Supporting Information

Reduction of carbonyl compounds by 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 GC-MS-QP5050A Ultrahigh Performance Mass Spectrometer AOC-20I, 100V using a direct-inlet system. GLC analyses were performed with a Shimadzu gas chromatograph, GC-2010.

1.2 Reagent list

Raney Ni–Al alloy (50:50, wt %) (Wako), 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

To the mixture of substrate (20 mg, 0.11mmol) (Wako), Raney Ni–Al alloy (50:50, wt %), Al powder (500 wt %) (53–150 μm, 99.5%) (Wako) and Pt/C, Pd/C, Ru/C and Rh/C (20 mg) (4.5 mole % metal) (Wako) was added H_2O (0.5 mL) (Wako distilled water). After heating at 60–80 °C for 3–18 h, the mixture was cooled to room temperature. The solution was diluted with 1 mL of water and then stirred overnight at room temperature in a sealed tube. After 24 h, the solution was extracted with diethyl ether (2 mL× 3) following the reported procedures [32]. The organic layer was combined, dried with $MgSO_4$, filtered through a cotton layer and concentrated in vacuum to give the corresponding hydrogenated product. The yields were determined by GLC analysis by using the standard compound (1,2,3,4-tetrahydronaphthalene) and products were identified by GC-MS.

Reduction of benzophenone (1a)

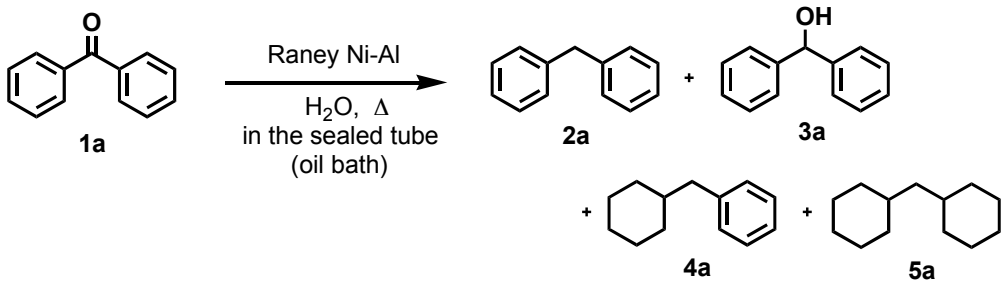


Table S1 Effects of the reaction temperature for hydrogenation of benzophenone (**1a**) by using Raney Ni–Al alloy in water[a,b]

Entry	Temp. (°C)	**2a**	**3a**	Yield(%)[d,e] **4a**	**5a**	recovery **1a**
1	r.t	0	0	0	0	100
2	r.t[c]	91	0	8	0	1
3	40	15	38	1	1	46
4	60	93[86]	0	7	0	0
5	80	77	0	18	3	2
6	100	49	0	46	4	0

[a]Substrate: 20 mg, Ni–Al alloy: 100 mg (500 wt%), H_2O: 0.5 mL, [b]Conditions: time: 3 h, [c]time: 24 h, [d]The yields were determined by GLC, [e]The Isolated yields are shown in square bracket.

Table S2 Effects of time for hydrogenation of benzophenone (**1a**) by using Raney Ni–Al alloy in water[a,b]

Entry	Time (h)			Yield(%)[c,d]		recovery
		2a	**3a**	**4a**	**5a**	**1a**
1	0.25	2	0	0	0	98
2	0.5	8	16	0	0	76
3	1	14	0	2	0	84
4	2	76	6	5	0	12
5	2.5	78	3	7	0	12
6	3	93[86]	0	7	0	0
7	4	90	2	7	0	0
8	8	88	1	10	0	0

[a] Substrate: 20 mg, Ni–Al alloy: 100 mg (500wt%), H_2O: 0.5 mL, [b] Condition: temp: 60 °C, [c] The yields were determined by GLC, [d] The Isolated yields are shown in square bracket.

