Supplementary Information

Comparison of Riboflavin-Derived Flavinium Salts Applied to Catalytic H_2O_2 Oxidations

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1. General

Melting points (Mp) were determined on a SANSYO SMP-300 (SANSYO, Tokyo, Japan) and are uncorrected. The IR spectra were recorded on a JASCO FT/IR-660 plus spectrophotometer (JASCO, Tokyo, Japan). The NMR spectra were measured using JEOL JNM-L400 and JNM ECX-500 spectrometers (JEOL, Akishima, Japan) operating at 400 and 500 MHz, respectively, for ^{1}H and 100 and 126 MHz, respectively, for ^{13}C using tetramethylsilane (TMS) or a solvent residual peak as the internal standard. The electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker microTOFII-SHIY3 mass spectrometer (Bruker, Billerica, MA) using the positive or negative mode ESI-TOF method for acetonitrile solutions and sodium formate as the reference. The GC measurements were performed on a Shimadzu GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) using Supelco Equity-5 (30 m x 0.25 mm) column. The absorption and fluorescence spectra were measured in a 1 cm quartz cell using a JASCO V-560 spectrophotometer and a JASCO FP-8300 spectrofluorometer, respectively.

2. Materials

All starting materials were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), Nacalai tesque (Kyoto, Japan), and Tokyo Kasei (TCI, Tokyo, Japan) and were used as received.

3. Investigation of redox and catalytic activity of flavinium salts

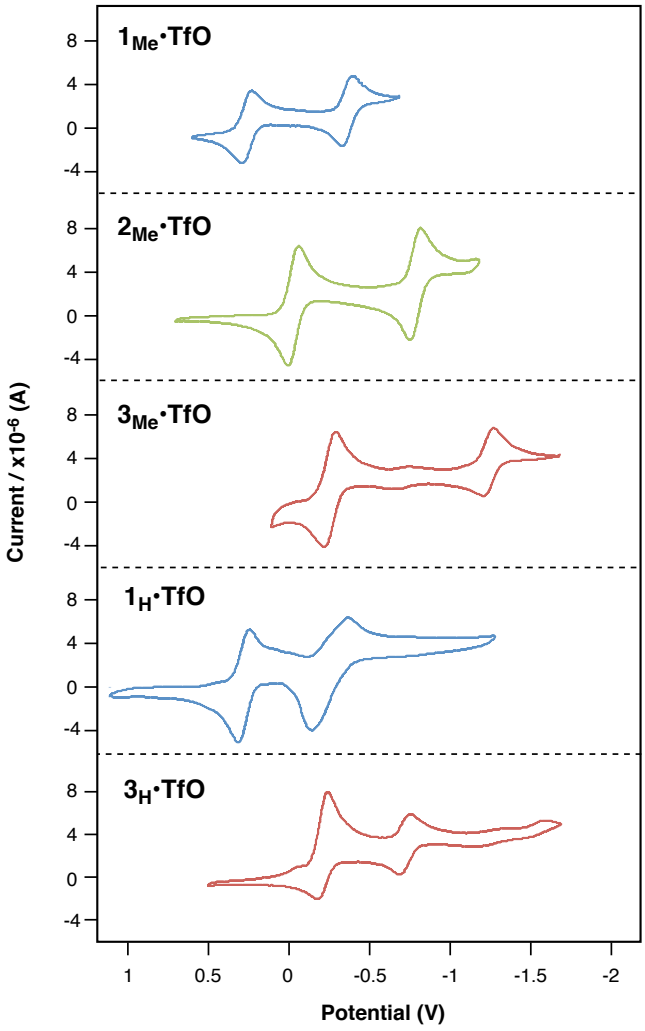


Fig. S1 Cyclic voltammograms of **1_{Me}•TfO**, **2_{Me}•TfO**, **3_{Me}•TfO**, **1_{H}•TfO**, and **3_{H}•TfO** measured in tetrabutylammonium perchlorate (0.1 M) containing CH_3CN.

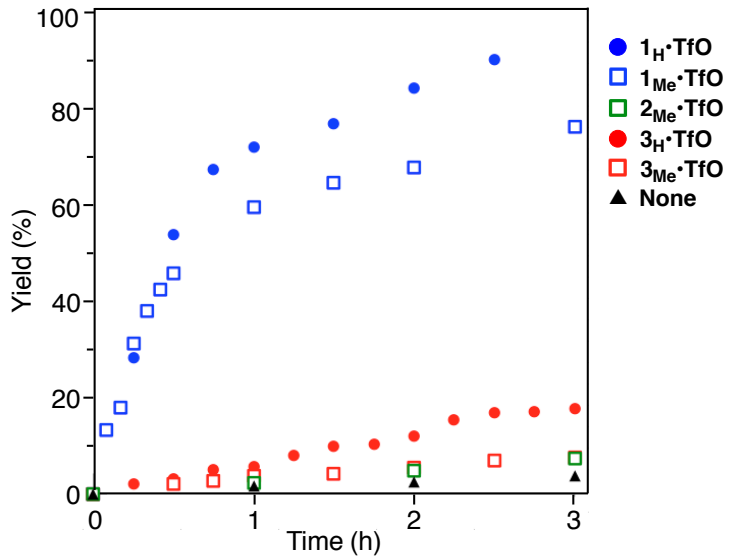


Figure S2. Comparison of flavinium catalysts in sulfoxidation of **14**.

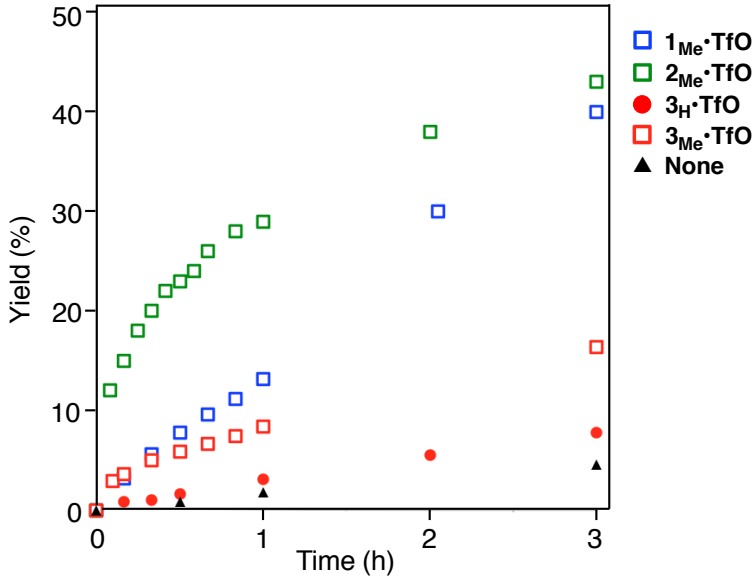


Figure S3. Comparison of flavinium catalysts in *N*-oxidation of **16**.

