Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information for

Lactam-Fused Tropolones: A New Tunable, Environmentally Sensitive Fluorophore Class

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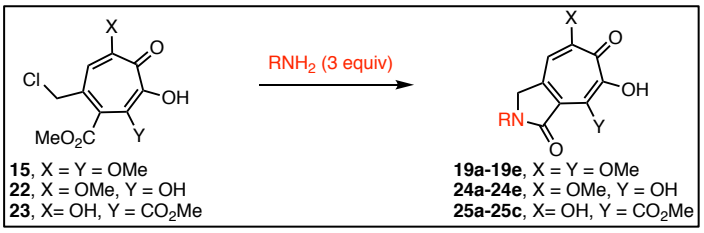
I. General Information.

All starting materials and reagents were purchased from commercially available sources and used without further purification. ^{1}H NMR shifts were measured using the solvent residual peak as the internal standard ($CDCl_3$ δ 7.26, DMSO-d_6 δ 2.50, CD_3OD δ 3.31, CD_3CN δ 1.94) and reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, m = multiplet), coupling constant (Hz), integration. $^{13}C\{^{1}H\}$ NMR shifts were measured using the solvent residual peak as the internal standard ($CDCl_3$ δ 77.2, DMSO-d_6 δ 39.5, CD_3OD δ 49.2, CD_3CN δ 118.7 and δ 1.4) and reported as chemical shifts. Infrared (IR) spectral bands are characterized as broad (br), strong (s), medium (m), and weak (w). Mass spectra were recorded on a spectrometer by the electrospray ionization (ESI) technique with a time-of-flight (TOF) mass analyzer. Microwave reactions were performed via the Biotage Initiator EXP US (manufacturer #: 355302) (external IR temperature sensor) in a sealed vessel. Where noted, reaction products were purified via reverse phase chromatography using a Biotage Isolera Prime, with Biotage C18 12g and 30g cartridges in a solvent system of H_2O/MeCN [0.05% TFA].

II. Synthesis and Characterization

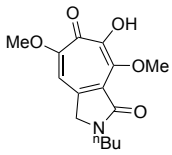
Synthesis of Lactam-Fused Tropolones



15, X = Y = OMe
22, X = OMe, Y = OH
23, X= OH, Y = CO_2Me

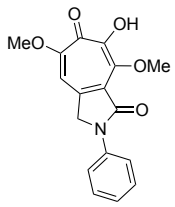
19a-19e, X = Y = OMe
24a-24e, X = OMe, Y = OH
25a-25c, X= OH, Y = CO_2Me

Methyl 5,7-dihydroxy-3,6-dioxo-2-phenyl-1,2,3,6-tetrahydrocyclohepta[c]pyrrole-4-carboxylate (19a). To a solution of tropolone (**15**) (20.0 mg, 0.069 mmol) in CH_2Cl_2 (3.0 mL) was added amine



(20.6 µL, 0.208 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-20% MeCN/H_2O [0.05% TFA] (10 CV); 10-30% MeCN/H_2O [0.05% TFA] (10 CV); 30- 65% MeCN/H_2O [0.05% TFA] (14 CV). Product fractions were concentrated to yield **19a** as a light yellow solid (9.8 mg, 49% yield). *Characterization data of **19a** are as follows.* **Melting Point (Mp):** 182-184 °C. **IR (thin film, KBr)** 3462 (br), 3205 (br), 2958 (w), 2933 (w), 2873(w), 1682 (s), 1601 (w), 1558 (m), 1456 (m), 1409 (w), 1379 (w), 1346 (m), 1285 (m), 1237 (s), 1126 (w), 1082 (w), 1060 (w), 950 (w), 844 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.94 (s, 1H), 4.37 – 4.31 (m, 2H), 4.08 (s, 3H), 4.04 (s, 3H), 3.61 – 3.55 (m, 2H), 1.67 – 1.60 (m, 2H), 1.42 – 1.34 (m, 2H), 0.98 – 0.93 (m, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** 170.9, 166.6, 160.5, 155.7, 150.5, 138.9, 126.8, 109.8, 62.0, 56.9, 52.3, 42.3, 30.4, 20.2, 13.9. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{15}H_{20}NO_5^+$: 294.1336. Found: 294.1341.

7-Hydroxy-5,8-dimethoxy-2-phenyl-2,3-dihydrocyclohepta[c]pyrrole-1,6-dione (19b). To a



solution of tropolone (**15**) (38.2 mg, 0.132 mmol) in CH_2Cl_2 (0.528 mL) was added amine (37.0 mg, 0.529 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 30 g C18 column, solvent gradient: 5% MeCN/H_2O [0.05% TFA] (3 CV); 5-25% MeCN/H_2O [0.05% TFA] (20 CV); 25-50% MeCN/H_2O [0.05% TFA] (20 CV). Product fractions were concentrated to yield **19b** as a yellow solid (29.9 mg, 72% yield).

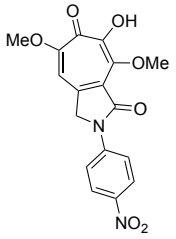
*Characterization data of **19b** are as follows.* **Mp**: 170-171 °C. IR (thin film, KBr) 3195 (br), 2925 (w), 2853 (w), 1696 (s), 1598 (m), 1559 (m), 1500 (w), 1459 (w), 1383 (m), 1338 (m), 1268 (s), 1224 (m), 1165 (w), 1121 (m), 1063 (w), 952 (w), 900 (w), 808 (w), 758 (w), 718 (w), 691 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.79 (m, *J* = 8.2 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.23 – 7.19 (m, *J* = 7.5 Hz, 1H), 7.01 – 6.99 (m, 1H), 4.81 (s, 2H), 4.12 (s, 3H), 4.09 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 167.9, 166.8, 158.4, 156.5, 150.4, 147.2, 133.2, 130.2, 120.2, 115.2, 114.3, 61.5, 56.5, 55.0, 53.0. **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calc'd for $C_{17}H_{15}NO_5Na^+$: 336.0842. Found: 336.0845.

Methyl 5,7-dihydroxy-2-(4-methoxyphenyl)-3,6-dioxo-1,2,3,6-tetrahydrocyclohepta[c]pyrrole-4-carboxylate (19c). To a solution of tropolone (**15**) (35.2 mg, 0.122 mmol) in CH_2Cl_2 (1.22 mL) was added amine (45.1 mg, 0.366 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-25% MeCN/H_2O [0.05% TFA] (16 CV); 25-40% MeCN/H2O [0.05% TFA] (10 CV). Product fractions were concentrated to yield **19c** as a yellow solid (40.4 mg, >98% yield). *Characterization data of **19c** are as follows.* **Mp**: 161-164 °C. **IR (thin film, KBr)** 3407 (br), 3174 (br), 3008 (w), 2956 (w), 2924 (w), 2853 (w), 1684 (m), 1513 (w), 1441 (w), 1400 (m), 1345 (w), 1275 (m), 1261 (m), 1206 (w), 1122 (w), 1057 (w), 885 (w), 724 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.79 (m, *J* = 8.2 Hz, 2H), 7.46 – 7.41 (m, *J* = 7.9 Hz, 2H), 7.23 – 7.19 (m, *J* = 7.5 Hz, 1H), 7.01 – 6.99 (m, 1H), 4.81 (s, 2H), 4.12 (s, 3H), 4.09 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ170.9, 165.2, 160.9, 157.1, 155.7, 150.4, 138.2, 131.6, 126.6, 121.7, 114.5, 109.4, 62.0, 57.1, 55.6, 53.0. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{18}H_{18}NO_6^+$: 344.1129. Found: 344.1131.

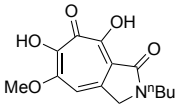
2-(4-(dimethylamino)phenyl)-7-hydroxy-5,8-dimethoxy-2,3dihydrocyclohepta[c]pyrrole1,6-dione (19d). To a solution of tropolone (**15**) (15.3 mg, 0.053 mmol) in CH_2Cl_2 (1.06 mL) was added amine (21.66 mg, 0.159 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 5% MeCN/H_2O [0.05% TFA] (3 CV); 5-20% MeCN/H_2O [0.05% TFA] (15 CV); 20-50% MeCN/H_2O [0.05%

TFA] (20 CV). Product fractions were concentrated to yield **19d** as a red solid (17.5 mg, 93% yield). *Characterization data of **19d** are as follows.* **Mp:** 190-193 °C. IR (thin film, KBr) 3442 (br), 3241 (br), 2970 (w), 2934 (w), 2850 (w), 2809 (w), 1616 (m), 1555 (m), 1520 (m), 1483 (w), 1444 (m), 1390 (w), 1338 (m), 1267 (s), 1223 (m), 1165 (m), 1065 (w), 946 (w), 902 (w), 812 (m), 768 (w), 731 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 8.9 Hz, 2H), 6.95 (s, 1H), 6.72 (d, *J* = 8.9 Hz, 2H), 4.68 (s, 2H), 4.09 (s, 3H), 4.05 (s, 3H), 2.92 (s, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 170.9, 164.9, 160.7, 155.7, 150.3, 147.9, 138.2, 128.6, 126.9, 121.4, 113.2, 109.5, 61.9, 57.0, 52.9, 40.9. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{19}H_{21}N_2O_5^+$: 357.1445. Found: 357.1444.

Methyl 5,7-dihydroxy-2-(4-nitrophenyl)-3,6-dioxo-1,2,3,6-tetrahydrocyclohepta[c]pyrrole-4-carboxylate (19e). To a solution of tropolone (**15**) (15.0 mg, 0.052 mmol) in CH_2Cl_2 (1.04 □L) was added amine (21.5 mg, 0.156 mmol). After stirring at 100 °C for 16 h, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-10% MeCN/H_2O [0.05% TFA] (10 CV); 10-50% MeCN/H_2O [0.05% TFA] (30 CV); 50- 65% MeCN/H_2O [0.05% TFA] (6 CV). Product fractions were concentrated to yield **19e** as a light yellow solid (16.3 mg, 87% yield). *Characterization data of **19e** are as follows.* **Mp:** 219-222 °C. IR (thin film, KBr) 3412 (br), 3226 (br), 2924 (w), 2852 (w), 1711 (m), 1592 (m), 1559 (w), 1503 (m), 1446 (w), 1375 (w), 1333 (s), 1274 (w), 1222 (w), 1167 (w), 1226 (w), 1058 (w), 805 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 9.4 Hz, 2H), 8.09 (d, *J* = 9.4 Hz, 2H), 7.02 (s, 1H), 4.90 (s, 2H), 4.16 (s, 3H), 4.14 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.3, 165.8, 161.6, 155.5, 150.0, 144.1, 143.9, 137.8, 125.7, 125.3, 118.4, 108.7, 62.0, 57.3, 52.2. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{17}H_{15}N_2O_7^+$: 359.0874. Found: 359.0877.



2-butyl-6,8-dihydroxy-5-methoxy-2,3-dihydrocyclohepta[c]pyrrole-1,7-dione (24a). To a solution of tropolone (**22**) (14.2 mg, 0.052 mmol) in CD_3CN (1.04 mL) was added amine (15.4 μL, 0.156 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-15% MeCN/H_2O [0.05% TFA] (16 CV); 15-



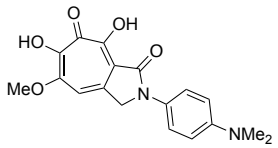
40% MeCN/H_2O [0.05% TFA] (20 CV); 40-100% MeCN/H2O [0.05% TFA] (12 CV). Product fractions were concentrated to yield **24a** as a yellow oil (6.4 mg, 44% yield). *Characterization data of **24a** are as follows.* **IR (thin film, KBr)** 3386 (br), 3104 (br), 2960 (w), 2873 (w), 1657 (s), 1516 (w), 1463 (w), 1400 (w), 1384 (w), 1295 (w), 1267 (w), 1172 (w), 1081 (m), 799 (w), 782 (w), 757 (w), 736 (w), 700 (w), 616 (w) cm^{-1}. **^{1}H NMR (400 MHz, CD_3CN)** δ 7.11 (s, 1H), 4.48 (s, 2H), 3.98 (s, 3H), 3.60 – 3.54 (m, 2H), 1.68 – 1.62 (m, 2H), 1.39 – 1.33 (m, 2H), 0.98 – 0.92 (m, 3H). **^{13}C {^{1}H} NMR (101 MHz, CD_3CN)** δ 207.5, 172.8, 169.0, 162.5, 151.4, 150.7, 140.9, 108.6, 57.7, 53.9, 42.6, 30.8, 30.7, 20.6, 13.9. **HRMS (ESI-TOF) m/z:** [M +Na]$^+$ Calc'd for $^+$: $C_{14}H_{17}NO_5Na^+$: 303.1038 Found: 303.1031

6,8-dihydroxy-5-methoxy-2-phenyl-2,3-dihydrocyclohepta[c]pyrrole-1,7-dione (24b). To a solution of tropolone (**22**) (15.7 mg, 0.057 mmol) in CH_2Cl_2 (1.1 mL) was added amine (15.6 μL, 0.171 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-10% MeCN/H_2O [0.05% TFA] (10 CV); 10-30% MeCN/H_2O [0.05% TFA] (20 CV); 30- 55% MeCN/H_2O [0.05% TFA] (8 CV). Product fractions were concentrated to yield **24b** as a yellow solid (13.3 mg, 79% yield). *Characterization data of **24b** are as follows.* **Mp:** decomposed at 201 °C. **IR (thin film, KBr)** 3400 (br), 3207 (br), 3064 (w), 2946 (w), 2849 (w), 1693 (s), 1599 (m), 1557 (m), 1500 (w), 1459 (w), 1446 (w), 1384 (m), 1341 (m), 1268 (m), 1226 (m), 1203 (m), 1168 (w), 1123 (m), 1064 (w), 951 (w), 902 (w), 810 (w), 759 (w), 735 (w), 719 (w), 692 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 – 7.73 (m, 2H), 7.51 – 7.45 (m, 2H), 7.31 – 7.27 (m, 1H), 6.90 (s, 1H), 4.94 (s, 2H), 4.09 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ170.9, 168.2, 162.4, 150.9, 150.8, 137.5, 137.4, 129.7, 126.3, 119.9, 118.2, 106.2, 57.3, 53.8. **HRMS (ESI-TOF) m/z:** [M + Na]$^+$ Calc'd for $C_{16}H_{13}NO_5Na^+$: 322.0686. Found: 322.0688.

6,8-dihydroxy-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrocyclohepta[c]pyrrole-1,7-dione (24c). To a solution of tropolone (**22**) (12.9 mg, 0.047 mmol) in CD_3Cl (0.94 μL) was added amine (17.4 mg, 0.141 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 5% MeCN/H_2O [0.05% TFA] (3 CV); 5-20% MeCN/H2O [0.05% TFA] (14 CV); 20-25% MeCN/H_2O [0.05%

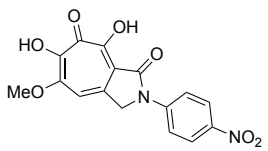
TFA] (5 CV); 25- 35% MeCN/H2O [0.05% TFA] (8 CV); 35- 45% MeCN/H_2O [0.05% TFA] (5 CV); 45- 100% MeCN/H_2O [0.05% TFA] (8 CV). Product fractions were concentrated to yield **24c** as a brown solid (11.7 mg, 76% yield). *Characterization data of **24c** are as follows*. **Mp:** 152-154 °C. **IR (thin film, KBr)** 3422 (br), 3175 (br), 3008 (w), 2977 (w), 2943(w), 2882 (w), 1671 (s), 1608 (m), 1566 (m), 1499 (w), 1409 (m), 1346 (w), 1295 (m), 1224 (m), 1156 (w), 1102 (w), 1060 (w), 975 (w), 866 (w), 761 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.89 (s, 1H), 4.89 (s, 2H), 4.08 (s, 3H), 3.85 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 170.6, 168.2, 162.3, 157.9, 150.9, 137.4, 130.3, 122.0, 118.3, 114.9, 106.3, 57.3, 55.7, 54.2. **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calc'd for $C_{17}H_{15}NO_6Na^+$: 352.0792. Found: 352.0793.

2-(4-(dimethylamino)phenyl)-6,8-dihydroxy-5-methoxy-2,3-dihydrocyclohepta[c]pyrrole-1,7-dione (24d). To a solution of tropolone (**22**) (15.3 mg, 0.056 mmol) in CH_2Cl_2 (1.1 mL) was added



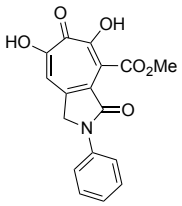
amine (22.9 mg, 0.168 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 5% MeCN/H_2O [0.05% TFA] (3 CV); 5-20% MeCN/H_2O [0.05% TFA] (10 CV); 20-30% MeCN/H_2O [0.05% TFA] (10 CV); 30-50% MeCN/H_2O [0.05% TFA] (20 CV). Product fractions were concentrated to yield **24d** as a dark red solid (13.3 mg, 71% yield). *Characterization data of **24d** are as follows.* **Mp:** 196-199 °C. **IR (thin film, KBr)** 3387 (br), 3180 (br), 2956 (w), 2924 (w), 2853(w), 1680 (s), 1520 (m), 1444 (w), 1400 (m), 1331 (w), 1275 (w), 1260 (w), 1204 (m), 1134 (m), 1069 (w), 801 (w), 750 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.58 (d, *J* = 9.1 Hz, 2H), 6.89 (s, 1H), 6.87 (d, *J* = 9.1 Hz, 2H), 4.86 (s, 2H), 4.08 (s, 3H), 3.01 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 170.3, 168.0, 162.0, 151.1, 151.0, 149.0, 137.4, 126.5, 122.0, 118.6, 112.9, 106.4, 57.2, 54.4, 40.7. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{18}H_{19}N_2O_5^+$: 343.1288. Found: 343.1293.

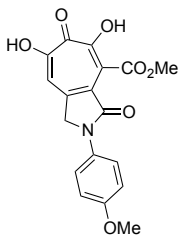
6,8-dihydroxy-5-methoxy-2-(4-nitrophenyl)-2,3-dihydrocyclohepta[c]pyrrole-1,7-dione (24e).



To a solution of tropolone (**22**) (16.5 mg, 0.060 mmol) in CD_3Cl (1.2 mL) was added amine (24.9 mg, 0.180 mmol). After stirring at 100 °C for 8 h, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-10% MeCN/H2O [0.05% TFA] (10 CV); 10-30% MeCN/H2O [0.05% TFA] (17 CV); 30- 65%

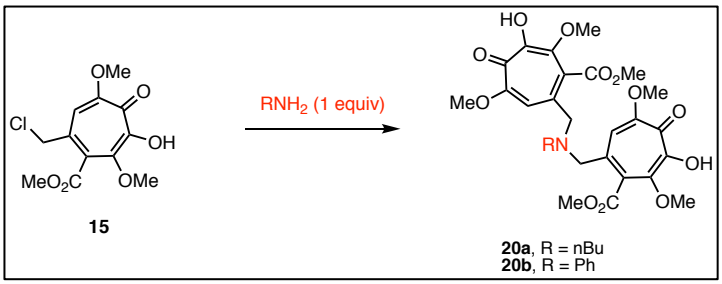
MeCN/H_2O [0.05% TFA] (15 CV). Product fractions were concentrated to yield **24e** as a yellow solid (14.9 mg, 73% yield). *Characterization data of **24e** are as follows.* **Mp:** decomposed at 218 °C. IR (thin film, KBr) 3383 (br), 3176 (br), 2956 (w), 2924 (w), 2853(w), 1736 (s), 1700 (m), 1685 (m), 1597 (m), 1504 (w), 1461 (w), 1442 (w), 1400 (m), 1328 (w), 1270 (w), 1242 (w), 1204 (w), 1112 (w), 1054 (w), 747 (w) cm^{-1}. **^{1}H NMR (400 MHz, Acetone-d6)** δ 8.34 (d, *J* = 9.4 Hz, 2H), 8.07 (d, *J* = 9.4 Hz, 2H), 7.17 (s, 1H), 5.03 (s, 2H), 4.05 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.5, 168.2, 163.0, 150.8, 150.4, 144.6, 142.9, 137.4, 125.5, 118.9, 117.7, 105.8, 57.4, 53.3. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{16}H_{13}N_2O_7^+$: 345.0717. Found: 345.0717.

Methyl 5,7-dihydroxy-3,6-dioxo-2-phenyl-1,2,3,6-tetrahydrocyclohepta[c]pyrrole-4-carboxylate (25a). 
To a solution of tropolone (**23**) (15.4 mg, 0.051 mmol) in CD_3Cl (1.02 mL) was added amine (14.0 μL, 0.153 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-10% MeCN/H_2O [0.05% TFA] (10 CV); 10-30% MeCN/H_2O [0.05% TFA] (14 CV); 30-45% MeCN/H_2O [0.05% TFA] (8 CV); 45-80% MeCN/H_2O [0.05% TFA] (8 CV). Product fractions were concentrated to yield **25a** as a yellow solid (9.6 mg, 58% yield). *Characterization data of **25a** are as follows.* **Mp:** decomposed at 225 °C. **IR (thin film, KBr)** 3250 (br), 2954 (w), 2926 (w), 2855 (w), 1729 (s), 1698 (s), 1598 (w), 1500 (m), 1445 (w), 1386 (s), 1292 (w), 1270 (m), 1140 (m), 1062 (w), 996 (w), 899 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 – 7.75 (m, 2H), 7.55 (s, 1H), 7.46 – 7.40 (m, 2H), 7.24 – 7.19 (m, 1H), 4.92 (d, *J* = 17.7 Hz, 1H), 4.83 (d, *J* = 17.7 Hz, 1H), 4.09 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, CD_3CN)** δ 170.7, 165.0, 164.9, 159.6, 154.0, 142.2, 138.0, 128.3, 125.6, 124.0, 121.0, 118.6, 113.6, 51.8, 51.4. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{17}H_{14}NO_6^+$: 328.0816. Found: 328.0819.

