Supplementary Information

Room temperature complete reduction of nitroarenes over novel $Cu/SiO_2@NiFe_2O_4$ nano-catalyst in aqueous medium – A kinetic and mechanistic study

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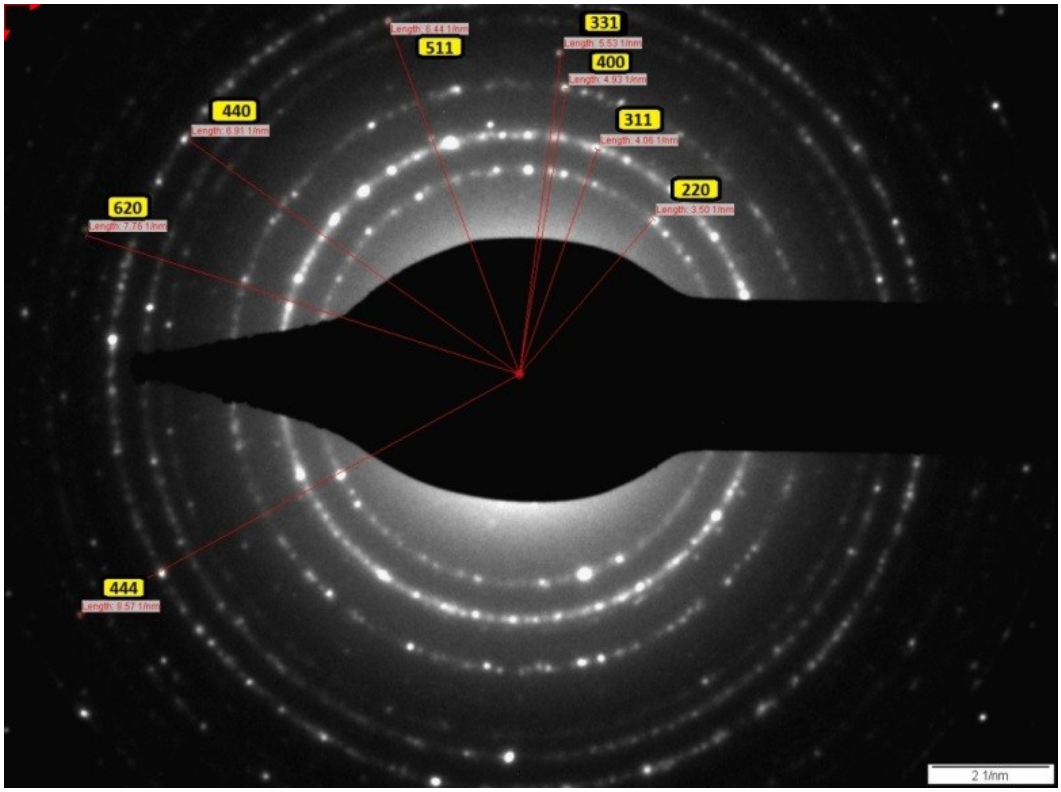


Fig. S1. ED indexing of $NiFe_2O_4$.

Supplementary Information

EDS data

MP1.1

Spectrum processing :

Peak possibly omitted : 0.271 keV

Processing option : All elements analyzed (Normalised)

Number of iterations = 3

Standard :

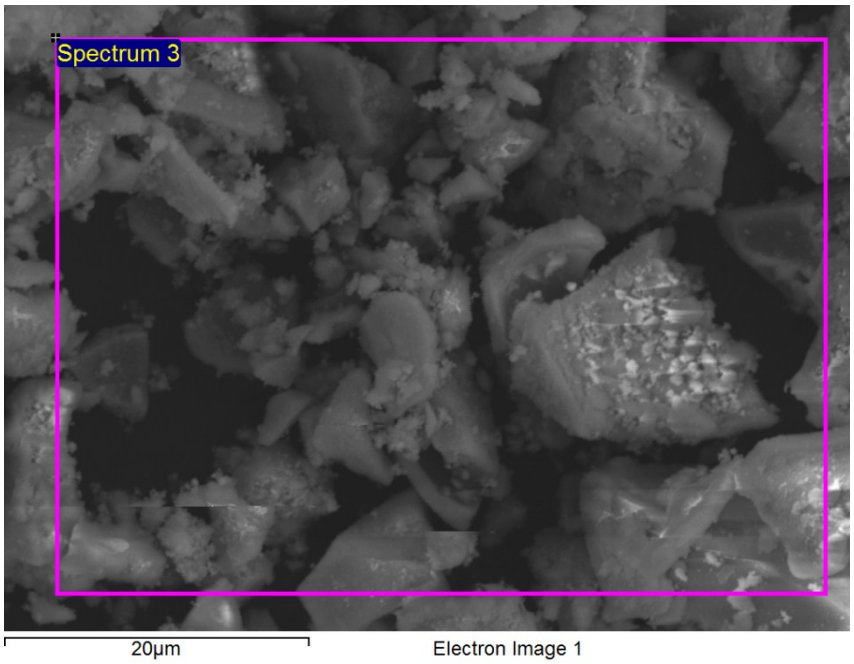
O SiO2 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

