

Determination of the photoisomerization quantum yield of a hydrazone photoswitch

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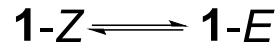
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1. A user guide to choose an appropriate procedure for determining the photoisomerization quantum yield of a bistable switch

Here we consider a bistable photoswitch **1** that shows a reversible photoswitching between **1-Z** and **1-E**. We assume that thermal relaxation of the metastable isomer, **1-E**, is very slow at room temperature.



In the reversible photoswitching between **1-Z** and **1-E**, the differential rate for the concentration of **1-Z** can be expressed as:^{S1}

$$VdC_Z = -\phi_{Z \rightarrow E}dn_{p,Z} + \phi_{E \rightarrow Z}dn_{p,E} \quad \text{Eq. 1}$$

where V is the sample volume; C_Z is the concentration of **1-Z**; $\phi_{Z \rightarrow E}$ and $\phi_{E \rightarrow Z}$ are the quantum yields for Z -to- E and E -to- Z photoisomerization processes, respectively; $n_{p,Z}$ and $n_{p,E}$ are the numbers of photons absorbed by **1-Z** and **1-E**, respectively.

The differential amounts of photons absorbed by **1-Z** and **1-E** during irradiation time dt are defined as:

$$dn_{p,Z} = I\varepsilon_Z^{irr}C_Z^t l \cdot \frac{1 - 10^{-A^{irr,t}}}{A^{irr,t}} dt = I\varepsilon_Z^{irr}C_Z^t l F(t) dt \quad \text{Eq. 2}$$

$$dn_{p,E} = I\varepsilon_E^{irr}C_E^t l F(t) dt \quad \text{Eq. 3}$$

where I is the molar photon flux; $A^{irr,t}$ is the absorbance of the isomeric mixture at the irradiation wavelength at time t ; ε_Z^{irr} and ε_E^{irr} are the molar extinction coefficients of **1-Z** and **1-E** at the irradiation wavelength, respectively; l is the optical path length; $F(t)$ stands for the photokinetic factor that is defined as:

$$F(t) = \frac{1 - 10^{-A^{irr,t}}}{A^{irr,t}} \quad \text{Eq. 4}$$

Therefore, Eq. 1 can be rearranged as below:

$$\frac{dC_Z^t}{dt} = \frac{-IlF(t)}{V} (\phi_{Z \rightarrow E}\varepsilon_Z^{irr}C_Z^t - \phi_{E \rightarrow Z}\varepsilon_E^{irr}C_E^t) \quad \text{Eq. 5}$$

By defining C_{tot} as the total concentration of the isomeric mixture ($C_{tot} = C_Z^t + C_E^t$), Eq. 5 can be rearranged to Eq. 6.

$$\frac{dC_Z^t}{dt} = \frac{-IlF(t)}{V} \{(\phi_{Z \rightarrow E}\varepsilon_Z^{irr} + \phi_{E \rightarrow Z}\varepsilon_E^{irr})C_Z^t - \phi_{E \rightarrow Z}\varepsilon_E^{irr}C_{tot}\} \quad \text{Eq. 6}$$

Pseudo quantum yield Q is defined as:

$$Q = \phi_{Z \rightarrow E}\varepsilon_Z^{irr} + \phi_{E \rightarrow Z}\varepsilon_E^{irr} \quad \text{Eq. 7}$$

Then Eq. 6 can be rewritten to:

$$\frac{dC_Z^t}{dt} = \frac{-IlF(t)}{V} (QC_Z^t - \phi_{E \rightarrow Z}\varepsilon_E^{irr}C_{tot}) \quad \text{Eq. 8}$$

When the photoisomerization process reaches the photostationary state (PSS) at $t = \infty$, there is no change in the concentration of 1-Z

$$\begin{aligned}\frac{dC_Z^\infty}{dt} &= 0 = \frac{-IlF(\infty)}{V}(QC_Z^\infty - \phi_{E \rightarrow Z}\varepsilon_E^{irr}C_{tot}) \\ QC_Z^\infty &= \phi_{E \rightarrow Z}\varepsilon_E^{irr}C_{tot}\end{aligned}\quad \text{Eq. 9}$$