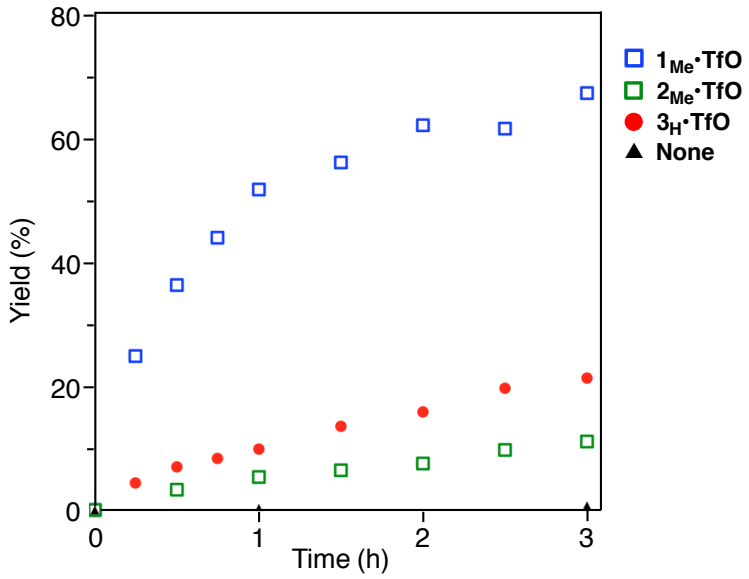
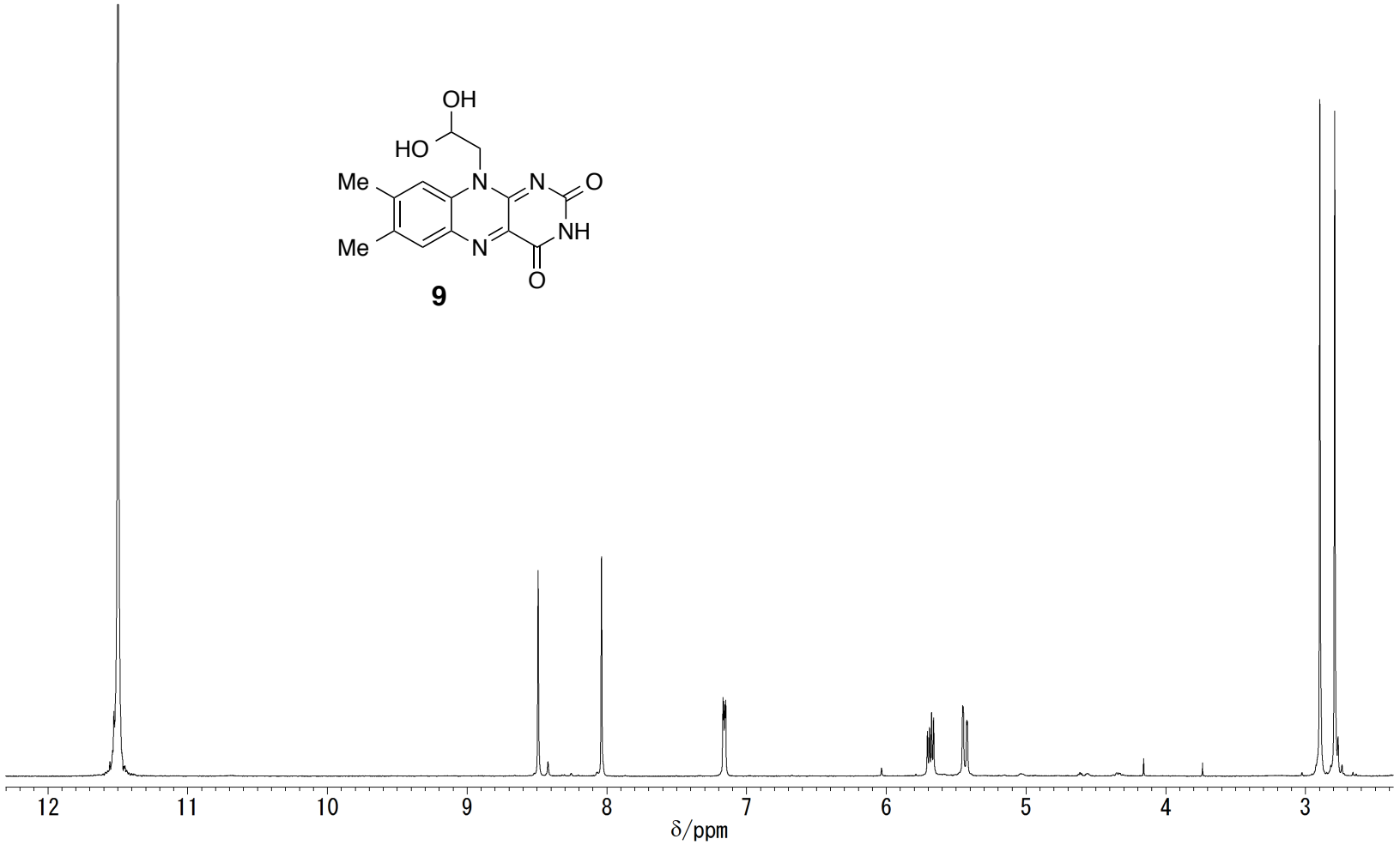
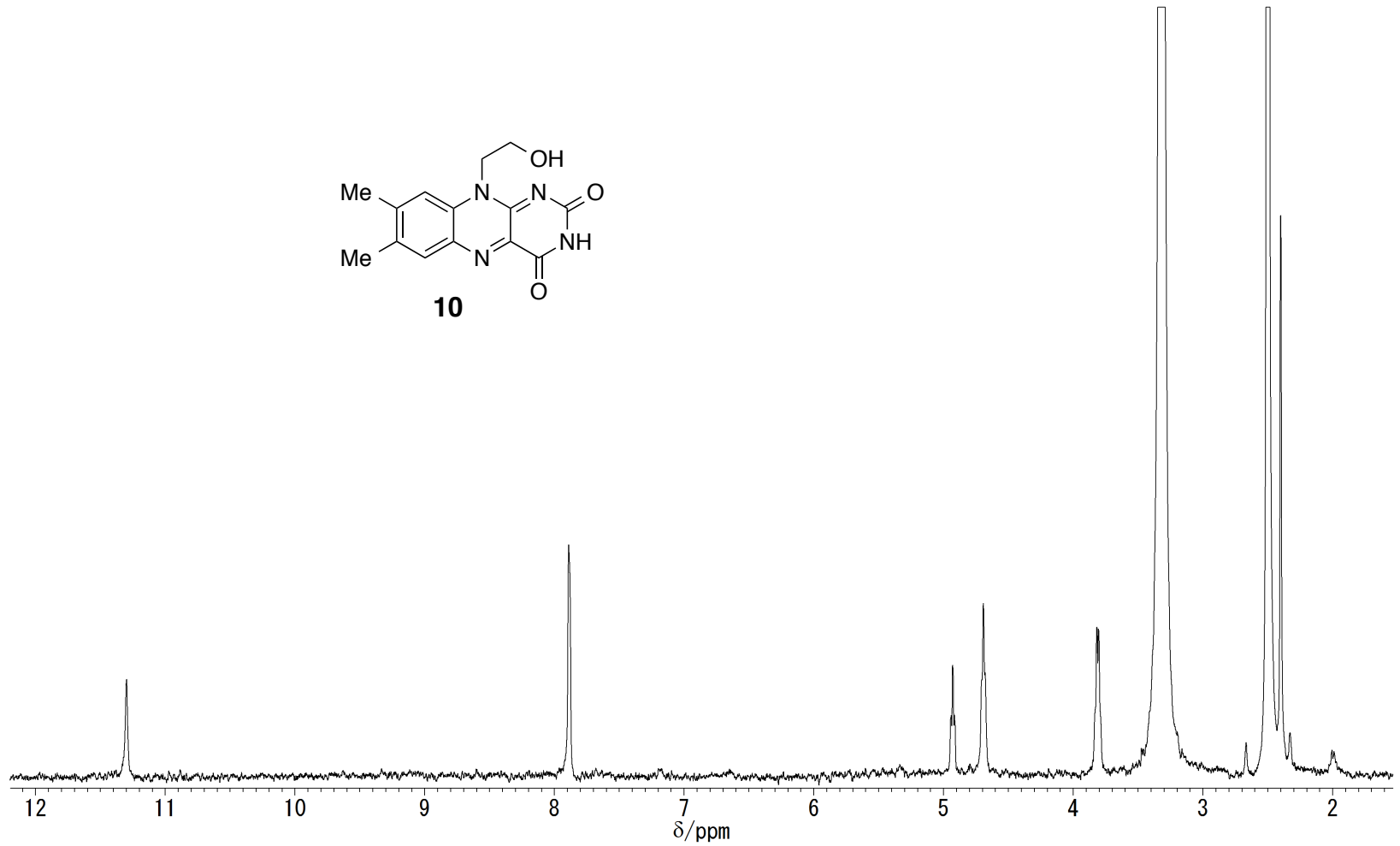


