

Electronic Supplementary Information (ESI) for Organic & Biomolecular Chemistry

## Reactions of Dehydrodiferulates with Ammonia

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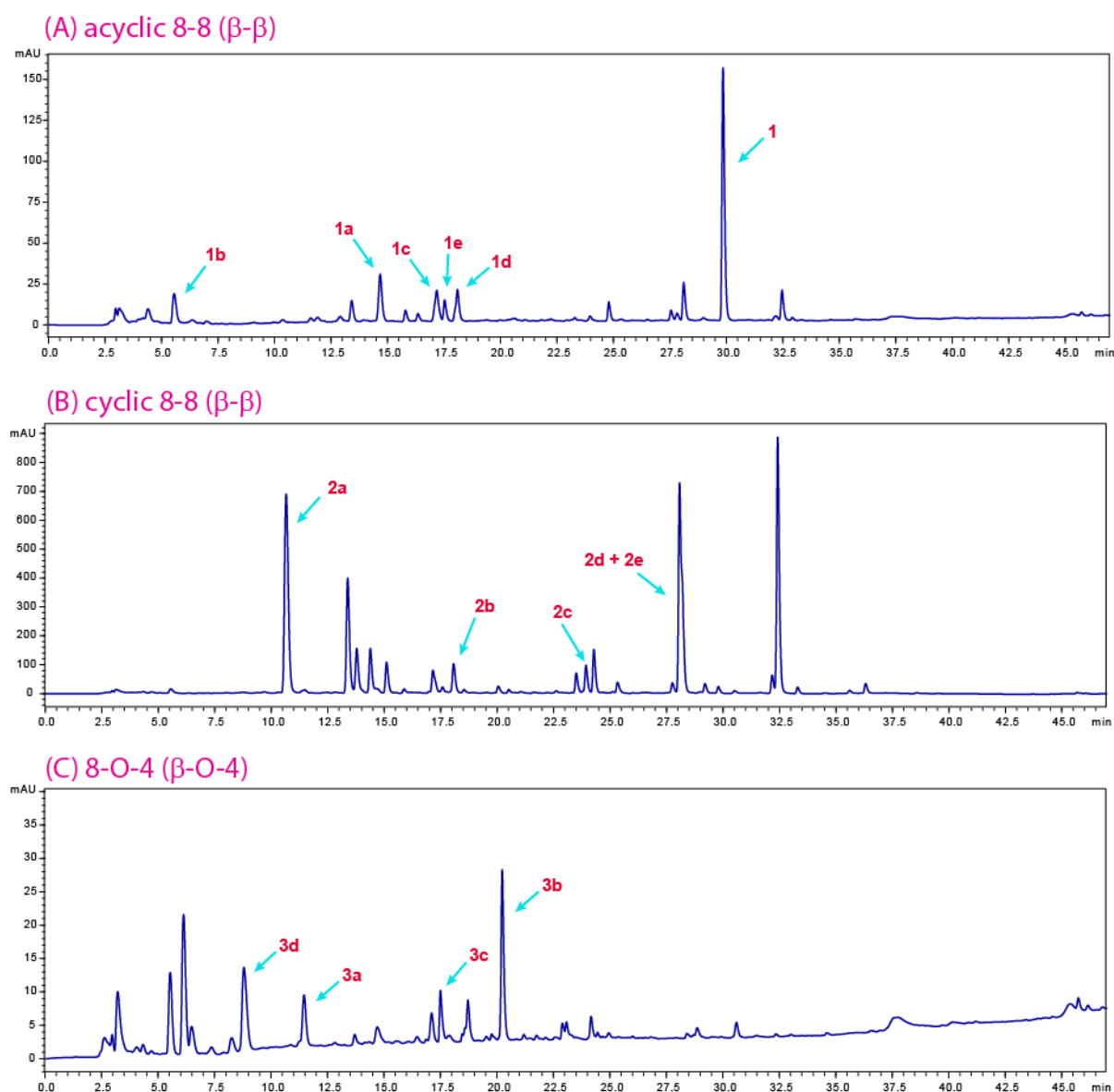
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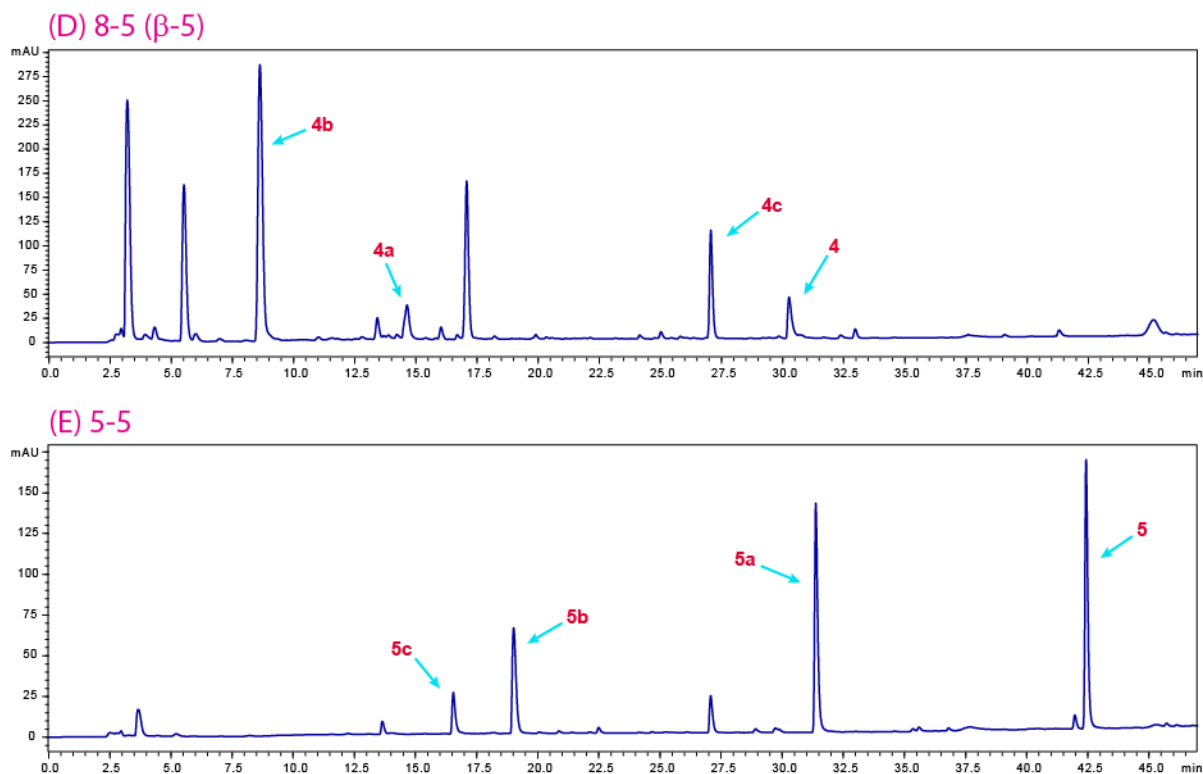
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## 1. HPLC chromatograms of crude reaction mixtures

After reaction completion (18 h), solvents were removed under vacuum and the product was dissolved in methanol (approximately 15 mL). The crude product, 1  $\mu$ L, was analyzed on a Shimadzu LCMS-2020 (using a Kinetex C18 (150  $\times$  4.6 mm, 2.6  $\mu$ m, Phenomenex column; detection was at 256 nm via a SPD-M20A photodiode array detector). Aqueous 0.1% formic acid (v/v, solvent system A) and methanol (0.1% formic acid, solvent system B) served as the mobile phase at flow rate of 0.5 mL/min in a gradient mode (Solvent B from 20 to 95% in 35 min, kept at 95% for 7 min, from 45 to 20% in 5 min). Compounds were characterized by their retention times and their ESIMS (in positive and negative modes) and compared with the isolated and structurally characterized compounds (as labeled; see Scheme 1 and Fig. 3 in the main paper).



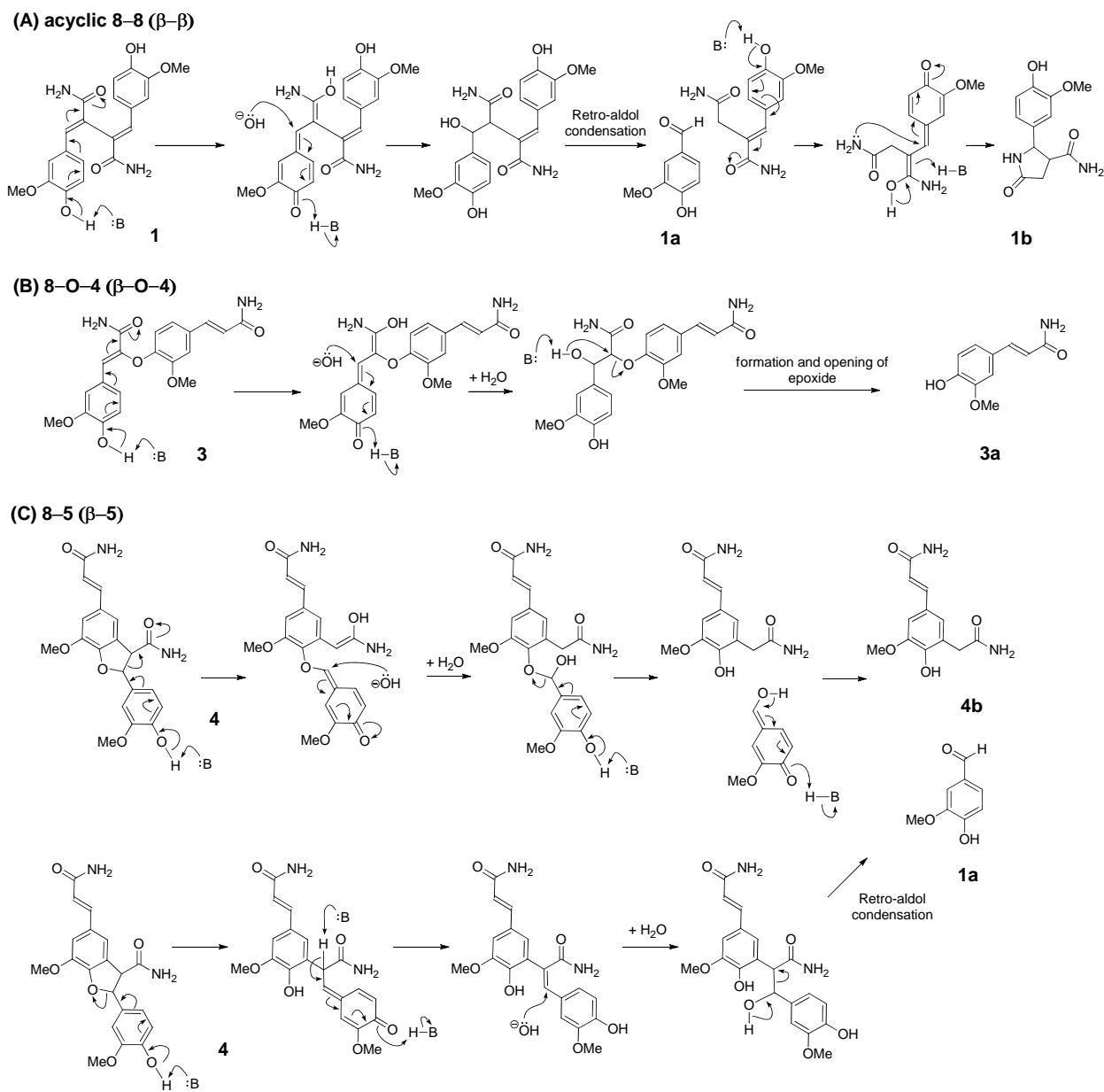


**Fig. S1.** HPLC chromatograms of crude reaction mixtures.

## 2. Proposed mechanisms for some of the reactions

In Scheme S1 (A), acyclic 8–8-diferulate **1** produces a quinone methide intermediate which, after the addition of a hydroxyl group *via* conjugate addition (Michael reaction) and then breaking of the bond through a retro-Aldol type reaction, could form vanillin **1a**.<sup>1-3</sup> Intra-molecular attack of the amide nitrogen to the newly formed quinone methide could form compound **1b**. In Scheme S1 (B), similarly, a quinone methide could form from 8–O–4-linked diferulate **3**. Following addition of hydroxide ion to the  $\alpha$ -carbon, it could ionize and attack the  $\beta$ -carbon of the  $\beta$ -aryl ether bond (forming an epoxide intermediate through neighboring group participation) to cleave the ether linkage. In Scheme S1 (C), the tetrahydrofuran ring in the 8–5-linked diferulate (compound **4**) could open during the formation of quinone methide followed by abstraction of a proton and re-aromatization. The final retro-Aldol type reaction could yield compounds **4b** and **1a**. In compound **2**, aromatization of ring B to form a naphthalene structure could be the driving force to assist the elimination of H-7' and H-8'. We couldn't explain the formation of some of

the products (i.e., **2b-2e**, **1c** and **1d**) by similar nucleophilic type mechanisms; possibly some other types of reactions (e.g., radical reactions via the presence of oxygen as a radical initiator) could promote them.<sup>4,5</sup>



**Scheme S1.** Proposed mechanisms for some of the reactions.

### 3. Photograph of the pressure vessel

Photograph of the used 16 ml stainless steel (grade 316, HEL Inc. USA) pressure vessel with a multi-port lid standing inside a heating block. It was used to perform the AFEX reactions.



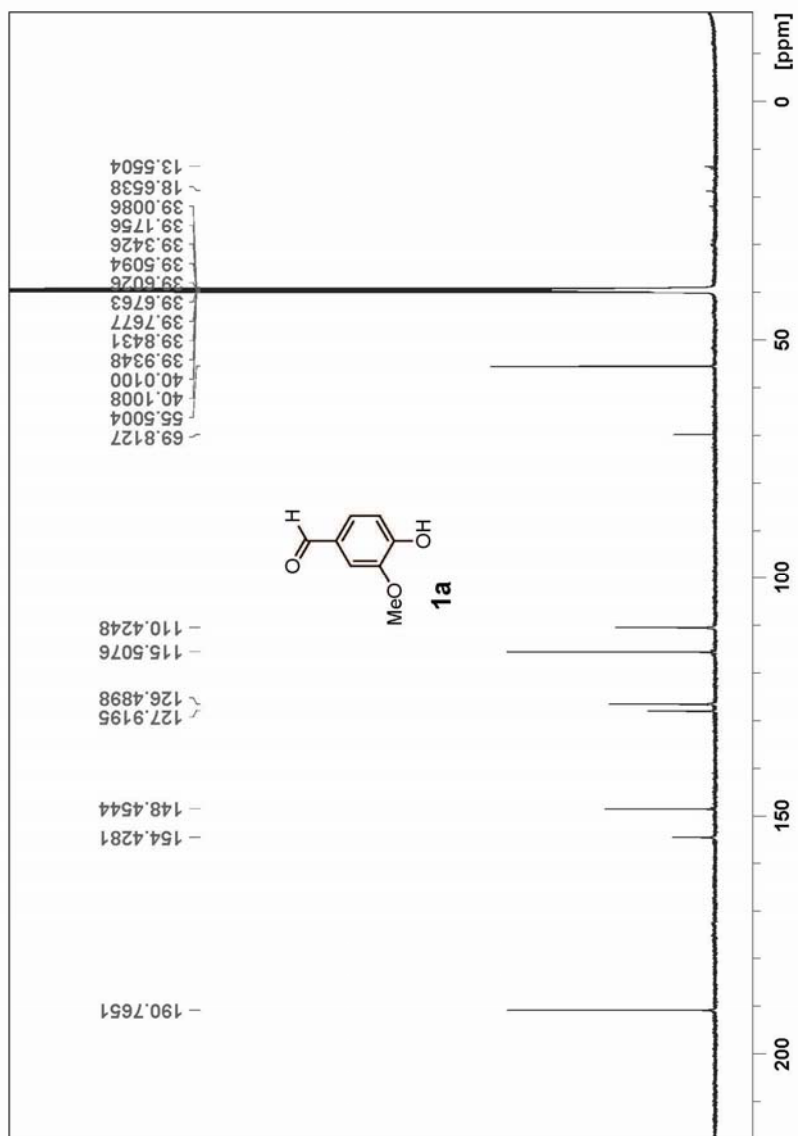
**Fig. S2.** Pressure vessel with a multi-port lid used for AFEX

### 4. References

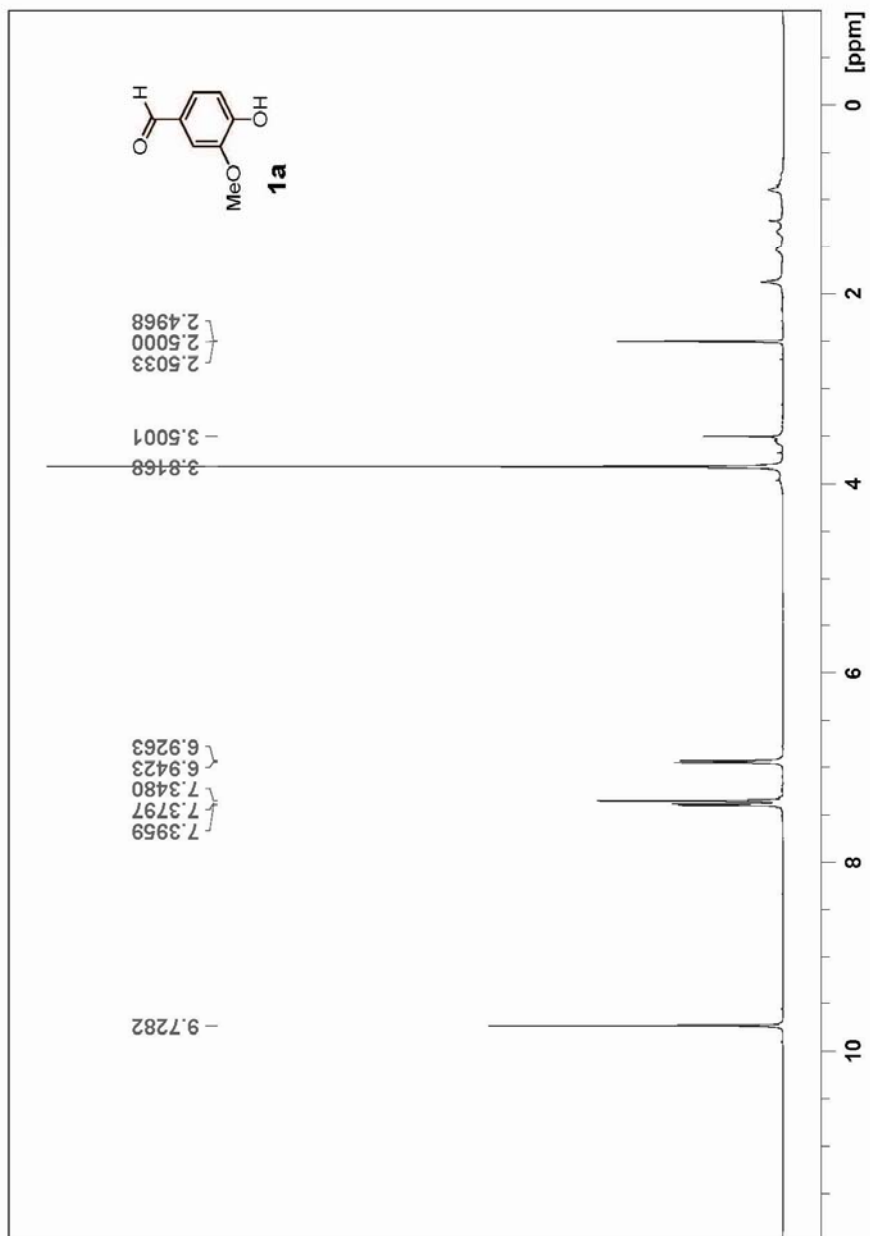
1. J. Gierer, *Holzforschung*, 1982, **36**, 43-51.
2. V. E. Tarabanko, Y. V. Hendogina, D. V. Petuhov and E. P. Pervishina, *React. Kinet. Catal. Lett.*, 2000, **69**, 361-368.
3. V. E. Tarabanko, D. V. Petukhov and G. E. Selyutin, *Kinetics and Catalysis (Translation of Kinetika i Kataliz)*, 2004, **45**, 569-577.
4. V. E. Tarabanko, N. A. Fomova, B. N. Kuznetsov, N. M. Ivanchenko and A. V. Kudryashev, *React. Kinet. Catal. Lett.*, 1995, **55**, 161-170.
5. J. Gierer, *Wood Science and Technology*, 1986, **20**, 1-33.