Table S3 Effects of catalysis for hydrogenation of benzophenone (**1a**) in water[a,b]

Entry	Raney Ni–Al (wt%)	**2a**	**3a**	Yield(%)[c,d] **4a**	**5a**	recovery **1a**
1	50	0	0	0	0	100
2	100	0	0	0	0	100
3	200	2	0	0	0	98
4	300	79	13	3	0	5
5	400	85	0	7	0	6
6	500	93[86]	0	7	0	0

[a] Substrate: 20 mg, H_2O: 0.5 mL, [b] Conditions: time: 3 h, temp: 60 °C, [c] The yields were determined by GLC, [d] The Isolated yields are shown in square bracket.

Table S4 Effects of amount of water for hydrogenation of benzophenone (**1a**) by using Raney Ni–Al alloy [a,b]

Entry	H_2O (mL)			Yield(%)[c,d]		recovery
		2a	**3a**	**4a**	**5a**	**1a**
1	0.25	84	5	9	0	2
2	0.50	93[86]	0	7	0	0
3	0.75	87	0	12	1	0
4	1.0	82	1	10	1	6
5	1.5	73	1	9	1	16
6	2.0	73	1	11	2	13

[a] Substrate: 20 mg, Ni–Al alloy: 100 mg (500wt%), [b] Conditions: time: 3 h, temp: 60 °C, [c] The yields were determined by GLC, [d] The Isolated yields are shown in square bracket.

Reduction of diphenylmethanol (3a)

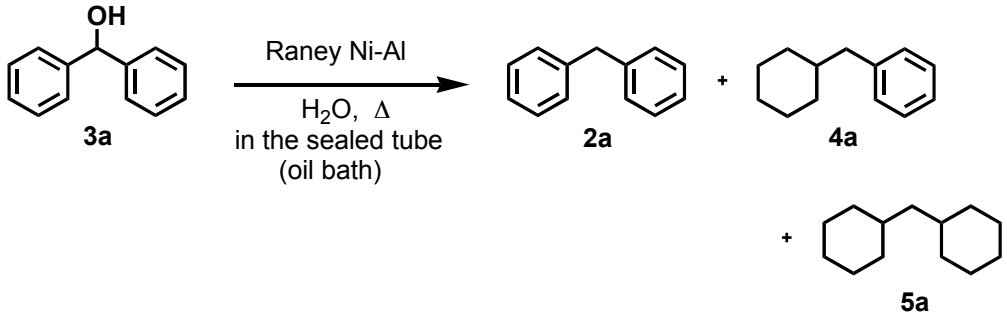


Table S5 Reduction of diphenylmethanol (**3a**) by using Raney Ni–Al alloy in water[a,b]

Entry	Time (h)		Yield(%)[c,d]		recovery
		2a	**4a**	**5a**	**3a**
1	0.25	0	0	0	100
2	0.50	10	0	0	89
3	0.75	24	1	0	75
4	1	27	1	0	72
5	1.5	62	3	0	36
6	2	83	4	0	13
7	2.5	94	6	0	0
8	3	93[86]	7	0	0
9	12	84	16	0	0
10	24	75	25	0	0

[a] Substrate: 20 mg, Ni–Al alloy: 100 mg (500 wt%), H_2O: 0.5 mL, [b] Condition: temp: 60 °C, [c] The yields were determined by GLC, [d] The Isolated yields are shown in square bracket.

Kinetic study of reduction of benzophenone:

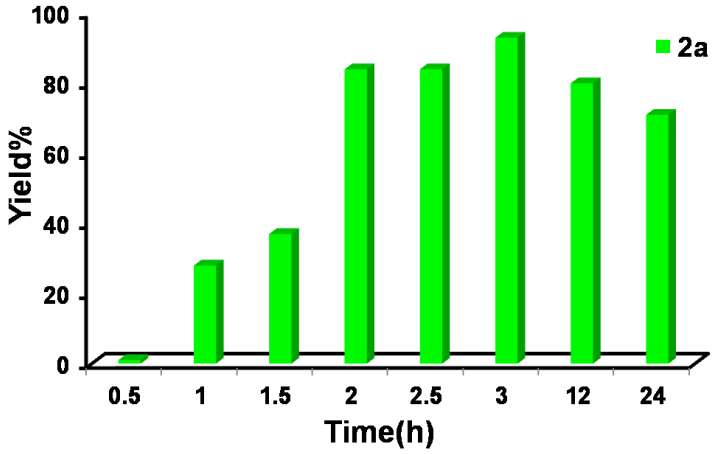


Fig S6: Reduction of benzophenone by using Raney Ni–Al alloy in water; Time effect.

