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Electronic Supplementary Information

A serendipitous crossed aldol reaction in the ligand periphery of a Ru(II) polypyridyl complex in silica bed: prospects for delivering anticancer agents for photoactivated chemotherapy

Ramranjan Mishra,[a] Pritha Chatterjee,[a] Ray J. Butcher[b] and Ashis K. Patra*[a]

[a]*Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, Uttar Pradesh, India. E-mail: akpatra@iitk.ac.in*

[b]*Department of Chemistry, Howard University, Washington, DC 20059, USA*

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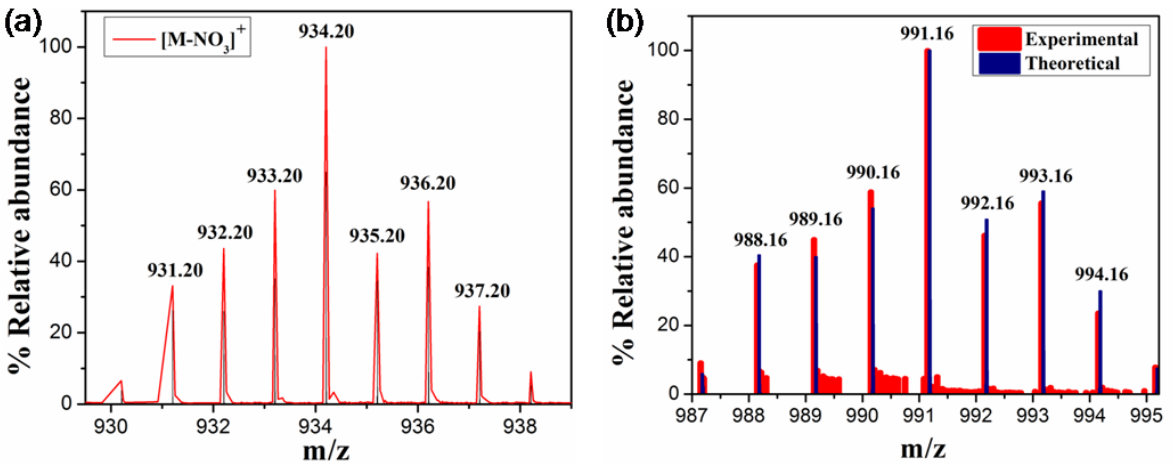

Figure S1. ESI-MS spectra of the compounds obtained in MeOH (a) Experimental (red lines) and the calculated (black lines) isotopic pattern of the crossed aldol product [**1-Ac**]. (b) Isotopic pattern for [**1**]$(PF_6)_2$ obtained experimentally (red column) compared to the calculated isotopic distributions.

