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

Supplementary Material

Aqueous Phase Semihydrogenation of Alkynes over Ni-Fe Bimetallic catalysts

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SI-1. Chemicals and Materials

Polyvinylpyrrolidone (PVP ~ 40,000 mwt, Sigma-Aldrich, 99%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 98%), $FeSO_4 \cdot 7H_2O$, and sodium borohydride were purchased from Alfa Aesar. All chemicals were of analytical grade and used without further purification. Substrates **1a, 1f, 1m and 1n** are commercially available. Remaining substrates was prepared according to the literature procedures.

SI-2. Characterization and physical measurements

High purity metal salts and chemicals were used for the experiments. NMR spectra were recorded with a Bruker Avance 400 (400 MHz and 600 MHz) spectrometer. Chemical shifts are reported in ppm relative to the center of the singlet at $\delta = 7.26$ ppm for $CDCl_3$, ^{13}C NMR in $CDCl_3$ at the center of triplet at $\delta = 77.0$ ppm. Powder X-ray diffraction (XRD) measurements were per-formed on a Bruker D8 Advance reflection diffractometer equipped with a LynxEye energy-discriminating position-sensitive detector (1D-PSD) using Cu $K\alpha1+2$ radiation. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were recorded by using a Carl Zeiss Supra-55 scanning electron microscope and an EDS Oxford instruments model X-Max, energy-dispersive X-ray spectrometer (Au-sputtered samples were used). High resolution transmission electron microscopy (HR-TEM) images were obtained by using a JEM-1400 microscope (JEOL) and Titan Themis-Z microscope from Thermo-Fisher Scientific by operating it at the accelerating voltage of 300 kV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo-Electron 3580 instrument and ARCOS (Spectro, Kleve, Germany). For ICP-OES analysis, 5 mg catalysts were digested overnight in 7 mL of aqua regia solution. Further, the digested solution was diluted to 20 mL using deionized water and the solution was analyzed using ICP-OES. ICP-OES analysis technique has a detection limit of 0.01 PPM. Before the ICP analysis, the synthesized catalysts were washed with copious amount of deionized water and ethanol to remove any unreacted metal salts and other impurities. After washing, catalysts were dried in vacuum oven for overnight. The dynamic light scattering (DLS) studies were performed in water-ethanol mixture on a Micromeritics Nanoplus 3 instrument. GC-MS analysis was performed on a Shimadzu GCMS-QP2010 Ultra and GC-2010 Plus system in EI (electron impact) mode using Rtx5MS column, and an Agilent 7890A series instrument coupled with an Agilent 5975C Series instrument equipped with a column HP-5MS. H_2-TPD were obtained on AutoChem II 2920 apparatus from Micromeritics equipped with Cirrus 2 mass spectrometry.

SI-3. Preparation of catalysts

Syntheses of Ni_1Fe_1, Ni_3Fe_1 and Ni_1Fe_3 catalysts

Bimetallic Ni-Fe catalysts with different Ni/Fe molar ratio were synthesized using polyvinylpyrrolidone (PVP) stabilized aqueous phase co-reduction process.[S1] Typically, 0.012 g of $NiCl_2 \cdot 6H_2O$ and 0.042 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 5 mL of distilled water containing 0.100 g of PVP and sonicated for 5 min. An aqueous solution of sodium borohydride (5 mL, 0.050 g) was added drop wise to the above mixture and sonicated again for 5 min to obtain a black suspension of Ni_1Fe_3 catalyst, which was magnetically separated out under inert gas protection using a Schlenk line, and washed with copious amount of deionized water and ethanol. Analogously, Ni_1Fe_1 and Ni_3Fe_1 catalysts along with the monometallic Ni and Fe catalysts were also synthesized. It should be noted that all catalysts were magnetically separated out under inert gas protection in a Schlenk line except Ni catalyst, which is separated out by centrifugation at 5000 rpm for 10 min. For characterization, washed catalysts were dried in vacuum and then used for SEM, TEM, EDX, powder XRD, XPS, H_2-TPD and ICP-OES analyses.

Synthesis of Ni/Fe_3O_4 catalyst. In round bottom flask, Fe_3O_4 magnetic nanoparticles (0.0173 g), $NiCl_2 \cdot 6H_2O$ (0.006 g) and PVP (0.0125 g) were dispersed in water (5 mL). An aqueous solution of sodium borohydride (5 mL, 0.0125 g) was added drop wise to the above mixture and sonicated for 5 min to obtain the black suspension of Ni/Fe_3O_4. The obtained solid was magnetically separated and washed with ethanol.

Bulk scale synthesis of Ni_1Fe_3 catalysts

Typically, 0.12 g of $NiCl_2 \cdot 6H_2O$ and 0.42 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 50 mL of distilled water containing 1.0 g of PVP and sonicated for 10 min. An aqueous solution of sodium borohydride (50 mL, 0.50 g) was added drop wise to the above mixture and sonicated again for 10 min to obtain a black suspension of Ni_1Fe_3 catalyst, which was magnetically separated out under inert gas protection in a Schlenk line and washed with copious amount of deionized water and ethanol.[S1]

SI-4. Catalytic semihydrogenation of alkynes

Reaction flask was charged with the freshly prepared catalyst (10.0 mol%) dispersed in water/ethanol (20 mL, 1:1 v/v), and was purged with N_2 gas. After that alkynes (1.0 mmol) and *n*-butyl amine (0.55 mmol) was added in the solution and the reaction mixture was stirred at 40 °C equipped with a H_2 balloon. After completion of the reaction, catalyst was magnetically separated from the reaction mixture. The reaction mixture was extracted with dichloromethane (3 × 5 mL), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Products were characterized by ^1H NMR, ^{13}C NMR and GC-MS.

General procedure for the synthesis of alkynes

For the synthesis of different internal alkynes, we followed previously reported procedure with minor modification.[S2,S3] In general, a dry round bottle flask was charged with the corresponding aryl iodide (5 equiv.), CuI (1-2 mol%), $PdCl_2(PPh_3)_2$ (1-2 mol%), PPh_3 (1-2 mol%), phenylacetylene (5.5 equiv.) and triethylamine (10 mL) in dry THF (10 mL). Reaction mixture was flushed thrice with N_2 gas and stirred overnight at 70 °C under N_2 atmosphere. After completion of the reaction, 10 mL of deionized water was added to the reaction mixture and was extracted with ethyl acetate (5 × 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and all the volatiles were removed under reduced pressure. The obtained crude products were purified by column chromatography using ethyl acetate and hexane as the eluent. ^{1}H NMR and ^{13}C NMR of the obtained products matches well with the reported literature data.[S2-S5]

SI-5. Characterization of catalyst

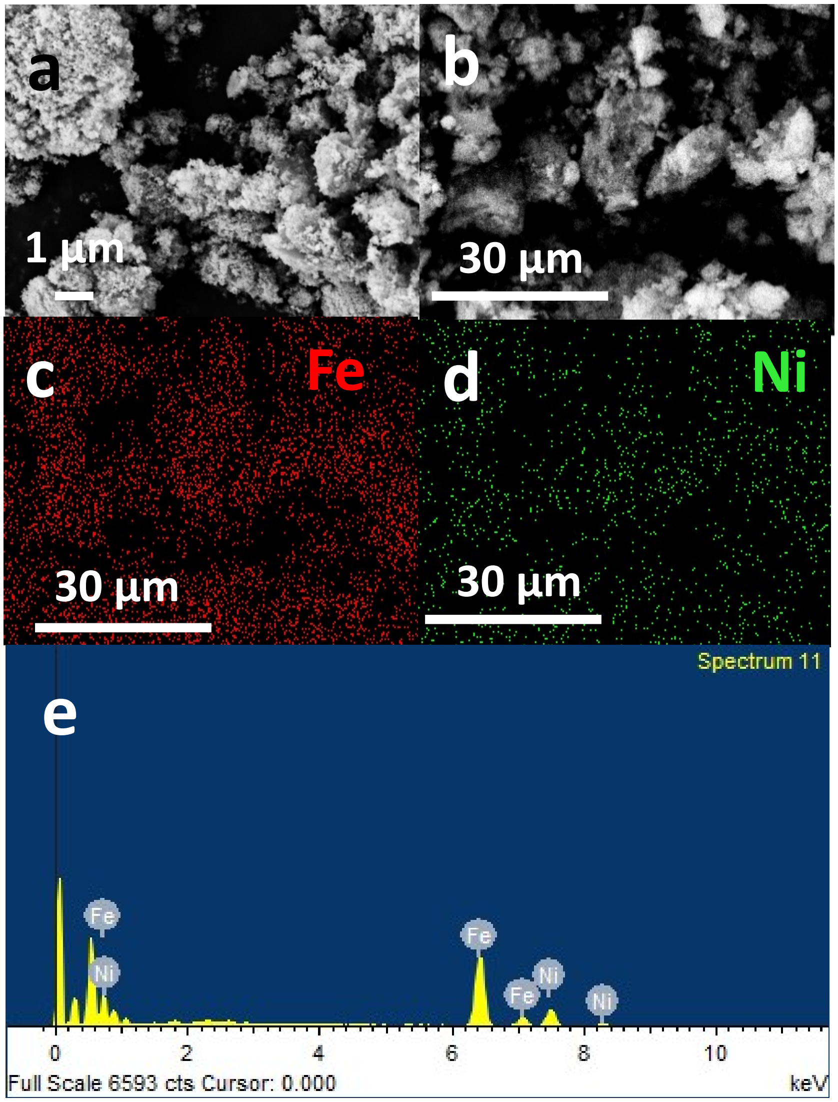


Fig. S1 (a) SEM image, (b-d) SEM image and the corresponding elemental mapping, and (e) SEM-EDS of Ni_1Fe_3 catalyst.

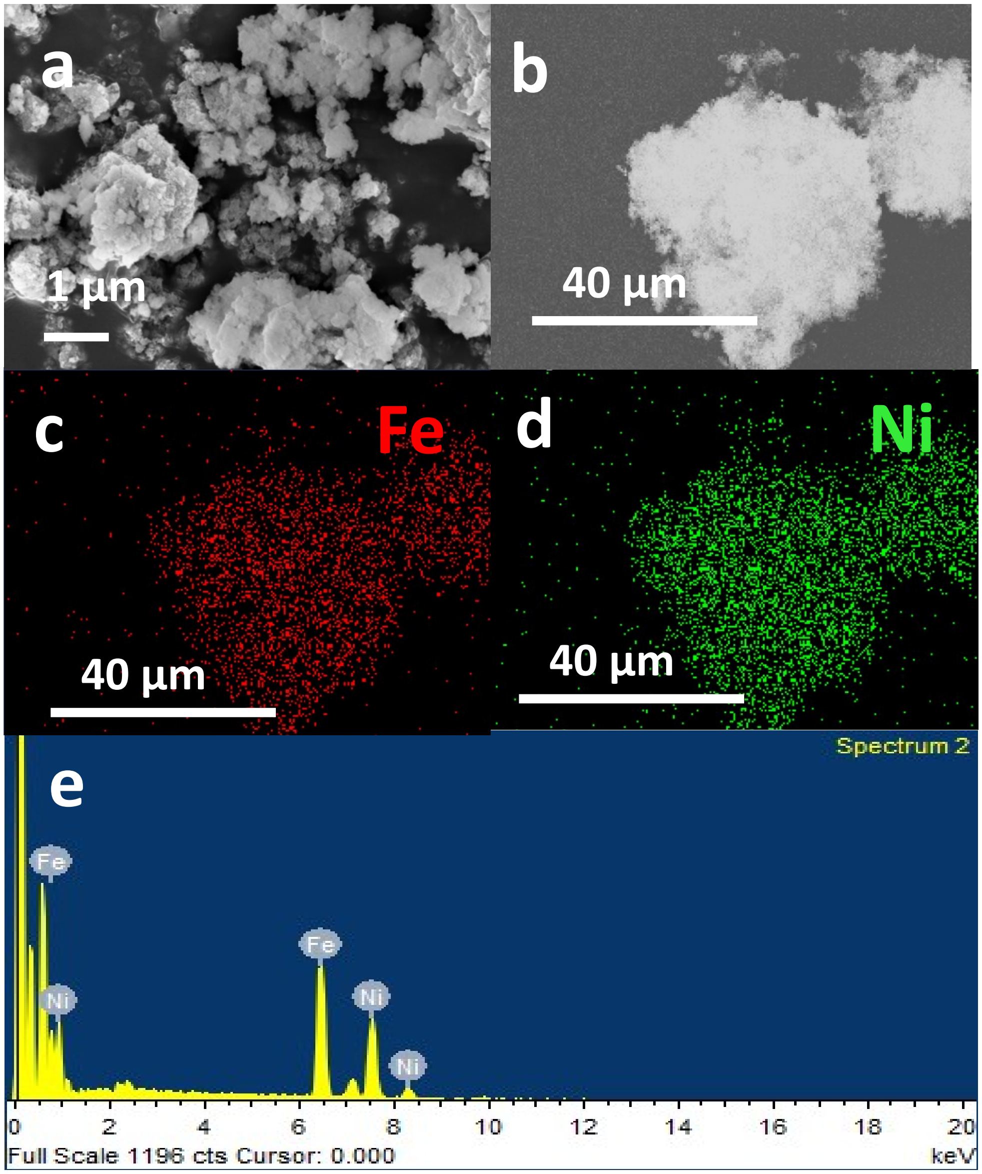


Fig. S2 (a) SEM image, (b-d) SEM image and the corresponding elemental mapping, and (e) SEM-EDS of Ni_1Fe_1 catalyst.

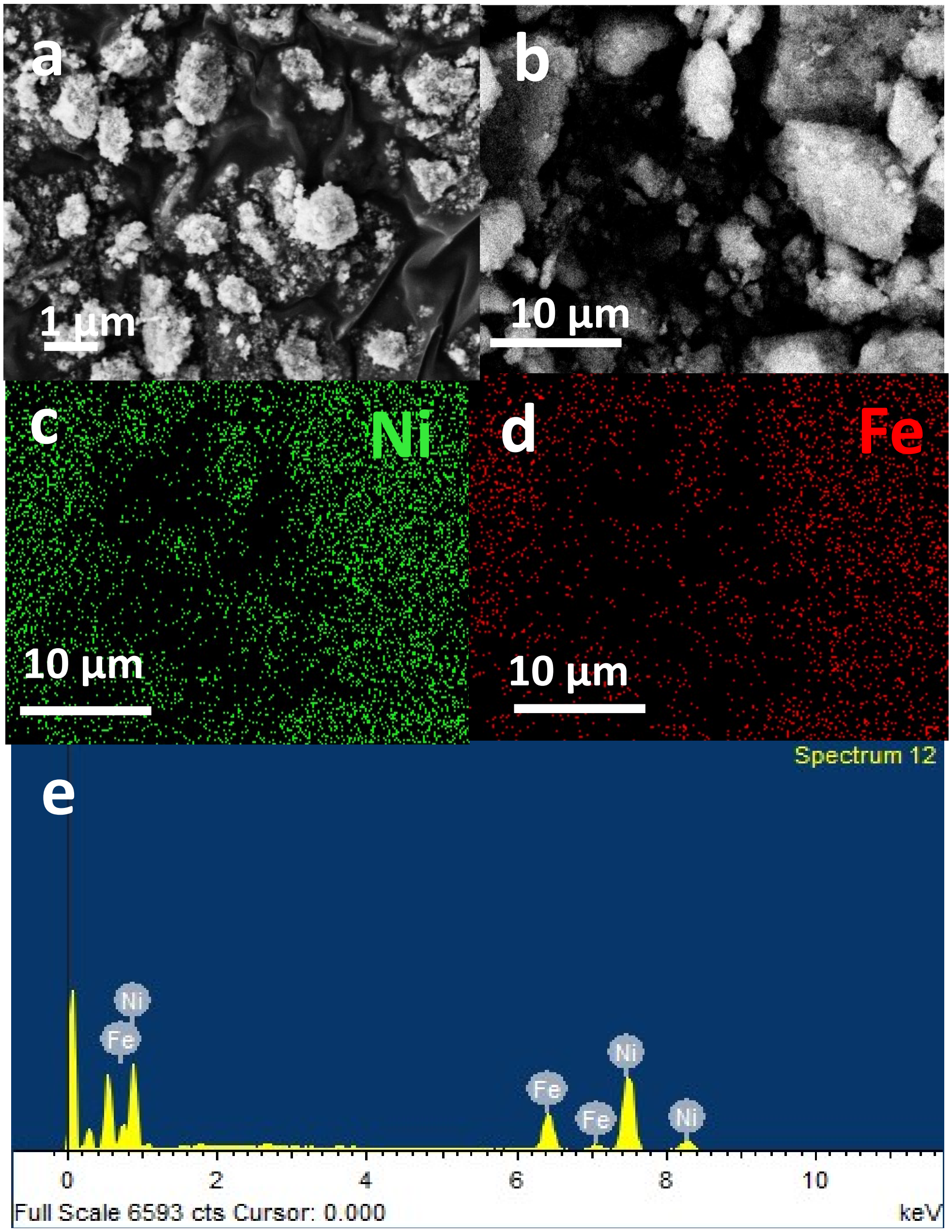


Fig. S3 (a) SEM image, (b-d) SEM image and the corresponding elemental mapping, and (e) SEM-EDS of Ni_3Fe_1 catalyst.

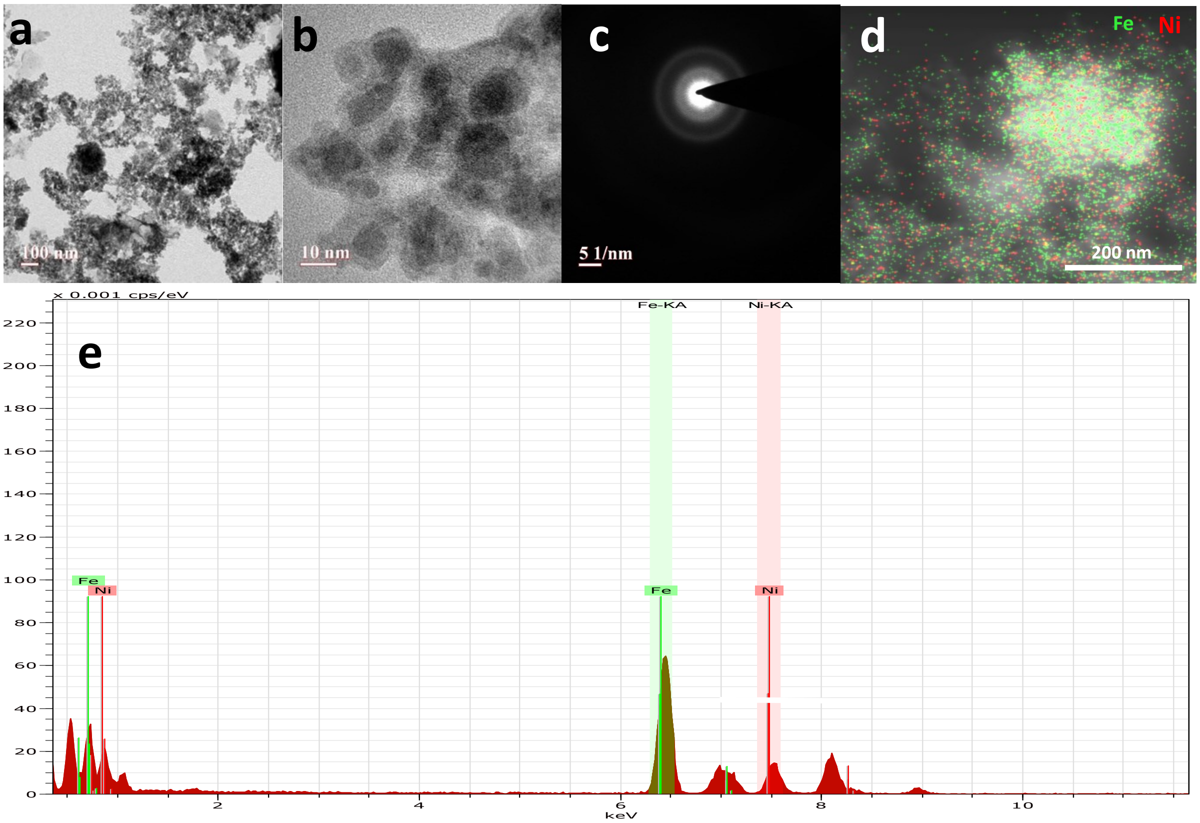


Fig. S4 (a,b) TEM images. (c) SEAD. (d) Overlay image of elemental mapping. (e) TEM-EDS of Ni_1Fe_3 fresh catalyst.

