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Supporting Information

Titania supported dioxidotungsten(VI) complex as bio-mimic for the *type II* copper-containing oxidase enzyme phenoxazinone synthase

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FT-IR spectral study

The FT-IR spectra of homogeneous ligand and complex are represented in Fig. S1. Complex **1** is dominated by two new bands at 879 and 965 cm^{-1} due to *cis*-[WO₂] structure.^{1,2} The stretching frequency of the azomethine nitrogen (C=N) at 1612 cm^{-1} in H₃hptb (**I**) shifts to 1603 cm^{-1} in [W^{VI}O₂(CH₃-hptb)(H₂O)] (**1**), indicating the coordination of tungsten to nitrogen of the azomethine group. After complex formation, the stretching frequency due to (N–N) bond appears at 1017 cm^{-1} after shifting from 977 cm^{-1} in the free ligand. The conversion of the carboxylic group to methyl ester causes the shifting of $\nu(\text{C}=\text{O})$ stretch from 1685 cm^{-1} to 1709 cm^{-1} . Since a broad band at ca. 3400 cm^{-1} is possibly due to coordinated water molecule to tungsten, the coordination of phenolic oxygen could not be confirmed unequivocally. But in the light of the crystal structure reported for the analogous *cis*-[MoO₂] complex, the coordination of phenolic oxygen may also be considered here as well.³

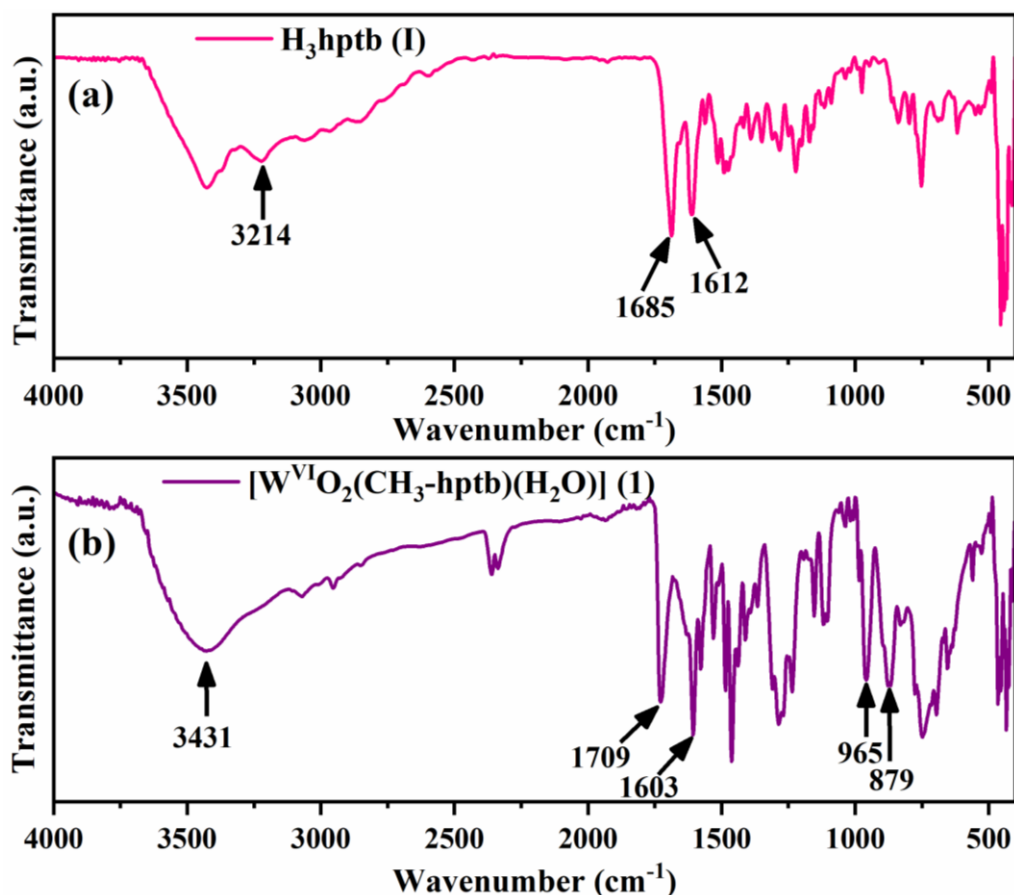


Fig. S1 FT-IR spectra of homogeneous ligand H_3hptb (I) (a), and its complex $[\text{W}^{\text{VI}}\text{O}_2(\text{CH}_3\text{-hptb})(\text{H}_2\text{O})]$ (1) (b).

