

Supporting Information for

Model Studies of the (6–4) Photoproduct
Photoreactivation: Efficient Photosensitized Splitting of
Thymine Oxetane Units by Covalently Linked
Tryptophan in High Polarity Solvents

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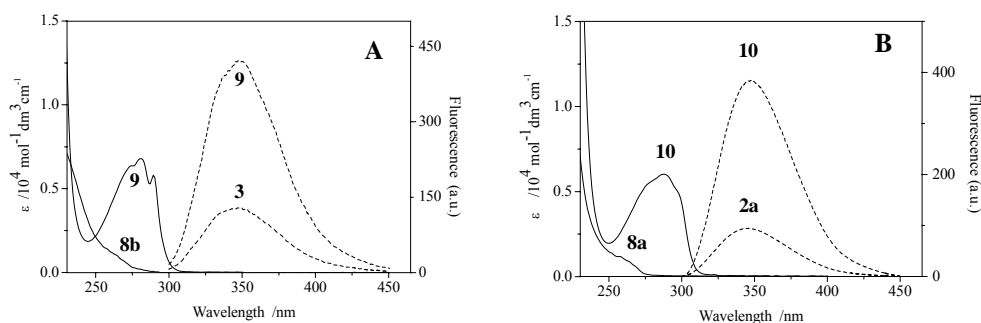


Fig. S1 UV absorption spectra (solid) and/or fluorescence emission spectra (dash) ($\lambda_{\text{ex}} = 290 \text{ nm}$) of compounds **9**, **8b** and **3** (A), **10**, **8a** and **2a** (B), in methanol.

The detail for measurement of splitting quantum yields

The absorbances at 270 nm (A_{270}) were measured at certain time intervals. The A_{270} change (ΔA_{270}) of the solution depends on the splitting reaction. The change of mole extinction coefficients ($\Delta \epsilon_{270}$) were obtained from those measured of model compounds **1–3** and the splitting products **4**, **5** and benzophenone or benzaldehyde at 270 nm, and the value of $\Delta \epsilon_{270}$ employed was $1.80 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^{-3}$ for **1** and **2**, $1.18 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^{-3}$ for **3**, respectively. The splitting concentration (c_{spl}) of the model compound was obtained from $\Delta A_{270} / \Delta \epsilon_{270}$. The plot of c_{spl} against the irradiation time (t , min) is fitted as a well straight line. The rate of splitting reaction was obtained from the slope (B) of the line (Fig. S2). The intensity of the incident light I_0 was measured using ferrioxalate actinometry. The rate of photon absorbed (I_a) by solution was obtained in term of Beer's law, $I_a = I_0 (1 - 10^{-A_{290}})$. The absorbance of the model compound at 290 nm, A_{290} was determined before irradiation. Above these values allow the calculation of the quantum yield in terms of $\Phi_{\text{spl}} = (\text{rate of oxetane split}) / (\text{rate of photon absorbed}) = BV_0 / I_a$, wherein V_0 was the volume of irradiation solution, $3 \times 10^{-3} \text{ L}$.

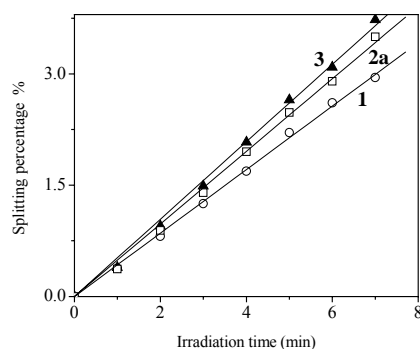


Fig. S2 Splitting rates determined for the model compounds **1**(\circ), **2a**(\square) and **3**(\blacktriangle) in methanol.

