Electronic Supplementary Information (ESI)

Pt-catalyzed selective oxidation of alcohols to aldehydes by hydrogen peroxide using continuous flow reactors

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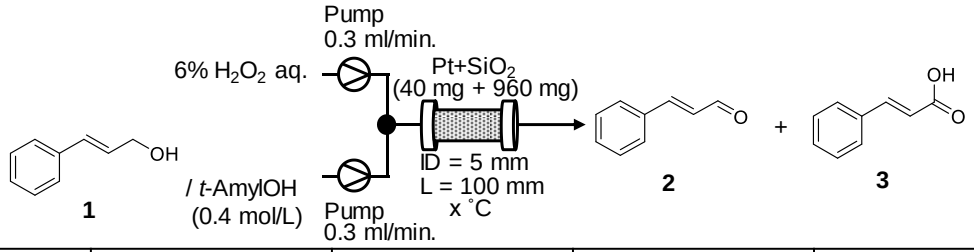
1. Optimization of the reaction conditions

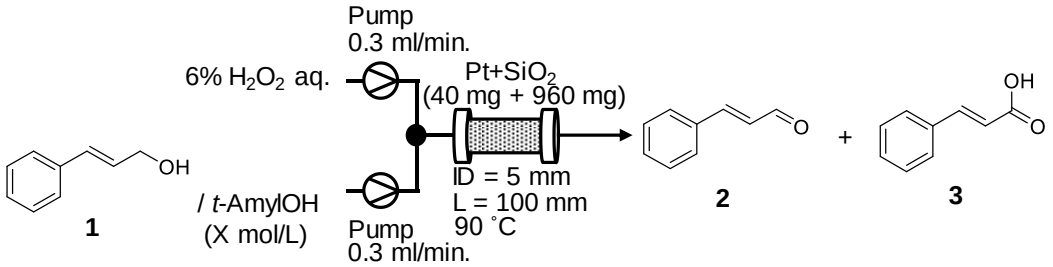
Table S1. Screening of reaction temperature. [a]



Temp (˚C)	60			70			80			90		
Time (min.)	15	30	60	15	30	60	15	30	60	15	30	60
Conv. of **1** (%)[b]	79	79	79	91	90	89	97	99	99	100	100	100
Yield of **2** (%)[b]	78	78	78	91	90	89	96	97	97	97	97	97
Yield of **3** (%)[b]	0	0	0	0	0	0	1	2	2	2	2	2

[a]The base reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

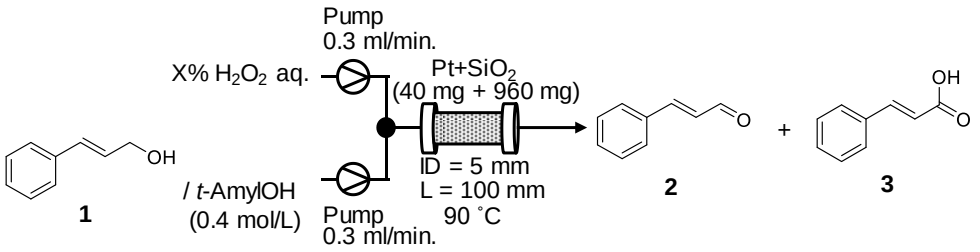
Table S2. Optimization about the concentration of **1**. [a]



Concentration of **1** (mol/L)	0.2			0.4			0.6		
Time (min.)	15	30	60	15	30	60	15	30	60
Conv. of **1** (%)[b]	100	100	100	100	100	100	79	84	79
Yield of **2** (%)[b]	93	93	94	97	97	97	78	83	79
Yield of **3** (%)[b]	7	7	6	2	2	2	0	0	0

[a]The base reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2, **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

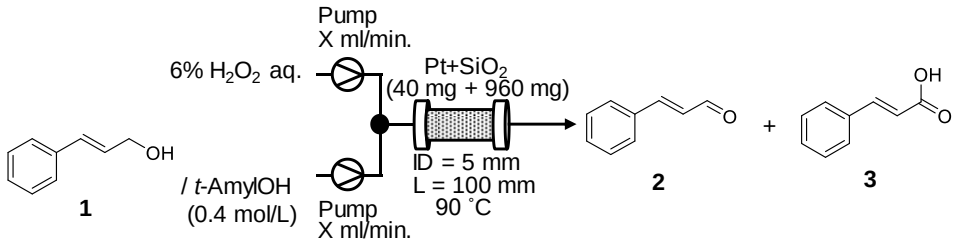
Table S3. Optimization about the concentration of H_2O_2 aq. [a]



Concentration of H_2O_2 (wt%)	2			6			10		
Time (min.)	15	30	60	15	30	60	15	30	60
Conv. of **1** (%)[b]	93	95	96	100	100	100	100	100	100
Yield of **2** (%)[b]	92	92	94	97	97	97	92	93	93
Yield of **3** (%)[b]	1	1	2	2	2	2	8	7	7

[a]The base reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of **1** in *t*-amylOH solution, H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

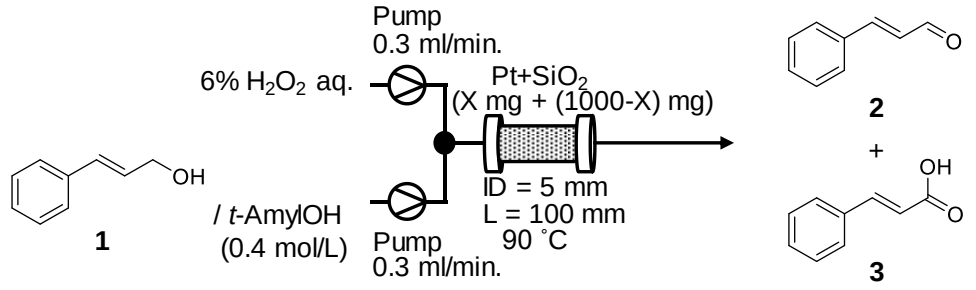
Table S4. Screening of flow rate. [a]



Flow rate (ml/min.)	0.1			0.3			0.5		
Time (min.)	15	30	60	15	30	60	15	30	60
Conv. of **1** (%)[b]	100	100	100	100	100	100	98	98	98
Yield of **2** (%)[b]	89	91	91	97	97	97	95	96	96
Yield of **3** (%)[b]	10	9	9	2	2	2	2	2	2

[a]The base reaction conditions are as follows: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C. [b]Determined by GC analysis based on **1**.

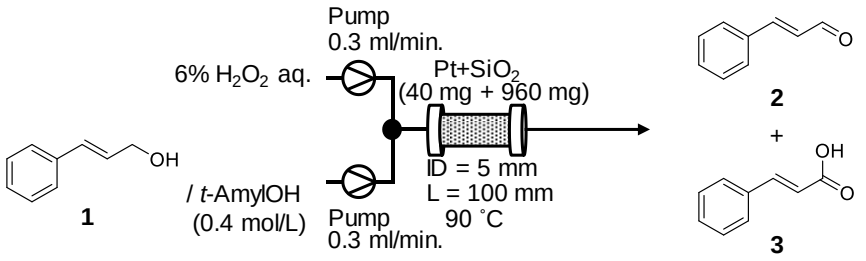
Table S5. Optimization about catalyst amounts. [a]



Amounts of Pt black (mg)	20			40			60		
Time (min.)	15	30	60	15	30	60	15	30	60
Conv. of **1** (%)[b]	75	71	68	100	100	100	99	100	100
Yield of **2** (%)[b]	73	69	67	97	97	97	93	93	94
Yield of **3** (%)[b]	2	1	0	2	2	2	6	6	6

[a]The base reaction conditions are as follows: 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

