Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Versatile etherification of alcohols with allyl alcohol by a titanium oxide-supported molybdenum oxide catalyst: gradual generation from titanium oxide and molybdenum oxide

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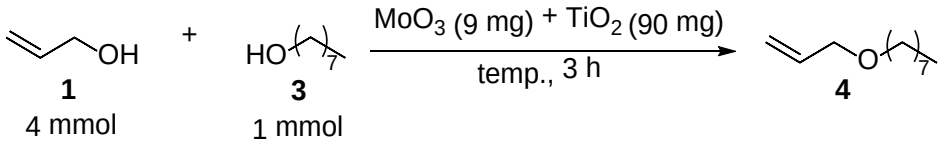
Contents

1. Screening of reaction temperature

Table S1. Influence of the reaction temperature for the reaction of allyl alcohol (**1**) and 1-octanol (**3**) using MoO_3 + TiO_2.

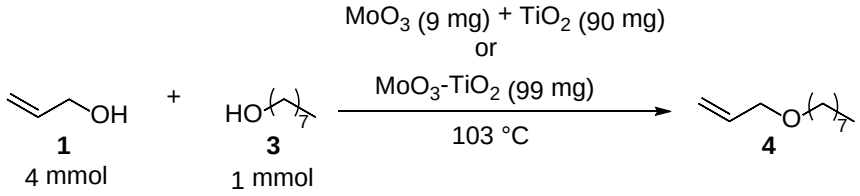


Oil bath Temp. (Inside Temp.)	Conversion of 1-octanol (**3**)[a]	Yield of allyl octyl ether (**4**) [a]	Selectivity [b]
(°C)	(%)	(%)	(%)
130 (101)	70	65	92
140 (103)	92	86	93
150 (107)	92	81	88

Reaction conditions: **1** (4.0 mmol), **3** (1.0 mmol), 500 rpm, 3 h, unless otherwise stated. [a] Conversion and yield on the basis of **3**, determined by GC analysis using biphenyl as an internal standard. [b] Selectivity = (yield of **4**) / (conversion of **3**) x 100.

2. Reaction profile about etherification

Table S2. Etherification of allyl alcohol (**1**) and 1-octanol (**3**) using MoO_3 + TiO_2 and MoO_3-TiO_2 catalysts.



Entry	Time (h)	Conversion of **3** (%)[a]	Yield of **4** (%)[a]
1[b]	0.2	1	0
2[b]	0.5	31	28
3[b]	1.0	78	75
4[b]	2.0	86	83
5[b]	3.0	90	86
6[c]	0.2	55	52
7[c]	0.5	87	84
8[c]	1.0	93	87
9[c]	3.0	93	87
10[d]	0.15	10	5
11[d]	0.5	30	25
12[d]	1.0	42	37
13[d]	3.0	72	63
14[d]	5.0	75	65

Reaction conditions: **1** (4.0 mmol), **3** (1.0 mmol), 500 rpm, 3 h, unless otherwise stated. [a] Conversion and yield on the basis of **3**, determined by GC analysis using biphenyl as an internal standard. [b] reaction using MoO_3 + TiO_2. [c] reaction using MoO_3-TiO_2 after calcination at 500 °C for 3 h . [d] reaction using MoO_3-TiO_2 without calcination.

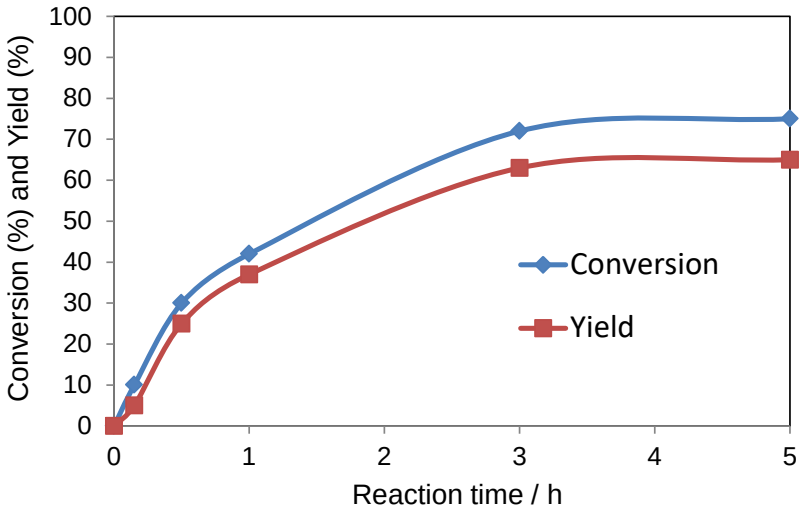


Fig. S1. Time course reaction profile of etherification of **1** and **3** using MoO_3-TiO_2 catalyst without calcination (a second cycle).

3. NH_3-TPD analyses of MoO_3-TiO_2, MoO_3-SiO_2, and MoO_3-Al_2O_3.

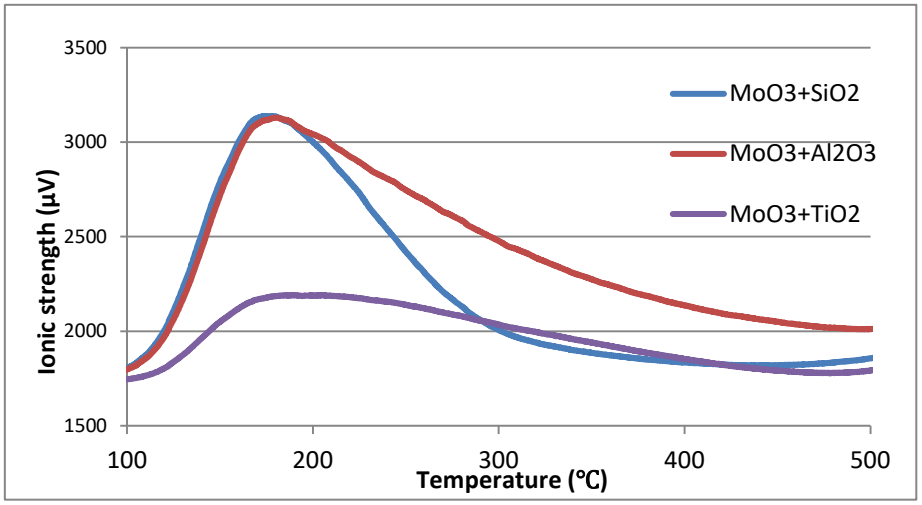
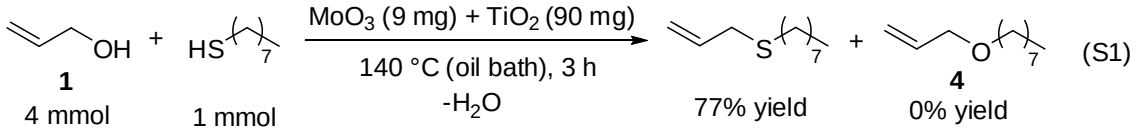


Fig. S2. NH_3-TPD analyses of MoO_3-TiO_2, MoO_3-SiO_2, and MoO_3-Al_2O_3.

4. Etherification of allyl alcohol and 1-octanethiol.



1
4 mmol

1 mmol

77% yield

4
0% yield

Etherification of 1-octanethiol with allyl alcohol (1) using MoO_3 and TiO_2 catalysts: A pressure-resistant glass tube equipped with a magnetic stirring bar was loaded with MoO_3 (9 mg), TiO_2 P25 (90 mg), **1** (230 mg, 4.0 mmol), and 1-octaniethiol (146 mg, 1.0 mmol). The vessel was tightly sealed by a screw cap and the mixture was stirred (500 rpm) in an oil bath maintained at 140 °C for 3 h. After the reaction, the solution was cooled to room temperature and then diluted with 12 ml of acetonitrile. Biphenyl (40 mg, 0.25 mmol) was added to the solution as an internal standard for gas chromatography (GC) analysis. The solution was placed under ultrasonic irradiation for 10 min. to ensure a good homogeneity of the mixture. The conversion and yield were determined on the basis of the analysis of the mixture by GC. The yield in allyl octyl sulfide was 77 %, the yield in allyl octyl ether (**4**) was 0%, the conversion of 1-octanethiol was over 99 %.

5. NMR data for compounds

Allyl octyl ether[1]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.97-5.87 (m, 1H), 5.27 (dd, J= 17.6, 1.2 Hz, 1H), 5.16 (d, J= 10.0, 1H), 3.96 (d, J= 5.6 Hz, 2H), 3.42 (t, J= 6.6 Hz, 2H), 1.58 (m, 2H), 1.38-1.18 (m, 10H), 0.88 (t, J= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=135.1, 116.7, 71.8, 70.5, 31.8, 29.8, 29.5, 29.3, 26.2, 22.7, 14.1.

