

Supporting Information

Iodine-Mediated Synthesis of Benzopyridothiazines via Tandem C–H Thiolation and Amination

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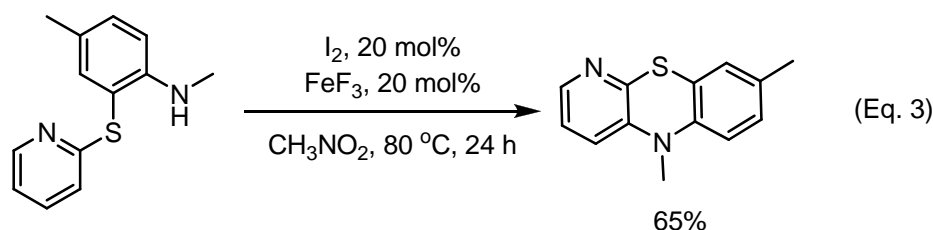
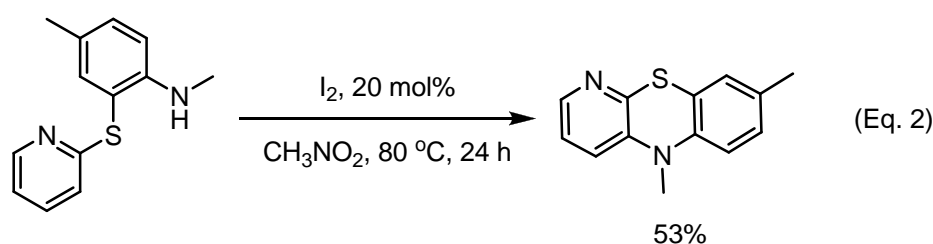
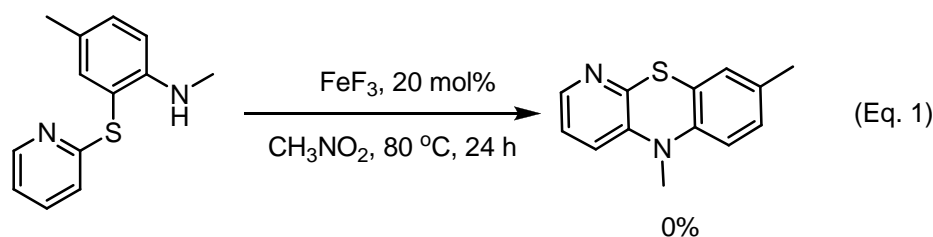
1. General Information

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-III 500 instrument (500 MHz for ^1H , 125 MHz for ^{13}C NMR spectroscopy) using CDCl_3 as the solvent. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker micrOTOF-Q II instrument. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR analysis was measured on Nicolet IS10 spectrometer (ATR).

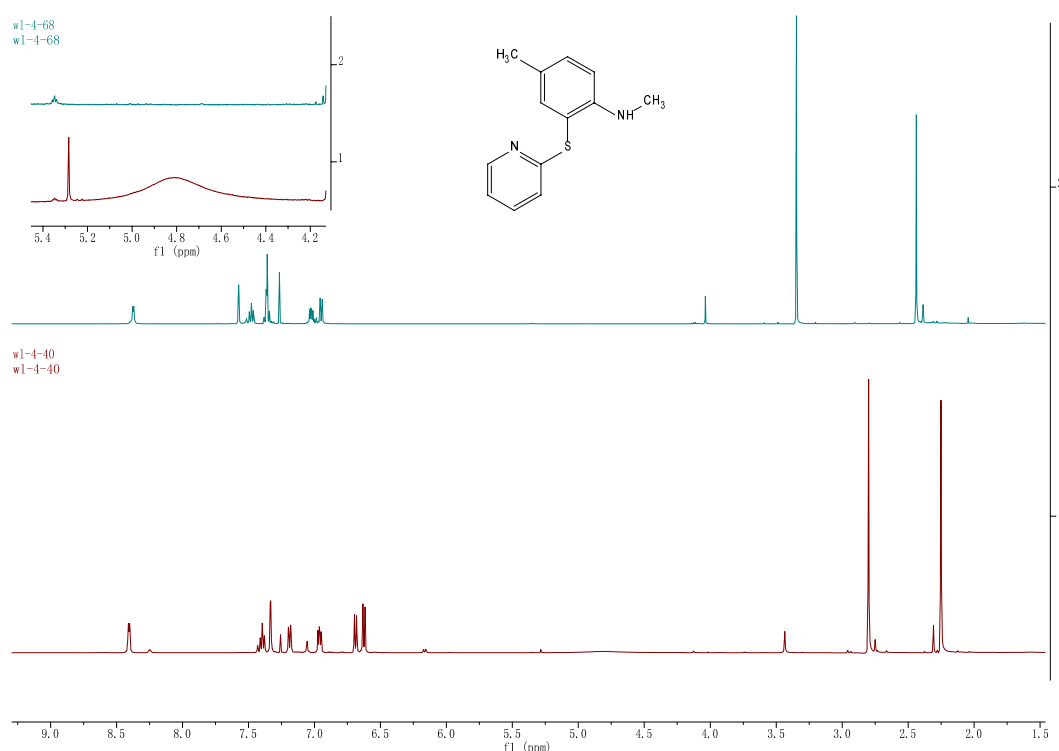
2. Typical Experimental Procedure

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with **1a** (0.2 mmol), **2a** (0.15 mmol), FeF_3 (0.04 mmol), I_2 (0.04 mmol) in CH_3NO_2 (2 mL) under air atmosphere. The reaction mixture was stirred at 80 °C for the indicated time. After the reaction finished, the mixture was poured into ethyl acetate, washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ and then brine. The aqueous layer was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product **3a**.

3. Control experiments

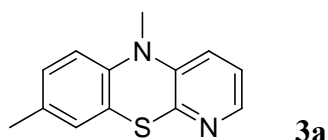


4. NMR study for the mixture of I₂ and intermediate B



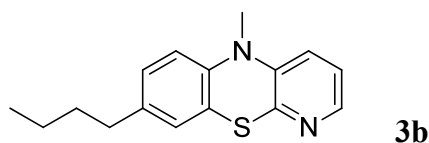
Note: the spectra in blue (w1-4-68): The mixture of **1a** and I₂ (1 equiv.) in CD₃CN at room temperature, stir for 24 hours. The spectra in red (w1-4-40): **1a** in CD₃CN at room temperature, stir for 24 hours.

5. NMR data and spectra for products 3a–3t and intermediate B



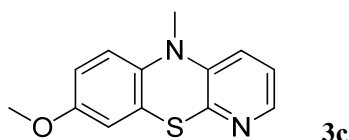
5,8-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (**3a**):

Yield: 28 mg (63%). Yellow solid, mp 88.6–90.3 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 4.8 Hz, 1H), 7.28 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.90 (s, 1H), 6.77 – 6.72 (m, 2H), 3.43 (s, 3H), 2.24 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 154.6, 144.1, 140.7, 133.0, 131.5, 127.2, 126.3, 119.7, 116.4, 116.1, 113.5, 32.3, 19.2. LRMS (EI, 70 eV) *m/z* (%): 228 (100), 213 (48), 227 (35), 195 (31), 229 (16) HRMS (ESI) for C₁₃H₁₃N₂S [M+H]⁺: calcd 229.0794, found 229.0798. IR (ATR, cm⁻¹): 3649, 3563, 1570, 1404, 1145, 812, 794, 764.



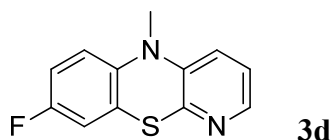
8-butyl-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (**3b**):

Yield: 35 mg (64%). Brown oil. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 4.6$ Hz, 1H), 7.26 (d, $J = 7.4$ Hz, 1H), 6.96 (d, $J = 8.2$ Hz, 1H), 6.90 (s, 1H), 6.74 (d, $J = 7.6$ Hz, 2H), 3.42 (s, 3H), 2.49 (t, $J = 7.6$ Hz, 2H), 1.55 (m, 2H), 1.32 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 145.1, 141.9, 137.7, 134.0, 127.6, 126.7, 120.7, 117.4, 117.2, 114.6, 34.5, 33.5, 33.3, 22.2, 13.9. LRMS (EI, 70 eV) m/z (%): 270 (95), 227 (100), 271 (17), 228 (15), 212 (10). HRMS (ESI) for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 271.1263, found 271.1266. IR (ATR, cm^{-1}): 3649, 2914, 1546, 1434, 1394, 1139, 812, 766.



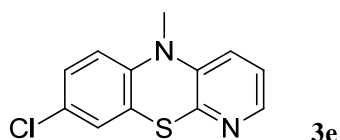
8-methoxy-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3c):

Yield: 32 mg (65%). Brown oil. ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, $J = 4.8$ Hz, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 8.8$ Hz, 1H), 6.75 (d, $J = 5.4$ Hz, 1H), 6.73 (d, $J = 3.0$ Hz, 1H), 6.69 (s, 1H), 3.76 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.8, 145.1, 137.7, 134.1, 122.2, 121.2, 117.3, 116.8, 115.3, 114.6, 112.8, 55.7, 33.5. LRMS (EI, 70 eV) m/z (%): 244 (100), 229 (79), 201 (26), 186 (19), 245 (16). HRMS (ESI) for $\text{C}_{13}\text{H}_{13}\text{ON}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 245.0743, found 245.0736. IR (ATR, cm^{-1}): 3556, 2855, 2352, 1550, 1394, 1248, 1023, 870.



8-fluoro-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3d):

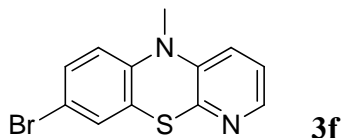
Yield: 19 mg (41%). Light yellow solid, mp 69.8–71.2 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 4.8$ Hz, 1H), 7.28 (d, $J = 7.4$ Hz, 1H), 6.85 (dd, $J = 16.8, 8.1$ Hz, 2H), 6.81 – 6.74 (m, 2H), 3.42 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) ^{13}C NMR (126 MHz, CDCl_3) δ 158.9 (d, $J_{\text{C-F}} = 254.6$ Hz), 155.4, 145.5, 140.5 (d, $J_{\text{C-F}} = 2.4$ Hz), 134.2, 122.9 (d, $J_{\text{C-F}} = 8.3$ Hz), 117.8, 116.3, 115.2 (d, $J_{\text{C-F}} = 8.3$ Hz), 114.0 (d, $J_{\text{C-F}} = 3.2$ Hz), 113.8, 33.6. LRMS (EI, 70 eV) m/z (%): 232 (100), 217 (57), 231 (41), 199 (33), 233 (16). HRMS (ESI) for $\text{C}_{12}\text{H}_{10}\text{FN}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 233.0542 found 233.0548. IR (ATR, cm^{-1}): 3636, 2908, 1497, 1430, 1407, 1268, 859, 767.