Figure S3 The ^1H NMR spectrum of compound **4**

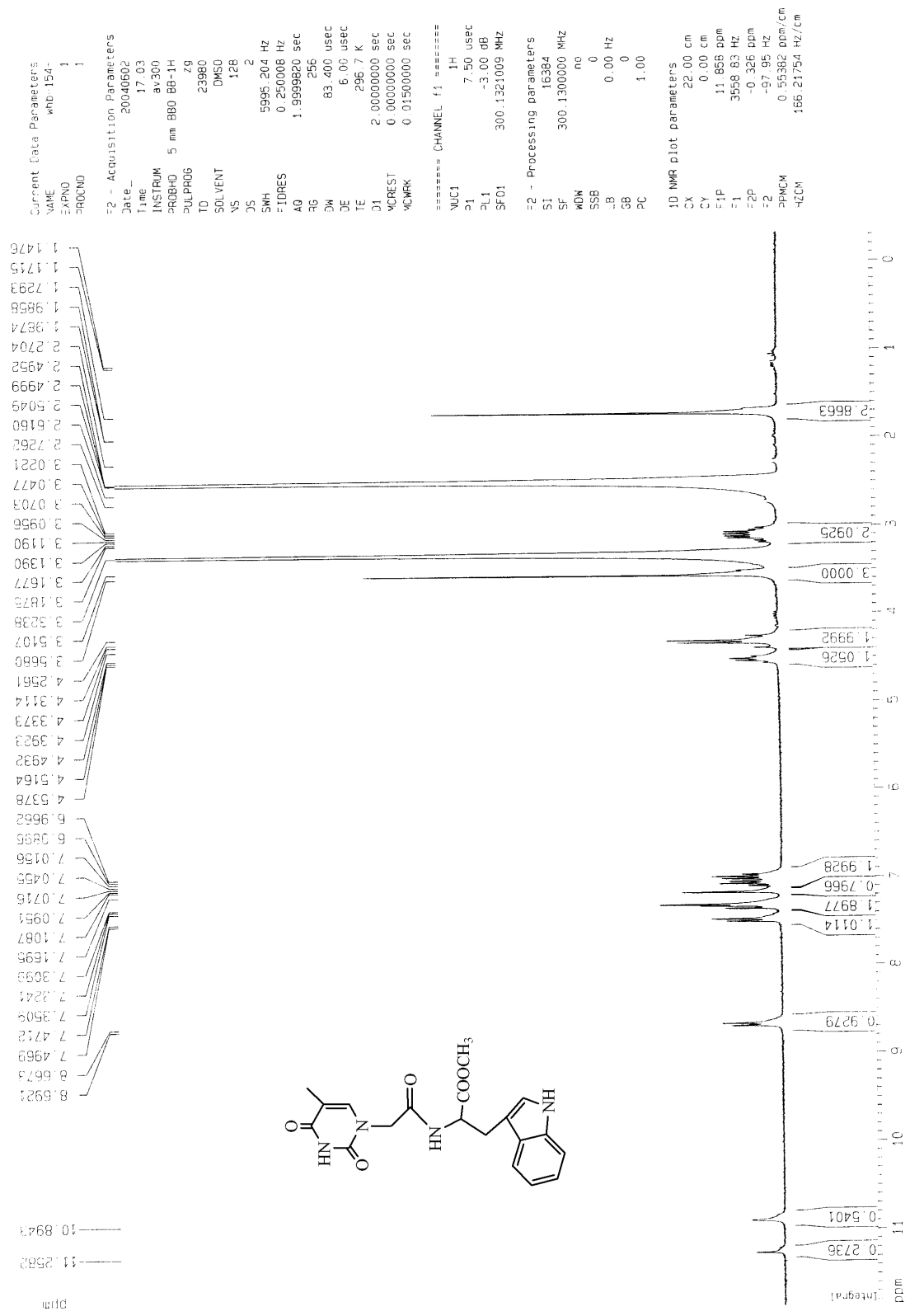


Figure S4 The ¹H NMR spectrum of compound **5**

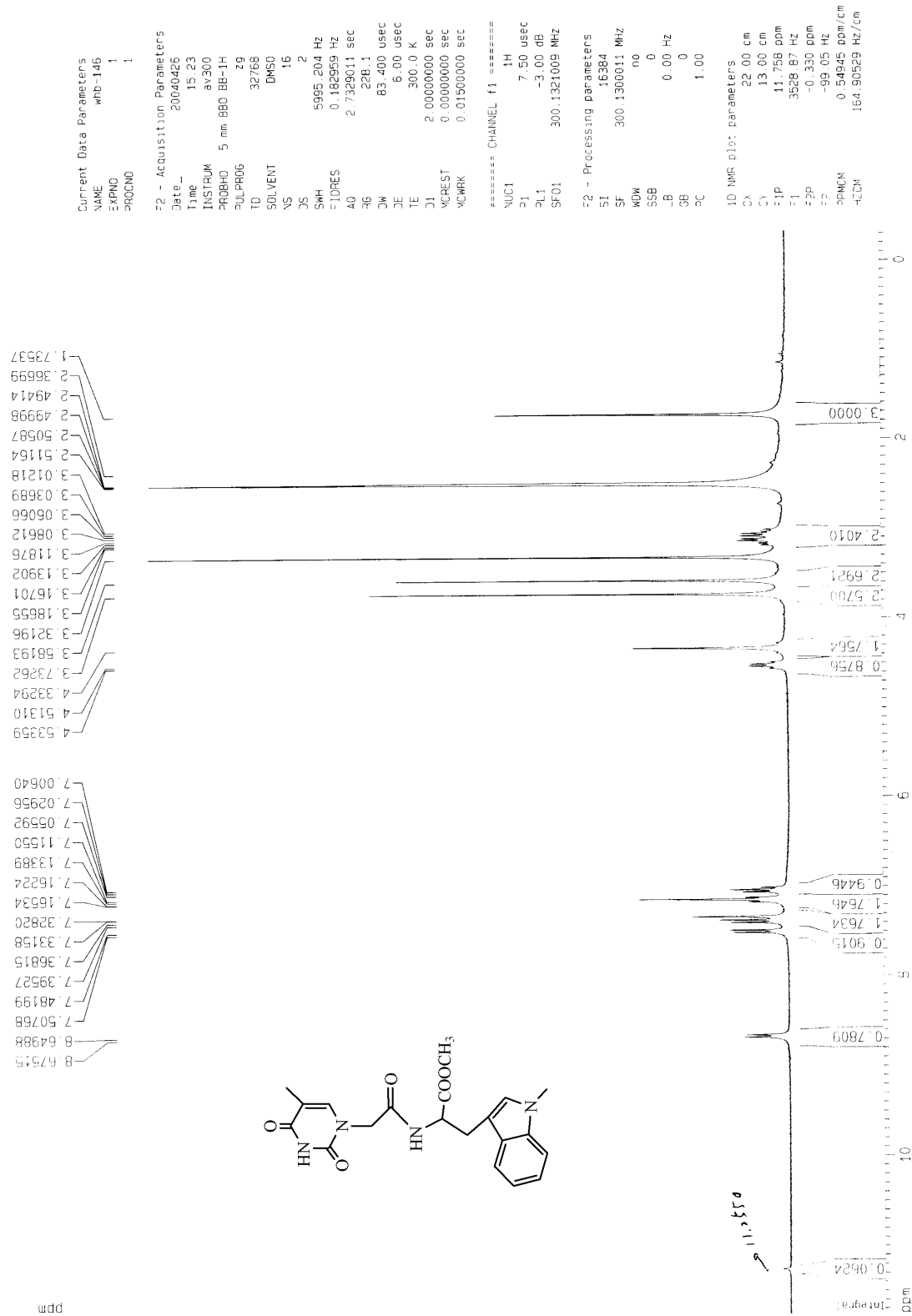


Figure S5 The ¹H NMR spectrum of compound 8a