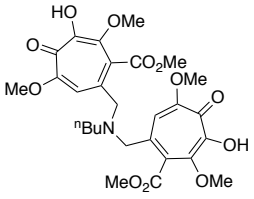
Methyl 5,7-dihydroxy-2-(4-methoxyphenyl)-3,6-dioxo-1,2,3,6-tetrahydrocyclohepta[c]pyrrole-4-carboxylate (25b). 
To a solution of tropolone (**23**) (28.7 mg, 0.095 mmol) in CH_2Cl_2 (1.9 mL) was added amine (35.1 mg, 0.285 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-10% MeCN/H_2O [0.05% TFA] (10 CV); 10-30% MeCN/H_2O [0.05% TFA] (20 CV); 30-50% MeCN/H2O [0.05% TFA] (15 CV). Product fractions were

concentrated to yield **25b** as a yellow solid (18.8 mg, 55% yield). *Characterization data of **25b** are as follows.* **Mp:** decomposed at 212 °C. **IR (thin film, KBr)** 3282 (br), 3023 (w), 2959 (w), 2923 (w), 2850 (w), 1736 (s), 1690 (m), 1613 (w), 1551 (m), 1514 (s), 1455 (w), 1392 (m), 1366 (w), 1299 (w), 1253 (m), 1208 (w), 1139 (w), 1058 (w), 1031 (w), 996 (w), 829 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 9.1 Hz, 2H), 7.53 (s, 1H), 6.95 (d, *J* = 9.1 Hz, 2H), 4.88 (d, *J* = 17.3 Hz, 1H), 4.78 (d, *J* = 17.3 Hz, 1H), 4.08 (s, 3H), 3.82 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 171.1, 165.8, 165.3, 160.0, 157.4, 155.3, 141.6, 131.2, 127.9, 123.0, 121.8, 114.7, 114.6, 55.7, 53.4, 53.1. **HRMS (ESI-TOF) m/z:** $[M + Na]^+$ Calc'd for $C_{18}H_{15}NO_7Na^+$: 380.0741. Found: 380.0742.

Synthesis of 2:1 Tropolone to Amine Adducts

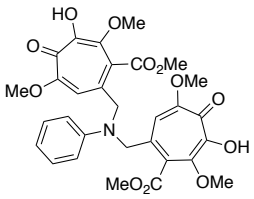


Dimethyl 2,2'-((butylazanediyl)bis(methylene))bis(6-hydroxy-4,7-dimethoxy-5-oxocyclohepta-1,3,6-triene-1-carboxylate) (20a). To a solution of tropolone (**23**) (15.0 mg, 0.050 mmol) in CD_3Cl (1.0 mL) was added amine (4.9 µL, 0.050 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 0% MeCN/H_2O [0.05% TFA] (3 CV); 0-20% MeCN/H_2O [0.05% TFA] (10 CV); 20-30% MeCN/H_2O [0.05% TFA] (10 CV); 30- 55% MeCN/H_2O [0.05% TFA] (10 CV); 55-70% MeCN/H_2O [0.05% TFA] (10 CV). Product fractions were concentrated to yield **20a** as a light yellow oil (10.5 mg, 36% yield). *Characterization data of **20a** are as follows.* **IR (thin film, KBr)** 3448 (br), 3207 (br), 2997 (w), 2954 (w), 2874 (w), 1733 (s), 1685 (w), 1561 (m), 1460 (w), 1436 (w), 1336 (m), 1217 (w), 1138 (m), 1276 (w), 975 (w), 946 (w), 921 (w), 875 (w), 800 (w), 669 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (M, 2H), 4.00 (d, *J* = 5.8 Hz, 9H), 3.94 (s, 5H), 3.86 (s, 2H), 2.89 – 2.69 (m, 2H), 1.60 – 1.43 (m, 2H), 1.31 – 1.20 (m, 2H), 0.92 – 0.76 (m, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ169.8, 167.1, 159.2, 155.4, 148.8, 135.7, 116.9, 61.5, 58.8, 57.1, 54.4,



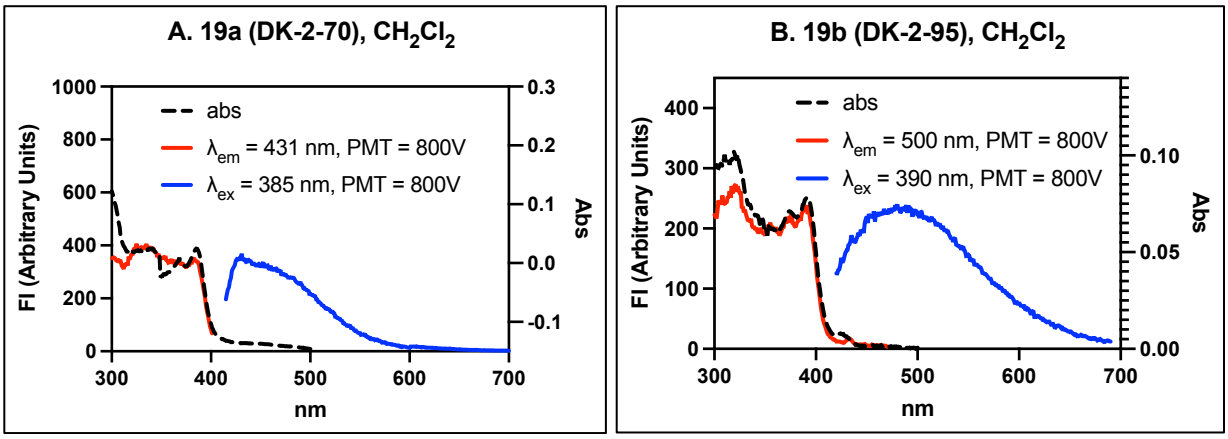
53.2, 20.4, 13.7. **HRMS (ESI-TOF) m/z:** $[M + H]^+$ Calc'd for $C_{28}H_{36}NO_{12}^+$: 578.2232. Found: 578.2234.

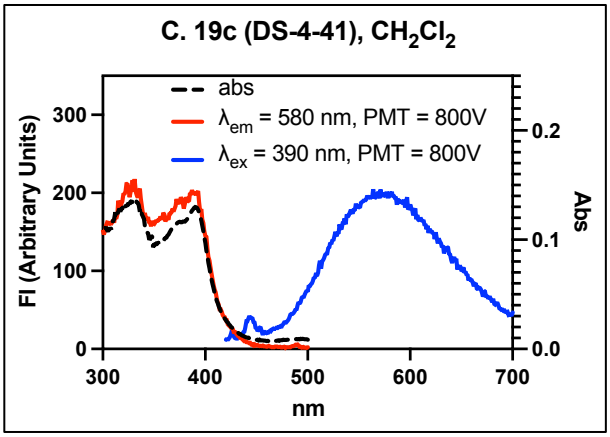
Dimethyl 2,2'-((phenylazanediyl)bis(methylene))bis(6-hydroxy-4,7-dimethoxy-5-oxocyclohepta-1,3,6-triene-1-carboxylate) (20b). To a solution of tropolone (**23**) (20.0 mg, 0.066 mmol) in CH_2Cl_2 (1.3 mL) was added amine (6.0 μL, 0.066 mmol). After stirring at rt for 10 min, the reaction mixture was purified by reverse phase chromatography (Biotage Isolera Prime, 12 g C18 column, solvent gradient: 5% MeCN/H_2O [0.05% TFA] (3 CV); 5-10% MeCN/H_2O [0.05% TFA] (10 CV); 10-20% MeCN/H_2O [0.05% TFA] (10 CV); 20- 35% MeCN/H_2O [0.05% TFA]. Product fractions were concentrated to yield **20b** as a light yellow oil (9.3 mg, 24% yield). *Characterization data of **20b** are as follows.* **IR (thin film, KBr)** 3440 (br), 3201 (br), 3063 (w), 2976 (w), 2942 (w), 2843 (w), 1699 (m), 1597 (w), 1561 (m), 1495 (w), 1473 (w), 1458 (w), 1443 (w), 1384 (m), 1333 (m), 1285 (w) 1269 (m), 1222 (m), 1165 (w), 1122 (m), 1063 (w), 948 (w), 900 (w), 808 (w), 765 (w), 730 (w), 718 (w), 691 (w) cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.23 (m, *J* = 7.5 Hz, 2H), 6.99 (s, 3H), 6.88 – 6.84 (m, *J* = 7.4 Hz, 2H), 6.79 – 6.75 (m, *J* = 8.0 Hz, 3H), 4.49 (s, 6H), 3.98 (s, 9H), 3.86 (s, 9H), 3.62 (s, 9H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ 167.9, 166.8, 158.4, 156.5, 150.4, 147.2, 133.2, 130.2, 120.2, 115.2, 114.3, 61.5, 56.5, 54.9, 52.9. **20b** converted to lactam **19b** during storage and shipping on two separate occasions, preventing the acquisition of HRMS data.

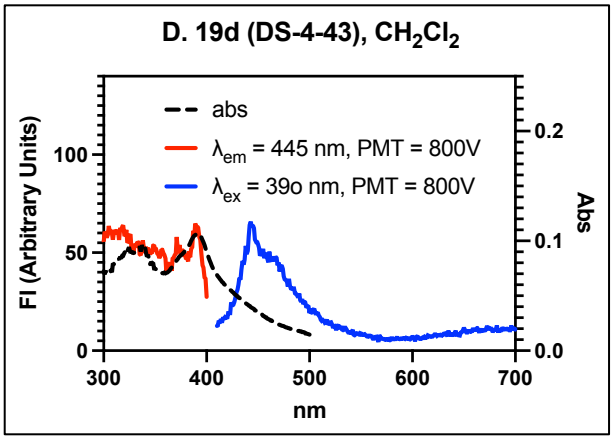


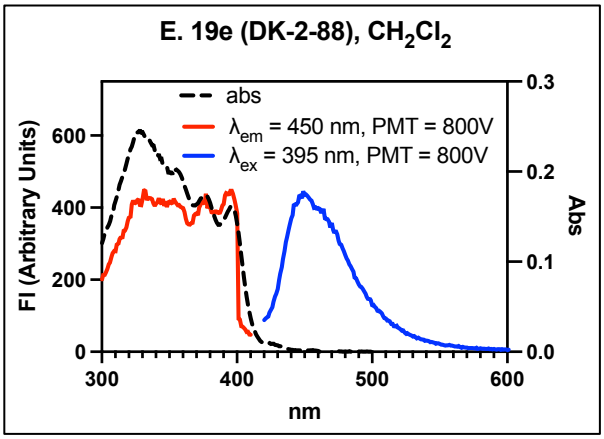
III. Absorbance and Fluorescence Data

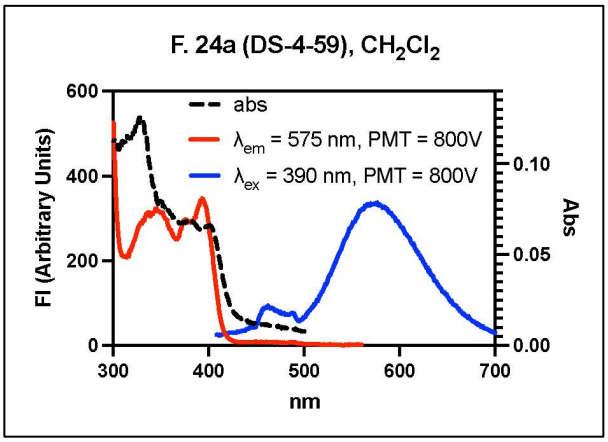
IIIa. Absorbance, Excitation and Emission Spectra Determination. 10 μM solution of samples were prepared by dissolving molecules in DMSO to a achieve a final concentration of 10 mM, and further diluting in solvent or buffer by adding 3 μL of DMSO solutions to 3 mL of solvent or buffer. Stock DMSO solutions were stored in freezer when not in use. UV-Vis spectra were obtained on a Cary 100 Bio UV-Visible Spectrophotometer with solutions in a Quartz Spectrophotometer Cell (standard rectangular cell, 10 mm, Vernier Software). Fluorescence Excitation and Emission spectra were obtained on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies), with solutions in a Quartz Fluorometer Cell (Rectangular, 10 mm, Starna Cells, Inc). All samples were collected using a 5 nm excitation and emission slit. The local absorbance maximum with the longest wavelength were used for the excitation unless otherwise described, and are listed on the following spectra. Similarly, PMT detector voltage was varied on a sample-by-sample basis based on fluorescence intensity, and are listed on the spectra below. Upon completing above sequence of experiments, samples were transferred to a 1 dram vial, and photographs used in publication (**Figure 1A**) were taken upon irradiation in a dark room (unless otherwise noted) with a UVGL-58 Handheld UV Lamp (6 Watt, 365 nm).

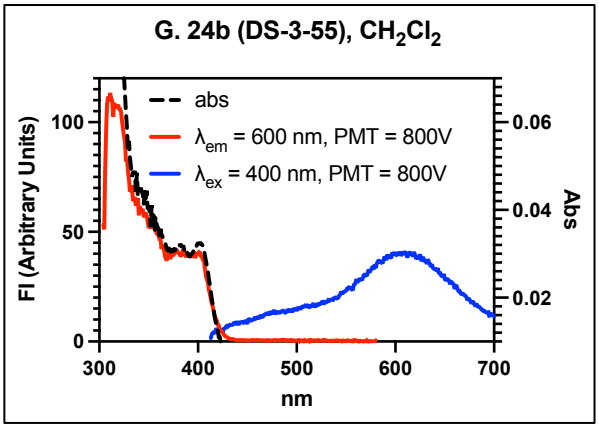


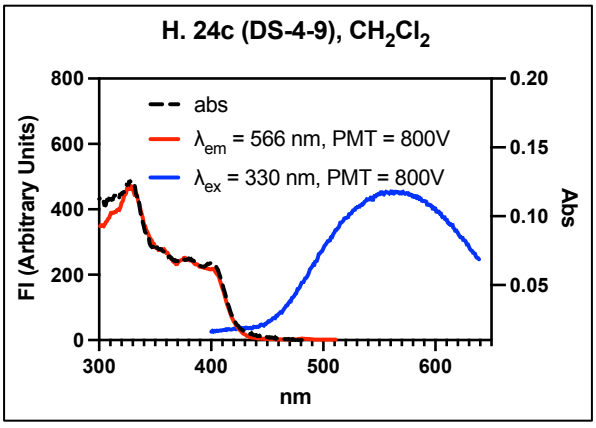

C. 19c (DS-4-41), CH_2Cl_2
abs
λ_{em} = 580 nm, PMT = 800V
λ_{ex} = 390 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

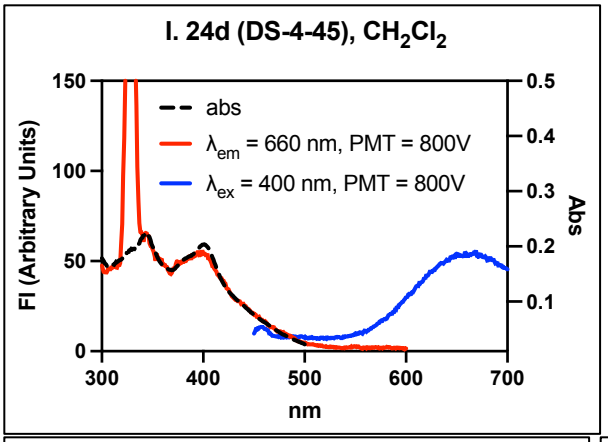

D. 19d (DS-4-43), CH_2Cl_2
abs
λ_{em} = 445 nm, PMT = 800V
λ_{ex} = 39o nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

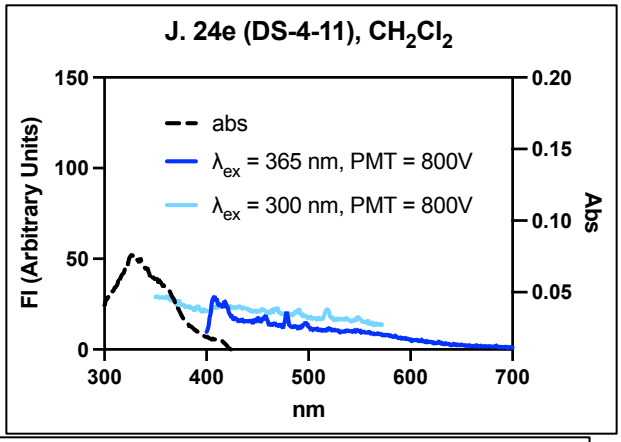

E. 19e (DK-2-88), CH_2Cl_2
abs
λ_{em} = 450 nm, PMT = 800V
λ_{ex} = 395 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

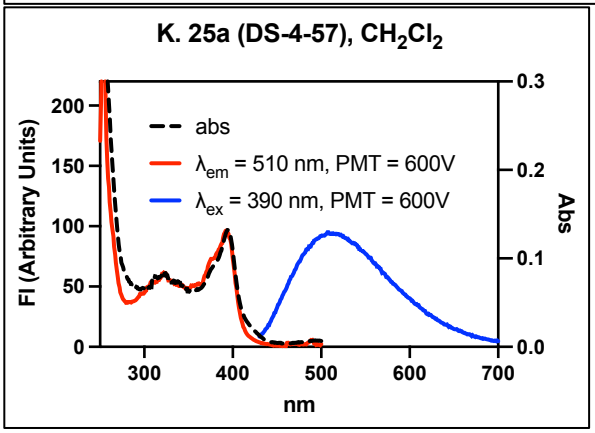

F. 24a (DS-4-59), CH_2Cl_2
abs
λ_{em} = 575 nm, PMT = 800V
λ_{ex} = 390 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

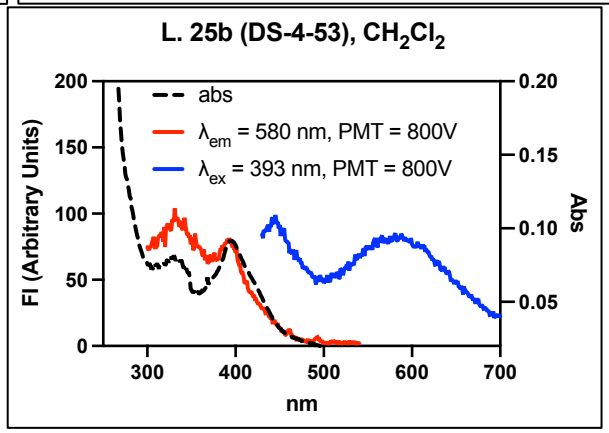

G. 24b (DS-3-55), CH_2Cl_2
abs
λ_{em} = 600 nm, PMT = 800V
λ_{ex} = 400 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

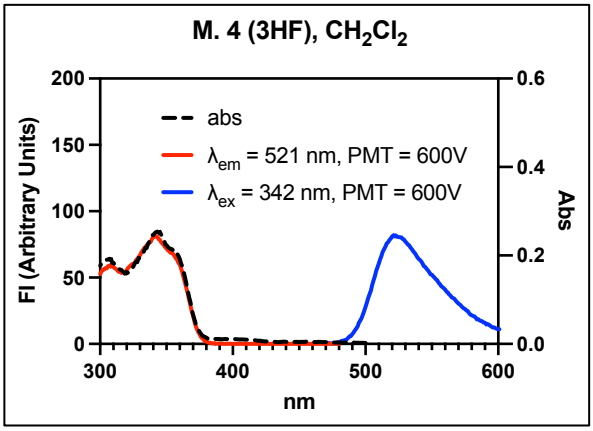

H. 24c (DS-4-9), CH_2Cl_2
abs
λ_{em} = 566 nm, PMT = 800V
λ_{ex} = 330 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

