

Supporting Information

for

Formal synthesis of (–)-agelastatin A: an iron(II)-mediated cyclization strategy

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Experimental procedures, characterization data of new compounds, and $^1\text{H}/^{13}\text{C}$ NMR spectra

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General. Melting points are uncorrected. All reagents were used as received from commercial suppliers unless otherwise noted. ^1H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were measured in the specified solvents. Chemical shifts are reported in ppm relative to the internal solvent signal [chloroform-*d*: 7.26 ppm (^1H NMR), 77. ppm (^{13}C NMR); methanol-*d*: 3.30 ppm (^1H NMR), 49.0 ppm (^{13}C NMR); DMSO-*d*₆: 2.49 ppm (^1H NMR), 39.5 ppm (^{13}C NMR)]. FTIR spectra were recorded for samples loaded as neat films on NaCl plates or dispersed in KBr pellets. Mass spectra were obtained according to the specified technique. Analytical thin layer chromatography (TLC) was performed using Kieselgel 60 F₂₅₄. Compounds were visualized with UV light and stained with anisaldehyde solution or phosphomolybdic acid solution.

Preparation of *N*-tosyloxycarbamate **8 from alcohol (+)-**6**:**

Preparation of *N*-hydroxycarbamate **7:** To a stirred solution of alcohol (+)-**6** [1] (300 mg, 1.56 mmol) in THF (14 mL) was added CDI (303 mg, 1.87 mmol). After 4.5 h at room temperature, TLC analysis indicated complete conversion of the starting material into the corresponding imidazolidine. To this mixture was added hydroxylamine hydrochloric acid salt (302 mg, 4.68 mmol), and stirring was continued for an additional 23.5 h at room temperature. The reaction mixture was then poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The organic layer was separated, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc → MeOH/EtOAc 1:30 v/v) to afford *N*-hydroxycarbamate **7** (255 mg, 67%) as a colorless solid. $[\alpha]_{\text{D}}^{22} +105.3$ (*c* 0.485, MeOH); IR (KBr) ν 3464, 3246, 1718, 1647 cm⁻¹; ^1H NMR (400 MHz, CD₃OD) δ 6.91-6.77 (m, 2H), 6.50 (m, 1H), 6.27-6.16 (m, 2H), 6.09 (m, 1H), 5.79 (m, 1H), 2.51 (ddd, 1H, *J* = 15.2, 8.0, 2.4 Hz), 2.09 (ddd, 1H, *J* = 14.4, 7.6, 2.0 Hz); ^{13}C NMR (100 MHz, CD₃OD) δ 166.6, 160.5, 138.4, 134.9, 125.9, 124.2, 115.6, 109.2, 80.9, 63.1, 41.5; MS *m/z*: 251 (*M*⁺), 174 (100%); HRMS–EI (*m/z*): [*M*]⁺ calcd for C₁₁H₁₃N₃O₄, 251.0906; found, 251.0922.

Preparation of *N*-tosyloxycarbamate **8:** To a solution of *N*-hydroxycarbamate **7** (228 mg, 0.908 mmol) in THF (12.5 mL) at 0 °C were added Et₃N (190 µL, 1.36 mmol) and TsCl (190 mg, 0.998 mmol), and the mixture was warmed to room temperature. After being stirred for 30 min at room temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1 v/v) to afford *N*-tosyloxycarbamate **8** (341 mg, 92%) as a colorless solid. $[\alpha]_D^{20} +71.6$ (*c* 0.485, CHCl₃); IR (neat) ν 3468, 3374, 2926, 1761, 1645 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.37 (brs, 1H), 7.89 (d, 2H, *J* = 8.2 Hz), 7.37 (d, 2H, *J* = 8.7 Hz), 6.75-6.61 (m, 2H), 6.42 (m, 1H), 6.19-6.06 (m, 2H), 6.03 (m, 1H), 5.92-5.52 (m, 3H), 2.46 (s, 3H), 2.36 (ddd, 1H, *J* = 15.1, 7.8, 2.7 Hz), 2.04 (ddd, 1H, *J* = 15.1, 7.3, 4.1 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 155.4, 146.1, 137.4, 133.4, 130.3, 129.7, 129.6, 124.0, 123.3, 114.0, 108.3, 81.2, 61.8, 39.8, 21.8; MS *m/z*: 406 (MH⁺), 154 (100%); HRMS–FAB [*M* + H]⁺ calcd for C₁₈H₂₀N₃O₆S, 406.1073; found, 406.1073.

Protocols for aminohalogenation of *N*-tosyloxycarbamate **8 with FeX₂/Bu₄NX:**

Table 1, entry 4

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in *t*-BuOH (1 mL) were added Bu₄NCl (16.4 mg, 0.059 mmol) and FeCl₂ (3.2 mg, 0.025 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 2.5 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1→3:1→EtOAc v/v) to afford chloride **5b** (6.3 mg, 48%) carbamate **9** (1.2 mg, 9%), and enone **10** (0.9 mg, 9%), all as colorless solids. **Chloride 5b**: IR (KBr) ν 3339, 2928, 1746, 1653 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 7.15 (dd, 1H, *J* = 2.8, 1.8 Hz), 6.81 (dd, 1H, *J* = 3.7, 1.8 Hz), 6.19 (dd, 1H, *J* = 3.7, 2.8 Hz), 5.92 (ddd, 1H, *J* = 11.5, 11.4,

