SUPPORTING INFORMATION

FOR

# What is the Structure of the Antitubercular Natural Product Eucapsitrione?

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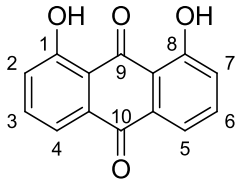
# I. Additional $^{13}$C and $^{1}$H NMR Data




**2**

**1,8-Dihydroxy-9,10-anthraquinone (*chrysazin*, 2)**

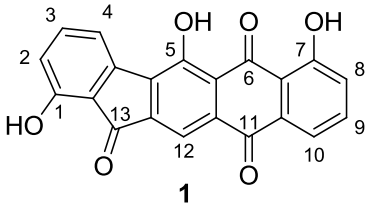
$^{1}$H NMR (500 MHz, $d_6$-DMSO) δ 11.90 (s, 2H, 2 × OH), 7.80 (dd, $J$ = 8.0, 7.5 Hz, 2H, H3, H6), 7.70 (dd, $J$ = 7.5, 1.0 Hz, 2H, H4, H5), 7.37 (dd, $J$ = 8.5, 1.0 Hz, 2H, H2, H7). $^{1}$H NMR (500 MHz, $d_5$-pyridine) δ 12.20 (s, 2H, 2 × OH), 7.87 (dd, $J$ = 7.5, 1.0 Hz, 1H, H4, H5), 7.62 (dd, $J$ = 8.5, 7.5 Hz, 1H, H3, H6), 7.35 (dd, $J$ = 8.3, 0.8 Hz, 1H, H2, H7); $^{13}$C NMR (125 MHz, $d_5$-pyridine) δ 193.4 (C9), 182.0 (C10), 163.0 (C1, C8), 138.0 (C3, C6), 134.4 (C4a, C10a), 125.1 (C2, C7), 120.2 (C4, C5), 116.7 (C8a, C9a). NMR assignments made with the assistance of COSY, HSQC and HMBC experiments.

**Table S1.** Spectroscopic data for chrysazin (**2**). All data except the $^{13}$C NMR data in $d_6$-DMSO were obtained by the authors.

| **$^{13}$C NMR (ppm)** | | **$^{1}$H NMR (ppm)** | |
|---|---|---|---|
| $d_5$-pyridine[a] | Kukushkina *et al.*[1] $d_6$-DMSO[b] | $d_5$-pyridine[c] | $d_6$-DMSO[c] |
| 193.4 | 192.9 | 12.20 (s, OH) | 11.90 (s, OH) |
| 182.0 | 182.2 | 7.87 (dd) | 7.80 (dd) |
| 163.0 | 162.3 | 7.62 (dd) | 7.70 (dd) |
| 138.0 | 138.3 | 7.35 (dd) | 7.37 (dd) |
| 134.4 | 134.1 | | |
| 125.1 | 125.3 | | |
| 120.2 | 120.2 | | |
| 116.7 | 116.8 | | |

[a] 125 MHz. [b] 22.5 MHz.[2] [c] 500 MHz.

# II. Additional $^{13}$C NMR Data and Chemical Shift Calculations




**1**

**Table S2.** Experimental $^{13}$C NMR chemical shifts for **1** ($d_5$-pyridine) compared with the calculated $^{13}$C NMR shifts (DMSO) and with the shifts of eucapsitrione ($d_6$-DMSO).[3]

| $\delta_{exp}$ **1** ($d_5$-pyr)[a] | $\delta_{exp}$ eucapsitrione[3] ($d_6$-DMSO)[b] | $\delta_{calc}$ **1** HF/ 6-31G* (DMSO) | $\delta_{calc}$ **1** B3LYP/ 6-31G* // HF/6-311G+(2d,p) (DMSO) | $\delta_{calc}$ **1** B3LYP/ 6-31G* (DMSO) | $\delta_{calc}$ **1** B3LYP/ 6-31G*//B3LYP/ 6-311+G(2d,p) (DMSO) |
|---|---|---|---|---|---|
| 193.7 | 187.1 | 192.6 | 209.3 | 182.8 | 205.3 |
| 191.0 | 184.8 | 192.0 | 207.5 | 179.8 | 202.0 |
| 181.3 | 180.2 | 177.7 | 194.5 | 169.3 | 191.0 |
| 163.2 | 177.2 | 158.3 | 174.4 | 150.5 | 172.3 |
| 159.0 | 161.9 | 156.8 | 169.6 | 146.2 | 168.0 |
| 158.3 | 161.1 | 154.8 | 166.8 | 145.7 | 166.9 |
| 143.6 | 137.2 | 141.7 | 153.6 | 130.4 | 149.8 |
| 141.7 | 135.2 | 140.2 | 152.4 | 129.1 | 148.4 |
| 138.3 | 135.1 | 138.7 | 151.1 | 127.1 | 147.4 |
| 138.3 | 134.5 | 137.7 | 149.9 | 126.3 | 146.0 |
| 136.0[c] | 131.0 | 137.4 | 143.7 | 125.7 | 145.1 |
| –[d] | 130.3 | 135.5 | 143.2 | 123.1 | 142.9 |
| 134.4 | 126.3 | 133.8 | 141.9 | 121.2 | 140.9 |
| 125.2 | 124.6 | 121.0 | 130.0 | 112.8 | 132.1 |
| 121.7 | 122.8 | 120.8 | 126.5 | 111.4 | 128.7 |
| 121.6 | 121.6 | 117.5 | 126.3 | 109.9 | 127.2 |
| 120.5 | 118.3 | 117.4 | 123.1 | 106.9 | 125.1 |
| 119.0 | 118.2 | 114.7 | 121.4 | 106.6 | 124.5 |
| 118.0 | 117.3 | 113.7 | 120.2 | 106.3 | 122.9 |
| 116.8 | 116.4 | 113.3 | 117.7 | 105.2 | 121.7 |
| 114.5 | 116.2 | 106.5 | 117.4 | 105.0 | 121.2 |
| **Mean \|Δδ\|**[e] | 3.7 | 2.8 | 8.1 | 11.9 | 7.5 |
| **Max \|Δδ\|**[e] | 14.0 | 8.0 | 16.5 | 13.6 | 11.6 |
| 3.7 | **Mean \|Δδ\|**[f] | 5.3 | 9.8 | 10.5 | 9.5 |
| 14.0 | **Max \|Δδ\|**[f] | 18.9 | 22.7 | 26.7 | 18.2 |

|Δδ| = Absolute chemical shift difference.

[a] 125 MHz. [b] 225 MHz. [c] This signal is obscured by a solvent peak in the $^{13}$C NMR; the chemical shift is approximated from correlations observed in the HMBC spectrum. [d] A $^{13}$C NMR resonance of C11a or C12a in **1** could not be experimentally observed. It is expected to be obscured by the solvent peak at 136.5−135.5 ppm based upon $^{13}$C NMR chemical shift predictions (see also experimental for **1**), and so was excluded from these shift difference calculations.[e] Mean and maximum |Δδ| calculated with respect to the experimental $^{13}$C NMR chemical shifts of **1** in $d_5$-pyridine. [f] Mean and maximum |Δδ| calculated with respect to the $^{13}$C NMR chemical shifts reported for eucapsitrione in $d_6$-DMSO.[3]

# III. References


(1) Kukushkina, M. L.; Gorelik, M. V.; Shapet'ko, N. N.; Bogachev, Y. S. *Zh. Obshch. Khim.* **1990**, *60*, 920.

(2) Kukushkina, M. L.; Shapet'ko, N. N.; Bogachev, Y. S.; Gorelik, M. V. *Zh. Obshch. Khim.* **1990**, *60*, 914.

(3) Sturdy, M.; Krunic, A.; Cho, S.; Franzblau, S.; Orjala, J. *J. Nat. Prod.* **2010**, *73*, 1441.

