

Synthesis of diversely substituted bis-pyrrolizidino/thiopyrrolizidino oxindolo/acenaphthylene curcuminoids via sequential azomethine ylide cycloaddition

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Supplementary information and Documents:

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Experimental Section:

General Information:

Chemistry:

All the compounds evaluated in this work were synthesized in two step sequences. Melting points were determined in capillaries and are uncorrected. IR spectra were recorded as KBr pellets using a JASCO 410 FTIR spectrometer. The NMR spectra were recorded using a Bruker 600 DPX spectrometer operating at 600 MHz for ^1H and 150 MHz for ^{13}C in *Pyridine- d_5* with TMS as internal standard and the chemical shifts are reported in δ units. Mass spectra (positive mode) were obtained on a LC-ESI-Q-TOF micro mass spectrometer in the electrospray ionization mode. Curcumin was isolated from *Curcuma longa* in the usual way. Isatins, acenaphthoquinone and α -amino acids were purchased from Alfa-Aesar Company. All other solvents and chromatographic absorbents were procured from E. Merck (Germany) and SRL (India) Ltd. unless otherwise indicated. Thin layer chromatography was performed on pre-coated silica gel 60 F₂₅₄ aluminum sheets (E. Merck, Germany) using the solvent system 5% MeOH in CHCl_3 and spots were developed using UV irradiation, Iodine and Liebermann-Burchard reagent. Compounds were separated using AKROS –“Automatic TLC Smart Flash” of Yamazen Corporation.

Typical experimental procedure for synthesis of mono cycloaddition products 3Aa ($\pm$):

A mixture of **1** (13.6 mmol, 5 g), isatin (13.6 mmol, 2.00 g) and proline (13.6 mmol, 1.56 g) was taken in a round bottom flask, dissolved in 50 mL methanol, and heated to reflux for 8 h. After completion of the reaction as evident from TLC, the solvent was removed and the crude product was subjected to column chromatography using gradual increasing methanol in chloroform as eluant using flash chromatography. The product was crystallized from chloroform-methanol mixture (85%, 6.56 g).

Typical experimental procedure for synthesis of mixed cycloaddition products:

A mixture of **3Aa** ($\pm$) (1.76 mmol, 1 g), 5-iodoisatin (1.76 mmol, 481 mg) and proline (1.76 mmol, 205 mg) or thioproline (1.76 mmol, 235 mg) was taken in a round bottom flask, dissolved in 50 mL methanol, and heated to reflux for 8 h. The solvent was removed after completion of the reaction, evident from TLC, and the crude product was subjected to column chromatography using gradual increasing methanol in chloroform as eluant using flash chromatography to isolate diastereomeric mixed pyrrolizidino/pyrrilizidino-thiopyrrolizidino

dispiro oxindolo curcuminoids. The product was crystallized from chloroform-methanol mixture.

Compound 4Aa ($\pm$):

Color: Obtained as white solid; **Yield:** 20% (314 mg); **Mp:** 219-221 °C; **R_f** 0.49 (6 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ Cm^{-1}): 3376, 2960, 2869, 1722, 1612;

^1H NMR (Py-d_5): δ 11.51 (1H, s, -NH), 11.19 (1H, s, -NH), 7.97 (1H, s), 7.75 (1H, d, $J=7.8$ Hz), 7.38 (2H, m), 7.29 (2H, m), 7.22 (2H, m), 7.13 (1H, d, $J=1.2$ Hz), 6.99 (1H, t, $J=7.8$ Hz), 6.96 (1H, d, $J=6.6$ Hz), 6.87 (1H, d, $J=8.4$ Hz), 6.75 (1H, dd, $J=1.8, 8.4$ Hz), 5.80 (1H, s), 4.59 (1H, d, $J=12.6$ Hz), 4.43 (1H, d, $J=12.6$ Hz), 4.21 (2H, m), 3.82 (3H, s), 3.75 (1H, m), 3.66 (3H, s), 3.64 (1H, m), 2.74 (2H, m), 2.62 (2H, m), 1.87 (3H, m), 1.82 (2H, m), 1.70 (3H, m).

^{13}C NMR (Py-d_5): δ 191.8 (-C=O), 190.8 (-C=O), 181.1 (-C=O), 180.2 (-C=O), 149.6 (-C), 149.2 (-C), 147.7 (-C), 147.6 (-C), 143.9 (-C), 143.6 (-C), 138.9 (-CH), 135.8 (-CH), 131.9 (-C), 130.9 (-C), 129.7 (-CH), 129.5 (-C), 127.1 (-C), 126.9 (-CH), 121.7 (2 $\times$ -CH), 121.0 (-CH), 117.4 (-CH), 117.1 (-CH), 113.2 (-CH), 111.7 (-CH), 111.4 (-CH), 110.6 (-CH), 101.4 (-CH), 84.7 (-C), 74.49 (-C), 74.46 (-C), 74.42 (-CH), 73.5 (-CH), 65.2 (-CH), 63.6 (-CH), 56.3 (-OMe), 56.1 (-OMe), 52.8 (-CH), 52.6 (-CH), 48.6 (-CH₂), 48.3 (-CH₂), 31.13 (-CH₂), 31.06 (-CH₂), 28.1 (-CH₂), 27.8 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 895 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₃N₄O₈I; found m/z 917.2042 [M+Na]⁺ [calcd. 917.2023].

Compound 4Ab ($\pm$):

Color: Obtained as white solid; **Yield:** 23% (362 mg); **Mp:** 192-194 °C; **R_f** 0.43 (6 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ Cm^{-1}): 3383, 2960, 2872, 1718, 1611.

^1H NMR (Py-d_5): δ 12.18 (1H, s, -NH), 11.81 (1H, s, -NH), 7.91 (1H, d, $J=1.8$ Hz), 7.63 (1H, dd, $J=1.8, 8.4$ Hz), 7.25 (2H, m), 7.19 (1H, m), 7.17 (2H, d, $J=7.8$ Hz), 7.07 (1H, d, $J=1.8$ Hz), 7.00 (2H, m), 6.92 (1H, d, $J=7.2$ Hz), 6.85 (2H, m), 5.94 (1H, s), 4.42 (2H, t, $J=12.0$ Hz), 4.20 (1H, m), 4.10 (1H, m), 3.85 (1H, m), 3.79 (3H, s), 3.70 (1H, m), 3.67 (3H, s), 2.69 (2H, m), 2.61 (2H, m), 1.86 (2H, m), 1.79 (1H, m), 1.69 (5H, m).

¹³C NMR (Py-d₅): δ 191.6 (-C=O), 189.7 (-C=O), 181.2 (-C=O), 180.5 (-C=O), 149.2 (-C), 149.1 (-C), 147.52 (-C), 147.50 (-C), 143.9 (-C), 143.5 (-C), 138.8 (-CH), 135.8 (-CH), 131.4 (-C), 131.2 (-C), 129.8 (-CH), 129.5 (-C), 127.1 (-CH), 126.6 (-C), 121.8 (-CH), 120.7 (2×-CH), 117.2 (-CH), 117.0 (-CH), 113.0 (-CH), 112.2 (-CH), 112.1 (-CH), 110.6 (-CH), 101.3 (-CH), 84.7 (-C), 74.9 (2×-C), 73.7 (-CH), 73.6 (-CH), 65.1 (-CH), 64.3 (-CH), 56.2 (-OMe), 56.1 (-OMe), 52.5 (-CH), 51.8 (-CH), 48.5 (-CH₂), 48.2 (-CH₂), 31.4 (-CH₂), 31.3 (-CH₂), 28.4 (-CH₂), 28.0 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 895 [M+H]⁺, 917 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₃N₄O₈I; found *m/z* 917.2034 [M+Na]⁺ [calcd. 917.2023].

Compound 4Ac (±):

Color: Obtained as white solid; **Yield:** 21% (330 mg); **Mp:** 175-177 °C; **R_f** 0.39 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.93 (1H, s, -NH), 11.54 (1H, s, -NH), 8.26 (1H, s), 7.60 (1H, m), 7.35 (1H, s), 7.28 (1H, t, *J*=7.8 Hz), 7.23 (2H, m), 7.16 (1H, m), 7.05 (2H, m), 6.93 (1H, d, *J*=8.4 Hz), 6.89 (2H, m), 6.54 (1H, d, *J*=7.8 Hz), 6.05 (1H, s), 4.71 (1H, m), 4.62 (1H, d, *J*=12 Hz), 4.33 (1H, m), 4.11 (1H, d, *J*=12 Hz), 3.95 (1H, m), 3.71 (3H, s), 3.55 (3H, s), 3.23 (1H, m), 2.83 (2H, m), 1.96 (1H, m), 1.90 (2H, m), 1.74 (2H, m), 1.64 (2H, m), 1.40 (2H, m).

¹³C NMR (Py-d₅): δ 196.3 (-C=O), 194.5 (-C=O), 181.2 (-C=O), 179.4 (-C=O), 149.3 (-C), 148.3 (-C), 147.7 (-C), 147.5 (-C), 144.6 (-C), 144.1 (-C), 138.7 (-CH), 136.2 (-CH), 131.4 (-C), 131.0 (-C), 129.9 (-CH), 127.7 (-CH), 126.9 (-C), 126.8 (-C), 124.1 (-CH), 121.7 (-CH), 121.4 (-CH), 117.1 (-CH), 116.5 (-CH), 113.0 (-CH), 112.6 (-CH), 112.3 (-CH), 110.7 (-CH), 102.9 (-CH), 84.3 (-C), 76.5 (-C), 75.1 (-C), 73.8 (-CH), 65.7 (-CH), 64.6 (-CH), 56.1 (-OMe), 55.7 (-OMe), 53.3 (-CH), 52.7 (-CH), 52.0 (-CH), 51.5 (-CH₂), 48.5 (-CH₂), 31.3 (-CH₂), 29.9 (-CH₂), 28.2 (-CH₂), 26.8 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 895 [M+H]⁺, 917 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₃N₄O₈I; found *m/z* 917.2017 [M+Na]⁺ [calcd. 917.2023].

Compound 4Ad (±):

Color: Obtained as white solid; **Yield:** 24% (378 mg); **Mp:** 218-220 °C; **R_f** 0.38 (6 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ cm^{-1}): 3391, 2960, 1720, 1613;

^1H NMR (Py-d_5): δ 11.77 (1H, s, -NH), 11.51 (1H, s, -NH), 8.33 (1H, s), 7.67 (1H, d, $J=7.2$ Hz), 7.60 (1H, d, $J=8.4$ Hz), 7.36 (1H, s), 7.30 (1H, t, $J=7.8$ Hz), 7.20 (1H, m), 7.15 (2H, m), 7.01 (1H, d, $J=7.8$ Hz), 6.97 (1H, m), 6.92 (1H, m), 6.89 (1H, s), 6.54 (1H, d, $J=8.4$ Hz), 5.97 (1H, s), 4.96 (1H, m), 4.67 (1H, q, $J=8.4$ Hz), 4.59 (1H, d, $J=12.6$ Hz), 4.37 (1H, m), 4.23 (1H, d, $J=12.0$ Hz), 3.98 (1H, m), 3.70 (3H, s), 3.56 (3H, s), 3.15 (1H, m), 2.88 (1H, m), 2.74 (2H, m), 1.96 (1H, m), 1.89 (2H, m), 1.77 (1H, m), 1.67 (1H, m), 1.61 (1H, m), 1.51 (1H, m), 1.23 (1H, m).

^{13}C NMR (Py-d_5): δ 197.7 (-C=O), 186.0 (-C=O), 181.2 (-C=O), 179.5 (-C=O), 149.3 (-C), 148.3 (-C), 147.7 (-C), 147.5 (-C), 144.6 (-C), 144.0 (-C), 138.7 (-CH), 136.0 (-CH), 131.5 (-C), 131.0 (-C), 129.9 (-CH), 128.0 (-CH), 127.2 (-C), 126.9 (-C), 121.7 (-CH), 121.4 (-CH), 121.3 (-CH), 117.1 (-CH), 116.5 (-CH), 113.3 (-CH), 112.6 (-CH), 112.4 (-CH), 110.8 (-CH), 102.9 (-CH), 84.3 (-C), 76.4 (-C), 75.4 (-C), 73.7 (-CH), 65.6 (-CH), 64.5 (-CH), 56.1 (-OMe), 55.8 (-OMe), 53.8 (-CH), 52.6 (-CH), 51.5 (-CH₂), 51.1 (-CH), 48.6 (-CH₂), 31.3 (-CH₂), 29.4 (-CH₂), 28.2 (-CH₂), 26.8 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 895 $[\text{M}+\text{H}]^+$, 917 $[\text{M}+\text{Na}]^+$.

HRMS [ESI-MS, positive mode]: MF: $\text{C}_{45}\text{H}_{43}\text{N}_4\text{O}_8\text{I}$; found m/z 895.2209 $[\text{M}+\text{H}]^+$ [calcd. 895.2204].

Compound 4Ba ($\pm$):

Color: Obtained as white solid; **Yield:** 19% (266 mg); **Mp:** 172-174 °C; **R_f** 0.50 (6 % MeOH in CHCl_3);

^1H NMR (Py-d_5): δ 10.94 (1H, s, -NH), 10.91 (1H, s, -NH), 7.31 (1H, d, $J=7.8$ Hz), 7.27 (3H, m), 7.21 (1H, s), 7.18 (2H, m), 7.12 (1H, d, $J=7.8$ Hz), 6.92 (2H, m), 6.88 (1H, d, $J=7.8$ Hz), 6.77 (1H, s), 5.77 (1H, s), 4.50 (1H, d, $J=12.0$ Hz), 4.40 (1H, d, $J=12.0$ Hz), 4.31 (1H, m), 4.21 (1H, m), 3.82 (1H, m), 3.77 (3H, s), 3.74 (1H, m), 3.71 (3H, s), 2.80 (2H, m), 2.65 (1H, m), 2.60 (1H, m), 2.26 (3H, s), 2.22 (3H, s), 1.86 (4H, m), 1.78 (2H, m), 1.68 (2H, m).

^{13}C NMR (Py-d_5): δ 192.1 (-C=O), 190.3 (-C=O), 181.3 (-C=O), 181.1 (-C=O), 149.24 (-C), 149.18 (-C), 147.5 (-C), 147.4 (-C), 143.5 (-C), 139.9 (-C), 131.9 (-CH), 131.8 (-C), 131.5 (-C), 130.6 (-C), 129.7 (-CH), 127.3 (-CH), 126.6 (-C), 126.2 (-C), 125.5 (-CH), 121.6 (-CH), 121.13 (-CH), 121.07 (-CH), 119.4 (-C), 117.2 (-CH), 117.1 (-CH), 112.2 (-CH), 111.8 (-CH), 110.6 (-CH), 101.6 (-CH), 74.9 (-C), 74.5 (-C), 73.7 (-CH), 73.5 (-CH), 65.1 (-CH),

64.2 (-CH), 56.2 (-OMe), 56.1 (-OMe), 52.53 (-CH), 52.50 (-CH), 48.6 (-CH₂), 48.4 (-CH₂), 31.2 (-CH₂), 30.9 (-CH₂), 28.1 (-CH₂), 27.6 (-CH₂), 21.2 (-CH₃), 17.2 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 797 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₈; found m/z 819.3361 [M+Na]⁺ [calcd. 819.3370].

Compound 4Bb (±):

Color: Obtained as white solid; **Yield:** 22% (308 mg); **Mp:** 188-190 °C; **R_f** 0.44 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.85 (1H, s, -NH), 11.73 (1H, s, -NH), 7.25 (2H, m), 7.21 (1H, m), 7.18 (2H, d, $J=7.8$ Hz), 7.11 (2H, m), 7.03 (1H, d, $J=7.8$ Hz), 6.97 (1H, d, $J=7.8$ Hz), 6.91 (2H, m), 6.75 (1H, s), 6.00 (1H, s), 4.48 (1H, d, $J=12.0$ Hz), 4.41 (1H, d, $J=12.0$ Hz), 4.18 (2H, m), 3.87 (1H, m), 3.74 (3H, s), 3.71 (3H, s), 3.66 (1H, m), 2.80 (1H, m), 2.73 (1H, m), 2.66 (1H, m), 2.61 (1H, m), 2.31 (3H, s), 2.16 (3H, s), 1.90 (1H, m), 1.83 (3H, m), 1.71 (3H, m), 1.63 (1H, m).

¹³C NMR (Py-d₅): δ 191.7 (-C=O), 190.1 (-C=O), 181.6 (-C=O), 181.2 (-C=O), 149.3 (-C), 149.2 (-C), 147.63 (-C), 147.57 (-C), 143.9 (-C), 140.0 (-C), 131.9 (-CH), 131.7 (-C), 131.5 (-C), 130.7 (-C), 129.8 (-CH), 127.1 (-CH), 126.7 (-C), 126.4 (-C), 125.3 (-CH), 121.6 (-CH), 120.9 (-CH), 120.8 (-CH), 119.4 (-C), 117.1 (2×-CH), 112.2 (-CH), 112.0 (-CH), 110.5 (-CH), 101.0 (-CH), 75.1 (-C), 74.8 (-C), 73.8 (-CH), 73.7 (-CH), 64.7 (-CH), 64.2 (-CH), 56.12 (-OMe), 56.09 (-OMe), 52.4 (-CH), 52.2 (-CH), 48.6 (-CH₂), 48.3 (-CH₂), 31.5 (-CH₂), 31.2 (-CH₂), 28.3 (-CH₂), 27.9 (-CH₂), 21.4 (-CH₃), 17.3 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 797 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₈; found m/z 819.3351 [M+Na]⁺ [calcd. 819.3370].

Compound 4Bc (±):

Color: Obtained as white solid; **Yield:** 21% (294 mg); **Mp:** 169-171 °C; **R_f** 0.40 (6 % MeOH in CHCl₃);

¹H NMR (DMSO-d₆): δ 10.36 (1H, s, -NH), 9.93 (1H, s, -NH), 8.84 (1H, d, $J=4.2$ Hz), 7.46 (1H, d, $J=7.2$ Hz), 7.17 (1H, m), 7.02 (1H, s), 6.95 (1H, m), 6.74 (4H, m), 6.41 (1H, m), 6.26 (1H, s), 6.18 (1H, d, $J=6.6$ Hz), 5.62 (1H, s), 4.24 (1H, m), 4.02 (1H, m), 3.78 (3H, s), 3.72

(2H, m), 3.56 (2H, m), 2.97 (1H, m), 2.42 (2H, m), 2.36 (1H, m), 2.25 (3H, s), 2.07 (3H, m), 1.96 (3H, s), 1.82 (2H, m), 1.68 (3H, m), 1.40 (1H, m), 1.15 (1H, m), 0.86 (1H, m).

¹³C NMR (DMSO-*d*₆): δ 197.2 (-C=O), 183.6 (-C=O), 179.2 (-C=O), 178.7 (-C=O), 147.6 (-C), 146.6 (-C), 145.4 (-C), 145.1 (-C), 142.3 (-C), 139.3 (-C), 130.8 (-CH), 130.3 (-C), 129.9 (-C), 129.1 (-CH), 127.0 (-CH), 126.5 (-C), 126.3 (-C), 125.2 (-C), 124.6 (-CH), 120.7 (-CH), 119.9 (-CH), 119.7 (-CH), 118.2 (-C), 115.6 (-CH), 114.9 (-CH), 111.8 (2×-CH), 109.8 (-CH), 101.6 (-CH), 74.8 (-C), 73.6 (-C), 72.5 (-CH), 64.1 (-CH), 62.3 (-CH), 55.6 (-OMe), 54.9 (-OMe), 52.6 (-CH), 50.4 (-CH), 50.3 (-CH₂), 48.9 (-CH), 47.4 (-CH₂), 30.1 (-CH₂), 28.0 (-CH₂), 27.2 (-CH₂), 25.6 (-CH₂), 20.7 (-CH₃), 16.2 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 797 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₈; found *m/z* 819.3395 [M+Na]⁺ [calcd. 819.3370].

Compound 4Bd (±):

Color: Obtained as white solid; **Yield:** 23% (322 mg); **Mp:** 170-172 °C; **R_f** 0.39 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3390, 2960, 1713, 1618;

¹H NMR (Py-*d*₅): δ 11.84 (1H, s, -NH), 11.17 (1H, s, -NH), 7.69 (1H, d, *J*=7.2 Hz), 7.43 (1H, s), 7.38 (1H, s), 7.31 (1H, t, *J*=7.2 Hz), 7.22 (1H, d, *J*=7.2 Hz), 7.18 (1H, d, *J*=1.2 Hz), 7.16 (1H, t, *J*=7.8 Hz), 7.06 (1H, d, *J*=7.8 Hz), 6.93 (3H, m), 6.81 (1H, s), 6.04 (1H, s), 4.99 (1H, m), 4.73 (1H, q, *J*=7.8 Hz), 4.64 (1H, d, *J*=6.6 Hz), 4.39 (1H, m), 4.25 (1H, d, *J*=12 Hz), 3.99 (1H, dd, *J*=9.6, 12 Hz), 3.75 (3H, s), 3.56 (3H, s), 3.23 (1H, m), 2.86 (1H, m), 2.79 (1H, t, *J*=7.2 Hz), 2.73 (1H, m), 2.38 (3H, s), 2.01 (3H, s), 1.97 (1H, m), 1.90 (2H, m), 1.76 (2H, m), 1.65 (1H, m), 1.59 (1H, m), 1.30 (1H, m).

¹³C NMR (Py-*d*₅): δ 198.0 (-C=O), 186.2 (-C=O), 181.4 (-C=O), 180.6 (-C=O), 149.3 (-C), 148.3 (-C), 147.6 (-C), 147.3 (-C), 143.9 (-C), 141.0 (-C), 131.8 (-CH), 131.6 (2×-C), 130.9 (-C), 130.0 (-CH), 128.0 (-CH), 127.9 (-C), 126.9 (-C), 125.4 (-CH), 121.8 (-CH), 121.7 (-CH), 121.5 (-CH), 119.4 (-C), 117.1 (-CH), 116.4 (-CH), 113.2 (-CH), 112.4 (-CH), 110.9 (-CH), 102.9 (-CH), 76.5 (-C), 75.4 (-C), 73.8 (-CH), 65.5 (-CH), 64.4 (-CH), 56.2 (-OMe), 55.7 (-OMe), 54.3 (-CH), 52.6 (-CH), 51.5 (-CH₂), 50.9 (-CH), 48.6 (-CH₂), 31.3 (-CH₂), 29.4 (-CH₂), 28.2 (-CH₂), 26.8 (-CH₂), 21.4 (-CH₃), 17.1 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 797 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₈; found *m/z* 819.3378 [M+Na]⁺ [calcd. 819.3370].

Compound 4Ca (±):

Color: Obtained as white solid; **Yield:** 17% (230 mg); **Mp:** 183-185 °C; **R_f** 0.48 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3391, 2961, 2868, 1722, 1615;

¹H NMR (Py-*d*₅): δ 11.28 (1H, s, -NH), 10.88 (1H, s, -NH), 7.59 (1H, dd, *J*=4.8, 6.6 Hz), 7.34 (1H, s), 7.24 (2H, m), 7.22 (1H, m), 7.18 (2H, m), 7.00 (3H, m), 6.85 (2H, m), 5.70 (1H, s), 4.52 (1H, d, *J*=12.0 Hz), 4.37 (1H, d, *J*=12.0 Hz), 4.29 (1H, m), 4.20 (1H, m), 3.81 (2H, m), 3.73 (3H, s), 3.70 (3H, s), 2.83 (1H, m), 2.77 (1H, m), 2.62 (2H, m), 2.16 (3H, s), 1.85 (4H, m), 1.78 (2H, m), 1.69 (2H, m).

¹³C NMR (Py-*d*₅): δ 191.2 (-C=O), 190.9 (-C=O), 181.0 (-C=O), 180.8 (-C=O), 149.22 (-C), 149.16 (-C), 147.5 (-C), 147.4 (-C), 142.4 (-C), 141.2 (-C), 131.6 (-C), 131.5 (-C), 130.8 (-C), 130.2 (-CH), 129.7 (-CH), 128.6 (-C), 128.0 (-CH), 127.5 (-CH), 126.7 (-C), 126.6 (-C), 120.8 (2×-CH), 117.1 (2×-CH), 112.2 (-CH), 111.8 (-CH), 111.7 (-CH), 110.4 (-CH), 101.7 (-CH), 74.7 (-C), 74.5 (-C), 73.7 (-CH), 73.2 (-CH), 65.1 (-CH), 64.0 (-CH), 56.1 (-OMe), 56.0 (-OMe), 52.2 (2×-CH), 48.54 (-CH₂), 48.51 (-CH₂), 31.0 (-CH₂), 30.6 (-CH₂), 27.9 (-CH₂), 27.7 (-CH₂), 21.2 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₈Cl; found *m/z* 839.2817 [M+Na]⁺ [calcd. 839.2824].

Compound 4Cb (±):

Color: Obtained as white solid; **Yield:** 20% (271 mg); **Mp:** 208-210 °C; **R_f** 0.43 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3382, 1711, 1613, 1516;

¹H NMR (Py-*d*₅): δ 12.14 (1H, s, -NH), 11.77 (1H, s, -NH), 7.59 (1H, m), 7.35 (1H, s), 7.20 (1H, m), 7.15 (2H, d, *J*=8.4 Hz), 7.10 (1H, d, *J*=1.8 Hz), 7.05 (1H, d, *J*=1.2 Hz), 6.94 (1H, d, *J*=7.8 Hz), 6.86 (1H, d, *J*=7.8 Hz), 6.84 (1H, d, *J*=1.2 Hz), 6.82 (1H, d, *J*=7.8 Hz), 6.80 (1H, dd, *J*=1.2, 8.4 Hz), 5.92 (1H, s), 4.39 (2H, d, *J*=12.0 Hz), 4.20 (1H, m), 4.12 (1H, m), 3.92 (1H, m), 3.82 (1H, m), 3.66 (3H, s), 3.65 (3H, s), 2.82 (1H, m), 2.65 (3H, m), 2.11 (3H, s), 1.85 (5H, m), 1.71 (3H, m).

¹³C NMR (Py-d₅): δ 191.2 (-C=O), 189.8 (-C=O), 181.2 (-C=O), 180.9 (-C=O), 149.0 (2×-C), 147.42 (-C), 147.36 (-C), 142.6 (-C), 141.2 (-C), 131.6 (-C), 131.2 (-C), 130.7 (-C), 130.3 (-CH), 129.9 (-CH), 128.7 (-C), 128.2 (-CH), 127.5 (-CH), 126.7 (-C), 126.6 (-C), 120.35 (-CH), 120.31 (-CH), 116.99 (-CH), 116.97 (-CH), 112.5 (-CH), 112.3 (-CH), 111.7 (-CH), 110.3 (-CH), 101.5 (-CH), 75.25 (-C), 75.22 (-C), 73.7 (-CH), 73.4 (-CH), 65.3 (-CH), 64.9 (-CH), 56.0 (2×-OMe), 51.8 (-CH), 51.6 (-CH), 48.3 (-CH₂), 48.2 (-CH₂), 31.4 (2×-CH₂), 28.4 (-CH₂), 28.3 (-CH₂), 21.3 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₈Cl; found *m/z* 839.2820 [M+Na]⁺ [calcd. 839.2824].

Compound 4Cc (±):

Color: Obtained as white solid; **Yield:** 20% (271 mg); **Mp:** 174-176 °C; **R_f** 0.36 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 12.14 (1H, s, -NH), 11.20 (1H, s, -NH), 7.90 (1H, d, *J*=1.8 Hz), 7.53 (1H, s), 7.39 (1H, dd, *J*=1.8, 7.8 Hz), 7.30 (1H, m), 7.17 (1H, d, *J*=7.8 Hz), 7.07 (1H, d, *J*=8.4 Hz), 7.04 (1H, d, *J*=8.4 Hz), 7.01 (1H, d, *J*=8.4 Hz), 6.91 (1H, m), 6.86 (2H, m), 6.67 (1H, d, *J*=7.8 Hz), 6.21 (1H, s), 5.04 (1H, m), 4.86 (1H, m), 4.66 (1H, d, *J*=12.6 Hz), 4.31 (1H, m), 4.25 (1H, d, *J*=12.0 Hz), 4.01 (1H, m), 3.68 (3H, s), 3.51 (3H, s), 3.34 (1H, m), 2.88 (1H, m), 2.82 (1H, m), 2.74 (1H, m), 2.34 (3H, s), 1.94 (3H, m), 1.88 (1H, m), 1.78 (4H, m).

¹³C NMR (Py-d₅): δ 197.5 (-C=O), 187.4 (-C=O), 181.0 (-C=O), 180.2 (-C=O), 149.3 (-C), 148.2 (-C), 147.7 (-C), 147.4 (-C), 143.0 (-C), 142.4 (-C), 131.1 (-C), 131.0 (-C), 130.2 (-CH), 130.0 (-CH), 129.2 (-C), 128.4 (-C), 128.1 (-CH), 127.7 (-CH), 127.3 (-C), 127.0 (-C), 121.6 (-CH), 121.2 (-CH), 117.2 (-CH), 116.4 (-CH), 112.9 (-CH), 112.4 (-CH), 112.0 (-CH), 110.2 (-CH), 103.0 (-CH), 76.6 (-C), 75.2 (-C), 74.0 (-CH), 65.9 (-CH), 64.6 (-CH), 56.1 (-OMe), 55.7 (-OMe), 53.9 (-CH), 52.4 (-CH), 52.1 (-CH), 51.5 (-CH₂), 48.5 (-CH₂), 31.3 (-CH₂), 29.1 (-CH₂), 28.4 (-CH₂), 27.0 (-CH₂), 21.5 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₈Cl; found *m/z* 839.2839 [M+Na]⁺ [calcd. 839.2824].

Compound 4Cd (±):

Color: Obtained as white solid; **Yield:** 23% (311 mg); **Mp:** 172-174 °C; **R_f** 0.35 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 12.20 (1H, s, -NH), 11.24 (1H, s, -NH), 7.91 (1H, s), 7.56 (1H, m), 7.39 (1H, m), 7.31 (1H, s), 7.17 (1H, m), 7.07 (3H, m), 7.00 (1H, d, *J*=7.2 Hz), 6.92 (1H, m), 6.86 (1H, m), 6.67 (1H, d, *J*=7.8 Hz), 6.21 (1H, s), 4.87 (1H, m), 4.67 (1H, d, *J*=12.6 Hz), 4.30 (2H, m), 4.03 (1H, m), 3.71 (1H, m), 3.68 (3H, s), 3.51 (3H, s), 2.87 (3H, m), 2.34 (3H, s), 2.23 (1H, s), 1.92 (5H, m), 1.78 (3H, m).

¹³C NMR (Py-d₅): δ 198.4 (-C=O), 185.7 (-C=O), 181.0 (-C=O), 180.1 (-C=O), 149.2 (-C), 148.2 (-C), 147.7 (-C), 147.4 (-C), 142.9 (-C), 142.4 (-C), 131.3 (-C), 130.9 (-C), 130.1 (-CH), 129.9 (-CH), 129.1 (-C), 128.4 (-C), 128.1 (-CH), 128.0 (-CH), 127.6 (-C), 126.8 (-C), 121.4 (-CH), 121.3 (-CH), 117.1 (-CH), 116.4 (-CH), 113.2 (-CH), 112.4 (-CH), 111.9 (-CH), 110.1 (-CH), 103.0 (-CH), 76.5 (-C), 75.3 (-C), 73.7 (-CH), 65.5 (-CH), 64.7 (-CH), 56.0 (-OMe), 55.7 (-OMe), 54.0 (-CH), 52.4 (-CH), 51.5 (-CH₂), 50.9 (-CH), 48.7 (-CH₂), 31.0 (-CH₂), 29.9 (-CH₂), 28.1 (-CH₂), 23.2 (-CH₂), 21.5 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₈Cl; found *m/z* 839.2812 [M+Na]⁺ [calcd. 839.2824].

Compound 4Da (±):

Color: Obtained as white solid; **Yield:** 18% (246 mg); **Mp:** 238-240 °C; **R_f** 0.47 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3399, 2959, 2868, 1719, 1605;

¹H NMR (Py-d₅): δ 11.19 (1H, s, -NH), 10.89 (1H, s, -NH), 7.30 (1H, dd, *J*=2.4 Hz), 7.28 (1H, d, *J*=8.4 Hz), 7.25 (1H, d, *J*=7.8 Hz), 7.22 (1H, d, *J*=1.8 Hz), 7.20 (1H, d, *J*=1.2 Hz), 7.14 (1H, d, *J*=1.8 Hz), 7.08 (1H, dd, *J*=1.8, 8.4 Hz), 7.00 (1H, td, *J*=2.4, 8.4 Hz), 6.89 (3H, m), 6.85 (1H, q, *J*=4.2), 5.75 (1H, s), 4.49 (2H, m), 4.20 (2H, m), 3.75 (3H, s), 3.72 (1H, m), 3.70 (3H, s), 3.69 (3H, s), 3.68 (1H, m), 2.82 (1H, m), 2.73 (1H, m), 2.63 (2H, m), 1.88 (2H, m), 1.78 (4H, m), 1.69 (2H, m).

¹³C NMR (Py-d₅): δ 191.15 (-C=O), 191.11 (-C=O), 180.9 (-C=O), 180.8 (-C=O), 158.7 (-C, ¹*J*_{C-F}=237.0 Hz), 155.4 (-C), 149.3 (-C), 149.2 (-C), 147.6 (-C), 147.5 (-C), 139.8 (-C), 137.1 (-C), 131.5 (-C), 131.3 (-C), 128.6 (-C), 127.9 (-C), 121.2 (-CH), 121.0 (-CH), 117.2 (-CH), 117.1 (-CH), 116.1 (-CH, ²*J*_{C-F}=24.0 Hz), 115.3 (-CH), 114.8 (-CH, ²*J*_{C-F}=24.0 Hz), 114.3 (-

CH), 111.9 (-CH), 111.5 (-CH), 111.1 (-CH, $^3J_{C-F}=9.0$ Hz), 110.9 (-CH), 101.6 (-CH), 74.9 (-C), 74.8 (-C), 73.8 (-CH), 73.5 (-CH), 64.6 (-CH), 64.5 (-CH), 56.2 (-OMe), 56.1 (-OMe), 56.0 (-OMe), 52.6 (-CH), 52.4 (-CH), 48.4 (2 $\times$ -CH₂), 31.1 (-CH₂), 30.9 (-CH₂), 28.0 (-CH₂), 27.9 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₉F; found m/z 839.3084 [M+Na]⁺ [calcd. 839.3068].

Compound 4Db ($\pm$):

Color: Obtained as white solid; **Yield:** 22% (300 mg); **Mp:** 178-180 °C; **R_f** 0.43 (6 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ cm^{-1}): 3385, 2961, 2870, 1721, 1605;

¹H NMR (Py-*d*₅): δ 11.91 (1H, s, -NH), 11.74 (1H, s, -NH), 7.33 (1H, dd, $J=2.4, 8.4$ Hz), 7.18 (2H, m), 7.14 (1H, d, $J=7.8$ Hz), 7.11 (2H, dd, $J=1.8, 7.8$ Hz), 7.01 (1H, td, $J=2.4, 9.0$ Hz), 6.96 (1H, d, $J=8.4$ Hz), 6.87 (3H, m), 6.83 (1H, dd, $J=2.4, 8.4$ Hz), 5.96 (1H, s), 4.44 (2H, m), 4.13 (2H, m), 3.84 (1H, m), 3.76 (1H, m), 3.73 (3H, s), 3.71 (3H, s), 3.63 (3H, s), 2.76 (1H, m), 2.65 (3H, m), 1.86 (2H, m), 1.78 (2H, m), 1.69 (4H, m).

¹³C NMR (Py-*d*₅): δ 191.4 (-C=O), 189.5 (-C=O), 181.14 (-C=O), 181.08 (-C=O), 158.7 (-C, $^1J_{C-F}=237$ Hz), 155.4 (-C), 149.1 (2 $\times$ -C), 147.42 (-C), 147.40 (-C), 139.9 (-C), 137.1 (-C), 131.5 (-C), 131.2 (-C), 128.4 (-C, $^3J_{C-F}=7.5$ Hz), 128.0 (-C), 120.7 (-CH), 120.6 (-CH), 117.1 (-CH), 117.0 (-CH), 116.2 (-CH, $^2J_{C-F}=24.0$ Hz), 115.4 (-CH), 114.9 (-CH, $^2J_{C-F}=25.5$ Hz), 114.0 (-CH), 112.2 (-CH), 112.1 (-CH), 111.2 (-CH, $^3J_{C-F}=9$ Hz), 110.9 (-CH), 101.5 (-CH), 75.4 (-C), 75.3 (-C), 73.9 (-CH), 73.6 (-CH), 65.0 (-CH), 64.5 (-CH), 56.08 (-OMe), 56.06 (-OMe), 55.9 (-OMe), 51.9 (-CH), 51.8 (-CH), 48.2 (2 $\times$ -CH₂), 31.6 (-CH₂), 31.5 (-CH₂), 28.41 (-CH₂), 28.40 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₉F; found m/z 839.3062 [M+Na]⁺ [calcd. 839.3068].

Compound 4Dc ($\pm$):

Color: Obtained as white solid; **Yield:** 21% (286 mg); **Mp:** 196-198 °C; **R_f** 0.37 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.81 (1H, s, -NH), 11.39 (1H, s, -NH), 7.66 (1H, dd, *J*=2.4, 8.4 Hz), 7.40 (1H, d, *J*=1.8 Hz), 7.34 (1H, s), 7.15 (1H, d, *J*=7.8 Hz), 7.09 (1H, d, *J*=9.0 Hz), 7.03 (1H, m), 7.00 (1H, dd, *J*=2.4, 8.4 Hz), 6.92 (3H, m), 6.86 (1H, d, *J*=7.8 Hz), 6.64 (1H, q, *J*=4.2 Hz), 6.11 (1H, s), 4.97 (1H, m), 4.77 (1H, m), 4.66 (1H, d, *J*=12.6 Hz), 4.31 (1H, m), 4.19 (1H, d, *J*=12.0 Hz), 3.97 (1H, m), 3.71 (3H, s), 3.68 (3H, s), 3.53 (3H, s), 3.25 (1H, m), 2.90 (1H, m), 2.83 (1H, m), 2.74 (1H, m), 1.93 (1H, m), 1.86 (3H, m), 1.72 (4H, m).

¹³C NMR (Py-d₅): δ 195.7 (-C=O), 189.0 (-C=O), 181.2 (-C=O), 180.1 (-C=O), 158.9 (-C, ¹*J*_{C-F}=235.5 Hz), 155.6 (-C), 149.2 (-C), 148.3 (-C), 147.64 (-C), 147.56 (-C), 140.9 (-C), 137.5 (-C), 131.5 (-C), 129.9 (-C, ³*J*_{C-F}=9.4 Hz), 128.4 (-C), 126.9 (-C), 121.8 (-CH), 121.2 (-CH), 117.1 (-CH), 116.5 (-CH), 116.1 (-CH, ²*J*_{C-F}=22.5 Hz), 115.7 (-CH), 115.2 (-CH, ²*J*_{C-F}=24.0 Hz), 113.8 (-CH), 112.7 (-CH), 112.4 (-CH), 110.9 (-CH, ³*J*_{C-F}=7.5 Hz), 110.8 (-CH), 102.7 (-CH), 76.8 (-C), 75.4 (-C), 73.9 (-CH), 65.8 (-CH), 64.7 (-CH), 56.1 (-OMe), 56.0 (-OMe), 55.7 (-OMe), 53.4 (-CH), 52.5 (-CH), 52.1 (-CH), 51.5 (-CH₂), 48.5 (-CH₂), 31.4 (-CH₂), 28.9 (-CH₂), 28.3 (-CH₂), 26.9 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₉F; found *m/z* 839.3059 [M+Na]⁺ [calcd. 839.3068].

Compound 4Dd (±):

Color: Obtained as white solid; **Yield:** 24% (327 mg); **Mp:** 189-191 °C; **R_f** 0.36 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.66 (1H, s, -NH), 11.37 (1H, s, -NH), 7.72 (1H, d, *J*=8.4 Hz), 7.45 (1H, s), 7.37 (1H, s), 7.18 (1H, d, *J*=8.4 Hz), 7.10 (1H, d, *J*=7.8 Hz), 7.02 (2H, m), 6.95 (3H, m), 6.92 (1H, m), 6.66 (1H, q, *J*=3.6 Hz), 5.97 (1H, s), 4.93 (1H, t, *J*=10.2 Hz), 4.71 (1H, m), 4.60 (1H, d, *J*=11.4 Hz), 4.41 (1H, m), 4.25 (1H, d, *J*=12.0 Hz), 4.01 (1H, m), 3.80 (3H, s), 3.69 (3H, s), 3.52 (3H, s), 3.20 (1H, m), 2.97 (1H, m), 2.78 (2H, m), 1.91 (4H, m), 1.77 (2H, m), 1.65 (1H, m), 1.60 (1H, m).

¹³C NMR (Py-d₅): δ 194.0 (-C=O), 187.2 (-C=O), 181.3 (-C=O), 180.1 (-C=O), 158.9 (-C, ¹*J*_{C-F}=235.5 Hz), 155.6 (-C), 149.3 (-C), 148.3 (-C), 147.6 (-C), 147.5 (-C), 140.9 (-C), 137.5 (-C), 131.7 (-C), 130.0 (-C), 128.5 (-C), 127.4 (-C), 121.8 (-CH), 121.6 (-CH), 117.0 (-CH), 116.4 (-CH), 116.0 (-CH, ²*J*_{C-F}=24.0 Hz), 115.8 (-CH), 115.3 (-CH, ²*J*_{C-F}=24.0 Hz), 114.3 (-CH), 113.1 (-CH), 112.3 (-CH), 110.9 (-CH), 110.8 (-CH), 102.8 (-CH), 76.8 (-C), 75.7 (-C), 73.6 (-CH), 65.8 (-CH), 65.0 (-CH), 56.3 (-OMe), 56.1 (-OMe), 55.8 (-OMe), 53.9 (-CH),

52.7 (-CH), 51.45 (-CH), 51.41 (-CH₂), 48.6 (-CH₂), 31.2 (-CH₂), 29.3 (-CH₂), 28.1 (-CH₂), 26.8 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₆H₄₅N₄O₉F; found m/z 839.3059 [M+Na]⁺ [calcd. 839.3068].

Compound 4Ea (±):

Color: Obtained as white solid; **Yield:** 18% (250 mg); **Mp:** 180-182 °C; **R_f** 0.47 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3397, 2959, 2868, 1720, 1615;

¹H NMR (Py-*d*₅): δ 11.02 (1H, s, -NH), 10.96 (1H, s, -NH), 7.32 (1H, dd, $J=2.4, 8.4$ Hz), 7.28 (2H, m), 7.23 (1H, d, $J=1.8$ Hz), 7.21 (1H, m), 7.17 (1H, d, $J=1.2$ Hz), 7.09 (1H, dd, $J=1.2, 7.8$ Hz), 6.97 (2H, m), 6.81 (1H, m), 6.77 (1H, s), 5.74 (1H, s), 4.52 (1H, d, $J=12.6$ Hz), 4.38 (1H, d, $J=12.0$ Hz), 4.33 (1H, m), 4.17 (1H, m), 3.79 (2H, m), 3.75 (3H, s), 3.70 (3H, s), 2.82 (1H, m), 2.76 (1H, m), 2.63 (2H, m), 2.24 (3H, s), 2.20 (3H, s), 1.82 (6H, m), 1.69 (2H, m).

¹³C NMR (Py-*d*₅): δ 192.4 (-C=O), 190.2 (-C=O), 181.2 (-C=O), 181.0 (-C=O), 158.7 (-C, $^1J_{C-F}=235.5$ Hz), 149.22 (-C), 149.17 (-C), 147.5 (-C), 147.4 (-C), 139.8 (-C), 139.6 (-C), 131.9 (-CH), 131.7 (-C), 131.5 (-C), 130.6 (-C), 128.3 (-C), 126.1 (-C), 125.4 (-CH), 120.91 (-CH), 120.87 (-CH), 119.3 (-C), 117.2 (-CH), 117.1 (-CH), 116.1 (-CH, $^2J_{C-F}=22.5$ Hz), 115.1 (-CH, $^2J_{C-F}=24.0$ Hz), 112.4 (-CH), 111.6 (-CH), 111.1 (-CH), 101.6 (-CH), 74.9 (-C), 74.8 (-C), 73.8 (-CH), 73.3 (-CH), 65.6 (-CH), 63.6 (-CH), 56.1 (-OMe), 56.0 (-OMe), 52.4 (-CH), 52.3 (-CH), 48.5 (-CH₂), 48.4 (-CH₂), 31.1 (-CH₂), 30.7 (-CH₂), 28.0 (-CH₂), 27.7 (-CH₂), 21.2 (-CH₃), 17.1 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found m/z 837.3240 [M+Na]⁺ [calcd. 837.3276].

Compound 4Eb (±):

Color: Obtained as white solid; **Yield:** 22% (305 mg); **Mp:** 182-184 °C; **R_f** 0.43 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3403, 3208, 2964, 2871, 1713, 1605;

¹H NMR (Py-d₅): δ 12.03 (1H, s, -NH), 11.73 (1H, s, -NH), 7.28 (1H, d, *J*=7.8 Hz), 7.17 (2H, m), 7.13 (2H, m), 7.08 (1H, s), 6.98 (1H, m), 6.82 (3H, m), 6.69 (1H, s), 5.93 (1H, s), 4.38 (2H, m), 4.20 (1H, m), 4.13 (1H, m), 3.92 (1H, m), 3.78 (1H, m), 3.67 (3H, s), 3.64 (3H, s), 2.84 (1H, m), 2.68 (3H, m), 2.28 (3H, s), 2.12 (3H, s), 1.92 (1H, m), 1.84 (4H, m), 1.72 (3H, m).

¹³C NMR (Py-d₅): δ 190.7 (-C=O), 190.3 (-C=O), 181.5 (-C=O), 181.3 (-C=O), 158.6 (-C, ¹*J*_{C-F}=237.0 Hz), 149.0 (2×-C), 147.44 (-C), 147.38 (-C), 139.9 (2×-C), 131.9 (-CH), 131.6 (-C), 131.3 (-C), 130.6 (-C), 128.3 (-C), 126.2 (-C), 125.5 (-CH), 120.3 (-CH), 120.2 (-CH), 119.4 (-C), 117.0 (-CH), 116.9 (-CH), 116.2 (-CH, ²*J*_{C-F}=24.0 Hz), 115.1 (-CH, ²*J*_{C-F}=24.0 Hz), 112.6 (-CH), 112.3 (-CH), 111.0 (-CH, ³*J*_{C-F}=7.5 Hz), 101.4 (-CH), 75.4 (2×-C), 73.6 (-CH), 73.4 (-CH), 65.2 (-CH), 64.9 (-CH), 56.04 (-OMe), 55.98 (-OMe), 51.8 (-CH), 51.5 (-CH), 48.33 (-CH₂), 48.29 (-CH₂), 31.5 (-CH₂), 31.3 (-CH₂), 28.4 (-CH₂), 28.2 (-CH₂), 21.3 (-CH₃), 17.2 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found *m/z* 837.3305 [M+Na]⁺ [calcd. 837.3276].

Compound 4Ec (±):

Color: Obtained as white solid; **Yield:** 21% (292 mg); **Mp:** 172-174 °C; **R_f** 0.38 (6 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 12.01 (1H, s, -NH), 11.15 (1H, s, -NH), 7.66 (1H, dd, *J*=2.4, 8.4 Hz), 7.37 (1H, s), 7.31 (1H, d, *J*=1.8 Hz), 7.17 (1H, m), 7.13 (2H, m), 7.01 (1H, m), 6.92 (2H, m), 6.85 (1H, m), 6.79 (1H, s), 6.15 (1H, s), 4.99 (1H, dd, *J*=9.6, 12.0 Hz), 4.80 (1H, q, *J*=8.4 Hz), 4.66 (1H, d, *J*=12.0 Hz), 4.31 (1H, m), 4.23 (1H, d, *J*=12.0 Hz), 4.00 (1H, dd, *J*=9.6, 12.0 Hz), 3.70 (3H, s), 3.52 (3H, s), 3.21 (1H, m), 2.83 (2H, m), 2.74 (1H, m), 2.33 (3H, s), 1.99 (3H, s), 1.91 (3H, m), 1.83 (2H, m), 1.76 (2H, m), 1.69 (1H, m).

¹³C NMR (Py-d₅): δ 196.8 (-C=O), 188.2 (-C=O), 181.3 (-C=O), 180.4 (-C=O), 158.9 (-C, ¹*J*_{C-F}=237.0 Hz), 149.3 (-C), 148.2 (-C), 147.7 (-C), 147.4 (-C), 141.0 (-C), 140.2 (-C), 131.8 (-CH), 131.2 (-C), 130.8 (-C), 128.8 (-C, ³*J*_{C-F}=7.5 Hz), 127.8 (-C), 127.5 (-C), 125.3 (-CH), 121.7 (-CH), 121.2 (-CH), 119.3 (-C), 117.1 (-CH), 116.4 (-CH), 116.3 (-CH, ²*J*_{C-F}=24.0 Hz), 115.4 (-CH, ²*J*_{C-F}=24.0 Hz), 113.0 (-CH), 112.3 (-CH), 111.2 (-CH, ³*J*_{C-F}=7.5 Hz), 102.8 (-CH), 76.6 (-C), 75.4 (-C), 73.9 (-CH), 65.6 (-CH), 64.7 (-CH), 56.1 (-OMe), 55.6 (-OMe),

54.0 (-CH), 52.3 (-CH), 51.7 (-CH), 51.5 (-CH₂), 48.4 (-CH₂), 31.3 (-CH₂), 29.0 (-CH₂), 28.3 (-CH₂), 26.9 (-CH₂), 21.4 (-CH₃), 17.0 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found m/z 837.3284 [M+Na]⁺ [calcd. 837.3276].

Compound 4Ed (±):

Color: Obtained as white solid; **Yield:** 23% (319 mg); **Mp:** 170-172 °C; **R_f** 0.37 (6 % MeOH in CHCl₃);

¹H NMR (Py-*d*₅): δ 11.87 (1H, s, -NH), 11.14 (1H, s, -NH), 7.74 (1H, dd, $J=2.4, 8.4$ Hz), 7.40 (1H, s), 7.31 (1H, d, $J=1.8$ Hz), 7.27 (1H, m), 7.18 (1H, m), 7.12 (2H, m), 6.95 (2H, m), 6.91 (1H, d, $J=8.4$ Hz), 6.80 (1H, s), 6.04 (1H, s), 5.05 (1H, dd, $J=9.6, 12.0$ Hz), 4.68 (1H, m), 4.61 (1H, d, $J=12.0$ Hz), 4.37 (1H, m), 4.25 (1H, d, $J=12.0$ Hz), 4.00 (1H, m), 3.66 (3H, s), 3.54 (3H, s), 3.29 (1H, m), 2.77 (2H, m), 2.38 (3H, s), 1.99 (3H, s), 1.93 (2H, m), 1.76 (3H, m), 1.64 (2H, m), 1.55 (2H, m).

¹³C NMR (Py-*d*₅): δ 198.0 (-C=O), 186.2 (-C=O), 181.2 (-C=O), 180.4 (-C=O), 158.9 (-C, $^1J_{C-F}=237.0$ Hz), 149.3 (-C), 148.3 (-C), 147.7 (-C), 147.4 (-C), 141.0 (-C), 140.1 (-C), 131.8 (-CH), 131.2 (-C), 130.8 (-C), 128.8 (-C, $^3J_{C-F}=7.5$ Hz), 127.8 (-C), 127.3 (-C), 125.4 (-CH), 121.7 (-CH), 121.3 (-CH), 119.3 (-C), 117.14 (-CH), 117.08 (-CH), 116.3 (-CH, $^2J_{C-F}=24.0$ Hz), 115.6 (-CH, $^2J_{C-F}=24.0$ Hz), 113.1 (-CH), 112.3 (-CH), 111.3 (-CH, $^3J_{C-F}=7.5$ Hz), 102.9 (-CH), 76.5 (-C), 75.7 (-C), 73.7 (-CH), 65.5 (-CH), 64.7 (-CH), 56.1 (-OMe), 55.7 (-OMe), 54.2 (-CH), 52.4 (-CH), 51.5 (-CH₂), 50.8 (-CH), 48.5 (-CH₂), 31.2 (-CH₂), 29.9 (-CH₂), 28.3 (-CH₂), 26.8 (-CH₂), 21.4 (-CH₃), 17.0 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found m/z 837.3264 [M+Na]⁺ [calcd. 837.3276].

Compound 4Fa (±):

Color: Obtained as white solid; **Yield:** 17% (232 mg); **Mp:** 182-184 °C; **R_f** 0.47 (6 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ Cm⁻¹): 3385, 2959, 2868, 1719, 1607;

¹H NMR (Py-*d*₅): δ 10.96 (2H, s, -NH), 7.32 (1H, dd, $J=2.4, 8.4$ Hz), 7.27 (2H, m), 7.23 (1H, d, $J=1.8$ Hz), 7.22 (1H, m), 7.16 (1H, d, $J=1.8$ Hz), 7.09 (1H, dd, $J=1.8, 7.8$ Hz), 6.96 (2H,

m), 6.80 (1H, m), 6.77 (1H, s), 5.74 (1H, s), 4.52 (1H, d, $J=12.6$ Hz), 4.38 (1H, d, $J=12.0$ Hz), 4.33 (1H, m), 4.16 (1H, m), 3.79 (2H, m), 3.75 (3H, s), 3.70 (3H, s), 2.80 (1H, m), 2.76 (1H, m), 2.62 (2H, m), 2.24 (3H, s), 2.20 (3H, s), 1.82 (6H, m), 1.69 (2H, m).

^{13}C NMR (Py- d_5): δ 192.3 (-C=O), 190.2 (-C=O), 181.2 (-C=O), 181.0 (-C=O), 158.7 (-C, $^1J_{\text{C-F}}=240.0$ Hz), 149.21 (-C), 149.16 (-C), 147.5 (-C), 147.4 (-C), 139.8 (-C), 139.6 (-C), 131.9 (-CH), 131.6 (-C), 131.5 (-C), 130.6 (-C), 128.3 (-C, $^3J_{\text{C-F}}=7.5$ Hz), 126.1 (-C), 125.4 (-CH), 120.91 (-CH), 120.87 (-CH), 119.3 (-C), 117.2 (-CH), 117.1 (-CH), 116.1 (-CH, $^2J_{\text{C-F}}=22.5$ Hz), 115.1 (-CH, $^2J_{\text{C-F}}=24.0$ Hz), 112.4 (-CH), 111.6 (-CH), 111.1 (-CH), 101.7 (-CH), 74.9 (-C), 74.8 (-C), 73.8 (-CH), 73.3 (-CH), 65.6 (-CH), 63.8 (-CH), 56.1 (-OMe), 56.0 (-OMe), 52.4 (-CH), 52.3 (-CH), 48.5 (-CH₂), 48.4 (-CH₂), 31.1 (-CH₂), 30.7 (-CH₂), 28.0 (-CH₂), 27.7 (-CH₂), 21.2 (-CH₃), 17.1 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found m/z 815.3458 [M+H]⁺ [calcd. 815.3456].

Compound 4Fb ($\pm$):

Color: Obtained as white solid; **Yield:** 20% (273 mg); **Mp:** 184-186 °C; **R_f** 0.43 (6 % MeOH in CHCl₃);

IR (KBr, ν_{max} cm^{-1}): 3402, 2958, 2869, 1714, 1613, 1518;

^1H NMR (Py- d_5): δ 12.03 (1H, s, -NH), 11.73 (1H, s, -NH), 7.28 (1H, dd, $J=2.4, 7.8$ Hz), 7.19 (1H, s), 7.16 (1H, d, $J=8.4$ Hz), 7.13 (2H, m), 7.08 (1H, d, $J=1.8$ Hz), 6.98 (1H, td, $J=2.4, 9.0$ Hz), 6.82 (3H, m), 6.69 (1H, s), 5.92 (1H, s), 4.38 (2H, m), 4.20 (1H, m), 4.13 (1H, m), 3.92 (1H, m), 3.78 (1H, m), 3.67 (3H, s), 3.64 (3H, s), 2.85 (1H, m), 2.67 (3H, m), 2.28 (3H, s), 2.12 (3H, s), 1.92 (1H, m), 1.85 (2H, m), 1.81 (2H, m), 1.71 (3H, m).

^{13}C NMR (Py- d_5): δ 190.6 (-C=O), 190.3 (-C=O), 181.5 (-C=O), 181.3 (-C=O), 158.6 (-C, $^1J_{\text{C-F}}=237.0$ Hz), 149.0 (2 $\times$ -C), 147.44 (-C), 147.38 (-C), 139.9 (2 $\times$ -C), 131.9 (-CH), 131.6 (-C), 131.3 (-C), 130.6 (-C), 128.4 (-C, $^3J_{\text{C-F}}=7.5$ Hz), 126.2 (-C), 125.5 (-CH), 120.3 (-CH), 120.2 (-CH), 119.4 (-C), 117.0 (-CH), 116.9 (-CH), 116.2 (-CH, $^2J_{\text{C-F}}=24.0$ Hz), 115.1 (-CH, $^2J_{\text{C-F}}=24.0$ Hz), 112.6 (-CH), 112.3 (-CH), 111.0 (-CH, $^3J_{\text{C-F}}=7.5$ Hz), 101.4 (-CH), 75.44 (-C), 75.41 (-C), 73.6 (-CH), 73.4 (-CH), 65.3 (-CH), 64.9 (-CH), 56.03 (-OMe), 55.98 (-OMe), 51.8 (-CH), 51.5 (-CH), 48.33 (-CH₂), 48.29 (-CH₂), 31.5 (-CH₂), 31.3 (-CH₂), 28.4 (-CH₂), 28.2 (-CH₂), 21.3 (-CH₃), 17.2 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 $[M+H]^+$, 837 $[M+Na]^+$.

HRMS [ESI-MS, positive mode]: MF: $C_{47}H_{47}N_4O_8F$; found m/z 815.3456 $[M+H]^+$ [calcd. 815.3456].

Compound 4Fc ($\pm$):

Color: Obtained as white solid; **Yield:** 20% (273 mg); **Mp:** 173-175 °C; **R_f** 0.37 (6 % MeOH in $CHCl_3$);

1H NMR (Py- d_5): δ 11.77 (1H, s, -NH), 11.38 (1H, s, -NH), 7.63 (1H, m), 7.44 (1H, s), 7.34 (1H, s), 7.16 (1H, d, $J=8.4$ Hz), 7.12 (1H, m), 7.00 (1H, td, $J=2.4, 9.0$ Hz), 6.91 (2H, m), 6.86 (2H, m), 6.64 (1H, q, $J=4.2$ Hz), 6.10 (1H, s), 4.99 (1H, m), 4.74 (1H, m), 4.65 (1H, d, $J=12.0$ Hz), 4.33 (1H, m), 4.14 (1H, d, $J=12.0$ Hz), 4.05 (1H, m), 3.67 (3H, s), 3.51 (3H, s), 3.22 (1H, m), 2.95 (1H, m), 2.83 (1H, m), 2.75 (1H, m), 2.39 (3H, s), 2.28 (3H, s), 1.95 (3H, m), 1.78 (3H, m), 1.69 (2H, m).

^{13}C NMR (Py- d_5): δ 195.7 (-C=O), 189.0 (-C=O), 181.6 (-C=O), 180.1 (-C=O), 158.9 (-C, $^1J_{C-F}=235.5$ Hz), 149.2 (-C), 148.3 (-C), 147.61 (-C), 147.58 (-C), 140.9 (-C), 140.3 (-C), 131.9 (-CH), 131.6 (-C), 130.8 (-C), 129.8 (-C, $^3J_{C-F}=7.4$ Hz), 126.8 (-C), 126.7 (-C), 125.7 (-CH), 121.7 (-CH), 121.2 (-CH), 119.5 (-C), 117.1 (-CH), 116.4 (-CH), 116.1 (-CH, $^2J_{C-F}=22.5$ Hz), 115.2 (-CH, $^2J_{C-F}=24.0$ Hz), 112.7 (-CH), 112.4 (-CH), 110.9 (-CH, $^3J_{C-F}=7.5$ Hz), 102.8 (-CH), 76.8 (-C), 75.2 (-C), 73.8 (-CH), 65.9 (-CH), 64.6 (-CH), 56.1 (-OMe), 55.7 (-OMe), 53.2 (-CH), 52.6 (-CH), 52.0 (-CH), 51.5 (-CH₂), 48.6 (-CH₂), 31.3 (-CH₂), 29.0 (-CH₂), 28.2 (-CH₂), 26.9 (-CH₂), 21.3 (-CH₃), 17.4 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 815 $[M+H]^+$, 837 $[M+Na]^+$.

HRMS [ESI-MS, positive mode]: MF: $C_{47}H_{47}N_4O_8F$; found m/z 815.3462 $[M+H]^+$ [calcd. 815.3456].

Compound 4Fd ($\pm$):

Color: Obtained as white solid; **Yield:** 22% (300 mg); **Mp:** 186-188 °C; **R_f** 0.36 (6 % MeOH in $CHCl_3$);

1H NMR (Py- d_5): δ 11.73 (1H, s, -NH), 11.37 (1H, s, -NH), 7.66 (1H, d, $J=7.8$ Hz), 7.54 (1H, s), 7.41 (1H, s), 7.18 (2H, s), 7.01 (1H, td, $J=3.0, 9.0$ Hz), 6.95 (1H, dd, $J=1.8, 8.4$ Hz), 6.90 (3H, m), 6.68 (1H, q, $J=4.2$ Hz), 6.00 (1H, s), 4.91 (1H, m), 4.71 (1H, m), 4.64 (1H, d, $J=12.0$ Hz), 4.40 (1H, m), 4.29 (1H, d, $J=12.0$ Hz), 4.12 (1H, m), 3.70 (3H, s), 3.49 (3H, s), 3.18 (1H, m), 2.97 (1H, m), 2.76 (2H, m), 2.37 (3H, s), 2.34 (3H, s), 2.25 (1H, m), 1.96 (3H, m), 1.79 (1H, m), 1.73 (1H, m), 1.63 (1H, m), 1.58 (1H, m).

¹³C NMR (Py-*d*₅): δ 195.2 (-C=O), 190.8 (-C=O), 185.8 (-C=O), 180.3 (-C=O), 158.9 (-C, ¹*J*_{C-F}=235.5 Hz), 149.2 (-C), 148.2 (-C), 147.45 (-C), 147.37 (-C), 140.9 (-C), 140.2 (-C), 131.9 (-CH), 130.7 (-C), 130.2 (-C), 129.6 (-C), 127.75 (-C), 127.0 (-C), 126.1 (-CH), 121.6 (-CH), 121.4 (-CH), 119.5 (-C), 117.0 (-CH), 116.3 (-CH), 116.0 (-CH, ²*J*_{C-F}=24.0 Hz), 115.9 (-CH, ²*J*_{C-F}=25.5 Hz), 113.3 (-CH), 112.5 (-CH), 110.8 (-CH, ³*J*_{C-F}=7.5 Hz), 102.85 (-CH), 76.8 (-C), 75.7 (-C), 73.7 (-CH), 65.1 (-CH), 64.7 (-CH), 56.1 (-OMe), 55.7 (-OMe), 54.4 (-CH), 52.6 (-CH), 51.3 (-CH, CH₂), 48.7 (-CH₂), 31.3 (-CH₂), 29.2 (-CH₂), 28.2 (-CH₂), 26.8 (-CH₂), 21.4 (-CH₃), 17.4 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 815 [M+H]⁺, 837 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₇N₄O₈F; found *m/z* 815.3452 [M+H]⁺ [calcd. 815.3456].

Compound 5Aa (±):

Color: Obtained as white solid; **Yield:** 30% (655 mg); **Mp:** 230-232 °C; **R_f** 0.65 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3336, 2927, 1725, 1615, 1517;

¹H NMR (Py-*d*₅): δ 11.26 (2H, s, -NH), 7.64 (2H, d, *J*=7.8 Hz), 7.31 (2H, m), 7.25 (2H, dd, *J*=0.6, 7.8 Hz), 7.22 (2H, m), 6.99 (4H, m), 6.93 (2H, d, *J*=7.8 Hz), 5.74 (1H, s), 4.36 (2H, d, *J*=12.6 Hz), 4.33 (2H, m), 3.92 (2H, d, *J*=10.2 Hz), 3.76 (6H, s), 3.65 (4H, m), 3.11 (2H, dd, *J*=2.4, 11.4 Hz), 3.00 (2H, m).

¹³C NMR (Py-*d*₅): δ 190.5 (-C=O), 180.0 (-C=O), 149.5 (-C), 148.0 (-C), 143.8 (-C), 130.5 (-C), 130.3 (-CH), 128.5 (-CH), 124.5 (-C), 121.7 (-CH), 121.5 (-CH), 117.3 (-CH), 111.7 (-CH), 110.5 (-CH), 101.4 (-CH), 76.7 (-CH), 75.1 (-C), 62.6 (-CH), 56.2 (-OMe), 54.9 (-CH₂), 51.5 (-CH), 36.7 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 827 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₃H₄₀N₄O₈S₂; found *m/z* 827.2180 [M+Na]⁺ [calcd. 827.2185].

Compound 5Ab (±):

Color: Obtained as white solid; **Yield:** 35% (765 mg); **Mp:** 242-244 °C; **R_f** 0.55 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3407, 2928, 1718, 1617, 1518;

¹H NMR (Py-d₅): δ 11.94 (2H, s, -NH), 7.43 (4H, m), 7.30 (2H, d, *J*=1.8 Hz), 7.20 (1H, d, *J*=1.8 Hz), 7.18 (3H, t, *J*=7.8 Hz), 6.94 (4H, m), 5.98 (1H, s), 4.36 (2H, d, *J*=13.2 Hz), 4.32 (2H, t, *J*=7.8 Hz), 3.92 (2H, d, *J*=10.8 Hz), 3.86 (6H, s), 3.63 (4H, m), 3.15 (2H, d, *J*=11.4 Hz), 3.00 (2H, dd, *J*=6.6, 11.4 Hz).

¹³C NMR (Py-d₅): δ 190.5 (-C=O), 180.3 (-C=O), 148.2 (2×-C), 144.0 (-C), 130.3 (-CH), 130.2 (-C), 128.4 (-CH), 123.5 (-C), 121.8 (-CH), 121.6 (-CH), 117.5 (-CH), 111.7 (-CH), 110.5 (-CH), 101.1 (-CH), 76.9 (-CH), 75.5 (-C), 61.6 (-CH), 56.3 (-OMe), 55.9 (-CH₂), 51.9 (-CH), 36.9 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 827 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₃H₄₀N₄O₈S₂; found *m/z* 827.2167 [M+Na]⁺ [calcd. 827.2185].

Compound 5Ba (±):

Color: Obtained as white solid; **Yield:** 31% (700 mg); **Mp:** 216-218 °C; **R_f** 0.60 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3379, 2923, 1718, 1602, 1521;

¹H NMR (Py-d₅): δ 10.96 (2H, s, -NH), 7.52 (2H, s), 7.27 (2H, d, *J*=8.4 Hz), 7.22 (2H, m), 7.00 (2H, dd, *J*=1.8, 8.4 Hz), 6.94 (2H, d, *J*=8.4 Hz), 6.84 (2H, d, *J*=7.8 Hz), 5.66 (1H, s), 4.36 (2H, m), 4.30 (2H, d, *J*=12.0 Hz), 3.88 (2H, d, *J*=10.2 Hz), 3.78 (2H, m), 3.73 (6H, s), 3.60 (2H, d, *J*=9.6 Hz), 3.10 (2H, dd, *J*=2.4, 10.8 Hz), 2.98 (2H, m), 2.12 (6H, s).

¹³C NMR (Py-d₅): δ 190.2 (-C=O), 180.2 (-C=O), 149.3 (-C), 147.7 (-C), 141.1 (-C), 130.9 (-C), 130.724 (-C), 130.716 (-CH), 129.1 (-CH), 124.6 (-C), 121.2 (-CH), 117.3 (-CH), 112.2 (-CH), 110.3 (-CH), 101.6 (-CH), 76.4 (-CH), 75.2 (-C), 62.9 (-CH), 56.2 (-OMe), 54.6 (-CH₂), 50.9 (-CH), 36.7 (-CH₂), 21.3 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 855 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₄N₄O₈S₂; found *m/z* 855.2495 [M+Na]⁺ [calcd. 855.2498].