^1H NMR spectral study

In the ^1H NMR spectrum of the ligand H_3hptb (I), the peaks due to two phenolic $-\text{OH}$ appear at $\delta = 8.82$ and 10.58 ppm and the carboxylic acid proton appears at $\delta = 11.88$ ppm. Signals due to the phenolic protons ($-\text{OH}$) vanish due to the coordination of both the phenolic oxygen to W (Fig. S2). Further, the disappearance of the carboxylic acid proton at $\delta = 11.88$ ppm (s, 1H) of ligand while the appearance of a new peak at $\delta = 3.93$ ppm (s, 3H) in complex confirms the esterification of the carboxylic acid group. Signals due to the aromatic protons appear in the expected range for both ligand and complex but with a slight shift of the peaks in the complex. All these observations confirm the coordination of ligand to W.

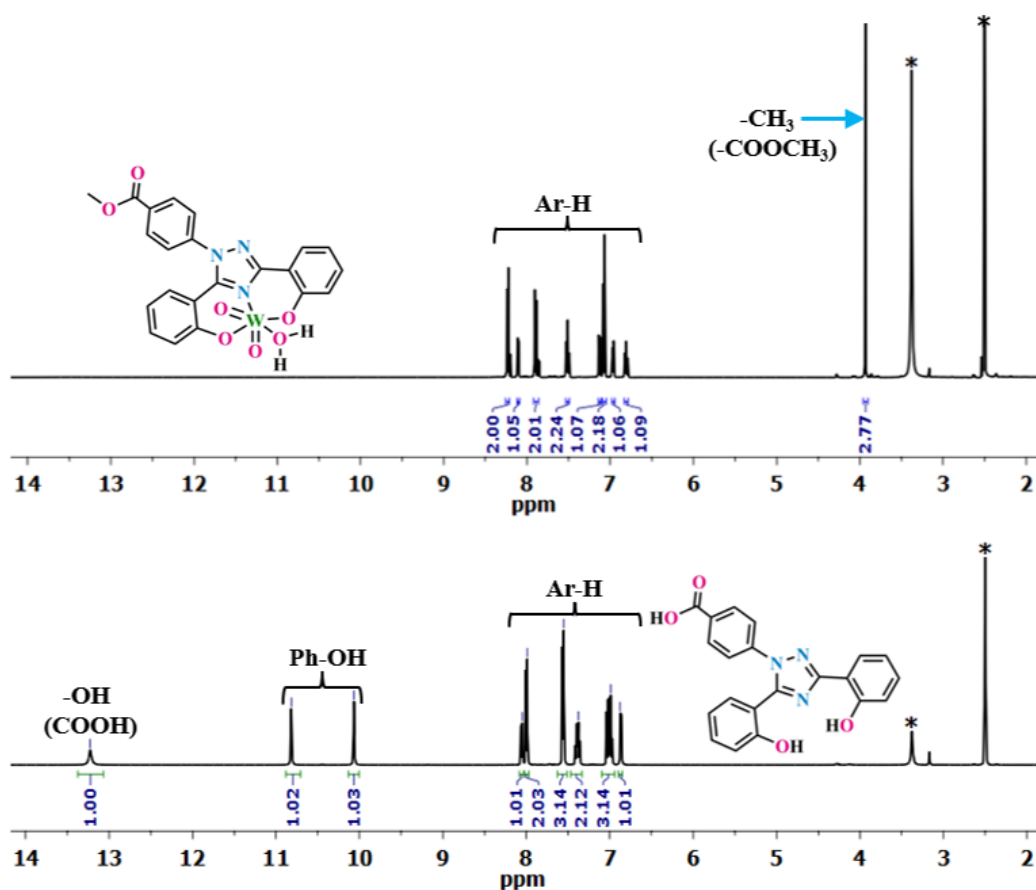


Fig. S2 The ^1H NMR spectra of H_3hptb (**I**) and $[\text{W}^{\text{VI}}\text{O}_2(\text{CH}_3\text{-hptb})(\text{H}_2\text{O})]$ (**1**) recorded in DMSO-d_6 .

