

## **Synthesis of Cobalt(II) Phenolate Selenoether Complexes to Mimic Hydrogenase like Activity for Hydrogen Gas Production**

Aditya Upadhyay<sup>a</sup>, Kanika<sup>a</sup>, Yogesh Mandhar<sup>a</sup>, Monojit Batabyal<sup>a</sup>, Saravanan Raju<sup>a</sup>, Svastik  
Jaiswal<sup>a</sup>, Ray J. Butcher<sup>b</sup> and Sangit Kumar<sup>a\*</sup>

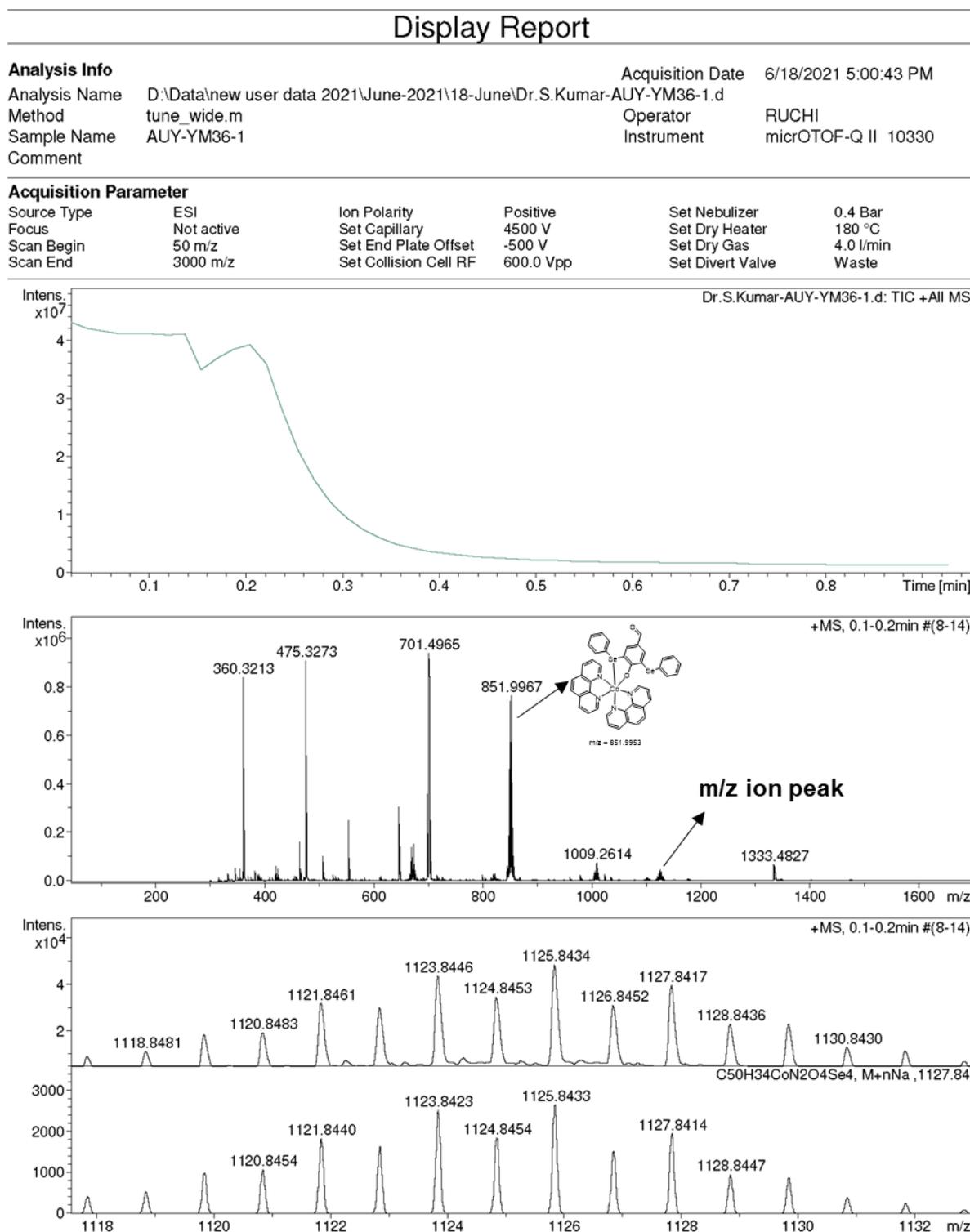
<sup>a</sup>Department of Chemistry, Indian Institute of Science Education and Research, Bhopal By-  
Pass Road, Bhauri, Bhopal 462 066, Madhya Pradesh, India

<sup>b</sup>Department of Chemistry, Howard University, Washington ,D. C. 20059, United States

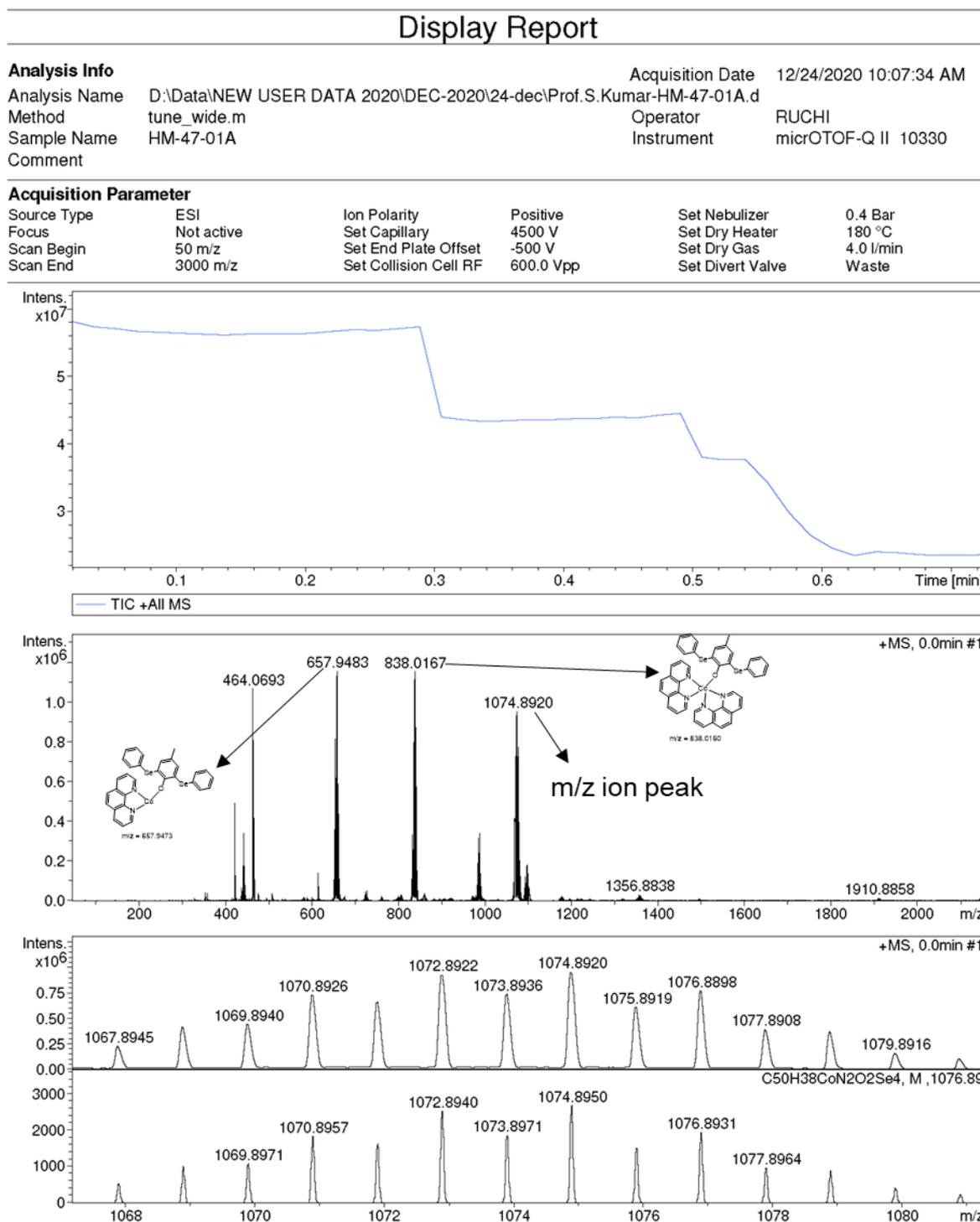
## Table of Contents

HRMS mass spectra of <b>3a-3d</b>	S3–S6
CV of Complexes <b>3a-3d</b>	S7-S8
CV of <b>3a-3d</b> at various scan rates	S9
$i_p$ vs scan rate graphs for <b>3a-3d</b>	S10-S11
CV study of <b>1b</b> in the presence of AcOH	S12
$i_{cat}$ vs [AcOH] graphs for <b>3a-3d</b>	S13-S14
Post dip analysis test for <b>3a-3d</b>	S15
GCTCD read out of hydrogen production	S16
EPR study of acidic solution of <b>3a</b> and <b>3d</b>	S17
UV-Vis titration of <b>1b</b> in the presence of AcOH	S18
$^{77}\text{Se}$ NMR data of acidic mixture of ligand <b>2a</b>	S19