Compound 5Bb (±):

Color: Obtained as white solid; **Yield:** 35% (791 mg); **Mp:** 260-262 °C; **R_f** 0.53 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3388, 2921, 1708, 1617, 1516;

¹H NMR (Py-d₅): δ 11.93 (2H, s, -NH), 7.55 (2H, s), 7.17 (2H, d, *J*=7.8 Hz), 7.11 (2H, d, *J*=1.8 Hz), 6.93 (2H, d, *J*=7.8 Hz), 6.88 (2H, dd, *J*=1.2, 7.8 Hz), 6.79 (2H, d, *J*=7.8 Hz), 5.88 (1H, s), 4.30 (2H, m), 4.27 (2H, d, *J*=12.0 Hz), 3.95 (2H, d, *J*=10.2 Hz), 3.86 (2H, m), 3.70 (2H, d, *J*=10.2 Hz), 3.67 (6H, s), 3.15 (2H, dd, *J*=1.8, 11.4 Hz), 3.02 (2H, m), 2.08 (6H, s).

¹³C NMR (Py-d₅): δ 189.9 (-C=O), 180.3 (-C=O), 149.2 (-C), 147.8 (-C), 141.4 (-C), 130.8 (-CH), 130.7 (-C), 130.5 (-C), 129.2 (-CH), 124.6 (-C), 120.8 (-CH), 117.2 (-CH), 112.4 (-CH), 110.0 (-CH), 101.3 (-CH), 76.7 (-CH), 75.9 (-C), 63.0 (-CH), 56.0 (-OMe), 55.1 (-CH₂), 50.8 (-CH), 37.0 (-CH₂), 21.3 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 855 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₄N₄O₈S₂; found *m/z* 855.2498 [M+Na]⁺ [calcd. 855.2498].

Compound 6Aa (±):

Color: Obtained as white solid; **Yield:** 30% (431 mg); **Mp:** 172-174 °C; **R_f** 0.60 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3290, 2926, 1720, 1608, 1520;

¹H NMR (Py-d₅): δ 11.13 (2H, s, -NH), 7.61 (1H, s), 7.32 (2H, d, *J*=8.4 Hz), 7.26 (1H, d, *J*=8.4 Hz), 7.18 (2H, m), 7.15 (1H, m), 7.13 (1H, s), 6.94 (4H, m), 6.81 (1H, m), 5.77 (1H, s), 4.49 (1H, d, *J*=12.0 Hz), 4.36 (1H, d, *J*=12.6 Hz), 4.32 (1H, m), 4.23 (1H, m), 3.96 (1H, d, *J*=9.6 Hz), 3.81 (3H, s), 3.73 (3H, s), 3.70 (1H, m), 3.68 (3H, s), 3.63 (2H, m), 3.08 (1H, d, *J*=10.2 Hz), 2.98 (1H, m), 2.76 (1H, m), 2.61 (1H, m), 1.89 (1H, m), 1.79 (2H, m), 1.67 (1H, m).

¹³C NMR (Py-d₅): δ 191.8 (-C=O), 189.9 (-C=O), 181.0 (-C=O), 179.9 (-C=O), 155.2 (-C), 149.4 (-C), 149.3 (-C), 147.9 (-C), 147.6 (-C), 143.8 (-C), 137.2 (-C), 131.8 (-C), 130.2 (-C), 129.7 (-CH), 126.94 (-C), 126.89 (-CH), 125.9 (-C), 121.8 (-CH), 121.6 (-CH), 121.1 (-CH), 117.3 (-CH), 117.2 (-CH), 116.4 (-CH), 115.0 (-CH), 111.8 (-CH), 111.5 (-CH), 110.8 (-CH), 110.6 (-CH), 101.6 (-CH), 76.5 (-CH), 75.7 (-C), 74.4 (-C), 73.9 (-CH), 64.0 (-CH), 63.0 (-CH), 56.19 (-OMe), 56.16 (-OMe), 56.12 (-OMe), 55.1 (-CH₂), 52.7 (-CH), 51.6 (-CH), 48.6 (-CH₂), 36.7 (-CH₂), 30.9 (-CH₂), 27.6 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₄N₄O₉S; found *m/z* 839.2722 [M+Na]⁺ [calcd. 839.2727].

Compound 6Ab (±):

Color: Obtained as white solid; **Yield:** 35% (503 mg); **Mp:** 176-178 °C; **R_f** 0.55 (5 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.91 (1H, s, -NH), 11.78 (1H, s, -NH), 7.49 (1H, d, *J*=2.4 Hz), 7.22 (2H, m), 7.19 (1H, m), 7.16 (2H, dd, *J*=1.8, 7.8 Hz), 7.13 (1H, d, *J*=7.2 Hz), 7.01 (1H, dd, *J*=1.8, 7.8 Hz), 6.94 (4H, m), 6.87 (1H, dd, *J*=2.4, 8.4 Hz), 5.95 (1H, s), 4.38 (2H, m), 4.28 (1H, m), 4.16 (1H, m), 3.97 (1H, d, *J*=10.8 Hz), 3.79 (1H, m), 3.76 (3H, s), 3.72 (3H, s), 3.68 (1H, m), 3.63 (3H, s, 1H, m), 3.13 (1H, dd, *J*=1.8, 11.4 Hz), 3.00 (1H, m), 2.69 (1H, m), 2.60 (1H, m), 1.85 (1H, m), 1.68 (3H, m).

¹³C NMR (Py-d₅): δ 191.2 (-C=O), 189.6 (-C=O), 181.1 (-C=O), 180.3 (-C=O), 155.1 (-C), 149.3 (-C), 149.2 (-C), 147.9 (-C), 147.6 (-C), 143.8 (-C), 137.3 (-C), 131.3 (-C), 130.6 (-C), 129.7 (-CH), 127.1 (-CH), 126.6 (-C), 125.8 (-C), 121.7 (-CH), 121.3 (-CH), 120.9 (-CH), 117.2 (-CH), 117.1 (-CH), 115.8 (-CH), 115.3 (-CH), 112.1 (-CH), 111.9 (-CH), 110.7 (-CH), 110.6 (-CH), 101.2 (-CH), 76.7 (-CH), 76.1 (-C), 74.9 (-C), 73.8 (-CH), 64.1 (-CH), 62.7 (-CH), 56.15 (-OMe), 56.11 (-OMe), 55.90 (-OMe), 55.6 (-CH₂), 52.3 (-CH), 51.2 (-CH), 48.5 (-CH₂), 37.0 (-CH₂), 31.3 (-CH₂), 28.0 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 817 [M+H]⁺, 839 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₅H₄₄N₄O₉S; found *m/z* 839.2728 [M+Na]⁺ [calcd. 839.2727].

Compound 6Ba (±):

Color: Obtained as white solid; **Yield:** 32% (508 mg); **Mp:** 212-214 °C; **R_f** 0.56 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3511, 3209, 2924, 1713, 1606, 1515;

¹H NMR (Py-d₅): δ 11.73 (1H, s, -NH), 11.29 (1H, s, -NH), 8.38 (1H, d, *J*=1.2 Hz), 7.84 (1H, d, *J*=7.8 Hz), 7.42 (1H, d, *J*=1.2 Hz), 7.37 (1H, d, *J*=7.8 Hz), 7.28 (3H, m), 7.08 (1H, d, *J*=1.8 Hz), 7.01 (1H, m), 6.85 (2H, m), 6.60 (1H, dd, *J*=1.8, 7.8 Hz), 5.79 (1H, s), 4.64 (1H, d, *J*=12.0 Hz), 4.32 (1H, d, *J*=12.6 Hz), 4.26 (1H, m), 4.17 (1H, m), 3.94 (1H, d, *J*=10.8 Hz), 3.88 (3H, s), 3.80 (1H, m), 3.69 (1H, m), 3.62 (3H, s), 3.48 (1H, m), 3.04 (1H, m), 2.95 (1H, m), 2.66 (2H, m), 1.86 (3H, m), 1.66 (1H, m).

¹³C NMR (Py-d₅): δ 193.3 (-C=O), 188.9 (-C=O), 180.8 (-C=O), 179.3 (-C=O), 158.7 (-C, ¹*J*_{C-F}=239.1 Hz), 149.6 (-C), 149.5 (-C), 148.1 (-C), 147.8 (-C), 143.8 (-C), 140.1 (-C), 139.6

(-CH), 137.1 (-CH), 132.0 (-C), 129.6 (-C), 129.4 (-C), 127.1 (-C), 122.4 (-CH), 120.8 (-CH), 117.7 (-CH), 117.2 (-CH), 115.9 (-CH, $^2J_{C-F}=22.5$ Hz), 114.3 (-CH, $^2J_{C-F}=24$ Hz), 112.9 (-CH), 112.0 (-CH), 111.0 (-CH, $^3J_{C-F}=6.45$ Hz), 110.7 (-CH), 101.0 (-CH), 84.4 (-C), 76.6 (-CH), 75.5 (-C), 74.9 (-CH), 74.6 (-C), 64.1 (-CH), 62.6 (-CH), 56.5 (-OMe), 56.0 (-OMe), 55.7 (-CH₂), 52.5 (-CH), 51.7 (-CH), 48.2 (-CH₂), 36.9 (-CH₂), 31.1 (-CH₂), 28.0 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 953 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₄H₄₀N₄O₈IFS; found m/z 953.1488 [M+Na]⁺ [calcd. 953.1493].

Compound 6Bb (±):

Color: Obtained as white solid; **Yield:** 37% (587 mg); **Mp:** 220-222 °C; **R_f** 0.48 (5 % MeOH in CHCl₃);

¹H NMR (Py-*d*₅): δ 12.25 (1H, s, -NH), 11.88 (1H, s, -NH), 8.31 (1H, s), 7.59 (1H, d, $J=7.8$ Hz), 7.30 (1H, d, $J=7.8$ Hz), 7.14 (1H, d, $J=7.8$ Hz), 7.09 (1H, d, $J=8.4$ Hz), 7.06 (1H, s), 7.02 (1H, s), 6.96 (1H, m), 6.81 (2H, m), 6.76 (2H, d, $J=7.8$ Hz), 5.82 (1H, s), 4.32 (1H, d, $J=12.0$ Hz), 4.25 (1H, m), 4.21 (1H, d, $J=12.0$ Hz), 4.14 (1H, m), 3.93 (1H, d, $J=10.8$ Hz), 3.83 (1H, m), 3.73 (3H, s), 3.71 (1H, m), 3.65 (1H, m), 3.63 (3H, s), 3.12 (1H, d, $J=12.0$ Hz), 2.99 (1H, m), 2.63 (2H, m), 1.84 (1H, m), 1.76 (1H, m), 1.67 (2H, m).

¹³C NMR (Py-*d*₅): δ 190.4 (-C=O), 189.2 (-C=O), 181.0 (-C=O), 179.6 (-C=O), 158.6 (-C, $^1J_{C-F}=237.0$ Hz), 149.1 (-C), 149.0 (-C), 147.8 (-C), 147.4 (-C), 143.5 (-C), 139.8 (-C), 139.1 (-CH), 137.4 (-CH), 131.1 (-C), 130.1 (-C), 128.3 (-C), 127.0 (-C), 120.7 (-CH), 120.3 (-CH), 117.2 (-CH), 117.1 (-CH), 116.2 (-CH, $^2J_{C-F}=24.0$ Hz), 115.0 (-CH, $^2J_{C-F}=24$ Hz), 112.6 (-CH), 112.5 (2×-CH), 111.2 (-CH, $^3J_{C-F}=7.5$ Hz), 101.7 (-CH), 84.5 (-C), 76.4 (-CH), 76.0 (-C), 75.3 (-C), 73.6 (-CH), 64.8 (-CH), 63.5 (-CH), 56.1 (-OMe), 56.0 (-OMe), 55.5 (-CH₂), 51.9 (-CH), 51.0 (-CH), 48.2 (-CH₂), 37.1 (-CH₂), 31.4 (-CH₂), 28.3 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 953 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₄H₄₀N₄O₈IFS; found m/z 953.1487 [M+Na]⁺ [calcd. 953.1493].

Compound 6Ca (±):

Color: Obtained as white solid; **Yield:** 31% (455 mg); **Mp:** 180-182 °C; **R_f** 0.54 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3514, 3200, 1713, 1610, 1515;

¹H NMR (Py-d₅): δ 11.61 (1H, s, -NH), 11.39 (1H, s, -NH), 8.29 (1H, s), 7.76 (1H, d, *J*=7.8 Hz), 7.57 (1H, m), 7.34 (2H, m), 7.28 (2H, m), 7.18 (1H, d, *J*=7.8 Hz), 7.13 (1H, s), 6.88 (1H, d, *J*=7.8 Hz), 6.80 (1H, d, *J*=7.8 Hz), 6.77 (1H, d, *J*=8.4 Hz), 5.74 (1H, s), 4.57 (1H, d, *J*=12.0 Hz), 4.38 (1H, m), 4.27 (1H, m), 4.20 (1H, m), 3.92 (1H, d, *J*=10.8 Hz), 3.82 (1H, m), 3.80 (3H, s), 3.67 (3H, s), 3.64 (1H, m), 3.57 (1H, m), 3.08 (1H, d, *J*=11.4 Hz), 2.96 (1H, m), 2.71 (1H, m), 2.61 (1H, m), 1.82 (3H, m), 1.66 (1H, m).

¹³C NMR (Py-d₅): δ 192.8 (-C=O), 189.0 (-C=O), 180.5 (-C=O), 179.3 (-C=O), 149.9 (-C), 149.5 (-C), 148.0 (-C), 147.7 (-C), 143.7 (-C), 142.6 (-C), 139.4 (-CH), 137.0 (-CH), 131.9 (-C), 130.0 (-CH), 129.8 (-C), 129.3 (-C), 127.2 (-C), 126.9 (-CH), 126.6 (-C), 121.9 (-CH), 120.9 (-CH), 117.5 (-CH), 117.3 (-CH), 112.8 (-CH), 112.0 (-CH), 111.8 (-CH), 111.2 (-CH), 101.1 (-CH), 84.5 (-C), 76.7 (-CH), 75.2 (2×-C), 74.4 (-CH), 64.6 (-CH), 62.4 (-CH), 56.3 (-OMe), 56.1 (-OMe), 55.3 (-CH₂), 52.4 (-CH), 51.4 (-CH), 48.2 (-CH₂), 36.9 (-CH₂), 31.0 (-CH₂), 27.9 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 947 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₄H₄₀ClIN₄O₈S; found *m/z* 947.1375 [M+H]⁺ [calcd. 947.1378].

Compound 6Cb (±):

Color: Obtained as white solid; **Yield:** 35% (549 mg); **Mp:** 230-232 °C; **R_f** 0.46 (5 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 12.23 (1H, s, -NH), 12.06 (1H, s, -NH), 8.30 (1H, s), 7.59 (1H, m), 7.55 (1H, dd, *J*=1.8, 8.4 Hz), 7.17 (1H, dd, *J*=1.8, 8.4 Hz), 7.10 (2H, dd, *J*=3.0, 8.4 Hz), 7.02 (2H, m), 6.79 (1H, d, *J*=8.4 Hz), 6.75 (2H, m), 6.68 (1H, d, *J*=7.8 Hz), 5.80 (1H, s), 4.28 (2H, d, *J*=12.0 Hz), 4.18 (1H, m), 4.14 (1H, m), 3.92 (1H, d, *J*=10.8 Hz), 3.82 (2H, t, *J*=10.8 Hz), 3.68 (3H, s), 3.64 (3H, s), 3.62 (1H, m), 3.10 (1H, m), 2.99 (1H, m), 2.67 (1H, m), 2.60 (1H, m), 1.85 (1H, m), 1.79 (1H, m), 1.70 (2H, m).

¹³C NMR (Py-d₅): δ 189.8 (2×-C=O), 180.8 (-C=O), 179.5 (-C=O), 149.0 (-C), 148.9 (-C), 147.7 (-C), 147.3 (-C), 143.5 (-C), 142.4 (-C), 139.1 (-CH), 137.4 (-CH), 131.1 (-C), 130.1 (-C), 129.9 (-CH), 128.5 (-C), 127.6 (-CH), 127.0 (-C), 126.7 (-C), 120.5 (-CH), 120.1 (-CH), 117.1 (-CH), 117.0 (-CH), 112.8 (-CH), 112.6 (-CH), 112.5 (-CH), 111.8 (-CH), 101.7 (-CH), 84.5 (-C), 76.3 (-CH), 76.1 (-C), 75.3 (-C), 73.3 (-CH), 65.5 (-CH), 63.6 (-CH), 56.13 (-OMe), 56.06 (-OMe), 55.5 (-CH₂), 51.7 (-CH), 50.9 (-CH), 48.2 (-CH₂), 37.1 (-CH₂), 31.3 (-CH₂), 28.4 (-CH₂).

MS [ESI-MS, positive mode]: found m/z 947 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₄H₄₀ClIN₄O₈S; found m/z 969.1193 [M+Na]⁺ [calcd. 969.1198].

Compound 6Da (±):

Color: Obtained as white solid; **Yield:** 32% (452 mg); **Mp:** 202-204 °C; **R_f** 0.55 (5 % MeOH in CHCl₃);

IR (KBr, ν_{max} Cm⁻¹): 3411, 2930, 1721, 1604, 1518;

¹H NMR (Py-*d*₅): δ 11.26 (1H, s, -NH), 10.63 (1H, s, -NH), 7.43 (1H, s), 7.28 (2H, t, *J*=8.4 Hz), 7.23 (2H, m), 7.10 (1H, d, *J*=2.4 Hz), 7.06 (1H, dd, *J*=1.2, 7.8 Hz), 7.01 (1H, dd, *J*=1.2, 7.8 Hz), 6.86 (1H, d, *J*=7.8 Hz), 6.81 (1H, dd, *J*=2.4, 8.4 Hz), 6.75 (1H, s), 5.72 (1H, s), 4.38 (3H, m), 4.28 (1H, m), 3.95 (1H, m), 3.81 (1H, m), 3.75 (3H, s), 3.74 (3H, s), 3.71 (2H, m), 3.64 (3H, s), 3.17 (1H, m), 3.00 (1H, m), 2.88 (1H, m), 2.62 (1H, m), 2.23 (3H, s), 2.15 (3H, s), 1.88 (1H, m), 1.79 (1H, m), 1.70 (2H, m).

¹³C NMR (Py-*d*₅): δ 194.0 (-C=O), 187.9 (-C=O), 180.9 (-C=O), 180.4 (-C=O), 155.4 (-C), 149.4 (-C), 149.1 (-C), 147.7 (-C), 147.5 (-C), 140.0 (-C), 136.8 (-C), 132.3 (-CH), 132.0 (-C), 130.6 (-C), 130.5 (-C), 127.8 (-C), 126.5 (-CH), 124.2 (-C), 121.3 (-CH), 121.0 (-CH), 119.0 (-C), 117.3 (-CH), 117.1 (-CH), 115.0 (-CH), 114.5 (-CH), 112.4 (-CH), 111.7 (-CH), 110.8 (-CH), 101.9 (-CH), 77.1 (-CH), 75.5 (-C), 74.8 (-C), 72.9 (-CH), 66.1 (-CH), 61.5 (-CH), 56.13 (2×-OMe), 56.09 (-OMe), 55.2 (-CH₂), 52.5 (-CH), 51.1 (-CH), 48.5 (-CH₂), 36.7 (-CH₂), 30.6 (-CH₂), 27.5 (-CH₂), 21.1 (-CH₃), 17.2 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 845 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₉S; found m/z 845.3238 [M+H]⁺ [calcd. 845.3220].

Compound 6Db (±):

Color: Obtained as white solid; **Yield:** 36% (508 mg); **Mp:** 182-184 °C; **R_f** 0.47 (5 % MeOH in CHCl₃);

¹H NMR (Py-*d*₅): δ 11.83 (1H, s, -NH), 11.79 (1H, s, -NH), 7.47 (1H, s), 7.18 (1H, dd, *J*=1.2, 7.8 Hz), 7.12 (2H, m), 7.07 (2H, m), 6.84 (3H, m), 6.77 (1H, dd, *J*=2.4, 8.4 Hz), 6.69 (1H, s), 5.87 (1H, d, *J*=1.2 Hz), 4.33 (2H, m), 4.27 (1H, d, *J*=12.6 Hz), 4.19 (1H, m), 3.98 (1H, d, *J*=10.2 Hz), 3.90 (1H, m), 3.80 (1H, t, *J*=10.2 Hz), 3.75 (1H, d, *J*=10.2 Hz), 3.68 (3H,

s), 3.64 (3H, s), 3.54 (3H, s), 3.17 (1H, m), 3.04 (1H, m), 2.81 (1H, m), 2.64 (1H, m), 2.26 (3H, s), 2.10 (3H, s), 1.87 (1H, m), 1.79 (1H, m), 1.69 (2H, m).

¹³C NMR (Py-d₅): δ 191.0 (-C=O), 189.3 (-C=O), 181.2 (-C=O), 180.6 (-C=O), 155.4 (-C), 149.1 (-C), 149.0 (-C), 147.7 (-C), 147.4 (-C), 140.0 (-C), 137.1 (-C), 132.3 (-CH), 131.6 (-C), 130.7 (-C), 130.4 (-C), 127.9 (-C), 126.5 (-CH), 124.3 (-C), 120.7 (-CH), 120.3 (-CH), 119.1 (-C), 117.2 (-CH), 116.9 (-CH), 115.3 (-CH), 114.1 (-CH), 112.6 (-CH), 112.4 (-CH), 110.7 (-CH), 101.4 (-CH), 76.6 (-CH), 76.1 (-C), 75.5 (-C), 73.4 (-CH), 65.2 (-CH), 63.3 (-CH), 56.1 (-OMe), 56.0 (-OMe), 55.8 (-OMe), 55.0 (-CH₂), 51.8 (-CH), 50.7 (-CH), 48.4 (-CH₂), 36.9 (-CH₂), 31.3 (-CH₂), 28.1 (-CH₂), 21.3 (-CH₃), 17.2 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 845 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₈N₄O₉S; found *m/z* 845.3209 [M+H]⁺ [calcd. 845.3220].

Compound 6Ea (±):

Color: Obtained as white solid; **Yield:** 31% (441 mg); **Mp:** 172-174 °C; **R_f** 0.51 (5 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.16 (1H, s, -NH), 10.69 (1H, s, -NH), 7.46 (1H, s), 7.30 (2H, m), 7.28 (1H, s), 7.25 (2H, d, *J* = 9.6 Hz), 7.08 (1H, d, *J* = 7.8 Hz), 7.03 (1H, d, *J* = 7.8 Hz), 6.95 (1H, d, *J* = 7.8 Hz), 6.83 (1H, d, *J* = 7.8 Hz), 6.73 (1H, s), 5.73 (1H, s), 4.37 (3H, m), 3.95 (1H, d, *J* = 10.2 Hz), 3.87 (1H, m), 3.81 (1H, m), 3.76 (3H, s), 3.73 (3H, s), 3.71 (1H, m), 3.16 (1H, m), 3.01 (1H, m), 2.86 (1H, m), 2.63 (1H, m), 2.24 (3H, s), 2.15 (6H, s), 2.01 (1H, m), 1.90 (1H, m), 1.82 (2H, m), 1.69 (1H, m).

¹³C NMR (Py-d₅): δ 192.6 (-C=O), 187.8 (-C=O), 180.5 (-C=O), 179.9 (-C=O), 148.7 (-C), 148.5 (-C), 147.1 (-C), 146.8 (-C), 140.4 (-C), 139.3 (-C), 131.7 (-CH), 131.4 (-C), 130.2 (3×-C), 129.9 (-C), 129.6 (-CH), 127.5 (-CH), 126.0 (-C), 125.9 (-CH), 120.5 (-CH), 120.3 (-CH), 118.4 (-C), 116.7 (-CH), 116.5 (-CH), 111.8 (-CH), 111.4 (-CH), 109.7 (-CH), 101.2 (-CH), 76.2 (-CH), 75.0 (-C), 74.1 (-C), 72.6 (-CH), 65.0 (-CH), 61.4 (-CH), 55.5 (2×-OMe), 54.4 (-CH₂), 51.7 (-CH), 50.5 (-CH), 48.0 (-CH₂), 36.1 (-CH₂), 30.2 (-CH₂), 27.0 (-CH₂), 20.7 (-CH₃), 20.6 (-CH₃), 16.6 (-CH₃).

MS [ESI-MS, positive mode]: found *m/z* 829 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₉N₄O₈S; found *m/z* 829.3268 [M+H]⁺ [calcd. 829.3271].

Compound 6Eb (±):

Color: Obtained as white solid; **Yield:** 36% (512 mg); **Mp:** 169-171 °C; **R_f** 0.45 (5 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ Cm^{-1}): 3404, 2926, 1712, 1605, 1517, 1485;

¹H NMR (Py-*d*₅): δ 7.41 (1H, s), 7.17 (2H, m), 7.09 (3H, m), 6.90 (1H, d, $J=7.8$ Hz), 6.82 (2H, m), 6.78 (1H, d, $J=7.8$ Hz), 6.64 (1H, s), 5.85 (1H, s), 4.27 (3H, m), 4.16 (1H, m), 3.93 (1H, d, $J=9.6$ Hz), 3.83 (2H, q, $J=9.6$, 21 Hz), 3.70 (1H, d, $J=9.6$ Hz), 3.63 (3H, s), 3.58 (3H, s), 3.13 (1H, m), 2.99 (1H, m), 2.78 (1H, m), 2.59 (1H, m), 2.21 (3H, s), 2.05 (3H, s), 2.00 (3H, s), 1.84 (1H, m), 1.75 (2H, m), 1.64 (1H, m).

¹³C NMR (Py-*d*₅): δ 190.6 (-C=O), 188.8 (-C=O), 180.8 (-C=O), 180.1 (-C=O), 148.6 (-C), 148.4 (-C), 147.2 (-C), 146.8 (-C), 140.7 (-C), 139.5 (-C), 131.8 (-CH), 131.1 (-C), 130.2 (2 $\times$ -C), 130.1 (-C), 129.8 (-C), 129.7 (-CH), 127.5 (-CH), 126.0 (-C), 125.9 (-CH), 120.1 (-CH), 119.7 (-CH), 118.5 (-C), 116.6 (-CH), 116.4 (-CH), 111.9 (-CH), 111.7 (-CH), 109.7 (-CH), 100.7 (-CH), 76.1 (-CH), 75.5 (-C), 74.7 (-C), 73.0 (-CH), 64.5 (-CH), 62.5 (-CH), 55.5 (-OMe), 55.4 (-OMe), 54.5 (-CH₂), 51.1 (-CH), 50.2 (-CH), 47.9 (-CH₂), 36.3 (-CH₂), 30.7 (-CH₂), 27.5 (-CH₂), 20.8 (-CH₃), 20.7 (-CH₃), 16.7 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 829 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₇H₄₉N₄O₈S; found m/z 829.3268 [M+H]⁺ [calcd. 829.3271].

Compound 7A (±):

Color: Obtained as white solid; **Yield:** 54% (636 mg); **Mp:** 192-194 °C; **R_f** 0.52 (5 % MeOH in CHCl₃);

IR (KBr, $\nu_{\max}$ Cm^{-1}): 3511, 2960, 1720, 1607, 1515;

¹H NMR (Py-*d*₅): δ 11.82 (1H, s, -NH), 7.87 (2H, m), 7.84 (2H, m), 7.76 (1H, t, $J=7.2$ Hz), 7.69 (1H, d, $J=7.2$ Hz), 7.41 (1H, t, $J=7.2$ Hz), 7.37 (1H, d, $J=1.2$ Hz), 7.30 (1H, t, $J=7.8$ Hz), 7.16 (3H, m), 7.02 (1H, d, $J=7.8$ Hz), 6.79 (1H, dd, $J=1.2$, 8.4 Hz), 6.75 (1H, d, $J=8.4$ Hz), 6.70 (1H, s), 6.03 (1H, s), 4.96 (1H, m), 4.61 (2H, m), 4.45 (1H, d, $J=11.4$ Hz), 4.38 (1H, m), 4.01 (1H, dd, $J=9.6$, 12 Hz), 3.71 (3H, s), 3.36 (3H, s), 3.14 (1H, m), 2.90 (1H, m), 2.74 (1H, m), 2.54 (1H, t, $J=7.2$ Hz), 1.98 (1H, m), 1.90 (2H, m), 1.78 (1H, m), 1.70 (1H, m), 1.64 (1H, m), 1.50 (1H, m), 1.31 (1H, m).

¹³C NMR (Py-*d*₅): δ 204.6 (-C=O), 197.4 (-C=O), 186.5 (-C=O), 181.2 (-C=O), 149.3 (-C), 148.1 (-C), 147.7 (-C), 147.2 (-C), 144.0 (-C), 143.2 (-C), 138.1 (-C), 133.2 (-C), 131.7 (-CH), 131.5 (-C), 131.3 (-C), 129.9 (-CH), 128.83 (-CH), 128.79 (-CH), 128.0 (-CH), 127.5 (-C), 126.9 (-C), 125.9 (-CH), 123.7 (-CH), 121.9 (-CH), 121.8 (-CH), 121.7 (-CH), 121.4 (-CH), 117.1 (-CH), 116.3 (-CH), 113.2 (-CH), 112.3 (-CH), 110.8 (-CH), 103.0 (-CH), 79.3 (-C), 75.3 (-C), 73.7 (-CH), 66.0 (-CH), 64.6 (-CH), 56.1 (-OMe), 55.6 (-OMe), 54.8 (-CH), 52.6 (-CH), 51.8 (-CH₂), 50.7 (-CH), 48.6 (-CH₂), 31.3 (-CH₂), 29.5 (-CH₂), 28.2 (-CH₂), 26.7 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 804 [M+H]⁺, 826 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₉H₄₅N₃O₈; found *m/z* 826.3113 [M+Na]⁺ [calcd. 826.3104].

Compound 7B (±):

Color: Obtained as yellowish white solid; **Yield:** 56% (629 mg); **Mp:** 163-165 °C; **R_f** 0.50 (5 % MeOH in CHCl₃);

¹H NMR (Py-*d*₅): δ 12.17 (1H, s, -NH), 8.06 (2H, d, *J* = 7.2 Hz), 7.88 (1H, d, *J* = 8.4 Hz), 7.84 (1H, s), 7.67 (2H, m), 7.62 (1H, t, *J* = 7.2 Hz), 7.47 (1H, d, *J* = 7.2 Hz), 7.34 (1H, d, *J* = 7.8 Hz), 7.30 (1H, s), 7.19 (1H, d, *J* = 8.4 Hz), 7.15 (1H, d, *J* = 8.4 Hz), 7.03 (1H, s), 6.91 (1H, d, *J* = 8.4 Hz), 6.83 (1H, d, *J* = 7.8 Hz), 5.81 (1H, s), 4.52 (1H, d, *J* = 11.4 Hz), 4.30 (1H, d, *J* = 12.0 Hz), 4.23 (1H, m), 4.09 (1H, m), 3.88 (3H, s), 3.74 (2H, m), 3.66 (3H, s), 2.62 (2H, m), 2.52 (1H, m), 2.35 (1H, m), 1.84 (2H, m), 1.70 (5H, m), 1.58 (1H, m).

¹³C NMR (Py-*d*₅): δ 205.1 (-C=O), 191.4 (-C=O), 189.4 (-C=O), 179.9 (-C=O), 148.8 (-C), 148.6 (-C), 147.1 (-C), 147.0 (-C), 142.9 (-C), 142.2 (-C), 138.2 (-CH), 135.0 (-CH), 132.1 (-C), 131.8 (-CH), 130.75 (-C), 130.67 (-C), 130.45 (-C), 128.9 (-C), 128.2 (-CH), 128.1 (-CH), 125.3 (-CH), 123.6 (-C), 122.9 (-CH), 121.6 (-CH), 120.4 (-CH), 120.3 (-CH), 116.7 (-CH), 116.4 (-CH), 112.4 (-CH), 111.5 (-CH), 111.1 (-CH), 100.7 (-CH), 84.2 (-C), 77.5 (-C), 74.1 (-C), 73.5 (-CH), 73.0 (-CH), 64.5 (-CH), 62.9 (-CH), 55.7 (-OMe), 55.4 (-OMe), 52.9 (-CH), 51.4 (-CH), 48.2 (-CH₂), 47.7 (-CH₂), 30.7 (-CH₂), 30.4 (-CH₂), 27.7 (-CH₂), 27.0 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 930 [M+H]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₉H₄₅IN₃O₈; found *m/z* 930.2252 [M+H]⁺ [calcd. 930.2251].

Compound 7C (±):

Color: Obtained as white solid; **Yield:** 50% (607 mg); **Mp:** 204-206 °C; **R_f** 0.49 (5 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 11.78 (1H, s, -NH), 8.08 (1H, dd, *J*=2.4, 6.6 Hz), 8.05 (1H, dd, *J*=2.4, 8.4 Hz), 7.83 (1H, dd, *J*=2.4, 8.4 Hz), 7.74 (1H, m), 7.62 (2H, m), 7.47 (1H, dd, *J*=1.8, 7.8 Hz), 7.41 (1H, dd, *J*=1.8, 7.8 Hz), 7.31 (1H, s), 7.26 (1H, d, *J*=8.4 Hz), 7.18 (2H, m), 7.12 (1H, d, *J*=7.8 Hz), 6.96 (1H, d, *J*=7.8 Hz), 6.91 (2H, m), 5.86 (1H, s), 4.46 (1H, m), 4.32 (2H, m), 4.11 (1H, m), 3.87 (3H, s), 3.82 (3H, s), 3.76 (2H, m), 3.49 (1H, m), 3.24 (1H, d, *J*=10.8 Hz), 3.20 (1H, d, *J*=11.4 Hz), 3.02 (1H, m), 2.57 (2H, m), 1.86 (1H, m), 1.71 (2H, m), 1.64 (1H, m).

¹³C NMR (Py-d₅): δ 205.0 (-C=O), 190.9 (-C=O), 190.5 (-C=O), 180.9 (-C=O), 149.8 (-C), 149.6 (-C), 148.3 (-C), 147.9 (-C), 143.9 (-C), 143.4 (-C), 133.2 (-C), 132.51 (-CH), 132.47 (-C), 131.2 (-C), 131.0 (-C), 130.3 (-C), 129.7 (-CH), 128.7 (-CH), 128.6 (-CH), 126.8 (-CH), 126.4 (-C), 126.2 (-CH), 125.1 (-CH), 122.4 (-CH), 121.9 (-CH), 121.7 (-CH), 121.5 (-CH), 117.5 (-CH), 117.3 (-CH), 111.9 (-CH), 111.3 (-CH), 110.6 (-CH), 100.9 (-CH), 78.7 (-C), 77.4 (-CH), 74.4 (-C), 73.8 (-CH), 63.8 (-CH), 61.2 (-CH), 56.3 (-OMe), 56.2 (-OMe), 55.9 (-CH₂), 53.0 (-CH), 52.4 (-CH), 48.4 (-CH₂), 37.2 (-CH₂), 31.3 (-CH₂), 27.9 (-CH₂).

MS [ESI-MS, positive mode]: found *m/z* 822 [M+H]⁺, 844 [M+Na]⁺.

HRMS [ESI-MS, positive mode]: MF: C₄₈H₄₃N₃O₈S; found *m/z* 844.2670 [M+Na]⁺ [calcd. 844.2669].

Compound 7D (±):

Color: Obtained as yellowish white solid; **Yield:** 49% (588 mg); **Mp:** 160-162 °C; **R_f** 0.48 (5 % MeOH in CHCl₃);

¹H NMR (Py-d₅): δ 8.05 (2H, m), 7.87 (1H, d, *J*=8.4 Hz), 7.76 (1H, d, *J*= 8.4 Hz), 7.65 (1H, t, *J*= 7.8 Hz), 7.60 (1H, d, *J*=7.2 Hz), 7.39 (1H, d, *J*=7.8 Hz), 7.31 (1H, d, *J*=1.2 Hz), 7.27 (1H, d, *J*=8.4 Hz), 7.20 (1H, m), 7.15 (1H, s), 7.07 (2H, m), 7.01 (1H, d, *J*= 7.8 Hz), 6.96 (1H, dd, *J*= 1.2, 7.8 Hz), 5.88 (1H, s), 4.46 (1H, d, *J*= 12.6 Hz), 4.33 (2H, m), 4.12 (1H, m), 3.88 (3H, s), 3.76 (2H, m), 3.73 (3H, s), 3.70 (1H, m), 3.24 (1H, d, *J*=10.8 Hz), 3.12 (1H, d, *J*=11.4 Hz), 3.00 (1H, m), 2.72 (1H, m), 2.63 (1H, m), 2.13 (3H, s), 1.87 (1H, m), 1.77 (2H, m), 1.68 (1H, m).

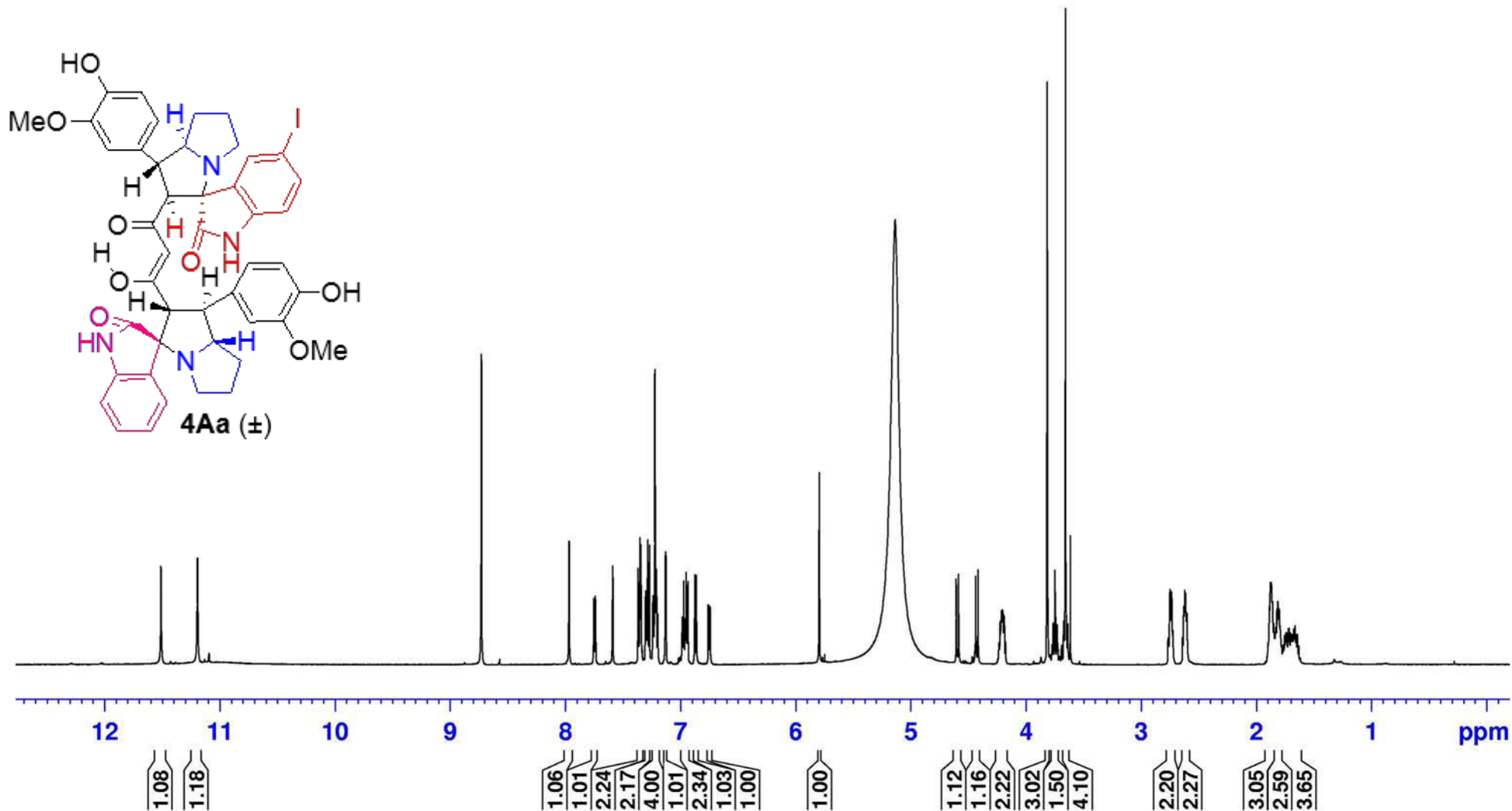
¹³C NMR (Py-d₅): δ 204.5 (-C=O), 192.0 (-C=O), 188.1 (-C=O), 180.4 (-C=O), 149.0 (-C), 148.7 (-C), 147.6 (-C), 147.1 (-C), 142.8 (-C), 140.8 (-C), 132.8 (-C), 131.9 (-CH), 131.8 (-

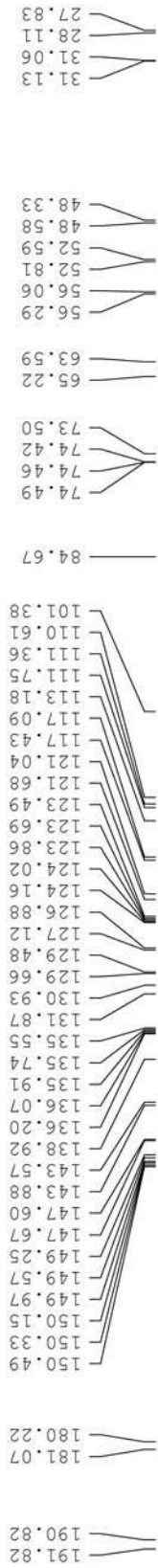
C), 130.8 (-C), 130.5 (-C), 130.3 (-C), 129.8 (-CH, -C), 128.1 (-CH), 128.0 (-CH), 127.3 (-CH), 126.1 (-C), 125.5 (-CH), 124.3 (-CH), 121.8 (-CH), 120.9 (-CH), 120.6 (-CH), 116.8 (-CH), 116.5 (-CH), 111.4 (-CH), 110.8 (-CH), 109.9 (-CH), 100.4 (-CH), 78.2 (-C), 77.1 (-CH), 74.1 (-C), 73.1 (-CH), 64.1 (-CH), 60.5 (-CH), 55.6 (-OMe), 55.5 (-OMe), 55.2 (-CH₂), 51.8 (-CH), 51.6 (-CH), 47.7 (-CH₂), 36.8 (-CH₂), 30.8 (-CH₂), 27.7 (-CH₂), 20.8 (-CH₃).

MS [ESI-MS, positive mode]: found m/z 836 [M+H]⁺.

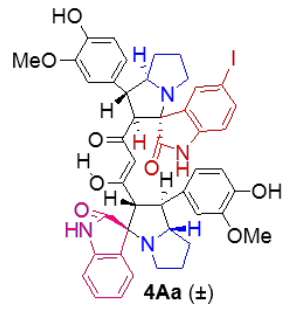
HRMS [ESI-MS, positive mode]: MF: C₄₉H₄₆N₃O₈S; found m/z 836.3009 [M+H]⁺ [calcd. 836.3006].

11.508	11.194	8.730	7.970	7.755	7.742	7.590	7.368	7.355	7.347	7.345	7.303	7.291	7.285	7.272	7.240	7.237	7.223	7.211	7.198	7.131	7.129	6.986	6.973	6.950	6.938	6.876	6.862	6.759	6.756	6.745	6.742	5.796	5.136	4.606	4.585	4.439	4.418	4.216	4.211	4.206	4.200	4.190	3.817	3.750	3.659	3.616	2.752	2.748	2.739	2.632	2.629	2.621	2.616	2.605	1.886	1.876	1.871	1.864	1.860	1.823	1.813	1.805
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DEPT-135



56.29
56.06
52.81
52.59

65.22
63.59

74.43
73.50

101.38

110.61
111.36
111.74
113.18
117.09
117.43
121.04
121.68
124.15

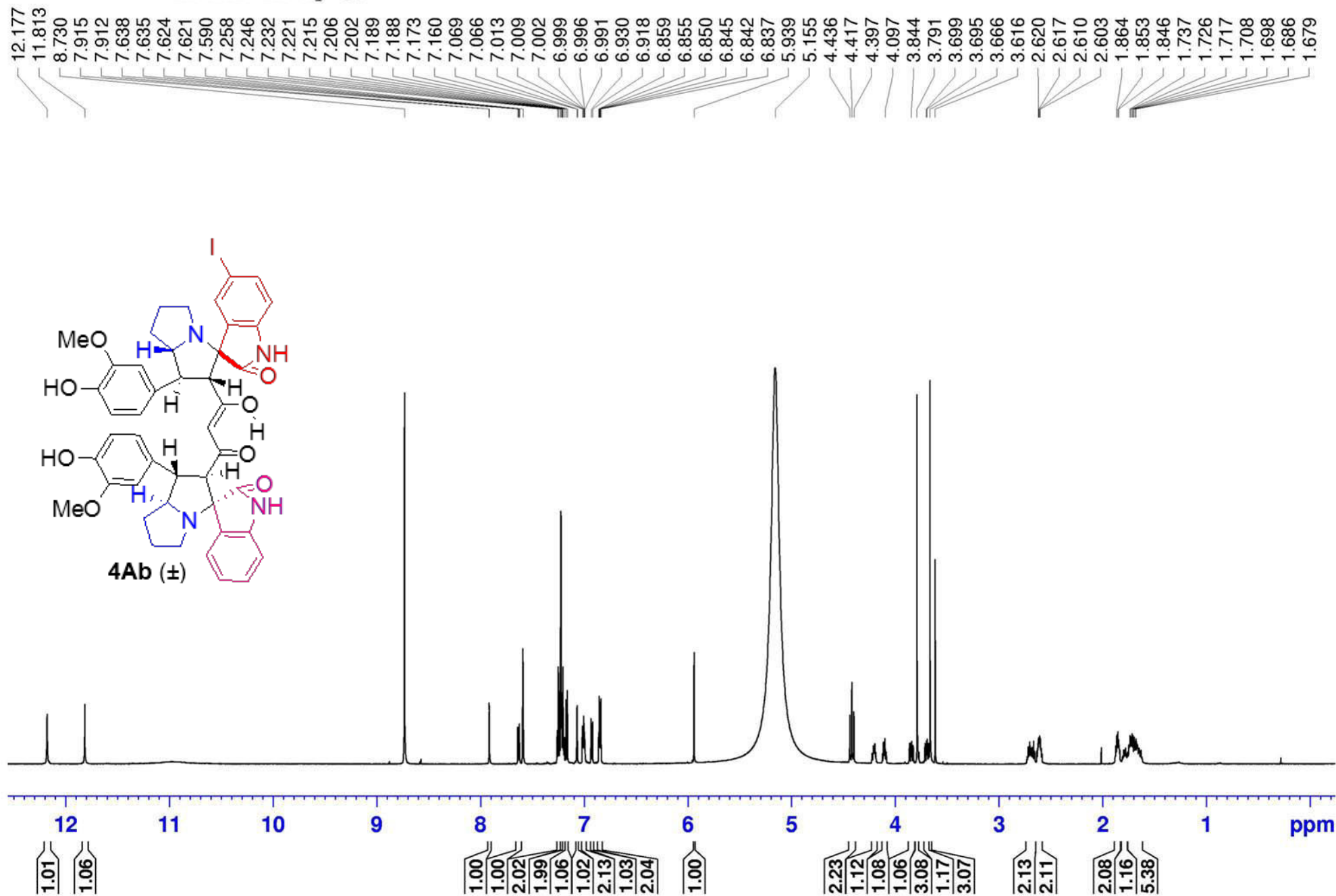
126.88
129.66

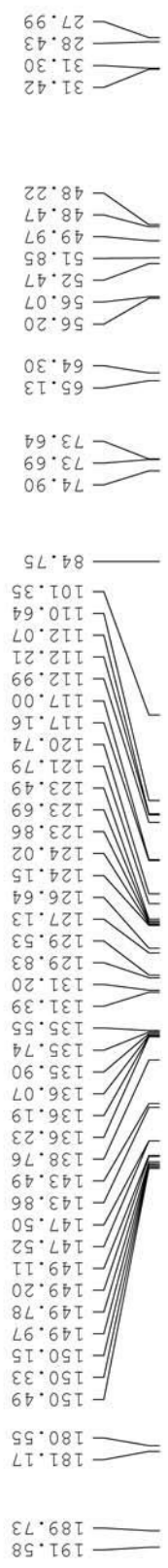
135.81
138.92

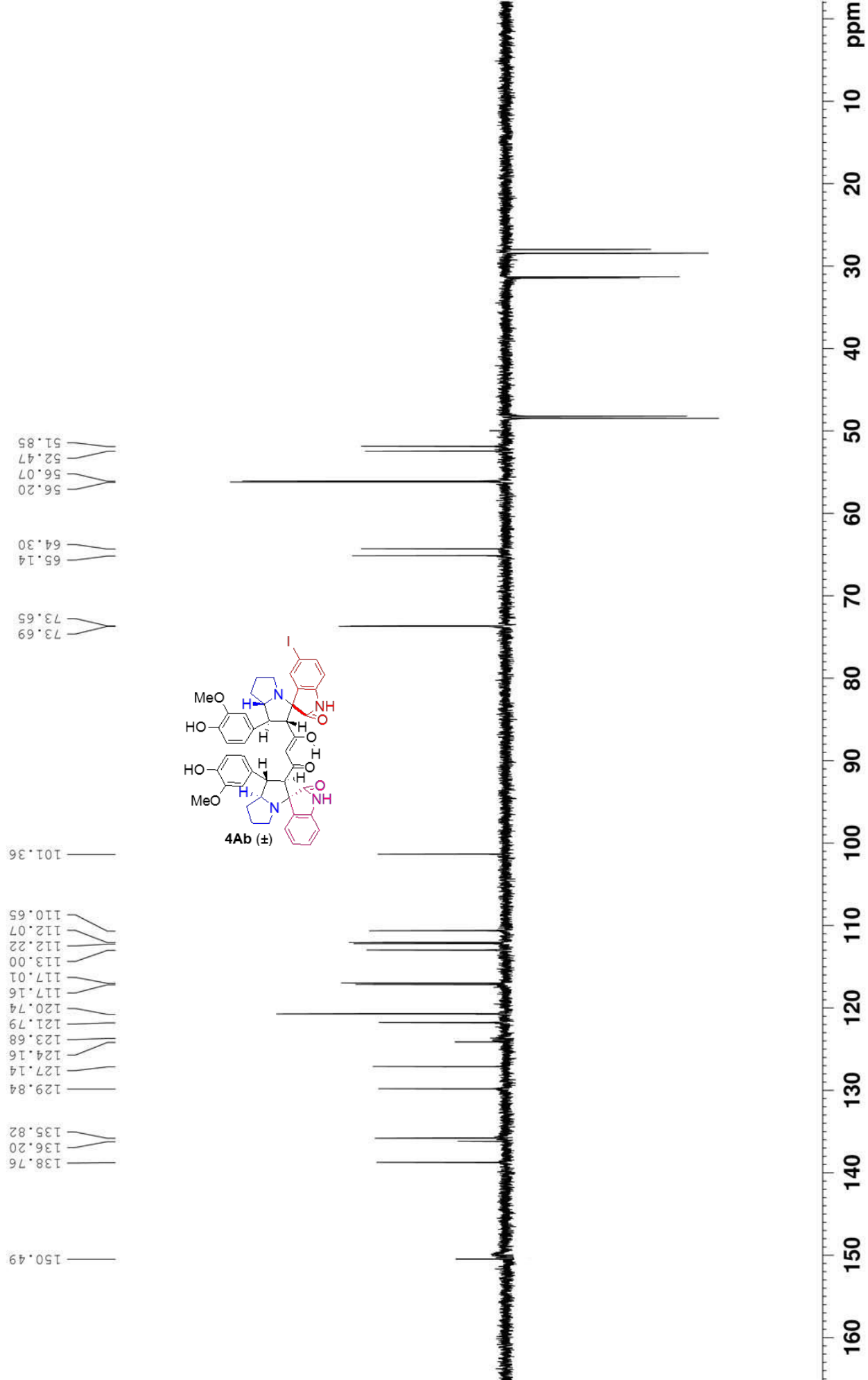
150.48

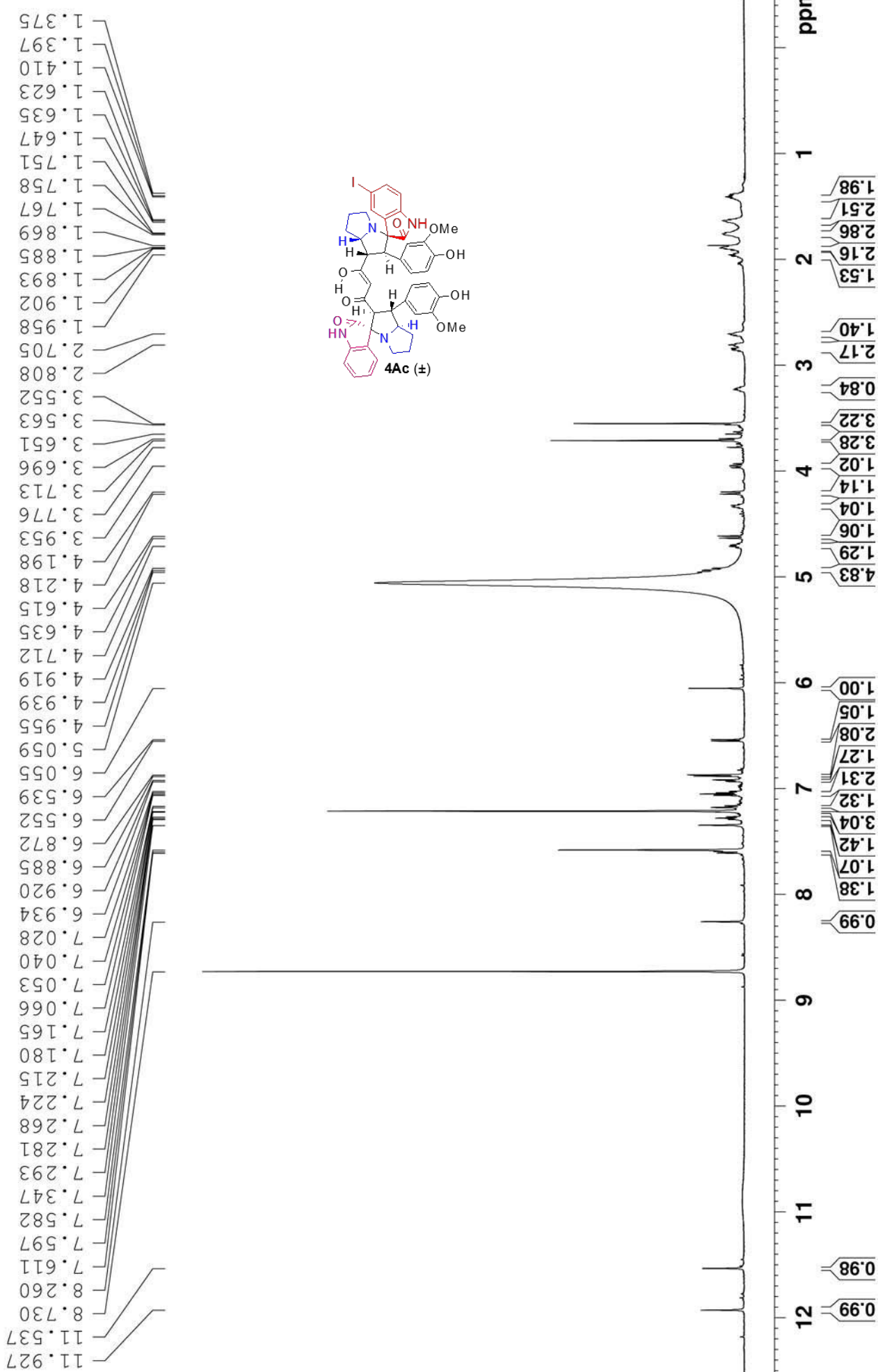
ppm

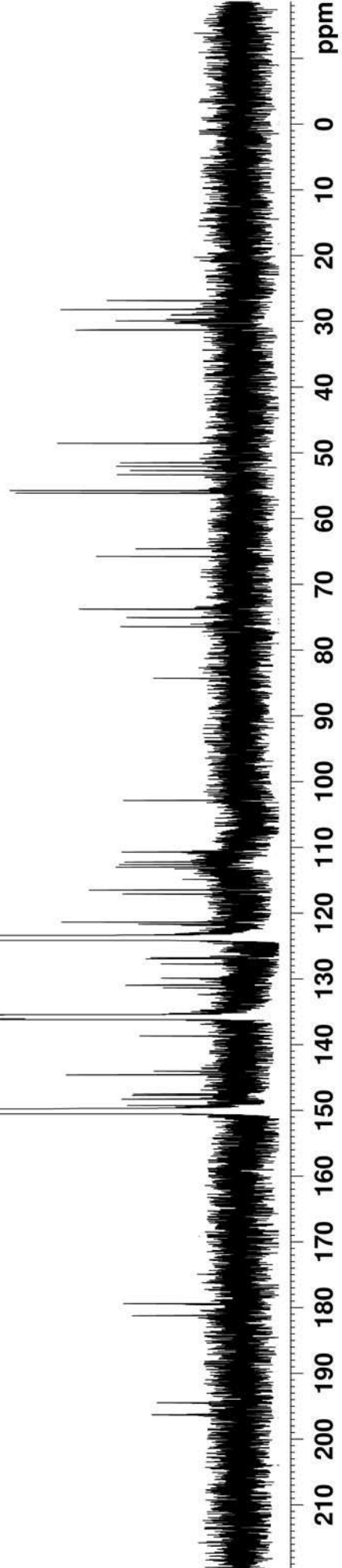
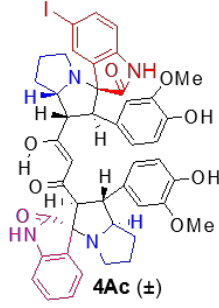
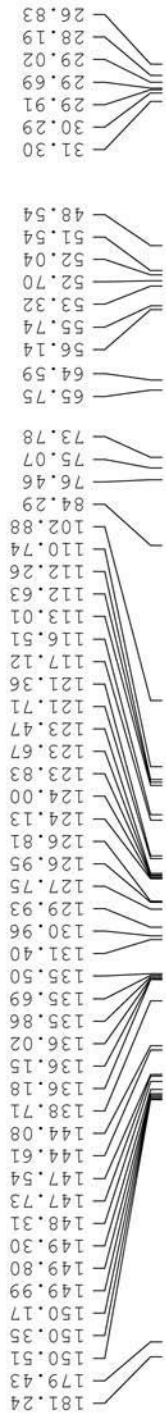
¹H NMR in Py-d₅

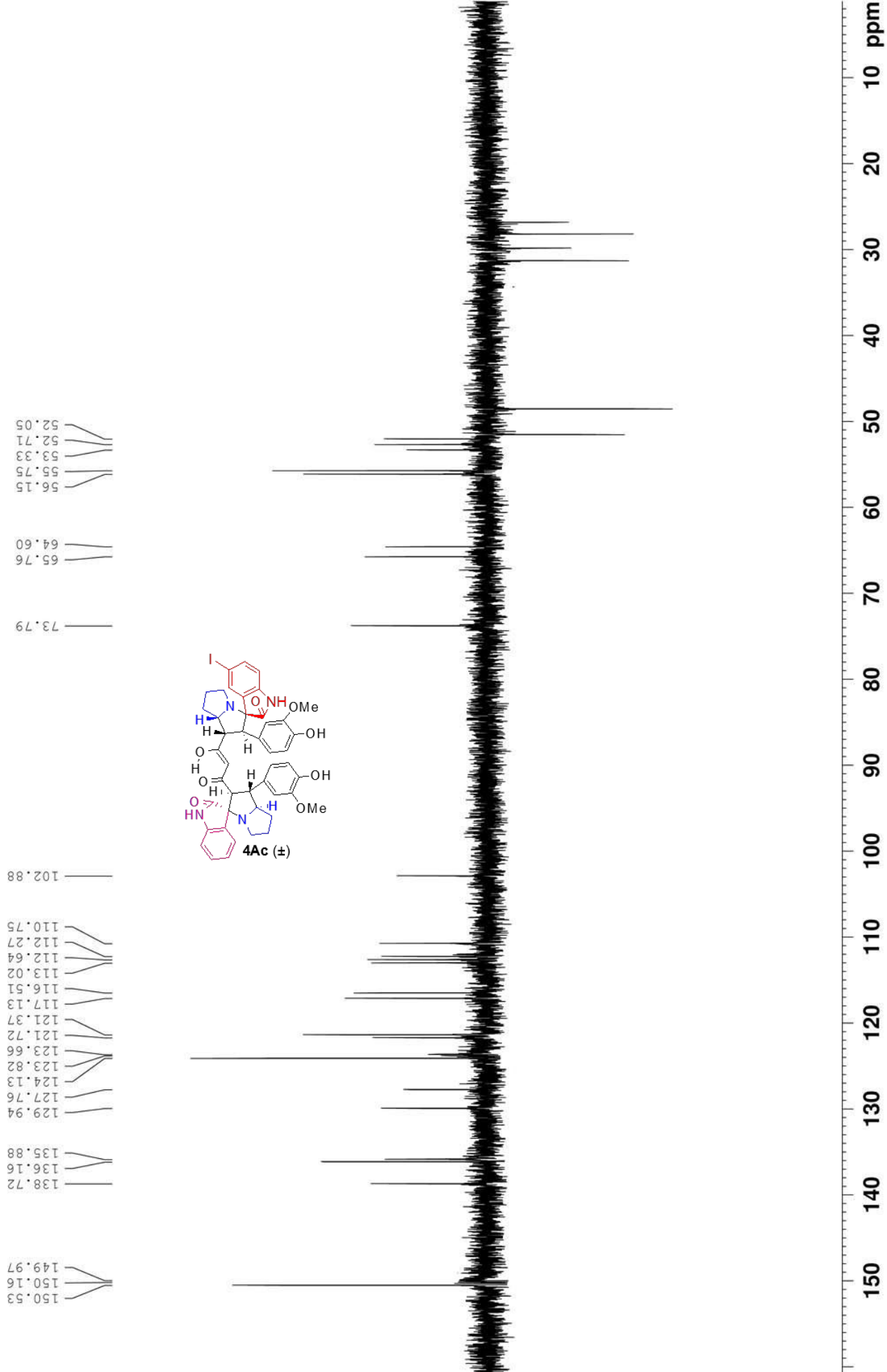




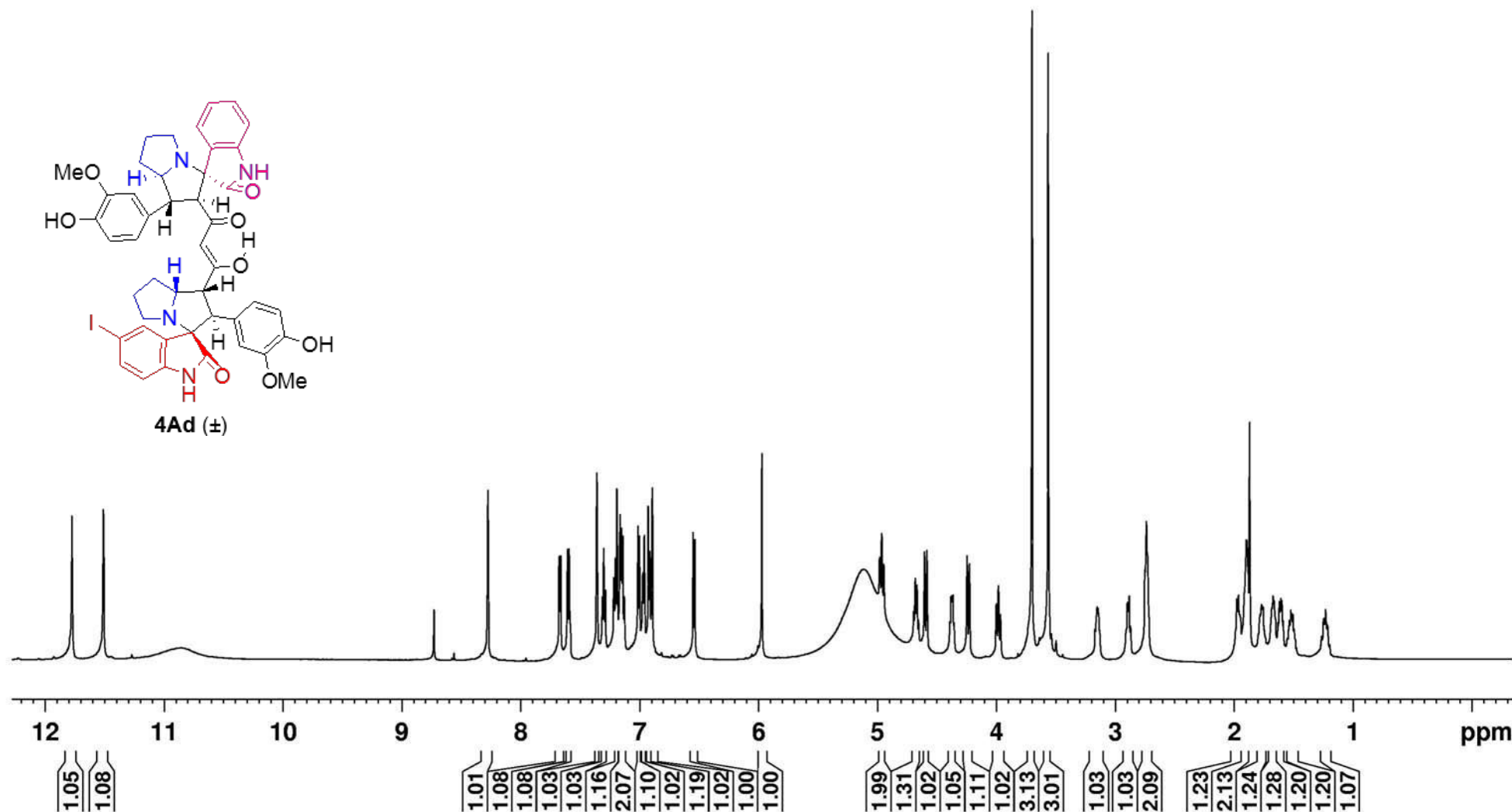
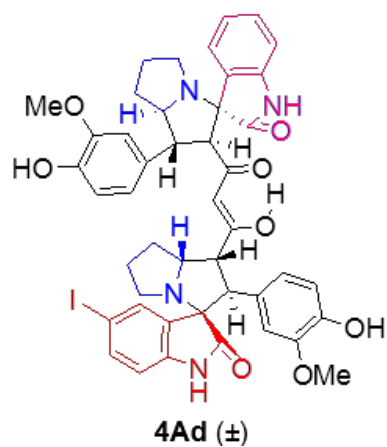
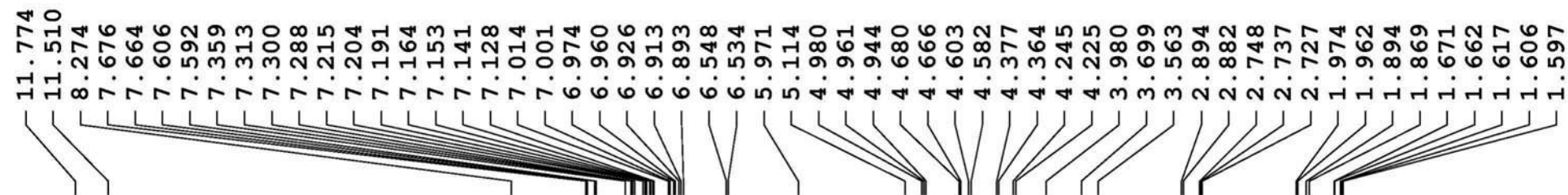