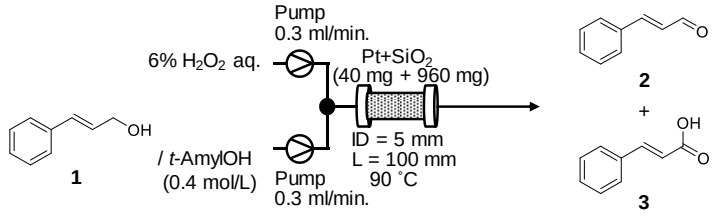
Table S6. Screening of column length. [a]



Column length (cm)	5			10		
Amounts of Pt black (mg)	20			40		
Amounts of SiO_2 (mg)	480			960		
Time (min.)	15	30	60	15	30	60
Conv. of **1** (%)[b]	70	63	58	100	100	100
Yield of **2** (%)[b]	70	63	58	97	97	97
Yield of **3** (%)[b]	0	0	0	2	2	2

[a]The base reaction conditions are as follows: 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

Table S7. Oxidation of **1** without air trap during 50-100 h. [a]

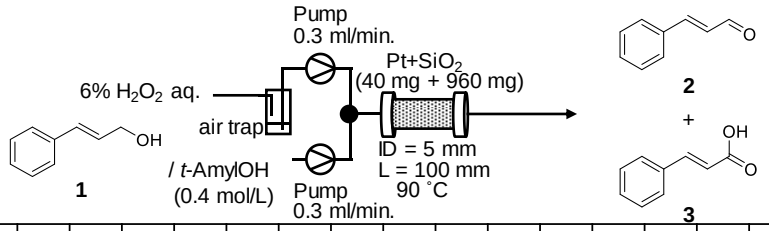


Time (h)	50	52	54	56	58	60	62	64	66	68	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	100
Conv. of **1** (%)[b]	97	97	99	99	98	95	98	97	88	71	98	97	97	98	98	97	97	96	96	93	92	93	75	77	95	93
Yield of **2** (%)[b]	94	94	95	96	95	93	95	95	87	69	94	94	95	95	95	95	95	94	94	91	91	92	74	75	93	91
Yield of **3** (%)[b]	3	3	4	3	3	2	3	2	1	0	4	3	2	3	3	2	2	2	2	2	1	1	0	0	2	2

[a]Reaction conditions: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

2. Continuous flow oxidation for 120 hours

Table S8. Oxidation of **1** to **2** for over 120 h [a]



Time (h)	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
Conv. of **1** (%)[b]	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Yield of **2** (%)[b]	95	96	97	97	98	97	98	98	98	98	98	98	98	98	98	98	98	98	98	98
Yield of **3** (%)[b]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1

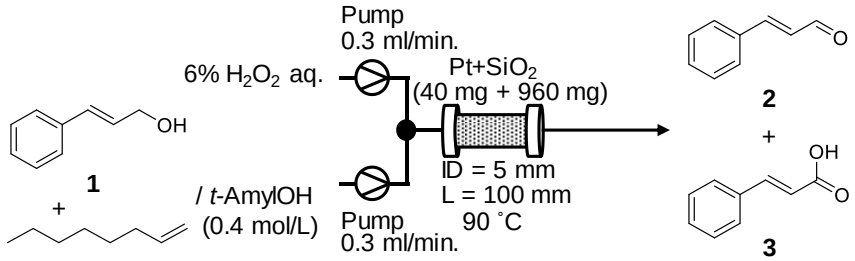
Time (h)	42	44	46	48	50	52	54	56	58	60	62	64	66	68	70	72	74	76	78	80
Conv. of **1** (%)[b]	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Yield of **2** (%)[b]	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98
Yield of **3** (%)[b]	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Time (h)	82	84	86	88	90	92	94	96	98	100	102	104	106	108	110	112	114	116	118	120
Conv. of **1** (%)[b]	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Yield of **2** (%)[b]	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98
Yield of **3** (%)[b]	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

[a]Reaction conditions: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

3. Oxidation of *(E)*-cinnamyl alcohol in the presence of 1-octene

Table S9. Oxidation of **1** in the presence of 1-octene [a]



Time (min.)	15	30	60
Conv. of **1** (%)[b]	66	67	66
Yield of **2** (%)[b]	64	65	65
Yield of **3** (%)[b]	0	0	0

[a]Reaction conditions: 40 mg of Pt black, 960 mg of SiO_2, 0.4 mol/L of 1-octene and 0.4 mol/L of **1** in *t*-amylOH solution, 6wt% H_2O_2 aq., 90 °C, flow rate: each 0.3 ml/min. [b]Determined by GC analysis based on **1**.

4. NMR Spectra

The NMR spectroscopic data of the synthesized compounds **2**–**14** agreed well with the NMR data reported by the production through another methods.[ref]

(E)-Cinnamaldehyde (**2**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.71 (d, *J* = 8.0 Hz, 1H), 7.59-7.56 (m, 2H), 7.50-7.43 (m, 4H), 6.73 (dd, *J* =16.0, 7.6 Hz, 1H).

(E)-Cinnamic acid (**3**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 7.80 (d, *J* =16.0 Hz, 1H), 7.60-7.52 (m, 2H), 7.45-7.38 (m, 3H), 6.46 (d, *J* =16.0 Hz, 1H).

(E)-α-Methylcinnamaldehyde (**4**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.59 (s, 1H), 7.54-7.38 (m, 5H), 7.27 (s, 1H), 2.08 (s, 3H).

(E)-4-Nitrocinnamaldehyde (**5**):[(b)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.79 (d, *J* = 8.0 Hz, 1 H), 8.30 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 16.0 Hz, 1H), 6.82 (dd, *J* = 16.0, 8.0 Hz, 1H).

(E)-2-Octenal (**6**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.51 (d, *J* = 8.0 Hz, 1H), 6.86 (m, 1H), 6.12 (m, 1H), 2.37-2.31 (m, 2H), 1.55-1.48 (m, 2H), 1.35-1.31 (m, 4H), 0.91(t, *J* = 6.6 Hz, 3H).

(E)-2-Nonenal (**7**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.51 (d, *J* = 8.0 Hz, 1H), 6.86 (m, 1H), 6.13 (m, 1H), 2.37-2.31 (m, 2H), 1.53-1.47 (m, 2H), 1.36-1.31 (m, 6H), 0.89(t, *J* = 6.0 Hz, 3H).

Citral (**8**):[(c)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.99 (d, *J* = 8.4 Hz, 1H), 5.88 (d, *J* = 8.4 Hz, 1H), 5.08-5.06 (m, 1H), 2.24-2.17 (m, 4H), 2.17 (s, 3H), 1.69 (s, 3H), 1.61(s, 3H).

Benzaldehyde (**9**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 10.03 (s, 1H), 7.90-7.88 (m, 2H), 7.66-7.62 (m, 1H), 7.56-7.52 (m, 2H).

Benzoic acid (**10**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.15-8.12 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H).

4-Methoxybenzaldehyde (**11**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.89 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H).

4-Bromobenzaldehyde (**12**):[(d)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.98 (s, 1H), 7.76 (d, *J* = 12.0 Hz, 2H), 7.69 (d, *J* = 12.0 Hz, 2H).

