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Design and Synthesis of N-Doped Carbons as Efficient Metal-Free Catalysts in the Hydrogenation of 1-Chloro-4-Nitrobenzene

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Supplementary Materials:

Table S1. Relative percentages obtained from the deconvolution of the XPS high resolution N1s spectra of melamine-citrate carbons obtained after pyrolysis at 750 ºC of different mixtures of melamine-citrate.

Sample	Energy (eV)	Species	at. %	%
MelCit 4:1	398.22	Pyridinic	14.27	62
	400.01	Pyrrolic	8.37	36
	401.58	Quaternary	0.48	2
MelCit 3:1	398.16	Pyridinic	11.86	58
	399.96	Pyrrolic	8.72	42
MelCit 2:1	398.24	Pyridinic	13.23	52
	400.01	Pyrrolic	10.72	42
	401.23	Quaternary	1.50	6
MelCit 1:1	398.23	Pyridinic	4.92	35
	400.07	Pyrrolic	8.61	61
	401.74	Quaternary	0.61	4
MelCit 1:2	398.24	Pyridinic	2.31	42
	400.03	Pyrrolic	2.60	48
	401.18	Quaternary	0.54	10

Table S2. Relative percentages obtained from the deconvolution of the XPS high resolution O 1s spectra of melamine-citrate carbons obtained after pyrolysis at 750 ºC of different mixtures of melamine-citrate.

Sample	Energy (eV)	Species	at. %	%
MelCit 4:1	531.28	O=C	4.91	64
	532.93	O-C	2.82	36
MelCit 3:1	531.20	O=C	5.28	68
	532.76	O-C	2.49	32
MelCit 2:1	531.11	O=C	4.33	57
	532.83	O-C	2.79	36
	533.93	O-C=O	0.56	7
MelCit 1:1	530.86	O=C	4.52	60
	532.51	O-C	2.47	32
	533.65	O-C=O	0.59	8
MelCit 1:2	531.23	O=C	6.78	56
	532.50	O-C	3.71	30
	533.91	O-C=O	1.75	14

Table S3. Relative percentages obtained from the deconvolution of the XPS high resolution C 1s spectra of melamine-citrate carbons obtained after pyrolysis at 750 ºC of different mixtures of melamine-citrate.

Sample	Energy (eV)	Species	at. %	%
MelCit 4:1	284.62	C-C, C-H, C=C	37.83	55
	285.85	C-N, C-O	22.15	32
	287.17	C=N, C=O	7.13	10
	288.78	COOH	2.03	3
MelCit 3:1	284.57	C-C, C-H, C=C	33.62	49
	285.71	C-N, C-O	24.53	35
	287.15	C=N, C=O	8.01	12
	288.9	COOH	2.98	4
MelCit 2:1	284.60	C-C, C-H, C=C	33.65	49
	285.77	C-N, C-O	16.53	24
	286.99	C=N, C=O	14.03	21
	288.84	COOH	4.22	6
MelCit 1:1	284.64	C-C, C-H, C=C	52.45	67
	285.91	C-N, C-O	15.38	20
	287.28	C=N, C=O	7.39	9
	288.73	COOH	2.81	4
MelCit 1:2	284.62	C-C, C-H, C=C	54.14	68
	285.78	C-N, C-O	19.71	25
	287.42	C=N, C=O	4.44	5
	289.00	COOH	1.54	2

Table S4. Relative percentages obtained from the deconvolution of the XPS high resolution C 1s spectra of MelCit 2:1 carbons obtained after pyrolysis at different temperatures.

