

Oxalate capped Iron Nano: From Methylene blue degradation to Bis(indolyl)methane synthesis

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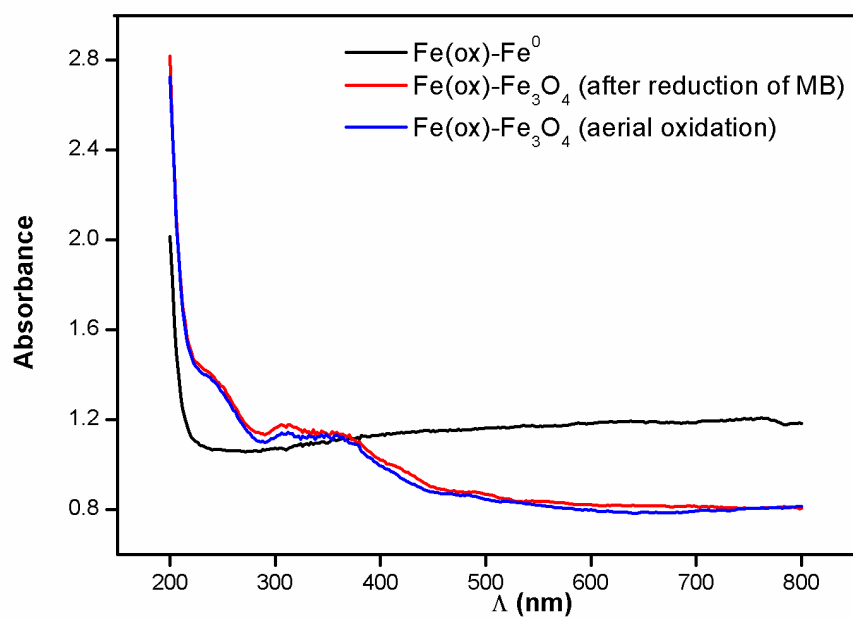


Fig. S1. UV-vis spectrum of Fe(ox)-Fe⁰, before and after the oxidation.

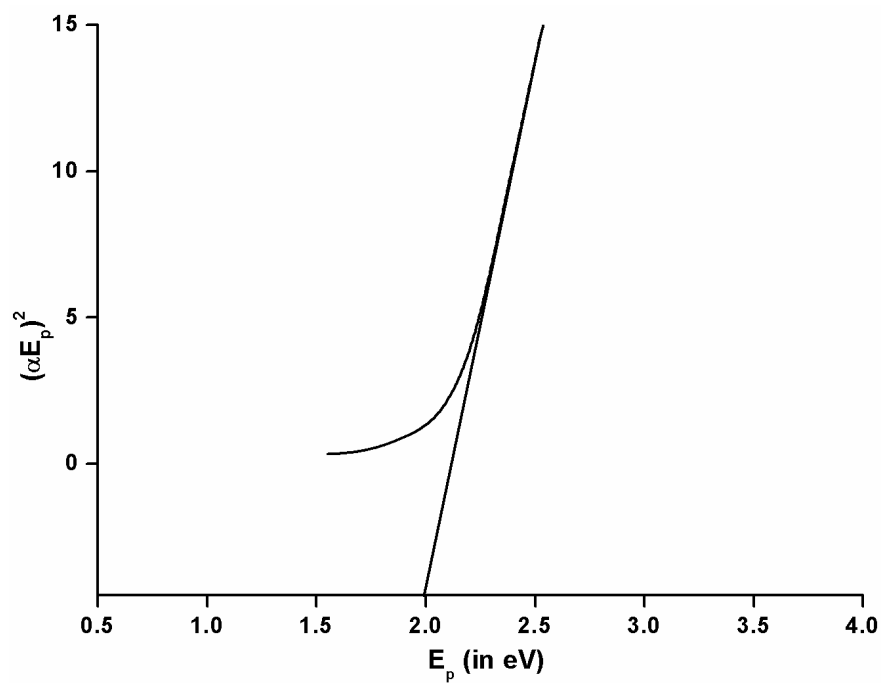


Fig. S2. Band gap value of Fe(ox)-Fe₃O₄.

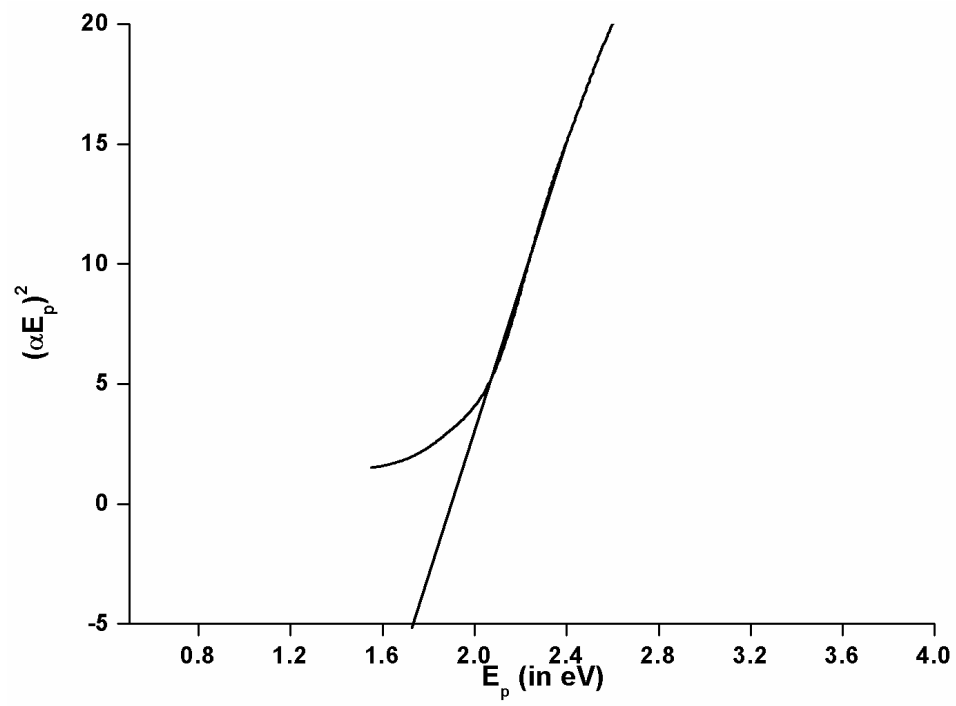


Fig. S3. Band gap value of Fe_3O_4 .

Synthesis of Iron Nano [Fe(ox)-Fe⁰]. . .

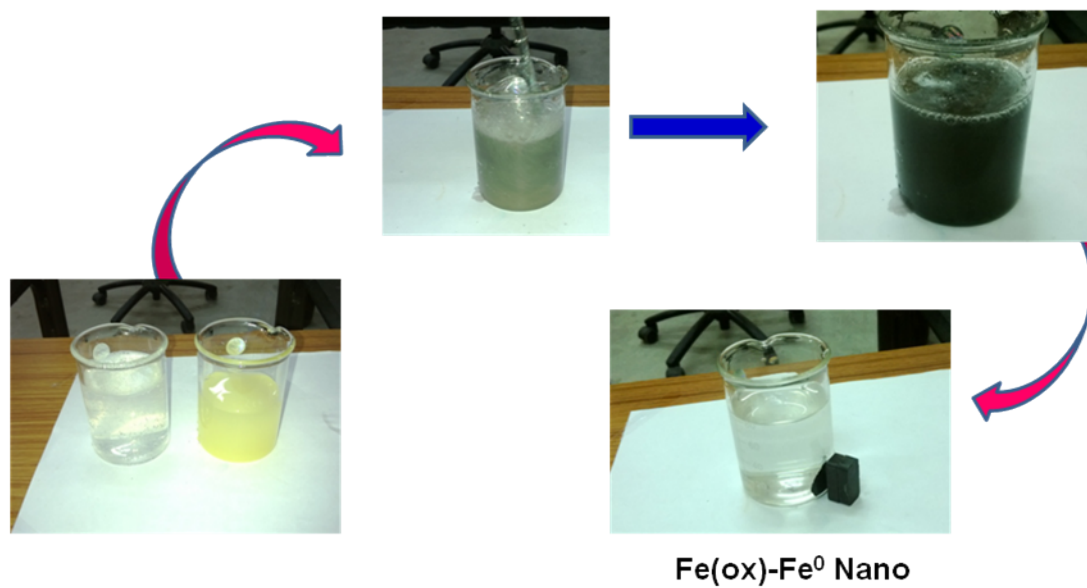


Fig. S4. Synthetic procedure of Fe(ox)-Fe⁰.

Characterization of Oxidized product (Reddish-Brown Material) . . .

