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Supporting Information for

Regiocontrolled Synthesis of the Trimeric Quinone Framework of Conocurvone

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PART I - EXPERIMENTAL SECTION

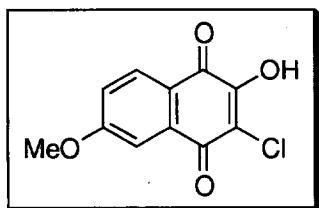
General Methods: Unless otherwise indicated, all NMR spectra were collected at room temperature in CDCl₃ with CHCl₃ as the internal reference (δ 7.26 ppm for ¹H and δ 77.25 ppm for ¹³C). IR spectra were measured in KBr pellets or neat as thin films on NaCl plates. MS were measured under fast atom bombardment (FAB) or electron impact (EI) conditions. Melting points were taken in open capillary tubes and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Analytic thin-layer chromatography (TLC) was performed on commercial Uniplat silica gel plates (Analtech), 250 μ m thickness, with fluorescent indicator (F-254). Flash chromatography was carried out using 35-70 μ m silica gel purchased from Acros. Anhydrous CH₂Cl₂, CHCl₃, CH₃CN, DMF, acetone & dioxane were purchased from Aldrich and used as received. Diisopropylethylamine was distilled from CaH₂ and stored over 4Å molecular sieves under an atmosphere of dry argon. Other solvents and reagents from commercial suppliers were used as received. Unless otherwise specified, all manipulations involving air-sensitive reagents were carried out under an atmosphere of dry argon using standard Schlenck techniques in oven dried (at least 6 h at 140°C) glassware. Extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure using a rotary evaporator. 2-Hydroxy-1,4-naphthoquinones **5b** & **5c** were prepared according to previously described procedures¹. The quinone 1,4-dipole **8** was prepared as described by Varvoglis.²

(1) Kasturi, T. R.; Arunachalam, T. *Can. J. Chem.* **1966**, *44*, 1086-1089.

(2) Varvoglis, A.; Hatzigrigoriou, E.; Spyroudis, S. *Liebigs Ann. Chem.* **1989**, 167-170.

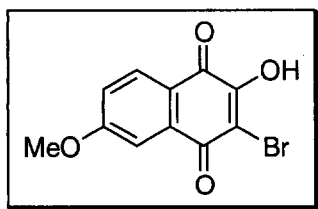
General Procedure for the Synthesis of 2-Hydroxy-3-halo-6-methoxy-1,4-naphthoquinones

To a vigorously stirred suspension of the dipole **8** (1 mmol)² in anhydrous CHCl₃ (20 mL) under argon and at room temperature, was injected the hydrohalic acid (10 mmol). The brilliant yellow suspension was stirred for 48 h at room temperature during which time a yellow solution formed. The solution was poured into 50 mL of water and the organic layer separated and washed with water (2 X 150 mL). The yellow organic layer was extracted with 10% aqueous NaHCO₃ (3 X 150 mL). The dark red aqueous layer was washed with ether and then acidified in a spacious Erlenmeyer flask with concentrated HCl to pH = 2 (litmus). The yellow suspension was extracted with chloroform and the organic layer was dried (MgSO₄), filtered and evaporated to yield the halohydroxyquinone **9**.

**3-Chloro-2-hydroxy-6-methoxy-1,4-dihydro-1,4-naphthalenedione**

(**9a**). The dipole **8** (2.03 g, 5 mmol) was treated with concentrated HCl (4.2 mL, 50 mmol), according to the general procedure described above, to yield 1.03 g (86%) of **9a** as an orange solid: mp = 179-181

°C (EtOH); R_f = 0.20 (EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 3.99 (s, 3H), 7.18 (dd, J = 8.4, 2.7 Hz, 1H), 7.66 (d, J = 2.4 Hz, 1H), 7.77 (s, 1H, broad), 8.08 (d, J = 8.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 56.44, 112.08, 119.79, 121.94, 122.32, 129.75, 134.82, 153.27, 165.71, 178.00, 178.25; FT-IR (film) 3339, 1662, 1646, 1634, 1584, 1296, 771, 745, 651 cm⁻¹; Anal. calcd. for C₁₁H₇ClO₄: C, 55.37; H, 2.96. Found: C, 54.96; H, 2.95.

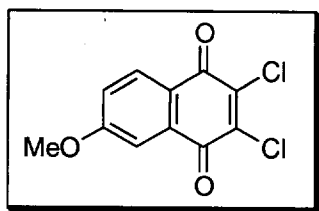
**3-Bromo-2-hydroxy-6-methoxy-1,4-dihydro-1,4-naphthalenedione**

(**9b**). The dipole **8** (1.50 g, 3.7 mmol) was treated with 48% aqueous HBr (4.2 mL, 37 mmol), according to the general procedure described above, to yield 0.817 g (78%) of **9b** as an orange solid: mp = 176-

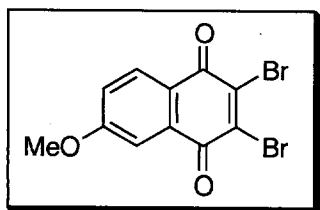
179°C (CHCl₃); R_f = 0.23 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 3.98 (s, 3H), 7.18 (dd, J = 8.8, 2.8 Hz, 1H), 7.65 (d, J = 2.8 Hz, 1H), 7.90 (s, 1H), 8.08 (d, J = 8.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 56.18, 109.95, 112.19, 119.61, 121.76, 129.72, 134.79, 155.48, 165.60, 177.36, 178.06; FT-IR (film) 3301, 1664, 1652, 1626, 1576, 1253, 1132, 1003, 915, 839, 745, 730 cm⁻¹; Anal. calcd. for C₁₁H₇BrO₄: C, 46.67; H, 2.49. Found: C, 46.80; H, 2.68.

General Procedure for the Synthesis of 2,3-Dihalo-6-methoxy-1,4-naphthoquinones

The 3-halo-2-hydroxyquinone **9** (1 mmol) was placed in a 15 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles, the thionyl halide (30 mmol) was injected followed by the addition of anhydrous DMF (5 drops). Reactions involving thionyl bromide were stirred for 48 h at room temperature, while reactions involving thionyl chloride were refluxed for 5 h. In a well-ventilated hood, the solution was cooled to room temperature and slowly poured into 100 mL of water (CAUTION!) followed by extraction of the reaction mixture with CHCl_3 (70 mL). The organic layer was washed successively with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2 X 50 mL) (thionyl bromide reactions only) followed by 10% aqueous NaHCO_3 (2 X 50 mL). The organic layer was dried (MgSO_4), filtered and evaporated using a minimum amount of heat to yield the dihaloquinone **10**.

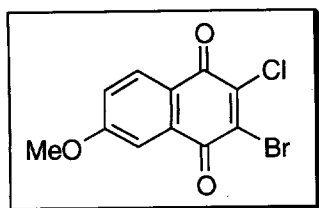
**2,3-Dichloro-6-methoxy-1,4-dihydro-1,4-naphthalenedione (10c).**

The chlorohydroxyquinone **9a** (0.444 g, 1.86 mmol) was refluxed with thionyl chloride (4.1 mL, 56 mmol) and DMF for 5 h, according to the general procedure described above, to yield 0.368 g (77%) of the dichloroquinone **10c** as a yellow solid: mp = 120-124 °C; R_f = 0.31 (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 3.97 (s, 3H), 7.25-7.28 (dd, J = 8.6 Hz, 2.7 Hz, 1H), 7.63 (d, J = 2.6 Hz, 1H), 8.15 (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.56, 111.84, 121.35, 124.59, 130.73, 133.41, 143.17, 144.32, 165.13, 175.38, 176.62; FT-IR 3334, 1678, 1648, 1600, 1561, 1503, 1456, 1302, 1242, 1140, 1076 cm^{-1} ; MS (FAB) m/z (relative intensity) 259 $[(\text{M}+2+\text{H})^+]$, 7], 257 $[(\text{M}+\text{H})^+]$, 12], 221 (16), 207 (20), 154 (100); HRMS (FAB) calcd. for $\text{C}_{11}\text{H}_7^{35}\text{Cl}_2\text{O}_3$ ($\text{M}+\text{H})^+$ 256.9772, found 256.9767.

**2,3-Dibromo-6-methoxy-1,4-dihydro-1,4-naphthalenedione (10d).**

The bromohydroxyquinone **9b** (0.50 g, 1.77 mmol) was stirred with thionyl bromide (4.1 mL, 53 mmol) and DMF at room temperature for 48 hours, according to the general procedure described above. The crude product was purified by flash chromatography on silica eluting with 10% ethyl acetate in hexanes to yield 0.268 g (44%) of the dibromoquinone **10d** as yellow needles: mp = 138-142

$^{\circ}\text{C}$; $R_f = 0.30$ (10% EtOAc in hexanes), ^1H NMR (500 MHz, CDCl_3) δ 3.97 (s, 3H), 7.24-7.26 (dd, $J = 8.7$ Hz, 2.7 Hz, 1H), 7.63 (d, $J = 2.6$ Hz, 1H), 8.15 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 55.93, 111.56, 120.71, 123.85, 130.53, 132.65, 141.36, 143.04, 164.37, 174.60, 175.81; FT-IR 3091, 2987, 2847, 1674, 1597, 1575, 1541, 1496, 1461, 1348, 1294, 1229, 1125, 1067, 1015 cm^{-1} ; MS (EI) m/z (relative intensity) 346 $[(\text{M}+2+\text{H})^+]$, 51], 344 $[(\text{M}+\text{H})^+]$, 100], 316 (27), 273 (22), 258 (12), 164 (21), 130 (19); HRMS (EI) calcd. for $\text{C}_{11}\text{H}_7^{79}\text{Br}_2\text{O}_3$ $(\text{M}+\text{H})^+$ 344.8762, found 344.8591.



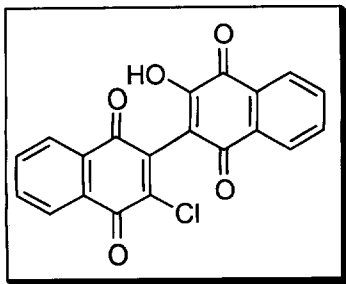
3-Bromo-2-chloro-6-methoxy-1,4-dihydro-1,4-naphthalenedione

(10e). The bromohydroxyquinone **9b** (1.04 g, 3.68 mmol) was refluxed with thionyl chloride (7.7 mL, 112 mmol) and DMF for 5 h, according to the general procedure described above. The crude

product was purified by flash chromatography on silica eluting with 10% ethyl acetate in hexanes to yield 0.611 g (55%) of **10e** as a yellow solid: mp = 124-127 $^{\circ}\text{C}$; $R_f = 0.26$ (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 3.97 (s, 3H), 7.22-7.25 (dd, $J = 8.7$ Hz, 2.6 Hz, 1H), 7.60 (d, $J = 2.6$ Hz, 1H), 8.12 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.13, 111.41, 120.92, 124.17, 130.30, 132.99, 142.74, 143.90, 164.70, 174.94, 176.18; FT-IR 3008, 2948, 2842, 1675, 1598, 1577, 1560, 1495, 1460, 1349, 1296, 1232, 1139, 1074, 1022 cm^{-1} ; MS (FAB) m/z (relative intensity) 303 $[(\text{M}+2+\text{H})^+]$, 100], 301 $[(\text{M}+\text{H})^+]$, 71], 265 (12), 257 (22), 221 (20), 147 (39); HRMS (FAB) calcd. for $\text{C}_{11}\text{H}_7^{79}\text{Br}^{35}\text{ClO}_3$ $(\text{M}+\text{H})^+$ 300.9267, found 300.9259.

General Procedure for the Synthesis of 3'-Halo-3-hydroxy-2,2'-binaphthalenyl-1,4,1',4'-tetraones

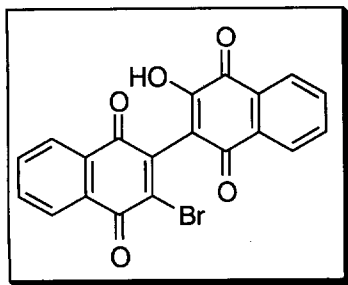
The 2,3-dihaloquinone **10** (1 mmol), hydroxyquinone **5** (1 mmol) and cesium carbonate (2 mmol) were placed in a 25 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles 10 mL of anhydrous CH_3CN was added, and the suspension stirred at room temperature for *seven days* during which time the color changed from orange to dark red. The mixture was acidified with concentrated HCl to pH = 2 (litmus) forming the biquinone as a yellow precipitate. The suspension was poured into 100 mL of water and stirred for 1 hour to dissolve remaining traces of cesium carbonate. The precipitate was filtered and the product air-dried for 3 days at room temperature.

**3'-Chloro-3-hydroxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (6a).**

Method A: Reaction of 2,3-dichloro-1,4-naphthoquinone **10a** (1.70 g, 7.5 mmol) with 2-hydroxy-1,4-naphthoquinone **5a** (1.31 g, 7.5 mmol) for 7 days, according to the general procedure described above, yielded 2.54 g (93%) of the chlorohydroxybiquinone **6a** as a yellow solid: mp = 296-300°C; R_f = 0.19 (EtOAc); ^1H NMR (500

MHz, CDCl_3) δ 7.74 (s, 1H, broad), 7.77-7.82 (m, 3H), 7.83-7.86 (m, 1H), 8.14-8.17 (m, 1H), 8.18-8.21 (m, 2H), 8.22-8.26 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 115.72, 127.19, 127.78 (2 C), 127.93, 129.71, 131.80, 132.23, 133.11, 133.98, 134.62, 134.93, 136.09, 139.09, 146.42, 153.54, 177.74, 180.74, 181.14, 181.86; FT-IR 3339, 3106, 3072, 1675, 1644, 1591, 1459, 1369, 1337, 1302, 1275 cm^{-1} ; MS (FAB) m/z (relative intensity) 367 [(M+2H) $^+$, 54], 365 [(M+H) $^+$, 98], 330 (27), 307 (29), 286 (100), 219 (26), 154 (95), 132 (86); HRMS (FAB) calcd. for $\text{C}_{20}\text{H}_{10}^{35}\text{ClO}_5$ (M+H) $^+$ 365.0217, found 365.0228.

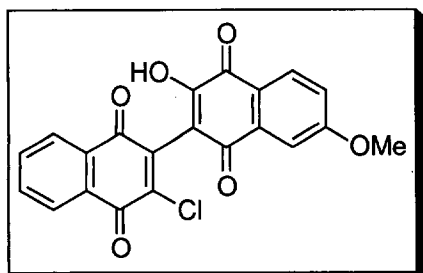
Method B: 2,3-Dichloro-1,4-naphthoquinone **10a** (0.235 g, 1.04 mmol), potassium salt of lawsone **12a** (0.220 g, 1.04 mmol) and 18-crown-6 (0.274 g, 1.04 mmol) were placed in a 25 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles, 20 mL of anhydrous CH_3CN was added and the suspension stirred at room temperature for 24 hours. The mixture was acidified with concentrated HCl to pH = 2 (litmus), and the suspension was poured into 50 mL of water and stirred for 1 hour. The precipitate was filtered and the product air-dried for 3 days at room temperature. The yellow precipitate was dissolved in CH_2Cl_2 and the organic layer extracted with 10% NaHCO_3 . The red aqueous solution was acidified then extracted with CH_2Cl_2 . The organic layer was dried (MgSO_4), filtered, and evaporated to yield 0.294 g (78%) of **6a** as a yellow solid.

**3-Bromo-3'-hydroxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (6b).**

Reaction of 2,3-dibromo-1,4-naphthoquinone **10b** (4.74 g, 15 mmol) with 2-hydroxy-1,4-naphthoquinone **5a** (2.61 g, 15 mmol) for 7 days, according to the general procedure described above, yielded 5.83 g (94%) of the bromohydroxybiquinone **6b** as a yellow solid: mp = 219-221°C; R_f = 0.23 (EtOAc); ^1H NMR (500

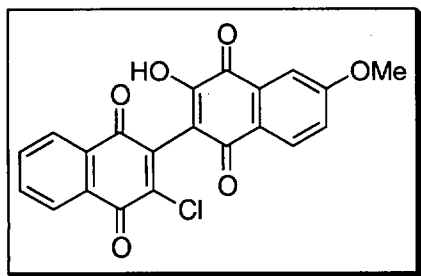
MHz, CDCl_3) δ 7.71 (s, 1H, broad), 7.77-7.82 (m, 3H), 7.83-7.87 (m, 1H), 8.14-8.16 (m, 1H),

8.18-8.21 (m, 2H), 8.22-8.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 117.31, 126.73, 127.32, 127.42, 127.80, 129.35, 131.13, 131.71, 132.65, 133.54, 134.15, 134.42, 135.61, 141.75, 142.59, 152.71, 177.29, 179.83, 180.81, 181.29; FT-IR 3336, 3111, 3072, 1676, 1644, 1590, 1459, 1371, 1336, 1301, 1270 cm^{-1} ; MS (FAB) m/z (relative intensity) 411 $[(\text{M}+2\text{H})^+]$, 58], 409 $[(\text{M}+\text{H})^+]$, 46], 371 (13), 347 (8), 330 (100), 176 (9); HRMS (FAB) calcd. for $\text{C}_{20}\text{H}_{10}^{79}\text{BrO}_5$ $(\text{M}+\text{H})^+$ 408.9712, found 408.9711.