6.9 Hz), 5.15 (t, 1H, $J = 6.9$ Hz), 4.55 (dd, 1H, $J = 11.5, 6.0$ Hz), 4.46 (m, 1H), 2.54 (dd, 1H, $J = 14.7, 6.9$ Hz), 2.31 (ddd, 1H, $J = 14.7, 11.4, 6.0$ Hz); ^1H NMR (400 MHz, DMSO- d_6) δ 8.14 (d, 1H, $J = 0.9$ Hz), 7.55 (brs, 1H), 7.23 (dd, 1H, $J = 2.8, 1.8$ Hz), 6.93 (brs, 1H), 6.79 (dd, 1H, $J = 3.6, 1.8$ Hz), 6.12 (dd, 1H, $J = 3.6, 2.8$ Hz), 5.95 (ddd, 1H, $J = 11.9, 11.4, 7.3$ Hz), 5.05 (dd, 1H, $J = 6.9, 6.8$ Hz), 4.67 (dd, 1H, $J = 11.4, 5.5$ Hz), 4.37 (m, 1H), 2.31 (dd, 1H, $J = 13.7, 7.3$ Hz), 2.19 (ddd, 1H, $J = 13.7, 11.9, 6.0$ Hz), ^{13}C NMR (125 MHz, DMSO- d_6) δ 163.1, 158.5, 126.3, 122.7, 113.6, 108.3, 75.9, 63.9, 58.5, 56.9, 37.7. **Carbamate 9**: IR (KBr) ν 3389, 2951, 1690, 1663 cm^{-1} ; ^1H NMR (400 MHz, CD_3OD) δ 6.86-6.77 (m, 2H), 6.49 (m, 1H), 6.21-6.13 (m, 2H), 6.08 (dd, 1H, $J = 3.7, 2.7$ Hz), 5.69 (m, 1H), 2.49 (ddd, 1H, $J = 15.1, 7.8, 2.7$ Hz), 2.06 (ddd, 1H, $J = 15.1, 7.3, 4.6$ Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 166.6, 159.7, 137.9, 135.3, 125.9, 124.2, 115.6, 109.1, 80.1, 63.1, 41.5. **Enone 10**: IR (neat) ν 3349, 2926, 1715, 1645 cm^{-1} ; ^1H NMR (400 MHz, CD_3OD) δ 7.76 (dd, 1H, $J = 5.5, 2.7$ Hz), 6.90-6.80 (m, 2H), 6.66 (m, 1H), 6.39 (dd, 1H, $J = 5.5, 2.3$ Hz), 6.15 (dd, 1H, $J = 4.1, 2.8$ Hz), 3.02 (dd, 1H, $J = 18.8, 6.4$ Hz), 2.27 (dd, 1H, $J = 18.8, 2.3$ Hz); ^1H NMR (300 MHz, CDCl_3) δ 7.65 (dd, 1H, $J = 5.9, 2.4$ Hz), 6.86-6.72 (m, 3H), 6.42 (dd, 1H, $J = 5.9, 1.7$ Hz), 6.19 (dd, 1H, $J = 3.7, 2.8$ Hz), 5.60 (brs, 2H), 3.12 (dd, 1H, $J = 19.3, 6.5$ Hz), 2.31 (dd, 1H, $J = 19.3, 2.4$ Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 208.9, 166.3, 163.1, 136.7, 126.0, 124.7, 115.7, 109.9, 58.1, 45.0. All the spectroscopic and analytical data of chloride **5b**, carbamate **9**, and enone **10** were identical with those reported in the previous study [2]. The chemical shifts in the ^{13}C NMR spectrum of carbamate **9** in the literature [2] were erroneous due to the incorrect assignment of reference solvent signal (CD_3OD for 49.0 ppm). The corrected data are given above.

Table 1, entry 1

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in EtOH (1 mL) were added Bu_4NBr (23.8 mg, 0.074 mmol) and FeBr_2 (5.4 mg, 0.025 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 1.75 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H_2O . The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic

extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1→EtOAc v/v) to afford bromide **5a** (2.0 mg, 13%), enone **10** (2.8 mg, 30%), and carbamate **9** (4.5 mg, 39%). **Bromide 5b**: IR (KBr) ν 3376, 2955, 1751, 1647 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 7.13 (dd, 1H, *J* = 2.8, 1.4 Hz), 6.81 (dd, 1H, *J* = 3.7, 1.4 Hz), 6.19 (dd, 1H, *J* = 3.7, 2.8 Hz), 5.97 (ddd, 1H, *J* = 11.5, 11.0, 7.3 Hz), 5.17 (t, 1H, *J* = 6.9 Hz), 4.57 (dd, 1H, *J* = 11.0, 6.0 Hz), 4.47 (m, 1H), 2.55 (dd, 1H, *J* = 14.2, 7.3 Hz), 2.29 (ddd, 1H, *J* = 14.2, 11.5, 6.0 Hz); ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.11 (d, 1H, *J* = 0.9 Hz), 7.55 (brs, 1H), 7.21 (dd, 1H, *J* = 2.7, 1.4 Hz), 6.92 (brs, 1H), 6.78 (dd, 1H, *J* = 3.7, 1.4 Hz), 6.11 (dd, 1H, *J* = 3.7, 2.7 Hz), 6.00 (ddd, 1H, *J* = 12.4, 11.4, 7.3 Hz), 5.06 (dd, 1H, *J* = 6.9, 6.4 Hz), 4.69 (dd, 1H, *J* = 11.4, 5.5 Hz), 4.37 (m, 1H), 2.31 (dd, 1H, *J* = 13.7, 7.3 Hz), 2.15 (ddd, 1H, *J* = 13.7, 12.4, 6.4 Hz), ¹³C NMR (125 MHz, DMSO-*d*₆) δ 163.1, 158.4, 126.3, 122.6, 113.5, 108.3, 76.3, 58.8, 57.1, 56.0, 38.0. The spectroscopic and analytical data of bromide **5a** were exactly matched with those reported in the previous study [2].

Table 1, entry 2

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.0493 mmol in EtOH (1 mL) were added Bu₄NCl (16.4 mg, 0.0592 mmol) and FeCl₂ (3.2 mg, 0.0247 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 0.75 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1→EtOAc v/v) to afford chloride **5b** (5.2 mg, 39%), enone **10** (1.8 mg, 19%), and carbamate **9** (2.4 mg, 20%). The yields of the materials were determined by ¹H NMR analysis.

Table 1, entry 3

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in *t*-BuOH (1 mL) were added Bu₄NBr (19.1 mg, 0.059 mmol) and FeBr₂ (5.4 mg, 0.025 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 0.5 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1→EtOAc v/v) to afford bromide **5a** (5.8 mg, 38%), carbamate **9** (2.5 mg, 22%), and enone **10** (1.8 mg, 19%). The yields of the materials were determined by ¹H NMR analysis.

Table 1, entry 5

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in *t*-BuOH (1 mL) were added Bu₄NBr (19.1 mg, 0.059 mmol) and FeBr₂ (2.2 mg, 0.01 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 3.3 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1 v/v → EtOAc) to afford bromide **5a** (3.8 mg, 25%), carbamate **9** (1.9 mg, 16%), and enone **10** (0.5 mg, 5%), and unreacted *N*-tosyloxycarbamate **8** (4.4 mg, 22%). The yields of the materials were determined by ¹H NMR analysis.

Table 1, entry 6

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in *t*-BuOH (1 mL) were added Bu₄NCl (16.4 mg, 0.059 mmol) and FeCl₂ (1.3 mg, 0.01 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 3.3 h at the same temperature, the mixture was poured into a

separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 2:1 v/v → EtOAc) to afford chloride **5b** (4.1 mg, 31%), carbamate **9** (1.1 mg, 9%), and enone **10** (1.3 mg, 14%), and unreacted *N*-tosyloxycarbamate **8** (6.0 mg, 30%). The yields of the materials were determined by ¹H NMR analysis.