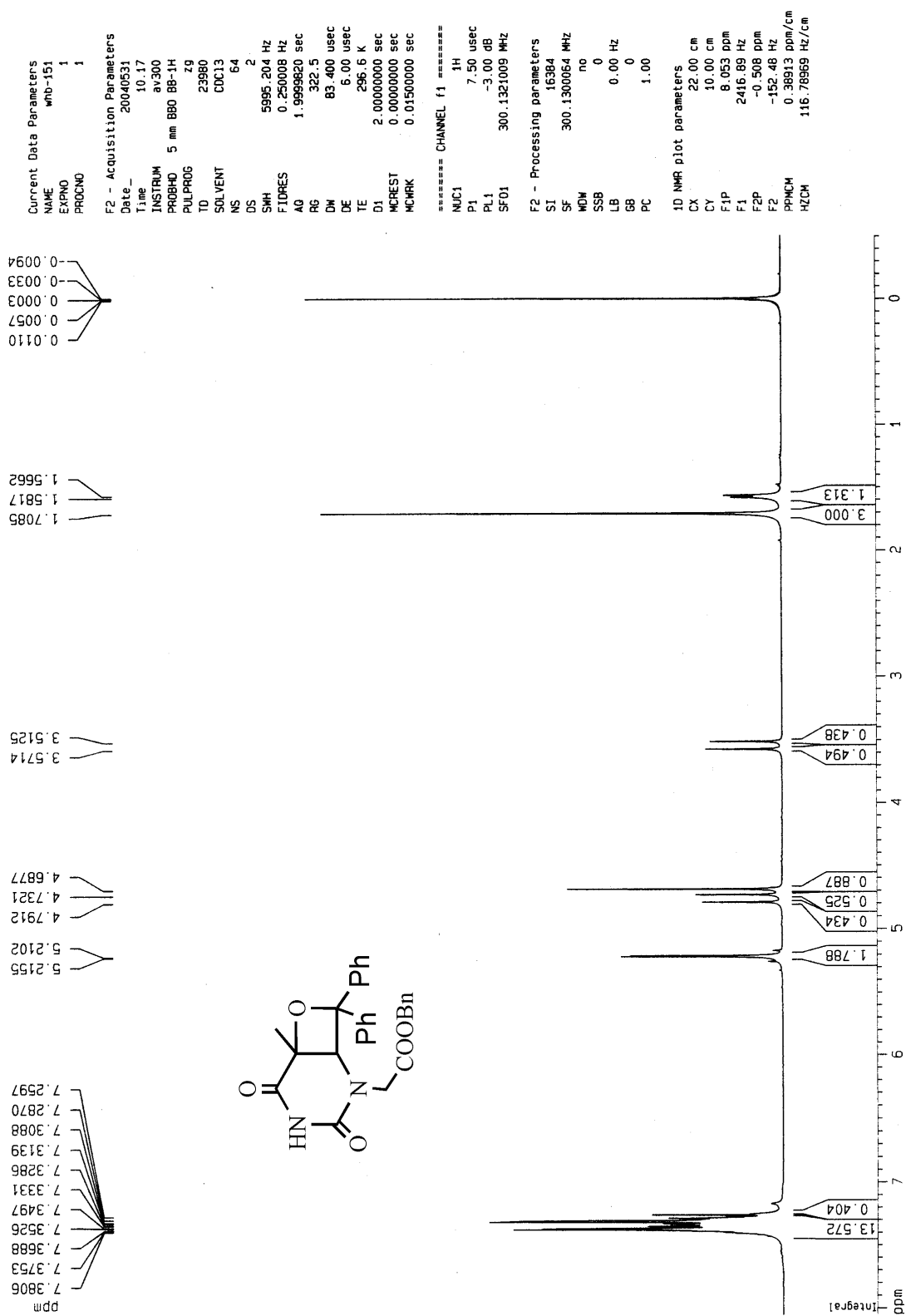


Figure S6 The ¹H NMR spectrum of compound 8b

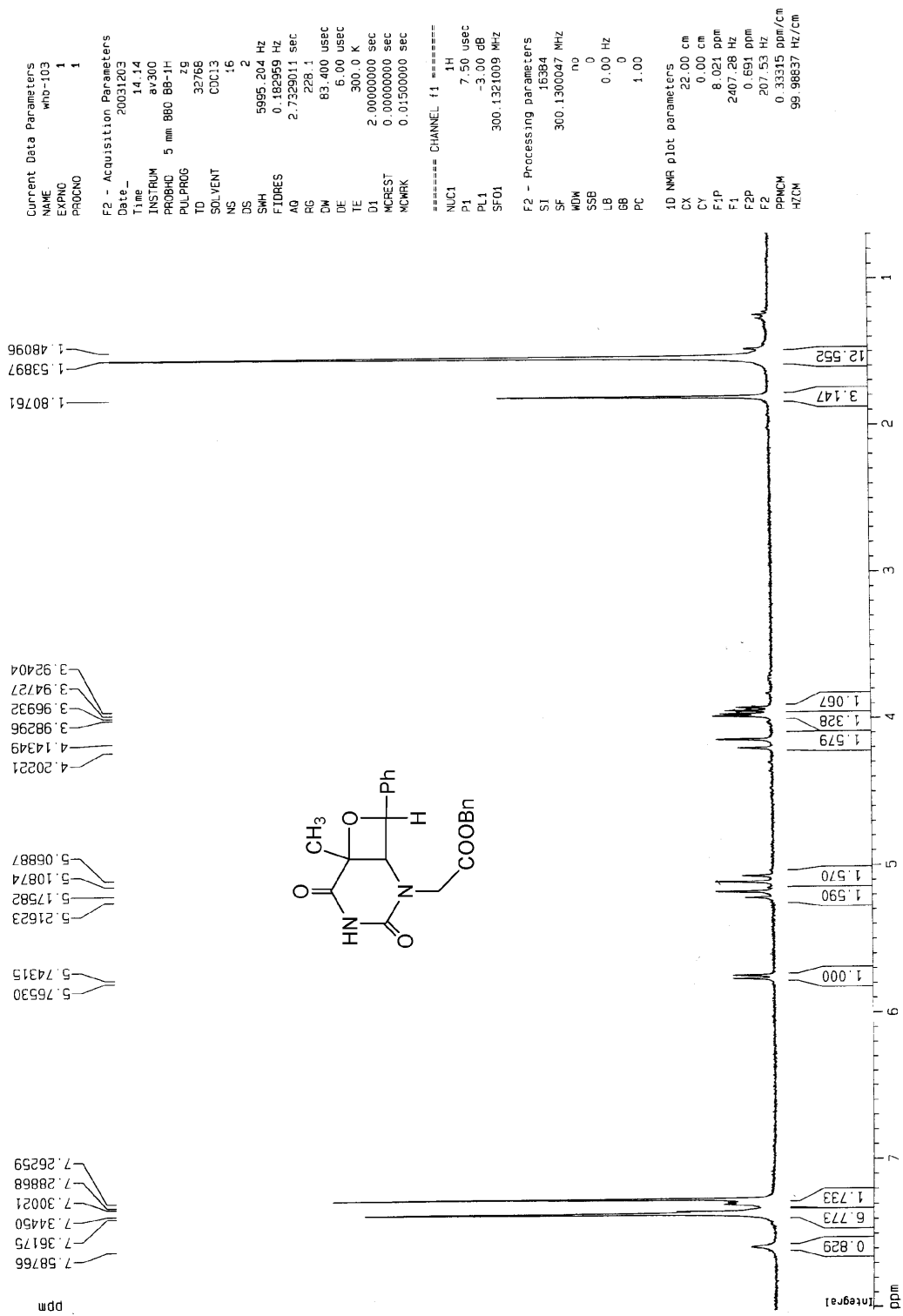


Figure S7 The ¹H NMR spectrum of compound **1**

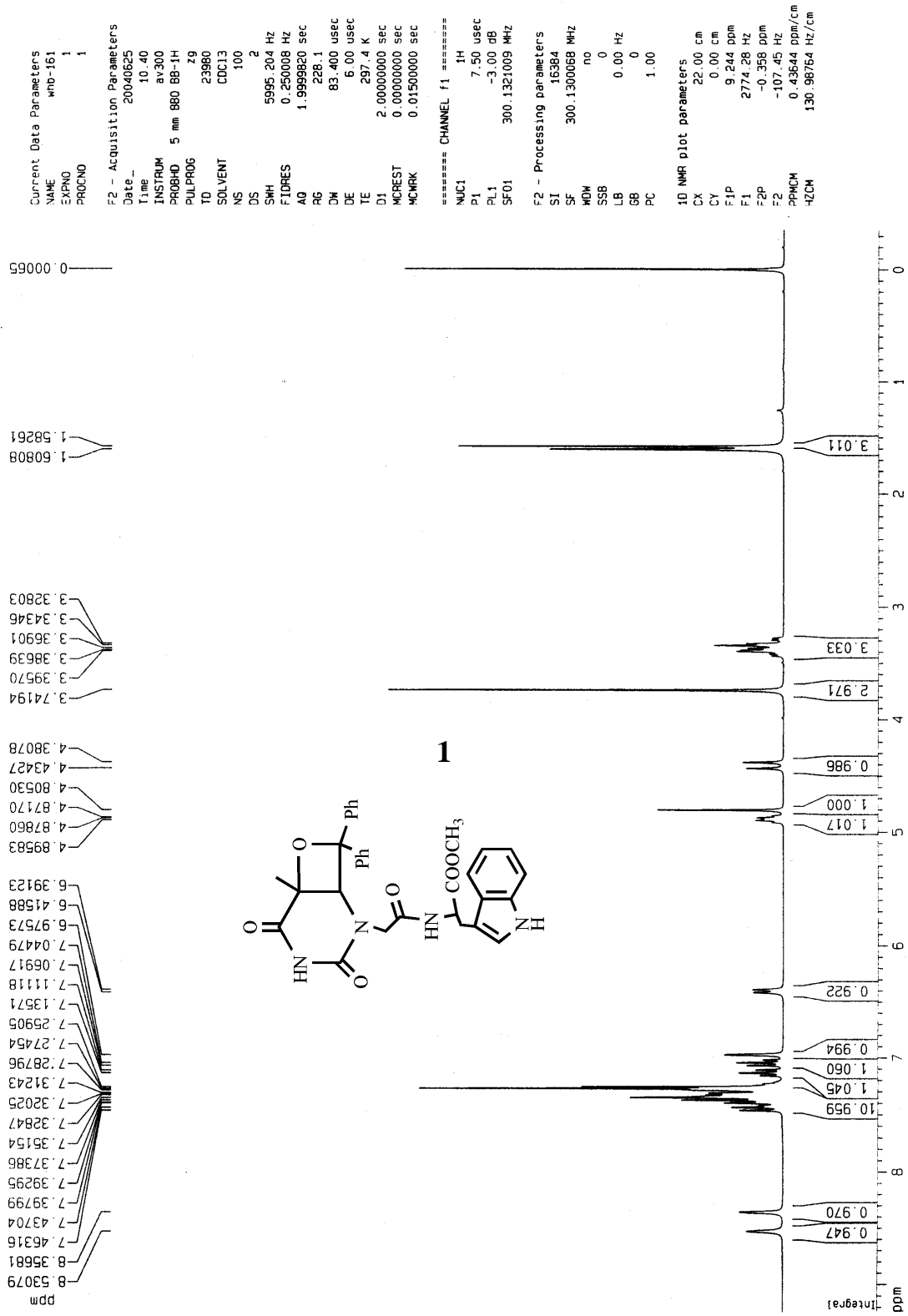