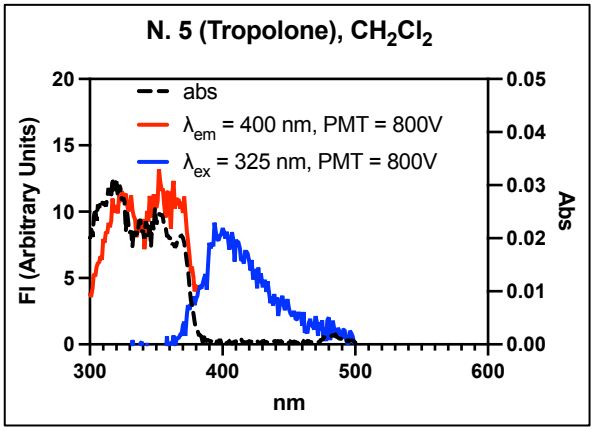

I. 24d (DS-4-45), CH2Cl2
abs
λem = 660 nm, PMT = 800V
λex = 400 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

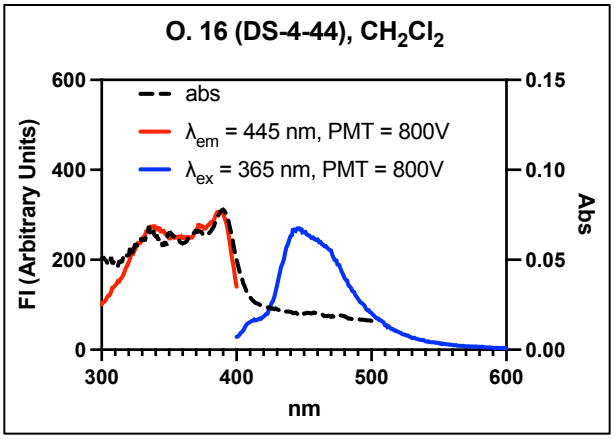

J. 24e (DS-4-11), CH2Cl2
abs
λex = 365 nm, PMT = 800V
λex = 300 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

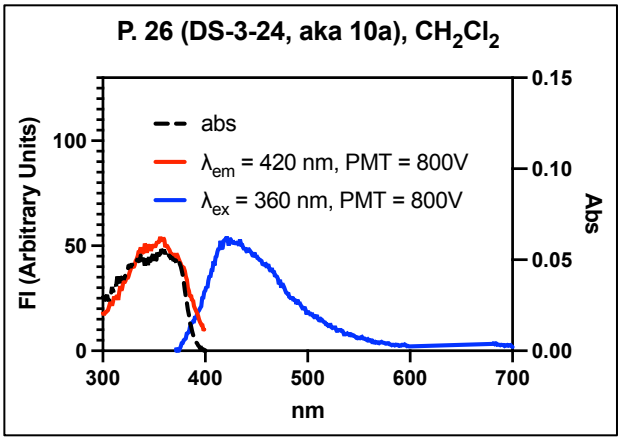

K. 25a (DS-4-57), CH2Cl2
abs
λem = 510 nm, PMT = 600V
λex = 390 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

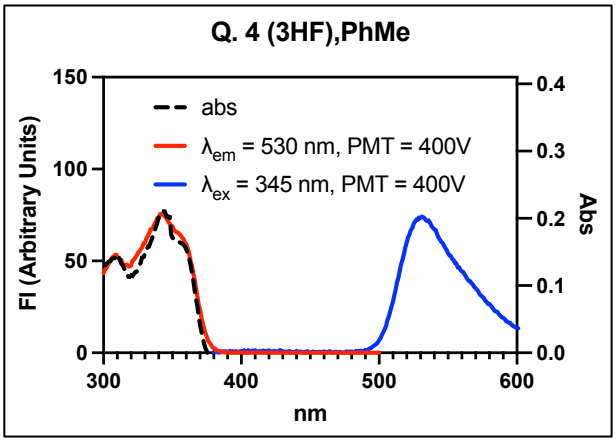

L. 25b (DS-4-53), CH2Cl2
abs
λem = 580 nm, PMT = 800V
λex = 393 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

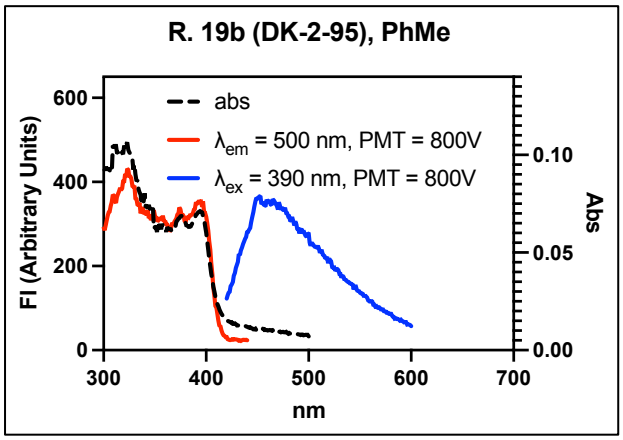

M. 4 (3HF), CH2Cl2
abs
λem = 521 nm, PMT = 600V
λex = 342 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

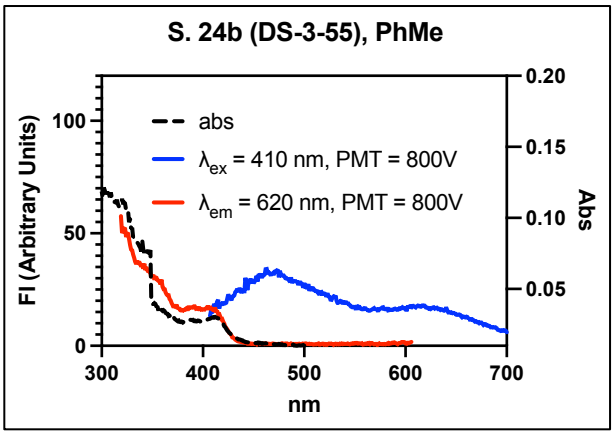

N. 5 (Tropolone), CH2Cl2
abs
λem = 400 nm, PMT = 800V
λex = 325 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

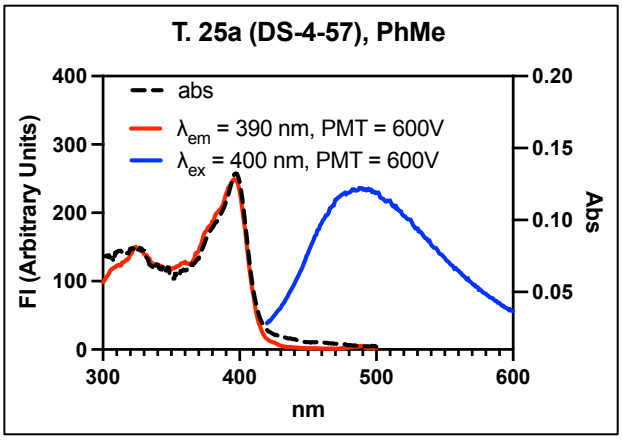

O. 16 (DS-4-44), CH2Cl2
abs
λem = 445 nm, PMT = 800V
λex = 365 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

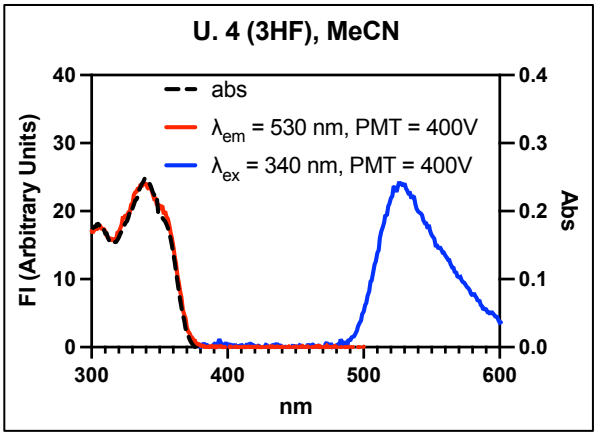

P. 26 (DS-3-24, aka 10a), CH2Cl2
abs
λem = 420 nm, PMT = 800V
λex = 360 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

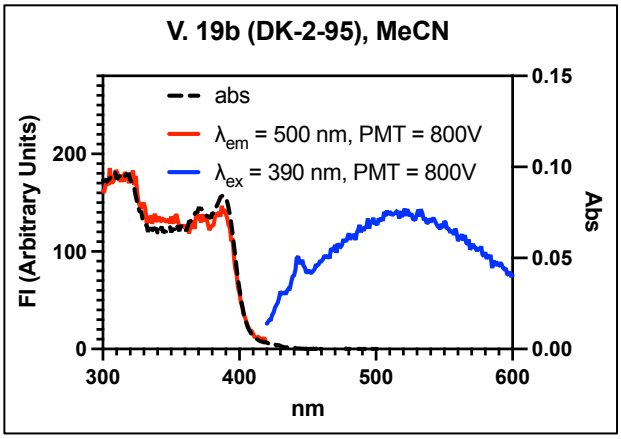

Q. 4 (3HF),PhMe
abs
λem = 530 nm, PMT = 400V
λex = 345 nm, PMT = 400V
Fl (Arbitrary Units)
Abs
nm

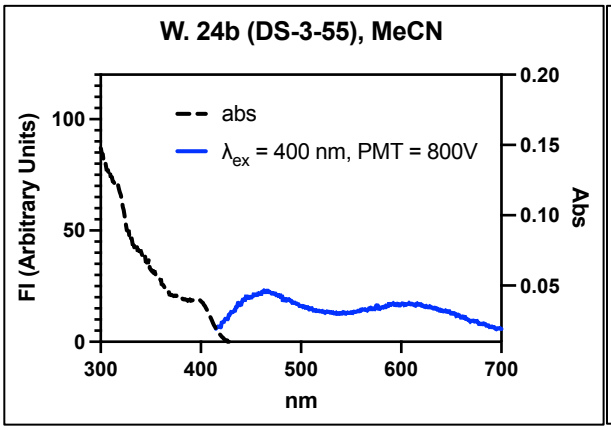

R. 19b (DK-2-95), PhMe
abs
λem = 500 nm, PMT = 800V
λex = 390 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

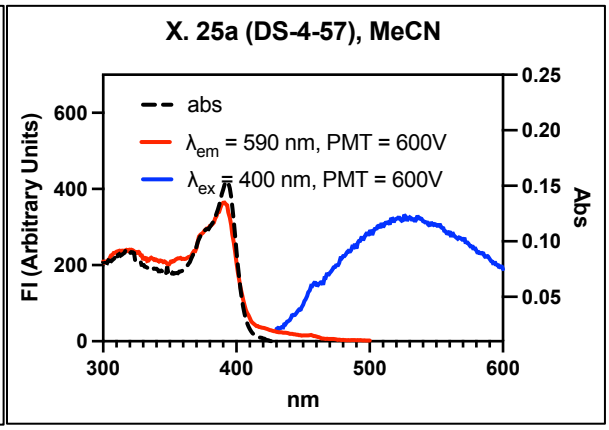

S. 24b (DS-3-55), PhMe
abs
λex = 410 nm, PMT = 800V
λem = 620 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

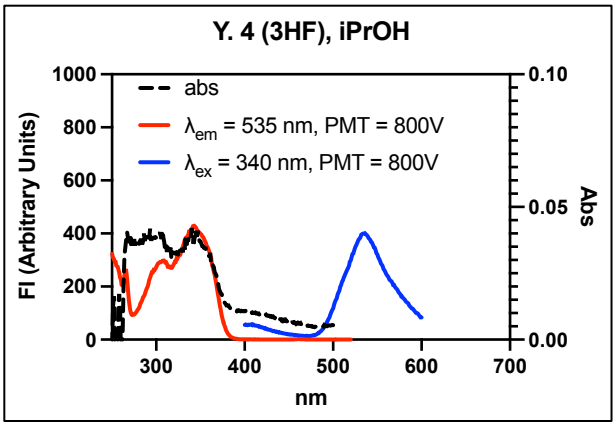

T. 25a (DS-4-57), PhMe
abs
λem = 390 nm, PMT = 600V
λex = 400 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

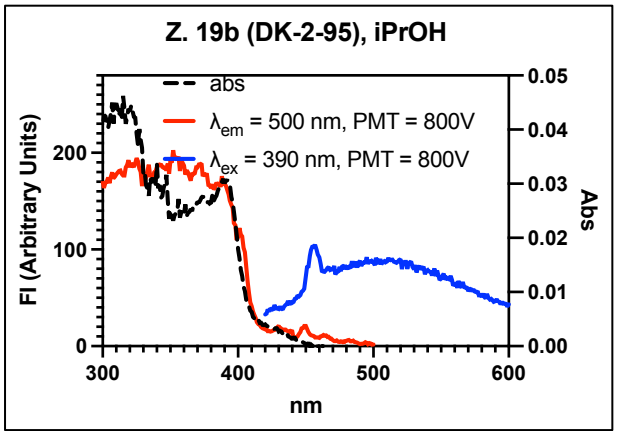

U. 4 (3HF), MeCN
abs
λem = 530 nm, PMT = 400V
λex = 340 nm, PMT = 400V
Fl (Arbitrary Units)
Abs
nm

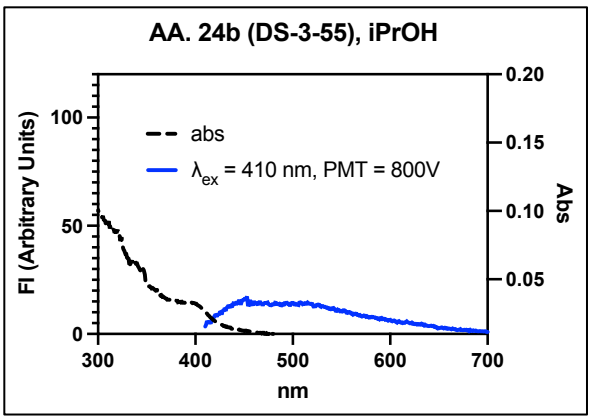

V. 19b (DK-2-95), MeCN
abs
λem = 500 nm, PMT = 800V
λex = 390 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

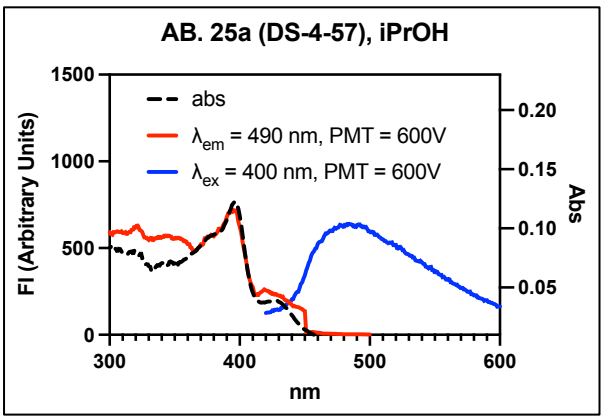

W. 24b (DS-3-55), MeCN
abs
λex = 400 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

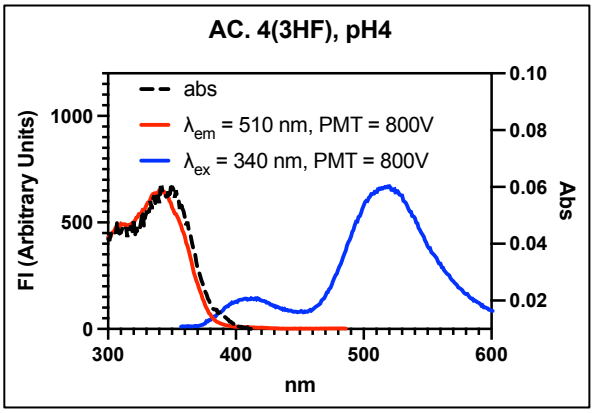

X. 25a (DS-4-57), MeCN
abs
λem = 590 nm, PMT = 600V
λex = 400 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

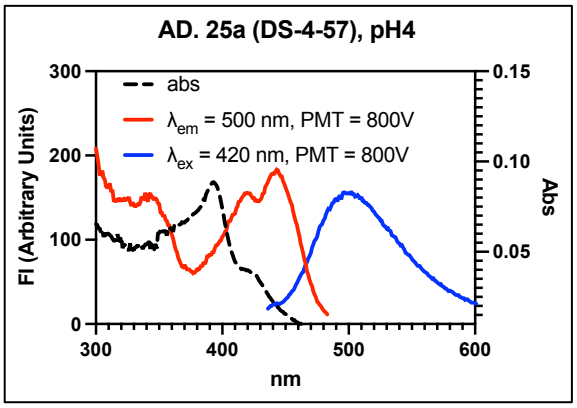

Y. 4 (3HF), iPrOH
abs
λem = 535 nm, PMT = 800V
λex = 340 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

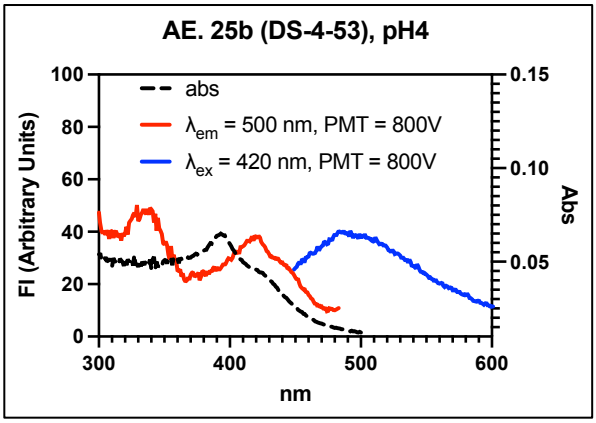

Z. 19b (DK-2-95), iPrOH
abs
λem = 500 nm, PMT = 800V
λex = 390 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

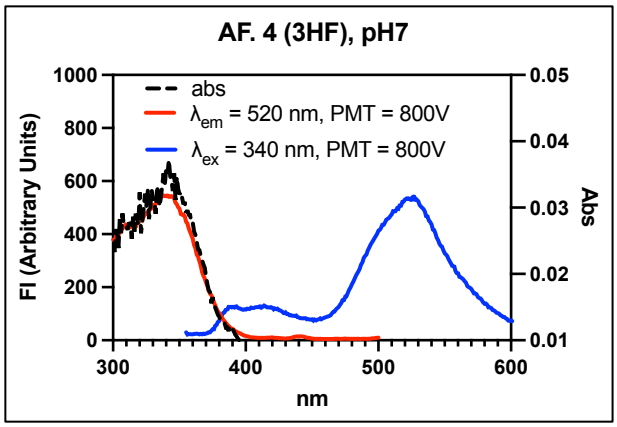

AA. 24b (DS-3-55), iPrOH
abs
λex = 410 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

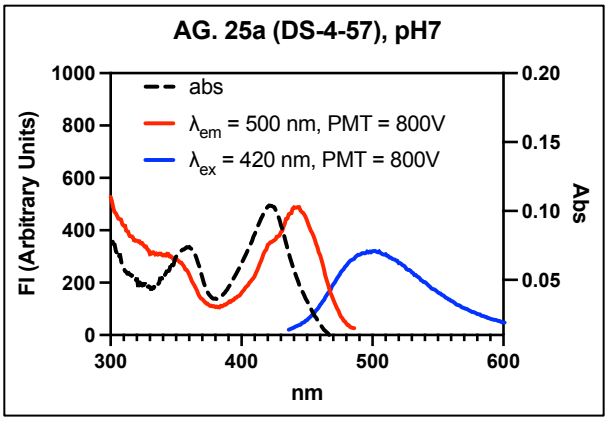

AB. 25a (DS-4-57), iPrOH
abs
λem = 490 nm, PMT = 600V
λex = 400 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

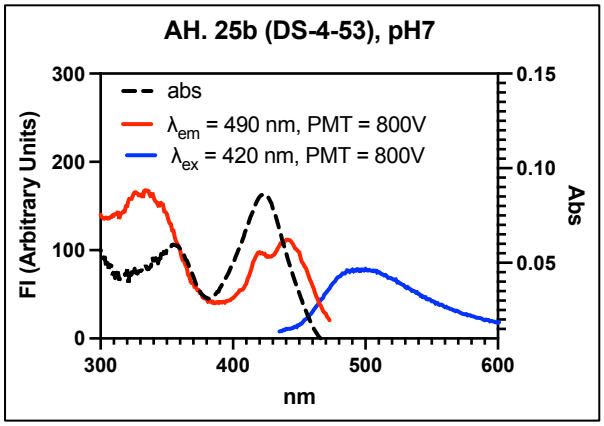

AC. 4(3HF), pH4
abs
λem = 510 nm, PMT = 800V
λex = 340 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

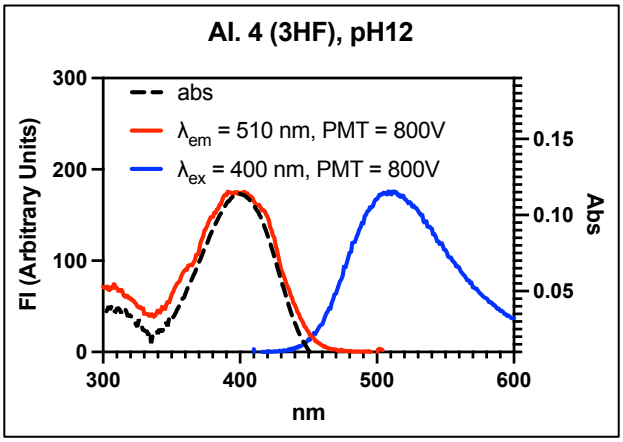

AD. 25a (DS-4-57), pH4
abs
λem = 500 nm, PMT = 800V
λex = 420 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

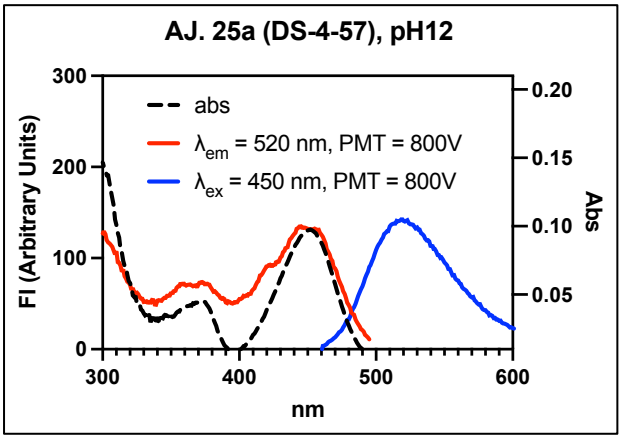

AE. 25b (DS-4-53), pH4
abs
λem = 500 nm, PMT = 800V
λex = 420 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

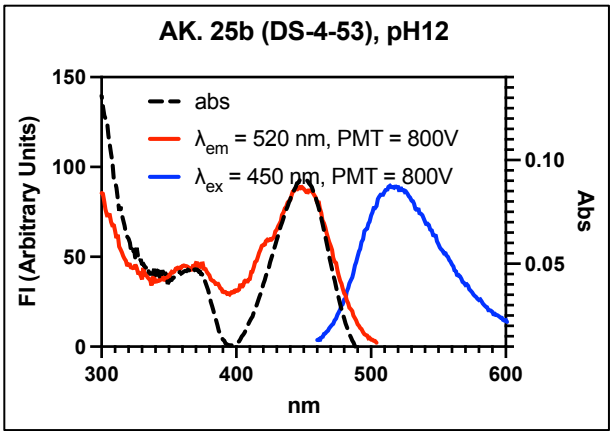

AF. 4 (3HF), pH7
abs
λem = 520 nm, PMT = 800V
λex = 340 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

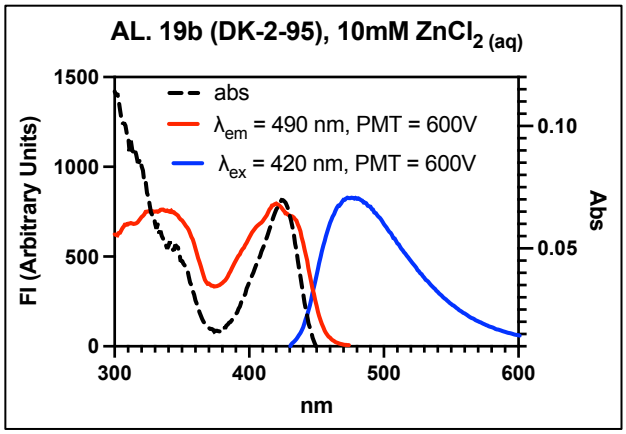

AG. 25a (DS-4-57), pH7
abs
λem = 500 nm, PMT = 800V
λex = 420 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

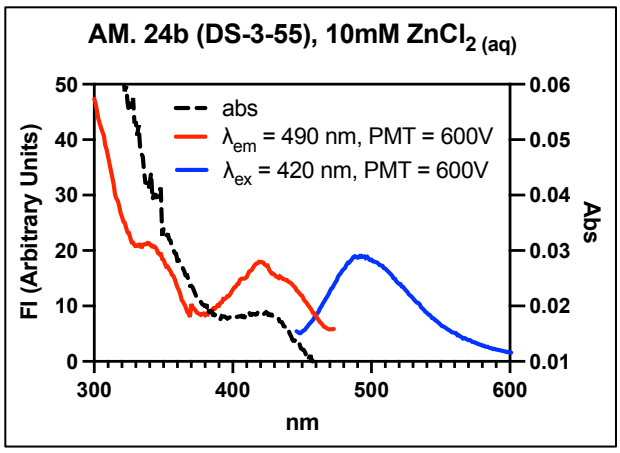

AH. 25b (DS-4-53), pH7
abs
λem = 490 nm, PMT = 800V
λex = 420 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