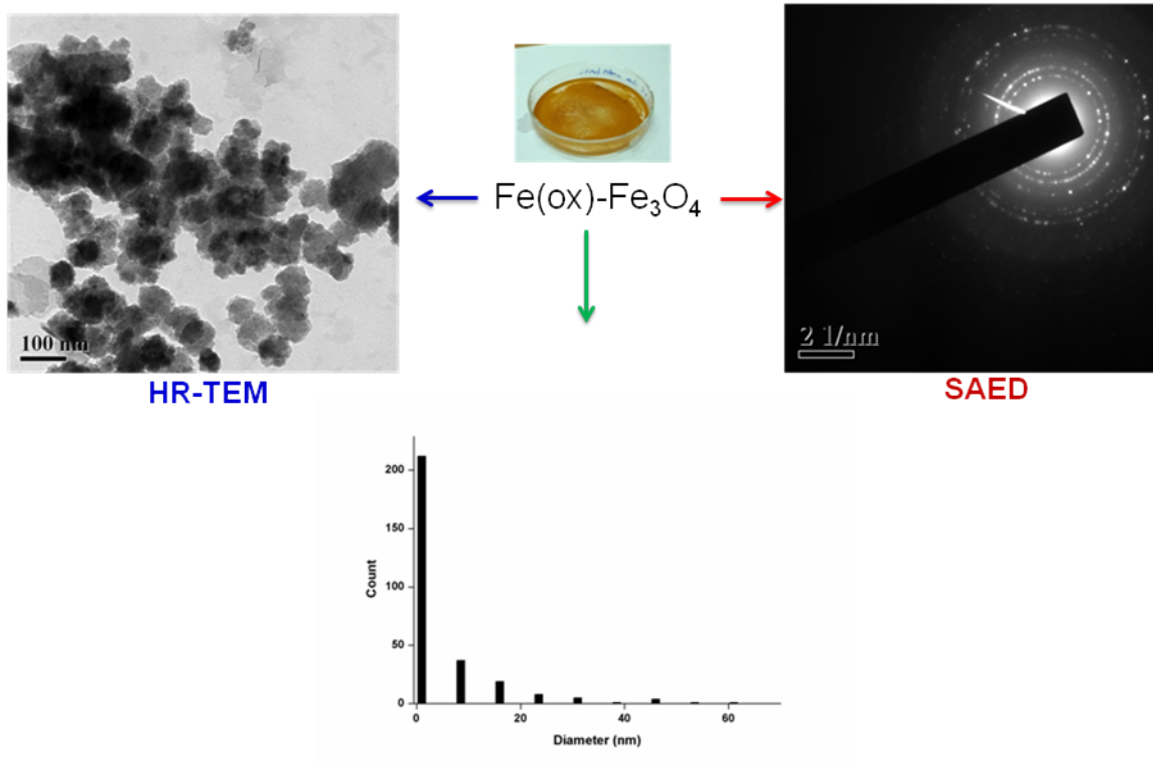


Fig. S5. TEM, particle distribution, and SAED pattern of Fe₃O₄.

TEM and Particle Distribution of Iron Nano [Fe(ox)-Fe⁰]. . .

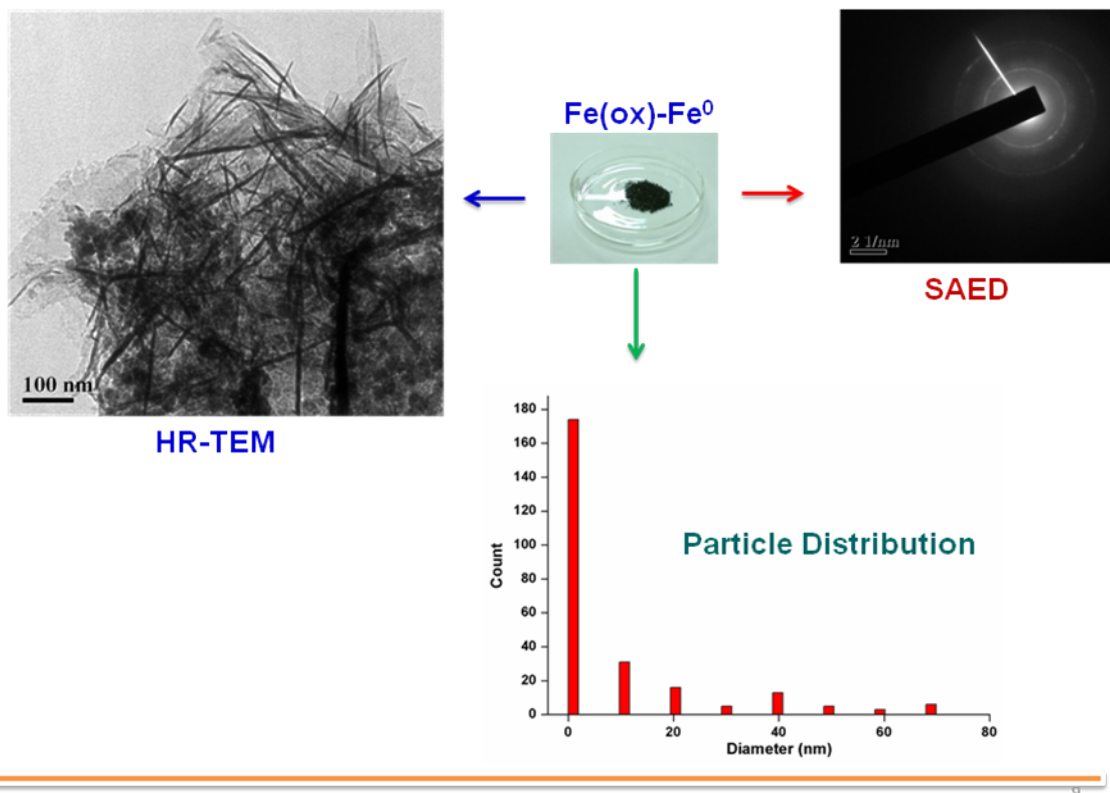
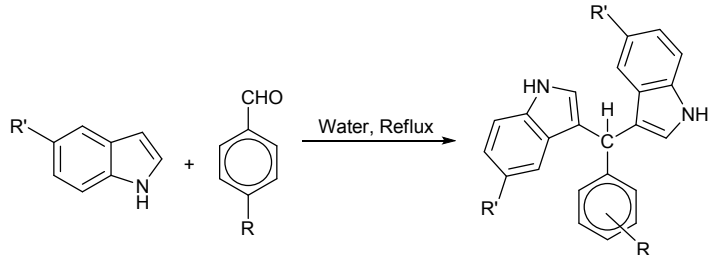


Fig. S6. TEM, particle distribution, and SAED pattern of Fe(ox)-Fe⁰.

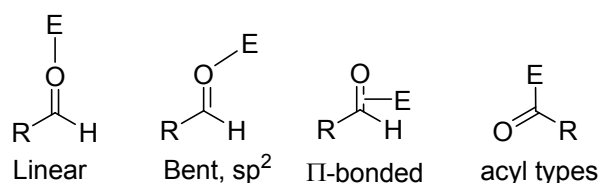
Table S1 condensation reaction between aldehyde and indoles in water


#	R	R'	Product	Time (h)	Yield (%)
3	Br	H	1c	6	21
4	Me	H	1b	6	8
7	NO ₂	Br	1g	6	12
8	Me	OMe	1h	6	10
10	H	OMe	1j	6	<5

Involvement of Fe(ox)-Fe₃O₄ as a catalyst in the condensation reaction between aldehydes and indoles:

There are several different possible modes of coordination of carbonyl group to metal catalysts. Mainly four types of coordination modes of aldehyde have been proposed (scheme 1).¹

Scheme 1. Possible coordination mode of aldehyde with metal catalyst



It is expected that after binding of C=O to metal catalyst, there must be a shift in both the C=O and C-H stretching band of aldehyde as compared to free aldehyde. The material was prepared for the study by grinding the 1:1 mixture of aldehyde and catalyst in a motor pestle for 0.5 h. The two material; Fe₃O₄ and Fe(ox)-Fe₃O₄ was chosen for the study. The FTIR spectra of free 4-bromo benzaldehyde (**2a**) shows two peaks at 2763 and 2855 cm⁻¹ due to C-H stretching vibration and another two peaks at 1693 and 1577 cm⁻¹ due the C=O stretching vibration of **2a**. In the mixture of **2a** and Fe(ox)-Fe₃O₄, the C-H stretching vibration at 2763 cm⁻¹ of **2a** shifted to lower wavenumber, which indicates the binding of **2a** with Fe(ox)-Fe₃O₄ catalyst (Fig. S7). On the other hand the C=O stretching vibration at 1693 for free **2a** also shifted to lower wavenumber in the mixture of **2a** and Fe(ox)-Fe₃O₄ sample (Fig. S8), which also suggested the interaction of

2a with Fe(ox)-Fe₃O₄. In case of Fe₃O₄ material, less shift of C=O and C-H stretching vibration was observed as compared to Fe(ox)-Fe₃O₄.