Figure S4. Comparison of flavinium catalysts in Baeyer-Villiger oxidation of **18**.

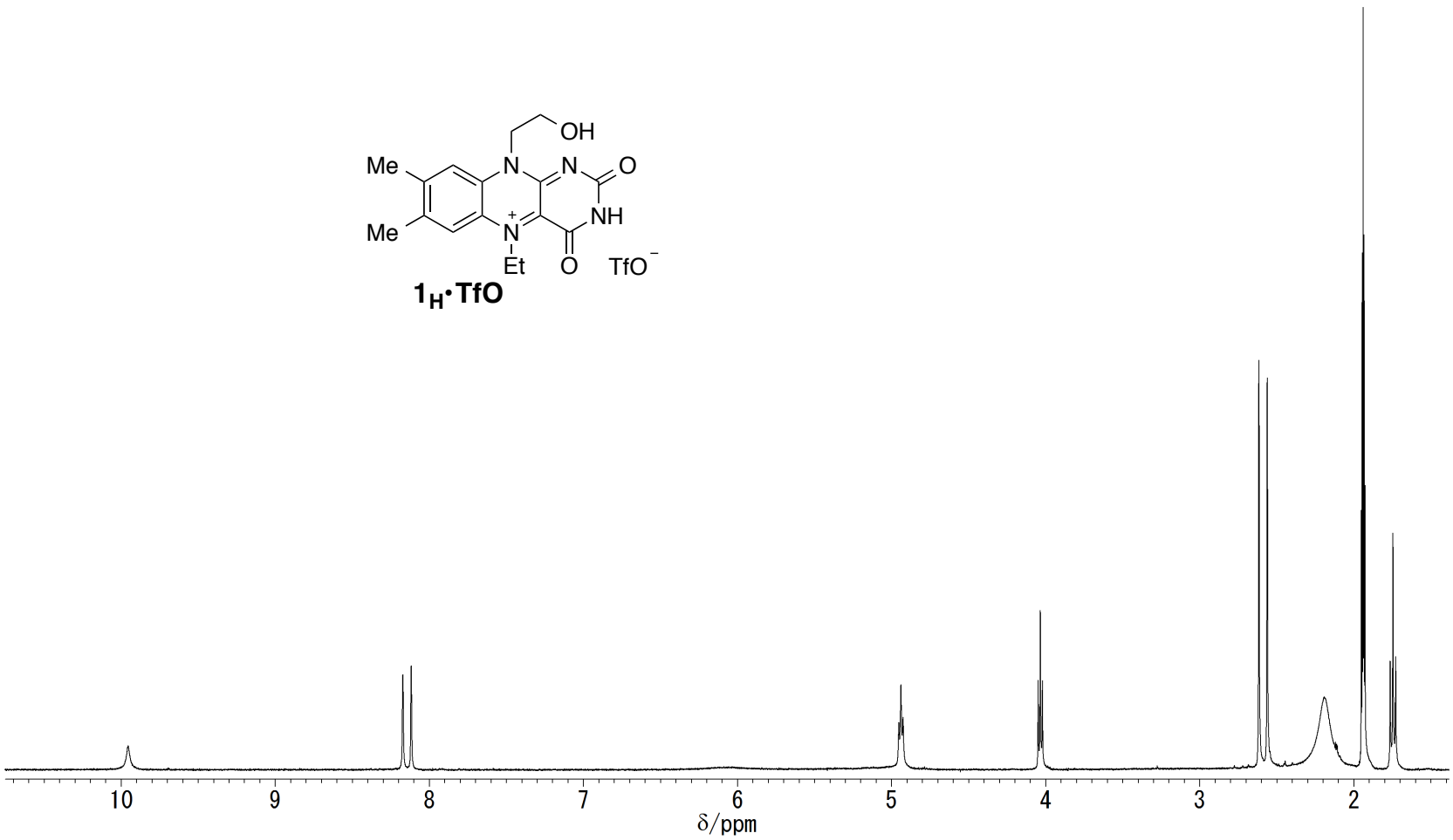
4. ^{1}H and ^{13}C NMR Spectra



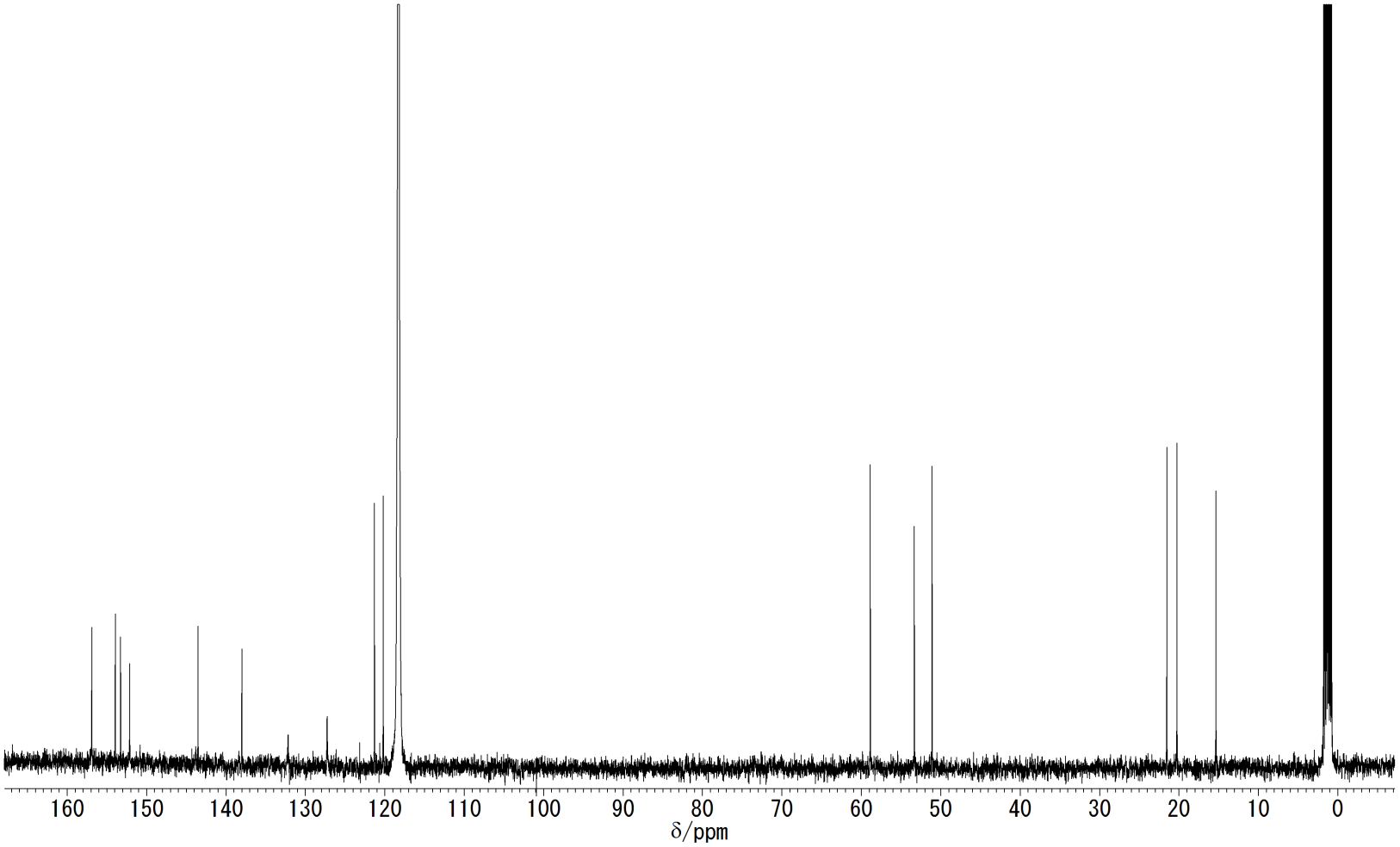
Spectrum S1. ^{1}H NMR (TFA-*d*, 500 MHz) spectrum of compound **9**.



