Supporting Information

Correlation between Functionality Preference of Ru Carbenes and *Exo*/*Endo* Product Selectivity for Clarifying the Mechanism of Ring-Closing Enyne Metathesis

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1. Time-dependent change of the fluorescence spectra

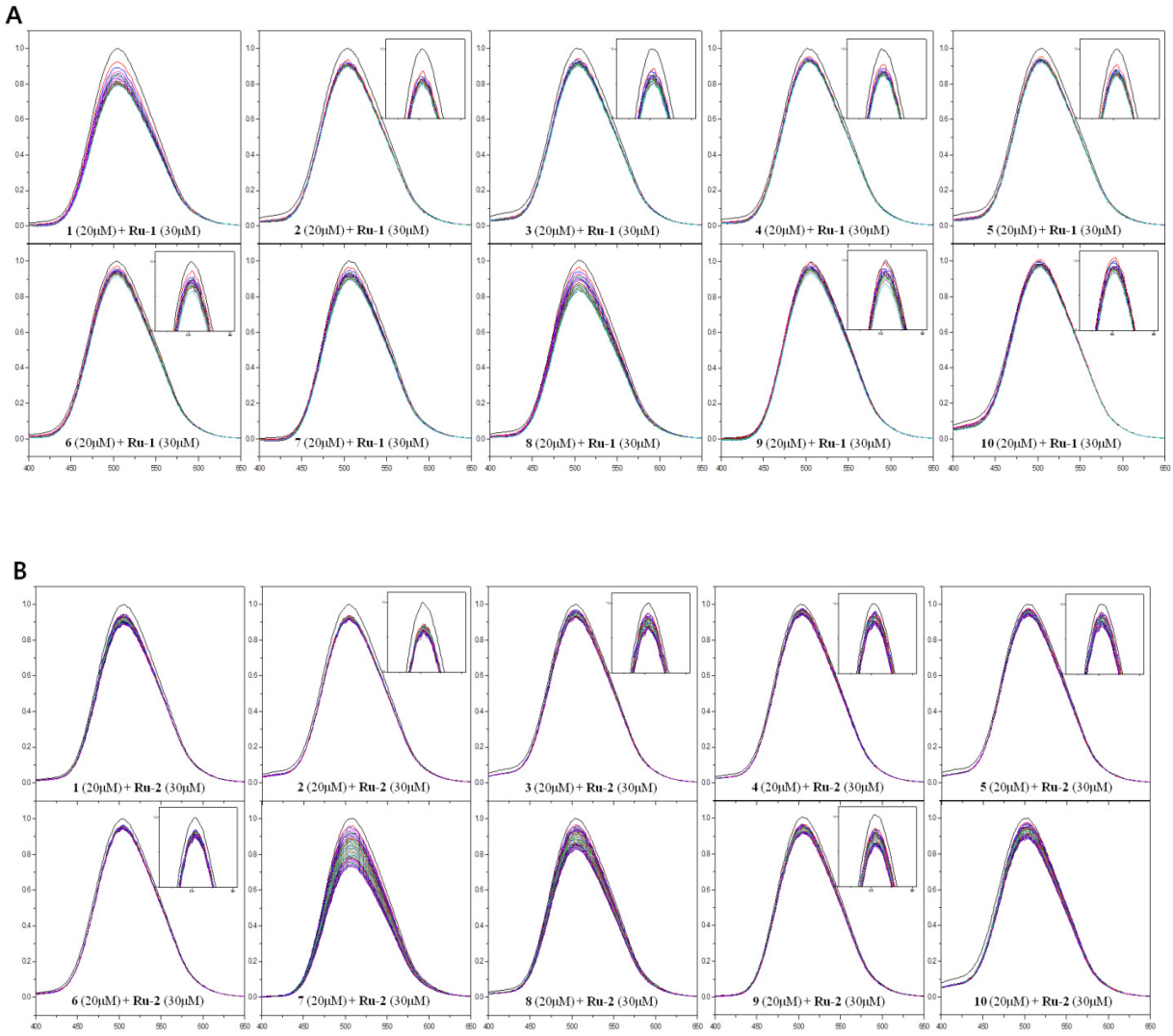


Figure S1. Time-dependent change of the fluorescence spectra of dye-alkene (**1-6**) and dye-alkyne (**7-10**) due to the reaction with the (A) **Ru-1** and (B) **Ru-2** catalysts**.**

2. Photostability of substrate and time-dependent change of fluorescence spectra of control

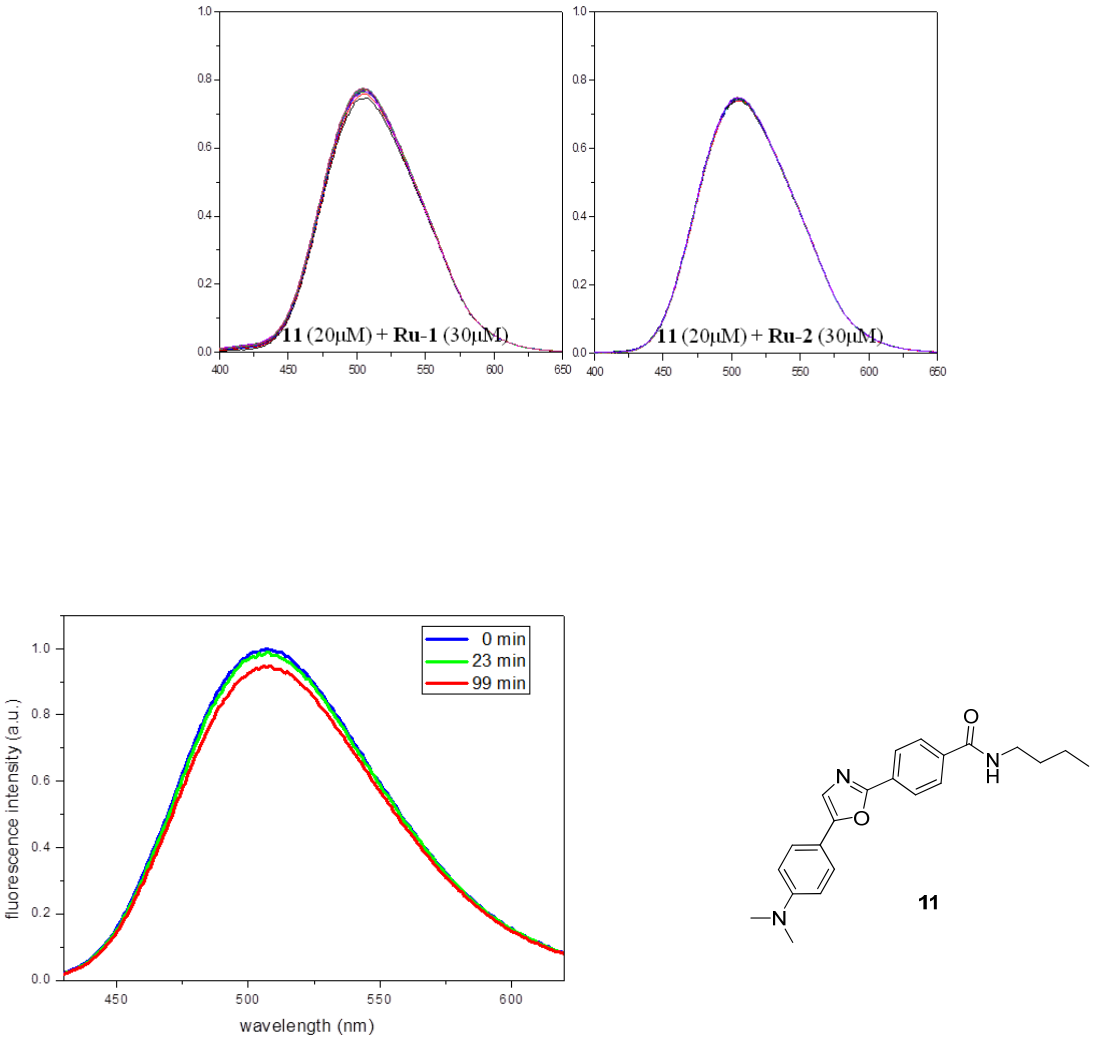
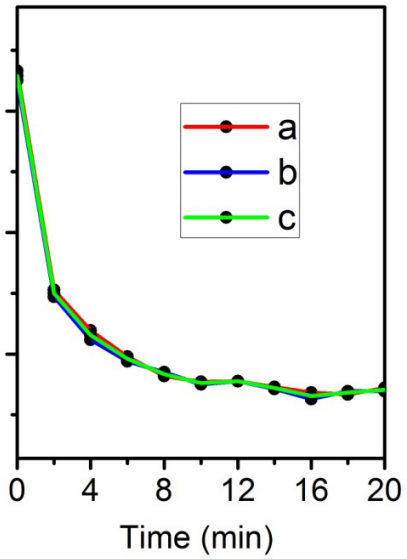


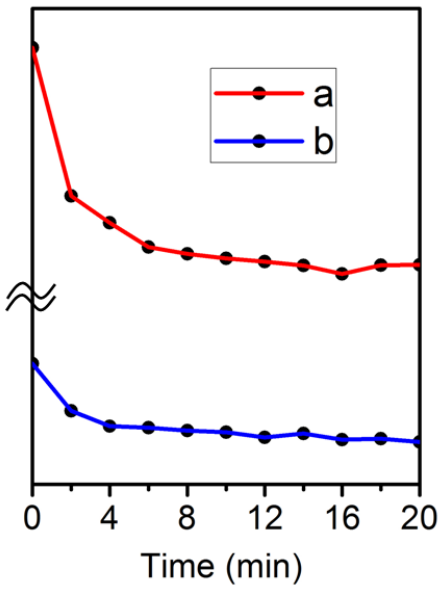
Figure S2. Time-dependent change of the fluorescence spectra and photostability of control **11**.

3. Time-dependent fluorescence quenching traces at various conditions



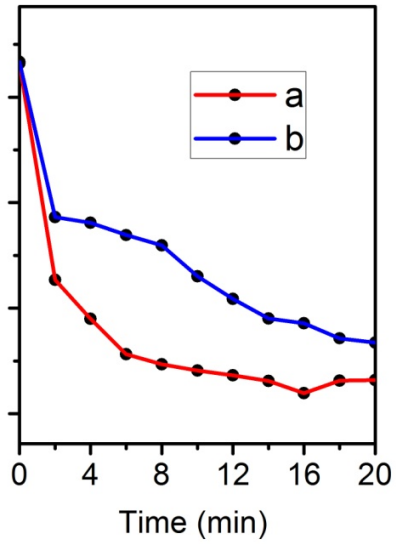
Index	Condition
a	**3** (20 μM) + **Ru-1** (30 μM)
b	**3** (20 μM) + **Ru-1** (30 μM)
c	Average of a and b

Figure S3. Reproducibility test of time-dependent fluorescence quenching traces at the same conditions. The experimental data curve is reproduced well and the averaged curve is used for the analysis. In this figure, the time-dependent fluorescence quenching traces of *cis*-alkene (**3**) is presented as an example.



Index	Condition
a	**3** (20 μM) + **Ru-1** (30 μM)
b	**3** (10 μM) + **Ru-1** (15 μM)

Figure S4. Time-dependent fluorescence quenching traces at different concentration of the substrate with the same equivalent (1.5 equiv) catalyst concentration. These curves share the same rate constants (k and k_{-1}) and it increases the data/parameter ratio at the fitting analysis. In this figure, the time-dependent fluorescence quenching traces of *cis*-alkene (**3**) is presented as an example.



Index	Condition
a	**3** (20 μM) + **Ru-1** (30 μM)
b	**3** (20 μM) + **Ru-1** (20 μM)

Figure S5. Time-dependent fluorescence quenching traces at different concentration of the catalyst (1.0 and 1.5 equiv) with the same substrate concentration. These curves share the same rate constants (k and k_{-1}) and it increases the data/parameter ratio at the fitting analysis. In this figure, the time-dependent fluorescence quenching traces of *cis*-alkene (**3**) is presented as an example.

4. Global fitting analysis of FRET data

The detailed describtion on the quantitative analysis of FRET data was reported in our previous publications[1,2]. In the following pages, we briefly describe how we quantitatively analyzed FRET data.,

Reaction scheme

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

$$\mathbf{substrate} + \mathbf{catalyst} \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} \mathbf{substrate{:}catalyst}$$

Rate equations

We set up the rate equations as follows:

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

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

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

Concentrations of each species at a certain time, t + Δt, 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:

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

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:

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

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

Definition of χ^2

The definition of the χ^2 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.[3] 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 21 parameters (20 rate constants and B value) have been optimized with 16 to 20 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.