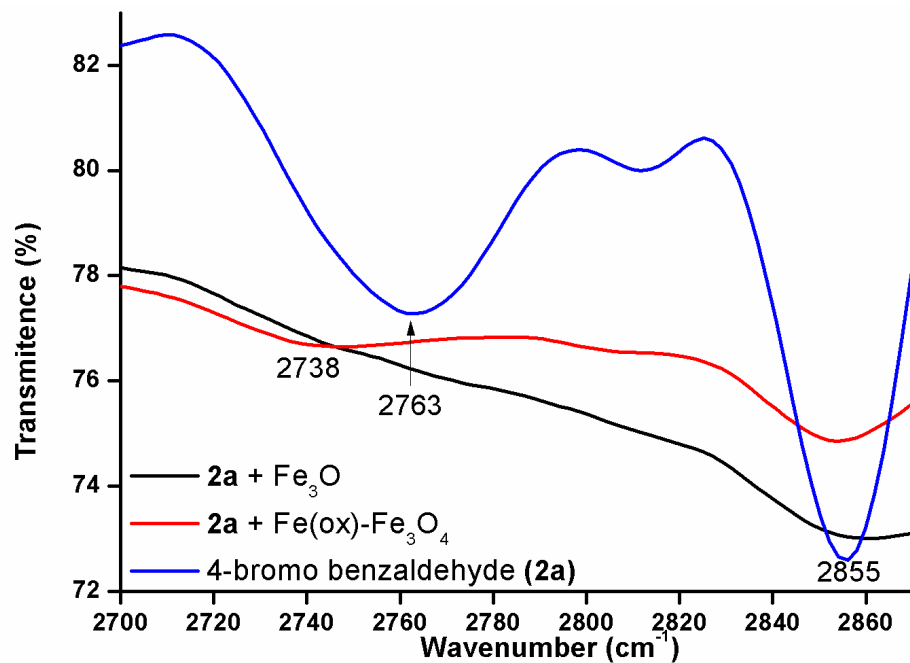


Fig. S7. FTIR spectra of 4-bromo benzaldehyde (C-H stretching band) on Fe₃O₄ and Fe(ox)-Fe₃O₄.

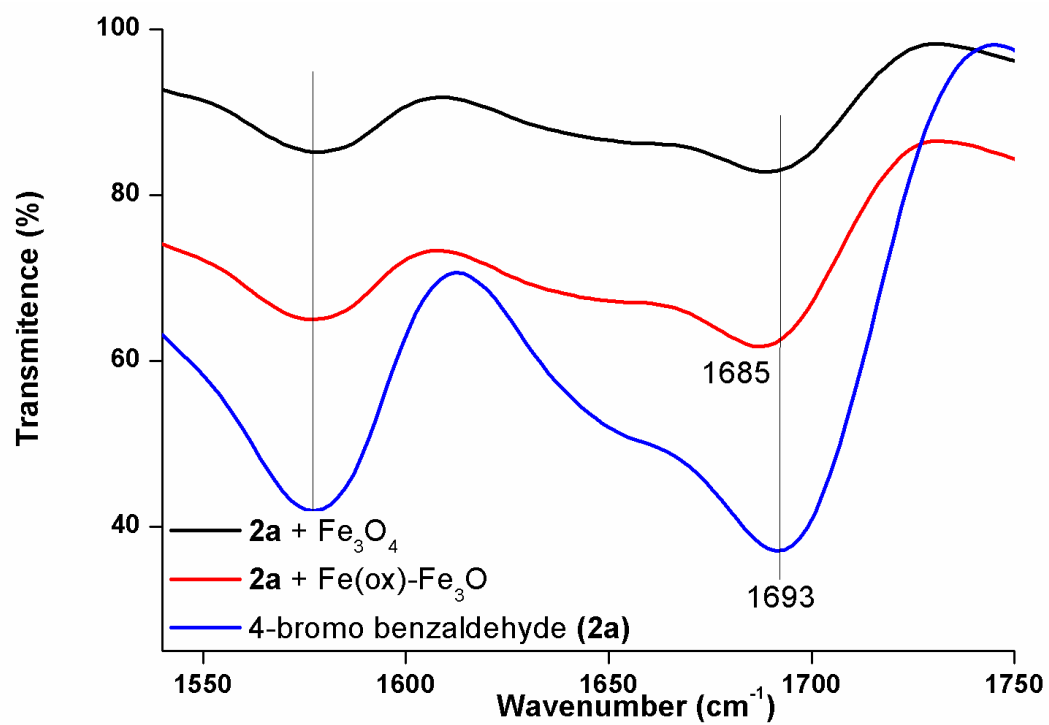


Fig. S8. FTIR spectra of 4-bromo benzaldehyde (C-O stretching band) on Fe_3O_4 and Fe(ox)- Fe_3O_4 .

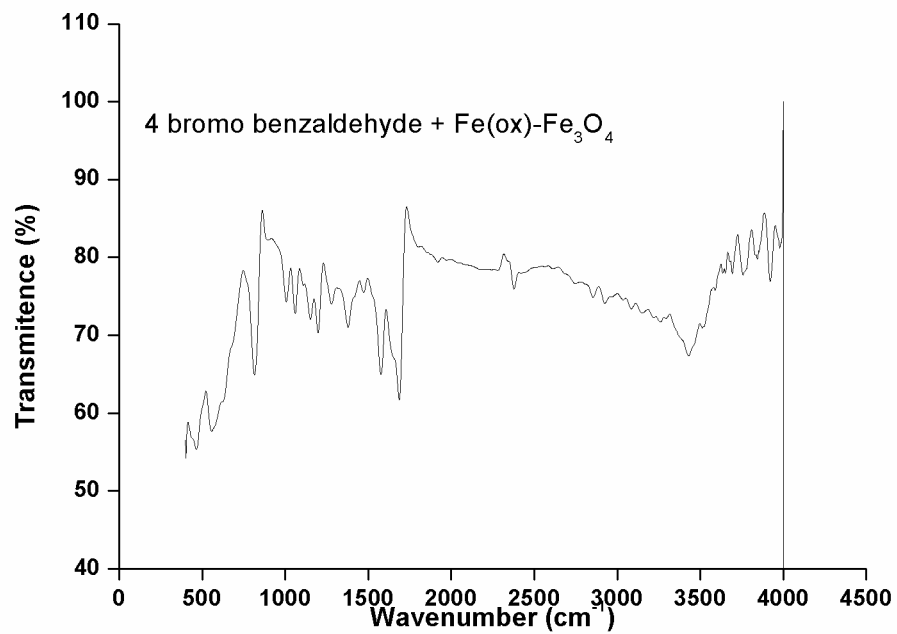


Fig. S9. FTIR spectra of 4-bromo benzaldehyde on $\text{Fe(ox)-Fe}_3\text{O}_4$.

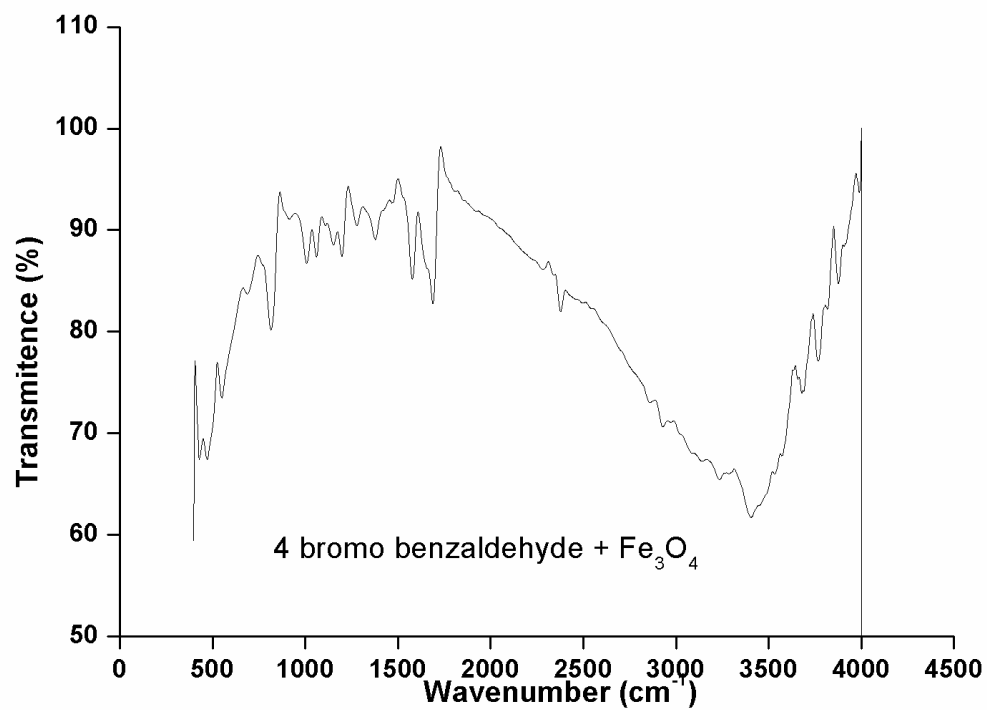


Fig. S10. FTIR spectra of 4-bromo benzaldehyde on Fe_3O_4 .

