Supporting Information

for

Pd- and Cu-catalyzed approaches in the syntheses of new cholane aminoanthraquinone pincer-like ligands

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Experimental procedures, characterization data, copies of the ^{1}H, ^{13}C NMR spectra, UV–vis data

General information

^{1}H and ^{13}C-NMR spectra were recorded at 400 and 100.6 MHz respectively with a Bruker Avance 400 and Agilent MR 400 spectrometers. Chemical shifts were measured relative to HMDS and solvent signal in ^{1}H and ^{13}C NMR spectra respectively. Only characteristic signals in ^{1}H-NMR of steroids are given. Column chromatography was carried out on Macherey-Nagel slilicagel 60 (0.040–0.063 mm). All procedures associated with oxygen- and water-sensitive compounds were conducted under dry argon atmosphere. Cs_2CO_3 was dried in vacuo at 120–150 °C for several hours, stored in a Schlenk tube, and weighed in an argon-flushed vessel.

UV–vis absorption spectra of a 50 μM solution of the ligands **5c** and **5d** in acetonitrile (3 ml placed into quartz cuvette with 1 cm optical path length) were recorded as a function of added $Cu(ClO_4)_2$, $Al(ClO_4)_3$ or $Cr(ClO_4)_3$ (0.01 M in acetonitrile) at a uniform data point interval of 1 nm with a Cary 60 (Agilent) spectrophotometer. All necessary aliquots of perchlorates (3.0 μl or 7.5 μl) were added manually with LLG-microliter pipette (0.5 to 10 μl). The calculation of stability constants was performed by nonlinear least-squares analysis with the Specfit program [1].

Experimental procedures and characterization data

General procedure for preparation of amides 2a–c [2]

To the suspension of bile acid (1.0 mmol) and Et_3N (1.5 equiv) in THF (2.5 ml) isobutyl chloroformate (1.1 equiv) was added at 10 °C and reaction was stirred at this temperature for 15 min. Conc. aqueous NH_3 (1.5 equiv) was added dropwise and stirring was continued for 30 min at 10 °C and 3 h at rt. Solvents were evaporated and the crude product was washed with H_2O followed by washing with Et_2O. The target product was dried in vacuo at 50–60 °C to constant mass and used without further purification.

(3α,5β)-3-Hydroxycholan-24-amide (2a)

Obtained from 1.50 g (4.0 mmol) of **1a**. White powder (84%, 1.26 g). M. p. 224-226 °C (lit. 214-216 °C [3], 208-210 °C [2]). ^{1}H NMR (400 MHz, DMSO-d_6): 0.60 (3H, s, 18-CH_3), 0.86 (6H, 19-CH_3, 21-CH_3), 2.01 (2H, m, 23-CH_2), 3.35 (1H, m, 3β-H), 4.43 (1H, d, *J* 4.5 Hz, 3-OH), 6.63 (1H, s, C(O)NH_2), 7.20 (1H, s, C(O)NH_2).

(3α,5β,12α)-3,12-Dihydroxycholan-24-amide (2b)

Obtained from 5.0 g (12.7 mmol) of **1b**. White powder (80%, 4.0 g). M. p. 213-215 °C (lit. 213-215 °C [2]). ^{1}H NMR (400 MHz, DMSO-d_6): 0.58 (3H, s, 18-CH_3), 0.83 (3H, s, 19-CH_3), 0.90 (3H, d, *J* 6.4 Hz, 21-CH_3), 1.98 (2H, m, 23-CH_2), 3.36 (1H, m, 3β-H), 3.59 (1H, m, 12β-H), 4.17 (1H, s, 12-OH), 4.45 (1H, s, 3-OH), 6.61 (1H, s, C(O)NH_2), 7.19 (1H, s, C(O)NH_2).

(3α,5β,7α,12α)-3,7,12-Trihydroxycholan-24-amide (2c)

Obtained from 5.0 g (12.2 mmol) of **1c**. White powder (85%, 4.3 g). M. p. 138-140°C (lit. 135-137°C [2]). ^{1}H NMR (400 MHz, DMSO-d_6): 0.57 (3H, s, 18-CH_3), 0.80 (3H, s, 19-CH_3), 0.91 (3H, d, *J* 5.4 Hz, 21-CH_3), 2.15 (2H, m, 23-CH_2), 3.17 (1H, m, 3β-H), 3.60 (1H, br.s, 12β-H), 3.77 (1H, br. s, 7β-H), 4.01 (1H, s, 7-OH), 4.10 (1H, s, 12-OH), 4.32 (1H, s, 3-OH), 6.63 (1H, s, C(O)NH_2), 7.21 (1H, s, C(O)NH_2).

General procedure for preparation of amines 3a–c [2]

To the cooled (with an ice bath) suspension of amide **2** (1.0 mmol) in THF (10 ml) $LiAlH_4$ (3 equiv) was added in small portions (**CAUTION**: exothermic reaction with hydrogen evolution) under argon atmosphere. When evolution of hydrogen ceased the mixture was refluxed for 15 h, cooled to rt, and excess of $LiAlH_4$ was quenched by dropwise addition of H_2O (3 ml). The suspension was half

concentrated and then filtered. The white solid was washed with hot THF until disappearance of the amine **3** in the filtrate (TLC control). The filtrate was evaporated and the product was purified by column chromatography.

(3α,5β)-3-Hydroxycholan-24-amine (3a)

Obtained from 1.26 g (3.4 mmol) of **2a**. Eluent CH_2Cl_2:CH_3OH:Et_3N 100:10:5, R_f 0.5. White powder (67%, 0.83 g). M. p. 158-160 °C (lit. 148-150 °C [2]). ^{1}H NMR (400 MHz, DMSO-d_6): 0.63 (3H, s, 18-CH_3), 0.90 (6H, s, 19-CH_3, 21-CH_3), 1.95 (2H, m, 24-CH_2), 2.64 (2H, m, NH_2), 3.58 (1H, m, 3β-H).

(3α,5β,12α)-3,12-Dihydroxycholan-24-amine (3b)

Obtained from 4.0 g (10.2 mmol) of **2b**. Eluent CH_2Cl_2:CH_3OH:Et_3N 100:10:5, R_f 0.3. White powder (68%, 2.6 g). M. p. 108-110°C. ^{1}H NMR (400 MHz, DMSO-d_6): 0.58 (3H, s, 18-CH_3), 0.83 (3H, s, 19-CH_3), 0.91 (3H, d, *J* 6.5 Hz, 21-CH_3), 2.45 (2H, m, NH_2), 3.35 (1H, m, 3β-H), 3.78 (1H, s, 12β-H). ^{13}C NMR (100.6 MHz, DMSO-d_6): 11.8, 12.5, 17.4, 23.1, 23.5, 26.1, 27.0, 27.4, 28.7, 30.1, 30.2, 32.9, 34.4, 34.9, 35.3, 36.3, 41.6, 42.3, 45.7, 45,9, 46.3, 47.5, 69.9, 71.0.

(3α,5β,7α,12α)-3,7,12-Trihydroxycholan-24-amine (3c)

Obtained from 4.3 g (10.4 mmol) of **2c**. Eluent CH_2Cl_2:CH_3OH:Et_3N 100:10:5, R_f 0.2. White powder (68%, 2.8 g, 7.1 mmol). M. p. 110-112°C. ^{1}H NMR (400 MHz, DMSO-d_6): 0.58 (3H, s, 18-CH_3), 0.80 (3H, s, 19-CH_3), 0.91 (3H, d, *J* 7.0 Hz, 21-CH_3), 3.17 (1H, m, 3β-H), 3.60 (1H, s, 12β-H), 3.78 (1H, s, 7β-H), 4.00 (1H, s, 7-OH), 4.09 (1H, s, 12-OH), 4.30 (1H, br. s, 3-OH). ^{13}C NMR (100.6 MHz, DMSO-d_6): 11.8, 12.4, 17.4, 23.1, 23.5, 26.1, 27.0, 27.3, 28.6, 30.1, 30.2, 32.9, 33.8, 35.1, 35.3, 35.4, 41.3, 41.5, 42.3, 45.7, 46.2, 66.2, 70.3, 71.0.

General procedure of Cu-catalyzed amination

A mixture of amine **3** (0.3 mmol), aryl halide (0.1 mmol), CuI (0.02 mmol), L-proline (0.04 mmol) and K_2CO_3 (0.4 mmol) in DMSO (1 ml) was stirred at 110 °C in a glass vial with a screw cap under argon atmosphere for 24 h. The reaction mixture was cooled to rt, diluted with CH_2Cl_2 (15 ml) and washed with H_2O (3 × 10 ml). The organic layer was dried over Na_2SO_4, evaporated, and the product was purified by column chromatography.

4-[(3*α*,5β,12*α*)-3,12-Dihydroxycholan-24-ylamino]toluene (4)

Obtained from 56.7 mg (0.15 mmol) of **3b**, 21.8 mg (0.1 mmol) of 4-iodotoluene, 3.8 mg (0.02 mmol) of CuI, 4.6 mg (0.04 mmol) of L-proline, 27.6 mg (0.2 mmol) of K_2CO_3 in DMSO (1 ml). Pale-brown powder (95%, 44.4 mg). ^{1}H NMR (400 MHz, DMSO-d_6): 0.59 (3H, s, 18-CH_3), 0.83 (3H, s, 19-CH_3), 0.93 (3H, d, *J* 6.5 Hz, 21-CH_3), 2.12 (3H, s, CH_3), 3.78 (1H, s, 12β-H), 4.19 (1H, d, *J* 3.8 Hz, 12-OH), 4.47 (1H, d, *J* 3.8 Hz , 3-OH), 5.22 (1H, t, *J* 5.6 Hz., NH), 6.43 (2H, d, *J* 8.2 Hz), 6.85 (2H, d, *J* 8.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.7, 17.6, 20.3, 23.1, 23.6, 26.1, 26.3, 27.1, 27.6, 28.5, 30.4, 33.2, 33.6, 34.1, 35.2, 35.4, 36.0, 36.4, 42.0, 44.9, 46.4, 47.5, 48.2, 71.7, 73.14, 112.9, 126.3, 129.6, 146.2

1,3-Bis[(3α,5β)-3-hydroxycholan-24-ylamino]benzene (5a)

Pale-brown powder (40%, 31.9 mg). M.p. 123-125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.63 (6H, s, 18-CH_3), 0.91 (6H, s, 19-CH_3), 0.92 (6H, d, *J* 6.4 Hz, 21-CH_3), 3.03 (4H, m, 24-CH_2), 3.61 (2H, m, 3β-H), 5.85 (1H, t, *J* 1.9 Hz, 2-H_{Ar}), 5.98 (2H, dd, *J* 8.0 Hz, 1.9 Hz, 4-H_{Ar} and 6-H_{Ar}), 6.95 (1H, t, *J* 8.0 Hz, 5-H_{Ar}). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.0, 18.6, 20.8, 23.3, 24.2, 26.2, 26.4, 27.2, 28.3, 30.5, 33.3, 34.5, 35.3, 35.6, 35.8, 36.4, 40.1, 40.4, 42.0, 42.7, 44.6, 56.1, 56.4, 71.8, 76.7, 77.0, 77.3, 96.9, 102.7, 129.8, 149.7.

Calculated ($C_{54}H_{88}N_2O_2$): C 81.35%, H 11.13%, N 3.51%.Found: C 81.47%, H 11.12%, N 3.55%.

4,4'-Bis[(3α,5β)-3-hydroxycholan-24-ylamino]biphenyl (5b)

White powder (41%, 35.8 mg). M.p. 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.64 (6H, s, 18-CH_3), 0.91 (6H, s, 19-CH_3), 0.92 (6H, d, *J* 6.5 Hz, 21-CH_3), 3.08 (4H, m., 24-CH_2), 3.61 (2H, m, 3β-H), 6.64 (4H, d, *J* 7.6 Hz, *m*-H_{Ar}), 7.35 (4H, d, *J* 7.6 Hz, *o*-H_{Ar}). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.0, 18.7, 20.8, 23.3, 24.2, 26.2, 26.4, 27.2, 28.3, 30.5, 33.3, 34.6, 35.3, 35.6, 35.8, 36.5, 40.2, 40.4, 42.1, 42.7, 44.8, 56.2, 56.5, 71.9, 113.1, 127.1, 130.6, 146.9.

Calculated ($C_{60}H_{92}N_2O_2 \cdot CH_2Cl_2$): C 76.45%, H 9.89%, N 2.92%. Found: C 76.22%, H 9.60%, N 3.11 %.

General procedure of Pd-catalyzed amination

A mixture of amine **3** (0.3 mmol), aryl halide (0.1 mmol), $Pd(dba)_2$ (0.012 mmol), BINAP (0.015 mmol) and Cs_2CO_3 (0.4 mmol) in dioxane (2 ml) was stirred at 100 °C in a glass vial with a screw cap under argon atmosphere for 24 h. The reaction mixture was cooled to rt, diluted with CH_2Cl_2 (15 ml) and washed with H_2O (3 × 10 ml). The organic layer was dried over Na_2SO_4, evaporated, and the product was purified by column chromatography.

1,3-bis[(3α,5β)-3-hydroxycholan-24-ylamino]benzene (5a)

Obtained from 65.1 mg (0.18 mmol) of **3a**, 7.1 μl (0.06 mmol) of 1,3-dibromobenzene, 4.1 mg (0.0072 mmol) of $Pd(dba)_2$, 5.6 mg (0.009 mmol) of BINAP, 34.6 mg (0.36 mmol) of *t*-BuONa in dioxane (1 ml). Pale-brown powder (61%, 29.2 mg).

1,8-Bis[(3*α*,5β)-3-hydroxycholan-24-ylamino]-9,10-anthraquinone (5c)

Obtained from 108.5 mg (0.3 mmol) of **3a** and 27.7 mg (0.1 mmol) of 1,8-dichloro-9,10-anthraquinone. Dark-violet powder (88%, 81,6 mg). M.p. 156-158 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.62 (6H, s, 18-CH_3), 0.90 (6H, s, 19-CH_3), 0.94 (6H, d, *J* 6.5 Hz, 21-CH_3), 3.25 (4H, m, 24-CH_2), 3.61 (2H, m, 3β-H), 6.99 (2H, d, *J* 8.4 Hz, *o*-H_{Ar}), 7.45 (2H, t, *J* 8.4 Hz, *m*-H_{Ar}), 7.52 (2H, d, *J* 7.3 Hz, *p*-H_{Ar}), 9.66 (2H, t, *J* 4.9 Hz, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.1, 18.7, 20.8, 23.4, 24.3, 25.8, 26.5, 27.2, 28.3, 30.6, 33.5, 34.6, 35.4, 35.7, 35.9, 36.5, 40.2, 40.4, 42.1, 42.7, 43.6, 56.1, 56.5, 71.8, 114.3, 114.8, 117.7, 134.1, 134.4, 151.2, 184.8, 188.9.

Calculated ($C_{62}H_{90}N_2O_4$): C 80.30%, H 9.78%, N 3.02%. Found: C 80.63%, H 9.60%, N 2.91 %.

1,8-bis[(3*α*,5β,12*α*)-3,12-dihydroxycholan-24-ylamino]-9,10-anthraquinone (5d)

Obtained from 108.5 mg (0.3 mmol) of **3b**, 27.7 mg (0.1 mmol) of **6a**, 2.3 mg (0.004 mmol) of $Pd(dba)_2$, 3.1 mg (0.005 mmol) of BINAP, 130.3 mg (0.4 mmol) of Cs_2CO_3 and 0.4 ml of dioxane. Dark-violet powder (74%, 71 mg). M.p. 180-182 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.67 (6H, s, 18-CH_3), 0.89 (6H, s, 19-CH_3), 1.03 (6H, d, *J* 6.4 Hz, 21-CH_3), 3.24 (4H, m, 24-CH_2), 3.59 (2H, m, 3β-H), 3.99 (2H, br. s., 12β-H), 6.98 (2H, d, *J* 8.4 Hz, *o*-H_{Ar}), 7.44 (2H, t, *J* 8.3 Hz, *m*-H_{Ar}) 7.50 (2H, d, *J* 7.3 Hz, *p*-H_{Ar}), 9.61 (2H, br. s., NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.7, 17.8, 23.1, 23.7, 25.7, 26.1, 27.1, 27.6, 28.6, 30.5, 33.5, 33.6, 34.1, 35.2, 35.4, 36.0, 36.4, 42.0, 43.6, 46.5, 47.4, 48.3, 71.7, 73.2, 114.3, 114.7, 117.7, 134.0, 134.3, 151.2, 184.7, 188.9.