$$\Delta G = -RT \ln K$$
$$K = k / k_{-1}$$

5. FRET data with Ru isopentenylidene

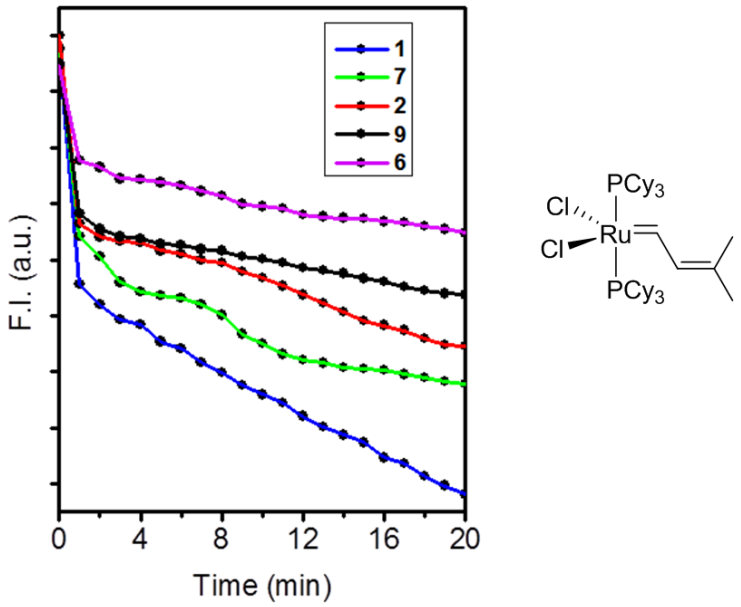
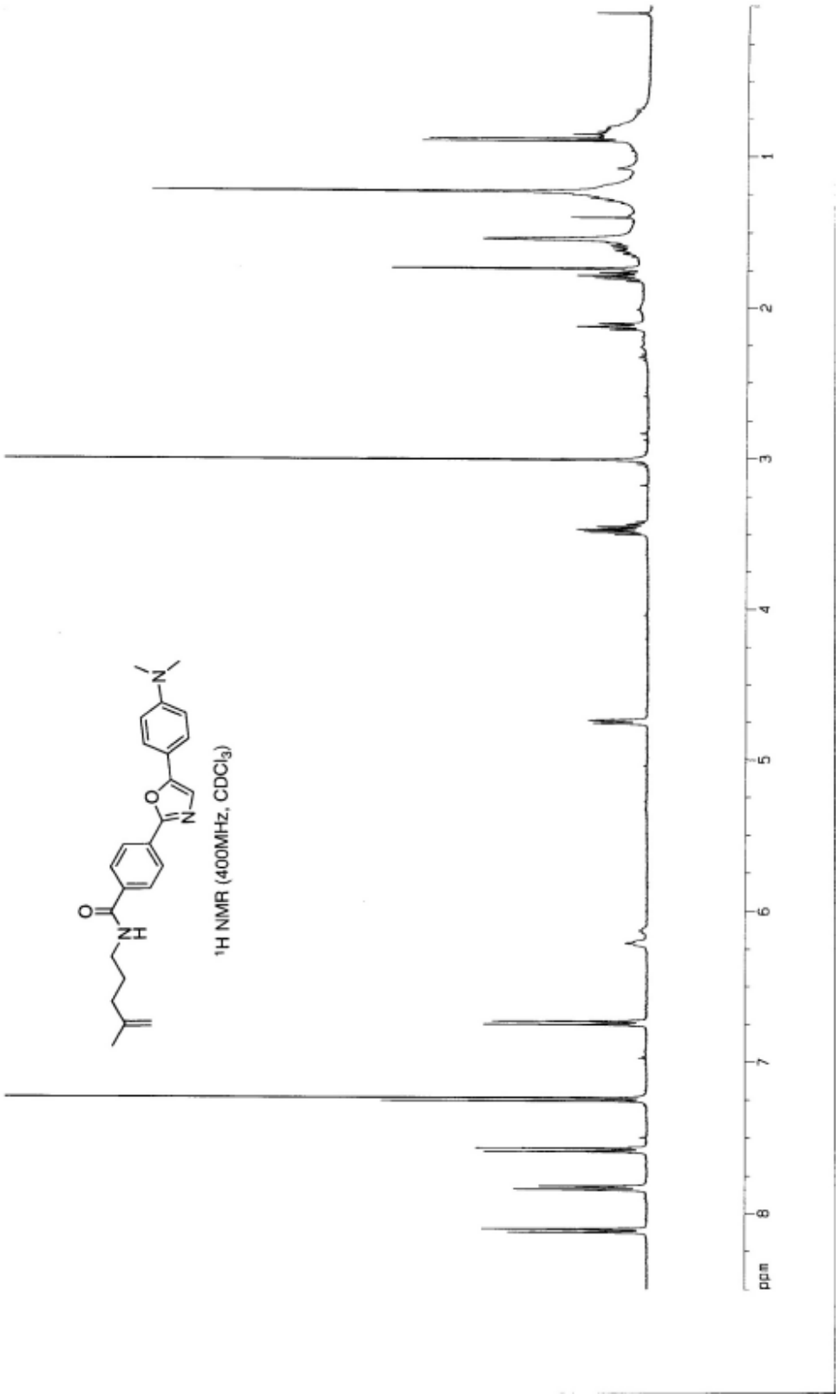
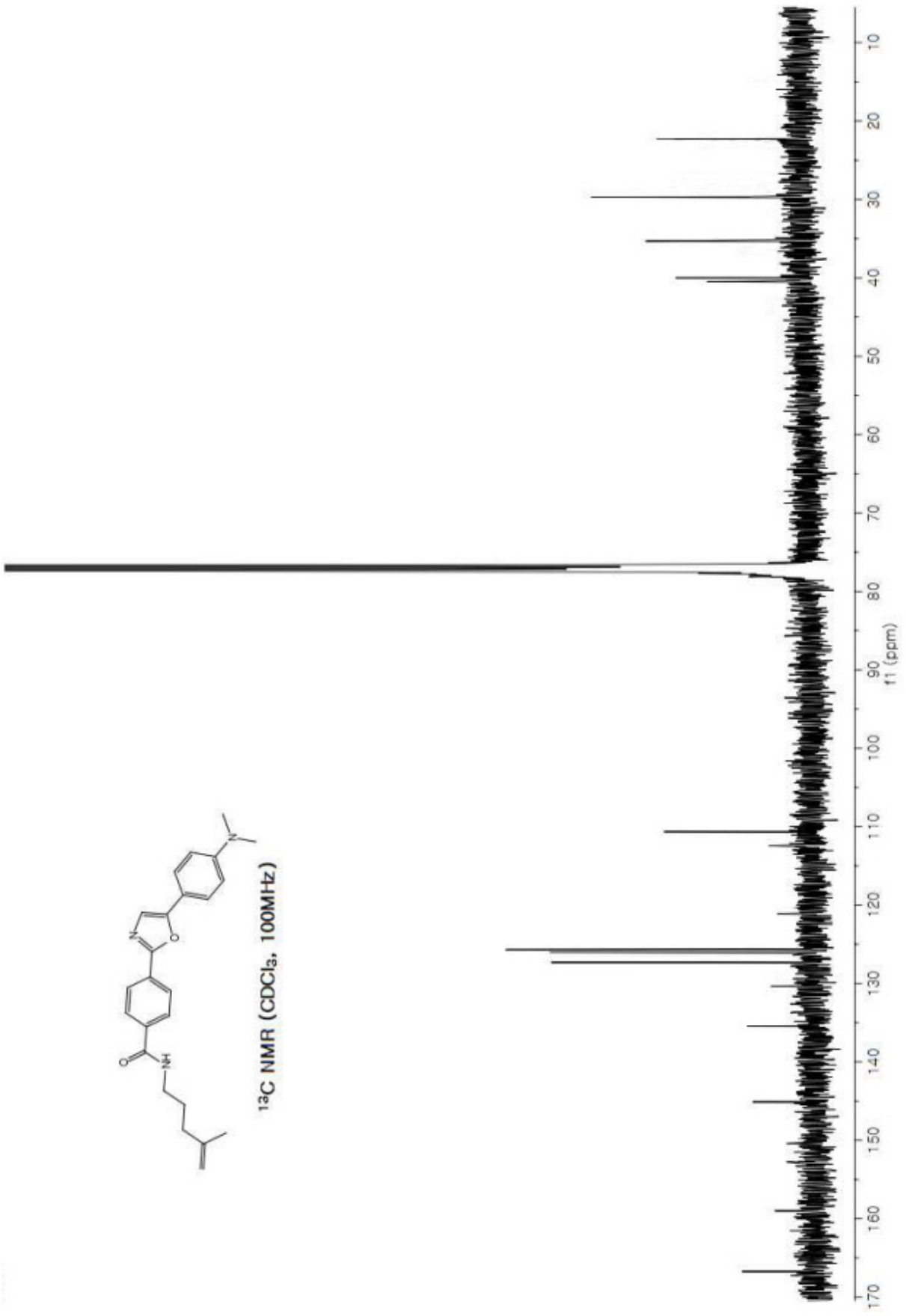


Figure S6. Time-dependent fluorescence quenching traces of **1**, **2**, **6**, **7** and **9**, whose functional groups are the components of the enyne substrates in Table 2, by the **Ru-1** analogue, Ru isopentenylidene. The Ru isopentenylidene shows no change of the order of functionality preference to **Ru-1**. The functionality preference order is **1** > **7** > **2** > **9** > **6** (20 μM:30 μM of substrates vs. catalyst).

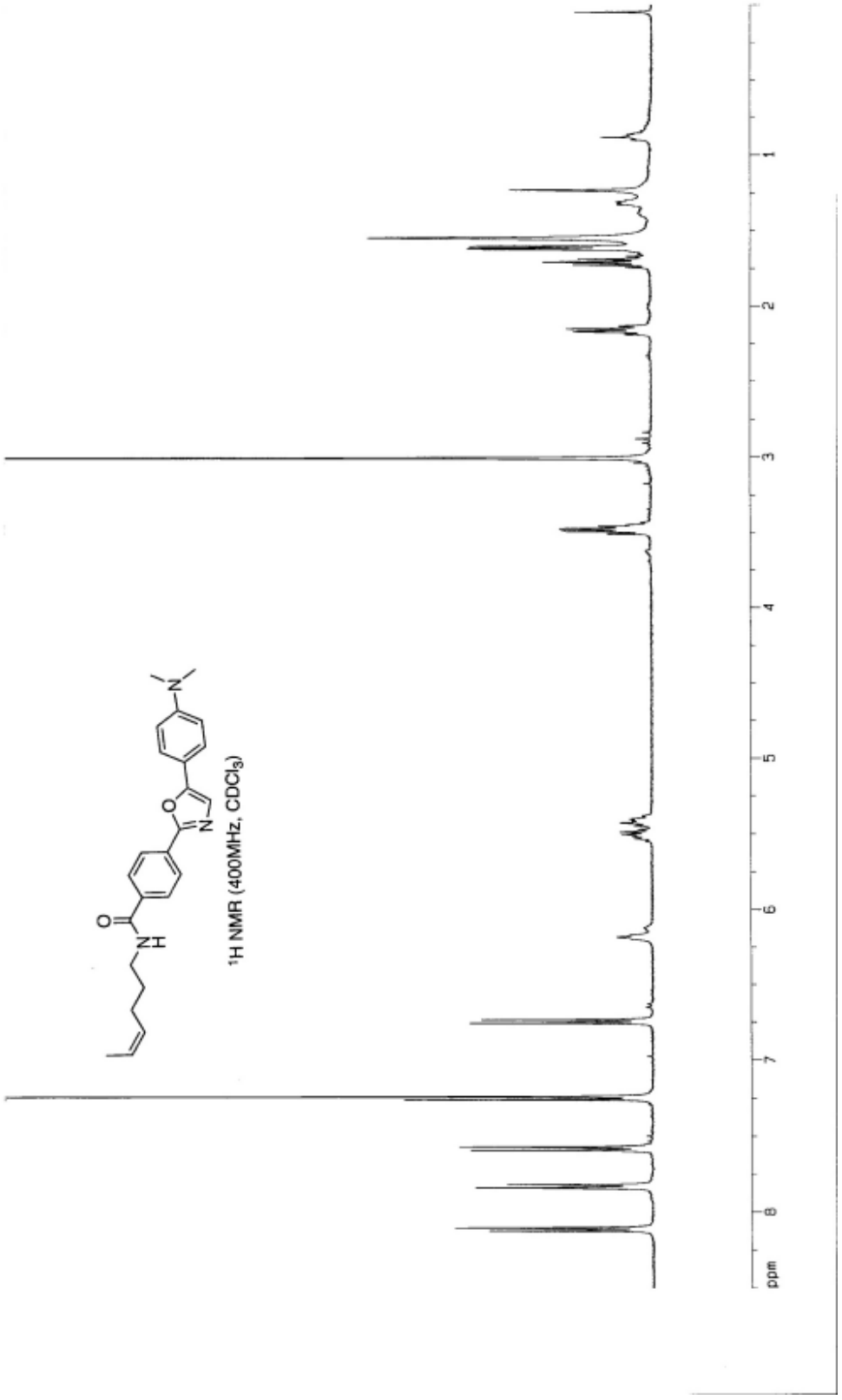
6. ^{1}H and ^{13}C NMR spectra of Compounds

Compound **2**



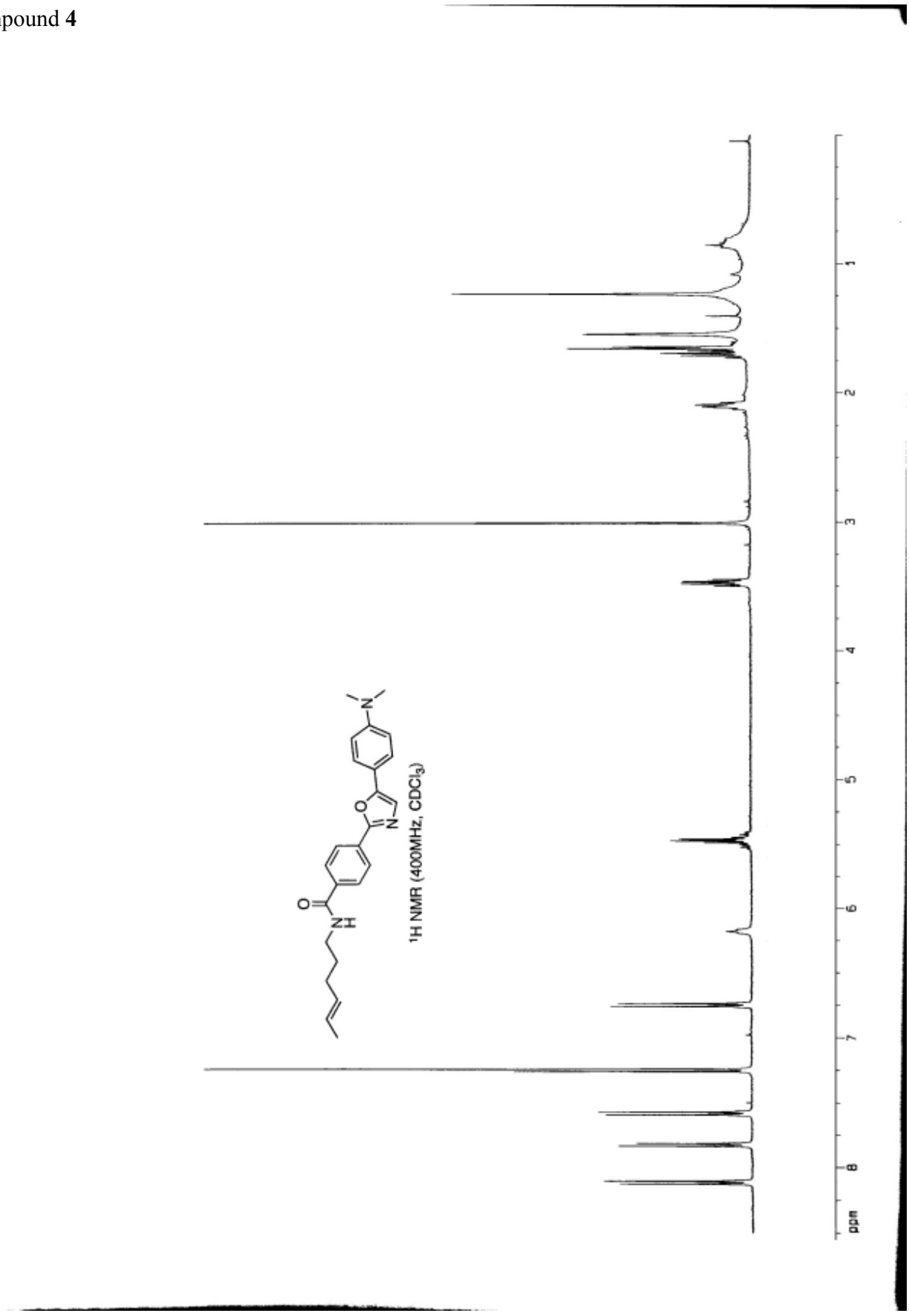

^{13}C NMR ($CDCl_3$, 100MHz)
f1 (ppm)