^{13}C NMR spectral study

The ^{13}C NMR spectral analysis of the homogeneous compounds was also executed to know the coordination modalities of the metal to the ligand. The ^{13}C NMR spectra of H_3hptb (**I**) and $[\text{W}^{\text{VI}}\text{O}_2(\text{CH}_3\text{-hptb})(\text{H}_2\text{O})]$ (**1**) are displayed in Fig. S3. The ^{13}C NMR of ligand **I** matches well with the earlier reported data in the literature.⁴ After coordinating tungsten to the ligand, there is an apparent shift in the signals of carbon atoms corresponding to C6/C6' and C8/C8'. The esterification of the carboxylic acid group causes an up-field shift in the signal of the carbon atom corresponding to C1. In addition, a new peak at $\delta = 53.19$ ppm arises in the spectrum of complex **1**, signifying the esterification of the carboxylic acid group present in the ligand **I**. All other signals are within the predicted range with minor shifts in their positions. The spectral data of ligand and complex related to ^{13}C NMR are organized in Table S1.

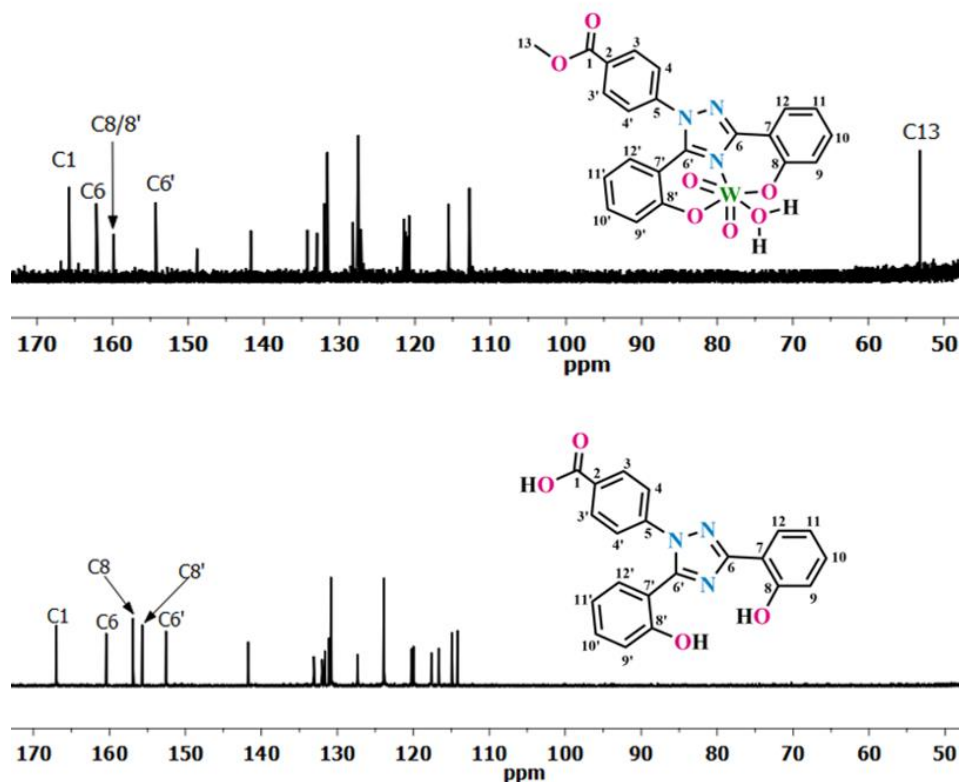


Fig. S3 The ^{13}C NMR spectra of H_3hptb (**I**) and $[\text{W}^{\text{VI}}\text{O}_2(\text{CH}_3\text{-hptb})(\text{H}_2\text{O})]$ (**1**) recorded in DMSO-d_6 .