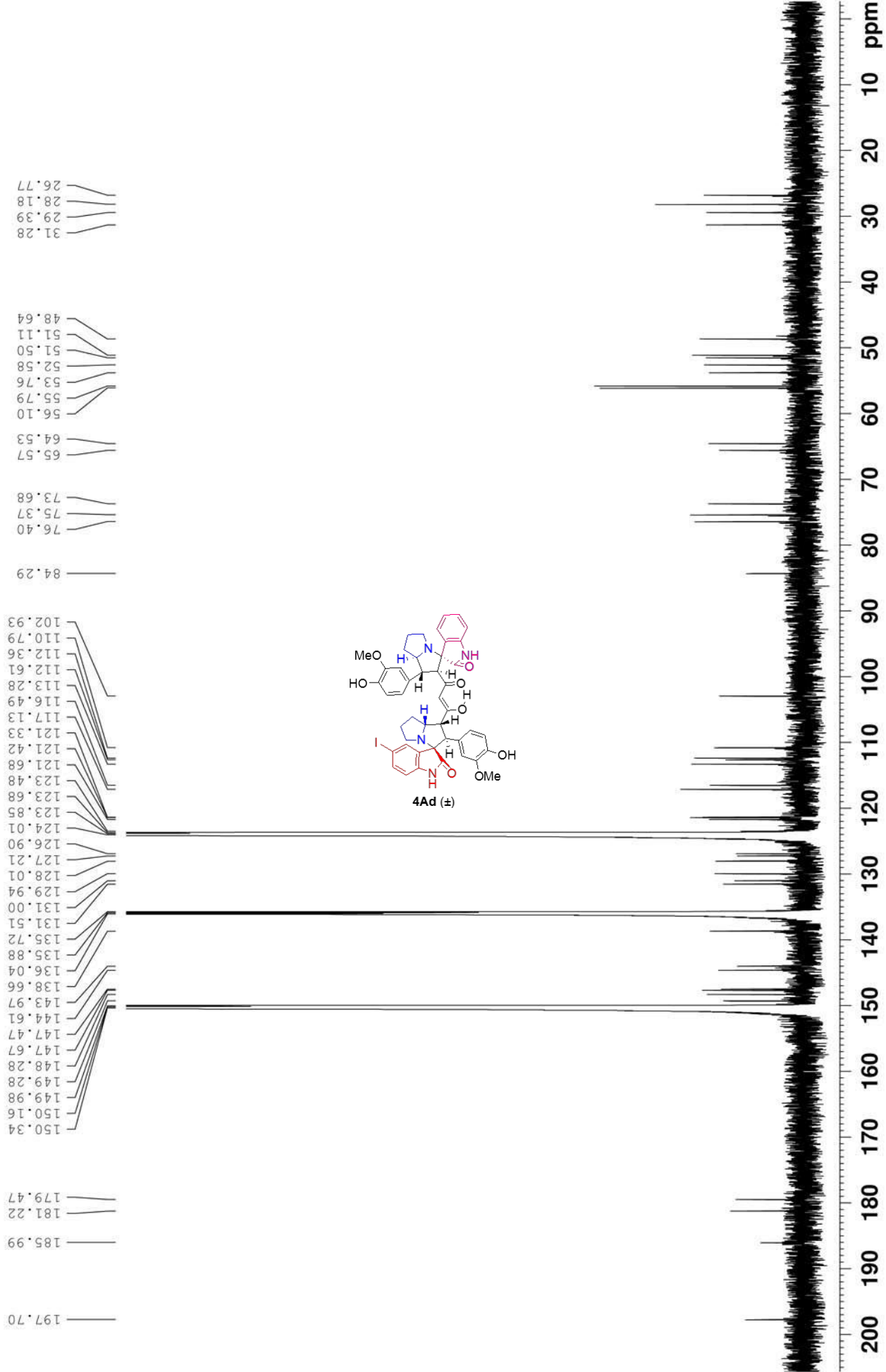


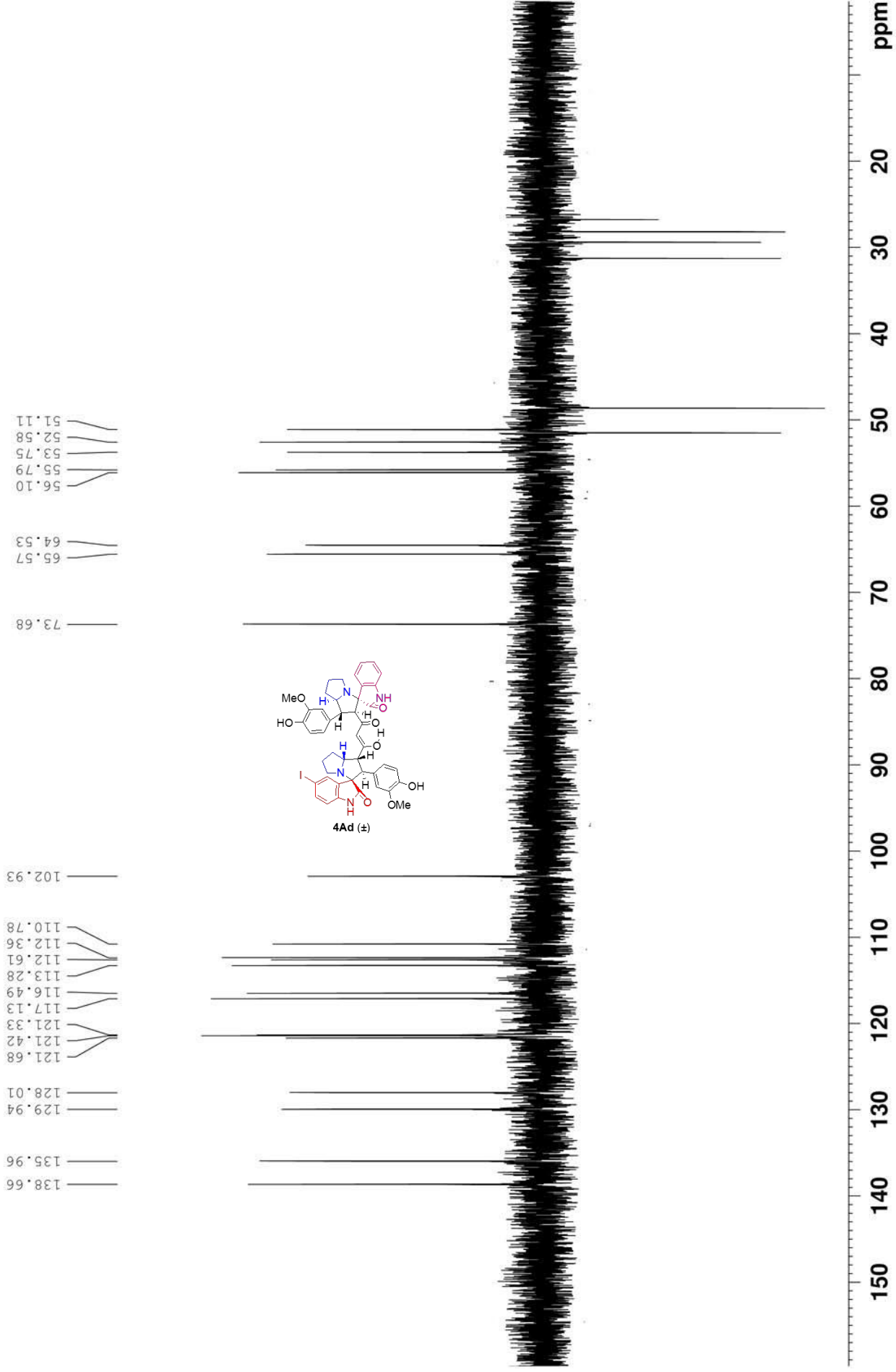


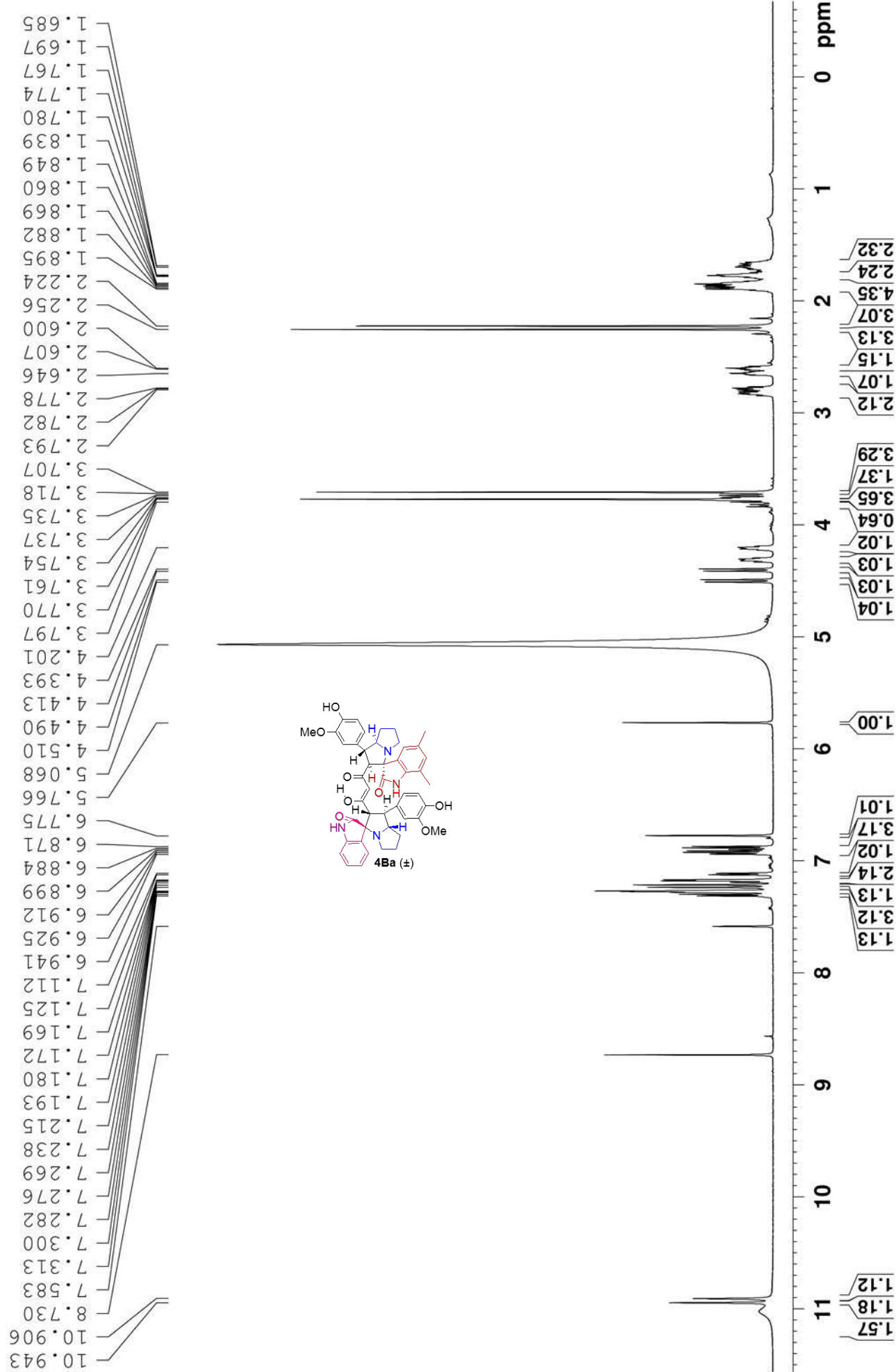


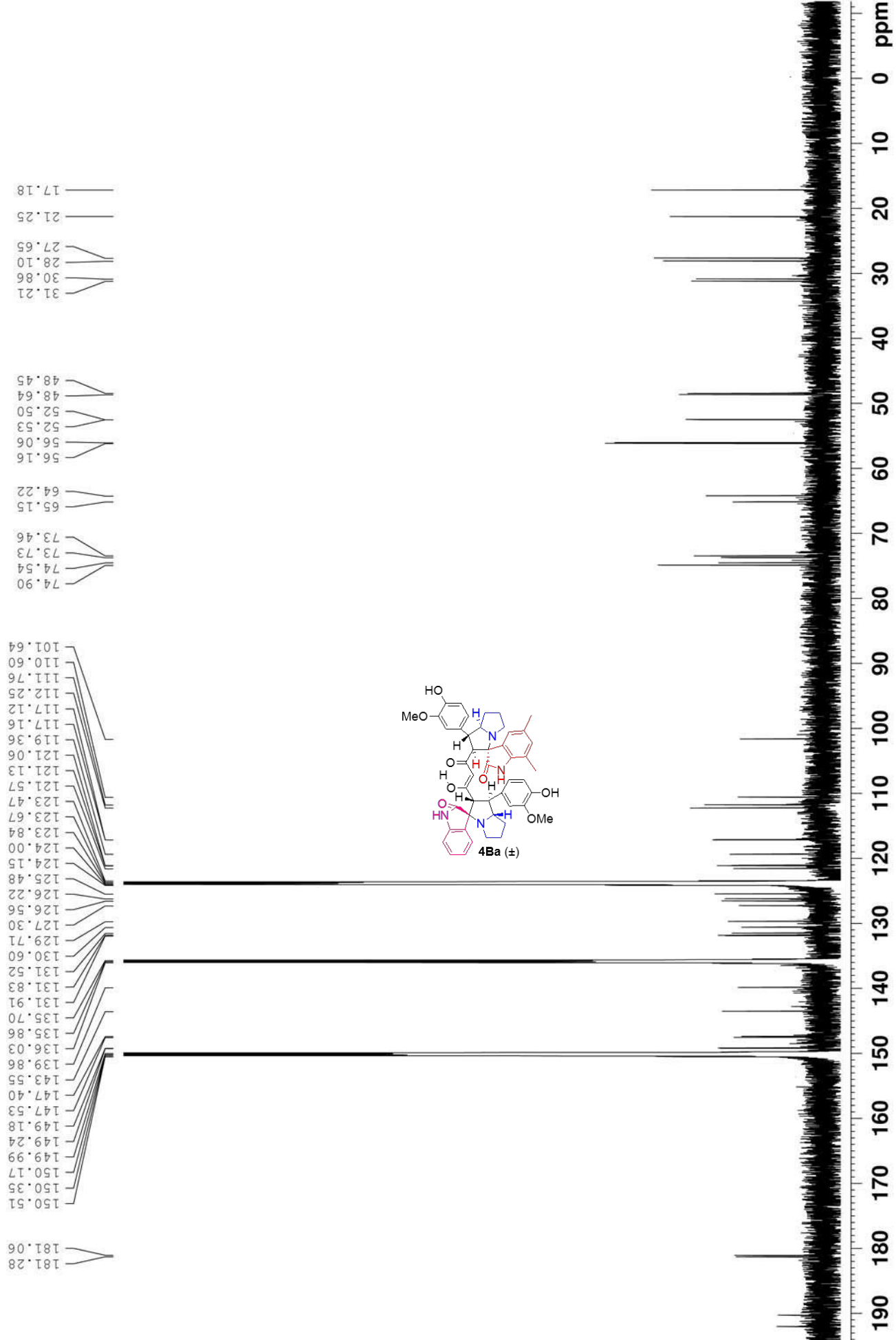
¹H NMR in Py-d₅



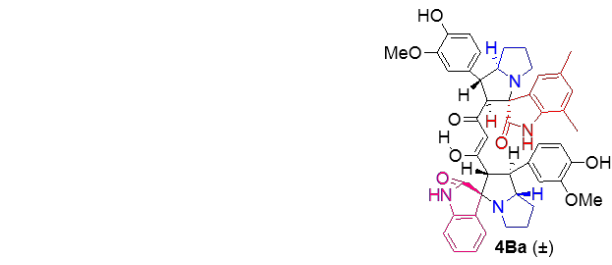




¹H NMR in Py-d5



DEPT-135

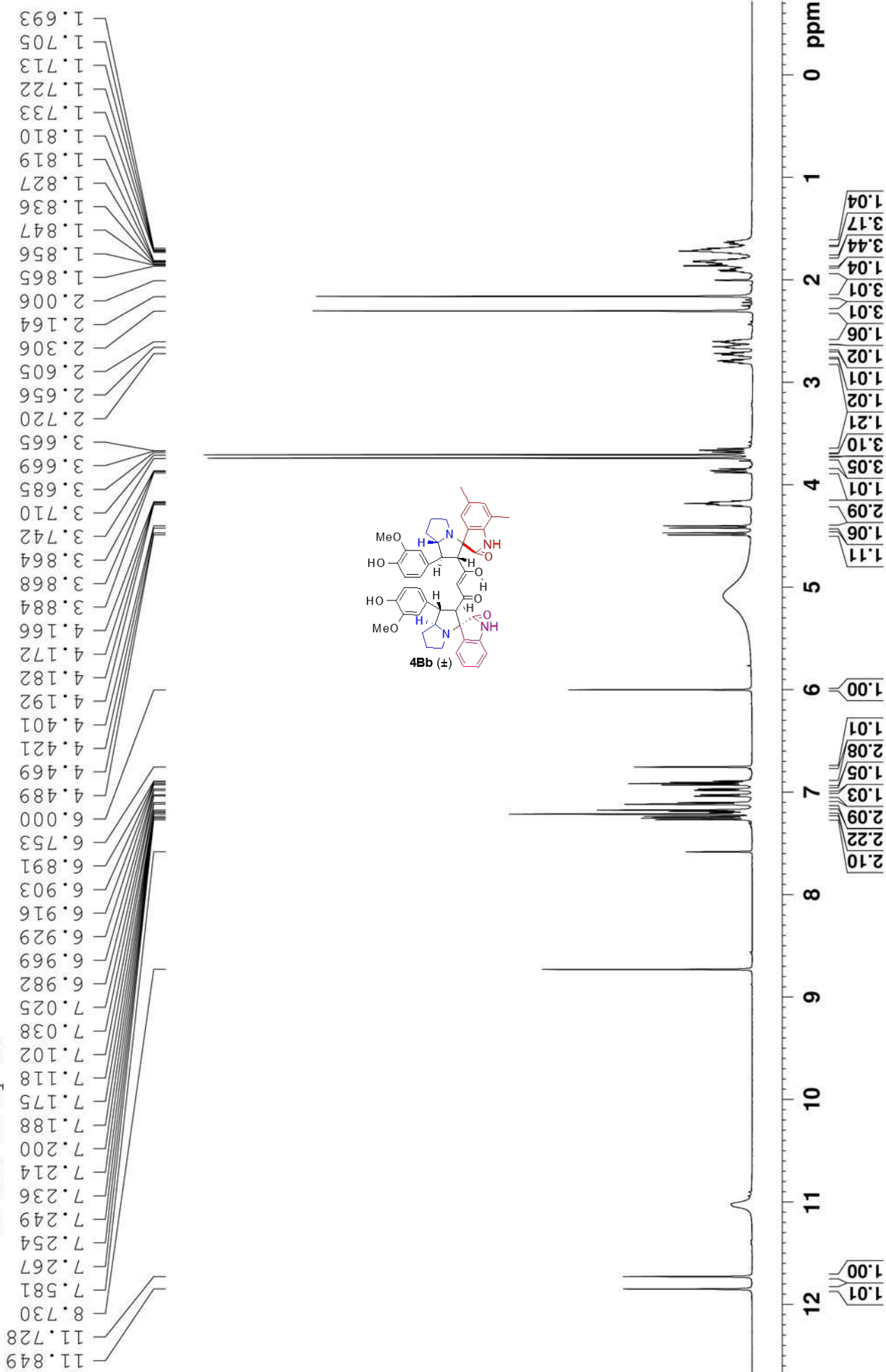


131.91
129.71
127.30
125.48
124.13
121.57
121.13
121.07
117.16
117.12
112.25
111.76
110.60

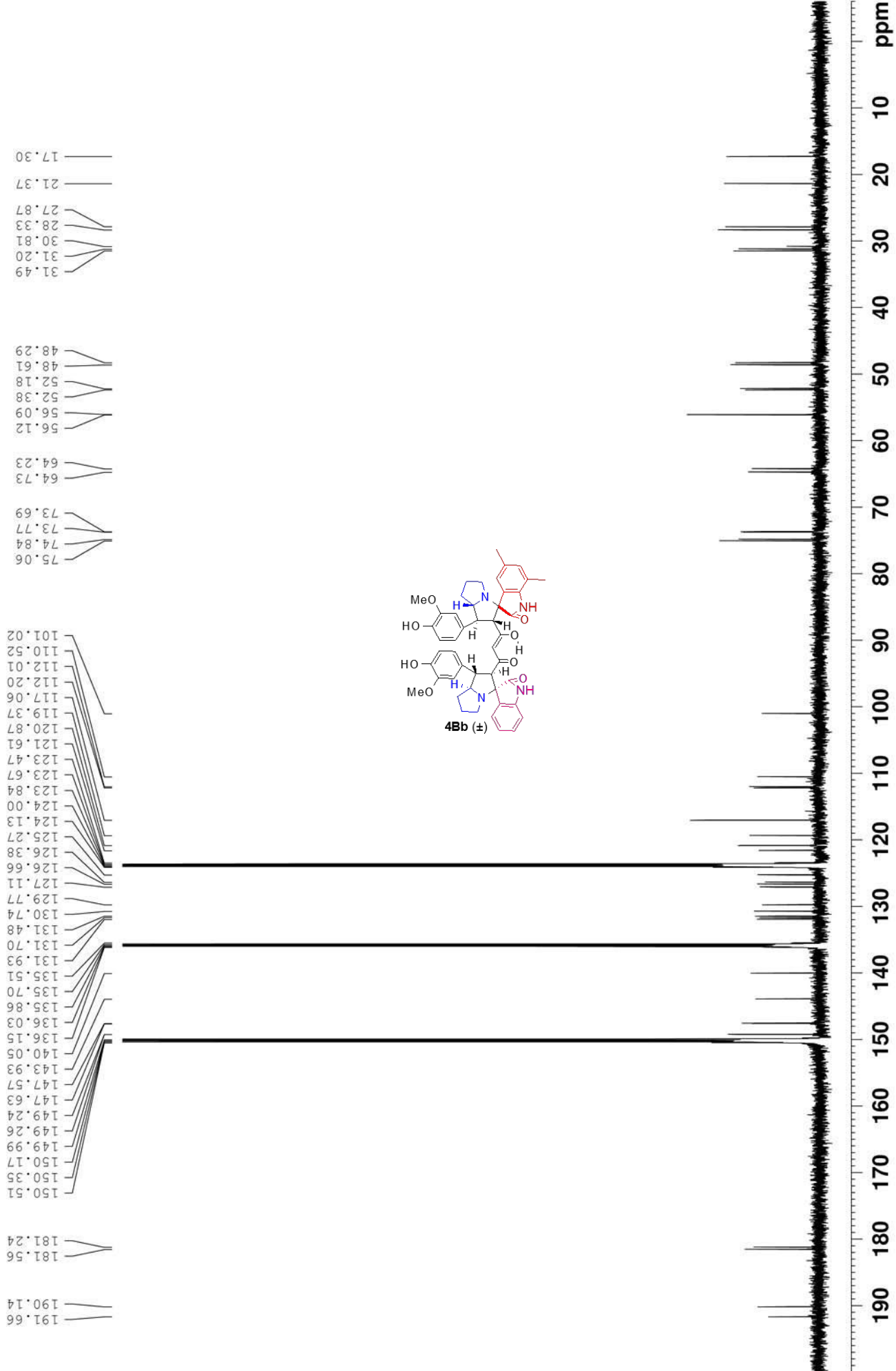
73.74
73.46
65.15
64.22
56.17
56.06
52.53
52.50
21.25
17.18

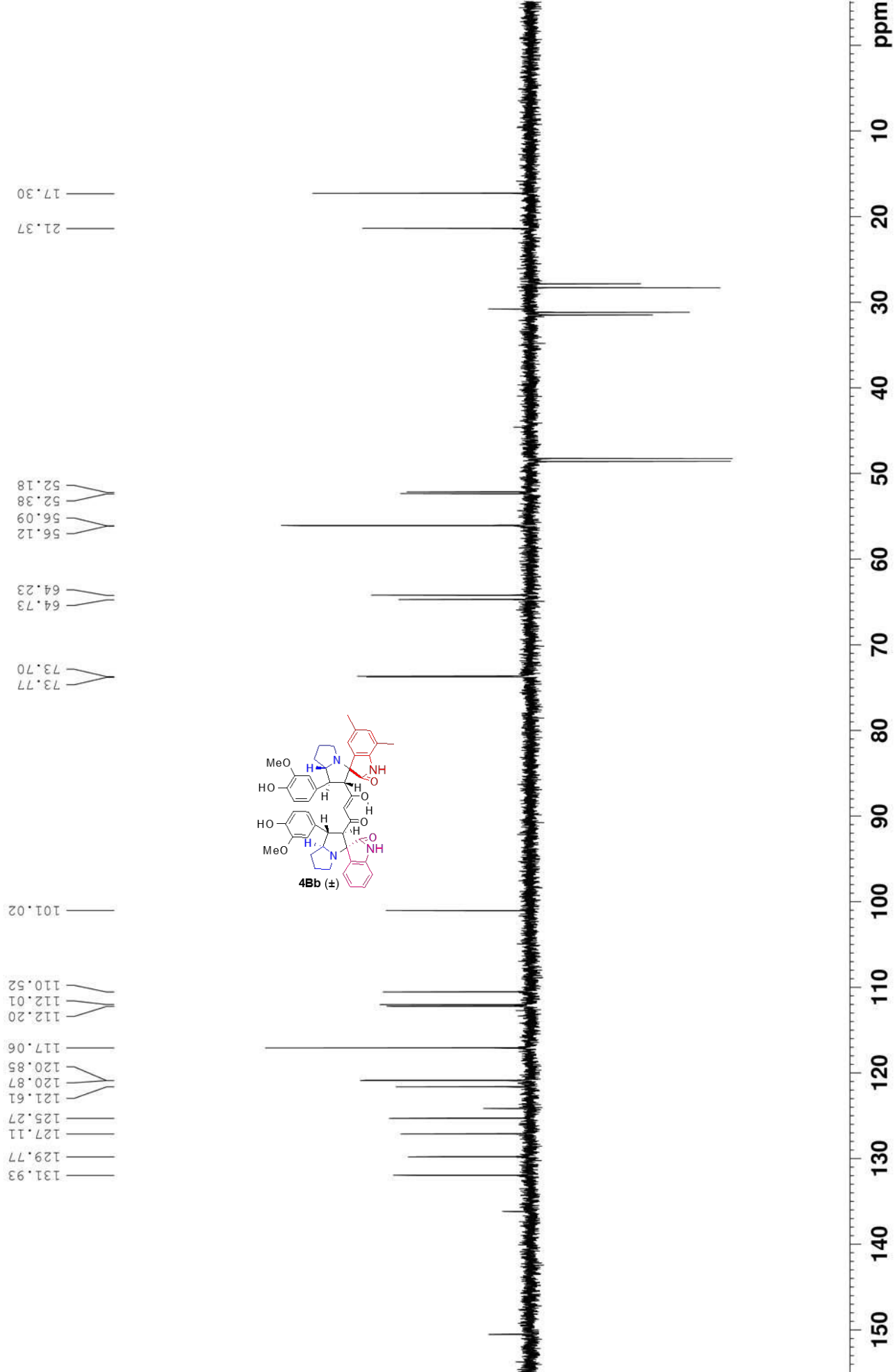
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

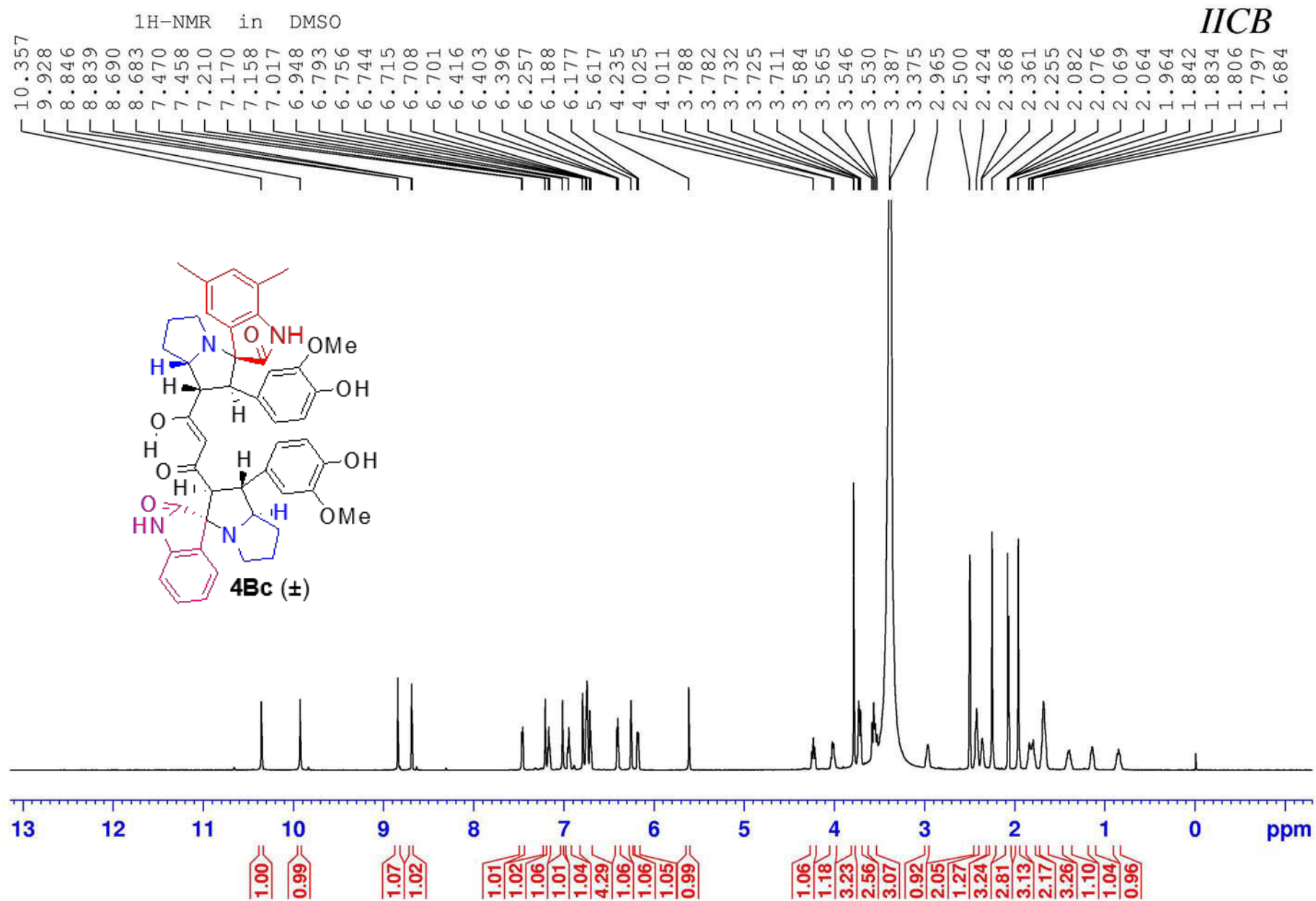
¹H NMR in Py-d5



¹³C-NMR in Py-d5

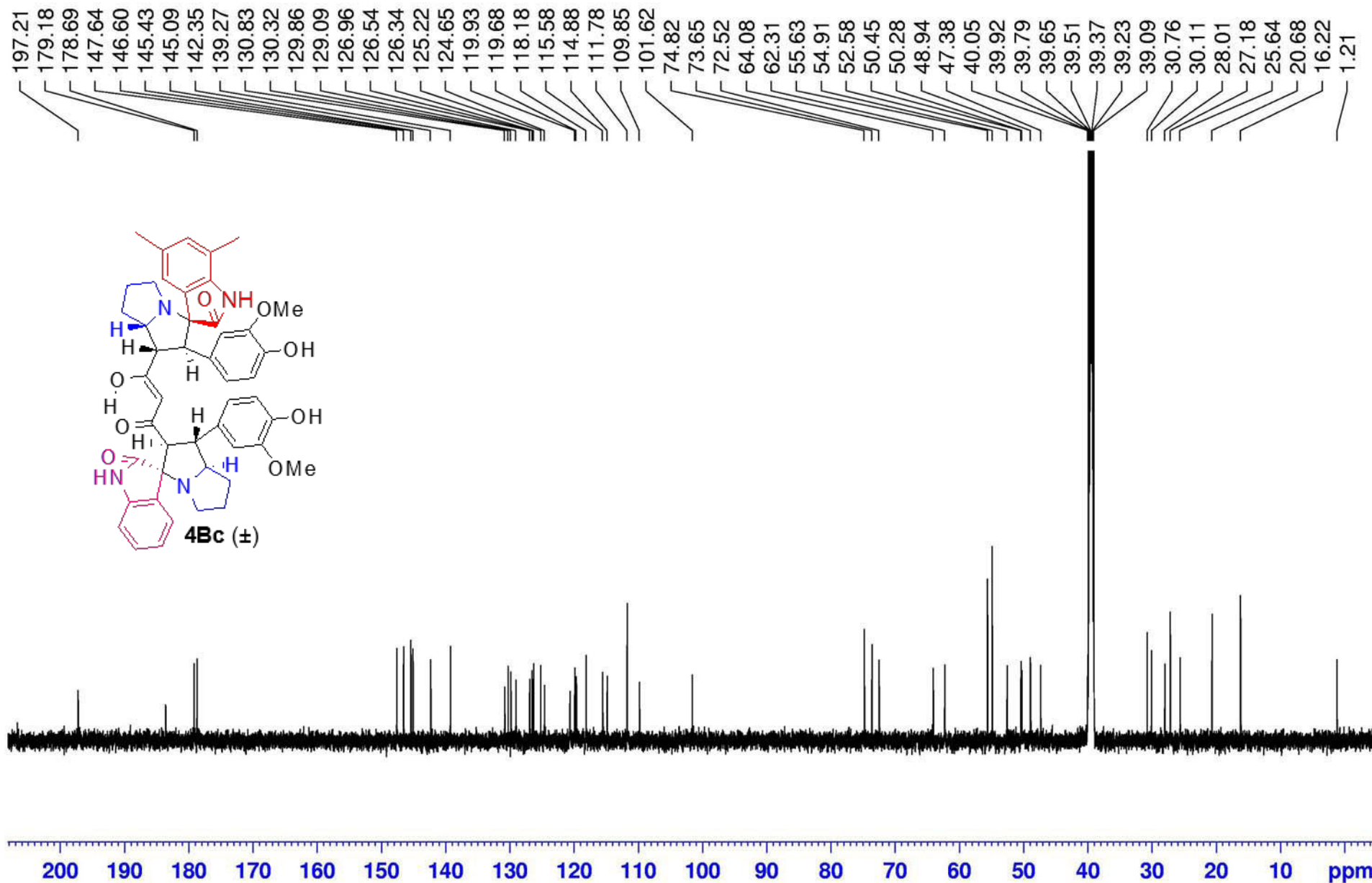






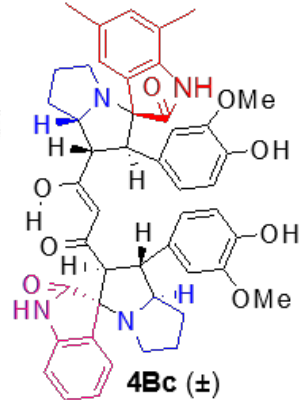
^{13}C -NMR in DMSO

HCB



DEPT-90

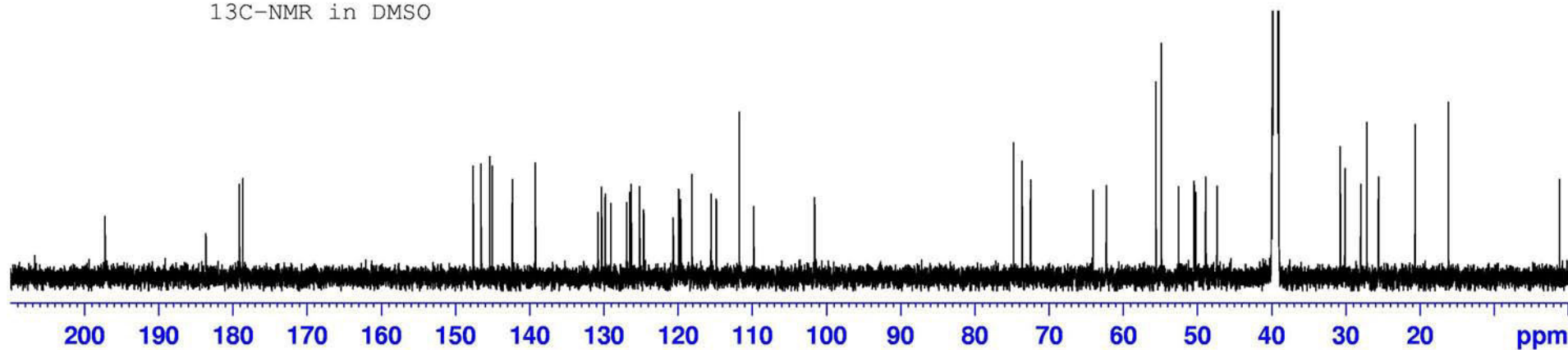
IICB



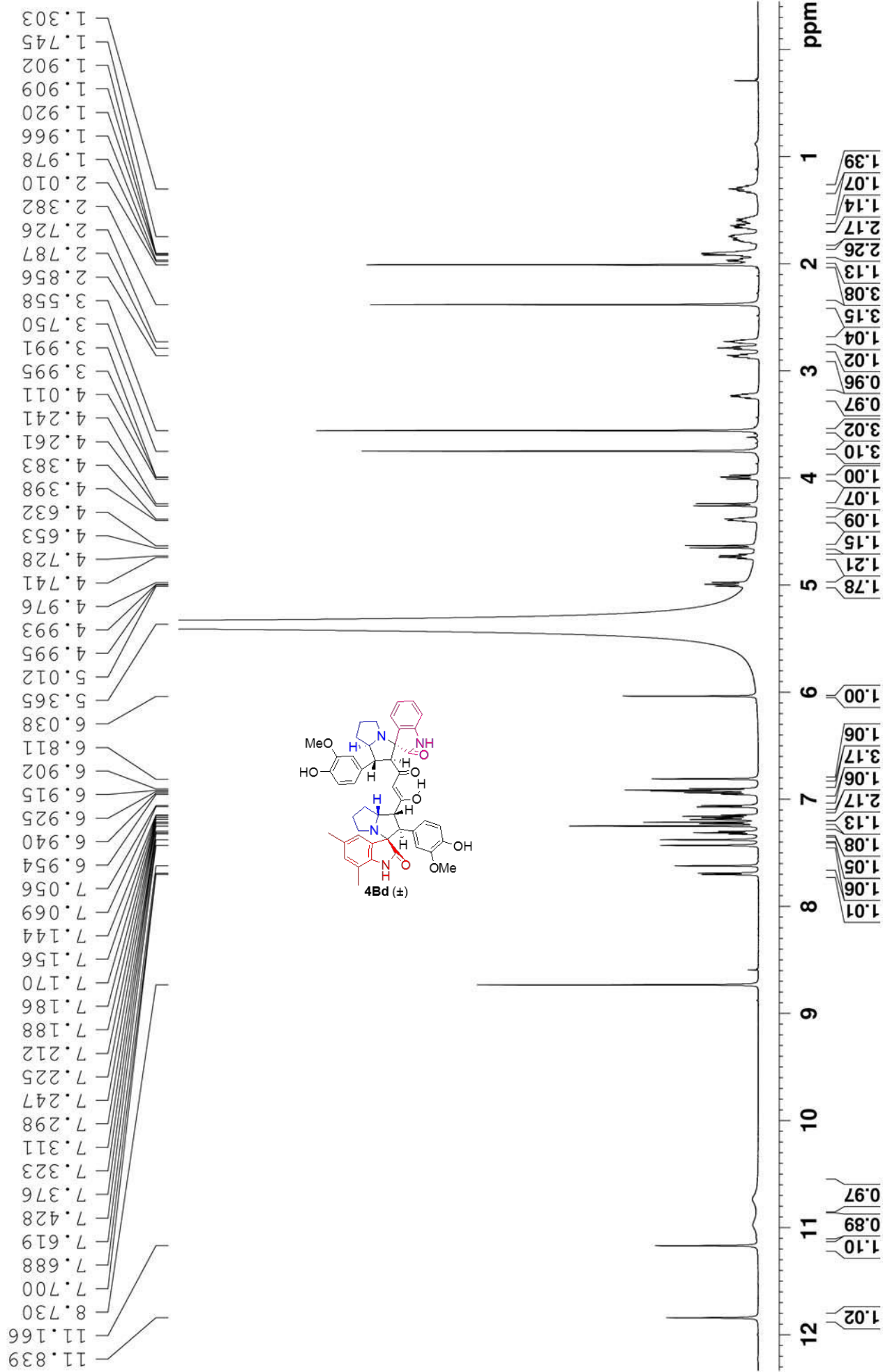
4Bc (±)

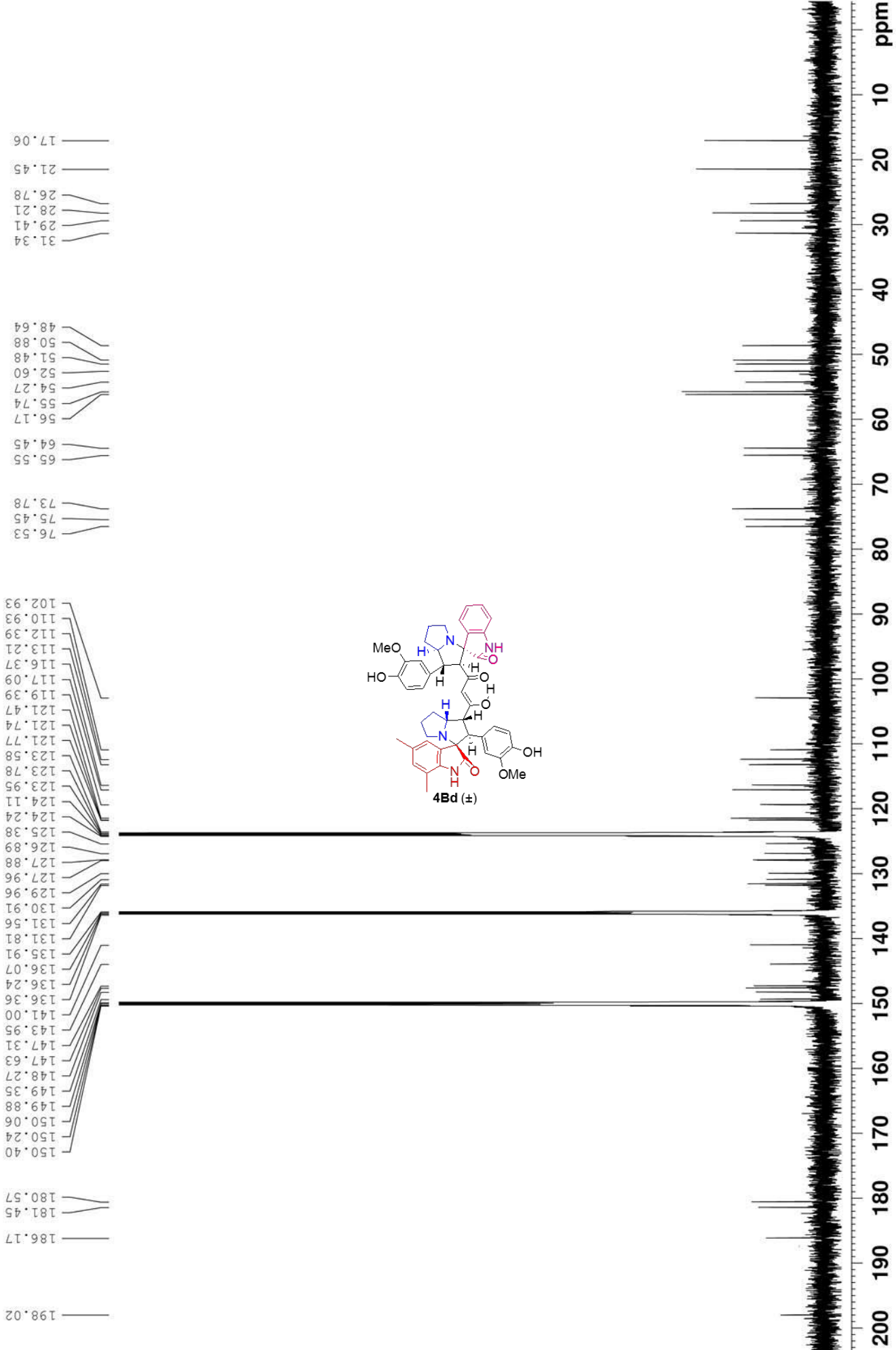
DEPT-135

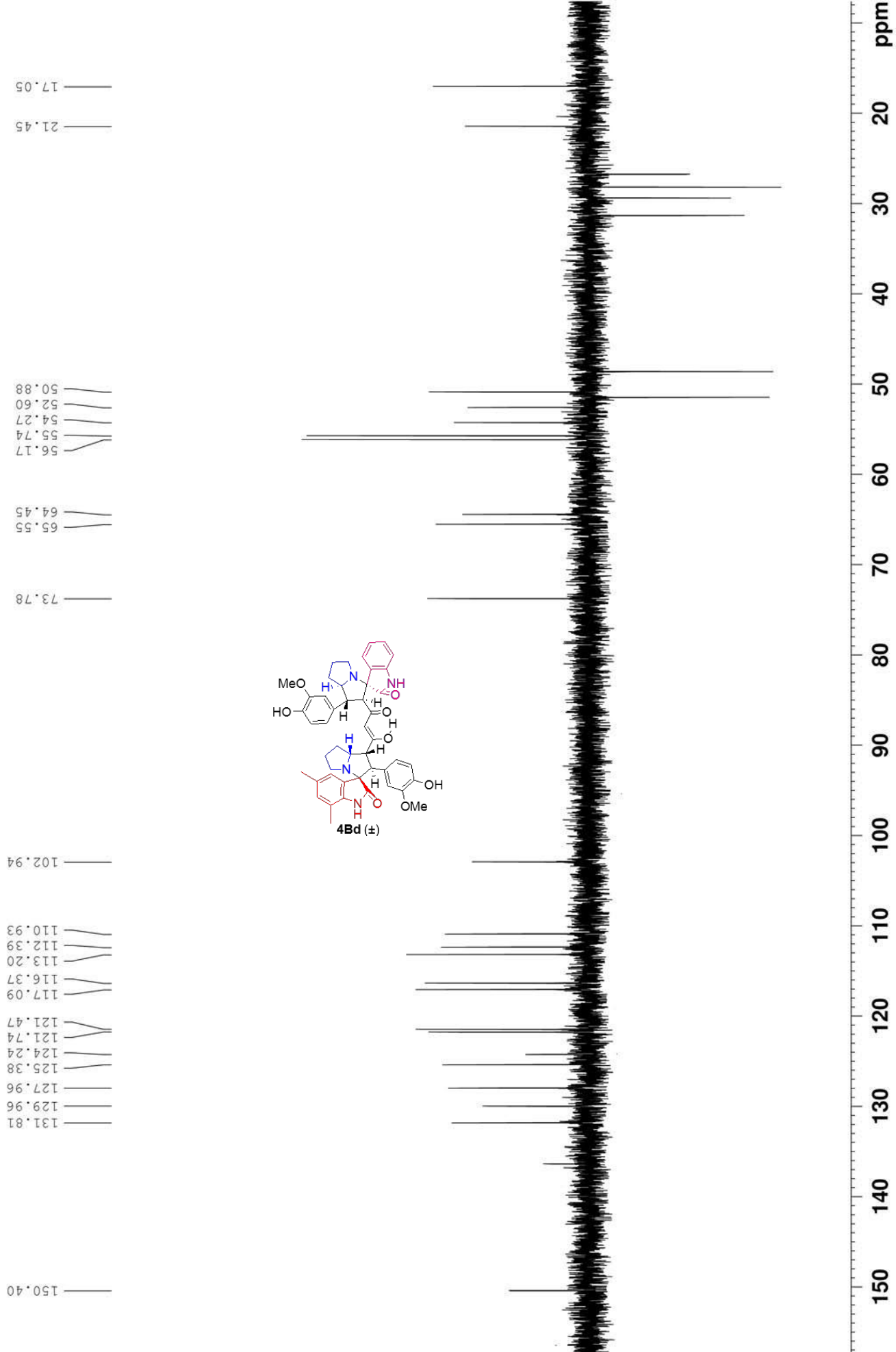
¹³C-NMR in DMSO

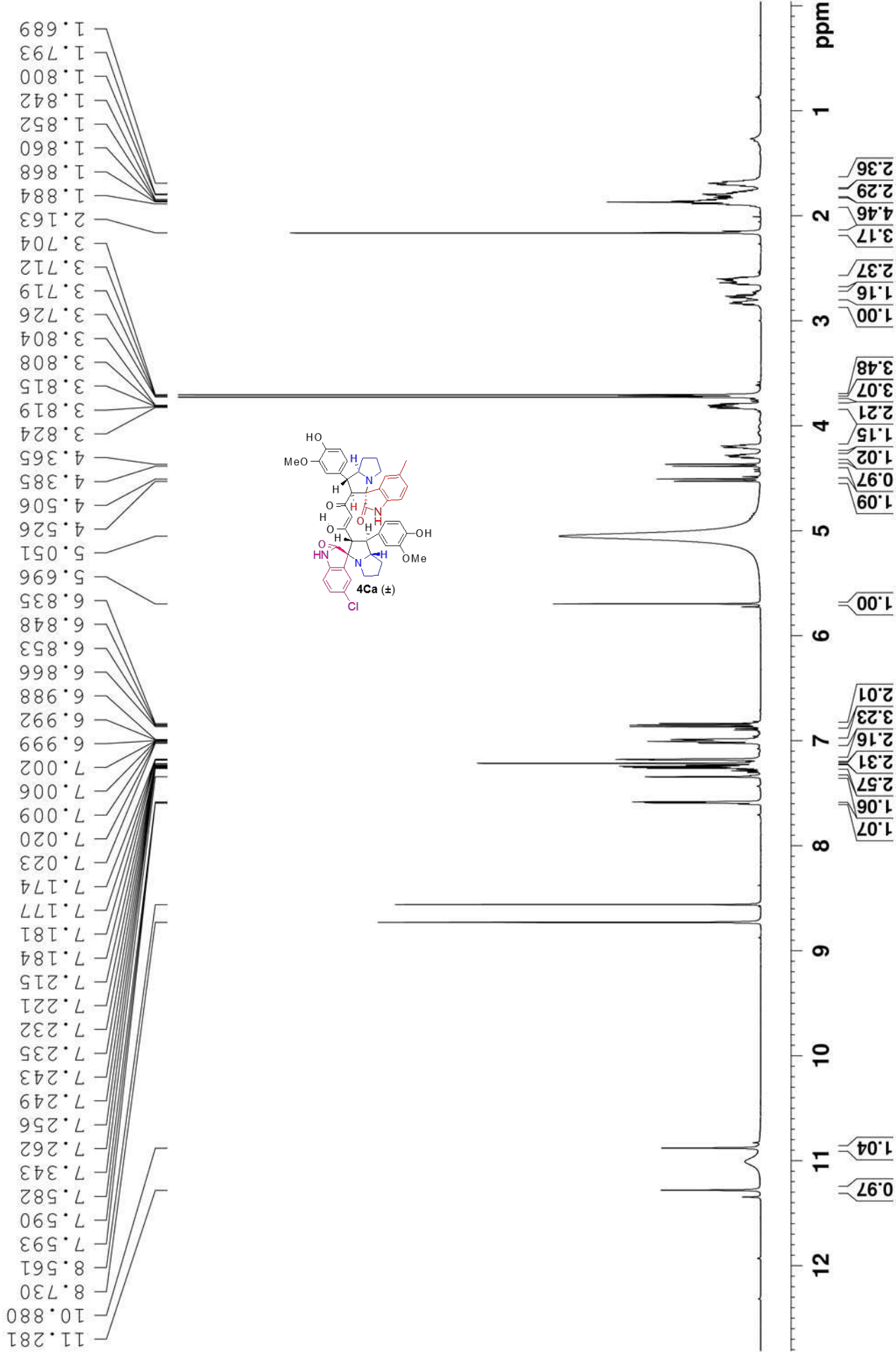


¹H NMR in Py-d5

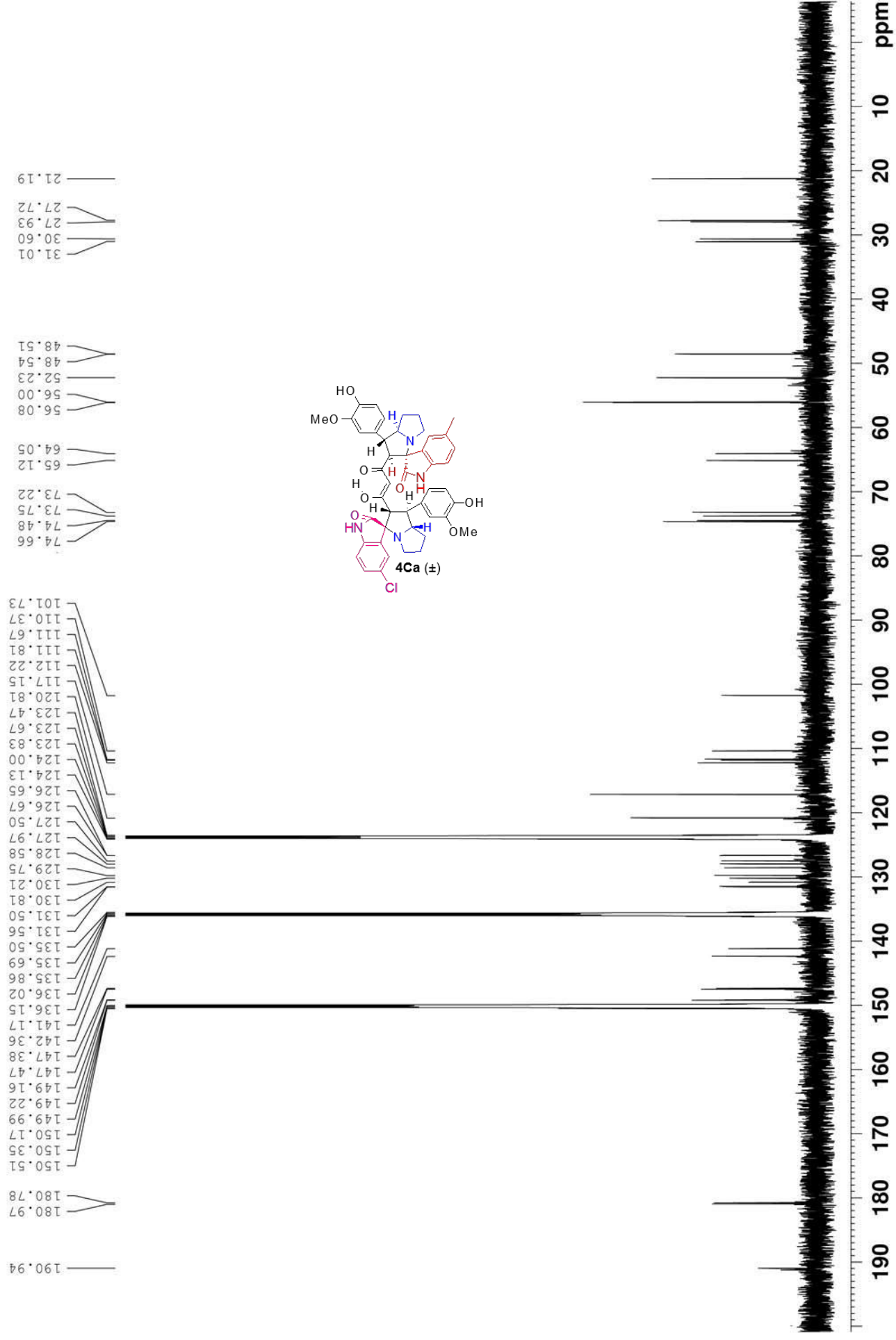




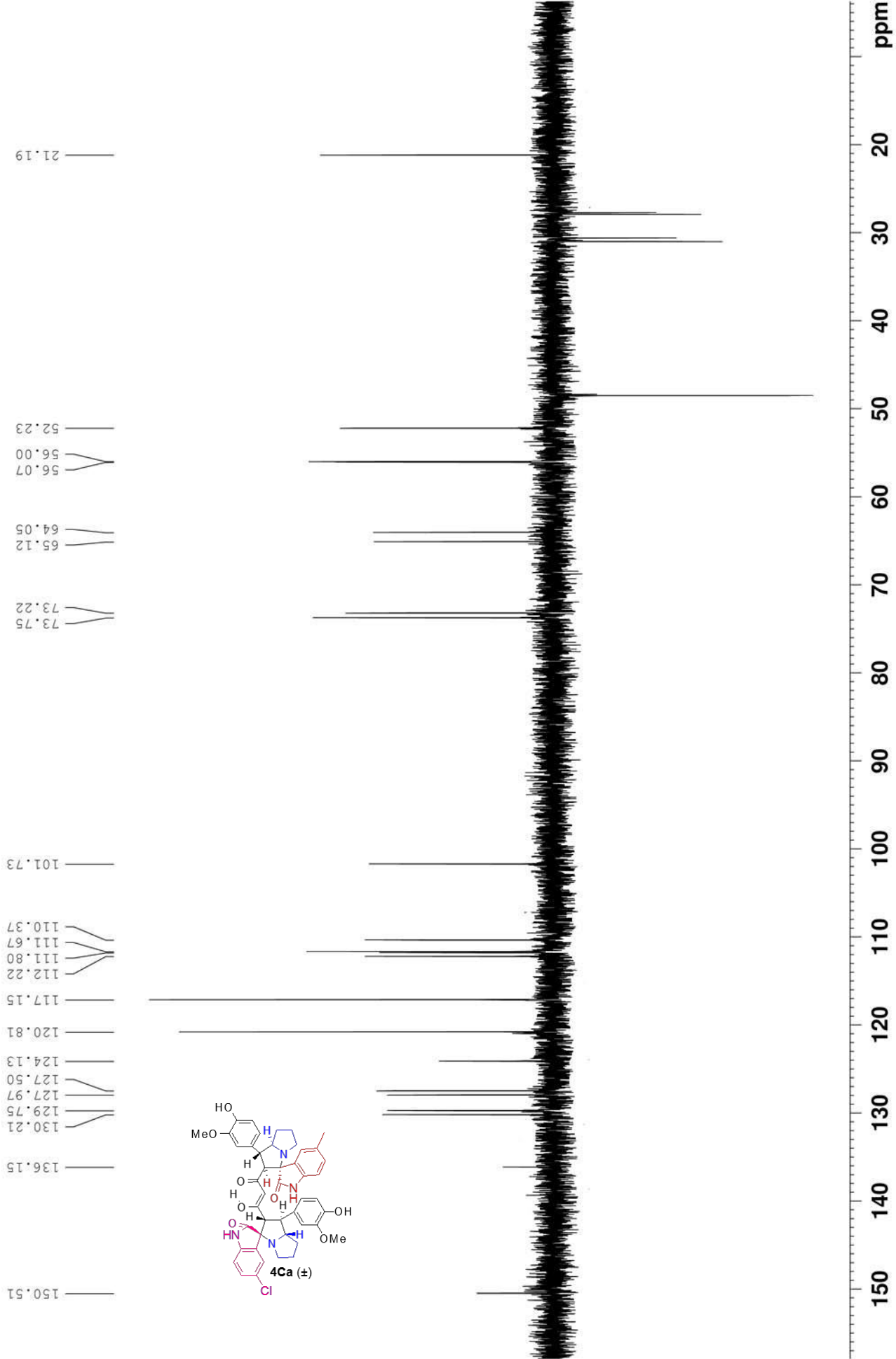


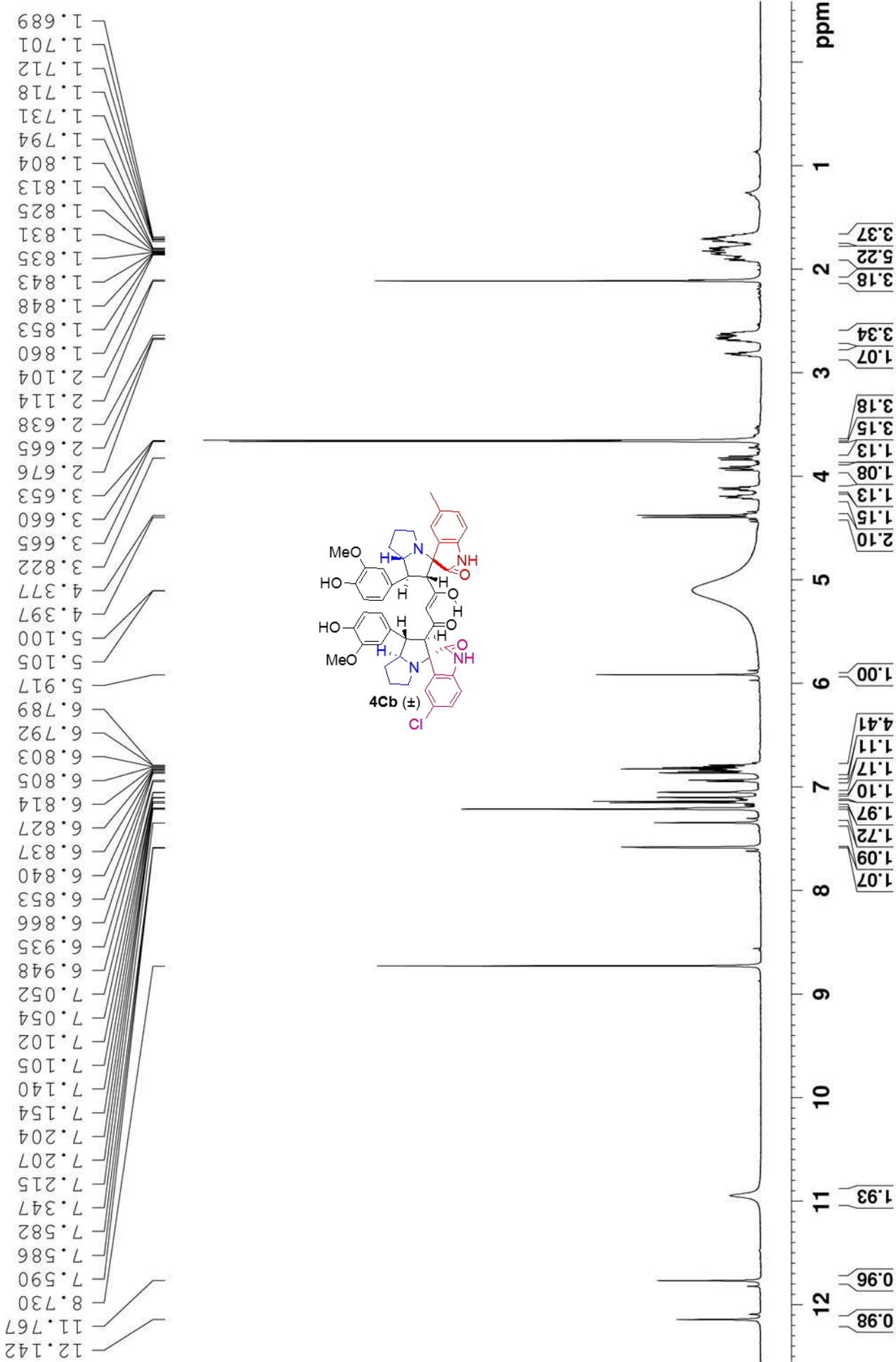


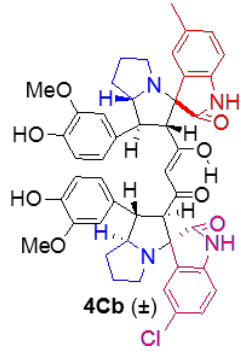
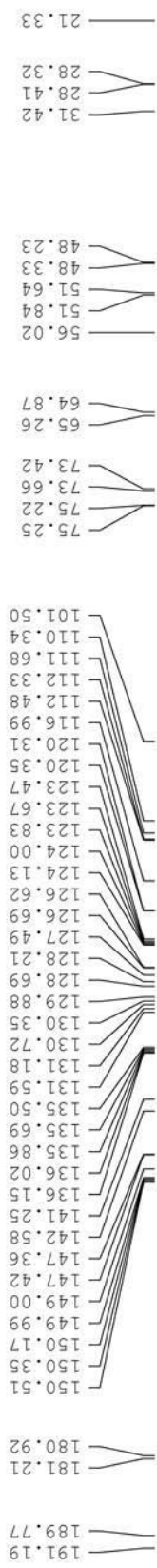
¹³C-NMR in Py-d5