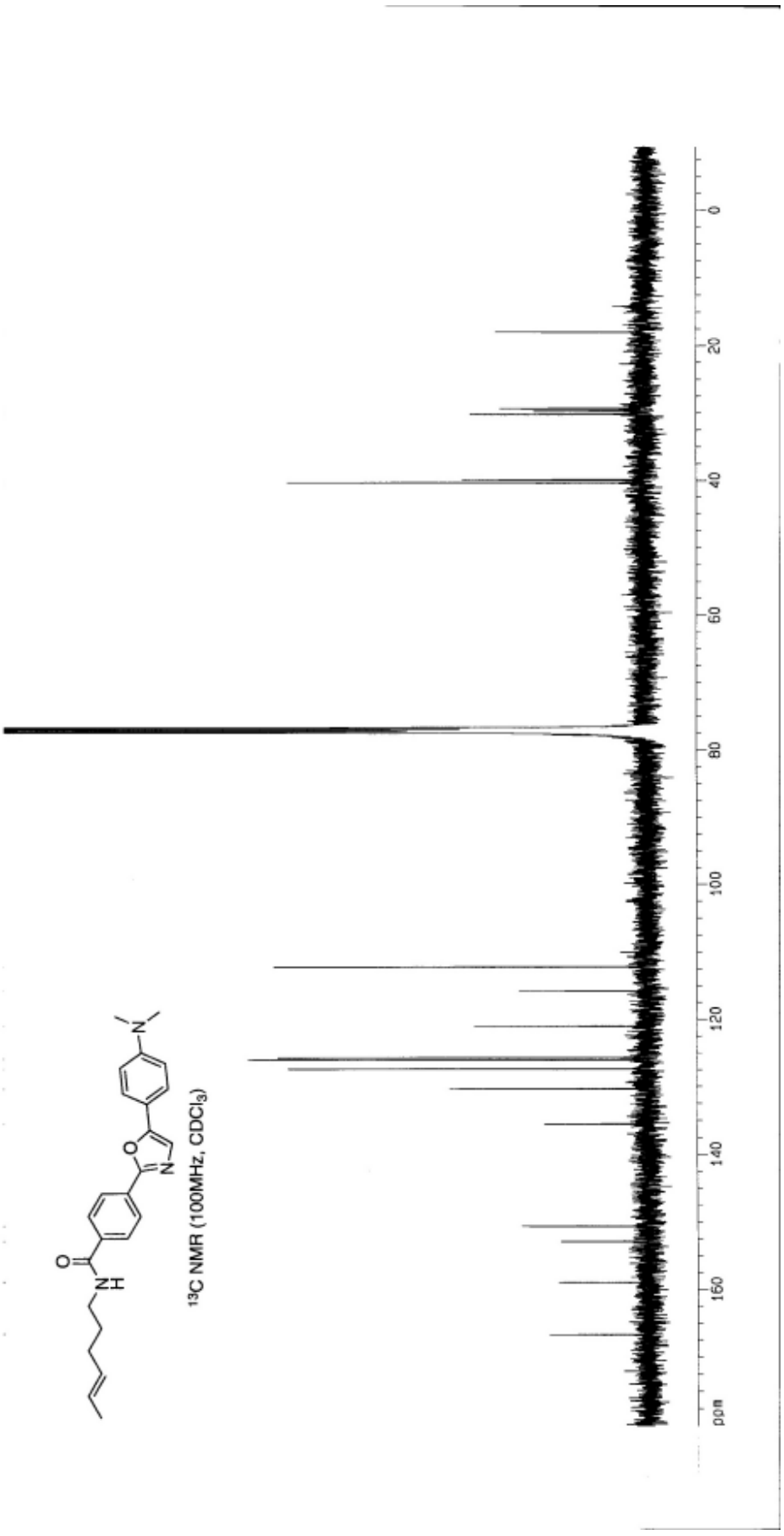
Compound **3**



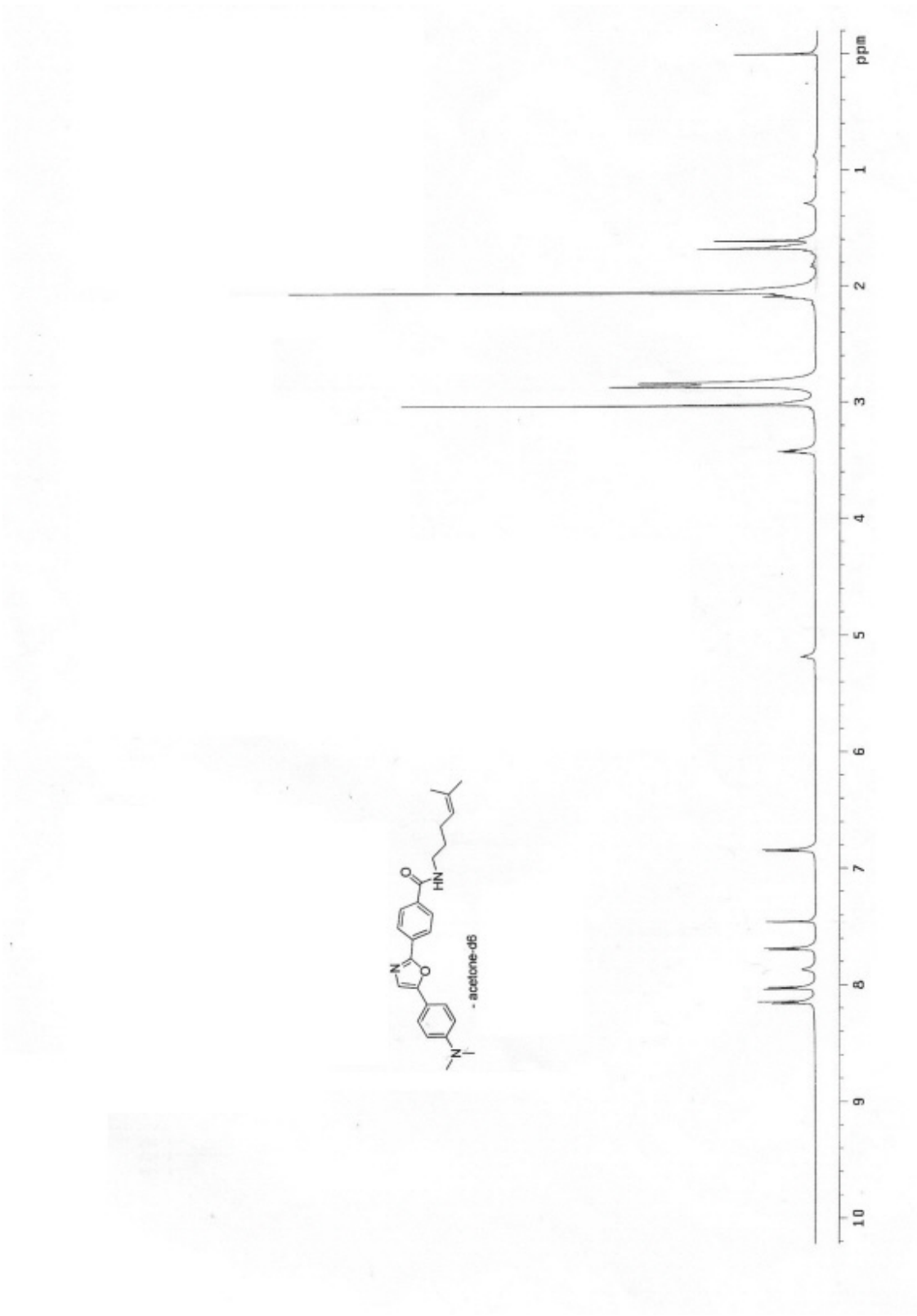
^{13}C NMR (100MHz, $CDCl_3$)
ppm
0
20
40
60
80
100
120
140
160