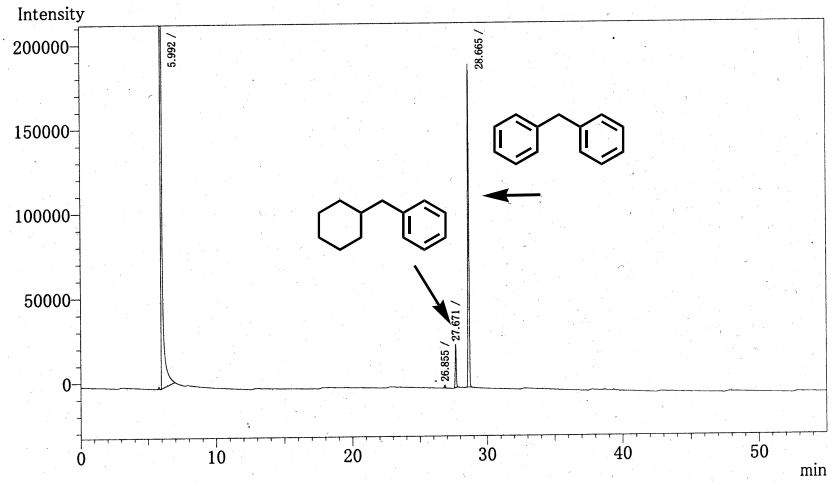
GC Condition:

	Rate (°C/min)	Temperature (°C)	Hold (min)
1	-	100	-
2	2	200	5

and

	Rate (°C/min)	Temperature (°C)	Hold (min)
1	-	100	-
2	4	280	5

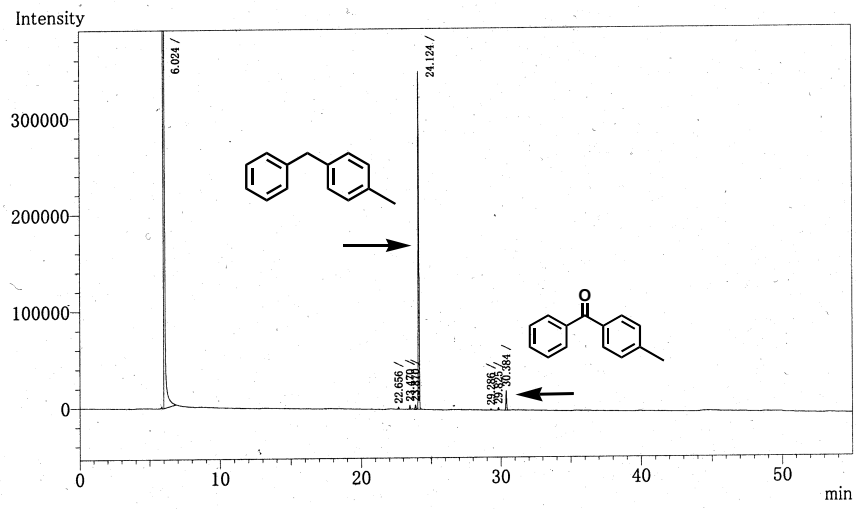
GC of Table 2 Entry 1



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	5.992	107663475	39109268	98.883				
2	26.855	9995	1847	0.009				
3	27.671	138830	25565	0.128				
4	28.665	1067188	189617	0.980				
合計		108879488	39326297					