Sample	Energy (eV)	Species	at. %	%
MelCit P500	284.56	C-C, C-H, C=C	8.76	18
	286.22	C-N, C-O	5.07	11
	288.18	C≡N-C	32.91	69
	289.81	COOH	0.70	2
MelCit P600	284.64	C-C, C-H, C=C	11.33	23
	286.23	C-N, C-O	8.47	17
	288.13	C≡N-C	29.15	60
MelCit P700	284.58	C-C, C-H, C=C	20.90	37
	285.93	C-N, C-O	8.45	15
	287.21	C≡N-C, C=O	23.04	40
	288.86	COOH	4.46	8
MelCit P750	284.60	C-C, C-H, C=C	33.65	49
	285.77	C-N, C-O	16.53	24
	286.99	C=N, C=O	14.03	21
	288.84	COOH	4.22	6
MelCit P800	284.59	C-C, C-H, C=C	45.97	62
	286.05	C-N, C-O	21.05	28
	287.92	C=N, C=O	5.65	8
	289.61	COOH	1.88	2
MelCit P850	284.58	C-C, C-H, C=C	52.49	67
	285.98	C-N, C-O	20.07	26
	287.68	C=N, C=O	4.21	5
	288.84	COOH	1.33	2
MelCit P900	284.60	C-C, C-H, C=C	54.78	67
	285.81	C-N, C-O	14.83	18
	286.96	C=N, C=O	8.81	11
	288.96	COOH	3.13	4
MelCit P950	284.63	C-C, C-H, C=C	67.00	75
	285.83	C-N, C-O	9.93	11
	286.74	C=N, C=O	9.52	11
	288.71	COOH	2.57	3

Table S5. Relative percentages obtained from the deconvolution of the XPS high resolution N 1s spectra of MelCit 2:1 carbons obtained after pyrolysis at different temperatures.

Sample	Energy (eV)	Species	at. %	%
MelCit P500	398.78	C≡N-C	35.13	71
	400.40	Pyrrolic	11.05	23
	401.47	Quaternary	2.11	4
	404.38	N-oxide	0.97	2
MelCit P600	398.57	C≡N-C	29.02	65
	400.27	Pyrrolic	15.88	35
MelCit P700	398.31	Pyridinic	21.49	60
	400.09	Pyrrolic	14.42	40
MelCit P750	398.24	Pyridinic	13.23	52
	400.01	Pyrrolic	10.72	42
	401.23	Quaternary	1.50	6
MelCit P800	398.11	Pyridinic	9.25	50
	399.91	Pyrrolic	8.05	43
	401.26	Quaternary	1.25	7
MelCit P850	398.12	Pyridinic	8.21	53
	399.97	Pyrrolic	6.48	42
	401.52	Quaternary	0.72	5
MelCit P900	398.12	Pyridinic	5.19	49
	399.83	Pyrrolic	3.86	40
	401.14	Quaternary	1.17	11
MelCit P950	398.19	Pyridinic	2.83	48
	399.87	Pyrrolic	2.48	40
	401.3	Quaternary	0.87	12

Table S6. Conversion (%) vs time during the five cyclic experiments showing the reusability of Mel-Cit P850 carbon in the hydrogenation of 1-chloro-4-nitrobenzene.

Time (min)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
0	0.78	0.58	0.32	0.15	0.22
15	4.00	1.50	1.40	1.28	0.10
30	5.97	3.62	3.25	2.95	2.53
60	10.53	5.27	4.12	4.35	4.57
120	17.87	10.17	8.23	8.10	7.98
180	22.51	15.63	12.54	10.92	11.02
300	30.97	25.24	22.13	20.12	19.85
360	35.27	29.52	26.32	25.12	24.98
480	44.40	39.25	35.41	34.23	33.12
600	54.48	49.32	46.85	43.68	41.95
900	75.32	65.45	62.12	58.21	55.23
1200	92.60	82.05	77.85	69.45	65.21
1440	100.00	91.45	85.63	77.19	72.85
1800		100.00	90.23	82.35	80.12