## 5. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for all isolated products

$^{13}\text{C}$  NMR spectrum of **1a** (125 MHz,  $\text{DMSO-d}_6$ )

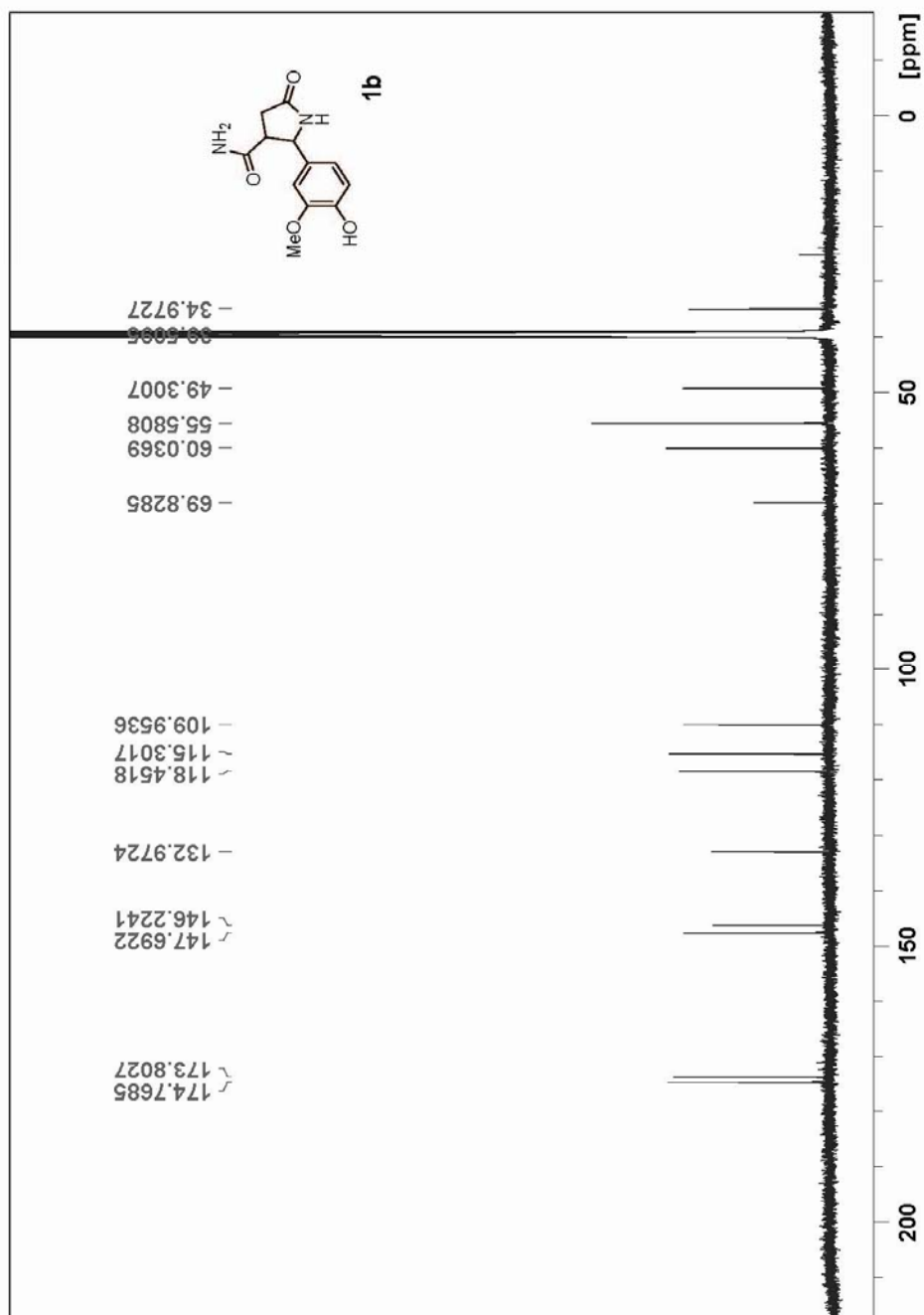


$^1\text{H}$  NMR spectrum of **1a** (500 MHz,  $\text{DMSO-d}_6$ )

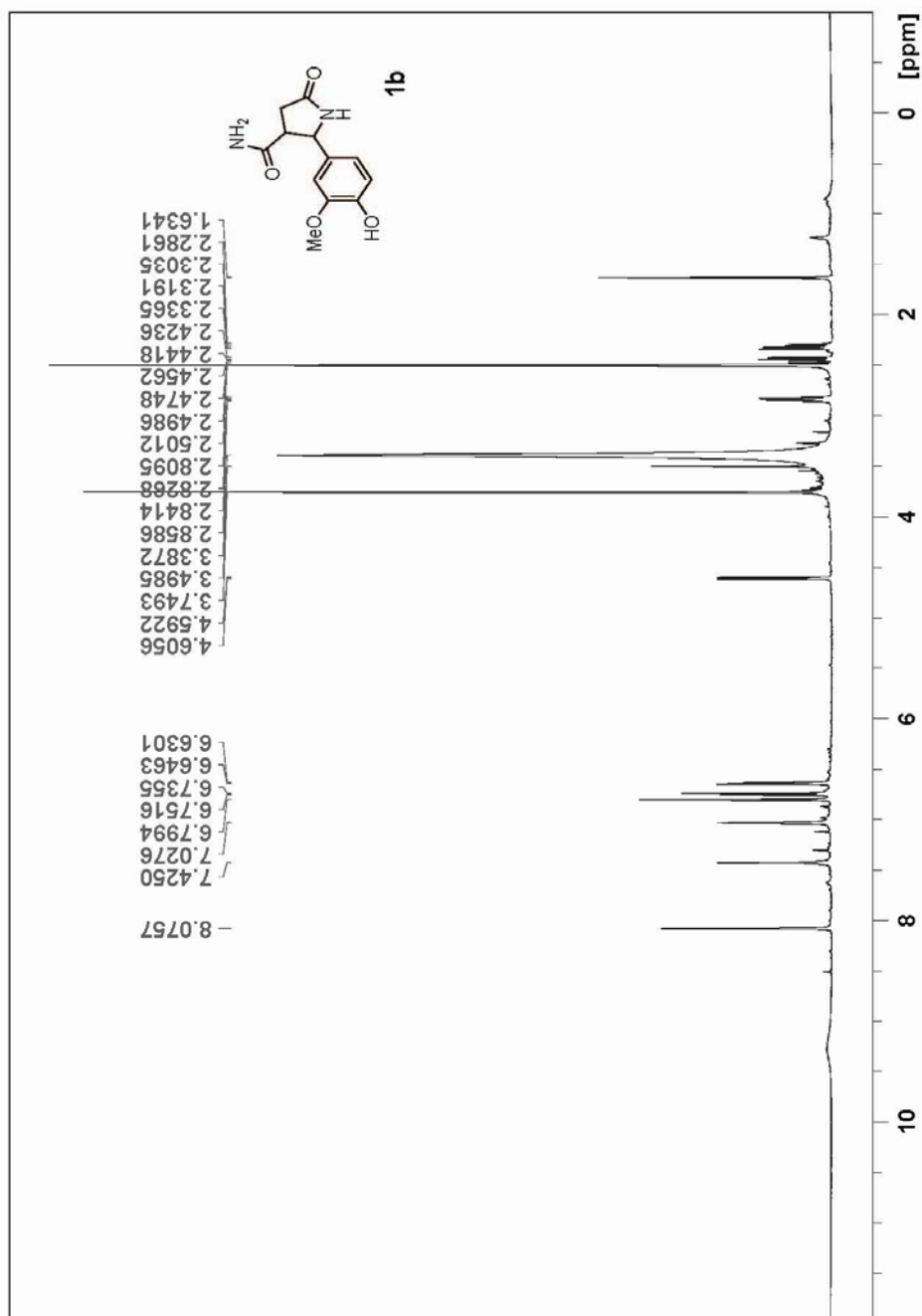




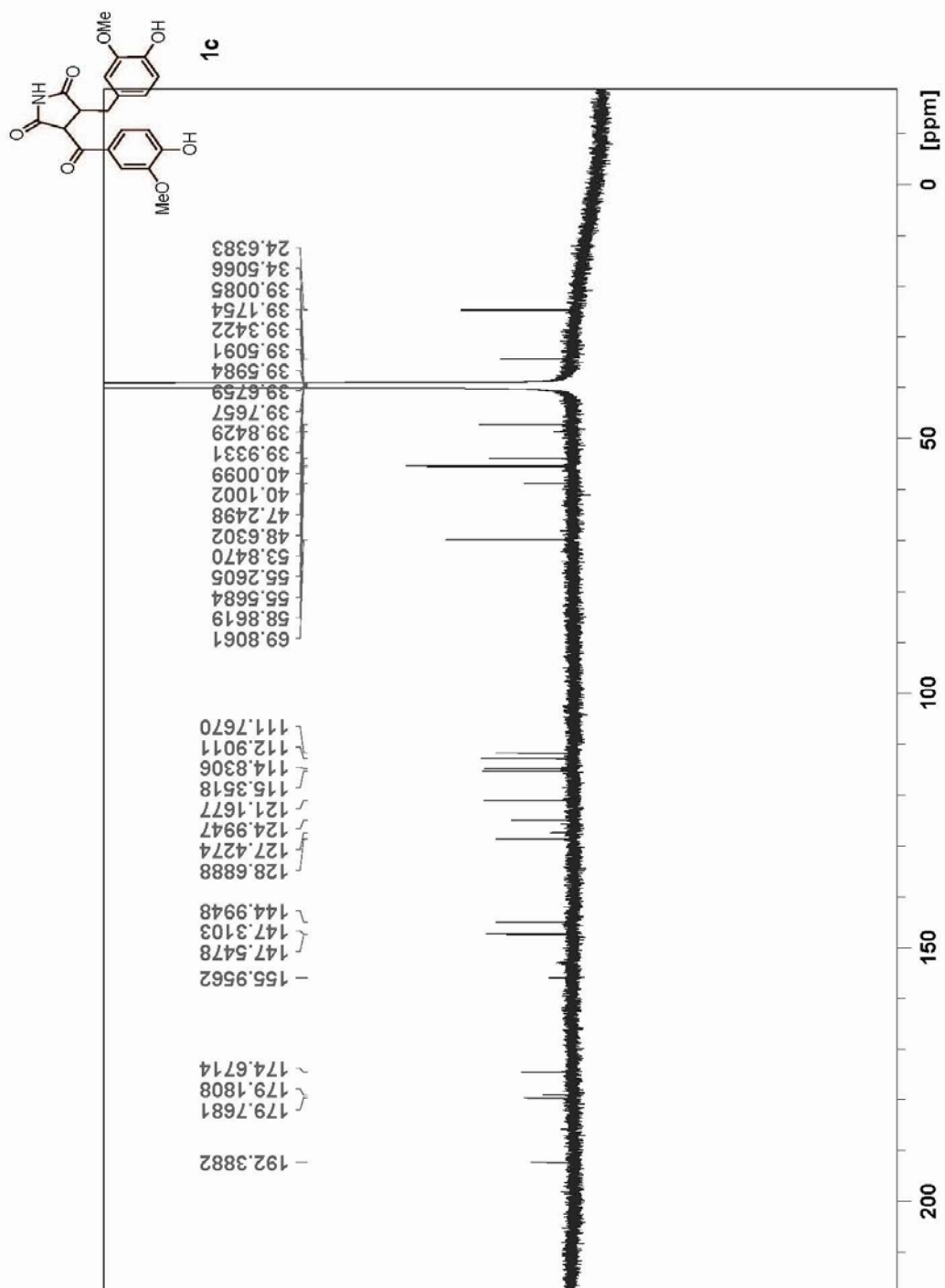
$^{13}\text{C}$  NMR spectrum of **1b** (125 MHz, DMSO- $d_6$ )



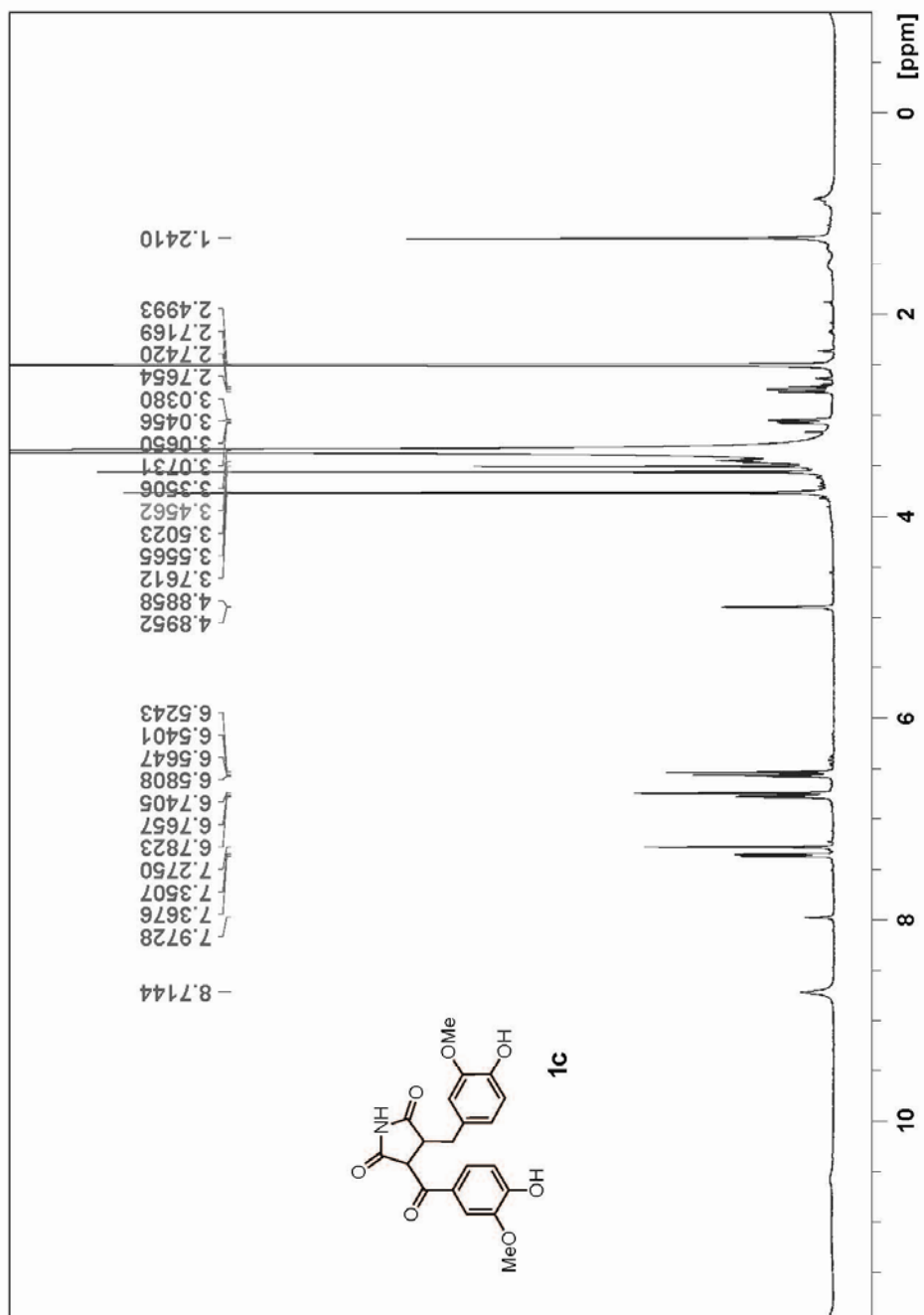
$^1\text{H}$  NMR spectrum of **1b** (500 MHz, DMSO- $d_6$ )



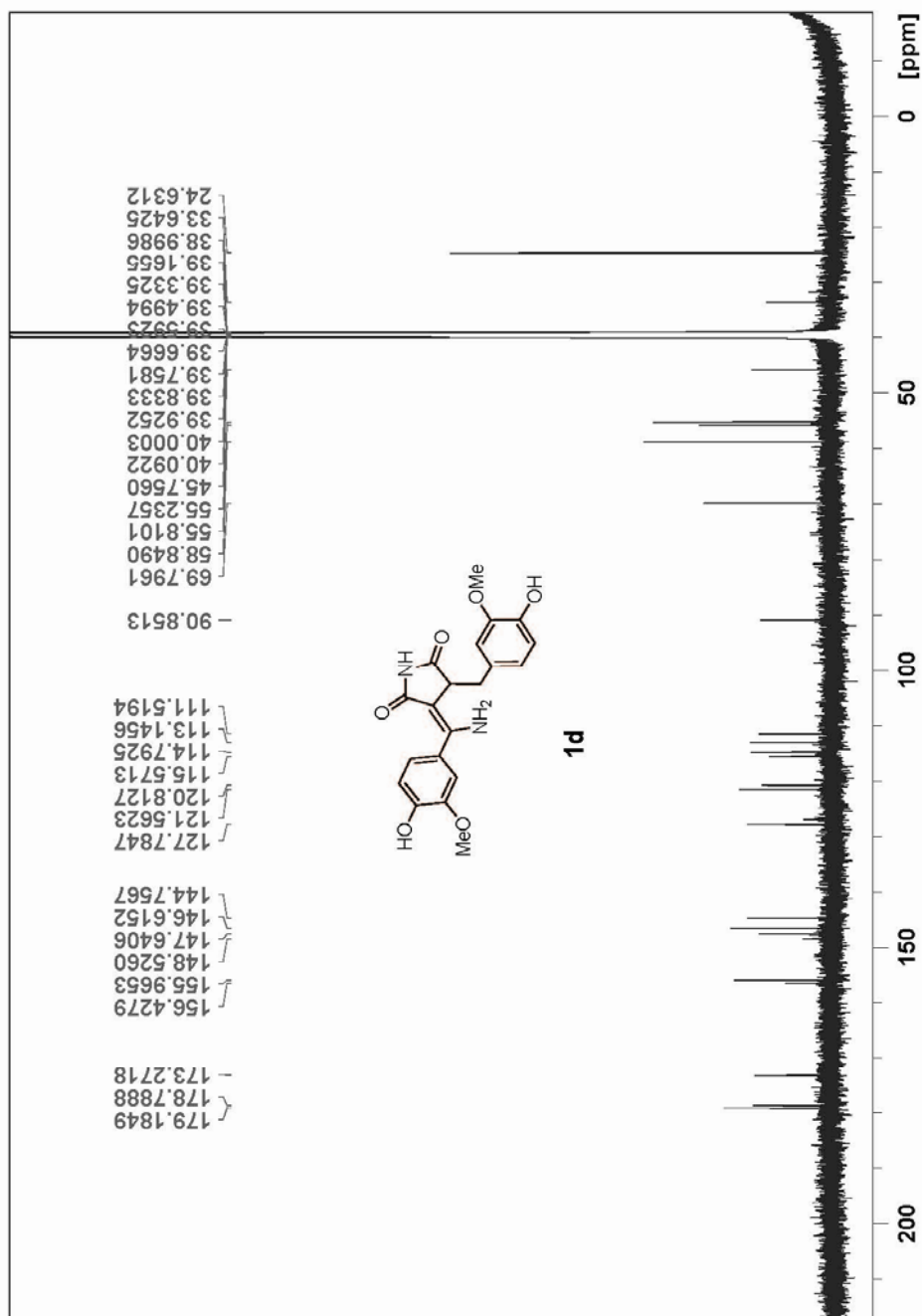
$^{13}\text{C}$  NMR spectrum of **1c** (125 MHz, DMSO- $d_6$ )



