Supplementary Information (SI) for Green Chemistry.

Supplementary Information

Reductive amidation of polylactic acid with nitro compounds using nickel based nanocatalysts

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S1. Materials and methods

Polylactic acid (4032D size) was bought from Nature Works, USA. All nitro compounds were obtained commercially from various chemical companies. Nickel nitrate hexahydrate ($Ni(NO_3)_2$•$6H_2O$) and methanol solvent (HPLC grade, ≥99.8%) were obtained from Fisher Chemical. iso-Propanol was obtained from Across organics.

XRD powder patterns were recorded on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD) using Cu Kα radiation (λ = 1.5406 Å).

XPS measurements were performed in VG ESCALAB220iXL with monochromate AlKα radiation (E = 1486.6 eV).

TEM measurements were performed on a JEM-2100 operating at an accelerated voltage of 200 kV. The sample was ultrasonicated in ethanol solution, and a drop was deposited on a copper grid covered with a holey carbon membrane for observation.

The surface area and porosity were carried out by the N_2 adsorption isotherm using the Brunauer-Emmett-Teller (BET) method on an ASAP 2020 Micromeritics instrument. Before analysis, all samples were degassed at 200 °C for 6 h to desorb moisture and impurities from their surfaces. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model from the desorption branch.

Raman spectroscopy with excitation wavelength of 532 nm was performed using a RENISHAW inVia Raman microscope equipped with a CCD detector.

^1H spectra were recorded on Bruker AV 300 using DMSO-d6 solvents. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) in Hz.

All catalytic reactions were performed in glass vials by placing them in 250 mL quartz fitted autoclaves.

S2. Procedure for catalyst preparation

All catalysts mentioned in this work were prepared via the same procedure. A typical procedure for the preparation of optimal catalyst (Ni-L@C-800) is as follows: In a round bottomed flask, 0.574 g of $Ni(NO_3)_2$•$6H_2O$ and 0.376 g o-Phenylenediamine are stirred in methanol (50 mL) for 10 h at room temperature. Then, the active carbon support (2.0 g) was added, and the mixture was stirred for another 12 h at room temperature. After that, menthol was removed by rotary evaporation at 50 °C/350 mPa, the material obtained was dried at 100 °C in oven for 8 h. Finally, the resulting black colored solid material was grinded to fine powder and pyrolyzed at 800 °C/ 2 h under argon.

S3. Catalyst Characterization

Table S1. Hydrogenation of 4-fluoronitrobenzene.

Entry	Solvent	T(°C)/t(h)	Conversion, %	Yield, %
1	Toluene	140/2	78	78
2	Methanol	140/2	65	65
3	Ethanol	140/2	60	60
4	Cyclohexane	140/2	24	24

Reaction conditions: 0.5 mmol 4-fluoronitrobenzene, 20 mg Ni-L@C-800 (3 mol% Ni) , 20 bar H_2, 2mL solvent, 140 °C, GC yield.

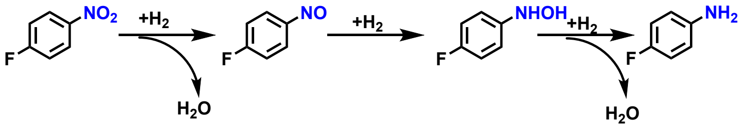


Figure S1. The mechanism of nitro compound reduction.