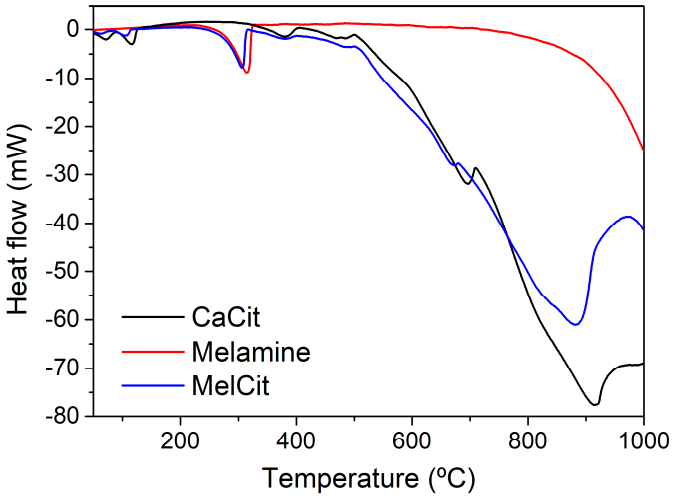


Figure S1. DSC profiles of calcium citrate tetrahydrate, melamine, and the corresponding physical mixture of both (2:1 w/w ratio). Heating rate: 5 ºC/min; N_2 atmosphere.

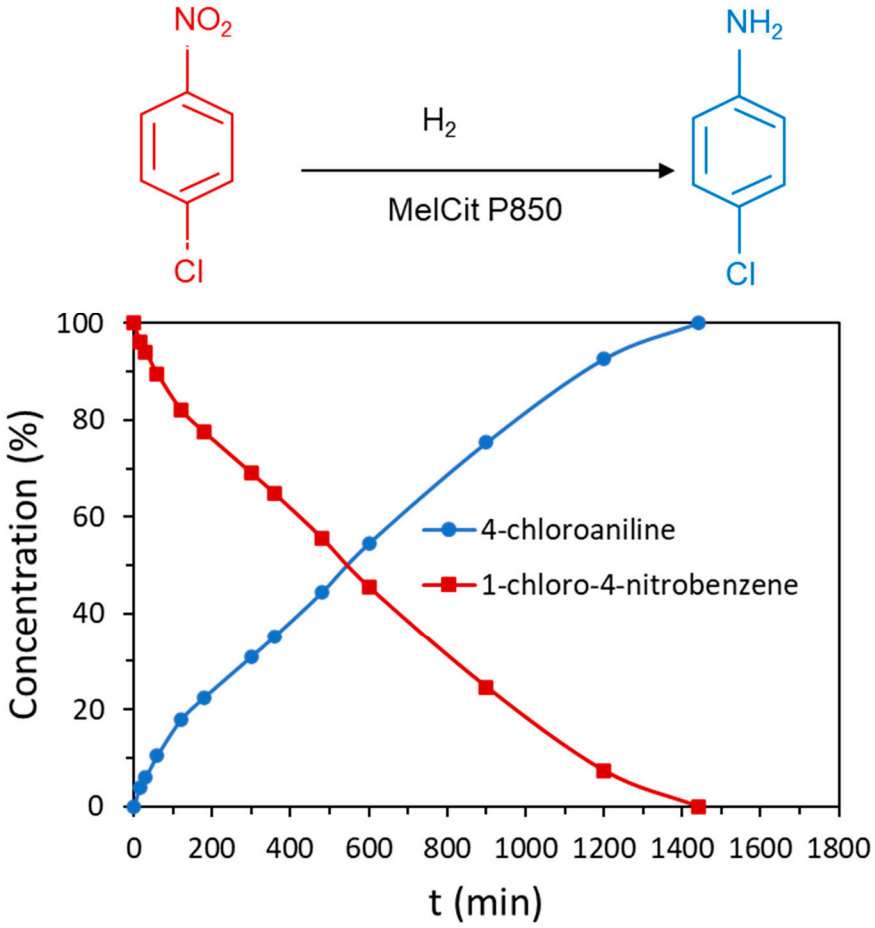


Figure S2. Evolution of compounds over the course of the hydrogenation reaction in the presence of MelCit P850 carbon.