Calculated ($C_{62}H_{90}N_2O_6 \cdot 3CH_2Cl_2$): C 65.30%, H 7.97%, N 2.31%. Found: C 65.68%, H 7.88%, N 2.27%.

1,8-bis[(3α,5β,12α)-3,7,12-Trihydroxycholan-24-ylamino]-9,10-anthraquinone (5e)

Obtained from 118.1 mg (0.3 mmol) of **3c**, 27.7 mg (0.1 mmol) of **6a**, 2.3 mg (0.004 mmol) of $Pd(dba)_2$, 3.1 mg (0.005 mmol) of BINAP, 130.3 mg (0.4 mmol) of Cs_2CO_3 and 0.4 ml of dioxane. Violet powder (34%, 33.7 mg). M.p. 171-173 ^oC. ^1H NMR (400 MHz, $CDCl_3$): 0.63 (6H, s, 18-CH_3), 0.82 (6H, s, 19-CH_3), 1.02 (6H, d, *J* 6.4 Hz, 21-CH_3), 3.25 (2H, m, 3β-H), 3.35 (4H, m, 24-CH_2), 3.8 (2H, br. s., 7β-H), 3.96 (2H, br. s., 12β-H), 7.01 (2H, d, *J* 8.4 Hz, *o*-H_{Ar}), 7.44 (2H, t, *J* 8.3 Hz, *m*-H_{Ar}) 7.50 (2H, d, *J* 7.3 Hz, *p*-H_{Ar}), 9.70 (2 H, br. s., NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.3, 17.8, 22.4, 23.3, 25.1, 26.3, 28.0, 28.1, 30.5, 33.6, 34.7, 34.9, 35.3, 35.6, 39.3, 41.5, 41.70, 43.2, 46.4, 47.2, 68.5, 72.1, 73.3, 114.5, 114.9, 117.8, 134.1, 134.4, 151.1, 184.6, 188.8.

Calculated ($C_{62}H_{90}N_2O_8 \cdot 3CH_3OH$): C 71.79%, H 9.45%, N 2.58%. Found: C 71.93%, H 9.41%, N 2.45%.

1,5-bis[(3α,5β)-3-Hydroxycholan-24-ylamino]-9,10-anthraquinone (5f)

Obtained from 108.5 mg (0.3 mmol) of **3a** and 27.7 mg (0.1 mmol) **6b**. Dark-violet powder (76%, 70,5 mg). M.p. 152-154 ^oC. ^1H NMR (400 MHz, $CDCl_3$): 0.64 (6H, s, 18-CH_3), 0.91 (6H, s, 19-CH_3), 0.95 (6H, d, *J* 6.4 Hz, 21-CH_3), 3.26 (4H, m, 24-CH_2), 3.61 (2H, m, 3β-H), 6.94 (2H, d, *J* 8.1 Hz, *o*-H_{Ar}), 7.51 (4H, m, *m*-H_{Ar} and *p*-H_{Ar}), 9.69 (2H, t, *J* 4.9 Hz, NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.0, 18.6, 20.8, 23.4, 24.2, 25.8, 26.4, 27.2, 28.3, 30.5, 33.4, 34.5, 35.3, 35.6, 35.8, 36.4, 40.1, 40.4, 42.1, 42.7, 43.5, 56.0, 56.5, 71.8, 112.8, 114.6, 116.3, 135.1, 136.3, 151.4, 185.4.

Calculated ($C_{62}H_{90}N_2O_4$): C 80.30%, H 9.78%, N 3.02%. Found: C 79.97%, H 9.57%, N 2.78 %.

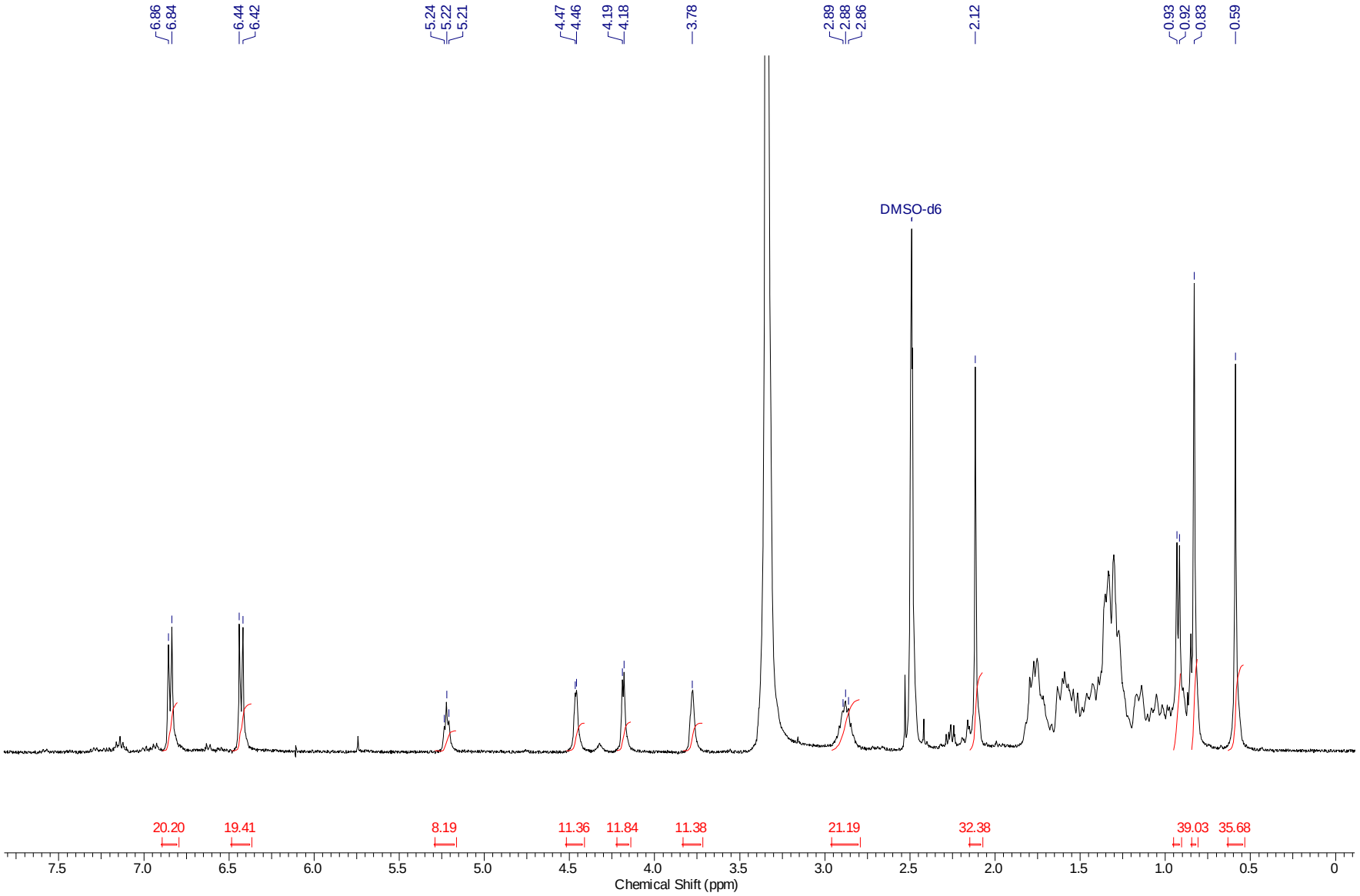
1,8-Bis[(3α,5β)-3-methoxycholan-24-ylamino]-9,10-anthraquinone (S1)

A mixture of **5c** (46 mg, 0.05 mmol) and trimethyloxonium tetrafluoroborate (17.7 mg, 0.12 mmol) in dry CH_2Cl_2 (5 ml) was stirred at ambient temperature under argon atmosphere for 24 h. The

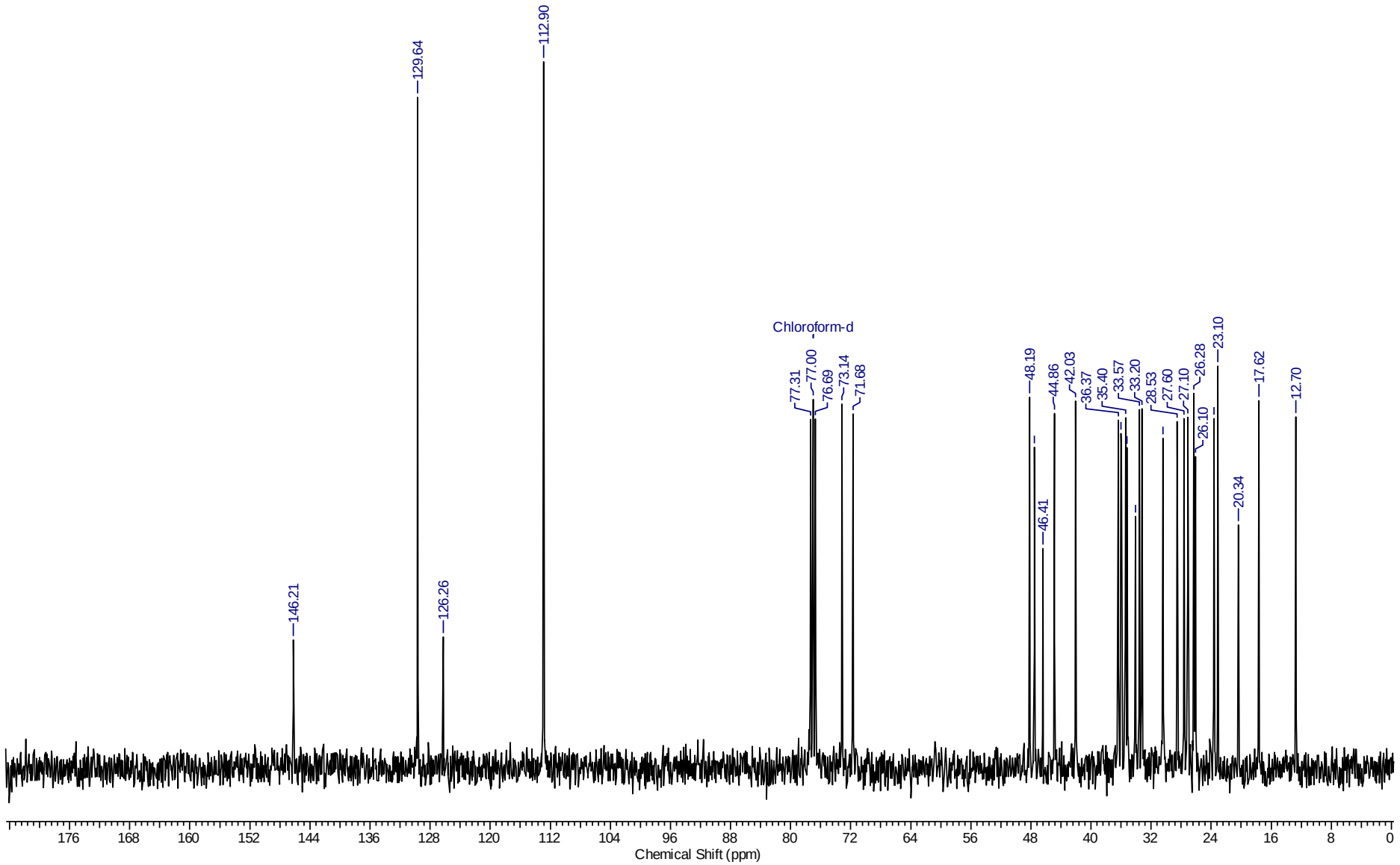
reaction mixture was diluted with CH_2Cl_2 (15 ml) and washed with H_2O (10 ml). The organic layer was dried over Na_2SO_4, evaporated, and the product was purified by column chromatography. Dark-violet powder (29%, 14 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 0.66 (6H, s, 18-CH_3), 0.92 (6H, s, 19-CH_3), 0.98 (6H, d, *J* 6.5 Hz, 21-CH_3), 3.16 (2H, m, 3β-H), 3.26 (4H, m, 24-CH_2), 3.35 (6H, s, 3-OCH_3), 7.00 (2H, d, *J* 8.1 Hz, *o*-H_{Ar}), 7.46 (2H, t, *J* 8.1 Hz, *m*-H_{Ar}) 7.52 (2H, d, *J* 7.3 Hz, *p*-H_{Ar}), 9.63 (2H, t, J 4.9 Hz., NH). ^{13}C NMR (100.6 MHz, $CDCl_3$): 12.1, 18.7, 20.8, 23.4, 24.3, 25.8, 26.4, 27.3, 28.3, 29.7, 32.7, 33.4, 34.9, 35.3, 35.6, 35.9, 40.2, 40.3, 42.0, 42.7, 43.5, 55.5, 56.1, 56.5, 80.4, 114.3, 114.7, 117.6, 134.0, 134.3, 151.2, 184.8, 188.9.

Copies of the ^{1}H and ^{13}C NMR spectra

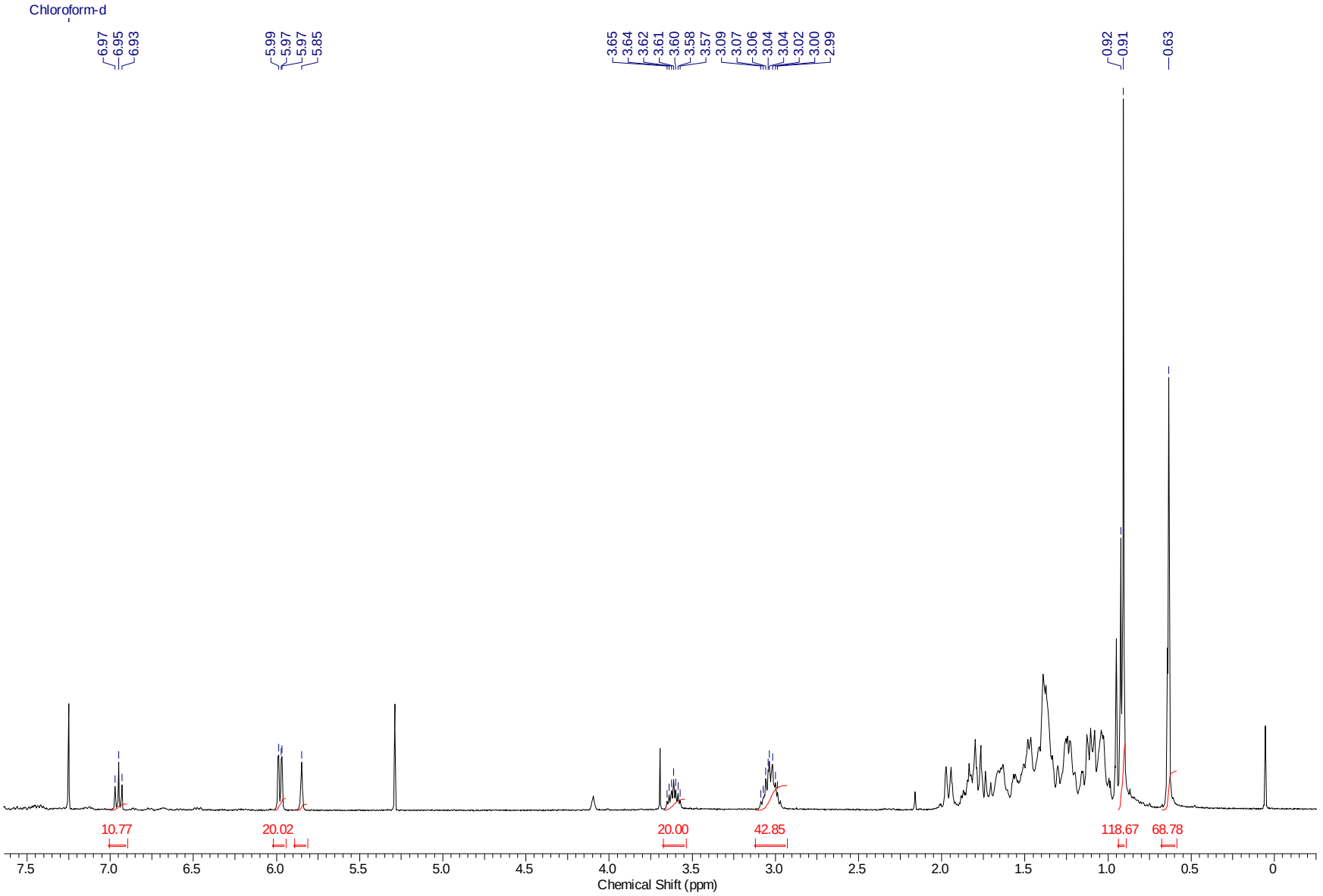
^{1}H NMR spectrum of 4-[(3α,5β,12α)-3,12-dihydroxycholan-24-ylamino]toluene (**4**) (DMSO-d_6, 400 MHz, 300 K)