Table S1 ^{13}C NMR data of homogeneous compounds (in ppm).

Compound	C6	C6'	C8	C8'	C1	Other Carbons	C13
H_3hptb (I)	160.49	152.55	156.85	155.72	166.96	141.73, 133.09, 132.02, 131.60, 131.07, 130.83, 127.31, 123.86, 120.23, 119.99, 117.60, 116.66, 114.93, 114.17	---
$[\text{W}^{\text{VI}}\text{O}_2(\text{CH}_3\text{-hptb})(\text{H}_2\text{O})]$ (1)	162.13	154.29	159.85	159.85	165.76	148.82, 141.70, 134.22, 132.95, 131.96, 131.61, 128.25, 127.48, 127.13, 121.44, 121.27, 121.03, 120.74, 115.63, 112.74	53.19
($\Delta\delta$)	(1.64)	(1.74)	(3.00)	(4.13)	(-1.20)		

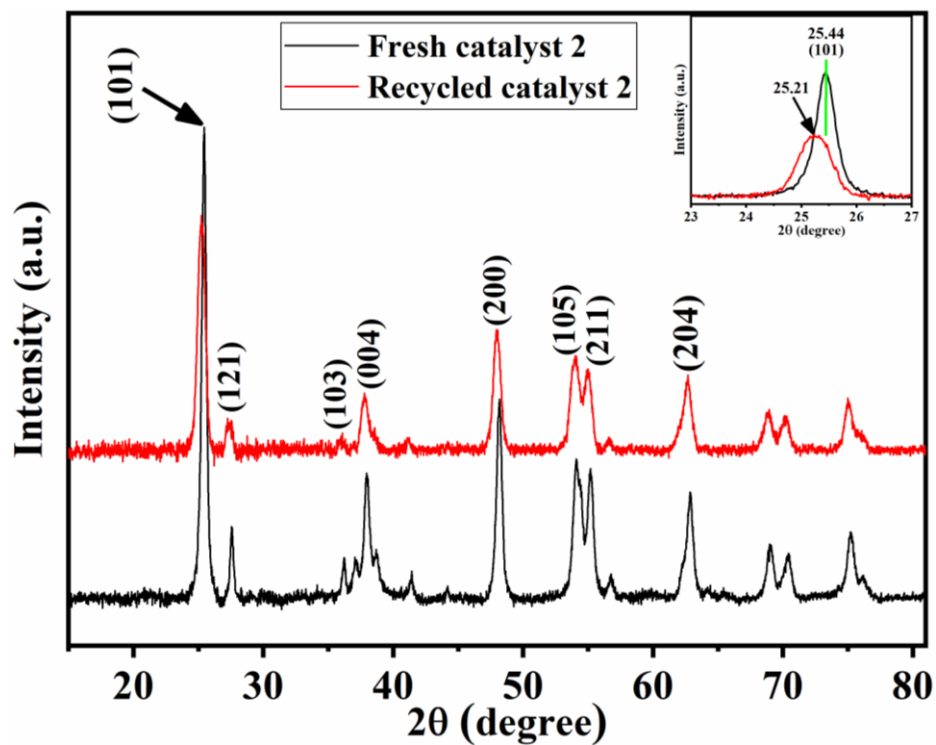


Fig. S4 XRD pattern of fresh and recycled catalyst $[W^{VI}O_2(hptb)(H_2O)]@APTMS-TiO_2$ (2). Inset shows the shift in the peak of (101) plane after the functionalization of titania.