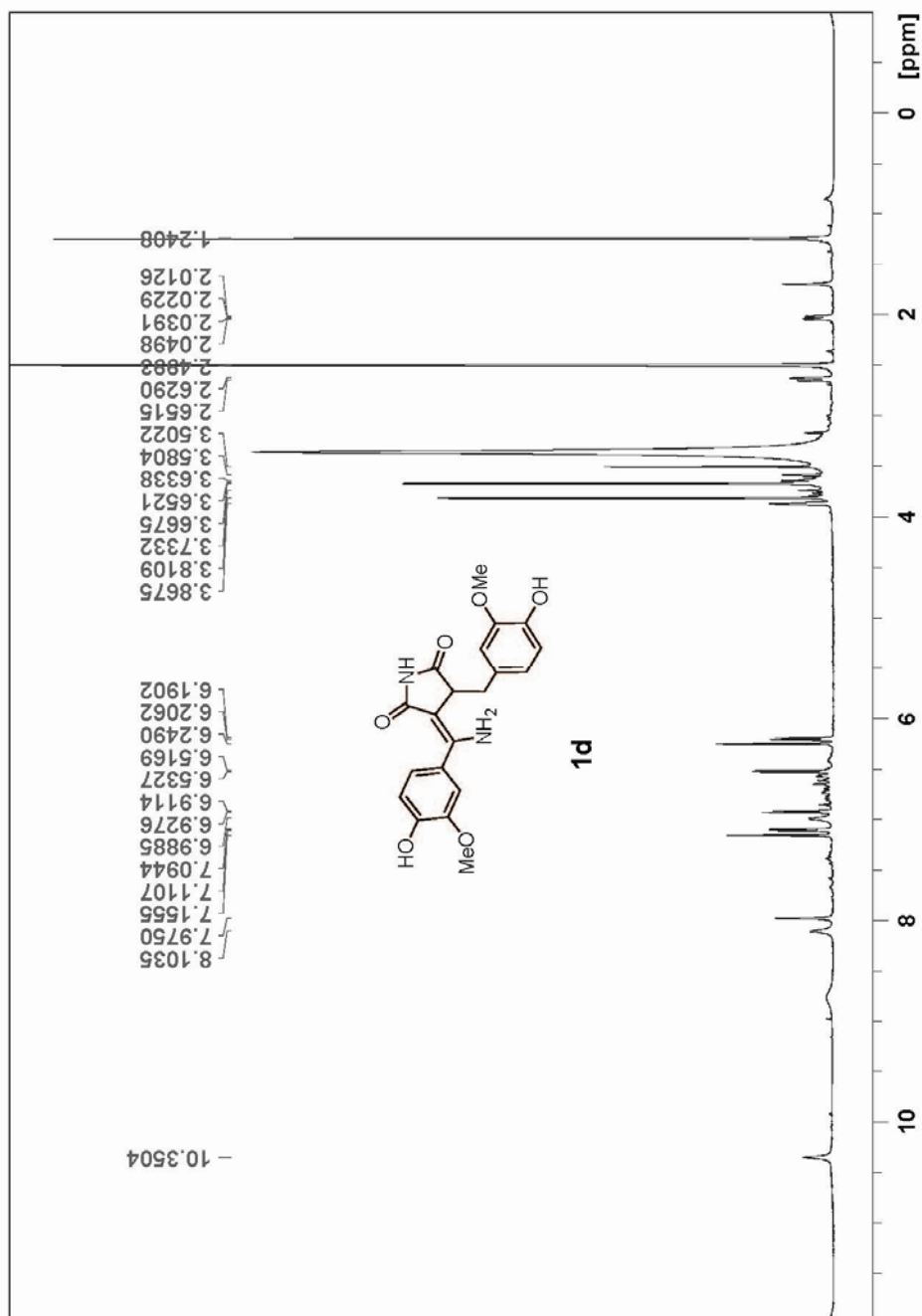
$^1\text{H}$  NMR spectrum of **1c** (500 MHz,  $\text{DMSO-d}_6$ )



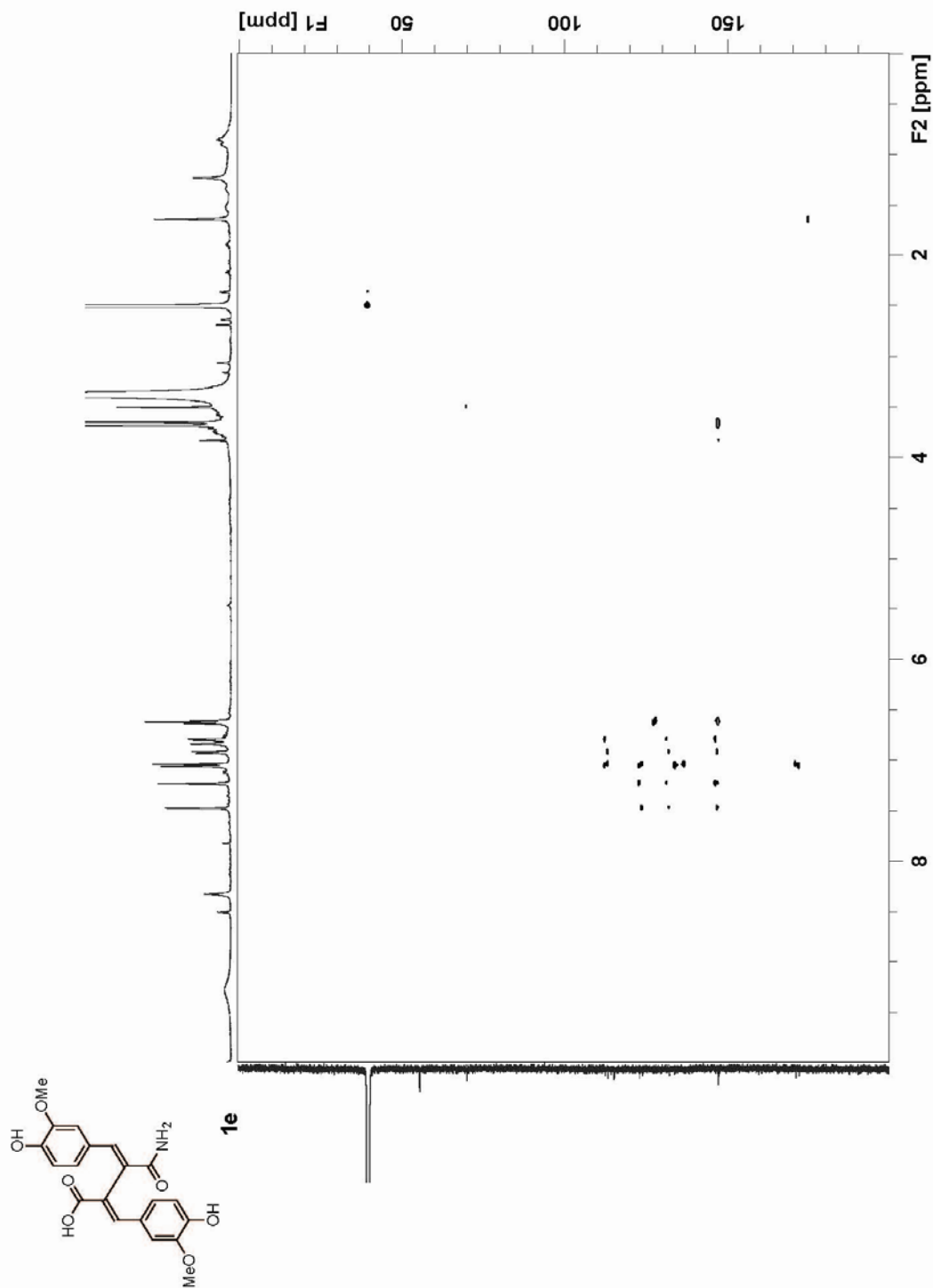
$^{13}\text{C}$  NMR spectrum of **1d** (125 MHz, DMSO- $d_6$ )



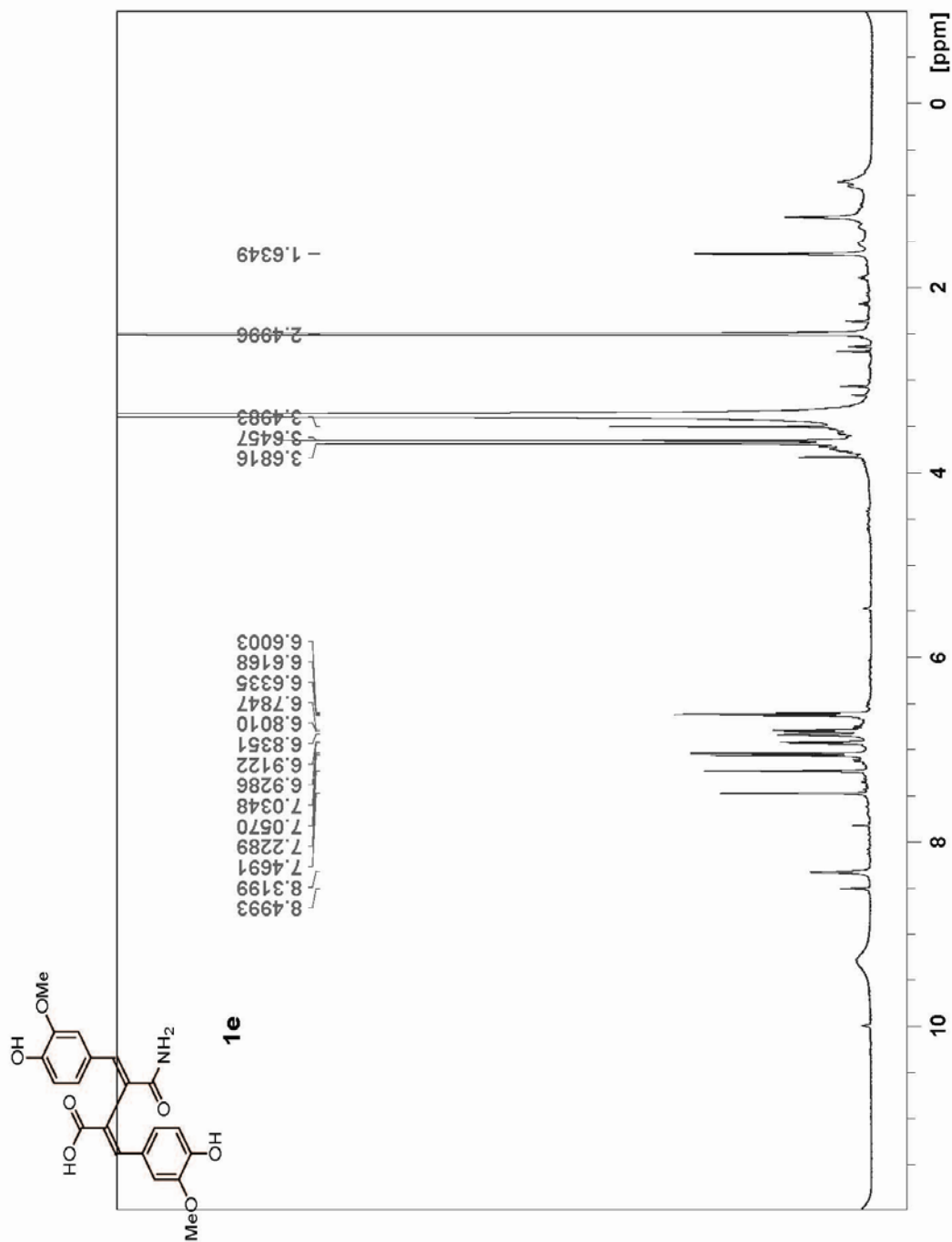
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HMBC spectrum of **1e** (DMSO-d<sub>6</sub>)

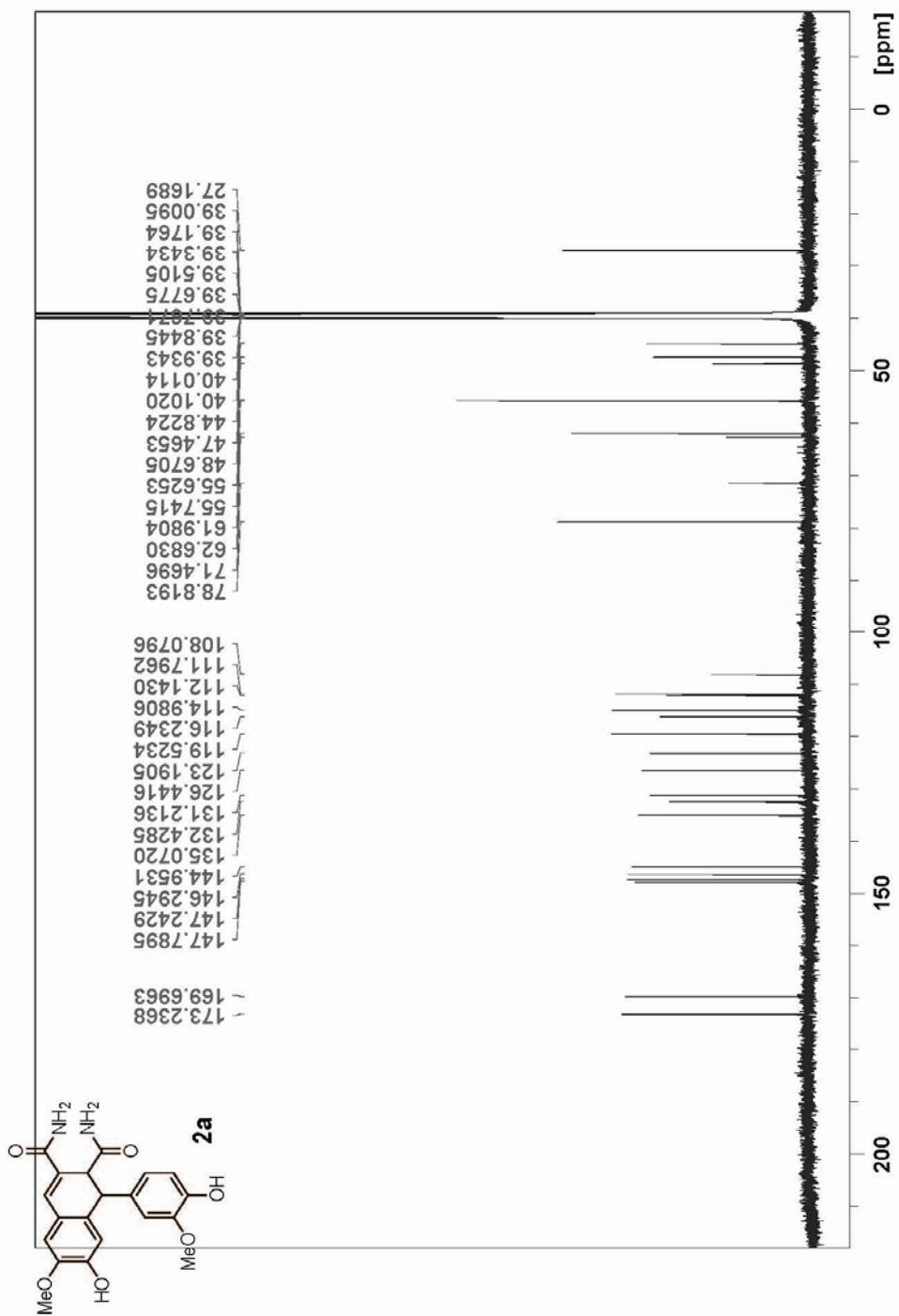


$^1\text{H}$  NMR spectrum of **1e** (500 MHz, DMSO- $d_6$ )

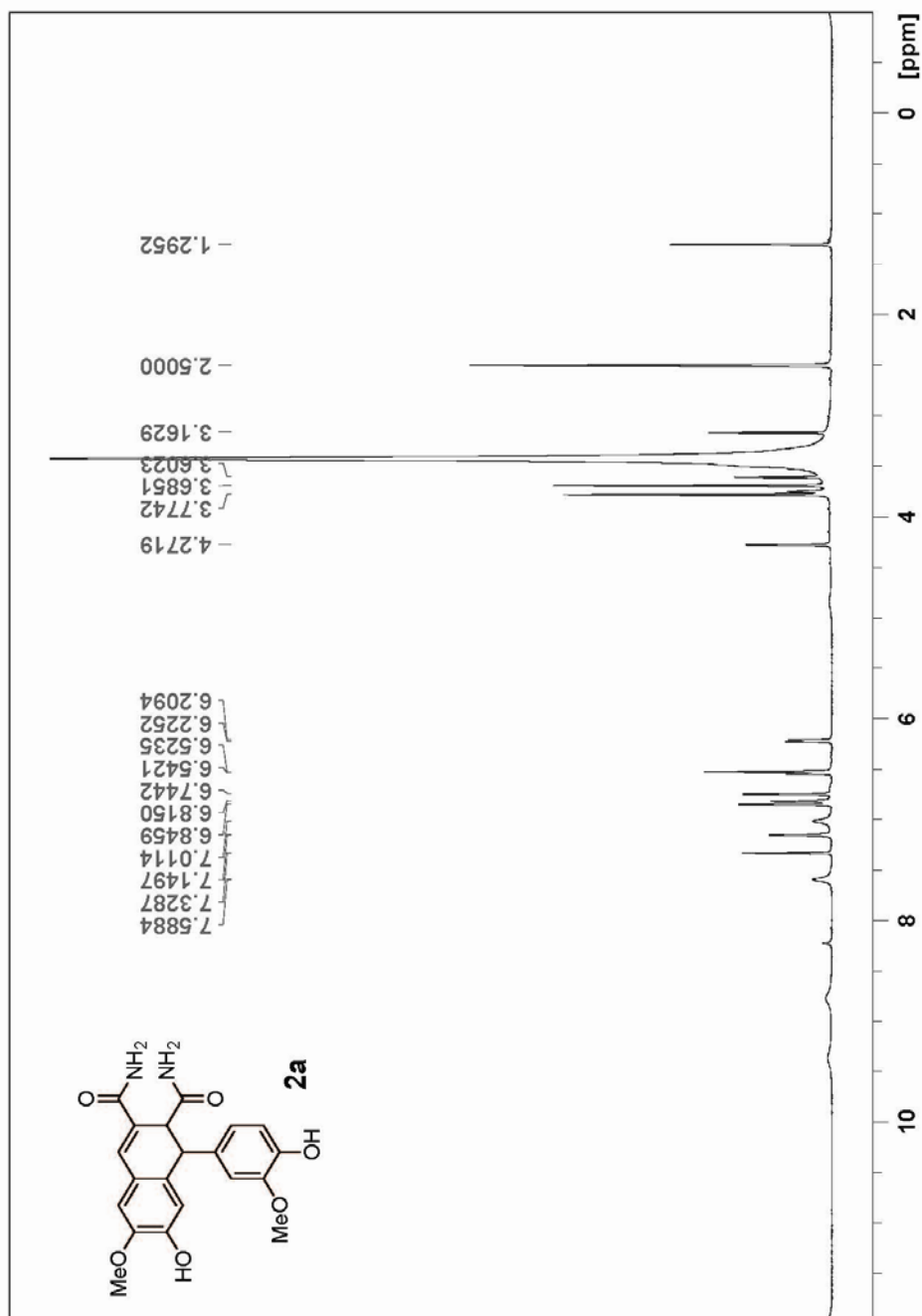




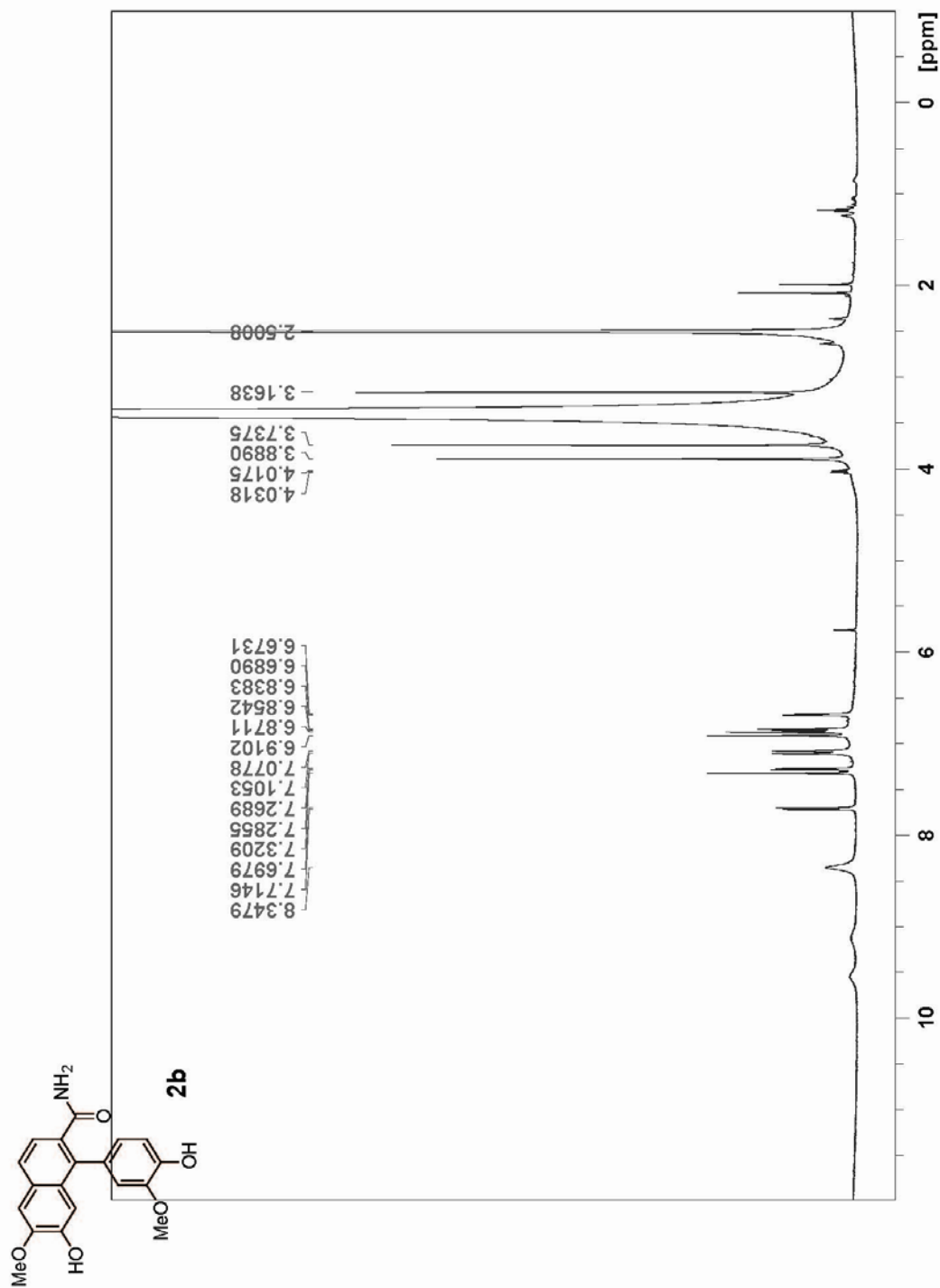
$^{13}\text{C}$  NMR spectrum of **2a** (125 MHz, DMSO- $d_6$ )