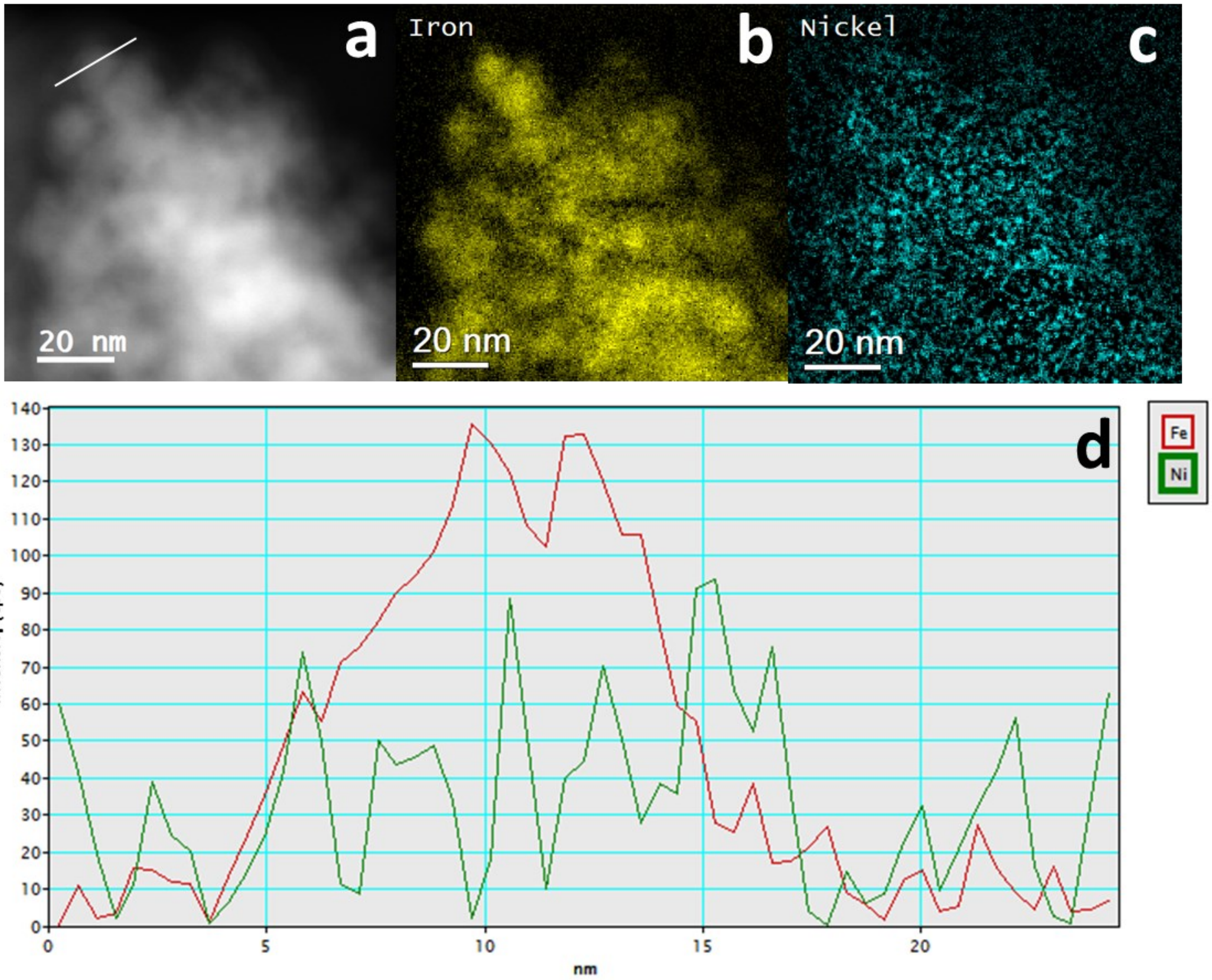


Fig. S5 (a) TEM image and the corresponding (b-c) elemental mapping for Ni and Fe metals, and (d) the line scanning profile of Ni_1Fe_3 catalyst.

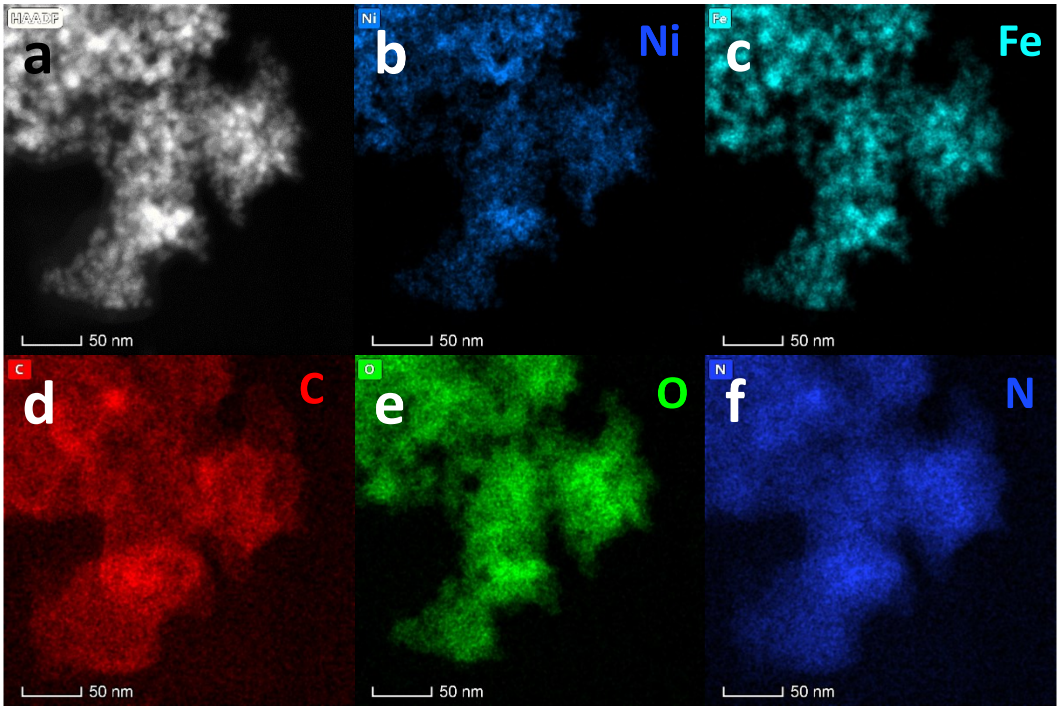


Fig. S6 (a) HAADF-TEM image and the corresponding (b-f) EDS elemental mapping of Ni_1Fe_3 catalyst.

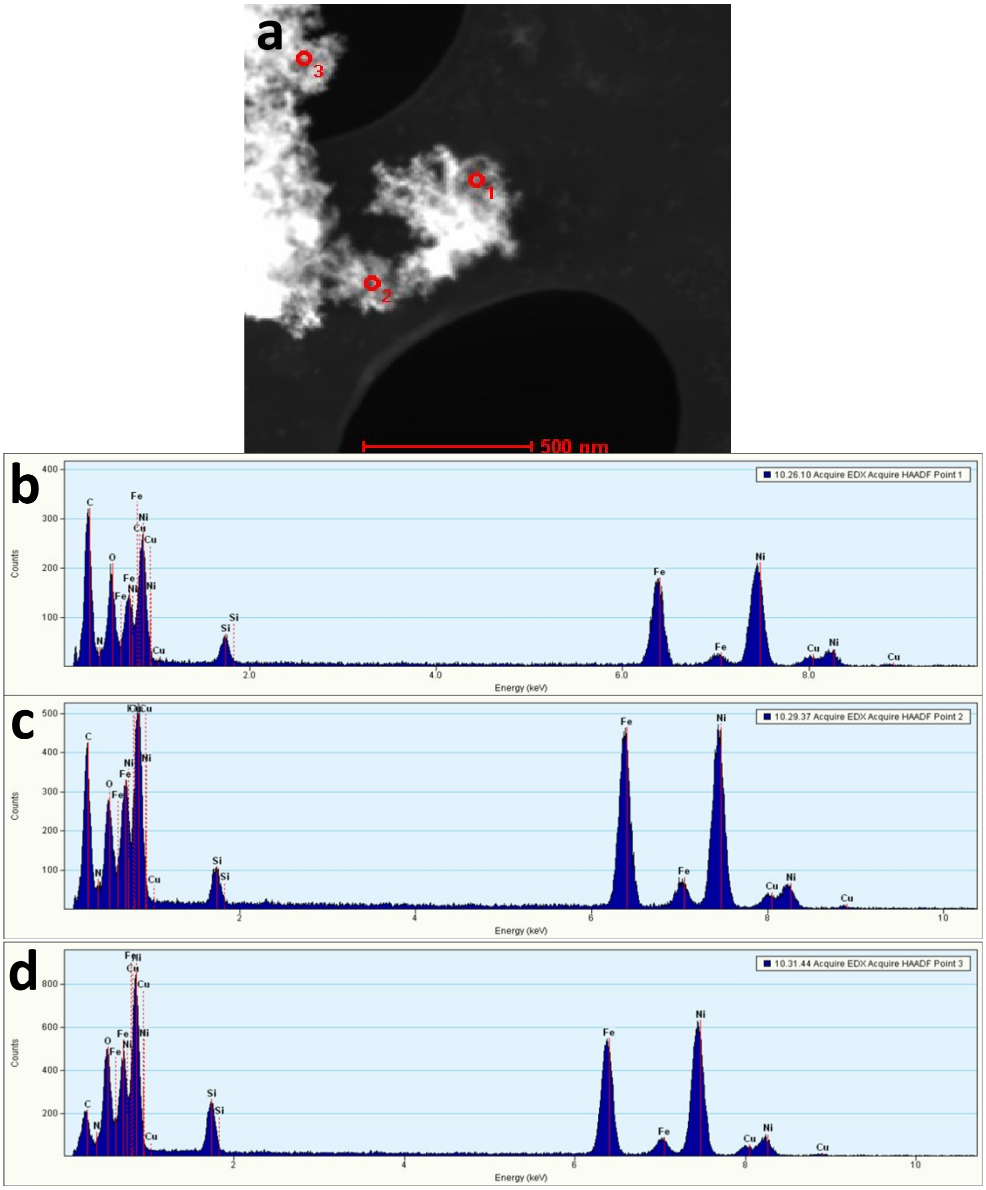


Fig. S7 (a) HAADF-STEM image with the corresponding (b-d) EDS spectra of randomly chosen nanoparticles of Ni_1Fe_1 catalyst.

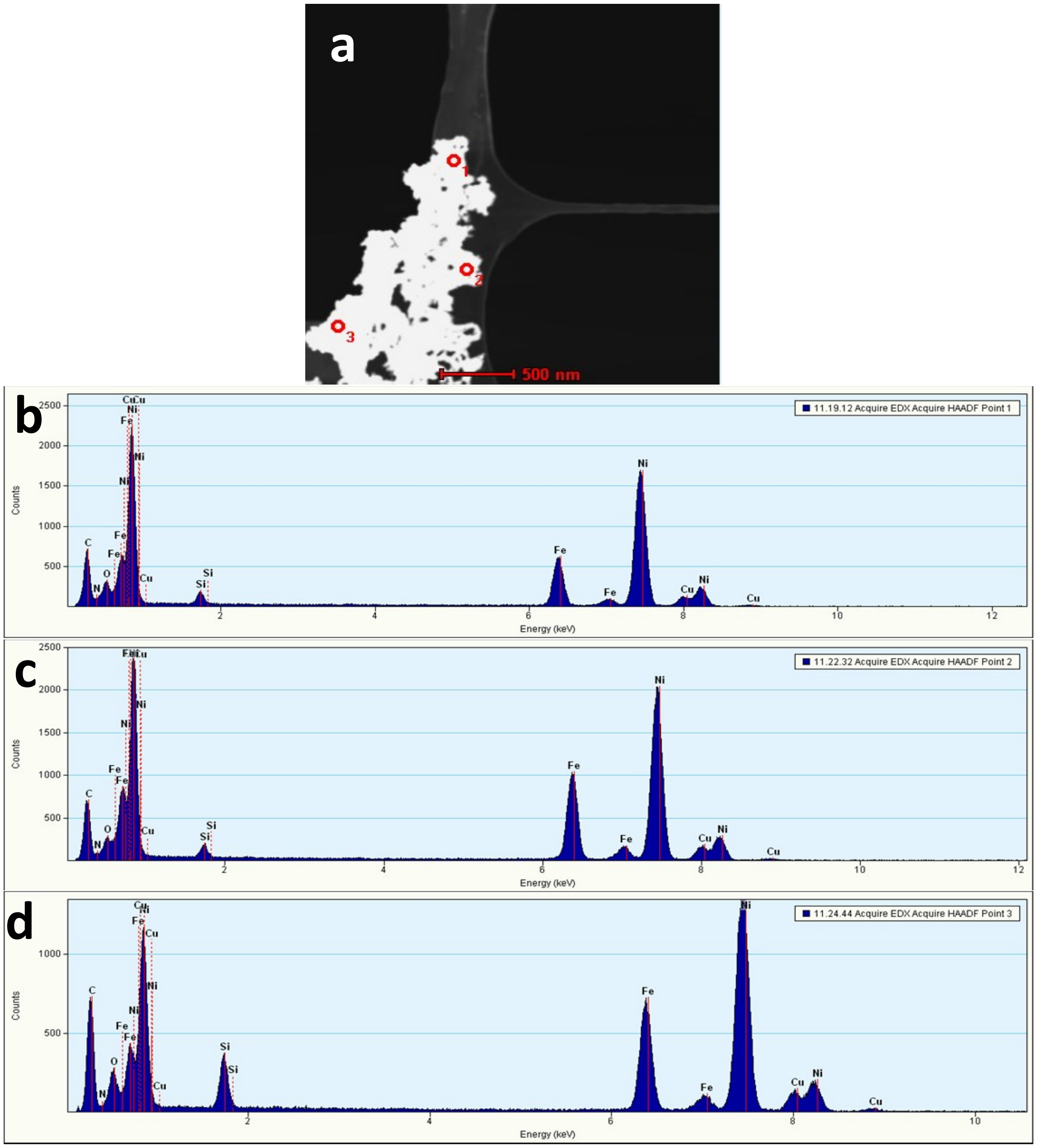


Fig. S8 (a) HAADF-STEM image with the corresponding (b-d) EDS spectra of randomly chosen nanoparticles of Ni_3Fe_1 catalyst.

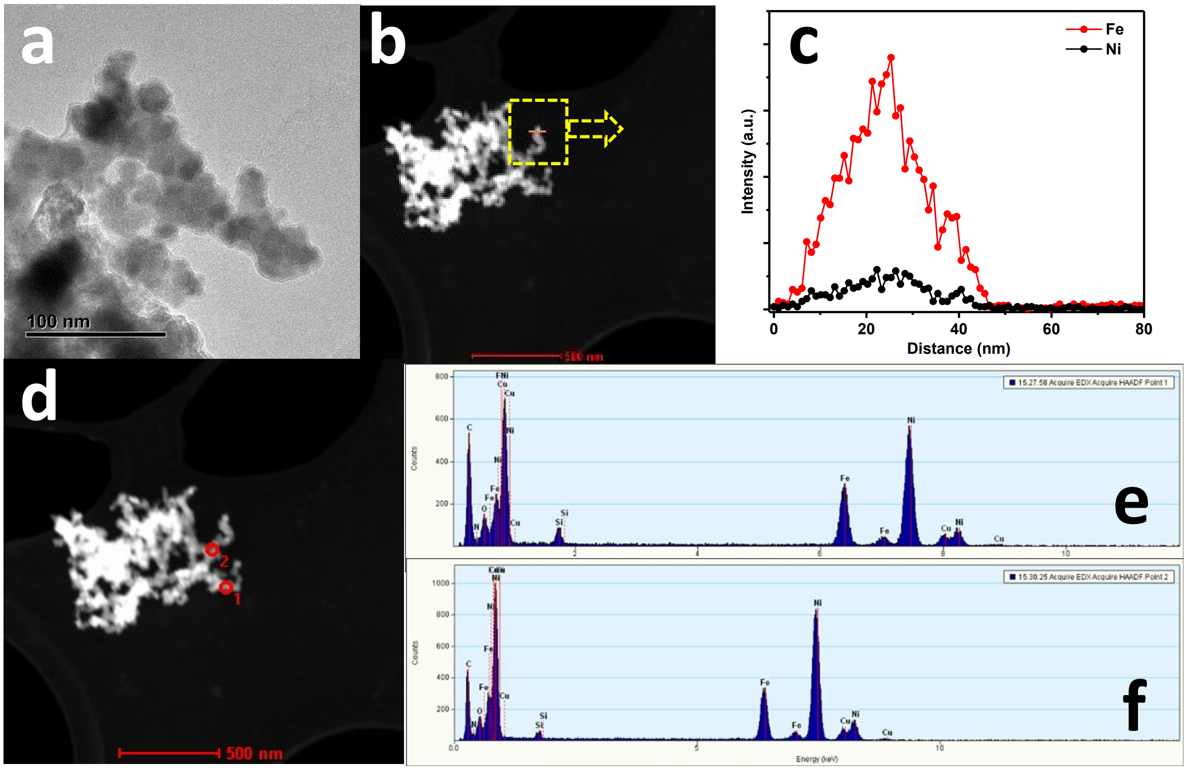


Fig. S9 (a) TEM image. (b) HAADF-STEM image with corresponding (c) EDS line scanning profiles of Ni and Fe and (d-f) EDS spectra of randomly chosen nanoparticles of Ni_1Fe_3 catalyst synthesized without PVP ligand.

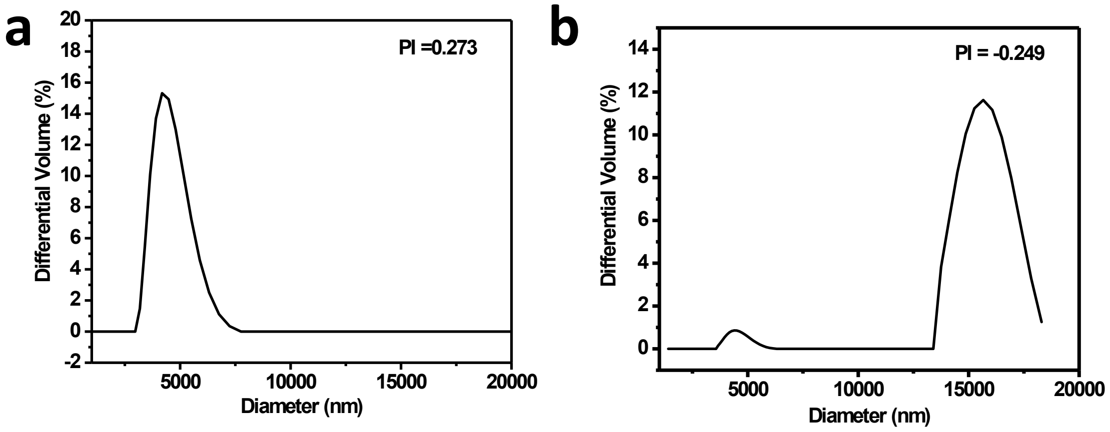


Fig. S10 DLS spectra of Ni_1Fe_3 catalysts synthesized (a) with PVP and (b) without PVP.

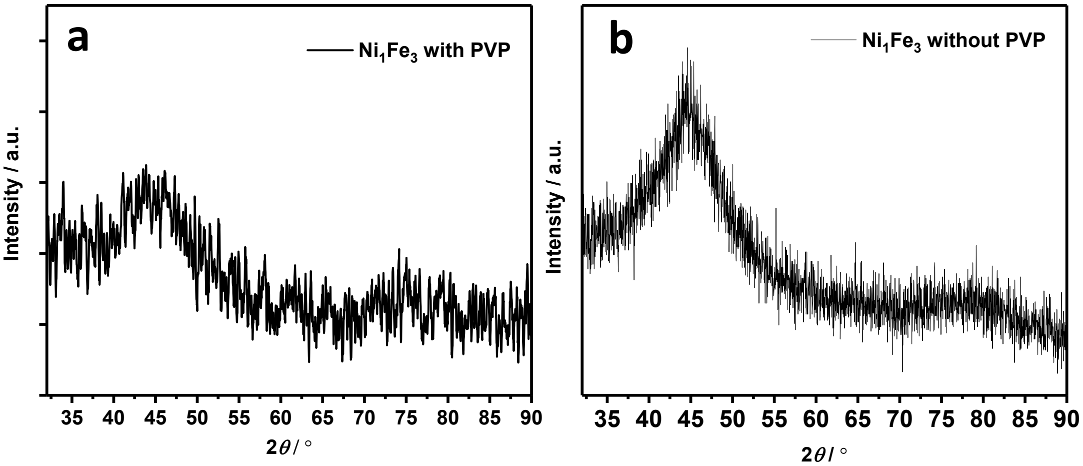


Fig. S11 P-XRD of Ni_1Fe_3 catalyst synthesized (a) with and (b) without PVP.

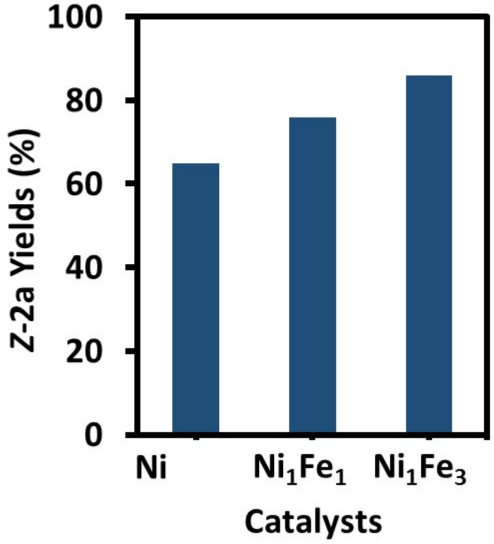


Fig. S12 Catalytic hydrogenation of **1a** to *Z*-**2a**. Reaction conditions: **1a** (1.0 mmol), catalyst (10 mol%), *n*-butyl amine (0.55 mmol) under H_2 atmosphere at 40 °C for 4 h.