Allyl hexyl ether[2]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.97-5.87 (m, 1H), 5.27 (dd, J= 17.2, 1.2 Hz, 1H), 5.16 (d, J= 10.0 Hz, 1H), 3.96 (d, J= 5.2 Hz, 2H), 3.42 (t, J= 6.6 Hz, 2H), 1.62-1.55 (m, 2H), 1.41-1.24 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=135.1, 116.6, 71.8, 70.5 31.7, 29.7, 25.9, 22.6, 14.0.

Allyl decyl ether[3]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.97-5.87 (m, 1H), 5.27 (dd, J= 17.2, 1.2 Hz, 1H), 5.16 (d, J= 10.0 Hz, 1H), 3.96 (d, J= 5.6 Hz, 2H), 3.42 (t, J= 6.6 Hz, 2H), 1.62-1.55 (m, 2 H), 1.39-1.21 (m, 14 H), 0.88 (t, J= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ=135.1, 116.6, 71.8, 70.5 31.9, 29.8, 29.6, 29.5, 29.3, 26.2, 22.7, 14.1.

Allyl (4-methoxy) butyl ether : ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.96-5.86 (m, 1H), 5.27 (dd, J= 17.2, 1.2 Hz, 1H), 5.17 (d, J= 10.8 Hz, 1H), 3.96 (d, J= 5.6 Hz, 2H), 3.47-3.38 (m, 4H), 3.33 (s, 3 H), 1.67-1.64 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=135.0, 116.6, 72.5, 71.7, 70.0, 58.4, 26.4, 26.4. Elemental analysis: calcd (%) for $C_8H_{16}O_2$: C 66.63, H 11.18; found: C 66.46, H 11.24.

Allyl 2-octyl ether : ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.97-5.88 (m, 1H), 5.25 (dd, J= 17.2, 1.2 Hz,1H), 5.14 (d, J= 10.0 Hz, 1H), 4.05-3.90 (m, 2H), 3.47-3.39 (m, 1H), 1.63-1.28 (m, 10H), 1.13 (d, J= 6.4 Hz, 3H), 0.88 (t, J= 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=135.6, 116.2, 74.9, 69.3, 36.7, 31.9, 29.4, 25.5, 22.6, 19.7, 14.1. Elemental analysis: calcd (%) for $C_{11}H_{22}O$: C 78.58, H 13.02; found: C 77.19, H 12.94.

Allyl cyclohexyl ether[2]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.98-5.88 (m, 1H), 5.27 (dd, J= 17.6, 1.2 Hz, 1H), 5.14 (d, J= 10.0 Hz, 1H), 4.02-4.00 (m, 2H), 3.31-3.25 (m, 1H), 1.99-1.11 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 135.7, 116.2, 68.8, 32.3, 25.8, 24.2.

Allyl phenyl ether[4]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 7.30-7.23 (m, 2H), 6.96-6.91 (m, 3H), 6.11-6.01 (m, 1H), 5.41 (d, J= 17.6 Hz, 1H), 5.29-5.28 (d, J= 10.4 Hz, 1H), 4.52 (d, J= 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 158.5, 133.3, 129.4, 120.8, 117.6, 114.7, 68.7.

Allyl benzyl ether[5]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 7.35 – 7.26 (m, 5H), 6.00 – 5.91 (m, 1H), 5.31 (dd, J= 17.2, 1.2 Hz, 1H), 5.20 (d, J= 10.0 Hz, 1H), 4.52 (s, 2H), 4.03 (dt, J= 5.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 138.3, 134.7, 128.3, 127.7, 127.5, 117.1, 72.1, 71.1.

Allyl (2-phenyl) cyclohexyl ether[6]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 7.30-7.17 (m, 5H), 5.62-5.52 (m, 1H), 4.97-4.95 (m, 1H), 4.94-4.91 (m, 1H), 3.79 (dd, J = 13.2, 5.6 Hz, 1H), 3.58 (dd, J = 13.2, 5.2 Hz, 1H), 3.37-3.31 (m, 1H), 2.54 (ddd, J = 22.0, 12.0, 3.2 Hz, 1H), 2.21–2.13 (m, 1H), 1.90–1.82 (m, 2H),1.76–1.70 (m, 1H), 1.57–1.47 (m, 1H), 1.38–1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 144.7, 135.4, 128.0, 127.8, 126.0, 116.0, 81.5, 70.1, 51.2, 33.8, 32.6, 26.0, 25.1.

Allyl (2-phenylthio) ethyl ether : ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 7.37-7.35 (m, 2H), 7.29-7.26 (m, 2H), 7.20-7.16 (m, 1H), 5.94-5.84 (m, 1H), 5.29-5.23 (m, 1H), 5.19-5.16 (m, 1H), 4.00-3.98 (m, 2H), 3.63 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ= 136.0, 134.4, 129.3, 128.9, 126.1, 117.2, 71.9, 68.7, 33.2. Elemental analysis: calcd (%) for $C_{11}H_{14}OS$: C 68.00, H 7.26, S 16.50; found: C 67.68, H 7.30, S 16.61.

2-buten-1-yl octyl ether (mixture of (*E*), (*Z*) isomers)[7] : ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.74-5.55 (m, 2H), 4.03-3.88 (m, 2H), 3.47-3.26 (m, 2H), 1.72-1.70 (m, 3H), 1.38-1.20 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=129.1, 127.8, 71.5, 70.3, 31.8, 29.8, 29.5, 29.3, 26.2, 22.7, 17.8, 14.1.

3-buten-2-yl octyl ether[8] : ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.78-5.69 (m, 1H), 5.18-5.09 (m, 2H), 3.83-3.76 (m, 1H), 3.47-3.26 (m, 2H), 1.59-1.52 (m, 2H), 1.38-1.20 (m, 10H), 1.23 (d, J= 6.4 Hz, 3H), 0.88 (t, J= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=140.7, 115.3, 76.8, 68.4, 31.8, 30.0, 29.5, 29.3, 26.2, 22.7, 21.3, 14.1.

Allyl octyl sulfide[9]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ= 5.84-5.74 (m, 1H), 5.10-5.06 (m, 2H), 3.12 (d, J = 7.2, 2H), 2.45 (t, J = 7.2 Hz, 2H), 1.59-1.52 (m, 2H), 1.40-1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=134.6, 116.6, 34.8, 31.8, 30.7, 29.3, 29.2, 29.2, 28.9, 22.7, 14.1.

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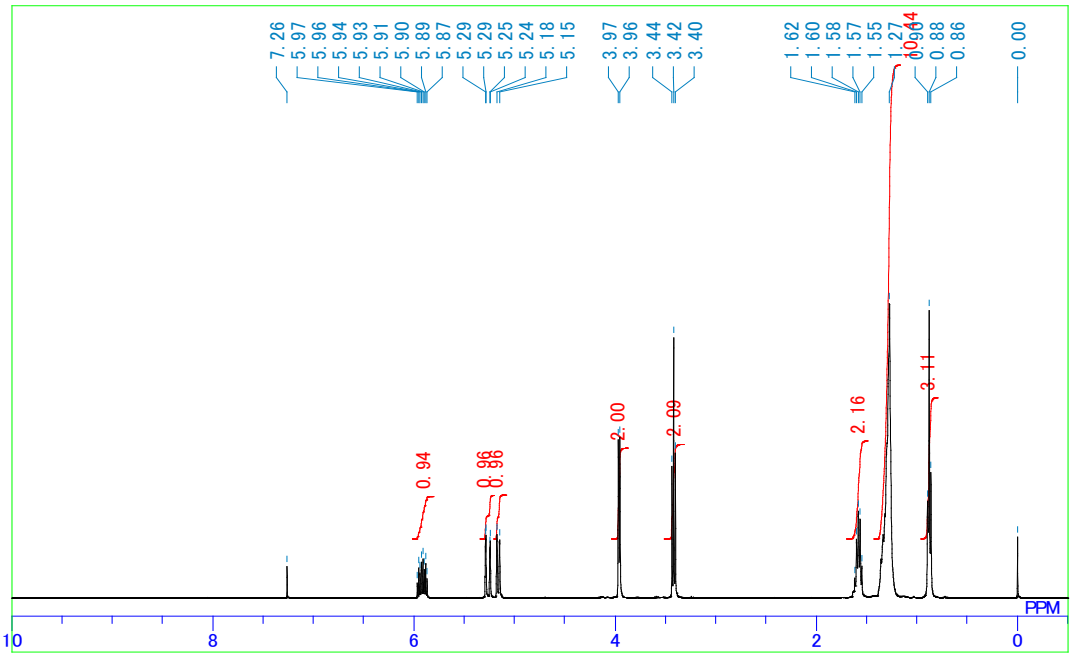
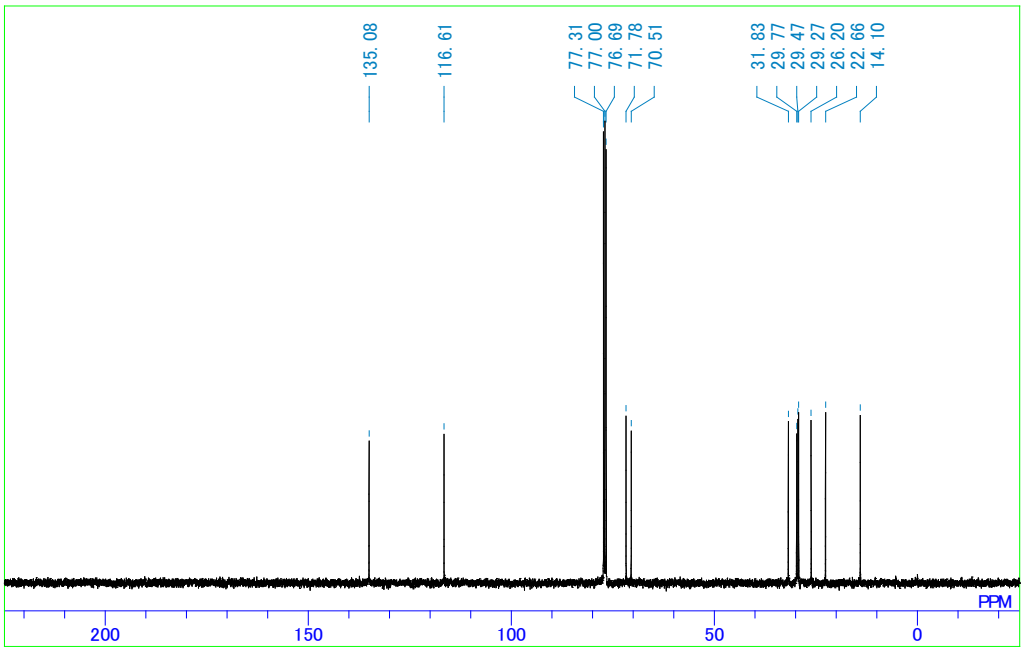
6. ^{1}H and ^{13}C NMR spectra