Fig S7: Reduction of Benzophenone using Ni–Al alloy and H_2O at 60 °C for 3 h

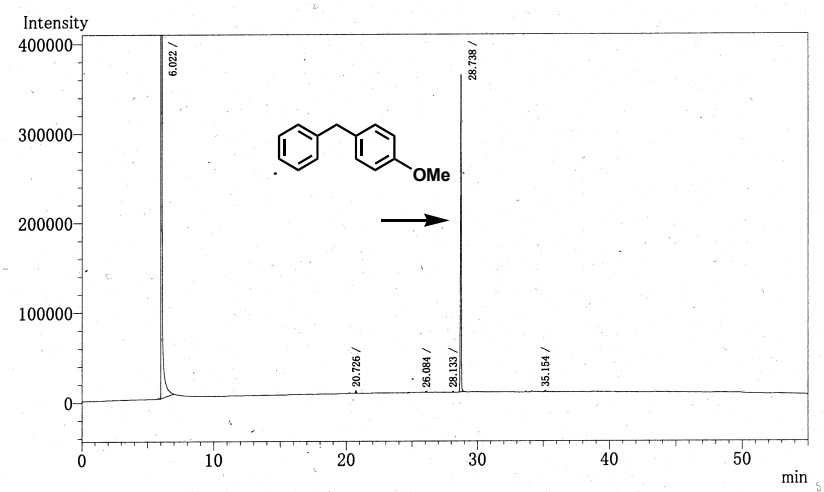
GC of Table 2 Entry 2



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	6.024	109540127	39435692	98.611				
2	22.656	8765	2251	0.008				
3	23.470	16683	4245	0.015				
4	23.870	18745	4690	0.017				
5	24.124	1396341	348337	1.257				
6	29.286	4848	1222	0.004				
7	29.825	11383	2752	0.010				
8	30.384	86065	20560	0.077				
合計		111082957	39819749					

Fig S8: Reduction of 4-Methylbenzophenone using Ni–Al alloy and H_2O at 60 °C for 3 h

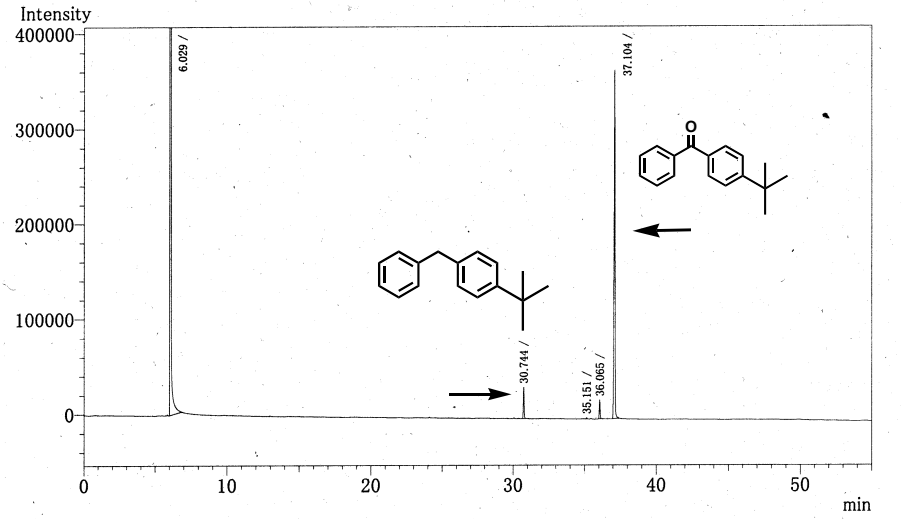
GC of Table 2 Entry 3



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	6.022	108740493	39616917	98.578				
2	20.726	11797	3143	0.011				
3	26.084	5763	1452	0.005				
4	28.133	5501	1359	0.005				
5	28.738	1538628	349785	1.395				
6	35.154	6440	1496	0.006				
合計		110308622	39974152					

Fig S9: Reduction of 4-Methoxybenzophenone using Ni–Al alloy and H_2O at 60 °C for 3 h