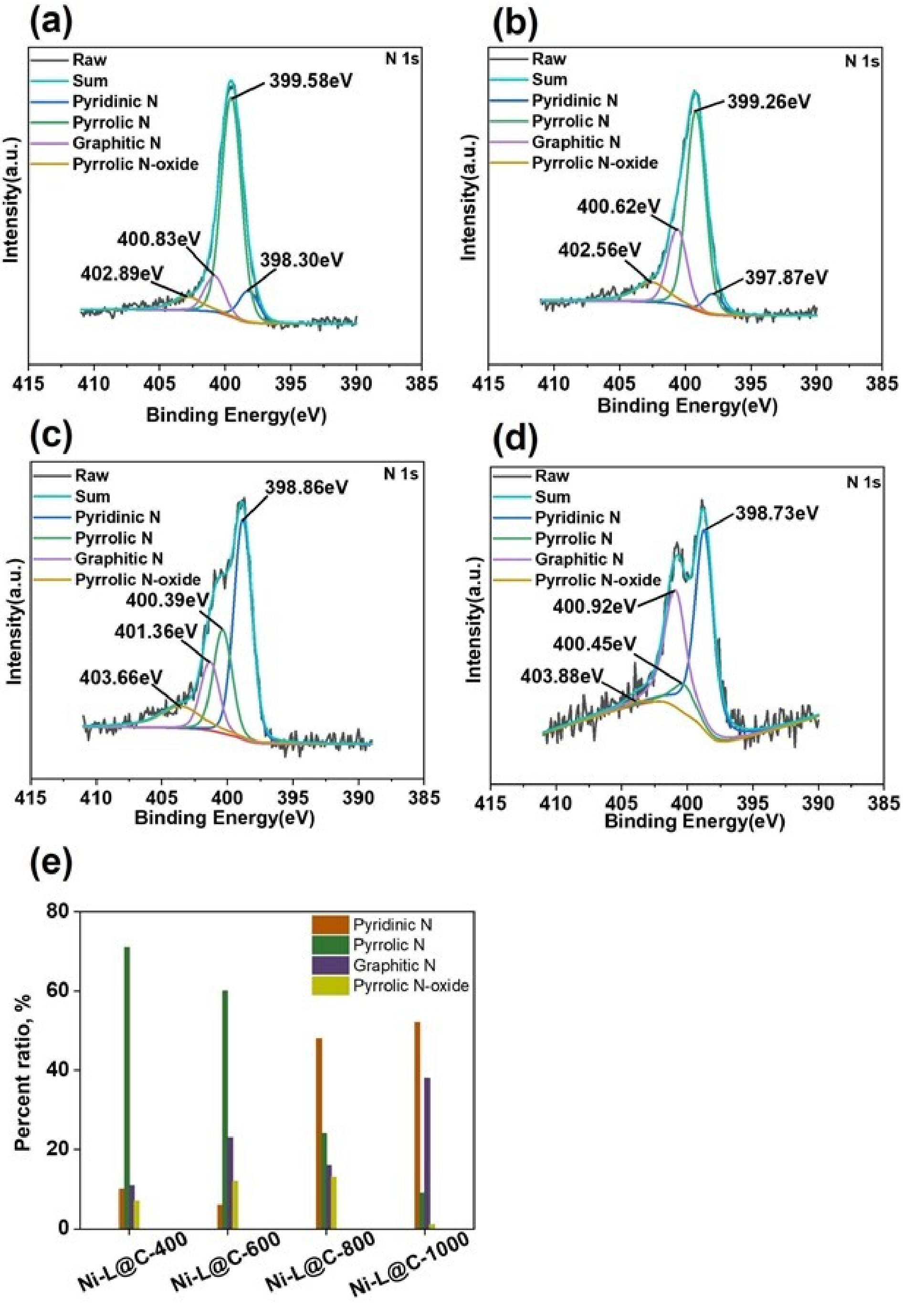


Figure S2. N 1S XPS spectra of selected samples and the percent of these four types of nitrogen species. (a) Ni-L@C-400, (b) Ni-L@C-600, (c) Ni-L@C-800, (d) Ni-L@C-1000.

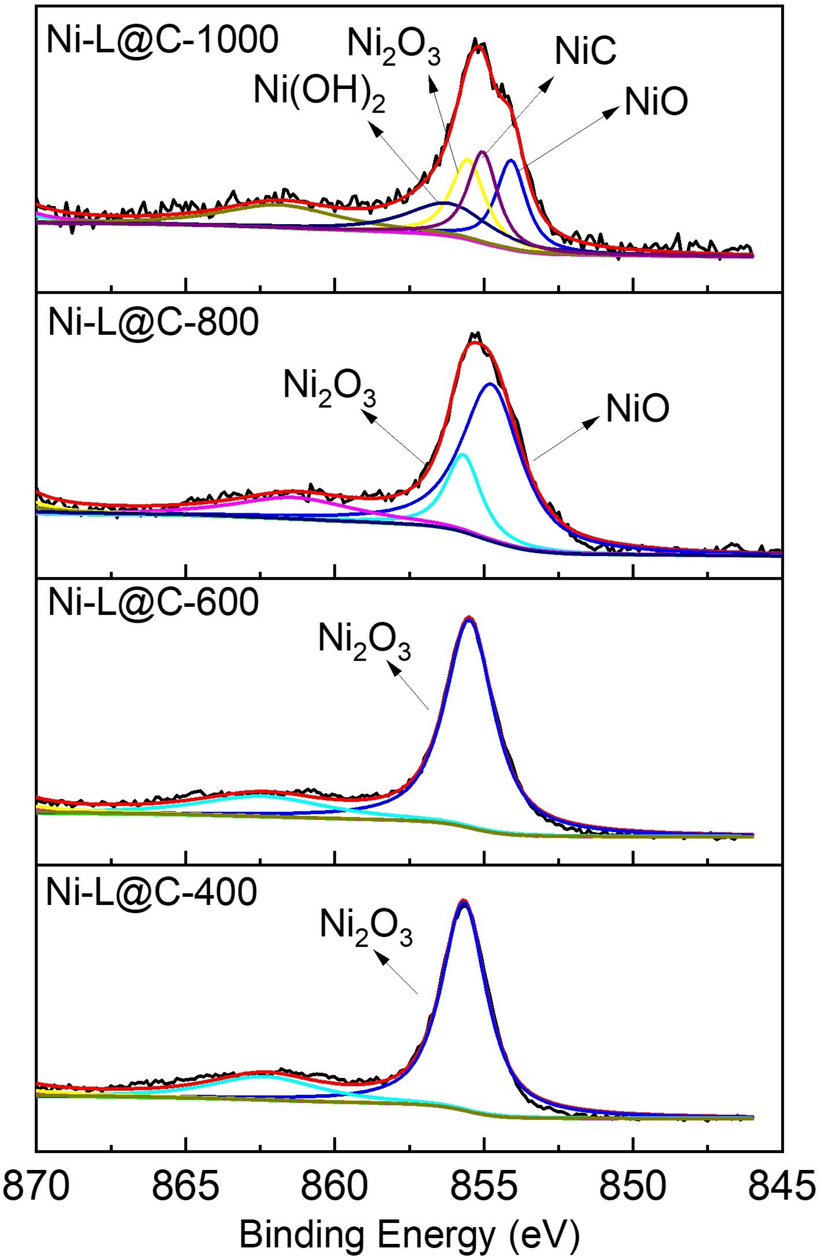


Figure S3. The Ni2P$_{3/2}$ XPS spectra of Ni-L@C-400, Ni-L@C-600, Ni-L@C-800 and Ni-L@C-1000.

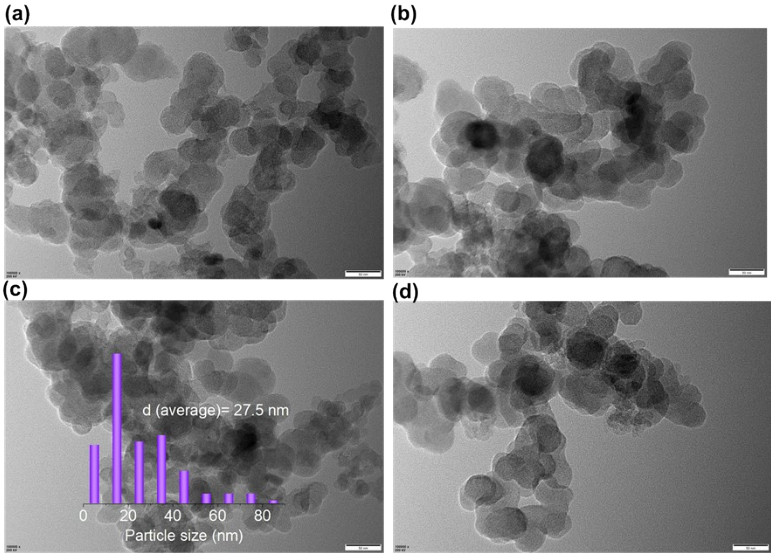


Figure S4. The TEM images of Ni-L@C-600.