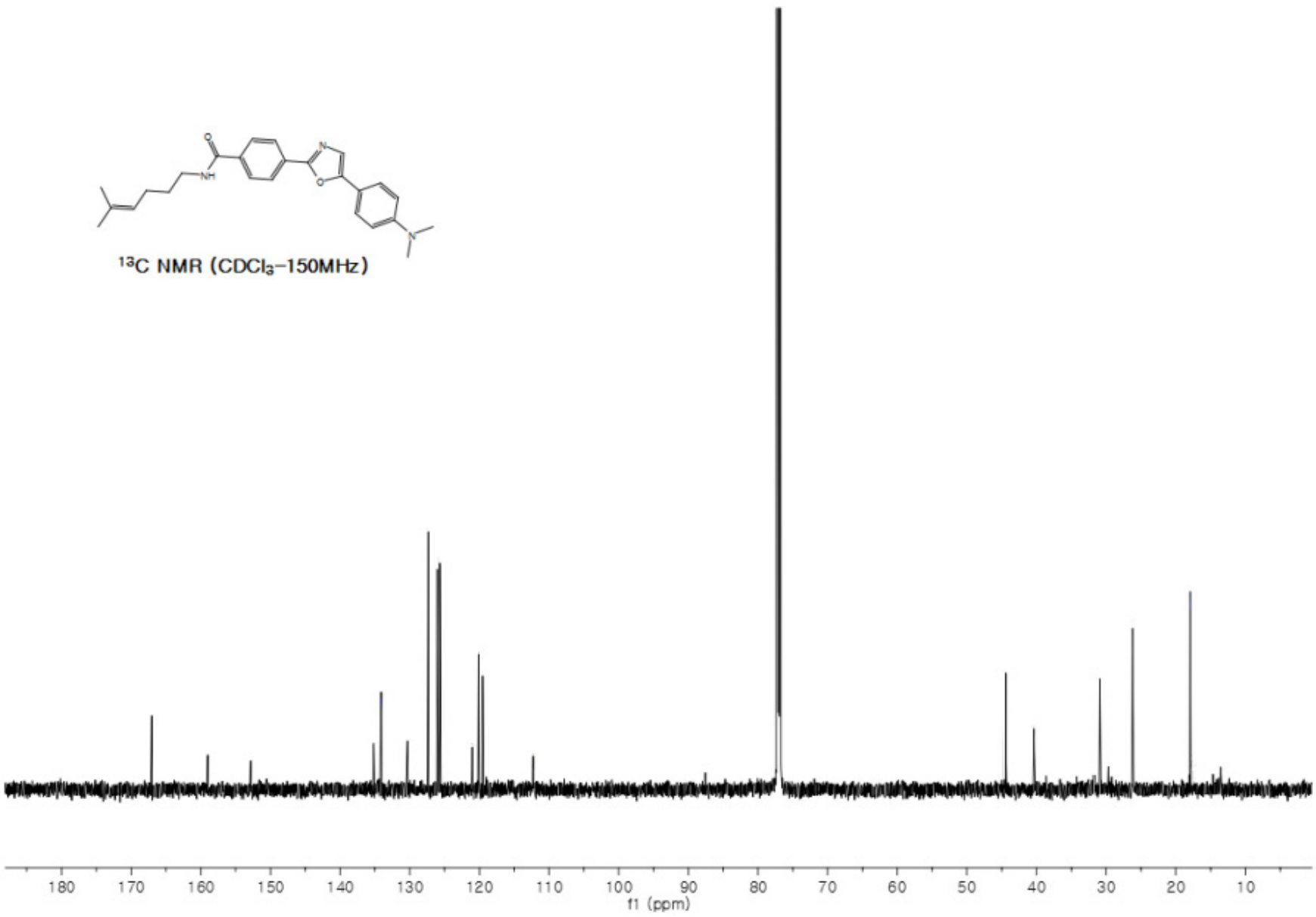
Compound **4**



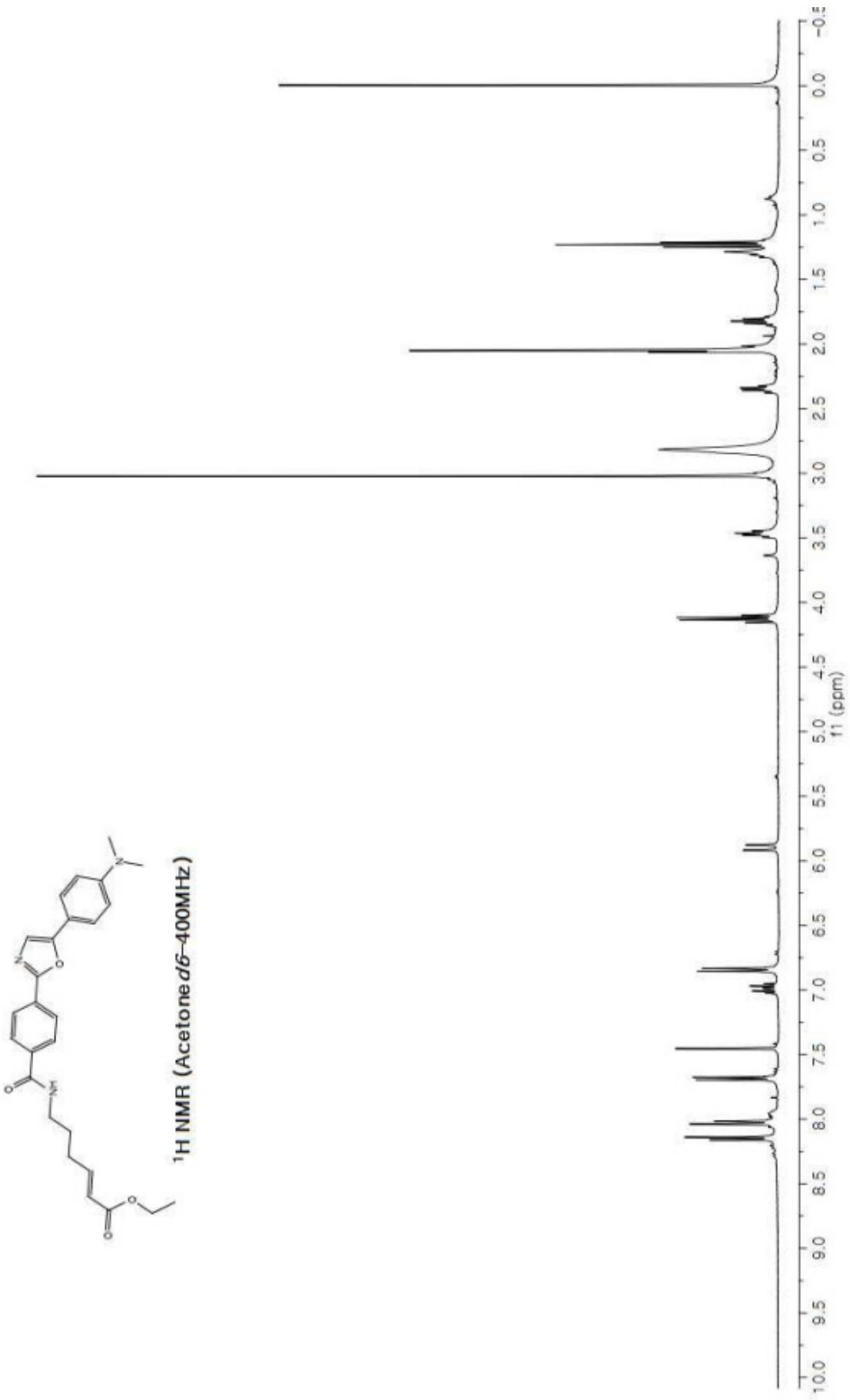

^{13}C NMR (100MHz, $CDCl_3$)
ppm

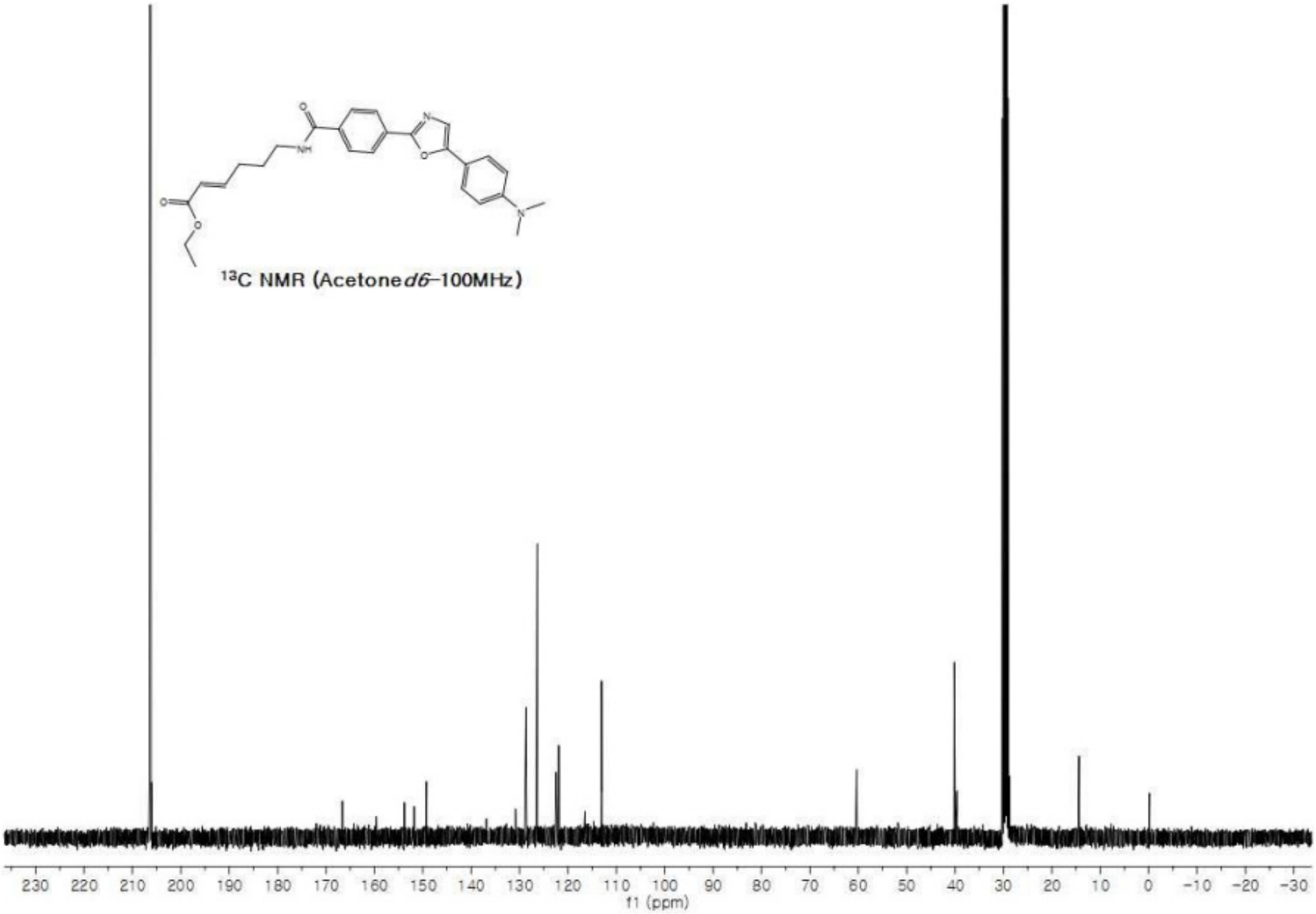
Compound **5**



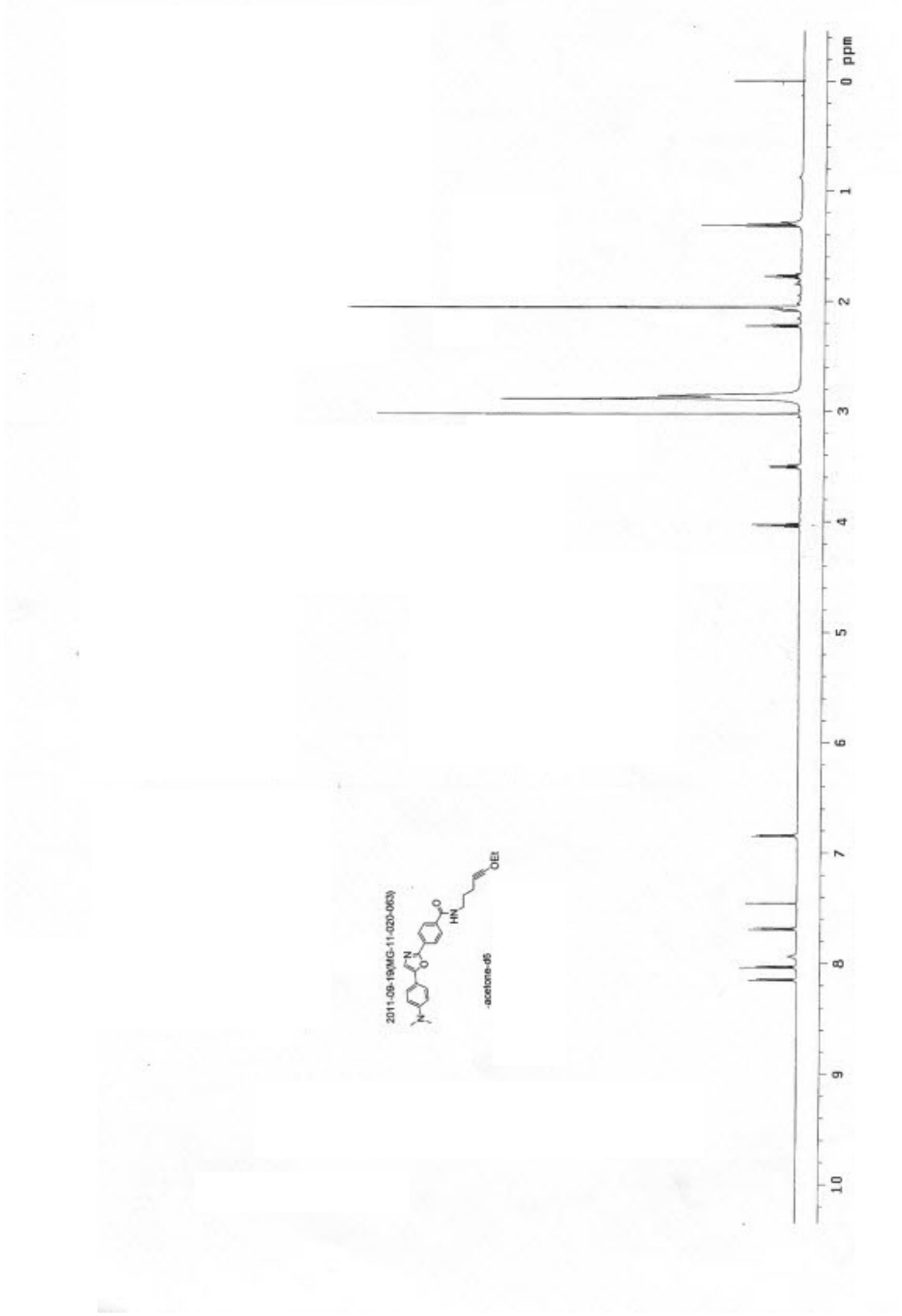

^{13}C NMR ($CDCl_3$–150MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

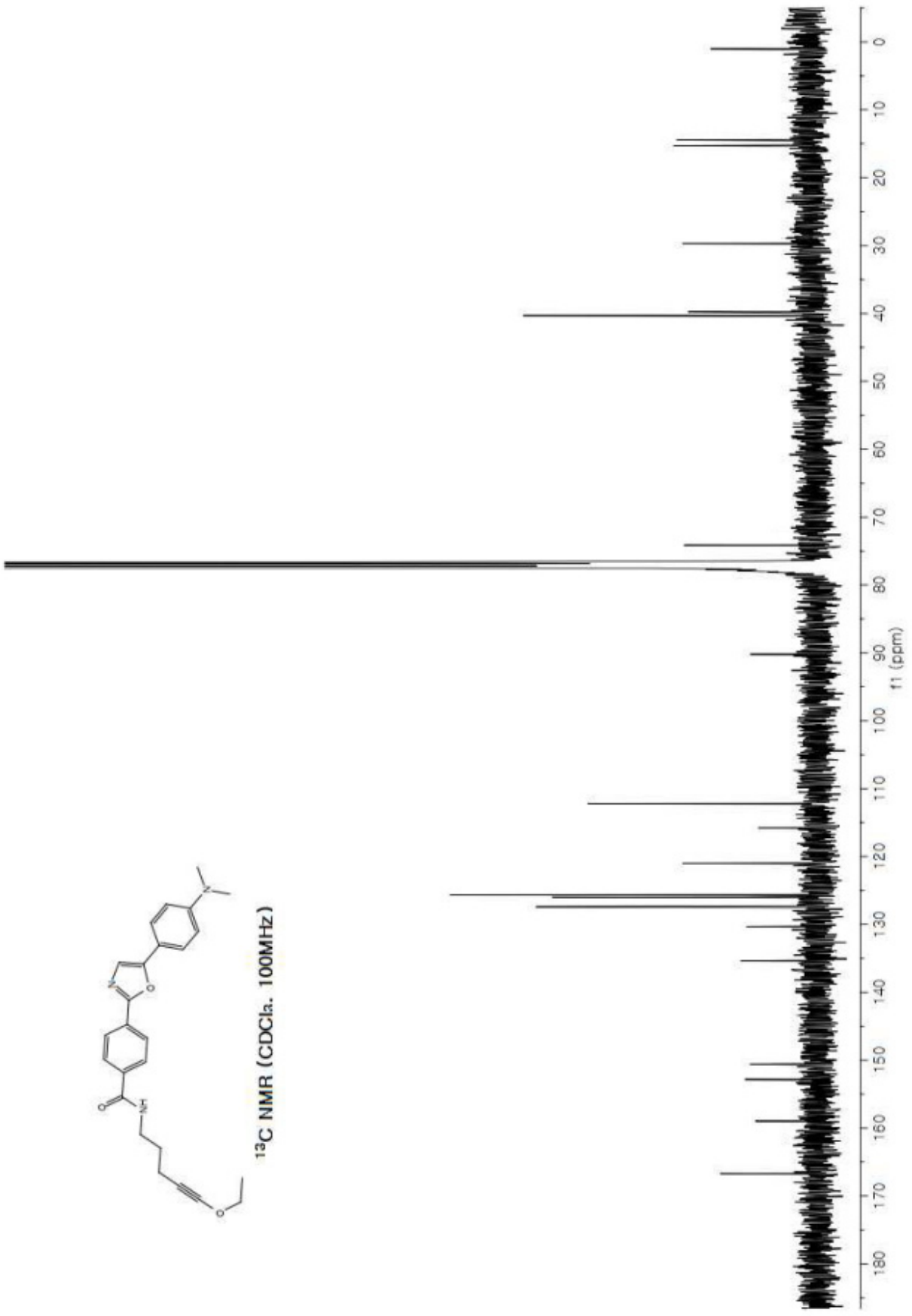
Compound **6**



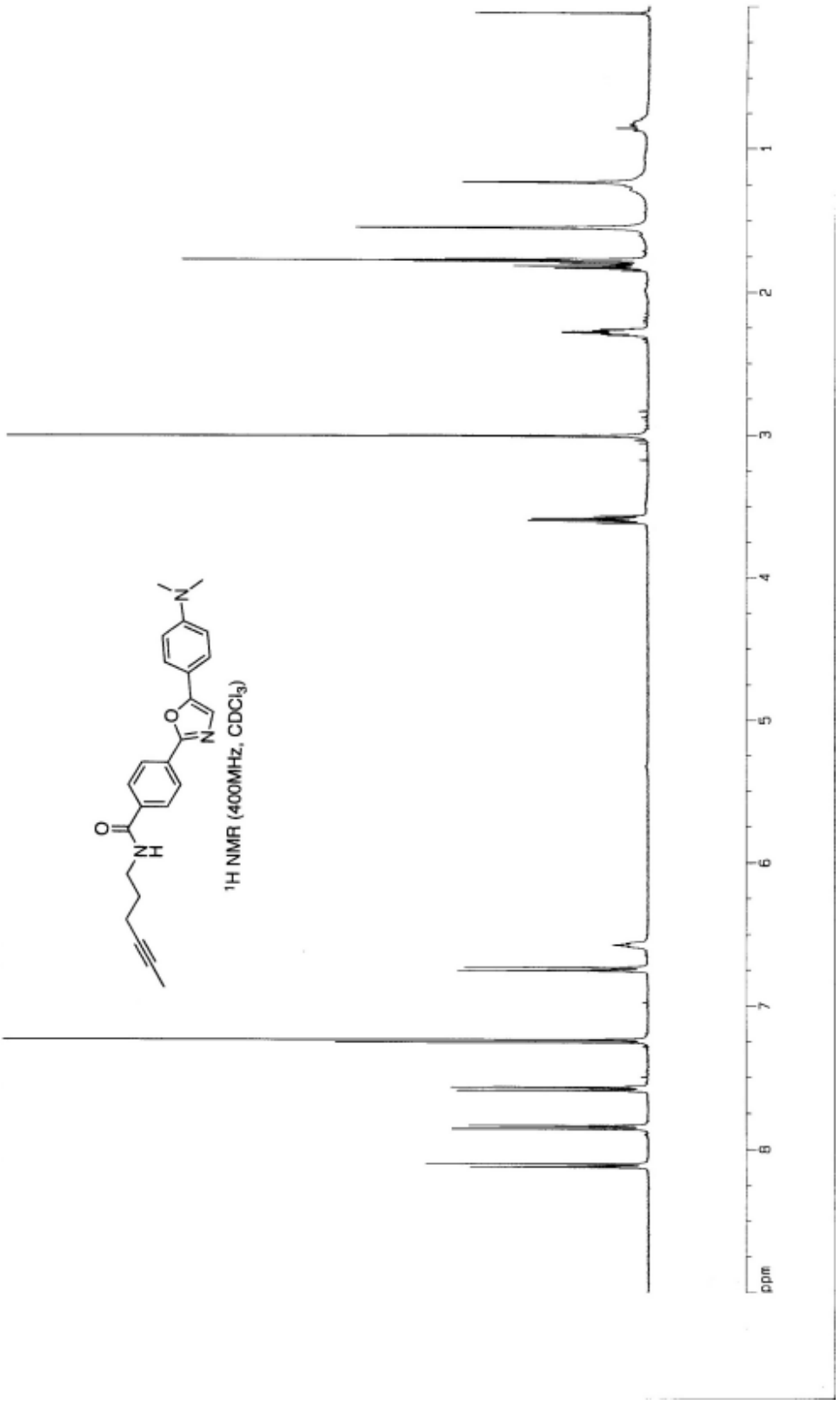

^{13}C NMR (Acetone*d6*–100MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