Table 1, entry 7

To a solution of *N*-tosyloxycarbamate **8** (20 mg, 0.049 mmol) in EtOH (1 mL) were added TMSCl (9.4 μL, 0.073 mmol) and FeCl₂ (3.2 mg, 0.025 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 16 h at the same temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H₂O. The phases were separated, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 4:1 → EtOAc) to afford chloride **5b** (3.9 mg, 29%), carbamate **9** (1.4 mg, 12%), diethyl ketal **12** (1.8 mg, 14%), and ketone **11** (1.5 mg, 16%). The yields of the materials were determined by ¹H NMR analysis. **Ketone 11**: colorless solid; $[\alpha]_D^{21} -10.1$ (*c* 0.14, MeOH); IR (neat) ν 3223, 2926, 1748, 1645 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 7.05 (dd, 1H, *J* = 2.7, 1.4 Hz), 6.91 (dd, 1H, *J* = 3.7, 1.4 Hz), 6.27 (dd, 1H, *J* = 3.7, 2.7 Hz), 4.95 (ddd, 1H, *J* = 12.4, 7.3, 5.0 Hz), 4.53 (m, 1H), 2.84 (dd, 1H, *J* = 18.3, 7.3 Hz), 2.71 (dd, 1H, *J* = 18.3, 6.0 Hz), 2.57 (ddd, 1H, *J* = 18.7, 7.3, 1.8 Hz), 2.44 (ddd, 1H, *J* = 18.7, 3.7, 1.4 Hz); ¹³C NMR (100 MHz, CD₃OD) δ 213.0, 162.4, 125.4, 122.9, 115.6, 111.4, 54.9, 53.4, 45.4, 43.7; MS *m/z*: 190 (*M*⁺), 190 (100%); HRMS–EI (*m/z*): [*M*]⁺ calcd for C₁₀H₁₀N₂O₂, 190.0742; found, 190.0741. **Diethyl ketal 12**: colorless solid; $[\alpha]_D^{22} +1.8$ (*c* 0.18, CHCl₃); IR (neat) ν 3206, 2974, 1651 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.97 (dd, 1H, *J* = 3.7, 1.4 Hz), 6.44 (dd, 1H, *J* = 2.9, 1.4 Hz), 6.27 (dd, 1H, *J* = 3.7, 1.4 Hz), 5.92 (brs, 1H), 4.56 (m, 1H), 4.26 (m, 1H), 3.55-3.33 (m, 4H), 2.47 (dd, 1H, *J* = 13.3, 6.9 Hz), 2.42-2.29 (m, 2H), 2.02 (dd, 1H, *J* = 13.7, 5.0 Hz), 1.20 (t, 3H, *J* = 6.9 Hz), 1.12

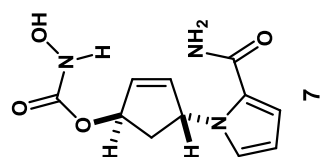
(t, 3H, $J = 6.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 122.8, 122.3, 114.0, 110.2, 107.5, 57.8, 56.4, 55.0, 53.4, 42.3, 41.6, 15.3, 15.1; MS m/z : 264 (M^+), 135 (100%); HRMS–EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_3$, 264.1474; found, 264.1475.

Aminobromination of azidoformate 3 with $\text{FeBr}_2/\text{Bu}_4\text{NBr}$: To a stirred solution of azidoformate **3** (2.0 g, 7.66 mmol) in EtOH (100 mL) were added Bu_4NBr (3.7 g, 11.4 mmol) and FeBr_2 (843 mg, 3.81 mmol). The mixture was warmed to 28 °C in a water bath and sonicated for ca. 1 min to dissolve all the reagents. After being stirred for 10 h at the same temperature, the mixture was filtered through a pad of celite/florisil, and the filtrate was concentrated under reduced pressure. The residue was diluted with EtOAc and poured into a separatory funnel where it was partitioned between EtOAc and H_2O . The organic extracts were combined, dried over MgSO_4 , filtered, and concentrated. The residue was rinsed with MeOH and filtered to give bromide **5a** (1.61 g, 67%) as a colorless solid. The filtrate was concentrated under reduced pressure to provide a residue, which was further purified by flash silica gel column chromatography (EtOAc/*n*-hexane 4:1 v/v \rightarrow EtOAc) to afford carbamate **9** (281 mg, 16%), enone **10** (51 mg, 3%), and additional bromide **5a** (67 mg, 3%), all as colorless solids.

Reaction of enone 10 with TMSCl in EtOH: To a solution of enone **10** (15 mg, 0.08 mmol) in EtOH (1 mL) was added TMSCl (12 μL , 0.09 mmol). After being stirred for 3 h at room temperature, the mixture was poured into a separatory funnel where it was partitioned between EtOAc and H_2O . The phases were separated and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (EtOAc/*n*-hexane 4:1 \rightarrow 6:1 \rightarrow EtOAc v/v) to give ketone **11** (1.5 mg, 10%) and diethyl ketal **12** (4.0 mg, 19%), both as colorless solids.

References

- 1) Yoshimitsu, T.; Ino, T.; Tanaka, T. *Org. Lett.* **2008**, *10*, 5457.
- 2) Yoshimitsu, T.; Ino, T.; Futamura, N.; Kamon, T.; Tanaka, T. *Org. Lett.* **2009**, *11*, 3402.



2.01

1.00

2.00

1.00

1.00

1.00

1.00

1.00

1.00

PPM

0

1

2

3

4

5

6

7

8

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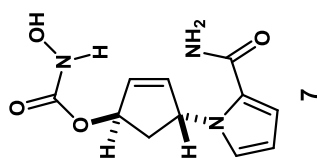
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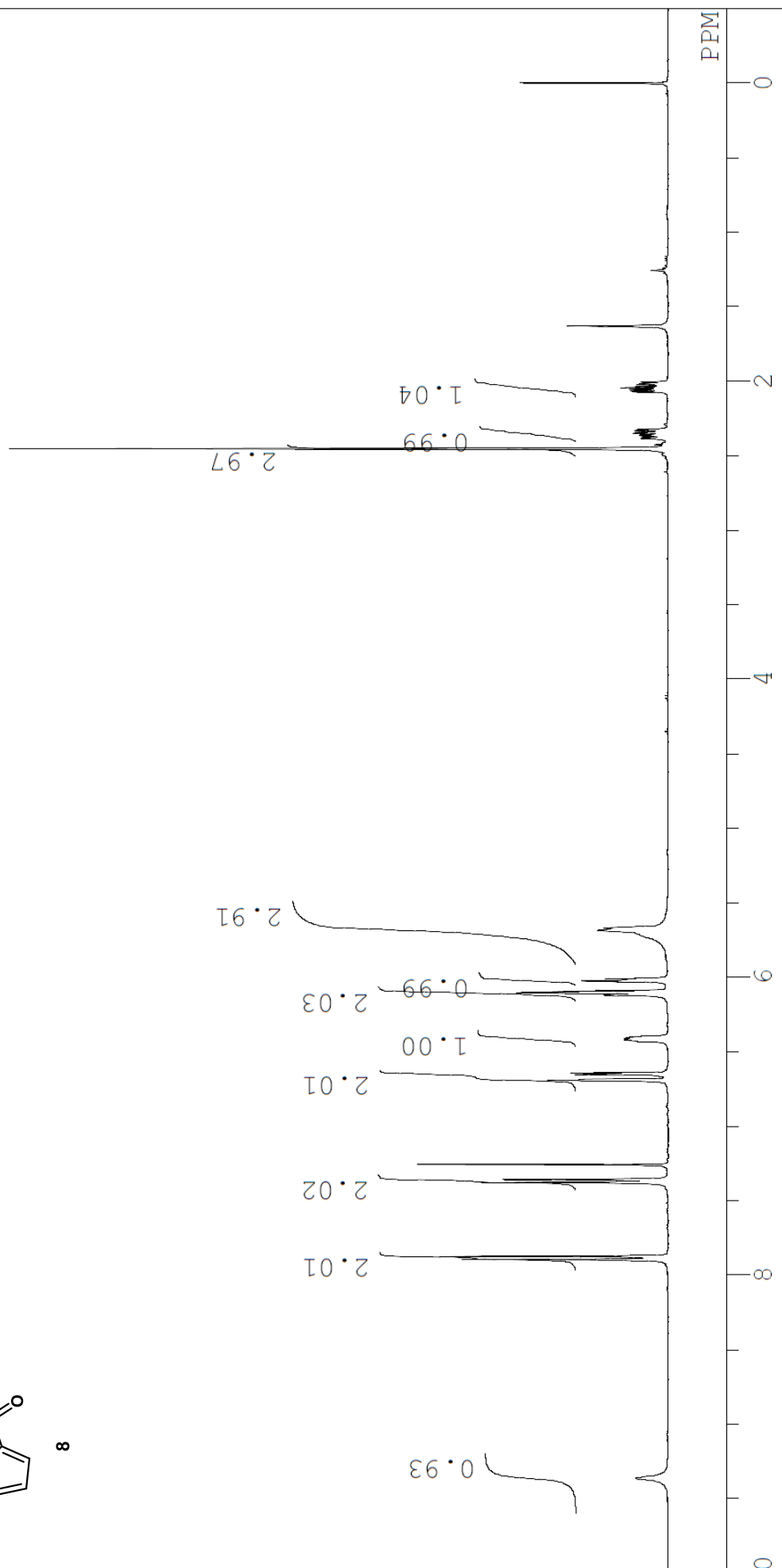
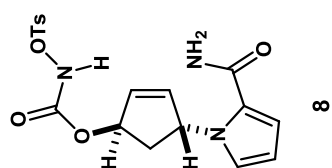
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100MHz, CDCl₃

