Supporting Information

Preference of Ruthenium-Based Metathesis Catalyst toward *Z*- and *E*-Alkene as a Guide for Selective Reaction to Alkene Stereoisomer

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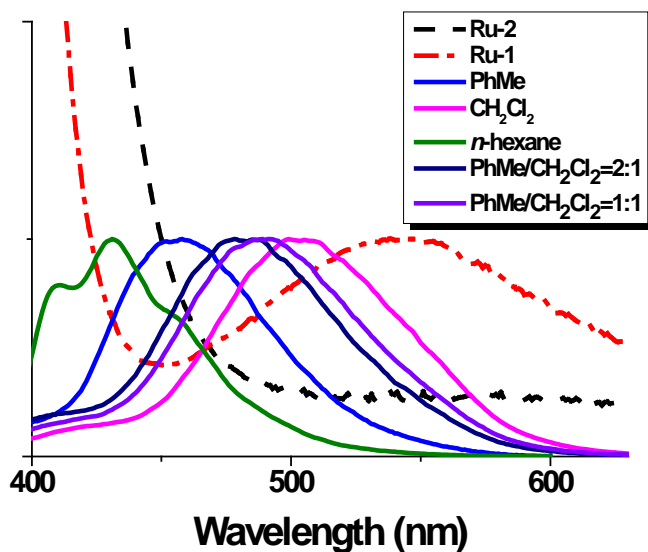## 1. UV-vis spectra of Ru catalysts and fluorescence spectra of substrates

Figure S1. Red dashed/dotted and black dashed lines are the UV-vis spectra of **Ru-1** and **Ru-2**, respectively. Colored solid lines are the fluorescence spectra of the dye-conjugated substrates in PhMe (blue), CH_2Cl_2 (pink), n-hexane (green), PhMe/ CH_2Cl_2 = 2:1 (navy), PhMe/ CH_2Cl_2 = 1:1 (violet).

2. Fitting analysis of FRET data[1]

Reaction scheme

We assumed the substrate-catalyst association and dissociation steps have the following reaction schemes.

$$\text{substrate + catalyst} \xrightleftharpoons[k_{-1}]{k} \text{substrate:catalyst}$$
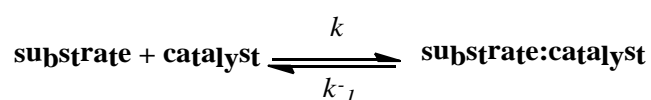
Rate equations

We set up the rate equations as follows:

$$\frac{d[\textbf{substrate}]}{dt} = -k[\textbf{substrate}][\textbf{catalyst}] + k_{-1}[\textbf{substrate:catalyst}]$$

$$\frac{d[\textbf{substrate:catalyst}]}{dt} = k[\textbf{substrate}][\textbf{catalyst}] - k_{-1}[\textbf{substrate:catalyst}]$$

$$\frac{d[\textbf{catalyst}]}{dt} = -k[\textbf{substrate}][\textbf{catalyst}] + k_{-1}[\textbf{substrate:catalyst}]$$

Although these equations have an analytical solution, numerical approximation has been employed for convenience. Δt is 0.01 minute.

$$\frac{\Delta[\mathbf{substrate}]}{\Delta t} = -k[\mathbf{substrate}][\mathbf{catalyst}] + k_{-1}[\mathbf{substrate\!:\!catalyst}]$$

$$\frac{\Delta[\mathbf{substrate\!:\!catalyst}]}{\Delta t} = k[\mathbf{substrate}][\mathbf{catalyst}] - k_{-1}[\mathbf{substrate\!:\!catalyst}]$$

$$\frac{\Delta[\mathbf{catalyst}]}{\Delta t} = -k[\mathbf{substrate}][\mathbf{catalyst}] + k_{-1}[\mathbf{substrate\!:\!catalyst}]$$

Concentrations of each species at a certain time, $t + \Delta t$, are,

$$[\mathbf{substrate}]_{t+\Delta t} = [\mathbf{substrate}]_t + (-k[\mathbf{substrate}]_t[\mathbf{catalyst}]_t + k_{-1}[\mathbf{substrate\!:\!catalyst}]_t)\Delta t$$

$$[\mathbf{substrate\!:\!catalyst}]_{t+\Delta t} = [\mathbf{substrate\!:\!catalyst}]_t + (k[\mathbf{substrate}]_t[\mathbf{catalyst}]_t - k_{-1}[\mathbf{substrate\!:\!catalyst}]_t)\Delta t$$

$$[\mathbf{catalyst}]_{t+\Delta t} = [\mathbf{catalyst}]_t + (-k[\mathbf{substrate}]_t[\mathbf{catalyst}]_t + k_{-1}[\mathbf{substrate\!:\!catalyst}]_t)\Delta t$$

Theoretical curves

Theoretical fluorescence intensity, I_{theory} has been calculated by the following expressions:

$$I_{theory} = A[\mathbf{substrate}] + B[\mathbf{substate\!:\!catalyst}] + C$$

The values of A, B and C are assumed to be the same for all kinds of substrates because they have the same dye and other conditions such as amount of solvent or sample cell are exactly same.

Fitting parameters

The fitting parameters are defined as follows:

Parameter	Definition
k	Binding rate constant between substrate and catalyst
k_{-1}	Dissociation rate constant of substrate:catalyst
A	PL intensity of substrate per unit mole.
B	PL intensity of substrate:catalyst per unit mole.
C	Background PL intensity.

A and C values

In order to reduce the number of parameters to be optimized together, the values of A and C were determined experimentally. If we measure fluorescence intensity at t=0, [substrate:catalyst] should be zero and above equations are reduced to:

$$I_{theory,t=0} = A[\textbf{substrate}]_{t=0} + C$$

By plotting [substrate]$_{t=0}$ vs. fluorescence intensity, A and C have been determined.

Definition of χ2

The definition of the χ2 is as follows:

$$\chi^2 = \sum_{I=\text{curve \#}} \chi_i^2$$

$$\chi_i^2 = \sum_j (I_{exp}(t_j, i) - I_{theory}(t_j, i))^2$$

Least-squares fit

The least-squares fit of the model against the experimental data was done using the minimization package MINUIT written at CERN.[2] The quantity minimized is χ^2. The errors of the fitted parameters have been calculated by MINUIT and they represent one standard deviation. In total 17 parameters (16 rate constants and B value) have been optimized with 8 experimental curves. Since each experimental curve contains many data points, the data-to-parameter ration is sufficiently high enough.

Gibbs free energy change

The Gibbs free energy change was obtained using the following standard equations.

$$\Delta G = -RT\ln K$$

$$K = k/k_{-1}$$

3. References

1. a) J. –H. Sohn, K. H. Kim, H. –Y. Lee, Z. S. No, H. Ihee, *J. Am. Chem. Soc.* **2008**, *130*, 16506-16507; b) K. H. Kim, T. Ok, K. Lee, H. –S. Lee, K. T. Chang, H. Ihee, J. –H. Sohn, *J. Am. Chem. Soc*. **2010**, *132*, 12027-12033; c) O. S. Lee, K. H. Kim, J. Kim, K. Kwon, T. Ok, H. Ihee, H. –Y. Lee, J. –H. Sohn, *J. Org. Chem*. **2013**, *78*, 8242-8249.