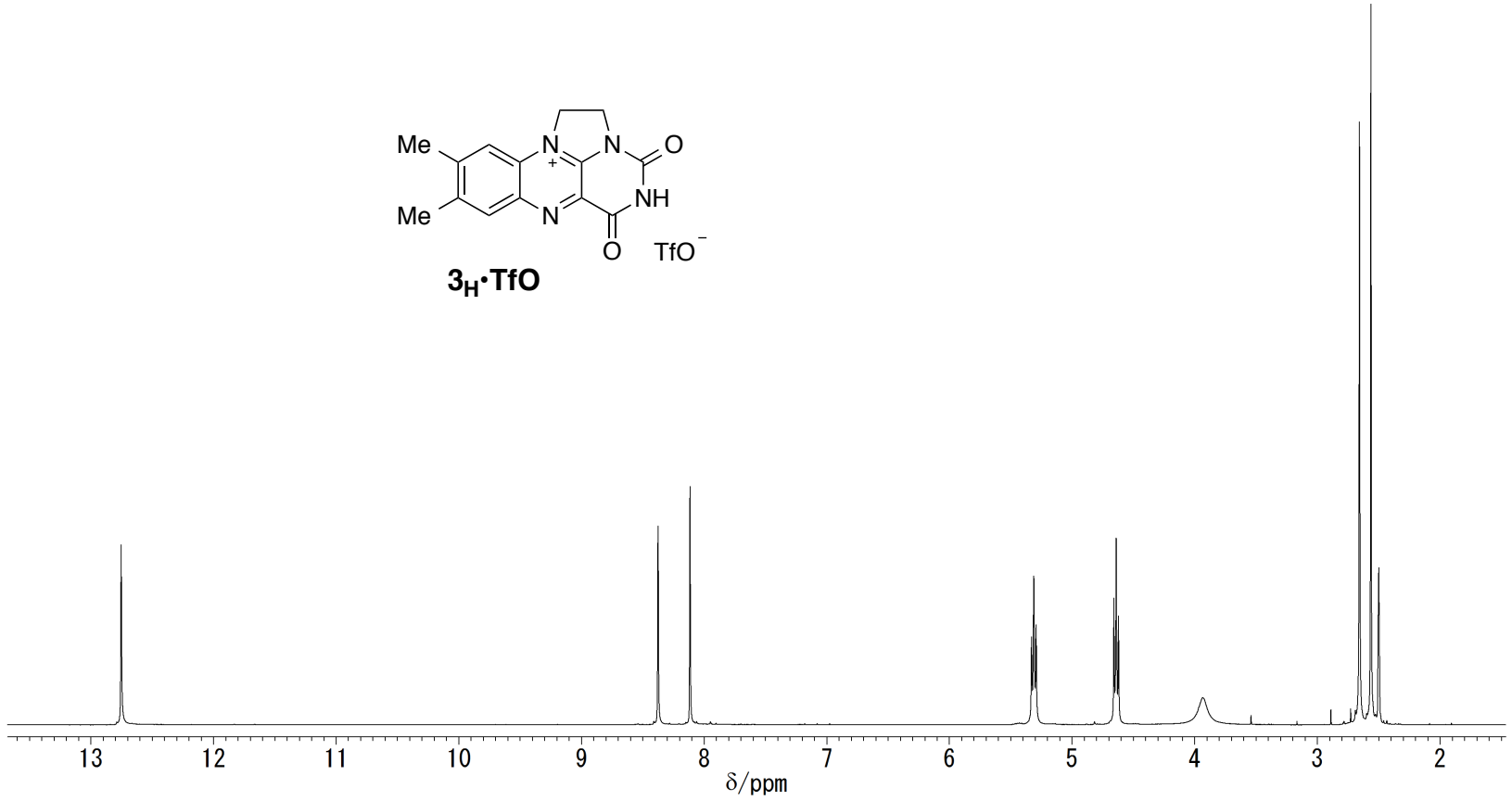
Spectrum S2. ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **10**.



