Unique nanocages of $12CaO•7Al_2O_3$ boost heterolytic hydrogen activation and selective hydrogenation of heteroarenes over ruthenium catalyst

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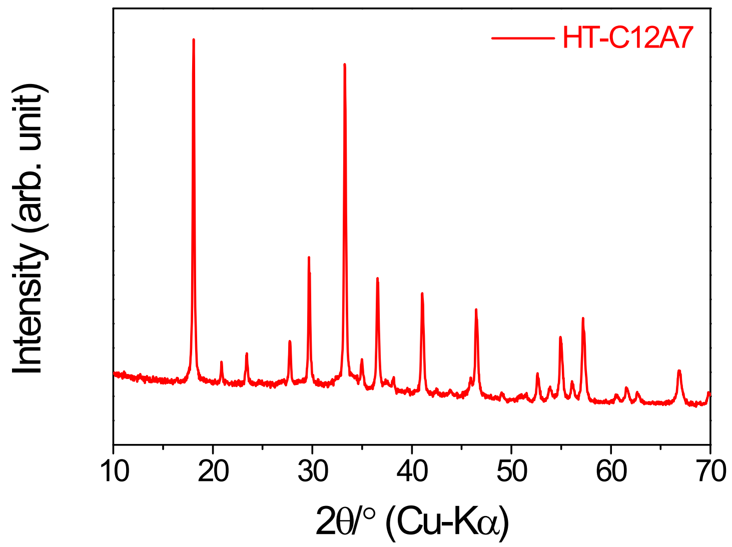


Fig. S1 XRD pattern of HT-C12A7.

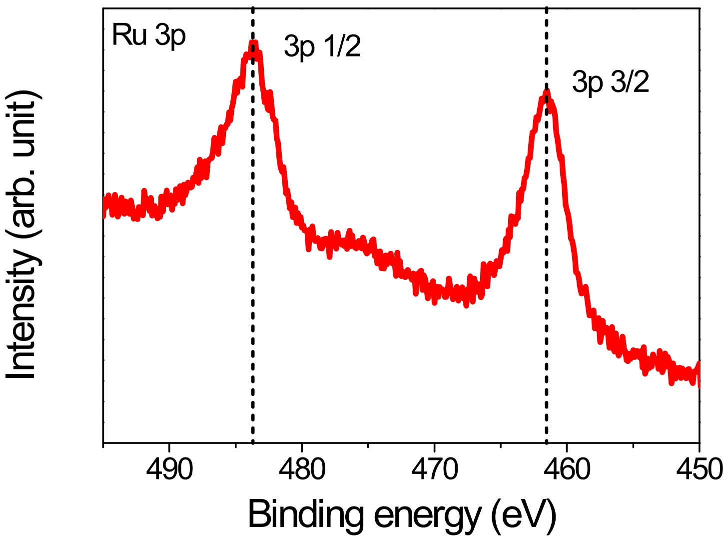


Fig. S2 XPS Ru 3p spectrum for Ru/HT-C12A7. The dotted lines indicate the Ru 3p peaks derived from bulk Ru metal respectively.

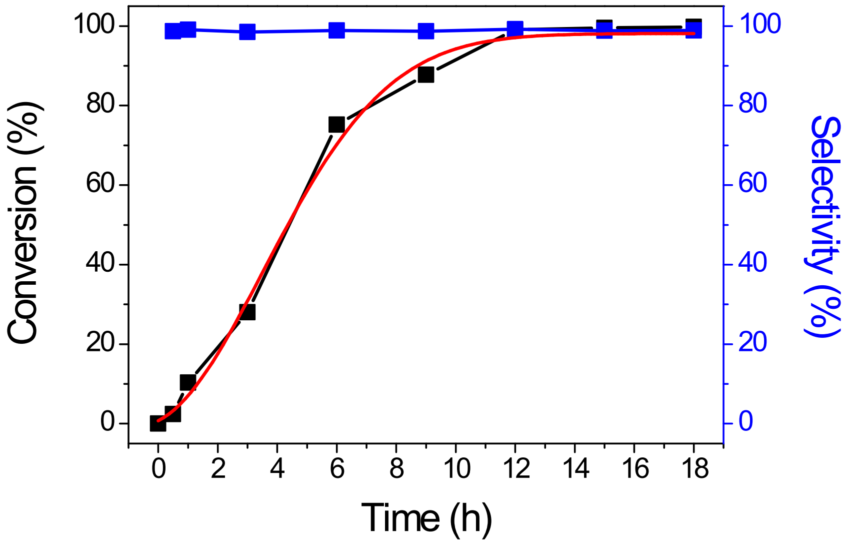


Fig. S3 Kinetic data of the hydrogenation of quinoline with 2wt% Ru/HT-C12A7 catalyst. Reaction condition: 5 mmol substrate, catalyst 40 mg, H_2 (1.0 MPa), 80 °C. Yield was determined by gas GC and GCMS analysis.

Table S1. Summary of reported Ru, Pt and other transition metal based heterogeneous catalysts for hydrogenation of various quinolines.

Catalyst	Solvent	B.E.T. [m^2g^{-1}]	H_2 [MPa]	Temp. [°C]	Time [h]	Yield [%]	Ref.
Ru/HT-C12A7	**---**	**54**	**1.0**	**80**	**12**	**98.3**	**This work**
Ru/HT-C12A7[a]	**---**	**54**	**1.0**	**60**	**12**	**95.4**	**This work**
Au/HAS-TiO_2[a]	toluene	124	2.0	25	16	92	*J. Am. Chem. Soc.* 2012, 134, 17592.
Ru/HAS-TiO_2[a]	toluene	124	2.0	60	3	81.8	*J. Am. Chem. Soc.* 2012, 134, 17592.
Au/HAS-TiO_2	---	124	2.0	140	48	100	*J. Am. Chem. Soc.* 2012, 134, 17592.
Rh/Al_2O_3	---	---	3.0	80	115	72.9	*ACS Catal.* 2012, 2, 1524.
Rh/MgO	---	---	2.0	100	24	100	*Applied Catalysis A: General* 2014, 477, 117.
RhNP/Lewic acidic IL	---	---	3.0	80	15-48	95	*Angew. Chem. Int. Ed.* 2016, 55, 292.

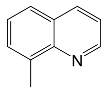
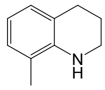
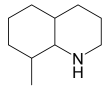
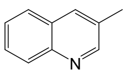
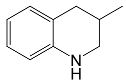
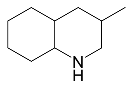
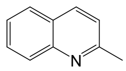
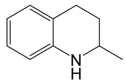
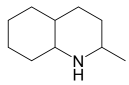
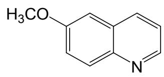
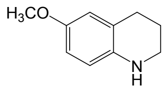
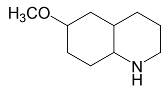
[a] 6-chloroquinoline was used as a substrate instead of quinoline.

Table S2. Characterization of Ru catalysts on various supports.

Catalyst	Surface area (m^2g^{-1})	Ru loading (wt%)	Dispersion (%)[a]	Particle size [nm][a]
Ru/HT-C12A7	**54**	**2.0**	**37.3**	**3.6**
Ru/HT-C12A7	**54**	**5.0**	**32.5**	**4.1**
Ru/Al_2O_3	85	5.0	19.6	6.8
Ru/CaO	77	5.0	26.3	5.0
Ru/SiO_2-Al_2O_3	420	5.0	37.1	3.6
Ru/MgO	34	5.0	22.7	5.8
Ru/ZrO_2	9.2	5.0	13.3	10.0
Ru/TiO_2	112	5.0	19.0	7.0

[a] Dispersion and particle size were calculated on the basis of CO chemisorption values, assuming spherical metal particles and that the stoichiometry of Ru/CO = 1.

Table S3. Main side products of the substrates with low selectivites.

Entry	Substrate	product	Yield (%)[c]	Side product	Yield (%)[c]
1[a]			89.1		10.9
2[b]			91.4		8.6
3[b]			87.7		12.3
4[a]			87.4		12.6

[a] Reaction condition: 5 mmol substrate, 40 mg catalyst (2 wt% Ru/HT-C12A7), 1.0 MPa H_2, 15 h, 80 °C; [b] 12 h; [c] isolated yield.

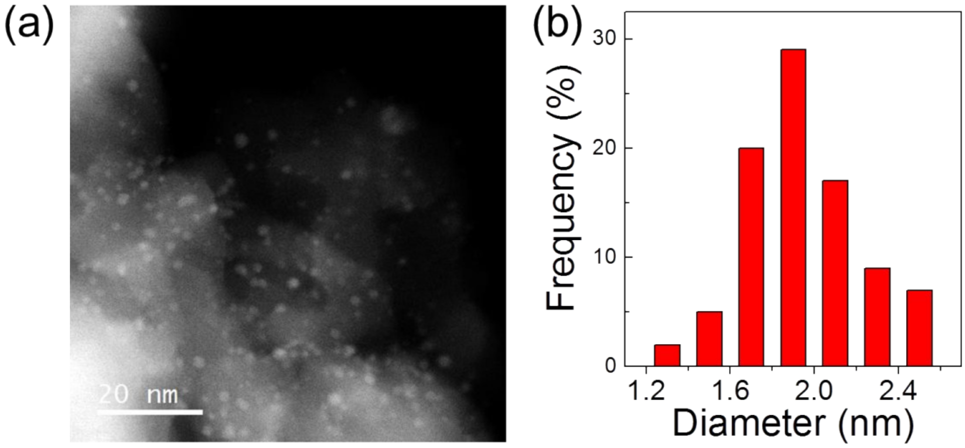


Fig. S4 HAADF STEM image of Ru/HT-C12A7 after the reaction of chemoselective hydrogenation of quinoline. (a) Overview image of Ru/HT-C12A7 and (b) metal particle size distribution histogram.

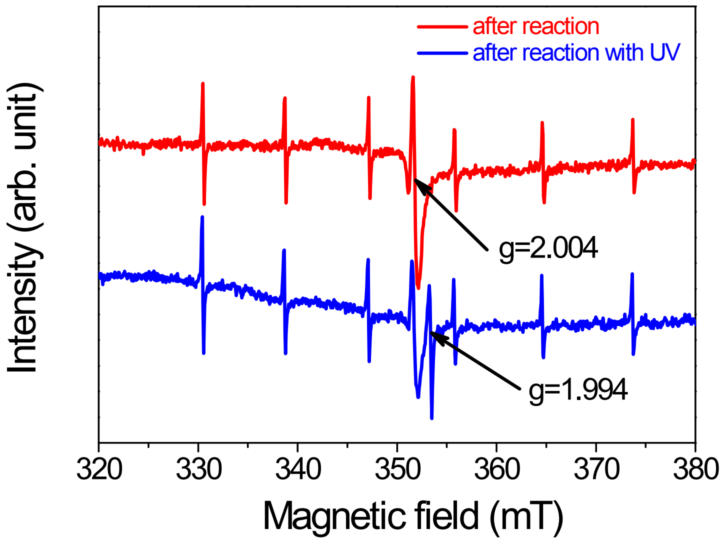


Fig. S5 EPR spectra of Ru/HT-C12A7 catalyst after hydrogenation reaction and that after reaction then irradiated by UV light (microwave frequency = 9.7 GHz, temperature = 25 °C). The sextet with a separation of ~8mT is due to Mn^{2+} in MgO as a standard.

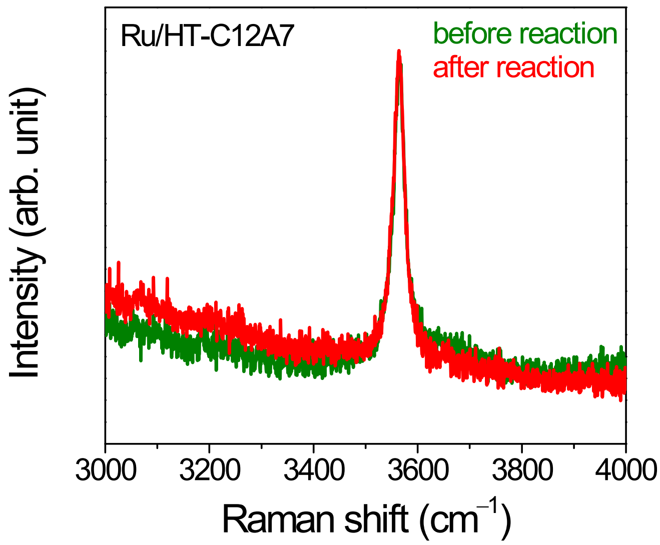


Fig. S6 Raman spectra of Ru/HT-C12A7 catalyst before and after hydrogenation reaction.

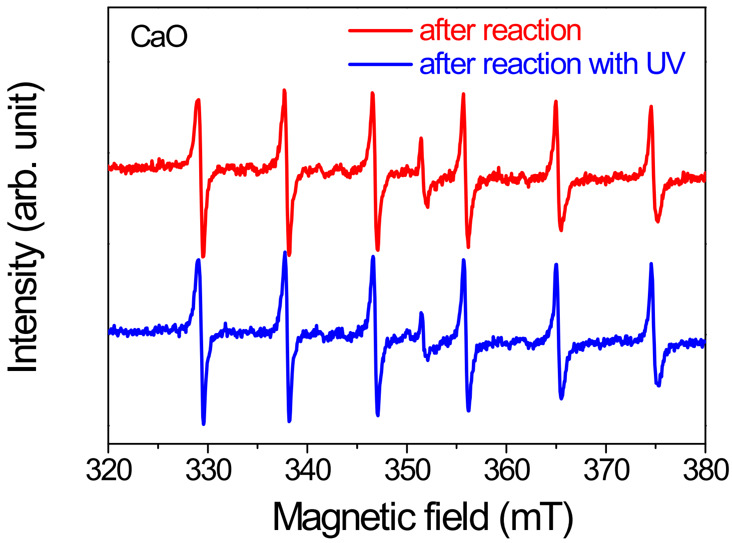


Fig. S7 EPR spectra of Ru/CaO catalyst after the hydrogenation reaction and the catalyst after reaction and then irradiated by UV light (microwave frequency = 9.7 GHz, temperature = 25 °C). The sextet with a separation of ~8mT is due to Mn^{2+} in MgO as a standard.

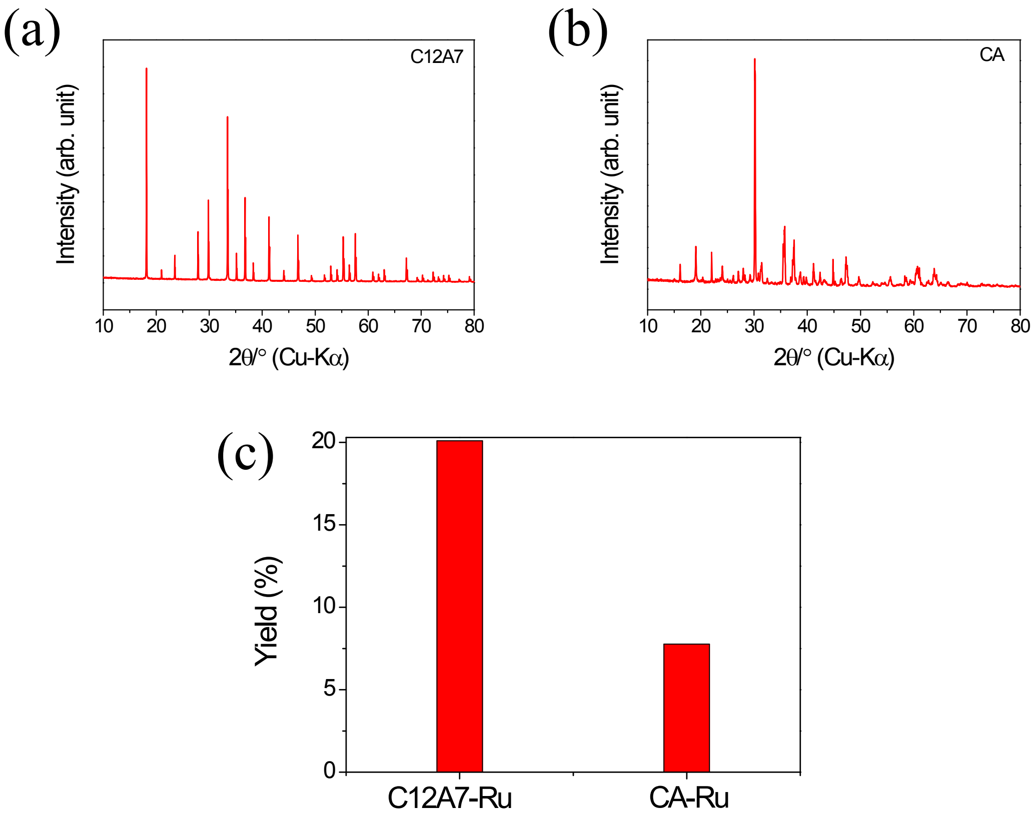


Fig. S8 XRD patterns of solid-state reaction prepared (a) C12A7 and (b) CaO·Al_2O_3 (CA). Catalytic activities (c) of quinoline hydrogenation by C12A7 and CA loaded with 10wt% Ru, respectively. Reaction condition: 5 mmol substrate, catalyst 40 mg, H_2 (1.0 MPa), 80 °C, 12h.

