SUPPORTING INFORMATION

Unusual Friedlander Reactions: a Route to Novel Quinoxaline-based Heterocycles‡

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Characterizations: All chemicals and solvents were purchased from commercial suppliers. The ^{1}H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as the internal standard using a Bruker wide bore *Avance* 300 NMR Spectrometer. ^{1}HNMR spectra often include a water peak. The quoted chemcial shifts are in ppm and J values are expressed in Hz. The signals have been designed as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), and m (multiplets). IR spectra were recorded as KBr pellets using a Nicolet AVATAR 360 FTIR ESP spectrometer with a Hewlett Packard Desk jet 840C plotter. Mass spectra were measured using direct injection probe Q-MS. High resolution MS spectra were recorded using Apex-IV mass spectrometer and JEOL GCmate. X-ray crystallography data collection was recorded using an Apex2 Bruker 2005.

Experimental Section

General procedure A

Benzofurazan oxide (**3**) and any of its derivatives were synthesised according to a modified literature procedure.[1]

Derivatives of *o*-nitroaniline (43.5 mmol) were dissolved in 20% ethanol/ KOH (250 mL). The deep red solution was cooled in an ice bath (0-5 ^{o}C). Commercial Clorox (NaOCl) (200 mL) was added with stirring until no *o*-nitroaniline was present in the solution, that is, when the solution no longer changed color from yellow to red upon the addition of Chlorox . The bright yellow precipitate was collected by suction filtration and was washed with cold water. The solid was dried under vacuum. Recrystallization, when needed, was performed using a solution of 1:3 water-ethanol solution, yielded yellow crystalline benzofurazan oxide **3** or its derivatives (80-92% yield).

2,3-Dihydro-1H-cyclopenta[b]quinoxaline-4,9-dioxide (2a)

In 200ml beaker, Benzofurazan oxide (**1a**) (5 g, 36 mmol) and cyclopentanone (11 g, 131 mmol) were dissolved in minimum amount of acetonitrile (25-30 mL). The solution was heated to its boiling point. The effervescent solution was left to stand at room temperature for 1 minute. To the hot solution, pyrrolidine (5 mL) was added drop-wise resulting in an exothermic reaction (effervescent) with a color change from brown-yellow to dark black. The reaction mixture was left to stand under room temperature for 30 minutes. The yellowish crystals were formed in the bottom of the flask. The latter were collected by suction filtration, washed with cold methanol, dried under vacuum, and identified as 2,3-dihydro-1H-cyclopenta[b]quinoxaline-4,9-dioxide (**2a**) (60% yield; m.p. 186-187 ^{o}C). When it was necessary, recrystallization was performed using methanol. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.55-8.59(2H, m), 7.78-7.83(2H, m), 3.33-3.42(4H, m), 2.28-2.42(2H, m). ^{13}C NMR (75 MHz , $CDCl_3$): δ 145.02, 138.31, 130.64, 120.01, 29.21, 19.60. FTIR (KBr): 3078(w), 2969(w), 1547(s), 1503(m), 1428(w), 1315(s), 1295(s), 1099(m), 1045(s), 872(m), 789(s), 699(s), 631(s) cm^{-1}. HRMS calculated for $C_{11}H_{10}N_2Na_1O_2$ (M+Na) *m/z* 225.05617, found 225.06345.

6,7-Dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4,9-dioxide (2b)

6,7-dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4,9-dioxide (**2b**) was collected in 67% yield; m.p. 197 ^{o}C. FTIR (KBr): 3484(w, b), 2950(w), 1556(m), 1494(m), 1340(s), 1186(w), 1118(m), 1025(s), 886(m), 775(m), 683(s), 578(w) cm^{-1}.

1,2,3,4-tetrahydrophenazine-5,10-dioxide (3a)[2]

In 200ml beaker, Benzofurazan oxide (**1a**) (5 g, 36 mmol) and cyclohexanone (11 g, 112.2 mmol) were dissolved in minimum amount of acetonitrile (25-30 mL). The solution was heated

to its boiling point. The effervescent solution was left to stand at room temperature for 1 minute. To the hot solution, pyrrolidine (5 mL) was added drop-wise resulting in an exothermic reaction (effervescent) with a color change from brown-yellow to dark black. The reaction mixture was left to stand at room temperature for 30 minutes. The yellowish crystals were formed in the bottom of the flask. The latter were collected by suction filtration, washed with cold methanol, dried under vacuum, and identified as 1,2,3,4-tetrahydrophenazine-5,10-dioxide **(3a)** (57% yield; m.p. 183-184 ^{o}C).

7,8-Dimethyl-1,2,3,4-tetrahydrophenazine-5,10-dioxide (3b)

7,8-Dimethyl-1,2,3,4-tetrahydrophenazine-5,10-dioxide (3b) was collected in 63% yield; m.p. 211-213 ^{o}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.94 (4H, m), 2.50 (6H, s), 3.11 (4H, m), 8.35 (2H, s).^{13}C-NMR (75 MHz ,$CDCl_3$) δ 20.34, 20.71, 21.65, 24.29, 29.08, 29.70, 118.76, 119.00, 134.97, 141.55, 142.00. FTIR: 2940, 2872, 1517, 1503, 1452, 1422, 1344, 1332, 1307, 1133, 1072, 972, 879,676 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_2O_2$ (244.29): C, 68.83; N, 11.47. Found: C, 68.87; N, 11.57.

7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoxaline-5,11-dioxide (4a)

Benzofurazan oxide (**1a**) (5 g, 36.8 mmol) and cycloheptanone (11 g, 98 mmol) were dissolved in acetonitrile (30-35 mL). The solution was heated to the boiling point. The effervescent solution was left to stand under room temperature for 1 minute. To the hot solution, pyrrolidine (5 mL) was added drop-wise resulting in an exothermic reaction, effervescent, with a color change from orange-yellow to dark black. The reaction mixture was left to stand at room temperature for 30 minutes. The yellow crystals were formed in the bottom of the flask. The

latter was collected by suction filtration, washed with cold methanol (until no more pyrrolidine was found), dried under vacuum, and identified as 7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoxaline-5,11-dioxide (**4a**) (61% yield; m.p. 160 ^{o}C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.64-8.53 (2H, m), 7.81-7.78 (2H, m), 3.47-3.35 (4H, m), 2.42-2.38 (4H, m), 1.62-1.48 (m, 2H). (FTIR (KBr): 2934(m), 2856(m), 1513(m), 1442(m), 1348(s), 1305(s), 1266(m), 1206(s), 1044(s), 963(s), 916(s), 865(s), 785(s), 647(s), 611(s) cm^{-1}.

2,3-Dihydro-1H-cyclopenta[b]quinoxalin-1-yl acetate-4-oxide (5a)

2,3-Dihydro-1H-cyclopenta[b]quinoxaline-4,9-dioxide (**2a**) (1 g, 5 mmol) was dissolved in a mixture of acetic anhydride (4 mL) and acetic acid (1 mL). The mixture was stirred at room temperature for 12 hours. The blue black reaction mixture was poured over crushed ice (20 g) with vigorous stirring for 1 hour. The aqueous mixture was left to stand at 0-5 ^{o}C for 12 hours. The pale yellow precipitate was collected by suction filtration, washed with cold water, dried under vacuum, and identified as 2,3-dihydro-1H-cyclopenta[b]quinoxalin-1-yl acetate-4-oxide (**5a**) (50%; m.p. 95-97 ^{o}C). When recrystallization was required, it was performed using methanol. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.62-8.65(1H, dd, J_1=9Hz, J_2=1.5Hz), 8.16-8.19(1H, dd, J_1=8.4Hz, J_2=1.2Hz), 7.73-7.84(2H, m), 6.27-6.31(1H, dd, J_1=7.5Hz, J_2=5.1Hz), 3.39-3.44(1H, m), 3.25-3.30(1H, m), 2.79-2.84(1H, m), 2.21-2.29(3H, m), 2.17(3H, s). ^{13}C NMR (75 MHz , $CDCl_3$): δ 170.31, 158.36, 145.73, 141.71, 136.99, 131.07, 130.32, 130.03, 118.37, 75.39, 28.59, 25.05, 21.10. FTIR (KBr): 2957(m), 1741(s), 1570(m), 1497(s), 1358(m), 1232(s, b), 1043(s), 974(m), 903(s), 765(s), 733(m), 677(m), 651(s), 615(m), 541(s), 469(m), 440(s) cm^{-1}. MS calculated for $C_{13}H_{13}N_2O_3$ (M+H) *m/z* 245.1, found 245.1.

6,7-Dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxalin-1-yl acetate-4-oxide (5b)

6,7-dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxalin-1-yl acetate-4-oxide (**5b**) was collected in 55% yield; m.p. 162-163^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32-8.34(1H, d, J=6Hz), 7.89-7.90(1H, d, J=4.5Hz), 6.24-6.28(1H, dd, J_1=7.5Hz, J_2=5.1Hz), 3.36-3.47(1H, m), 3.18-3.28(1H, m), 2.77-2.86(1H, m), 2.52(3H, s), 2.48(3H, s), 2.21-2.28(1H, m), 2.17(1H, s). FTIR (KBr): 2956(w), 1734(s), 1585(s), 1489(s), 1448(m), 1360(m), 1335(m). 1233(s, b), 1121(m), 1025(m), 961(s), 909(m), 865(s), 785(s), 704(s), 565(s), 446(m) cm^{-1}. MS calculated for $C_{15}H_{16}N_2O_3$ (M+H) *m/z* 273.1, found 273.4.

1-Acetoxy-1,2,3,4-tetrahydrophenazine-5-oxide (6a)

1,2,3,4-tetrahydrophenazine-5,10-dioxide **(3a)** (1 g, 3.8 mmol) was dissolved in a mixture of acetic anhydride (4 mL) and acetic acid (1 mL). The mixture was stirred at room temperature for 12 hours. The deep black reaction mixture was poured over crushed ice (20 g) with vigorous stirring for 1 hour. The aqueous mixture was left to stand at 0-5 ^{o}C for 12 hours. The pale yellow precipitate was collected by suction filtration, washed with cold water, dried under vacuum, and identified as 1-Acetoxy-1,2,3,4-tetrahydrophenazine-5-oxide **(6a)** (50%; m.p. 141-143 ^{o}C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.17 (7H, m), 3.07 (1H, m), 3.22 (1H, m), 6.14 (1H, t, *J* = 6 Hz), 7.77 (2H, m), 8.10 (1H, d, *J* = 6 Hz), 8.56 (1H, d, *J* = 6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 16.71, 21.27, 24.59, 27.87, 70.68, 118.47, 130.57, 130.78, 136.24, 140.64, 143.41, 152.14, 153.81, 170.13. FTIR: 1728, 1575, 1485, 1432, 1341, 1239, 1103, 1056, 1013, 969, 908, 768 cm^{-1}. MS: *m/z* calcd for $C_{14}H_{14}N_2O_3$ 258.4, Found 259.2.

1-Acetoxy-7,8-dimethyl-1,2,3,4-tetrahydrophenazine-5-oxide (6b)

1-Acetoxy-7,8-dimethyl-1,2,3,4-tetrahydrophenazine-5-oxide **(6b)** was collected in 43% yield; m.p. 150-152^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (7H, m), 2.48 (6H, d, *J*=12 Hz), 3.01

(1H, m), 3.23 (1H, m), 6.11 (1H, t, *J*=0.3 Hz), 7.83 (1H, s), 8.29 (1H, s). ^{13}C NMR (75 MHz, CDCl3): δ 16.34, 19.71, 20.14, 20.89, 24.09, 27.50, 30.54, 117.15, 128.68, 134.19, 139.44, 140.97, 141.92, 150.43, 169.76. FTIR: 1733, 1700, 1569, 1506, 1483, 1380, 1368, 1351, 1238, 1198, 1064, 1049, 991, 955, 912 cm^{-1}. MS: *m/z* calcd for $C_{16}H_{18}N_2O_3$ 286.3**,** Found 286.1.

7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoxalin-6-yl acetate-11-oxide (7a)

In a 2-necked round bottom flask, 7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoxaline-5,11-dioxide (**4a**) (2.5 g, 11 mmol) was dissolved in acetic acid (20 mL). The mixture was heated to the reflux temperature. Acetic anhydride (1.63 g, 16 mmol) was added dropwise, over 20 minutes. After cooling, the solution was poured over crushed ice (20 g) and stirred for 12 hours. The pale yellow solid was collected by suction filtration, washed with cold water, dried by vacuum, and identified as 7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoxalin-6-yl acetate-5-oxide (**7a**) (57%; m.p. 78-80 ^{o}C). When recrystallization was required, it was performed using methanol.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54-8.58(1H, dd, J_1=7.8Hz, J_2=2.1Hz), 8.01-8.05(1H, dd, J_1=6.9Hz, J_2=2.2Hz), 7.70-7.77(2H, m), 6.06-6.09(1H, dd, J_1=7.2Hz, J_2=5.4Hz), 3.86-3.95(1H, m), 3.23-3.36(1H, m), 2.25(3H, s), 2.05-2.14(3H, m), 1.90-1.95(2H, m), 1.67-1.78(1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.97, 156.57, 143.09, 142.30, 135.73, 130.72, 130.08, 130.00, 119.27, 75.94, 31.49, 27.01, 25.37, 24.18, 21.06. FTIR (KBr): 2939(m), 2861(w), 1725(s), 1576(m), 1487(s), 1445(w), 1380(s), 1339(s), 1220(s), 1154(m), 1038(s), 964(m), 919(m), 896(w), 876(w), 768(s), 617(m) cm^{-1}. MS calculated for $C_{15}H_{17}N_2O_3$ (M+H) *m/z* 273.1, found 273.1.

1-Hydroxy-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4-oxide (8a)

1-Acetoxy-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4-oxide (**5a**) (2 g, 8.2 mmol) was dissolved in the minimum amount (10 mL) of methanol and placed in an ice bath for 5 minutes. 2% methanolic base (30 mL) was added to the cold solution. The solution was kept in an ice bath at 0 ^{o}C for 5 minutes. The reaction was halted by the addition of cold water (50 mL). The black-green mixture was extracted with ethyl acetate, dried over $MgSO_4$ and concentrated under vacuum. The crude product was then purified via silica gel column chromatography (Hexane: Ethyl acetate, 7:3) to yield 1-hydroxy-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4-oxide (**8a**) (56% yield; m.p. 162-163 ^{o}C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.57-8.60(1H, dd, J_1=8.4Hz, J_2=1.5Hz), 8.11-8.14(1H, dd, J_1=8.4Hz, J_2=1.5Hz), 7.70-7.81(2H, m), 5.41-5.46(1H, t, J=6.9Hz), 4.60(1H, s), 3.41-3.51(1H, m), 3.10-3.22(1H, m), 2.72-2.78(1H, m), 2.23-2.30(1H, m). ^{13}C NMR (75 MHz , $CDCl_3$): δ 162.49, 145.26, 141.31, 136.92, 131.05, 129.65, 129.51, 118.45, 73.44, 30.59, 24.70. FTIR (KBr): 3353(s, b), 2964(w), 1734(s), 1570(s), 1493(s), 1435(m), 1350(m), 1101(m), 1060(s), 970(s), 896(s), 782(s), 647(m), 612(w) cm^{-1}. HRMS calculated for $C_{11}H_{10}N_2Na_1O_2$ (M+Na) *m/z* 225.05617, found 225.06345.

6,7-Dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxalin-1-ol-4-oxide (8b)

6,7-dimethyl-2,3-dihydro-1H-cyclopenta[b]quinoxalin-1-ol-4-oxide (**8b**) was obtained in 55% yield; m.p. 175-176 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25(1H, s), 7.75(1H, s), 5.38-5.43(1H, dd, J_1=7.5Hz, J_2=6Hz), 3.38-3.47(1H, m), 3.09-3.18(1H, m), 2.69-2.74(1H, m), 2.48(3H, s), 2.45(3H, s), 2.23-2.32(1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.38, 143.83, 141.59, 140.69, 135.03, 128.43, 117.48, 73.26, 30.67, 24.69, 20.44, 20.19. FTIR (KBr): 3255(m, b), 2969(w), 1569(s), 1484(m), 1458(w), 1359(m), 1337(w), 1223(w), 1102(m), 1050(s),

1011(m), 967(m), 905(w), 877(m), 790(m), 651(w, b) cm^{-1}. MS calculated for $C_{13}H_{15}N_2O_2$ (M+H) *m/z* 231.1, found 231.1.

7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoxalin-6-ol-11-oxide (9a)

7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoxalin-6-yl acetate-5-oxide (**7a**) (2 g, 7.35 mmol) was dissolved in 5% methanolic base (30 mL). The solution was refluxed for 10 minutes. After cooling, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2, dried over $MgSO_4$ and concentrated under vacuum. The crude product was then purified via silica gel column chromatography (Hexane: Ethyl acetate, 8:2) to yield 7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoxalin-6-ol-11-oxide (**9a**) (42% yield; m.p. 130 ^oC). ^1H NMR (300 MHz, $CDCl_3$): δ 8.58-8.61(1H, dd, J_1=8.7Hz, J_2=1.8Hz), 8.04-8.07(1H, dd, J_1=8.4Hz, J_2=1.2Hz), 7.71-7.81(2H, m), 5.46-5.47(1H, d, J=4.2Hz), 4.91-4.97(1H, m), 4.39-4.46(1H, m), 2.43-2.52(1H, m), 2.35-2.39(1H, m), 2.1-2.17(2H, m), 1.49-1.63(1H, m), 1.28-1.41(1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.56, 142.70, 141.03, 136.07, 131.03, 129.89, 129.07, 119.55, 71.99, 36.63, 28.76, 25.20, 24.73. FTIR (KBr): 3405(w, b), 2936(s), 2853(m), 1581(m), 1485(s), 1392(m), 1330(m), 1287(m), 1258(s), 1096(w), 1050(s), 959(s), 827(w), 771(s) cm^{-1}. MS calculated for $C_{13}H_{15}N_2O_2$ (M+H) *m/z* 231.1, found 231.1.

2,3-Dihydro-1H-cyclopenta[b]quinoxaline-4-oxide (10a)

Product **10a** was obtained as a side product in the hydrolysis reaction (formation of **8a**). It was purified via silica gel column chromatography, and collected in 27% yield; m.p. 52-53 ^oC. ^1H-NMR (300 MHz, $CDCl_3$): δ 8.48-8.51(1H, dd, J_1=8.4Hz, J_2=1.2Hz), 7.95-7.98(1H, d, J=8.4Hz), 7.61-7.73(2H, m), 3.20-3.32(4H, m), 2.25-2.35(2H, m). ^{13}C NMR (75 MHz , $CDCl_3$): δ 163.04, 144.84, 142.25, 135.78, 130.45, 129.08, 128.60, 118.09, 33.37, 27.62, 19.96. FTIR (KBr): 3067(w, b), 2965(w, b), 1590(m), 1485(s), 1426(w), 1382(m), 1358(m), 1308(m),

1085(s), 861(m), 796(s), 661(w), 607(w) cm^{-1}. MS calculated for $C_{11}H_{11}N_2O$ (M+H) *m/z* 187.1, found 187.1.

7,8,9,10-Tetrahydro-6H-cyclohepta[b]quinoxaline-11-oxide (11a)

Product **11a** was obtained as a side product in the hydrolysis reaction (formation of **9a**). It was purified via silica gel column chromatography, and collected in 24% yield; m.p.54-55 ^oC. Knowing that, the yield of this side product (**11a**) increases with increasing the reflux period. ^1H NMR (300 MHz, $CDCl_3$): δ 8.55-8.58(1H, dd, J_1=8.1Hz, J_2=1.8Hz), 7.79-8.00(1H, dd, J_1=7.8Hz, J_2=1.8Hz), 7.65-7.76(2H, m), 3.49-3.52(2H, m), 3.19-3.23(2H, m), 1.79-2.01(6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.15, 144.70, 142.61, 135.36, 130.57, 129.29, 129.22, 119.38, 39.05, 31.68, 26.46, 25.77, 25.65. FTIR (KBr): 3269(m, b), 2915(m), 2854(m), 1582(s), 1487(s), 1444(w), 1320(s), 1305(s), 1147(m), 1077(s), 960(s), 924(s), 770(s), 655(w) cm^{-1}. MS calculated for $C_{13}H_{15}N_2O_1$ (M+H) *m/z* 215.1, found 215.0.

2,3-Dihydro-1H-cyclopenta[b]quinoxaline-1-one (13a)

1-Hydroxy-2,3-dihydro-1H-cyclopenta[b]quinoxaline-4-oxide (**8a**) (1g, 5mmol) was dissolved in a solution of methanol (20 mL)/ acetic acid (10 mL). The reaction mixture was refluxed for 12 hours. The brownish solution was neutralized with 10% sodium carbonate solution (50 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$.The crude product was purified by column chromatography on silica gel (Hexane: Ethyl acetate, 8:2) to yield 2,3-dihydro-1H-cyclopenta[b]quinoxaline-1-one (**13a**) as greenish solid (67% yield; m.p. 150-151^oC). ^1H-NMR (300 MHz, $CDCl_3$): δ 8.33-8.36(1H, dd, J_1=8.1Hz, J_2=1.2Hz), 8.15-8.18(1H, dd, J_1=8.7Hz, J_2=1.5Hz), 7.84-7.97(2H, m), 3.52-3.56(2H, m), 3.02-3.07(2H, m). ^{13}C NMR (75 MHz , $CDCl_3$): δ 204.06, 164.58, 147.16, 144.28, 143.11, 133.15, 131.62, 130.75, 128.97, 35.38, 26.43. FTIR (KBr): 3037(w), 2935(w), 1720(s), 1653(w), 1556(m), 1500(m), 1435(w), 1402(m), 1360(m),

1271(w), 1150(s), 1116(s), 1046(s), 983(m), 804(m), 781(s), 521(s) cm^{-1}. HRMS calculated for $C_{11}H_8N_2Na_1O$ (M+Na) *m/z* 207.04561, found 207.05288.

6,7-Dimethyl-2,3-dihydrocyclopenta[b]quinoxalin-1-one (13b)

6,7-dimethyl-2,3-dihydrocyclopenta[b]quinoxalin-1-one (**13b**) was collected in 70% yield; m.p. 170-171 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.04(1H, s), 7.88(1H, s), 3.46-3.50(2H, m), 2.97-3.03(2H, m), 2.56(3H, s), 2.53(3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.34, 164.11, 146.25, 144.88, 143.44, 142.22, 141.74, 130.17, 127.82, 35.30, 26.33, 20.90, 20.46. FTIR (KBr): 2923(m, b), 1733(s), 1585(s), 1488(s), 1419(m), 1405(m), 1364(s), 1287(w), 1209(s), 1165(m), 1144(s), 1045(s), 1003(m), 879(w), 785(w), 722(m), 400(s) cm^{-1}. MS calculated for $C_{13}H_{13}N_2O_1$ (M+H) *m/z* 213.1, found 213.0.

7,8,9,10-Tetrahydrocyclohepta[b]quinoxalin-6-one (14)

7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoxalin-6-ol-11-oxide (**9a**) (1 g, 4.7 mmol) was dissolved in a solution of methanol (20 mL)/ acetic acid (10 mL). The reaction mixture was refluxed for 12 hours. The brownish solution was neutralized with 10% sodium carbonate solution (50 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$.The crude product was purified by column chromatography on silica gel (Hexane: Ethyl acetate, 8:2) to yield 7,8,9,10-tetrahydrocyclohepta[b]quinoxalin-6-one (**14**) as yellow solid (77% yield; m.p. 150-151^oC). ^1H NMR (300 MHz, $CDCl_3$): δ 8.21-8.25(1H, dd, J_1=8.4Hz, J_2=1.5Hz), 8.06-8.09(1H, dd, J_1=8.1Hz, J_2=1.8Hz), 7.75-7.86(2H, m), 3.29-3.33(2H, t, J=6Hz), 2.93-2.98(2H, m), 2.07-2.16(2H, m), 1.94-2.03(2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.38, 154.19, 151.23, 142.45, 141.12, 131.70, 130.27, 130.04, 128.55, 40.60, 34.83, 24.56, 22.14. FTIR (KBr): 2964(w), 2870(w), 1691(s), 1530(m), 1484(m), 1457(m), 1408(w), 1355(m), 1240(w), 1207(w), 1118(m), 1066(w), 1044(m), 533(m) cm^{-1}. MS calculated for $C_{13}H_{13}N_2O_1$ (M+H) *m/z* 213.1, found 213.0.

1-hydroxyphenazine (15a)[3]

1-Acetoxy-1,2,3,4-tetrahydrophenazine-5-oxide (0.5 g, 1.93 mmol) was dissolved in 5% KOH/MeOH (10 mL). The solution was refluxed for 15 minutes and then left to cool to room temperature. The violet solution was neutralized with HCl (5 mL), extracted with CH_2Cl_2. and dried over $MgSO_4$.The crude product was purified by column chromatography on silica gel (Hexane: Ethyl acetate, 8:2) to yield 1-hydroxyphenazine as yellow solid (37% yield; m.p. 156-157^oC).

8H-Indolo[3,2-a]phenazine (17a), Quinolino[2,3,c]cylclopentadienone[2,3-b]quinoxaline (18a)

2,3-Dihydro-1H-cyclopenta[b]quinoxaline-1-one (**13a**) (0.2 g, 1.1 mmol), and *o*-amino benzaldehyde (0.26 g, 2.2 mmol) were dissolved in a solution of methanol (20 mL) and acetic acid (10 mL). The reaction mixture was refluxed for 72 hour. The reaction mixture was neutralized with 10% sodium carbonate solution (20 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$.The crude product was loaded on a silica gel column and eluted with a 5:1 mixture of dichloromethane: hexane. Two main products were isolated. The major product was isolated as an orange solid and identified as quinolino[2,3,c]cylclopentadienone[2,3-b]quinoxaline (**18a**) (47% yield; m.p. 283-284 ^oC). ^1H NMR (300 MHz, $CDCl_3$): δ 8.75(1H, s), 8.43-8.47(2H, m), 8.34-8.35(1H, d, J=1.8Hz), 8.03-8.04(1H, d), 7.89-7.96(3H, m), 7.71-7.73(1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.8, 153.3, 152.6, 152.2, 145.3, 144.7, 144.2, 143.8, 134.15, 133.7, 133.3, 131.7, 131.6, 131.15, 130.9, 130.8, 129, 128.86. FTIR (KBr): 2924(m, b), 1726(s), 1584(m),

1492(w), 1453(w), 1333(s), 1285(s), 1056(w), 939(m), 758(m) cm^{-1}. MS calculated for $C_{18}H_{10}N_3O_1$ (M+H) *m/z* 284.1, found 284.0.

The minor product was isolated as a pale yellow solid and identified as 8H-indolo[3,2-a]phenazine (**17a**) (21% yield; m.p. above 300 ^oC). ^1H NMR (300 MHz, $CDCl_3$): δ 9.14-9.17(1H, dd, J_1=5.7Hz, J_2=2.7Hz), 8.74(1H, s, b), 8.35-8.39(1H, dd, J_1=8.7Hz, J_2=1.2Hz), 8.21-8.24(1H, dd, J_1=8.4Hz, J_2=1.2Hz), 8.07-8.10(1H, d, J=9.3Hz), 7.92-7.95(1H, d, J=9.3Hz), 7.72-7.85(2H, m), 7.56-7.59(1H, m), 7.43-7.48(2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.90, 140.83, 140.44, 140.09, 137.29, 137.07, 128.94, 128.51, 128.48, 127.63, 126.93, 124.13, 123.52, 122.64, 120.62, 118.69, 113.97, 110.26. FTIR (KBr): 3228(s, b), 2910(s), 2853(m), 1586(m), 1452(w), 1333(m), 1250(s), 1183(w), 1057(w), 800(s, b), 752(w) cm^{-1}. MS calculated for $C_{18}H_{12}N_3$ (M+H) *m/z* 270.1, found 270.1

2,3-Dimethyl-8H-indolo[3,2-a]phenazine (17b)

2,3-dimethyl-8H-indolo[3,2-a]phenazine (**17b**) was collected in 19% yield; m.p. above 300 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 9.10-9.2(1H, m), 8.8(1H, s, b), 8.18(1H, s), 8.10-8.13(1H, d, J=9.3Hz), 8.10(1H, s), 7.93-7.96(1H, d, J=9.3Hz), 7.6-7.63(1H, m), 7.47-7.50(2H, m), 2.58-2.6(6H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.24, 141.63, 141.41, 141.11, 140.82, 140.46, 139.60, 138.10, 128.09, 128.04, 127.90, 124.98, 124.76, 124.54, 123.65, 121.41, 118.72, 111.16, 20.69, 20.62. FTIR (KBr): 3227(m, b), 2924(m, b), 2853(w, b), 1478(w), 1372(w), 1333(w), 1230(s), 1053(m), 765(m) cm^{-1}. MS calculated for $C_{20}H_{16}N_3$ (M+H) *m/z* 298.1, found 298.2.

See X-Ray Fig.1 in the main text.

3,4-Dimethylquinolino[2,3,c]cylclopentadienone[2,3-b]quinoxaline (18b)

3,4-Dimethylquinolino[2,3,c]cylclopentadienone[2,3-b]quinoxaline (**18b**) was collected in 56% yield; m.p. 291-292 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69(1H, s), 8.41-8.44(1H, d, J=8.4Hz), 8.16(1H, s), 8.07(1H, s), 8.00-8.03(1H, dd, J_1=8.4Hz, J_2=1.2Hz), 7.88-7.94(1H, dt, J_1=7.2Hz, J_2=1.5Hz), 7.65-7.71(1H, dt, J_1=7.2Hz, J_2=1.2Hz), 2.58(3H, s), 2.56(3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.98, 158.27, 154.85, 151.85, 149.45, 144.85, 143.20, 142.93, 142.69, 133.73, 133.38, 131.03, 130.83, 130.57, 129.84, 128.80, 128.67, 128.41, 20.89, 20.58. FTIR (KBr): 2927(w, b), 1715(s), 1611(s), 1547(m), 1493(s), 1406(w), 1360(s), 1217(m), 1175(m), 1139(m), 1076(s), 868(m), 797(m), 761(m), 436(s) cm^{-1}. MS calculated for $C_{20}H_{14}N_3O_1$ (M+H) *m/z* 312.1, found 312.1.

See X-Ray, Fig. 2 in the main text.

12,13,14-Trihydroindolo[2,3-c]cyclohepta[2,3-b]quinoxaline (22)

This was accomplished via a modified literature procedure.[4] Briefly, small amount of trifluoroacetic acid (1 mL) was added to a solution of **14a** (0.1 g, 0.47 mmol) and phenylhydrazine (0.05 g, 0.47 mmol) in glacial acetic acid. The resulting reaction mixture was stirred at 90°C for 2hours. After cooling, the reaction mixture was neutralized with 10% sodium carbonate solution (20 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (Hexane: Ethyl acetate, 7:3) to yield 12,13,14-Trihydroindolo[2,3-c]cyclohepta[2,3-b]quinoxaline (**22**) in 74% yield as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.83-8.80(1H, d, J=9.3Hz), 8.61-8.59(1H, dd, J_1=8.7Hz, J_2=1.2Hz), 8.33(1H, s, b), 8.30-8.29(1H, d, J=2.1Hz), 8.17-8.15(1H, dd, J_1=8.1Hz, J_2=0.9Hz), 7.76-7.73(1H, t, d, J_1=8.7Hz, J_2=1.5Hz), 7.65-7.63(1H, t, d, J_1=6.9Hz, J_2=1.2Hz), 7.39-7.35(1H, m), 7.30-

7.29(1H, d, J=3.6Hz), 3.65-3.62(2H, m), 3.30-3.25(2H, m), 2.36-2.30(2H, m). MS calculated for $C_{19}H_{14}N_3$ (M-H) *m/z* 284.1, found 284.1.