Therefore, Eq. 8 can be rewritten to:

$$\begin{aligned}\frac{dC_Z^t}{dt} &= \frac{-IlF(t)Q}{V}(C_Z^t - C_Z^\infty) \\ \frac{dC_Z^t}{(C_Z^t - C_Z^\infty)} &= \frac{-IlF(t)Q}{V}dt\end{aligned}\quad \text{Eq. 10}$$

Integrating Eq. 10 from time t_1 to t_2 gives:

$$\begin{aligned}\ln \left[\frac{C_Z^{t_1} - C_Z^\infty}{C_Z^{t_2} - C_Z^\infty} \right] &= \frac{IlQ}{V} \int_{t_1}^{t_2} F(t)dt \\ \therefore Q &= \frac{V}{Il \int_{t_1}^{t_2} F(t)dt} \ln \left[\frac{C_Z^{t_1} - C_Z^\infty}{C_Z^{t_2} - C_Z^\infty} \right]\end{aligned}\quad \text{Eq. 11}$$

The absorbance of mixture at the observed wavelength at time t , $A^{obs,t}$, is defined as:

$$A^{obs,t} = (\varepsilon_Z^{obs}C_Z^t + \varepsilon_E^{obs}C_E^t)l = \{(\varepsilon_Z^{obs} - \varepsilon_E^{obs})C_Z^t + \varepsilon_E^{obs}C_{tot}\}l \quad \text{Eq. 12}$$

where ε_Z^{obs} and ε_E^{obs} are the molar extinction coefficients of 1-Z and 1-E at the observed wavelength, respectively. Accordingly, the absorbance of mixture at the observed wavelength at PSS is given as below:

$$A^{obs,\infty} = \{(\varepsilon_Z^{obs} - \varepsilon_E^{obs})C_Z^\infty + \varepsilon_E^{obs}C_{tot}\}l \quad \text{Eq. 13}$$

Subtracting Eq. 13 from Eq. 12 gives:

$$A^{obs,t} - A^{obs,\infty} = (\varepsilon_Z^{obs} - \varepsilon_E^{obs})(C_Z^t - C_Z^\infty)l \quad \text{Eq. 14}$$

Therefore, Eq. 11 can be rewritten to:

$$Q = \frac{V}{Il \int_{t_1}^{t_2} F(t)dt} \ln \left[\frac{A^{obs,t_1} - A^{obs,\infty}}{A^{obs,t_2} - A^{obs,\infty}} \right] \quad \text{Eq. 15}$$

where A^{obs,t_1} , A^{obs,t_2} , and A_{obs}^∞ are the absorbances at the observed wavelength at time t_1 , t_2 , and at photostationary state, respectively.

Direct integration of the photokinetic factor cannot be achieved when ε_E^{irr} is not zero (i.e. absorption by both isomers at the irradiation wavelength). To determine the pseudo quantum yield Q , approximation of the photokinetic factor in different circumstances can be obtained as described below.

➤ **Case 1:** If the absorbance at the irradiation wavelength is low ($A^{irr,t} \ll 0.1$), the photokinetic factor can be approximated to:

$$F(t) = \frac{1 - 10^{-A^{irr,t}}}{A^{irr,t}} \approx \ln 10 \quad \text{Eq. 16}$$

Inserting Eq. 16 into Eq. 10 gives:

$$\frac{dC_Z^t}{(C_Z^t - C_Z^\infty)} = \frac{-IlQ \ln(10)}{V} dt \quad \text{Eq. 17}$$

Integration of Eq. 17 from time 0 to t gives:

$$Qt = \frac{V}{Il \ln(10)} \ln \left[\frac{C_Z^0 - C_Z^\infty}{C_Z^t - C_Z^\infty} \right] = \frac{V}{Il \ln(10)} \ln \left[\frac{A^{obs,0} - A^{obs,\infty}}{A^{obs,t} - A^{obs,\infty}} \right]$$

$$\therefore Q = \frac{V}{Il t \ln(10)} \ln \left[\frac{A^{obs,0} - A^{obs,\infty}}{A^{obs,t} - A^{obs,\infty}} \right] \quad \text{Eq. 18}$$