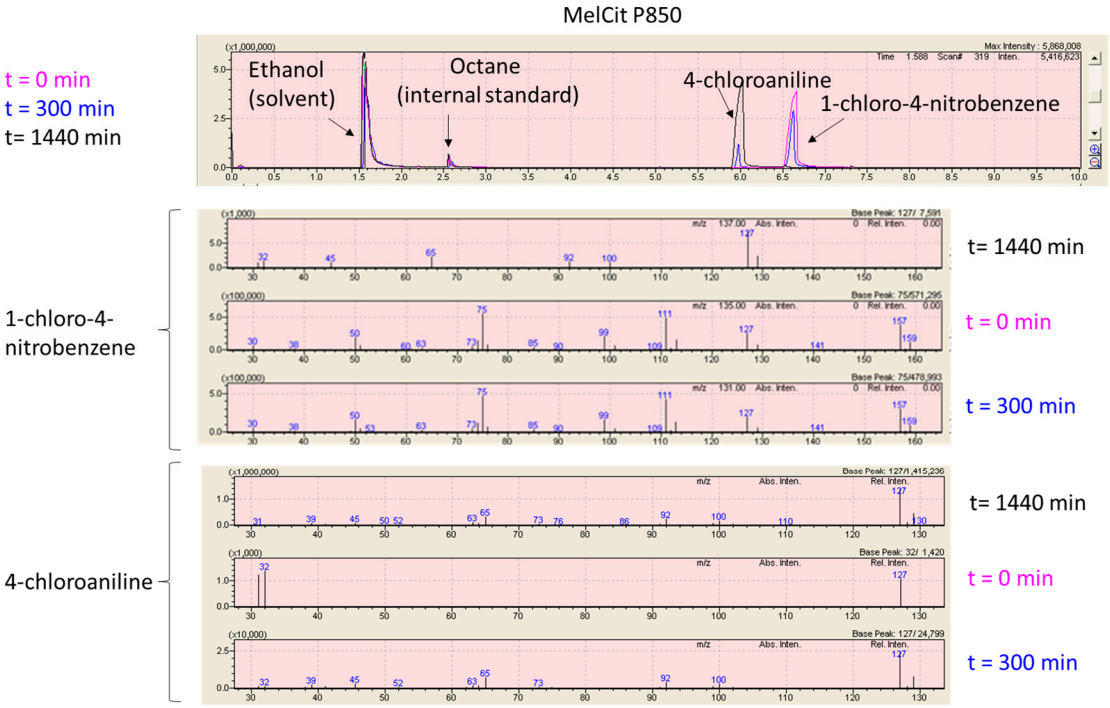
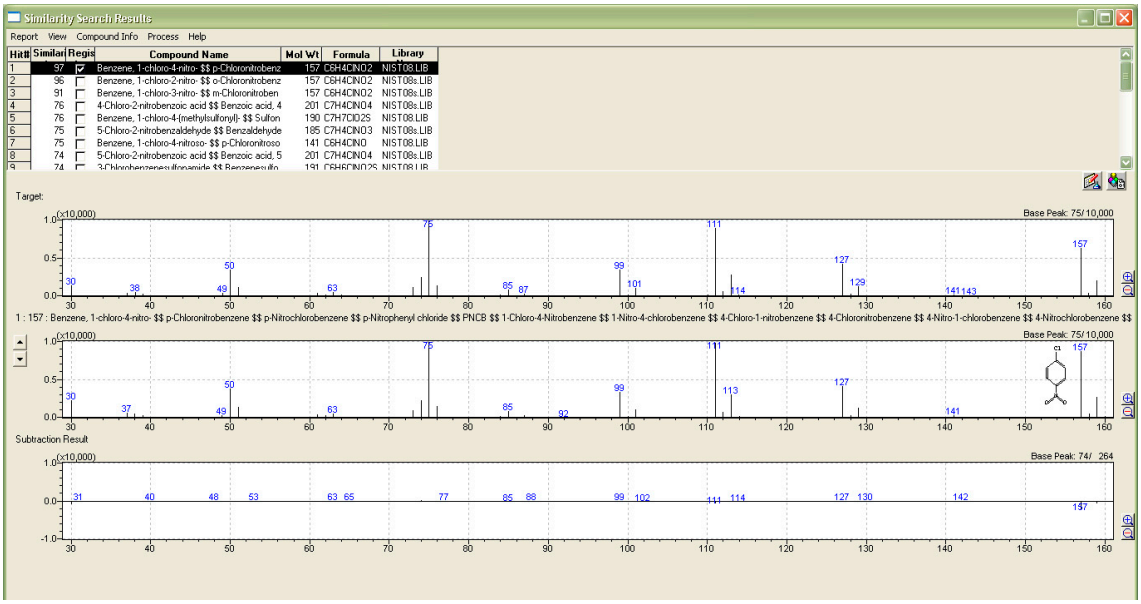