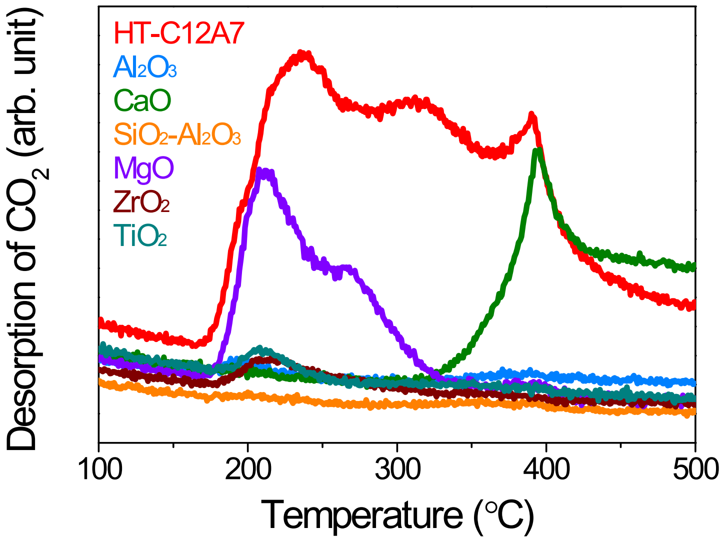
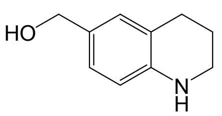
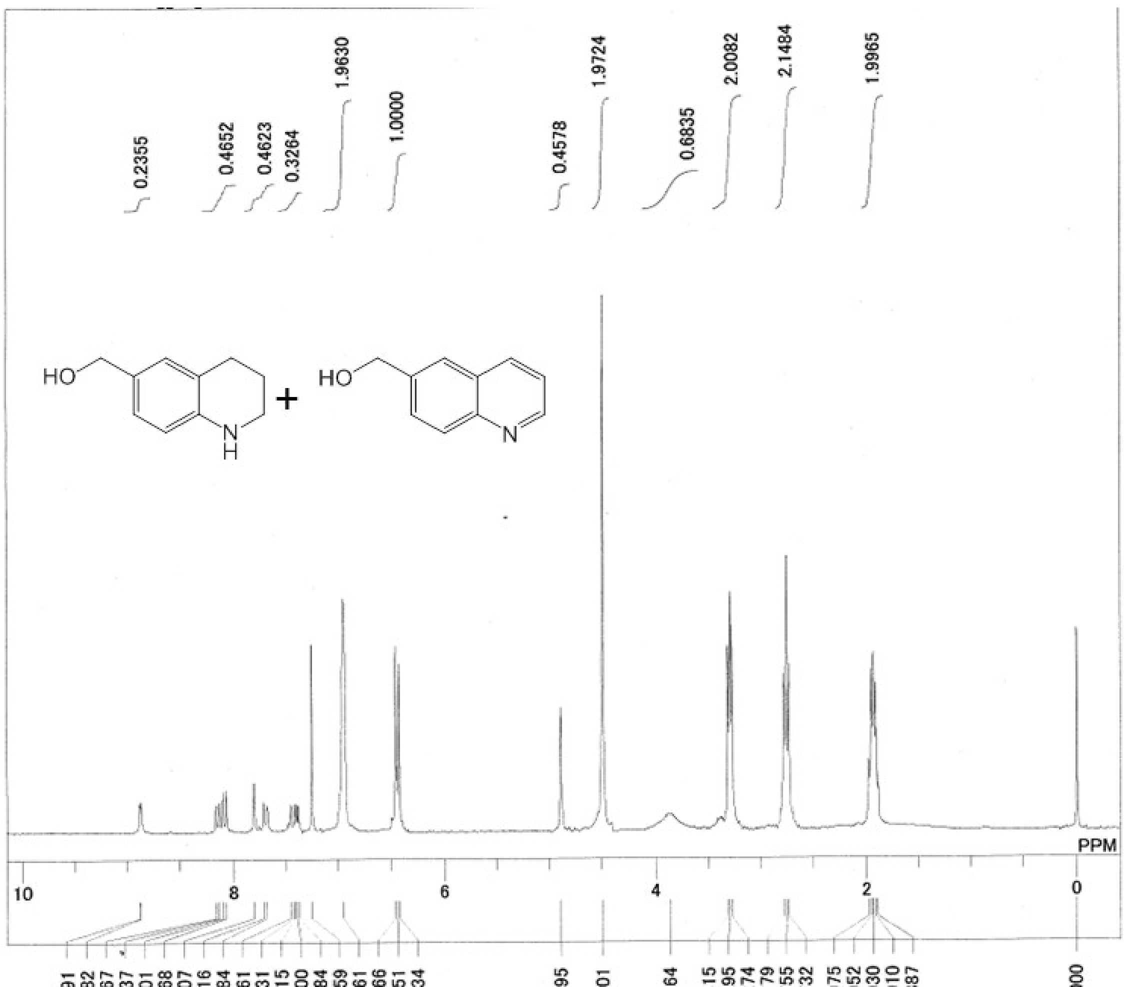
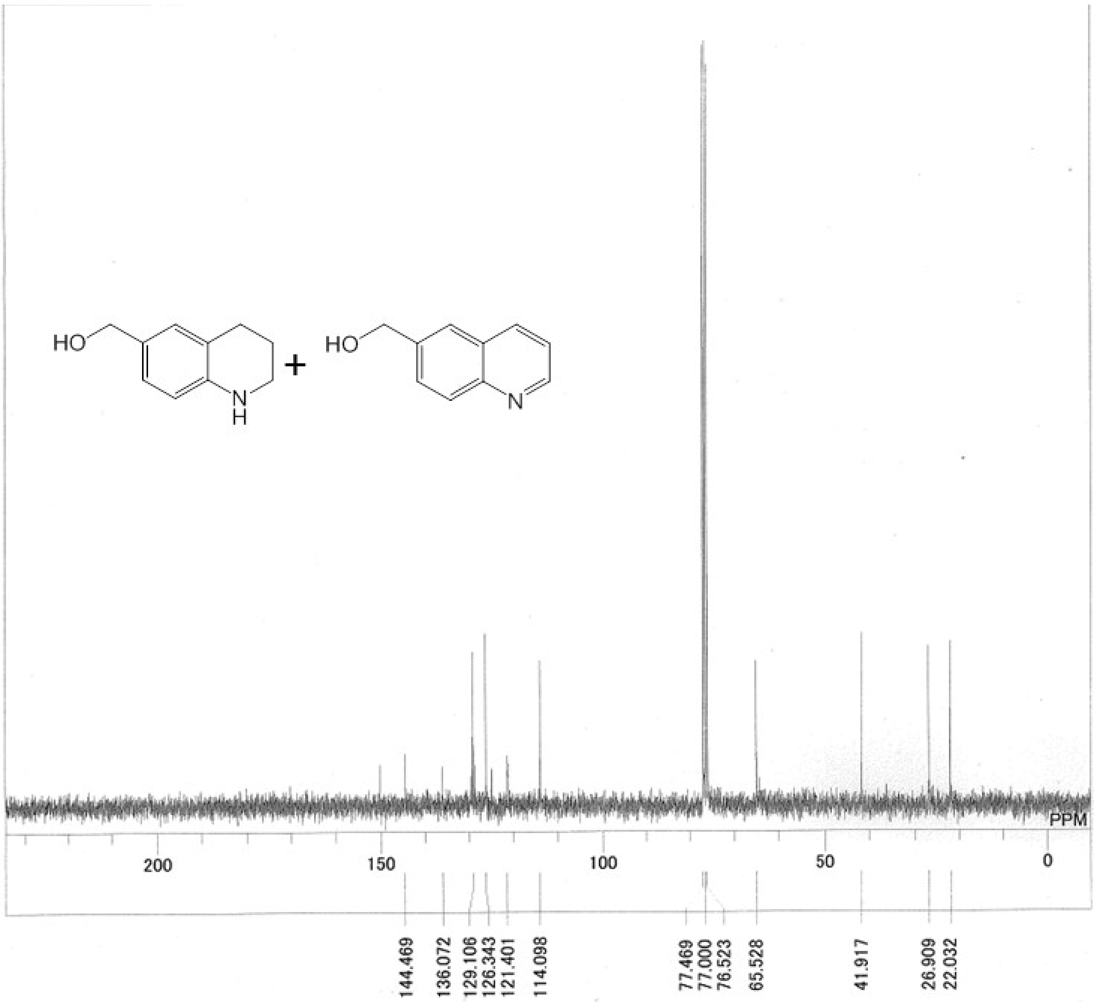


Fig. S9 CO_2-TPD profiles of various Ru-based catalysts with different supports.



[1]H NMR ($CDCl_3$, 300 MHz): δ = 6.96 (s, 2H), 6.52-6.39 (m, 1H), 4.50 (s, 2H), 3.86 (brs, 1H), 3.36-3.22 (m, 2H), 2.76 (t, 2H), 2.02-1.85 (m, 2H); [13]C NMR ($CDCl_3$, 75 MHz): δ = 144.5, 136.1, 129.1, 126.3, 121.4, 114.1, 65.5, 41.9, 26.9, 22.0.

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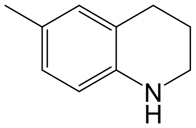
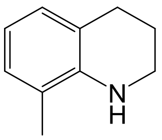
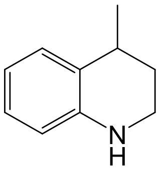
26.909
22.032



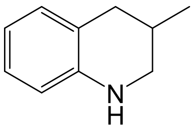
[1]H NMR ($CDCl_3$, 300 MHz): δ = 6.78 (s, 2H), 6.52-6.41 (m, 1H), 3.65-2.89 (m, 3H), 2.73 (t, 2H), 2.20 (s, 3H), 2.08-1.81 (m, 2H); [13]C NMR ($CDCl_3$, 75 MHz): δ = 142.2, 130.0, 127.2, 126.3, 121.7, 114.5, 42.1, 26.9, 22.4, 20.4.



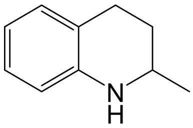
[1]H NMR ($CDCl_3$, 300 MHz): δ = 6.85 (t, 2H), 6.54 (t, 1H), 3.62 (s, 1H), 3.39-3.28 (m, 2H), 2.77 (t, 2H), 2.06 (s, 3H), 2.05-1.85 (m, 2H); [13]C NMR ($CDCl_3$, 75 MHz): δ = 142.6, 127.7, 127.3, 121.1, 120.7, 116.3, 42.2, 27.2, 22.1, 17.1.



[1]H NMR ($CDCl_3$, 300 MHz): δ = 7.04 (d, 1H), 6.95 (t, 1H), 6.62 (t, 1H), 6.45 (d, 1H), 3.83 (s, 1H), 3.41-3.11 (m, 2H), 2.99-2.78 (m, 1H), 2.08-1.82 (m, 1H), 1.76-1.53 (m, 1H), 1.28 (d, 3H); [13]C NMR ($CDCl_3$, 75 MHz): δ = 144.2, 128.3, 126.6, 116.8, 114.0, 38.9, 30.1, 29.7, 22.6.

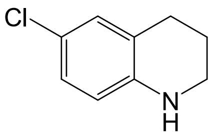


[1]H NMR ($CDCl_3$, 300 MHz): δ = 7.05-6.83 (m, 2H), 6.58 (t, 1H), 6.43 (d, 1H), 3.78 (s, 1H), 3.30-3.10 (m, 1H), 2.91-2.62 (m, 2H), 2.45-2.30 (m, 1H), 2.15-1.95 (m, 1H), 1.01 (d, 3H); [13]C NMR ($CDCl_3$, 75 MHz): δ = 144.2, 129.4, 126.5, 120.9, 116.7, 113.7, 48.7, 35.3, 27.0, 18.9.

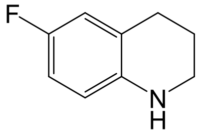


[1]H NMR ($CDCl_3$, 300 MHz): δ = 7.02-6.88 (m, 2H), 6.60 (t, 1H), 6.46 (d, 1H), 3.65 (brs, 1H), 3.48-3.25 (m, 1H), 2.93-2.55 (m, 2H), 2.01-1.76 (m, 1H), 1.70-1.45 (m, 1H), 1.19 (d, 3H); [13]C

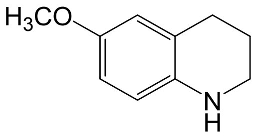
NMR ($CDCl_3$, 75 MHz): δ = 144.7, 129.2, 126.6, 121.1, 116.9, 114.0, 47.1, 30.1, 26.6, 22.6.



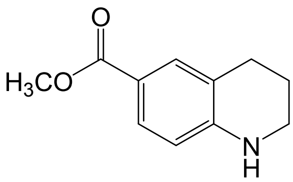
[1]H NMR ($CDCl_3$, 300 MHz): δ = 7.02-6.91 (m, 2H), 6.43-6.35 (m, 1H), 3.65 (s, 1H), 3.35-3.15 (m, 2H), 2.70 (t, 2H), 2.04-1.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.1, 128.9, 126.4, 122.8, 121.1, 115.1, 41.7, 26.7, 21.6.



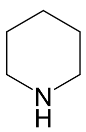
[1]H NMR ($CDCl_3$, 300 MHz): δ = 6.78-6.55 (m, 2H), 6.51-6.22 (m, 1H), 3.51 (s, 1H), 3.28 (t, 2H), 2.75 (t, 2H), 2.08-1.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 157.1, 140.9, 122.7 (d), 115.5 (d), 114.8 (d), 113.1 (d), 42.0, 27.0, 21.9.



[1]H NMR ($CDCl_3$, 300 MHz): δ = 6.65-6.46 (m, 2H), 6.45-6.35 (m, 1H), 3.70 (s, 3H), 3.57 (brs, 1H), 3.20 (t, 2H), 2.72 (t, 2H), 1.98-1.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 151.5, 138.7, 122.6, 115.3, 114.6, 112.7, 55.5, 55.3, 42.1, 27.0, 22.2.

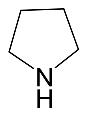


[1]H NMR ($CDCl_3$, 300 MHz): δ = 7.68-7.57 (m, 2H), 6.37 (d, 1H), 4.36 (s, 1H), 3.83 (s, 3H), 3.40-3.27 (m, 2H), 2.76 (t, 2H), 2.01-1.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.5, 148.7, 131.2, 129.0, 119.8, 117.3, 112.6, 51.4, 41.6, 26.8, 21.3.

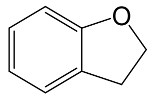


[1]H NMR ($CDCl_3$, 300 MHz): δ = 2.99-2.69 (m, 2H), 1.72-1.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 75

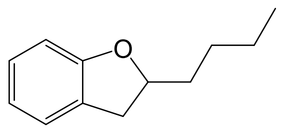
MHz): δ = 47.3, 27.1, 25.0.



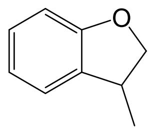
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.01-2.62 (m, 4H), 1.88-1.43 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 46.9, 25.4.



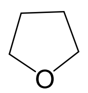
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-6.98 (m, 2H), 6.95-6.83 (m, 2H), 4.55 (t, 2H), 3.20 (t, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.9, 127.9, 126.8, 124.9, 120.3, 109.3, 71.0, 27.0.



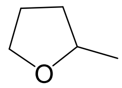
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19-7.01 (m, 2H), 6.88-6.65 (m, 2H), 4.84-6.63 (m, 1H), 3.35-3.16 (m, 1H), 2.91-2.72 (m, 1H), 1.91-1.73 (m, 1H), 1.71-1.56 (m, 1H), 1.55-1.18 (m, 4H), 0.93 (t, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.5, 127.8, 126.9, 124.8, 120.0, 109.2, 83.3, 35.8, 35.4, 27.6, 22.6, 14.0.