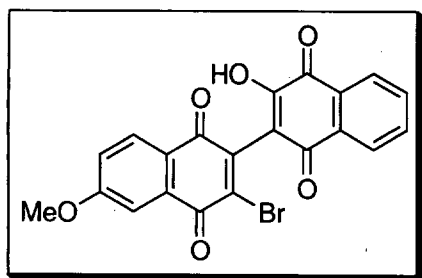
3'-Chloro-3-hydroxy-7-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (6c). Reaction of 2,3-dichloro-1,4-naphthoquinone **10a** (1.70 g, 7.5 mmol) with 2-hydroxy-6-methoxy-1,4-naphthoquinone **5b** (1.53 g, 7.5 mmol) for 7 days, according to the general procedure described above, yielded 2.7

g (91%) of the chlorohydroxybiquinone **6c** as a yellow solid: mp = 211-216 °C; R_f = 0.11 (33% hexanes in EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 3.98 (s, 3H), 7.20-7.23 (dd, J = 8.6 Hz, 2.6 Hz, 1H), 7.63 (d, J = 2.6 Hz, 1H), 7.78-7.83 (m, 2H), 8.14 (d, J = 8.6 Hz, 1H), 8.15-8.16 (m, 1H), 8.23-8.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.58, 111.70, 114.97, 120.28, 122.89, 127.76, 127.91, 129.92, 131.82, 132.26, 134.57, 134.91, 135.74, 139.21, 146.40, 154.03, 166.26, 177.81, 179.54, 180.77, 181.85; FT-IR 3350, 3106, 3081, 2951, 2848, 1678, 1658, 1646, 1590, 1500, 1375, 1313, 1274, 1250, 1134, 1014 cm^{-1} ; MS (FAB) m/z (relative intensity) 397 $[(\text{M}+2\text{H})^+]$, 49], 395 $[(\text{M}+\text{H})^+]$, 86], 360 (28), 329 (16), 307 (29), 219 (24), 176 (24), 154 (100); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{12}^{35}\text{ClO}_6$ $(\text{M}+\text{H})^+$ 395.0322, found 395.0317.



3'-Chloro-3-hydroxy-6-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (6d). Reaction of 2,3-dichloro-1,4-naphthoquinone **10a** (0.334 g, 1.47 mmol) with 2-hydroxy-7-methoxy-1,4-naphthoquinone **5c** (0.300 g, 1.47 mmol) for 7 days, according to the general procedure described above, yielded 0.396 g (68%) of the chlorohydroxybiquinone **6d** as a brown solid: mp = 220-224 °C; R_f = 0.27 (33% hexanes in EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 3.98 (s, 3H), 7.28-7.31 (dd, J = 8.6 Hz, 2.7 Hz, 1H), 7.62 (d, J = 2.7 Hz, 1H), 7.78-7.82 (m, 2H), 8.11 (d, J = 8.6 Hz, 1H), 8.14-8.16 (m, 1H), 8.22-8.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.47, 110.85, 115.52, 122.02,

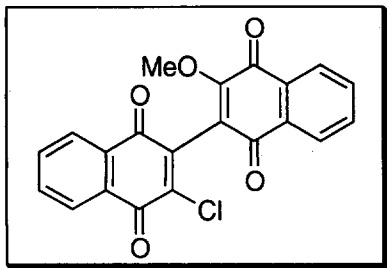
126.37, 127.76, 127.90, 130.08, 131.46, 131.81, 132.25, 134.58, 134.90, 139.28, 146.33, 153.28, 164.23, 177.77, 180.82, 181.31, 181.40; FT-IR 3311, 2976, 2843, 1680, 1663, 1635, 1589, 1492, 1366, 1348, 1277, 1231, 1118, 1018 cm^{-1} ; MS (FAB) m/z (relative intensity) 397 $[(M+2+H)^+$, 52], 395 $[(M+H)^+$, 100], 360 (30), 329 (12), 219 (18), 176 (23), 154 (27); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{12}^{35}\text{ClO}_6$ $(M+H)^+$ 395.0322, found 395.0304.



3-Bromo-3'-hydroxy-6-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (6e) The bromochloroquinone **10e** (0.178 g, 0.59 mmol) was reacted with 2-hydroxy-1,4-naphthoquinone **5a** (0.103 g, 59 mmol) for 1 day, according to the general procedure described above. The reaction yielded 0.232 g (90 %) of a 8.5:1.5 mixture of biquinones as determined by comparing the integration of the signals of the methoxyl protons common to both 3-bromo-3'-hydroxy-6-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone **6e** and 3-chloro-3'-hydroxy-7-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone. Three successive triturations in 75% aqueous acetone yielded 0.118 g (46%) of the major regioisomer **6e** as a brilliant yellow solid which was > 95% pure: mp = 199-203°C; R_f = 0.23 (33% hexanes in EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 3.99 (s, 3H), 7.24-7.26 (dd, J = 8.6 Hz, 2.6 Hz, 1H), 7.66 (d, J = 2.6 Hz, 1H), 7.73 (s, 1H, broad), 7.77-7.80 (dt, J = 7.6 Hz, 1.1 Hz, 1H), 7.83-7.86 (dt, J = 7.6 Hz, 1.1 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 8.17-8.21 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.07, 111.17, 117.52, 120.96, 125.13, 126.70, 127.33, 129.34, 129.86, 132.68, 133.11, 133.50, 135.60, 140.80, 142.68, 152.57, 164.31, 177.44, 178.90, 180.83, 181.33; FT-IR 3267 (broad), 3068, 2842, 1675, 1653, 1576, 1499, 1457, 1375, 1298, 1280, 1237, 1134, 1072, 1012 cm^{-1} ; MS (FAB) m/z (relative intensity) 441 $[(M+2+H)^+$, 8], 439 $[(M+H)^+$, 7], 360 (14), 307 (42), 219 (11), 154 (100); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{12}^{79}\text{BrO}_6$ $(M+H)^+$ 438.9817, found 438.9805.

General Procedure for the Synthesis of 3'-Halo-3-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraones The halohydroxybiquinone **6** (1 mmol) and trimethyloxonium tetrafluoroborate (2 mmol) were placed in a 100 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles 60 mL of anhydrous CH_2Cl_2 was added and the suspension stirred at room temperature for 30 min. N,N -diisopropylethylamine (1.5 mmol) was added and the dark

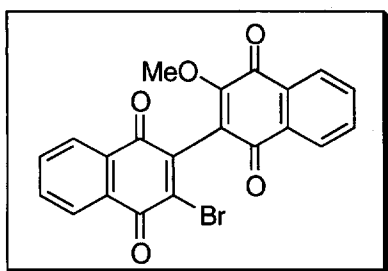
red solution stirred for an additional 3 hours during which time the color changed to dark yellow. The solution was diluted with 60 mL of CH_2Cl_2 and the mixture washed successively with water containing 3 drops of conc. HCl (2 X 150 mL) and 10% NaHCO_3 (1 X 150 mL). The organic layer was dried (MgSO_4), filtered, and evaporated to yield the biquinone methyl ether 7. Decomposition was noted to occur on contact of the methyl ethers with silica. Pure products could be obtained by trituration of the crude product with a small quantity of acetone.



3'-Chloro-3-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone

(7a). Reaction of the chlorohydroxybiquinone **6a** (1.00 g, 2.74 mmol) with trimethyloxonium tetrafluoroborate (0.81 g, 5.48 mmol) and N,N-diisopropylethylamine (0.53 g (0.71 mL), 4.11 mmol,) in methylene chloride (150 mL), according to the

general procedure described above, yielded 0.850 g (82%) of the chloromethoxybiquinone **7a** as a yellow solid: mp = 235-238 °C; R_f = 0.25 (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 4.19 (s, 3H), 7.75-7.82 (m, 4H), 8.08-8.11 (m, 1H), 8.12-8.16 (m, 2H), 8.22-8.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 61.84, 123.89, 127.01, 127.10, 127.76, 127.91, 131.82, 131.92, 131.97, 132.19, 134.14, 134.64, 134.86, 134.91, 140.64, 145.74, 157.97, 177.68, 180.93, 181.44, 182.42; FT-IR 2954, 2852, 1675, 1648, 1593, 1573, 1457, 1337, 1304, 1280, 1270, 1218, 1148 cm^{-1} ; MS (FAB) m/z (relative intensity) 381 $[(\text{M}+2+\text{H})^+]$, 52], 379 $[(\text{M}+\text{H})^+]$, 100], 345 (13); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{12}^{35}\text{ClO}_5$ $(\text{M}+\text{H})^+$ 379.0373, found 379.0363.

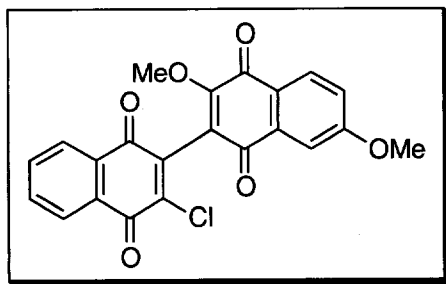


3'-Bromo-3-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone

(7b). Reaction of the bromohydroxybiquinone **6b** (0.100 g, 0.24 mmol) with trimethyloxonium tetrafluoroborate (0.071 g, 0.48 mmol) and N,N-diisopropylethylamine (0.047 g (0.063 mL), 0.36 mmol)) in methylene chloride (15 mL), according to

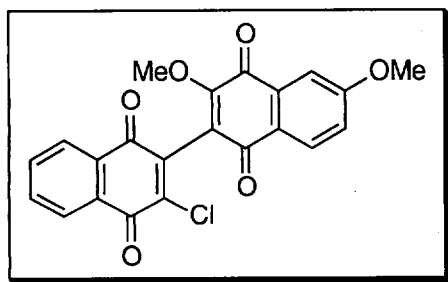
the general procedure described above, yielded 0.088 g (87%) of the bromomethoxybiquinone **7b** as a yellow solid: mp = 219-221 °C; R_f = 0.24 (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 4.18 (s, 3H), 7.75-7.81 (m, 4H), 8.09-8.11 (m, 1H), 8.12-8.16 (m, 2H), 8.22-8.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 61.81, 125.77, 127.01, 127.09, 127.86, 128.23, 131.58, 131.92, 131.96, 132.09, 134.15, 134.62, 134.85 (2C), 141.53, 144.55, 157.46, 177.63, 180.44, 181.50, 182.29; FT-IR 3071, 2954, 1675, 1616, 1592, 1571, 1453, 1337, 1268, 1218, 1144,

1048, 1019 cm^{-1} ; MS (FAB) m/z (relative intensity) 425 $[(M+2+H)^+]$, 100] 423 $[(M+H)^+]$, 89), 344 (48); HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{12}^{79}\text{BrO}_5$ $(M+H)^+$ 422.9868, found 422.9850.



3'-Chloro-3,7-dimethoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (7c). The chlorohydroxybiquinone **6c** (1.3 g, 3.29 mmol) and silver (I) oxide (2.29 g, 9.87 mmol) were placed in a 100 mL round bottom flask fitted with a T-bore stopcock. After 3 argon and vacuum cycles, dry acetone (50 mL) was added followed by 4.1 mL of iodomethane (66

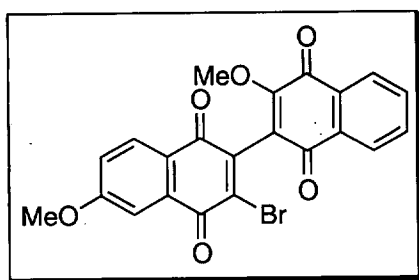
mmol). After stirring at room temperature for 2 hours, another 4.1 mL portion of iodomethane was added and the red suspension was stirred at room temperature for an additional 24 h. The resulting dark yellow suspension was filtered through a pad of Celite and the Celite was washed with acetone (2 X 30 mL). The acetone was evaporated and the residue triturated with a small amount of 75% aqueous acetone to yield 0.848 g (63%) of the dimethoxybiquinone **7c** as a dark yellow solid: mp = 292-295 $^{\circ}\text{C}$; R_f = 0.16 (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 3.95 (s, 3H), 4.18 (s, 3H), 7.20-7.22 (dd, J = 8.6 Hz, 2.7 Hz, 1H), 7.53 (d, J = 2.7 Hz, 1H), 7.77-7.82 (m, 2H), 8.08 (d, J = 8.7 Hz, 1H), 8.14-8.16 (m, 1H), 8.23-8.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.44, 61.92, 110.40, 120.67, 123.30, 125.32, 127.76, 127.90, 129.66, 131.84, 132.22, 134.25, 134.60, 134.88, 140.76, 145.73, 158.31, 165.11, 177.75, 180.32, 180.96, 182.45; FT-IR 3072, 2962, 2841, 1675, 1651, 1614, 1588, 1497, 1459, 1346, 1280, 1249, 1177, 1143, 1081, 1046, 1014 cm^{-1} ; MS (FAB) m/z (relative intensity) 411 $[(M+2+H)^+]$, 66], 409 $[(M+H)^+]$, 53], 371 (28), 330 (100), 289 (14), 219 (29), 154 (64); HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{14}^{35}\text{ClO}_6$ $(M+H)^+$ 409.0479, found 408.9698.



3'-Chloro-3,6-dimethoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (7d). Reaction of the chlorohydroxybiquinone **6d** (0.20 g, 0.51 mmol) with trimethyloxonium tetrafluoroborate (0.151 g, 1.02 mmol) and N,N -diisopropylethylamine (0.10 g (0.135 mL), 0.77 mmol) in methylene chloride (30 mL), according to the general

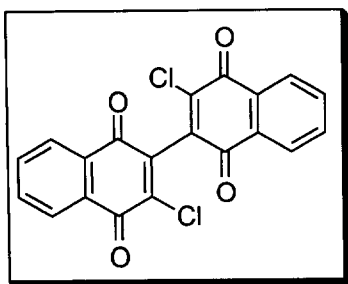
procedure described above, yielded 0.181 g (87%) of the dimethoxybiquinone **7d** as a dark yellow solid: mp = 204-207 $^{\circ}\text{C}$; R_f = 0.16 (10% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3)

δ 3.96 (s, 3H), 4.14 (s, 3H), 7.21-7.23 (dd, J = 8.6 Hz, 2.6 Hz, 1H), 7.57 (d, J = 2.6 Hz, 1H), 7.77-7.81 (m, 2H), 8.03 (d, J = 8.6 Hz, 1H), 8.12-8.15 (m, 1H), 8.21-8.23 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.40, 61.69, 110.73, 121.10, 124.00, 125.38, 127.75, 127.89, 129.39, 131.83, 132.20, 133.79, 134.61, 134.88, 140.81, 145.64, 157.77, 164.51, 177.69, 181.00, 181.51, 181.70; FT-IR 3076, 2949, 2840, 1675, 1643, 1616, 1588, 1498, 1458, 1333, 1277, 1246, 1206, 1148, 1086, 1050, 1018 cm^{-1} ; MS (FAB) m/z (relative intensity) 411 $[(\text{M}+2+\text{H})^+]$, 26], 409 $[(\text{M}+\text{H})^+]$, 44], 307 (18), 154 (100); HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{14}^{35}\text{ClO}_6$ $(\text{M}+\text{H})^+$ 409.0479, found 409.0486.



3-Bromo-6,3'-dimethoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraone (7e). Reaction of the bromohydroxybiquinone **6e** (0.200 g, 0.46 mmol) with trimethyloxonium tetrafluoroborate (0.136 g, 0.92 mmol) and *N,N*-diisopropylethylamine (0.089 g (0.120 mL), 0.69 mmol,) in

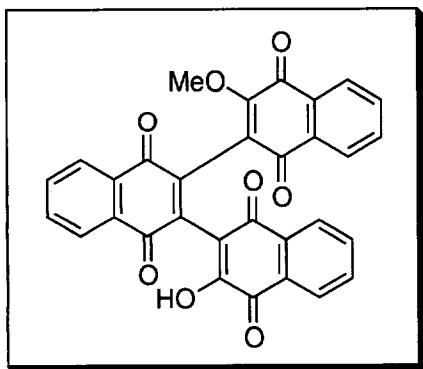
methylene chloride (25 mL), according to the general procedure described above, yielded 0.200 g (96%) of the dimethoxybiquinone **7e** as a bronze sponge, mp = 103-106 °C; R_f = 0.22 (20% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 4.01 (s, 3H), 4.20 (s, 3H), 7.26-7.28 (dd, J = 8.6 Hz, 2.7 Hz, 1H), 7.68 (d, J = 2.6 Hz, 1H), 7.78-7.81 (m, 2H), 8.10 (d, J = 8.6 Hz, 1H), 8.11-8.14 (m, 1H), 8.16-8.18 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 56.51, 61.75, 111.61, 121.34, 125.48, 125.93, 127.00, 127.06, 130.30, 131.92, 132.00, 133.57, 134.11, 134.82, 140.58, 144.71, 157.42, 164.76, 177.79, 179.51, 181.50, 182.36; FT-IR 3073, 2950, 2842, 1676, 1650, 1624, 1589, 1497, 1457, 1337, 1287, 1217, 1141, 1071, 1047, 1018 cm^{-1} ; MS (FAB) m/z (relative intensity) 455 $[(\text{M}+2+\text{H})^+]$, 13], 453 $[(\text{M}+\text{H})^+]$, 10], 373 (12), 307 (21), 219 (7), 154 (100); HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{14}^{79}\text{BrO}_6$ $(\text{M}+\text{H})^+$ 452.9974, found 452.9968.



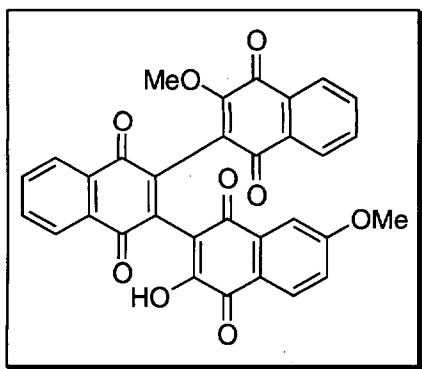
3,3'-Dichloro-2,2'-binaphthalenyl-1,4,1',4'-tetraone (11).

The hydroxychlorobiquinone **6a** (0.800 g, 2.2 mmol) was placed in a 25 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles, thionyl chloride (10 mL, 137.7 mmol) was injected followed by the addition of anhydrous DMF (1 mL). The reaction mixture was refluxed for 3.5 h and then cooled to room temperature. The orange solution was slowly poured into 150 mL of water (CAUTION!).

