

## SUPPORTING INFORMATION

**A FRET Approach to Phosgene Detection**

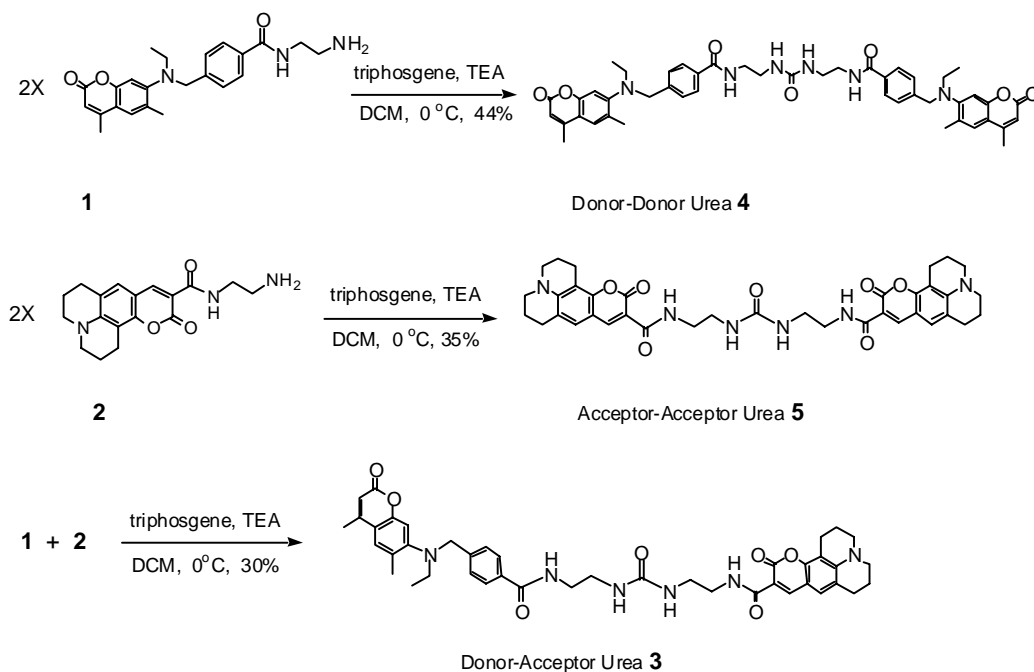
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**General.** Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, COSY and HMBC NMR spectra were recorded at  $295 \pm 1$  K on JEOL 300 and 500 MHz spectrometers. Chemical shifts were measured relative to residual non-deuterated solvent resonances. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. UV-vis spectra were measured on a Varian Cary-50 spectrophotometer. Fluorescence spectra were recorded on a JOBIN YVON FluoroMax-3 spectrofluorometer. ESI-TOF high resolution mass spectra were recorded on an Agilent ESI-TOF mass spectrometer at the Scripps Center for Mass Spectrometry (La Jolla, CA). Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. All experiments with moisture- and/or air-sensitive compounds were run under a dried nitrogen atmosphere. For column chromatography, Silica Gel 60 Å (Sorbent Technologies, Inc.; 200–425 mesh) was used.

Coumarin 2, coumarin 343, triphosgene, and methyl 4-(bromomethyl)benzoate were purchased from Acros Organics (Morris Plains, NJ), *t*-butyl *N*-(2-aminoethyl)carbamate was purchased from AK Scientific (Mountain View, CA), *N*-ethyl-*N'*-(3-dimethyl aminopropyl)carbodiimide hydrochloride (EDC•HCl) and 1-hydroxy-benzotriazole (HOBt) were delivered from Sigma-Aldrich (St. Louis, MO). The reagents were used as received.



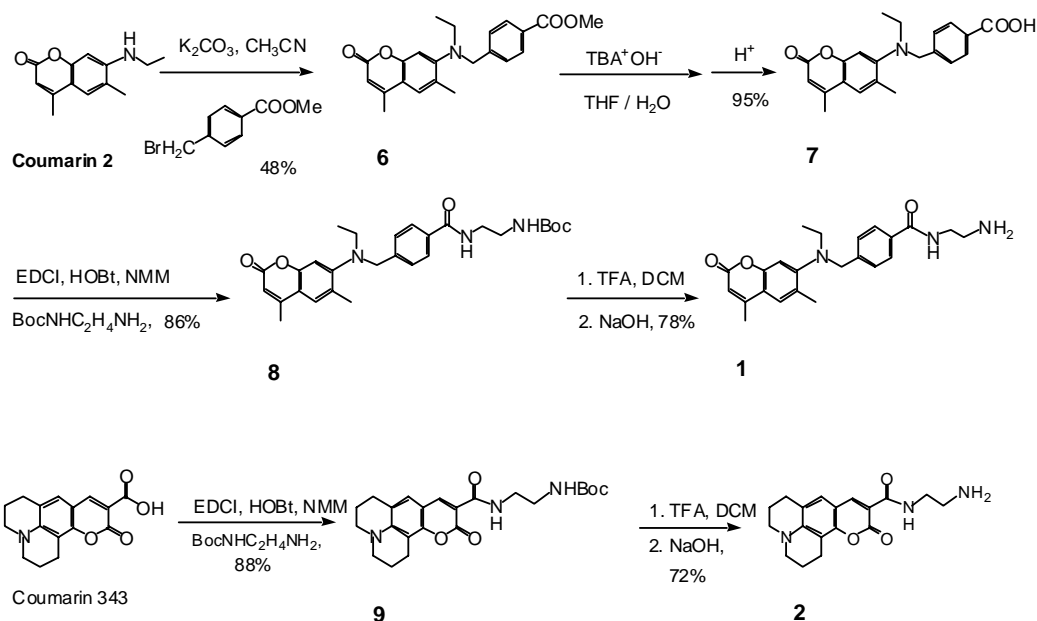
**Scheme 1.** Preparation of ureas 3-5.

**Donor-Acceptor Urea (3).** To a dried  $\text{CH}_2\text{Cl}_2$  (5 mL) solution of coumarin **1** (40 mg, 0.1 mmol) and TEA (0.1 mL), triphosgene (9.9 mg, 0.033 mmol) was added. The mixture was stirred at  $0^\circ\text{C}$  for 15 min after which coumarin **2** (33 mg, 0.1 mmol) was added in  $\text{CH}_2\text{Cl}_2$  (5 mL). The reaction mixture was stirred for an hour, the solvent was removed in vacuo, and the residue was applied to column chromatography, ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 15:1) to give product **3** as a yellow solid,  $R_f = 0.2$ . Yield 23 mg, 0.031 mmol, (30%), mp  $>300^\circ\text{C}$  (decomp); IR (KBr):  $\nu$  3295, 2928, 2490, 1689, 1616, 1531, 1309, 1175, 1062;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz):  $\delta$  8.70 (br, 1 H), 8.49 (s, 1 H), 8.41 (br, 1 H), 7.75 (d,  $J = 8.0$  Hz,

2 H), 7.51 (s, 1 H), 7.37 (d,  $J = 8.0$  Hz, 2 H), 7.05, (s, 1 H), 6.98 (s, 1 H), 6.16 (s, 1 H), 6.10 (br, 2 H), 4.29 (s, 2 H), 3.5-3.0 (m, 12 H), 2.71 (q,  $J = 7.0$  Hz, 2 H), 2.58-2.40 (m, 4 H), 2.36 (s, 3 H), 2.35 (s, 3 H), 1.92-1.80 (m, 4 H), 1.04 (t,  $J = 7.0$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  167.8, 164.8, 163.1, 161.8, 160.0, 153.7, 152.7, 152.6, 148.5, 148.0, 141.8, 135.3, 133.3, 129.7, 128.2, 127.4, 127.2, 126.7, 122.1, 121.9, 119.9, 114.9, 112.6, 109.2, 108.2, 108.1, 105.6, 56.3, 50.3, 49.9, 46.7, 42.5, 40.8, 39.9, 27.5, 21.1, 20.2, 20.1, 18.7, 18.6, 11.9; ESI-TOF MS: calcd for  $[\text{MH}^+]$   $\text{C}_{42}\text{H}_{47}\text{N}_6\text{O}_7$  747.3501, found 747.3492.

**Donor-Donor Urea (4).** To a  $\text{CH}_2\text{Cl}_2$  (5 mL) solution of coumarin **1** (80 mg, 0.2 mmol) and TEA (0.1 mL), triphosgene (9.9 mg, 0.033 mmol) was added. The mixture was stirred at  $0^\circ\text{C}$  for 1 h. The solvent was removed in vacuo, and the residue was applied to column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 15:1) to give urea **4** as a pale yellow solid, 35 mg, 0.043 mmol, (44%),  $R_f = 0.21$ , mp  $>300^\circ\text{C}$  (decomp); IR (KBr):  $\nu$  3382, 2926, 2855, 1717, 1613, 1547, 1502, 1391, 1267, 1158, 1060;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.71 (d,  $J = 8.2$  Hz, 4 H), 7.67 (br, 2 H), 7.33 (s, 2 H), 7.25 (d,  $J = 8.2$  Hz, 4 H), 6.79 (s, 2 H), 6.08 (s, 2 H), 5.79 (br., 2 H), 4.20 (s, 4 H), 3.48-3.36 (m, 4 H), 3.36-3.26 (m, 4 H), 3.02 (q,  $J = 6.9$  Hz, 4 H), 2.38 (s, 6 H), 2.35 (s, 6 H), 1.05 (t,  $J = 6.9$  Hz, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  167.9, 161.7, 160.5, 153.4, 152.7, 152.6, 141.8, 133.1, 129.6, 128.3, 127.3, 126.7, 114.9, 112.6, 109.3, 56.1, 47.1, 41.9, 40.1, 18.7, 18.6, 12.0; ESI-TOF high MS: calcd for  $[\text{MH}^+]$   $\text{C}_{47}\text{H}_{53}\text{N}_6\text{O}_7$  813.3970, found 813.3966.

**Acceptor-Acceptor Urea (5).** Prepared similarly to urea **4** by starting with coumarin **2** (66 mg, 0.2 mmol).  $R_f = 0.17$ . Yield bright yellow solid 25 mg, 0.036 mmol, (35%); ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  15:1), mp  $>300^\circ\text{C}$  (decomp); IR (KBr):  $\nu$  3337, 2941, 2845, 1687, 1616, 1519, 1457, 1367, 1309, 1211, 1176;  $^1\text{H}$  NMR ( $\text{CDCl}_3 + 10\% \text{CD}_3\text{OD}$ , 500 MHz):  $\delta$  8.40 (s, 2 H), 6.91 (s, 2 H), 3.50-3.40 (m, 4 H), 3.40-3.20 (m, 12 H), 2.85-2.60 (m, 8 H), 2.00-1.80 (m, 8 H);  $^{13}\text{C}$  NMR could not be obtained due to the low solubility. ESI-TOF MS: calcd for  $[\text{MH}^+]$   $\text{C}_{37}\text{H}_{41}\text{N}_6\text{O}_7$  681.3031, found 681.3032.



**Scheme 2.** Preparation of amines **1** and **2**.

**4-(N-coumarin)methylbenzoate (6).**<sup>1</sup> Coumarin **2** (217 mg, 1.0 mmol), methyl 4-(bromomethyl)benzoate (275 mg, 1.2 mmol) and  $\text{K}_2\text{CO}_3$  (690 mg, 5.0 mmol) were mixed in freshly distilled MeCN (30 mL) and refluxed for 72 h. The solvent was evaporated in vacuo and the residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  50:1) to give product **6** as a pale yellow solid (175 mg, 0.48 mmol, 48%), mp 92-93 °C;  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 500 MHz):  $\delta$  7.87 (d,  $J = 8.3$  Hz, 2 H), 7.54 (s, 1 H), 7.46 (d,  $J = 8.3$  Hz, 2 H), 7.01 (s, 1 H), 6.18 (s, 1 H), 4.36 (s, 2 H), 3.23 (s, 3 H), 3.07 (q,  $J = 6.8$  Hz, 2 H), 2.37 (s, 3 H), 2.36 (s, 3 H), 1.05 (t,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  167.0, 161.6, 153.4, 152.7, 152.4, 143.7, 129.9, 129.8, 128.1, 126.6, 126.5, 115.1, 112.8, 109.4, 56.4, 52.1, 47.0, 18.7, 18.6, 11.9.

**4-(N-Coumarin)methylbenzoic Acid (7).** Compound **6** (175 mg, 0.48 mmol) and tetrabutylammonium hydroxide ( $\text{TBA}^+\text{OH}^-$ , 40% w/w, 0.78 mL, 1.2 mmol) were added to a mixture of THF (5 mL) and water (5 mL) and stirred overnight. The reaction mixture was then treated with aq HCl (1 M) until pH~4. The precipitate was filtered, washed with

water (3 x 20 mL) and dried to yield acid **7** as a white powder; yield 160 mg, 0.46 mmol, (95%), mp 203-204 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 7.85 (d, *J* = 8.2 Hz, 2 H), 7.54 (s, 1 H), 7.43 (d, *J* = 8.2 Hz, 2 H), 7.01 (s, 1 H), 6.18 (s, 1 H), 4.35 (s, 2 H), 3.08 (q, *J* = 6.4 Hz, 2 H), 2.38 (s, 3 H), 2.37 (s, 3 H), 1.05 (t, *J* = 6.4 Hz, 3 H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 167.7, 160.8, 153.6, (two peaks), 152.6, 144.4, 130.1, 129.9, 129.7, 128.6, 127.6, 114.8, 112.4, 109.1, 55.3, 47.6, 18.8, 18.5, 12.4.

***N*-Boc Donor Amine (8).** *N*-Boc-Ethylenediamine (0.13 mL, 0.8 mmol) and acid **7** (140 mg, 0.4 mmol) were mixed with EDC•HCl (153 mg, 0.8 mmol), HOBT (108 mg, 0.8 mmol) and NMM (0.1 mL) in dry CH<sub>2</sub>Cl<sub>2</sub> (25 mL) and stirred at 0 °C overnight. The solution was evaporated to dryness. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with 5% aq HCl (50 mL). The organic layer was separated, washed with water (3 x 50 mL), and evaporated. Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 50:1) afforded product **8** as a yellow powder; yield 169 mg, 0.34 mmol, (86%), mp 86–87 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 8.40-8.30 (br, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.52 (s, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 6.98 (s, 1 H), 6.90-6.82 (br, 1 H), 6.16 (s, 1 H), 4.32 (s, 2 H), 3.30-3.20 (m, 2 H), 3.15-2.99 (m, 6 H), 2.37 (s, 3 H), 2.36 (s, 3 H), 1.34 (s, 9 H), 1.05 (t, *J* = 6.4 Hz, 3 H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 166.7, 160.8, 156.3, 153.7, 153.6, 152.6, 142.4, 133.8, 129.6, 128.3, 127.8, 127.6, 114.7, 112.3, 109.2, 78.2, 55.1, 47.7, 40.3, 40.1, 28.8, 18.8, 18.6, 12.4.

**Donor Amine (1).** Compound **8** (148 mg, 0.3 mmol) and TFA (5.0 mL, 0.07 mol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred overnight. The solvent was evaporated, and the product was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with 5% aq NaOH (25 mL) and water (3 x 25 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated to obtain amine **1** as a yellowish solid (92 mg, 0.23 mmol, 0.78%), mp 97-98 °C; IR (KBr): ν 3361, 2928, 2869, 1718, 1612, 1540, 1502, 1390, 1350, 1268, 1158, 1060; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): δ 8.32 (br, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.52 (s, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 6.99 (s, 1 H), 6.16 (s, 1 H), 4.32 (s, 2 H), 3.31-3.15 (m, 2 H), 3.08 (q, *J* =

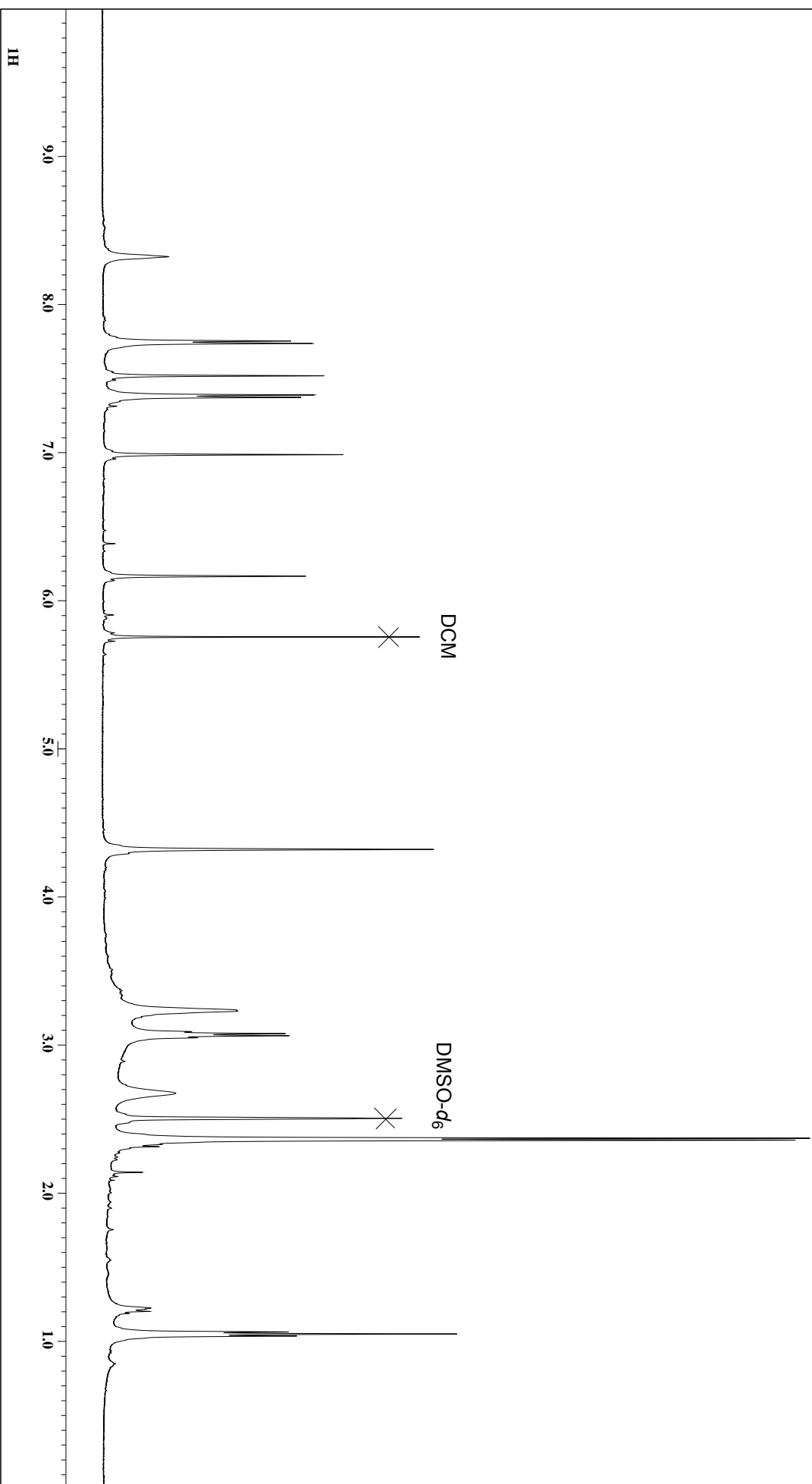
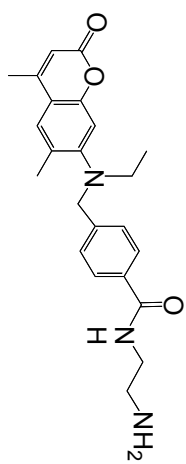
6.8 Hz, 2 H), 2.67 (br, 2 H), 2.37 (s, 3 H), 2.36 (s, 3 H), 1.05 (t,  $J = 6.8$  Hz, 3 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  166.8, 160.8, 153.7 (two peaks), 152.6, 142.3, 134.0, 129.6, 128.3, 127.8, 127.6, 114.7, 112.3, 109.1, 55.1, 47.6, 43.5, 41.8, 18.8, 18.6, 12.4; ESI-TOF MS: calcd for  $[\text{MH}^+]$   $\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_3$  394.2125, found 394.2130.

***N*-Boc Acceptor Amine (9).** *N*-Boc Ethylenediamine (0.20 mL, 1.3 mmol), coumarin 343 (185 mg, 0.65 mmol), EDC•HCl (248 mg, 1 mmol), HOBT (175 mg, 1.3 mmol) and NMM (0.1 mL) were mixed in dried  $\text{CH}_2\text{Cl}_2$  (25 mL) and stirred at 0 °C overnight. The solution was evaporated to dryness. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) and washed with 5% aq HCl (50 mL). The organic layer was separated, washed with water (3 x 50 mL), and evaporated. Column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  50:1) afforded product **9** as a bright yellow powder (245 mg, 0.57 mmol, 88%),  $R_f = 0.16$ , mp 220 °C;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  8.72 (t,  $J = 5.8$  Hz, 1 H), 8.47 (s, 1 H), 7.20 (s, 1 H), 6.91 (t,  $J = 4.6$  Hz, 1 H), 3.40-3.25 (m, 6 H), 3.08 (q,  $J = 6.0$  Hz, 2 H), 2.75-2.65 (m, 4 H), 1.94-1.81 (m, 4 H), 1.37 (s, 9 H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 300 MHz):  $\delta$  163.3, 162.2, 156.3, 152.6, 148.5, 148.0, 127.6, 119.9, 108.4, 107.8, 105.1, 78.2, 50.1, 49.5, 40.0, 39.7, 28.7, 27.3, 21.0, 20.1 (two peaks).

