Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Efficient bifunctional reactivity of K-doped CrO(OH) nanosheets: Exploiting the combined role of Cr(III) and surface -OH groups in tandem catalysis

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S1 Experimental Section:

Materials used: Potassium chromate K_2CrO_4, Chromium Nitrate nonahydrate $Cr(NO_3)_2.9H_2O$, tetraethyl orthosilicate (TEOS), aminopropyl triethoxysilane (APTES), Benzyl alcohol, 1-phenyl ethanol, Benzaldehyde, Malononitrile, Aniline, Ethyl cyano acetate, acetophenone, aniline, Acetonitrile, xylene.

Synthesis of K-α-CrO(OH): A quartz boat, loaded with K_2CrO_4 particles was put in the tube furnace. Hydrogen was then introduced at a constant flow rate into the tube to keep the reductive atmosphere. The reaction temperature was raised to the ramping rate 10 ºC/min and kept at 500 ºC for 1 h and naturally cooled to the ambient temperature. The product was washed by distilled water several times until the dissolvable components were completely removed. After that, the black green intermediate was dried at 60 °C.

Synthesis of α-CrO(OH): 1g of K-α-CrO(OH) was taken in 50mL of 0.01N HCL solution and stirred for 48h at 70°C and filtered. The obtained residue was stirred again in distilled water, filtered and dried at 60°C.

Synthesis of γ-CrO(OH)[1] 15 g of $Cr(NO_3)_2.9H_2O$ was taken and dissolved in 75 mL of distilled water. 10% Ammonia solution was added dropwise with constant stirring till the pH attained the value 5. The solution was allowed to stir for further 30 min, centrifuged and washed to obtain the precipitate. This wet precipitate was transferred into a beaker and was placed in a teflon lined autoclave containing 2 mL of water. The sample was sealed and heated for 12 h at 170 ºC. The resultant product was washed, centrifuged and dried. Cr_2O_3 was obtained by calcining γ-CrO(OH) in a muffle furnace at 800 °C.

Synthesis of K-γ-CrO(OH): In the synthesis procedure of γ-CrO(OH), 0.5g KNO_3 was additionally added in 75mL of distilled water containing 15g of $Cr(NO_3).9H_2O$. 10% Ammonia solution was added dropwise to the above solution with constant stirring till the pH attained the value 5. The solution was allowed to stir for further 30 min, centrifuged and washed to obtain the precipitate. This wet precipitate was transferred into a beaker and was placed in a teflon lined autoclave containing 2 mL of water. The sample was sealed and heated for 12 h at 170 ºC. The resultant product was washed, centrifuged and dried. The elemental analysis showed K loading of 3.0 wt %

Synthesis of SiO_2-NH_2: 0.5mL of Ammonia stock solution (30%) was taken along with 3.77mL of distilled water and 15mL of isopropanol and stirred for 10min. Then 7.44mL of Tetraethylorthosilicate was added dropwise with stirring. A white silica suspension was obtained which was stirred for further 5h and then centrifuged washed with ethanol and dried at 150 ºC for 5h. For amine functionalization 5 mmol of amino propyl triethoxysilane was taken in dry toluene along with 1g of SiO_2 powder obtained above. This was refluxed overnight at 110 ºC then filtered washed with ethanol and dried to obtain SiO_2-NH_2.

Characterization: Transmission electron microscopy (TEM) images were obtained using FEI Technai TF-20 electron microscope operating at 200kV. Specimens of the samples were prepared by drop-casting well-dispersed ethanol particle suspensions onto a carbon coated copper grids. Infrared Spectroscopy measurements were done using Bruker FT-IR. The samples were analyzed as solids. XRD was measured using PANalytical X'pert Pro diffractometer working under 40kV and 20 mA with CuKα (0.154 nm) radiation using a Ni filter. X-ray photoelectron spectroscopy (XPS) study of K-α-CrO(OH) was done using VG Microtech model ESCA 3000 instrument. The organic reaction was monitored using an Agilent Technologies GC (7890B) equipped with a Flame Ionization Detector using a HP-5 capillary column. CO_2 TPD measurements were performed on Micromeritics ChemiSorb 2720 instrument equipped with a TCD detector.

Catalytic Reaction:

Knoevenagel Condensation: In a typical reaction 1 mmol of benzaldehyde was taken along with 2 mmol of malononitrile **(2a)** / ethylcyanoacetate **(2b)** in a 25 mL round bottomed flask with 0.1 g of catalyst using 5mL of acetonitrile and heated at 80 ºC for required amount of time in nitrogen atmosphere. The reaction mixture was cooled and then centrifuged. The supernatant was analyzed using GC.

C-C & C-N coupling reaction : In a typical reaction 1 mmol of benzaldehyde (1) was taken along with 2 mmol of acetophenone **(2c)** / aniline **(2d)** in a 25 mL round bottomed flask with 0.4 g of catalyst using 5mL of xylene and heated at 110 ºC for 12h in nitrogen atmosphere to yield **3c** & **3d** respectively. The reaction mixture was cooled and then centrifuged. The supernatant was analyzed using GC.

Benzyl alcohol oxidation: In a typical procedure, 1 mmol alcohol and 5 mL xylene was taken in a 25 mL round bottomed flask along with the required amount of catalyst. The suspension was refluxed at 110 °C for suitable time under oxygen atmosphere. The reaction mixture was cooled and then centrifuged and the supernatant was analyzed using GC.

Sequential oxidation-condensation: In a typical procedure, 1 mmol benzyl alcohol and 5 mL xylene was taken in a 25 mL RBF along with 0.4 g of catalyst and refluxed for suitable time under balloon oxygen pressure. After which 2 mmol malononitrile/ethyl cyanoacetate was injected into the reaction mixture and the reaction allowed to proceed for further time The reaction mixture was cooled and centrifuged with the supernatant liquid analyzed using GC.

One pot Oxidation-C-C coupling reaction: 1 mmol of benzyl alcohol and 2 mmol of 1-phenyl ethanol were taken in a 25 mL round bottom flask dissolved in 5mL of xylene together with 0.4 g of K-α-CrO(OH). This was refluxed for 48h under balloon oxygen to give **3c** The reaction mixture was cooled and then centrifuged and the supernatant was analyzed using GC.

One pot Oxidation- C-N coupling reaction: 1 mmol benzyl alcohol and 2 mmol of aniline were taken in a 25 mL round bottom flask dissolved in 5 mL of xylene together with 0.4g of K-α-CrO(OH). This was refluxed for 24h under balloon oxygen pressure to give **3d**. The reaction mixture was cooled and then centrifuged and the supernatant was analyzed using GC.

Recyclability: After the one pot reaction synthesis of **3c** the catalyst was separated by centrifugation washed thoroughly with CH_3OH and dried to be used for the next cycle.

In-situ Infrared Spectroscopy: CO_2 adsorption on K-α-CrO(OH)/ α-CrO(OH) was done using a praying mantis assembly equipped to a Perkin Elmer FT-IR using a MCT detector cooled using Liquid Nitrogen. The sample holder and the sample were first degassed under N_2 gas flow at 300 °C. The IR of the bare sample was then recorded. CO_2 was subsequently purged on K-α-CrO(OH)/ α-CrO(OH) held in the sample holder cavity in N_2 flow at room temperature. IR of the CO_2 adsorbed sample was measured. The difference spectra was obtained using the *difference function* inbuilt in the *Spectrum* Software.