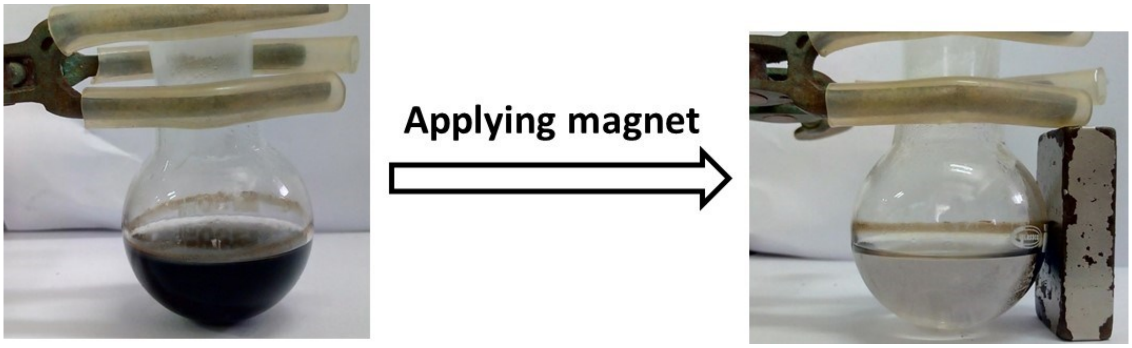


Fig. S13 Magnetic separation of Ni_1Fe_3 catalyst after the catalytic reaction.

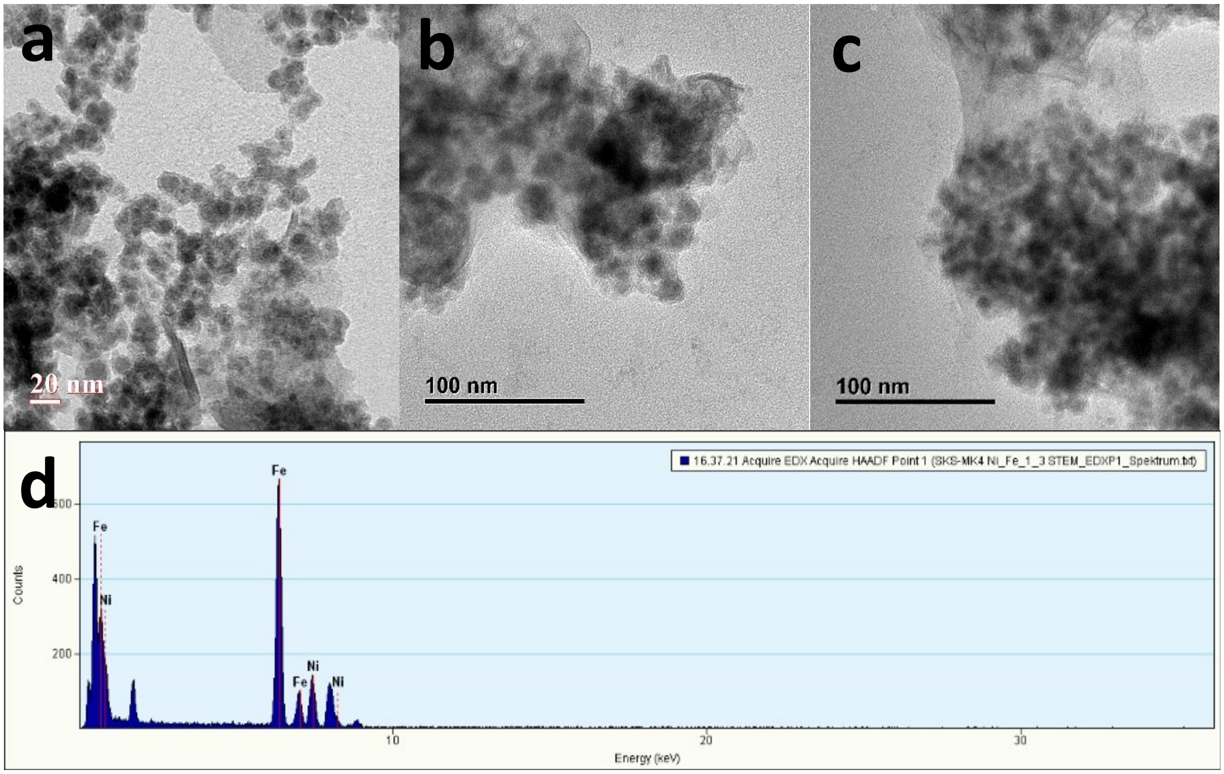


Fig. S14 TEM images of (a) fresh and (b-c) spent Ni_1Fe_3 nanoparticle catalyst. (d) EDS spectra of the spent Ni_1Fe_3 nanoparticle catalyst.

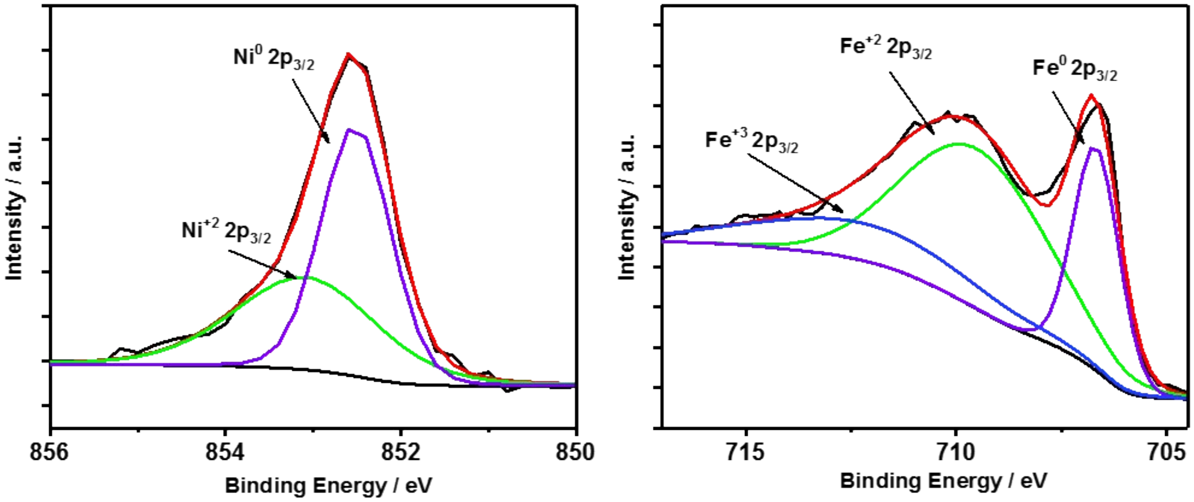


Fig. S15 XPS spectra of Ni_1Fe_3 spent catalysts after reaction.

SI-6. CS_2 poisoning experiment

The aqueous-ethanolic solution (1:1 v/v, 20.0 mL) of Ni_1Fe_3 catalyst (10 mol%) was added CS_2 (0.1, 0.25, 0.5 and 1 equiv. with reference to Ni metal in Ni_1Fe_3), and the reaction mixture was stirred at 40 °C for 1 h under H_2 balloon. Then diphenylacetylene (1.0 mmol) was added, and the reaction mixture was further stirred for 4 h in H_2 atmosphere (using a H_2 balloon) under the optimized reaction conditions. After 4 h of reaction, catalyst was magnetically separated from the reaction mixture. The reaction mixture was extracted with dichloromethane (3 × 5 mL), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Products were characterized by ^1H NMR.

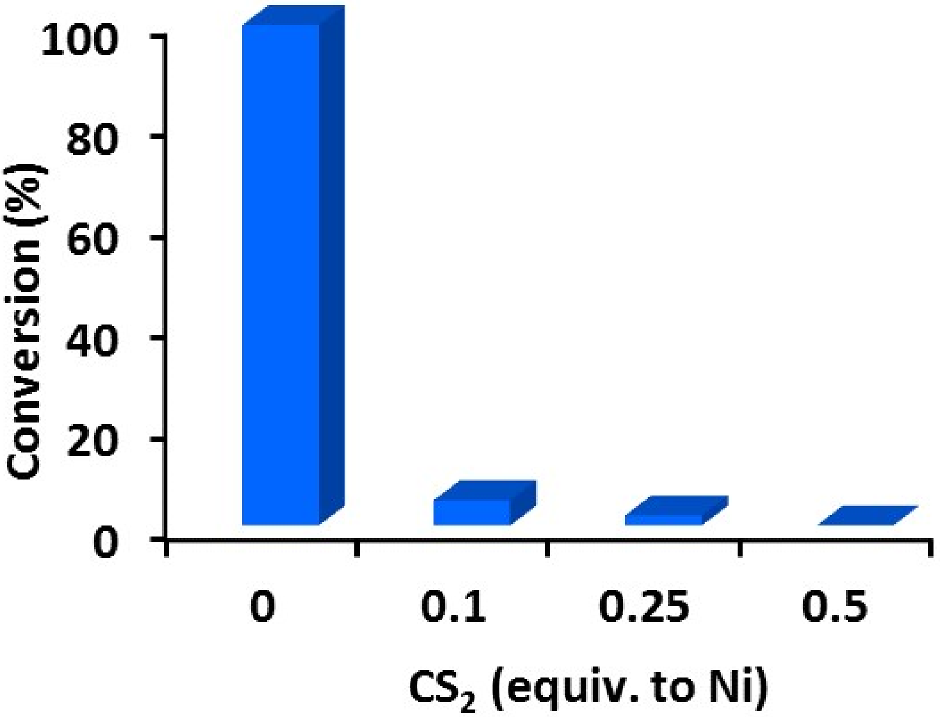
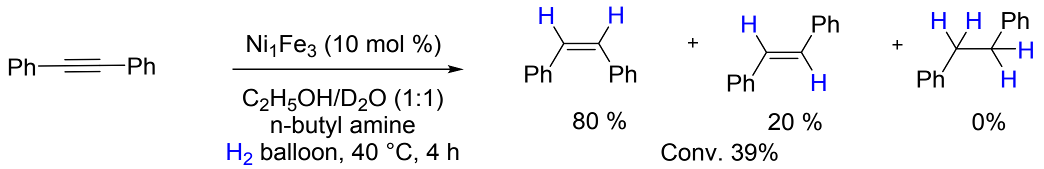


Fig. S16 Heterogeneity test of Ni_1Fe_3 catalyst using varying content of CS_2 poison.

SI-7. Deuterium labeling experiments

Experiment S1: To the fresh catalyst (10 mol%), C_2H_5OH/D_2O (1:1, 2 mL) diphenylacetylene (0.1 mmol) and *n*-butyl amine (0.055 mmol) was added. The reaction mixture was stirred at 40 °C for 4 h under H_2 atmosphere (using a H_2 balloon). After that, liquid aliquot was analyzed by GC-MS.



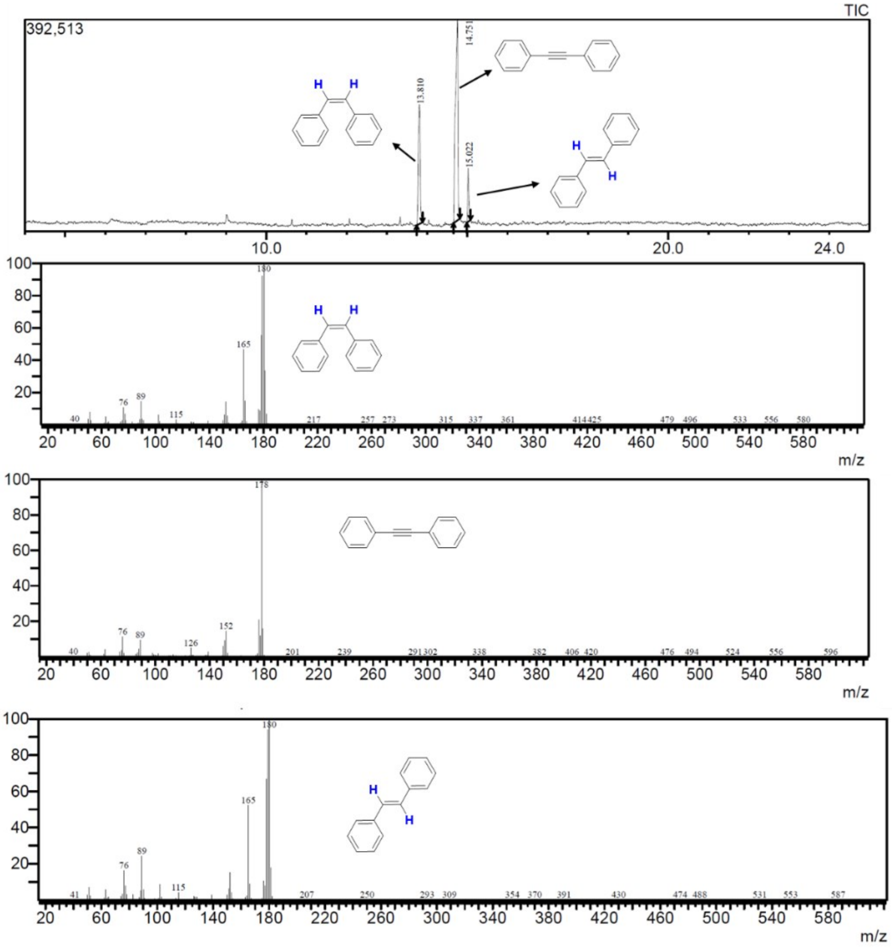
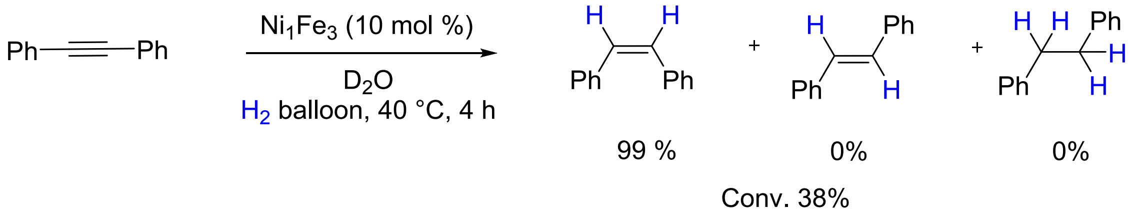


Fig. S17 GC-MS spectra of Deuterium-labeling experiment for the semihydrogenation of diphenylacetylene in presence of C_2H_5OH/D_2O.

Experiment S2: To the fresh Ni_1Fe_3 catalyst (10 mol%), D_2O (2 mL) and diphenylacetylene (0.1 mmol) was added, and the reaction mixture was stirred at 40 °C for 4 h under H_2 atmosphere (using a H_2 balloon). After 4h, the reaction aliquot was analyzed by GC-MS.



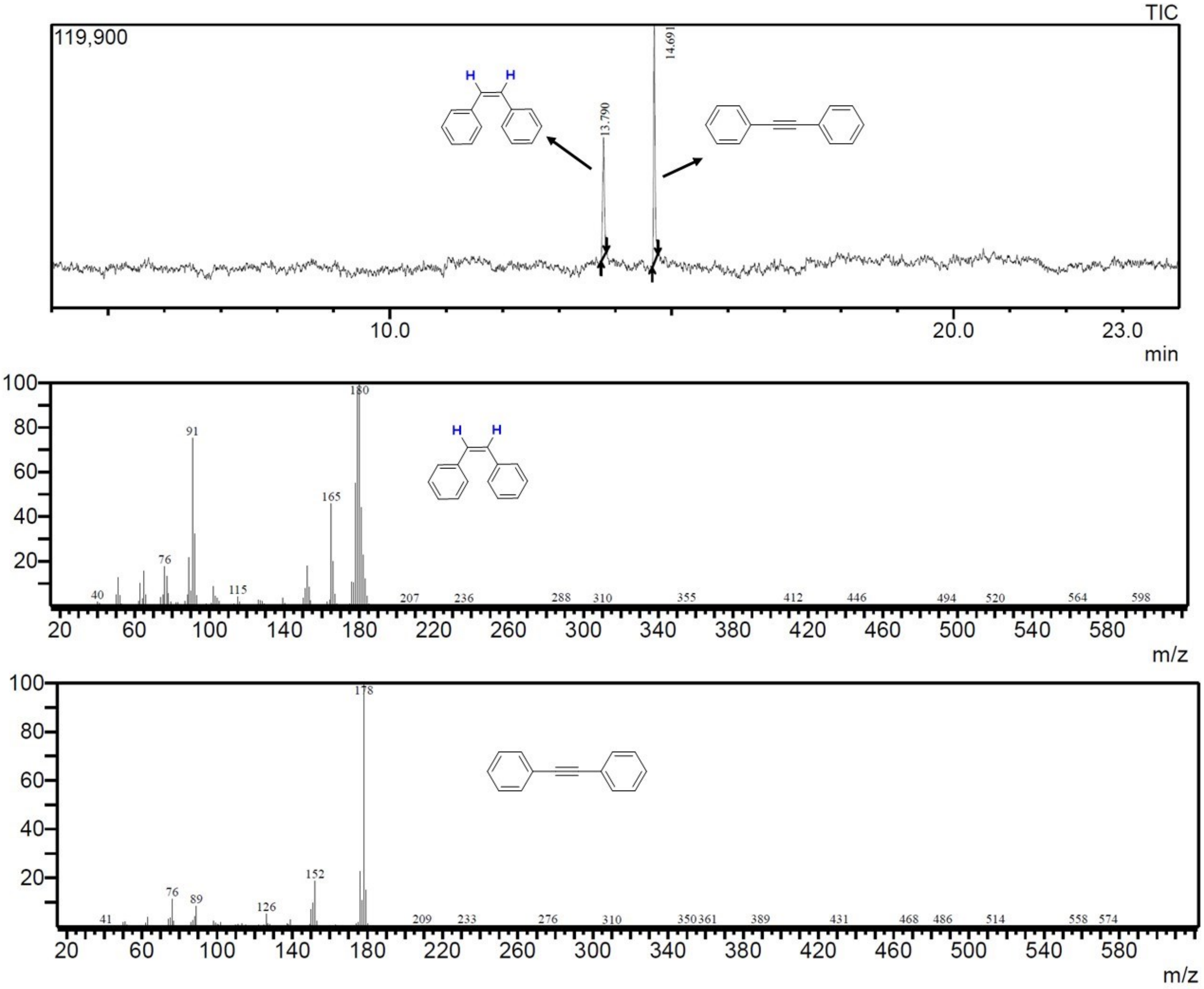
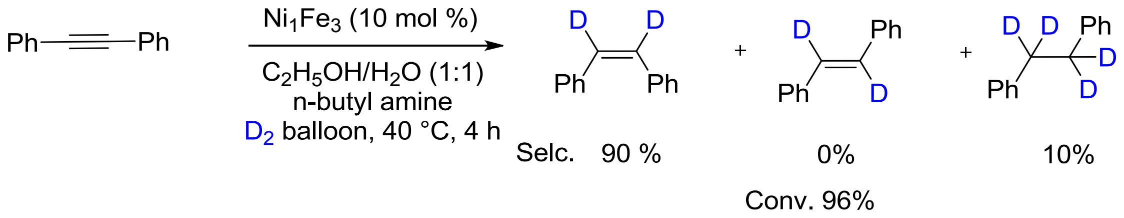
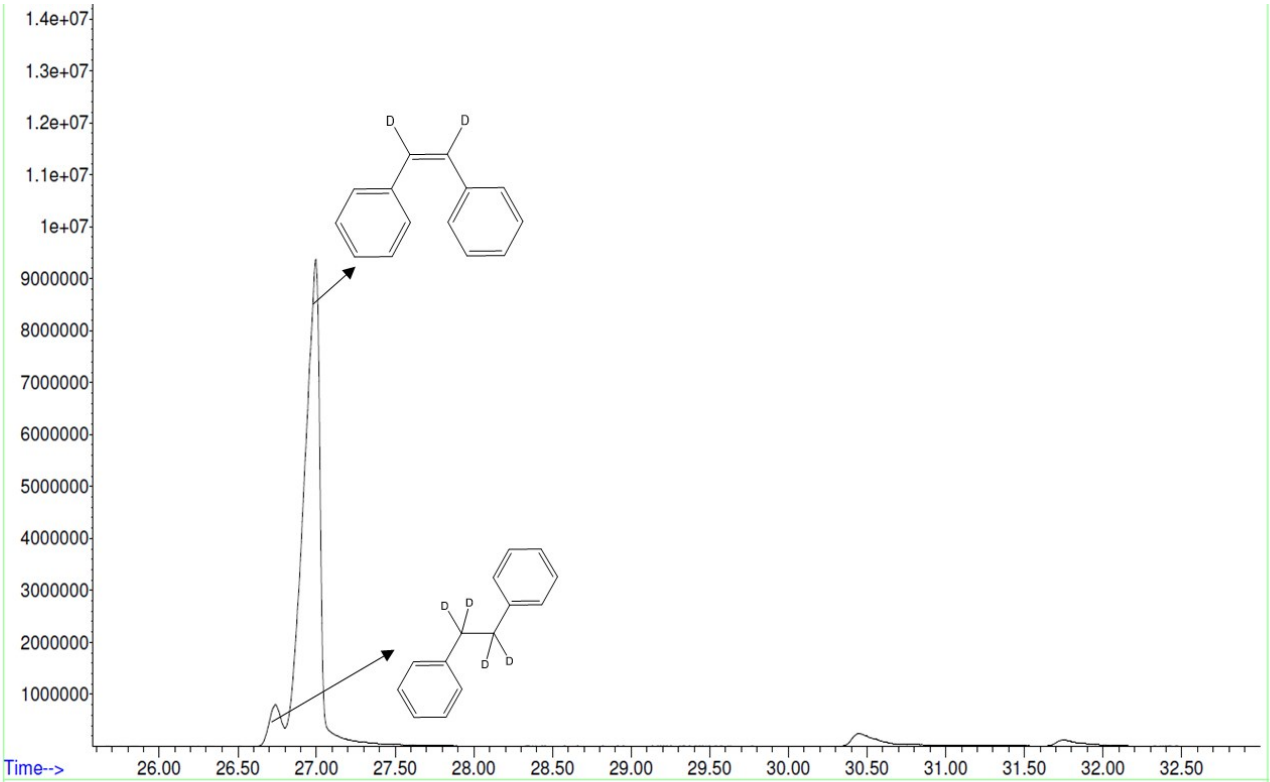


Fig. S18 GC-MS spectra of deuterium-labeling experiment for the semihydrogenation of diphenyl acetylene in presence of D_2O only.