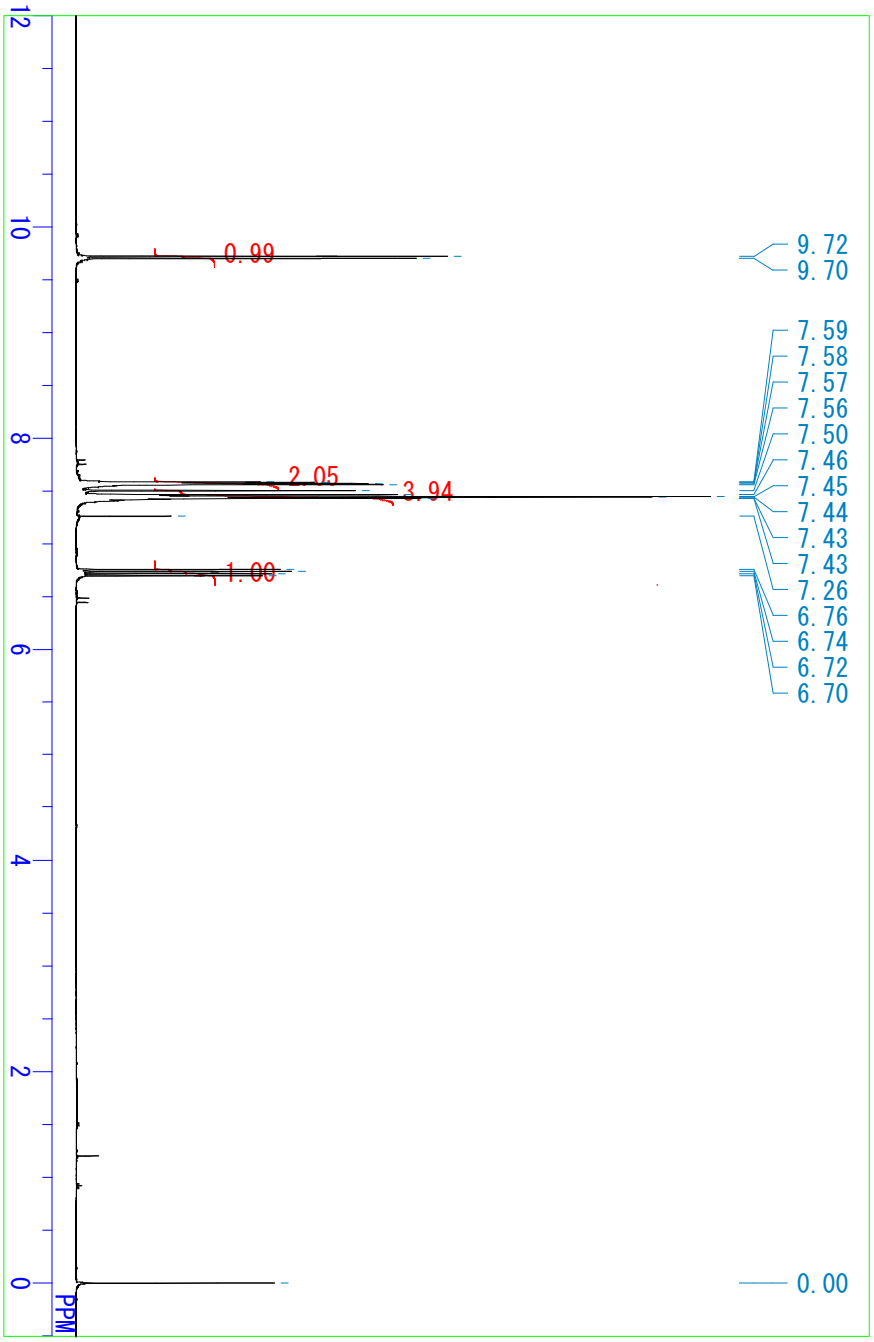
1-Octanal (**13**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 9.77 (t, *J* = 1.8 Hz, 1H), 2.42 (m, 2H), 1.65-1.61 (m, 2H), 1.30-1.28 (m, 8H), 0.88 (m, 3H).

1-Octanoic acid (**14**):[(a)] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 2.35 (t, *J* = 7.6 Hz, 2H), 1.65-1.62 (m, 2H), 1.39-1.25 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

Ref). (a) SDBSWeb: https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, Dec. 8, 2020); (b) C. J. Pouchert and J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1st ed.* Vol. 2, Aldrich Chemical, Milwaukee, 1993, 930-C; (c) C. J. Pouchert and J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1st ed.* Vol. 1, Aldrich Chemical, Milwaukee, 1993, 743-A; (d) C. J. Pouchert and J. Behnke, *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, 1st ed.* Vol. 2, Aldrich Chemical, Milwaukee, 1993, 940-C.