Cyclic Voltametry: The electrochemical analysis of all the synthesized samples were carried out by using the cyclic voltammetry technique. Prior to the measurement, glassy carbon electrodes were well polished by alumina slurry (of size 1 μ, 0.3 μ, 0.05 μ sequentially), sonicated in double distilled water and dried in the vacuum desiccator. In the meantime, the sample ink has been prepared by mixing the powdered sample (1mg) with absolute ethanol (95) and Nafion followed by ultrasonication for 5 minutes. An optimized amount of the sample ink has been drop casted onto the polished glassy carbon electrode and dried in the vacuum desiccator. The CV profiles were recorded by using Metrohm Electrochemical workstation in a two compartment three electrode electrochemical cell with a bare platinum (as auxiliary electrode), aqueous Ag/AgCl (as reference) and sample modified glassy carbon (as working electrode) in the electrolyte solutions (neutral: Na_2SO_4, acidic: 0.5M H_2SO_4, and alkaline: 1M KOH) at different sweep rates (10, 50 and 100 mV/s).

Fig. S1: BET Hysteresis plot for K-α-CrO(OH)

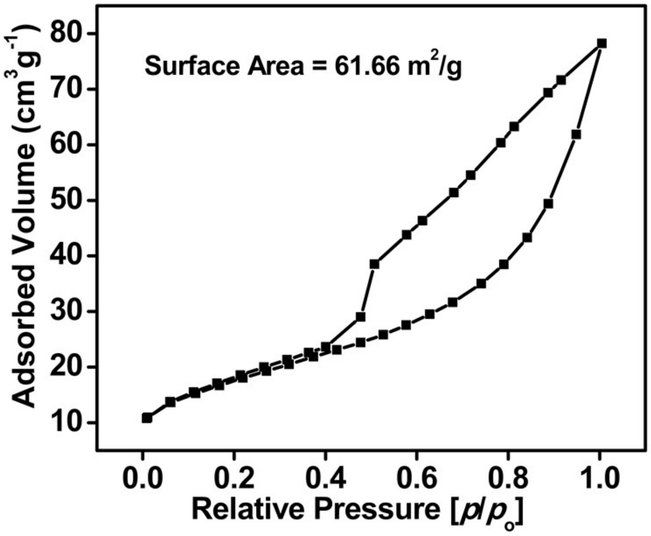


Fig. S2: Atomic Force Microscopy images of K-α-CrO(OH). Inset of b) shows thickness of sheet along the line between the dotted boundaries

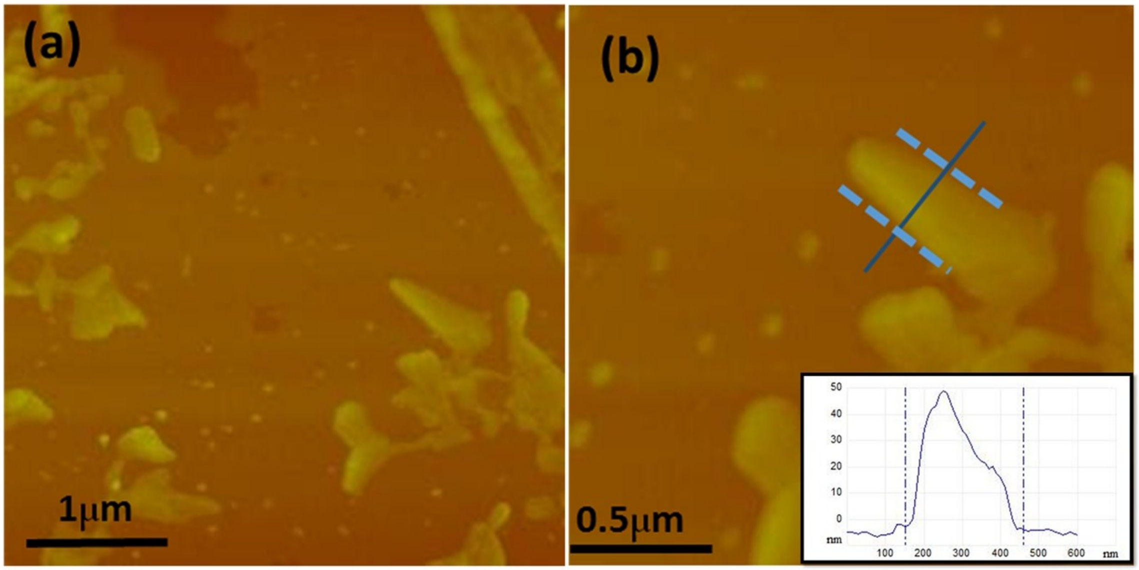
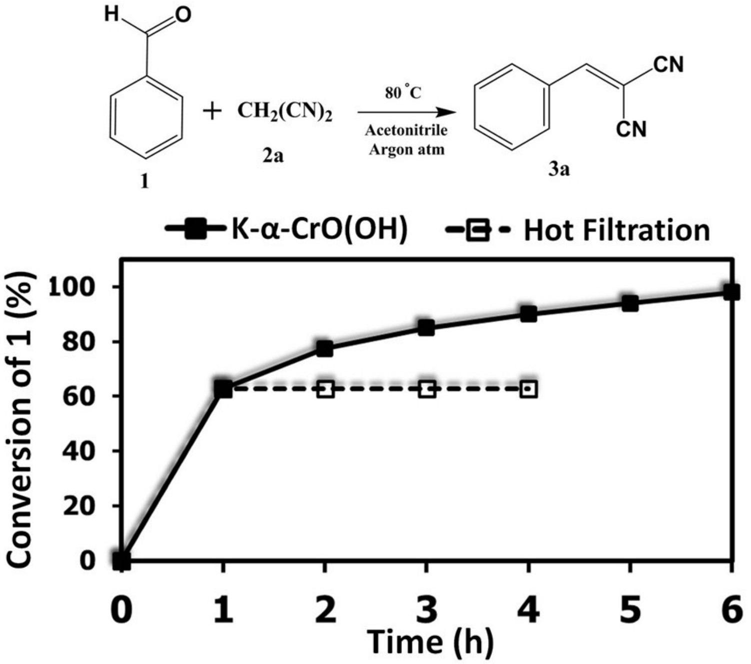


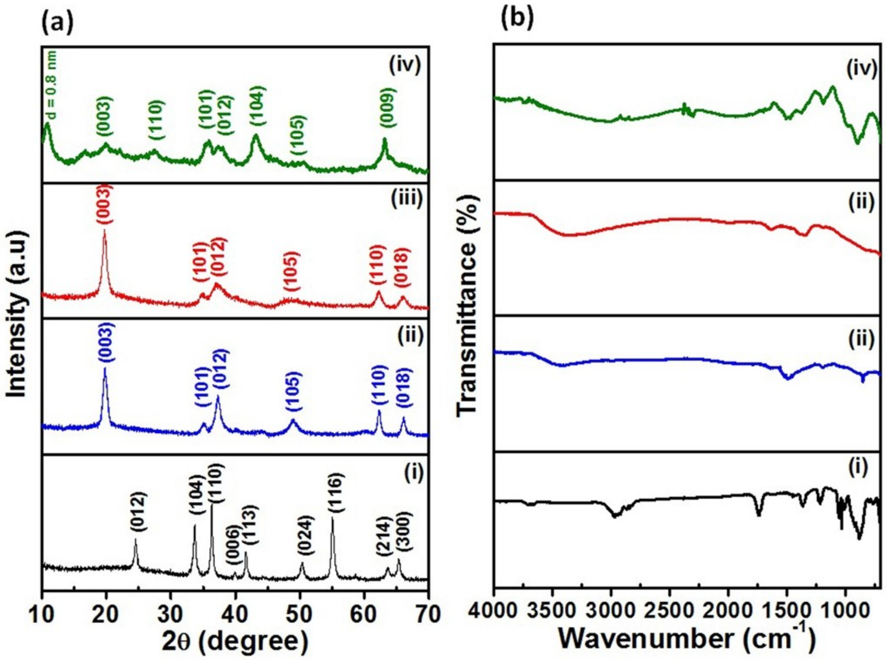
Fig. S3: Time dependent conversion for Knoevenagel Condensation using K-α-CrO(OH) and Hot filtration test for K-α-CrO(OH) for Knoevenagel Condensation.