8-chloro-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3e):

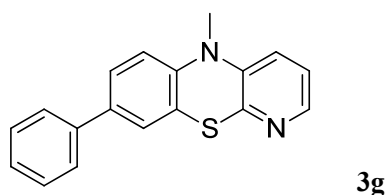
Yield: 25 mg (50%). Yellow solid, mp 105.4–107.1 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 4.9$ Hz, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.14 – 7.10 (m, 1H), 7.06 (d, $J = 2.1$ Hz, 1H), 6.79 (d, $J = 7.4$ Hz, 1H), 6.75 (d, $J = 8.7$ Hz, 1H), 3.42 (s, 3H). ^{13}C NMR

(125 MHz, CDCl₃) δ 155.1, 145.5, 143.0, 134.3, 128.0, 127.5, 126.4, 122.8, 118.0, 116.4, 115.4, 33.5. LRMS (EI, 70 eV) m/z (%): 248 (100), 233 (44), 350 (37), 247 (32), 213 (31). HRMS (ESI) for C₁₂H₁₀ClN₂S [M+H]⁺: calcd 249.0248, found 249.0255. IR (ATR, cm⁻¹): 3748, 3655, 2338, 1427, 1401, 1142, 804, 792.



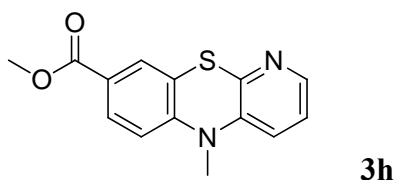
8-bromo-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3f):

Yield: 23 mg (40%). Light grey solid, mp 122.9–124.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (dd, J = 4.8, 1.3 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.18 (d, J = 2.1 Hz, 1H), 6.79 (dd, J = 7.4, 5.0 Hz, 1H), 6.68 (d, J = 8.7 Hz, 1H), 3.41 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 155.0, 145.4, 143.5, 134.3, 130.4, 129.1, 123.2, 118.0, 116.4, 115.8, 115.2, 33.4. LRMS (EI, 70 eV) m/z (%): 292 (100), 294 (99), 213 (80), 279 (34), 277 (34). HRMS (ESI) for C₁₂H₁₀BrN₂S [M+H]⁺: calcd 292.9743, found 292.9753. IR (ATR, cm⁻¹): 3642, 2345, 1662, 1480, 1430, 1145, 796, 758.



5-methyl-8-phenyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3g):

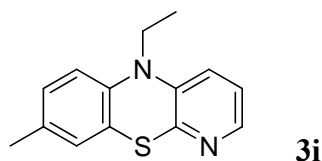
Yield: 40 mg (69%). Grey solid, mp 116.8–118.3 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (dd, J = 4.9, 1.3 Hz, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.31 – 7.26 (m, 3H), 6.88 (d, J = 8.4 Hz, 1H), 6.75 (dd, J = 7.4, 5.0 Hz, 1H), 3.46 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 155.2, 145.2, 143.4, 139.7, 136.1, 134.2, 128.8, 127.2, 126.5, 126.3, 125.3, 121.4, 117.8, 117.0, 115.0, 33.4. LRMS (EI, 70 eV) m/z (%): 290 (100), 275 (35), 289 (29), 291 (22), 257 (15). HRMS (ESI) for C₁₈H₁₅N₂S [M+H]⁺: calcd 291.0950, found 291.0955. IR (ATR, cm⁻¹): 3655, 2339, 1544, 1427, 1398, 1136, 820, 754.



methyl 5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine-8-carboxylate (3h):

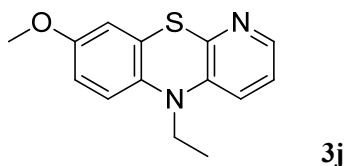
Yield: 17 mg (32%). Yellow solid, mp 120.7–122.0 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (dd, J = 4.9, 1.5 Hz, 1H), 7.83 (dd, J = 8.5, 1.9 Hz, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.28 (m, 1H), 6.85 – 6.80 (m, 2H), 3.88 (s, 3H), 3.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.2, 154.4, 148.2, 145.4, 134.3, 129.8, 128.0, 124.6, 120.8, 118.6, 116.8, 114.0, 52.0, 33.6. LRMS (EI, 70 eV) m/z (%): 272 (100), 213 (26), 241(20),

273 (20), 257 (17). HRMS (ESI) for $C_{14}H_{13}N_2O_2S$ $[M+H]^+$: calcd 273.0692, found 273.0722. IR (ATR, cm^{-1}): 3669, 2345, 1709, 1424, 1298, 1116, 787, 761.



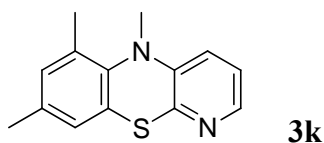
5-ethyl-8-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3i):

Yield: 19 mg (41%). Yellow oil. 1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, $J = 4.3$ Hz, 1H), 7.19 (d, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 6.84 (s, 1H), 6.77 (d, $J = 8.3$ Hz, 1H), 6.69 (t, $J = 5.9$ Hz, 1H), 4.12 – 4.07 (m, 2H), 2.22 (s, 3H), 1.38 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 144.9, 140.2, 133.8, 132.3, 128.0, 127.4, 120.8, 117.3, 116.7, 115.0, 39.8, 20.1, 12.5. LRMS (EI, 70 eV) m/z (%): 242 (100), 213 (77), 227 (62), 214 (44), 195 (24). HRMS (ESI) for $C_{14}H_{15}N_2S$ $[M+H]^+$: calcd 243.0950, found 243.0962. IR (ATR, cm^{-1}): 3748, 3642, 1659, 1546, 1407, 1109, 802.



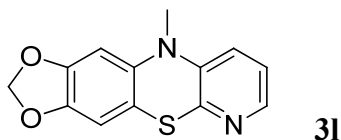
5-ethyl-8-methoxy-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3j):

Yield: 22 mg (42%). Brown oil. 1H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.20 (dd, $J = 7.4, 1.7$ Hz, 1H), 6.80 (d, $J = 8.9$ Hz, 1H), 6.71 – 6.66 (m, 2H), 6.63 (d, $J = 2.9$ Hz, 1H), 4.09 (q, $J = 6.9$ Hz, 2H), 3.75 (s, 3H), 1.37 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 155.0, 145.0, 136.1, 134.0, 122.3, 117.1, 116.3, 115.8, 112.7, 112.6, 55.7, 39.9, 12.6. LRMS (EI, 70 eV) m/z (%): 258 (100), 229 (73), 243 (46), 186 (23), 215 (22). HRMS (ESI) for $C_{14}H_{15}ON_2S$ $[M+H]^+$: calcd 259.0900, found 259.0891. IR (ATR, cm^{-1}): 3669, 2914, 2372, 1659, 1523, 1490, 1212, 837.



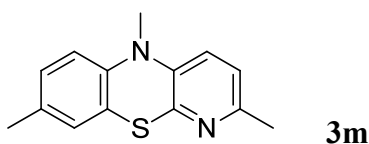
5,6,8-trimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3k):

Yield: 26 mg (54%). Brown oil. 1H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, $J = 4.9, 1.5$ Hz, 1H), 7.28 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.82 (s, 1H), 6.78 (s, 1H), 6.75 (dd, $J = 7.5, 5.0$ Hz, 1H), 3.58 (s, 3H), 2.35 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 145.2, 140.1, 133.8, 133.5, 132.4, 128.8, 127.9, 125.3, 120.6, 117.7, 40.0, 20.9, 20.2. LRMS (EI, 70 eV) m/z (%): 242 (100), 227 (87), 241 (30), 209 (24), 243 (17). HRMS (ESI) for $C_{14}H_{15}N_2S$ $[M+H]^+$: calcd 243.0950, found 243.0959. IR (ATR, cm^{-1}): 3561, 2346, 1570, 1449, 1399, 1126, 846, 772.



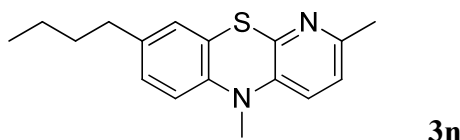
3l

10-methyl-10H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]pyrido[3,2-e][1,4]thiazine (3l): Yield: 35 mg (67%). Brown solid, mp 111.8–113.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 4.9 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 6.77 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.60 (s, 1H), 6.51 (s, 1H), 5.92 (s, 2H), 3.40 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 156.1, 148.0, 145.2, 143.5, 139.5, 134.1, 117.8, 117.5, 111.6, 107.2, 101.6, 97.8, 34.0. LRMS (EI, 70eV) *m/z* (%): 258 (100), 243 (37), 200 (25), 225 (20), 226 (19). HRMS (ESI) for C₁₃H₁₁O₂N₂S [M+H]⁺: calcd 259.0536, found 259.0543. IR (ATR, cm⁻¹): 3040, 2848, 1494, 1434, 1401, 1309, 846, 761.



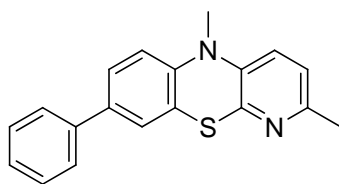
3m

2,5,8-trimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3m): Yield: 29 mg (60%). Grey oil. ¹H NMR (500 MHz, CDCl₃) δ 7.14 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.89 (s, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.58 (t, *J* = 10.9 Hz, 1H), 3.42 (s, 3H), 2.39 (s, 3H), 2.22 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 154.9, 154.3, 142.0, 134.3, 132.2, 128.0, 127.3, 121.1, 116.6, 114.5, 113.1, 33.2, 23.9, 20.2. LRMS (EI, 70 eV) *m/z* (%): 242 (100), 227 (43), 241 (42), 209 (38), 243 (17). HRMS (ESI) for C₁₄H₁₅N₂S [M+H]⁺: calcd 243.0950, found 243.0954. IR (ATR, cm⁻¹): 3649, 2961, 2372, 1500, 1434, 1142, 804, 658.



3n

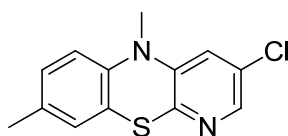
8-butyl-2,5-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3n): Yield: 29 mg (51%). Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.14 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 3.42 (s, 3H), 2.49 (t, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 1.54 (m, 2H), 1.32 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 155.0, 154.3, 142.2, 137.4, 134.3, 127.4, 126.6, 121.0, 116.6, 114.5, 113.1, 34.5, 33.5, 33.2, 23.9, 22.2, 13.9. LRMS (EI, 70 eV) *m/z* (%) 241 (100), 284 (95), 285 (19), 242 (18), 209 (15). HRMS (ESI) for C₁₇H₂₁N₂S [M+H]⁺: calcd 285.1420, found 285.1422. IR (ATR, cm⁻¹): 3662, 2914, 2345, 1639, 1546, 1377, 1142, 812.



