
Dioxane	481 (405)	365 (296)	492 (320, 396)	482 (403)	367, 486 (299)	526 (318)
DMF	551 (415)	504 (299)	575 (326, 410)	508 (419)	519 (299)	534 (322)
DMSO	561 (423)	526 (299)	585 (330, 420)	530 (424)	532 (301)	529 (306)
EtOAc	500 (403)	432 (295)	519 (318, 397)	518 (401)	432, 524 (297)	-
THF	503 (407)	419 (297)	521 (319, 400)	506 (409)	437, 526 (299)	-
Toluene	465 (406)	363 (297)	475 (320, 396)	-	-	-
Water[b]	498 (360, 422)	370 (290)	566 (355, 410)	521 (325)	536 (291)	497 (283, 315)
None, Solid[c]	516 (405)	347 (300)	575, 612 (405)	531 (415)	556 (350)	503, 530 (350)

[a] Absorbance λ_{max} shown in parentheses; [b] buffered in 10 mM MOPS to pH = 7.2; [c] Excitation λ shown in parentheses

Details on the Lippert-Magata calculations[1]

The change in dipole moment ($\Delta\mu = \mu_E - \mu_G$) between the ground and excited states of compounds **L1**-**L4** and **L4**-**Zn** were calculated from the Lippert-Mataga equation (**Eq S1**)

$$\tilde{\upsilon}_a - \tilde{\upsilon}_f = \Delta\tilde{\upsilon} = \frac{2\Delta f}{4\pi\varepsilon_0 hca^3}(\mu_E - \mu_G)^2 + const \quad \textbf{S1}$$

where $\tilde{\upsilon}_a$ and $\tilde{\upsilon}_f$ are the absorption and emission maxima (in m^{-1}), Δf is the solvent orientation polarizability as described in **Eq S2**, ε_0 is the vacuum permittivity constant (8.8542 x 10^{-12} F m^{-1}), h is Planck's constant (6.6256 x 10^{-34} J s), c is the speed of light (2.9979 x 10^8 m s^{-1}), a is the Onsager radius as described in **Eq S3**, and μ_E and μ_G are the dipole moments in the excited and ground state (in Cm). Solvent orientation polarizabilities (Δf) were calculated from **Eq S2**

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} + \frac{n^2 - 1}{2n^2 + 1} \quad \textbf{S2}$$

where ε and n are the dielectric constant and refractive index of a solvent, respectively (**Table S2**). The Onsager radii for **L1**-**L4** and **L4**-**Zn** were approximated from the crystal structure unit cell following **Eq S3**

$$a = \left(\frac{3V_m}{4\pi N_A}\right)^{1/3} \quad \textbf{S3}$$

where a is the Onsager radius (in m), V_m is the compound's molar volume (in m^3 mol^{-1}), and N_A is Avogadro's number (6.0221 x 10^{23} mol^{-1}). A constant of 0.5 Å, or 5 x 10^{-11} m is added to the calculated Onsager radius to account for the closest possible approach of solvent. The molar volume was calculated from the unit cell measurements of the crystal structures using **Eq S4**

$$V_m = \frac{N_A \times V_{cell}}{Z} \quad \textbf{S4}$$

where V_m is the compound's molar volume (in m^3 mol^{-1}), N_A is Avogadro's number (6.0221 x 10^{23} mol^{-1}), V_{cell} is the unit cell volume (in m^3), and Z is the number of formula units in the unit cell. For **L2**-**Zn**, where crystal data was missing, the molecular weight divided by density (cm^3 mol^{-1}), with d = 1 g cm^{-1}, was used instead of molar volume.[2]

Table S2. Solvent optical properties and calculated orientation polarizabilities.

Solvent	relative permittivity (ε)	optical refractive index (*n*)	orientation polarizability (Δ*f*)
Toluene	2.38	1.4969	0.0132
Dioxane	2.25	1.4224	0.0245
THF	7.58	1.4072	0.210
DCM	8.93	1.4241	0.217
EtOAc	6.02	1.3724	0.200
ACN	37.5	1.3441	0.305
DMF	36.7	1.4305	0.274
DMSO	46.7	1.4783	0.263

Table S3. Collection of the main crystal data and structure refinement details of compounds presented in this study.