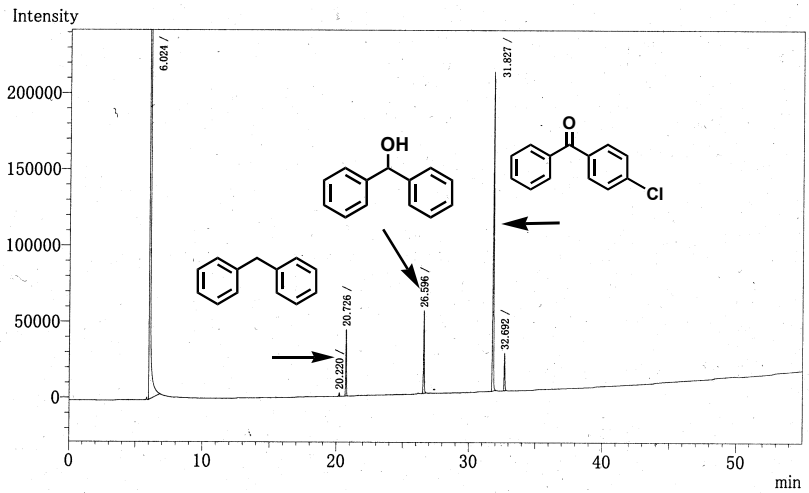
GC of Table 2 Entry 4



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	6.029	107830084	39542059	98.204				
2	30.744	130500	32664	0.119				
3	35.151	5599	1340	0.005				
4	36.065	83803	19576	0.076				
5	37.104	1751683	362514	1.595				
合計		109801669	39958153					

Fig S10: Reduction of 4-*tert*-butylbenzophenone using Ni–Al alloy and H_2O at 60 °C for 3 h

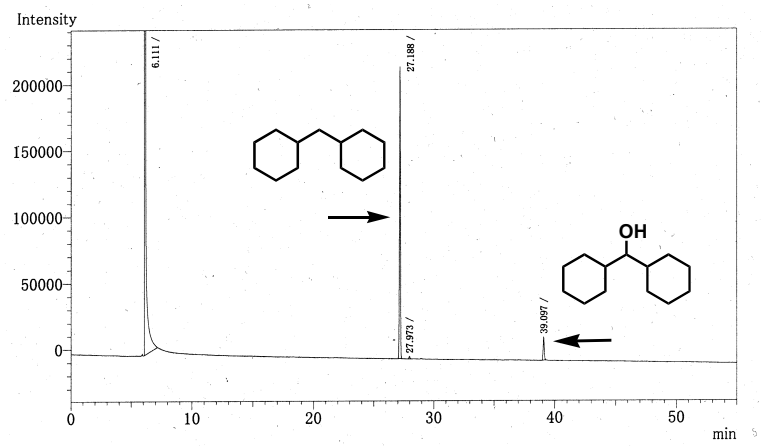
GC of Table 2 Entry 5



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	6.024	107551613	39200228	98.705				
2	20.220	8313	2224	0.008				
3	20.726	156788	43433	0.144				
4	26.596	223091	54101	0.205				
5	31.827	921853	208800	0.846				
6	32.692	101518	24746	0.093				
合計		108963176	39533532					

Fig S11: Reduction of 4-Chlorobenzophenone using Ni–Al alloy and H_2O at 60 °C for 3 h

GC of Table 7 Entry 1



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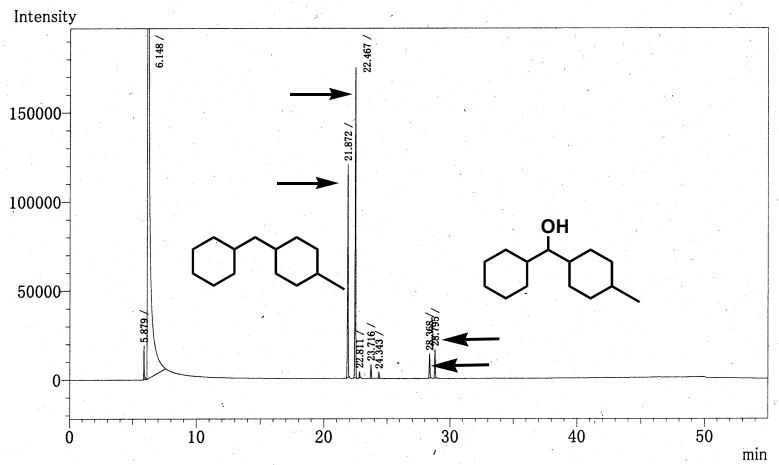
1	6.111	123543986	43163357	98.924				
2	27.188	1221626	220124	0.978				
3	27.973	10155	1889	0.008				
4	39.097	111491	17529	0.089				
合計		124887258	43402899					