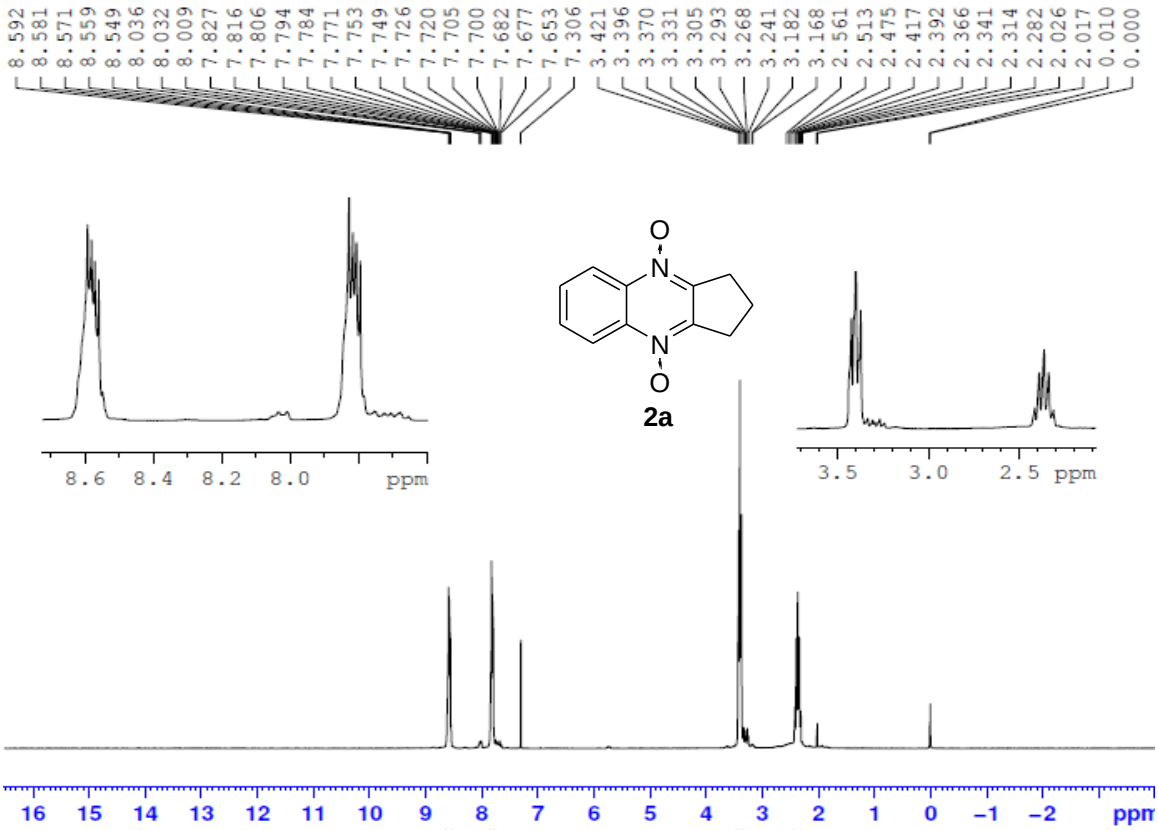
13,14,15-Trihydroquinolino[2,3-c]cyclohepta[2,3-b]quinoxaline (23)

7,8,9,10-Tetrahydrocyclohepta[b]quinoxalin-6-one (**14a**) (1 g, 5 mmol) and *o*-amino benzaldehyde (0.6 g, 5 mmol) were dissolved in a solution of methanol (20 mL) and acetic acid (10 mL). The reaction mixture was refluxed for 72 hour. The reaction mixture was neutralized with 10% sodium carbonate solution, extracted with CH_2Cl_2 and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (Hexane: Ethyl acetate, 8:2) to yield 13,14,15-trihydroquinolino[2,3-c]cyclohepta[2,3-b]quinoxaline (**23**) as a yellow solid (68% yield; m.p.167-168 ^oC). ^1H NMR (300 MHz, $CDCl_3$): δ 8.40-8.36(2H, m), 8.11-8.16(2H, m), 7.89-7.86(1H, d, J=8.1Hz), 7.84-7.73(3H, m), 7.64-7.59(1H, t, J=7.8Hz), 3.08-3.04(2H, m), 2.86-2.82(2H, m), 2.44-2.39(2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.59, 155.11, 153.32, 147.68, 142.15, 142.12, 135.60, 132.53, 130.42, 130.31, 130.27, 129.49, 129.36, 128.54, 128.51, 127.47, 126.97, 33.30, 29.85, 29.50. FTIR (KBr): 3369(w, b), 2957(m), 1666(w), 1620(w), 1493(m), 1450(w), 1356(m), 1260(w), 999(s), 912(m), 775(s), 612(m)cm^{-1}. MS calculated for $C_{20}H_{16}N_3$ (M+H) *m/z* 298.1, found 298.2.

13,14,15-Trihydroquinoxalino[2,3-c]cyclohepta[2,3-b]quinoxaline-1,6-dioxide (24)

7,8,9,10-tetrahydrocyclohepta[b]quinoxalin-6-one (**14**) (1 g, 5 mmol) and benzofurazan oxide (**1a**) (0.68 g, 5 mmol) were dissolved in acetonitrile (30-35 mL). The solution was heated to the boiling point. The effervescent solution was left to stand under room temperature for 1 minute. To the hot solution, pyrrolidine (5 mL) was added drop-wise resulting in an exothermic reaction, effervescent, with a color change from orange-yellow to dark black. The reaction mixture was left to stand under room temperature for 30 minutes. The reaction mixture was

extracted with ethyl acetate. The organic layer was collected, dried over Na_2SO_4, and evaporated to dryness under vacuum. The crude product was purified by silica gel column chromatography (the side products were eliminated with ethyl acetate and product **24** was eluted by MeOH) to yield a green product of 13,14,15-trihydroquinoxalino[2,3-c]cyclohepta[2,3-b]quinoxaline-1,6-dioxide (**24**) (65%; m.p. 210-212 ^{o}C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74-8.81(2H, m), 8.30-8.34(1H, m), 8.14-8.17(1H, m), 7.83-7.97(4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.46, 144.31, 142.53, 142.35, 141.30, 138.31, 138.04, 137.44, 132.48, 131.86, 131.56, 130.23, 129.94, 128.81, 121.14, 120.51, 32.86, 26.35, 23.08. FTIR (KBr): 3469(m, b), 1494(w), 1380(s), 1296(s), 1119(m), 1083(s), 991(s), 891(m), 766(s), 659(m) cm^{-1}. MS calculated for $C_{19}H_{15}N_4O_2$ (M+H) *m/z* 331.1, found 331.1.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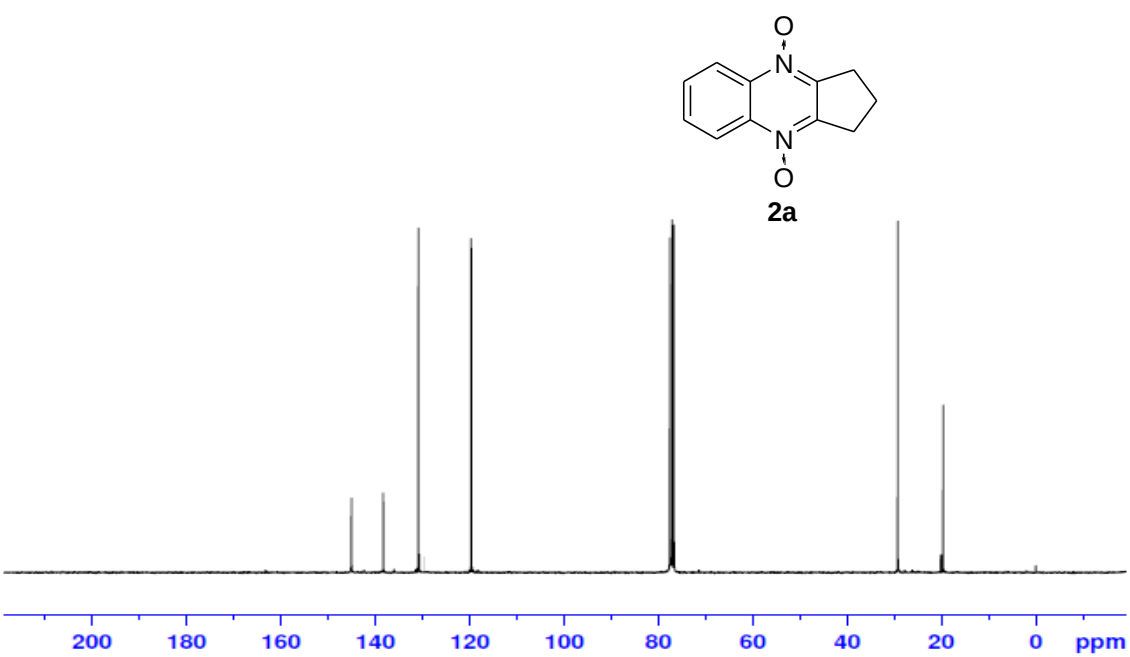
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2a

Mass Spectrum Deconvolution Report

Analysis Info

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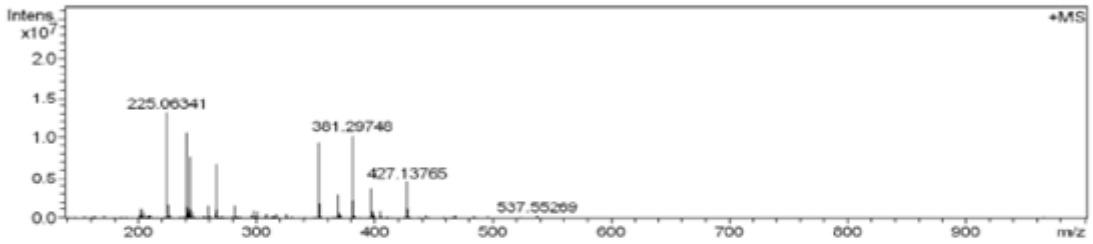

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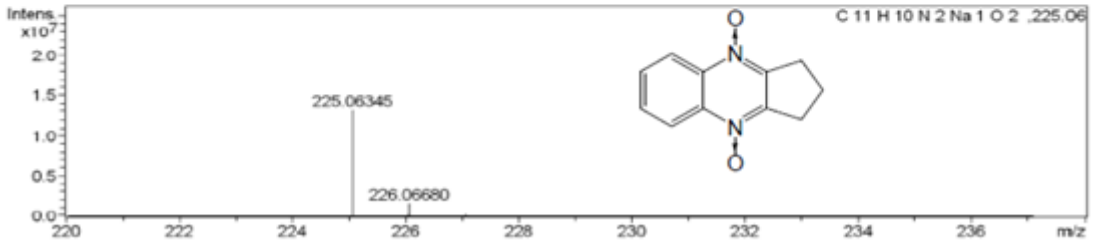

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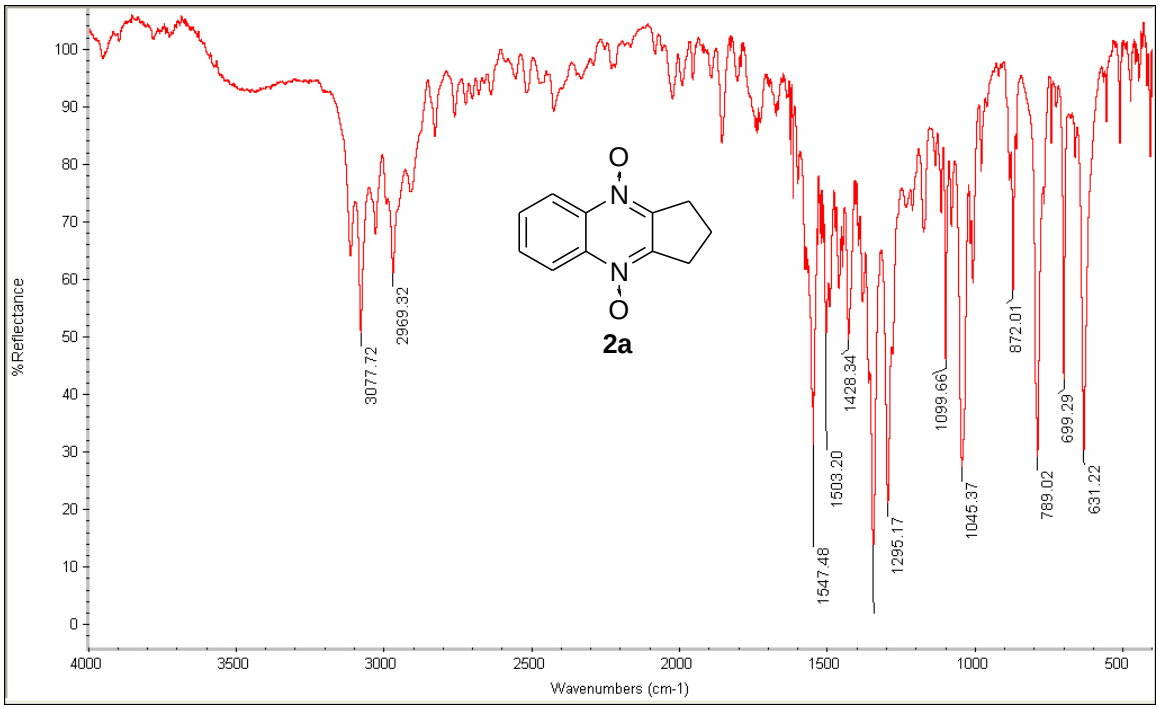

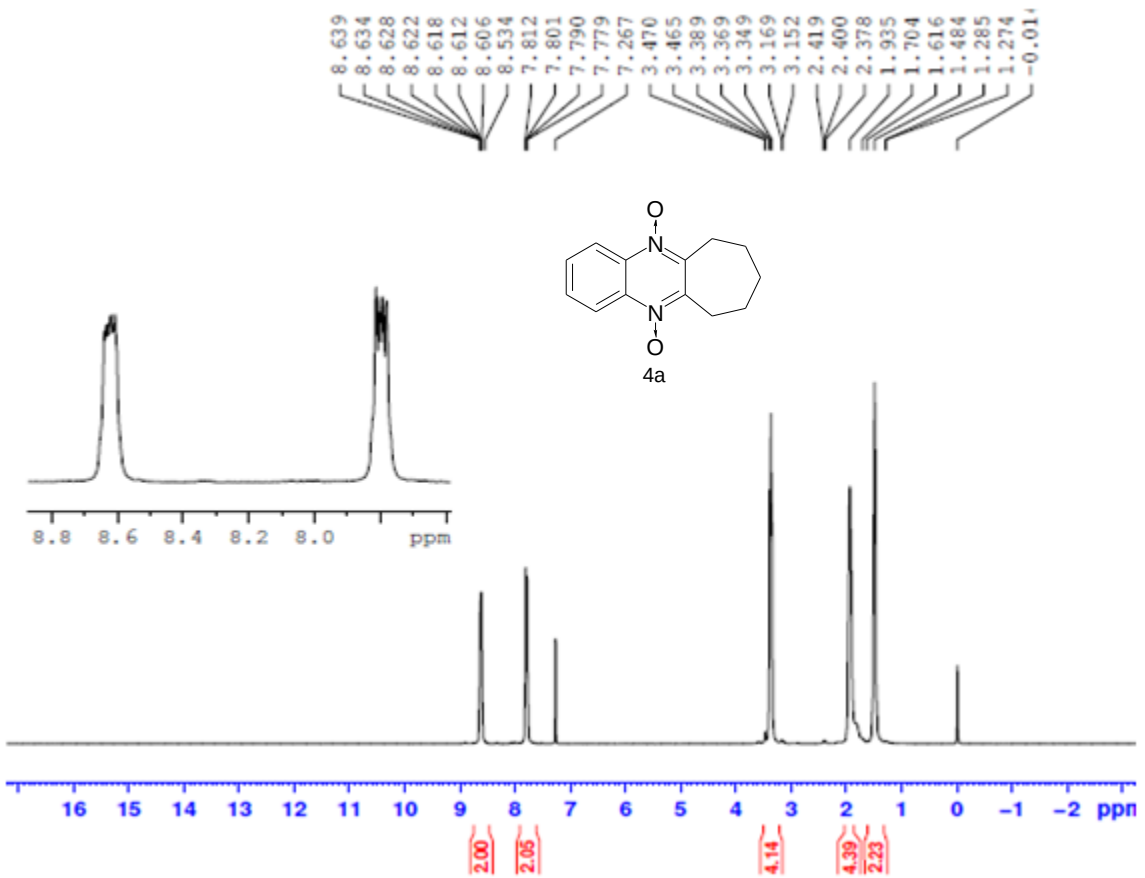
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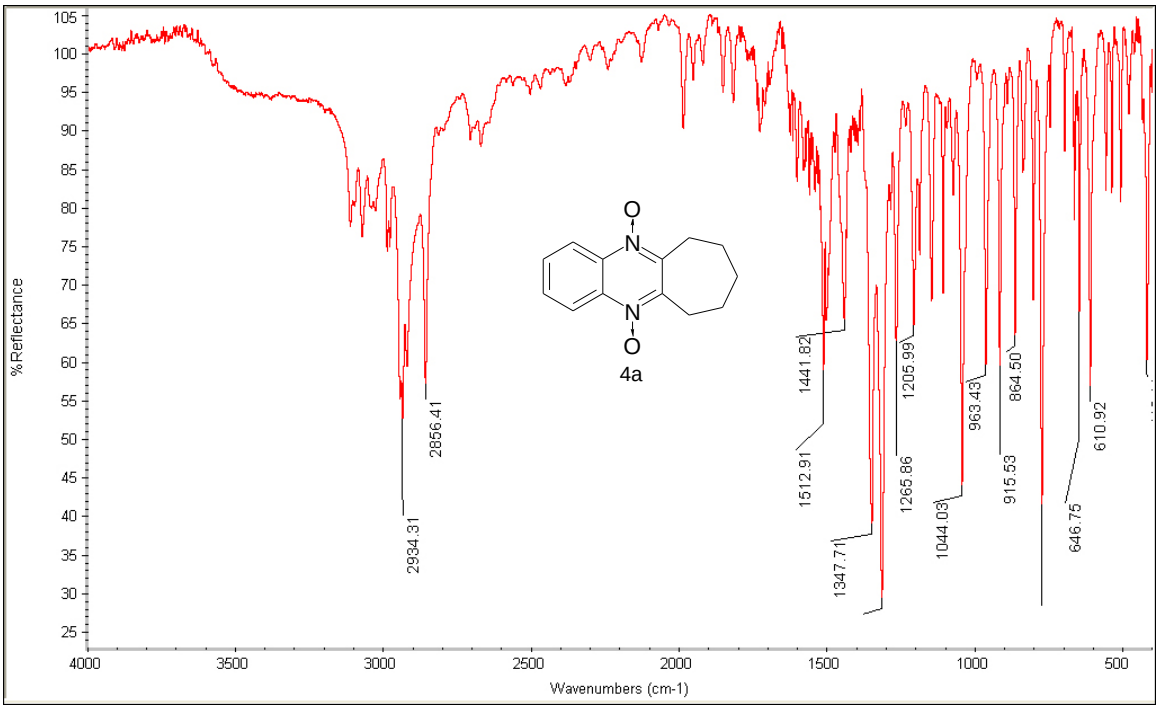
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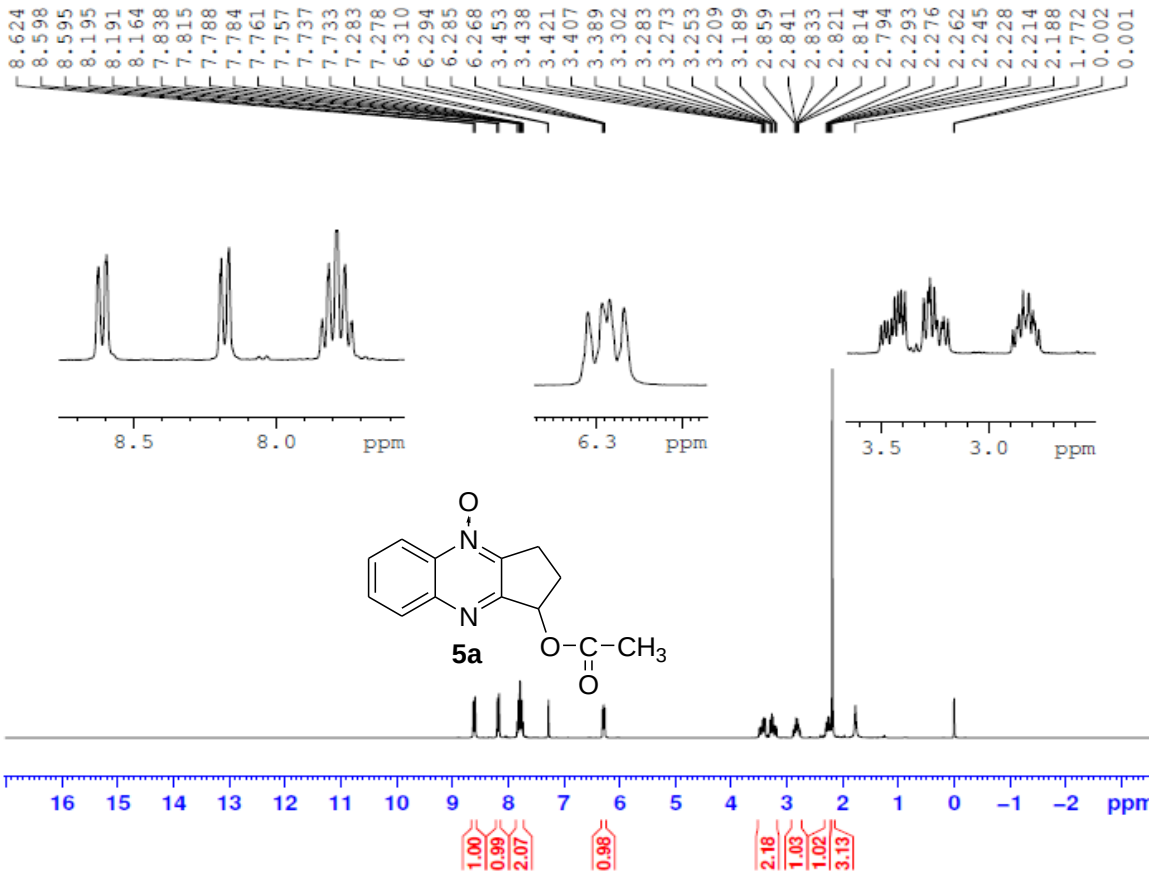
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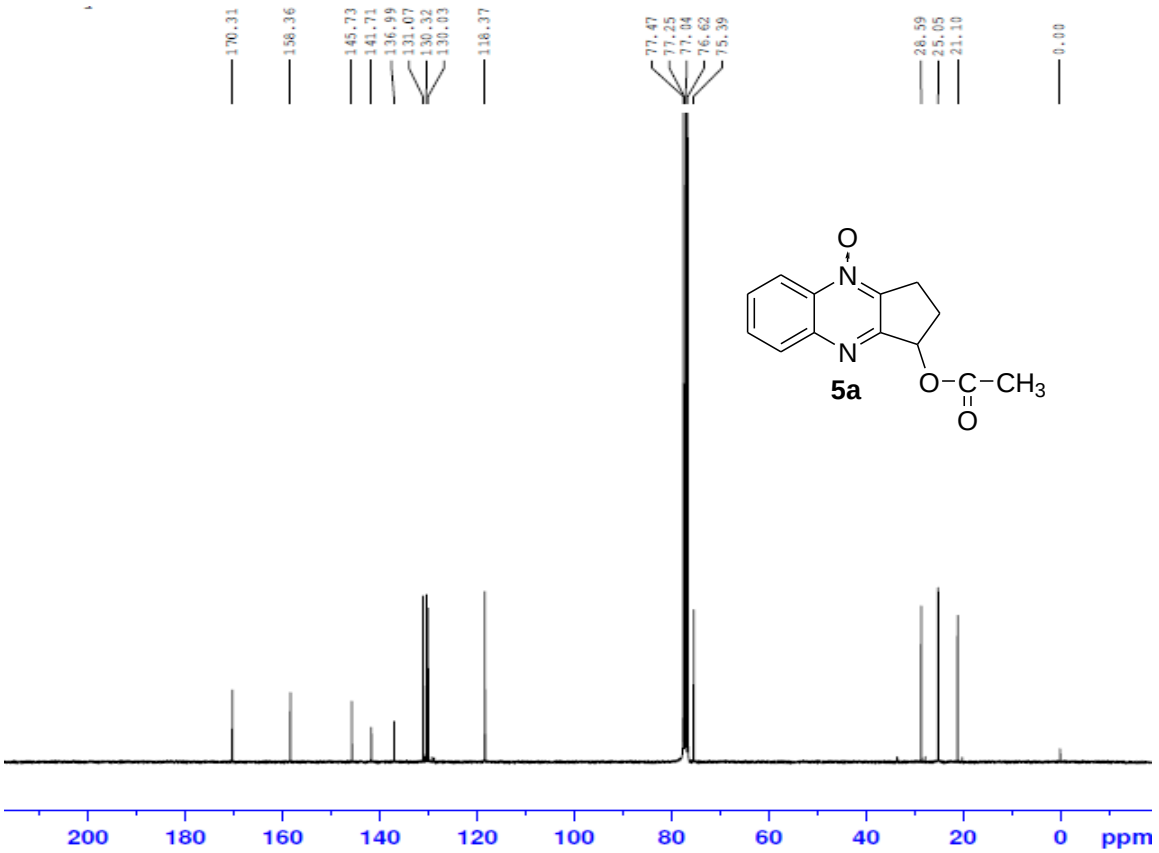
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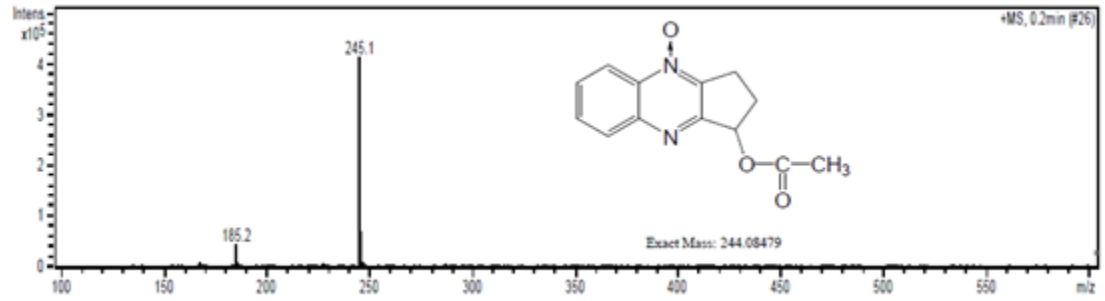
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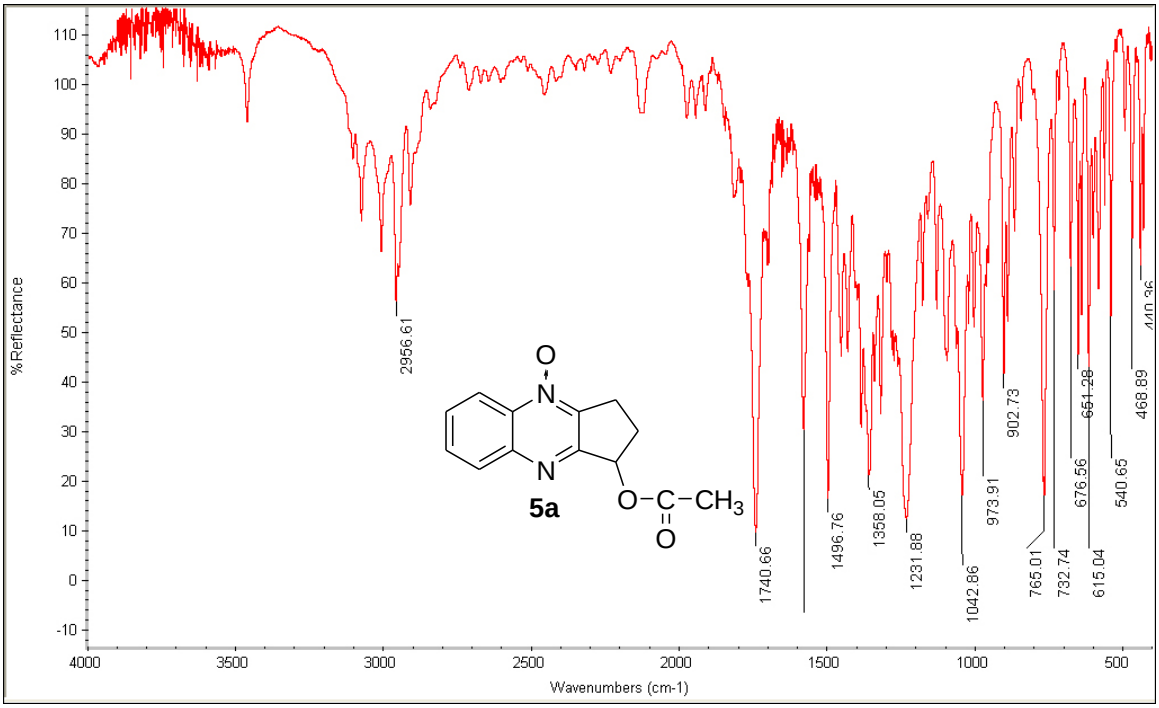
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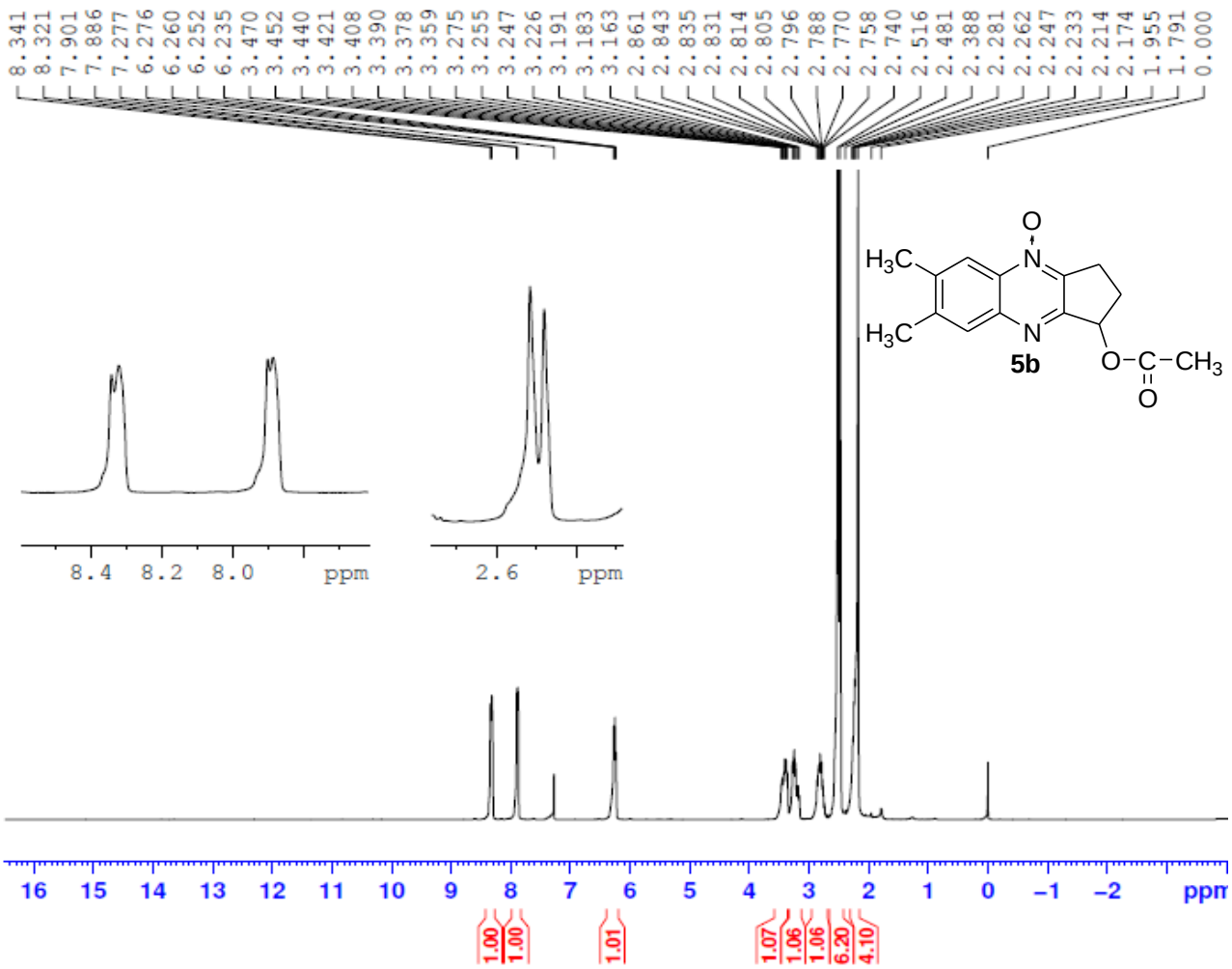
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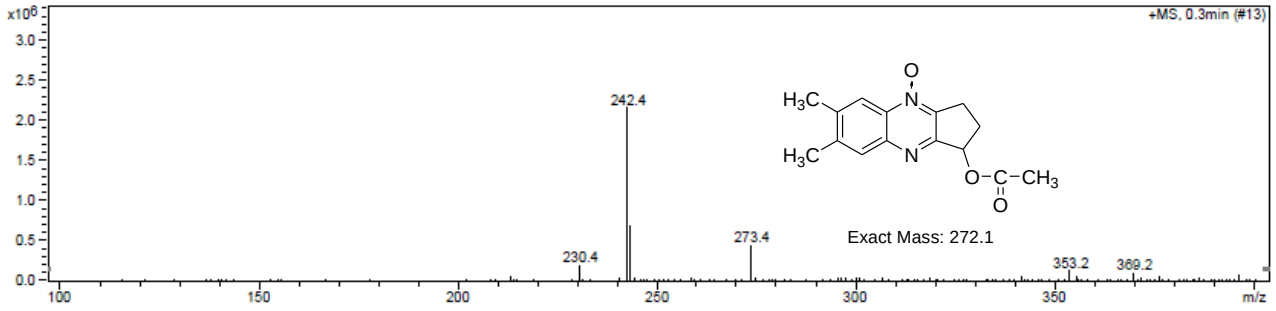
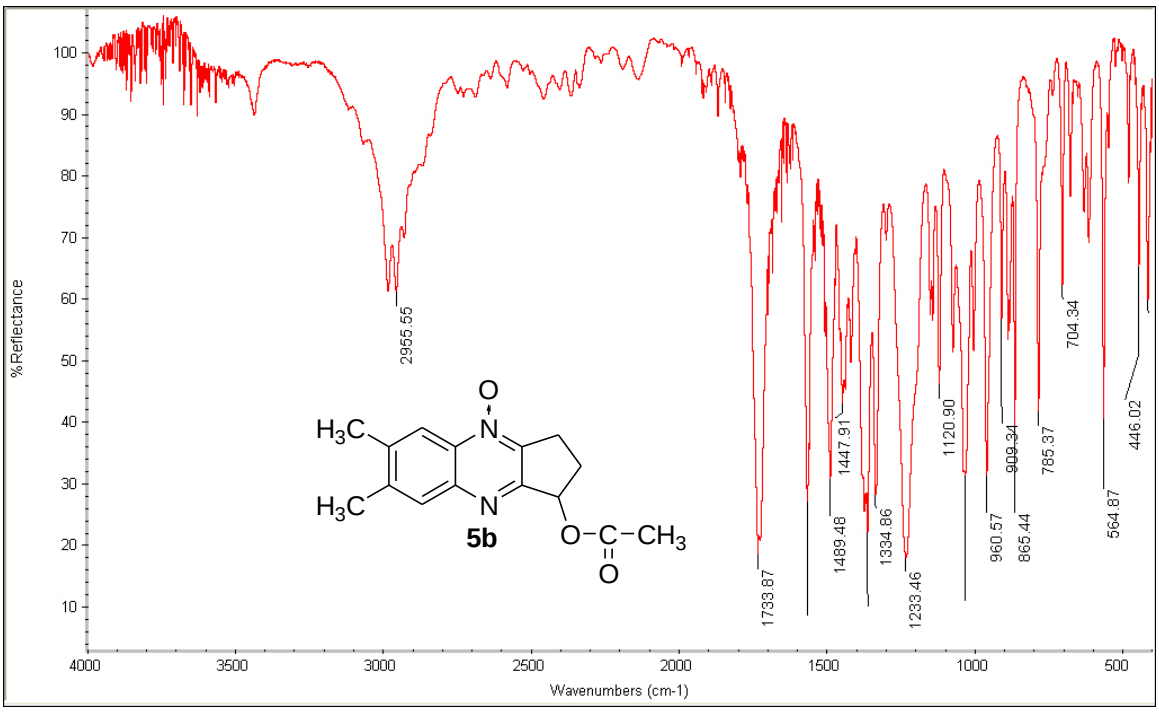
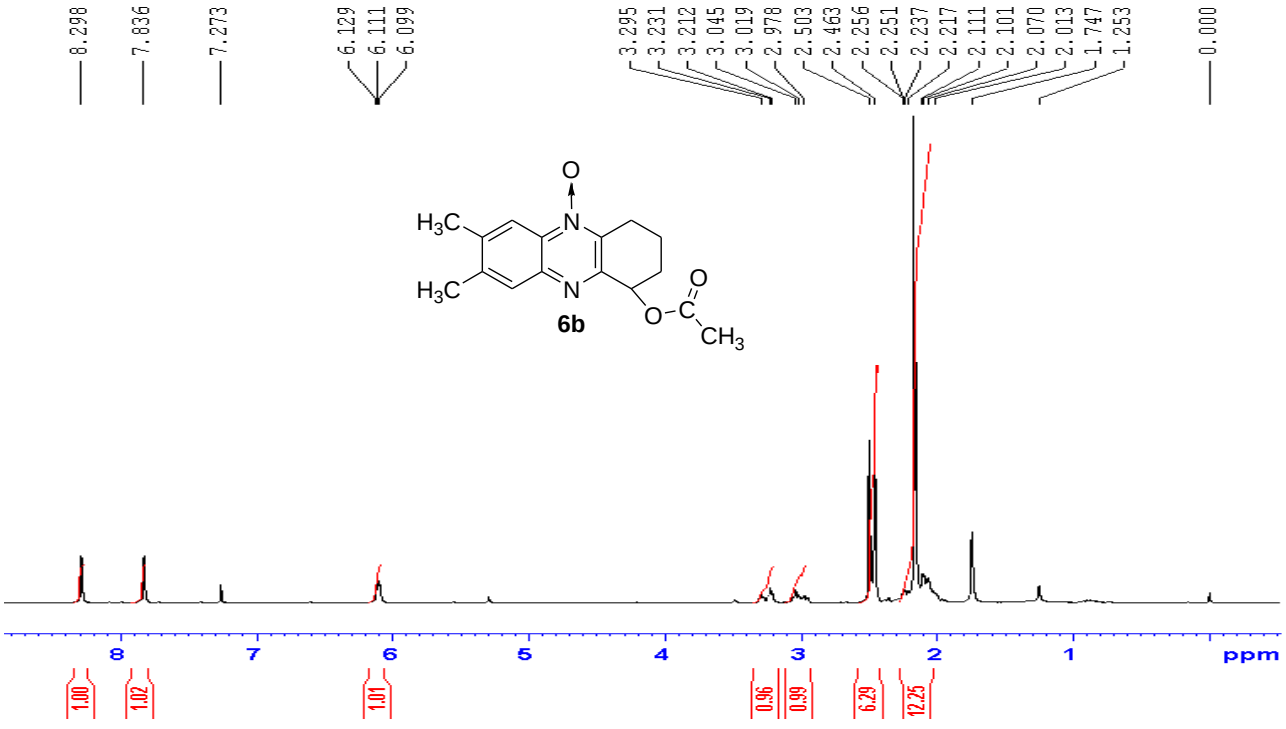
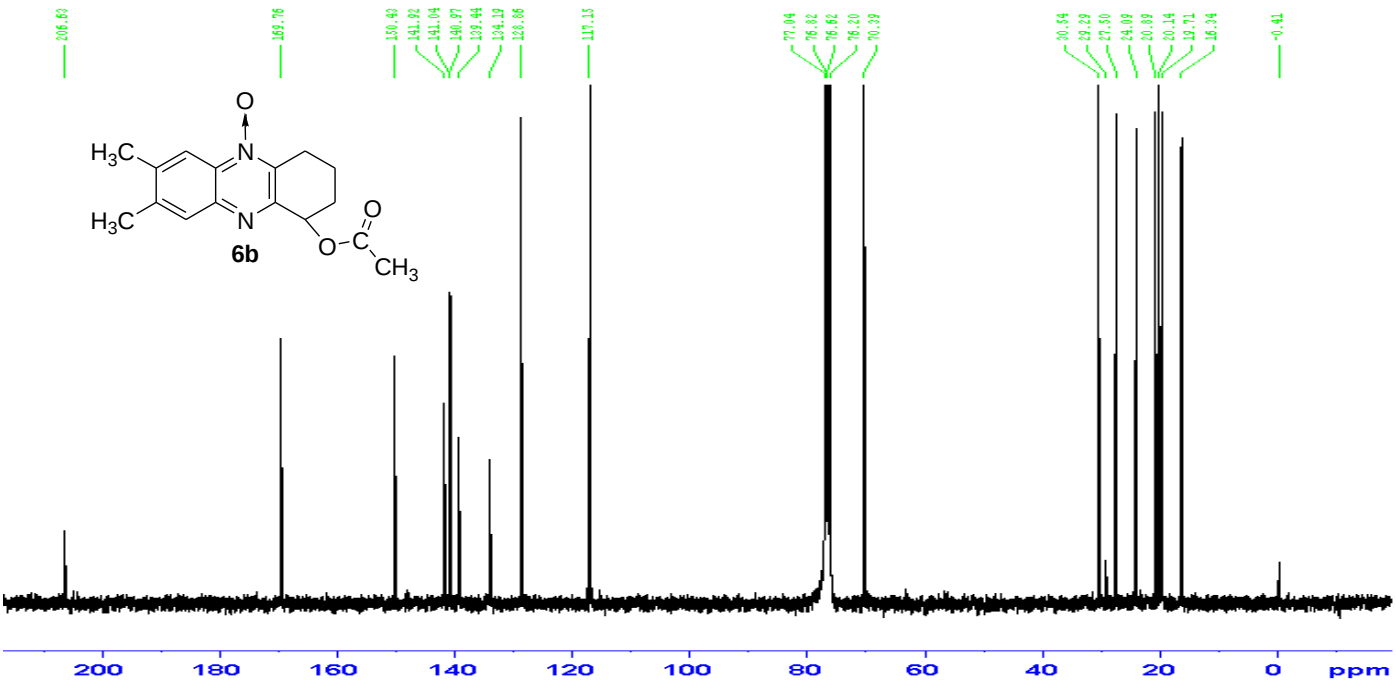
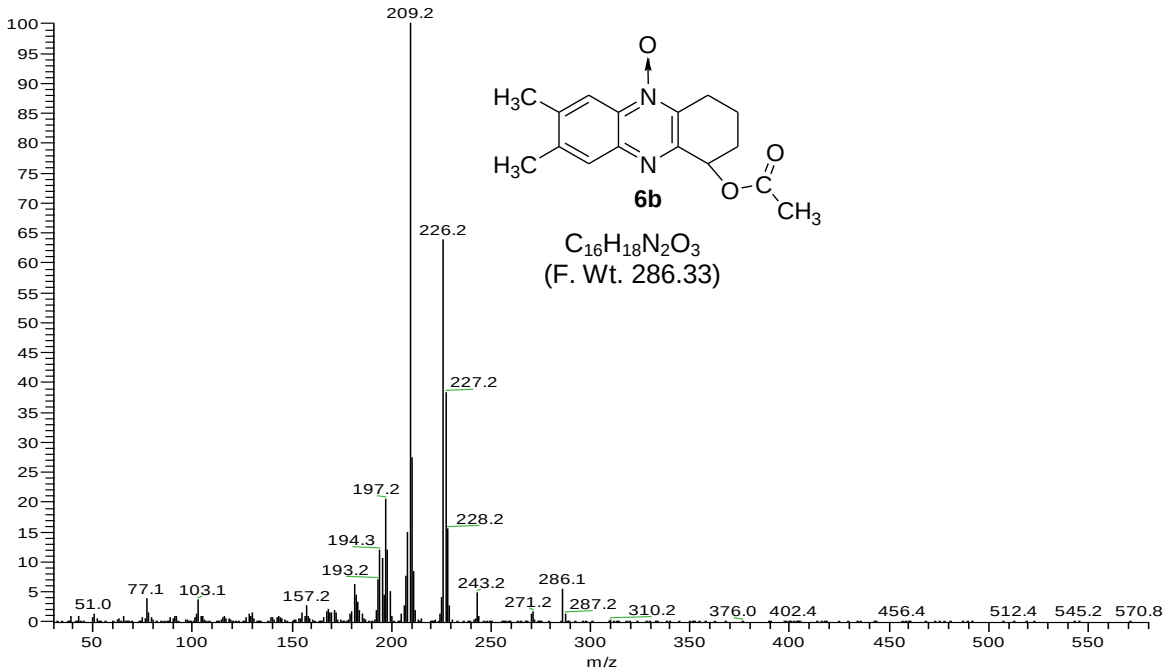
1.00
1.00
1.01
1.07
1.06
1.06
6.20
4.10