	L1	**L2**	**L3 (bis-β-ketoenol)**	**L3 (β-ketoenol-diketone)**	**L4**	**L4-Zn**
Empirical formula	$C_{16}H_{16}N_2O_2$	$C_{16}H_{16}N_4$	$C_{27}H_{27}N_3O_4$	$C_{27}H_{27}N_3O_4$	$C_{27}H_{27}N_7$	$C_{33}H_{41}Cl_2N_9O_2Zn$
FW	268.31	264.33	457.51	457.51	449.55	732.02
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	orthorhombic	Monoclinic
Space group	P 2_1/c (no. 14)	P 2_1/c (no. 14)	P 2_1/c (no. 14)	P 2_1/c (no. 14)	P 2_1 2_1 2_1 (no. 19)	P 2_1/c (no. 14)
Unit cell dimensions	*a* [Å] = 9.6366(3) *b* [Å] = 14.5962(5) *c* [Å] = 9.6954(3) α [°] = 90 β [°] = 98.9920(10) γ [°] = 90	*a* [Å] = 11.5707(3) *b* [Å] = 6.0057(2) *c* [Å] = 19.0933(6) α [°] = 90 β [°] = 98.018(1) γ [°] = 90	*a* [Å] = 6.098(3) *b* [Å] = 14.862(10) *c* [Å] = 24.487(15) α [°] = 90 β [°] = 92.87(3) γ [°] = 90	*a* [Å] = 8.1741(9) *b* [Å] = 10.6497(12) *c* [Å] = 26.131(3) α [°] = 90 β [°] = 96.891(4) γ [°] = 90	*a* [Å] = 9.8859(13) *b* [Å] = 10.8489(14) *c* [Å] = 20.943(3) α [°] = 90 β [°] = 90 γ [°] = 90	*a* [Å] = 13.2533(3) *b* [Å] = 11.8894(3) *c* [Å] = 23.1759(5) α [°] = 90 β [°] = 105.245(2) γ [°] = 90
V, Å^3	1346.97(8)	1313.83(7)	2217(2)	2258.3(4)	2246.2(5)	3523.40(15)
Z	4	4	4	4	4	4
Dcalc, mg/m^3	1.323	1.336	1.371	1.346	1.329	1.380
Abs coeff, mm^{-1}	0.089	0.652	0.754	0.740	0.651	2.717
F(000)	568	560	968	968	952	1528
Crystal size, mm	0.33 x 0.226 x 0.113	0.038 x 0.186 x 0.205	0.201 x 0.178 x 0.105	0.28 x 0.14 x 0.03	0.217 x 0.163 x 0.128	0.22 x 0.154 x 0.031
θ range for collection, [°]	2.54 to 25.68	3.86 to 71.81	4.45 to 76.12	4.48 to 69.79	4.47 to 72.35	3.95 to 72.30
Index ranges	$-14 \le h \le 12$ $-22 \le k \le 22$ $-14 \le l \le 14$	$-14 \le h \le 14$ $-7 \le k \le 7$ $-20 \le l \le 23$	$-7 \le h \le 7$ $-18 \le k \le 18$ $-29 \le l \le 29$	$-9 \le h \le 9$ $0 \le k \le 12$ $0 \le l \le 31$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-25 \le l \le 23$	$-16 \le h \le 16$ $-14 \le k \le 14$ $-28 \le l \le 28$
Reflns (meas., uniq., obs.)	48893/5122/4579	23491/2580/2291	24670/4179/3066	5479/4380/3020	9767/4421/4322	64548/6948/5709
Rint	0.0271	0.0418	0.0928	0.0792	0.0355	0.0866
Completeness to θ_{max}	99.8 (θ = 33.141°)	99.5 (θ = 72.005°)	98.4 (θ = 70.404°)	98.6 (θ = 70.054°)	99.5 (θ = 72.344°)	99.9 (θ = 72.296°)
Data / restraints / parameters	5122 / 0 / 189	2580 / 0 / 186	4179 / 2 / 317	4380 / 1 / 312	4421 / 0 / 317	6948 / 0 / 438
GOF on F^2	1.037	1.049	1.086	1.086	1.044	1.064
Final *R* indices (obs data)	*R1* = 0.0386 *wR2* = 0.1139	*R1* = 0.0366 *wR2* = 0.0942	*R1* = 0.0555 *wR2* = 0.1322	*R1* = 0.0896 *wR2* = 0.1801	*R1* = 0.0262 *wR2* = 0.0663	*R1* = 0.0462 *wR2* = 0.1047
R indices (all data)	*R1* = 0.0428 *wR2* = 0.1185	*R1* = 0.0415 *wR2* = 0.0982	*R1* = 0.0923 *wR2* = 0.1601	*R1* = 0.1374 *wR2* = 0.2120	*R1* = 0.0270 *wR2* = 0.0670	*R1* = 0.0627 *wR2* = 0.1154
Largest diff peak and hole, [e Å^3]	0.460 and -0.272	0.174 and -0.248	0.283 and -0.344	0.293 and -0.359	0.147 and -0.141	0.372 and -0.487