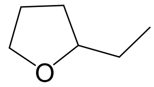
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.19-7.03 (m, 2H), 6.91-6.58 (m, 2H) 4.65 (t, 1H), 4.05 (t, 1H), 3.61-3.38 (m, 1H), 1.30 (d, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.7, 132.2, 128.0, 123.8, 120.4, 109.4, 78.4, 78.3, 36.5, 19.3.



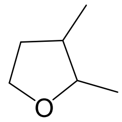
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.91-3.58 (m, 4H), 2.03-1.71 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 67.9, 25.6.



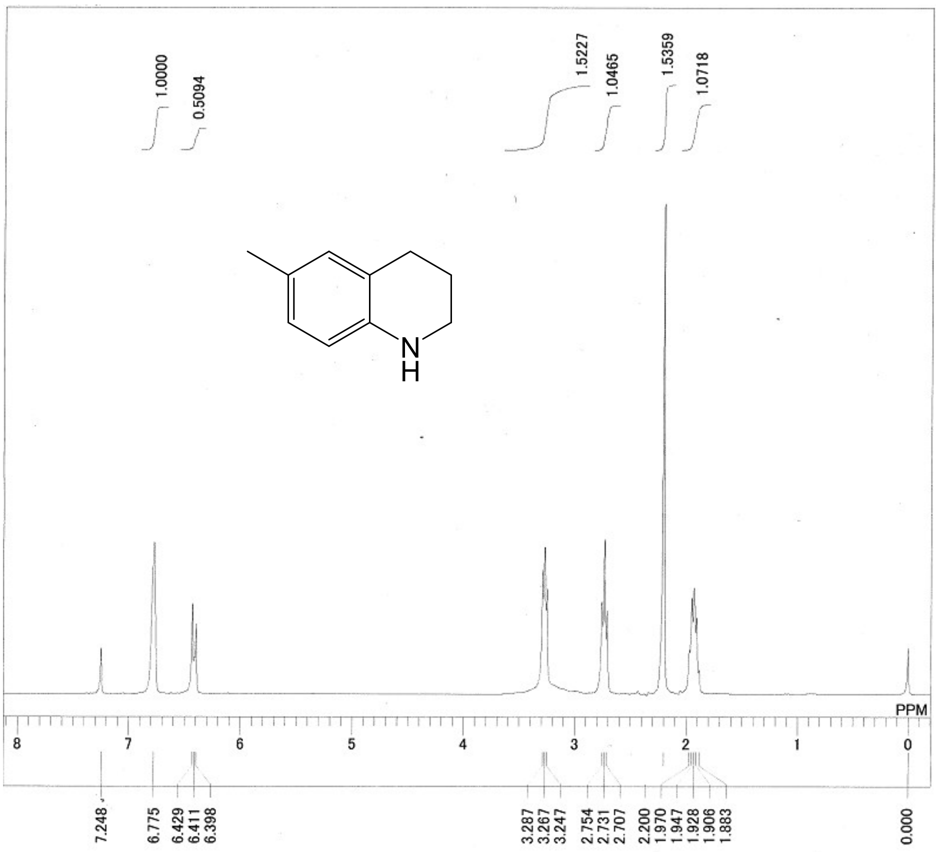
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.05-3.80 (m, 2H), 3.79-3.58 (m, 1H), 2.09-1.66 (m, 3H), 1.51-1.29 (m, 1H), 1.23 (d, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 75.2, 67.7, 33.0, 25.8, 20.9.



^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.85-3.49 (m, 3H), 1.99-1.65 (m, 3H), 1.63-1.21 (m, 3H), 0.86 (t, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 80.6, 67.5, 30.7, 28.4, 25.6, 10.3.



^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.01-3.75 (m, 2H), 3.71-3.49 (m, 1H), 2.25-1.84 (m, 2H), 1.61-1.36 (m, 1H), 1.02 (d, 3H), 0.85 (d, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 77.1, 66.0, 35.8, 33.6, 15.8, 14.1.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H
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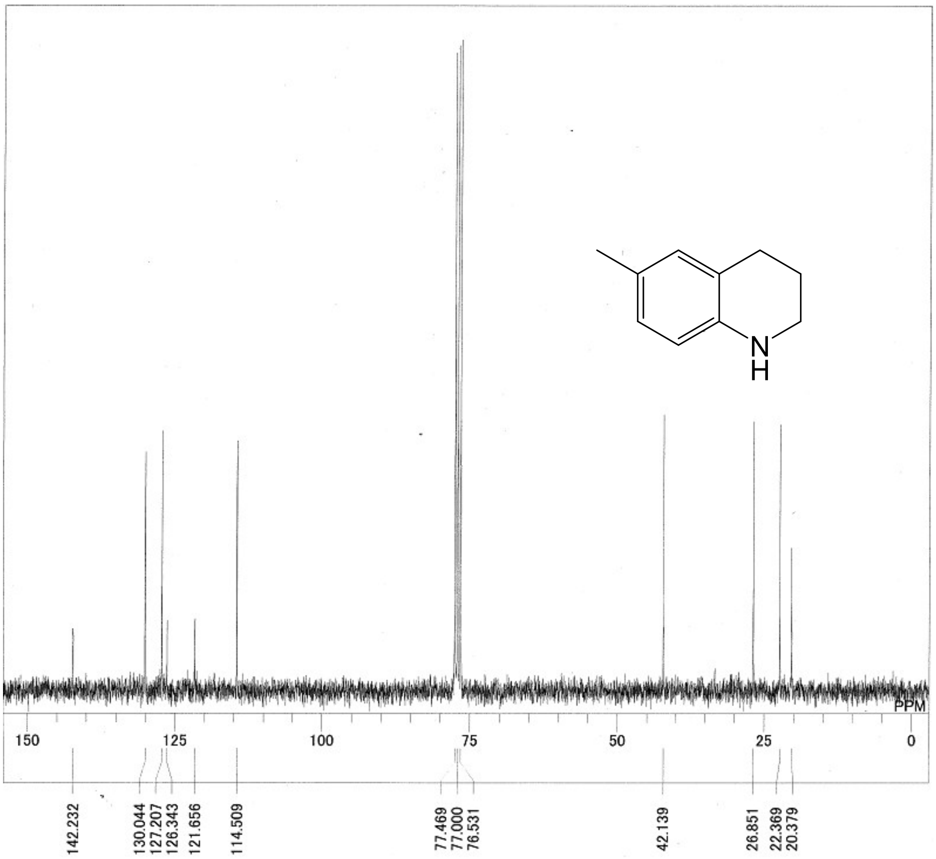
7
6
5
4
3
2
1
0
7.248
6.775
6.429
6.411
6.398
3.287
3.267
3.247
2.754
2.731
2.707
2.200
1.970
1.947
1.928
1.906
1.883
0.000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H
PPM
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125
100
75
50
25
0
142.232
130.044
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121.656
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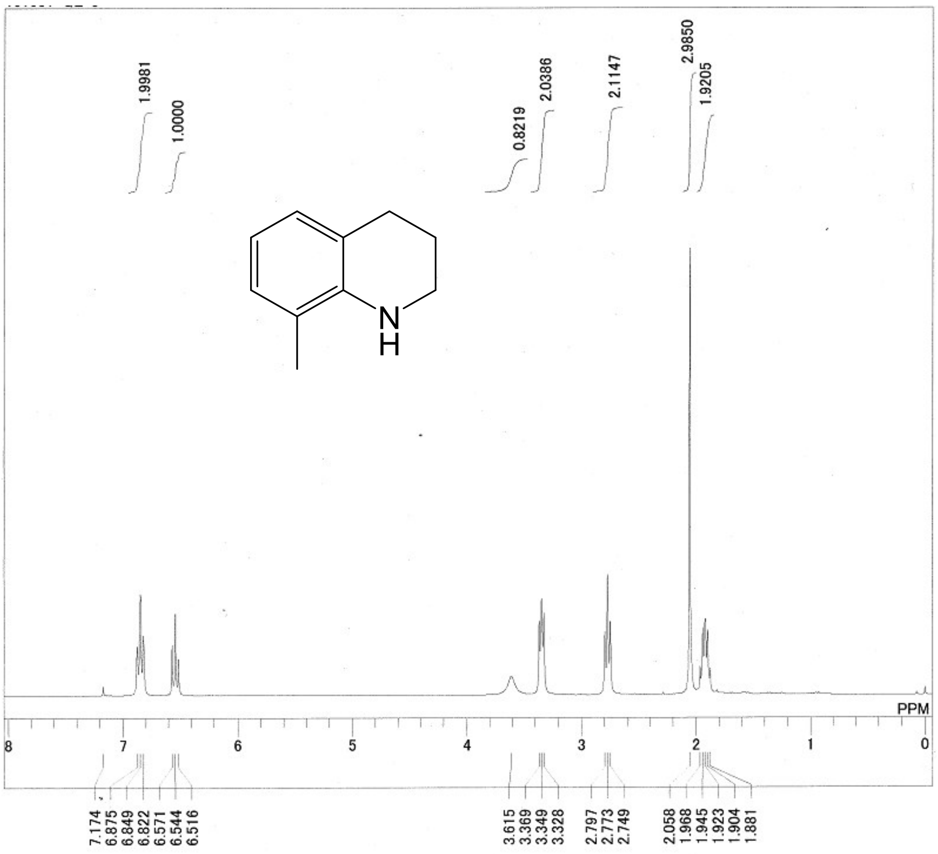
77.469
77.000
76.531
42.139
26.851
22.369
20.379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1.9205
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H
PPM
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6.875
6.849
6.822
6.571
6.544
6.516
3.615
3.369
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3.328
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2.773
2.749
2.058
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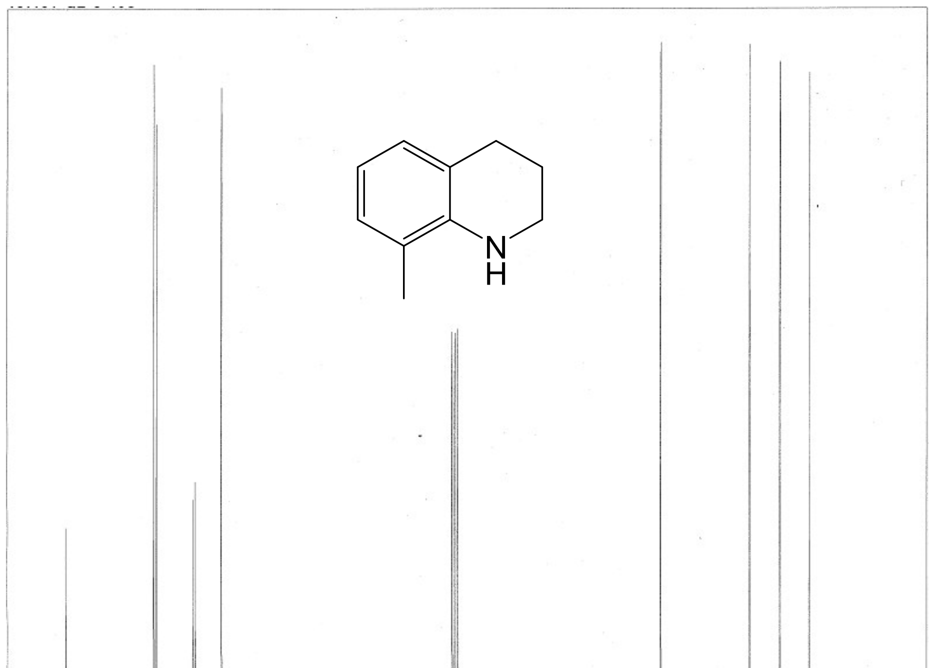
1.945
1.923
1.904
1.881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77.000
76.523
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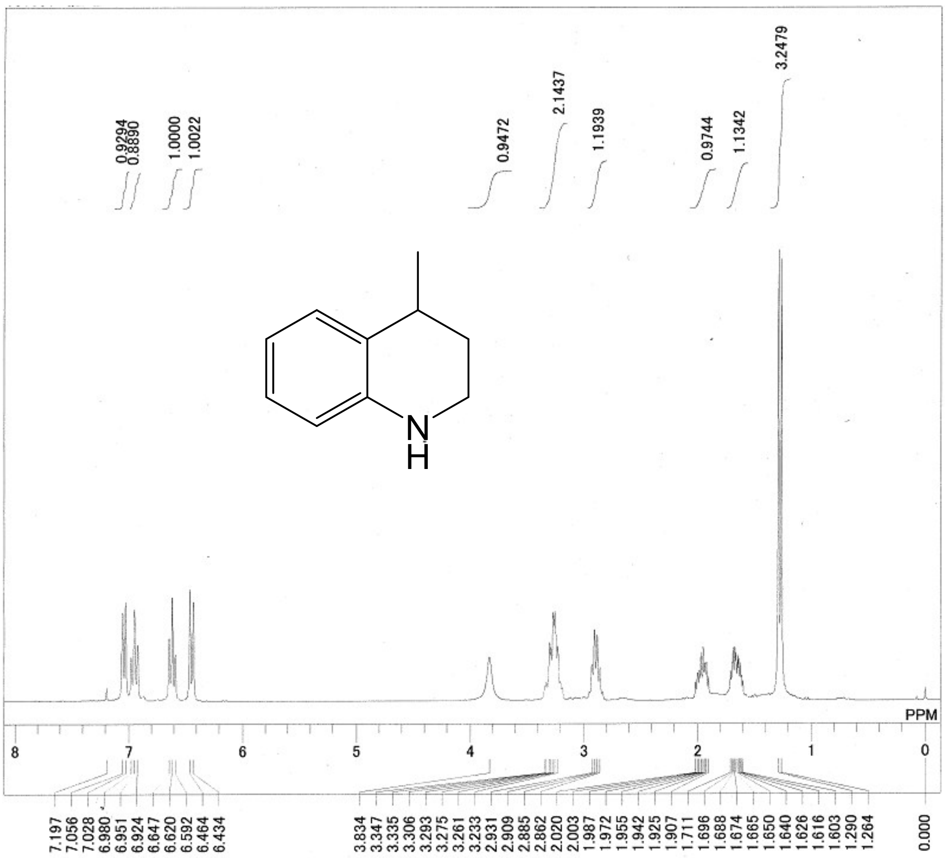
17.073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1.1939
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N
H
PPM
8
7
6
5
4
3
2
1
0
7.197
7.056
7.028
6.980
6.951
6.924
6.647
6.620
6.592
6.464
6.434
3.834
3.347
3.335
3.306
3.293
3.275
3.261
3.233
2.931
2.909
2.885
2.862
2.020
2.003
1.987
1.972
1.955
1.942
1.925
1.907
1.711
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1.674
1.665
1.650
1.640
1.626
1.616
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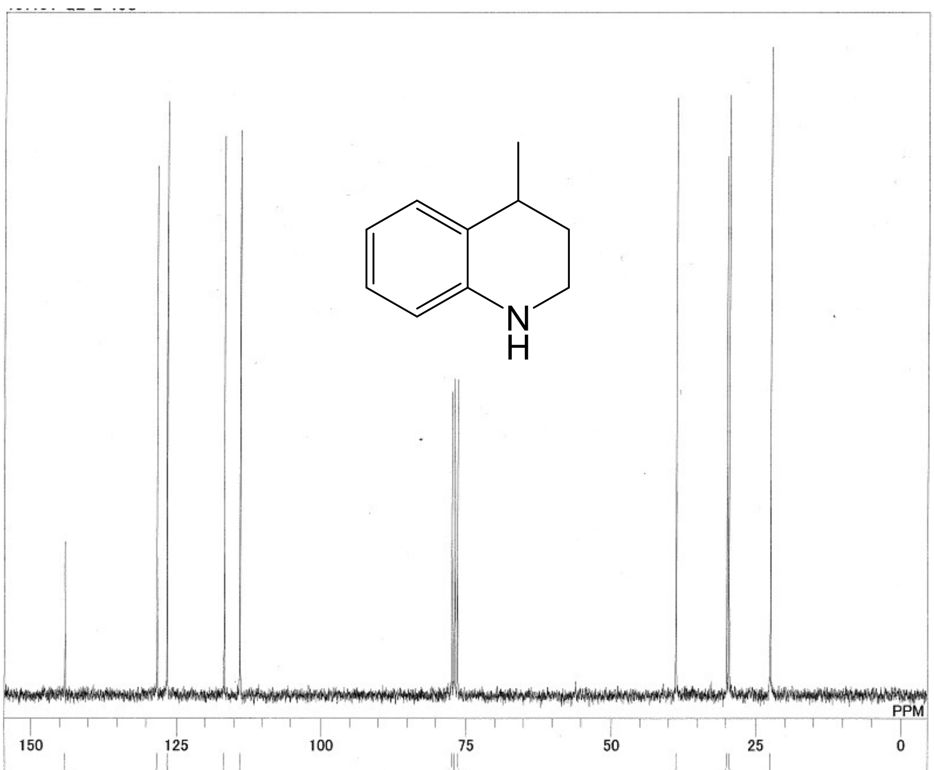
1.264
0.000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H
PPM
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75
50
25
0
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116.795
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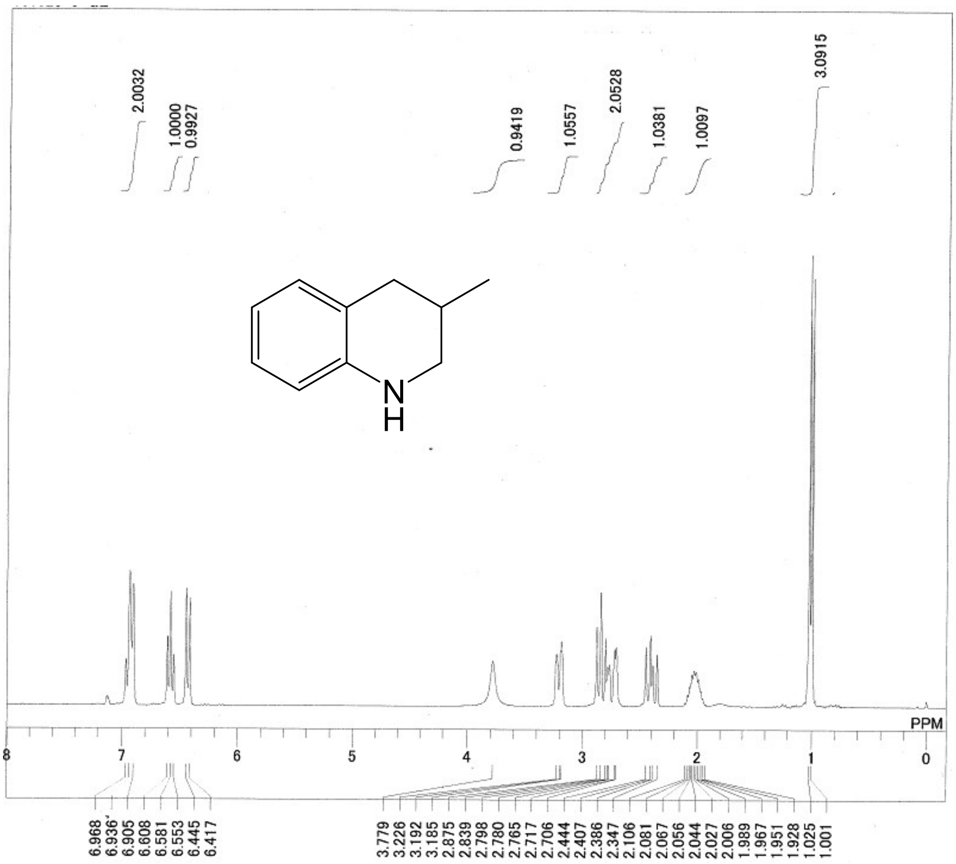
77.477
77.000
76.531
38.882
30.116
29.746
22.566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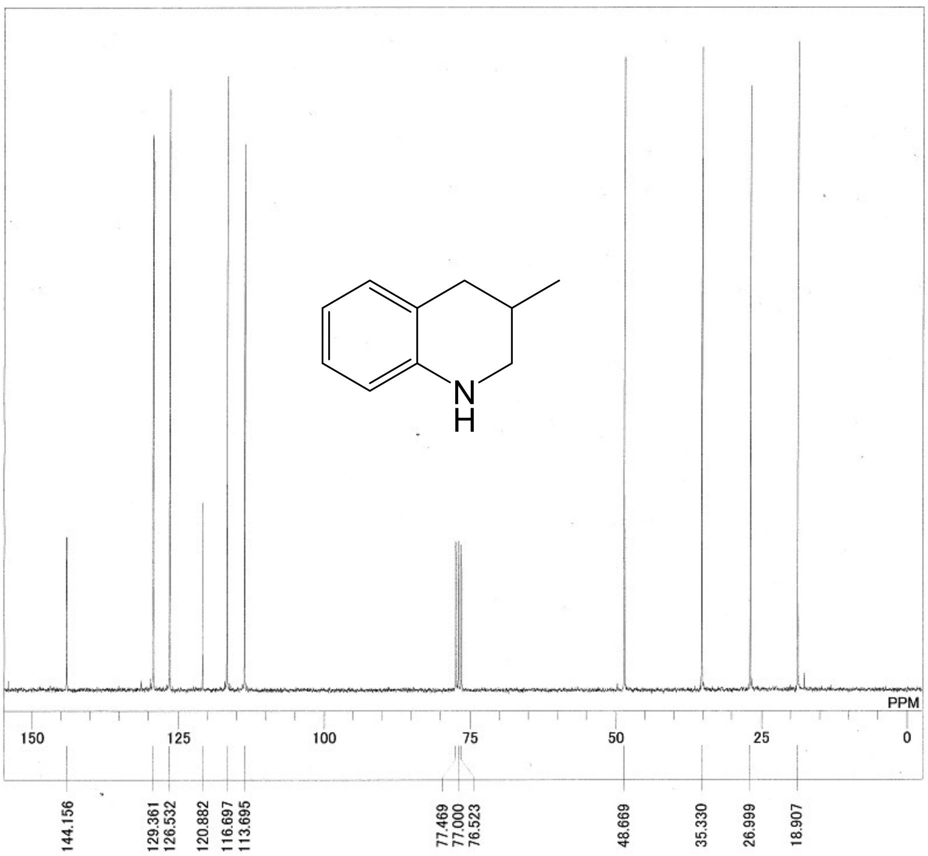
H
PPM
8
7
6
5
4
3
2
1
0
6.968
6.936
6.905
6.608
6.581
6.553
6.445
6.417
3.779
3.226
3.192
3.185
2.875
2.839
2.798
2.780
2.765
2.717
2.706
2.444
2.407
2.386
2.347
2.106
2.081
2.067
2.056
2.044
2.027
2.006
1.989
1.967
1.951
1.928
1.025
1.001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H
PPM
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125
100
75
50
25
0
144.156
129.361
126.532
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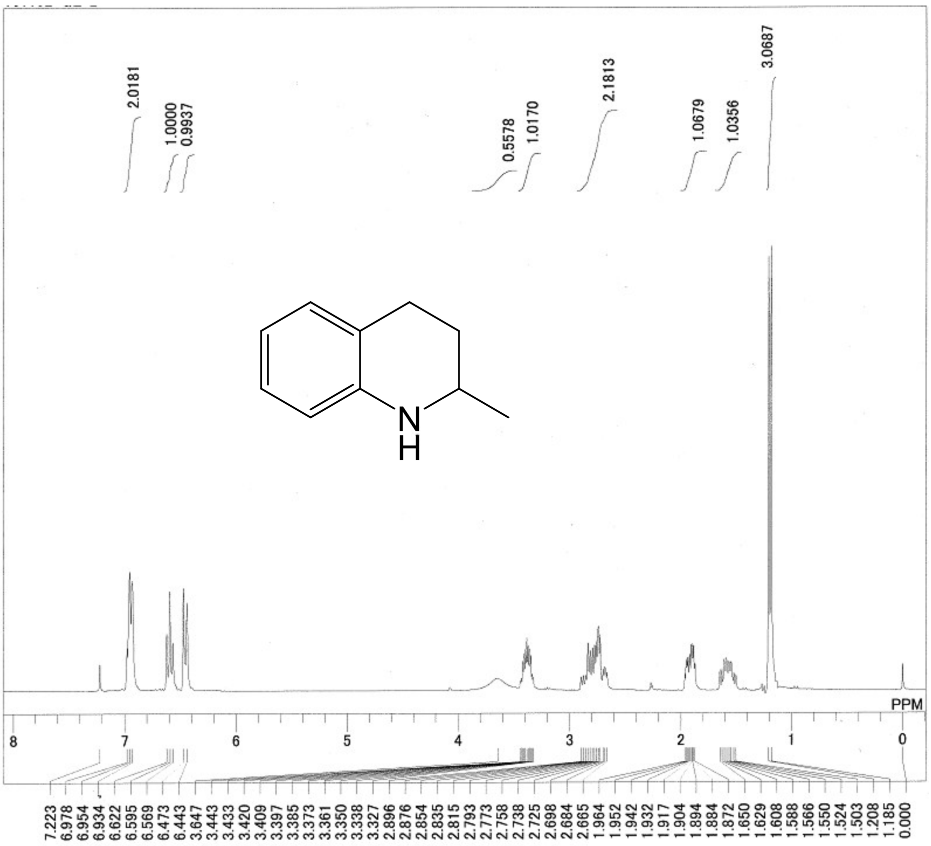
116.697
113.695
77.469
77.000
76.523
48.669
35.330
26.999
18.907