**Figure S1:** 500 MHz $^{1}$H NMR spectrum of 1-hydroxy-8-acetoxy-9,10-anthraquinone in $CDCl_3$

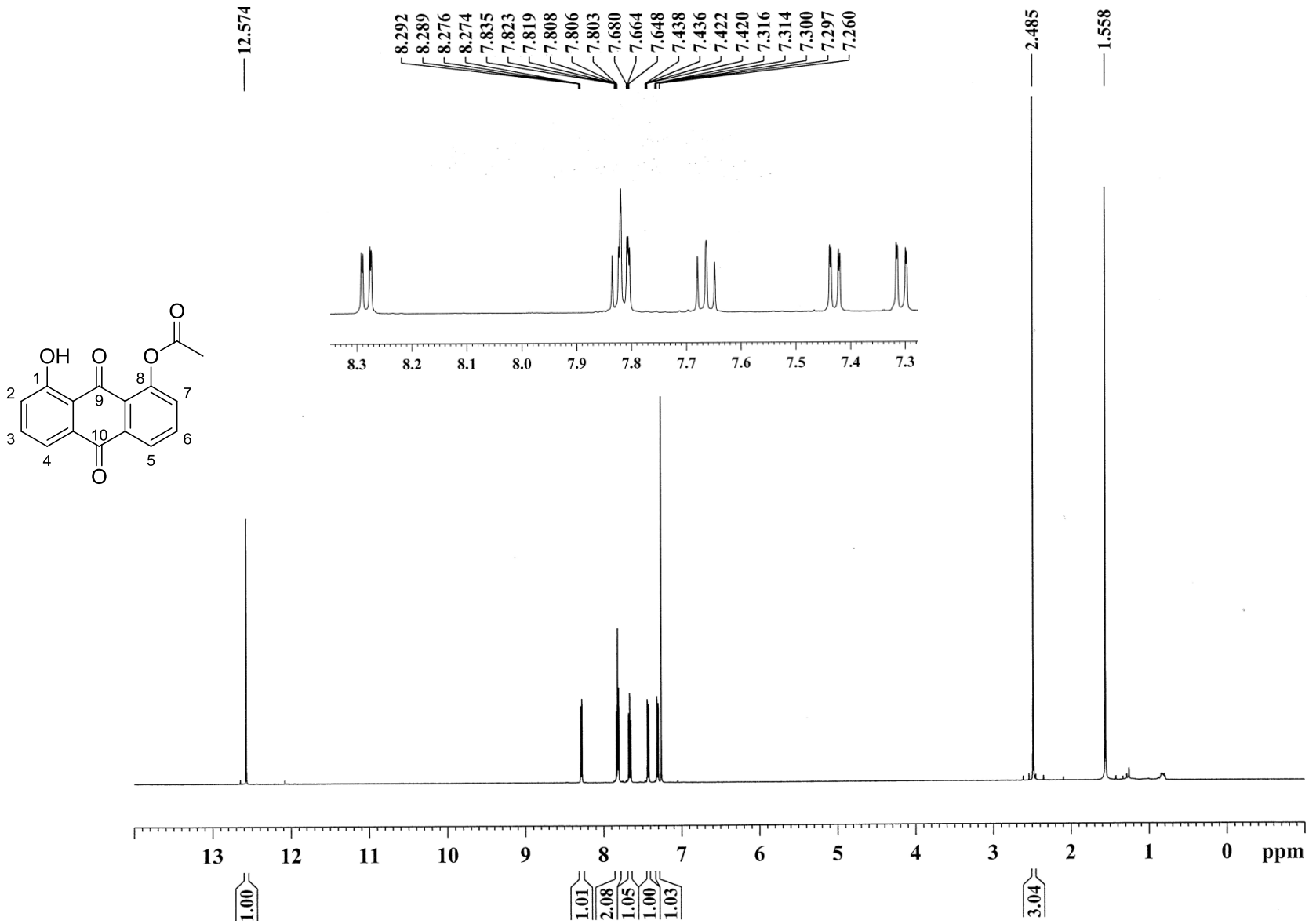


**Figure S2:** 400 MHz $^{1}$H NMR spectrum of **3** in $CDCl_3$

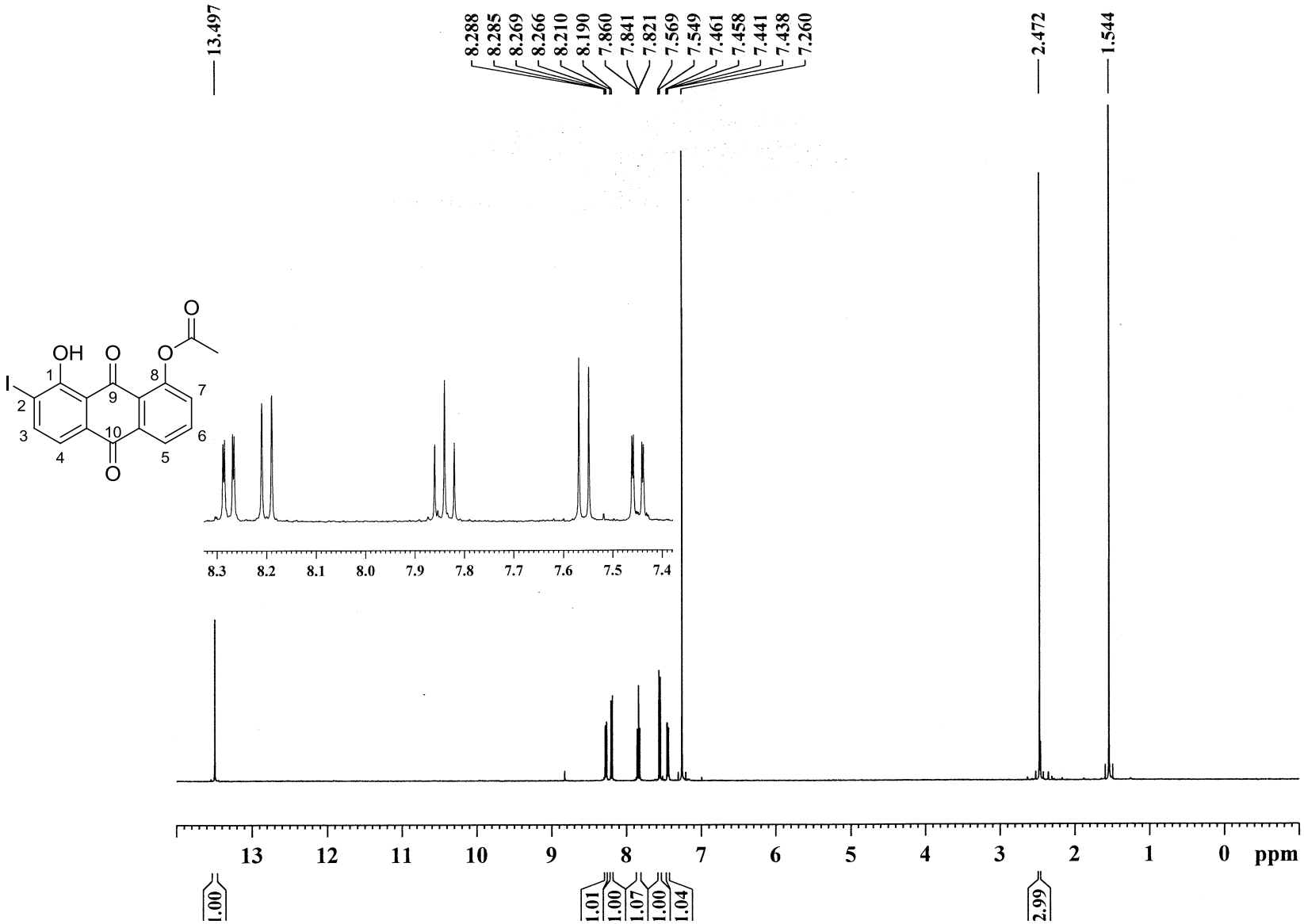


**Figure S3:** 100 MHz $^{13}C$ NMR spectrum of **3** in $CDCl_3$

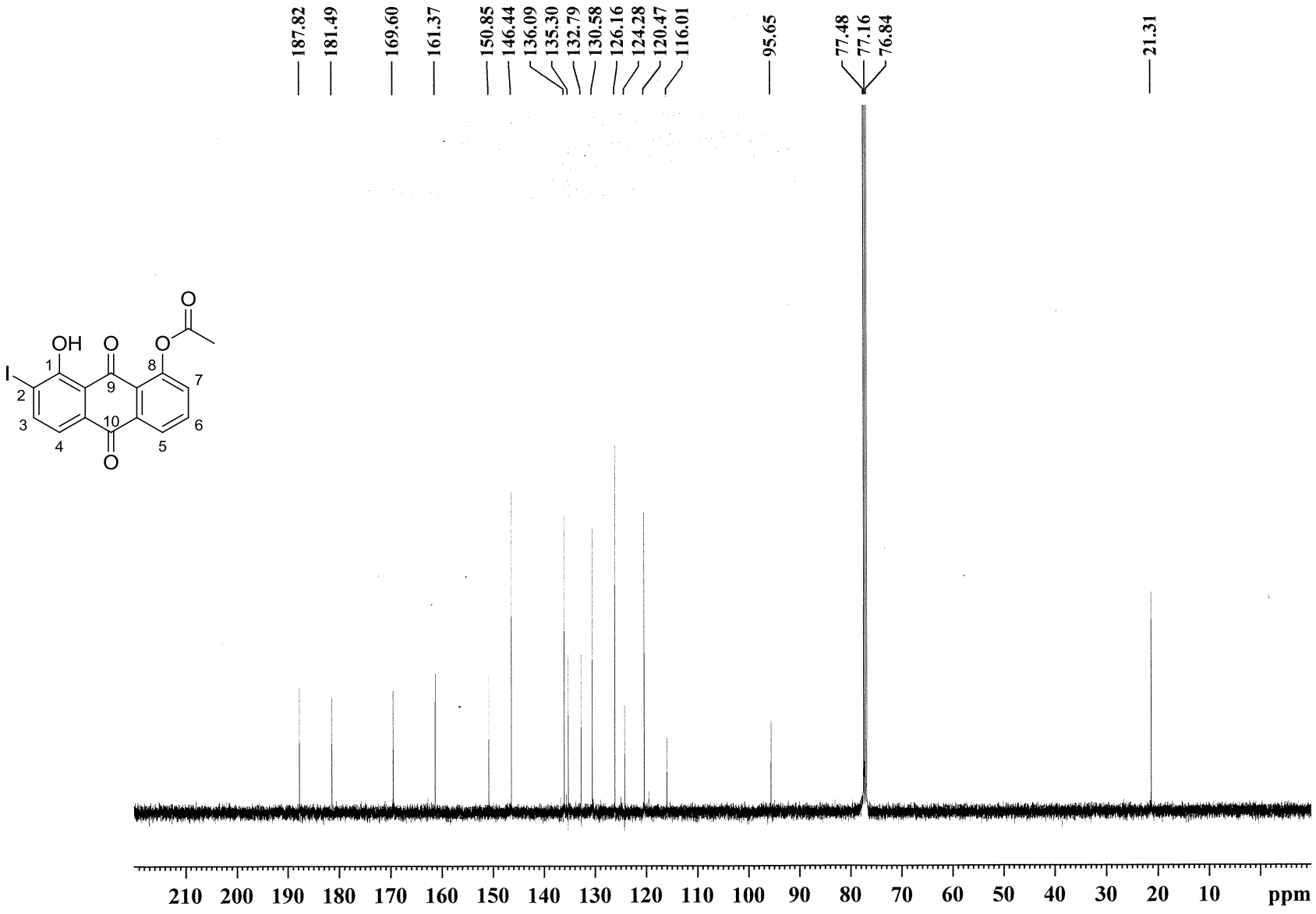


**Figure S4:** 400 MHz $^{1}$H NMR spectrum of **4** in $CDCl_3$

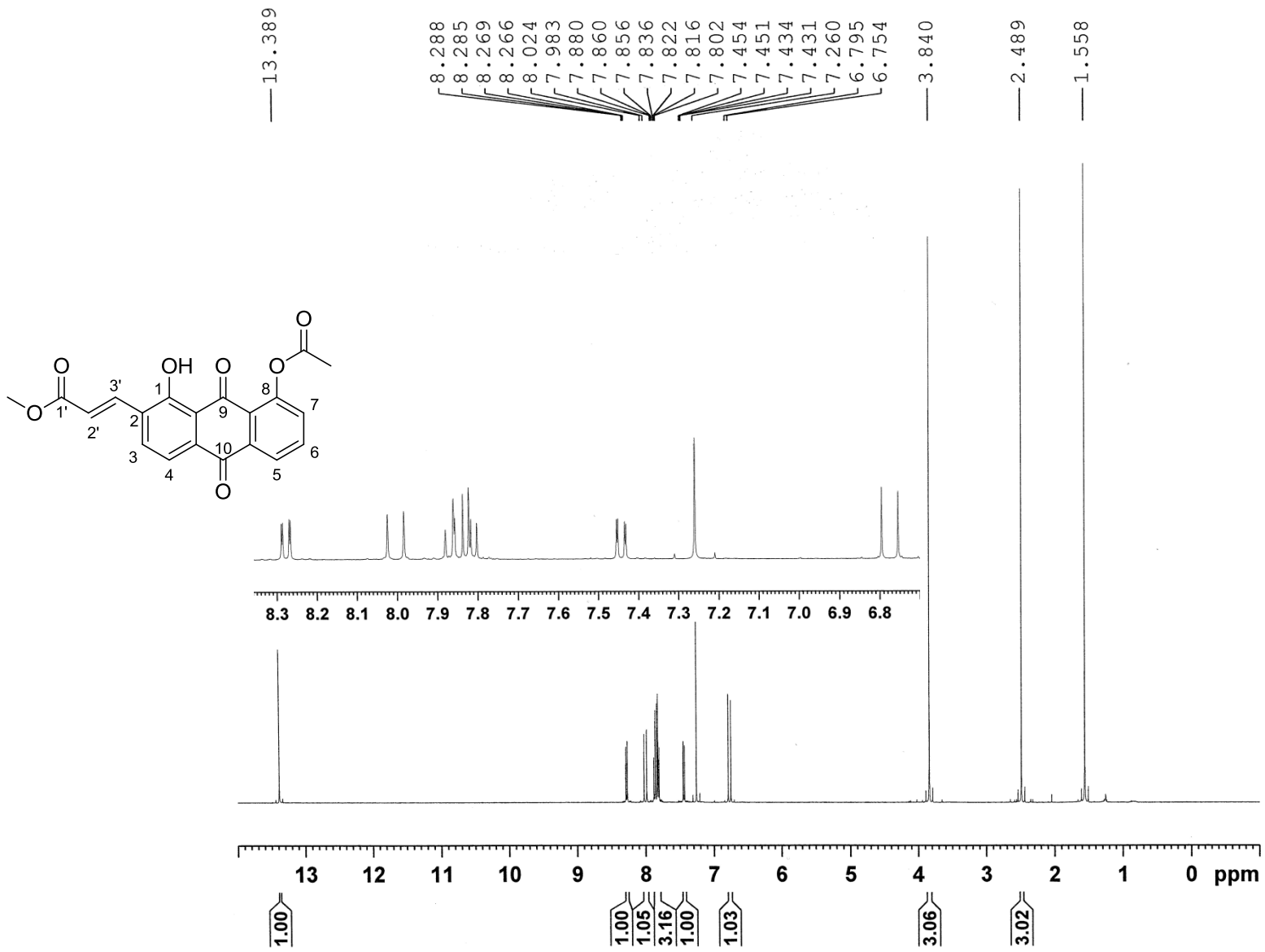


**Figure S5:** 100 MHz $^{13}$C NMR spectrum of **4** in $CDCl_3$

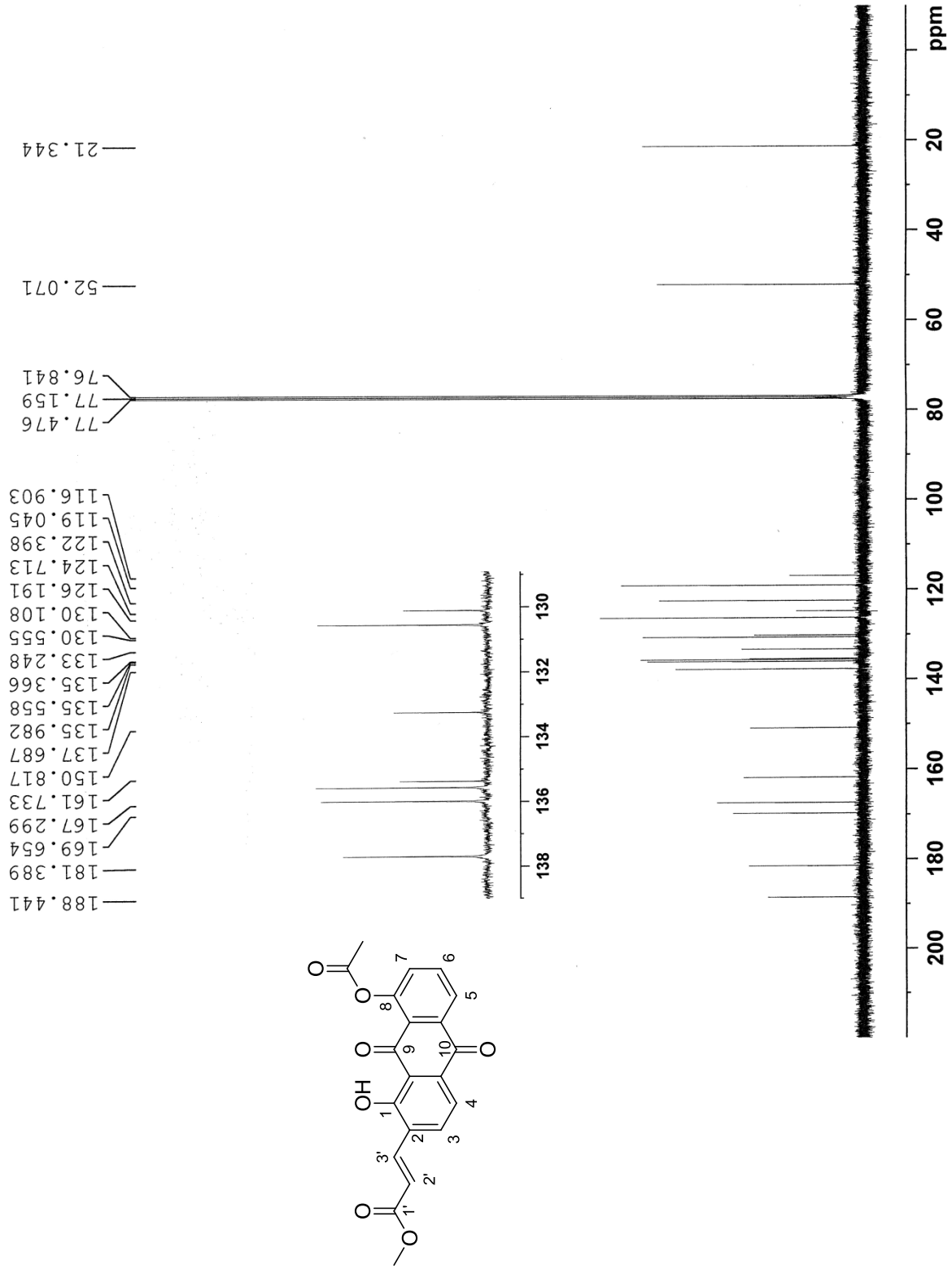


**Figure S6:** 400 MHz $^{1}$H NMR spectrum of **5** in $CDCl_3$

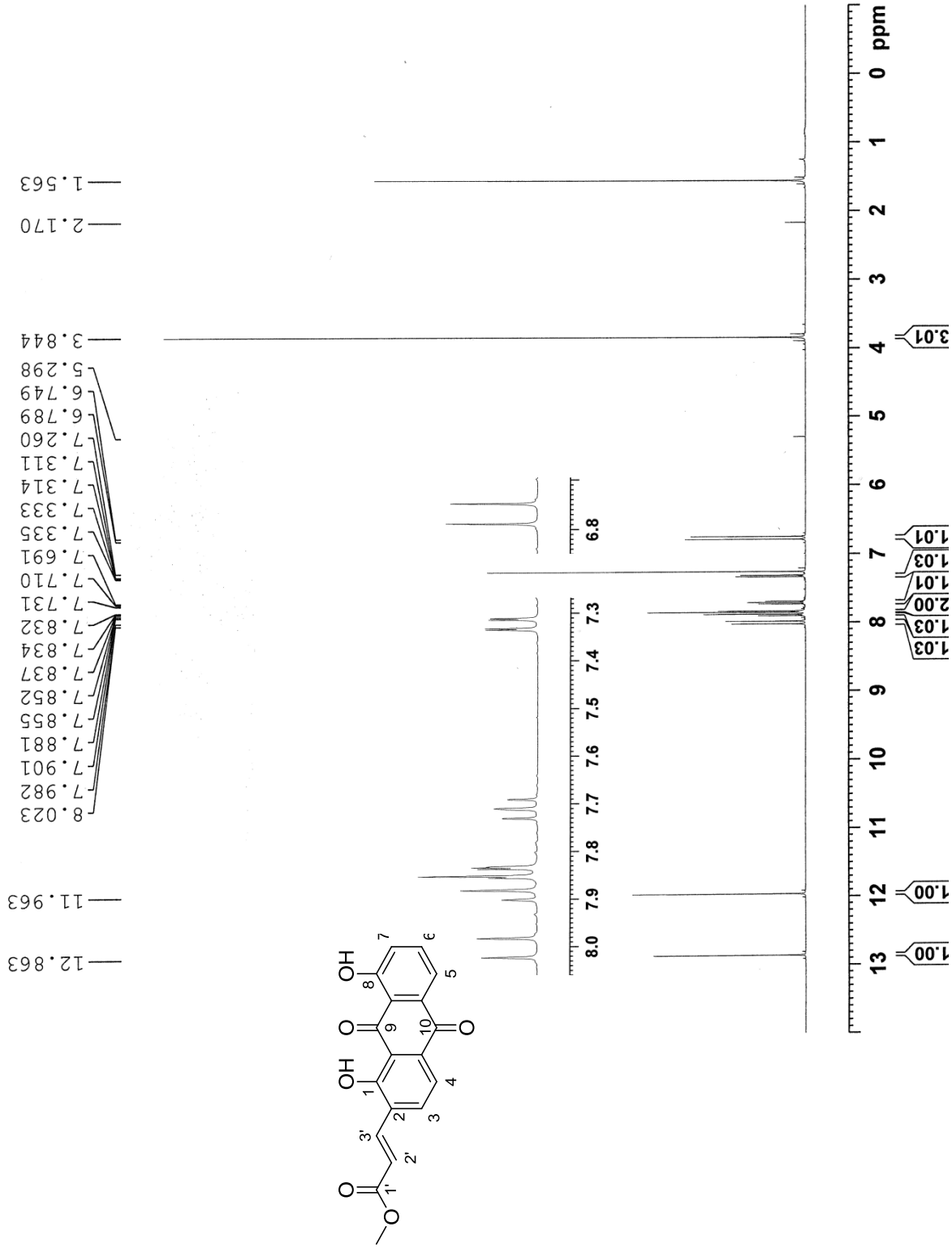


**Figure S7:** 100 MHz $^{13}$C NMR spectrum of **5** in $CDCl_3$

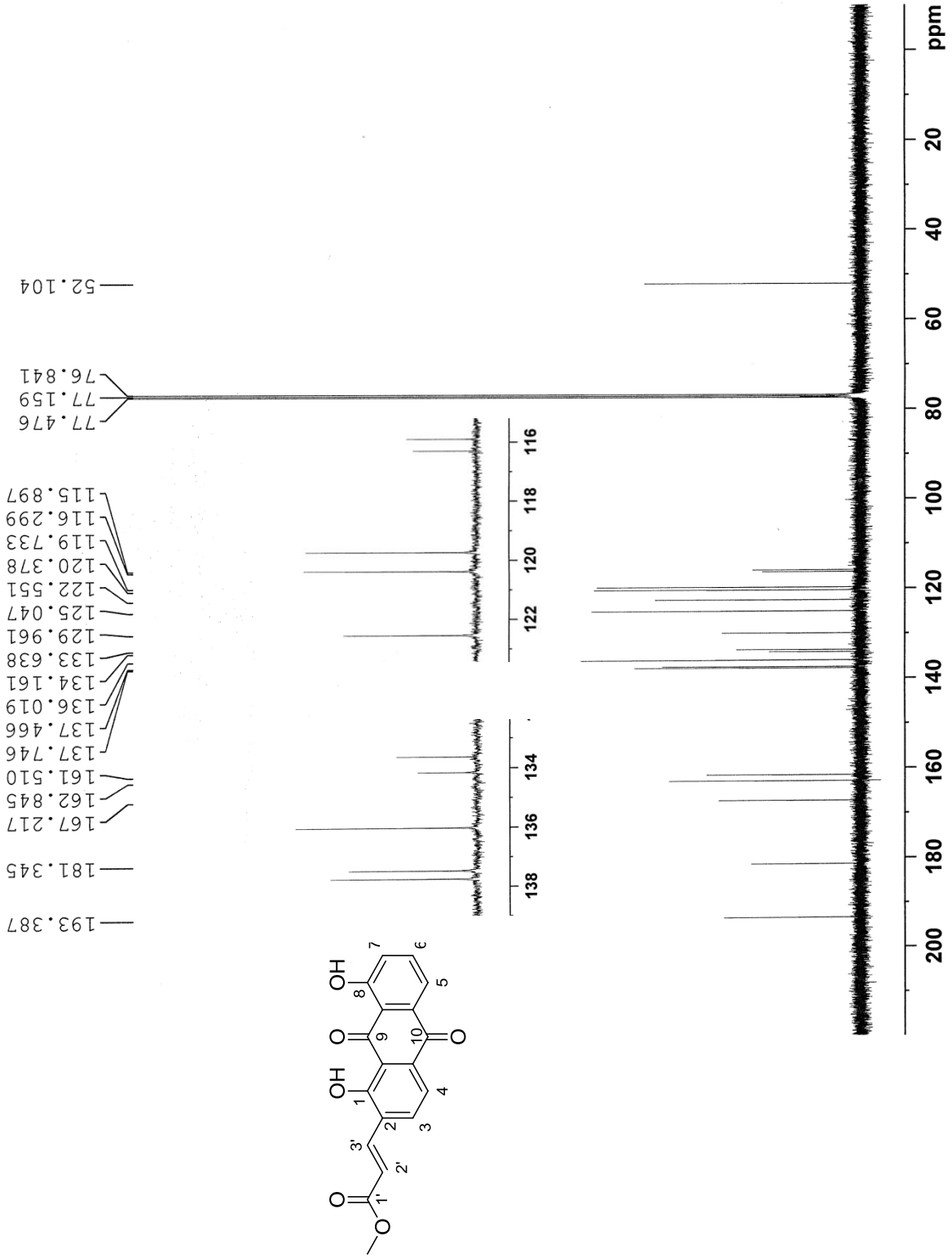


**Figure S8:** 500 MHz $^{1}$H NMR spectrum of **6** in $d_6$-DMSO

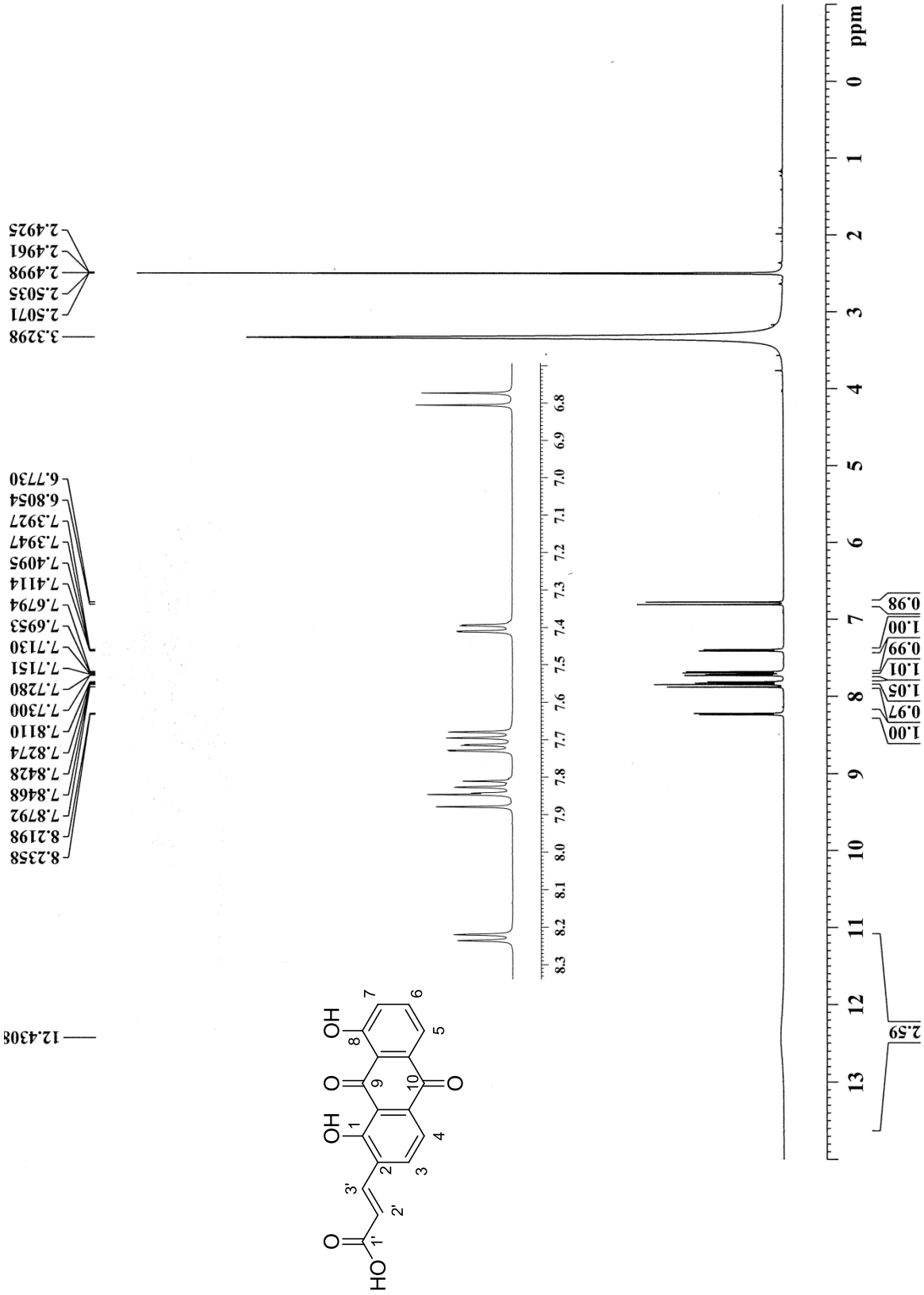