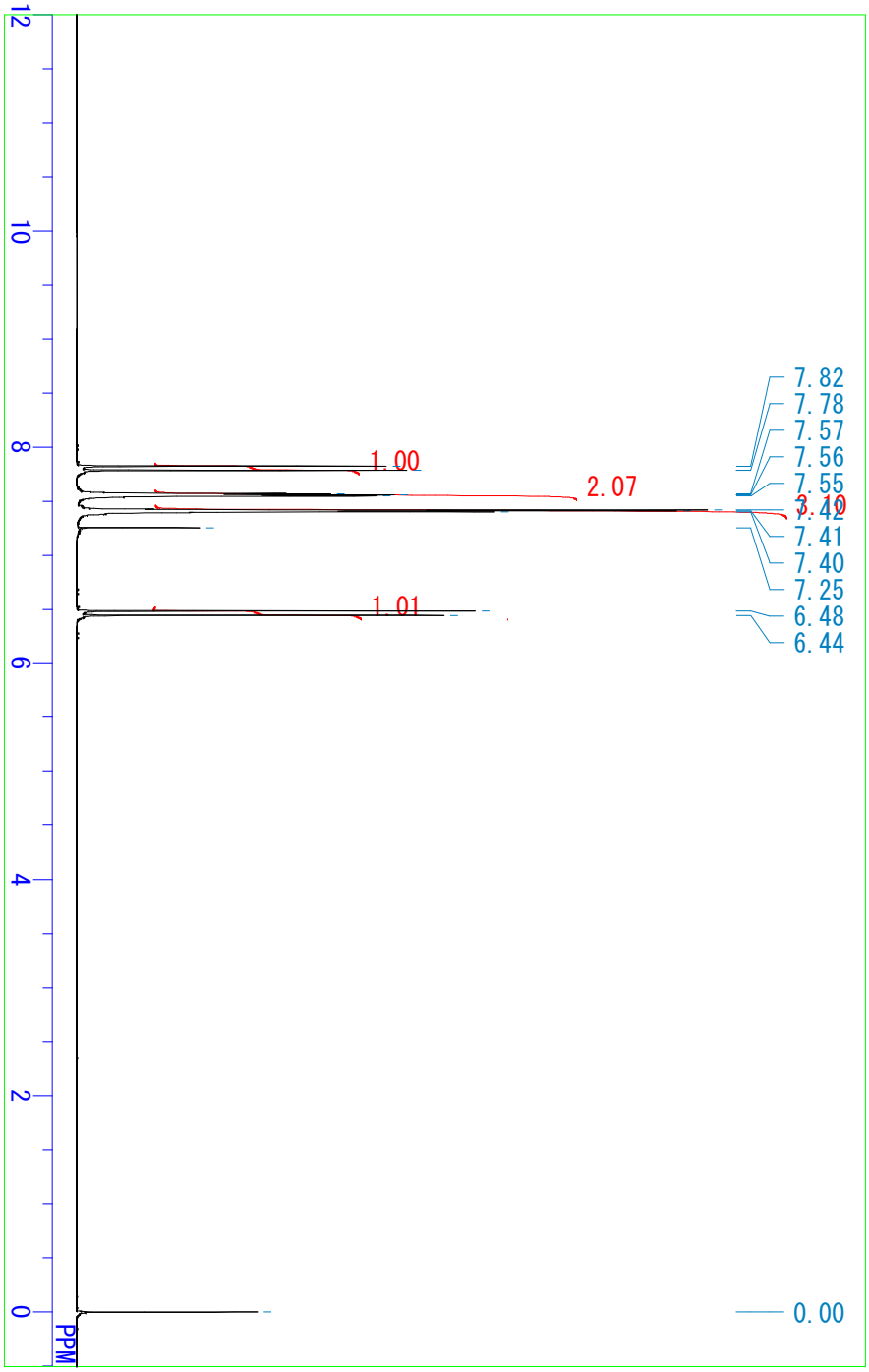
***(E)*-cinnamaldehyde**

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



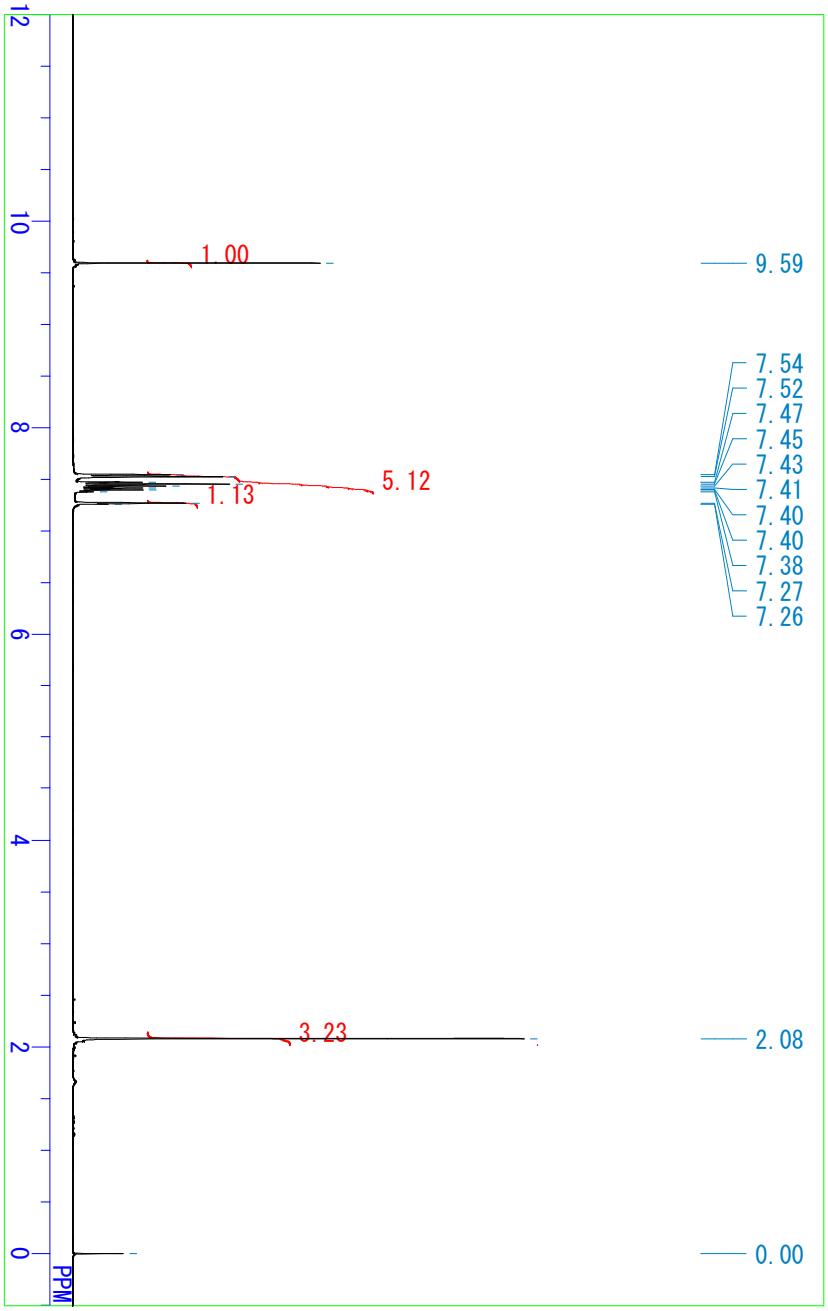
***(E)*-cinnamic acid**

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



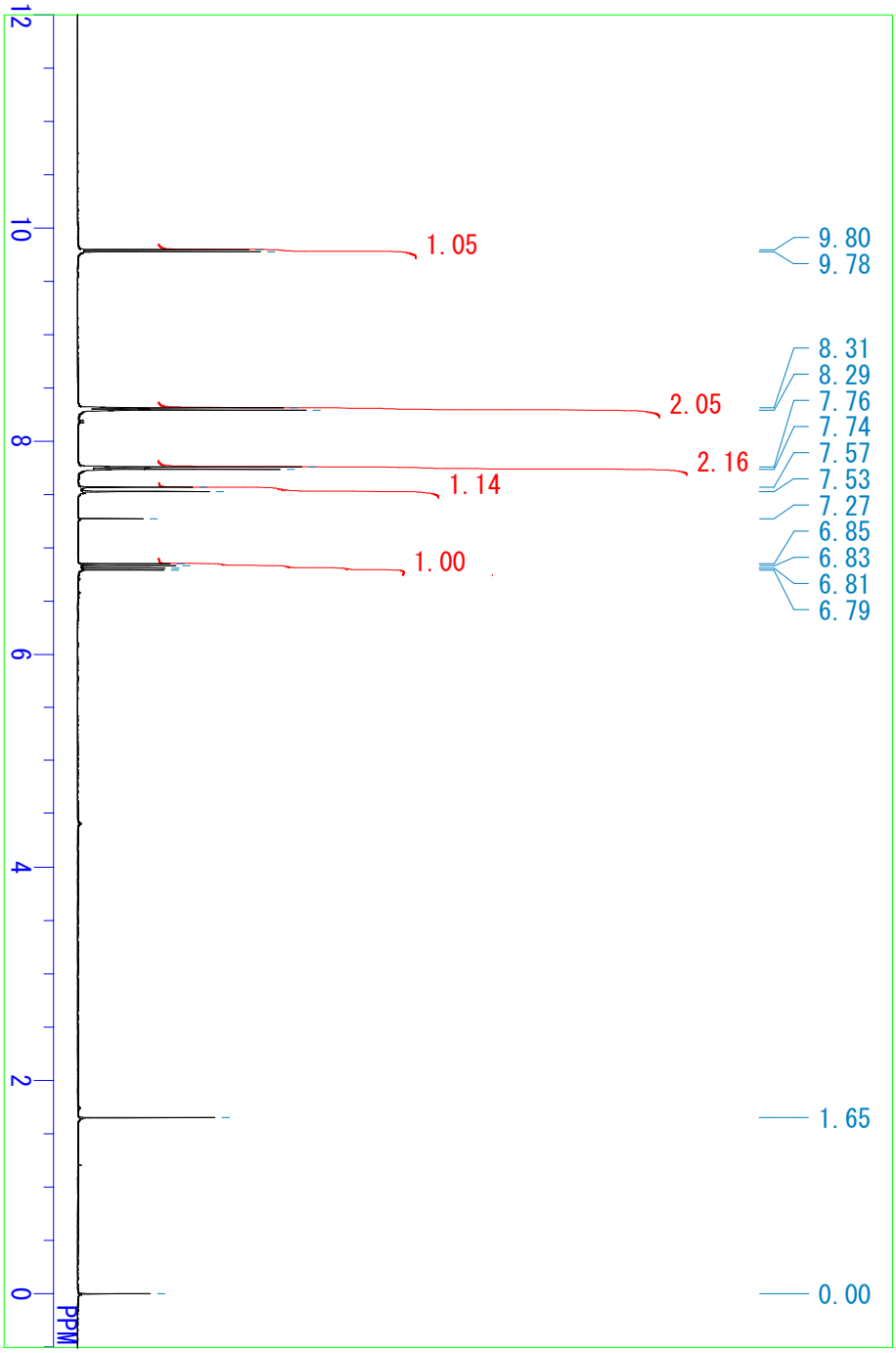