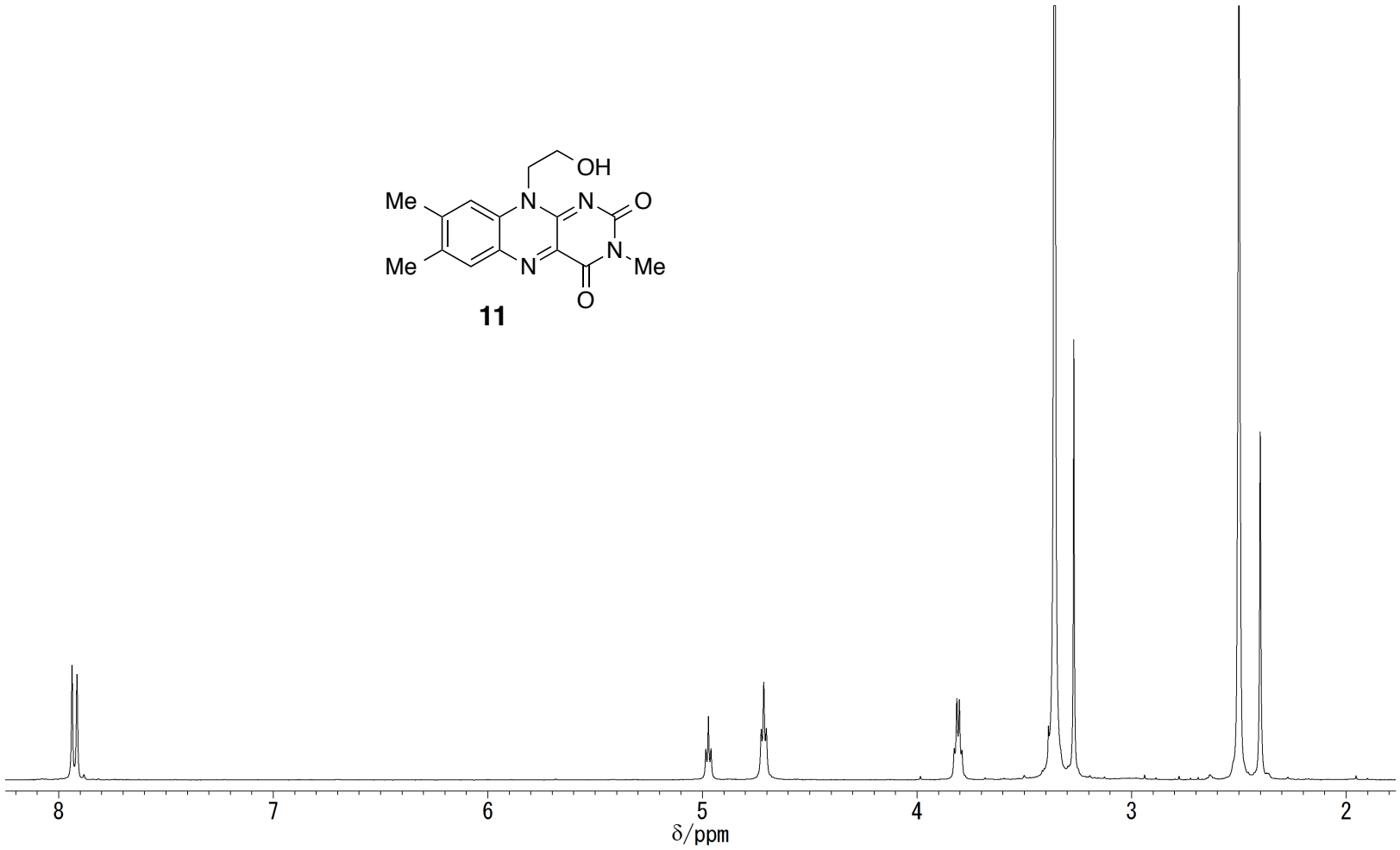
Spectrum S3. ^{1}H NMR (CD_3CN, 400 MHz) spectrum of compound **1_H•TfO**.



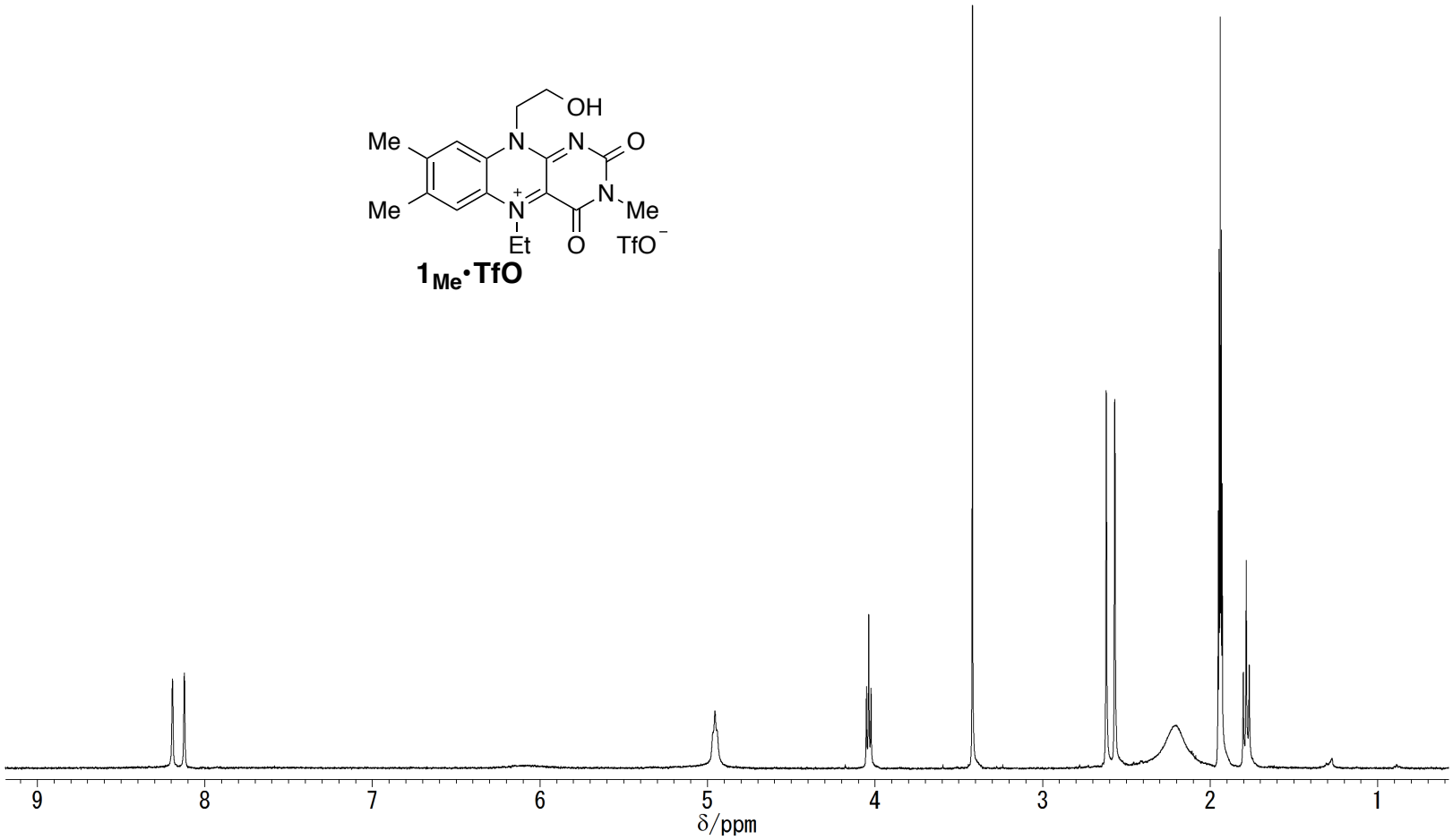
Spectrum S4. ^{13}C NMR (CD_3CN, 126 MHz) spectrum of compound **1_H•TfO**.