2. CERN, Minuit; Function Minimization and Error Analysis, http://wwwasdoc.web.cern.ch/wwwasdoc/minuit/minmain.html.

4. ¹H and ¹³C NMR Spectra of ZZ-ene, ZE-ene, EE-ene and their intermediates

ZZ-ene
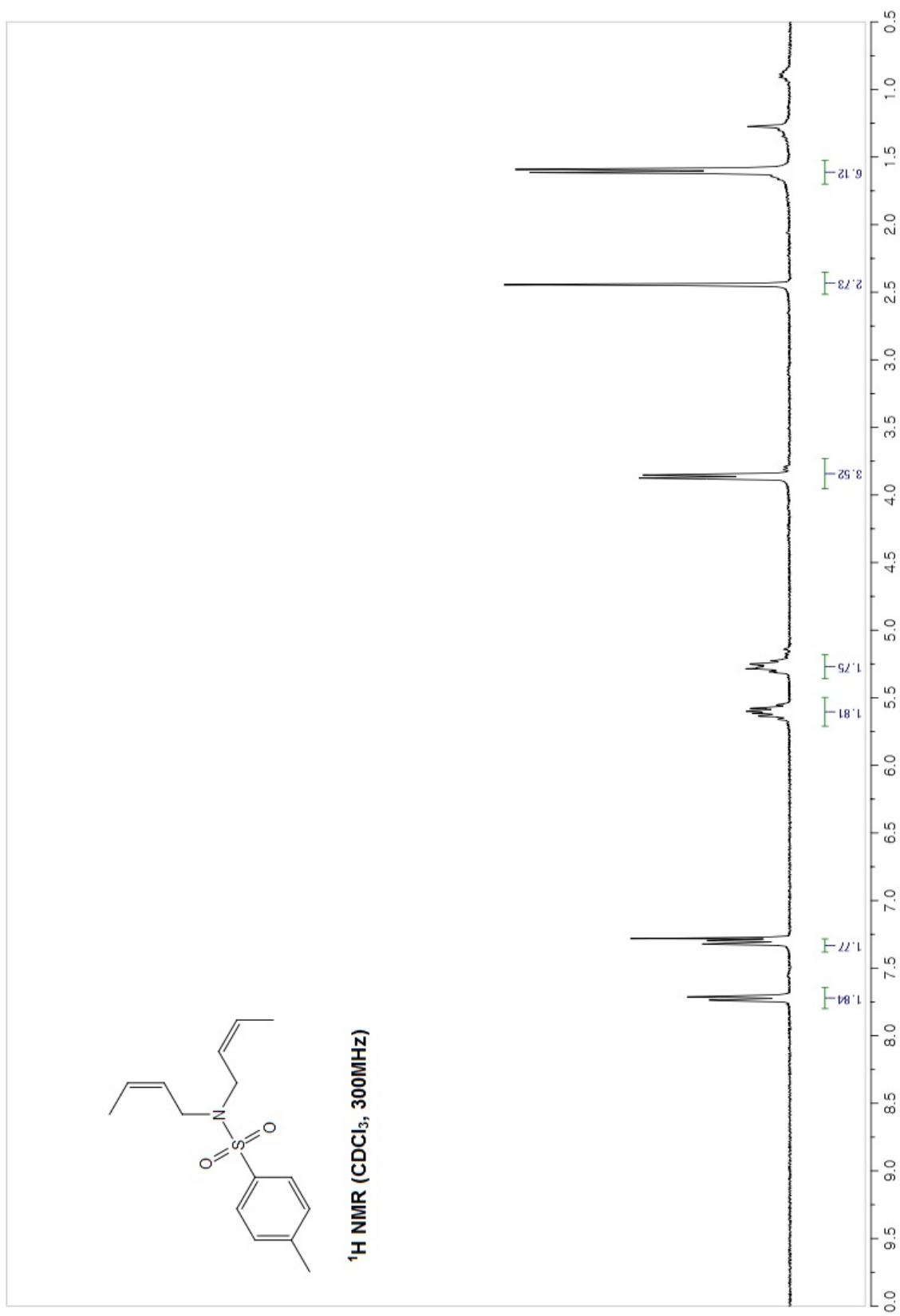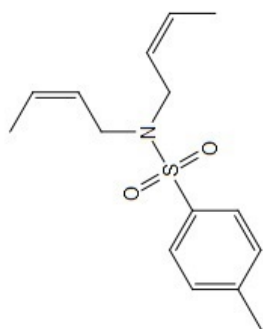