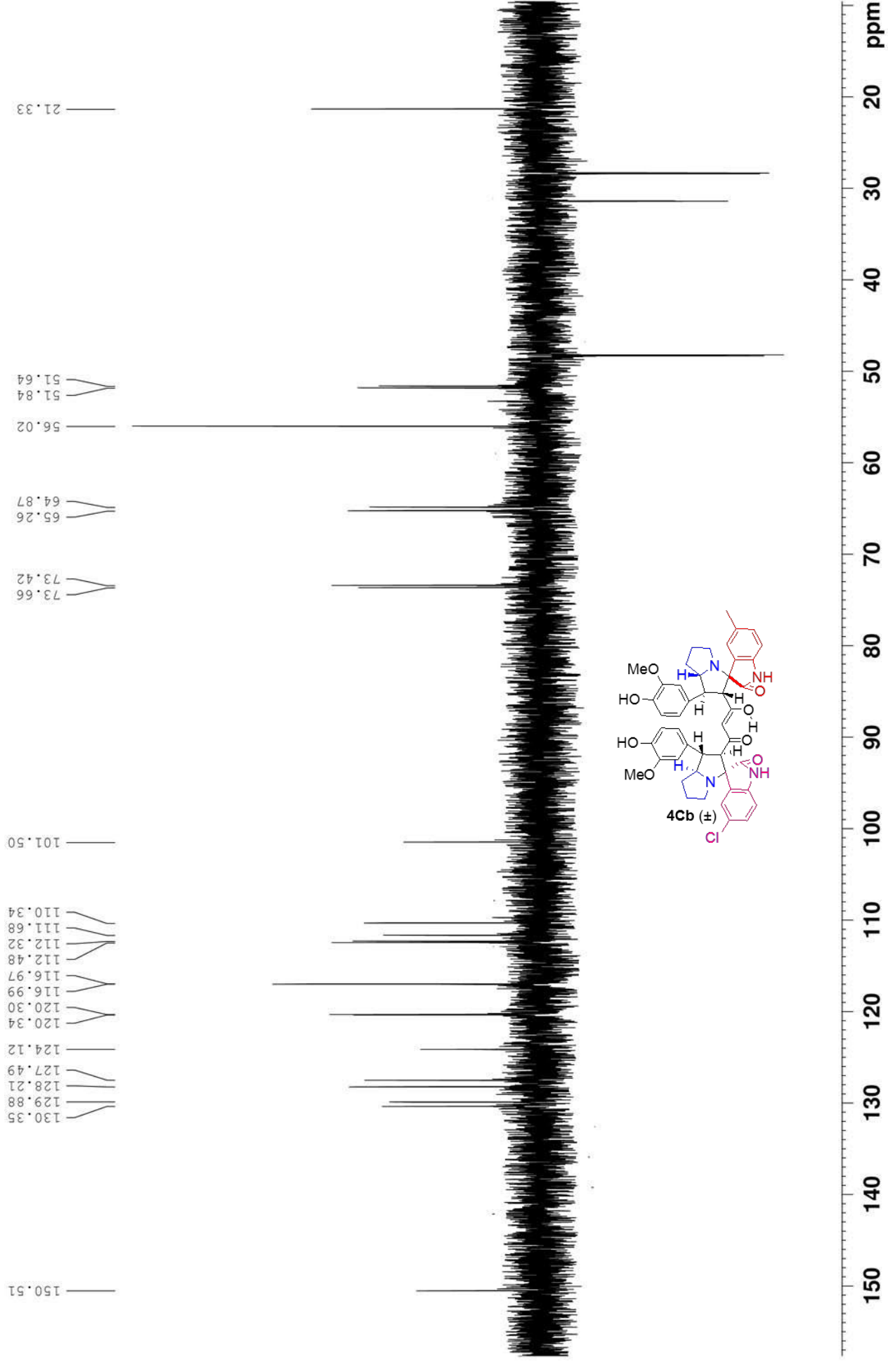
DEPT-135

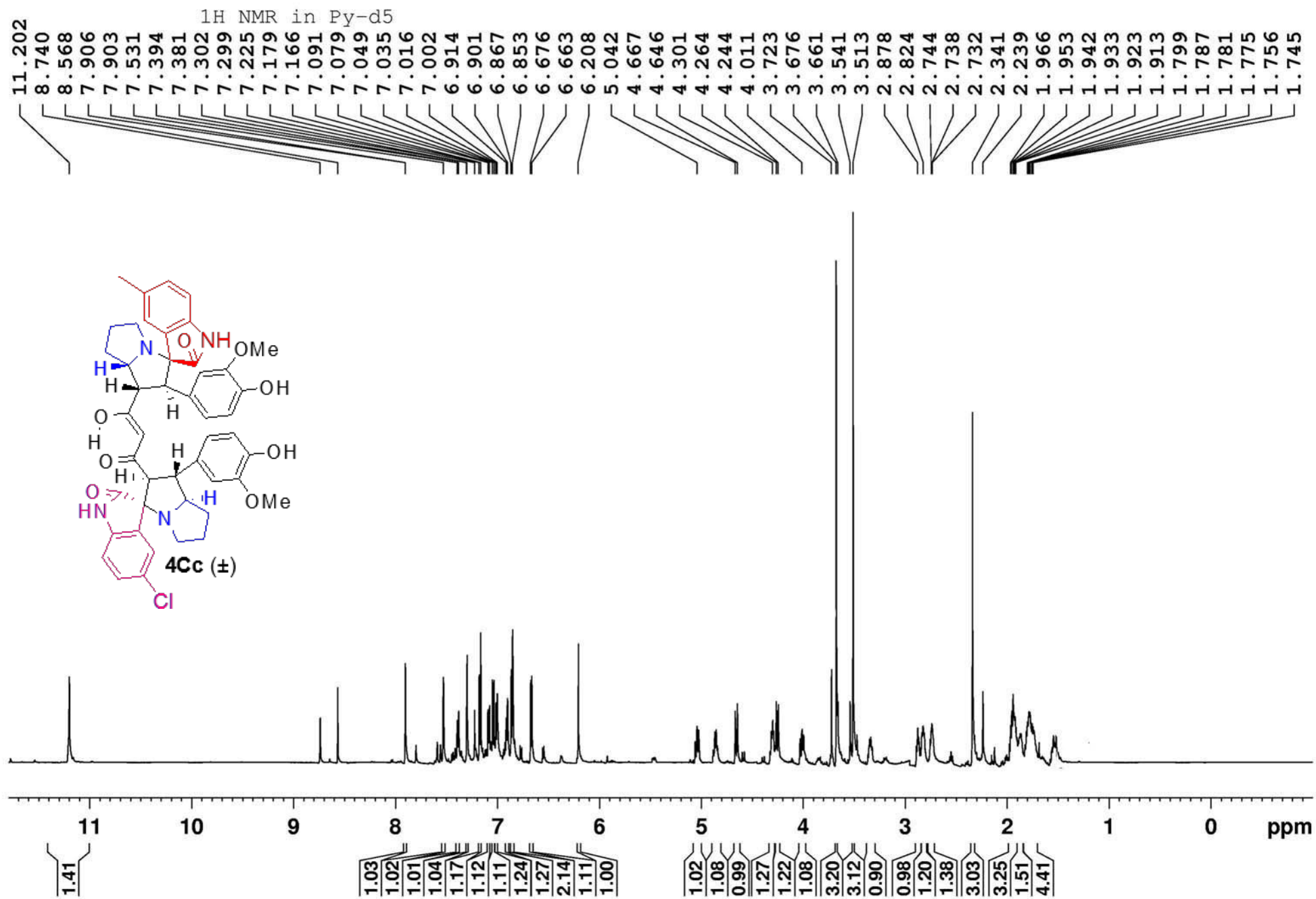


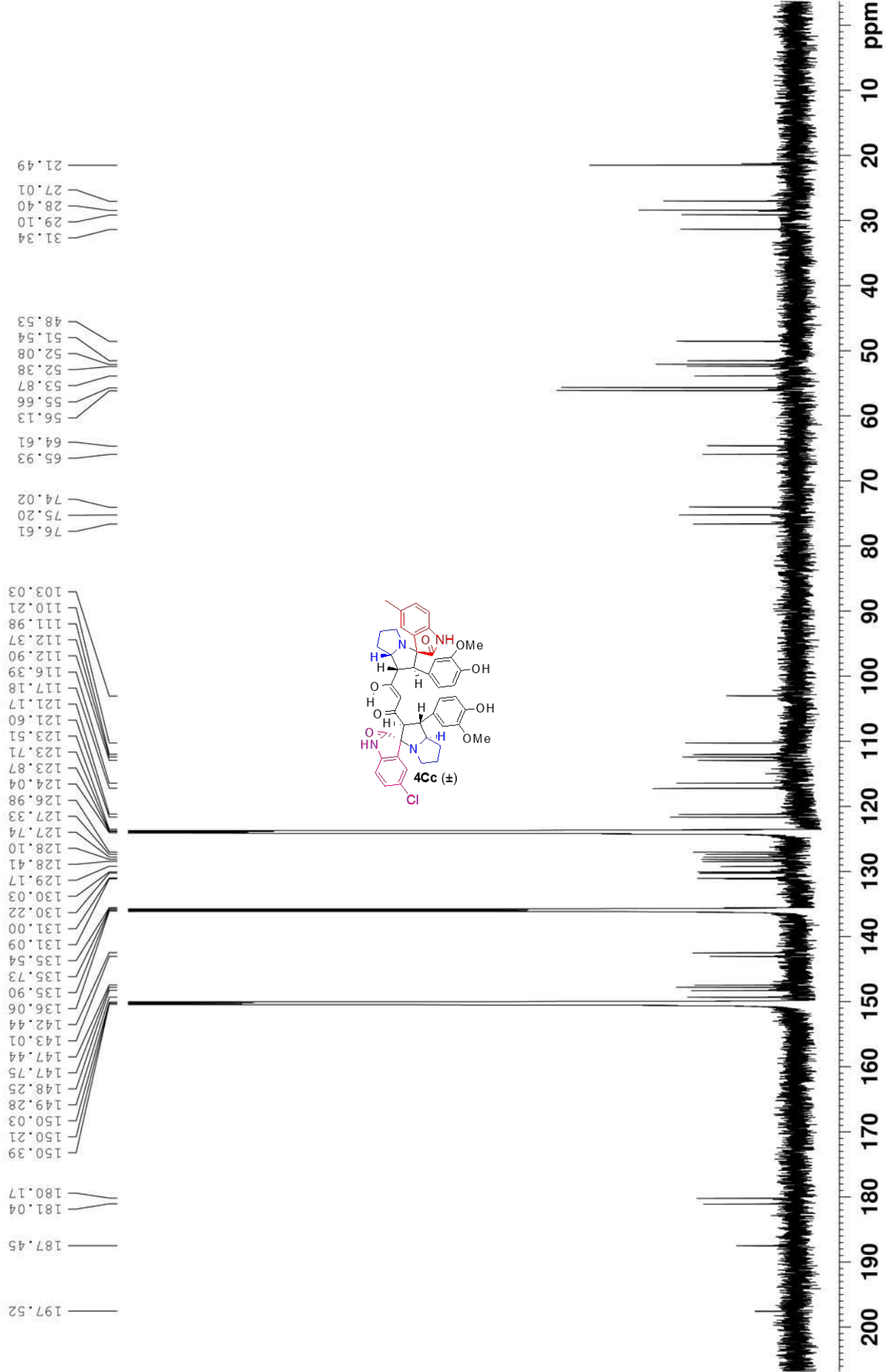
¹H NMR in Py-d5

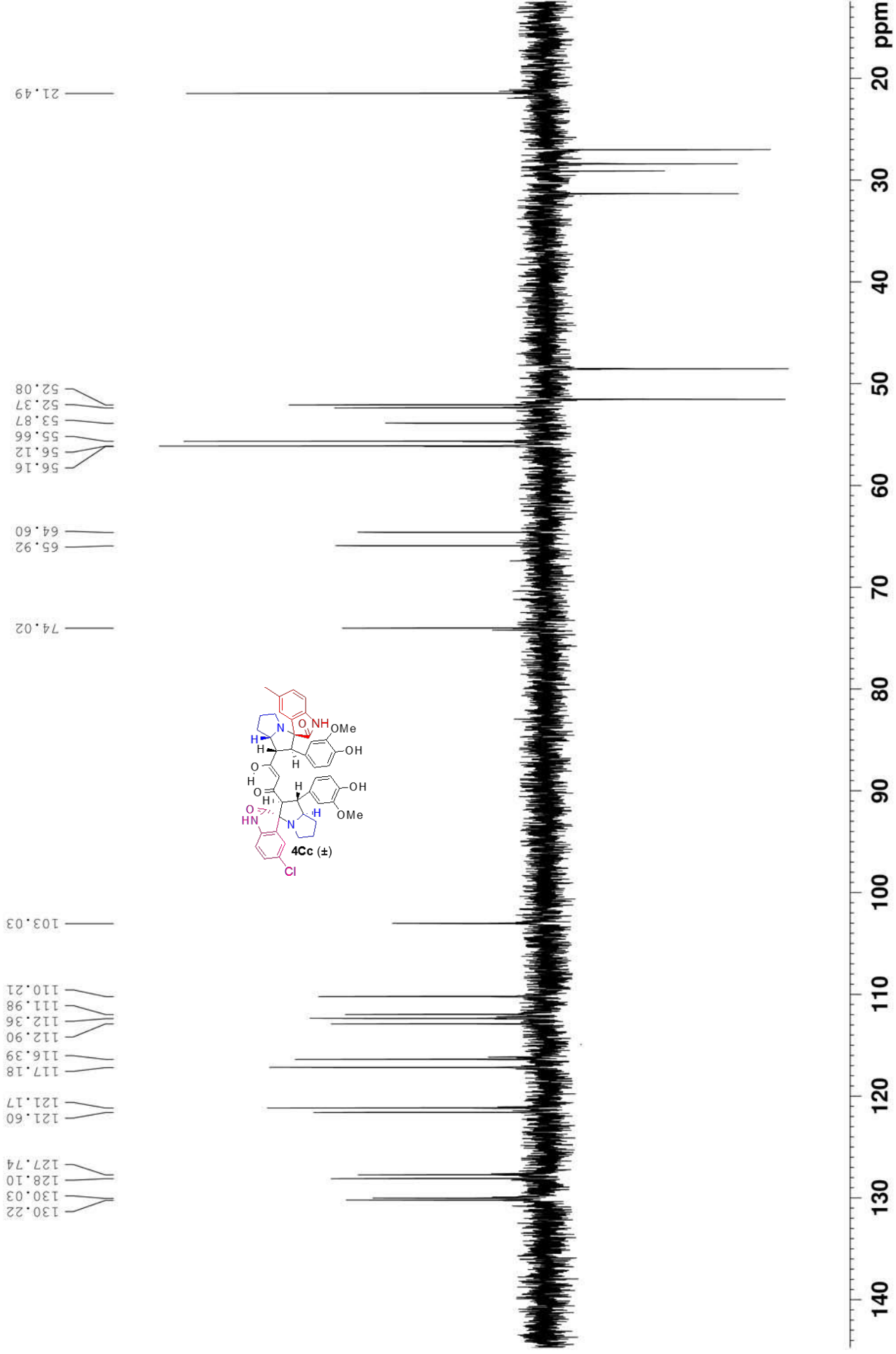


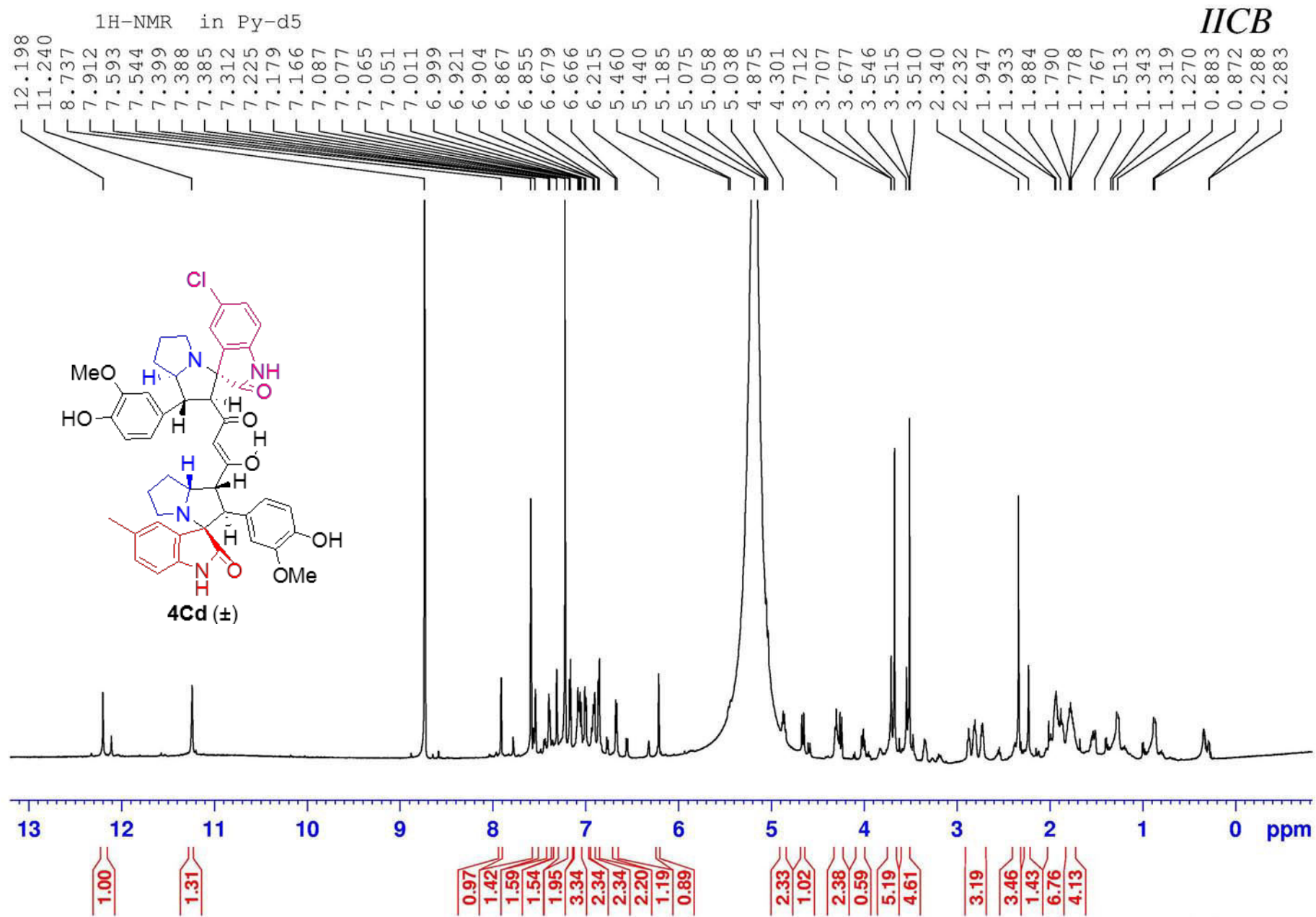
DEPT-135

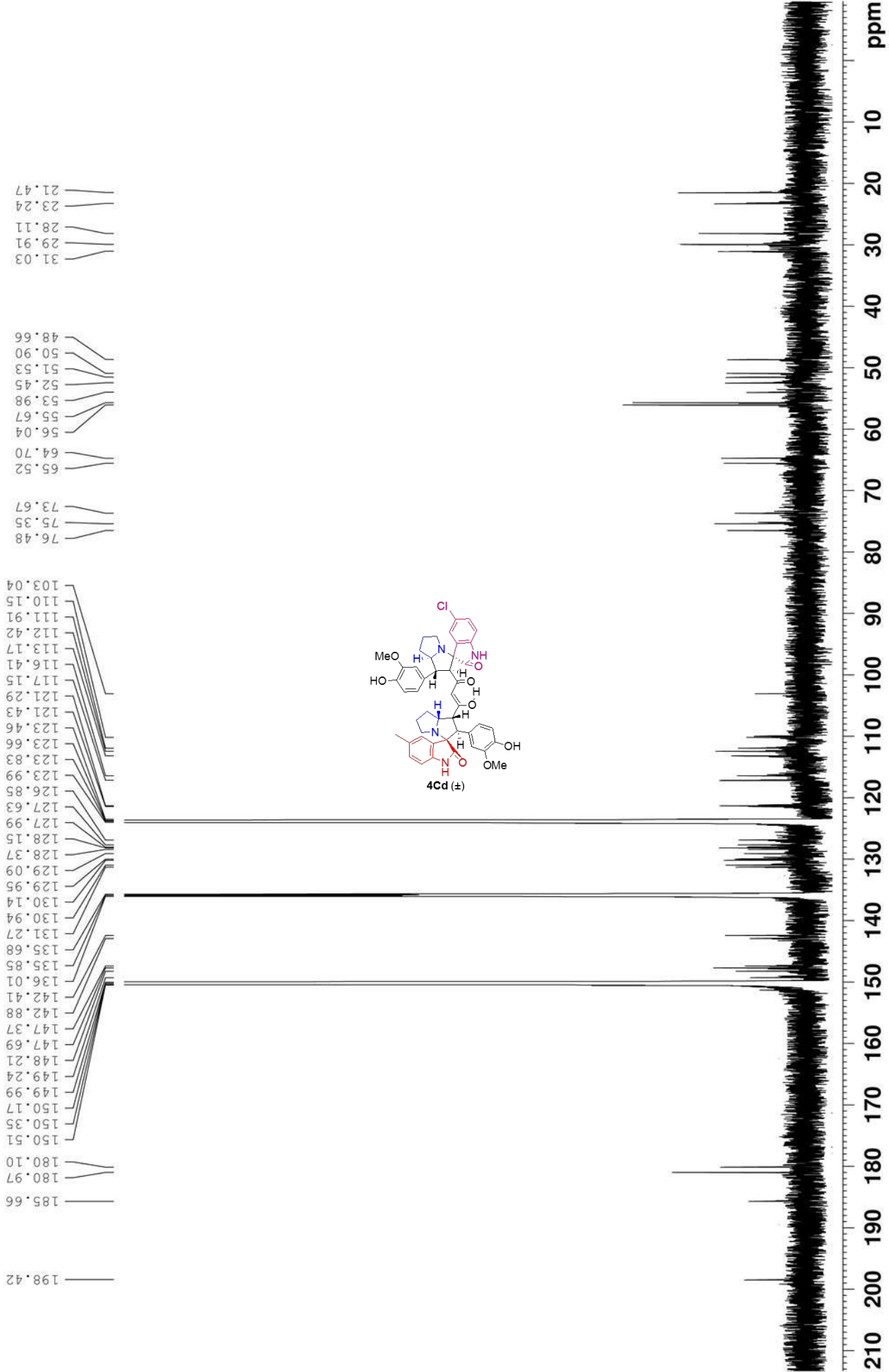


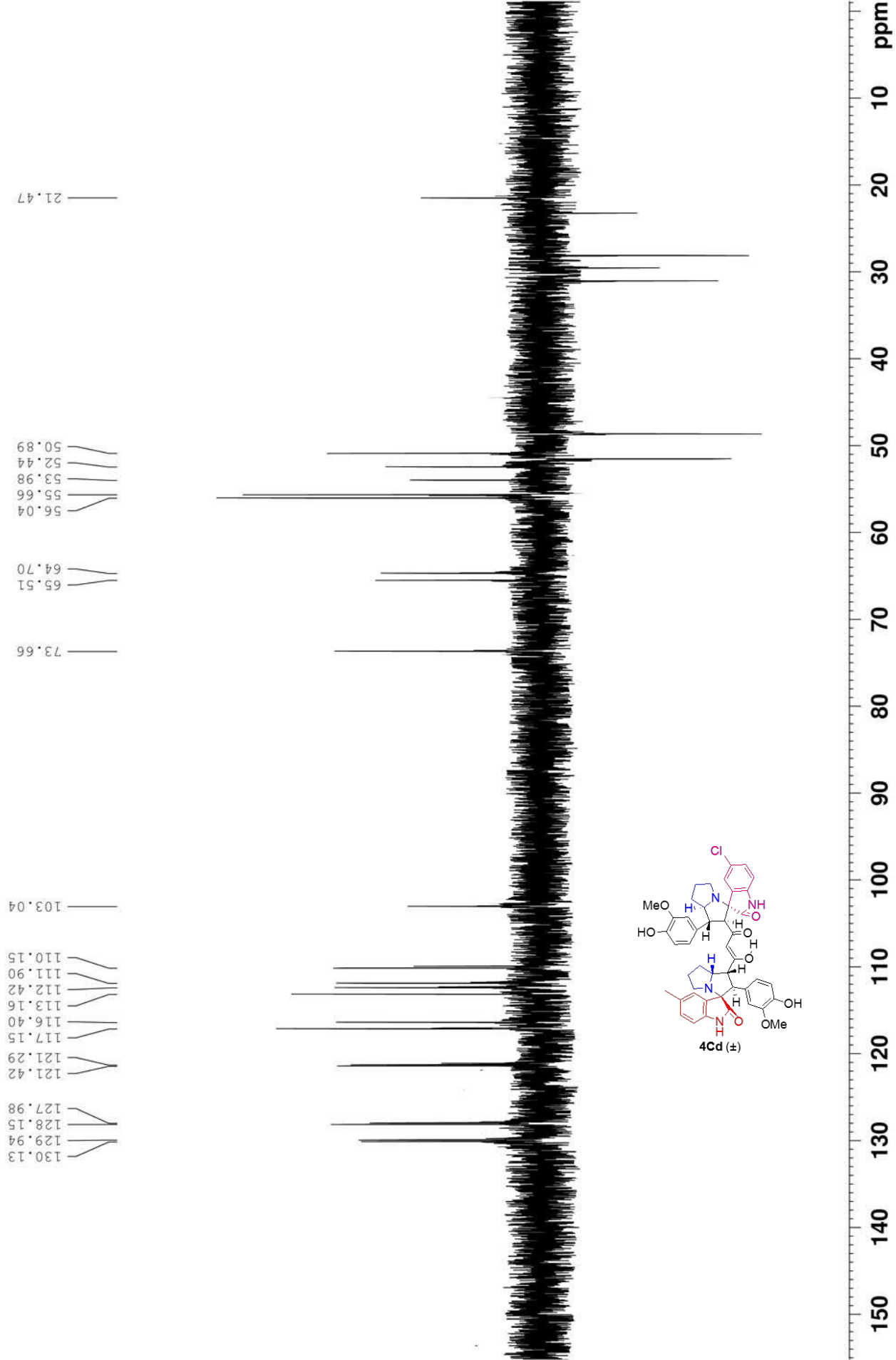




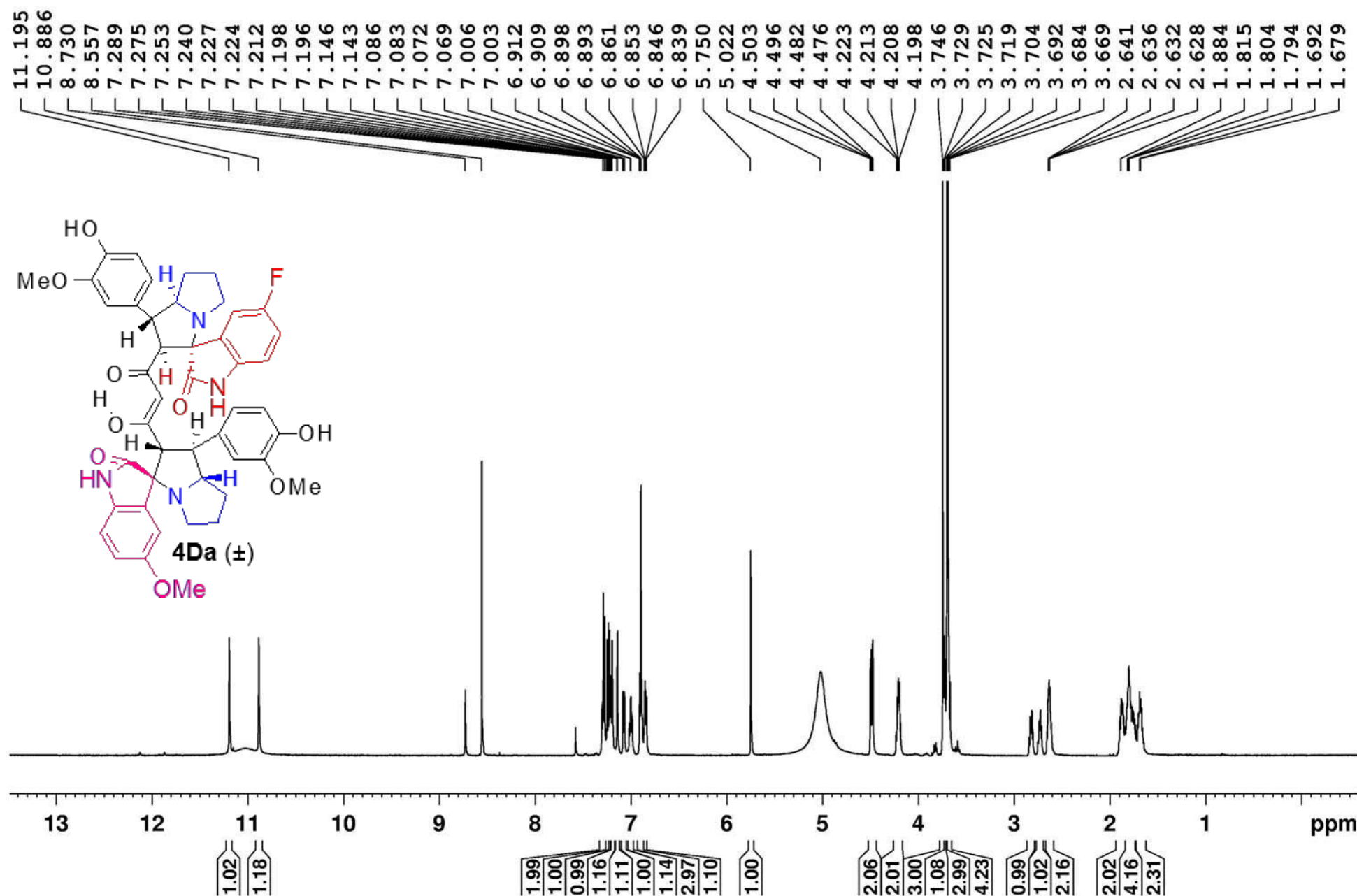




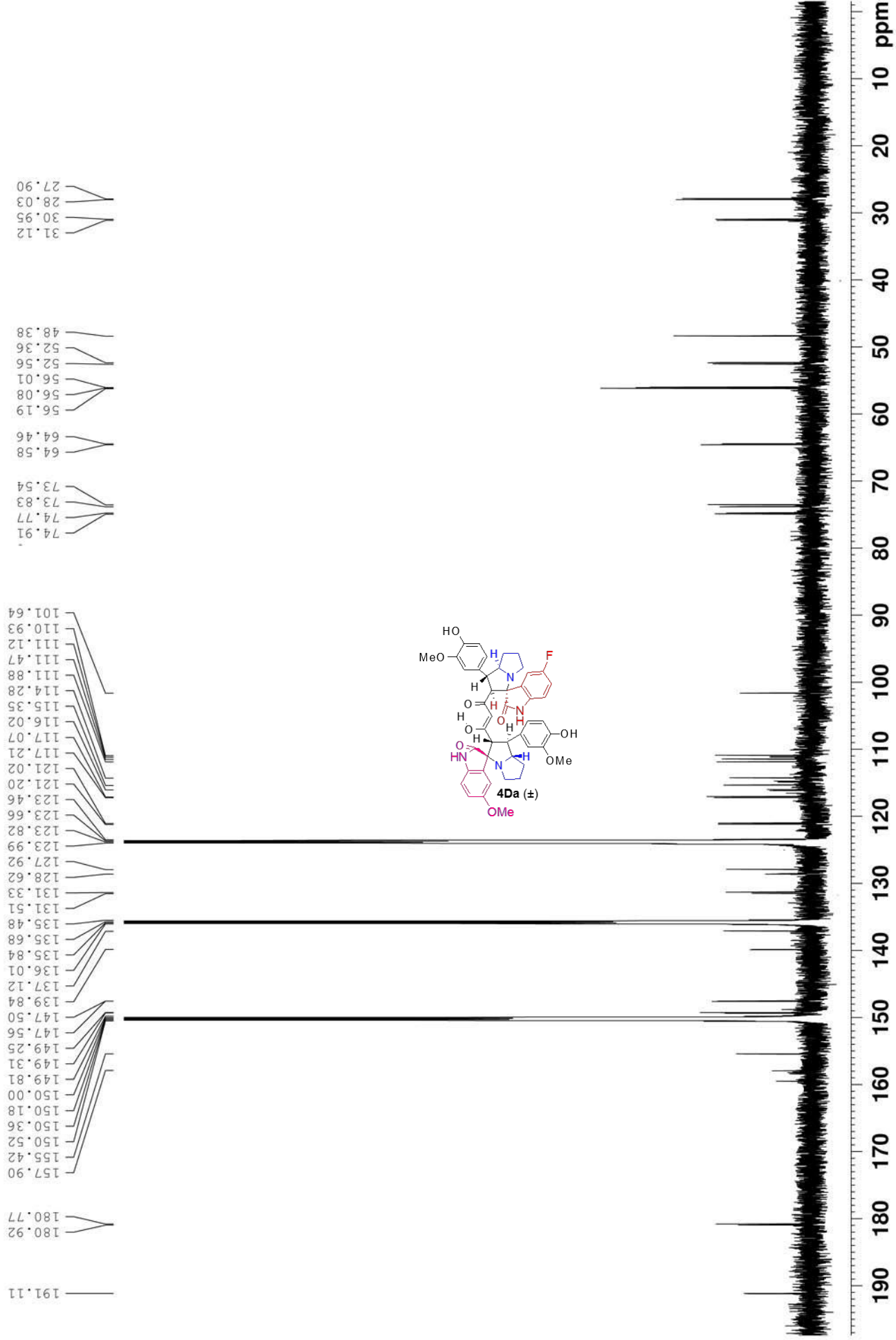




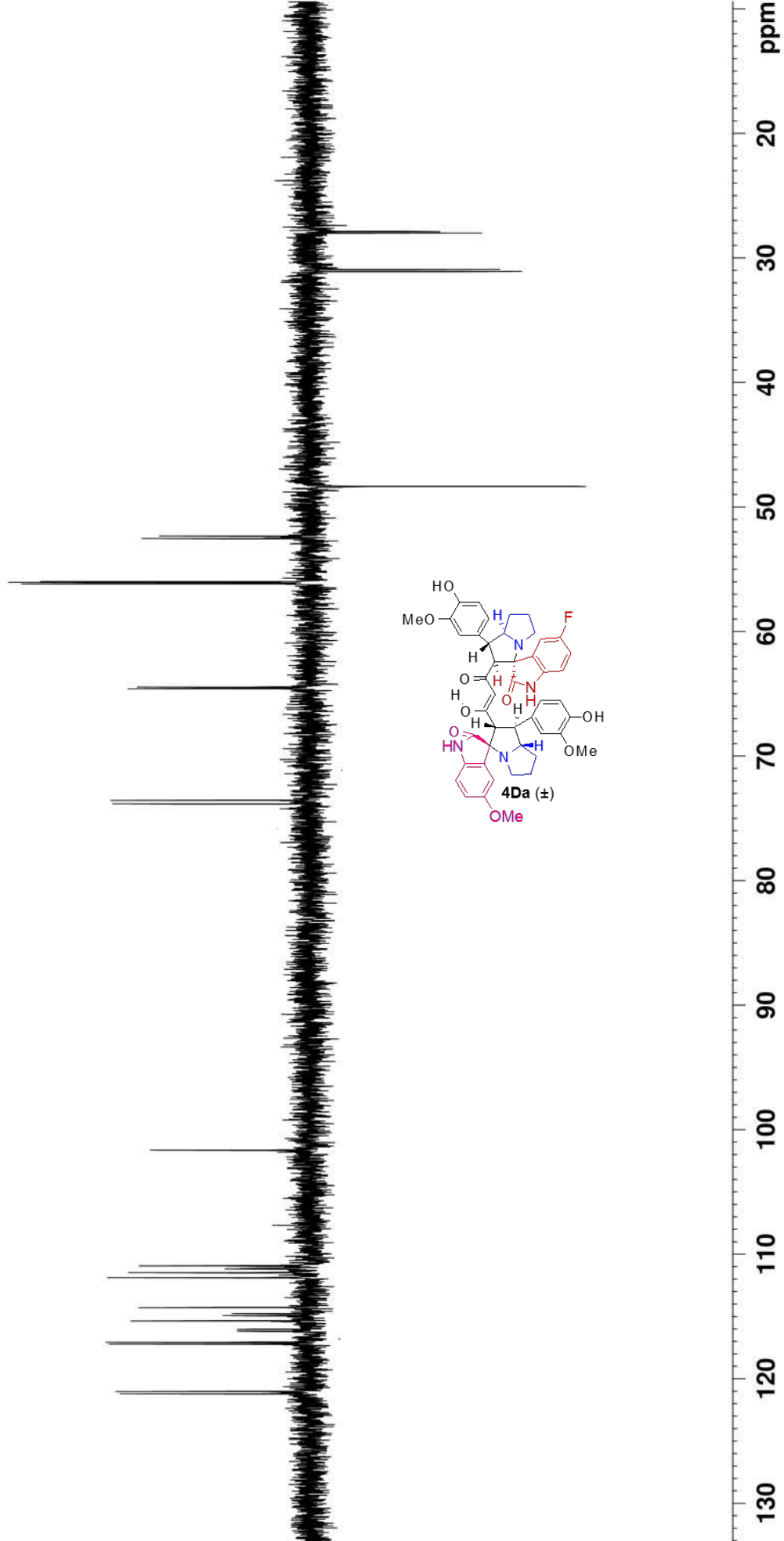
¹H NMR in Py-d₅

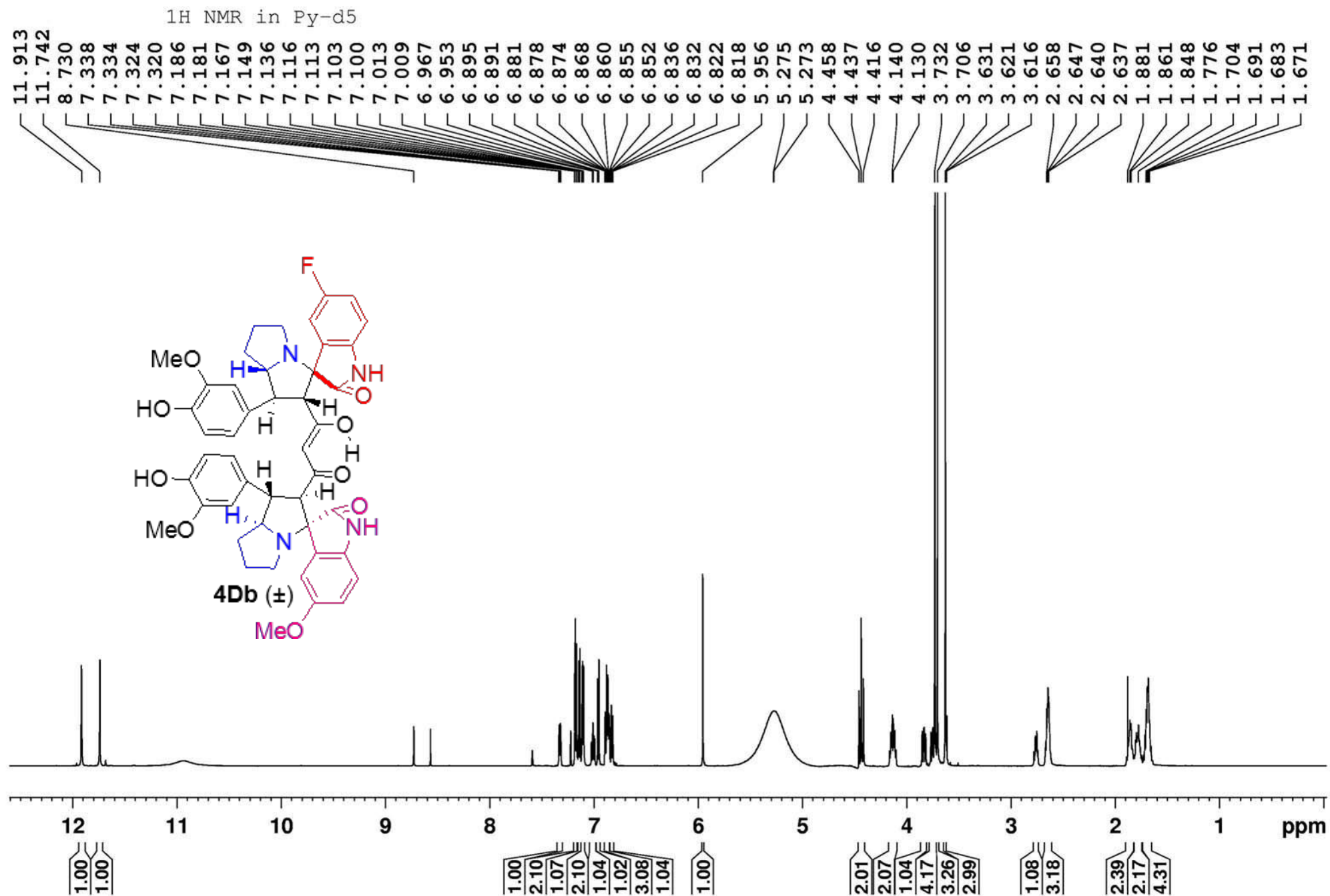


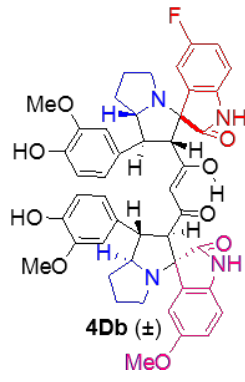
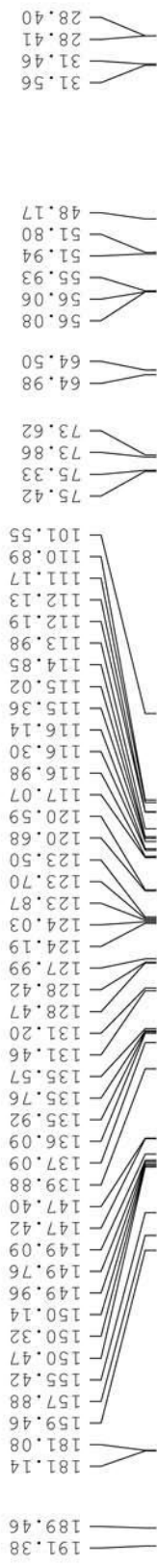
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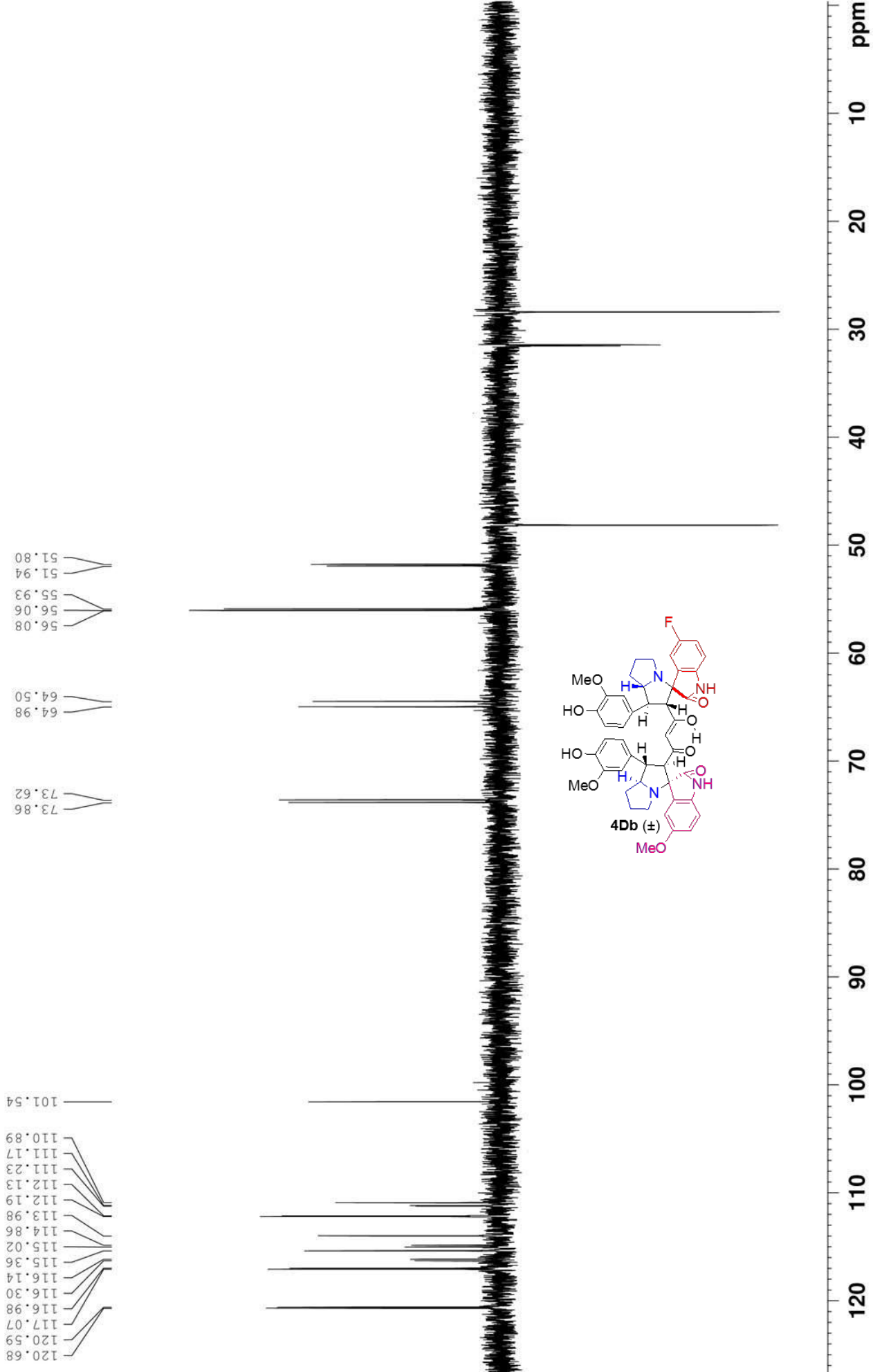


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121.02
117.21
117.07
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116.02
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114.92
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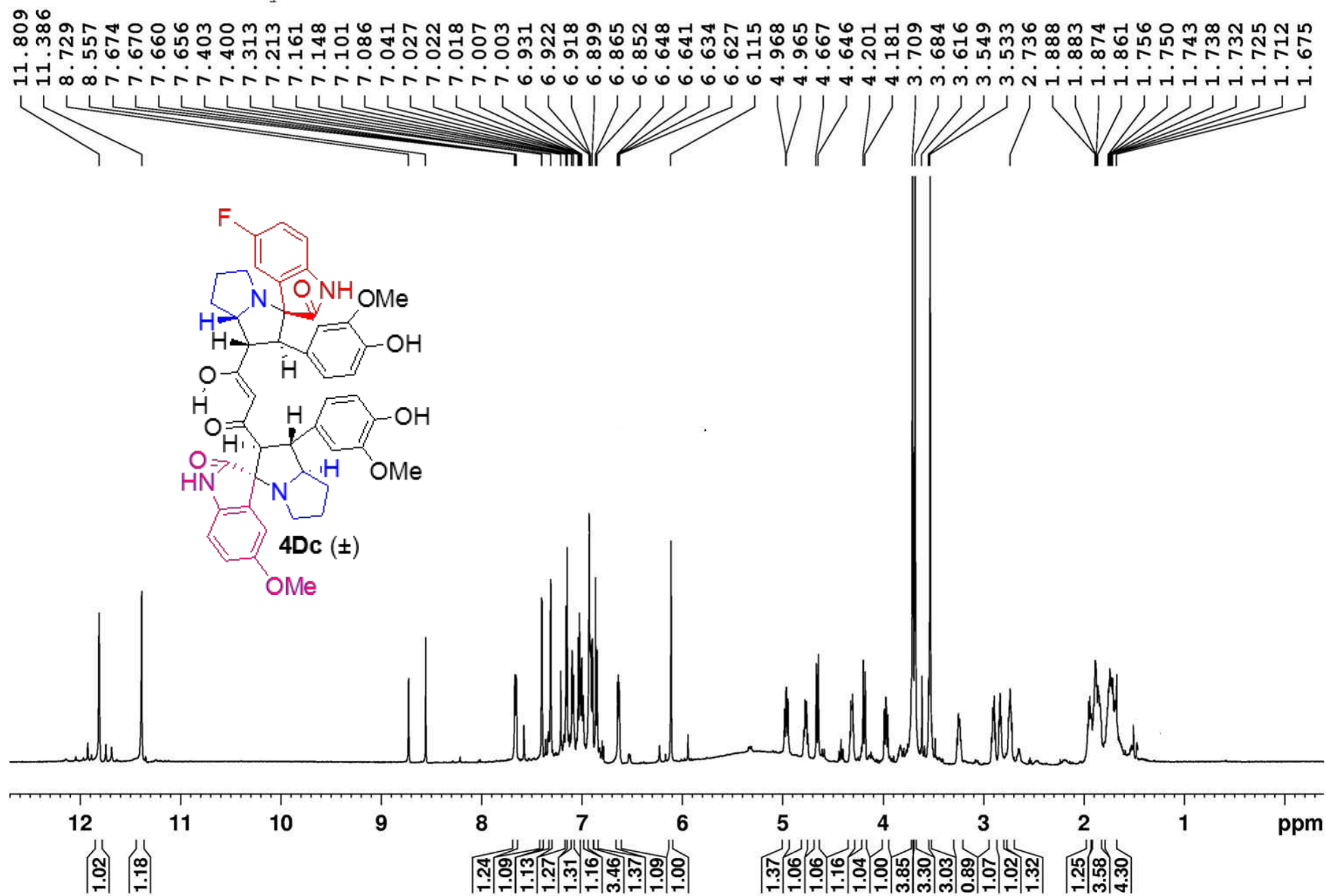


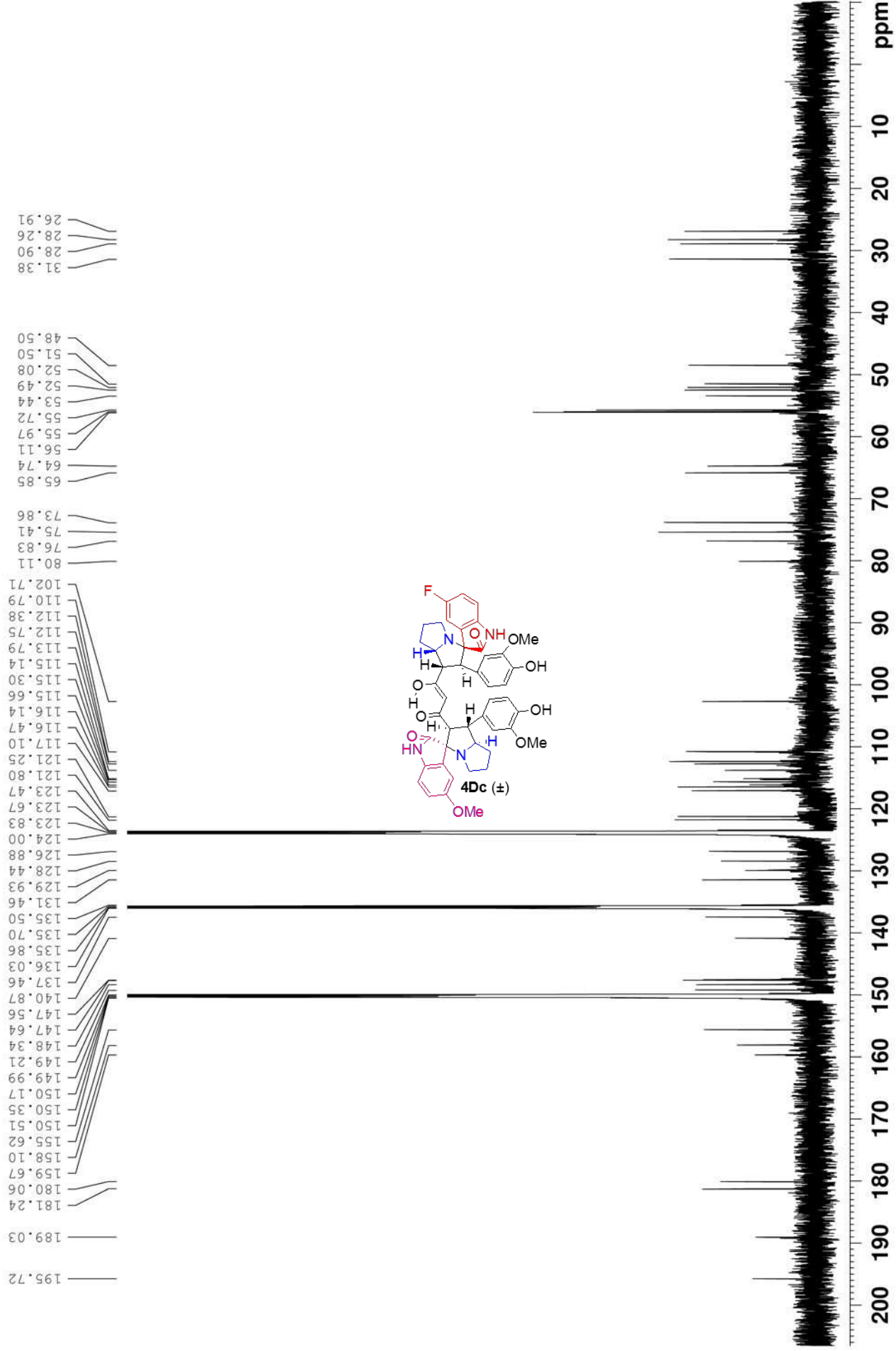


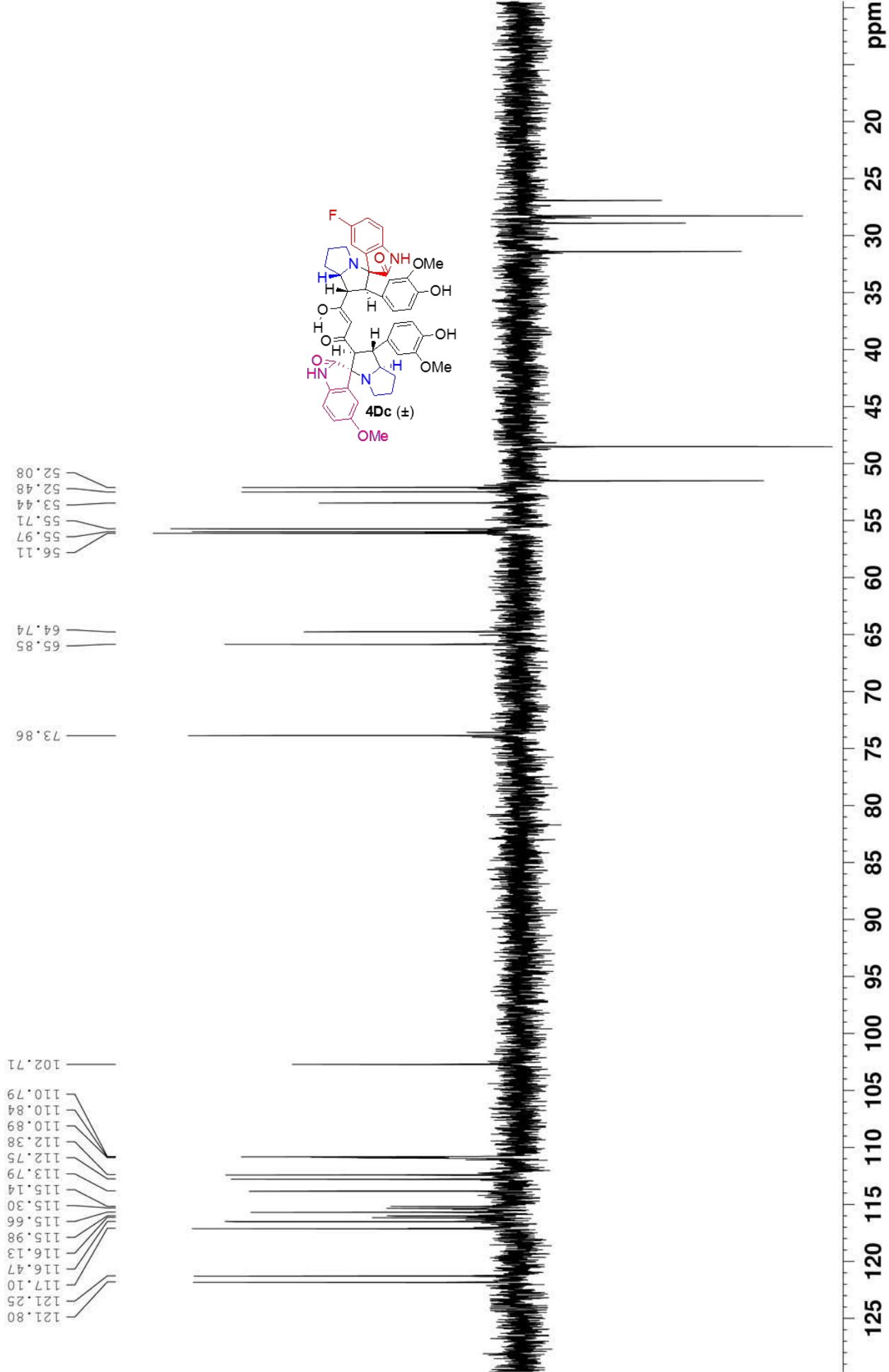




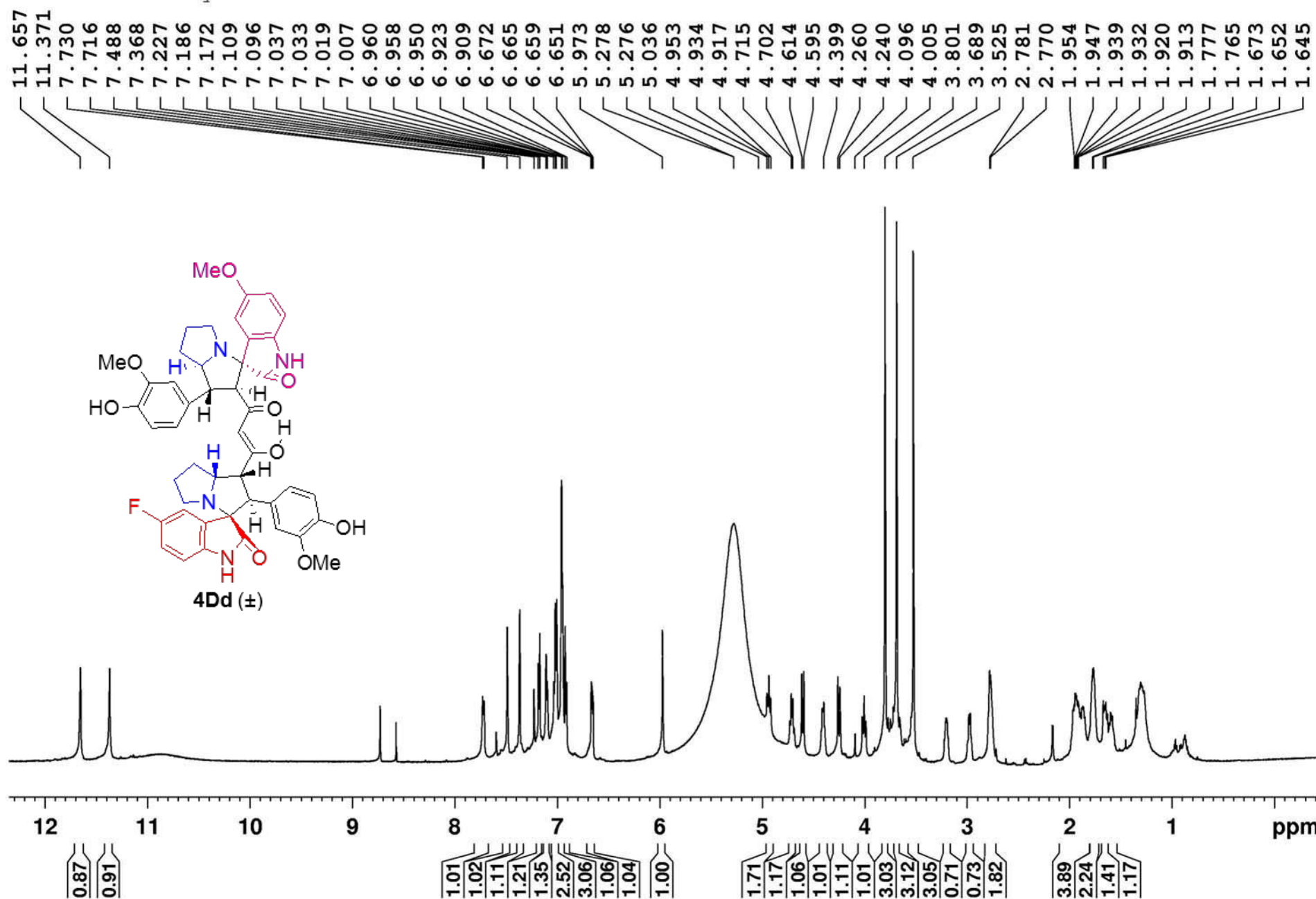
¹H NMR in Py-d₅

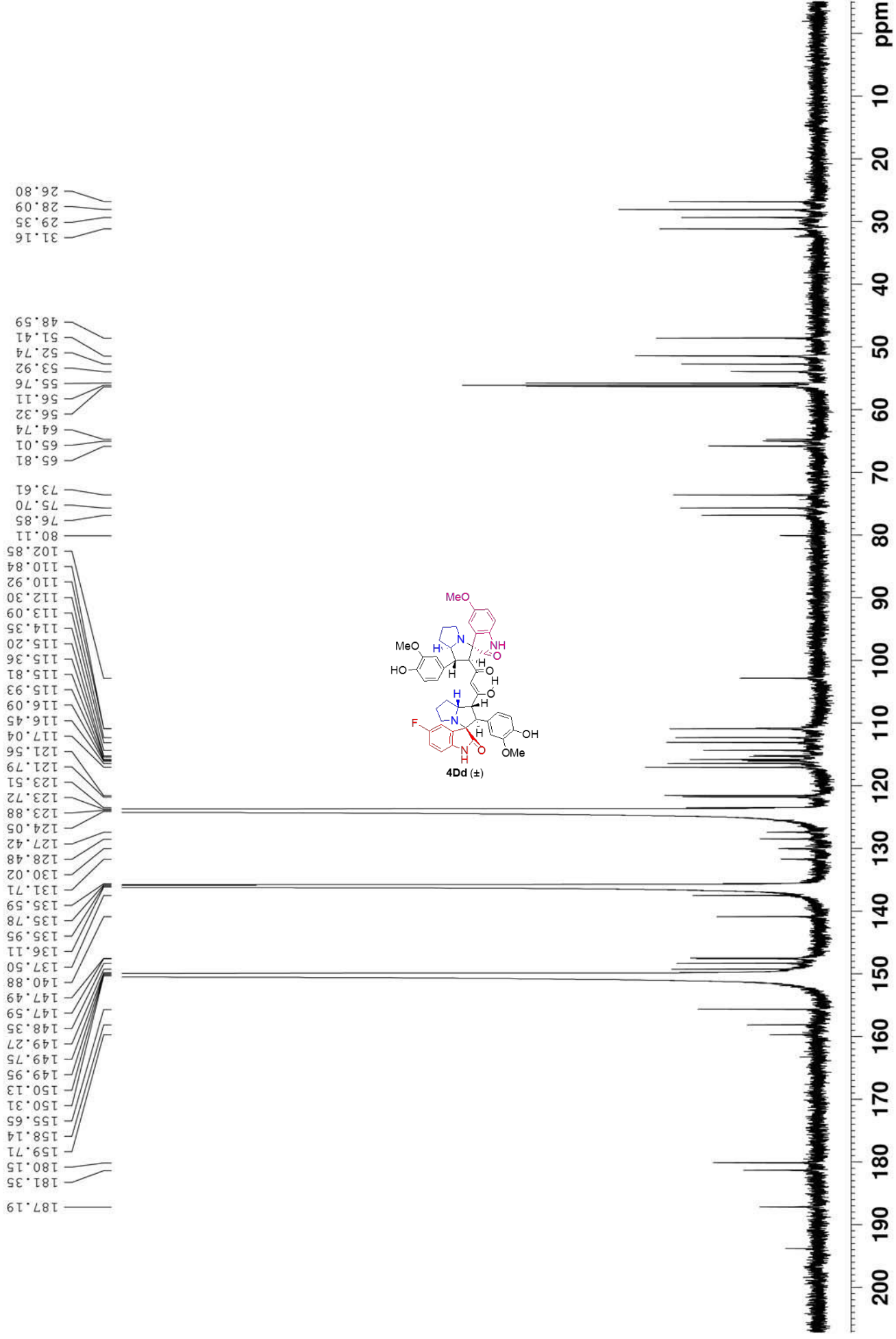






¹H NMR in Py-d₅



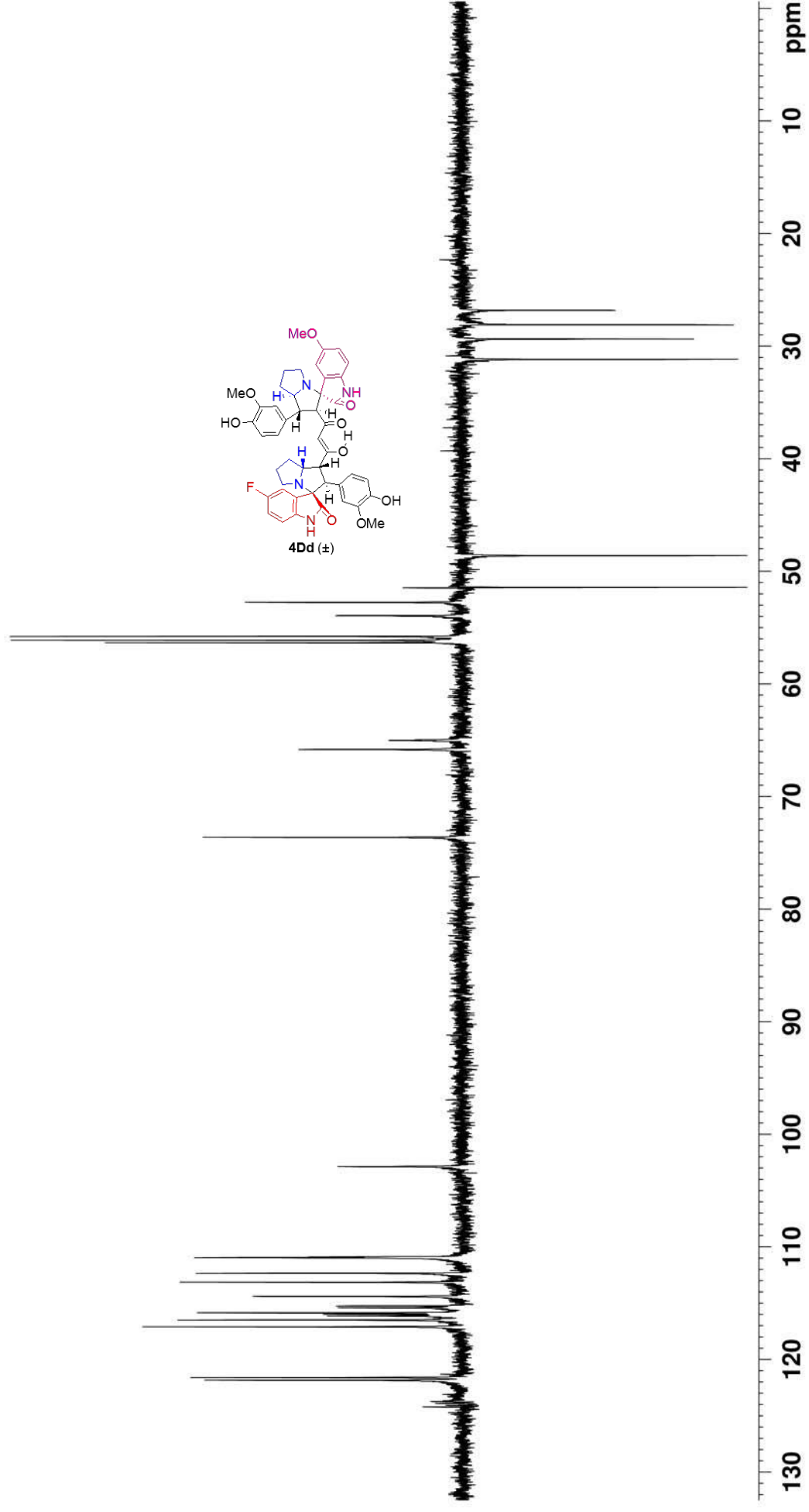
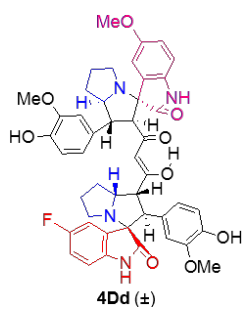


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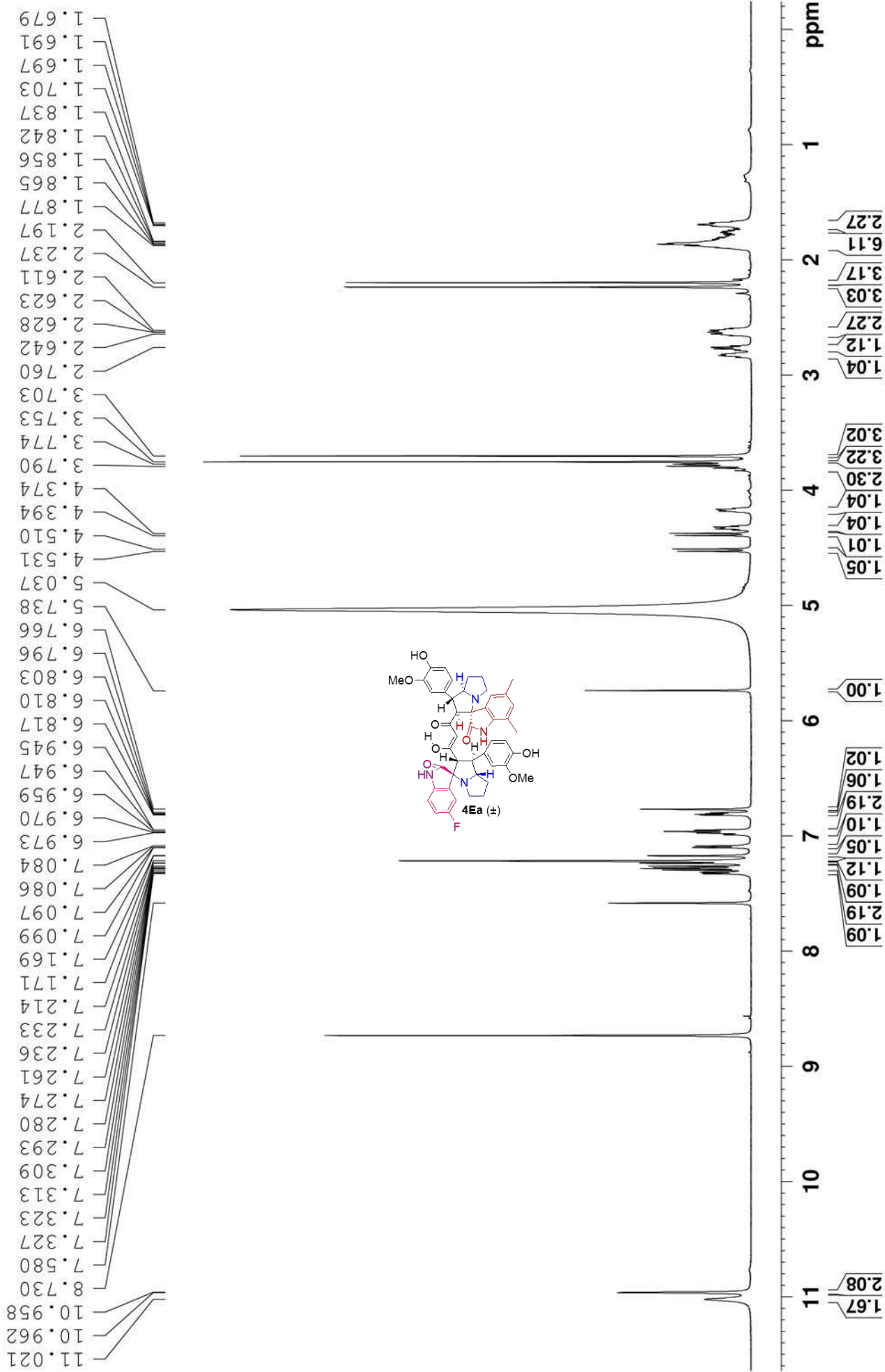
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123.70
121.80
121.56
117.05
116.45
116.09
115.94
115.81
115.36
115.20
114.35
113.09
112.30
110.92
110.84
102.85

