Synthesis of mesoporous iridium nanosponge: A highly active, thermally stable and efficient olefin hydrogenation catalyst

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EXPERIMENTAL SECTION

Turnover frequency calculation and H$_2$-TPD experiment

Temperature programmed desorption (H$_2$-TPD) experiment was performed with a multipurpose unit coupled to a quadrupole mass spectrometer (BELCAT II catalyst analyser, Japan). The H$_2$-TPD profile was given below (Fig. S1). It contains two peaks, one at 170 °C and other one appears at 395 °C. The first peak at 170 °C could be ascribed to desorption of weakly bound hydrogen from the metal surface whereas, broad peak at 395 °C refers to the strongly bound hydrogen on metallic iridium.
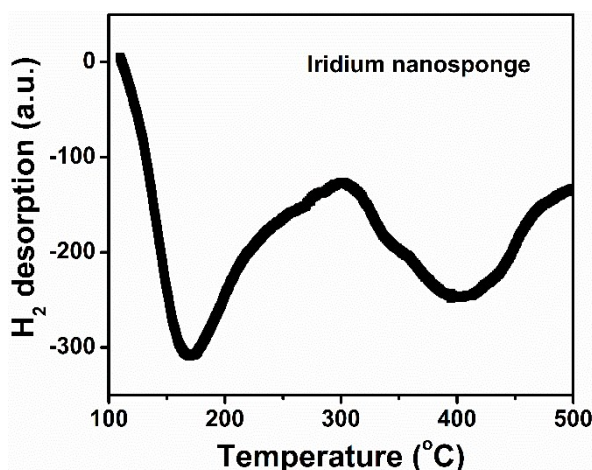
Figure S1. H_2-TPD profile of iridium nanosponge.

Based on the BET surface area data and H_2-TPD profile, we have calculated the fraction of iridium site is exposed for catalysis. Few assumptions were made for the calculation which are:

1.   Since, iridium nanosponge is mesoporous in nature, then all the exposed iridium atoms takes part in the catalysis step. There is no hindered diffusion as the pore size varies between 5-100 nm with a peak centered at 27.7 nm (Fig. 1g; main manuscript).

2.   The iridium lattice possess FCC (face-centred cubic) crystal structure. According to the surface energy value, the most atomically dense lattice plane (111) is having lowest surface energy among the other lattice planes ((110) and (100)). We assume that, only (111) lattice plane which is having lowest surface energy is exposed for iridium.

The FCC unit cell edge length for iridium is 3.833 Å.

The area occupied by (111) lattice plane of a FCC lattice is $= \dfrac{a^2 \times \sqrt{3}}{2}$, where a is the unit cell edge length (3.833 Å). The area was calculated to be 1.2724×10^{-19} m^2. The total occupancy for (111) lattice plane for a FCC system is 2 atom.

Therefore, 1.2724×10^{-19} m^2 of surface area contains 2 atoms;

33.5 m^2/g (BET surface area) contains 3.8668×10^{20} atoms.

1 gm of iridium, with a surface area of 33.5 m^2/g have 3.86668×10^{20} atoms exposed. Upon dividing with Avogadro's number ($N_A = 6.022 \times 10^{23}$ mol^{-1}), 1 gm of iridium nanosponge was found to have 0.8734 mmol of iridium exposed.

Deconvolution of H_2-TPD profile shows that, 0.337 mmol/g of hydrogen (which is strongly bound to the iridium surface) was desorbed from the iridium nanosponge. Since, each iridium atom can bind with single hydrogen atom [Ir (s) + ½ H_2 (g) = IrH (s)], then 0.674 mmol (2×0.337 mmol) of hydrogen atom was actually bound with the iridium metal. Now, assuming 1:1 stoichiometric binding of iridium and hydrogen, the exposed iridium atom concentration was calculated to be 0.674 mmol for 1 gm of iridium. But, from BET surface area measurement, the exposed iridium concentration was measured to be 0.8734 mmol for 1 gm of iridium. The lower value obtained from H_2-TPD experiment could be attributed to the fact that, all the iridium surface was not covered by (111) lattice plane. There are low density planes such as (110) and (100) present at the surfaces which causes decrement in the amount of hydrogen adsorption.

Turnover frequency was calculated on the basis of total iridium atom exposed (obtained from H_2-TPD experiment).

Turnover frequency (TOF) = moles of substrate transformed per mole of iridium per hour (for total metal)

Determination of concentration of surface exposed iridium metal

H_2-TPD study reveals that, 0.674 mmol of iridium is exposed at the surface per gram of iridium. Since, 0.05 mol% (0.01 mmol) iridium catalyst is the optimized catalyst concentration used for most of the hydrogenation reactions, the concentration of the surface exposed iridium was calculated for this particular concentration.

5.2 mmol (1 gm) of iridium has 0.674 mmol of surface exposed iridium atoms.

Then, 0.01 mmol of iridium has $\dfrac{0.674 \times 0.01}{5.2}$ = 0.0013 mmol of surface exposed iridium atoms.

Therefore, the surface atoms exposed for 0.01 mmol of iridium is (0.0013/0.01) = 13 %.

In parenthesis; Turnover frequency (TOF) = moles of substrate transformed per mole of exposed iridium per hour (for exposed metal)

Table S1. Hydrogenation of alkenes at different temperatures

Entry	Substrate	Solvent	T (^{o}C)	Time (h)	Conv. (%)[a]	TOF (h^{-1})[b]
1	Styrene	CH_2Cl_2	30	4	>99	500 (3846)
2	Styrene	n-heptane	30	1.75	>99	1143 (8791)
3	Styrene	n-heptane	50	0.75	>99	2667 (20512)
4	Styrene	n-heptane	75	0.42	>99	4762 (36630)
5	Cyclohexene	CH_2Cl_2	30	4	>99	500 (3846)
6	Cyclohexene	n-heptane	75	0.4	>99	5000 (38461)
7	1-Hexadecene	CH_2Cl_2	30	6	>99	333 (2564)
8	1-Hexadecene	n-heptane	75	0.3	>99	6667 (51282)

Substrate/iridium catalyst ratio was 2000 and 4 bar hydrogen gas pressure was maintained for all the reactions; [a]conversion determined by GC/MS analysis; [b]turnover frequency = mol (alkene)/mol (Ir nanosponge)·h based on total metal, in parenthesis based on available surface atoms of catalyst.

Table S2. Hydrogenation of 4-vinylcyclohexene by iridium nanosponge

Entry	Substrate	Time (h)	Conv. (%)[a]	TOF (h^{-1})[b]	Product
1	4-Vinylcyclohexene	3	26.5[c]	177 (1359)	Ethyl cyclohexane
2	4-Vinylcyclohexene	6	58.3[c]	194 (1495)	Ethyl cyclohexane

| 3 | 4-Vinylcyclohexene | 9 | >99[c] | 222 (1709) | Ethyl cyclohexane |

All reactions were carried out at a constant temperature of 30 °C and constant hydrogen gas pressure of 4 bar in CH_2Cl_2; [a]conversion determined by GC/MS analysis, [b]turnover frequency = mol (ethyl cyclohexane)/mol (Ir nanosponge) h, in parenthesis based on available surface atoms of catalyst; [c]conversion of 4-vinylcyclohexene to ethylcyclohexane.
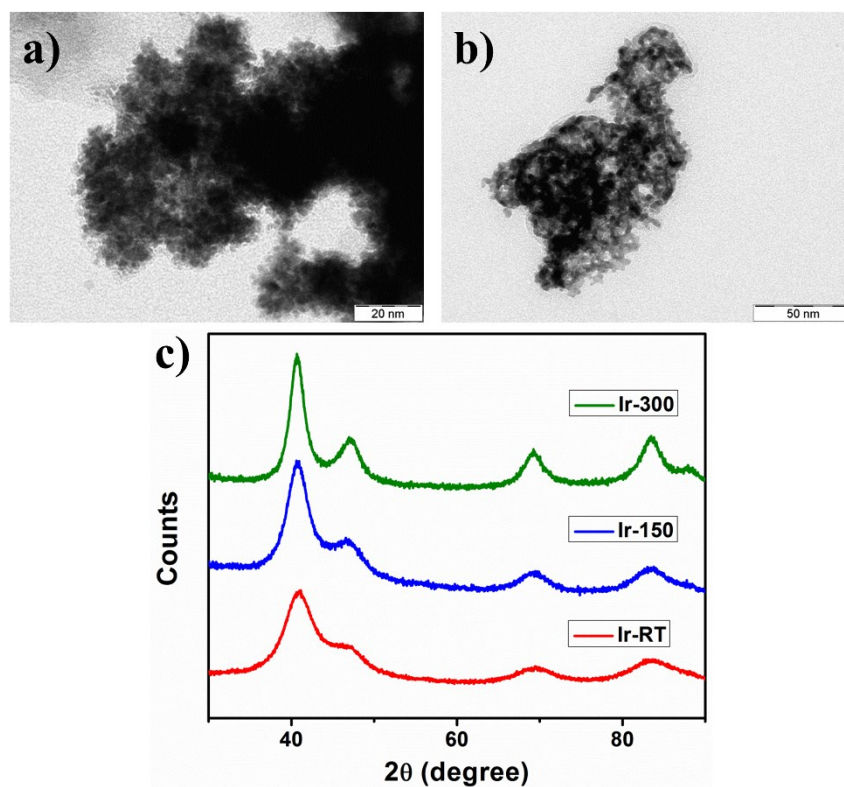
Figure S2. BF TEM images of iridium nanosponge annealed at a) 150 °C for 3 h and b) 300 °C for 3 h, c) powder XRD stack plot of annealed sample with as prepared sample.

Table S3. Hydrogenation of styrene using iridium nanosponge annealed at different temperatures

Entry	Catalyst	Time (h)	Conversion (%)[a]	TOF (h^{-1})[b]
1	Ir-RT[c]	4	>99	500
2	Ir-150	4	>99	500

3	Ir-300	4	95	475

All reactions were carried out at fixed styrene/iridium catalyst ratio of 2000 (20 mmol of styrene and 0.01 mmol of iridium nanosponge), 4 bar of hydrogen gas pressure, and at 30 °C in CH_2Cl_2; [a]conversion determined by GC/MS analysis; [b]turnover frequency = mol (product)/mol (Ir nanosponge)·h; [c]Iridium nanosponge as prepared sample (without any heat treatment).
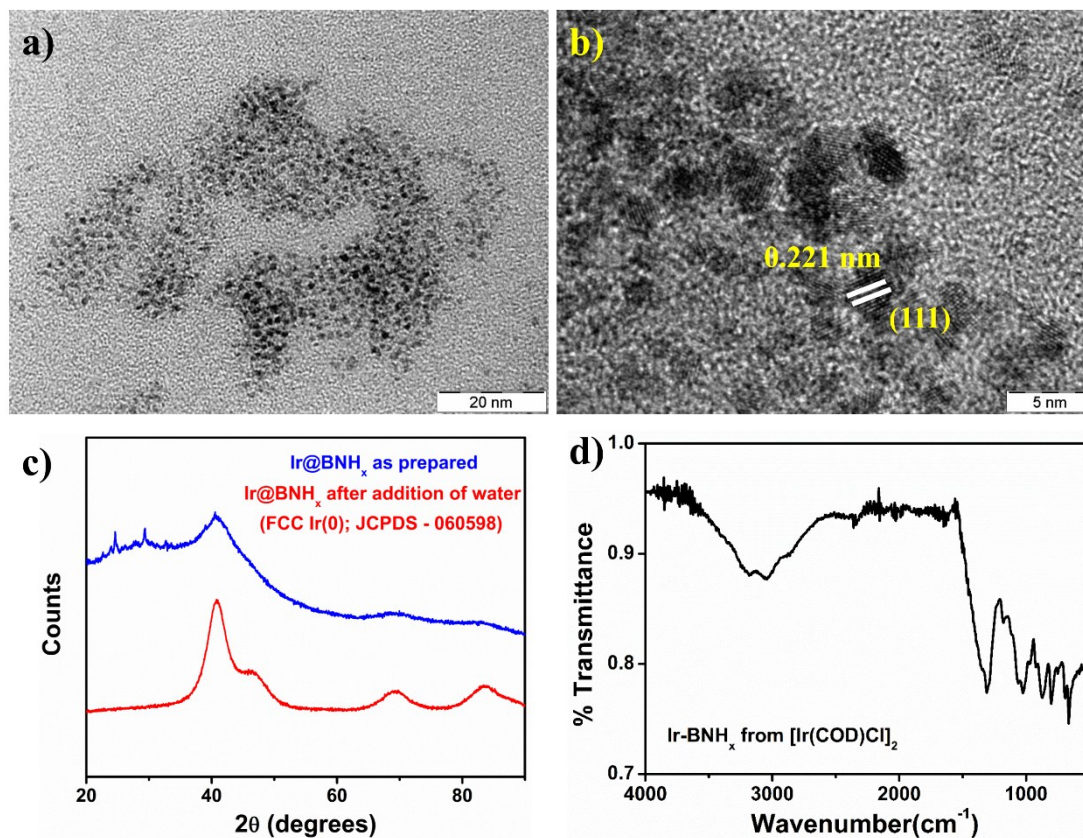
Figure S3. a) BF-TEM image, b) HRTEM image, c) powder XRD stack plot of Ir@BNH$_x$ polymer and iridium nanosponge, and d) FTIR spectra of iridium nanoparticle stabilized by BNH$_x$ polymer (Ir@BNH$_x$) synthesized from [Ir(COD)Cl]$_2$.
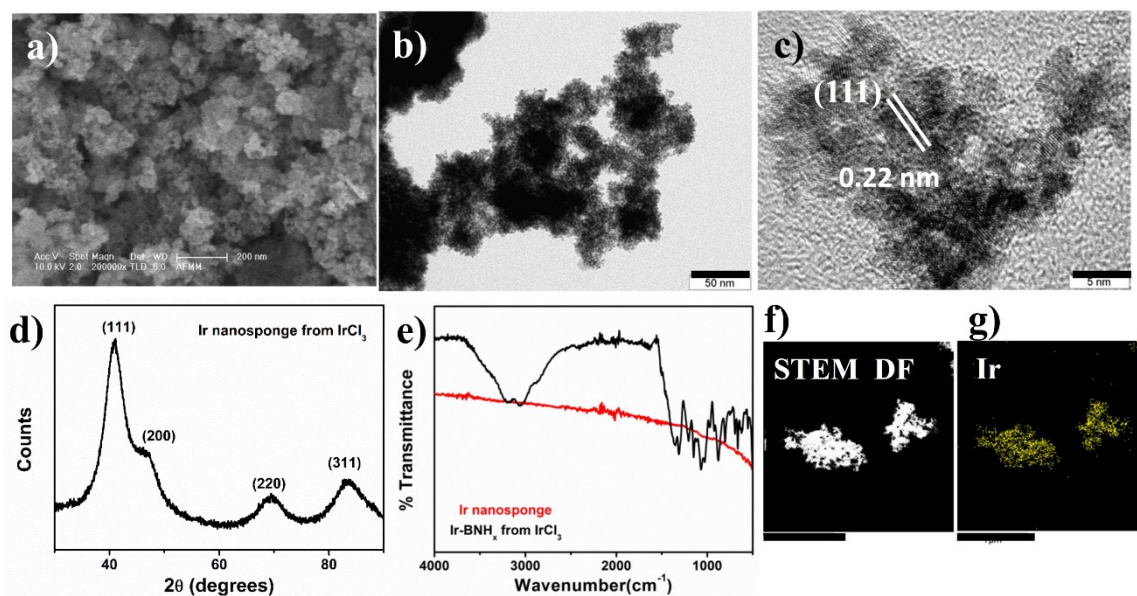
Figure S4. a) SEM image, b) BF TEM image, c) HRTEM image, d) PXRD pattern, e) FT-IR spectral comparison plot, f) STEM HAADF image (scale bar 1 micron) and g) STEM EDS elemental mapping (scale bar 1 micron) of iridium nanosponge synthesized from $IrCl_3$.
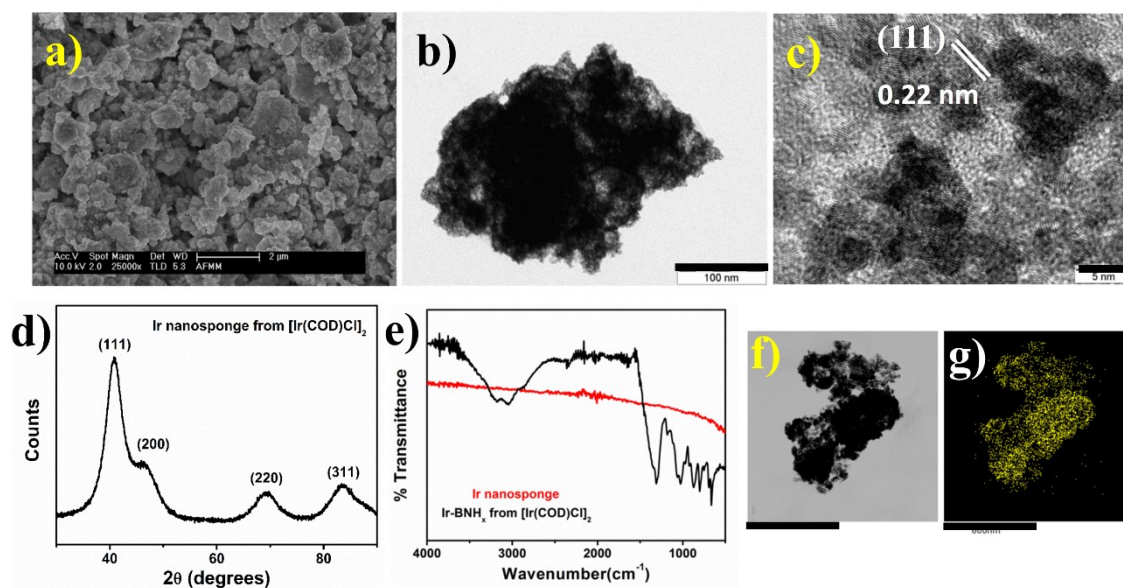
Figure S5. a) SEM image, b) BF TEM image, c) HRTEM image, d) PXRD pattern, e) FT-IR spectral comparison plot, f) STEM BF image (scale bar 600 nm) and g) STEM EDS elemental mapping (scale bar 600 nm) of iridium nanosponge synthesized from $[Ir(COD)Cl]_2$.
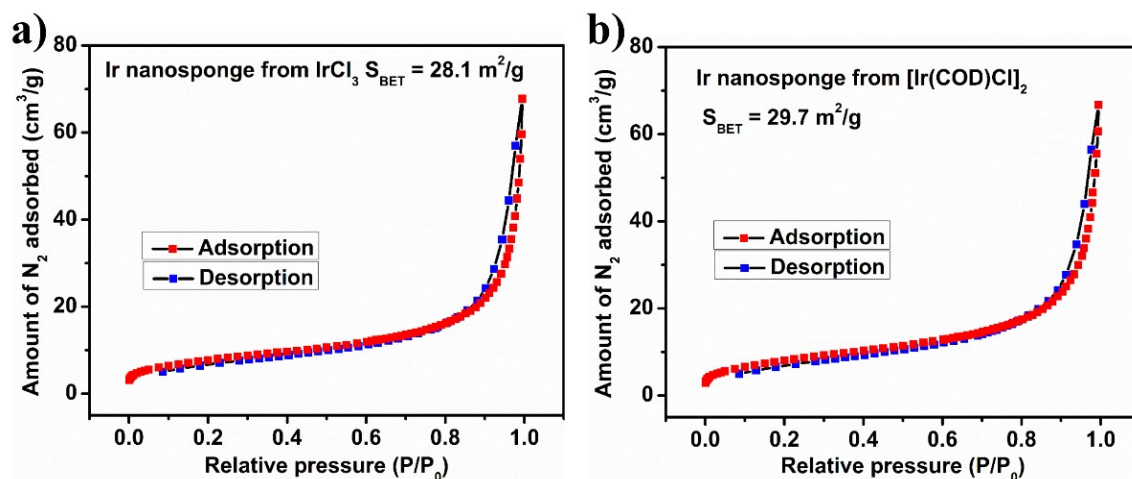
Figure S6. BET isotherms of iridium nanosponge synthesized from a) $IrCl_3$ and b) $[Ir(COD)Cl]_2$.

Table S4. Hydrogenation of styrene using iridium nanosponge prepared from different iridium precursors

Entry	Styrene/catalyst	Catalyst	Time (h)	Conversion (%)[a]	TOF (h^{-1})[b]
1	2000	Ir-1[c]	1[f]	53.6[f]	1072
2	2000	Ir-1[c]	4	>99	500
3	2000	Ir-2[d]	1[f]	53.9[f]	1078
4	2000	Ir-2[d]	4	>99	500
5	2000	Ir-3[e]	1[f]	53.4[f]	1068
6	2000	Ir-3[e]	4	>99	500

All reactions were carried out at 4 bar hydrogen gas pressure and at 30 °C in CH_2Cl_2; [a]conversion determined by GC/MS analysis; [b]turnover frequency = mol (styrene)/mol (Ir nanosponge) h; [c]iridium catalyst prepared from H_2IrCl_6; [d]iridium catalyst prepared from $IrCl_3.xH_2O$; [e]iridium catalyst prepared from $[Ir(1,5-COD)Cl]_2$; [f]reaction was stopped after 1 h and aliquot was drawn for ^{1}H-NMR and GC-MS study, % styrene converted to ethyl benzene.