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1.0356
3.0687
N
H
PPM
8
7
6
5
4
3
2
1
0
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6.954
6.934
6.622
6.595
6.569
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6.443
3.647
3.443
3.433
3.420
3.409
3.397
3.385
3.373
3.361
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3.338
3.327
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2.876
2.854
2.835
2.815
2.793
2.773
2.758
2.738
2.725
2.698
2.684
2.665
1.964
1.952
1.942
1.932
1.917
1.904
1.894
1.884
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1.608
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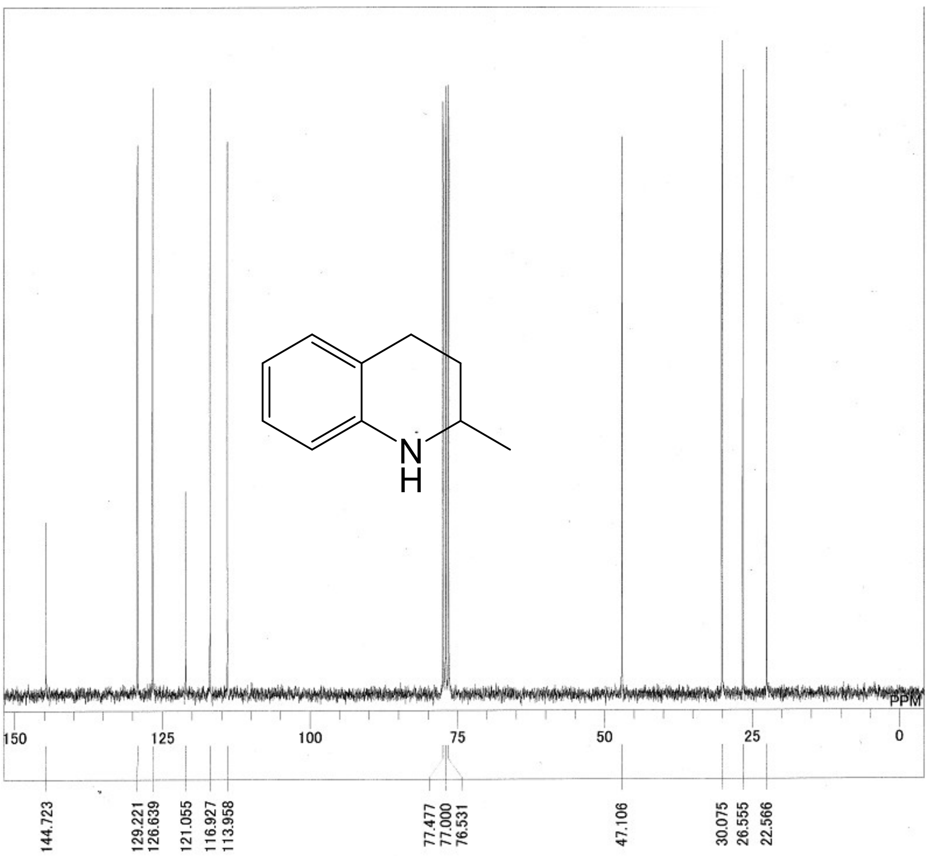
1.566
1.550
1.524
1.503
1.208
1.185
0.000



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PPM
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125
100
75
50
25
0
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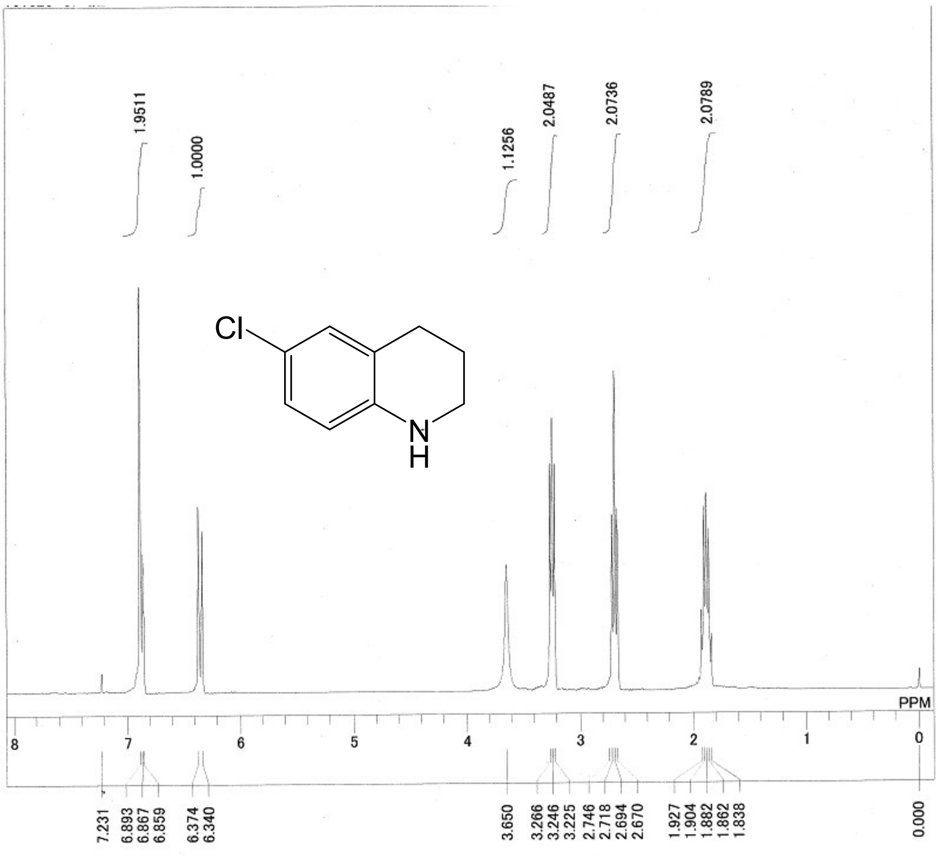
76.531
47.106
30.075
26.555
22.566



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2.0736
2.0789
Cl
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H
PPM
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6.867
6.859
6.374
6.340
3.650
3.266
3.246
3.225
2.746
2.718
2.694
2.670
1.927
1.904
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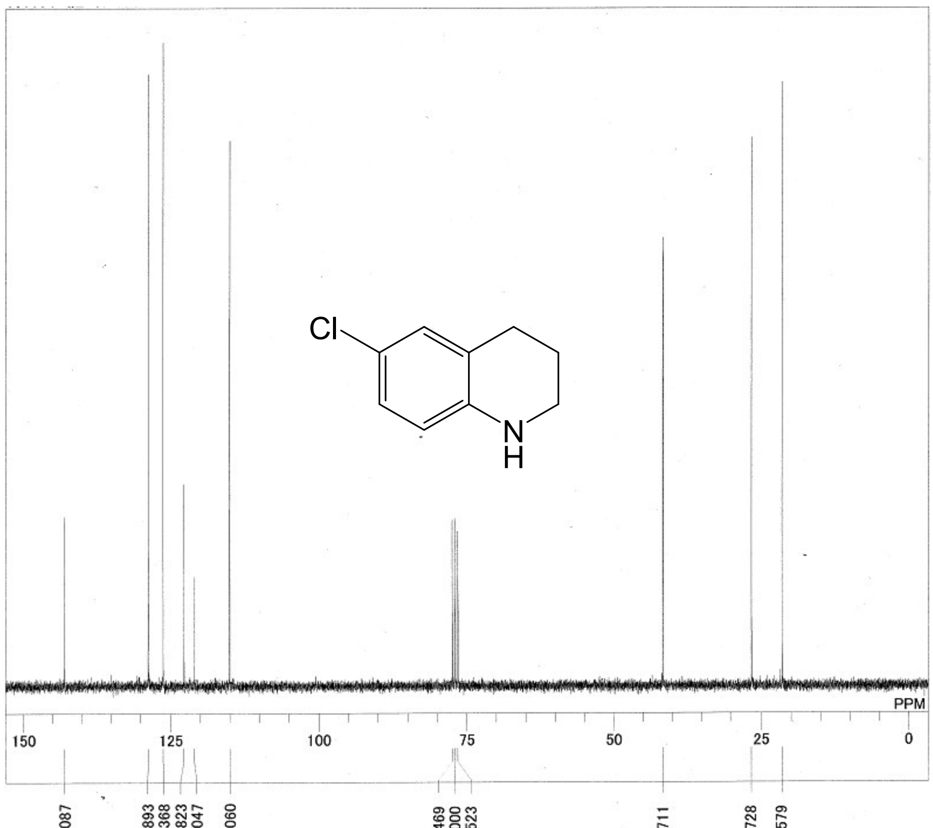
1.862
1.838
0.000