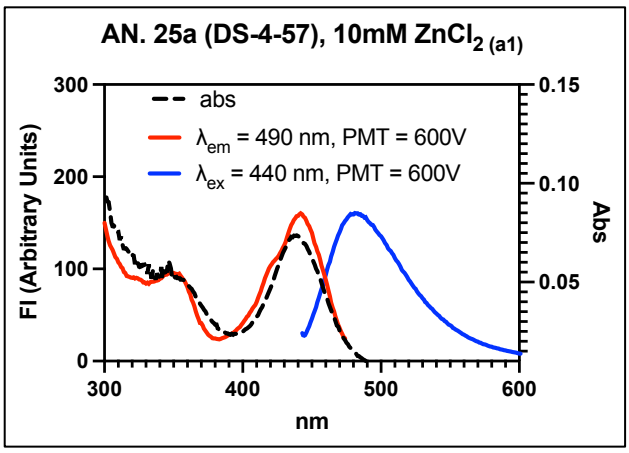

AI. 4 (3HF), pH12
abs
λem = 510 nm, PMT = 800V
λex = 400 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

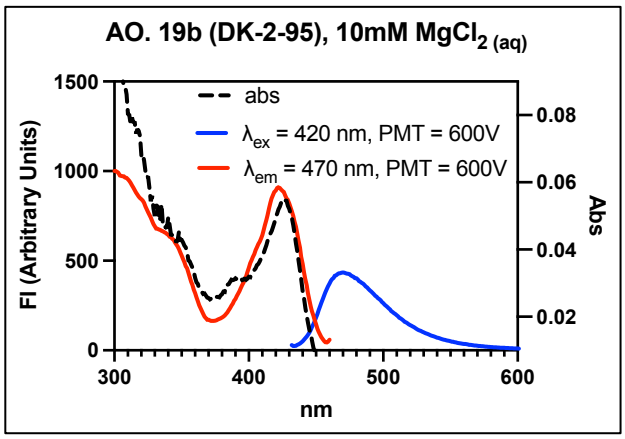

AJ. 25a (DS-4-57), pH12
abs
λem = 520 nm, PMT = 800V
λex = 450 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

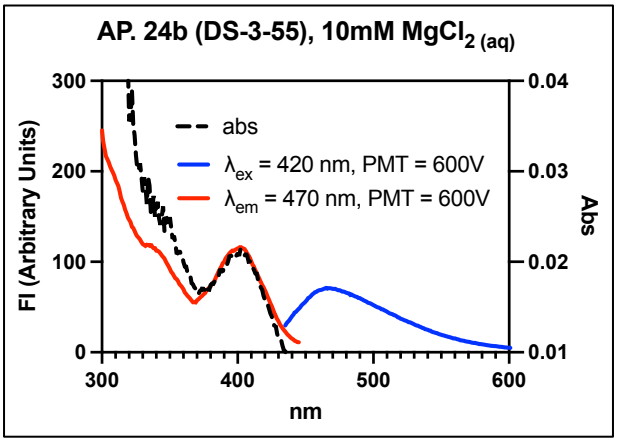

AK. 25b (DS-4-53), pH12
abs
λem = 520 nm, PMT = 800V
λex = 450 nm, PMT = 800V
Fl (Arbitrary Units)
Abs
nm

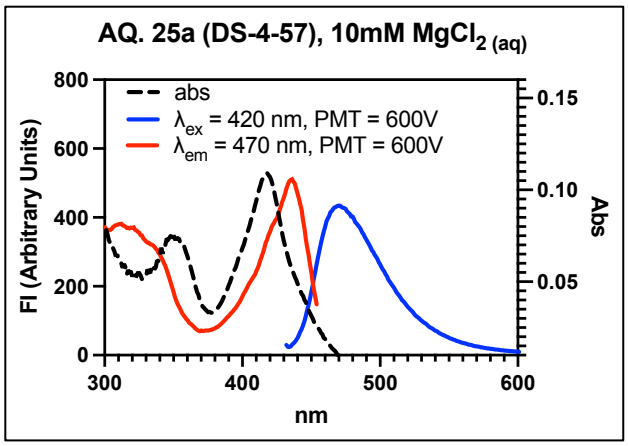

AL. 19b (DK-2-95), 10mM ZnCl2 (aq)
abs
λem = 490 nm, PMT = 600V
λex = 420 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm


AM. 24b (DS-3-55), 10mM ZnCl2 (aq)
abs
λem = 490 nm, PMT = 600V
λex = 420 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

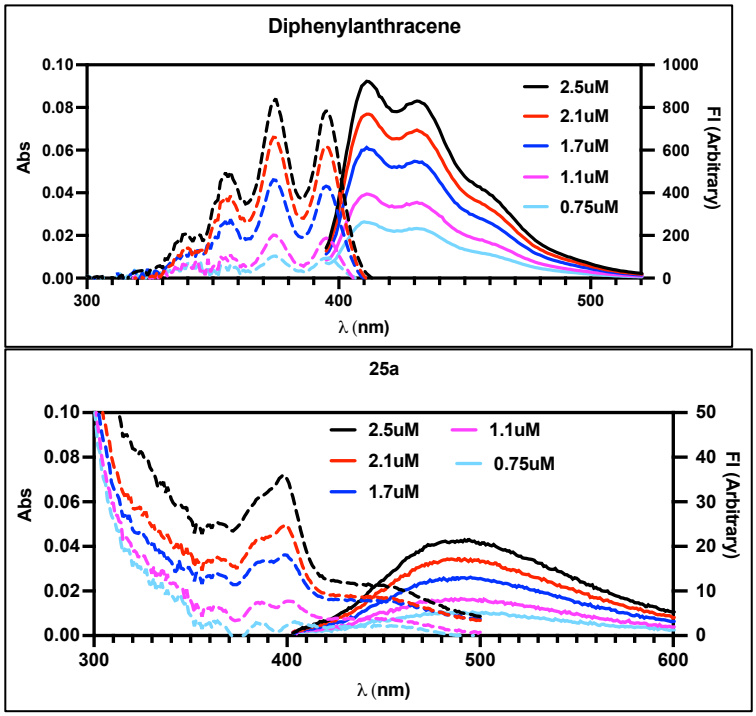

AN. 25a (DS-4-57), 10mM ZnCl2 (a1)
abs
λem = 490 nm, PMT = 600V
λex = 440 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm


AO. 19b (DK-2-95), 10mM MgCl2 (aq)
abs
λex = 420 nm, PMT = 600V
λem = 470 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm


AP. 24b (DS-3-55), 10mM MgCl2 (aq)
abs
λex = 420 nm, PMT = 600V
λem = 470 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

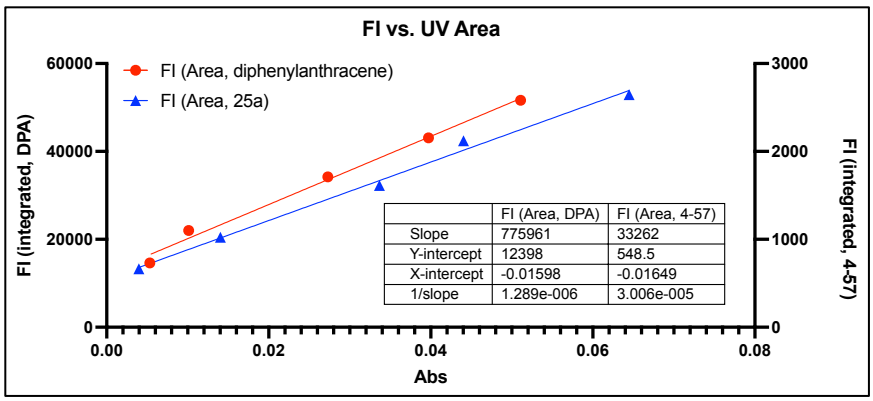

AQ. 25a (DS-4-57), 10mM MgCl2 (aq)
abs
λex = 420 nm, PMT = 600V
λem = 470 nm, PMT = 600V
Fl (Arbitrary Units)
Abs
nm

IIIb. Quantum Yield Determination. Absorbance and Emission Spectra (λ_{ex} = 390 nm, PMV = 500 V) were obtained for 3 mL solutions of **25a** (DS-4-47) in toluene and 2,4-diphenylanthracene in benzene. For **25a**, the beginning concentration was 6.6 μM, and for diphenylanthracene, the beginning concentration was 2.5 μM. Each solution was diluted by to 2.5/3, then subsequently by 2.3/3, 2/3, and 2/3, to obtain concentrations of 5.5 μM, 4.2 μM, 2.8 μM, and 1.9 μM for **25a** and 2.1 μM, 1.6 μM, 1.06 μM, 0.7 μM of diphenylantracene. Following background subtraction (PhMe or Benzene), the absorbance and emission graphs for each solution follow:



The absorbance of **25a** at 400 nm was plotted against concentration in molar, and the slope provided the molar extinction coefficient (ε = 33,500 $cm^{-1}M^{-1}$).

Integration under the fluorescence curve was plotted against the absorbance value at 390 nm to give the following graphs:



Using the following formula:

$$\Phi_{F,\,25a} = \Phi_{F,\,DPA} * (m_{25a}/\, m_{DPA}) * (n_{D,PhH}\, /n_{D,PhMe})$$

Where Φ_F is the quantum yield, m is the slope, and n_D is the solvent refractive index: (benzene = 1.5011; toluene = 1.4969). Using the literature quantum yield of diphenylanthracene in benzene (0.82), and the slopes determined above, a quantum yield for **25a** of 0.035 was determined.

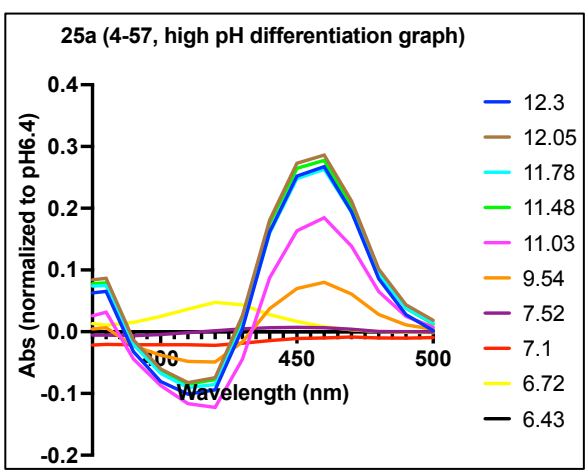
IIIc. UV-Vis-Based pKa Determination.

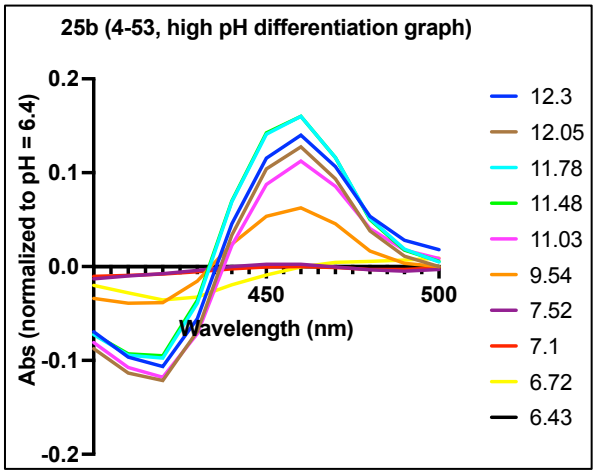
Stock Solutions of potassium phosphate buffers. 100 mM aqueous phosphate buffers were generated using potassium phosphate monobasic and tribasic salts dissolved in deionized water. The monobasic potassium phosphate solution also contained 200 mM of potassium chloride to maintain constant concentration of potassium ions in solution. The pH of these solutions were 4.4 and 12.3, as determined using an EcoSense pH10a meter . Mixtures of these solutions were created by combining 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, and 1:9 of the monobasic and tribasic solutions, which provided pHs of 6.0, 6.4, 6.7, 7.1, 7.5, 9.5, 11.0, 11.5, 11.8, and 12.0. Additional points between 4.4 and 6.0 were generated through fine-tuning the lower pH solutions to generate 4.7, 5.3, and 5.6, and for lower pH solutions, monobasic solution was acidified with aqueous HCl to generate aqueous solutions of pH of 1.4, 2.14, 2.72 and 3.13.

Determination of pKa by UV-Vis. Data was collected on a Syngery H1 microplate reader. 10 µM of 2.5 mM solutions of **25a (DS-4-57)** and **45b (DS-4-53)** in dmso were added to 190 µM of the buffered solutions in a clear 96-well flat bottom plate (Costar, polystyrene) well a final concentration of 125 µM. For background absorbance, 10 µM dmso was added to same set of

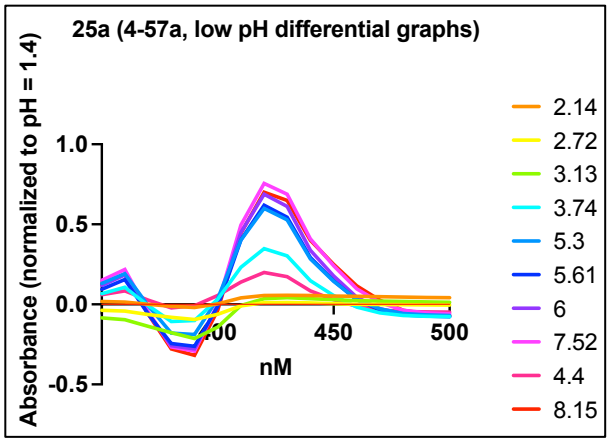
phosphate buffers. UV-Vis absorbance from 300 nm to 500 nm was collected. Data was processed by subtracting the background absorbance from that containing tropolones.

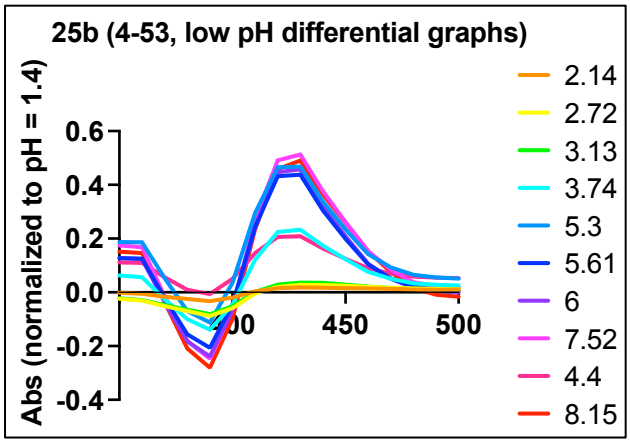
For high pKa, differential spectra were created by subtracting data at pH 6.4 to generate the following graphs:



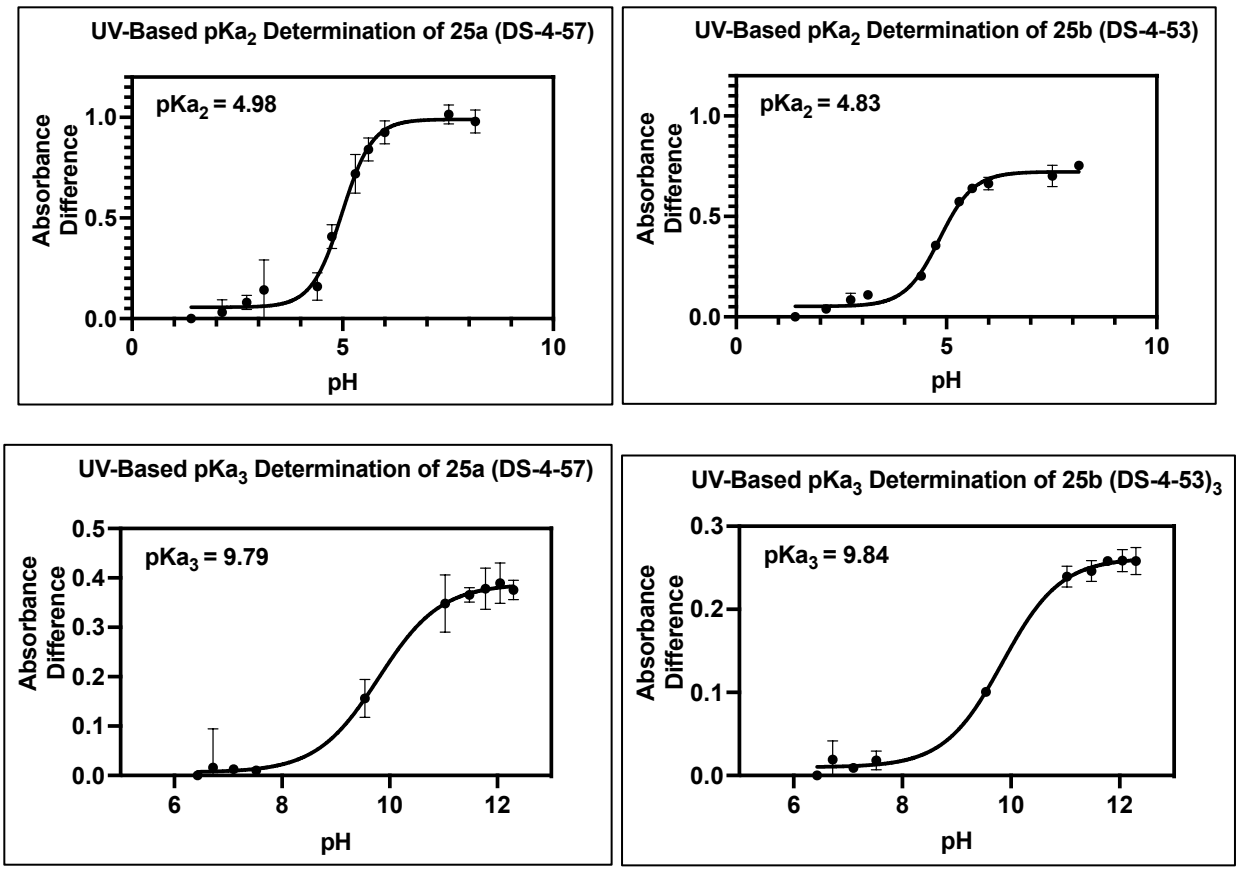


Similarly, for low pKa, differential spectra were created by subtracting data at pH 1.4 to generate the following graphs:





The above experiments were carried out twice, and from these data, the difference between 460 and 420nm were plotted versus pH to obtain pKa3 and 390 and 420 (4-57) and 390 and 430 (4-53). Data was processed using sigmoidal dose-response to obtain pKa values. Graphs from these experiments are as follows:

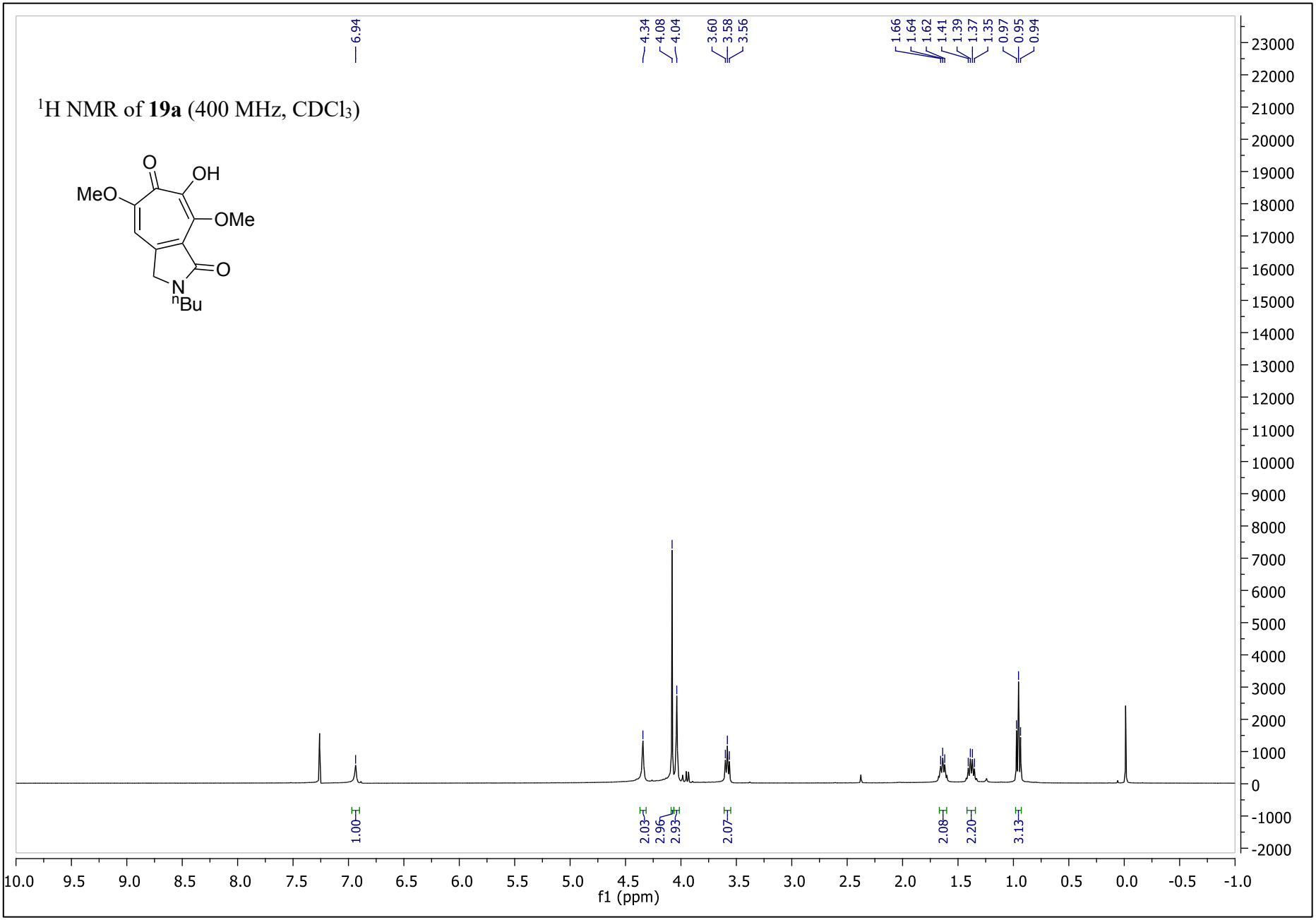


Fluorescence emission versus pH. Immediately following the collection of the UV data described above, fluorescence intensity was recorded at 500 nm following excitation at 450 nm in the same platereader. This data is presented as part of Figure 3B and 3C in the manuscript.