Table S5. Surface area, pore size, and pore volume of iridium nanosponges synthesize from different iridium precursors

Entry	Materials	S_{BET} (m²/g)	Pore size (nm)	Pore volume (cm³/g)
1	Ir from H_2IrCl_6	33.5	27.7	0.245
2	Ir from $IrCl_3$	28.1	16.7	0.104
3	Ir from $[Ir(COD)Cl]_2$	29.7	16.2	0.102
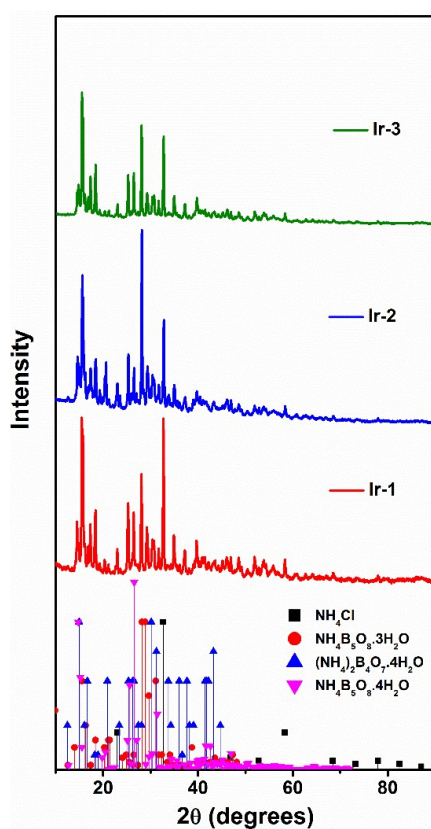
Figure S7. PXRD stack plot of dried filtrates obtained after the hydrolysis reaction of three different Ir@BNH$_x$ nanocomposite. The iridium precursors used for synthesis of Ir@BNH$_x$ nanocomposite are Ir-1: H_2IrCl_6, Ir-2: $IrCl_3$, and Ir-3: $[Ir(COD)Cl]_2$. JCPDS card number:

NH$_4$Cl: 07-0007; (NH$_4$)$_2$B$_4$O$_7$.4H$_2$O: 19-0061; NH$_4$B$_5$O$_8$.4H$_2$O: 74-1233; NH$_4$B$_5$O$_8$.3H$_2$O: 12-0637.
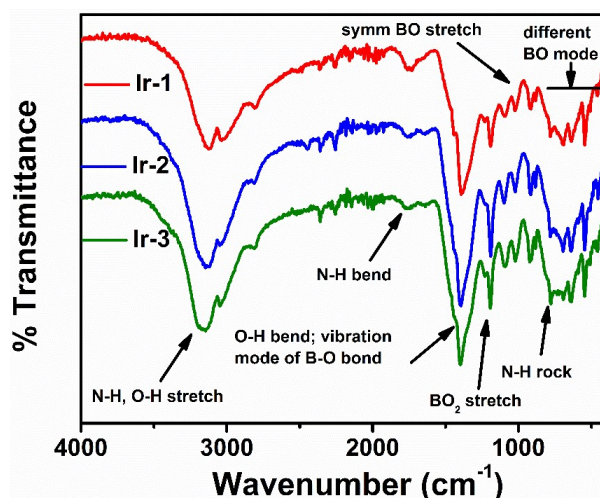
Figure S8. FT-IR spectral stack plot of dried filtrates obtained after the hydrolysis reaction of three different Ir@BNH$_x$ nanocomposite. The iridium precursors used for synthesis of Ir@BNH$_x$ nanocomposite are Ir-1: H$_2$IrCl$_6$, Ir-2: IrCl$_3$, and Ir-3: [Ir(COD)Cl]$_2$.
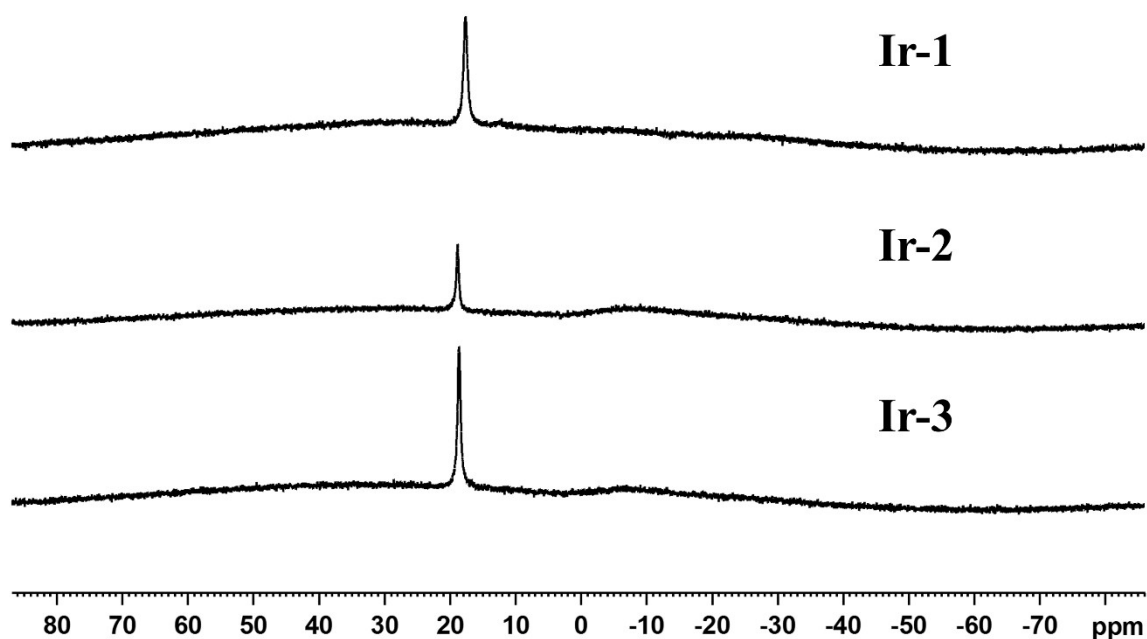
Figure S9. ^{11}B-NMR spectral stack plot of dried filtrates obtained after the hydrolysis reaction of three different Ir@BNH$_x$ nanocomposites. Dried filtrates were dissolved in milli Q water and NMR spectra was recorded. The iridium precursors used for synthesis of Ir@BNH$_x$ nanocomposite are Ir-1: H$_2$IrCl$_6$, Ir-2: IrCl$_3$, and Ir-3: [Ir(COD)Cl]$_2$.
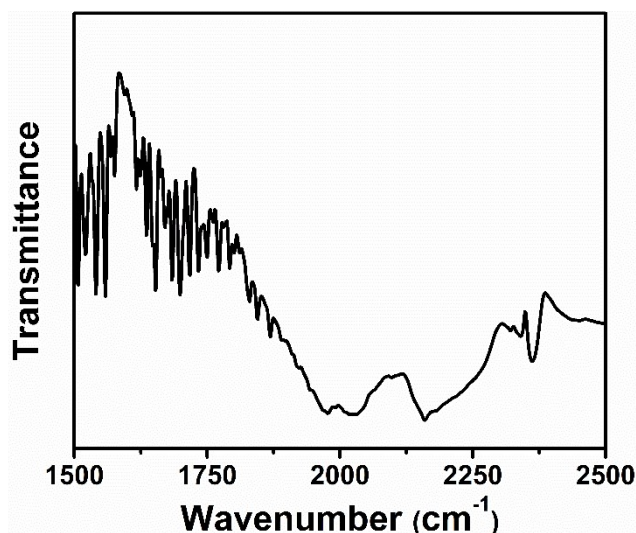
Figure S10. FT-IR spectrum of iridium nanosponge treated with CO.

General information

For optimization study (except table 2, table S1 entry number 6 and 8, and table S2), styrene was used as a model substrate and the product obtained was ethylbenzene. Here, GC-MS characterization of styrene and ethylbenzene were presented first as a model spectra. Afterwards, only gas chromatogram was attached for styrene and ethylbenzene.

3.95 min peak corresponds to ethylbenzene

Abundance [10981] | Scan 429 (3.947 min)

| NIST MS (MF=96) 1/5: >Ethylbenzene
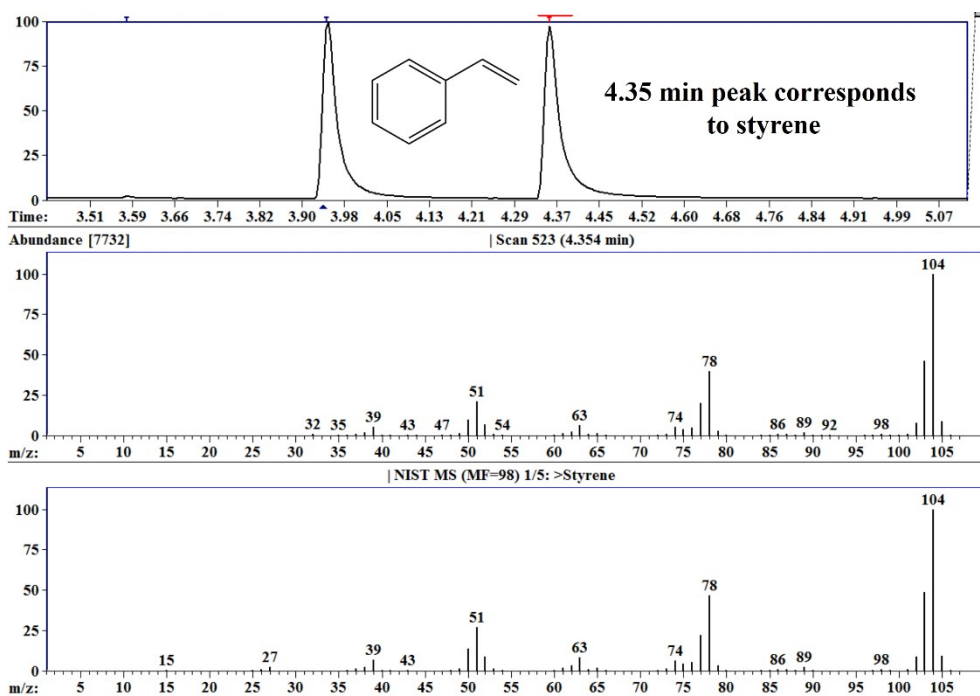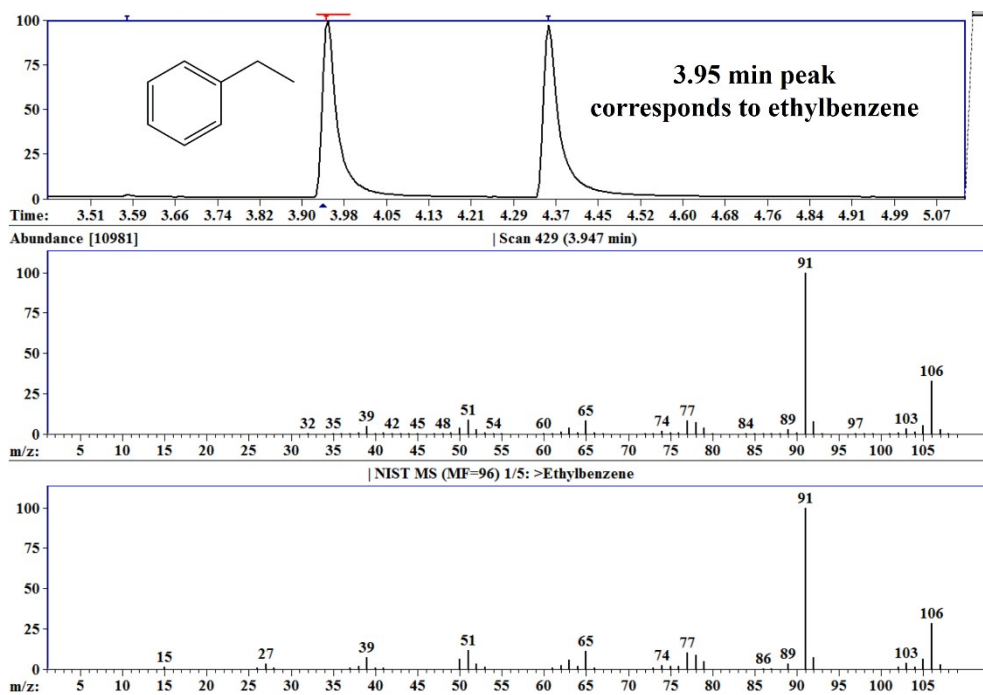
Table 1 (effect of substrate/catalyst ratio) – entry 1-4

Table 1 entry 1; S/C ratio 1000

Table 1 entry 2; S/C ratio 2000

Table 1 entry 3; S/C ratio 5000

Table 1 entry 4; S/C ratio 10000

Before

Table 1 entry 1; S/C ratio 1000

Table 1 entry 2; S/C ratio 2000

Table 1 entry 3; S/C ratio 5000

Table 1 entry 4; S/C ratio 10000
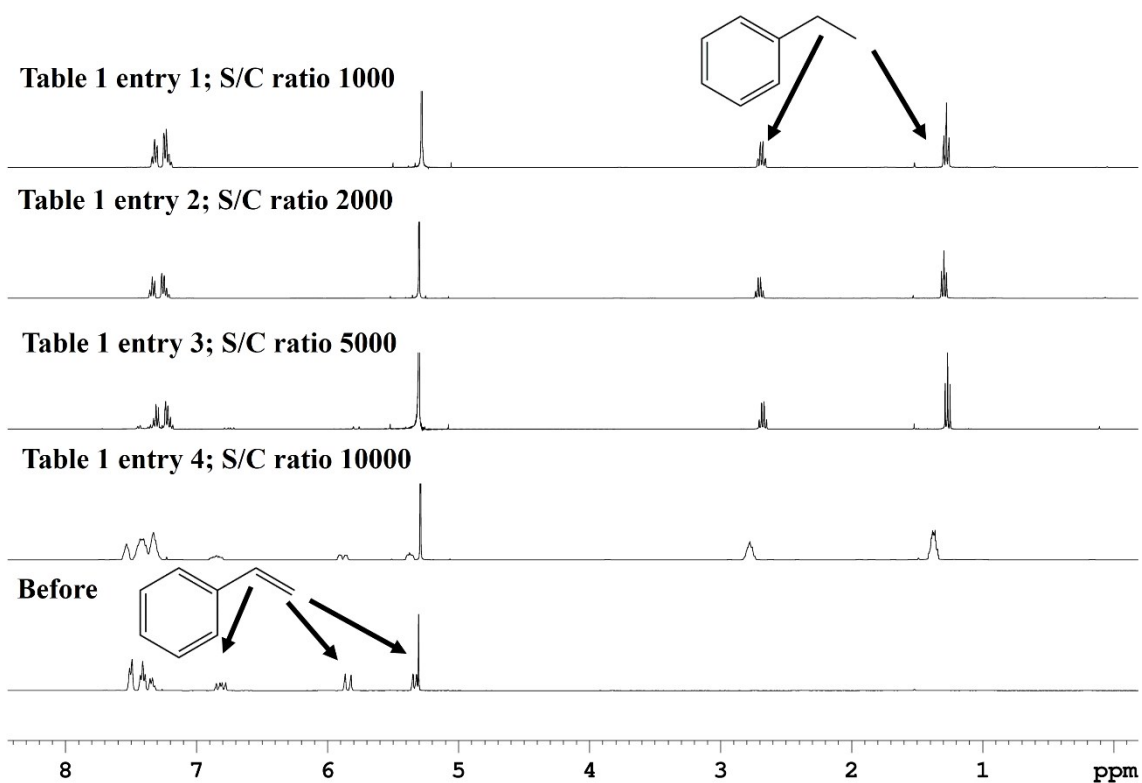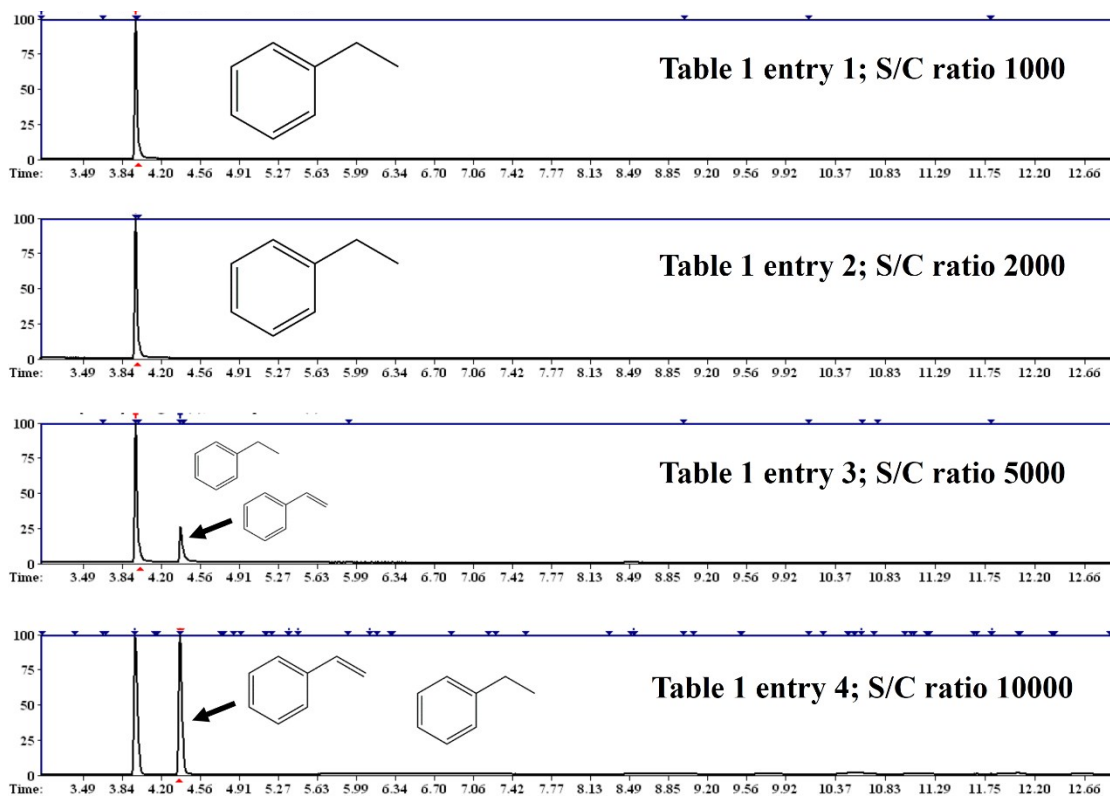
Table 1 (effect of pressure) – entry 5-8

Table 1 entry 5; 2 bar

Table 1 entry 6; 3 bar

Table 1 entry 2; 4 bar

Table 1 entry 7; 5 bar

Table 1 entry 8; 6 bar

Before

Table 1 entry 5; 2 bar

Table 1 entry 6; 3 bar

Table 1 entry 2; 4 bar

Table 1 entry 7; 5 bar
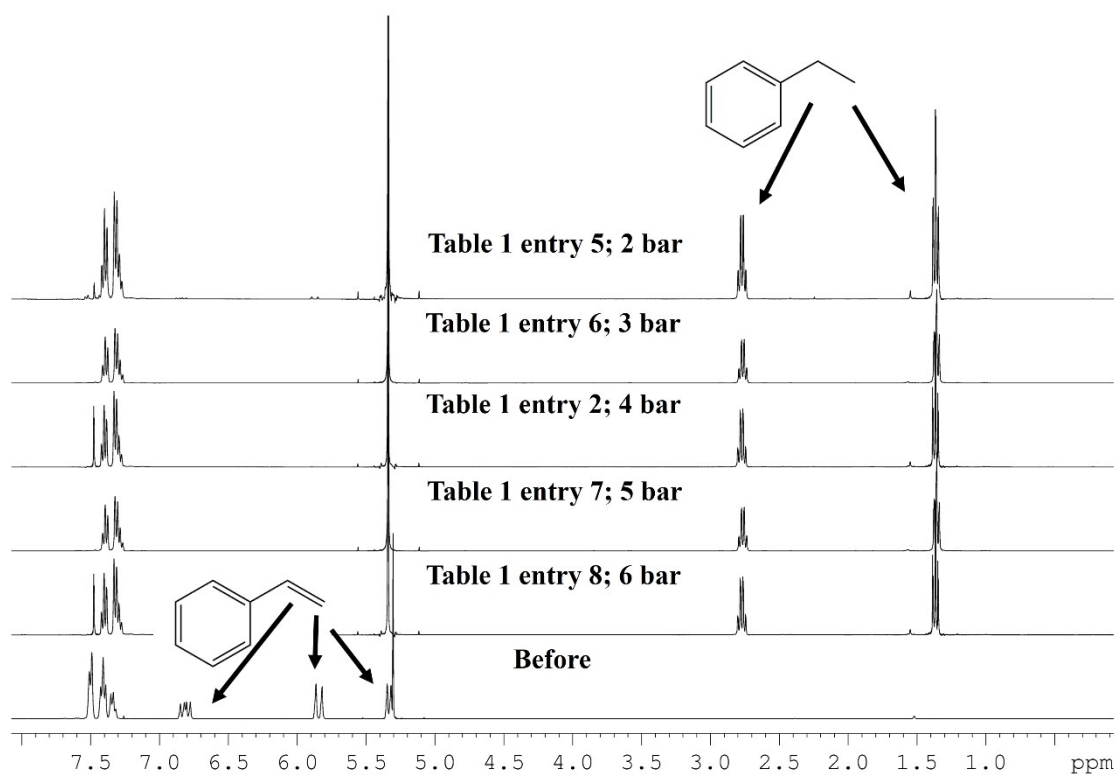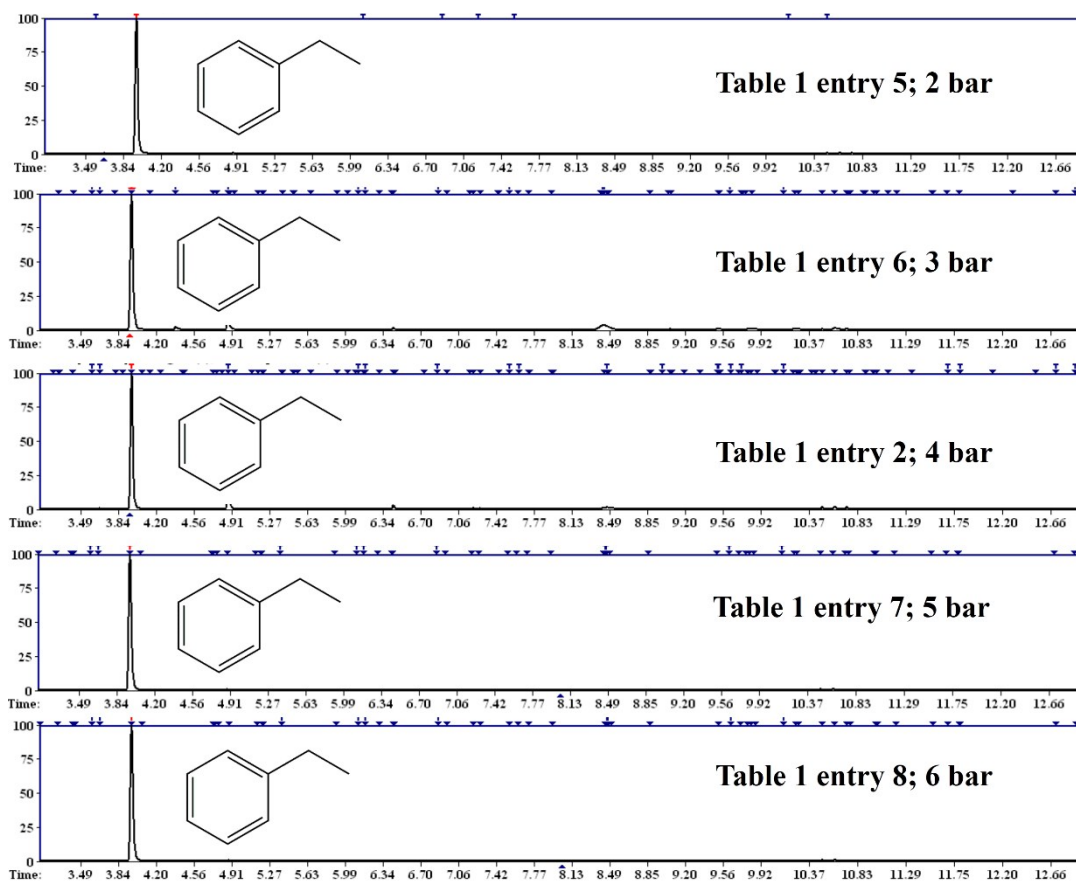
Table 1 entry 8; 6 bar

Blank experiment without hydrogen gas:

Gas Chromatogram

Reaction of styrene with iridium nanosponge in CH_2Cl_2 in absence of hydrogen
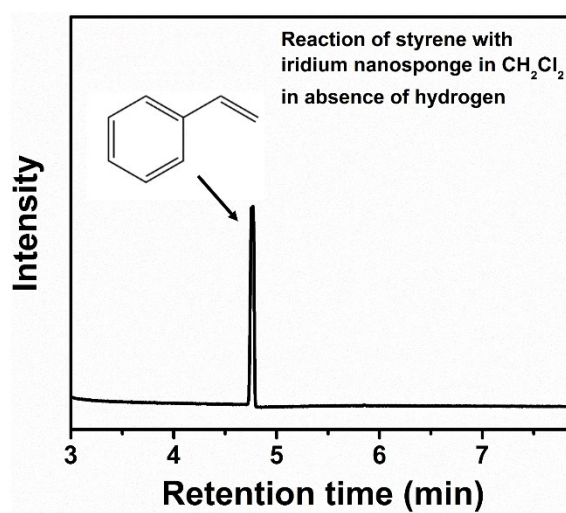
Table 1 (effect of temperature) - entry 9-11

Table 1 Entry 11 – n-heptane @ 75 ºC

Table 1 Entry 10 – n-heptane @ 50 ºC

Table 1 Entry 9 – n-heptane @ 30 ºC

Before

Table 1 Entry 11 – n-heptane @ 75 °C

Table 1 Entry 10 – n-heptane @ 50 °C

Table 1 Entry 9 – n-heptane @ 30 °C
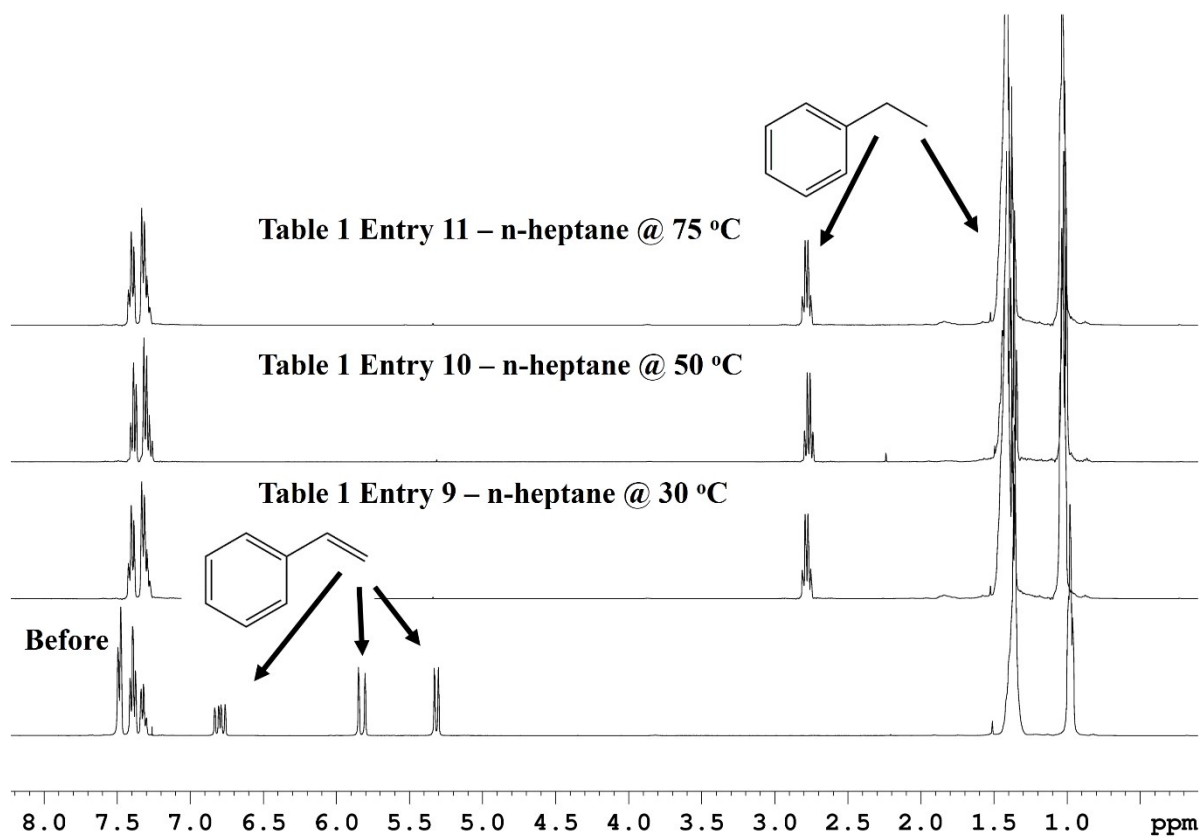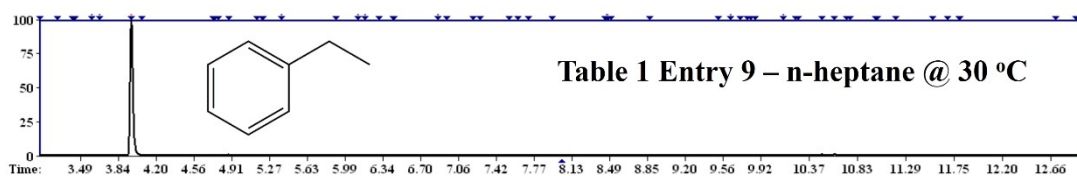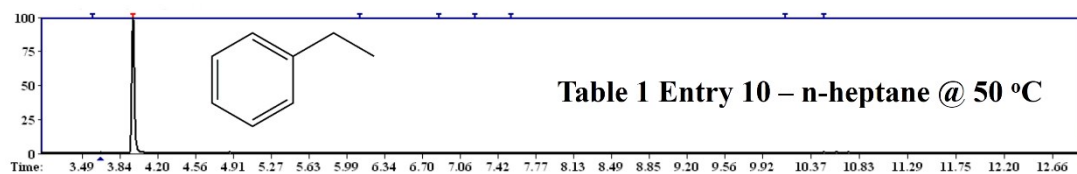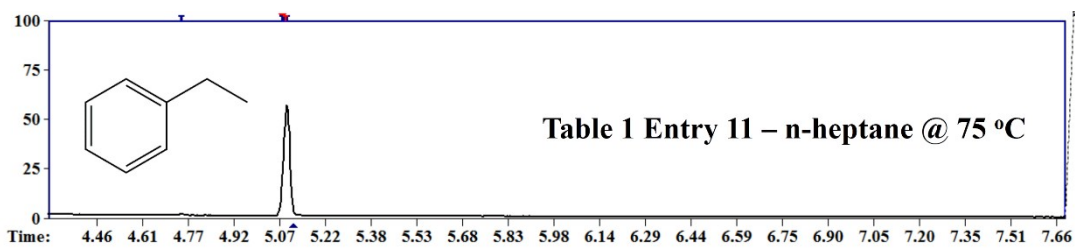
Table S1 (Hydrogenation of alkenes at different temperatures) entry 1-4 is same for the table 1 entry 2, 9-11. Table S1 entry 5 is same for the table 3 entry 9. Similarly, table S1 entry 7 is same for the table 3 entry 7.

Table S1 entry 6 [effect of temperature]

After
Table S1 Entry 6

Before

Alkene proton
(*sp²* H)

8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5   ppm
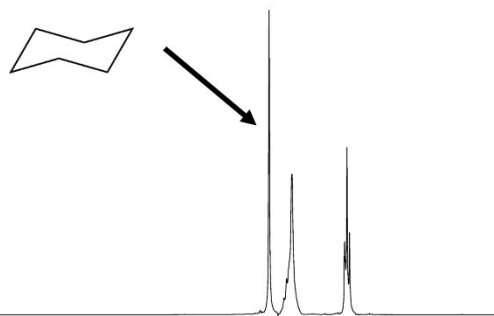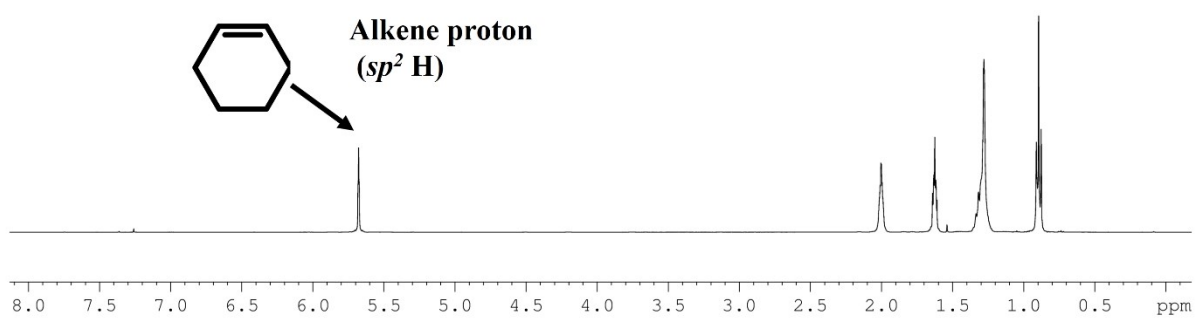
Table S1 entry 8 [effect of temperature]

After
Table S1 Entry 8

Before

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

After
Table S1 Entry 8

Time: 8.81 8.99 9.16 9.33 9.50 9.68 9.85 10.08 10.30 10.52 10.74 10.97 11.19 11.42 11.64 11.86 12.08 12.31

Abundance [5726] | Scan 2609 (11.371 min)

| NIST MS (MF=97) 1/19: >Hexadecane

Table 2 entry 1

Table 2 entry 1

Before

Hit	SI	RSI	Prob	Name	Library Name
1	935	936	47.44	Styrene	mainlib
2	916	917	23.03	Bicyclo[4.2.0]octa-1,3,5-triene	mainlib
3	915	915	22.14	1,3,5,7-Cyclooctatetraene	mainlib
4	855	857	3.93	1,3,7-Octatrien-5-yne	mainlib
5	832	838	1.43	Indan, epoxide	mainlib
6	798	800	0.36	Benzeneethanamine, N-[(4-hydroxy)hy...	mainlib
7	793	798	0.29	Phosphonic acid, (2-phenylethenyl)-	mainlib
8	792	793	0.28	2HInden-2-one, 1,3-dihydro-	mainlib
9	784	790	0.21	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-...	mainlib
10	780	783	0.17	3(2H)-Furanone, dihydro-2,2-dimethyl-5...	mainlib
11	769	775	0.12	Phensuximide	mainlib
12	753	844	0.07	Chromium, tricarbonyl[(1,2,3,4,5,6-ü)-1,3...	mainlib

Styrene
Formula C8H8, MW 104, CAS# 100-42-5, Entry# 69556
Benzene, ethenyl-

Table 2 entry 1

Table 2 entry 2

Table 2 entry 2
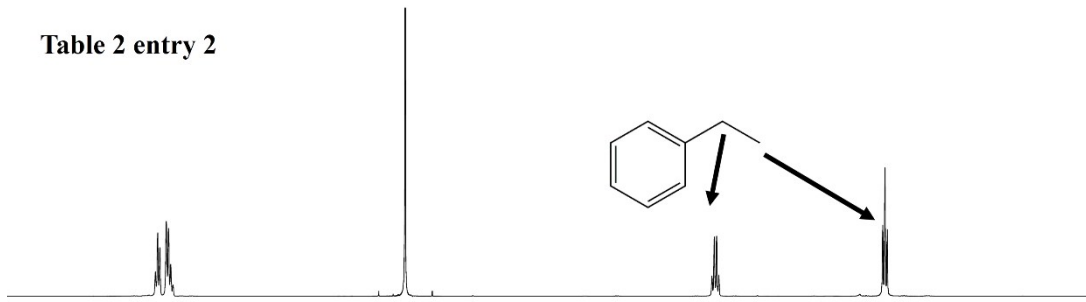
Before
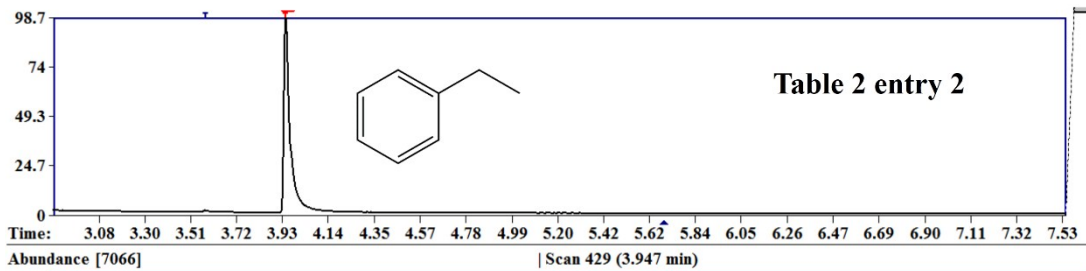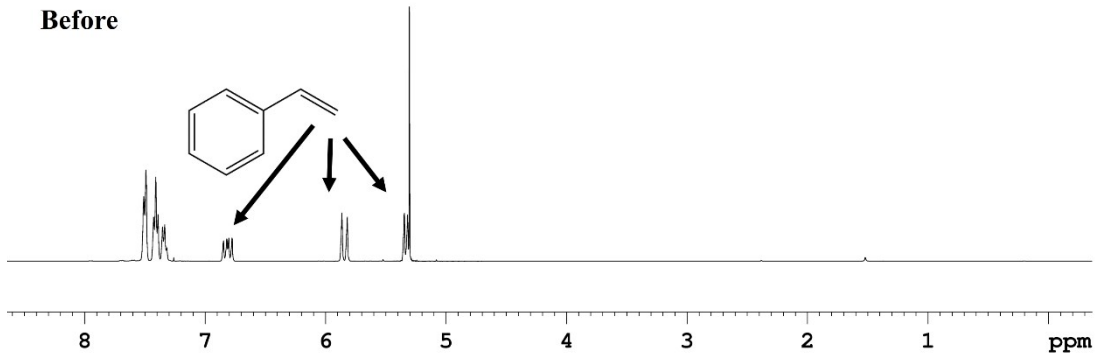
Table 2 entry 2

| NIST MS (MF=96) 1/5: >Ethylbenzene
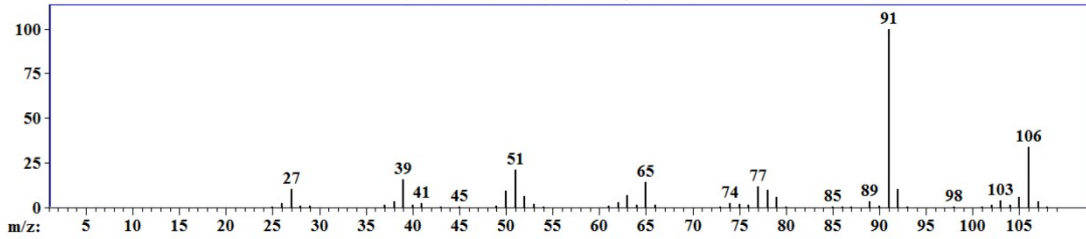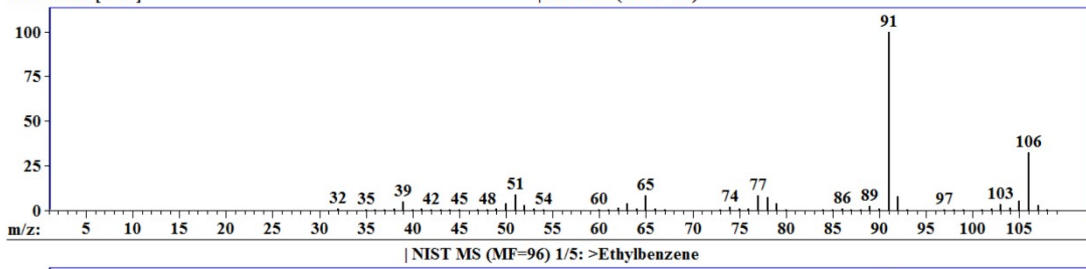
Table 2 entry 3

Table 2 entry 3

Before

Vinylic proton

Table 2 entry 3

Abundance [3197] | Scan 1106 (6.849 min)

| NIST MS (MF=94) 1/3: >Benzene, 1-chloro-4-ethyl-
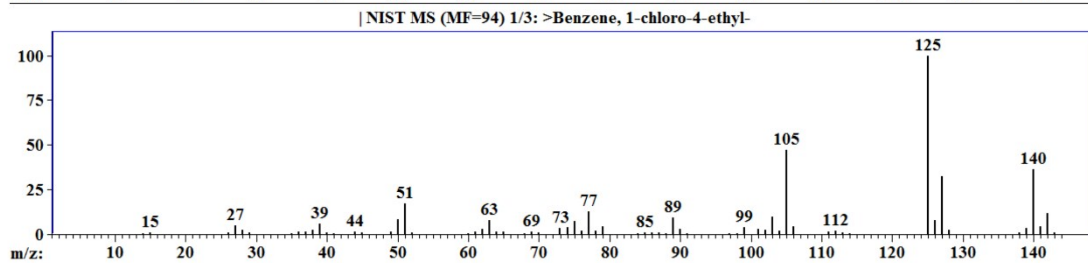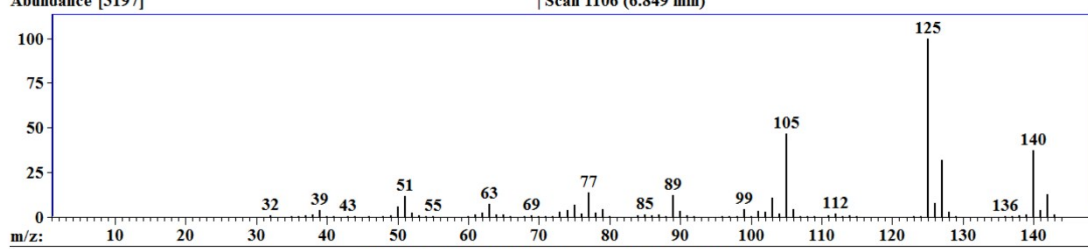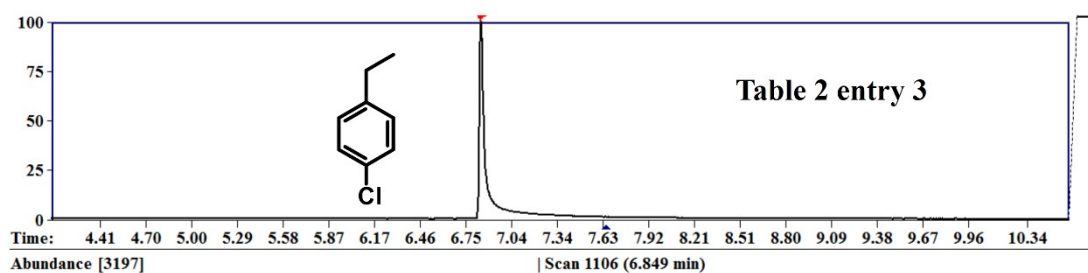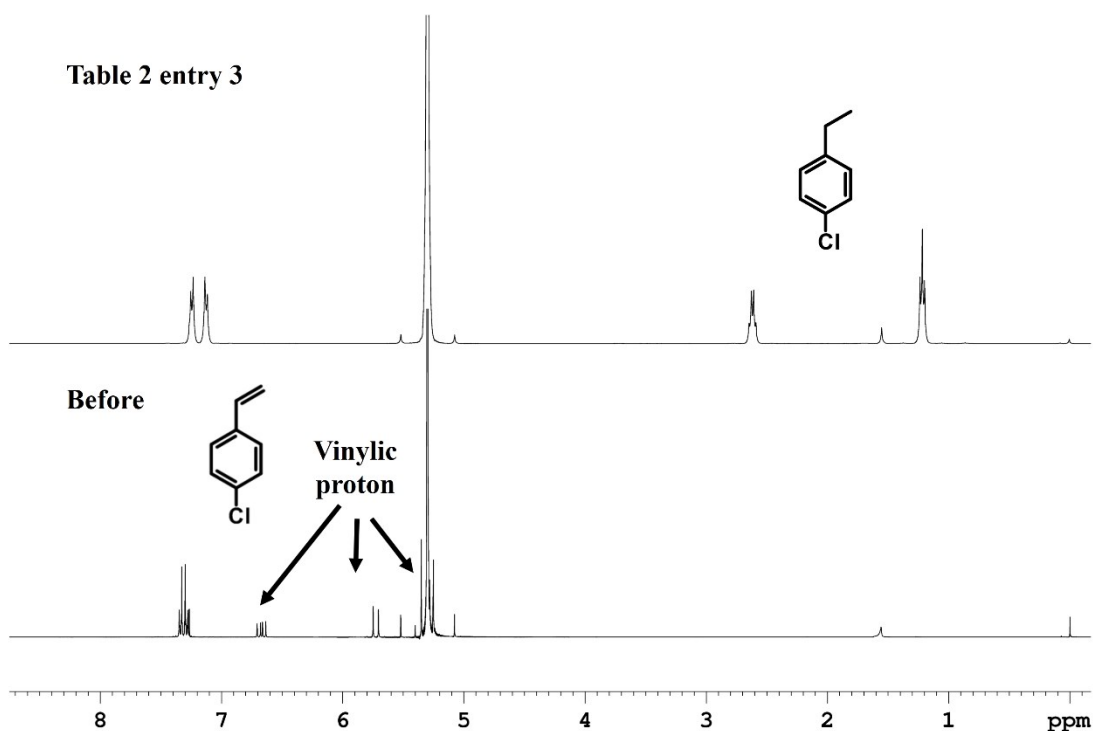
Table 2 entry 4