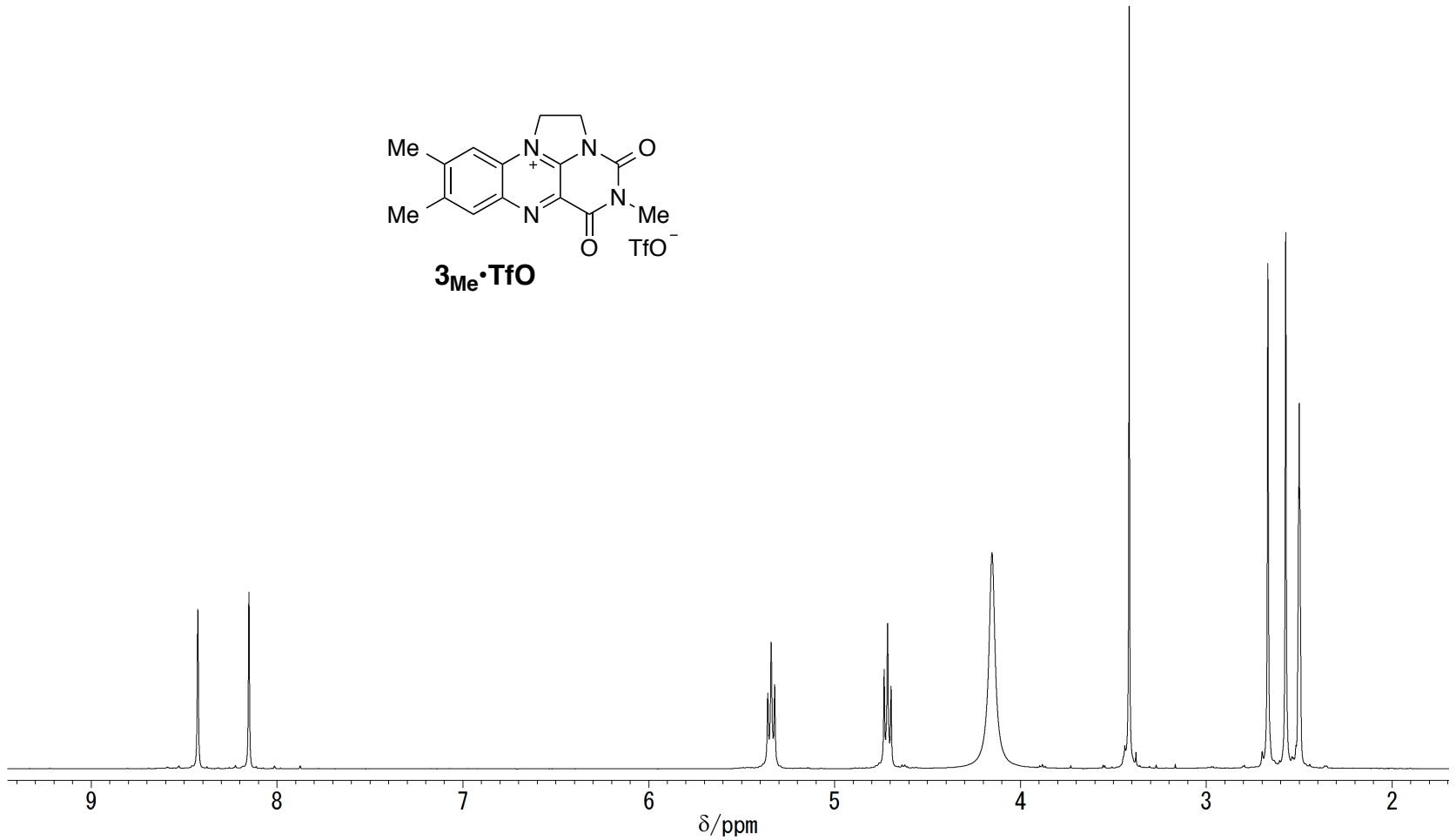
Spectrum S5. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3_H•TfO**.



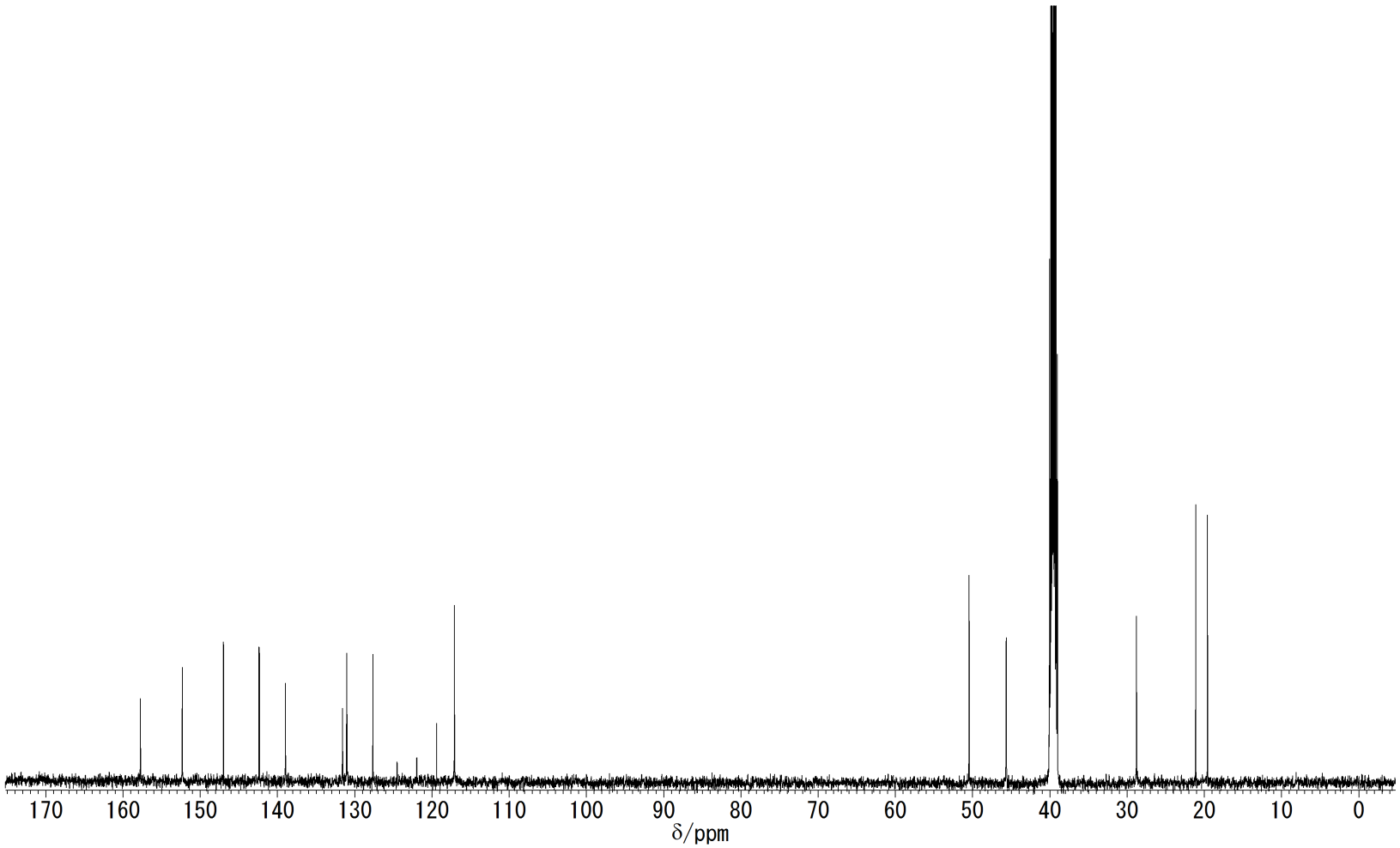
Spectrum S6. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **11**.