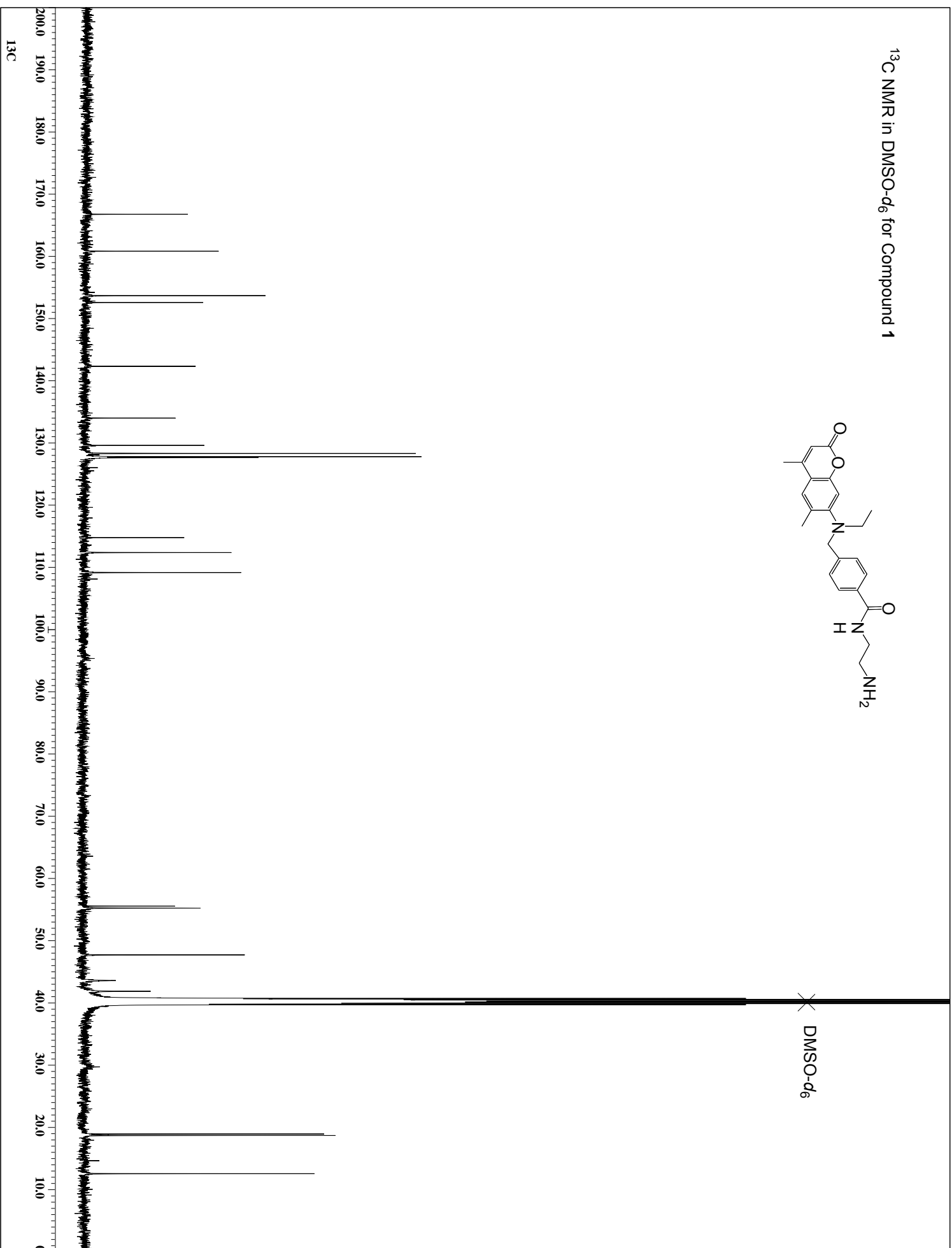
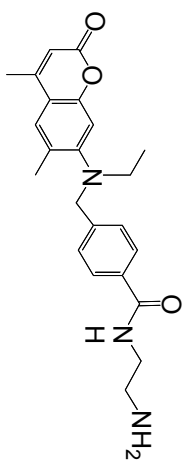
**Acceptor Amine (2).** Compound **9** (245 mg, 0.57 mmol) and TFA (5.0 mL, 0.07 mol) were dissolved in dried  $\text{CH}_2\text{Cl}_2$  (10 mL) and stirred overnight. The solvent was evaporated and the residue was redissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) and washed with 5% aq NaOH (25 mL) and water (3 x 25 mL). The organic layer was dried with  $\text{Na}_2\text{SO}_4$  and evaporated to yield amine **2** as a brown solid (135 mg, 0.41 mmol, 72%), mp >300 °C (decomp); IR (KBr):  $\nu$  3320, 2938, 2854, 1692, 1616, 1517, 1367, 1309, 1212, 1174;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  9.05 (t,  $J = 8.2$  Hz, 1 H), 8.52 (s, 1 H), 6.94 (s, 1 H), 3.62-3.50 (m, 2 H), 3.35-3.25 (m, 4 H), 3.02 (t,  $J = 5.0$  Hz, 2 H), 2.89-2.79 (m, 2 H), 2.78-2.69 (m, 2 H), 2.02-1.88 (m, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  164.5, 163.1, 152.8, 148.3, 148.2, 127.2, 119.7, 108.8, 108.3, 105.7, 50.3, 49.9, 41.8, 41.7, 27.5, 21.2, 20.3, 20.2. ESI-TOF MS: calculated for  $[\text{MH}^+]$   $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_3$  328.1656, found 328.1653.

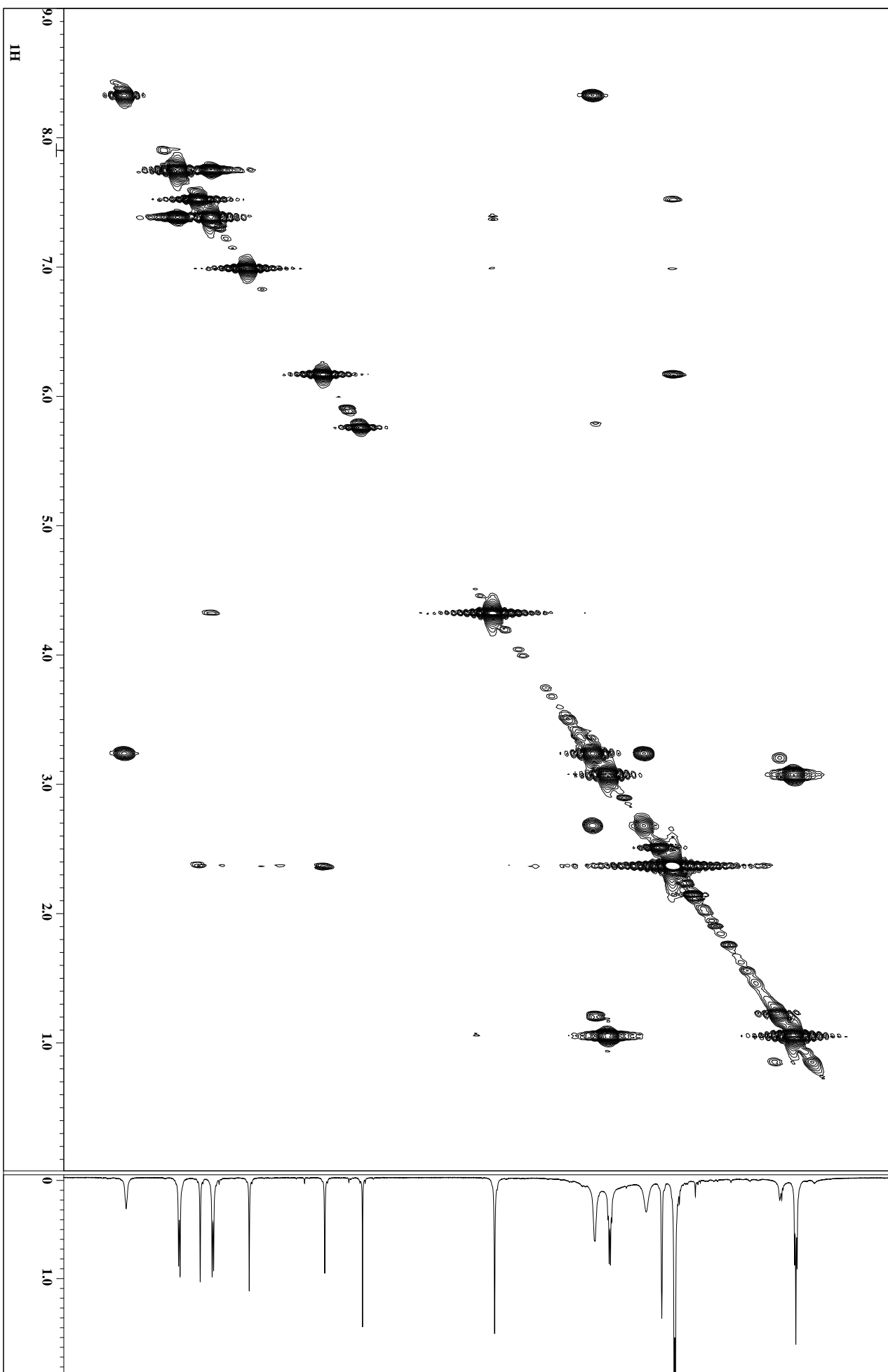
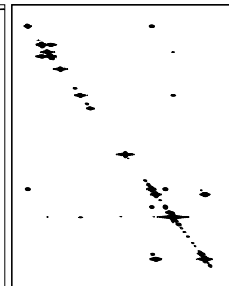
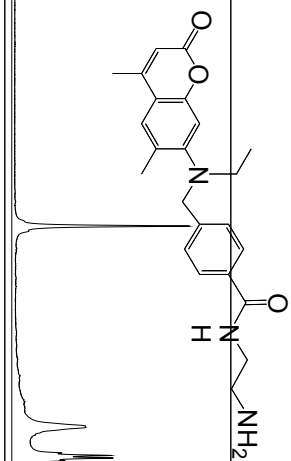
**Fluorescent Measurements:** In a typical experiment, an aliquot from the stock solution of triphosgene ( $[\text{triphosgene}] = 6.7 \times 10^{-3} \text{ M}$ ) in  $\text{CHCl}_3$  was added to the flask containing a mixture of donor amine **1** (2.0 mg, 0.005 mmol), acceptor amine **2** (1.7 mg, 0.005 mmol) and TEA (~10-15 eq) in  $\text{CHCl}_3$  (5 mL;  $[\mathbf{1}] = [\mathbf{2}] = 1 \times 10^{-3} \text{ M}$ ). After homogenization, an aliquot was taken and diluted 1000 times to  $10^{-6} \text{ M}$ . The fluorescence spectrum was recorded. The emission at  $\lambda = 464 \text{ nm}$  was monitored upon excitation at  $\lambda = 343 \text{ nm}$ . Additional aliquots of triphosgene were then added and, after dilution, the spectrum was recorded again. The triphosgene concentration ranged between  $3 \times 10^{-5}$  and  $1.5 \times 10^{-2} \text{ M}$ . In addition, solutions with concentrations  $[\mathbf{1}] = [\mathbf{2}]$  between  $5 \times 10^{-4}$  and  $1 \times 10^{-2} \text{ M}$  were tested. All titration experiments were performed at least in triplicate showing good reproducibility.

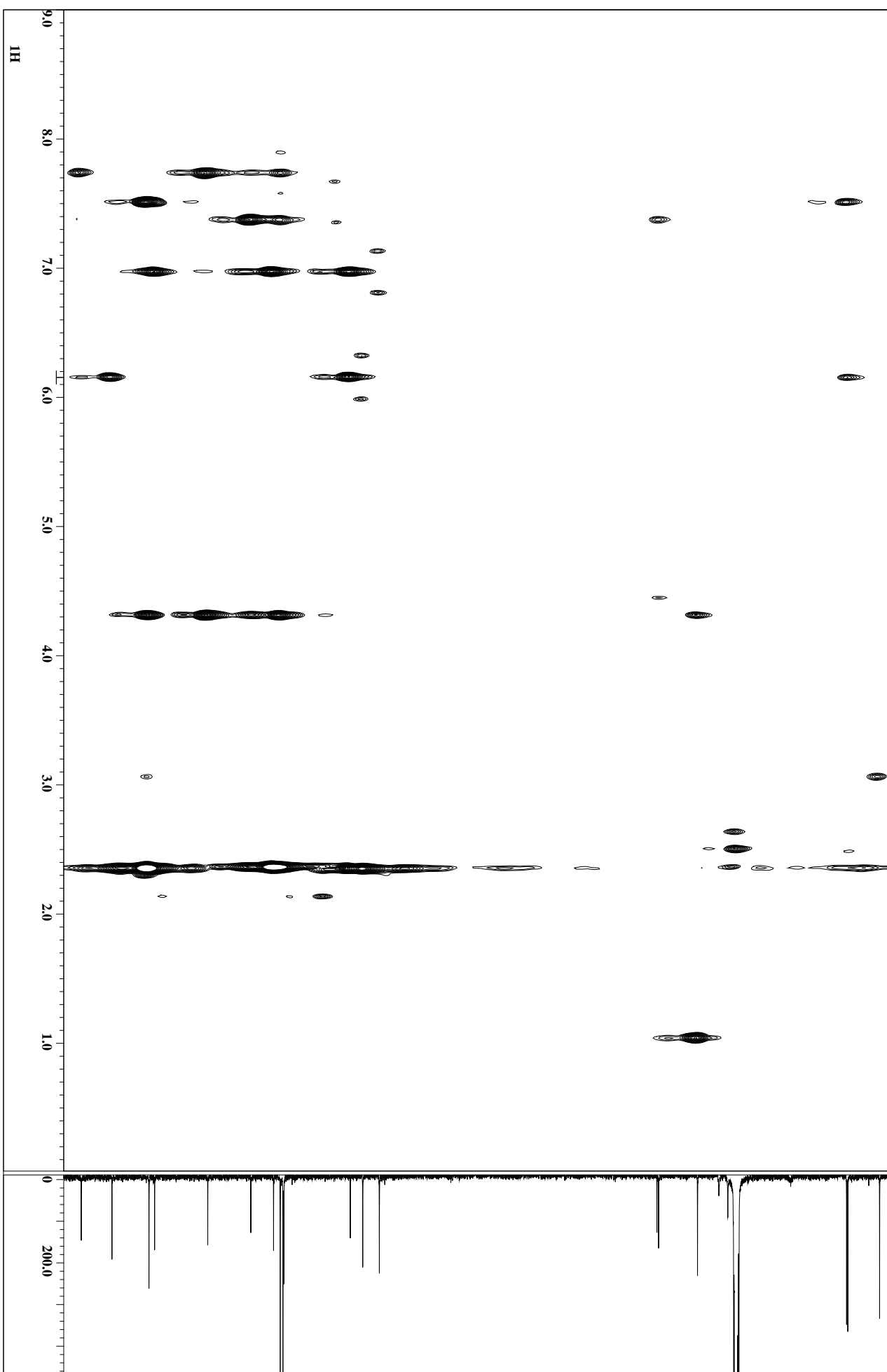
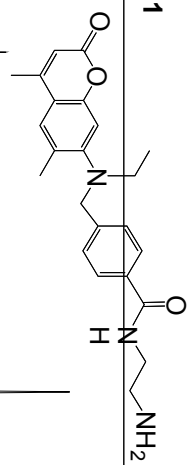
<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound 1



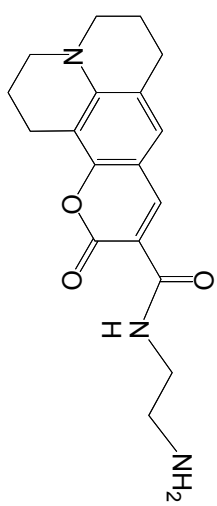
<sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> for Compound 1





HMBC NMR in DMSO- $d_6$  for compound **1**

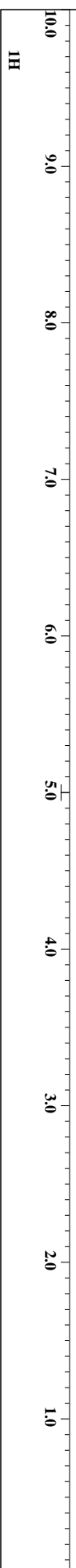
$^1\text{H}$  NMR in  $\text{CDCl}_3$  for Compound **2**