Eq. 18 can be rewritten to:

$$A^{obs,t} = (A^{obs,0} - A^{obs,\infty})e^{-at} + A^{obs,\infty} \quad \text{Eq. 19}$$

where a in the exponent $-at$ is defined as:

$$a = \frac{IlQ \ln(10)}{V} \quad \text{Eq. 20}$$

Then non-linear fitting of Eq. 20 from the plot of absorbance versus irradiation time gives exponential factor, a , which directly gives the value of pseudo quantum yield Q .

The individual quantum yields, $\phi_{Z \rightarrow E}$ and $\phi_{E \rightarrow Z}$, can then be obtained from Q .

At photostationary state, there is no change in concentration of **1-Z**.

$$\frac{dC_Z^\infty}{dt} = 0 = \frac{-IlF(t)}{V} (\phi_{Z \rightarrow E} \varepsilon_Z^{irr} C_Z^\infty - \phi_{E \rightarrow Z} \varepsilon_E^{irr} C_E^\infty) \quad \text{Eq. 21}$$

$$\phi_{Z \rightarrow E} \varepsilon_Z^{irr} C_Z^\infty = \phi_{E \rightarrow Z} \varepsilon_E^{irr} C_E^\infty \quad \text{Eq. 22}$$

Therefore, the relation between $\phi_{Z \rightarrow E}$ and $\phi_{E \rightarrow Z}$ can be described as:

$$\frac{\phi_{Z \rightarrow E}}{\phi_{E \rightarrow Z}} = \frac{\varepsilon_E^{irr} C_E^\infty}{\varepsilon_Z^{irr} C_Z^\infty} \quad \text{Eq. 23}$$

By using Eq. 23, the quantum yield for each direction of photoisomerization can be extracted from the pseudo quantum yield Q .

$$Q = \phi_{Z \rightarrow E} \varepsilon_Z^{irr} + \phi_{E \rightarrow Z} \varepsilon_E^{irr} = \phi_{Z \rightarrow E} \varepsilon_Z^{irr} + \phi_{Z \rightarrow E} \frac{\varepsilon_Z^{irr} C_Z^\infty}{\varepsilon_E^{irr} C_E^\infty} \varepsilon_E^{irr}$$

$$= \phi_{Z \rightarrow E} \varepsilon_Z^{irr} \left(1 + \frac{C_Z^\infty}{C_E^\infty} \right) = \frac{\phi_{Z \rightarrow E} \varepsilon_Z^{irr} C_{tot}}{C_E^\infty} \quad \text{Eq. 24}$$

From Eq. 24, individual quantum yields are obtained as below:

$$\phi_{Z \rightarrow E} = \frac{QC_E^\infty}{\varepsilon_Z^{irr} C_{tot}}, \phi_{E \rightarrow Z} = \frac{QC_Z^\infty}{\varepsilon_E^{irr} C_{tot}} \quad \text{Eq. 25}$$

➤ **Case 2:** If the absorbance at the irradiation wavelength is not sufficiently low for the approximation in Eq. 16 and the interval for absorbance measurement is short, integration of the photokinetic factor from time t_1 to t_2 can be approximated to:^{S2}

$$\int_{t_1}^{t_2} F(t) dt = \frac{F(t_1) + F(t_2)}{2} (t_2 - t_1) \quad \text{Eq. 26}$$

By inserting Eq. 26 into Eq. 15 gives:

$$Q = \frac{2V}{Il(t_2 - t_1)\{F(t_1) + F(t_2)\}} \ln \left[\frac{A^{obs,t_1} - A^{obs,\infty}}{A^{obs,t_2} - A^{obs,\infty}} \right] \quad \text{Eq. 27}$$

Pseudo quantum yield Q can be obtained experimentally by using Eq. 27. Determination of the individual quantum yields can be achieved as described in **Case 1**.