**Figure S9:** 125 MHz $^{13}$C NMR spectrum of **6** in $d_6$-DMSO

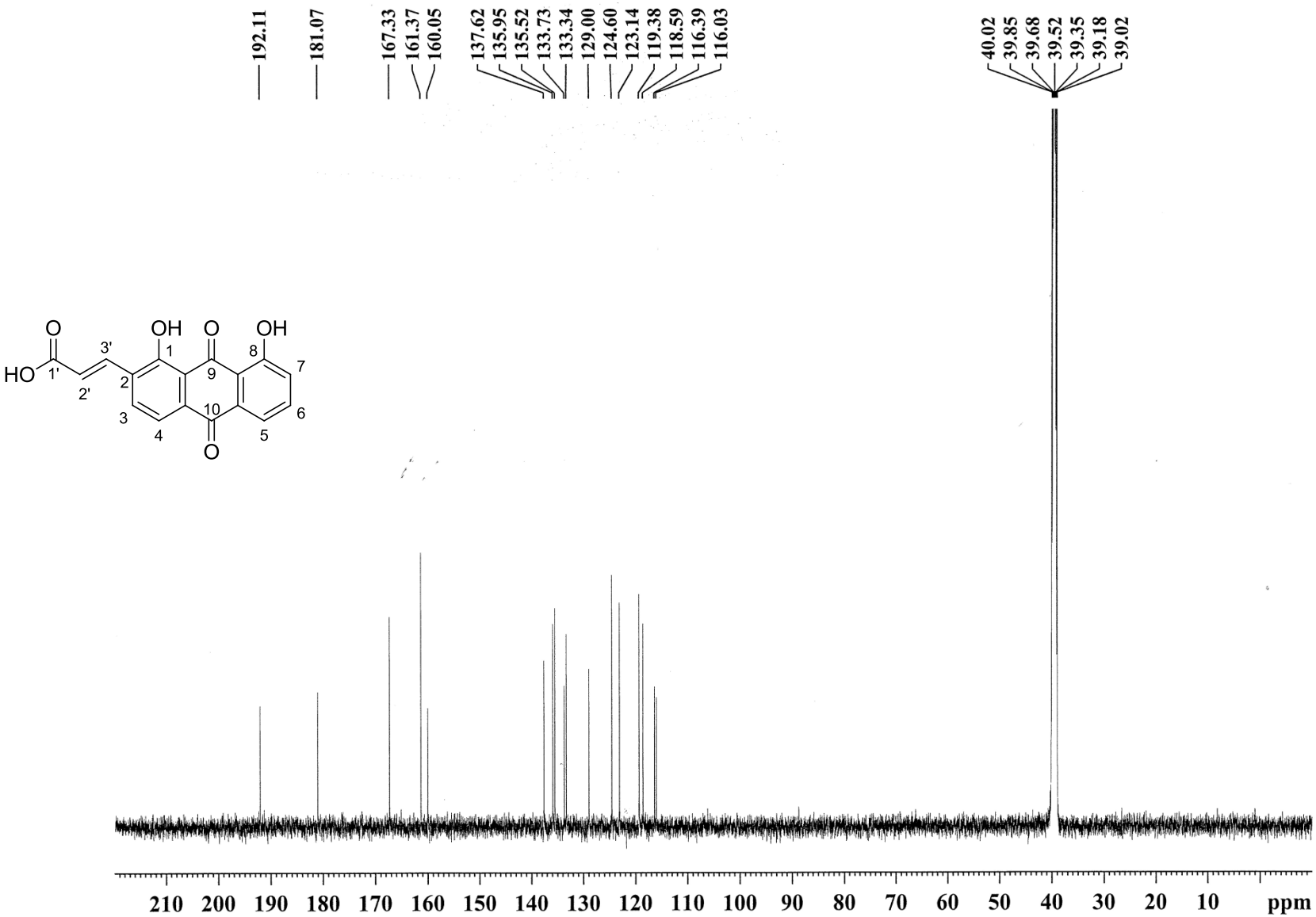


**Figure S10:** 500 MHz $^{1}$H NMR spectrum of **9a** in $CDCl_3$

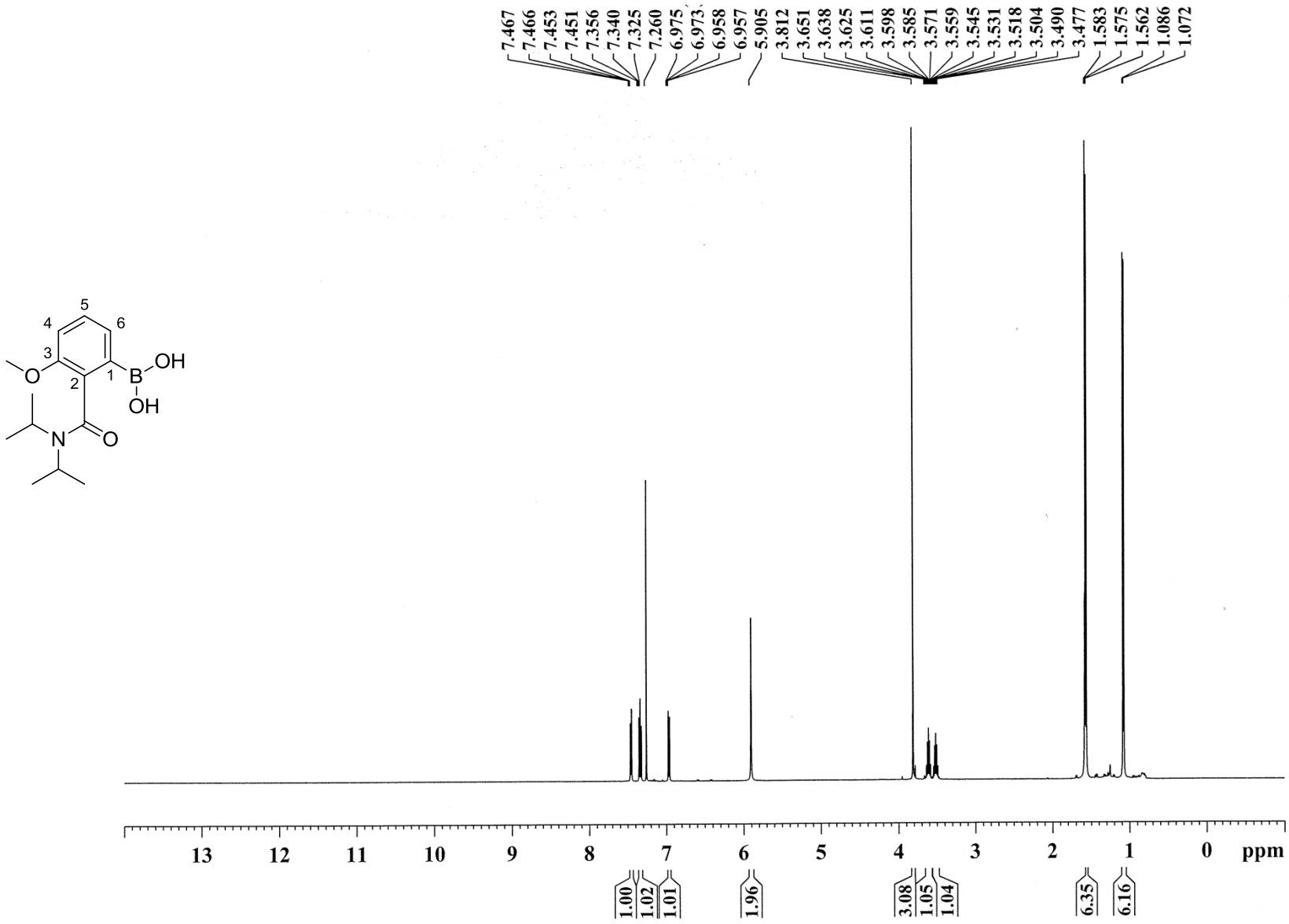


**Figure S11:** 500 MHz $^{1}$H NMR spectrum of **9c** in $CDCl_3$

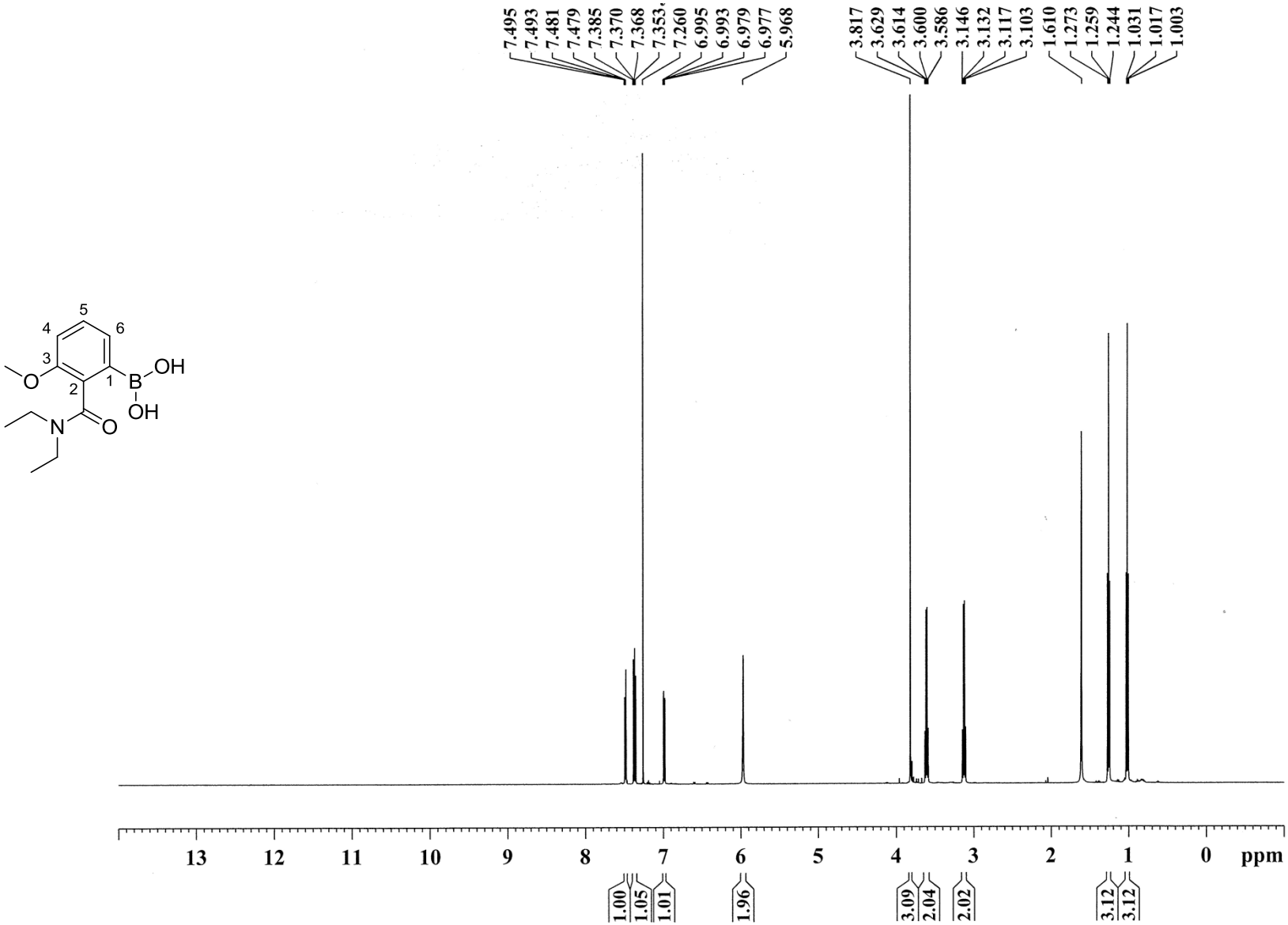


**Figure S12:** 125 MHz $^{13}C$ NMR spectrum of **9c** in $CDCl_3$

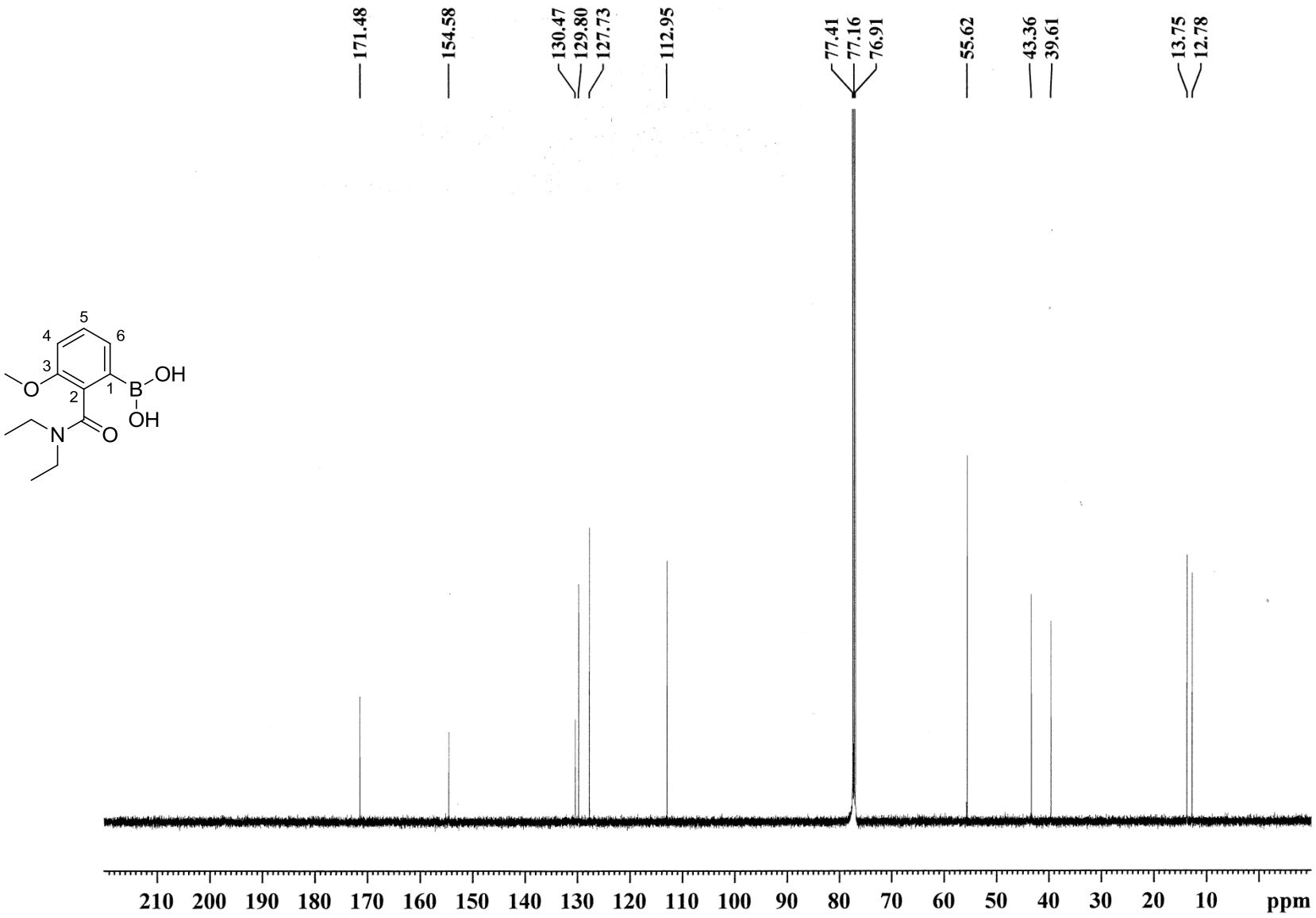


**Figure S13:** 400 MHz $^{1}$H NMR spectrum of **10a** in $CDCl_3$

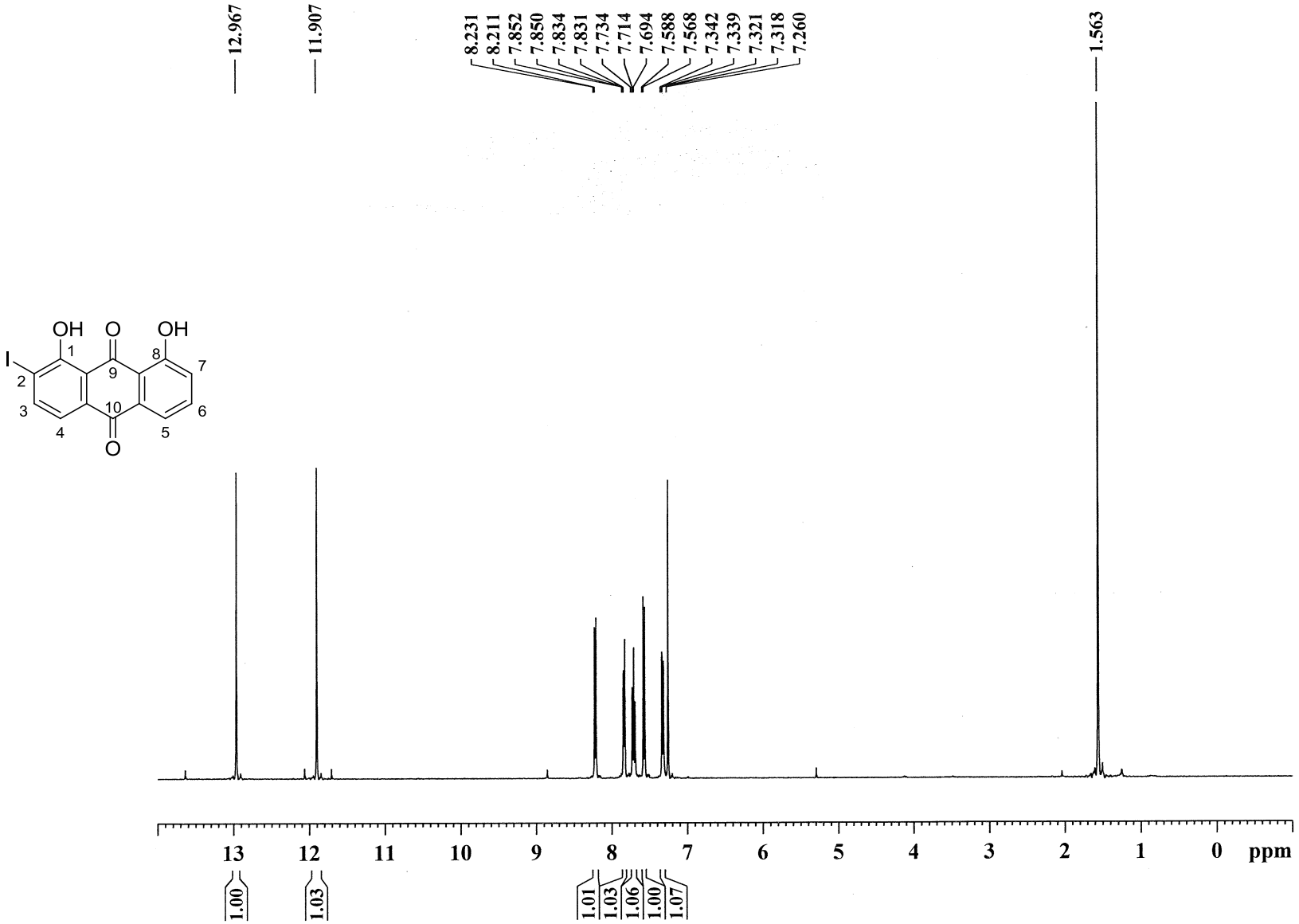


**Figure S14:** 100 MHz $^{13}C$ NMR spectrum of **10a** in $CDCl_3$

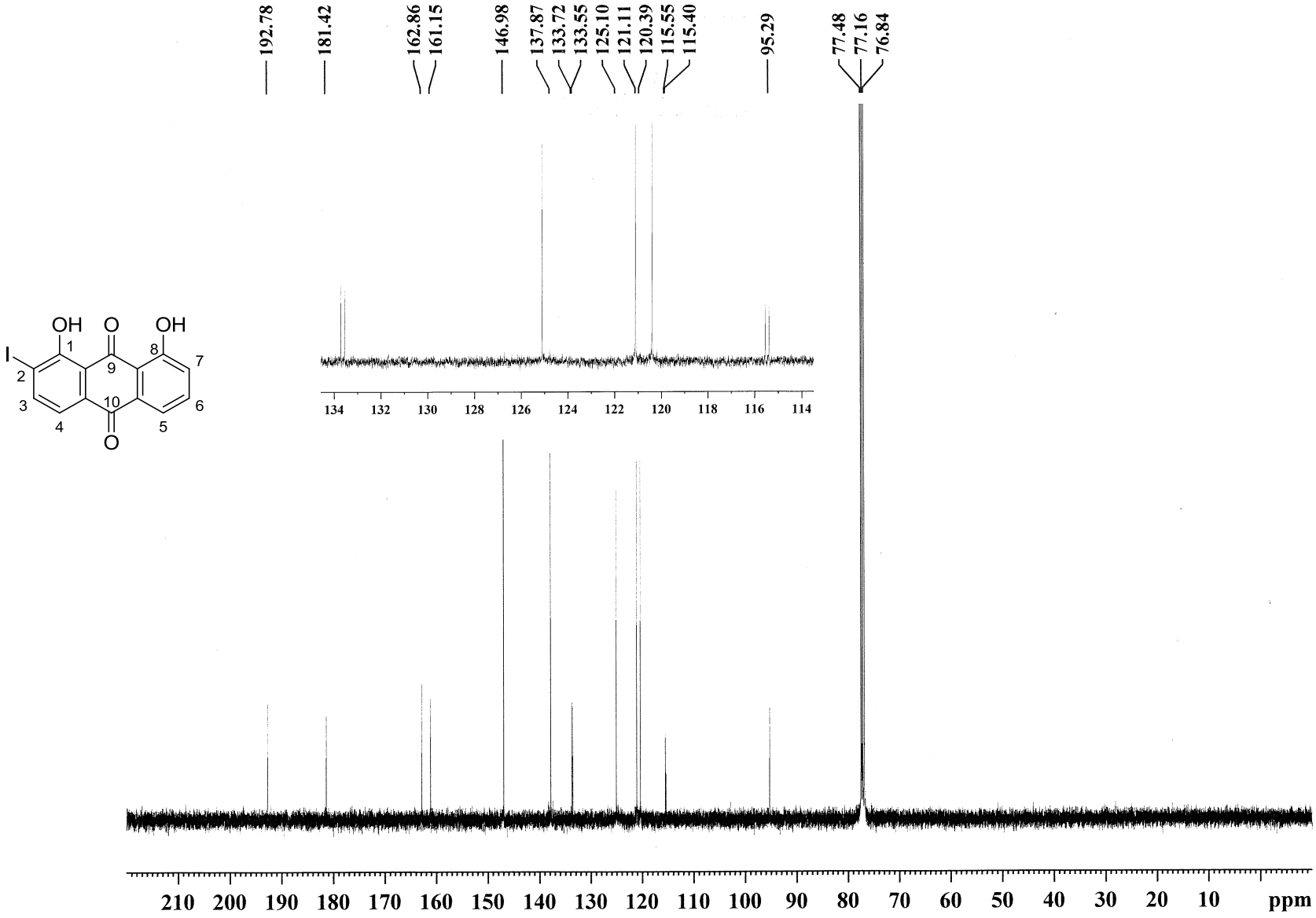


**Figure S15:** 500 MHz $^{1}$H NMR spectrum of **10b** in $CDCl_3$

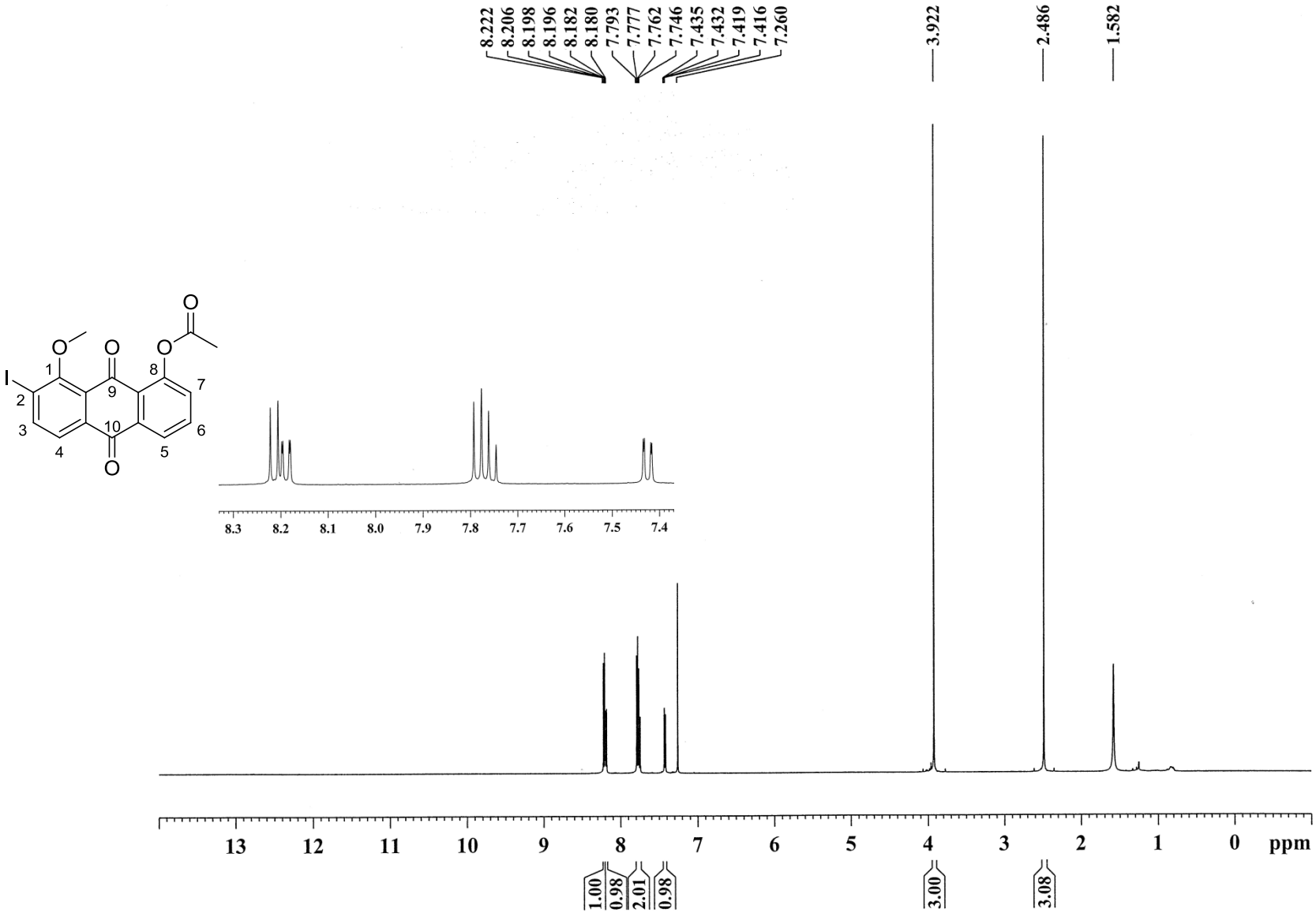


