Electronic Supplementary Information(ESI)

Selective Electro-oxidation of Phenol to 1,4-Hydroquinone Employing Carbonaceous Electrodes: Surface Modification is the Key

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Cyclic Voltammetry Mesurements :

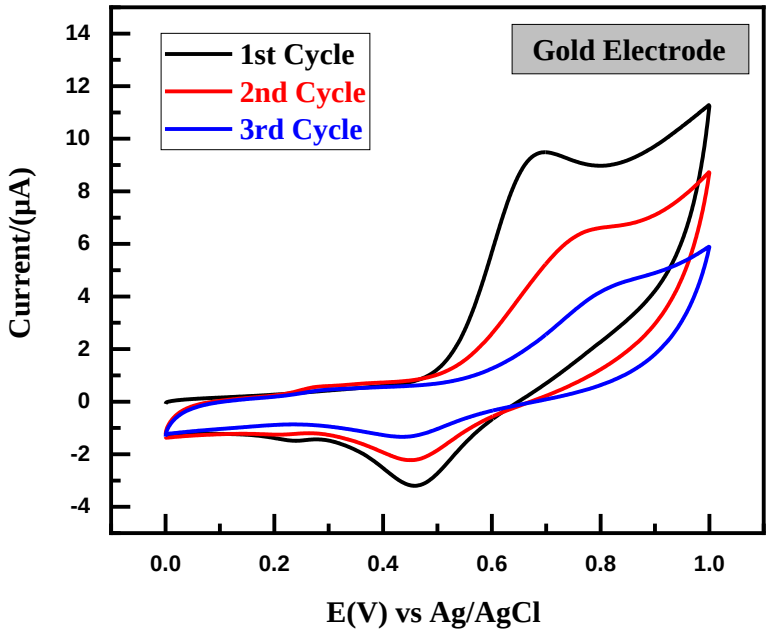


Figure S1. Cyclic voltammogram of phenol (1.0 mM) on gold electrode for 3 cycles with 0.1 M KNO_3 at a scan rate of 100 mVs^{-1}.

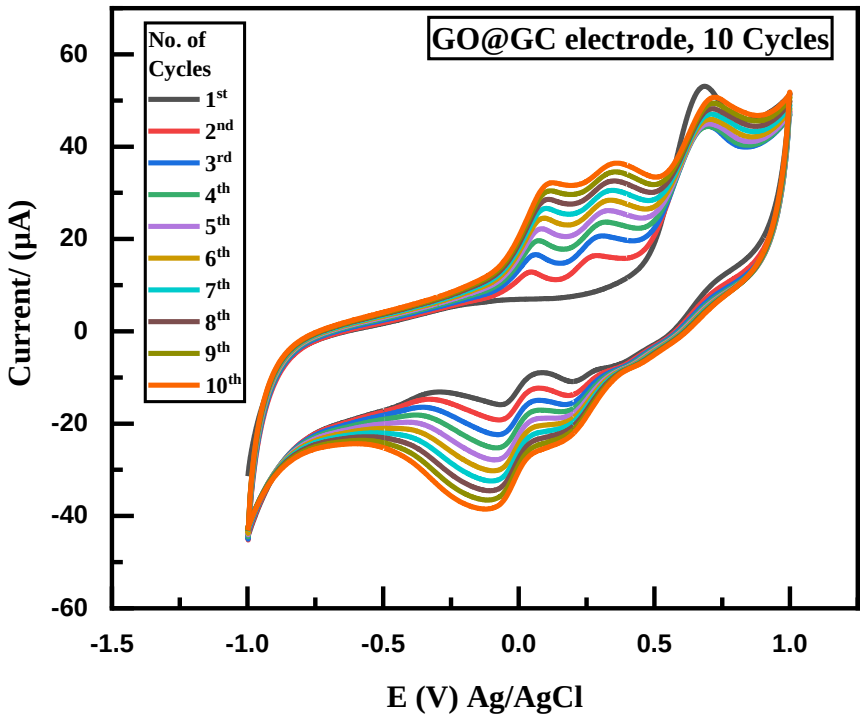


Figure S2. Cyclic voltammogram of phenol (1.0 mM) on GO coated glassy carbon electrode for 10 cycles with 0.1 M KNO_3 at a scan rate of 100 mVs^{-1}.

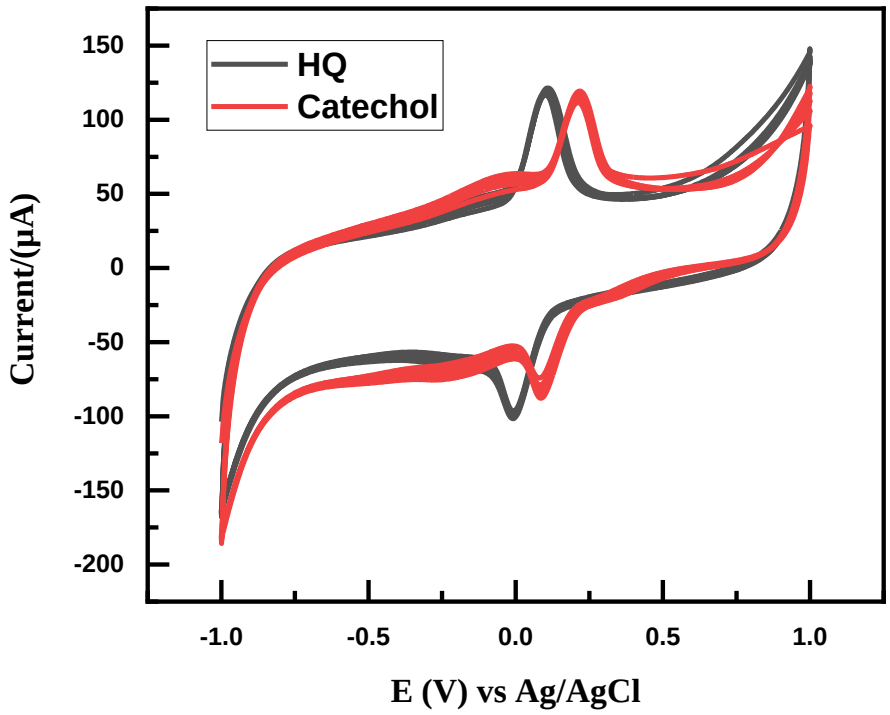


Figure S3. An overlayed cyclic voltammograms of hydroquinone (HQ; 1.0 mM) and catechol (1.0 mM) on GO@GCelectrode for 5 cycles each in 0.1 M KNO_3 at a scan rate of 100 mVs^{-1}.

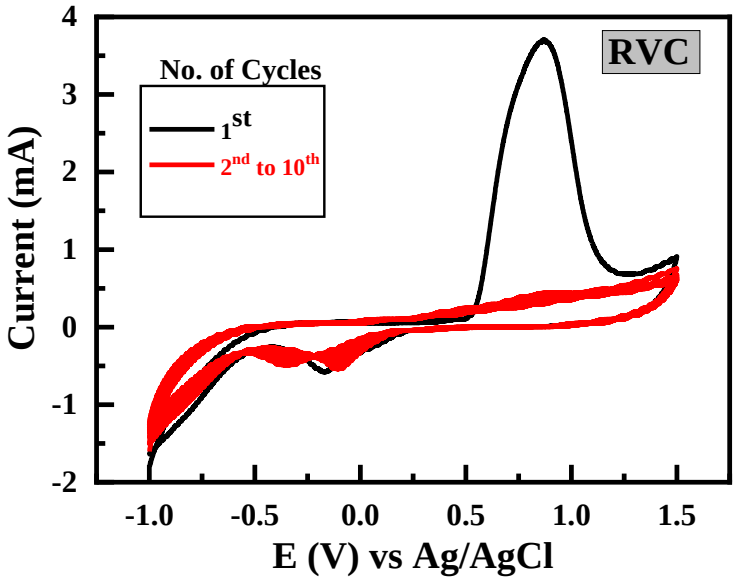


Figure S4. A cyclic voltammogram of of phenol (1.0 mM) on RVC for 10 cycles in 0.1 M PBS at a scan rate of 100 mVs^{-1}.

Raman Analysis of Carbonaceous Materials:

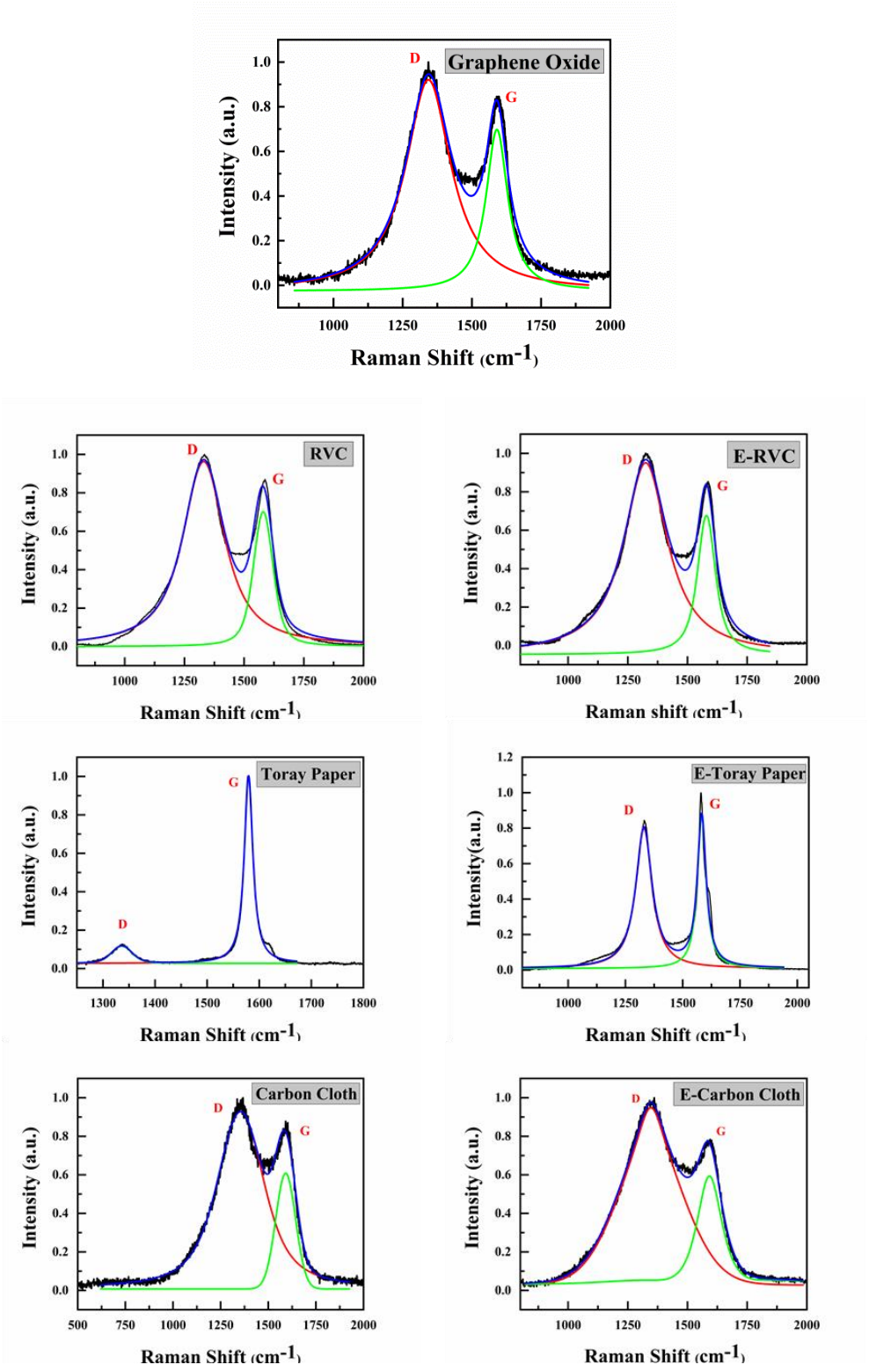


Figure S5. Raman spectra of various carbonaceous materials before and after electrochemical treatment under acidic conditions. The spectra have been de-convoluted to obtain the intensities of D and G bands. The letter "E" has been added to the respective names of electrochemically acid treated carbon materials.

Table S1. The ratios of intensity of G band to the D band (I_G/I_D) of different carbonaceous materials before and after electrochemical treatment.

Sr. No.	Carbonaceous material	I_G/I_D	
1	Graphene oxide	0.7303	
		Before electro-chemical treatment	After electro-chemical treatment
2	RVC	0.7560	0.7209
3	Toray Carbon Paper	8.8015	1.1111
4	Carbon Cloth	0.6584	0.6333

XPS Analysis of Carbonaceous Materials:

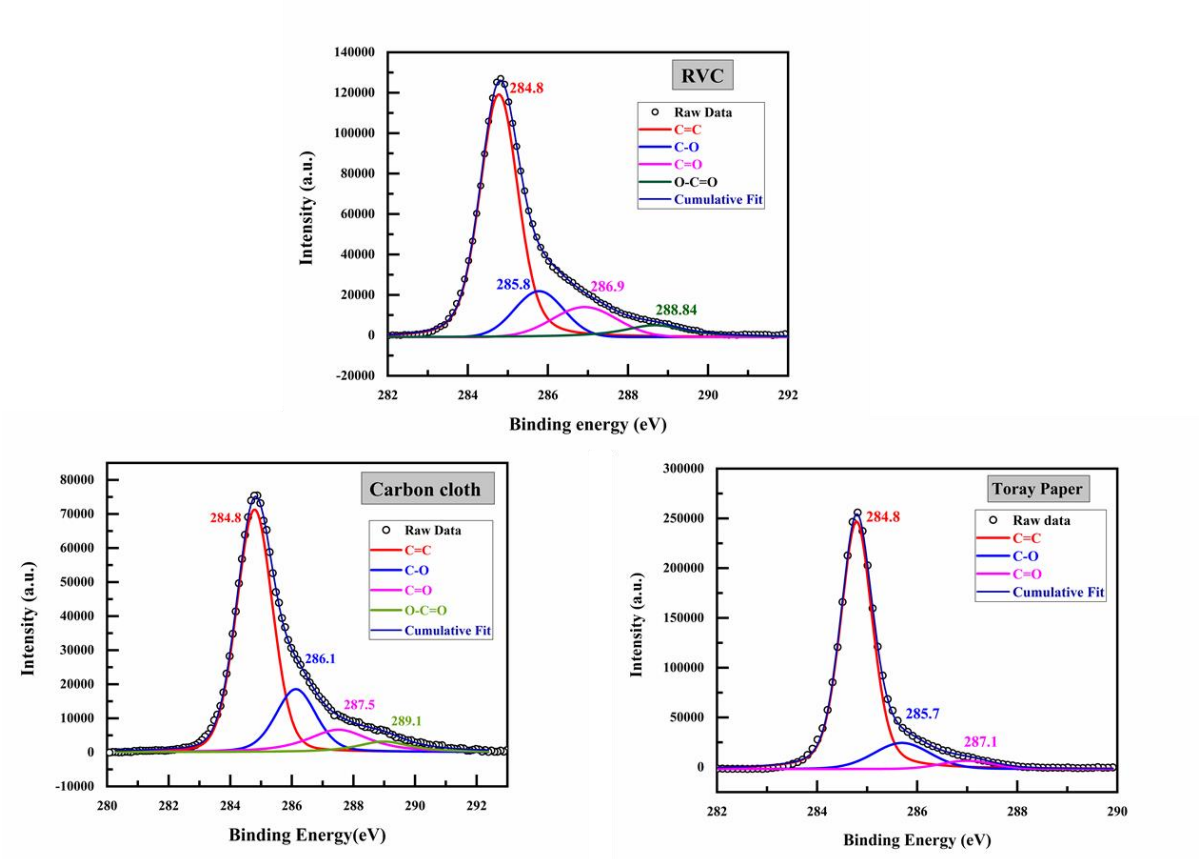


Figure S6. XPS spectra of various carbonaceous materials (RVC, carbon cloth, toray paper) with the information about carbon and oxygen contain in the particular sample.

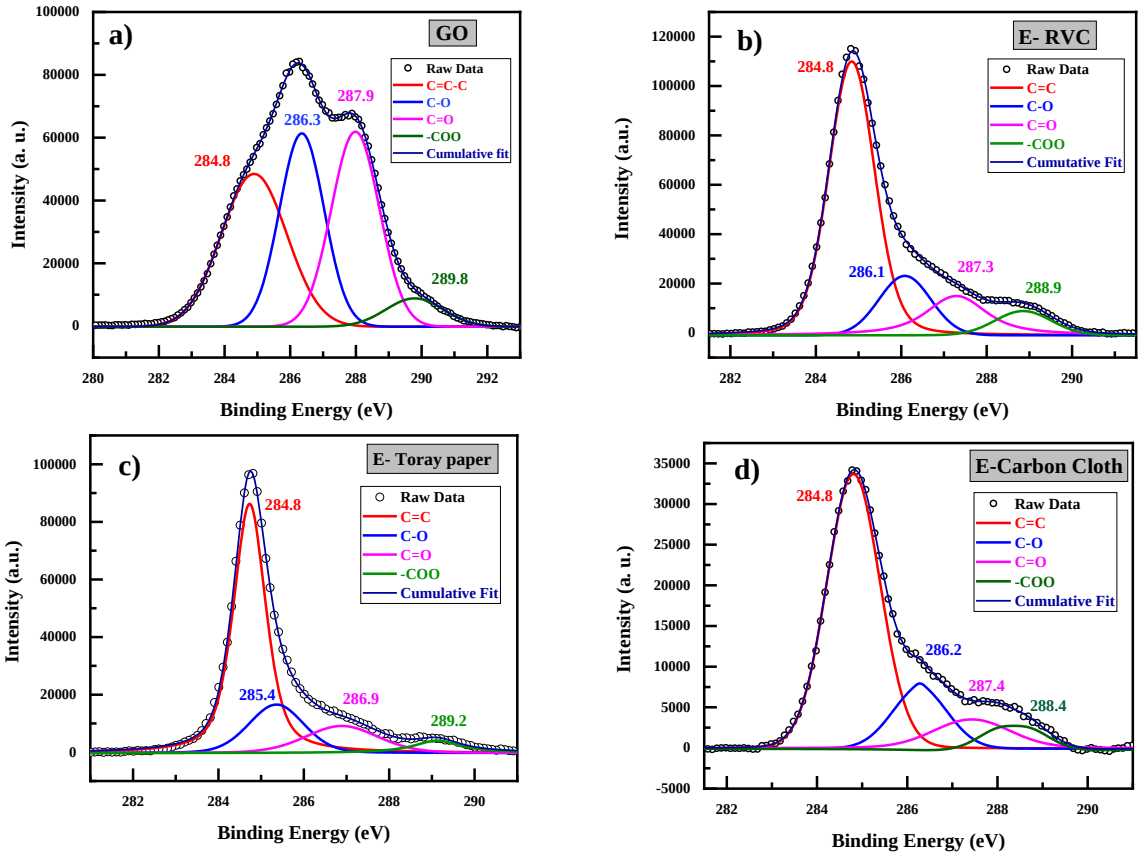
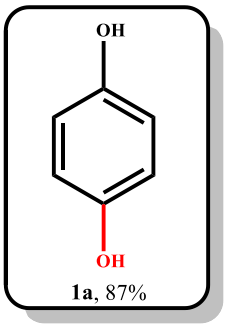


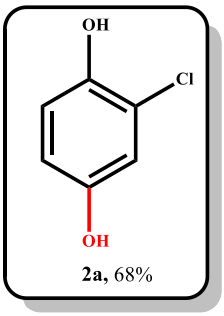
Figure S7. XPS spectra of carbonaceous materials **(7a-d)** after electrochemically treated in acidic condition. The spectra have been de-convoluted to obtain the each peak representing particular oxygen functionalities on the surface of carbonaceous materials. The letter "E" has been added to the respective names of electrochemically acid treated carbon materials.