Table S4. Hydrogen bond parameters for compounds **L3**, **L4** and **L4-Zn**.

Compound	**D–H···A**	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (º)**
L3	O1–H1···O2	0.862(10)	1.654(17)	2.469(3)	157(3)
	O3–H3···O4	0.860(10)	1.714(16)	2.534(3)	158(3)
L4	N2–H2···N5	0.89(2)	2.43(2)	3.1175(19)	134.0(17)
	N6–H6···N2	0.89(2)	2.60(2)	3.1753(19)	123.3(16)
	N6–H6···N3	0.89(2)	1.98(2)	2.806(2)	154.1(18)
L4-Zn	N3–H3···O1	0.91(4)	1.86(4)	2.773(3)	174(3)
	N6–H6···O2	0.93(4)	1.77(4)	2.703(3)	178(3)

Table S5. Select geometric parameters for **L1**-**L4** and **L4**-**Zn**.

	L1	L2	L3 (bis-β-ketoenol)	L3 (β-ketoenol-β-diketone)	L4	L4-Zn
Bond Lengths (Å)						
C6-O1	1.3043(8)	-	1.299(3)	1.297(5)	-	-
C6-N2	-	1.3526(16)	-	-	1.346(2)	1.340(4)
C6-C7	1.3897(9)	1.3815(16)	1.388(3)	1.389(5)	1.383(2)	1.404(4)
C7-C8	1.4189(9)	1.4091(16)	1.401(3)	1.404(6)	1.411(2)	1.392(4)
C8-O2	1.2961(8)	-	1.301(3)	1.303(5)	-	-
C8-N3	-	1.3432(15)	-	-	1.340(2)	1.358(4)
C12-N2	1.3602(9)	-	1.371(3)	1.380(5)	-	-
C12-N4	-	1.3830(15)	-	-	1.382(2)	1.375(4)
C17-O3	-	-	1.304(3)	1.221(5)	-	-
C17-N5	-	-	-	-	1.337(2)	1.330(3)
C17-C18	-	-	1.380(3)	1.514(5)	1.406(2)	1.404(4)
C18-C19	-	-	1.416(3)	1.508(6)	1.382(2)	1.397(4)
C19-O4	-	-	1.284(3)	1.226(5)	-	-
C19-N6	-	-	-	-	1.357(2)	1.360(3)
C23-N3	-	-	1.359(3)	1.379(5)	-	-
C23-N7	-	-	-	-	1.375(2)	1.373(4)
Zn1-N1	-	-	-	-	-	2.130(2)
Zn1-N2	-	-	-	-	-	2.165(2)
Zn1-N5	-	-	-	-	-	2.215(2)
Zn1-Cl1	-	-	-	-	-	2.2558(7)
Zn1-Cl2	-	-	-	-	-	2.2574(7)
Bond Angles (º)						
O1-C6-C7	122.24(6)	-	122.5(2)	122.3(4)	-	-
C6-C7-C8	119.68(6)	105.19(10)	120.1(2)	119.3(4)	105.33(14)	105.1(2)
O2-C8-C7	119.65(6)	-	119.6(2)	119.3(3)	-	-
C12-N2-C15	120.60(6)	-	121.0(2)	120.0(4)	-	-
C12-N2-C16	120.95(6)	-	119.8(2)	120.3(4)	-	-
C15-N2-C16	118.41(6)	-	119.0(2)	118.7(4)	-	-
C12-N4-C15	-	120.72(10)	-	-	119.30(14)	120.7(3)
C12-N4-C16	-	120.19(10)	-	-	119.77(14)	120.1(3)
C15-N4-C16	-	118.49(10)	-	-	118.86(15)	119.2(3)
O3-C17-C18	-	-	123.0(2)	121.7(4)	-	-
C17-C18-C19	-	-	121.2(2)	111.8(3)	105.44(14)	104.7(2)
O4-C19-C18	-	-	120.0(2)	120.3(3)	-	-
C23-N3-C26	-	-	120.1(2)	121.6(4)	-	-
C23-N3-C27	-	-	120.8(2)	119.9(4)	-	-
C26-N3-C27	-	-	116.6(2)	118.4(3)	-	-