Allyl octyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

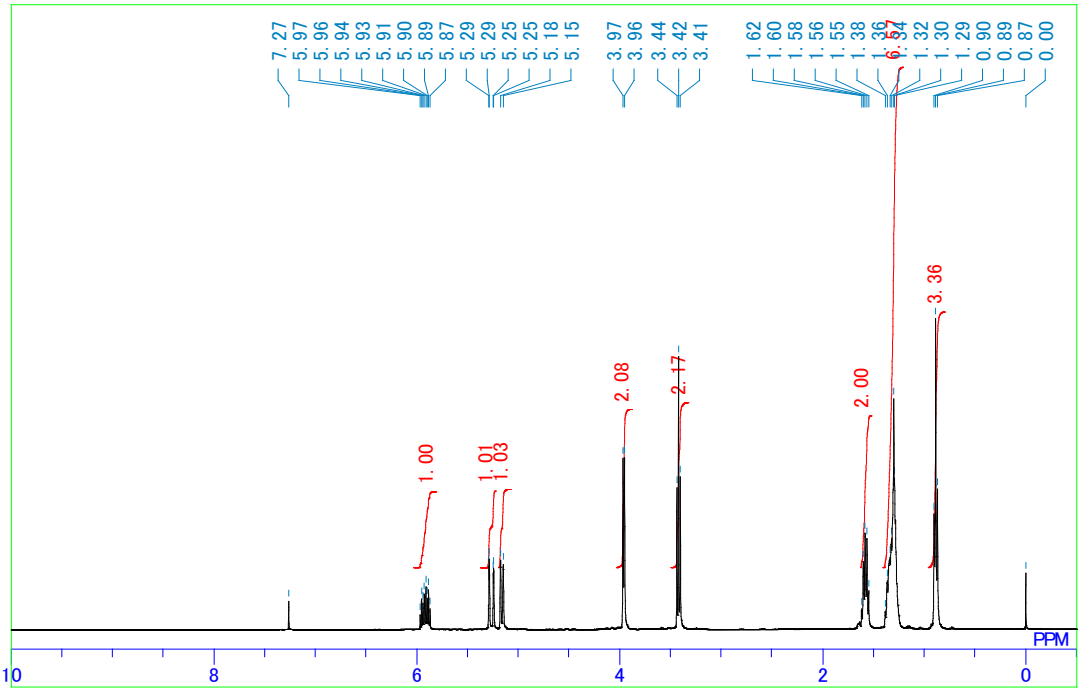


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

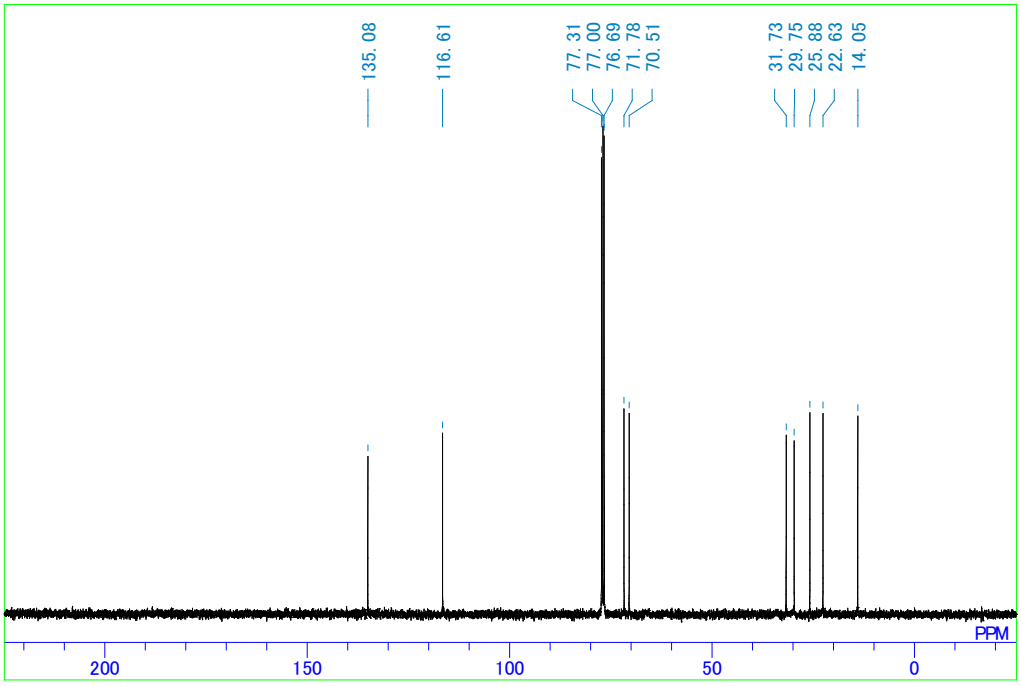


Allyl hexyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

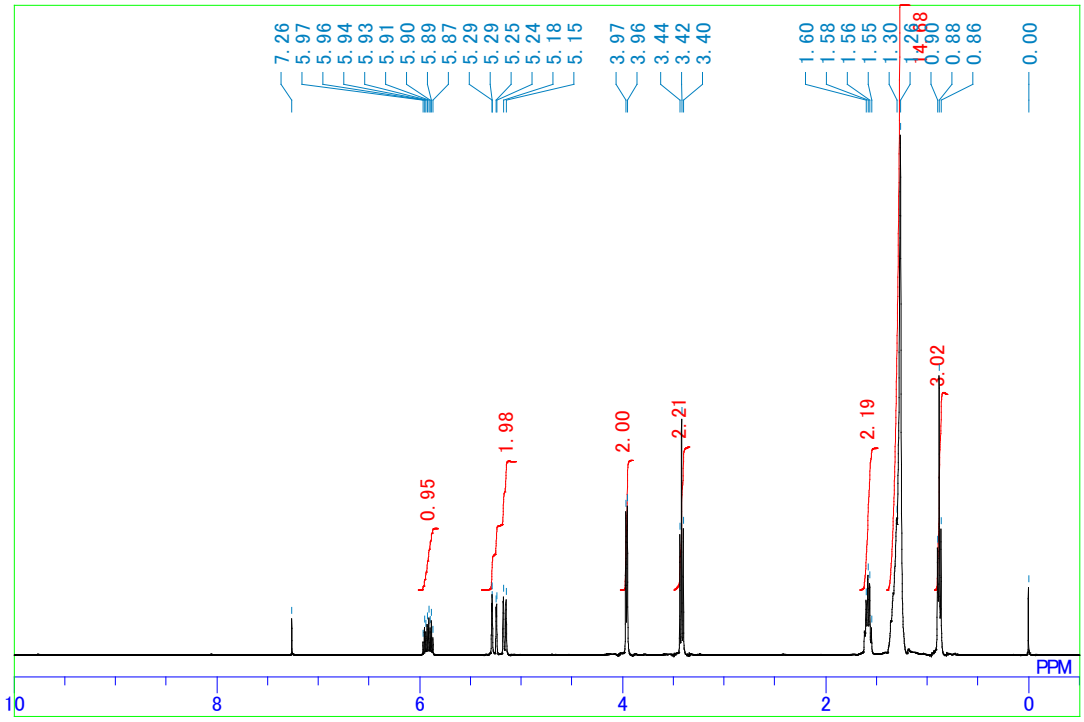


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

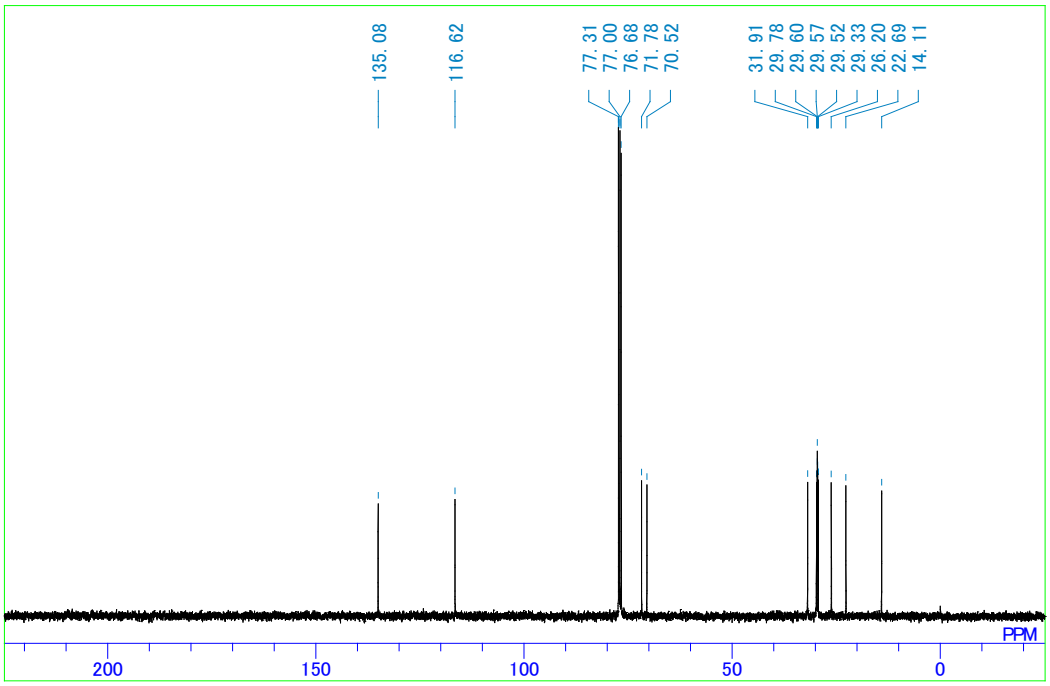