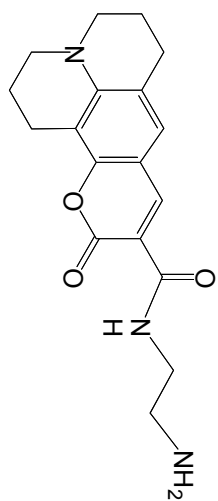
$\times$   $\text{CDCl}_3$

DCM

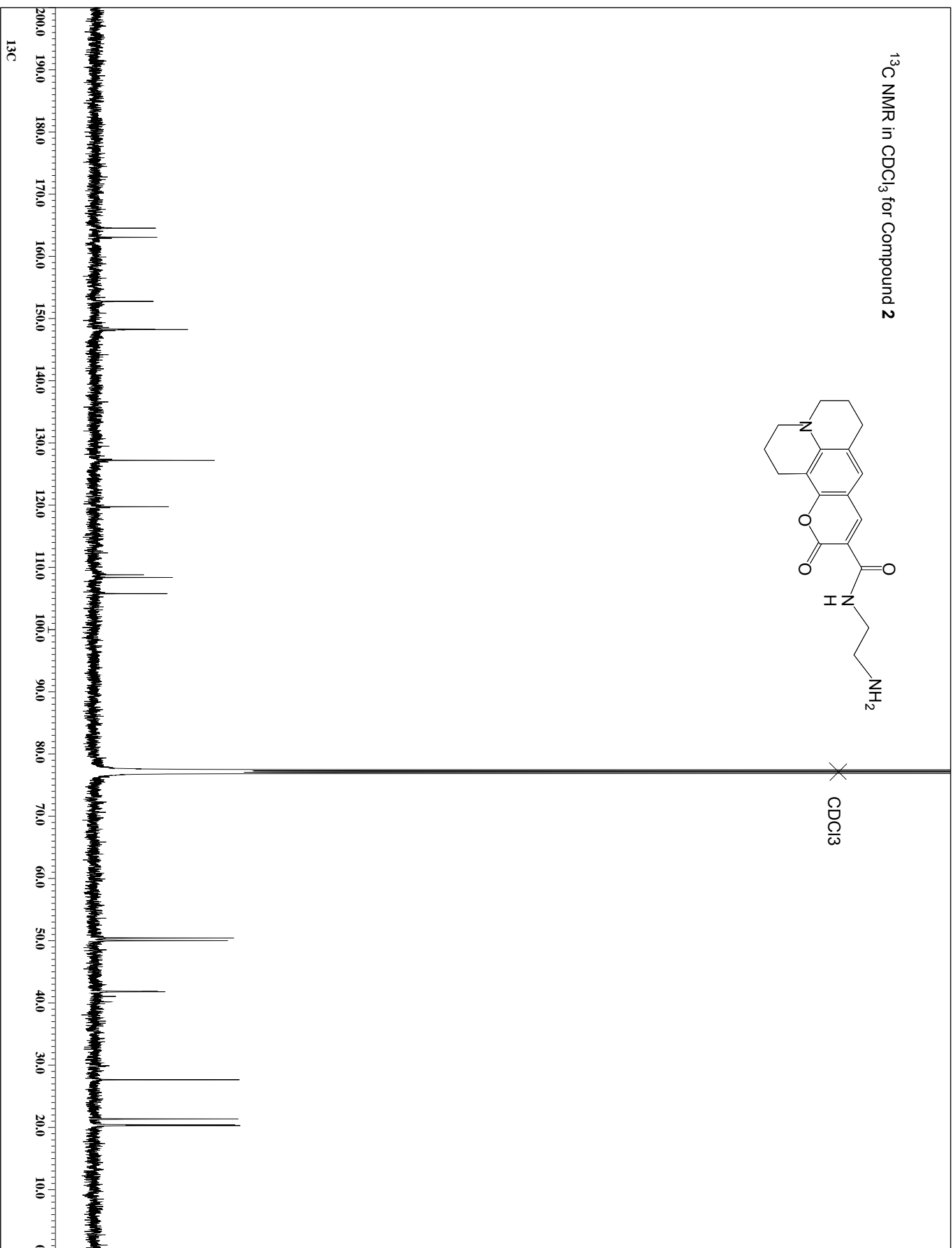
Acetone

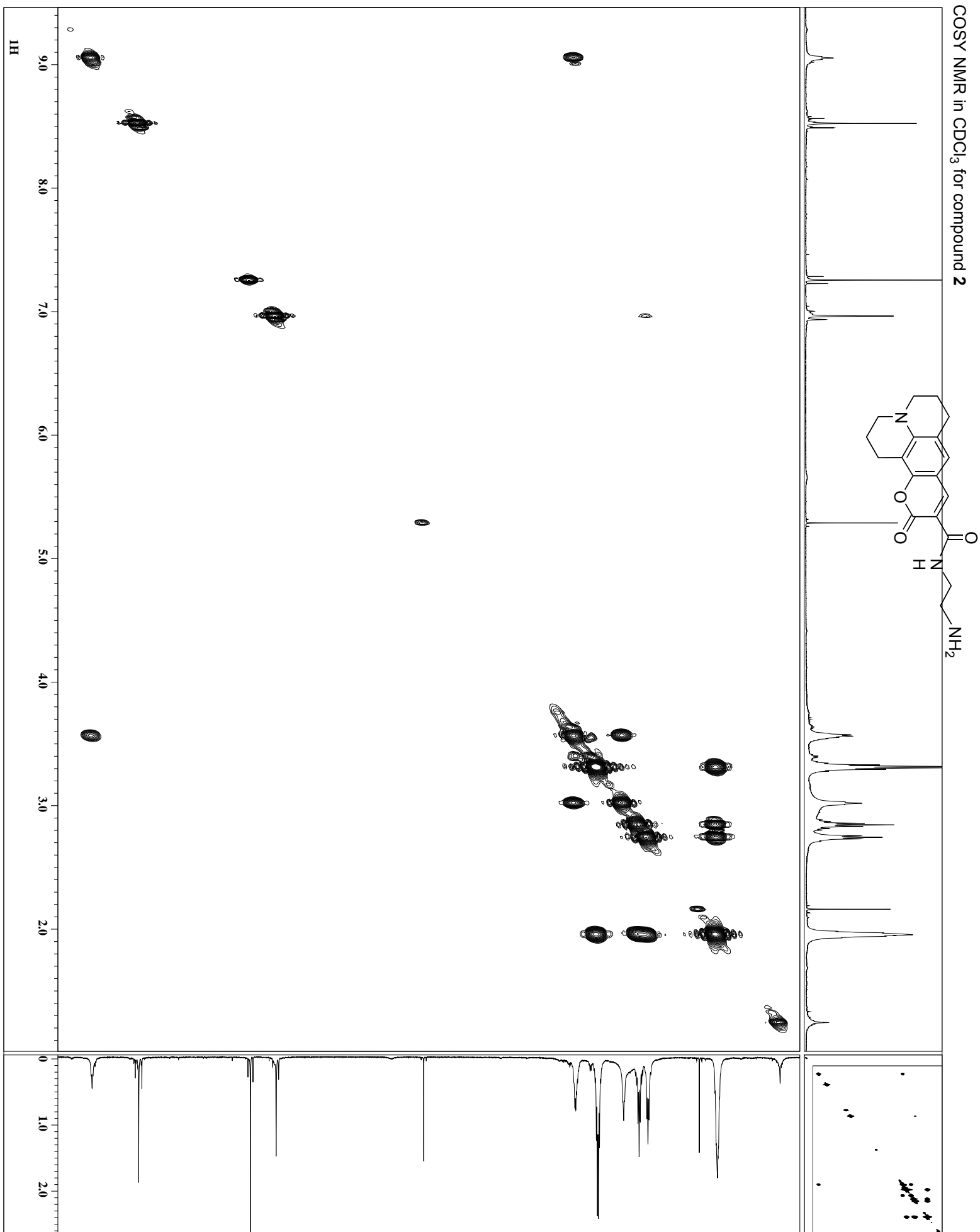


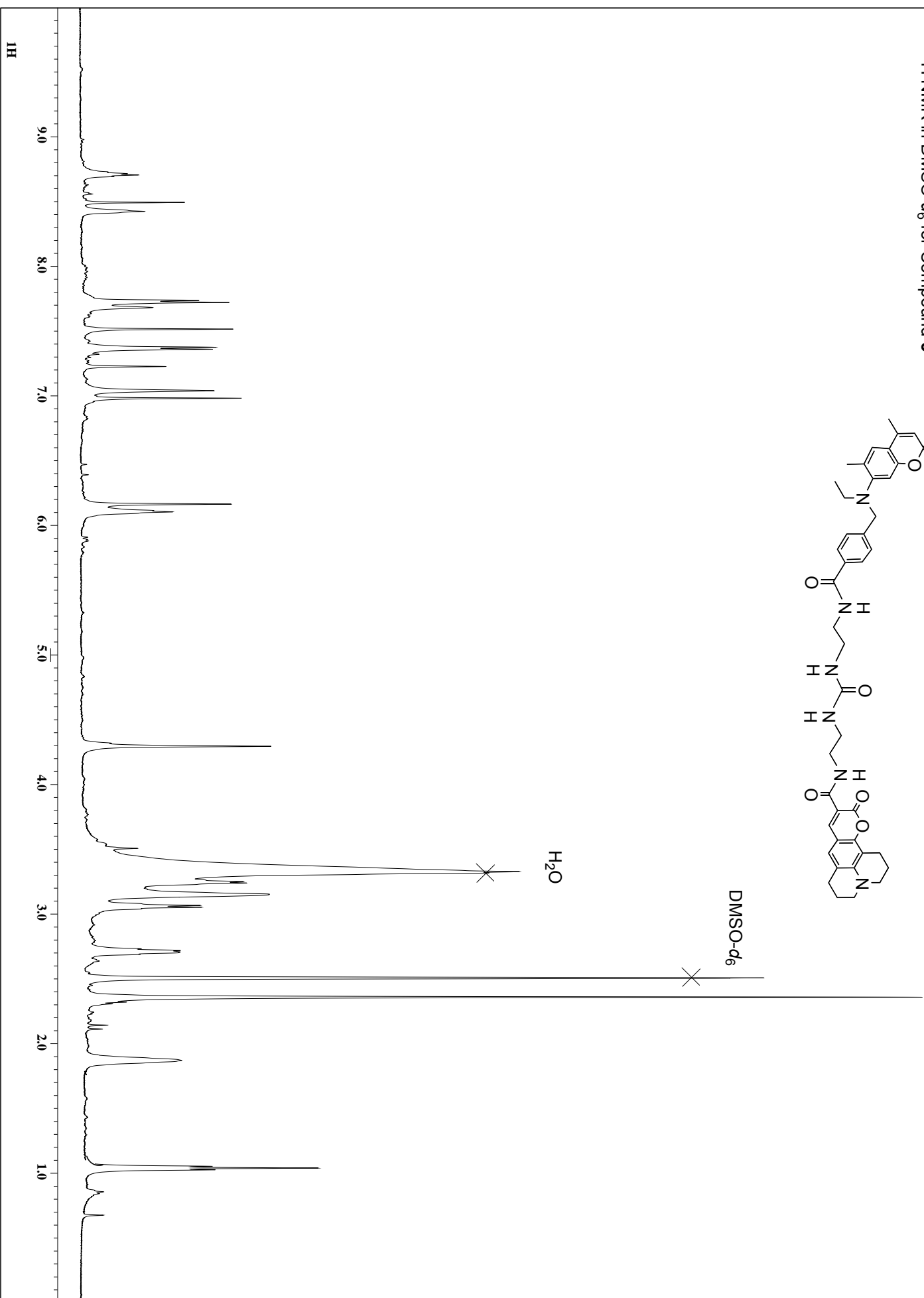
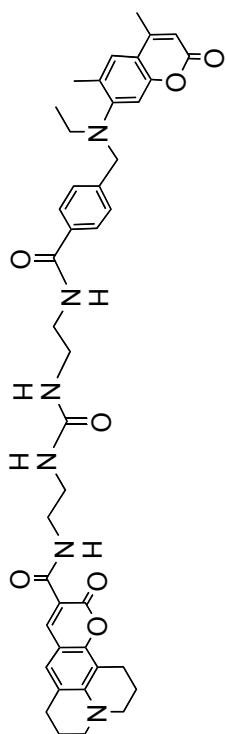
$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  for Compound **2**



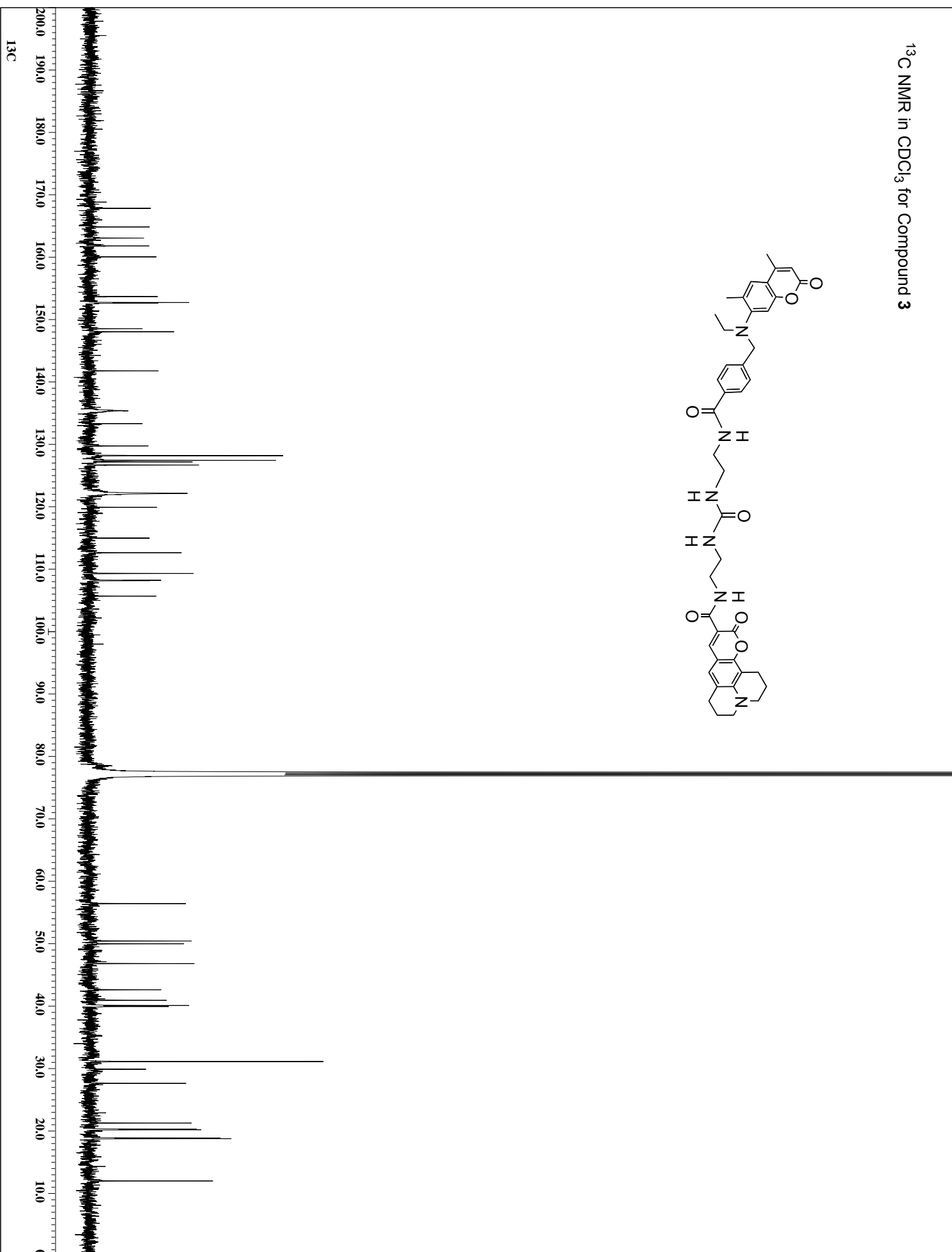
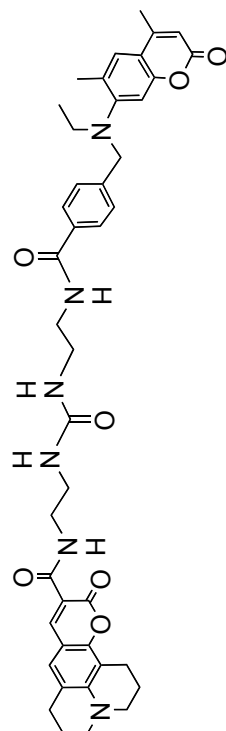
×  $\text{CDCl}_3$

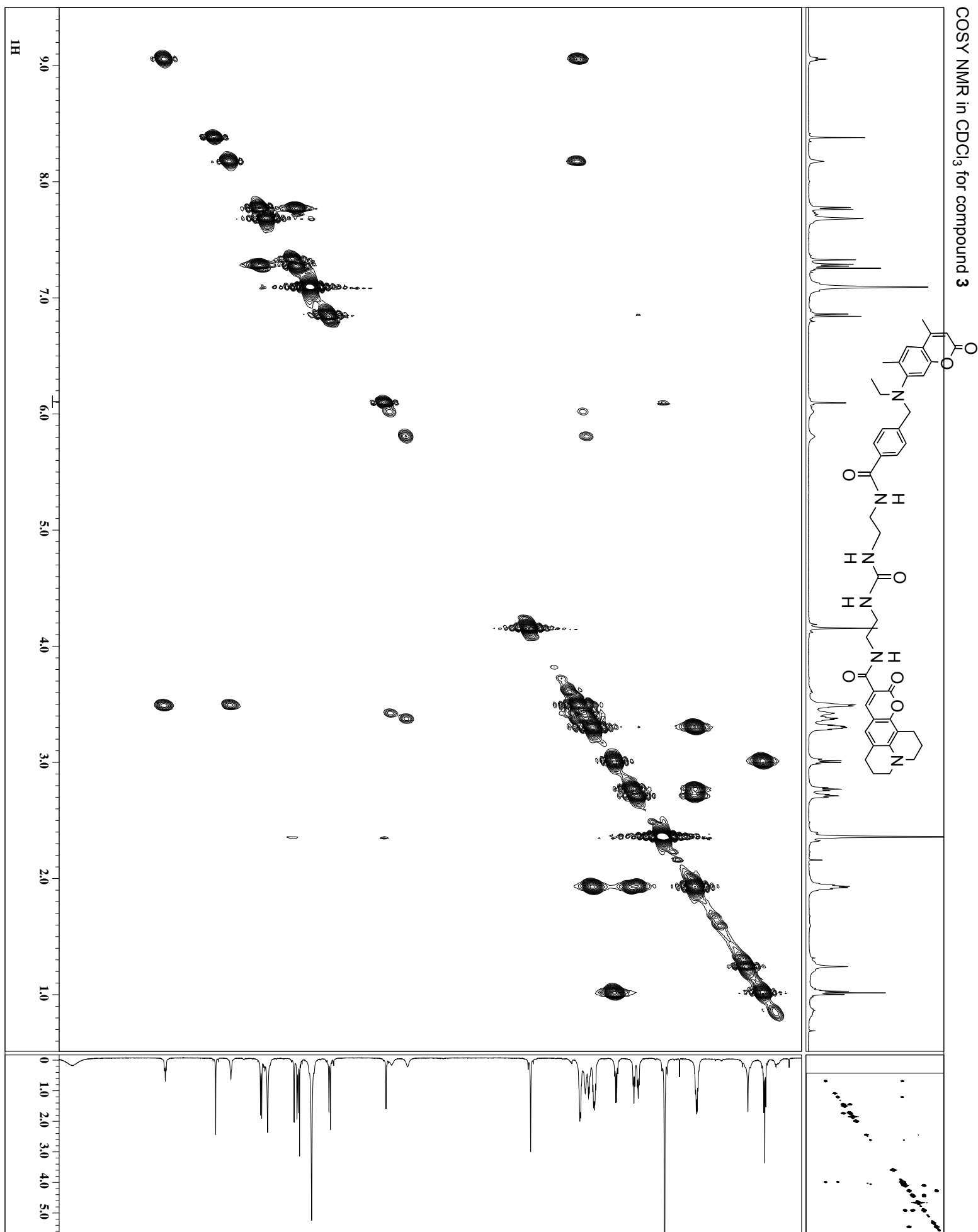


COSY NMR in CDCl<sub>3</sub> for compound **2**

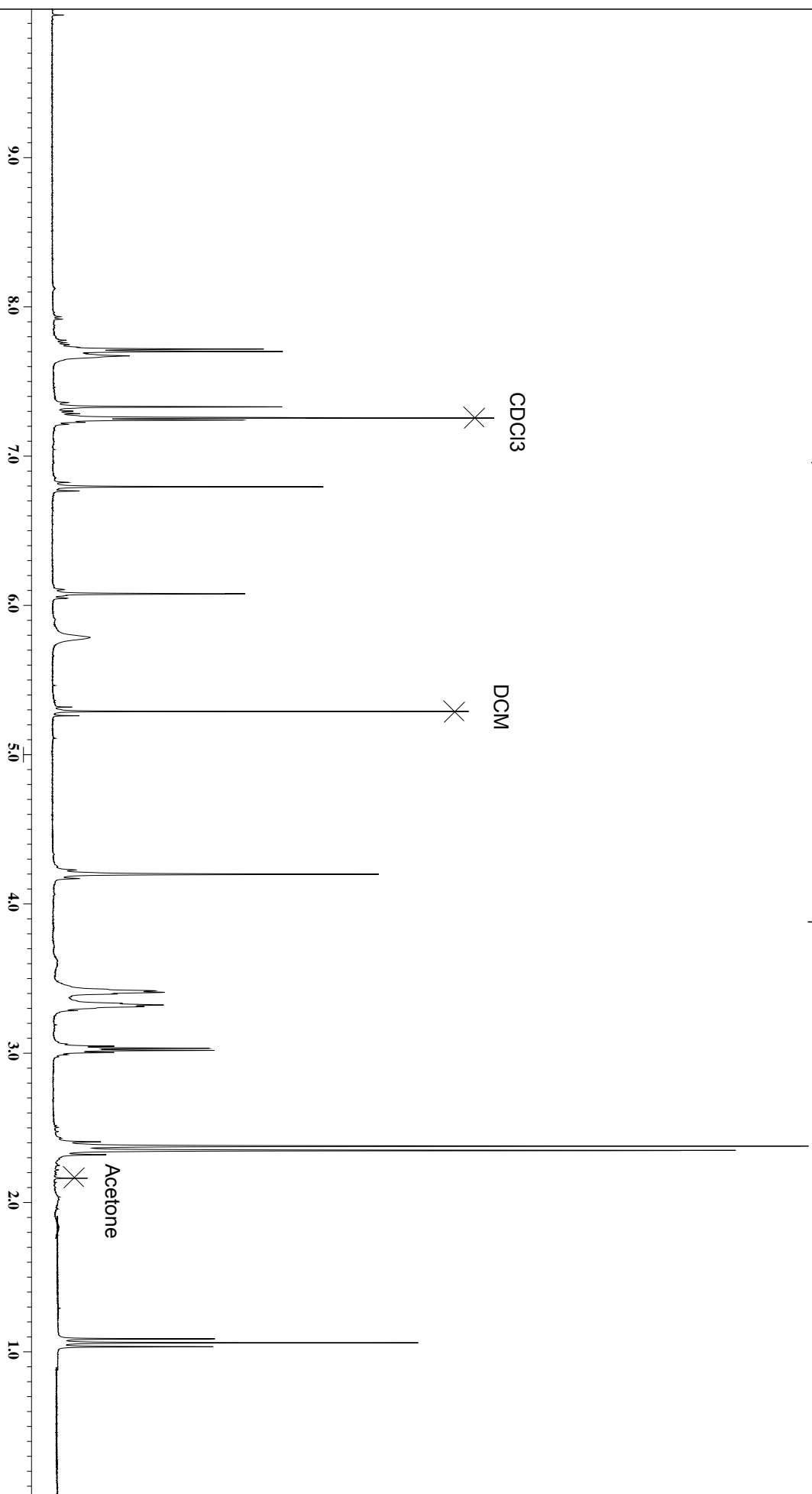
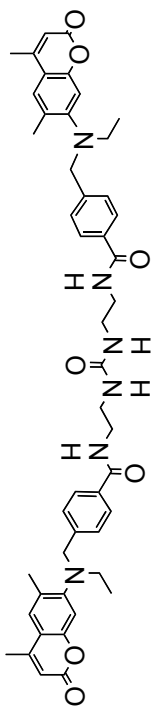
<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound **3**

$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  for Compound **3**

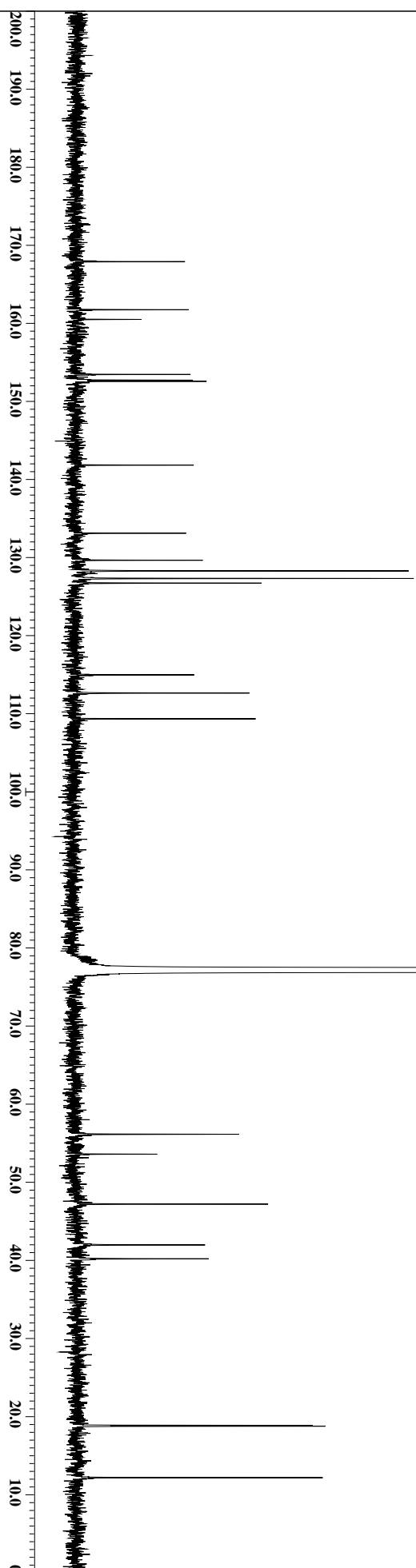
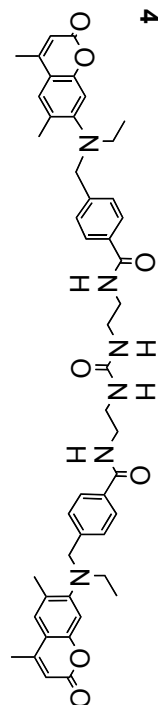