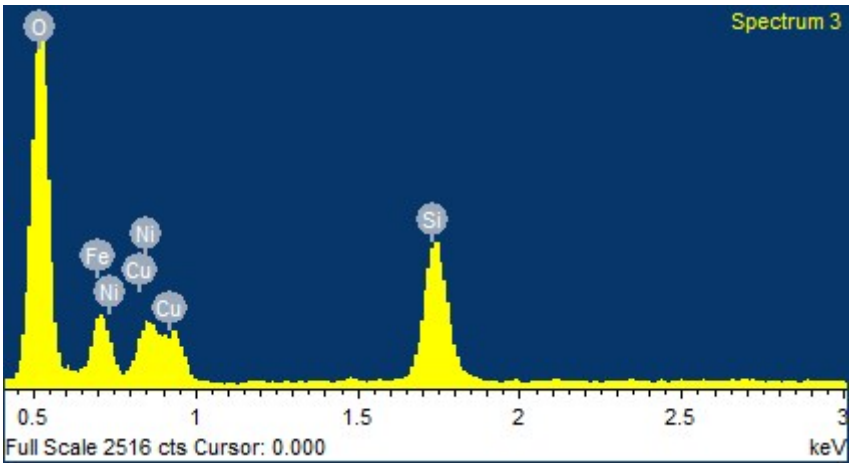
Fe Fe 1-Jun-1999 12:00 AM

Ni Ni 1-Jun-1999 12:00 AM

Cu Cu 1-Jun-1999 12:00 AM



Element	Weight%	Atomic%
O K	32.91	61.19
Si K	8.20	8.68
Fe K	29.85	15.90
Ni K	16.35	8.28
Cu L	12.69	5.94
Totals	100.00	