3o

2,5-dimethyl-8-phenyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3o):

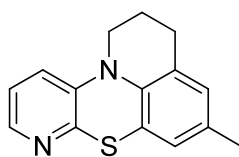
Yield: 33 mg (55%). Yellow solid, mp 97.5–98.8 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.23 (t, *J* = 5.4 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 3.40 (s, 3H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 154.5, 154.5, 143.7, 139.9, 135.8, 134.4, 128.8 (s, 2C), 127.1, 126.5 (s, 2C), 126.1, 125.2, 121.7, 116.9, 114.8, 112.9, 33.3, 23.9. LRMS (EI, 70 eV) *m/z* (%): 304 (100), 303 (36), 289 (28), 305 (23), 271 (14). HRMS (ESI) for C₁₉H₁₇N₂S [M+H]⁺: calcd 305.1107, found 305.1115. IR (ATR, cm⁻¹): 3642, 2956, 1507, 1437, 1377, 1145, 816, 758.



3p

3-chloro-5,8-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3p):

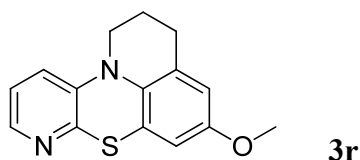
Yield: 32 mg (61%). Yellow solid, mp 117.7–119.4 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 1.9 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 3.39 (s, 3H), 2.24 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 153.9, 143.0, 141.2, 133.3, 132.9, 128.5, 127.4, 124.6, 119.8, 118.8, 114.7, 33.4, 20.2. LRMS (EI, 70 eV) *m/z* (%): 262 (100), 247 (61), 264 (39), 229 (25), 249 (22). HRMS (ESI) for C₁₃H₁₂ClN₂S [M+H]⁺: calcd 263.0404, found 263.0414. IR (ATR, cm⁻¹): 2974, 2908, 2338, 1646, 1430, 1245, 888, 789.



3q

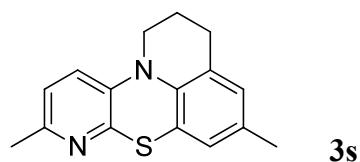
5-methyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3q):

Yield: 30 mg (59%). Yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 4.9 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 6.72 – 6.66 (m, 3H), 3.92 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 6.1 Hz, 2H), 2.18 (s, 3H), 2.04 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 154.7, 144.9, 137.3, 133.7, 132.0, 128.9, 125.7, 125.3, 118.6, 117.3, 116.3, 44.7, 28.0, 21.6, 20.1. LRMS (EI, 70 eV) *m/z* (%): 254 (100), 253 (23), 255 (18), 224 (18), 221 (17). HRMS (ESI) for C₁₅H₁₅N₂S [M+H]⁺: calcd 255.0950, found 255.0954. IR (ATR, cm⁻¹): 3053, 2941, 1570, 1411, 1125, 847, 789, 718.



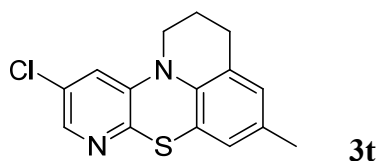
5-methoxy-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3r):

Yield: 24 mg (45%). Black oil. ^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, $J = 4.8$ Hz, 1H), 7.22 (d, $J = 7.4$ Hz, 1H), 6.70 (dd, $J = 7.3, 5.0$ Hz, 1H), 6.49 (d, $J = 2.7$ Hz, 1H), 6.45 (d, $J = 2.6$ Hz, 1H), 3.93 (t, $J = 6.0$ Hz, 2H), 3.72 (s, 3H), 2.72 (t, $J = 6.2$ Hz, 2H), 2.04 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.2, 154.9, 145.0, 133.8, 133.4, 126.8, 120.1, 117.1, 115.8, 113.5, 110.6, 55.6, 44.5, 28.3, 21.6. LRMS (EI, 70 eV) m/z (%): 270 (100), 255 (56), 271 (16), 227 (14), 199 (11). HRMS (ESI) for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$: calcd 271.0900, found 271.0900. IR (ATR, cm^{-1}): 3656, 2346, 1573, 1546, 1407, 1139, 1043, 758.



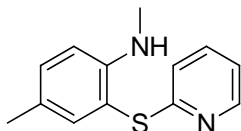
5,9-dimethyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3s):

Yield: 31mg (58%). Grey oil. ^1H NMR (500 MHz, CDCl_3) δ 7.00 (d, $J = 7.5$ Hz, 1H), 6.60 (d, $J = 5.1$ Hz, 1H), 6.58 (s, 1H), 6.48 (d, $J = 7.5$ Hz, 1H), 3.86 (t, $J = 6.0$ Hz, 2H), 2.60 (t, $J = 6.1$ Hz, 2H), 2.27 (s, 3H), 2.09 (s, 3H), 1.94 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 153.1, 153.0, 136.6, 132.9, 130.6, 127.7, 124.5, 124.2, 117.9, 115.3, 111.0, 43.4, 27.1, 22.9, 20.7, 19.1. LRMS (EI, 70 eV) m/z (%): 268 (100), 235 (24), 267 (23), 269 (19), 253 (15). HRMS (ESI) for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 269.1107, found 269.1105. IR (ATR, cm^{-1}): 3649, 2936, 1865, 1719, 1503, 1185, 849, 663.



10-chloro-5-methyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3t):

Yield: 37 mg (64%). Yellow solid, mp 138.6–140.2 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.88 (dd, $J = 2.2, 0.9$ Hz, 1H), 7.16 (t, $J = 2.1$ Hz, 1H), 6.67 (d, $J = 10.6$ Hz, 2H), 3.85 (t, $J = 6.0$, 2H), 2.68 (t, $J = 6.1$ Hz, 2H), 2.18 (s, 3H), 2.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 153.0, 142.8, 136.8, 132.9, 132.3, 129.1, 125.8, 125.4, 124.2, 117.8, 117.7, 44.9, 27.9, 21.5, 20.1. LRMS (EI, 70 eV) m/z (%): 288 (100), 290 (36), 289 (24), 287 (18), 258 (17). HRMS (ESI) for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{S}$ $[\text{M}+\text{H}]^+$: calcd 289.0561, found 289.0569. IR (ATR, cm^{-1}): 3642, 3556, 1716, 1500, 1420, 1102, 849, 746.

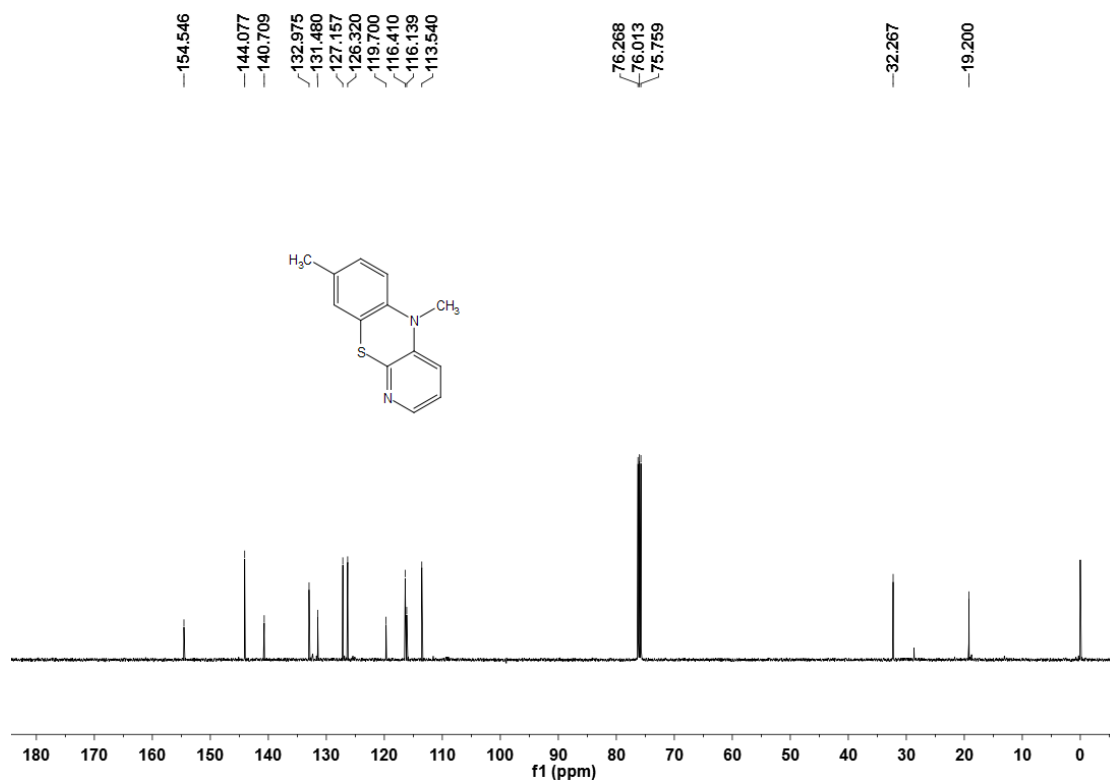
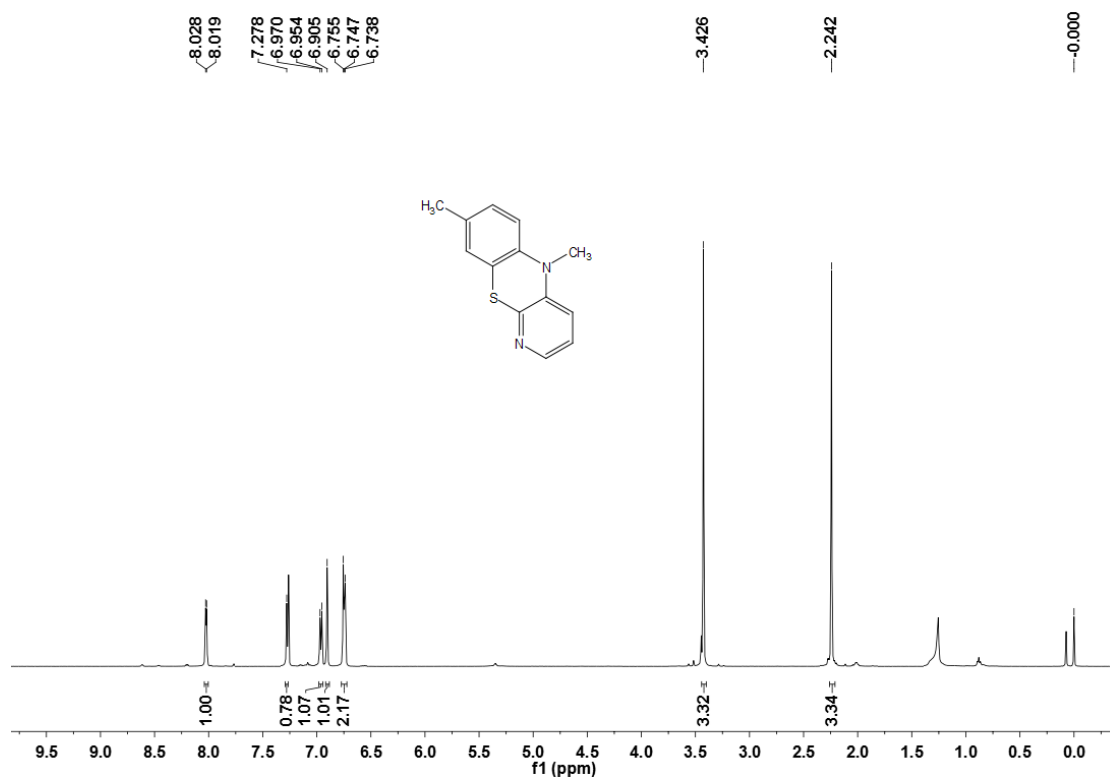


