

Support Information – New. J. Chem.

One-pot Mannich/aza-Wittig/deaminative aromatization reactions for the synthesis of 1,2,3,4-tetrahydronacridines and cyclohepta[*b*]quinolines

Wensheng Zhang,^a Wei Zheng,^a Guoqiang Zuo,^a Xiaole Li,^a Xiaofeng Zhang,^{b,c*} Wei Zhang^{b*}

^a *Jiyuan Vocational and Technical College, 88 Jiyuan Avenue, Jiyuan 459000, China.*

^b *Department of Chemistry and Centre for Green Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, USA.*

E-mail: xfxiaofengzhang@gmail.com ; wei2.zhang@umb.edu

^c *Department of Cancer Biology Dana-Farber Cancer Institute, Department of Medicine, Harvard Medical School, Boston, MA 02215, USA*

Content

1. General information.....	S2
2. General procedures	S2
3. Characterization data of products	S2
4. NMR spectra of products	S6

1. General information

Chemicals and solvents were purchased from commercial suppliers and used without further purification. Flash chromatography separations were performed on CHEETAH II medium pressure purification preparative chromatography system with Agela silica gel columns (230-400 μm mesh). Analytical thin-layer chromatography (TLC) was carried out on silica gel 60 F254 plates, which were visualized by exposure to ultraviolet light. Melting points were measured using WRS-2 digital melting point meter (uncorrected). ^1H NMR spectra were recorded on Bruker AV-400 NMR spectrometers with TMS as internal standard (Bruker, Switzerland). HRESIMS data were collected on a Thermo LTQ Orbitrap XL hybrid FTMS or an Agilent 6210 ESI-TOF mass spectrometer.

2. General Procedures for products 4

To a stirred solution of *o*-azidebenzaldehydes **1** (0.5 mmol) and 4-chloroaniline **2e** (0.525 mmol/1.05 eq, 67 mg) in MeCN (5 mL) was added cycloketones **3** (0.75 mmol/1.5 equiv.) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.075 mmol/0.15eq, 24 mg). After the reaction mixture was stirred at room temperature for 12 h, PPh_3 (0.6 mmol, 158 mg) was added and the mixture was stirred at room temperature for another 6 h. Upon completion of the reaction as monitored by TLC, the reaction mixture was filtered. The solution was then concentrated and the residue was purified by column chromatography to afford products **4**.

3. Characterization of products 4

1,2,3,4-Tetrahydroacridine **4a**. White solid. mp. 51.9-52.5 $^\circ\text{C}$ (lit. 52-53 $^\circ\text{C}$). Yield: 87%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.87-1.92 (2H, m), 1.96-2.00 (2H, m), 2.97 (2H, t, $J = 6.4$ Hz), 3.13 (2H, t, $J = 6.4$ Hz), 7.43 (1H, t, $J = 7.4$ Hz), 7.60 (1H, t, $J = 7.4$ Hz), 7.69 (1H, d, $J = 8.4$ Hz), 7.79 (1H, s), 7.98 (1H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 22.91, 23.23, 29.26, 33.55, 125.56, 126.89, 127.22, 128.24, 128.52, 130.98, 135.03, 146.56, 159.31. HRMS (ESI) m/z Calculated for $[\text{C}_{13}\text{H}_{13}\text{N}+\text{H}]^+$: 184.1121. Found: 184.1122.

2-Methyl-1,2,3,4-tetrahydroacridine **4b**. White solid. mp. 85.3-86.3 $^\circ\text{C}$. Yield: 84%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.10-1.12 (3H, m), 1.54-1.64 (1H, m), 1.92-2.09 (2H, m), 2.53-2.60 (1H, m), 2.97-3.26 (3H, m), 7.41 (1H, t, $J = 7.6$ Hz), 7.57-7.66 (2H, m), 7.75 (1H, s), 7.97 (1H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 21.59, 29.01, 31.33, 33.01, 37.72, 125.44, 126.81, 127.08, 128.18, 128.42, 130.50, 134.88, 146.57, 158.92. HRMS (ESI) m/z Calculated for $[\text{C}_{14}\text{H}_{15}\text{N}+\text{H}]^+$: 198.1277. Found: 198.1276.

2,2-Dimethyl-1,2,3,4-tetrahydroacridine **4c**. White solid. mp. 73.2-74.2 $^\circ\text{C}$. Yield: 85%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.04 (6H, s), 1.78 (1H, t, $J = 7.0$ Hz), 2.73 (1H, s), 3.16 (1H, d, $J = 7.0$ Hz), 7.40-7.44 (1H, m), 7.58-7.70 (2H, m), 7.78 (1H, s), 7.99 (1H, d, $J = 8.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 27.96 (2C), 29.64, 30.37, 35.97, 43.39, 125.52, 126.86, 127.21, 128.26, 128.53, 130.22, 135.55, 146.72, 158.51. HRMS (ESI) m/z Calculated for $[\text{C}_{15}\text{H}_{17}\text{N}+\text{H}]^+$: 212.1434. Found: 212.1435.

7-Chloro-1,2,3,4-tetrahydroacridine **4d**. White solid. mp. 91.2-91.8 $^\circ\text{C}$. Yield: 91%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.85-1.91 (2H, m), 1.95-2.01 (2H, m), 2.95 (2H, t, $J = 6.4$ Hz), 3.10 (2H, t, $J = 6.4$ Hz), 7.52 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.63 (1H, d, $J = 2.0$ Hz), 7.67 (1H, s), 7.89 (1H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 22.75, 23.08, 29.24, 33.49, 125.48, 127.75, 129.34, 129.91, 131.07, 132.03, 133.97, 144.91, 159.73. HRMS (ESI) m/z Calculated for $[\text{C}_{13}\text{H}_{12}\text{ClN}+\text{H}]^+$: 218.0731. Found: 218.0728.

7-Chloro-2-methyl-1,2,3,4-tetrahydroacridine **4e**. White solid. mp. 131.0-131.3 $^\circ\text{C}$. Yield: 84%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.11-1.13 (3H, m), 1.54-1.64 (1H, m), 1.94-2.09 (2H, m), 2.54-2.61 (1H, m), 2.97-3.23 (3H, m), 7.41 (1H, dd, $J_1 = 9.0$ Hz, $J_2 = 2.2$ Hz), 7.64-7.66 (2H, m), 7.89 (1H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 21.57, 28.94, 31.22, 32.97, 37.71, 125.45, 127.65, 129.34, 129.85, 131.04,

131.63, 133.92, 144.90, 159.40. HRMS (ESI) m/z Calculated for $[C_{14}H_{14}ClN+H]^+$: 232.0888. Found: 232.0886.

7-Chloro-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4f**. White solid. mp. 125.3-127.1 °C. Yield: 86%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.05 (6H, s), 1.79 (1H, t, $J = 6.8$ Hz), 2.73 (1H, s), 3.14 (1H, t, $J = 6.8$ Hz), 7.53 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz), 7.66 (1H, d, $J = 2.4$ Hz), 7.68 (1H, s), 7.91 (1H, d, $J = 9.2$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 27.93 (2C), 29.61, 30.29, 35.82, 43.33, 125.48, 127.76, 129.43, 129.87, 131.10, 131.33, 134.61, 145.00, 158.96. HRMS (ESI) m/z Calculated for $[C_{15}H_{16}ClN+H]^+$: 246.1044. Found: 246.1040.

7-Bromo-1,2,3,4-tetrahydroacridine **4g**. White solid. mp. 90.4-91.5 °C. Yield: 80%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.87-1.91 (2H, m), 1.95-2.00 (2H, m), 2.95 (2H, t, $J = 6.4$ Hz), 3.09 (2H, t, $J = 6.4$ Hz), 7.63-7.66 (2H, m), 7.81 (1H, d, $J = 2.0$ Hz), 7.83 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 22.75, 23.07, 29.25, 33.53, 119.19, 128.31, 128.86, 130.06, 131.87, 132.03, 133.87, 145.11, 159.90. HRMS (ESI) m/z Calculated for $[C_{13}H_{12}BrN+H]^+$: 262.0226. Found: 262.0225.

7-Bromo-2-methyl-1,2,3,4-tetrahydroacridine **4h**. White solid. mp. 132.5-133.0 °C. Yield: 82%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.11-1.13 (3H, m), 1.54-1.65 (1H, m), 1.93-2.09 (2H, m), 2.54-2.61 (1H, m), 2.98-3.23 (3H, m), 7.64-7.84 (4H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 21.57, 28.94, 31.20, 33.01, 37.71, 119.16, 128.22, 128.83, 129.99, 131.63, 131.86, 133.82, 145.10, 159.57. HRMS (ESI) m/z Calculated for $[C_{14}H_{14}BrN+H]^+$: 276.0382. Found: 276.0382.

7-Bromo-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4i**. White solid. mp. 120.9-121.9 °C. Yield: 78%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.05 (6H, s), 1.78 (1H, t, $J = 6.8$ Hz), 2.73 (1H, s), 3.12 (1H, d, $J = 8.8$ Hz), 7.66 (2H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.83-7.85 (2H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 27.93 (2C), 29.61, 30.34, 35.81, 43.34, 119.20, 128.31, 128.85, 130.03, 131.32, 131.94, 134.48, 145.20, 159.13. HRMS (ESI) m/z Calculated for $[C_{15}H_{16}BrN+H]^+$: 290.0539. Found: 290.0537.

6-Chloro-1,2,3,4-tetrahydroacridine **4j**. White solid. mp. 87.7-89.4 °C. Yield: 84%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.86-1.99 (4H, m), 2.92-3.11 (4H, m), 7.35 (1H, dd, $J_1 = 8.6$ Hz, $J_2 = 1.8$ Hz), 7.58 (1H, d, $J = 8.8$ Hz), 7.73 (1H, s), 7.96 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 22.77, 23.08, 29.20, 33.52, 125.51, 126.53, 127.27, 128.11, 131.30, 134.09, 134.77, 146.81, 160.51. HRMS (ESI) m/z Calculated for $[C_{13}H_{12}ClN+H]^+$: 218.0731. Found: 218.0727.

6-Chloro-2-methyl-1,2,3,4-tetrahydroacridine **4k**. White solid. mp. 137-137.8 °C. Yield: 85%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.07-1.10 (3H, m), 1.50-1.60 (1H, m), 1.89-2.06 (2H, m), 2.46-2.53 (1H, m), 2.90-3.19 (3H, m), 7.31 (1H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz), 7.53 (1H, d, $J = 8.4$ Hz), 7.64 (1H, s), 7.93 (1H, d, $J = 1.6$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 21.61, 28.96, 31.23, 37.66, 125.39, 126.42, 127.26, 128.08, 130.86, 134.02, 134.61, 146.85, 160.15. HRMS (ESI) m/z Calculated for $[C_{14}H_{14}ClN+H]^+$: 232.0888. Found: 232.0886.

6-Chloro-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4l**. White solid. mp. 107.3-108.2 °C. Yield: 79%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.05 (6H, s), 1.78 (1H, t, $J = 7.0$ Hz), 2.72 (1H, s), 3.13 (1H, t, $J = 7.0$ Hz), 7.37 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.61 (1H, d, $J = 8.4$ Hz), 7.74 (1H, s), 7.97 (1H, d, $J = 1.6$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 27.93 (2C), 29.61, 30.35, 35.81, 43.30, 125.52, 126.55, 127.29, 128.09, 130.58, 134.17, 135.37, 146.96, 159.76. HRMS (ESI) m/z Calculated for $[C_{15}H_{16}ClN+H]^+$: 246.1044. Found: 246.1043.

6,7,8,9-Tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4m**. White solid. mp. 163.7-165.1 °C. Yield: 87%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.83-1.93 (4H, m), 2.85-2.89 (2H, m), 3.01-3.05 (2H, m), 6.02 (2H, d, $J = 11.2$ Hz), 6.89 (2H, d, $J = 11.2$ Hz), 7.26 (2H, d, $J = 11.2$ Hz), 7.57 (2H, d, $J = 11.6$ Hz). ^{13}C NMR ($CDCl_3$, 100

MHz) δ (ppm) 23.00, 23.30, 28.94, 33.07, 101.37, 101.96, 104.82, 123.87, 128.97, 134.36, 144.54, 147.09, 150.00, 156.53. HRMS (ESI) m/z Calculated for $[C_{14}H_{13}NO_2+H]^+$: 228.1019. Found: 228.1016.

8-Methyl-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4n**. White solid. mp. 183.8-185.2 °C. Yield: 86%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.09-1.11 (3H, m), 1.50-1.60 (1H, m), 1.93-2.04 (2H, m), 2.47-2.54 (1H, m), 2.89-3.15 (3H, m), 6.03 (2H, s), 6.91 (1H, s), 7.27 (1H, s), 7.56 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 21.62, 29.09, 31.47, 32.58, 37.49, 101.36, 101.94, 104.79, 123.81, 128.58, 134.30, 144.56, 147.08, 149.98, 155.22. HRMS (ESI) m/z Calculated for $[C_{15}H_{15}NO_2+H]^+$: 242.1176. Found: 252.1175.

8,8-Dimethyl-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4o**. White solid. mp. 165.9-167.6 °C. Yield: 83%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.03 (6H, s), 1.74 (2H, t, $J = 6.2$ Hz), 2.65 (2H, s), 3.07 (2H, t, $J = 6.2$ Hz), 6.04 (2H, s), 6.92 (1H, s), 7.28 (1H, s), 7.57 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 27.92 (2C), 29.57, 29.93, 36.01, 43.08, 101.37, 101.92, 104.83, 123.88, 128.21, 134.85, 144.67, 147.06, 149.98, 155.69. HRMS (ESI) m/z Calculated for $[C_{16}H_{17}NO_2+H]^+$: 256.1332. Found: 256.1329.

7-Chloro-2,2-difluoro-1,2,3,4-tetrahydroacridine **4p**. White solid. mp. 117.0-117.6 °C. Yield: 63%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 2.39-2.49 (2H, m), 3.33-3.50 (2H, m), 7.59 (1H, dd, $J_1 = 9.2$ Hz, $J_2 = 2.4$ Hz), 7.70 (1H, d, $J = 2.4$ Hz), 7.78 (1H, s), 7.93 (1H, d, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 30.43, 30.49, 30.54, 30.86, 31.10, 31.35, 37.46, 37.74, 38.01, 119.75, 122.14, 124.53, 125.63, 126.24, 126.30, 126.36, 127.41, 130.13, 130.44, 131.97, 135.11, 145.37, 156.15. ^{19}F NMR ($CDCl_3$, 300 MHz) δ -94.50 (s). HRMS (ESI) m/z Calculated for $[C_{13}H_{10}ClF_2N+H]^+$: 254.0543. Found: 254.0540.

7-Bromo-2,2-difluoro-1,2,3,4-tetrahydroacridine **4q**. White solid. mp. 122.7-123.5 °C. Yield: 56%. 1H NMR ($DMSO-d_6$, 400 MHz) δ (ppm) 2.42-2.54 (2H, m), 3.23 (2H, t, $J = 7.0$ Hz), 3.58 (2H, t, $J = 8.8$ Hz), 7.79-7.88 (2H, m), 8.11 (1H, s), 8.17 (1H, d, $J = 2.0$ Hz). ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ (ppm) 29.79, 29.87, 29.92, 29.98, 30.03, 30.27, 36.42, 36.69, 36.97, 118.78, 120.76, 123.14, 125.53, 126.55, 126.61, 126.68, 127.61, 129.03, 130.14, 132.17, 134.82, 144.81, 156.36. ^{19}F NMR ($DMSO-d_6$, 300 MHz) δ -94.47 (s). HRMS (ESI) m/z Calculated for $[C_{13}H_{10}BrF_2N+H]^+$: 298.0037. Found: 298.0037.

6-Chloro-2,2-difluoro-1,2,3,4-tetrahydroacridine **4r**. White solid. mp. 151.6-152.3 °C. Yield: 60%. 1H NMR ($DMSO-d_6$, 400 MHz) δ (ppm) 2.42-2.49 (2H, m), 3.24 (2H, t, $J = 7.0$ Hz), 3.57 (2H, t, $J = 15.0$ Hz), 7.57 (1H, dd, $J_1 = 8.6$ Hz, $J_2 = 2.2$ Hz), 7.93-7.97 (2H, m), 8.18 (1H, s). ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ (ppm) 29.78, 29.88, 29.94, 30.02, 30.26, 36.39, 36.66, 36.93, 120.78, 123.16, 124.92, 125.54, 126.03, 126.09, 126.15, 126.57, 126.60, 129.15, 133.61, 135.74, 146.52, 157.04. ^{19}F NMR ($DMSO-d_6$, 300 MHz) δ -94.54 (s). HRMS (ESI) m/z Calculated for $[C_{13}H_{10}ClF_2N+H]^+$: 254.0543. Found: 254.0540.

8,8-Difluoro-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4s**. White solid. mp. 158.0-160.0 °C. Yield: 53%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 2.35-2.45 (2H, m), 3.27-3.43 (4H, m), 6.09 (2H, s), 6.96 (1H, s), 7.29 (1H, s), 7.67 (1H, s). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 30.05, 30.11, 30.1, 30.94, 31.18, 31.43, 37.20, 37.47, 37.75, 101.69, 101.95, 104.85, 120.04, 122.43, 123.22, 123.28, 123.34, 123.86, 124.82, 135.12, 145.22, 147.74, 150.83, 152.97. ^{19}F NMR ($CDCl_3$, 400 MHz) δ -96.33 (s). HRMS (ESI) m/z Calculated for $[C_{14}H_{11}F_2NO_2+H]^+$: 264.0831. Found: 264.0832.

7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline **4t**. White solid. mp. 89.8-91.7 °C (lit. 91-92.5 °C). Yield: 51%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.72-1.82 (4H, m), 1.86-1.92 (2H, m), 2.92 (2H, d, $J = 5.6$ Hz), 3.21 (2H, d, $J = 5.6$ Hz), 7.42-7.46 (1H, m), 7.56-7.63 (2H, m), 7.76 (1H, s), 8.00 (1H, d, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 28.97, 28.82, 32.17, 35.40, 39.99, 125.68, 126.74, 127.32, 128.37, 134.51, 136.44, 146.21, 164.60. HRMS (ESI) m/z Calculated for $[C_{14}H_{15}N+H]^+$: 198.1277. Found: 198.1275.