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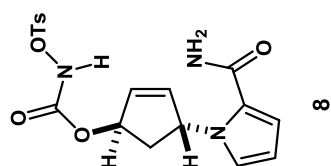
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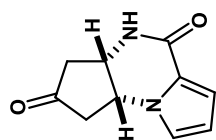
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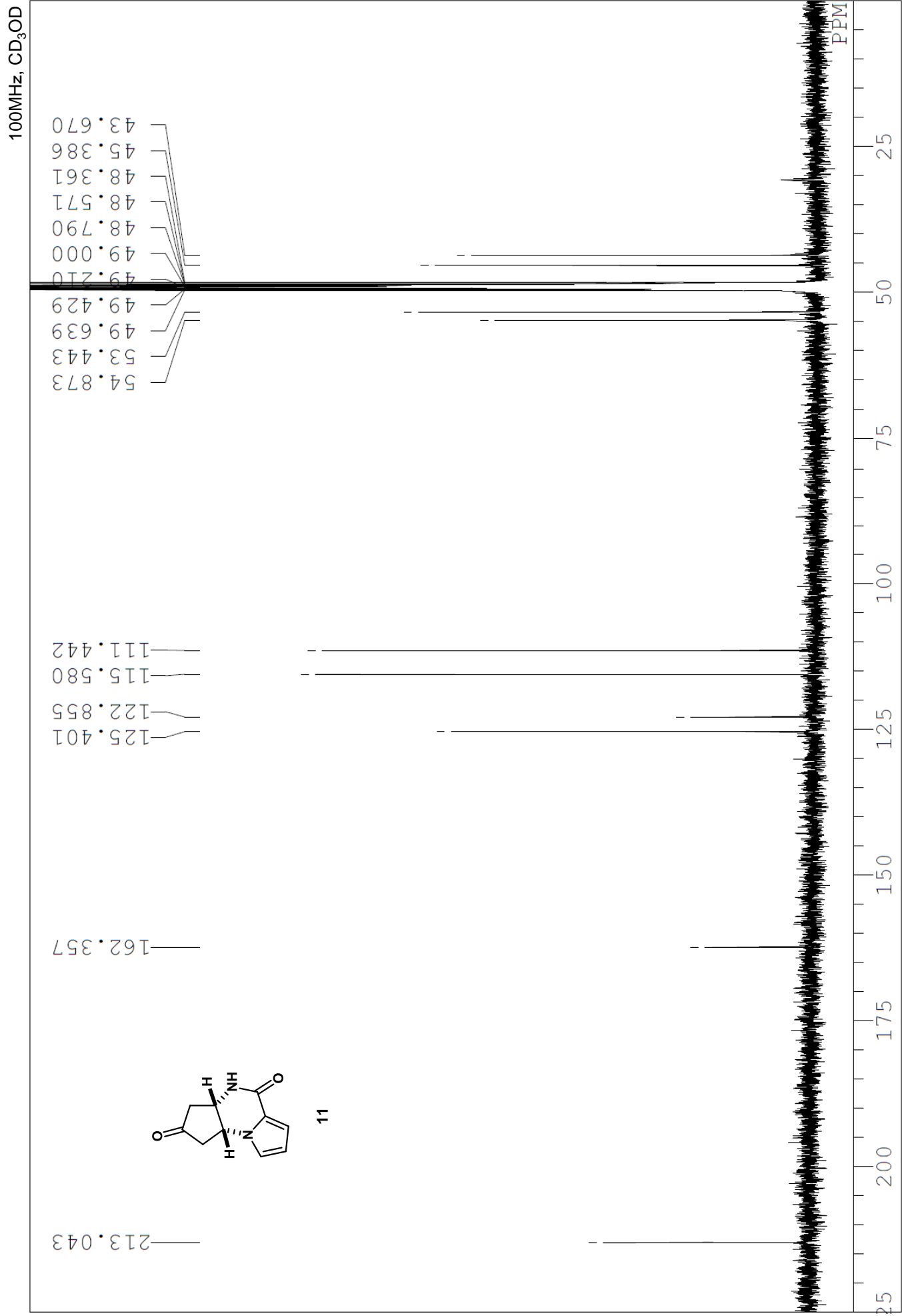
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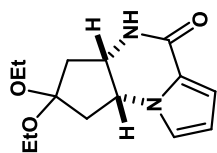
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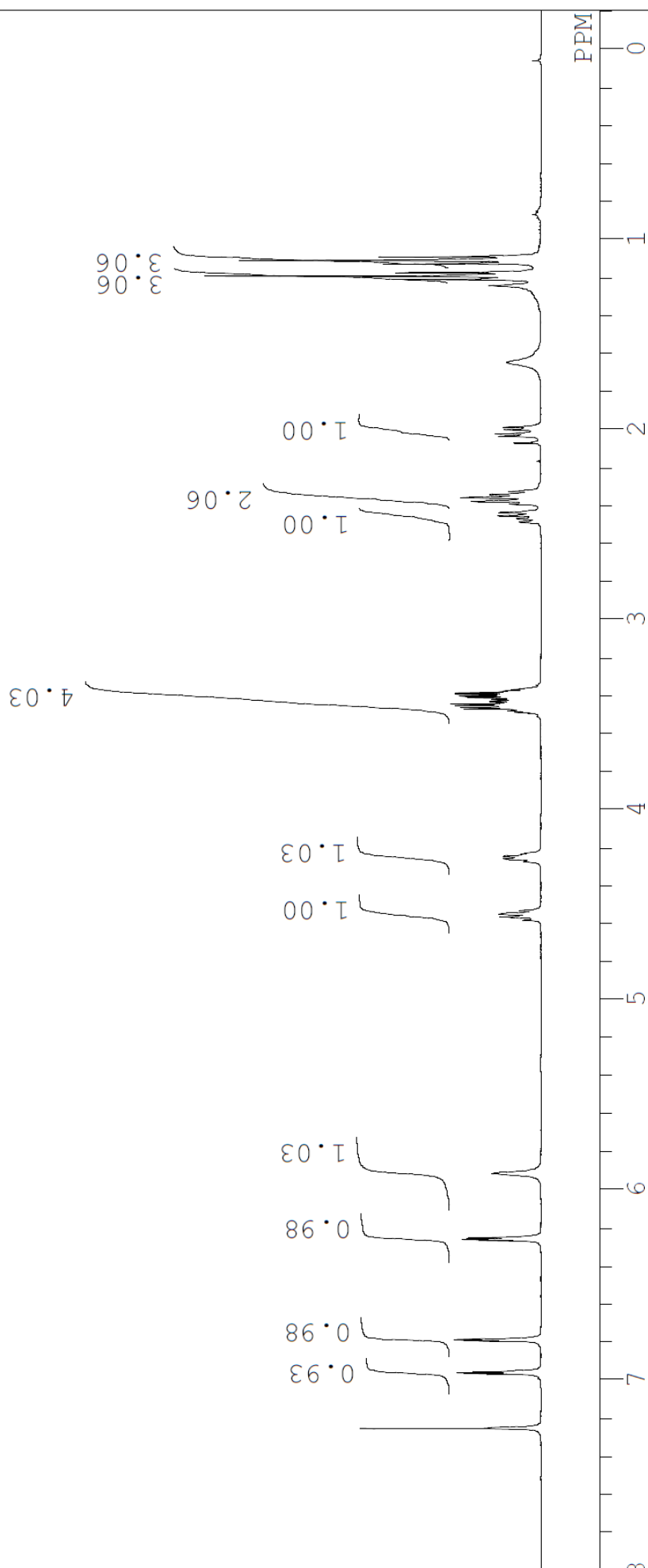
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0.93