Experiment S3: To the fresh catalyst (10 mol%), C_2H_5OH/H_2O (1:1, 20 mL) diphenylacetylene (1.0 mmol) and *n*-butyl amine (0.55 mmol) was added. The reaction mixture was stirred at 40 °C for 4 h under D_2 atmosphere (using a D_2 balloon). After that, liquid aliquot was analysed by GC-MS and NMR.





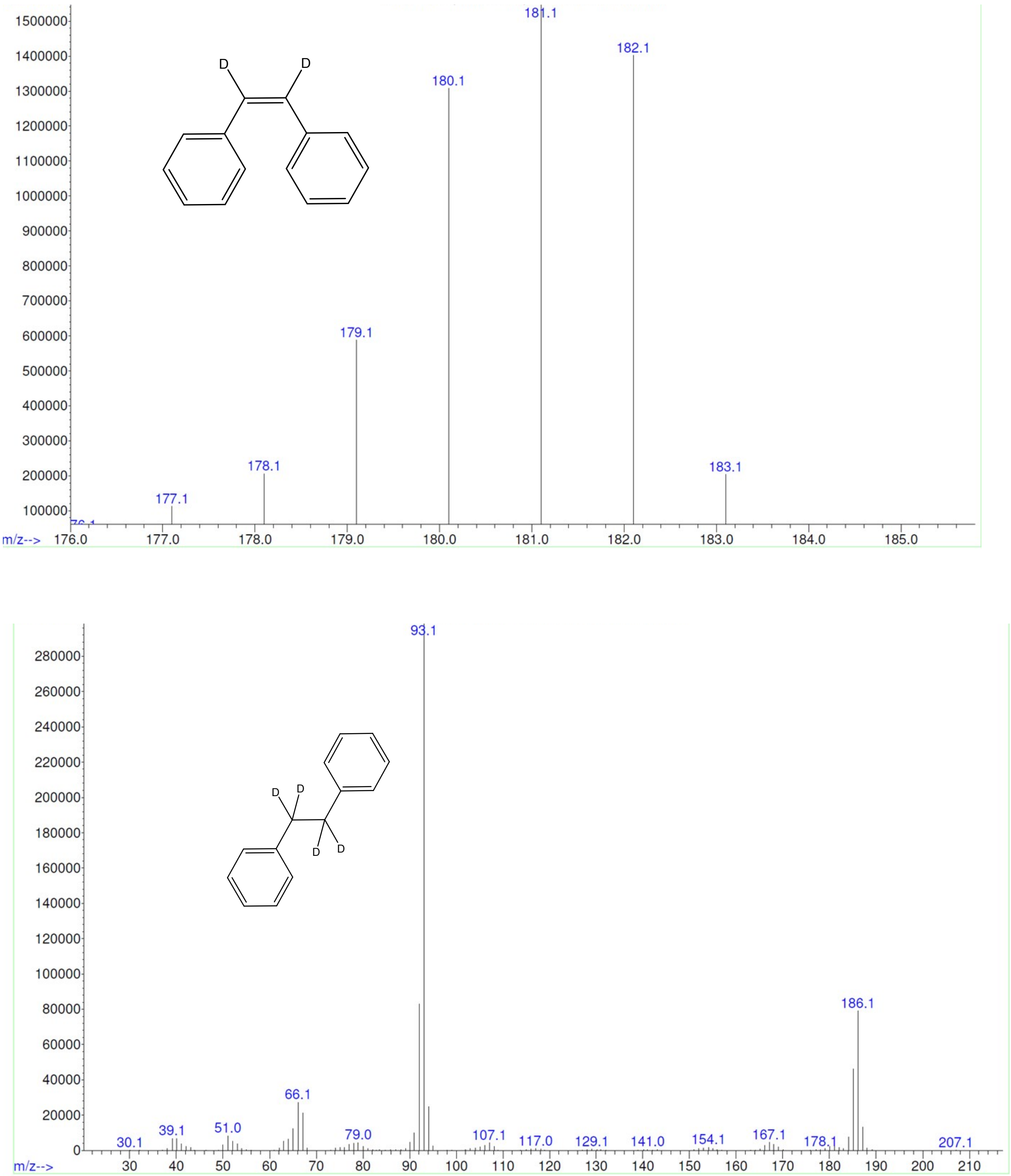
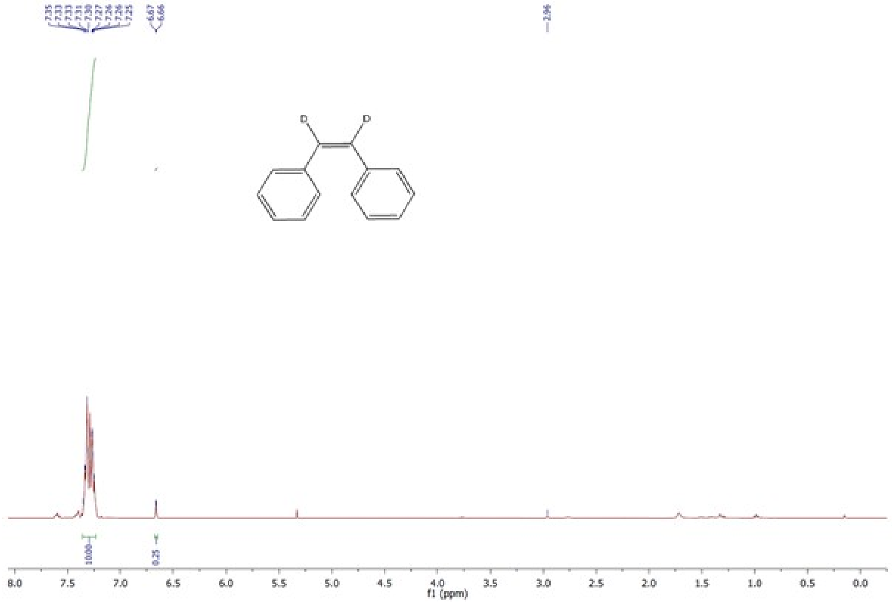


Fig. S19 GC-MS spectra of Deuterium-labeling experiment for the semihydrogenation of diphenylacetylene in the presence of D_2 gas.

^{1}H NMR



^{2}D NMR

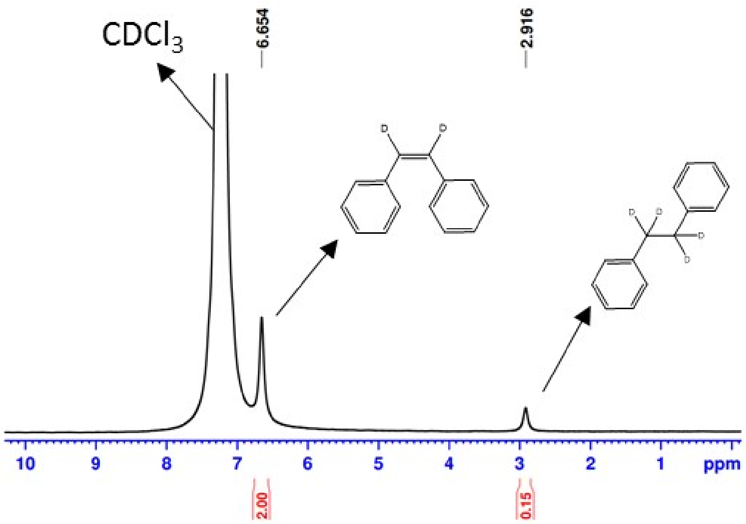


Fig. S20 ^{1}H NMR and ^{2}D NMR spectra of Deuterium-labeling experiment for the semihydrogenation of diphenylacetylene in the presence of D_2 gas.

SI-8. H_2-TPD experiment:

Experimental condition: For H_2-TPD measurements, 50 mg of catalyst was treated in H_2/Ar (1:9) flow (50 cc/min) at 300 ◦C for 4 h then cooled to ambient temperature at the same flow of gas. Then after, Ar gas flow (50 cc/min) was introduced and the catalyst was purged for 30 min to remove physisorbed H_2. After the stabilization of the base-line, TPD of desorbed H_2 was recorded up to 700 ˚C at a temperature ramp of 10 ˚C/min.

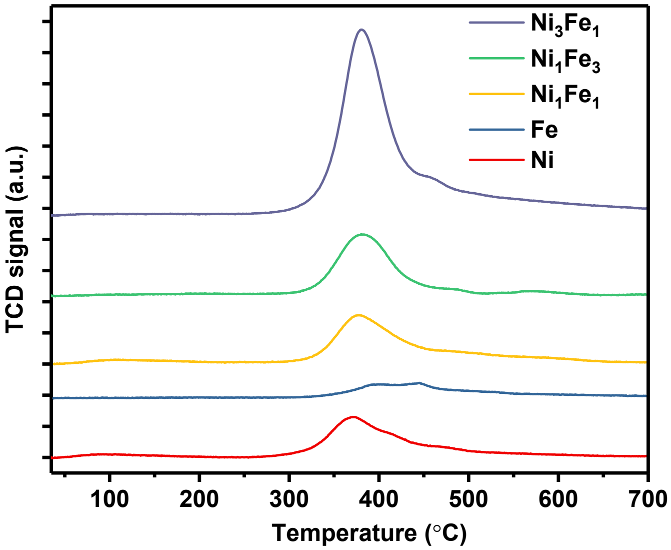


Fig. S21 H_2-TPD profile for the bimetallic Ni-Fe catalysts along with monometallic (Ni and Fe) catalysts.

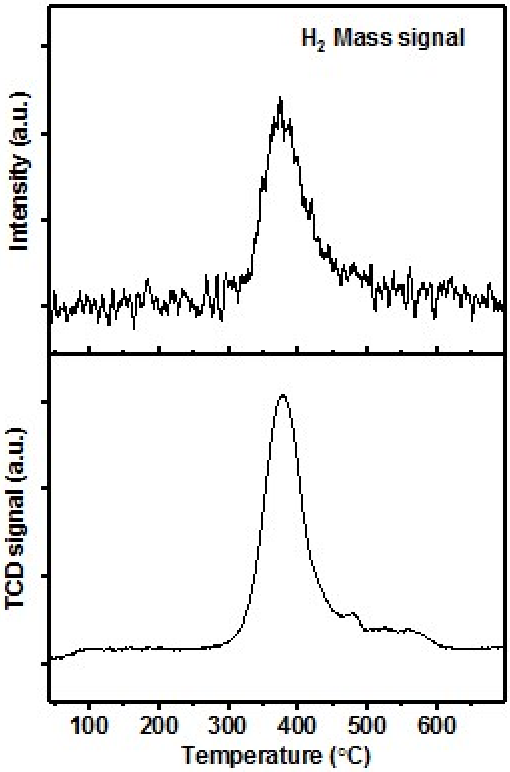


Fig. S22 H_2-TPD of Ni_1Fe_3 catalyst and their corresponding H_2 mass signal.

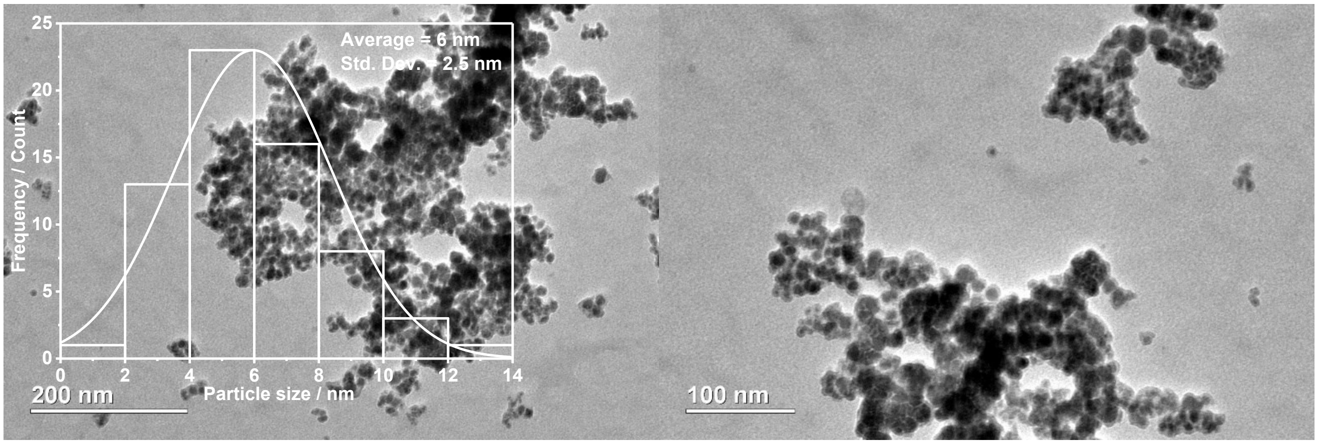


Fig. **S23** TEM image and particle size distribution curve of the Ni_1Fe_3 catalyst synthesized in bulk scale.

SI-10. XPS survey scan of different catalysts

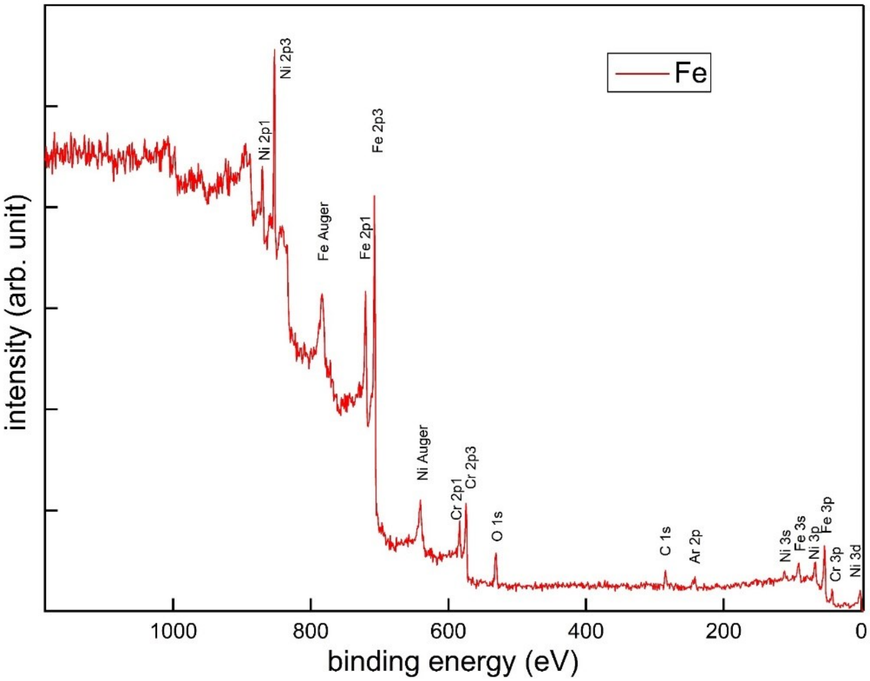


Fig. S24 XPS survey scan of freshly prepared Fe catalysts.

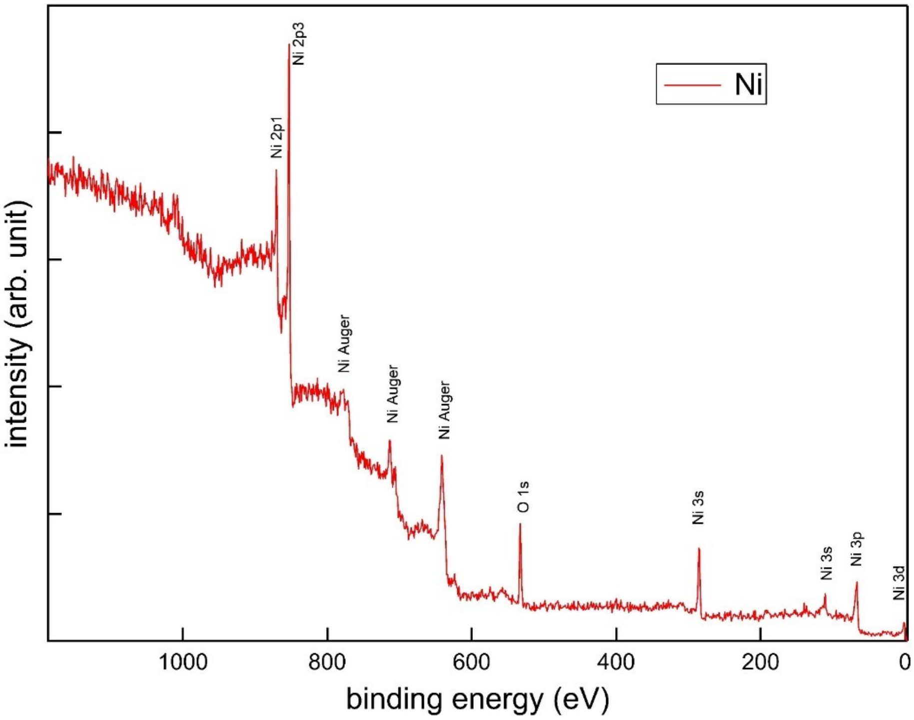


Fig. S25 XPS survey scan of freshly prepared Ni catalysts.

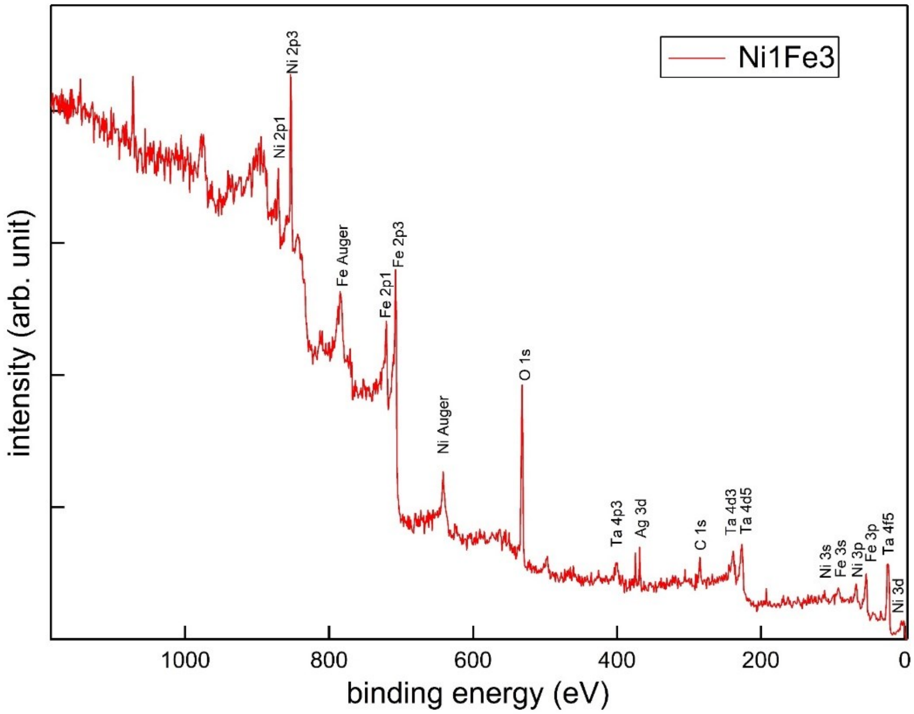


Fig. S26 XPS survey scan of freshly prepared Ni_1Fe_3 catalysts.