**Figure S16:** 125 MHz $^{13}C$ NMR spectrum of **10b** in $CDCl_3$

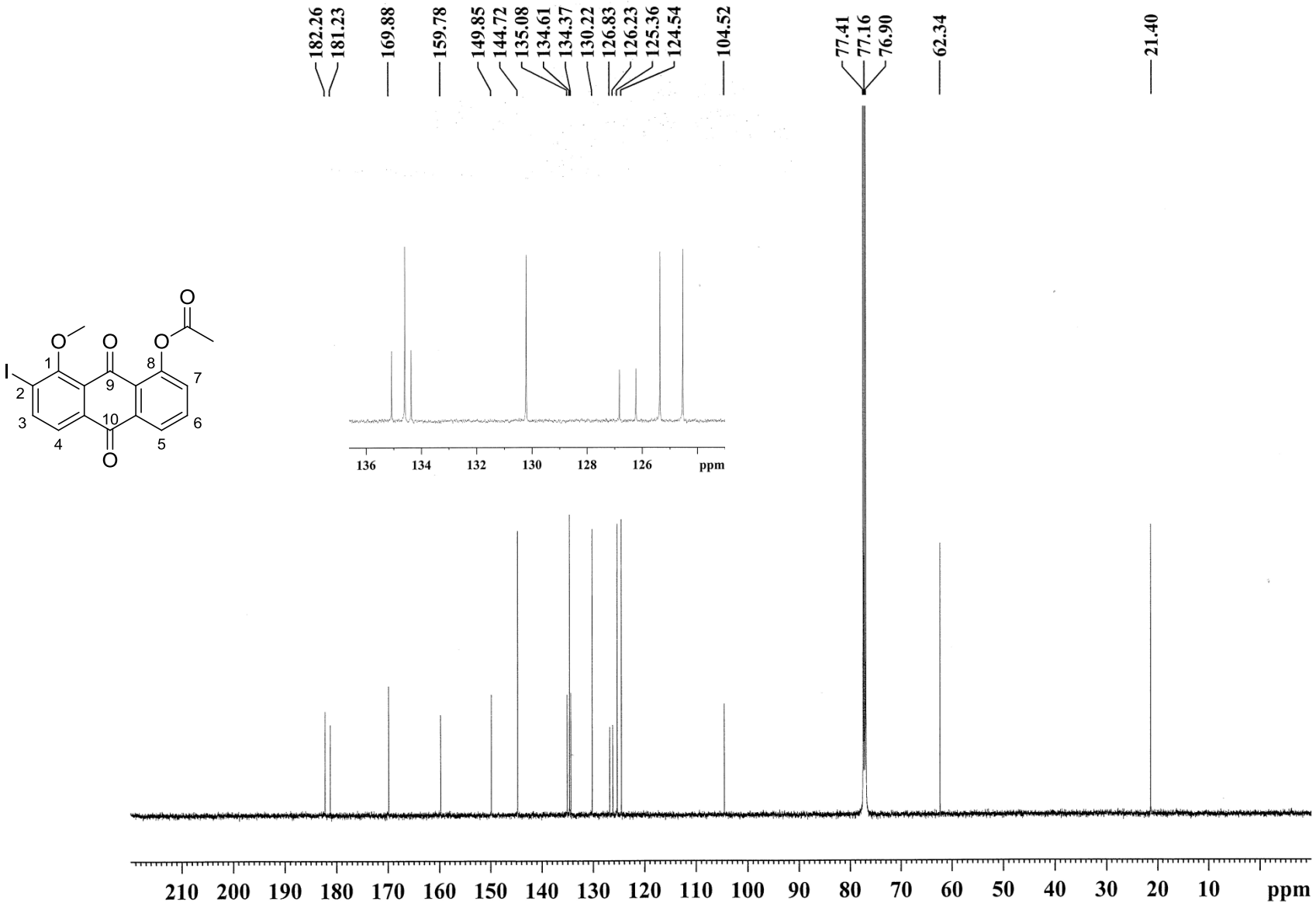


**Figure S17:** 500 MHz $^{1}$H NMR spectrum of **10c** in $CDCl_3$

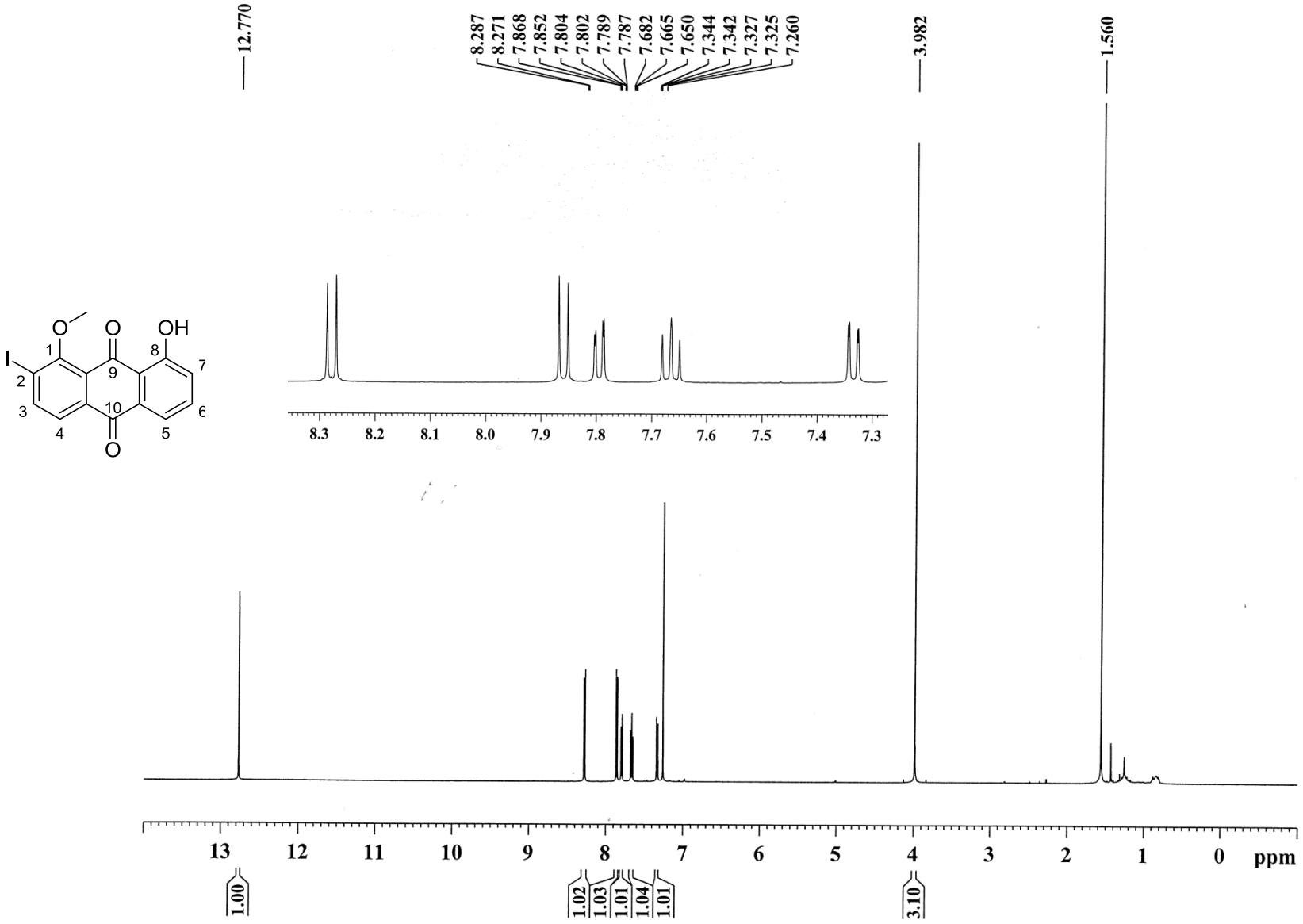


**Figure S18:** 125 MHz $^{13}C$ NMR spectrum of **10c** in $CDCl_3$

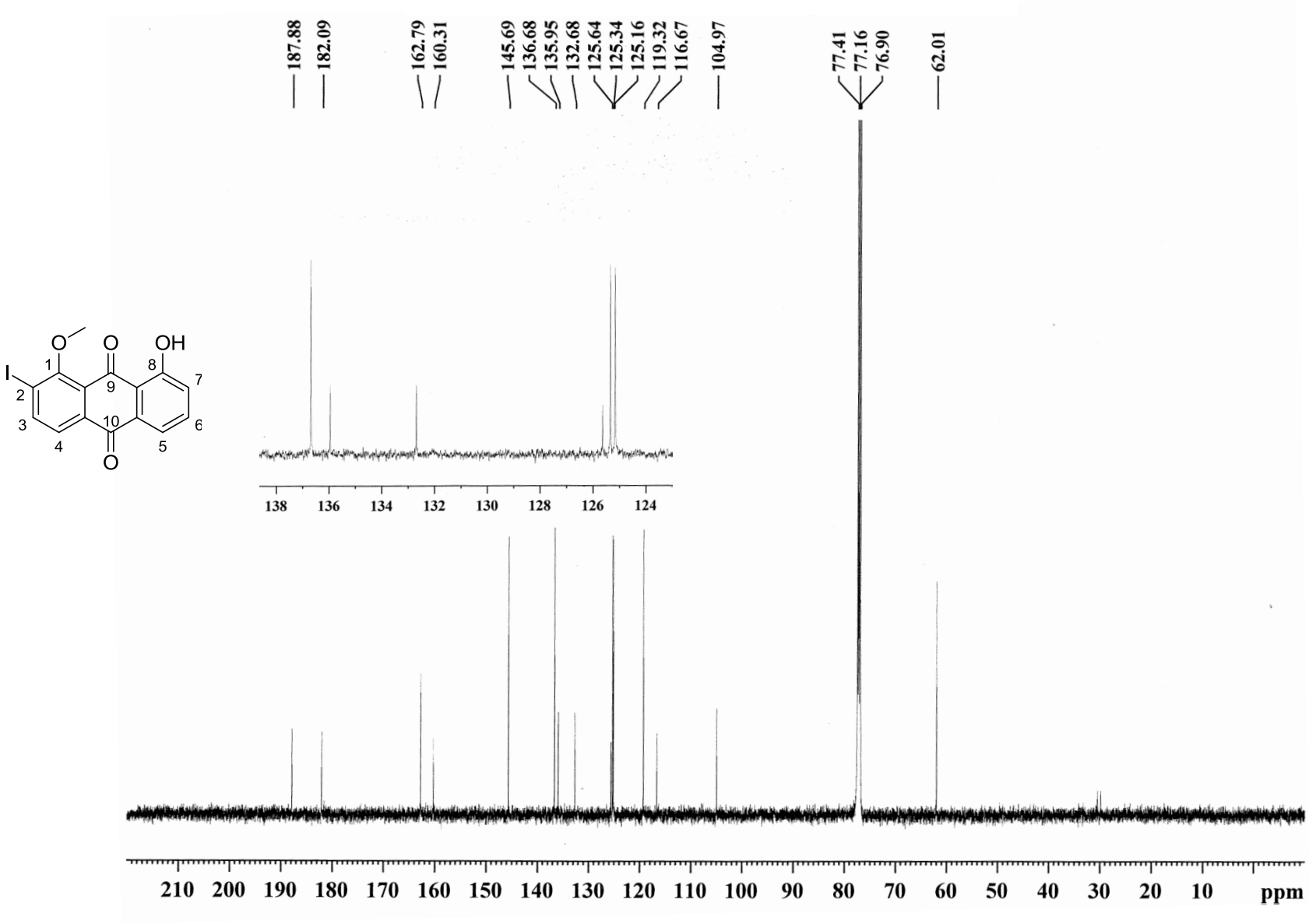


**Figure S19:** 400 MHz $^{1}$H NMR spectrum of **10e** in $CDCl_3$

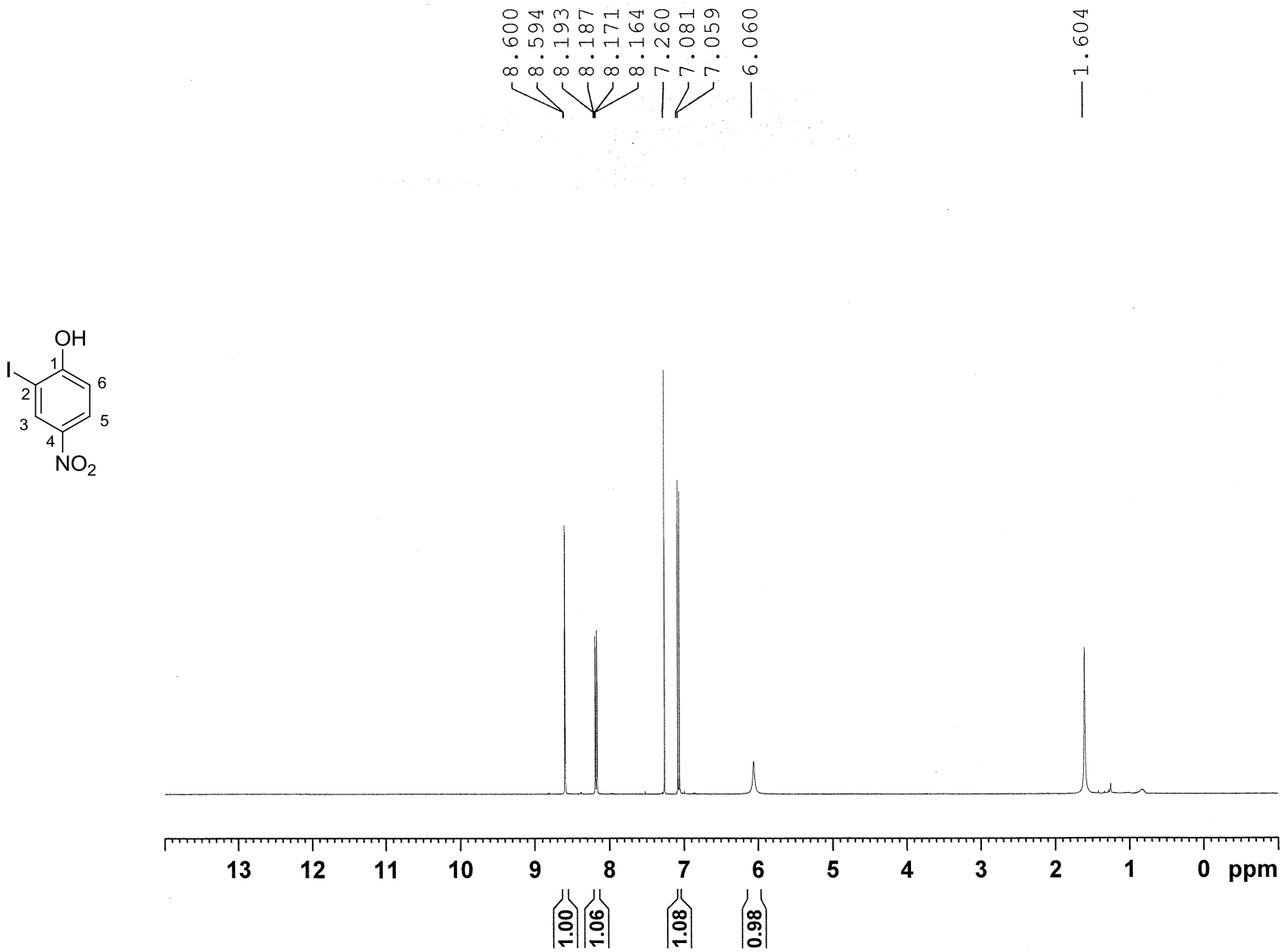


**Figure S20:** 500 MHz $^{1}$H NMR spectrum of **10f** in $CDCl_3$

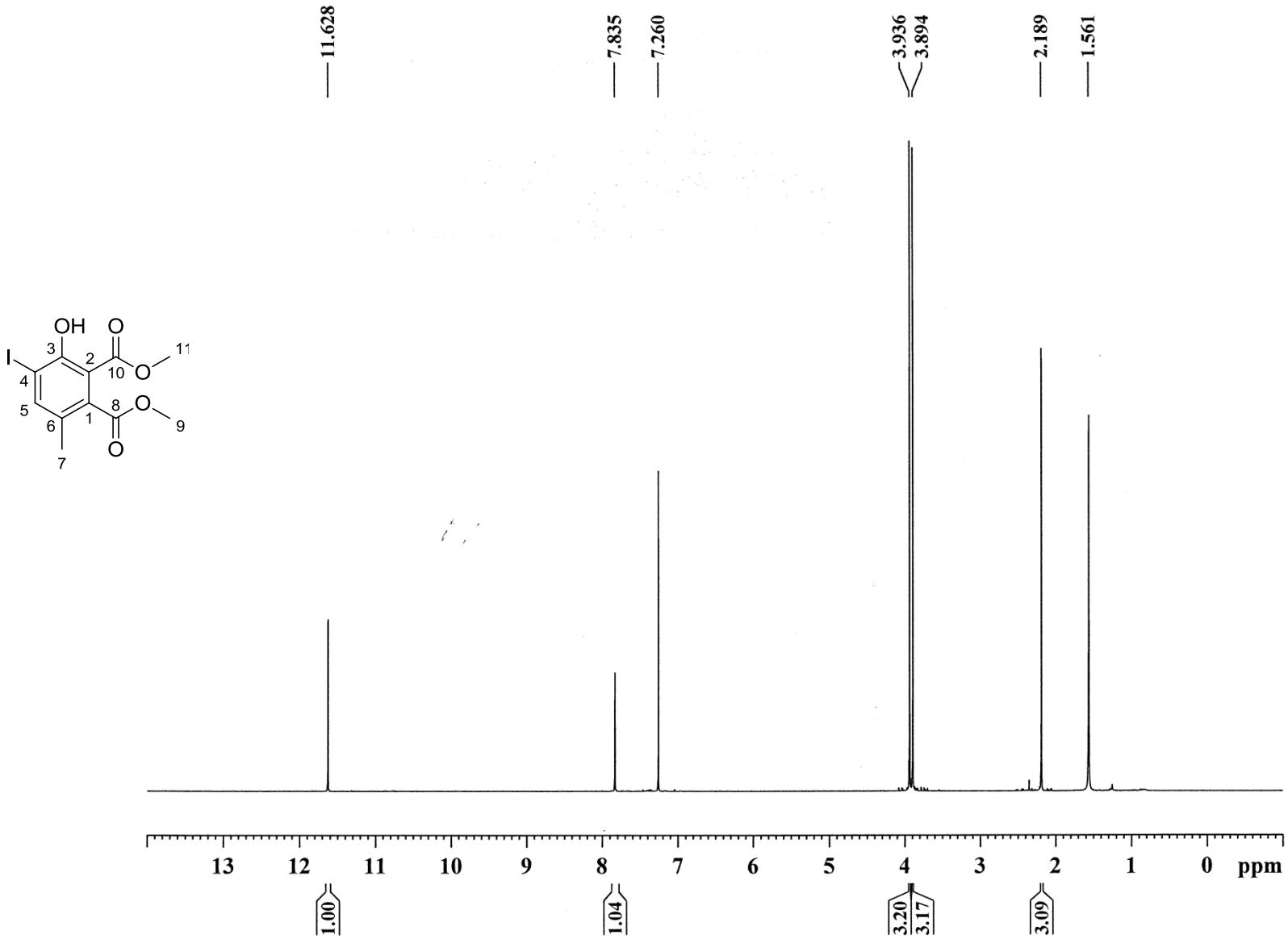


**Figure S21:** 125 MHz $^{13}C$ NMR spectrum of **10f** in $CDCl_3$

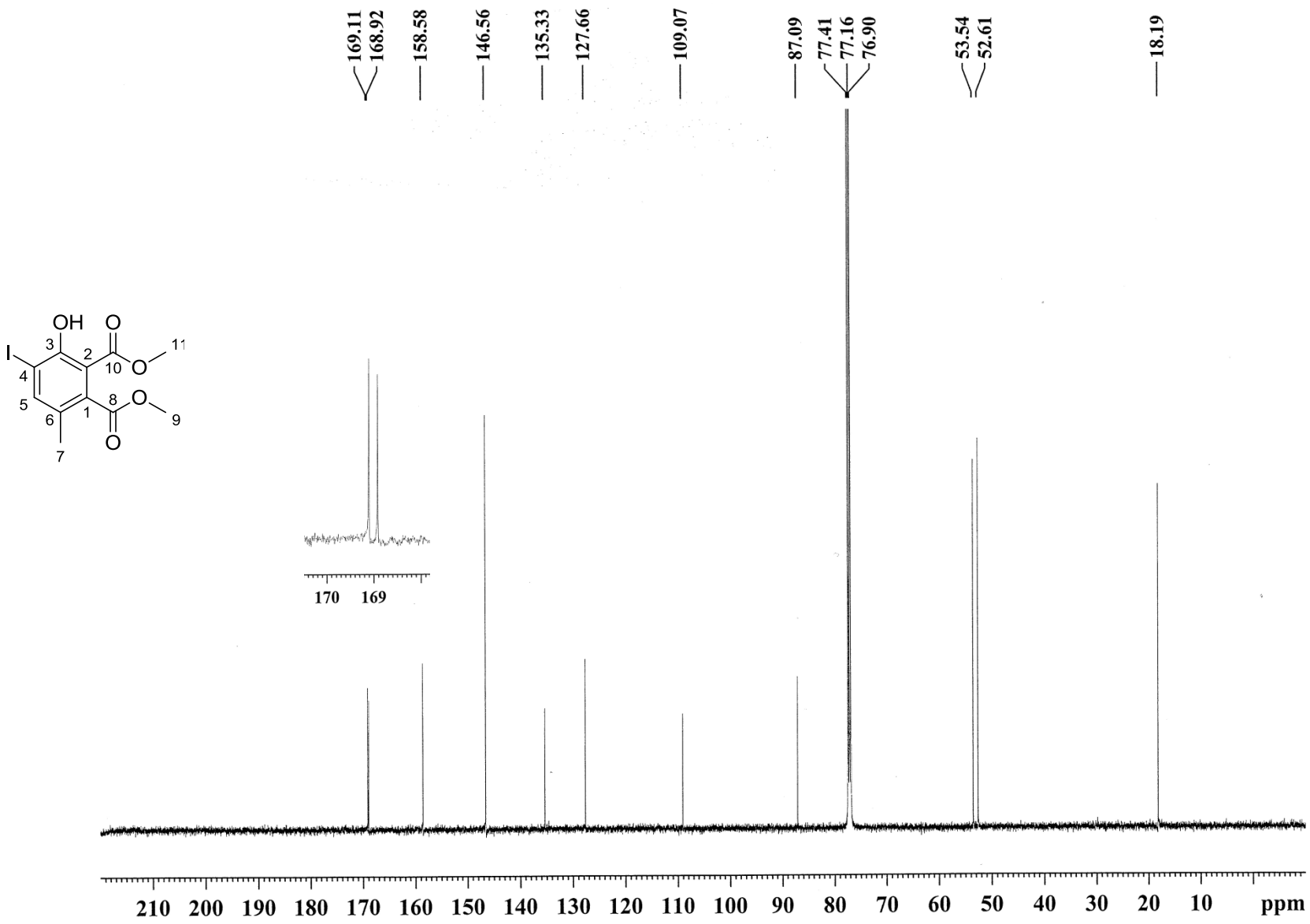


**Figure S22:** 500 MHz $^{1}$H NMR spectrum of **11a** in $CDCl_3$

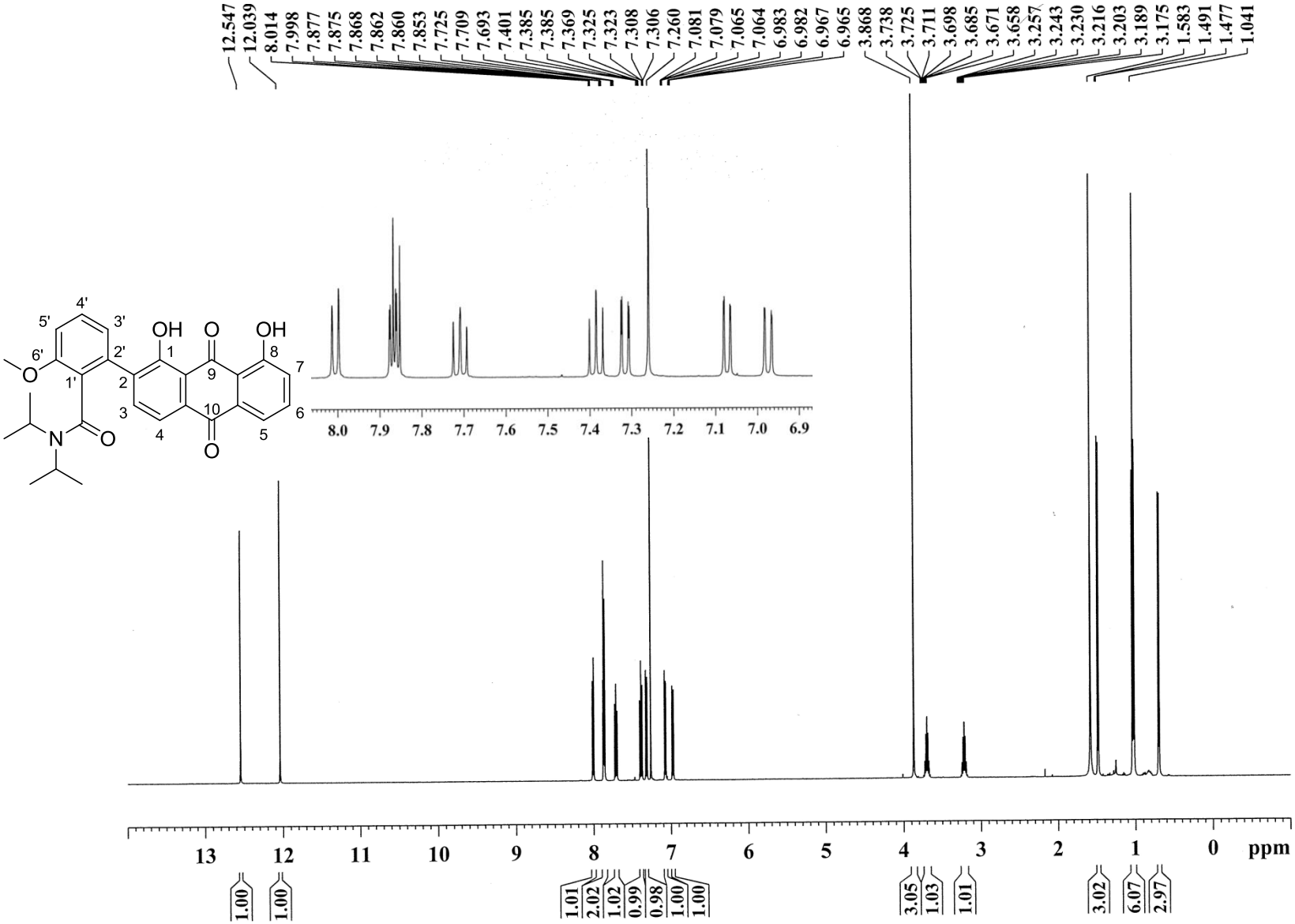


**Figure S23:** 125 MHz $^{13}C$ NMR spectrum of **11a** in $CDCl_3$

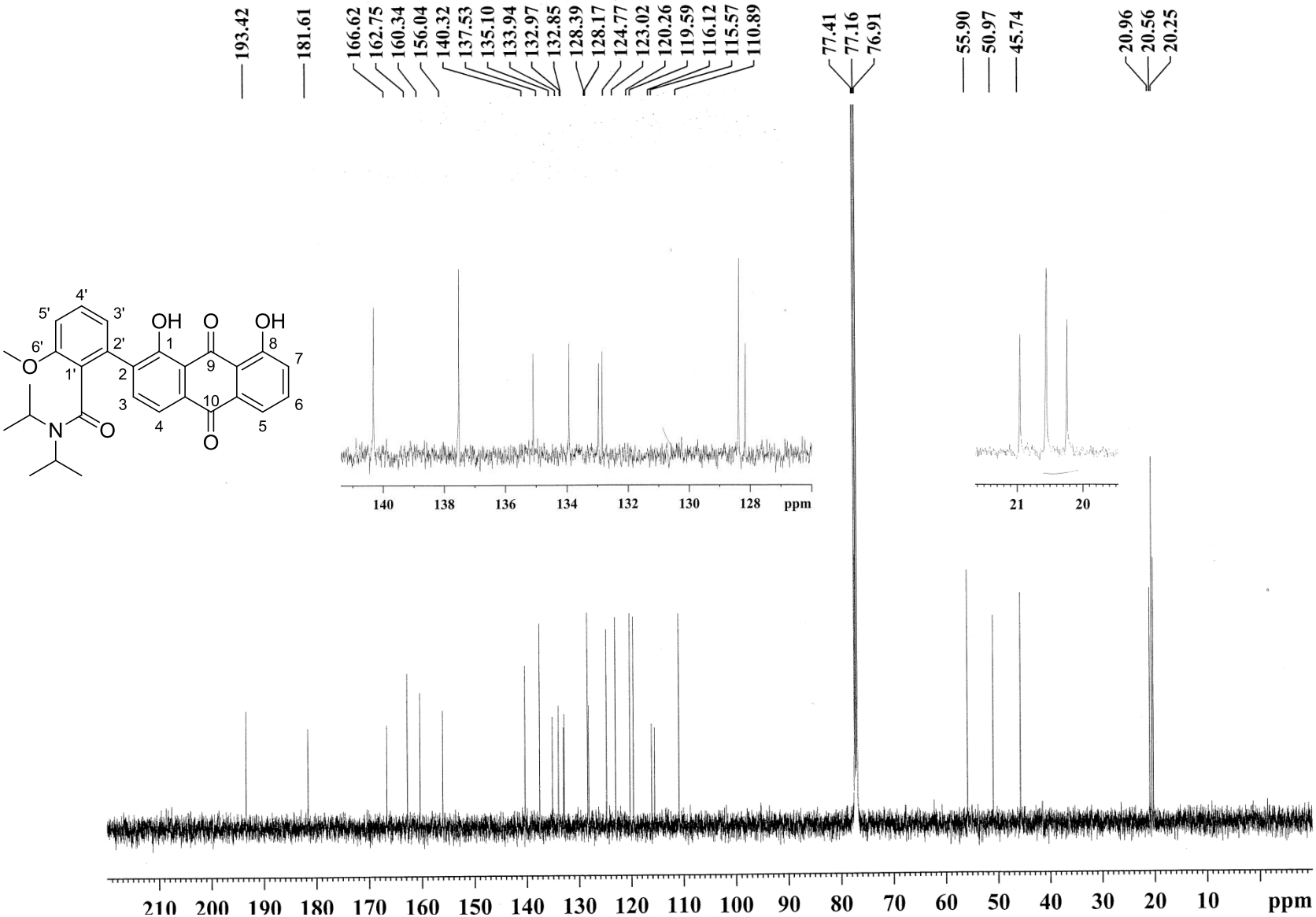