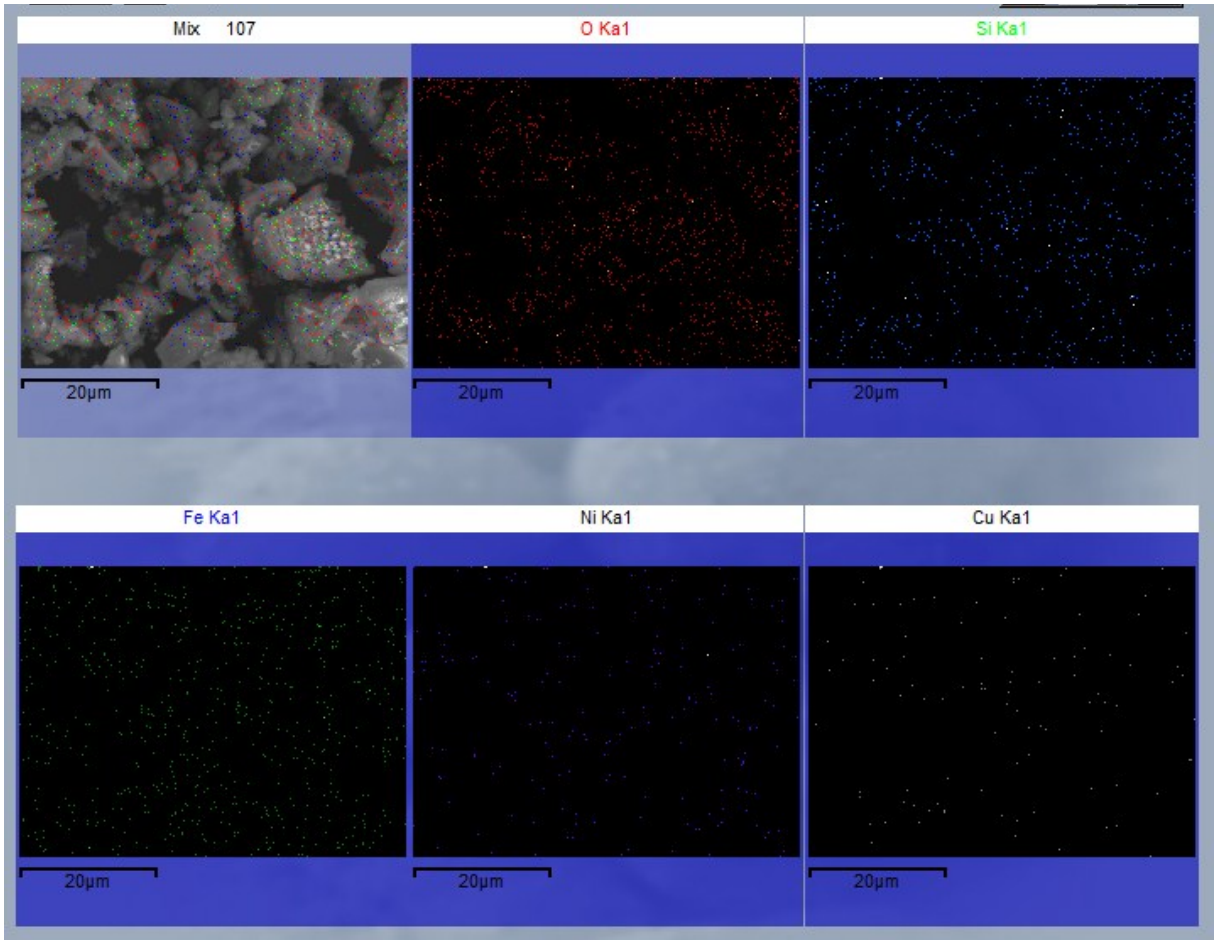


Supplementary Information

Elemental Mapping

The elemental mapping data showing uniform distribution of Si and Cu on the support.