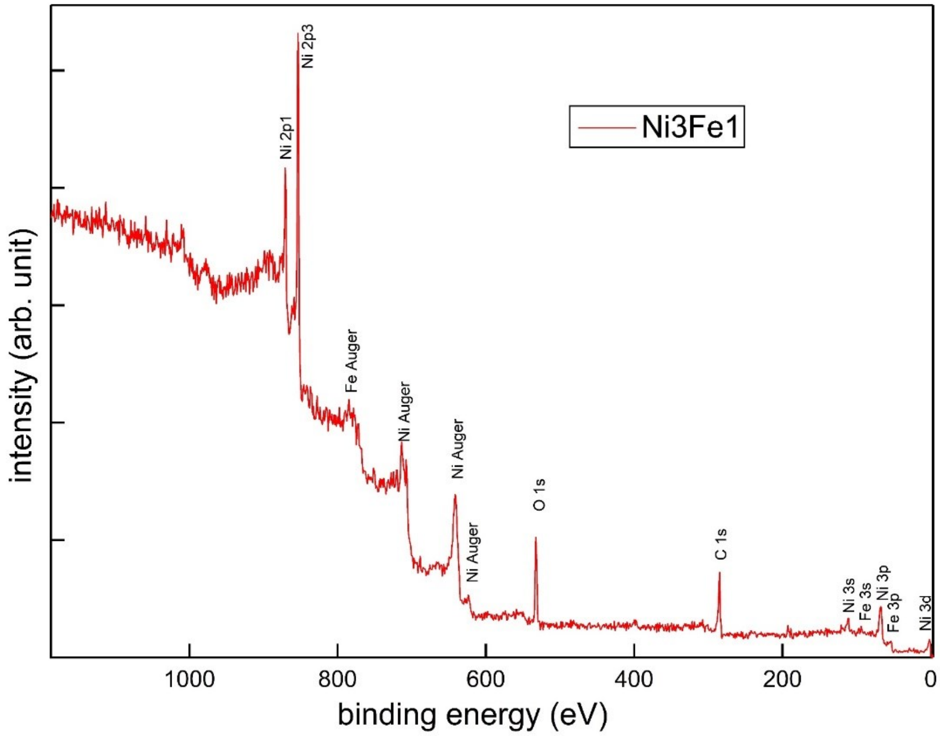


Fig. S27 XPS survey scan of freshly prepared Ni_3Fe_1 catalysts.

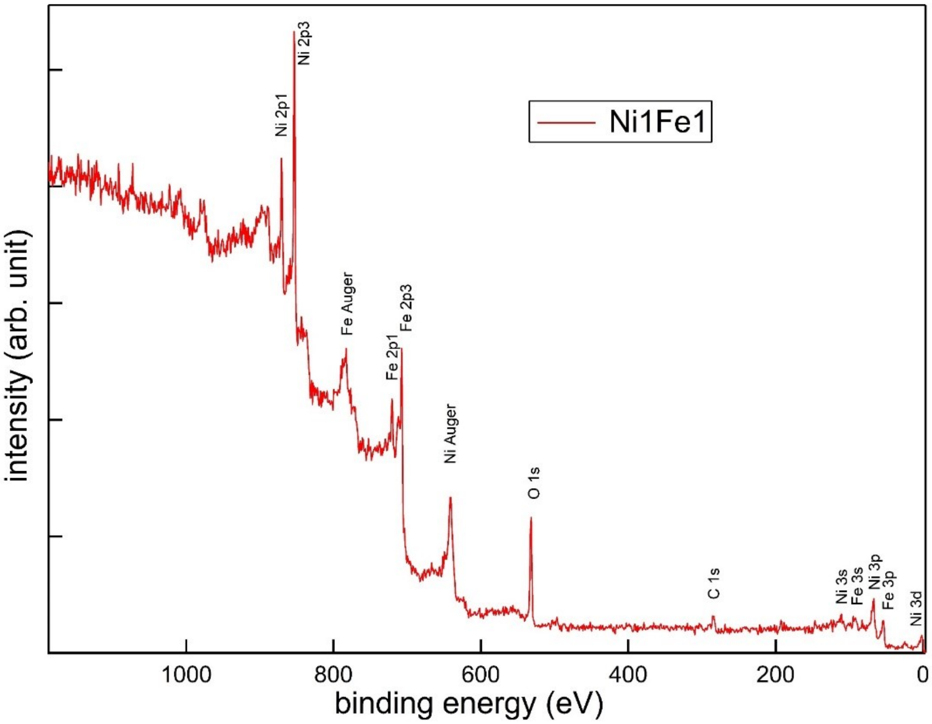
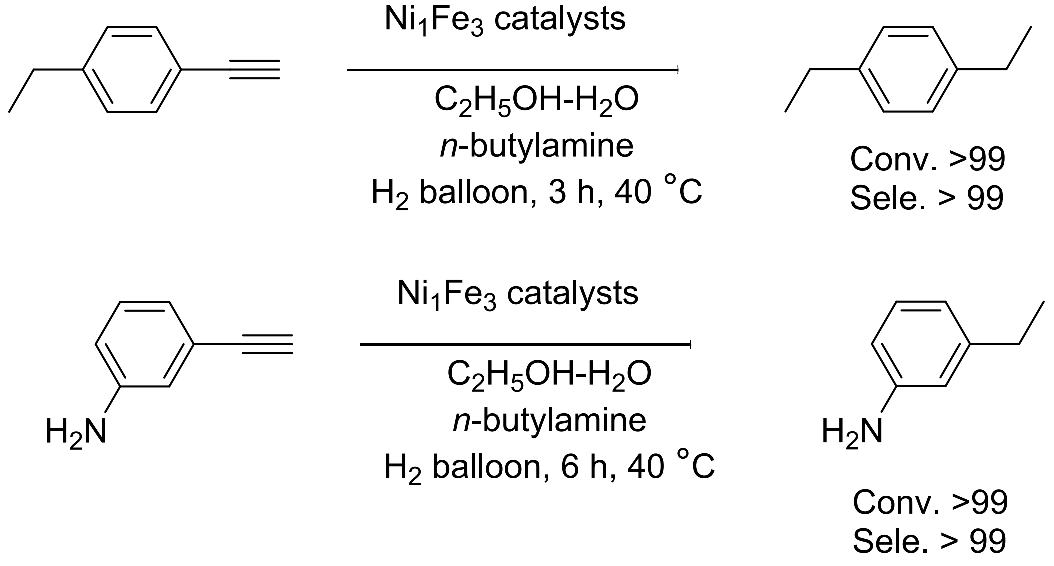


Fig. S28 XPS survey scan of freshly prepared Ni_1Fe_1 catalysts.

SI-10. Hydrogenation of terminal alkynes over Ni_1Fe_3 catalyst



Scheme S1 Hydrogenation of terminal alkynes over Ni_1Fe_3 catalyst. Reaction condition: terminal alkyne (1.0 mmol), catalyst (10 mol%), H_2 balloon, *n*-butyl amine (0.55 mmol), water-ethanol (1:1 v/v, 20.0 mL).

SI-11. ICP experiment under optimized reaction condition

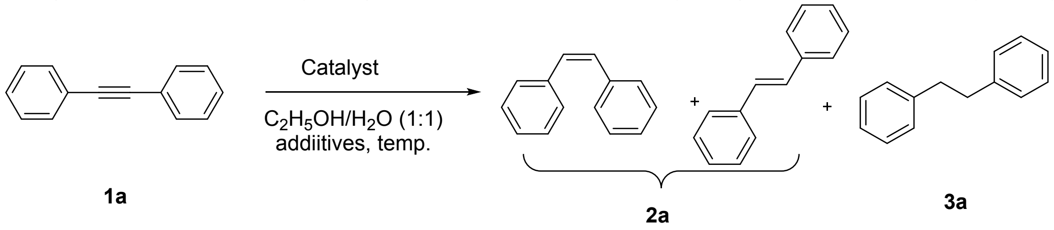
Table S1 ICP data of different synthesized catalysts.

S. No.	Catalysts	Ni/Fe atomic ratio
1	Ni_1Fe_3	1/2.7 (1/3)[a]
2	Ni_1Fe_1	1/1
3	Ni_3Fe_1	3/1

[a] For spent Ni_1Fe_3 catalyst recovered after the catalytic semihydrogenation reaction of diphenylacetylene (**1a**) under the optimized reaction condition.

SI-12. Screening of additives and hydrogen source for the semihydrogenation of diphenylacetylene

Table S2 Screening of additives and hydrogen source for the semihydrogenation of diphenylacetylene[a]

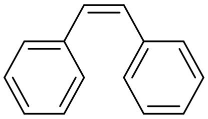


Entry	Catalysts	Temp. (°C)	Time (h)	Hydrogen source	Additives (mmol)	Conv. (%)[b]	Sele. (%)[b] (2a/3a)	Sele. (%)[b] (*Z/E*)
1.	Ni_1Fe_3	40	6	H_2	*n*-propyl amine (0.55)	99	54/46	89/11
2.	Ni_1Fe_3	50	5	H_2	*iso*propyl amine (0.55)	96	72/28	92/8
3.	Ni_1Fe_3	40	6	H_2	*n*-propyl amine (0.65)	70	93/7	96/4
4.	Ni_1Fe_3	40	5	H_2	*n*-propyl amine (0.45)	99	51/49	78/22
5.	Ni_1Fe_3	40	4	H_2	*n*-butyl amine (0.55)	99(94)[c] (77)[d] (23)[e]	91/9(89/11)[c] (95/5)[d] (97/3)[e]	96/4 (94/6)[c] (91/9)[d] (79/21)[e]
6.	Ni_1Fe_3 (without PVP)	40	5	H_2	No additive	47	99/-	92/8
7.	Ni_1Fe_3 (without PVP)	40	5	H_2	*n*-butyl amine (0.55)	26	99/-	90/10
8.	Ni_1Fe_3	40	4	H_2	*n*-butyl amine (0.55)	96	85/15	92/8[f]
9.	Ni_1Fe_3	40	4	H_2	*n*-butyl amine (0.45)	99	49/51	86/14
10.	Ni_1Fe_3	40	4	H_2	*n*-butyl amine (0.65)	90	92/8	93/7
11.	Ni_1Fe_3	40	5	H_2	*n*-butyl amine (0.55)	99	80/20	97/3
12.	Ni_1Fe_3	40	2	H_2	*n*-butyl amine (0.55)	47	93/7	95/5
13.	Ni/Fe_3O_4	50	5	H_2	*n*-butyl amine (0.55)	80	61/39	90/10
14.	Ni_1Fe_3	40	4	$NaBH_4$	*n*-butyl amine (0.55)	23	91/9	81/19
15.	Ni_1Fe_3	50	6	$N_2H_4·H_2O$	--	70	95/5	96/4

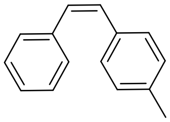
[a] Reaction conditions: Alkyne (1.0 mmol), catalyst (10 mol%), hydrogen source (H_2 balloon, $NaBH_4$ (1.0 mmol) or $N_2H_4·H_2O$ (2.0 mmol)). [b] Conversion of the substrate and selectivity of (*Z*) *cis*-alkene, (*E*) *trans*-alkene, alkane

was determined by ^{1}H NMR. ^{c}Repeat experiment. ^{d}2nd and ^{e}3rd cycle of Ni_1Fe_3 catalyst after fresh addition of diphenylacetylene (1.0 mmol) and *n*-butyl amine (0.55) for 4 h. ^{f} catalytic activity with catalysts prepared in bulk (10 times higher than the small scale synthesis)

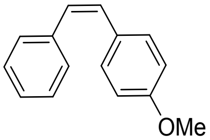
SI-13. Spectral data of semihydrogenated products



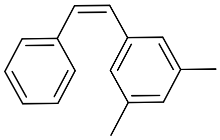
(*Z*)-1,2-diphenylethene: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 - 7.17 (m, 10H), 6.59 (s, 2H).



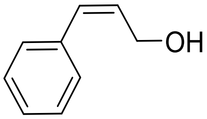
(*Z*)-1-methyl-4-styrylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.27 - 7.20 (m, 5H), 7.14 (d, 2H, *J* = 8.0 Hz), 7.02 (d, 2H, *J* = 8.0 Hz), 6.55 (s, 2H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) =137.67, 136.98, 134.45, 130.38, 129.73, 129.02, 128.98, 128.48, 128.35, 127.13, 21.38.



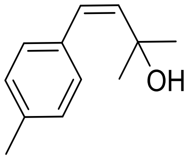
(*Z*)-1-methoxy-4-styrylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.28-7.17 (m, 7H), 6.75 (d, 2H, *J* = 8.0 Hz), 6.52 (s, 2H), 3.78 (s, 3H).



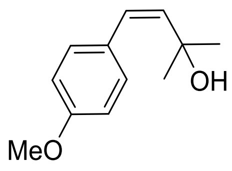
(*Z*)-1,3-dimethyl-5-styrylbenzene: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.27 - 7.17 (m, 5H), 6.87-6.83 (m, 3H) 6.54 (s, 2H), 2.21 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) =137.72, 137.51, 137.27, 130.58, 130.0, 129.0, 128.89, 128.21, 127.13, 126.73, 21.0.



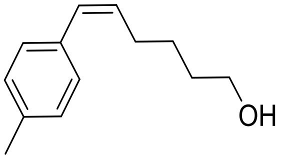
(*Z*)-3-phenylprop-2-en-1-ol: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.36-7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 (d, 2H, *J* = 8.0 Hz), 6.58 (d, 1H, *J* = 12.0 Hz), 5.90 – 5.84 (m, 1H), 4.44 (d, 2H, *J* = 8.0 Hz), 1.72 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 136.60, 131.37, 130.79, 128.81, 128.29, 127.24, 59.58.



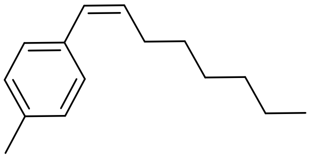
(*Z*)-2-methyl-4-(p-tolyl)but-3-en-2-ol: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.38 (d, 2H, *J* = 8.0 Hz), 7.23 (d, 2H, *J* = 8.0 Hz), 6.55 (d, 1H, *J* = 12.0 Hz), 6.85 (d, 1H, *J* = 12.0 Hz), 2.46 (s, 3H), 2.07 (s, 1H), 1.49 (s, 6H).



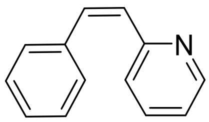
(*Z*)-4-(4-methoxyphenyl)-2-methylbut-3-en-2-ol: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.33 (d, 2H, *J* = 8.0 Hz), 6.85 (d, 2H, *J* = 8.0 Hz), 6.39 (d, 1H, *J* = 12.0 Hz), 5.69 (d, 1H, *J* = 12.0 Hz), 3.80 (s, 3H), 1.87 (s, 1H), 1.37 (s, 6H).



(Z)-6-(p-tolyl)hex-5-en-1-ol: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.18 - 7.12 (m, 4H), 6.39 (d, 1H *J* = 12.0 Hz), 5.62 - 5.59 (m, 1H), 3.63 (t, 2H, *J* = 8.0 Hz), 2.39 - 2.31 (m, 4H), 1.62-1.48 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 136.23, 134.85, 131.98, 129.03, 128.90, 128.72, 62.72, 32.29, 28.36, 26.16, 21.20.

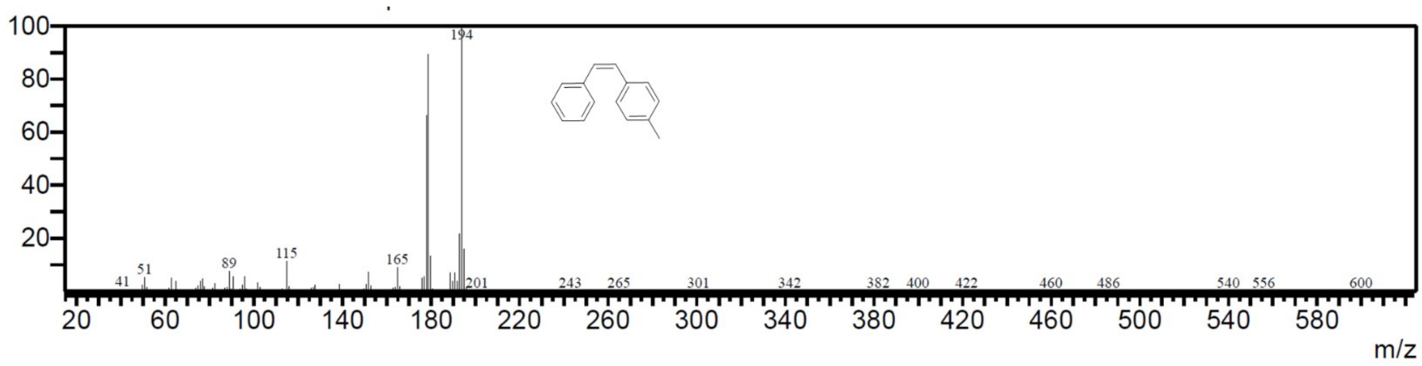


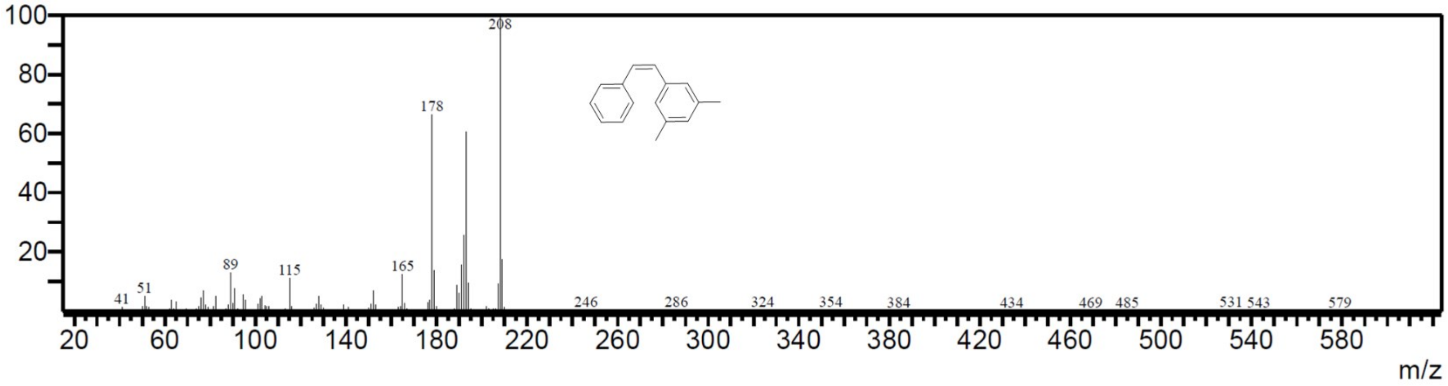
(Z)-1-methyl-4-(oct-1-en-1-yl)benzene: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.19 - 7.13 (m, 4H), 6.37 (d, 1H *J* = 12.0 Hz,), 5.65 - 5.58 (m, 1H), 2.34-2.29 (m, 5H), 1.46 - 1.40 (m, 2H), 1.36 - 1.26 (m, 6H), 0.88 (t, 3H *J* = 12 Hz).