**Figure S24:** 400 MHz $^{1}$H NMR spectrum of **11c** in $CDCl_3$

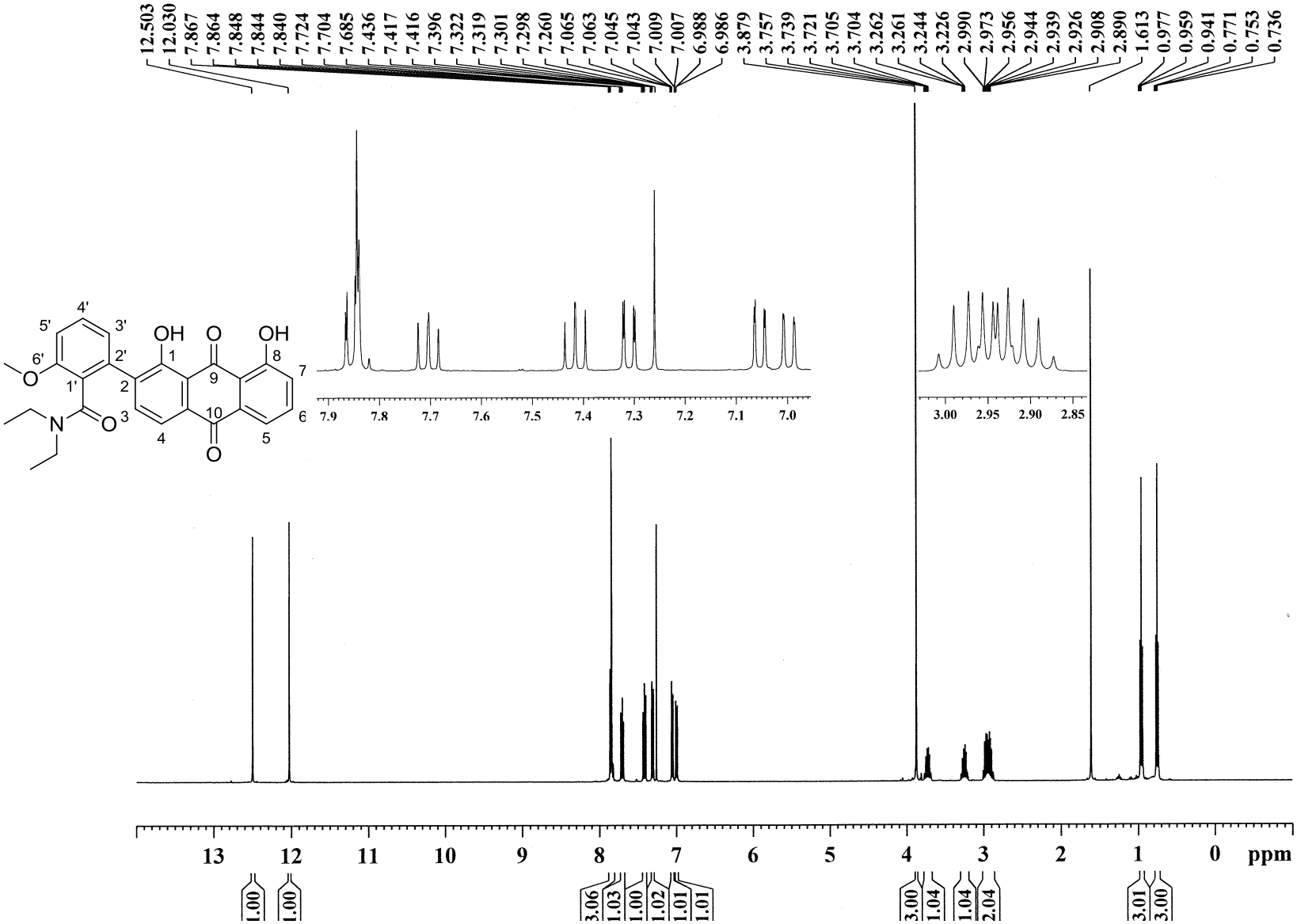


**Figure S25:** 100 MHz $^{13}C$ NMR spectrum of **11c** in $CDCl_3$

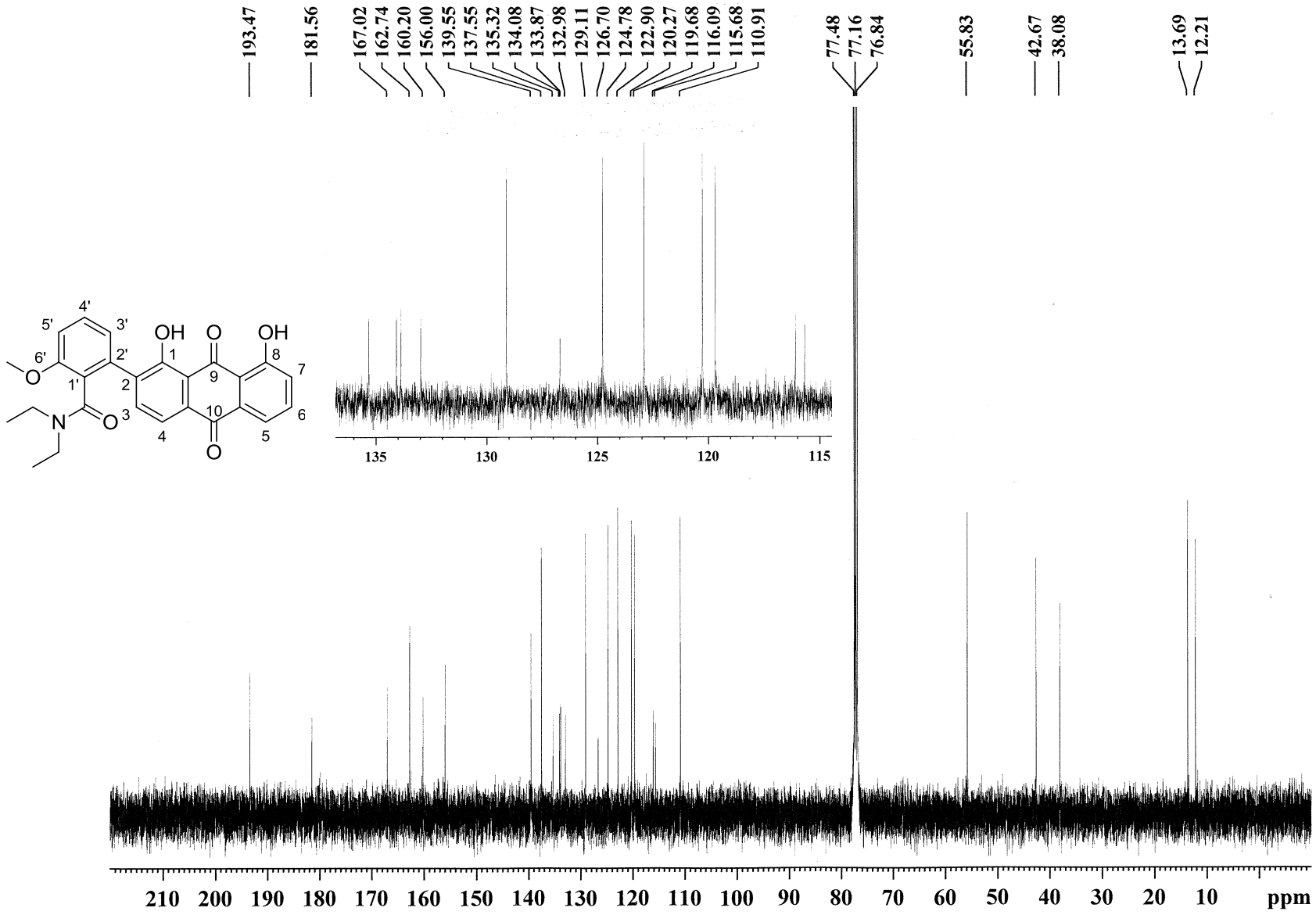


**Figure S26:** 500 MHz $^{1}$H NMR spectrum of **11d** in $CDCl_3$

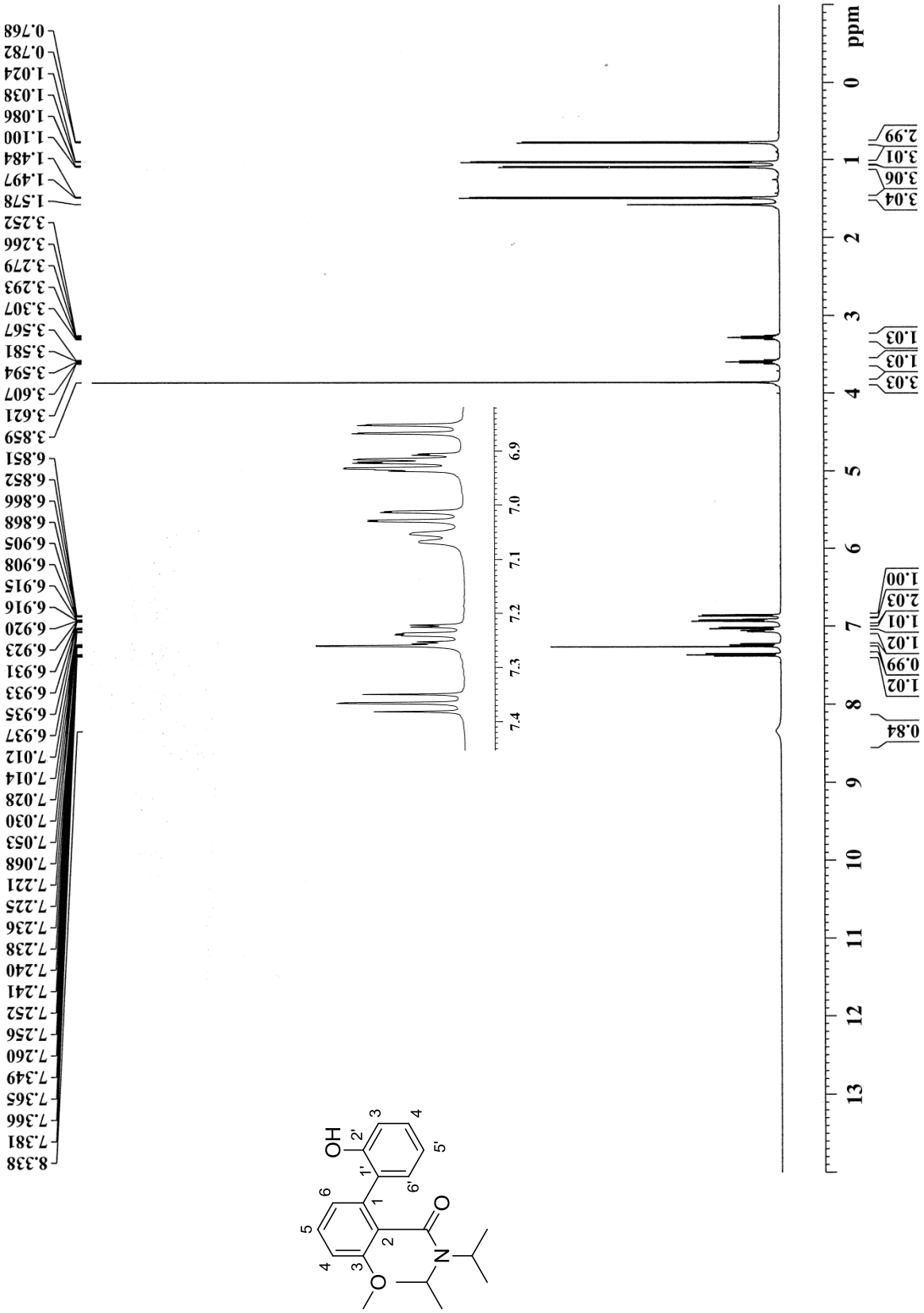


**Figure S27:** 125 MHz $^{13}C$ NMR spectrum of **11d** in $CDCl_3$

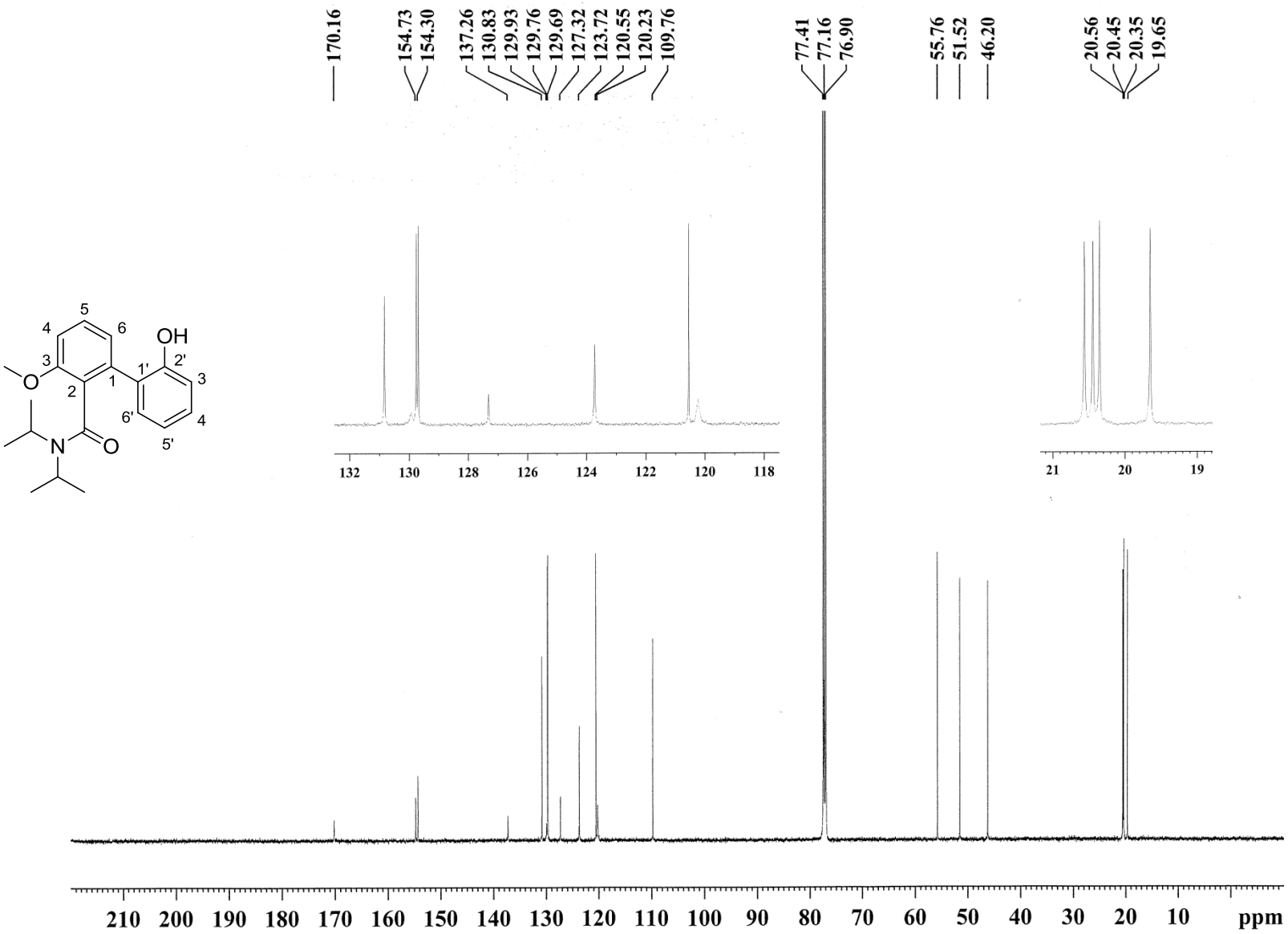


**Figure S28:** 500 MHz $^{1}$H NMR spectrum of **11f** in MeOD

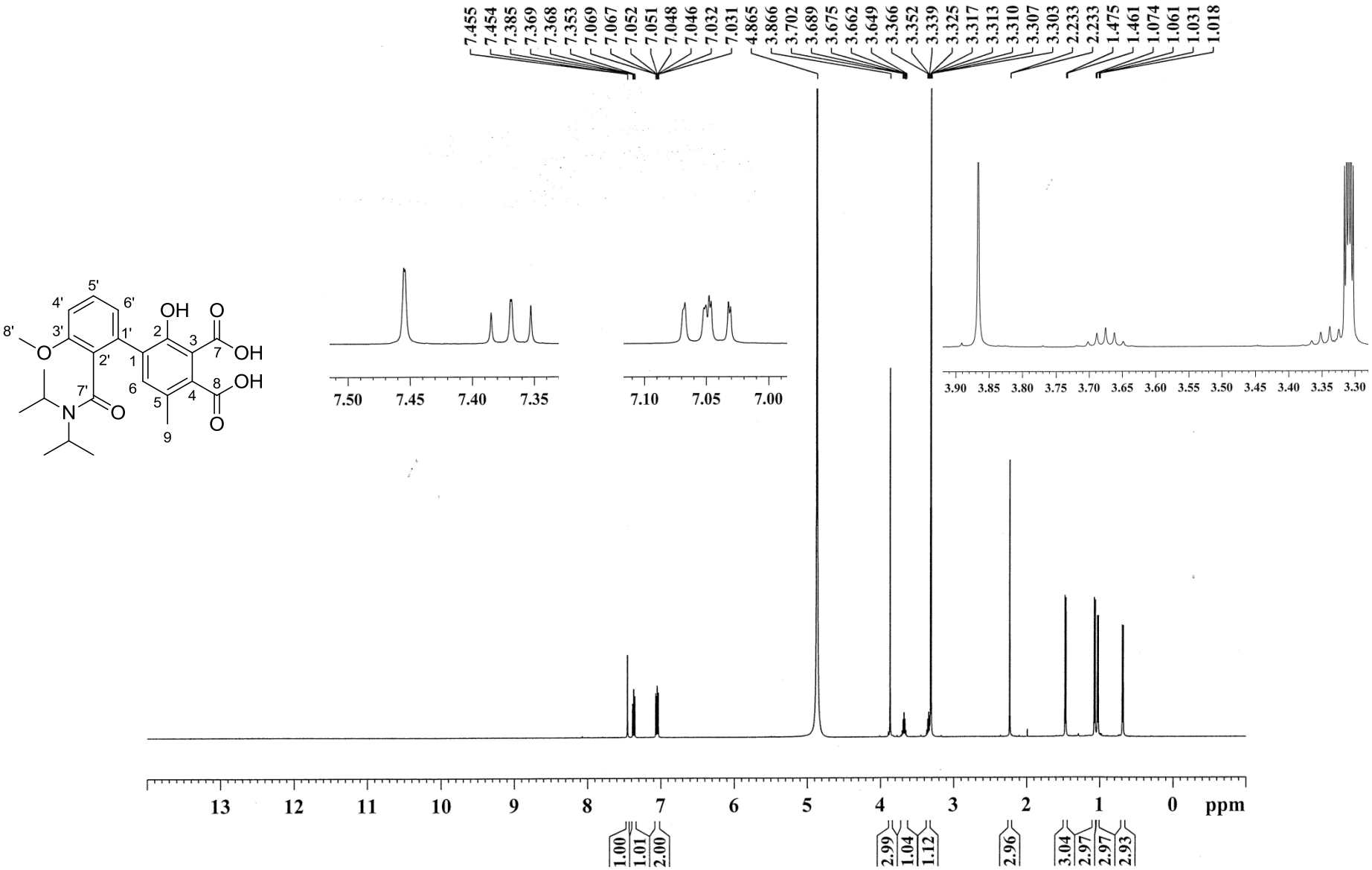


**Figure S29:** 125 MHz $^{13}$C NMR spectrum of **11f** in MeOD

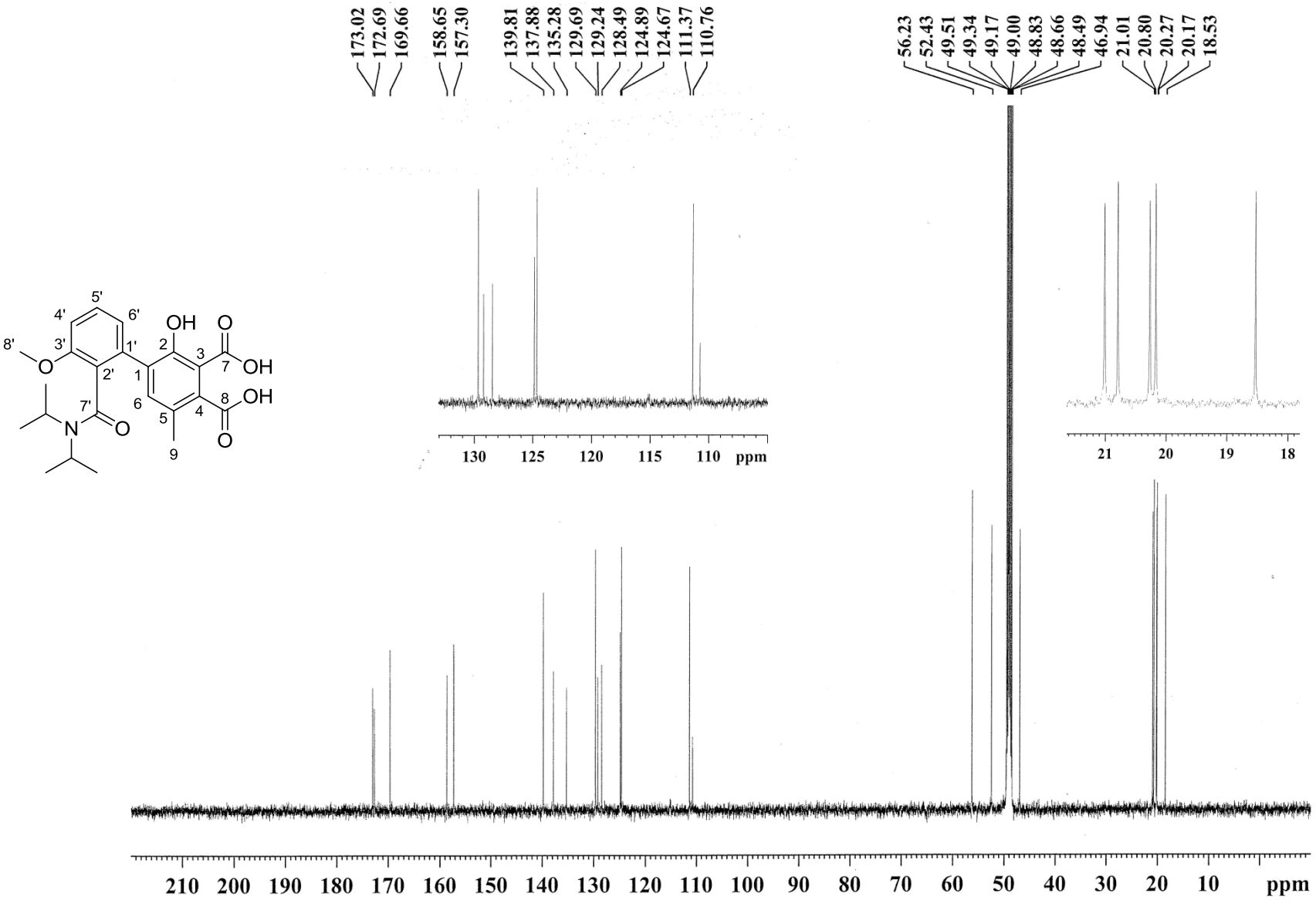


**Figure S30:** 500 MHz $^{1}$H NMR spectrum of **12a** in $CDCl_3$

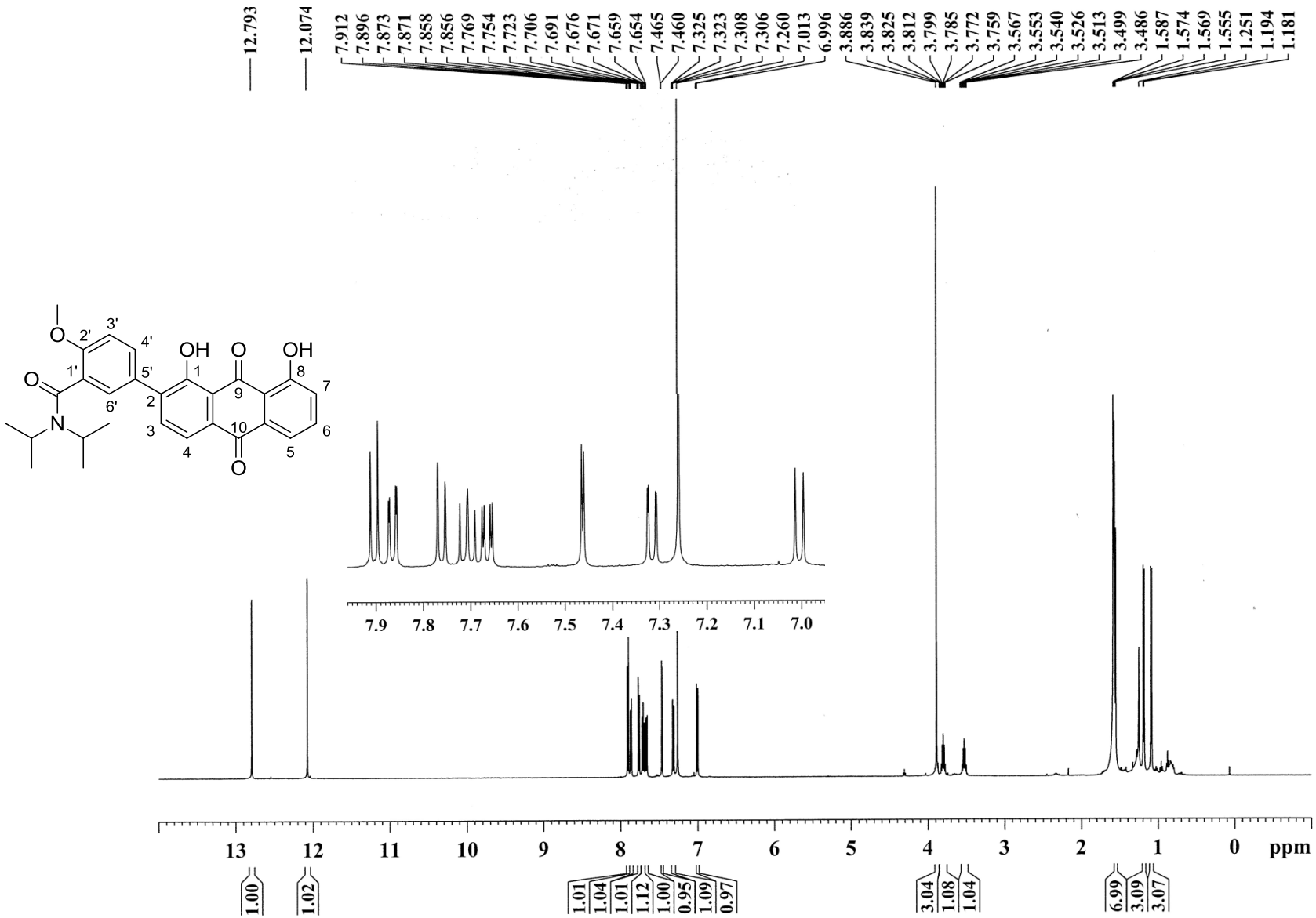


**Figure S31:** 125 MHz $^{13}C$ NMR spectrum of **12a** in $CDCl_3$

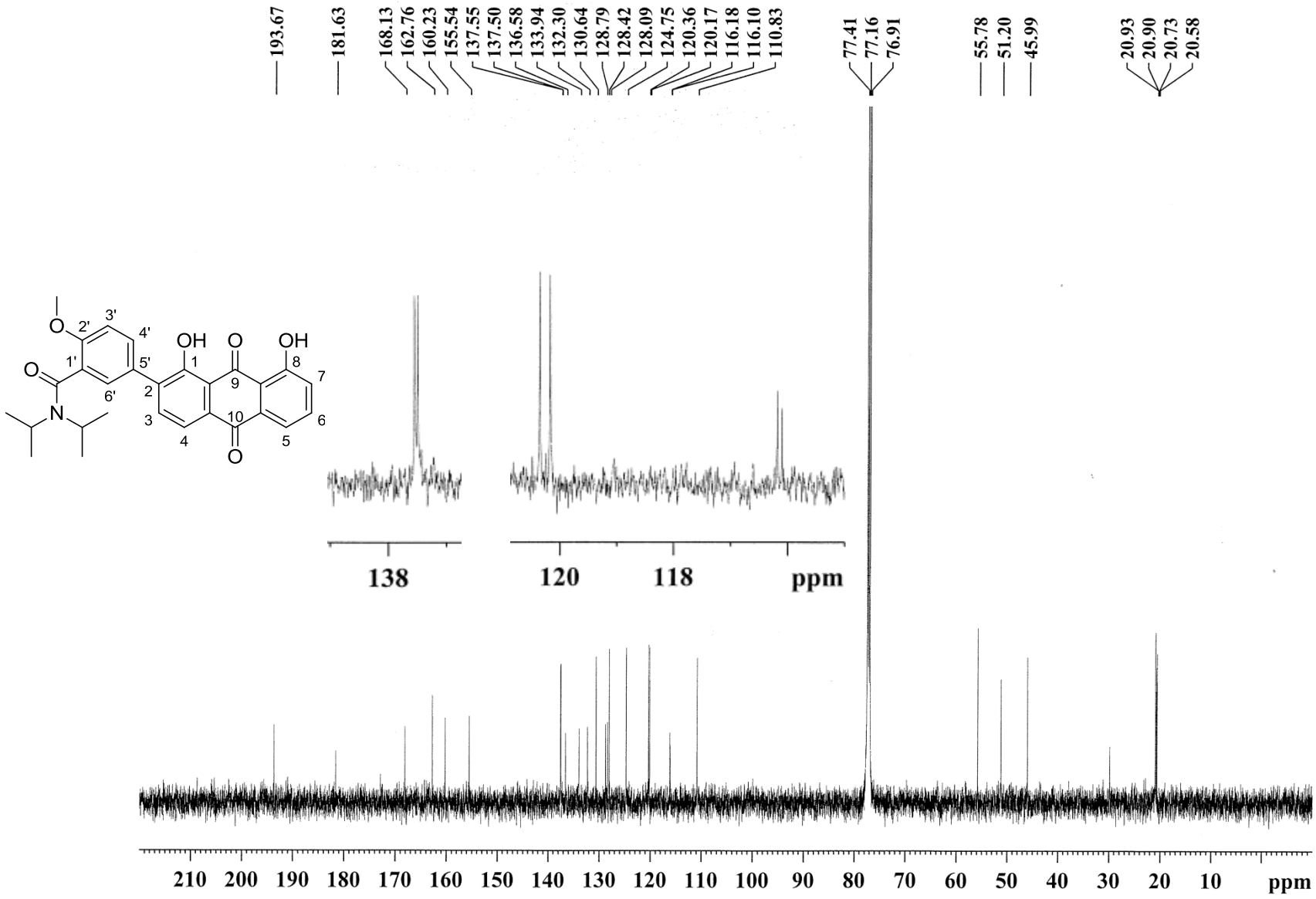


