Supplementary Material

Reduction of phenylacetylenes using Raney Ni–Al alloy, Al powder in the presence of noble metal catalysts in water

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1. Experimental Section

1.1 General remarks

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on Shimadzu GCMS-QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100V using a direct-inlet system. GLC analyses were performed by Shimadzu gas chromatographer, GC-2010.

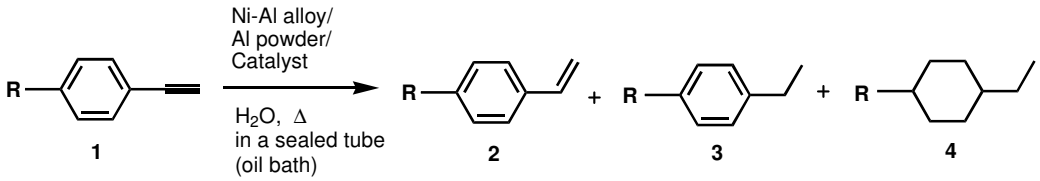
1.2 Reagent list

Raney Ni–Al alloy (500 wt%), Al powder (500 wt%) (53–150 μm, 99.5%) (Wako), Pt/C, Pd/C, Ru/C and Rh/C (5 wt%) (Wako), Distilled water (Wako).

1.3 Typical procedure

The mixture of a substrate (20 mg, 0.20 mmol) (Wako), Raney Ni–Al alloy (500 wt%), Al powder (500 wt%) (53–150 μm, 99.5%) (Wako) and Pt/C, Pd/C, Ru/C or Rh/C (20 mg) (4.5 mole % metal) was added to water (0.5 mL) (Wako distilled water). After heating the mixture at 60–120 °C for 6–12 h, it was cooled to room temperature. The solution was then diluted with 1 mL water and stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (3 × 2 mL) as per the reported procedure.[37] The combined organic layers were dried over anhydrous $MgSO_4$ and filtered through a porous cotton plug followed by concentrating in vacuum to afford the corresponding hydrogenated product. The yields were determined by GLC analysis using the standard compound (1,2,3,4-tetrahydronaphthalene), and the products were identified by GC–MS.

Reduction of phenylacetylenes (1)



1a : R = H ,
1b : R = CH_3 ,
1c : R = OCH_3 ,
1d : R = $C(CH_3)_3$

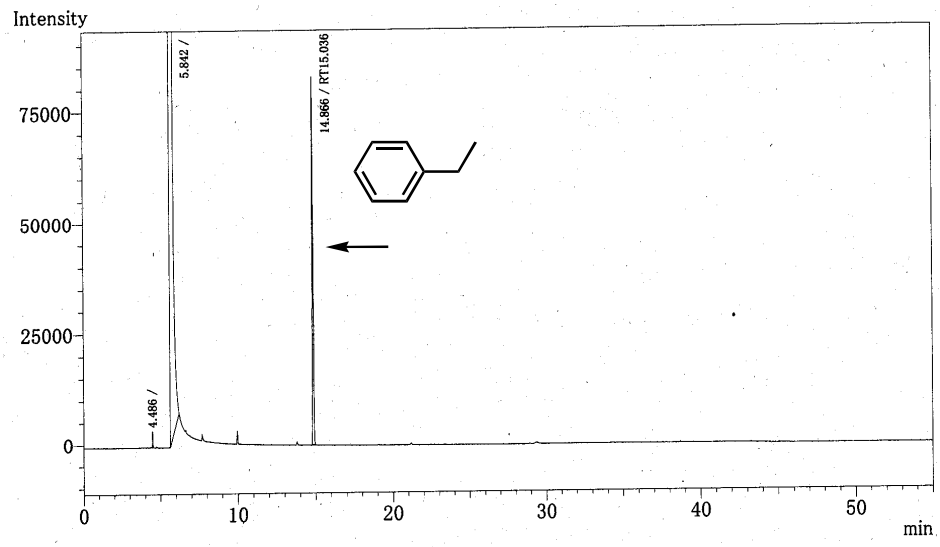
Scheme S1. Reduction of phenylacetylene by using Al powder in the presence of catalyst in water.