PPM





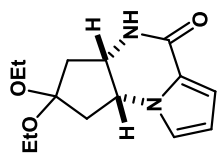
12



15.311
15.12141.636
42.33253.373
55.013
56.434
57.80776.676
77.000
77.315107.482
110.238
114.042122.261
122.814

159.531

PPM



12

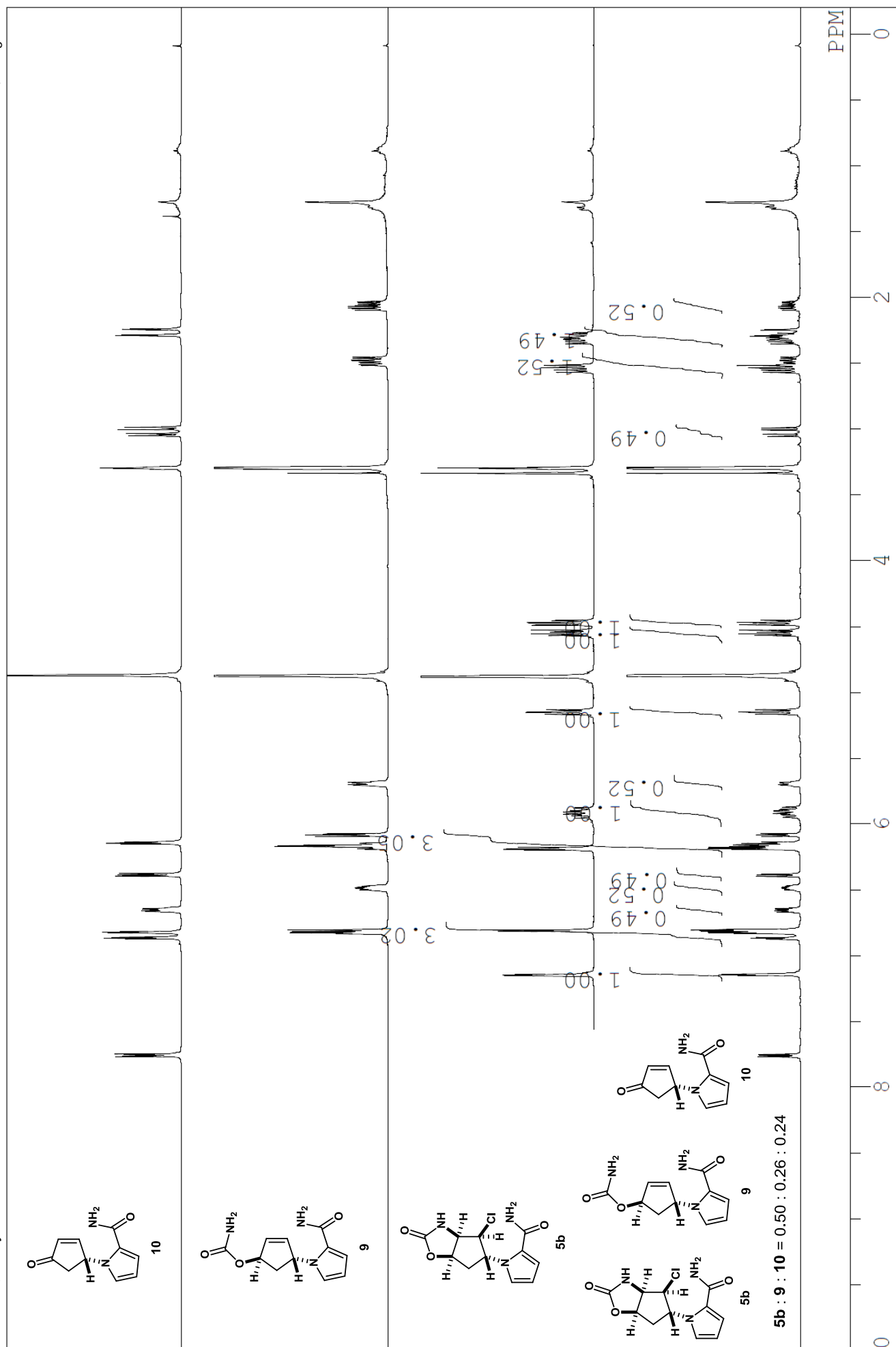
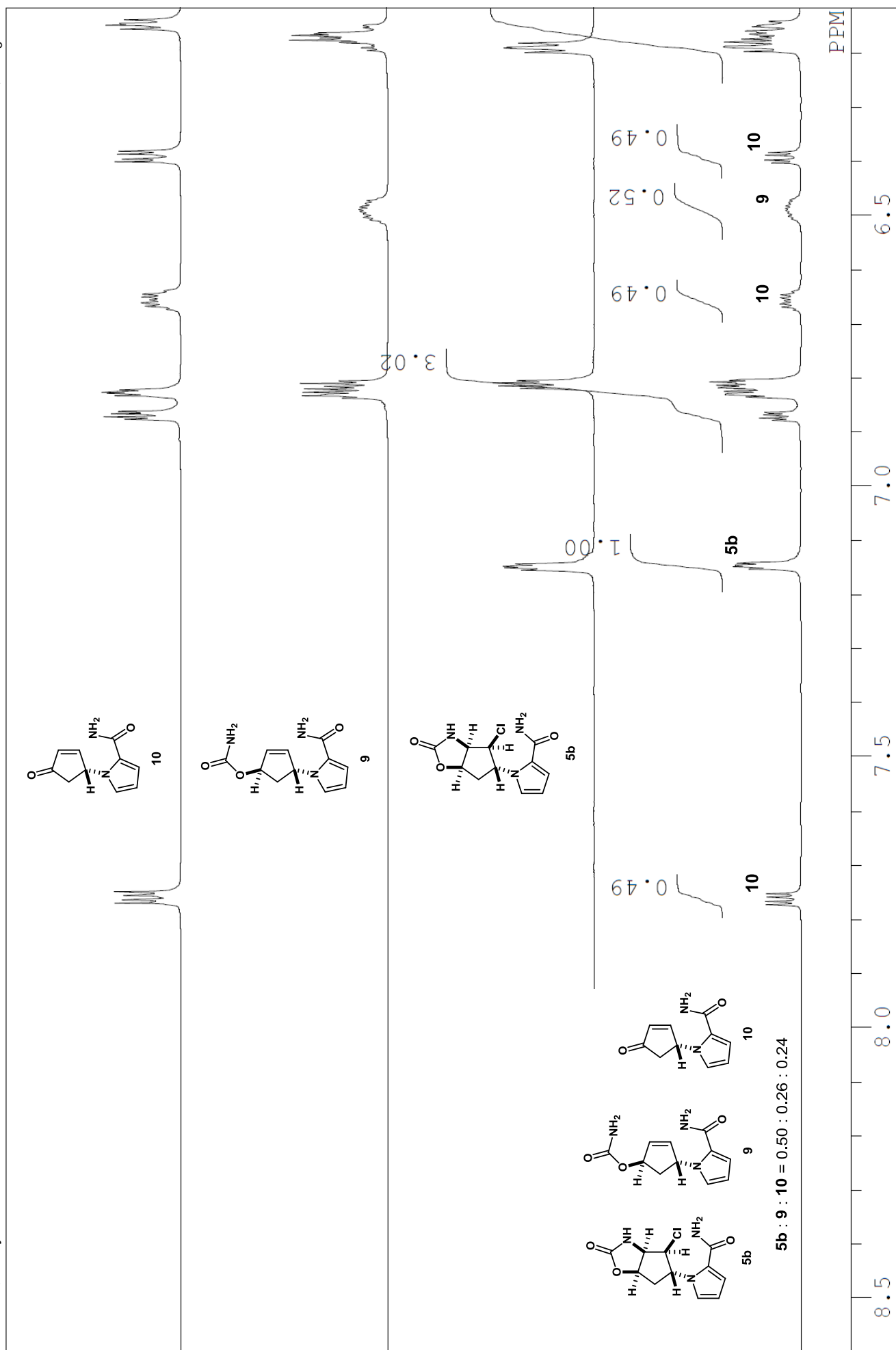