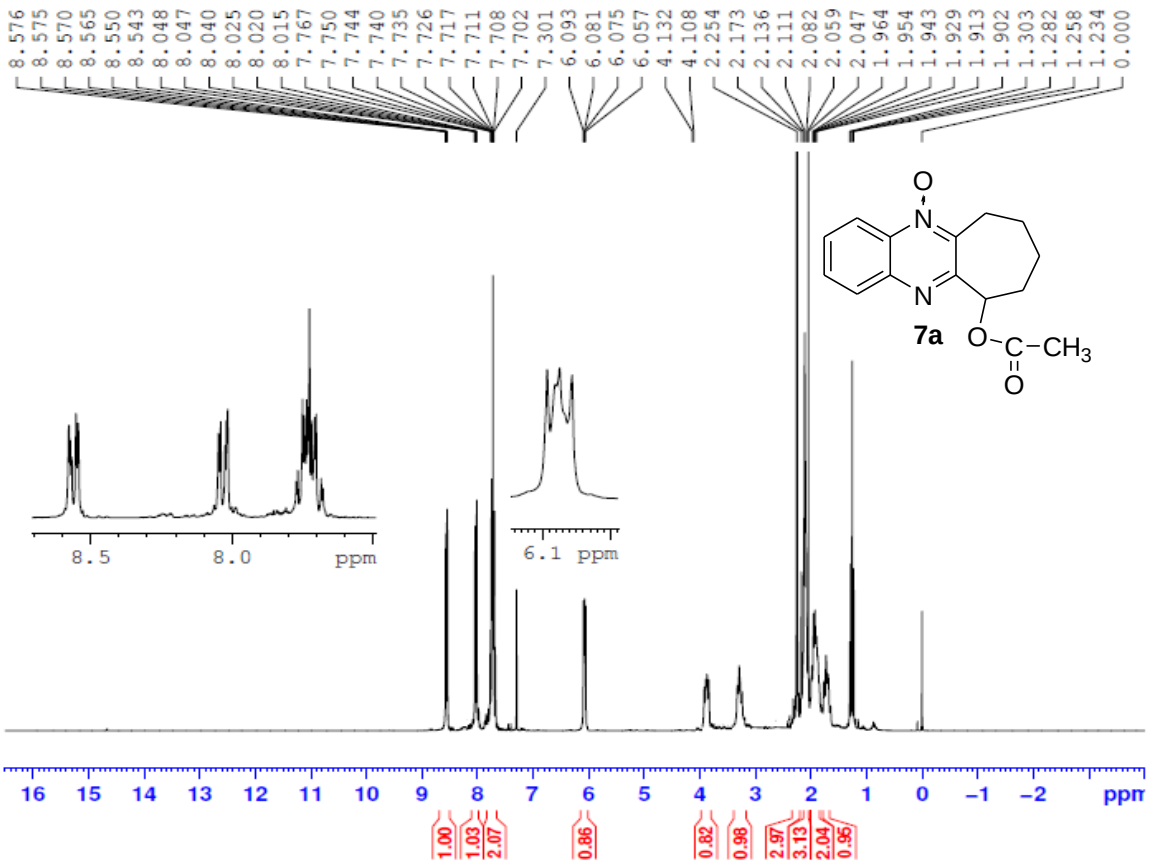

x10^6
3.0
2.5
2.0
1.5
1.0
0.5
0.0
+MS, 0.3min (#13)
242.4
230.4
273.4
353.2
369.2
100
150
200
250
300
350
m/z
H3C
H3C
O
N
N
O−C−CH3
O
Exact Mass: 272.1

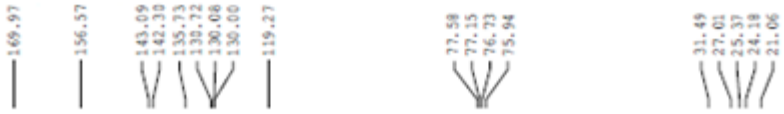

%Reflectance
Wavenumbers (cm-1)
2955.55
1733.87
1489.48
1447.91
1334.86
1233.46
1120.90
960.57
909.34
865.44
785.37
704.34
564.87
446.02
5b

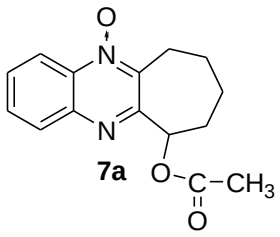

8.298
7.836
7.273
6.129
6.111
6.099
3.295
3.231
3.212
3.045
3.019
2.978
2.503
2.463
2.256
2.251
2.237
2.217
2.111
2.101
2.070
2.013
1.747
1.253
0.000
6b
ppm
1.00
1.02
1.01
0.96
0.99
6.29
12.25

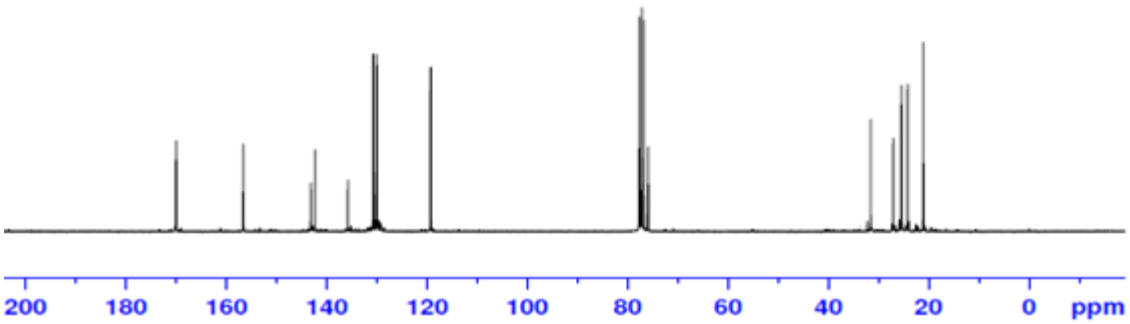

206.63
169.76
150.48
141.92
141.04
140.97
139.44
134.19
128.68
117.15
77.04
76.82
76.62
76.20
70.39
30.54
23.29
21.50
21.09
20.89
20.14
19.71
16.34
-0.41
O
N
H3C
H3C
N
O
O
C
O
CH3
6b
200
180
160
140
120
100
80
60
40
20
0
ppm

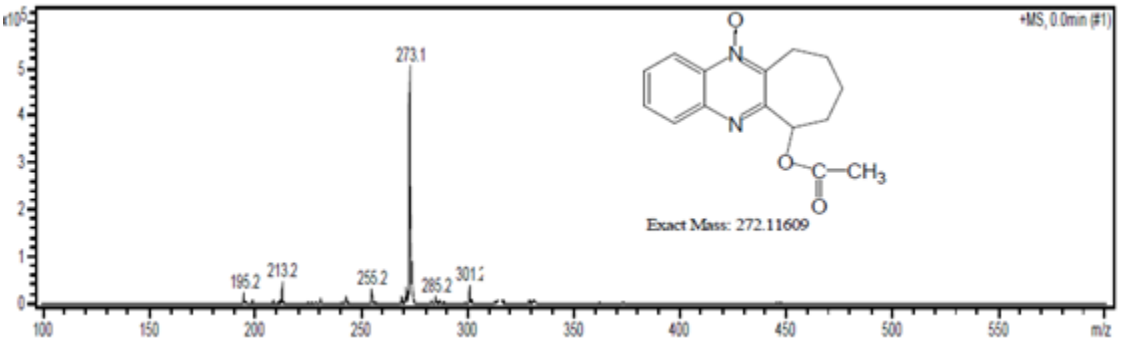

209.2
226.2
227.2
197.2
228.2
194.3
193.2
243.2
286.1
77.1
103.1
51.0
157.2
271.2
287.2
310.2
376.0
402.4
456.4
512.4
545.2
570.8
m/z
O
N
H3C
H3C
N
O
O
C
O
CH3
6b
C16H18N2O3
(F. Wt. 286.33)

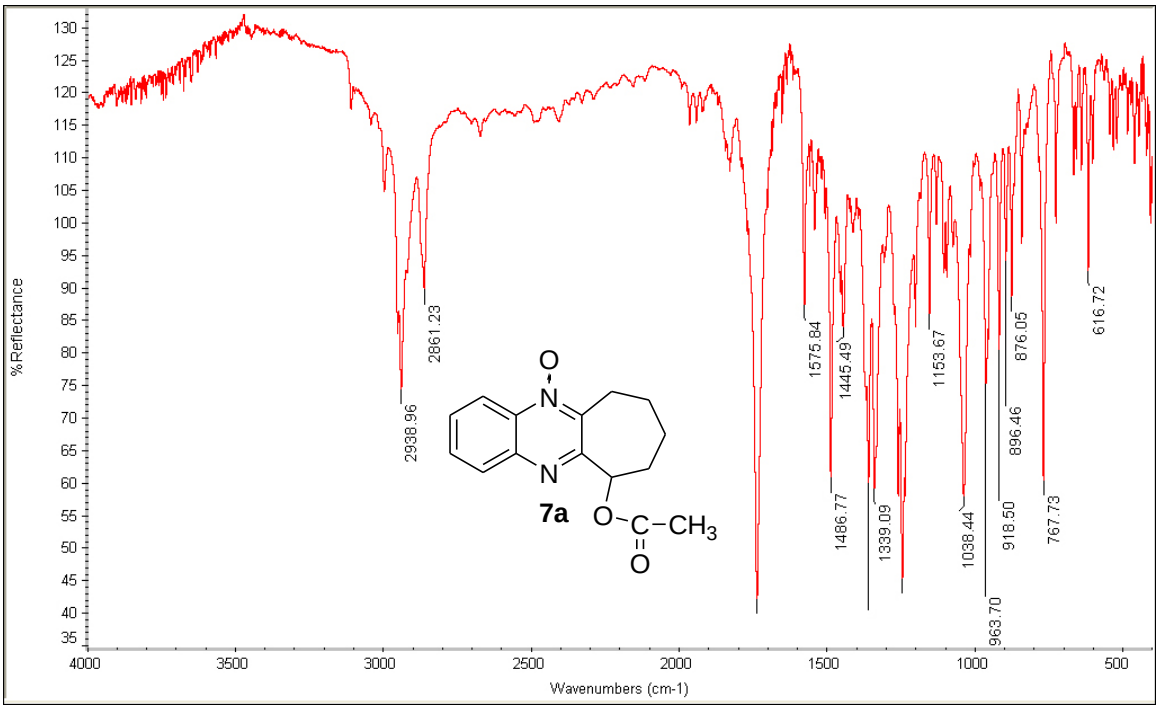

8.576
8.575
8.570
8.565
8.550
8.543
8.048
8.047
8.040
8.025
8.020
8.015
7.767
7.750
7.744
7.740
7.735
7.726
7.717
7.711
7.708
7.702
7.301
6.093
6.081
6.075
6.057
4.132
4.108
2.254
2.173
2.136
2.111
2.082
2.059
2.047
1.964
1.954
1.943
1.929
1.913
1.902
1.303
1.282
1.258
1.234
0.000
7a
8.5
8.0
ppm
6.1 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.03
2.07
0.86
0.82
0.98
2.97
3.13
2.04
0.95

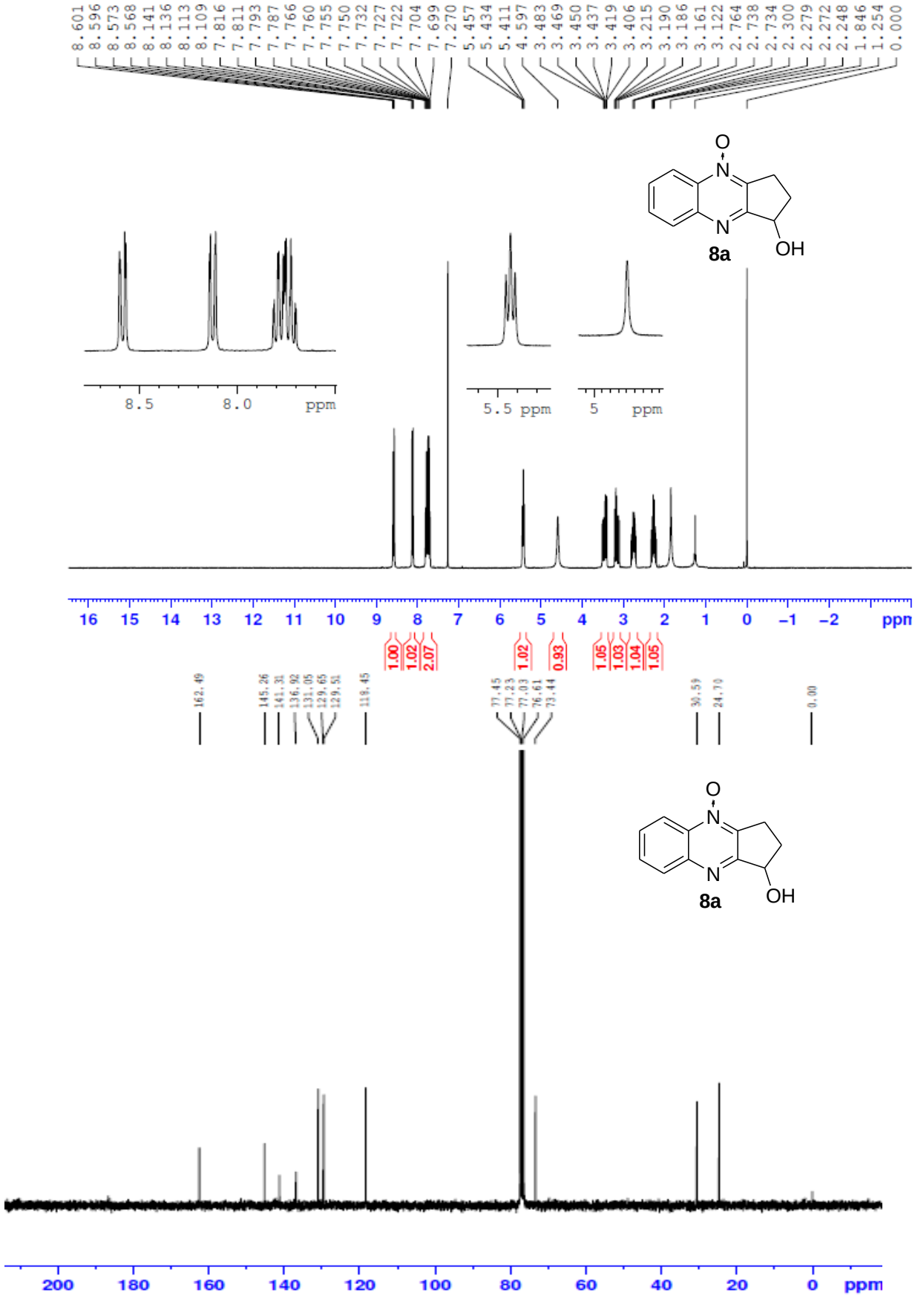

169.97
156.57
143.69
142.38
135.73
133.72
130.66
130.00
119.27
77.58
77.15
76.73
75.94
31.49
27.61
25.37
24.18
21.06


7a


200 180 160 140 120 100 80 60 40 20 0 ppm


+MS, 0.0min (#1)
273.1
195.2
213.2
255.2
285.2
301.2
Exact Mass: 272.11609
m/z


%Reflectance
2938.96
2861.23
1575.84
1445.49
1153.67
1486.77
1339.09
1038.44
963.70
918.50
896.46
876.05
767.73
616.72
7a
Wavenumbers (cm-1)

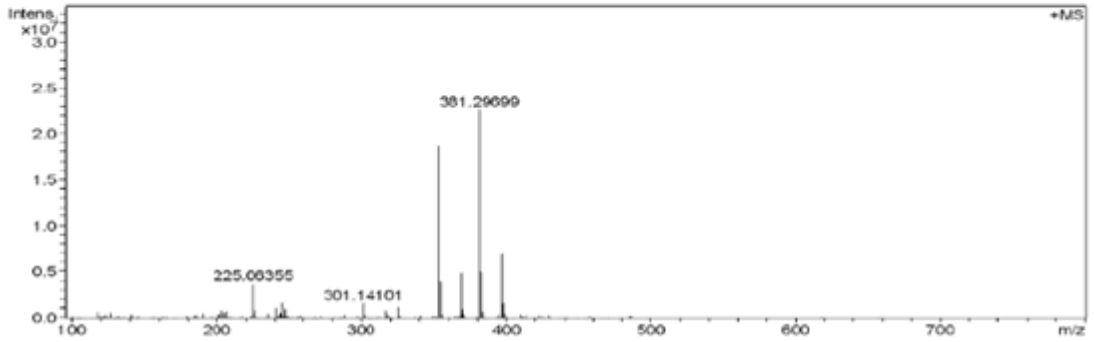

8.601
8.596
8.573
8.568
8.141
8.136
8.113
8.109
7.816
7.811
7.793
7.787
7.766
7.760
7.755
7.750
7.732
7.727
7.722
7.704
7.699
7.270
5.457
5.434
5.411
4.597
3.483
3.469
3.450
3.437
3.419
3.406
3.215
3.190
3.186
3.161
3.122
2.764
2.738
2.734
2.300
2.279
2.272
2.248
1.846
1.254
0.000
O
N
N
OH
8a
8.5
8.0
ppm
5.5 ppm
5
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.02
2.07
1.02
0.93
1.05
1.03
1.04
1.05
162.49
145.26
141.31
136.92
131.05
129.65
129.51
118.45
77.45
77.23
77.03
76.61
73.44
30.59
24.70
0.00
O
N
N
OH
8a
200 180 160 140 120 100 80 60 40 20 0 ppm