Figure S8 The ¹H NMR spectrum of compound 2a

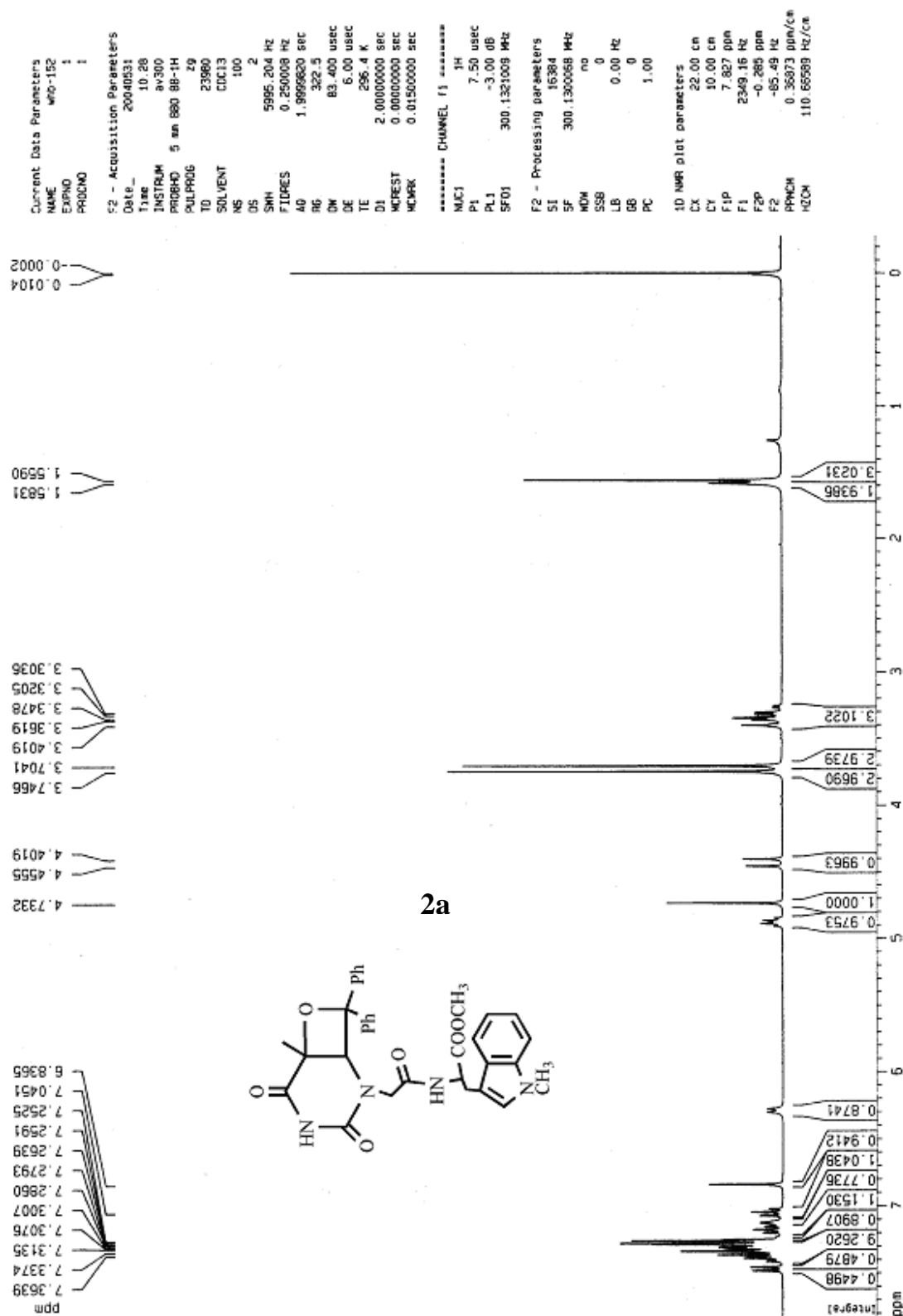


Figure S9 The ¹H NMR spectrum of compound 2b

Figure S10 The ¹H NMR spectrum of compound **3**

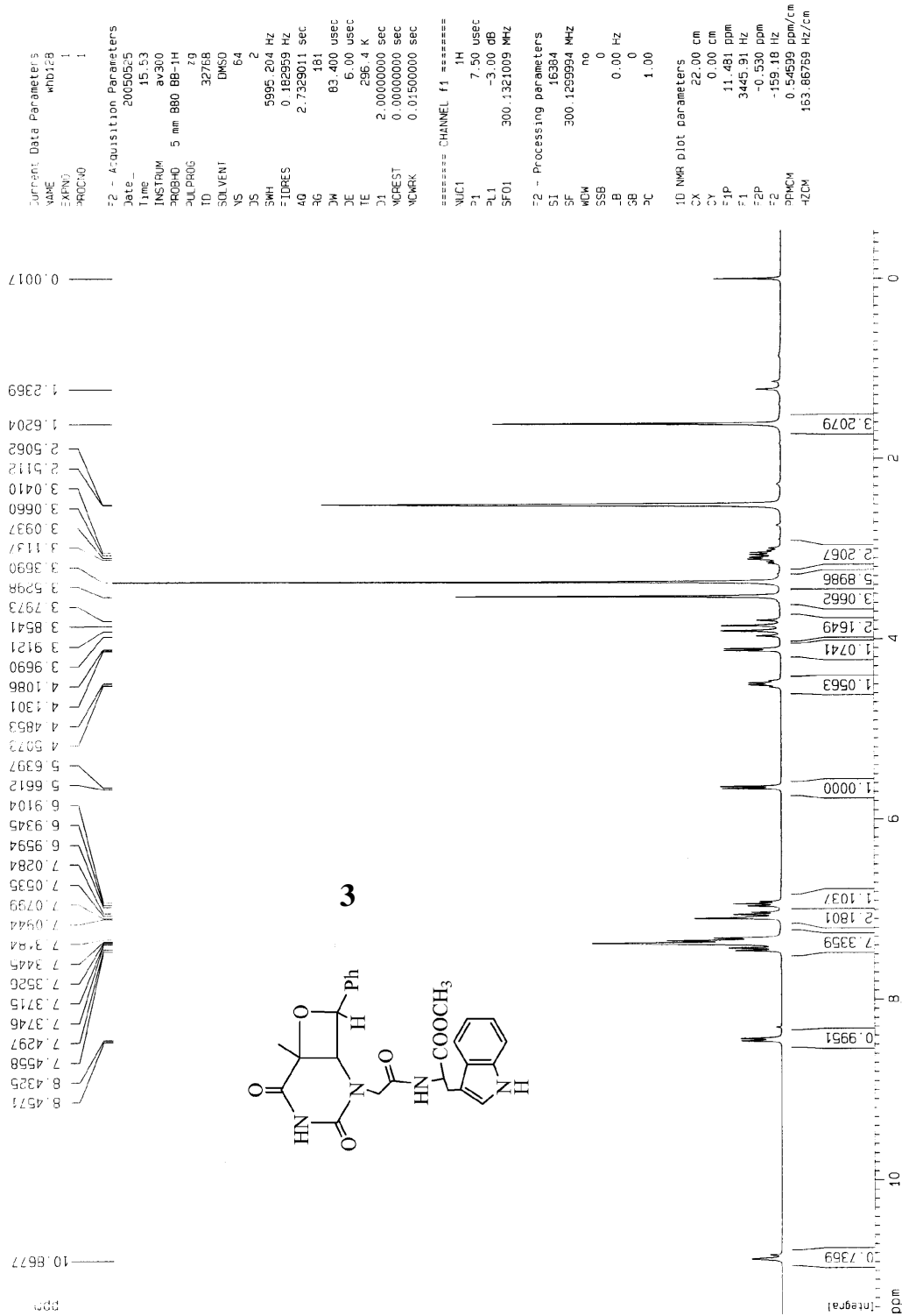