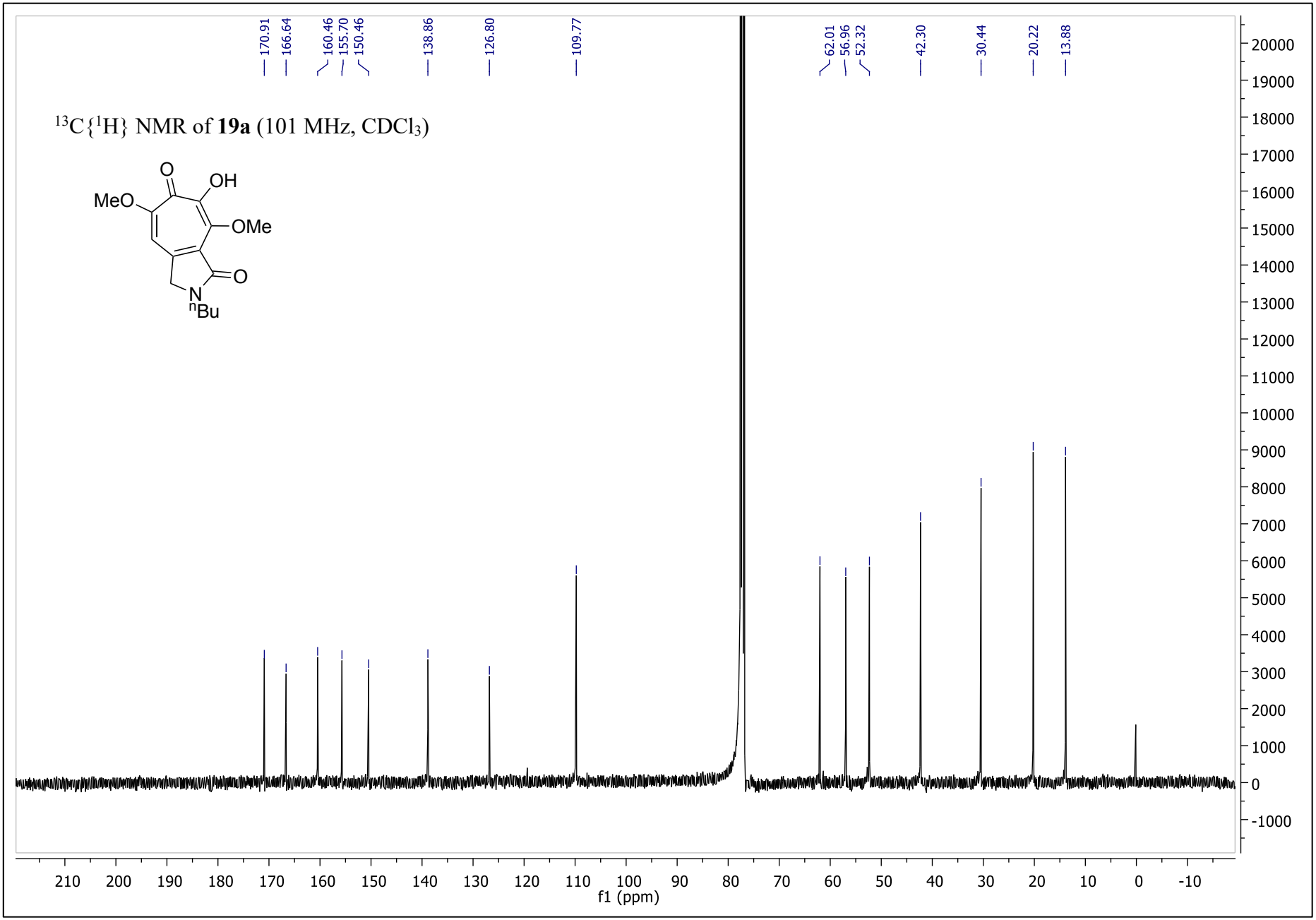
IIId. Fluorescence of Tropolones in Presence of Metals Across a Dilution Series.

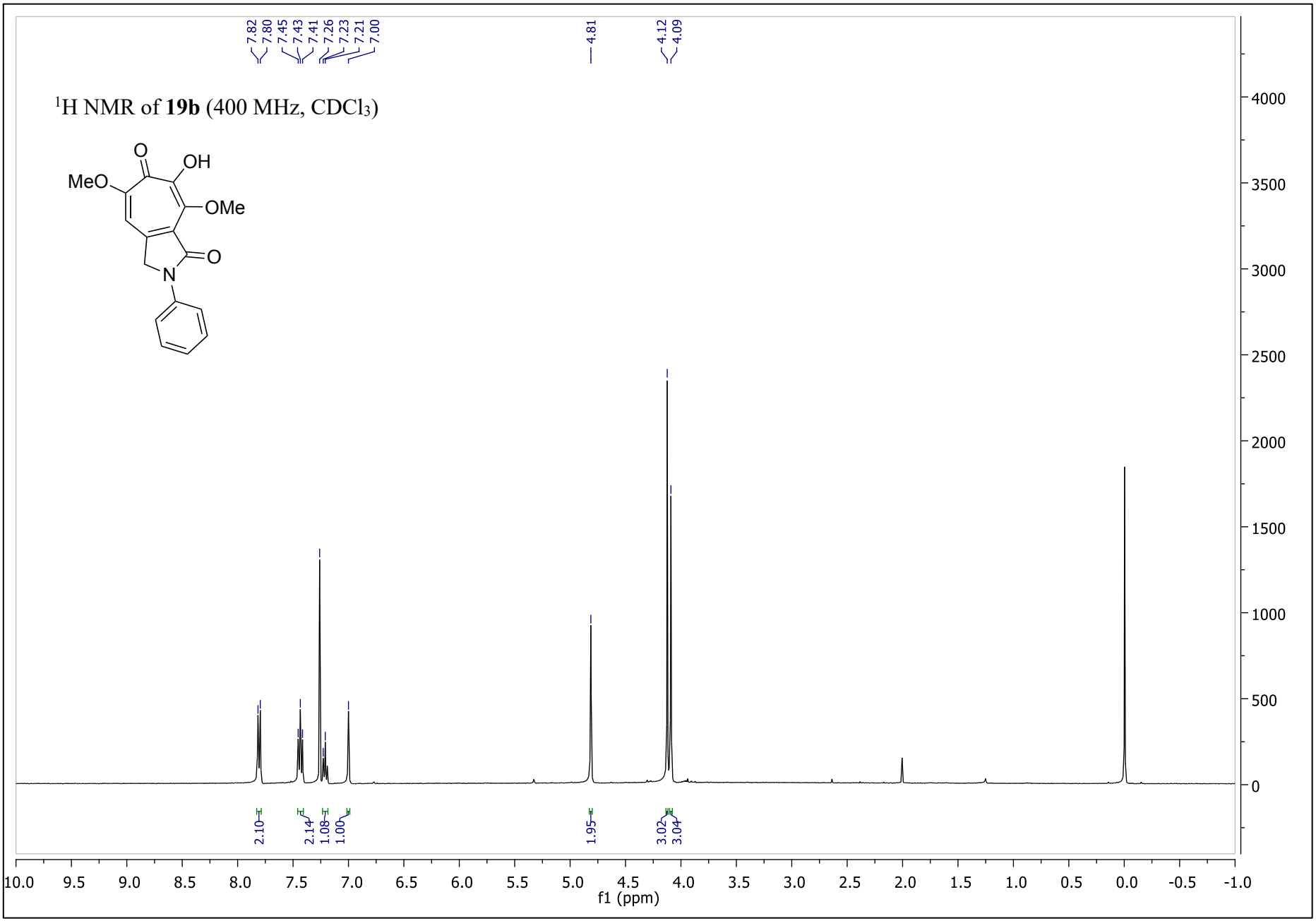
100 mM aqueous solutions of Zinc and Magnesium Chloride were made and diluted by factor of 3 across clear 96-well flat bottom plate (Costar, polystyrene). To accomplish this, 90 μL deionized water was mixed with 30 μL metal-containing solution in waterfall format across the plate (1 → 11), such that a dilution series was made across 11 of the 12 wells containing 90 μL of a dilution series of 100 mM, 33 mM, 11 mM, 3.6 mM, 1.2 mM, 0.4 mM, 130 μM, 44 μM, 15 μM, 5 μM, and 1.7 μM. The final series of wells contained 90 μL of deioinized water as a blank. Aqueous stock solutions containing 110 μM **19b**, **24b**, and **25a**, created by dilution of a 10 mM stock solution in dmso, were added to the wells in duplicate (**19b** across plate series 'c' and 'd', **24b** 'e' and 'f', and **25a** 'g' and 'h'. This provided 10 μM solutions of tropolones in solutions containing 90 mM, 30 mM, 10 mM, 3.3 mM, 1.1 mM, 0.37 mM, 12 μM, 40 μM, 14 μM, 4.6, and 1.5 μM

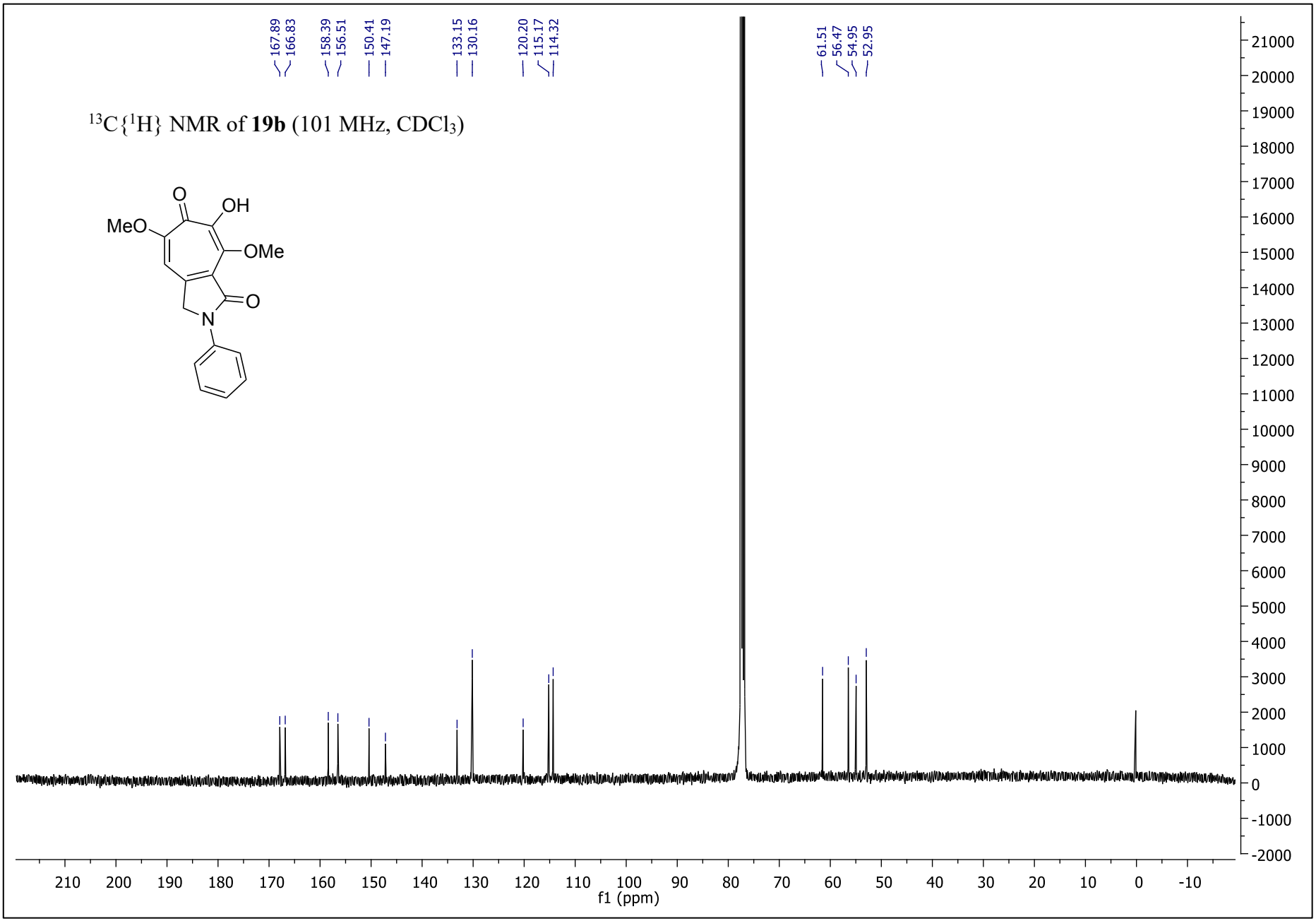
metals, as well as no metal. 10 μM water was added to plate series 'a' and 'b' for blanks. Fluroescence was recorded on a Syngery H1 microplate reader with excitation wavelength at 420 nm, and reading emission at either 460 nm or 480 nm for magnesium chloride and zinc chloride respectively. Data was processed by first subtracting the average of the background of magnesium or zinc solutions without tropolones from those with same concentration of metal but that contained tropolones. The corrected data series containing metals was then subtracted from that containing no metal. These numbers were inserted as sets of duplicates into Graphpad Prism used to create the data in figure 4C.

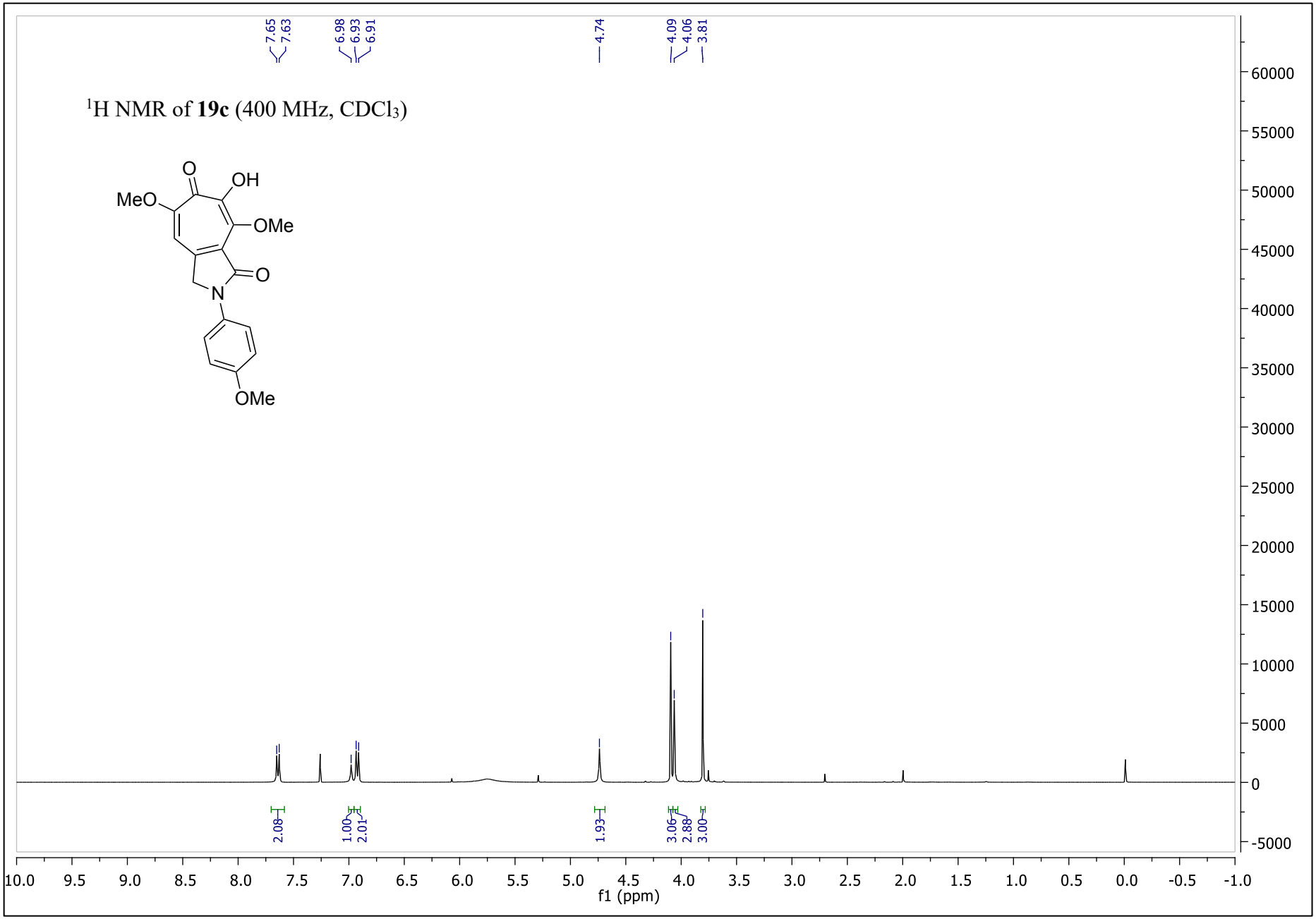


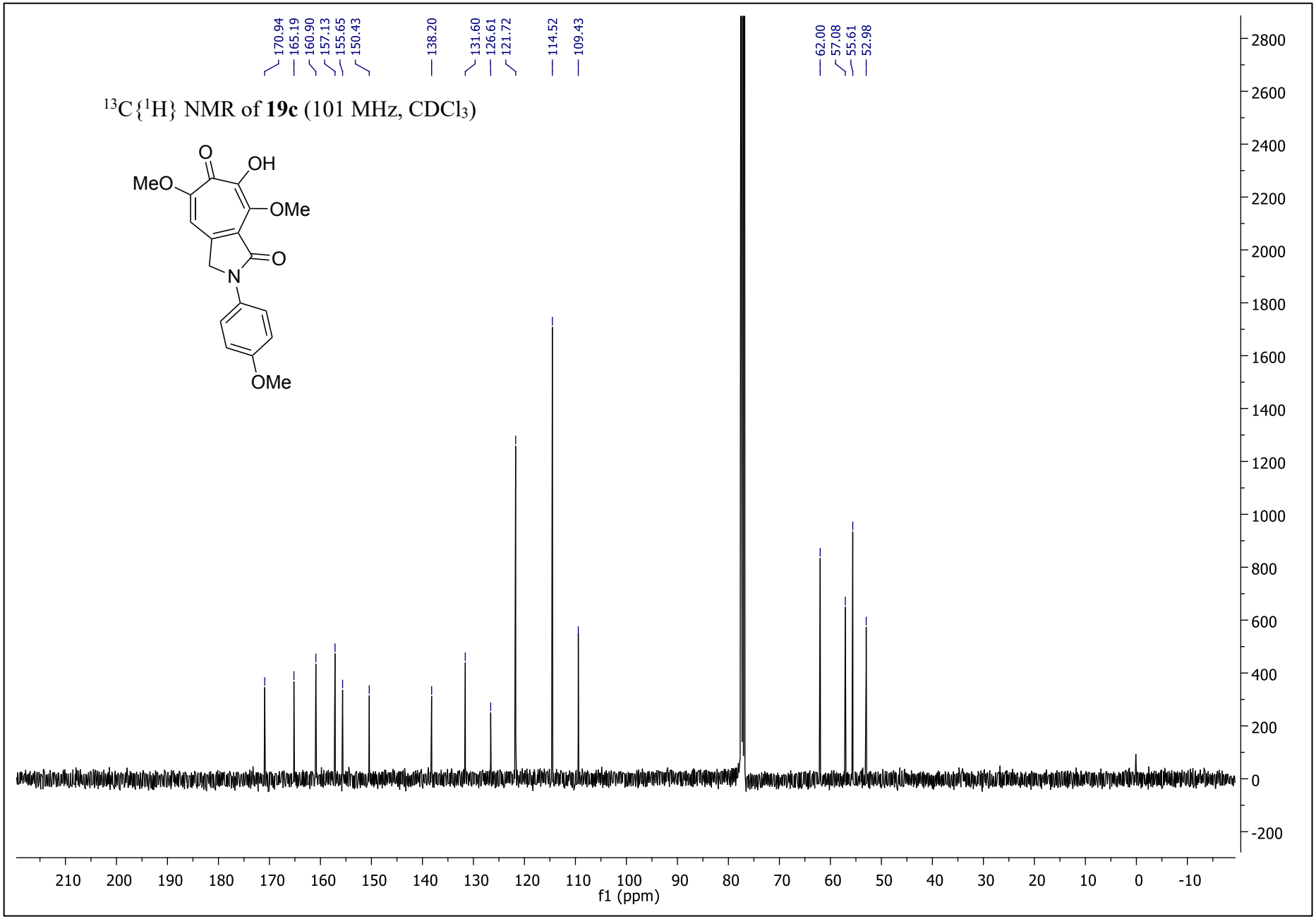
^{1}H NMR of **19a** (400 MHz, $CDCl_3$)


170.91
166.64
160.46
155.70
150.46
138.86
126.80
109.77
62.01
56.96
52.32
42.30
30.44
20.22
13.88
$^{13}C\{^{1}H\}$ NMR of **19a** (101 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
^{n}Bu
f1 (ppm)

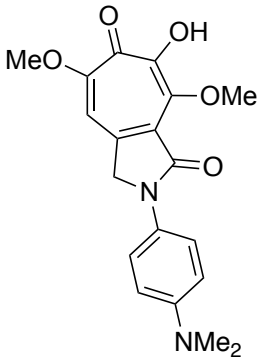

7.82
7.80
7.45
7.43
7.41
7.26
7.23
7.21
7.00
4.81
4.12
4.09
1H NMR of 19b (400 MHz, CDCl3)
O
OH
MeO
OMe
O
N
4000
3500
3000
2500
2000
1500
1000
500
0
2.10
2.14
1.08
1.00
1.95
3.02
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