➤ **Case 3:** When only 1-Z is excited at the irradiation wavelength ($\varepsilon_Z^{irr} > 0$, $\varepsilon_E^{irr} = 0$), the photokinetic factor can be obtained as below:^{S1,S3}

$$F(t) = \frac{1 - 10^{-A^{irr,t}}}{A^{irr,t}} = \frac{1 - 10^{-\varepsilon_Z^{irr} C_Z^t l}}{\varepsilon_Z^{irr} C_Z^t l} \quad \text{Eq. 28}$$

Then Eq. 5 can be rearranged as below:

$$\begin{aligned} \frac{dC_Z^t}{dt} &= \frac{-IlF(t)}{V} (\phi_{Z \rightarrow E} \varepsilon_Z^{irr} C_Z^t) = \frac{-Il}{V} (\phi_{Z \rightarrow E} \varepsilon_Z^{irr} C_Z^t) \frac{1 - 10^{-A^{irr,t}}}{\varepsilon_Z^{irr} C_Z^t l} = \frac{-I\phi_{Z \rightarrow E}}{V} (1 - 10^{-A^{irr,t}}) \\ dC_Z^t &= \frac{-I\phi_{Z \rightarrow E}}{V} (1 - 10^{-A^{irr,t}}) dt \end{aligned} \quad \text{Eq. 29}$$

Multiplying $\varepsilon_Z^{irr} l$ on both sides of Eq. 29 gives:

$$\begin{aligned} \varepsilon_Z^{irr} l dC_Z^t &= \frac{-I\phi_{Z \rightarrow E} \varepsilon_Z^{irr} l}{V} (1 - 10^{-A^{irr,t}}) dt \\ dA^{irr,t} &= \frac{-IlQ}{V} (1 - 10^{-A^{irr,t}}) dt \\ \frac{dA^{irr,t}}{1 - 10^{-A^{irr,t}}} &= \frac{-IlQ}{V} dt \end{aligned} \quad \text{Eq. 30}$$

Integrating Eq. 30 from time 0 to t gives:

$$\begin{aligned}
 \int_{A^{irr,0}}^{A^{irr,t}} \frac{dA^{irr,t}}{1 - 10^{-A^{irr,t}}} &= \frac{1}{\ln(10)} \int_{10^{A^{irr,0}}}^{10^{A^{irr,t}}} \frac{d(10^{A^{irr,t}})}{10^{A^{irr,t}} - 1} = - \int_0^t \frac{IlQ}{V} dt \\
 \frac{1}{\ln(10)} \ln \left[\frac{10^{A^{irr,t}} - 1}{10^{A^{irr,0}} - 1} \right] &= \frac{-IlQt}{V} \\
 Q &= \frac{V \log \left[\frac{10^{A^{irr,0}} - 1}{10^{A^{irr,t}} - 1} \right]}{Il t} \\
 \therefore \phi_{Z \rightarrow E} &= \frac{V \log \left[\frac{10^{A^{irr,0}} - 1}{10^{A^{irr,t}} - 1} \right]}{\varepsilon_Z^{irr} Il t} \quad \text{Eq. 31}
 \end{aligned}$$

➤ **Case 4:** If pure **1-Z** is available for photoswitching experiment, the unidirectional photoisomerization quantum yield ($\phi_{Z \rightarrow E}$) can be estimated very conveniently. To ignore the effect of reverse *E*-to-*Z* photoisomerization, photoswitching of pure **1-Z** is monitored until 5% of **1-Z** is converted to **1-E**.^{S4}