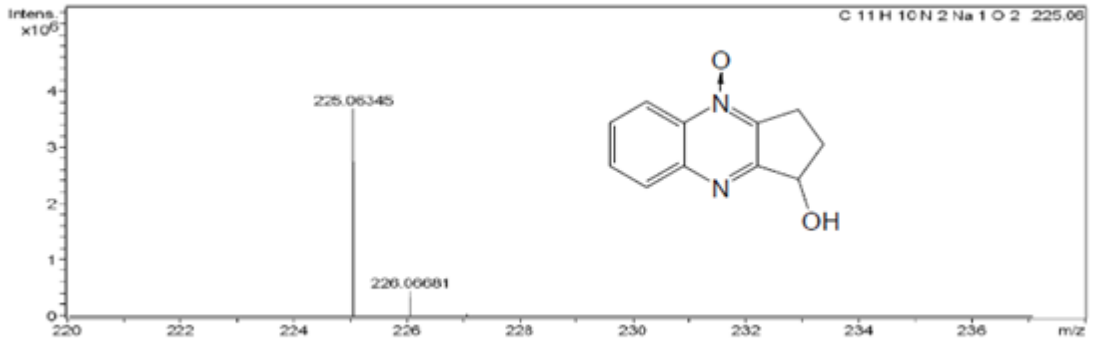
Mass Spectrum Molecular Formula Report

Analysis Info

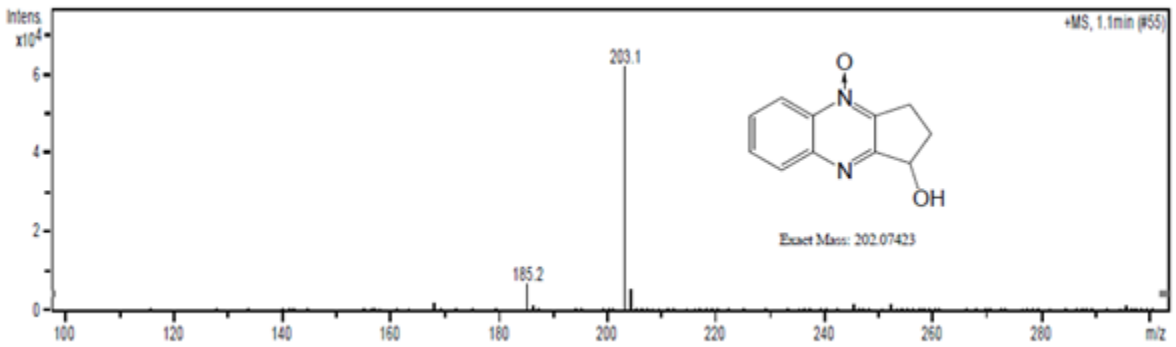
Analysis Name	D:\Data\2010mar18\zahra_000056.d	Acquisition Date	3/23/2010 3:42:11 PM
Method	ESI pos April 17 2009	Operator	FTMS_User
Sample Name	MZN25	Instrument	apex-IV
Comment	ACN		

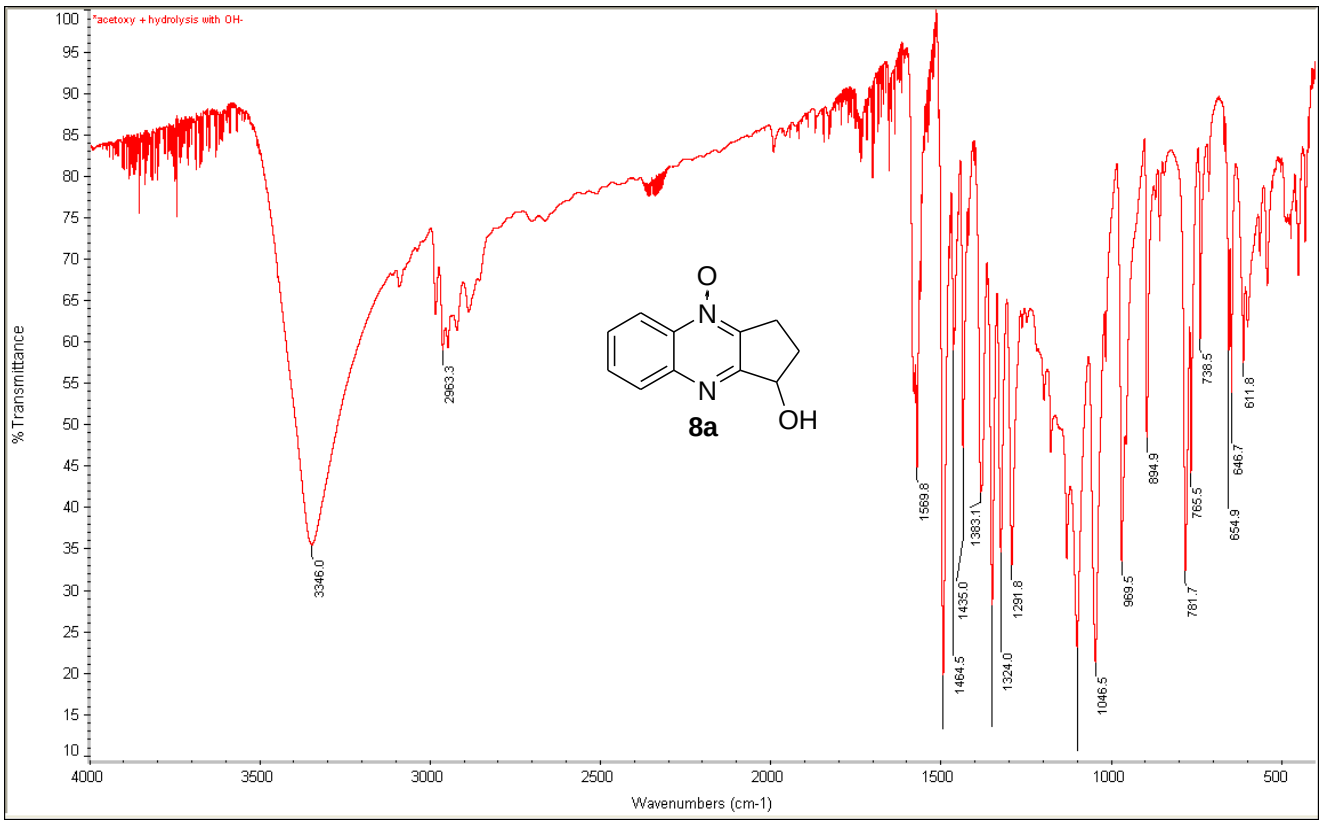
Acquisition Parameter

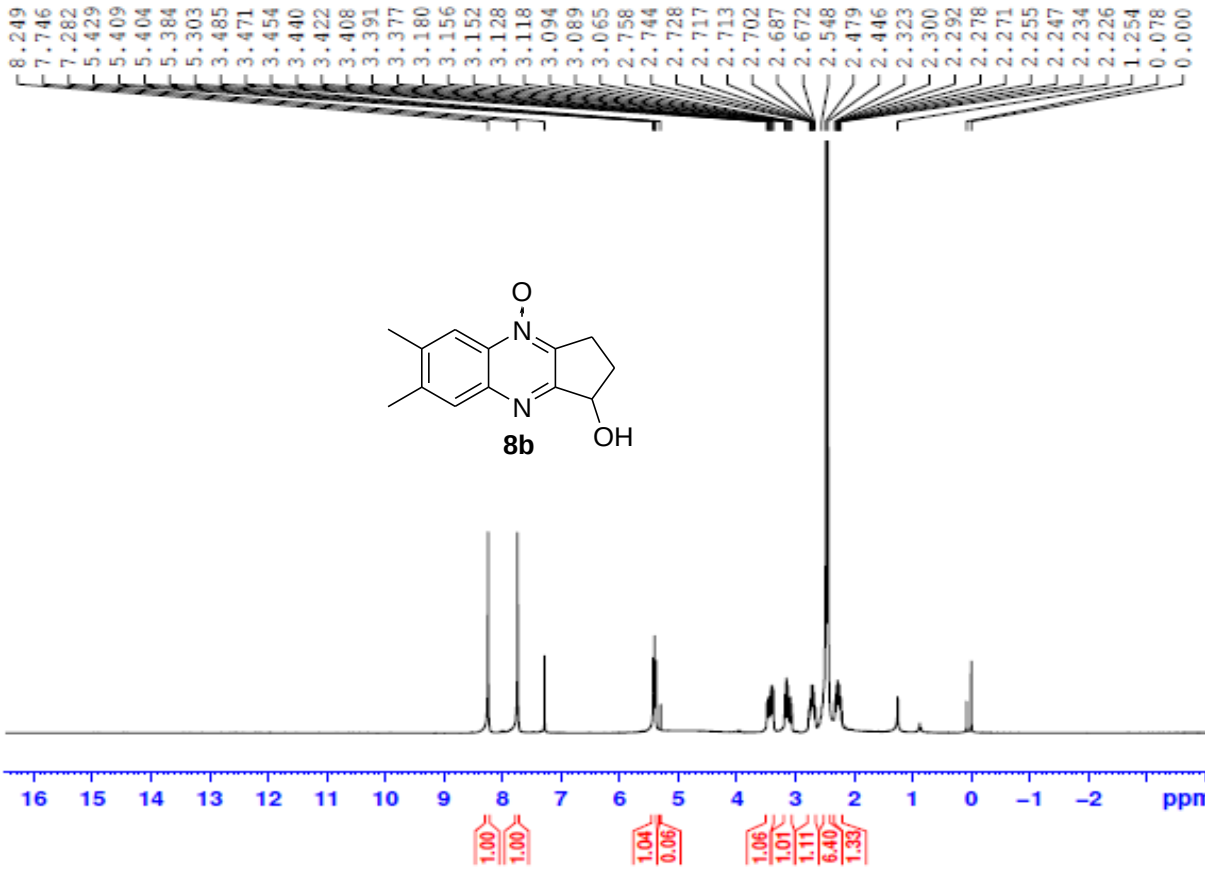


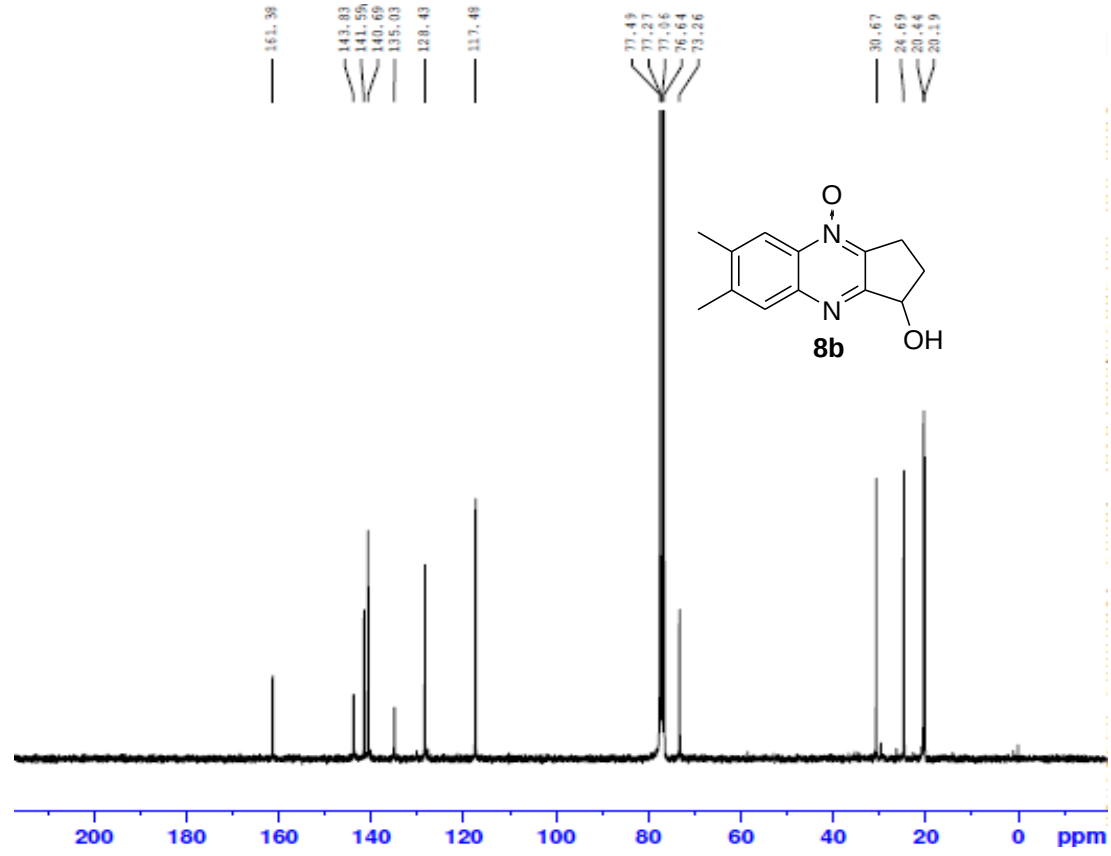


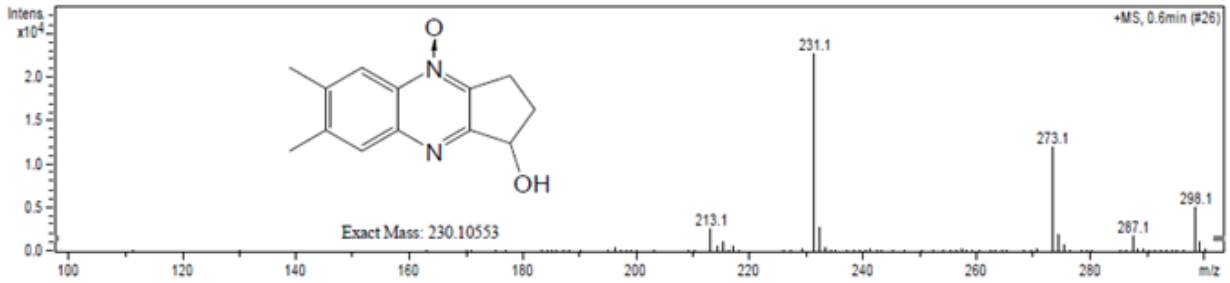
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 11 H 10 N 2 Na 1 O 2	0.006	225.06345	-0.45	-0.69	-0.10	7.50	ok	even

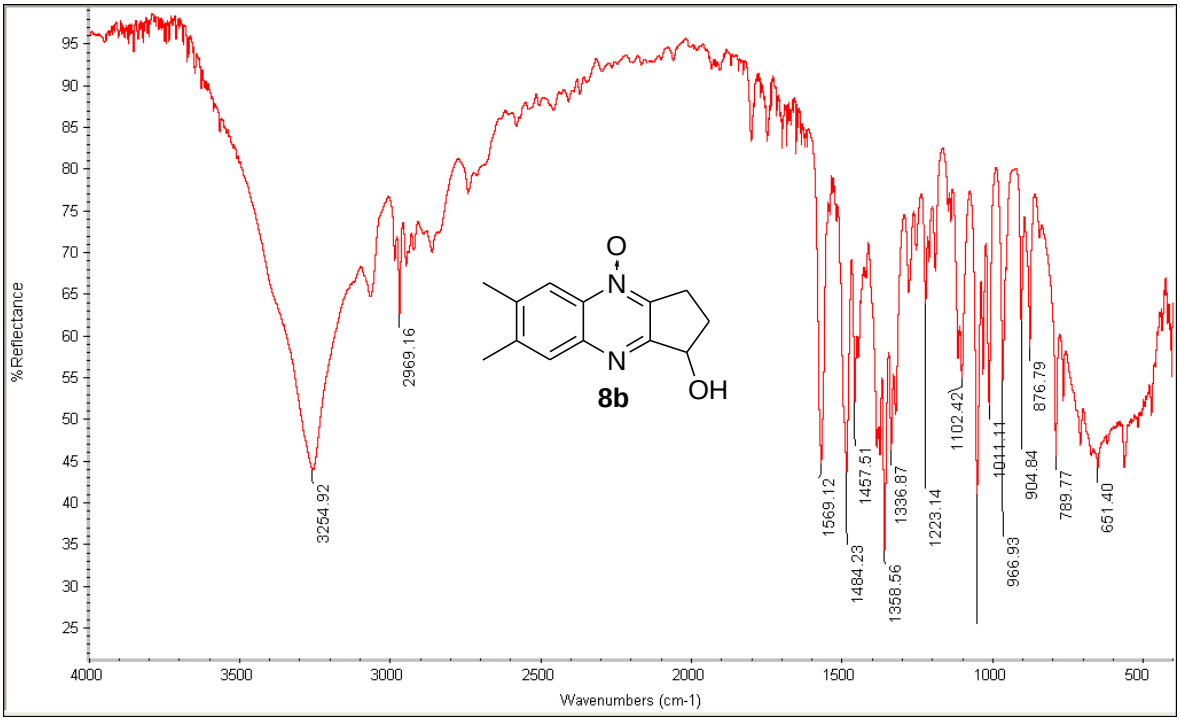


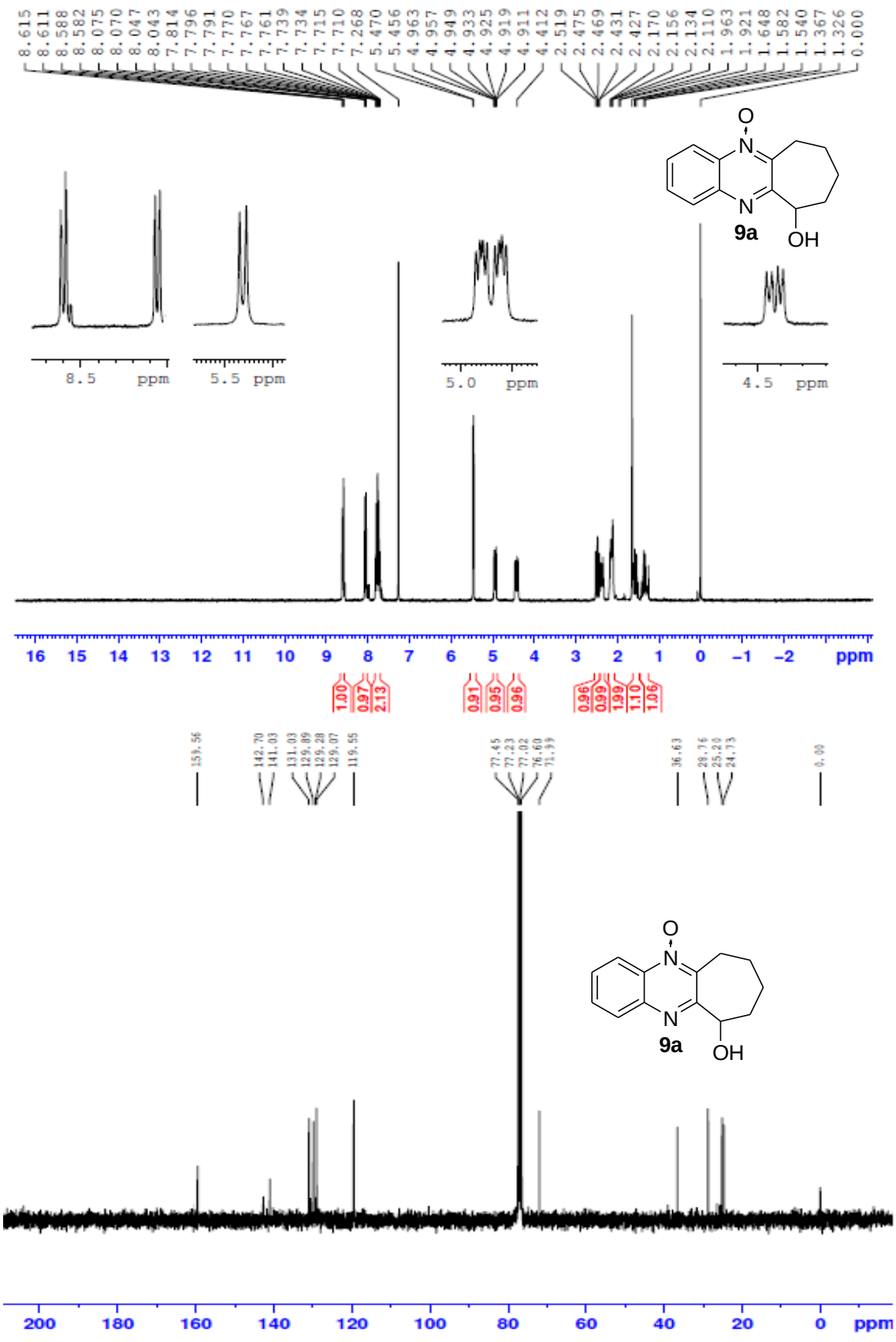

*acetoxy + hydrolysis with OH-
%Transmittance
Wavenumbers (cm-1)
3346.0
2963.3
1569.8
1464.5
1435.0
1383.1
1324.0
1291.8
1046.5
969.5
894.9
781.7
765.5
738.5
654.9
646.7
611.8
O
N
N
OH
8a

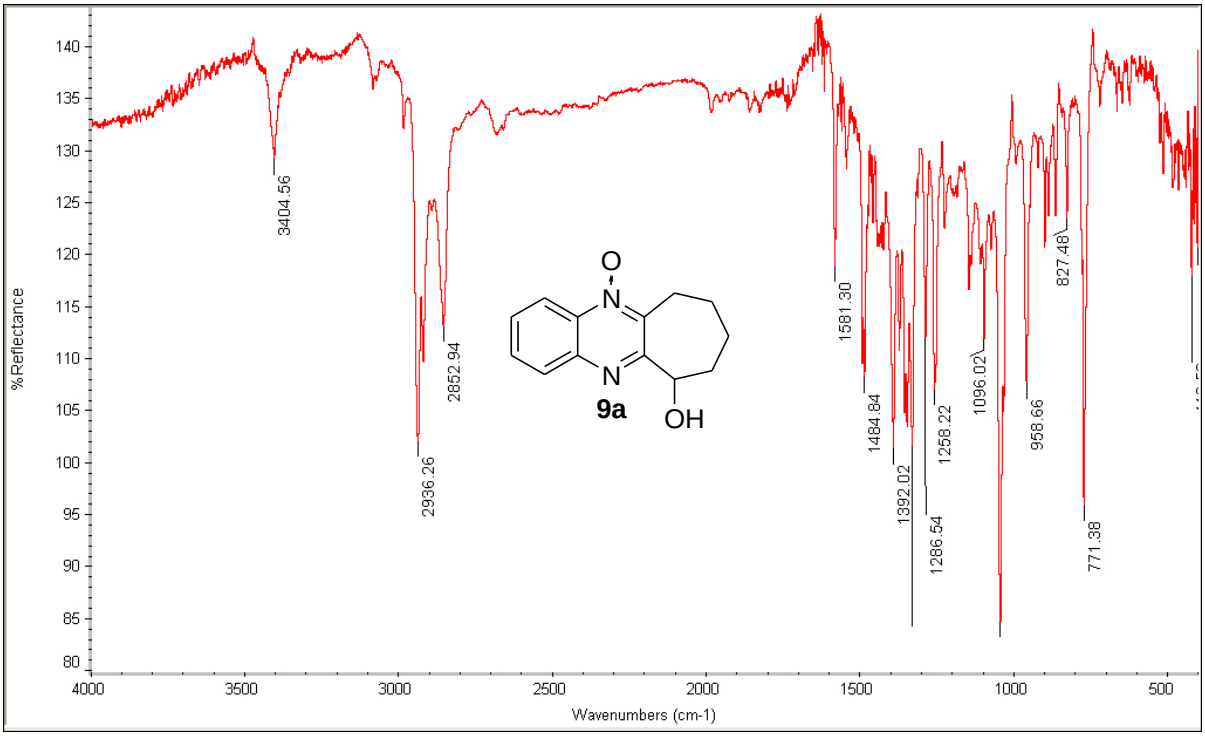

8.249
7.746
7.282
5.429
5.409
5.404
5.384
5.303
3.485
3.471
3.454
3.440
3.422
3.408
3.391
3.377
3.180
3.156
3.152
3.128
3.118
3.094
3.089
3.065
2.758
2.744
2.728
2.717
2.713
2.702
2.687
2.672
2.548
2.479
2.446
2.323
2.300
2.292
2.278
2.271
2.255
2.247
2.234
2.226
1.254
0.078
0.000
O
N
N
OH
8b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.00
1.04
0.06
1.06
1.01
1.11
6.40
1.33

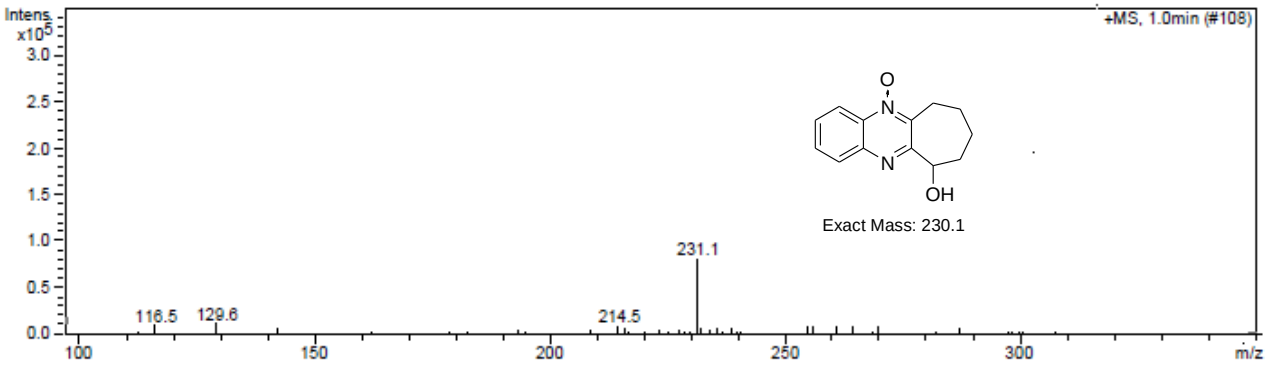

161.38
143.83
141.59
140.69
135.03
128.43
117.48
77.49
77.27
77.06
76.64
73.26
30.67
24.69
20.44
20.19
O
N
N
OH
8b
200 180 160 140 120 100 80 60 40 20 0 ppm

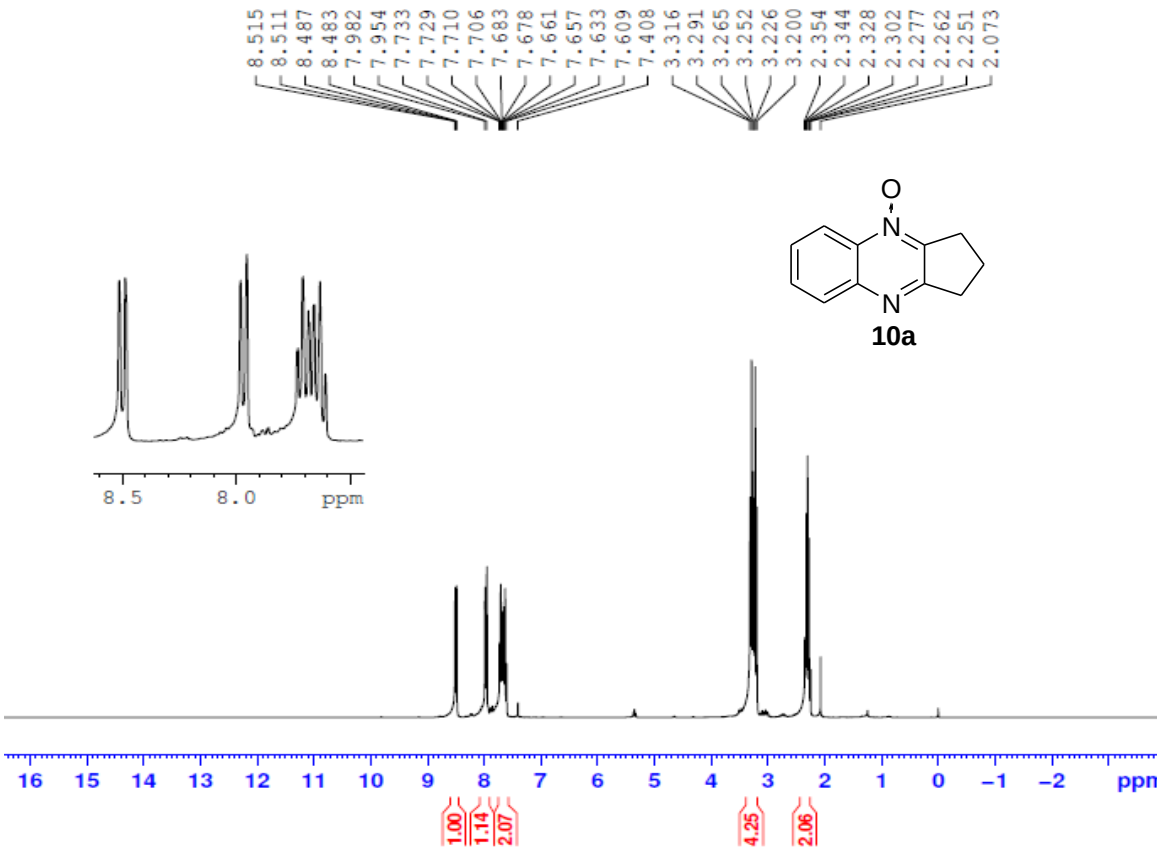

Intens.
x10^4
+MS, 0.6min (#26)
231.1
273.1
298.1
213.1
287.1
Exact Mass: 230.10553
m/z

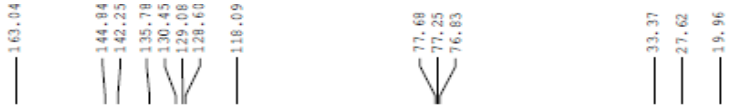

%Reflectance
3254.92
2969.16
1569.12
1484.23
1457.51
1358.56
1336.87
1223.14
1102.42
1011.11
966.93
904.84
876.79
789.77
651.40
8b
Wavenumbers (cm-1)