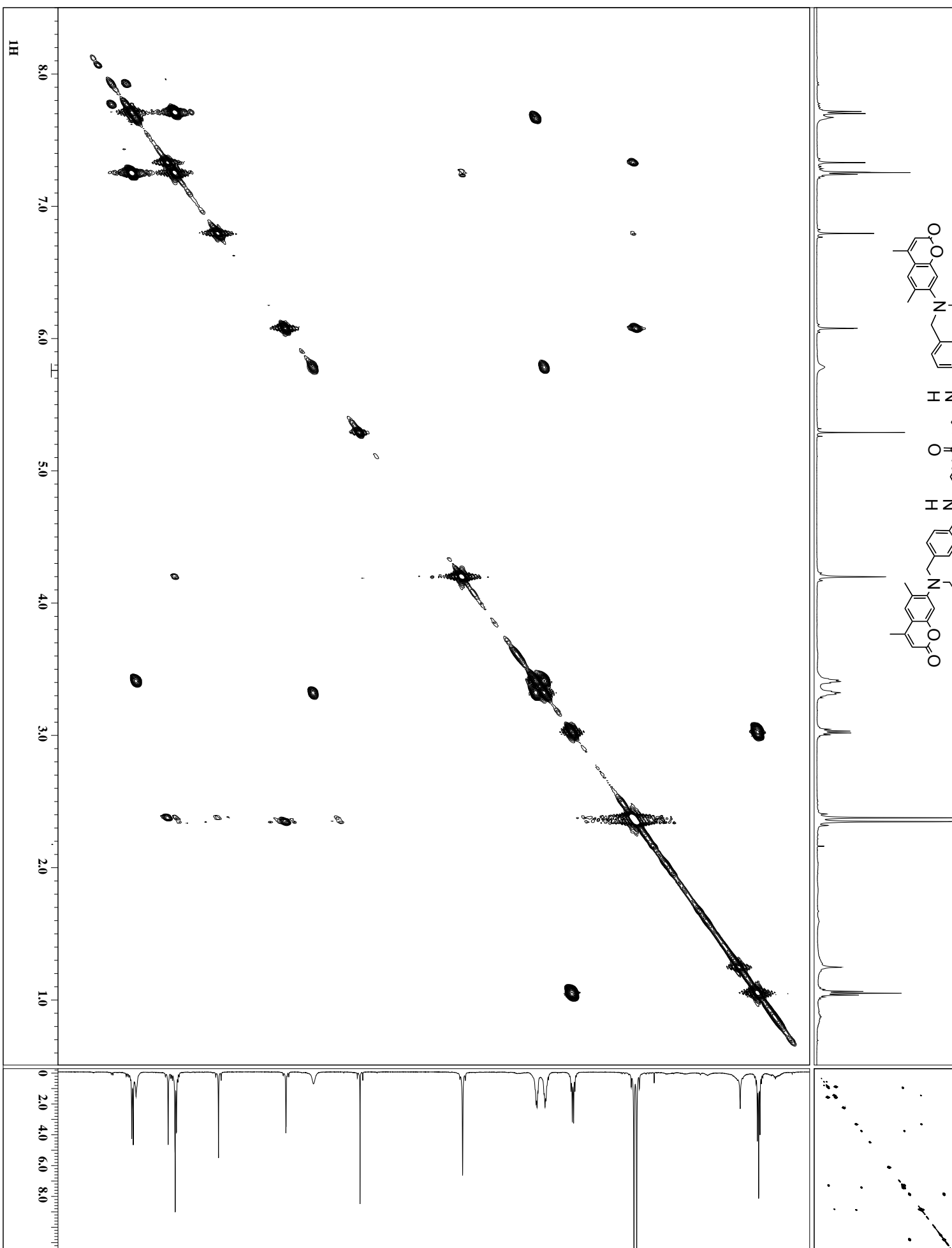
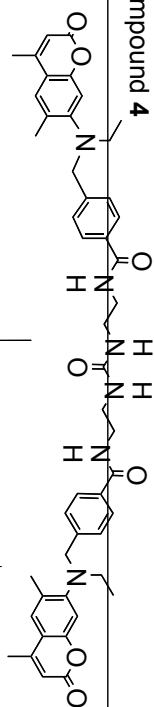


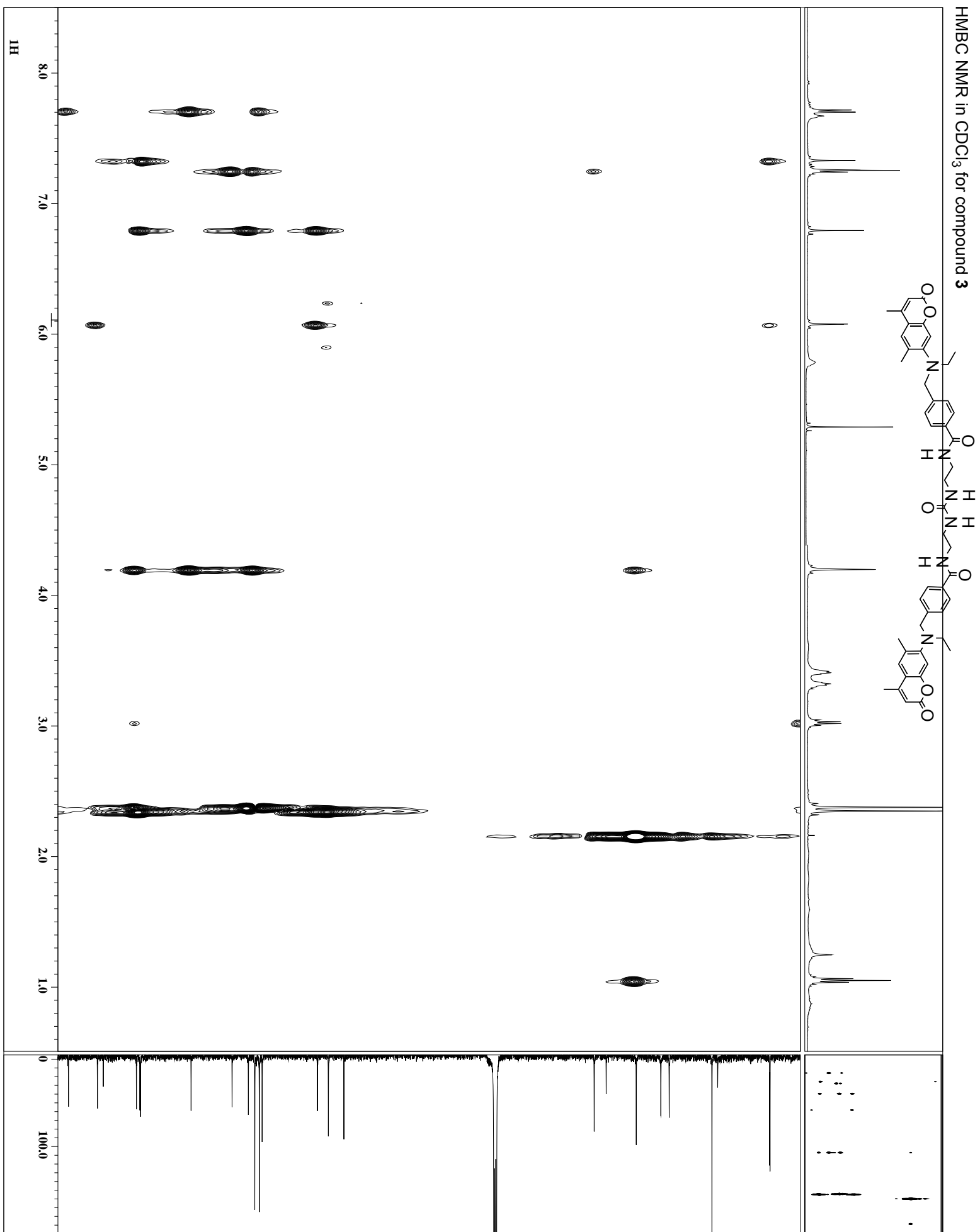
<sup>1</sup>H NMR in CDCl<sub>3</sub> for compound 4



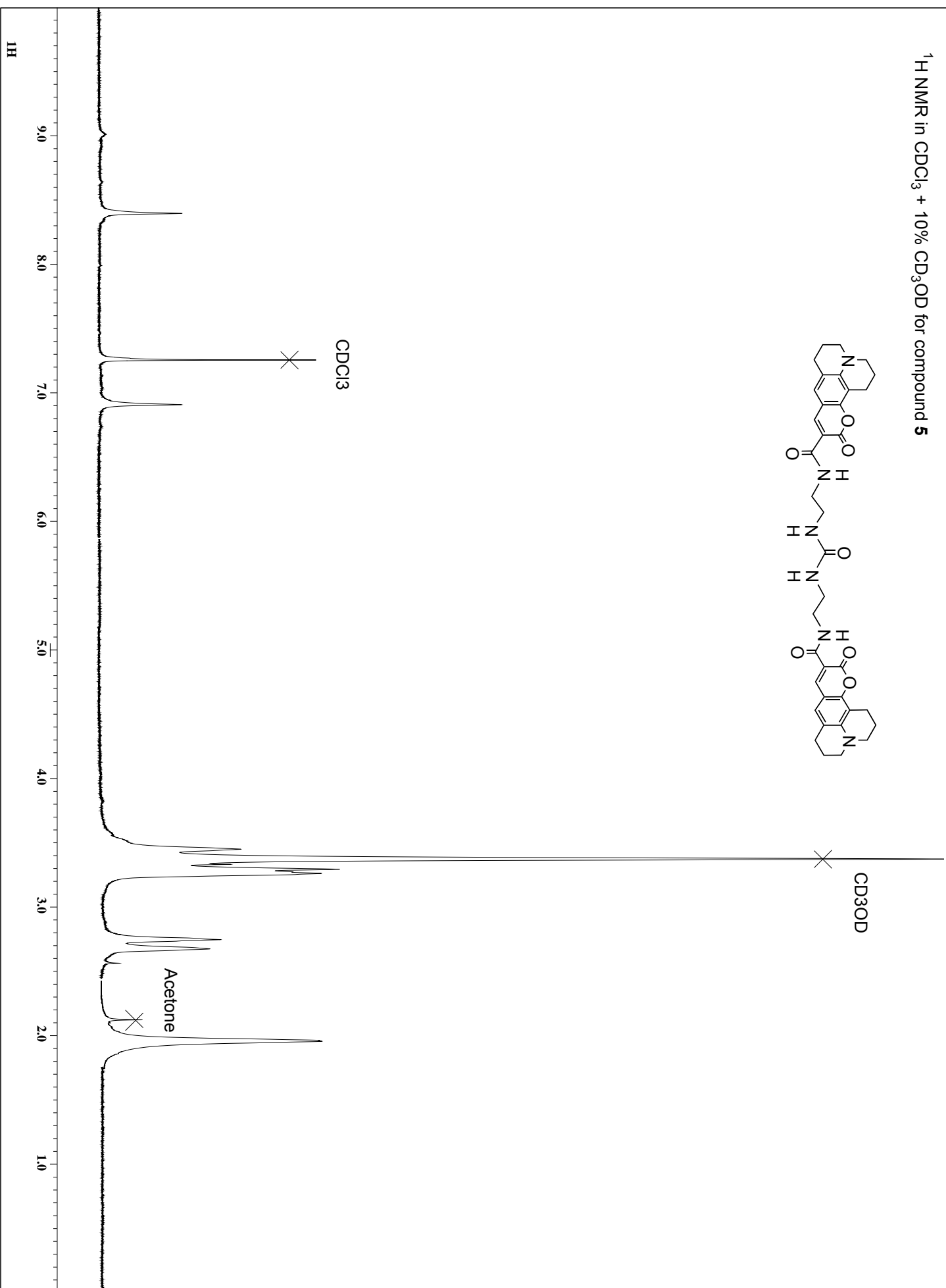
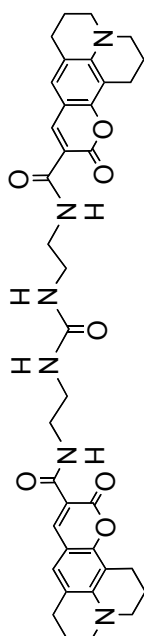
<sup>13</sup>C NMR in CDCl<sub>3</sub> for compound **4**



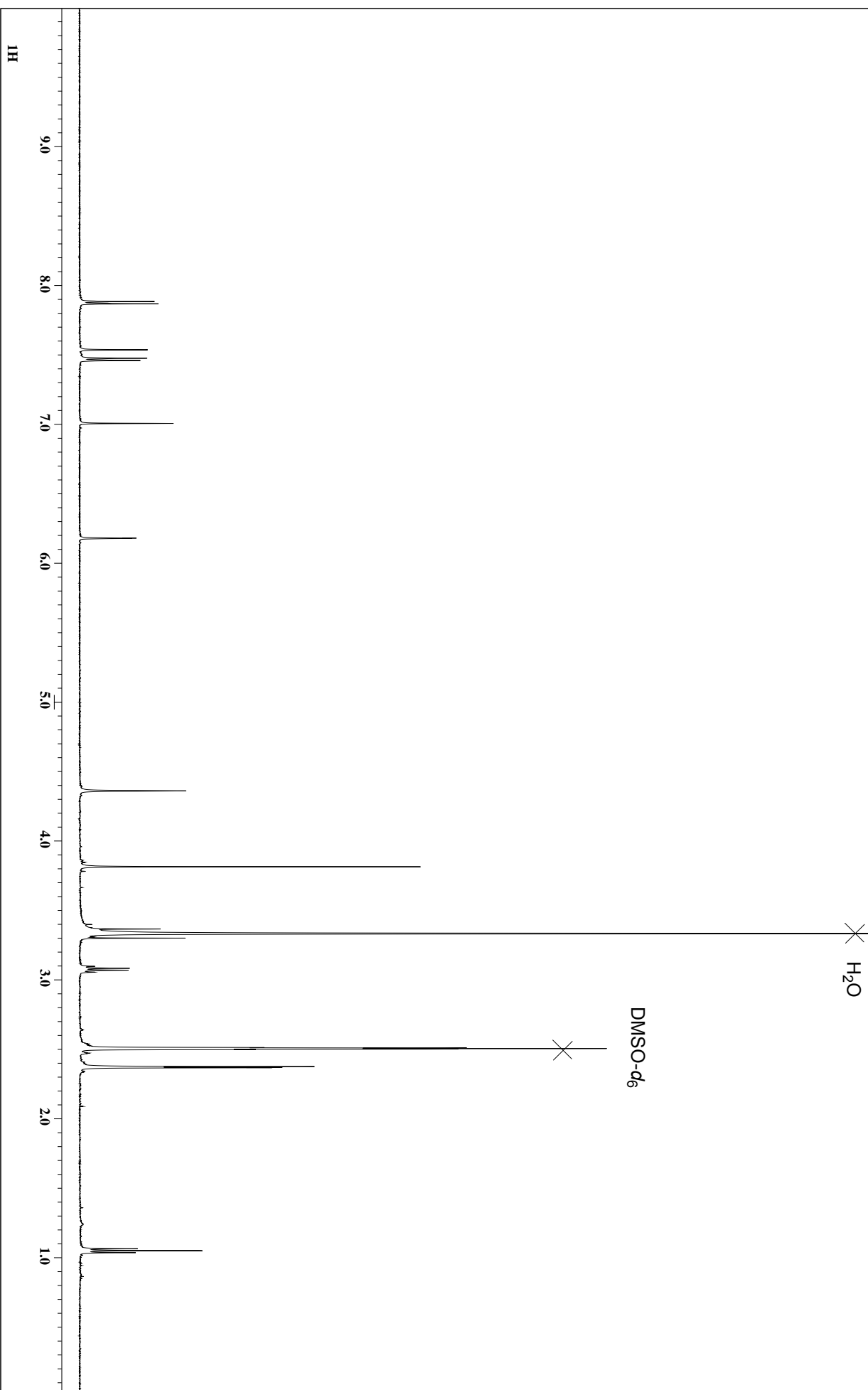
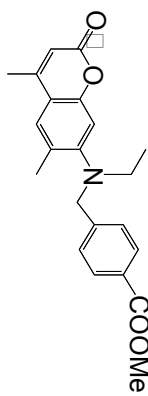
COSY NMR in CDCl<sub>3</sub> for compound 4

HMBC NMR in CDCl<sub>3</sub> for compound 3

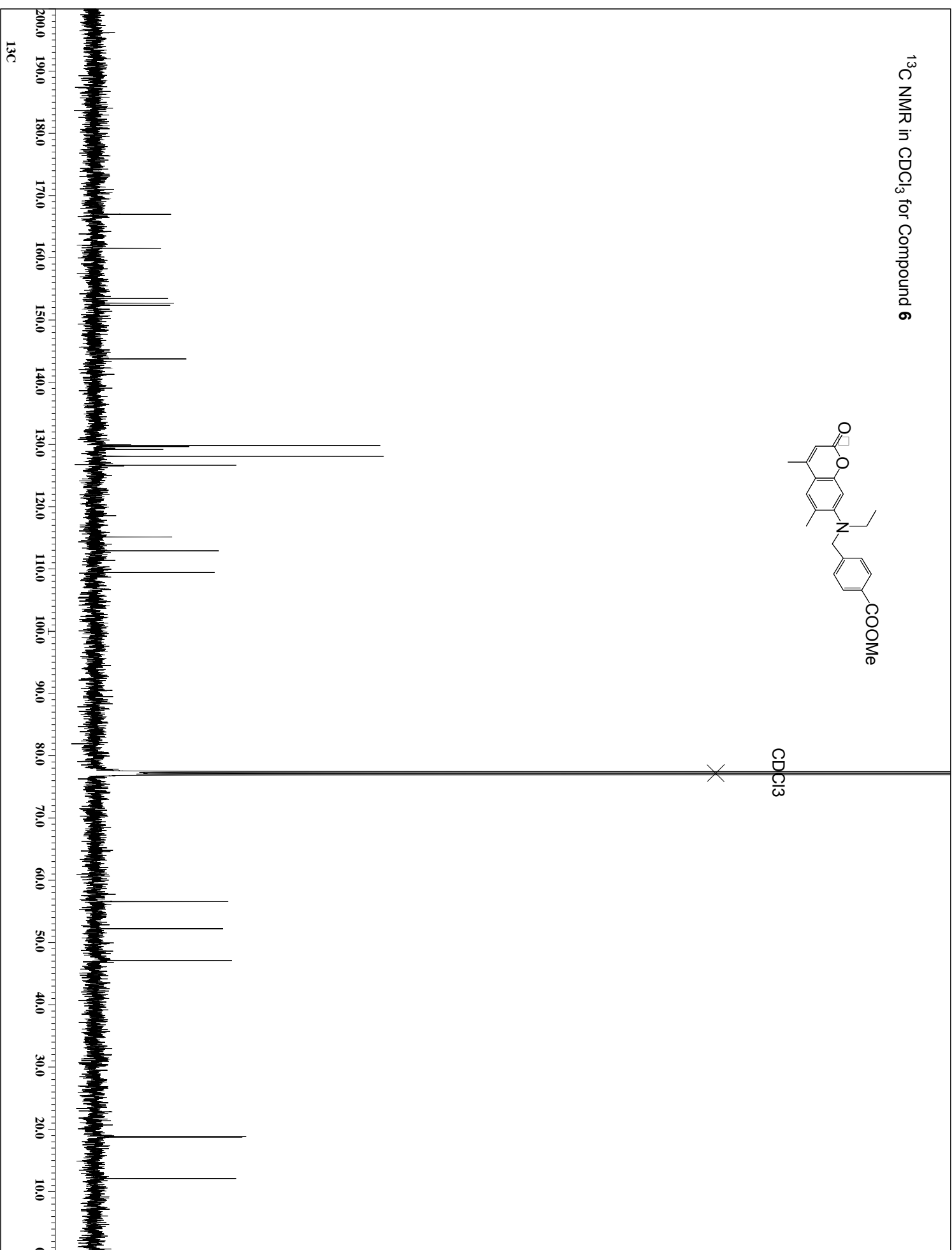
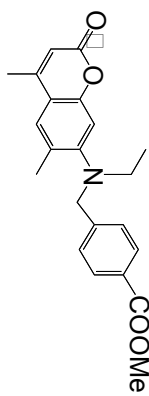
<sup>1</sup>H NMR in CDCl<sub>3</sub> + 10% CD<sub>3</sub>OD for compound **5**



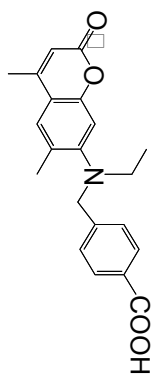
<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound **6**