**Figure S32:** 600 MHz $^{1}$H NMR spectrum of **13** in $CDCl_3$

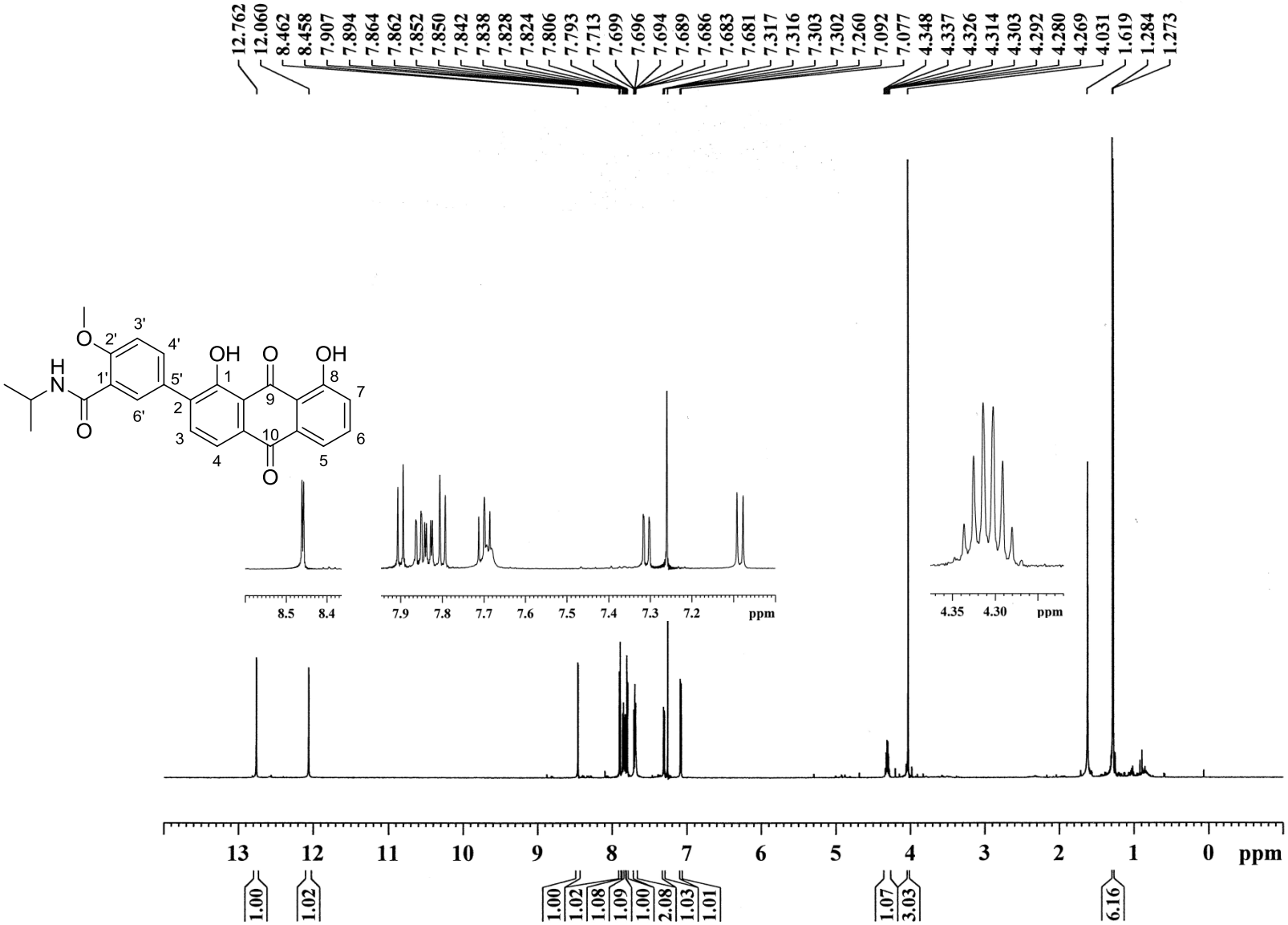


**Figure S33:** 150 MHz $^{13}C$ NMR spectrum of **13** in $CDCl_3$

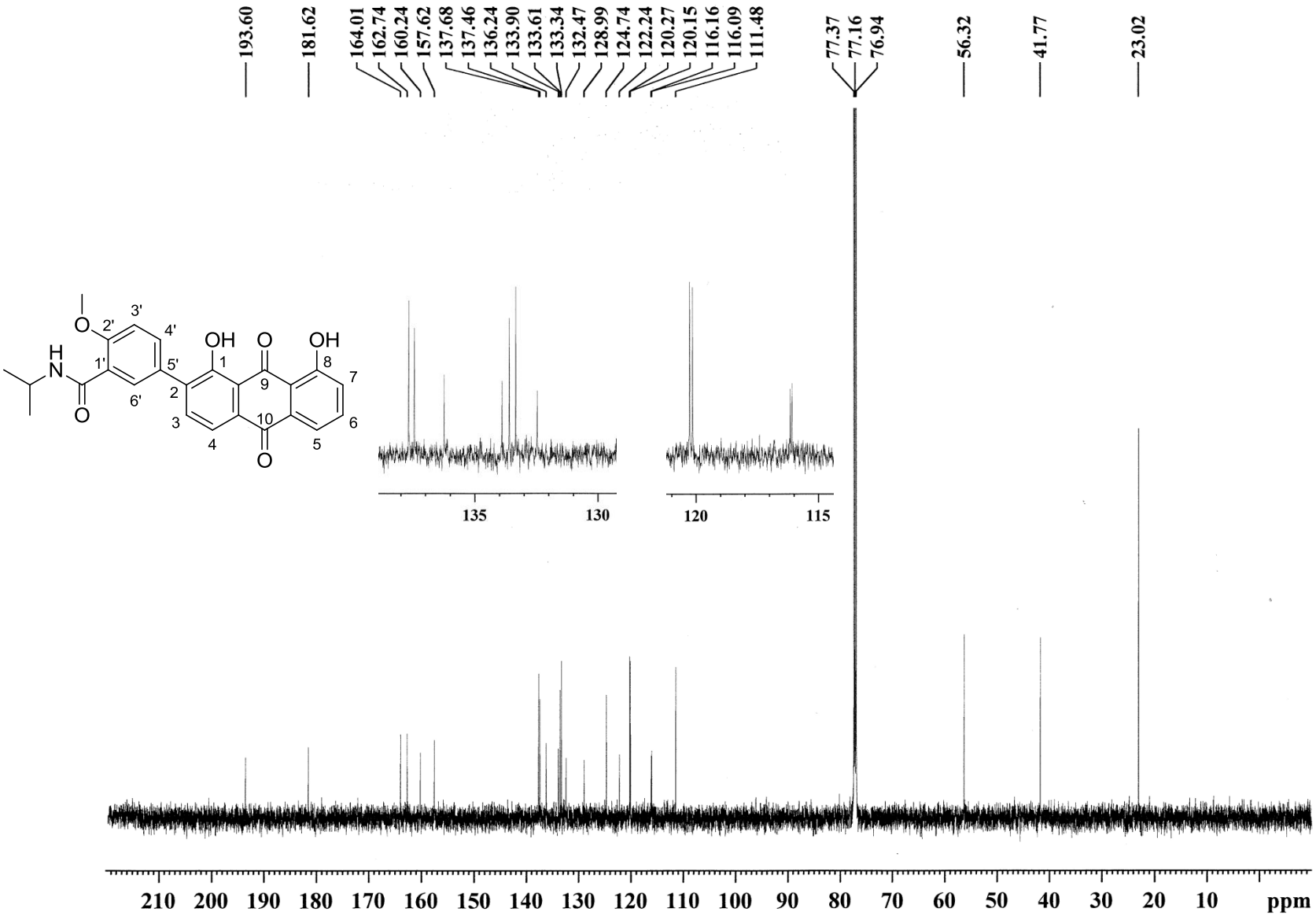


**Figure S34:** 600 MHz $^{1}$H NMR spectrum of **14** in $CDCl_3$

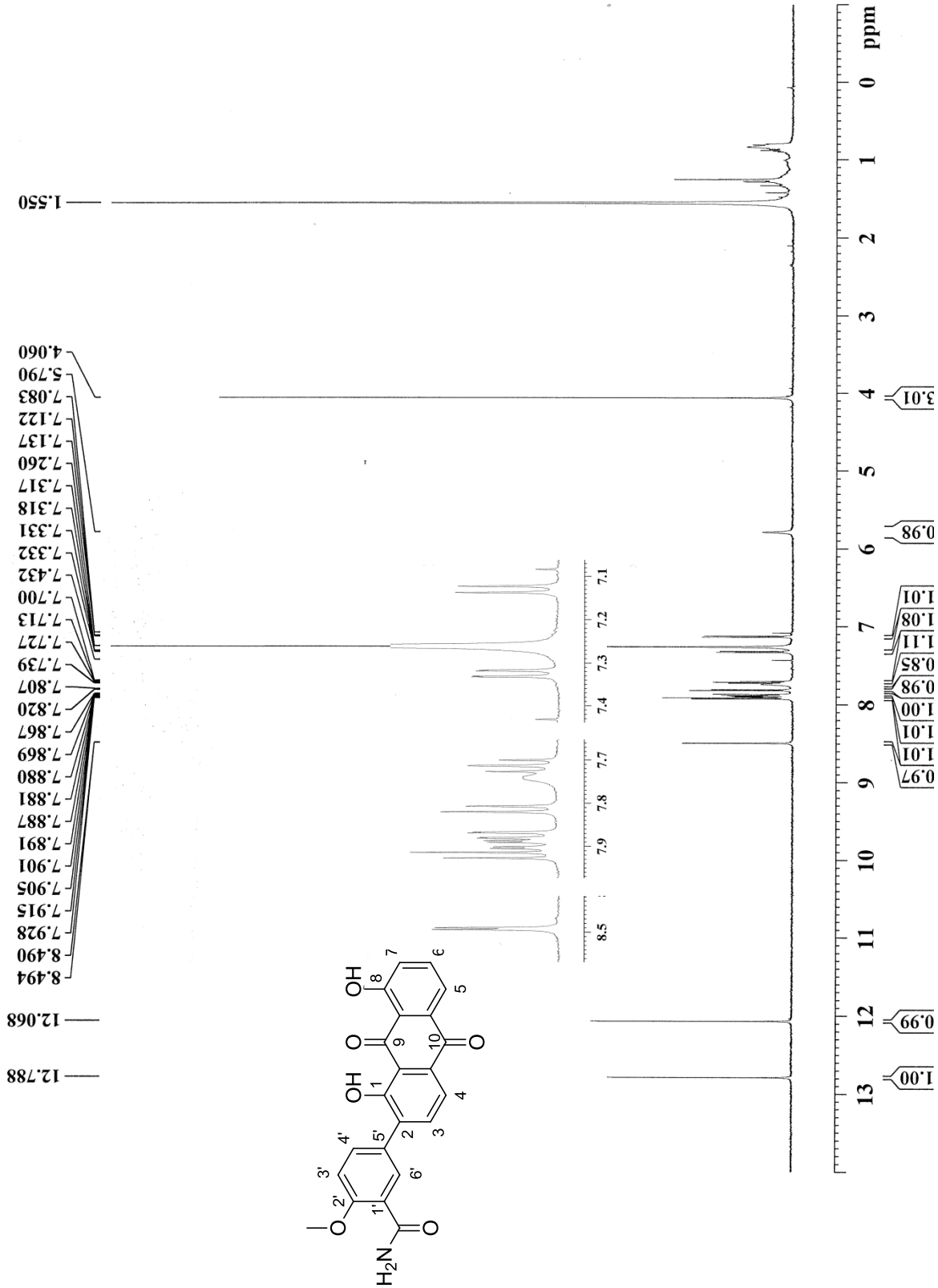


**Figure S35:** 600 MHz $^{1}$H NMR spectrum of **14** in $d_5$-pyridine

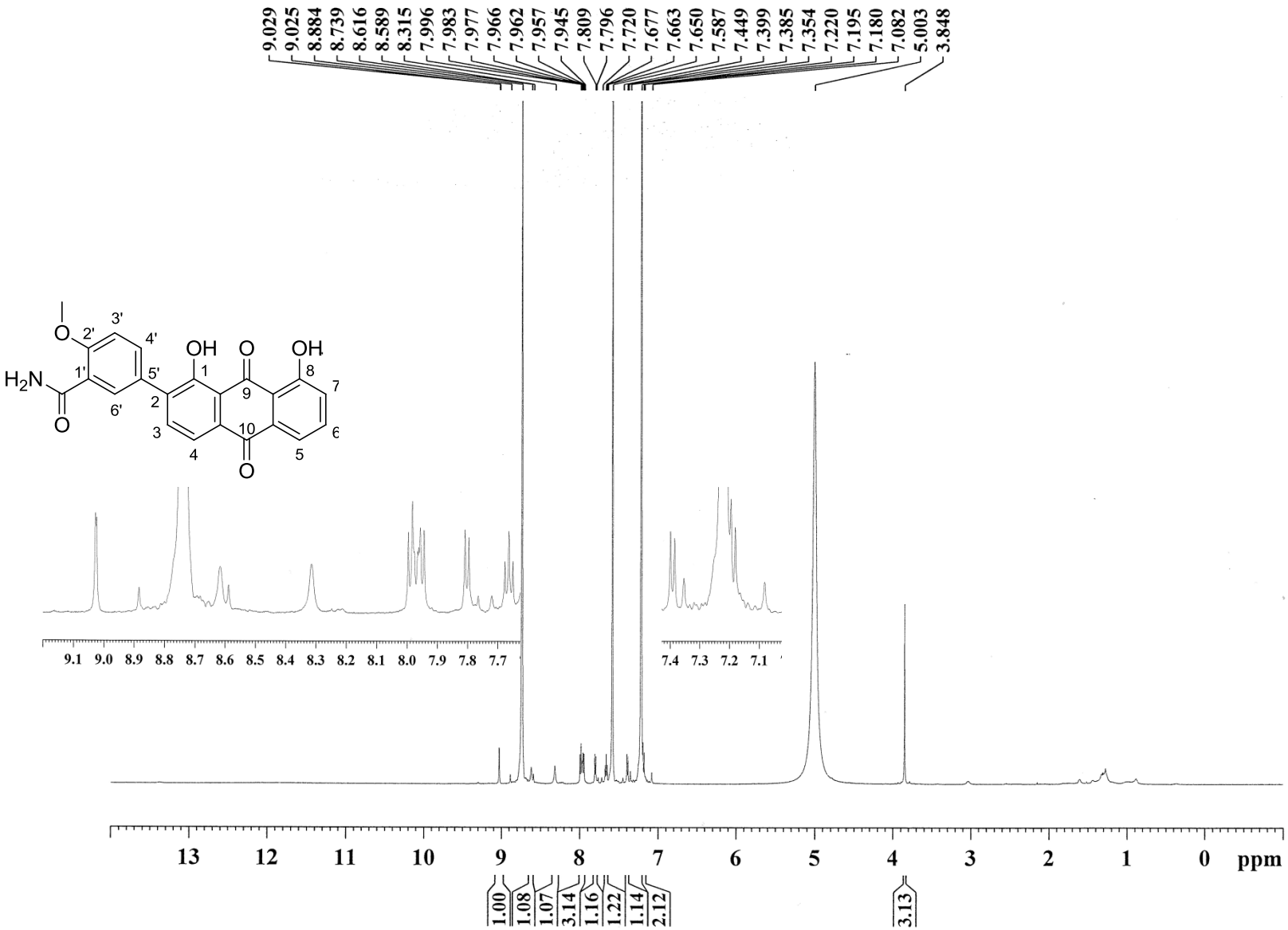


**Figure S36:** 150 MHz $^{13}$C NMR spectrum of **14** in $d_5$-pyridine

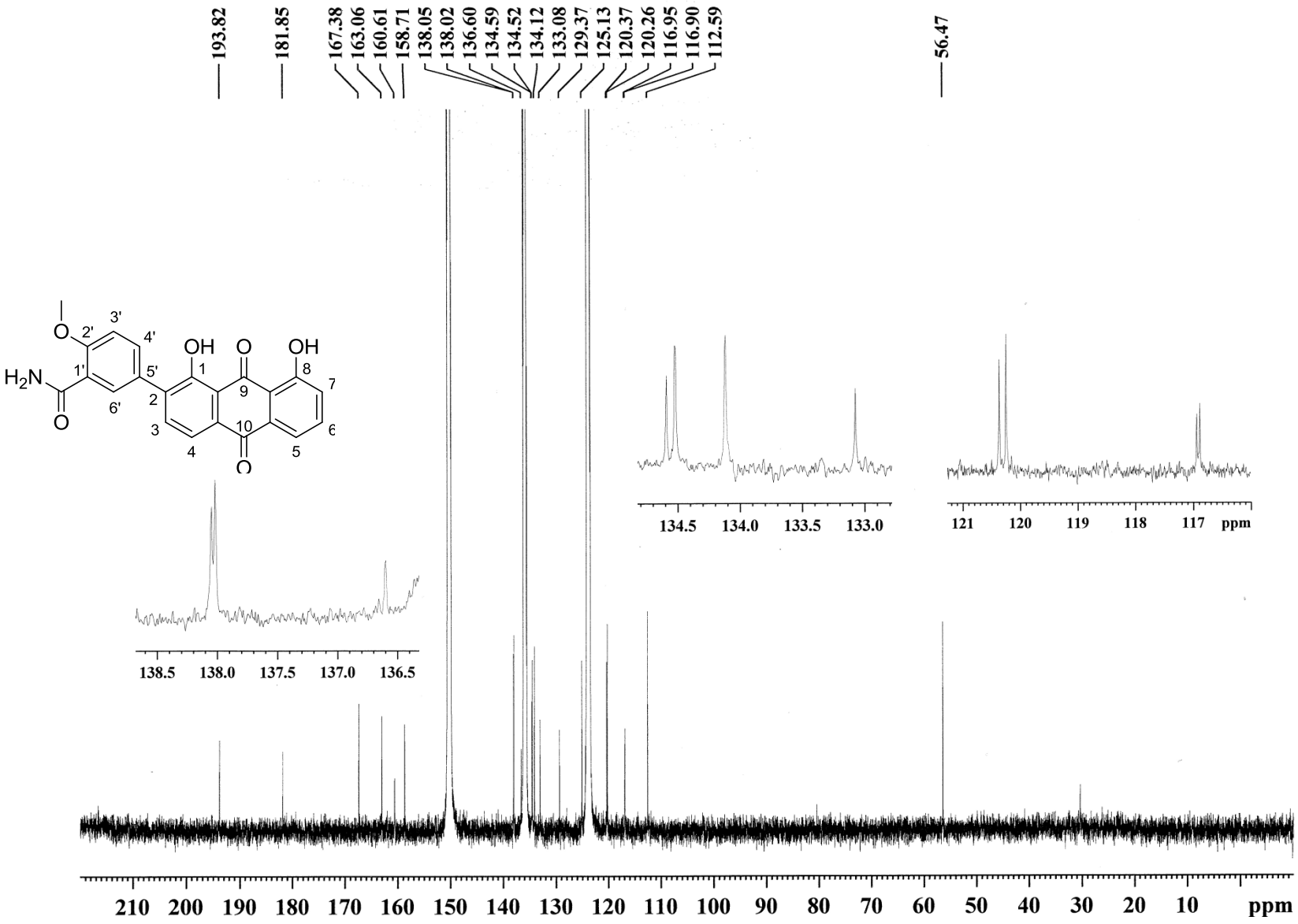


**Figure S37:** 400 MHz $^{1}$H NMR spectrum of **16** in $CDCl_3$

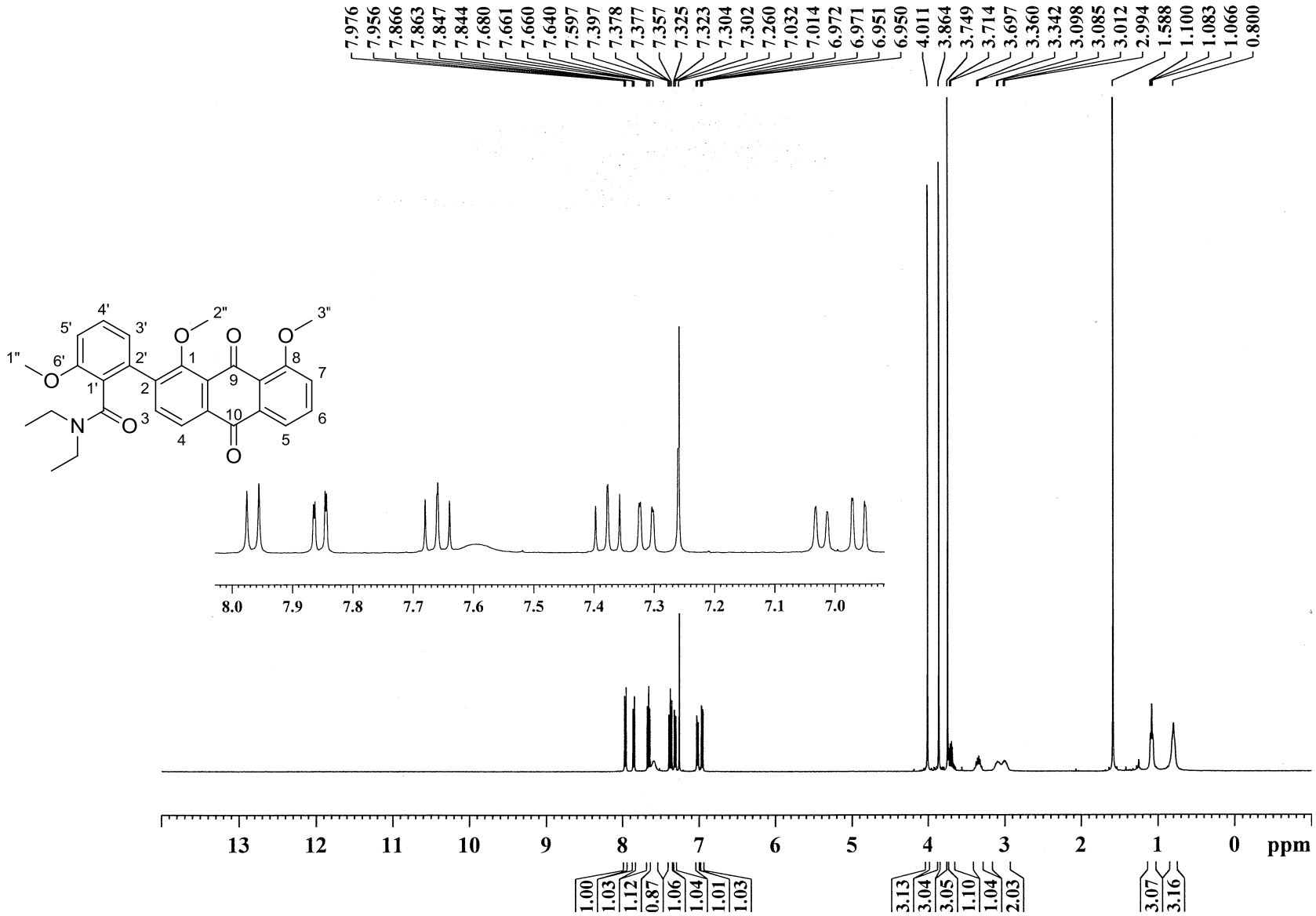


**Figure S38:** 100 MHz $^{13}C$ NMR spectrum of **16** in $CDCl_3$

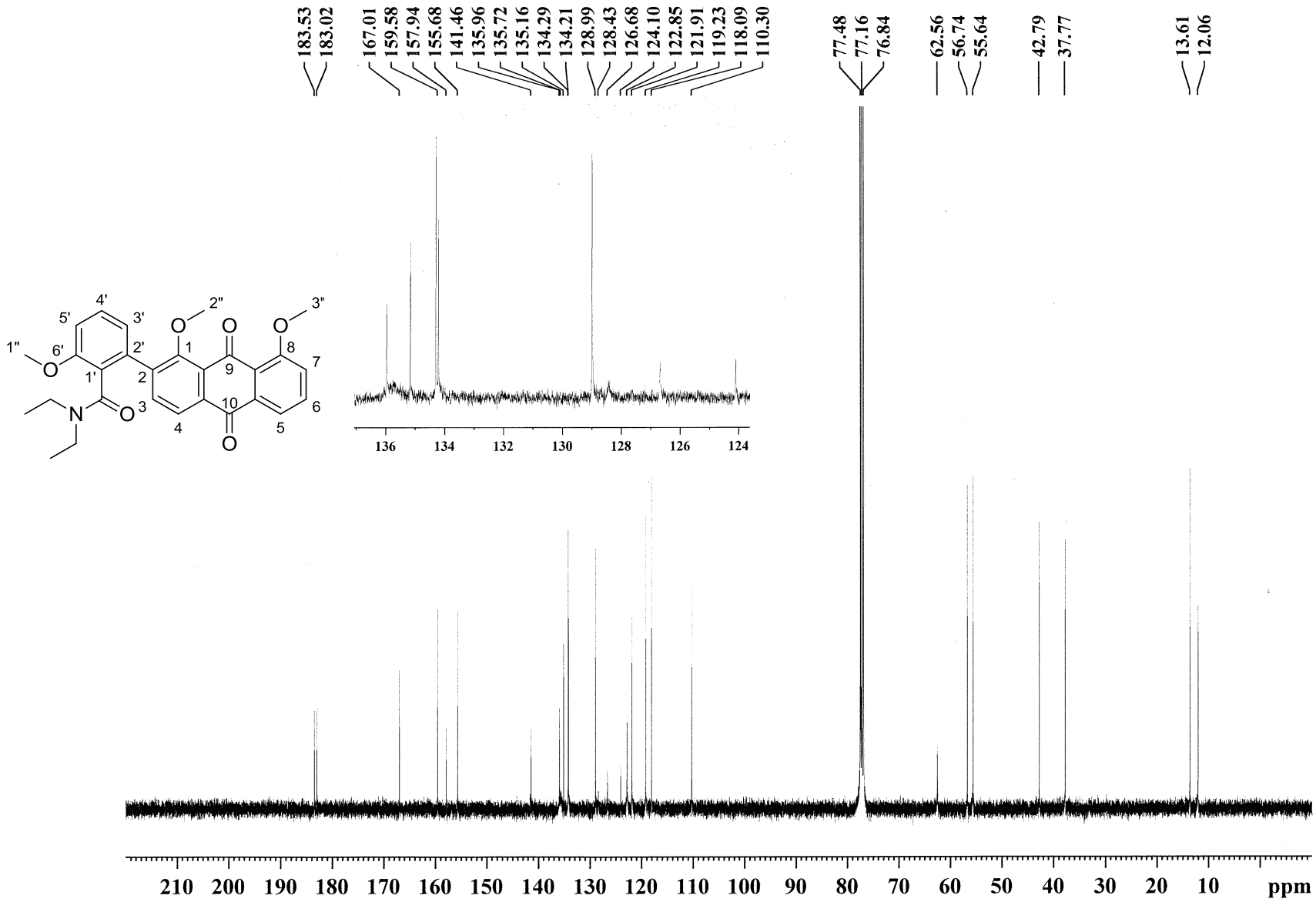