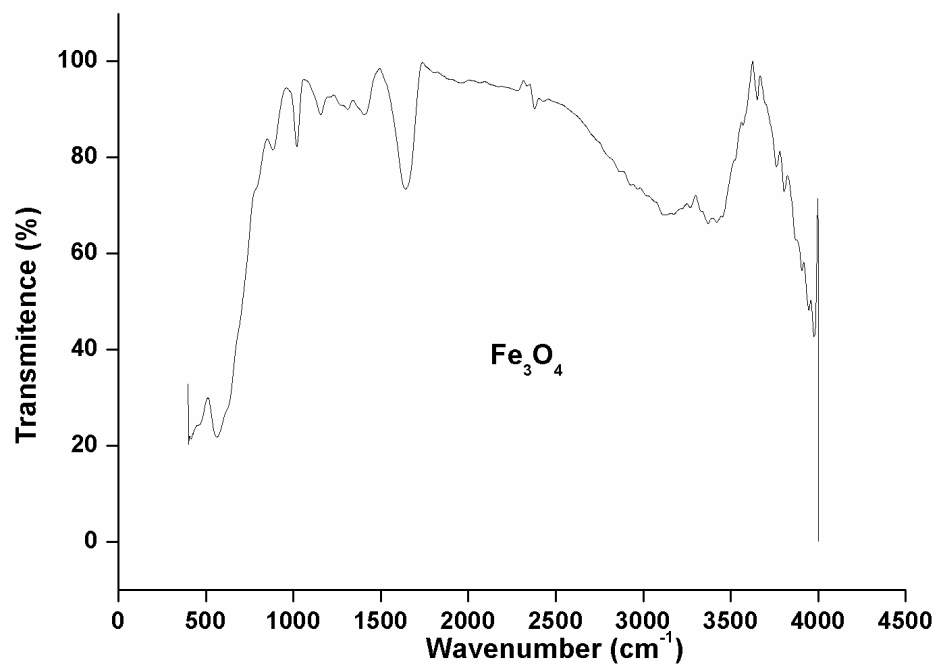


Fig S11. FTIR spectra of Fe_3O_4 .

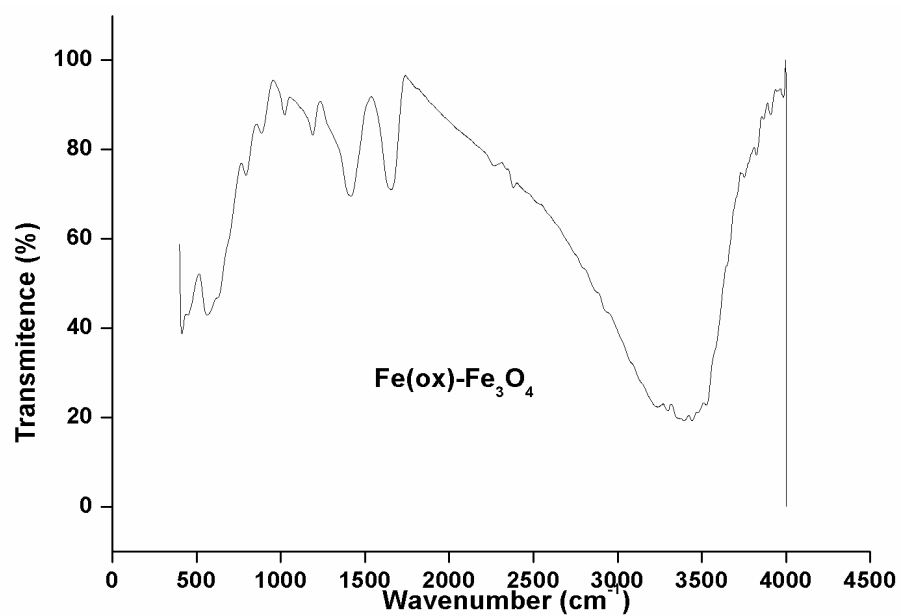


Fig S12. FTIR spectra of $\text{Fe(ox)-Fe}_3\text{O}_4$.

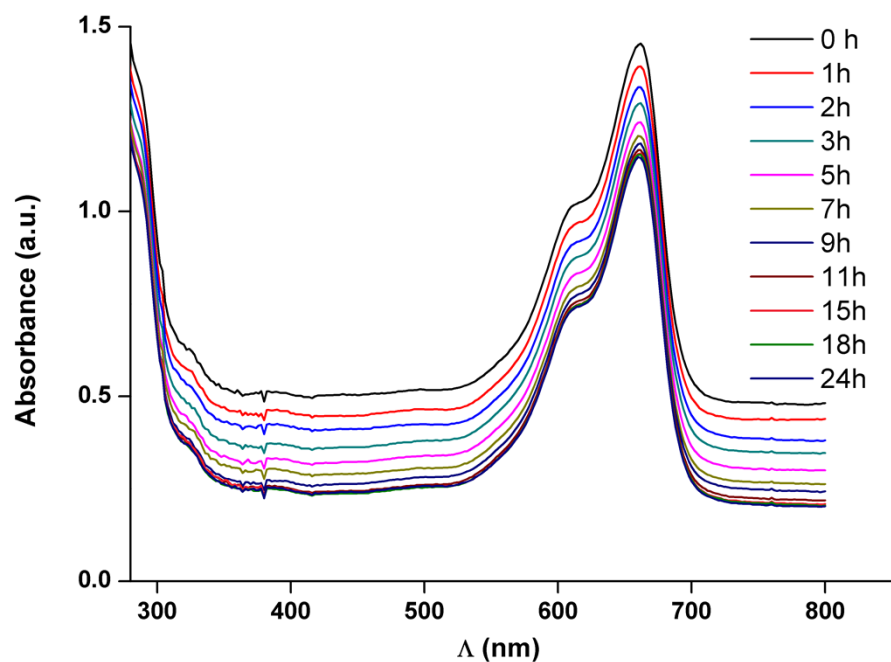


Fig S13. Absorbance *versus* wavelength plot of Fe(ox)-Fe₃O₄ promoted reaction of methylene blue in dark.

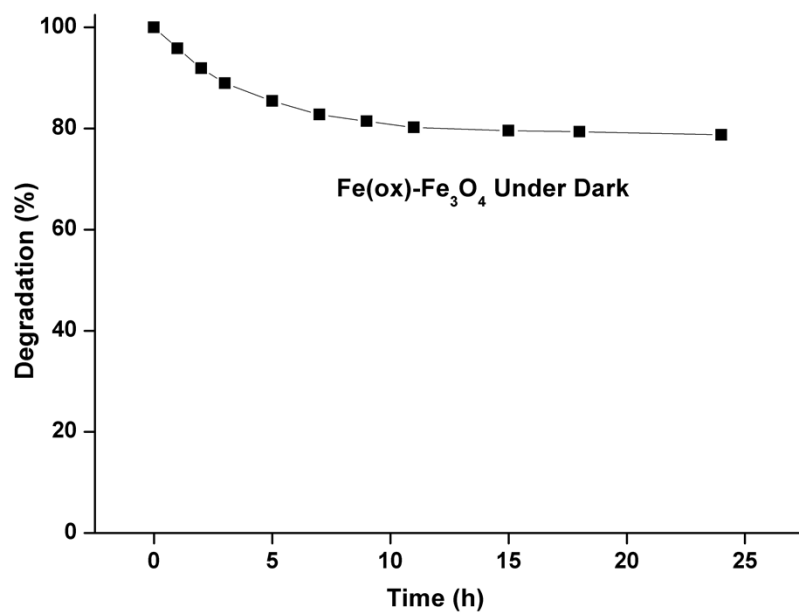


Fig S14. Degradation (%) *versus* time plot of Fe(ox)-Fe₃O₄ promoted reaction of methylene blue in dark.