Allyl decyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

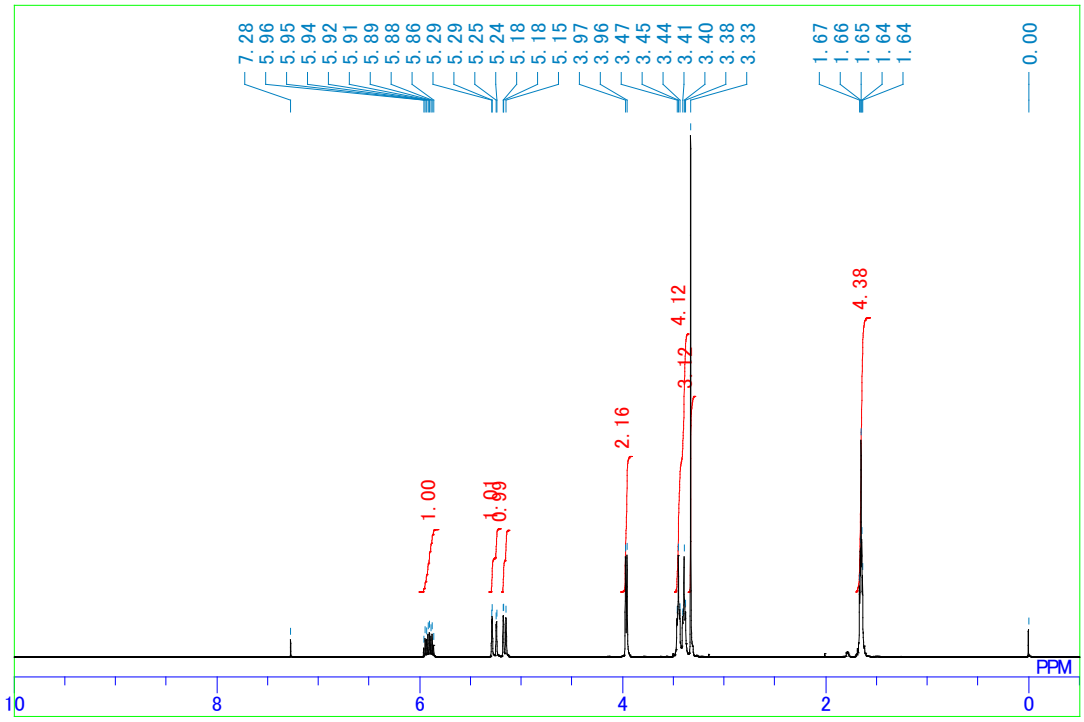


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

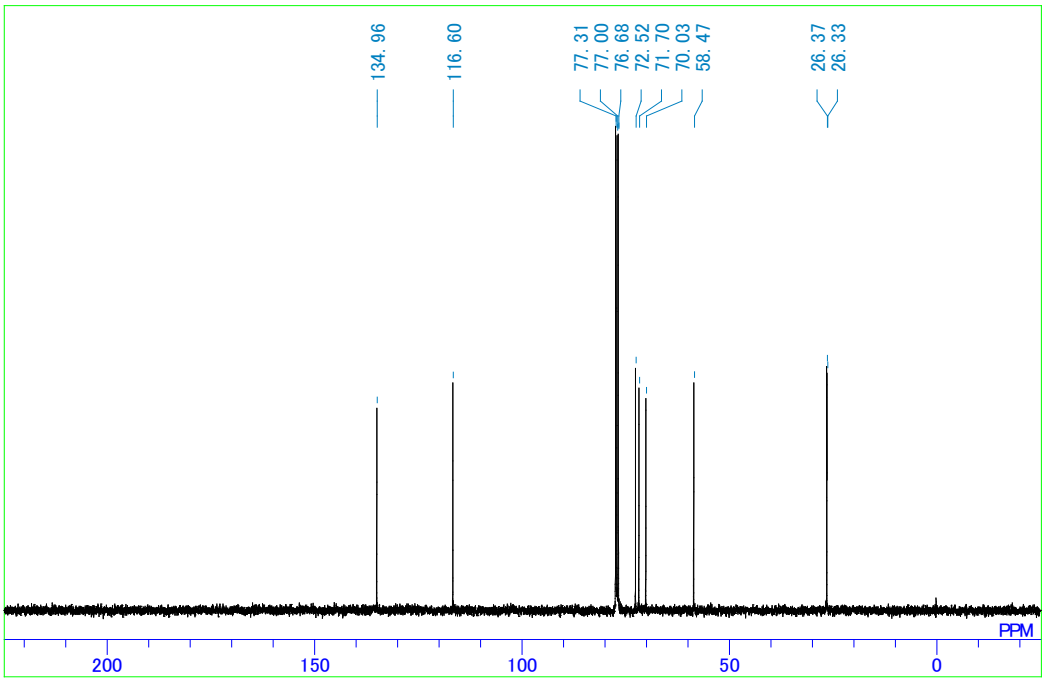


Allyl (4-methoxy) butyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

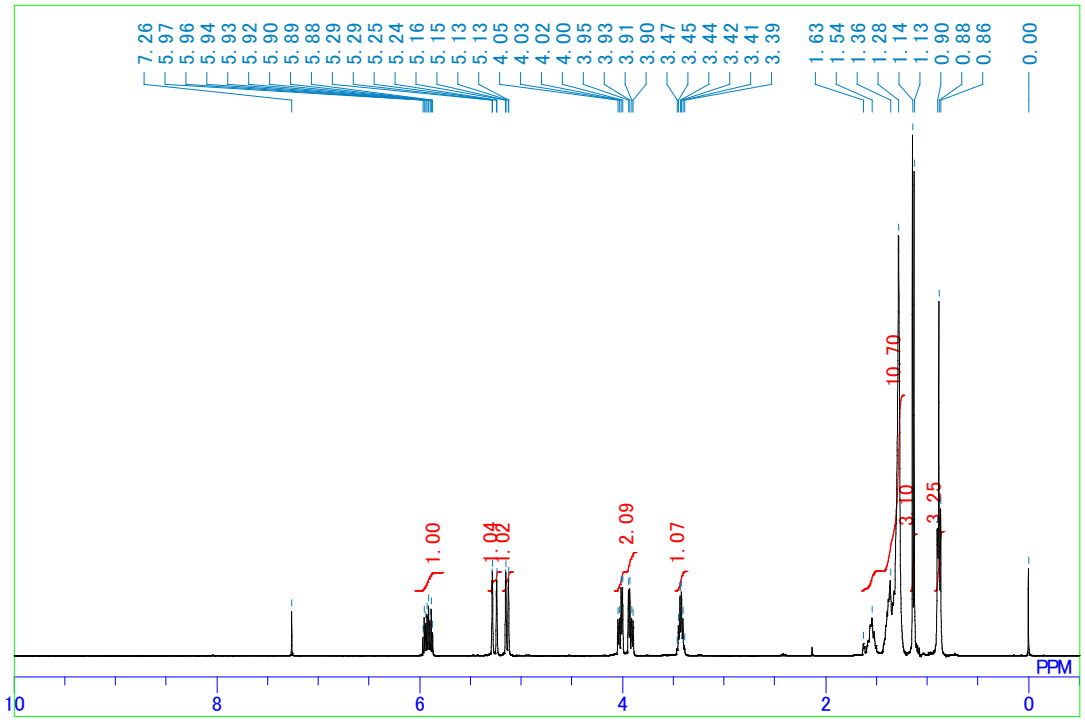


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

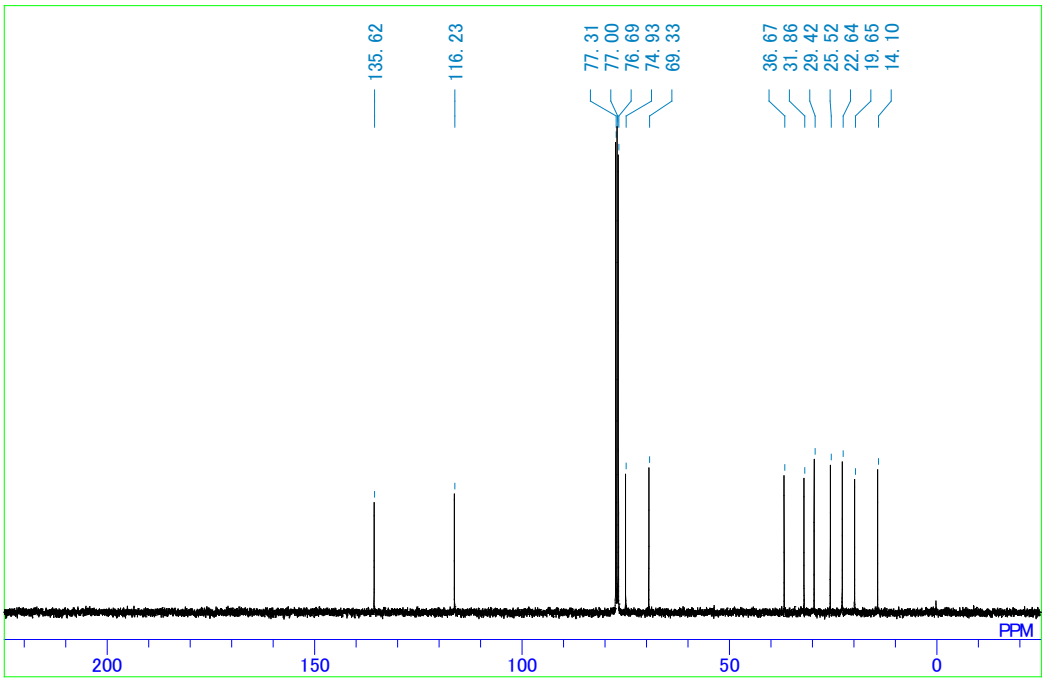