$^{13}\text{C}$  NMR in  $\text{CDCl}_3$  for Compound **6**



<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound 7



H<sub>2</sub>O

X

DMSO-*d*<sub>6</sub>

X

1H

9.0

8.0

7.0

6.0

5.0

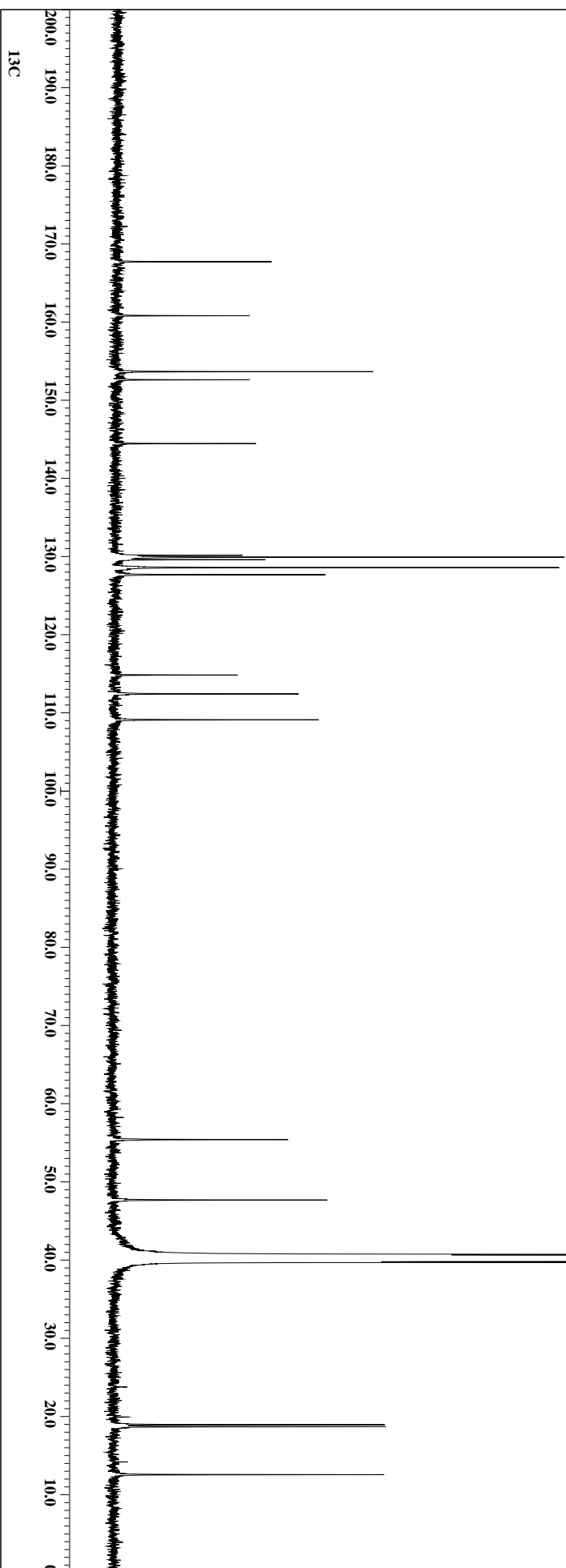
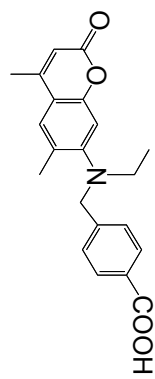
4.0

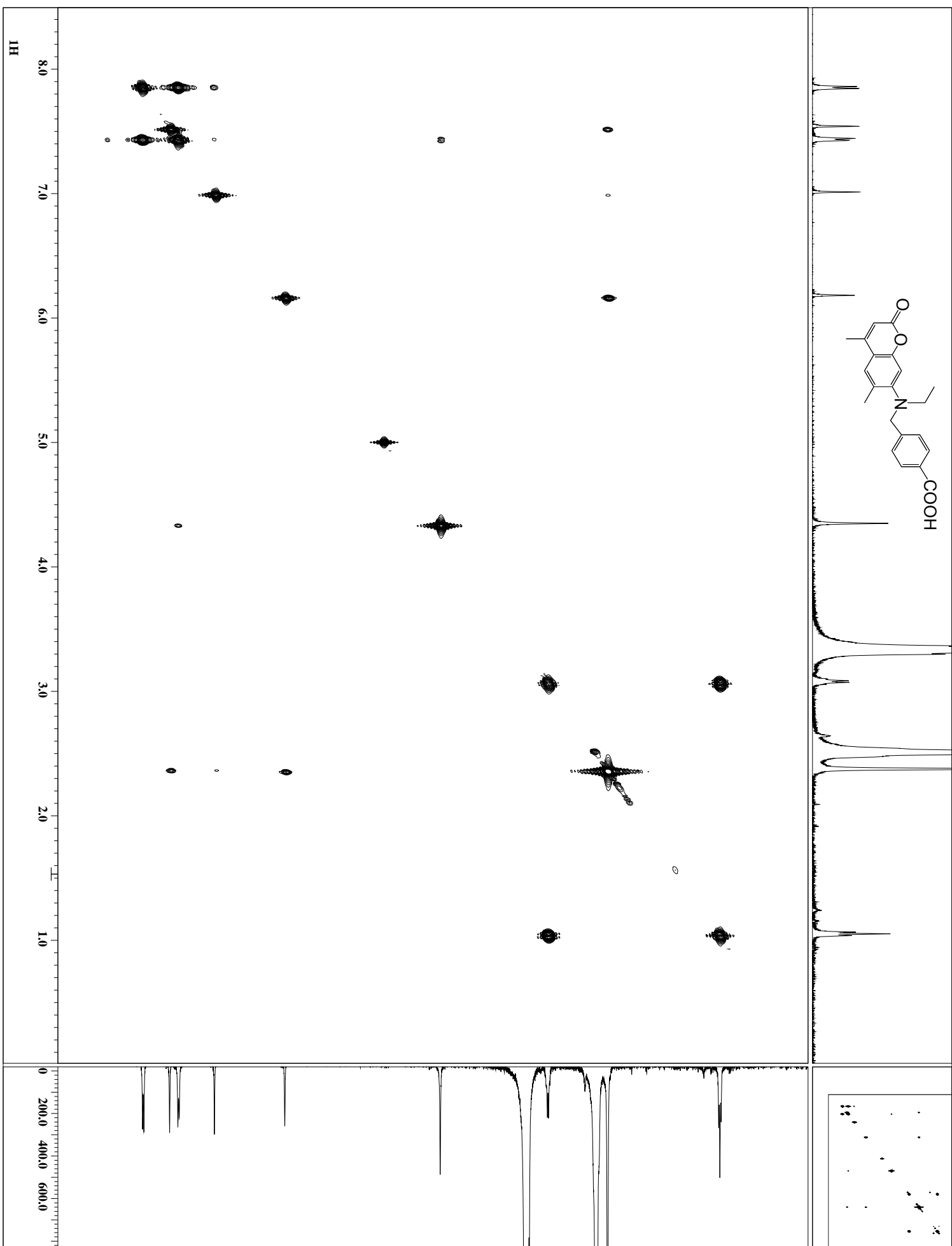
3.0

2.0

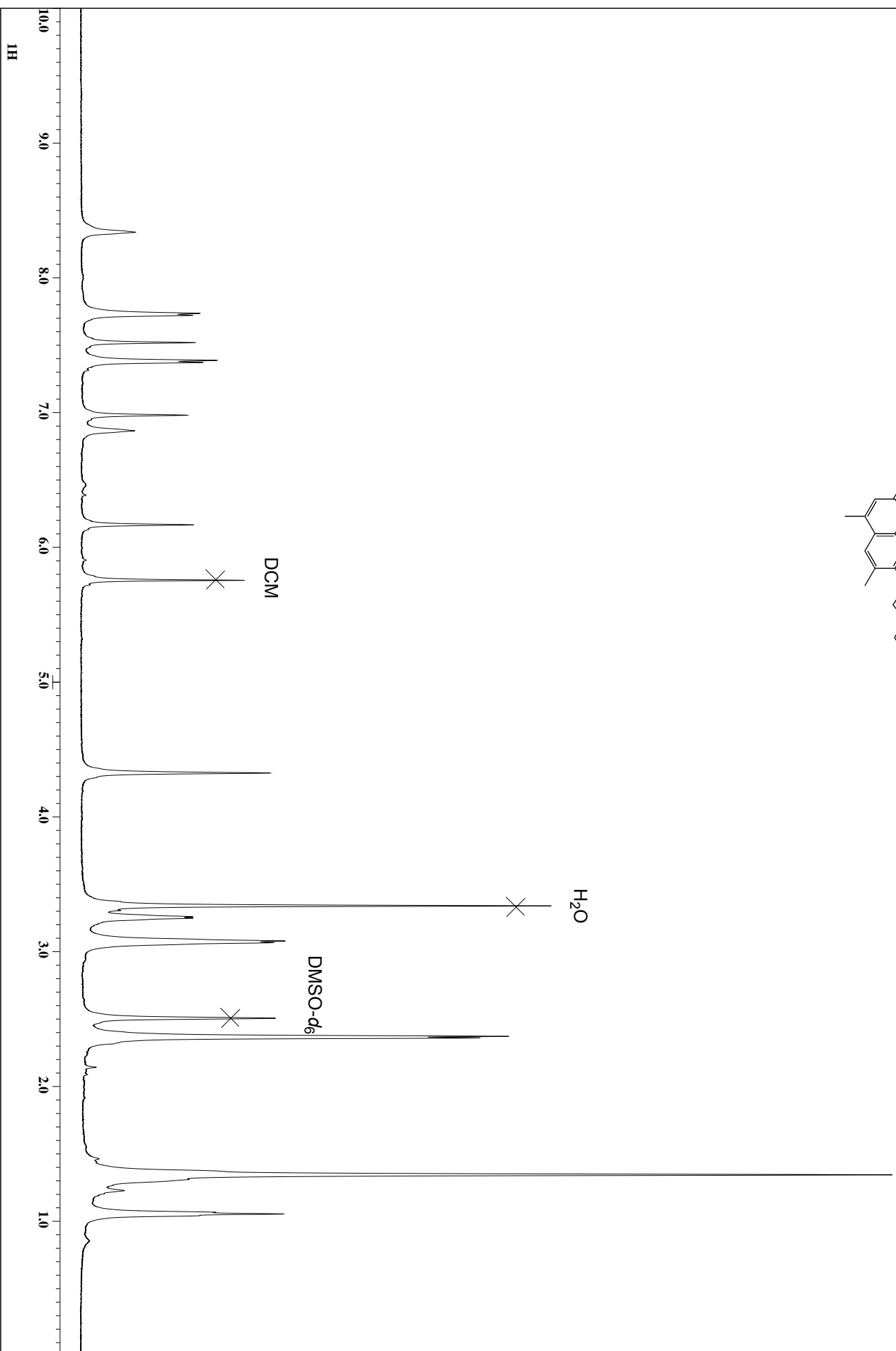
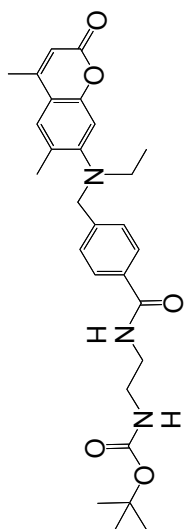
1.0

$^{13}\text{C}$  NMR in DMSO- $d_6$  for Compound 7

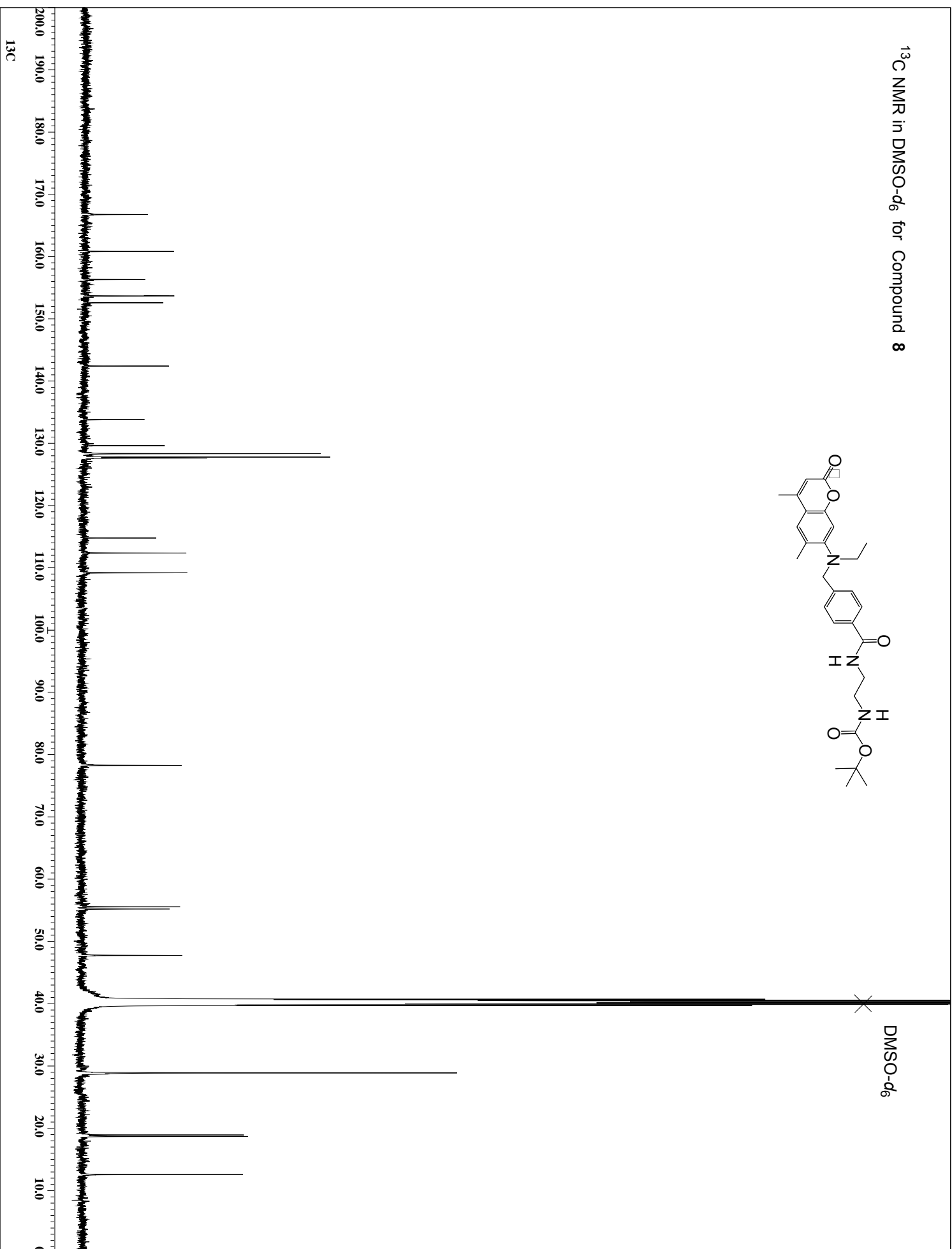
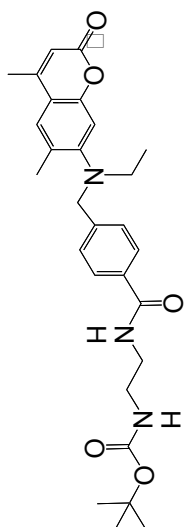


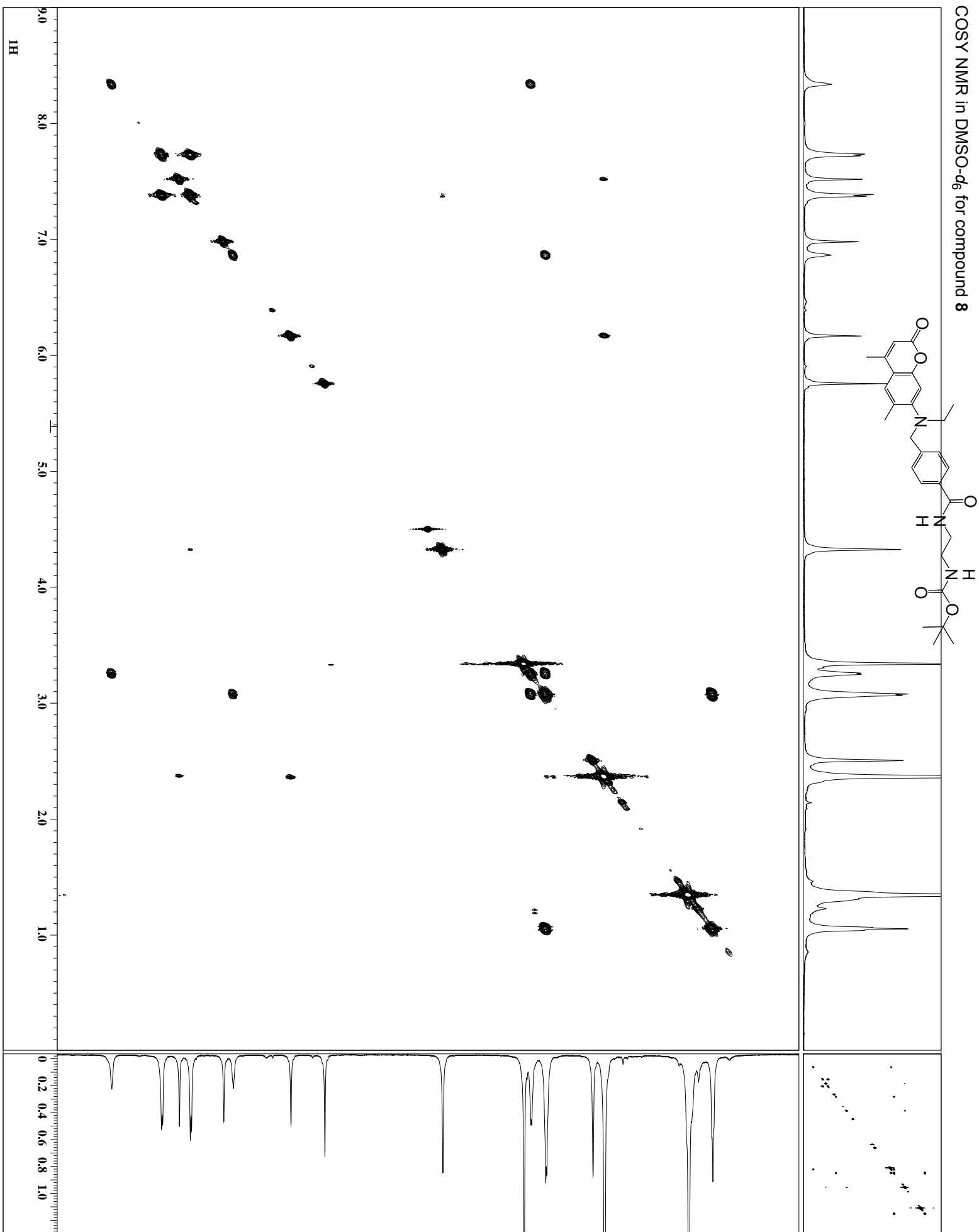


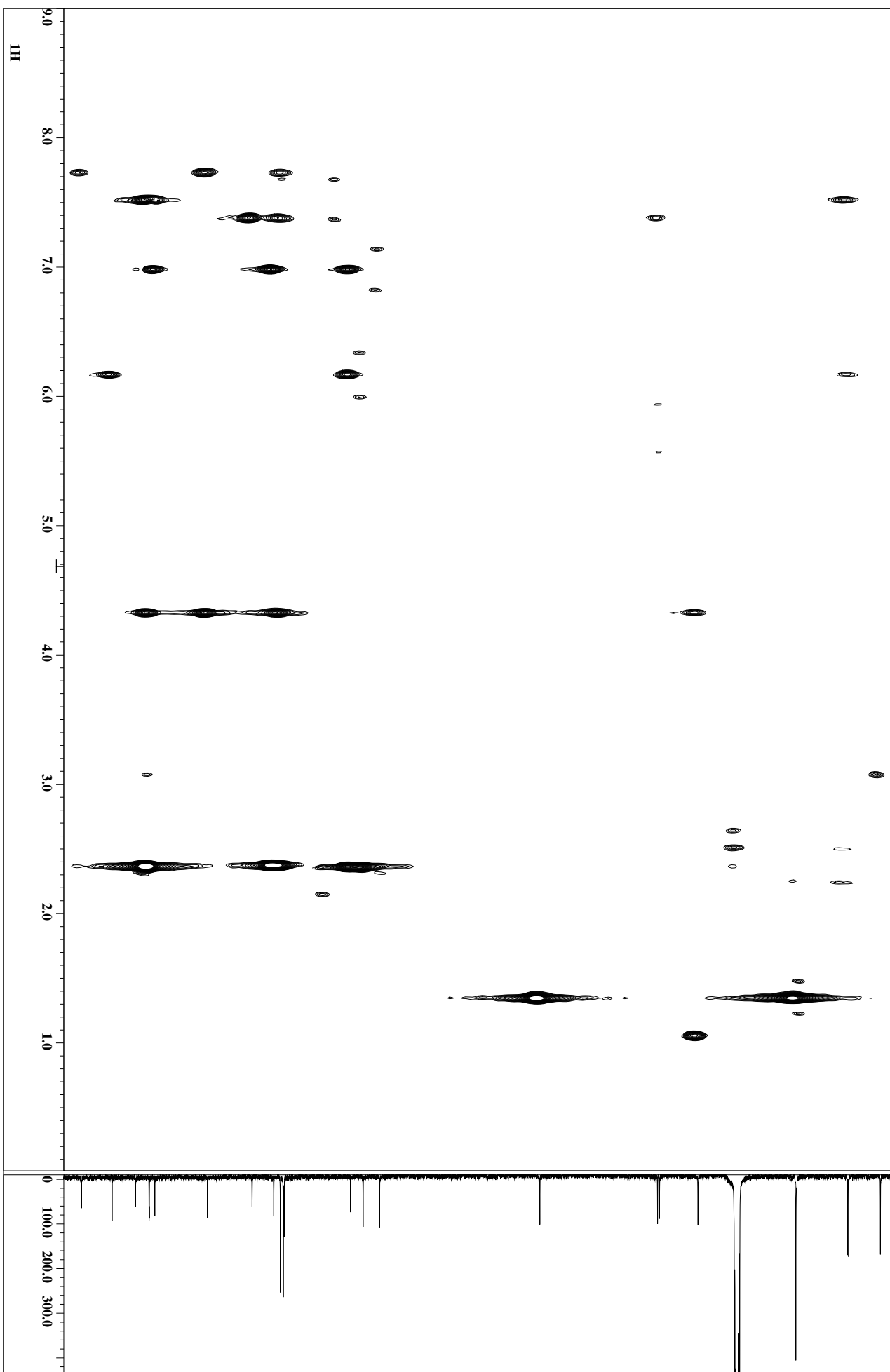
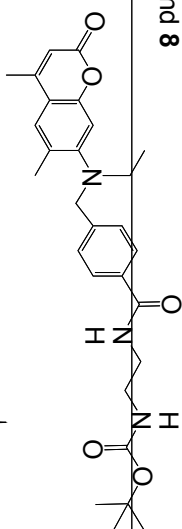
<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound 8