Intermediate **B**

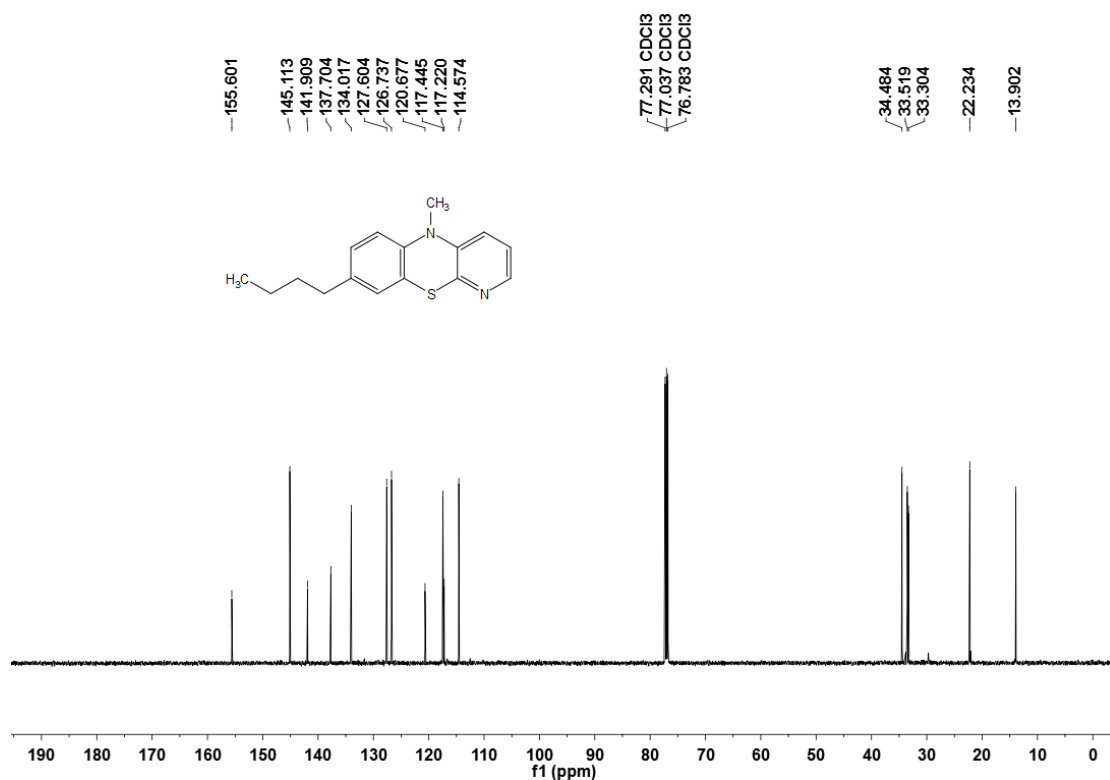
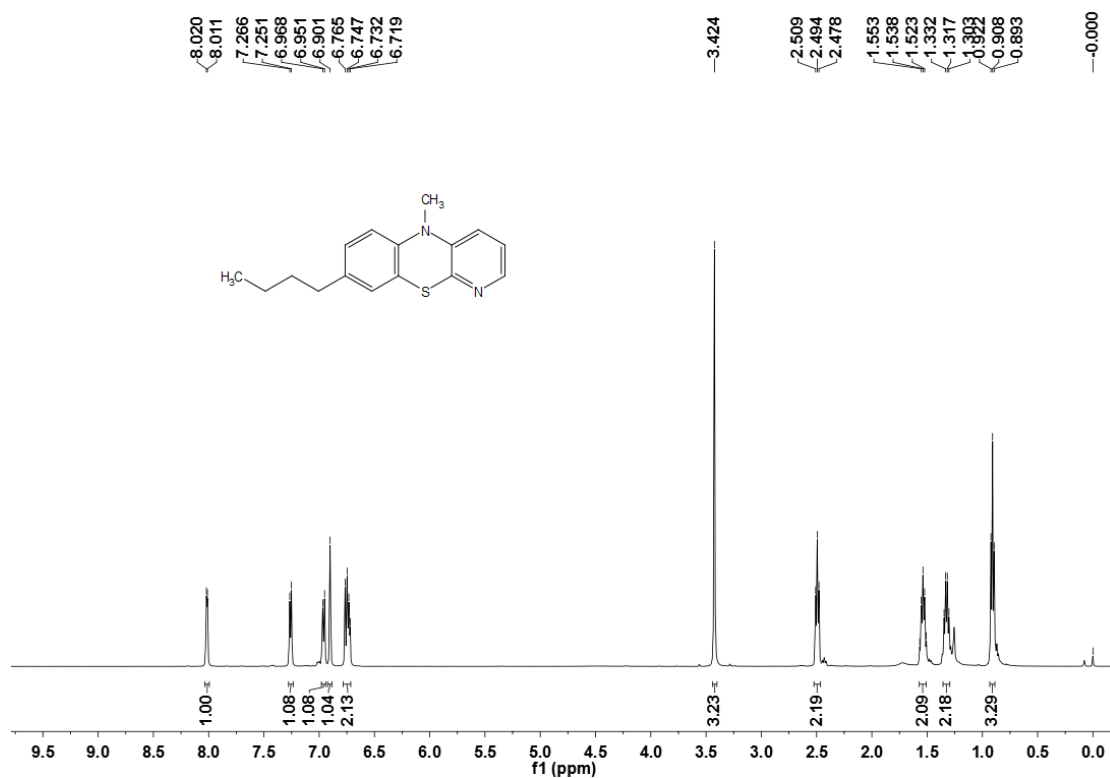
N,4-dimethyl-2-(pyridin-2-ylthio)aniline (B):

Yield: 110 mg (48%). Yellow solid, mp 70.6–72.3 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (d, *J* = 4.2 Hz, 1H), 7.47 – 7.35 (m, 1H), 7.33 (d, *J* = 1.0 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.96 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 4.79 (brs, 1H), 2.80 (s, 3H), 2.25 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 161.0, 149.5, 148.7, 138.1, 136.7, 132.7, 126.2, 119.8, 119.6, 112.2, 110.4, 30.7, 20.1. LRMS (EI, 70 eV) *m/z* (%): 197 (100), 230 (25), 182 (17), 200 (16), 198 (15). HRMS (ESI) for C₁₃H₁₅N₂S [M+H]⁺: calcd 231.0950, found 231.0953. IR (ATR, cm⁻¹): 3642, 2352, 1656, 1513, 1420, 1169, 809, 754.

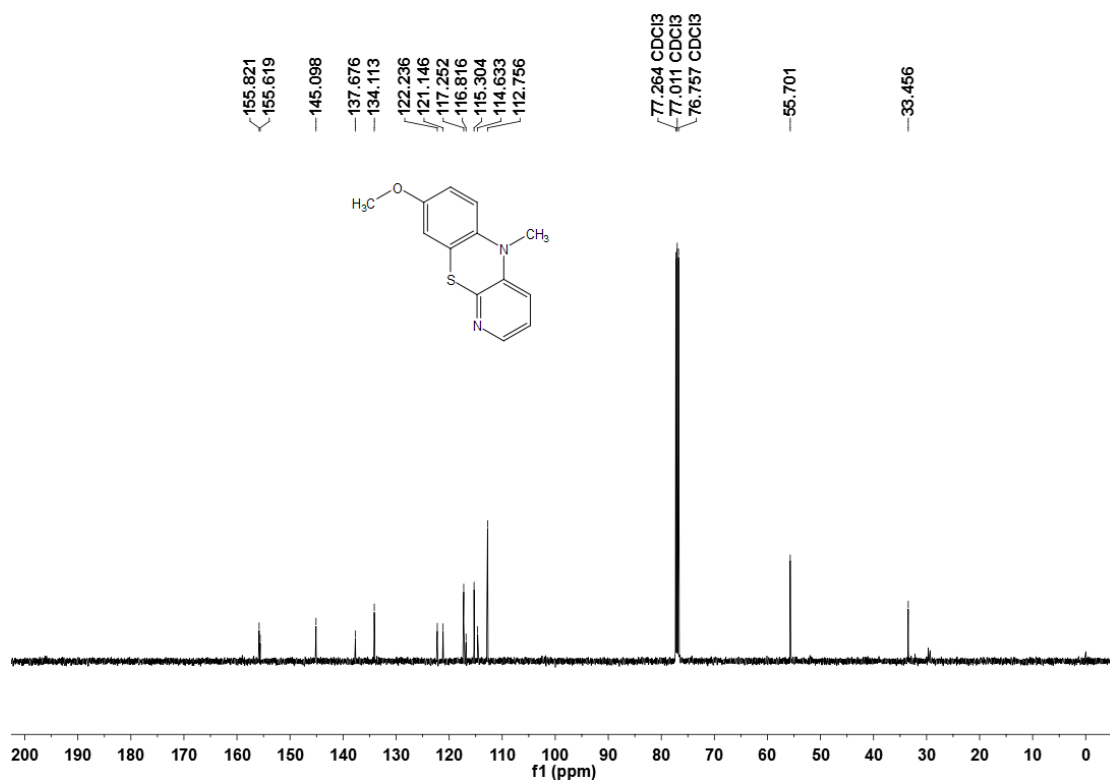
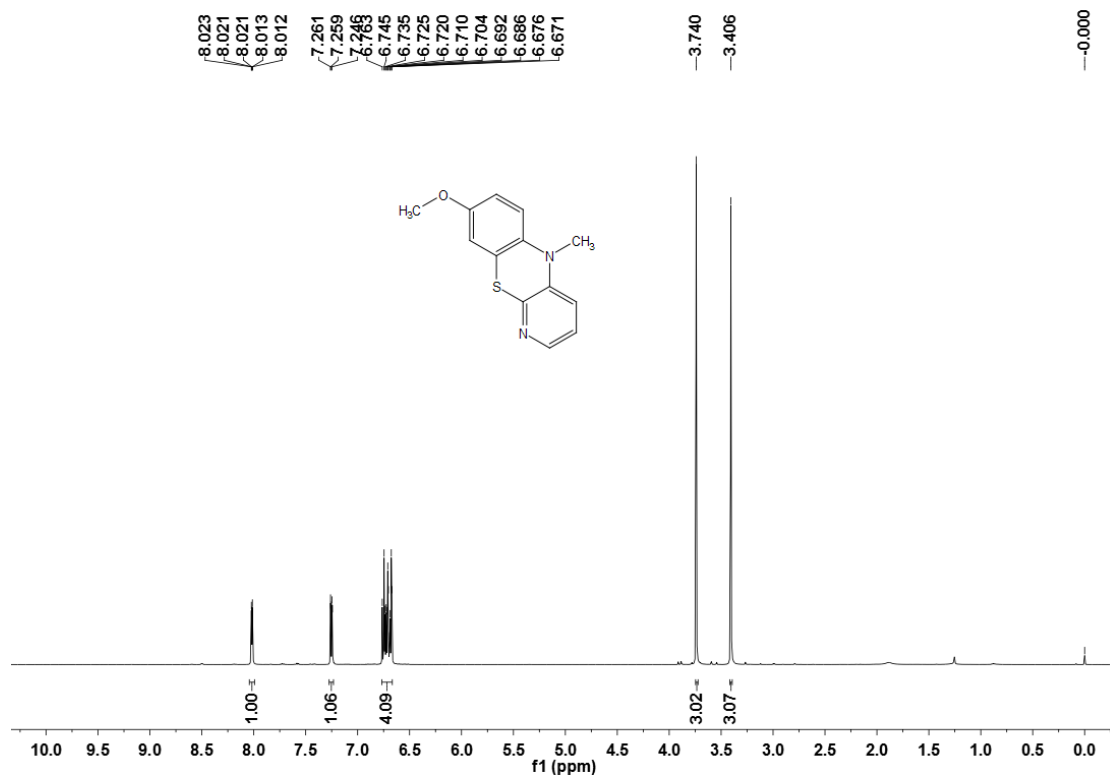
5,8-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3a)