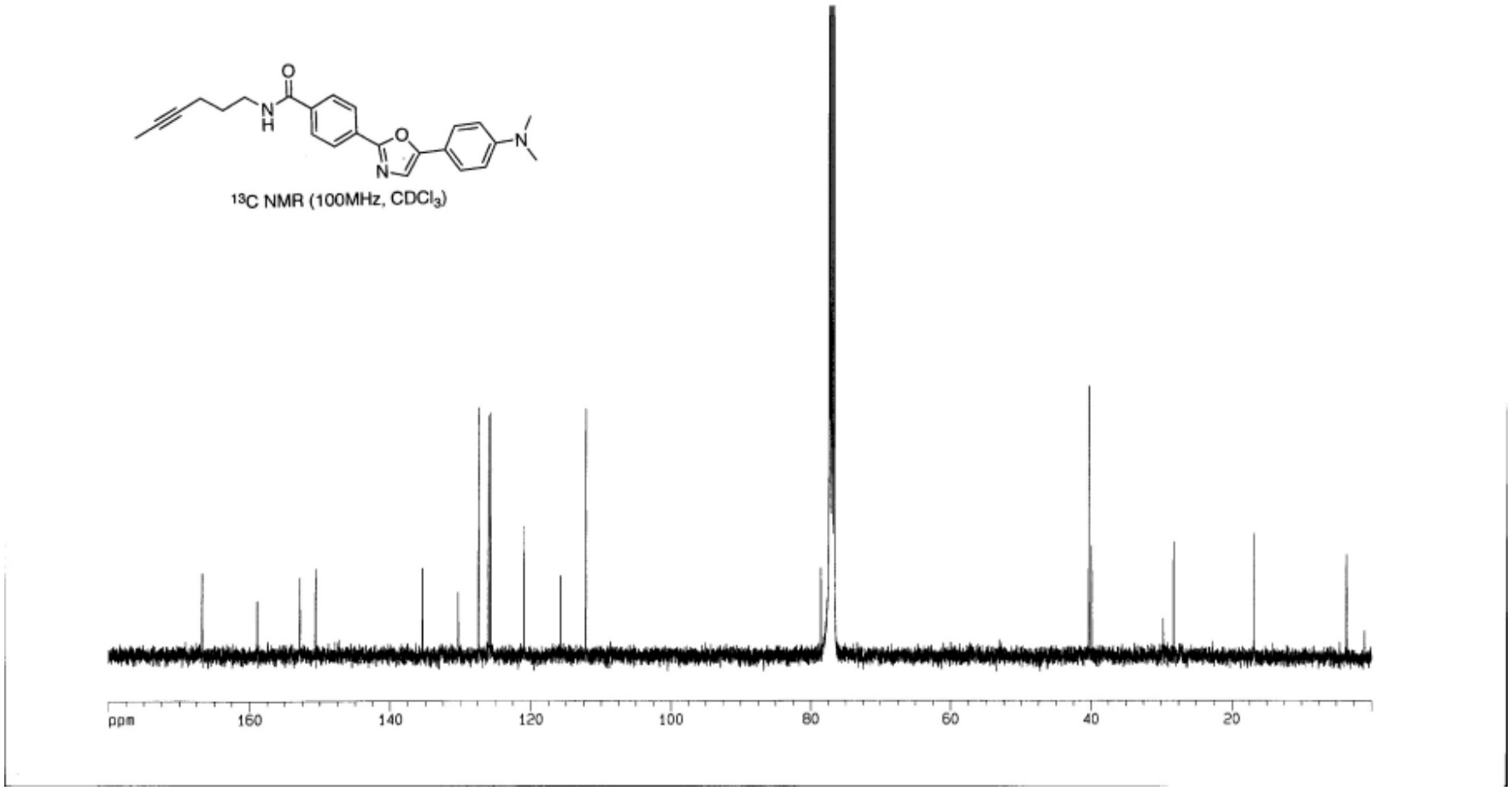
Compound **8**



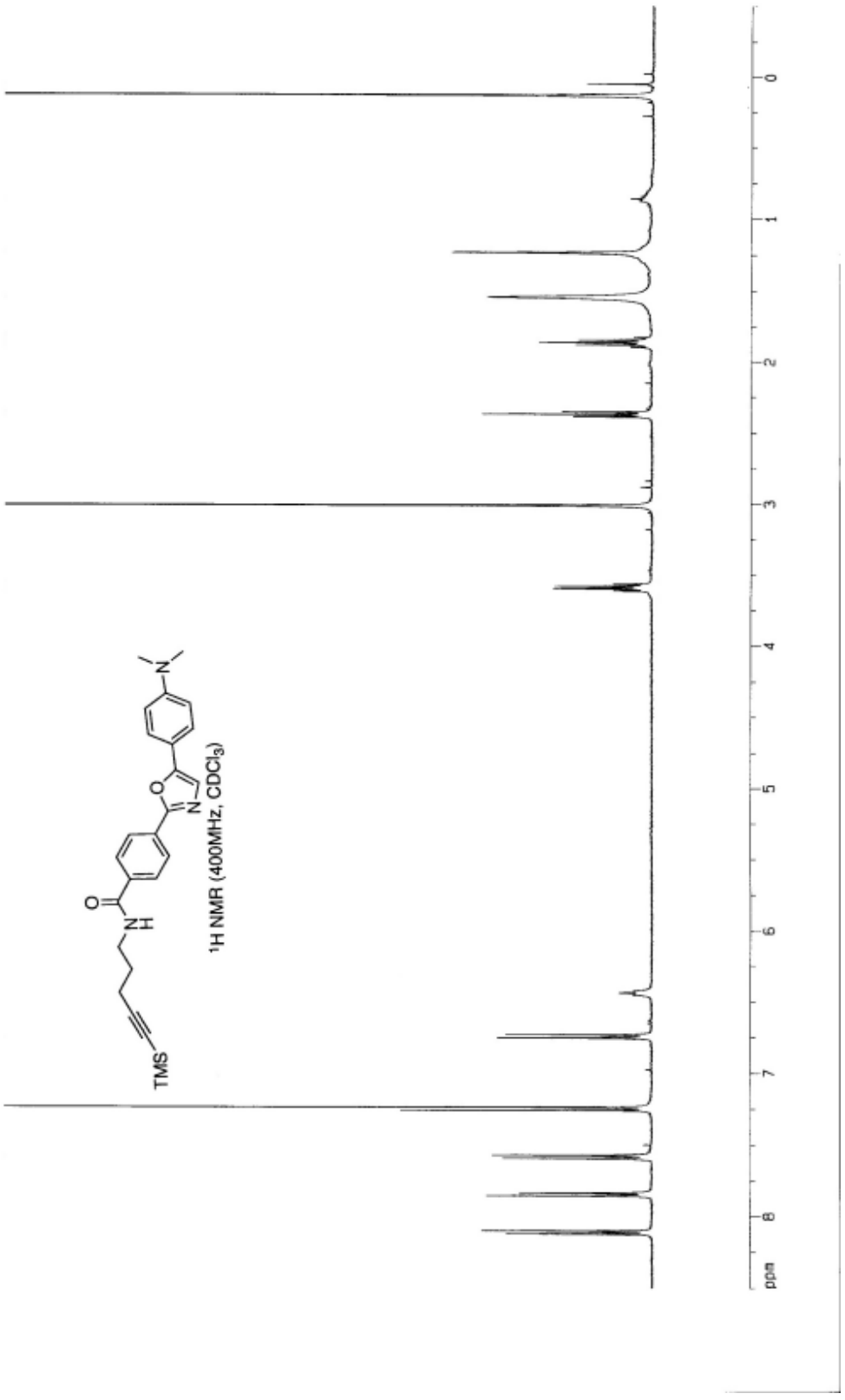

^{13}C NMR (CDCl$_3$, 100MHz)
f1 (ppm)