Figure S11 The ^{13}C NMR spectrum of compound 4

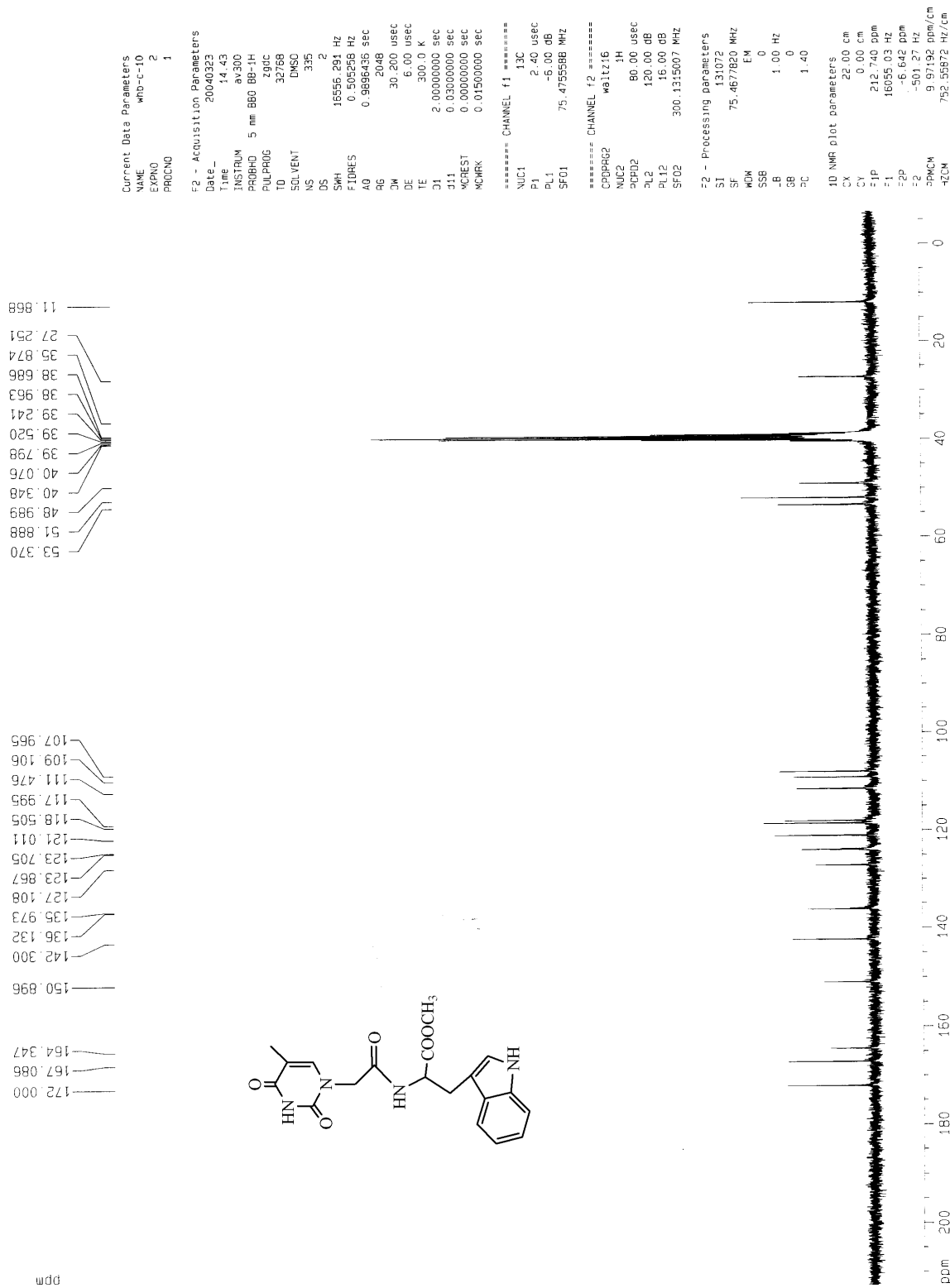


Figure S12 The ^{13}C NMR spectrum of compound **5**

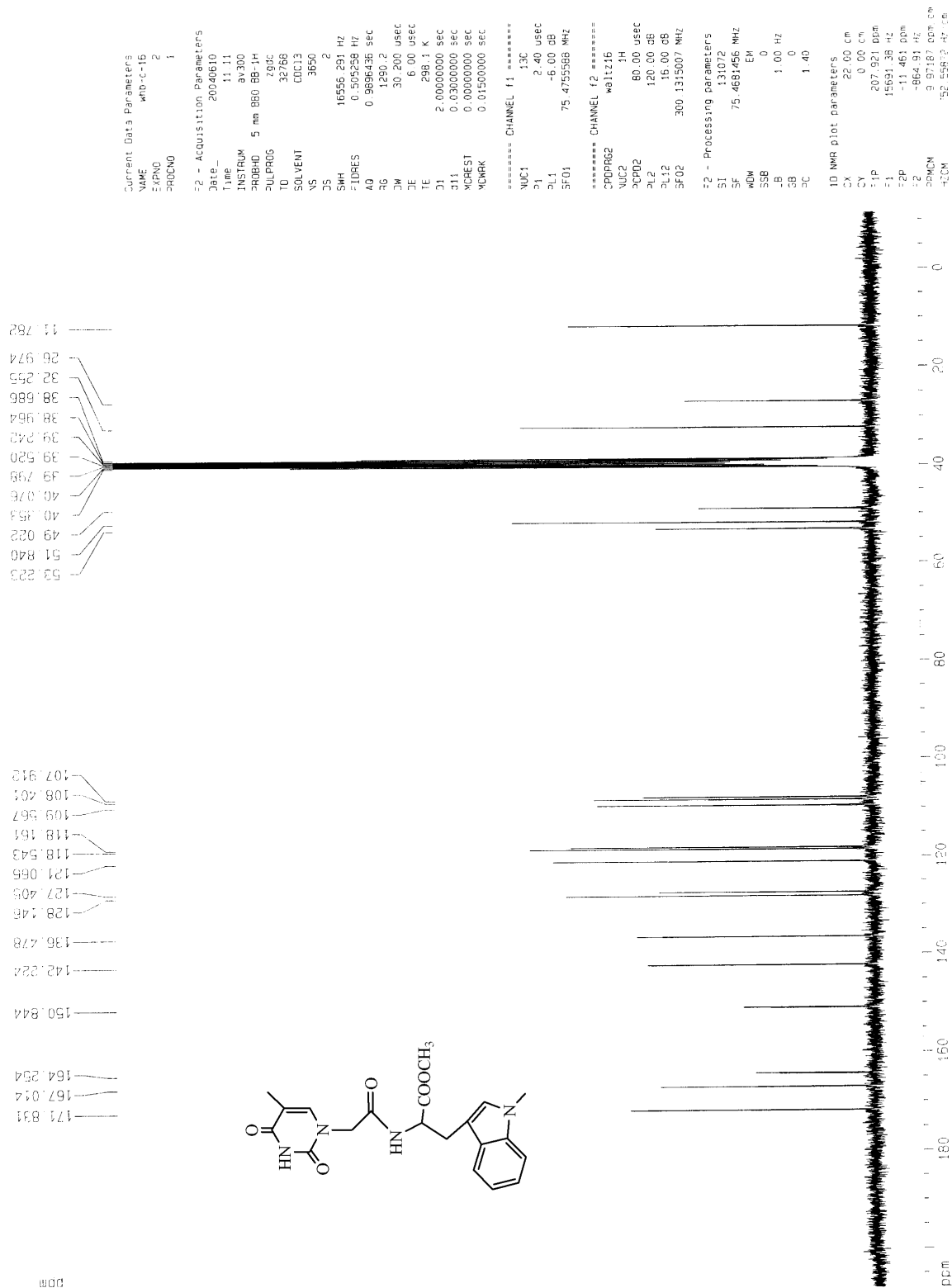


Figure S13 The ^{13}C NMR spectrum of compound **8a**