Table 2 entry 4

Before

Vinylic proton

Table 2 entry 4

Abundance [10.0] | Extracted spectrum (5.451 min)

| NIST MS (MF=96) 1/7: >Benzene, 1-ethyl-4-methyl–
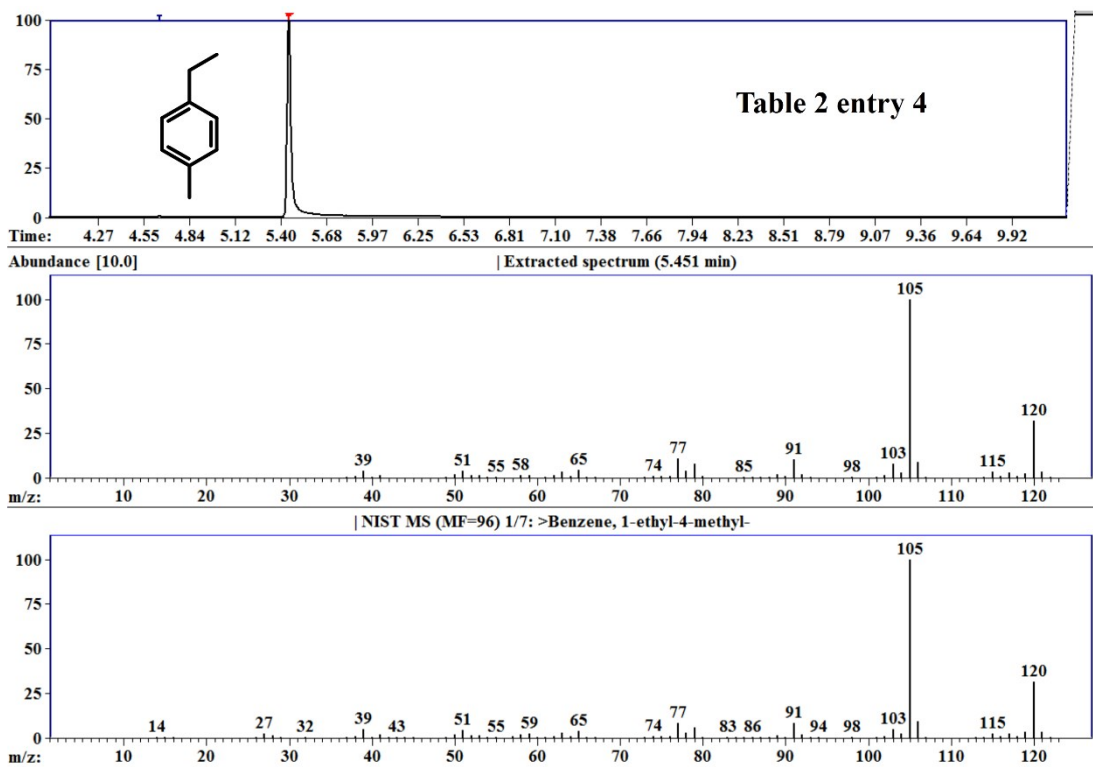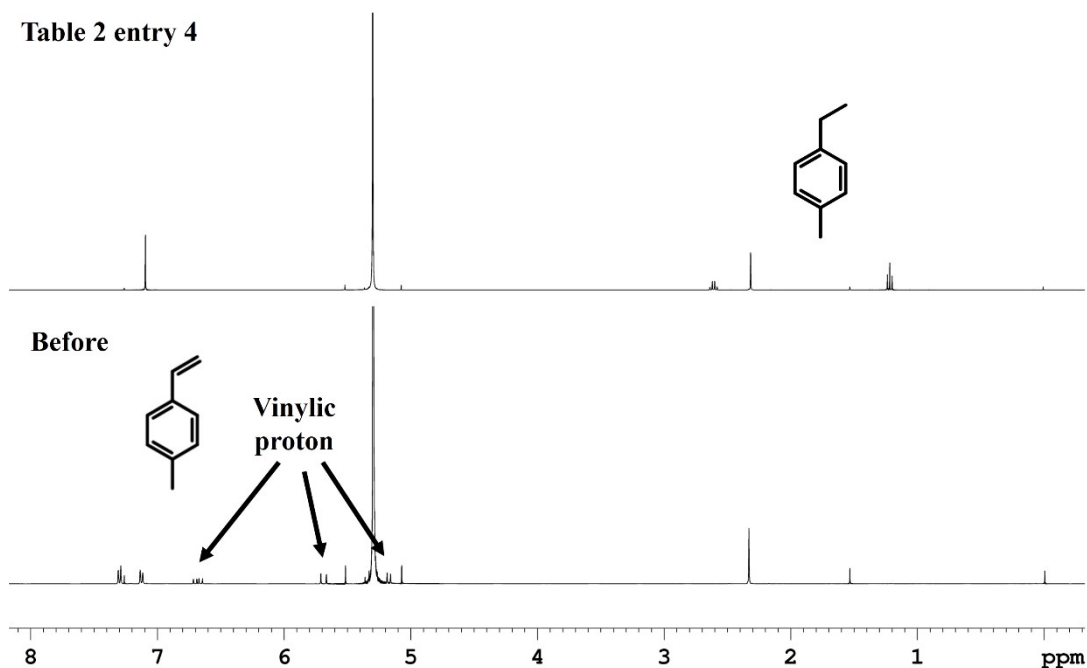
Table 2 entry 5

Table 2 entry 5

Before

Table 2 entry 5

Abundance [2739] | Scan 187 (1.667 min)
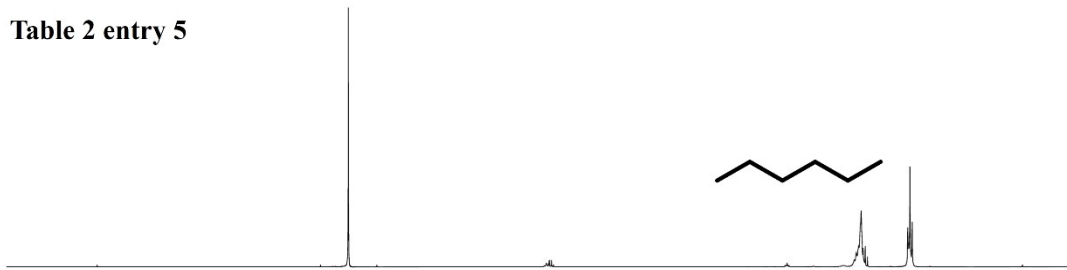
| NIST MS (MF=93) 1/5: >n-Hexane
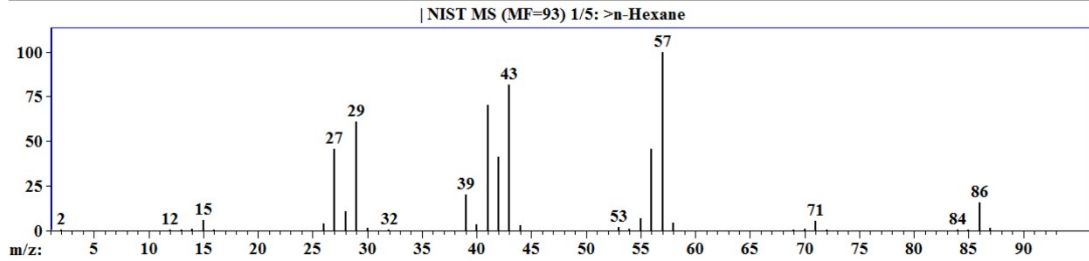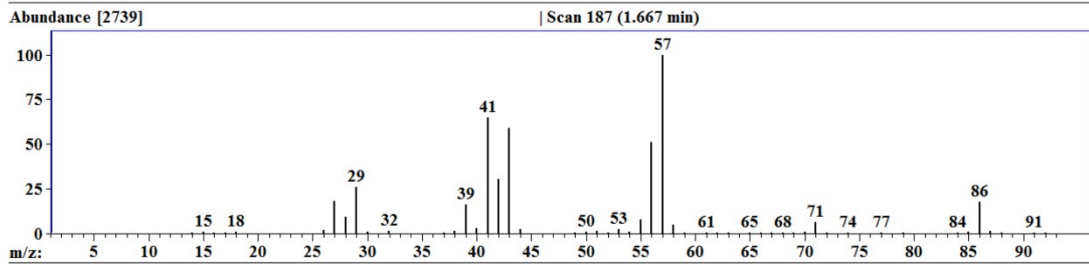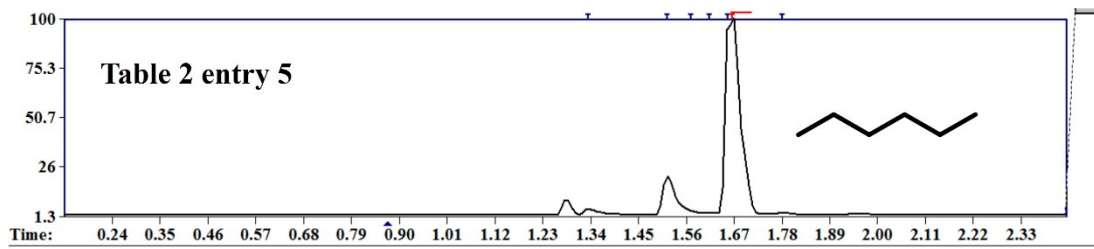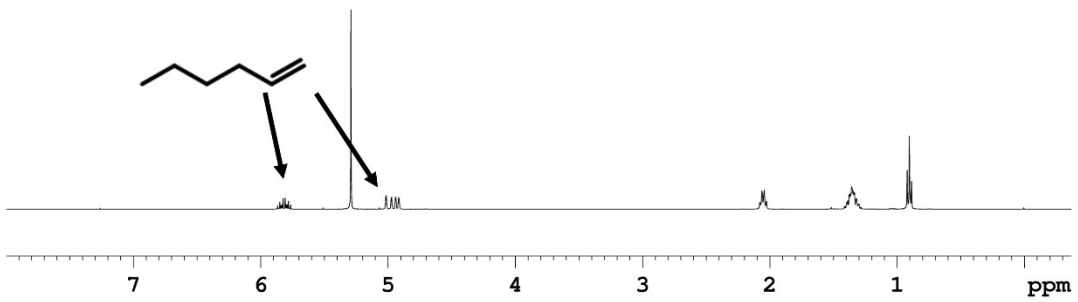
Table 2 entry 6

Table 2 entry 6

Before

Table 2 entry 6

Abundance [28783] | Scan 16 (3.156 min)
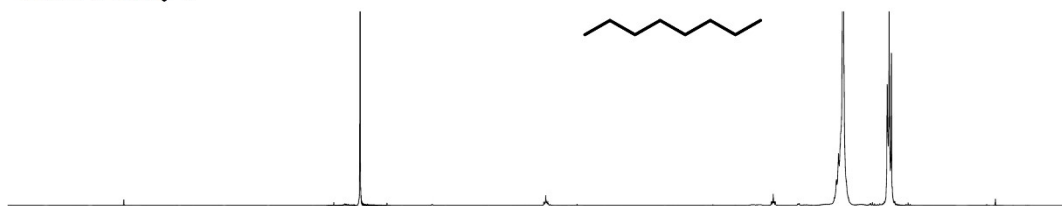
| NIST MS (MF=94) 1/4: >Octane
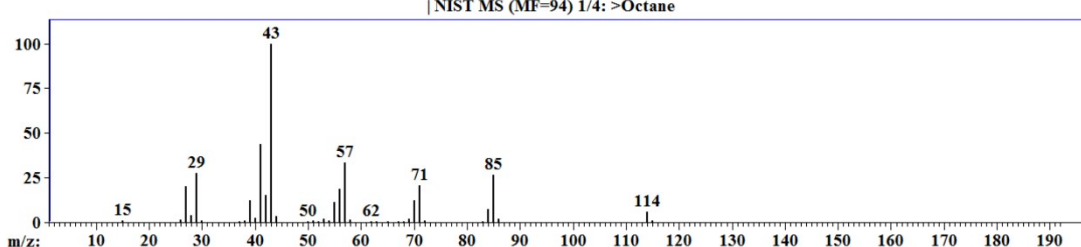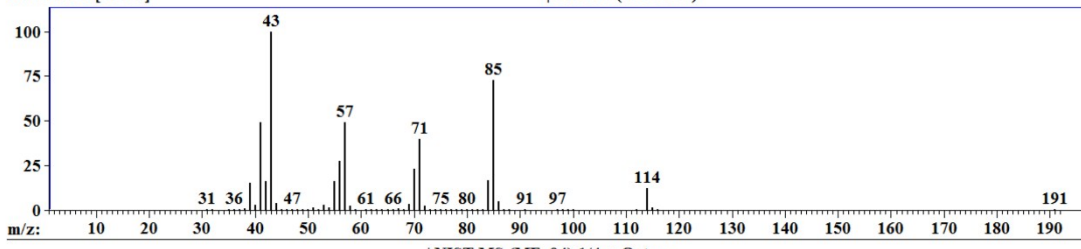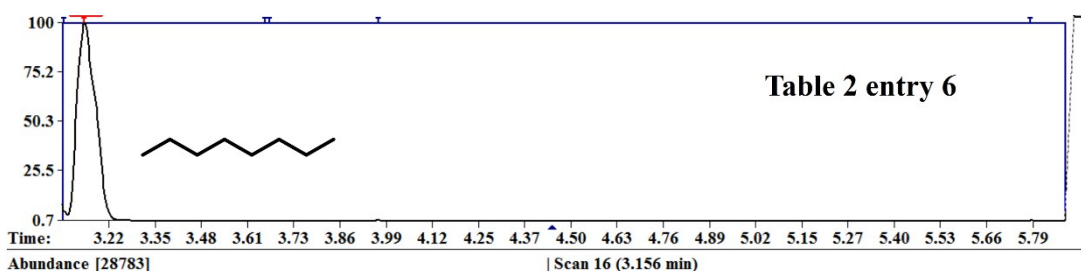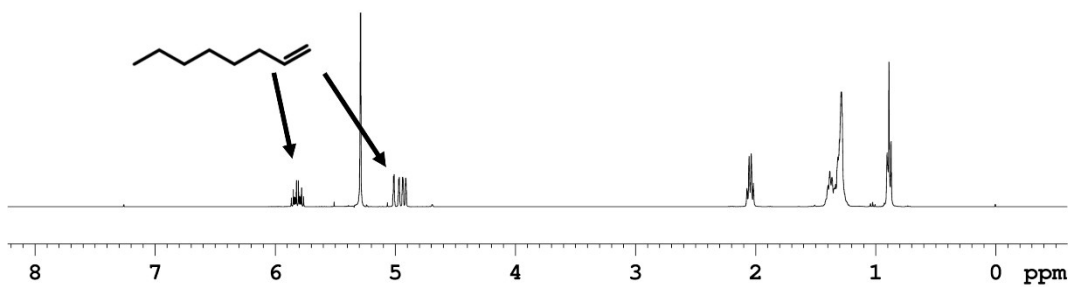
Table 2 entry 7

Table 2 entry 7

Before

Table 2 entry 7

Abundance [5726] | Scan 2609 (11.371 min)
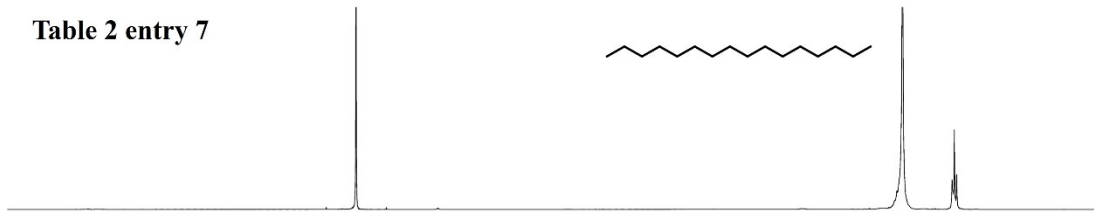
| NIST MS (MF=97) 1/19: >Hexadecane
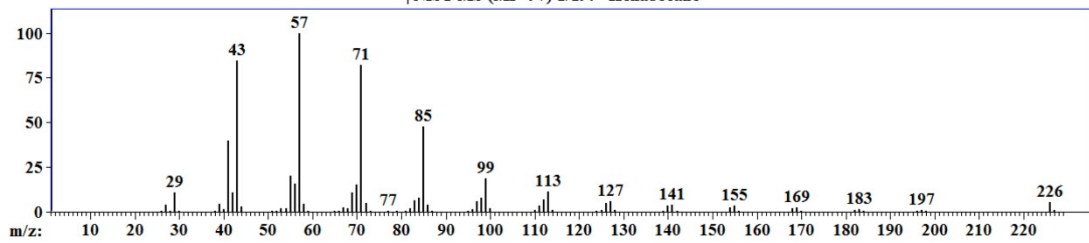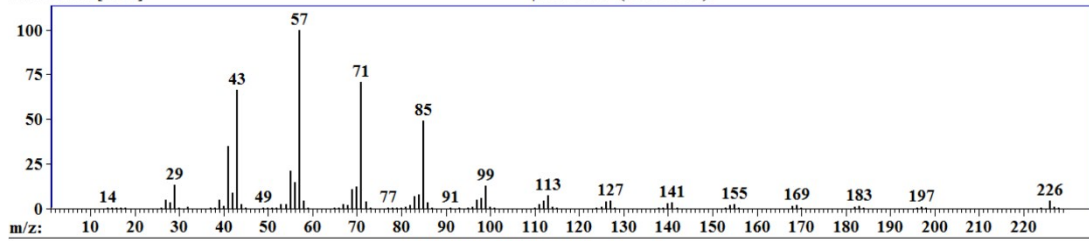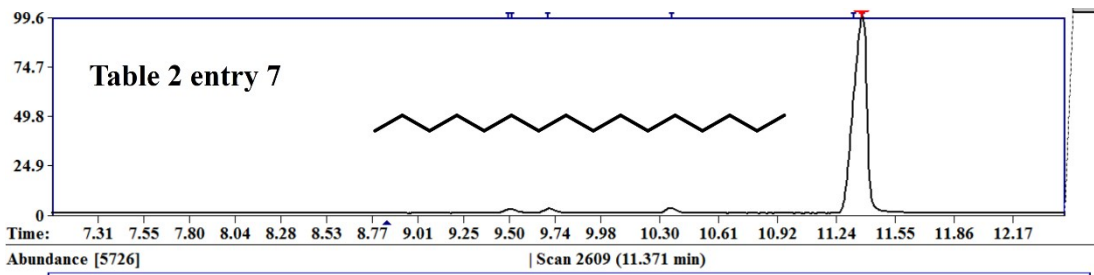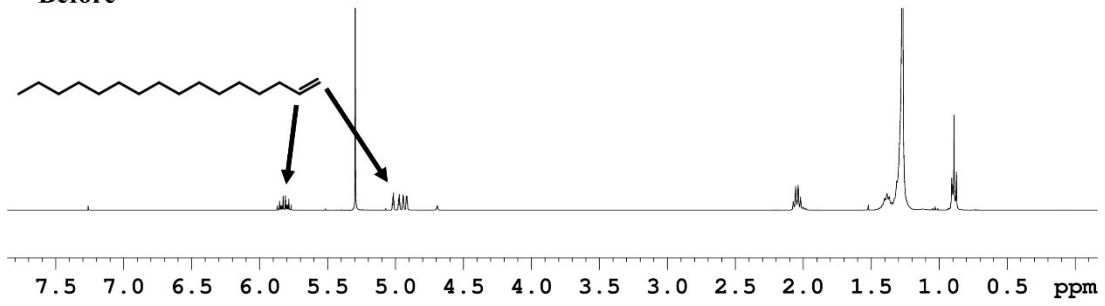
Table 2 entry 8

Table 2 entry 8
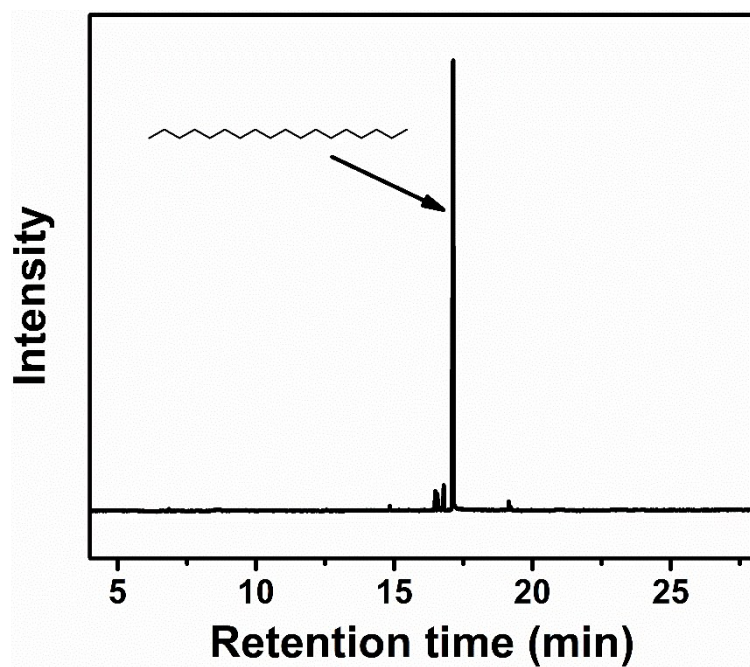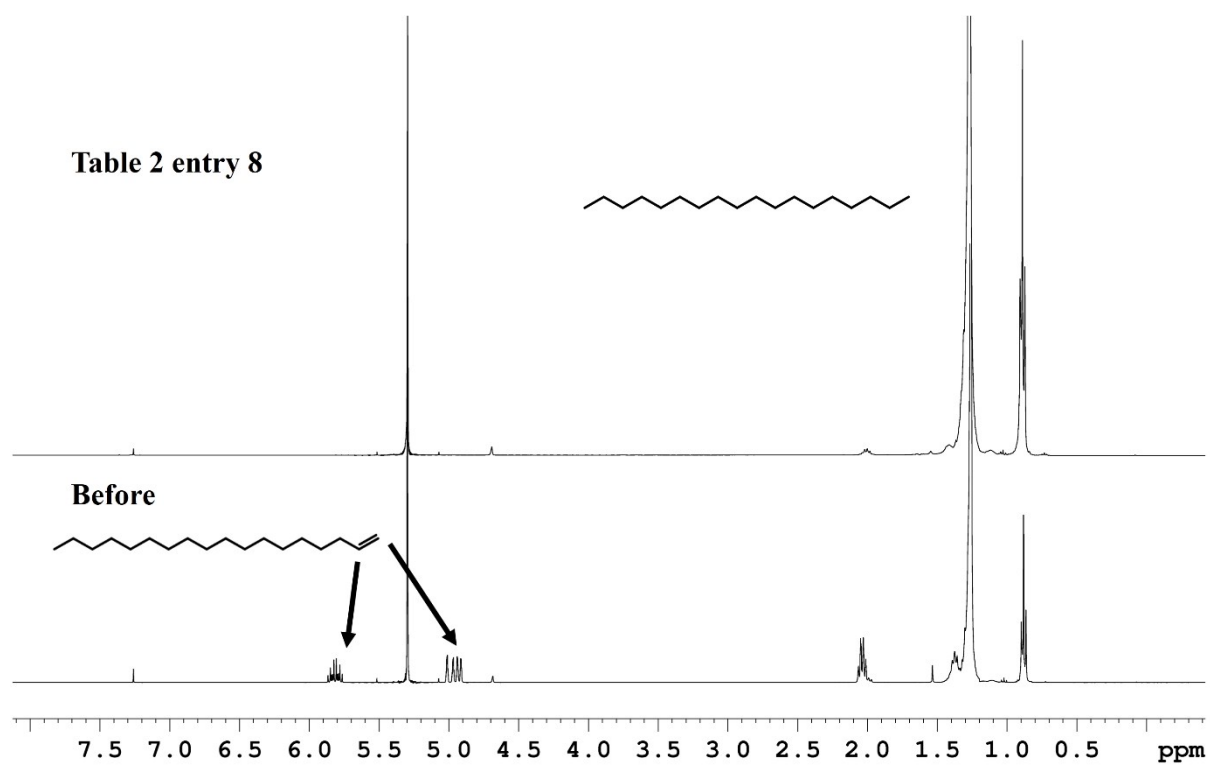
Before

Table 2 entry 9

Table 2 Entry 9

Before

Alkene proton (*sp²* H)