2-Chloro-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline **4u**. White solid. mp. 108.4-109.9 °C. Yield: 57%. 1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.73-1.81 (4H, m), 1.87-1.93 (2H, m), 2.92 (2H, dd, $J_1 = 6.6$ Hz, $J_2 =$

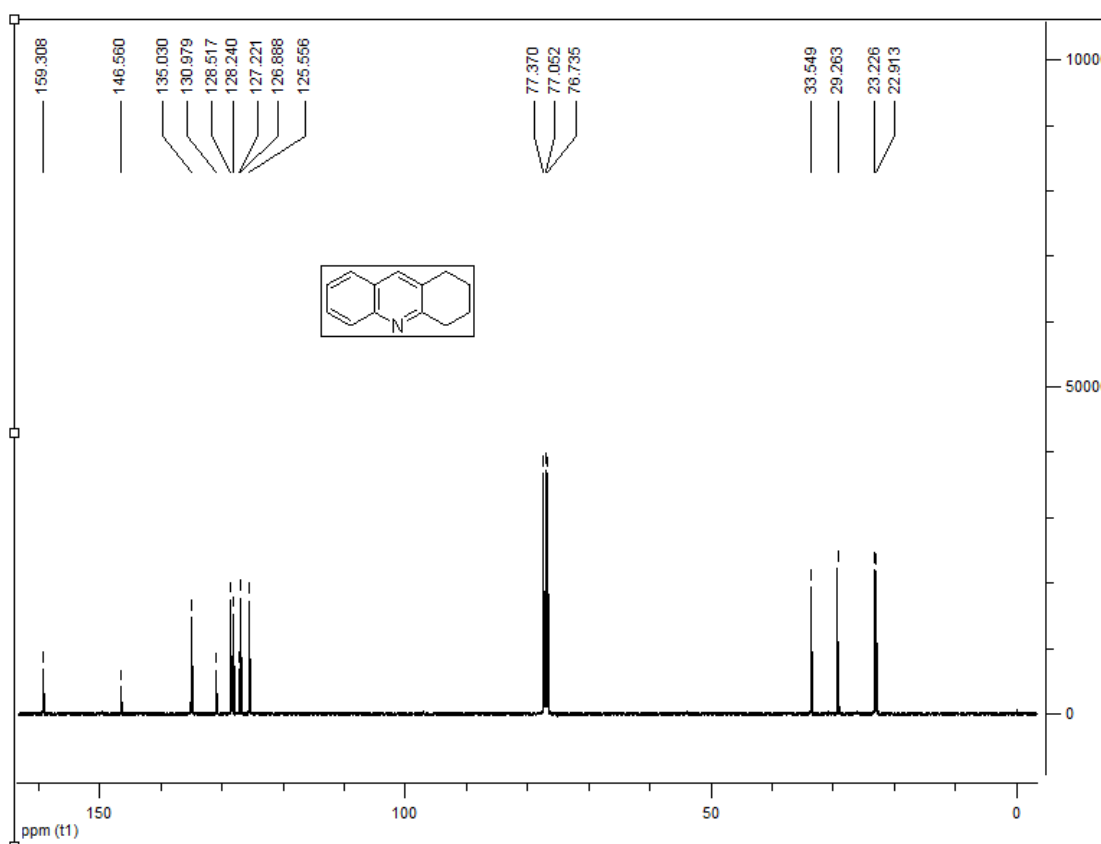
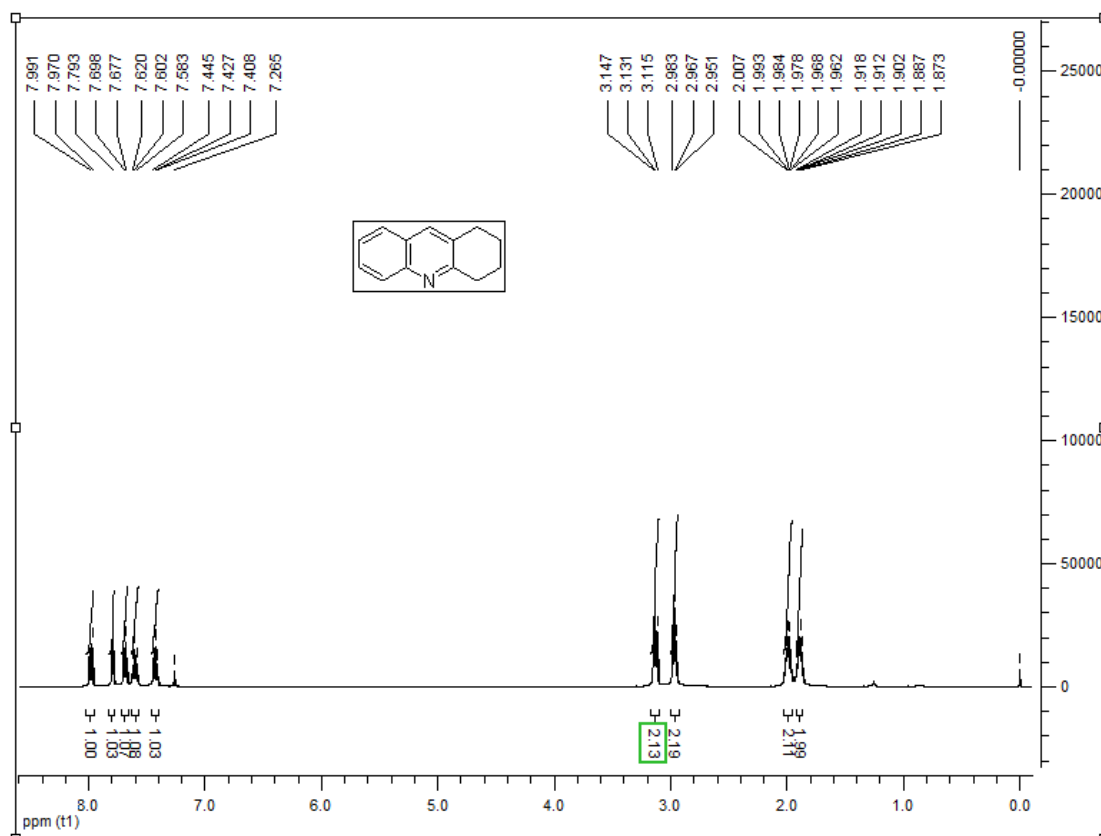
4.2 Hz), 3.19 (2H, d, $J = 5.6$ Hz), 7.54 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.4$ Hz), 7.67 (1H, d, $J = 2.4$ Hz), 7.70 (1H, s), 7.92 (1H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 26.91, 28.74, 32.16, 35.42, 39.96, 125.50, 128.01, 129.31, 130.04, 131.35, 133.63, 137.58, 144.54, 165.03. HRMS (ESI) m/z Calculated for $[\text{C}_{14}\text{H}_{14}\text{ClN}+\text{H}]^+$: 232.0888. Found: 232.0885.

2-Bromo-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline **4v**. White solid. mp. 127.8-128.9 °C. Yield: 52%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.73-1.90 (6H, m), 2.92 (2H, dd, $J_1 = 6.4$ Hz, $J_2 = 4.4$ Hz), 3.19 (2H, t, $J = 5.6$ Hz), 7.65-7.69 (2H, m), 7.74-7.86 (2H, m). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 26.86, 28.72, 32.11, 35.39, 39.99, 119.40, 128.53, 12.81, 130.20, 131.80, 133.45, 137.52, 144.78, 165.18. HRMS (ESI) m/z Calculated for $[\text{C}_{14}\text{H}_{14}\text{BrN}+\text{H}]^+$: 276.0382. Found: 276.0379.

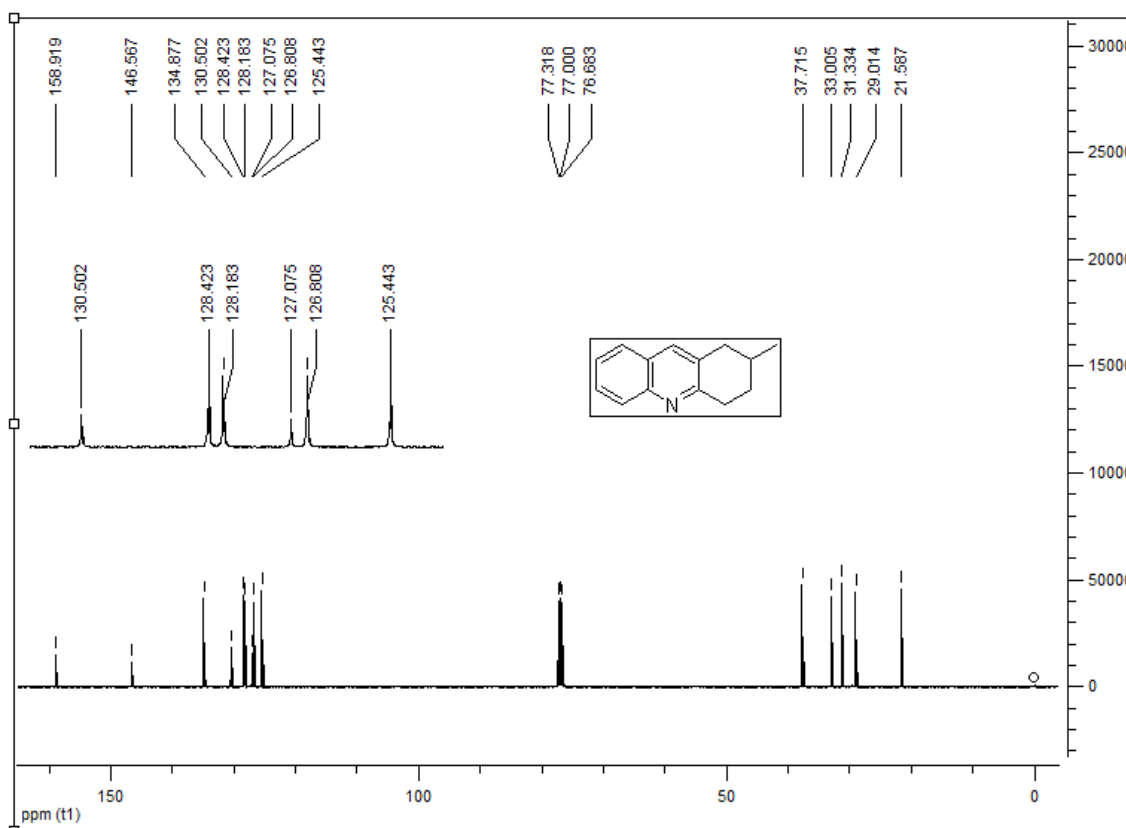
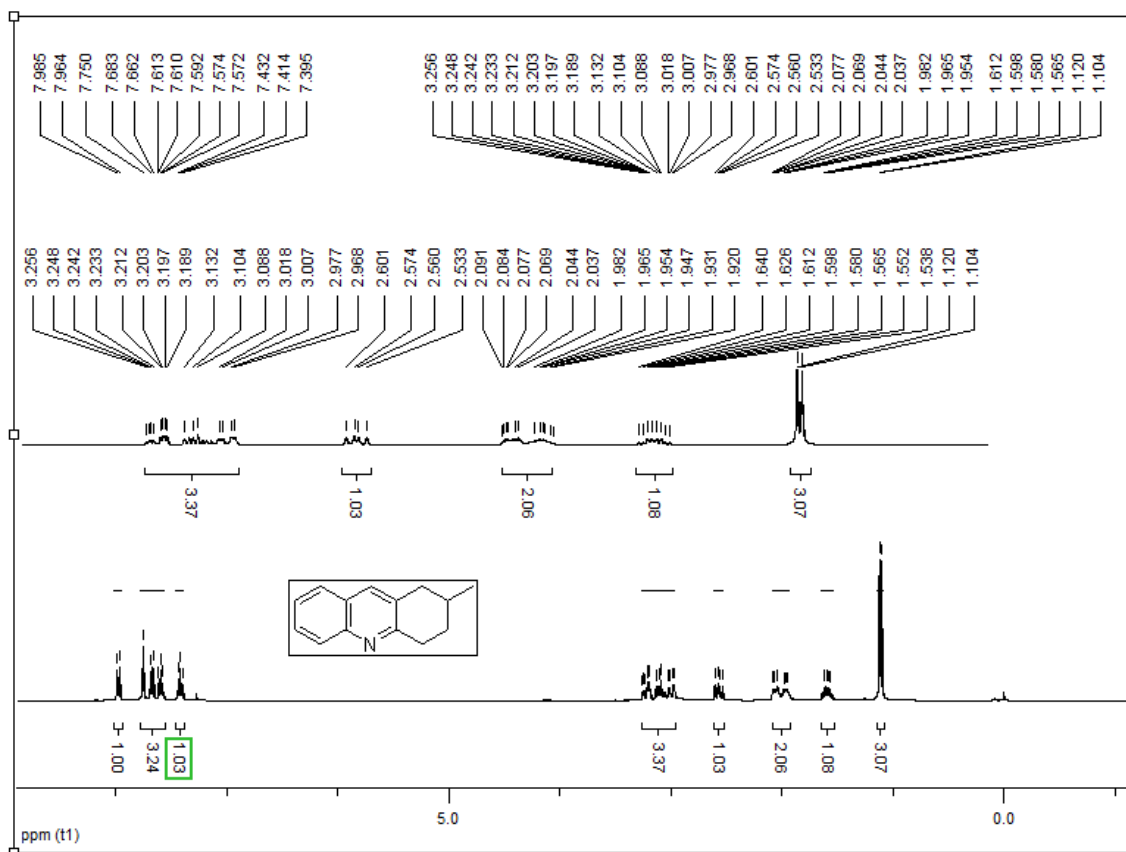
3-Chloro-7,8,9,10-tetrahydro-6H-cyclohepta[*b*]quinoline **4w**. White solid. mp. 105.0-107.0 °C. Yield: 60%. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 1.72-1.91 (6H, m), 2.91-2.93 (2H, m), 3.18-3.20 (2H, m), 7.39 (1H, dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz), 7.62 (1H, d, $J = 4.8$ Hz), 7.76 (1H, s), 7.99 (1H, d, $J = 0.4$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 26.85, 28.70, 32.11, 35.36, 39.94, 125.67, 126.68, 127.52, 127.96, 134.08, 134.29, 136.79, 148.53, 165.79. HRMS (ESI) m/z Calculated for $[\text{C}_{14}\text{H}_{14}\text{ClN}+\text{H}]^+$: 232.0888. Found: 232.0885.

4. NMR spectra of products 4

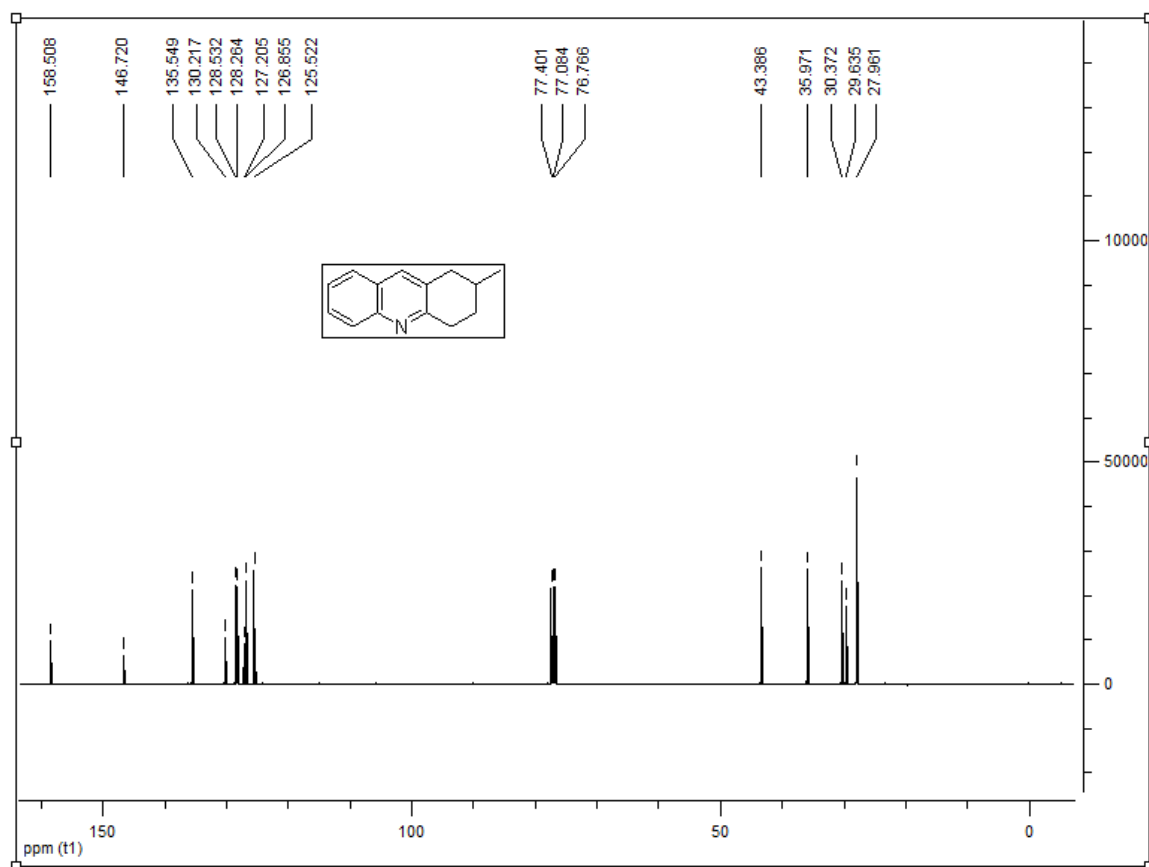
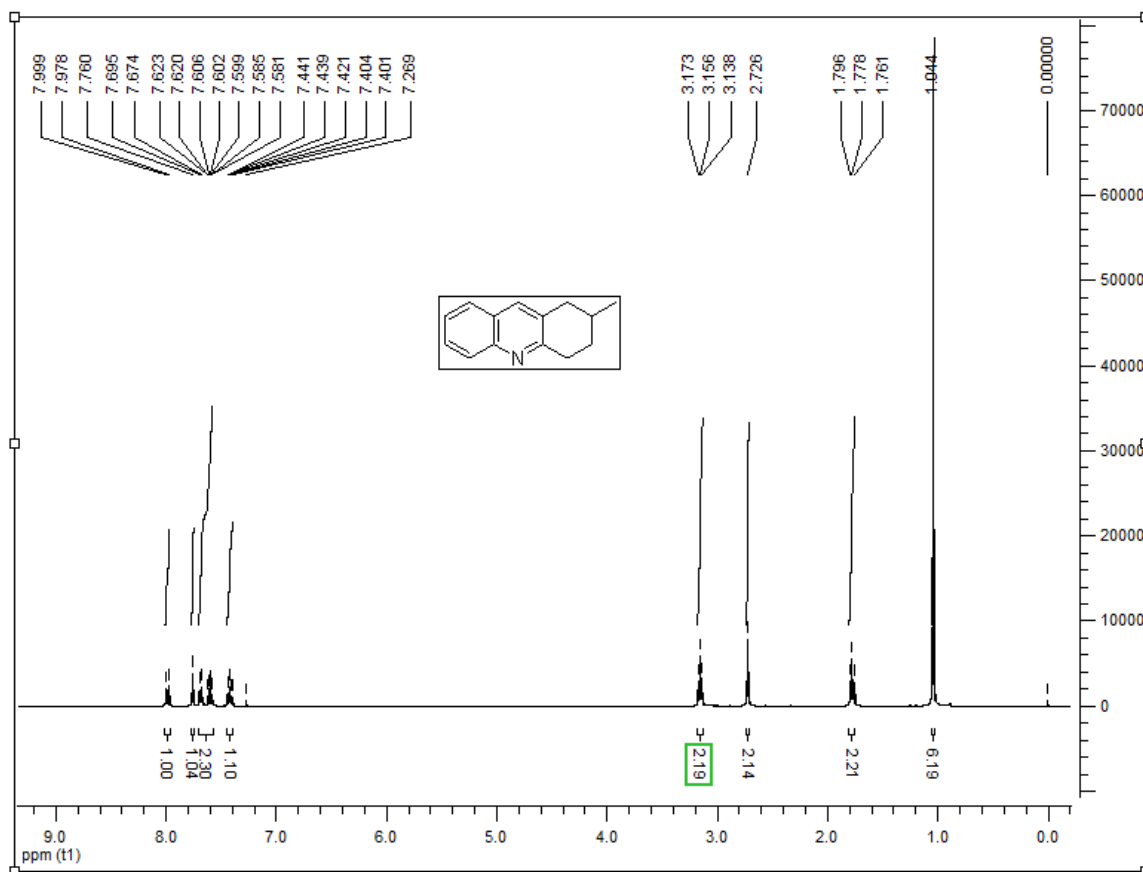
1,2,3,4-Tetrahydroacridine 4a