***(E)*-α-Methylcinnamaldehyde**

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



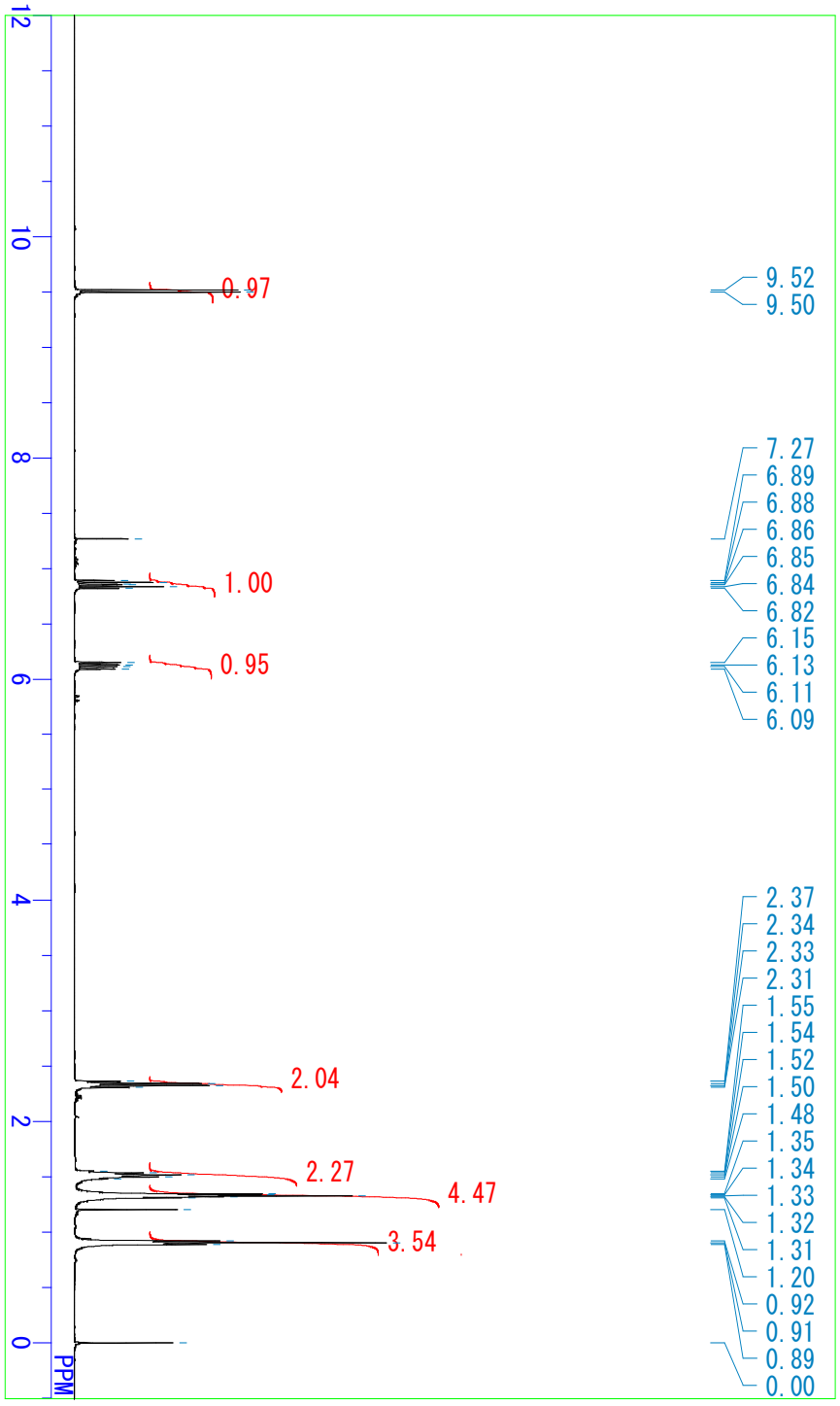
***(E)*-4-Nitrocinnamaldehyde**

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



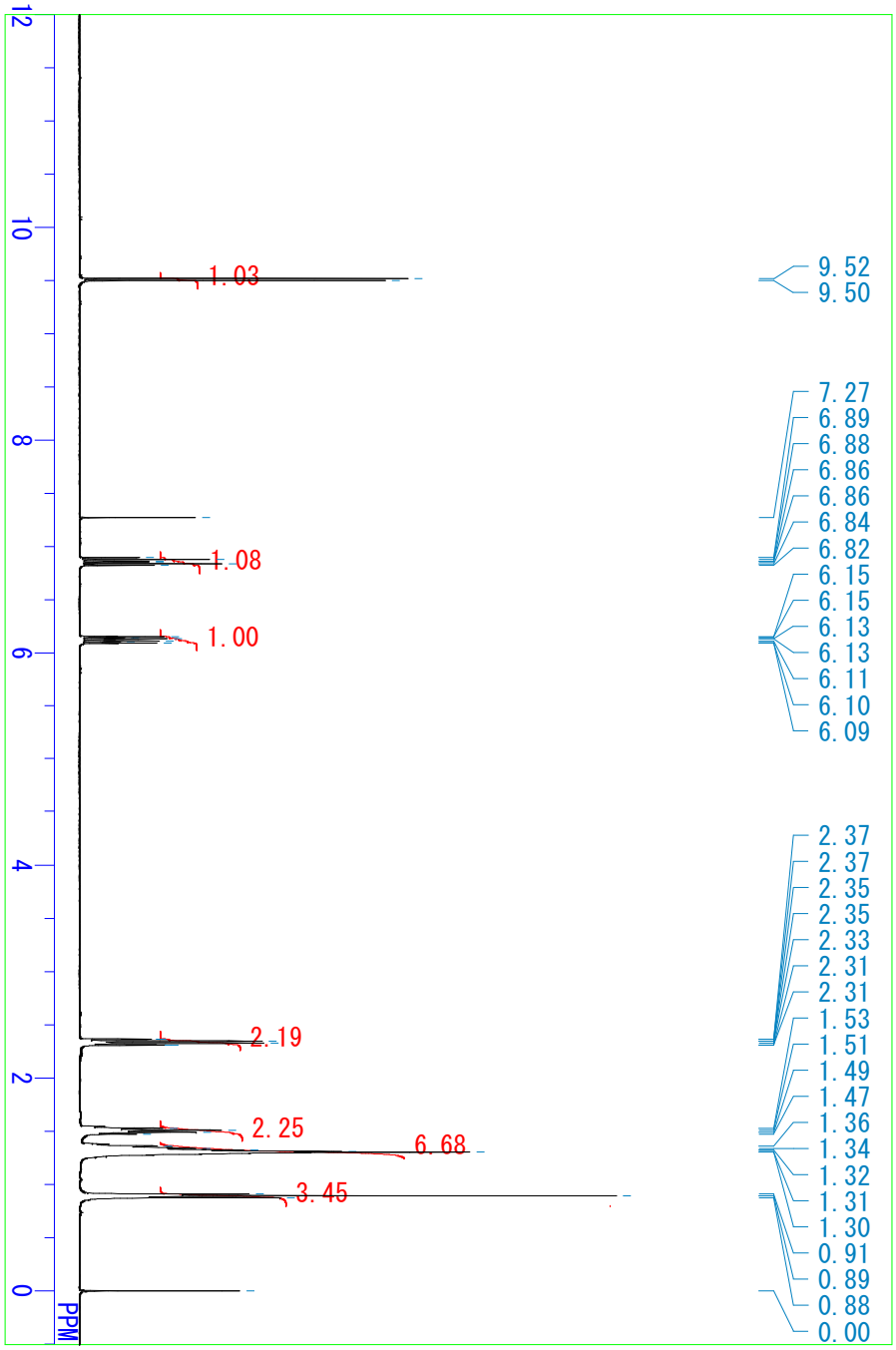
(E)-2-Octenal