**Figure S39:** 400 MHz $^{1}$H NMR spectrum of **17** in $CDCl_3$

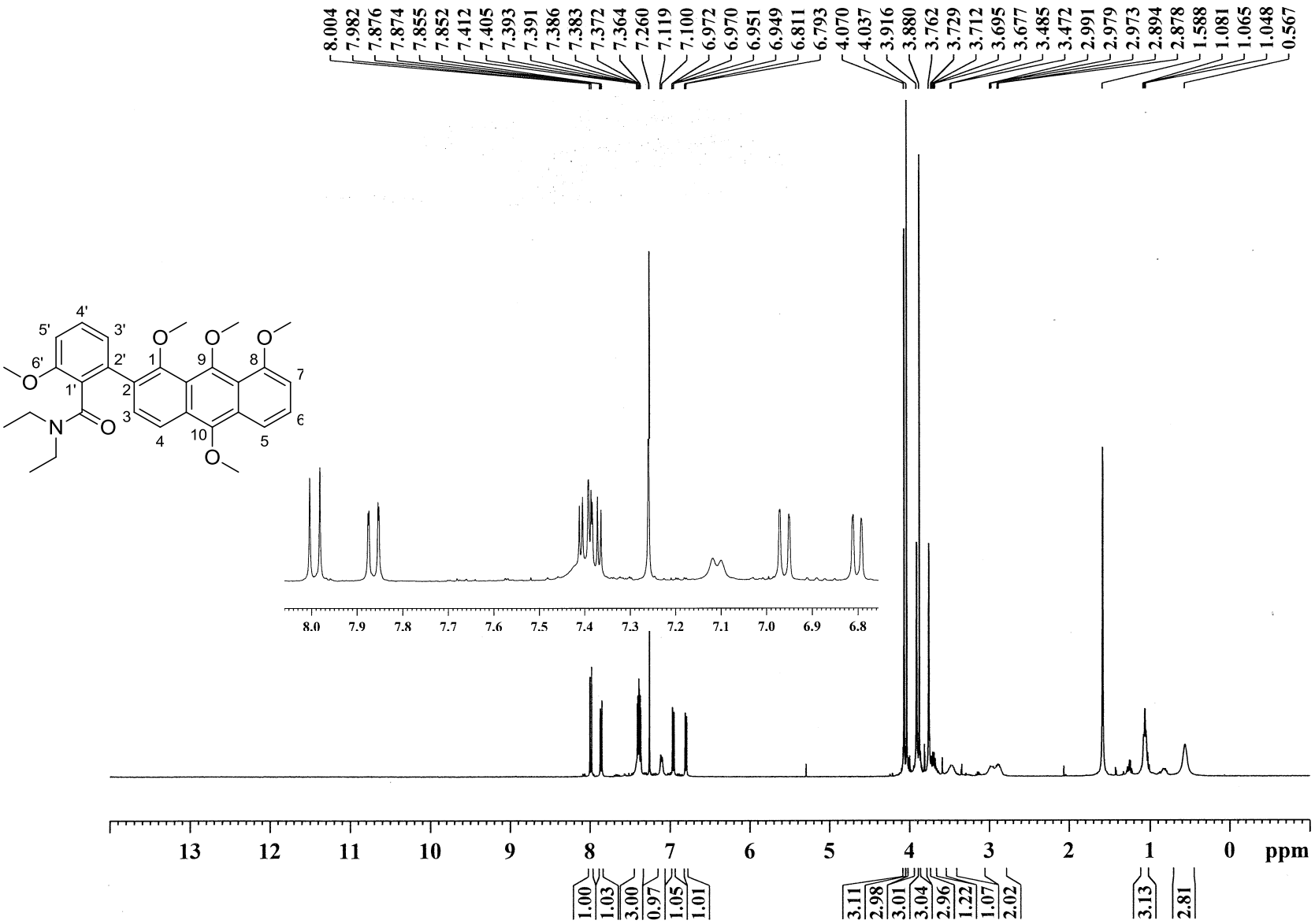


**Figure S40:** 125 MHz $^{13}C$ NMR spectrum of **17** in $CDCl_3$

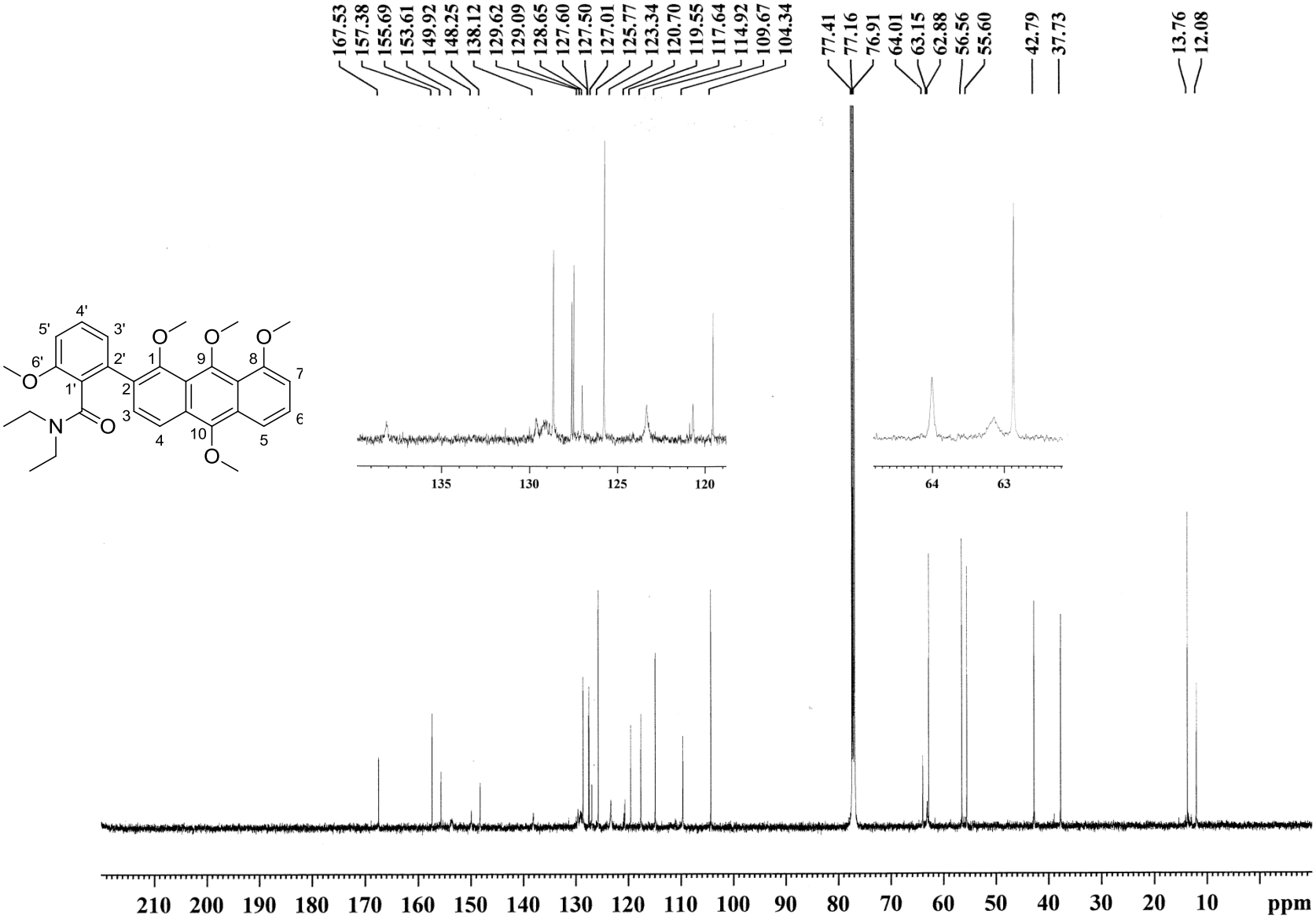


**Figure S41:** 600 MHz $^{1}$H NMR spectrum of crude **18** in $CDCl_3$

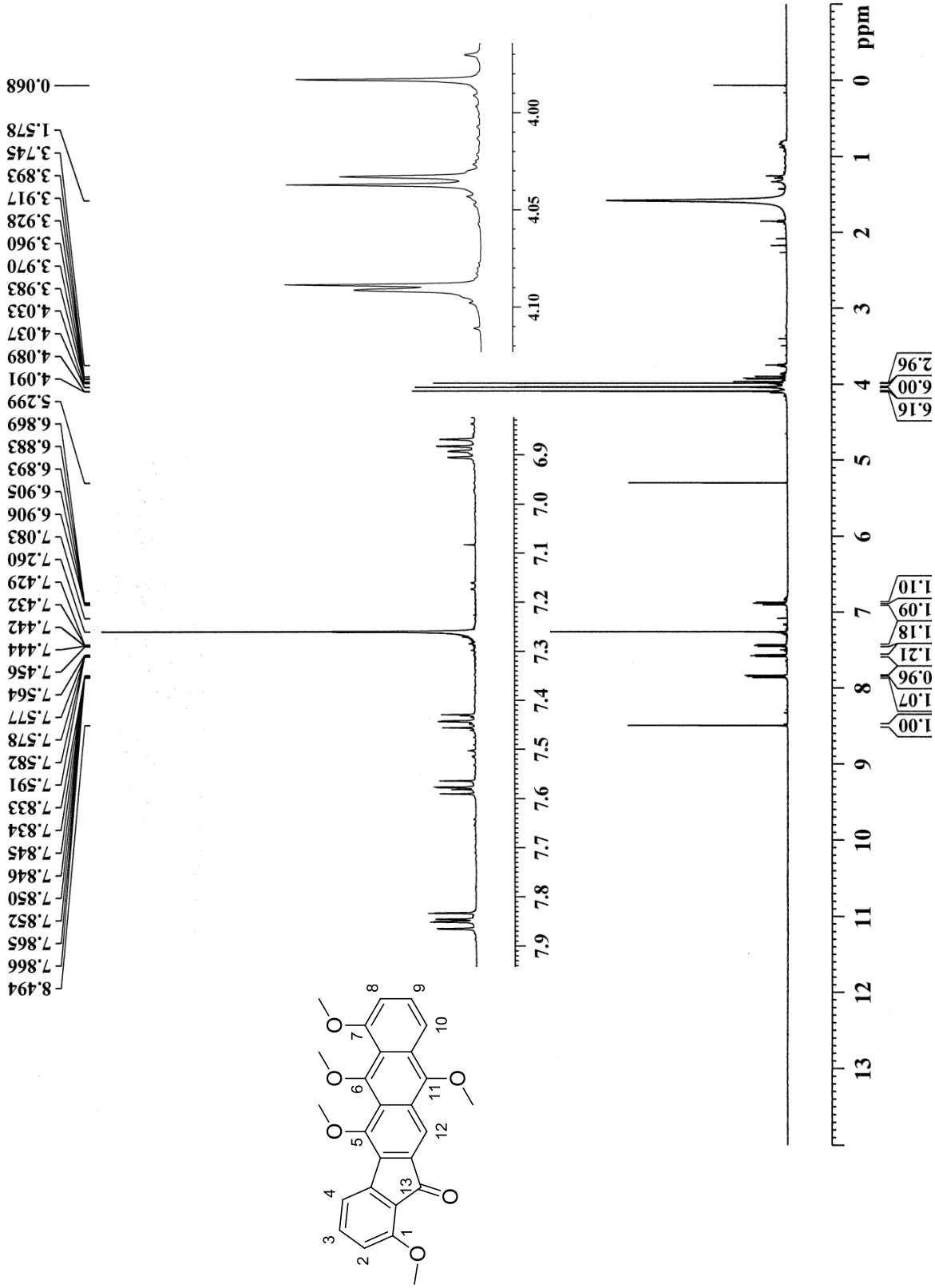


**Figure S42:** 500 MHz $^{1}$H NMR spectrum of crude **19** in $CDCl_3$

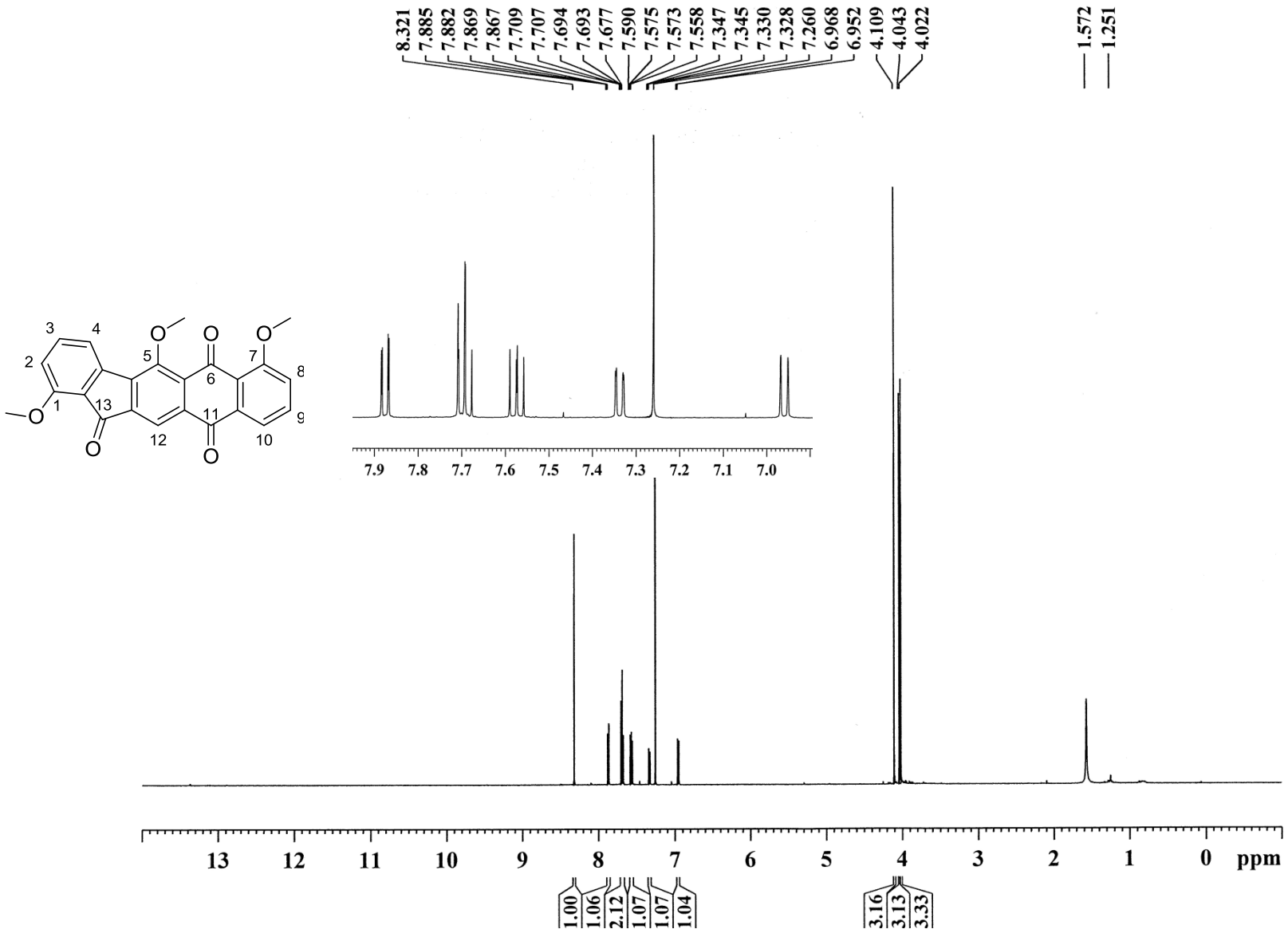


**Figure S43:** 125 MHz $^{13}$C NMR spectrum of **19** in $CDCl_3$

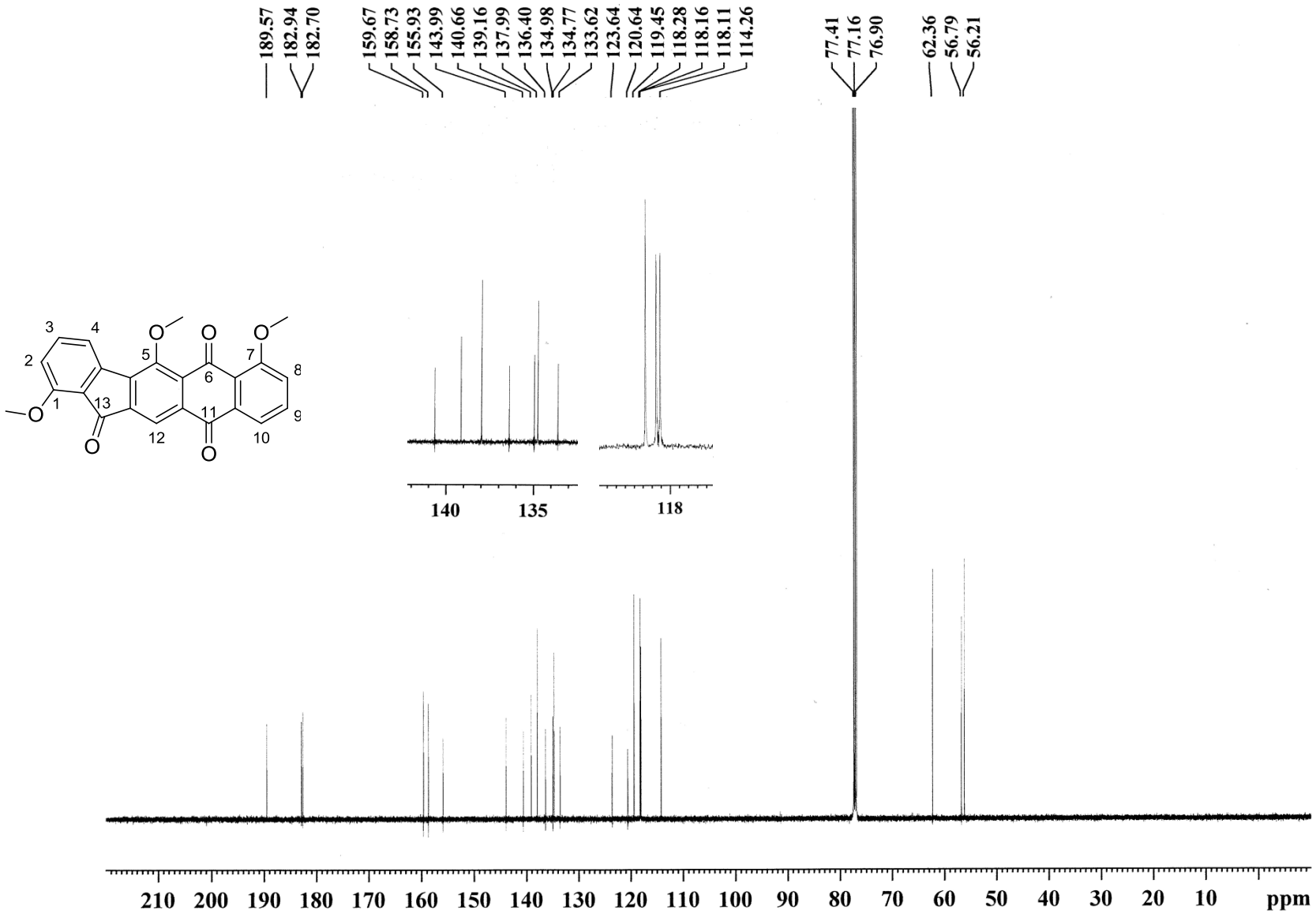


**Figure S44:** 500 MHz $^{1}$H NMR spectrum of **1** in $CDCl_3$

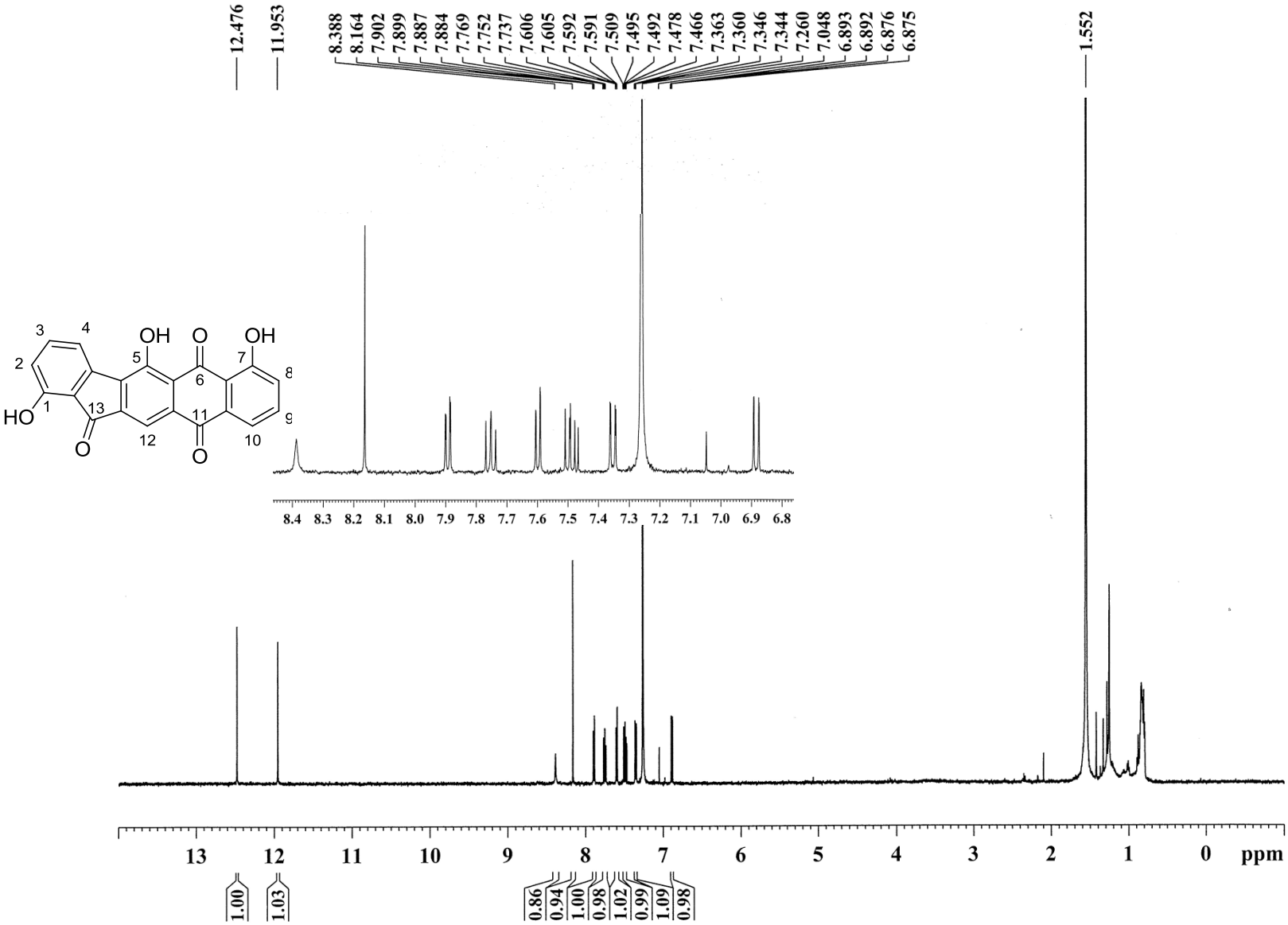


**Figure S45:** 500 MHz $^{1}$H NMR spectrum of **1** in $d_5$–pyridine

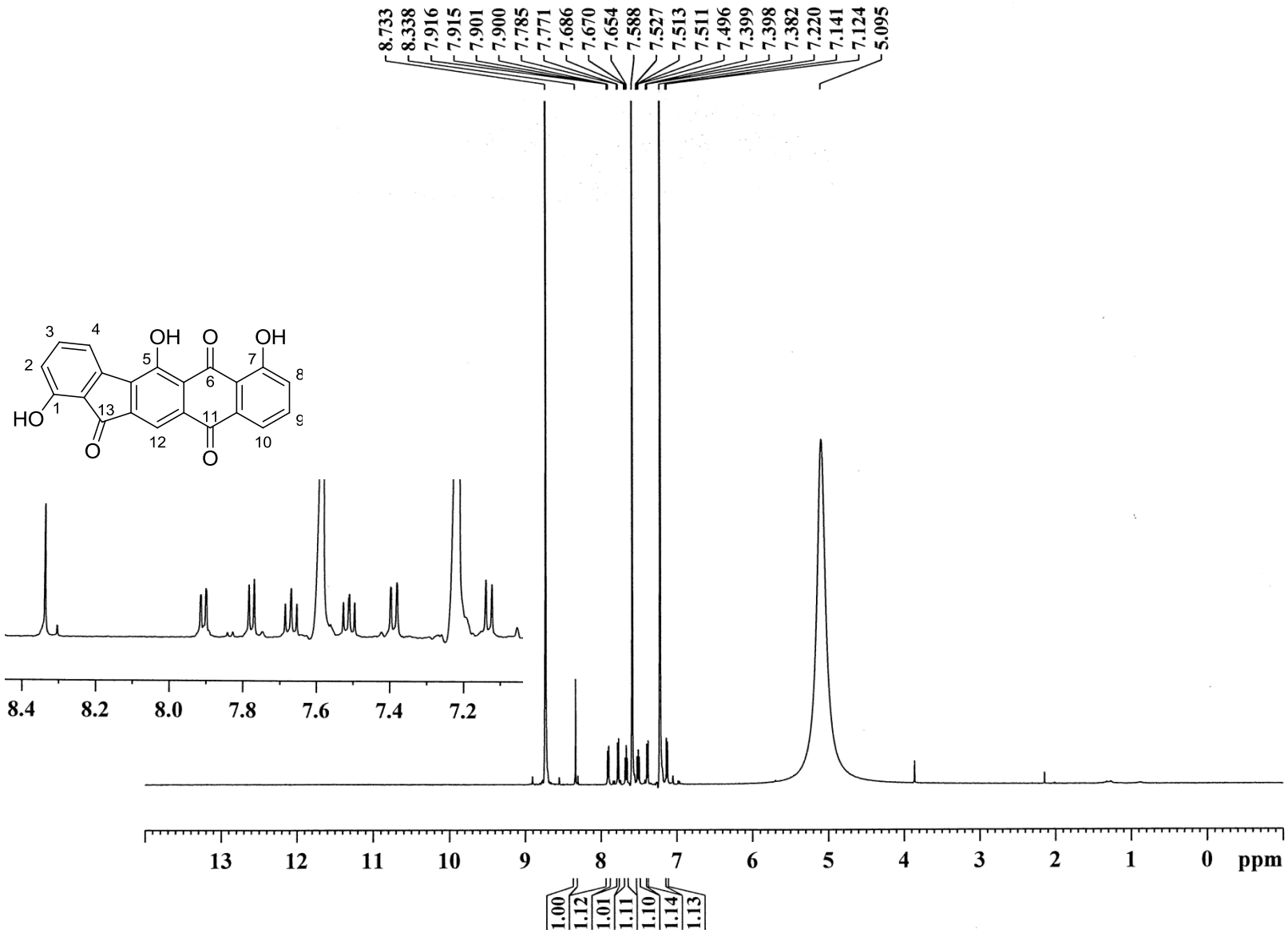


**Figure S46:** 125 MHz $^{13}$C NMR spectrum of **1** in $d_5$–pyridine

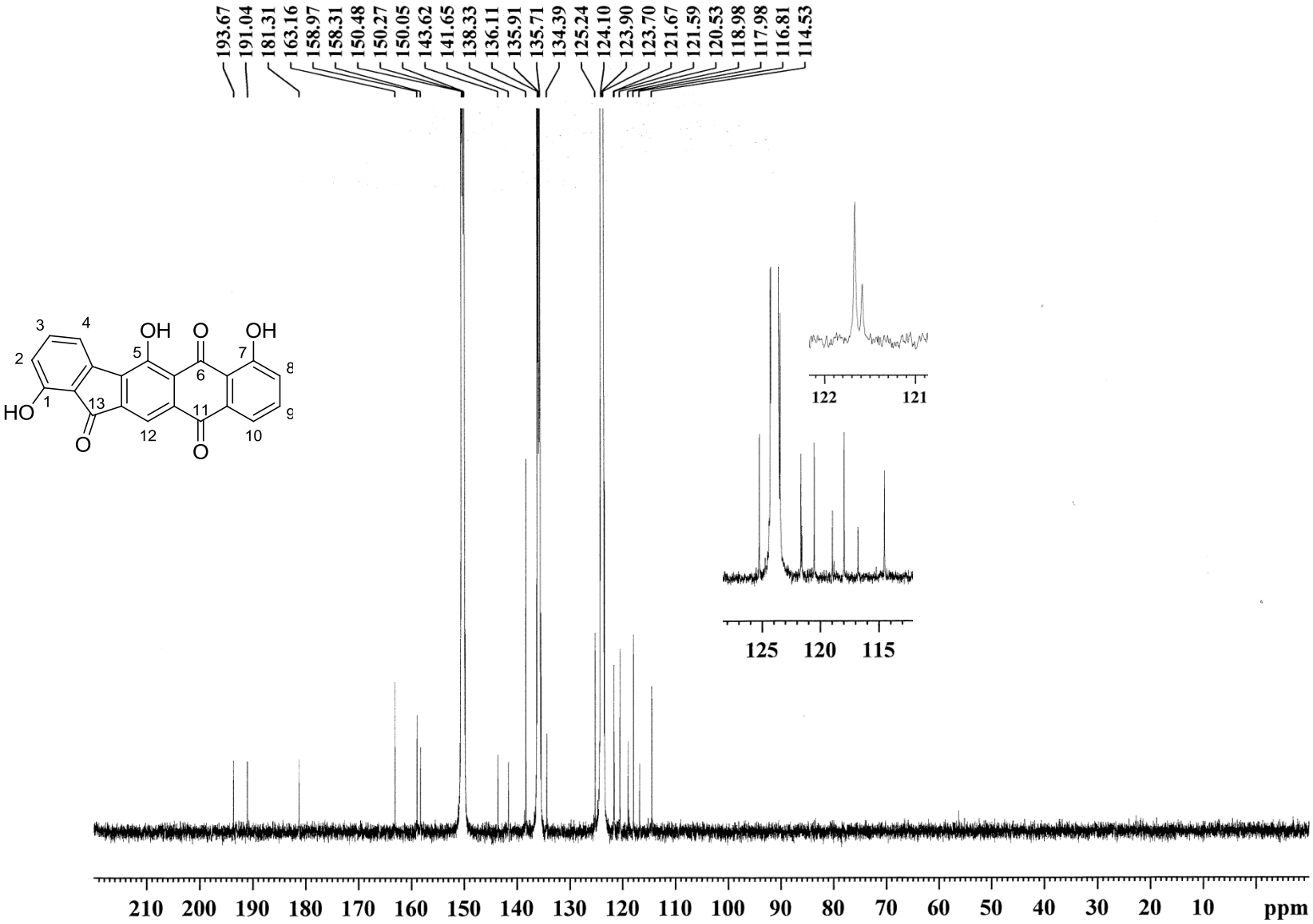