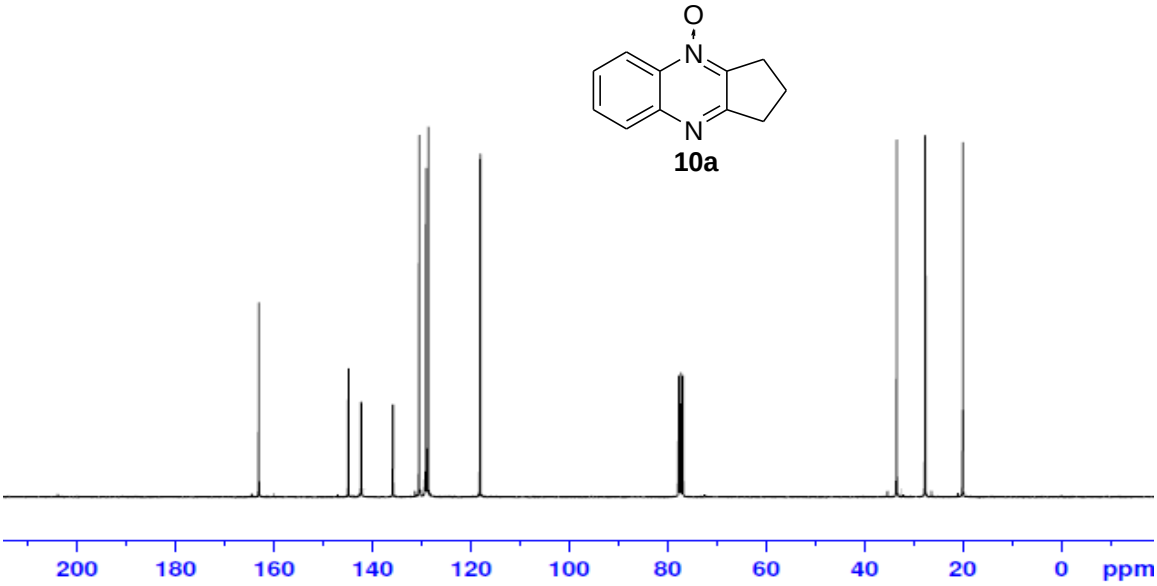

8.615
8.611
8.588
8.582
8.075
8.070
8.047
8.043
7.814
7.796
7.791
7.770
7.767
7.761
7.739
7.734
7.715
7.710
7.268
5.470
5.456
4.963
4.957
4.949
4.933
4.925
4.919
4.911
4.412
2.519
2.475
2.469
2.431
2.427
2.170
2.156
2.134
2.110
1.963
1.921
1.648
1.582
1.540
1.367
1.326
0.000
O
N
N
OH
9a
8.5 ppm
5.5 ppm
5.0 ppm
4.5 ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
0.97
2.13
0.91
0.95
0.96
0.96
0.99
1.99
1.10
1.06
159.56
142.70
141.03
131.03
129.89
129.28
129.07
119.55
77.45
77.23
77.02
76.60
71.99
36.63
28.76
25.20
24.73
0.00
O
N
N
OH
9a
200 180 160 140 120 100 80 60 40 20 0 ppm

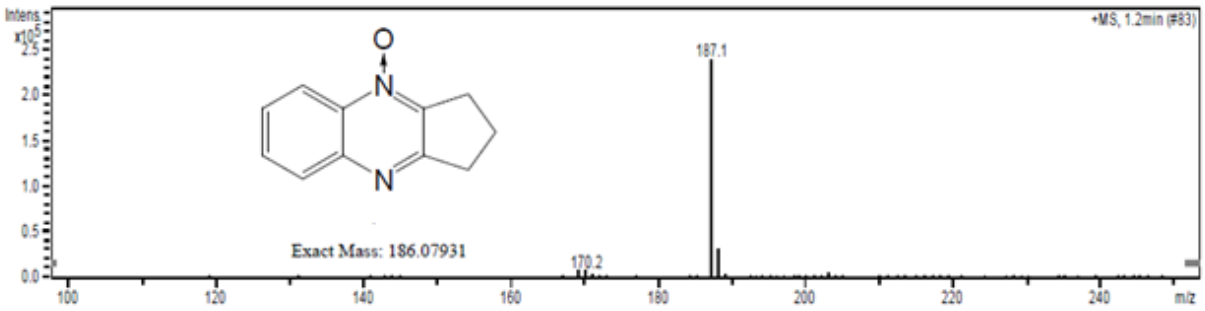

%Reflectance
Wavenumbers (cm-1)
3404.56
2936.26
2852.94
1581.30
1484.84
1392.02
1286.54
1258.22
1096.02
958.66
827.48
771.38
9a
OH

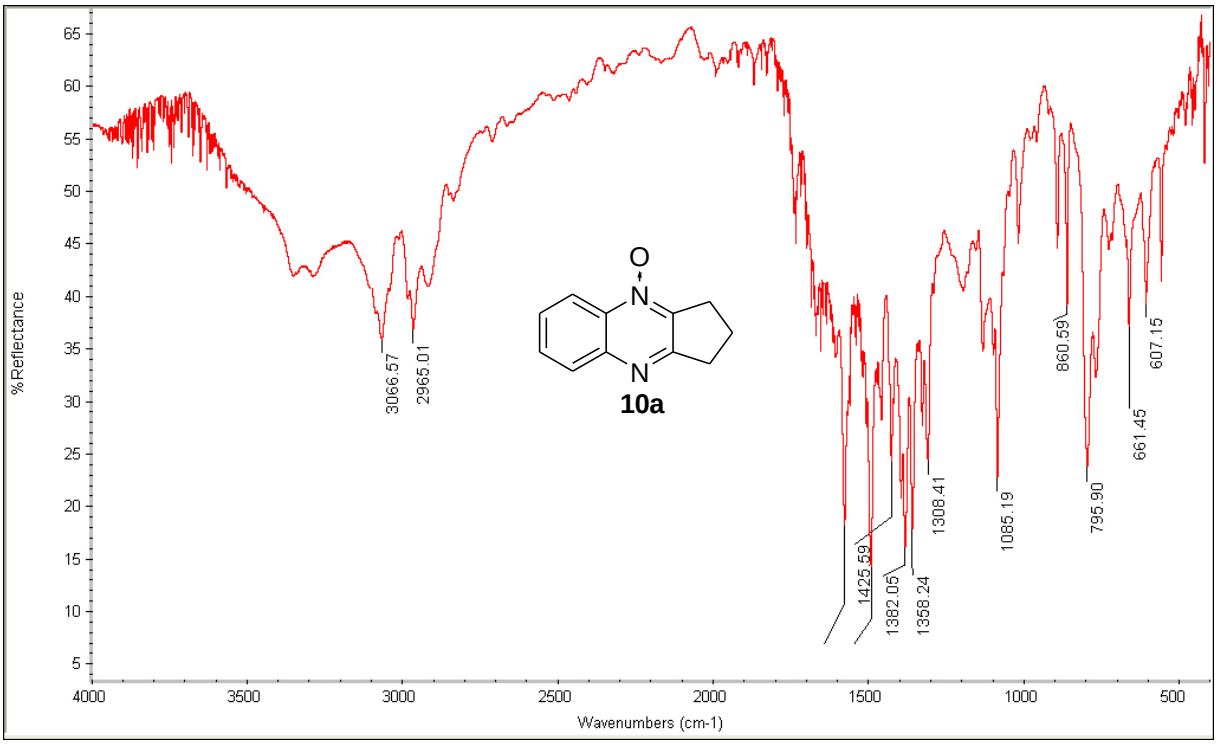

Intens.
x10^5
+MS, 1.0min (#108)
231.1
116.5
129.6
214.5
m/z
OH
Exact Mass: 230.1

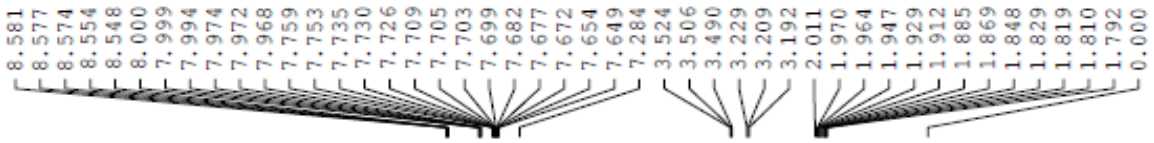

8.515
8.511
8.487
8.483
7.982
7.954
7.733
7.729
7.710
7.706
7.683
7.678
7.661
7.657
7.633
7.609
7.408
3.316
3.291
3.265
3.252
3.226
3.200
2.354
2.344
2.328
2.302
2.277
2.262
2.251
2.073
O
N
N
10a
8.5
8.0
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.14
2.07
4.25
2.06

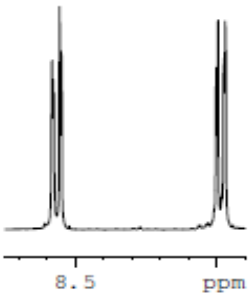

163.04
144.84
142.25
135.78
130.45
129.08
128.60
118.09
77.68
77.25
76.83
33.37
27.62
19.96

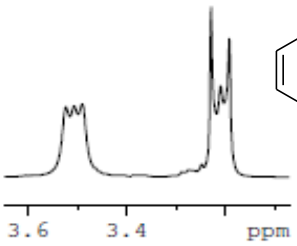

O
N
N
10a
200 180 160 140 120 100 80 60 40 20 0 ppm

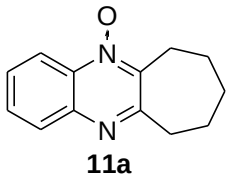

Intens.
x10^5
2.5
2.0
1.5
1.0
0.5
0.0
+MS, 1.2min (#83)
O
N
N
187.1
Exact Mass: 186.07931
170.2
100
120
140
160
180
200
220
240
m/z


%Reflectance
65
60
55
50
45
40
35
30
25
20
15
10
5
3066.57
2965.01
1425.59
1382.05
1358.24
1308.41
1085.19
860.59
795.90
661.45
607.15
O
N
N
10a
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

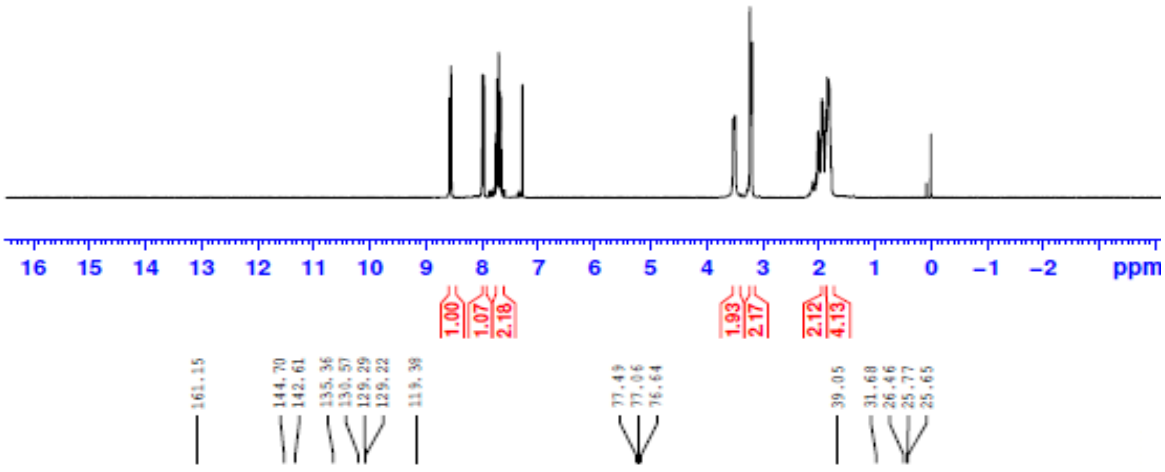

8.581
8.577
8.574
8.554
8.548
8.000
7.999
7.994
7.974
7.972
7.968
7.759
7.753
7.735
7.730
7.726
7.709
7.705
7.703
7.699
7.682
7.677
7.672
7.654
7.649
7.284
3.524
3.506
3.490
3.229
3.209
3.192
2.011
1.970
1.964
1.947
1.929
1.912
1.885
1.869
1.848
1.829
1.819
1.810
1.792
0.000

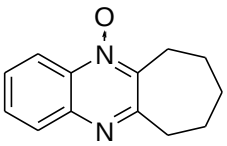

8.5
ppm


3.6
3.4
ppm

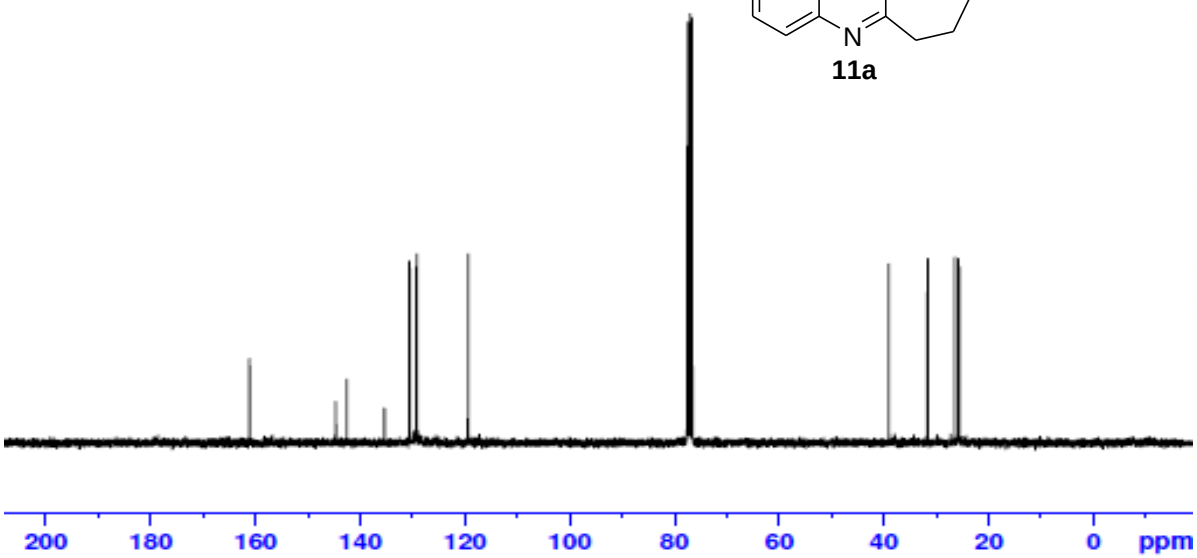

O
N
N

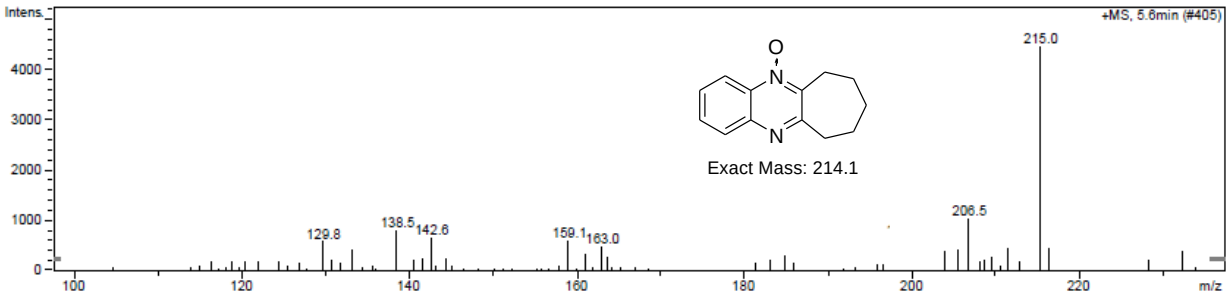
11a

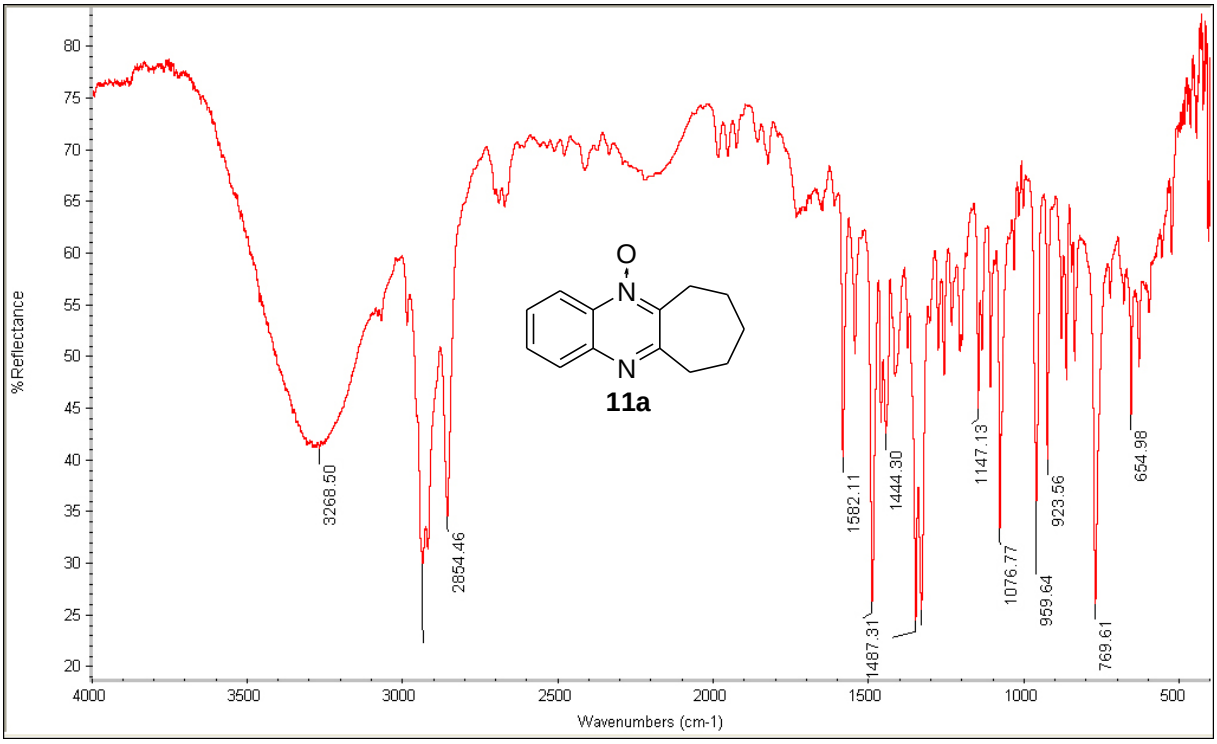

16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm
1.00
1.07
2.18
1.93
2.17
2.12
4.13
161.15
144.70
142.61
135.36
130.57
129.29
129.22
119.38
77.49
77.06
76.64
39.05
31.68
26.46
25.77
25.65

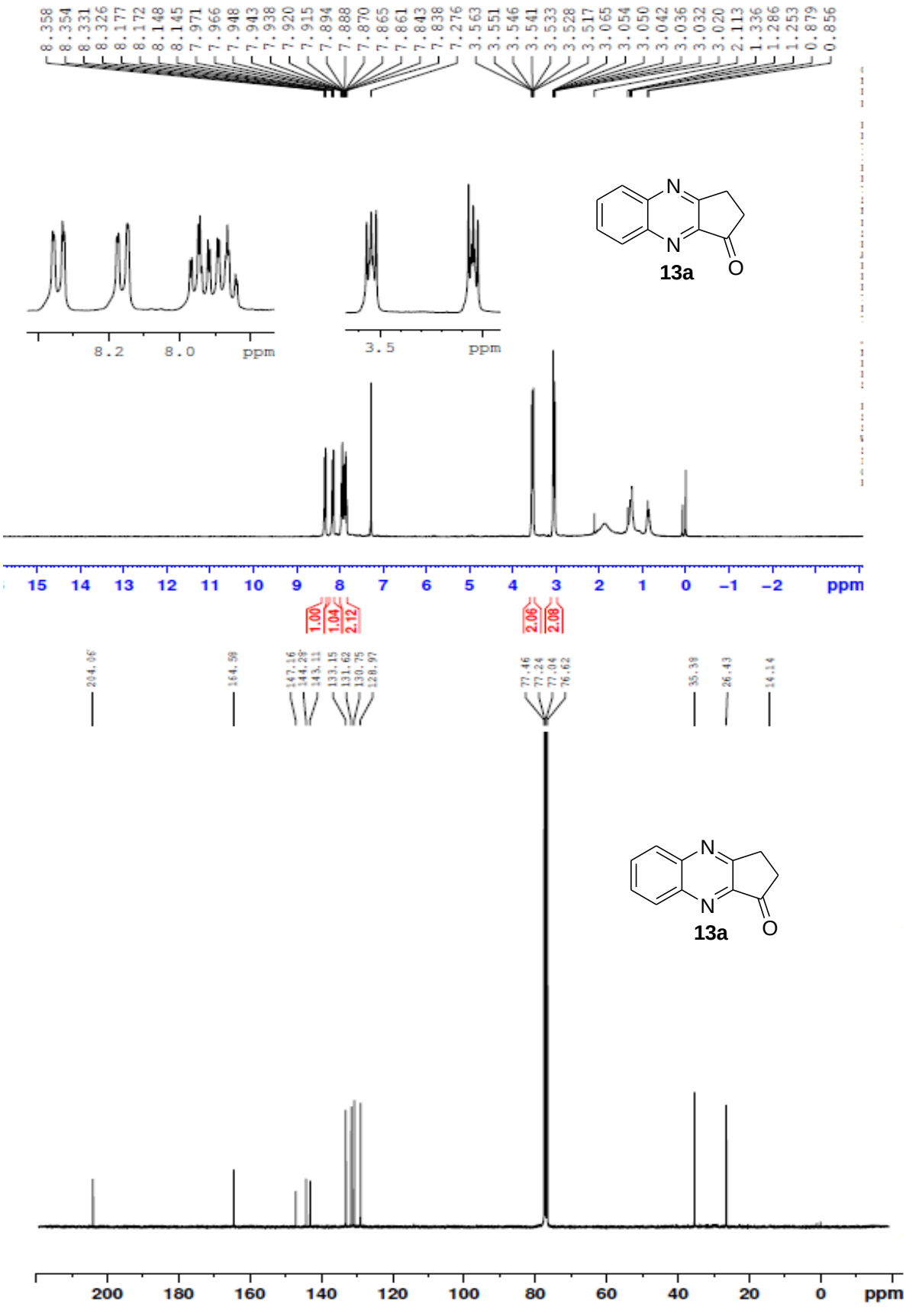

O
N
N

11a


200
180
160
140
120
100
80
60
40
20
0
ppm


Intens.
+MS, 5.6min (#405)
4000
3000
2000
1000
0
100
120
140
160
180
200
220
m/z
215.0
206.5
129.8
138.5
142.6
159.1
163.0
Exact Mass: 214.1


%Reflectance
80
75
70
65
60
55
50
45
40
35
30
25
20
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3268.50
2854.46
1582.11
1487.31
1444.30
1147.13
1076.77
959.64
923.56
769.61
654.98
11a

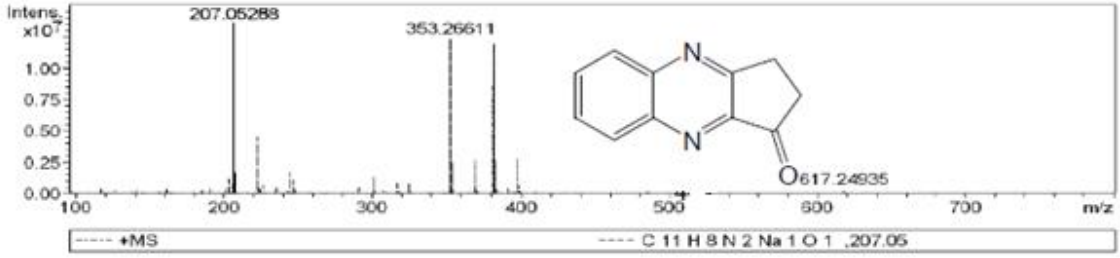

8.358
8.354
8.331
8.326
8.177
8.172
8.148
8.145
7.971
7.966
7.948
7.943
7.938
7.920
7.915
7.894
7.888
7.870
7.865
7.861
7.843
7.838
7.276
3.563
3.551
3.546
3.541
3.533
3.528
3.517
3.065
3.054
3.050
3.042
3.036
3.032
3.020
2.113
1.336
1.286
1.253
0.879
0.856
8.2
8.0
ppm
3.5
ppm
N
N
O
13a
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.04
2.12
2.06
2.08
204.06
164.58
147.16
144.28
143.11
133.15
131.62
130.75
128.97
77.46
77.24
77.04
76.62
35.38
26.43
14.14
N
N
O
13a
200 180 160 140 120 100 80 60 40 20 0 ppm

Mass Spectrum List Report

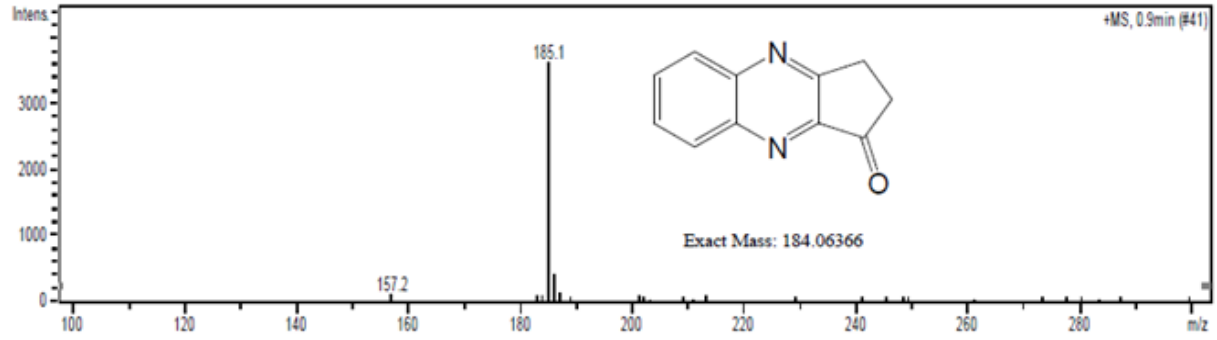
Analysis Info

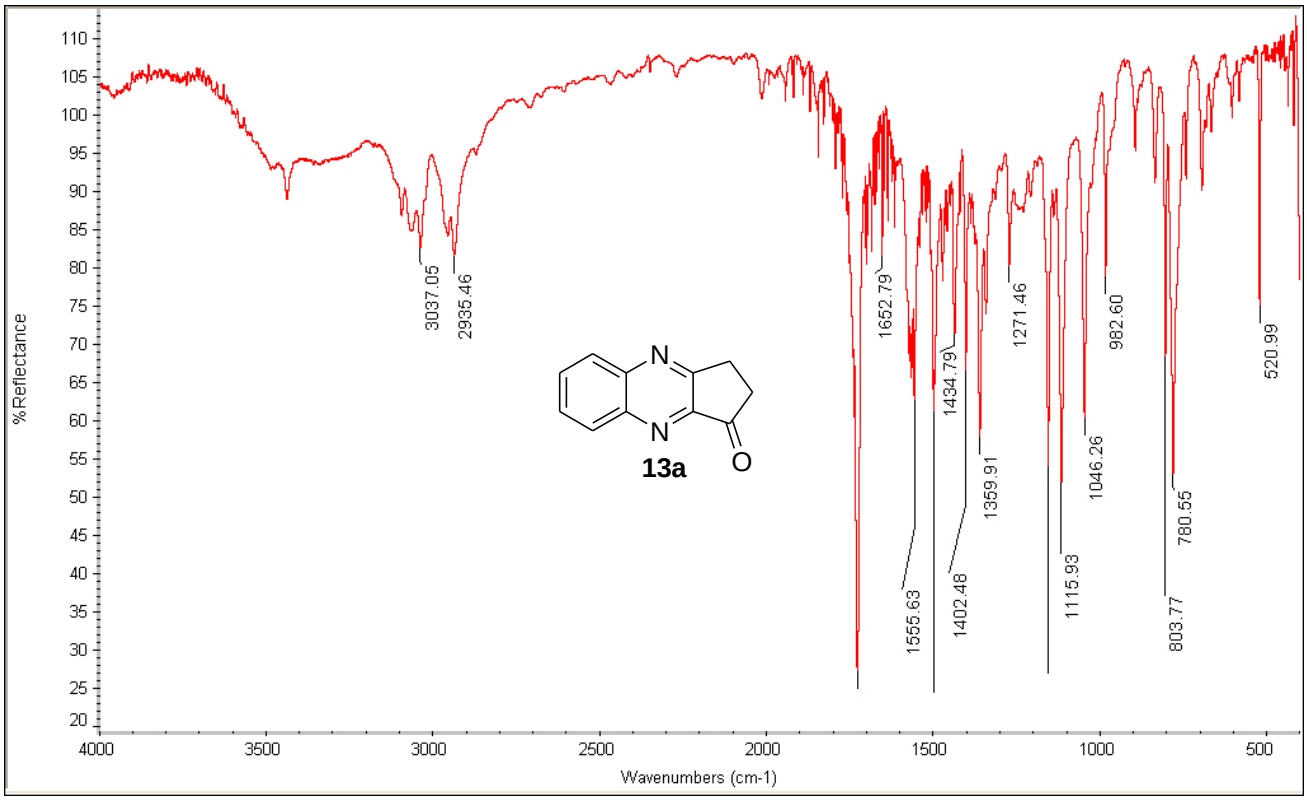
Analysis Name	zahra_000055.d	Acquisition Date	3/23/2010 3:37:21 PM
Method	ESI pos April 17 2009	Operator	FTMS_User
Sample Name	MZN26 ACN	Instrument	apex-IV