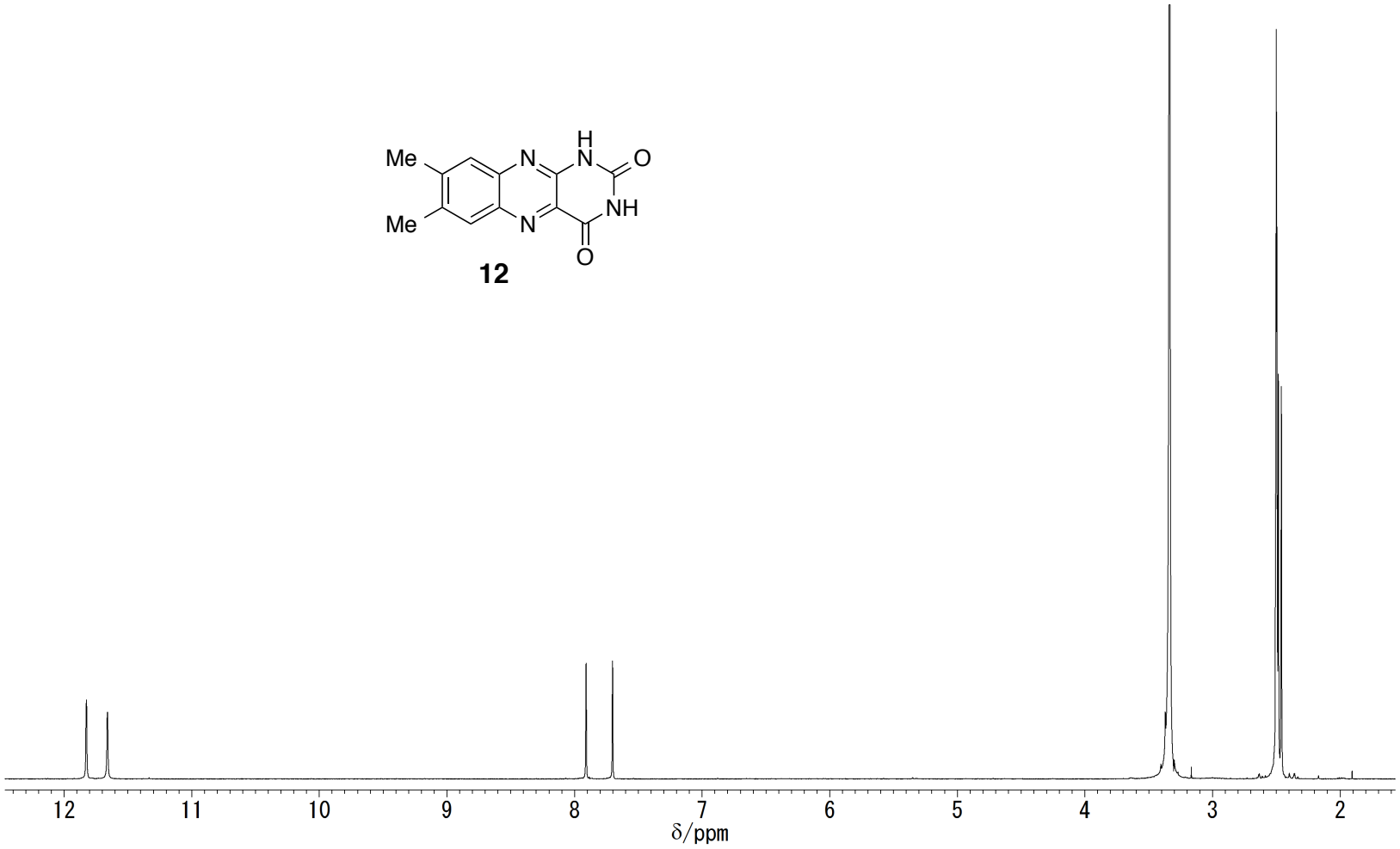
Spectrum S7. ^{1}H NMR (CD_3CN, 400 MHz) spectrum of compound **1_{Me}•TfO**.



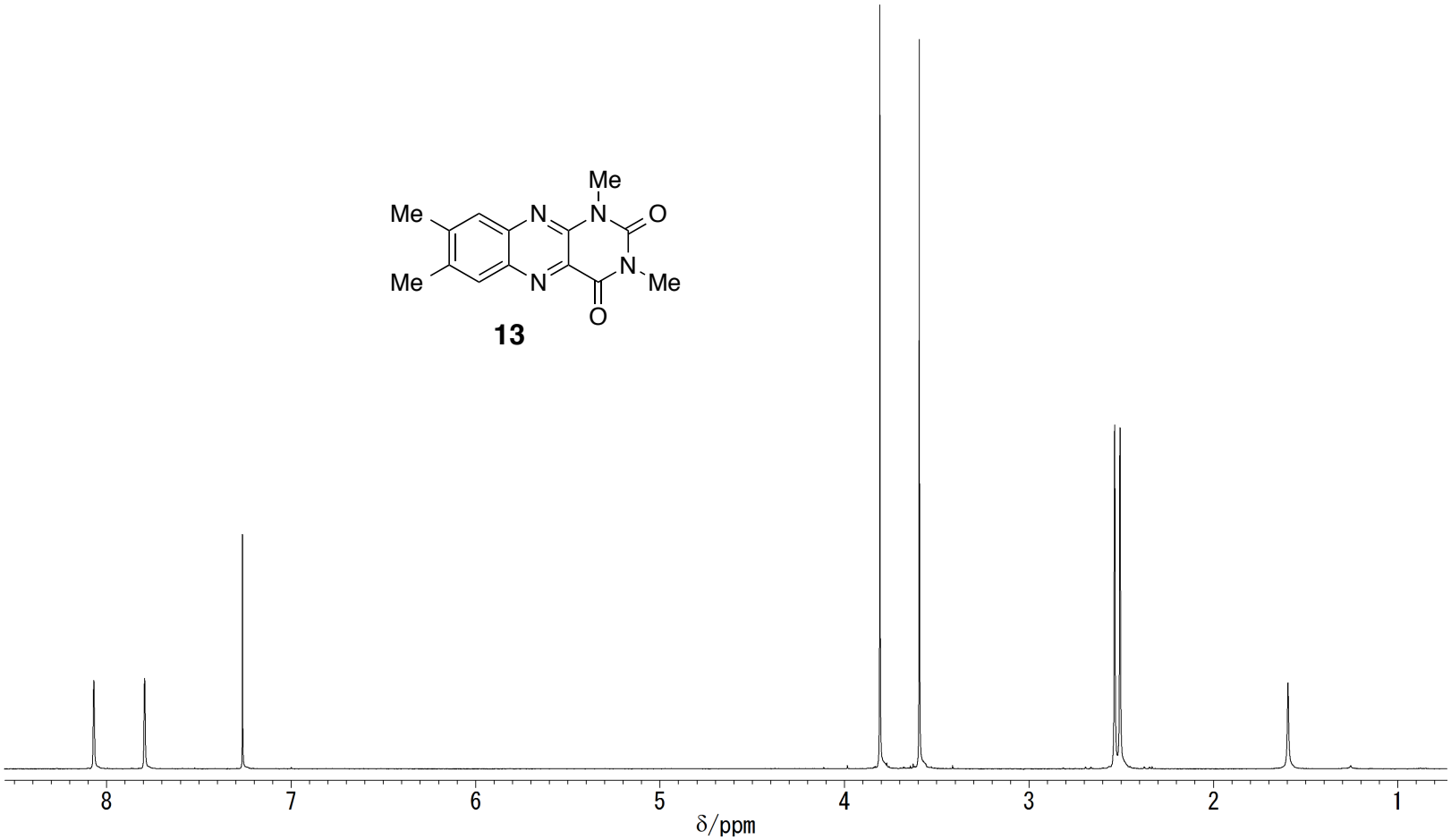
Spectrum S8. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3_{Me}•TfO**.