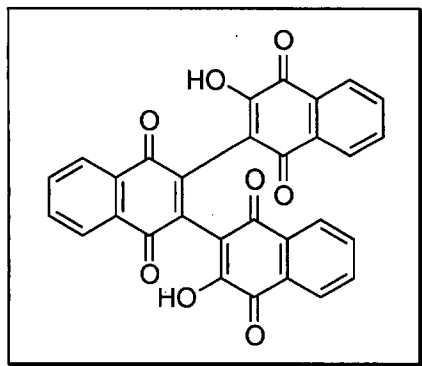
The mixture was extracted with CHCl_3 (100 mL) and the organic layer washed with 10% aqueous NaHCO_3 (2 X 150 mL), dried (MgSO_4), filtered and evaporated to yield 0.770 g (91%) of the dichlorobiquinone **11** as a yellow solid: mp = 265-268°C; R_f = 0.37 (20% EtOAc in hexanes); ^1H NMR (500 MHz, CDCl_3) δ 7.81-7.86 (m, 4H), 8.14-8.17 (m, 2H), 8.25-8.28 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 127.84, 128.12, 131.69, 131.89, 134.98, 135.19, 140.18, 145.49, 177.30, 180.12; FT-IR 3101, 1675, 1657, 1591, 1454, 1320, 1271, 1142, 1077 cm^{-1} ; MS (FAB) m/z (relative intensity) 385 $[(\text{M}+2\text{H})^+, 99]$, 383 $[(\text{M}+\text{H})^+, 94]$, 349 (39), 329 (45), 255 (33), 219 (43), 176 (72); HRMS (FAB) calcd. for $\text{C}_{20}\text{H}_9^{35}\text{Cl}_2\text{O}_4$ $(\text{M}+\text{H})^+$ 382.9878, found 382.9883.



3-Hydroxy-3''-methoxy-2,2',3',2''-ternaphthalene-1,4,1',4',1'',4''-hexaone (13a). The chloromethoxybiquinone **7a** (1.00 g, 2.64 mmol), the potassium salt **12a** (0.280 g, 1.32 mmol) and 18-crown-6 (0.349 g, 1.32 mmol) were placed in a 100 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles, 80 mL of anhydrous CH_3CN was added. The suspension was stirred at 65°C for 3 days during which time the mixture turned dark red. The suspension was acidified with concentrated HCl to pH = 2 (litmus) forming a red precipitate. The suspension was immediately filtered, and the red precipitate was washed on the filter paper with CH_2Cl_2 to yield 0.263 g (39%) of the trimeric quinone **13a** as a red solid: mp = 331-336 °C; R_f = 0.18 (20% methanol in chloroform); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 3.83 (s, 3H), 7.47-7.50 (t, J = 7.6 Hz, 1H), 7.52-7.56 (t, J = 7.6 Hz, 1H), 7.62-7.65 (t, J = 7.4 Hz, 2H), 7.69- 7.72 (t, J = 7.4 Hz, 2H), 7.83 (d, J = 7.4 Hz, 2H), 7.90-7.95 (m, 1H), 8.08 (d, J = 7.6 Hz, 2H), 8.14-8.17 (m, 1H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 52.79, 124.73, 125.51, 125.98, 126.61, 126.69, 127.38, 127.71, 128.06, 129.29, 131.06, 131.24, 131.93, 132.26, 133.01, 133.07, 133.61, 134.01, 134.64, 135.24, 136.78, 136.97, 139.48, 155.15, 160.27, 174.28, 177.81, 178.19, 180.21, 189.54, 197.51; FT-IR 3491, 3074, 2960, 1757, 1713, 1672, 1653, 1618, 1584, 1556, 1475, 1449, 1388, 1291, 1267, 1217, 1160, 1066, 1023 cm^{-1} ; MS (FAB) m/z (relative intensity) 517 $[(\text{M}+\text{H})^+, 7]$, 338 (13), 255 (64), 173 (100); HRMS (FAB) calcd. for $\text{C}_{31}\text{H}_{16}^7\text{LiO}_8$ $(\text{M}+\text{Li})^+$ 523.1005 found 523.1002.

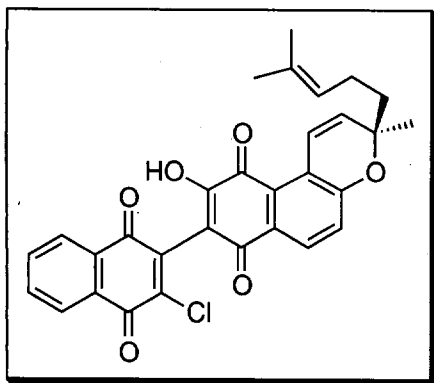


3-Hydroxy-6,3''-dimethoxy-2,2',3',2''-ternaphthalene-1,4,1',4',1'',4''-hexaone (13c). The chloromethoxybiquinone **7a** (0.80 g, 2.11 mmol), the potassium salt **12b** (0.254 g, 1.06 mmol) and 18-crown-6 (0.28 g, 1.06 mmol) were placed in a 100 mL round bottom flask fitted with a T-bore stopcock. After 3 vacuum and argon cycles, 70 mL of anhydrous acetonitrile was added. The suspension was stirred at 65°C for 3 days during which time the mixture turned dark red. The suspension was acidified with concentrated HCl to pH = 2 (litmus) and filtered. Water (200 mL) was added to the filtrate to yield a red precipitate. The aqueous solution was filtered and the red solid on the filter paper was washed with 200 mL of ether and air-dried to yield 0.202 g (49%) of the trimeric quinone **13c** as a brilliant red solid: mp = 279-282 °C; R_f = 0.28 (20% methanol in chloroform); ^1H NMR (500 MHz, DMSO- d_6) δ 3.64 (s, 3H), 3.80 (s, 3H), 6.98 (d, J = 2.5 Hz, 1H), 7.25-7.28 (dd, J = 8.4 Hz, 2.5 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.63-7.66 (dt, J = 7.4 Hz, 1.2 Hz, 2H), 7.70-7.73 (dt, J = 7.4 Hz, 1.2 Hz, 2H), 7.83-7.85 (dd, J = 7.5 Hz, 1.0 Hz, 2H), 8.07-8.08 (dd, J = 7.6 Hz, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, DMSO- d_6) δ 52.69, 55.86, 116.76, 117.76, 124.71 (2C), 125.53 (2C), 126.72 (2C), 127.57, 129.35 (2C), 130.53, 131.39, 132.31 (2C), 133.04 (2C), 133.99 (2C), 136.75 (2C), 138.71, 160.66, 161.19, 178.22 (2C), 180.19 (2C), 189.25, 197.15; FT-IR 3436, 3066, 2952, 2841, 1760, 1739, 1696, 1675, 1653, 1585, 1560, 1457, 1391, 1346, 1321, 1272, 1215, 1154, 1065, 1001 cm^{-1} ; MS (FAB) m/z (relative intensity) 547 (($\text{M}+\text{H}$) $^+$, 3), 307 (32), 154 (100); HRMS (FAB) calcd. for $\text{C}_{32}\text{H}_{19}\text{O}_9$ ($\text{M}+\text{H}$) $^+$ 547.1029 found 547.1005; Anal. calcd. for $\text{C}_{32}\text{H}_{18}\text{O}_9$: C, 70.33; H, 3.32. found: C, 69.61; H, 3.42.



3,3''-Dihydroxy-2,2'; 3',2''-ternaphthalene-1,4,1',4',1'',4''-hexaone (13b). The trimeric quinone monomethyl ether **13a** (0.05 g, 0.1 mmol) was placed in a 25 mL round bottom flask. THF (8 mL) and EtOH (8 mL) were added and the resulting red suspension stirred for 30 min at room temperature. 4M KOH (2 mL) was added and the resulting orange-brown suspension refluxed for 18 hours. The mixture was cooled to room temperature then acidified with concentrated HCl to pH = 2 (litmus) forming a spectacular

red precipitate. Water (50 mL) was added and the mixture extracted with CHCl_3 (250 mL). The organic layer was dried (MgSO_4), filtered, and evaporated to yield 0.042 g (84%) of the dihydroxy trimeric quinone **13b** as a red solid: mp = 325-329 °C; R_f = 0.15 (20% methanol in chloroform); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.33-7.36 (t, J = 7.51 Hz, 1H), 7.44-7.46 (d, J = 7.43 Hz, 1H), 7.50-7.52 (d, J = 7.78 Hz, 1H), 7.55-7.58 (t, J = 7.43 Hz, 1H), 7.62-7.65 (t, J = 7.44 Hz, 2H), 7.69-7.72 (t, J = 7.42 Hz, 2H), 7.81-7.83 (d, J = 7.59 Hz, 2H), 8.07-8.09 (d, J = 7.67 Hz, 2H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 124.70, 125.55 (2C), 126.69 (2C), 127.47 (2C), 128.92, 129.30 (2C), 130.38 (2C), 130.94 (2C), 132.24, 132.31, 133.03 (2C), 134.11, 134.74 (2C), 135.35 (2C), 136.80, 171.41, 178.30 (2C), 180.34 (2C), 194.96; FT-IR 3445 (very broad), 3069, 1734, 1652, 1584, 1554, 1437, 1388, 1293, 1267, 1217, 1159, 1064, 1022 cm^{-1} ; MS (FAB) m/z (relative intensity) 503 [($\text{M}+2+\text{H}$) $^+$, 2], 460 (8), 307 (33), 154 (100); HRMS (FAB) calcd. for $\text{C}_{30}\text{H}_{15}\text{O}_8$ ($\text{M}+\text{H}$) $^+$ 503.0767 found 503.0742; Anal. calcd. for $\text{C}_{30}\text{H}_{14}\text{O}_8$: C, 71.72; H, 2.81. Found: C, 71.14; H, 2.92.



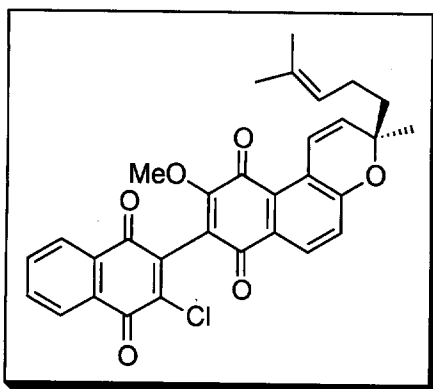
8-(3-Chloro-1,4-dioxo-1,4-dihydro-naphthalen-2-yl)-9-hydroxy-3-methyl-3-(4-methyl-pent-3-enyl)-3H-benzo [f]chromene-7,10-dione (15a).

Reaction of 2,3-dichloro-1,4-naphthoquinone **10a** (0.302 g, 1.33 mmol) with teretifolione B³ **14** (0.430 g, 1.33 mmol) for 7 days, according to the general procedure described above for the synthesis of the 3'-halo-3-hydroxy-2,2'-binaphthalenyl-

1,4,1',4'-tetraones **6**, yielded 0.650 g (95%) of the biquinone **15a** as a brilliant red solid: mp = 96-99 °C; R_f = 0.26 (40% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 1.47 (d, J = 3.0 Hz, 3H), 1.57 (d, J = 3.8 Hz, 3H), 1.66 (d, J = 4.0 Hz, 3H), 1.70-1.75 (m, 2H), 1.78-1.84 (m, 2H), 5.07-5.10 (m, 1H), 6.00 (d, J = 10.4 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 7.77-7.79 (m, 2H), 7.84 (d, J = 10.4 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 8.13-8.15 (m, 1H), 8.21-8.23 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 18.07, 23.07, 26.07, 27.07, 41.72, 80.06, 114.06, 120.37, 122.33, 122.94, 123.65, 123.84, 127.04, 127.75, 127.85, 129.82, 131.81, 132.28, 132.70, 134.52, 134.85, 136.33,

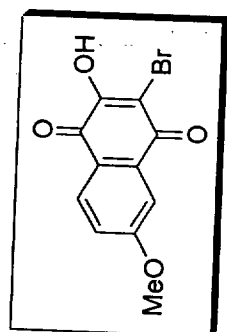
(3) Cannon, J. R.; Joshi, K. R.; McDonald, I. A.; Retallack, R. W.; Sierakowski, A. F.; Wong, L. C. H. *Tetrahedron Lett.* **1975**, 32, 2795-2798.

139.38, 146.22, 153.57, 158.98, 177.84, 180.79, 181.31, 183.06; FT-IR 3337, 2970, 2922, 1679, 1662, 1645, 1592, 1562, 1460, 1436, 1357, 1303, 1277, 1200, 1138, 1076 cm^{-1} ; MS (FAB) m/z (relative intensity) 517 $[(M+2+H)^+, 55]$, 515 $[(M+H)^+, 100]$, 397 (57), 297 (21), 213 (26), 154 (58); HRMS (FAB) calcd. for $\text{C}_{30}\text{H}_{24}^{35}\text{ClO}_6$ $(M+H)^+$ 515.1261, found 515.1279.

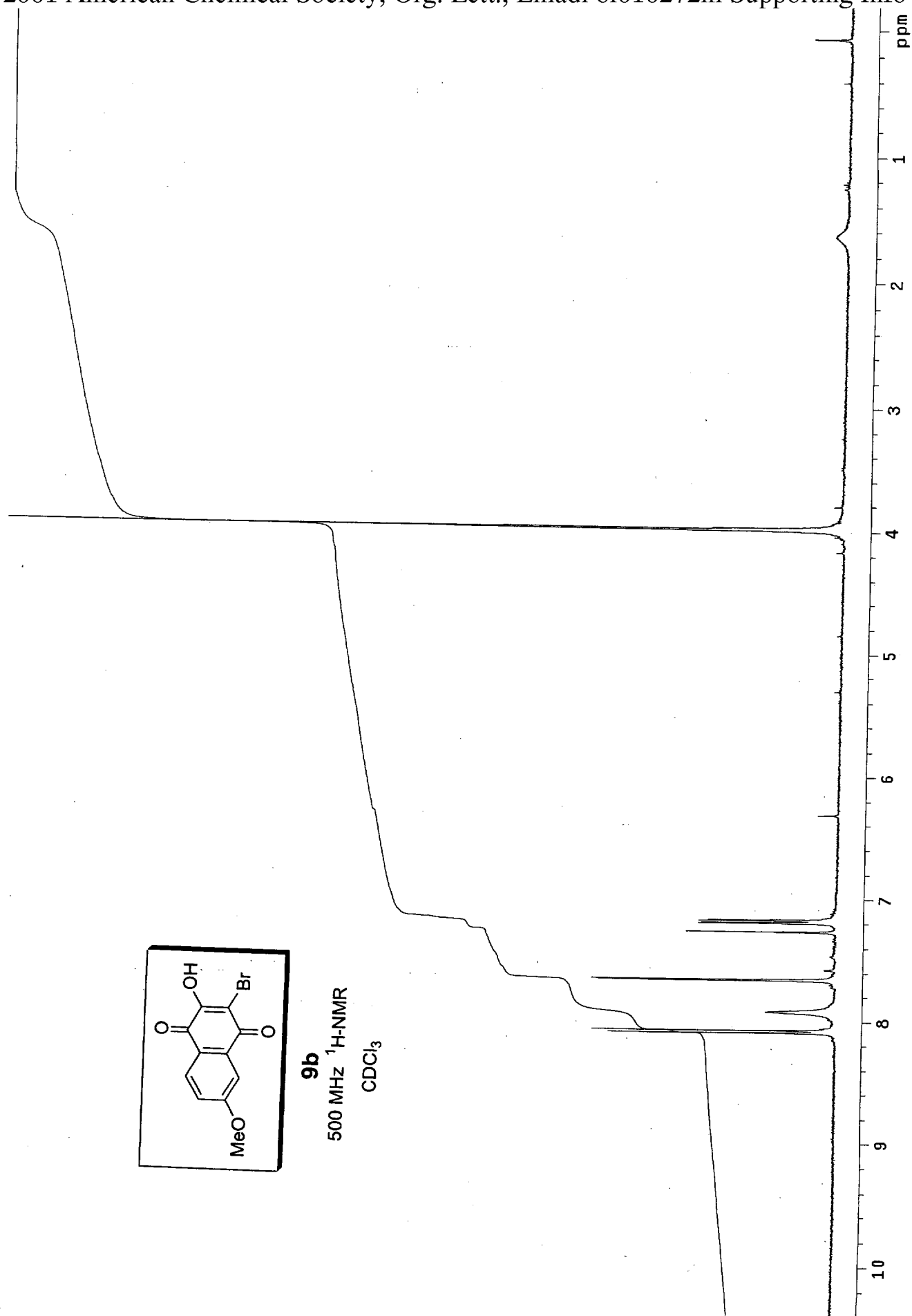


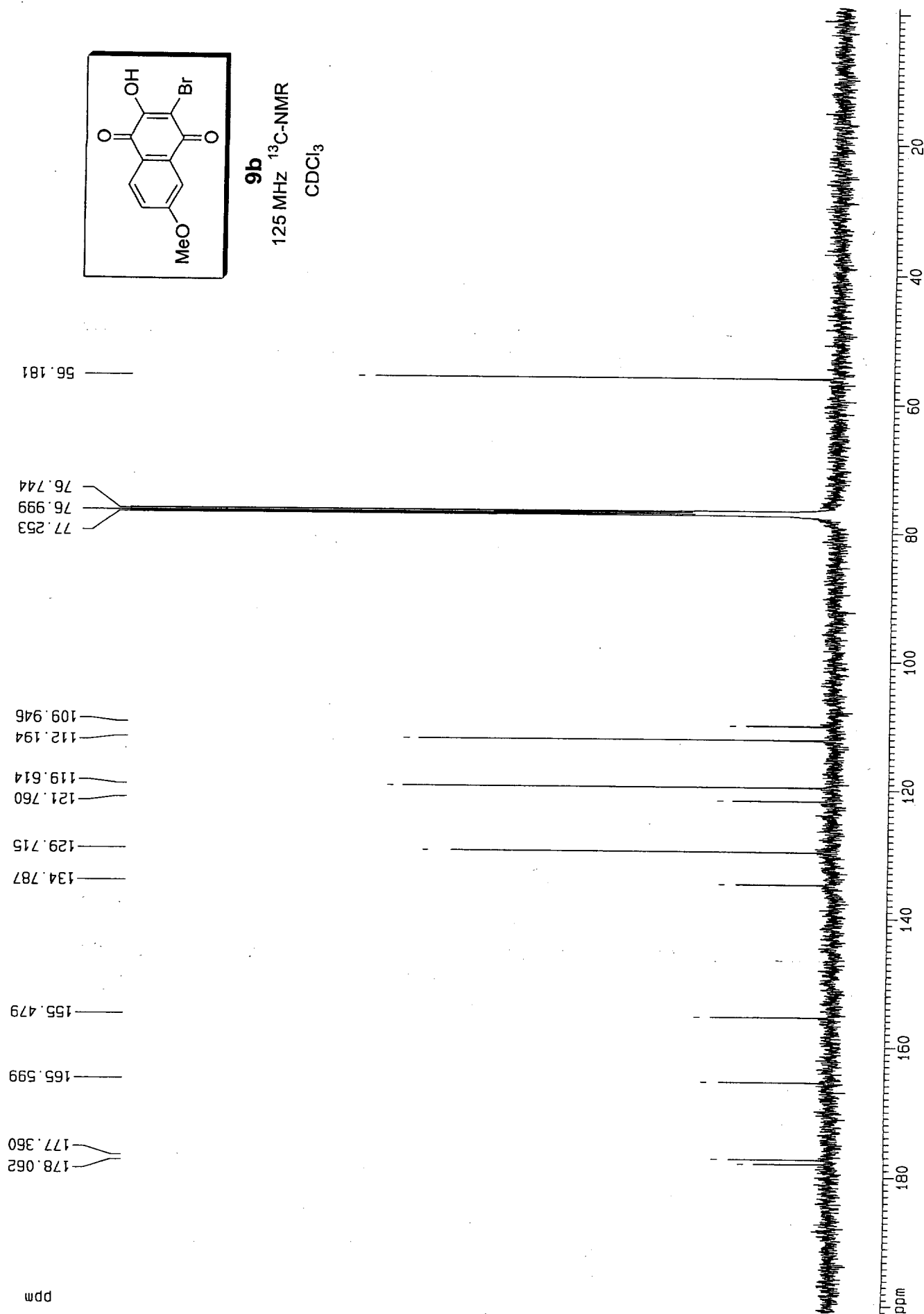
8-(3-Chloro-1,4-dioxo-1,4-dihydro-naphthalen-2-yl)-9-methoxy-3-methyl-3-(4-methyl-pent-3-enyl)-3H-benzo[f]chromene-7,10-dione (15b).