Allyl 2-octyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

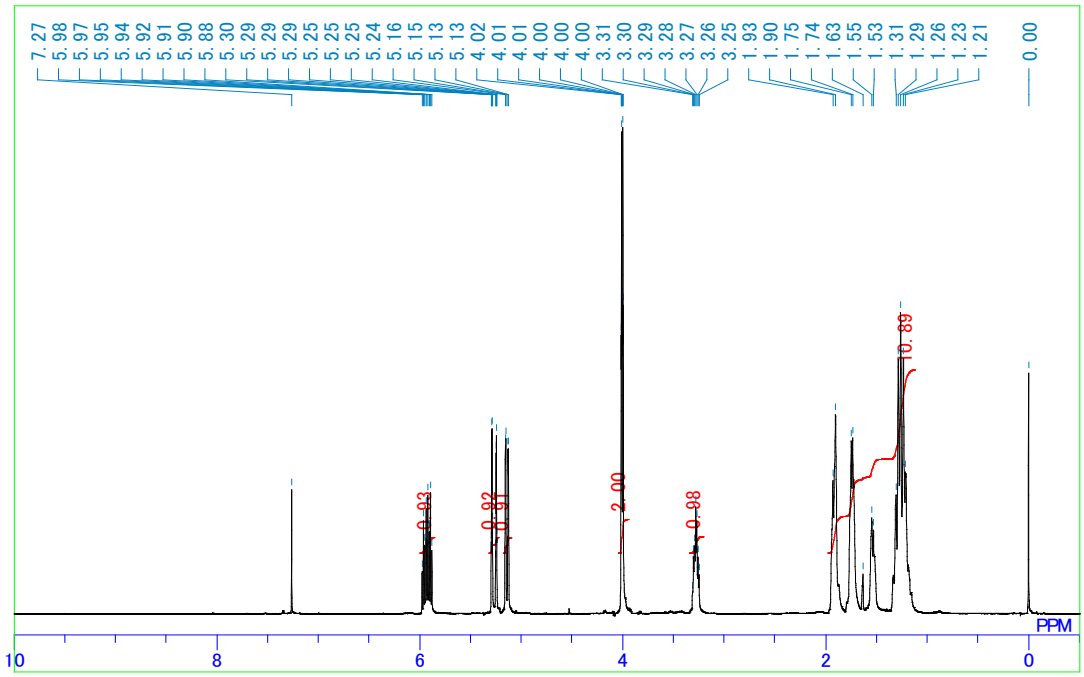


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

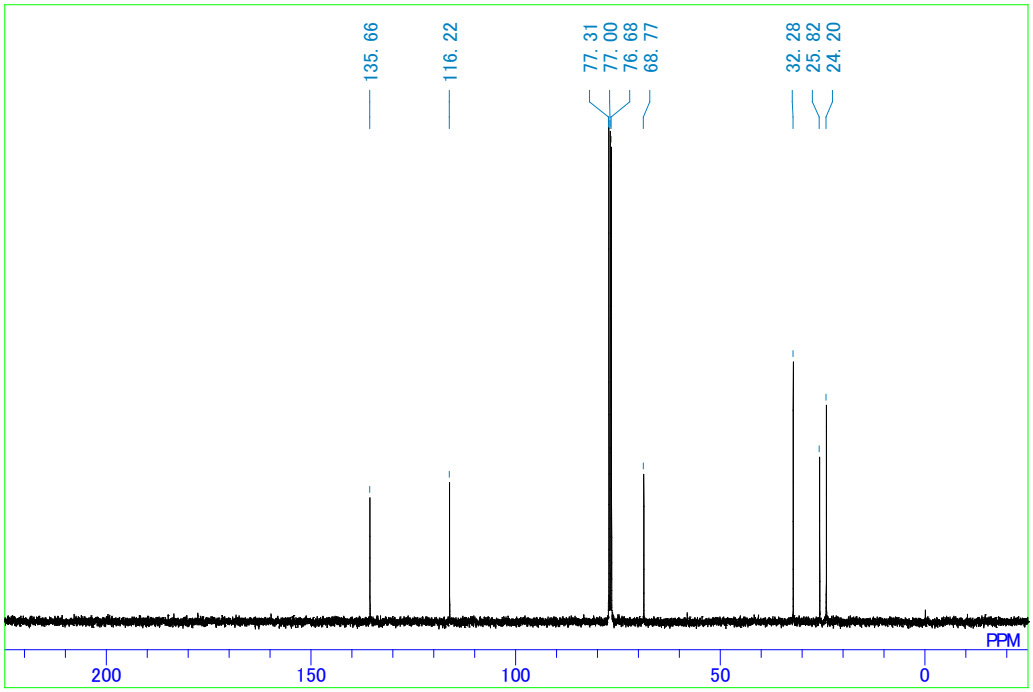


Allyl cyclohexyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

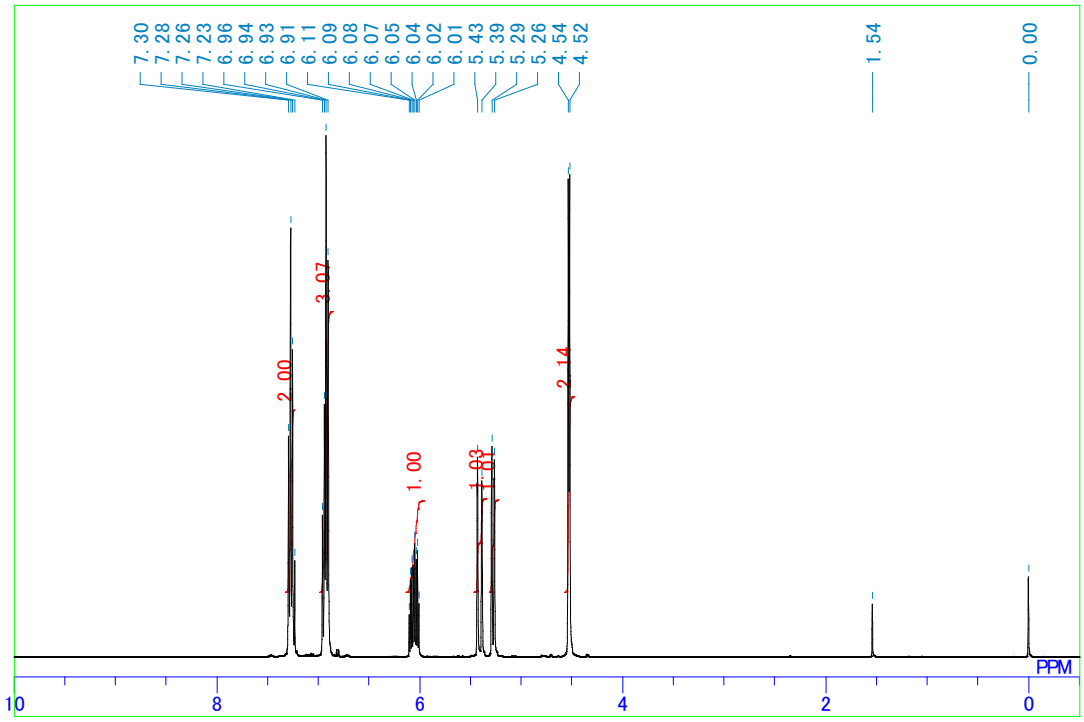


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

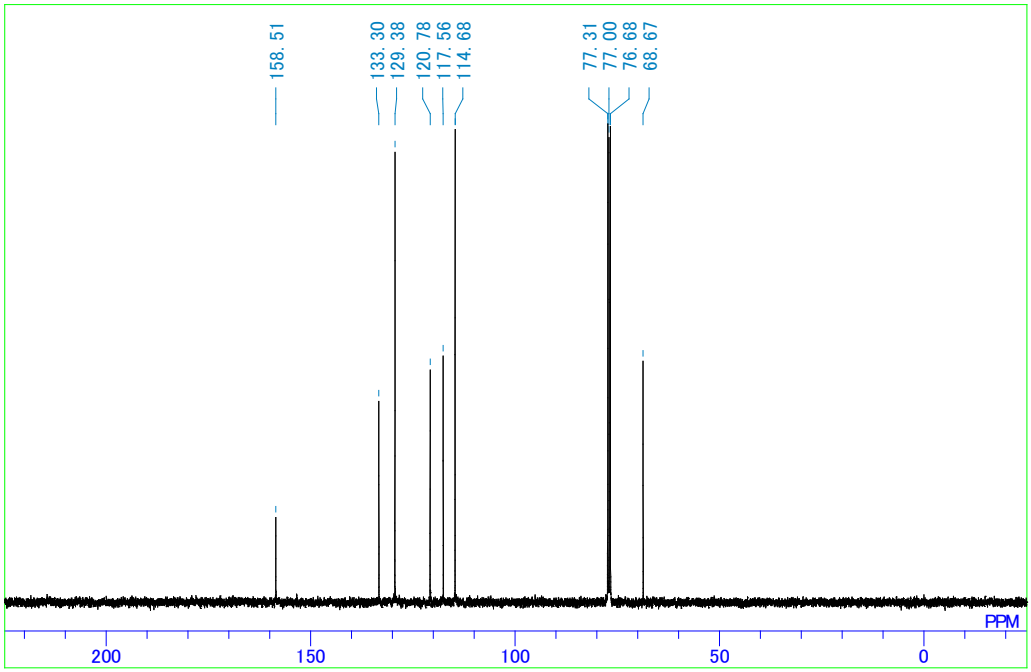