Reaction conditions: 1 (1 mmol), 2a (2 mmol), acetonitrile (5 mL), K-α-CrO(OH) 100mg,

Temperature: 80 °C , Nitrogen atmosphere.

Fig. S4: (a) XRD & (b) Infrared spectrum of i)Cr_2O_3 ii) γ-CrO(OH) iii)K- γ- CrO(OH) iv) α-CrO(OH)



XRD analysis (Fig S4a) of the control samples showed peaks due to respective phases and no impurity peaks were observed.

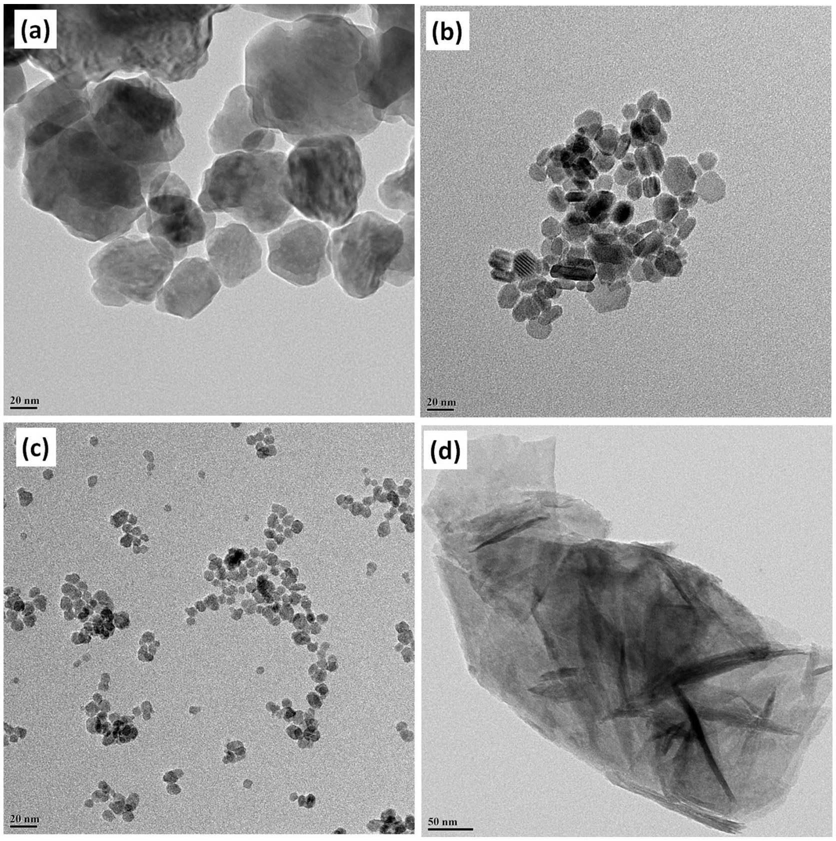
α-CrO(OH) - JCPDS-09-0331

γ-CrO(OH) - JCPDS-85-1373

Cr_2O_3 - JCPDS- 38-1479

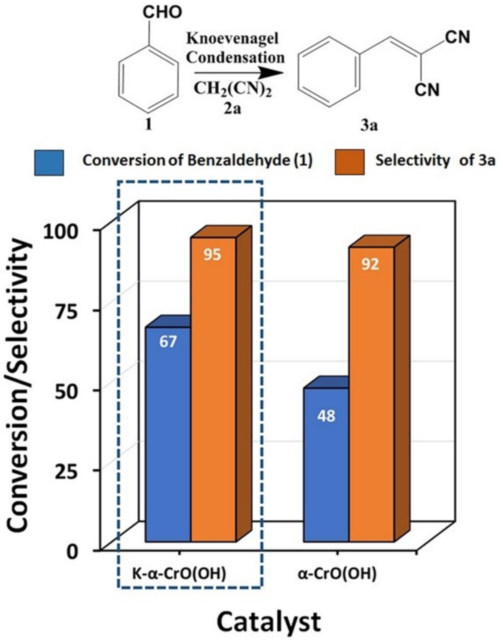
Infrared Spectroscopy (Fig S4b) indicated the presence of surface hydroxyl groups (3000-3700 cm^{-1}) in the case of γ-CrO(OH), K- γ- CrO(OH) and α-CrO(OH). Whereas surface hydroxyl groups are absent in the case of Cr_2O_3.

Fig S5: TEM images of a)Cr_2O_3 b) γ-CrO(OH) c)K- γ- CrO(OH) d) α-CrO(OH)



Cr_2O_3 has larger nanoparticle like morphology (Fig S5a). γ-CrO(OH) and K- γ-CrO(OH) are in the form of smaller nanoparticles (Fig 5b,c). α-CrO(OH) (Fig S5d) has a nanosheet like morphology intact, similar to K-α-CrO(OH).

Fig. S6: Knoevenagel condensation reaction for K doped and K free α-CrO(OH)



Reaction conditions: **1** (1 mmol), **2a** (2 mmol), acetonitrile (5 mL), K-α-CrO(OH)/ α-CrO(OH) 100mg, Temperature: 80 °C , Nitrogen atmosphere. 3h

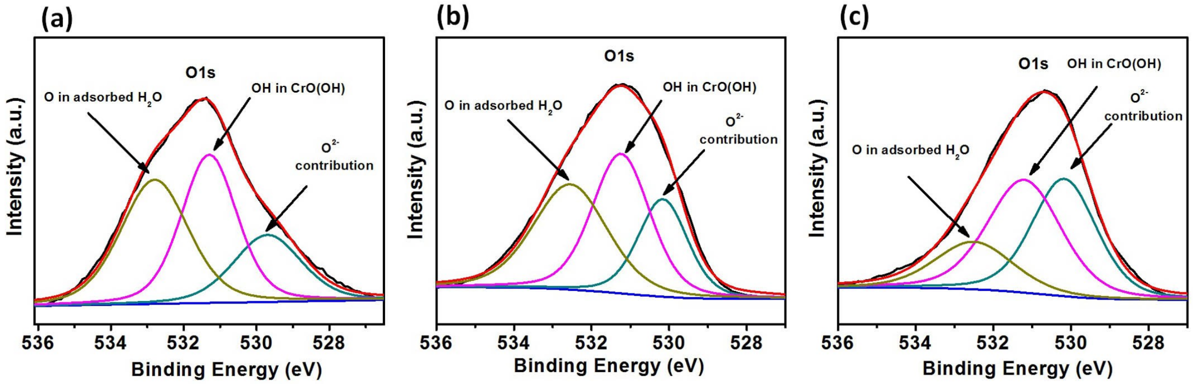
Table S7 : Textural properties and CO_2 TPD results of the samples.

Sr. No	Sample	Surface area (m^2/g)	Pore Volume cc/g	Weak/moderate Basicity (mmol/g of CO_2)
1.	Cr_2O_3	118.32	0.089	0.02
2.	γ-CrO(OH)	92.32	0.116	0.33
3.	K- γ-CrO(OH)	83.63	0.098	0.56
4.	α-CrO(OH)	68.35	0.086	0.59
5.	K-α-CrO(OH)	61.66	0.079	0.93

Table S8: Calculated weight loss of the samples obtained from TGA.