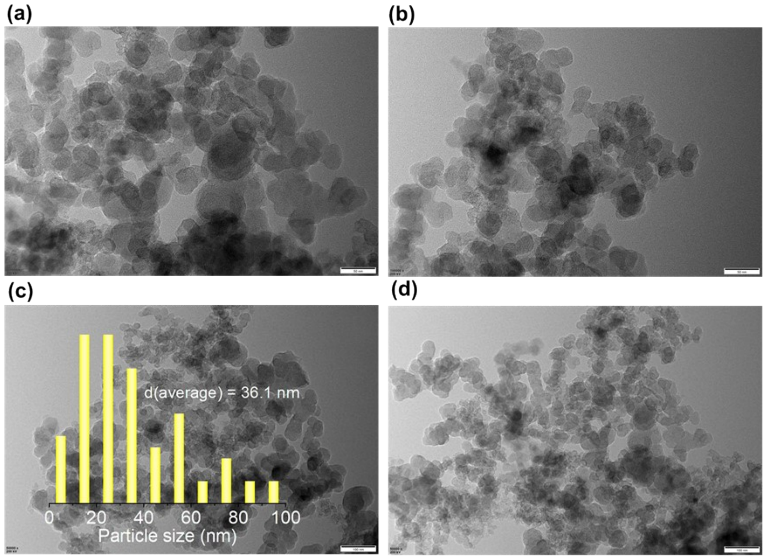


Figure S5. The TEM images of Ni-L@C-1000.

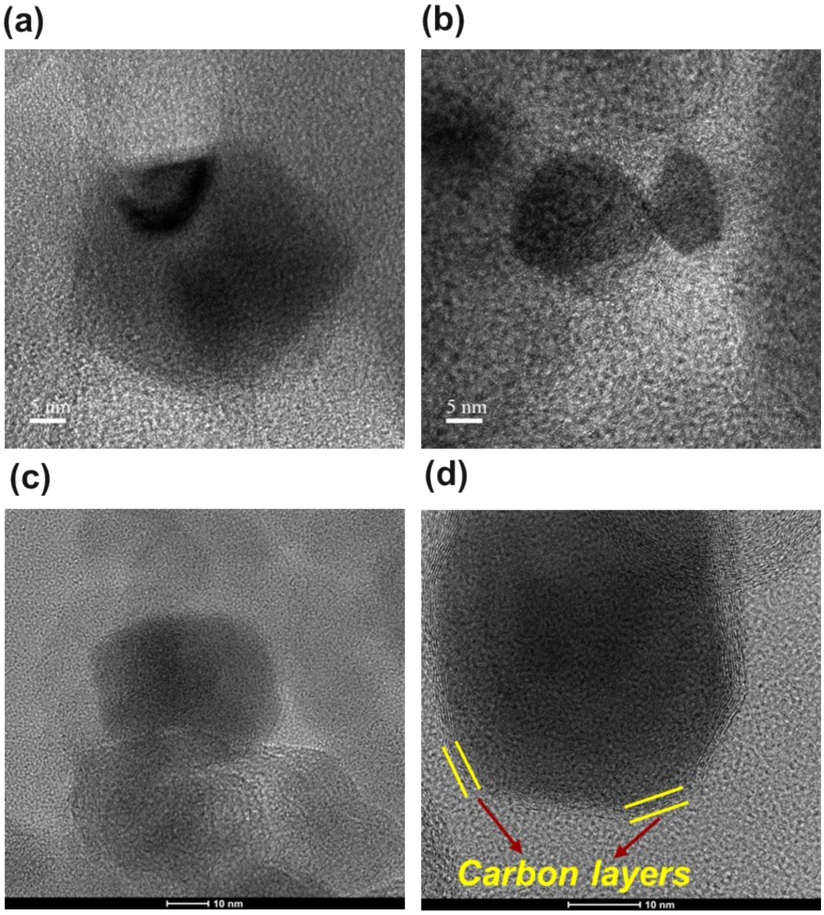


Figure S6. High resolution TEM images of (a)Ni-L@C-400, (b)Ni-L@C-600, (c)Ni-L@C-800, (d)Ni-L@C-1000.

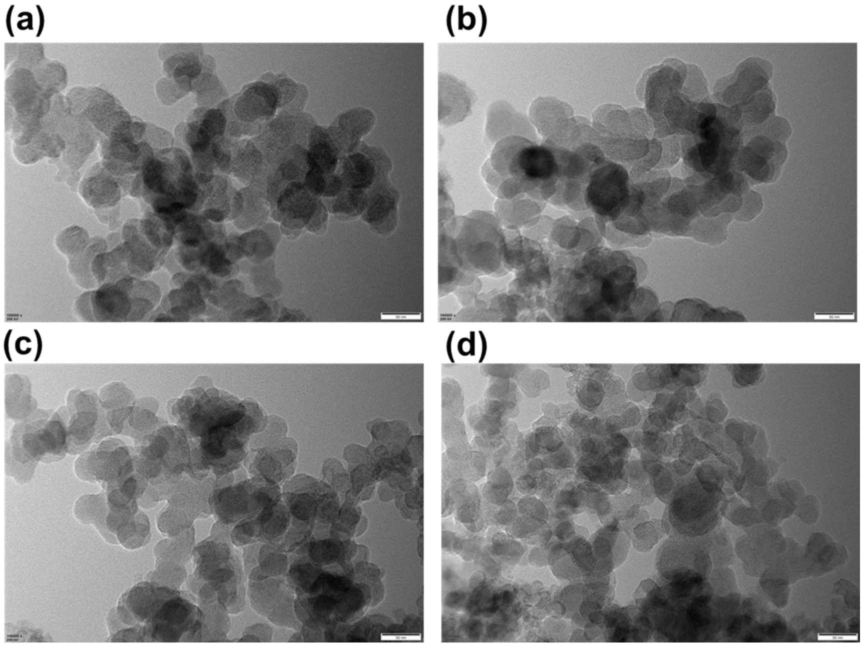


Figure S7. TEM images of (a)Ni-L@C-400, (b)Ni-L@C-600, (c)Ni-L@C-800, (d)Ni-L@C-1000.