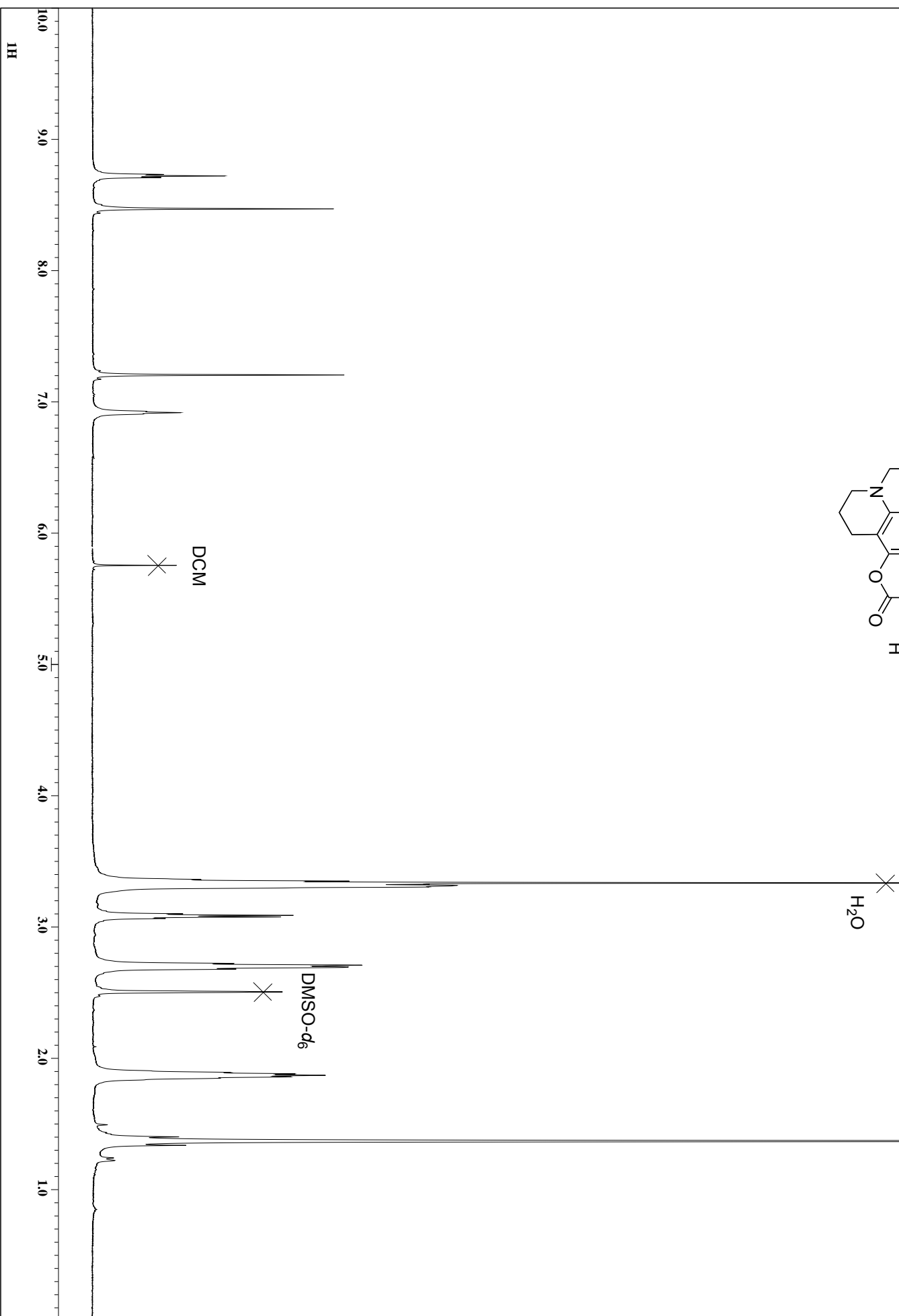
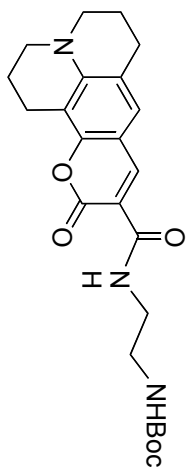


$^{13}\text{C}$  NMR in  $\text{DMSO-}d_6$  for Compound **8**

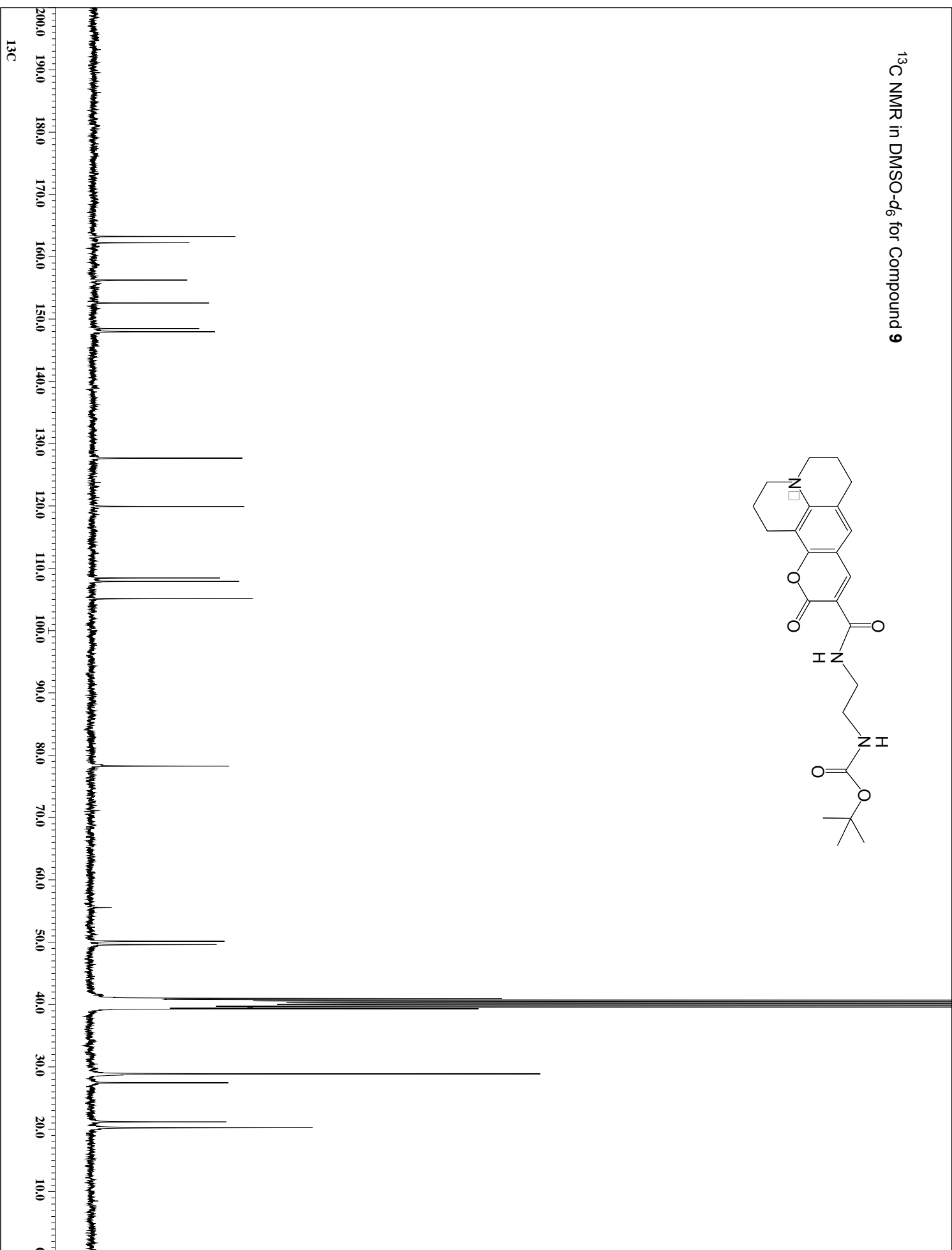
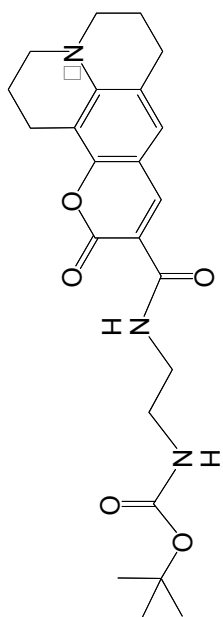


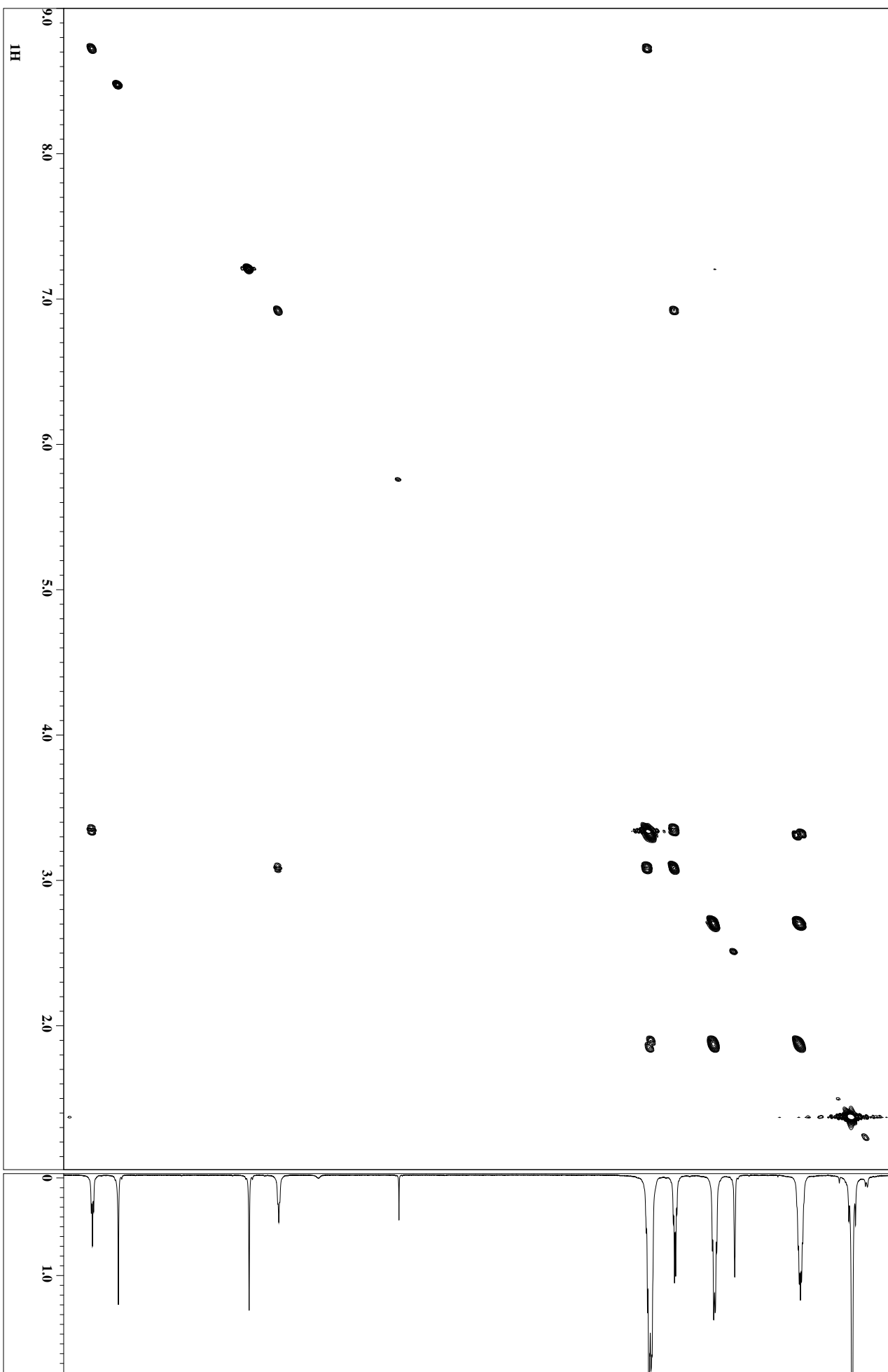
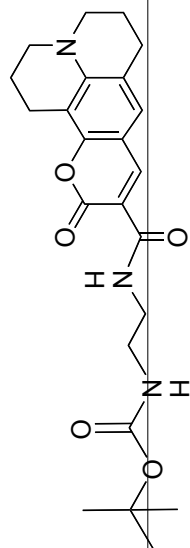


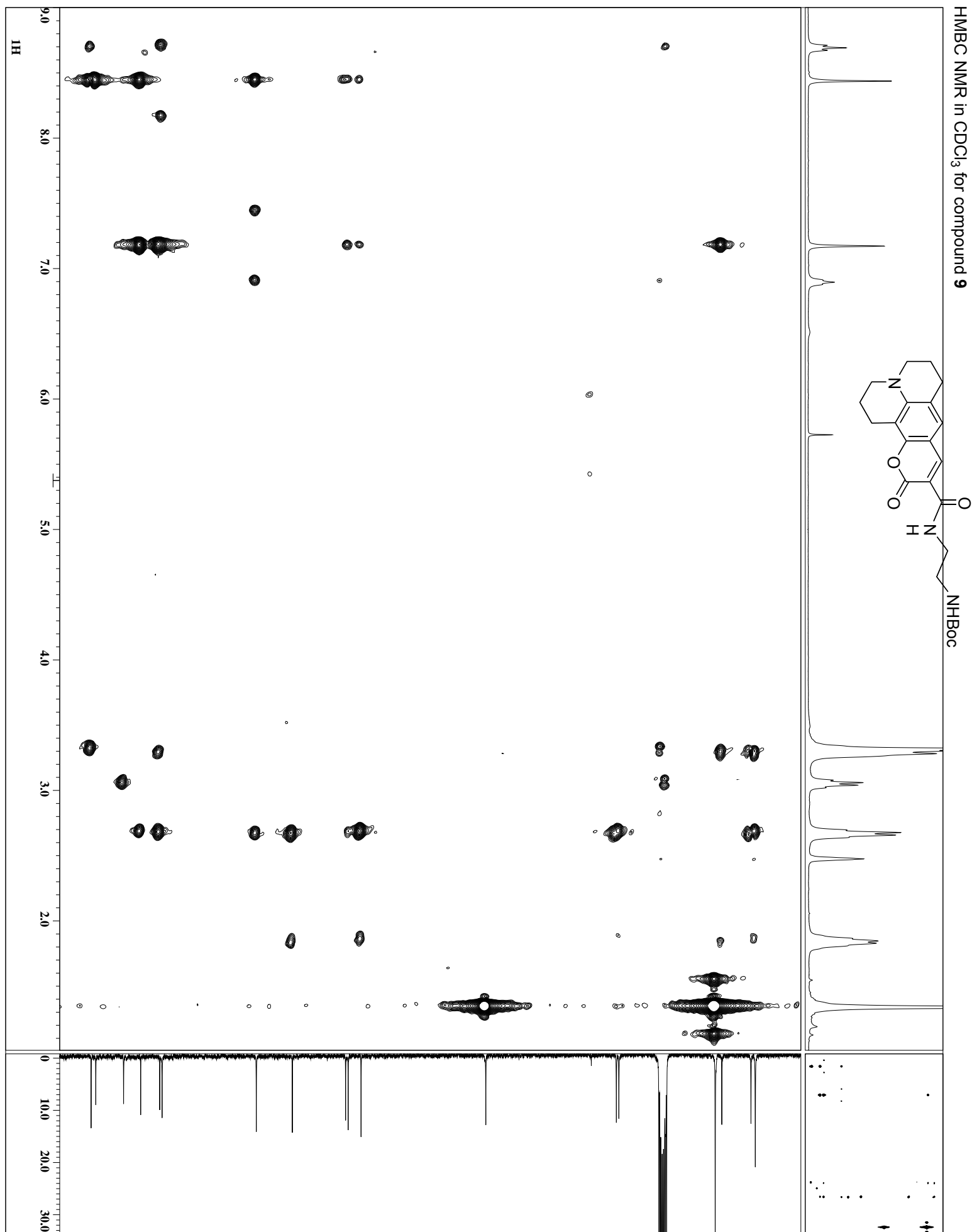


<sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> for Compound **9**

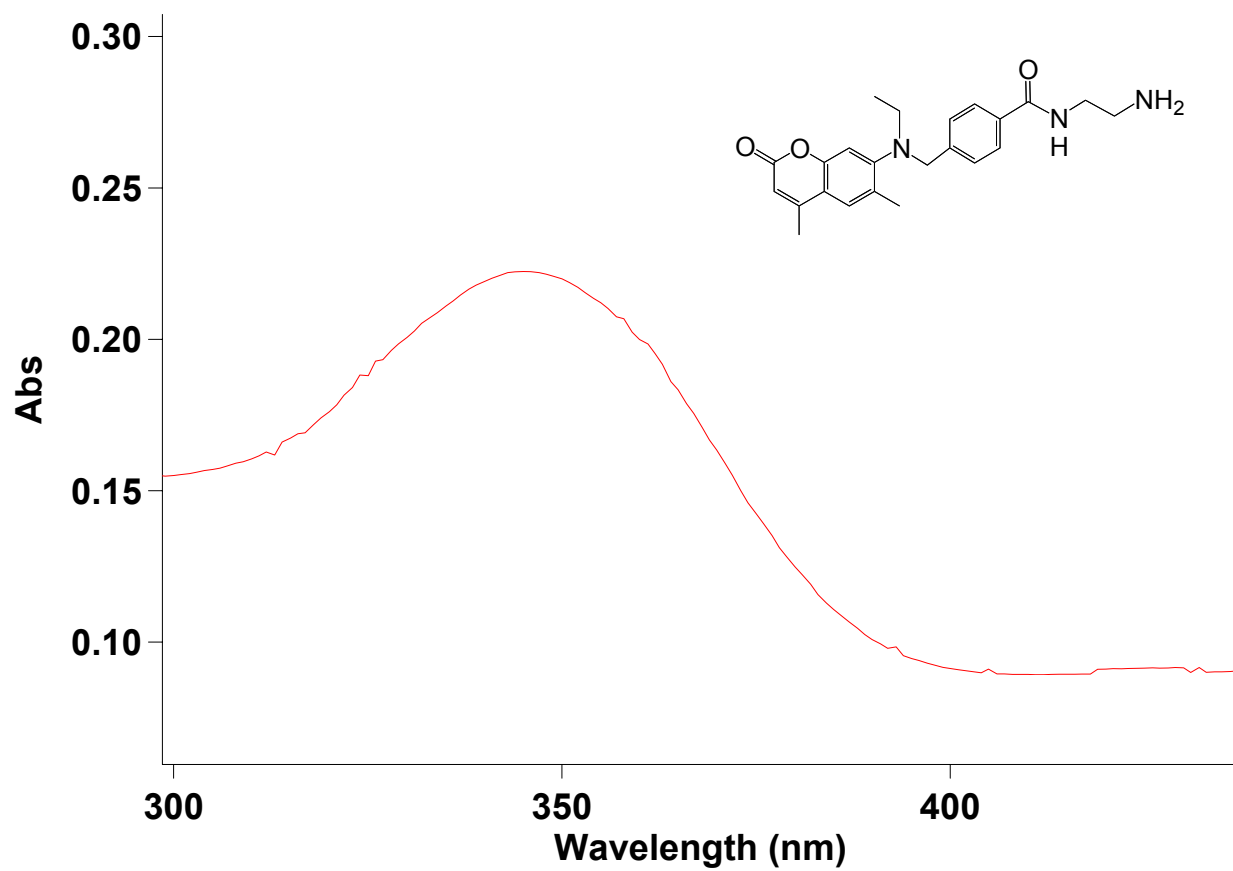
<sup>13</sup>C NMR in DMSO-*d*<sub>6</sub> for Compound **9**