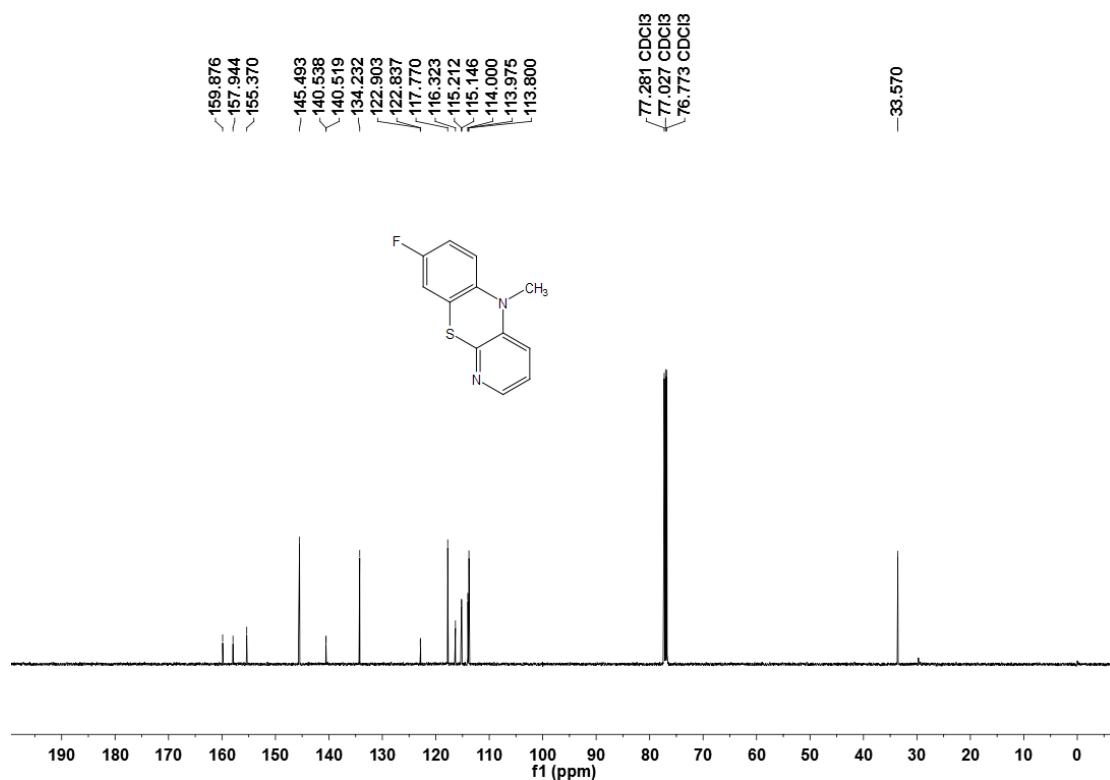
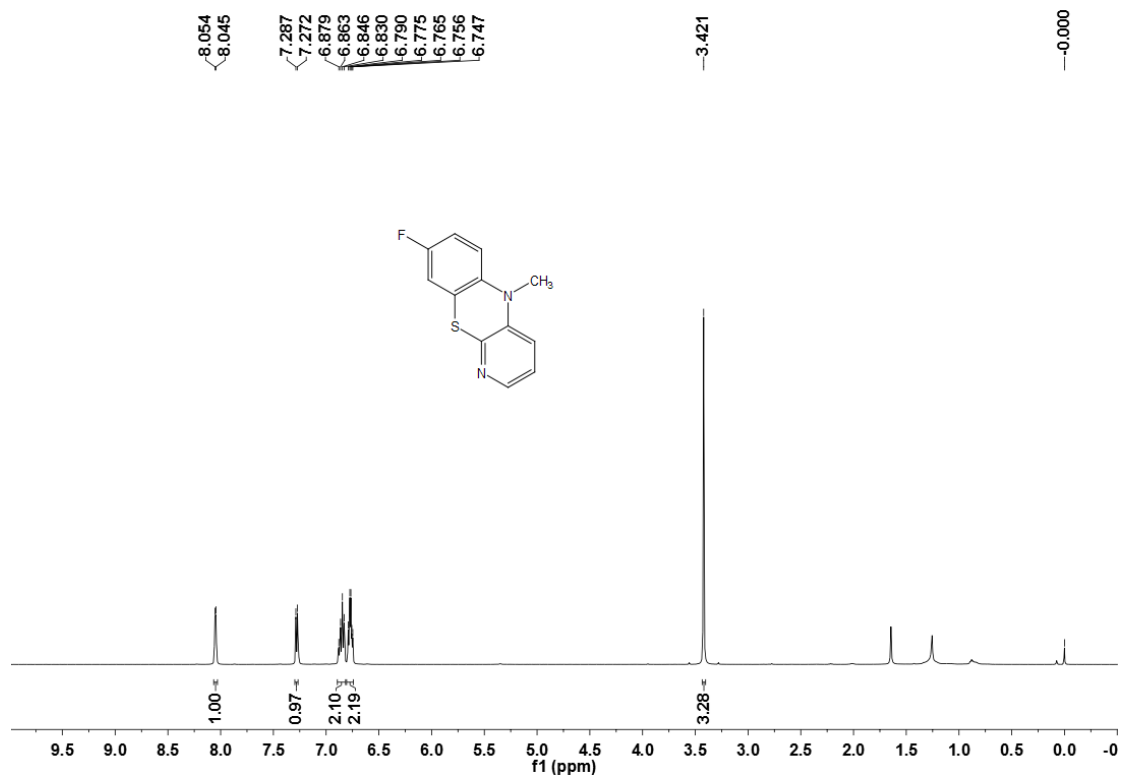
8-butyl-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3b)



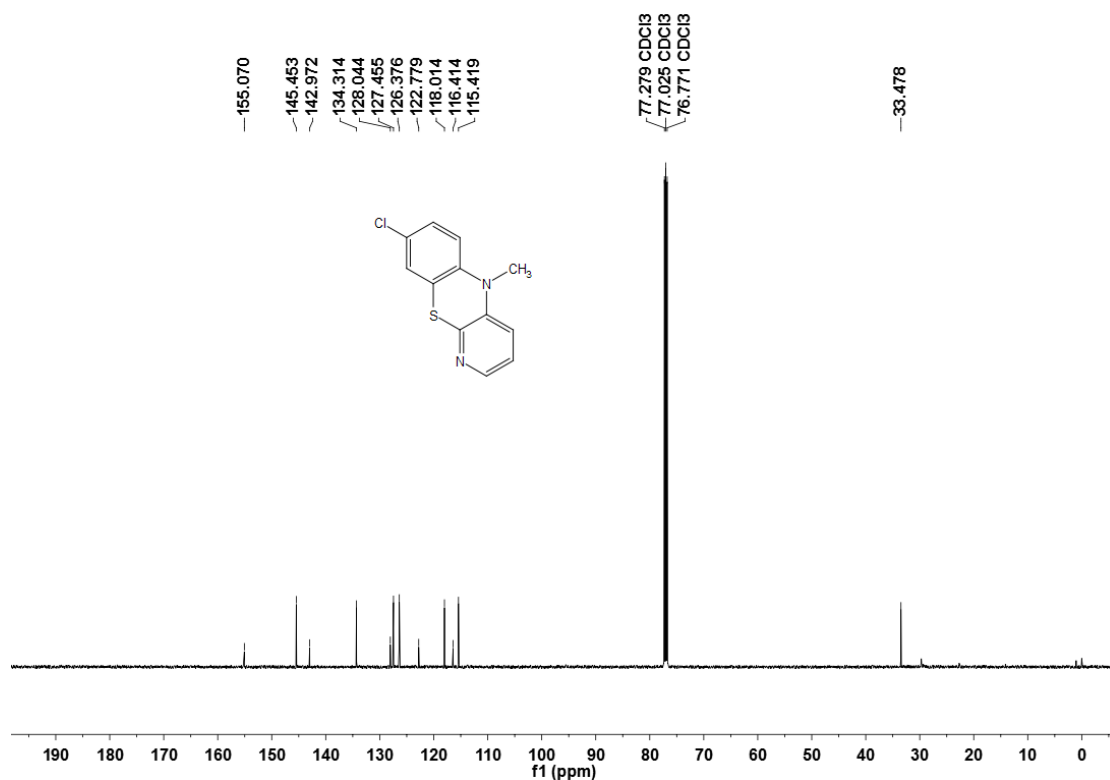
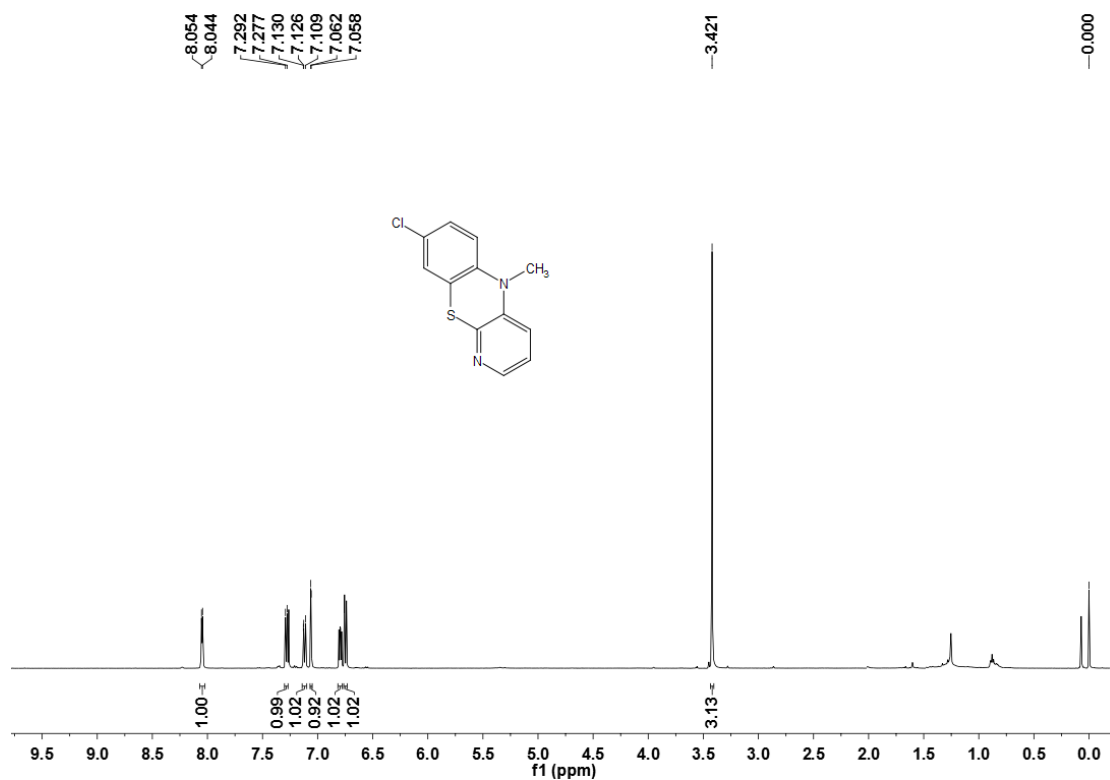
8-methoxy-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3c)