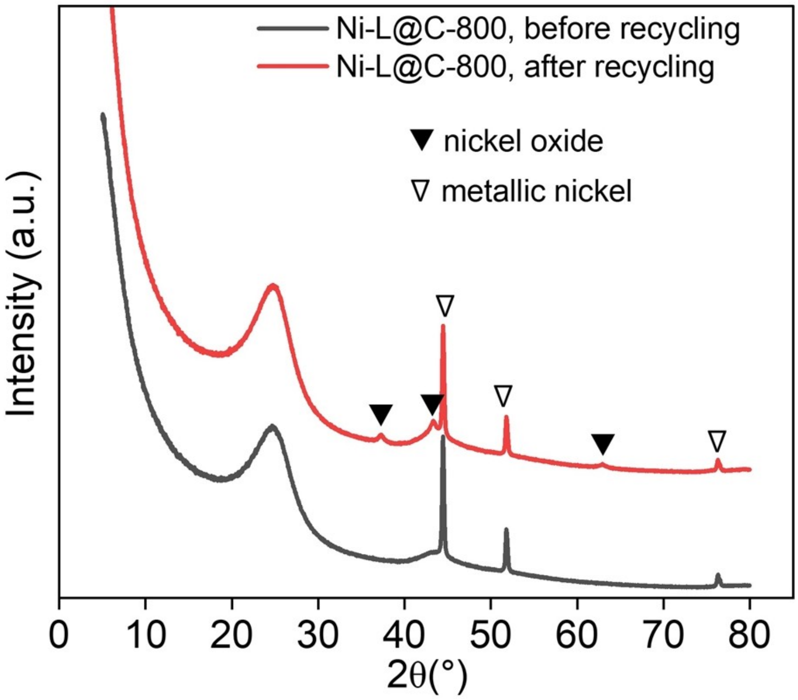


Figure S8. XRD spectra of Ni-L@C-800 material, before- and after- recycling experiments.

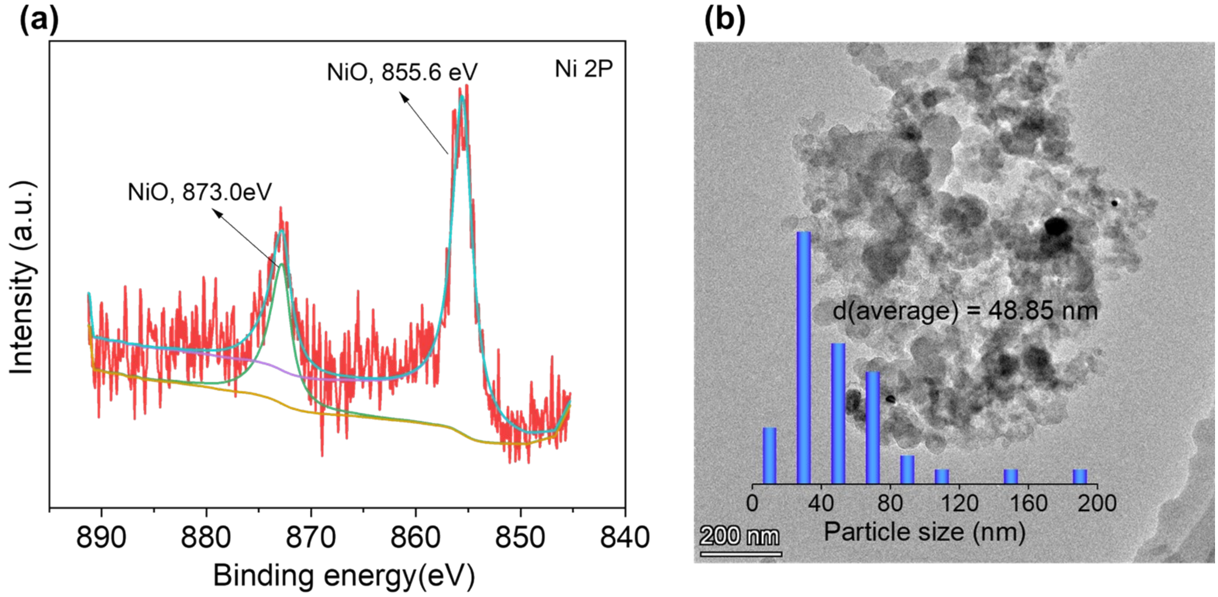


Figure S9. XPS and TEM characterization of Ni-L@C-800 material after- recycling experiments.

Table S2. The loading amount of Ni-L@C-800 catalysts.

Cycle	Loading amount (mg)	Nickel loading
0	30	4.4wt%
1	30	---
2	29	---
3	29	---
4	28	---
5	27	4.3wt%

Table S3. Textural properties of investigated samples.