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¹³C NMR (CDCl₃, 150MHz)
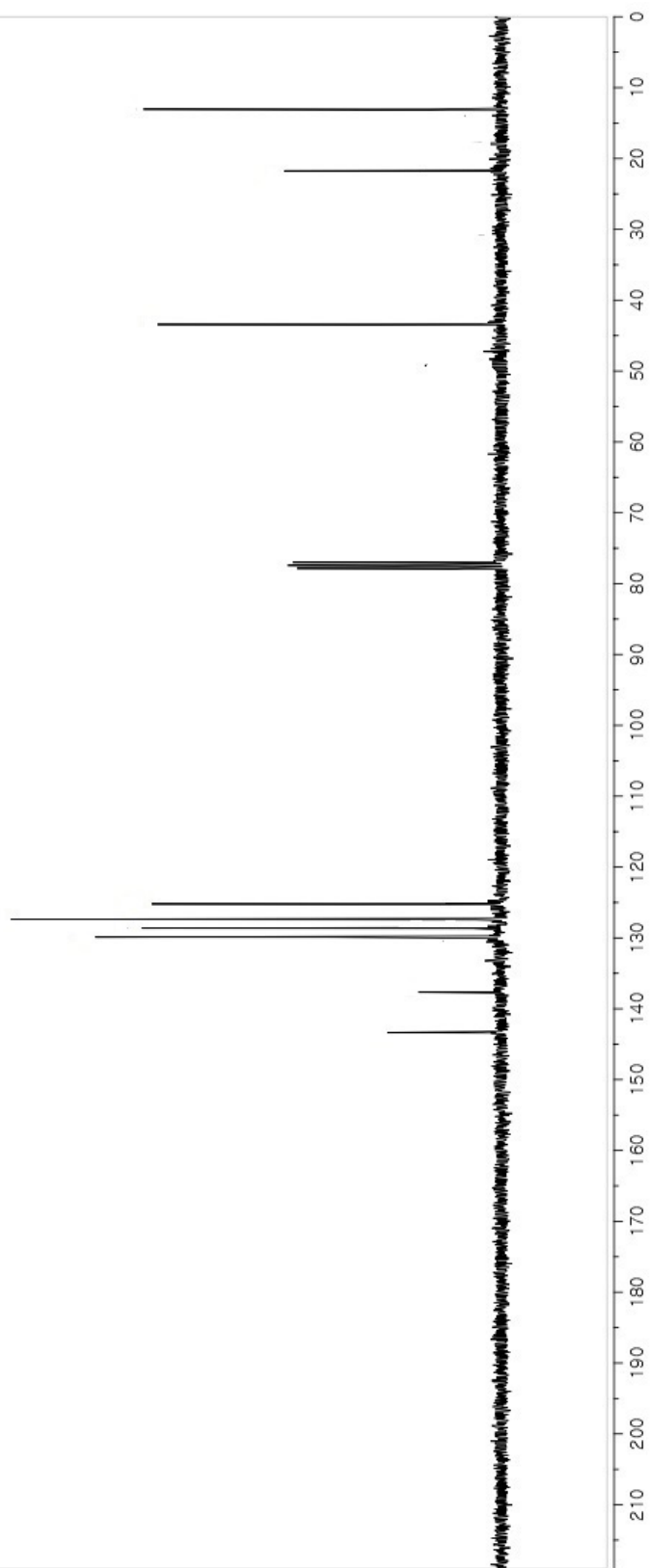
EE-ene
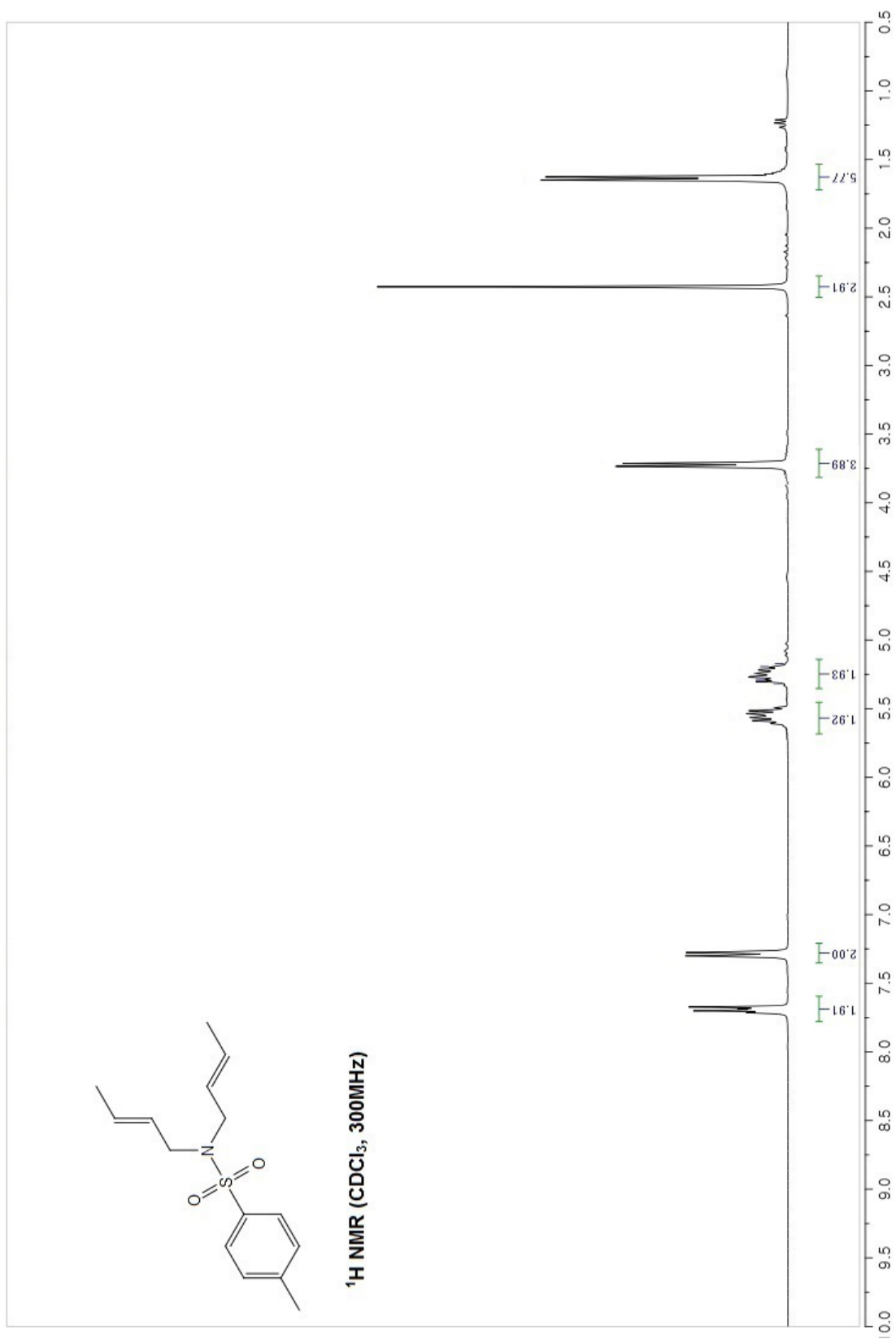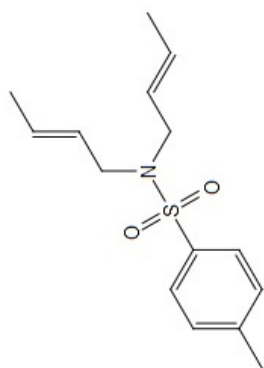
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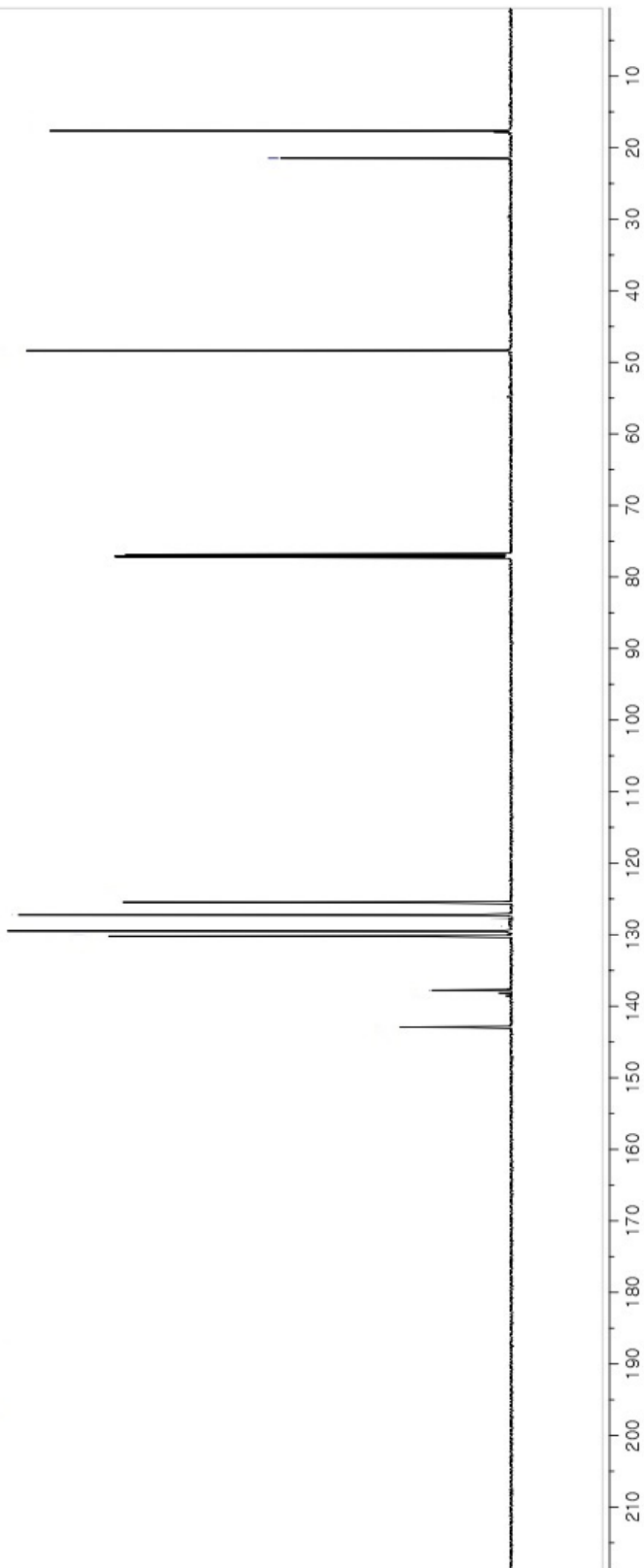
^{13}C NMR (CDCl$_3$, 150MHz)