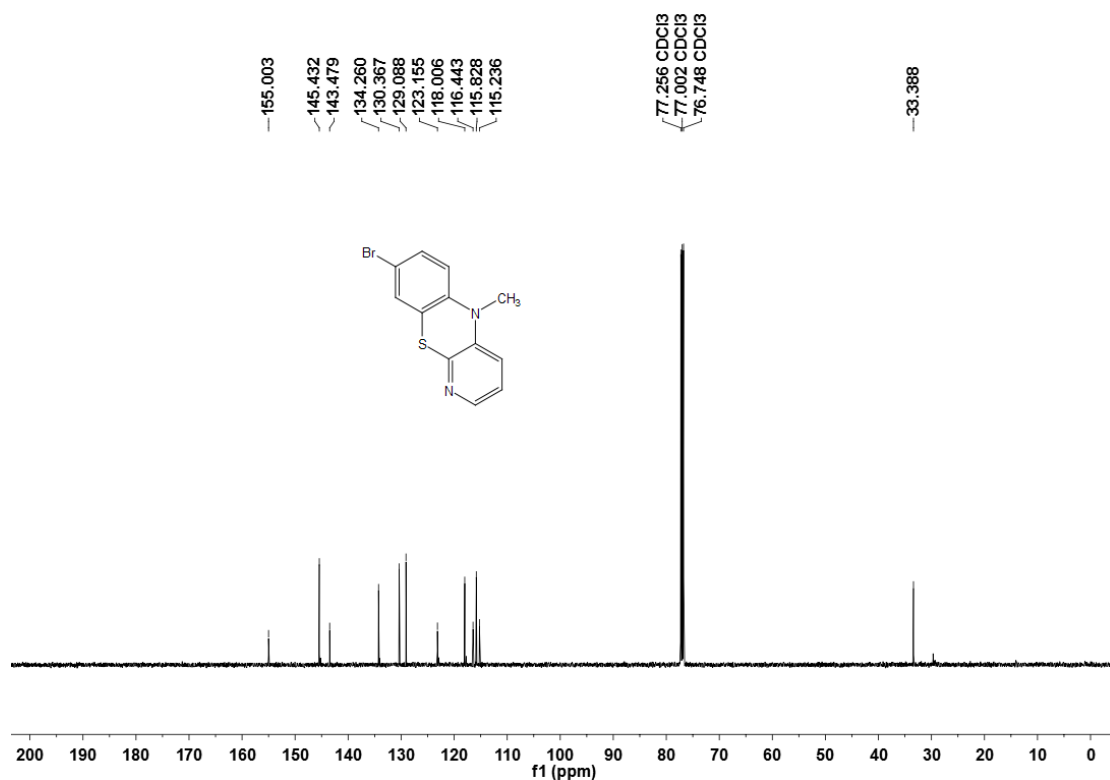
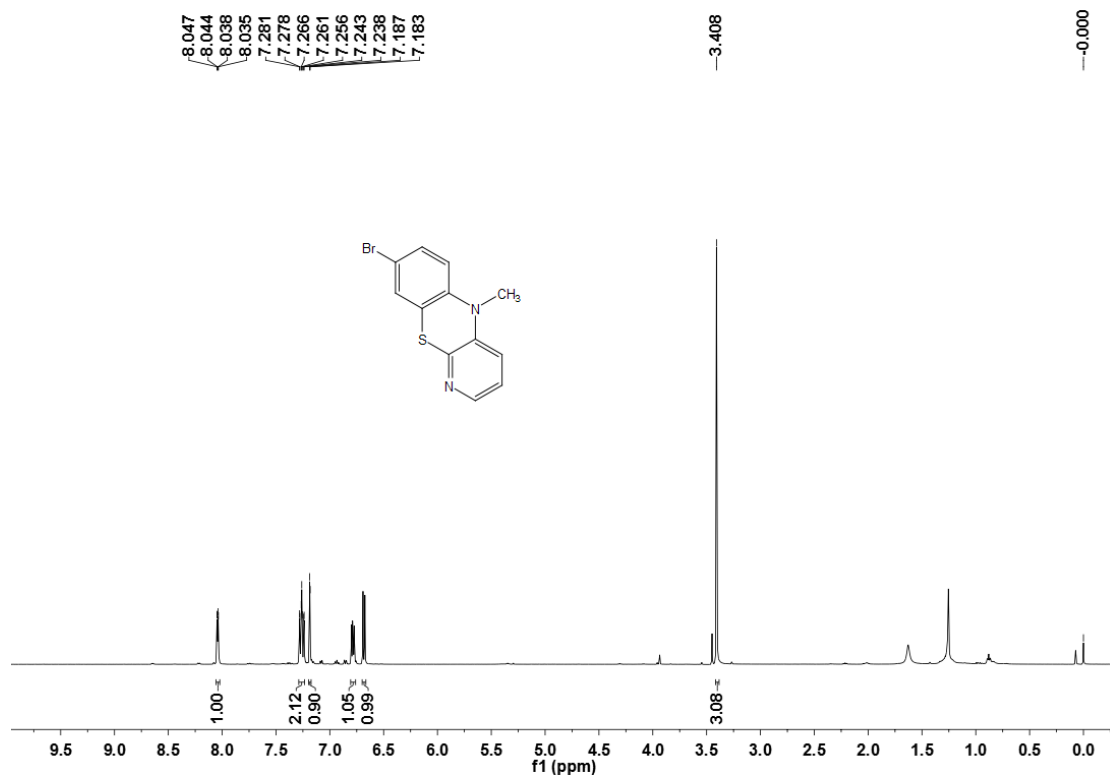
8-fluoro-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3d)



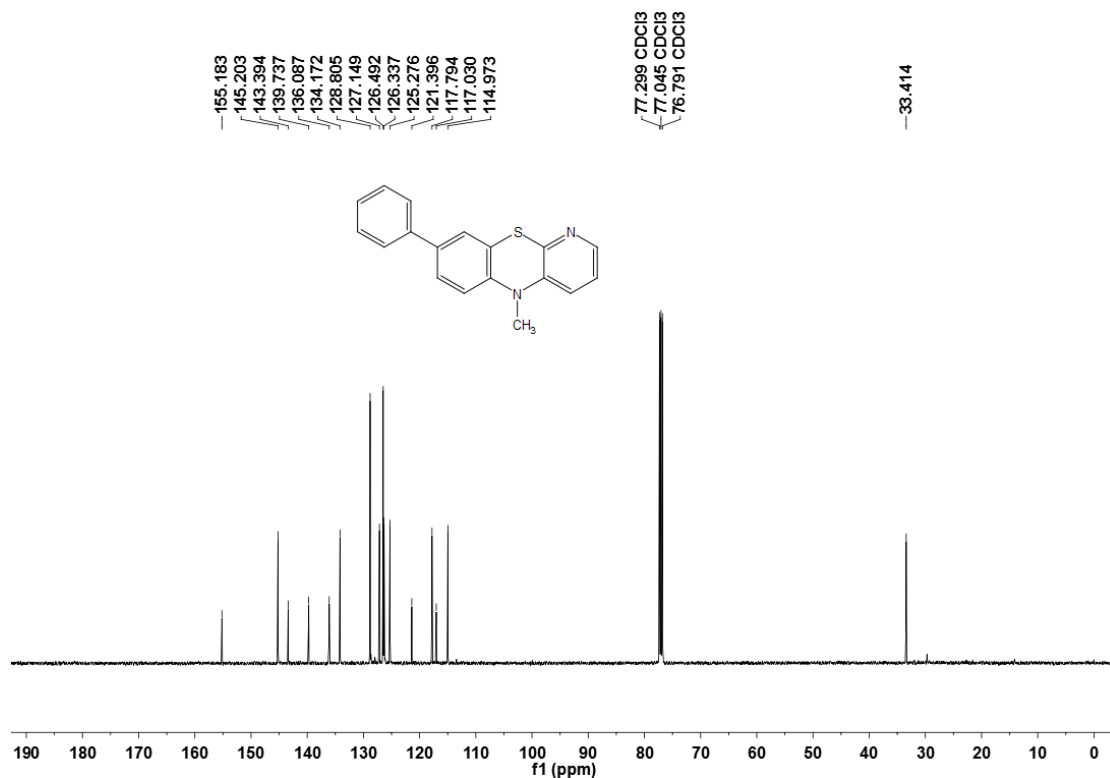
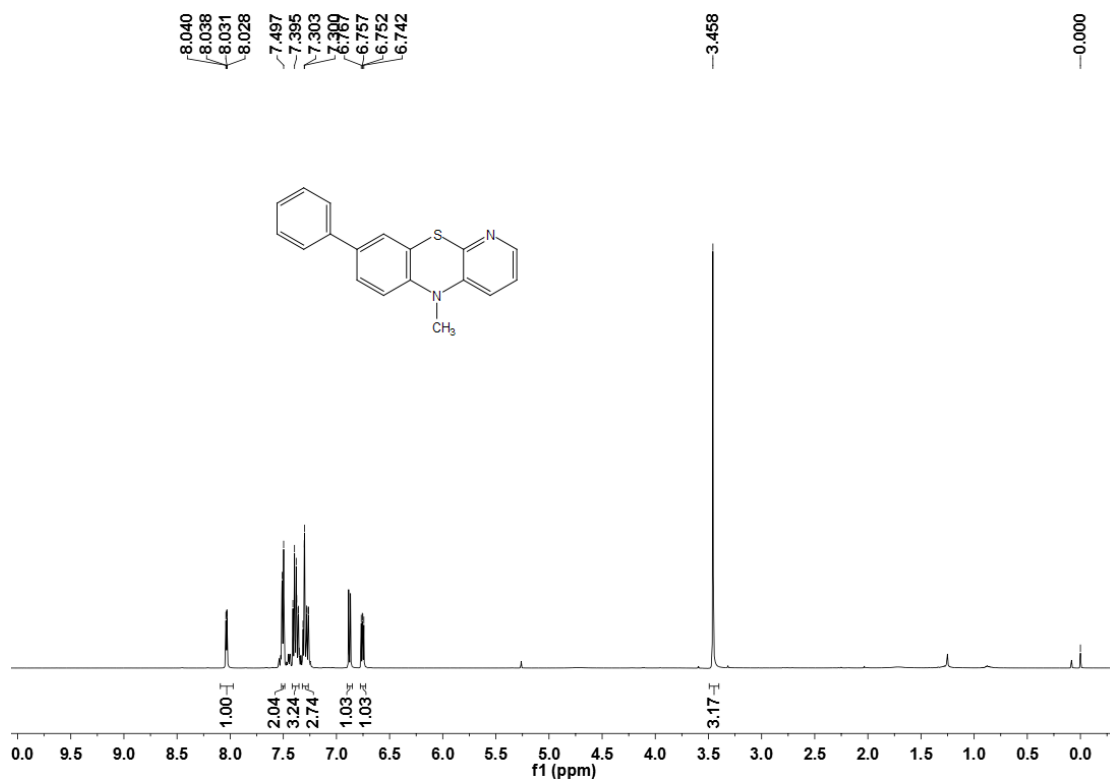
8-chloro-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3e)