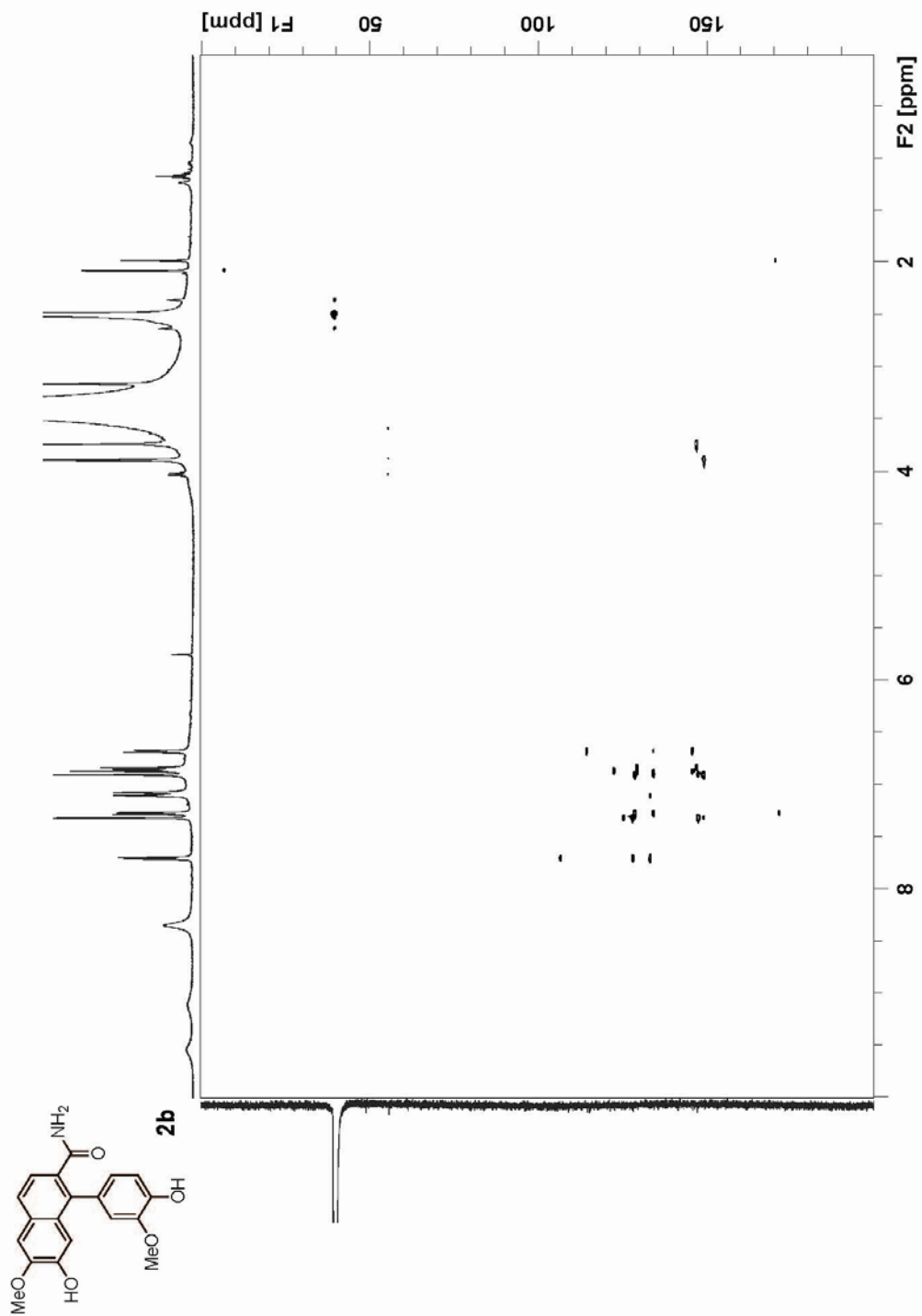
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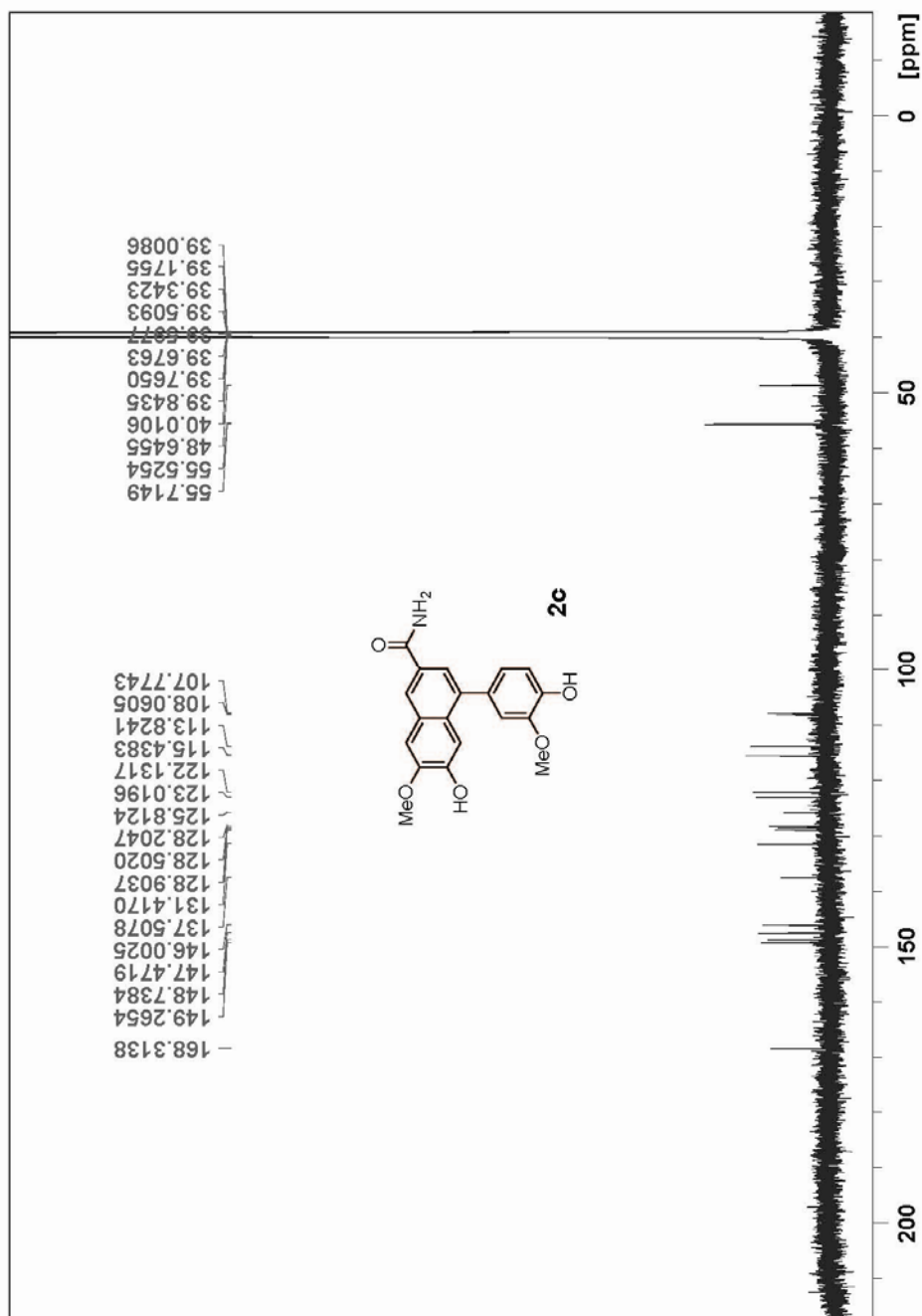
<sup>1</sup>H NMR spectrum of **2b** (500 MHz, DMSO-d<sub>6</sub>)



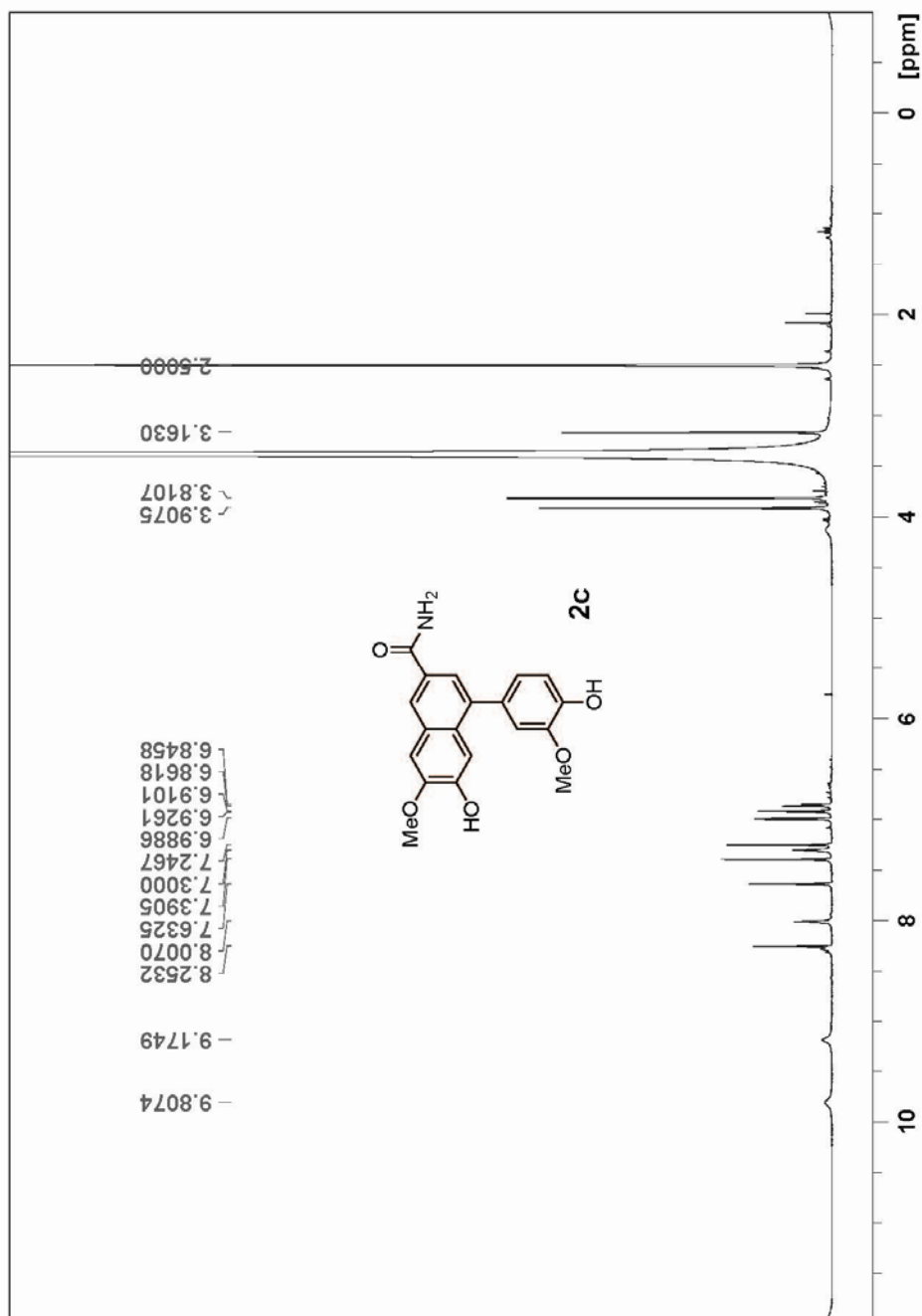
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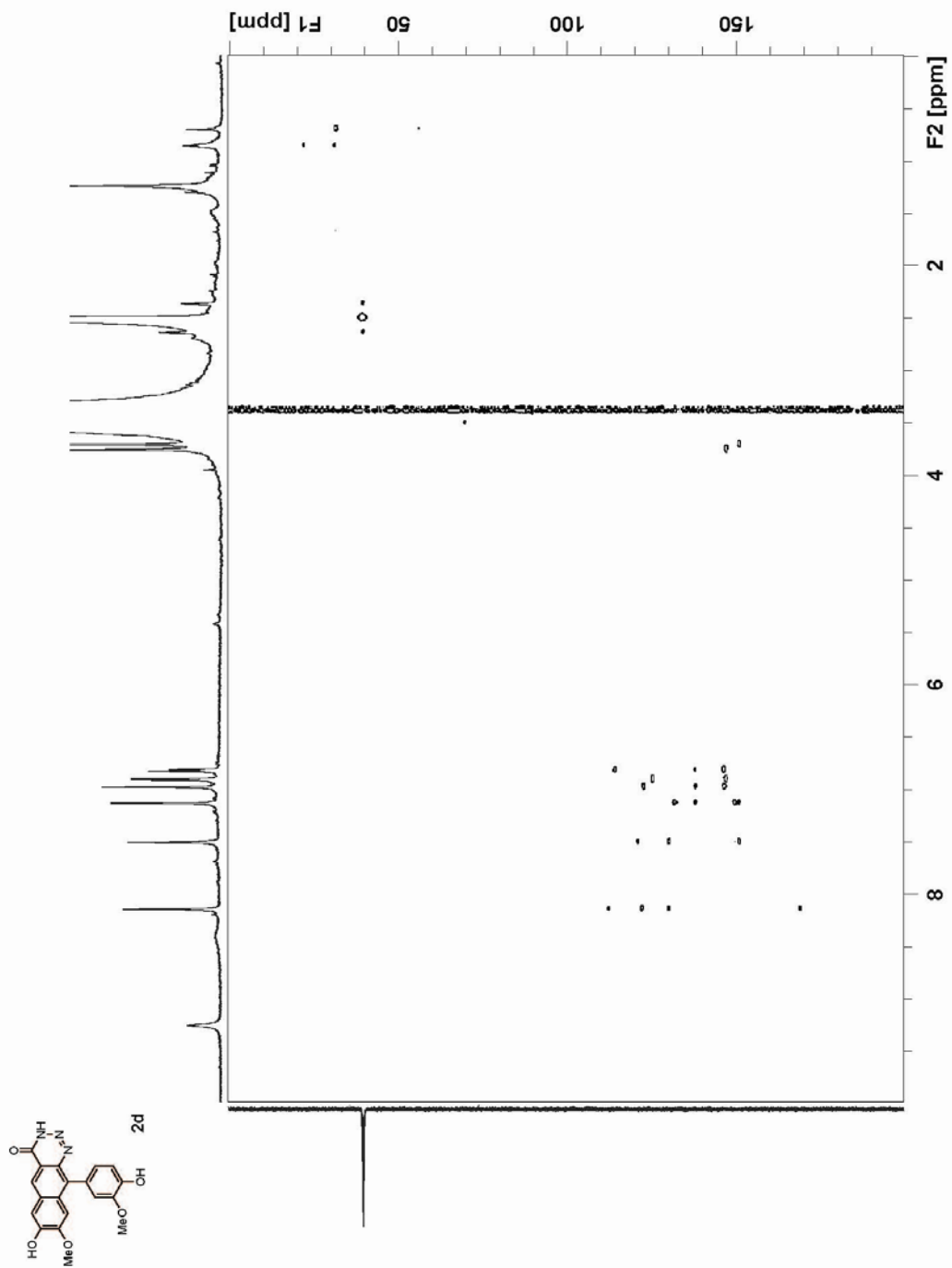
$^{13}\text{C}$  NMR spectrum of **2c** (125 MHz, DMSO- $d_6$ )



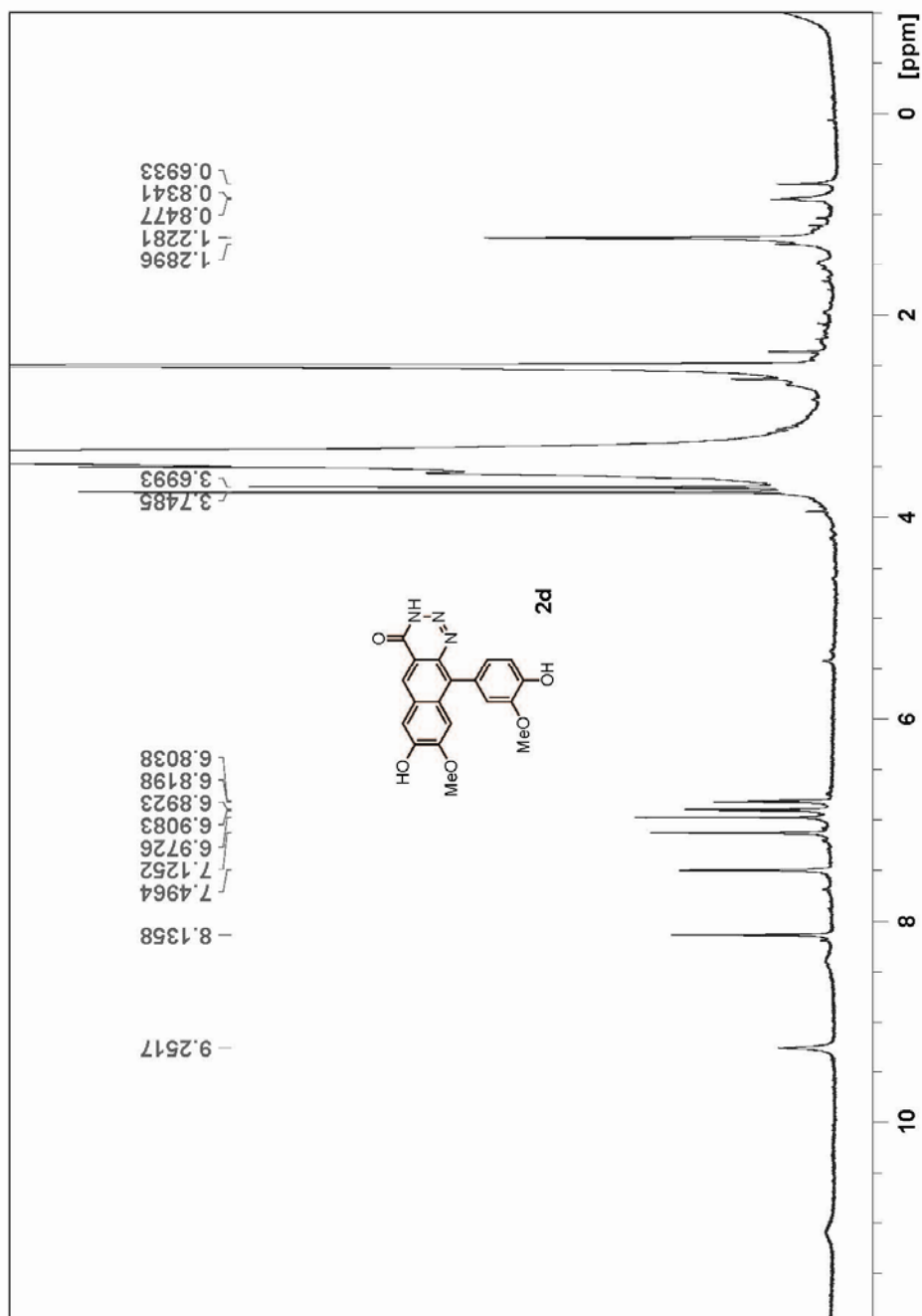
$^1\text{H}$  NMR spectrum of **2c** (500 MHz,  $\text{DMSO-d}_6$ )