ZE-ene
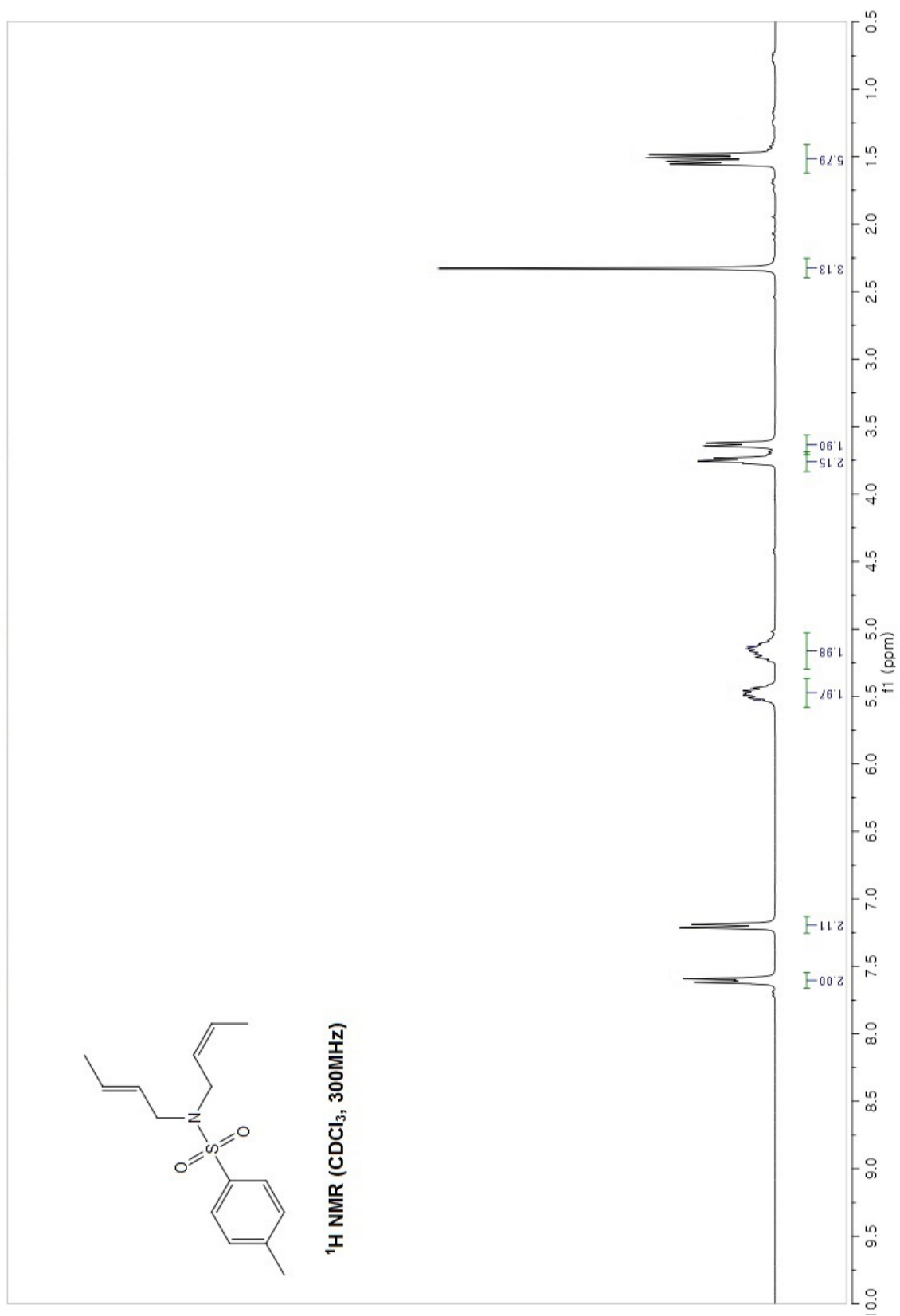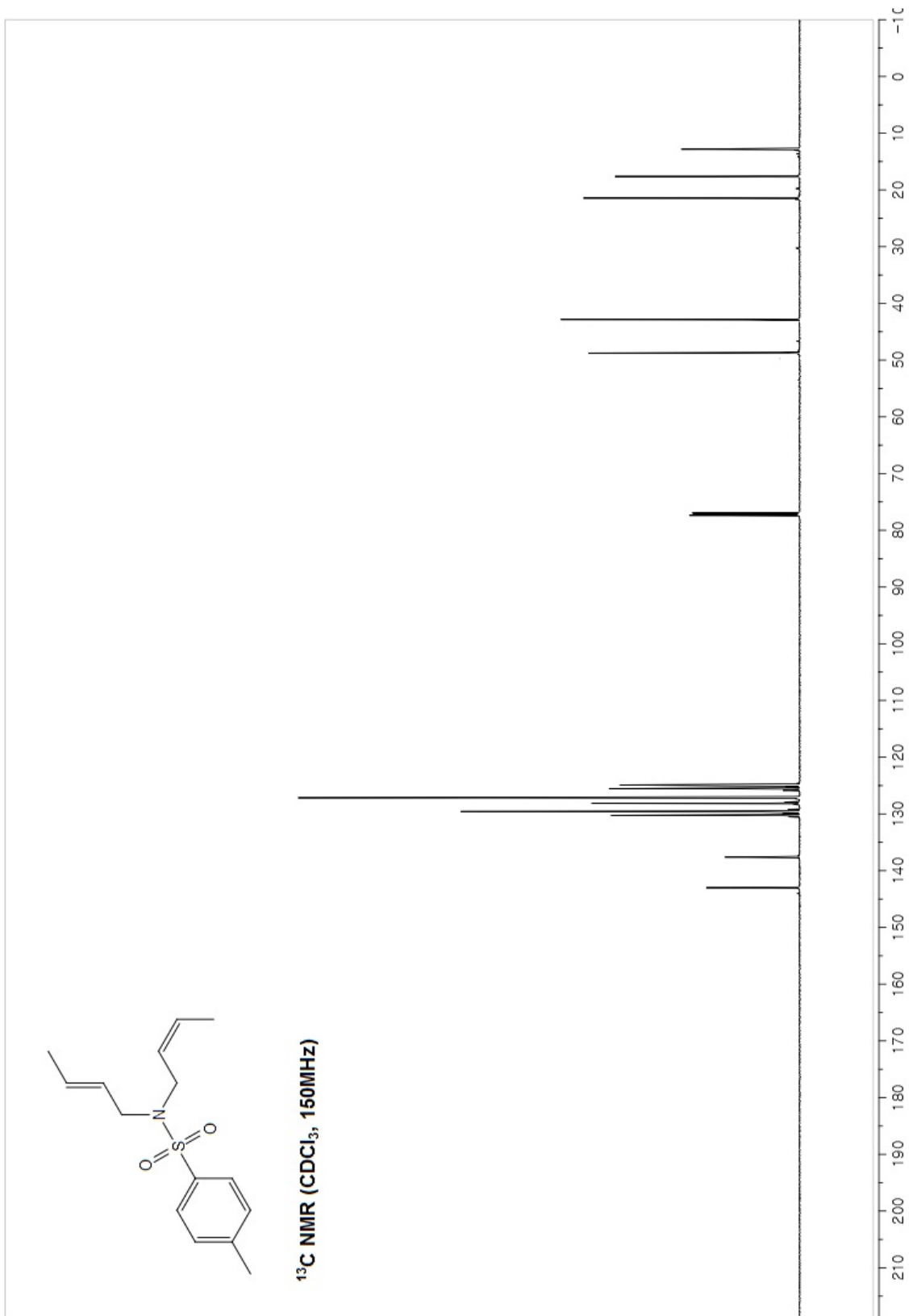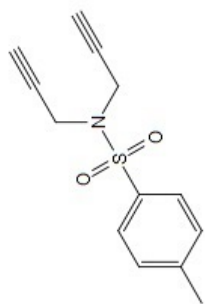
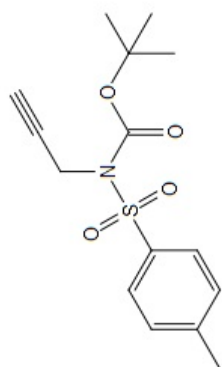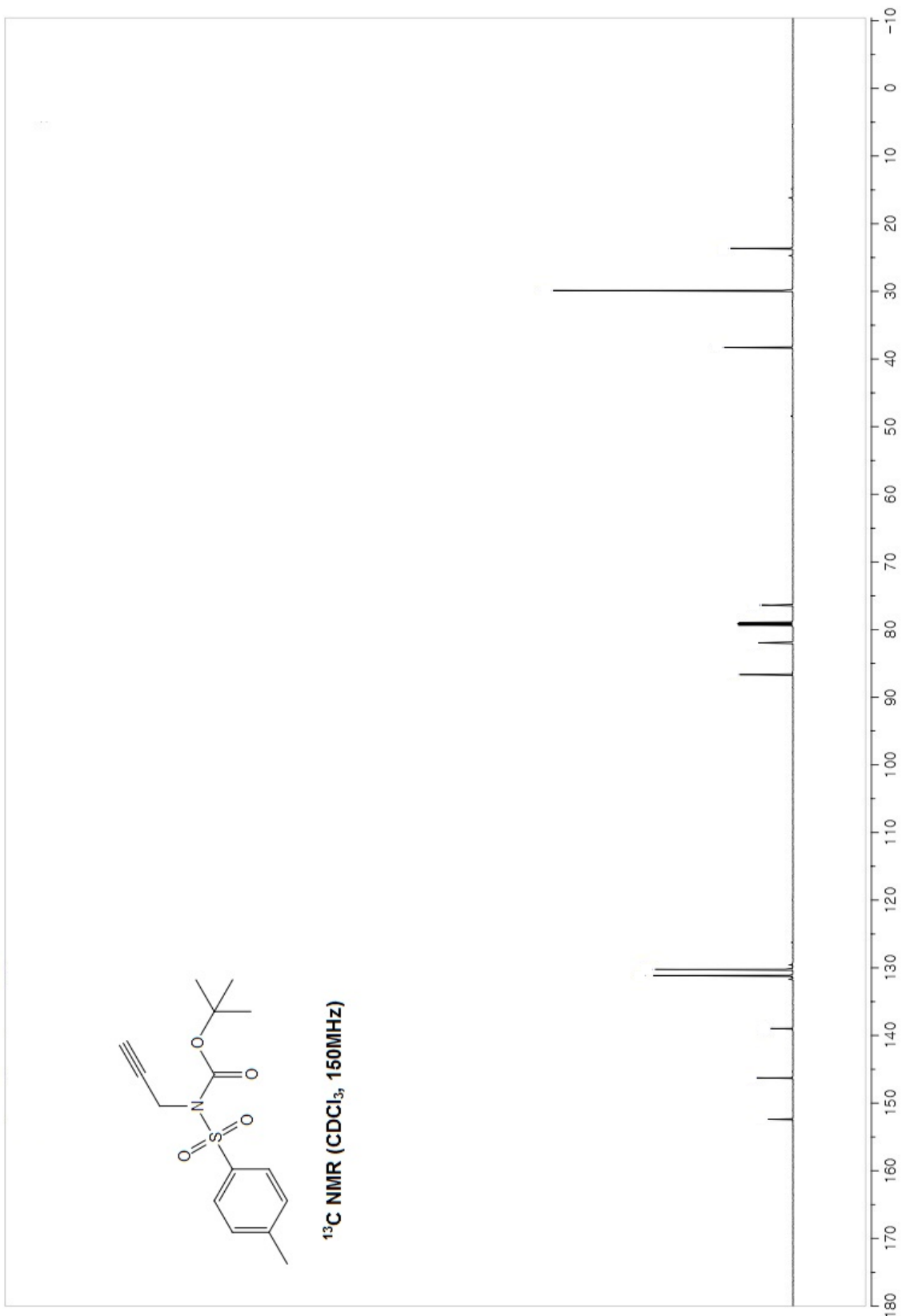