Table 1, entry 2

400MHz, CD₃OD



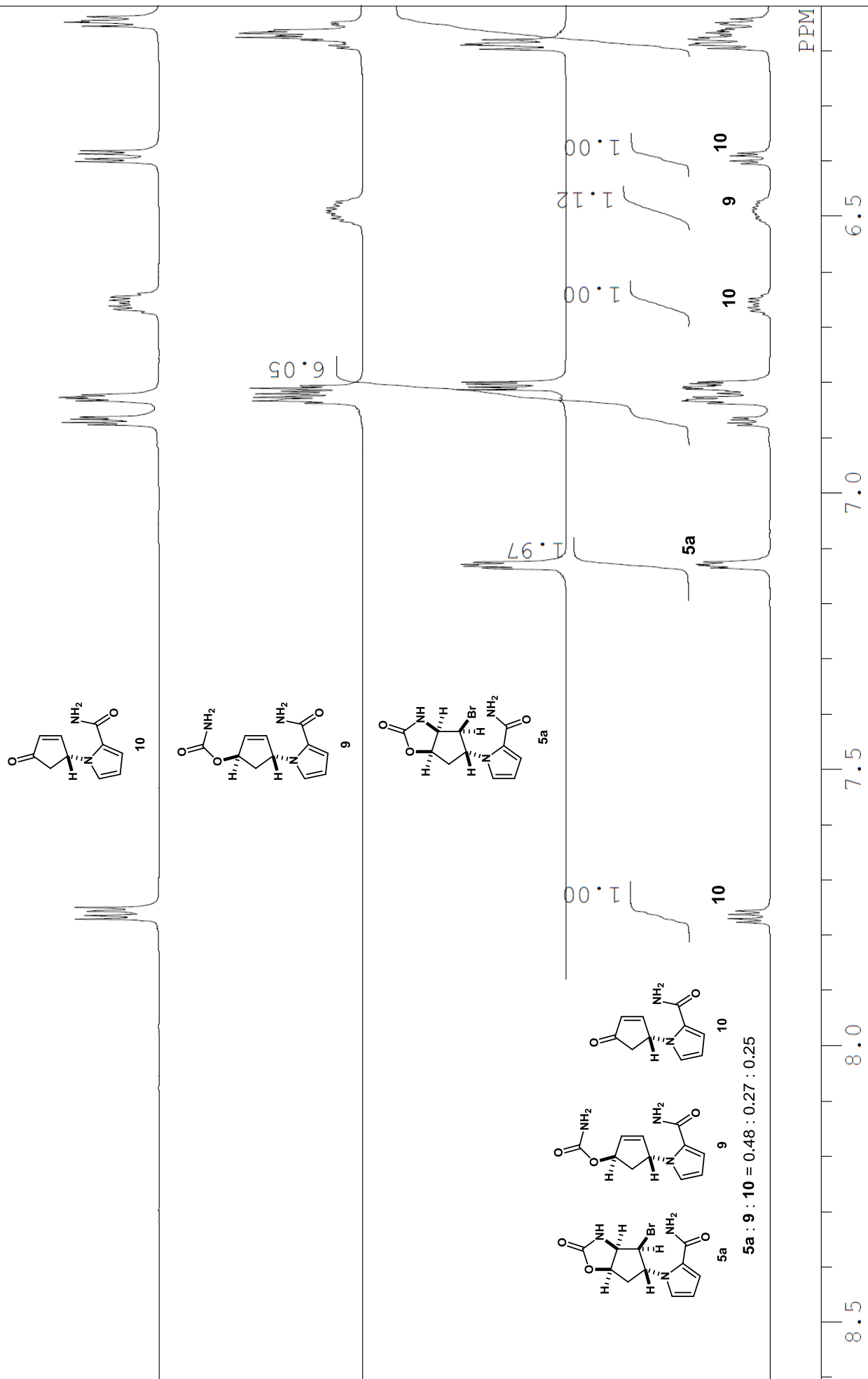
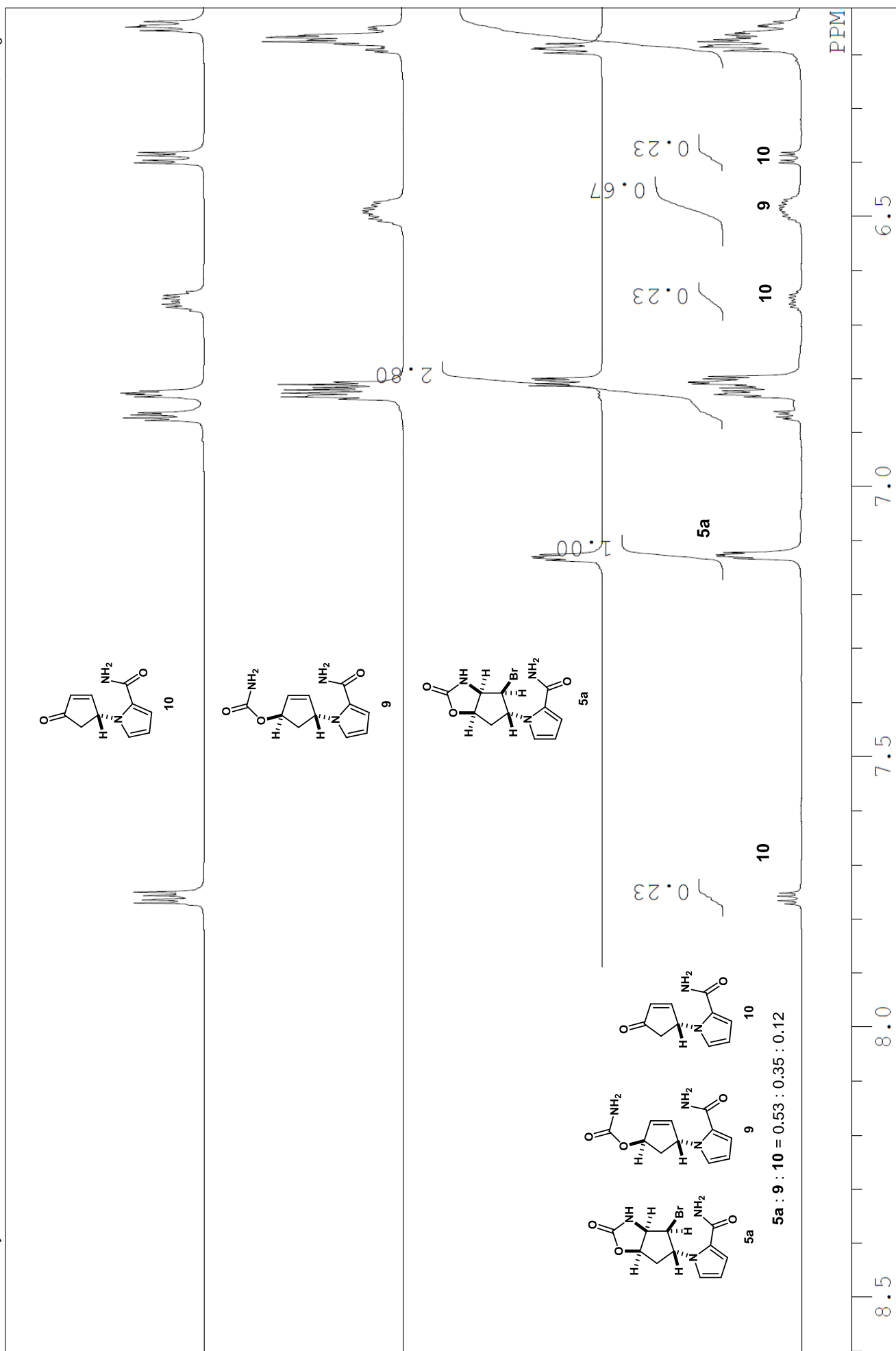




Table 1, entry 5