HMBC spectrum of **2d** (DMSO-d<sub>6</sub>)

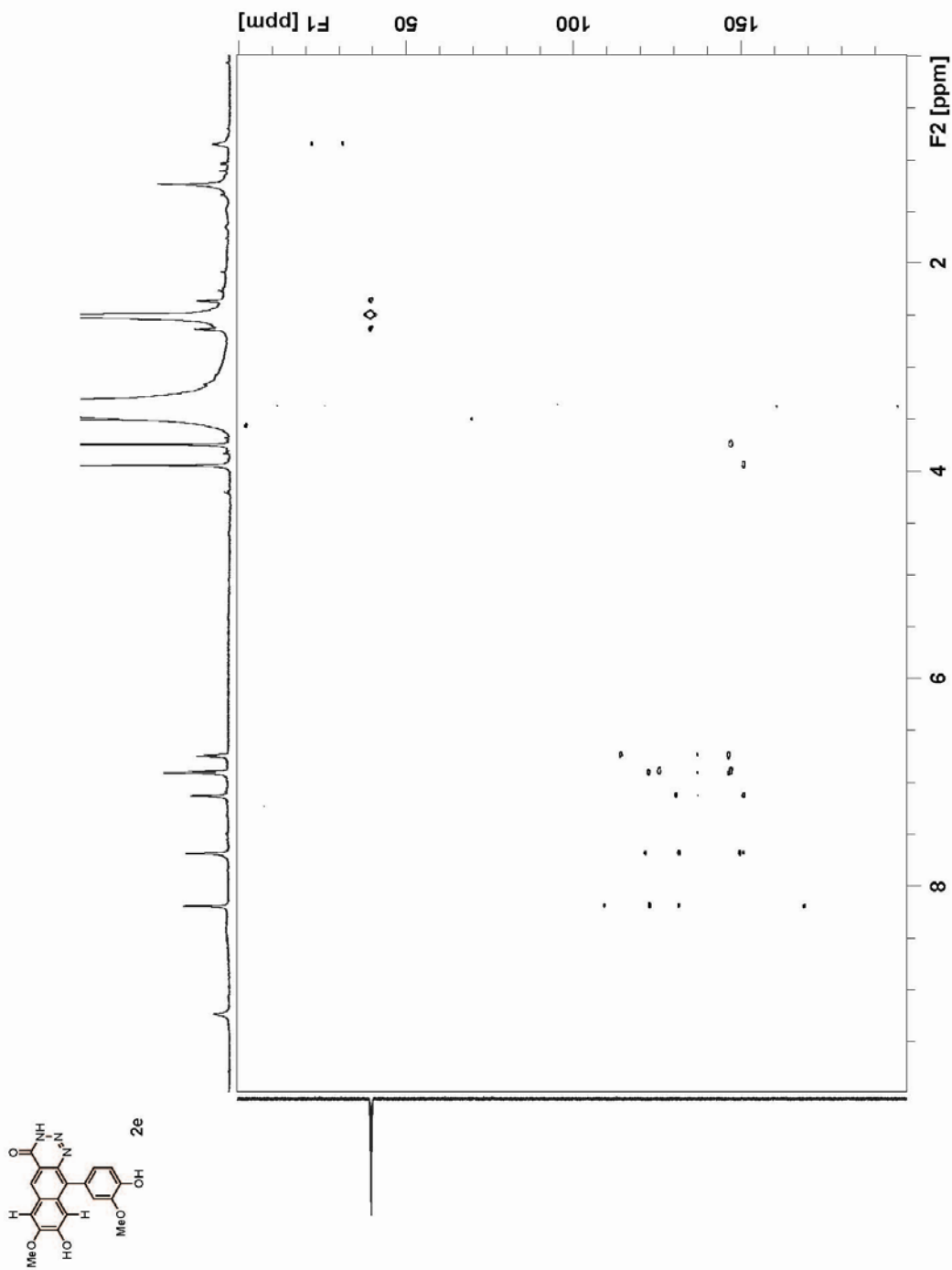


$^1\text{H}$  NMR spectrum of **2d** (500 MHz,  $\text{DMSO-d}_6$ )

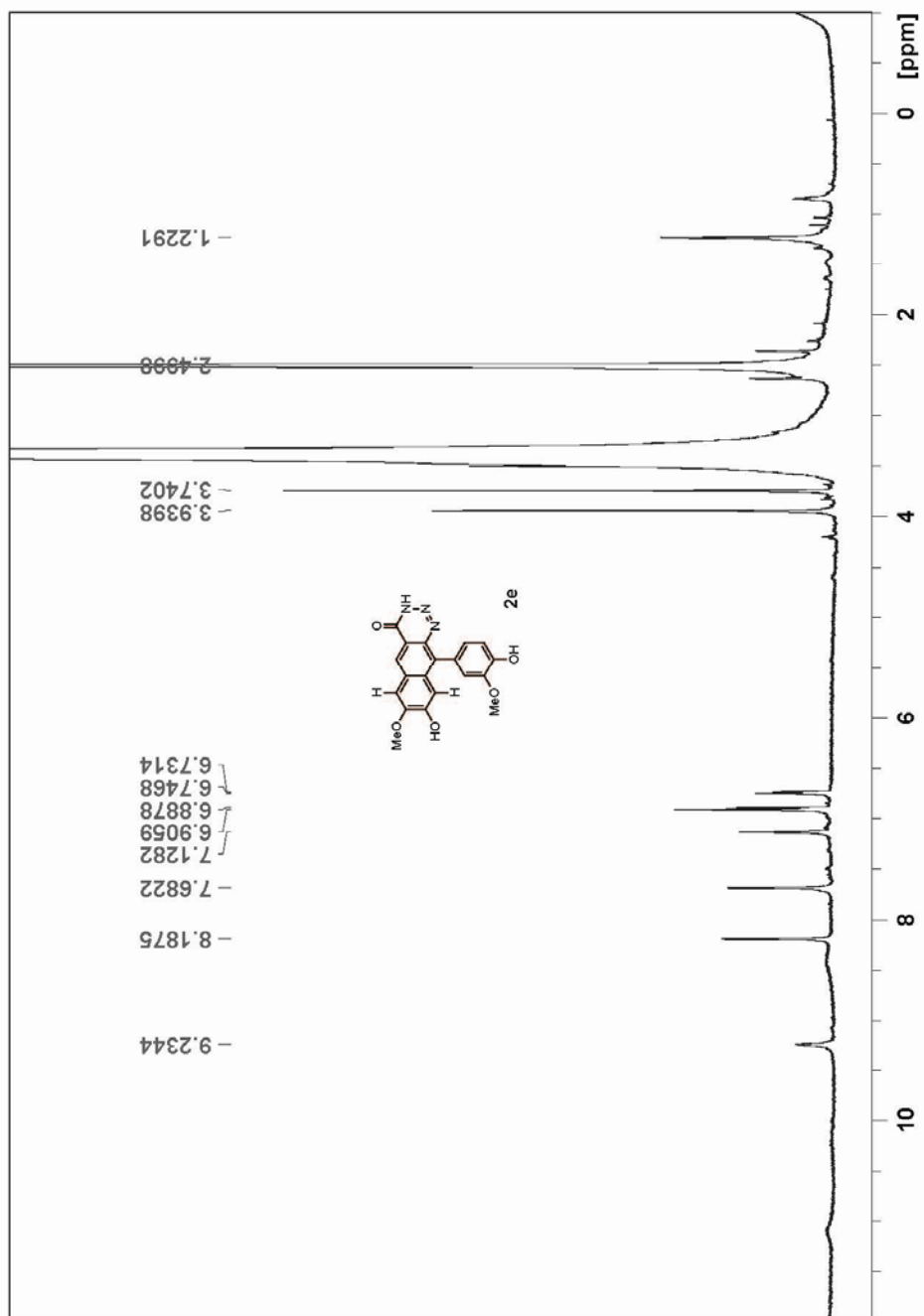




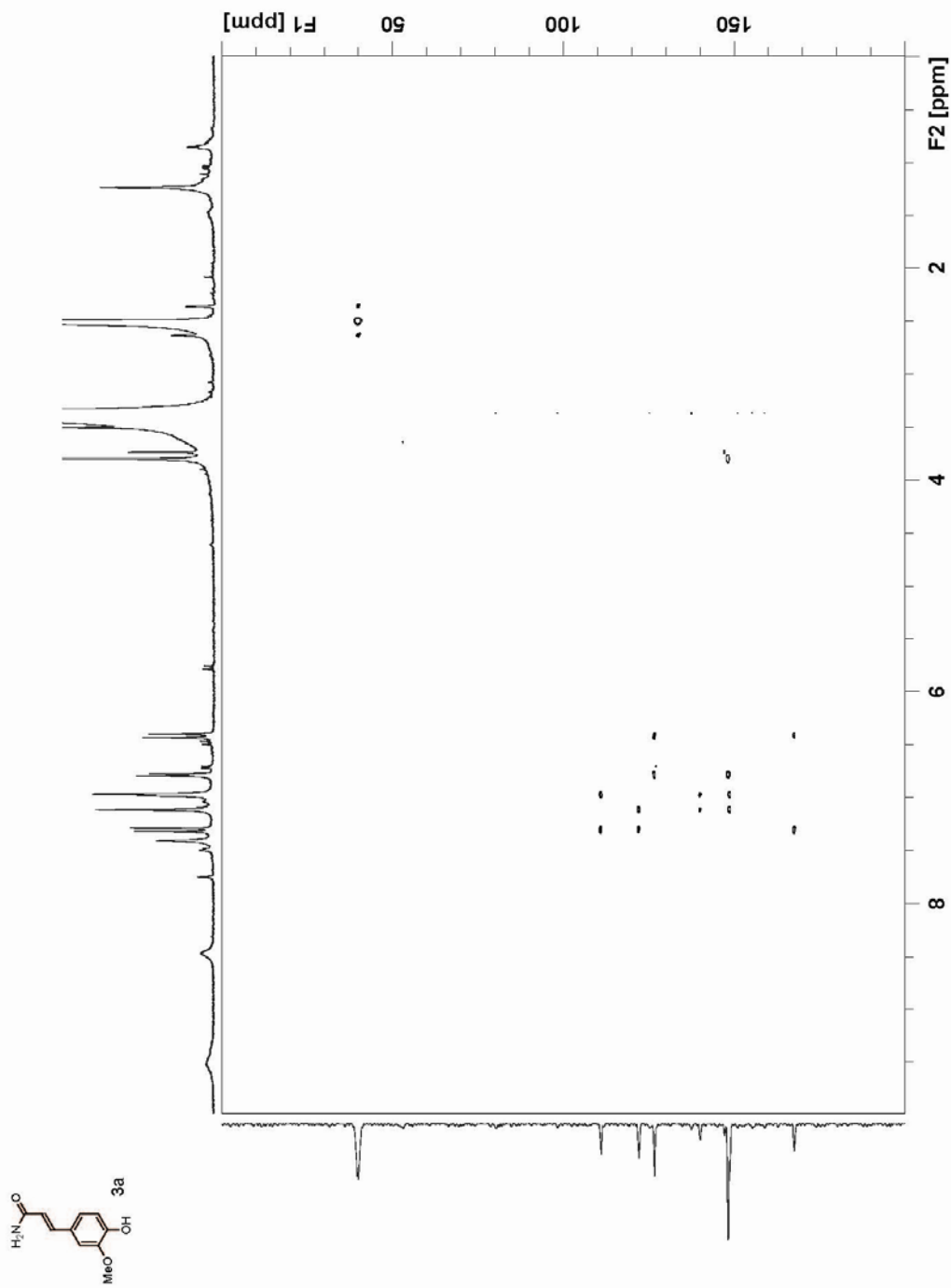
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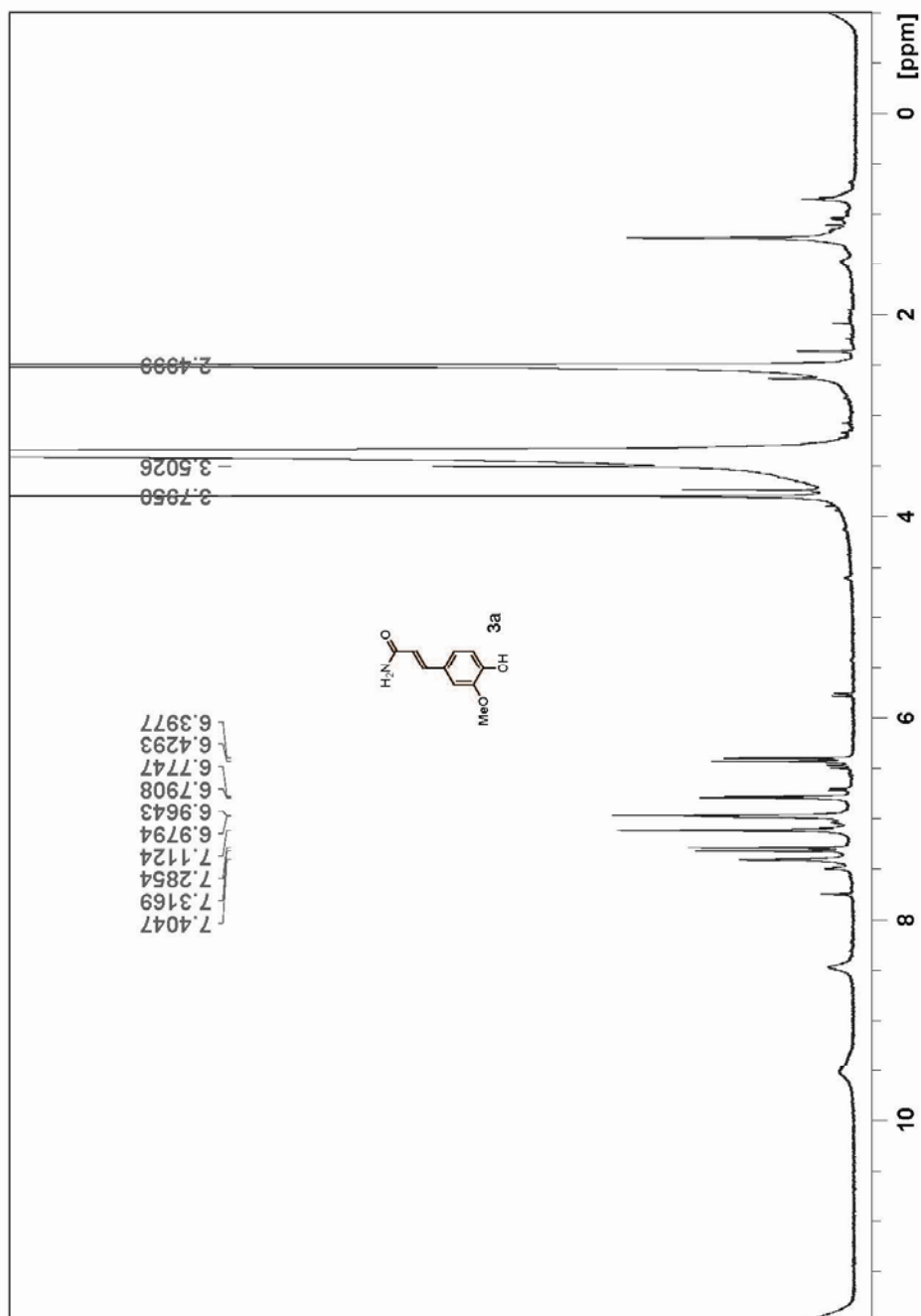
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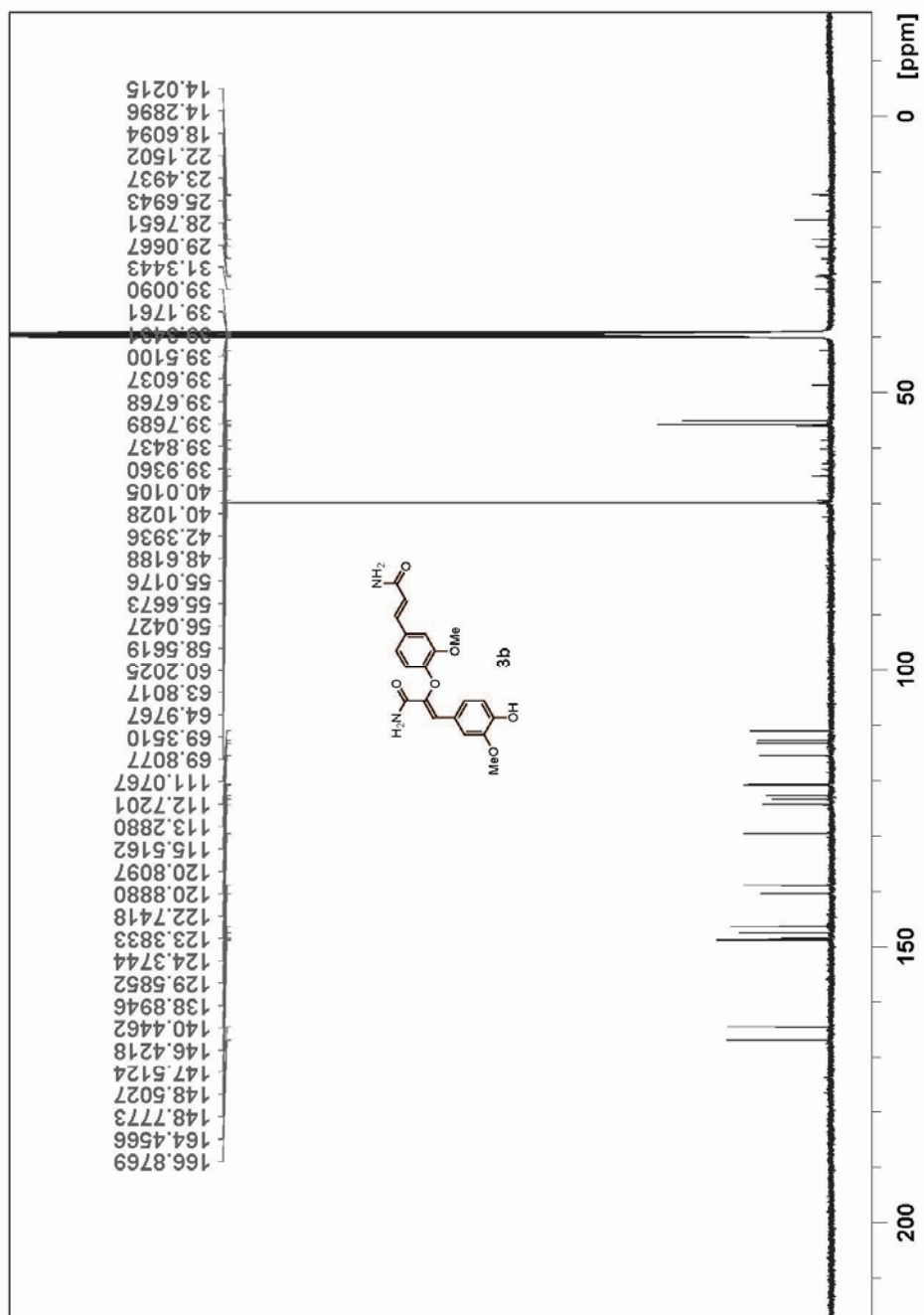
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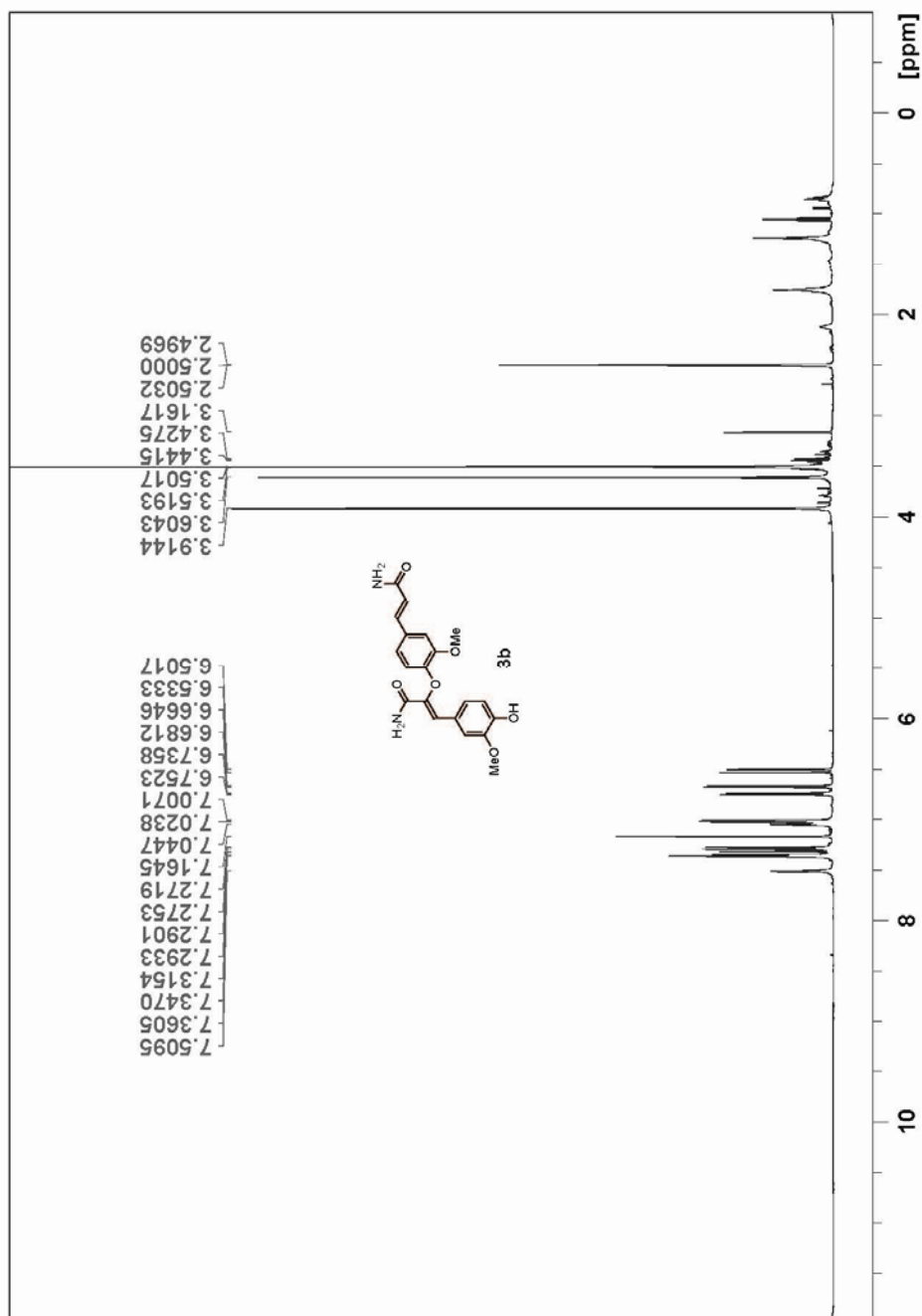
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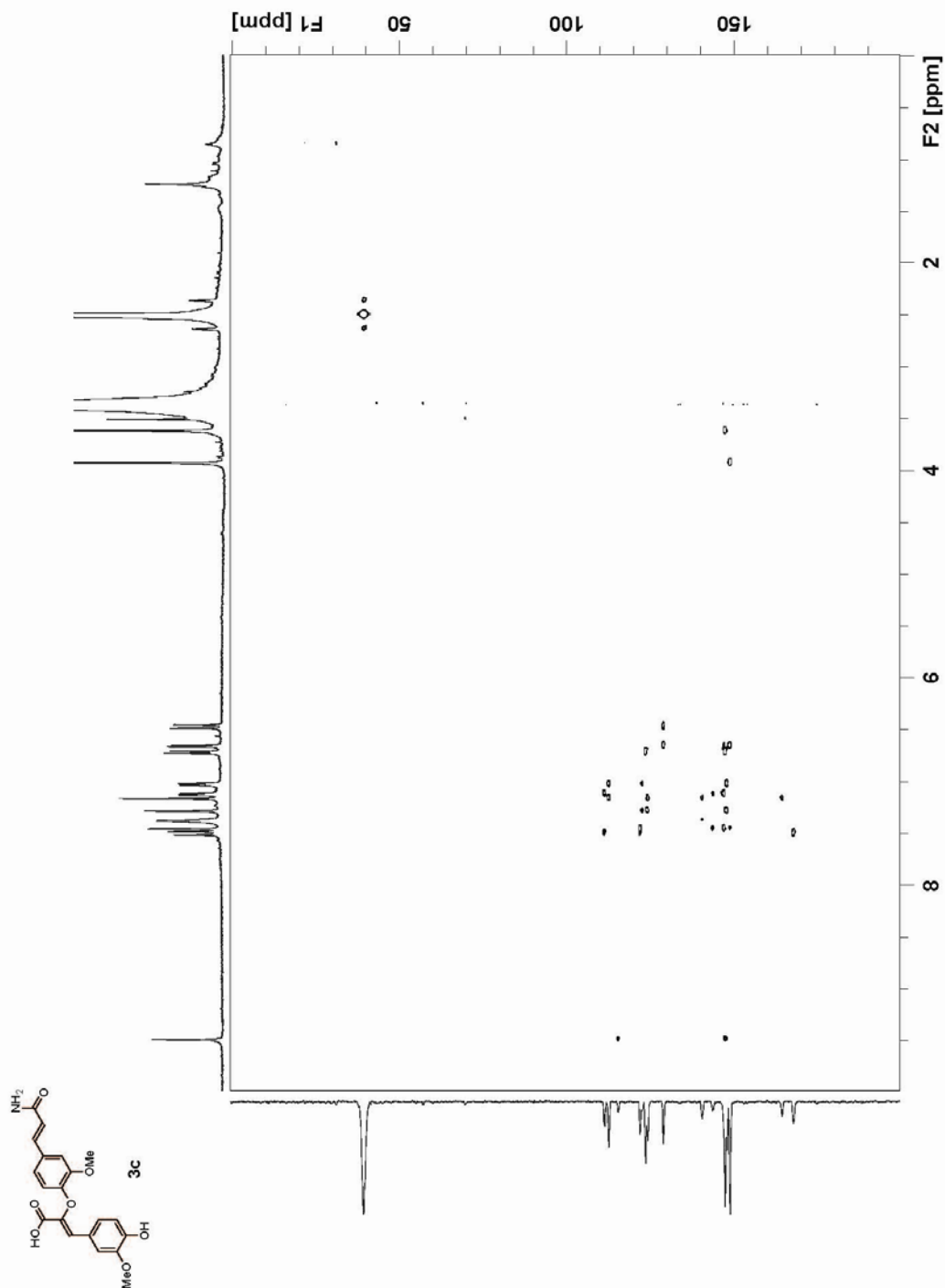
$^{13}\text{C}$  NMR spectrum of **3b** (125 MHz, DMSO- $d_6$ )