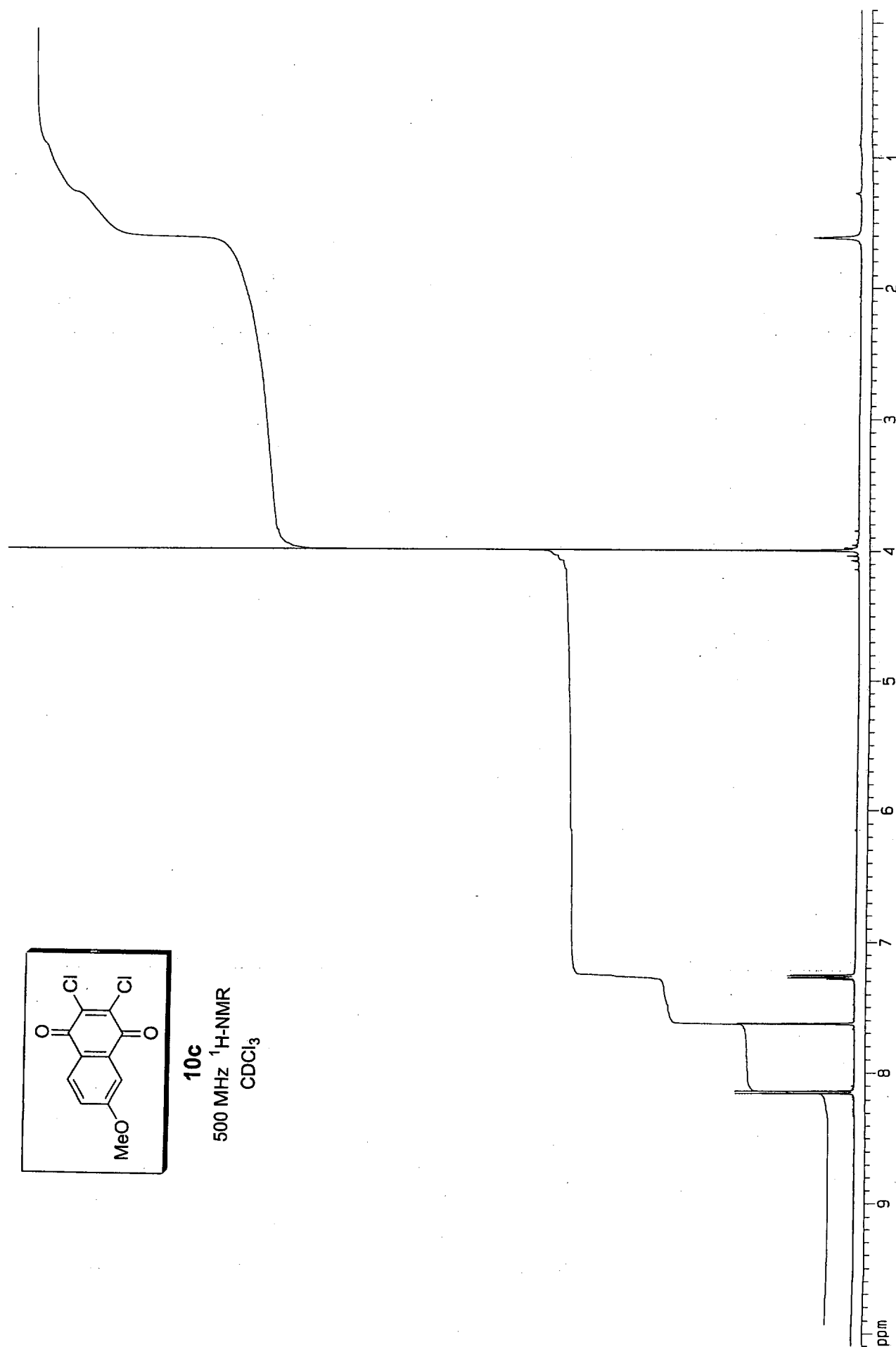
Reaction of the chlorohydroxybiquinone **15a** (0.250 g, 0.49 mmol) with trimethyloxonium tetrafluoroborate (0.145 g, 0.98 mmol) and *N,N*-diisopropylethylamine (0.096 g (0.129 mL), 0.74 mmol) in methylene chloride (40 mL) according to the general procedure described above for the synthesis of 3'-halo-3-methoxy-2,2'-binaphthalenyl-1,4,1',4'-tetraones **7**, yielded 0.166 g (64%) of the methyl ether **15b** as a bronze sponge: mp = 71–74°C; R_f = 0.21 (5% EtOAc in hexane); ^1H NMR (500 MHz, CDCl_3) δ 1.49 (d, J = 3.1 Hz, 3H), 1.60 (d, J = 2.7 Hz, 3H), 1.69 (d, J = 4.8 Hz, 3H), 1.71–1.77 (m, 2H), 1.80–1.85 (m, 2H), 4.11 (s, 3H), 5.10–5.12 (m, 1H), 5.96 (d, J = 10.4 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 10.5 Hz, 1H), 7.80–7.85 (m, 2H), 7.97 (d, J = 8.5 Hz, 1H), 8.16–8.18 (m, 1H), 8.22–8.26 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 18.08, 23.07, 26.07, 27.01, 41.67, 61.48, 79.89, 120.50, 121.56, 121.99, 122.47, 123.92, 126.16, 126.54, 127.76, 127.87, 129.12, 131.84, 132.22, 132.62, 134.57, 134.85, 135.04, 140.74, 145.62, 158.58, 159.48, 177.74, 180.99, 181.78, 183.49; FT-IR 3068, 2921, 2852, 1678, 1662, 1645, 1593, 1564, 1461, 1373, 1312, 1277, 1207, 1163, 1139, 1105, 1074, 1024 cm^{-1} ; MS (FAB) m/z (relative intensity) 531 $[(M+2+H)^+, 41]$, 529 $[(M+H)^+, 69]$, 445 (42), 154 (100); HRMS (FAB) calcd. for $\text{C}_{31}\text{H}_{26}^{35}\text{ClO}_6$ $(M+H)^+$ 529.1418, found 529.1427.