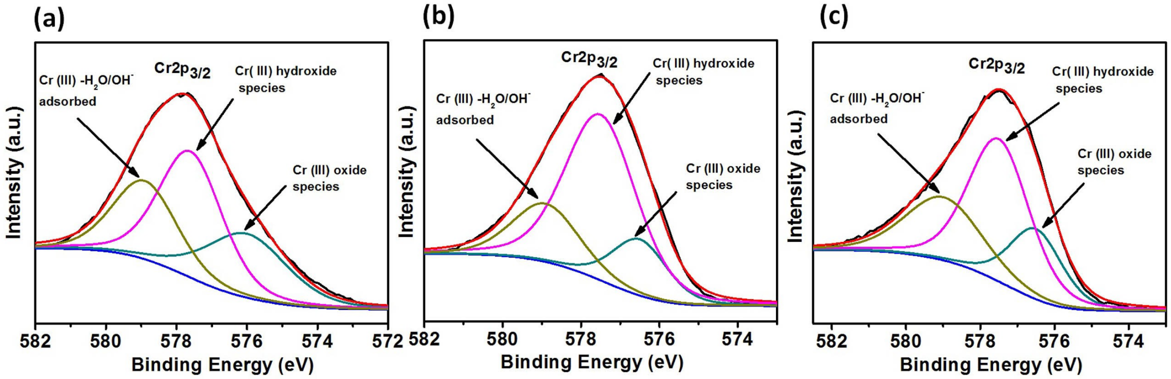
Sr No	Catalyst	Weight Loss from TGA (%) at various temperature ranges (°C)					Weight loss due to surface hydroxyl groups 150-350 °C (%)	Total weight loss @ 350 °C (%)
		25-150	**150-200**	**200-250**	**250-300**	**300-350**		
1.	K-α-CrO(OH)	4.83	2.92	2.67	1.47	1.40	8.48	13.31
2.	α-CrO(OH)	4.09	1.98	2.04	1.43	1.21	6.68	10.77
3.	K-γ-CrO(OH)	5.93	1.82	0.78	0.44	0.65	3.71	9.64
4.	γ-CrO(OH)	2.94	1.56	1.31	1.01	1.02	4.91	7.85
5.	Cr_2O_3	0.63	0.09	0.15	0.12	0.08	0.45	1.08

Fig S9: Deconvoluted O1s spectra of a) α-CrO(OH) b) γ-CrO(OH) c)K- γ- CrO(OH) with the calculated contributions of different Cr(III) species



Sr.No	**Catalyst**	**O^{2-} contribution (530.2eV) (%)**	**OH in CrO(OH) species (531.4 eV) (%)**	**O in adsorbed H_2O (532.4 eV) (%)**
1.	α-CrO(OH)	22	38	40
2.	K-α-CrO(OH)	32	34	36
3.	γ-CrO(OH)	23	39	38
4.	K-γ-CrO(OH)	39	37	24

Fig S10: Deconvoluted Cr2p$_{3/2}$ spectra of a) α-CrO(OH) b) γ-CrO(OH) c)K- γ- CrO(OH) with the calculated contributions of different Cr(III) species



Sr.No	Catalyst	Cr(III)-H$_2$O/OH- adsorbed (579.0 eV) (%)	Cr(III) hydroxide species (577.6 eV) (%)	Cr(III) oxide species (576.4 eV) (%)
1.	α-CrO(OH)	28	45	27
2.	K-α-CrO(OH)	23	52	25
3.	γ-CrO(OH)	20	63	17
4.	K-γ-CrO(OH)	28	51	21

Fig S11: Comparative FT-IR spectra of K-α-CrO(OH)-Rh-6G with bare K-α-CrO(OH) and Rh-6G in two different regions a) & b)

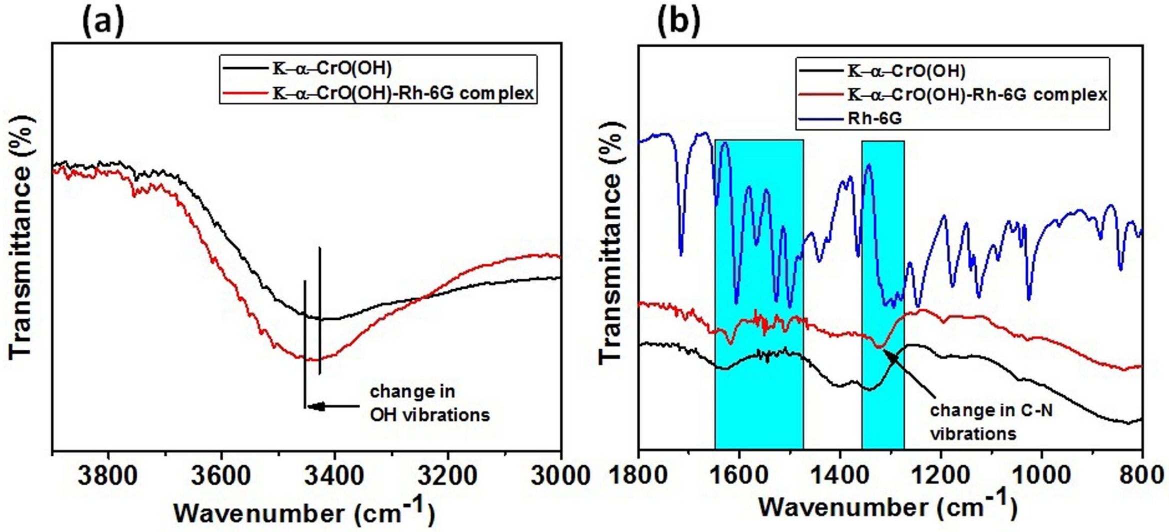
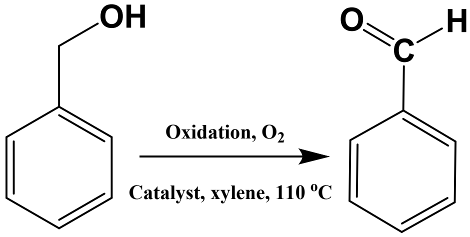


Table S12: Table showing the catalytic activity of K-α-CrO(OH) and other catalysts for benzyl alcohol oxidation



benzyl alcohol

1

Entry	Catalyst	Catalyst amount (g)	Conversion (%)	GC Selectivity (%)‡
1	No catalyst	-	0	-
2	K-α-CrO(OH)	0.1	64	99
3	K-α-CrO(OH)	0.4	100	95
4	α-CrO(OH)	0.4	83	96
5	γ-CrO(OH)	0.4	24	98
6	K- γ-CrO(OH)	0.4	38	96
7	Cr_2O_3	0.4	14	90

Reaction conditions: Benzyl alcohol (1 mmol), xylene (5mL), 110 °C, Time of reaction = 15h, ‡Apart from benzaldehyde, we also observed benzoic acid and benzyl benzoate as side products in low yields.

Fig S13: Cyclic Voltametry curves of a) α-CrO(OH) b)K- α- CrO(OH) c) γ-CrO(OH) d)K- γ- CrO(OH) e) Cr_2O_3