Spectroscopic Data of Products:



1,4-hydroquinone (1a): By the following typical procedures the product (**1a**) was isolated as a colourless solid, 101 mg (87% yield). Purification was done with column chromatography (Petrolium ether and ethyl acetate 4:1).

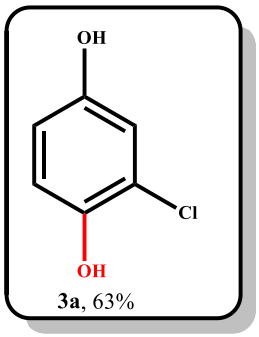
^{1}H NMR (200 MHz, DMSO-D6) δ 8.61 (s, 2H), 6.55 (s, 4H); **D_2O Exchange ^{1}H NMR** (200 MHz, DMSO-D6) δ 6.57(s, 4H); **^{13}C NMR** (400 MHz, DMSO-D6) δ 149.7, 115.7. ; **MS** m/z calculated for $C_6H_6O_2$ $[M]^+$ 110.04, GCMS found 110.1.



2a, 68%

2-chlorobenzene-1,4-diol (2a): By the following typical procedures the product (**2a**) was isolated as a white powder, 76 mg (68% yield). Purification was done with column chromatography (Petrolium ether and ethyl acetate 4:1).

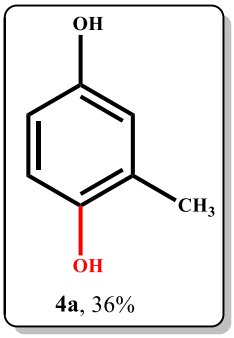
^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.36 (s, 1 H), 9.15 (s, 1 H), 6.76 (d, *J*=8.8 Hz, 1 H), 6.70 (d, *J*=2.9 Hz, 1 H), 6.55 (dd, *J*=8.8, 2.9 Hz, 1 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ ppm 150.78 (s), 146.09 (s), 120.06 (s), 117.74 (s), 116.60 (s), 115.36 (s), 40.56 (s), 40.35 (s), 40.14 (s), 39.93 (s), 39.72 (s), 39.31 (s); **MS** m/z calculated for $C_6H_5O_2Cl$ $[M]^+$ 144.0, GCMS found 144.0.



3a, 63%

2-chlorobenzene-1,4-diol (3a): By the following typical procedures the product (**3a**) was isolated as a white powder, 70 mg (63% yield). Purification was done with column chromatography (Petrolium ether and ethyl acetate 4:1).

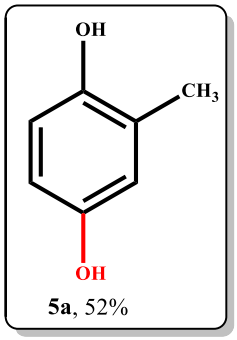
^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 9.36 (s, 1 H), 9.15 (s, 1 H), 6.76 (d, *J*=8.8 Hz, 1 H), 6.70 (d, *J*=2.9 Hz, 1 H), 6.55 (dd, *J*=8.8, 2.9 Hz, 1 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ ppm 150.36 (s), 145.67 (s), 119.64 (s), 117.32 (s), 116.18 (s), 114.94 (s), 40.14 (s), 39.93 (s), 39.72 (s), 39.31 (s), 39.09 (s), 38.89 (s); **MS** m/z calculated for $C_6H_5O_2Cl$ $[M]^+$ 144.0, GCMS found 144.0



4a, 36%

2-methylbenzene-1,4-diol (4a): By the following typical procedures the product (**4a**) was isolated as a white solid powder, 41 mg (36% yield). Purification was done with a column chromatography (Petrolium ether and ethyl acetate 4:1).

^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 8.55 (s, 1H), 8.50 (s, 1H), 6.55 (d, J = 8.5 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 6.37 (dd, J = 8.5, 2.8 Hz, 1H), 2.03 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ ppm 149.6 , 147.8 , 124.5 , 117.3 , 115.2 , 112.7 , 16.2 ; **MS** m/z calculated for $C_6H_5O_2Cl$ $[M]^+$ 124.14, GCMS found 124.1.



5a, 52%

2-methylbenzene-1,4-diol (5a): By the following typical procedures the product (**5a**) was isolated as a white solid powder, 59 mg (52 % yield). Purification was done with a column chromatography (Petrolium ether and ethyl acetate 4:1).

^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 8.55 (s, 1 H), 8.50 (s, 1 H), 6.52 - 6.57 (m, 1 H), 6.47 (br. s., 1 H), 6.34 - 6.40 (m, 1 H), 2.03 (s, 3 H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ ppm 149.6 , 147.8 , 124.5 , 117.3 , 115.2 , 112.7 , 16.2; **MS** m/z calculated for $C_6H_5O_2Cl$ $[M]^+$ 124.14, GCMS found 124.1.

NMR Spectra:

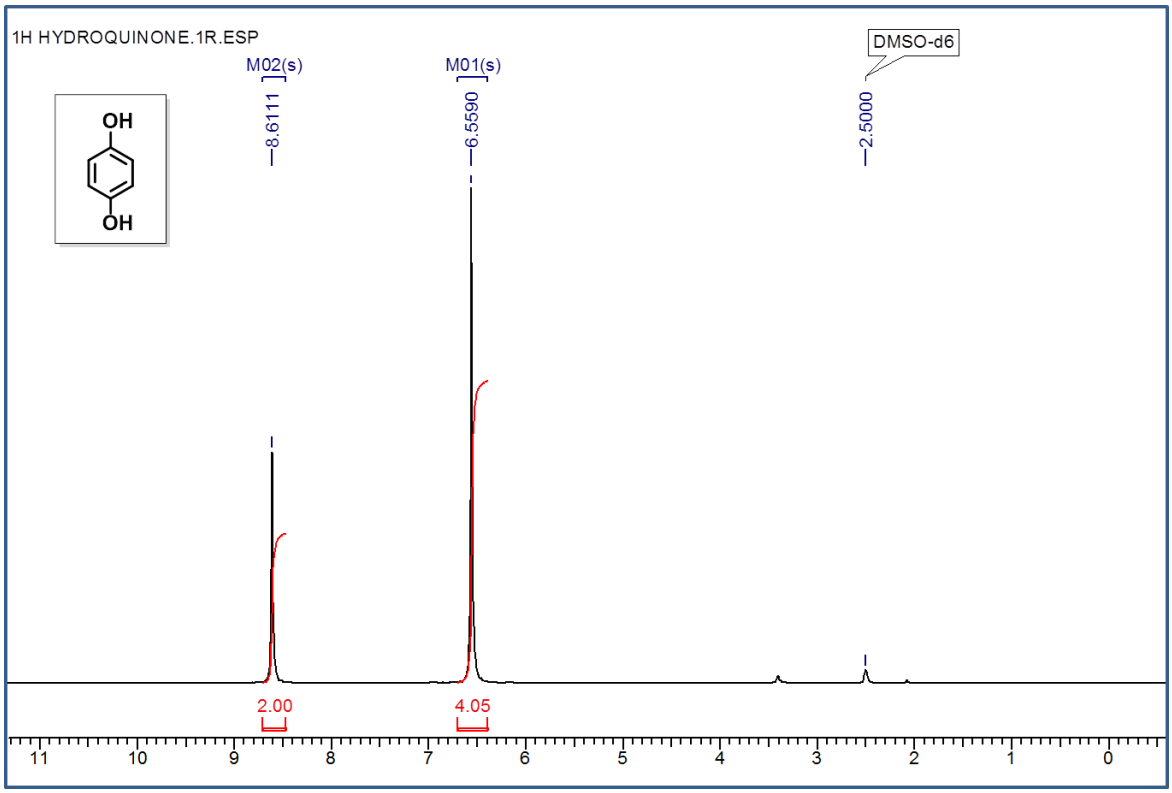


Figure S8. ^{1}H NMR spectrum of Hydroquinone (**1a)**

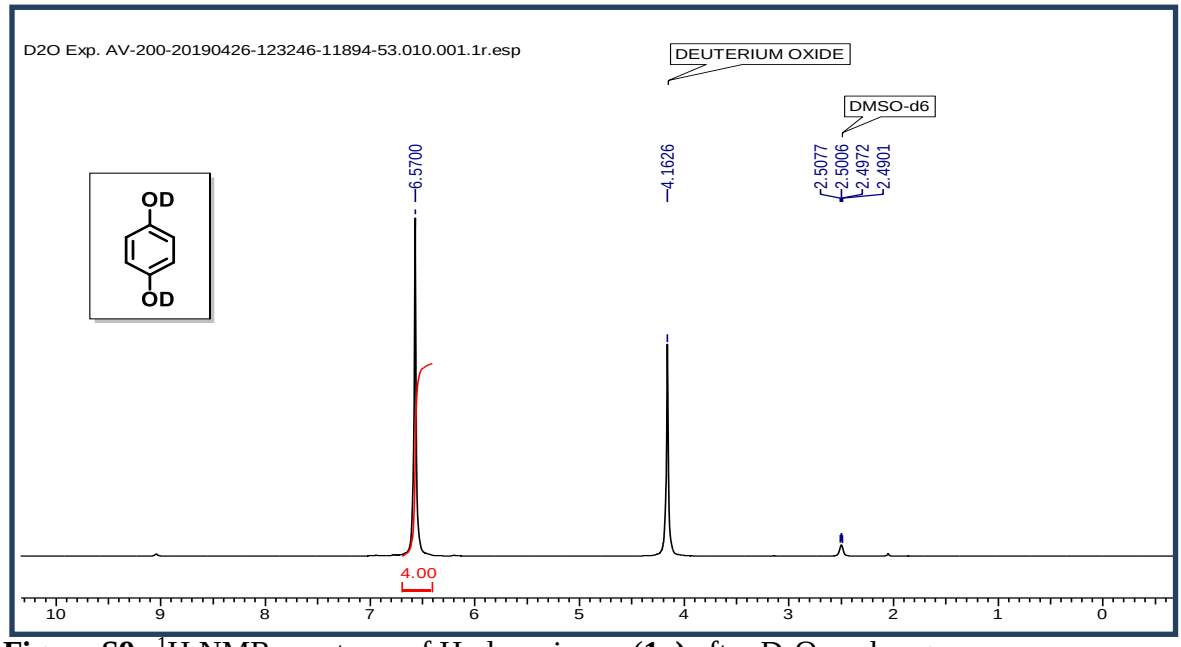


Figure S9. ^{1}H NMR spectrum of Hydroquinone (**1a)** after D_2O exchange.