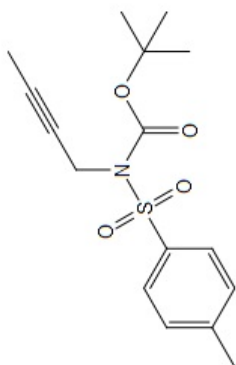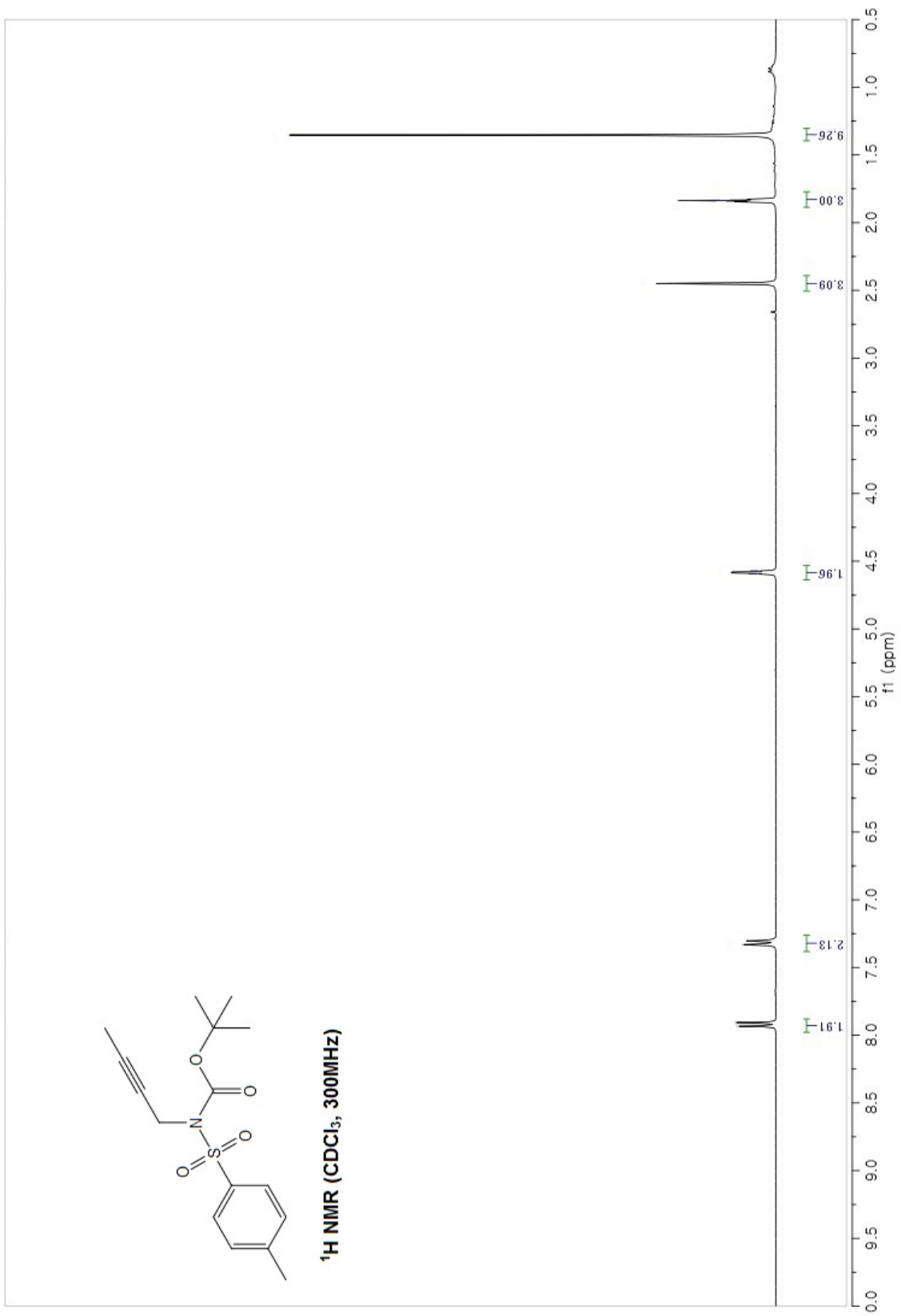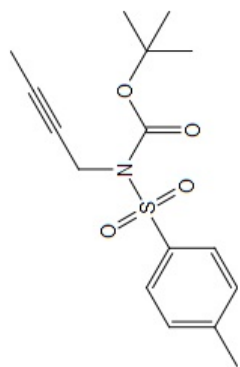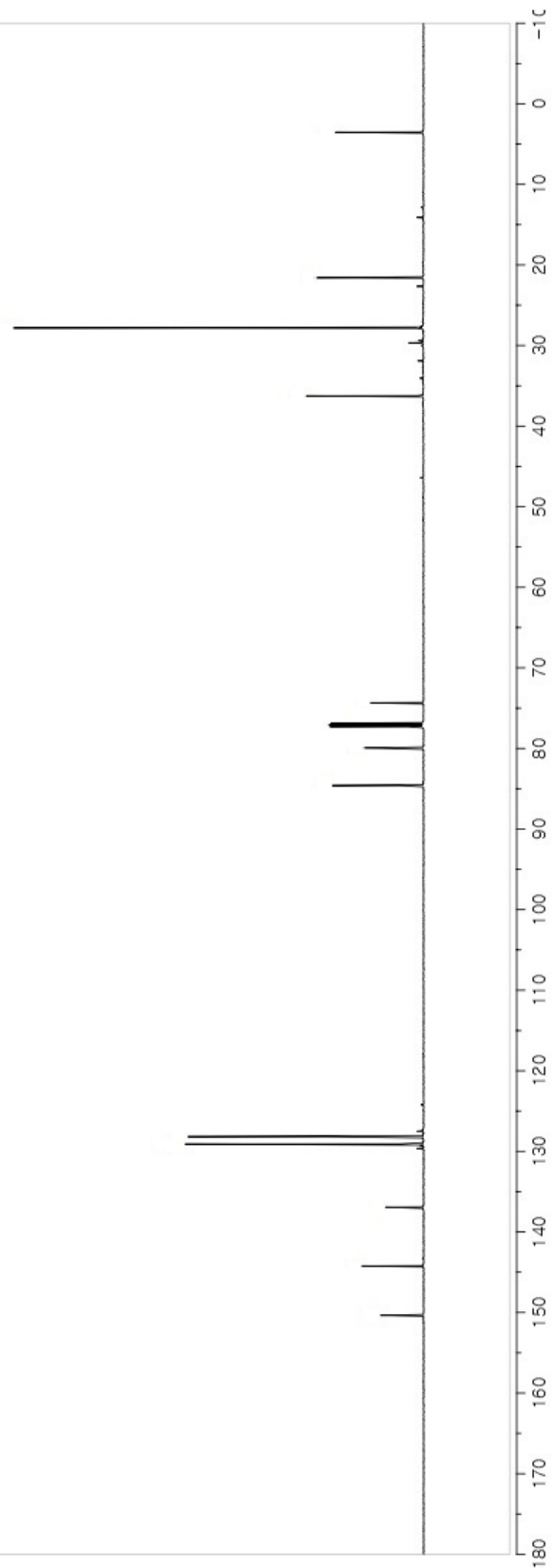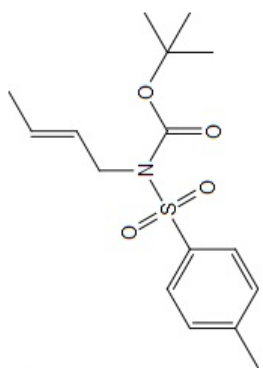