Fig S12: Reduction of Benzophenone using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h

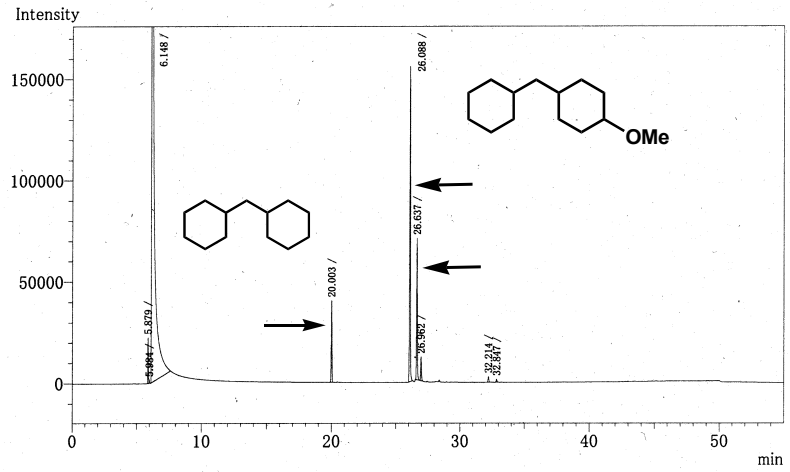
GC of Table 7 Entry 2



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	5.879	48065	18622	0.038				
2	6.148	123594708	42928764	98.920				
3	21.872	450943	118744	0.361				
4	22.467	665102	173346	0.532				
5	22.811	12641	3497	0.010				
6	23.716	31786	7956	0.025				
7	24.343	14407	3573	0.012				
8	28.368	59031	13655	0.047				
9	28.795	67794	16006	0.054				
合計		124944477	43284163					

Fig S13: Reduction of 4-Methylbenzophenone using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h

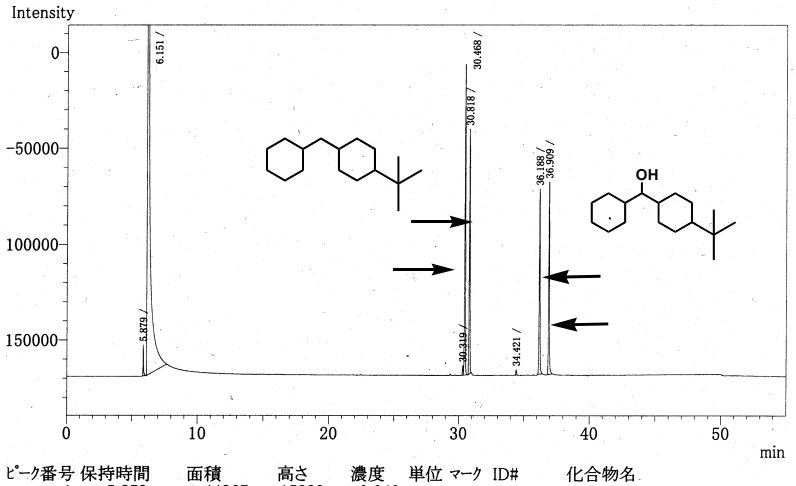
GC of Table 7 Entry 3



ﾋﾟｰｸ番号	保持時間	面積	高さ	濃度	単位	マーク	ID#	化合物名
1	5.879	55738	22055	0.046				
2	5.984	4461	1675	0.004		V		
3	6.148	120963889	42377073	99.021				
4	20.003	149875	40048	0.123				
5	26.088	635235	153734	0.520				
6	26.637	282056	69489	0.231				
7	26.962	50093	11658	0.041				
8	32.214	11798	2793	0.010				
9	32.847	6376	1520	0.005				
合計		122159521	42680045					