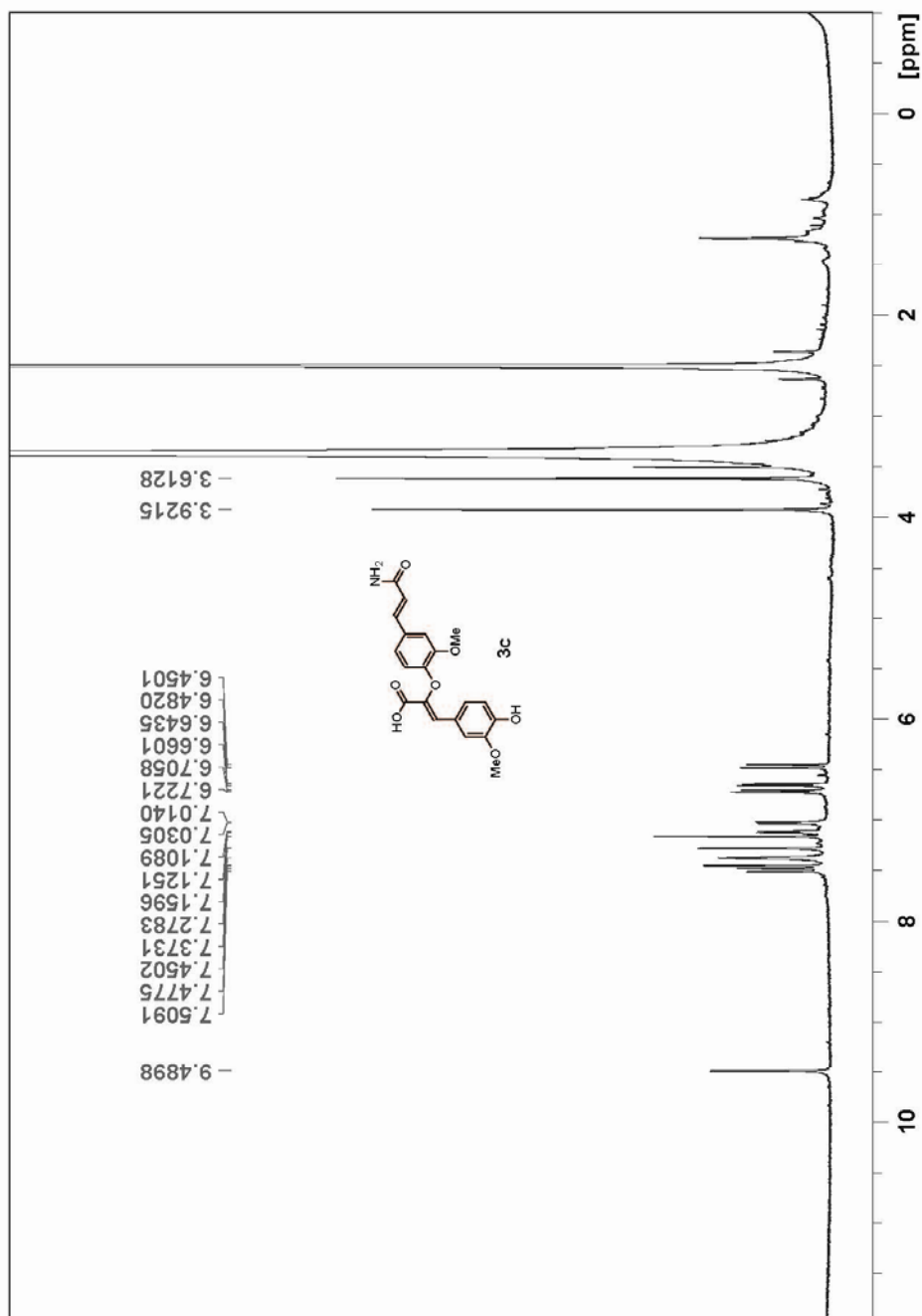
$^1\text{H}$  NMR spectrum of **3b** (500 MHz,  $\text{DMSO-d}_6$ )



HMBC spectrum of **3c** (DMSO-d<sub>6</sub>)

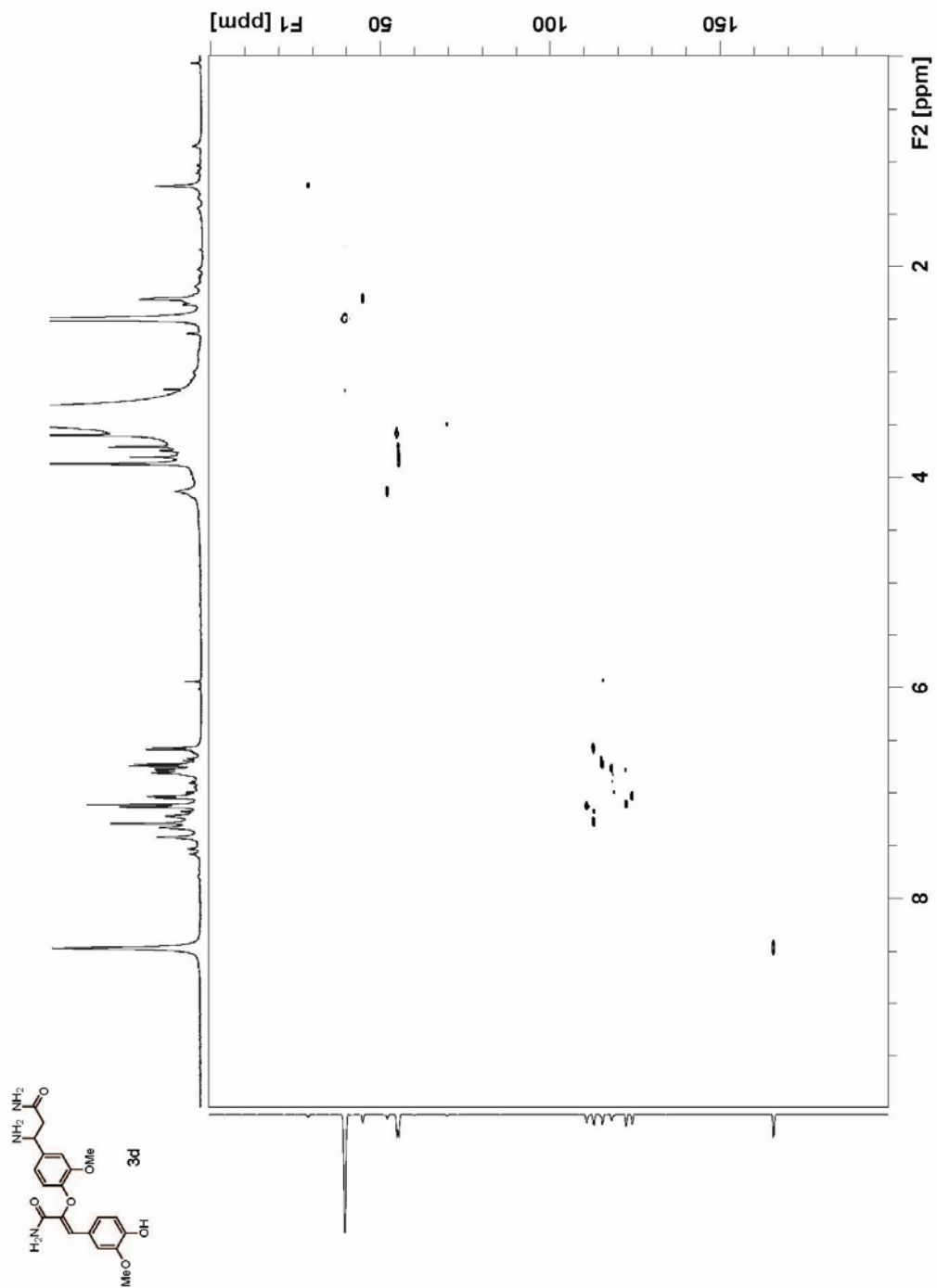


$^1\text{H}$  NMR spectrum of **3c** (500 MHz,  $\text{DMSO-d}_6$ )

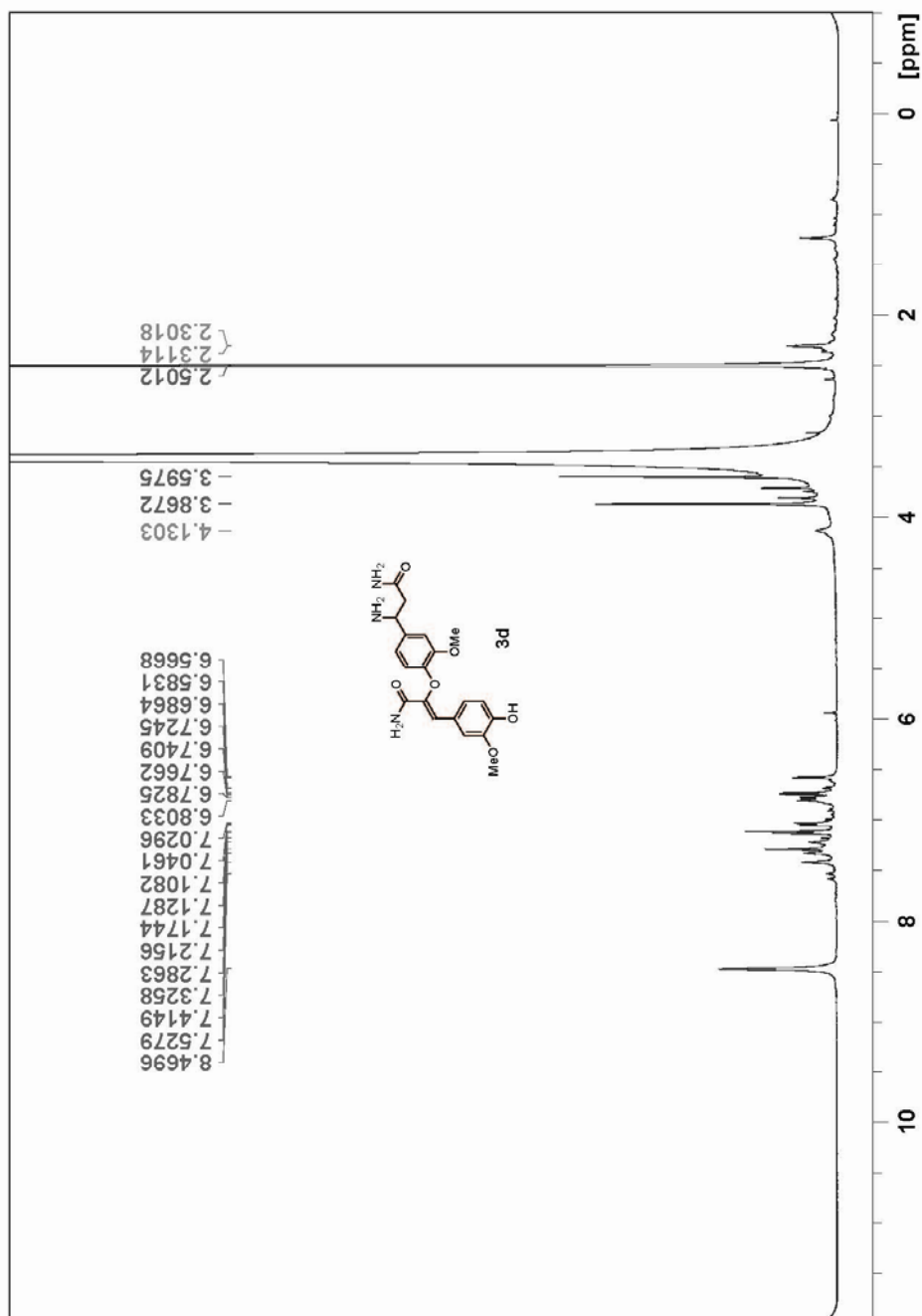




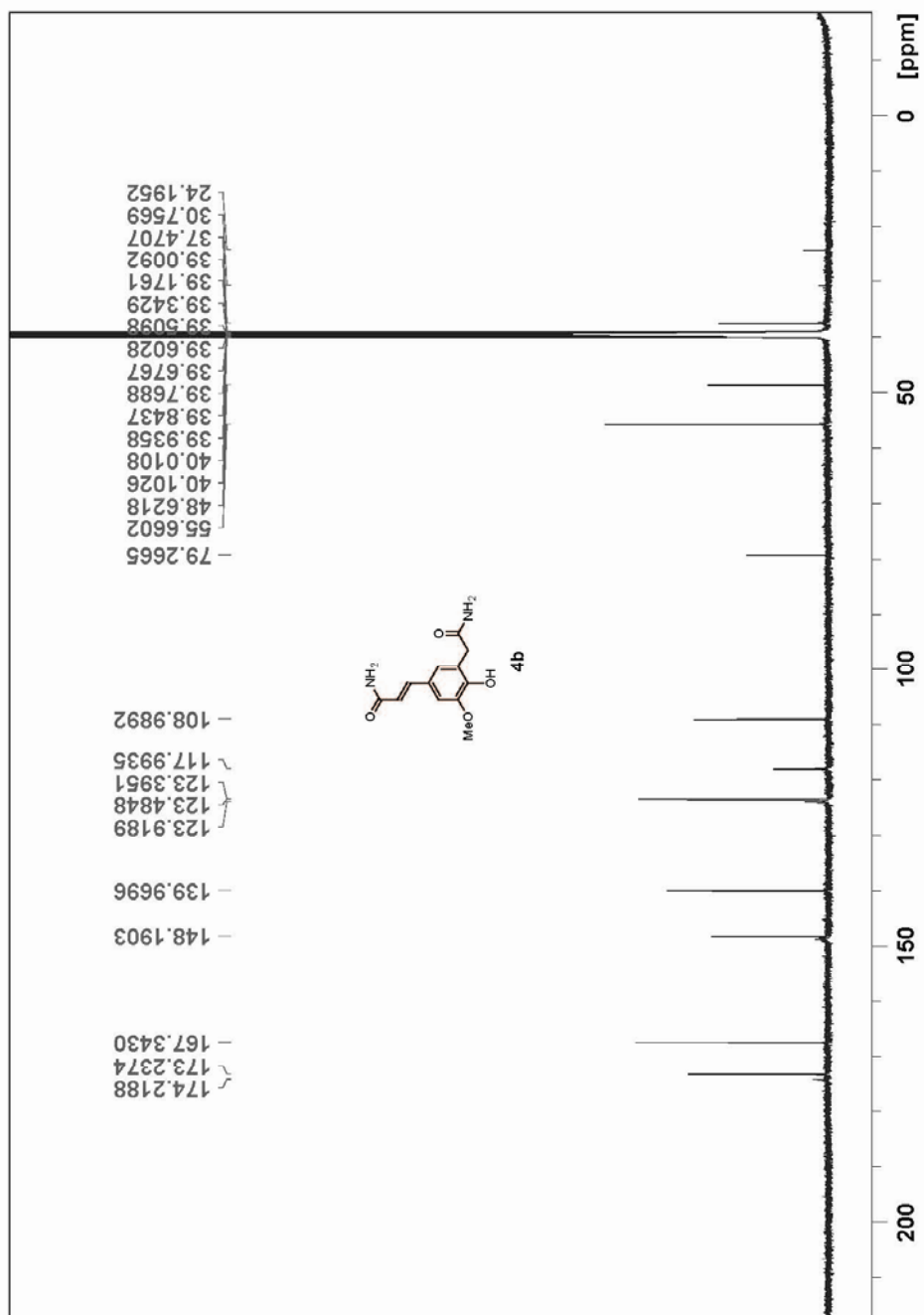
HMBC spectrum of **3d** (DMSO-d<sub>6</sub>)