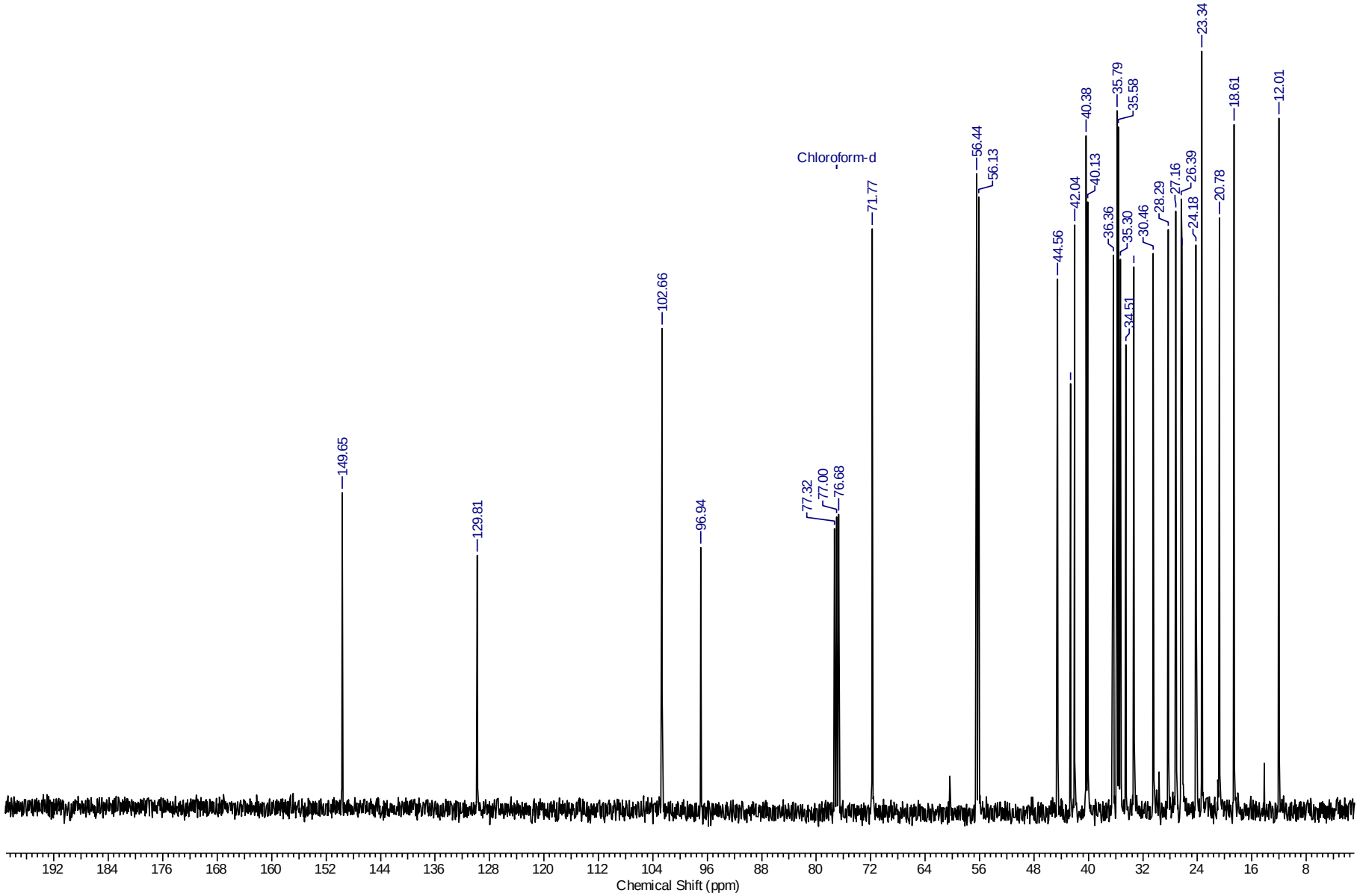
^{13}C NMR spectrum of 4-[(3α,5β,12α)-3,12-dihydroxycholan-24-ylamino]toluene (**4**) ($CDCl_3$, 100.6 MHz, 300 K)



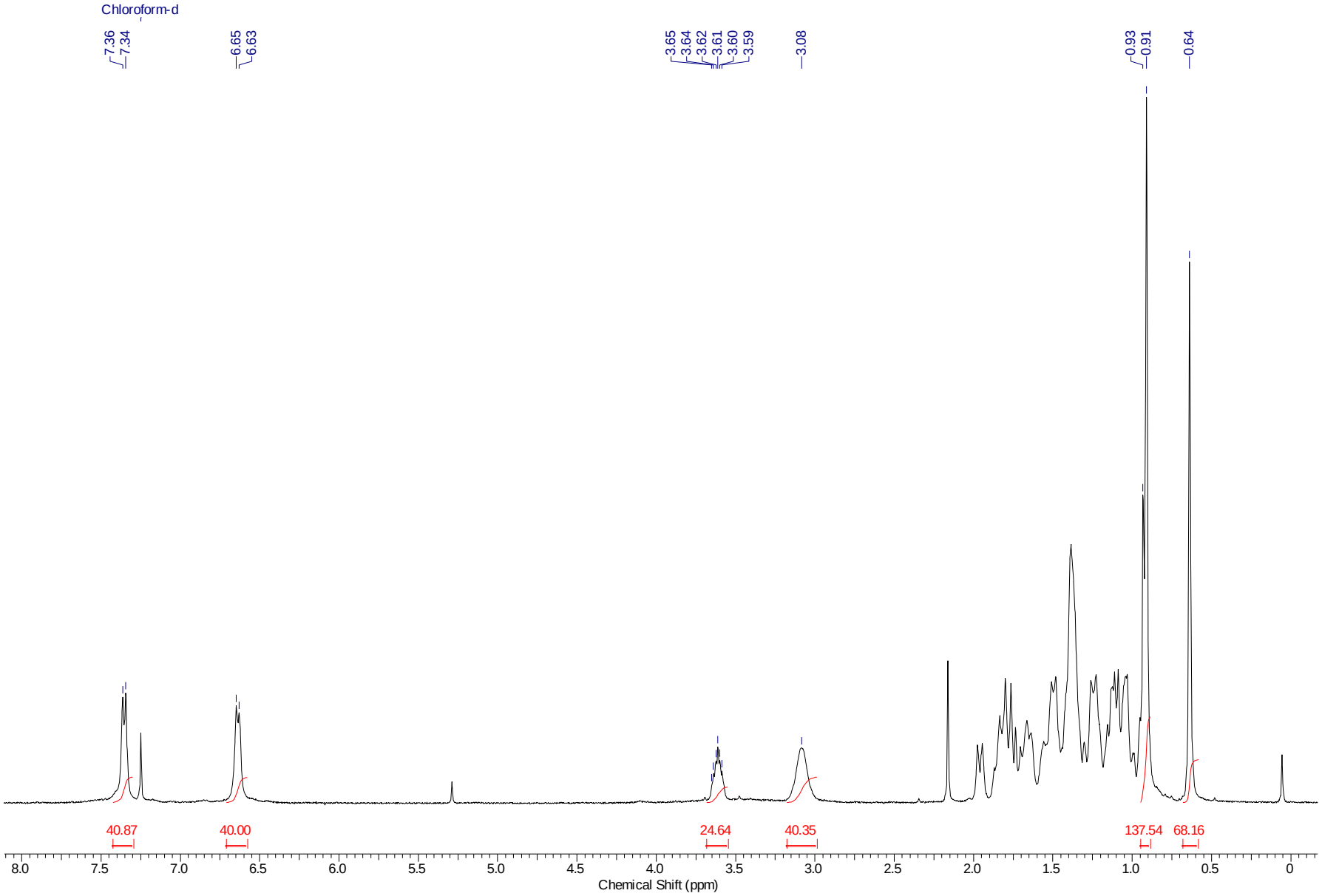
^{1}H NMR spectrum of 1,3-bis[(3α,5β)-3-hydroxycholan-24-ylamino]benzene (**5a**) ($CDCl_3$, 400 MHz, 300 K)



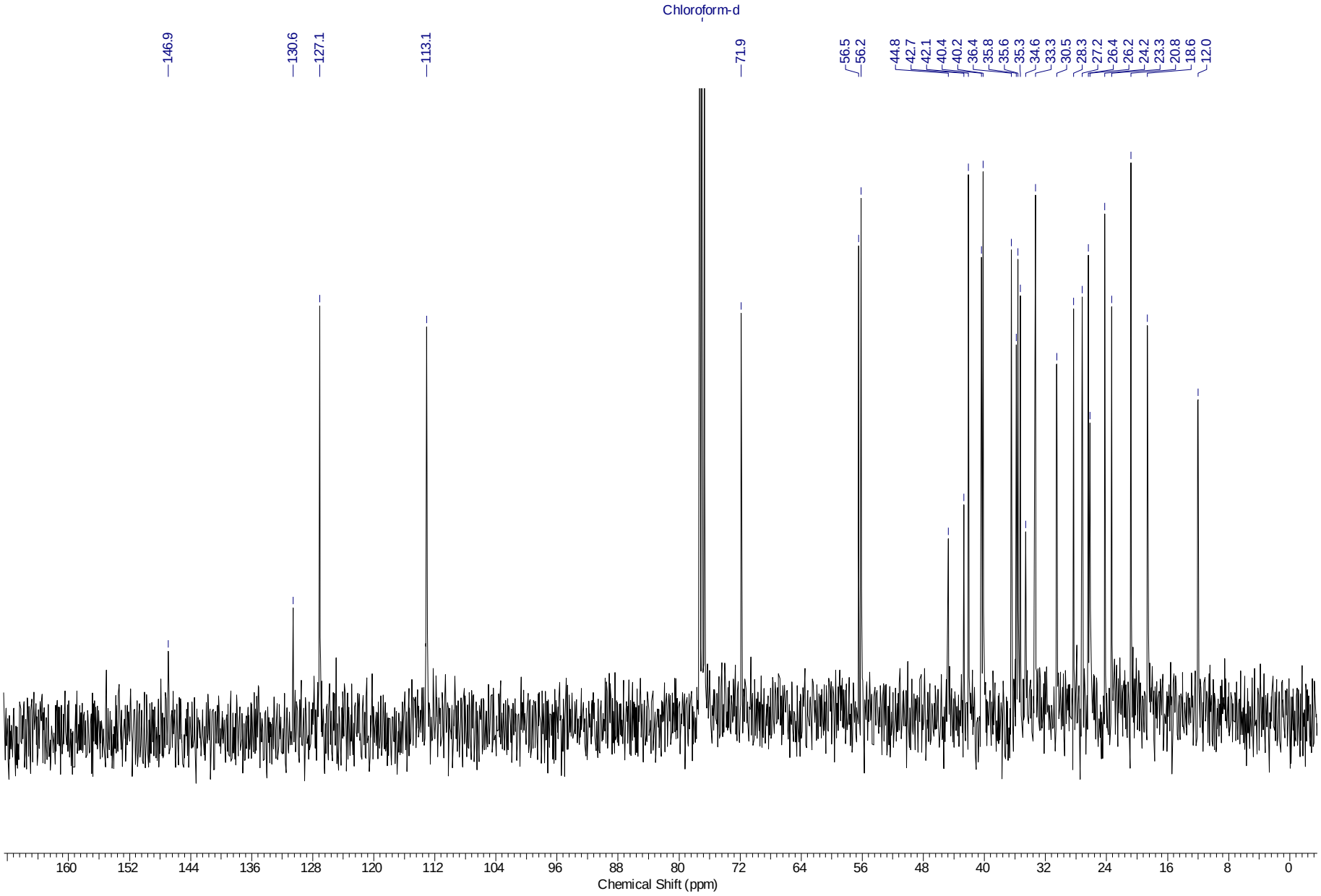
^{13}C NMR spectrum of 1,3-bis[(3α,5β)-3-hydroxycholan-24-ylamino]benzene (**5a**) ($CDCl_3$, 100.6 MHz, 300 K)



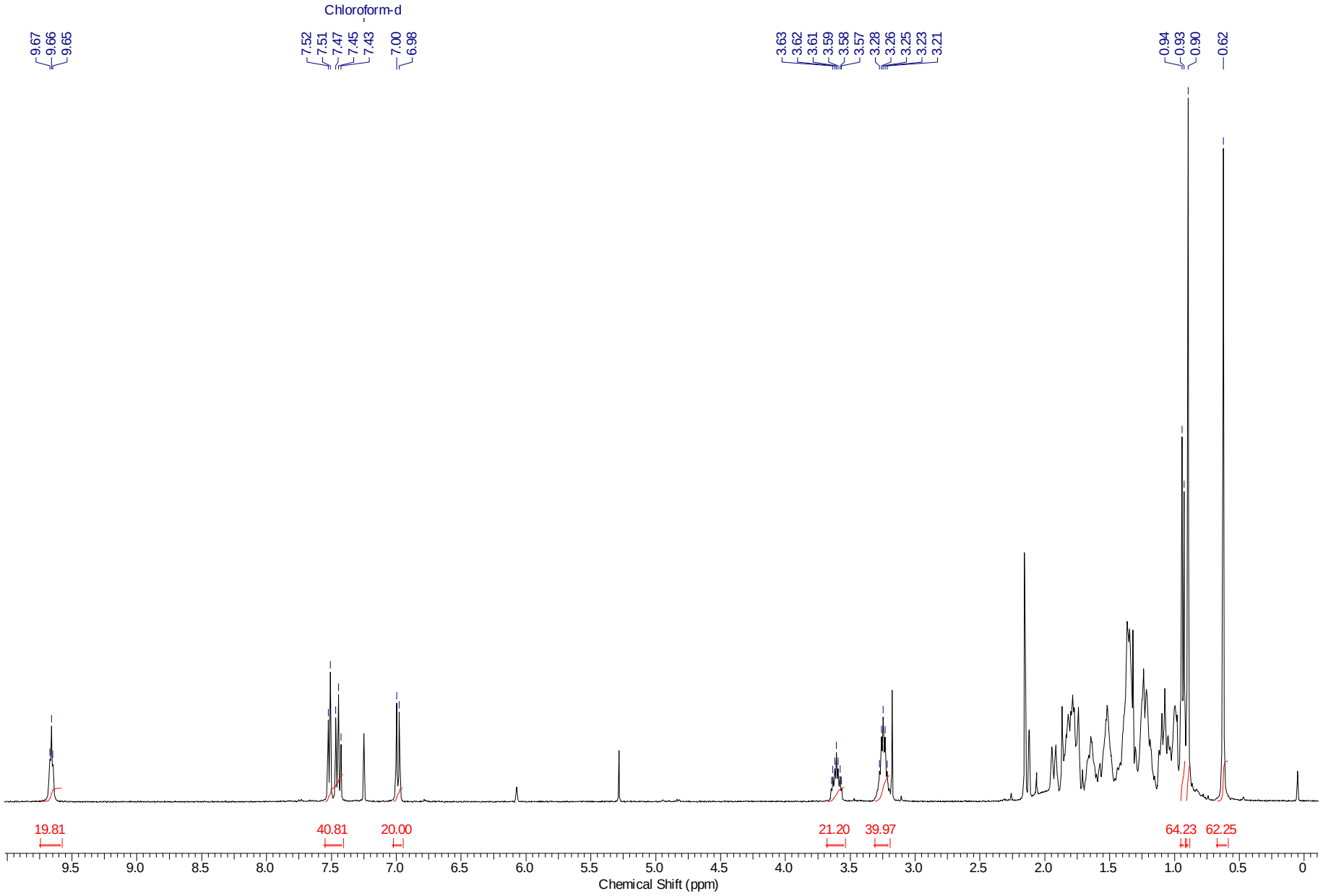
^{1}H NMR spectrum of 4,4’-bis[(3α,5β)-3-hydroxycholan-24-ylamino]biphenyl (**5b**) ($CDCl_3$, 400 MHz, 300 K)