MP1.1



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XPS of individual elements

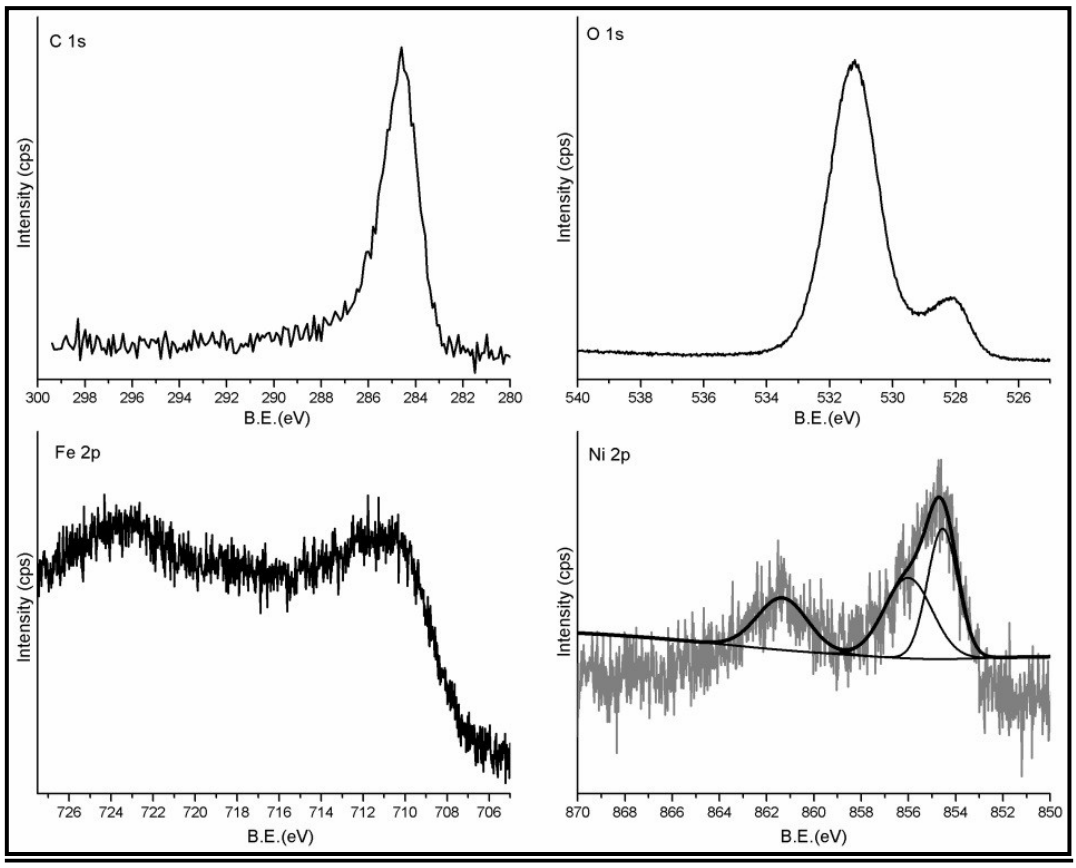

Fig. S2. XPS spectrum showing C 1s peak calibrated to 284.6eV. Remaining spectra are of individual elements present in the active catalyst sample $Cu/SiO_2@NiFe_2O_4$. Starting from left C 1s, O 1s, Fe 2p, Ni2p.

VSM

Table S1

Magnetisation data of the samples

Sample	Ms(emu/g)	Mr (emu/g)	Hc (Oe)
$Cu/SiO_2@NiFe_2O_4$	22.1165	2.6510	232
$SiO_2@NiFe_2O_4$	24.4882	2.3524	200
$NiFe_2O_4$	28.7444	2.5489	132

Ms- Saturation Magnetization

Mr- Remanent Magnetization

Hc - Coercivity

As expected the saturation magnetisation (Ms) was highest for $NiFe_2O_4$ which decreased after silica coating and was found lowest for $Cu/SiO_2@NiFe_2O_4$ as seen in the fig. S6.

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Product charaterisation

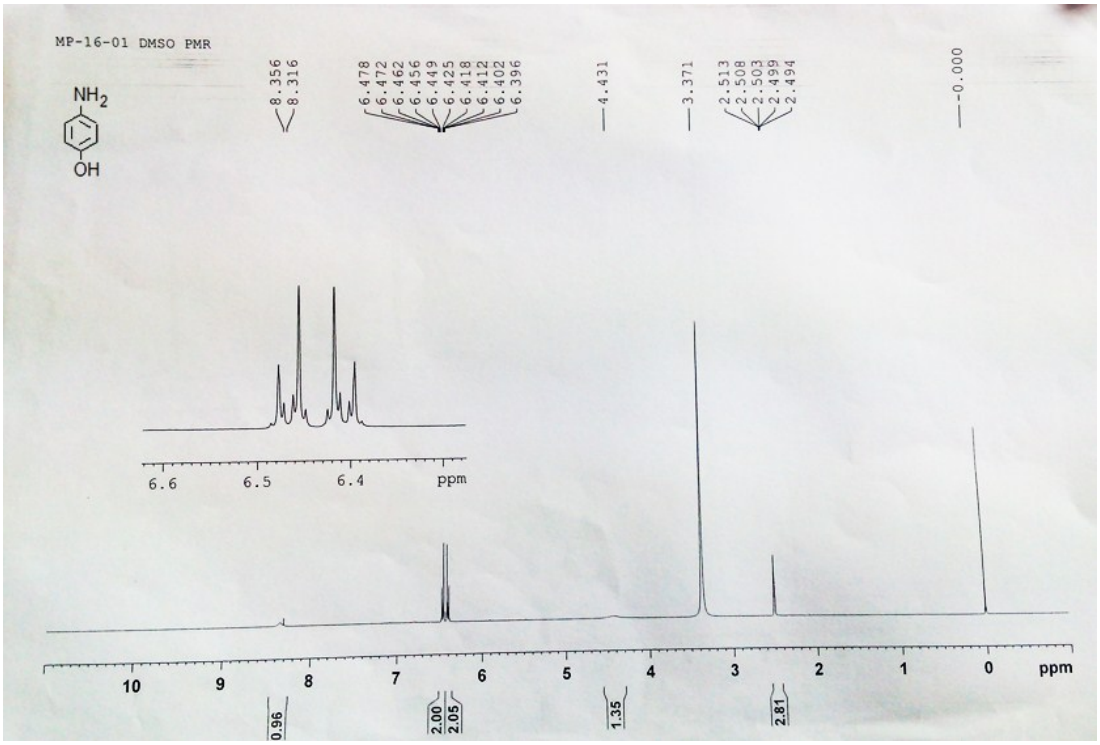


Fig. S3. ^{1}H NMR spectrum of the isolated product when performed on 1 mmol scale matches with reference [1].