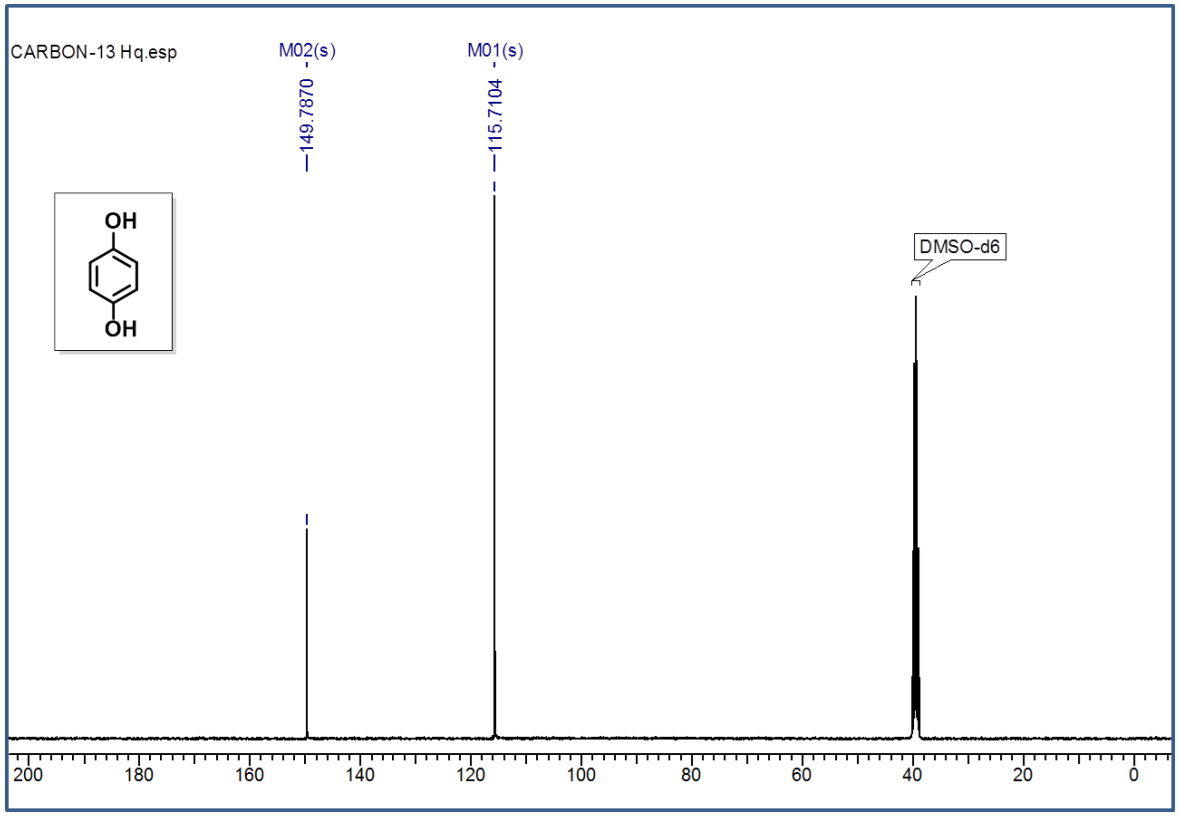


Figure S10. ^{13}C NMR spectrum of Hydroquinone (**1a)** in DMSO-d_6

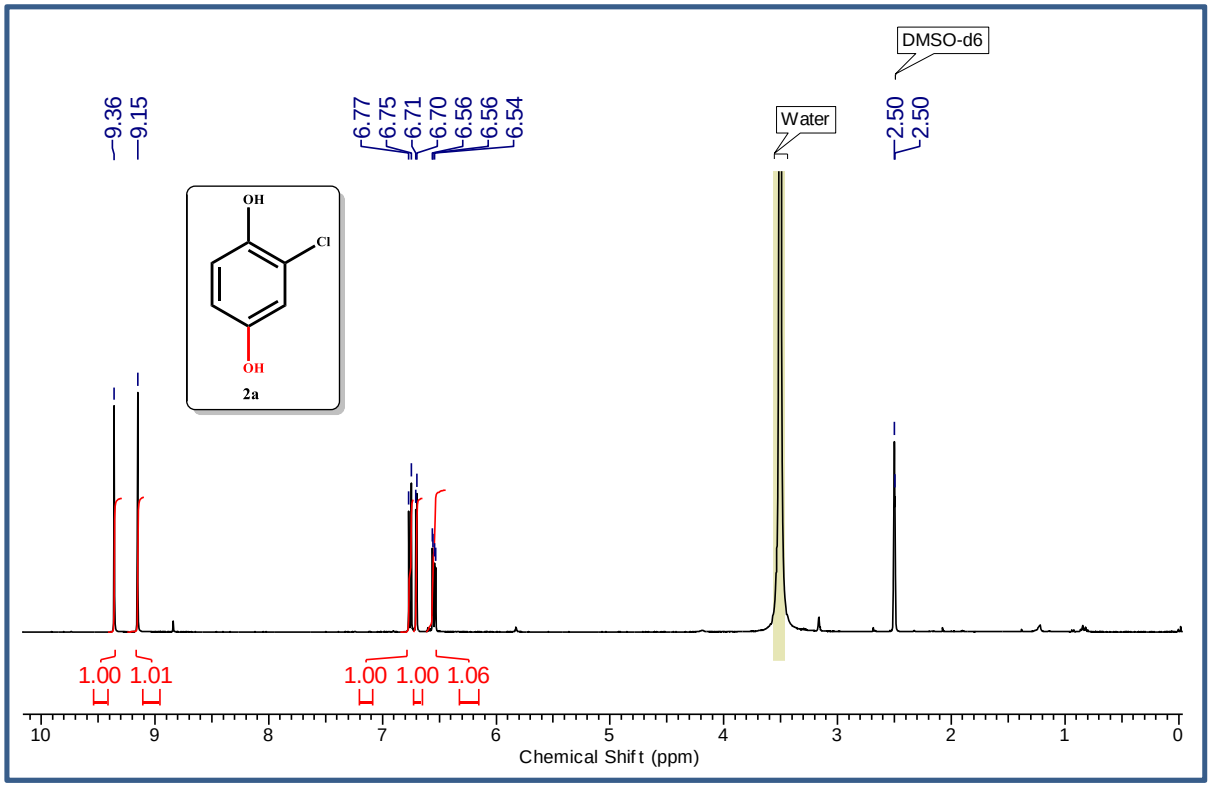


Figure S11. ^{1}H NMR spectrum of (**2a)** in DMSO-d_6

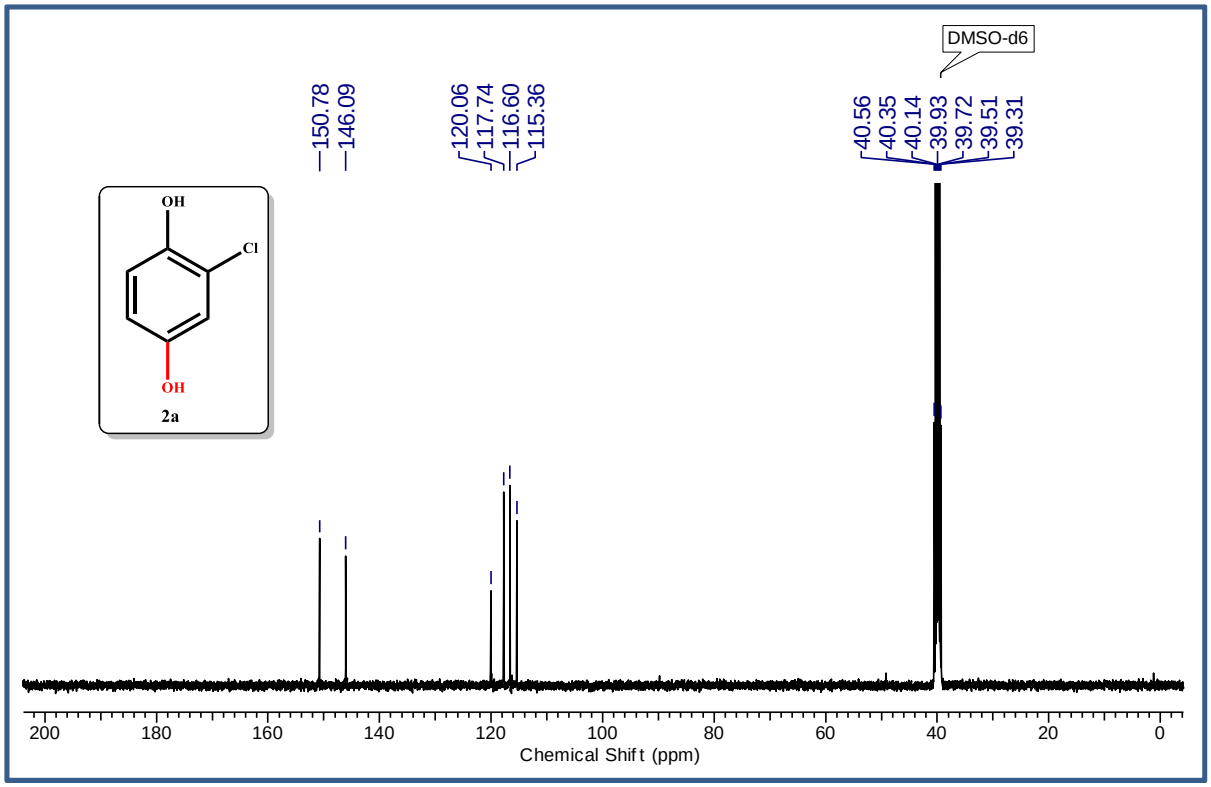


Figure S12. ^{13} C NMR spectrum of (**2a)** in DMSO-d_6