C23-N7-C26	-	-	-	-	121.05(14)	120.3(3)
C23-N7-C27	-	-	-	-	120.02(14)	120.2(2)
C26-N7-C27	-	-	-	-	118.93(14)	118.9(3)
N1-Zn1-Cl1	-	-	-	-	-	119.91(6)
N1-Zn1-Cl2	-	-	-	-	-	120.87(6)
N2-Zn2-N5	-	-	-	-	-	147.71(8)
Torsion Angles (º)						
N1-C5-C6-O1	176.05(6)	-	-174.9(2)	176.3(4)	-	-
N1-C5-C6-N2	-	0.43(16)	-	-	-15.6(2)	-8.5(3)
N1-C1-C17-O3	-	-	177.0(2)	179.6(4)	-	-
N1-C1-C17-N5	-	-	-	-	156.74(15)	9.1(3)
O1-C6-C7-C8	0.58(10)	-	2.0(4)	2.7(7)	-	-
C6-C7-C8-O2	0.36(10)	-	-1.2(4)	-2.2(6)	-	-
O2-C8-C9-C10	-170.60(6)	-	-178.8(2)	5.6(6)	-	-
N3-C8-C9-C10	-	-171.31(11)	-	-	147.12(16)	-162.6(3)
C11-C12-N2-C15	-2.77(11)	-	-5.4(4)	179.7(4)	-	-
C11-C12-N4-C15	-	-171.32(11)	-	-	-10.4(2)	2.2(5)
O3-C17-C18-C19	-	-	3.1(4)	-97.4(5)	-	-
C17-C18-C19-O4	-	-	-2.5(3)	8.5(6)	-	-
O4-C19-C20-C21	-	-	-173.8(2)	-168.4(4)	-	-
N6-C19-C20-C21	-	-	-	-	-22.2(2)	-177.7(3)
C22-C23-N3-C26	-	-	11.1(3)	171.9(4)	-	-
C22-C23-N7-C26	-	-	-	-	-7.1(2)	-5.7(5)

Computed XYZ coordinates of the ground state for compounds **L1**-**L4**.

*XYZ Coordinates for **L1***

Symbol	X	Y	Z
O	2.782097	-2.117632	0.000249
H	1.892443	-2.573433	0.000199
O	0.259431	-2.449643	0.000053
N	3.516443	1.385667	0.000521
N	-5.264877	0.739005	-0.00215
C	4.583526	2.181784	0.00044
H	4.382999	3.249804	0.000744
C	5.898077	1.710579	0.000045
H	6.728205	2.407237	-0.000001
C	6.103858	0.335694	-0.000288
H	7.107386	-0.07521	-0.000617
C	4.998311	-0.509921	-0.000202
H	5.113724	-1.585369	-0.000434
C	3.719452	0.056757	0.000207
C	2.515727	-0.809561	0.000214
C	1.240767	-0.314901	0.000104
H	1.131474	0.757231	0.000099
C	0.092022	-1.200034	-0.000039
C	-1.275538	-0.65224	-0.000292
C	-1.573507	0.723264	-0.000484
H	-0.778949	1.459845	-0.000282
C	-2.875645	1.187142	-0.00076
H	-3.043746	2.255547	-0.000555
C	-3.975693	0.289132	-0.001119
C	-3.673652	-1.100333	-0.000418
H	-4.470485	-1.832014	-0.000054
C	-2.366758	-1.542003	-0.000158
H	-2.162815	-2.606278	0.000257
C	-5.546683	2.169151	0.000565
H	-5.132876	2.664577	-0.883893
H	-5.139143	2.660663	0.890264
H	-6.623027	2.321045	-0.003183
C	-6.375092	-0.205803	0.001875
H	-7.312368	0.344754	-0.000508
H	-6.36055	-0.844161	0.891488
H	-6.360485	-0.850996	-0.882665