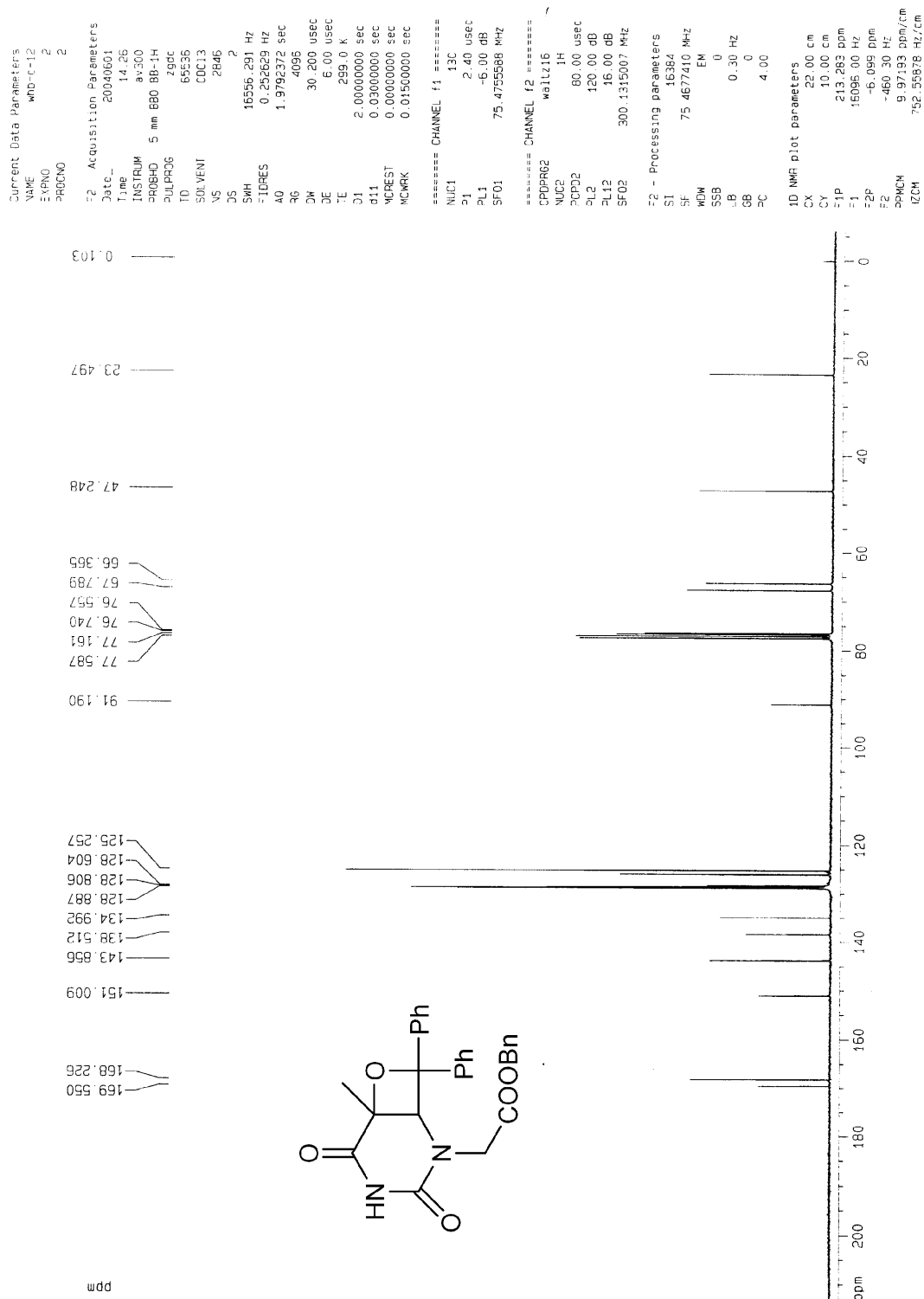


Figure S14 The ¹³C NMR spectrum of compound 8b

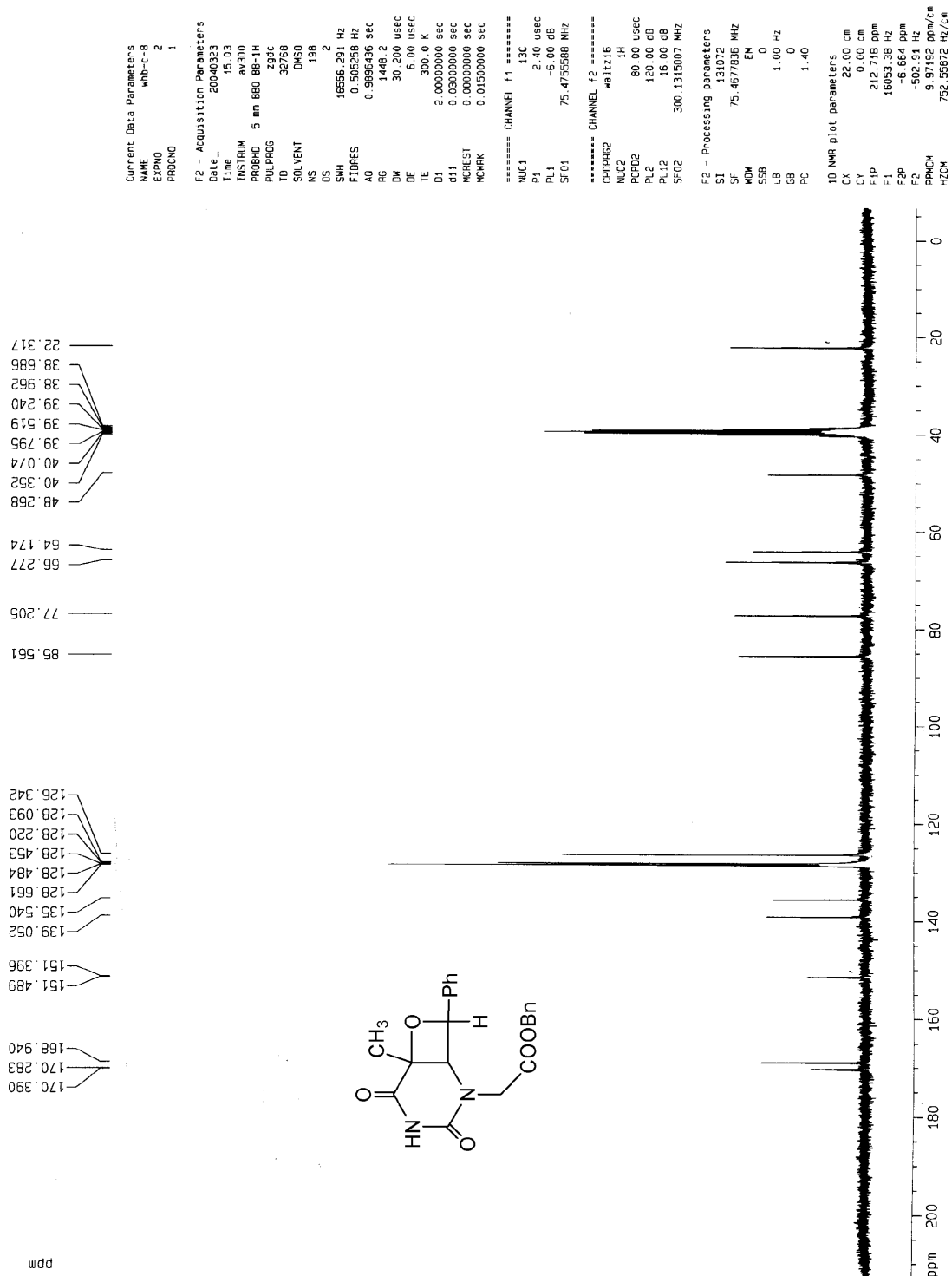


Figure S16 The ^{13}C NMR spectrum of compound **2a**

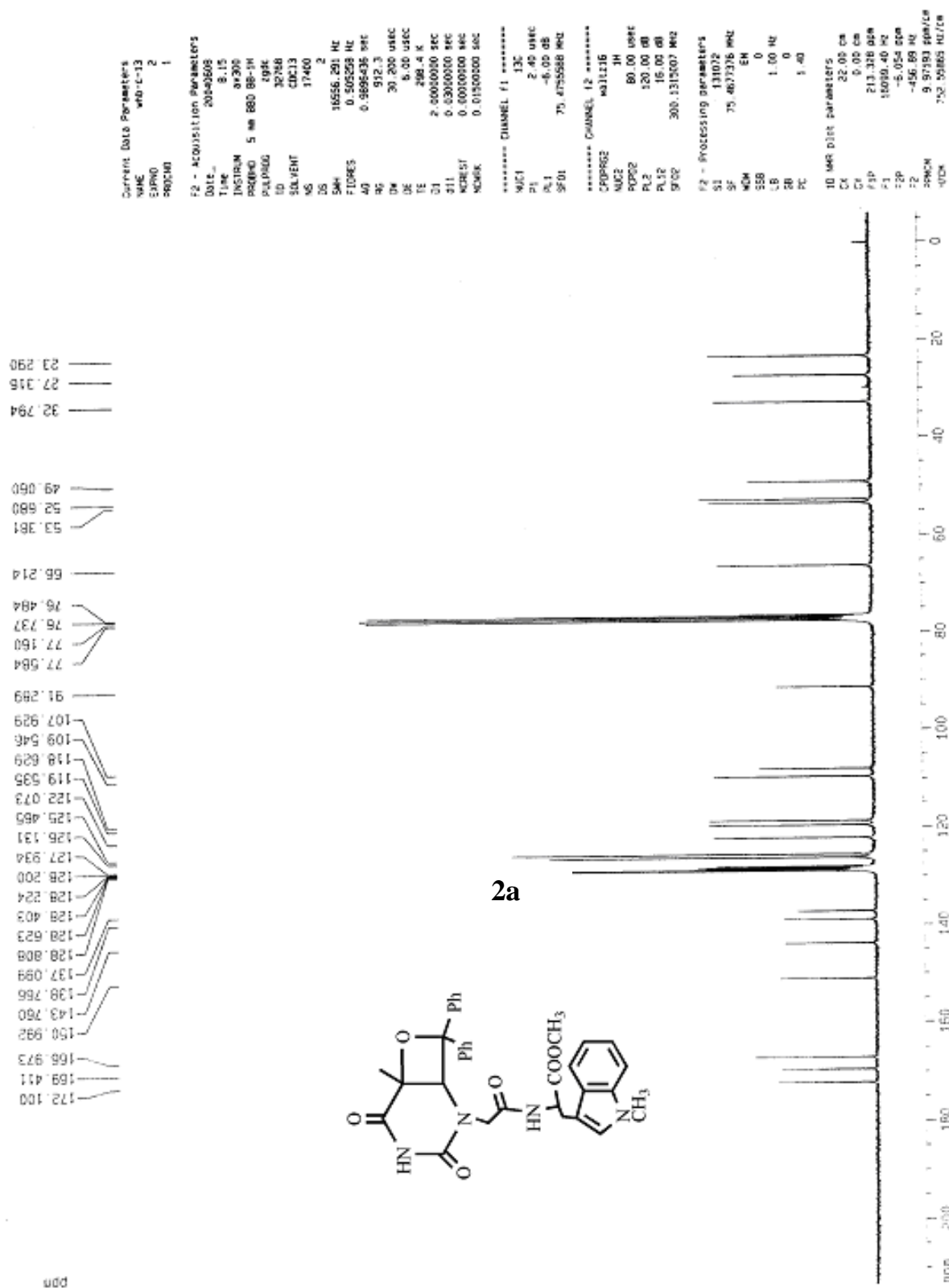