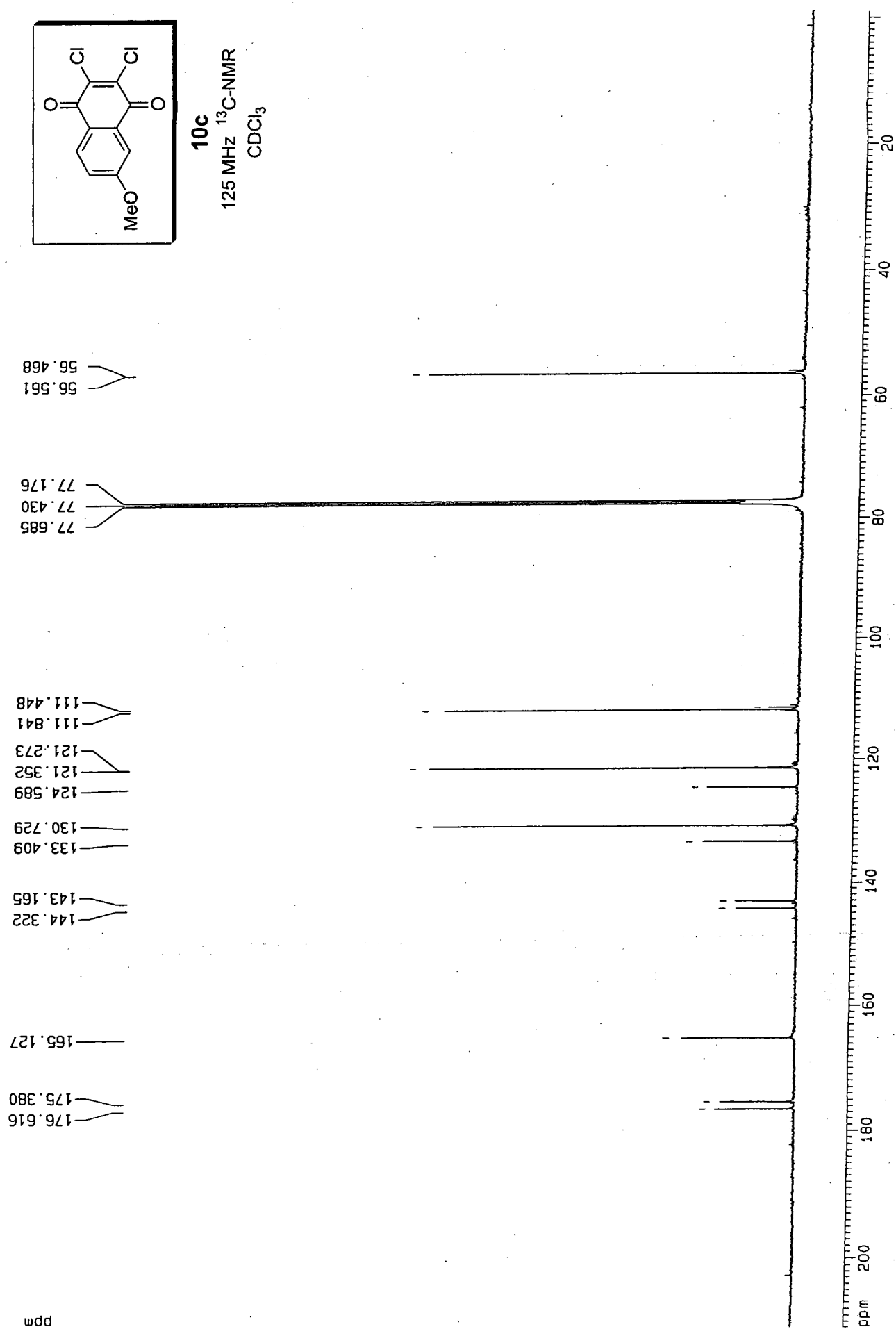


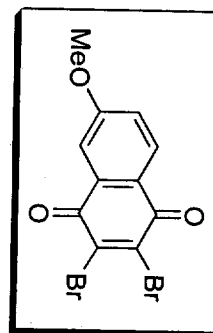
9b
500 MHz $^1\text{H-NMR}$
 CDCl_3







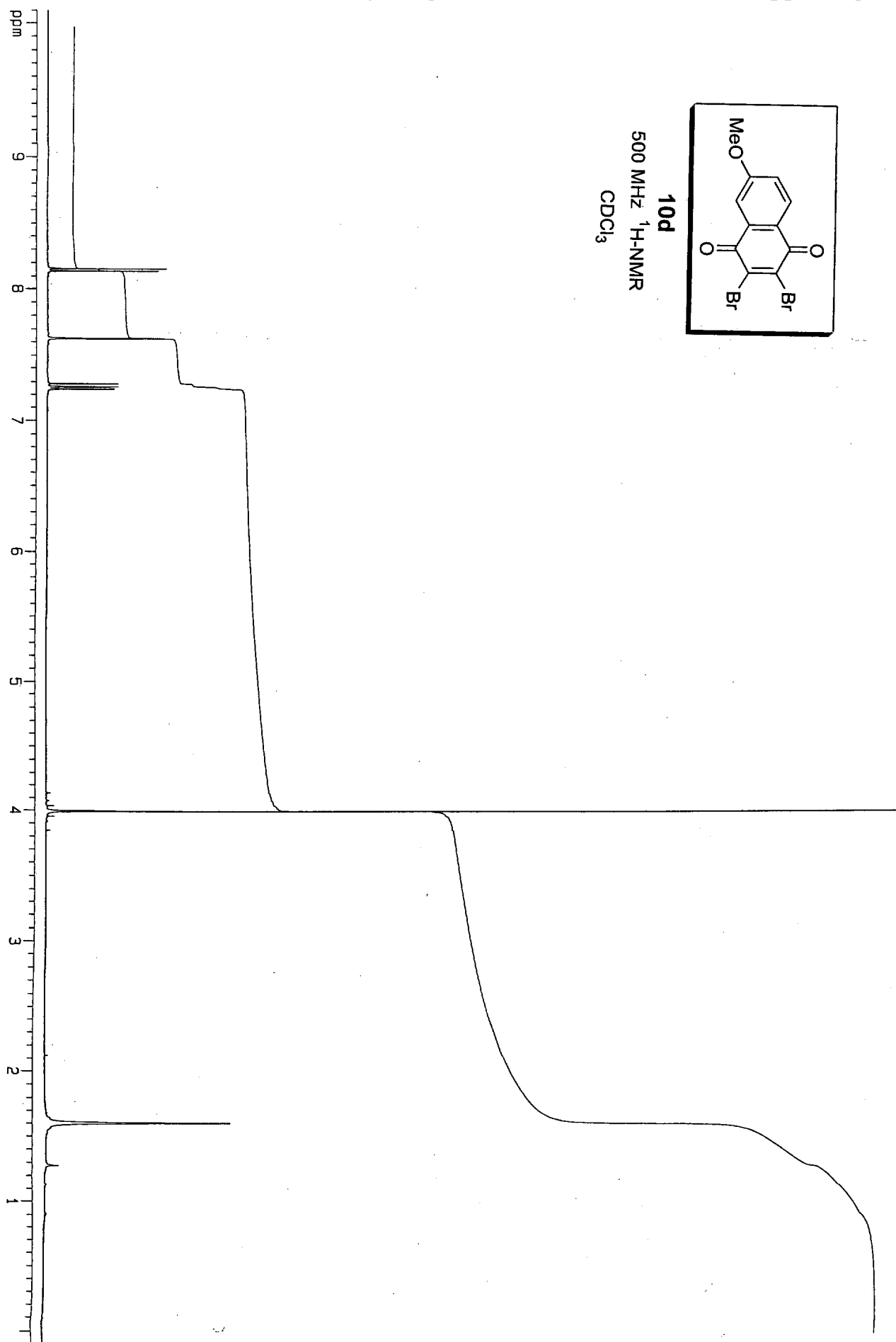


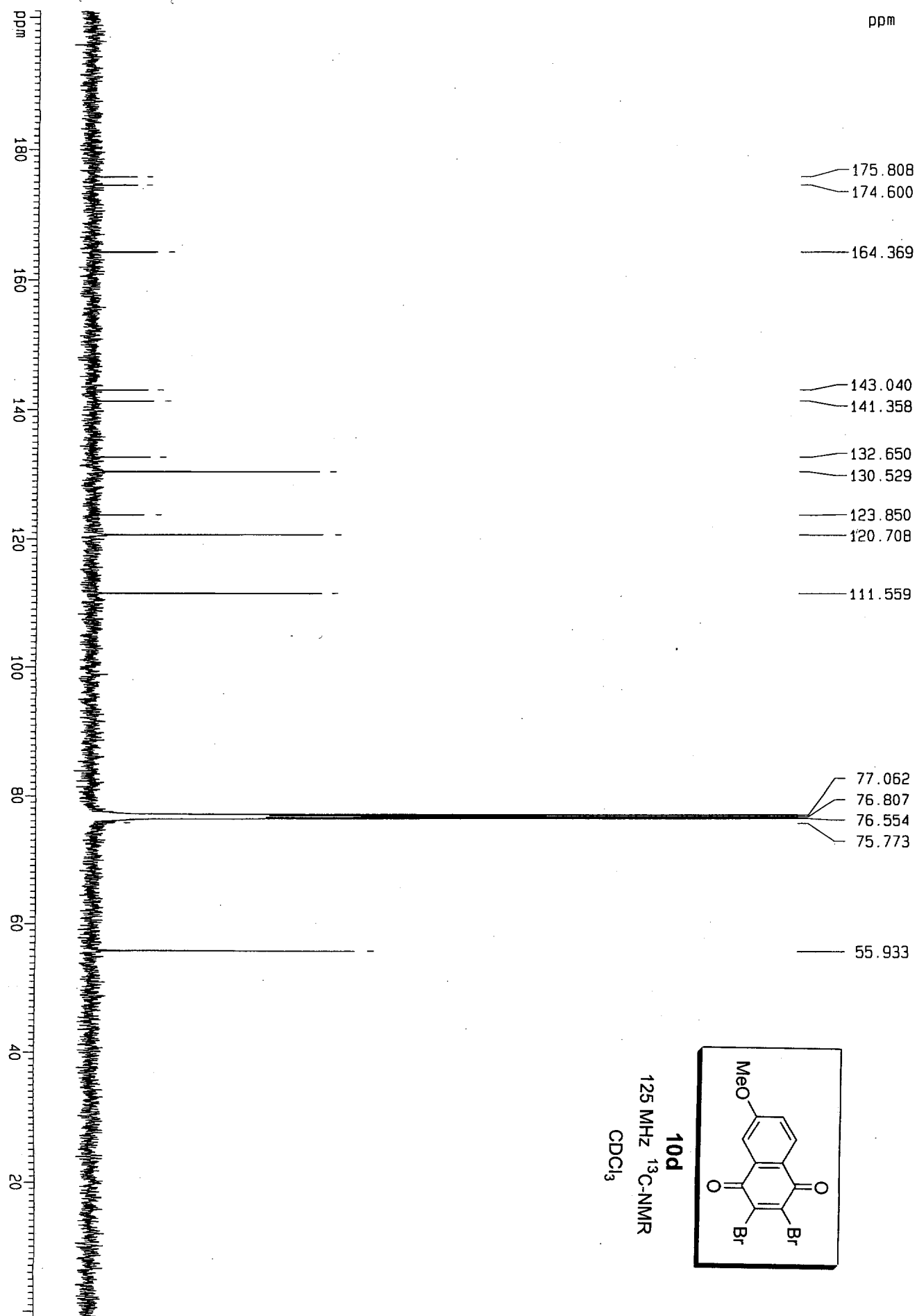


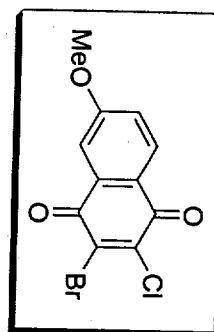
10d

500 MHz ^1H -NMR

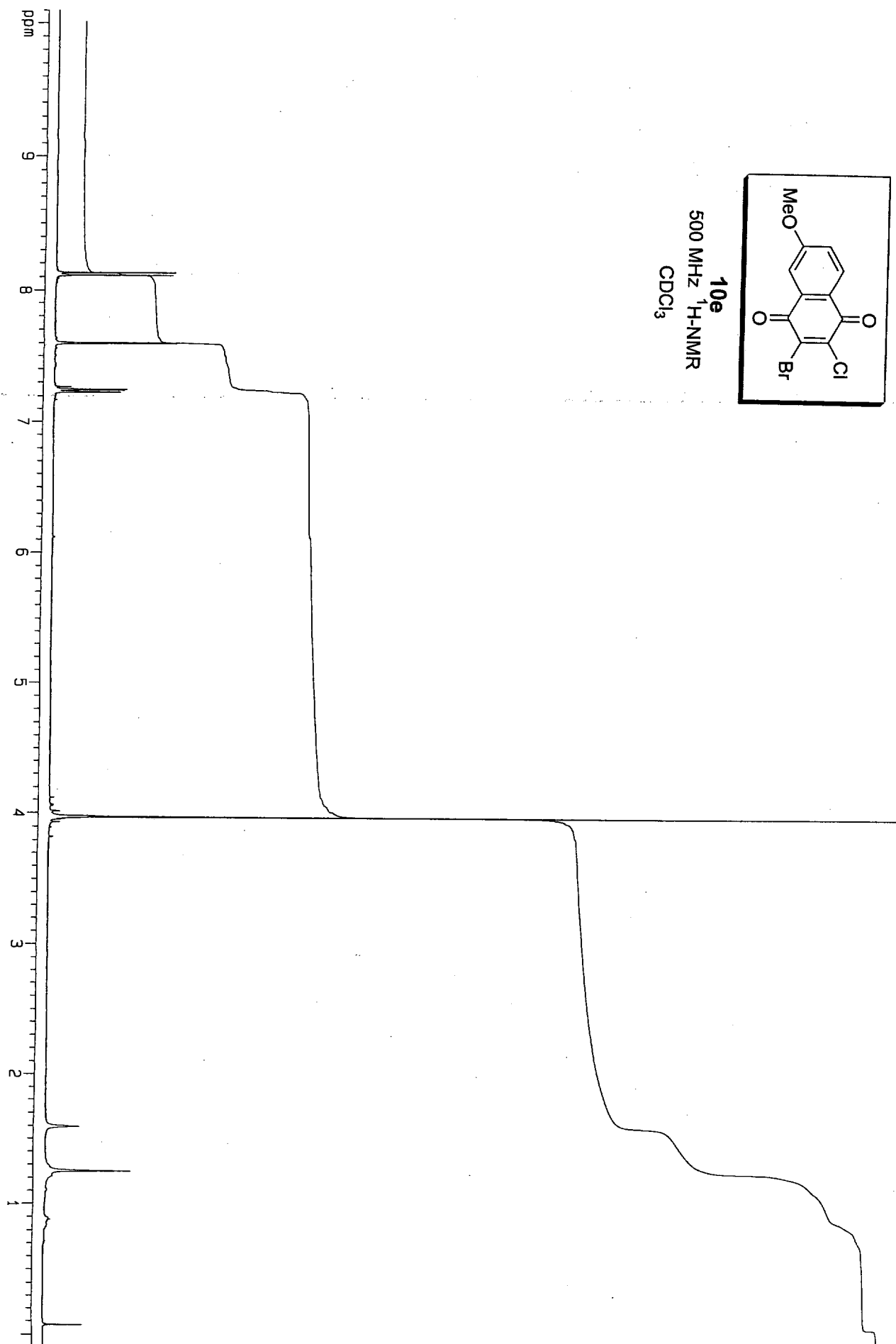
CDCl_3

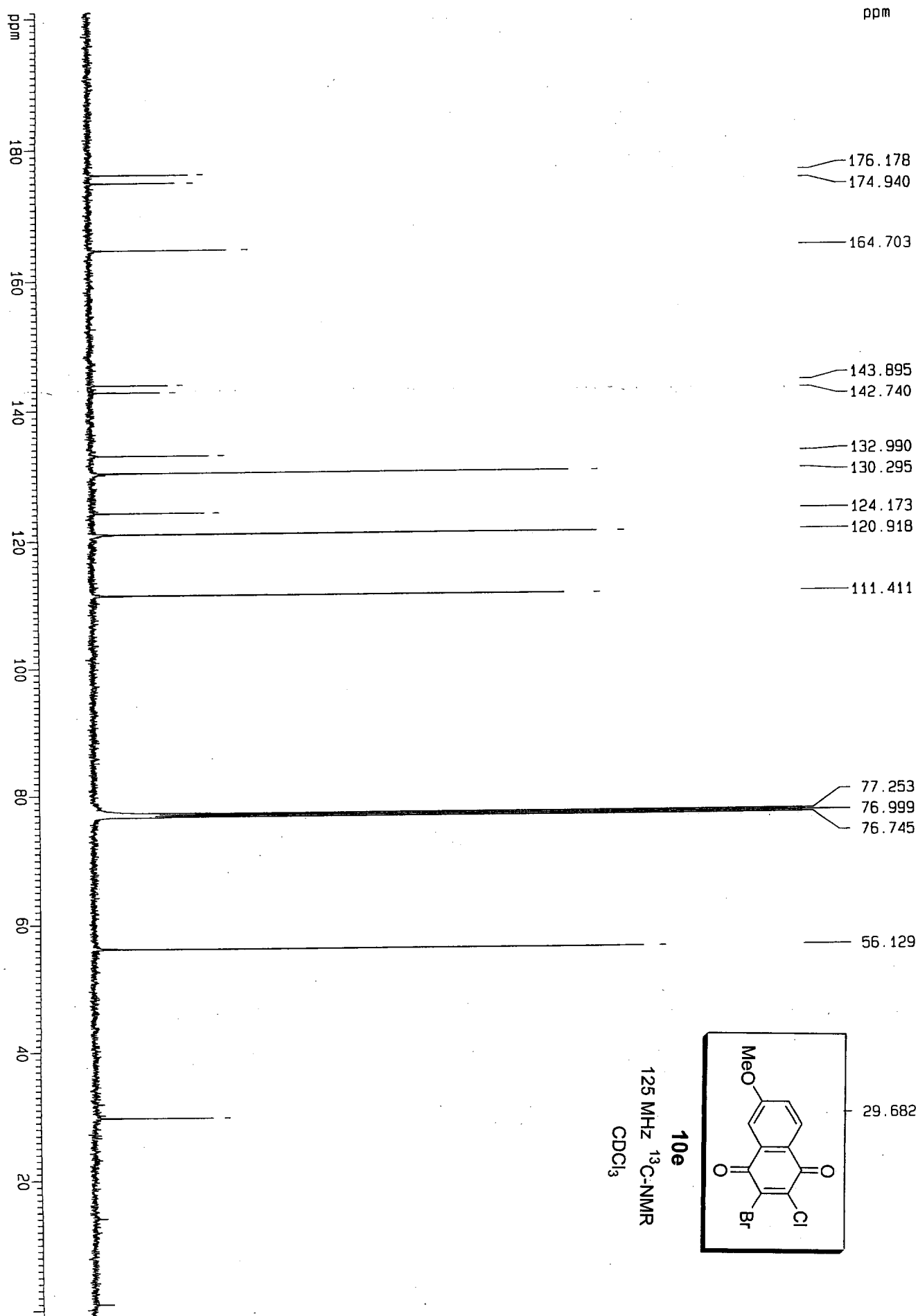