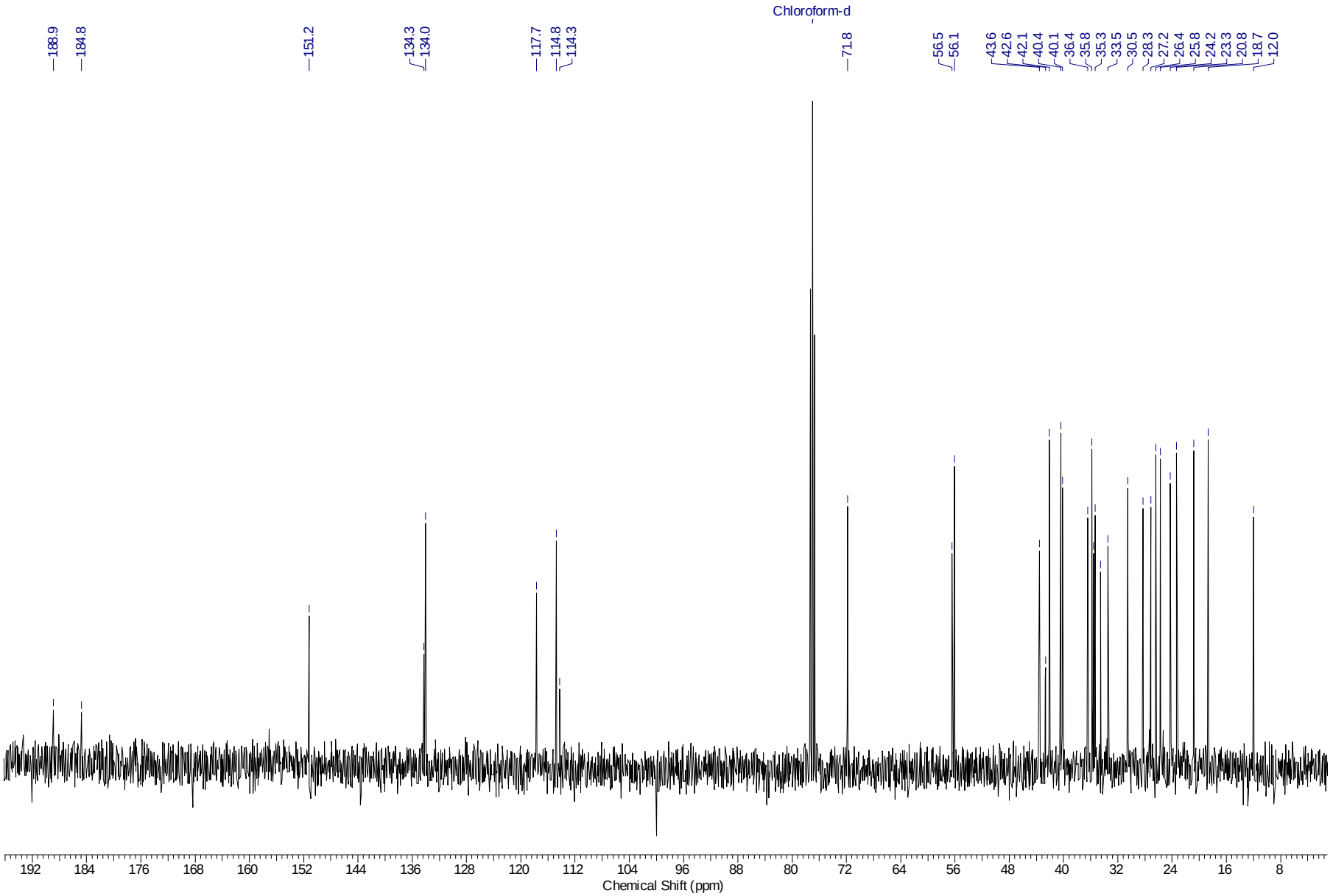
^{13}C NMR spectrum of 4,4’-bis[(3α,5β)-3-hydroxycholan-24-ylamino]biphenyl (**5b**) ($CDCl_3$, 100.6 MHz, 300 K)



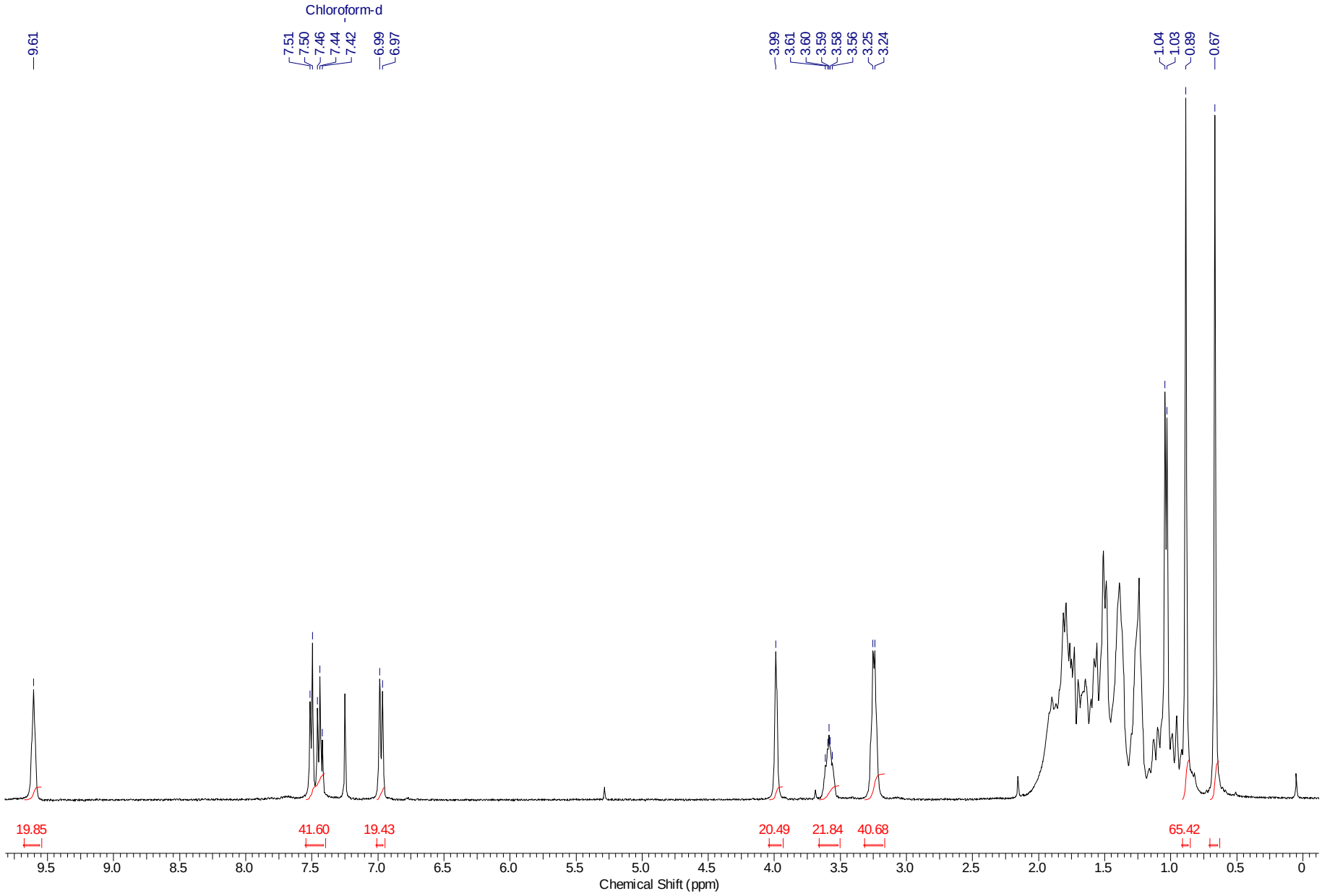
^{1}H NMR spectrum of 1,8-bis[(3α,5β)-3-hydroxycholan-24-ylamino]-9,10-anthraquinone (**5c**) ($CDCl_3$, 400 MHz, 300 K)



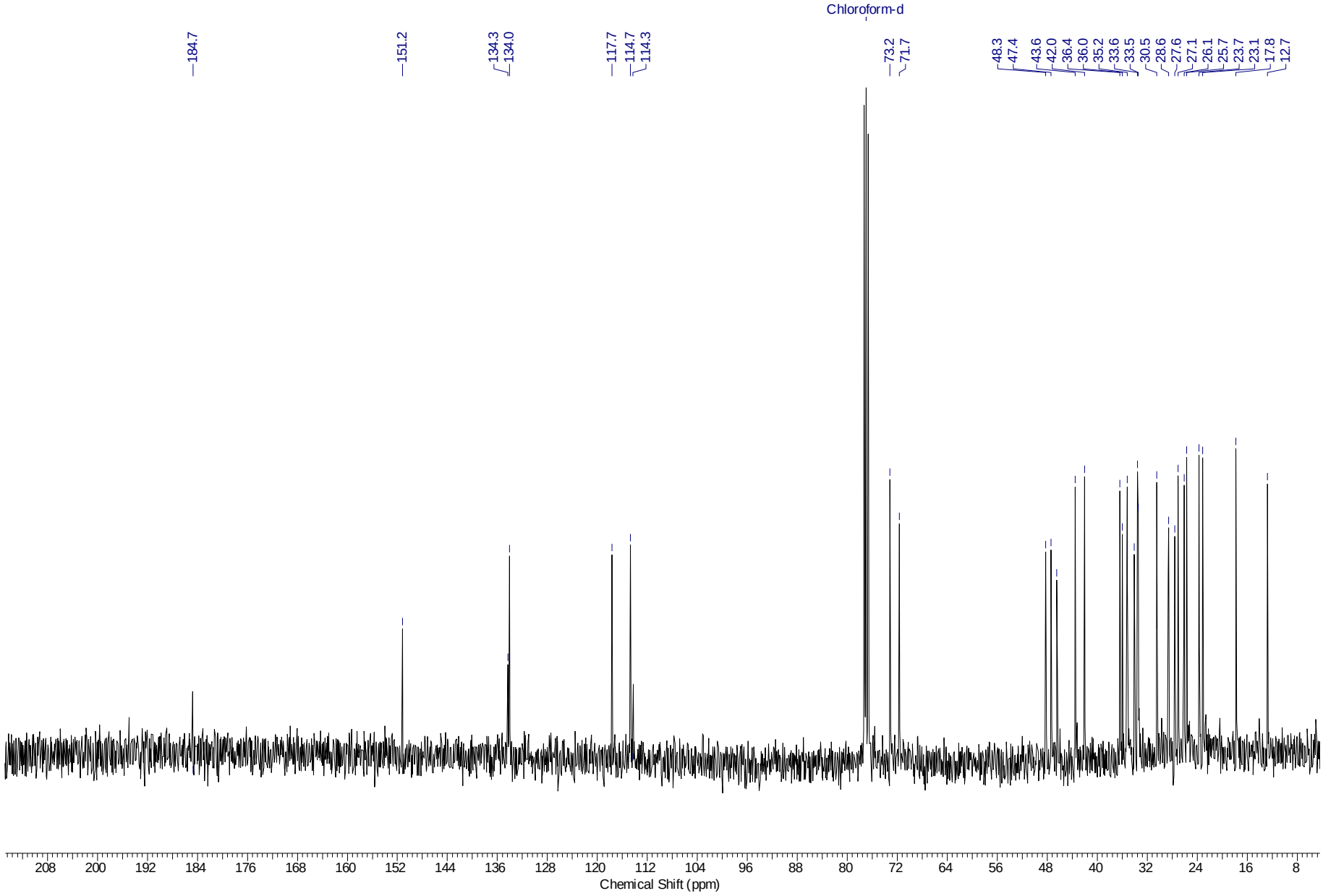
^{13}C NMR spectrum of 1,8-bis[(3α,5β)-3-hydroxycholan-24-ylamino]-9,10-anthraquinone (**5c**) ($CDCl_3$, 100.6 MHz, 300 K)



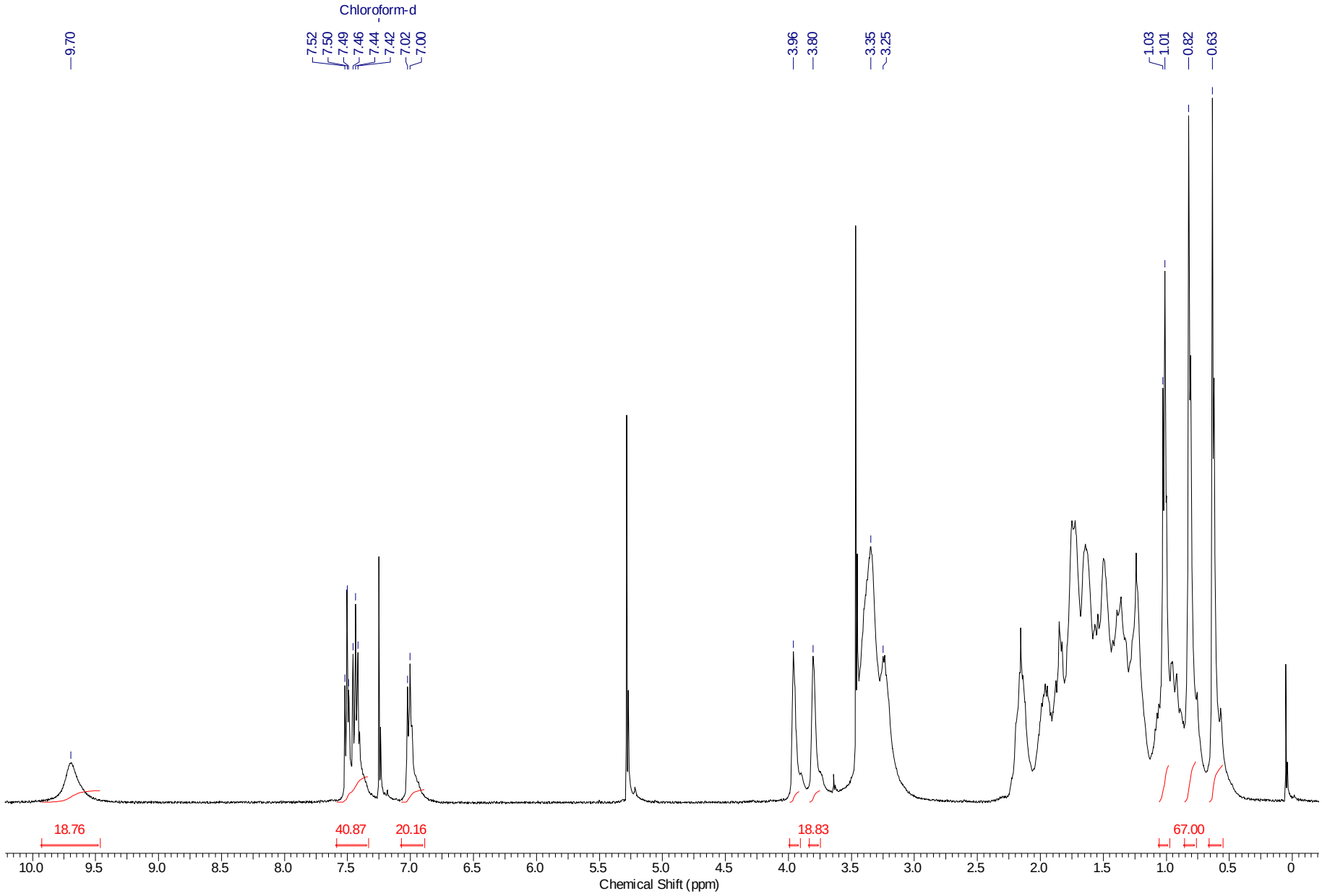
^{1}H NMR spectrum of 1,8-bis[(3α,5β,12α)-3,12-dihydroxycholan-24-ylamino]-9,10-anthraquinone (**5d**) ($CDCl_3$, 400 MHz, 300 K)