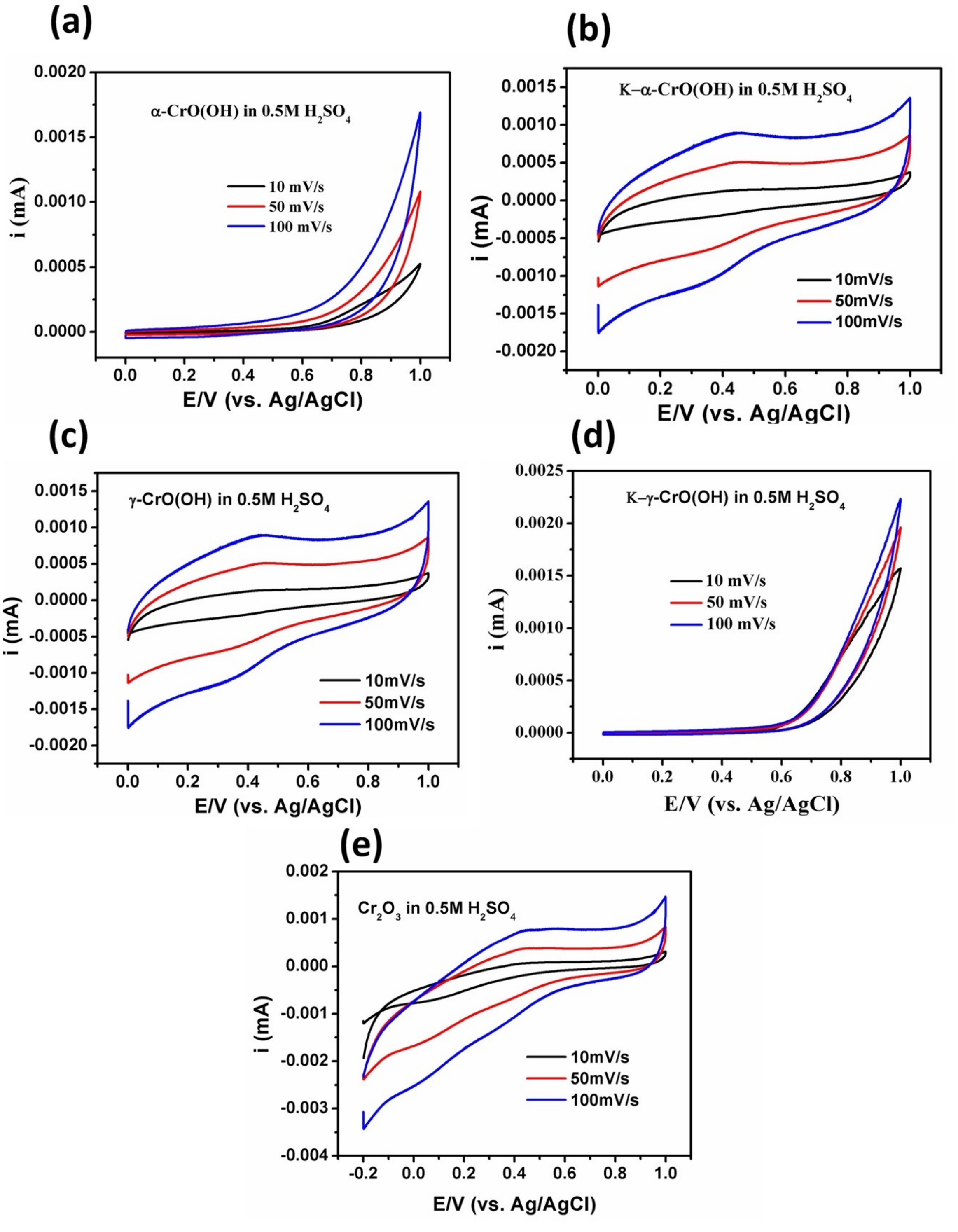
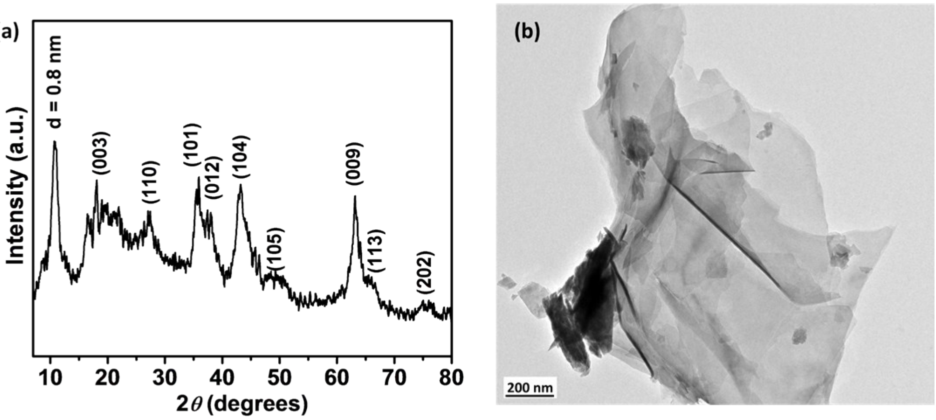
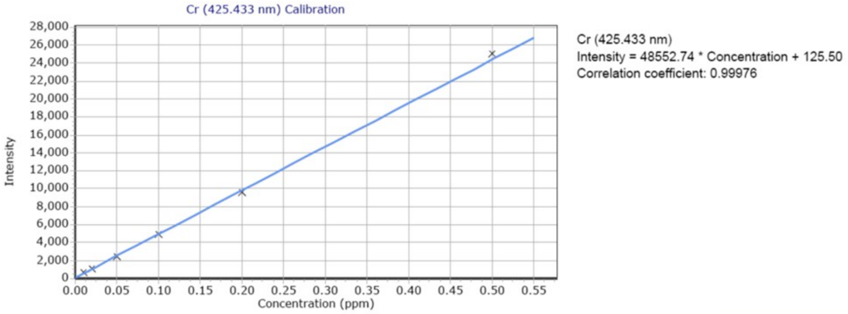


Fig. S14: a) XRD and b) TEM image of used K-α-CrO(OH).

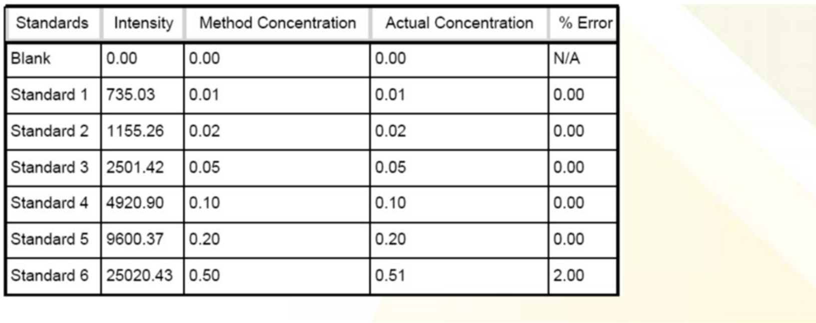


S2: Microwave plasma atomic emission spectroscopy results for leaching studies

a)Calibration Curves

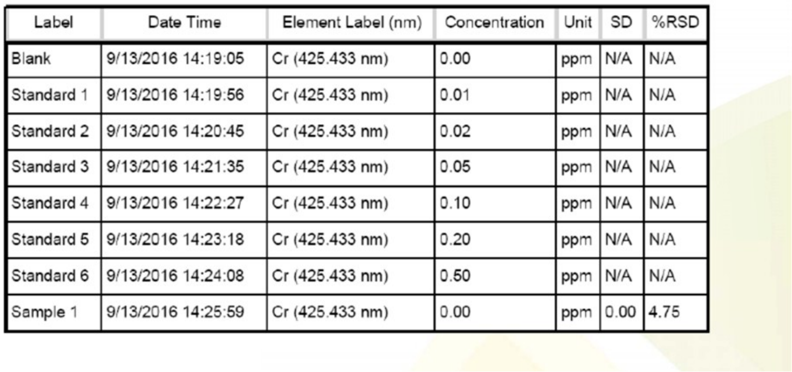


Cr (425.433 nm)
Intensity = 48552.74 * Concentration + 125.50
Correlation coefficient: 0.99976