*XYZ Coordinates for **L2***

Symbol	X	Y	Z
N	-4.684029	-0.923996	-0.028399
N	-2.016759	-1.570206	-0.024345
H	-2.643555	-2.359795	-0.044024
N	-0.6863	-1.738367	-0.018557
N	5.4763	0.351503	0.107208
C	-5.988821	-0.642761	-0.031311
H	-6.659788	-1.497363	-0.050829
C	-6.497063	0.654232	-0.010992
H	-7.567263	0.824046	-0.014376
C	-5.592806	1.713762	0.013555
H	-5.943195	2.740022	0.029899
C	-4.230779	1.439466	0.016828
H	-3.504652	2.243497	0.035526
C	-3.813354	0.10287	-0.004603
C	-2.396641	-0.267024	-0.002471
C	-1.218271	0.465196	0.019632
H	-1.127418	1.539221	0.043005
C	-0.175778	-0.495873	0.008651
C	1.276972	-0.27343	0.024456
C	1.827505	1.01558	0.015084
H	1.176865	1.883952	-0.009821
C	3.199115	1.22989	0.028007
H	3.55917	2.250028	0.010524
C	4.110625	0.148558	0.0613
C	3.552383	-1.15287	0.05504
H	4.194363	-2.023875	0.059967
C	2.179829	-1.347639	0.041827
H	1.793187	-2.360744	0.040596
C	6.377084	-0.777797	-0.070907
H	6.216388	-1.537837	0.6984
H	7.404651	-0.432165	0.022448
H	6.264781	-1.258637	-1.052438
C	6.010097	1.690045	-0.096187
H	5.765566	2.097489	-1.086894
H	7.093496	1.66069	0.001191
H	5.632348	2.385695	0.658016

*XYZ Coordinates for **L3***

Symbol	X	Y	Z
O	4.100081	-3.5031	0.143796
O	1.895743	-4.773491	0.139388
H	3.452756	-4.26477	0.160786
O	4.082337	3.523124	-0.143595
H	3.431169	4.281545	-0.160553
O	1.871843	4.782472	-0.139266
N	3.459052	0.008426	0.000091
N	-4.422118	-3.947269	-0.135037
N	-4.441821	3.925887	0.136055
C	4.13591	1.160551	-0.034343
C	5.536608	1.211793	-0.038128
H	6.044276	2.165967	-0.068376
C	6.242309	0.015464	-0.000377
H	7.326459	0.018204	-0.000561
C	5.542682	-1.184422	0.037599
H	6.055191	-2.136011	0.067664
C	4.14175	-1.140271	0.034276
C	3.354513	-2.398737	0.066887
C	1.989161	-2.428917	0.018509
H	1.476586	-1.482796	-0.039998
C	1.264567	-3.686111	0.054697
C	-0.206768	-3.703691	0.000547
C	-1.003269	-2.555704	-0.168745
H	-0.547693	-1.578461	-0.276341
C	-2.382885	-2.626467	-0.217632
H	-2.942612	-1.711348	-0.356181
C	-3.0599	-3.868764	-0.093319
C	-2.254047	-5.027981	0.07576
H	-2.713382	-6.002265	0.174939
C	-0.878463	-4.935748	0.117424
H	-0.2866	-5.834261	0.246406
C	-5.224443	-2.743106	-0.310986
H	-5.007111	-2.246381	-1.262517
H	-5.055287	-2.02405	0.497107
H	-6.277779	-3.011564	-0.305182
C	-5.090817	-5.237809	-0.020503
H	-4.798652	-5.918355	-0.827039
H	-6.165968	-5.089087	-0.080331
H	-4.870123	-5.724493	0.935115
C	3.342319	2.415031	-0.06678