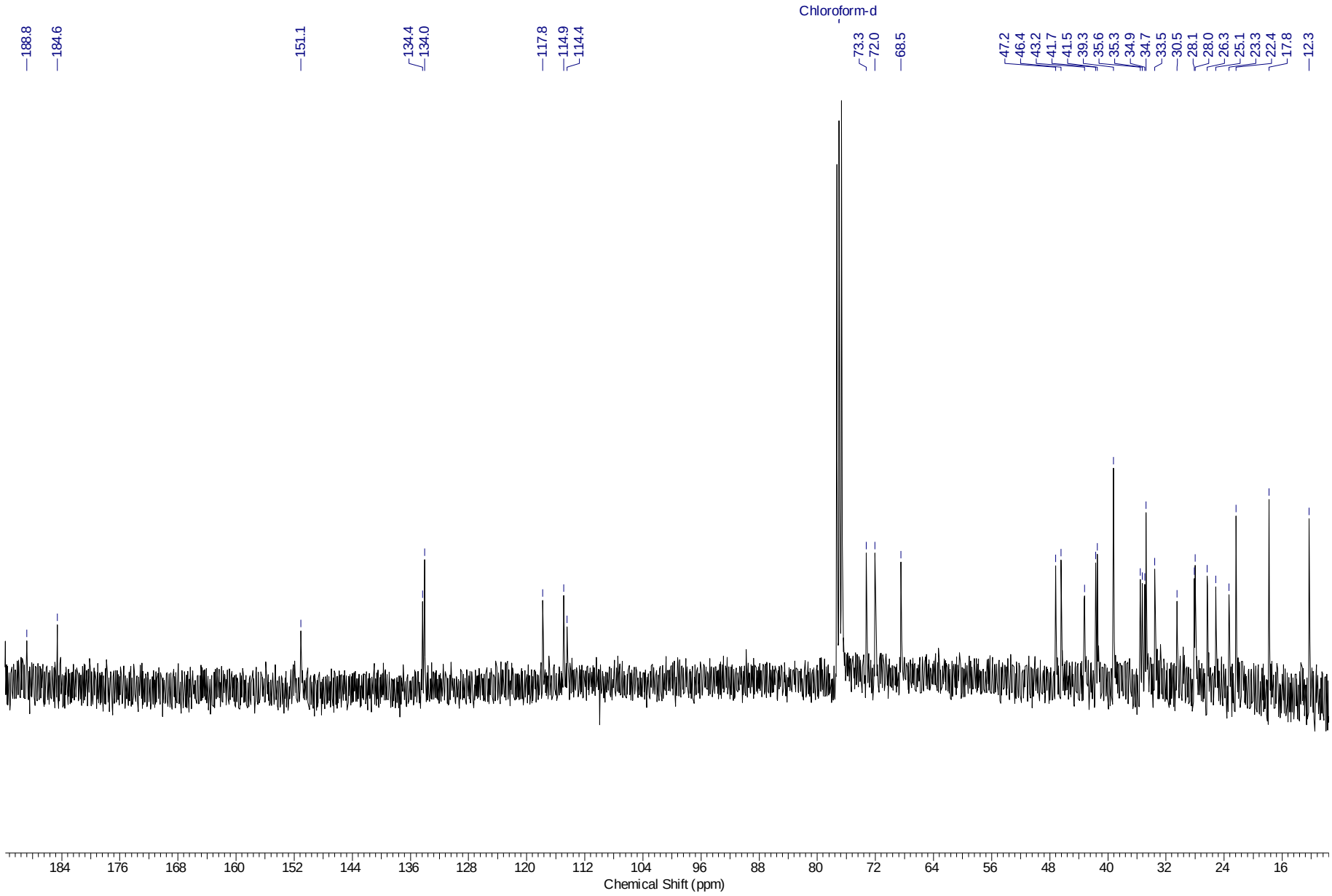
^{13}C NMR spectrum of 1,8-bis[(3α,5β,12α)-3,12-dihydroxycholan-24-ylamino]-9,10-anthraquinone (**5d**) ($CDCl_3$, 100.6 MHz, 300 K)



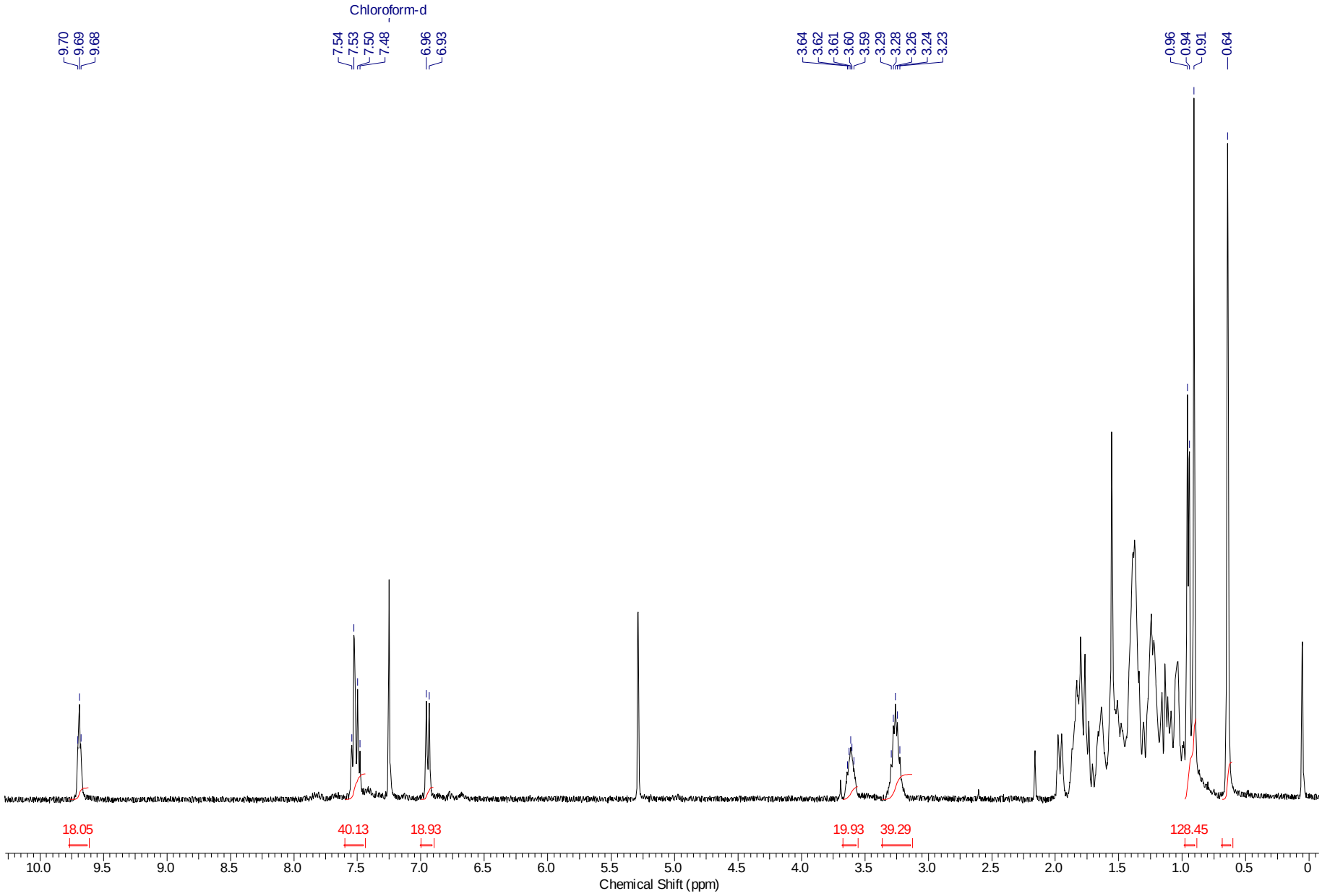
^{1}H NMR spectrum of 1,8-bis[(3α,5β,12α)-3,7,12-trihydroxycholan-24-ylamino]-9,10-anthraquinone (**5e**) ($CDCl_3$, 400 MHz, 300 K)



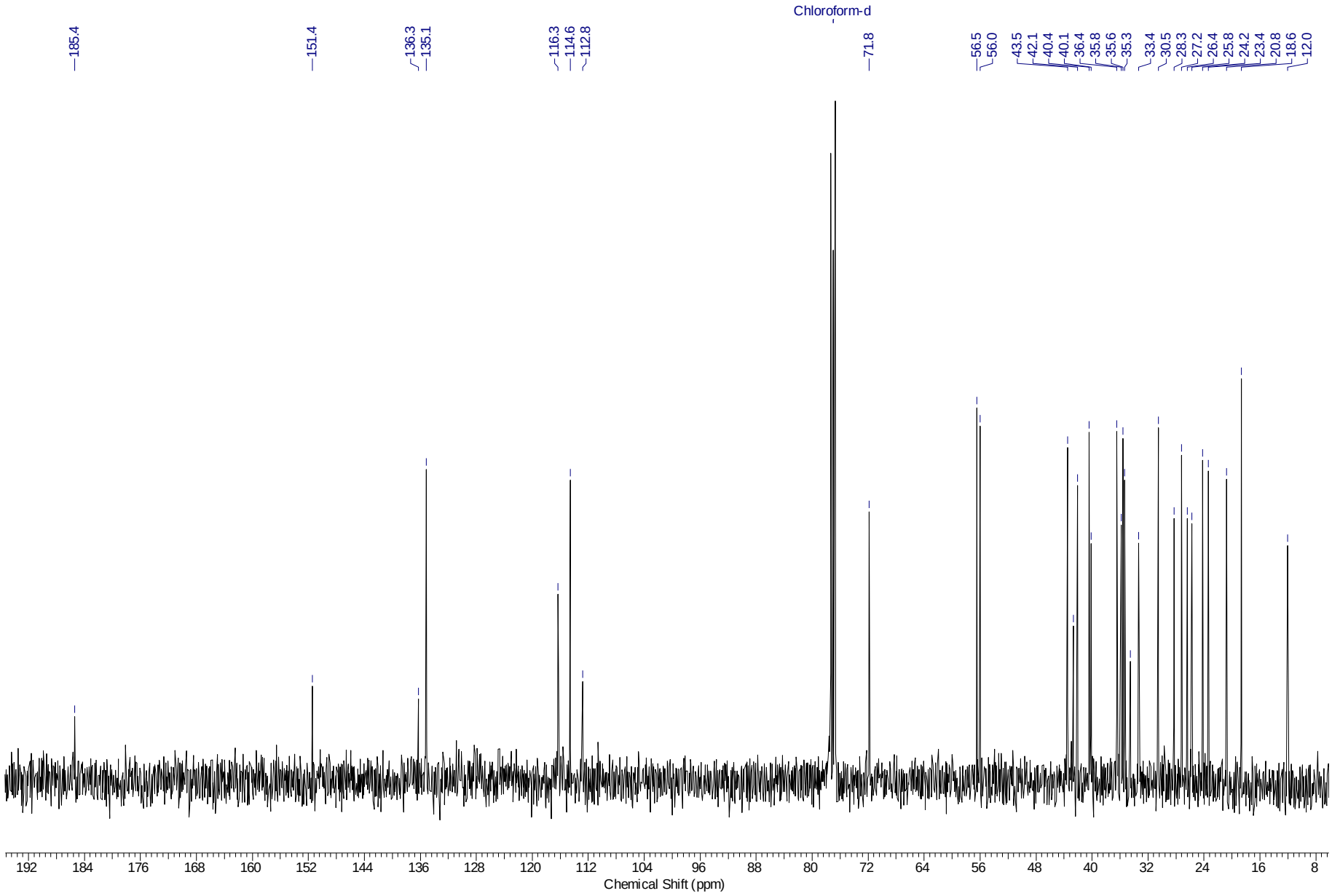
^{13}C NMR spectrum of 1,8-bis[(3α,5β,12α)-3,7,12-trihydroxycholan-24-ylamino]-9,10-anthraquinone (**5e**) ($CDCl_3$, 100.6 MHz, 300 K)



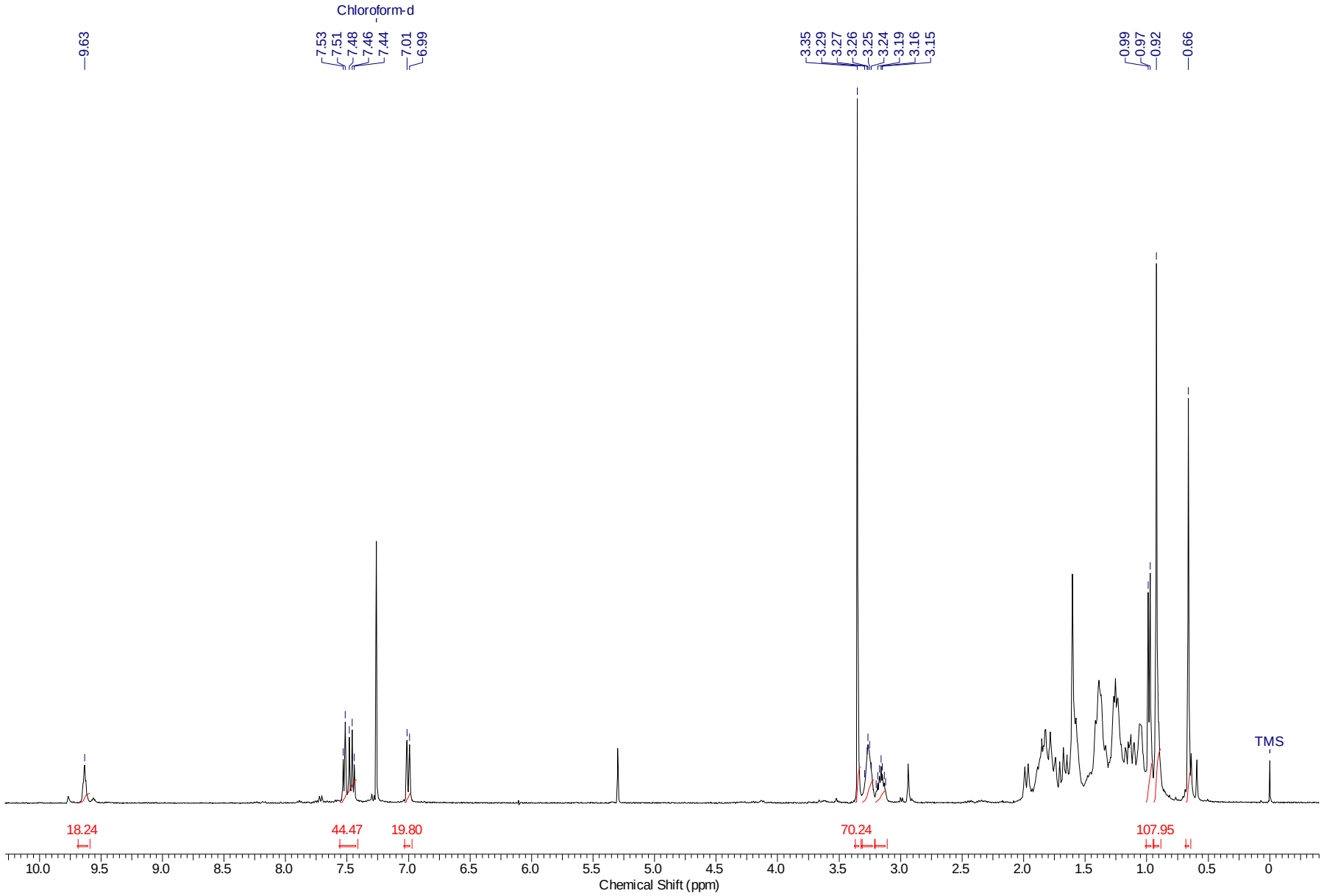
^{1}H NMR spectrum of 1,5-bis[(3α,5β)-3-hydroxycholan-24-ylamino]-9,10-anthraquinone (**5f**) ($CDCl_3$, 400 MHz, 300 K)