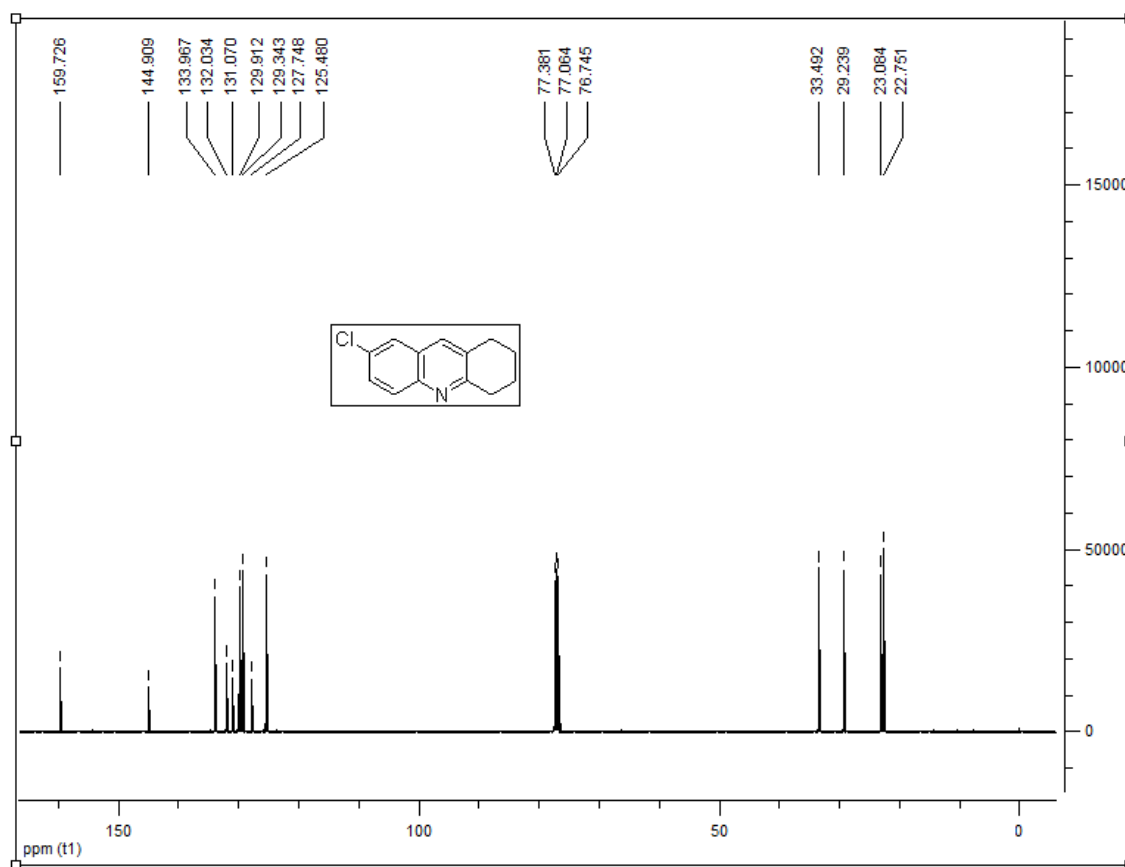
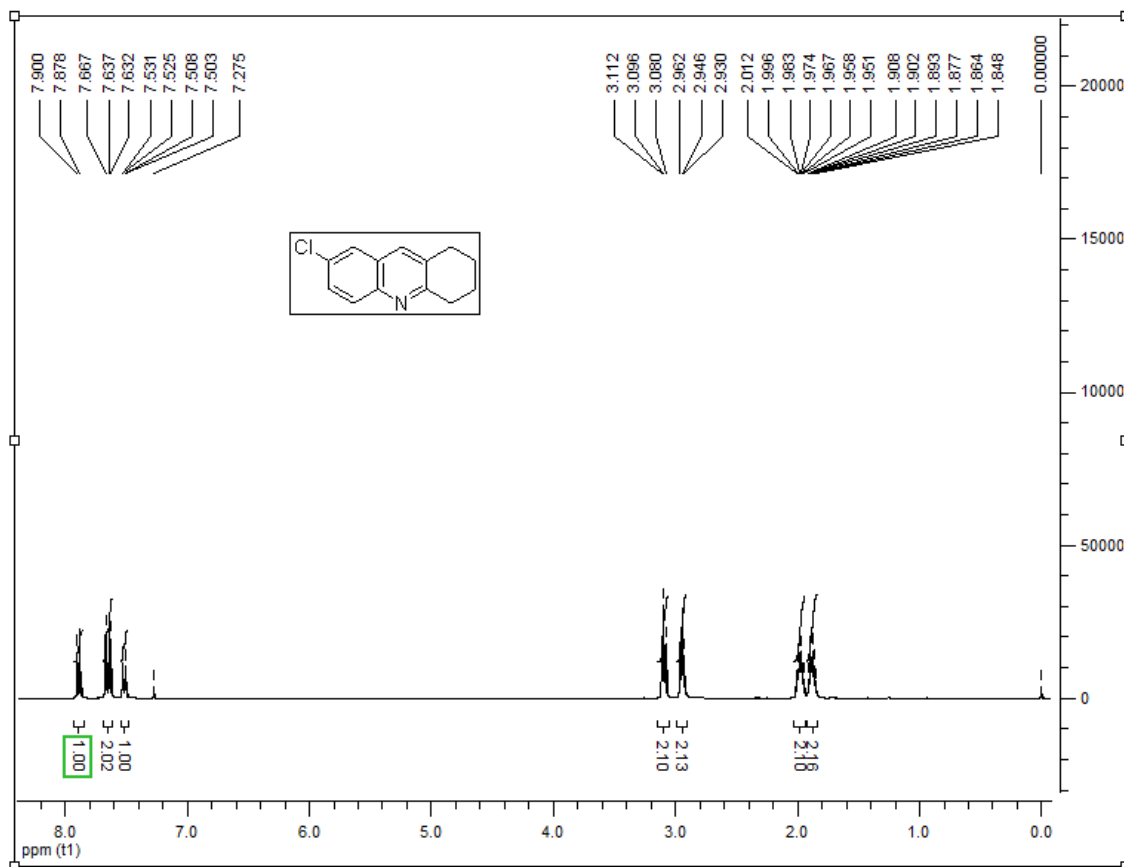
2-Methyl-1,2,3,4-tetrahydroacridine **4b**



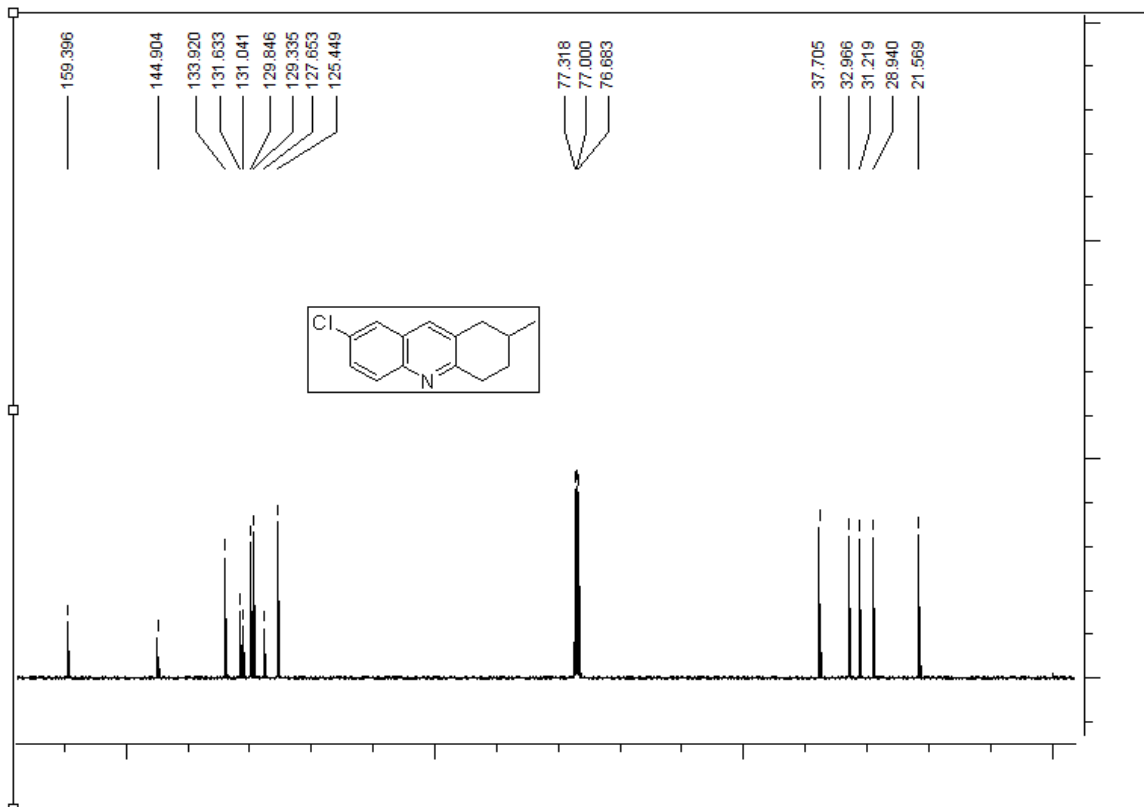
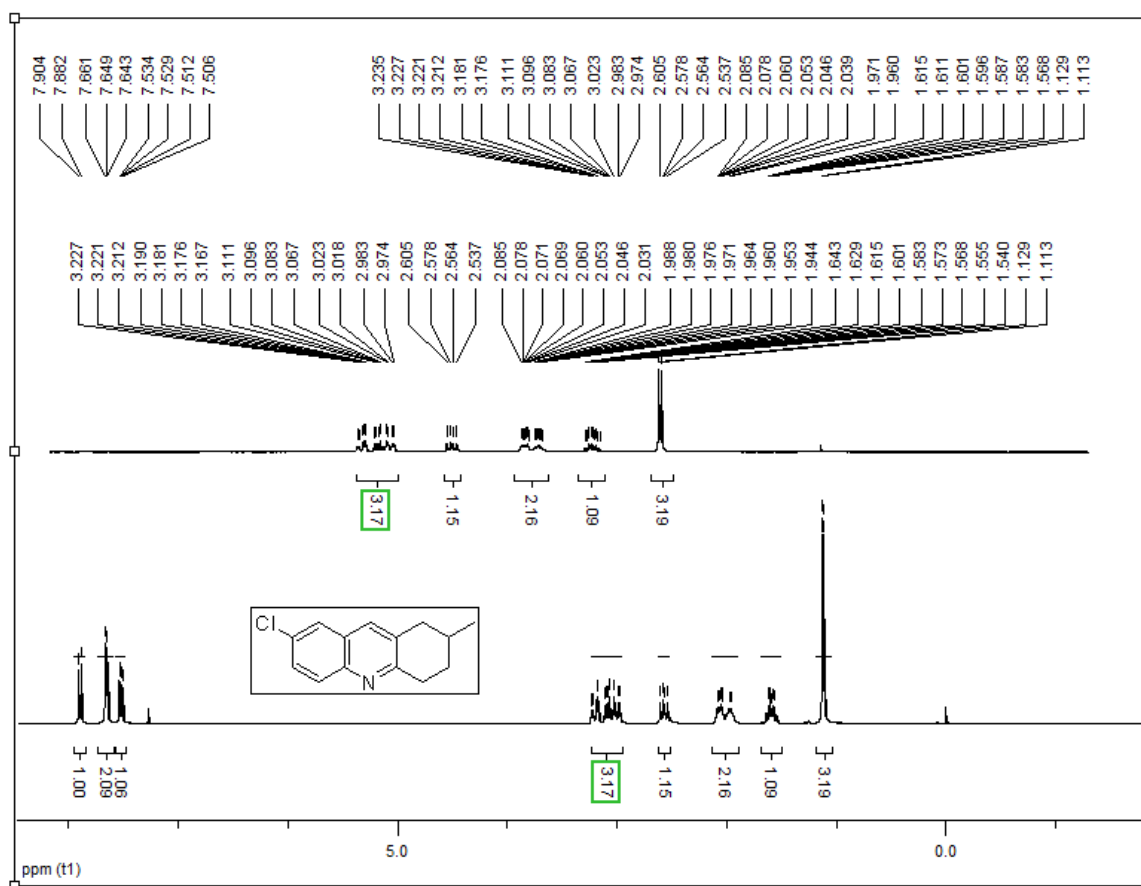
2,2-Dimethyl-1,2,3,4-tetrahydroacridine **4c**



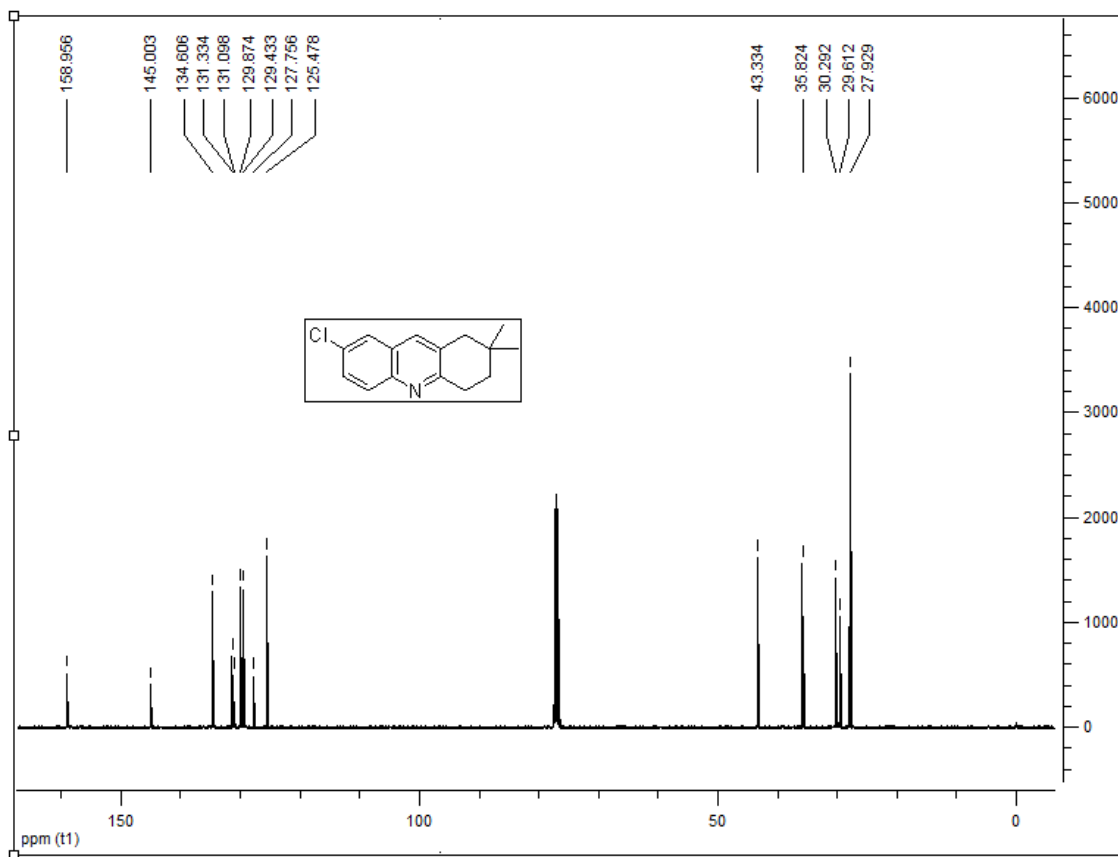
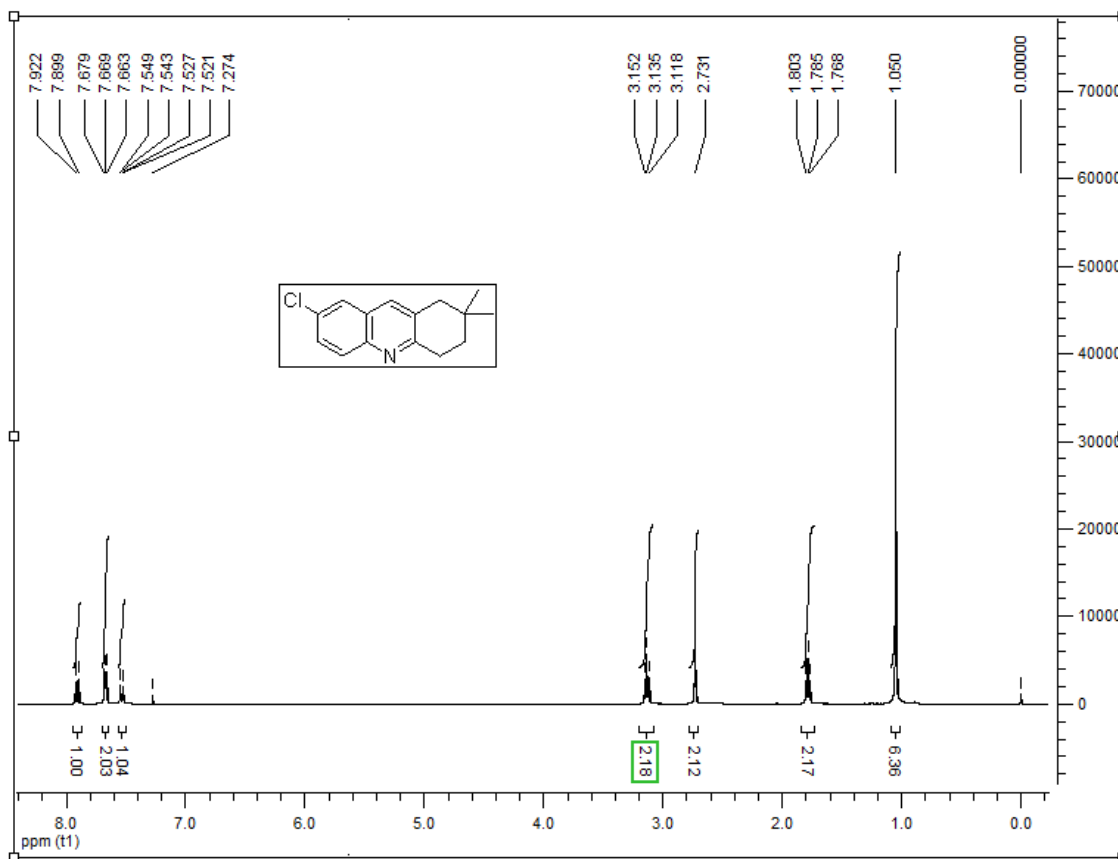
7-Chloro-1,2,3,4-tetrahydroacridine **4d**



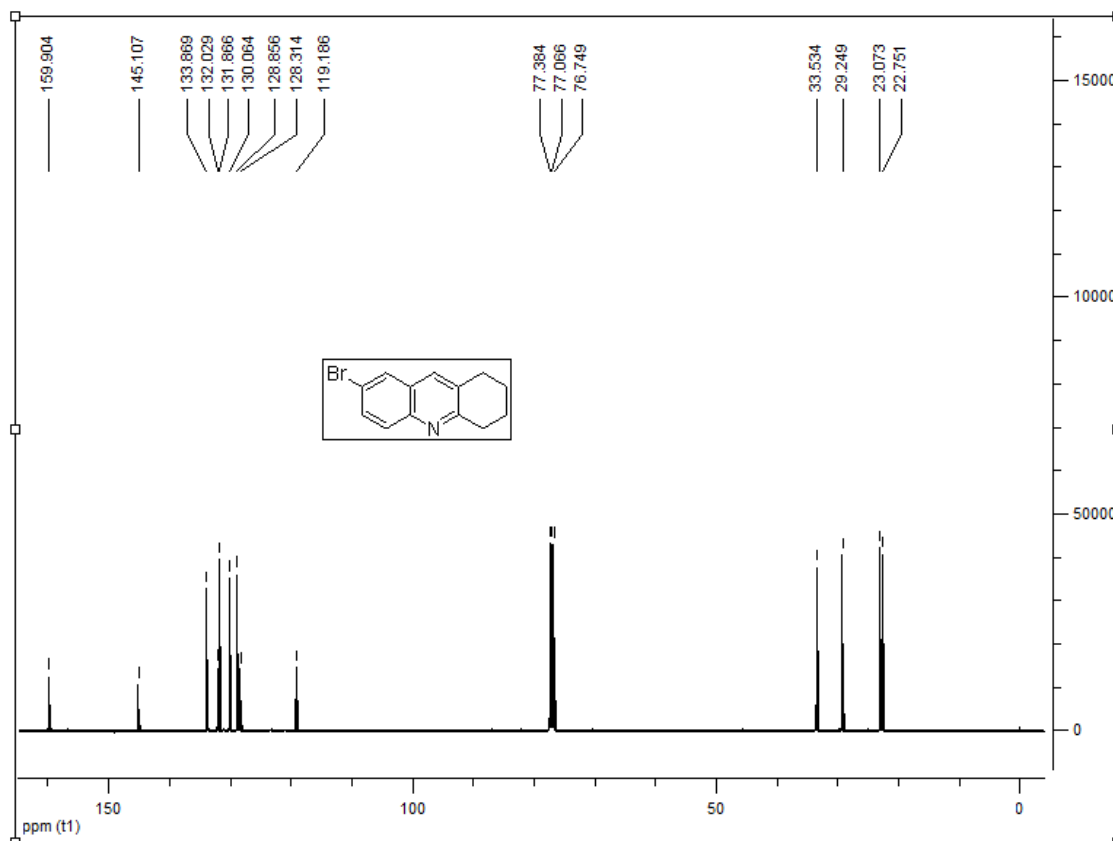
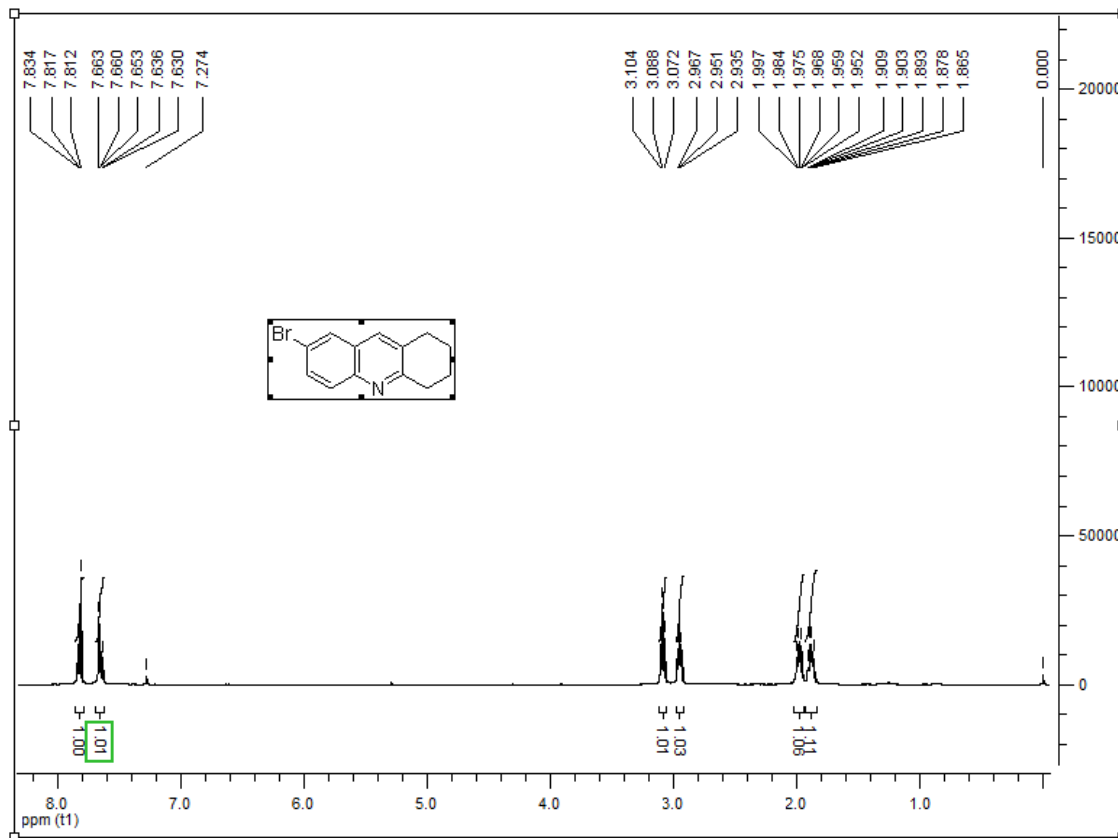
7-Chloro-2-methyl-1,2,3,4-tetrahydroacridine **4e**