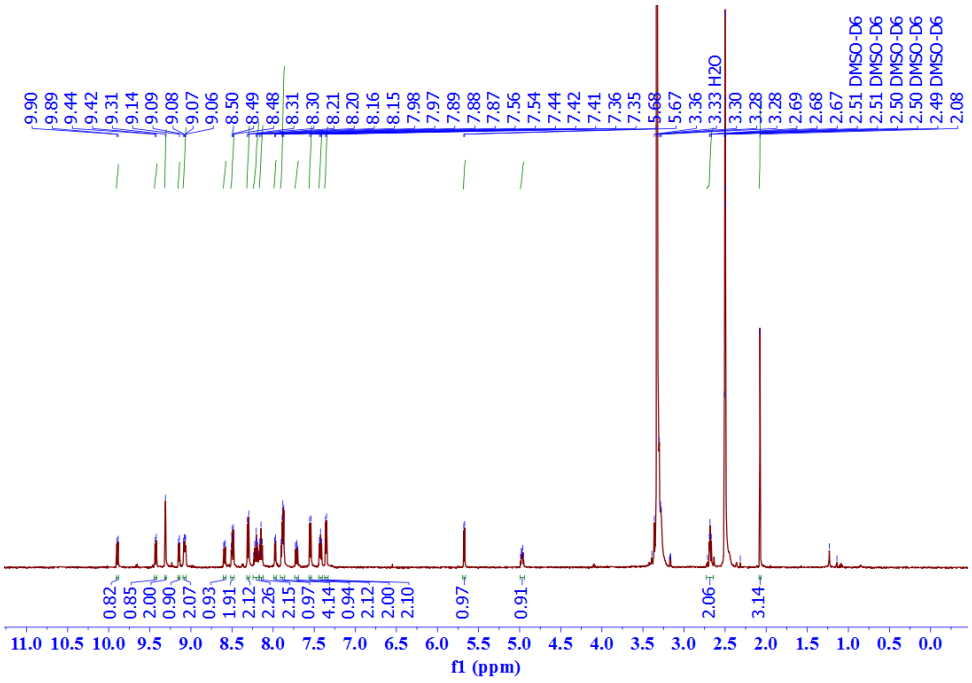

Figure S2. ^{1}H NMR of the pure product [**1-Ac**] obtained from column in DMSO-d_6.

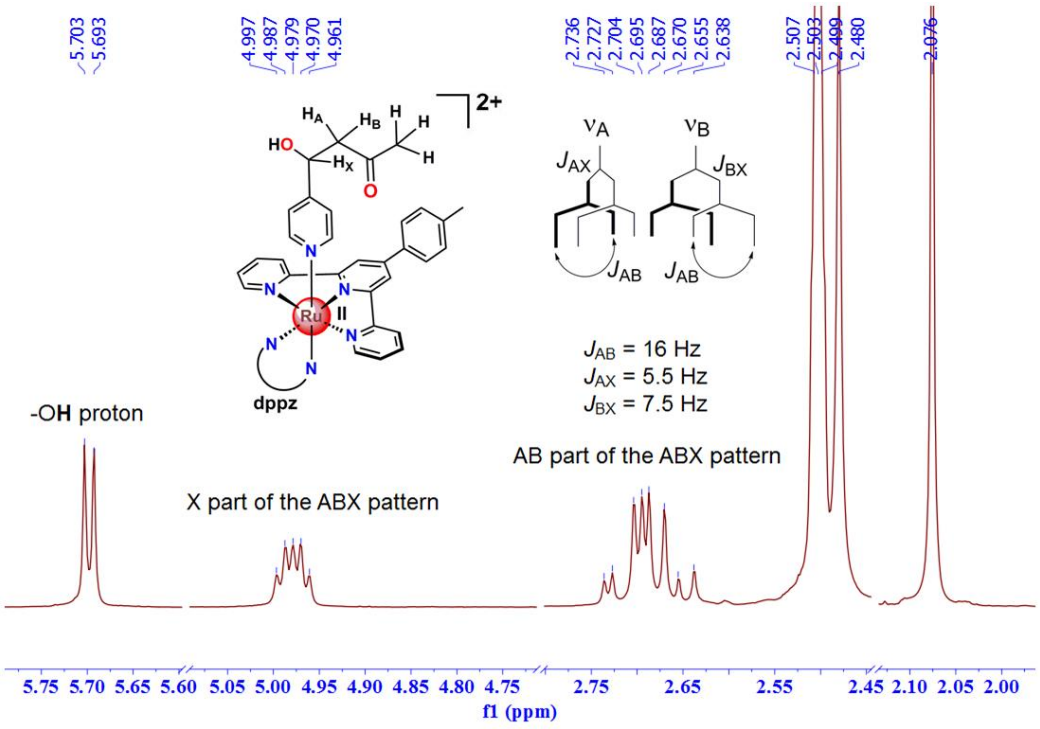

Figure S3. Second order complex coupling pattern in between the diastereotopic methylene protons A and B with the X proton in [**1-Ac**].