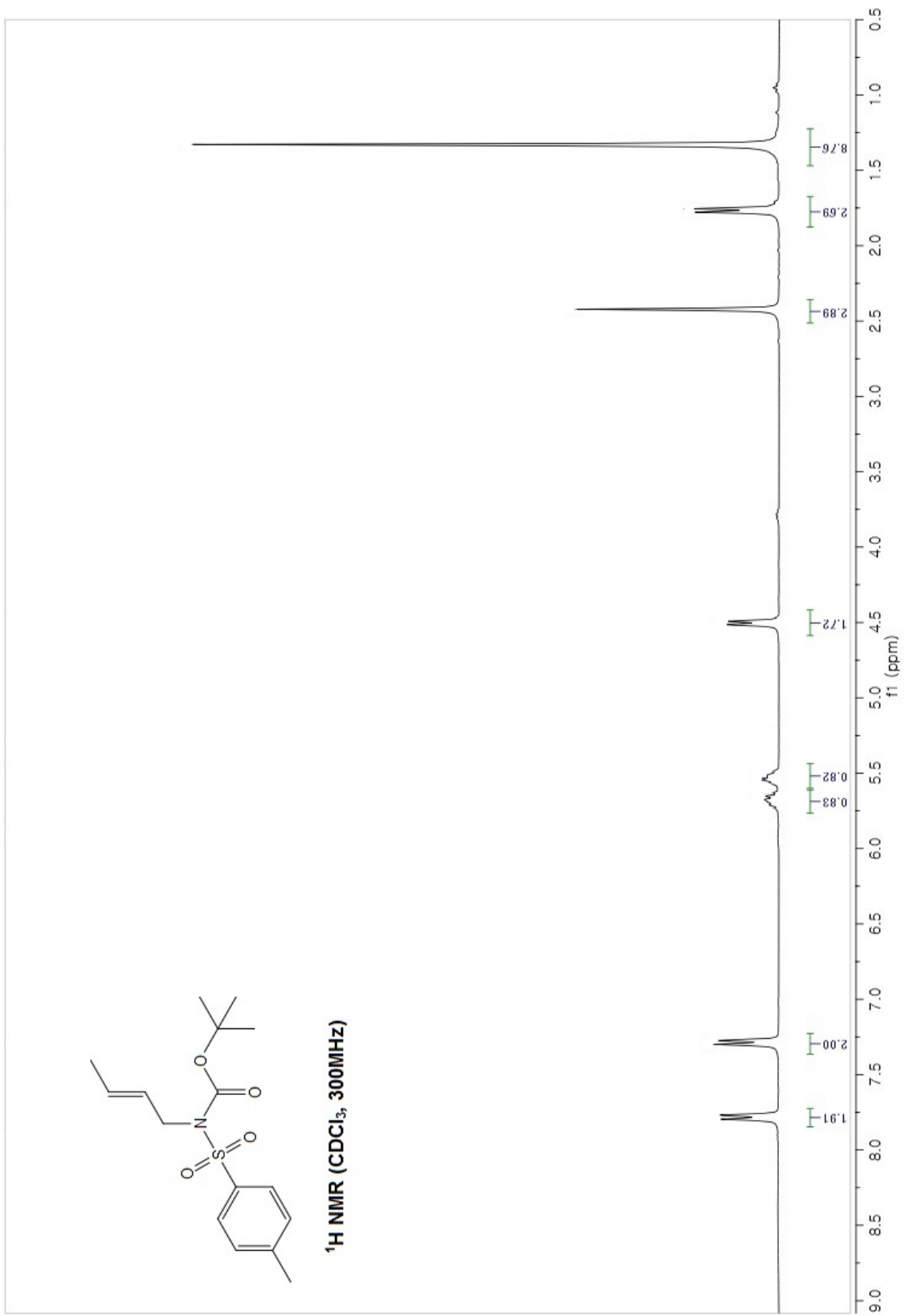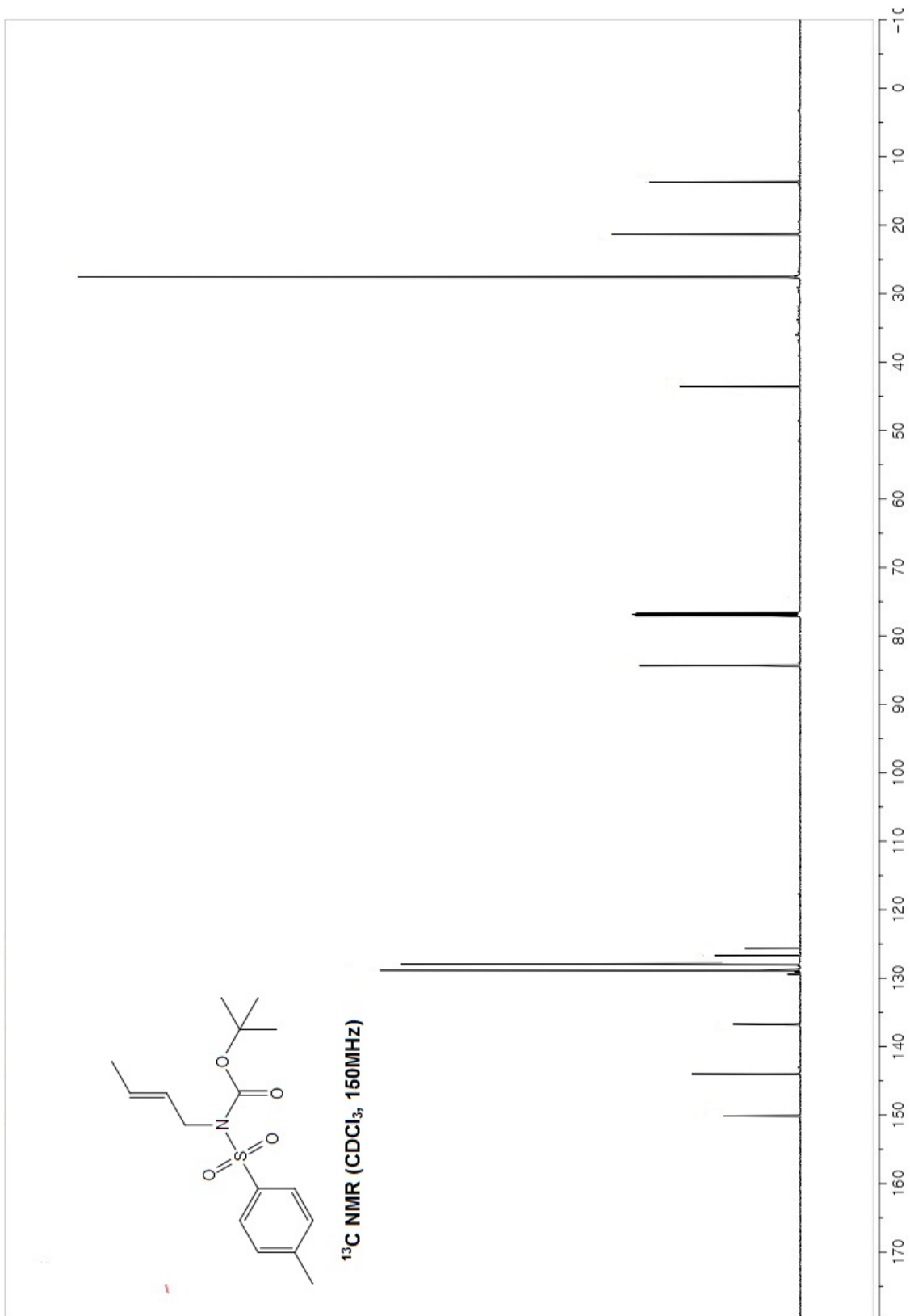¹H NMR (CDCl₃, 300MHz)
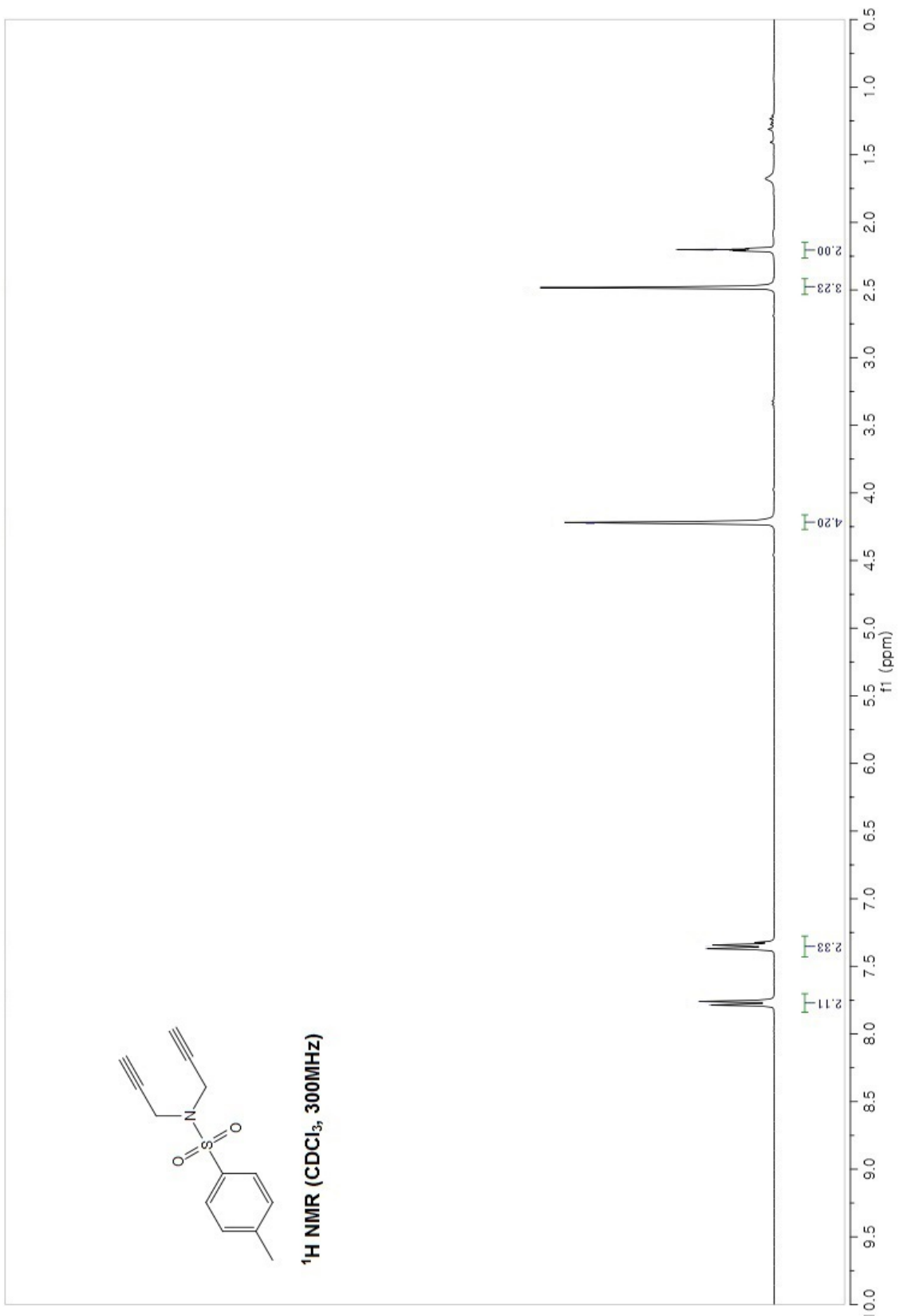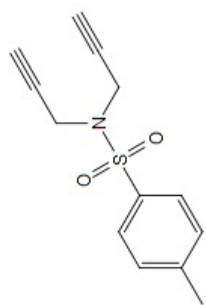
S10