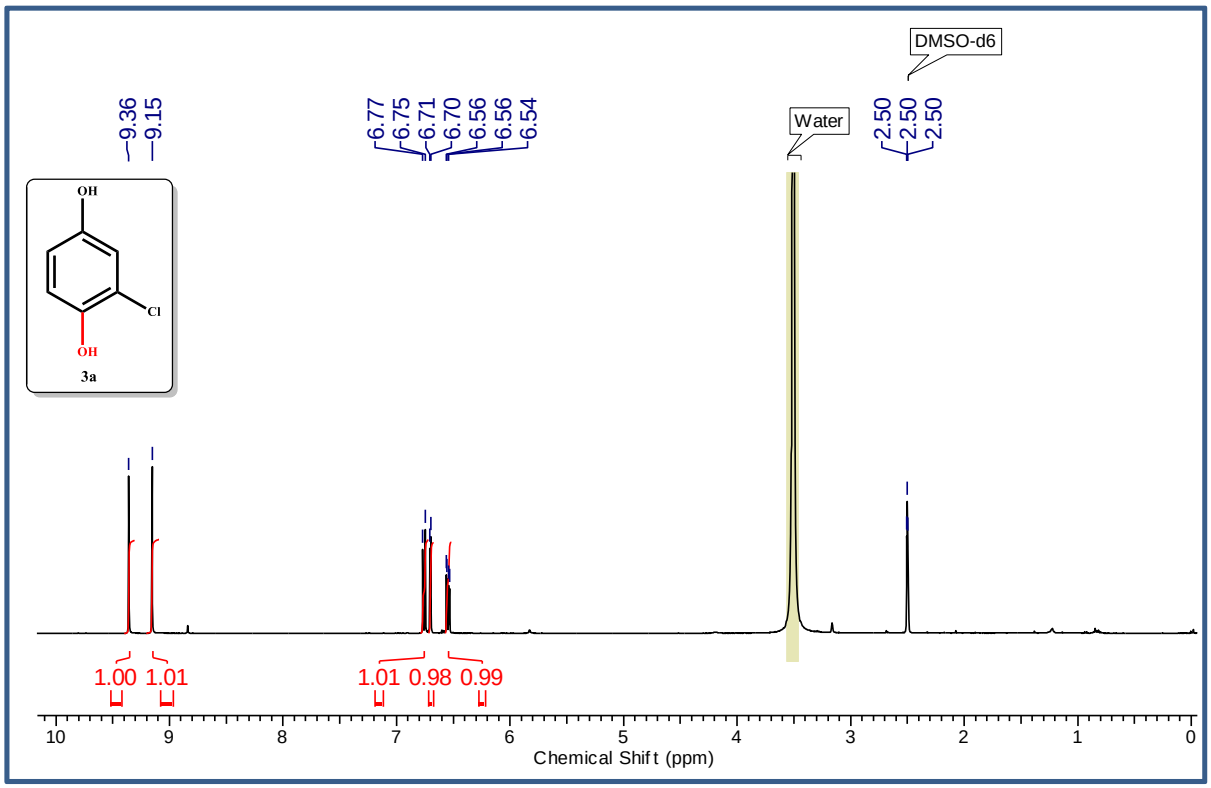


Figure S13. ^{1}H NMR spectrum of (**3a)** in DMSO-d_6

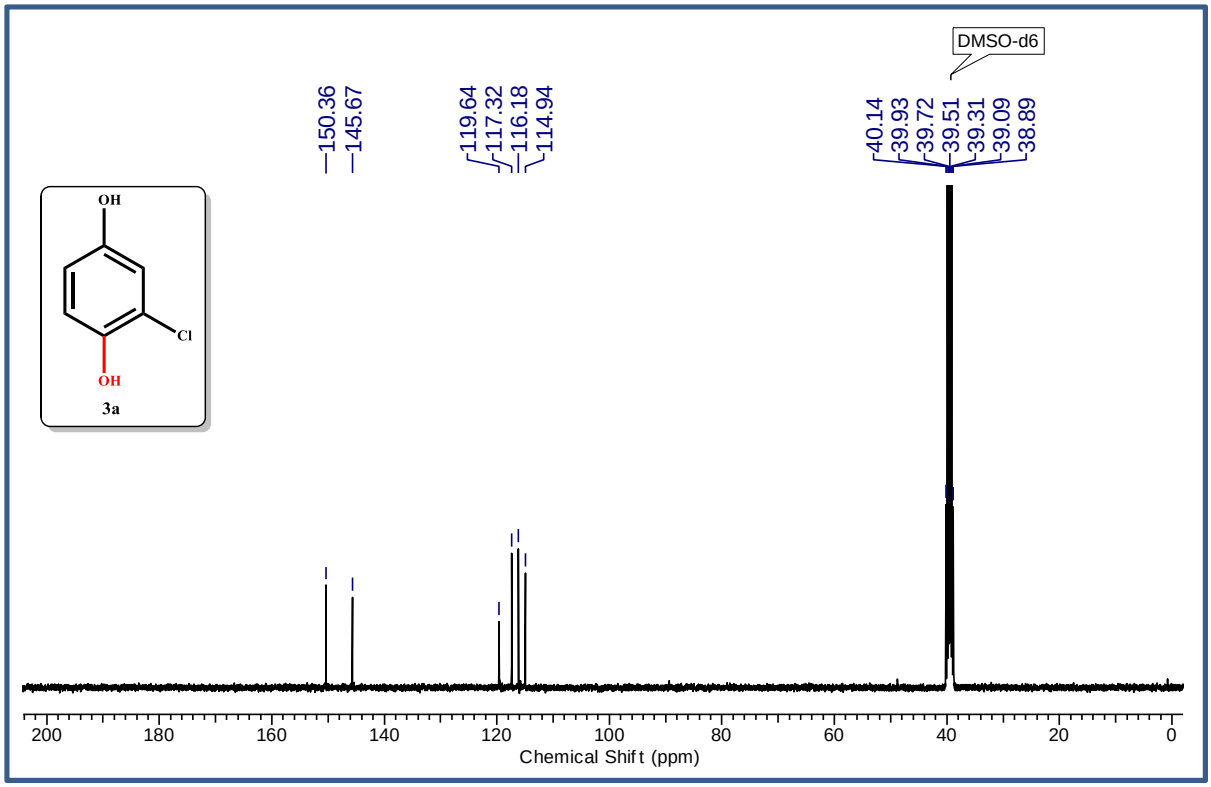


Figure S14. ^{13} C NMR spectrum of (**3a)** in DMSO-d_6

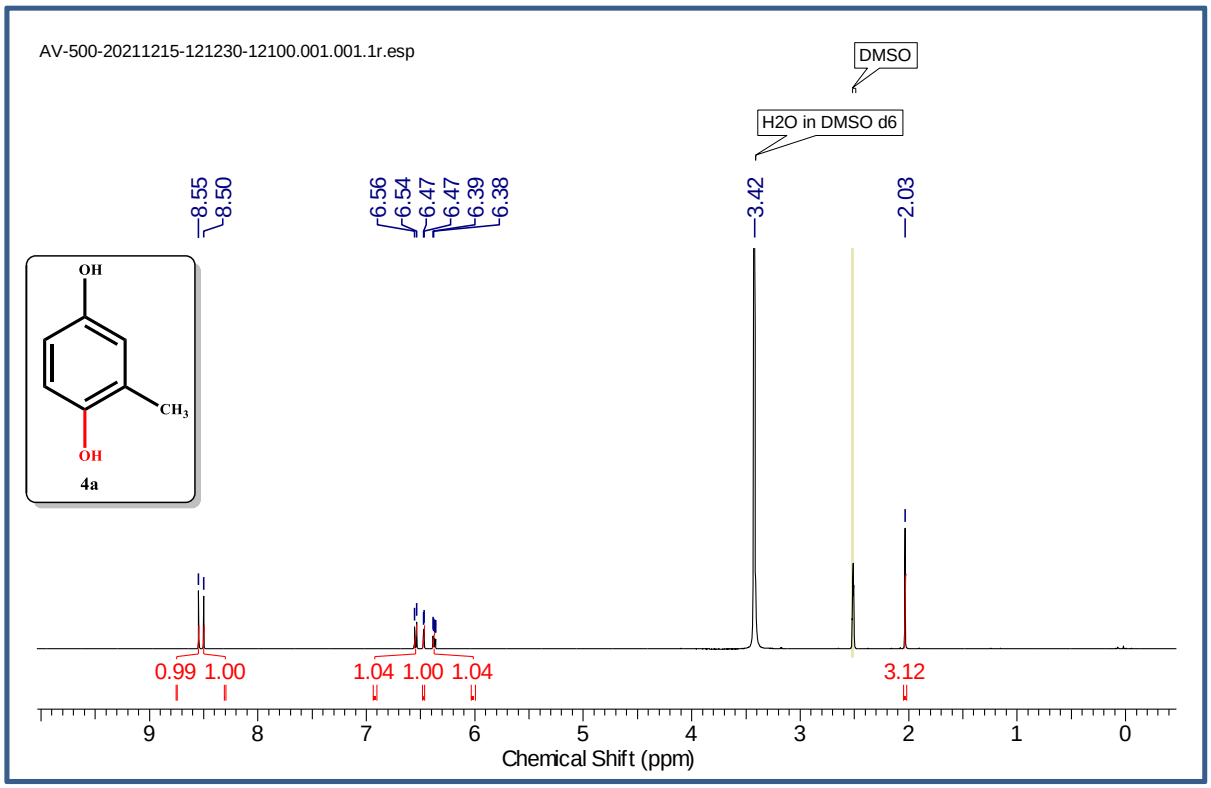


Figure S15. ^{1}H NMR spectrum of (**4a)** in DMSO-d_6

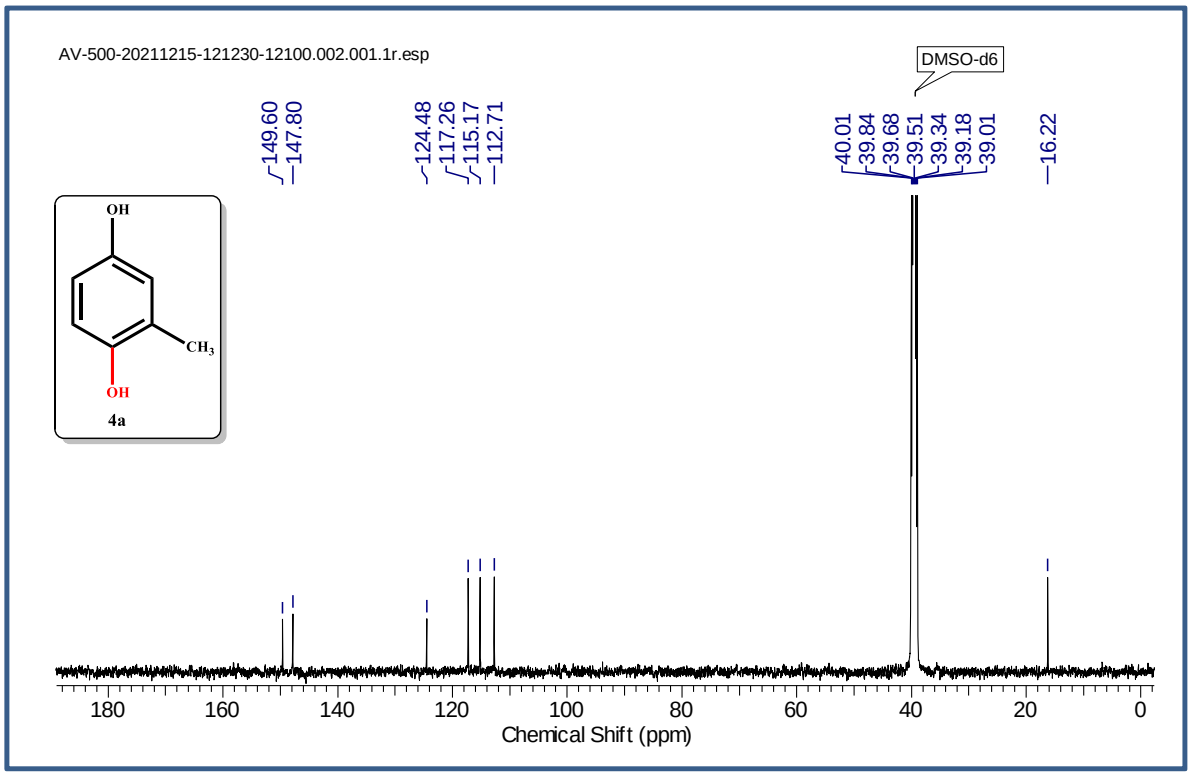