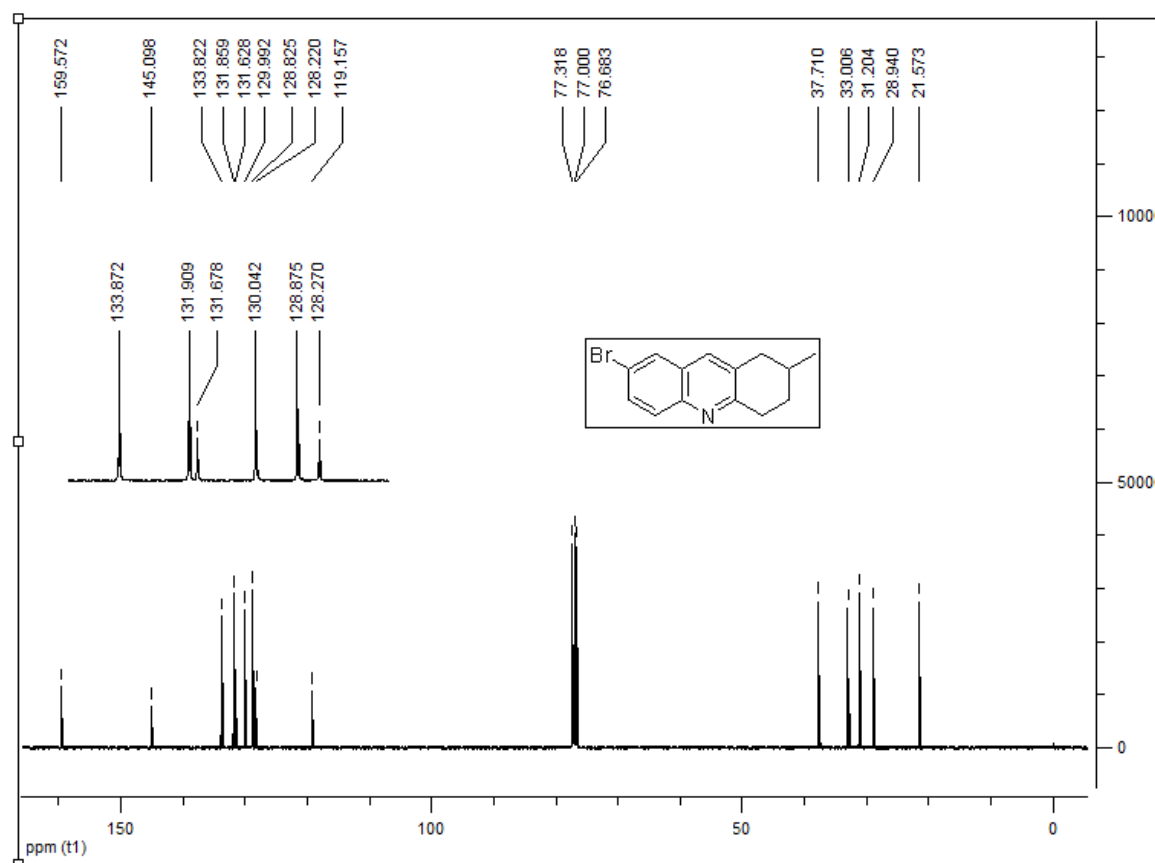
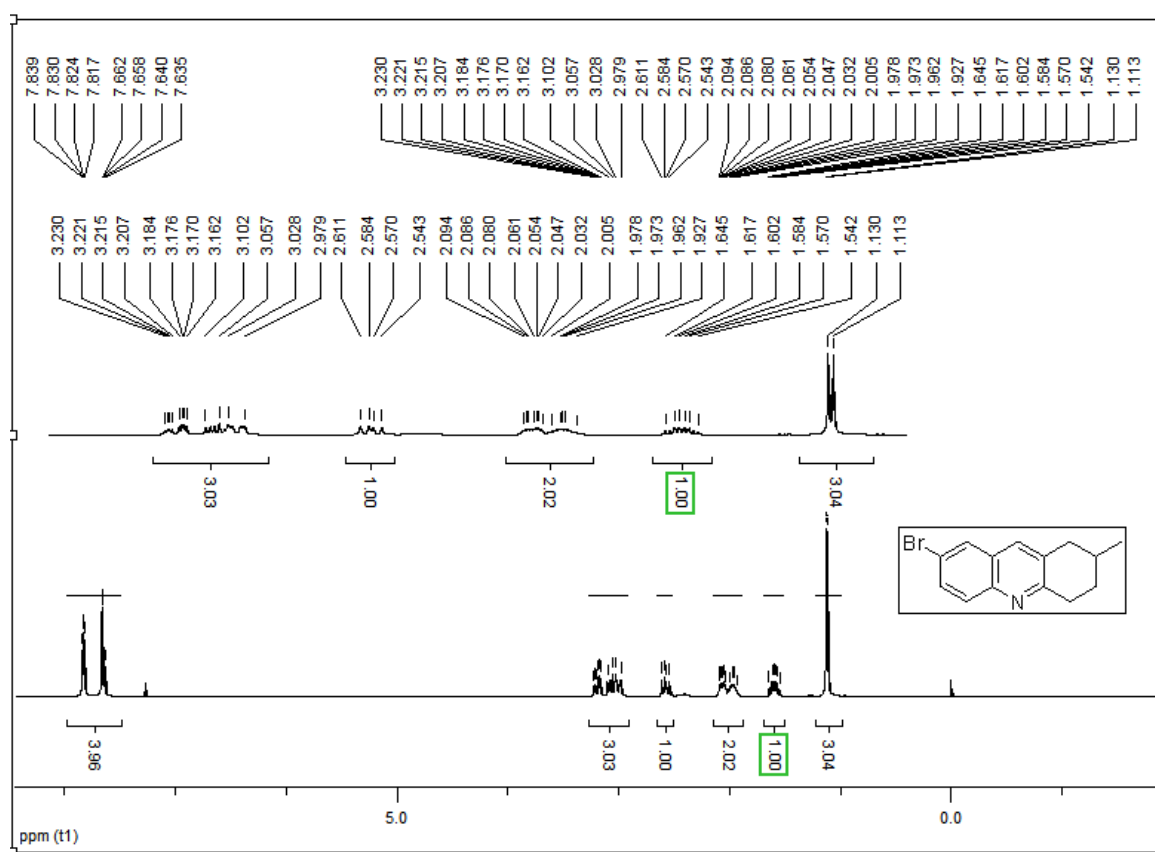
7-Chloro-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4f**



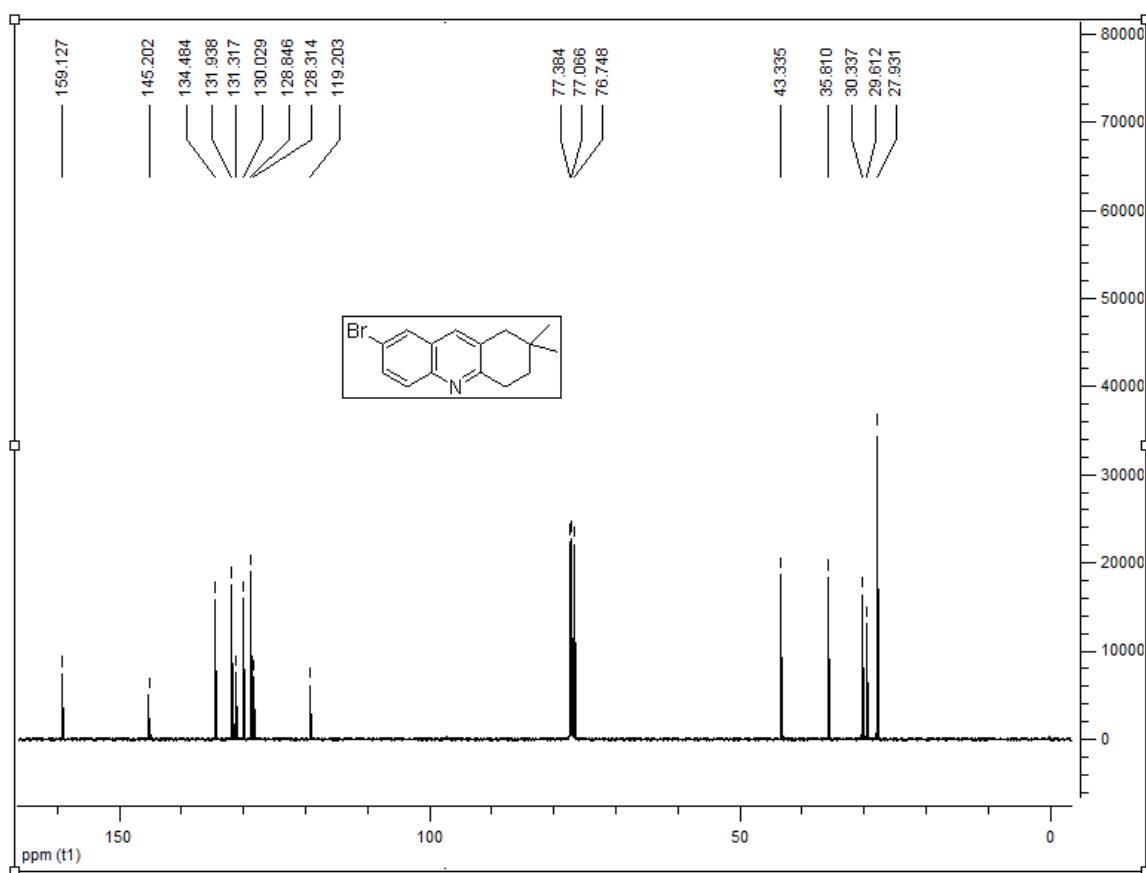
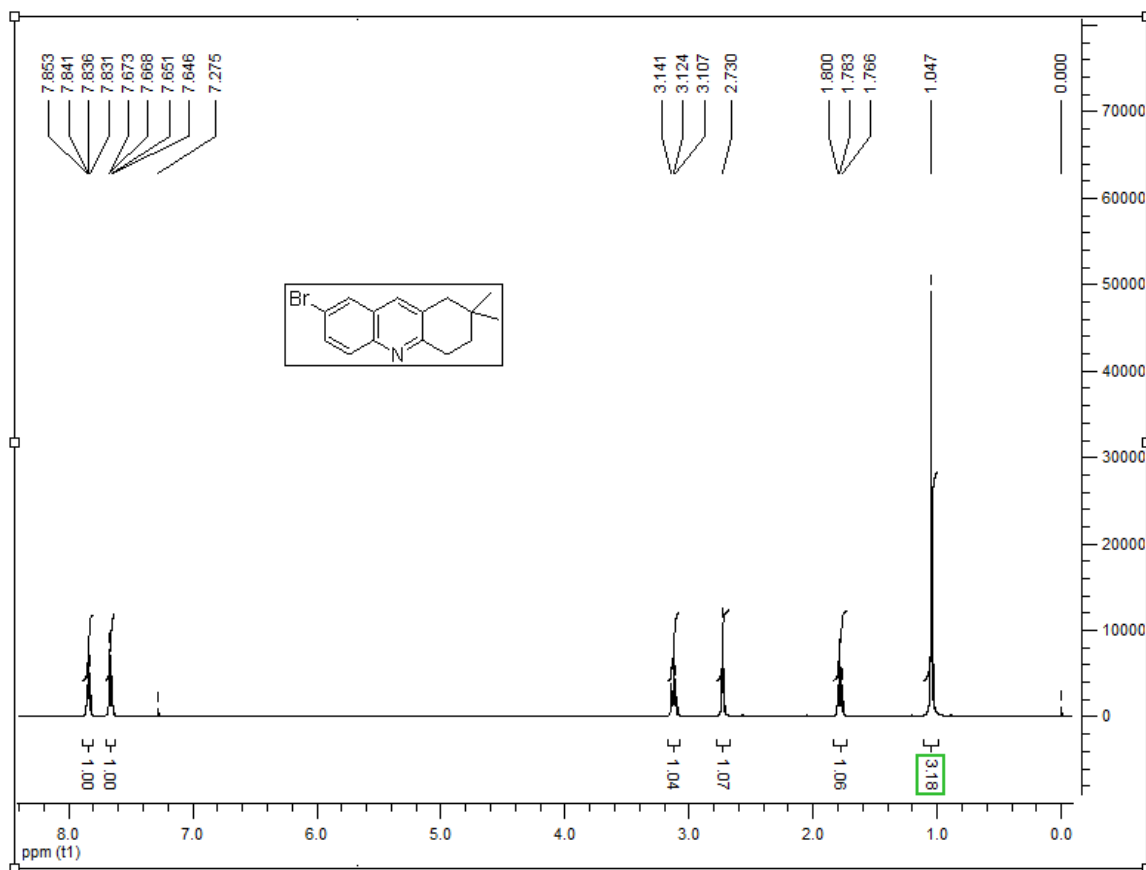
7-Bromo-1,2,3,4-tetrahydroacridine **4g**



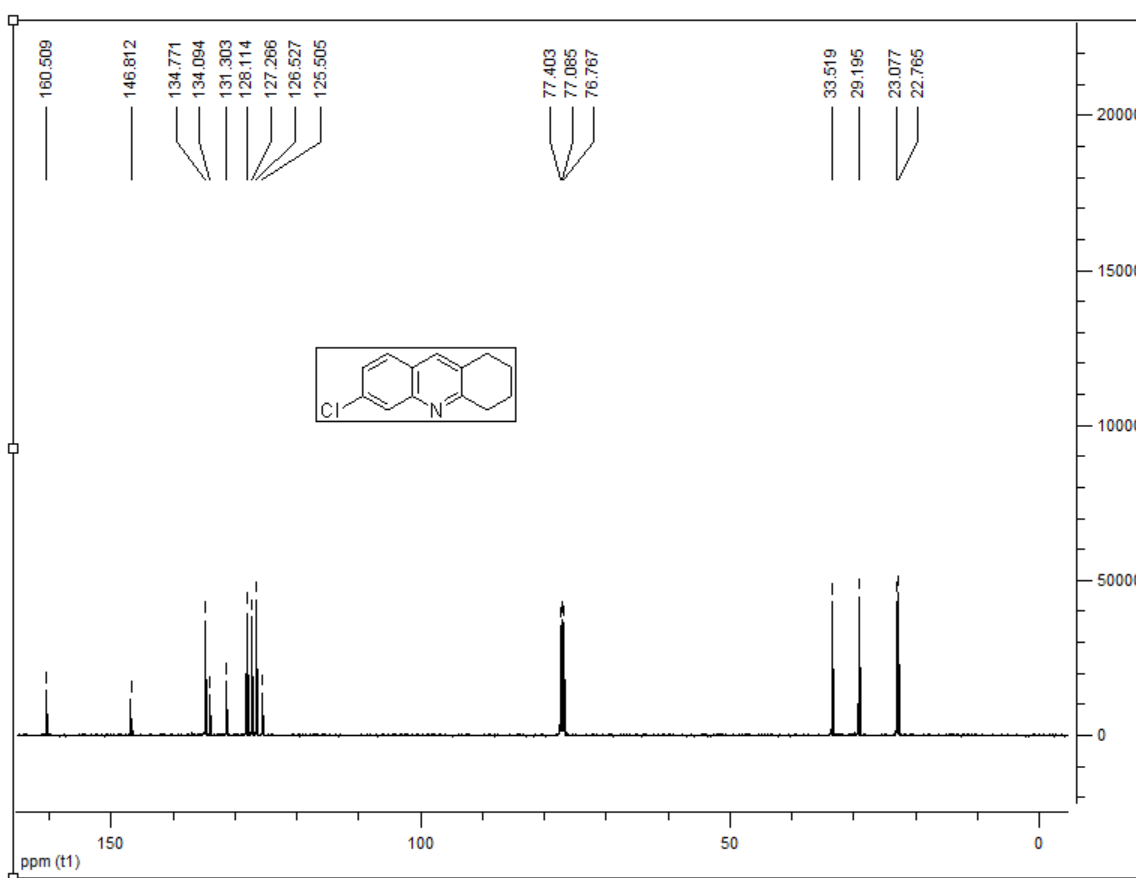
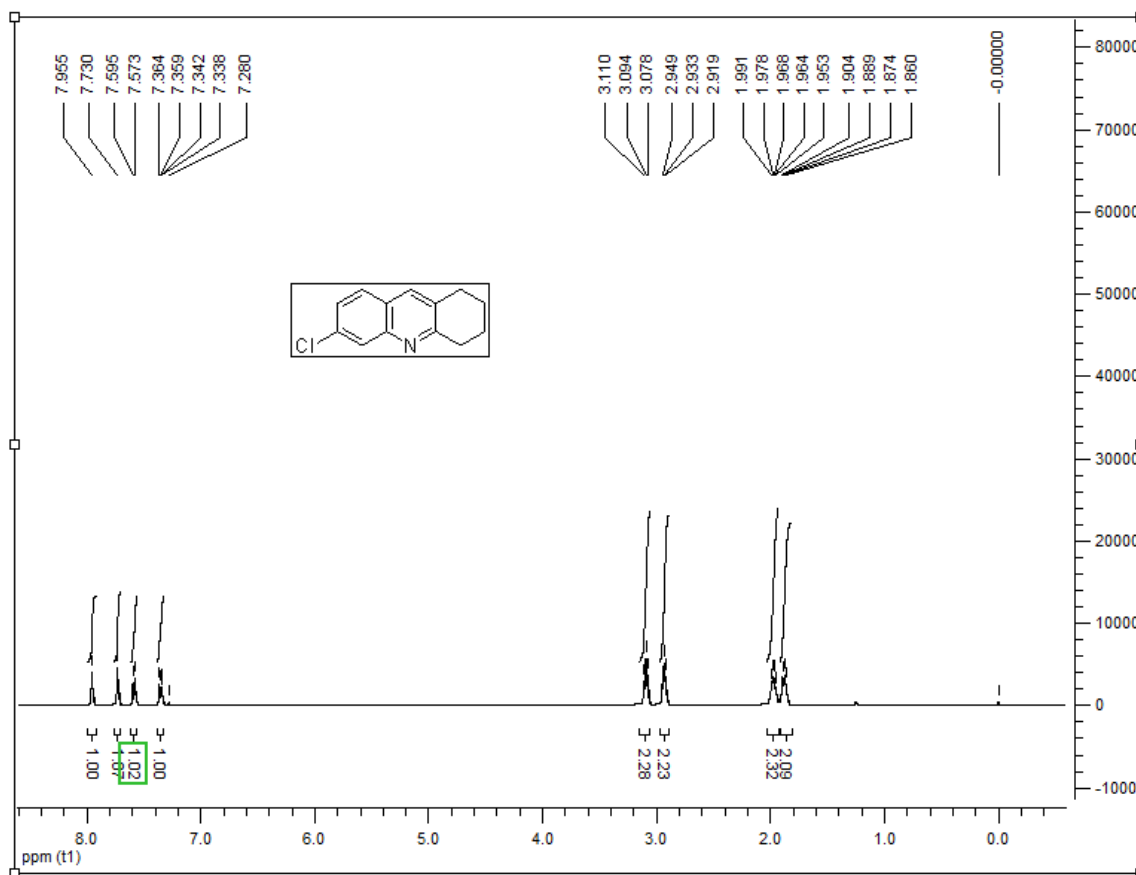
7-Bromo-2-methyl-1,2,3,4-tetrahydroacridine **4h**