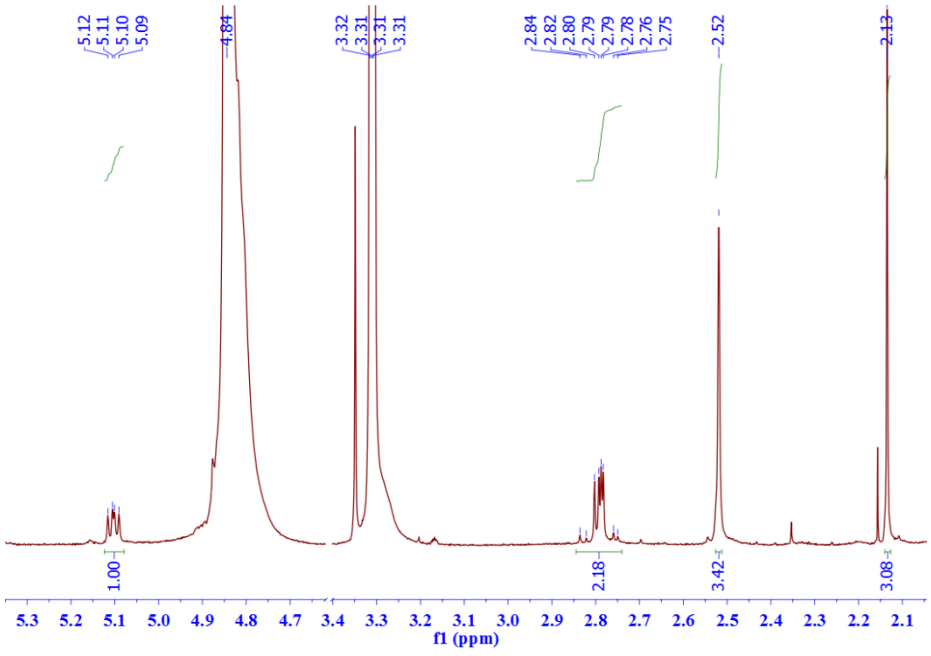

Figure S4. Expanded ^{1}H NMR spectrum of [**1-Ac**] in CD_3OD. The H_X proton was observed as a doublet of doublet at 5.11 ppm.

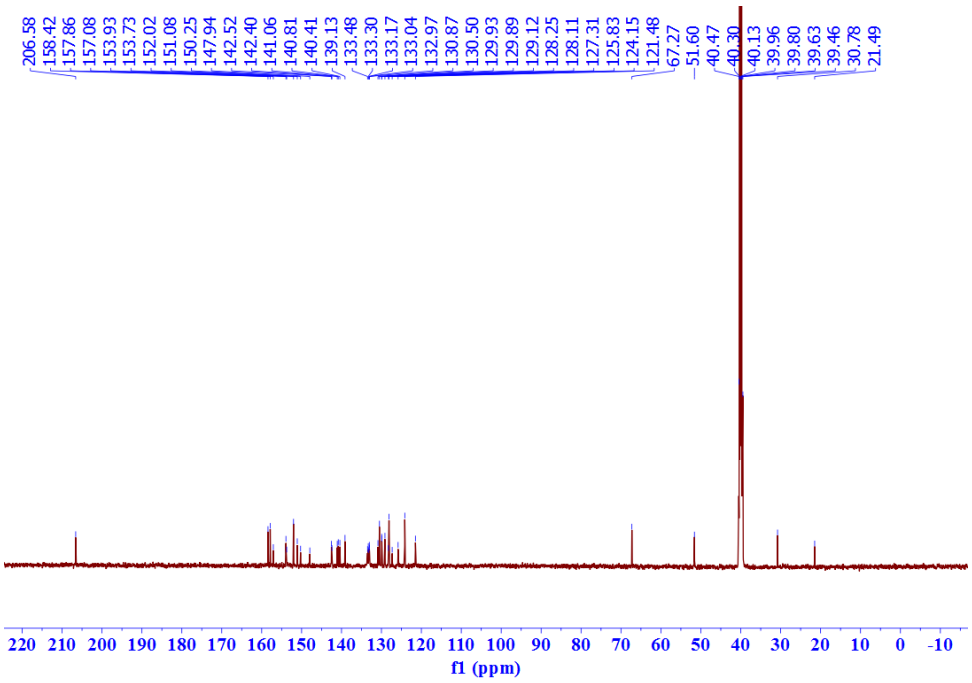

Figure S5. ^{13}C NMR spectra of [**1-Ac**] in DMSO-d_6 at 125 MHz.