Cl
N
H
PPM
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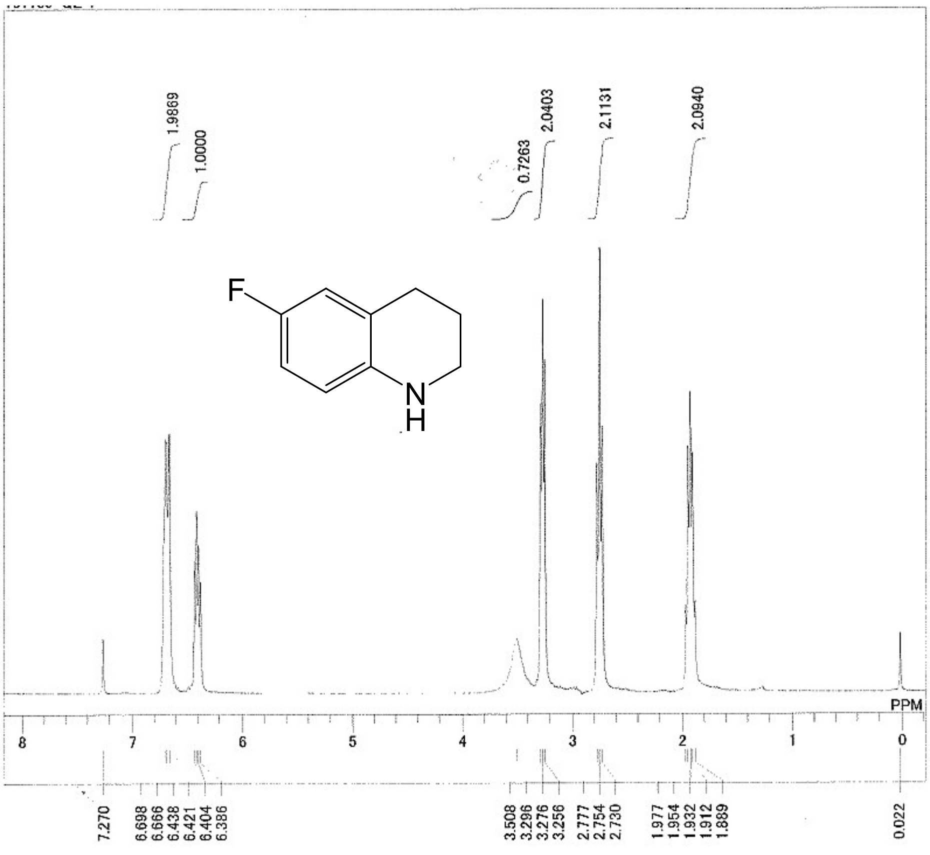
121.047
115.060
77.469
77.000
76.523
41.711
26.728
21.579



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F
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H
PPM
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7
6
5
4
3
2
1
0
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6.698
6.666
6.438
6.421
6.404
6.386
3.508
3.296
3.276
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2.777
2.754
2.730
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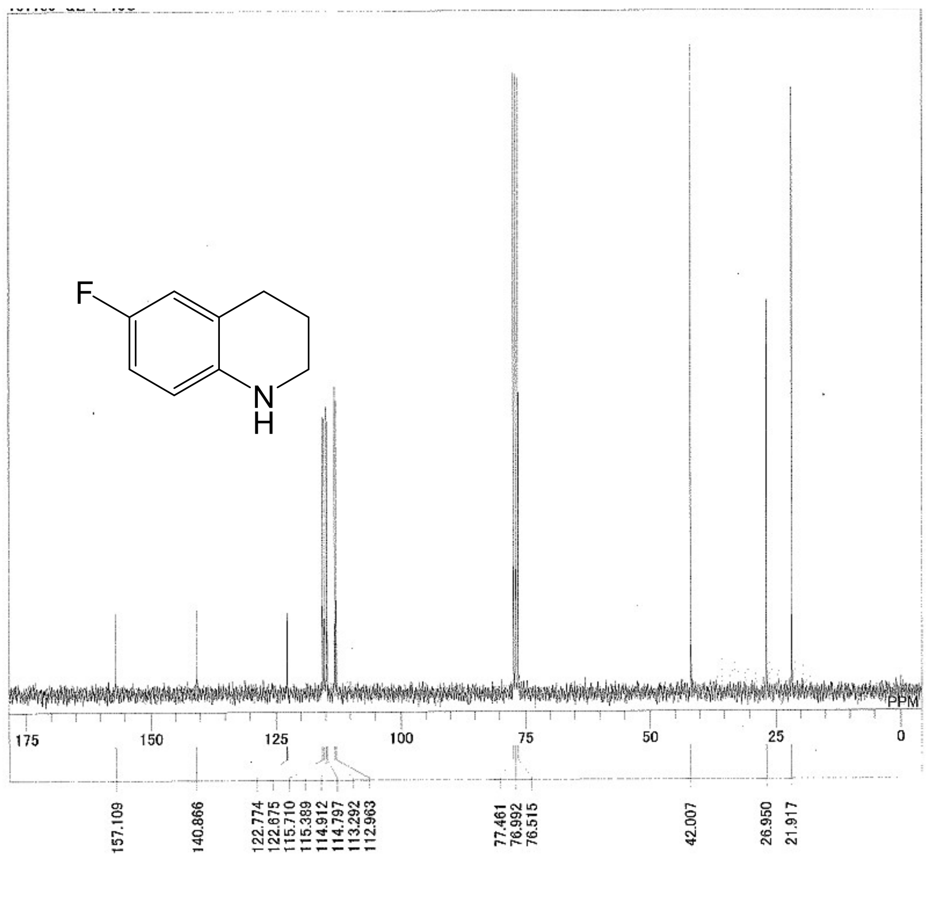
1.954
1.932
1.912
1.889
0.022



F
N
H
PPM
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150
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100
75
50
25
0
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122.774
122.675
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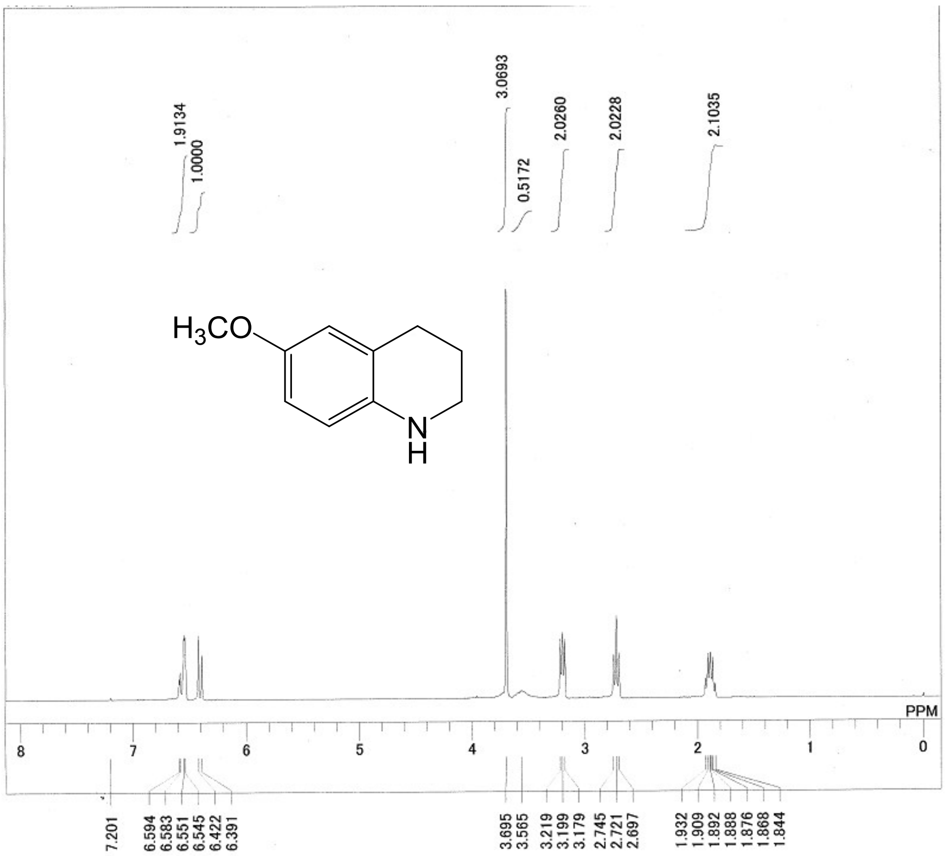
26.950
21.917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N
H
PPM
8
7
6
5
4
3
2
1
0
7.201
6.594
6.583
6.551
6.545
6.422
6.391
3.695
3.565
3.219
3.199
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2.721
2.697
1.932
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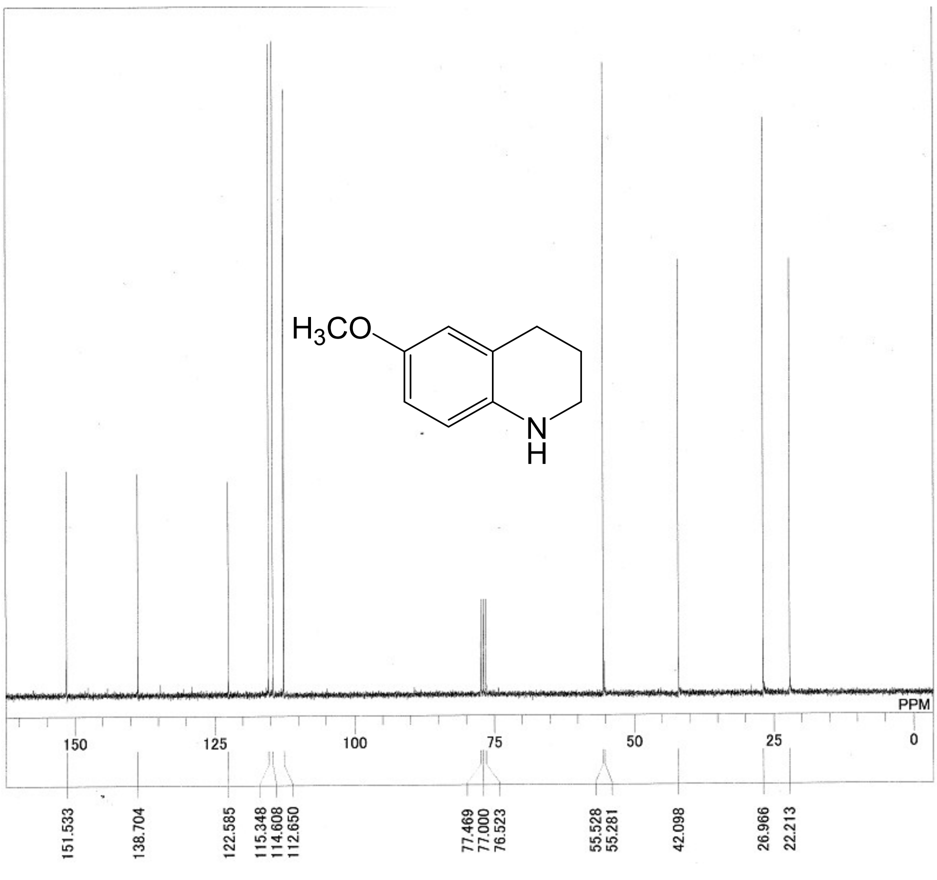
1.888
1.876
1.868
1.844


H_3CO
N
H
PPM
150
125
100
75
50
25
0
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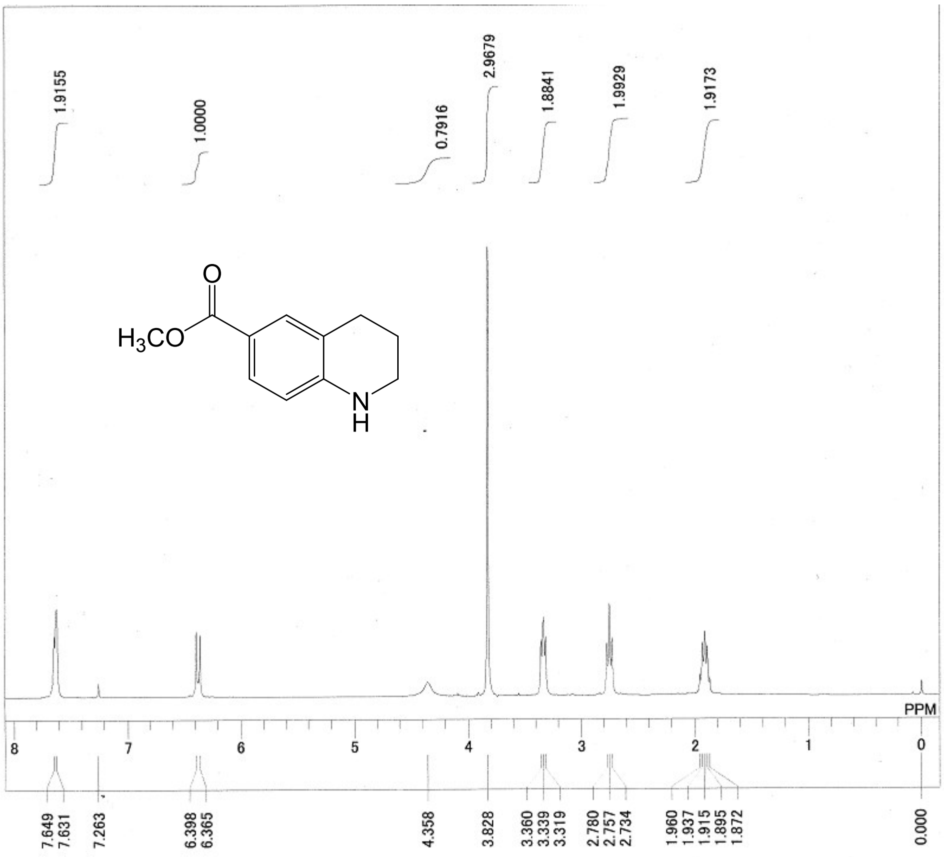
115.348
114.608
112.650
77.469
77.000
76.523
55.528
55.281
42.098
26.966
22.213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1.8841
1.9929
1.9173
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O
N
H
PPM
8
7
6
5
4
3
2
1
0
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7.631
7.263
6.398
6.365
4.358
3.828
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3.339
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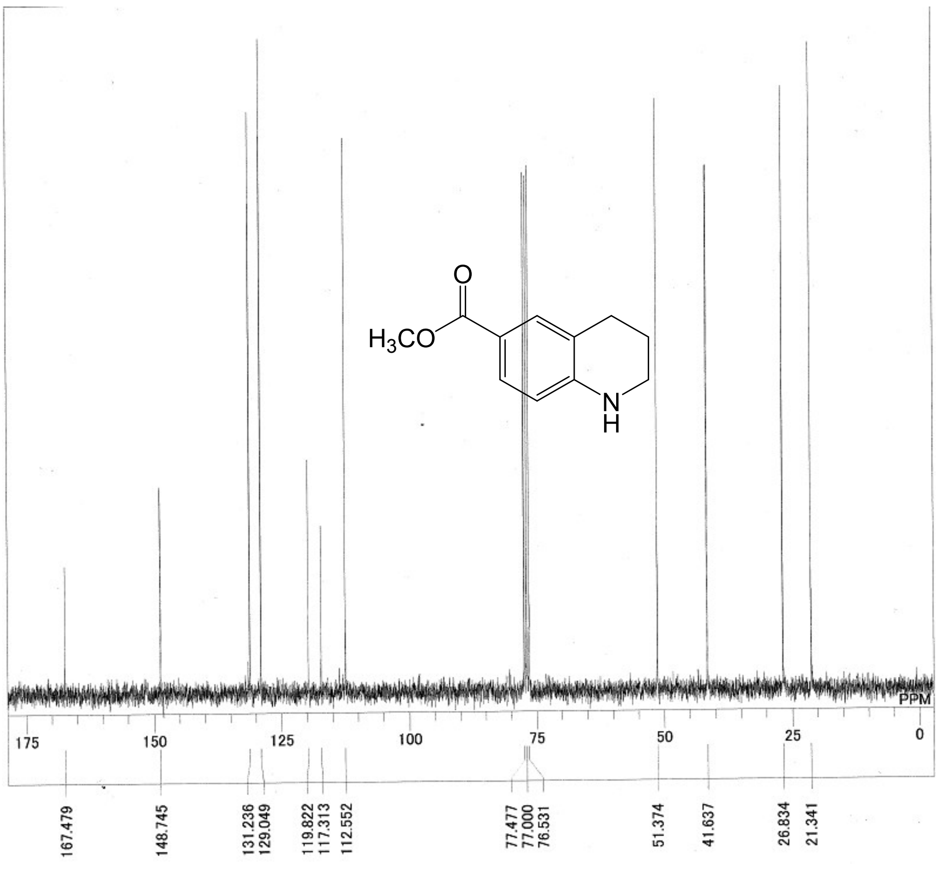
2.780
2.757
2.734
1.960
1.937
1.915
1.895
1.872
0.000