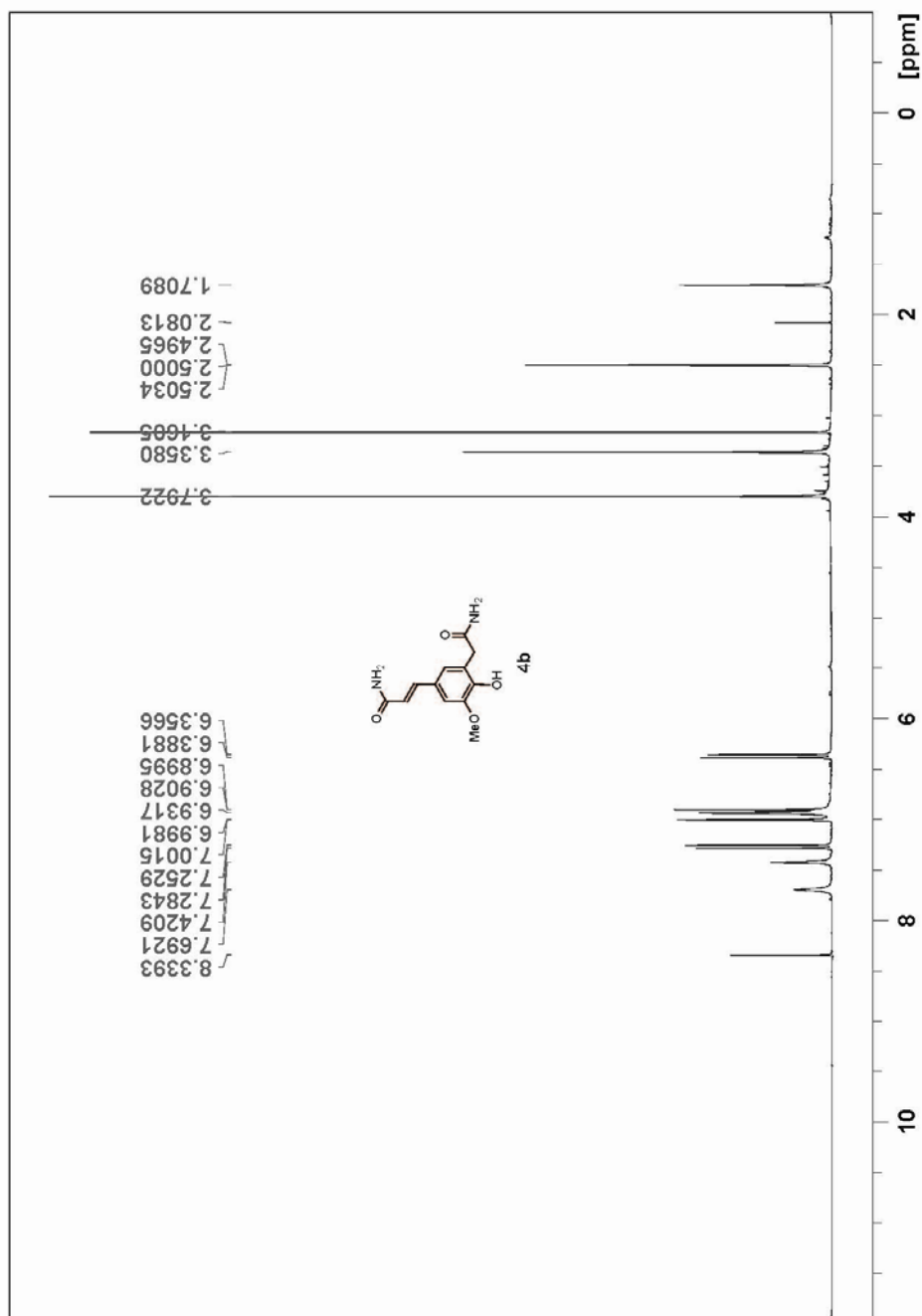
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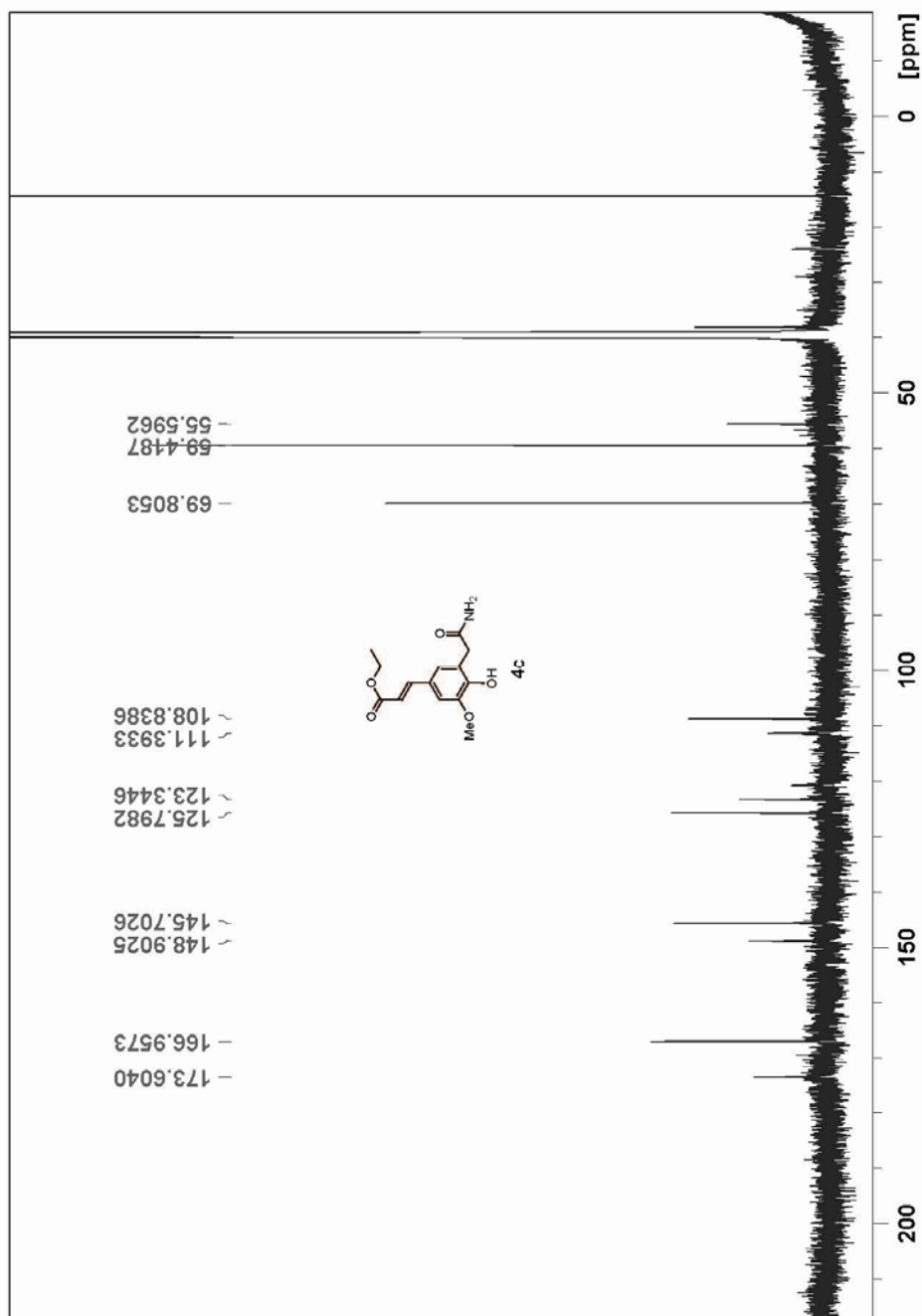
$^{13}\text{C}$  NMR spectrum of **4b** (125 MHz, DMSO- $d_6$ )



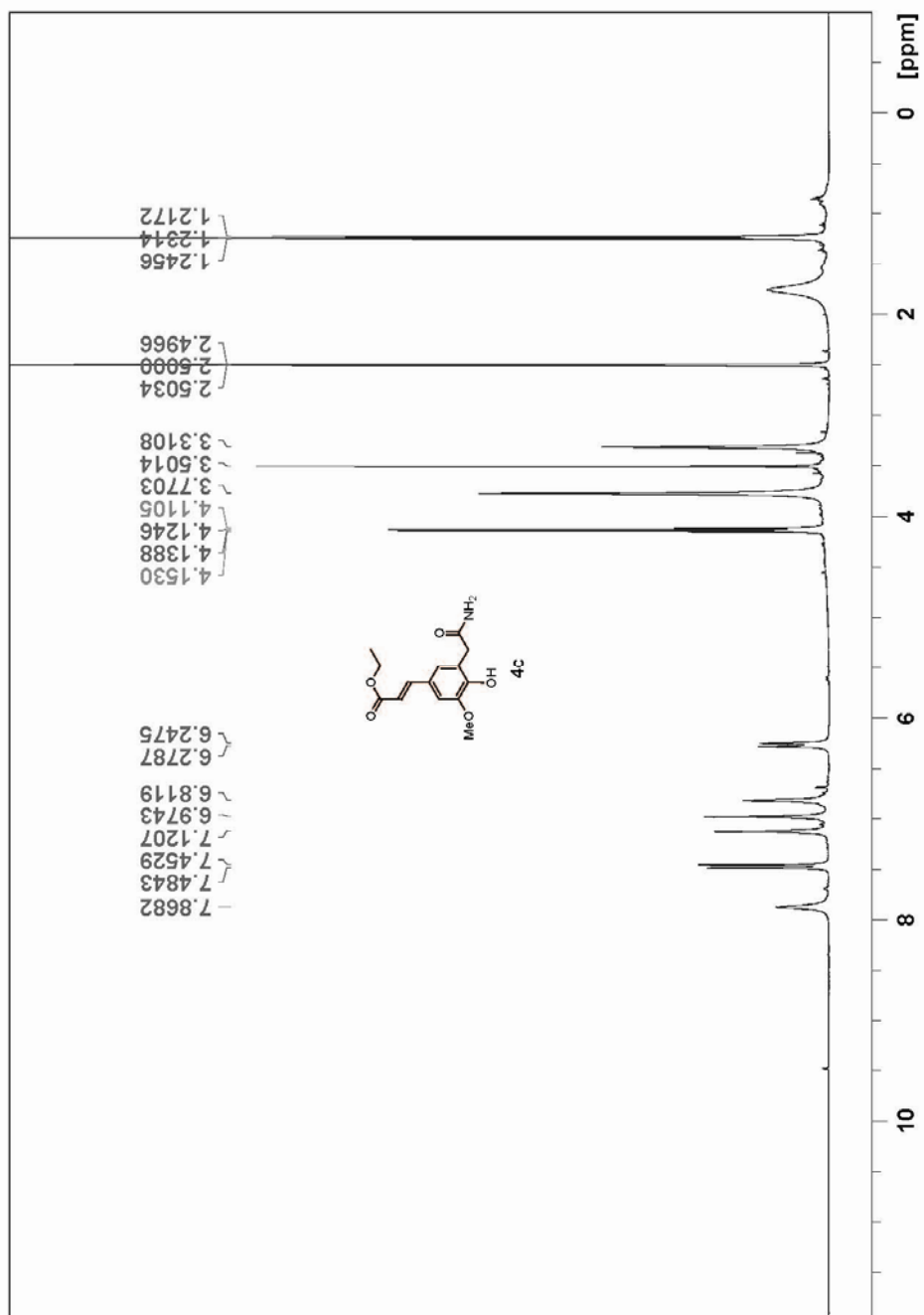
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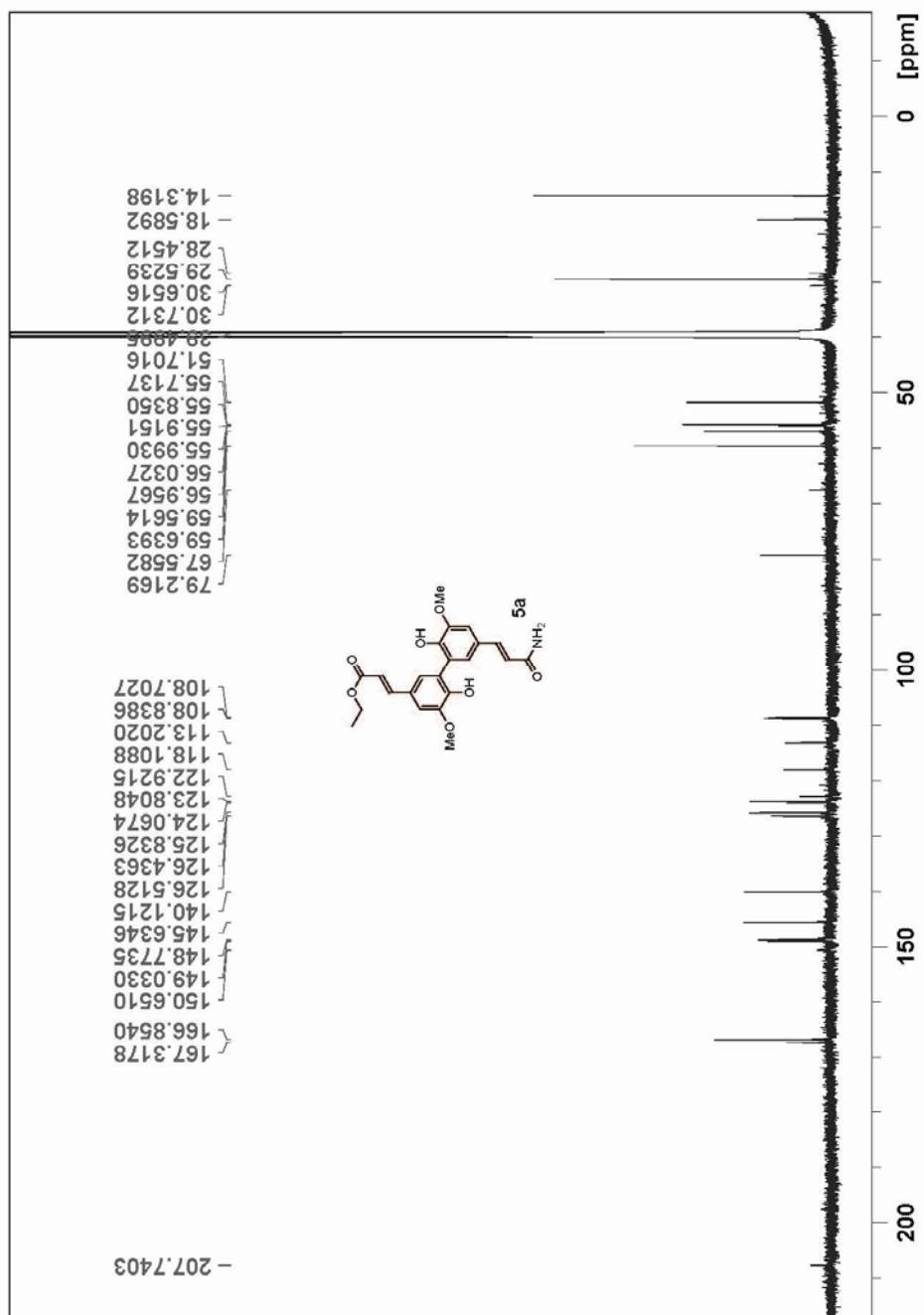
$^{13}\text{C}$  NMR spectrum of **4c** (125 MHz, DMSO- $d_6$ )



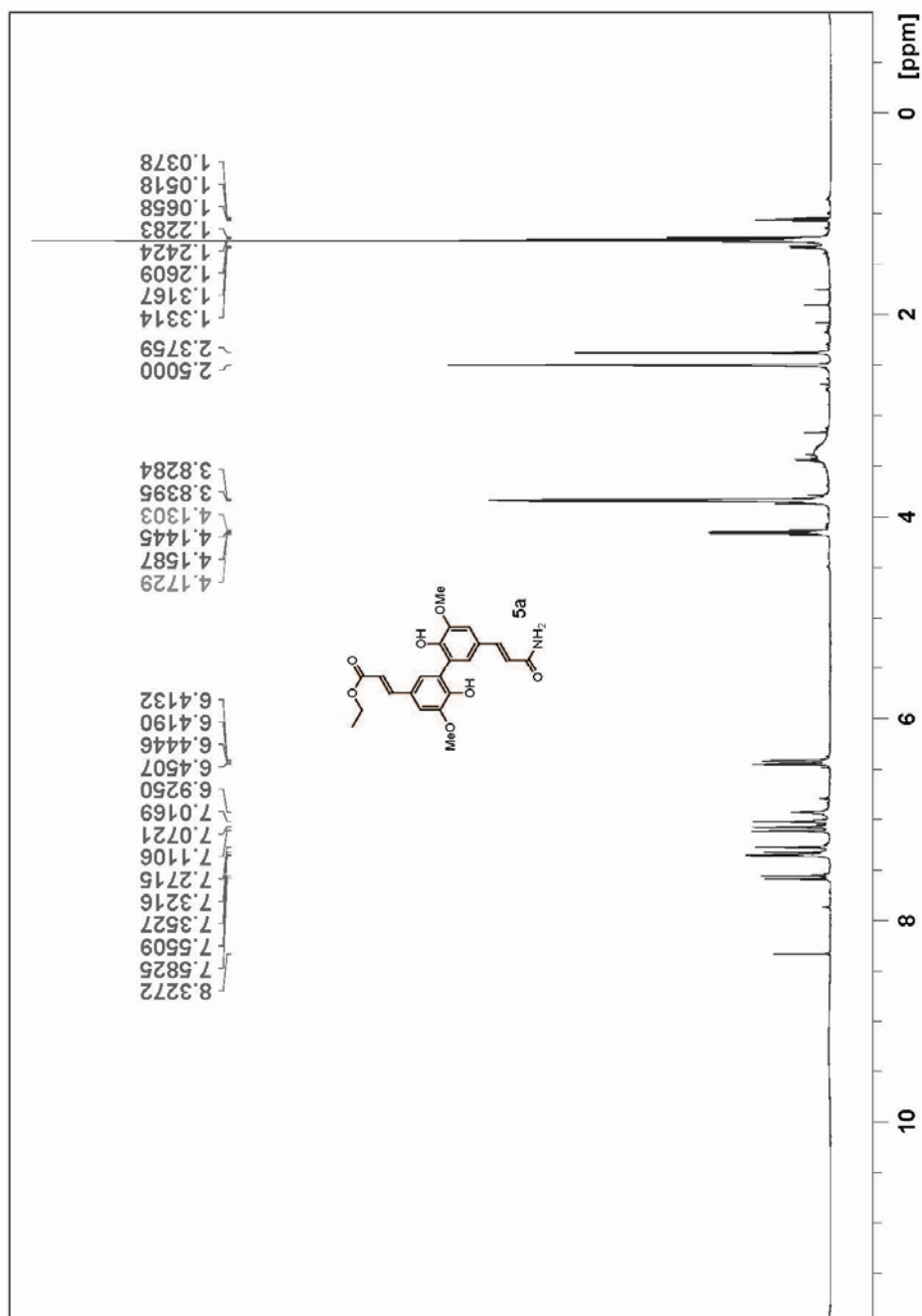
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$^{13}\text{C}$  NMR spectrum of **5a** (125 MHz, DMSO- $d_6$ )