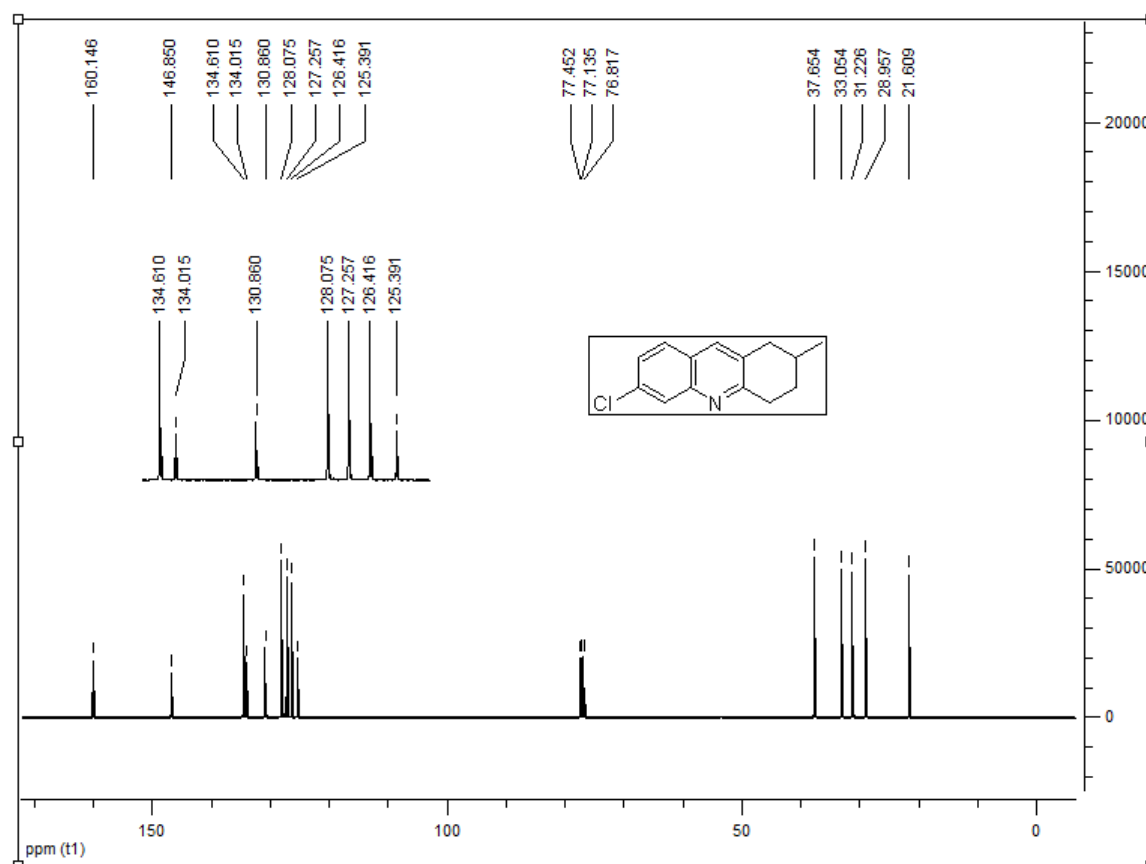
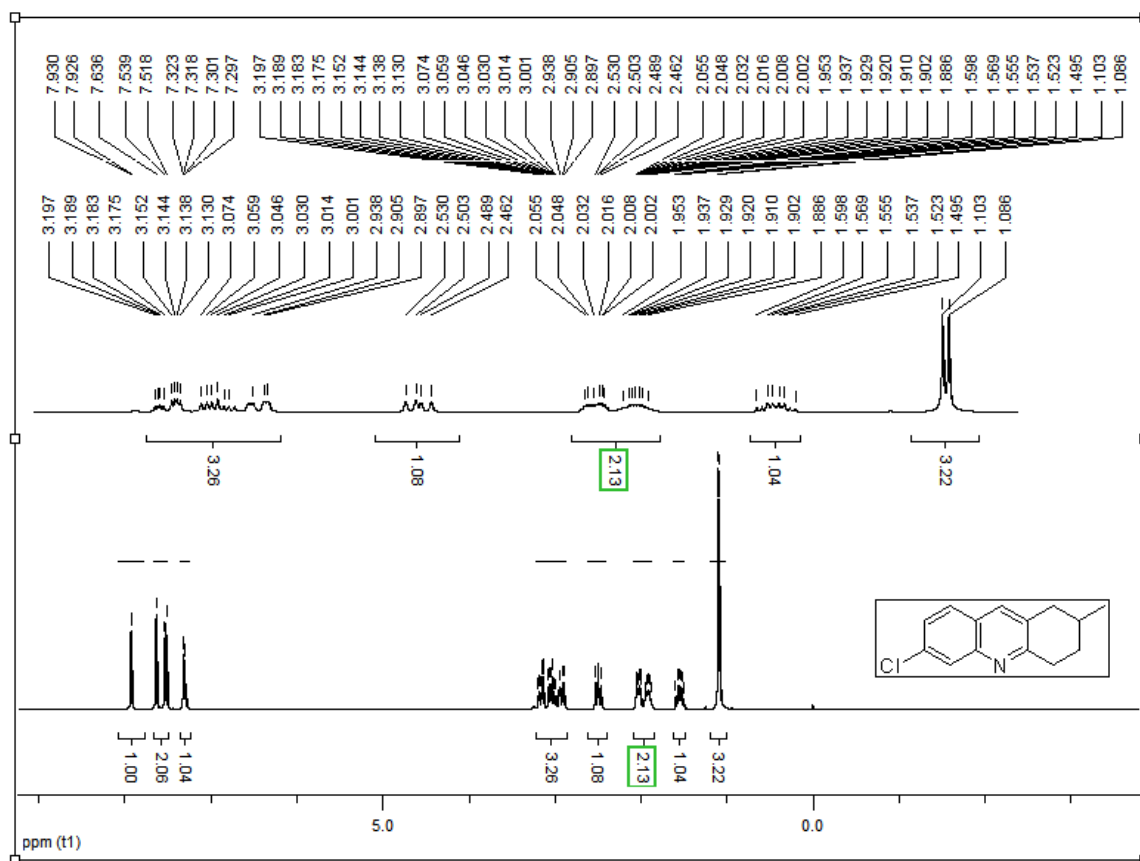
7-Bromo-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4i**



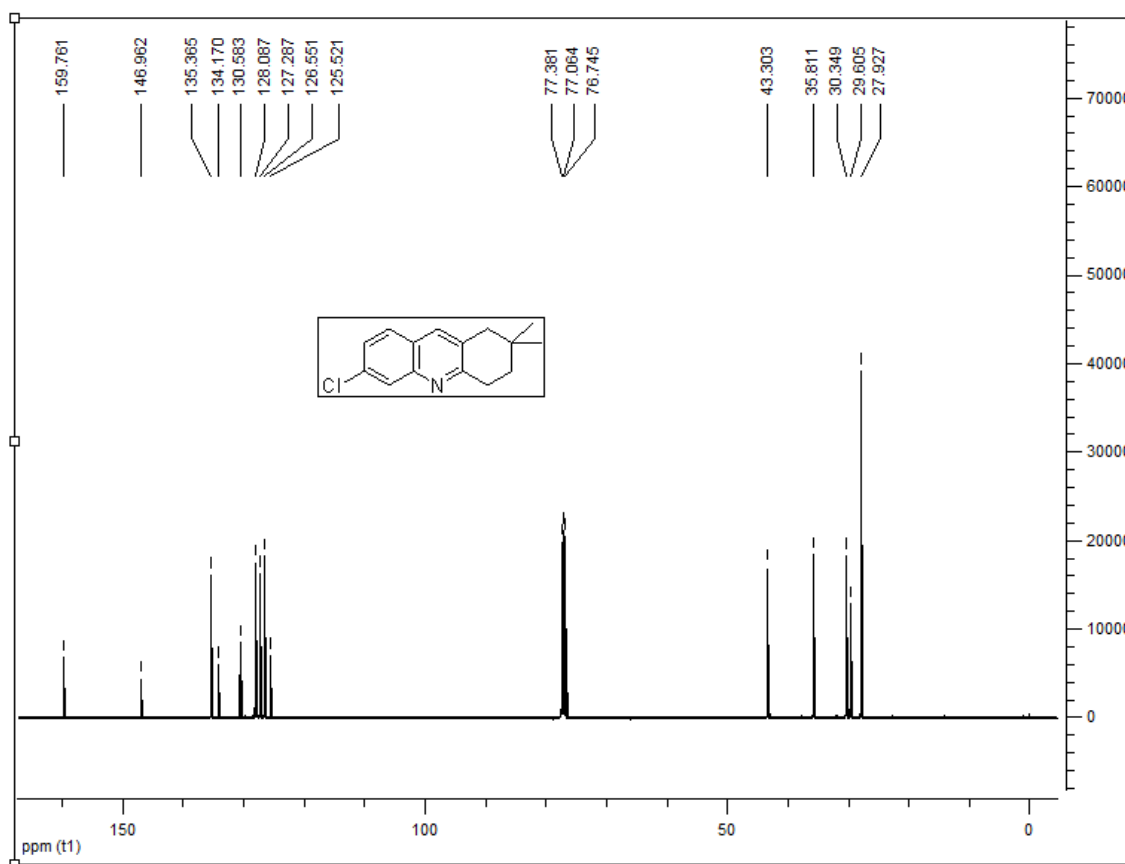
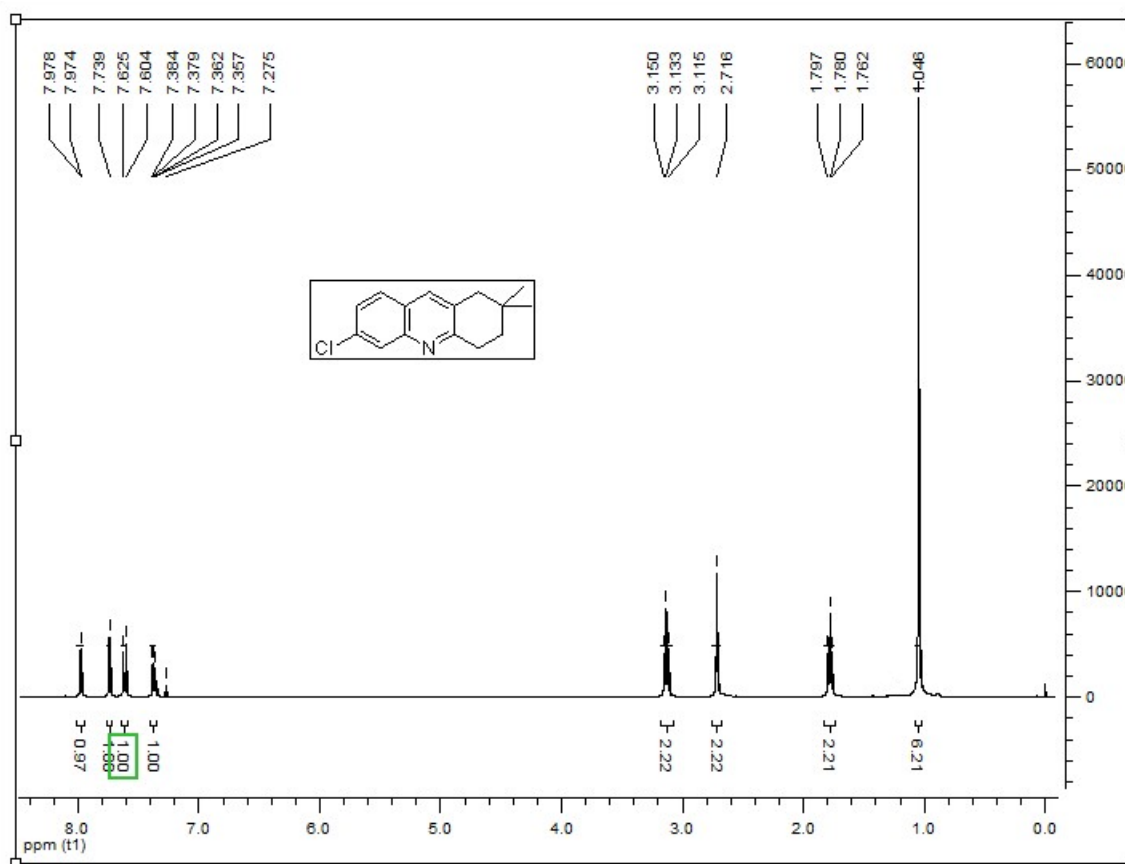
6-Chloro-1,2,3,4-tetrahydroacridine **4j**



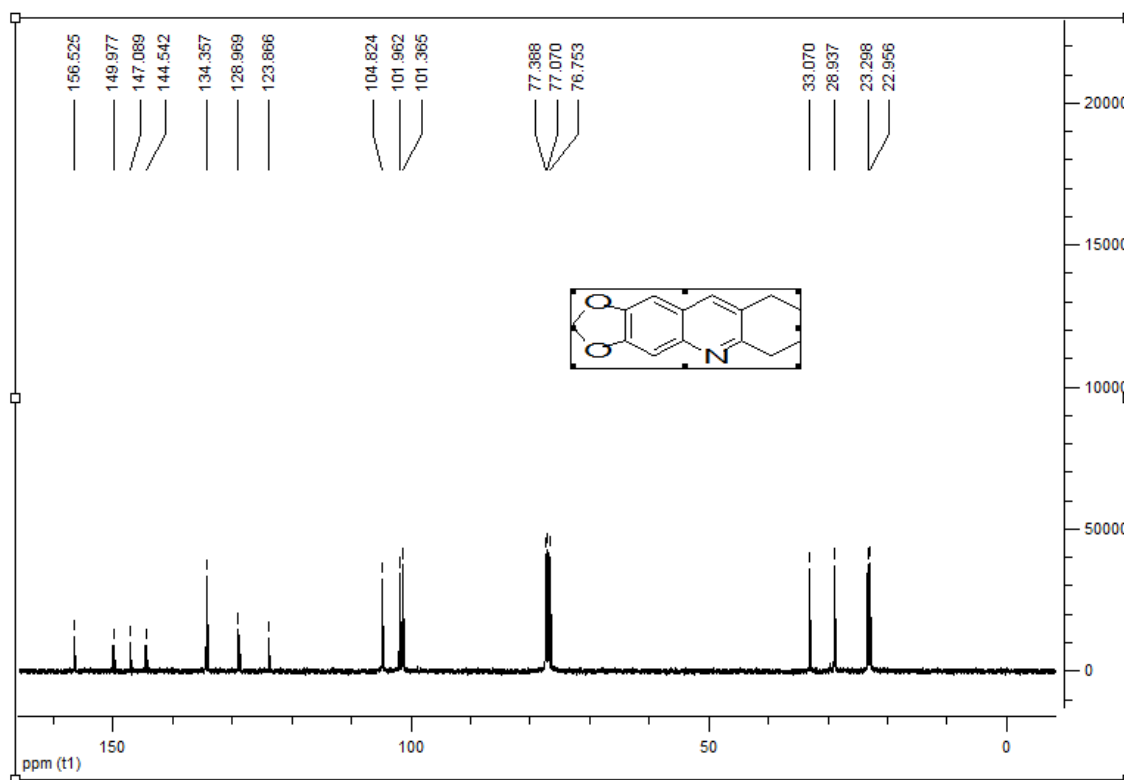
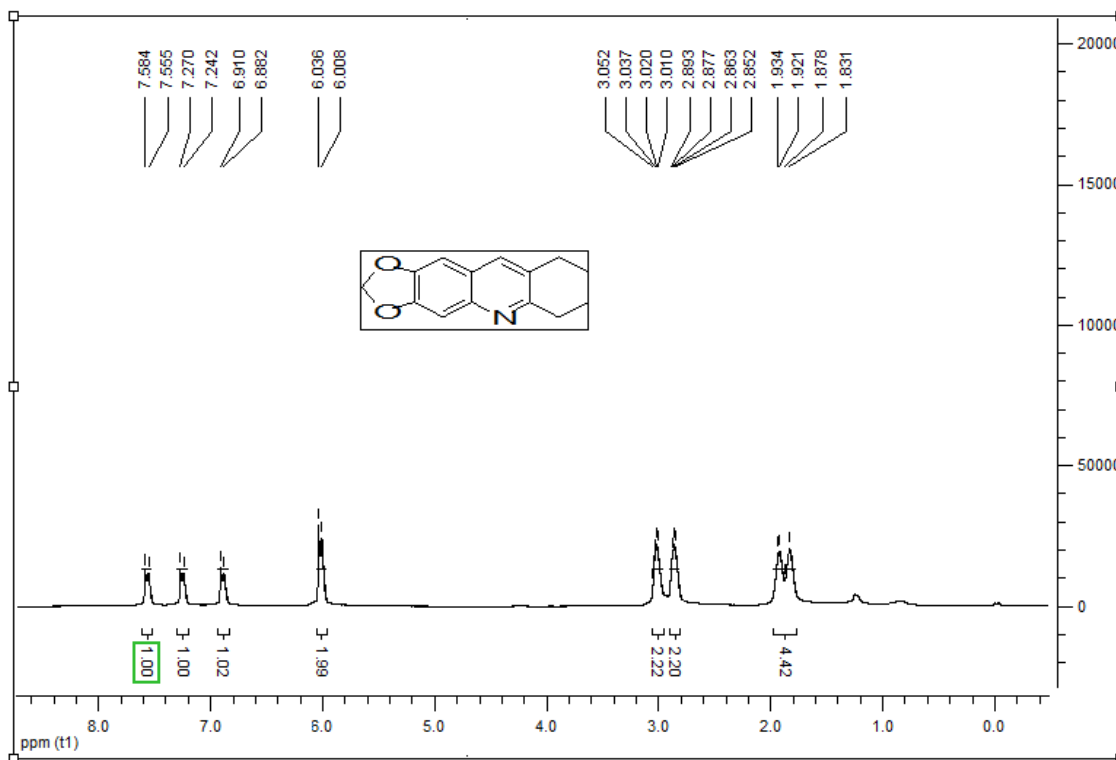
6-Chloro-2-methyl-1,2,3,4-tetrahydroacridine 4k



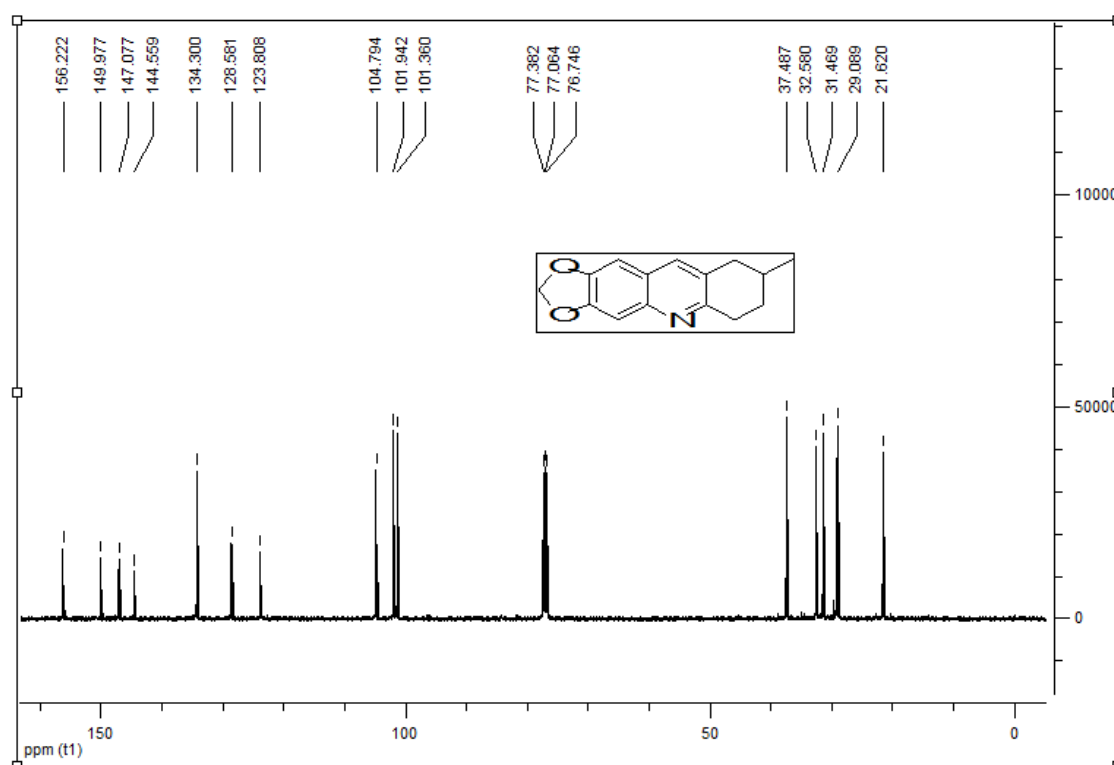
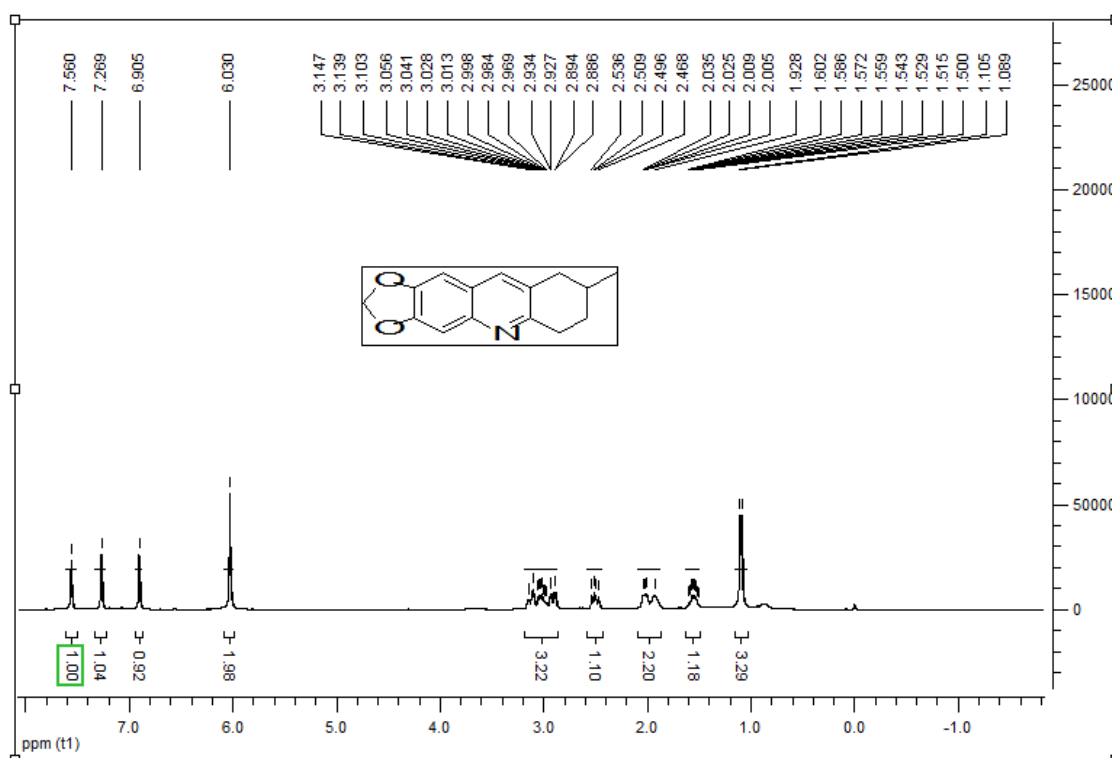
6-Chloro-2,2-dimethyl-1,2,3,4-tetrahydroacridine 4I