Reference

1 T. Aditya and T. Pal, *Chem. Commun.*, 2015, **51**, 9410–9431.

Supplementary Information

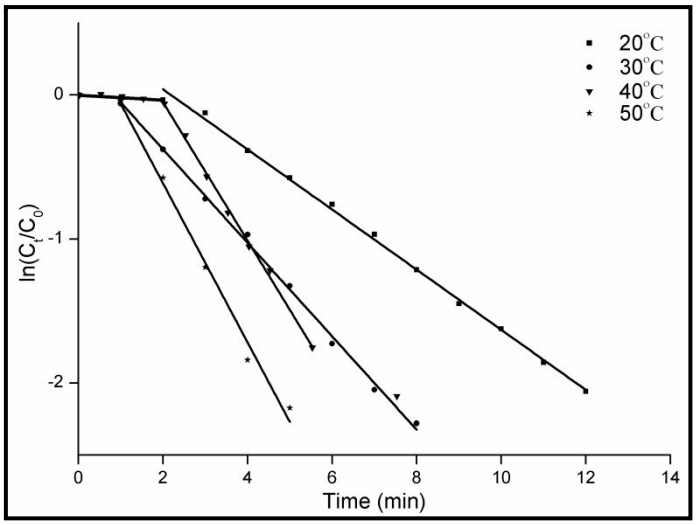


Fig. S4. Plot of *k* at different temperatures.

Table S2

Recyclability of the catalyst

Cycle	Time (min) for total conversion
1st	7
2nd	7
3rd	11
4th	14
5th	20

Table S3

Solvent Studies using Nitrobenzene (0.5 mmol), Catalyst (6 mg), NaBH4 (2.5 mmol)

Entry	Solvent system	Observations*
1	THF	no desired product
2	Acetonitrile	no desired product
3	Methanol	3.5h for complete conversion
4	Ethanol	5h for complete conversion
5	Water	2.5h for complete conversion
6	1:1 Water-THF	8h for complete conversion
7	1:1 Water-Acetonitrie	Multiple spots even after 5h
8	1:1 Water-Ethanol	Over 7h for complete conversion
9	**1:1 Water-Methanol**	**2h for complete conversion**

* Reactions were monitored on TLC.

Supplementary Information

GC CHROMATOGRAMS

Data File :	E:\Mira\nitro\rxn\nitrobenzene\nitrobenz+anilin+azobenz+nitroso std 120-160-180-220-260.Dat		
Method File :			
Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	9:18:17 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60