**Figure S1.** HRMS data of **3a**



**Figure S2. HRMS data of 3b**



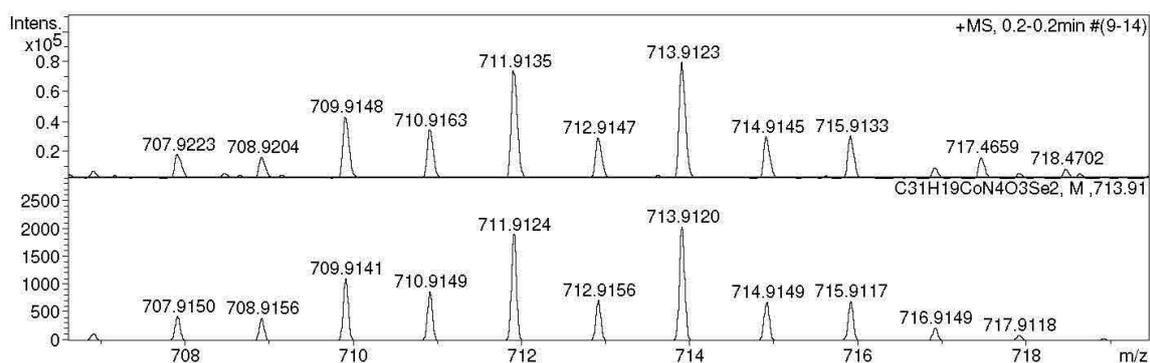
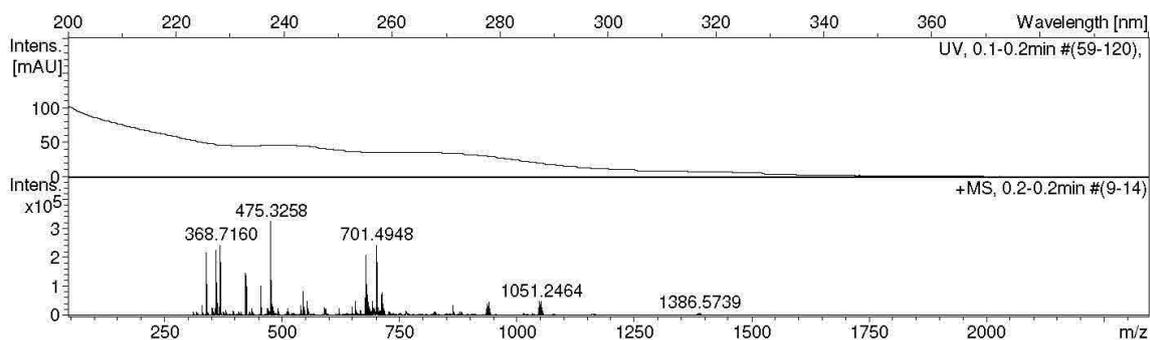
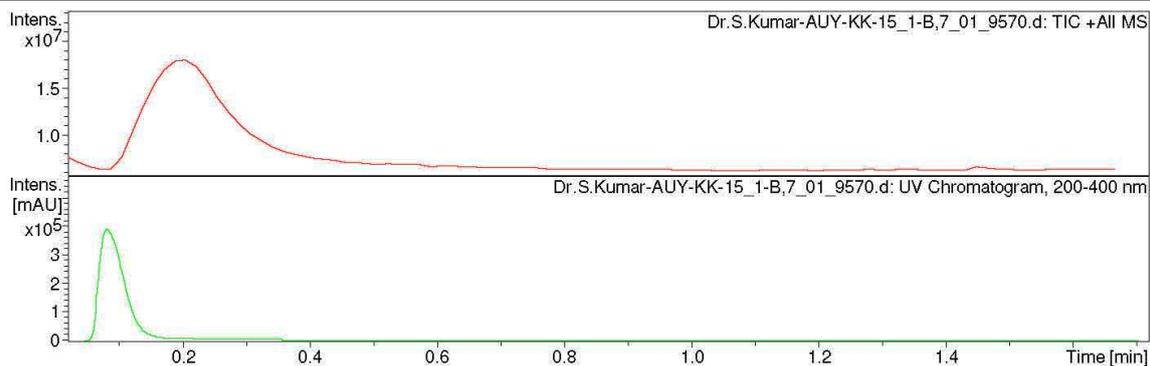
**Figure S3. HRMS data of 3c**

## Display Report

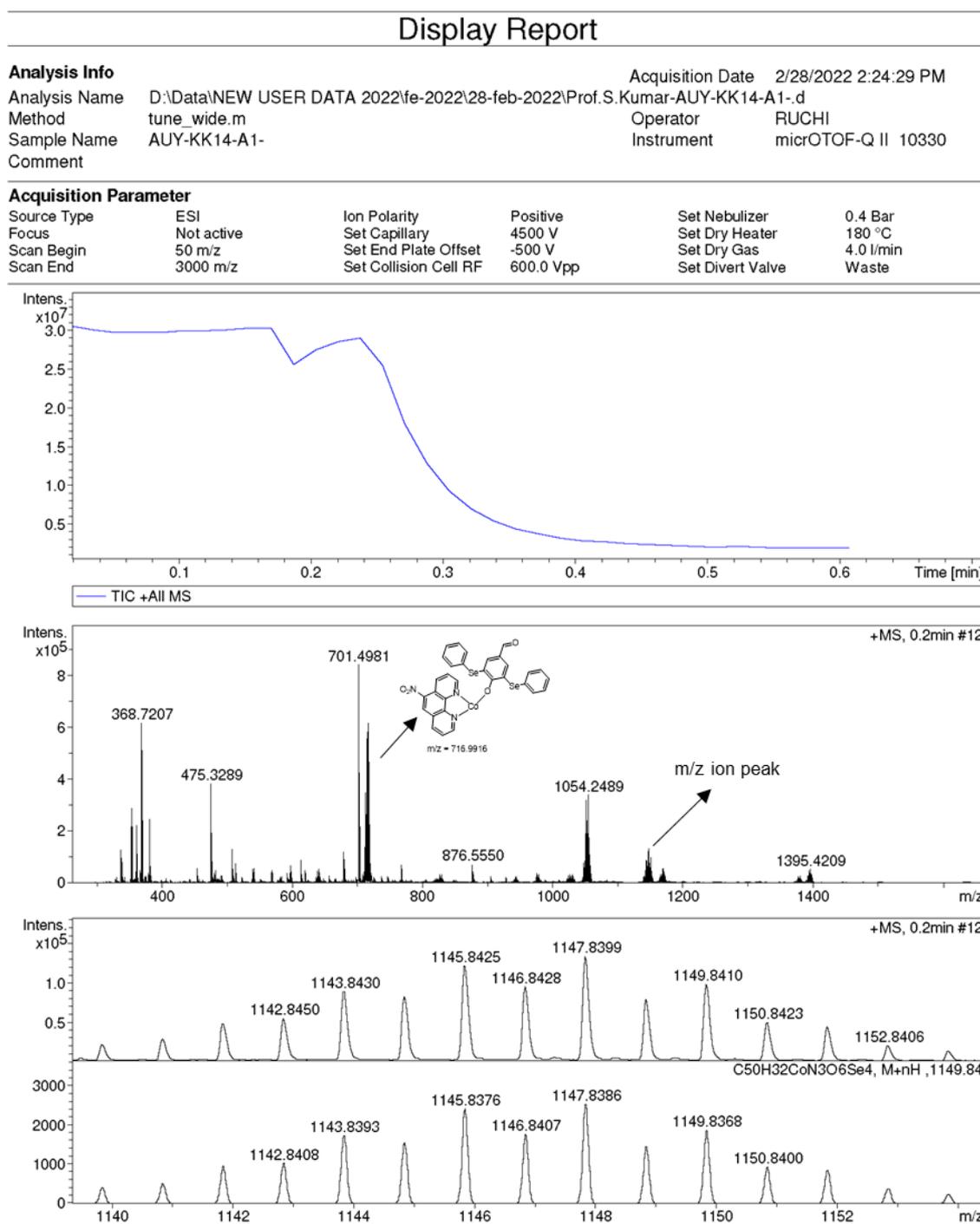
<b>Analysis Info</b>		Acquisition Date	9/22/2021 2:47:01 PM
Analysis Name	D:\Data\new user data 2021\Sept-2021\22-sept\Dr.S.Kumar-AUY-KK-15_1-B,7_01_9570.d	Operator	RUCHI
Method	hrlcms-20 sept--union-esi-tune wide-01-sept-2021.m	Instrument	micrOTOF-Q II 10330
Sample Name	Dr.S.Kumar-AUY-KK-15		
Comment			