GC Conditions:

	Rate (°C/min)	Temperature (°C)	Hold (min)
1	-	35	-
2	2	100	10

GC Spectra

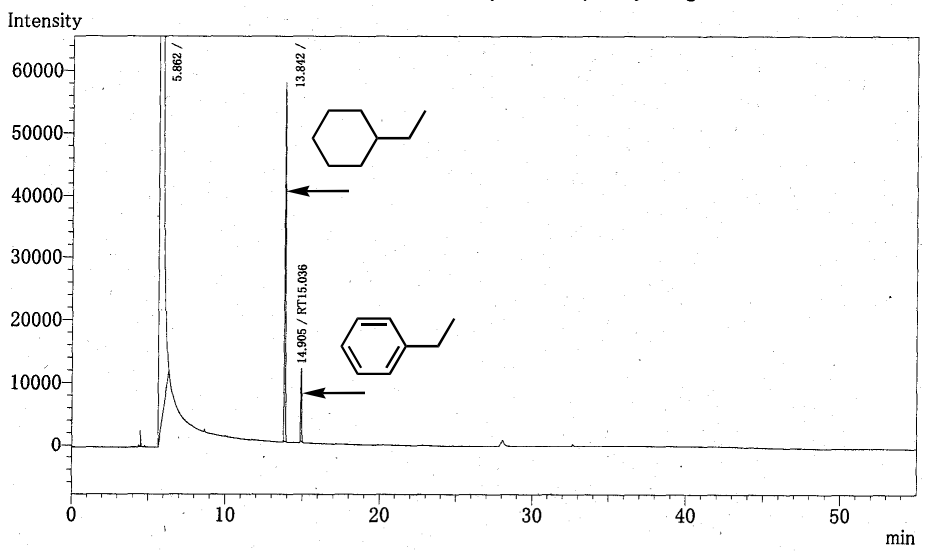
Table 2 Entry 3



ピーク番号	保持時間	面積	高さ	濃度	単位	マーク	ID#	化合物名
1	4.486	7377	3731	0.005				
2	5.842	157059673	21930309	99.772				
3	14.866	352021	82866	0.224	%		2	RT15.036
合計		157419071	22016906					

Reduction of phenylacetylene using Ni-Al and Al powder in H_2O at 120 °C for 6 h

Table 5 Entry 1



ピーク番号	保持時間	面積	高さ	濃度	単位	マーク	ID#	化合物名
1	5.862	155067651	21657575	99.813				
2	13.842	241182	57255	0.155				
3	14.905	48879	11602	0.031	%		2	RT15.036
合計		155357712	21726432					

Reduction of phenylacetylene using Ni-Al, Al powder and Pt/C in H_2O at 60 °C for 12

Table for figure 1

Reduction of phenylacetylene (**1a**) using Raney Ni–Al, Al powder and noble metal catalysts in H_2O[a,b]

Entry	Temp. (°C)	Pt/C	Pd/C	Ru/C	Rh/C
1	120	30.9	4.5	0	37
2	90	31.3	7.5	16	27.5
3	60	33.7	3.4	25.9	26.3

[a]Substrate: 20 mg (0.20 mmol), Raney Ni–Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol% (metal), H_2O: 0.5 mL.

[b]Conditions: time: 6 h.

[c]The yields were determined by GLC.

Table for figure 2

Reduction of phenylacetylene (**1a**) using Raney Ni–Al, Al powder and Pt/C in H_2O[a,b]

Entry	Temp. (°C)	Yield (%)[c] **3**	**4**
1	60	13.1	86.9
2	80	28.7	71.3
3	120	50	50

[a]Substrate: 20 mg (0.20 mmol), Raney Ni–Al: 100 mg (500 wt%), Al powder: 100 mg (500 wt%), catalyst: 4.5 mol% (metal), H_2O: 0.5 mL.

[b]Conditions: time: 12 h.

[c]The yields were determined by GLC.