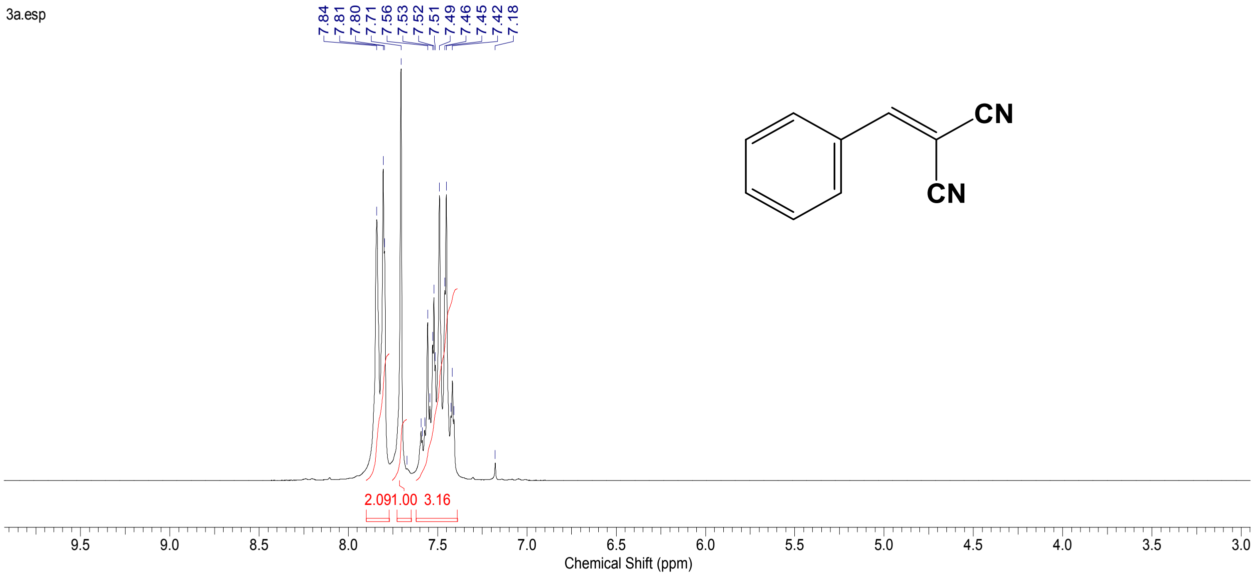
Standards	Intensity	Method Concentration	Actual Concentration	% Error
Blank	0.00	0.00	0.00	N/A
Standard 1	735.03	0.01	0.01	0.00
Standard 2	1155.26	0.02	0.02	0.00
Standard 3	2501.42	0.05	0.05	0.00
Standard 4	4920.90	0.10	0.10	0.00
Standard 5	9600.37	0.20	0.20	0.00
Standard 6	25020.43	0.50	0.51	2.00

b)ICP data

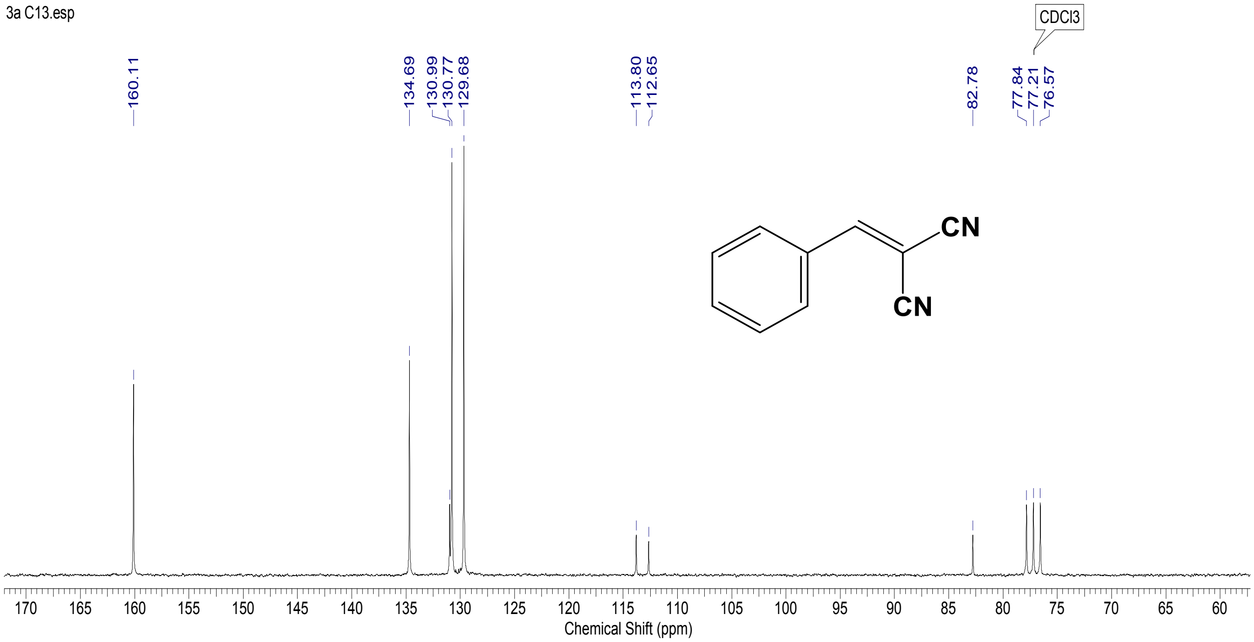


Label	Date Time	Element Label (nm)	Concentration	Unit	SD	%RSD
Blank	9/13/2016 14:19:05	Cr (425.433 nm)	0.00	ppm	N/A	N/A
Standard 1	9/13/2016 14:19:56	Cr (425.433 nm)	0.01	ppm	N/A	N/A
Standard 2	9/13/2016 14:20:45	Cr (425.433 nm)	0.02	ppm	N/A	N/A
Standard 3	9/13/2016 14:21:35	Cr (425.433 nm)	0.05	ppm	N/A	N/A
Standard 4	9/13/2016 14:22:27	Cr (425.433 nm)	0.10	ppm	N/A	N/A
Standard 5	9/13/2016 14:23:18	Cr (425.433 nm)	0.20	ppm	N/A	N/A
Standard 6	9/13/2016 14:24:08	Cr (425.433 nm)	0.50	ppm	N/A	N/A
Sample 1	9/13/2016 14:25:59	Cr (425.433 nm)	0.00	ppm	0.00	4.75