400MHz, CD₃OD



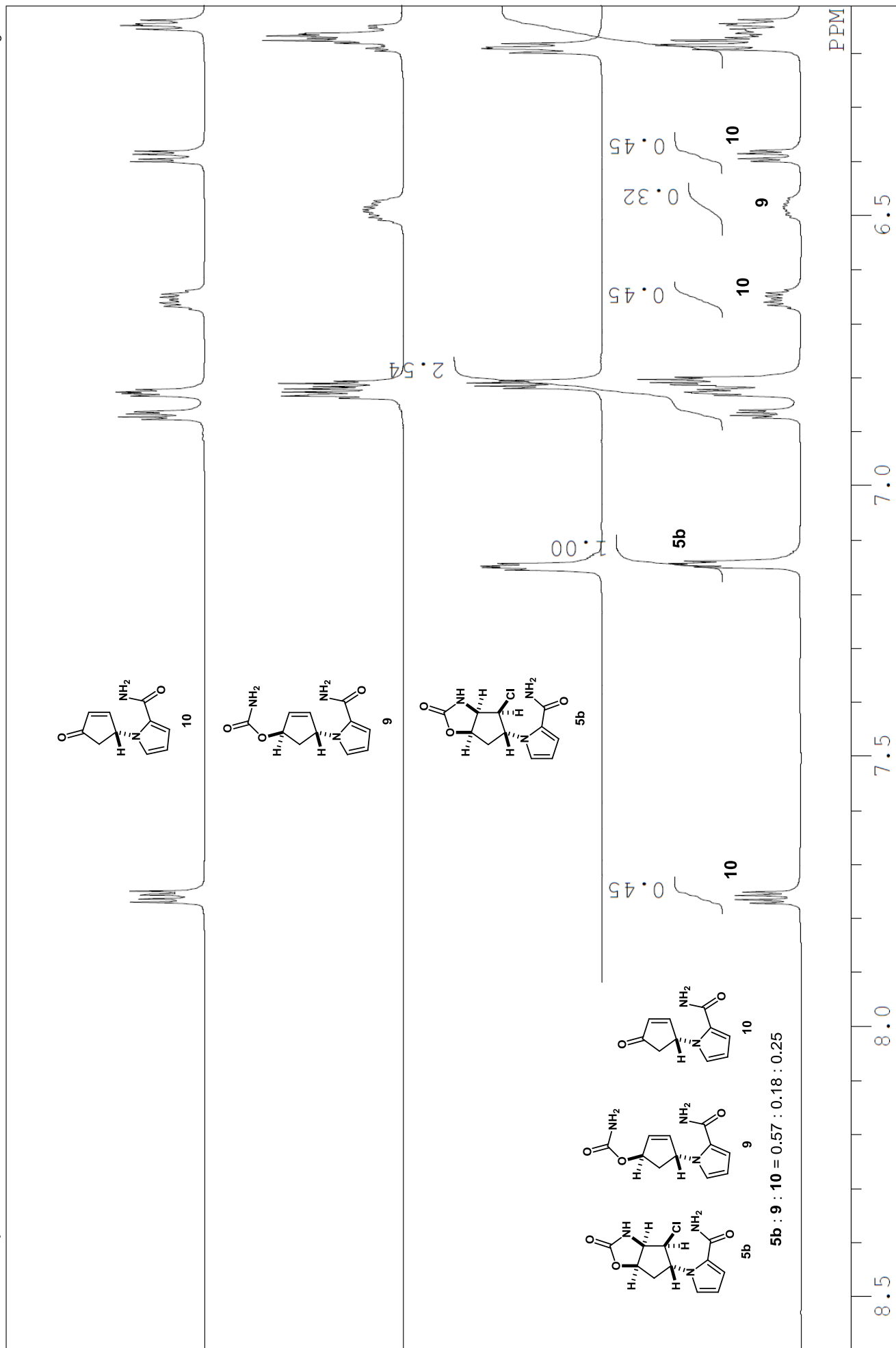
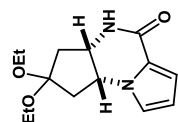
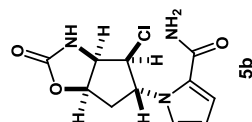