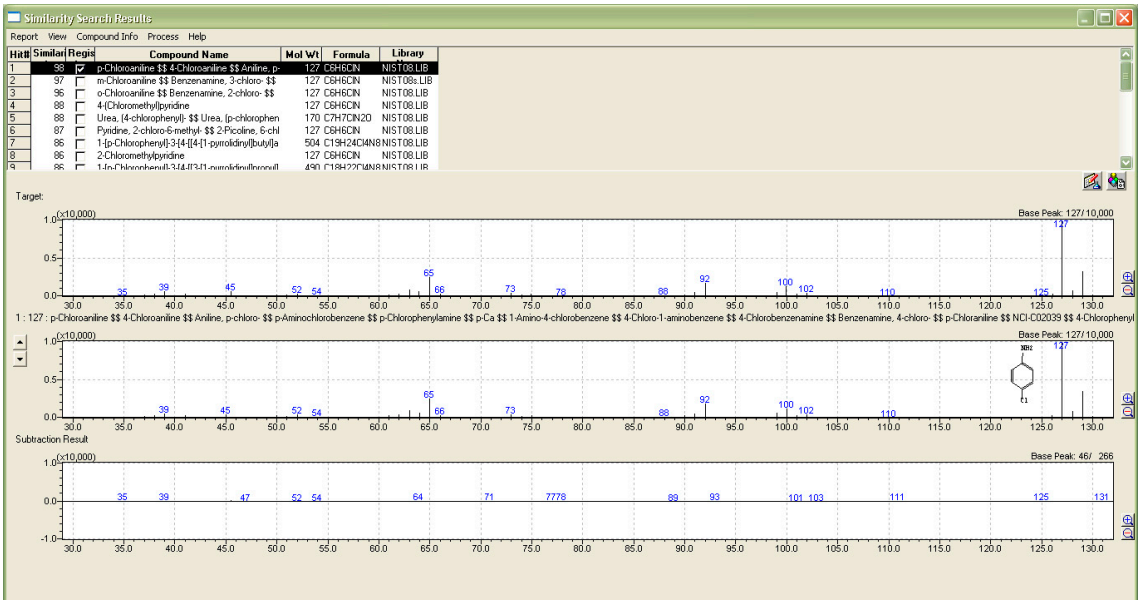