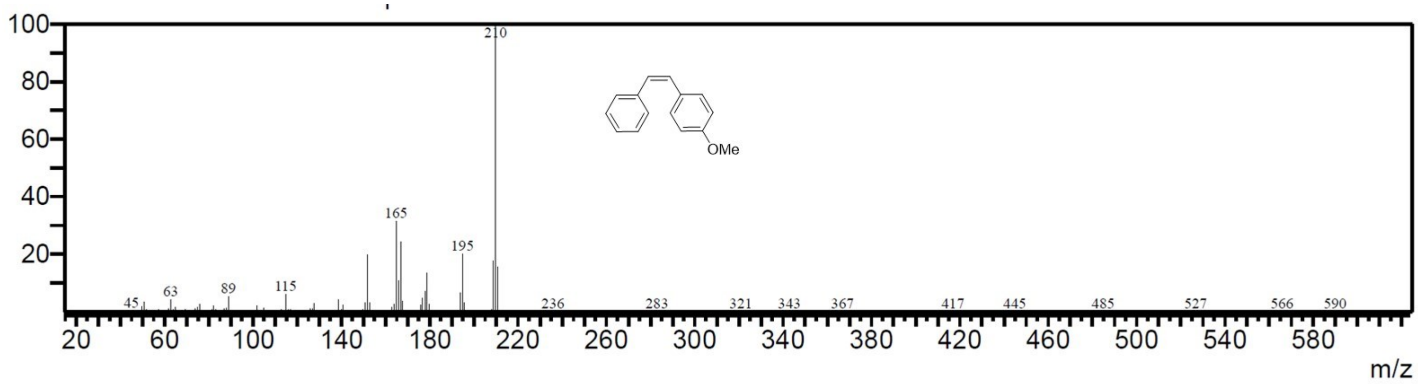


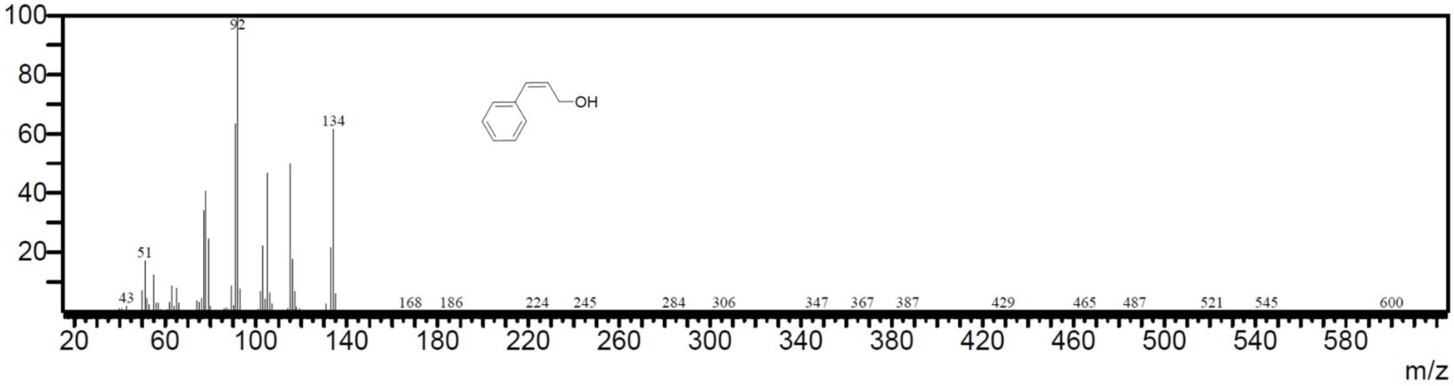
(Z)-2-styrylpyridine: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 8.61 (d, 1H, *J* = 4.0 Hz), 7.69-7.07 (m, 8H), 6.83 (d, 1H, *J* = 12.0 Hz), 6.70 (d, 1H, *J* = 12.0 Hz). {*J. Am. Chem. Soc.* **132**, 5018–5020 (2010)}

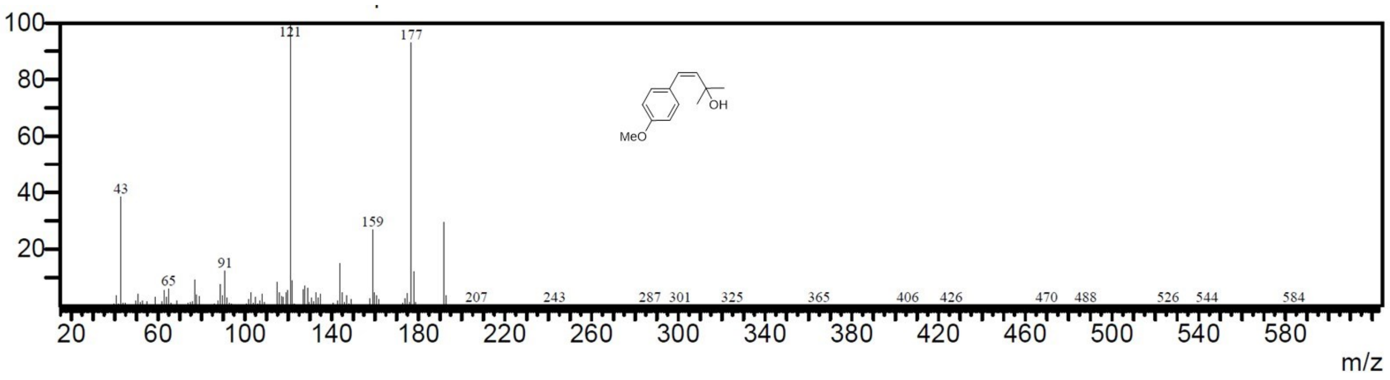
SI-14. GC-MS spectra for semihydrogenated products






100
80
60
40
20
210
165
195
45
63
89
115
236
283
321
343
367
417
445
485
527
566
590
OMe
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z


100
80
60
40
20
92
134
51
43
168
186
224
245
284
306
347
367
387
429
465
487
521
545
600
OH
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z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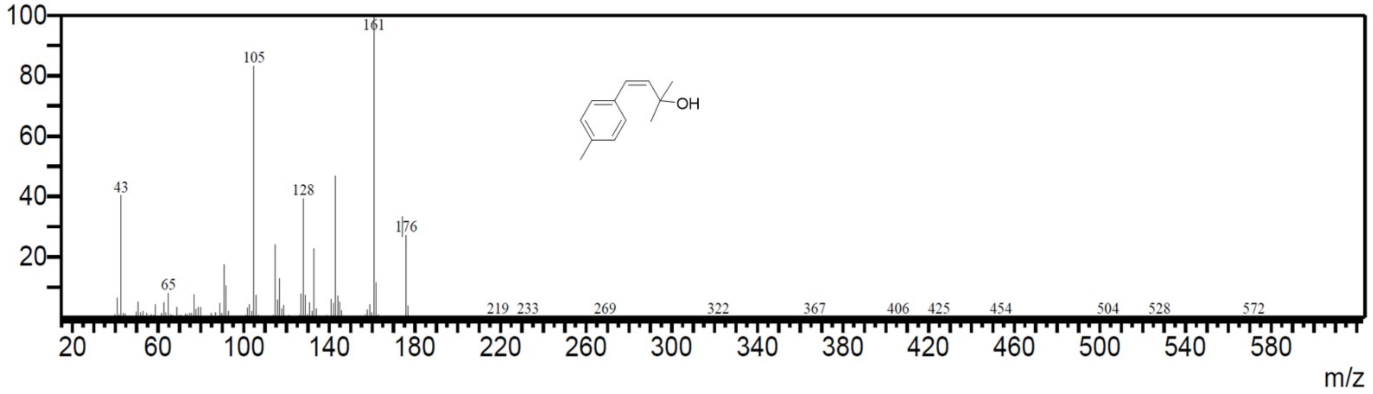
80
60
40
20
121
177
43
159
91
65
207
243
287
301
325
365
406
426
470
488
526
544
584
OH
MeO
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z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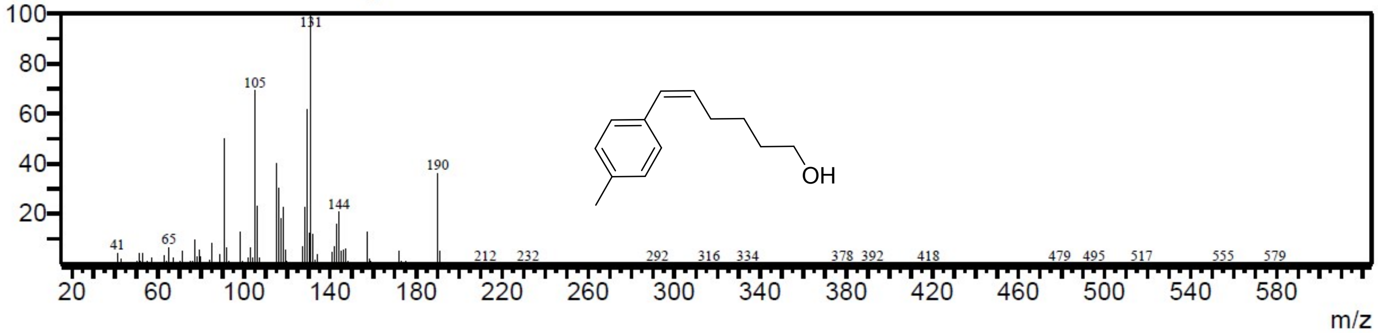
80
60
40
20
161
105
43
128
176
65
219
233
269
322
367
406
425
454
504
528
572
OH
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z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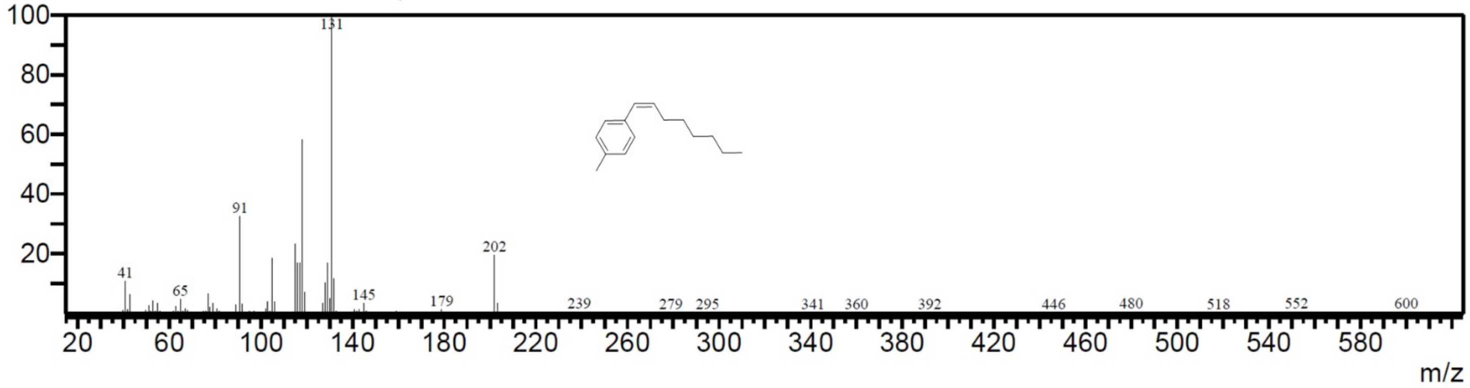
80
60
40
20
131
105
190
144
41
65
212
232
292
316
334
378
392
418
479
495
517
555
579
OH
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z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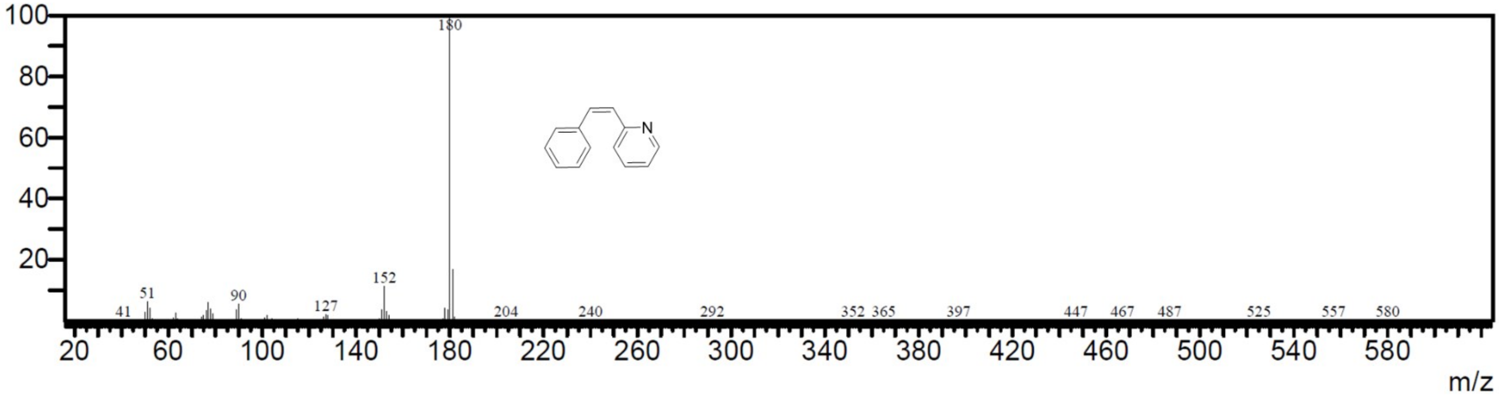
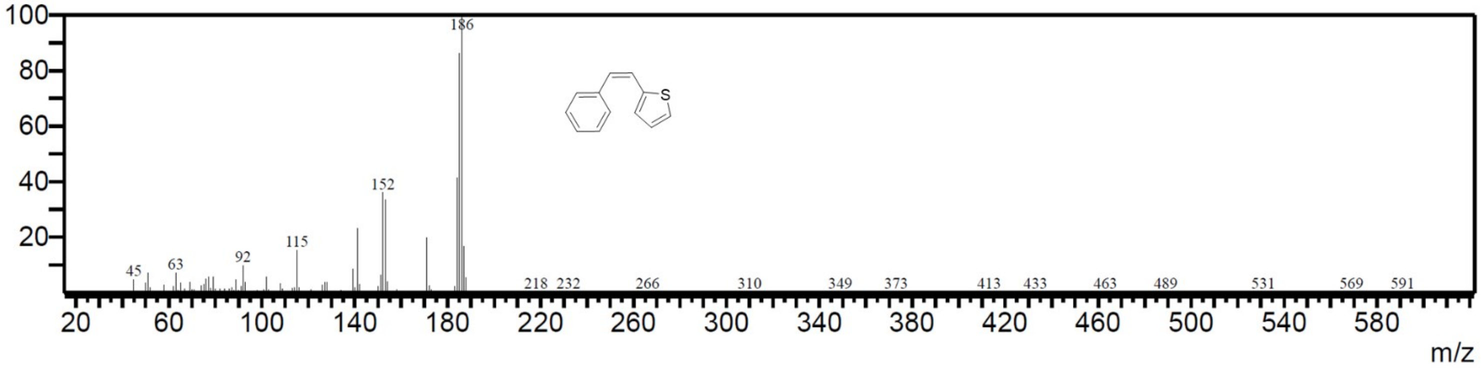
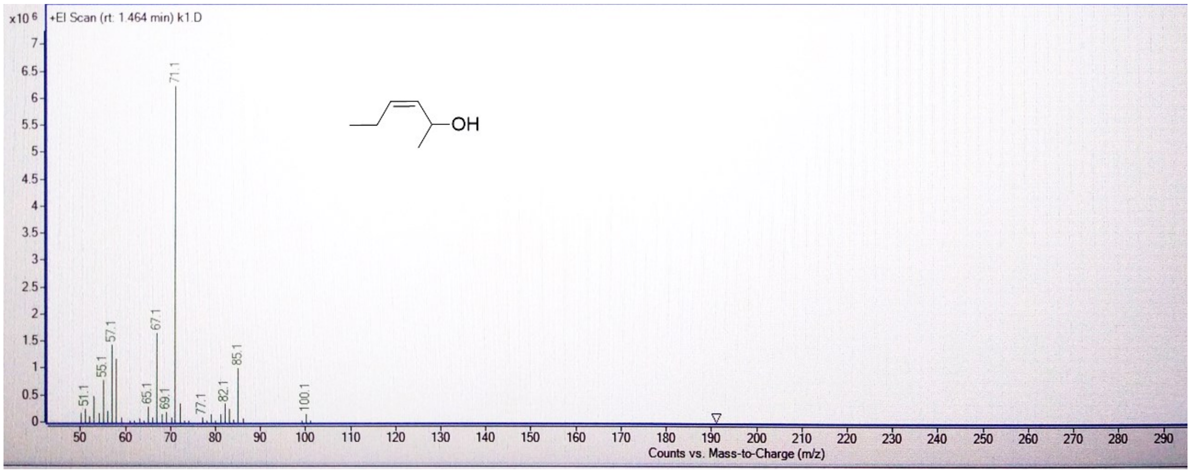
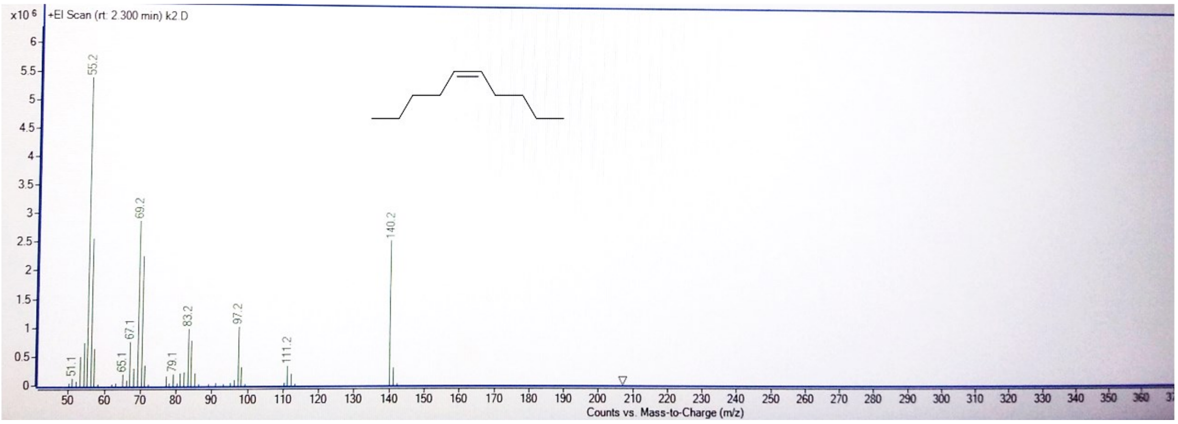
80
60
40
20
131
91
202
41
65
145
179
239
279
295
341
360
392
446
480
518
552
600
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z

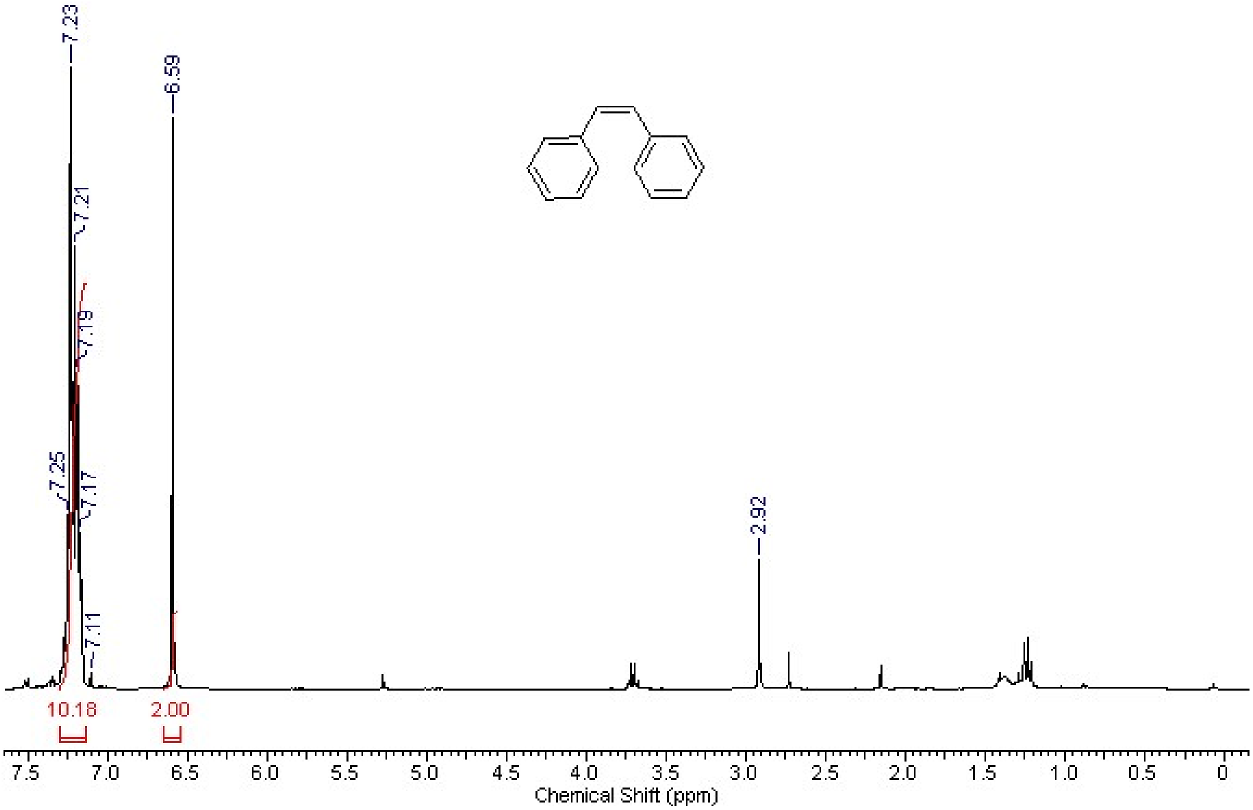

100
80
60
40
20
180
152
51
90
127
41
204
240
292
352
365
397
447
467
487
525
557
580
N
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z