8   7   6   5   4   3   2   1   ppm

Table 2 Entry 9

Abundance [2563] | Scan 219 (1.938 min)

| NIST MS (MF=97) 1/5: >Cyclohexane
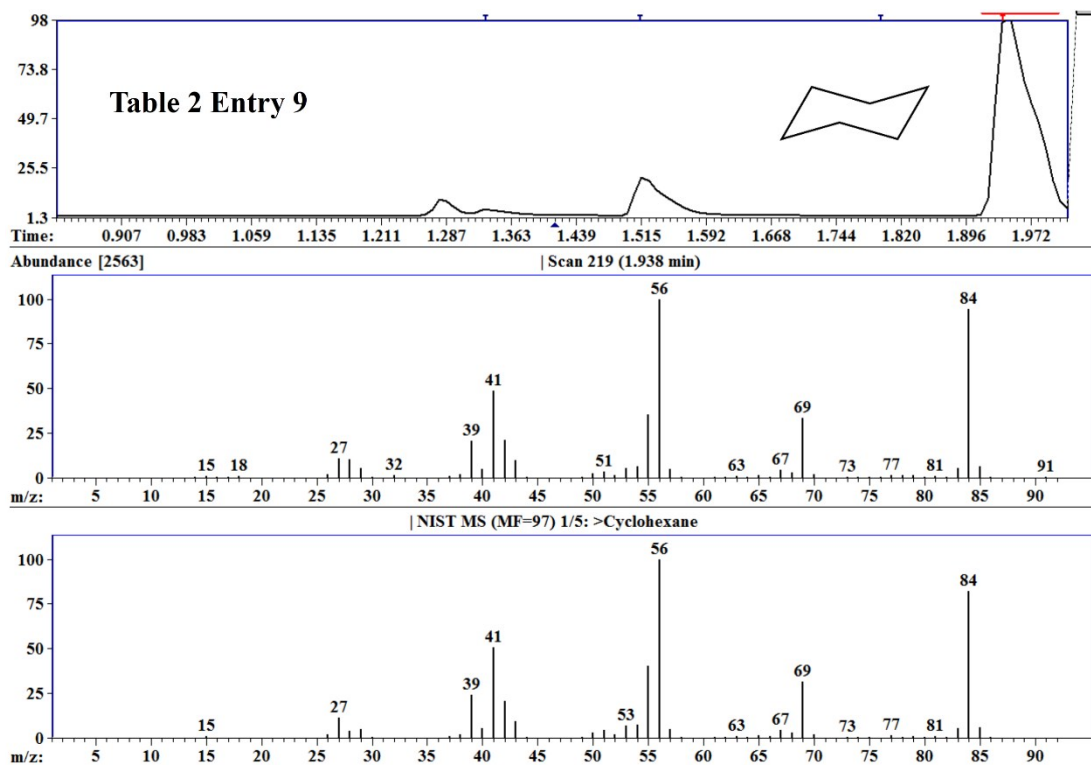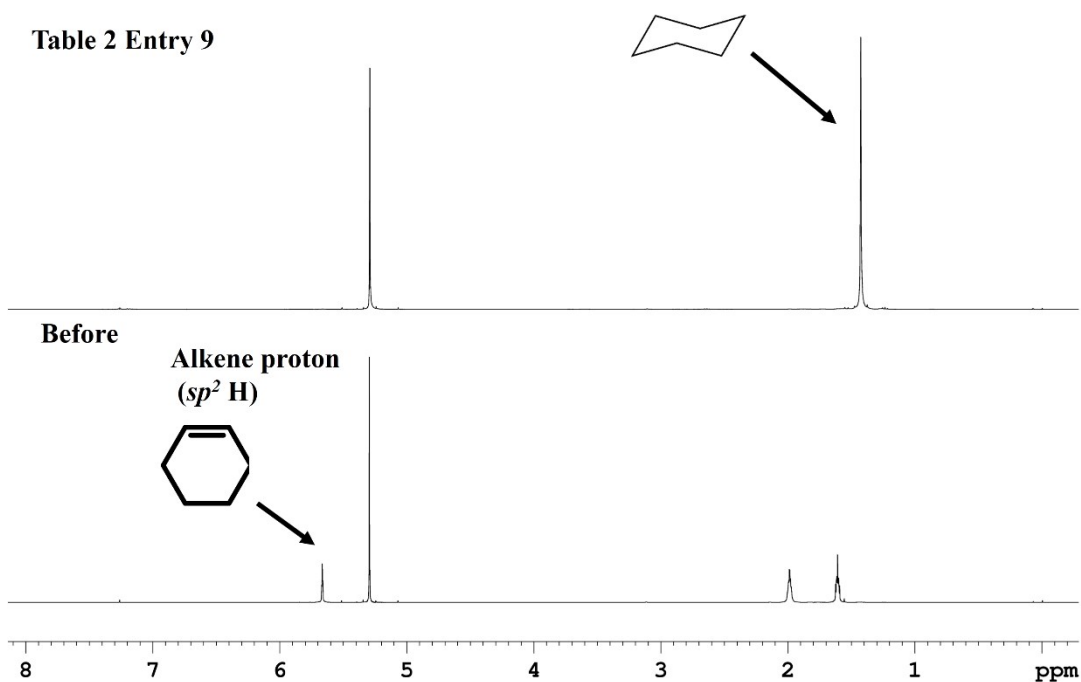
Table 2 entry 10

Table 2 Entry 10

Before
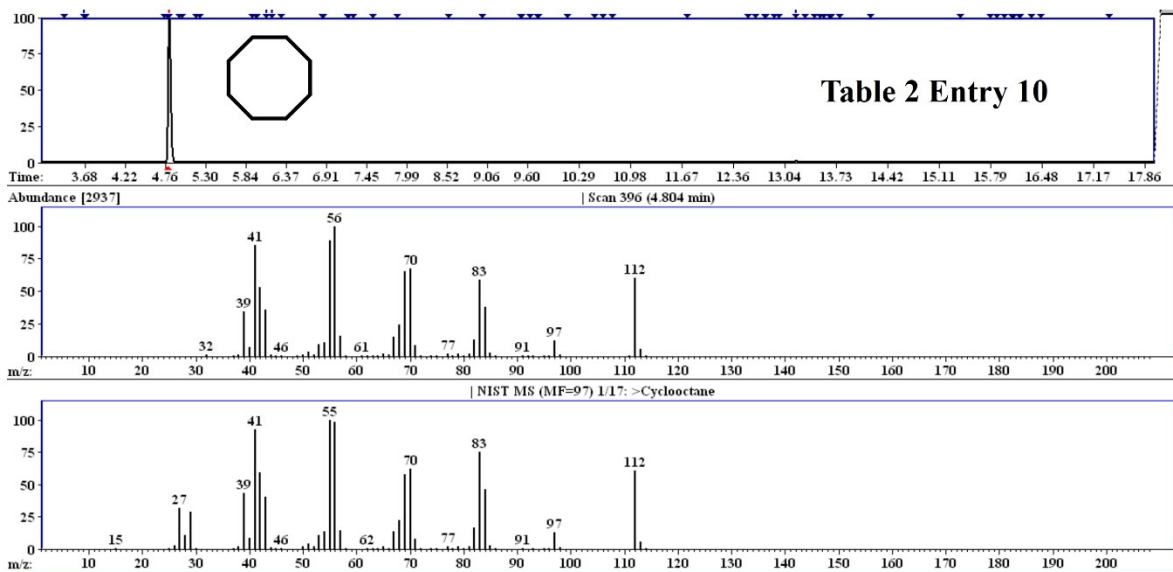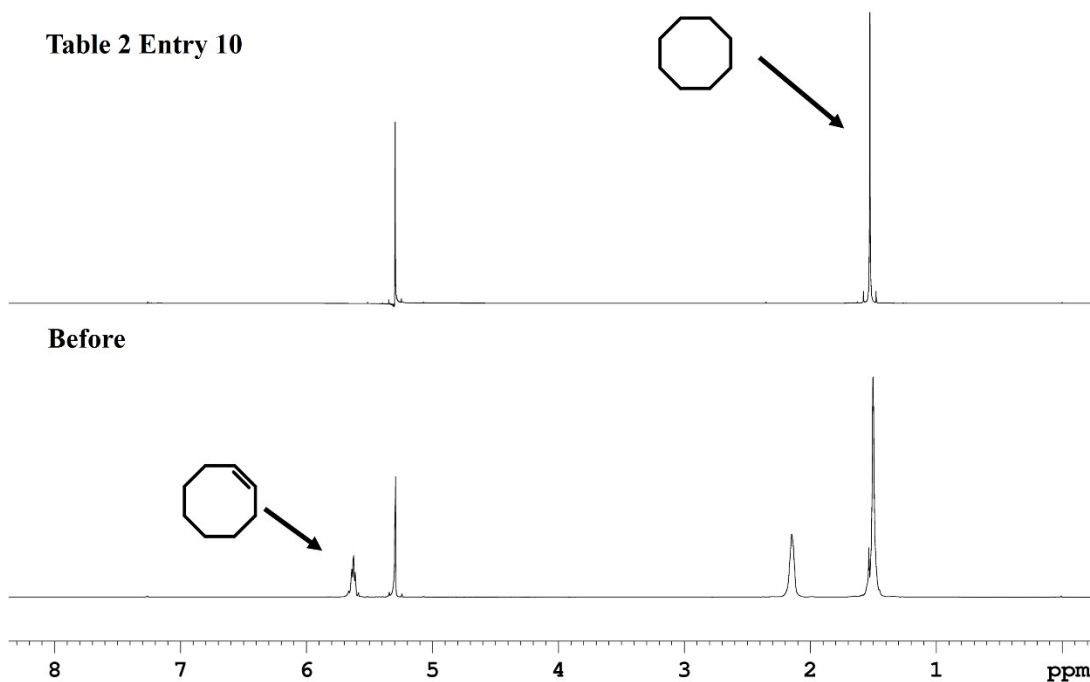
Table 2 Entry 10

Table 2 entry 11

Table 2 Entry 11
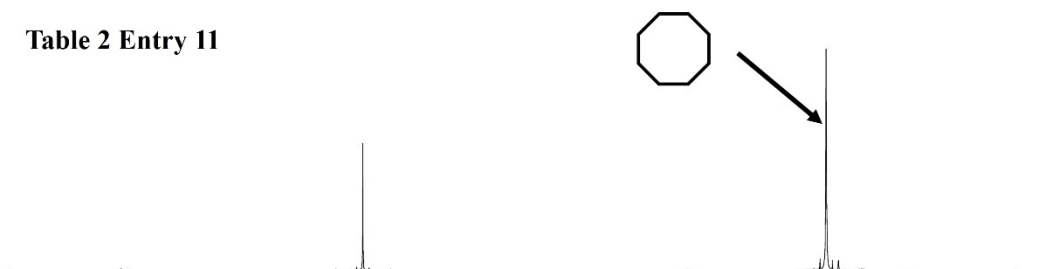
Before
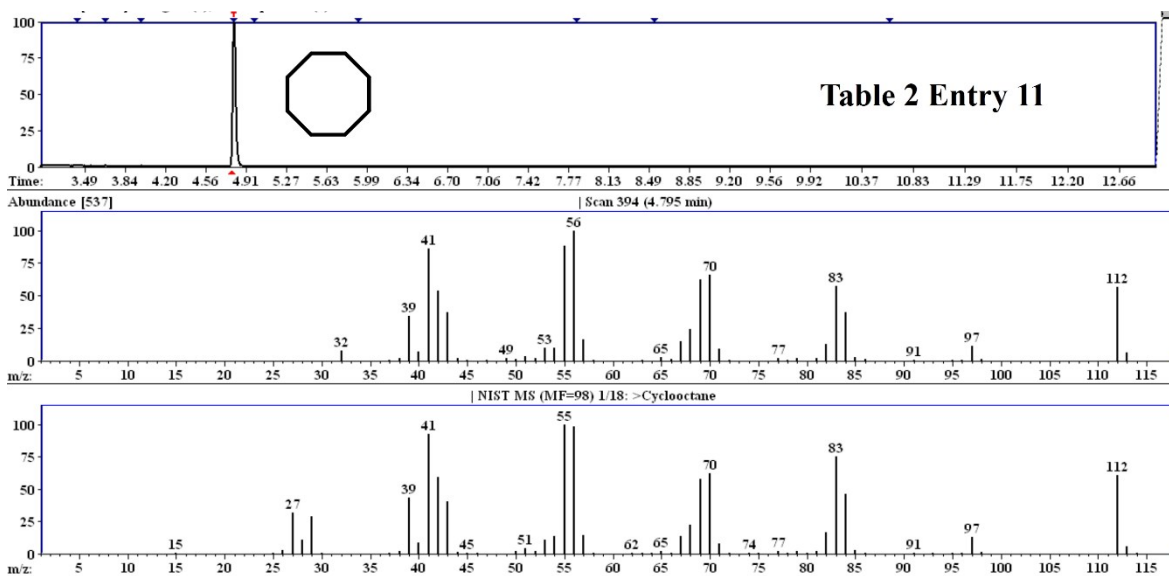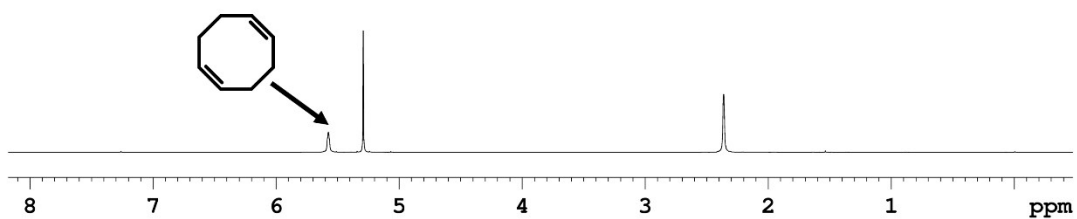
Table 2 Entry 11

Table 2 entry 12

Table 2 entry 12

Before

Table 2 entry 12

Abundance [87618] | Scan 60 (2.347 min)

| NIST MS (MF=92): >Propanoic acid, ethyl ester
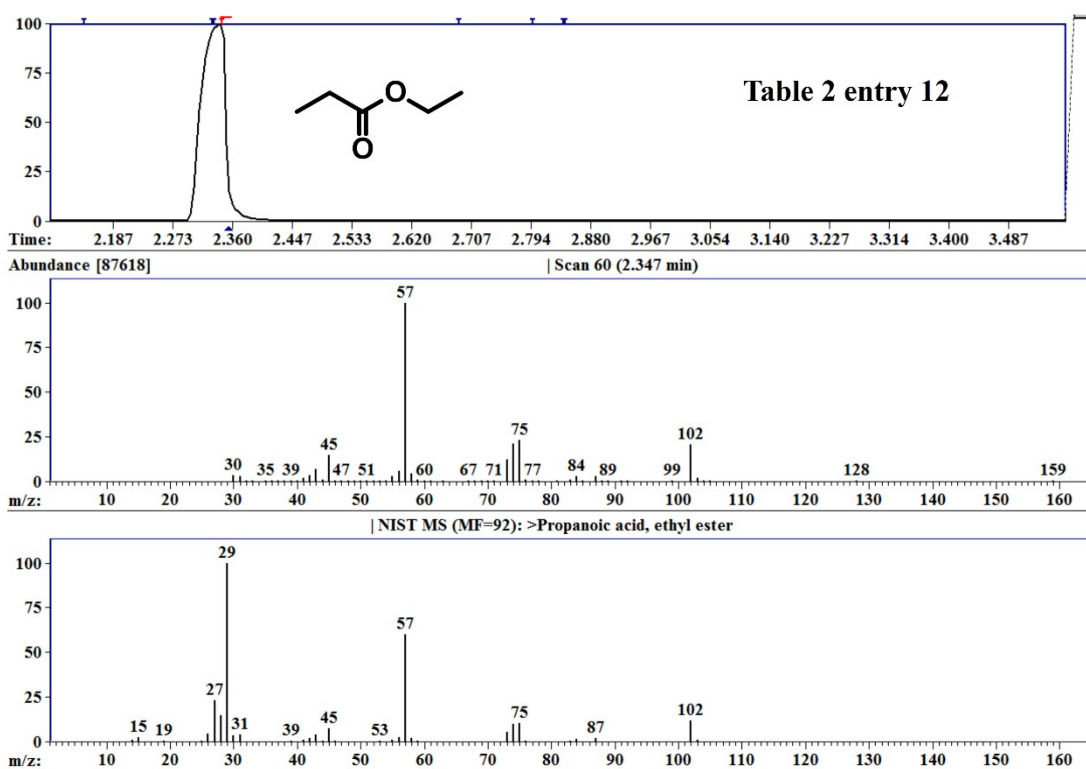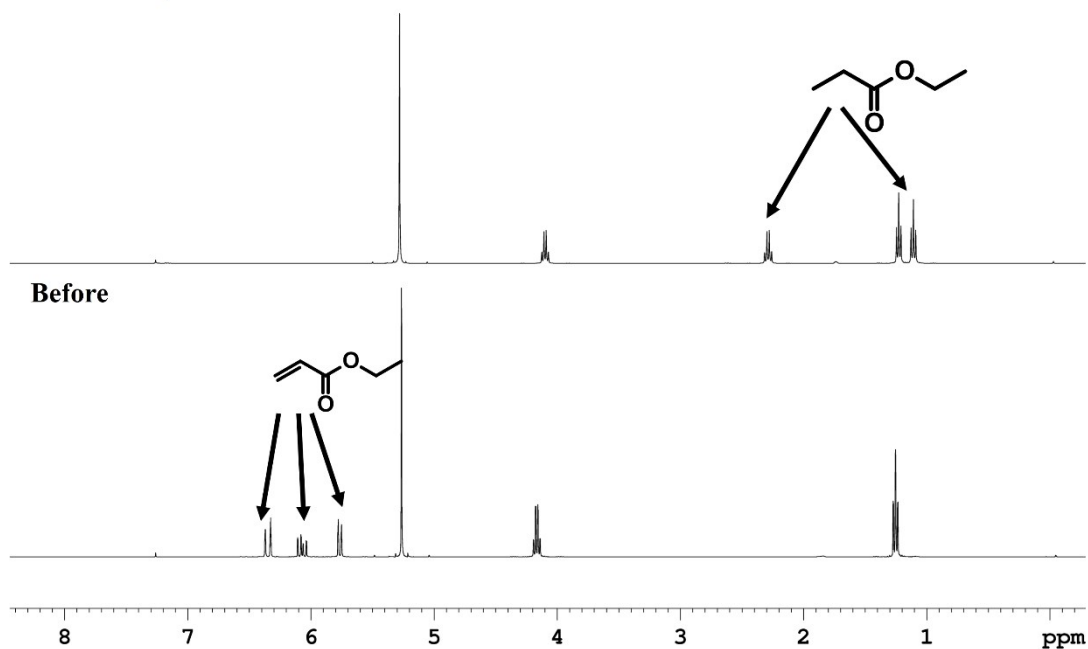
Table 2 entry 13

Table 2 entry 13

Before

Table 2 entry 13

| Scan 221 (3.045 min) |

Abundance [43118]

| NIST MS (MF=96): >Propanoic acid, 1,1-dimethylethyl ester
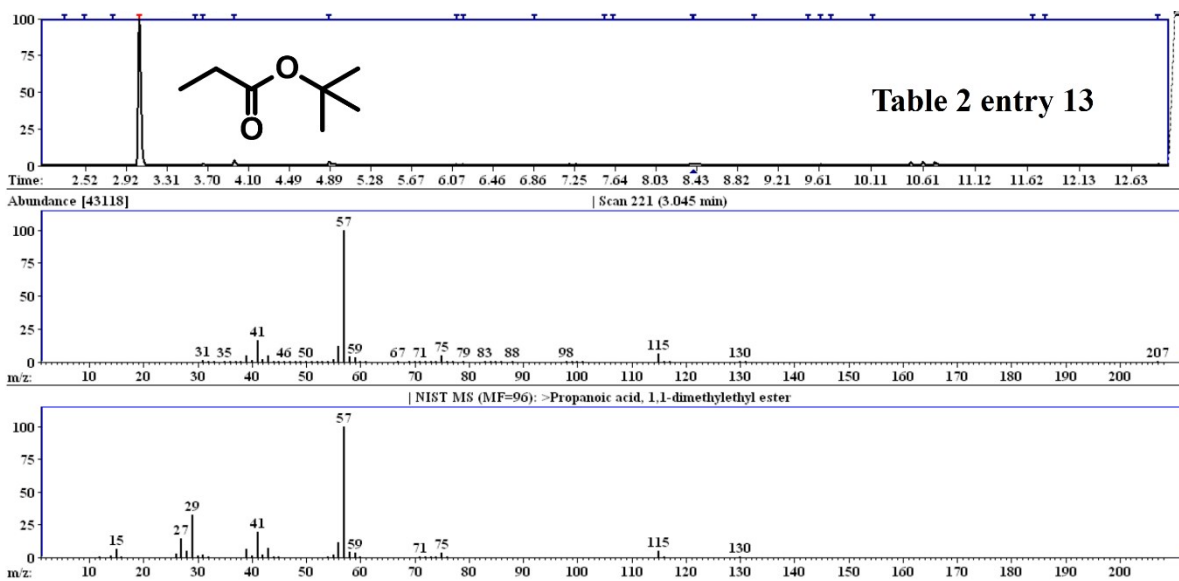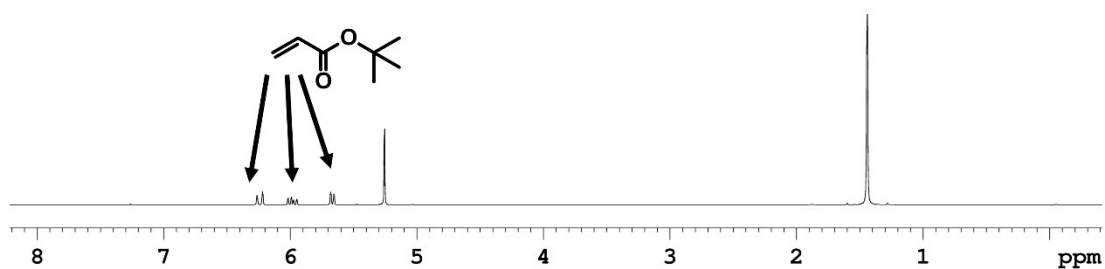
Table 2 entry 14