Sample	$S_{BET}(m^2g^{-1})$	Average pore Diameter (nm)
Ni-L@C-400	59	26.4
Ni-L@C-600	112	20.0
Ni-L@C-800	145	15.8
Ni-L@C-1000	151	13.4

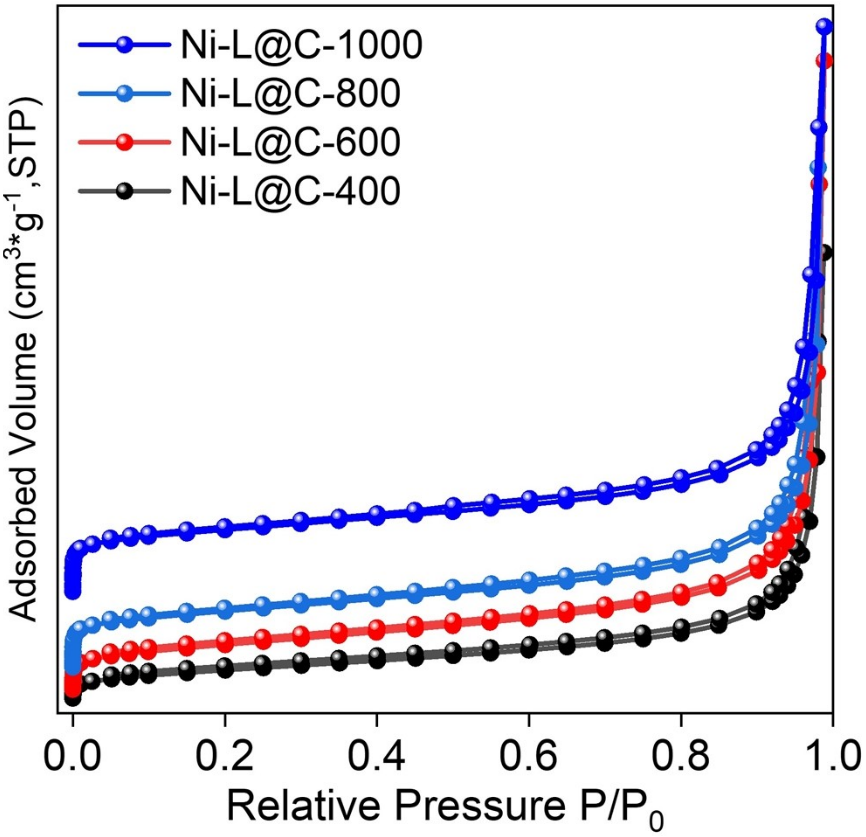


Figure S10. Nitrogen adsorption–desorption isotherms of Ni@C material calcined at different temperatures.

S4. General procedures for the reactions

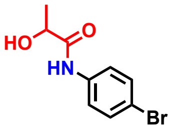
A 4 mL dried glass vial was charged with magnetic stirring bar, 0.5 mmol substrate nitro compounds, 30mg PLA. Then, 0.8 mL toluene and 0.2 mL H_2O were added followed by the addition of catalyst (20 mg). Then, the vial was fitted with septum, cap and needle and placed in into a 250 ml autoclave (7 vials at a time). The autoclave was flushed with H_2 gas twice and pressurized to 20 bar. Then, the autoclave was placed into an block preheated at 140 °C (Placed 30 minutes before counting the reaction time in order to attain reaction temperature) and the reactions were stirred for required time. After the completion of reaction, the autoclave was cooled to room temperature. The remaining H_2 in the autoclave was released and the reaction vials were taken out from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The resulting reaction products were purified by column chromatography (conditions: silica, n-hexane/ethyl acetate mixture). The purified products were characterized by NMR.

The upscaling reaction on 20 g scale was performed using 2 L autoclave.

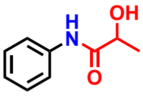
S5. Catalyst recycling

The reaction procedure is same with S4. After each run, the catalysts was filtered off and washed thoroughly with ethyl acetate. Then, dry it in a oven at 60°C. Next, it is used as the catalysts for the next run.

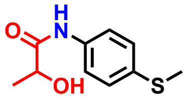
S6. NMR data



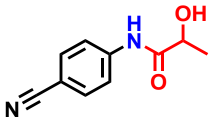
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.76 (s, 1H), 7.73 – 7.62 (m, 2H), 7.49 – 7.37 (m, 2H), 5.72 (d, *J* = 5.0 Hz, 1H), 4.18 – 4.03 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H).



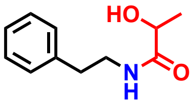
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.57 (s, 1H), 7.73 – 7.61 (m, 2H), 7.33 – 7.20 (m, 2H), 7.02 (tt, *J* = 7.3, 1.2 Hz, 1H), 5.70 (d, *J* = 5.2 Hz, 1H), 4.12 (qd, *J* = 6.7, 5.1 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H).



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.60 (s, 1H), 7.77 – 7.58 (m, 2H), 7.27 – 7.12 (m, 2H), 4.14 (t, *J* = 6.7 Hz, 1H), 2.41 (s, 3H), 1.31 (d, *J* = 6.8 Hz, 3H).