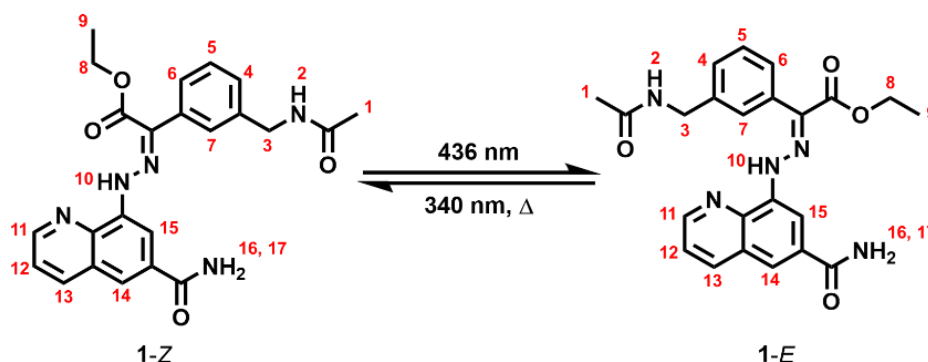
$$\begin{aligned}
 \phi_{Z \rightarrow E} &= \frac{V dC_Z}{dn_{p,z}} \\
 dA^{obs,t} &= \varepsilon_Z^{obs} l dC_Z^t \\
 dn_{p,z} &= I(1 - 10^{-A^{irr,t}}) dt \\
 \therefore \phi_{Z \rightarrow E} &= \frac{V}{I \varepsilon_Z^{obs} l (1 - 10^{-A^{irr,t}})} \cdot \frac{dA^{obs,t}}{dt} \quad \text{Eq. 32}
 \end{aligned}$$

In this case, it is approximated that the absorbance at the irradiation wavelength (A^{irr}) does not change during photoirradiation.

$$\therefore \phi_{Z \rightarrow E} = \frac{V}{I \varepsilon_Z^{obs} l (1 - 10^{-A^{irr}})} \cdot \frac{dA^{obs,t}}{dt} \quad \text{Eq. 33}$$

Therefore, the unidirectional photoisomerization quantum yield can be calculated directly from the observed slope, $\frac{dA^{obs,t}}{dt}$.

2. Characterization of compound 1



Synthetic procedure for compound **1** will be reported elsewhere. **1-Z**; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 13.36 (s, 1H, H_{10}), 9.00 (dd, $J = 4.2, 1.7$ Hz, 1H, H_{11}), 8.46 (dd, $J = 8.3, 1.7$ Hz, 1H, H_{13}), 8.42 (t, $J = 5.9$ Hz, 1H, H_2), 8.24 (s, 1H, H_{16}), 8.13 (d, $J = 1.8$ Hz, 1H, H_{15}), 8.10 (d, $J = 1.8$ Hz, 1H, H_{14}), 7.70 (dd, $J = 8.3, 4.2$ Hz, 1H, H_{12}), 7.62 (m, 2H, H_{6+7}), 7.54 (s, 1H, H_{17}), 7.40 (t, $J = 7.9$ Hz, 1H, H_5), 7.27 (d, $J = 8.0$ Hz, 1H, H_4), 4.40 (q, $J = 7.1$ Hz, 2H, H_8), 4.32 (d, $J = 5.9$ Hz, 2H, H_3), 1.90 (s, 3H, H_1), 1.35 (t, $J = 7.1$ Hz, 3H, H_9); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 169.23, 167.81, 163.66, 162.57, 150.32, 139.38, 138.45, 137.51, 137.36, 135.89, 133.30, 131.41, 127.88, 127.46, 127.02, 127.00, 122.92, 119.72, 107.77, 61.38, 42.13, 22.57, 13.90; **1-E**; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.15 (s, 1H, H_{10}), 8.74 (dd, $J = 4.3, 1.6$ Hz, 1H, H_{11}), 8.44 (m, 1H, H_2), 8.39 (dd, $J = 8.4, 1.6$ Hz, 1H, H_{13}), 8.21 (s, 1H, H_{16}), 8.12 (d, $J = 1.9$ Hz, 1H, H_{15}), 8.04 (d, $J = 1.8$ Hz, 1H, H_{14}), 7.64 – 7.57 (m, 2H, H_{5+12}), 7.54 (s, 1H, H_{17}), 7.46 (d, $J = 7.7$ Hz, 1H, H_4), 7.40 – 7.34 (m, 2H, H_{6+7}), 4.36 (d, $J = 6.1$ Hz, 2H, H_3), 4.30 (q, $J = 7.1$ Hz, 2H, H_8), 1.85 (s, 3H, H_1), 1.29 (t, $J = 7.1$ Hz, 3H, H_9); HRMS m/z (EI^+) calc. for $\text{C}_{23}\text{H}_{23}\text{N}_5\text{O}_4$ [M^+] = 433.1750, Found 433.1750.