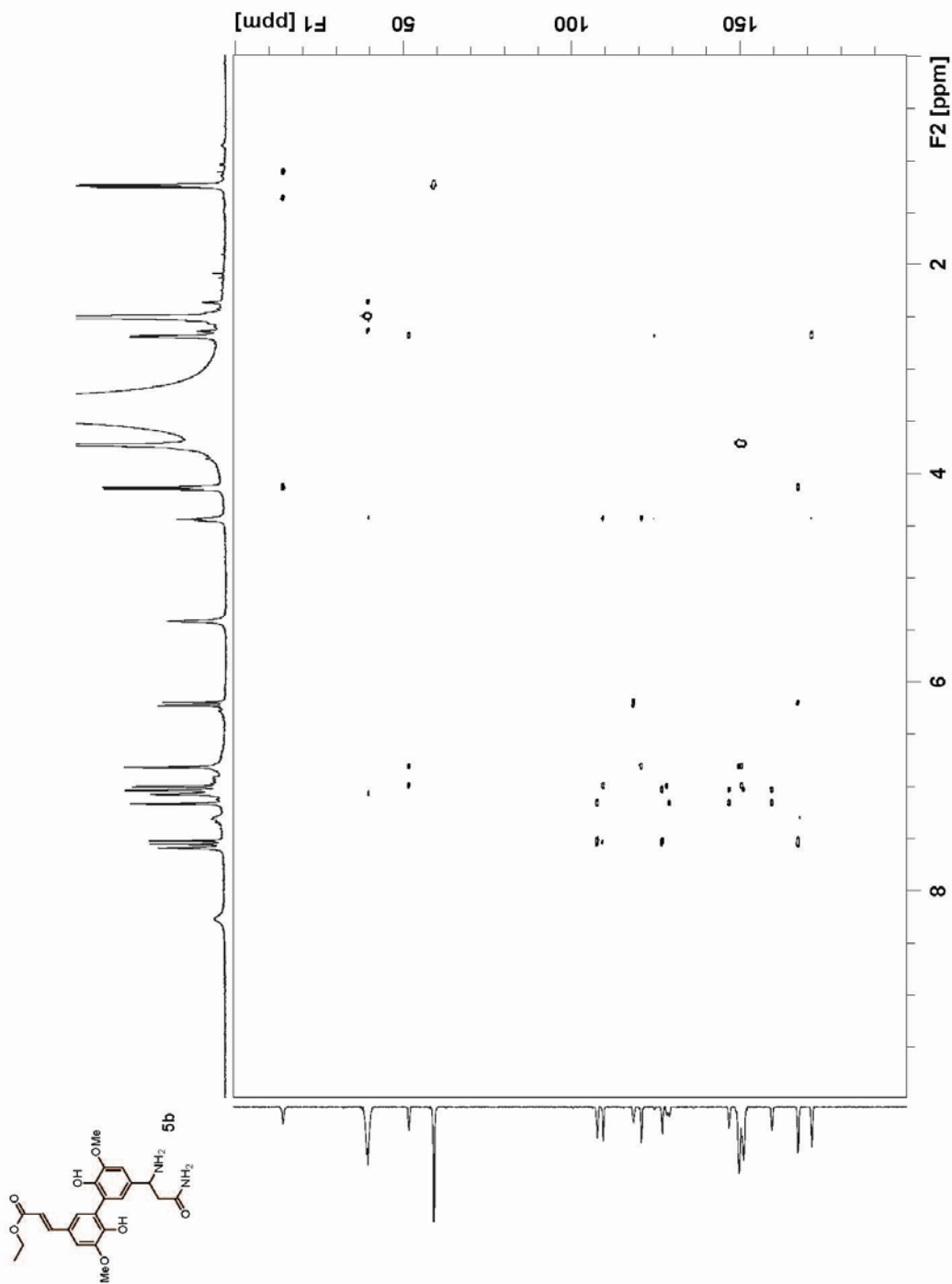


$^1\text{H}$  NMR spectrum of **5a** (500 MHz,  $\text{DMSO-d}_6$ )

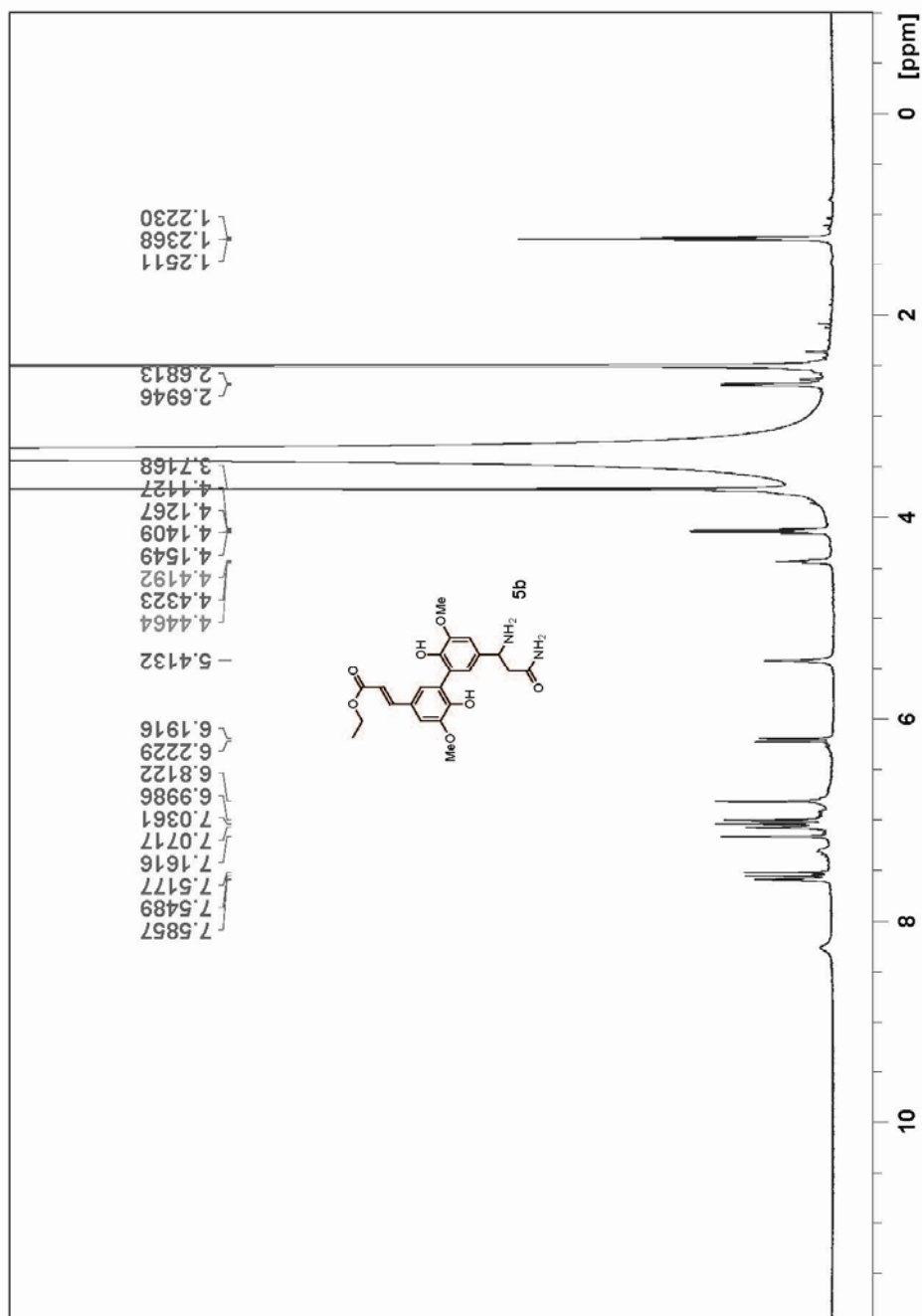




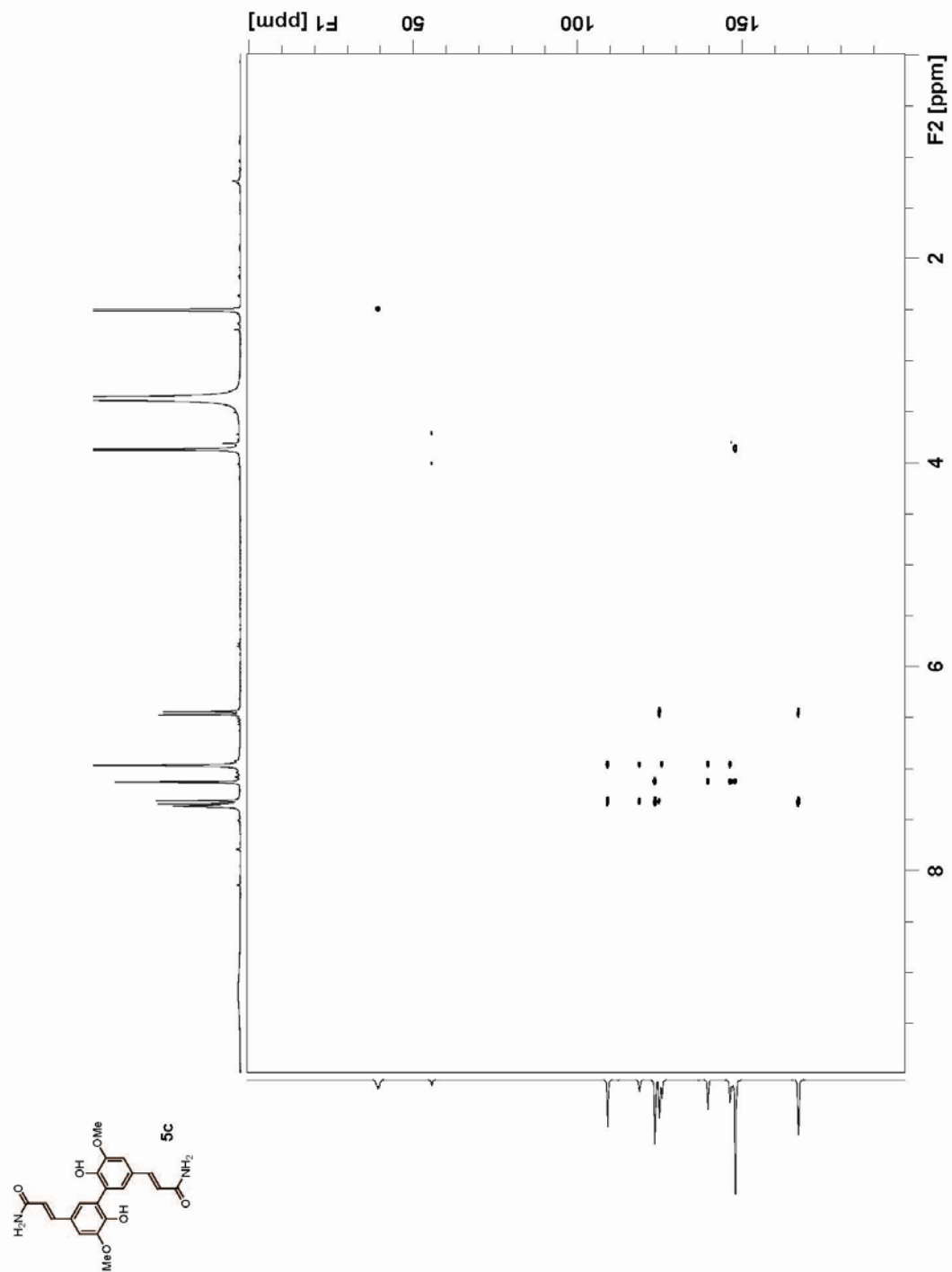
HMBC spectrum of **5b** (DMSO-d<sub>6</sub>)



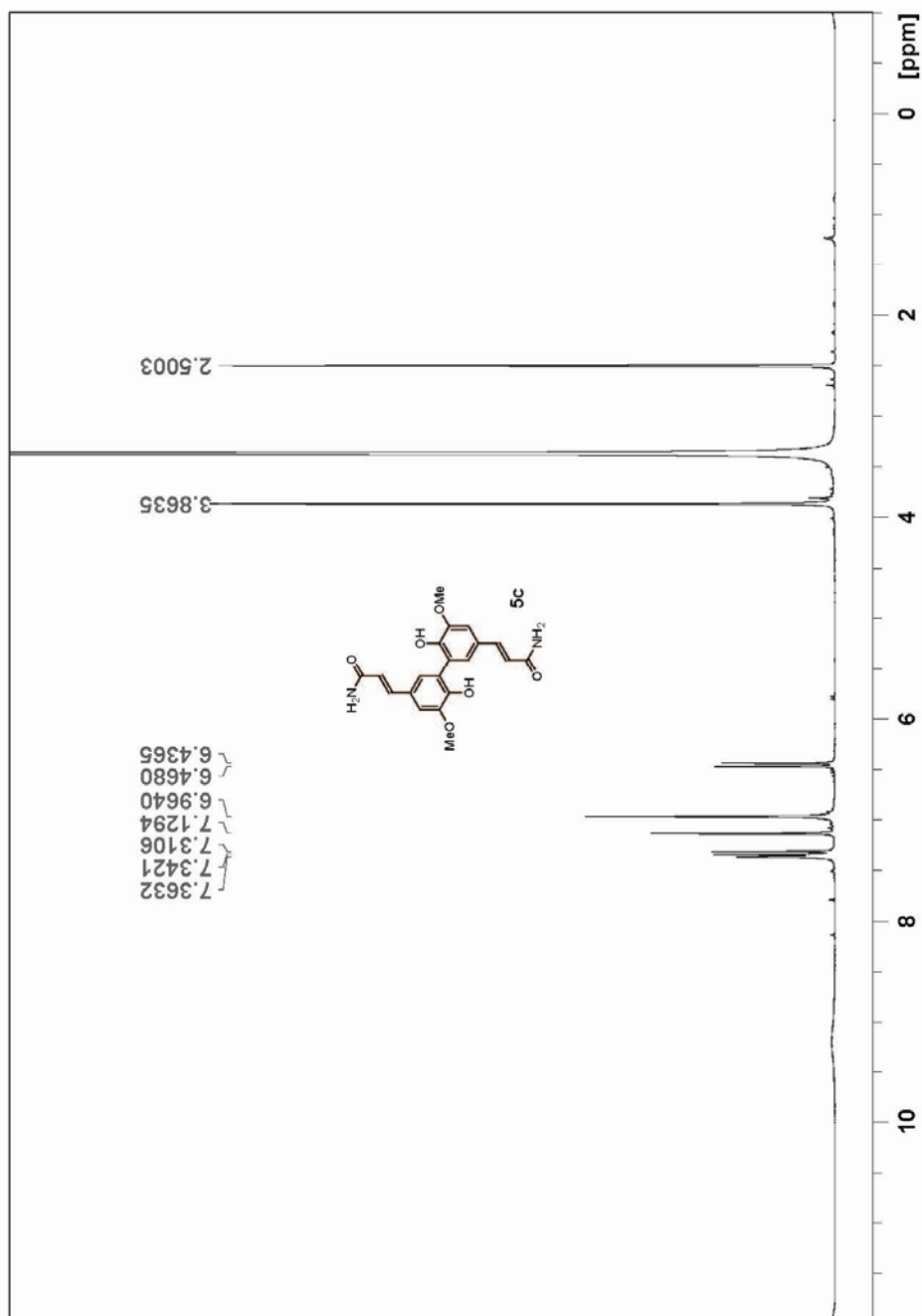
$^1\text{H}$  NMR spectrum of **5b** (500 MHz,  $\text{DMSO-d}_6$ )



HMBC spectrum of **5c** (DMSO-d<sub>6</sub>)



$^1\text{H}$  NMR spectrum of **5c** (500 MHz,  $\text{DMSO-d}_6$ )

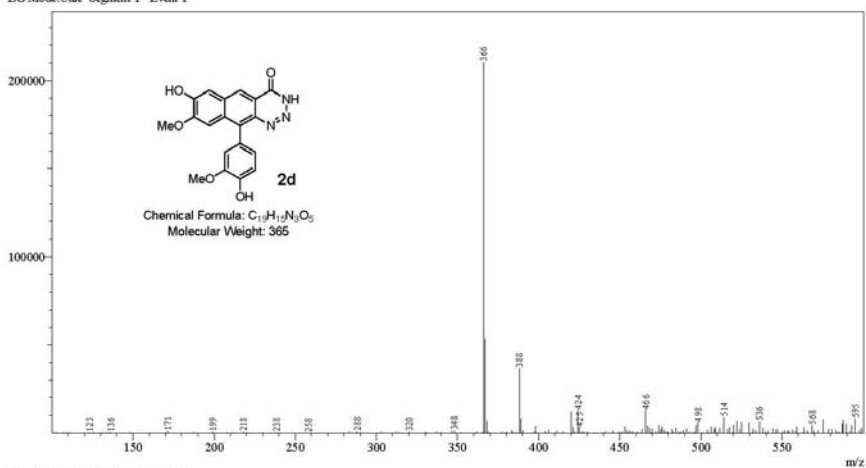


## 6. ESI spectra for 2d and 2e

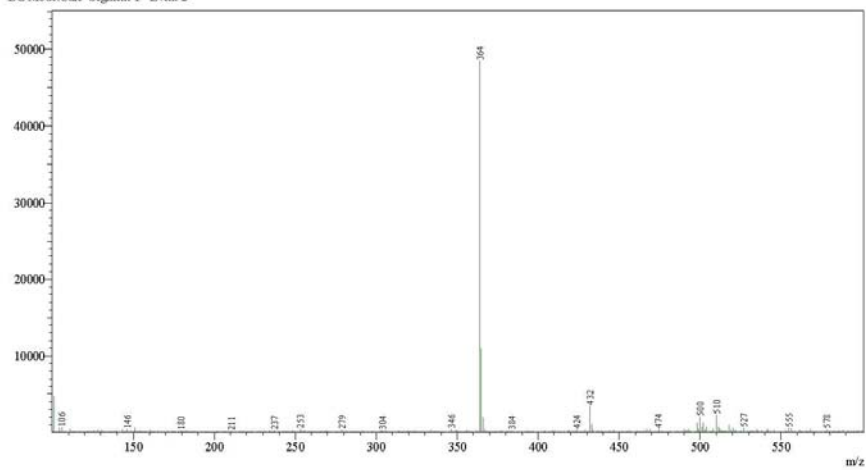
### ESI spectrum of 2d

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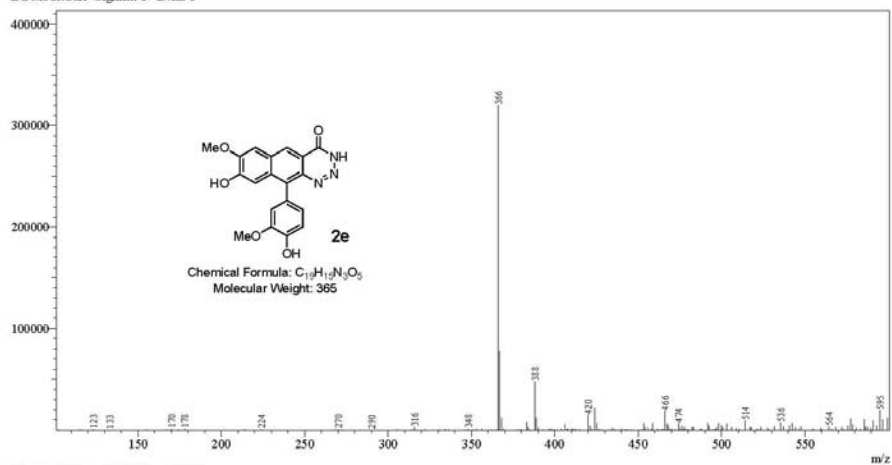
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## ESI spectrum of 2e

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