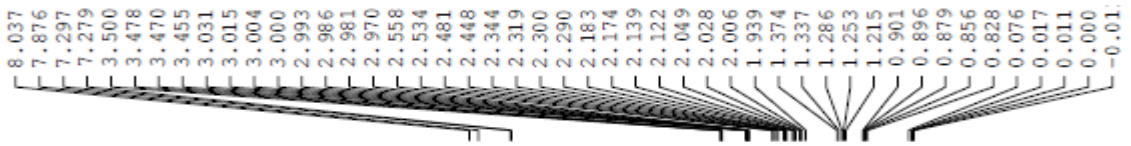
Acquisition Parameter

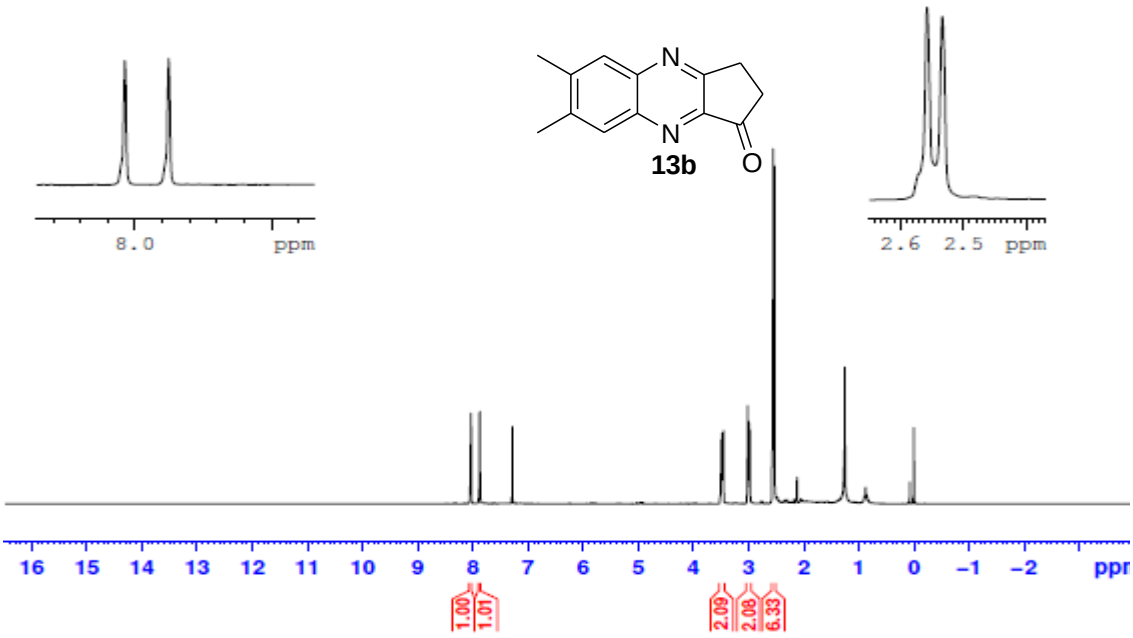


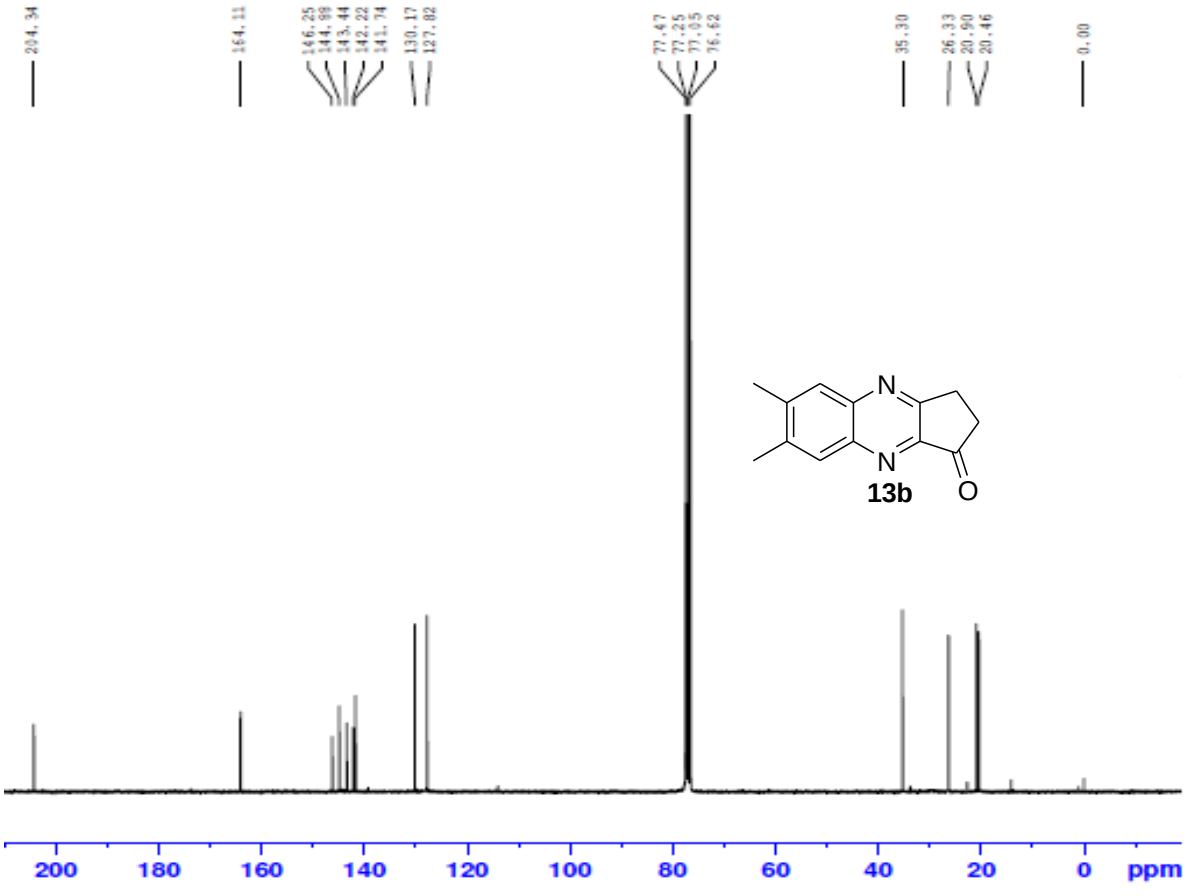
m/z	z	I	Res.	I %
201.97544		458713	76110	3.4
203.93049		1160691	74595	8.5
205.92751		771351	75060	5.7
207.04939		881892	146794	6.5
207.05258		13626668	73269	100.0
207.05585		907020	130590	6.7
208.05594		1701511	72538	12.5
223.02656		4523013	68224	33.2
224.02991		535935	68381	3.9
227.12513		720585	67385	5.3
236.07134		478885	65148	3.5
244.95703		1727018	63078	12.7
246.95407		1104901	61940	8.1
248.07919		482734	61893	3.5
292.08433		466453	52828	3.4
301.14085		1343820	51195	9.9
317.11485		813899	48667	6.0
325.23481		842274	47307	6.2
353.25677		845355	108747	6.2
353.26611		12361867	43414	90.7
353.27559		835835	94787	6.1
354.26946		2556510	43429	18.8
369.24010		2627766	41645	19.3
370.24342		539228	41539	4.0
381.28644		787276	81986	5.8
381.29738		11895228	40075	87.3
381.30840		795532	96681	5.8
382.30073		2680003	40049	19.7
397.27129		2847817	38523	20.9
398.27469		630797	38615	4.6

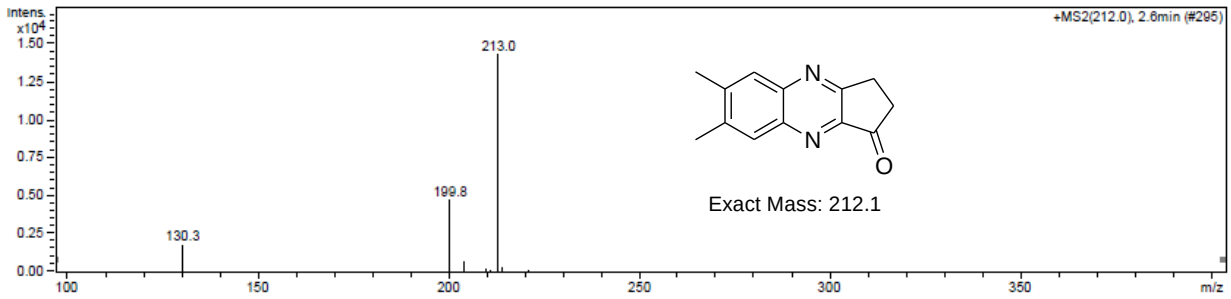


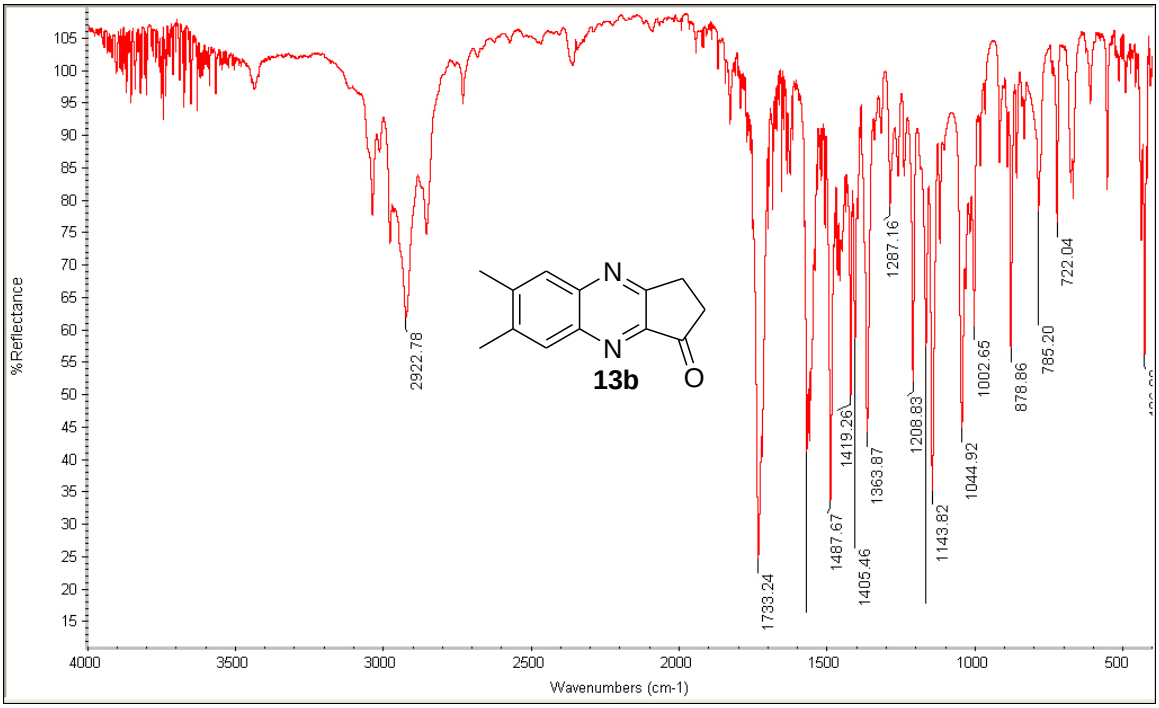

%Reflectance
Wavenumbers (cm-1)
3037.05
2935.46
1652.79
1555.63
1434.79
1402.48
1359.91
1271.46
1115.93
1046.26
982.60
803.77
780.55
520.99
N
N
O
13a

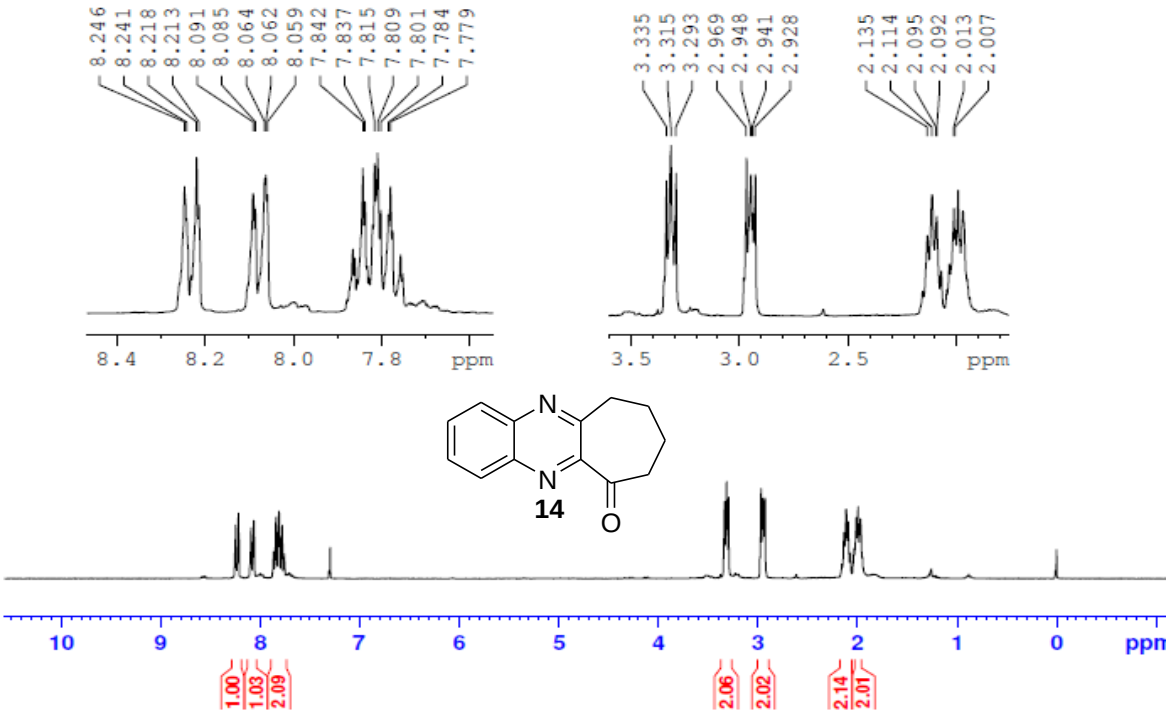

8.037
7.876
7.297
7.279
3.500
3.478
3.470
3.455
3.031
3.015
3.004
3.000
2.993
2.986
2.981
2.970
2.558
2.534
2.481
2.448
2.344
2.319
2.300
2.290
2.183
2.174
2.139
2.122
2.049
2.028
2.006
1.939
1.374
1.337
1.286
1.253
1.215
0.901
0.896
0.879
0.856
0.828
0.076
0.017
0.011
0.000
-0.01

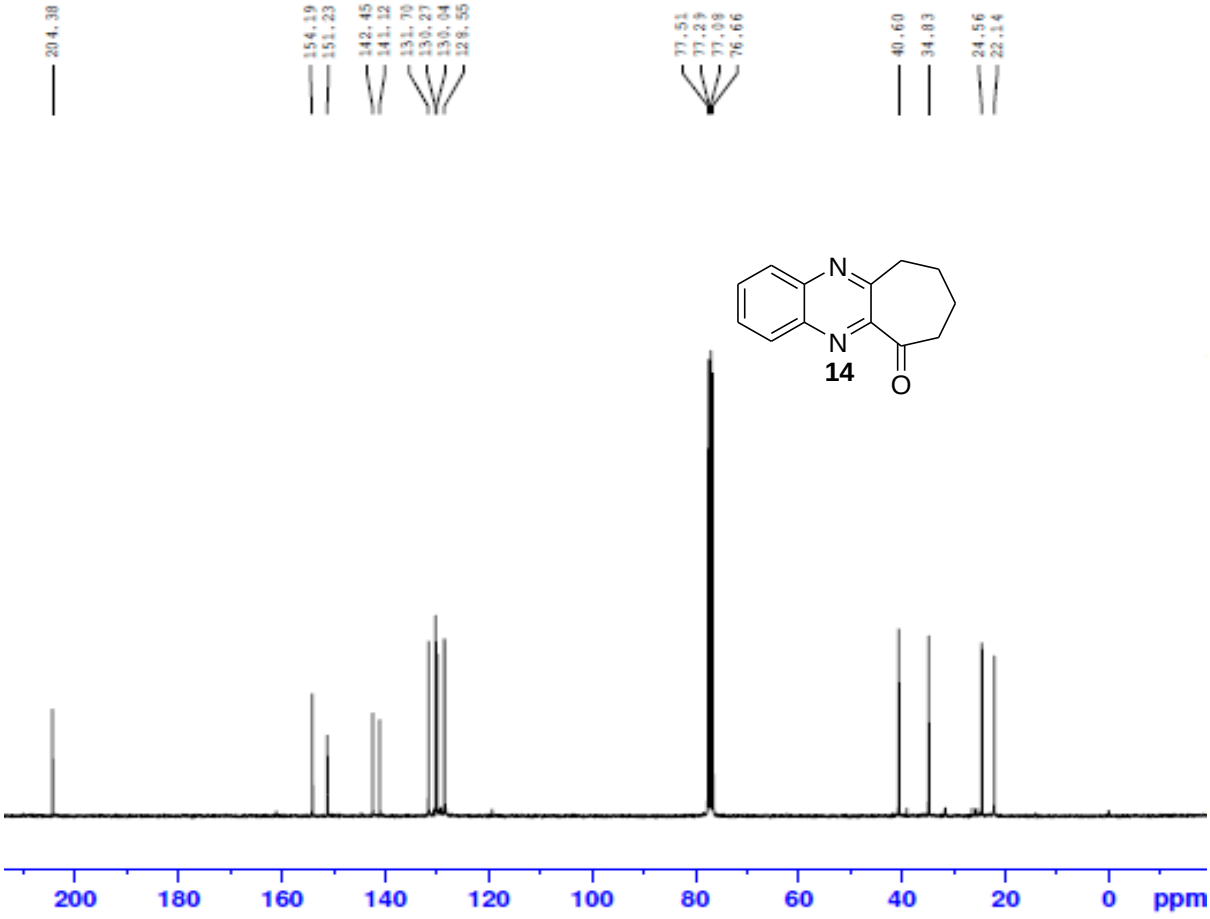

8.0
ppm
13b
2.6
2.5
ppm
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm
1.00
1.01
2.09
2.08
6.33

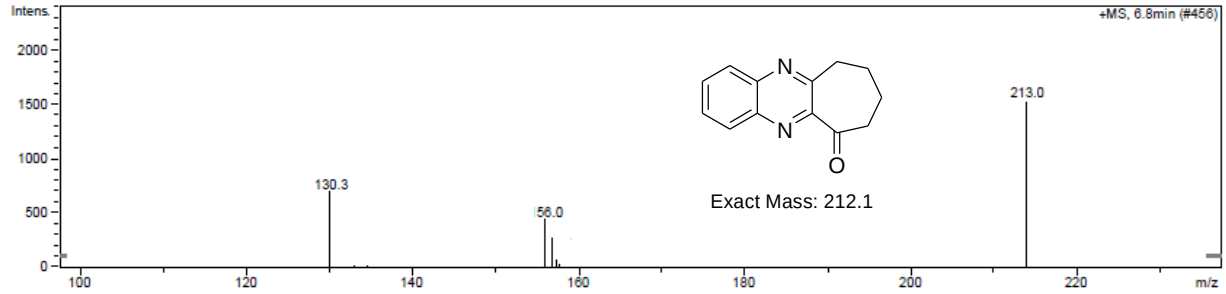

204.34
164.11
146.25
144.99
143.44
142.22
141.74
130.17
127.82
77.47
77.25
77.05
76.62
35.30
26.33
20.90
20.46
0.00
13b
200
180
160
140
120
100
80
60
40
20
0
ppm

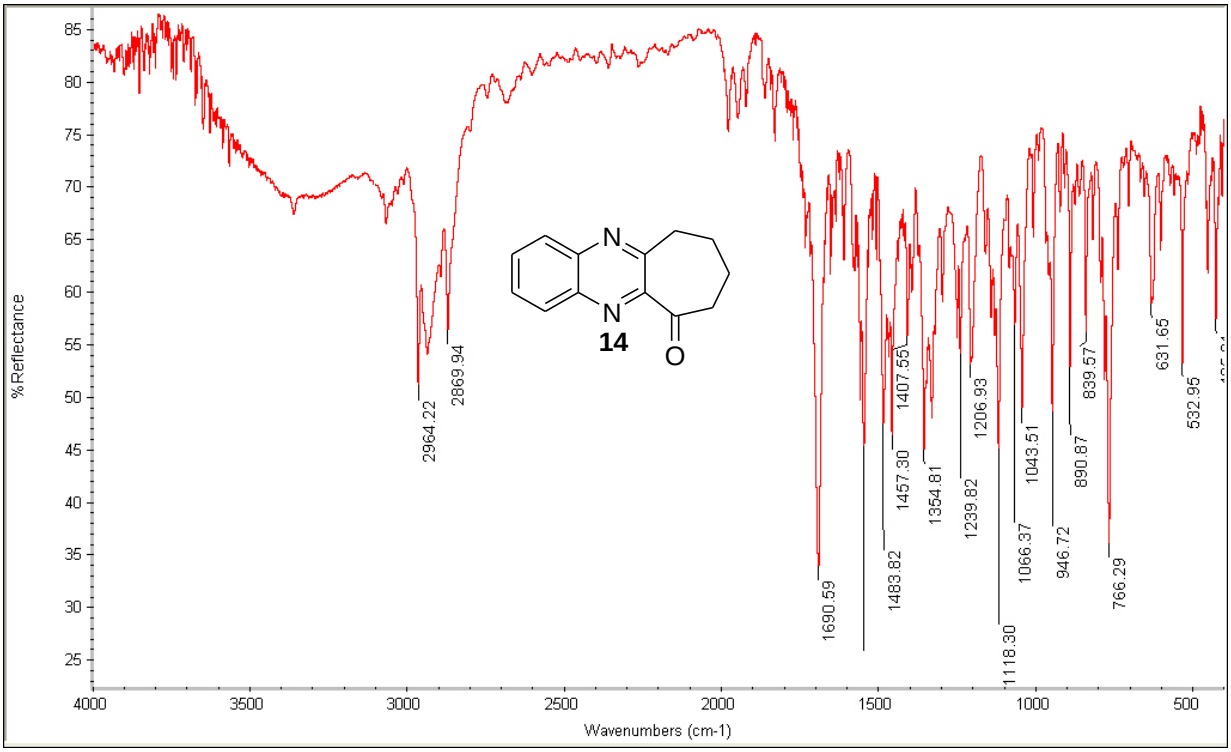

Intens.
x10^4
1.50
1.25
1.00
0.75
0.50
0.25
0.00
+MS2(212.0), 2.6min (#295)
213.0
199.8
130.3
100
150
200
250
300
350
m/z
N
N
O
Exact Mass: 212.1

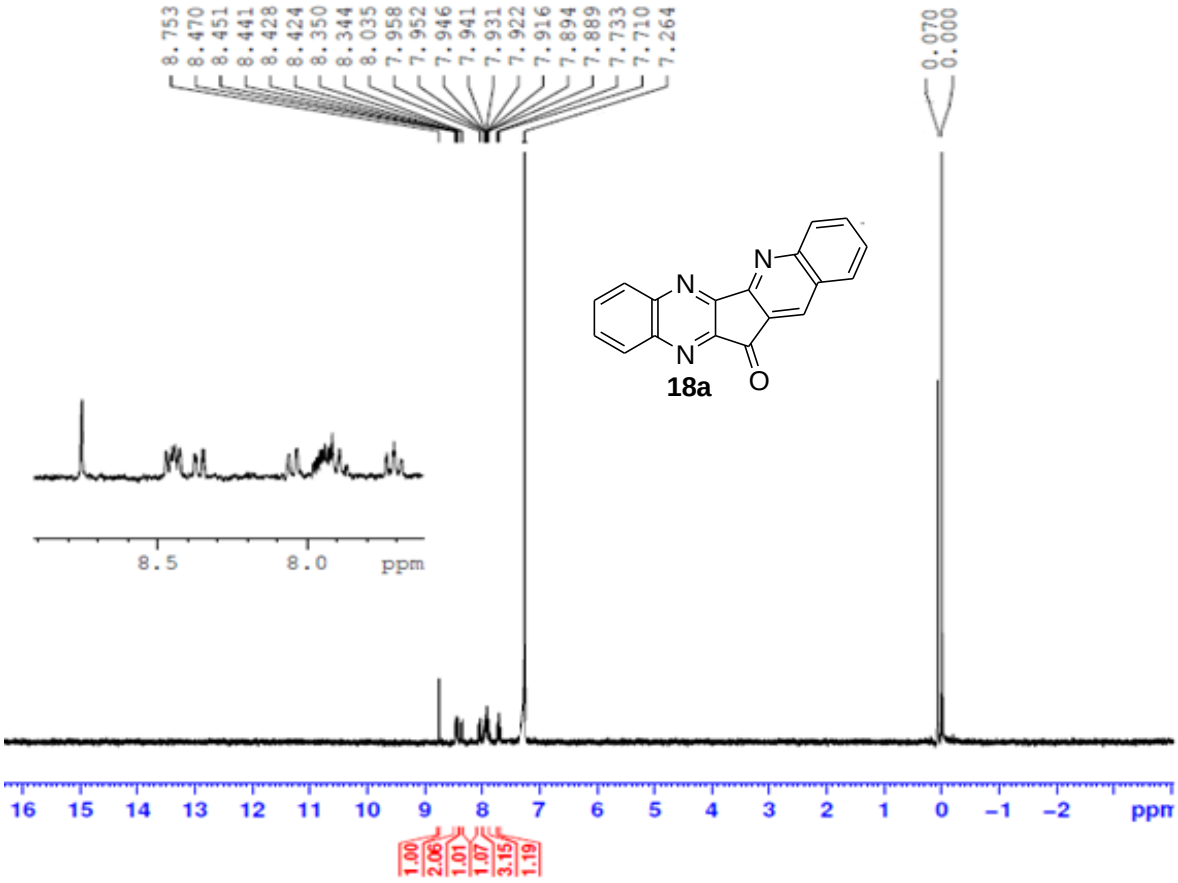

%Reflectance
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
2922.78
1733.24
1487.67
1419.26
1405.46
1363.87
1287.16
1208.83
1143.82
1044.92
1002.65
878.86
785.20
722.04
N
N
O
13b
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

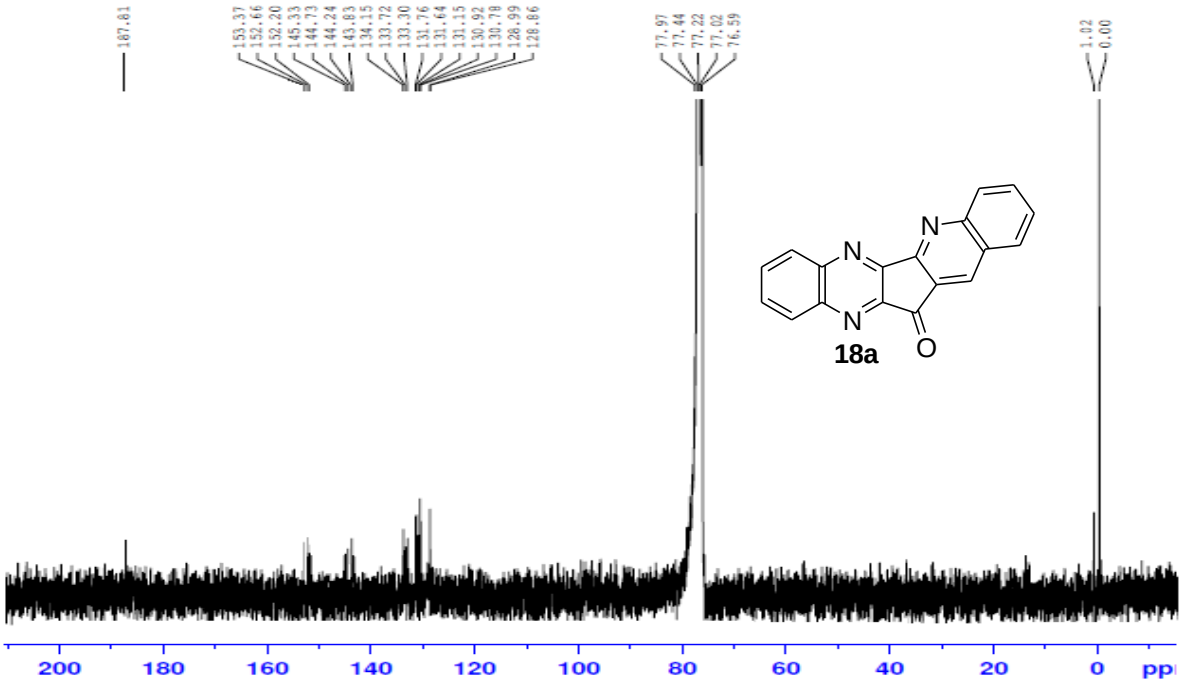

8.246
8.241
8.218
8.213
8.091
8.085
8.064
8.062
8.059
7.842
7.837
7.815
7.809
7.801
7.784
7.779
8.4
8.2
8.0
7.8
ppm
3.335
3.315
3.293
2.969
2.948
2.941
2.928
2.135
2.114
2.095
2.092
2.013
2.007
3.5
3.0
2.5
ppm
N
N
O
14
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.09
2.06
2.02
2.14
2.01

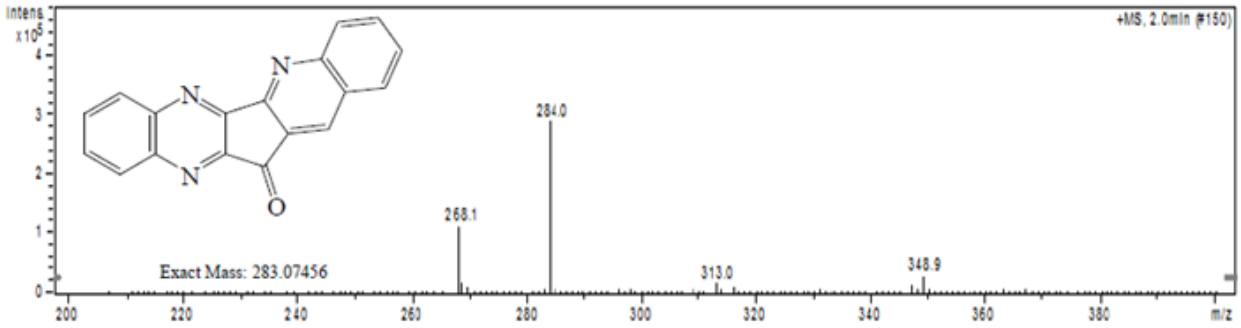

204.38
154.19
151.23
142.45
141.12
133.70
130.27
130.04
128.55
77.51
77.29
77.08
76.66
40.60
34.83
24.56
22.14
N
N
O
14
200
180
160
140
120
100
80
60
40
20
0
ppm

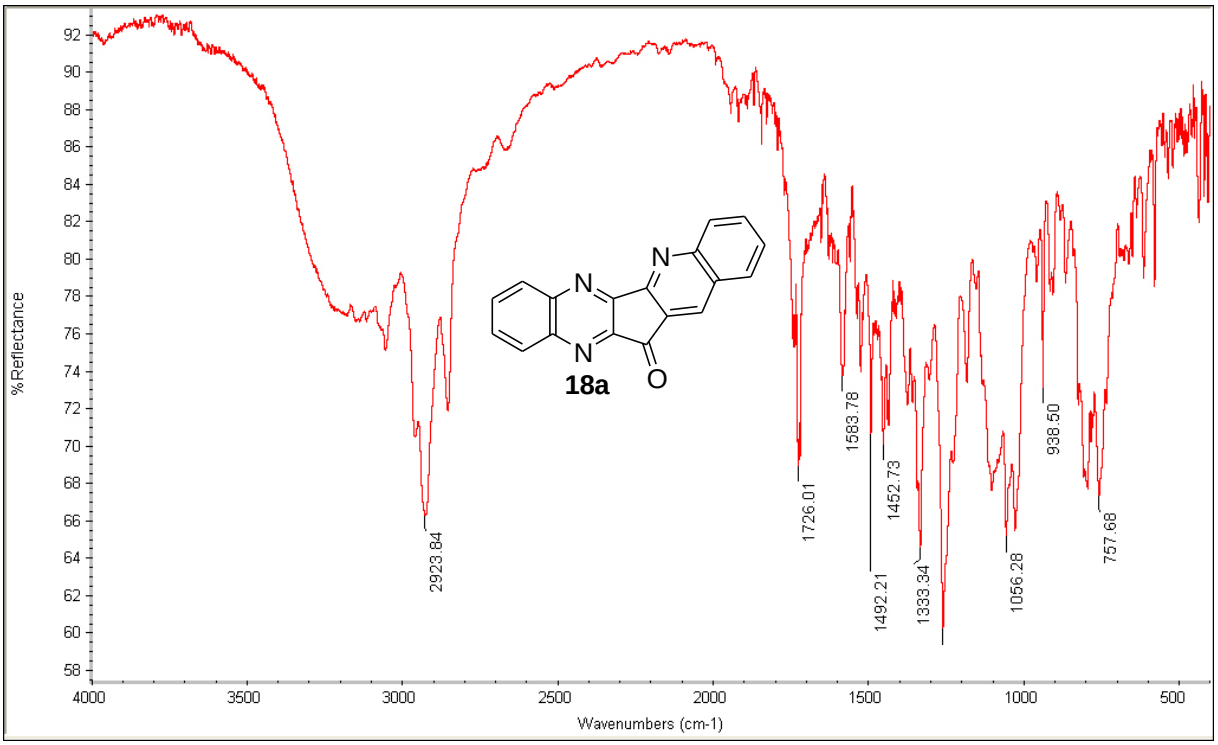

Intens.
+MS, 6.8min (#456)
2000
1500
1000
500
0
130.3
56.0
213.0
N
N
O
Exact Mass: 212.1
100
120
140
160
180
200
220
m/z