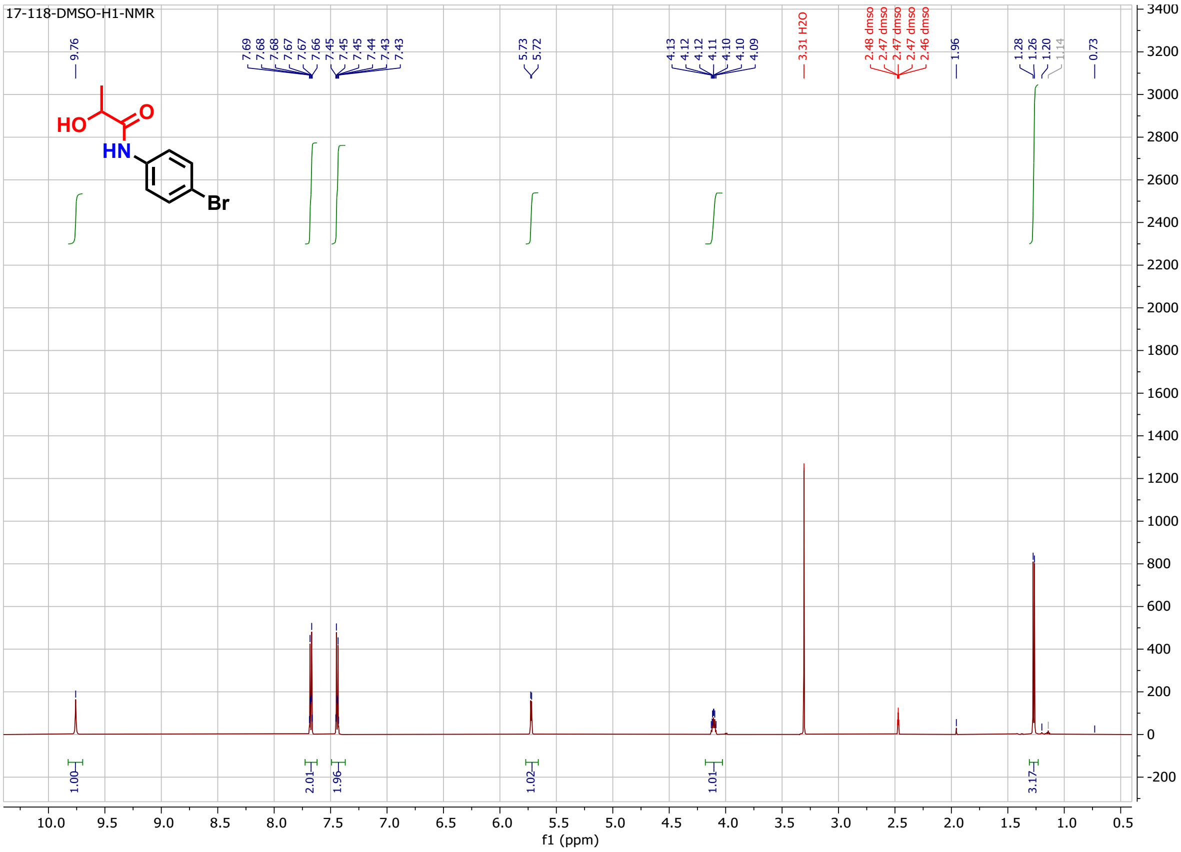


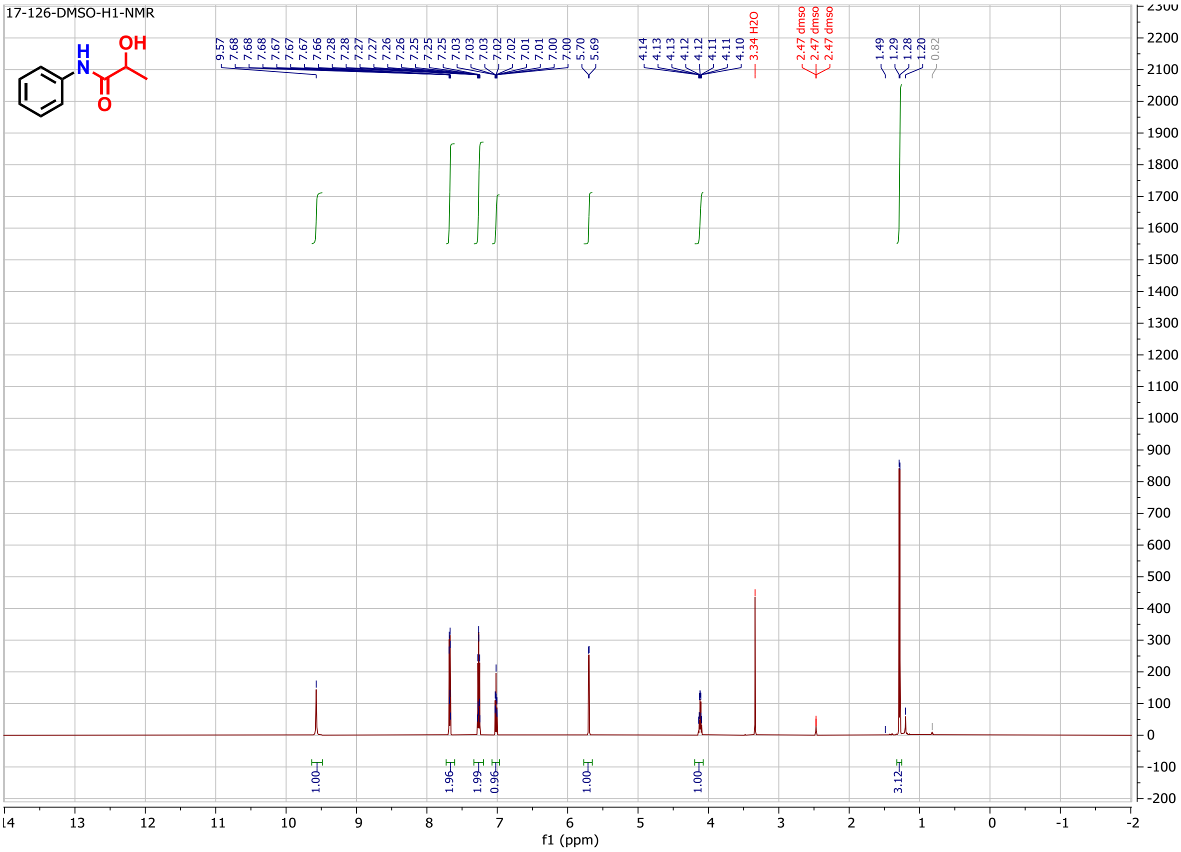
^{1}H NMR (600 MHz, DMSO-d_6) δ 9.63 (d, *J* = 5.7 Hz, 1H), 7.72 (td, *J* = 7.7, 6.8, 3.9 Hz, 2H), 7.21 – 6.97 (m, 2H), 5.69 (s, 1H), 4.18 (t, *J* = 6.9 Hz, 1H), 2.10 – 1.95 (m, 4H), 1.33 (t, *J* = 6.5 Hz, 3H).