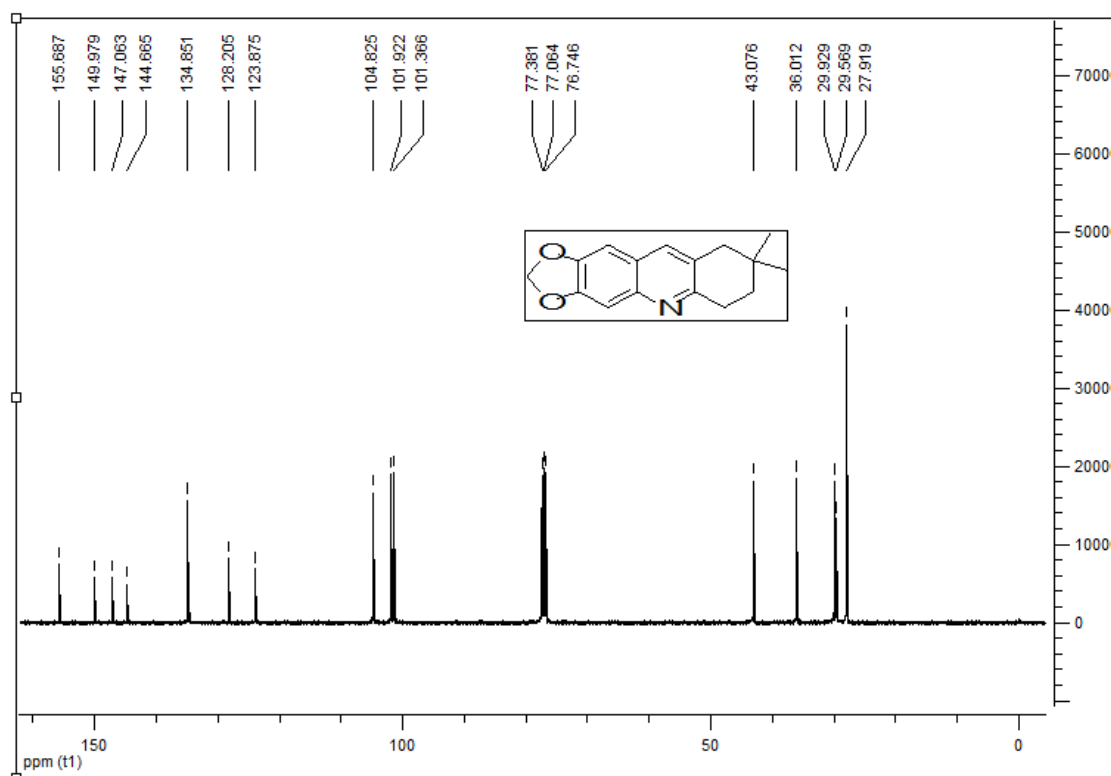
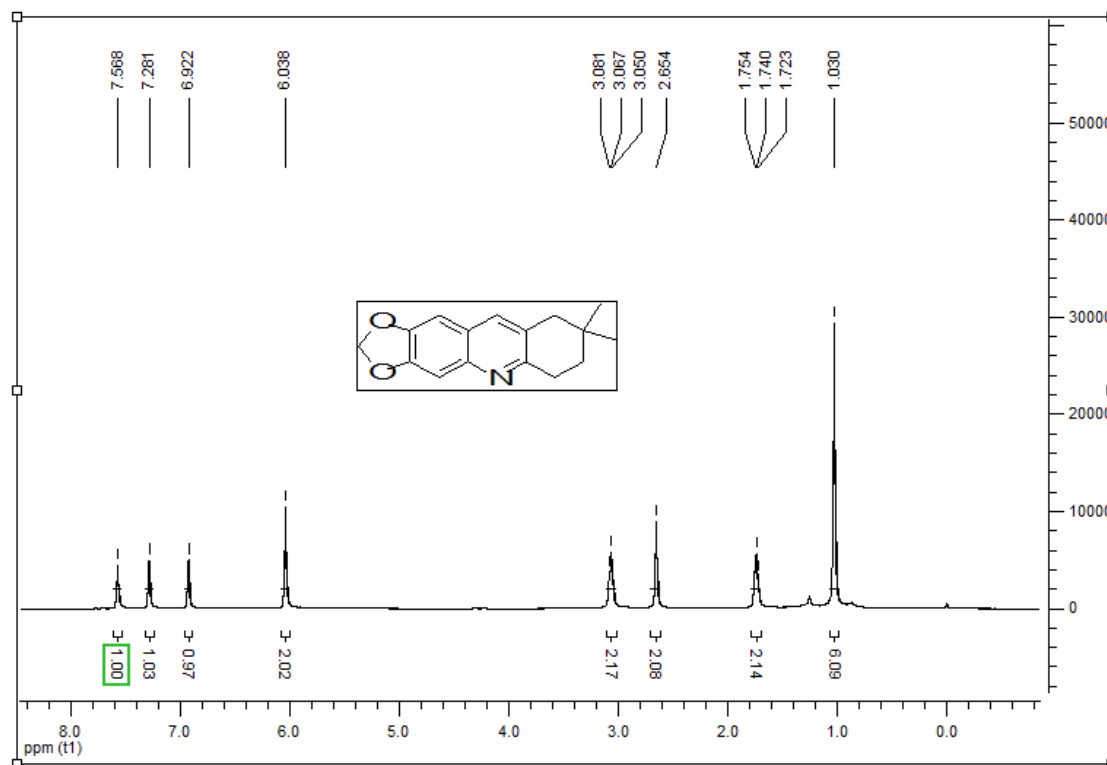
6,7,8,9-Tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4m**.



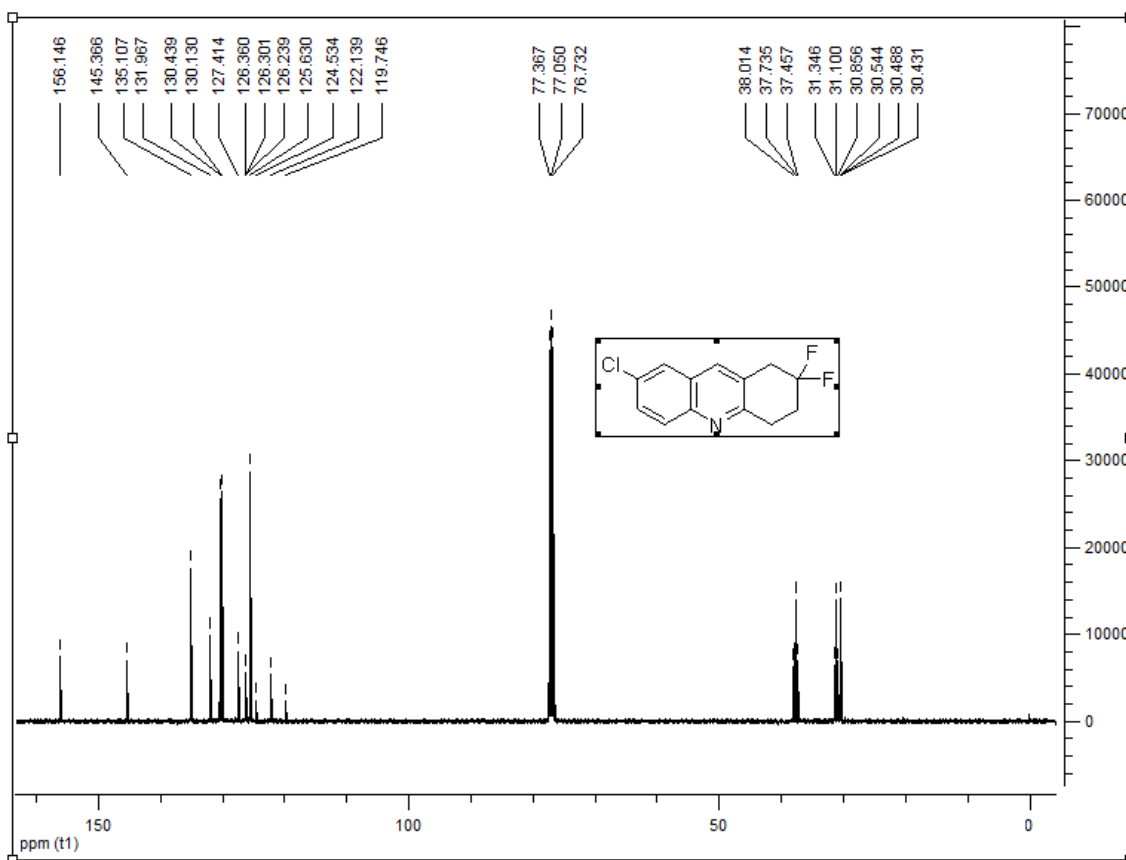
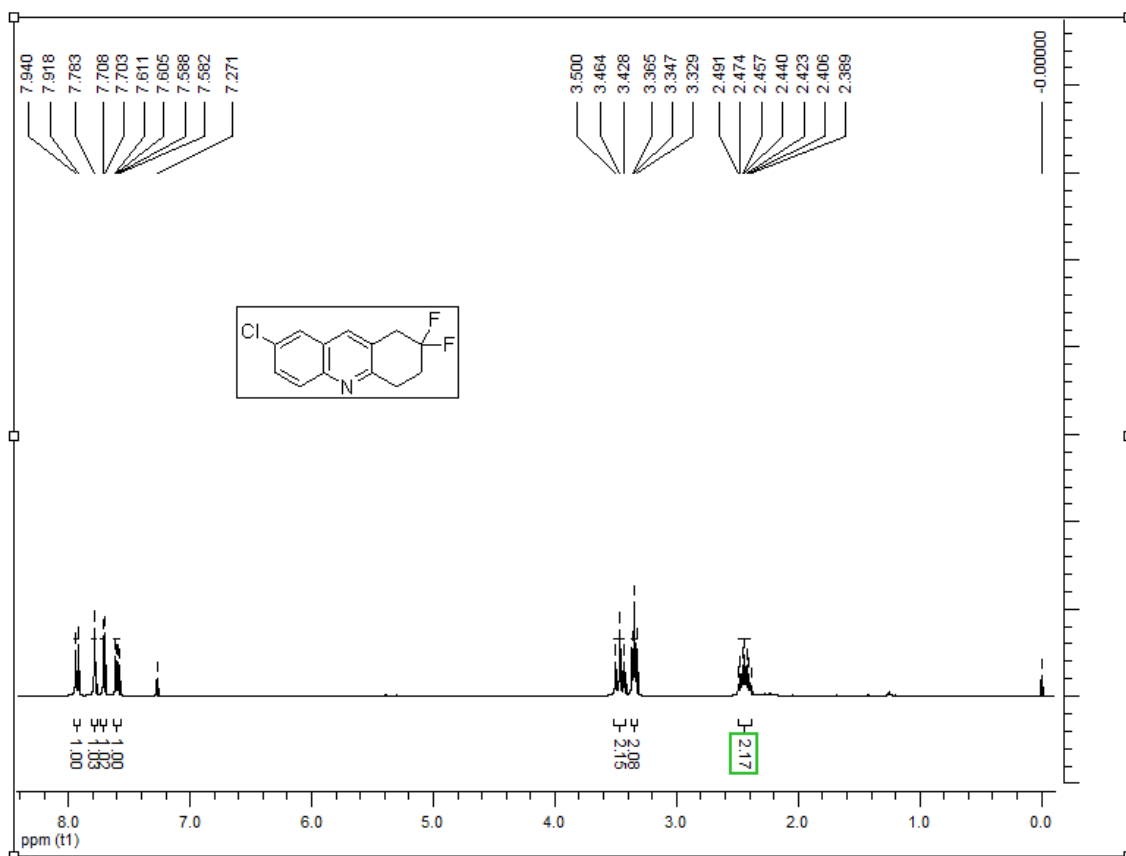
8-Methyl-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4n**.

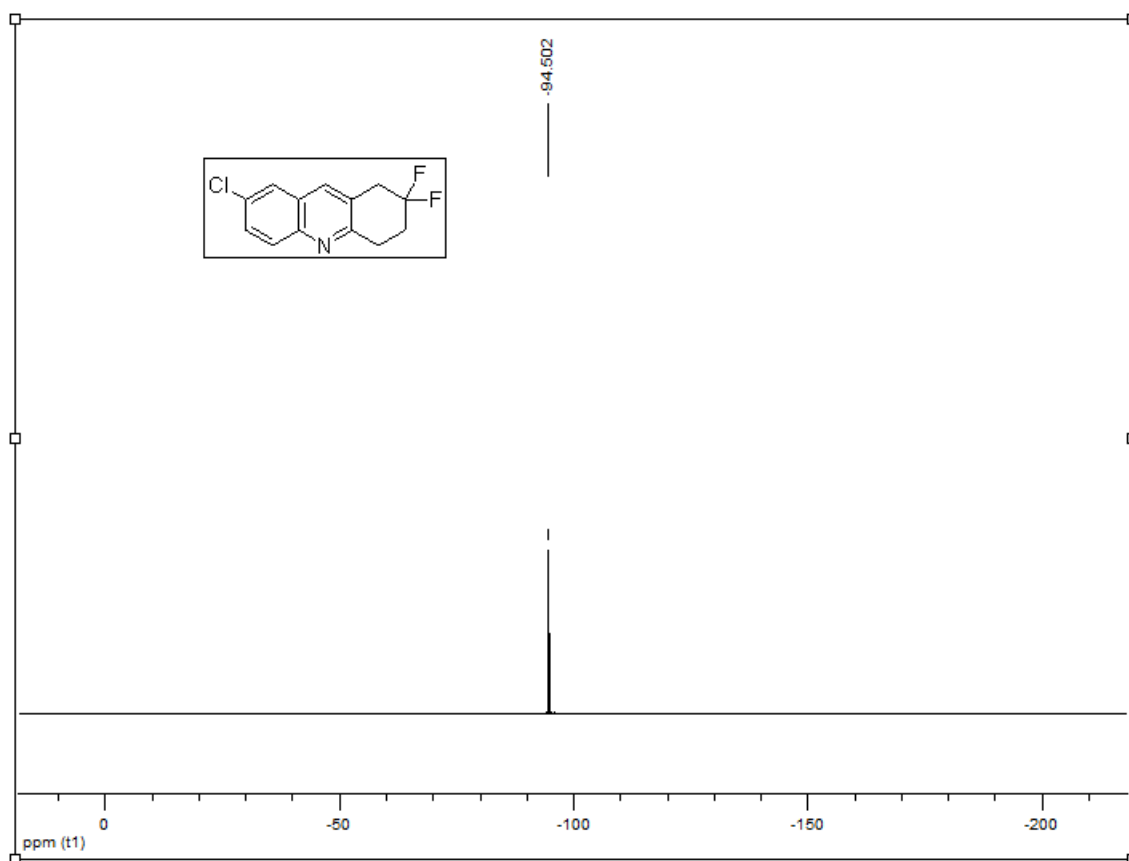


8,8-Dimethyl-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **40**.

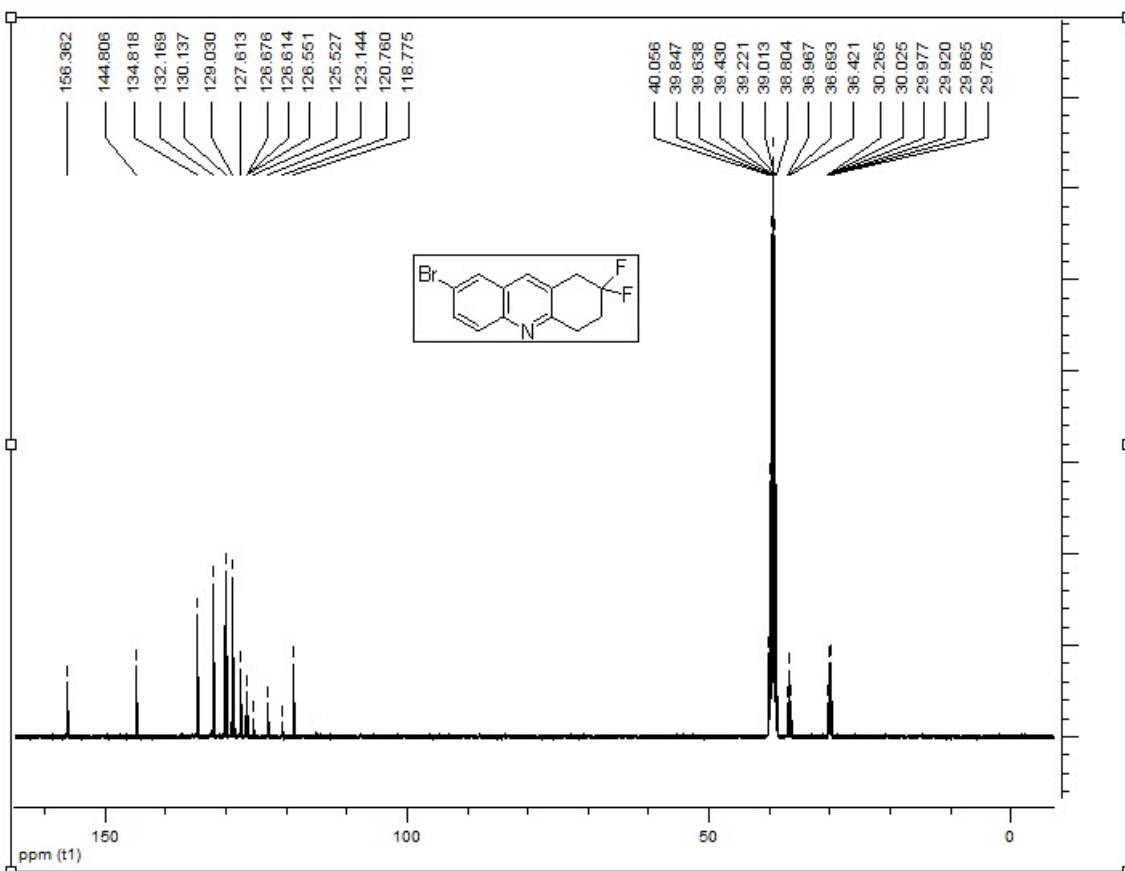
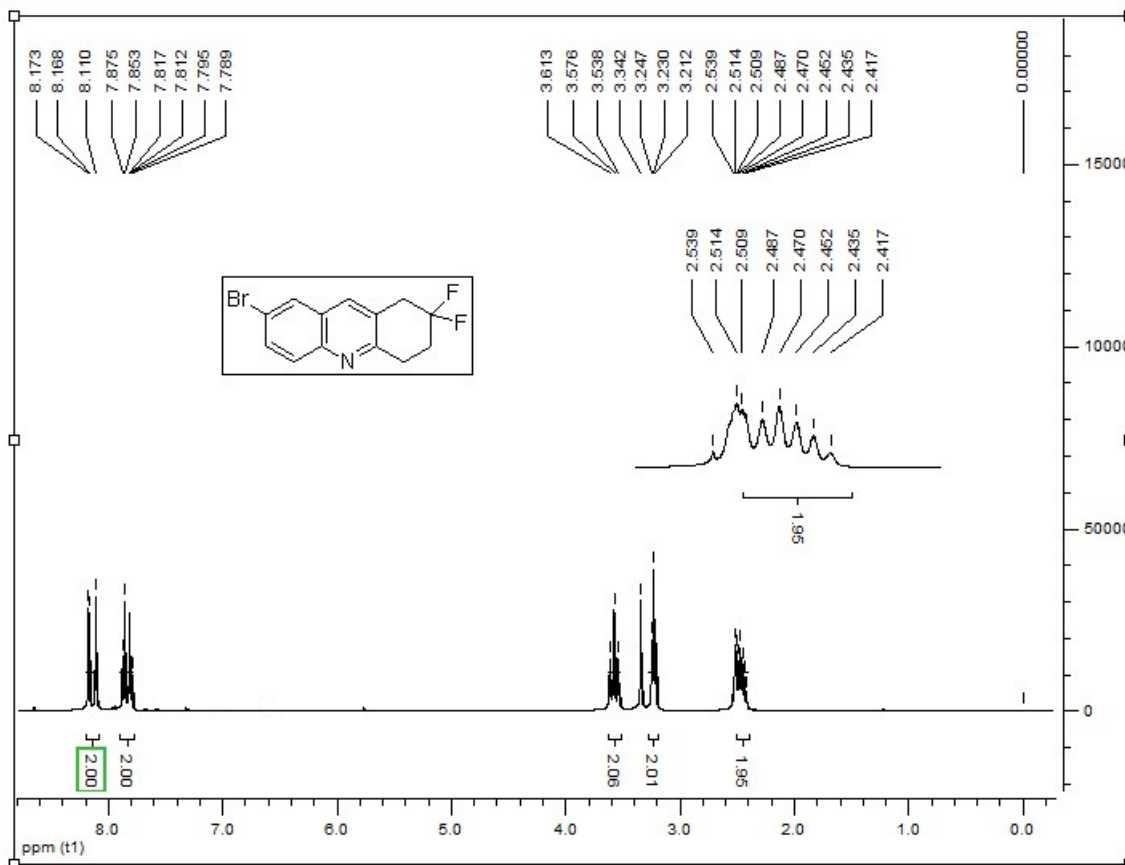