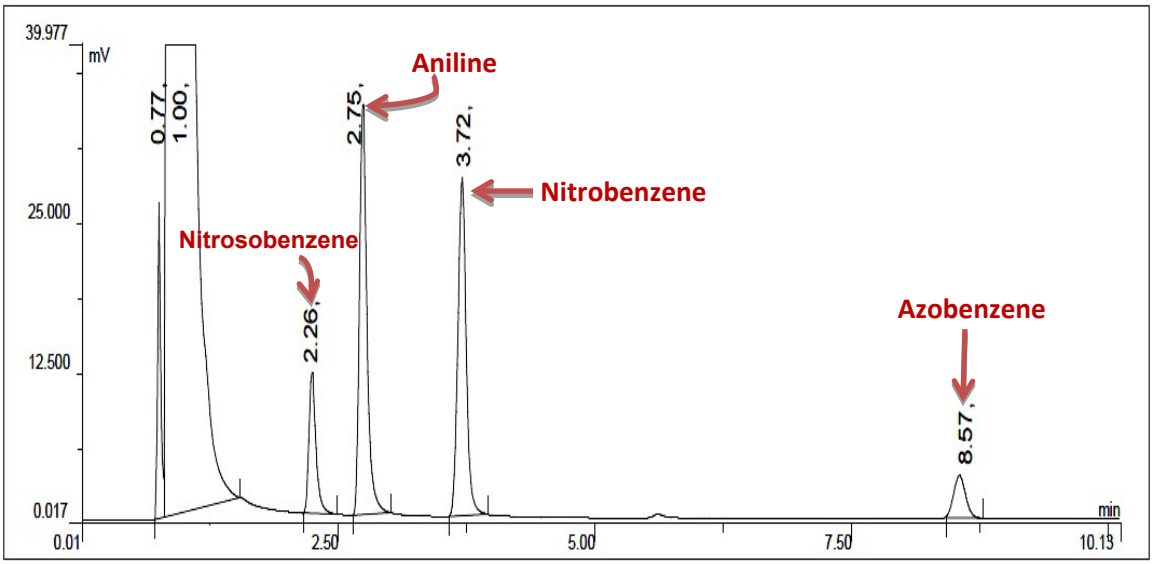


Fig. S5. A representative GC chromatogram showing Rt values of reactant Nitrobenzene, product aniline, and two intermediates Nitrosobenzene and Azobenzene.

All the GC runs were carried out using Ovi 101 column and same sequencer settings.

The above chromatograph displays the probable components of Nitrobenzene reduction. Authentic samples were injected individually to determine the retention time of the components with the set program. The subsequent chromatographs show the progress of the reaction with time in presence of $Cu/SiO_2@NiFe_2O_4$.

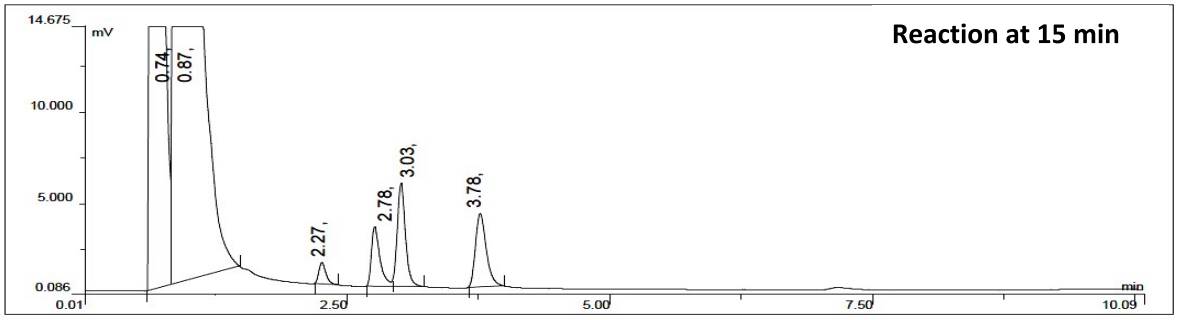
*NOTE: Since the boiling point of aniline (179ºC) and the internal standard used n-decane (174 ºC) are very closed and it couldn't be well resolved at the set program, internal standard wasn't used while performing the mechanistic studies.

Supplementary Information

Mechanistic Study using Nitrobenzene as substrate over time

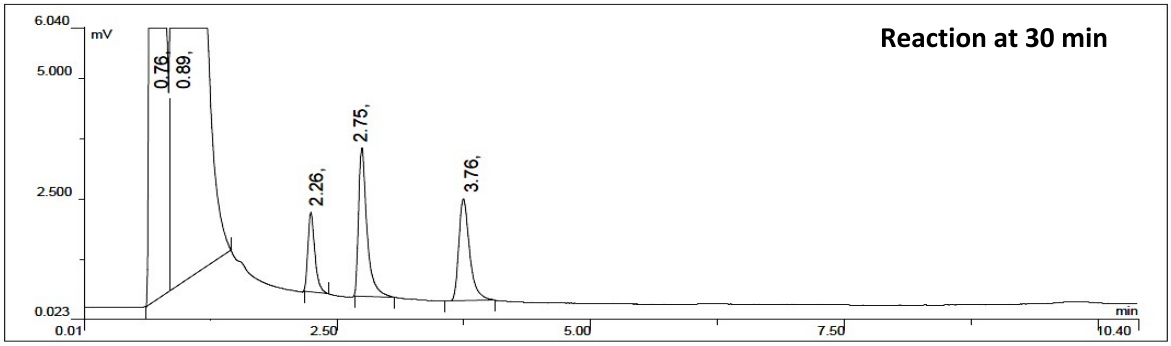
Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	5:33:06 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60