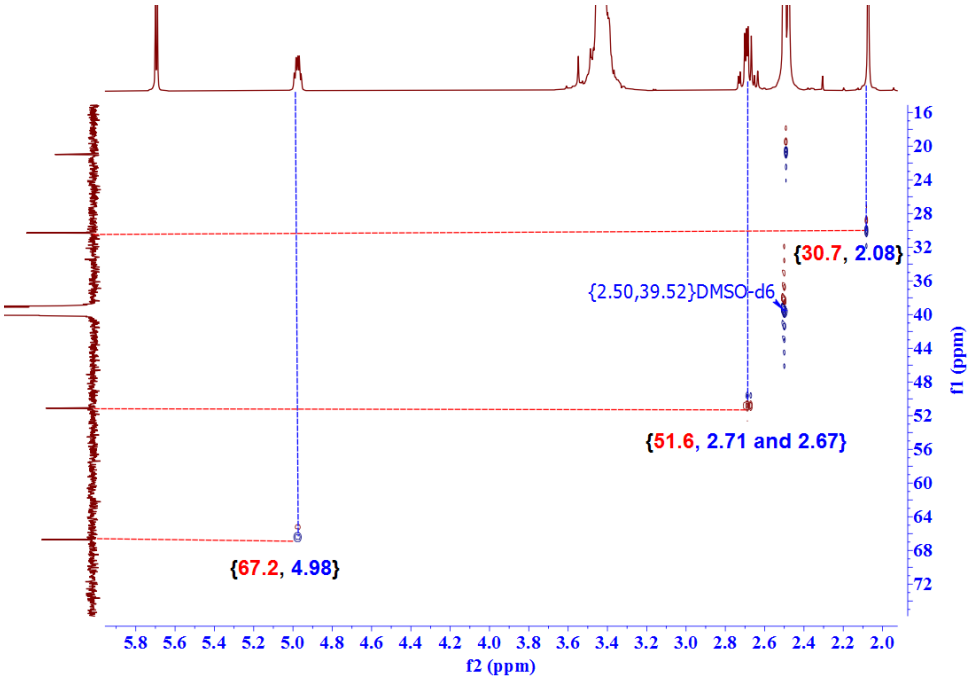

Figure S6. ^{1}H-^{13}C HSQC spectrum of [**1-Ac**] in DMSO-d_6 establishes the identity of the aliphatic region ^{13}C peaks associated with the aldol adduct of the coordinated 4-pyridine carboxaldehyde ligand.

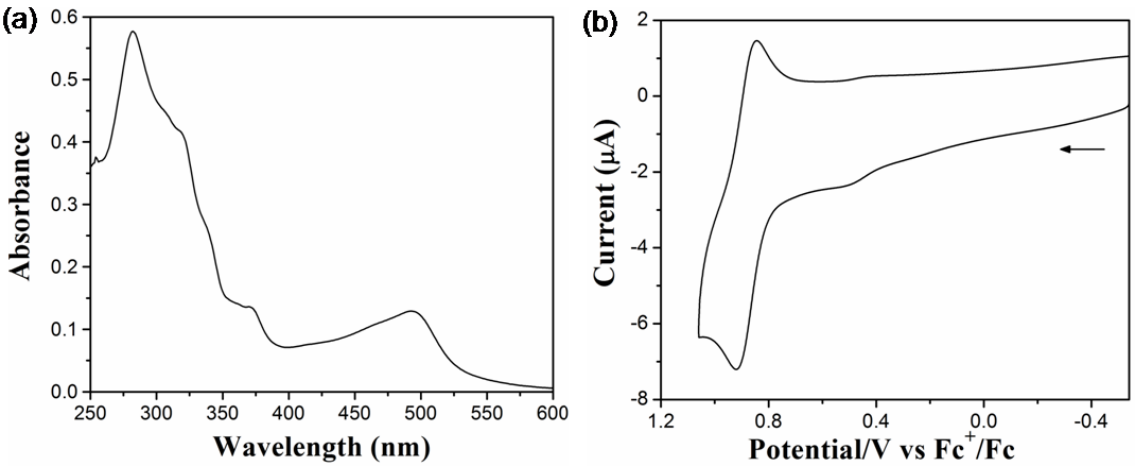

Figure S7. Electronic absorption spectra and cyclic voltammetry of [**1-Ac**]. (a) UV–vis spectrum of [**1-Ac**] in DMSO. (b) Cyclic voltammetric plot of [**1-Ac**] in acetonitrile depicting the oxidation side of the CV diagram.

Table S1. Selected bond distances (Å) of [**1-Ac**].

Compound	Ru1-N1	Ru1-N2	R1-N3	Ru1-N4	Ru1-N5	Ru1-N6
[**1-Ac**]	2.068(3)	1.957(4)	2.067(3)	2.093(4)	2.070(3)	2.120(3)

Table S2. Selected bond angles (degree) for [**1-Ac**].