Figure S16. ^{13} C NMR spectrum of (**4a)** in DMSO-d_6

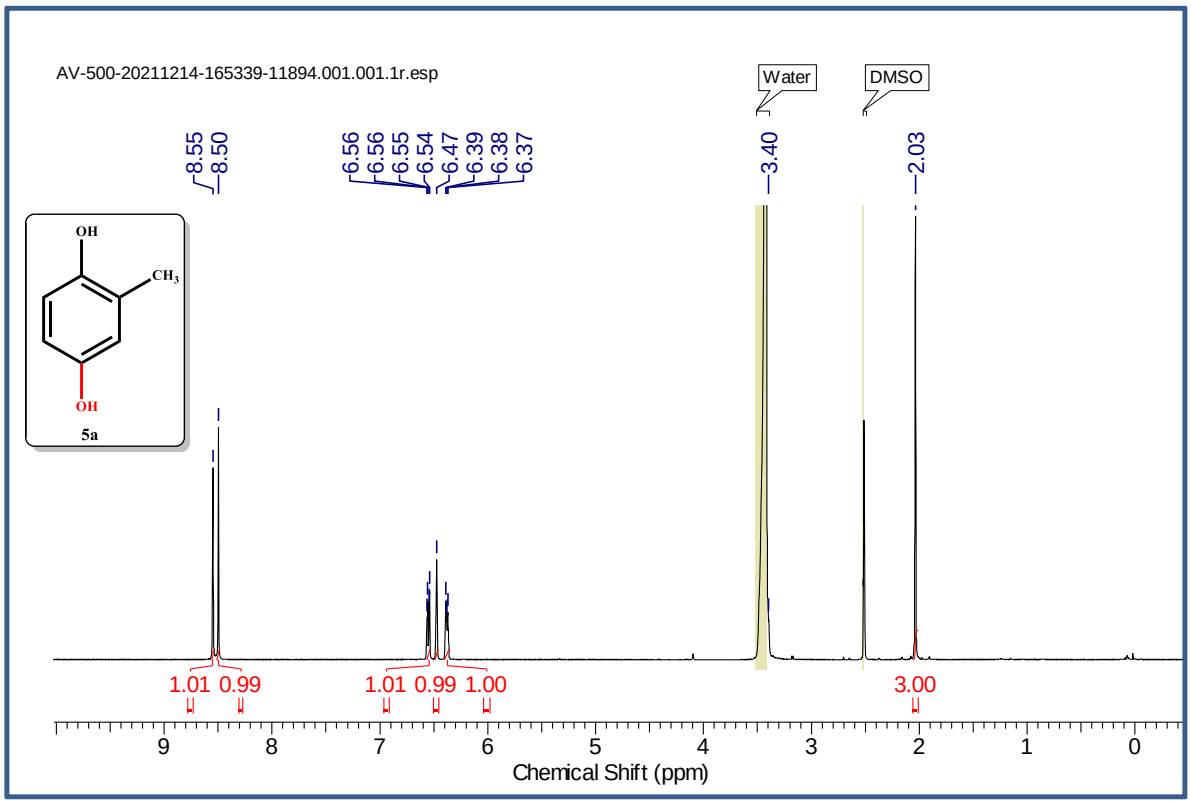


Figure S17. ^{1}H NMR spectrum of (**5a)** in DMSO-d_6

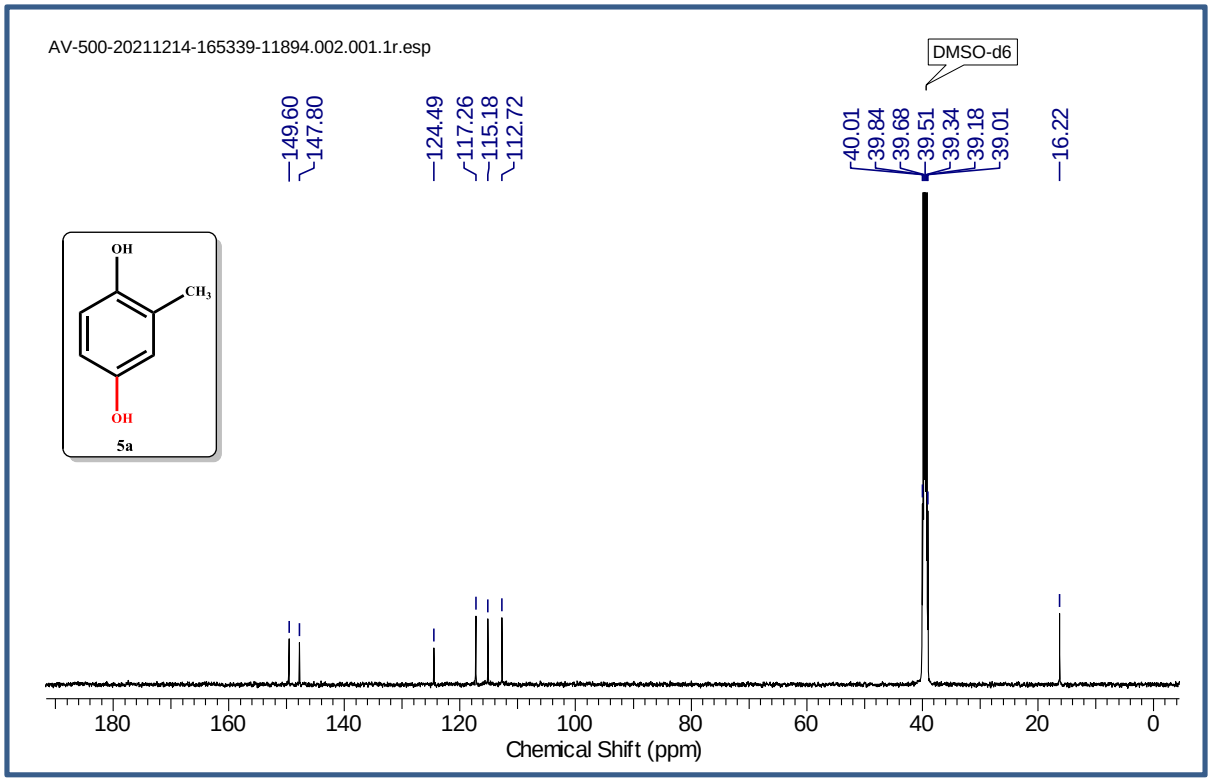


Figure S18. ^{13}C NMR spectrum of (**5a)** in DMSO-d_6

Gas Chromatography and Mass Spectrometry:

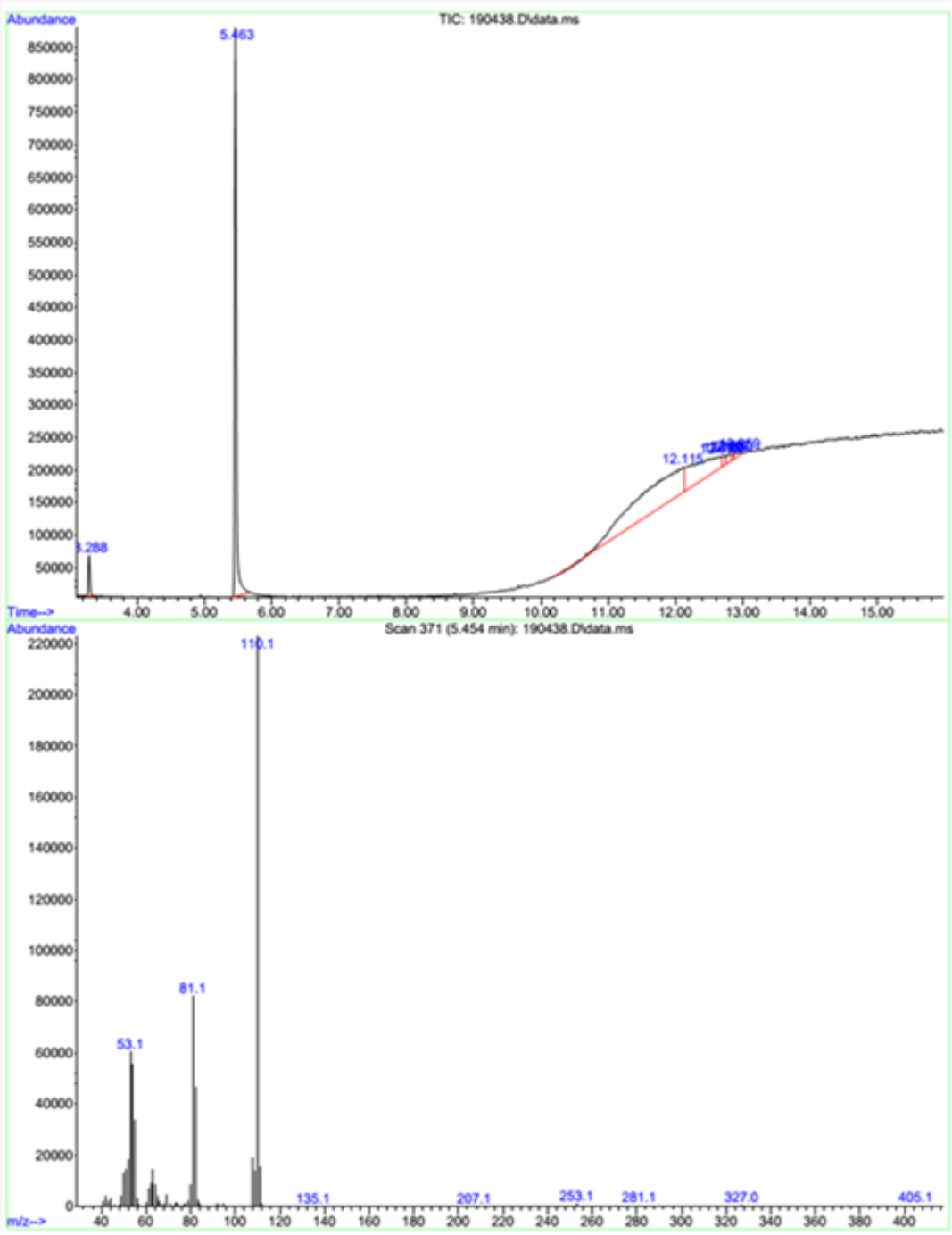


Figure S19. Gas chromatogram and mass spectrum of Hydroquinone (**1a)**

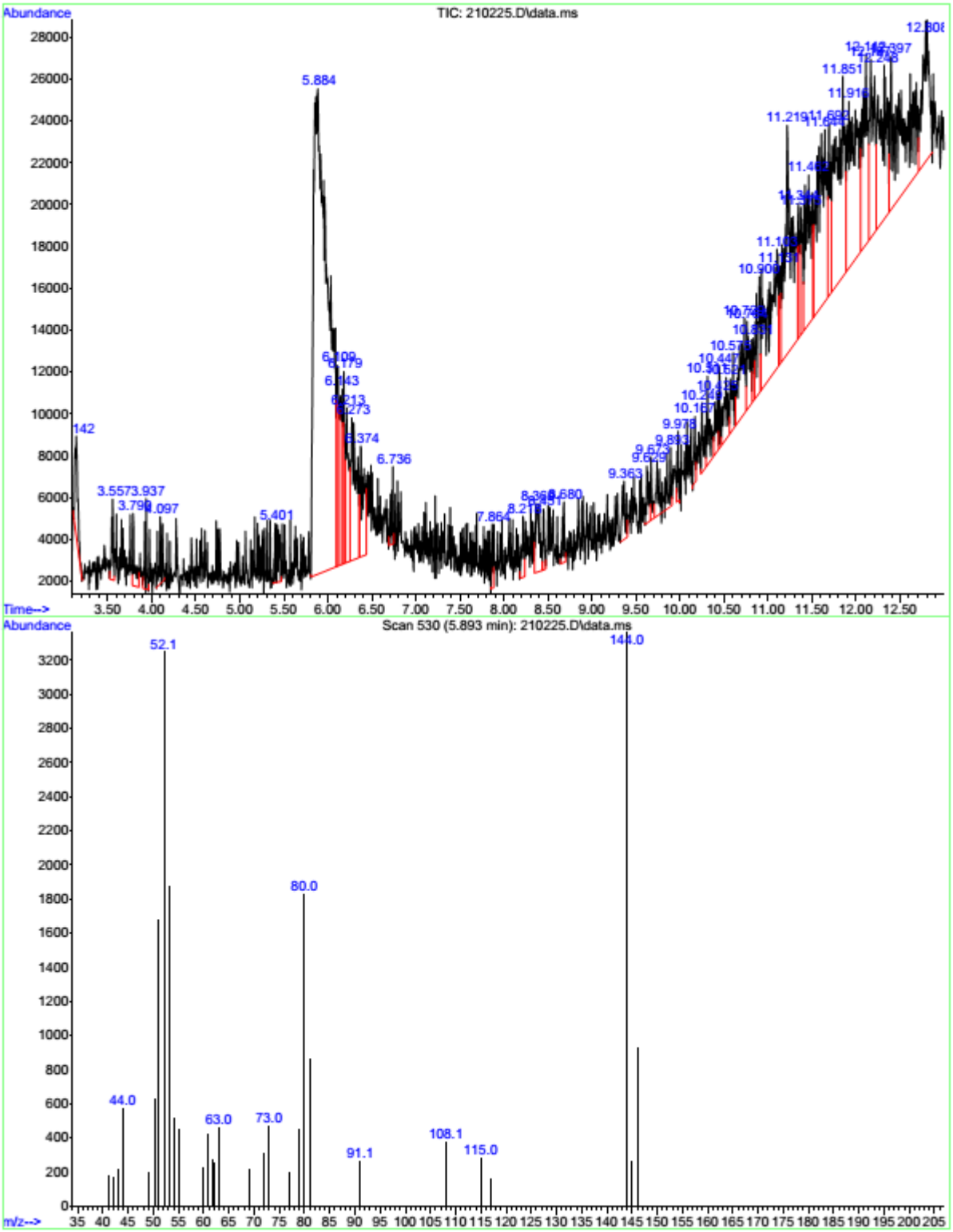


Figure S20. Gas chromatogram and mass spectrum of (**2a)**

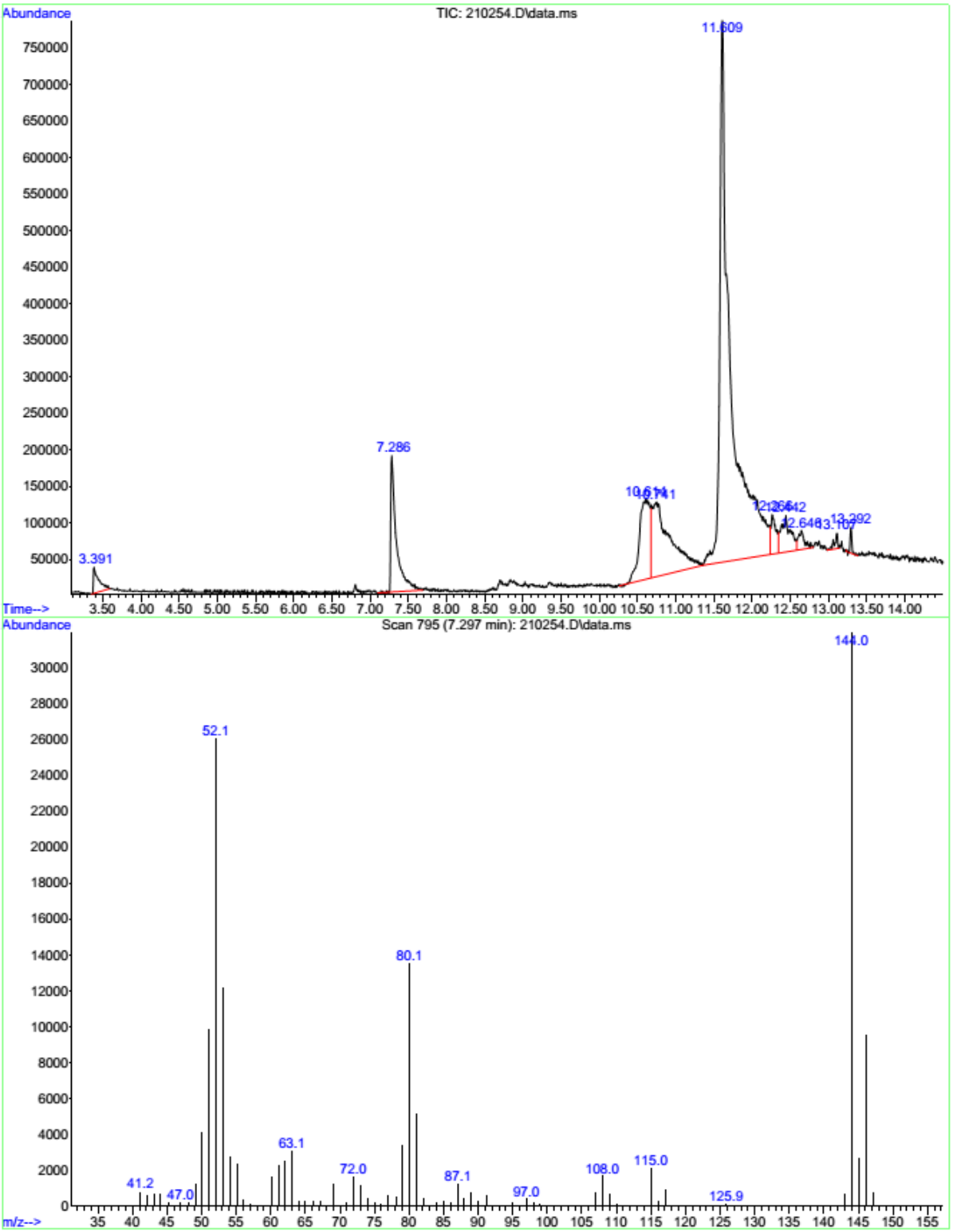