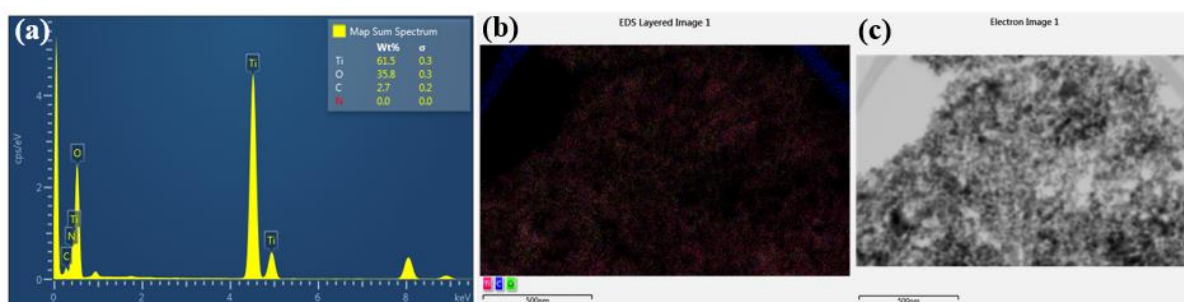


Fig. S5 (a) EDS spectrum, (b) EDS Layered image, and (c) Electron image of TiO_2 .

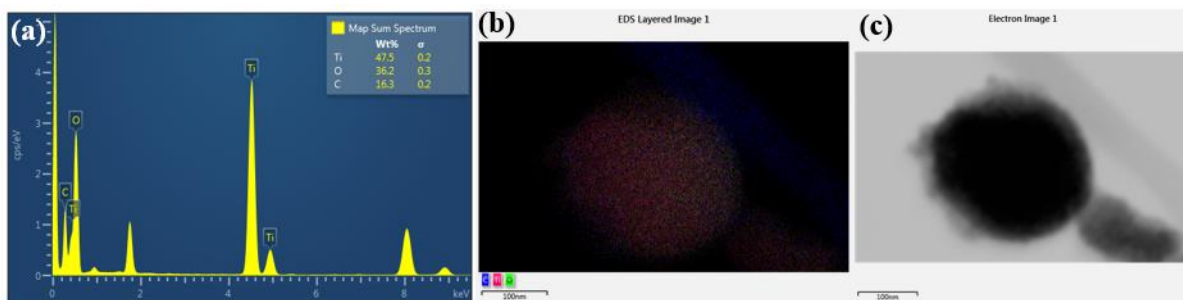


Fig. S6 (a) EDS spectrum, (b) EDS Layered image, and (c) Electron image of APTMS-TiO₂.

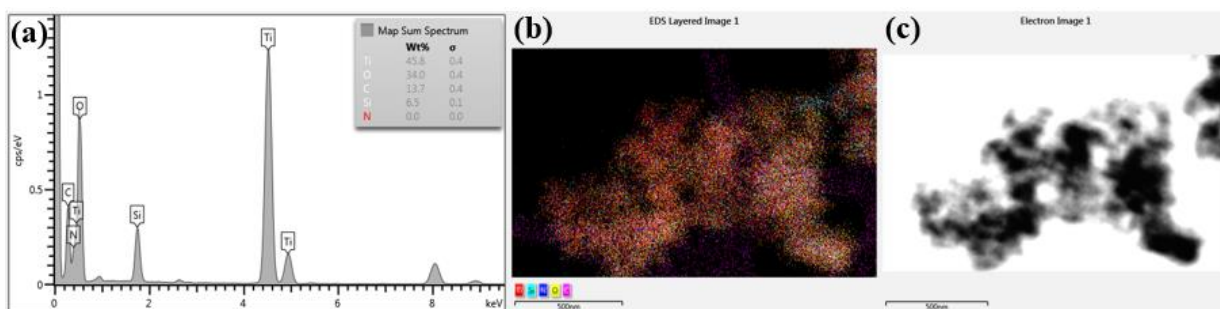


Fig. S7 (a) EDS spectrum, (b) EDS Layered image, and (c) Electron image of [H₂hptb]@APTMS-TiO₂ (II).