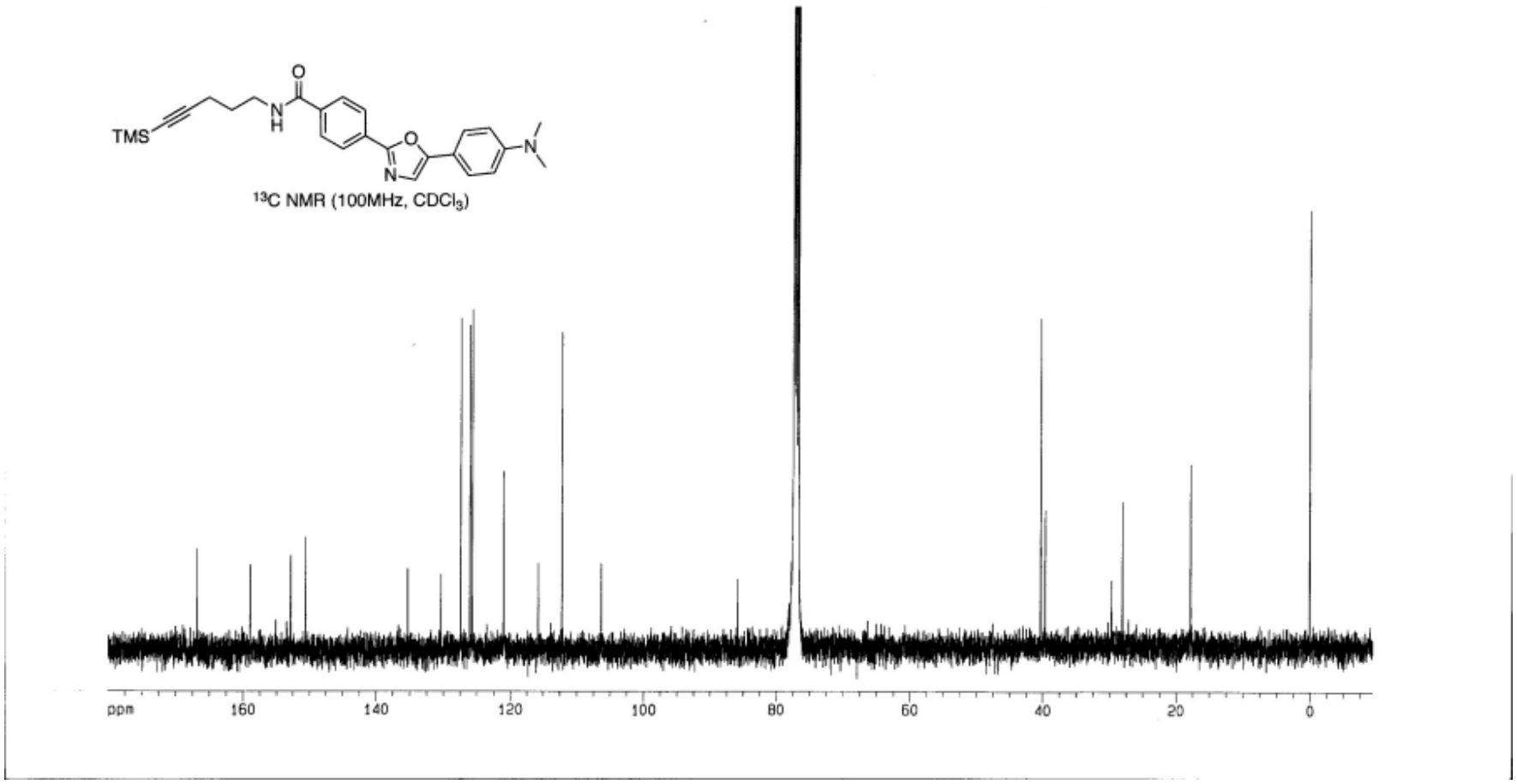
Compound **9**



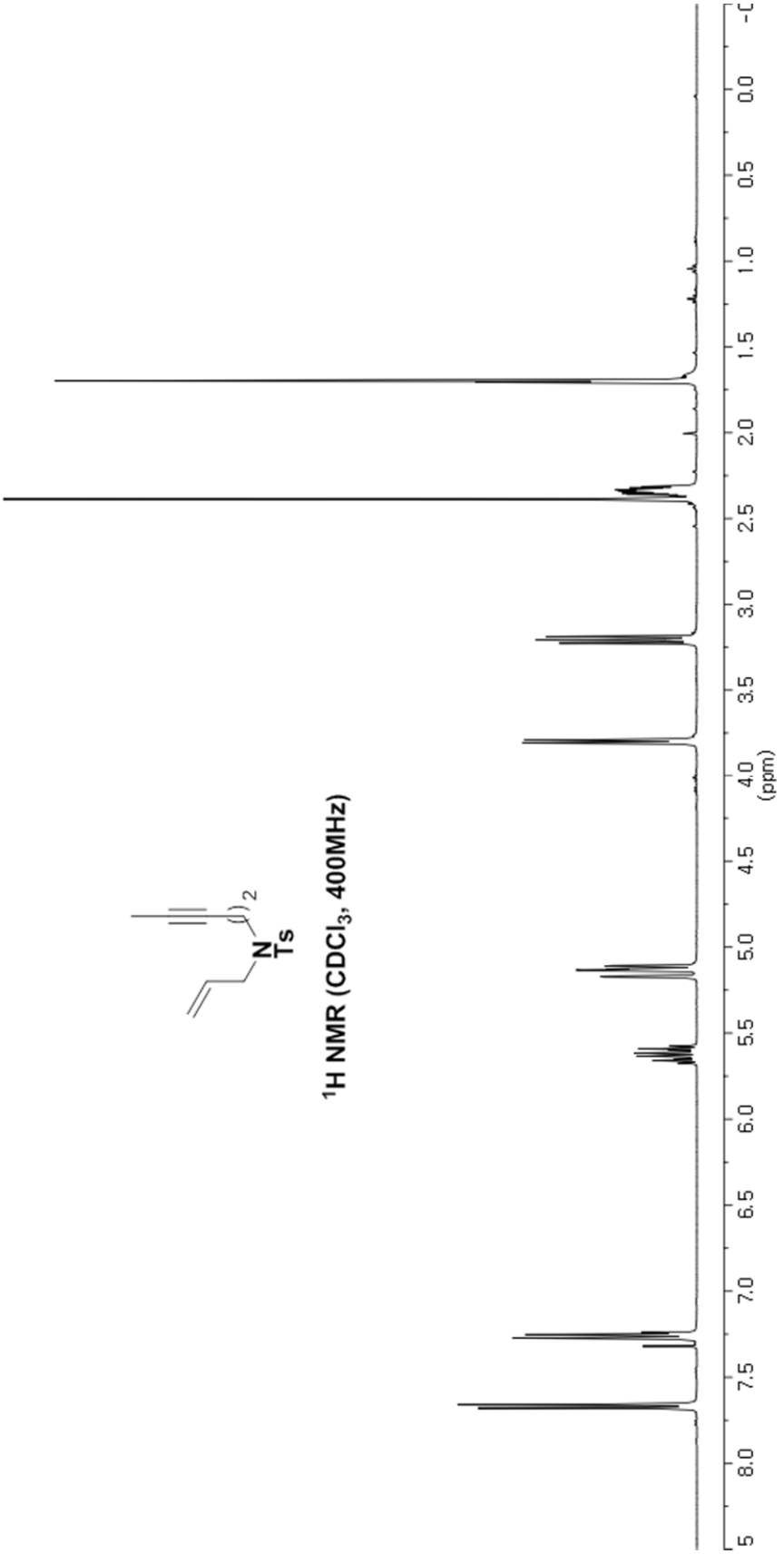

^{13}C NMR (100MHz, $CDCl_3$)
ppm
160
140
120
100
80
60
40
20

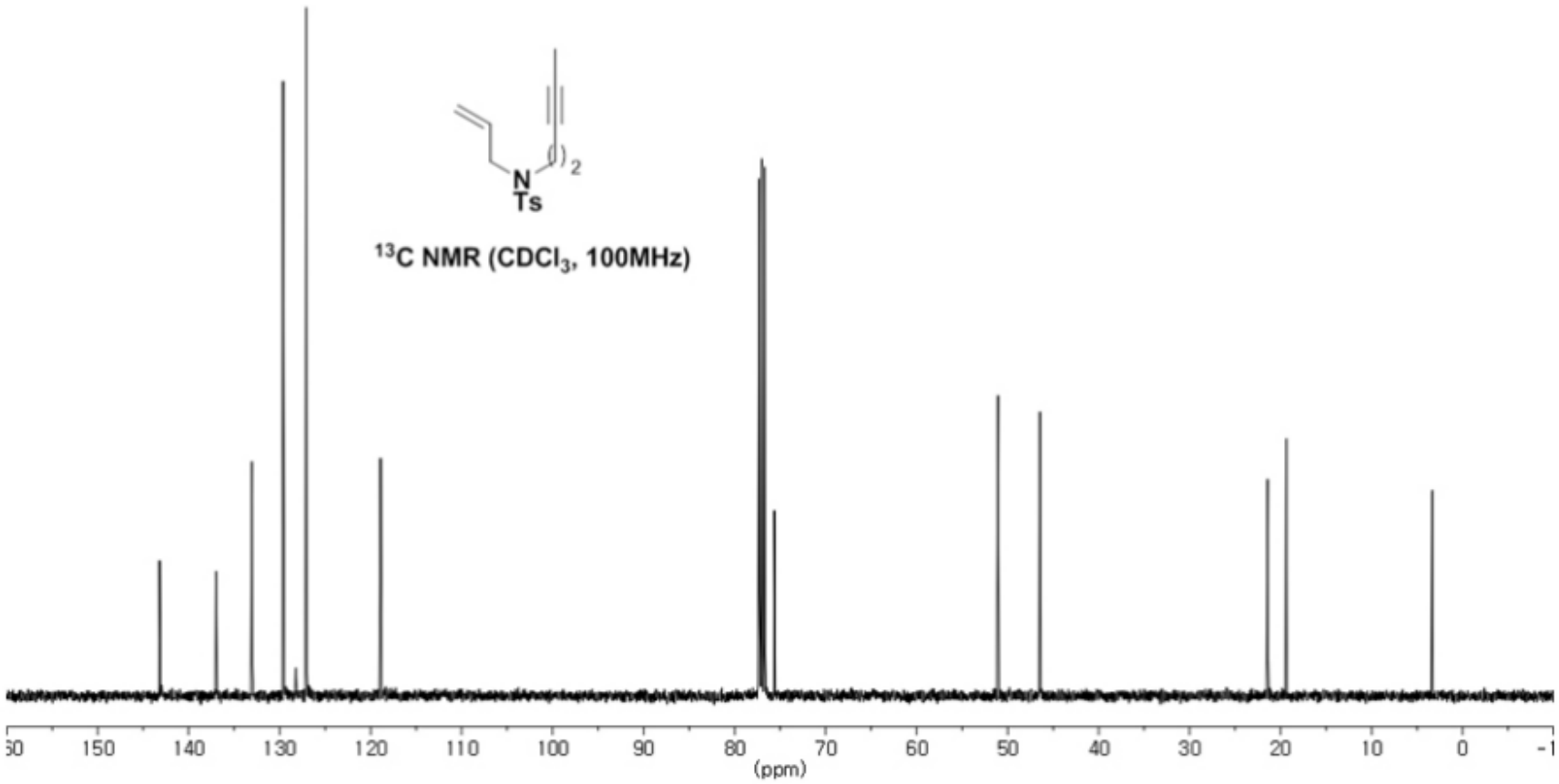
Compound **10**



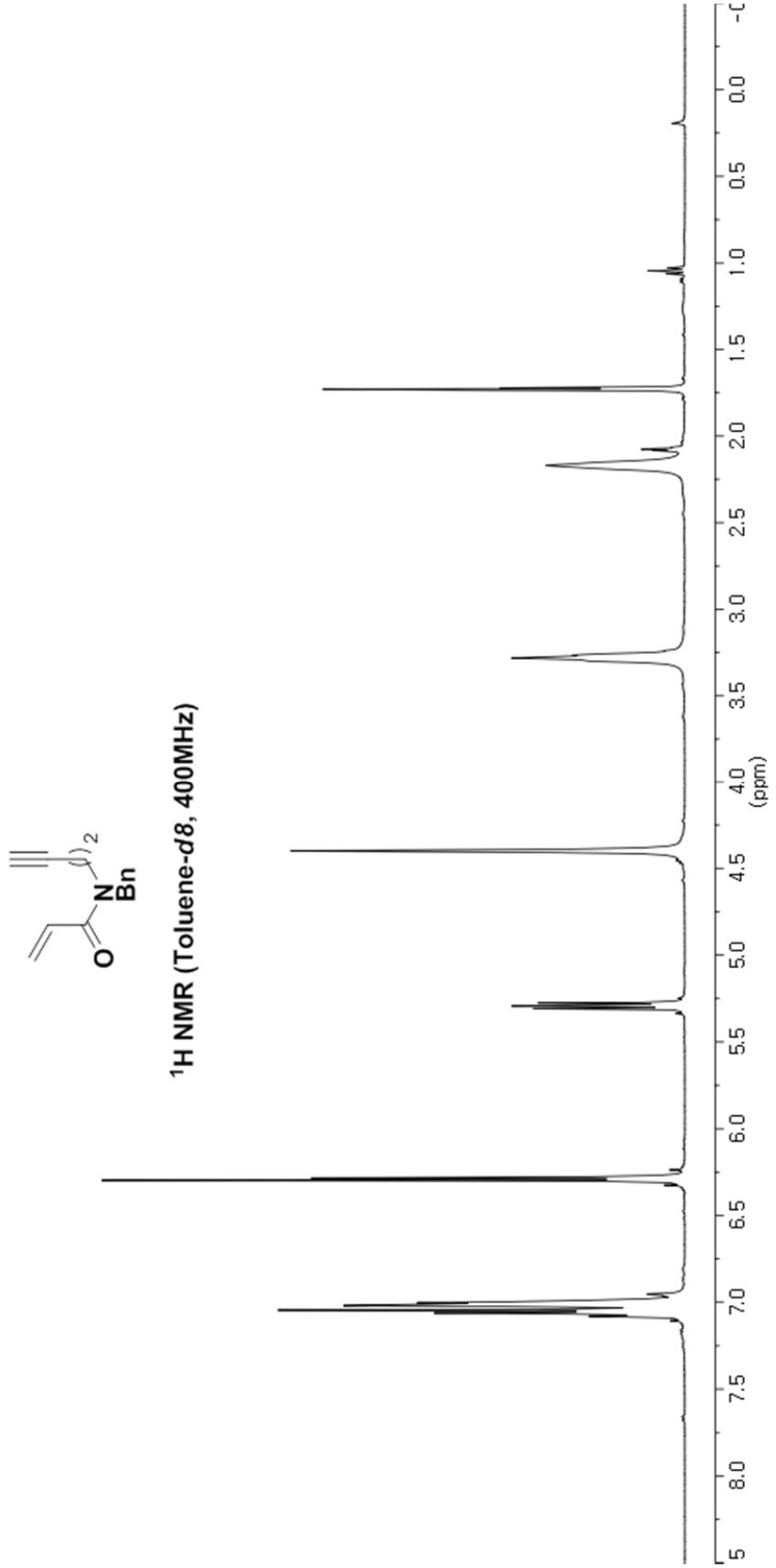

TMS
O
N
H
O
N
N
^{13}C NMR (100MHz, $CDCl_3$)
ppm
160
140
120
100
80
60
40
20
0

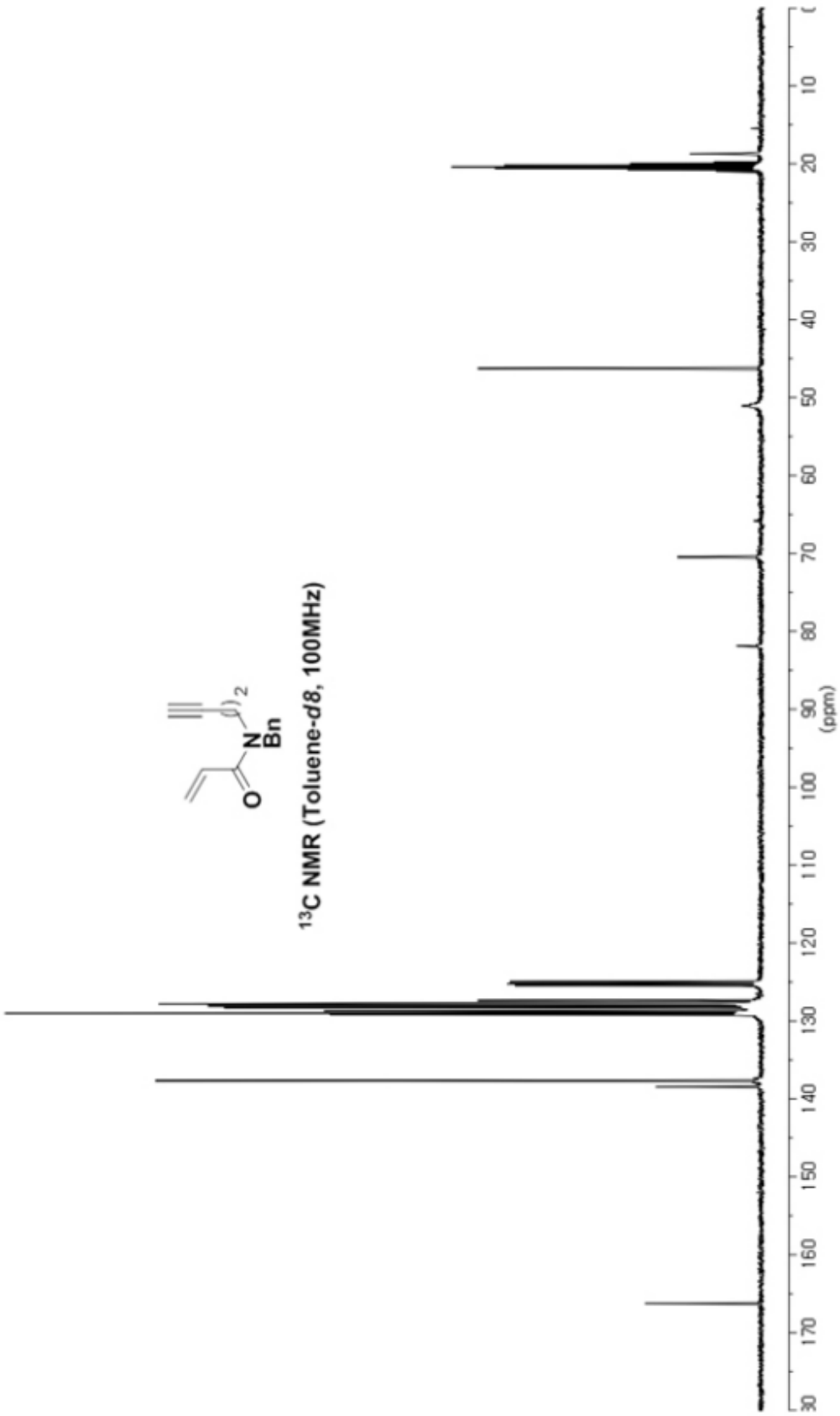
Compound **27**


Ts
N
2
^{1}H NMR ($CDCl_3$, 400MHz)
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
(ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