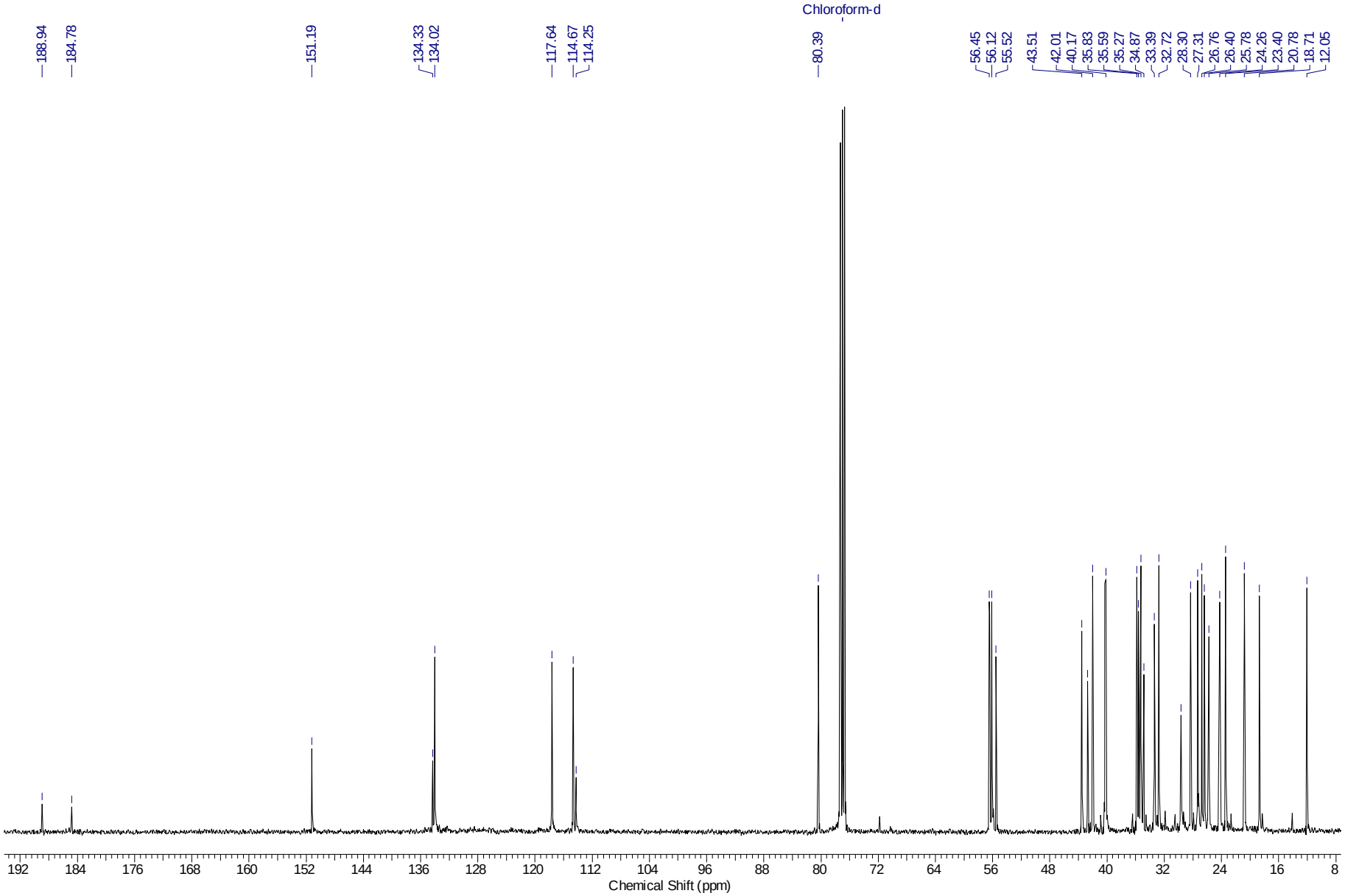
^{13}C NMR spectrum of 1,5-bis[(3α,5β)-3-hydroxycholan-24-ylamino]-9,10-anthraquinone (**5f**) ($CDCl_3$, 100.6 MHz, 300 K)



^{1}H NMR spectrum of 1,8-bis[(3α,5β)-3-methoxycholan-24-ylamino]-9,10-anthraquinone (**S1**) ($CDCl_3$, 400 MHz, 300 K)



^{13}C NMR spectrum of 1,8-bis[(3α,5β)-3-methoxycholan-24-ylamino]-9,10-anthraquinone (**S1**) ($CDCl_3$, 100.6 MHz, 300 K)



UV–vis titration

Figure S1: UV–vis spectra of the ligand **5c** (50 μM solution in MeCN) before and after addition of 5 equiv of metal perchlorates

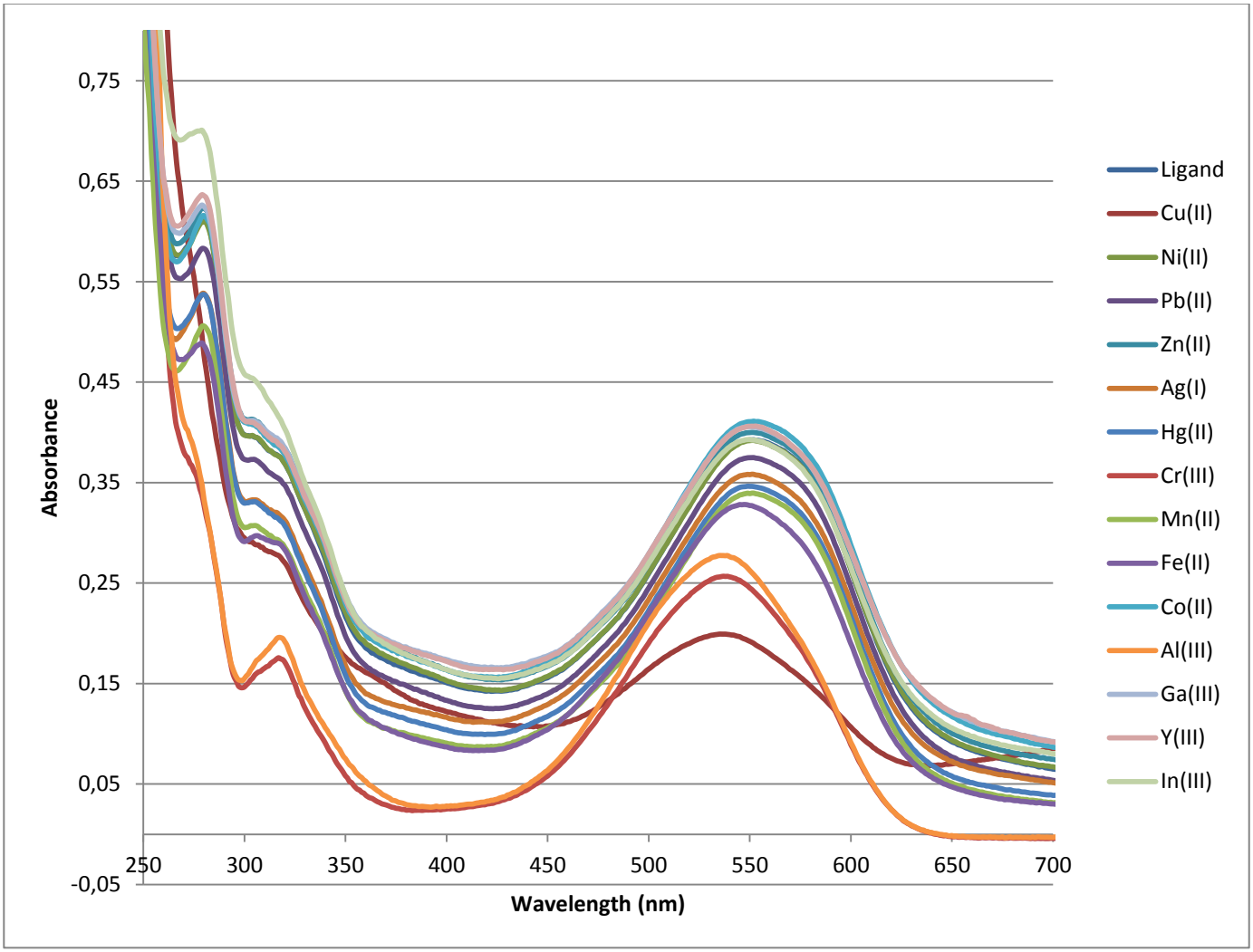


Figure S2: Evolution of UV–vis spectrum of **5c** (50 μM solution in MeCN) upon addition of $Cu(ClO_4)_2$ (0–5.0 equiv)

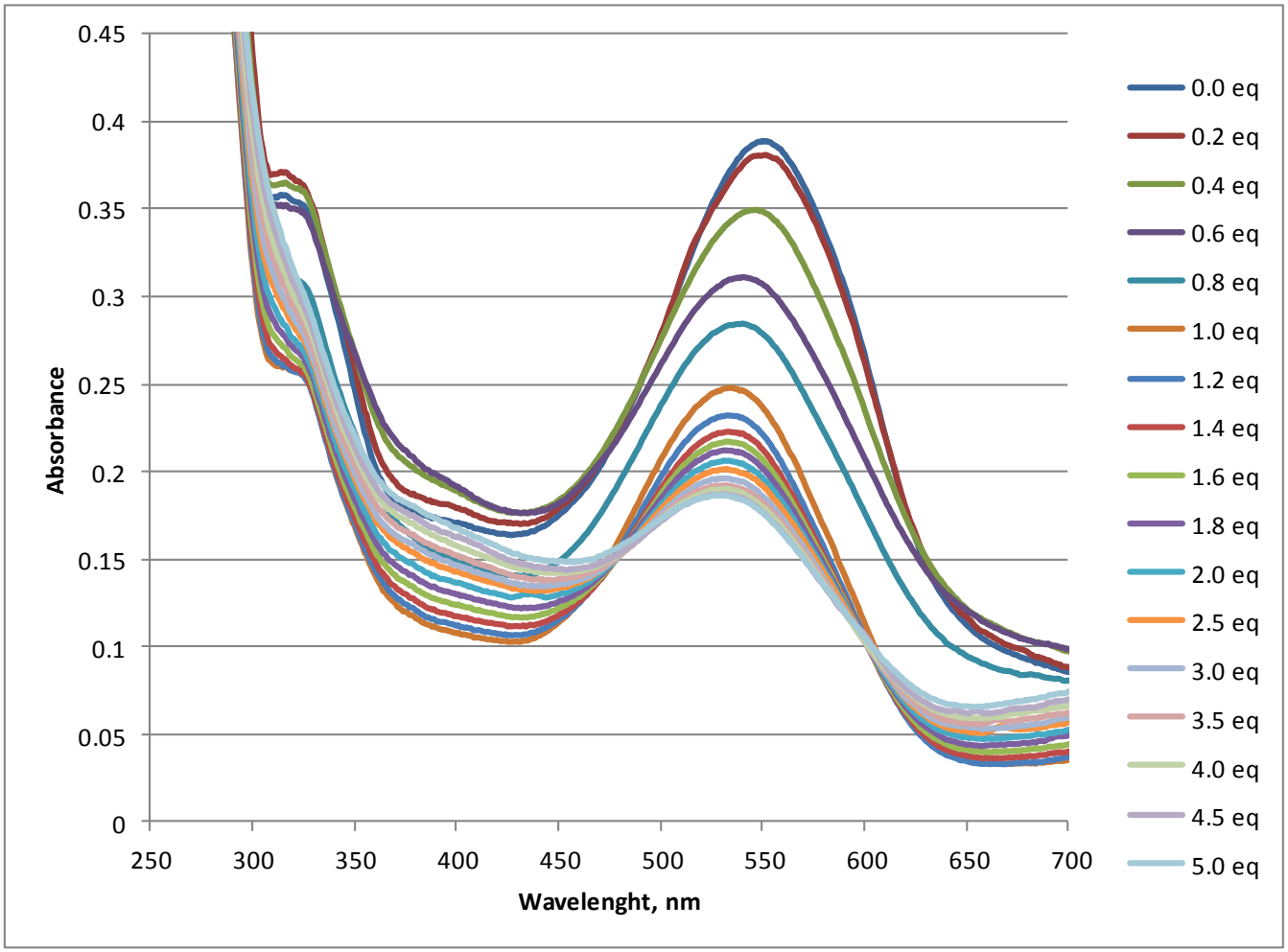


Figure S3: Changes of absorbance at 550 nm plotted against $[Cu(ClO_4)_2]/[\mathbf{5c}]_{total}$

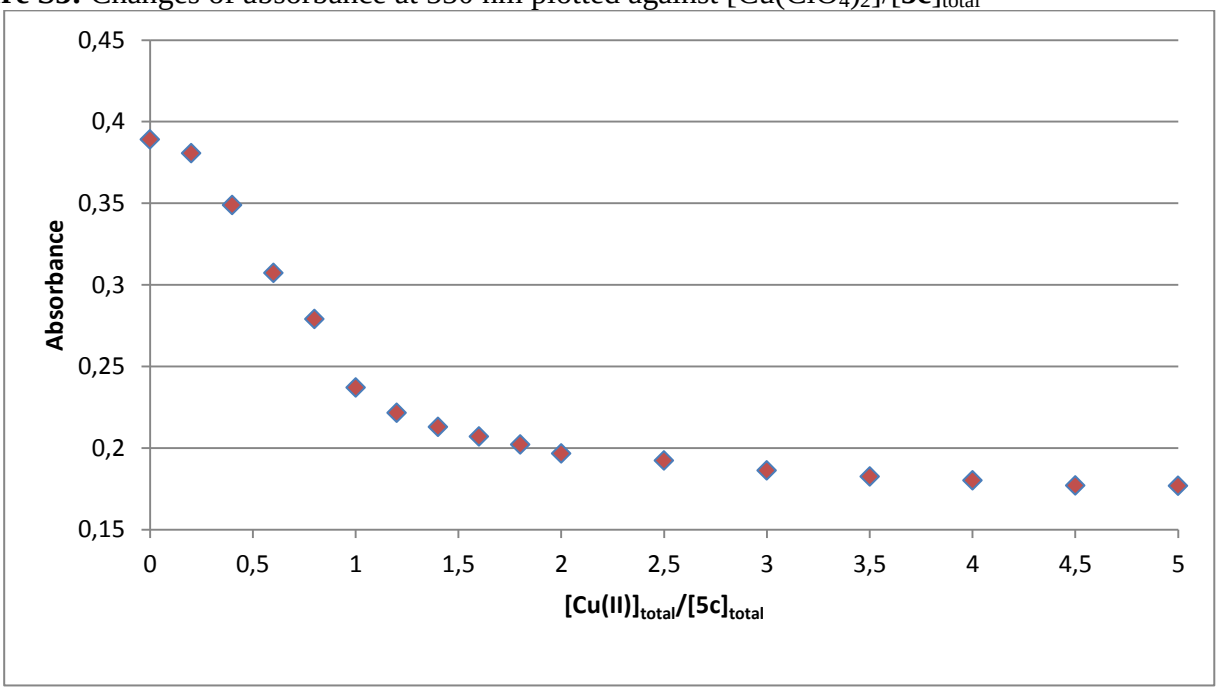


Figure S4: Evolution of UV–vis spectrum of **5c** (50 µM solution in MeCN) upon addition of $Al(ClO_4)_3$ (0–5.0 equiv)