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



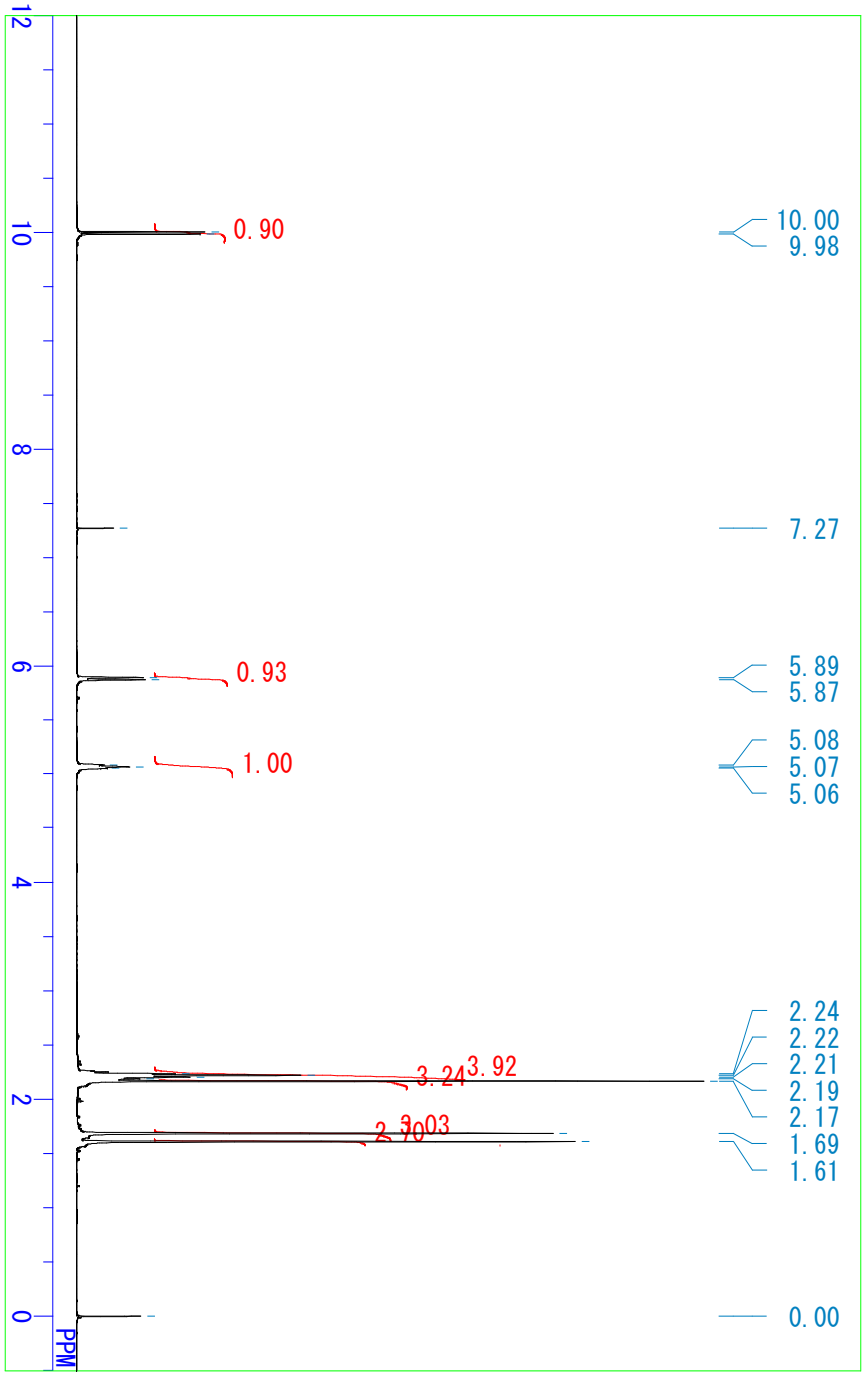
***(E)*-2-Nonenal**

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



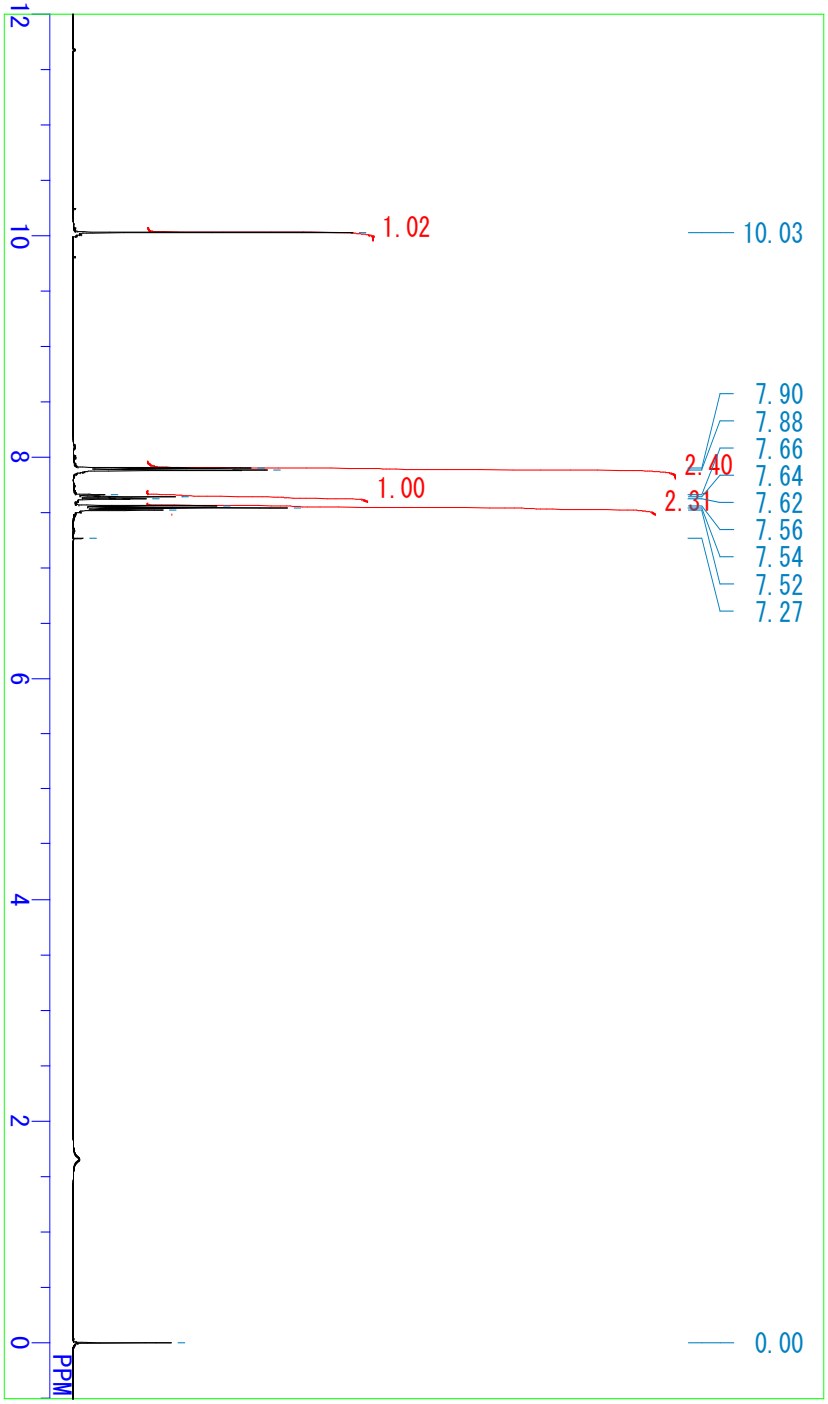
Citral

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