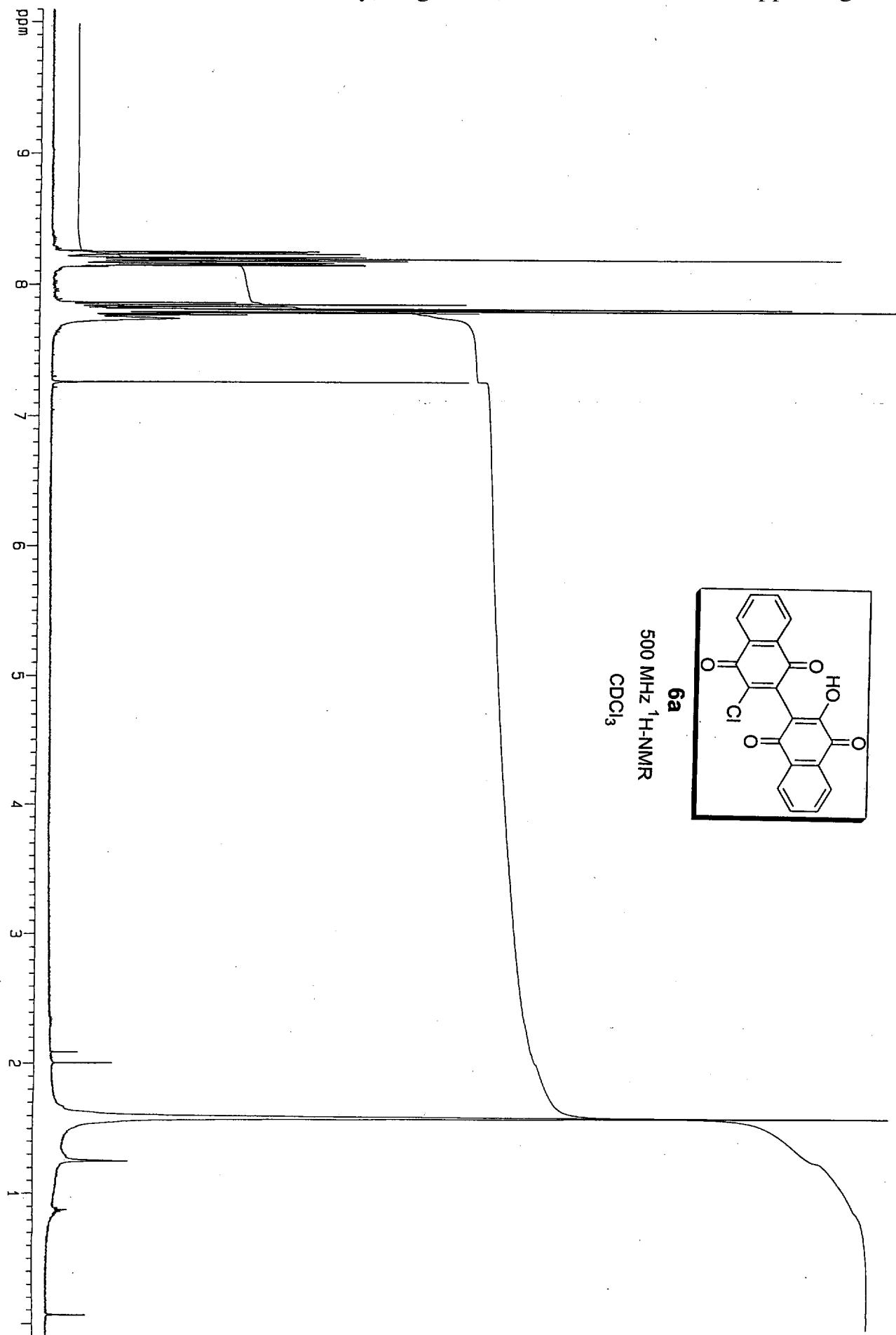


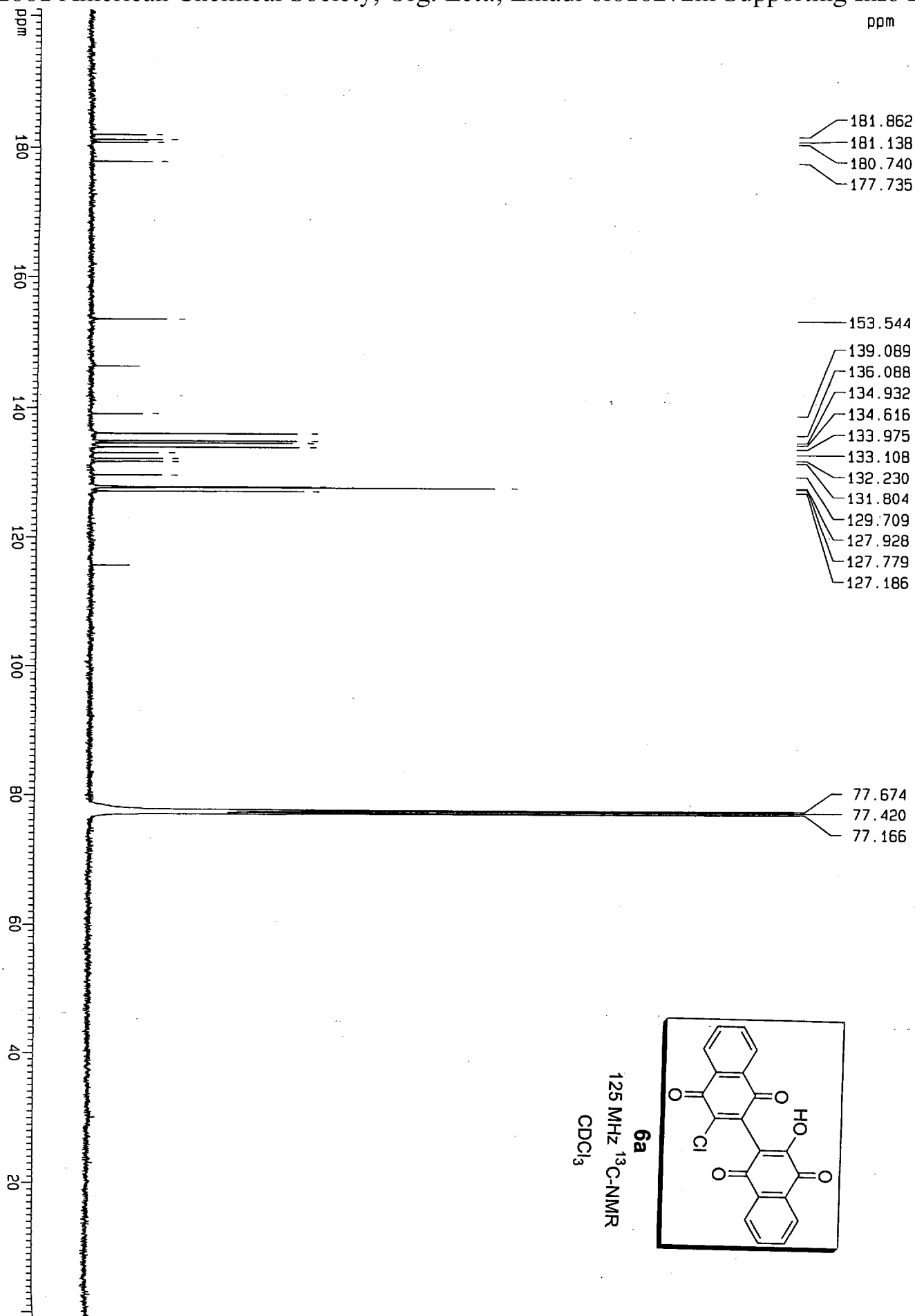


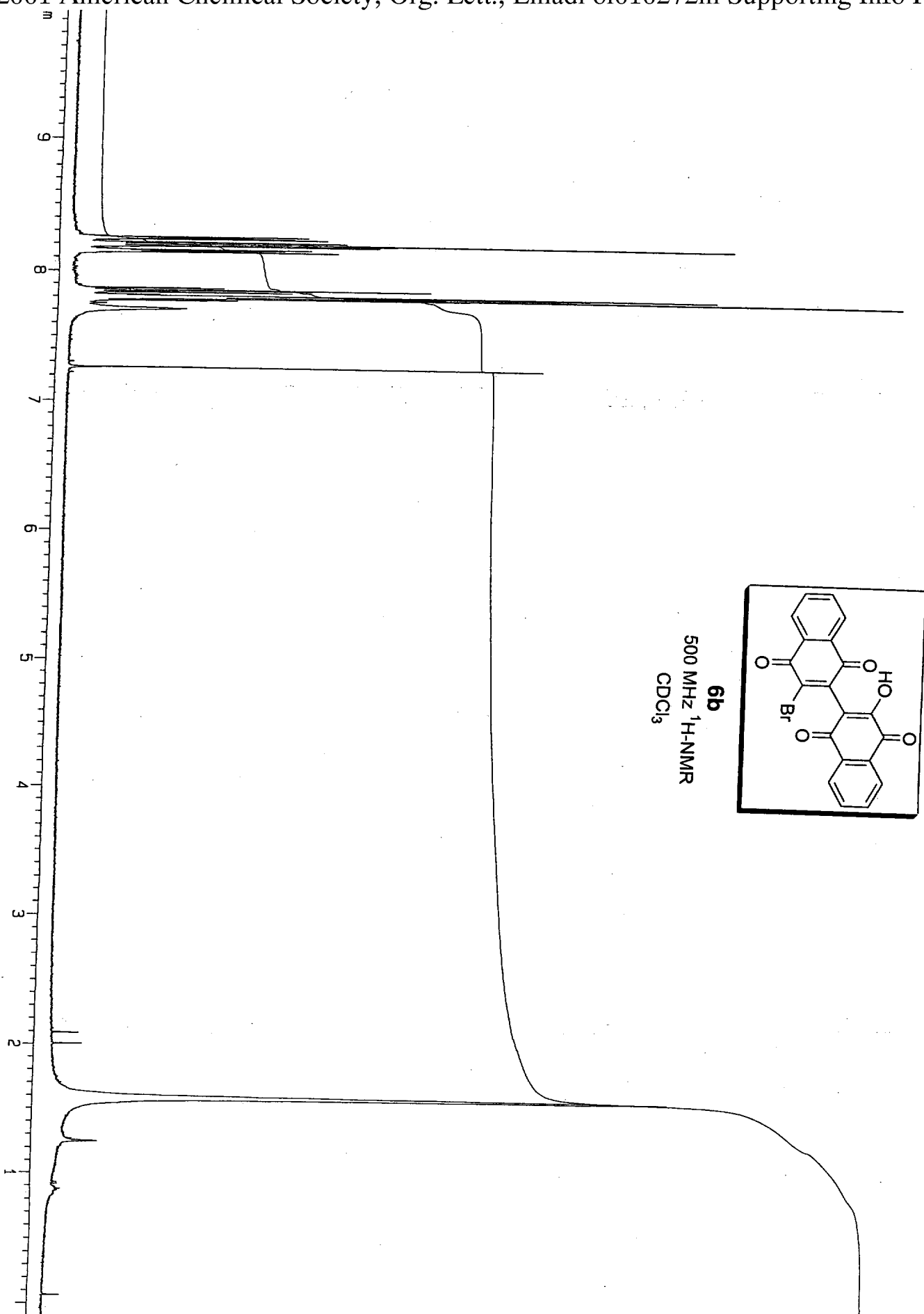
10e
500 MHz ^1H -NMR
 CDCl_3

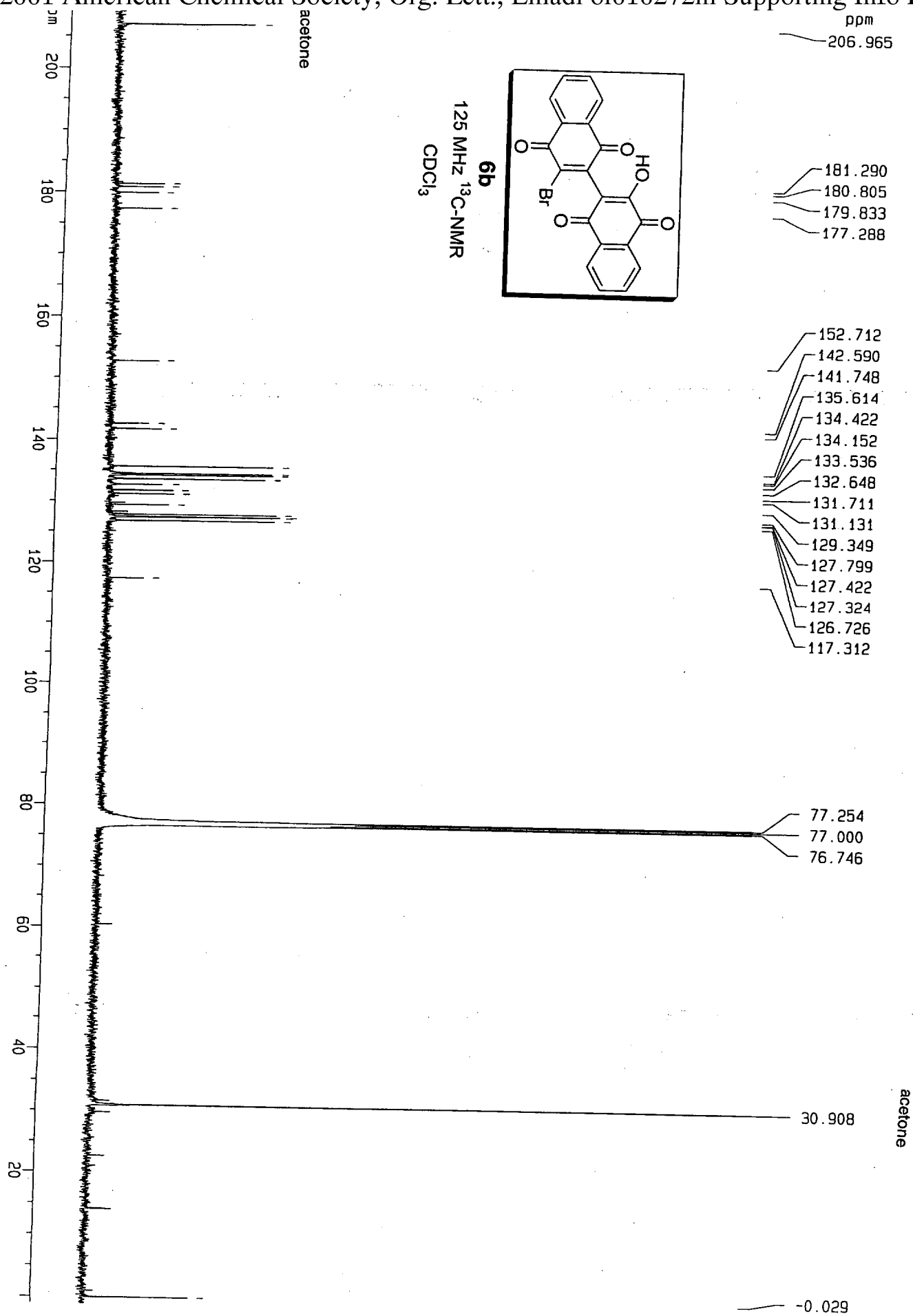


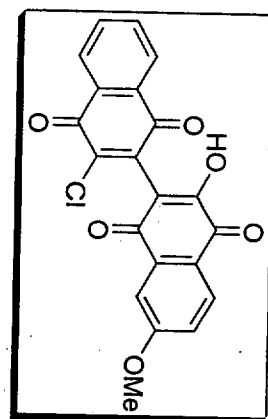








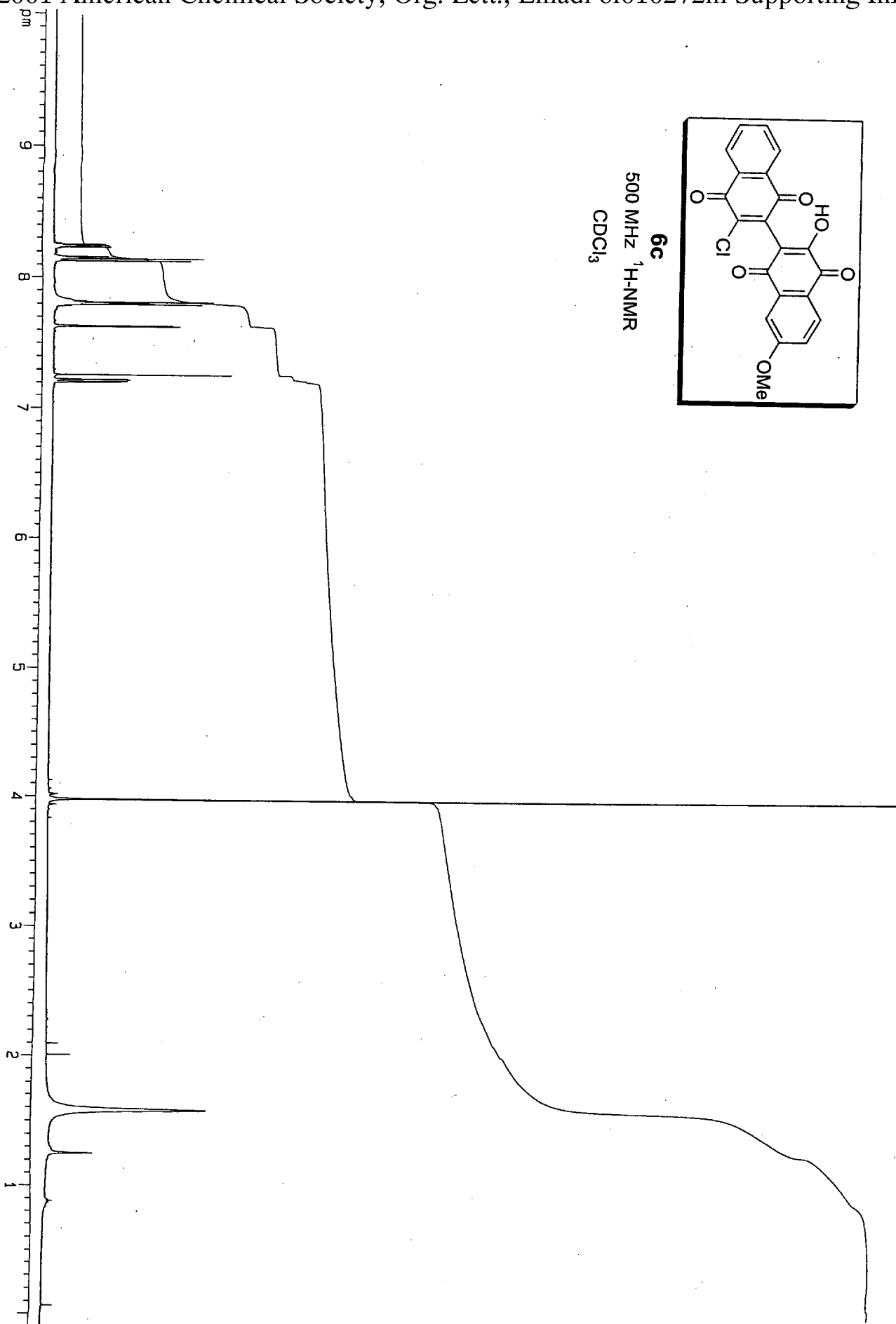


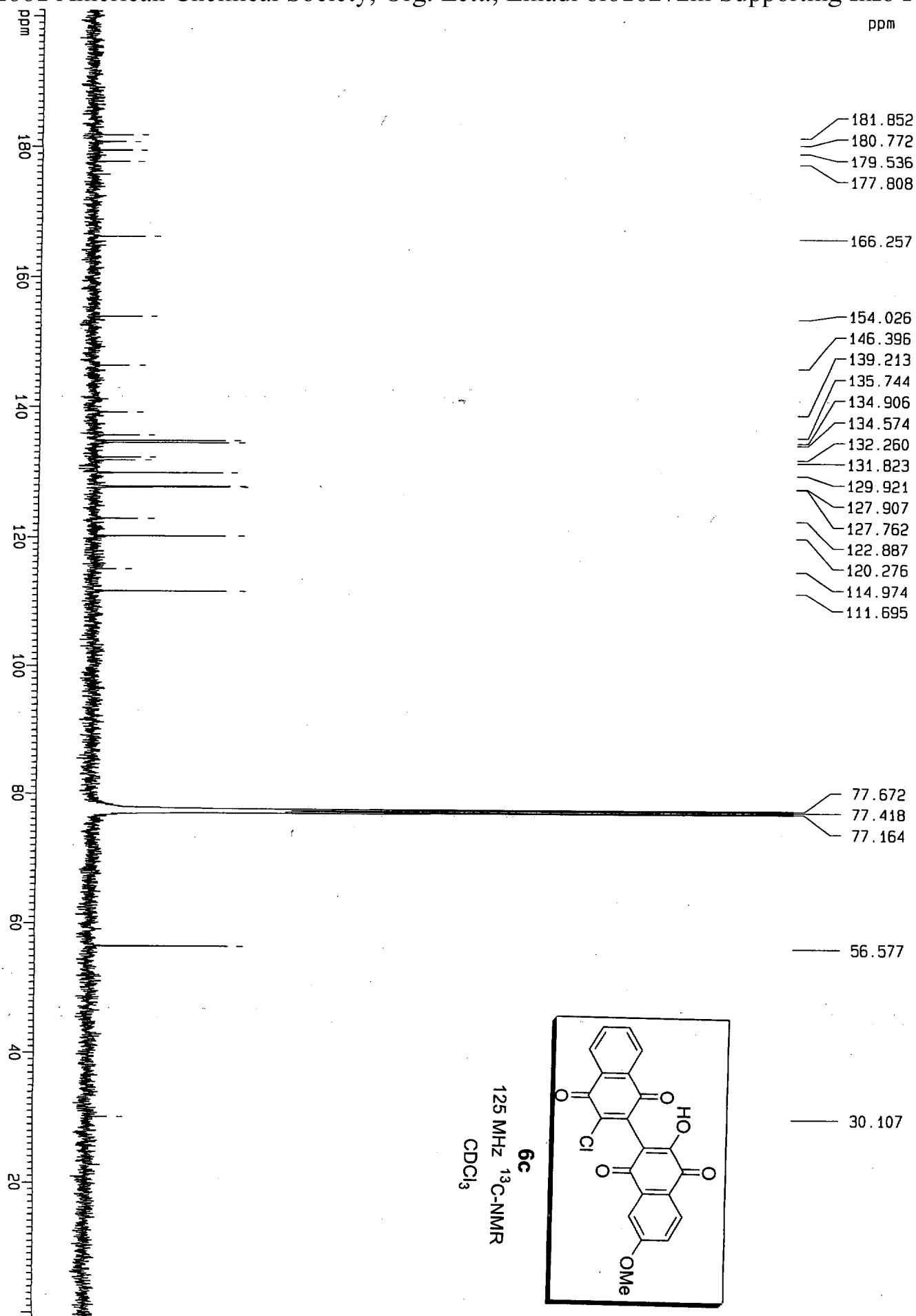


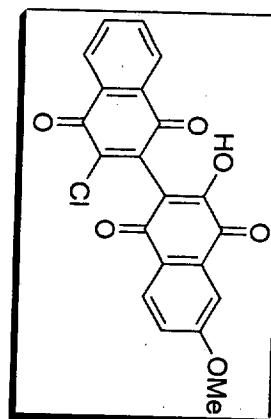