56.32
56.11
55.76
53.92
52.74
51.45

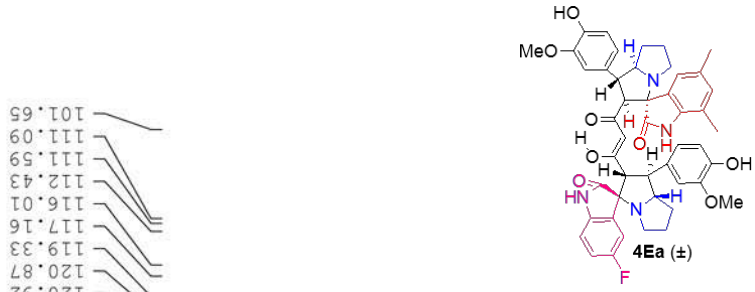
73.61
65.81
64.99



¹H NMR in Py-d₅



¹³C-NMR in Py-d₅



181.24

180.99

157.88

150.51

149.22

149.17

147.52

147.37

139.84

139.63

136.14

131.91

131.66

131.47

130.63

126.15

125.37

124.12

123.46

120.92

120.87

119.33

117.16

116.01

112.43

111.59

101.65

74.87

74.77

73.81

73.30

65.65

63.79

56.14

55.98

52.39

52.28

48.50

48.45

31.14

30.70

28.05

27.72

21.18

17.14

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160

150

140

130

120

110

100

90

80

70

60

50

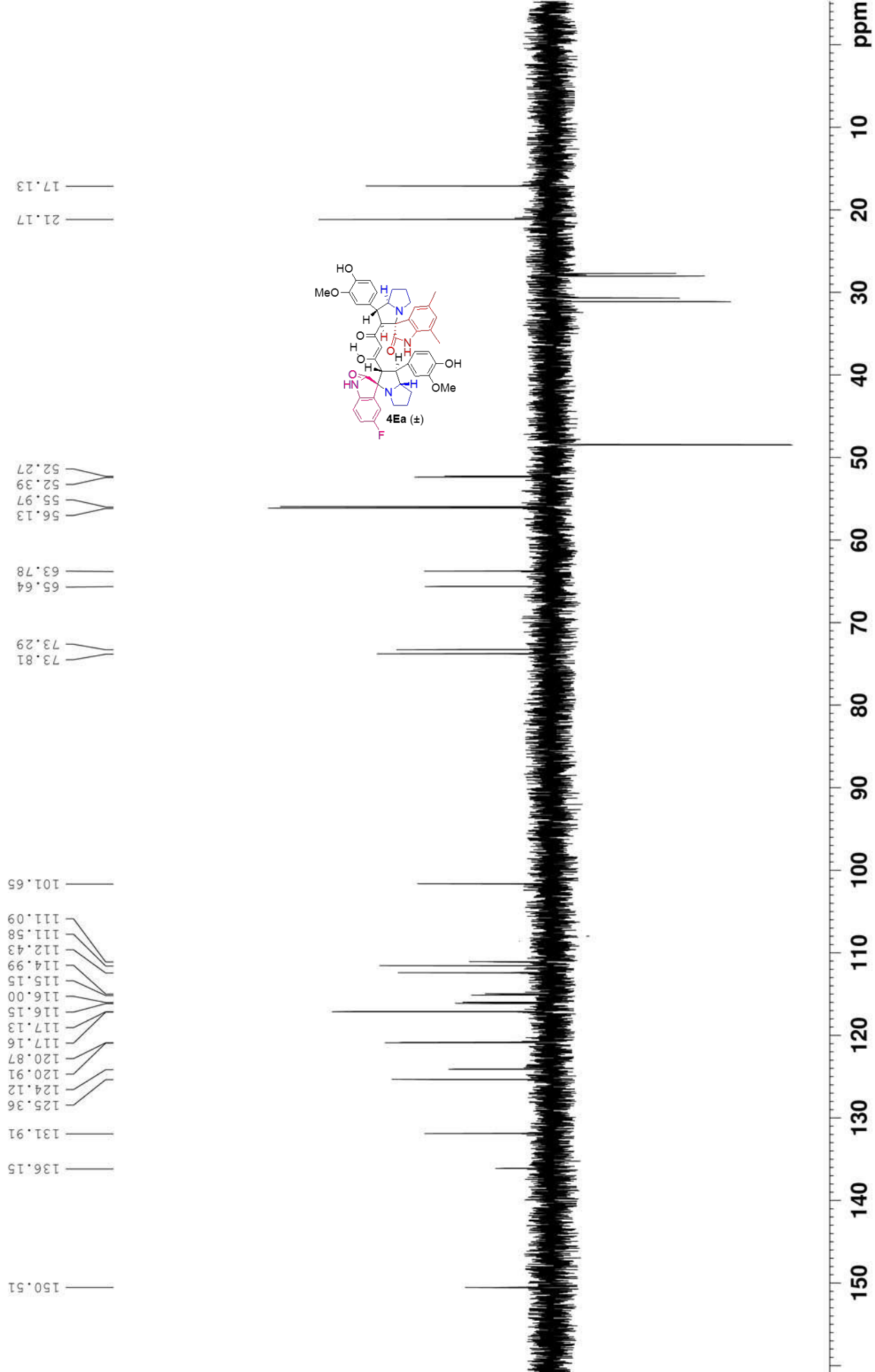
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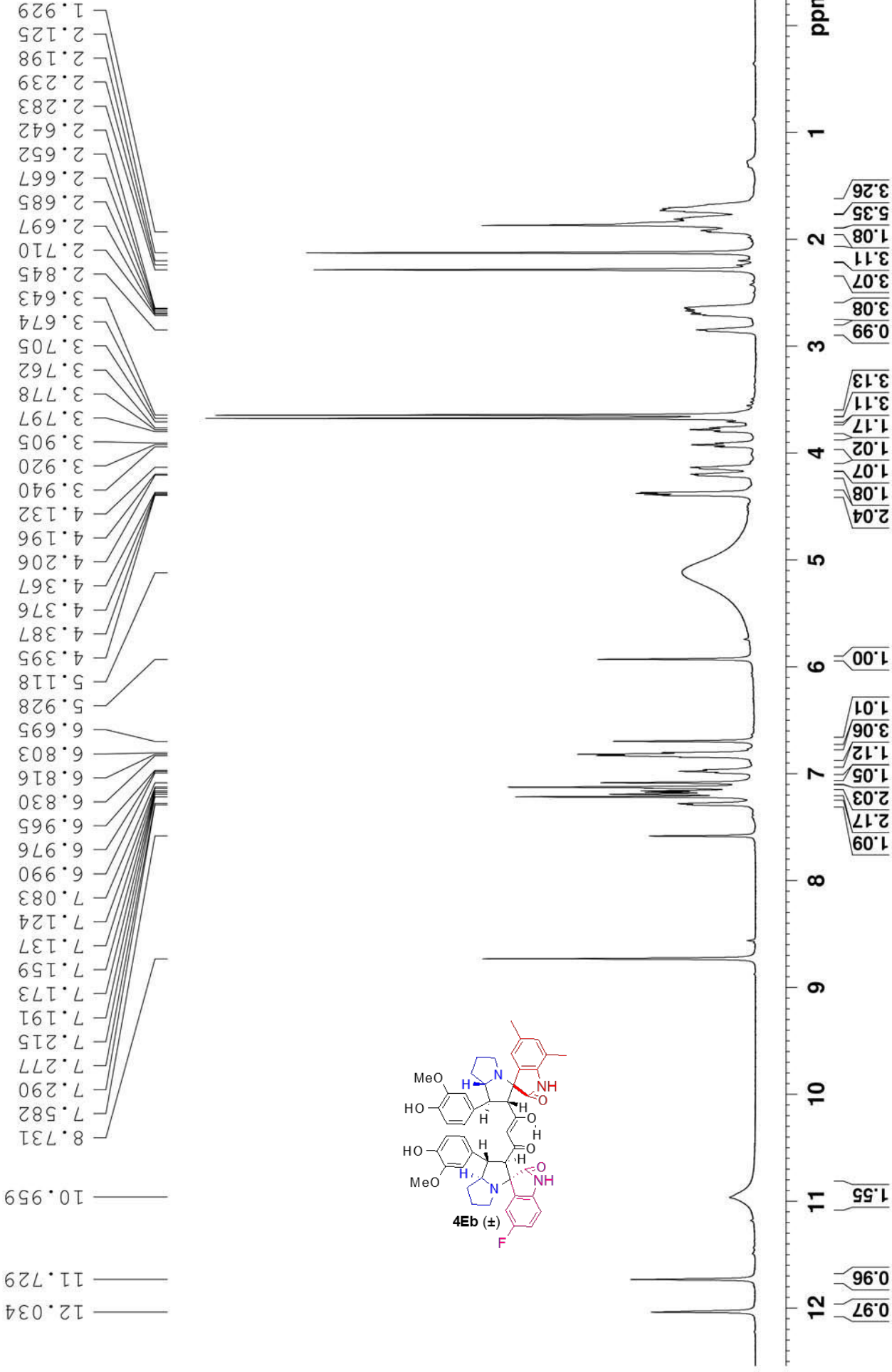
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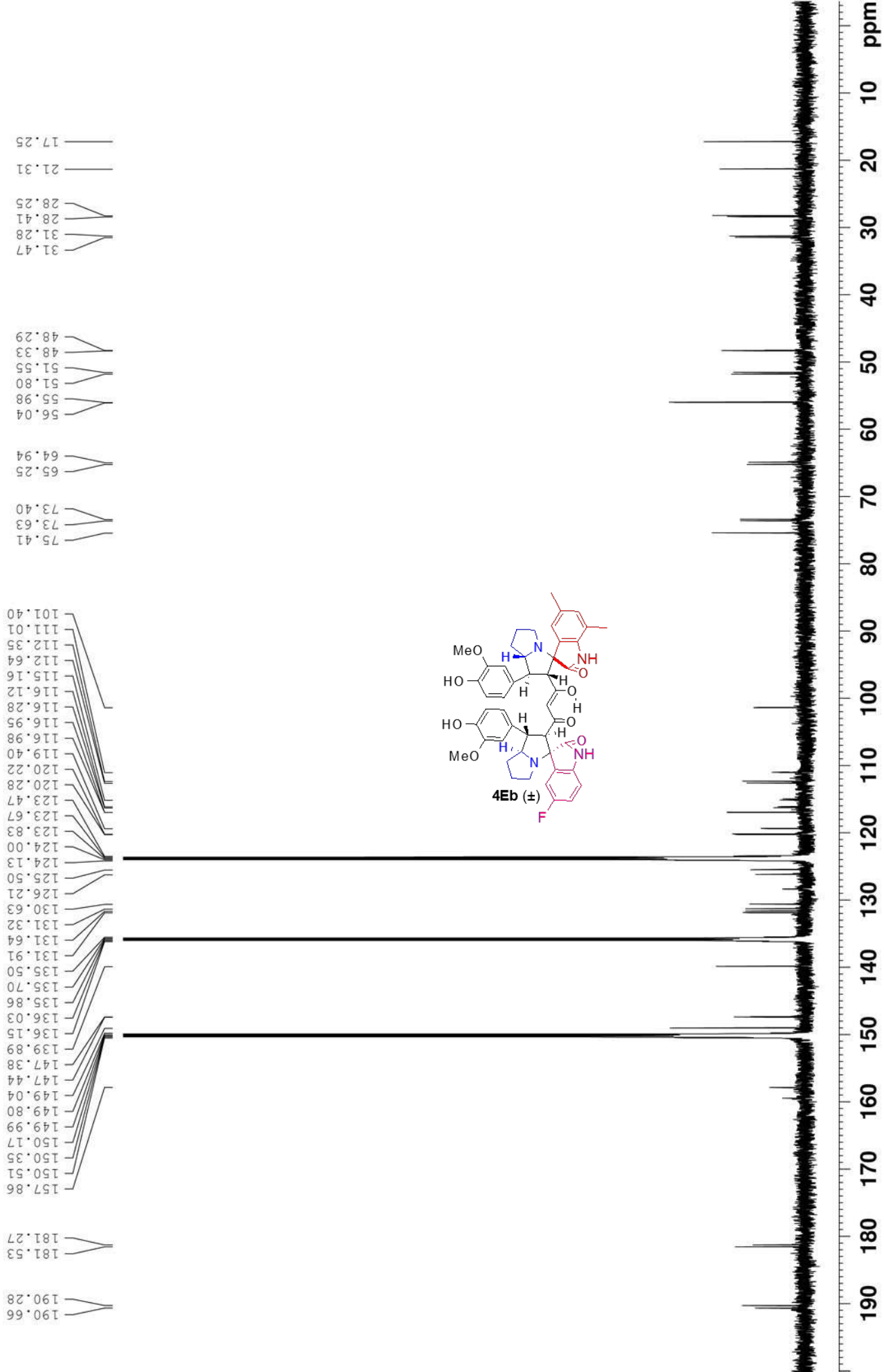
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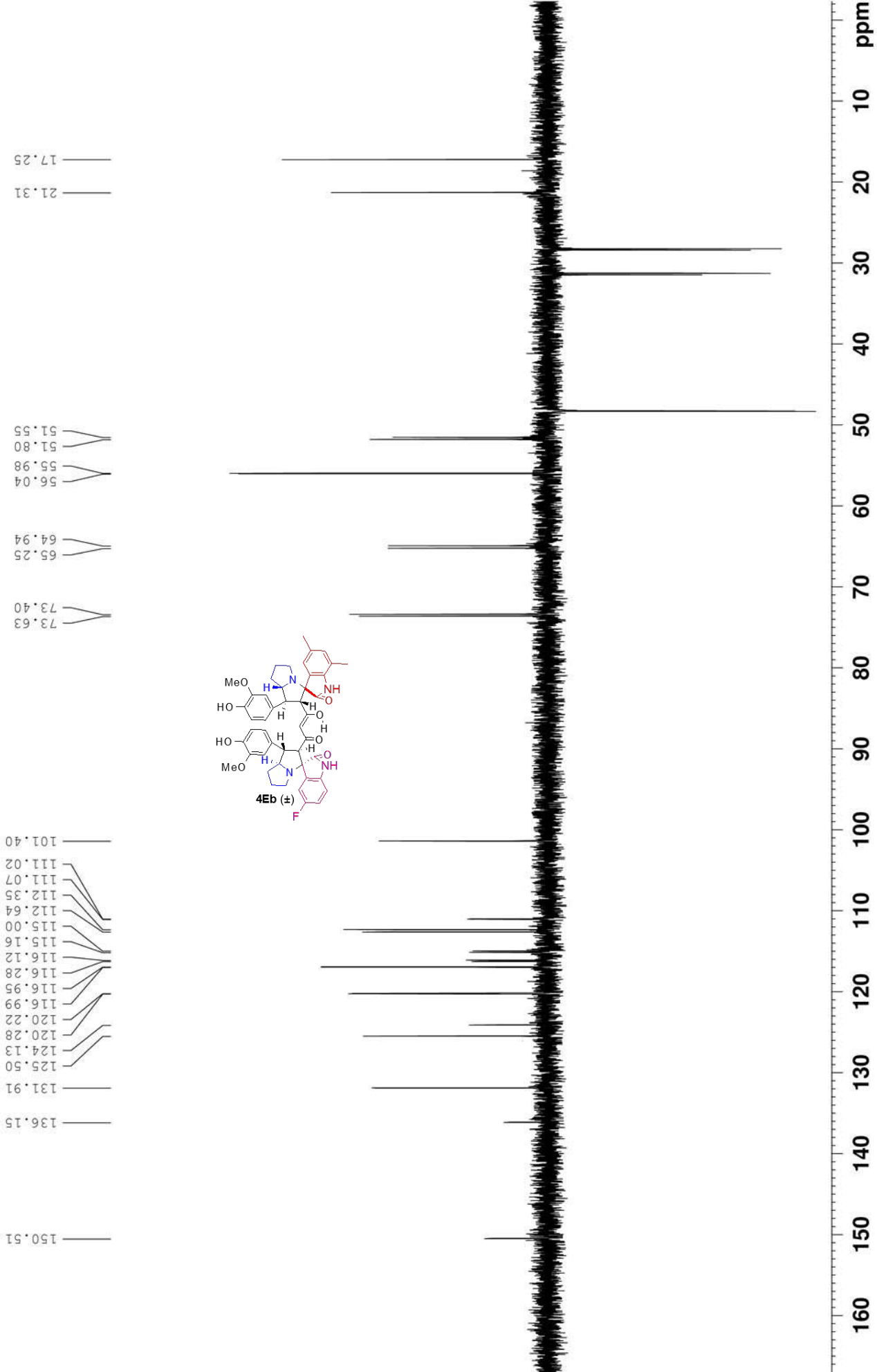
ppm



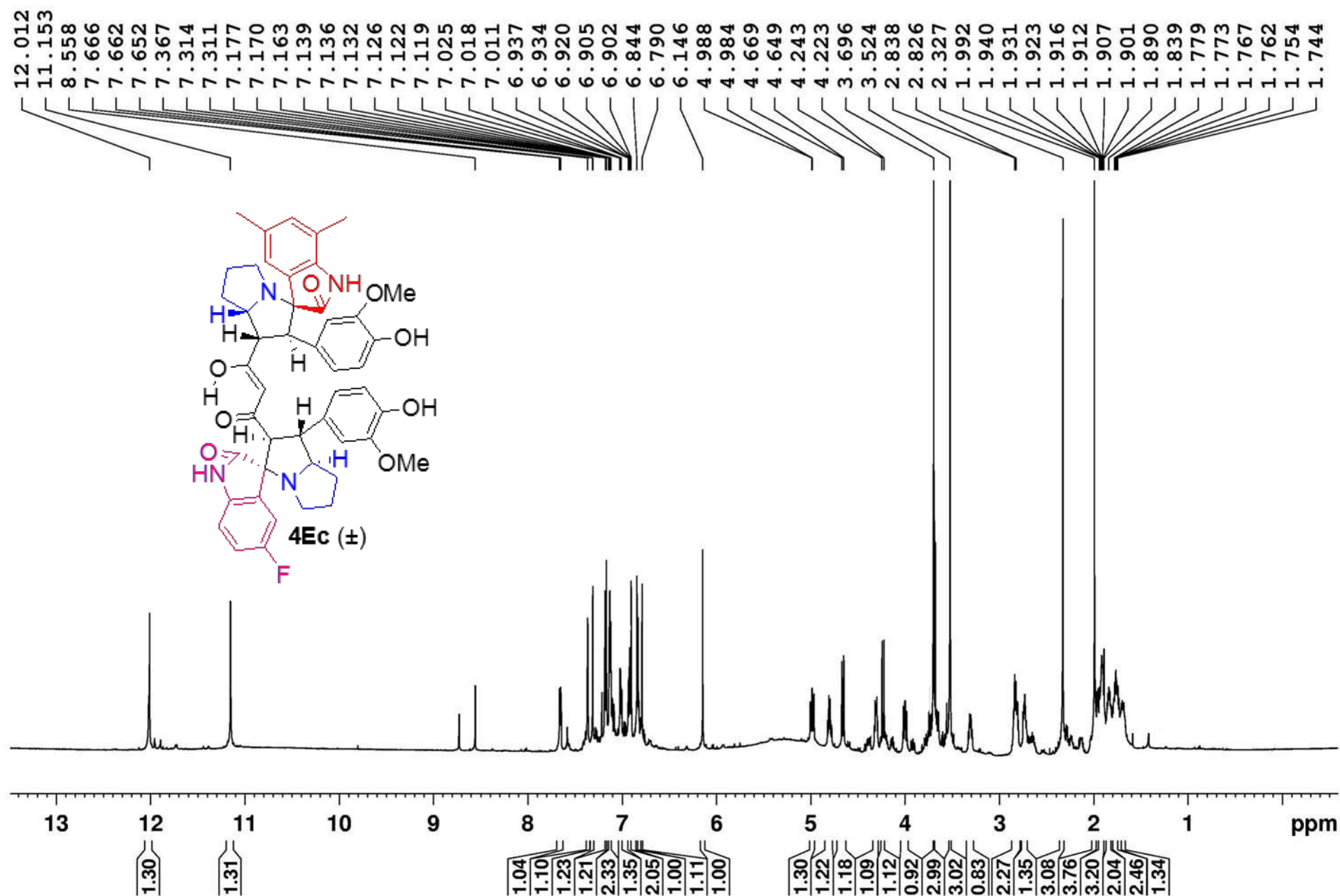
¹H NMR in Py-d5

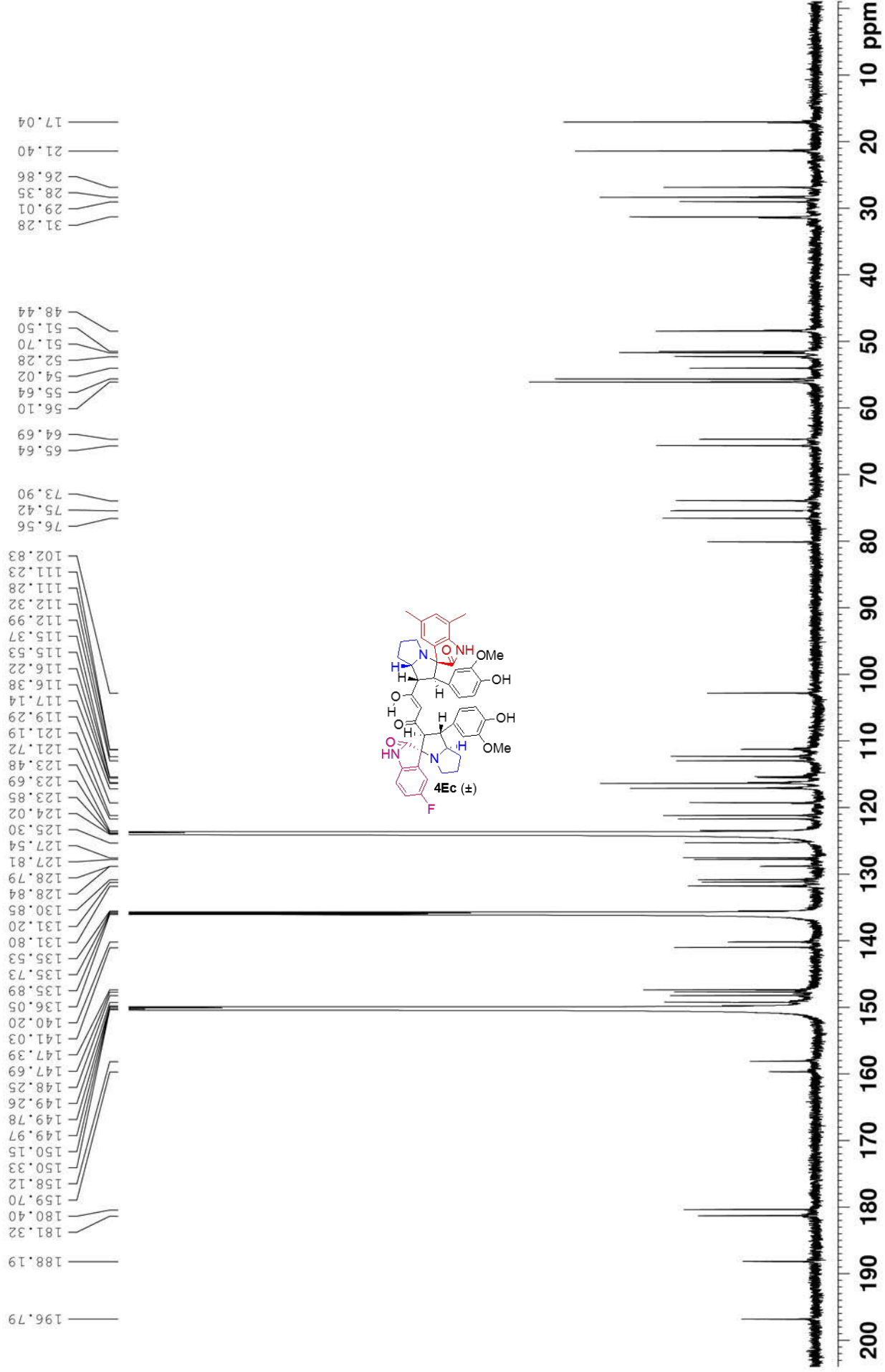


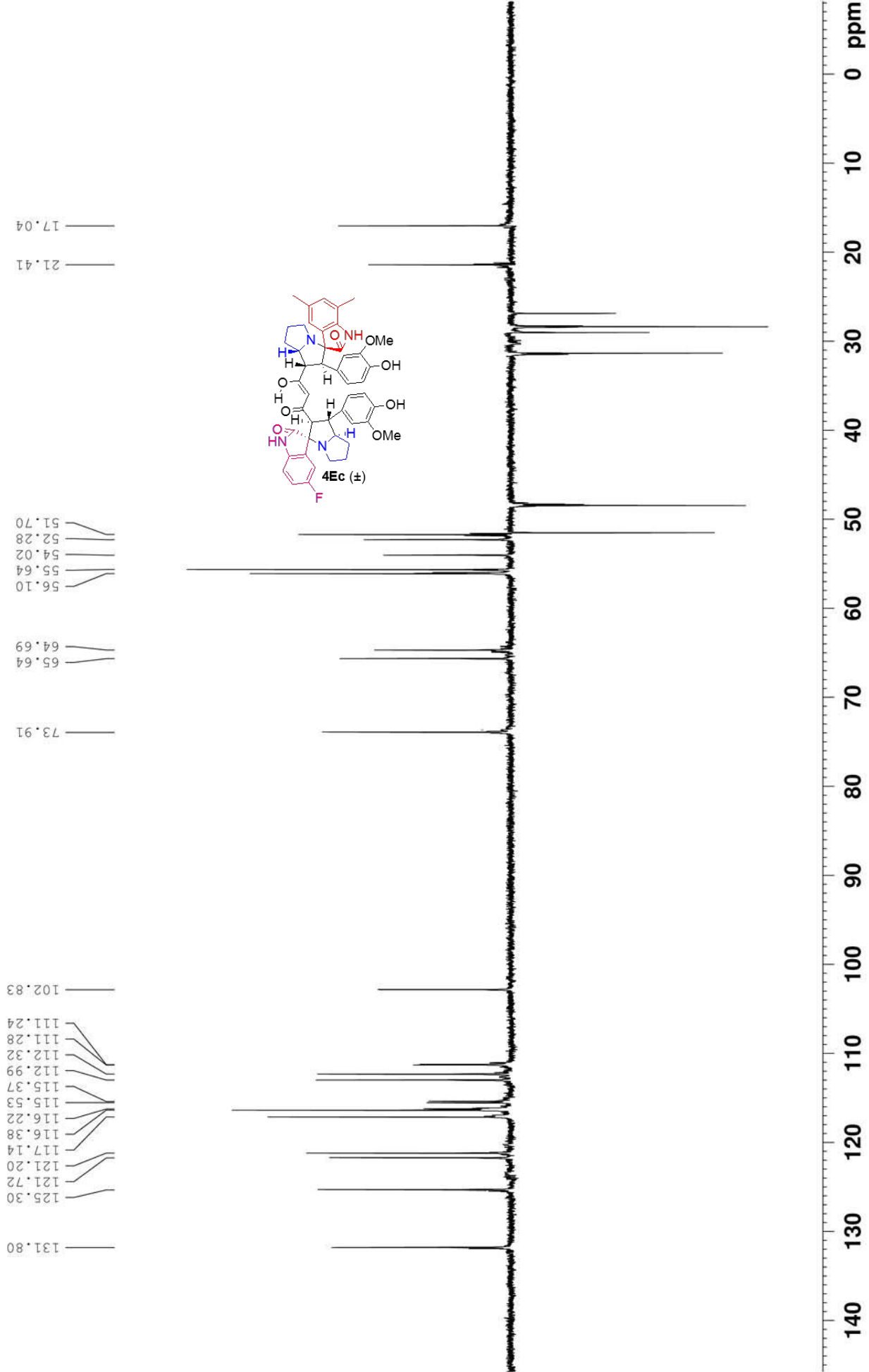




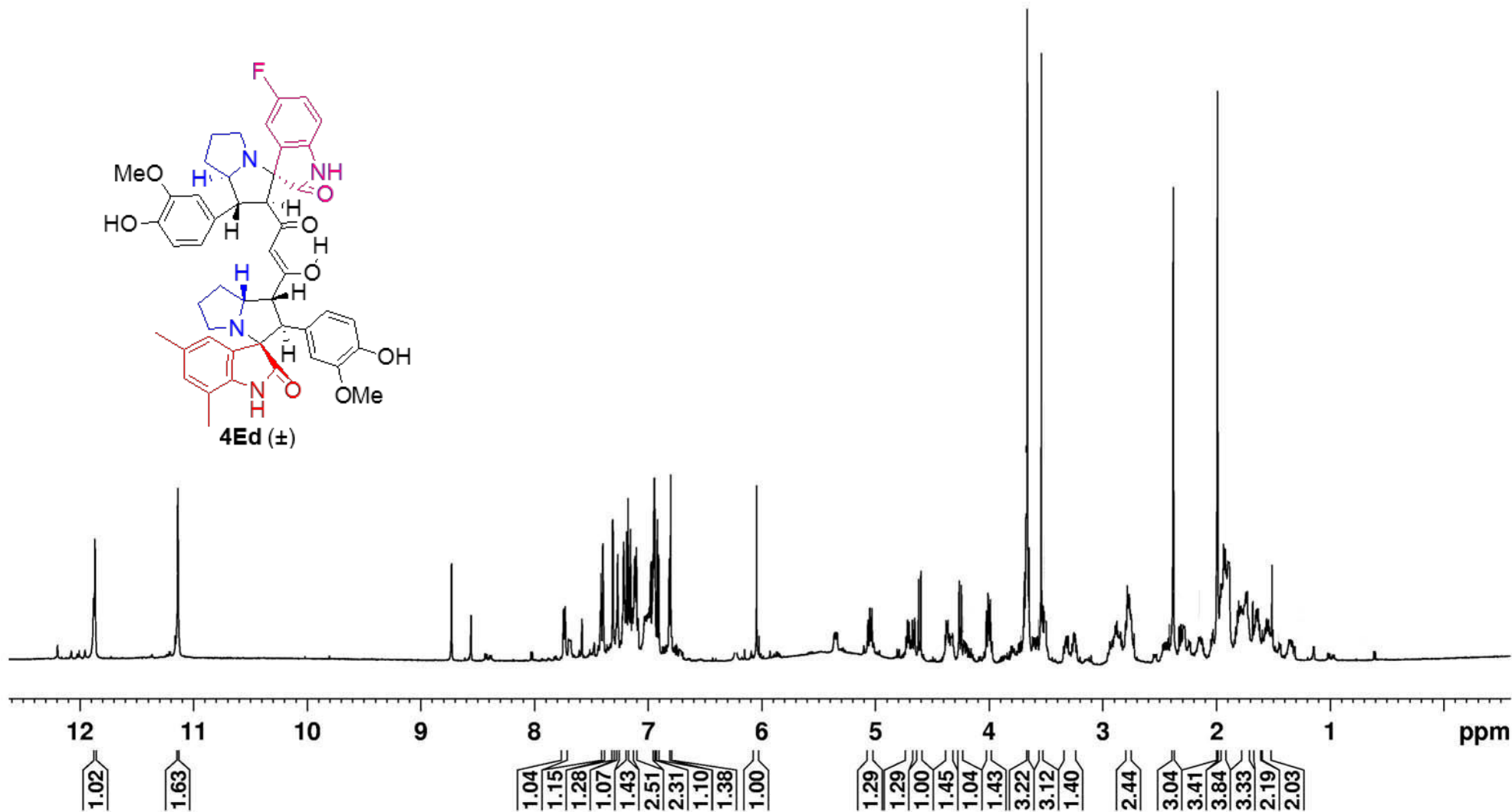
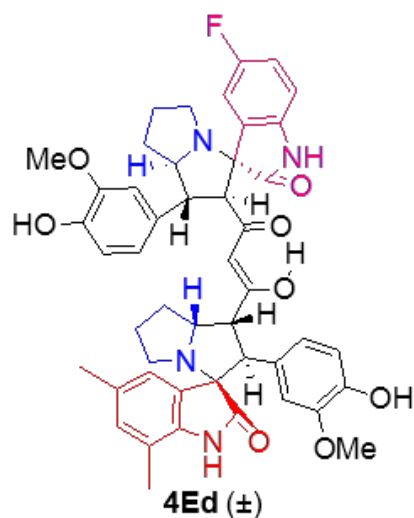
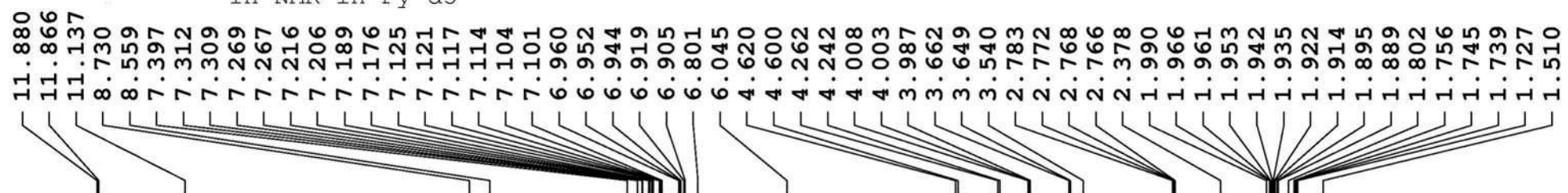
¹H NMR in Py-d₅



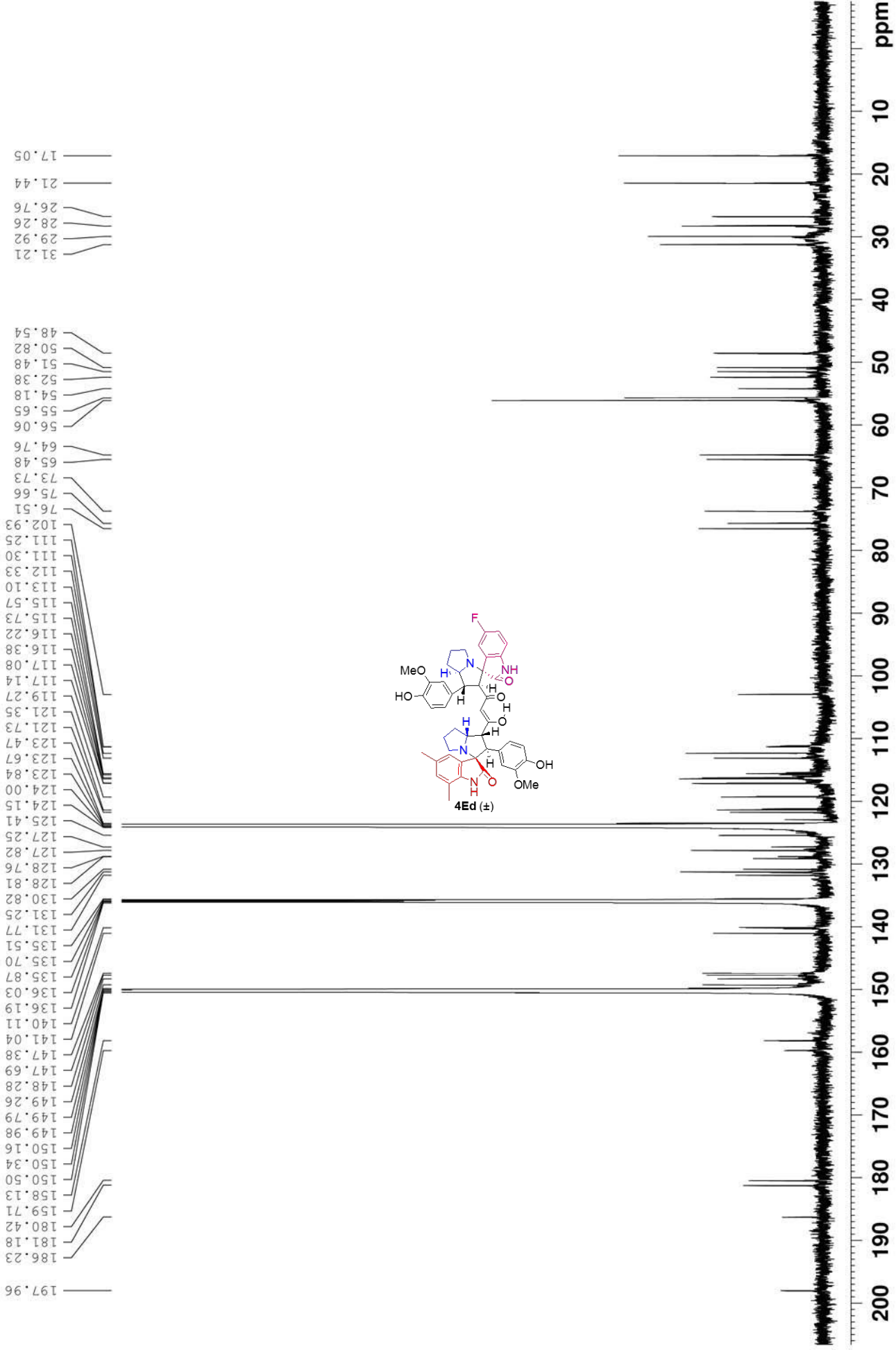


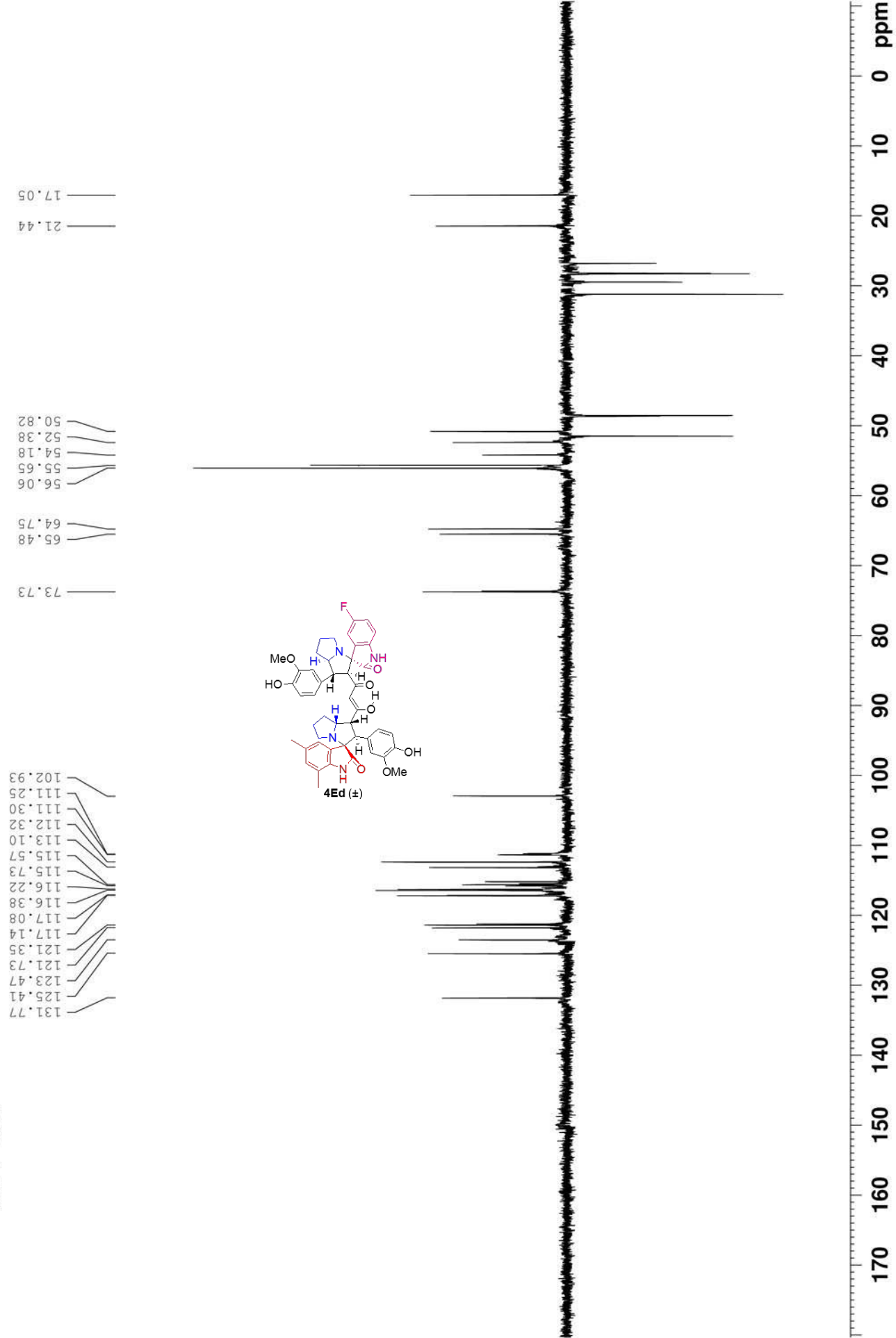


¹H NMR in Py-d₅

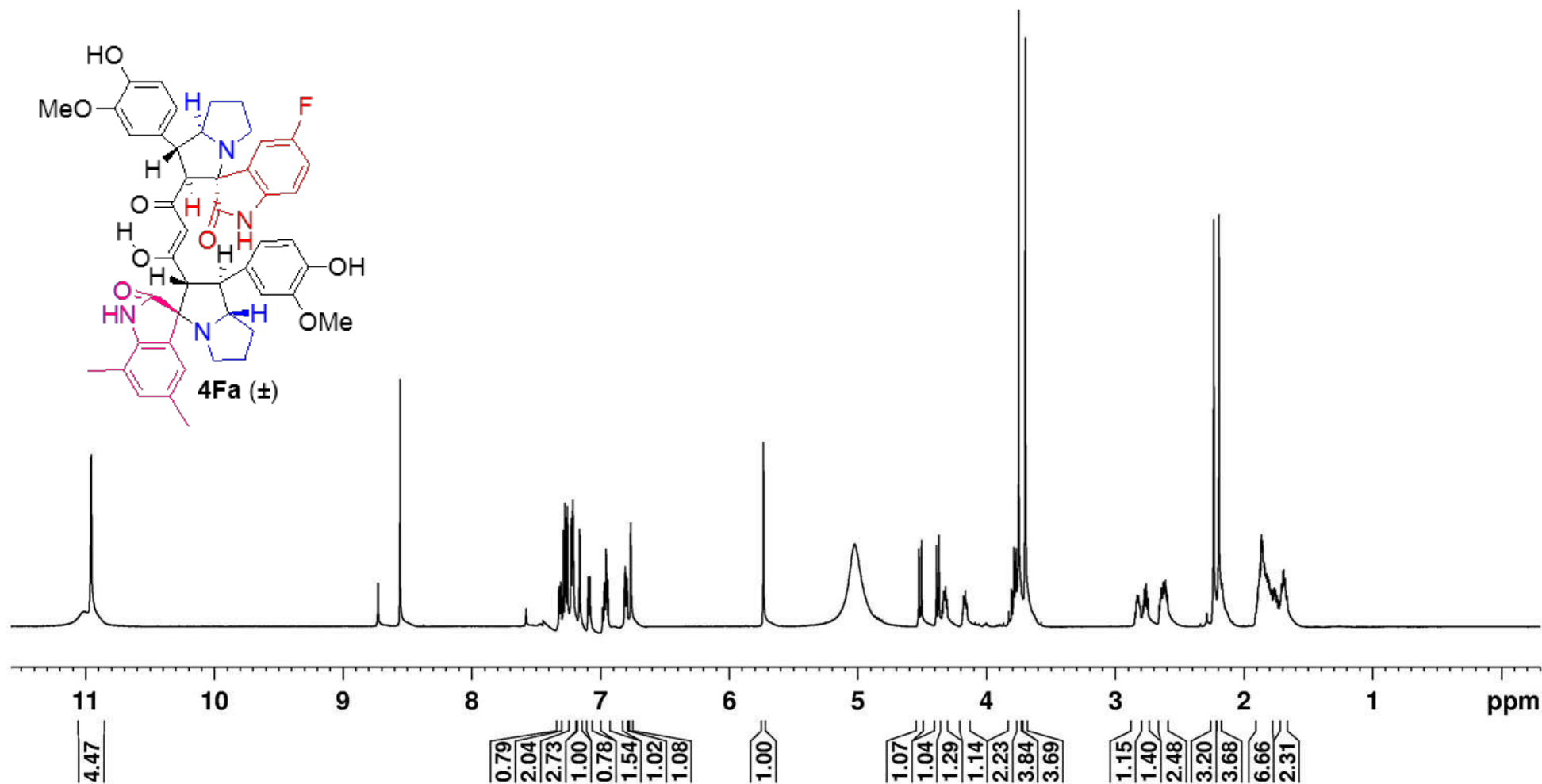
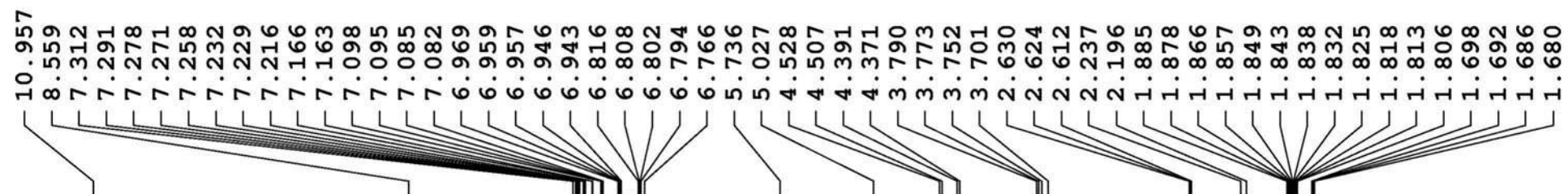


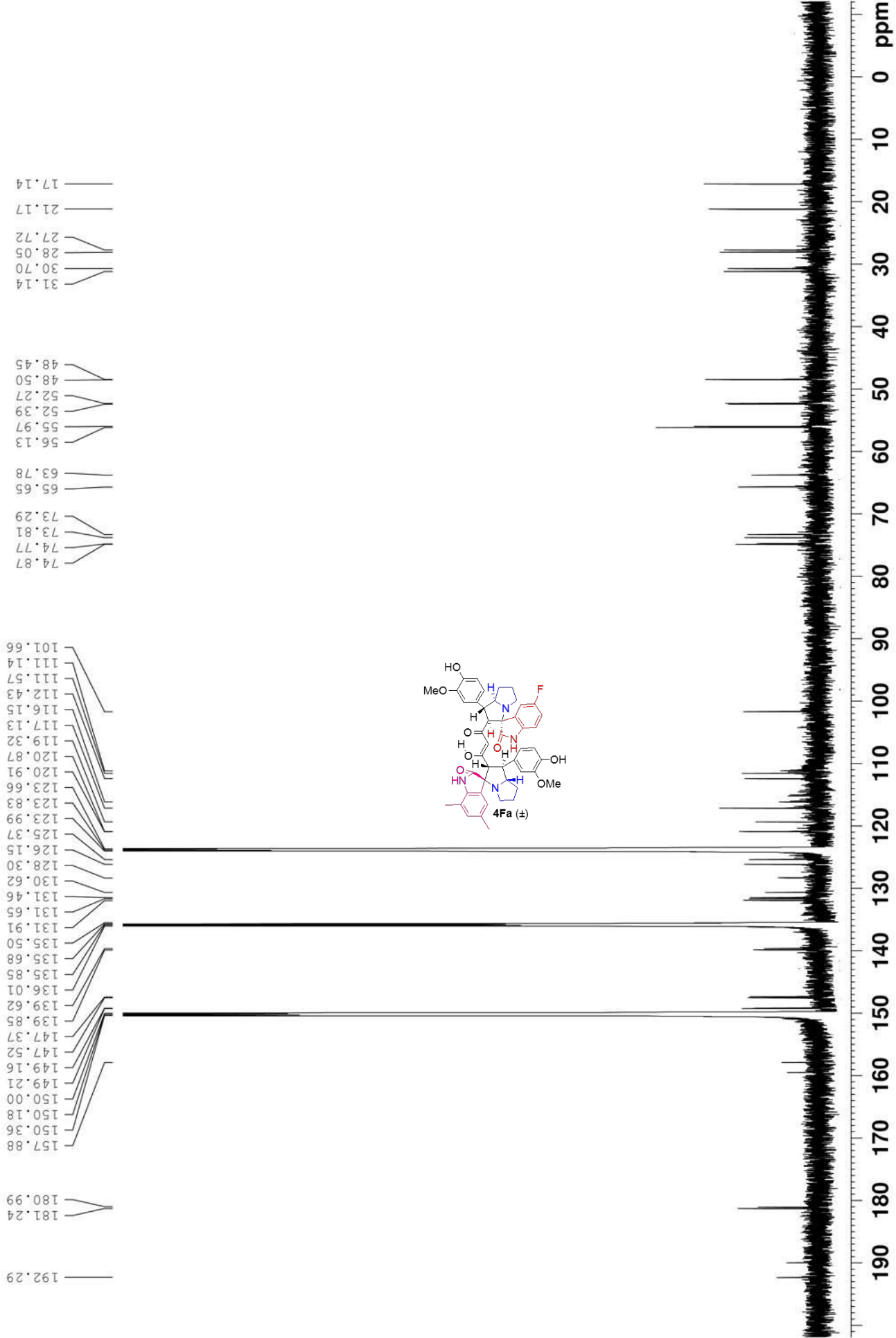
¹³C-NMR in Py-d₅

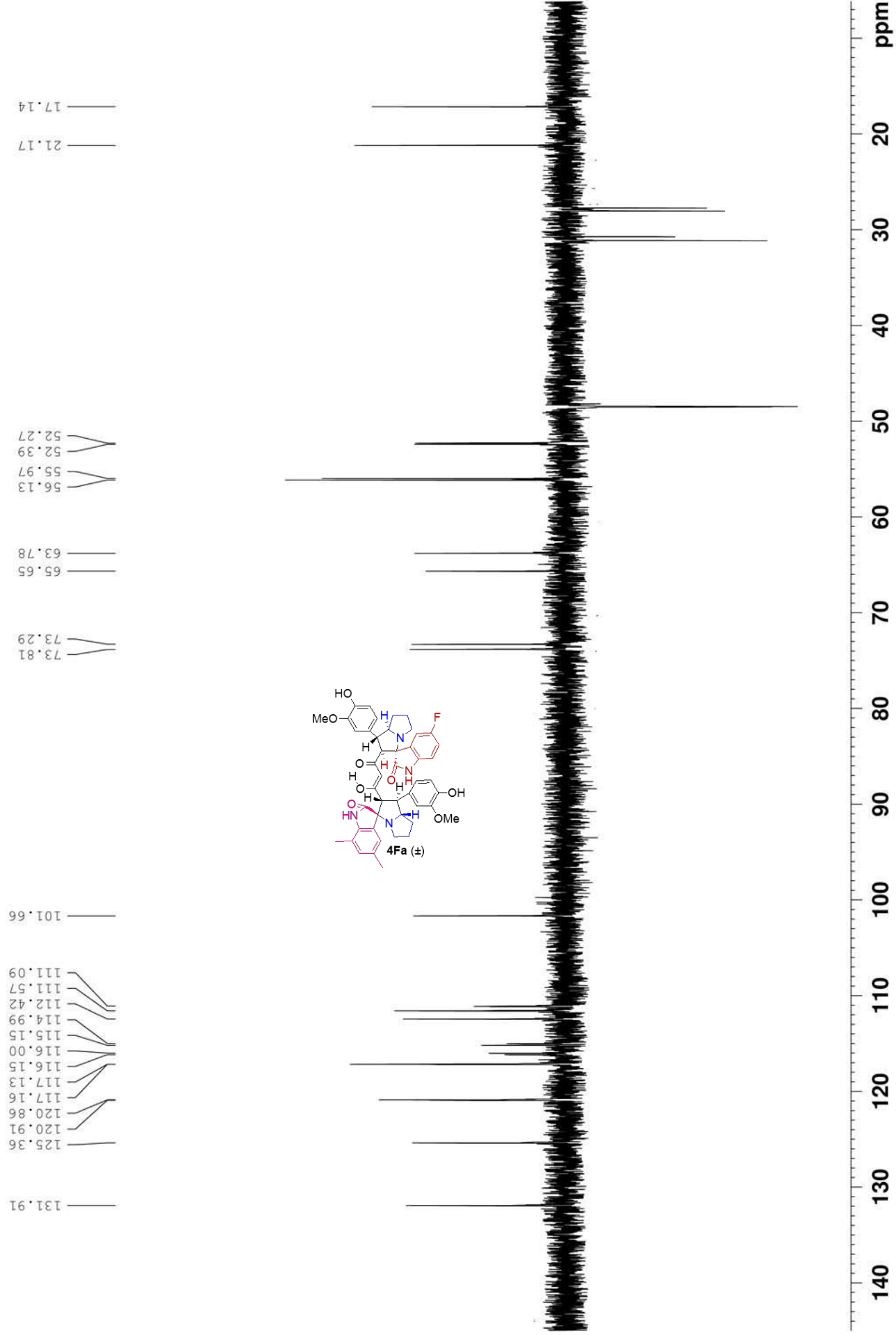




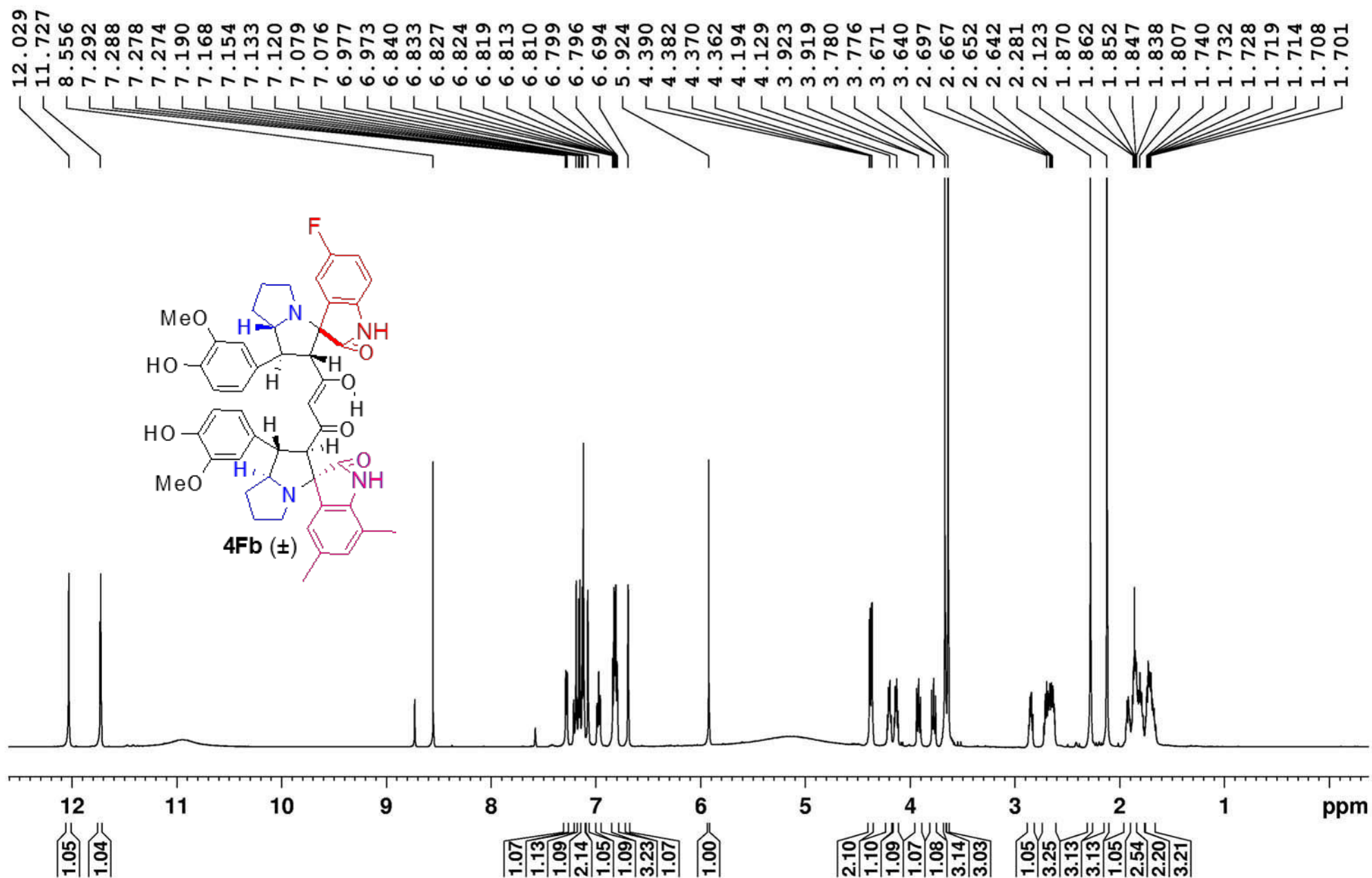
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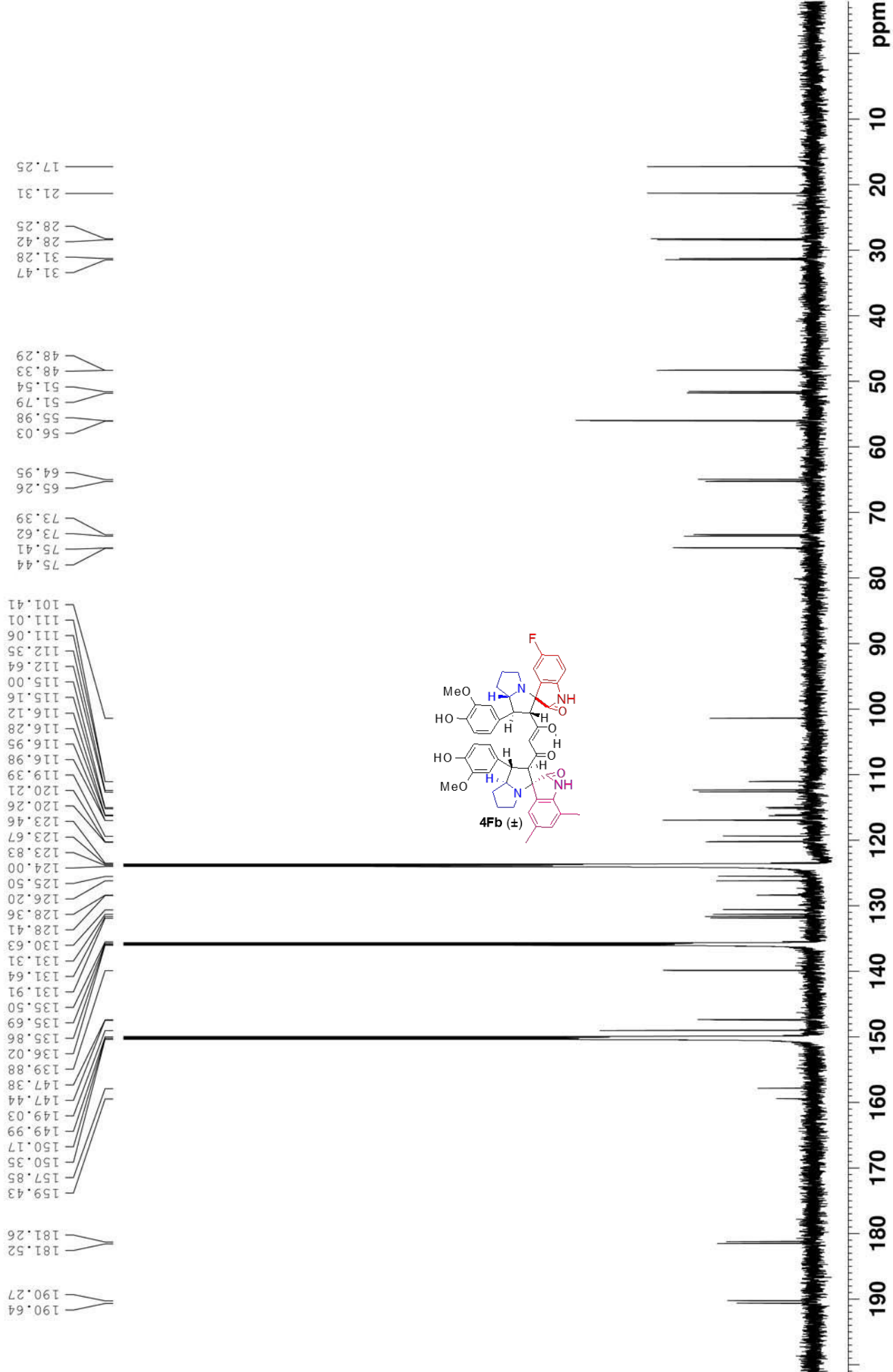


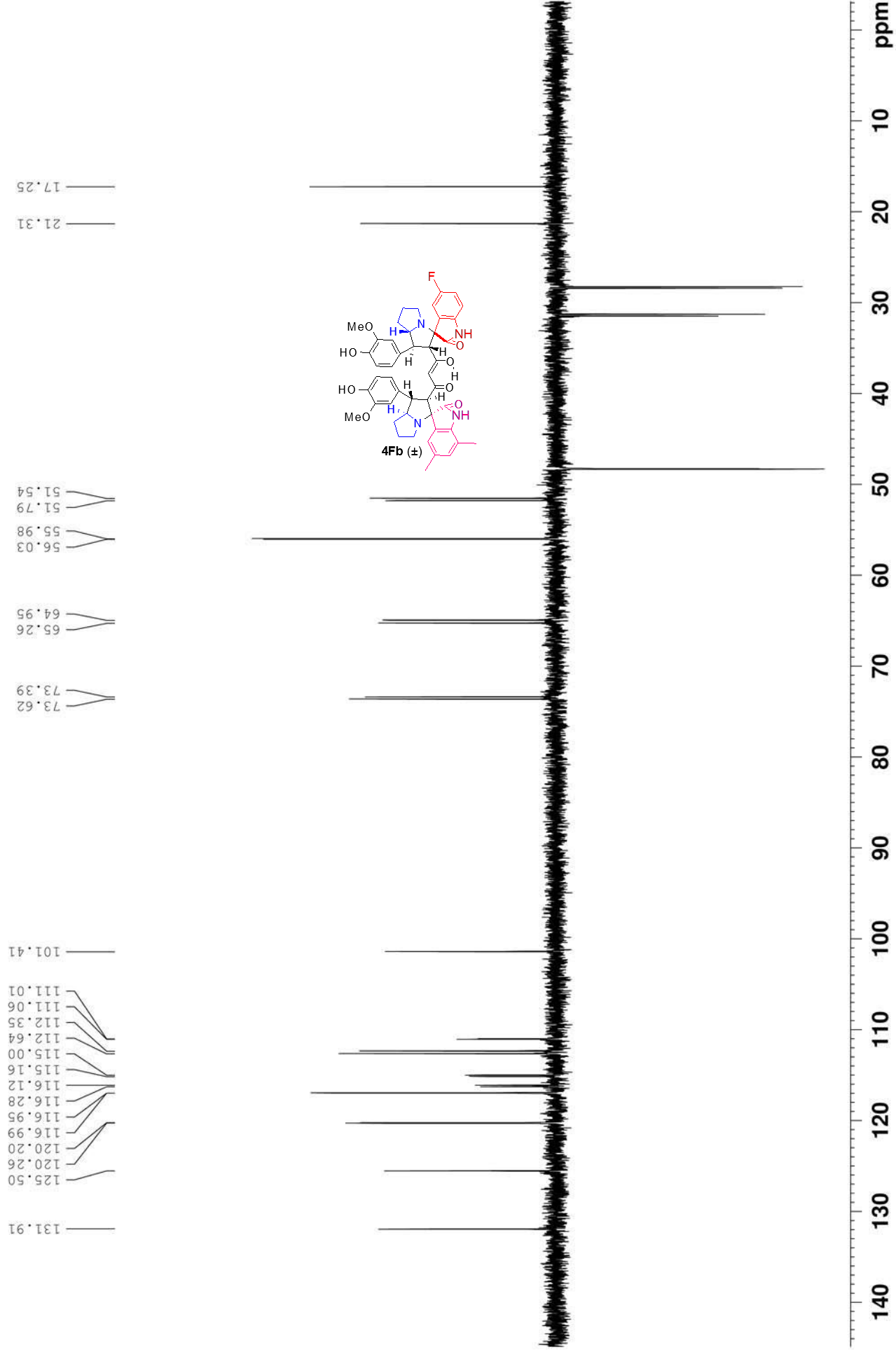




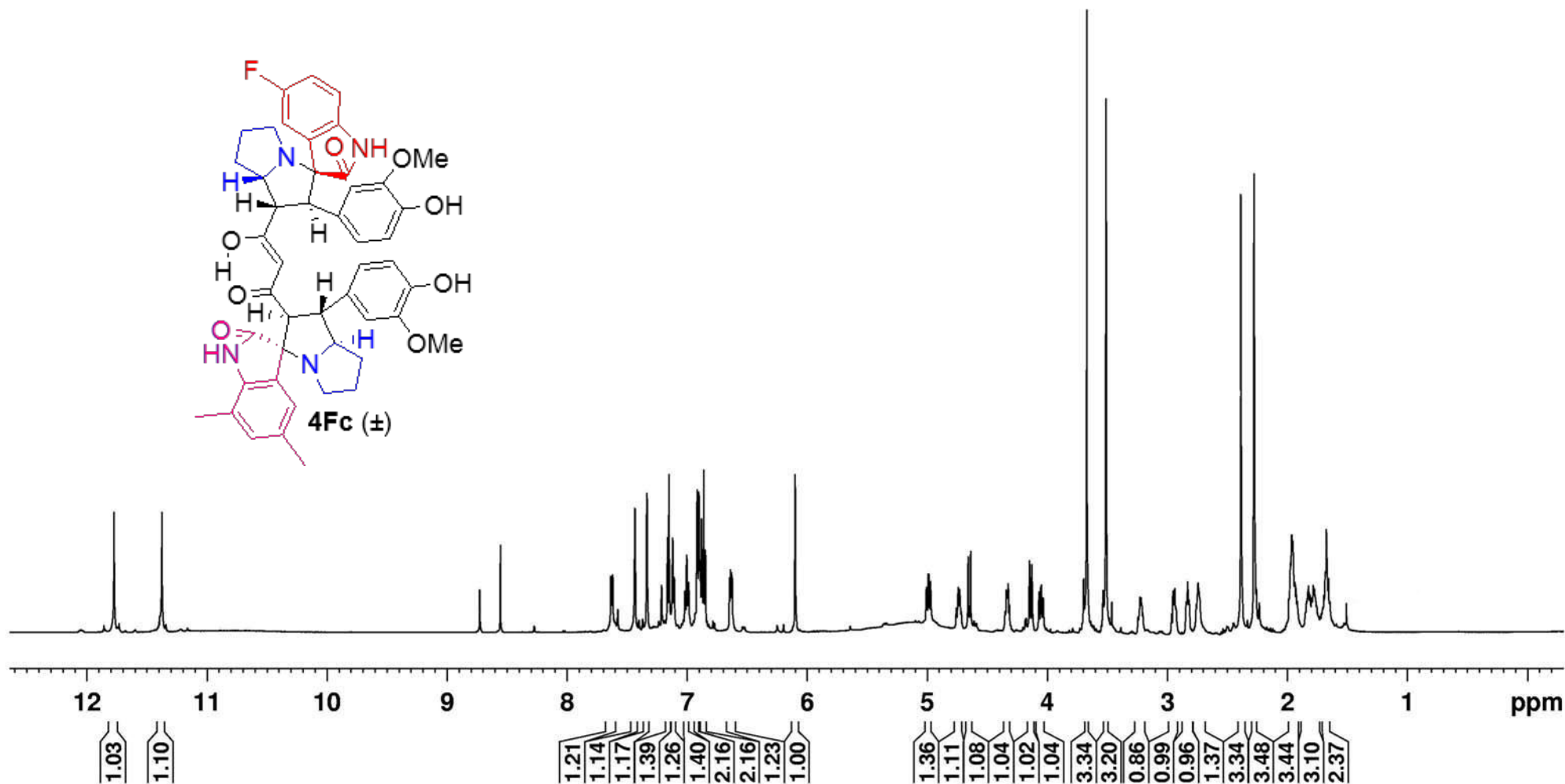
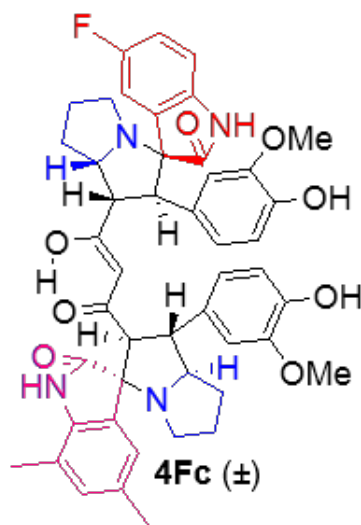
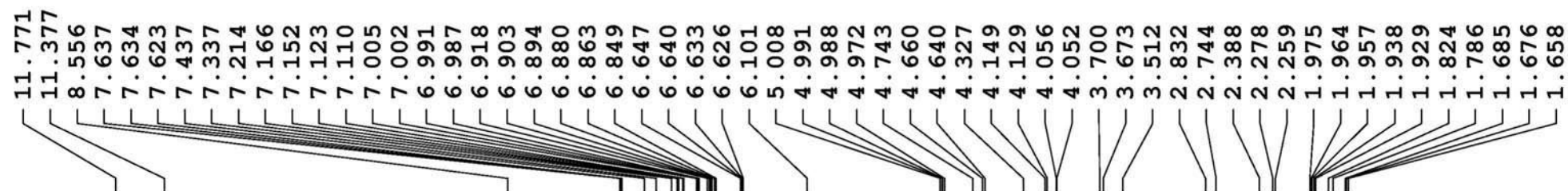
¹H NMR in Py-d₅