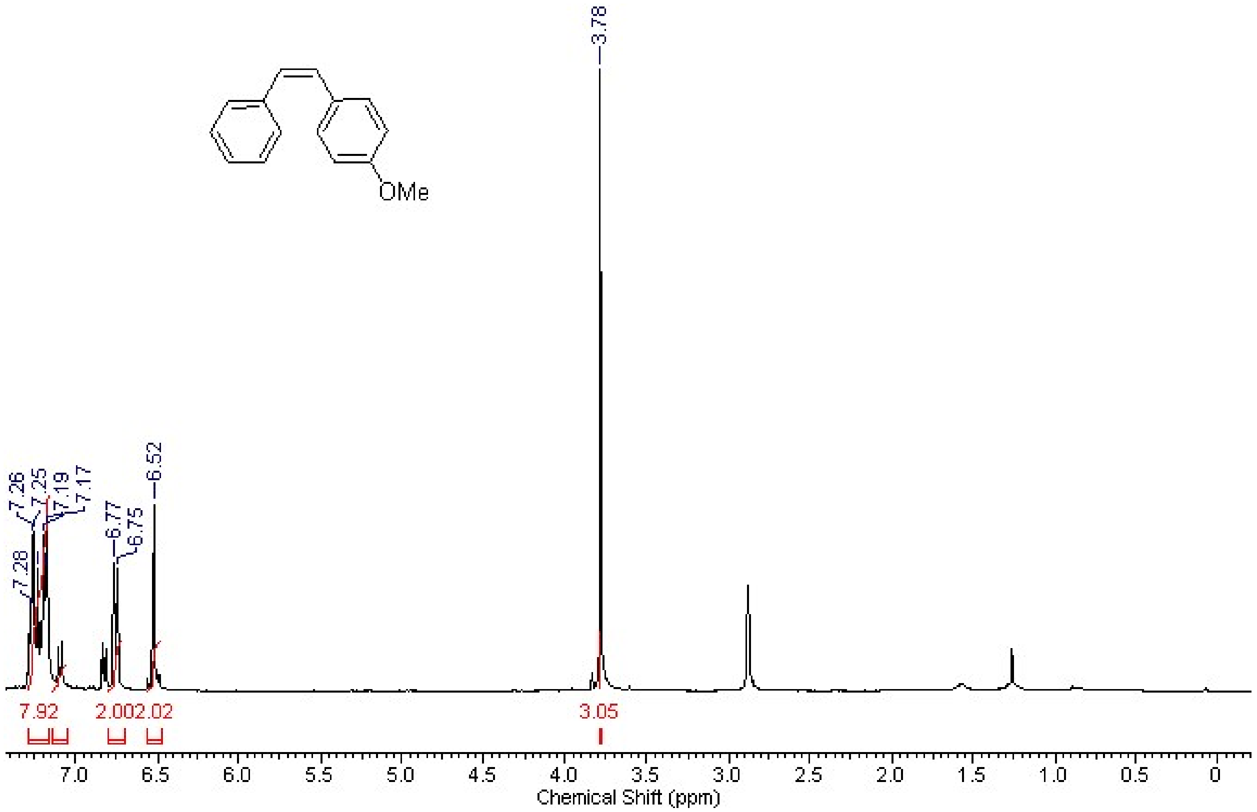

100
80
60
40
20
186
152
115
92
63
45
218
232
266
310
349
373
413
433
463
489
531
569
591
S
20
60
100
140
180
220
260
300
340
380
420
460
500
540
580
m/z

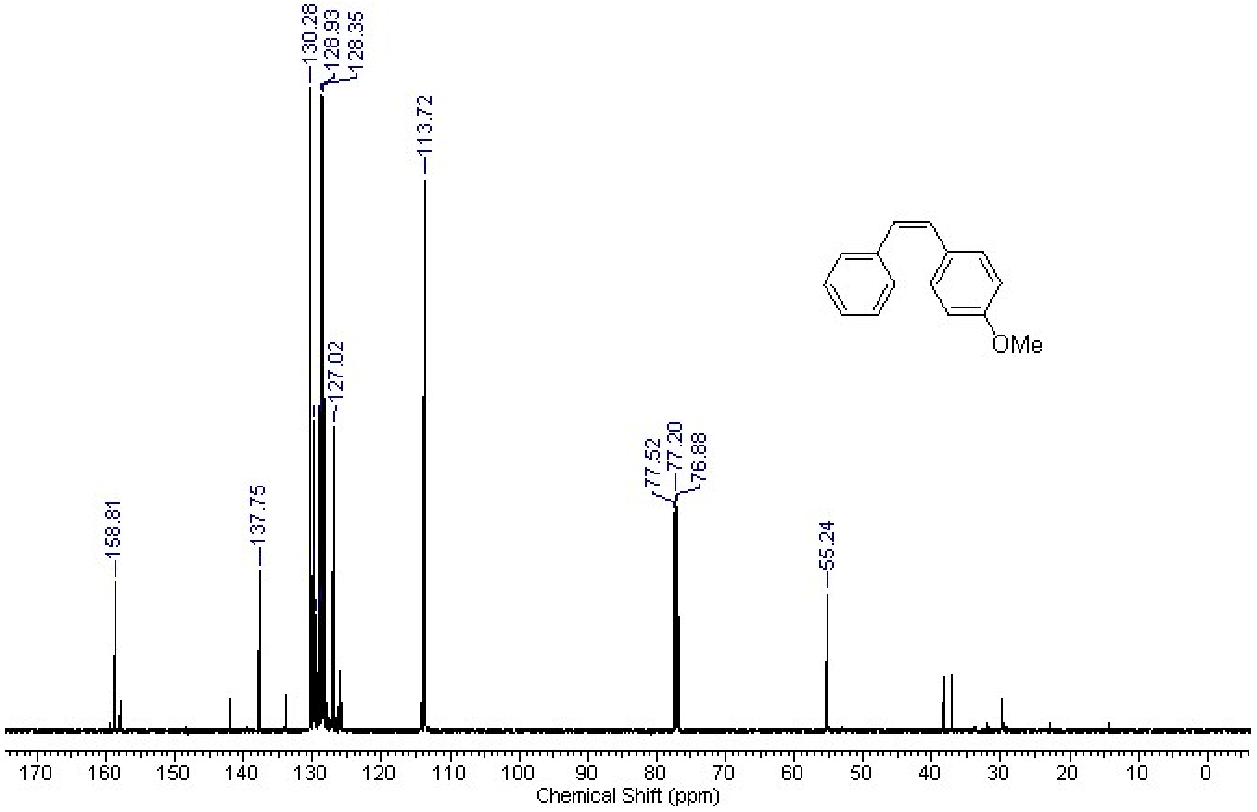

x10 6
+EI Scan (rt: 1.464 min) k1.D
OH
71.1
57.1
67.1
55.1
85.1
51.1
65.1
69.1
77.1
82.1
100.1
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290
Counts vs. Mass-to-Charge (m/z)

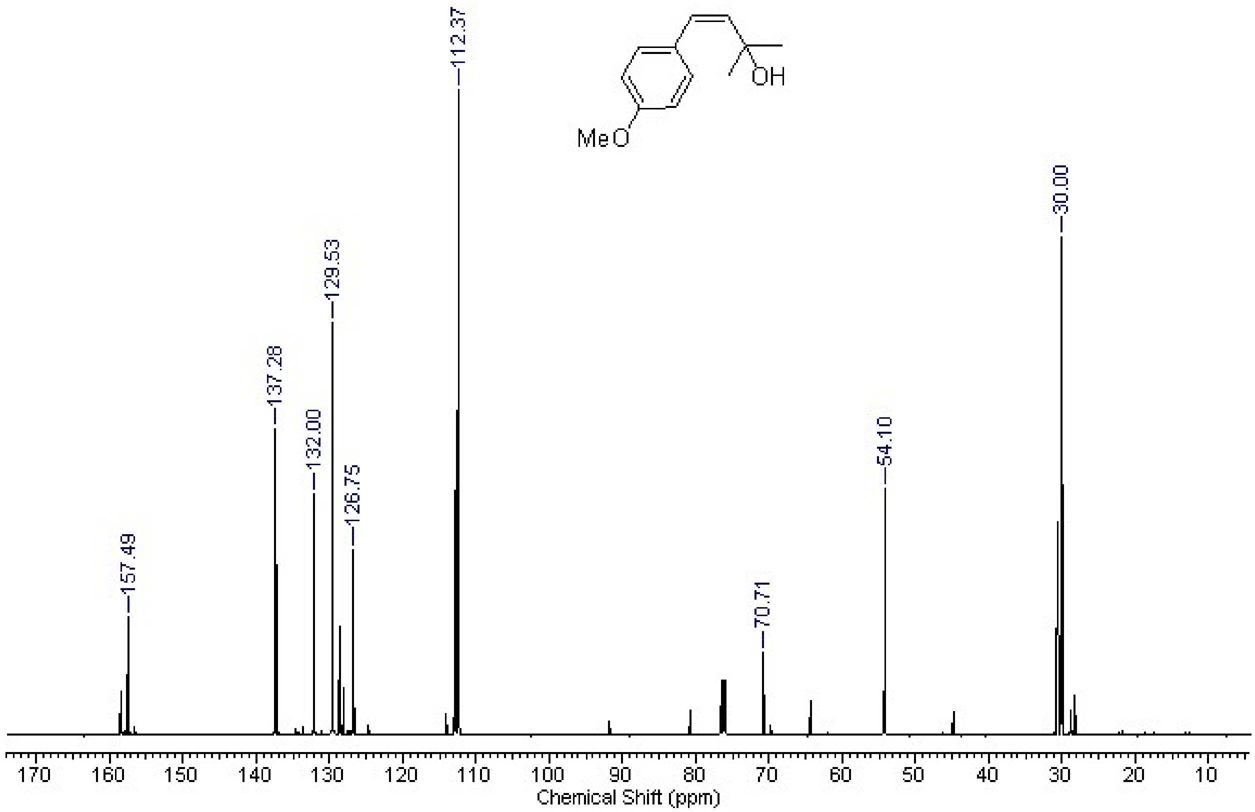

x10 6
+EI Scan (rt: 2.300 min) k2.D
55.2
69.2
140.2
83.2
97.2
67.1
111.2
51.1
65.1
79.1
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360
Counts vs. Mass-to-Charge (m/z)

SI-15. Spectra of semihydrogenated products

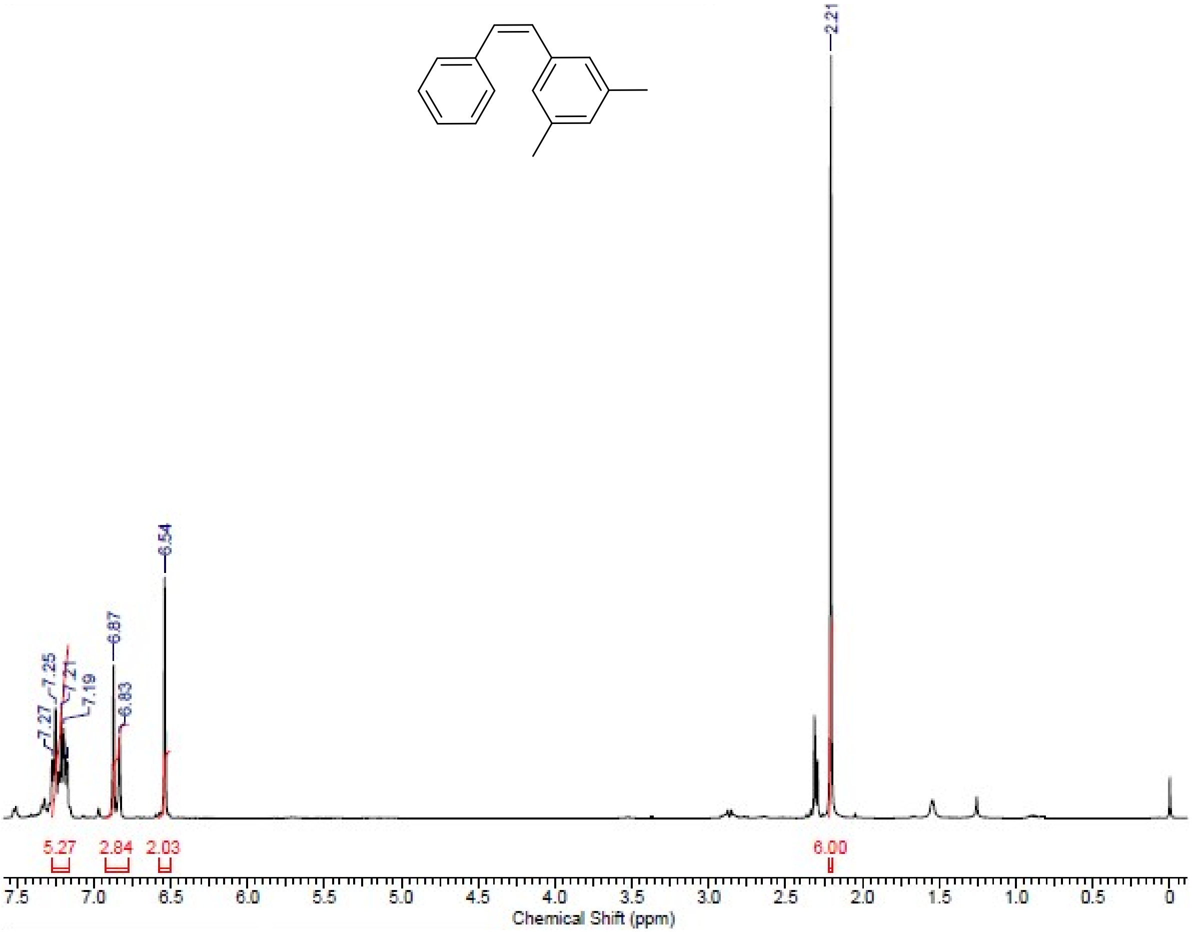


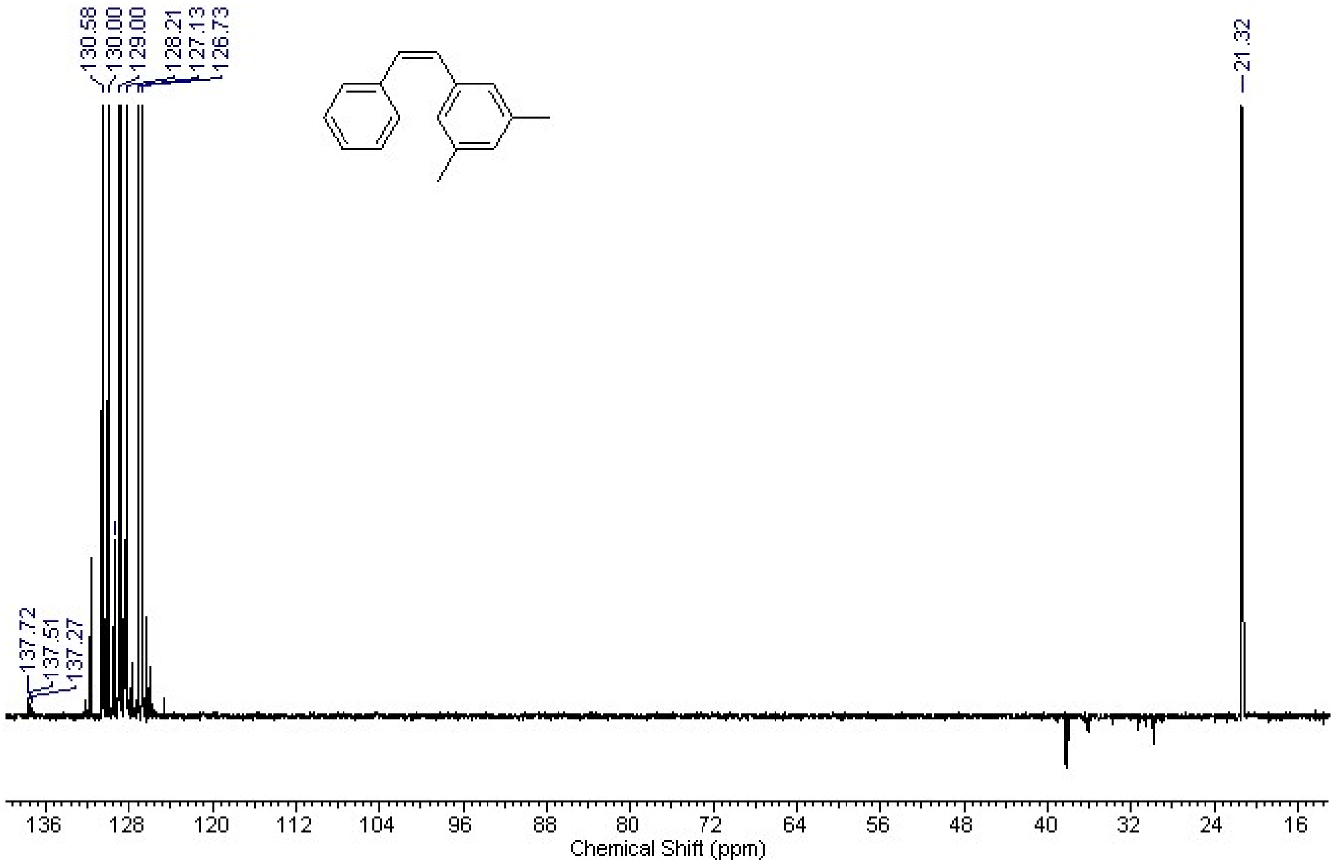

3.78
7.28
7.26
7.25
7.19
7.17
6.77
6.75
6.52
OMe
7.92
2.00
2.02
3.05
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

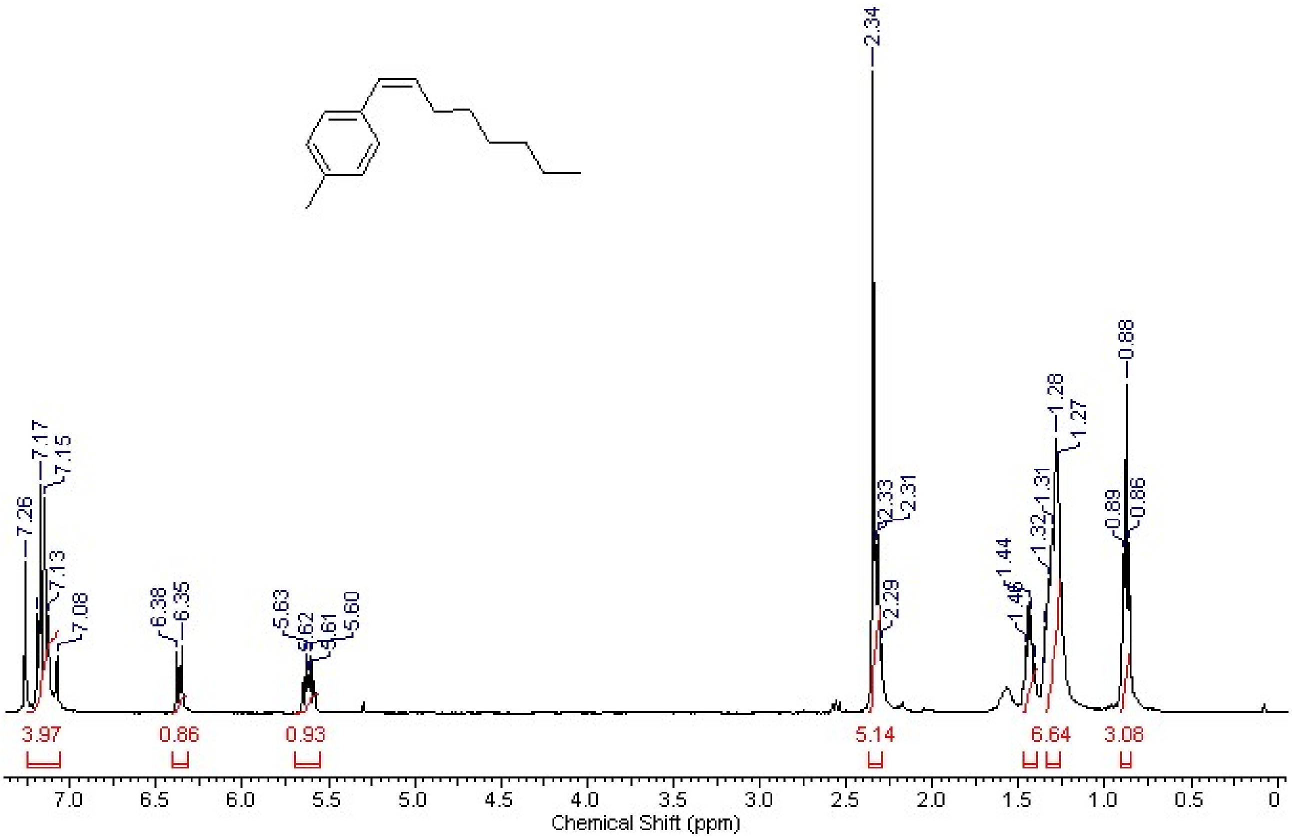

130.28
128.93
128.35
113.72
127.02
OMe
77.52
77.20
76.88
158.81
137.75
55.24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