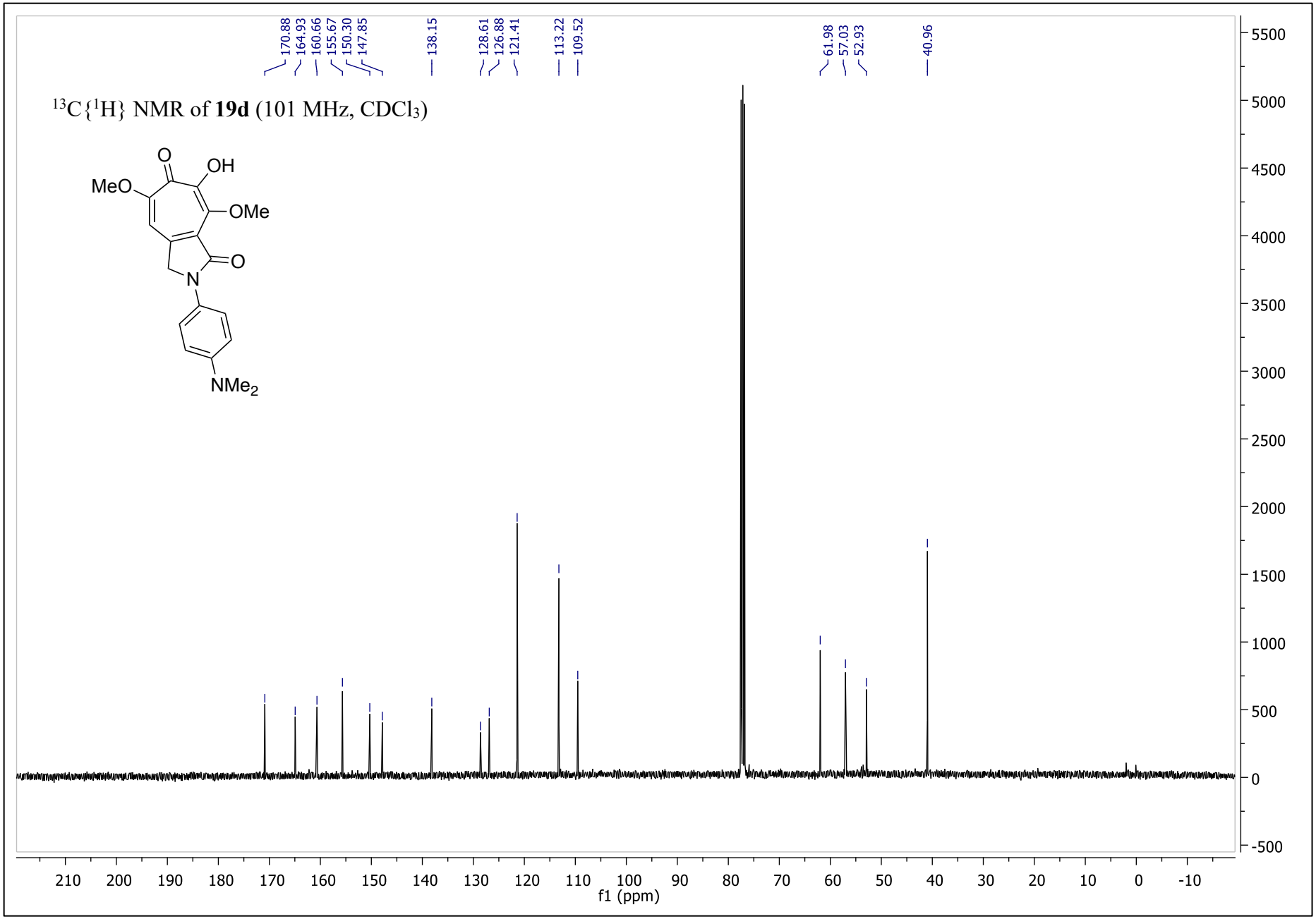

167.89
166.83
158.39
156.51
150.41
147.19
133.15
130.16
120.20
115.17
114.32
61.51
56.47
54.95
52.95
$^{13}C\{^{1}H\}$ NMR of **19b** (101 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
f1 (ppm)


7.65
7.63
6.98
6.93
6.91
4.74
4.09
4.06
3.81
^{1}H NMR of **19c** (400 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
OMe
2.08
1.00
2.01
1.93
3.06
2.88
3.00
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

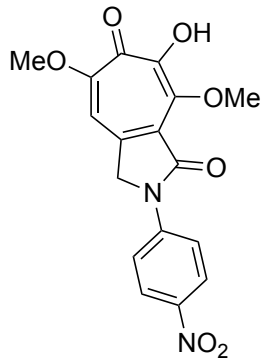

170.94
165.19
160.90
157.13
155.65
150.43
138.20
131.60
126.61
121.72
114.52
109.43
62.00
57.08
55.61
52.98
$^{13}C\{^{1}H\}$ NMR of **19c** (101 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
OMe
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

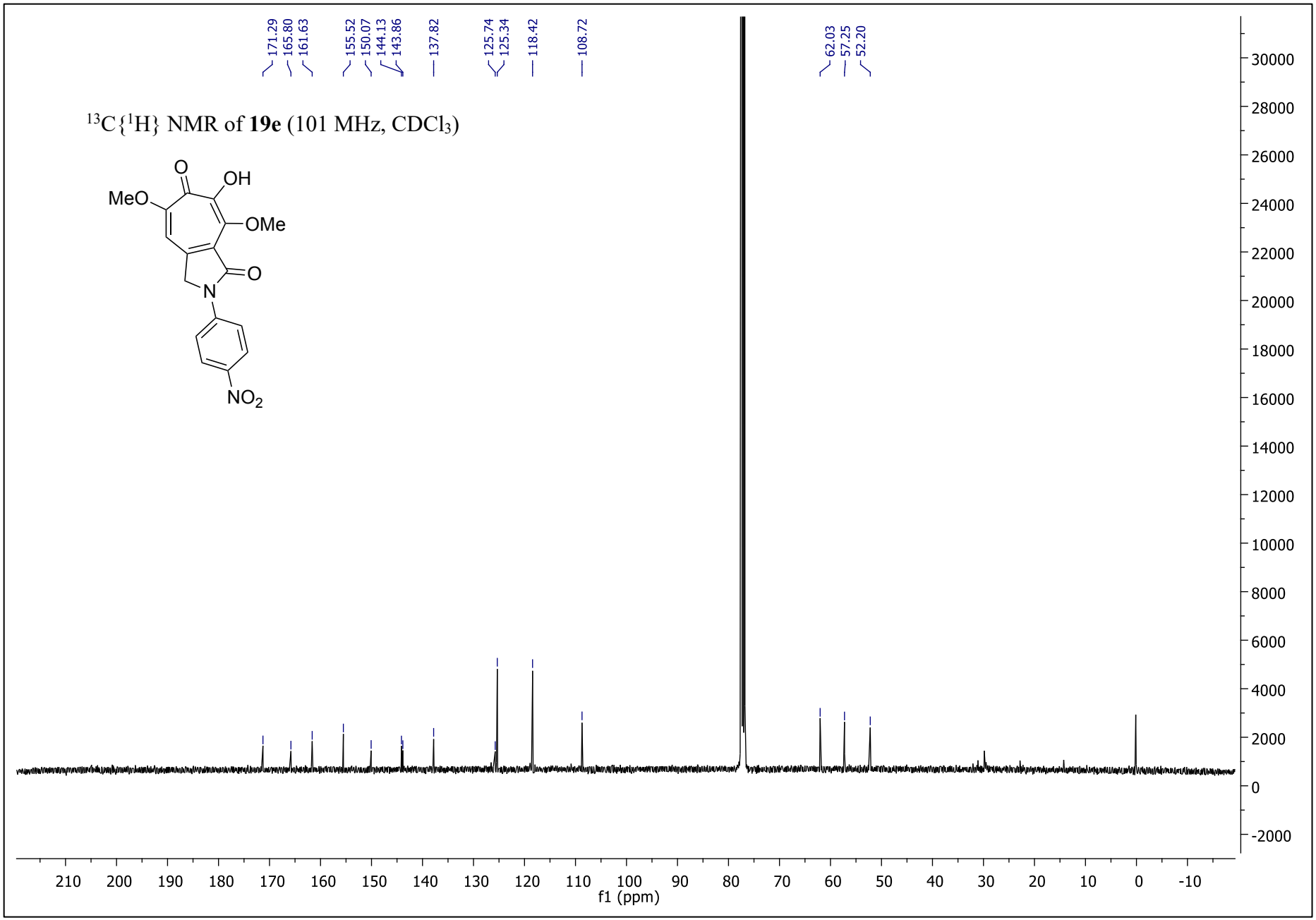
^{1}H NMR of **19d** (400 MHz, $CDCl_3$)



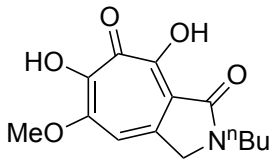

170.88
164.93
160.66
155.67
150.30
147.85
138.15
128.61
126.88
121.41
113.22
109.52
61.98
57.03
52.93
40.96
$^{13}C\{^{1}H\}$ NMR of **19d** (101 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
NMe_2
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

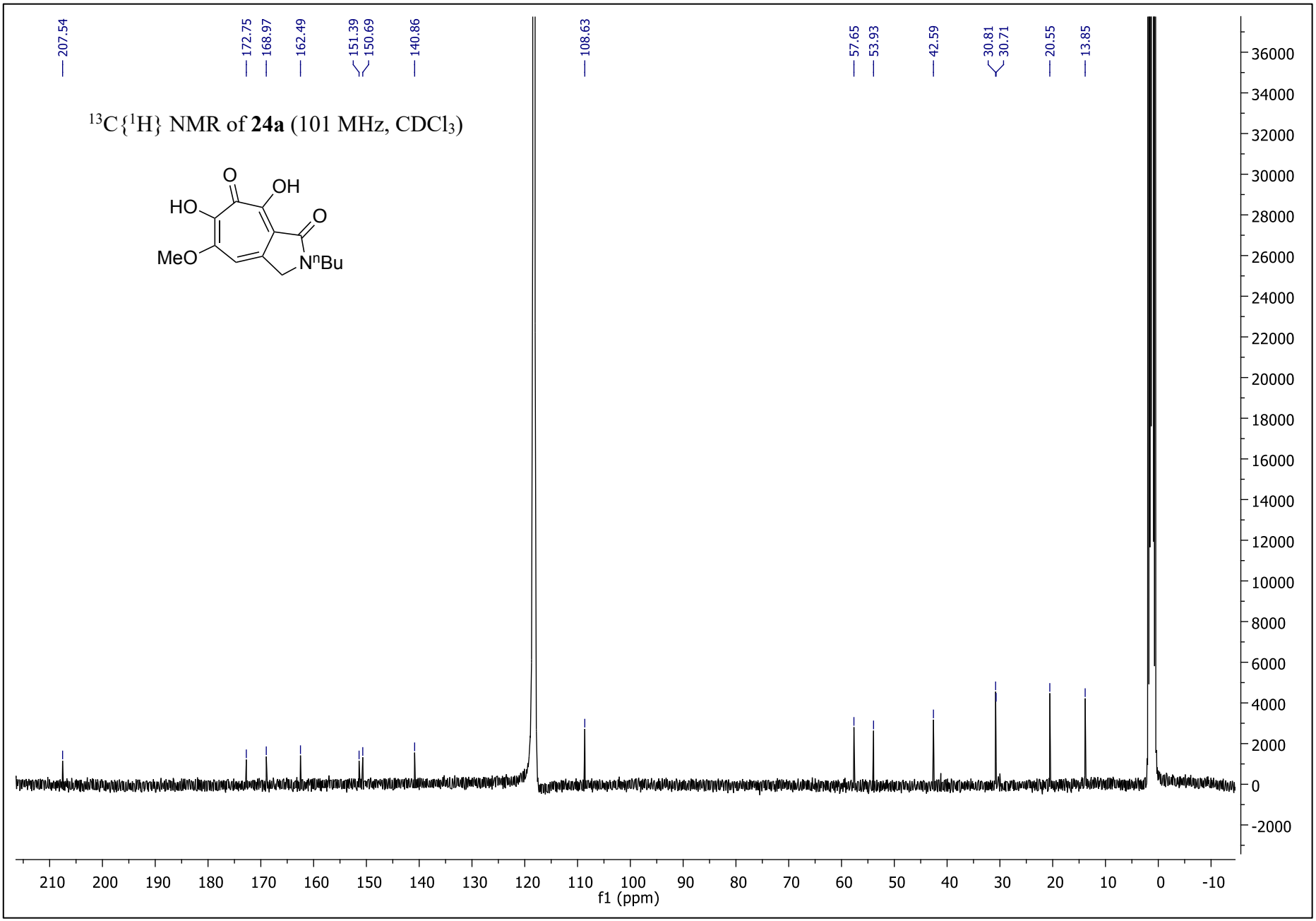
^{1}H NMR of **19e** (400 MHz, $CDCl_3$)

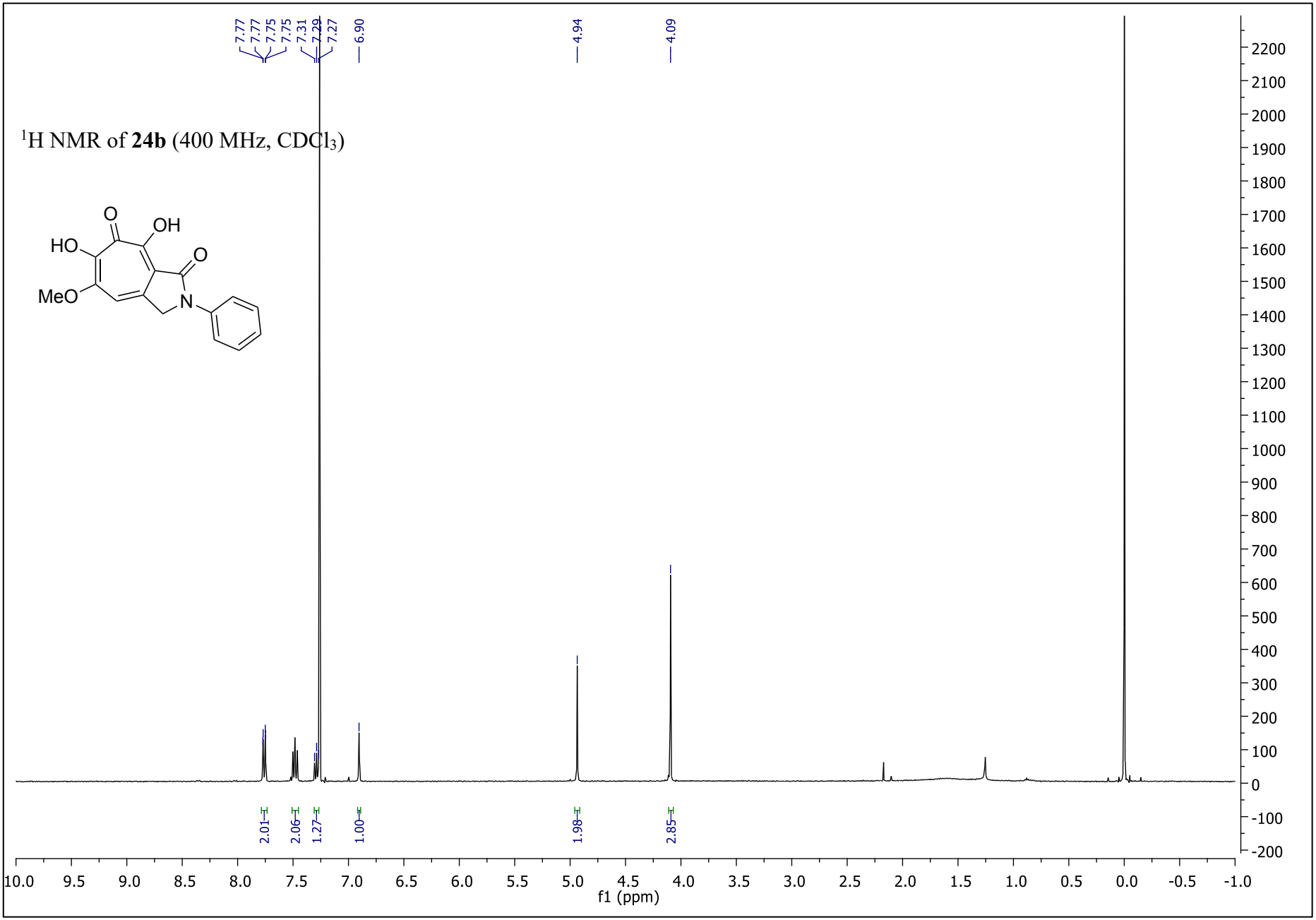


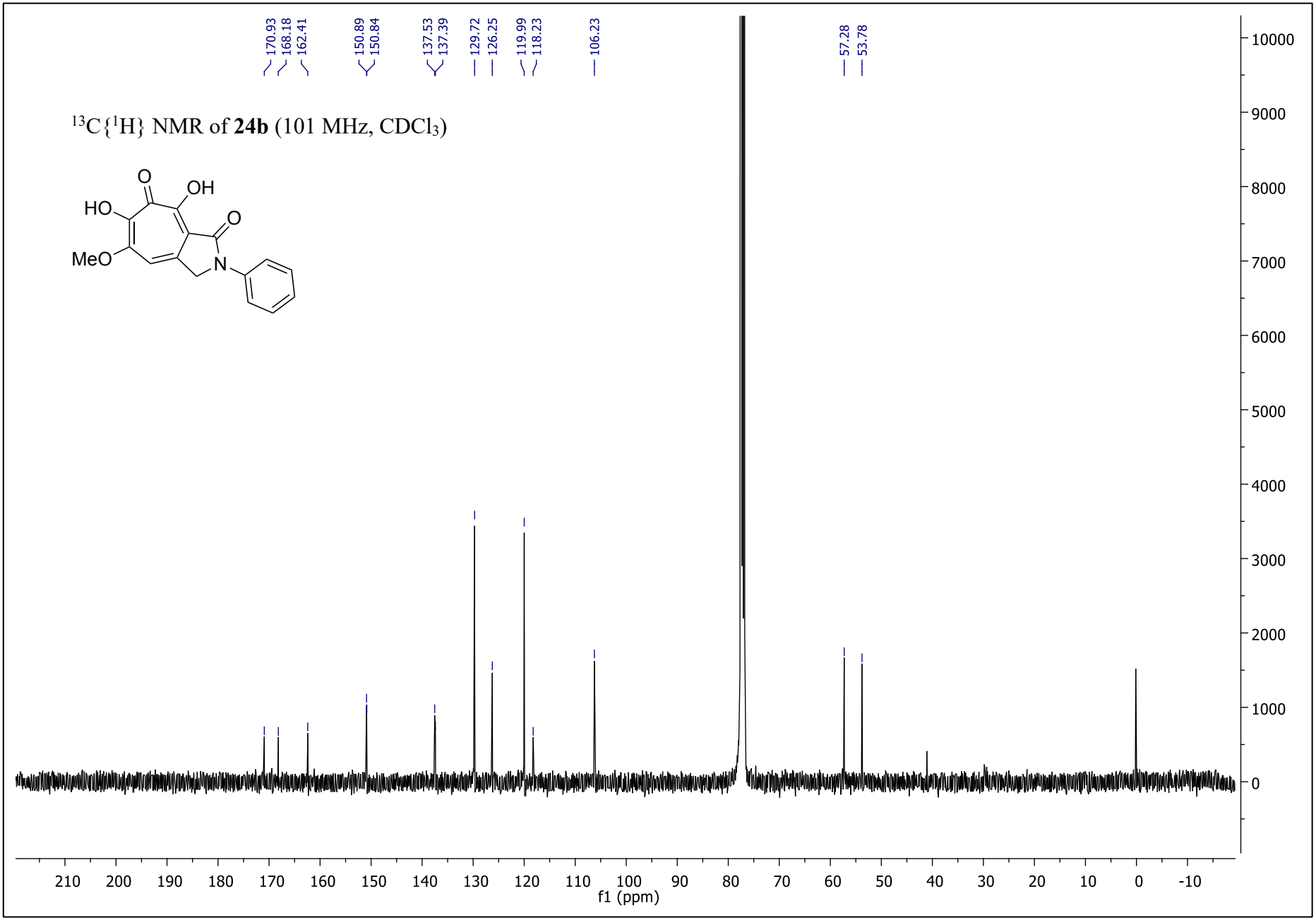

171.29
165.80
161.63
155.52
150.07
144.13
143.86
137.82
125.74
125.34
118.42
108.72
62.03
57.25
52.20
$^{13}C\{^{1}H\}$ NMR of **19e** (101 MHz, $CDCl_3$)
O
OH
MeO
OMe
O
N
NO_2
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of **24a** (400 MHz, $CDCl_3$)

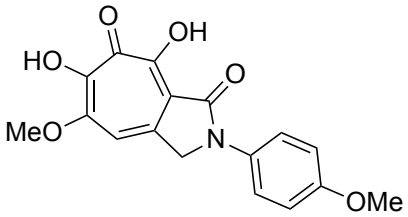


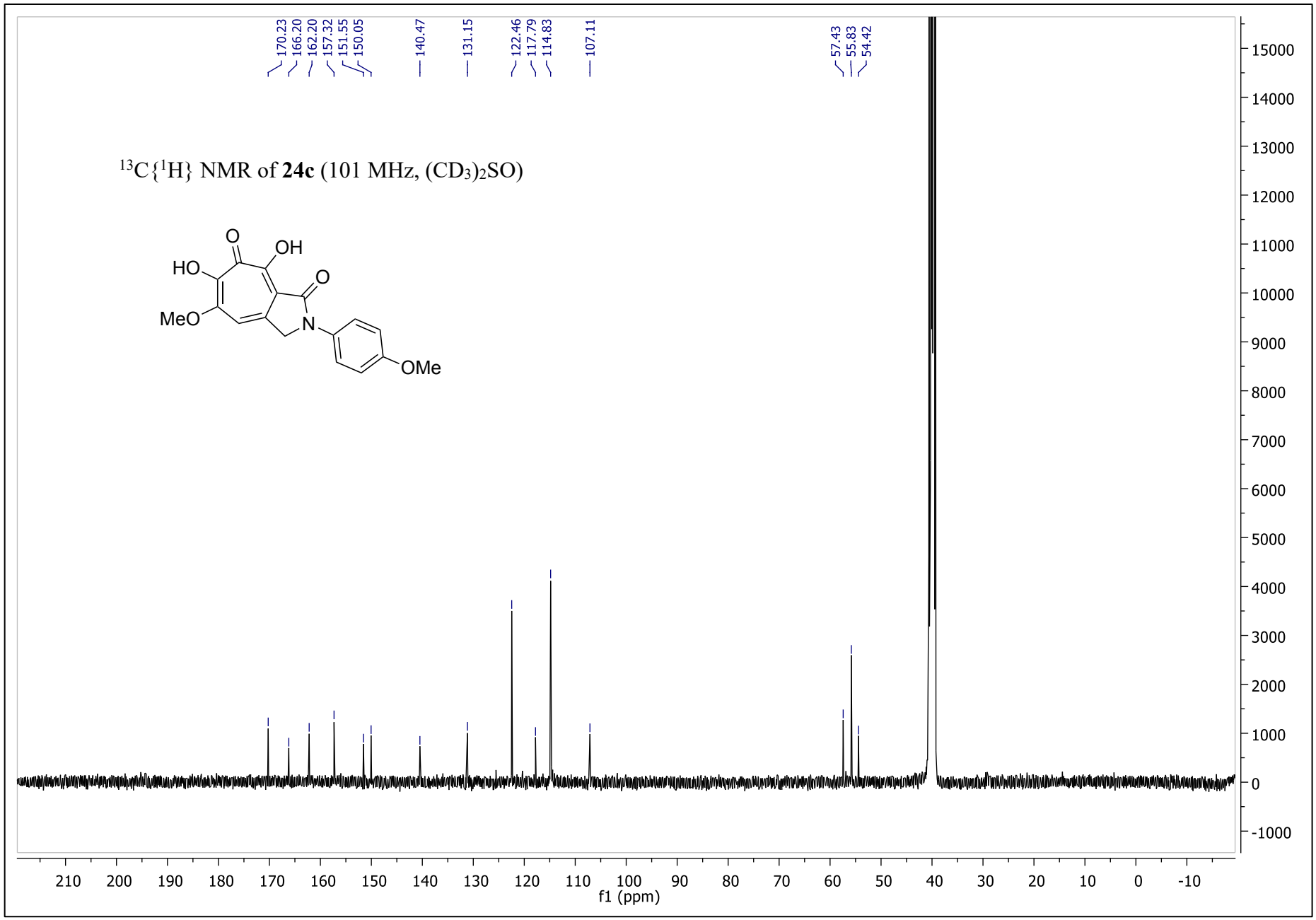

207.54
172.75
168.97
162.49
151.39
150.69
140.86
108.63
57.65
53.93
42.59
30.81
30.71
20.55
13.85
$^{13}C\{^{1}H\}$ NMR of **24a** (101 MHz, $CDCl_3$)
O
OH
HO
O
MeO
N^{n}Bu
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