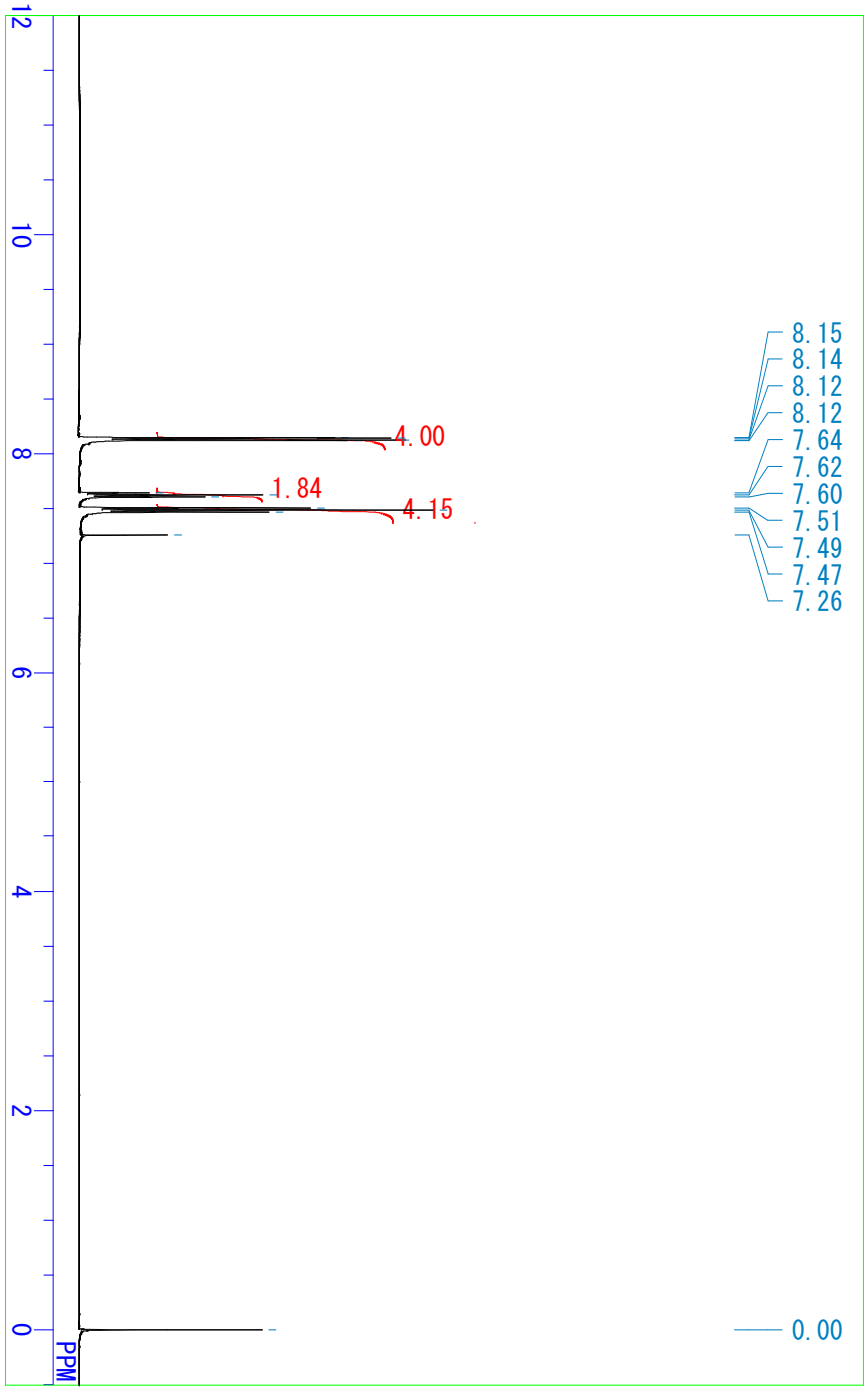
Benzaldehyde

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



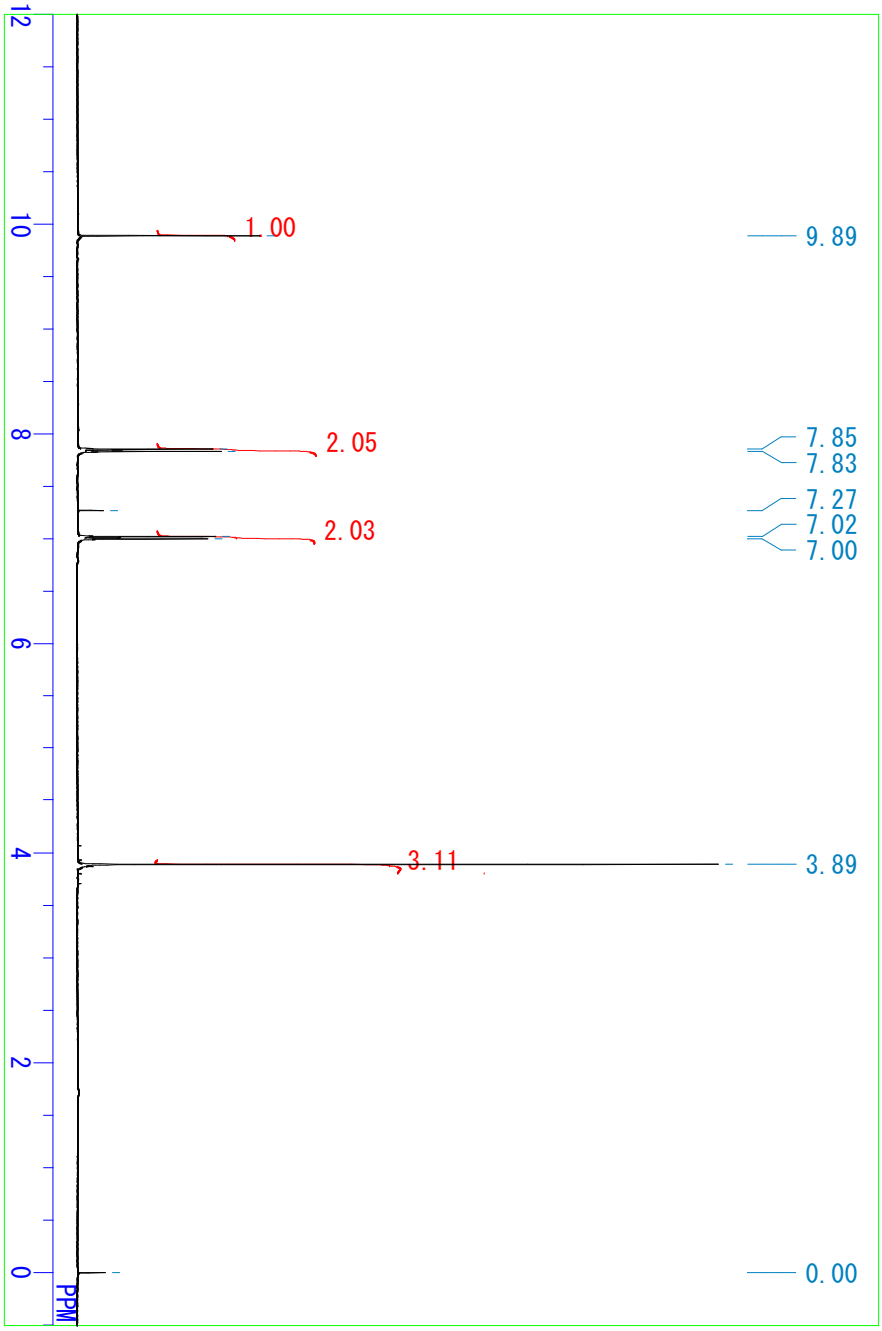
Benzoic acid

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



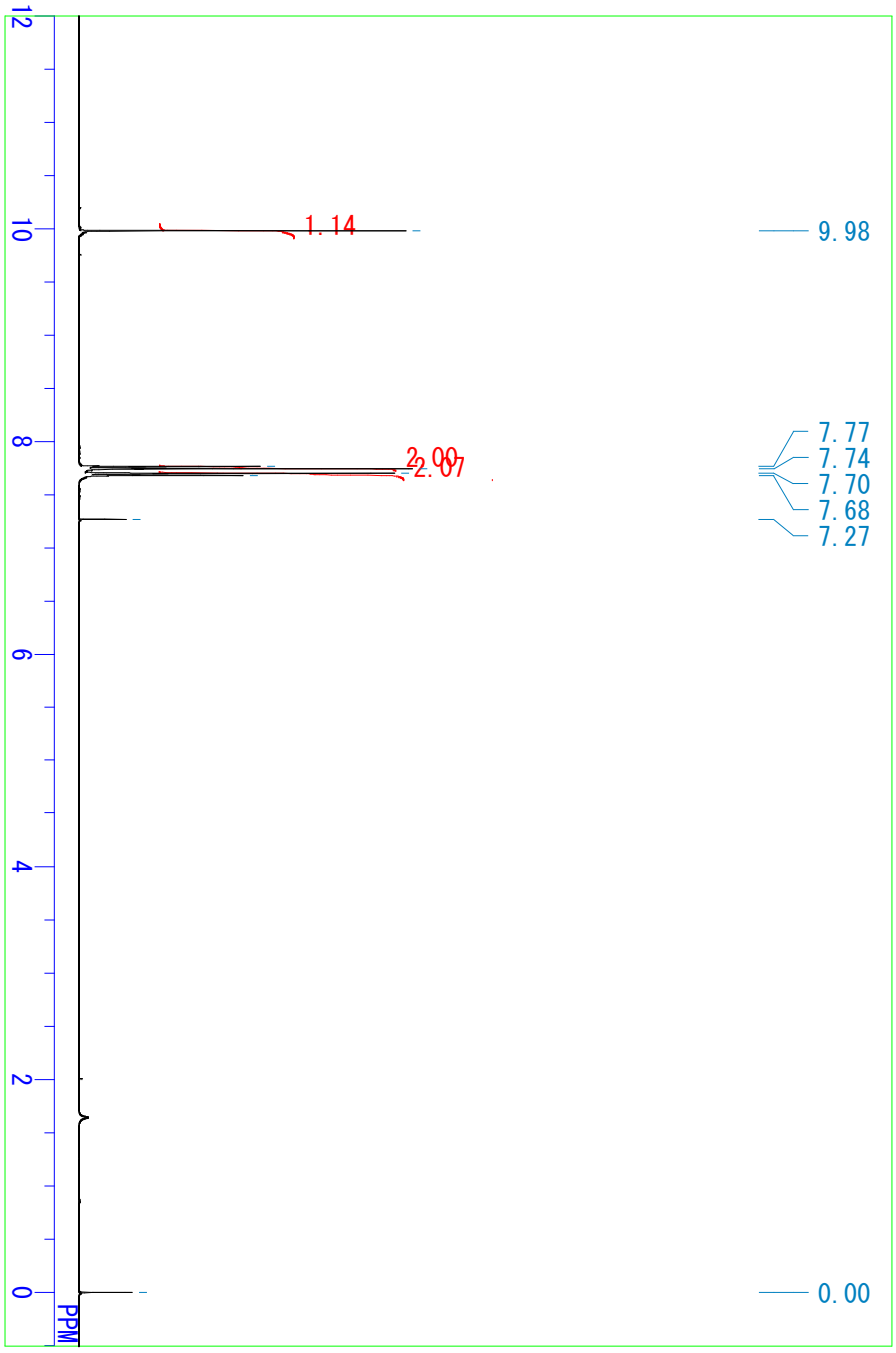
4-Methoxybenzaldehyde