H_3CO
O
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H
PPM
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150
125
100
75
50
25
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77.000
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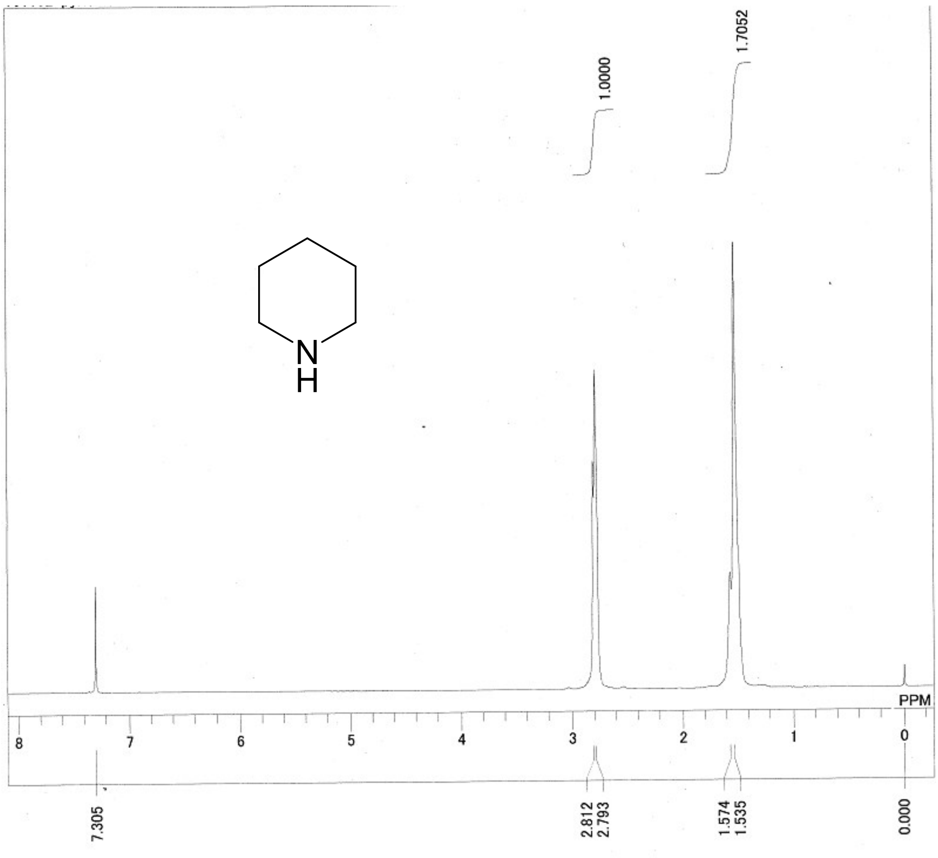
21.341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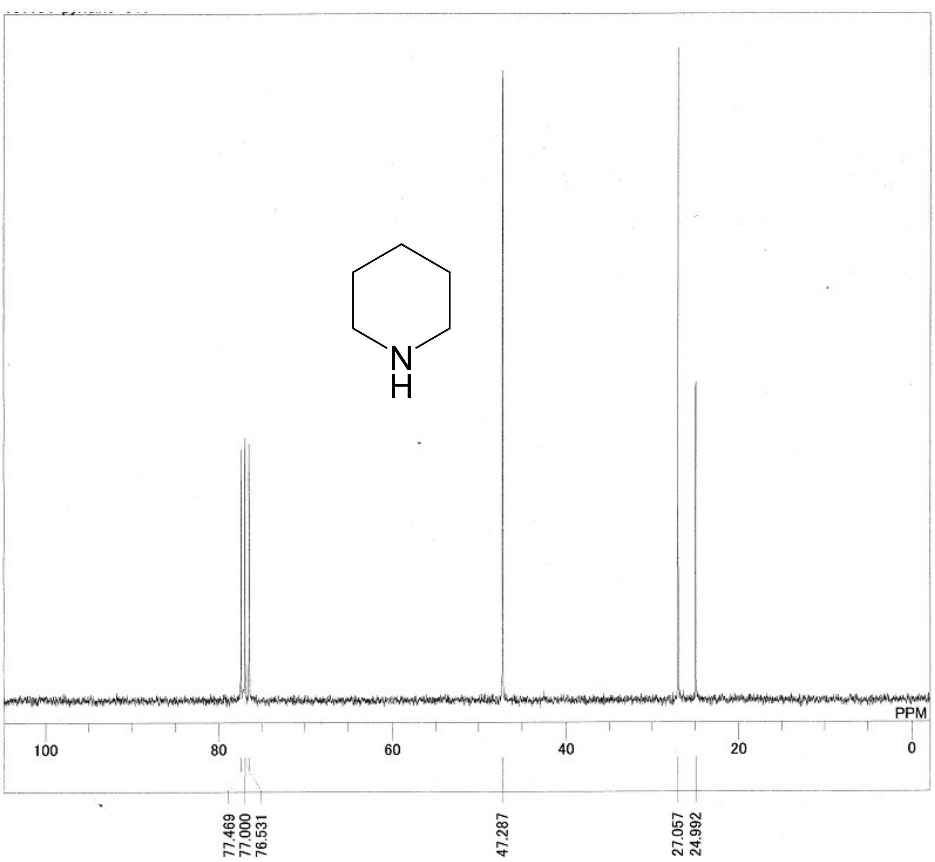
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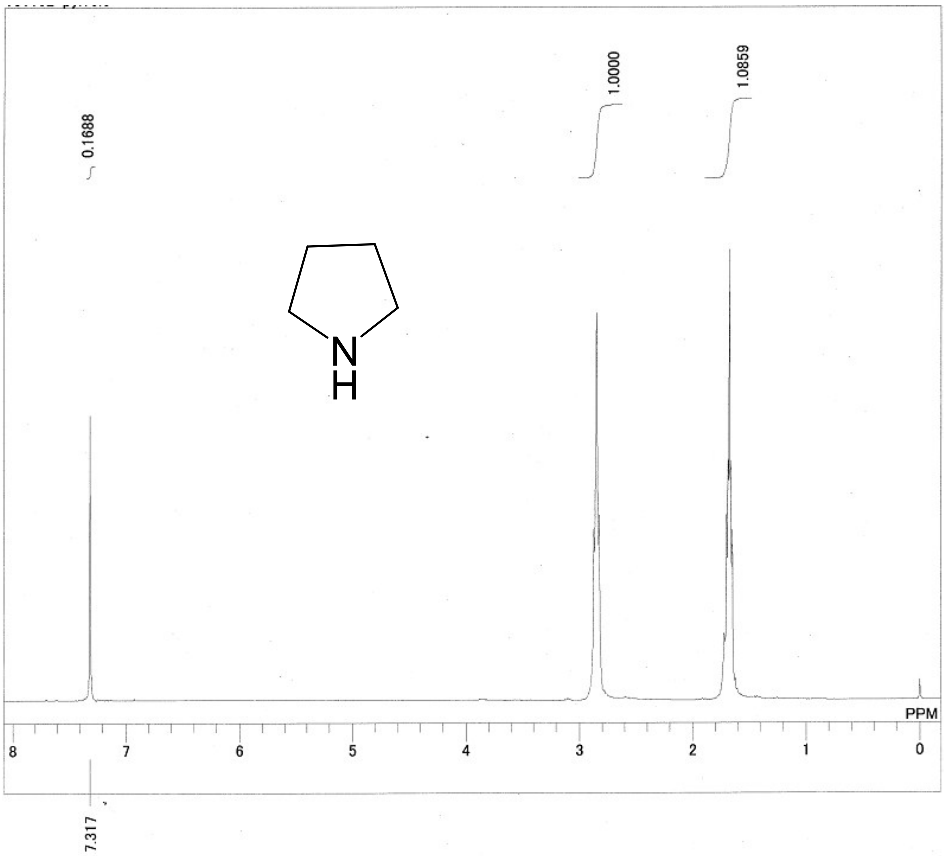
27.057
24.992



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1
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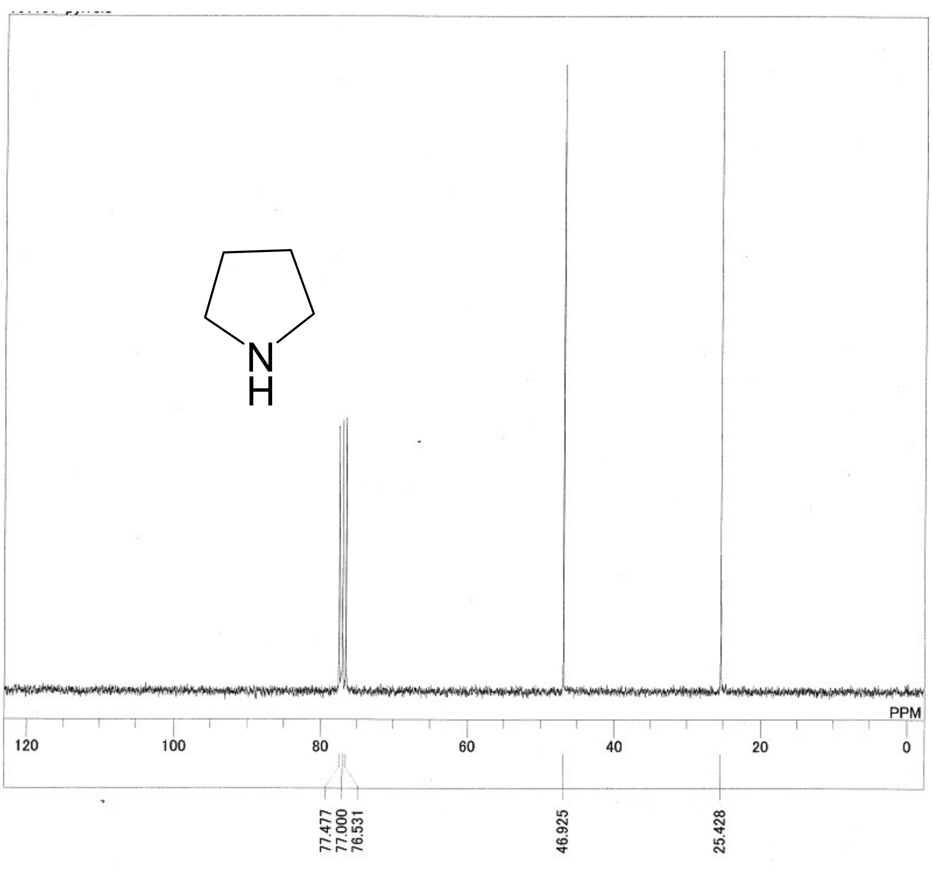

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20
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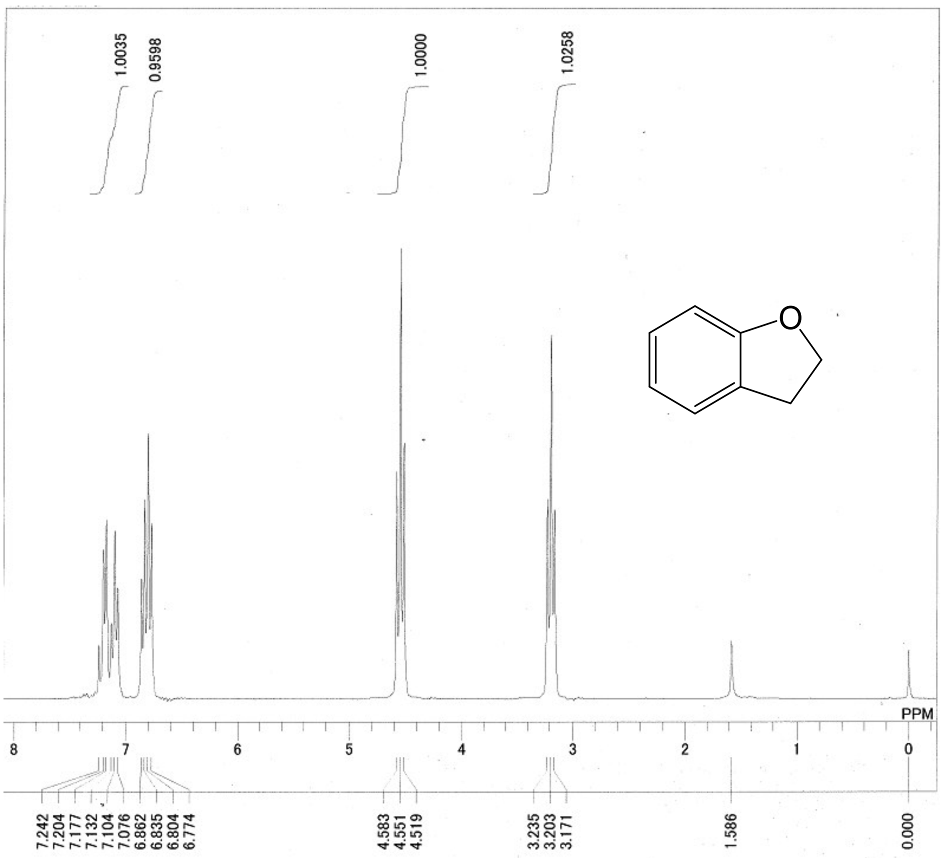
46.925
25.428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7.132
7.104
7.076
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6.835
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3.235
3.203
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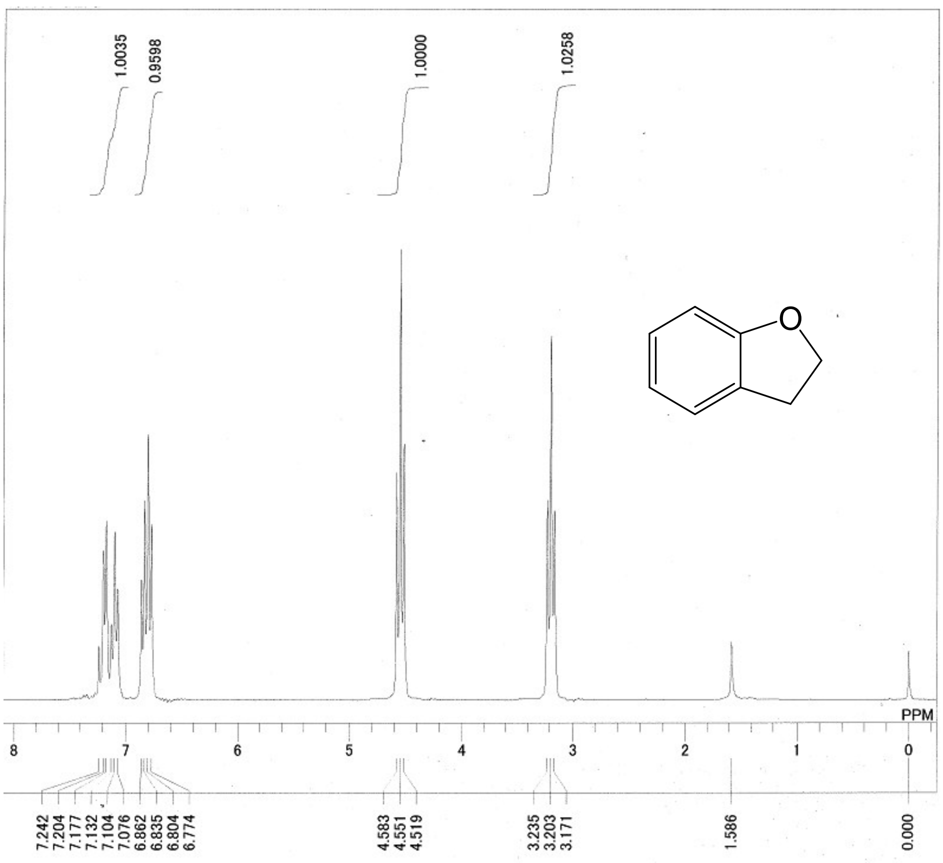
1.586
0.000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7.204
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7.132
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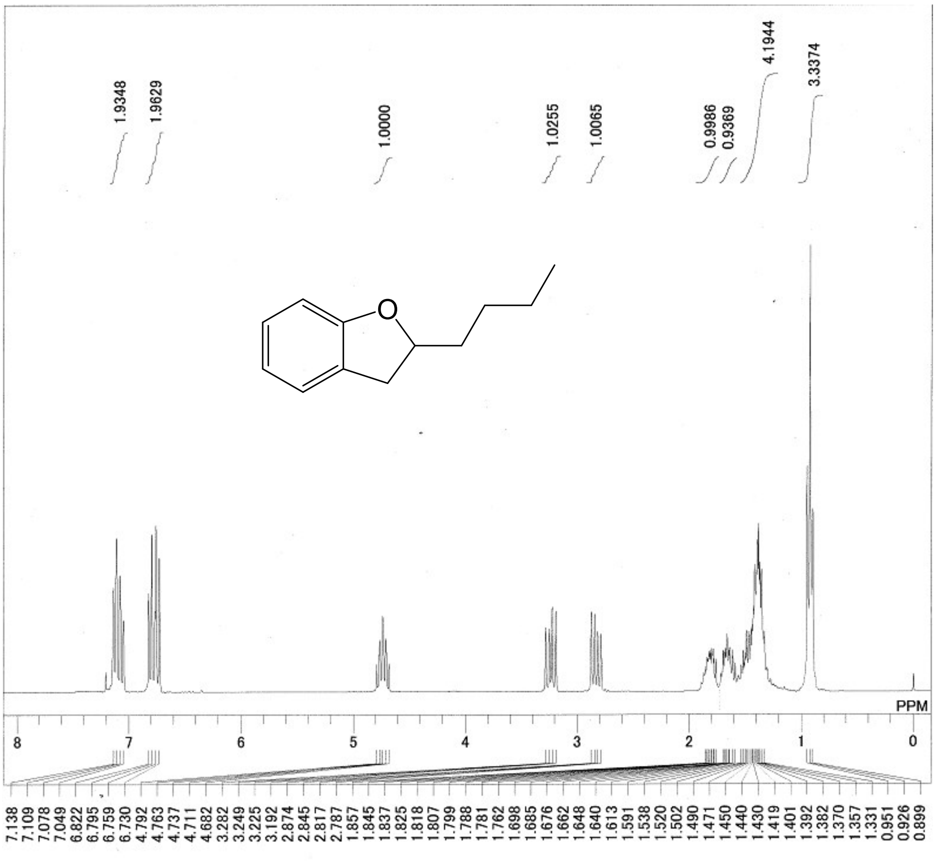