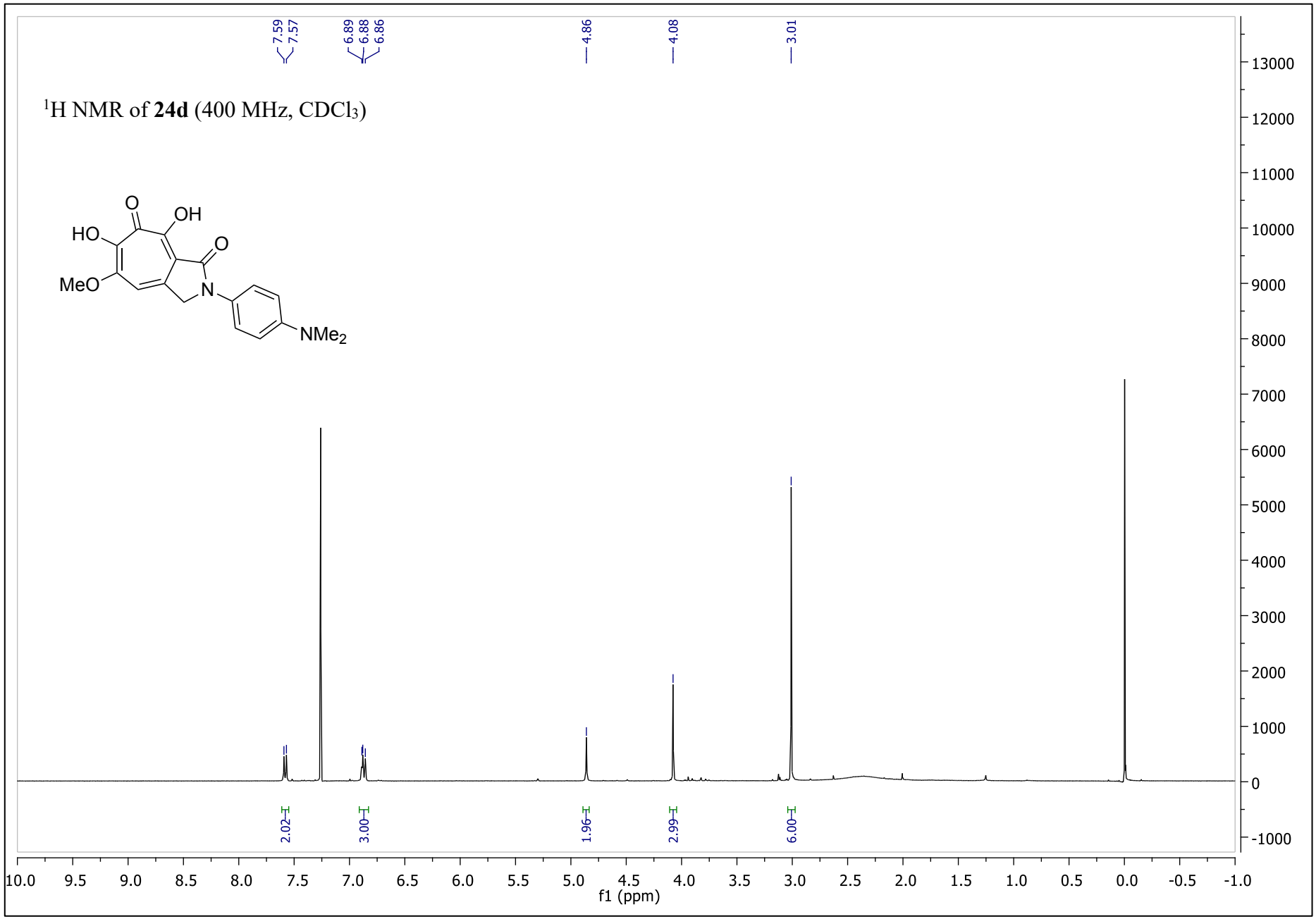

^{1}H NMR of **24b** (400 MHz, $CDCl_3$)
HO
OH
O
O
MeO
N
7.77
7.77
7.75
7.75
7.31
7.29
7.27
6.90
4.94
4.09
2.01
2.06
1.27
1.00
1.98
2.85
f1 (ppm)

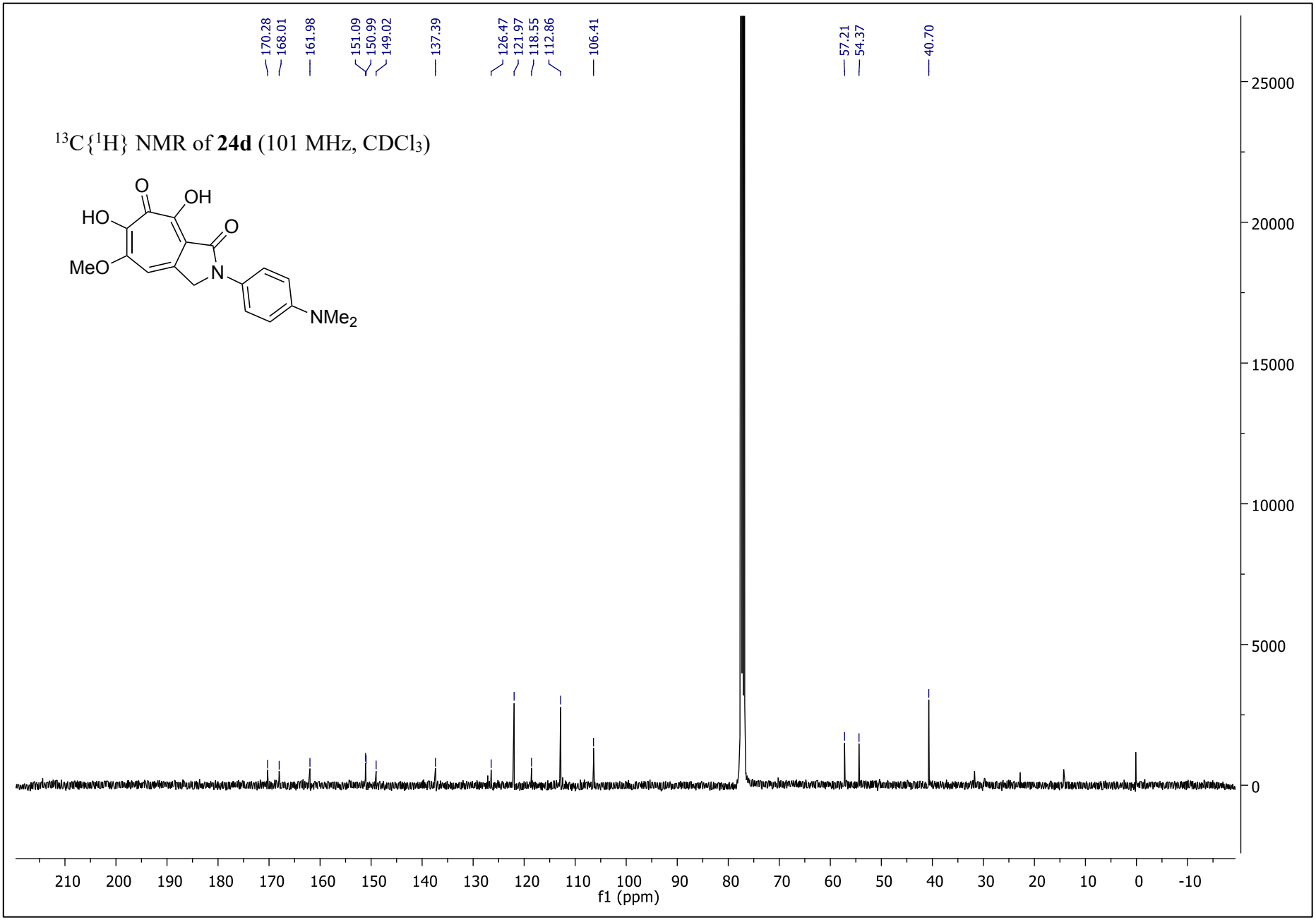

170.93
168.18
162.41
150.89
150.84
137.53
137.39
129.72
126.25
119.99
118.23
106.23
57.28
53.78
$^{13}C\{^{1}H\}$ NMR of **24b** (101 MHz, $CDCl_3$)
O
OH
HO
O
MeO
N
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

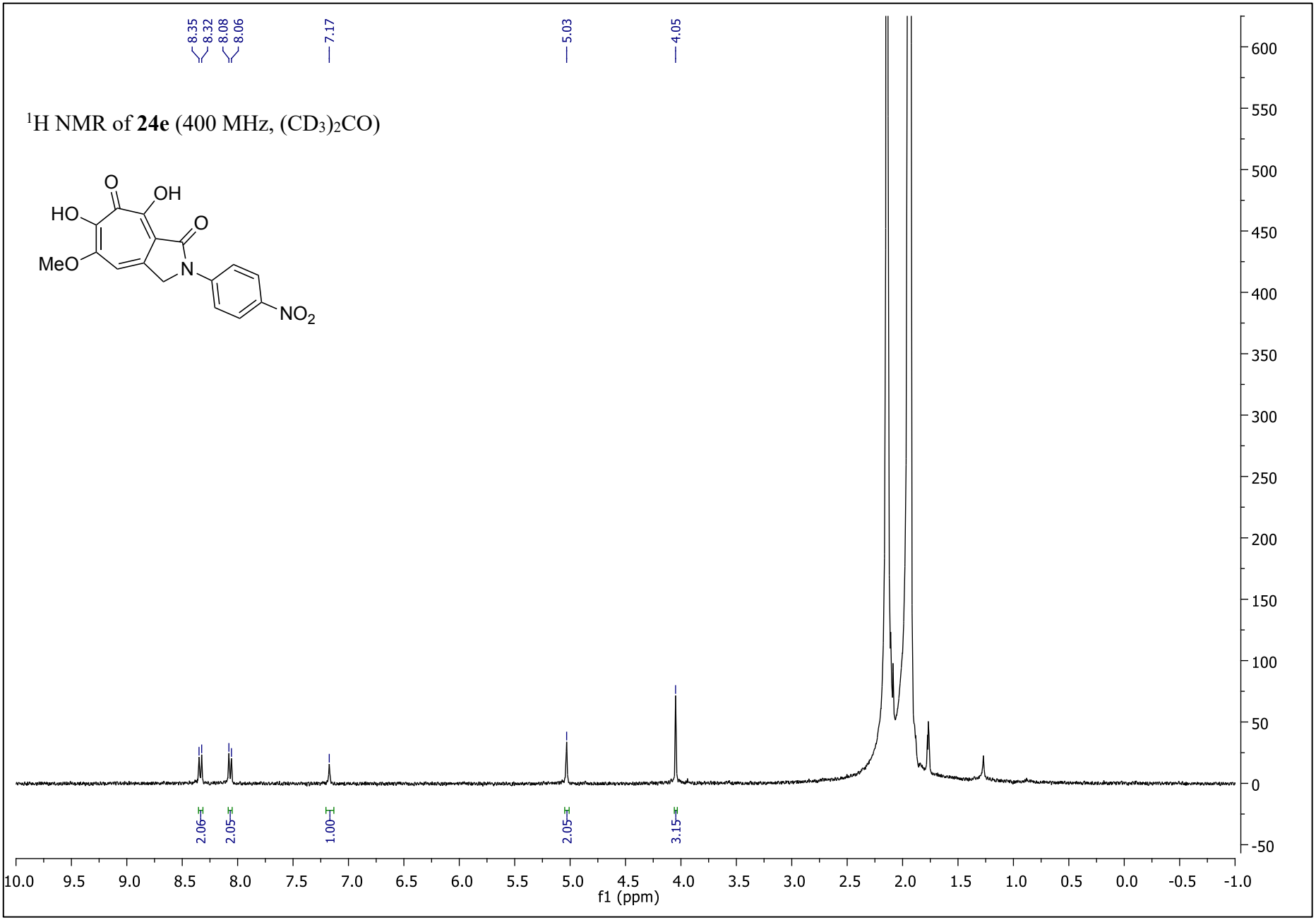
^{1}H NMR of **24c** (400 MHz, $CDCl_3$)

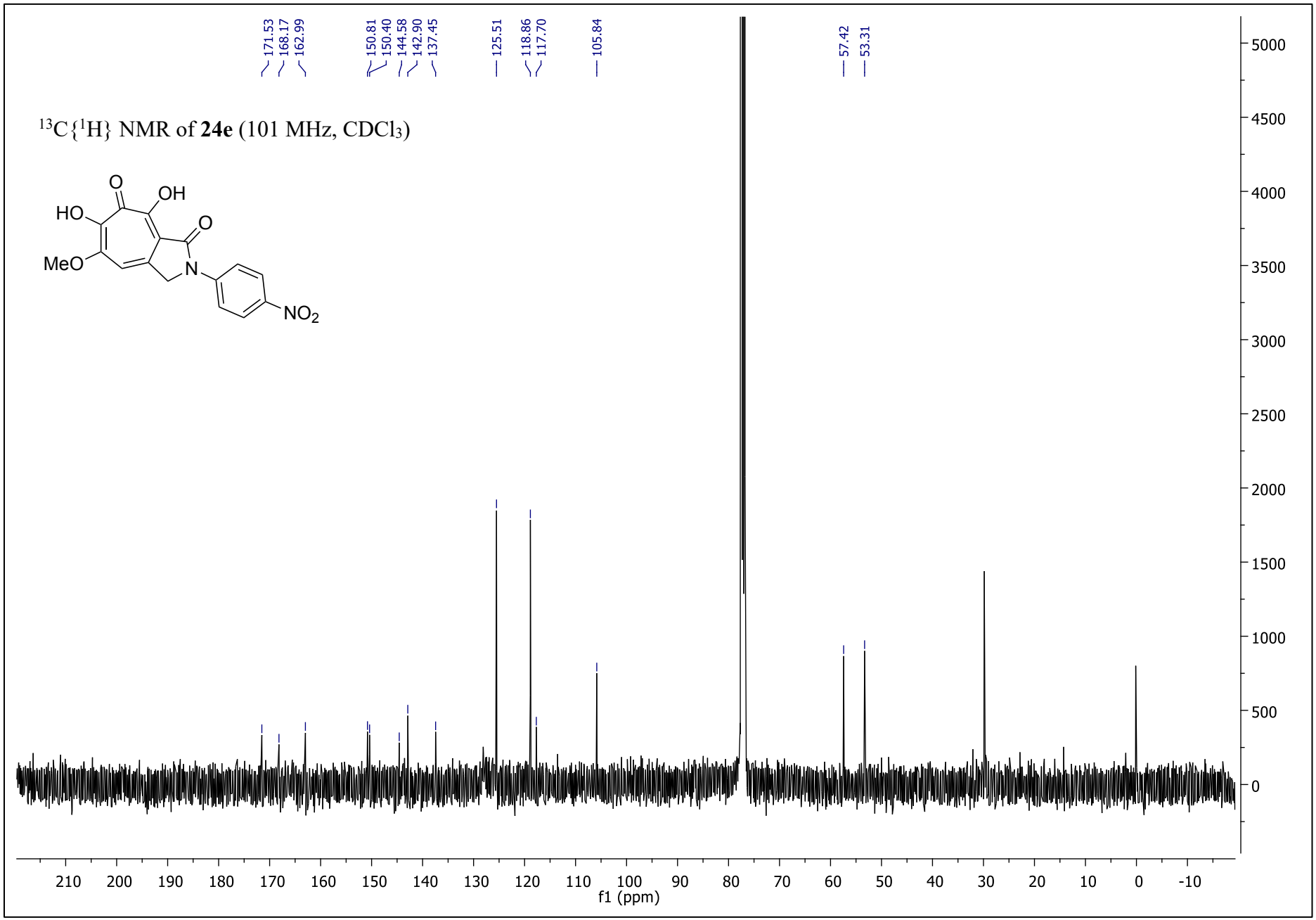


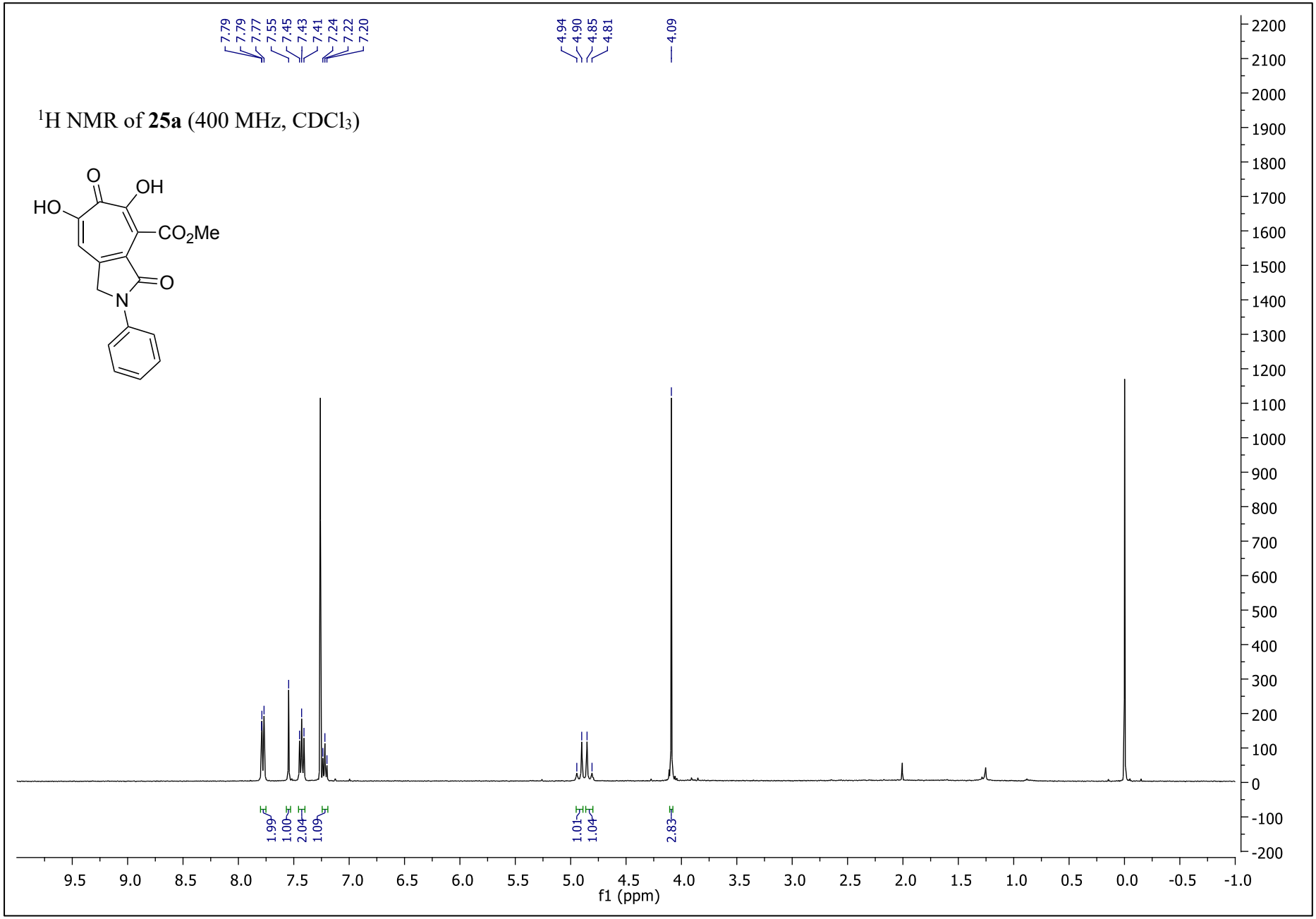

170.23
166.20
162.20
157.32
151.55
150.05
140.47
131.15
122.46
117.79
114.83
107.11
57.43
55.83
54.42
$^{13}C\{^{1}H\}$ NMR of **24c** (101 MHz, $(CD_3)_2SO$)
O
OH
HO
O
MeO
N
OMe
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