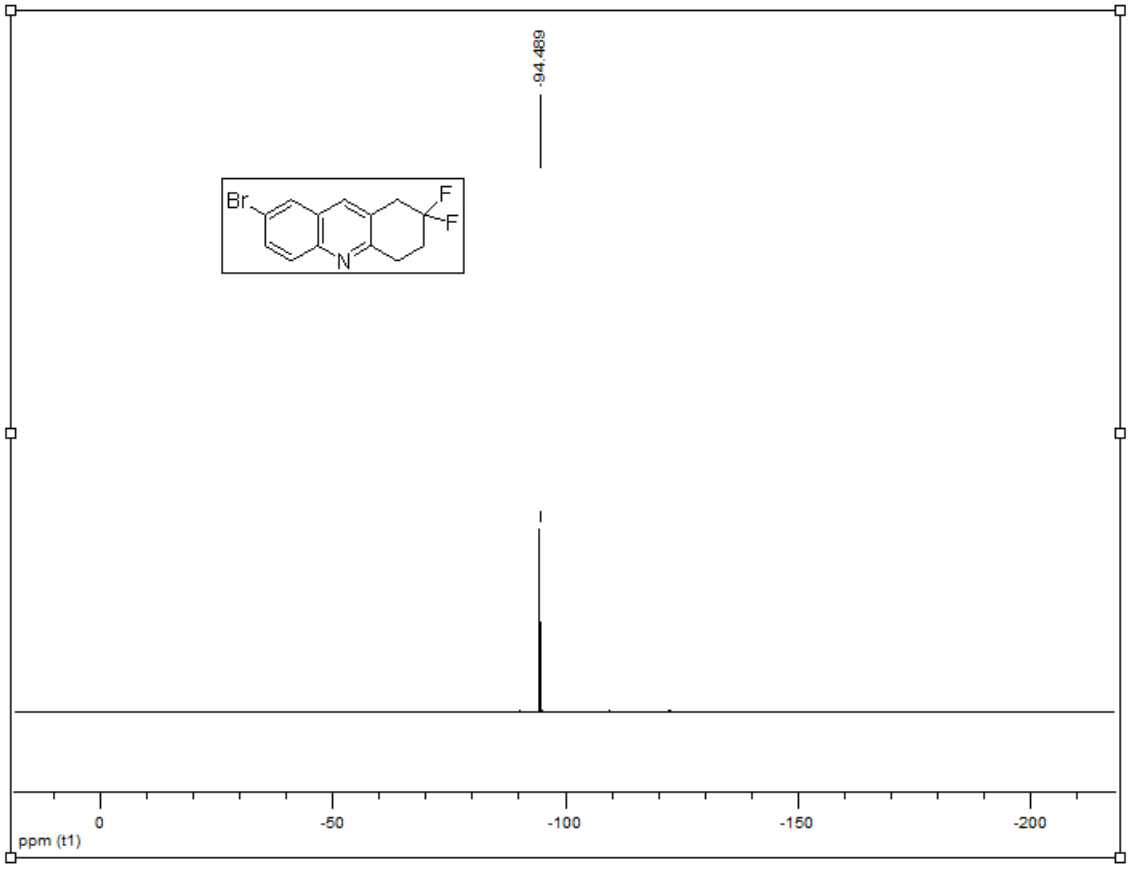
7-Chloro-2,2-difluoro-1,2,3,4-tetrahydroacridine **4p**



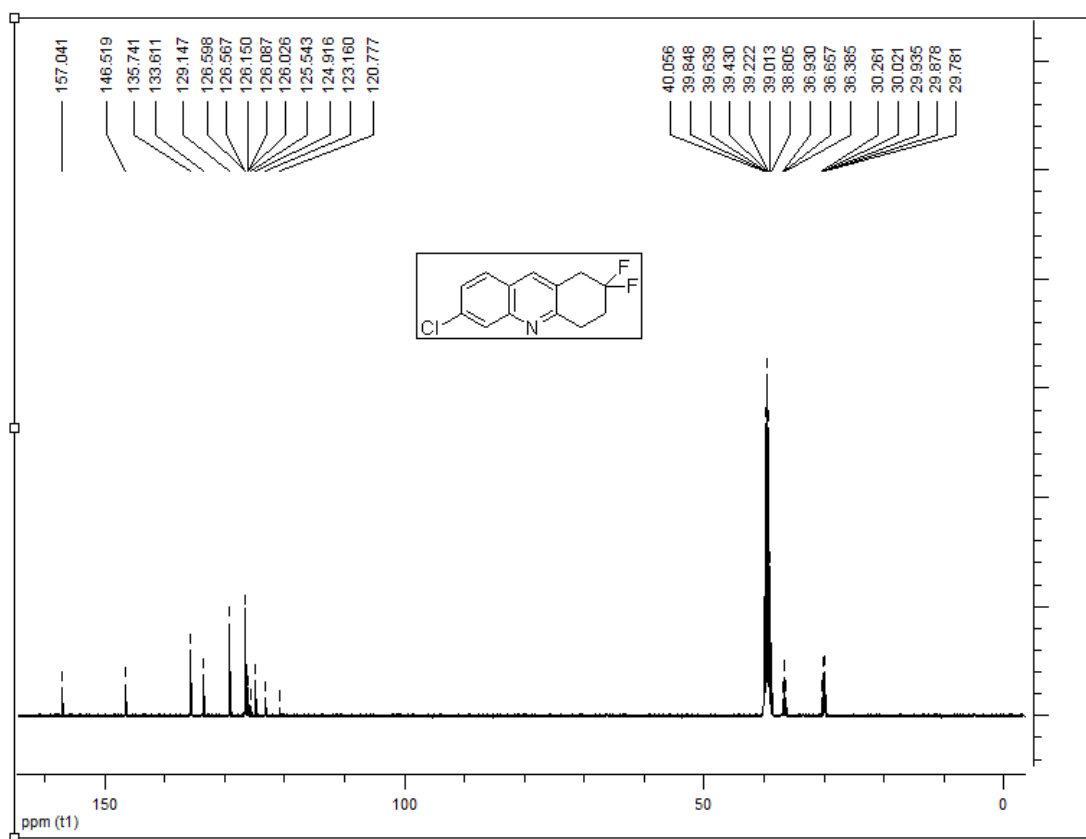
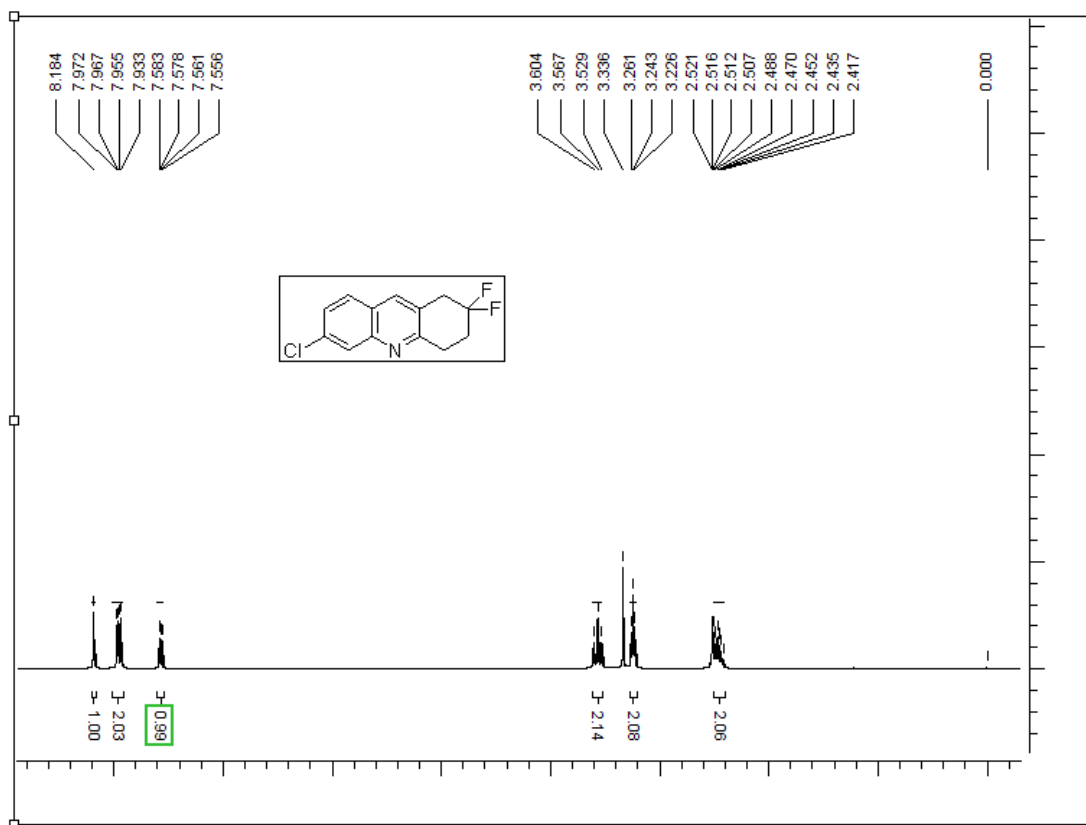


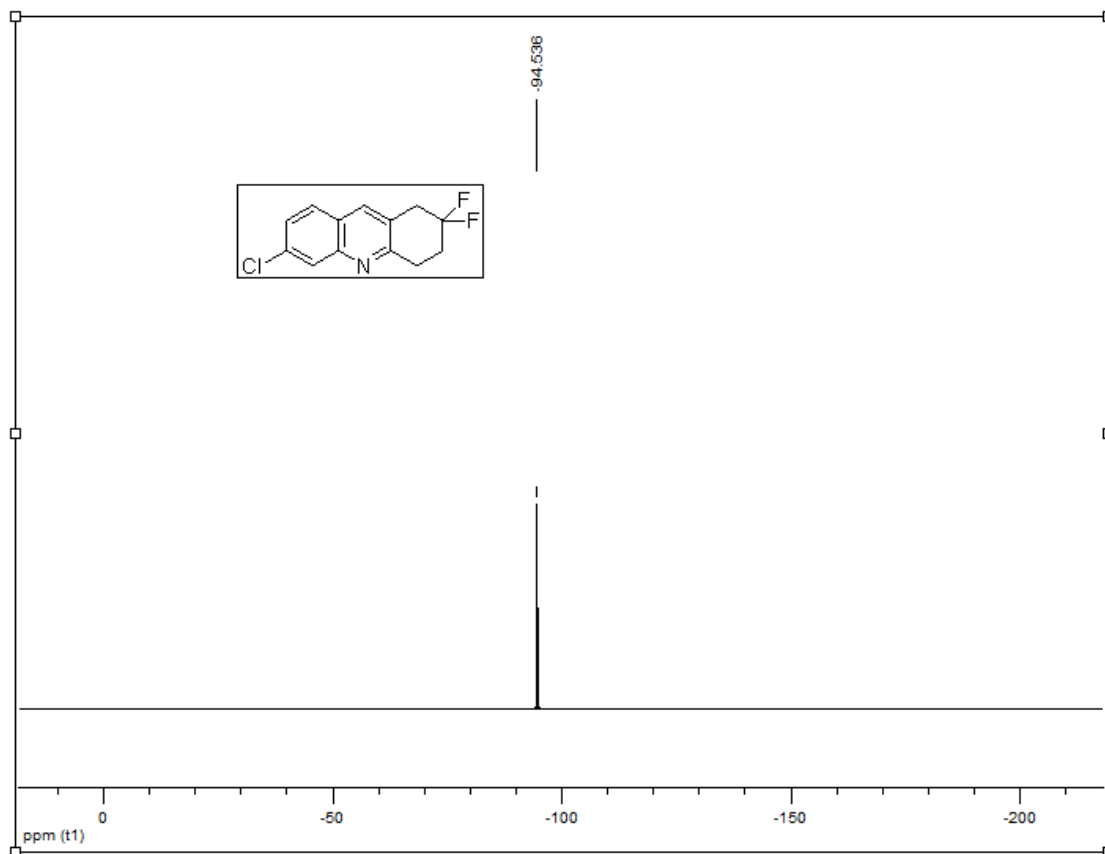
7-Bromo-2,2-dimethyl-1,2,3,4-tetrahydroacridine **4q**



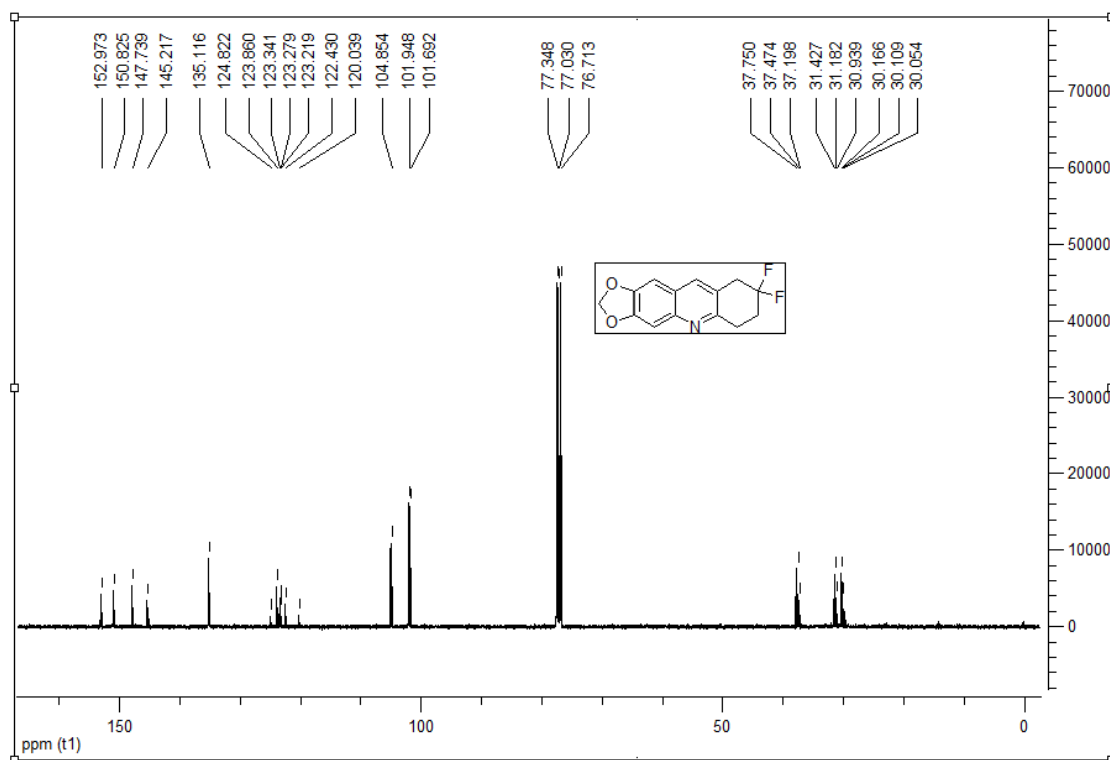
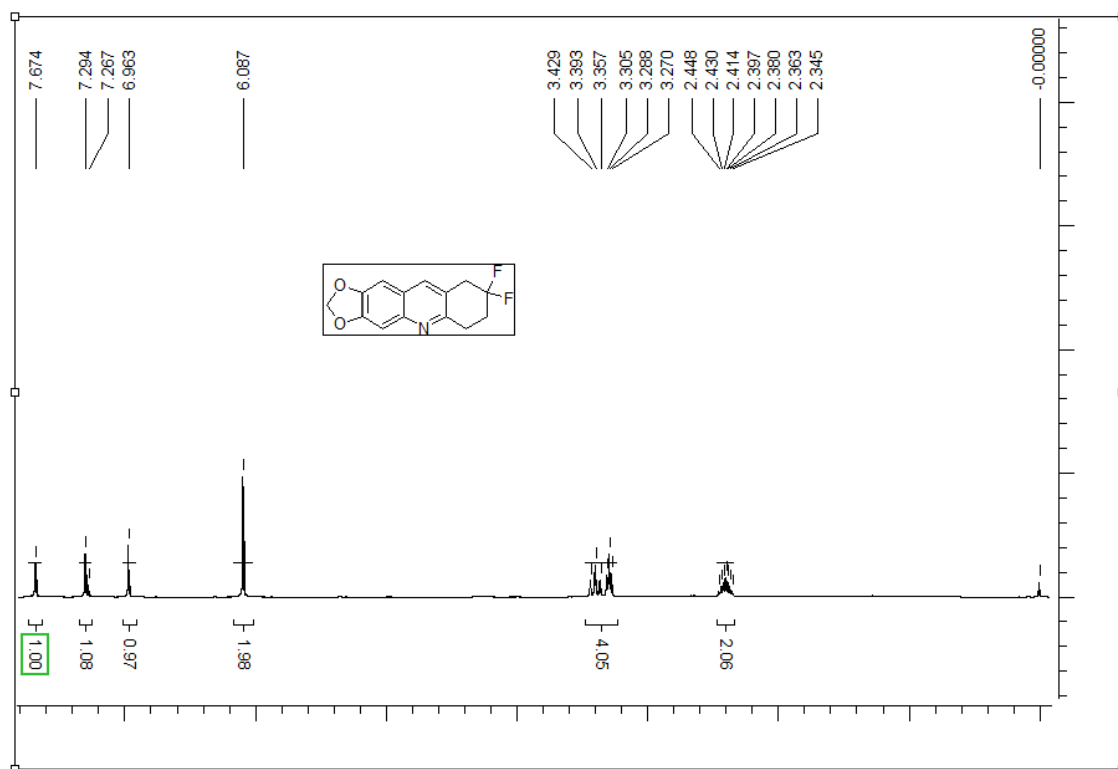