^{13}C NMR (CDCl$_3$, 150MHz)

¹H NMR (CDCl₃, 300MHz)

^{13}C NMR (CDCl$_3$, 150MHz)

S13

¹H NMR (CDCl₃, 300MHz)

S14

13C NMR (CDCl3, 150MHz)

S15
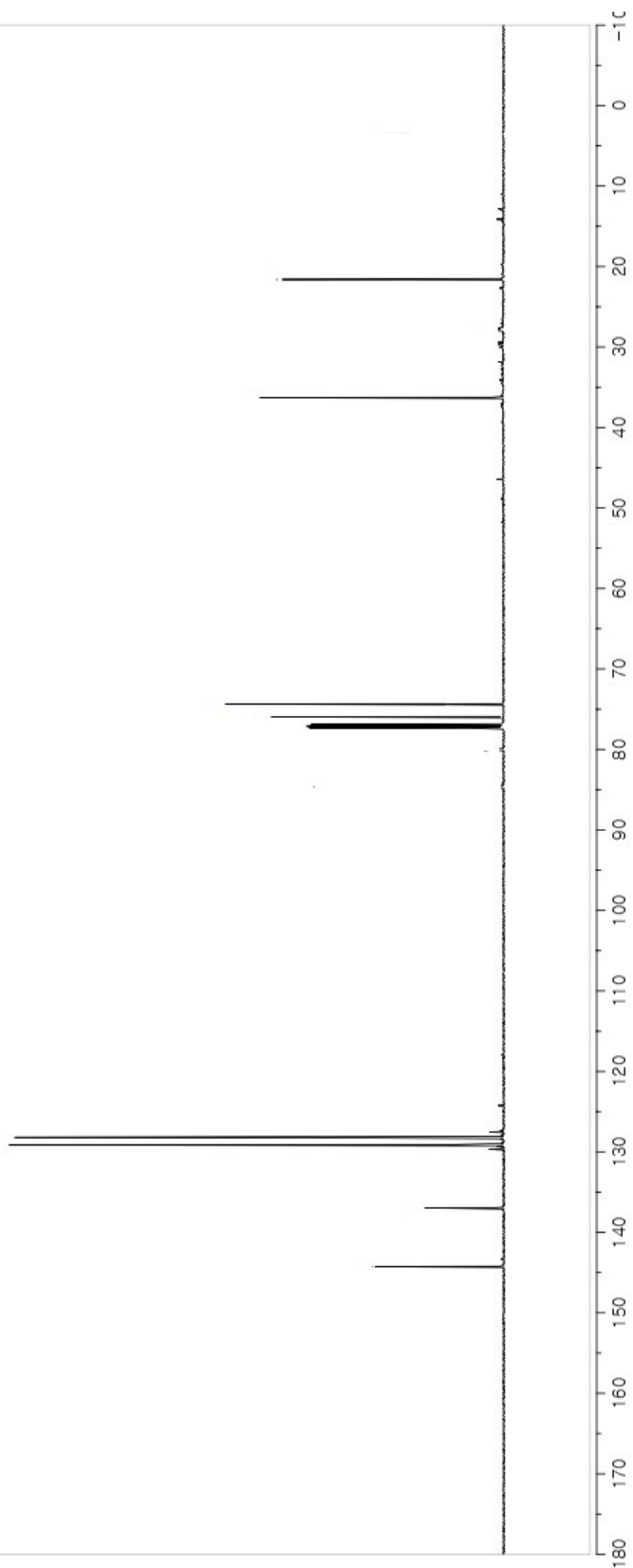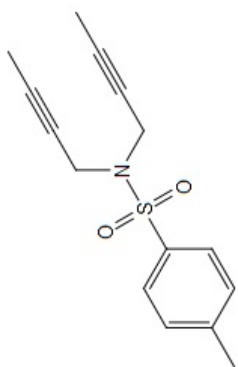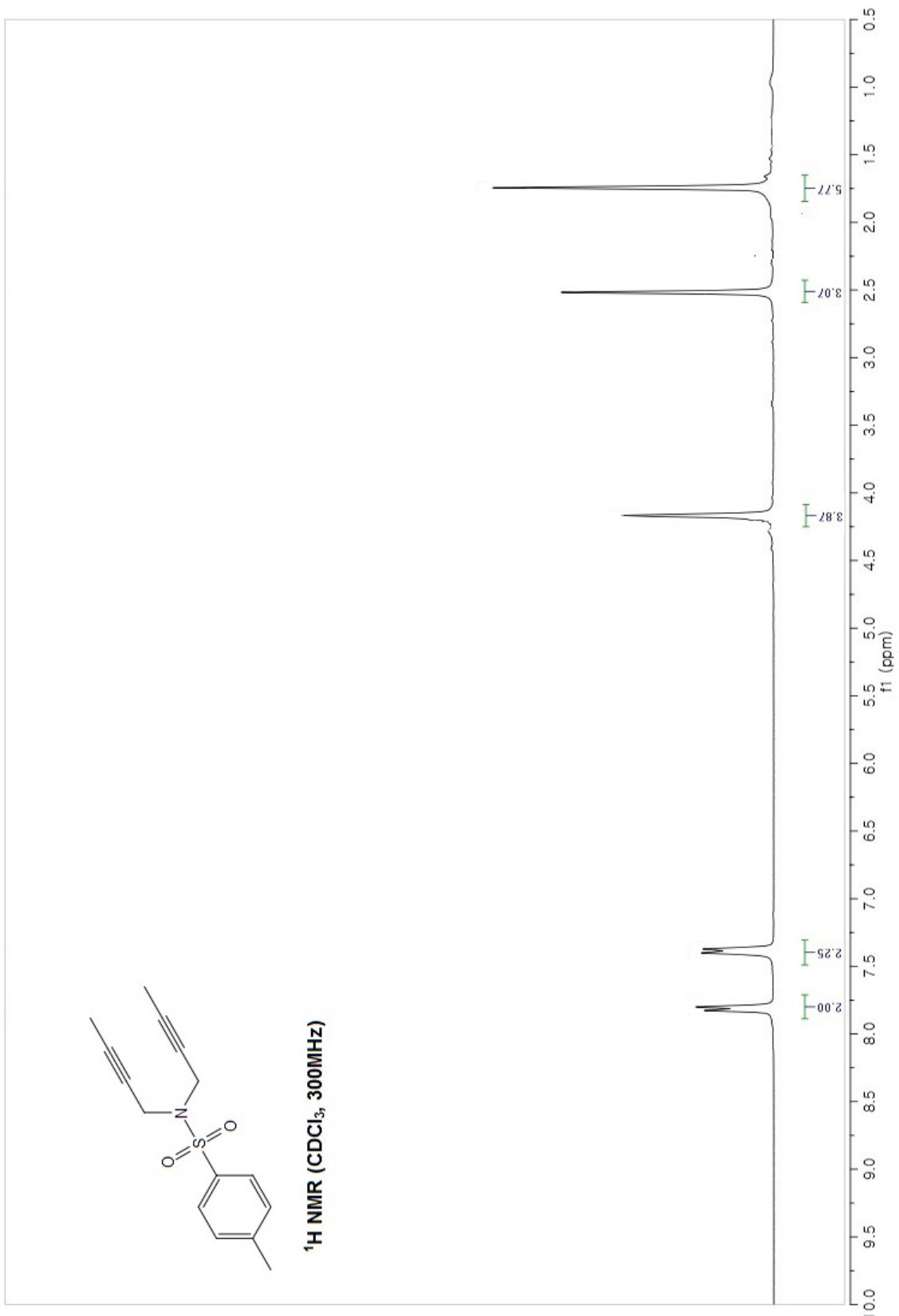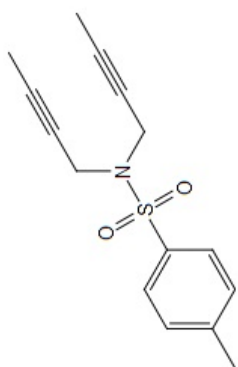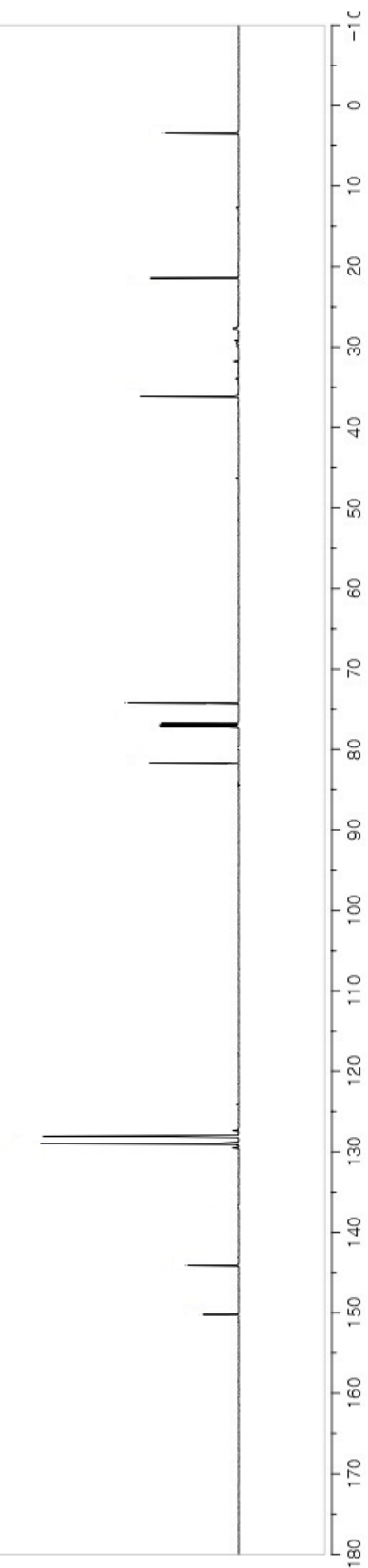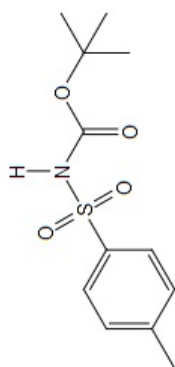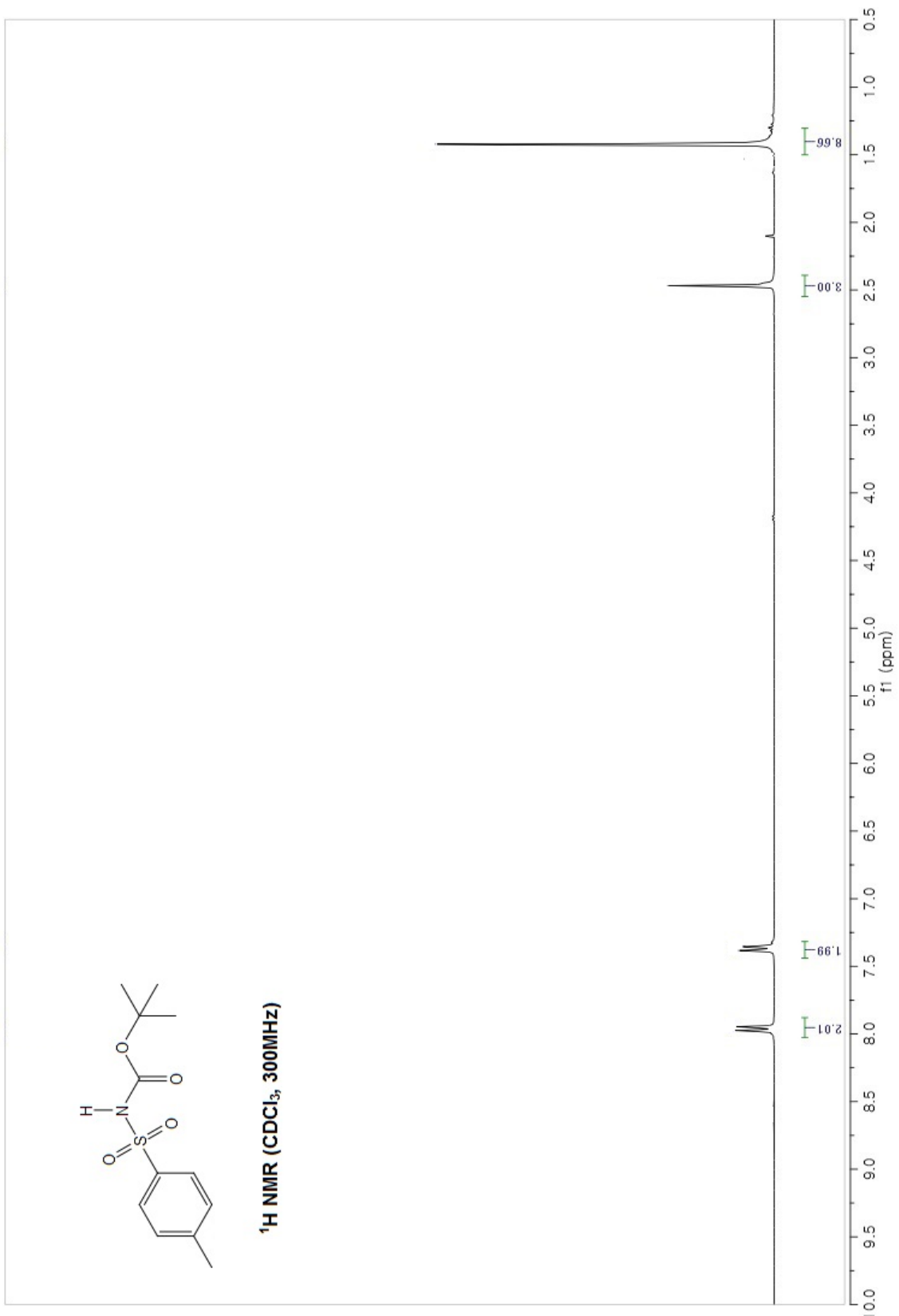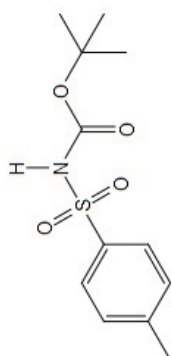
¹H NMR (CDCl₃, 300MHz)