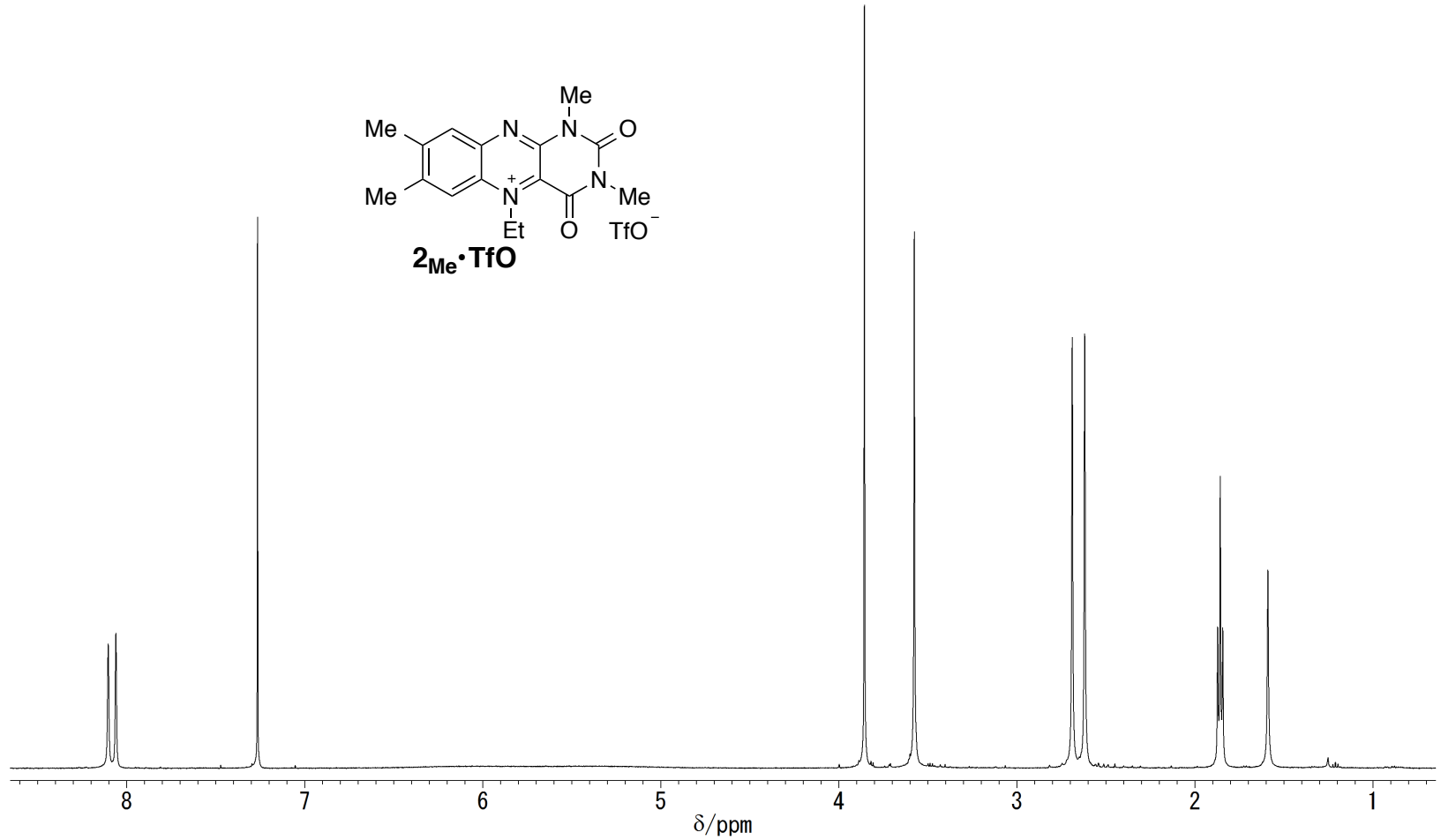
Spectrum S9. ^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of compound **3_{Me}•TfO**.



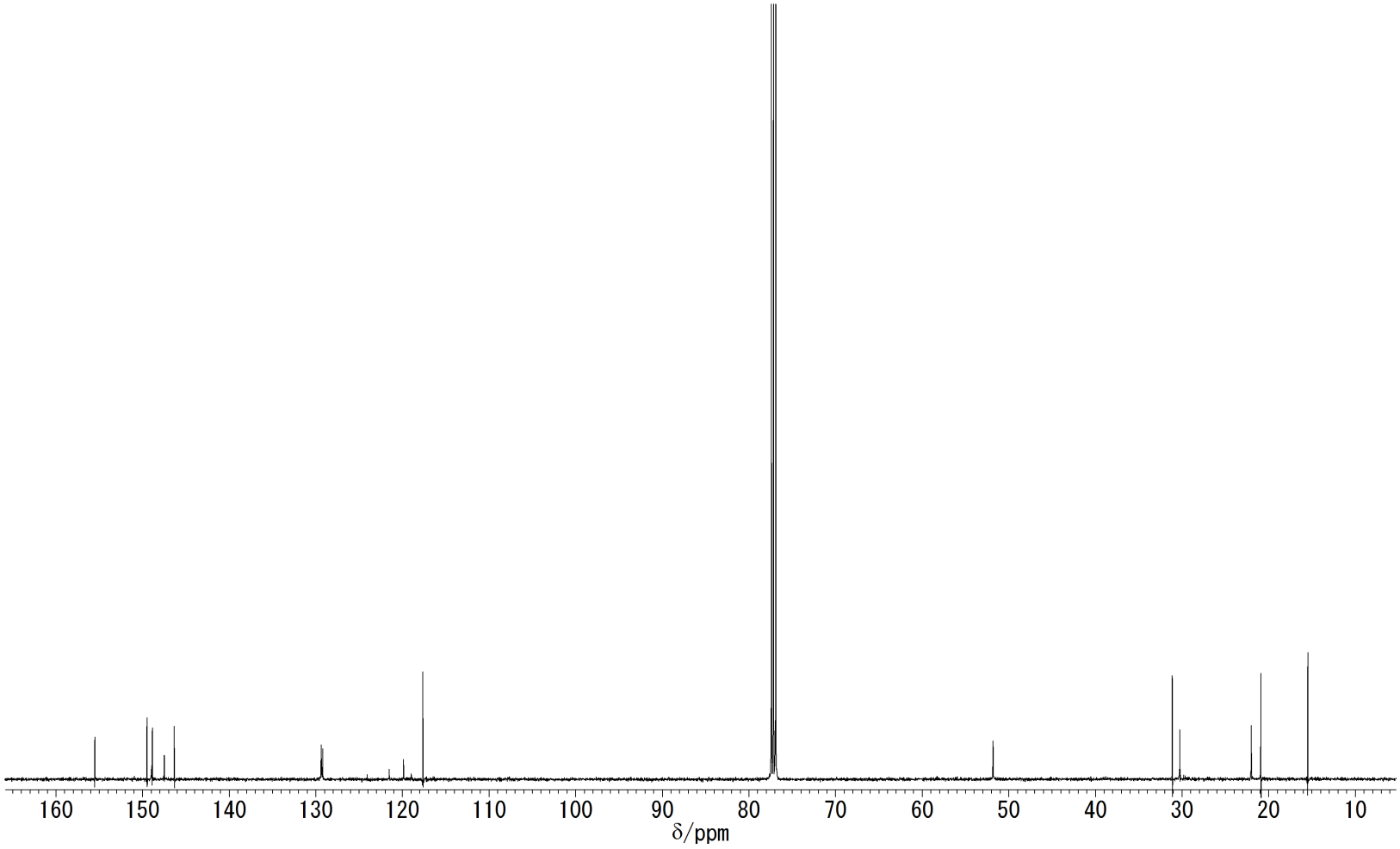
Spectrum S10. ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of compound **12**.



Spectrum S11. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **13**.



Spectrum S12. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **2_{Me}•TfO**.



Spectrum S13. ^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of compound $\mathbf{2_{Me}}$**•TfO**.