Figure S17 The ^{13}C NMR spectrum of compound **2b**


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PROCNO   1

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RG        5792.5
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DE        6.00 uSAC
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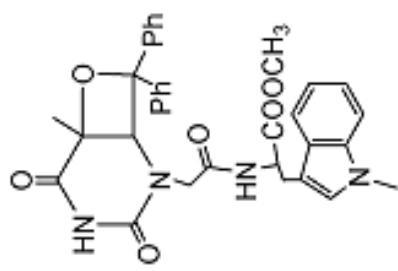
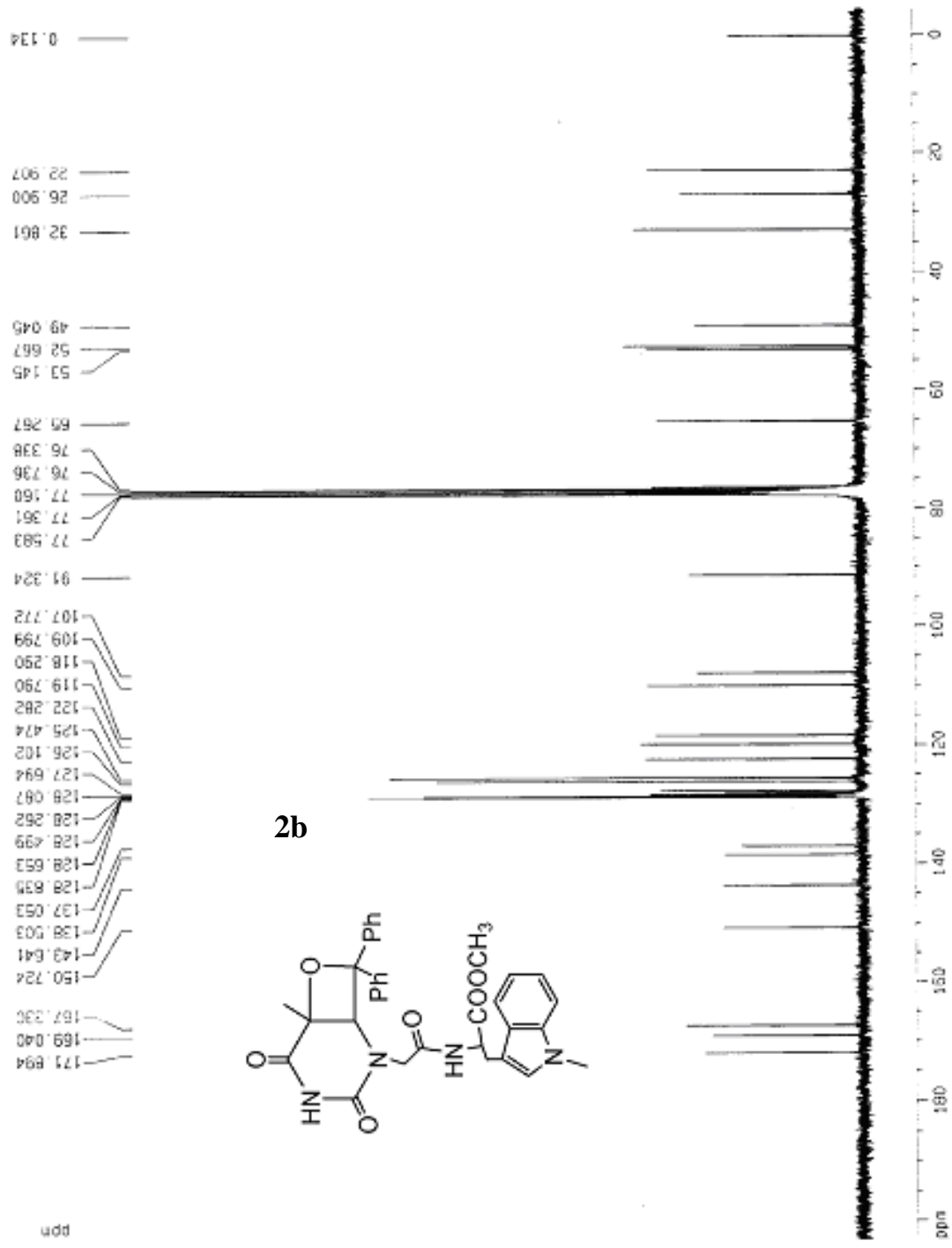


Figure S18 The ¹³C NMR spectrum of compound 3