Figure S3. GC-MS analysis of compounds at t = 0 min, t= 300 min and t= 1440 min during the course of the hydrogenation reaction in the presence of MelCit P850 carbon.

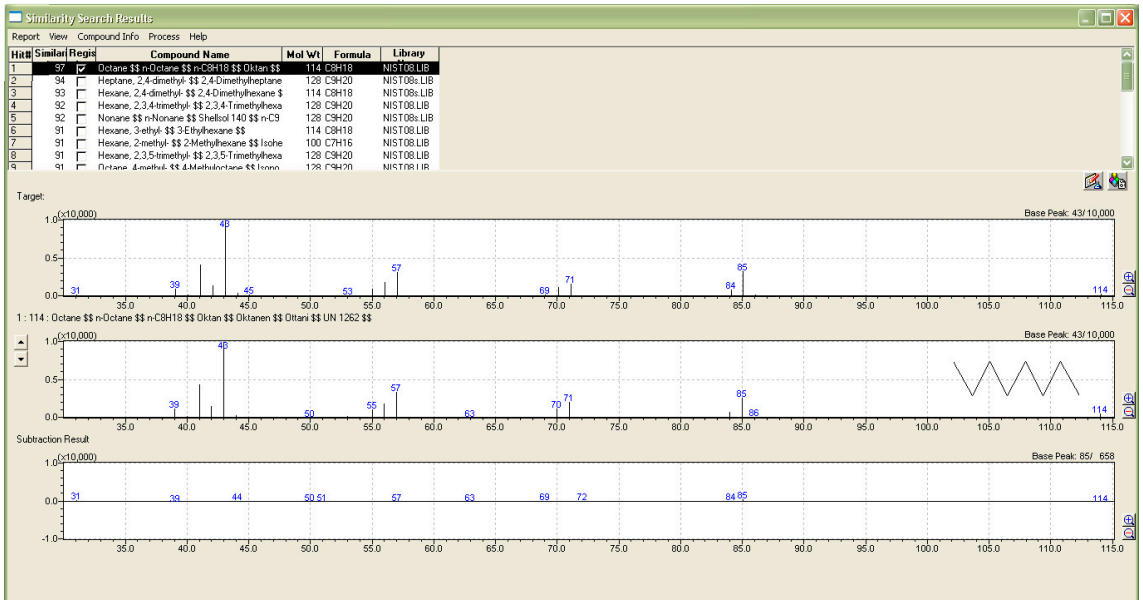
(a)


Similarity Search Results
Report View Compound Info Process Help
Hit# Similar Regis Compound Name Mol Wt Formula Library
1 97 Benzene, 1-chloro-4-nitro- $$ p-Chloronitrobenz 157 C6H4ClNO2 NIST08.LIB
2 96 Benzene, 1-chloro-2-nitro- $$ o-Chloronitrobenz 157 C6H4ClNO2 NIST08s.LIB
3 91 Benzene, 1-chloro-3-nitro- $$ m-Chloronitroben 157 C6H4ClNO2 NIST08s.LIB
4 76 4-Chloro-2-nitrobenzoic acid $$ Benzoic acid, 4 201 C7H4ClNO4 NIST08s.LIB
5 76 Benzene, 1-chloro-4-[(methylsulfonyl)- $$ Sulfon 190 C7H7ClO2S NIST08.LIB
6 75 5-Chloro-2-nitrobenzaldehyde $$ Benzaldehyde 185 C7H4ClNO3 NIST08s.LIB
7 75 Benzene, 1-chloro-4-nitroso- $$ p-Chloronitroso 141 C6H4ClNO NIST08.LIB
8 74 5-Chloro-2-nitrobenzoic acid $$ Benzoic acid, 5 201 C7H4ClNO4 NIST08s.LIB
Target:
Base Peak: 75/10,000
1 : 157 : Benzene, 1-chloro-4-nitro- $$ p-Chloronitrobenzene $$ p-Nitrochlorobenzene $$ p-Nitrophenyl chloride $$ PNCB $$ 1-Chloro-4-Nitrobenzene $$ 1-Nitro-4-chlorobenzene $$ 4-Chloro-1-nitrobenzene $$ 4-Chloronitrobenzene $$ 4-Nitro-1-chlorobenzene $$ 4-Nitrochlorobenzene $$
Base Peak: 75/10,000
Subtraction Result
Base Peak: 74/ 264

(b)