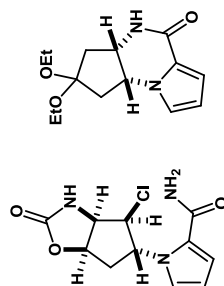
Table 1, entry 7

400MHz, CD₃OD

12

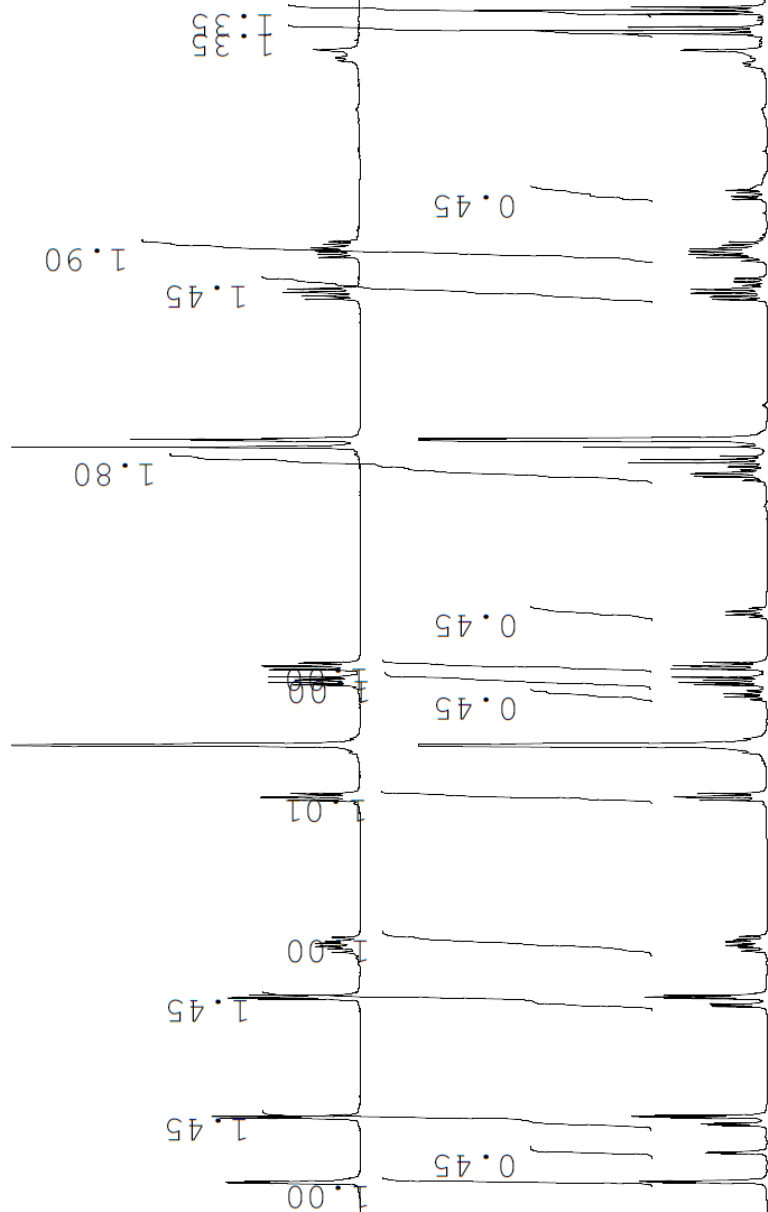


5b



12

5b : 12 = 0.69 : 0.31



PPM

0

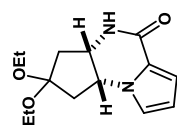
8

6

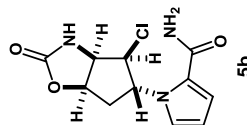
4

2

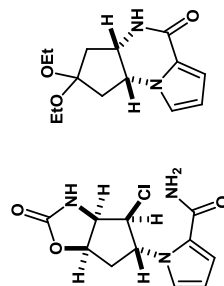
0



12



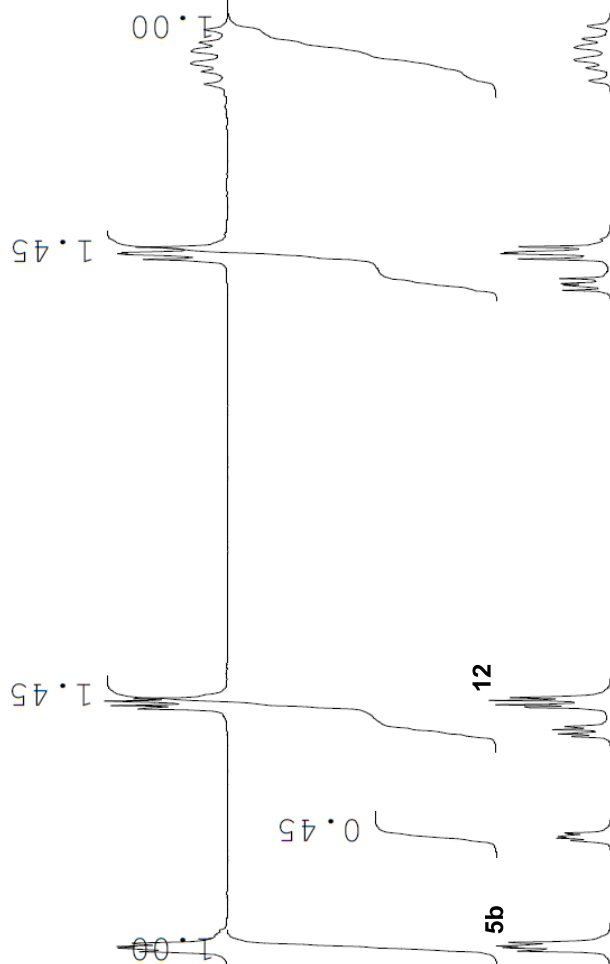
5b



12

5b

5b : 12 = 0.69 : 0.31



12

5b

PPM