6c

500 MHz $^1\text{H-NMR}$

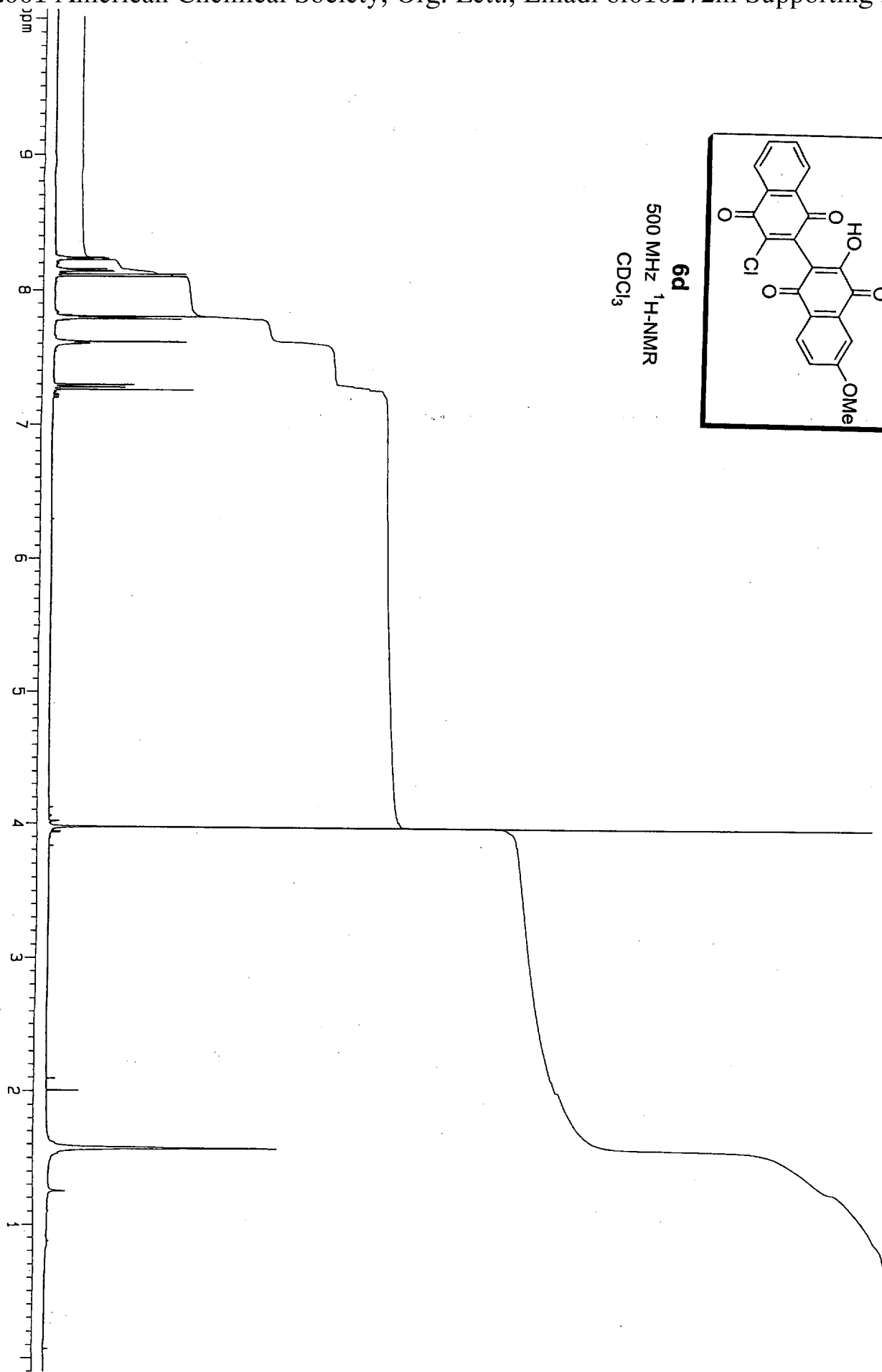
CDCl_3

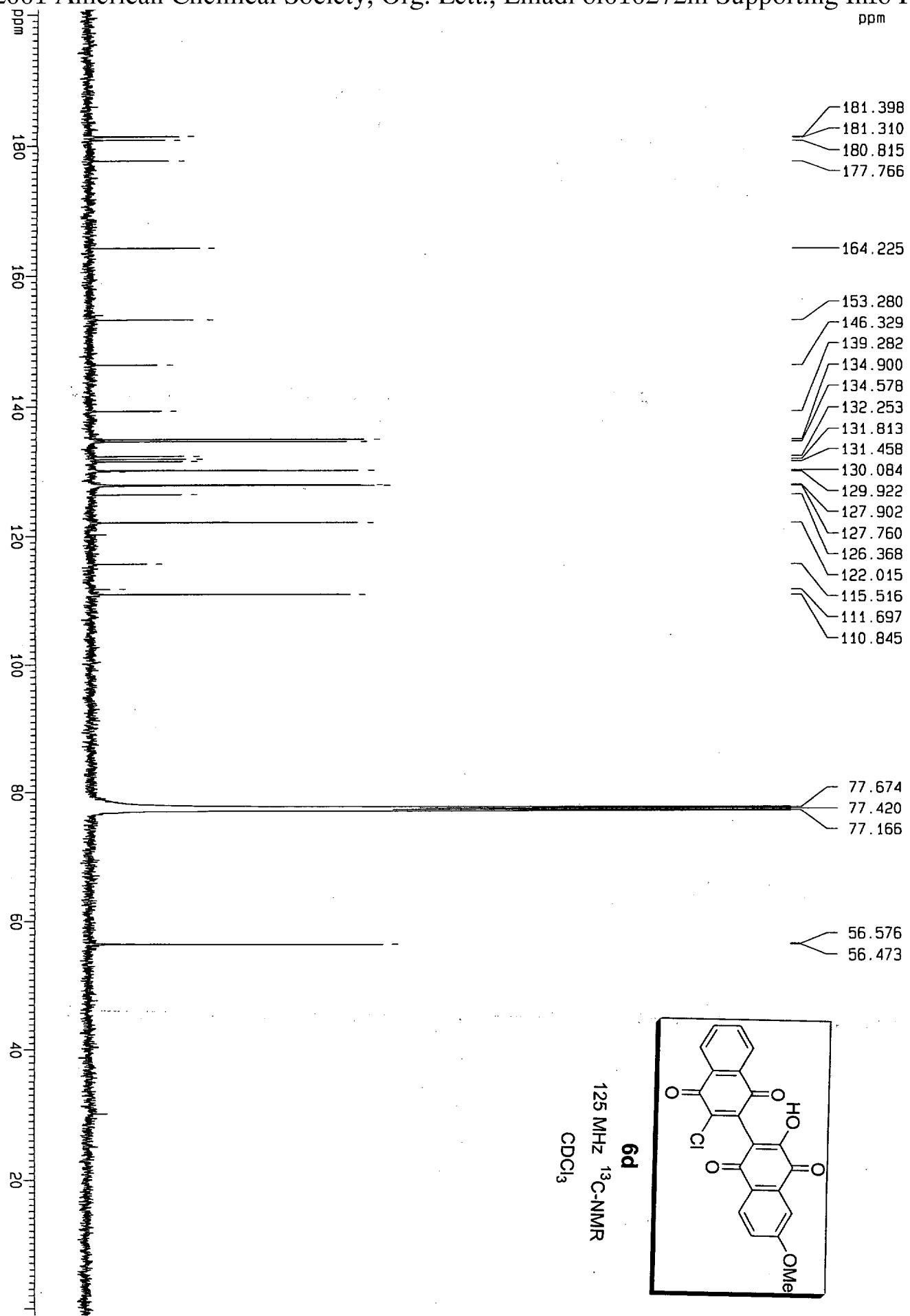


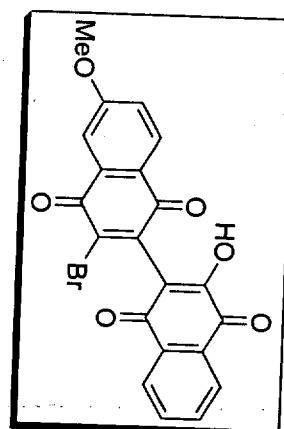




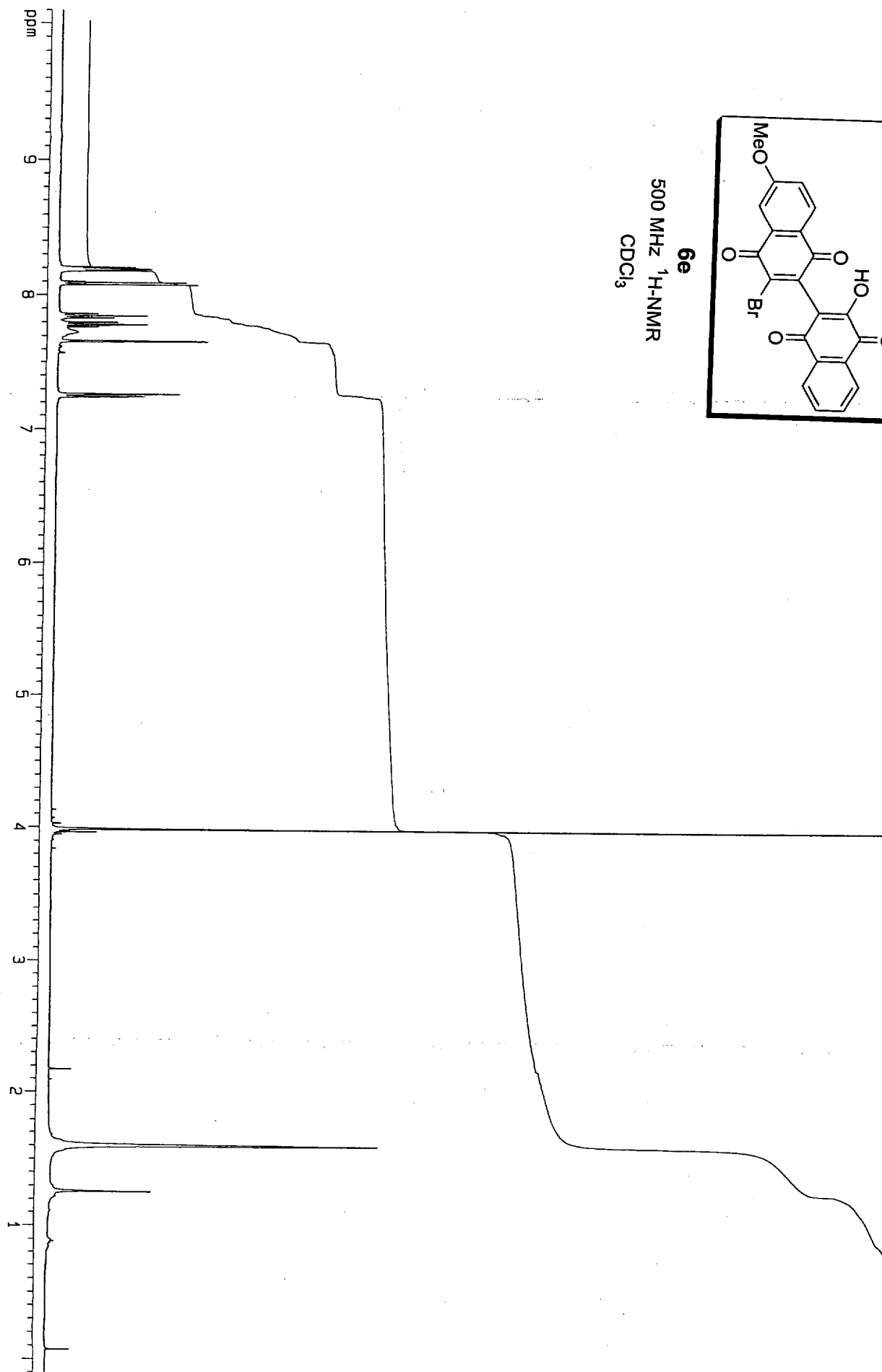
6d
500 MHz ^1H -NMR
 CDCl_3

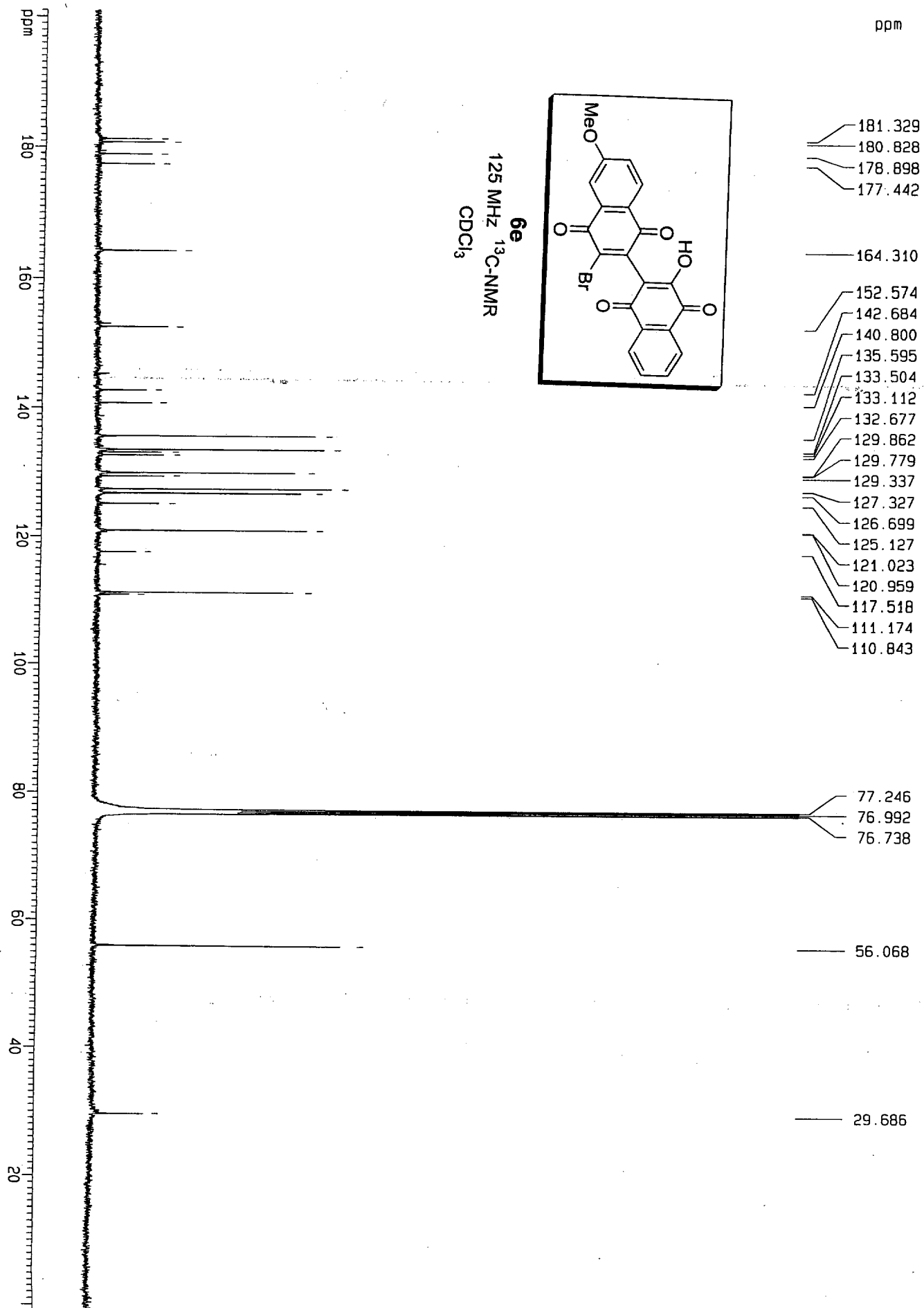


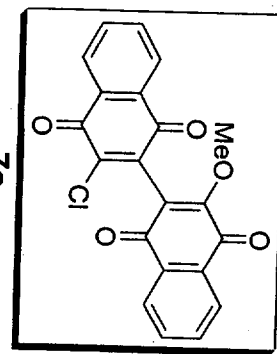
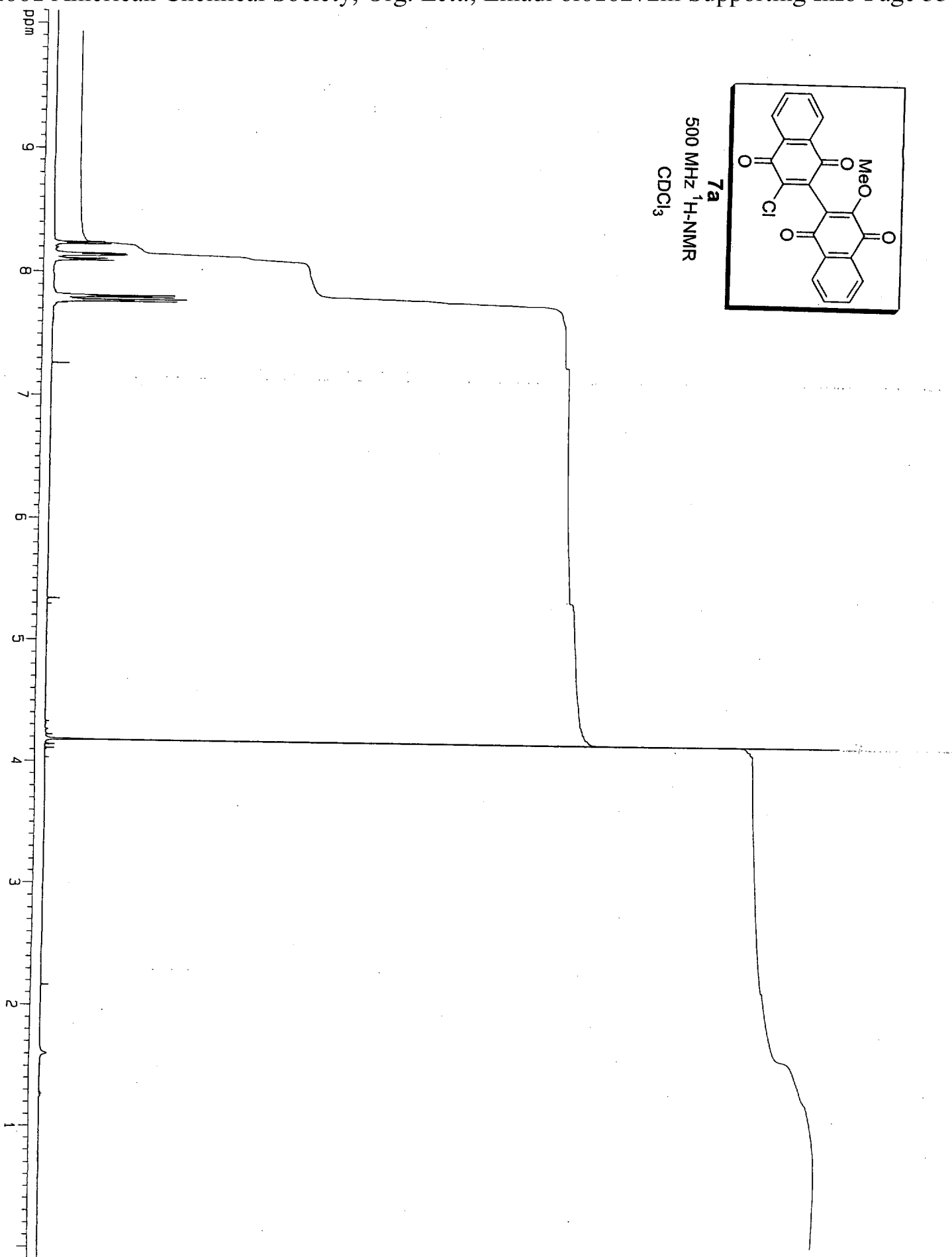