Allyl phenyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

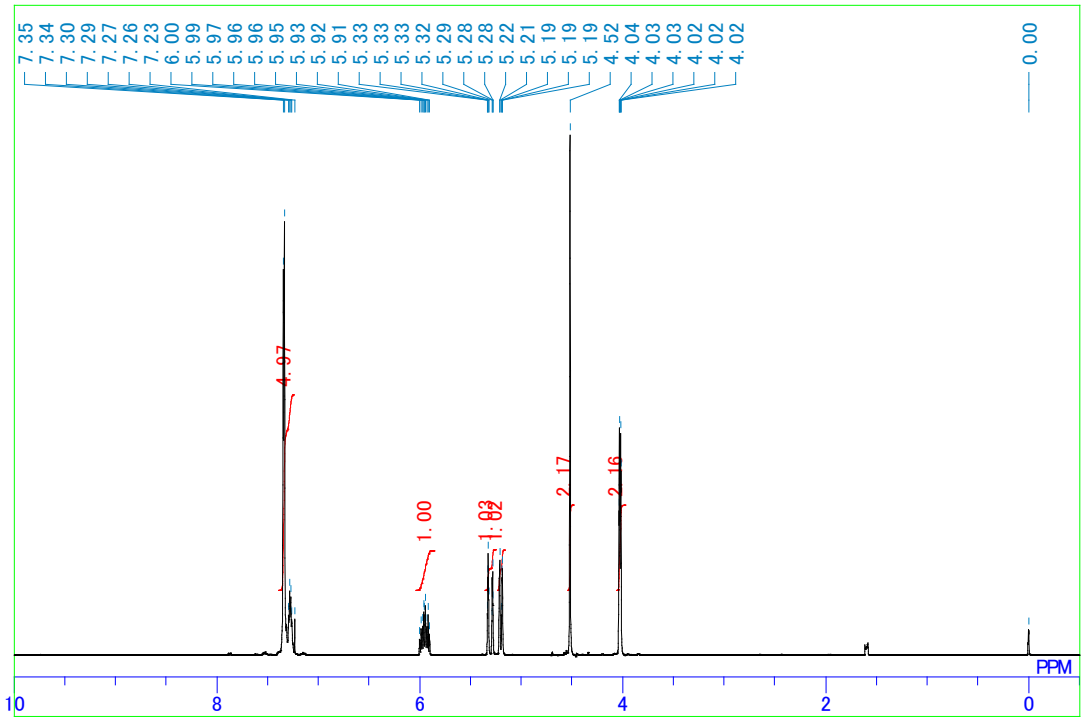


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

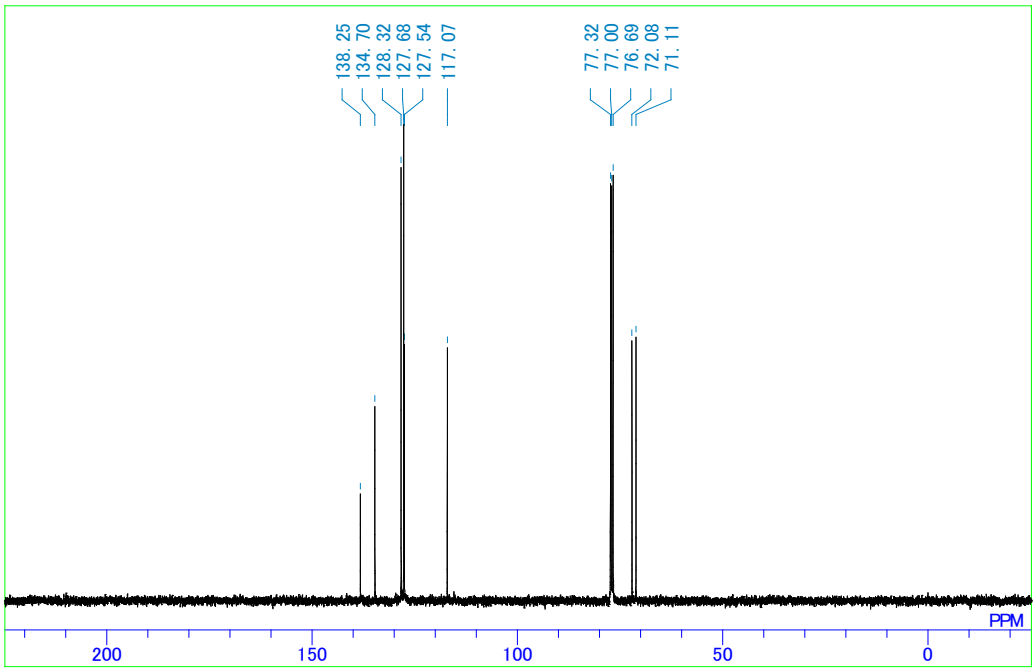


Allyl benzyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

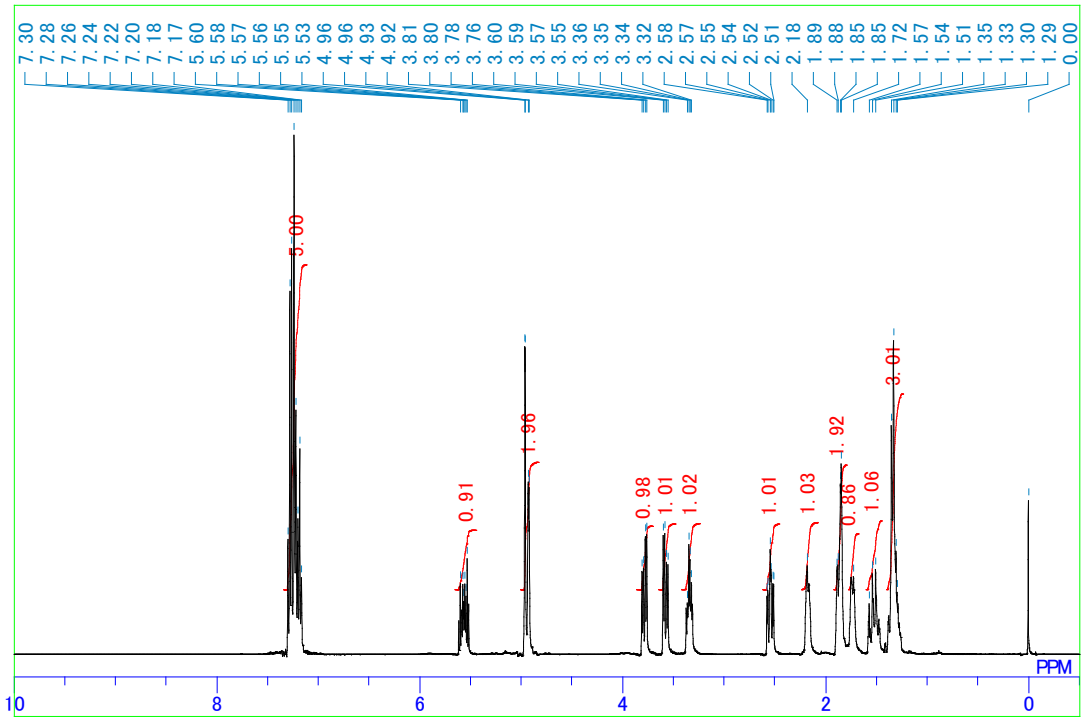


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

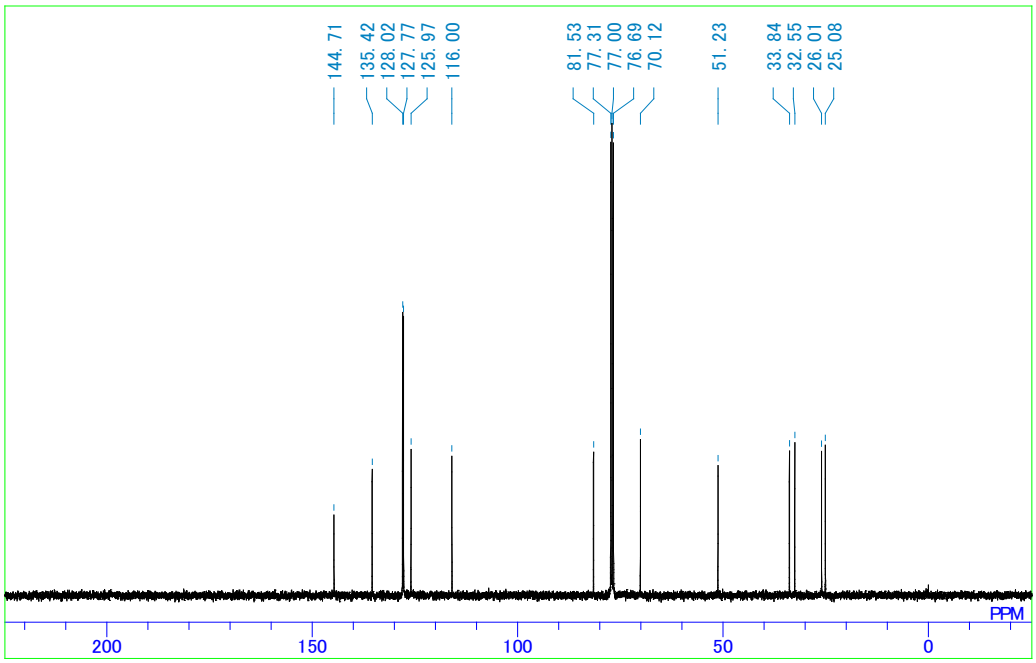