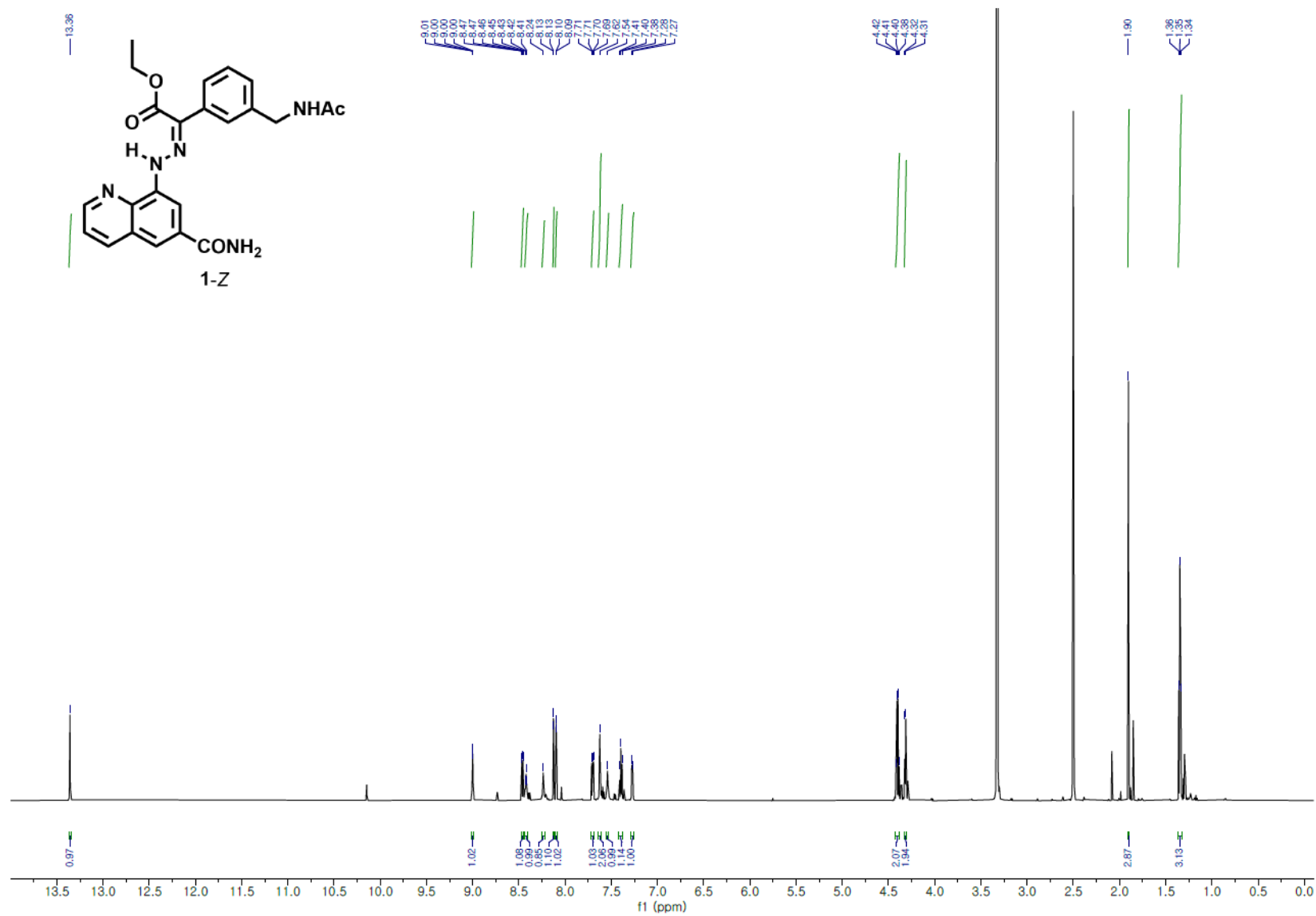


Figure S1. ¹H NMR spectrum of compound 1-Z in DMSO-*d*₆ at 298 K.