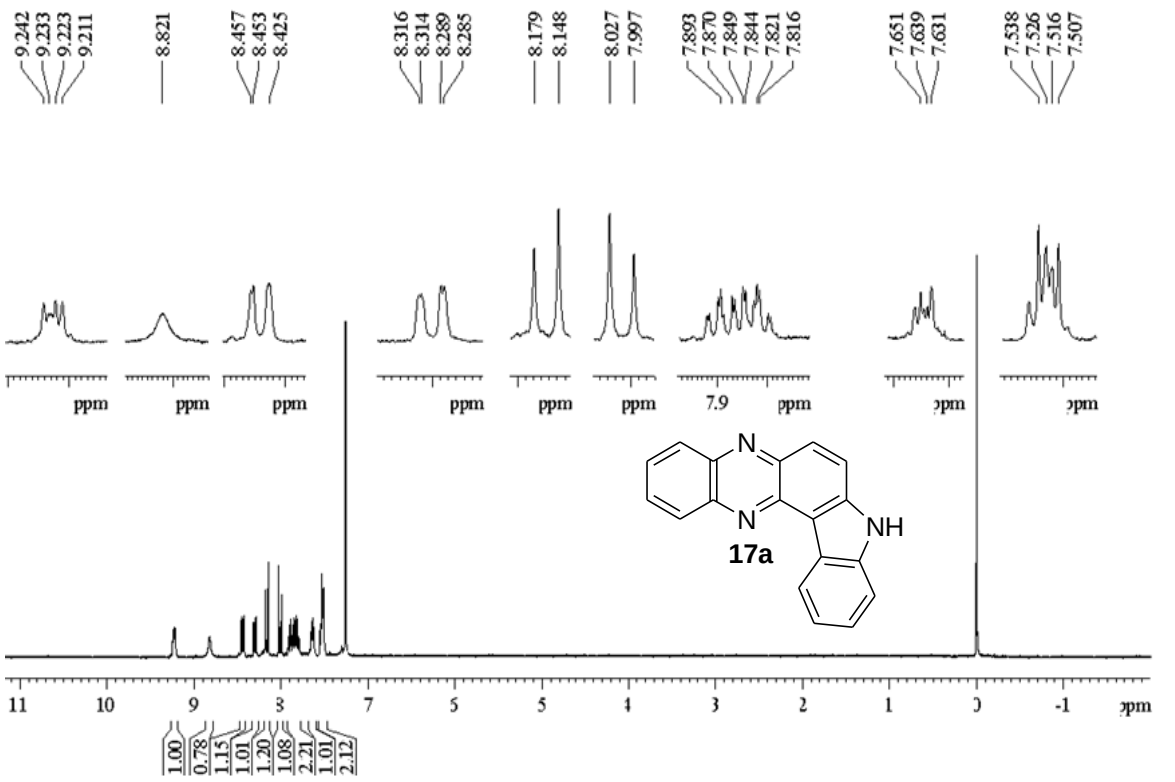

%Reflectance
85
80
75
70
65
60
55
50
45
40
35
30
25
2964.22
2869.94
1690.59
1483.82
1457.30
1407.55
1354.81
1239.82
1206.93
1118.30
1066.37
1043.51
946.72
890.87
839.57
766.29
631.65
532.95
N
N
14
O
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

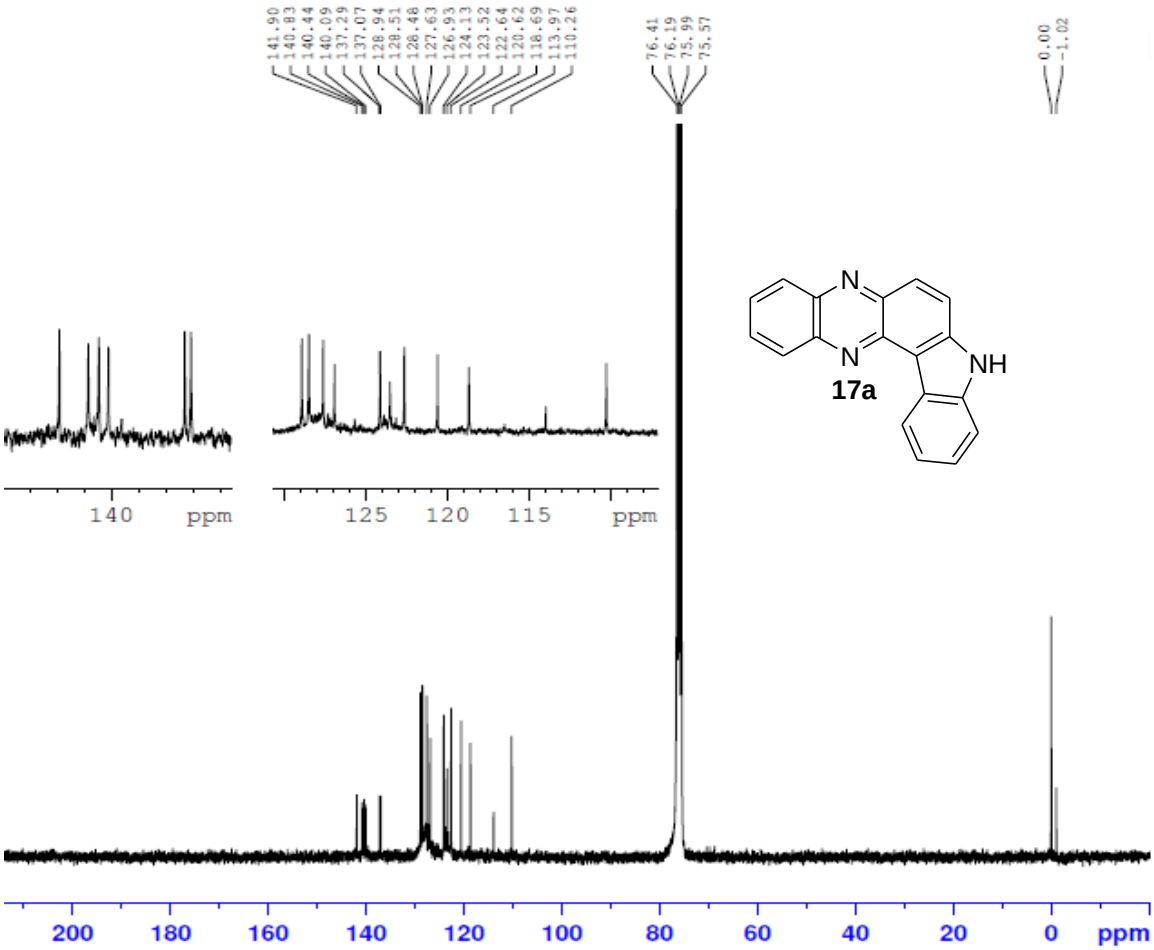

8.753
8.470
8.451
8.441
8.428
8.424
8.350
8.344
8.035
7.958
7.952
7.946
7.941
7.931
7.922
7.916
7.894
7.889
7.733
7.710
7.264
0.070
0.000
N
N
N
O
18a
8.5
8.0
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
2.06
1.01
1.07
3.15
1.19

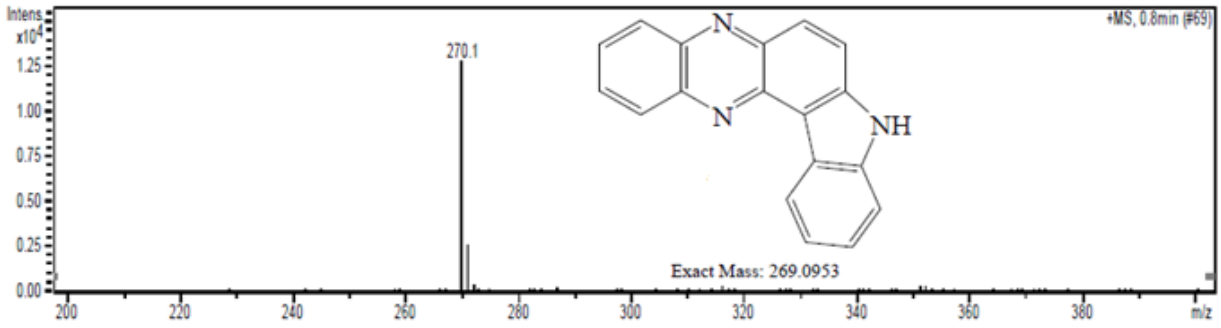

187.81
153.37
152.66
152.20
145.33
144.73
144.24
143.83
134.15
133.72
133.30
131.76
131.64
131.15
130.92
130.78
128.99
128.86
77.97
77.44
77.22
77.02
76.59
1.02
0.00
N
N
N
O
18a
200 180 160 140 120 100 80 60 40 20 0 ppm

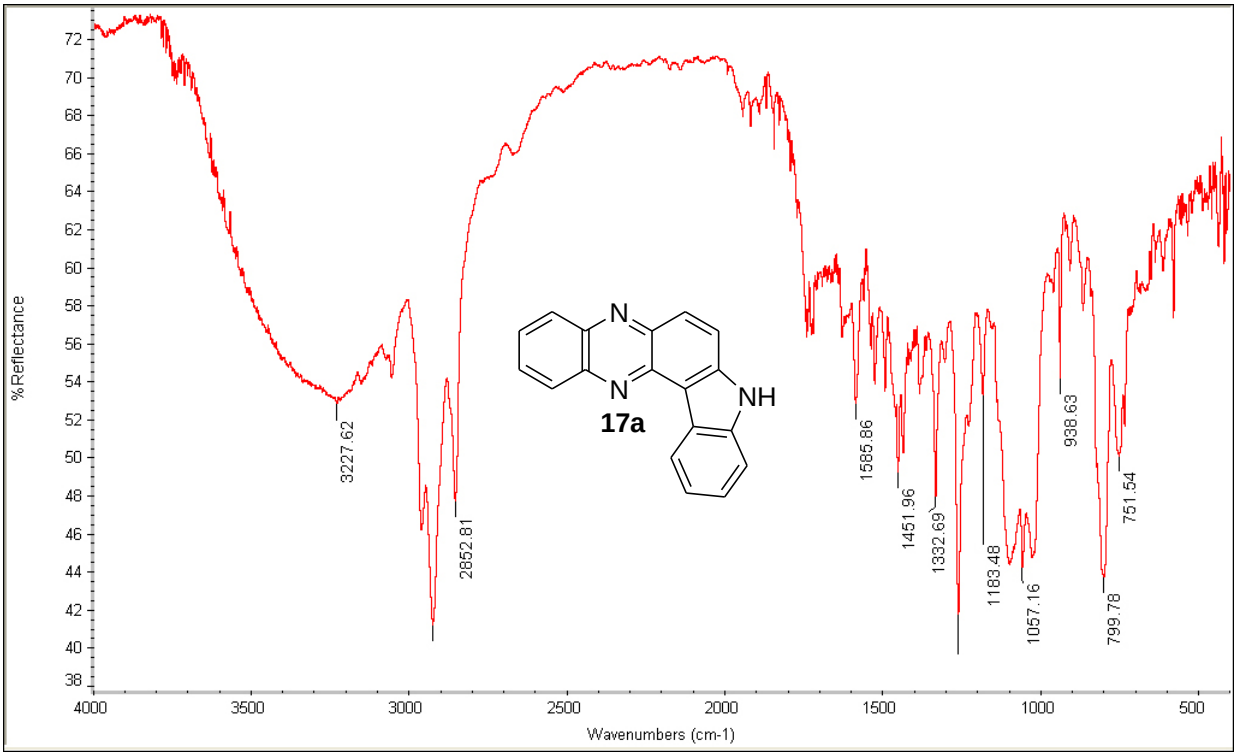

Intens.
x10^5
+MS, 2.0min (#150)
Exact Mass: 283.07456
268.1
284.0
313.0
348.9
m/z

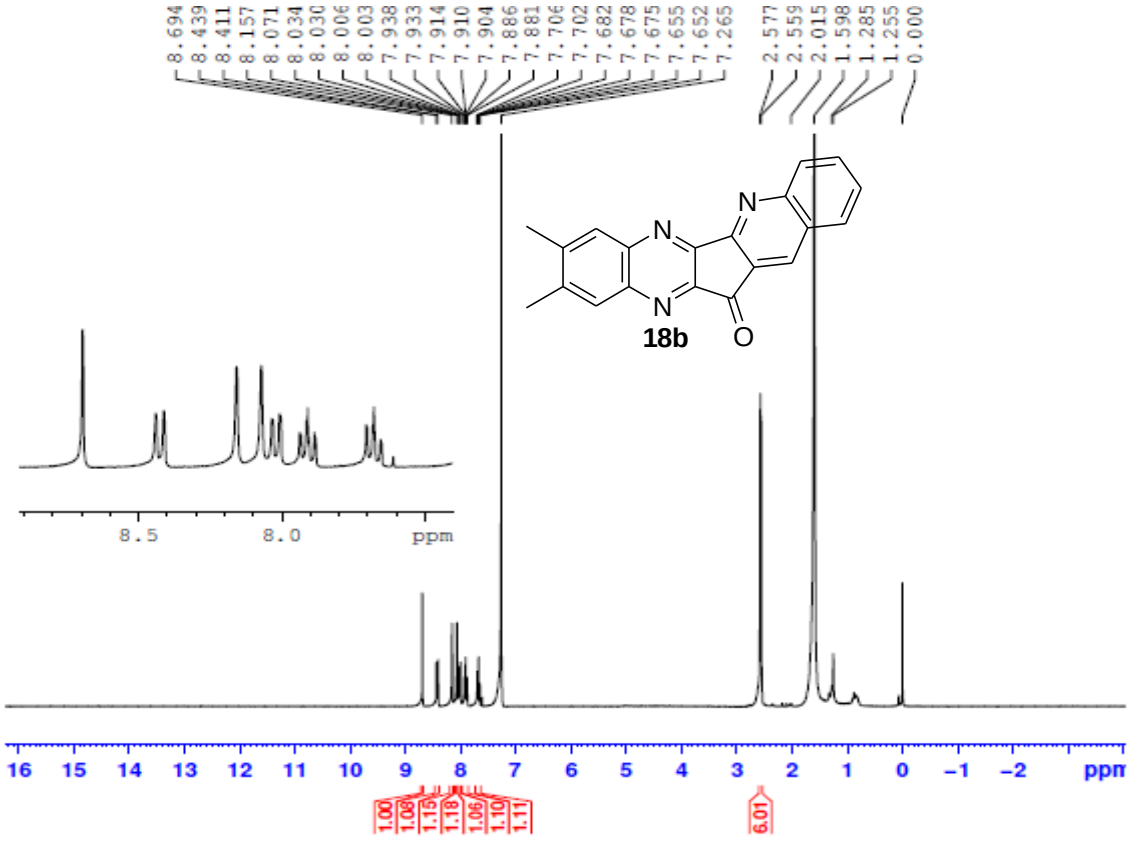

% Reflectance
Wavenumbers (cm-1)
2923.84
1726.01
1583.78
1492.21
1452.73
1333.34
1056.28
938.50
757.68
18a

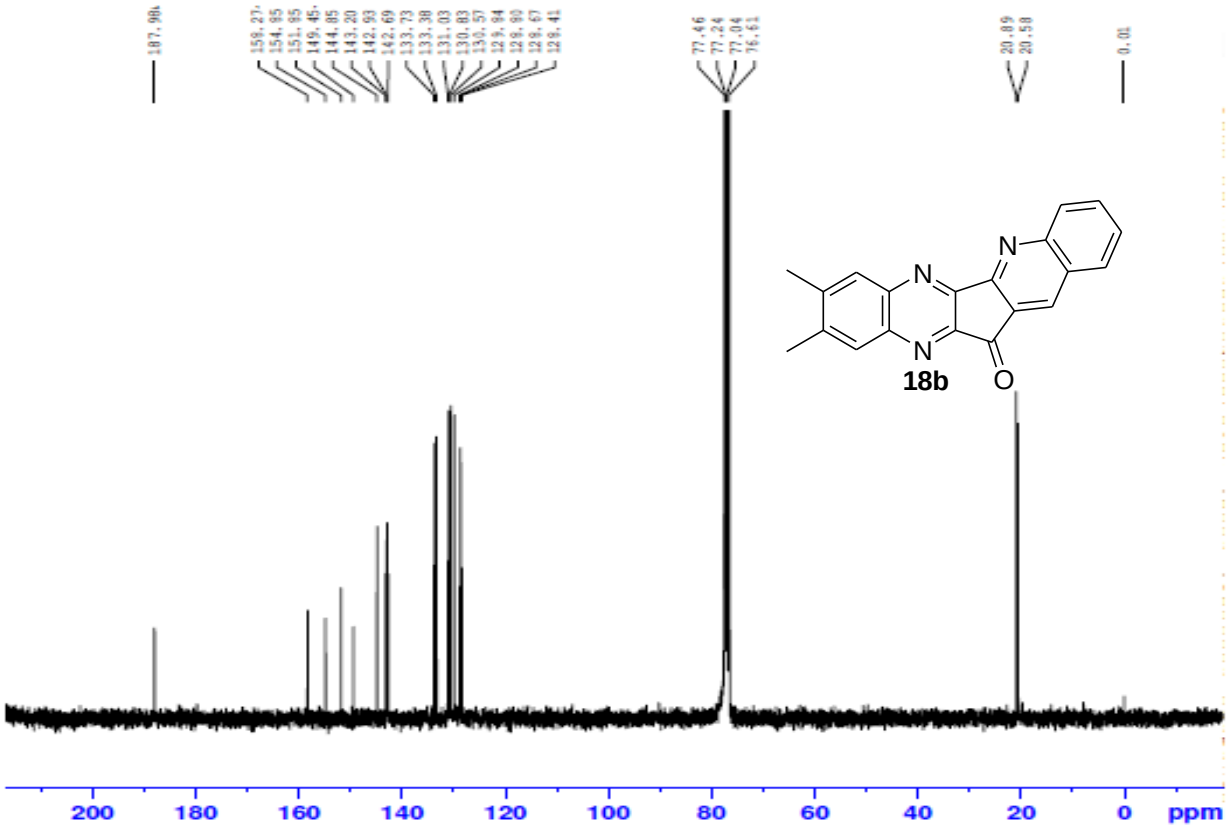

9.242
9.233
9.223
9.211
8.821
8.457
8.453
8.425
8.316
8.314
8.289
8.285
8.179
8.148
8.027
7.997
7.893
7.870
7.849
7.844
7.821
7.816
7.651
7.639
7.631
7.538
7.526
7.516
7.507
ppm
7.9
N
NH
17a
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
0.78
1.15
1.01
1.20
1.08
2.21
1.01
2.12

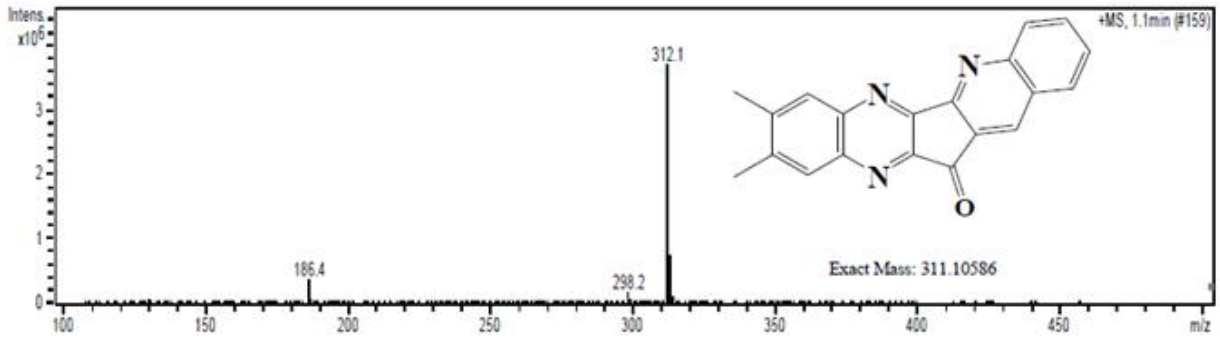

141.90
140.83
140.44
140.09
137.29
137.07
128.94
128.51
128.48
127.63
126.93
124.13
123.52
122.64
120.62
118.69
113.97
110.26
76.41
76.19
75.99
75.57
0.00
-1.02
N
NH
17a
140
ppm
125
120
115
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

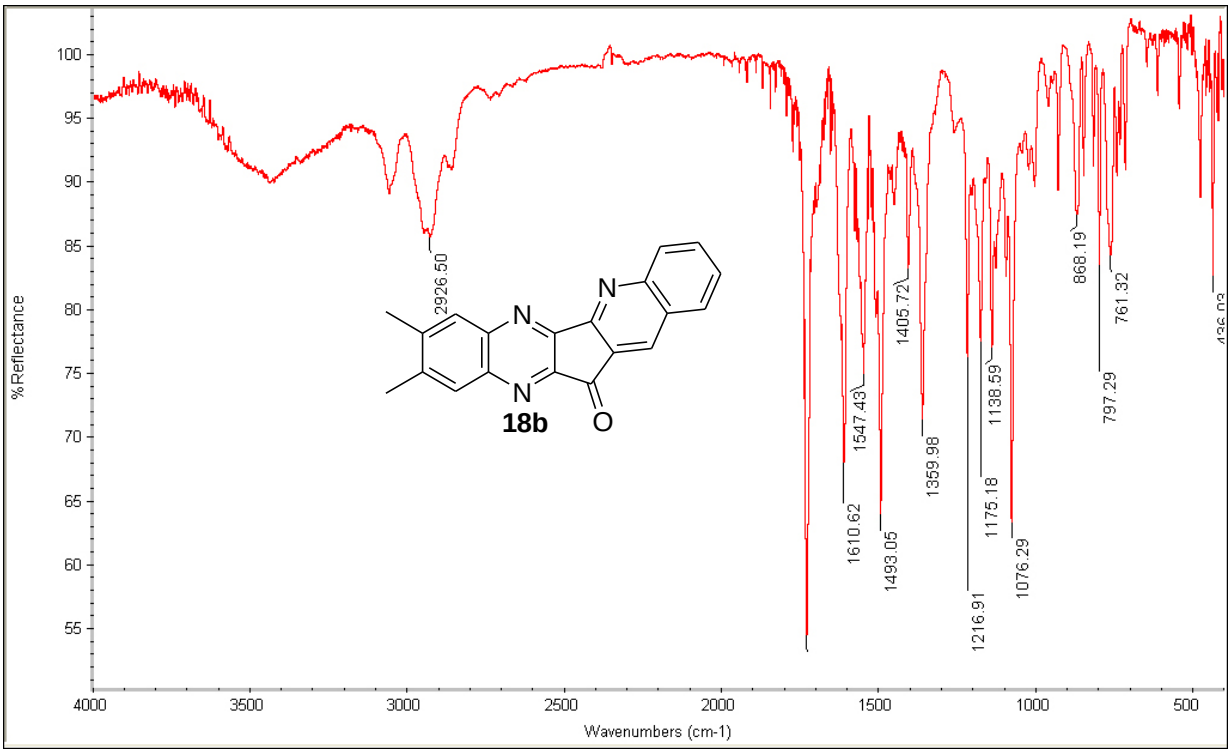

Intens.
x10^4
1.25
1.00
0.75
0.50
0.25
0.00
270.1
+MS, 0.8min (#69)
N
N
NH
Exact Mass: 269.0953
200
220
240
260
280
300
320
340
360
380
m/z

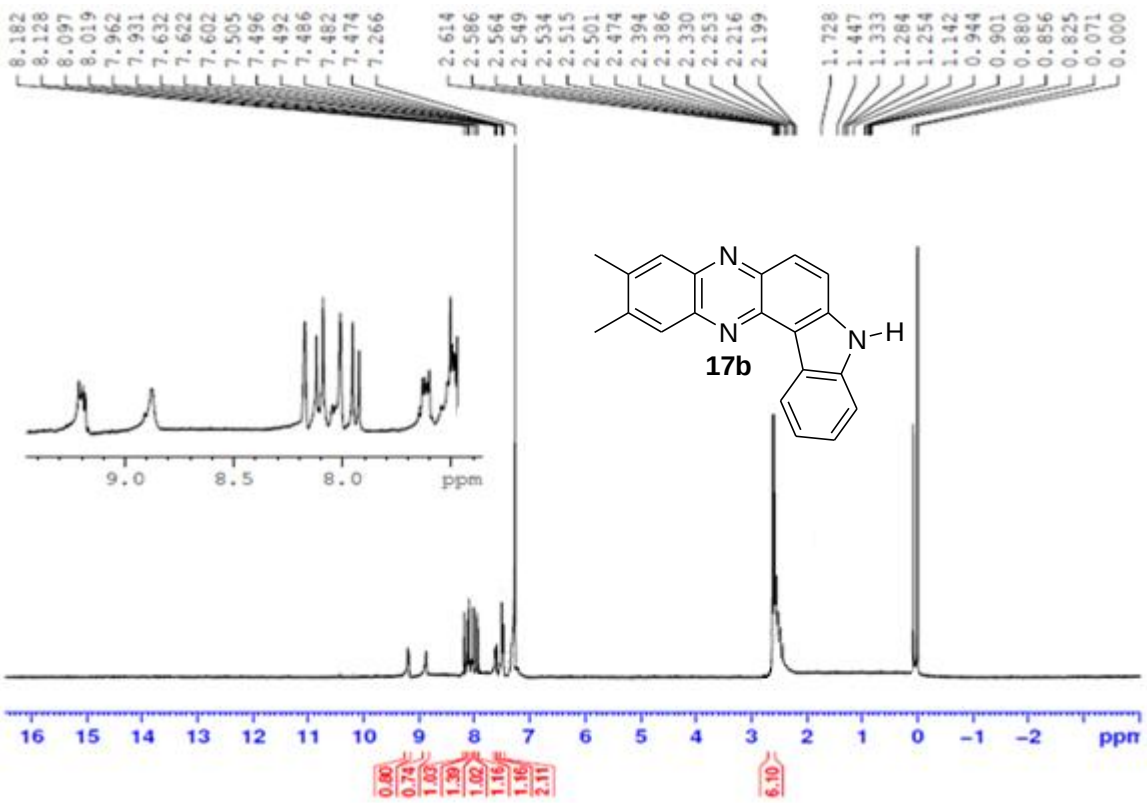

%Reflectance
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
3227.62
2852.81
1585.86
1451.96
1332.69
1183.48
1057.16
938.63
799.78
751.54
N
N
NH
17a
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

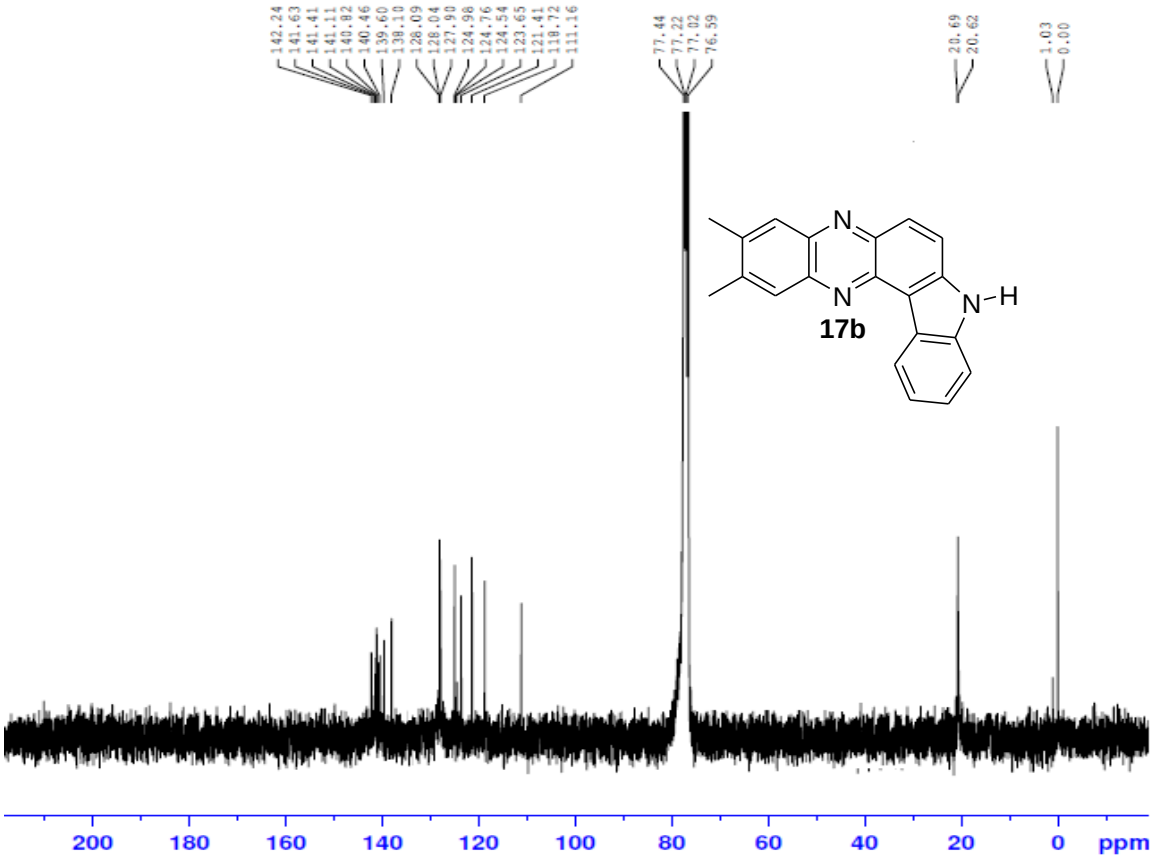

8.694
8.439
8.411
8.157
8.071
8.034
8.030
8.006
8.003
7.938
7.933
7.914
7.910
7.904
7.886
7.881
7.706
7.702
7.682
7.678
7.675
7.655
7.652
7.265
2.577
2.559
2.015
1.598
1.285
1.255
0.000
N
N
N
O
18b
8.5
8.0
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00
1.08
1.15
1.18
1.06
1.10
1.11
6.01

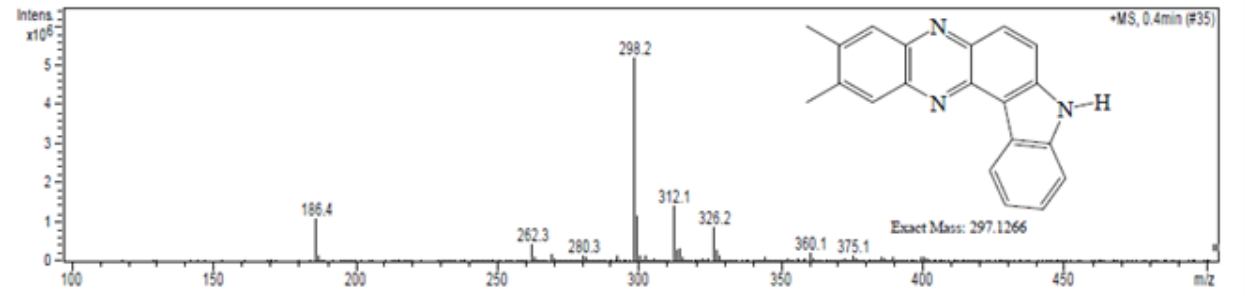

187.98
158.27
154.95
151.85
149.45
144.85
143.20
142.93
142.69
133.73
133.38
131.03
130.83
130.57
129.94
128.80
128.67
128.41
77.46
77.24
77.04
76.61
20.89
20.58
0.01
N
N
N
O
18b
200 180 160 140 120 100 80 60 40 20 0 ppm