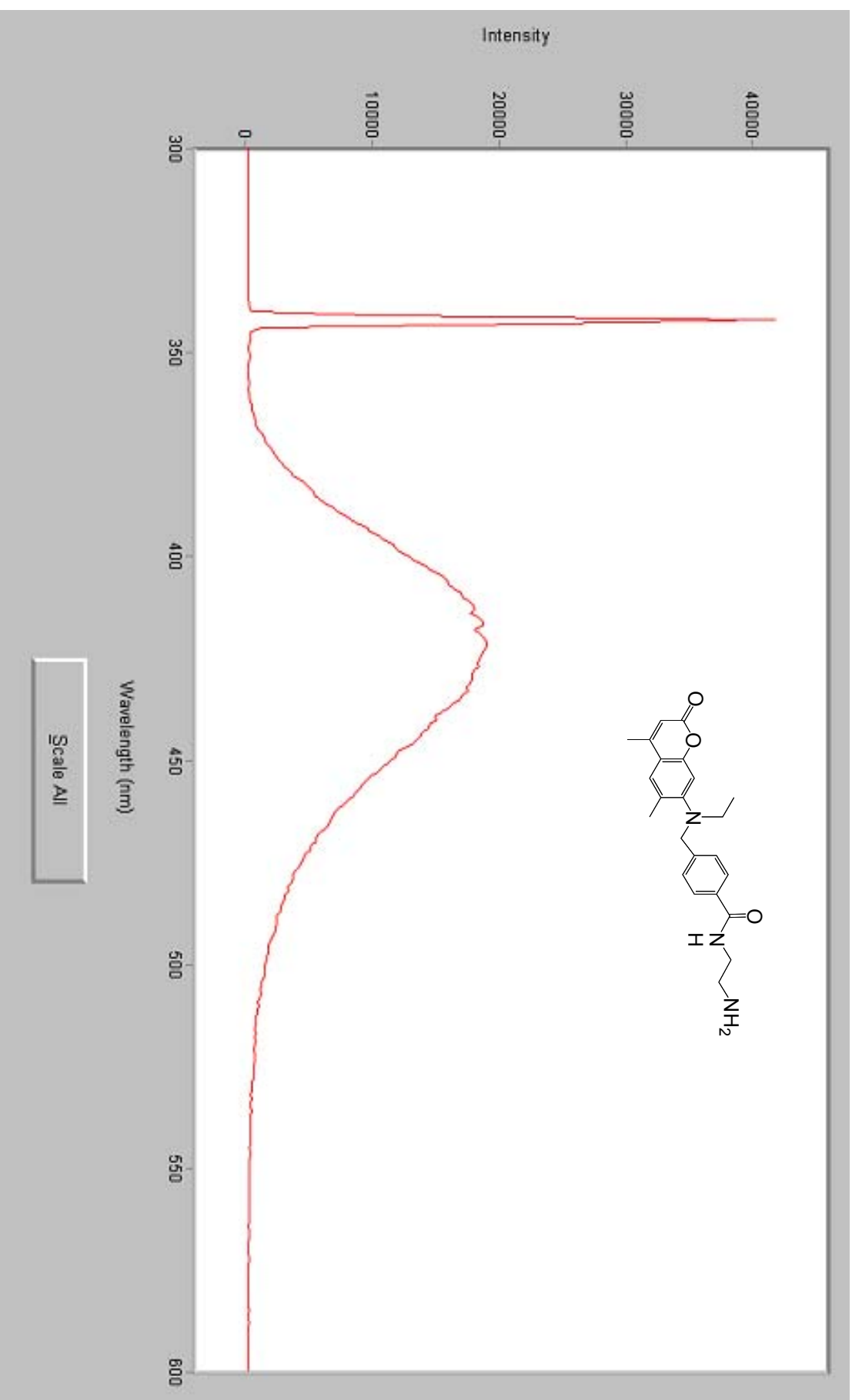


Compound 1:  $[c] = 1 \times 10^{-6}$  M,  $\lambda_{\max} = 343$  nm



**Fluorescence Spectrum:**

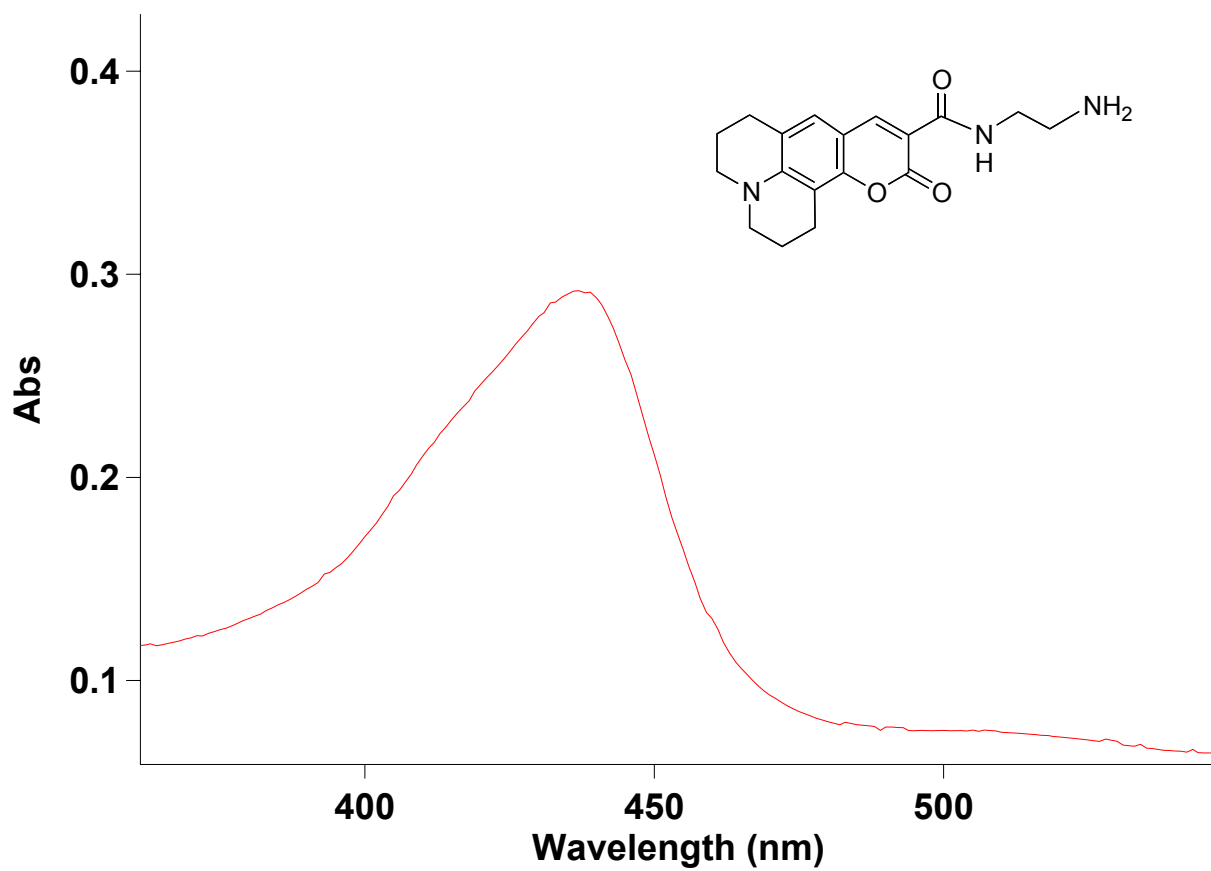
Compound 1:  $[c] = 1 \times 10^{-6}$  M.  $\lambda_{ex} = 343$  nm,  $\lambda_{em} = 425$  nm



# UV-vis Spectrum

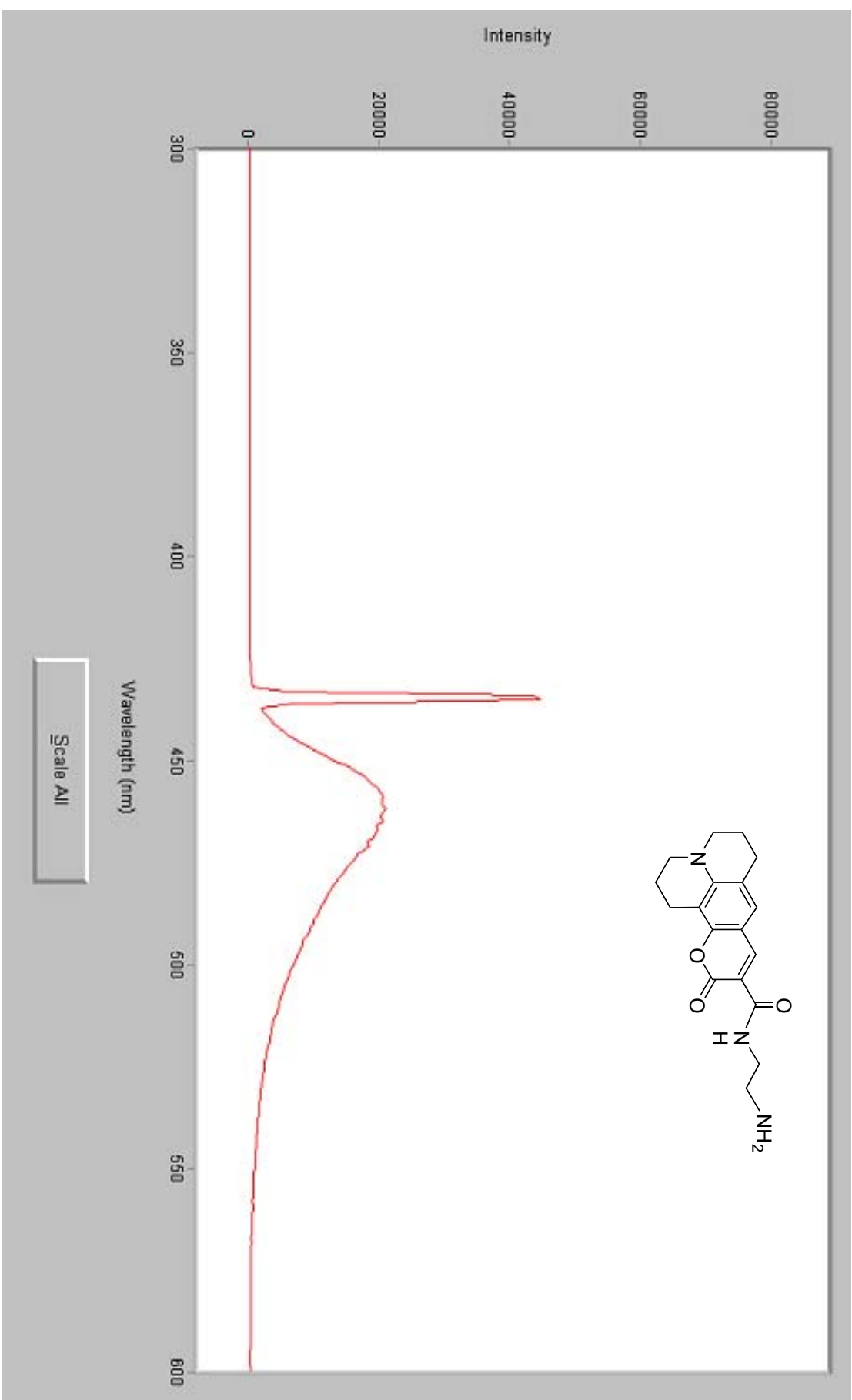
S38

Compound 2:  $[c] = 1 \times 10^{-6}$  M,  $\lambda_{\text{max}} = 435$  nm



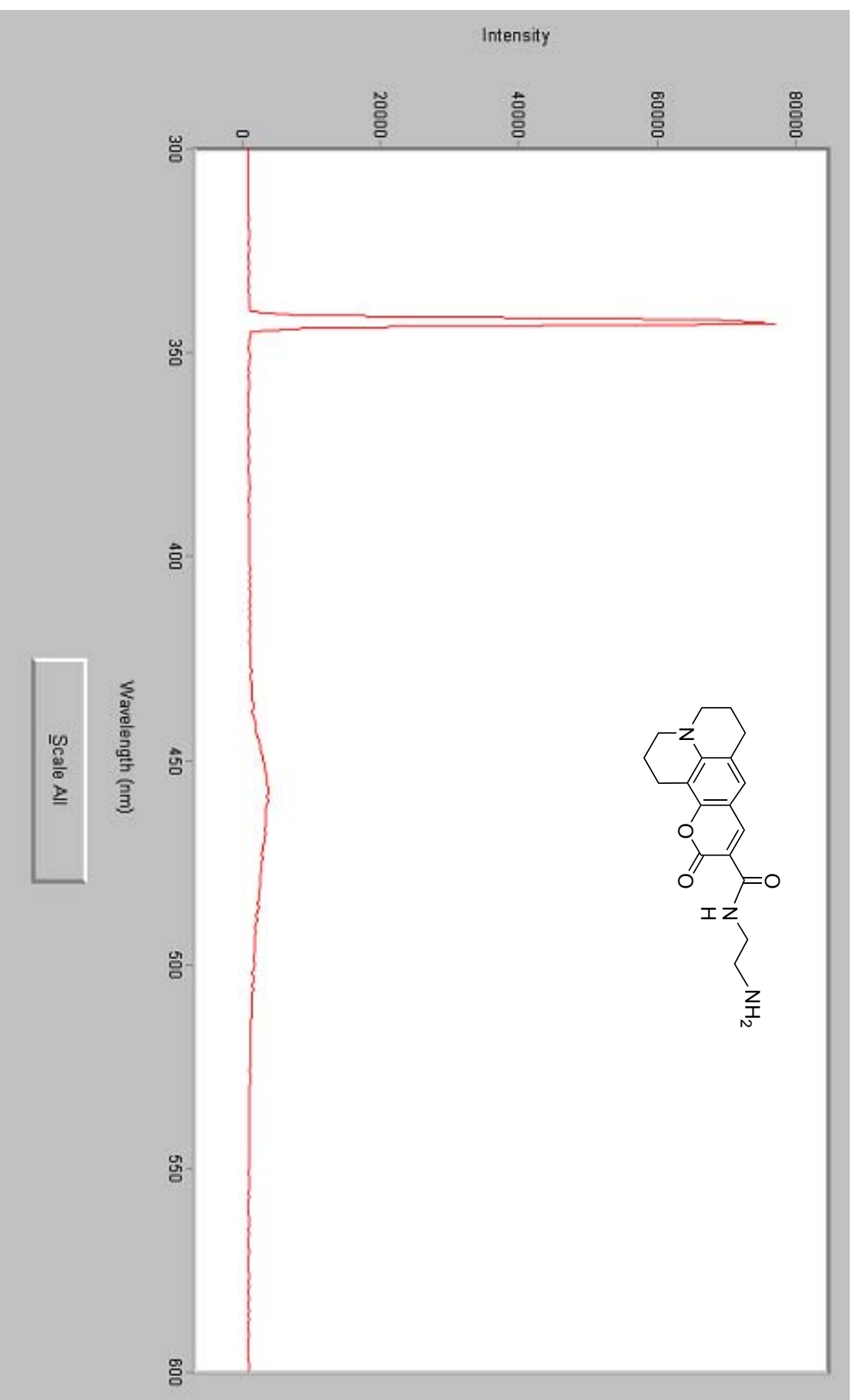
**Fluorescence Spectrum:**

Compound 2:  $[c] = 1 \times 10^{-6}$  M.  $\lambda_{ex} = 435$  nm,  $\lambda_{em} = 468$  nm



## Fluorescence Spectrum:

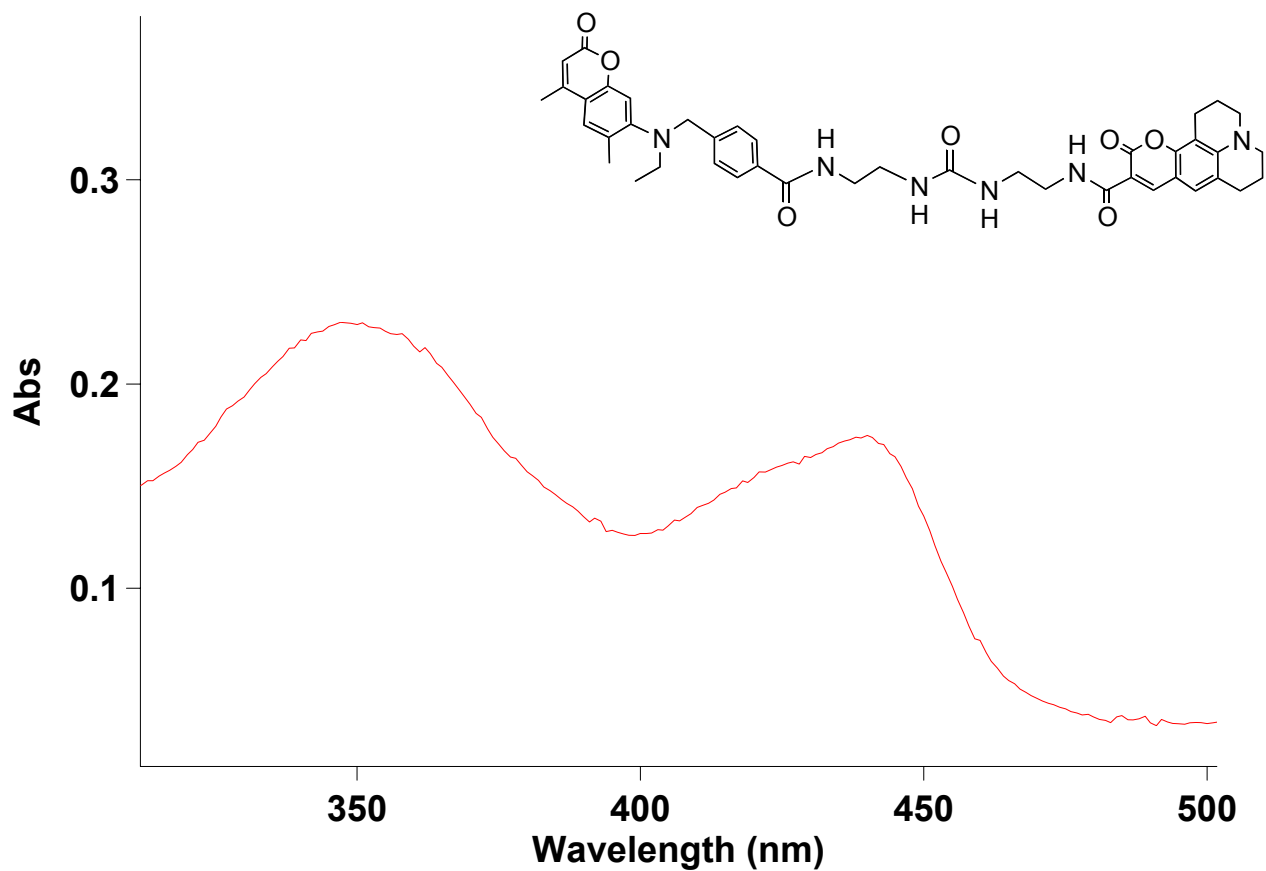
Compound **2**:  $[c] = 1 \times 10^{-6}$  M.  $\lambda_{ex} = 343$  nm, Emission is weak.



# UV-vis Spectrum

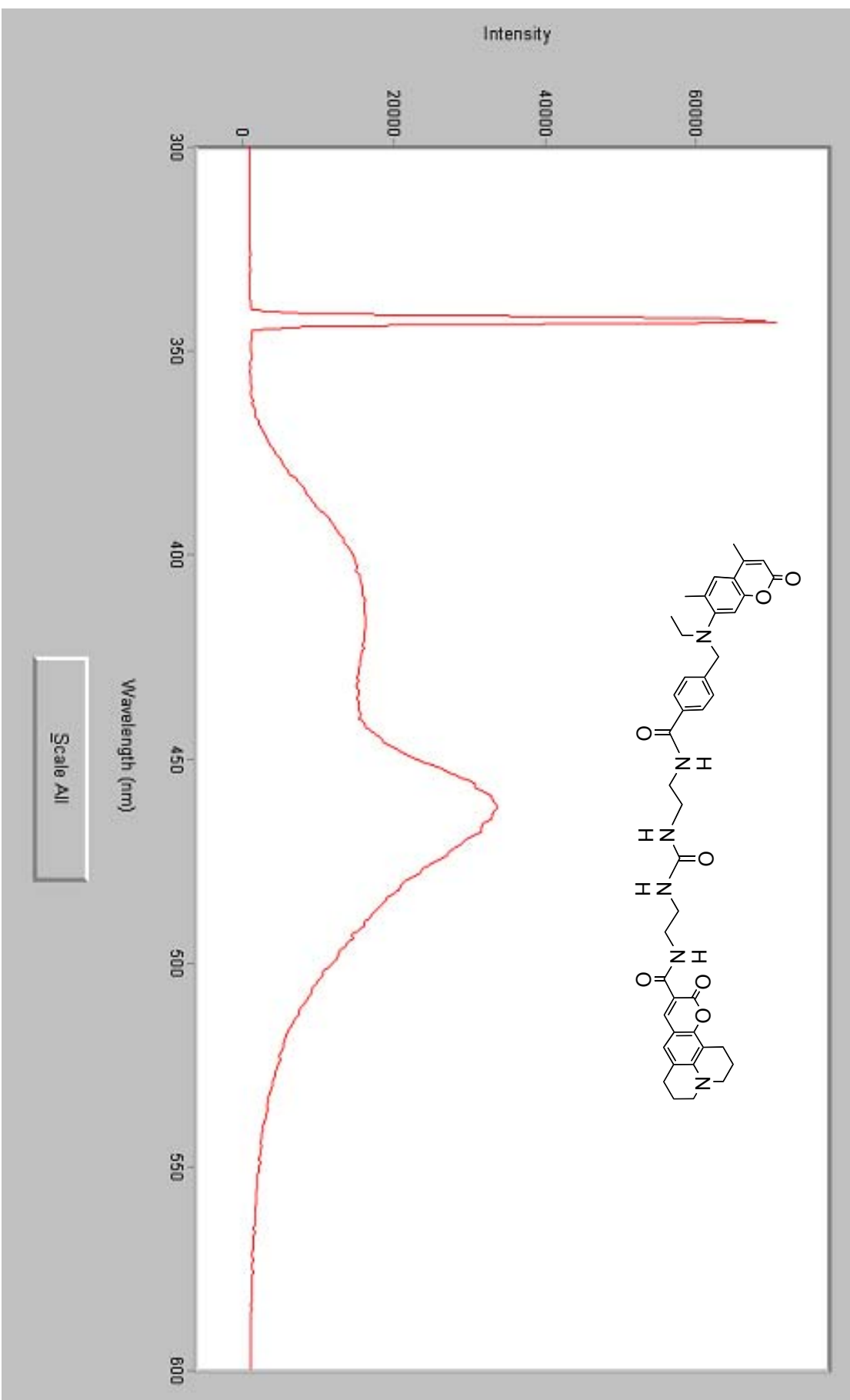
S41

Compound 3: [c] =  $1 \times 10^{-6}$  M,  $\lambda_{\text{max}1}$  = 343 nm,  $\lambda_{\text{max}2}$  = 438 nm



**Fluorescence Spectrum:**

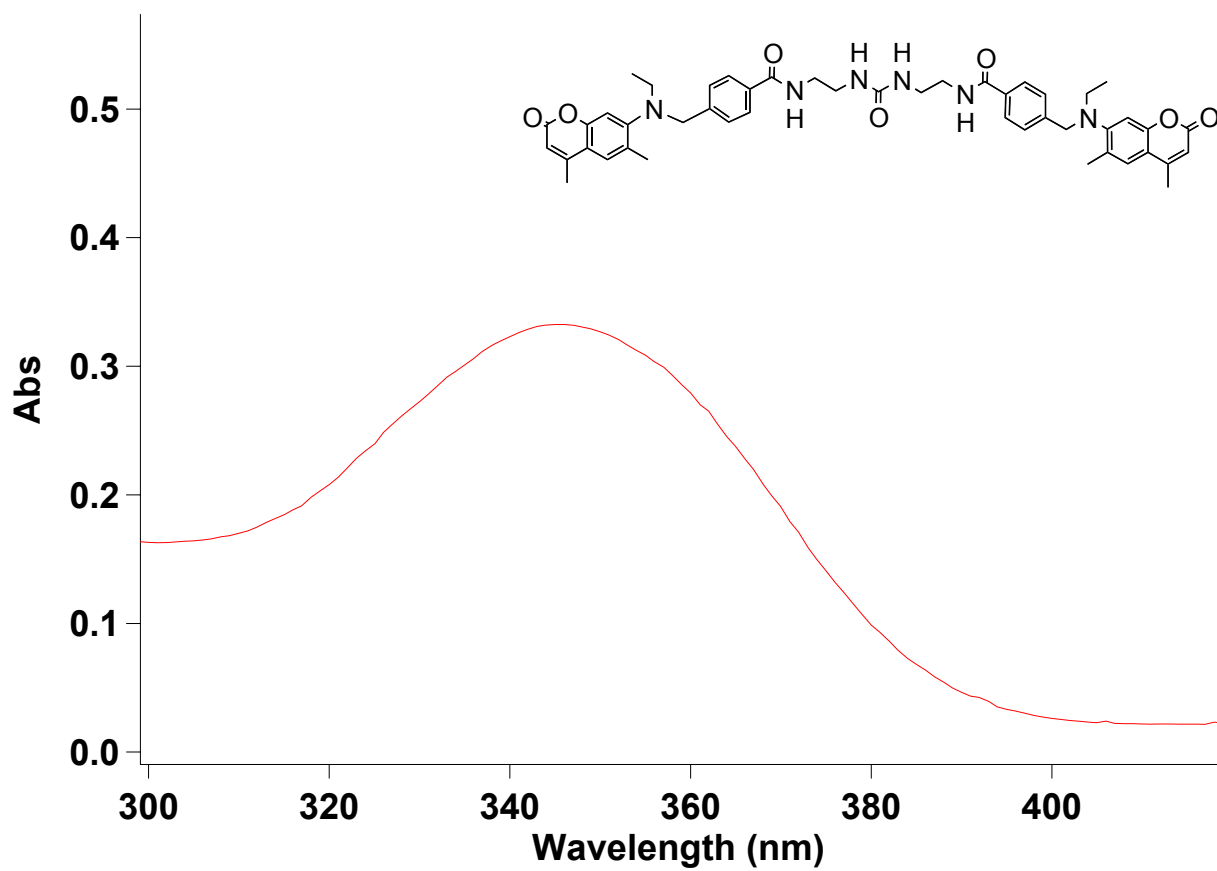
Compound **3**: [c] =  $1 \times 10^{-6}$  M.  $\lambda_{\text{ex}}$  = 343 nm,  $\lambda_{\text{em1}}$  = 422 nm,  $\lambda_{\text{em2}}$  = 464 nm.