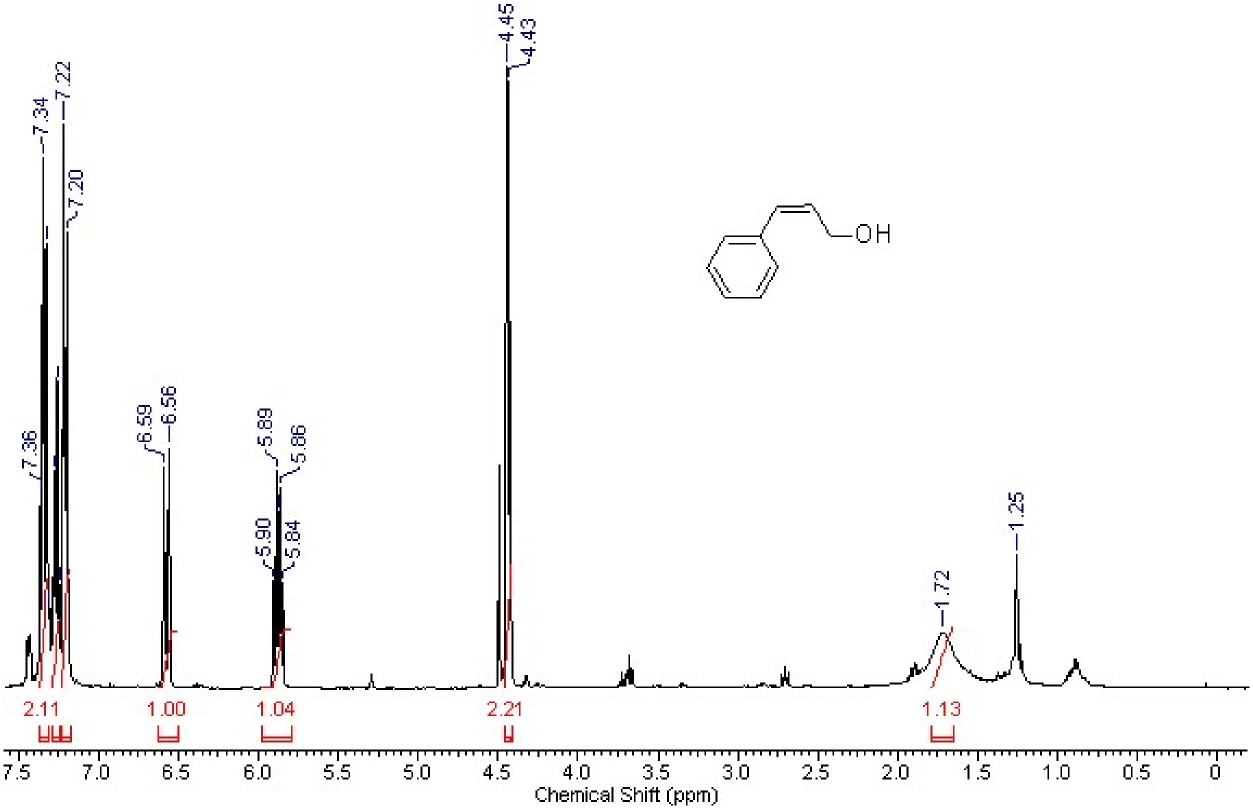


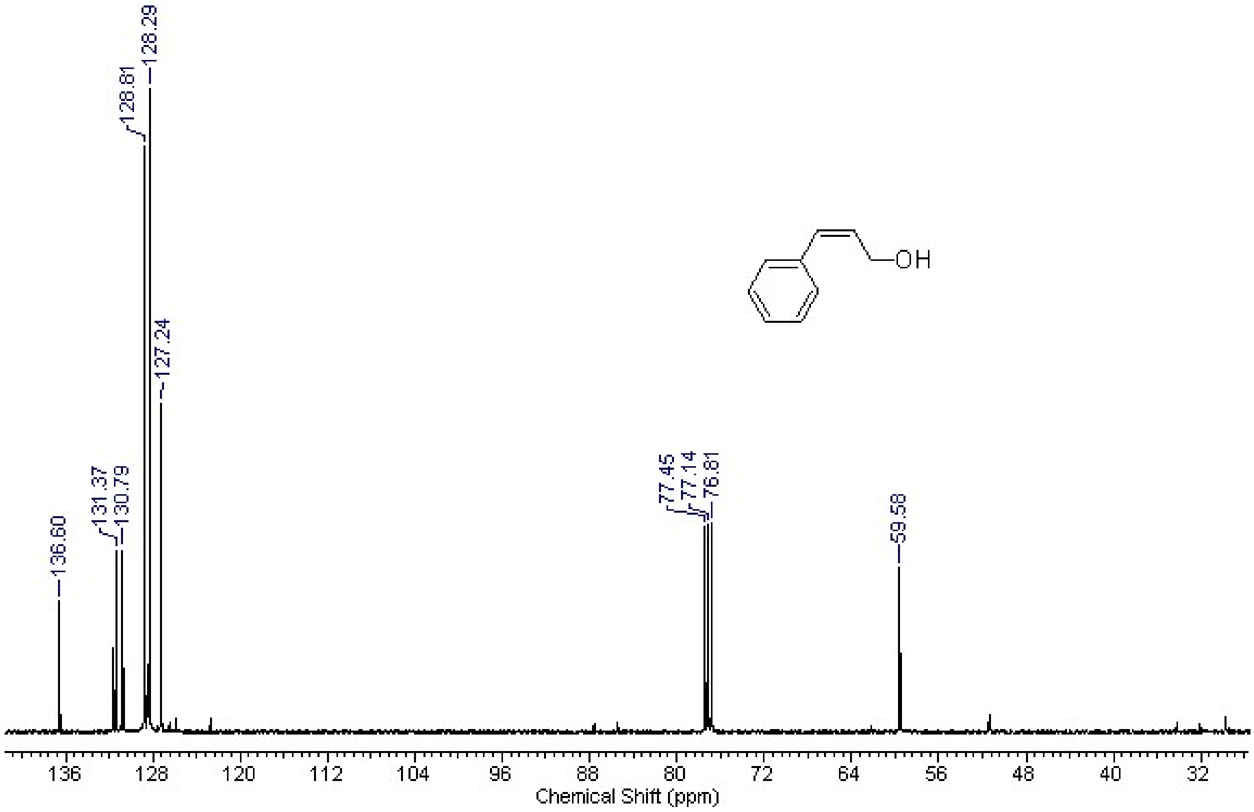
157.49
137.28
132.00
129.53
126.75
112.37
70.71
54.10
30.00
MeO
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

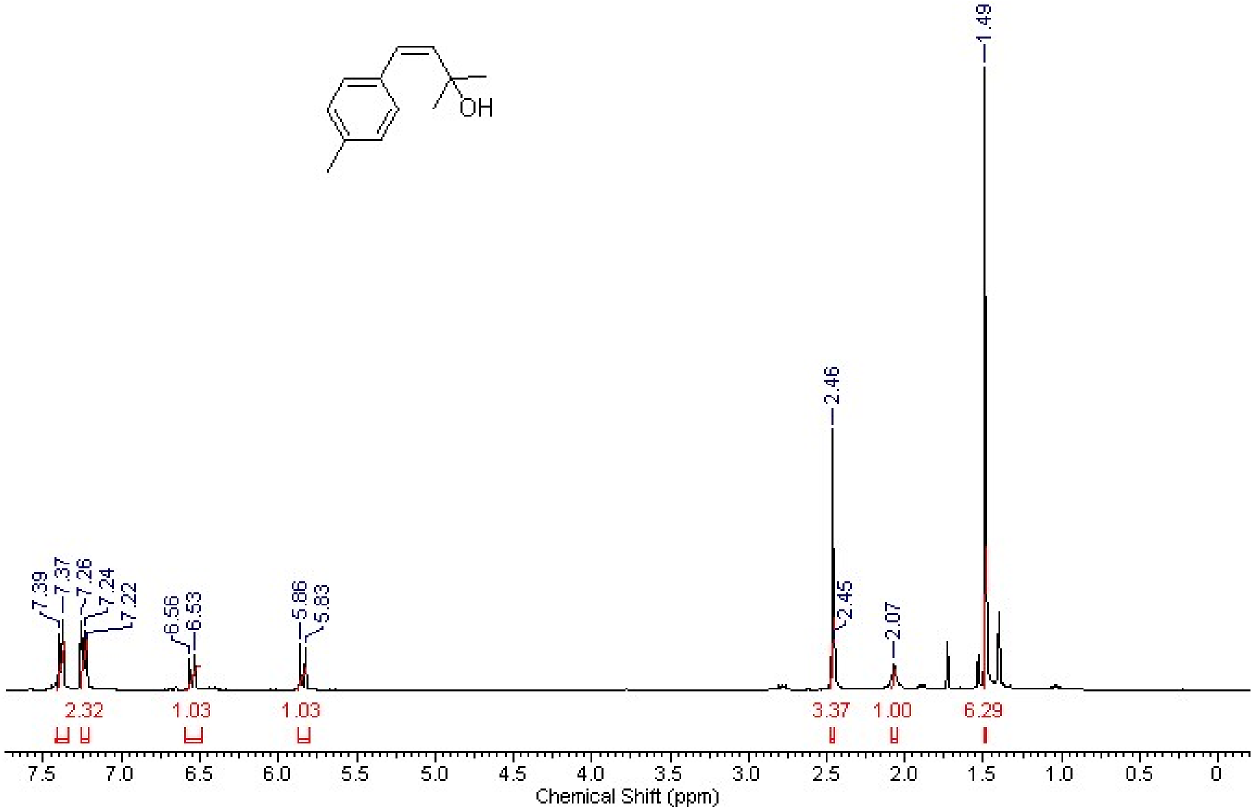

7.27
7.25
7.21
7.19
6.87
6.83
6.54
2.21
5.27
2.84
2.03
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

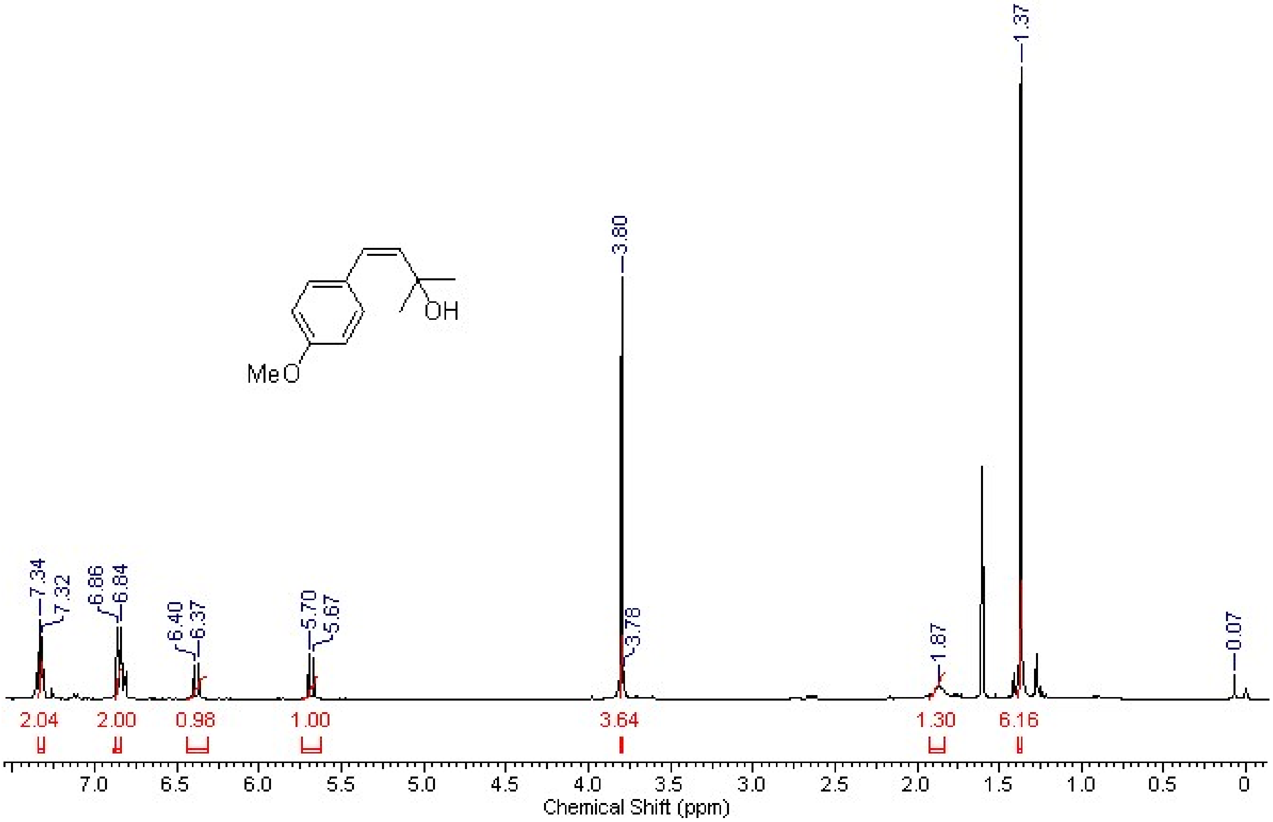

130.58
130.00
129.00
128.21
127.13
126.73
137.72
137.51
137.27
21.32
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


7.26
7.17
7.15
7.13
7.08
6.38
6.35
5.63
5.62
5.61
5.60
2.34
2.33
2.31
2.29
1.46
1.44
1.32
1.31
1.28
1.27
0.89
0.88
0.86
3.97
0.86
0.93
5.14
6.64
3.08
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 0
Chemical Shift (ppm)

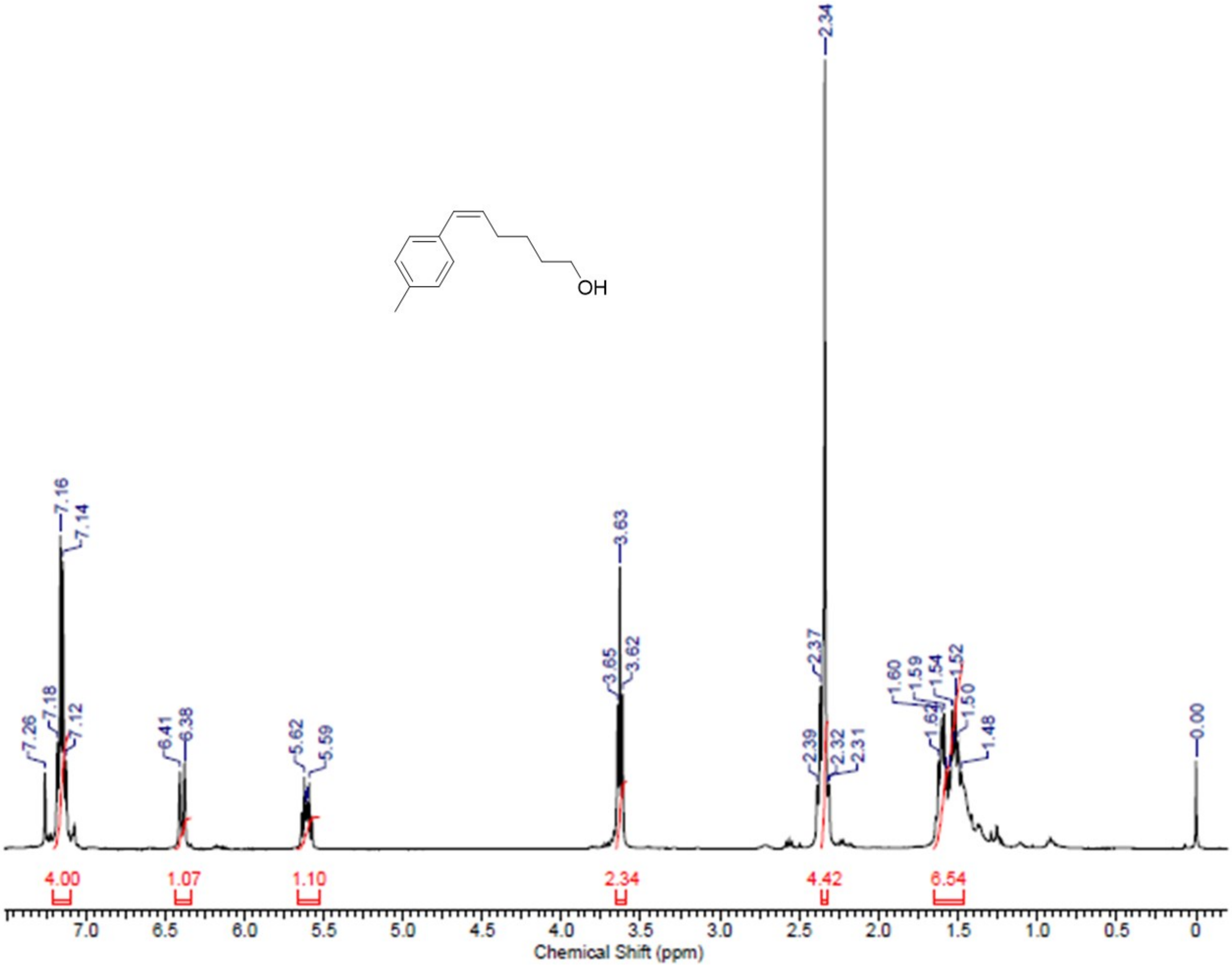

OH
7.36
7.34
7.22
7.20
6.59
6.56
5.90
5.89
5.86
5.84
4.45
4.43
1.72
1.25
2.11
1.00
1.04
2.21
1.13
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


136.60
131.37
130.79
128.81
128.29
127.24
77.45
77.14
76.81
59.58
OH
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)

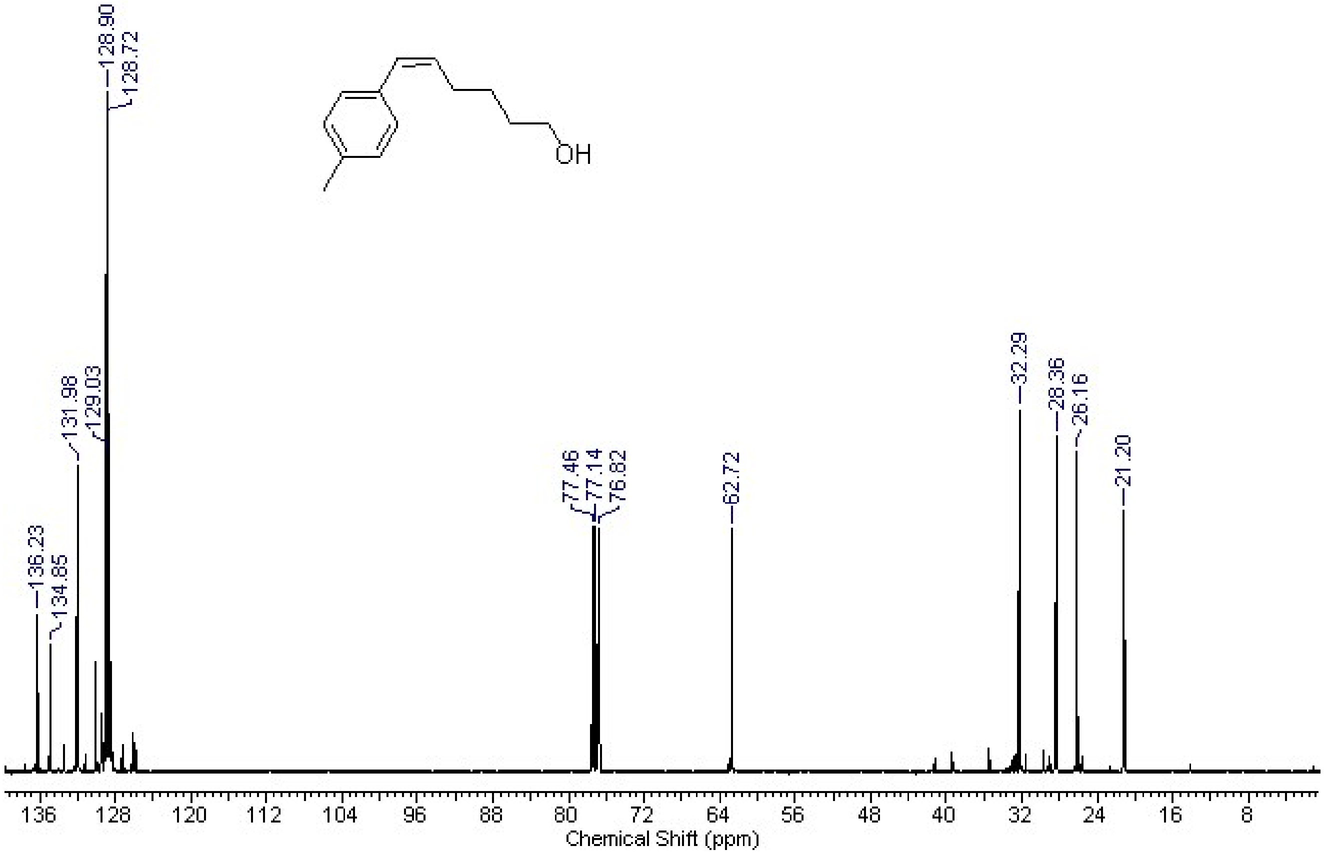

OH
7.39
7.37
7.26
7.24
7.22
6.56
6.53
5.86
5.83
2.46
2.45
2.07
1.49
2.32
1.03
1.03
3.37
1.00
6.29
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



MeO
OH
7.34
7.32
6.86
6.84
6.40
6.37
5.70
5.67
3.80
3.78
1.87
1.37
0.07
2.04
2.00
0.98
1.00
3.64
1.30
6.16
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
0
Chemical Shift (ppm)



OH
7.26
7.18
7.16
7.14
7.12
6.41
6.38
5.62
5.59
3.65
3.63
3.62
2.39
2.37
2.34
2.32
2.31
1.62
1.60
1.59
1.54
1.52
1.50
1.48
0.00
4.00
1.07
1.10
2.34
4.42
6.54
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
0
Chemical Shift (ppm)



OH
136.23
134.85
131.98
129.03
128.90
128.72
77.46
77.14
76.82
62.72
32.29
28.36
26.16
21.20
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

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