Fig S15. ^1H and ^{13}C NMR spectrum of compound **1a** in acetone- d_6

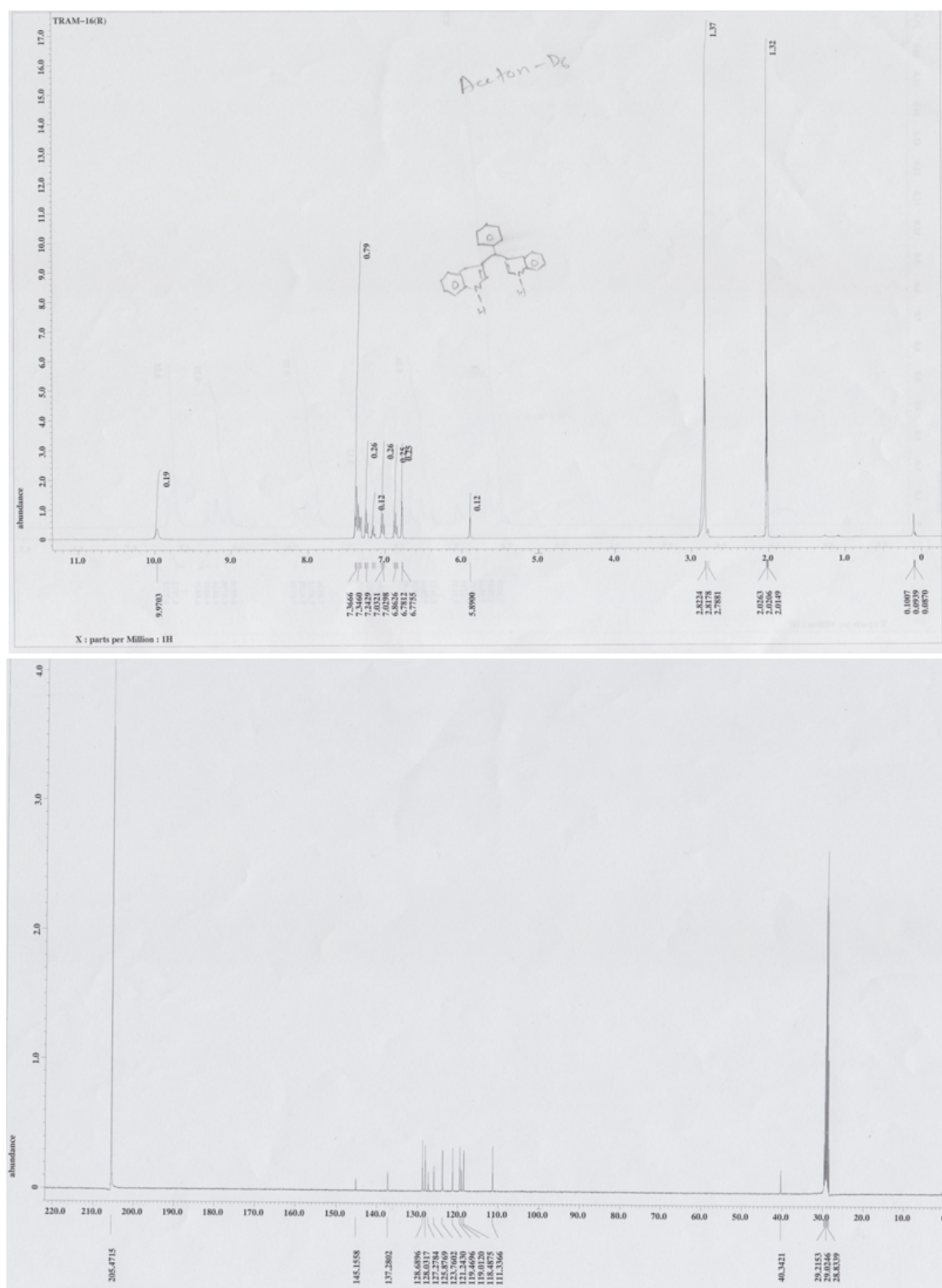


Fig S16. ^1H and ^{13}C NMR spectrum of compound **1b** in acetone- d_6

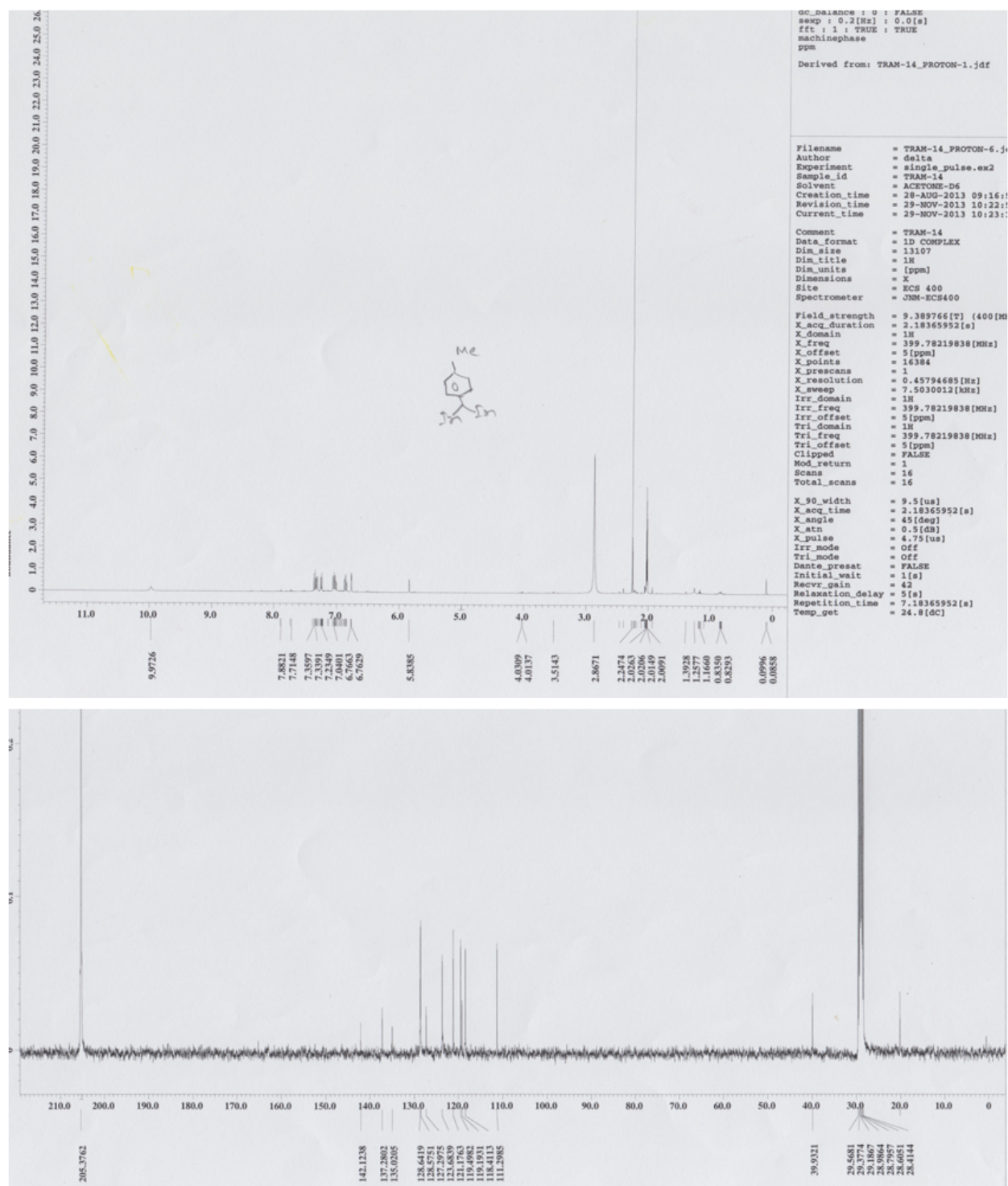


Fig S17. ^1H and ^{13}C NMR spectrum of compound **1c** in DMSO- d_6

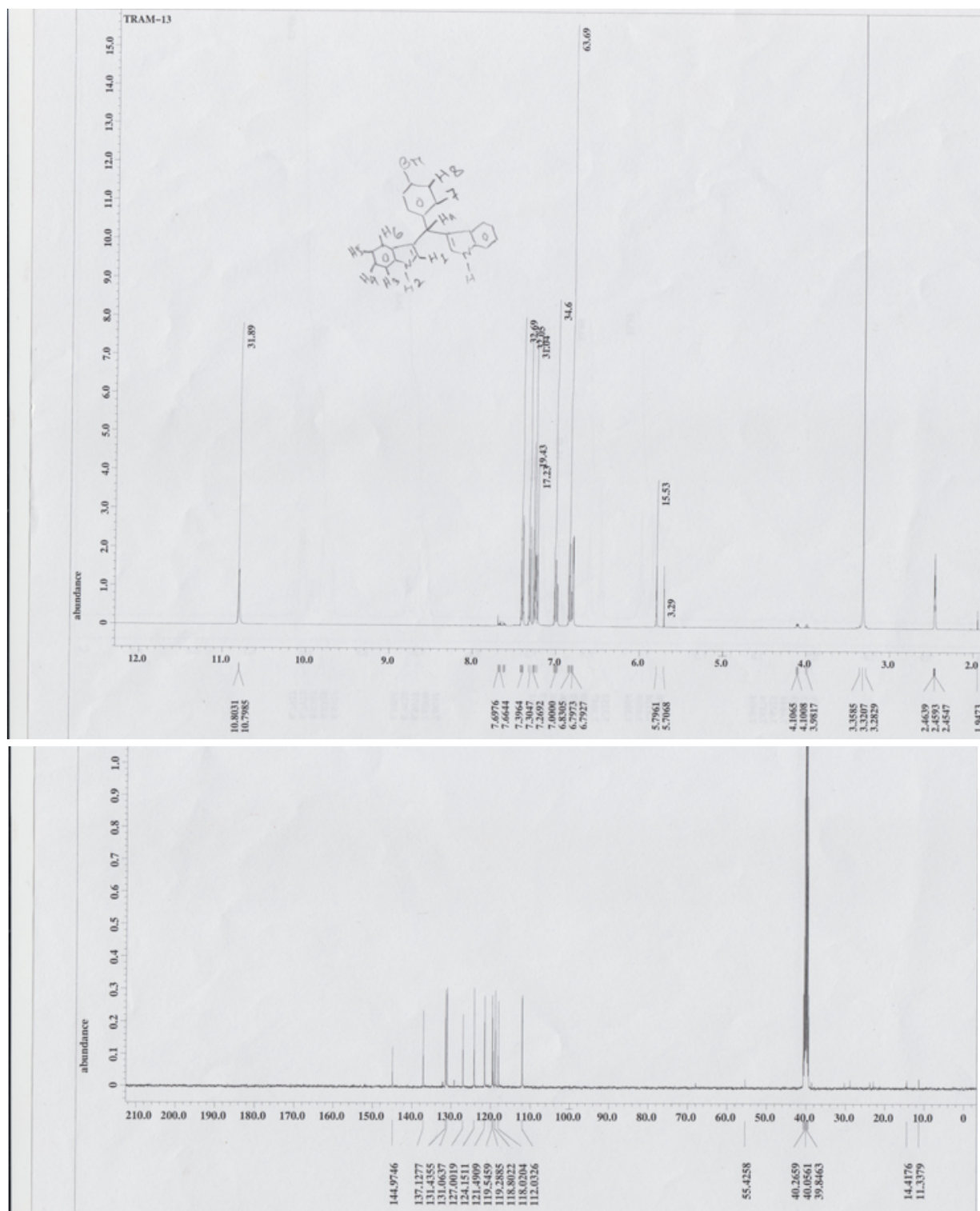


Fig S18. ^1H and ^{13}C NMR spectrum of compound **1d** in Acetone- d_6