C	1.97682	2.438386	-0.018418
H	1.468917	1.48973	0.040016
C	1.246025	3.69199	-0.054565
C	-0.225376	3.702414	-0.000361
C	-1.016352	2.550659	0.16925
H	-0.556126	1.575609	0.276944
C	-2.39629	2.614828	0.218267
H	-2.951616	1.697049	0.35694
C	-3.07926	3.853849	0.093868
C	-2.279001	5.016843	-0.075795
H	-2.743005	5.988866	-0.175408
C	-0.902998	4.931192	-0.117556
H	-0.315477	5.832487	-0.24695
C	-5.238446	2.717726	0.310497
H	-5.06644	2.000633	-0.498774
H	-6.293024	2.981302	0.305815
H	-5.018227	2.220627	1.261141
C	-5.116772	5.212982	0.019458
H	-4.826706	5.896597	0.82411
H	-6.191116	5.059328	0.081224
H	-4.899696	5.698669	-0.93753

*XYZ Coordinates for **L4***

Symbol	X	Y	Z
N	0.239568	2.040289	0.042982
N	-1.720371	0.111758	0.010896
H	-0.779441	-0.249973	0.018626
N	-2.778727	-0.712003	-0.012116
N	-9.144071	-2.059514	-0.163514
N	3.657195	3.242798	0.077021
N	4.725995	2.42926	0.056284
H	5.646331	2.83545	0.116783
N	8.253825	-3.104729	-0.089432
C	1.231484	2.942131	0.061101
C	0.982617	4.322401	0.080636
H	1.81159	5.018033	0.093835
C	-0.33428	4.76206	0.082718
H	-0.556967	5.823485	0.09878
C	-1.367029	3.830473	0.063766
H	-2.402805	4.147443	0.065215
C	-1.033179	2.472173	0.043205
C	-2.058936	1.426352	0.020141

C	-3.446153	1.454405	0.001603
H	-4.072413	2.331996	0.000447
C	-3.85199	0.095997	-0.018205
C	-5.214692	-0.454117	-0.044056
C	-6.346044	0.37336	-0.043476
H	-6.229867	1.45217	-0.018036
C	-7.634832	-0.142228	-0.068001
H	-8.465177	0.551356	-0.057527
C	-7.866573	-1.537288	-0.104861
C	-6.722445	-2.371631	-0.088828
H	-6.830056	-3.448316	-0.095329
C	-5.442829	-1.838668	-0.063985
H	-4.593268	-2.512481	-0.055312
C	-10.288329	-1.18088	0.027447
H	-10.296678	-0.705521	1.018022
H	-11.203876	-1.759136	-0.079557
H	-10.310469	-0.389938	-0.727155
C	-9.344398	-3.490801	0.00843
H	-8.81178	-4.060278	-0.758
H	-10.403711	-3.717381	-0.094673
H	-9.011104	-3.850163	0.991778
C	2.605422	2.415293	0.05922
C	3.019888	1.064248	0.032111
H	2.389647	0.191712	-0.011328
C	4.408212	1.100247	0.032031
C	5.407902	0.03331	0.003733
C	6.70874	0.237298	-0.482995
H	6.999863	1.206586	-0.876343
C	7.649459	-0.780893	-0.506552
H	8.634889	-0.560512	-0.894587
C	7.333509	-2.083556	-0.049278
C	6.020884	-2.285065	0.445336
H	5.722015	-3.252451	0.826385
C	5.09507	-1.254705	0.466273
H	4.107791	-1.453432	0.870649
C	9.630255	-2.828379	-0.473405
H	9.688842	-2.423163	-1.488226
H	10.198899	-3.755432	-0.456668
H	10.117889	-2.116815	0.205186
C	7.933444	-4.396592	0.499359
H	7.742228	-4.32859	1.578061
H	8.769071	-5.075884	0.346545
H	7.0536	-4.843448	0.02677

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