**Acquisition Parameter**

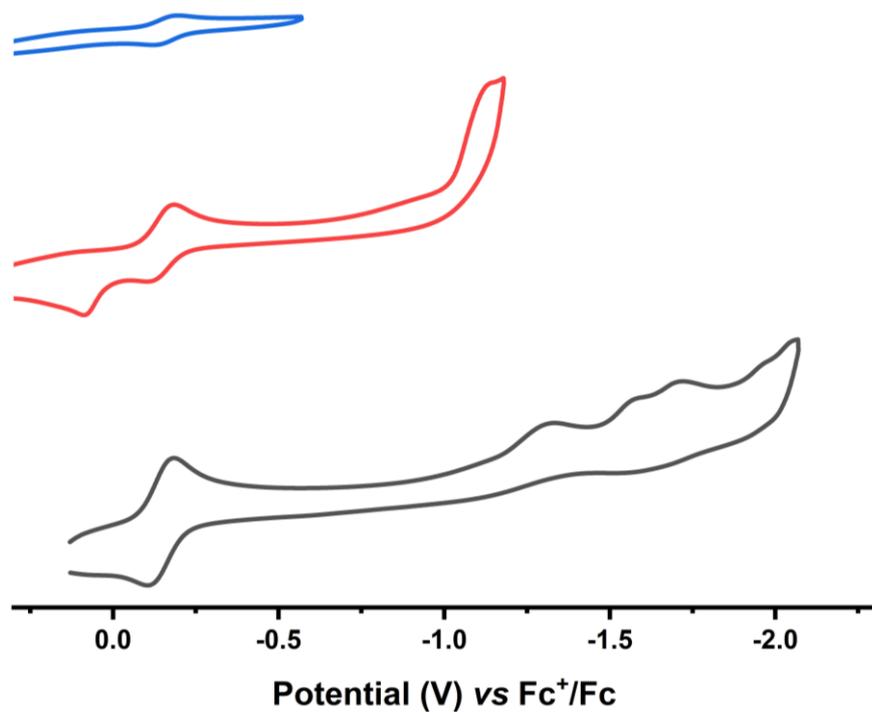
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste



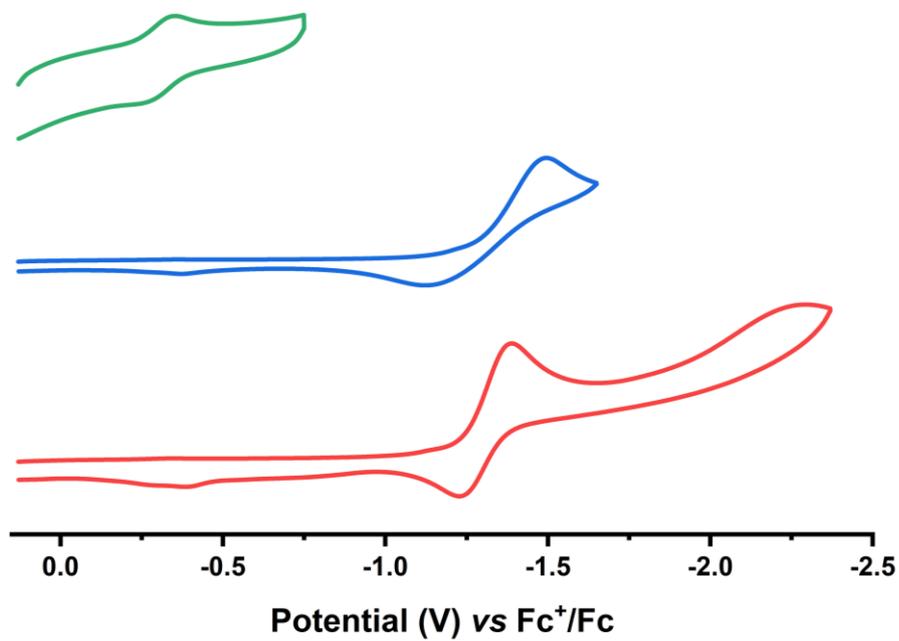
**Figure S4. HRMS data of 3d**



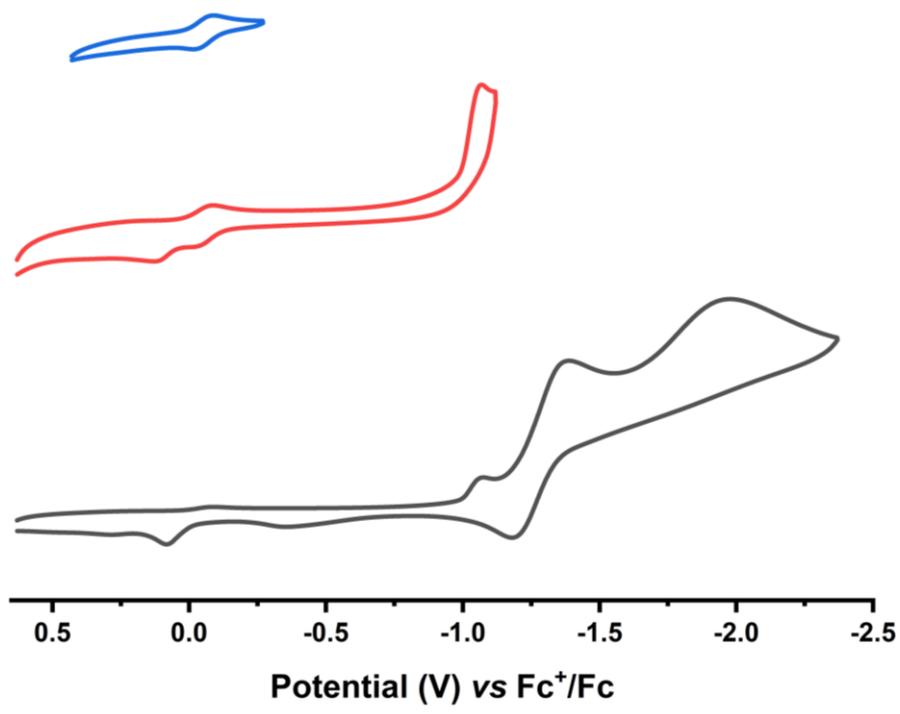
**Figure S5.** Rationalization of CV Peaks of **3a**



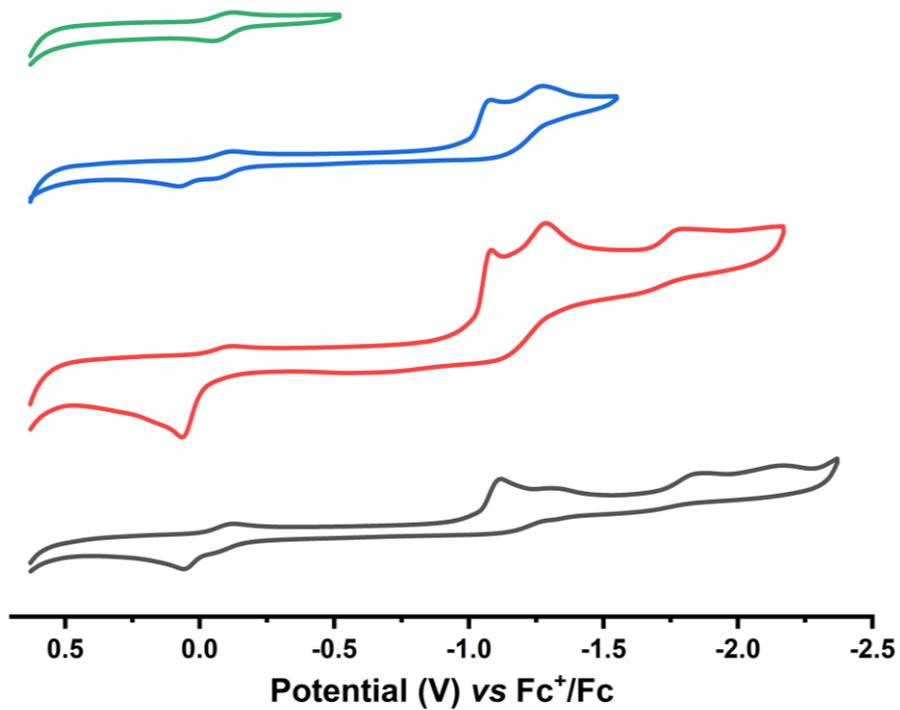
**Figure S6.** Rationalization of CV Peaks of **3b**