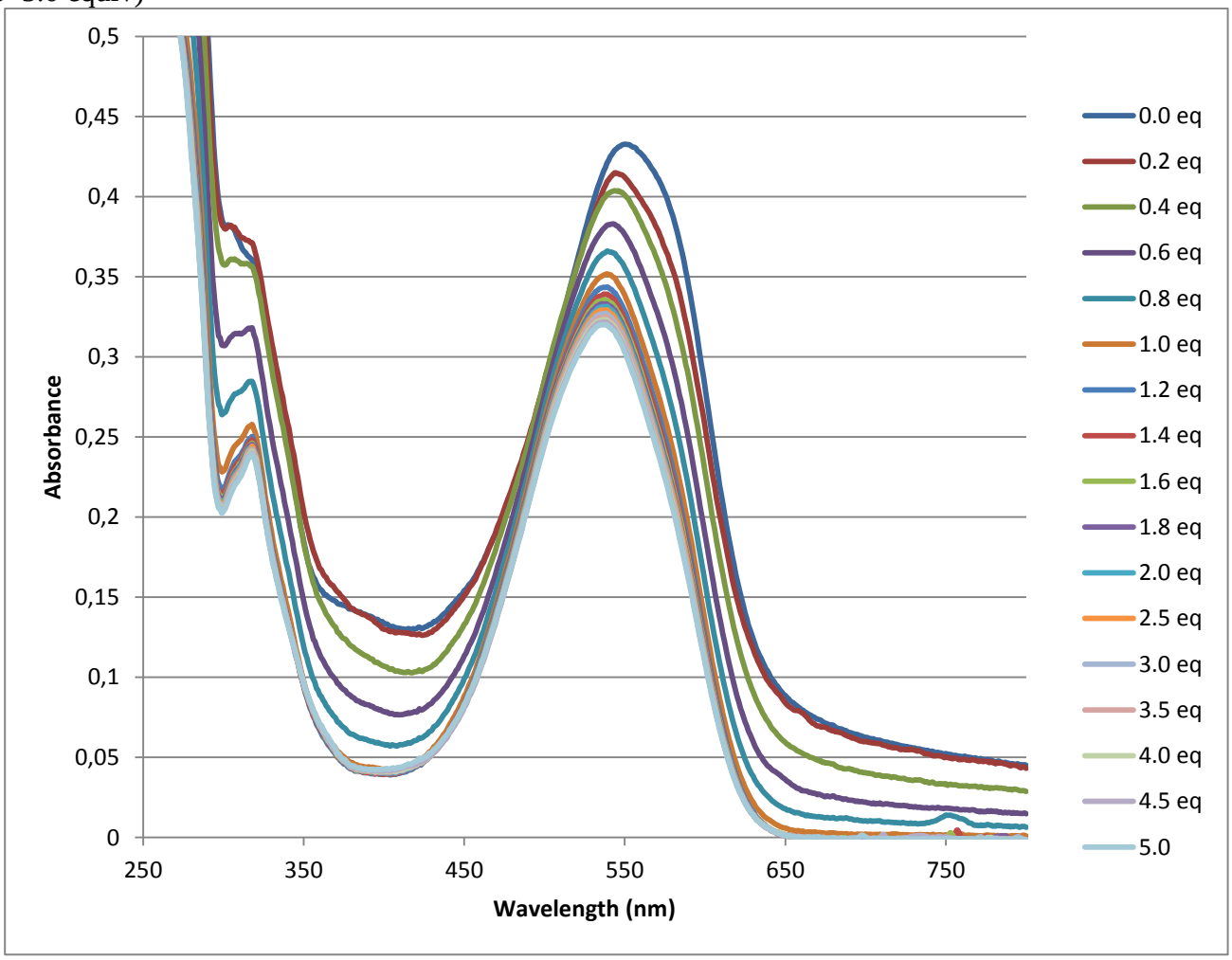


Figure S5: Changes of absorbance at 550 nm plotted against $[Al(ClO_4)_3]/[\mathbf{5c}]_{total}$

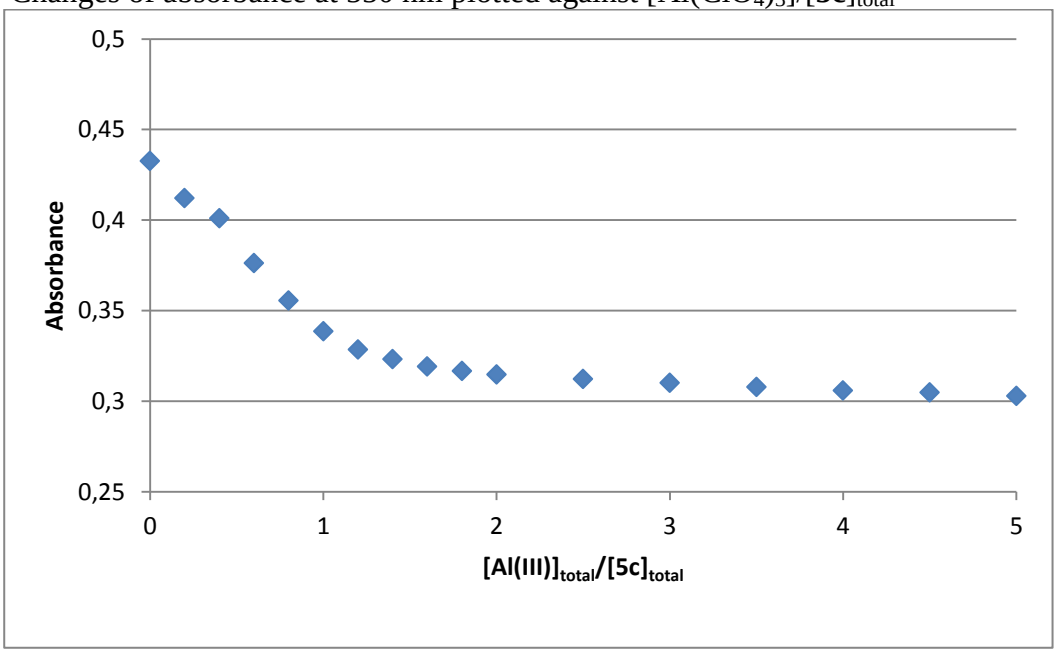


Figure S6: Evolution of UV–vis spectrum of **5c** (50 µM solution in MeCN) upon addition of $Cr(ClO_4)_3$ (0–5.0 equiv)

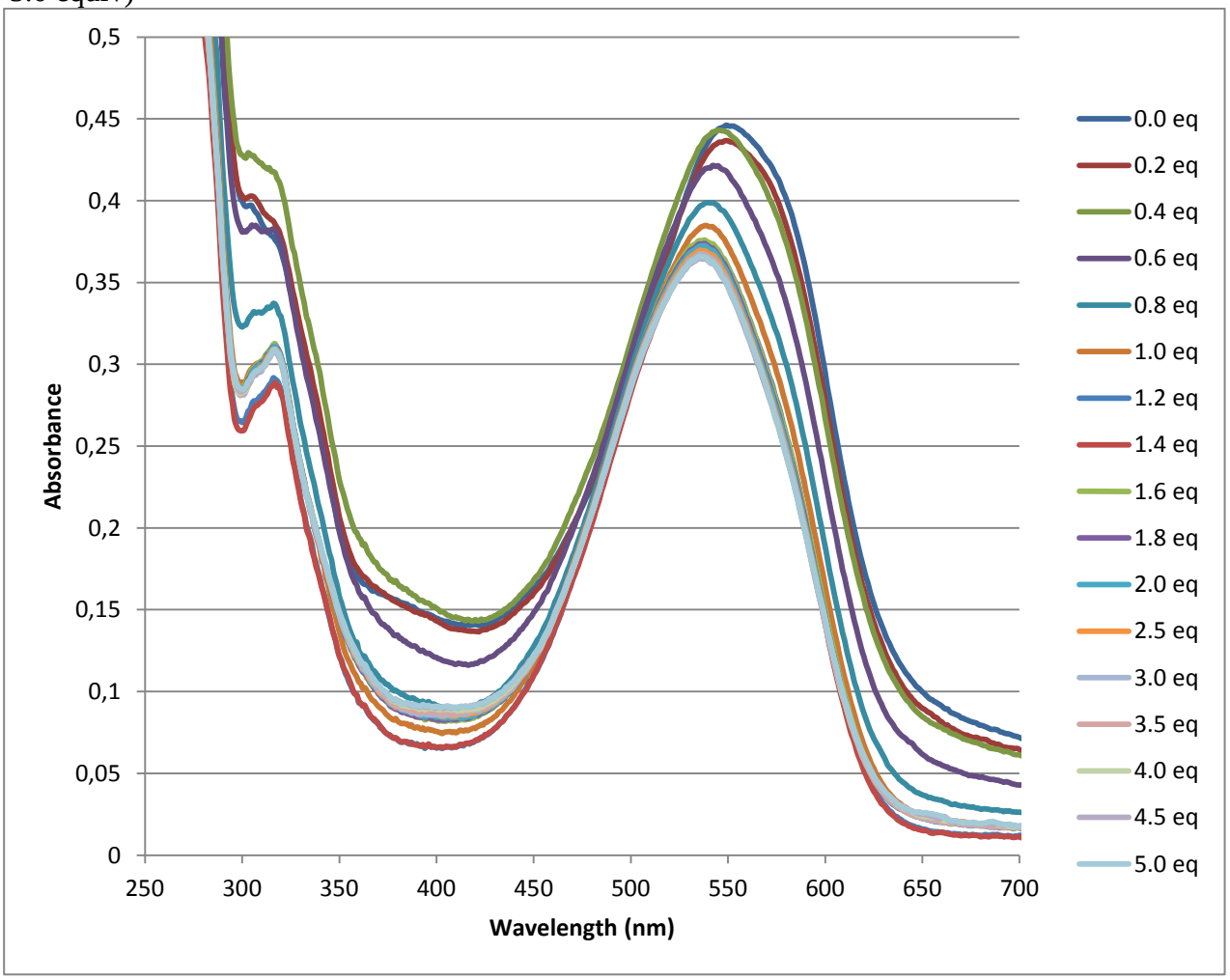


Figure S7: Changes of absorbance at 550 nm plotted against $[Cr(ClO_4)_3]/[\mathbf{5c}]_{total}$

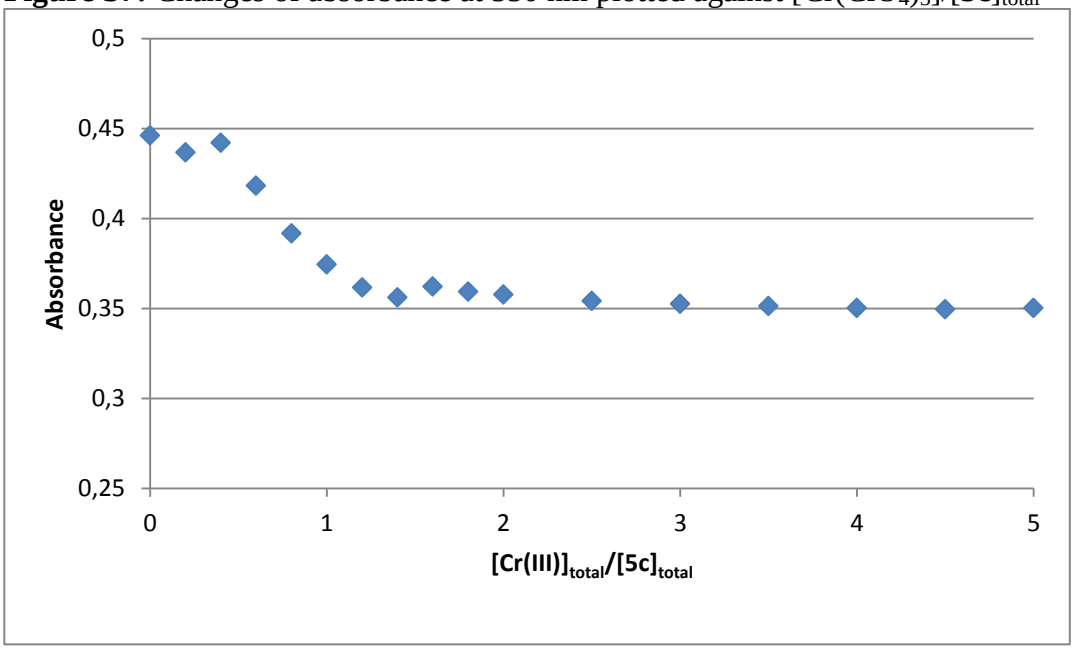


Figure S8: Evolution of UV–vis spectrum of **5d** (50 µM solution in MeCN) upon addition of $Cu(ClO_4)_2$ (0–5.0 equiv)

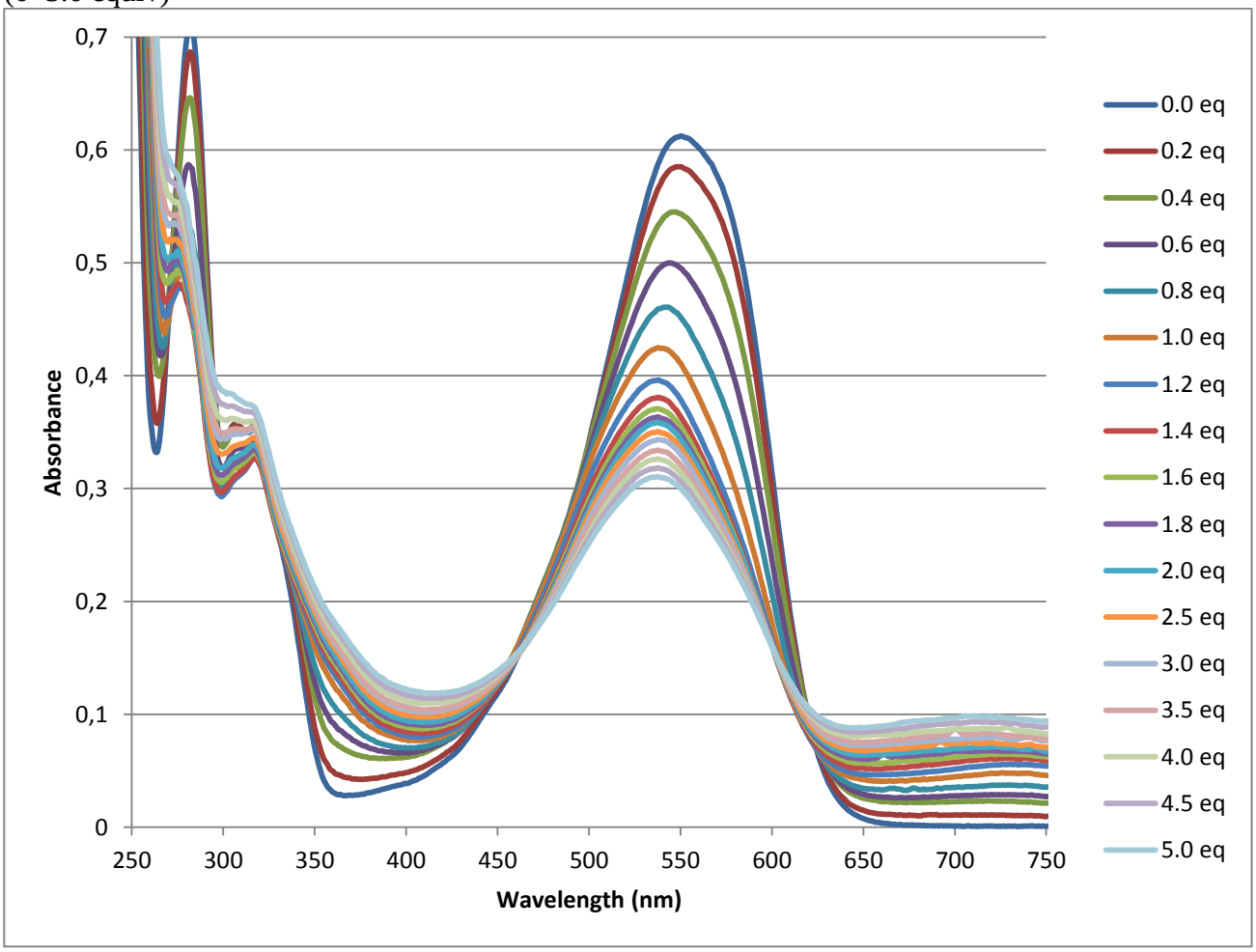


Figure S9: Changes of absorbance at 550 nm plotted against $[Cu(ClO_4)_2]/[\mathbf{5d}]_{total}$