Figure S21. Gas chromatogram and mass spectrum of (**3a)**

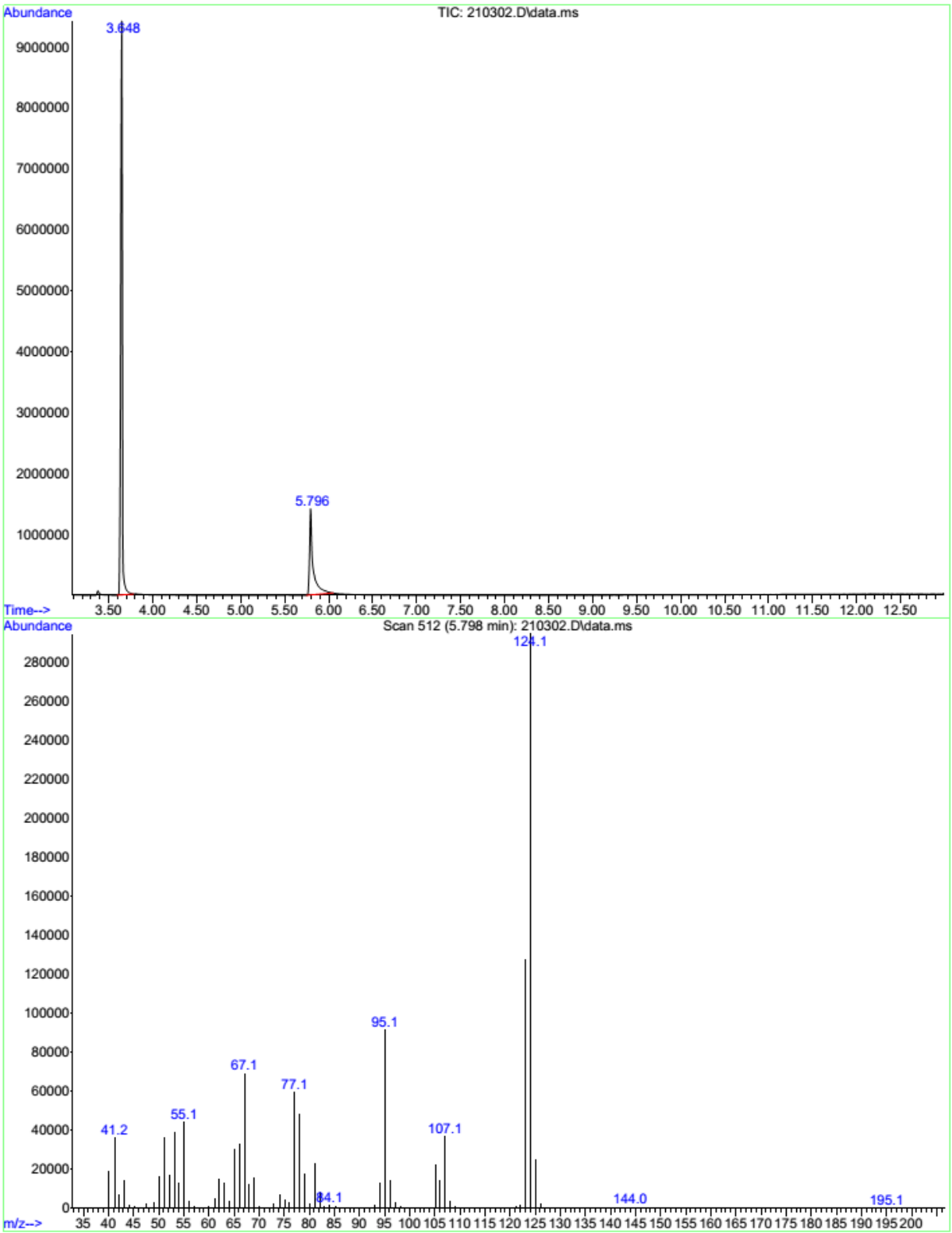


Figure S22. Gas chromatogram and mass spectrum of (**4a)**

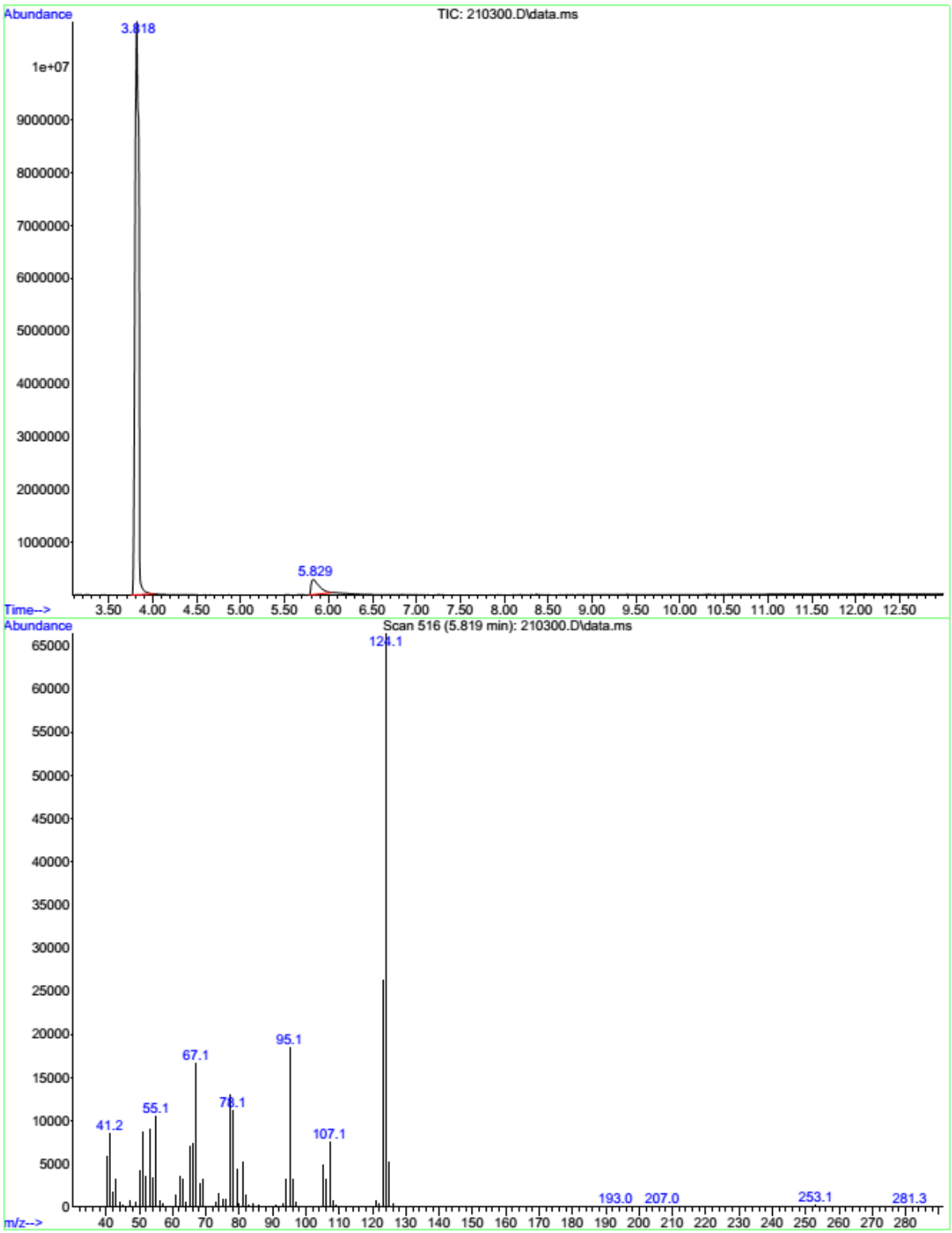


Figure S23. Gas chromatogram and mass spectrum of (**5a)**