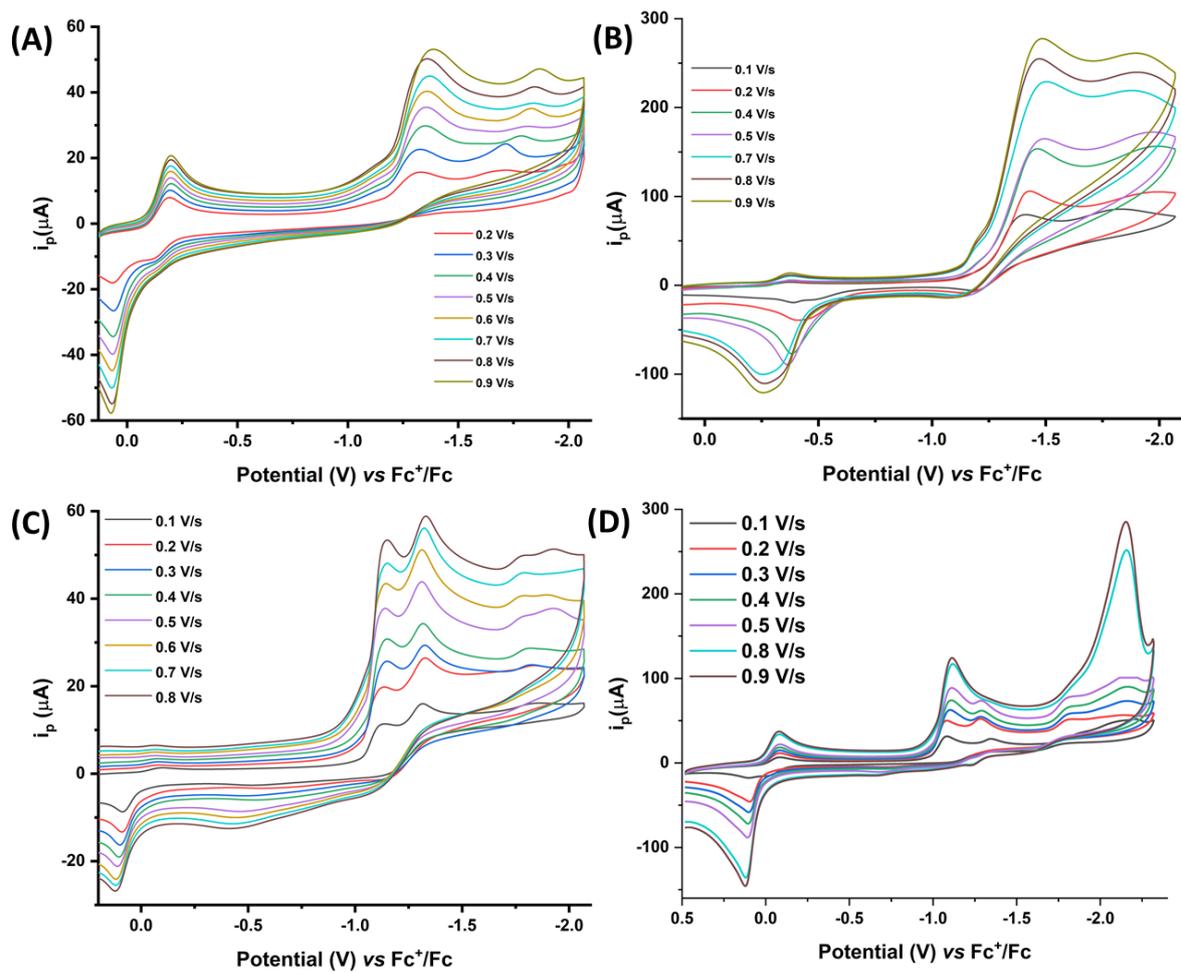
**Figure S7.** Rationalization of CV Peaks of **3c**



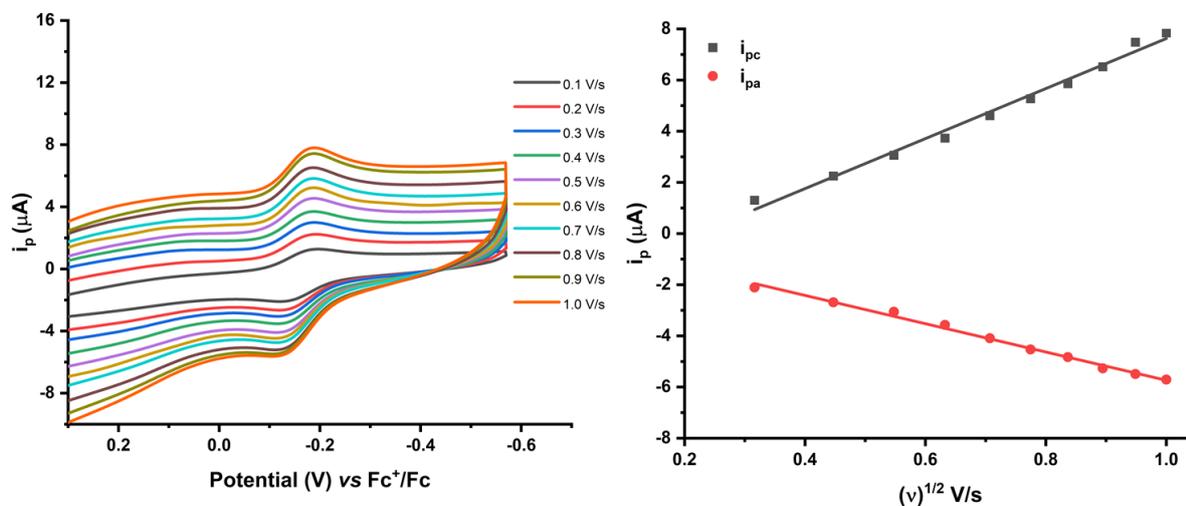
**Figure S8.** Rationalization of CV Peaks of **3d**



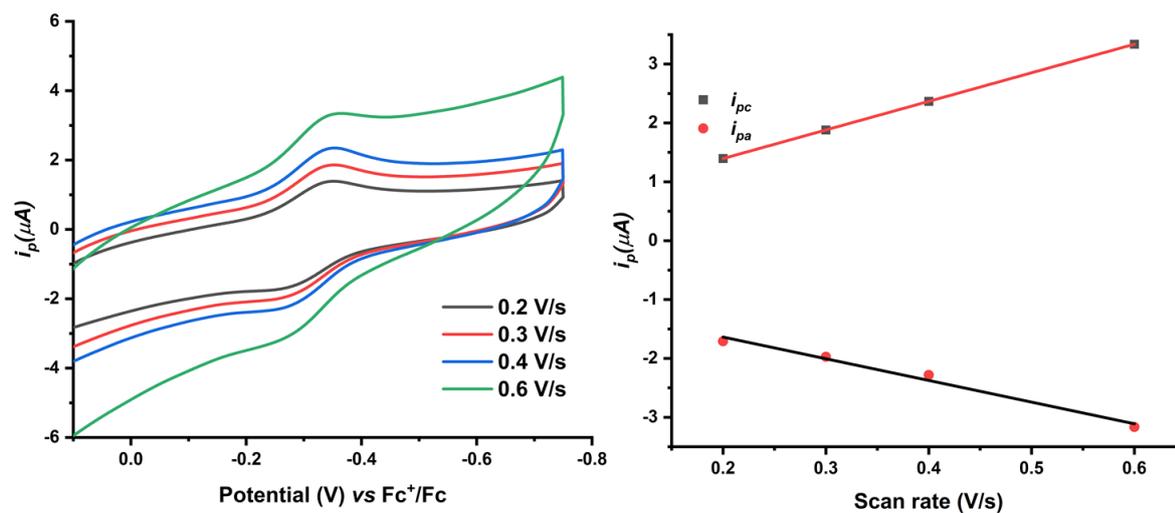
**Figure S9.** CV study of complexes **3a-3d** at various scan rates