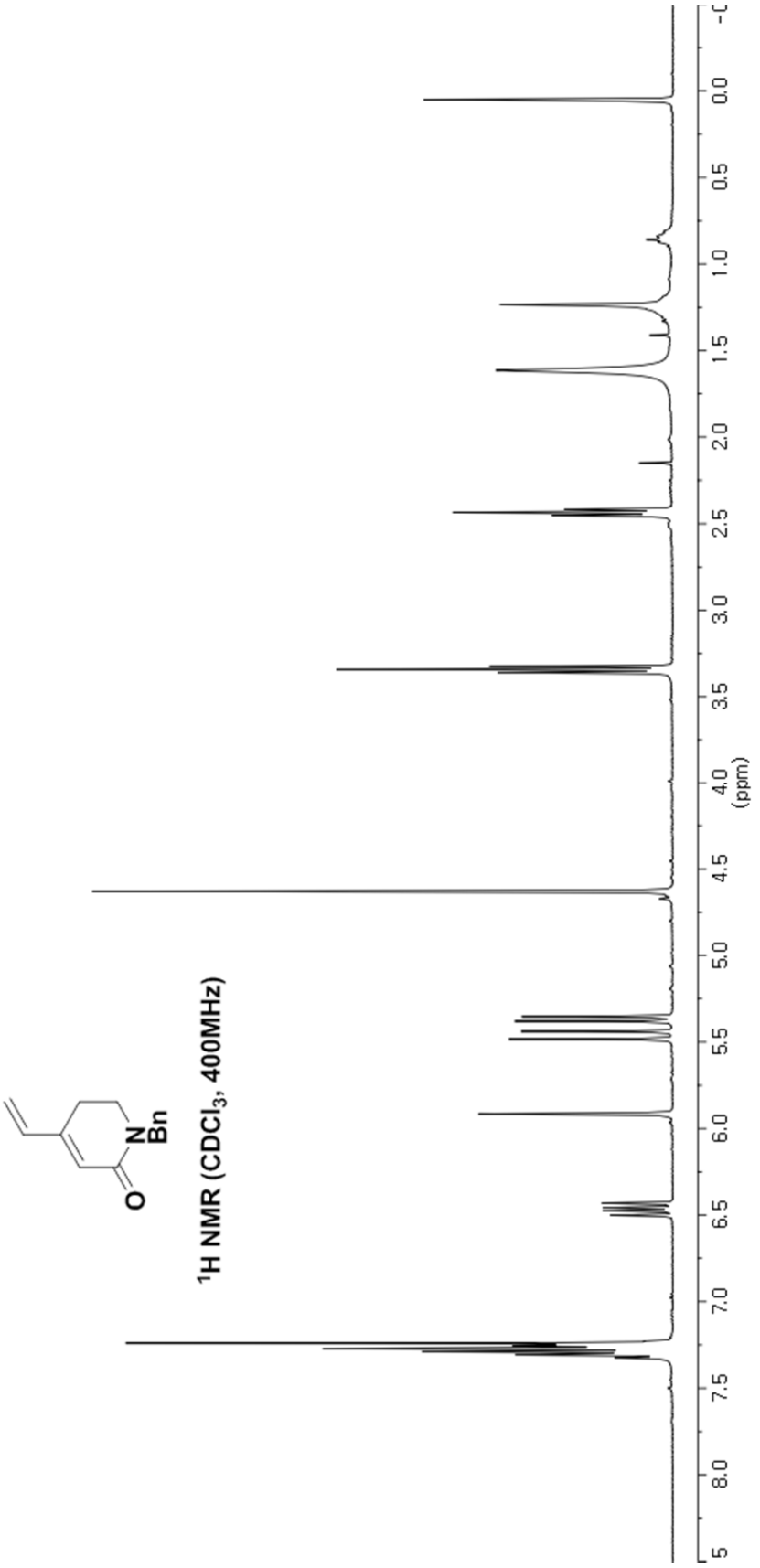

N
Ts
2
^{13}C NMR ($CDCl_3$, 100MHz)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

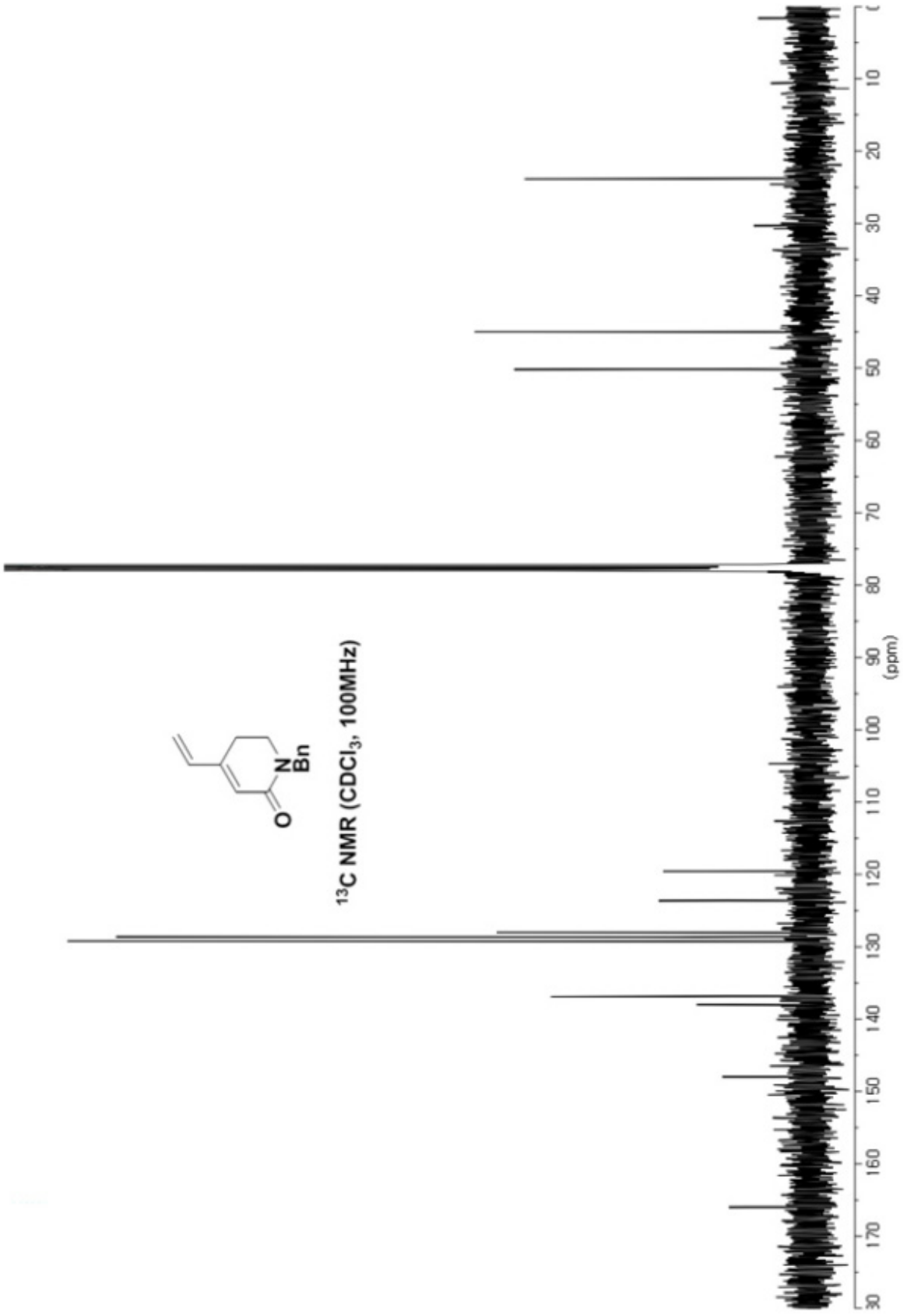
Compound **28**


^{1}H NMR (Toluene-*d8*, 400MHz)
N
Bn
O
2
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

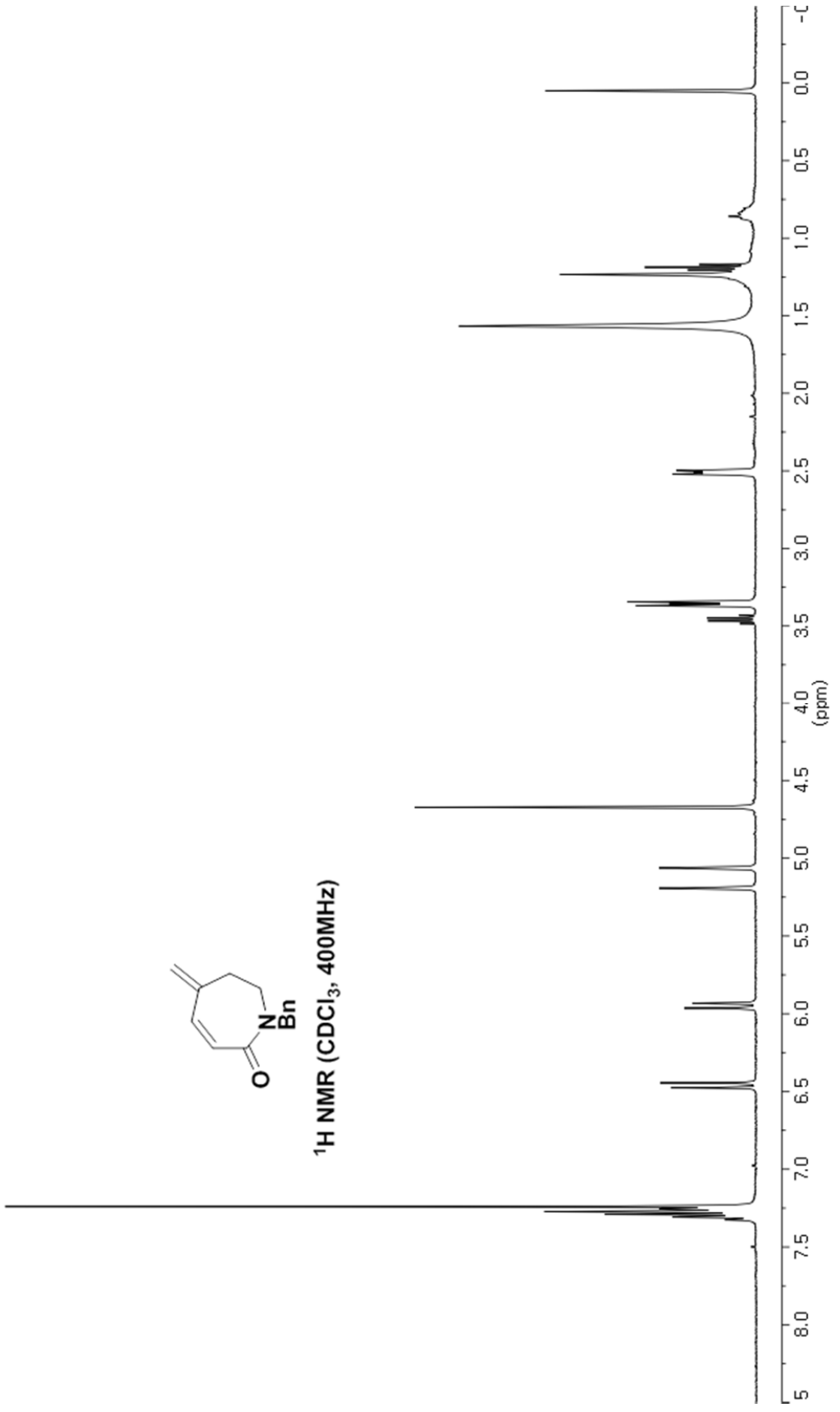

^{13}C NMR (Toluene-*d8*, 100MHz)
N
Bn
O
2
10
20
30
40
50
60
70
80
90
(ppm)
100
110
120
130
140
150
160
170
180