Table 2 entry 14

Before

Table 2 entry 14

| Scan 219 (2.031 min)

| NIST MS (MF=94): >Propanoic acid, 2-methyl-, methyl ester
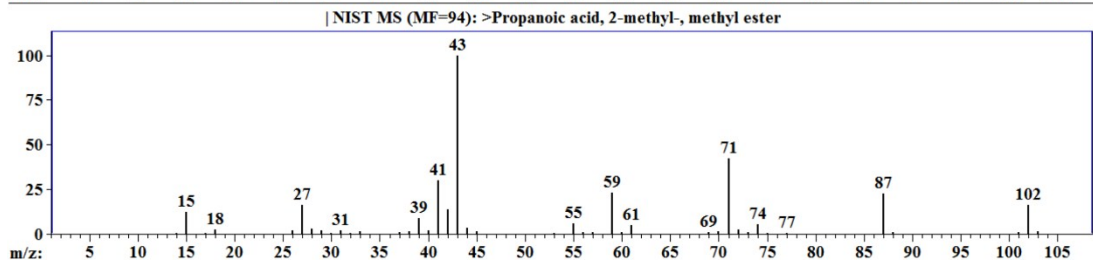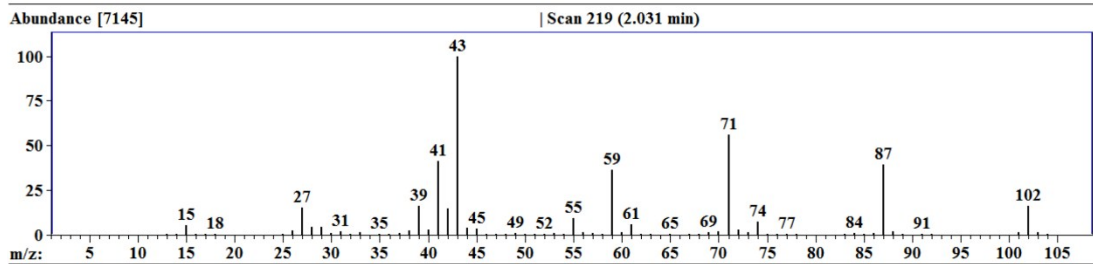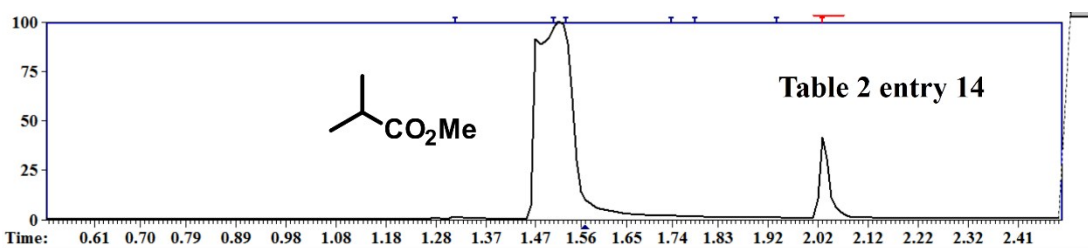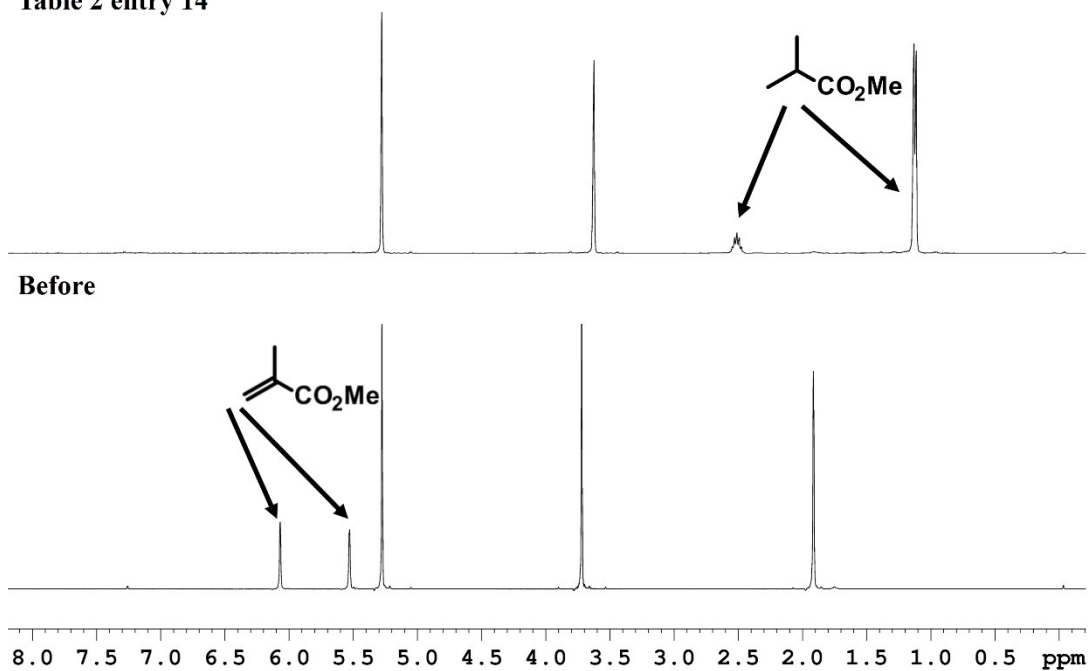
Table 2 entry 15

Table 2 entry 15

Before

Table 2 entry 15

Abundance [7203] | Scan 305 (4.409 min)

| NIST MS (MF=97) 1/2: >Cyclohexanone

Table 2 entry 15

Scan 271 (4.262 min)

| NIST MS (MF=97) 1/6: >Cyclohexanol
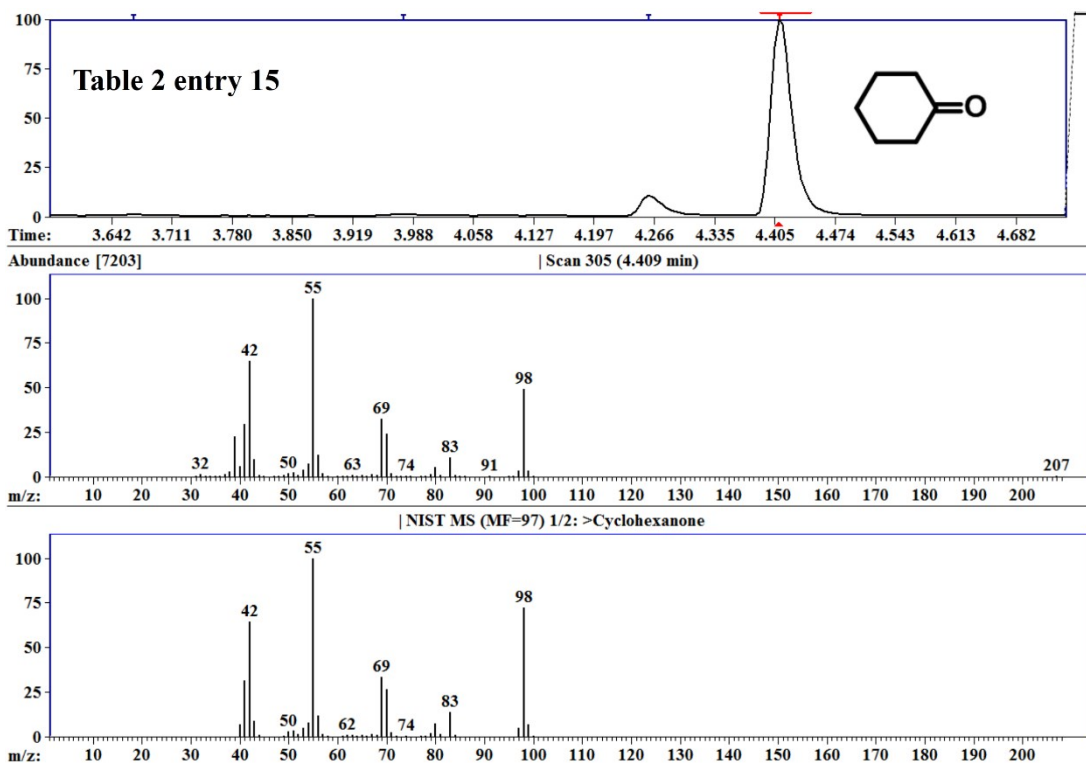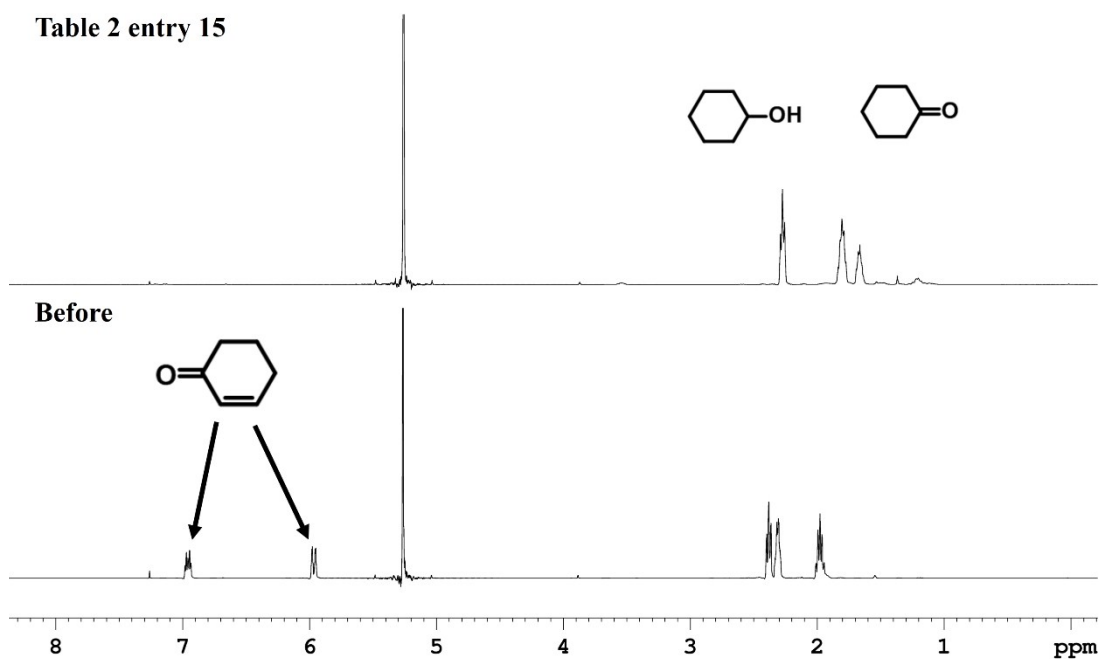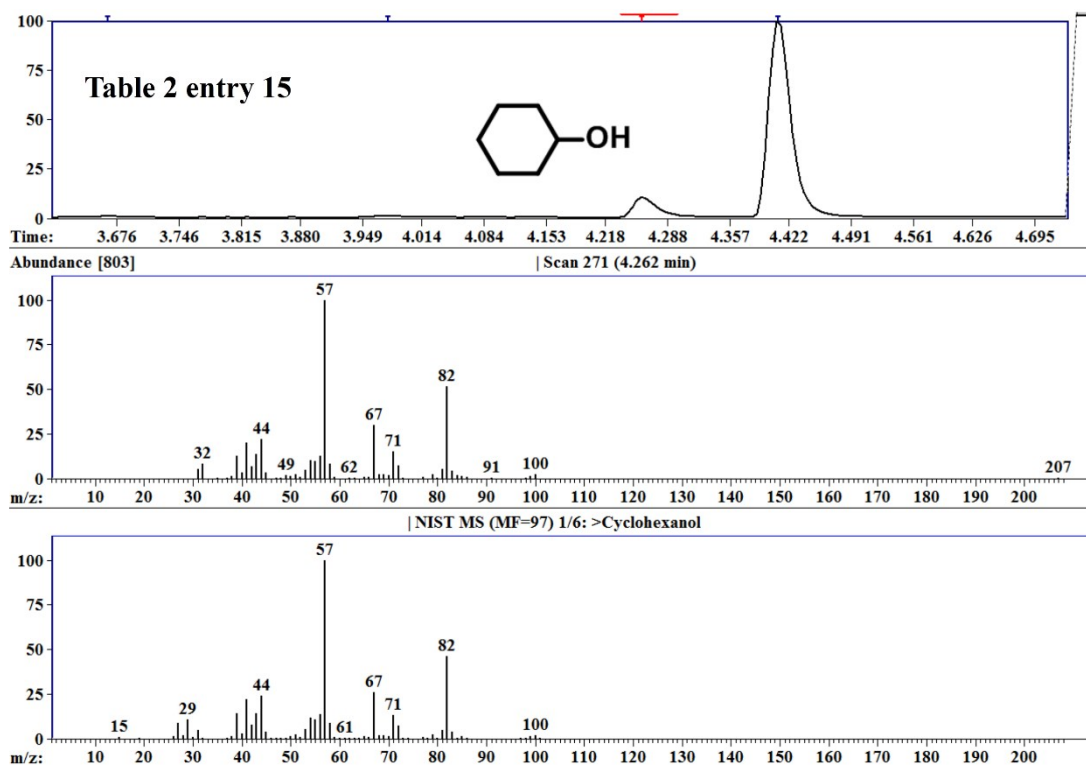
Table 2 entry 16 (Table S2 data) NMR stack plot

Table S2 entry 3
After 9 h

Table S2 entry 2
After 6 h

Table S2 entry 1
After 3 h

Before
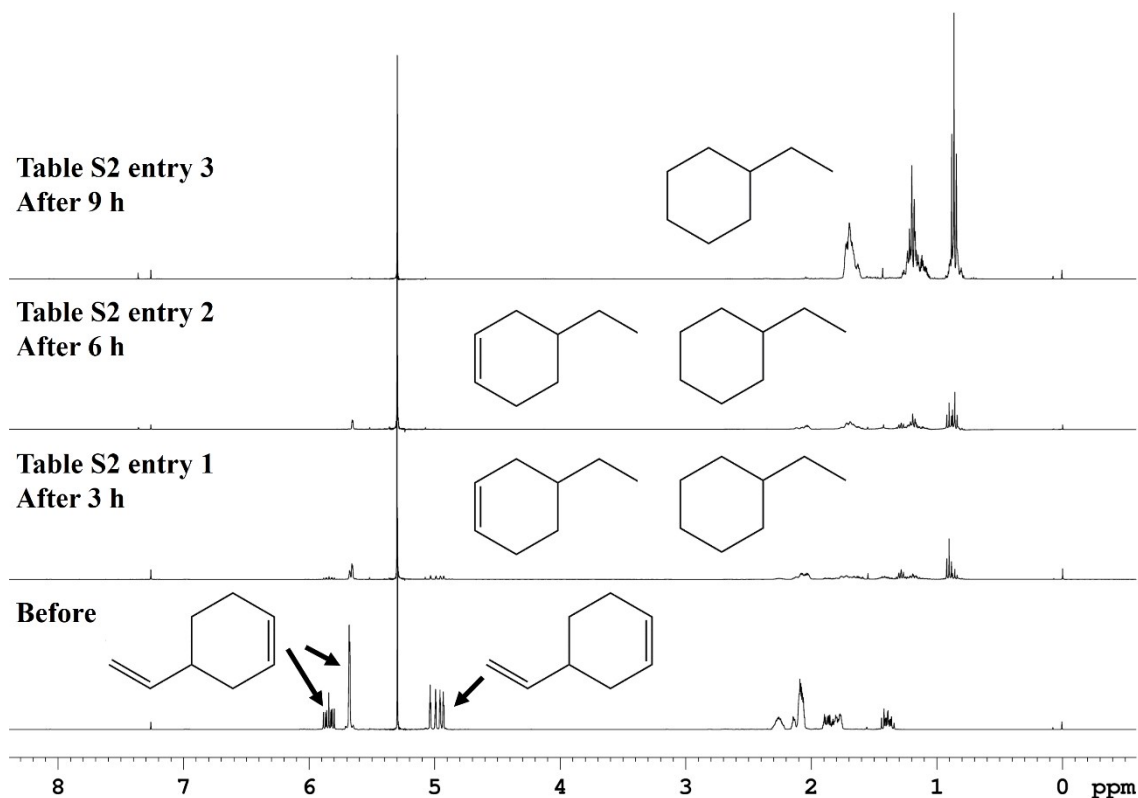
Table 2 entry 16 (Table S2 entry 1) GC-MS plot

Table S2 entry 1
After 3 h

| NIST MS (MF=92): >Cyclohexane, ethyl-

Table S2 entry 1
After 3 h

| NIST MS (MF=93) 1/15: >4-Ethylcyclohexene
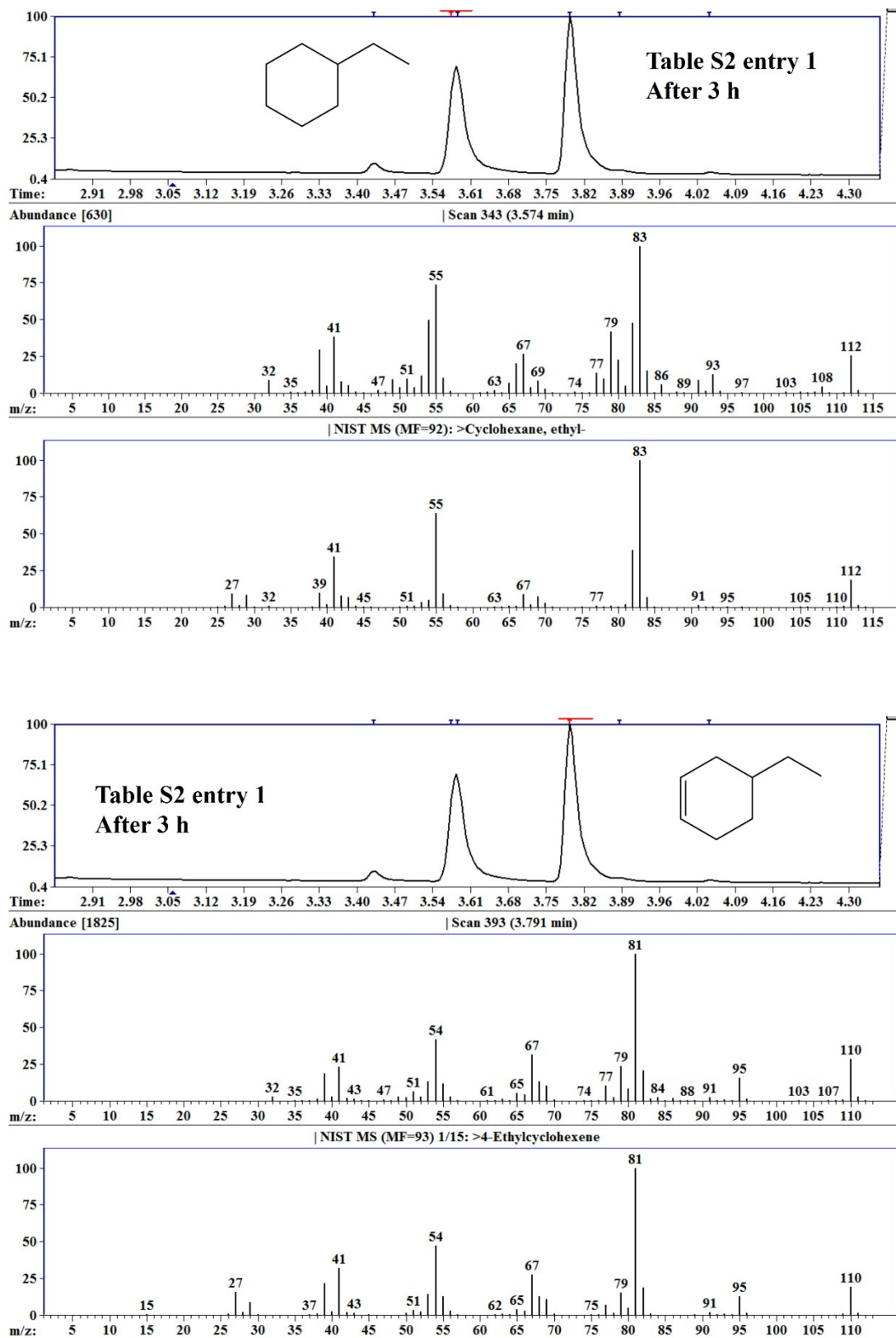
Table 2 entry 16 (Table S2 entry 2) GC-MS plot
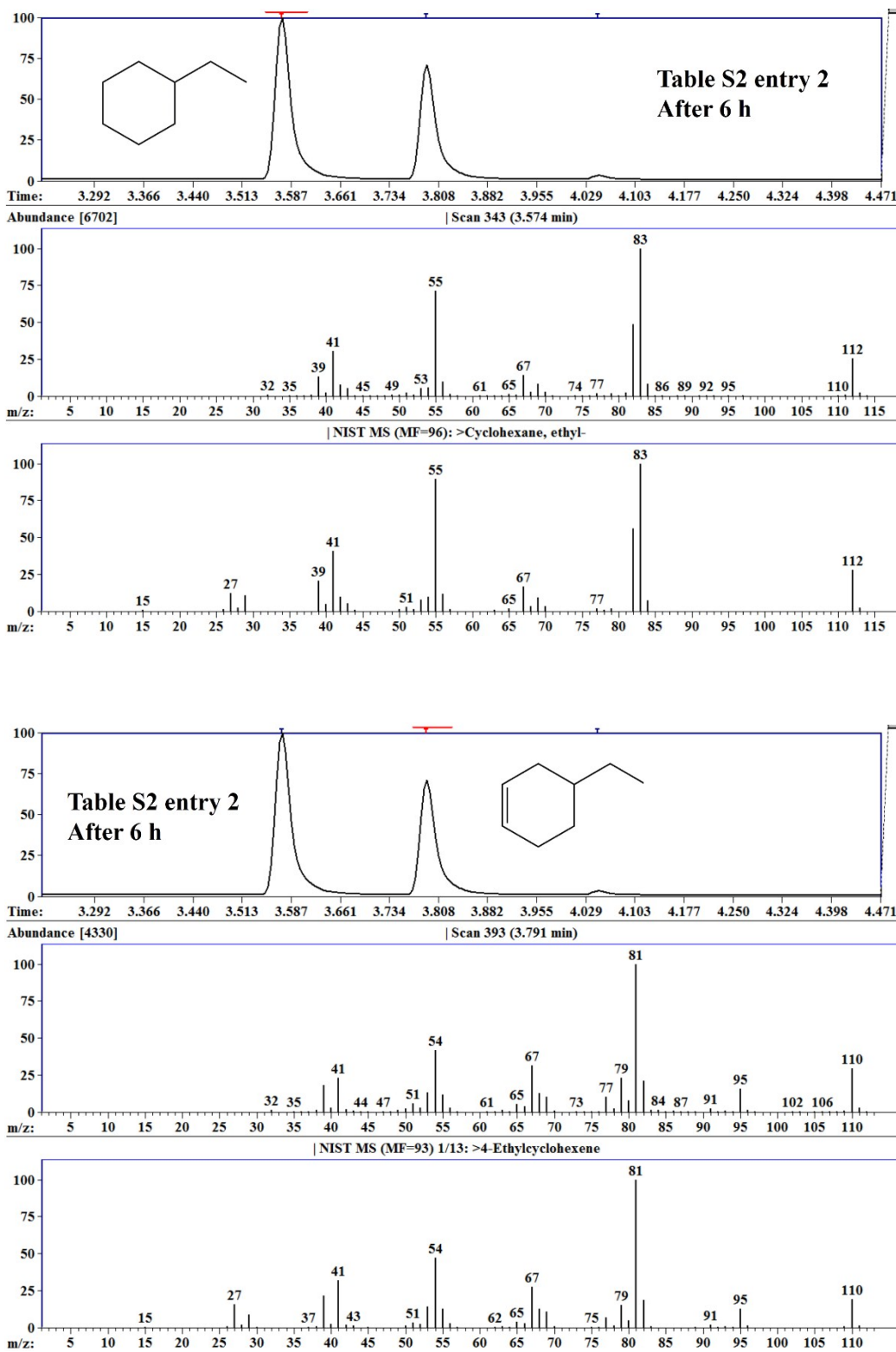
Table 2 entry 16 (Table S2 entry 3) GC-MS plot