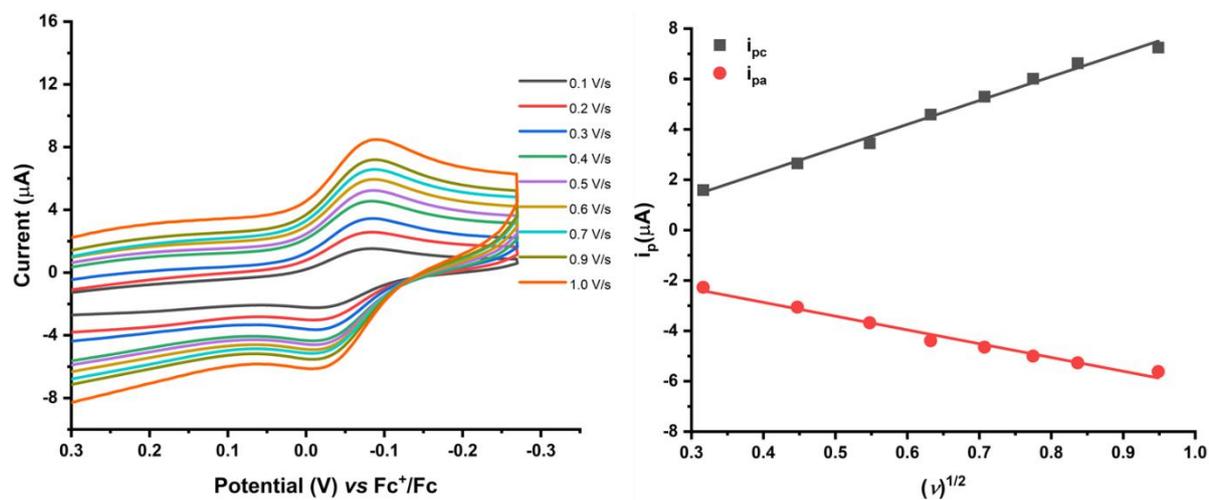
**Figure S10.** CV at various scan rate for Co(II/I) redox couple for **3a** and corresponding Cortrell Plot.



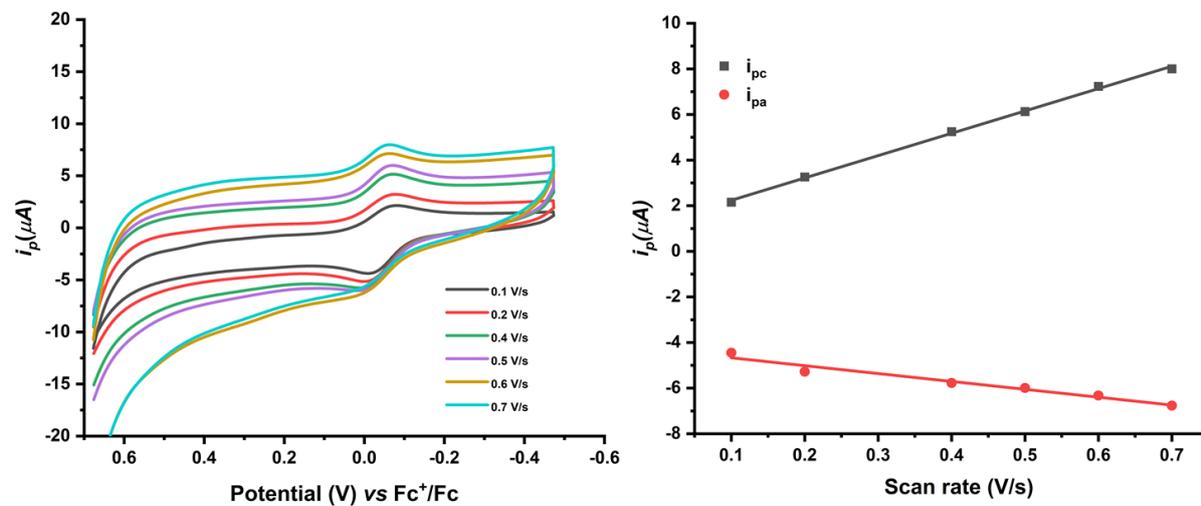
**Figure S11.** CV at various scan rate for Co(II/I) redox couple for **3b** and corresponding Cortrell Plot.



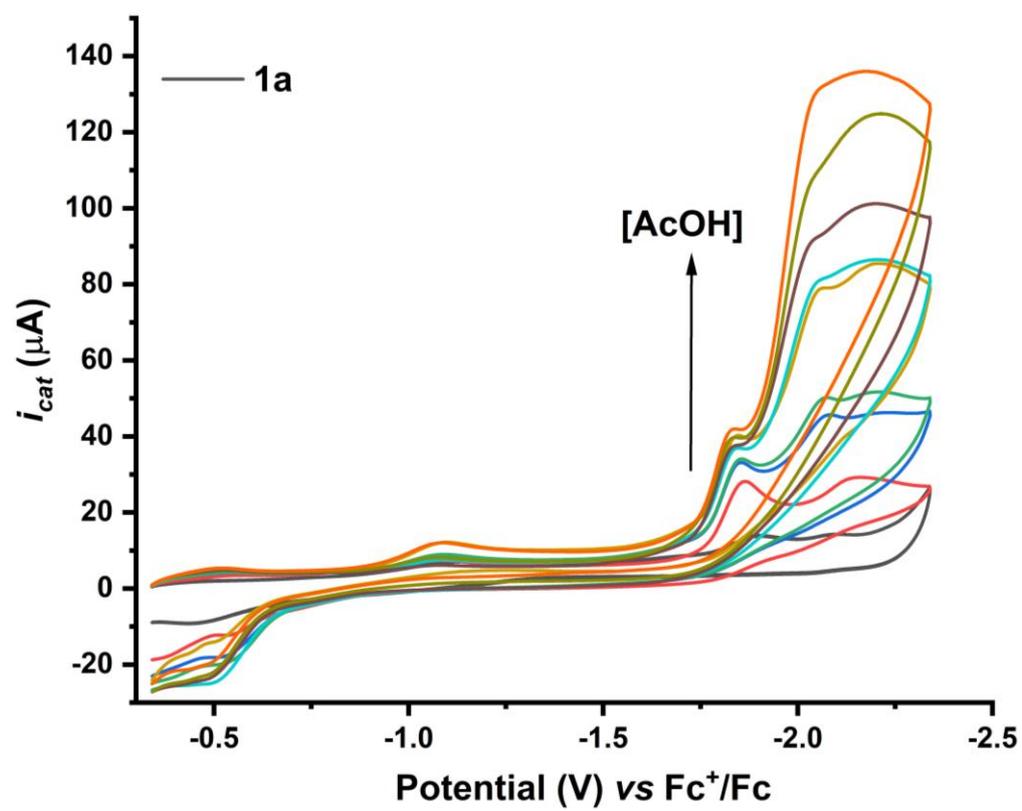
**Figure S12.** CV at various scan rate for Co(II/I) redox couple for **3c** and corresponding Cortrell Plot.