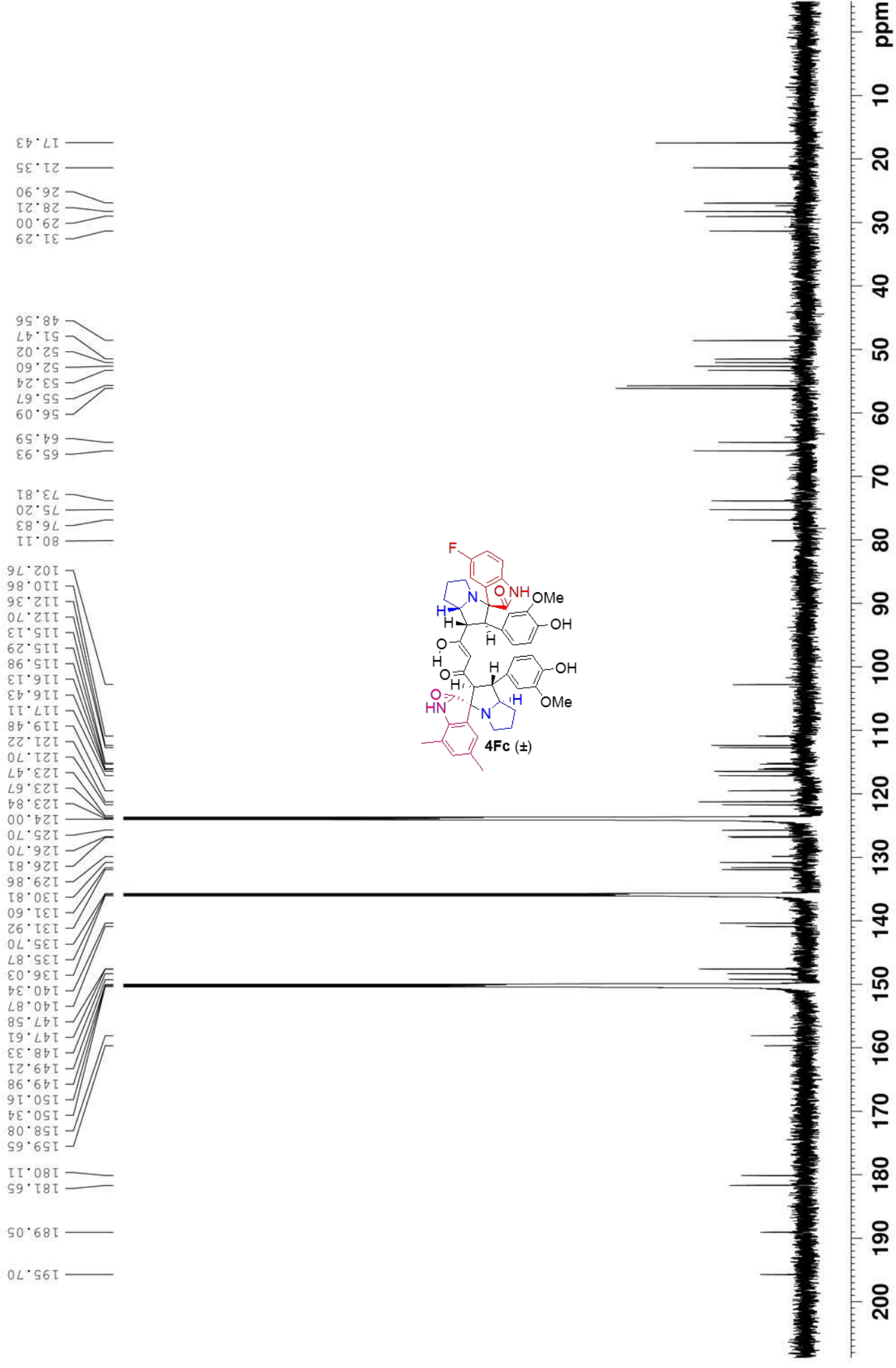


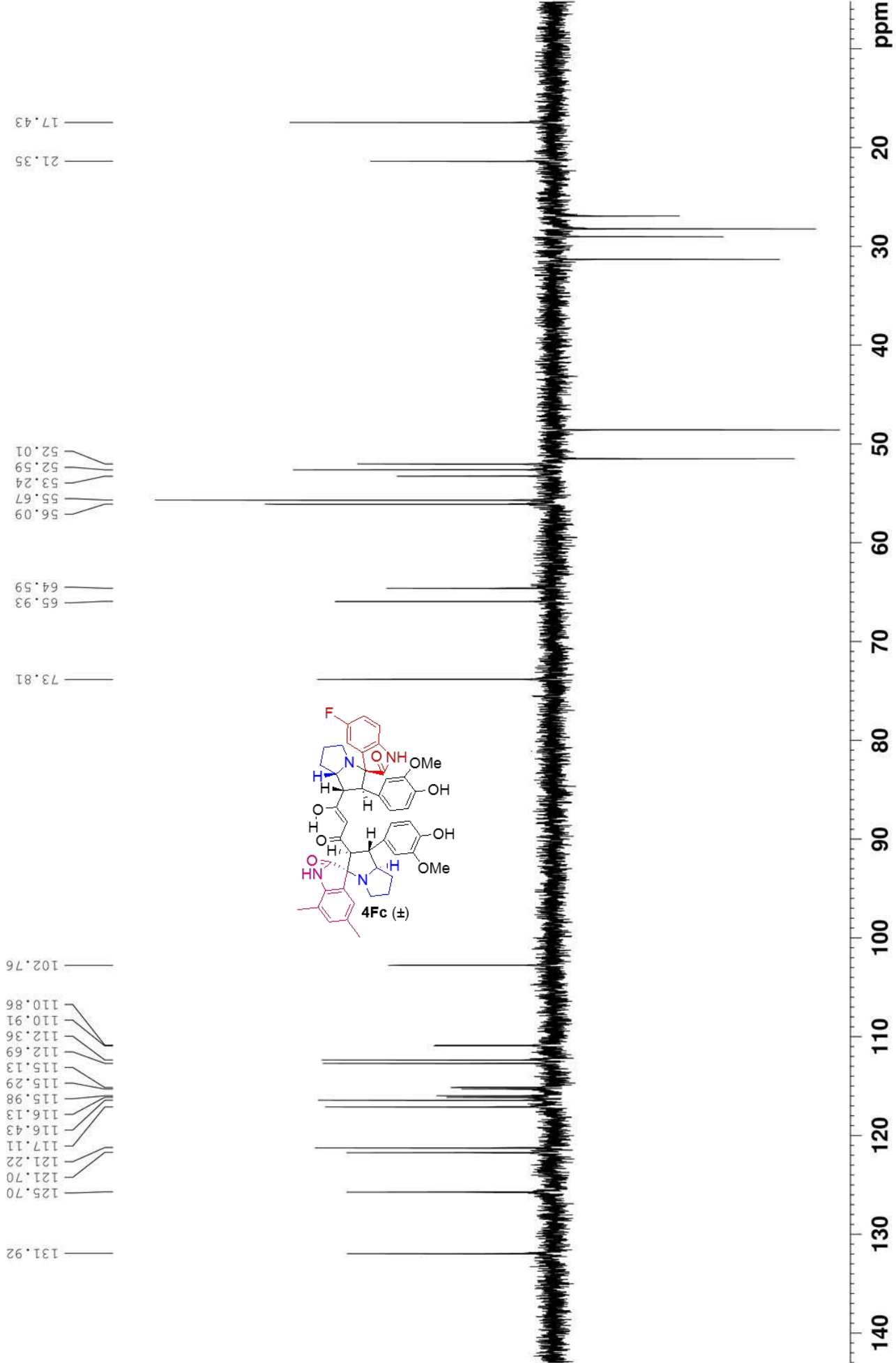


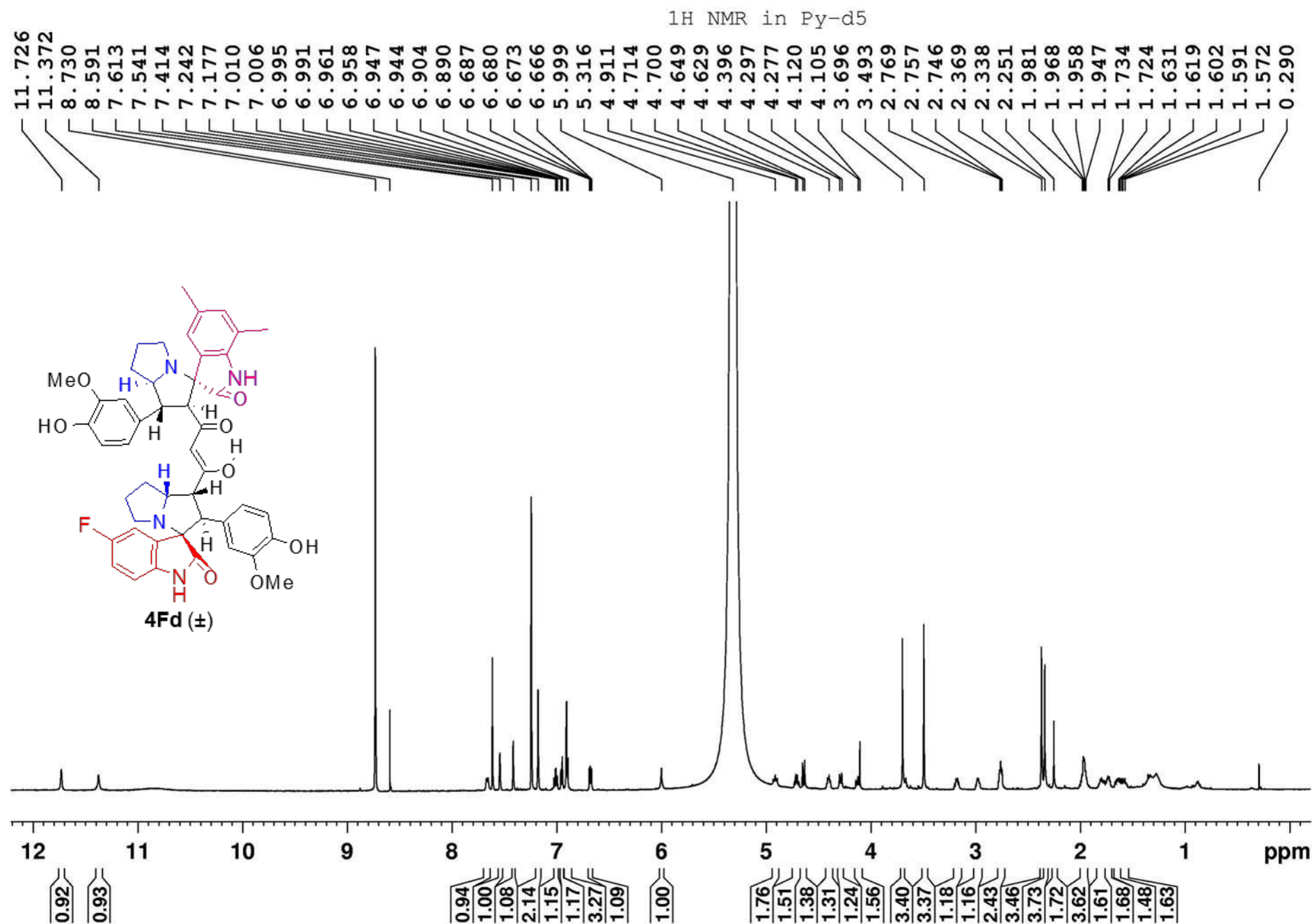


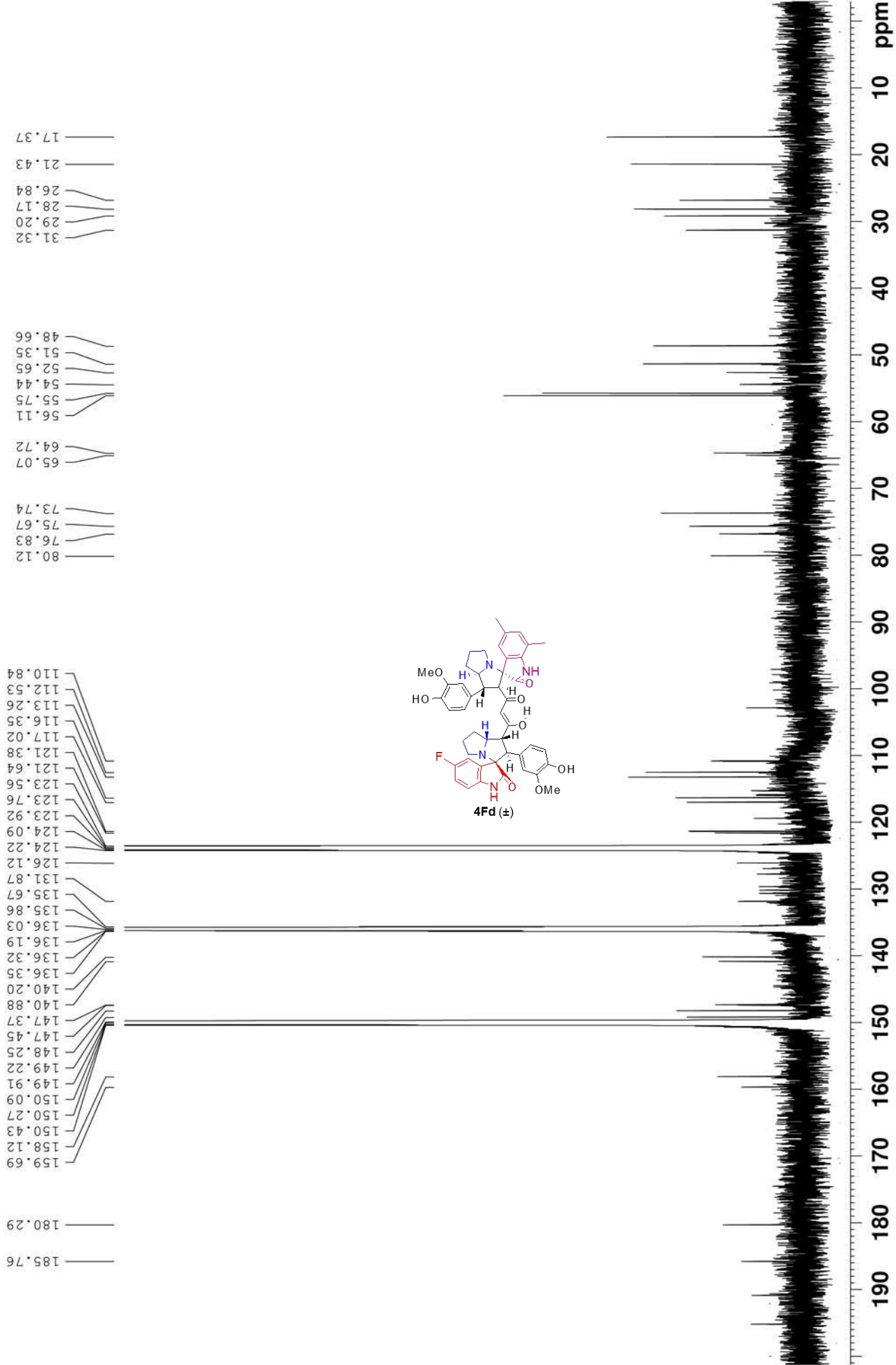
¹H NMR in Py-d₅



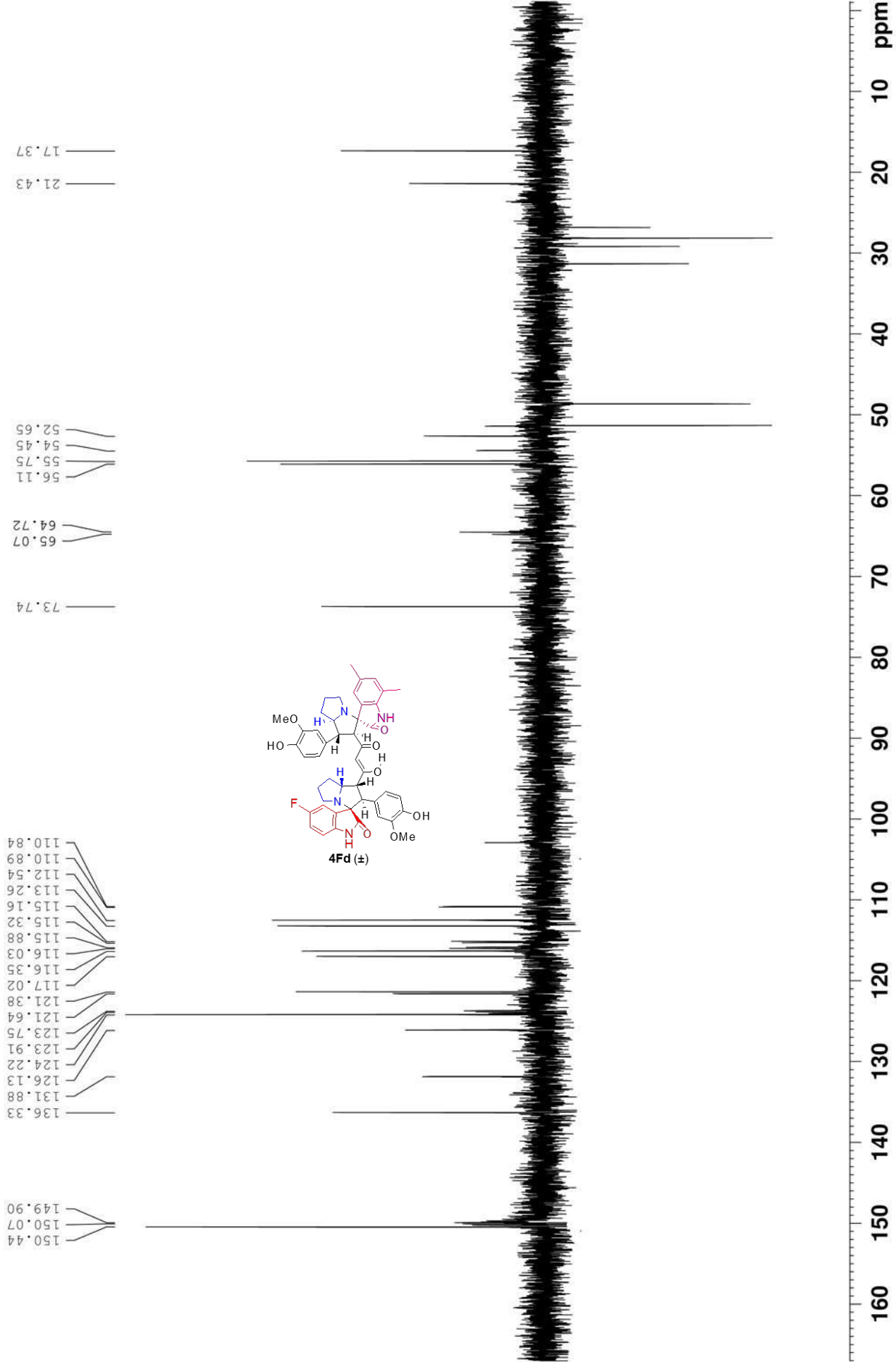


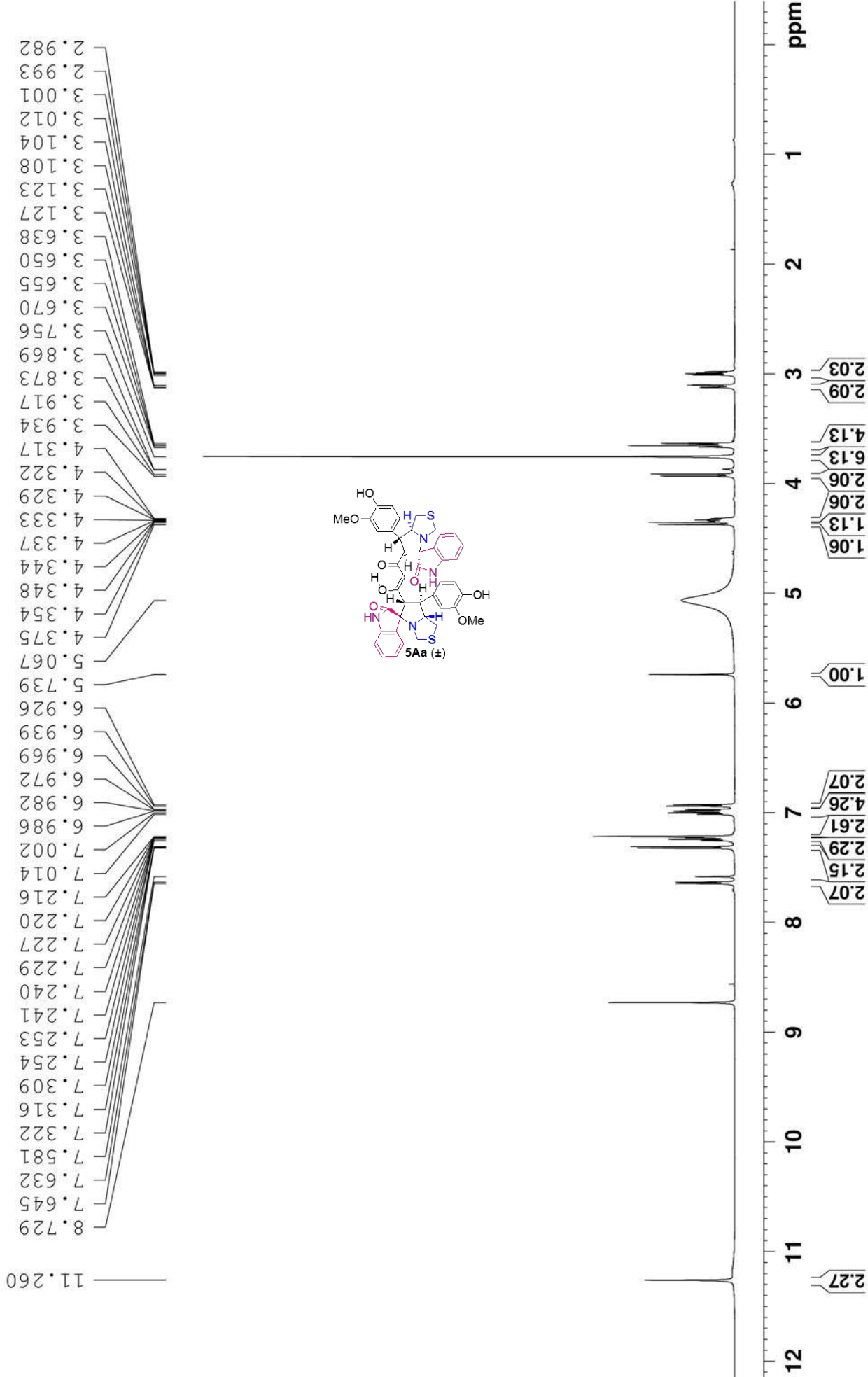


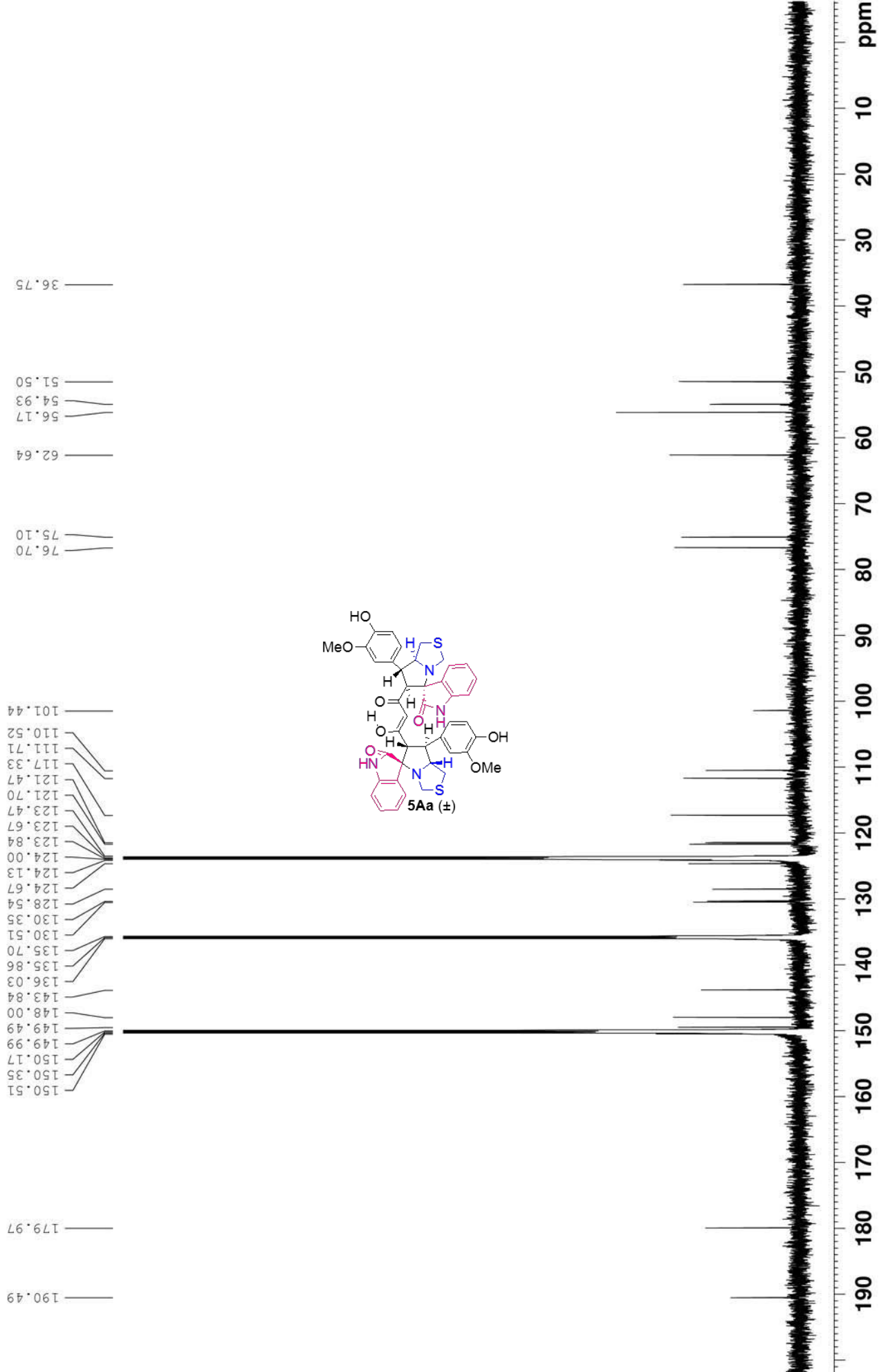




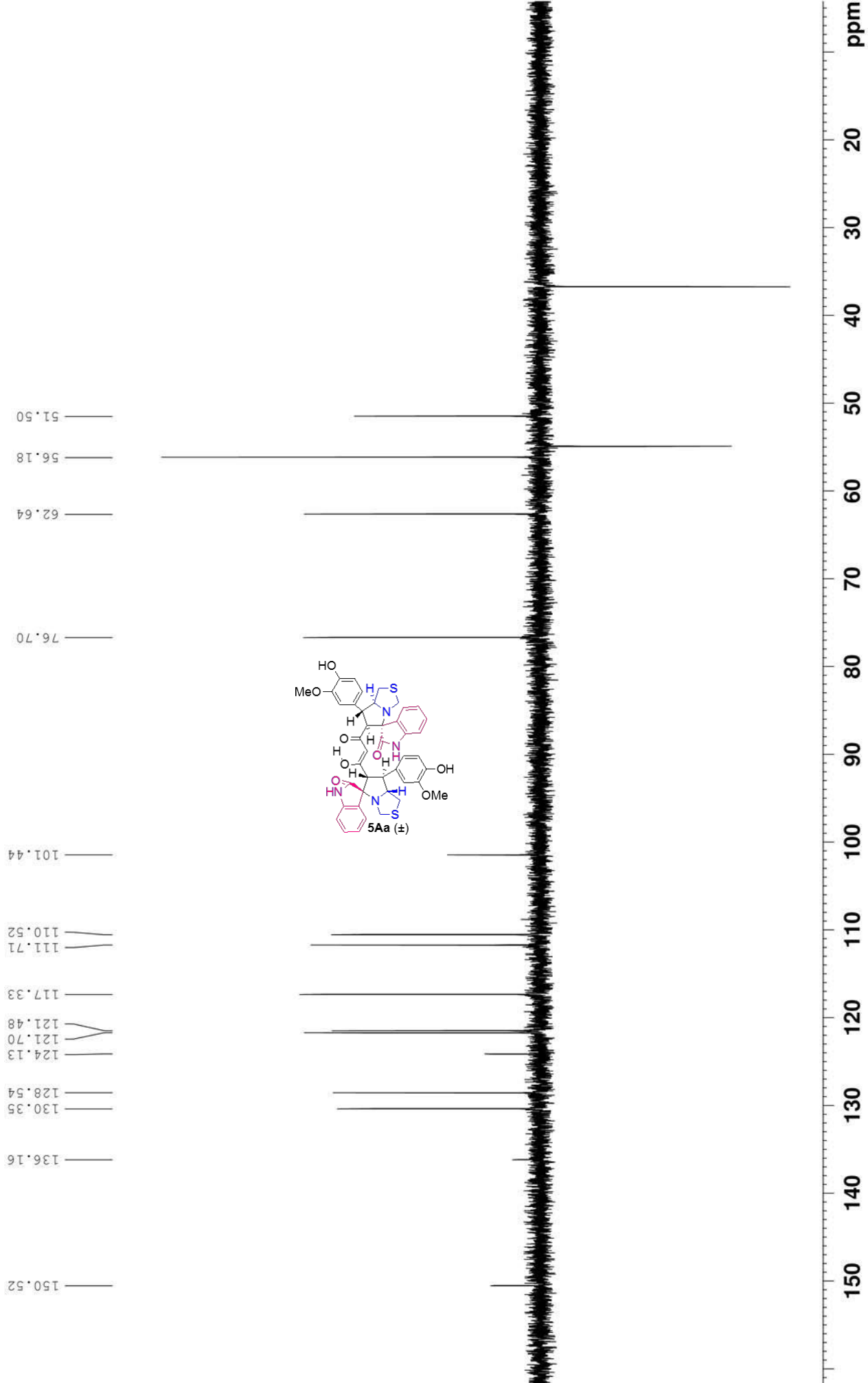
DEPT-135

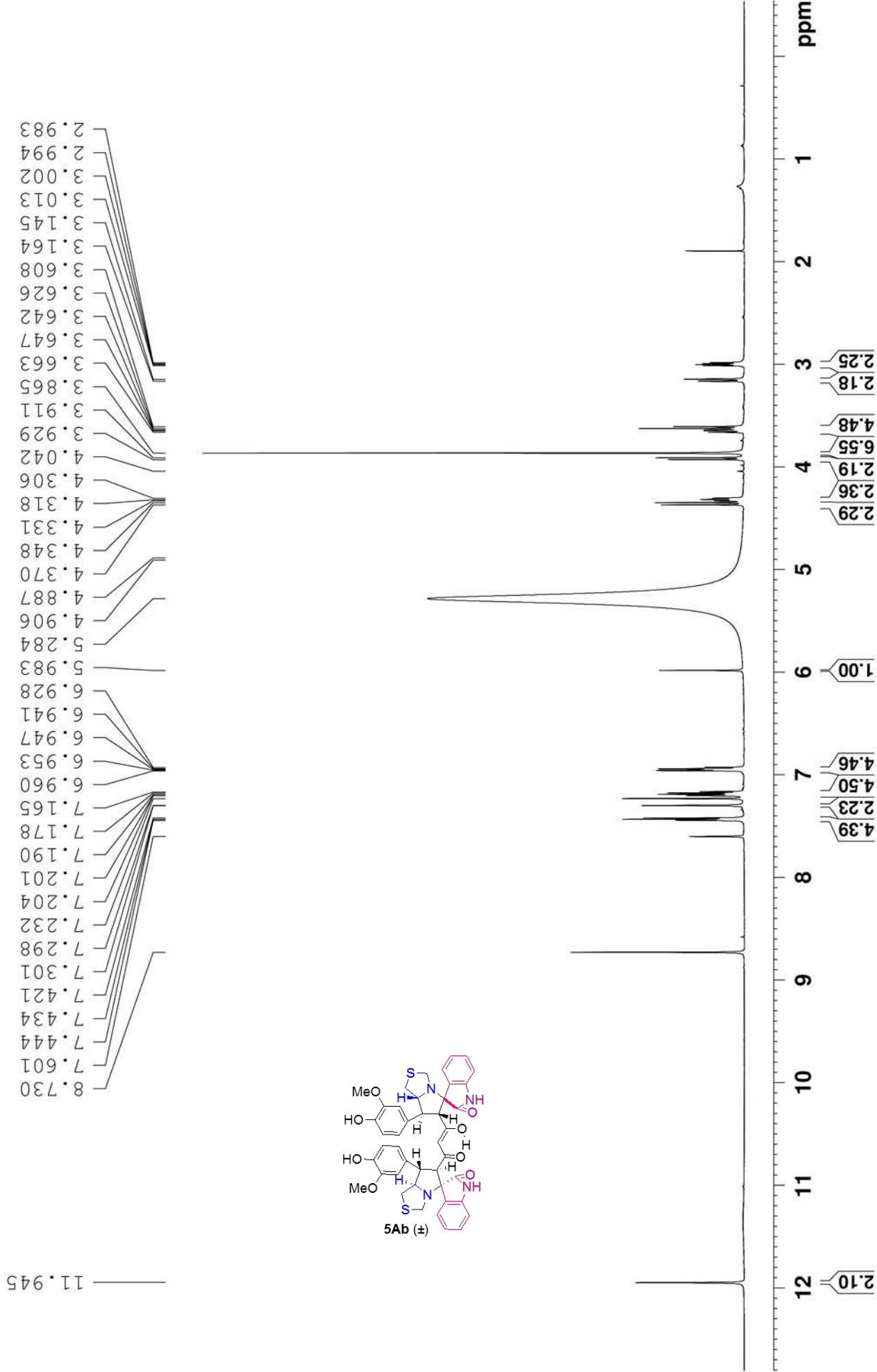
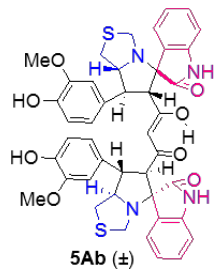


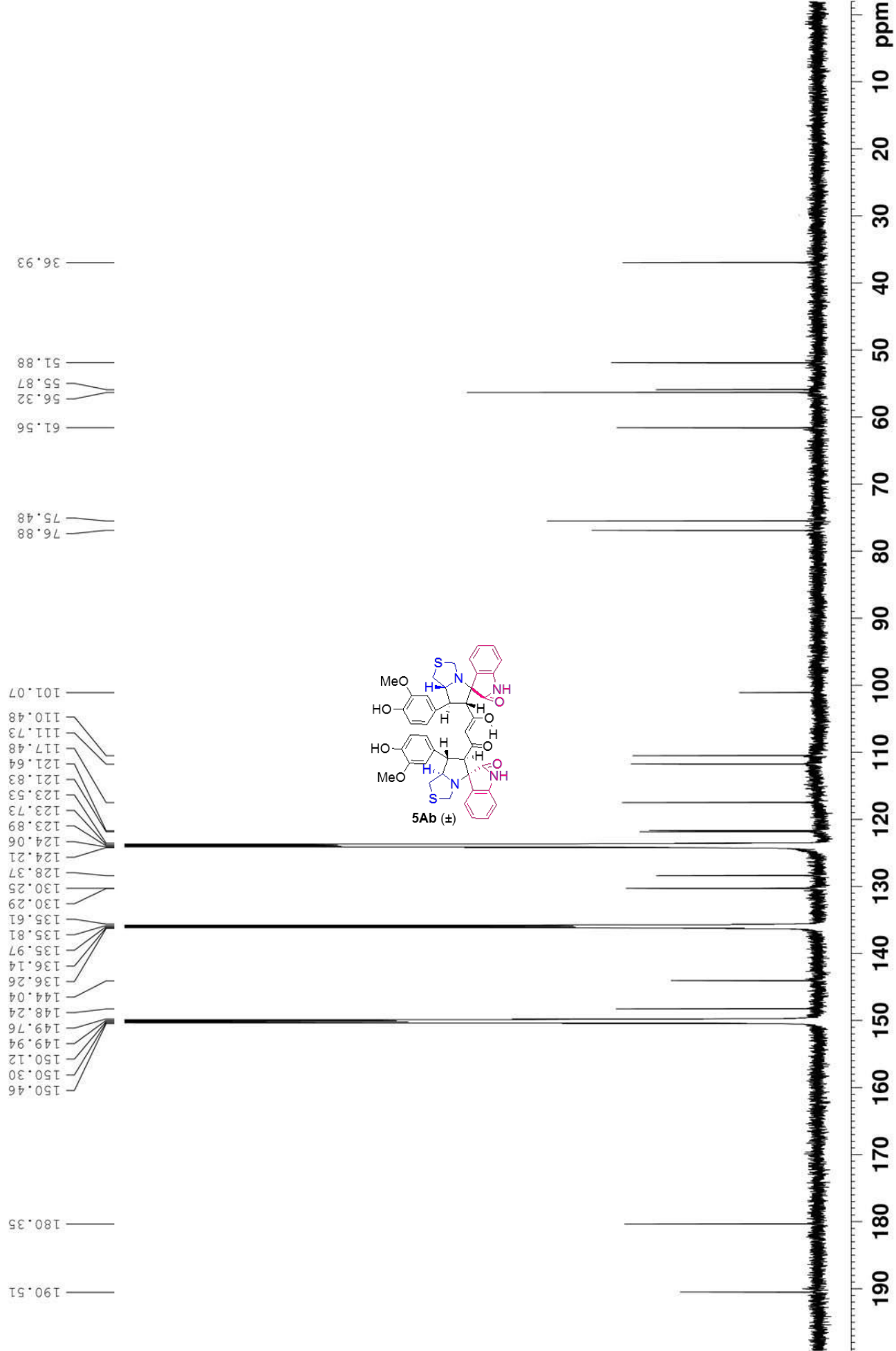


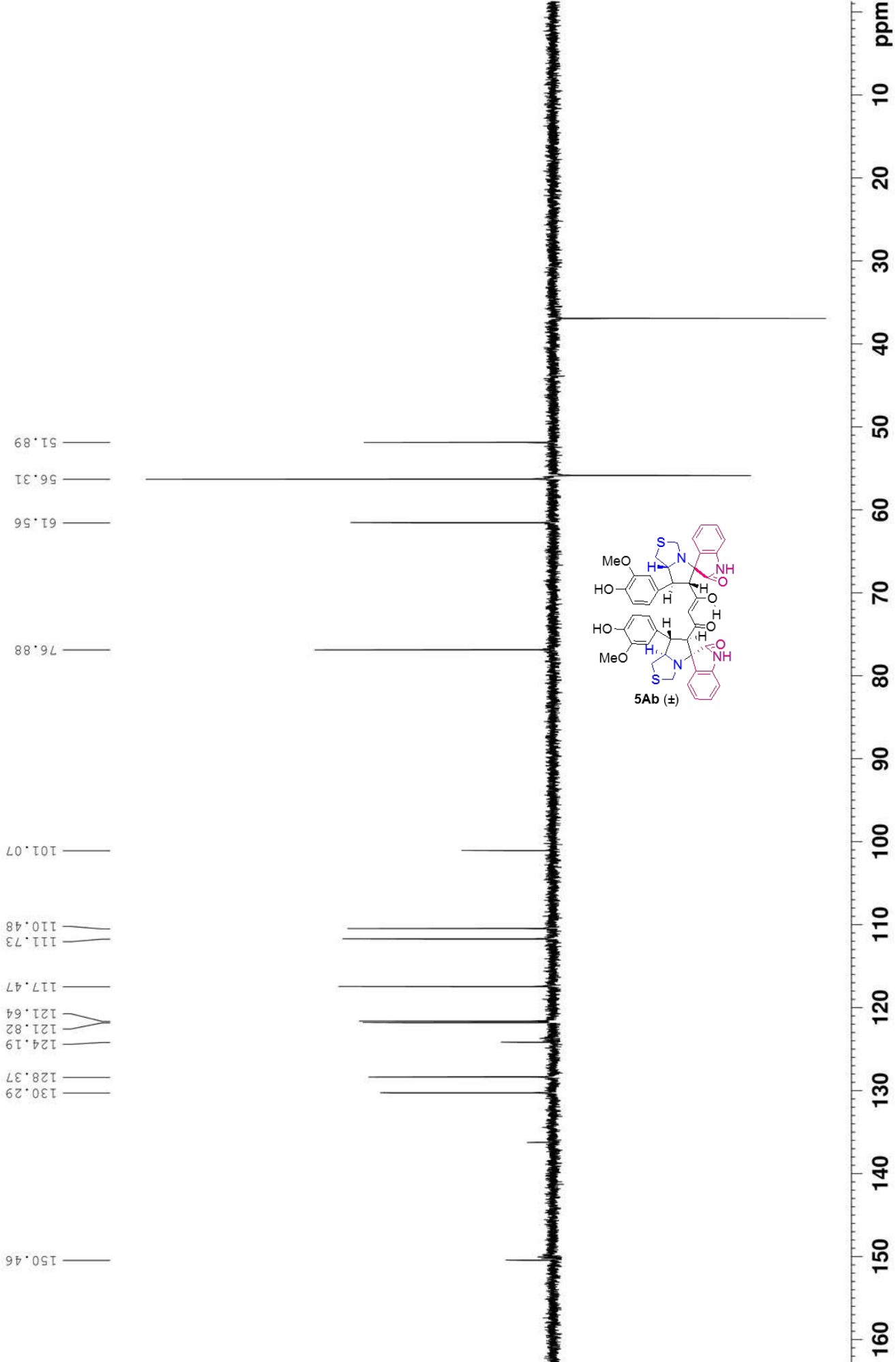


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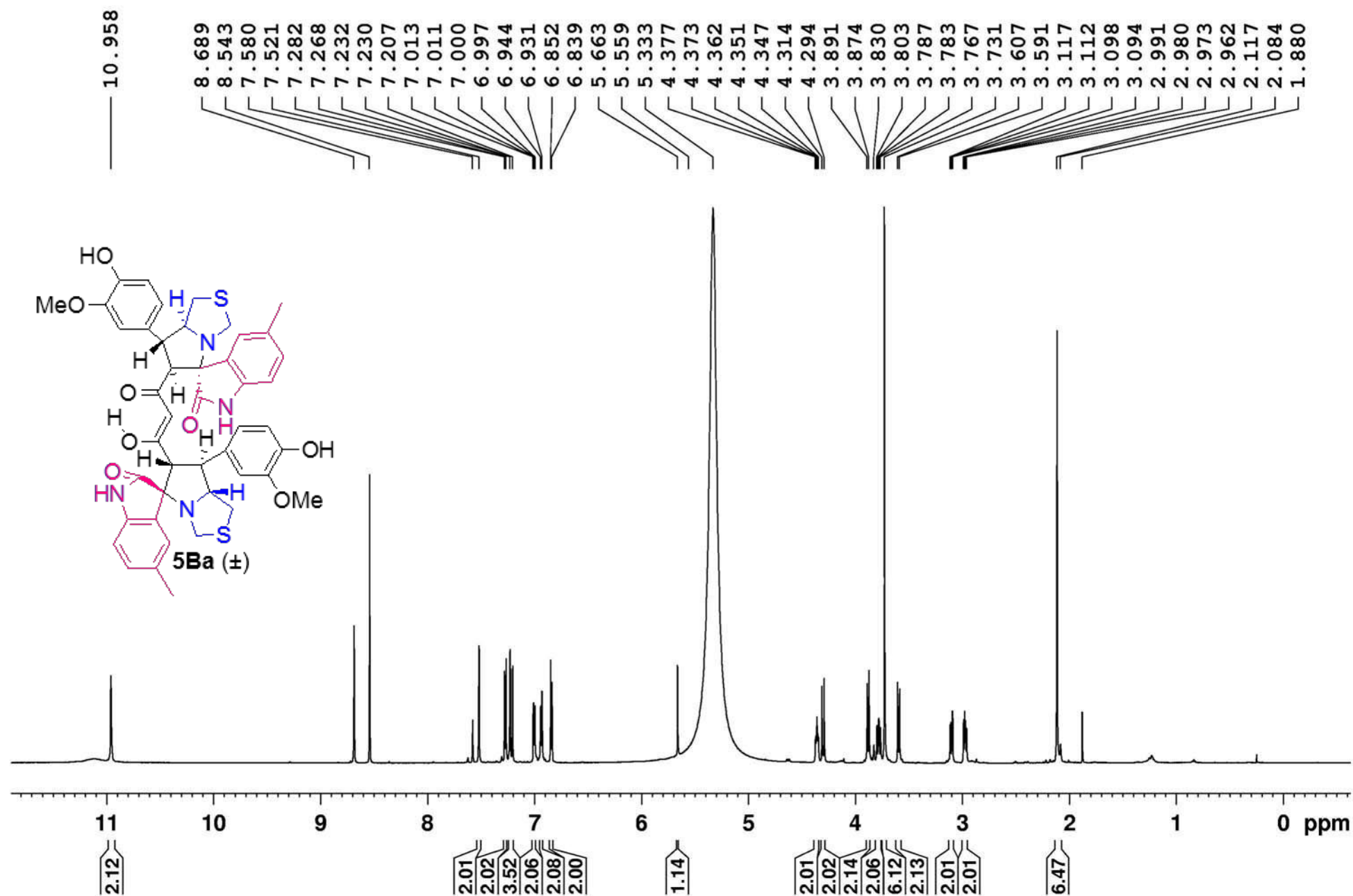