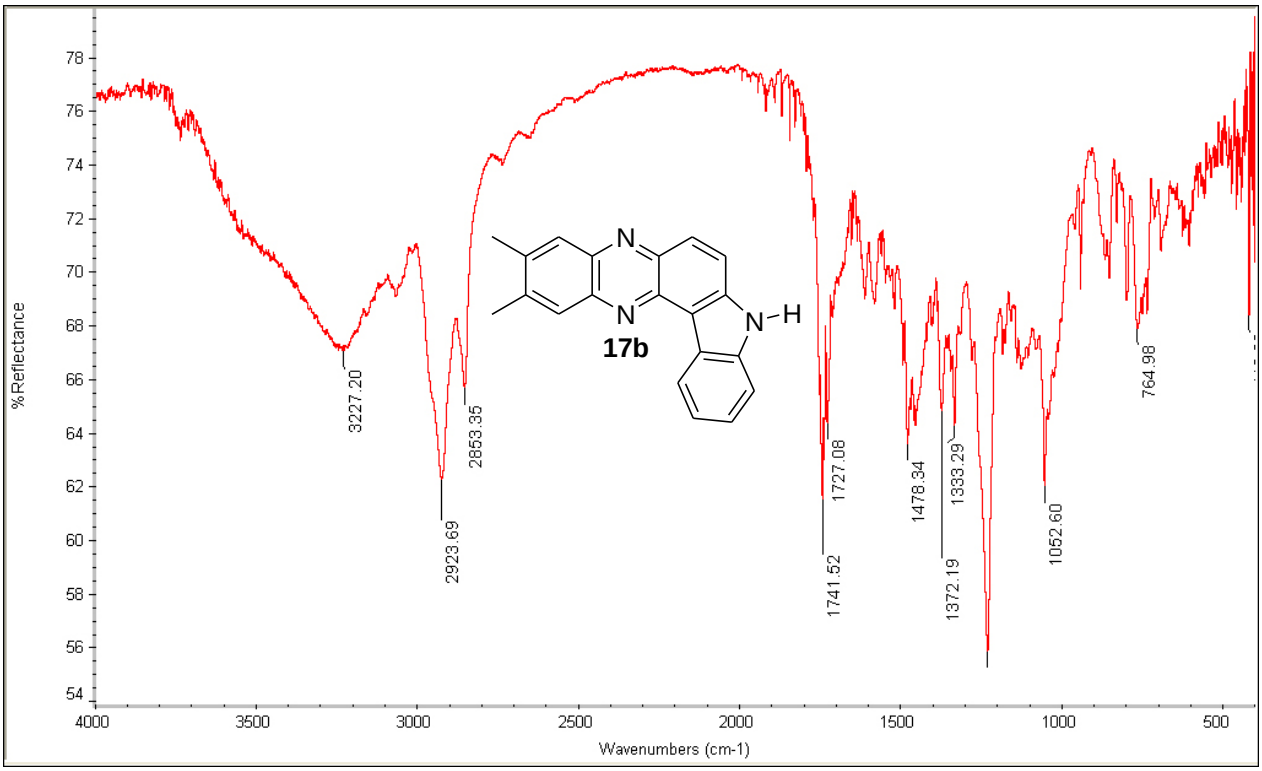

Intens.
x10^6
+MS, 1.1min (#159)
312.1
186.4
298.2
Exact Mass: 311.10586
m/z

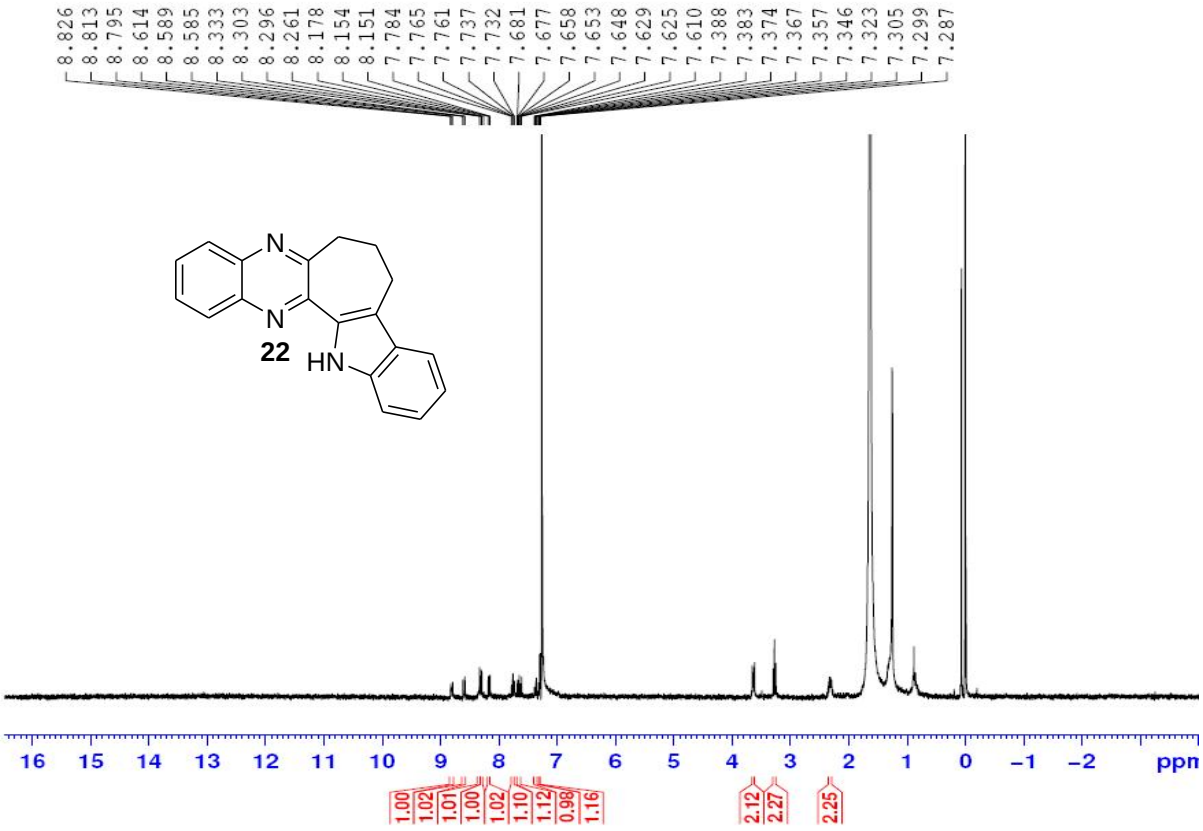

%Reflectance
2926.50
1610.62
1547.43
1493.05
1405.72
1359.98
1216.91
1175.18
1138.59
1076.29
868.19
797.29
761.32
18b
Wavenumbers (cm-1)

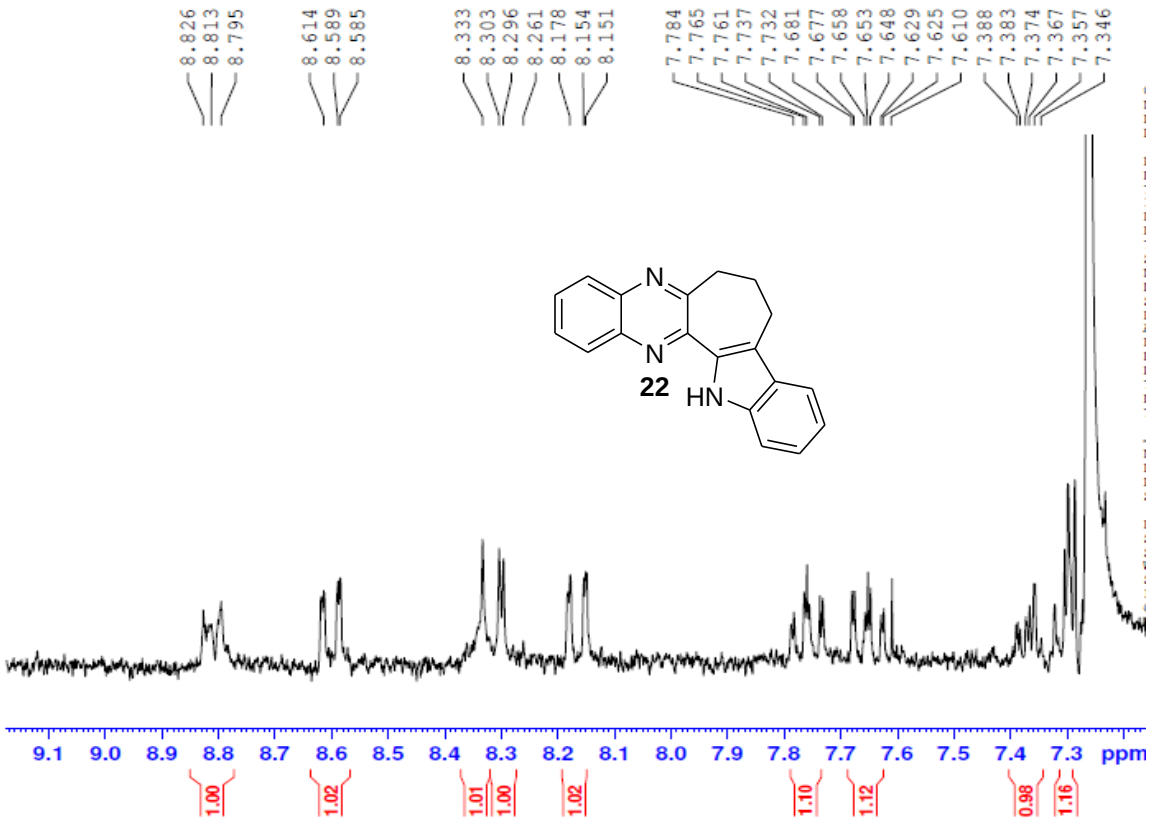

8.182
8.128
8.097
8.019
7.962
7.931
7.632
7.622
7.602
7.505
7.496
7.492
7.486
7.482
7.474
7.266
2.614
2.586
2.564
2.549
2.534
2.515
2.501
2.474
2.394
2.386
2.330
2.253
2.216
2.199
1.728
1.447
1.333
1.284
1.254
1.142
0.944
0.901
0.880
0.856
0.825
0.071
0.000
9.0
8.5
8.0
ppm
N
N
N-H
17b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
0.80
0.74
1.03
1.39
1.02
1.15
1.16
2.11
6.10

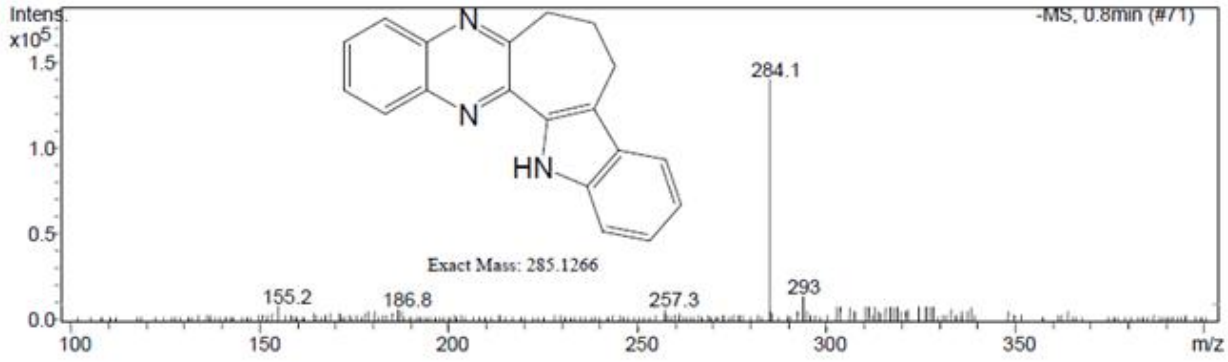

142.24
141.63
141.41
141.11
140.82
140.46
139.60
138.10
128.09
126.04
127.90
124.98
124.76
124.54
123.65
121.41
118.72
111.16
77.44
77.22
77.02
76.59
20.69
20.62
1.03
0.00
N
N
N-H
17b
200 180 160 140 120 100 80 60 40 20 0 ppm

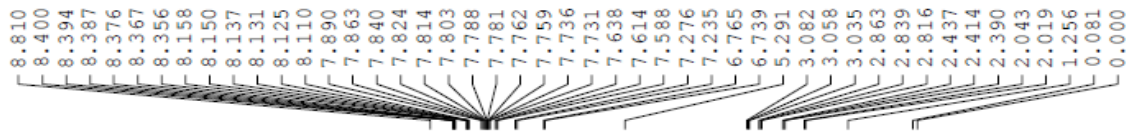

Intens.
x10^6
+MS, 0.4min (#35)
298.2
186.4
262.3
280.3
312.1
326.2
360.1
375.1
Exact Mass: 297.1266
m/z

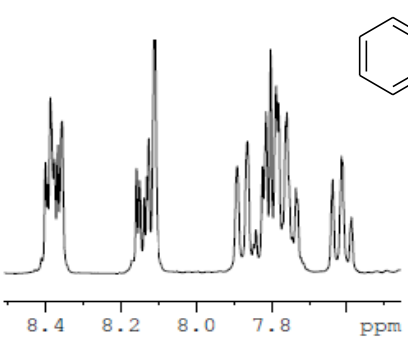

%Reflectance
3227.20
2923.69
2853.35
1741.52
1727.08
1478.34
1372.19
1333.29
1052.60
764.98
17b
Wavenumbers (cm-1)

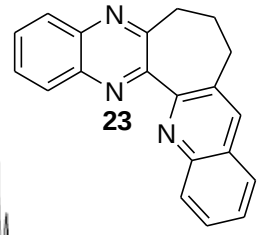

8.826
8.813
8.795
8.614
8.589
8.585
8.333
8.303
8.296
8.261
8.178
8.154
8.151
7.784
7.765
7.761
7.737
7.732
7.681
7.677
7.658
7.653
7.648
7.629
7.625
7.610
7.388
7.383
7.374
7.367
7.357
7.346
7.323
7.305
7.299
7.287
N
N
HN
22
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
1.00 1.02 1.01 1.00 1.02 1.10 1.12 0.98 1.16
2.12 2.27
2.25

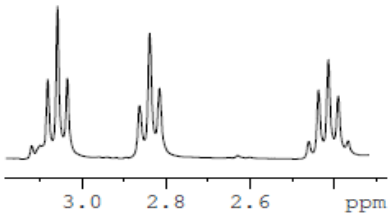

8.826
8.813
8.795
8.614
8.589
8.585
8.333
8.303
8.296
8.261
8.178
8.154
8.151
7.784
7.765
7.761
7.737
7.732
7.681
7.677
7.658
7.653
7.648
7.629
7.625
7.610
7.388
7.383
7.374
7.367
7.357
7.346
N
N
HN
22
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 ppm
1.00
1.02
1.01
1.00
1.02
1.10
1.12
0.98
1.16

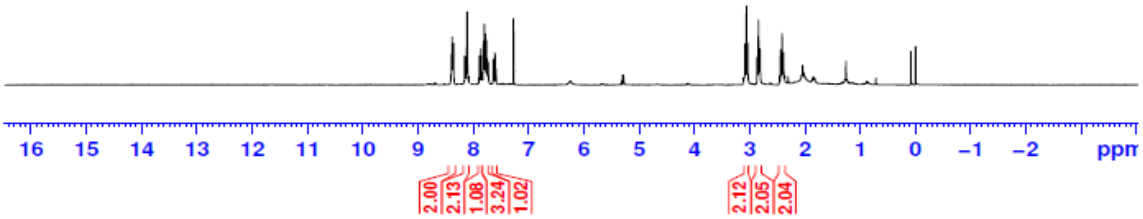

Intens.
x10^5
1.5
1.0
0.5
0.0
-MS, 0.8min (#71)
284.1
N
N
HN
Exact Mass: 285.1266
155.2
186.8
257.3
293
100
150
200
250
300
350
m/z

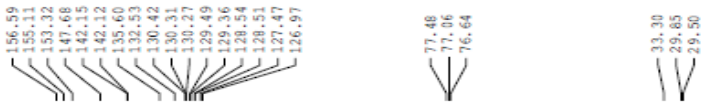

8.810
8.400
8.394
8.387
8.376
8.367
8.356
8.158
8.150
8.137
8.131
8.125
8.110
7.890
7.863
7.840
7.824
7.814
7.803
7.788
7.781
7.762
7.759
7.736
7.731
7.638
7.614
7.588
7.276
7.235
6.765
6.739
5.291
3.082
3.058
3.035
2.863
2.839
2.816
2.437
2.414
2.390
2.043
2.019
1.256
0.081
0.000

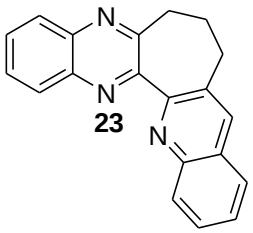

8.4
8.2
8.0
7.8
ppm


N
N
N
23

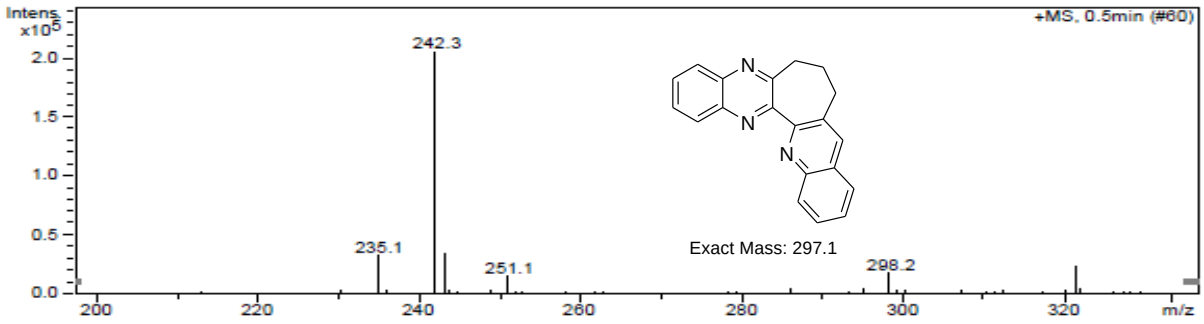

3.0
2.8
2.6
ppm

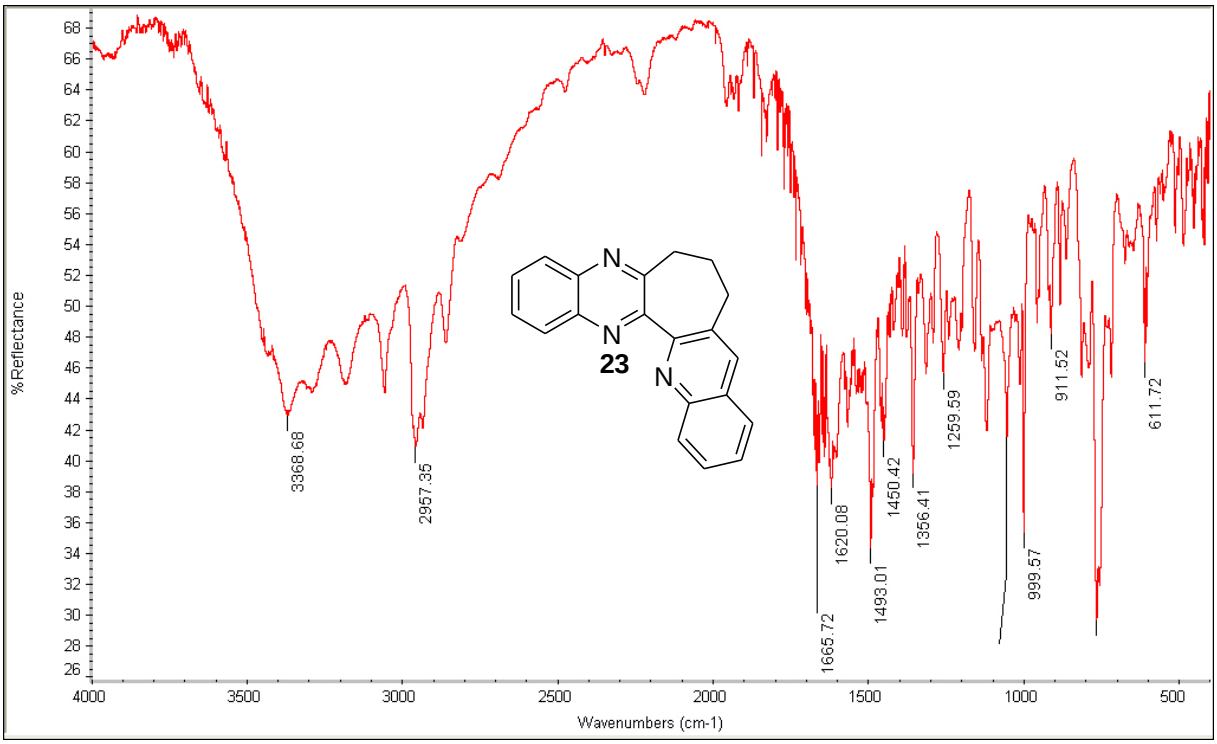

16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm
2.00
2.13
1.08
3.24
1.02
2.12
2.05
2.04

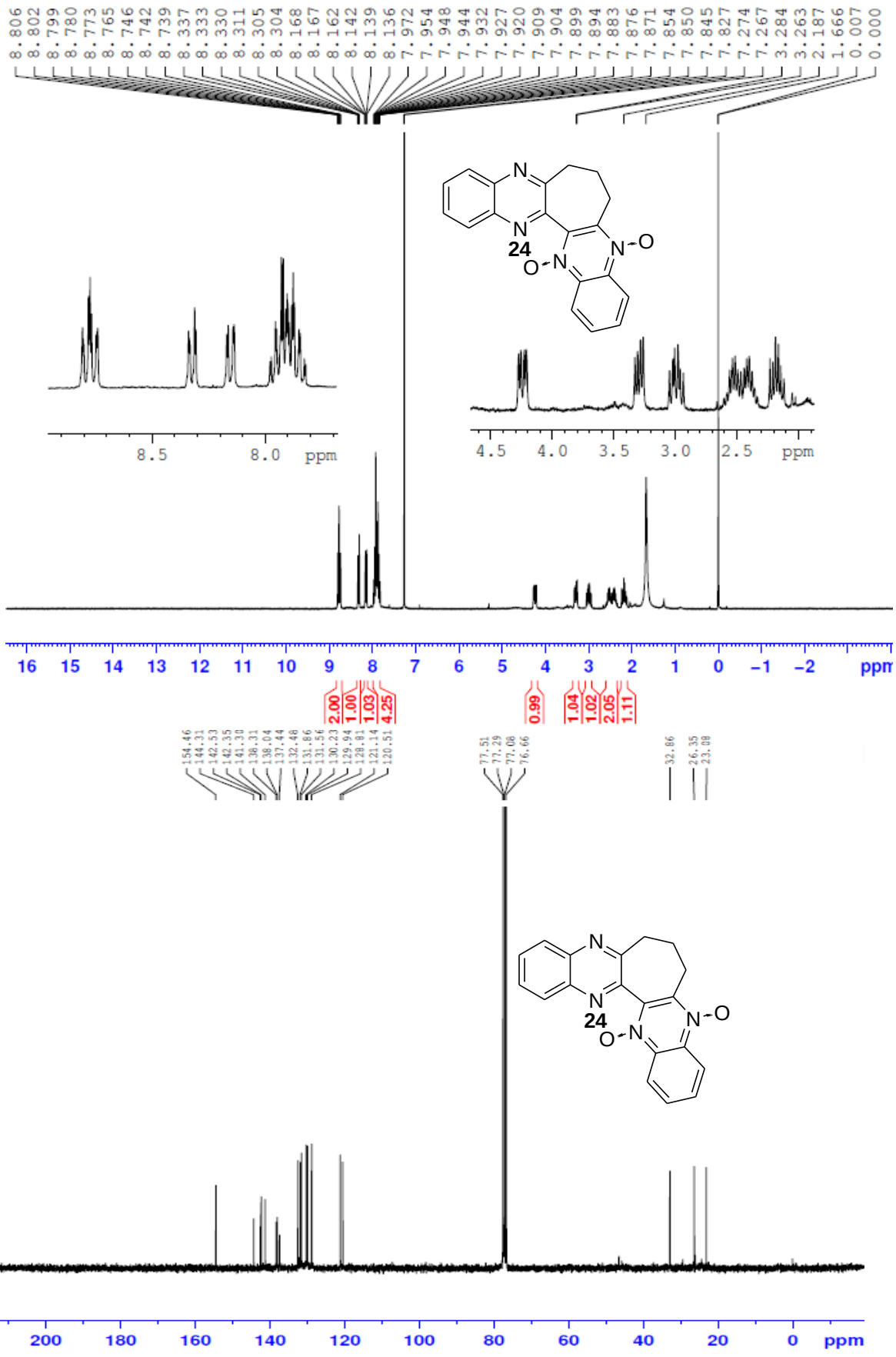

156.59
155.11
153.32
147.68
142.15
142.12
135.60
132.53
130.42
130.31
130.27
129.49
129.36
128.54
128.51
127.47
126.97
77.48
77.06
76.64
33.30
29.65
29.50

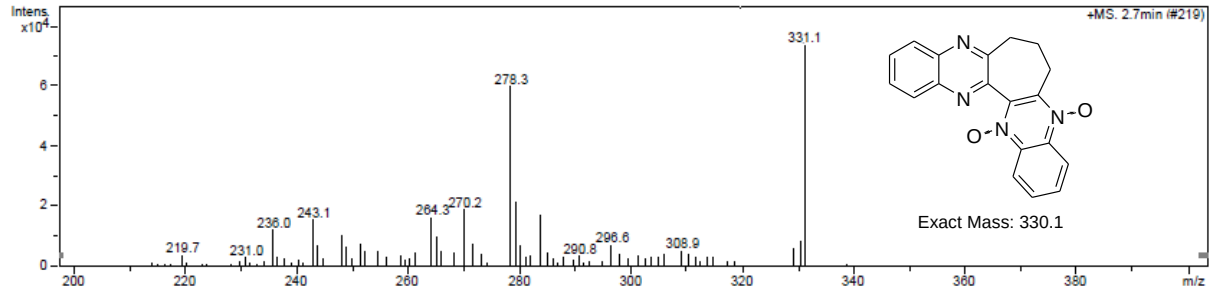

N
N
N
23

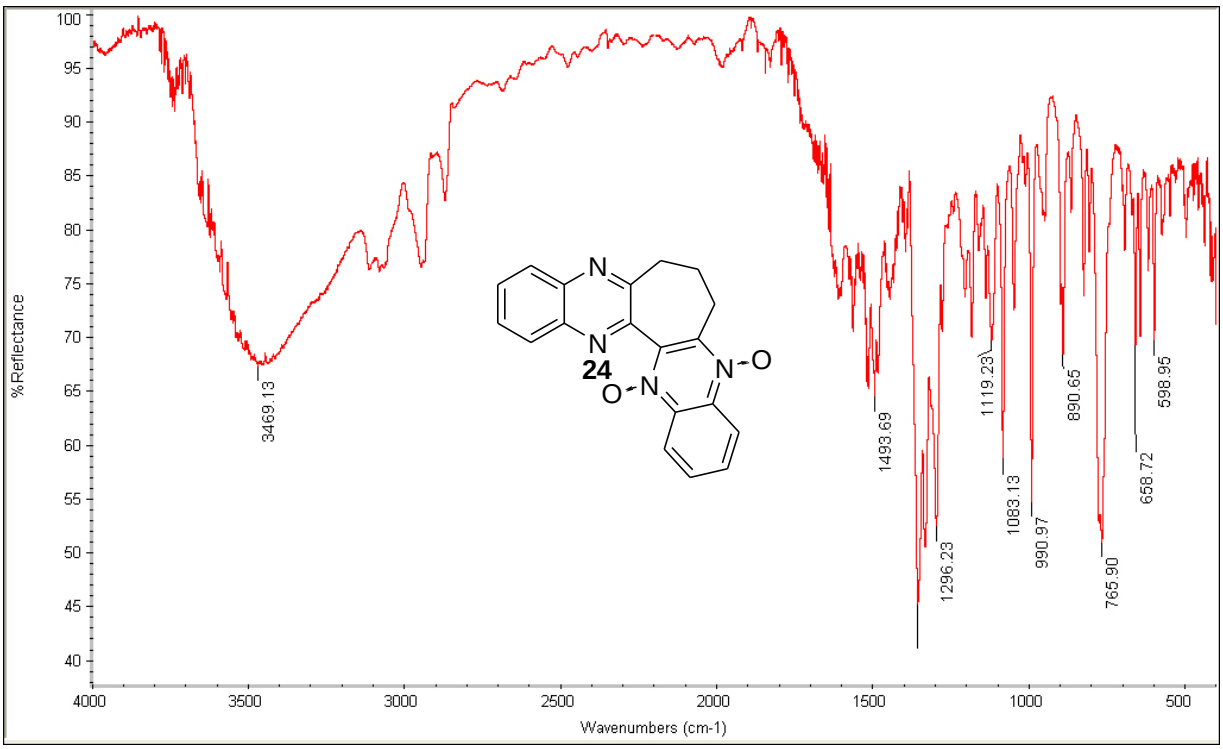
200
180
160
140
120
100
80
60
40
20
0
ppm


+MS, 0.5min (#60)
Intens
x10^5
2.0
1.5
1.0
0.5
0.0
242.3
235.1
251.1
298.2
200
220
240
260
280
300
320
m/z
N
N
N
Exact Mass: 297.1


%Reflectance
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
3368.68
2957.35
1665.72
1620.08
1493.01
1450.42
1356.41
1259.59
999.57
911.52
611.72
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
N
N
N
23


8.806
8.802
8.799
8.780
8.773
8.765
8.746
8.742
8.739
8.337
8.333
8.330
8.311
8.305
8.304
8.168
8.167
8.162
8.142
8.139
8.136
7.972
7.954
7.948
7.944
7.932
7.927
7.920
7.909
7.904
7.899
7.894
7.883
7.876
7.871
7.854
7.850
7.845
7.827
7.274
7.267
3.284
3.263
2.187
1.666
0.007
0.000
24
8.5
8.0
ppm
4.5
4.0
3.5
3.0
2.5
ppm
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
2.00
2.00
1.00
1.03
4.25
0.99
1.04
1.02
2.05
1.11
154.46
144.31
142.53
142.35
141.30
136.31
138.04
137.44
132.48
131.86
131.56
130.23
129.94
128.81
121.14
120.51
77.51
77.29
77.08
76.66
32.86
26.35
23.08
24
200 180 160 140 120 100 80 60 40 20 0 ppm


Intens.
x10^4
+MS, 2.7min (#219)
331.1
278.3
270.2
264.3
243.1
236.0
231.0
219.7
290.8
296.6
308.9
m/z
Exact Mass: 330.1


%Reflectance
3469.13
1493.69
1296.23
1119.23
1083.13
990.97
890.65
765.90
658.72
598.95
24
Wavenumbers (cm-1)

References:

1. Mallory, F. *Org. Synth. Coll.* **1963**, *IV*, 74.

2. Haddadin, M. J. and Issidorides, C. H. T*etrahedron Lett.*, **1965**,*36*, 3255-3256.

3. Issidorides, C.H.; Atfah, M, A,; Sabounji, J.J.; Sidani, A.R.; Haddadin, M.J. *Tetrahedron*, **1978**, *34*, 217

4. Talaz, O.; Saracoglu, N.; *Tetrahedron* **2010**, *66*, 1902–1910.