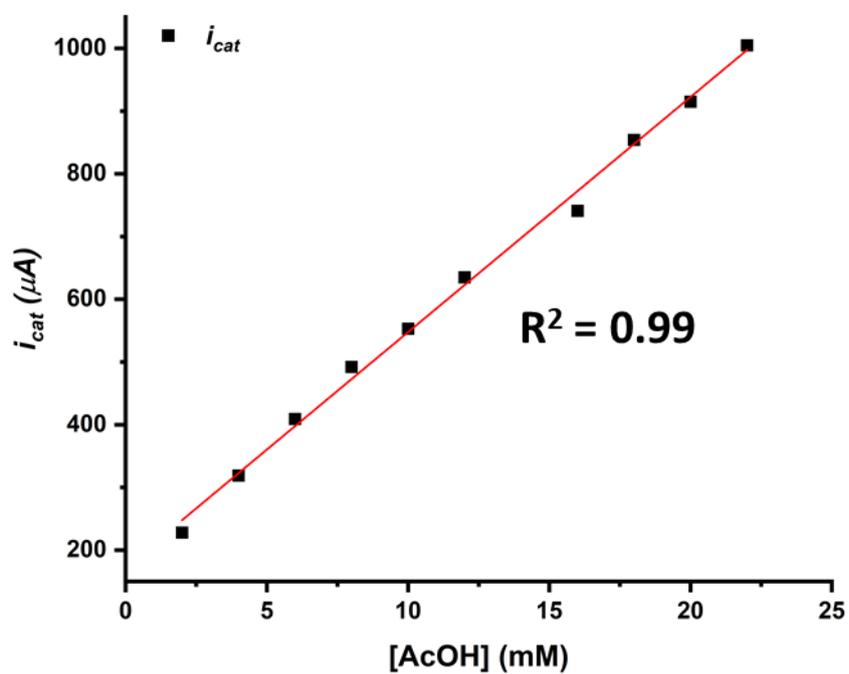
**Figure S13.** CV at various scan rate for Co(II/I) redox couple for **3d** and corresponding Cortrell Plot.