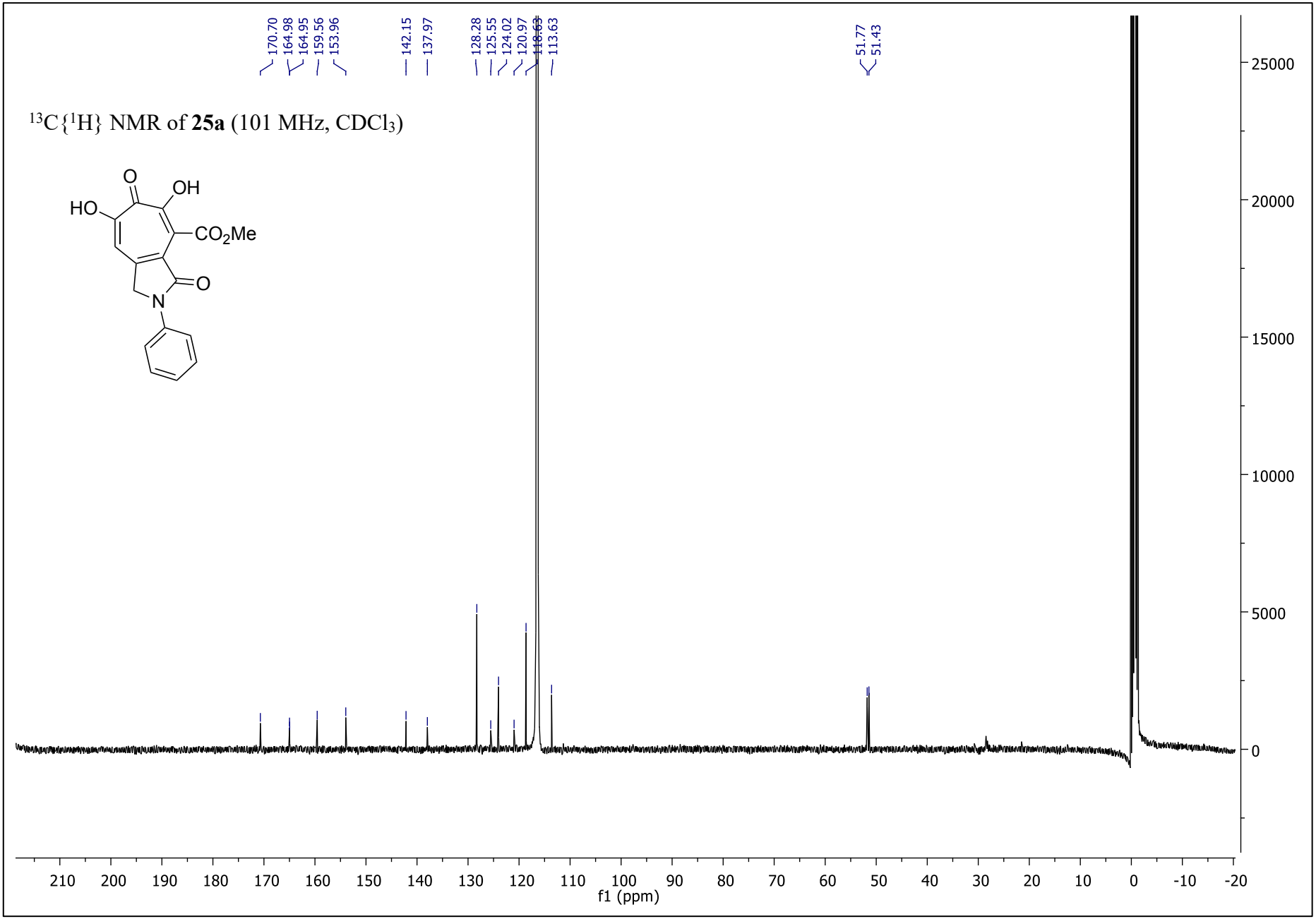

7.59
7.57
6.89
6.88
6.86
4.86
4.08
3.01
^{1}H NMR of **24d** (400 MHz, $CDCl_3$)
O
OH
HO
O
MeO
N
NMe_2
2.02
3.00
1.96
2.99
6.00
f1 (ppm)


170.28
168.01
161.98
151.09
150.99
149.02
137.39
126.47
121.97
118.55
112.86
106.41
57.21
54.37
40.70
$^{13}C\{^{1}H\}$ NMR of **24d** (101 MHz, $CDCl_3$)
O
OH
HO
O
MeO
N
NMe_2
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

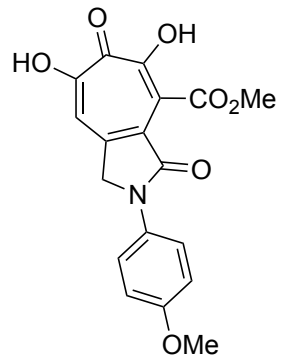

8.35
8.32
8.08
8.06
7.17
5.03
4.05
[1]H NMR of **24e** (400 MHz, $(CD_3)_2CO$)
O
OH
HO
O
MeO
N
NO_2
2.06
2.05
1.00
2.05
3.15
f1 (ppm)

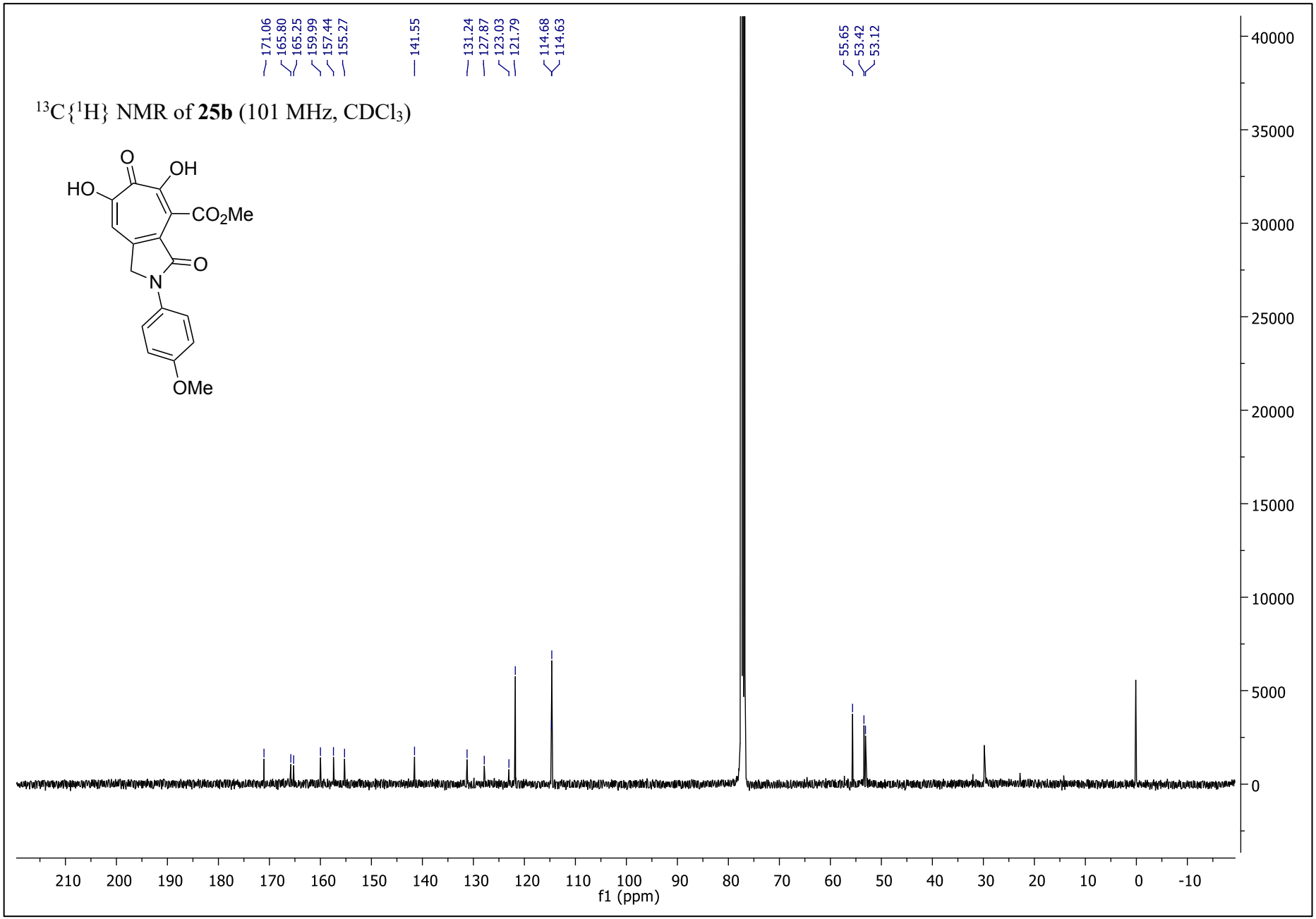

171.53
168.17
162.99
150.81
150.40
144.58
142.90
137.45
125.51
118.86
117.70
105.84
57.42
53.31
$^{13}C\{^{1}H\}$ NMR of **24e** (101 MHz, $CDCl_3$)
O
OH
HO
O
MeO
N
NO_2
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.79
7.79
7.77
7.55
7.45
7.43
7.41
7.24
7.22
7.20
4.94
4.90
4.85
4.81
4.09
1H NMR of 25a (400 MHz, CDCl3)
O
OH
HO
CO2Me
O
N
1.99
1.00
2.04
1.09
1.01
1.04
2.83
f1 (ppm)

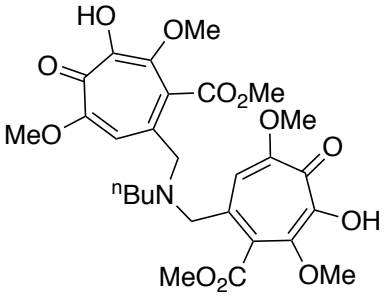

170.70
164.98
164.95
159.56
153.96
142.15
137.97
128.28
125.55
124.02
120.97
118.63
113.63
51.77
51.43
$^{13}C\{^{1}H\}$ NMR of **25a** (101 MHz, $CDCl_3$)
O
OH
HO
CO_2Me
O
N
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

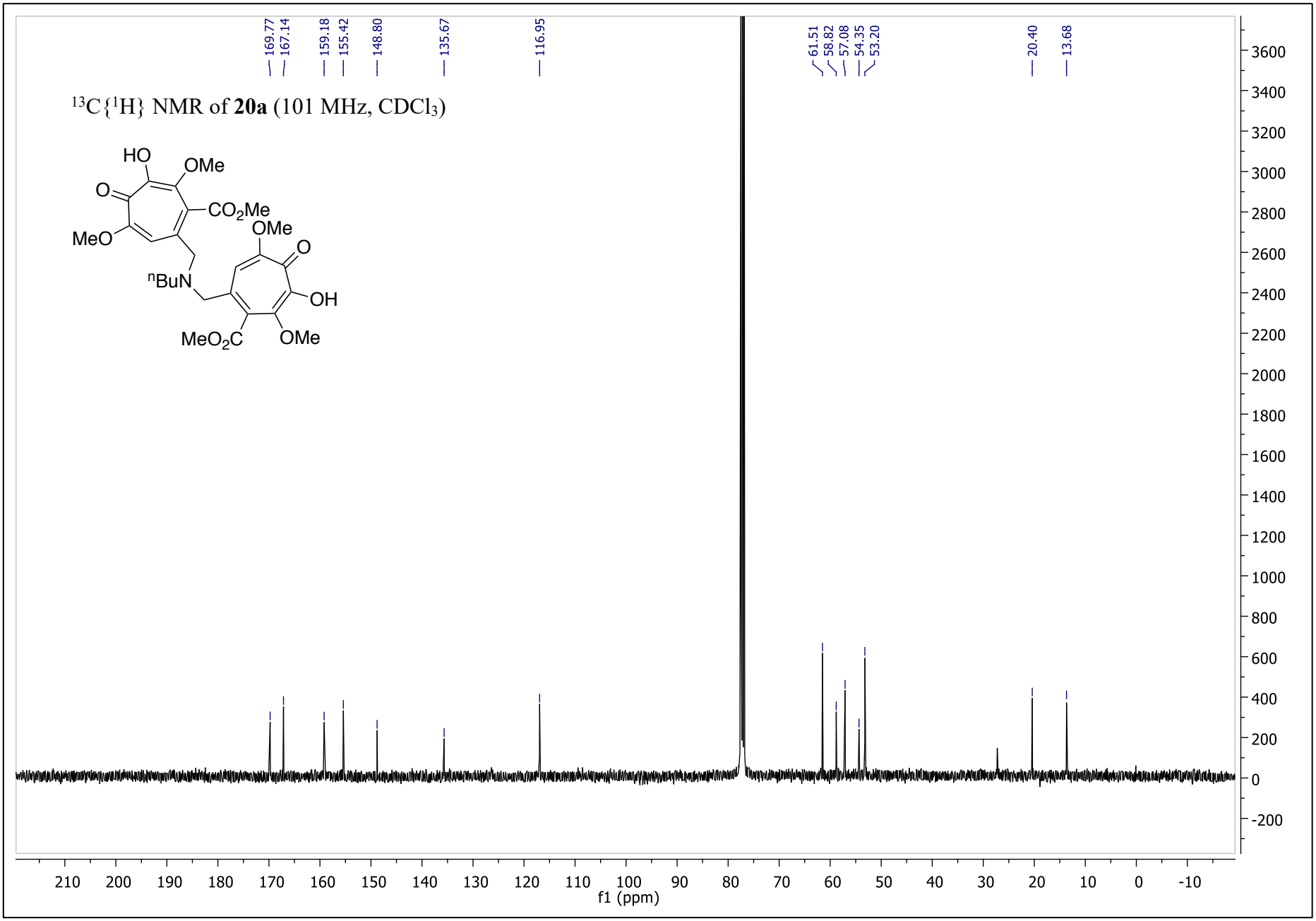
^{1}H NMR of **25b** (400 MHz, $CDCl_3$)

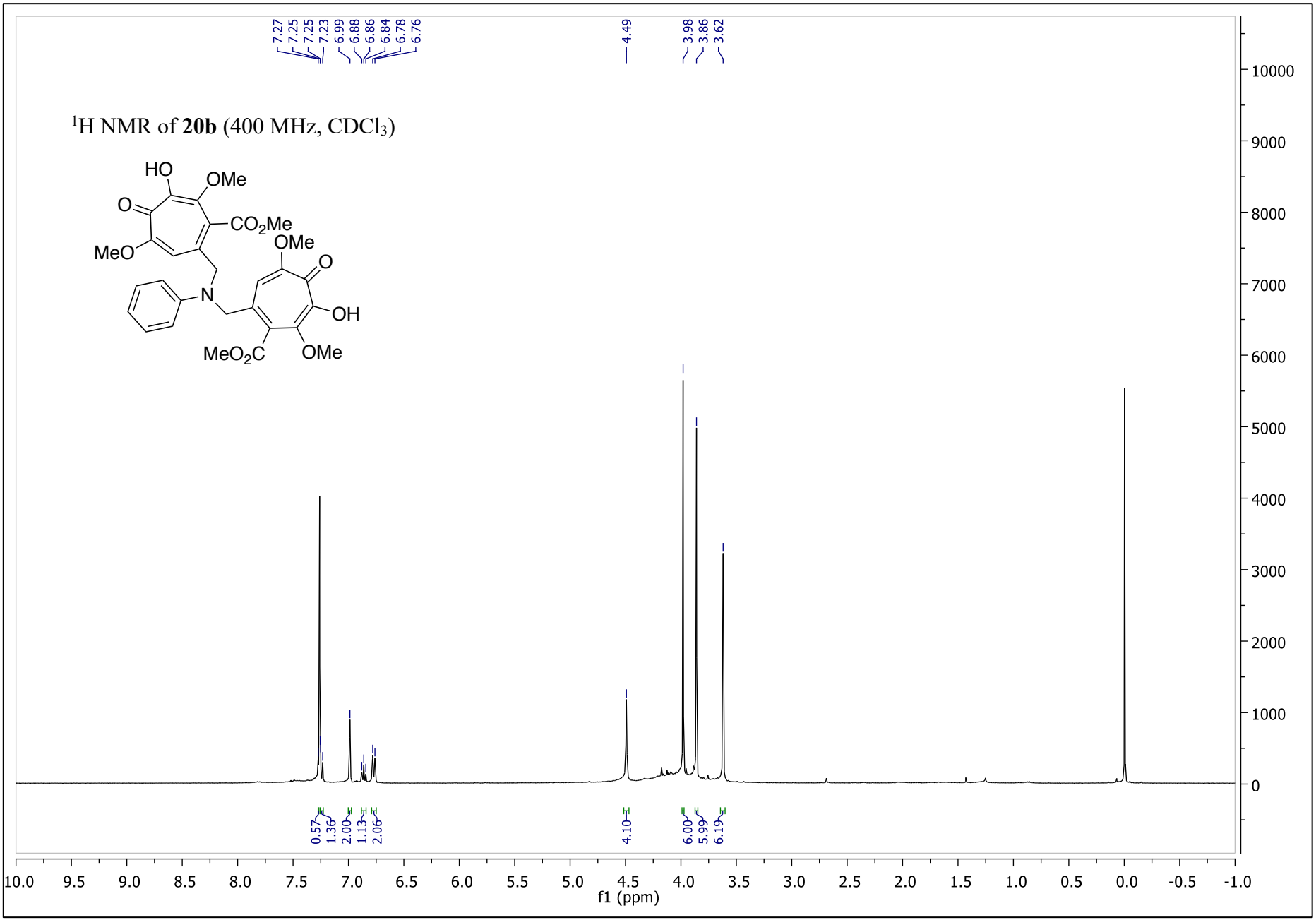


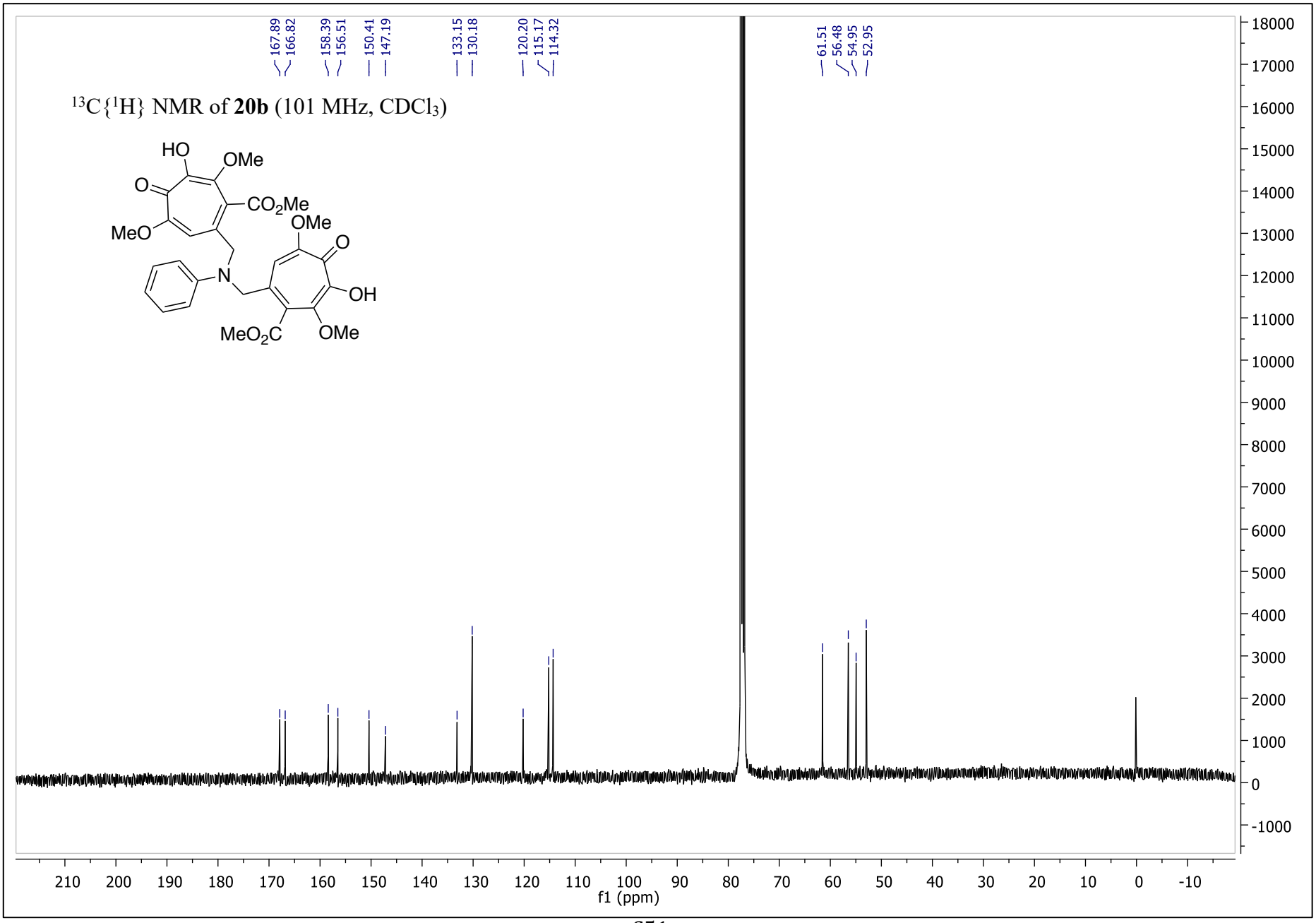

171.06
165.80
165.25
159.99
157.44
155.27
141.55
131.24
127.87
123.03
121.79
114.68
114.63
55.65
53.42
53.12
$^{13}C\{^{1}H\}$ NMR of **25b** (101 MHz, $CDCl_3$)
O
OH
HO
CO_2Me
O
N
OMe
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of **20a** (400 MHz, $CDCl_3$)




169.77
167.14
159.18
155.42
148.80
135.67
116.95
61.51
58.82
57.08
54.35
53.20
20.40
13.68
$^{13}C\{^{1}H\}$ NMR of **20a** (101 MHz, $CDCl_3$)
HO
OMe
O
CO_2Me
MeO
OMe
O
^{n}BuN
OH
MeO_2C
OMe
f1 (ppm)


7.27
7.25
7.25
7.23
6.99
6.88
6.86
6.84
6.78
6.76
4.49
3.98
3.86
3.62
^{1}H NMR of **20b** (400 MHz, $CDCl_3$)
HO
OMe
O
CO_2Me
MeO
OMe
O
N
OH
MeO_2C
OMe
0.57
1.36
2.00
1.13
2.06
4.10
6.00
5.99
6.19
f1 (ppm)


167.89
166.82
158.39
156.51
150.41
147.19
133.15
130.18
120.20
115.17
114.32
61.51
56.48
54.95
52.95
$^{13}C\{^{1}H\}$ NMR of **20b** (101 MHz, $CDCl_3$)
HO
OMe
O
CO_2Me
MeO
OMe
O
N
OH
MeO_2C
OMe
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)