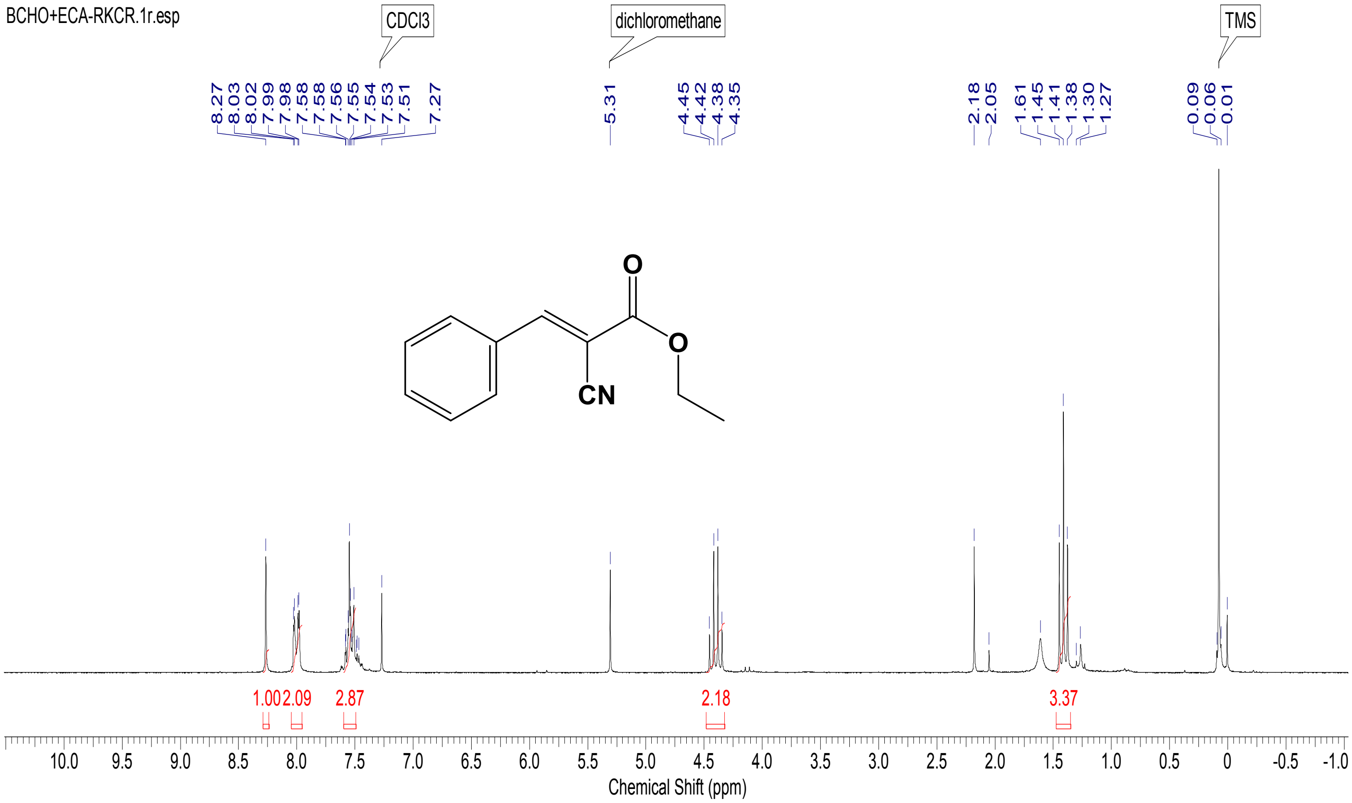
S3: NMR data



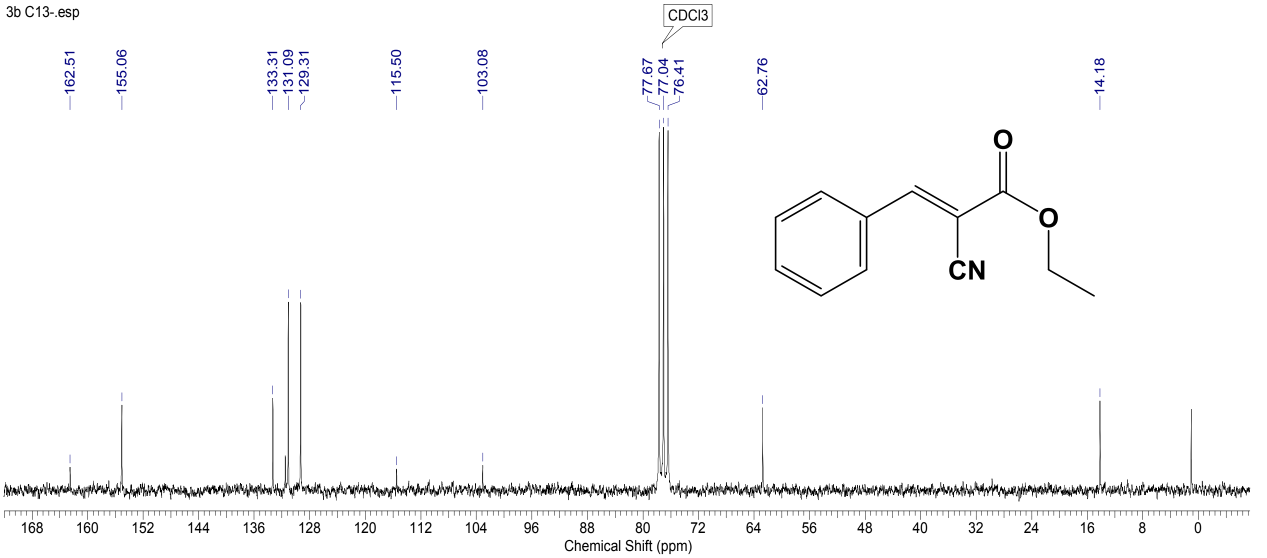
^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 7.39 - 7.62 (m, 4 H) 7.71 (s, 1 H) 7.77 - 7.90 (m, 2 H)



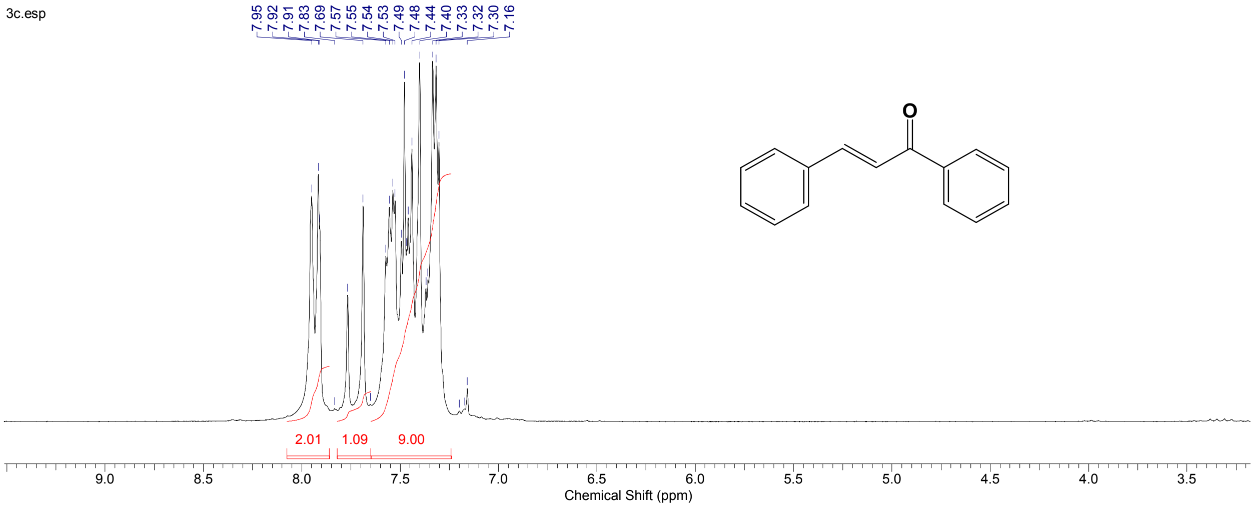
^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 76.57 (s, 1 C) 77.21 (s, 1 C) 77.84 (s, 1 C) 82.78 (s, 1 C) 112.65 (s, 1 C) 113.80 (s, 1 C) 129.68 (s, 1 C) 130.77 (s, 1 C) 130.99 (s, 1 C) 134.69 (s, 1 C) 160.11 (s, 1 C)



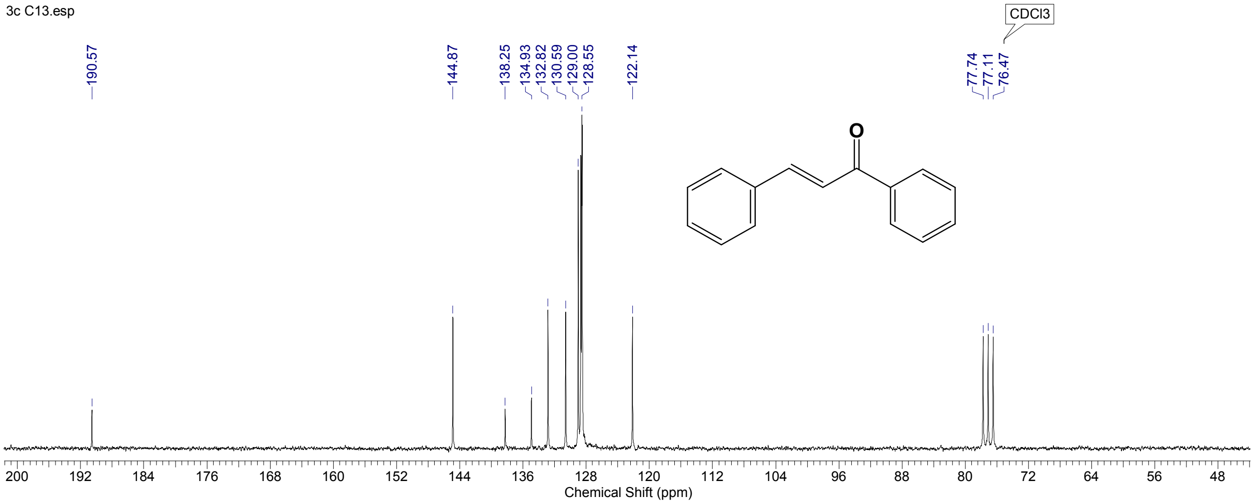
^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 1.41 (t, *J*=7.14 Hz, 4 H) 4.40 (q, *J*=7.20 Hz, 2 H) 7.49 - 7.60 (m, 3 H) 8.00 (dd, *J*=7.64, 1.71 Hz, 2 H) 8.27 (s, 1 H)