**Figure S47:** 125 MHz DEPTQ NMR spectrum of **1** in $d_5$–pyridine

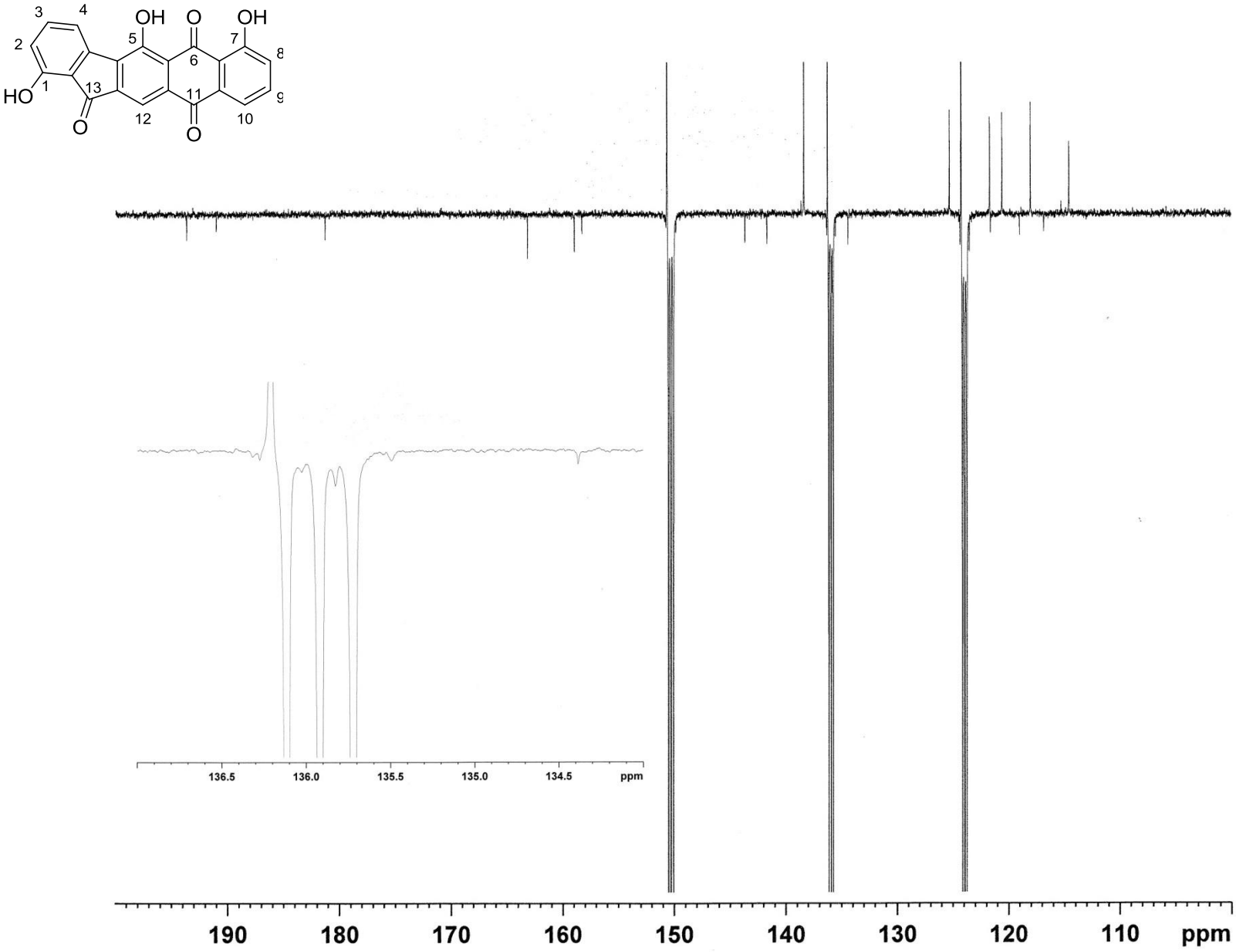


**Figure S48:** 500 MHz COSY NMR spectrum of **1** in $d_5$–pyridine

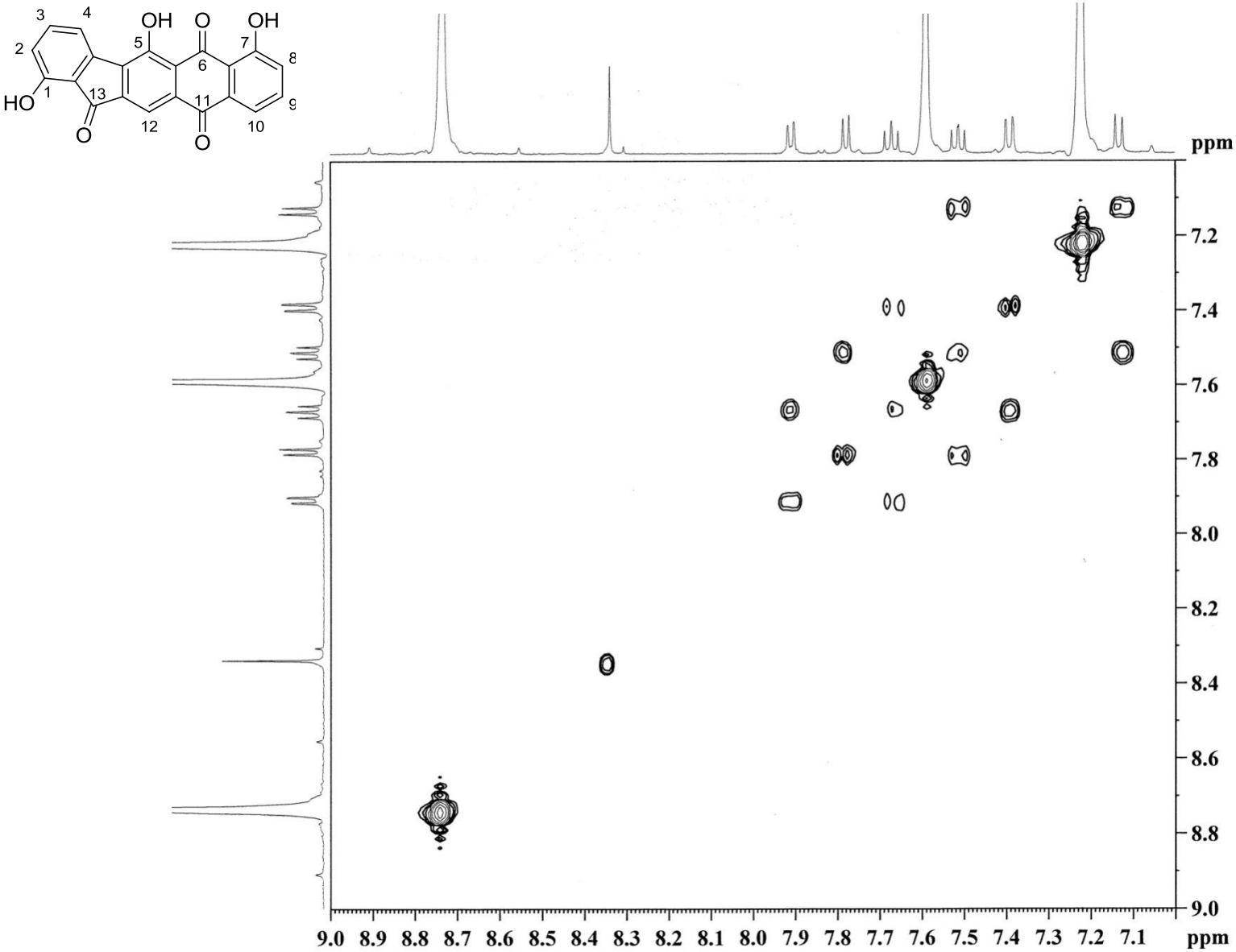


**Figure S49:** 500 MHz ($^{1}$H), 125 MHz ($^{13}$C) HSQC NMR spectrum of **1** in $d_5$–pyridine

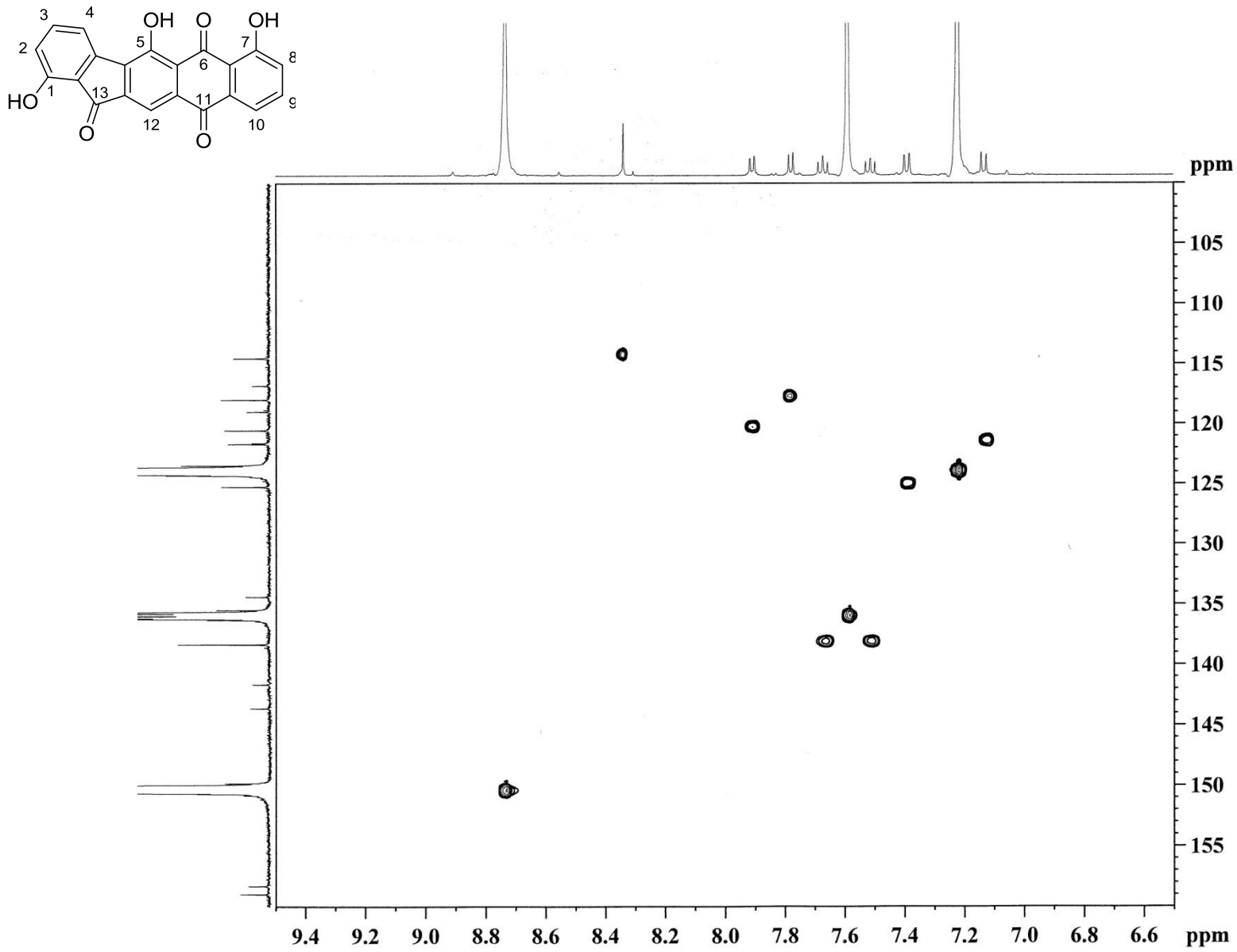


**Figure S50:** 500 MHz ($^{1}$H), 125 MHz ($^{13}$C) HMBC NMR spectrum of **1** in $d_5$–pyridine

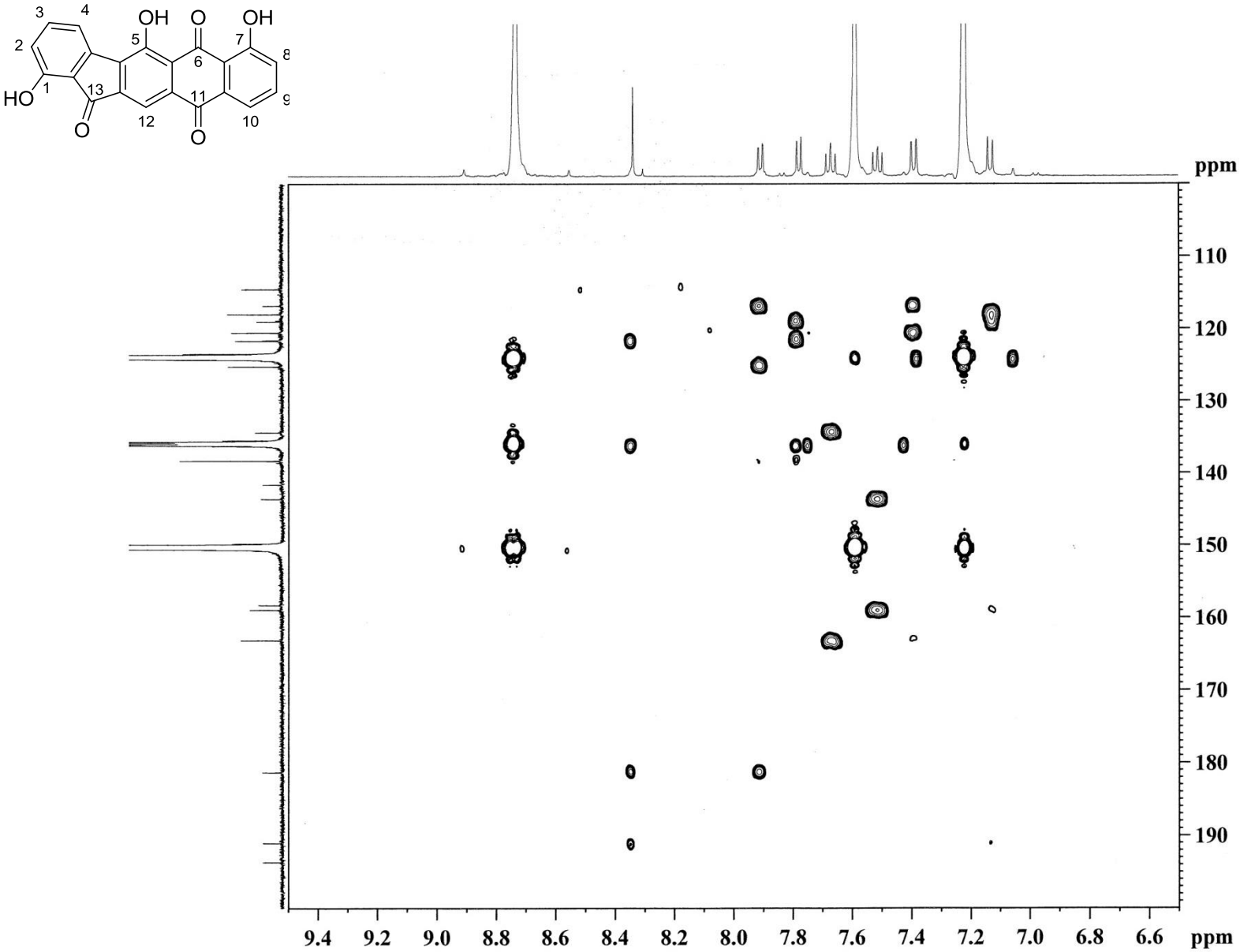


**Figure S51:** 500 MHz $^{1}$H NMR spectrum of **2** in $d_6$–DMSO

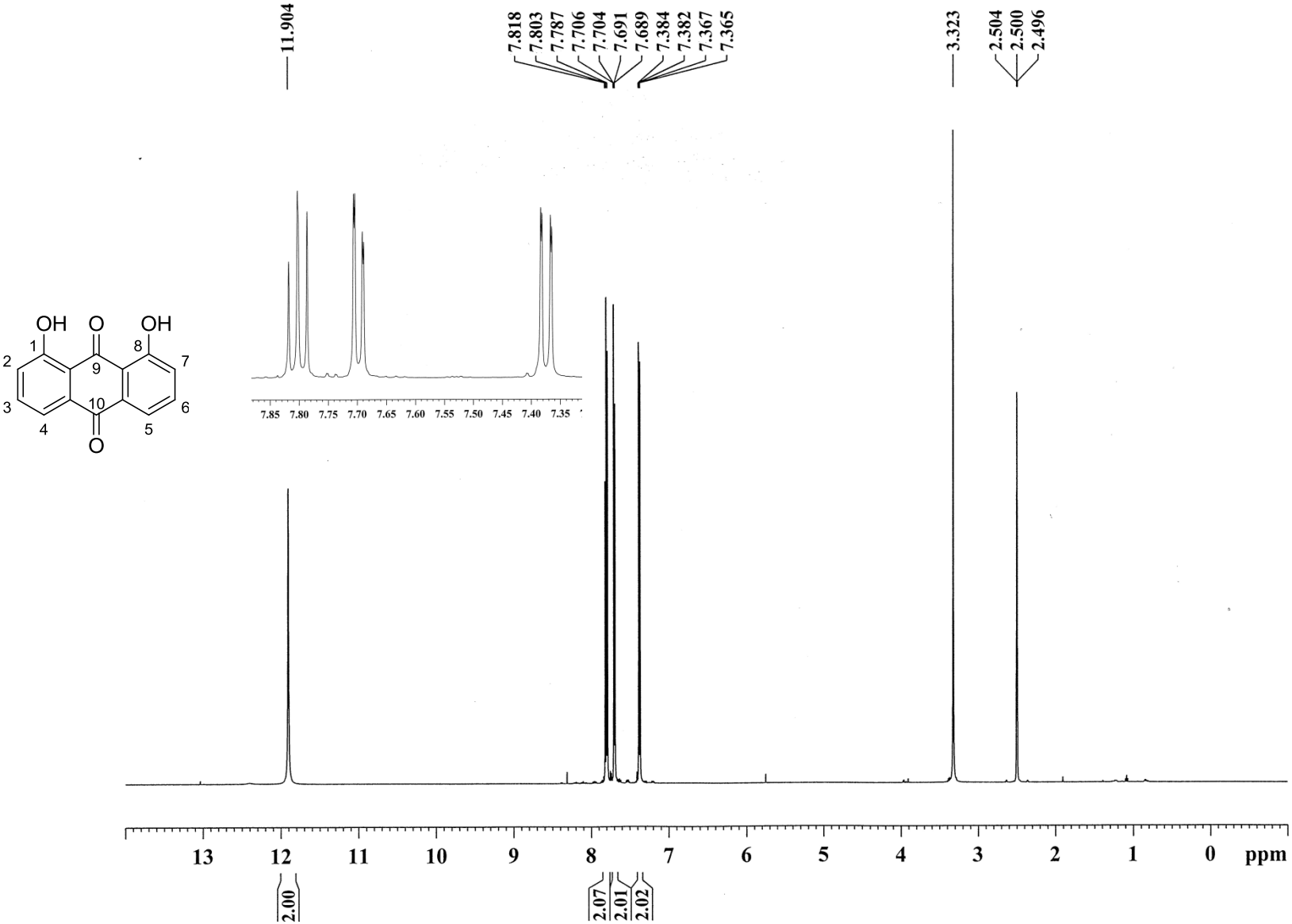


**Figure S52:** 500 MHz $^{1}$H NMR spectrum of **2** in $d_5$–pyridine

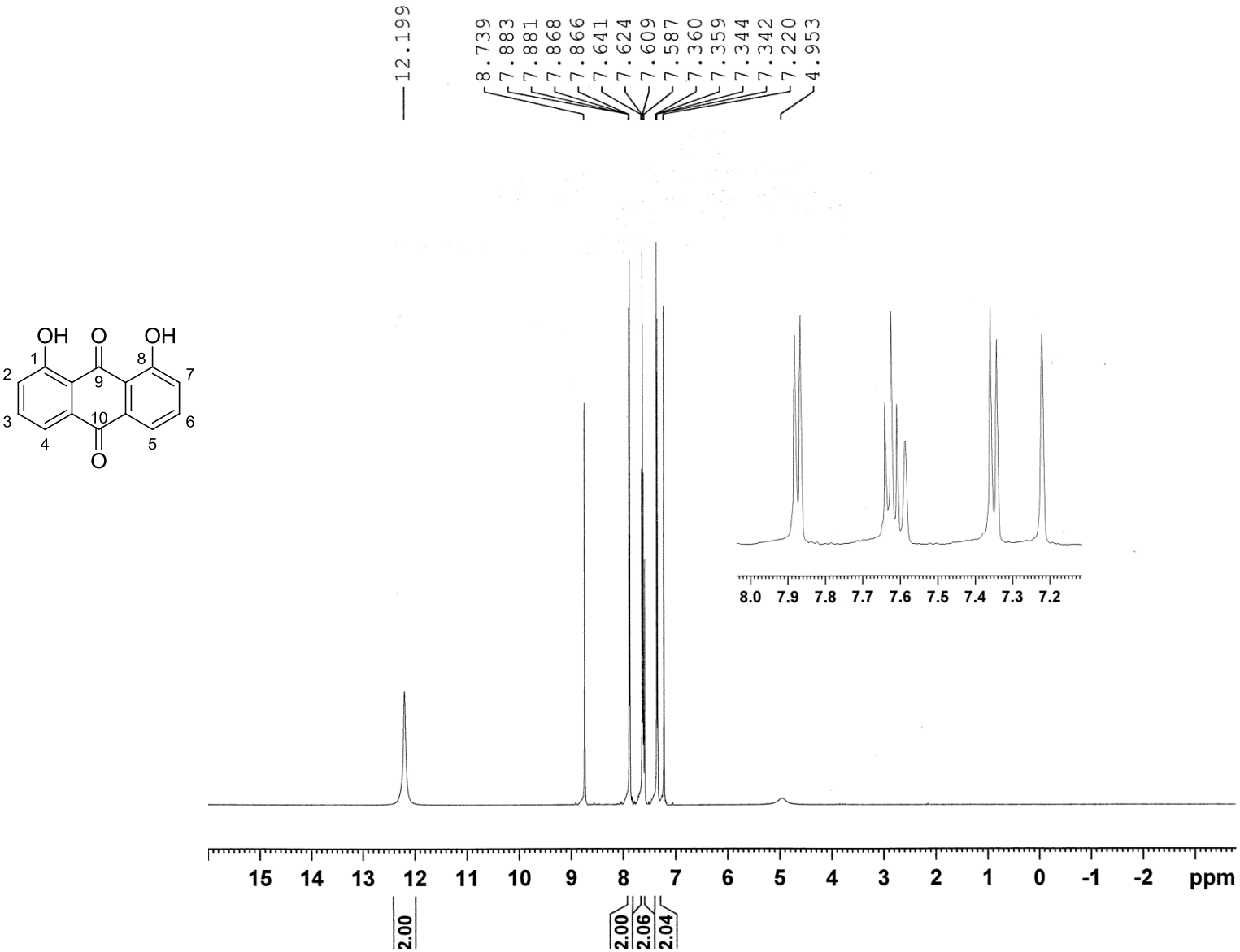


**Figure S53:** 125 MHz $^{13}$C NMR spectrum of **2** in $d_5$–pyridine