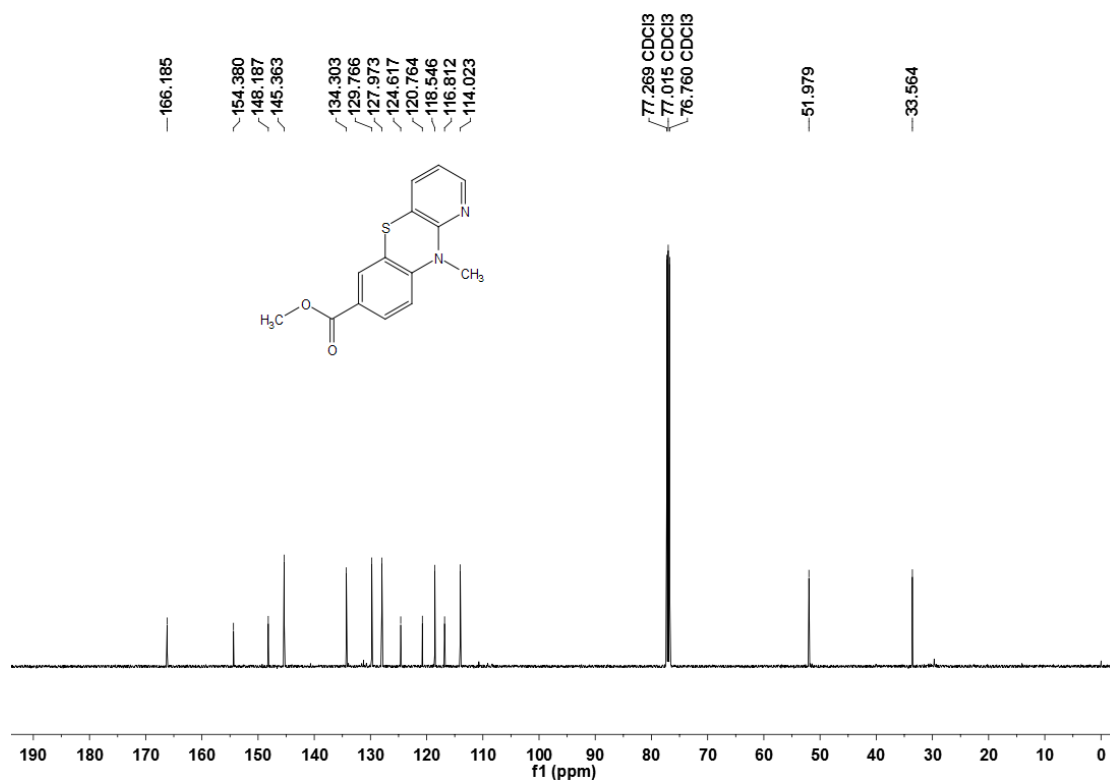
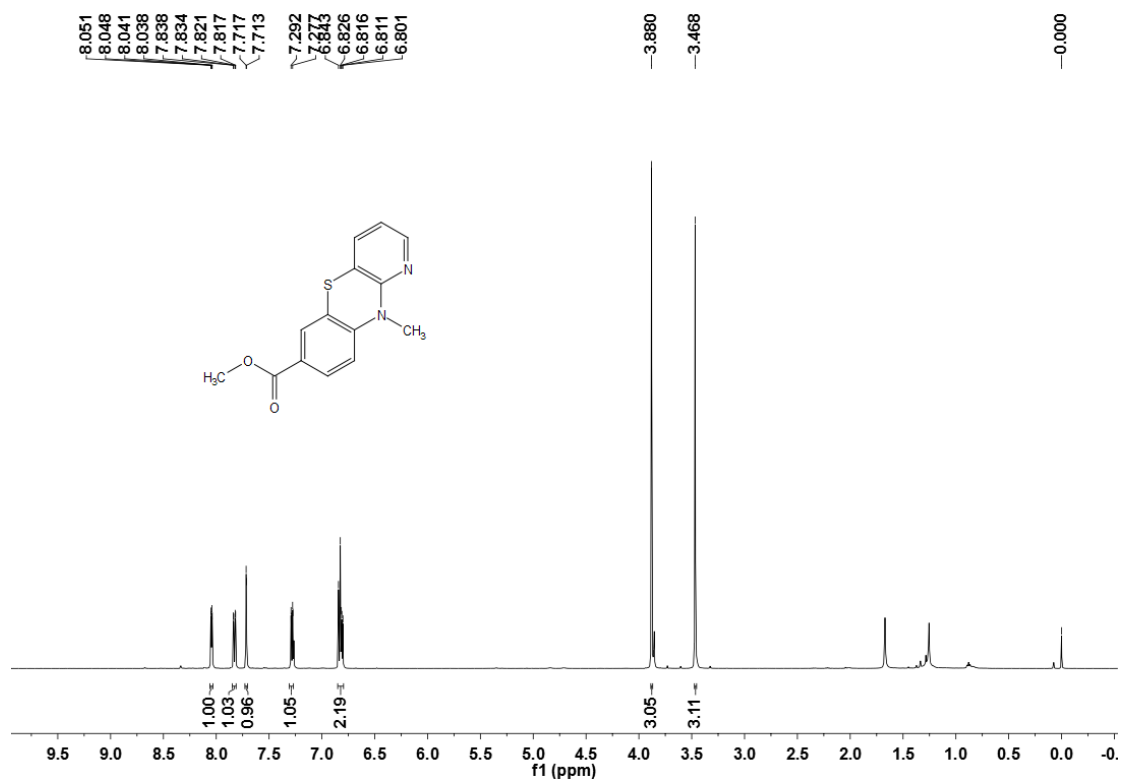
8-bromo-5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3f)



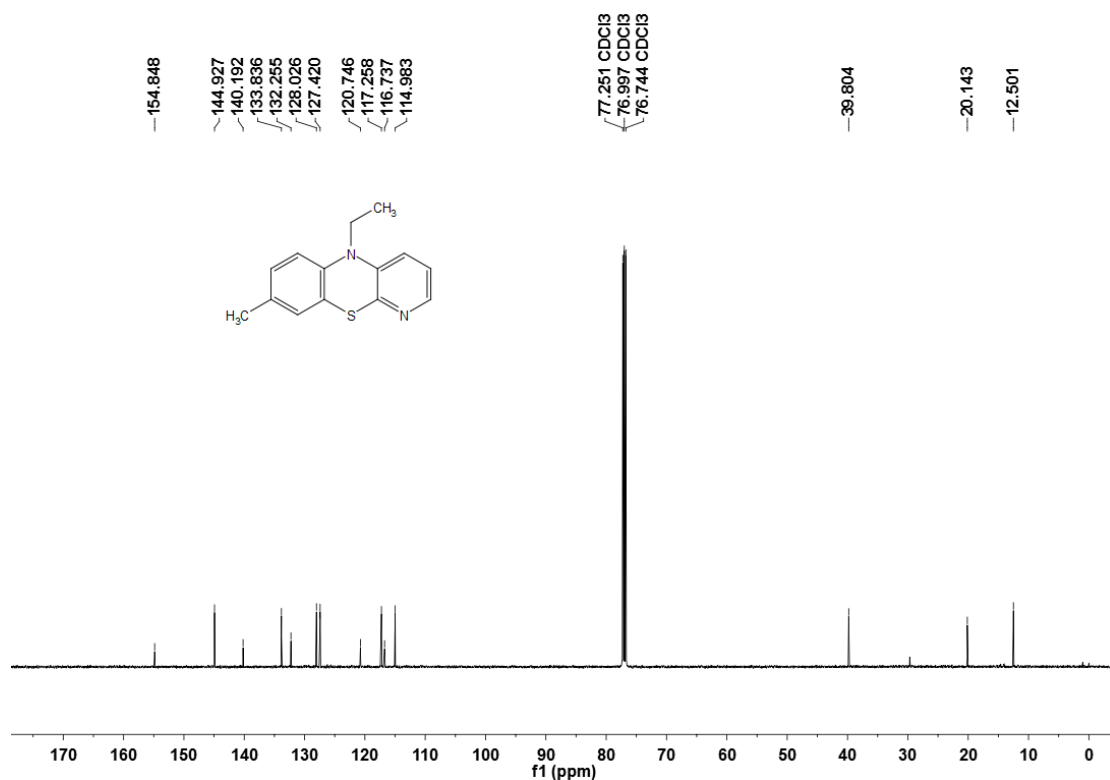
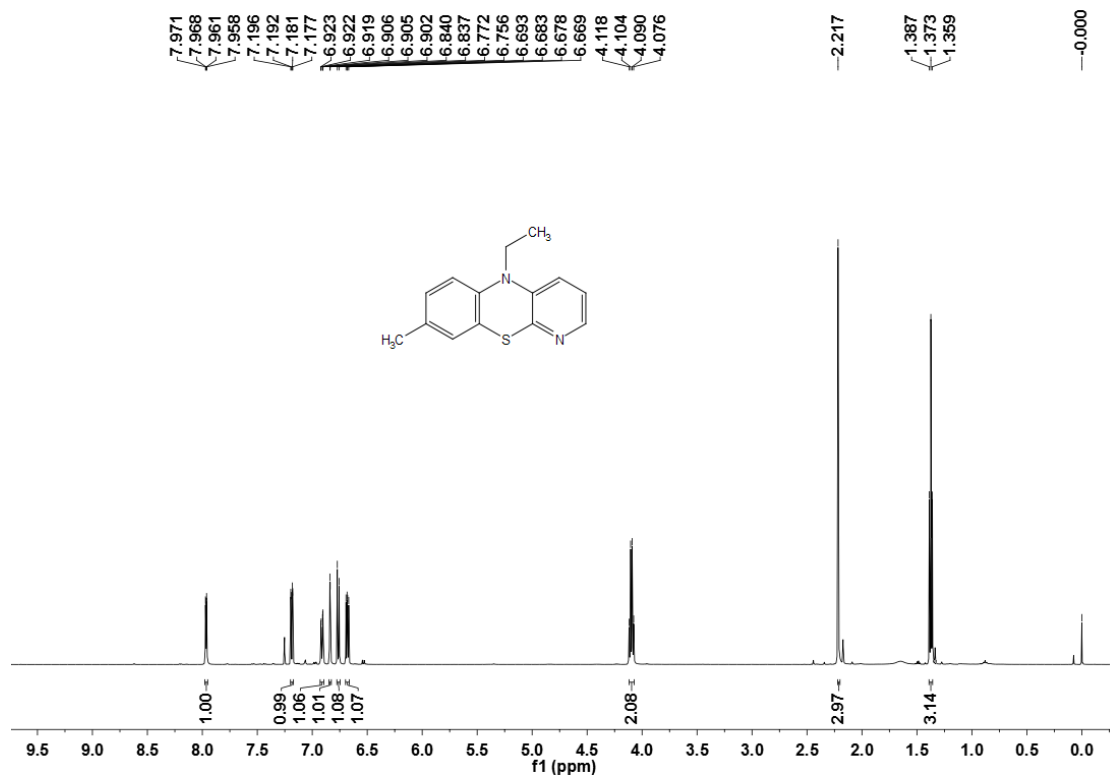
5-methyl-8-phenyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3g)