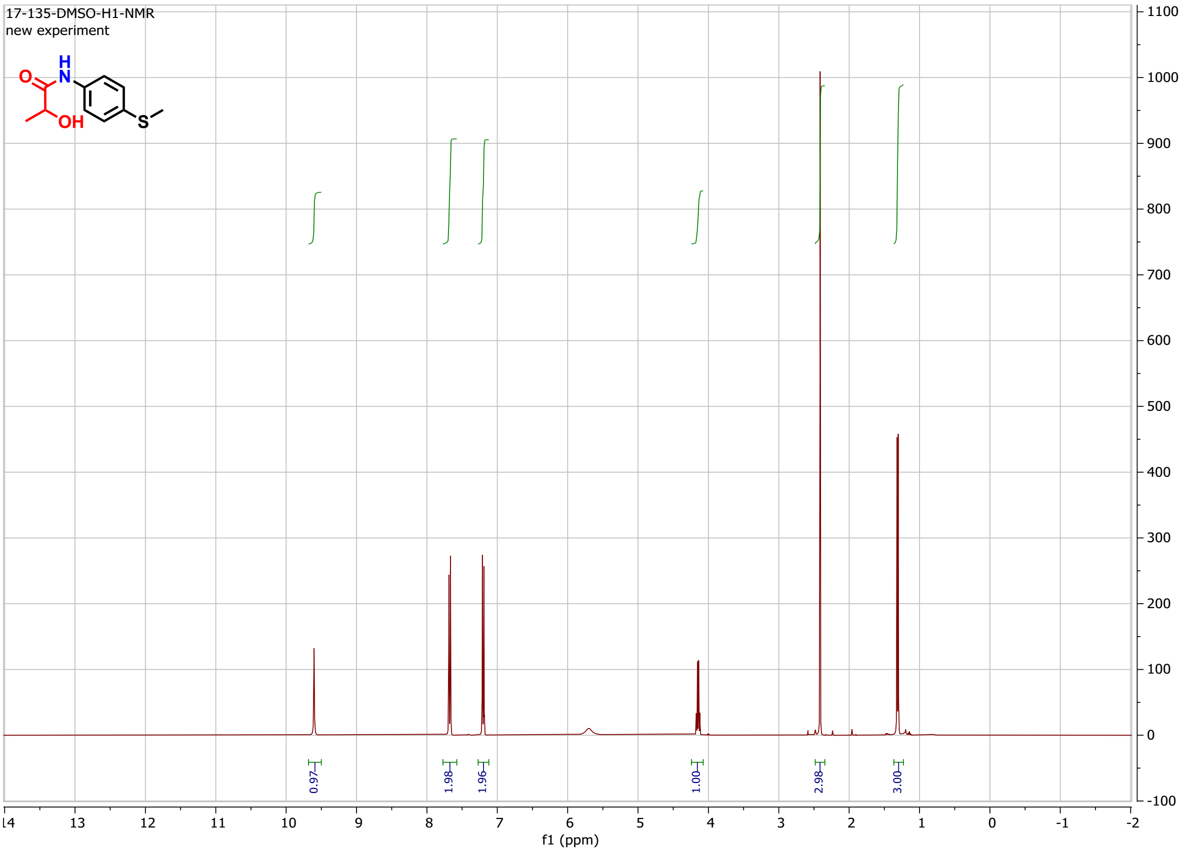


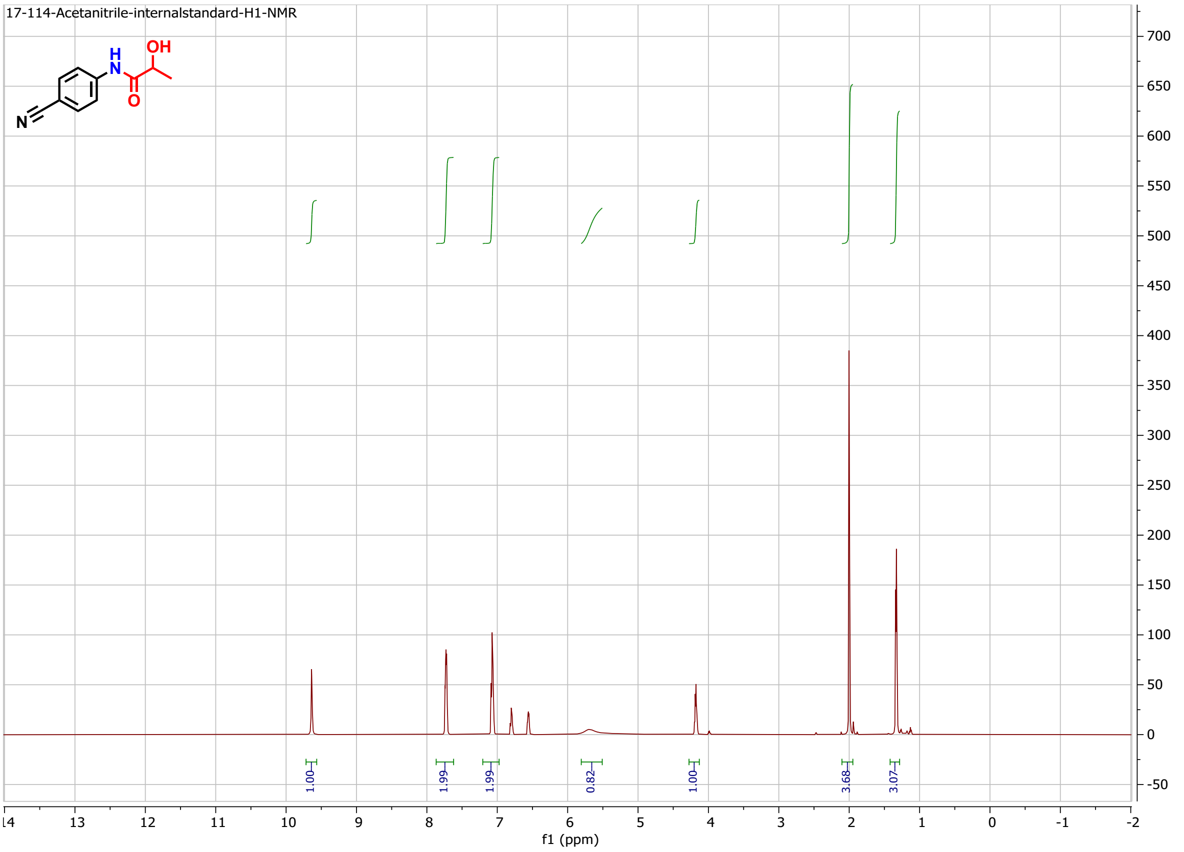
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 7.65 – 7.51 (m, 2H), 6.94 – 6.77 (m, 3H), 5.64 (d, *J* = 5.0 Hz, 1H), 4.16 – 4.03 (m, 1H), 3.70 (s, 4H), 1.27 (d, *J* = 6.7 Hz, 3H).