Allyl (2-phenyl) cyclohexyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

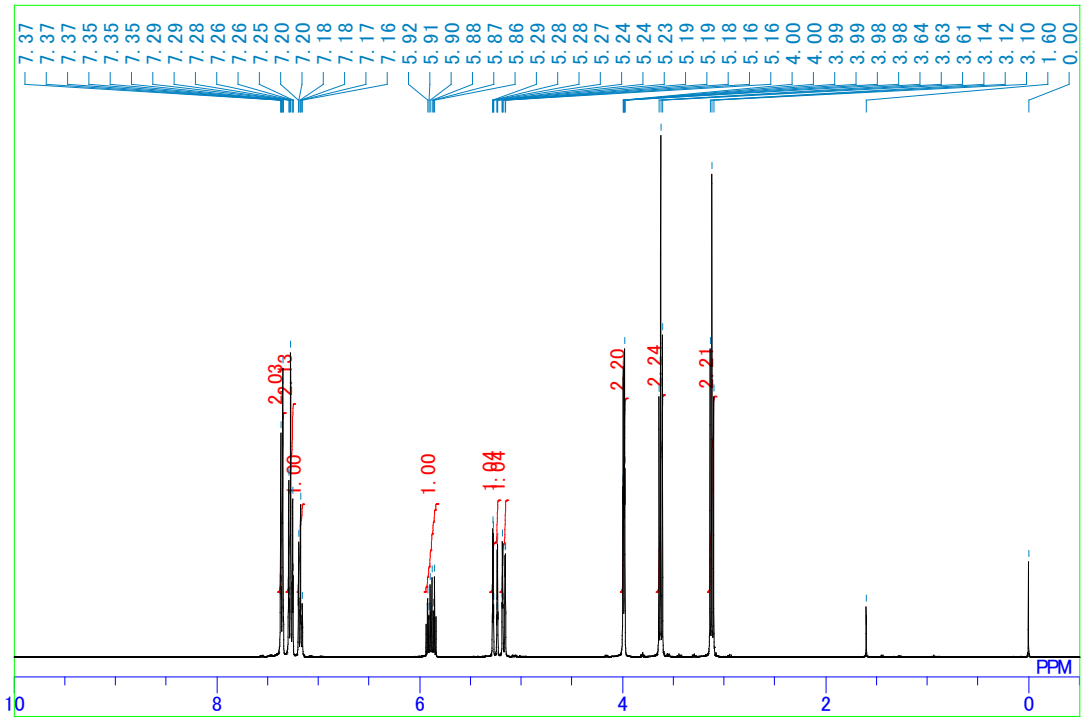


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

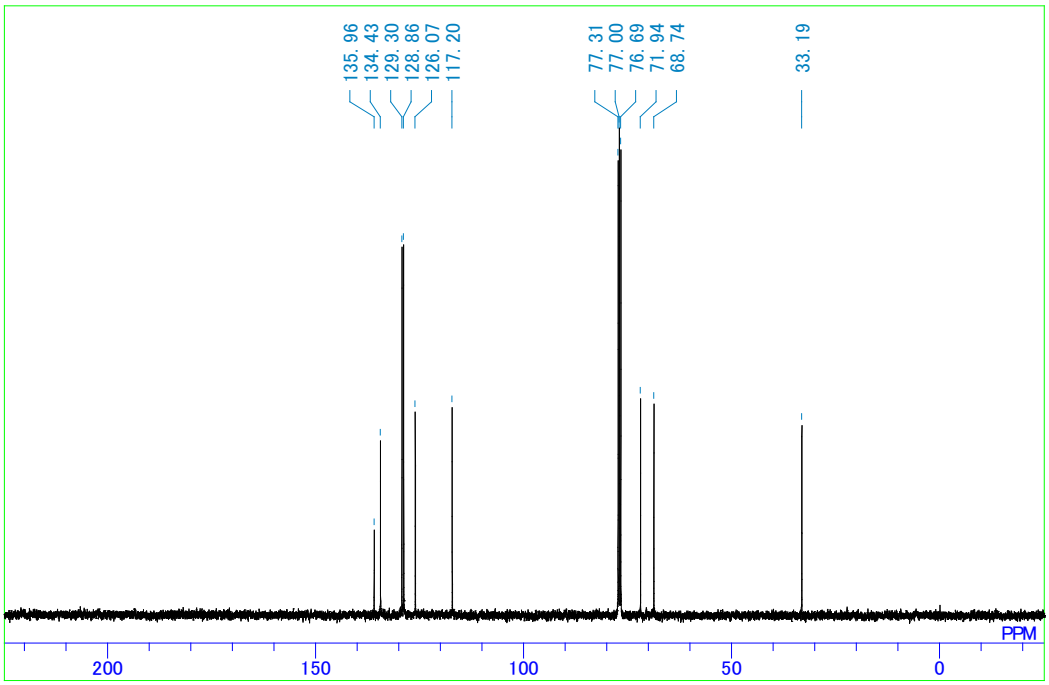


Allyl (2-phenylthio) ethyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

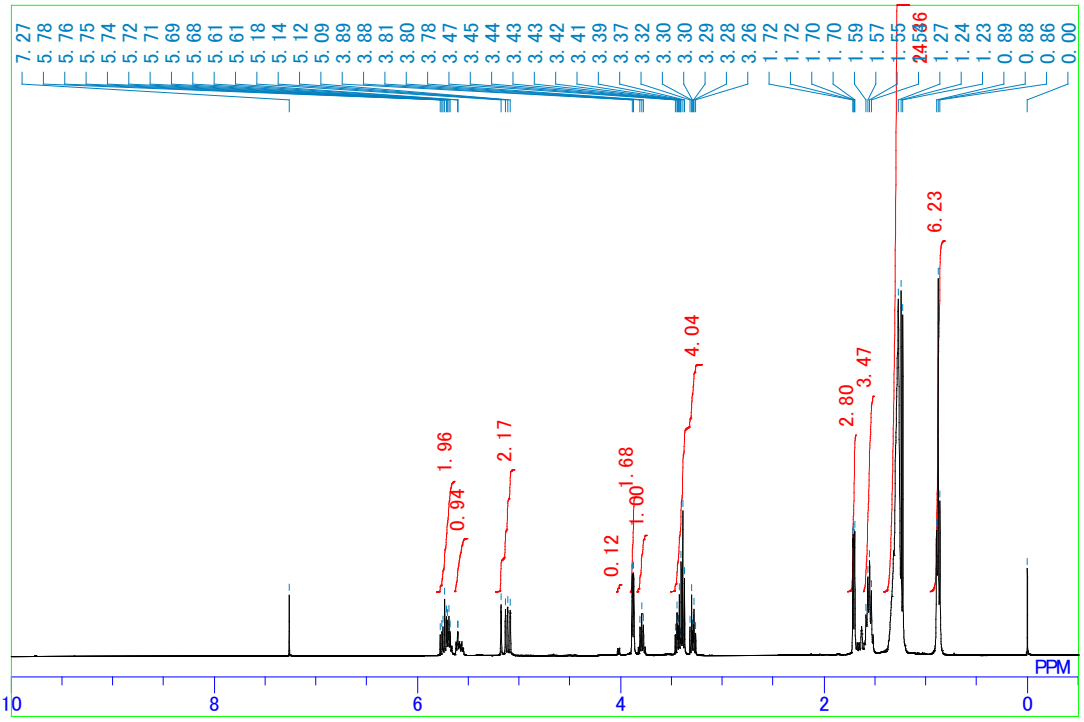


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)