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



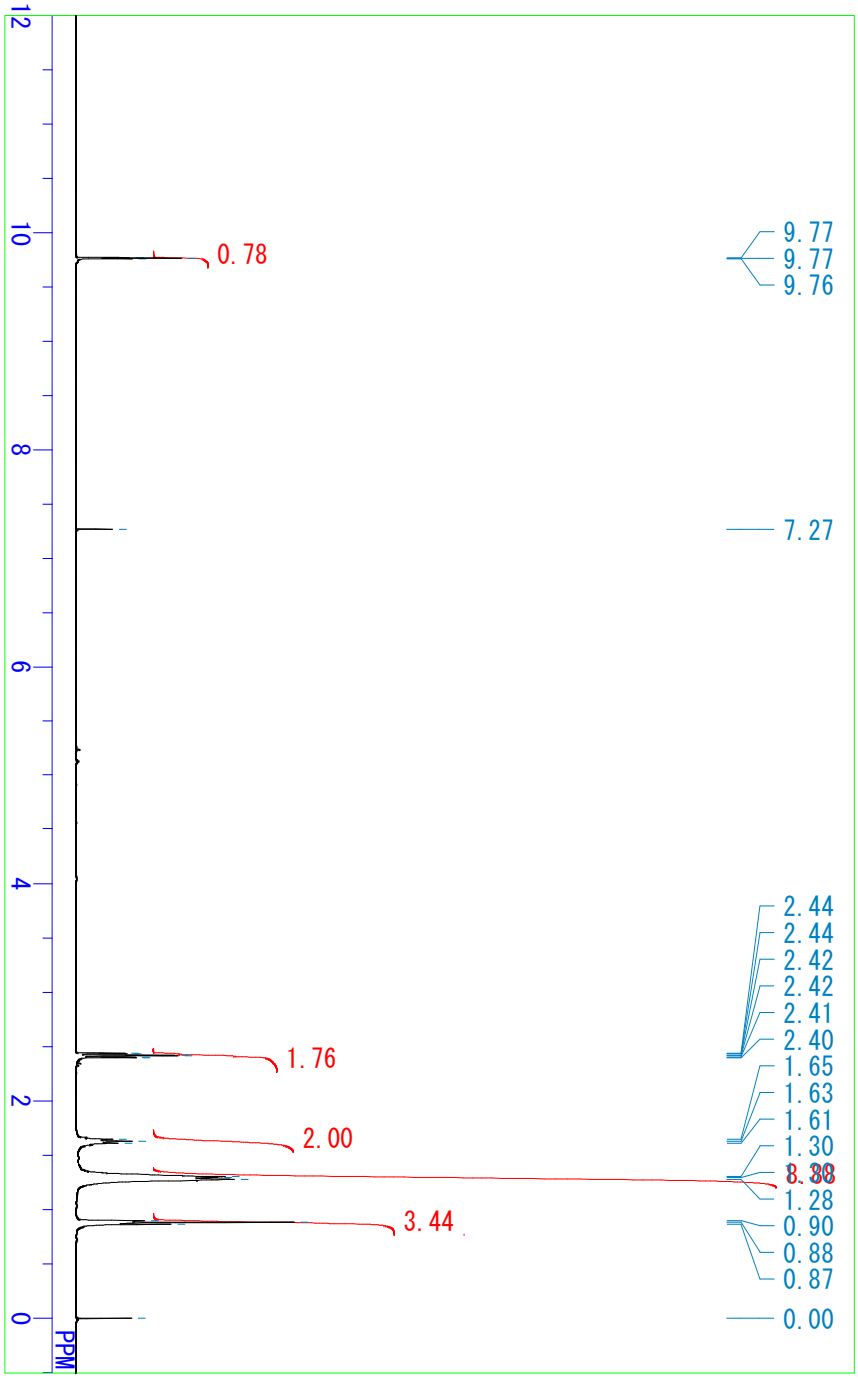
4-Bromobenzaldehyde

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



1-Octanal

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)



1-Octanoic acid

^{1}H NMR (400MHz, $CDCl_3$, 25 °C)