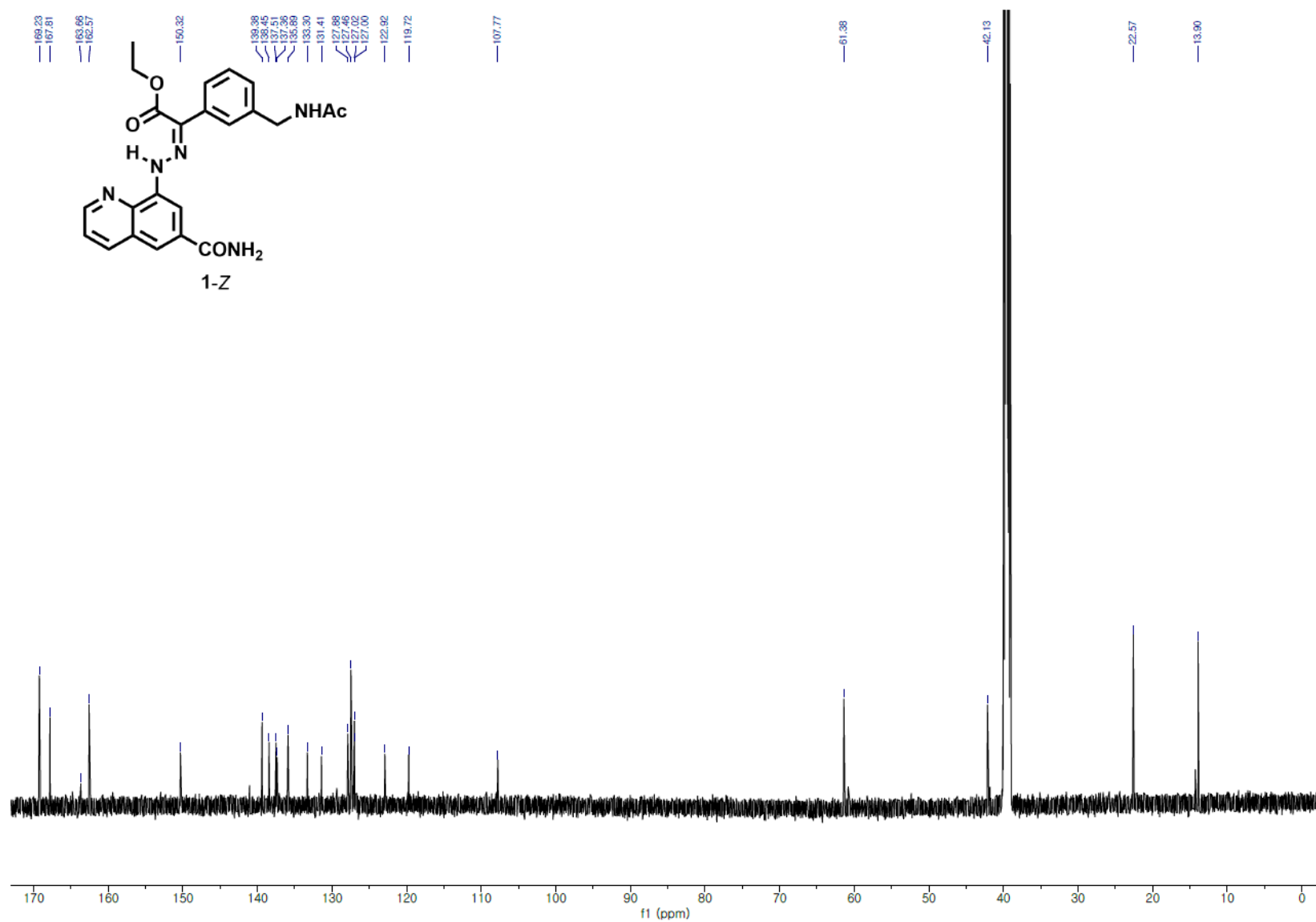


Figure S2. ^{13}C NMR spectrum of compound 1-Z in DMSO- d_6 at 298 K.