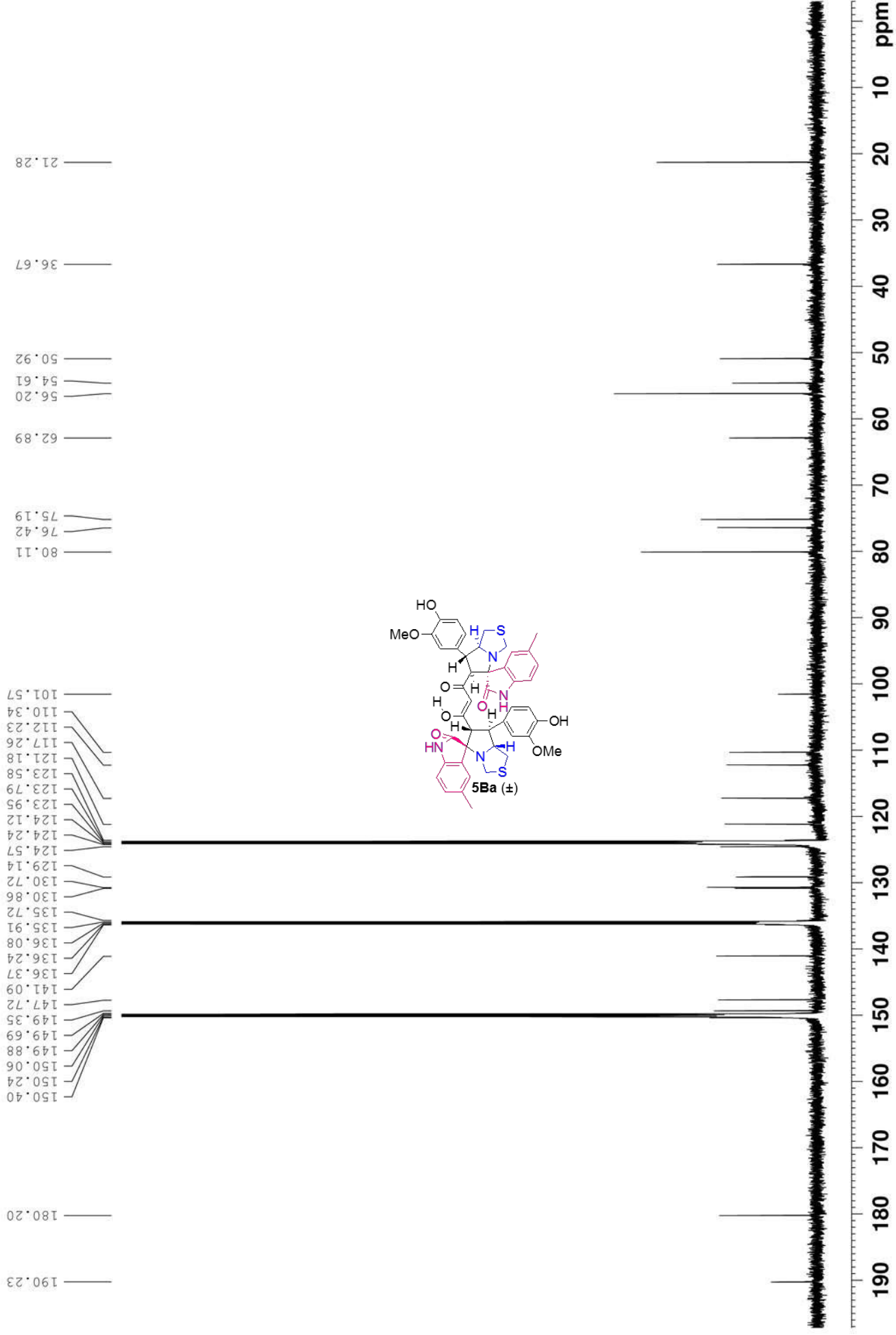


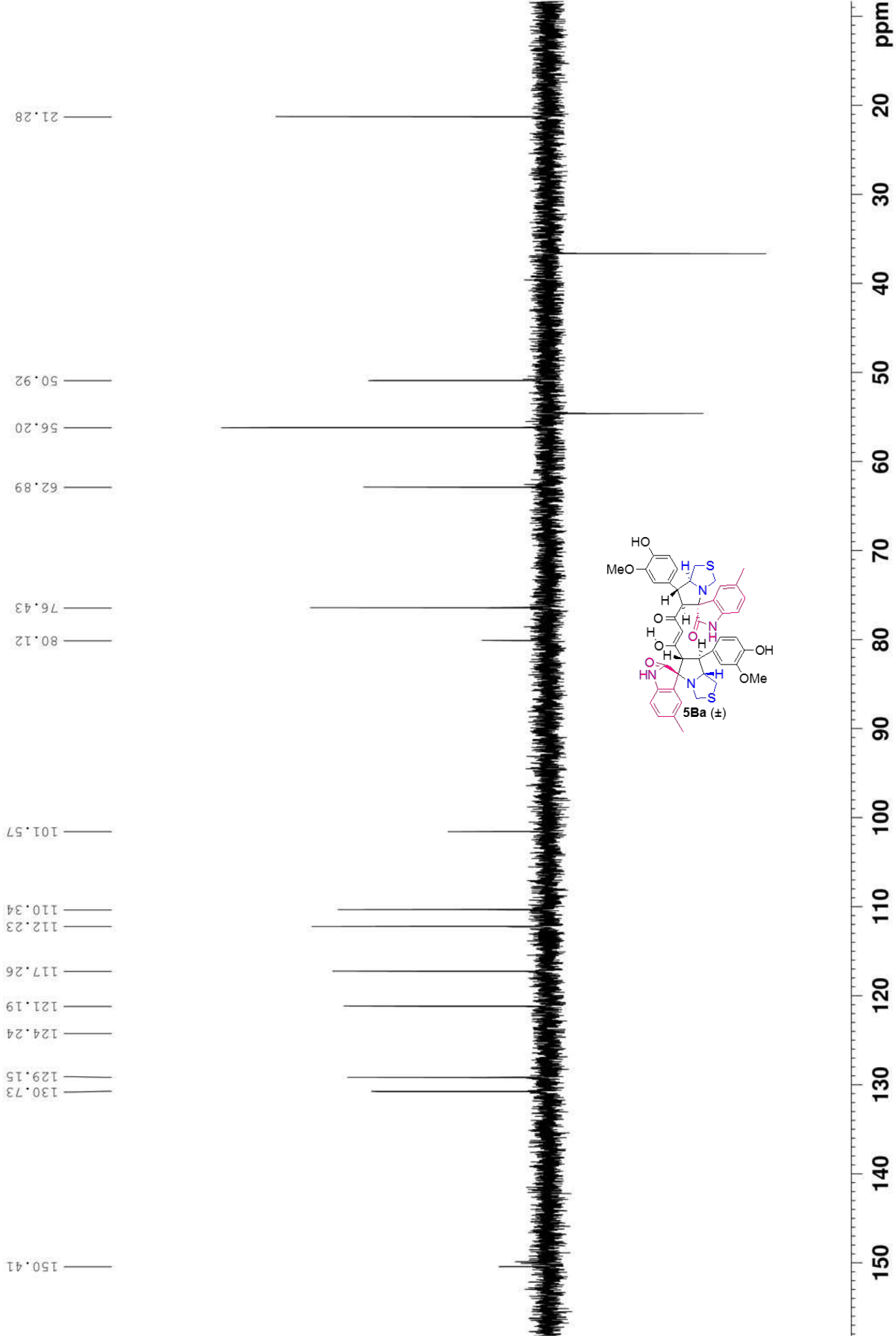


¹H NMR in Py-d₅

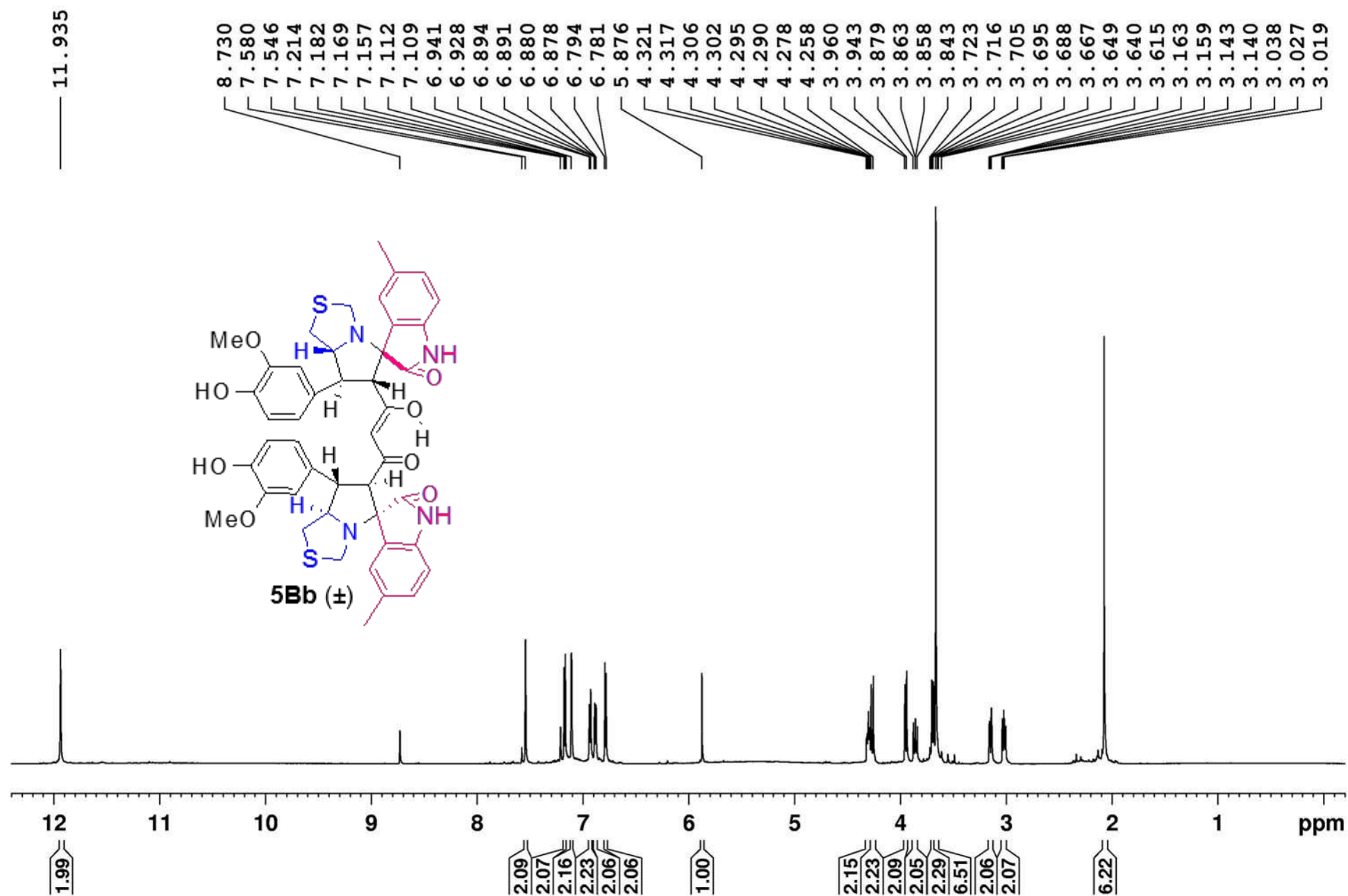


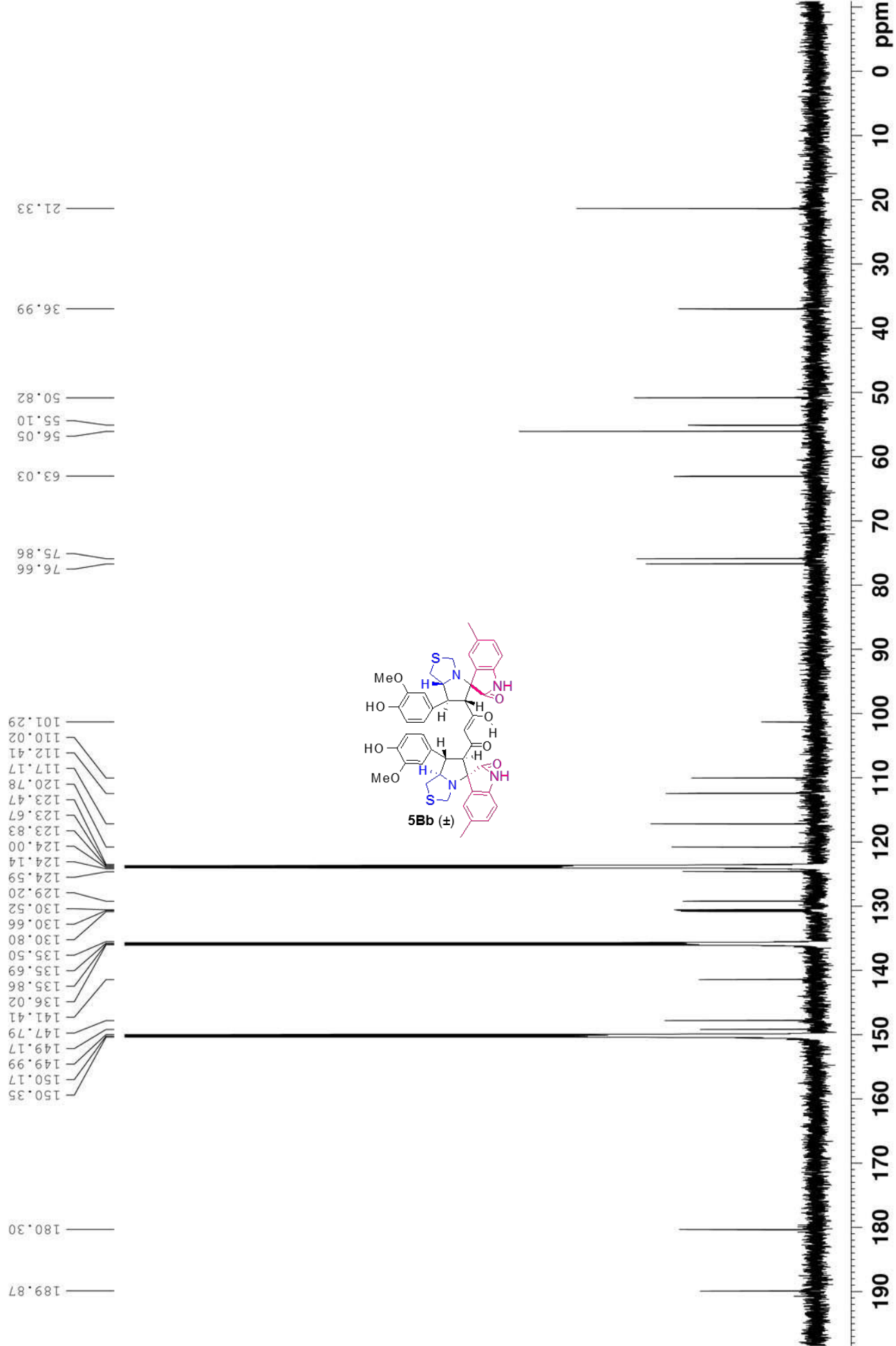
¹³C-NMR in Py-d₅

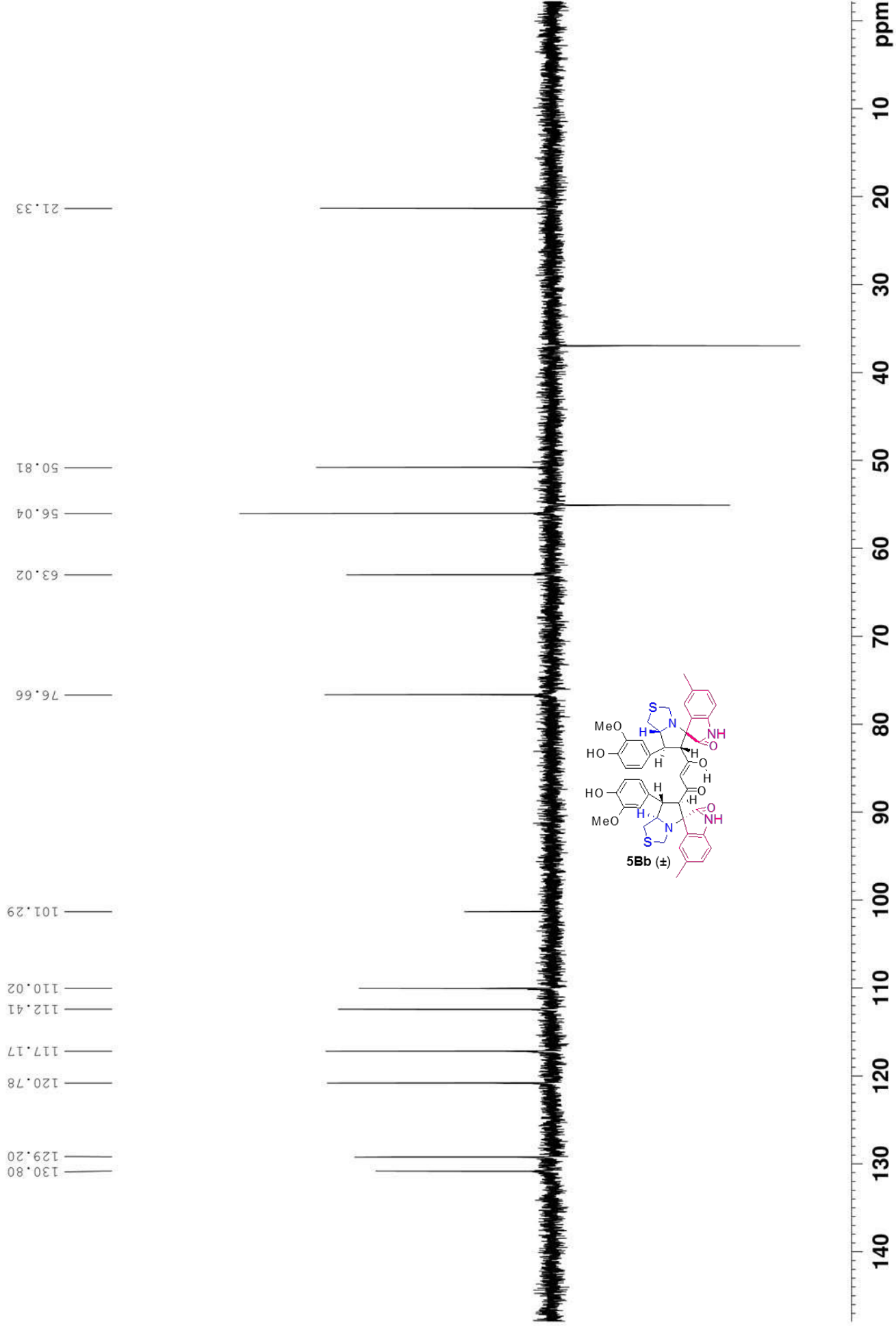


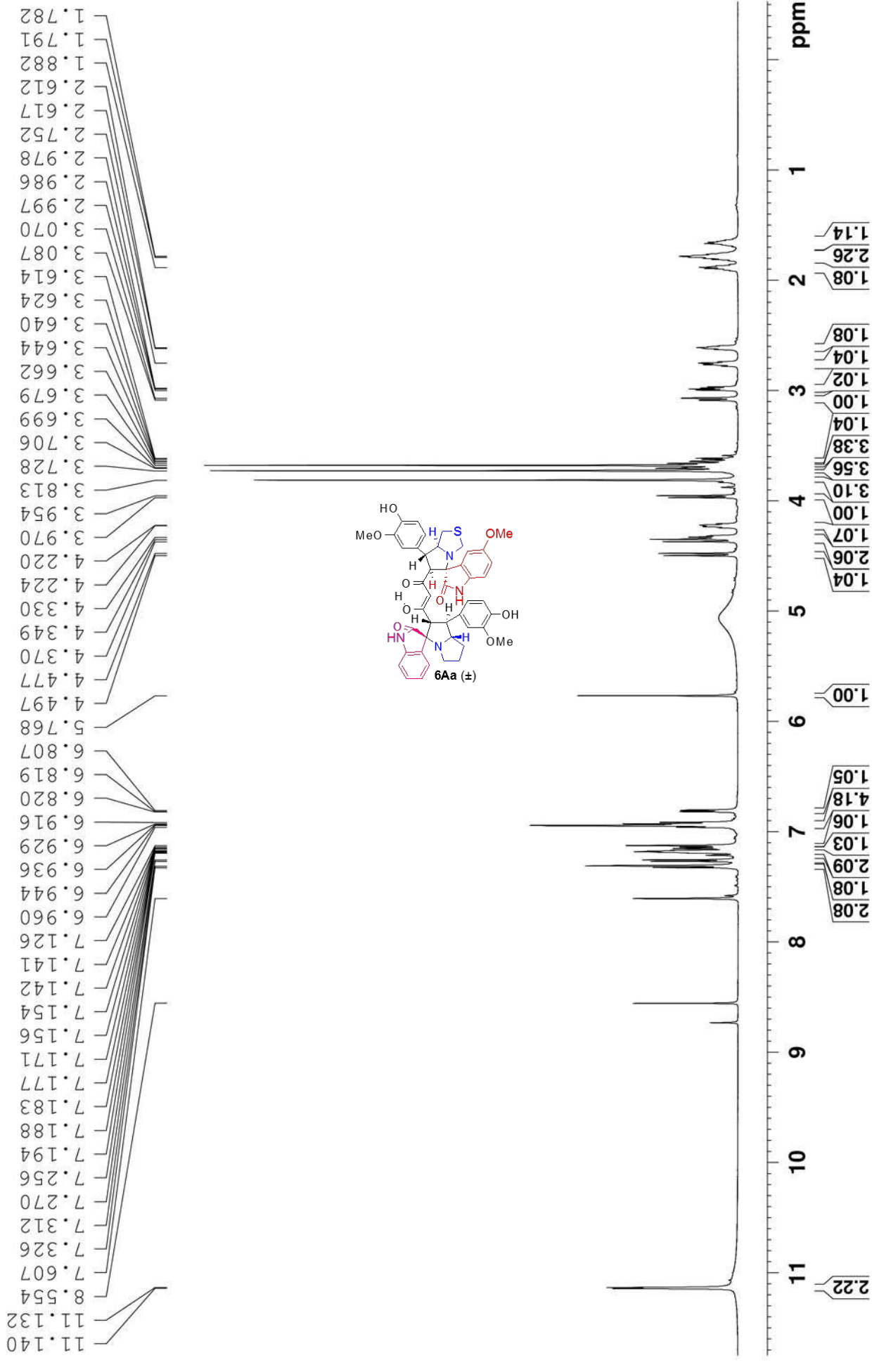


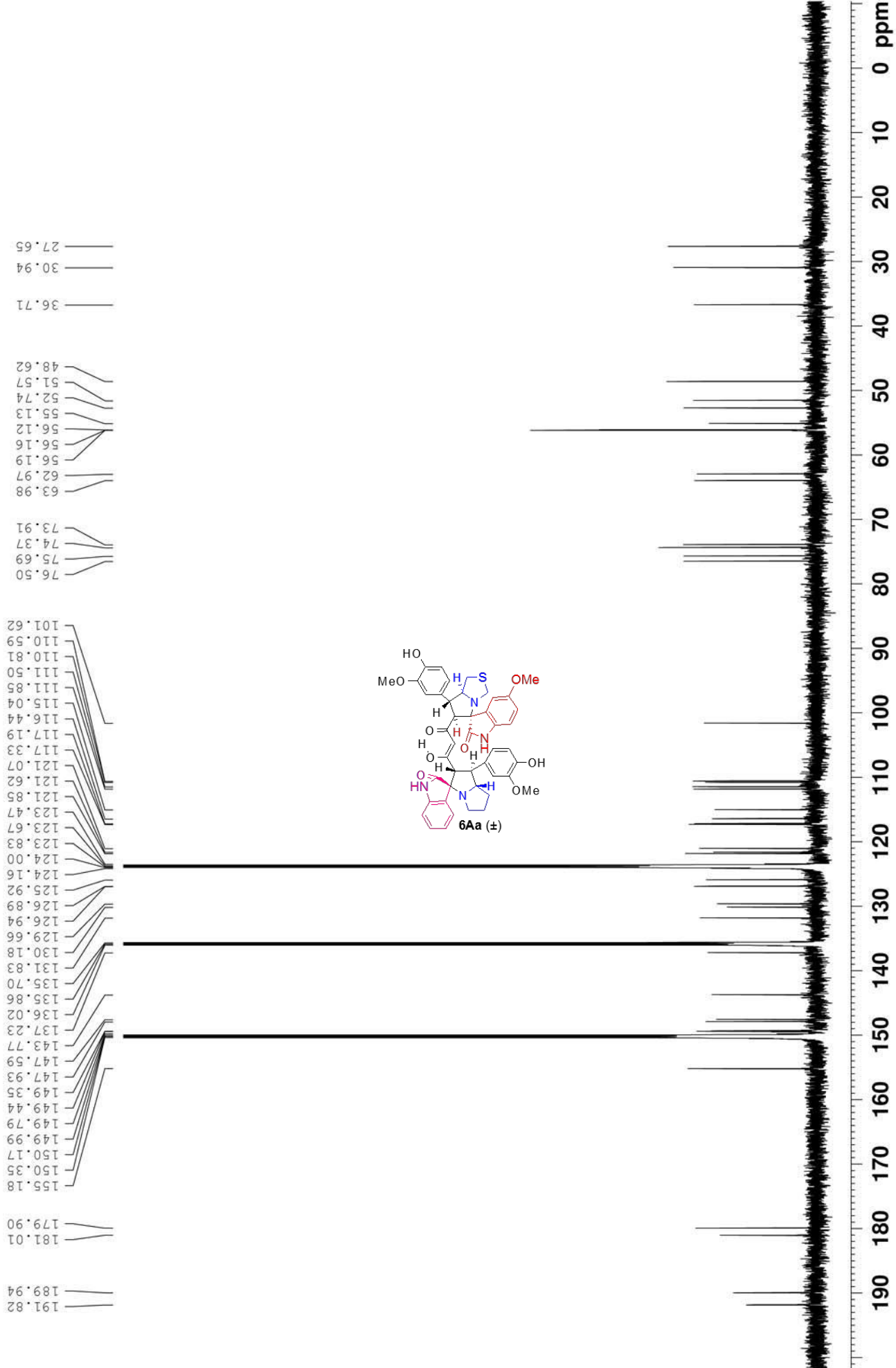
¹H NMR in Py-d₅

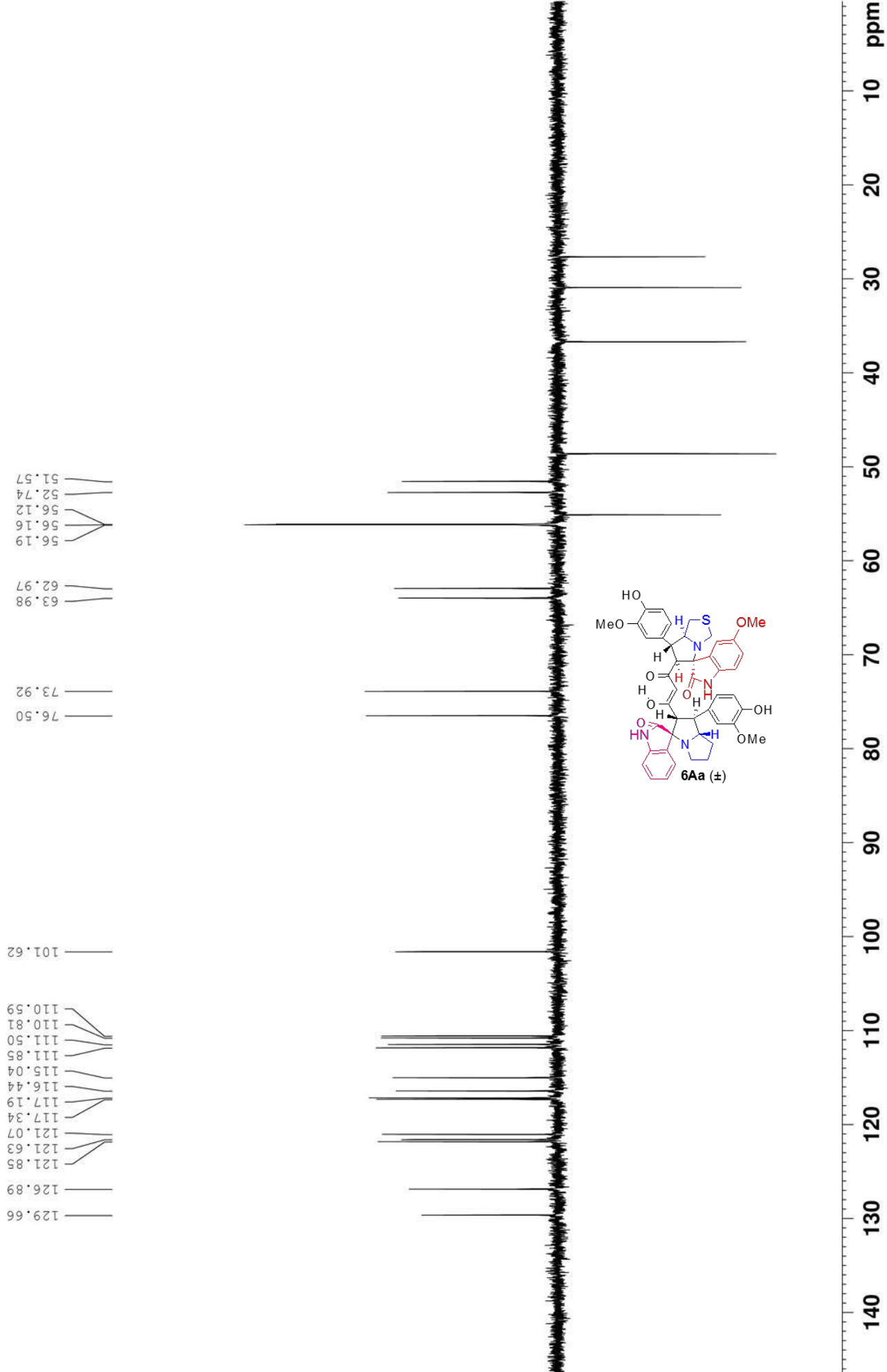




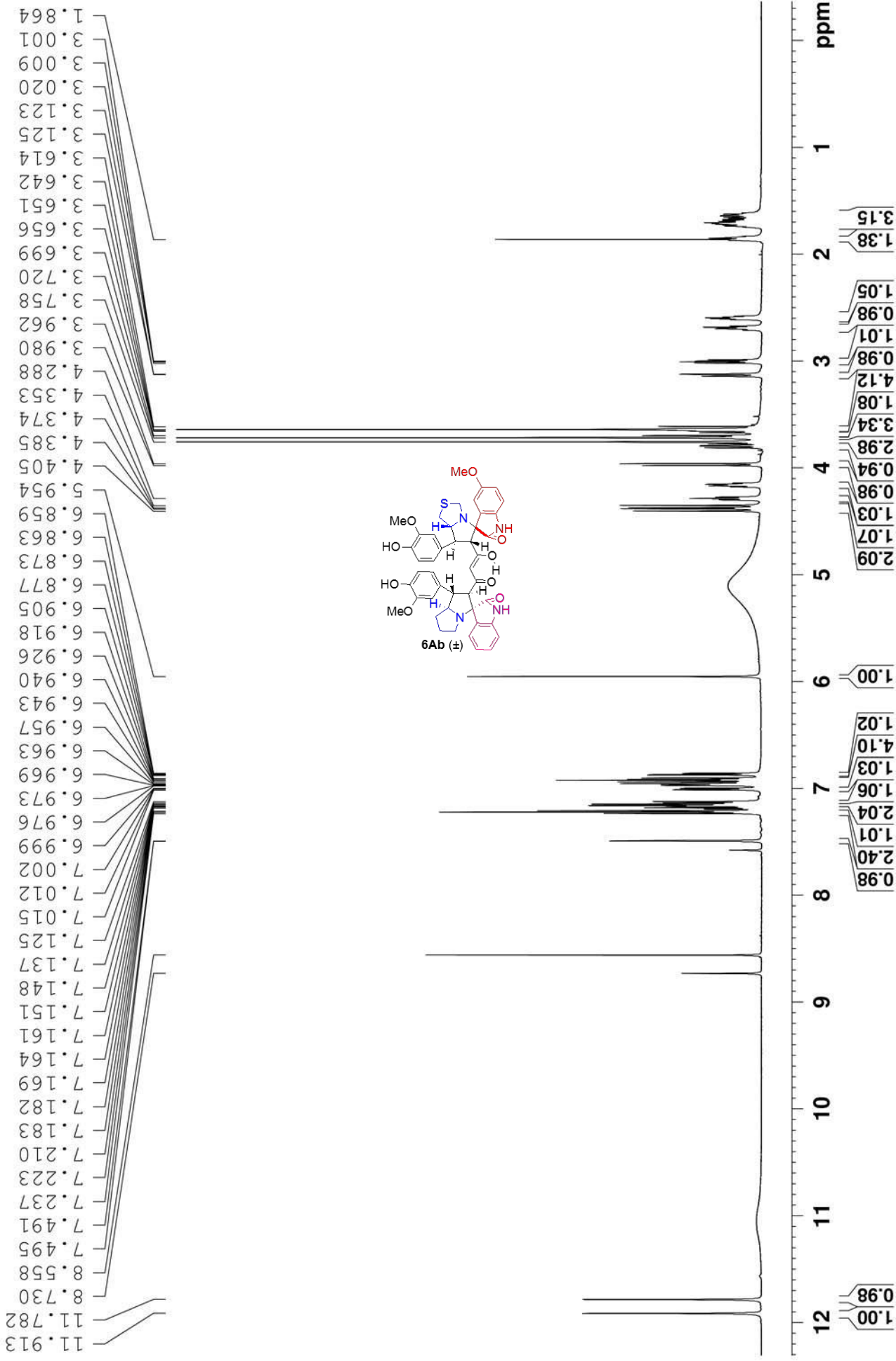




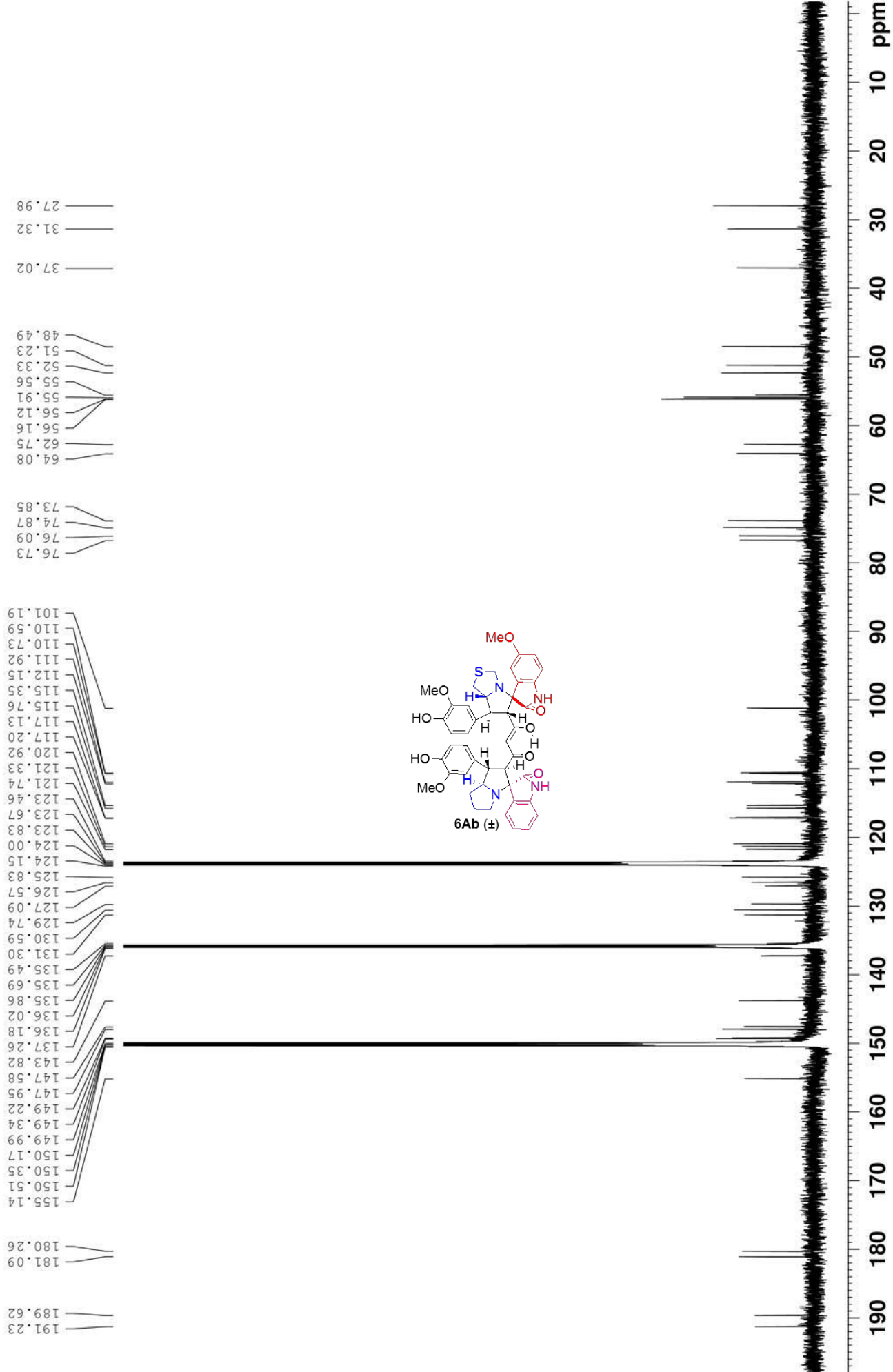


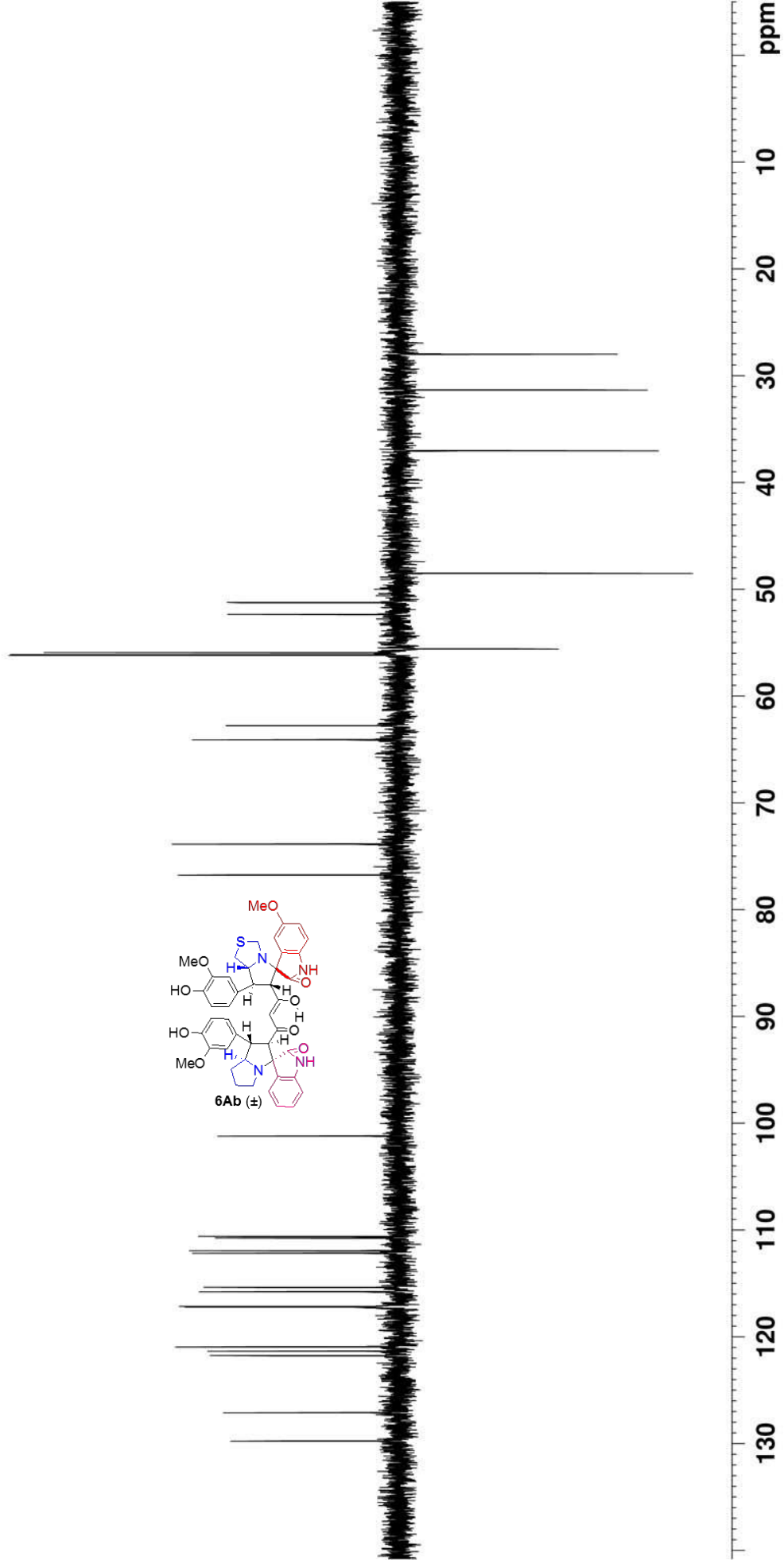
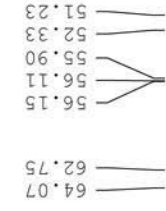
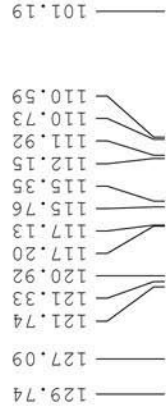


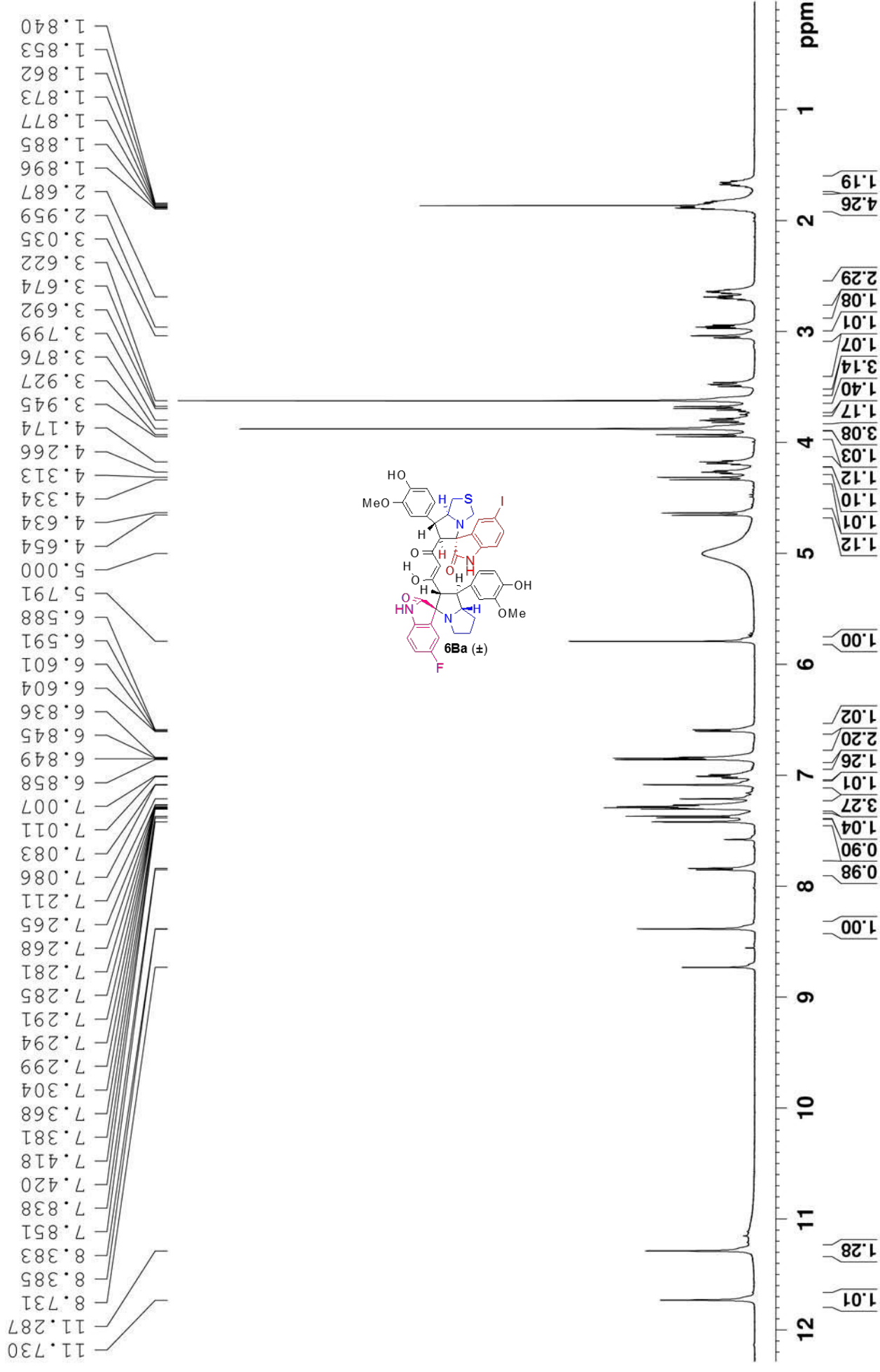
¹H NMR in Py-d5

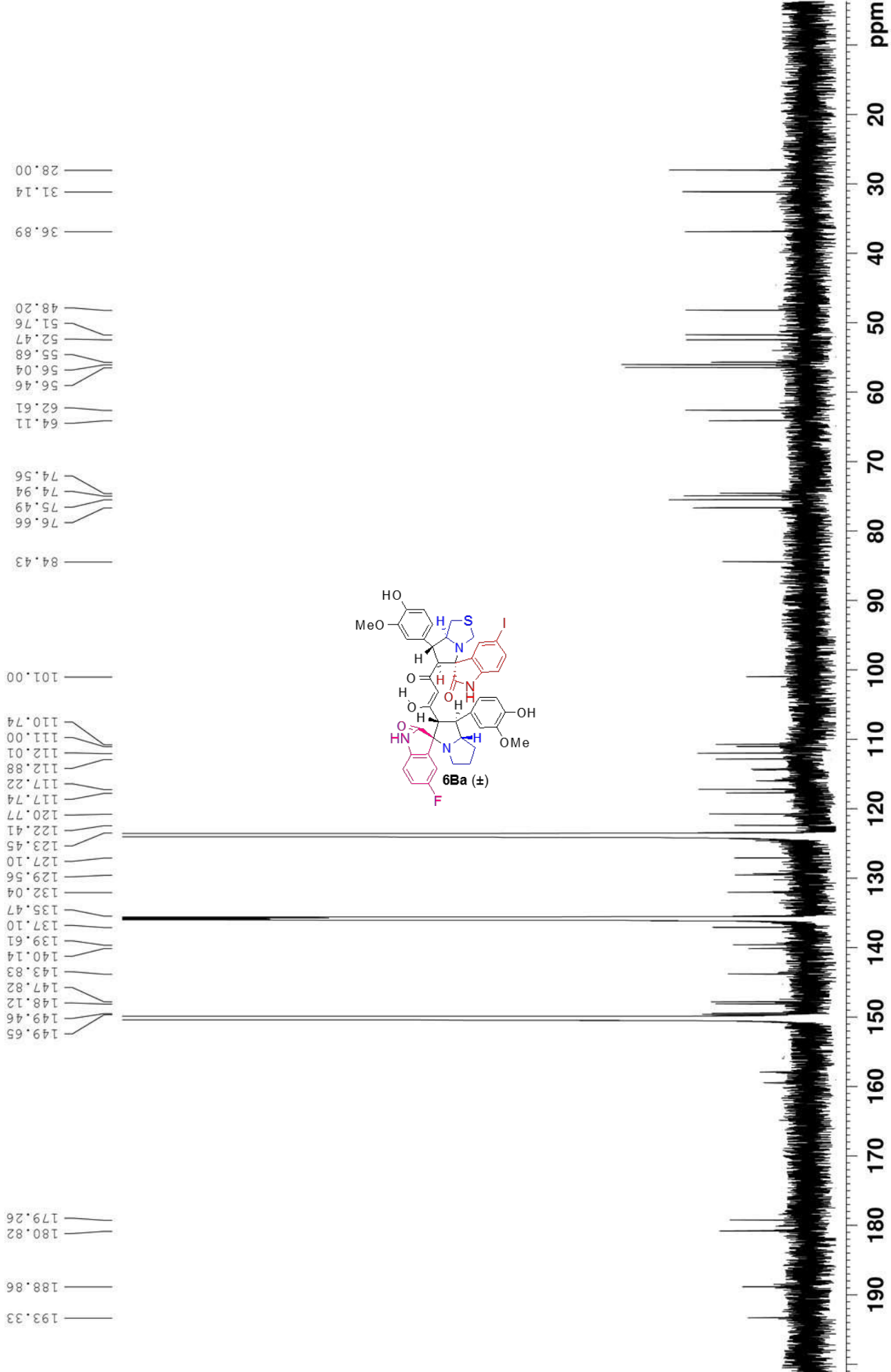


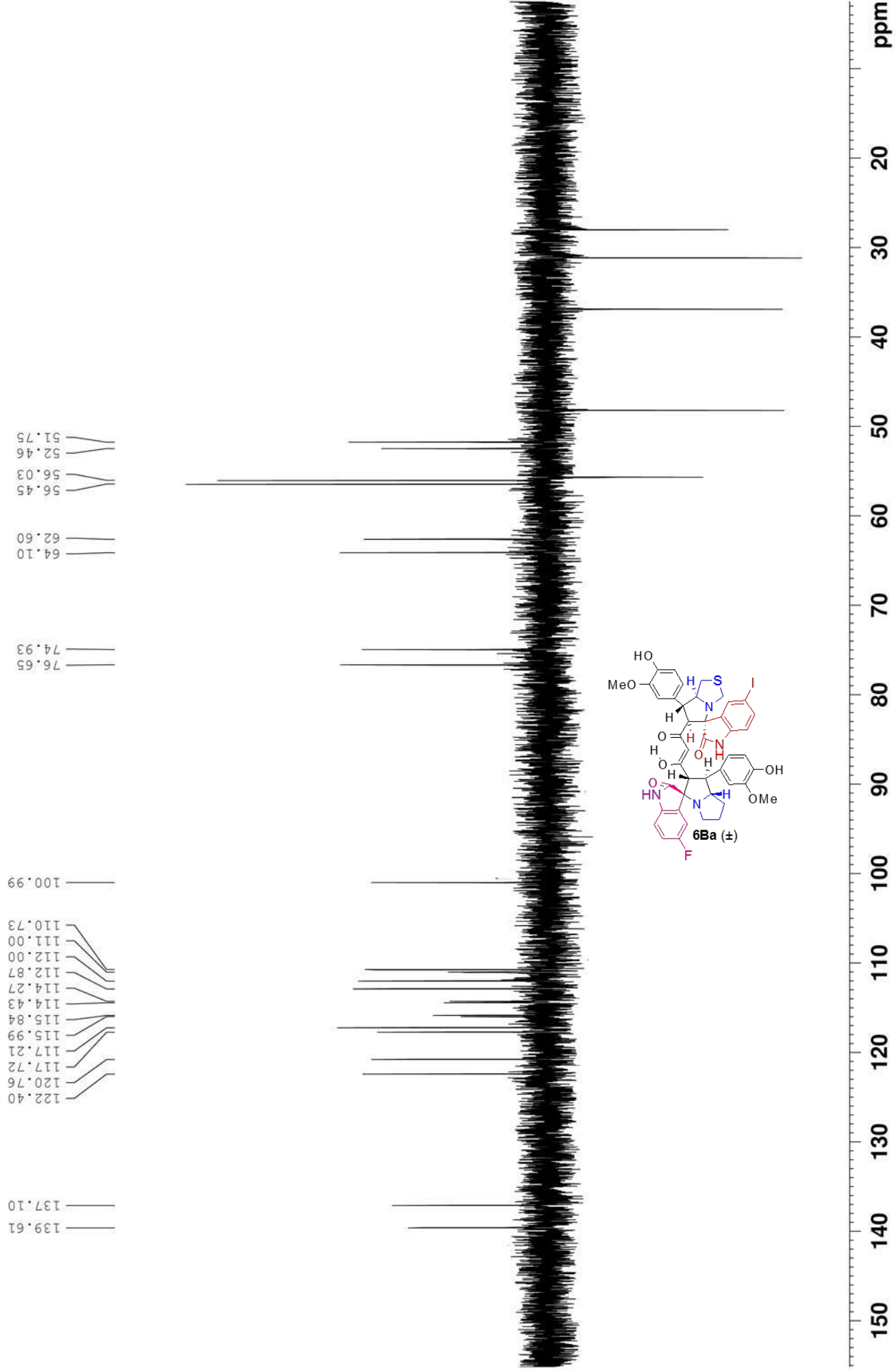
¹³C-NMR in Py-d₅



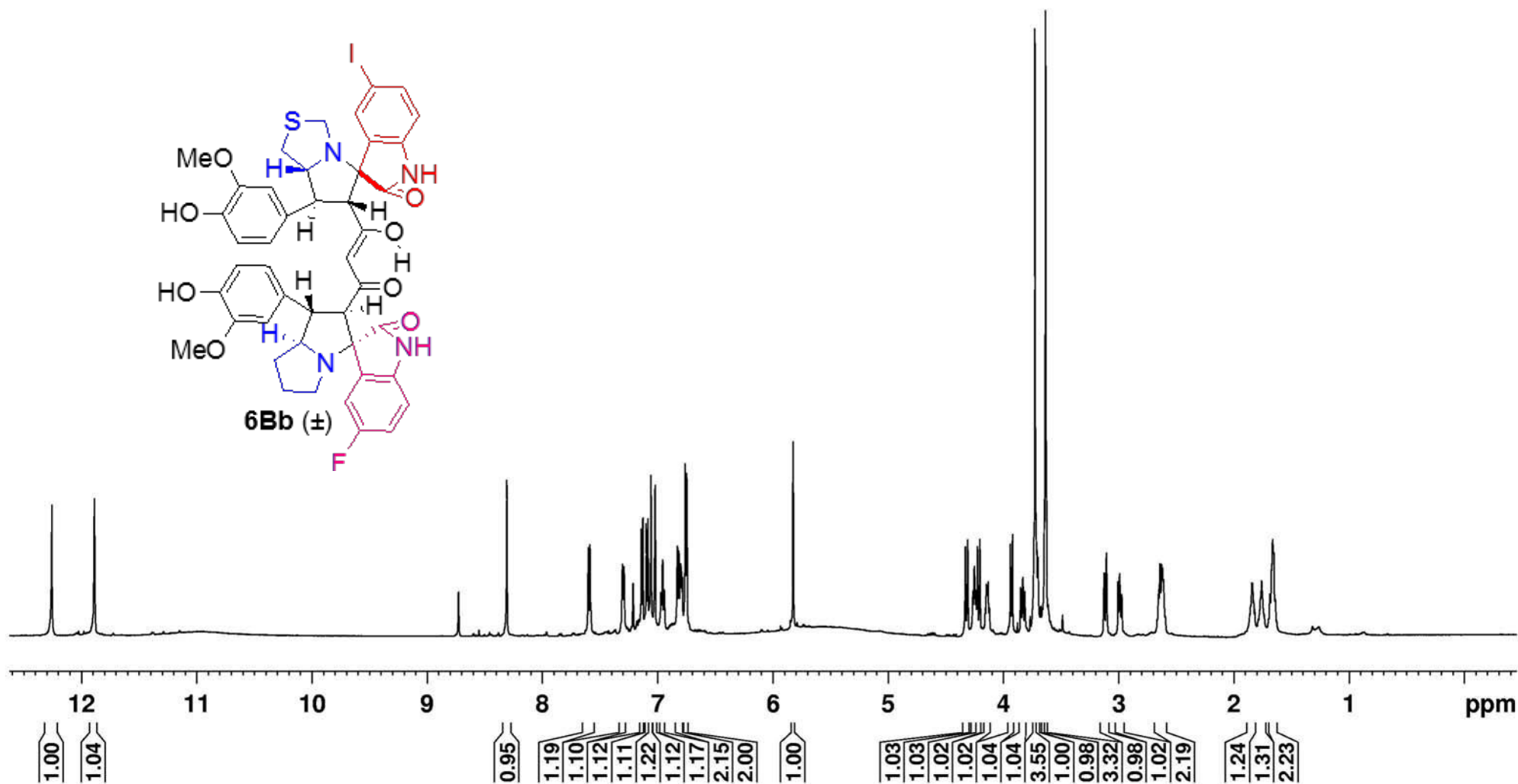
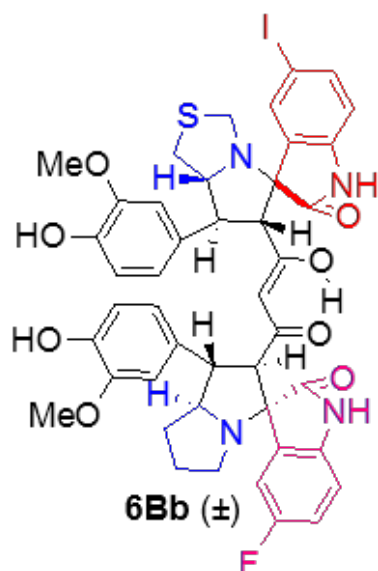
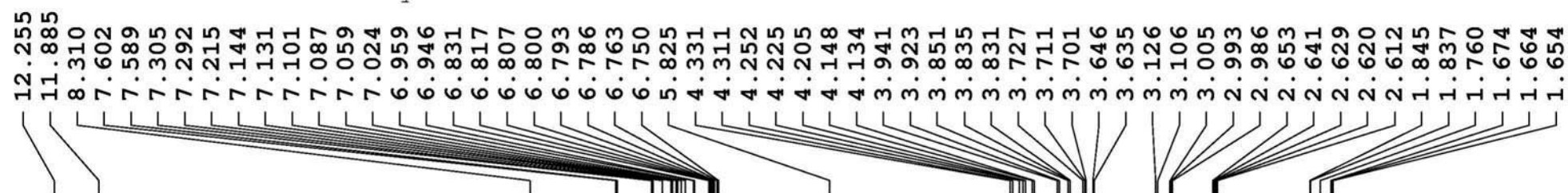


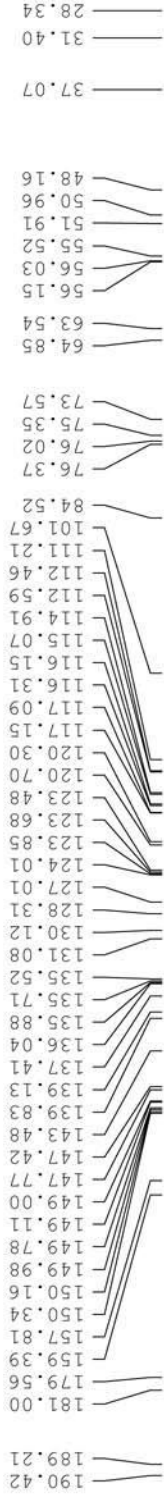


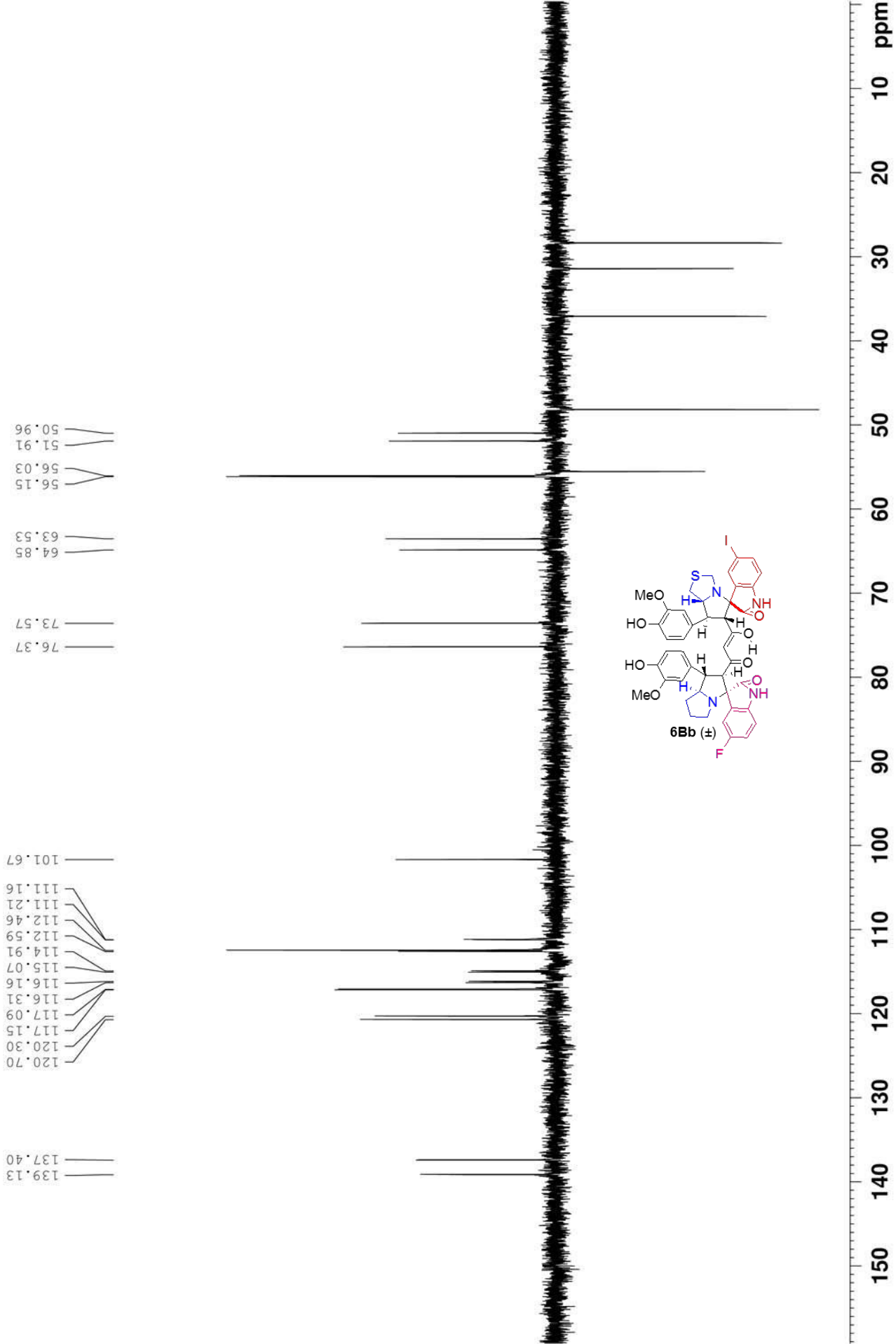




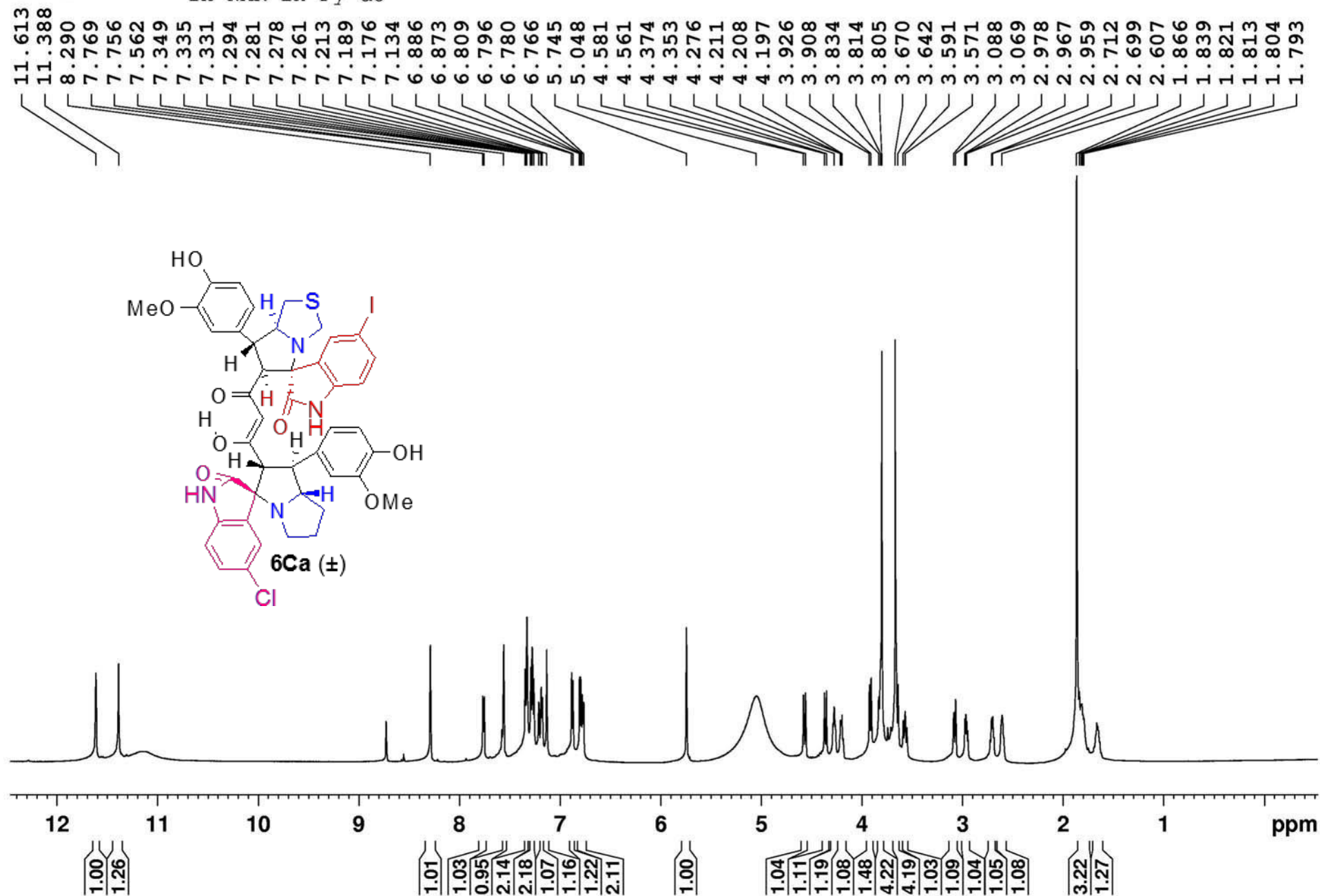
¹H NMR in Py-d₅







¹H NMR in Py-d₅





180.55
179.32

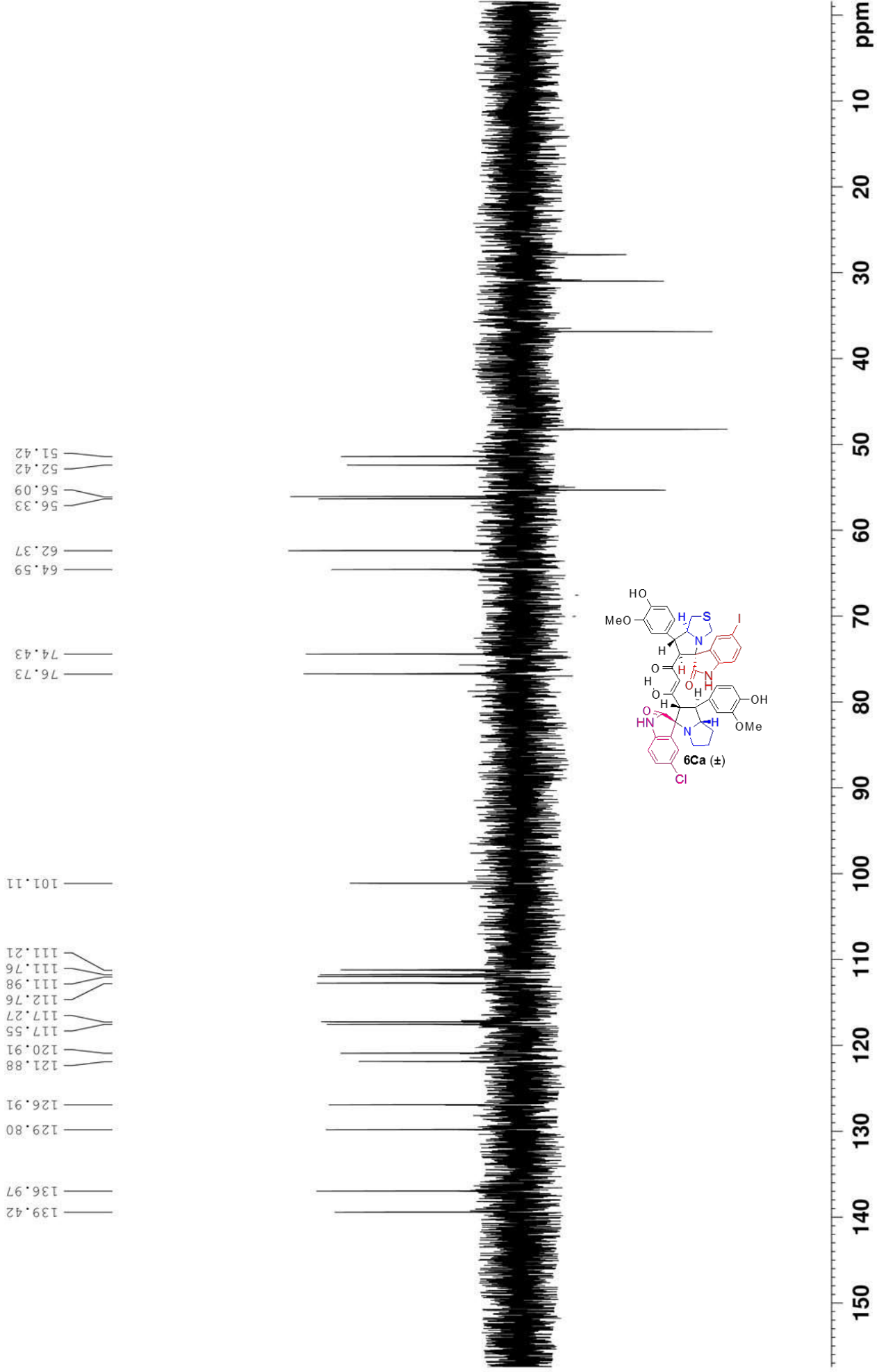
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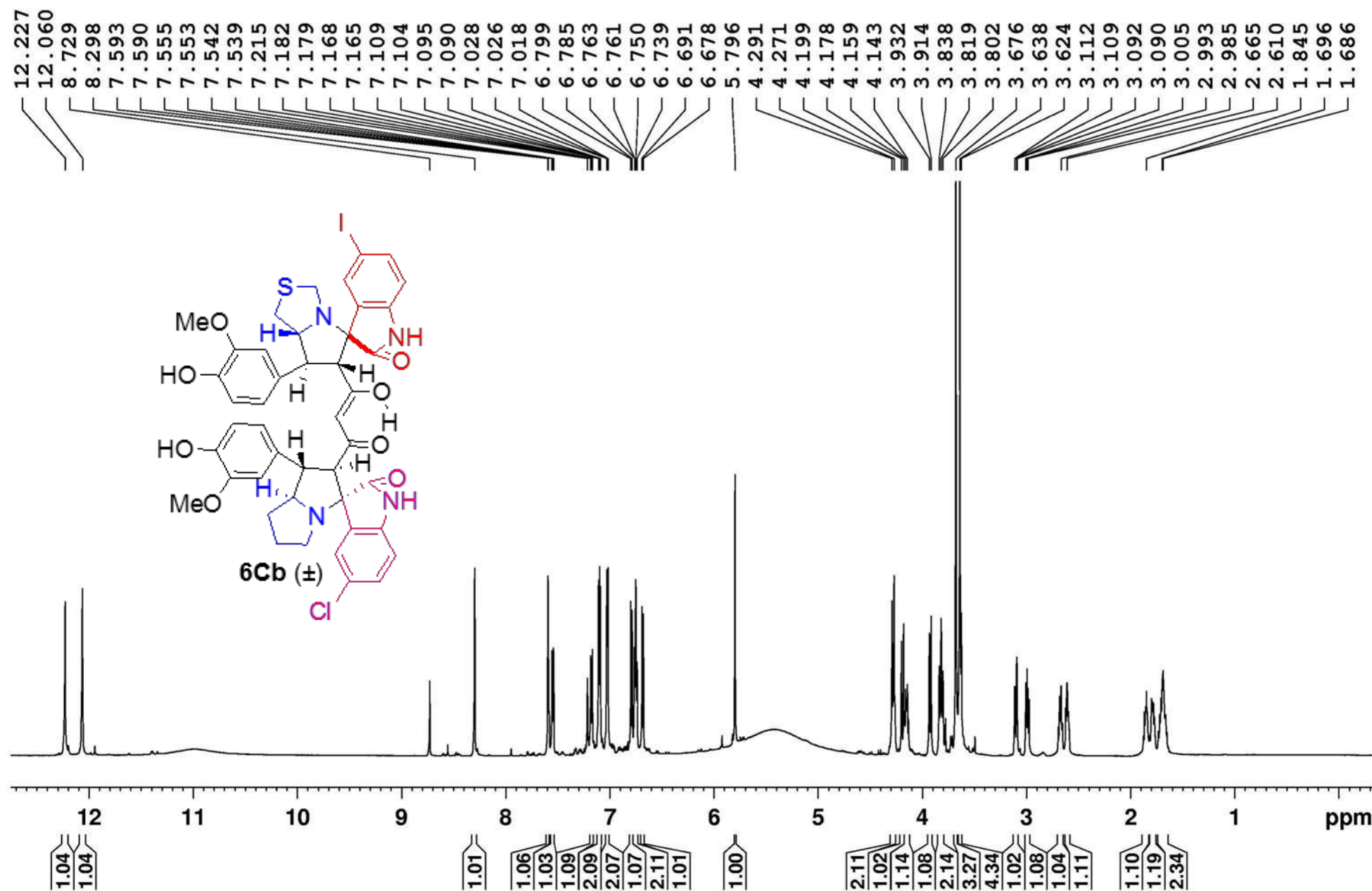
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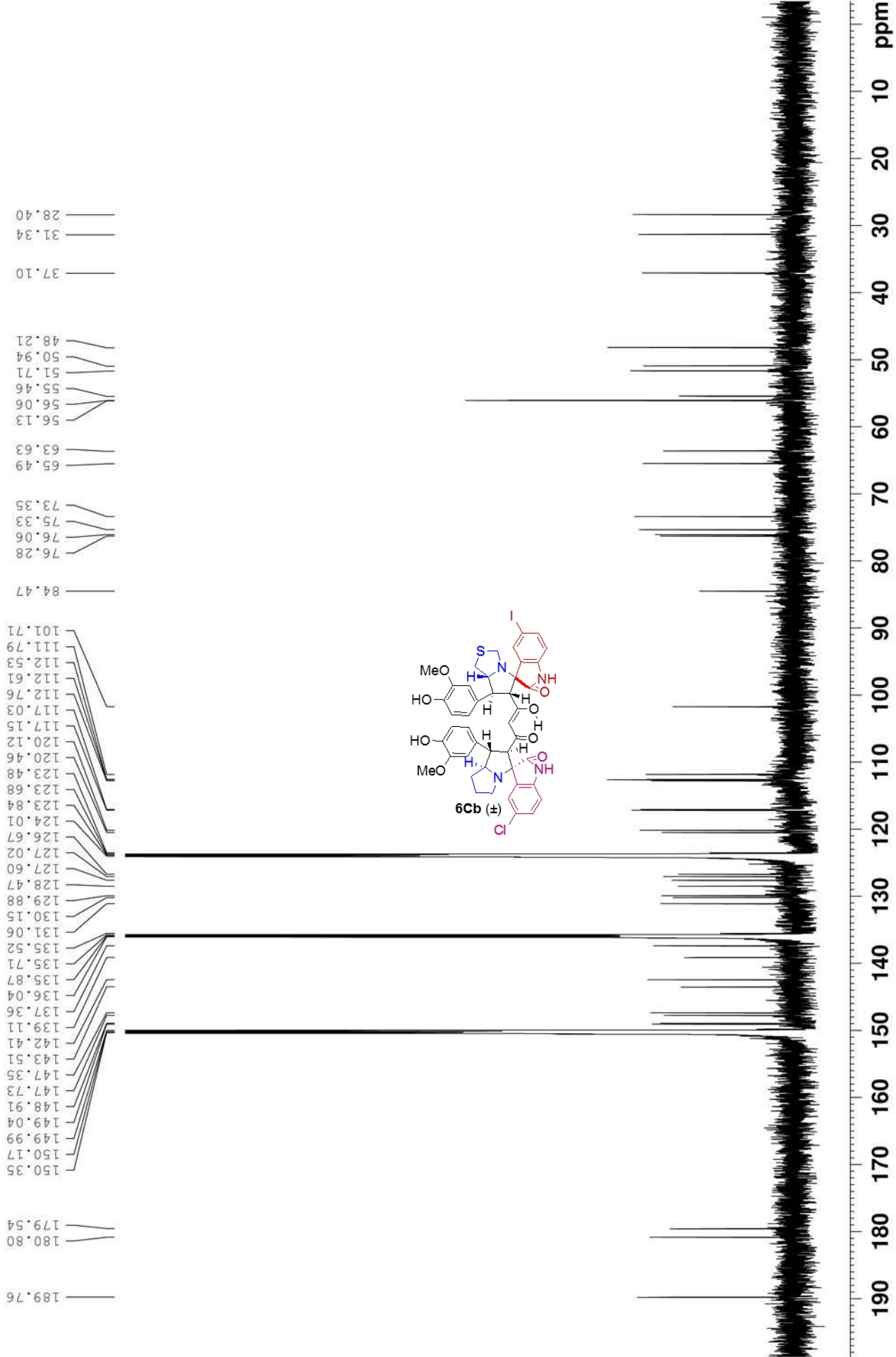
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51.41
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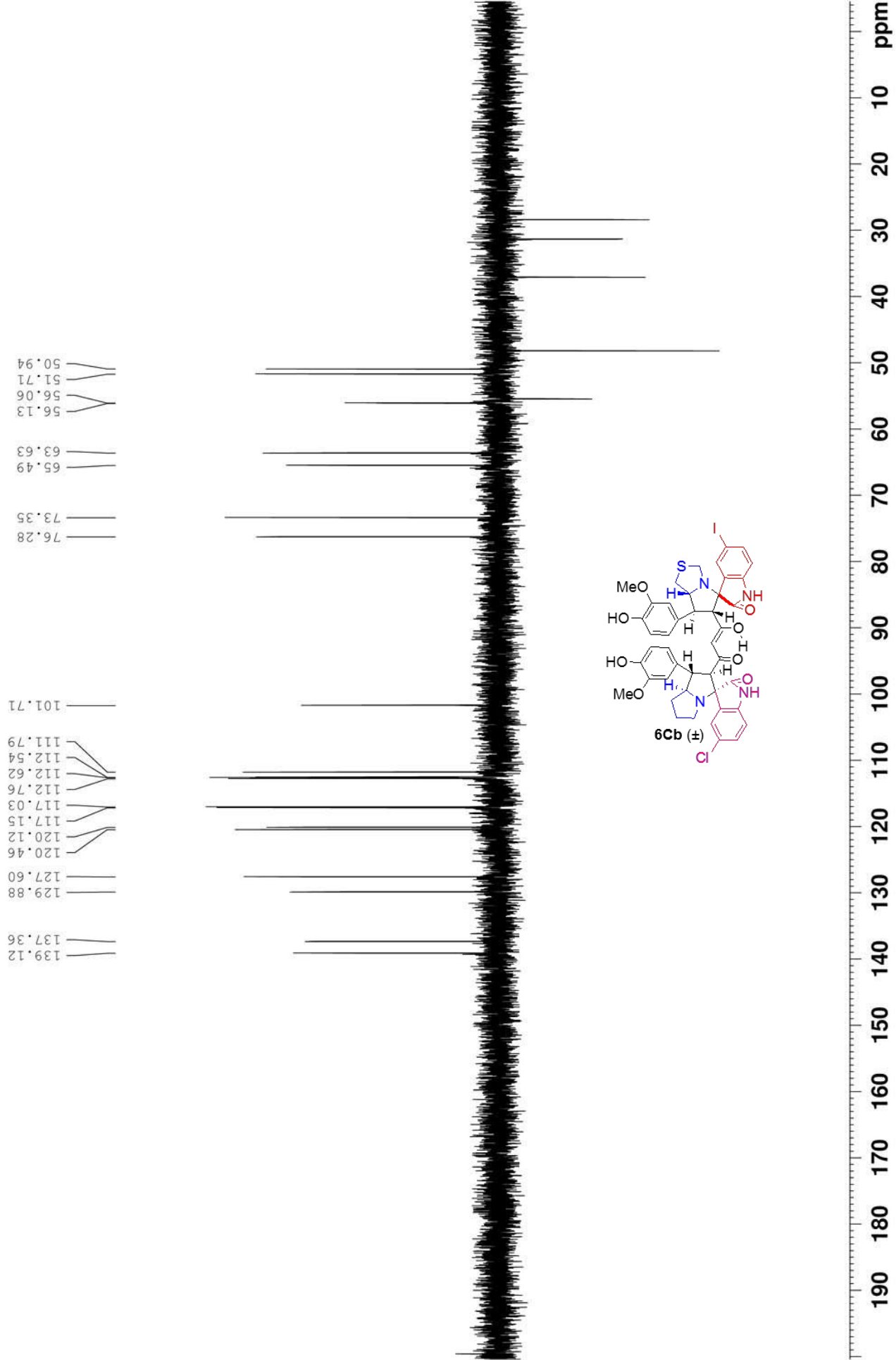
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1.34

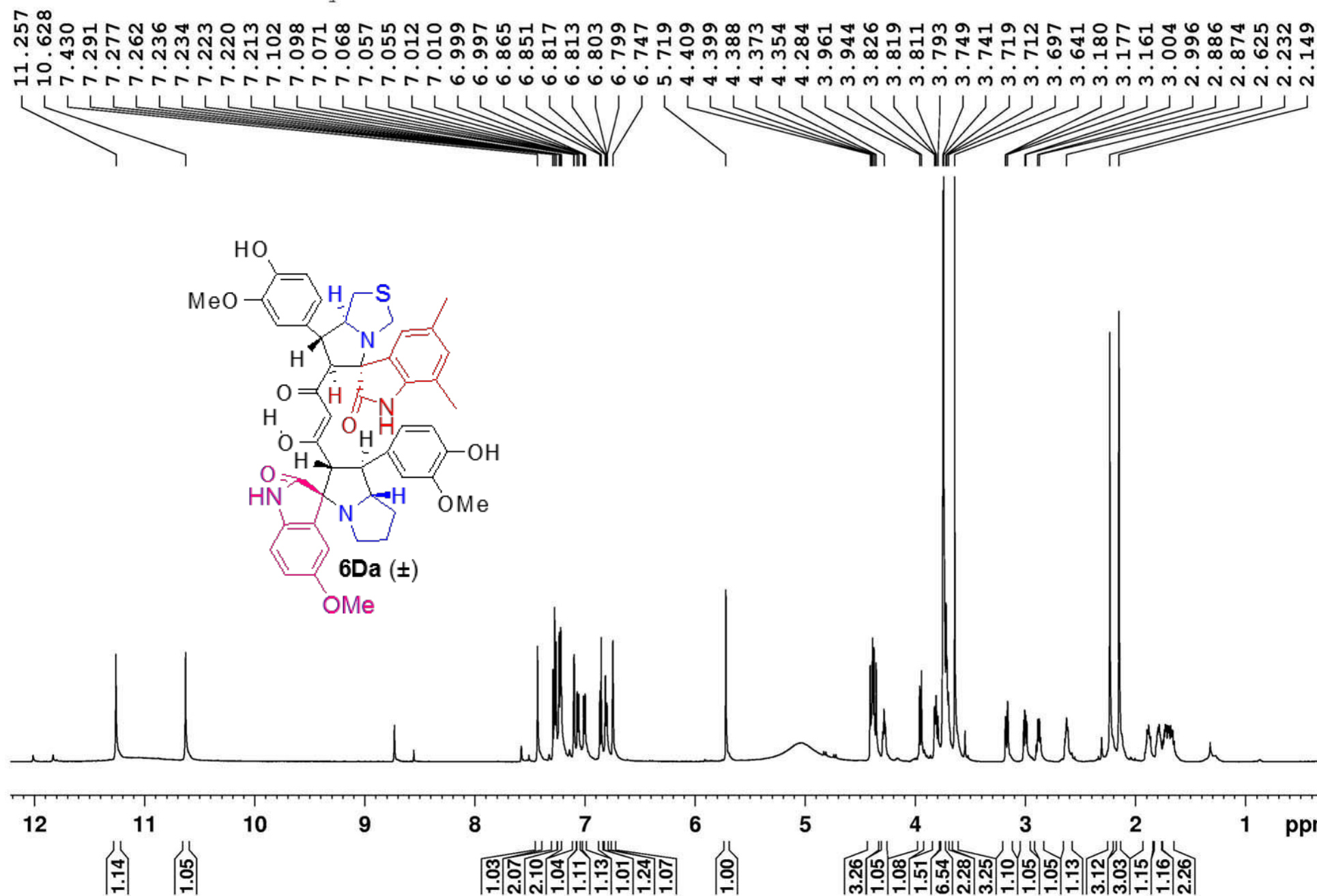


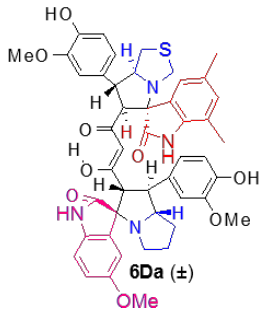
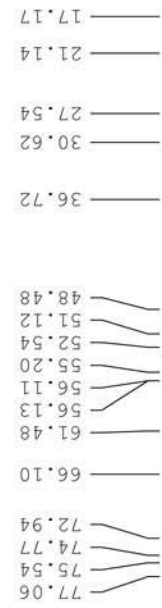
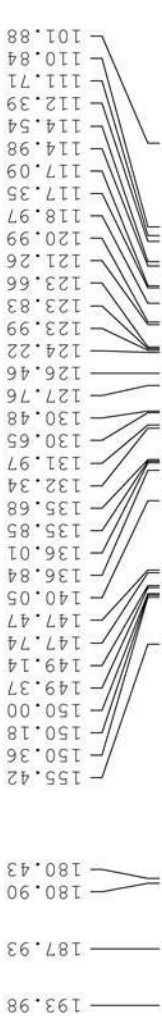




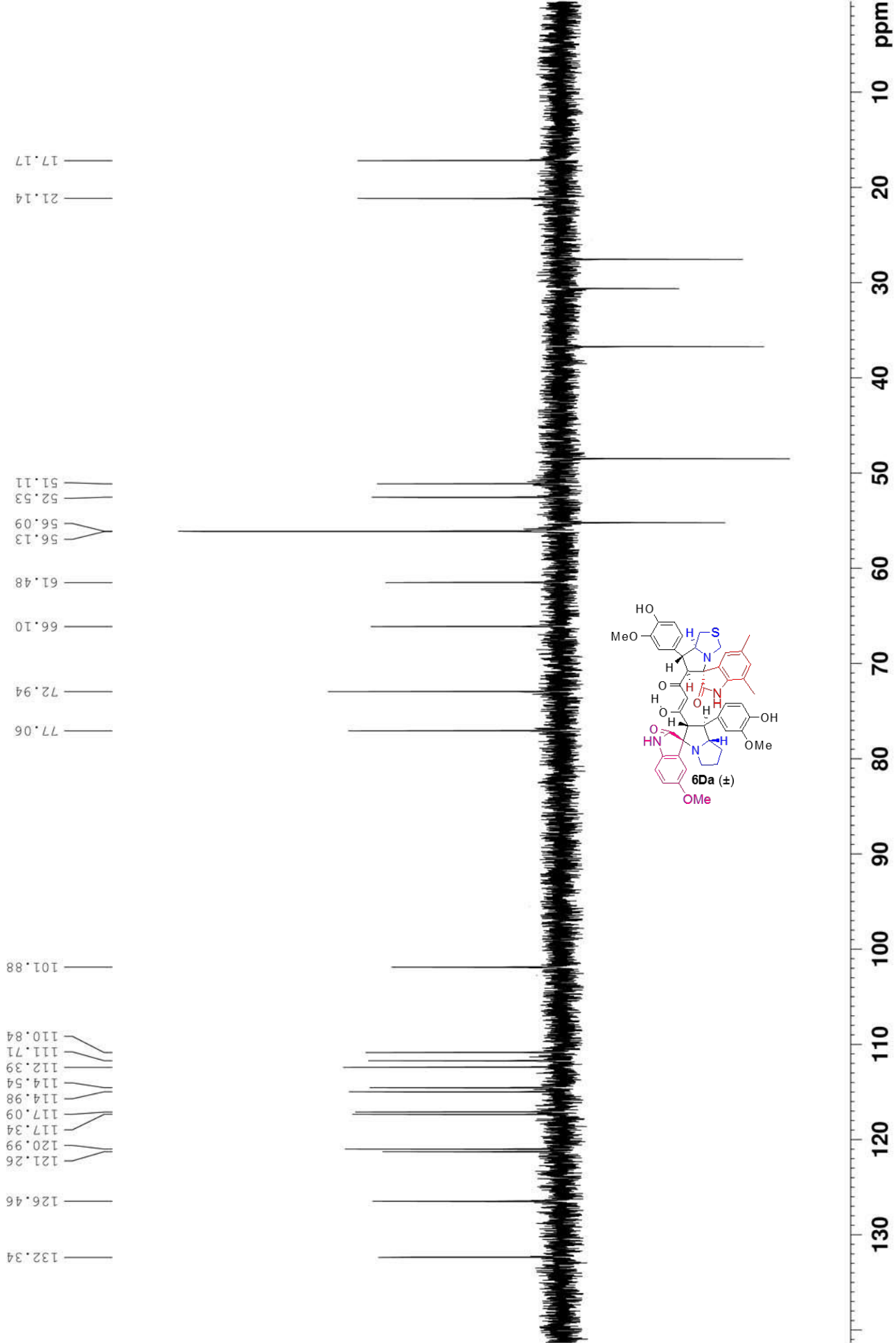


¹H NMR in Py-d₅

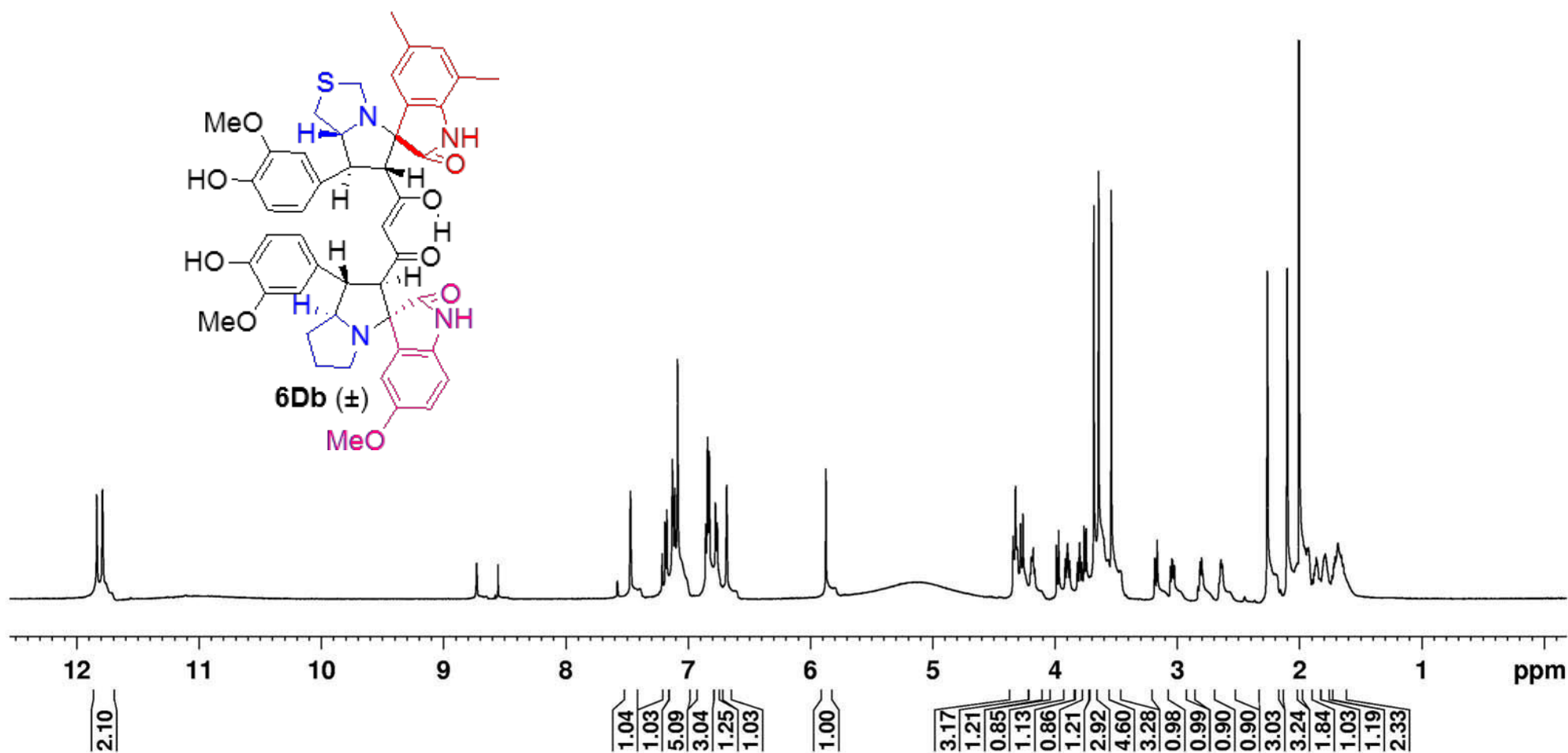
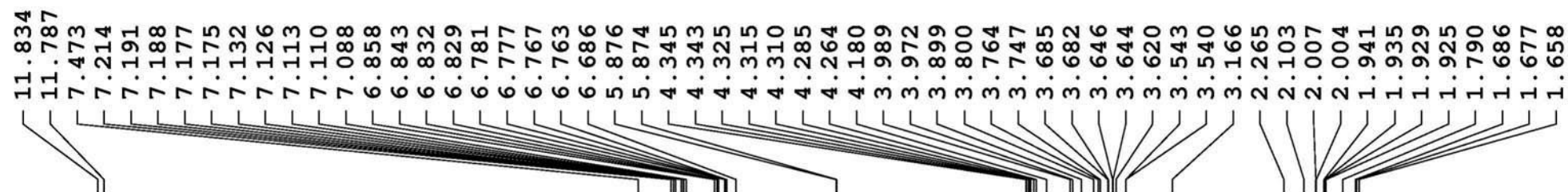