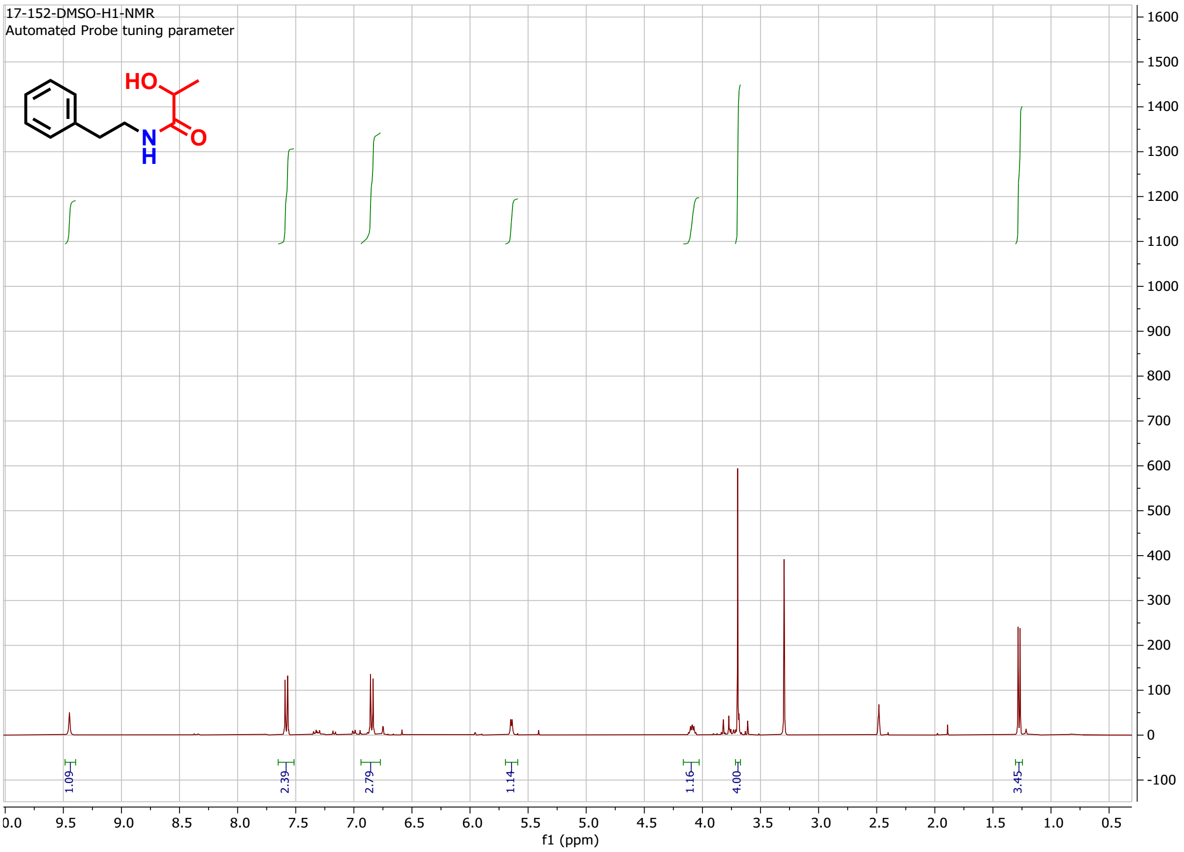
S7. NMR spectra


17-118-DMSO-H1-NMR
HO
O
HN
Br
9.76
7.69
7.68
7.68
7.67
7.67
7.66
7.45
7.45
7.45
7.44
7.43
7.43
5.73
5.72
4.13
4.12
4.12
4.11
4.10
4.10
4.09
3.31 H2O
2.48 dmso
2.47 dmso
2.47 dmso
2.47 dmso
2.46 dmso
1.96
1.28
1.26
1.20
1.14
0.73
1.00
2.01
1.96
1.02
1.01
3.17
10.0
9.5
9.0
8.5
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
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


17-126-DMSO-H1-NMR
H
N
OH
O
9.57
7.68
7.68
7.68
7.67
7.67
7.66
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.03
7.03
7.03
7.02
7.01
7.01
7.00
5.70
5.69
4.14
4.13
4.13
4.12
4.12
4.11
4.11
4.10
3.34 H2O
2.47 dmso
2.47 dmso
2.47 dmso
1.49
1.29
1.28
1.20
0.82
1.00
1.96
1.99
0.96
1.00
1.00
3.12
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


17-135-DMSO-H1-NMR
new experiment
H
N
O
OH
S
0.97
1.98
1.96
1.00
2.98
3.00
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


17-114-Acetanitrile-internalstandard-H1-NMR
H
N
OH
O
N
1.00
1.99
1.99
0.82
1.00
3.68
3.07
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)


17-152-DMSO-H1-NMR
Automated Probe tuning parameter
HO
N
H
O
1.09
2.39
2.79
1.14
1.16
4.00
3.45
0.0
9.5
9.0
8.5
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
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100