Similarity Search Results
Report View Compound Info Process Help
Hit# Similar Regis Compound Name Mol Wt Formula Library
1 98 p-Chloroaniline $$ 4-Chloroaniline $$ Aniline, p- 127 C6H6ClN NIST08.LIB
2 97 m-Chloroaniline $$ Benzenamine, 3-chloro- $$ 127 C6H6ClN NIST08s.LIB
3 96 o-Chloroaniline $$ Benzenamine, 2-chloro- $$ 127 C6H6ClN NIST08.LIB
4 88 4-(Chloromethyl)pyridine 127 C6H6ClN NIST08.LIB
5 88 Urea, [4-chlorophenyl]- $$ Urea, [p-chlorophen 170 C7H7ClN2O NIST08.LIB
6 87 Pyridine, 2-chloro-6-methyl- $$ 2-Picoline, 6-chl 127 C6H6ClN NIST08.LIB
7 86 1-[p-Chlorophenyl]-3-[4-[[4-[1-pyrrolidinyl][butyl]a 504 C19H24ClN8 NIST08.LIB
8 86 2-Chloromethylpyridine 127 C6H6ClN NIST08.LIB
Target:
Base Peak: 127/10,000
1 : 127 : p-Chloroaniline $$ 4-Chloroaniline $$ Aniline, p-chloro- $$ p-Aminochlorobenzene $$ p-Chlorophenylamine $$ p-Ca $$ 1-Amino-4-chlorobenzene $$ 4-Chloro-1-aminobenzene $$ 4-Chlorobenzenamine $$ Benzenamine, 4-chloro- $$ p-Chloraniline $$ NCI-C02039 $$ 4-Chlorophenyl
Base Peak: 127/10,000
Subtraction Result
Base Peak: 46/ 266

(c)



(d)

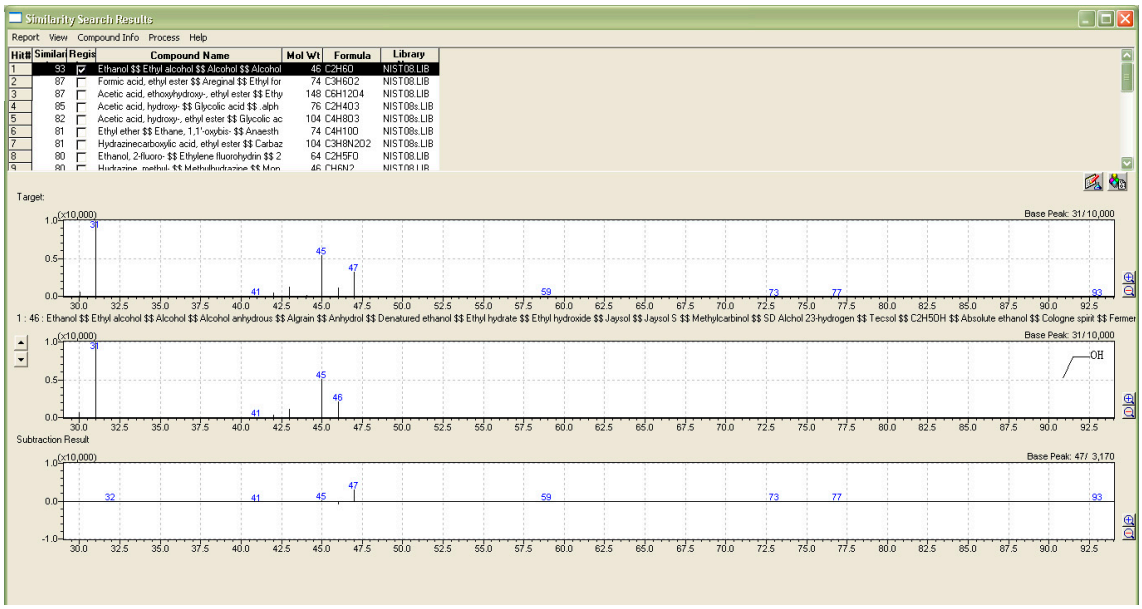


Figure S4. Mass spectra (MS) similarity search results of compounds detected during the course of the hydrogenation reaction in the presence of MelCit P850 carbon showing (a) 1-chloro-4-nitrobenzene, (b) 4-chloroaniline, (c) octane (internal standard) and (d) ethanol (solvent).