Angles	Values
N1-Ru1-N2	79.5(1)
N1-Ru1-N3	159.3(1)
N1-Ru1-N4	100.3(1)
N1-Ru1-N5	91.6(1)
N1-Ru1-N6	89.2(1)
N2-Ru1-N3	79.8(1)
N2-Ru1-N4	173.0(1)
N2-Ru1-N5	93.9(1)
N2-Ru1-N6	91.0(1)
N3-Ru1-N4	100.1(1)
N3-Ru1-N5	89.5(1)
N3-Ru1-N6	91.4(1)
N4-Ru1-N5	79.1(1)
N4-Ru1-N6	96.0(1)
N5-Ru1-N6	175.1(1)

Table S3. Refinement details and crystallographic parameters of the crystal structure of [**1-Ac**].

Empirical formula	$C_{106}H_{96}N_{26}O_{25}Ru_2$
Formula weight	2336.22
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.809(3)
b/Å	20.790(6)
c/Å	21.430(6)
α/°	90
β/°	102.404(8)
γ/°	90
Volume/Å^3	5138(2)
Z	2
ρ_{calc}g/cm^3	1.510
μ/mm^{-1}	0.385
F(000)	2404.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.66 to 56.812
Index ranges	$-15 \leq h \leq 15$, $-27 \leq k \leq 27$, $-28 \leq l \leq 28$
Reflections collected	105756
Independent reflections	12796 [R_{int} = 0.0930, R_{sigma} = 0.0535]
Data/restraints/parameters	12796/177/810
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0682, wR_2 = 0.1510
Final R indexes [all data]	R_1 = 0.0925, wR_2 = 0.1635
Largest diff. peak/hole / e Å^{-3}	1.38/-0.85

$$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|};\ wR_2 = \sqrt{\left\{\frac{\sum[w(Fo^2 - Fc^2)^2]}{\sum[w(Fo^2)^2]}\right\}}$$

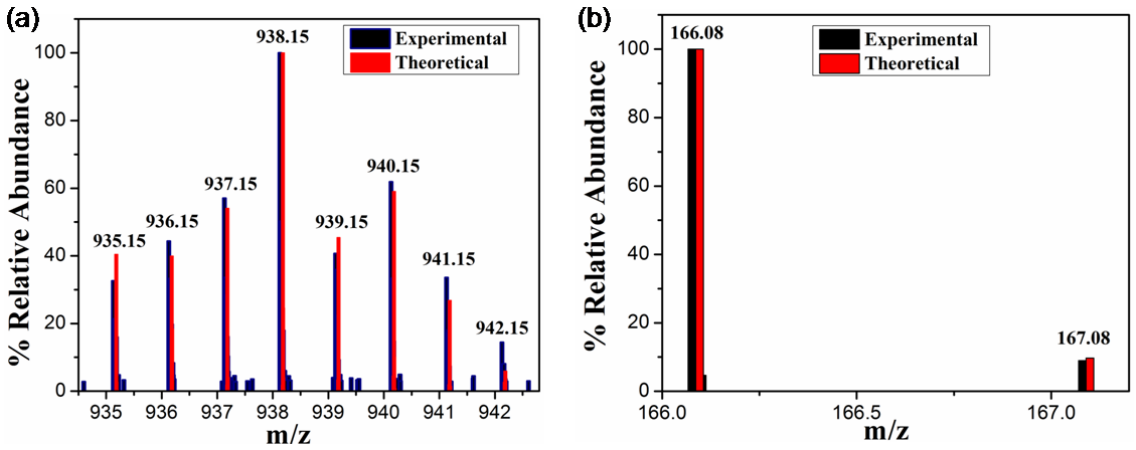

Figure S8. ESI-MS-based characterization of the photoproduct obtained from the photoreactivity study of [**1-Ac**] upon blue LED irradiation in DMSO-d_6. (a) The experimental isotopic pattern in comparison with the theoretically calculated values for {[Ru(ttp)(dppz)(DMSO-d_6]$^{2+}$+2[NO_3^-]+Na^+}. (b) ESI-MS plot of the released ligand obtained as $[M+H]^+$.