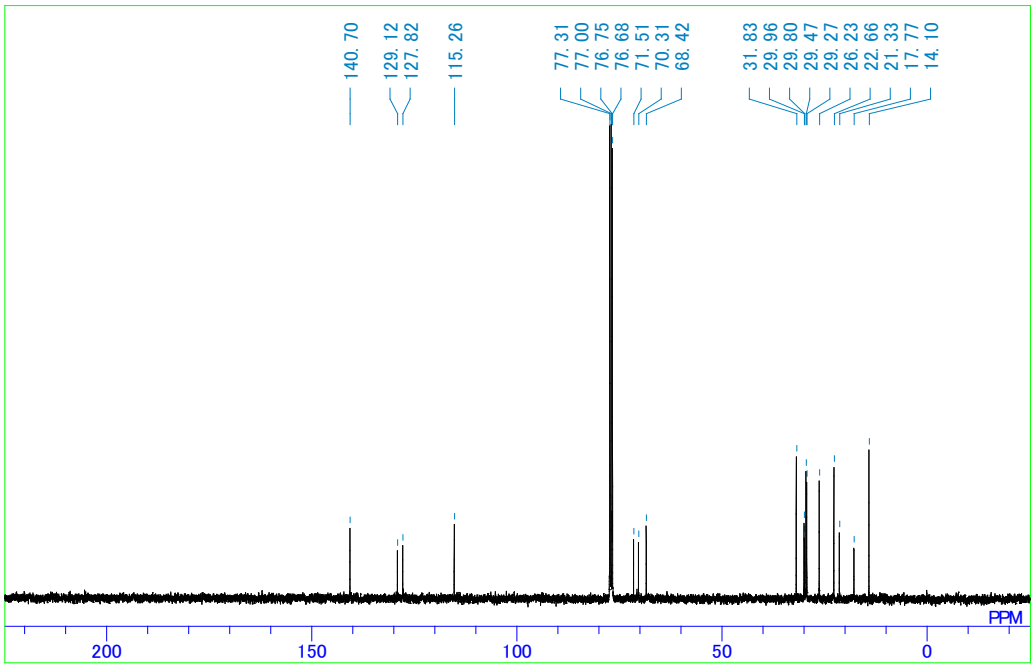


2-buten-1-yl octyl ether (mixture of (*E*), (*Z*) isomers) and 3-buten-2-yl octyl ether

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

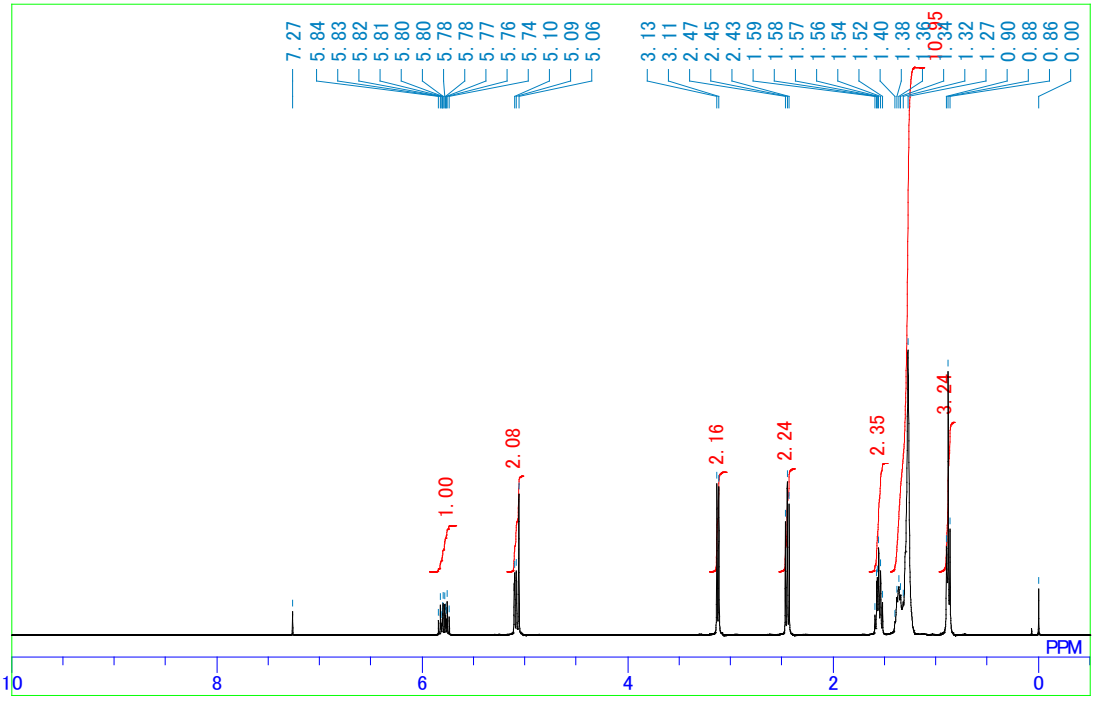


^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)



Allyl octyl sulfide

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



^{13}C NMR (100 MHz, $CDCl_3$, 25 °C)