Table S2 entry 3
After 9 h

Abundance [7459] | Scan 343 (3.574 min)

| NIST MS (MF=96): >Cyclohexane, ethyl-

Table S2 entry 3
After 9 h

Abundance [97.2] | Scan 394 (3.795 min)

| NIST MS (MF=94) 1/7: >4-Ethylcyclohexene
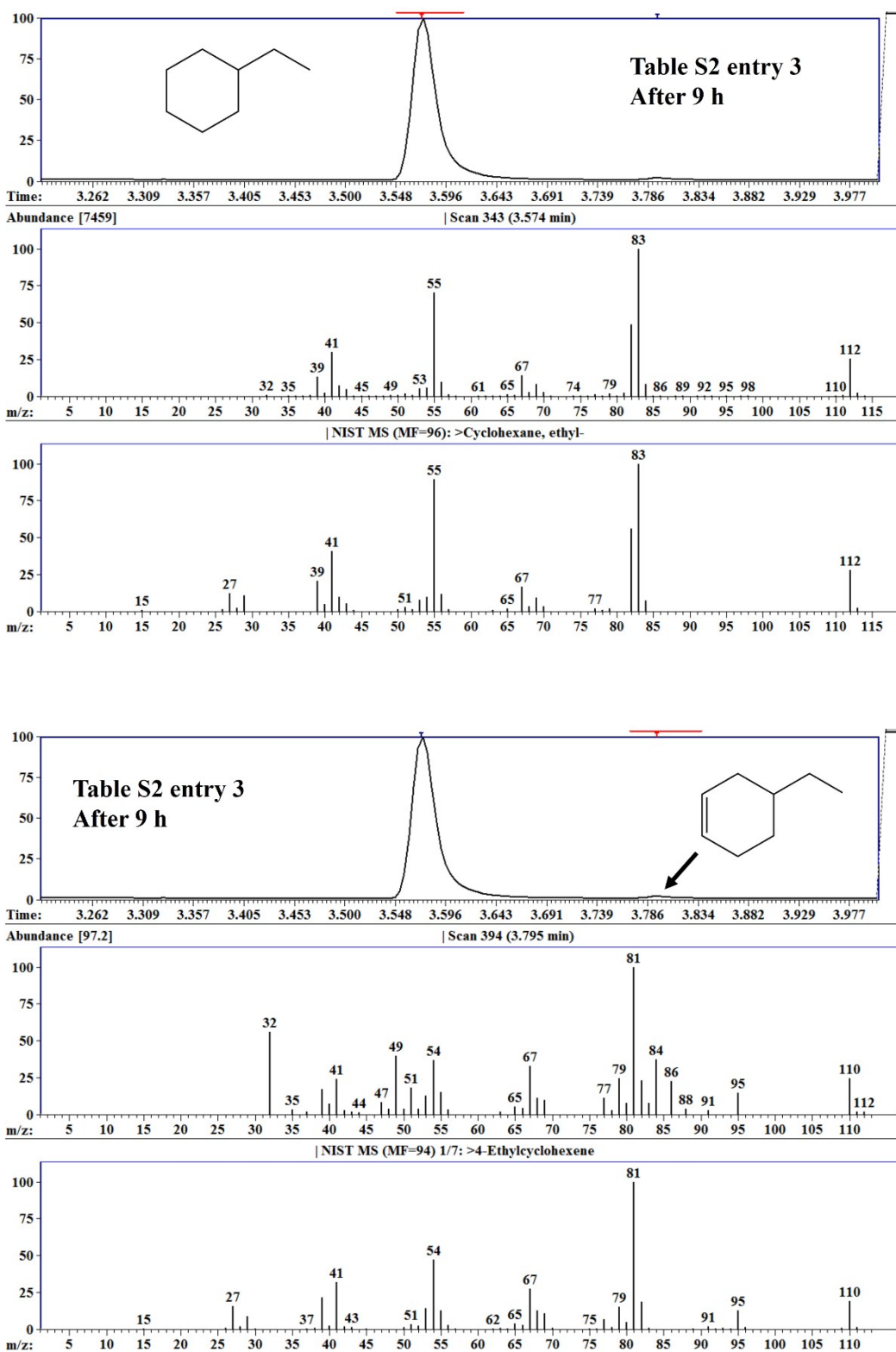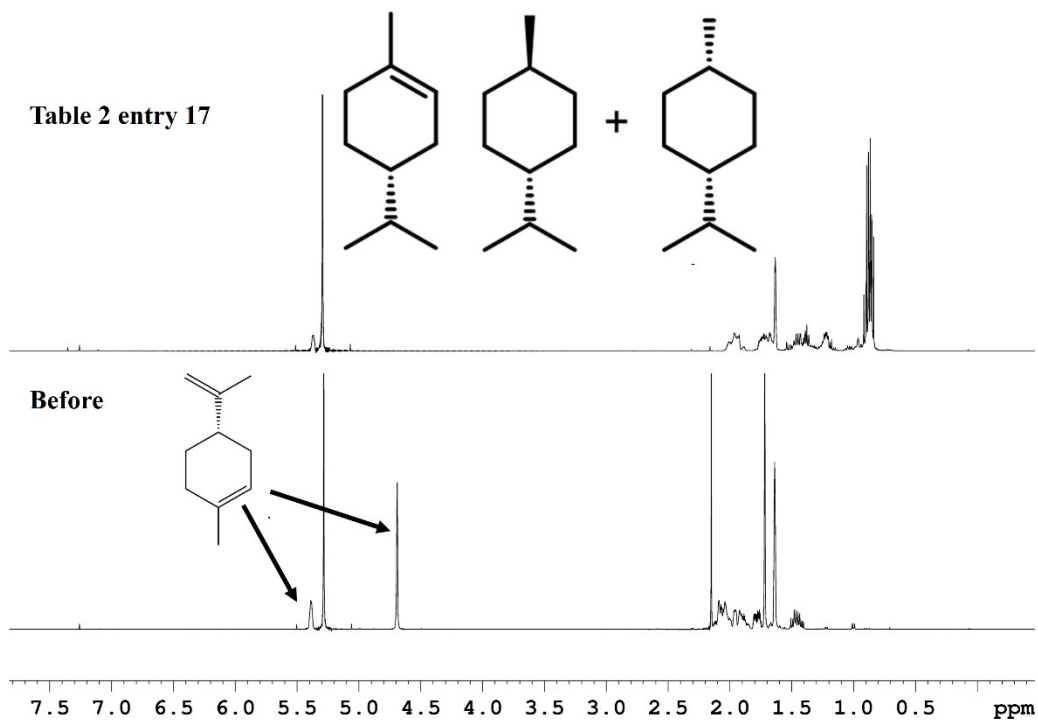
Table 2 entry 17 NMR
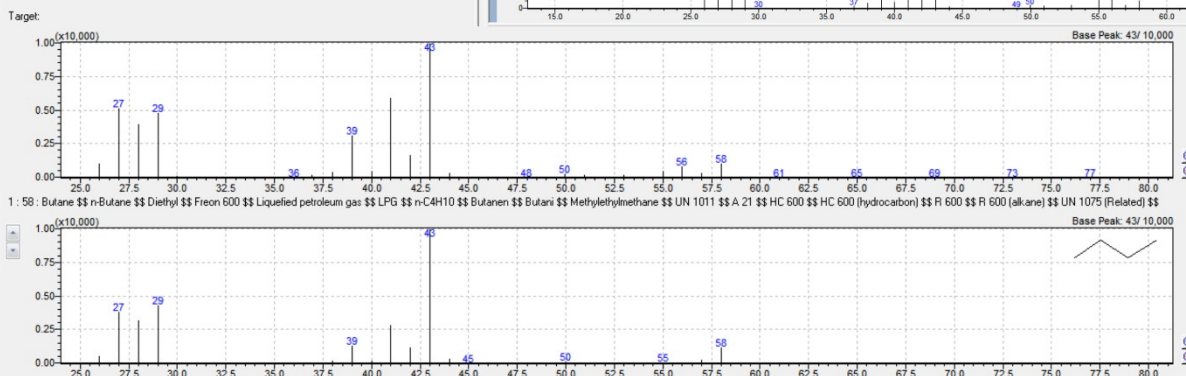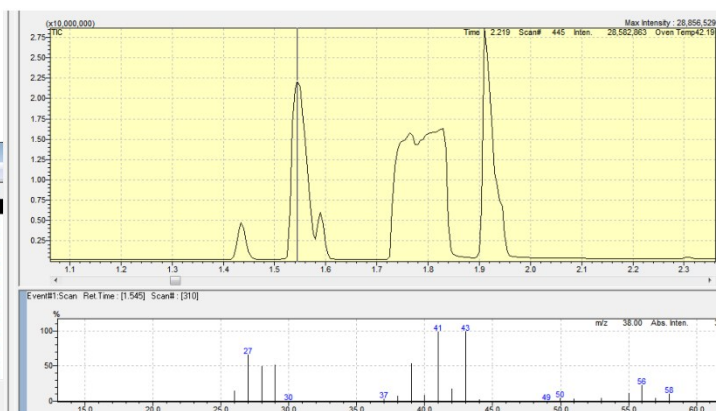

Table 2 entry 17 GC-MS plot

Gas chromatogram shows three peaks which correspond to the diastereomers of *p*-menthane (*cis* and *trans*) and 1-*p*-menthene. From the retention time and mass spectroscopic investigation the presence of *cis* and *trans* diastereomers could be ascertained. The stereochemistry of 1-*p*-menthene was established using specific rotation measurement. The specific rotation value for the starting material (*R*-limonene, 97%) is $[\alpha]_D^{22}$ +113.4 (*c* 2.0, CH$_2$Cl$_2$). Whereas, the specific rotation of product is $[\alpha]_D^{22}$ +101.9 (*c* 2.0, CH$_2$Cl$_2$), which matches with that of the *R* isomer of 1-*p*-menthene (83.5 % calculated from GC). Thus, there is retention of stereochemistry of the chiral center.
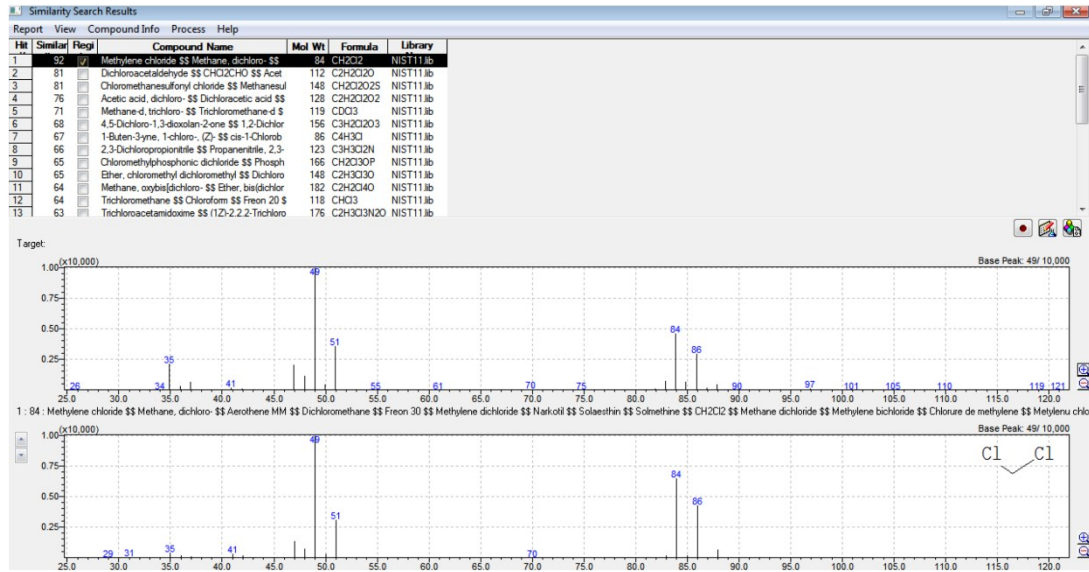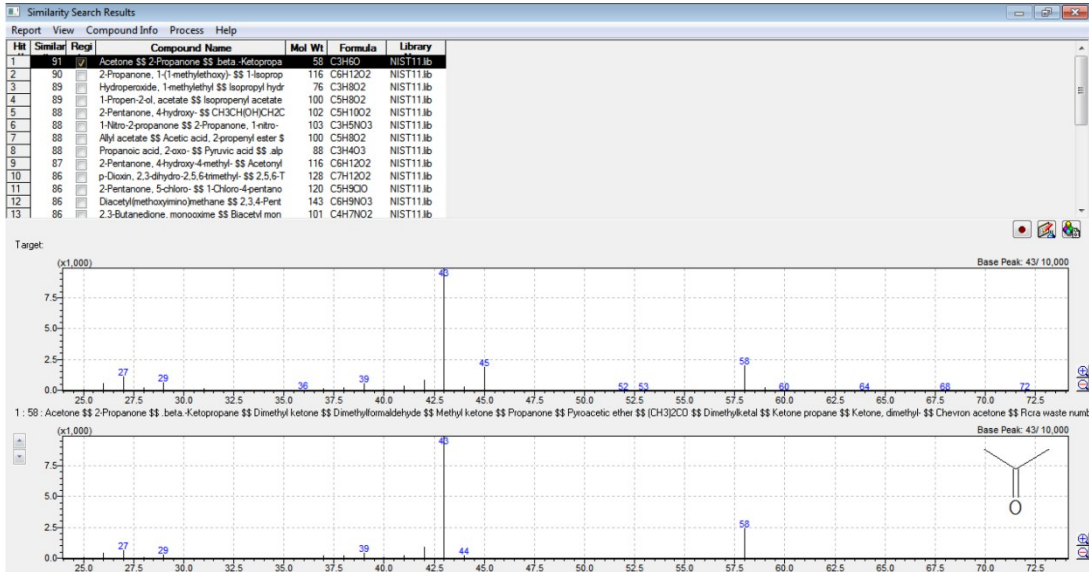
Table 2 entry 18 NMR stack plot
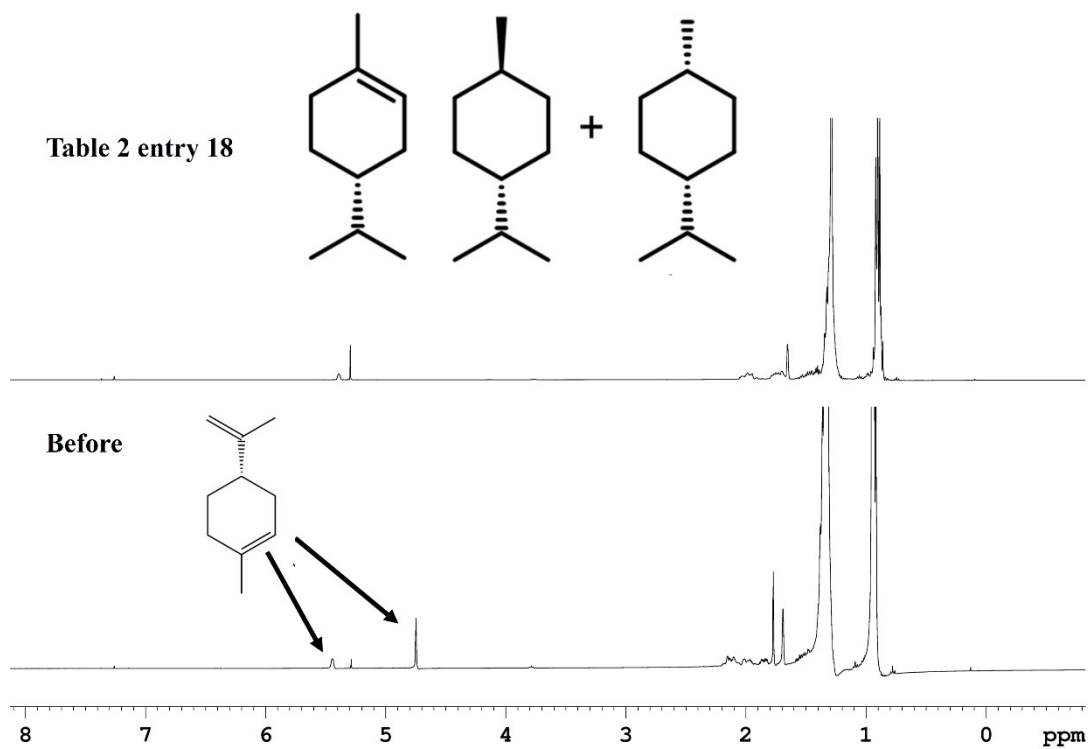
Table 2 entry 18 GC-MS plot

Gas chromatogram shows three peaks, corresponding to the diastereomers of *p*-menthane (*cis* and *trans*) and 1-*p*-menthene. From the retention time and mass spectroscopic investigation the presence of *cis* and *trans* diastereomers could be ascertained. The stereochemistry of 1-*p*-menthene was established using specific rotation measurement. The specific rotation value for the starting material (*R*-limonene, 97%) is $[\alpha]_D^{22}$ +113.4 (*c* 2.0, CH$_2$Cl$_2$). Whereas, specific rotation of the product is $[\alpha]_D^{22}$ +103.8 (*c* 2.0, CH$_2$Cl$_2$), which matches with that of the *R* isomer of 1-*p*-menthene (87.9 % calculated from GC). Thus, the stereochemistry of the chiral center was preserved.