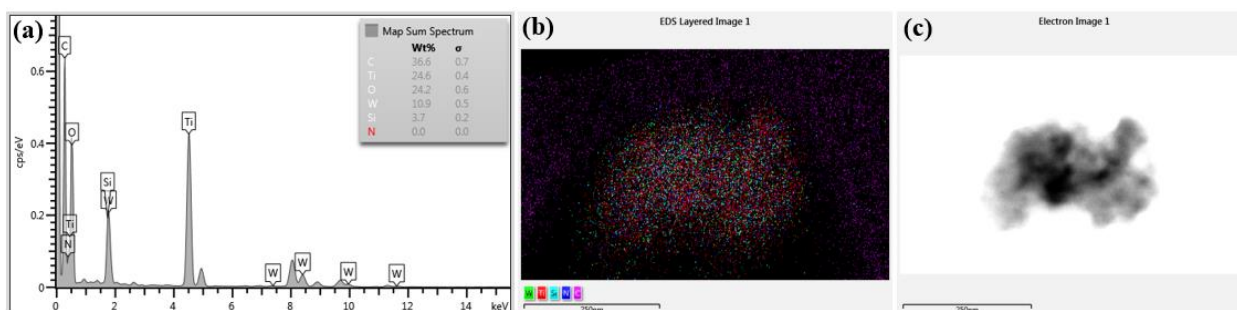


Fig. S8 (a) EDS spectrum, (b) EDS Layered image, and (c) Electron image of [W^{VI}O₂(hptb)(H₂O)]@APTMS-TiO₂ (2).

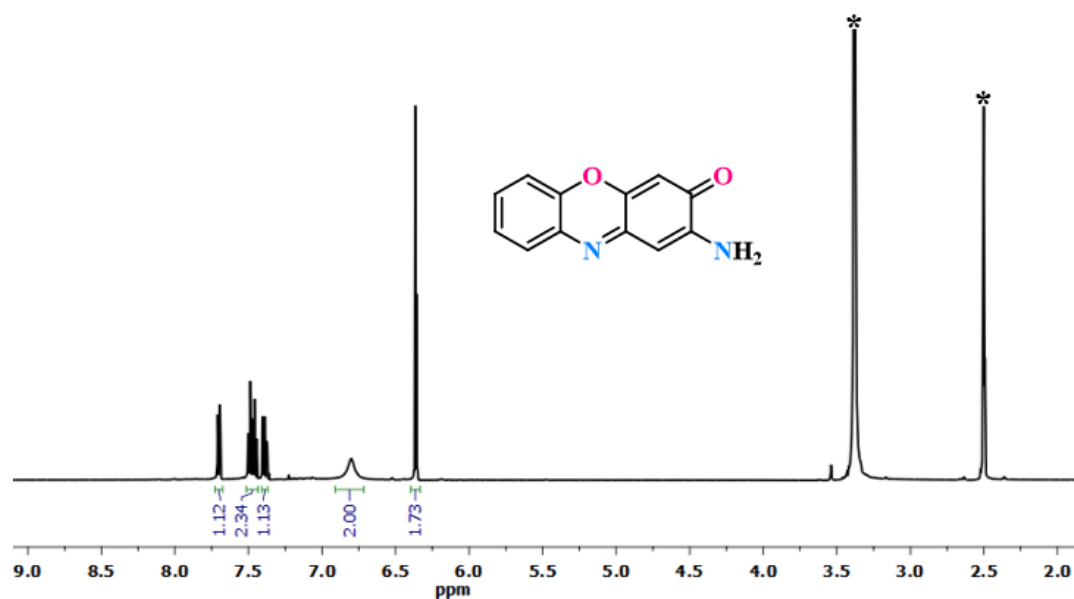


Fig. S9 ^1H NMR spectra of 2-amino-3H-phenoxazin-3-one (APX) recorded in DMSO- $[\text{d}_6]$. Asterisk (*) in the figure represents the proton impurity signal present in DMSO- d_6 at $\delta = 2.50$ ppm and that of moisture at $\delta = 3.35$ ppm.