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PPM
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7
6
5
4
3
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0
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6.759
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4.763
4.737
4.711
4.682
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3.249
3.225
3.192
2.874
2.845
2.817
2.787
1.857
1.845
1.837
1.825
1.818
1.807
1.799
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1.762
1.698
1.685
1.676
1.662
1.648
1.640
1.613
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1.520
1.502
1.490
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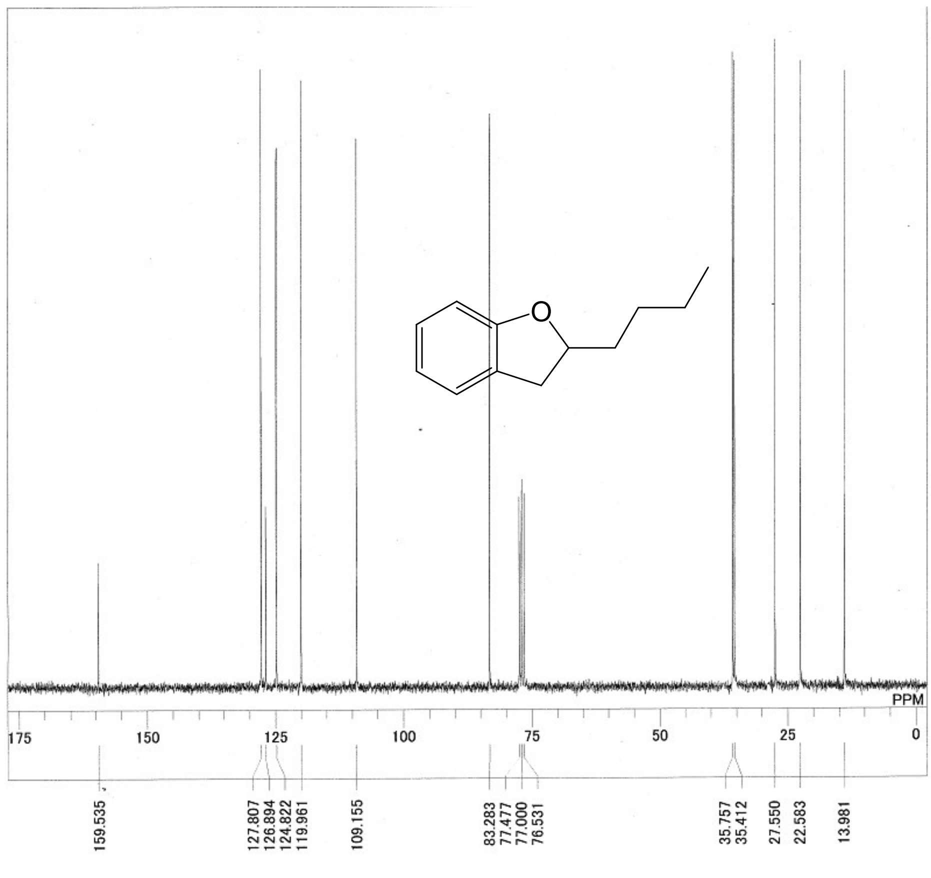
0.899



O
PPM
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125
100
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50
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0
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127.807
126.894
124.822
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83.283
77.477
77.000
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35.412
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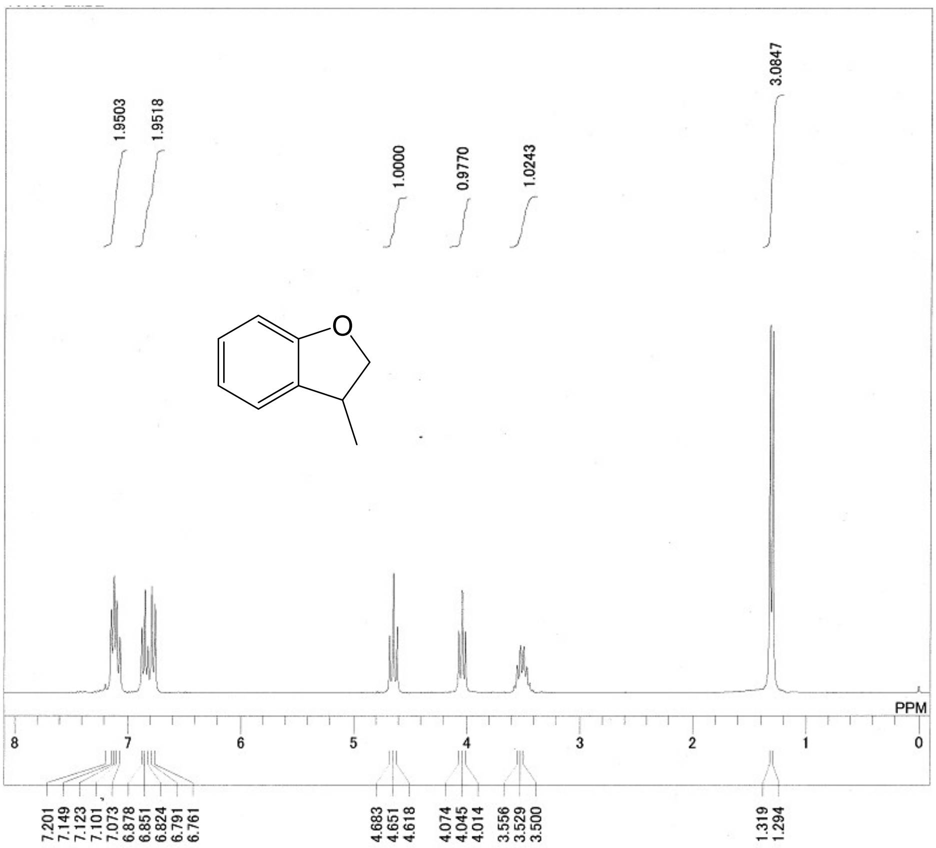
22.583
13.981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7
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5
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2
1
0
7.201
7.149
7.123
7.101
7.073
6.878
6.851
6.824
6.791
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4.651
4.618
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4.045
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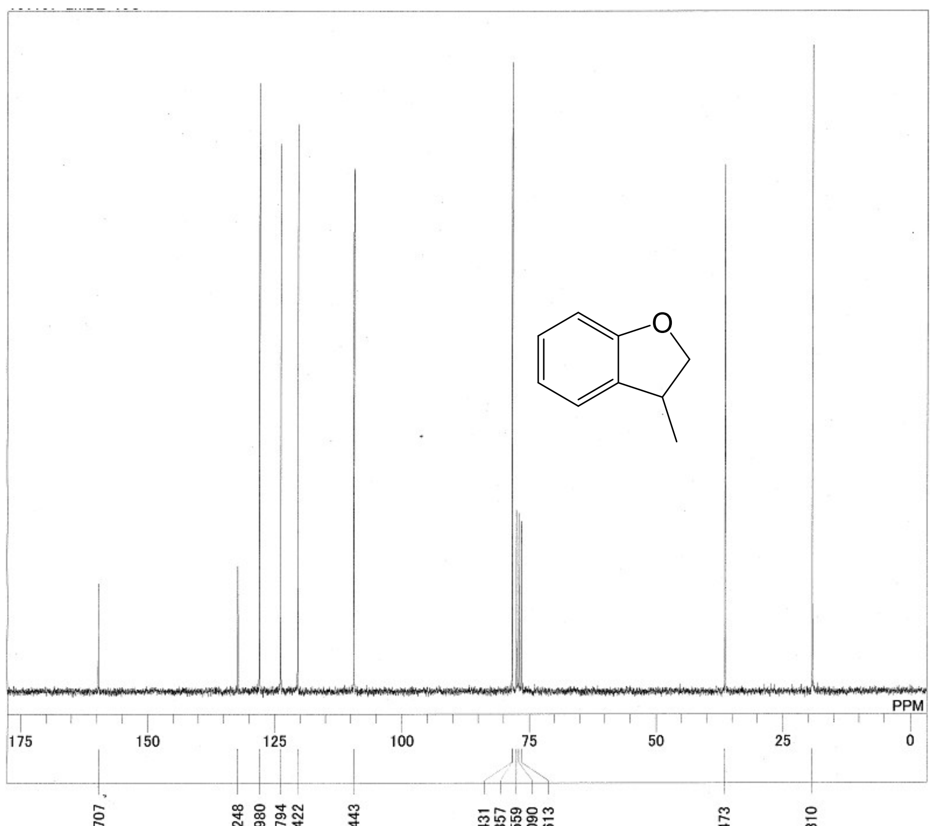
3.556
3.529
3.500
1.319
1.294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77.559
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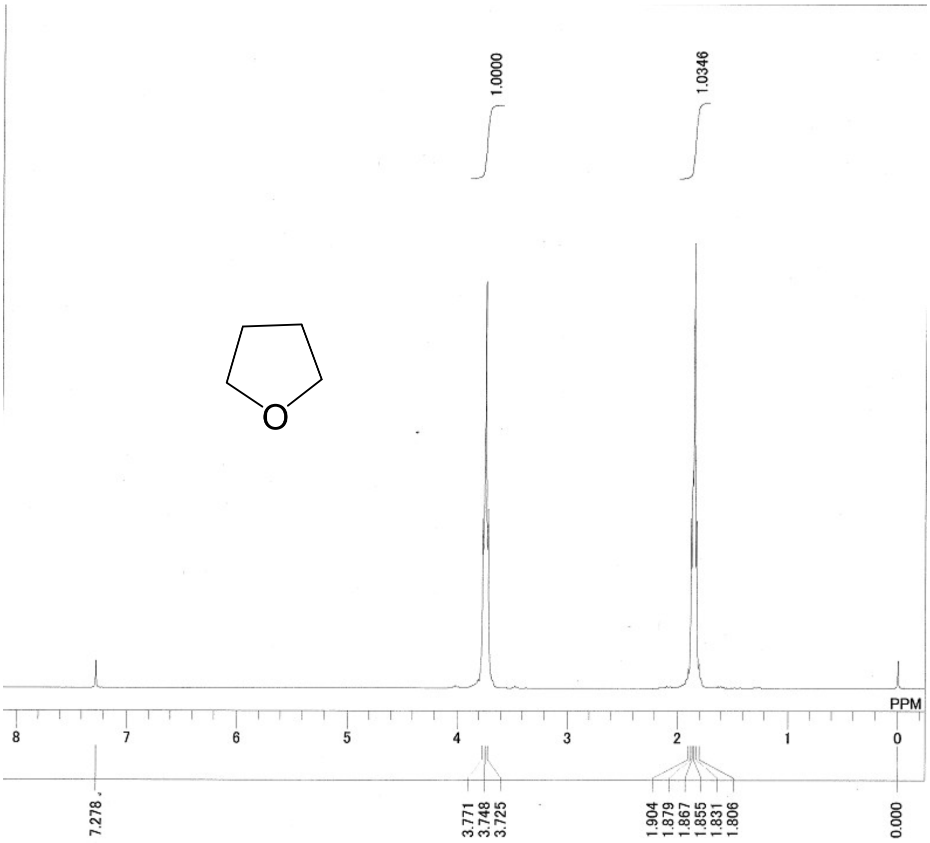
19.310



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4
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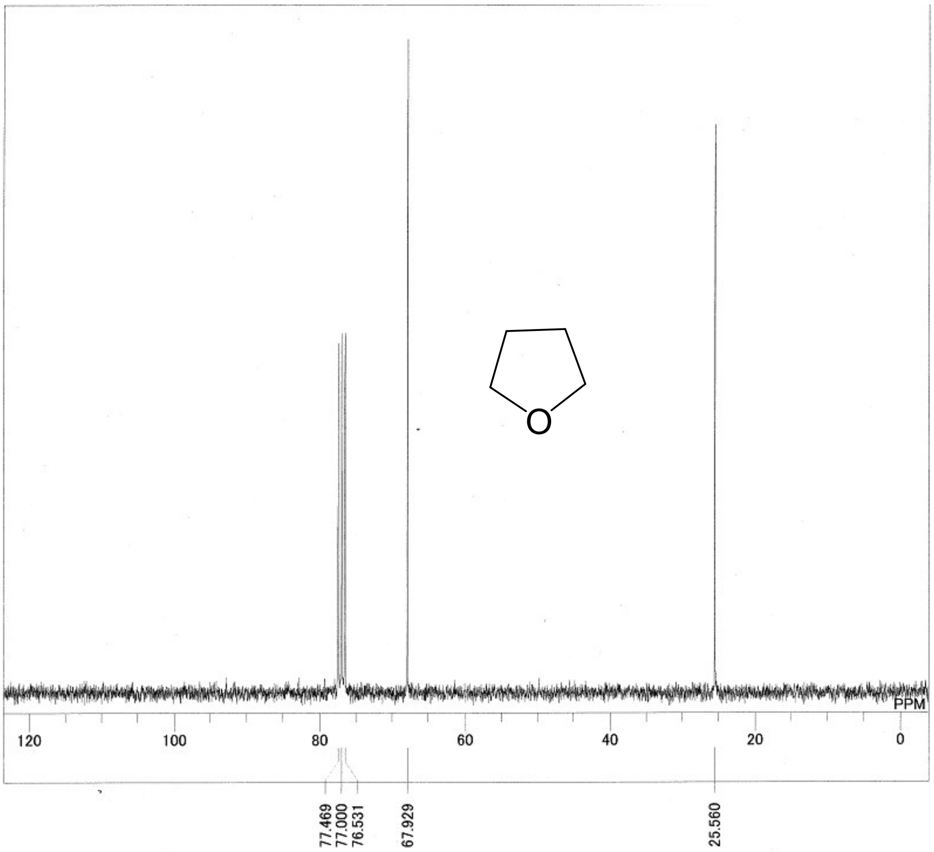
0.000