^{13}C NMR (CDCl$_3$, 75MHz)

^{1}H NMR (CDCl$_3$, 300MHz)

^{13}C NMR (CDCl$_3$, 150MHz)

¹H NMR (CDCl₃, 300MHz)

^{13}C NMR (CDCl$_3$, 150MHz)

¹H NMR (CDCl₃, 300MHz)

^{13}C NMR (CDCl$_3$, 150MHz)
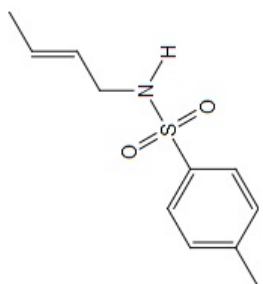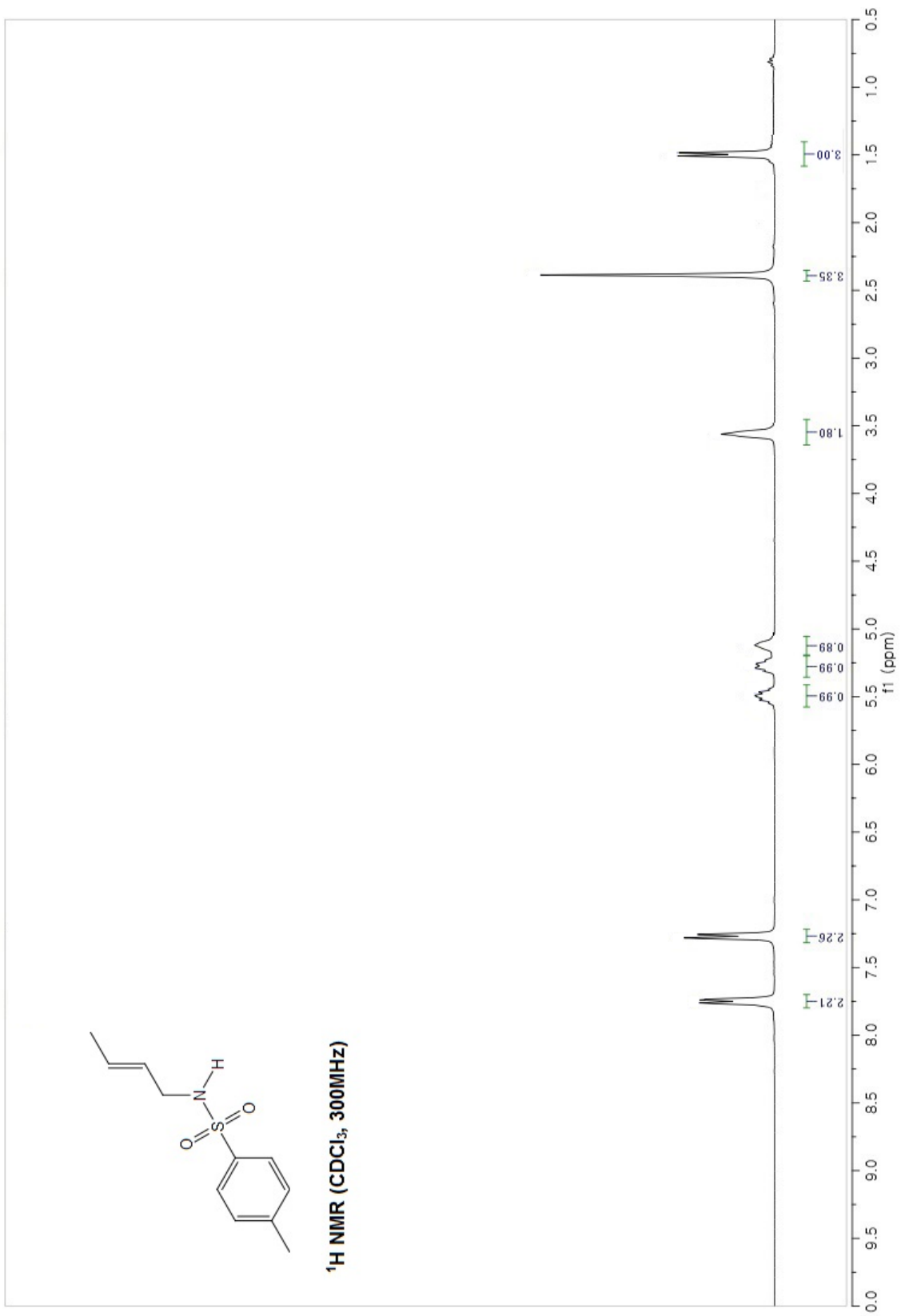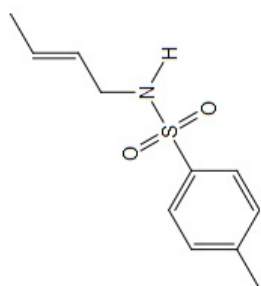
¹H NMR (CDCl₃, 300MHz)

¹³C NMR (CDCl₃, 150MHz)