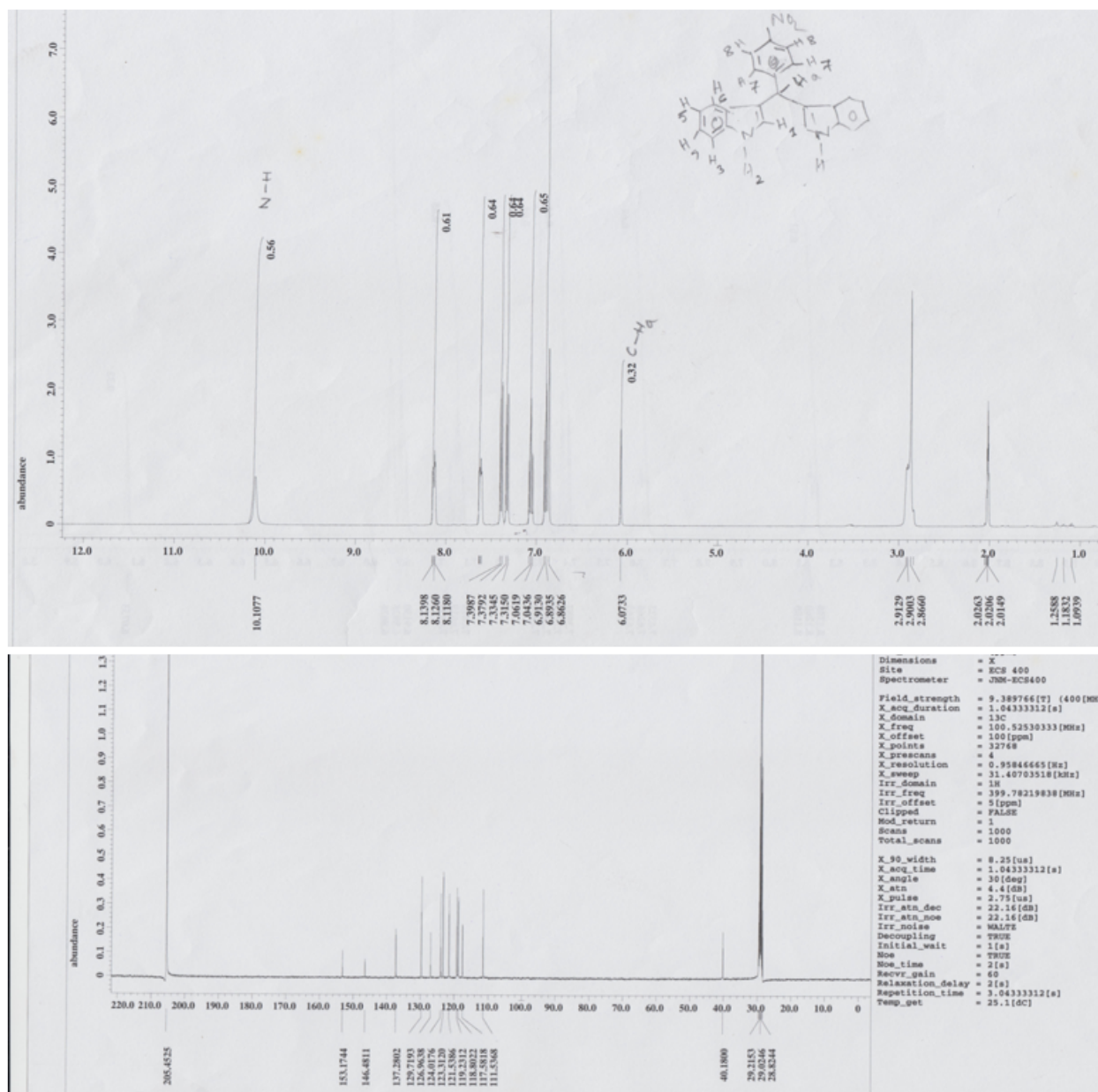


Fig S19. ^1H and ^{13}C NMR spectrum of compound **1e** in Acetone- d_6

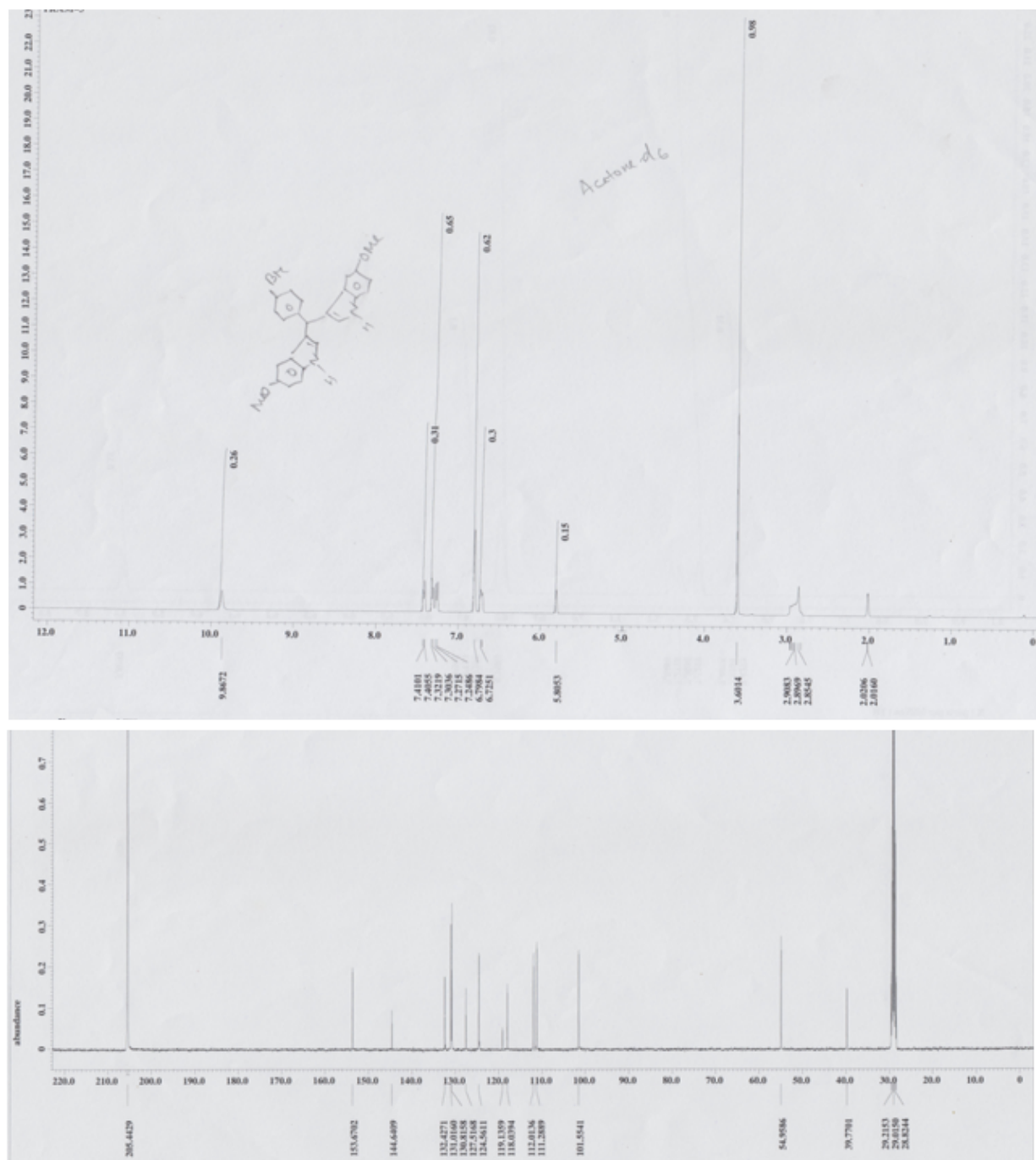


Fig S20. ^1H and ^{13}C NMR spectrum of compound **1f** in Acetone- d_6

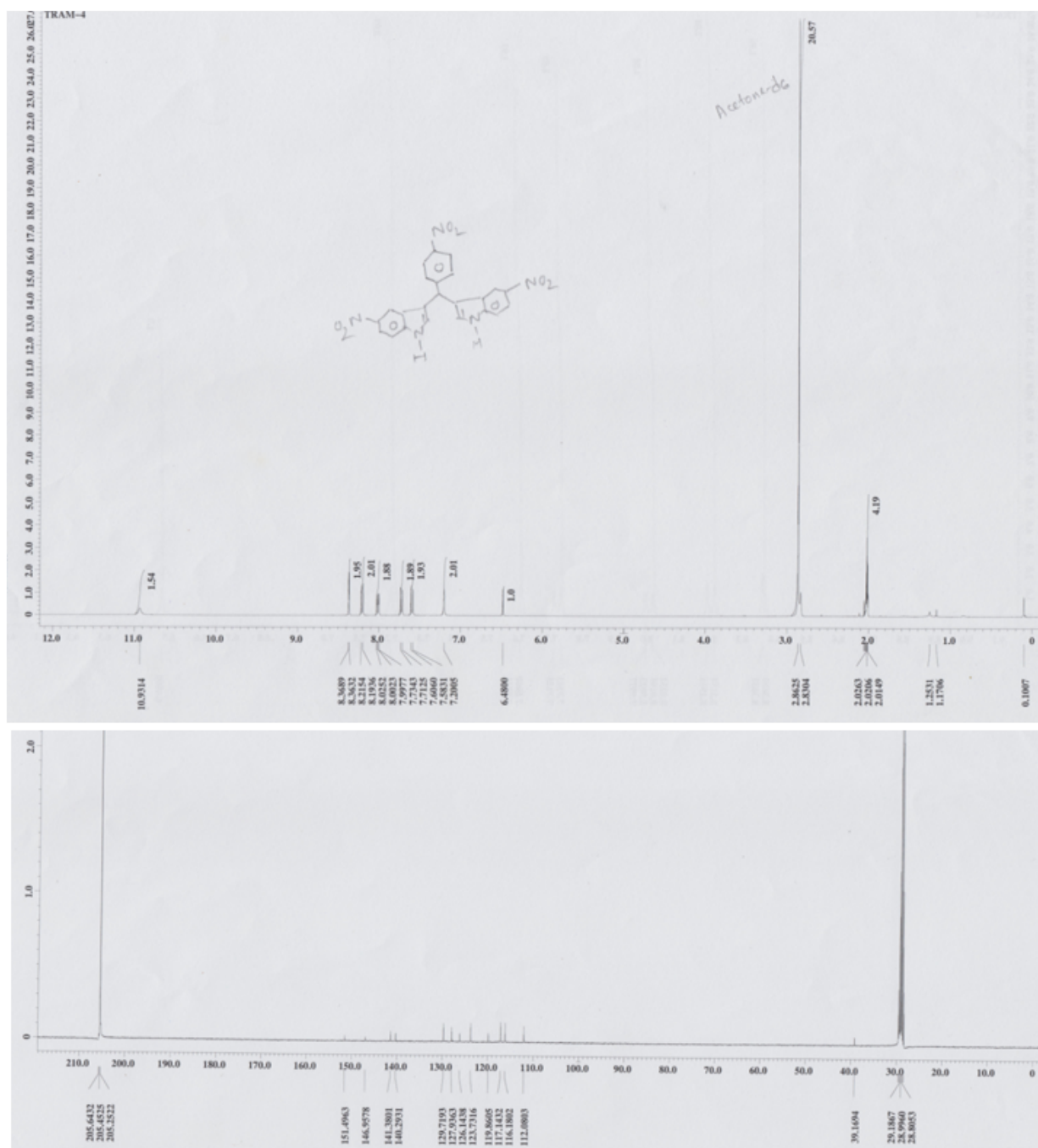


Fig S21. ^1H and ^{13}C NMR spectrum of compound **1g** in Acetone- d_6