O
PPM
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40
20
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77.000
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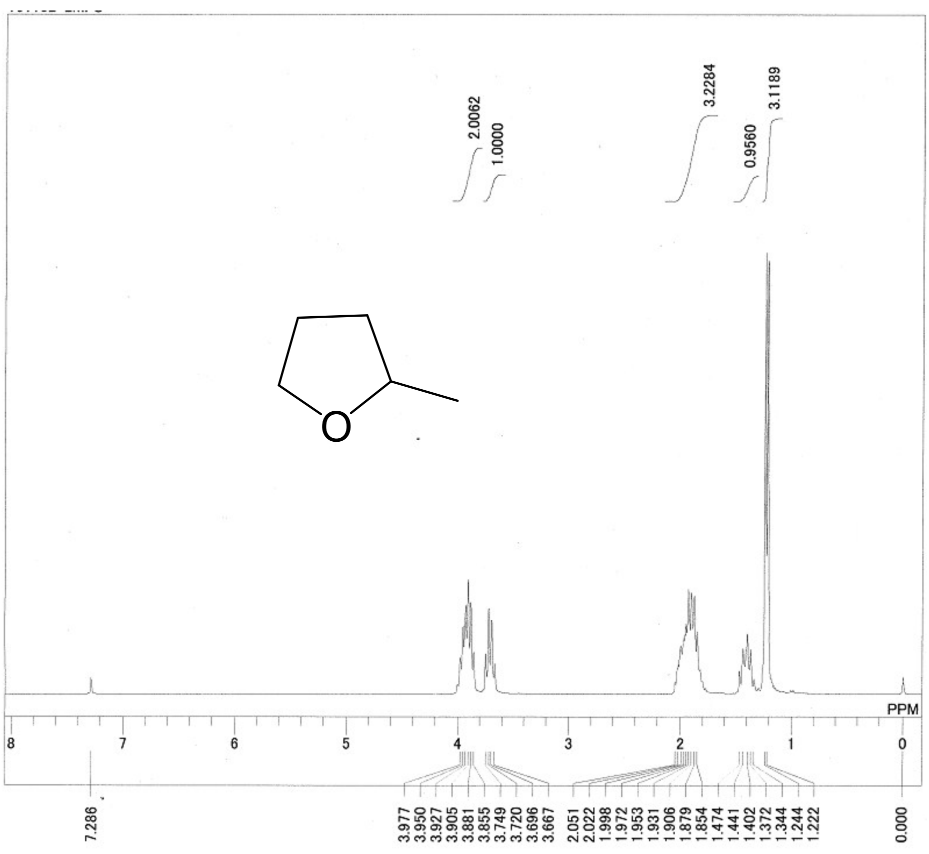
67.929
25.560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PPM
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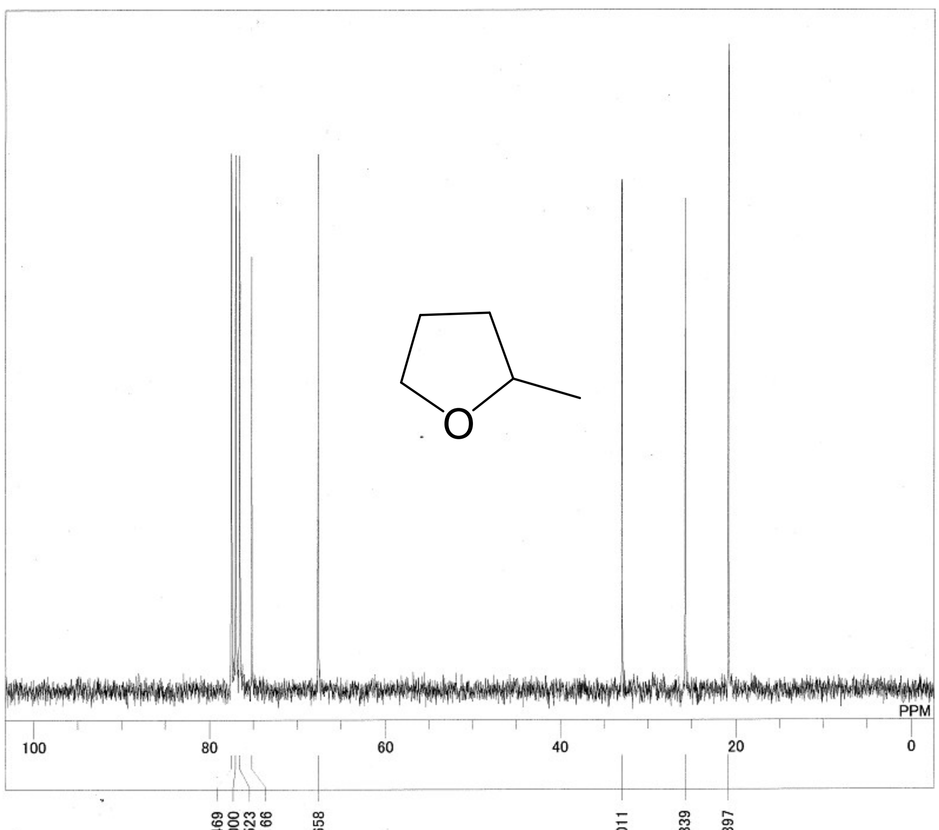
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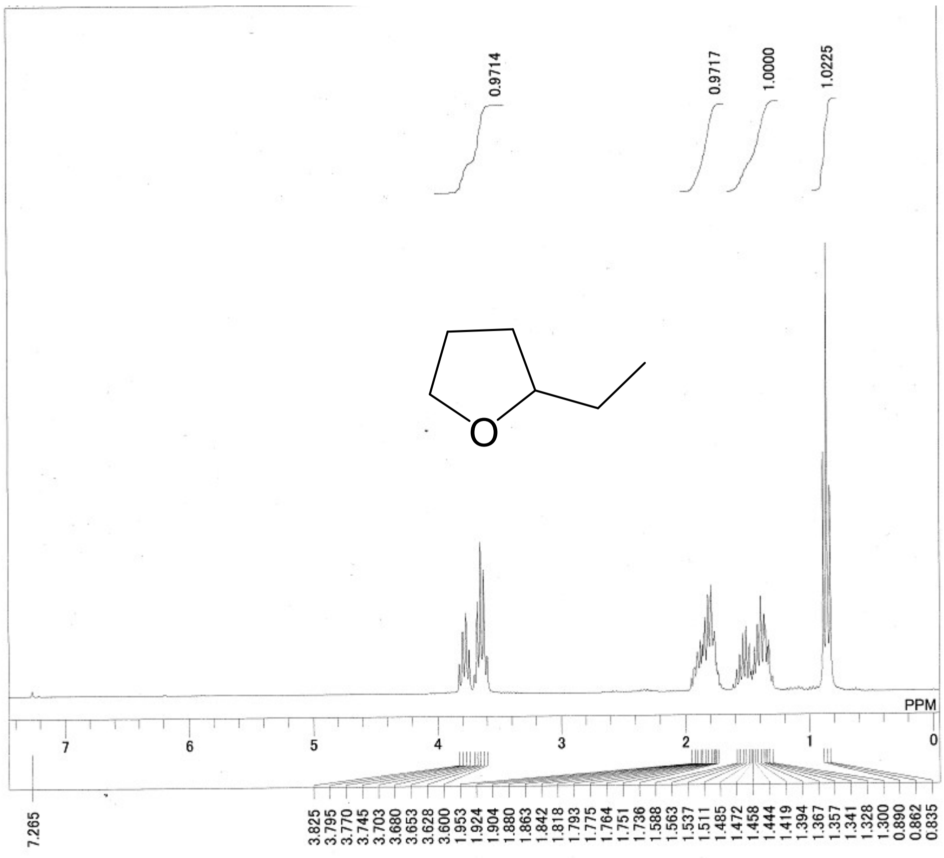
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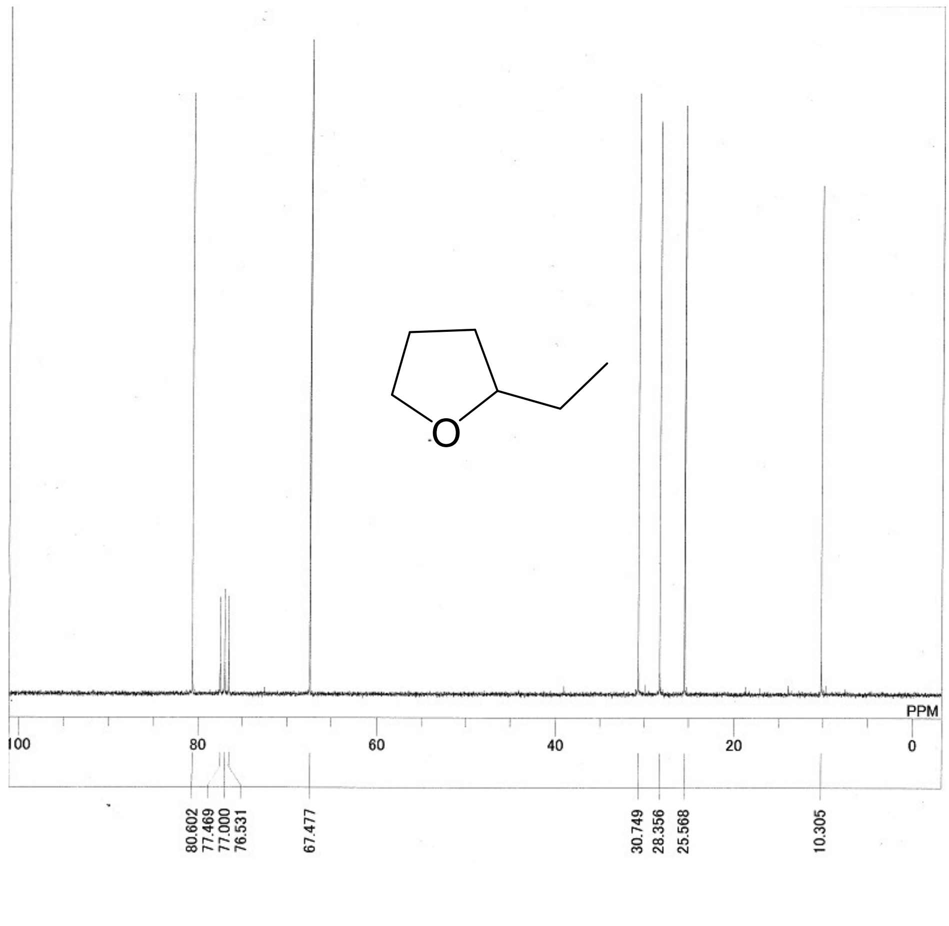
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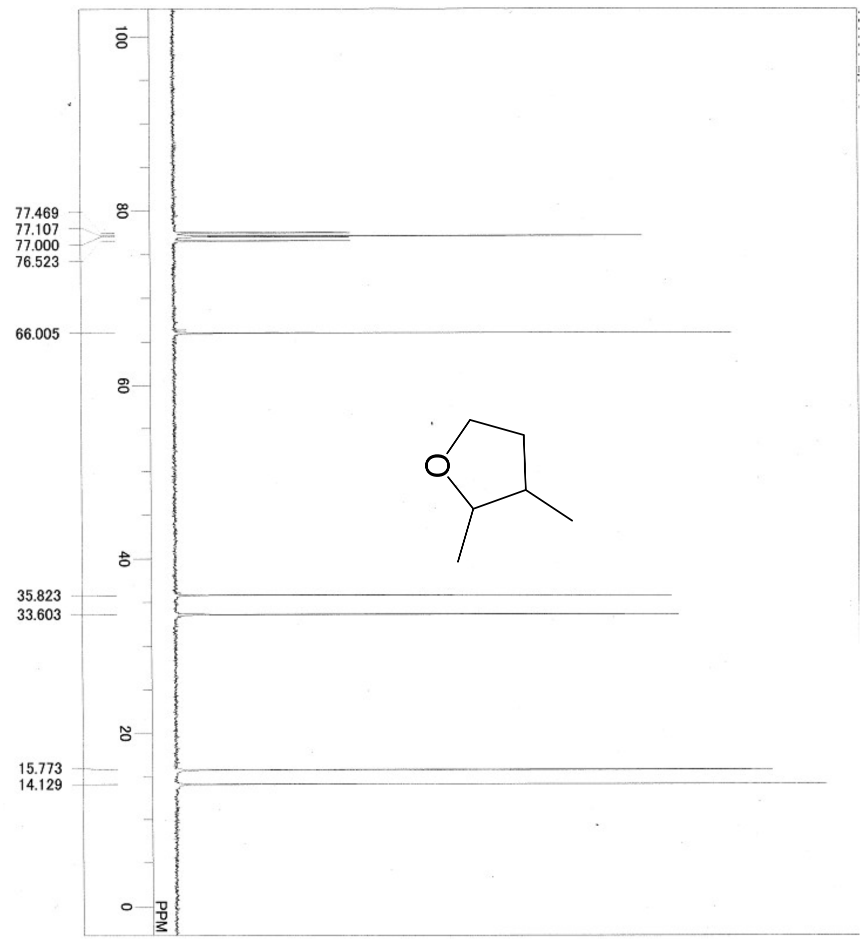

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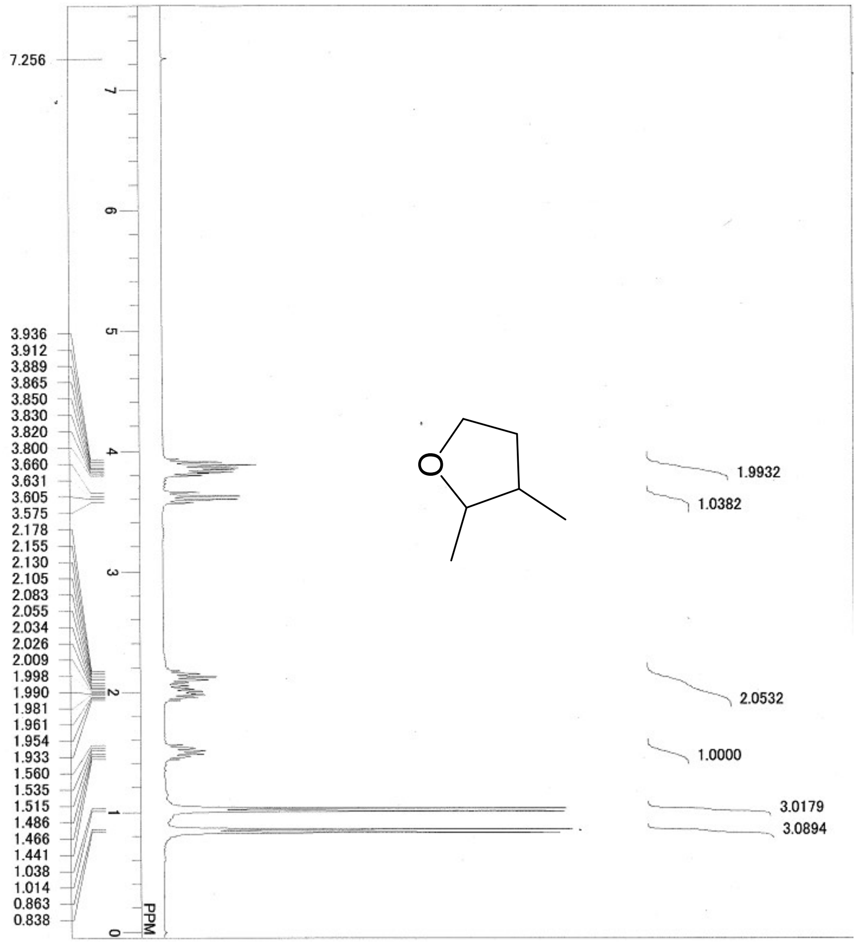

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