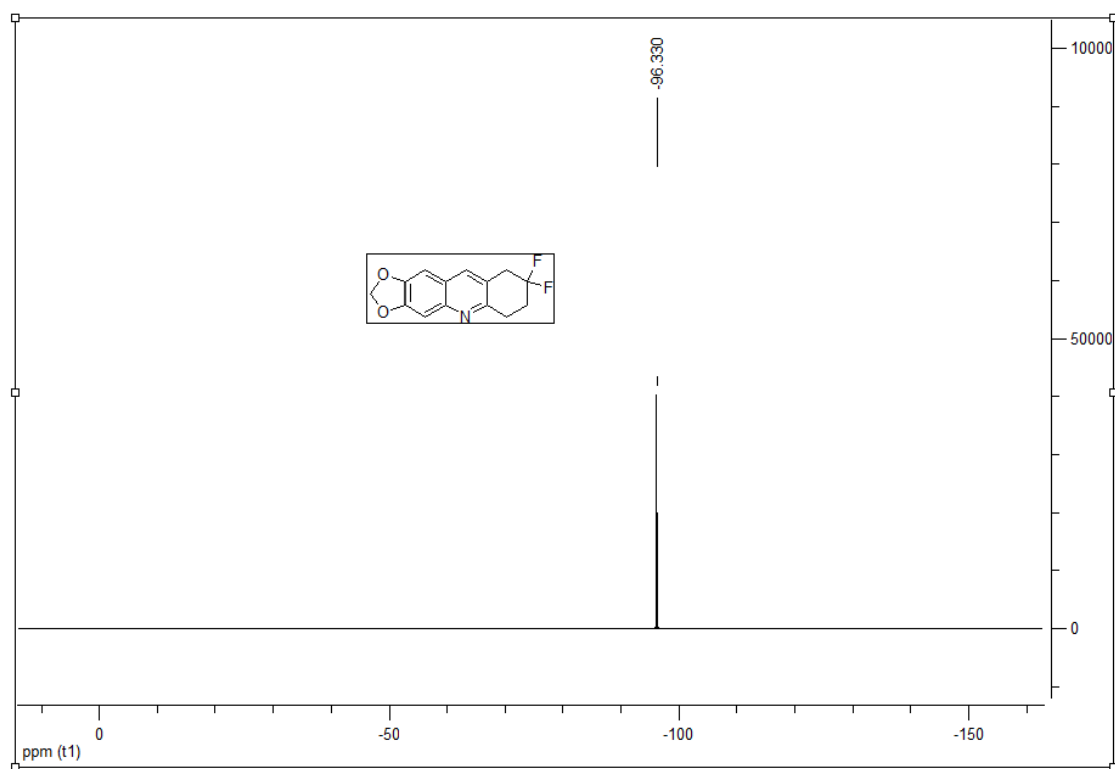
6-Chloro-2,2-difluoro-1,2,3,4-tetrahydroacridine **4r**



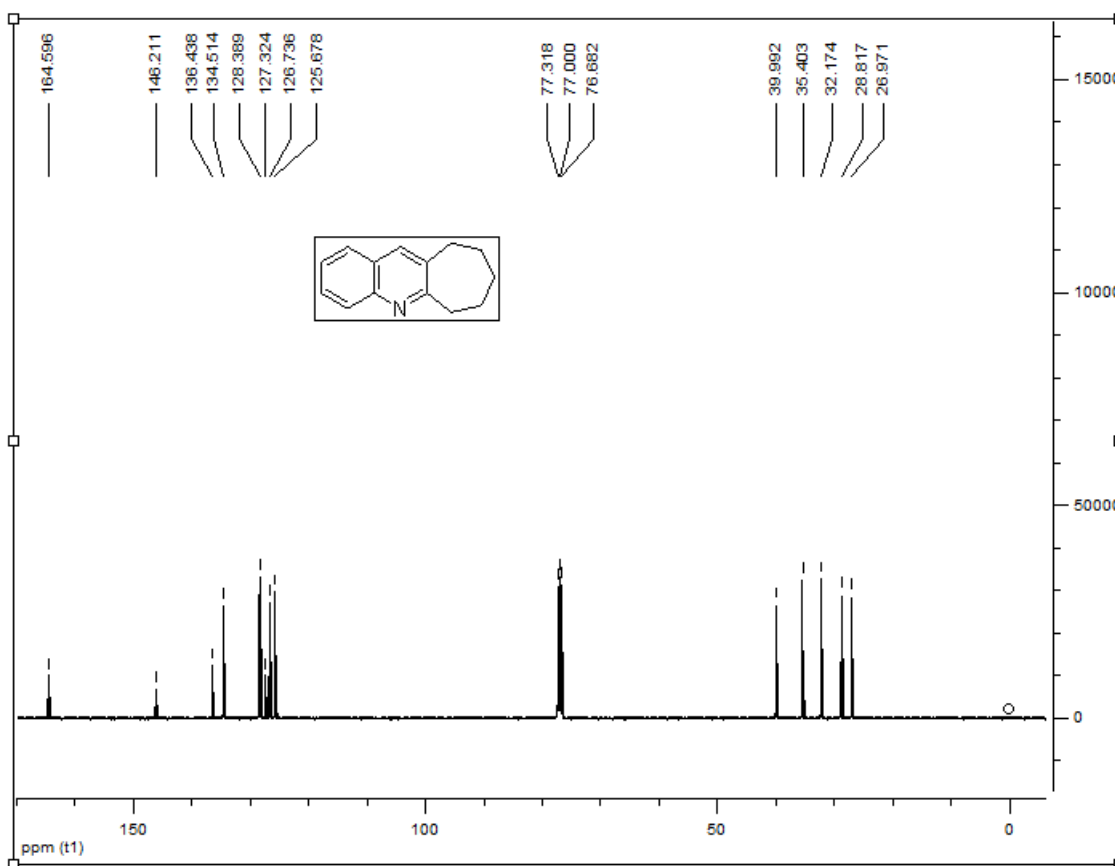
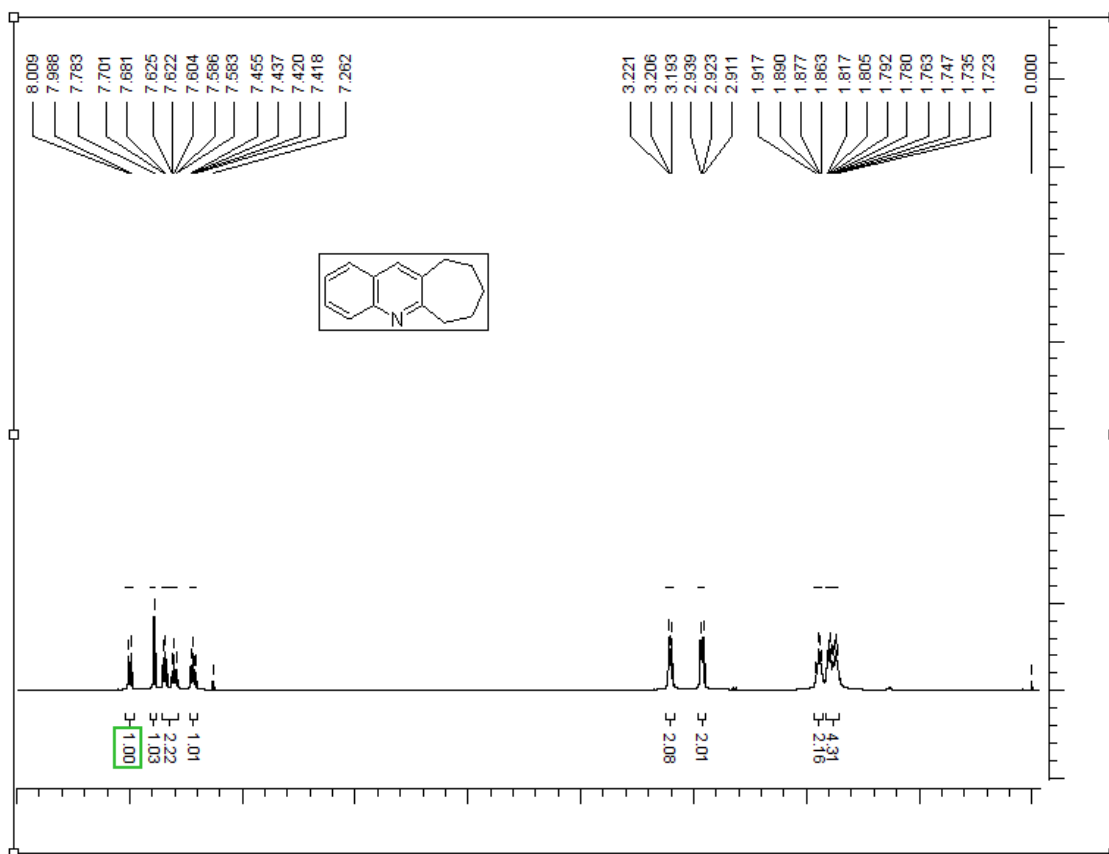


8,8-Difluoro-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-*b*]acridine **4s**.

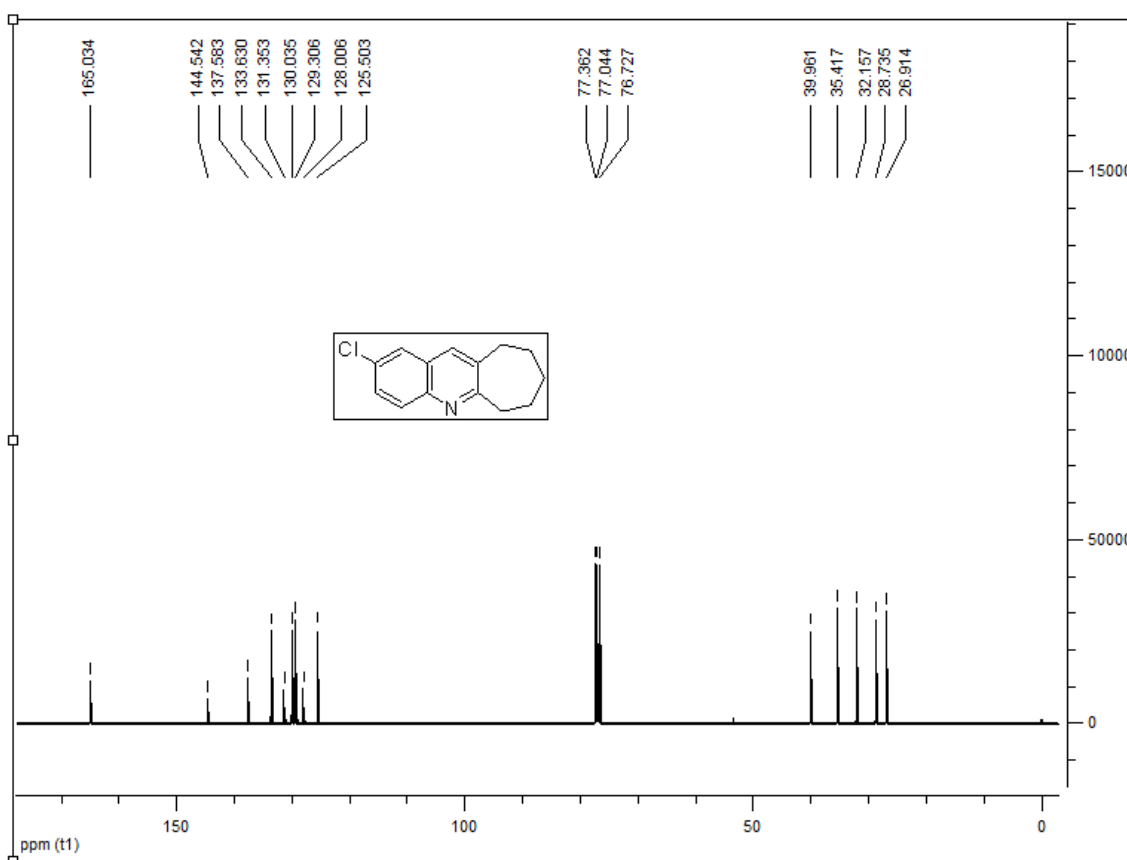
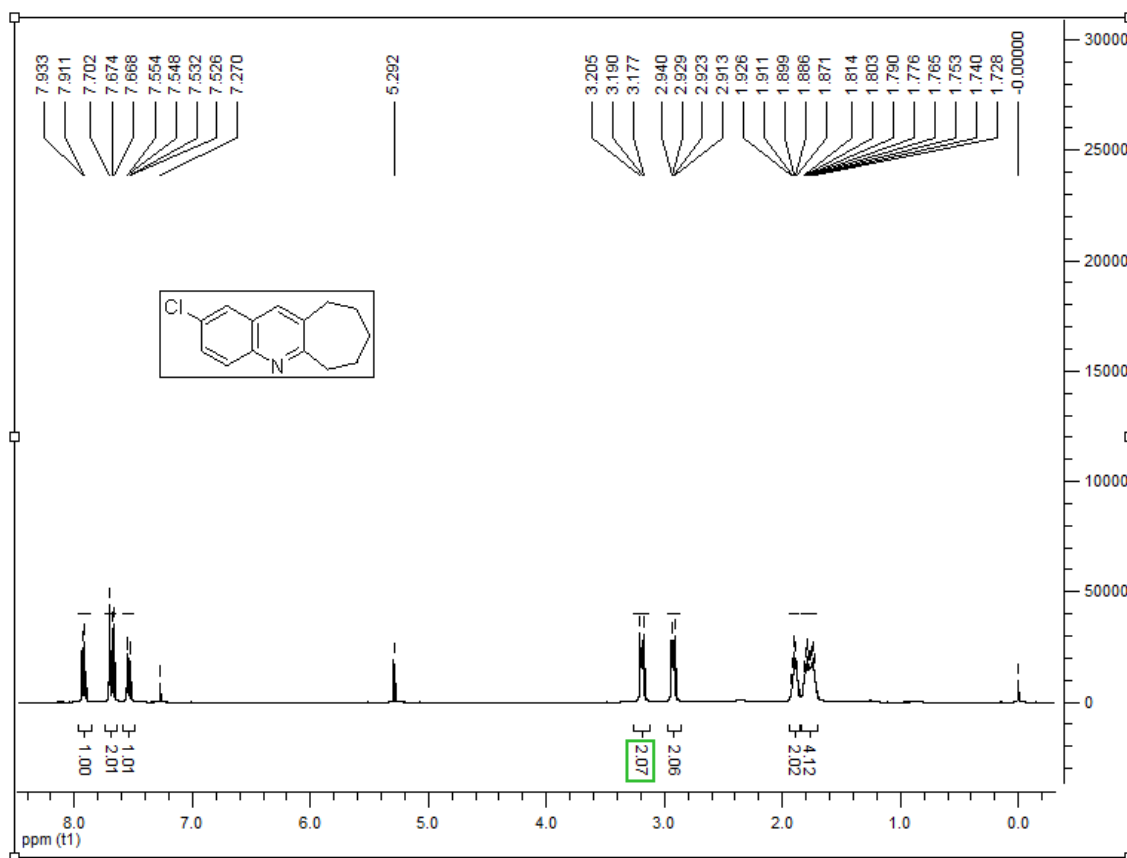




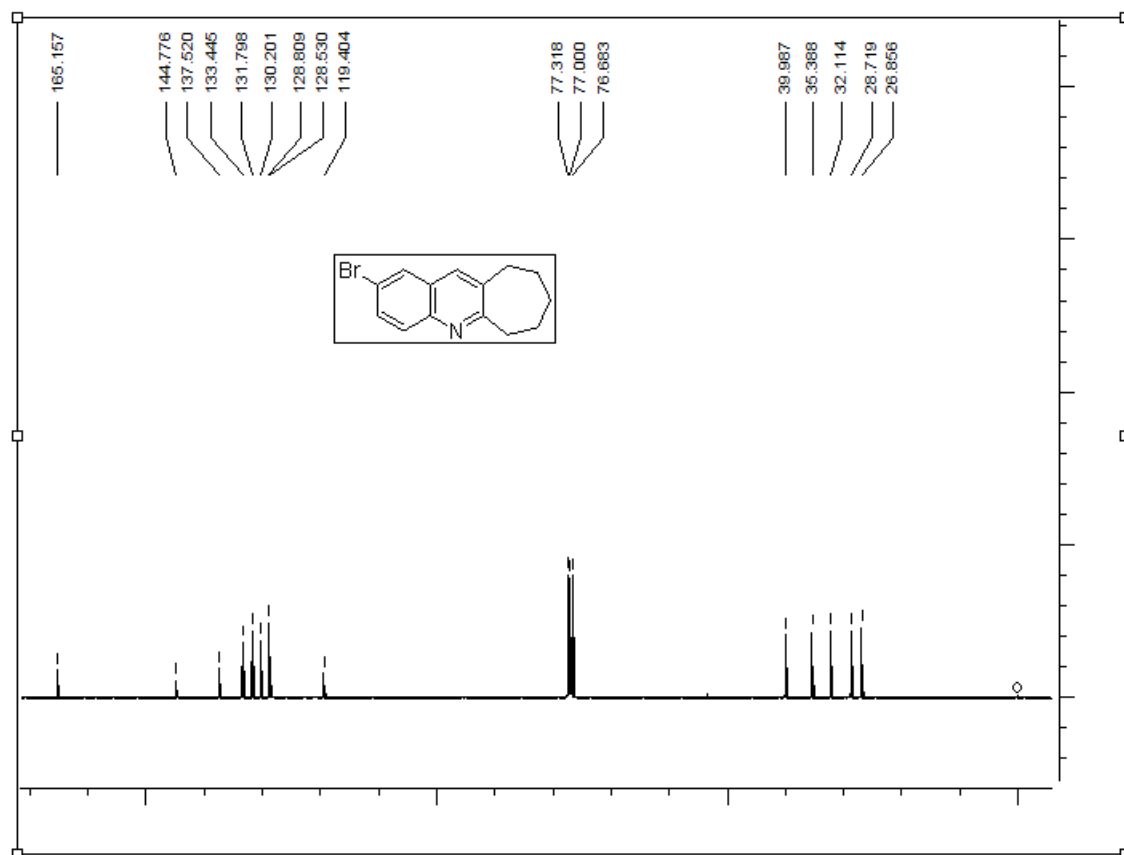
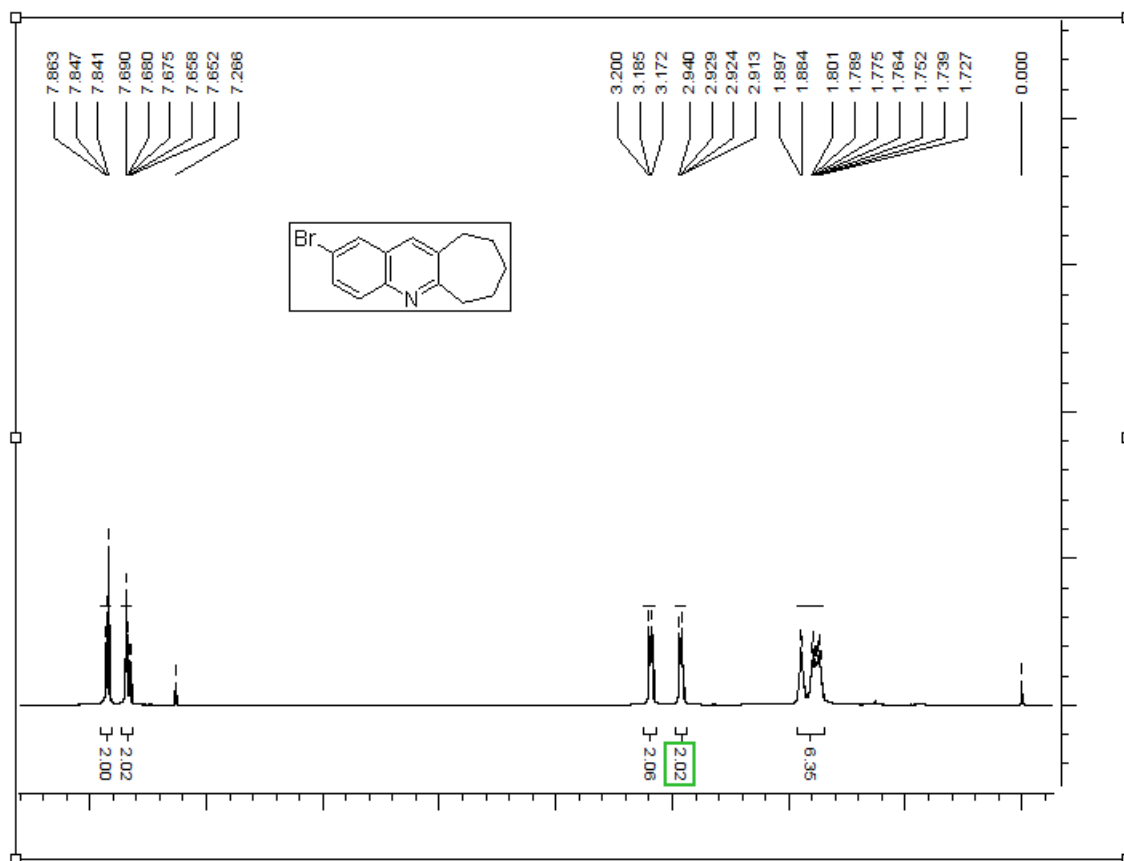
7,8,9,10-Tetrahydro-6H-cyclohepta[*b*]quinoline **4t**



2-Chloro-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline **4u**



2-Bromo-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline 4v



3-Chloro-7,8,9,10-tetrahydro-6H-cyclohepta[b]quinoline **4w**