Table 2 entry 19 GC-MS plot
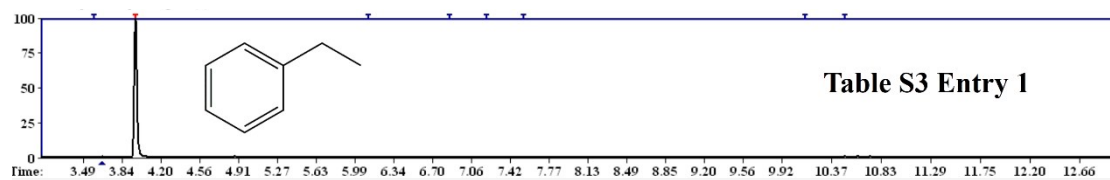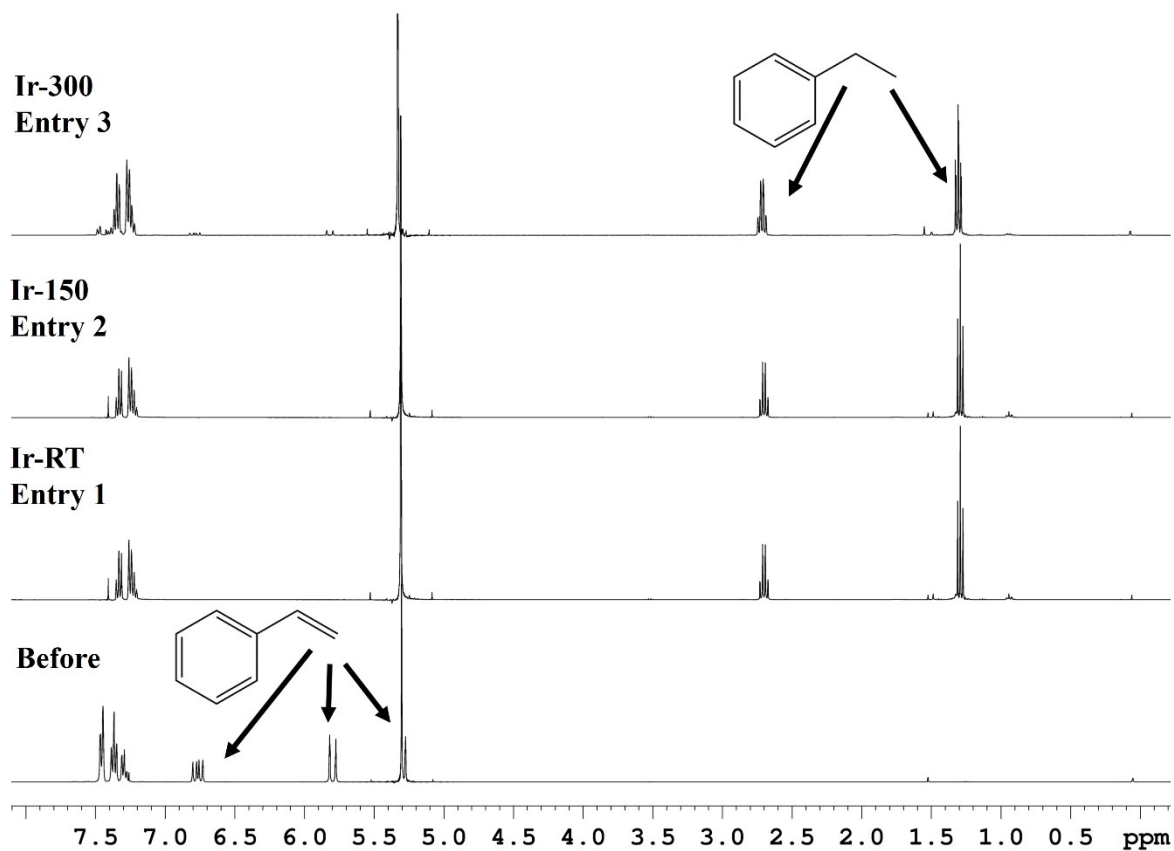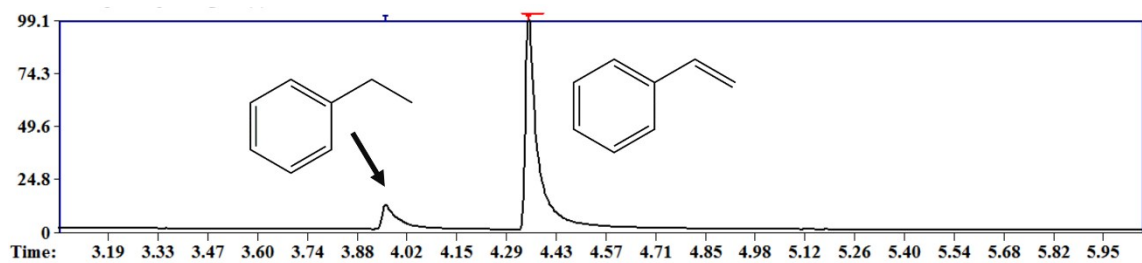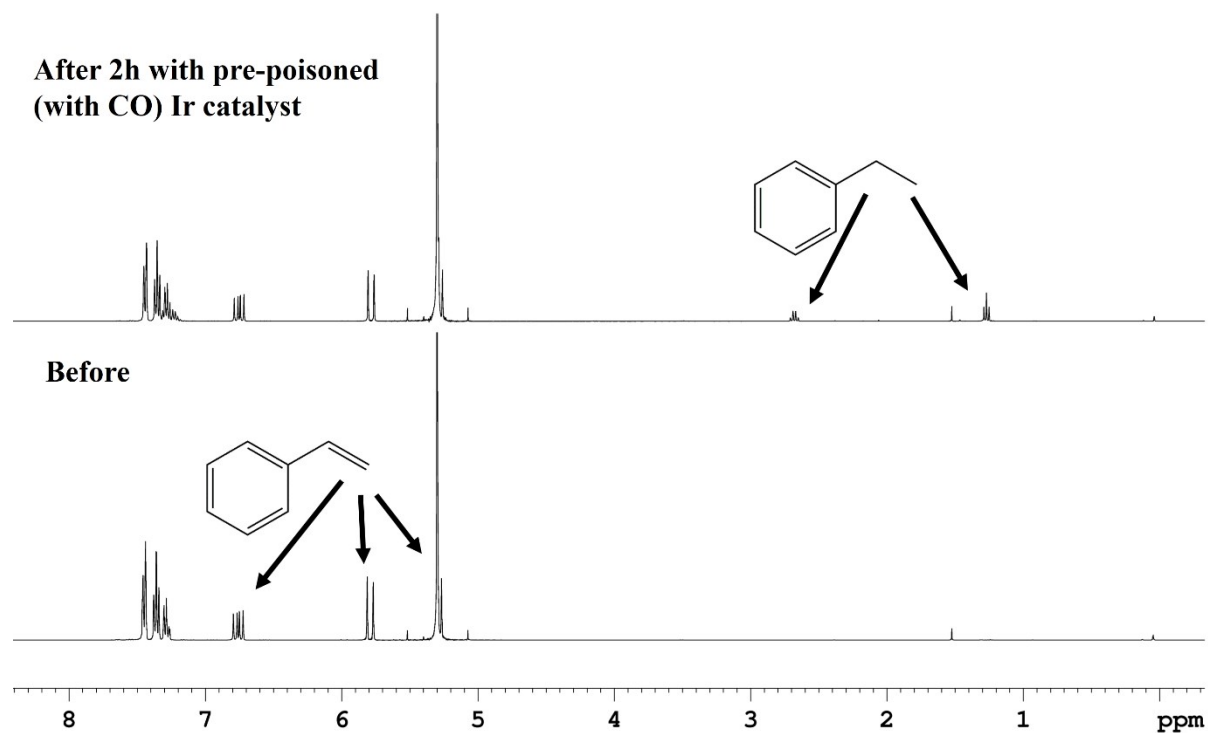
Catalyst recyclability test
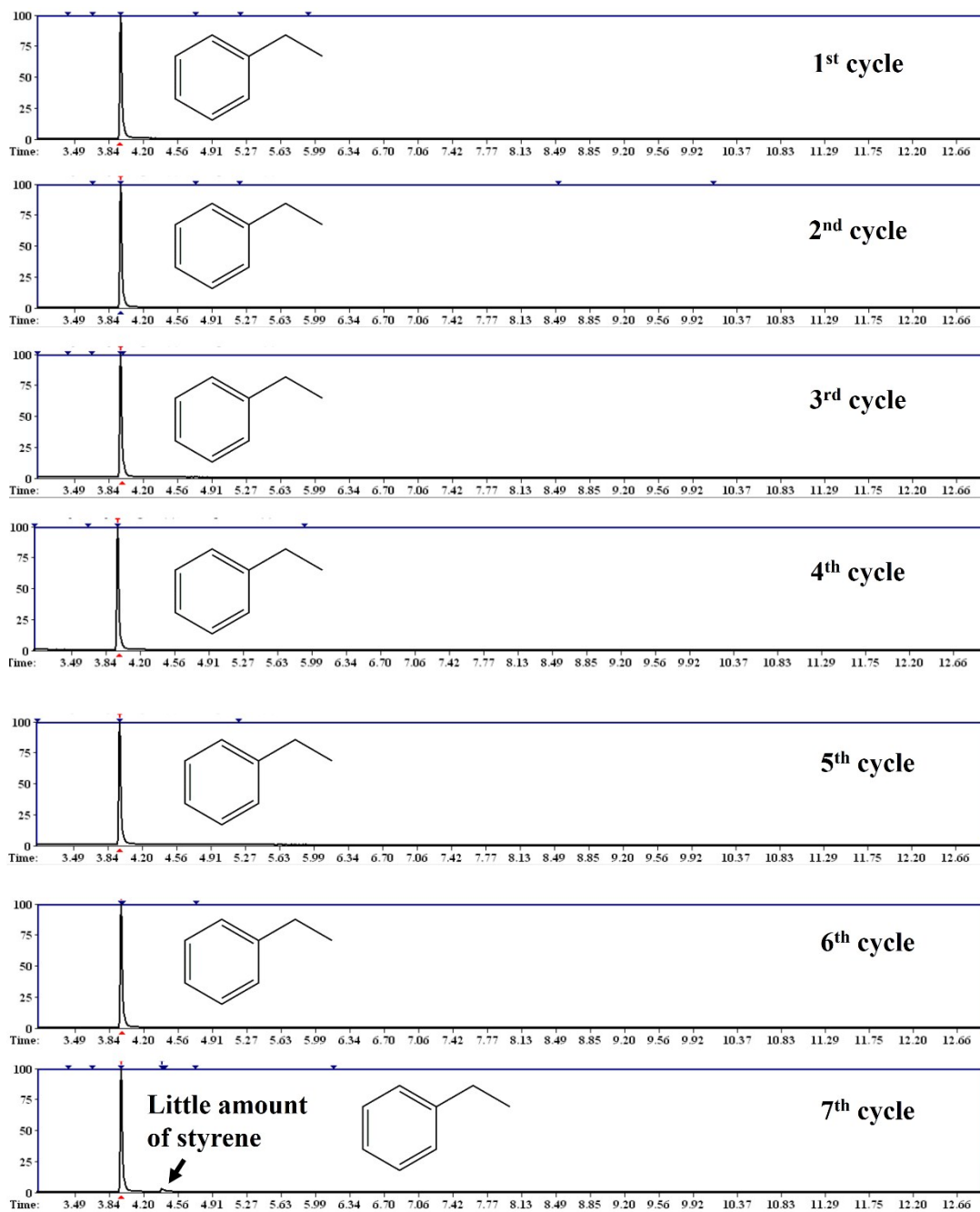
Table S3 (hydrogenation of styrene using annealed iridium nanosponges)
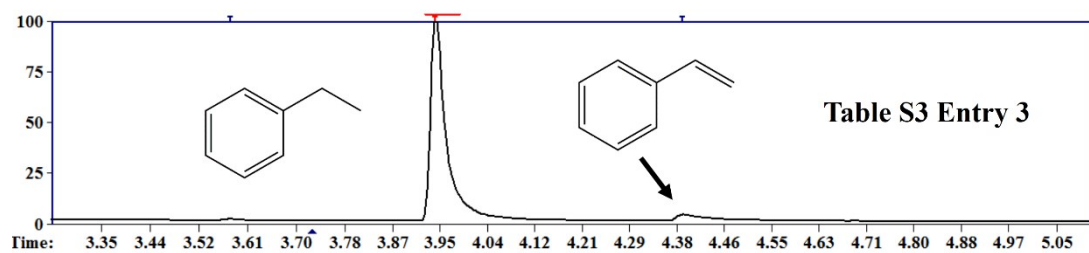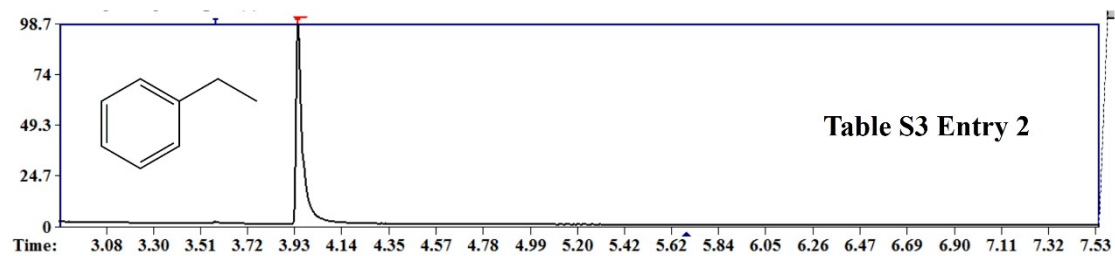
Catalyst poisoning experiment with CO

Hydrogenation of styrene using pre-poisoned iridium catalyst

Hydrogenation of styrene using post-poisoned iridium catalyst (with CO) after 1ˢᵗ step

2ⁿᵈ step - post-poisoned (with CO) Ir catalyst after 1ˢᵗ step then reaction carried out for 2 h

After 1 h 40 min – 1ˢᵗ step

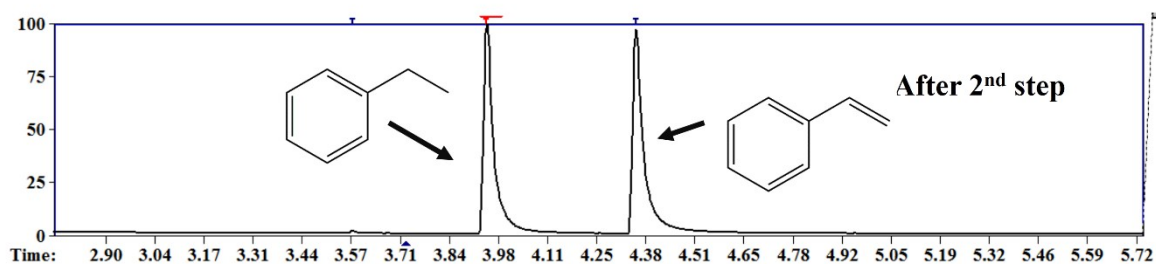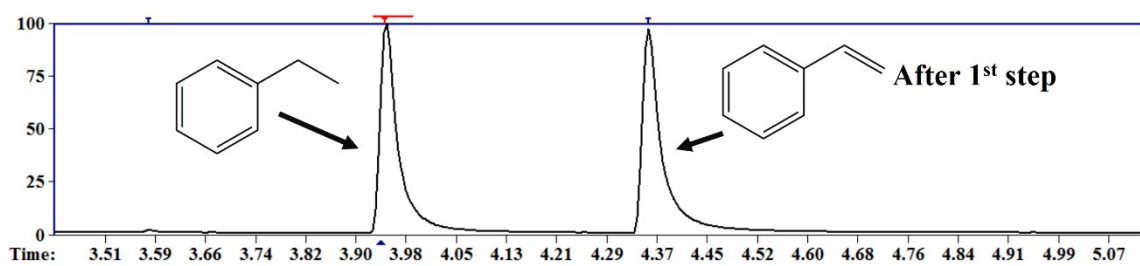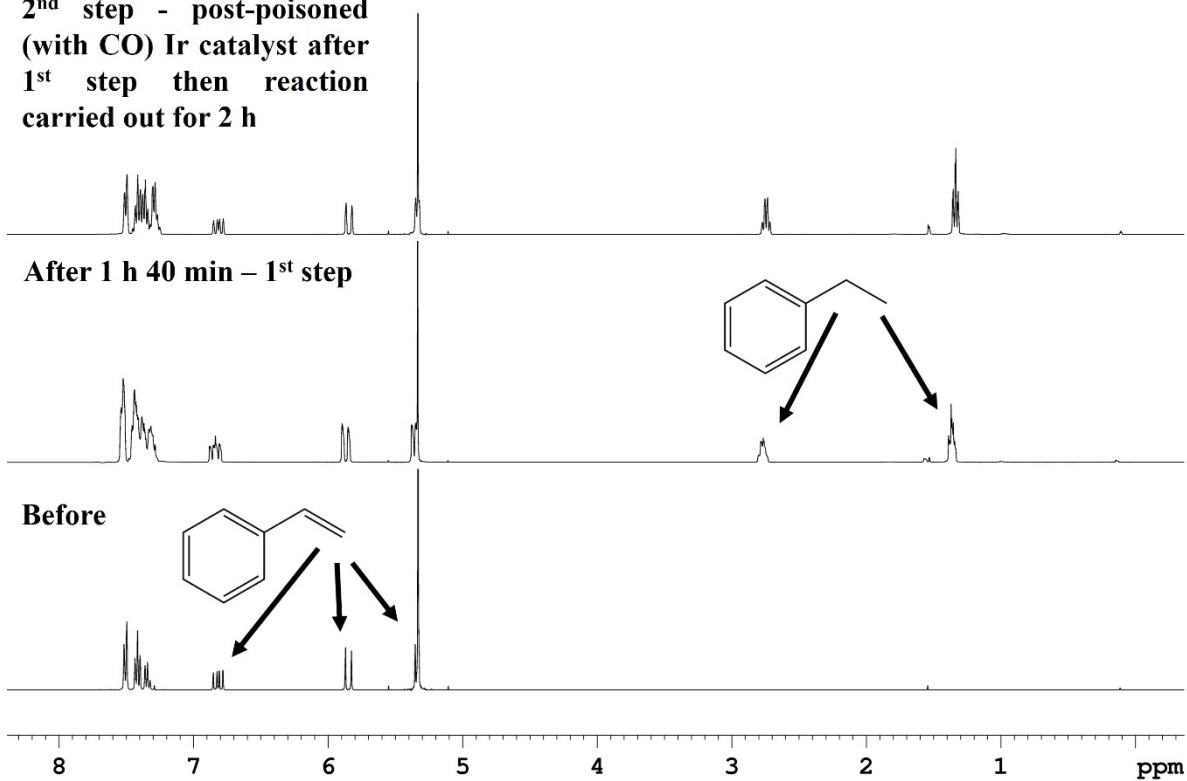**Before**

After 1ˢᵗ step

After 2ⁿᵈ step

Table S4 (hydrogenation styrene with iridium nanosponges synthesized from different precursors)
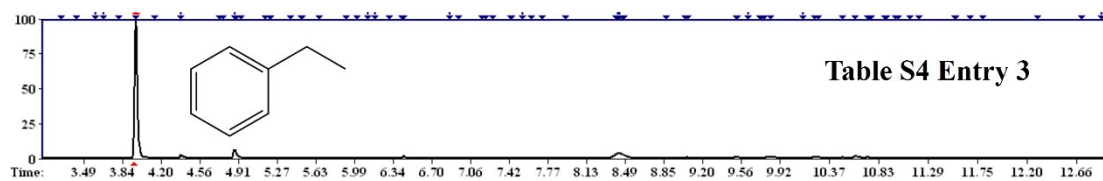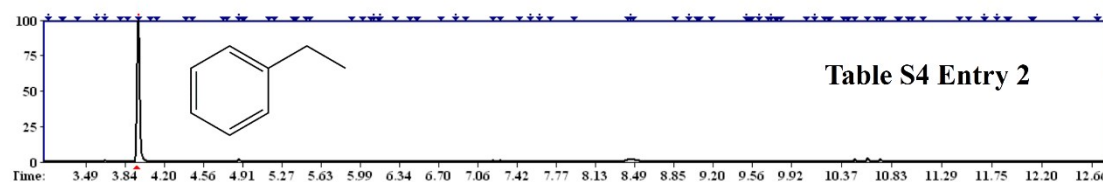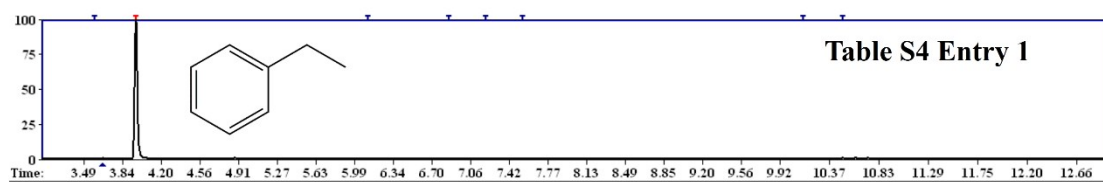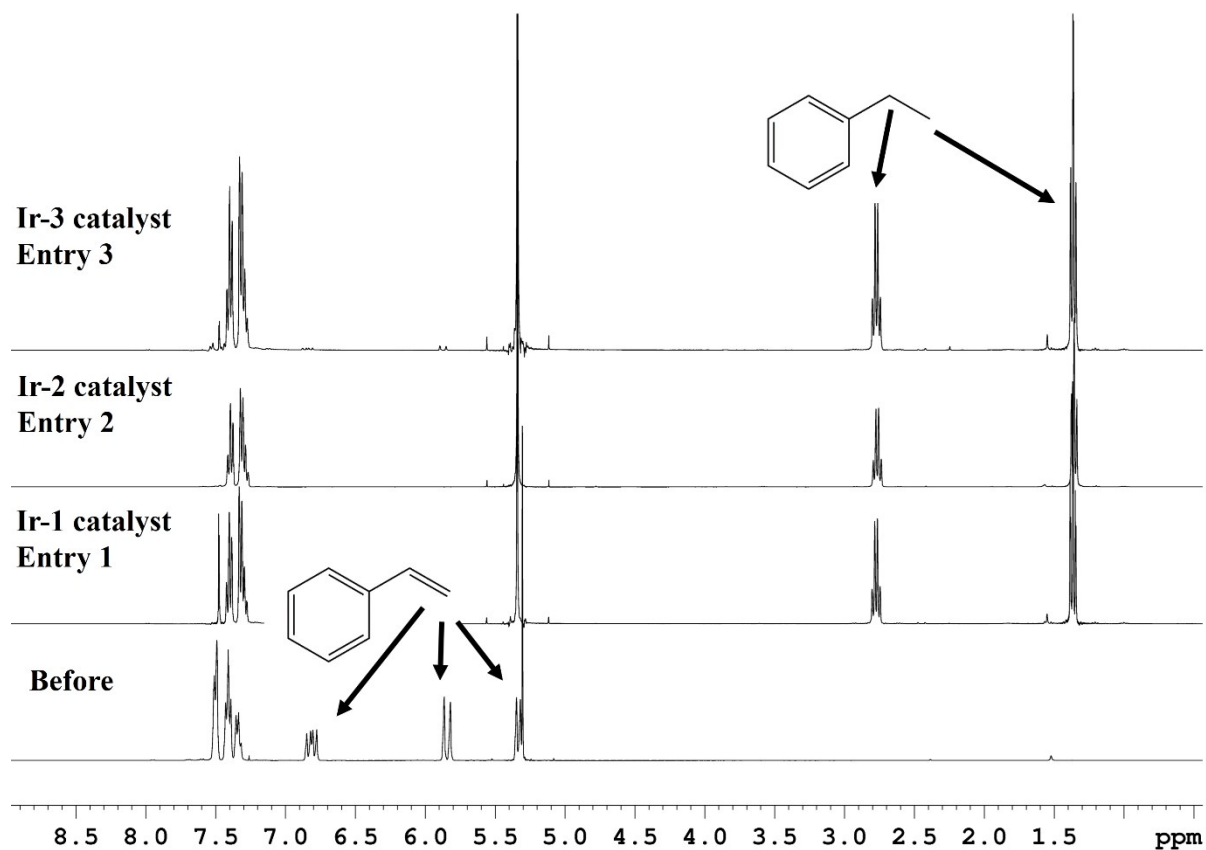
Table S4. Hydrogenation of styrene performed for 1 h using iridium nanosponge synthesized from different iridium precursors

Entry	Styrene/catalyst	Catalyst	Ratio of styrene to ethyl benzene[a]
1	2000	Ir from H_2IrCl_6	53.6:46.4
3	2000	Ir from $IrCl_3.xH_2O$	53.9:46.1
5	2000	Ir from $[Ir(COD)Cl]_2$	53.4:46.4

All reactions were carried out at 4 bar hydrogen gas pressure and at 30 °C in CH_2Cl_2 for 1 h; [a]conversion was determined by GC/MS analysis.
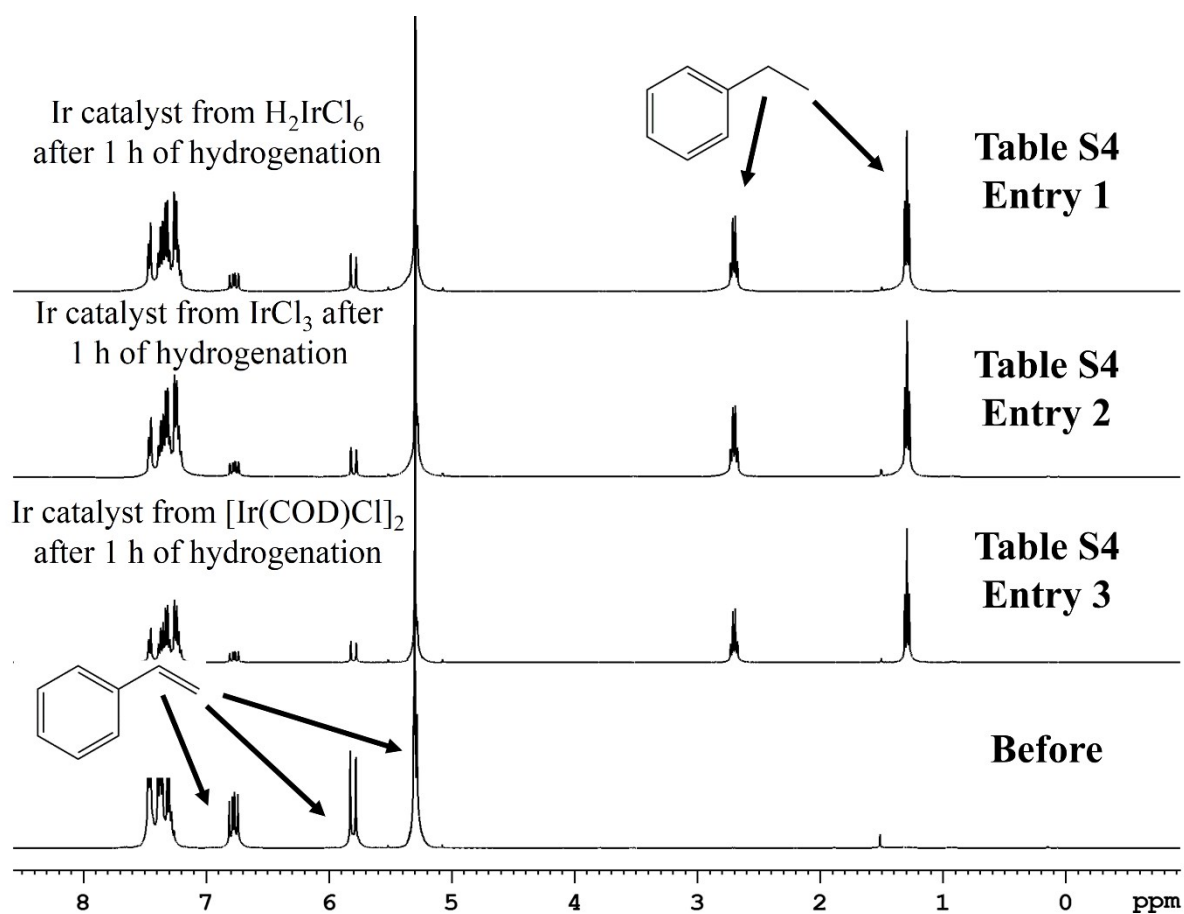
Table S4 ^{1}H-NMR stack plot

Table S4 GC stack plot