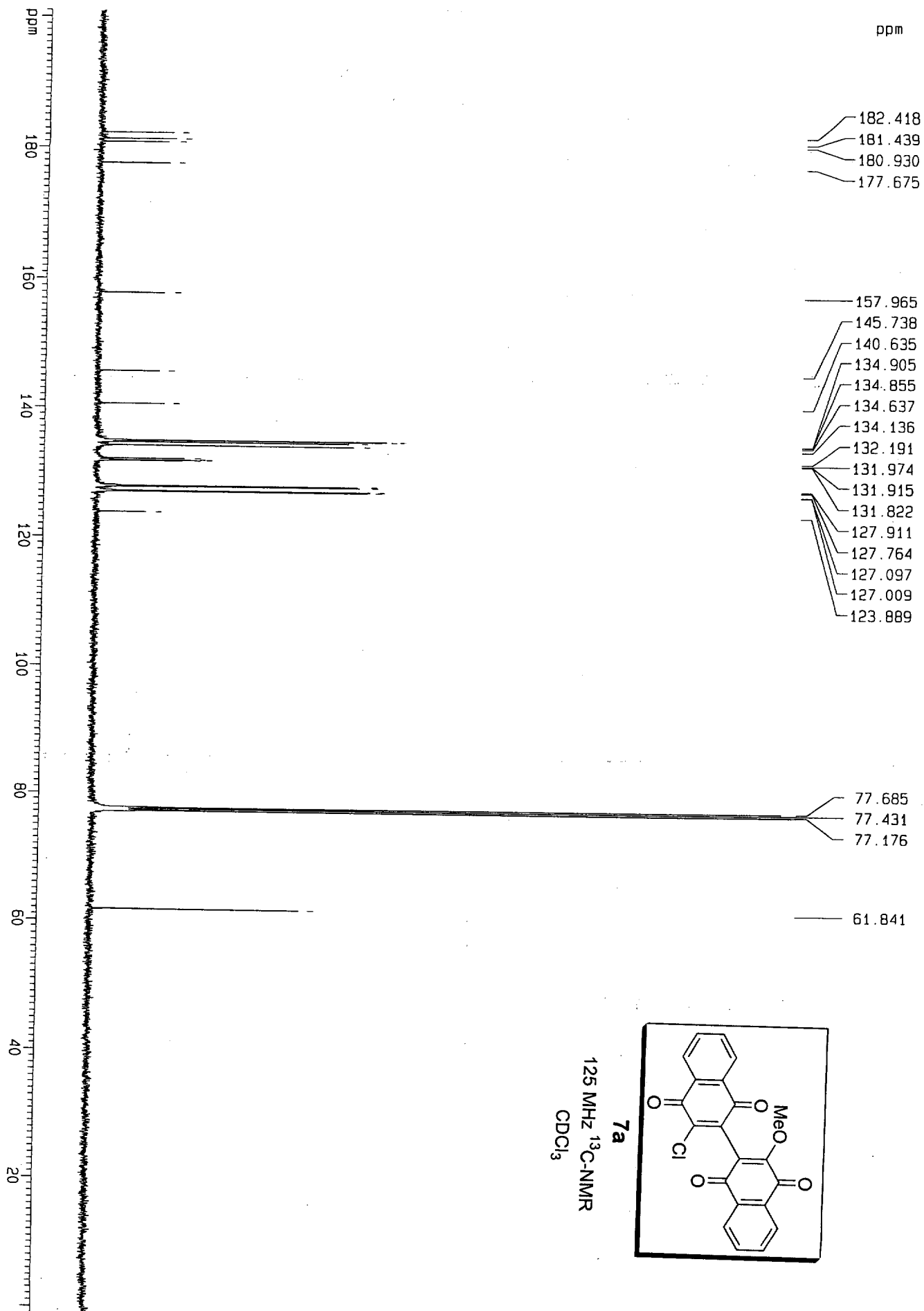
6e
500 MHz ^1H -NMR
 CDCl_3

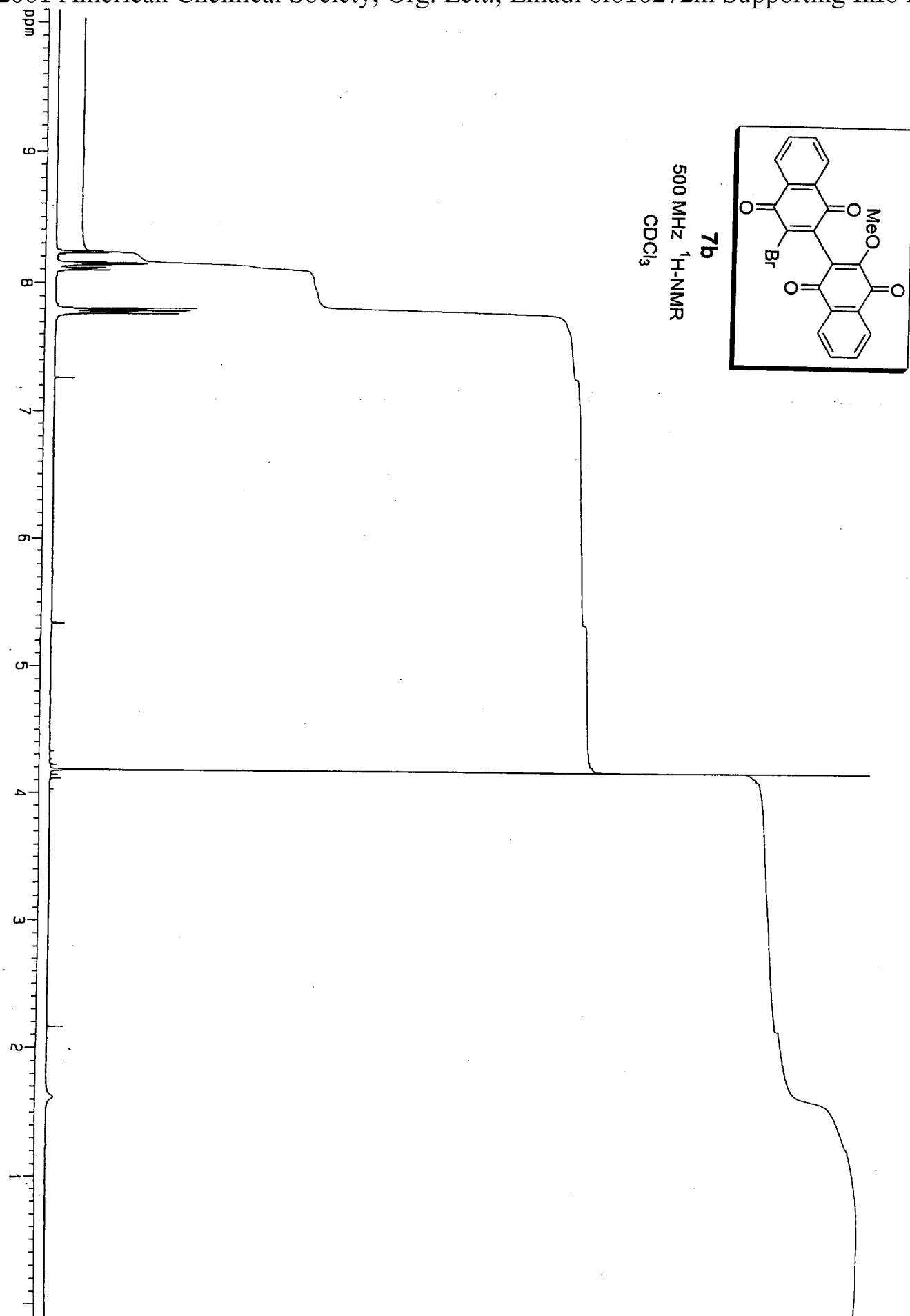


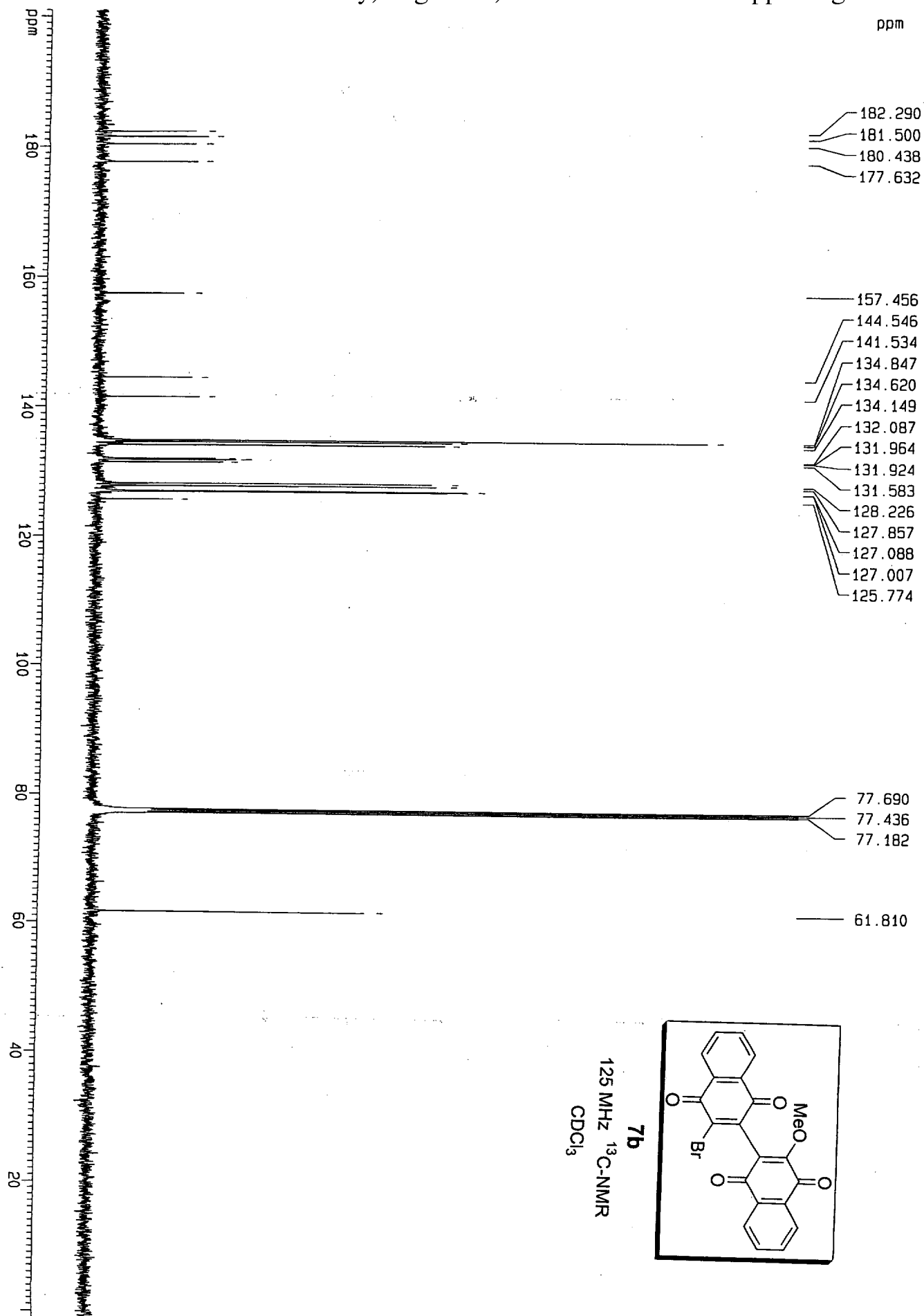


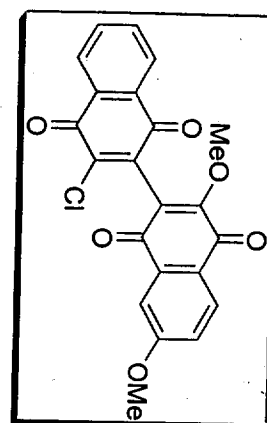


500 MHz ^1H -NMR
 CDCl_3

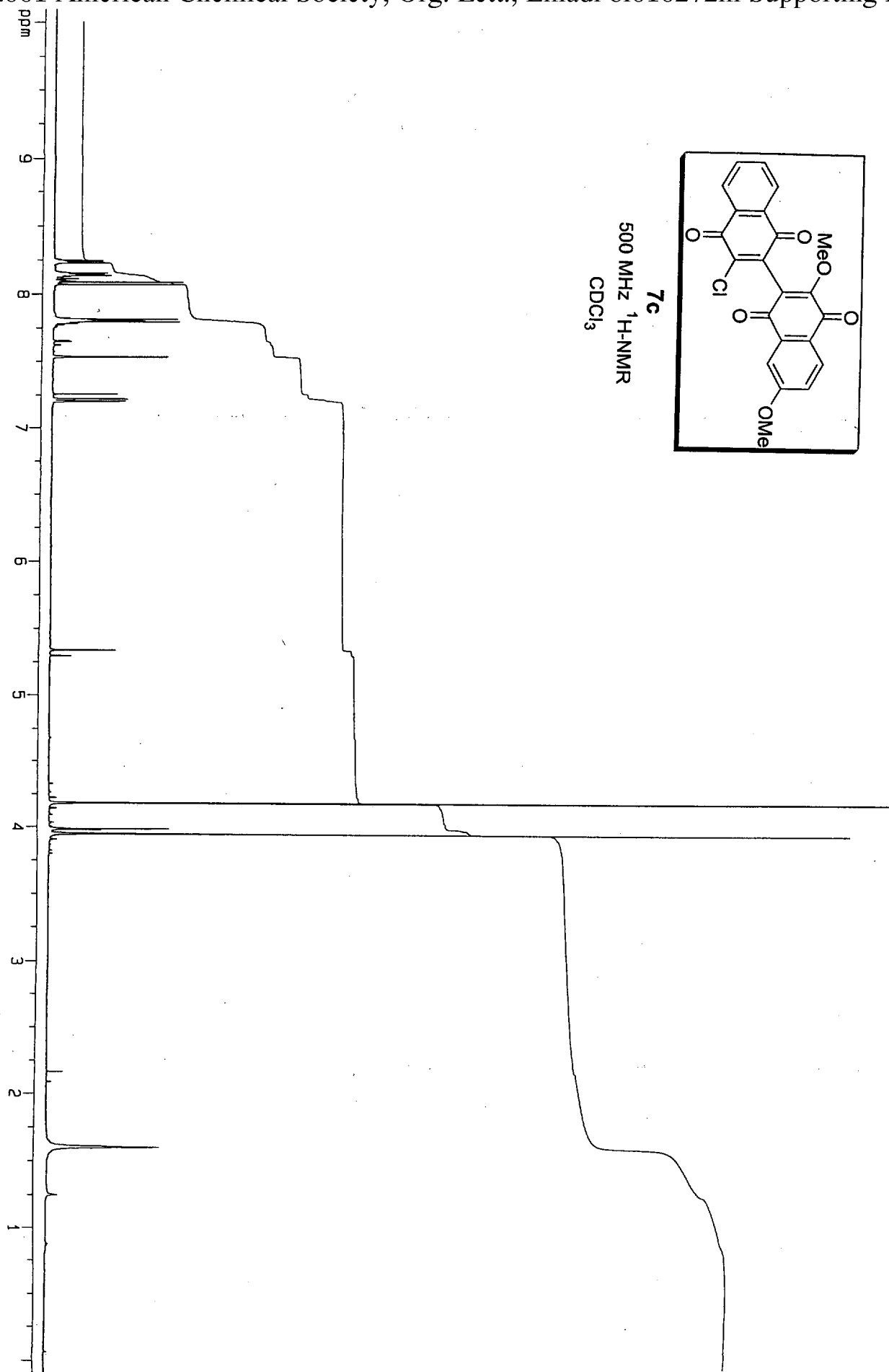


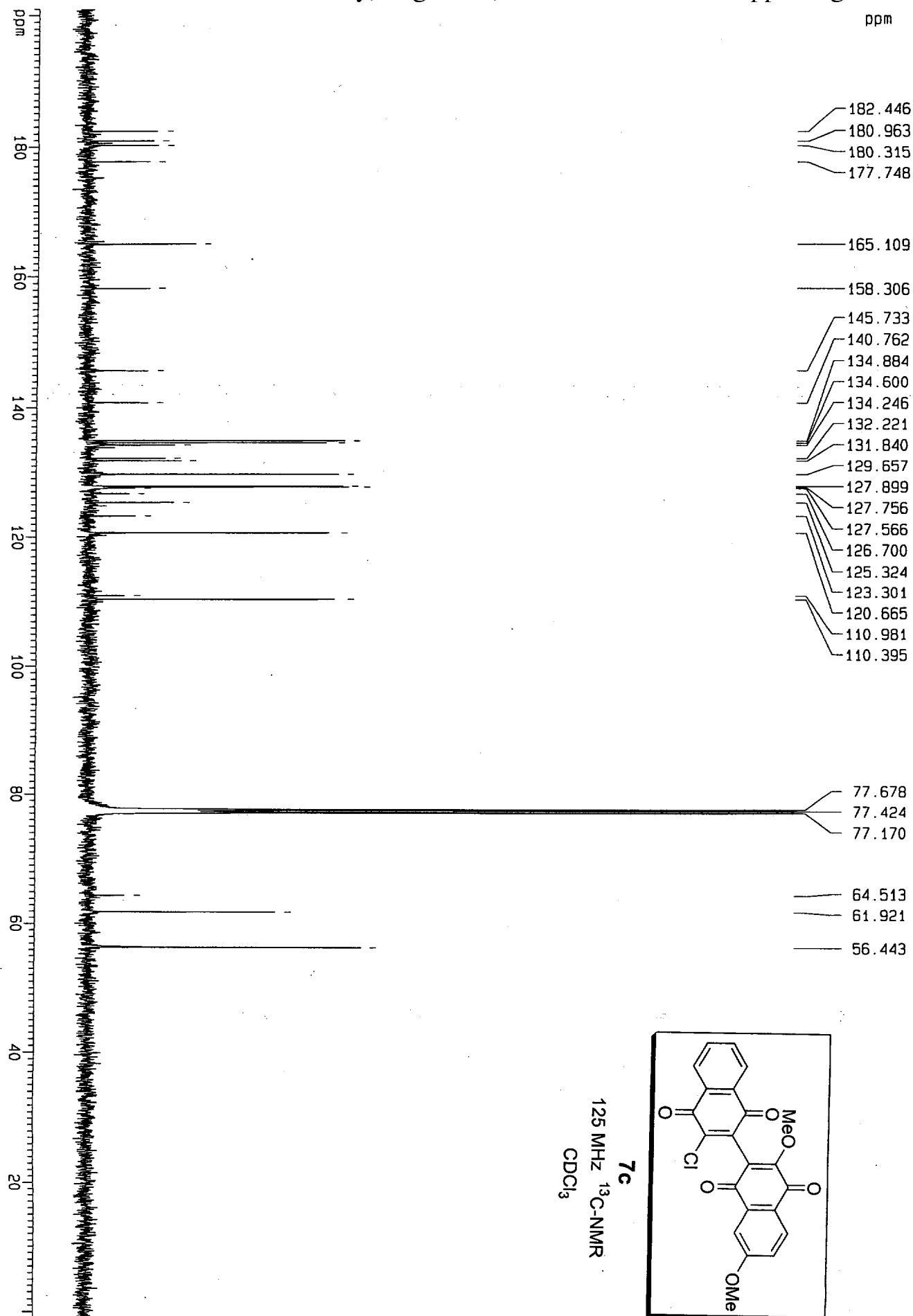


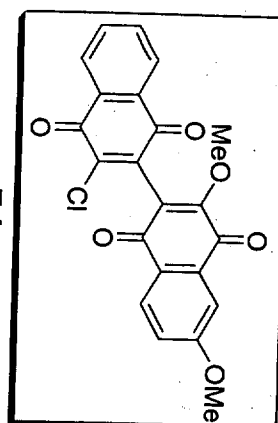




7c
500 MHz $^1\text{H-NMR}$
 CDCl_3







7d
500 MHz ^1H -NMR
 CDCl_3