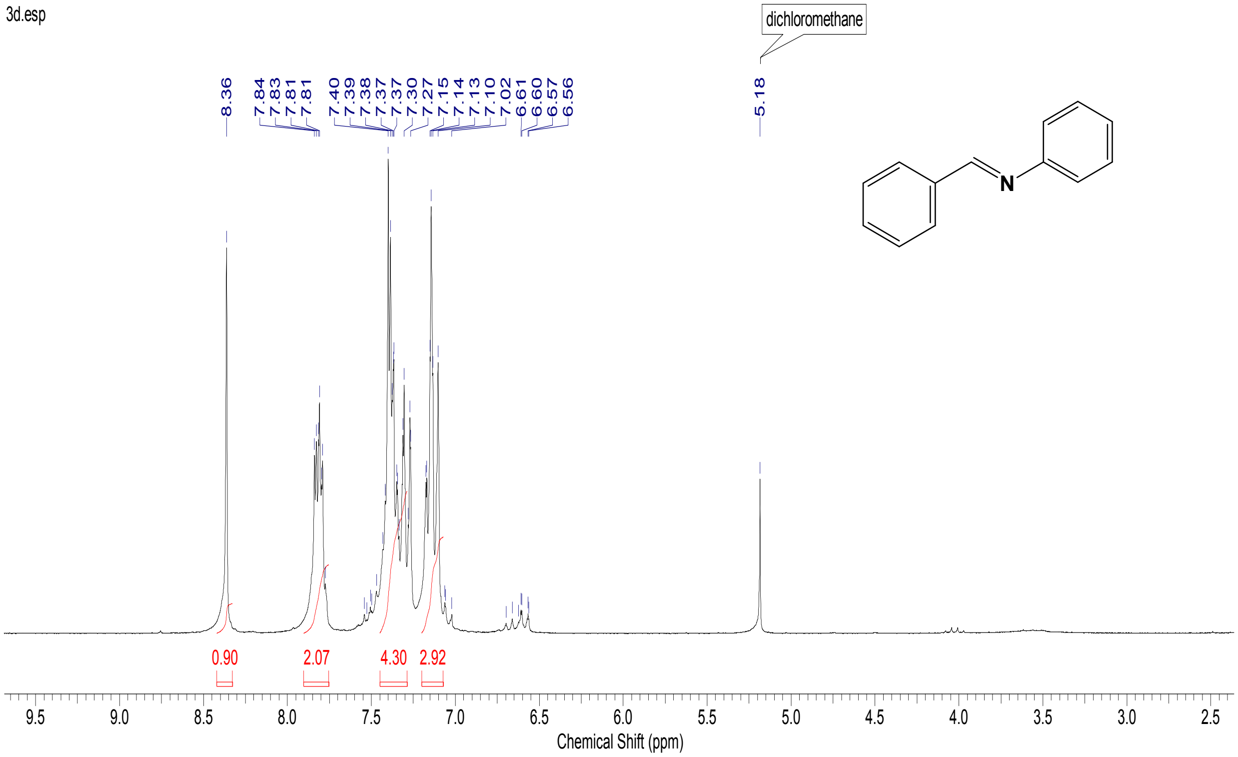
^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 14.18 (s, 1 C) 62.76 (s, 1 C) 76.41 (s, 1 C) 77.04 (s, 1 C) 77.67 (s, 1 C) 103.08 (s, 1 C) 115.50 (s, 1 C) 129.31 (s, 1 C) 131.09 (s, 1 C) 133.31 (s, 1 C) 155.06 (s, 1 C) 162.51 (s, 1 C)



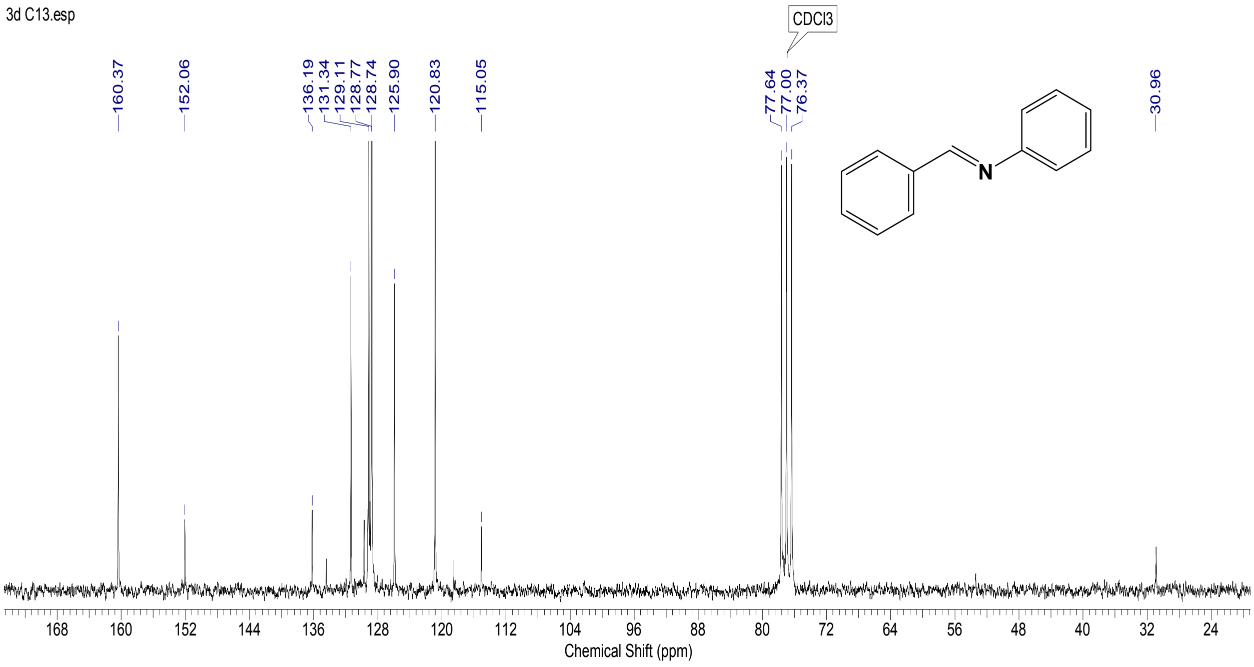
^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 7.24 - 7.65 (m, 10 H) 7.65 - 7.82 (m, 1 H) 7.86 - 8.08 (m, 2 H)



^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 76.47 (s, 1 C) 77.11 (s, 1 C) 77.74 (s, 1 C) 122.14 (s, 1 C) 128.55 (s, 1 C) 129.00 (s, 1 C) 130.59 (s, 1 C) 132.82 (s, 1 C) 134.93 (s, 1 C) 138.25 (s, 1 C) 144.87 (s, 1 C) 190.57 (s, 1 C)



^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 7.07 - 7.20 (m, 3 H) 7.29 - 7.45 (m, 5 H) 7.75 - 7.90 (m, 2 H) 8.36 (s, 1 H)



^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 30.96, 76.37 (s, 1 C) 77.64 (s, 1 C) 115.05 (s, 1 C) 120.83 (s, 1 C) 125.90 (s, 1 C) 128.74 (s, 1 C) 128.77 (s, 1 C) 129.11 (s, 1 C) 131.34 (s, 1 C) 136.19 (s, 1 C) 152.06 (s, 1 C) 160.37 (s, 1 C)

References

1. J. Yang, A. G. Baker, H. Liu, W. N. Martens and R. L. Frost*, Journal of materials scien*ce, 2010**,** 45, 6574-6585.