**Figure S14.** Electrolytic acid titration of 1,10-phenanthroline cobalt(II) chloride **1b**



**Figure S15.**  $i_{cat}$  vs [AcOH] Graph for **3a** at 0.1V/s



**Figure S16.**  $i_{cat}$  vs [AcOH] Graph for **3b** at 0.1V/s

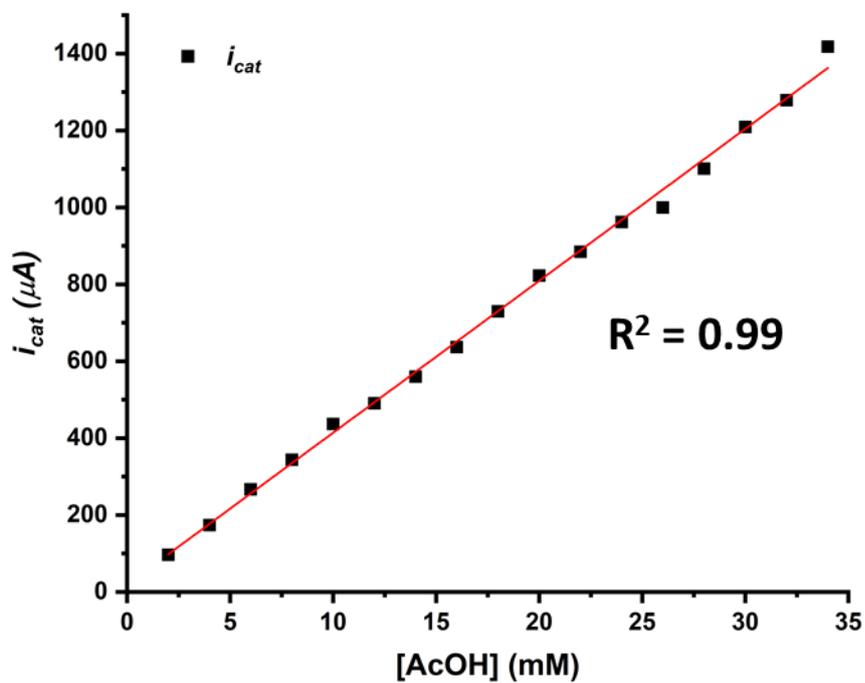


Figure S17.  $i_{cat}$  vs [AcOH] Graph for **3c** at 0.1V/s

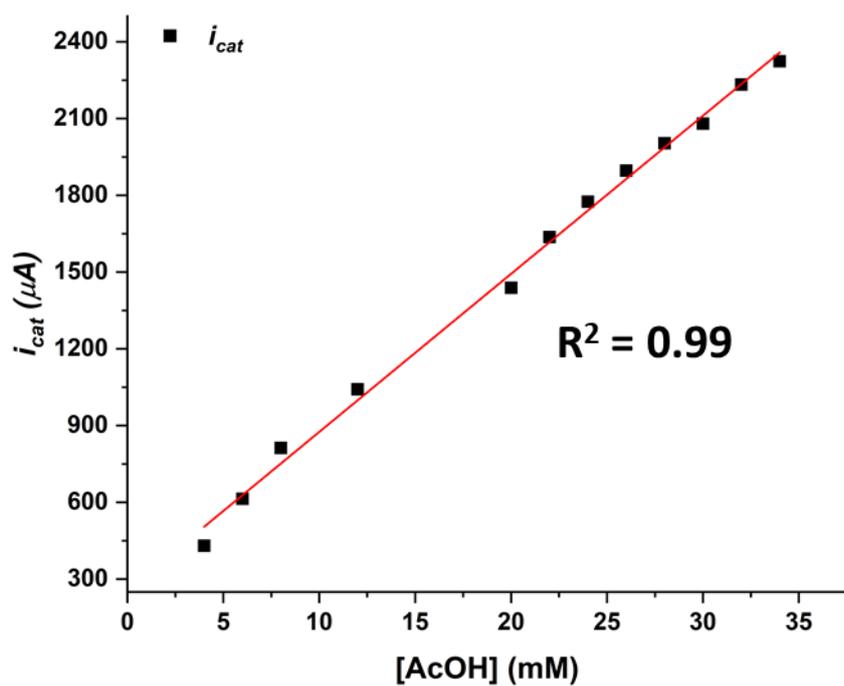


Figure S18.  $i_{cat}$  vs [AcOH] Graph for **3c** at 0.1V/s

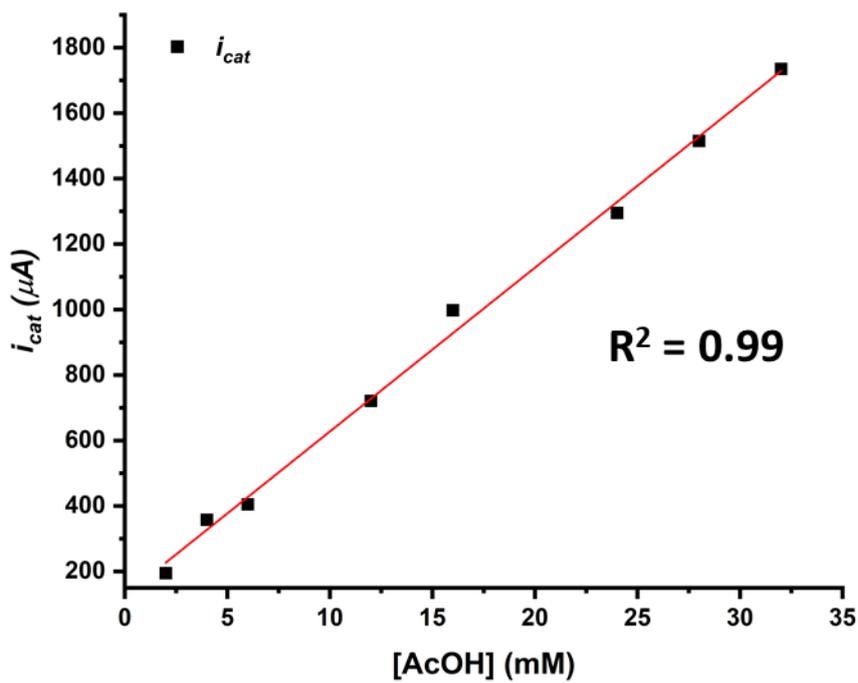
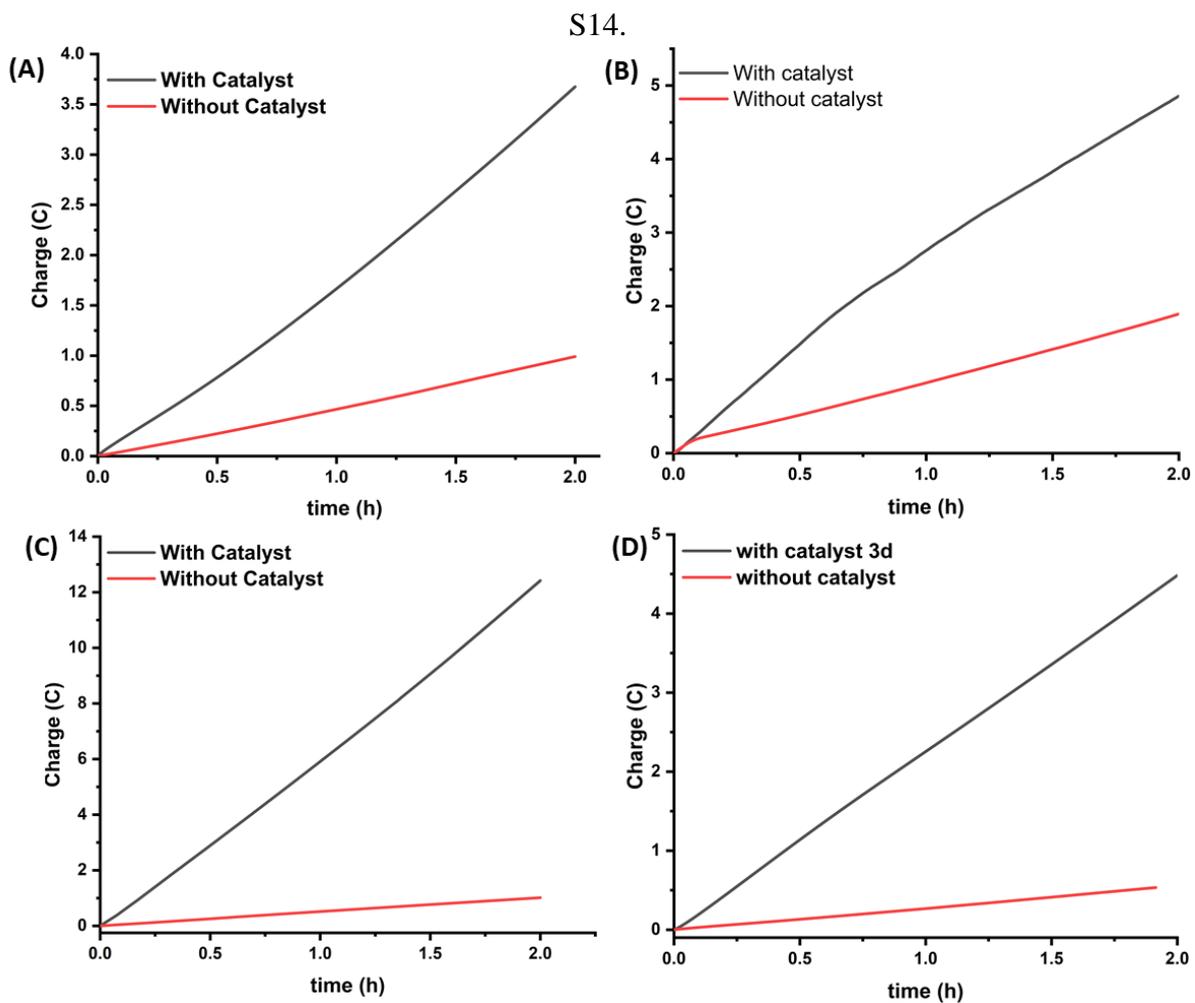
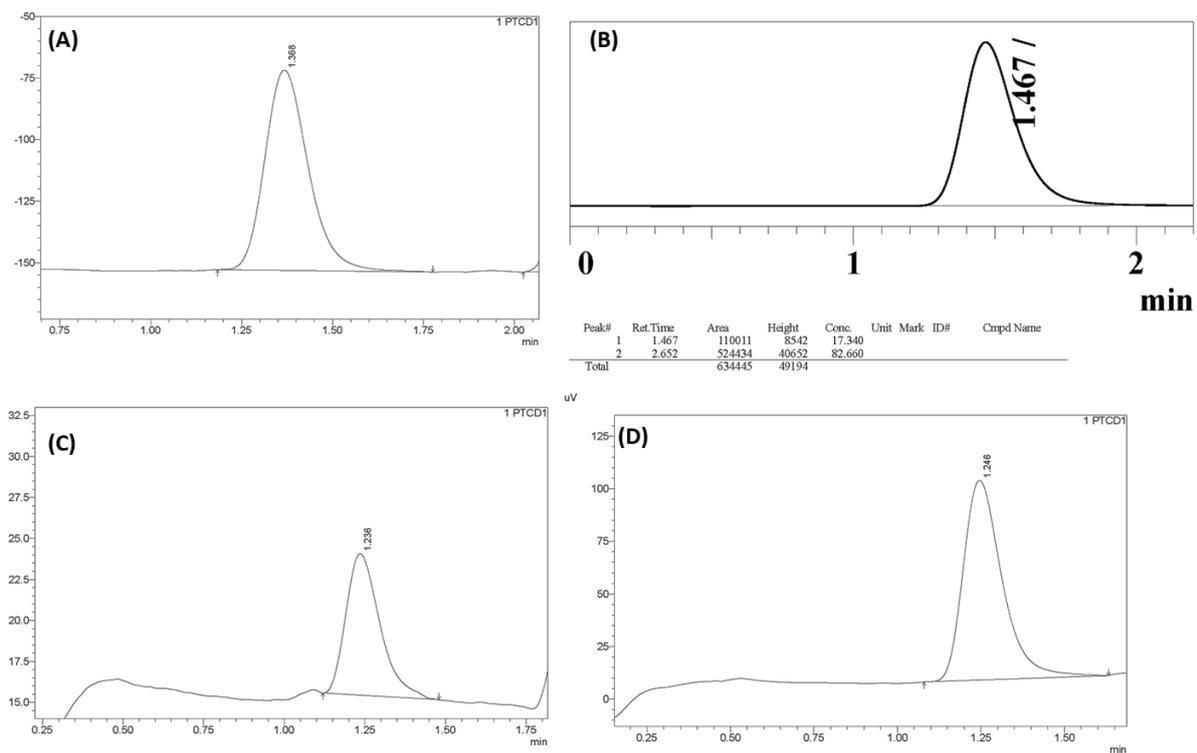


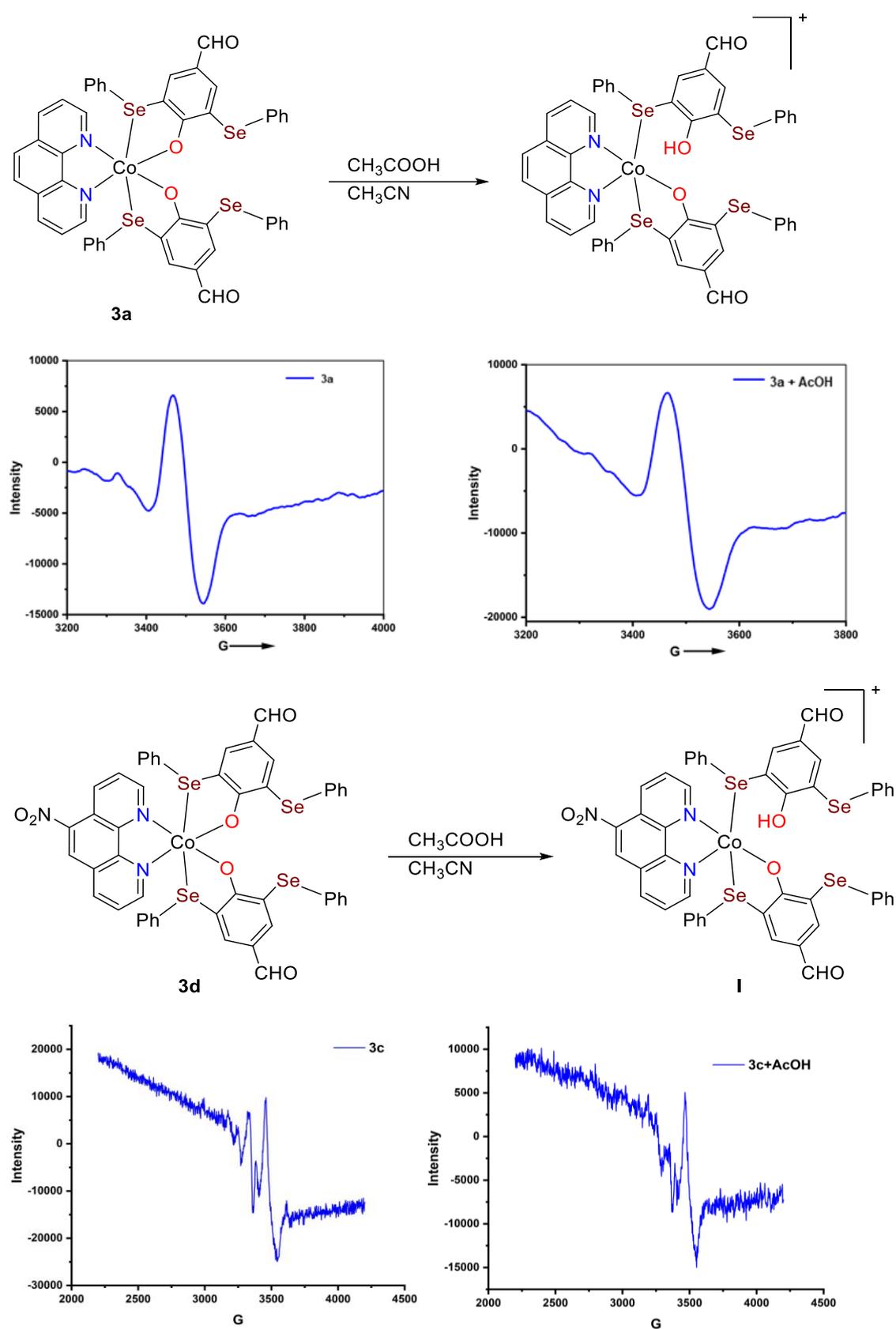
Figure S19A-D. Post Dip Analysis of Catalysts 3a (A), 3b (B), 3c (C), and 3d (D)