Fig S22. ^1H and ^{13}C NMR spectrum of compound **1h** in Acetone- d_6

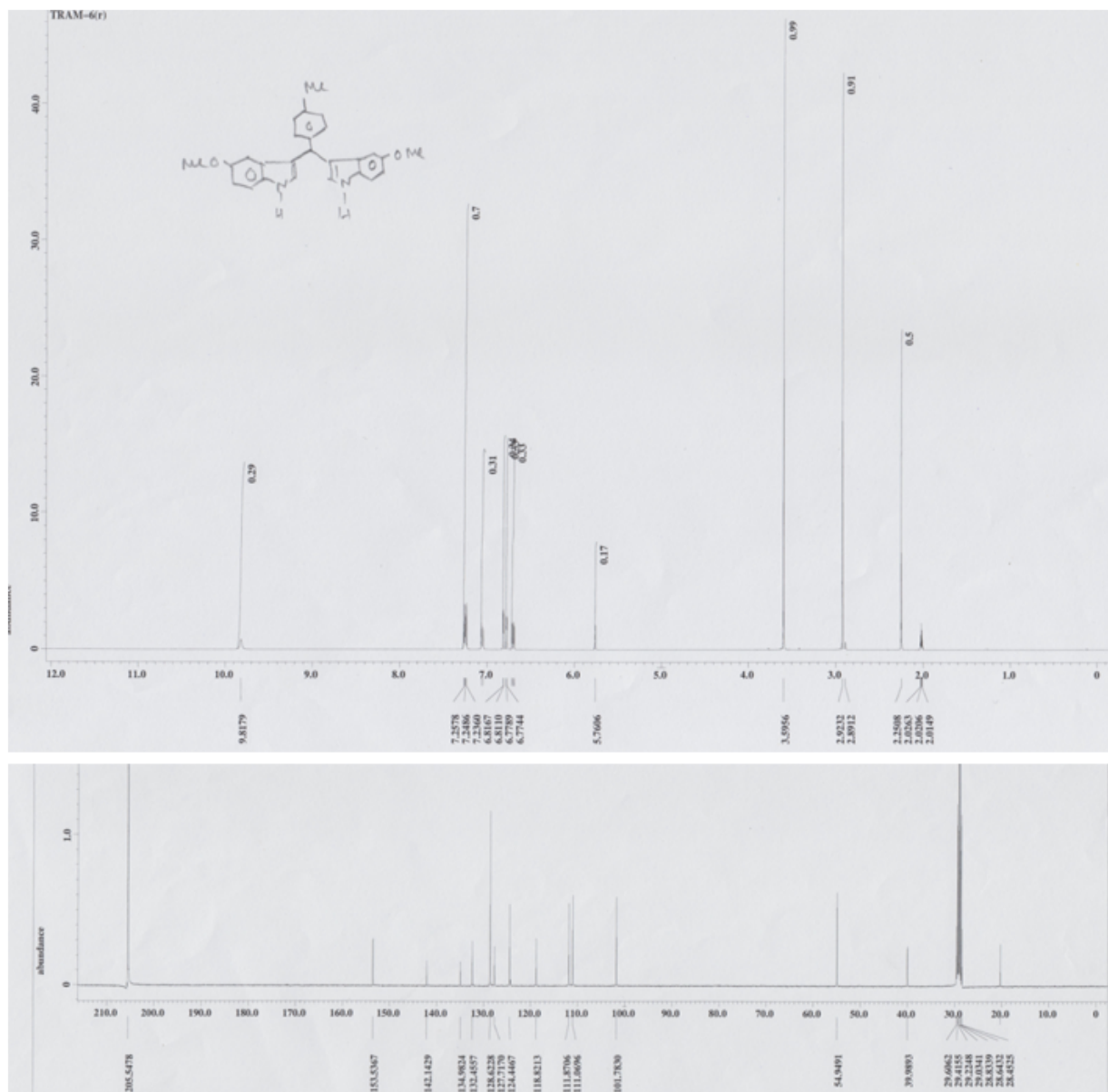


Fig S23. ^1H and ^{13}C NMR spectrum of compound **1i** in Acetone- d_6

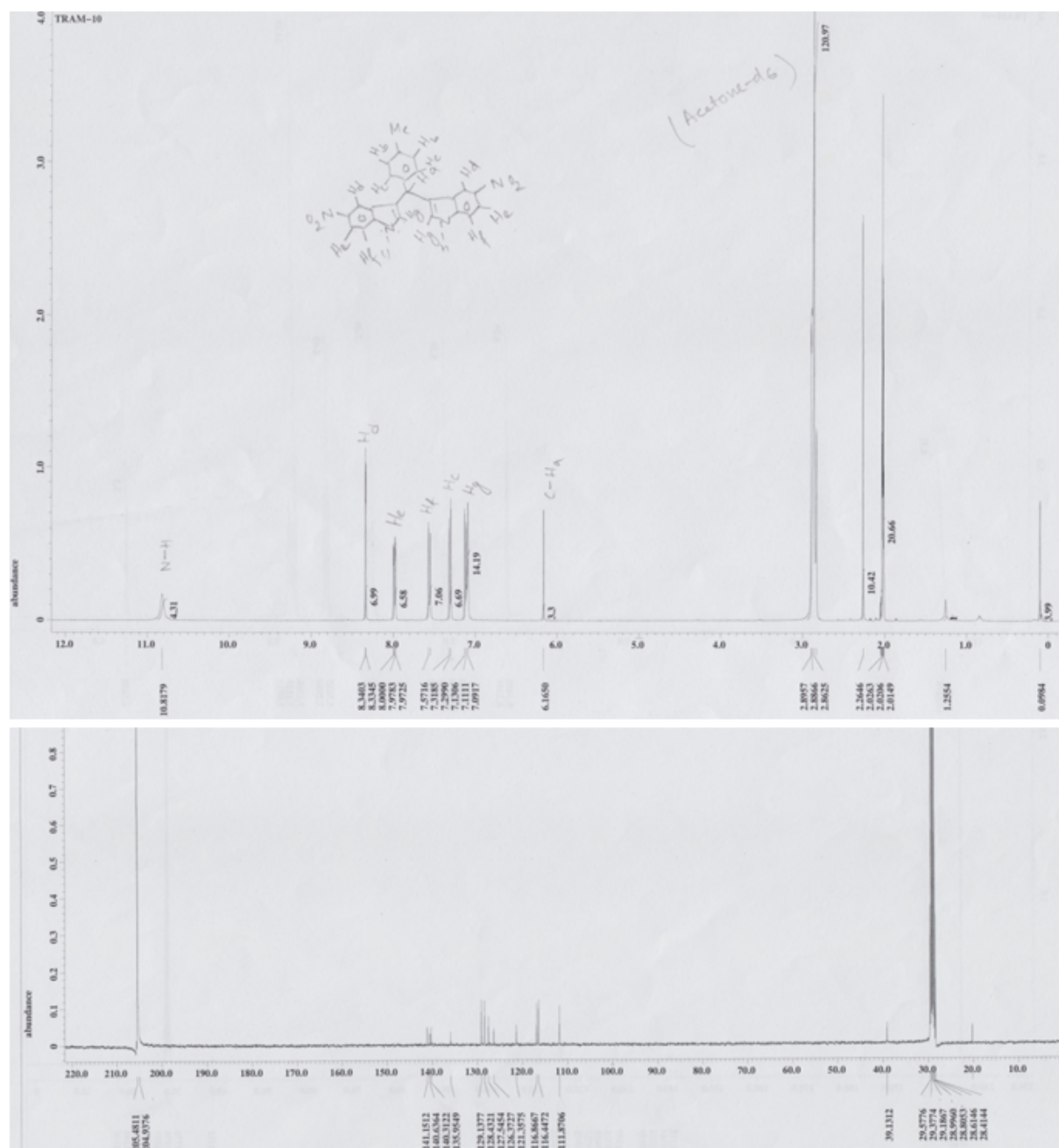
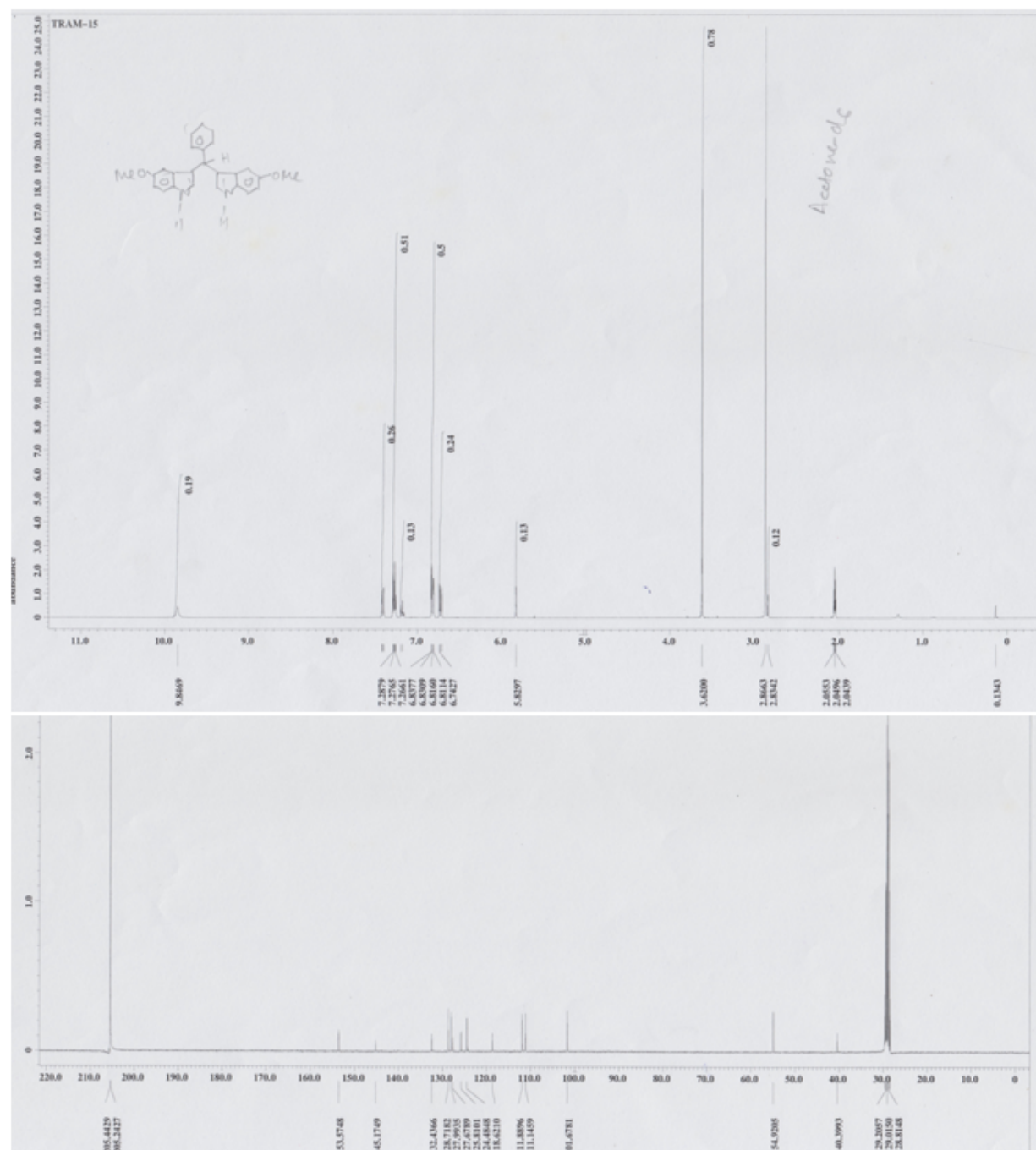


Fig S24. ^1H and ^{13}C NMR spectrum of compound **1j** in Acetone- d_6



References:

- ¹ (a) T. J. LuPage and Kenneth B. Wiberg, *J. Am. Chem. Soc.*, 1988, **110**, 6643. (b) R. Gaba, M. Bhandari and R. Kakkar, *Adv. Mat. Lett.* 2013, **4**, 769. (c) J. Álvarez-Rodríguez, M. Cerro-Aarçon, A. Guerrero-Ruiz, I. Rodríguez-Ramos and A. Arcoya, *Appl. Catal., A*, 2008, **348**, 241. (d) A. Stolle, T. Gallert, C. Schmöger and B. Ondruschka, *RSC Adv.*, 2013, **3**, 2112 and references therein.