# UV-vis Spectrum

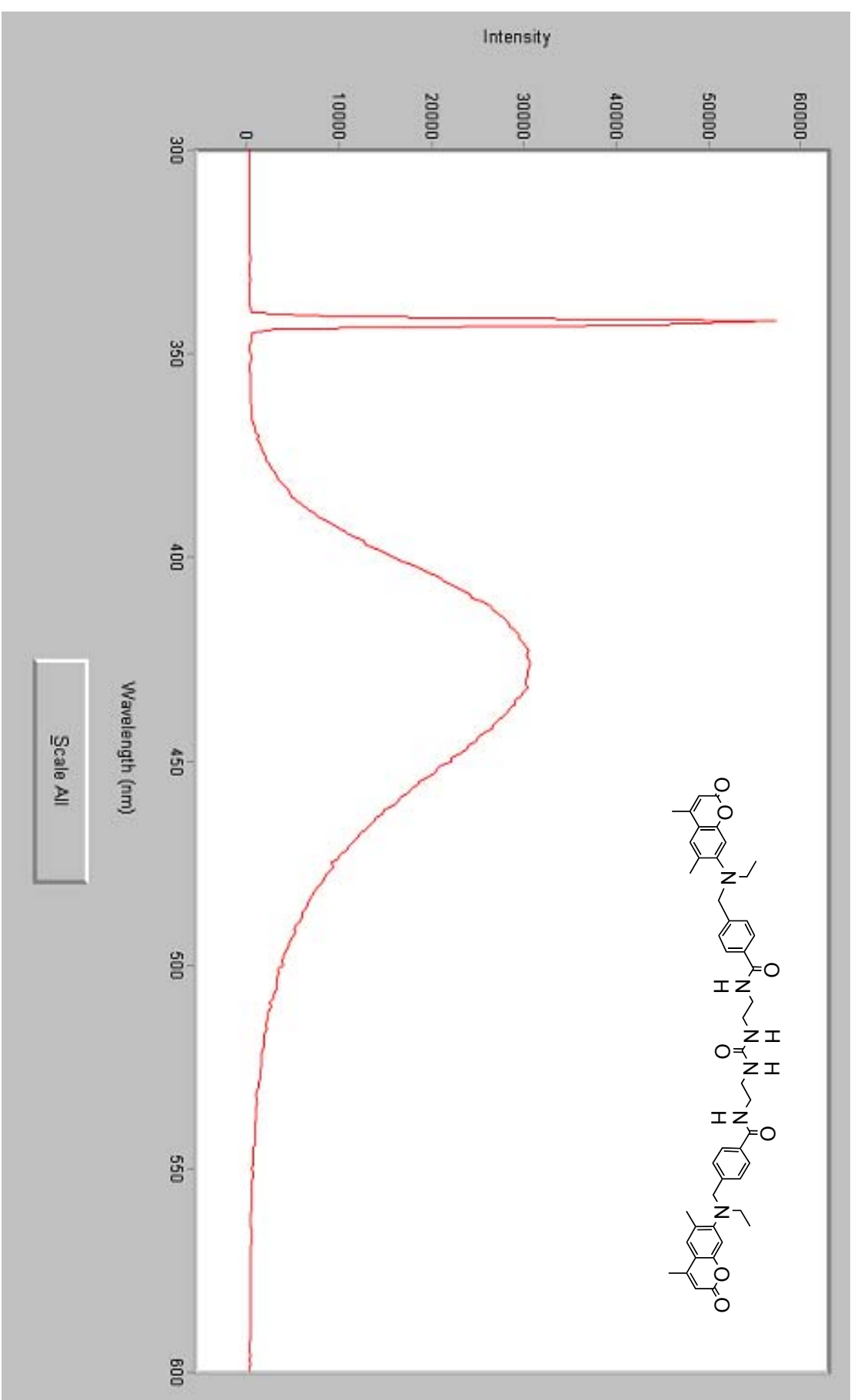
S43

Compound **4**:  $[c] = 1 \times 10^{-6}$  M,  $\lambda_{\text{max}} = 344$  nm

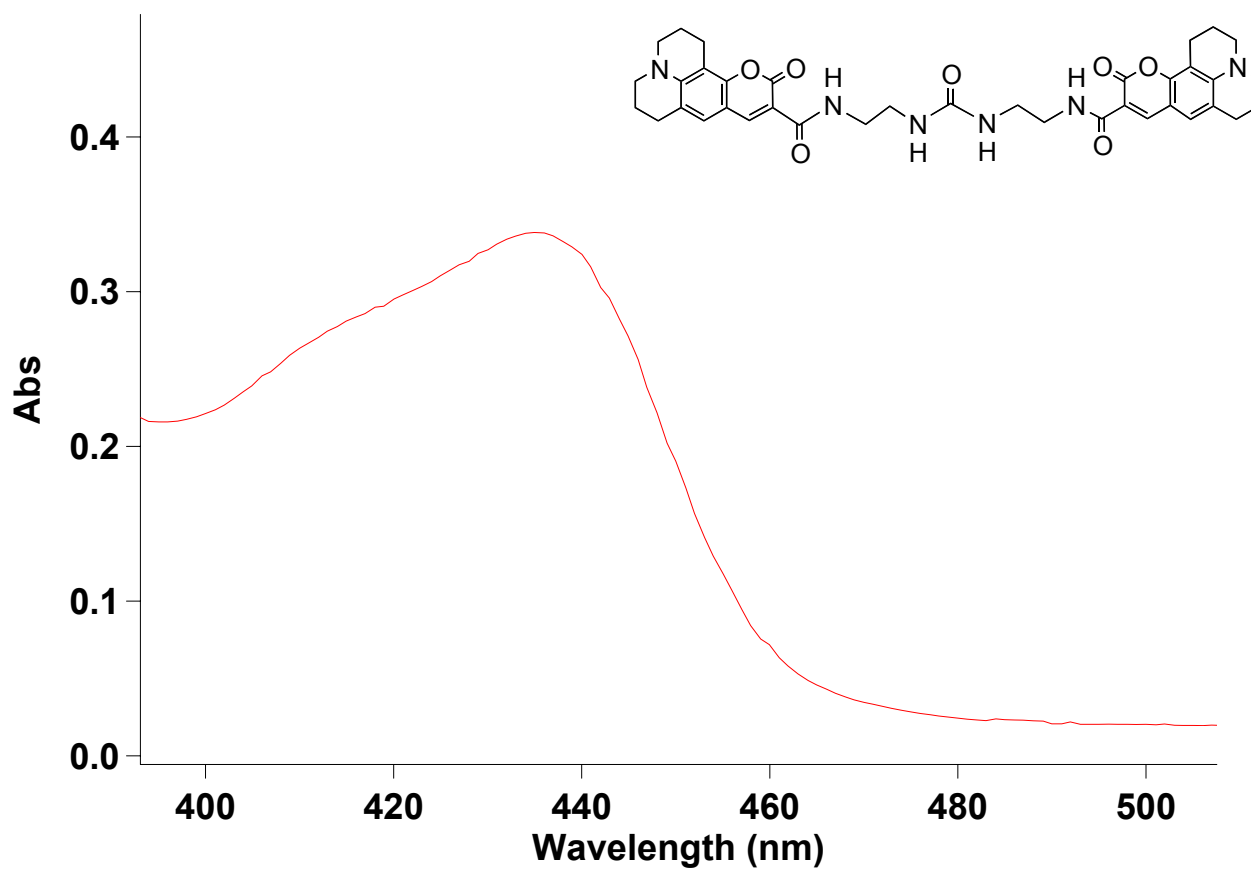


## Fluorescence Spectrum:

Compound 4:  $[c] = 1 \times 10^{-6}$  M.  $\lambda_{ex} = 344$  nm,  $\lambda_{em} = 424$  nm

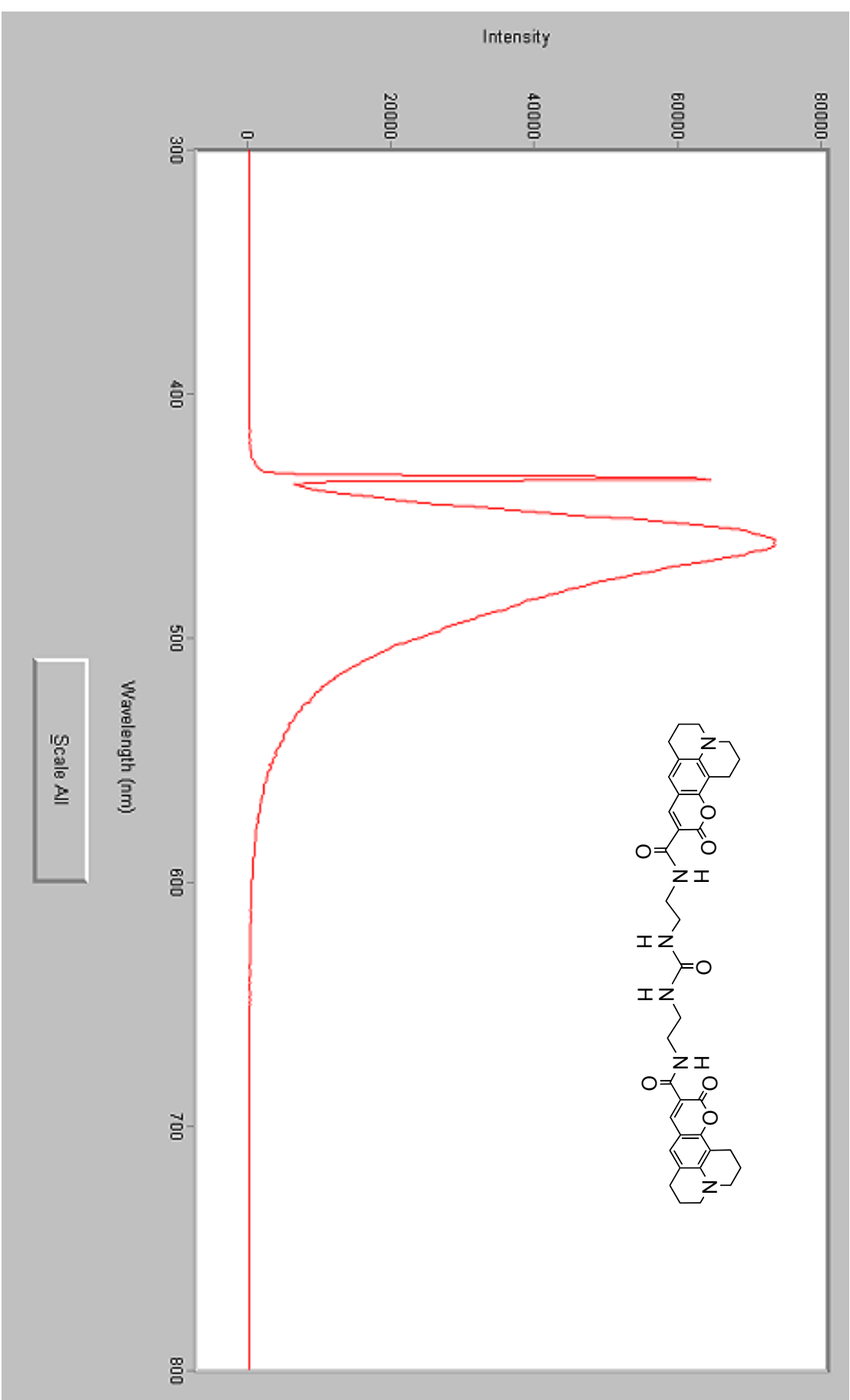


Compound **5**:  $[c] = 1 \times 10^{-6}$  M,  $\lambda_{\text{max}} = 435$  nm



## Fluorescence Spectrum:

Compound 5:  $[c] = 1 \times 10^{-6}$  M.  $\lambda_{ex} = 435$  nm,  $\lambda_{em} = 462$  nm



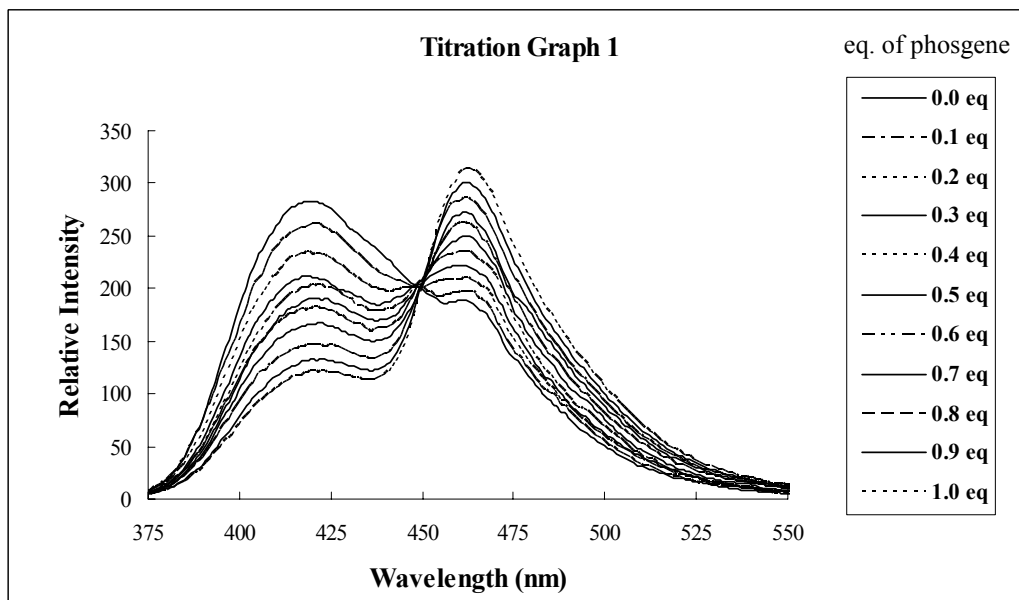
**Titration Results:**

Fig. 1. Fluorescence emission spectra on titration with triphosgene. Coumarins **1** and **2** were mixed in 1:1 ratio at  $1 \times 10^{-2}$  M in  $\text{CHCl}_3$ , TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted to  $10^{-5}$  M then emission spectra were recorded. The similar result was shown in  $10^{-6}$  M dilutions.

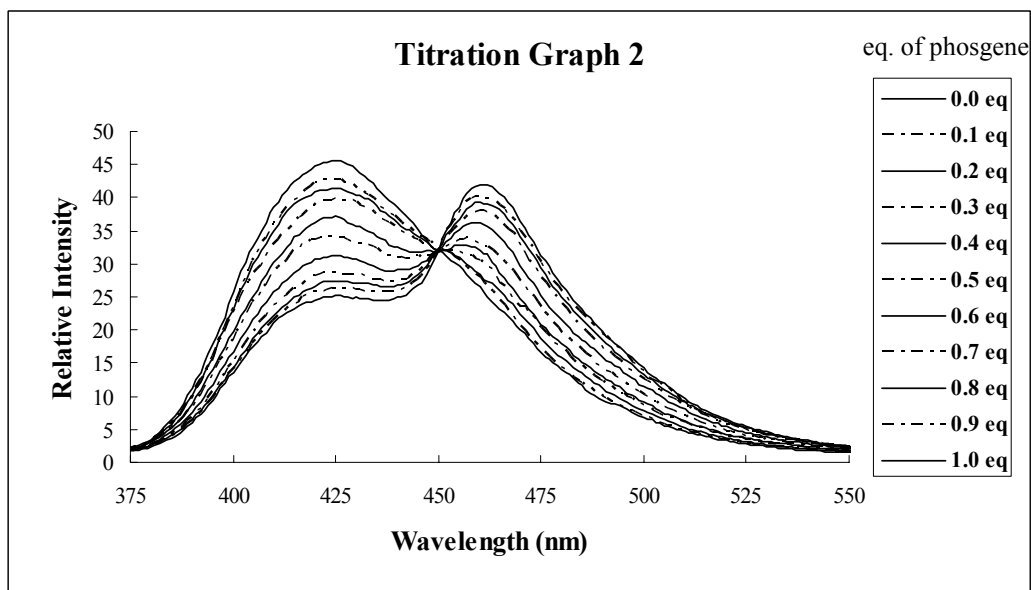


Fig. 2. Fluorescence emission spectra on titration with triphosgene. Coumarins **1** and **2** were mixed in 1:1 ratio at  $1 \times 10^{-3}$  M in  $\text{CHCl}_3$ , TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted  $10^{-6}$  M then emission spectra were recorded

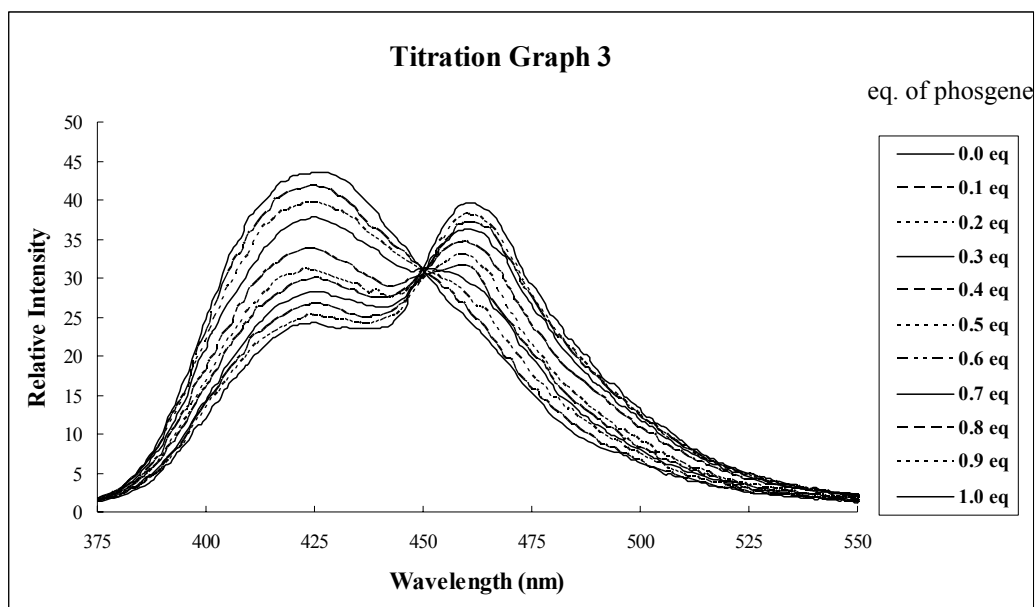


Fig. 3. Fluorescence emission spectra on titration with triphosgene. Coumarins **1** and **2** were mixed in 1:1 ratio at  $5 \times 10^{-4}$  M in  $\text{CHCl}_3$ , TEA (10 eq) was added. 1/3 equivalent triphosgene (equal to 1 equivalent phosgene) was added step by step. Aliquots were taken and diluted to  $10^{-6}$  M then emission spectra were recorded