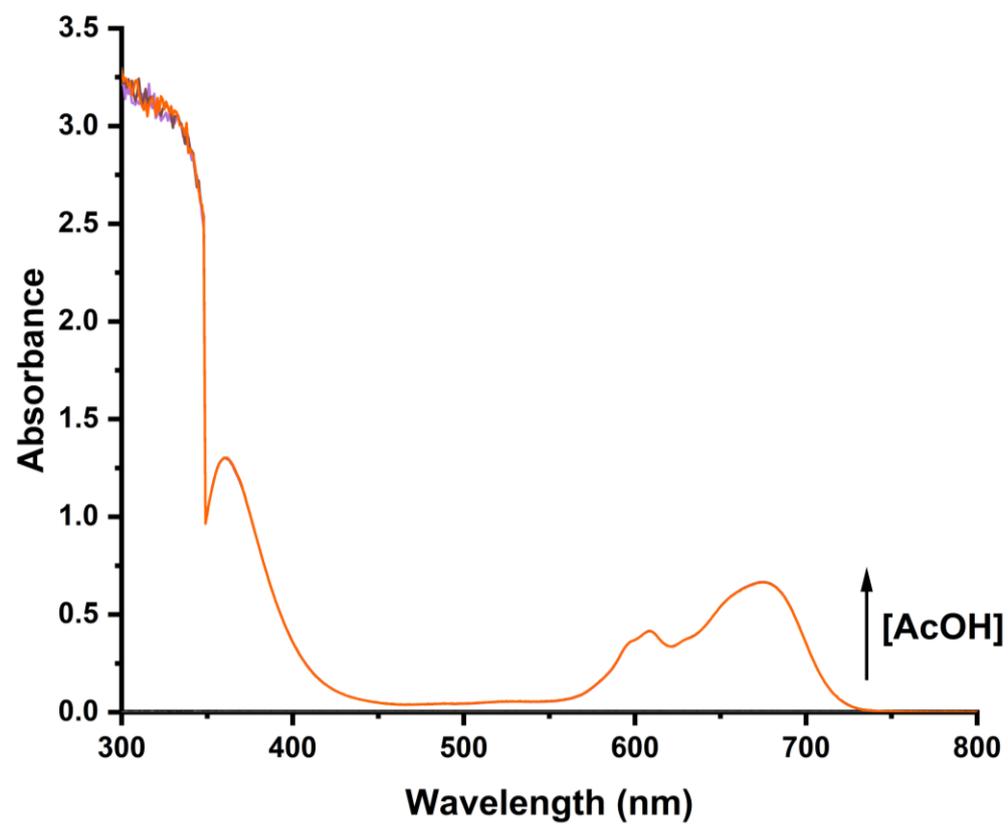
**Figure S20.** GCTCD Read out of Hydrogen Gas Production for Catalysts **3a-3d**



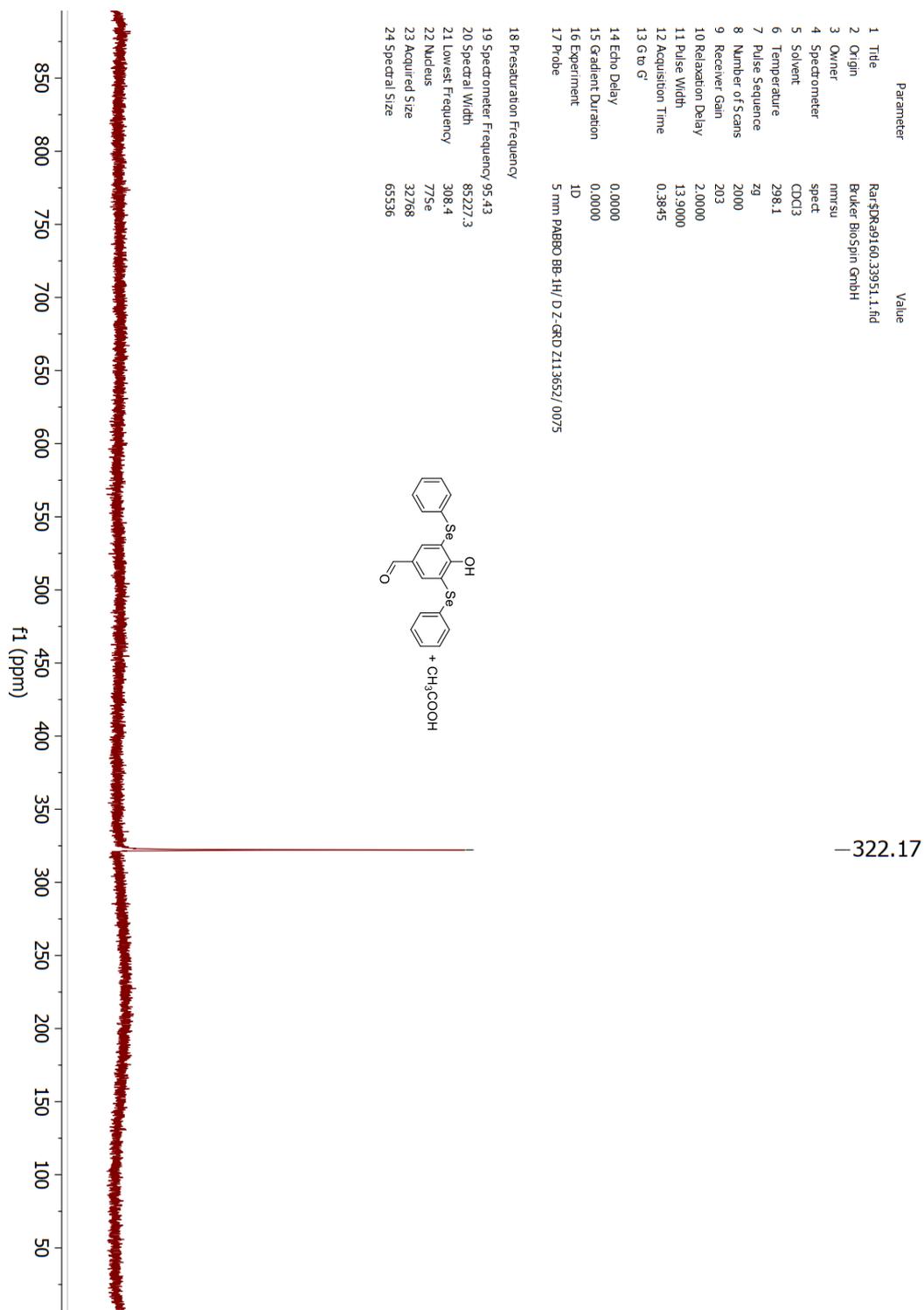
**Figure S21.** EPR Study of Acidic Solution of **3a** and **3d**



**Figure S22.** The UV-Visible titration of **1b** in the presence of acetic acid



**Figure S23.**  $^{77}\text{Se}$  NMR of a Reaction Mixture of Ligand **2a** and Acetic Acid in  $\text{CDCl}_3$



The  $^{77}\text{Se}$  NMR chemical shift value is similar to its actual bis-selenophenol which occurs at 320 ppm (*Chem. Asian J.* 2021, **16**, 966–973), which suggests that selenium has not protonated on the addition of acetic acid.