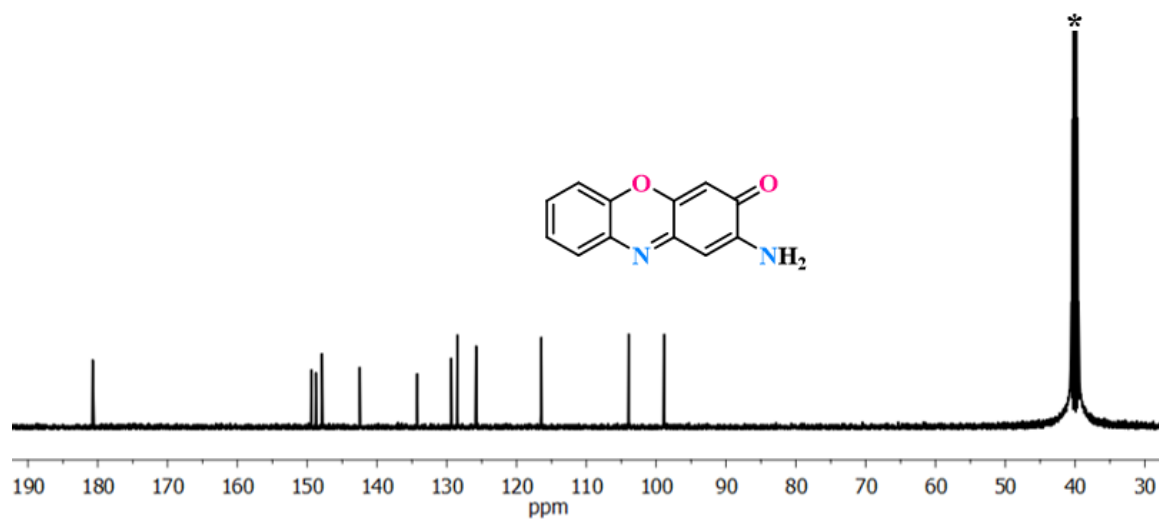


Fig. S10 ^{13}C NMR spectra of 2-amino-3H-phenoxazin-3-one (APX) recorded in DMSO- $[\text{d}_6]$.

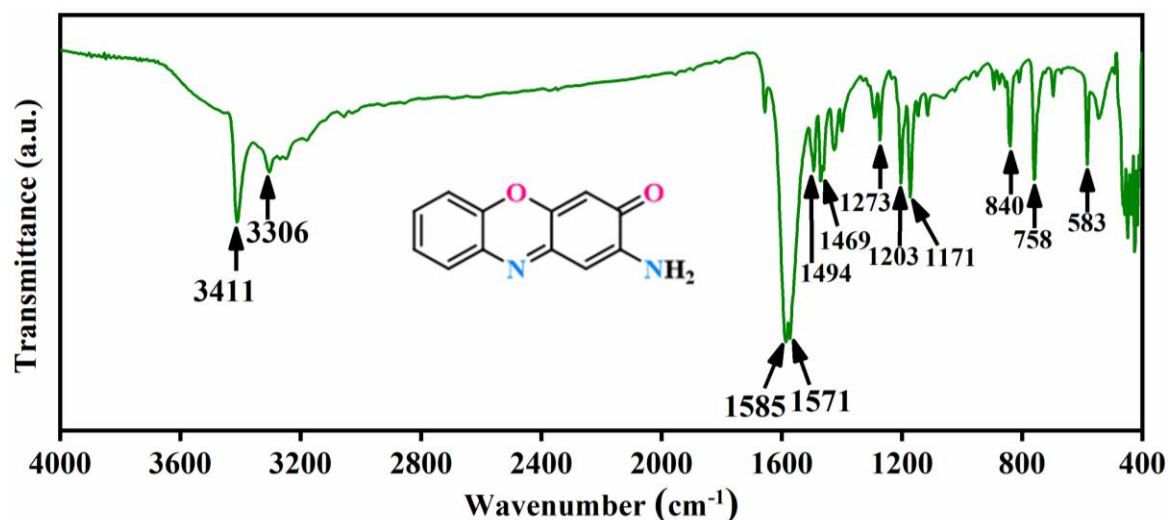


Fig. S11 IR spectrum of 2-amino-3H-phenoxazin-3-one (APX).

References

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