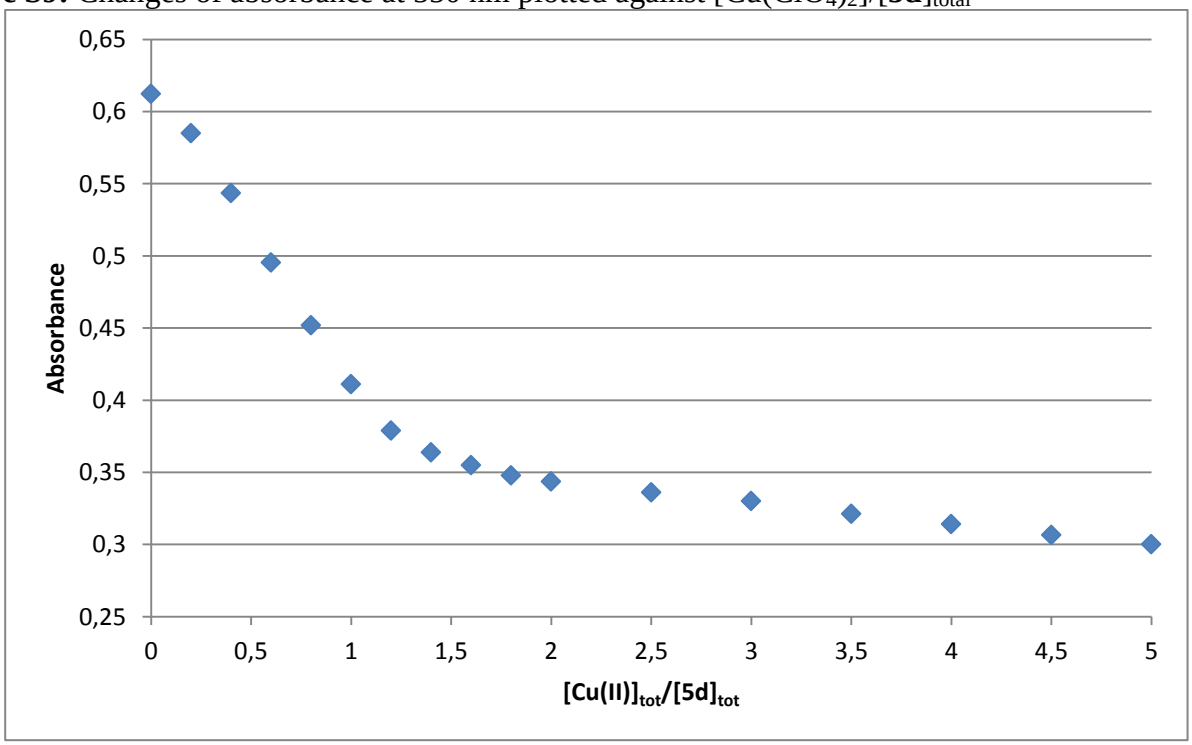


Figure S10: Evolution of UV–vis spectrum of **5d** (50 µM solution in MeCN) upon addition of $Al(ClO_4)_3$ (0–5.0 equiv)

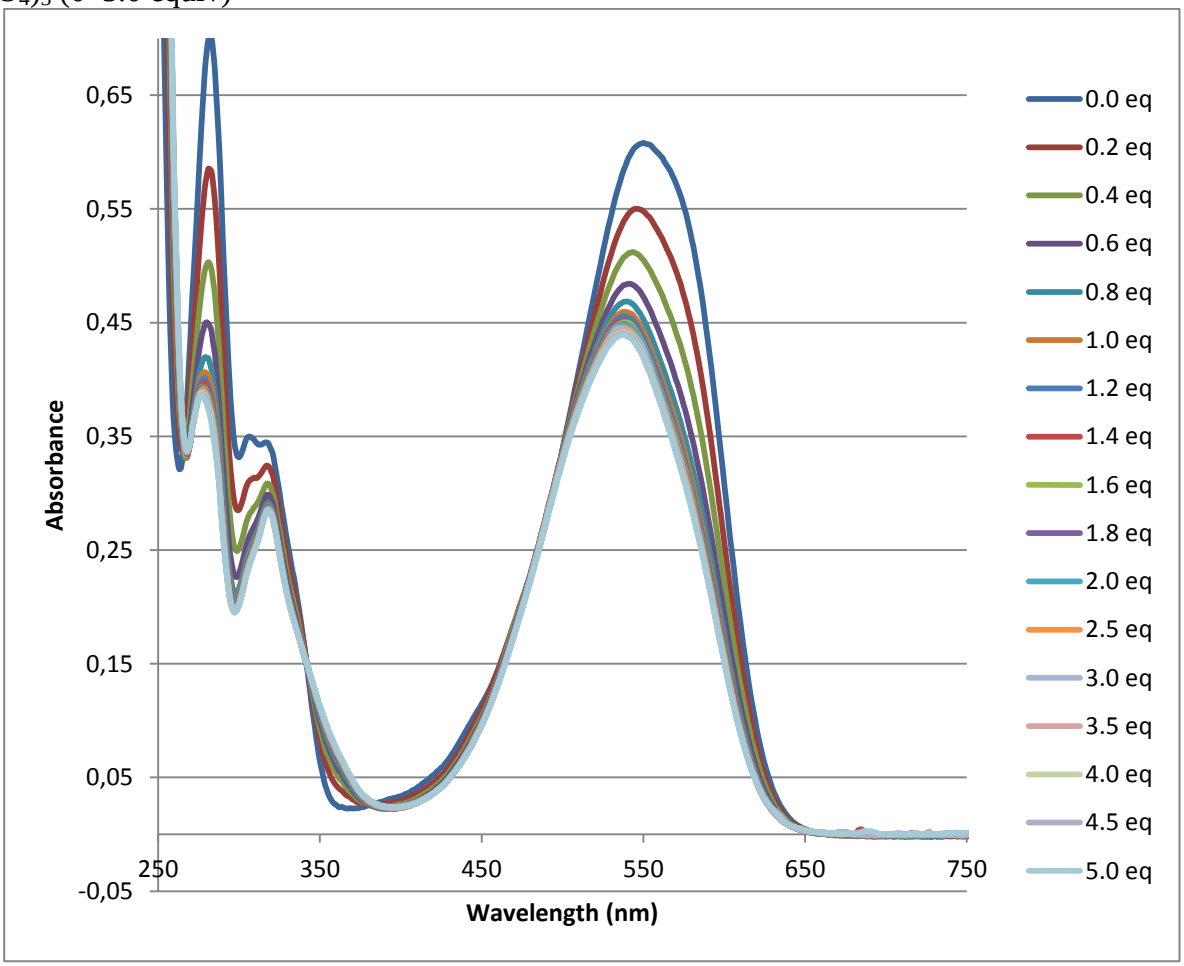


Figure S11: Changes of absorbance at 550 nm plotted against $[Al(ClO_4)_3]/[\mathbf{5d}]_{total}$

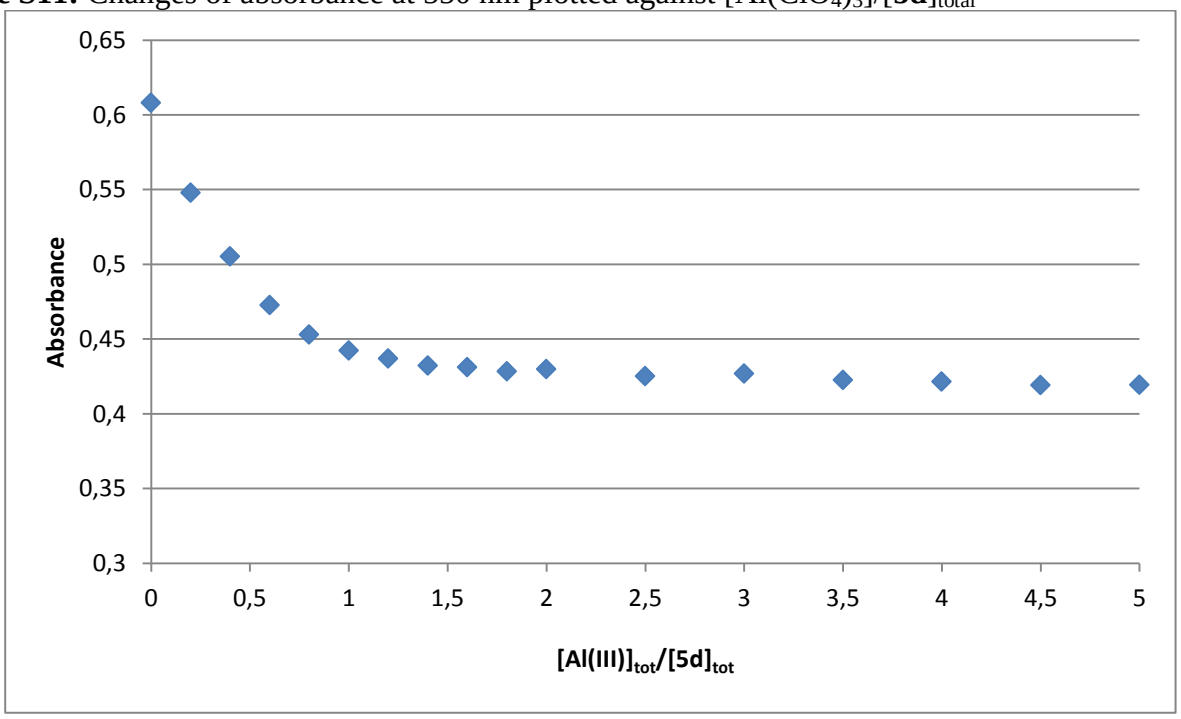


Figure S12: Evolution of UV–vis spectrum of **5d** (50 µM solution in MeCN) upon addition of $Cr(ClO_4)_3$ (0–5.0 equiv)

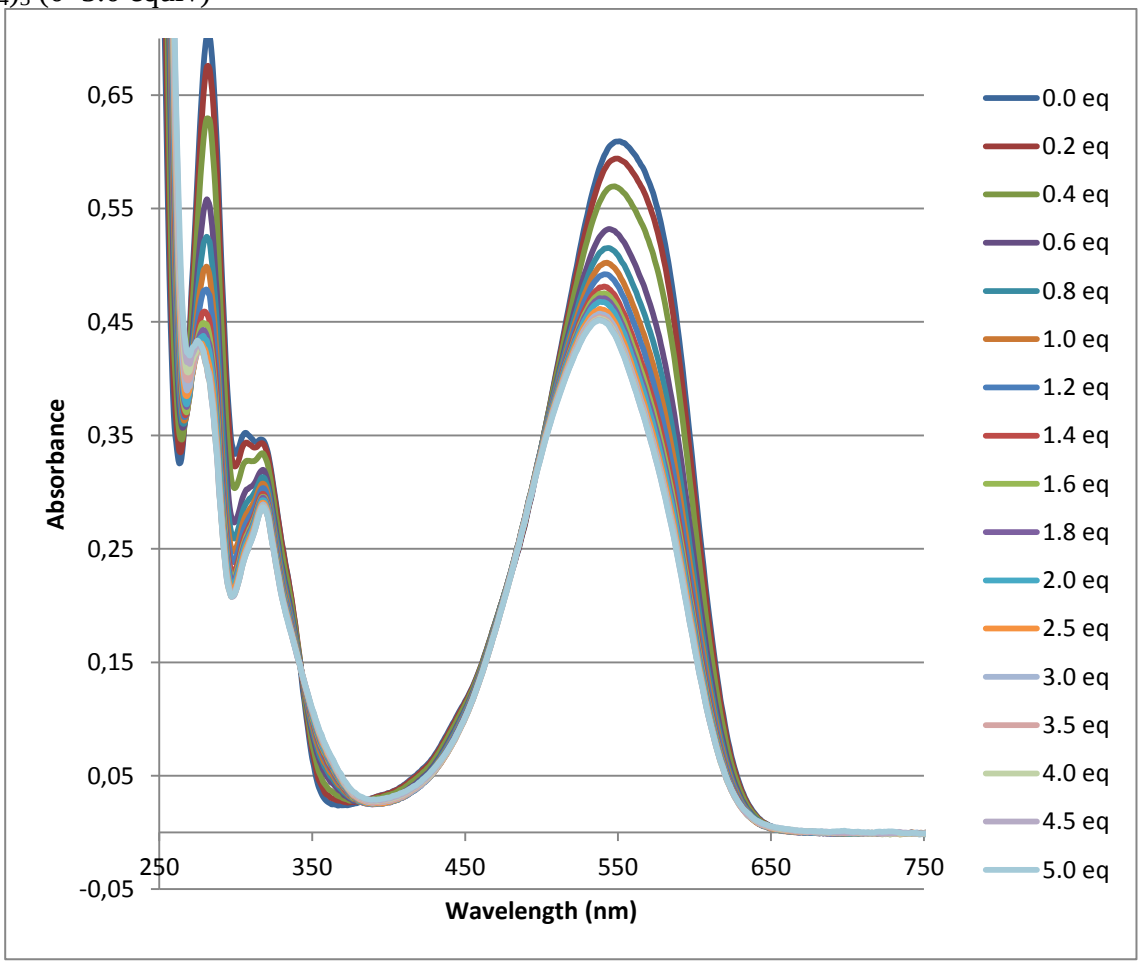
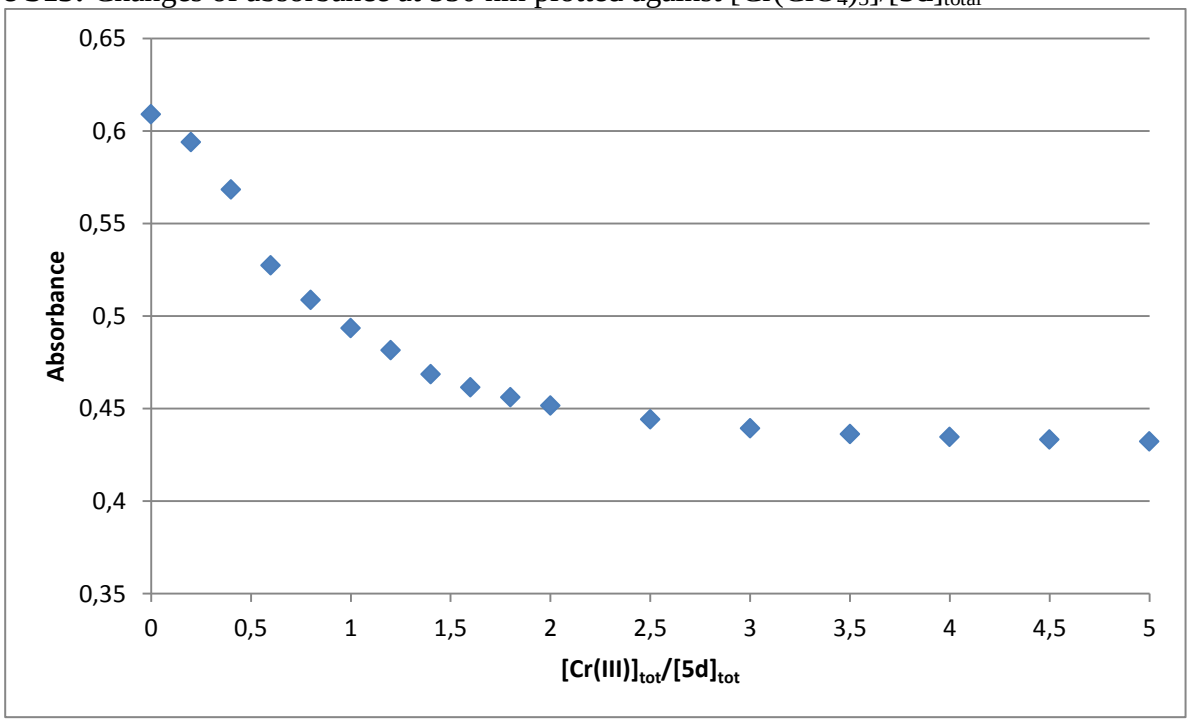


Figure S13: Changes of absorbance at 550 nm plotted against $[Cr(ClO_4)_3]/[\mathbf{5d}]_{total}$



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2. Fini, A.; Fazio, G.; Roda, A.; Bellini, A.M.; Mencini, E.; Guarneri, M. *J. Pharm Sci.* **1992**, *81*, 726-730.

3. Joachimiak, R.; Piasecka, M.; Paryzek, Z. *J. Chem. Res.*, **2008**, 260-265.