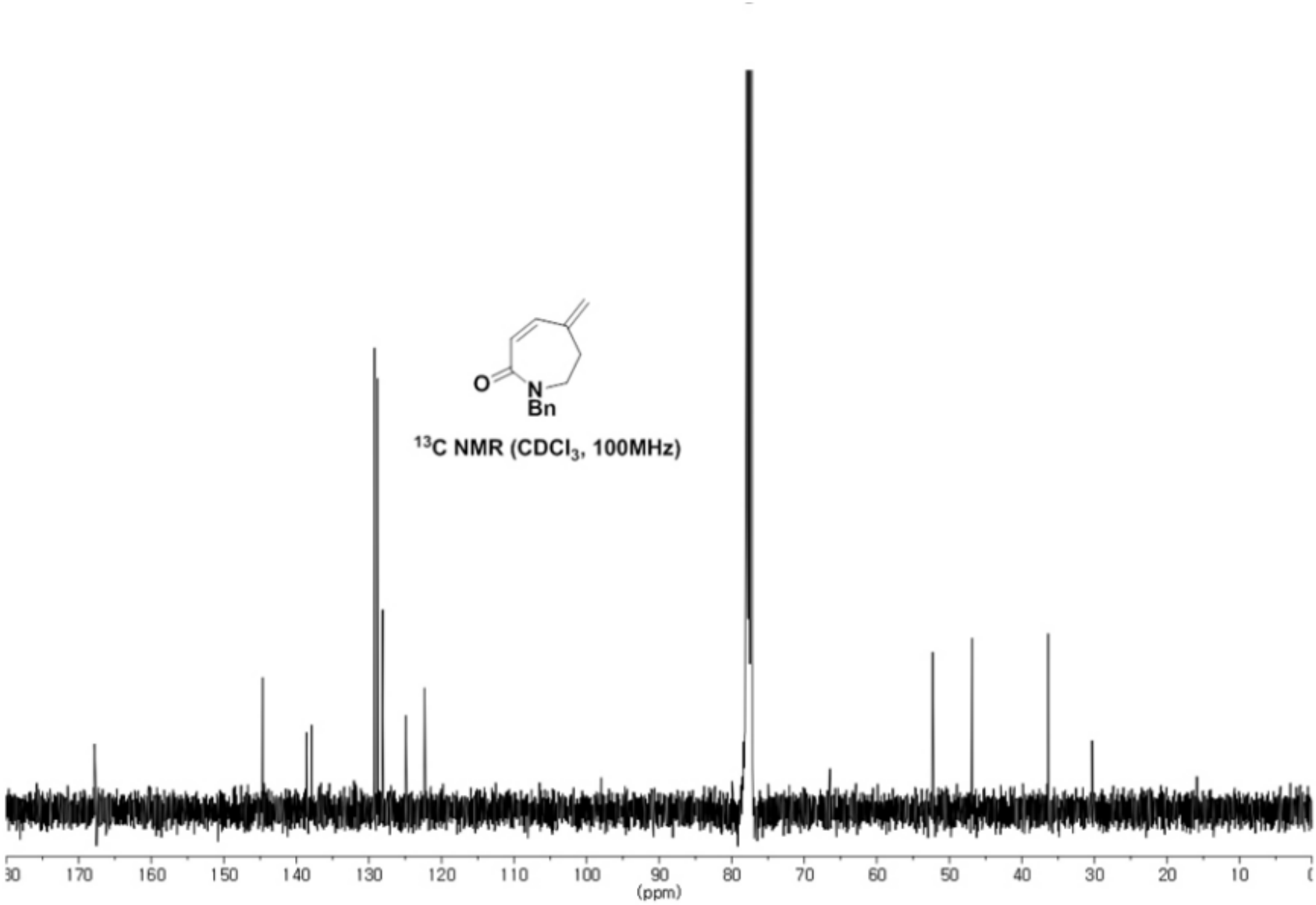
Compound **42**



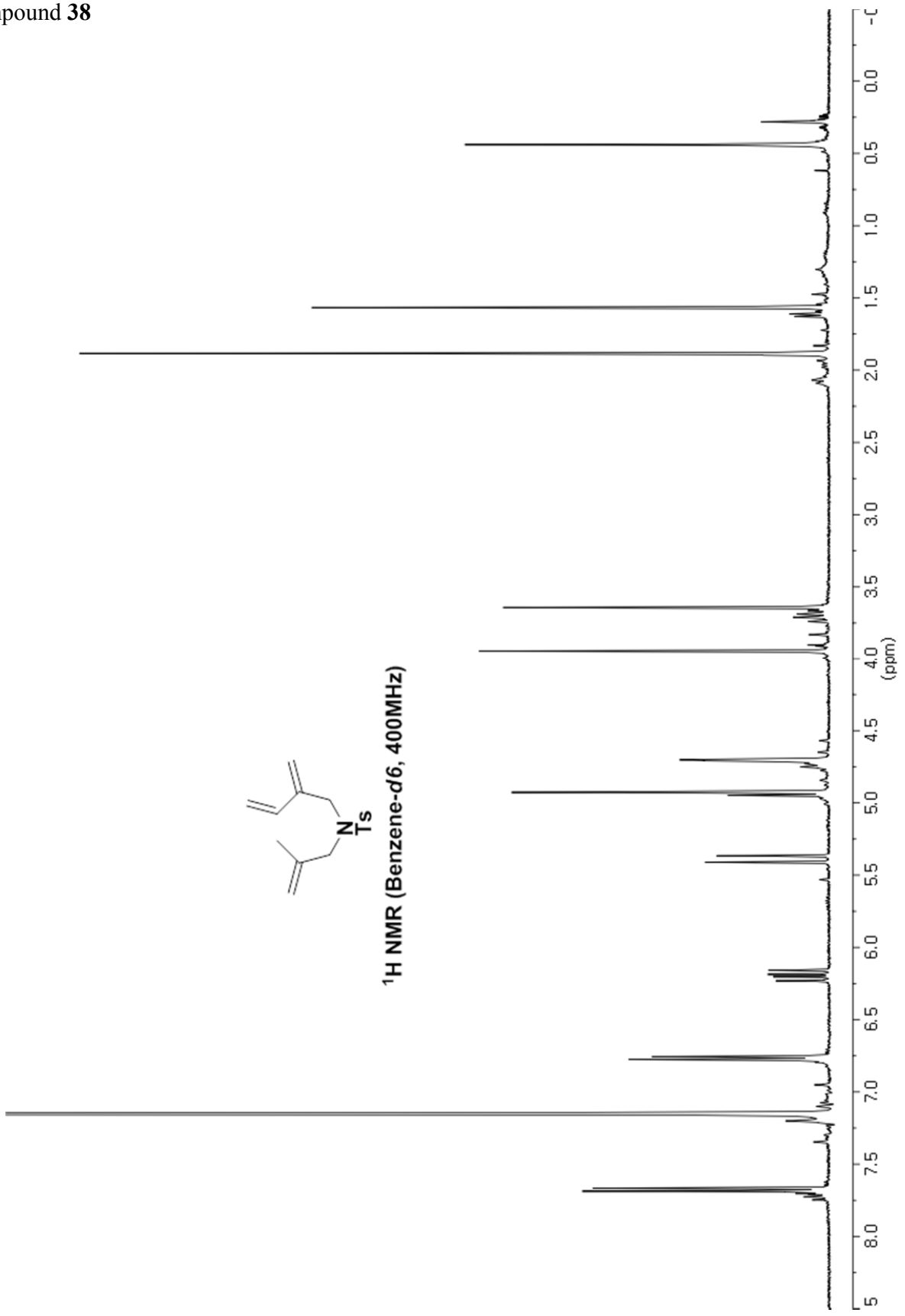

^{13}C NMR ($CDCl_3$, 100MHz)
N
Bn
O
(ppm)

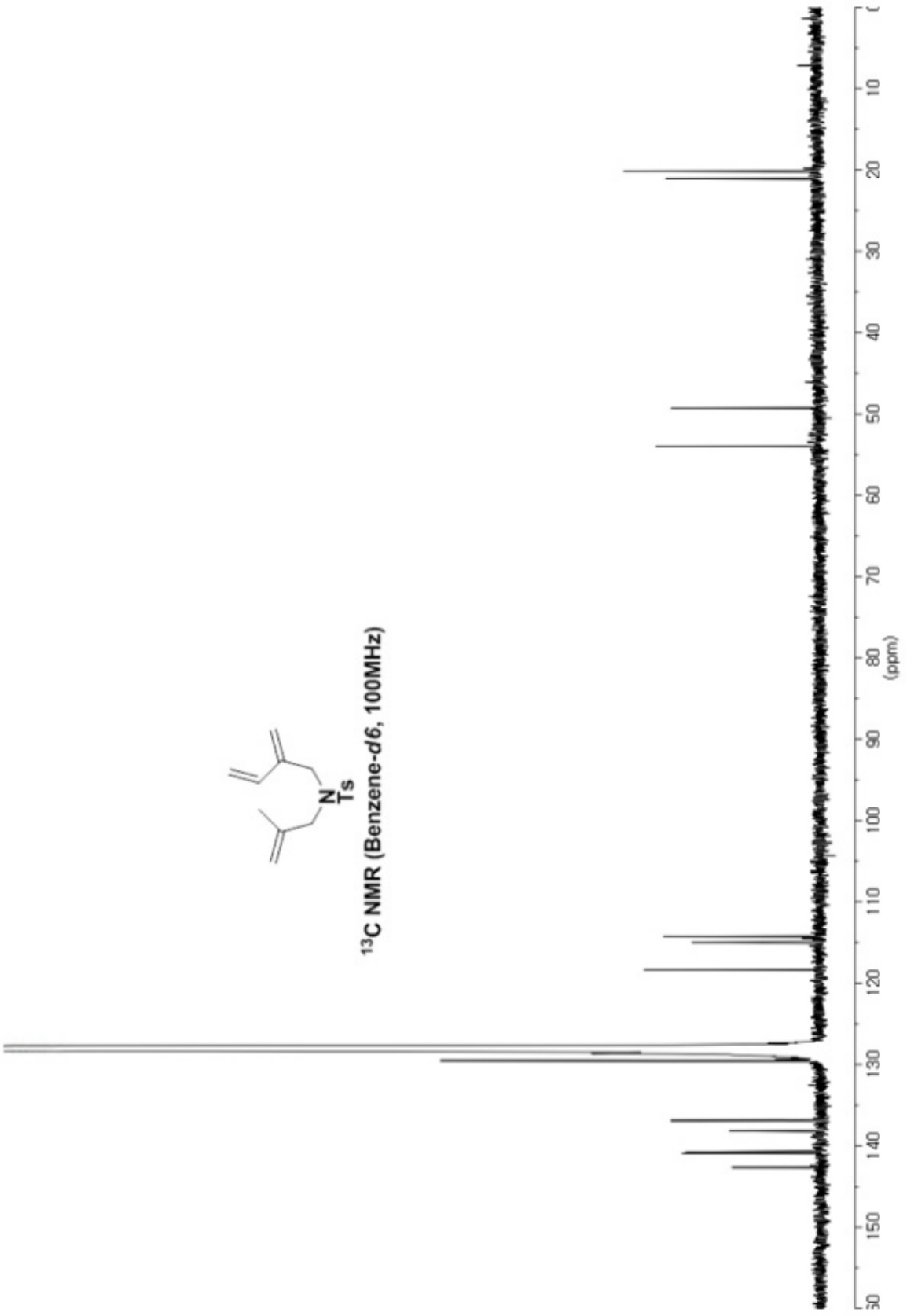
Compound **43**


N
Bn
O
^{1}H NMR ($CDCl_3$, 400MHz)
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
(ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

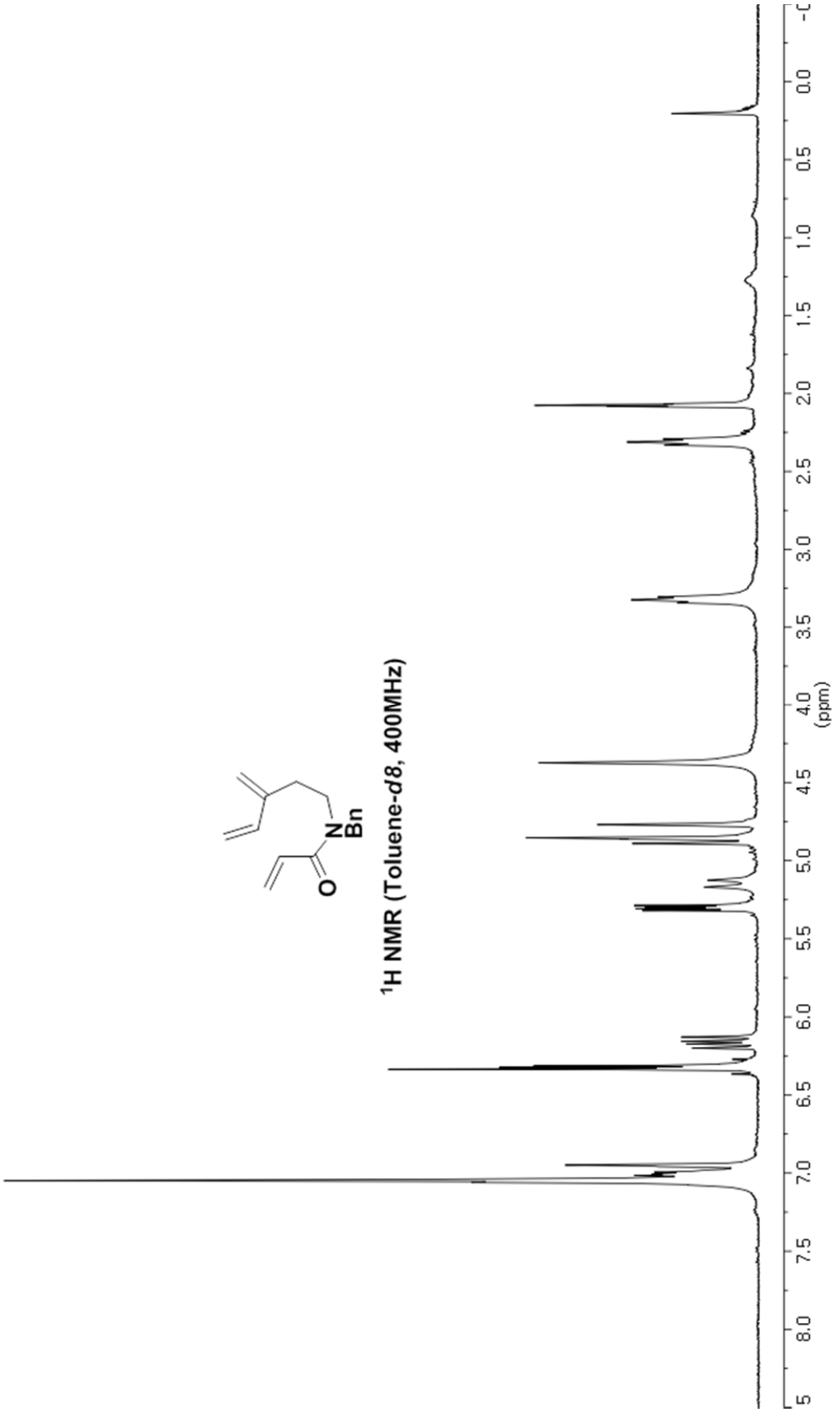

O
N
Bn
13C NMR (CDCl3, 100MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

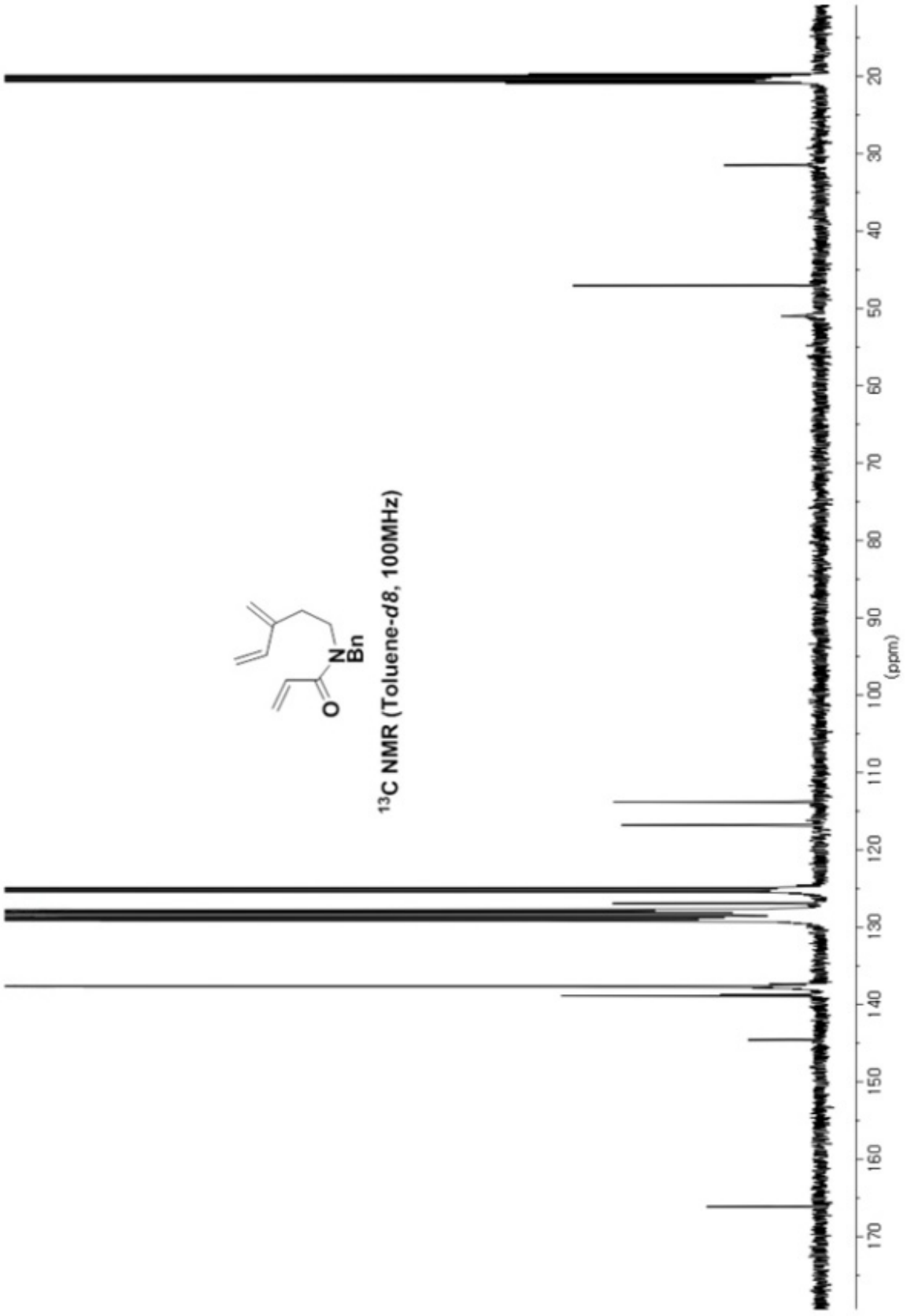
Compound **38**




^{13}C NMR (Benzene-*d6*, 100MHz)
N
Ts
(ppm)

Compound **44**


N
Bn
O
^{1}H NMR (Toluene-*d8*, 400MHz)
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
(ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


^{13}C NMR (Toluene-*d8*, 100MHz)
N
Bn
O
(ppm)

7. References

1. Sohn, J. –H.; Kim, K. H.; Lee, H. –Y.; No, Z. S.; Ihee, H. *J. Am. Chem. Soc.* **2008**, *130*, 16506-16507.

2. Kim, K. H.; Ok, T.; Lee, K.; Lee, H. –S.; Chang, K. T.; Ihee, H.; Sohn, J. –H. *J. Am. Chem. Soc.* **2010**, *132*, 12027-12033.

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