Fig S14: Reduction of 4-Methoxybenzophenone using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h

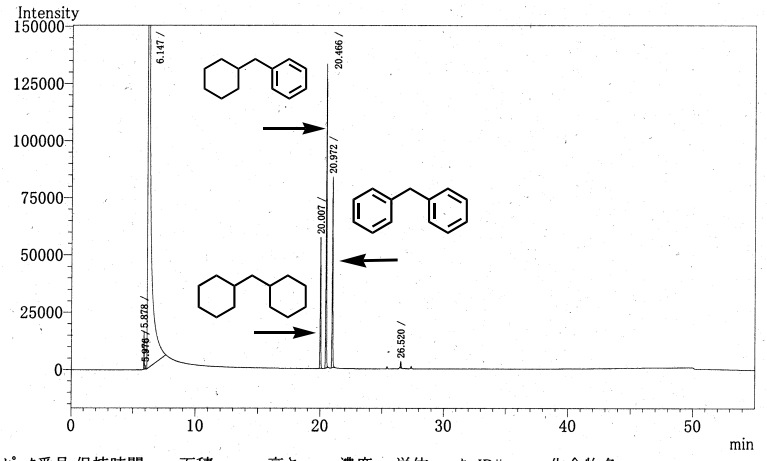
GC of Table 7 Entry 4



ﾋﾟｰｸ番号	保持時間	面積	高さ	濃度	単位	マーク	ID#	化合物名
1	5.879	44367	15839	0.040				
2	6.151	108715192	38744821	98.053				
3	30.319	21123	5073	0.019				
4	30.468	685642	161584	0.618		V		
5	30.818	523883	126542	0.473				
6	34.421	12989	2961	0.012				
7	36.188	424224	96494	0.383				
8	36.909	446725	100227	0.403				
合計		110874145	39253541					

Fig S15: Reduction of 4-*tert*-butylbenzophenone using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h

GC of Table 7 Entry 5



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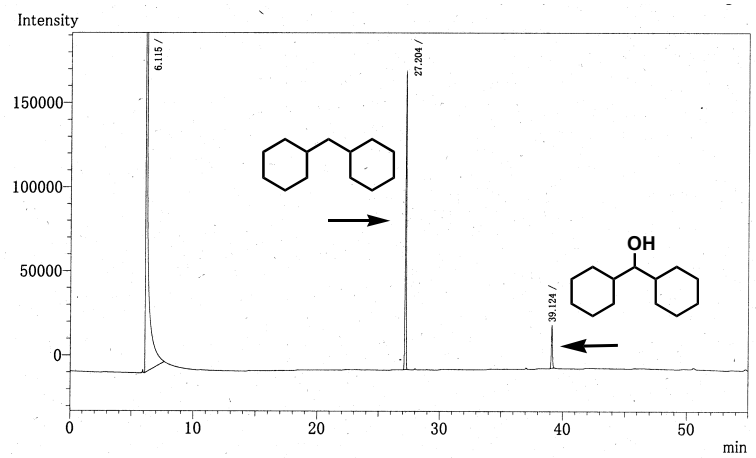
1	5.878	41987	16418	0.034				
2	5.976	4161	1749	0.003		V		
3	6.147	123486881	42434361	99.136				
4	20.007	209448	56761	0.168				
5	20.466	493503	131898	0.396				
6	20.972	314518	83080	0.252				
7	26.520	12063	2912	0.010				
合計		124562561	42727179					

Fig S16: Reduction of 4-Chlorobenzophenone using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h

GC of Table 9 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	6.115	126746667	43486438	99.108				
2	27.204	977622	176980	0.764				
3	39.124	162848	25442	0.127				
合計		127887137	43688860					

Fig S17: Reduction of Diphenylmethanol using Ni–Al alloy, Al powder, Pt/C and H_2O at 80 °C for 18 h