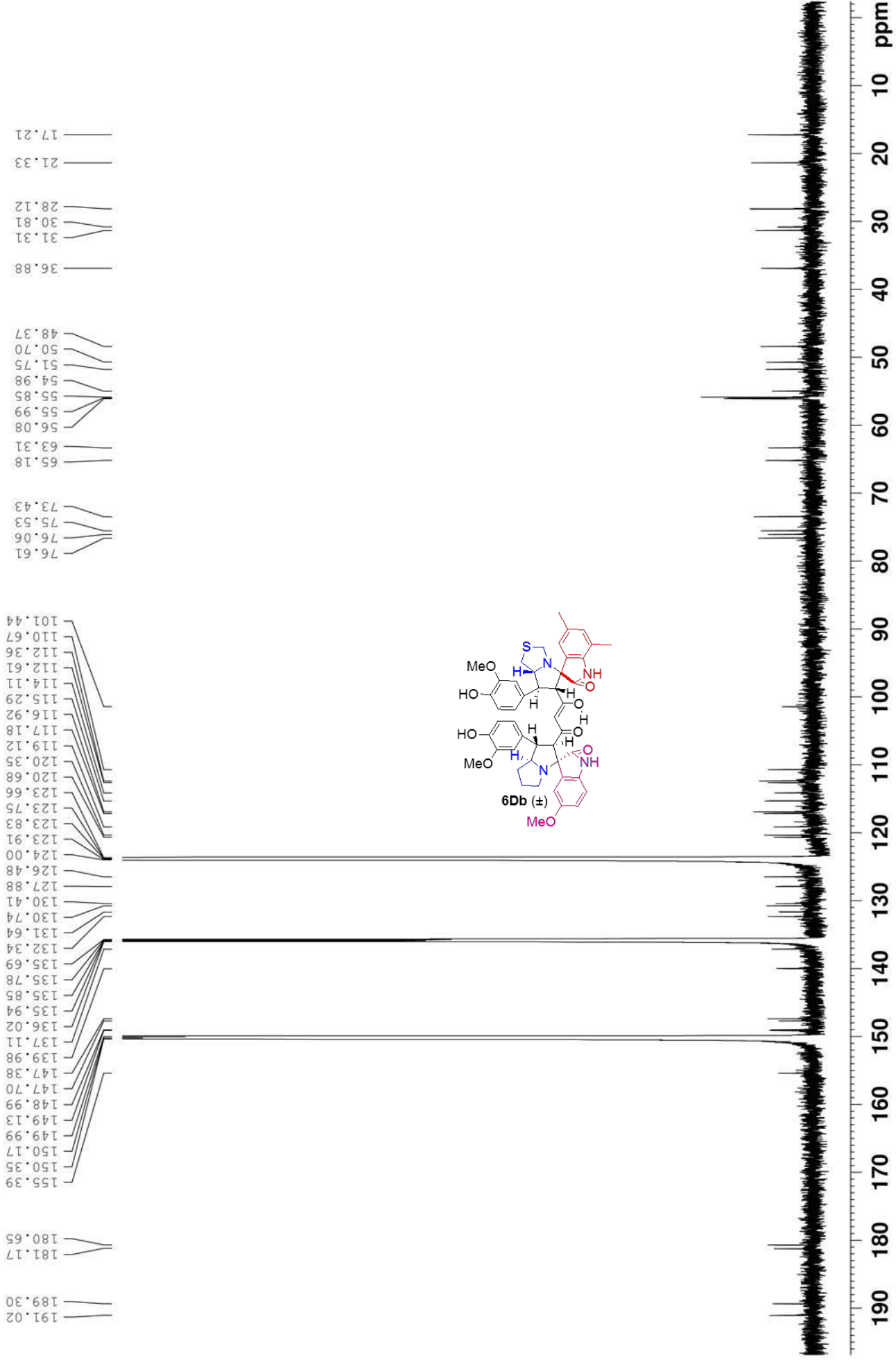


DEPT-135

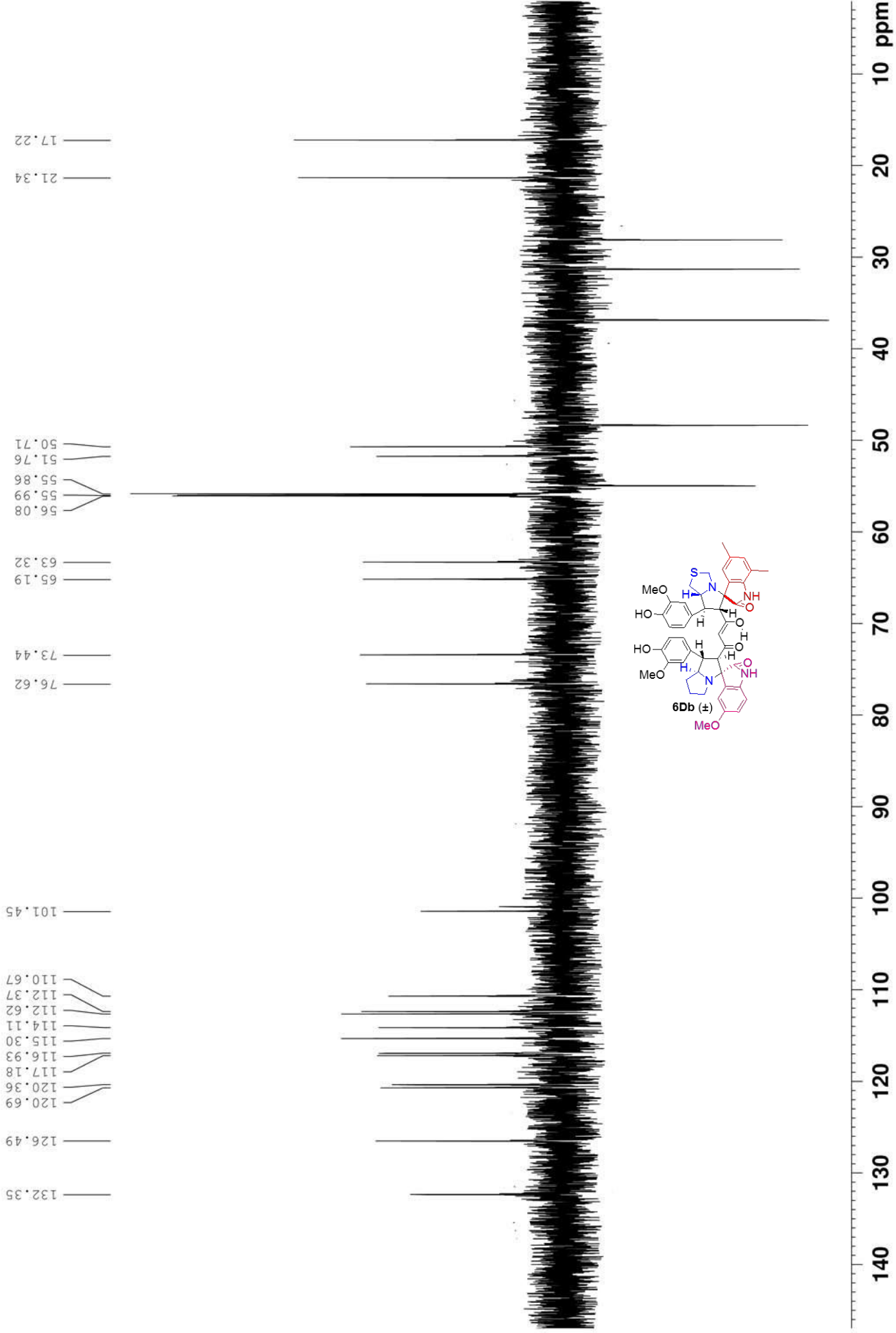


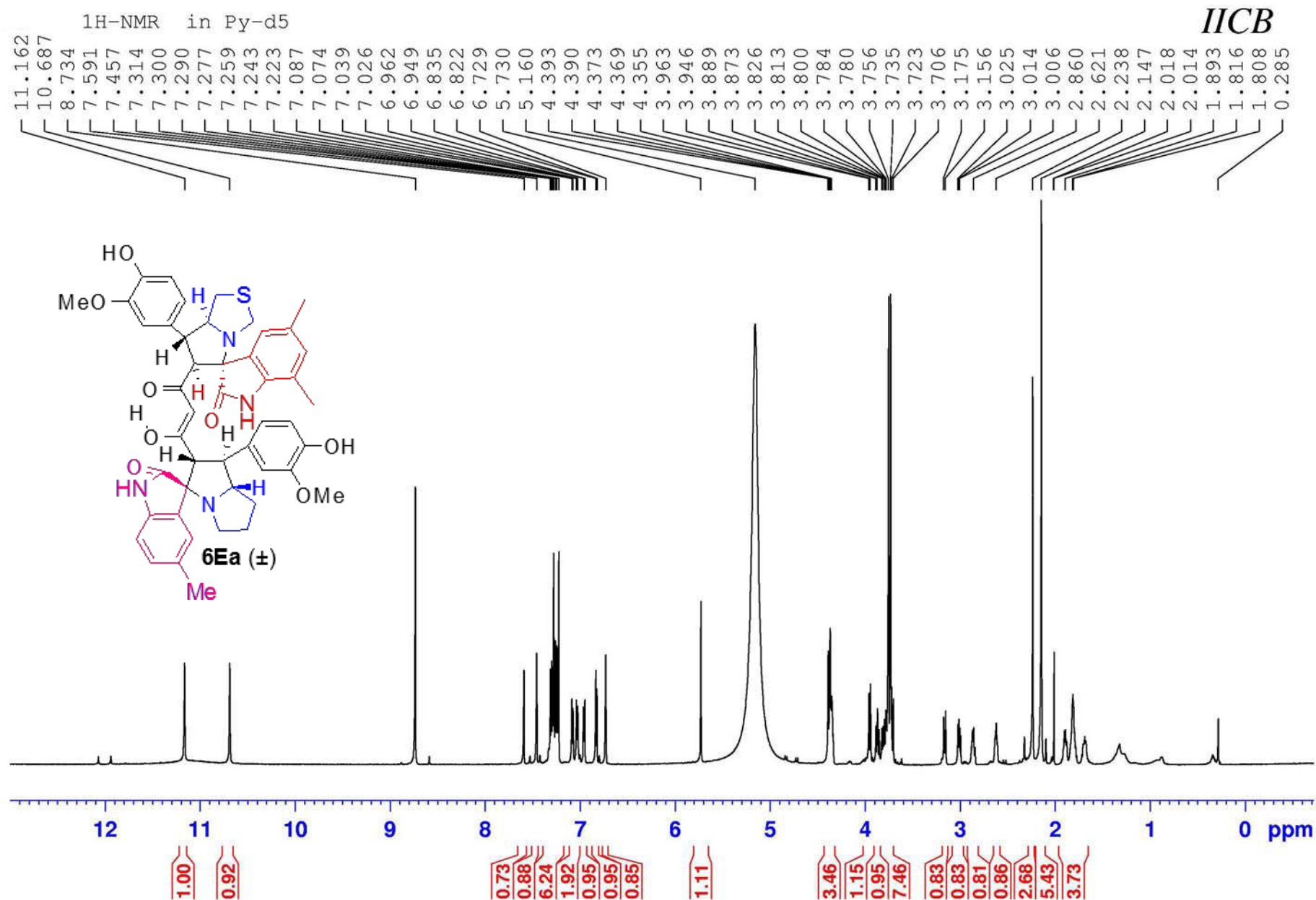
¹H NMR in Py-d5





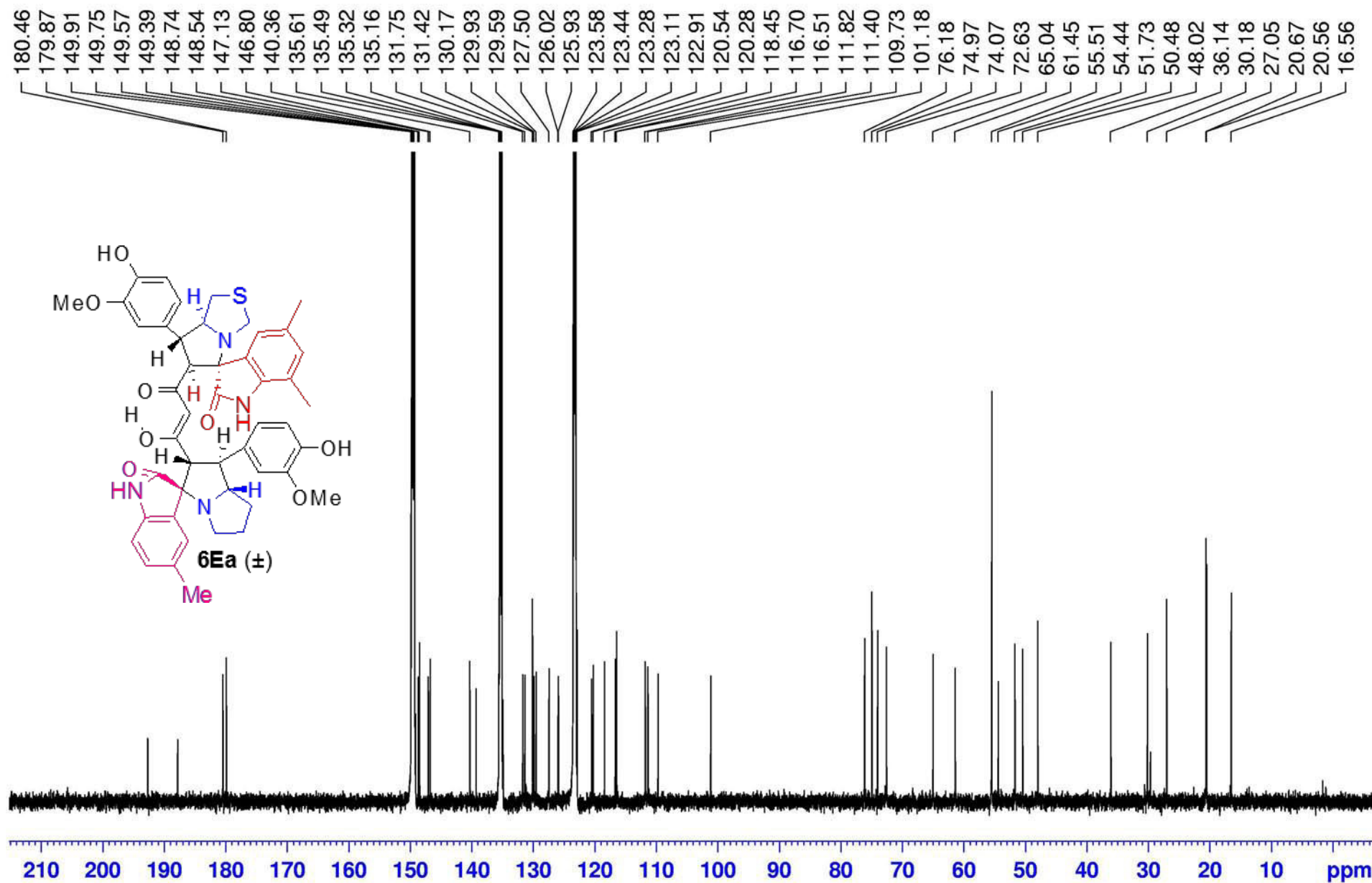
DEPT-135





^{13}C -NMR in Py-d₅

HCB

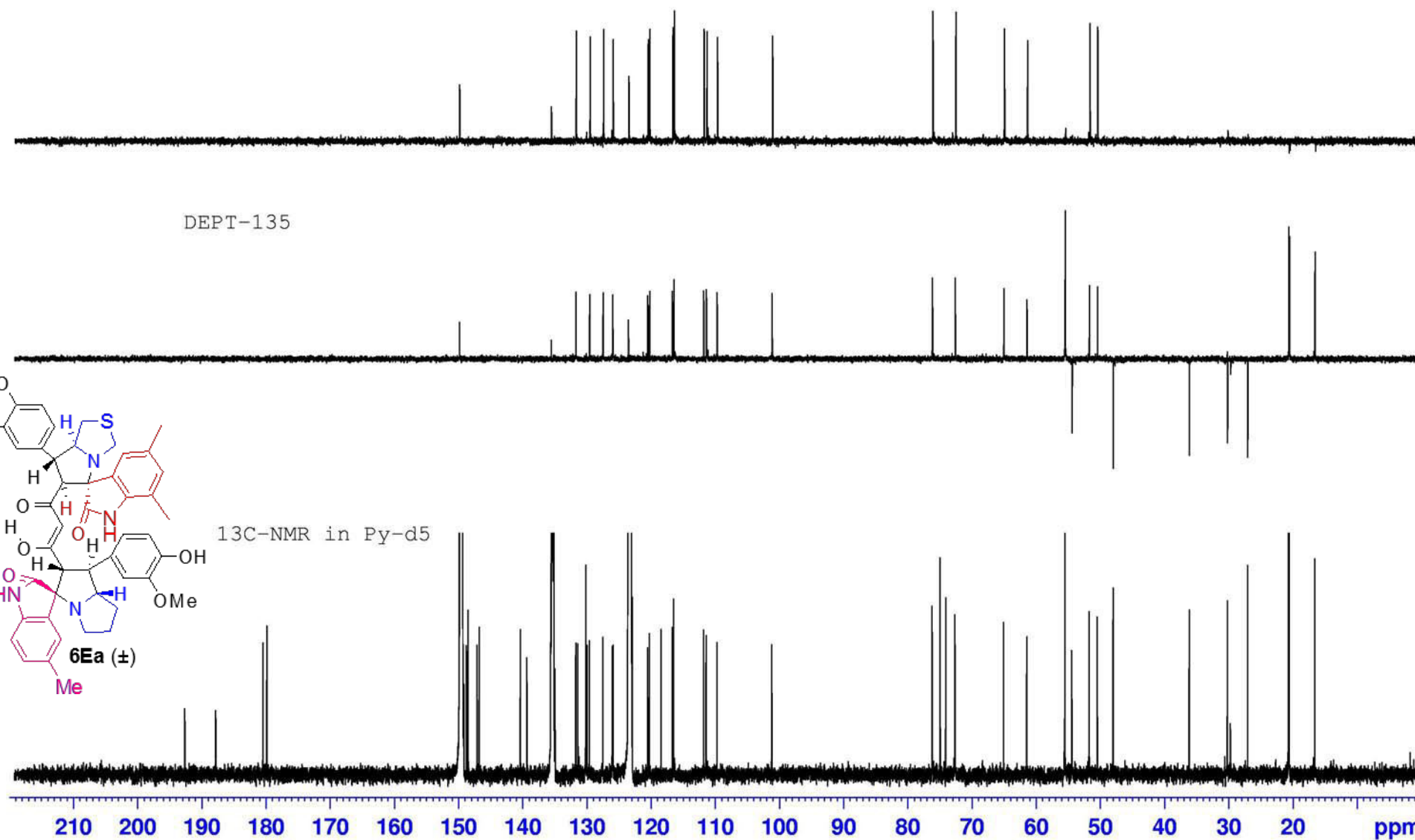
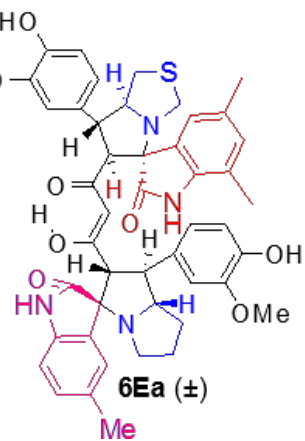


DEPT-90

IICB

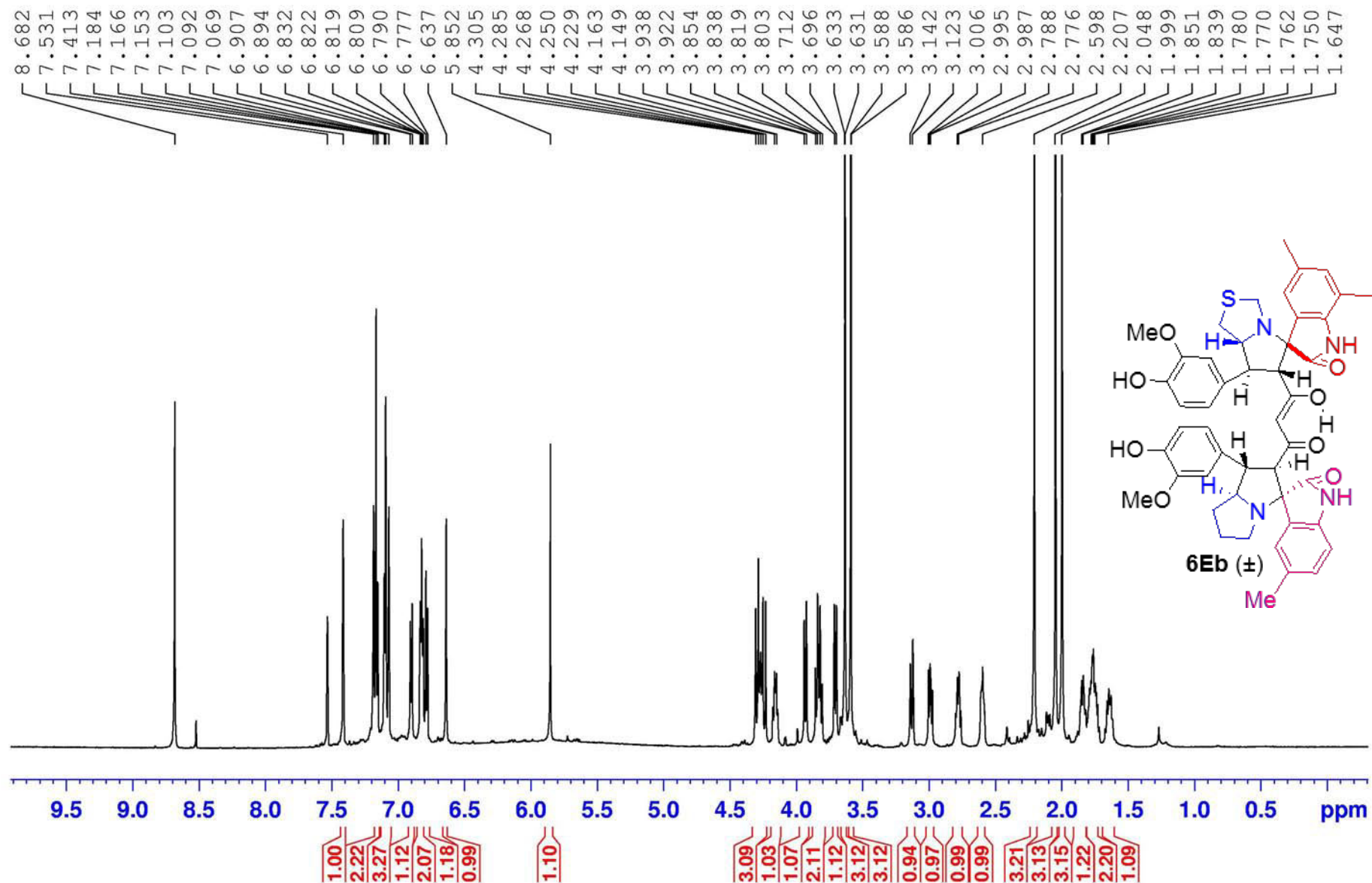
DEPT-135

^{13}C -NMR in Py-d₅



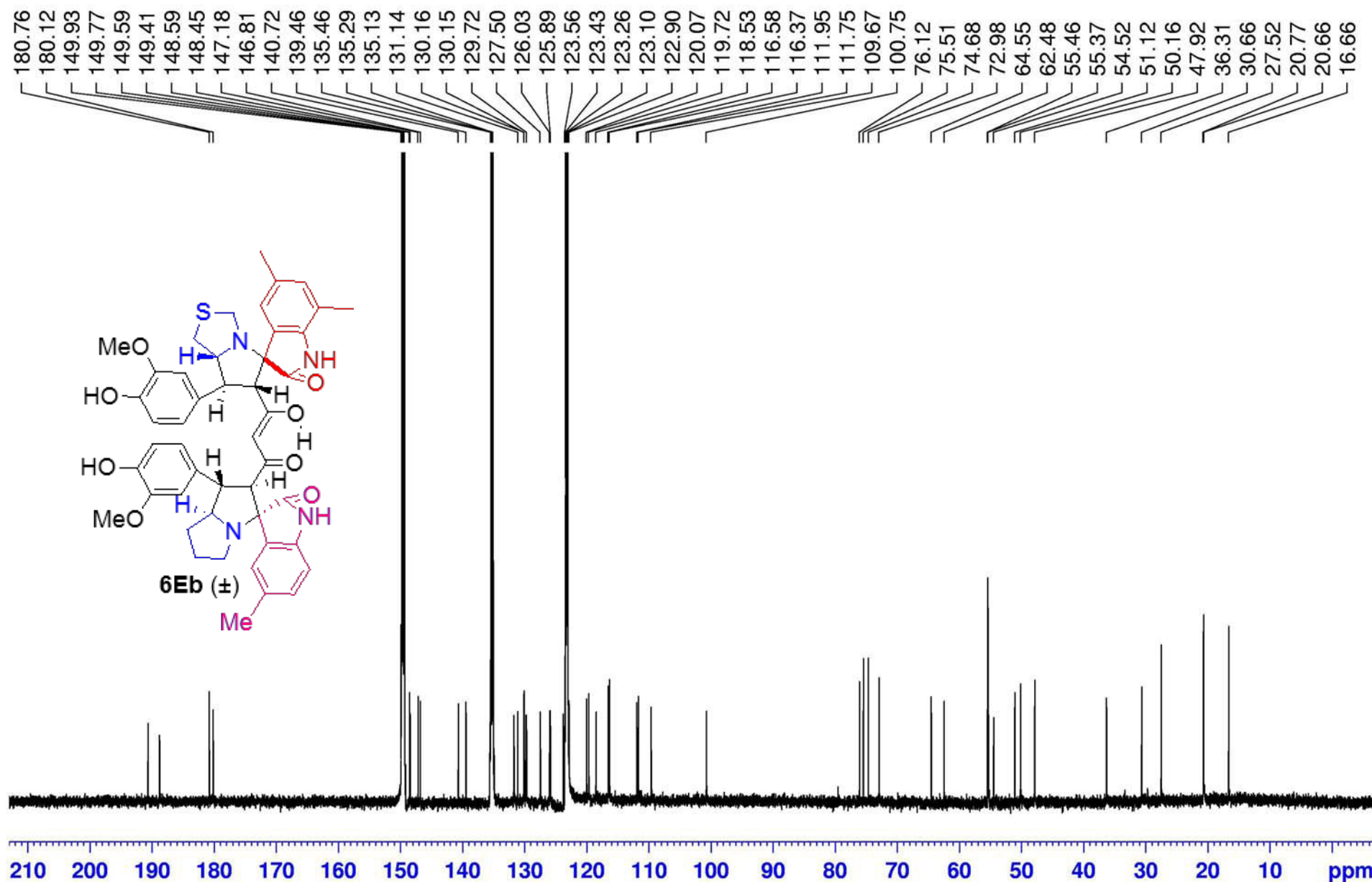
¹H-NMR in Py-d₅

IICB

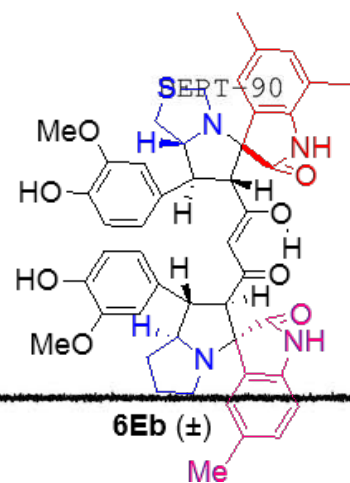


^{13}C -NMR in Py-d₅

HCB

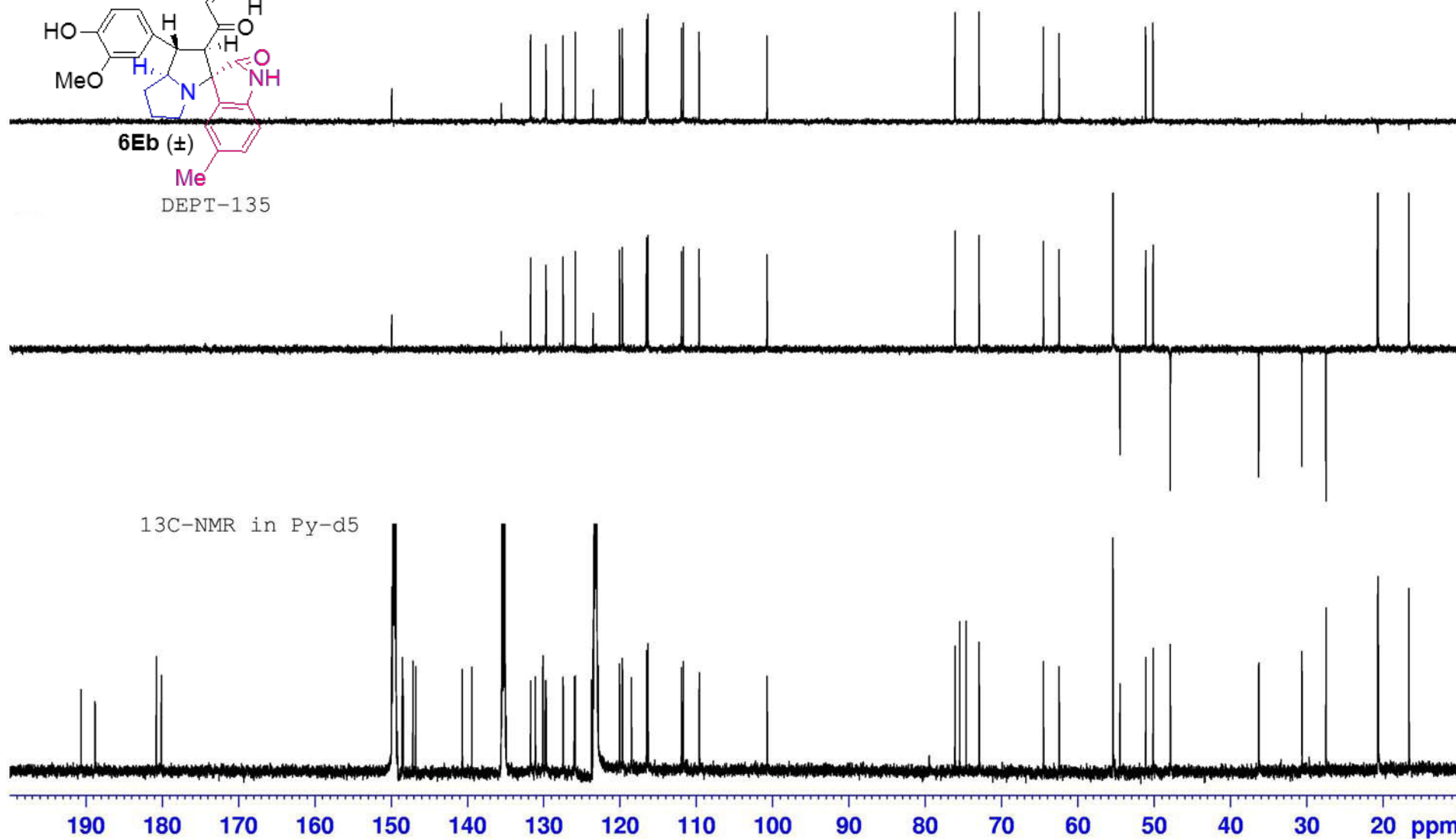


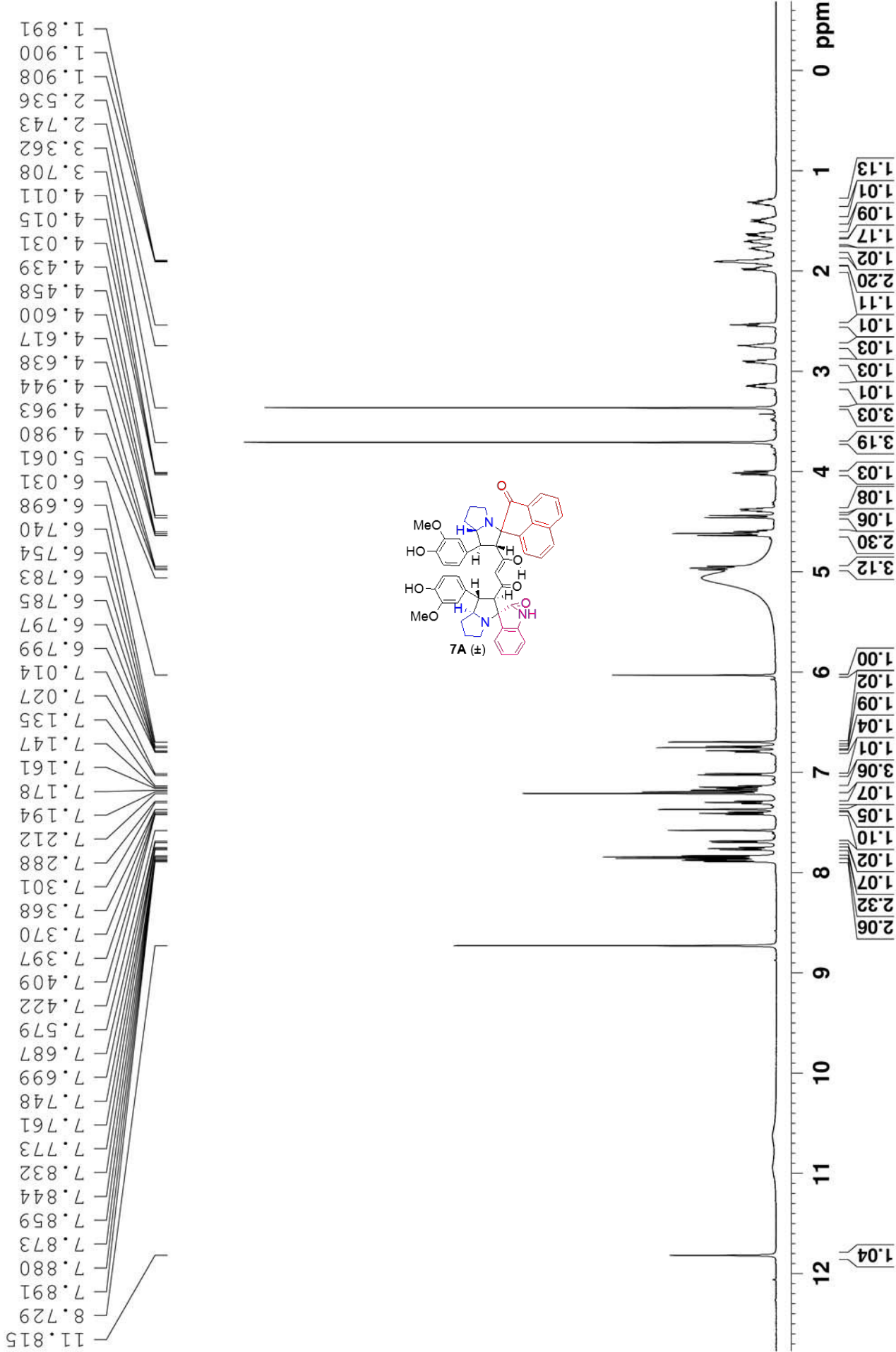
IICB

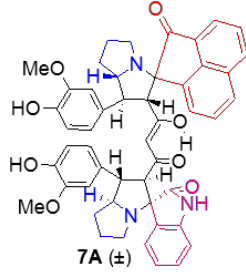
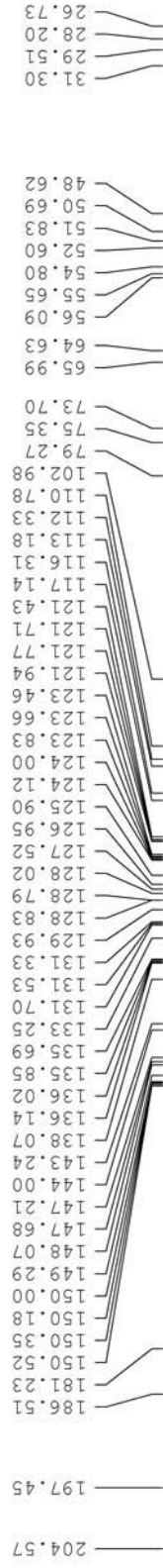


DEPT-135

¹³C-NMR in Py-d₅



¹H NMR in Py-d5



DEPT-135

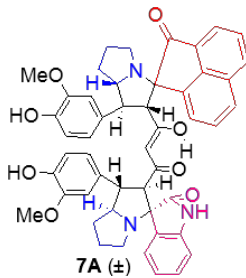
150.52
149.95

131.70
129.93
128.83
128.80
128.02
125.90
124.13
123.68
121.94
121.78
121.71
121.44
117.14
116.31
113.18
112.33
110.78
102.99

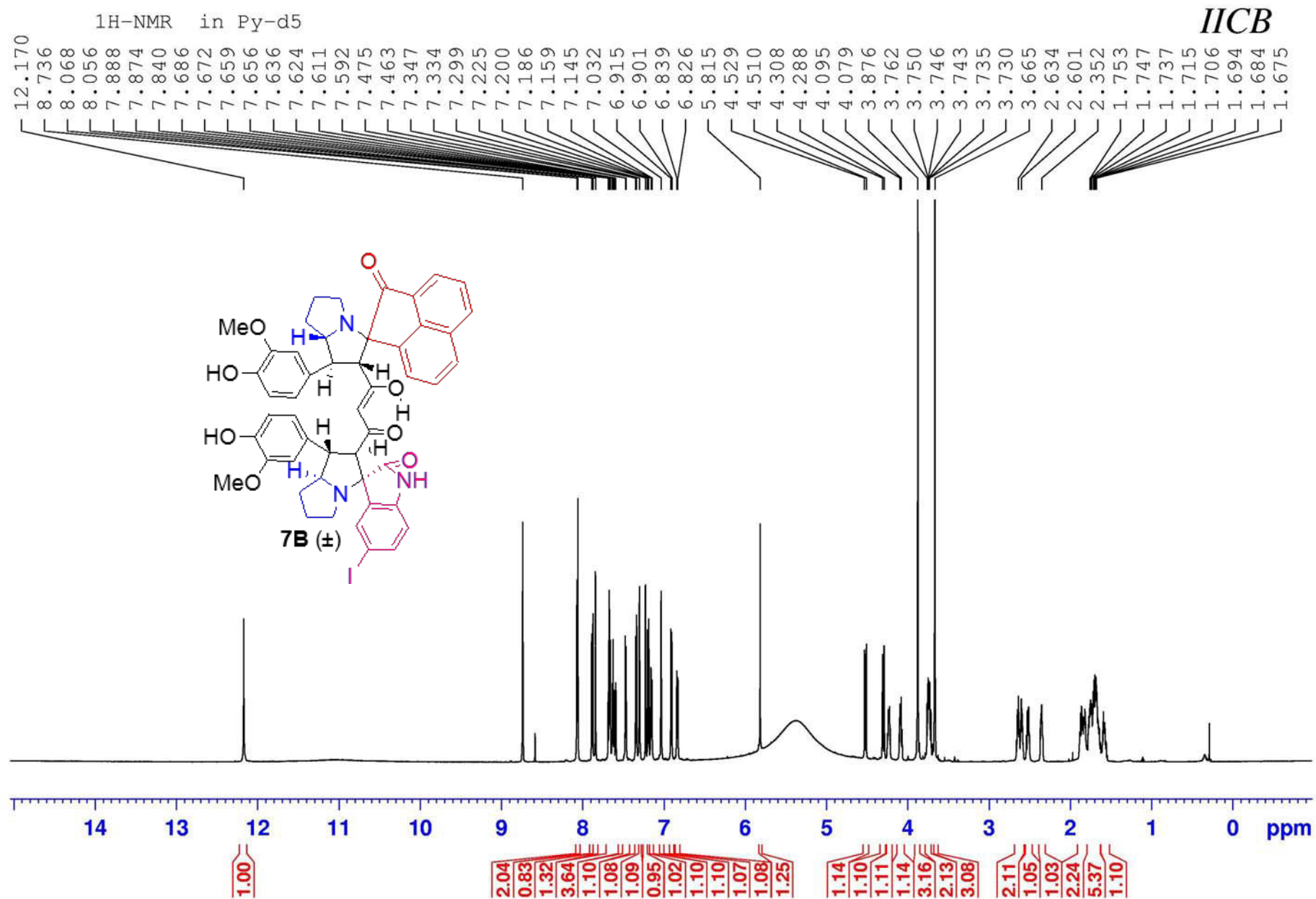
73.70

65.99
64.63

56.09
55.65
54.80
52.60
50.69

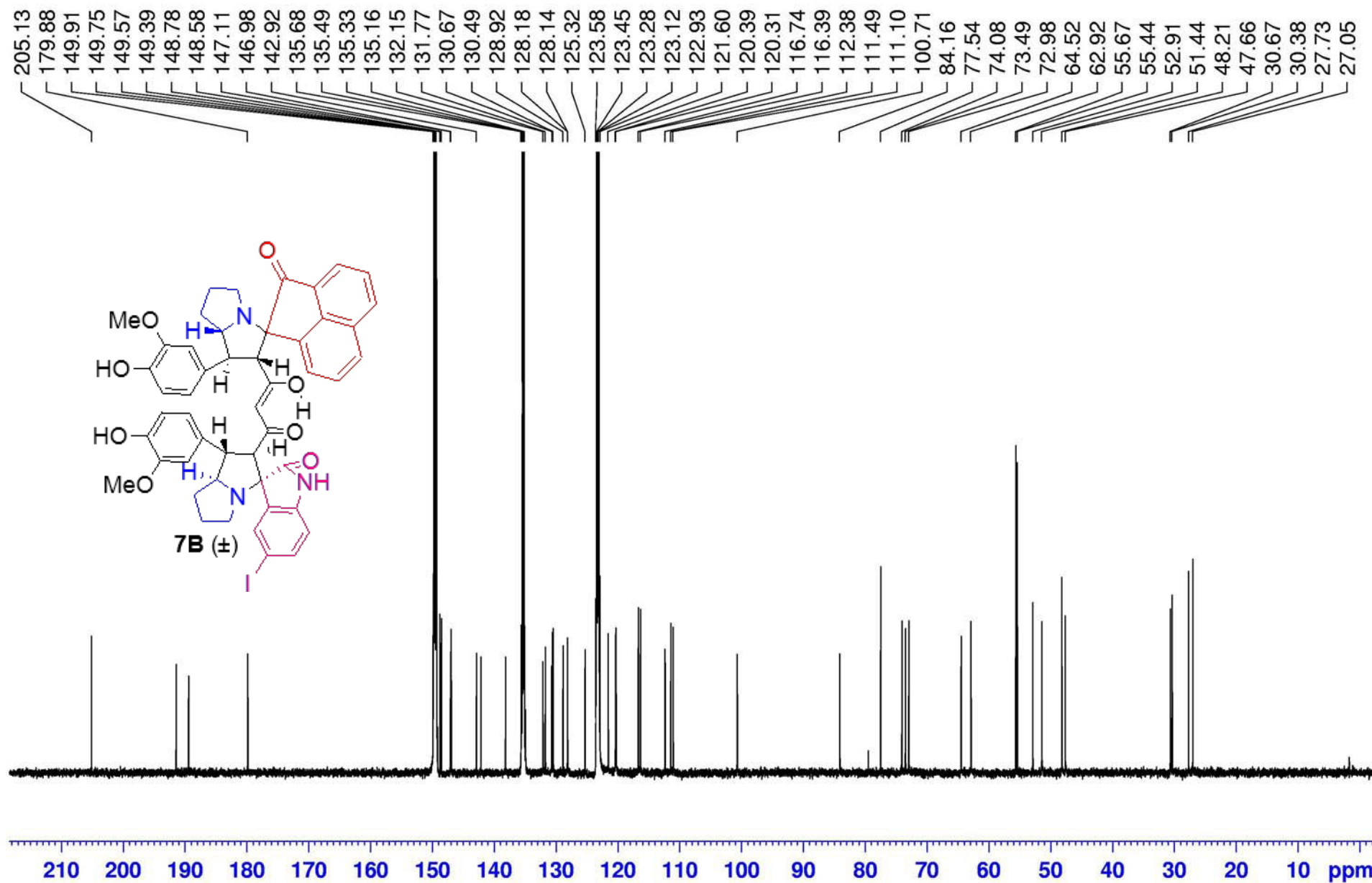


150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

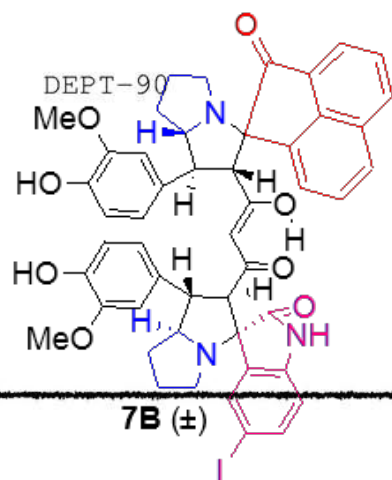


^{13}C -NMR in Py-d₅

HCB

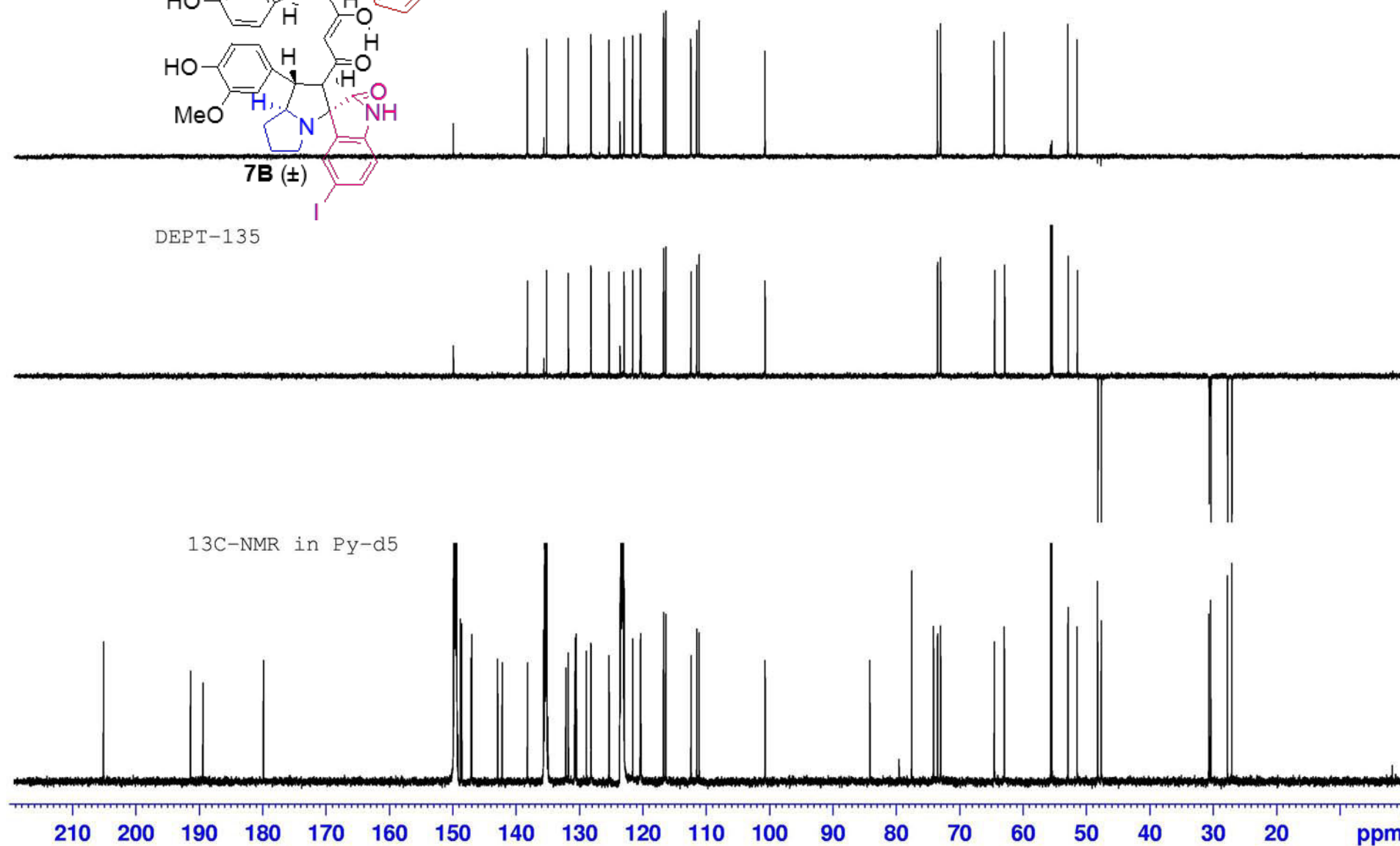


IICB

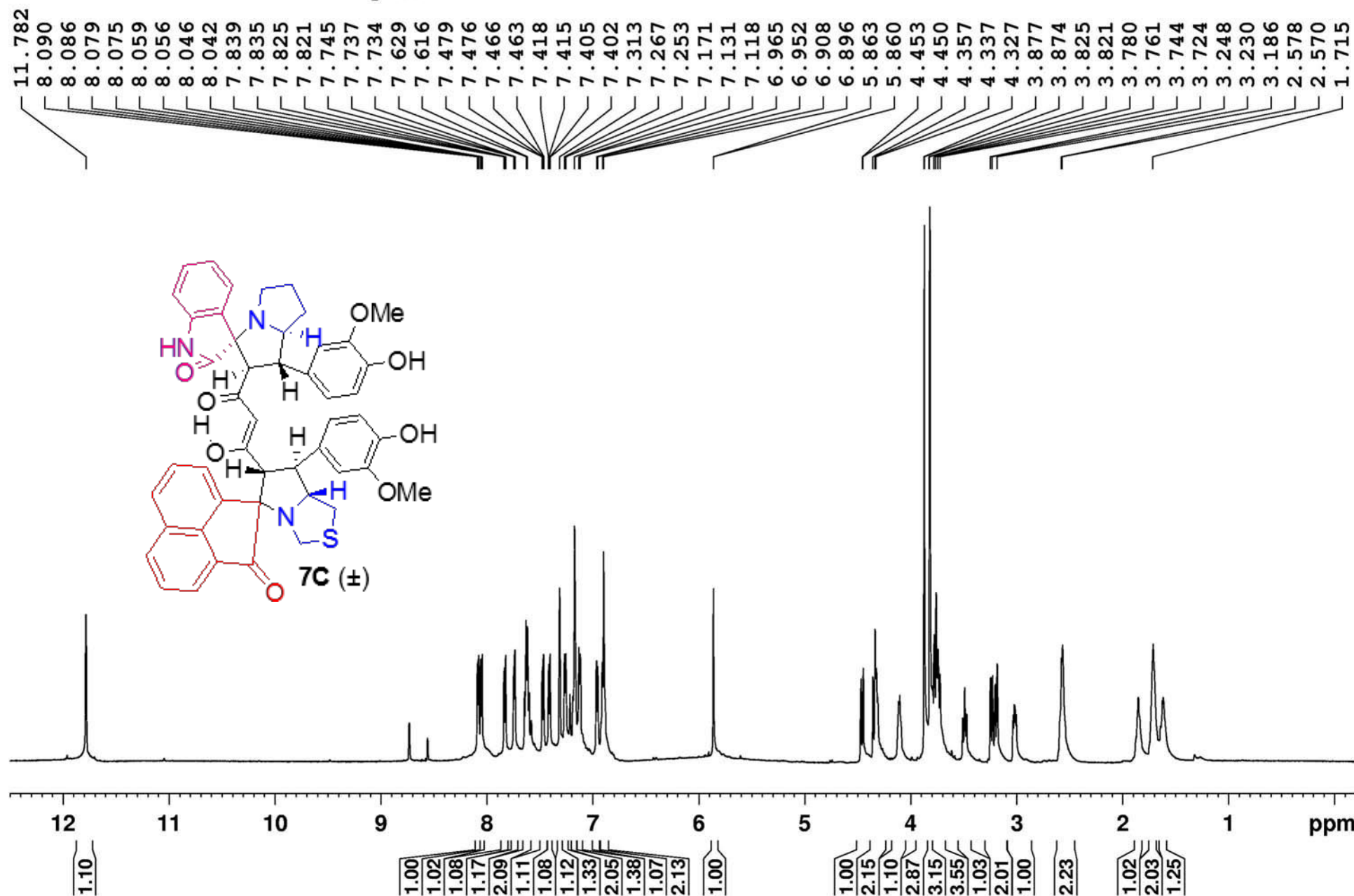


DEPT-135

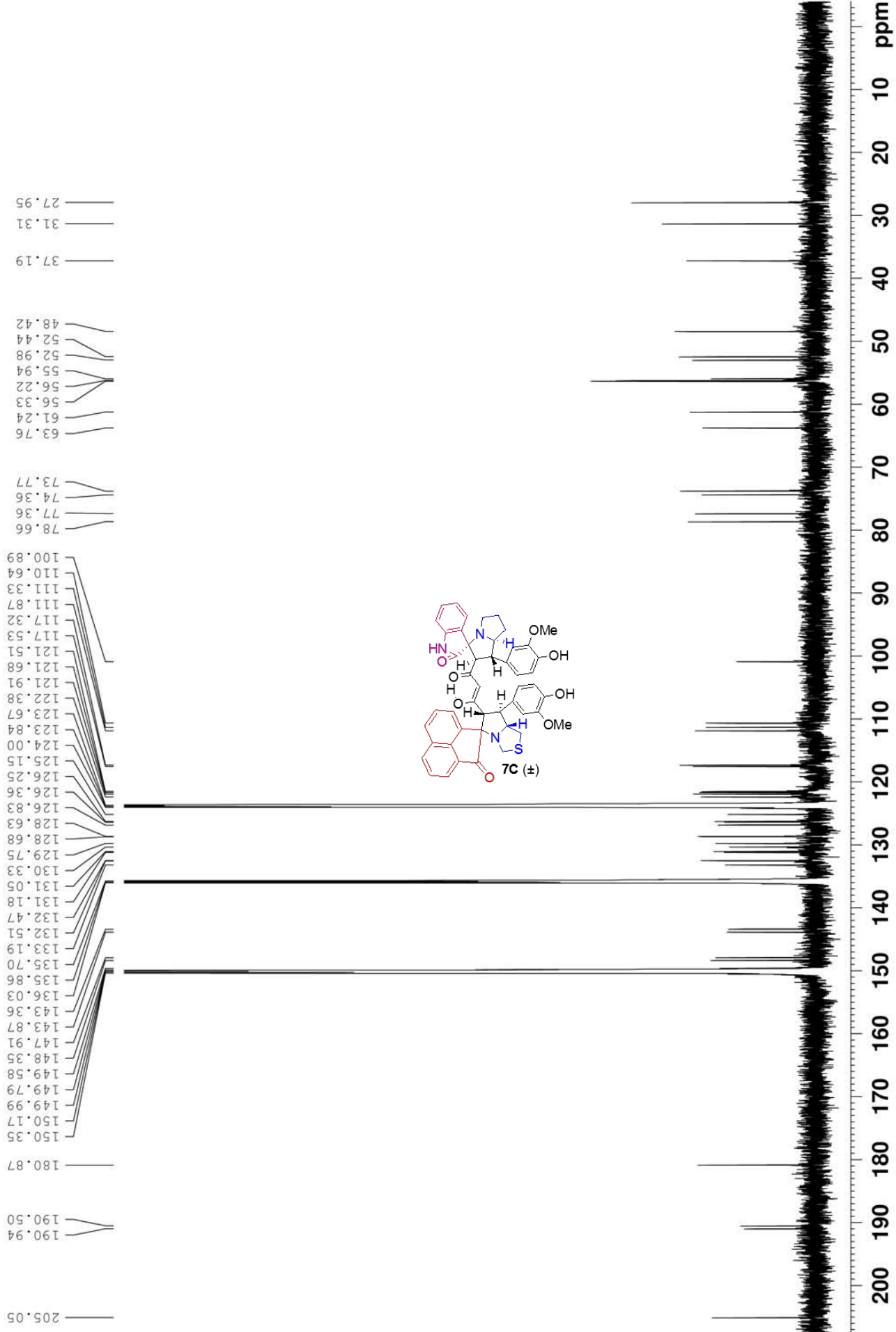
^{13}C -NMR in Py-d₅

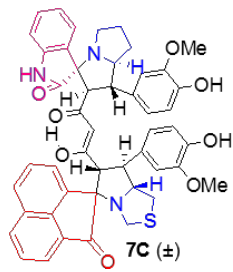


¹H NMR in Py-d₅



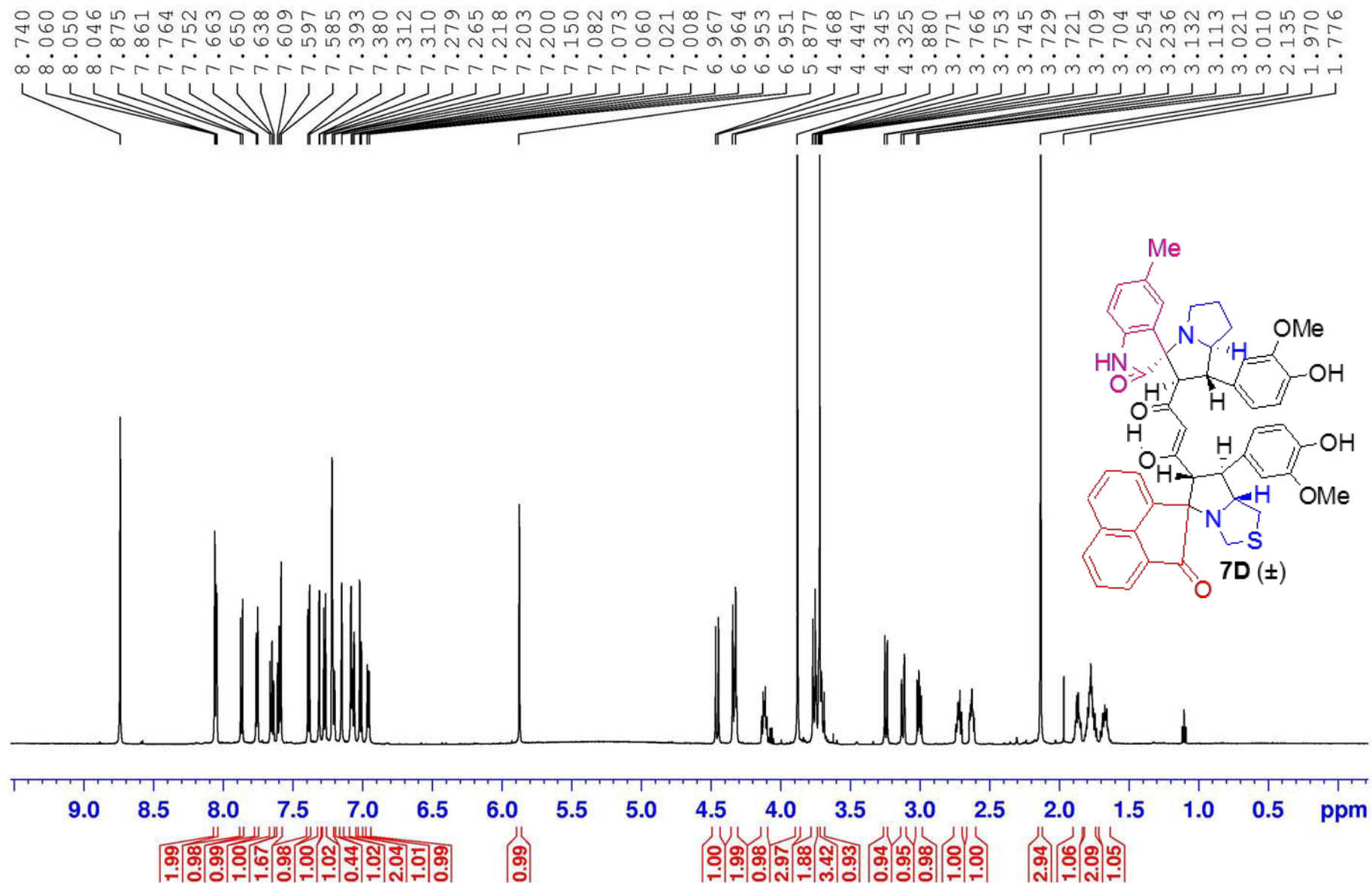
¹³C-NMR in Py-d₅





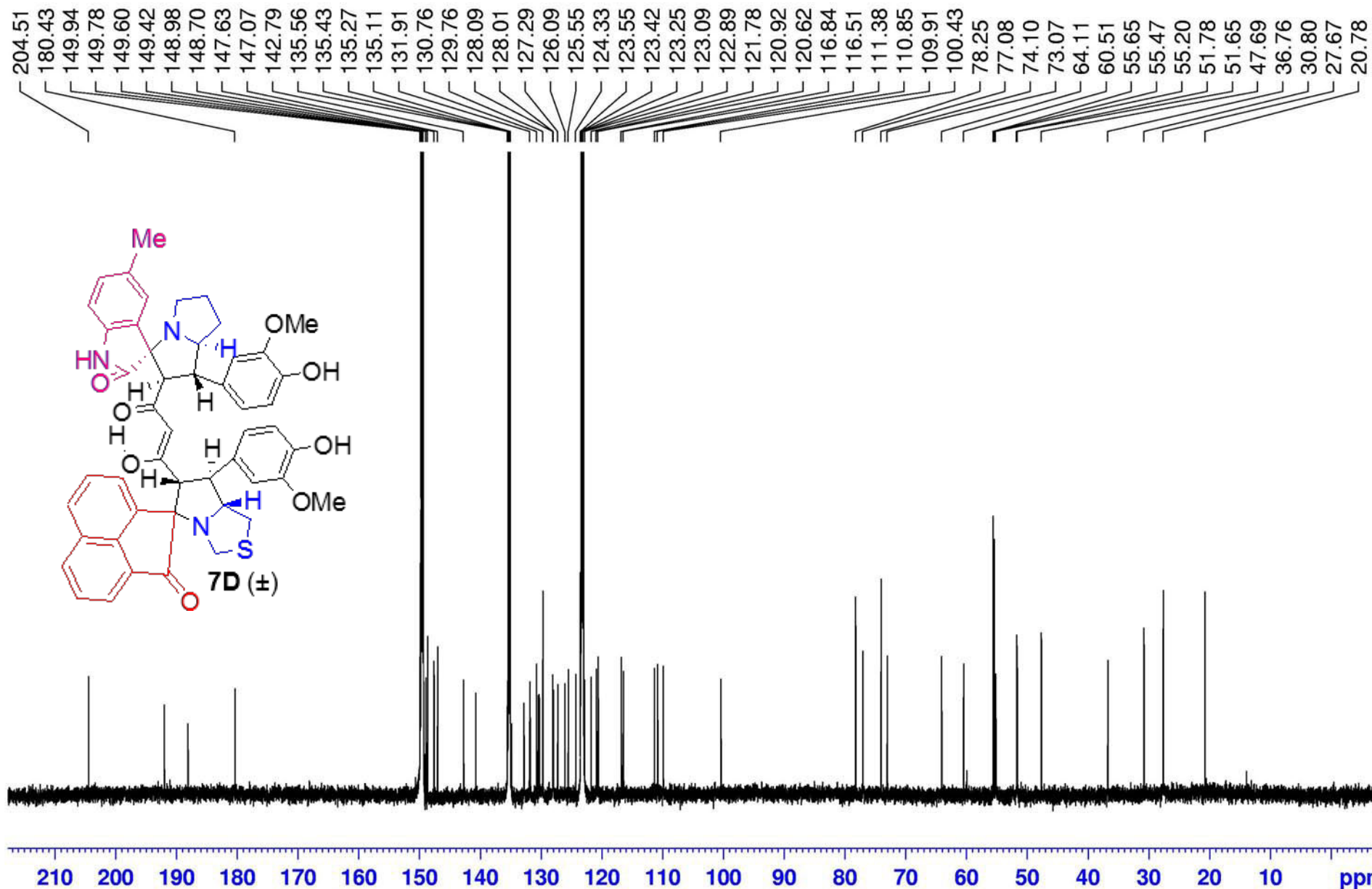
¹H-NMR in Py-d₅

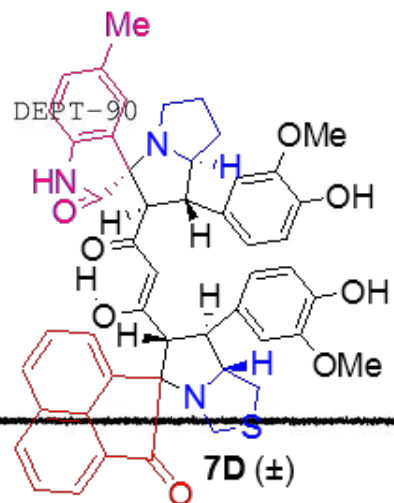
IICB



^{13}C -NMR in Py- d_5

HICB





IICB