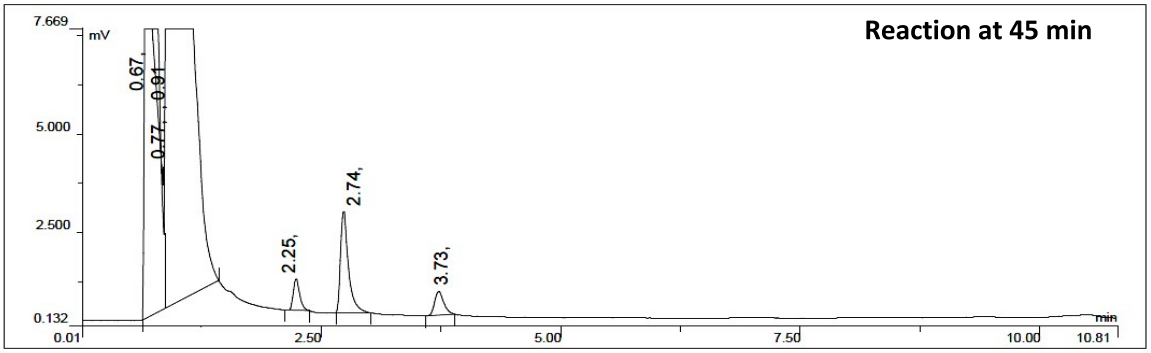
Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	5:52:38 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60



Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	6:06:52 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60



Supplementary Information

Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	6:21:29 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
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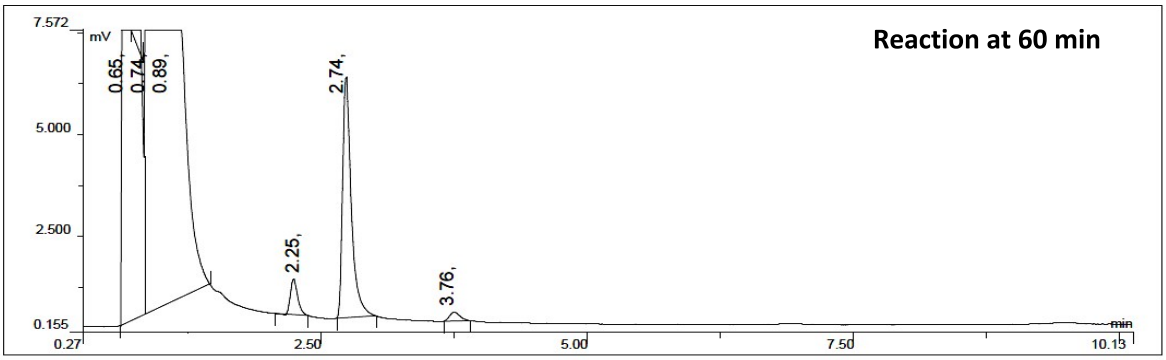
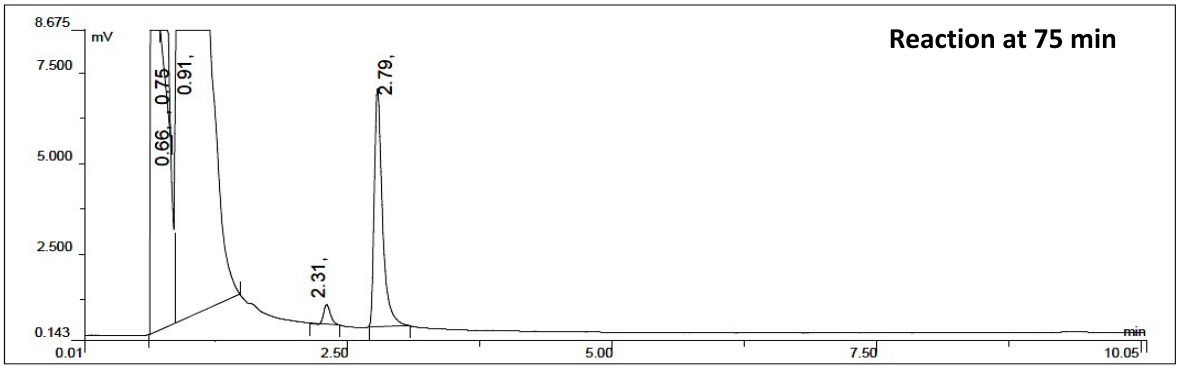


Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	6:34:37 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60



Sample Name :	Sample1	**Analysis Type :**	Percent Method
Detector :	FID	**Time :**	6:49:15 PM
System :	GC	**Chan No :**	Chan 2
Run Date :	8/5/2016		

Peak Width	Peak Threshold	Area Reject	Height Reject
16	60	500	60