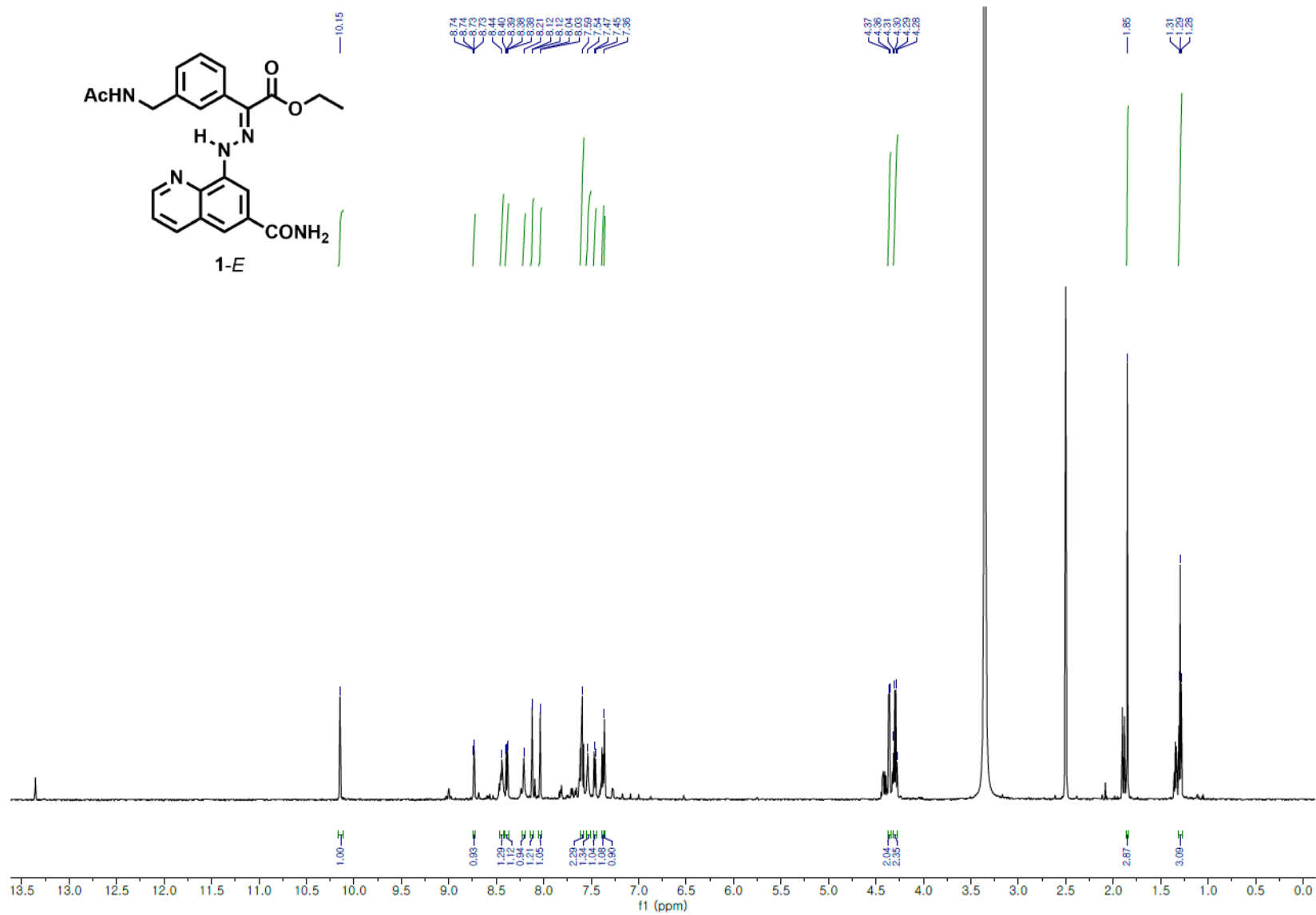


Figure S3. ^1H NMR spectrum of compound **1-E** in $\text{DMSO}-d_6$ at 298 K.

3. References

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