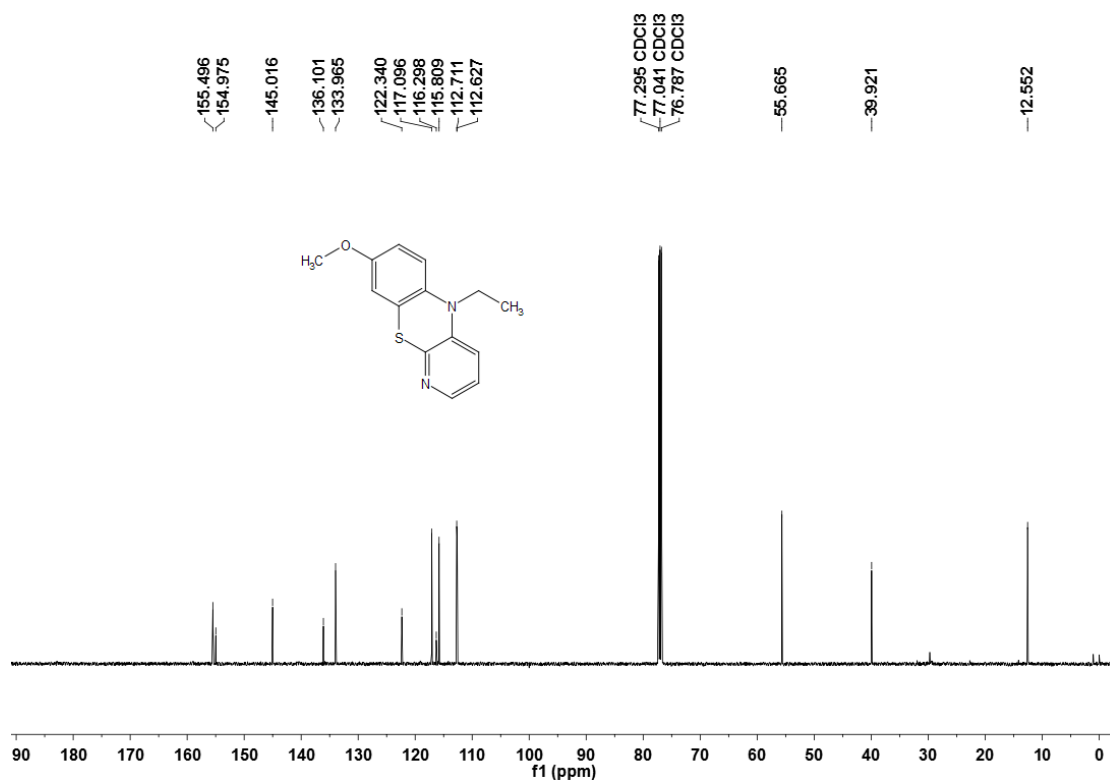
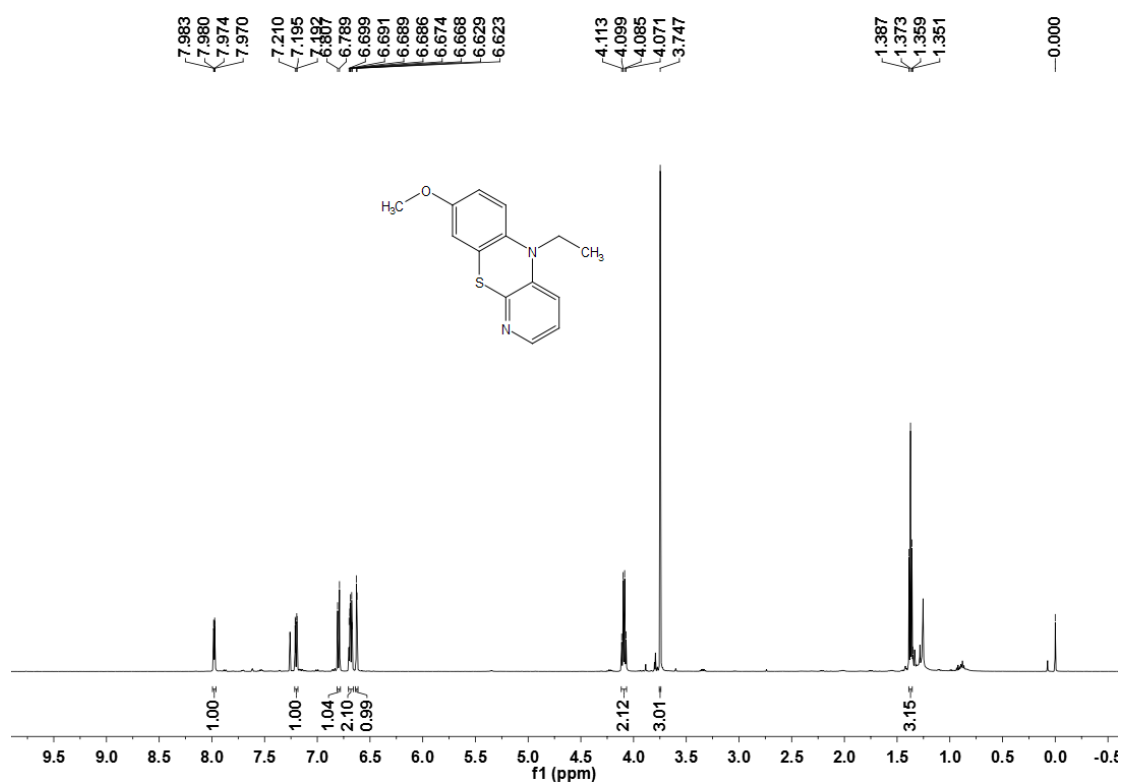
methyl 5-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine-8-carboxylate (3h)



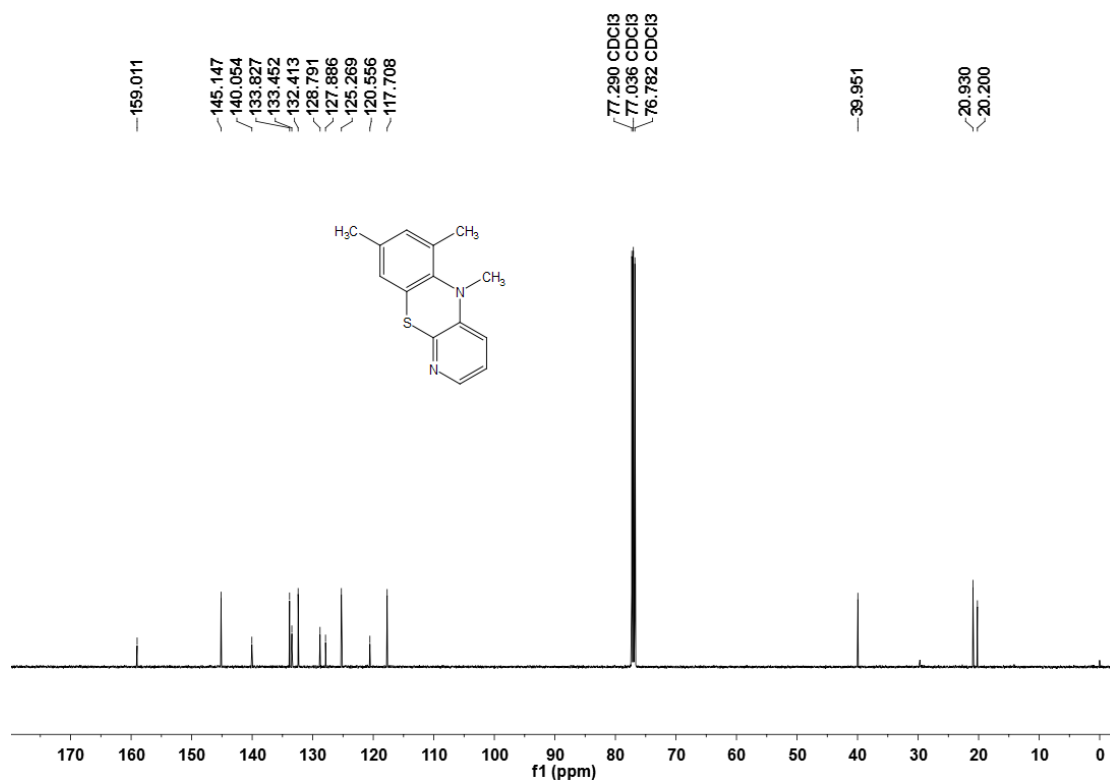
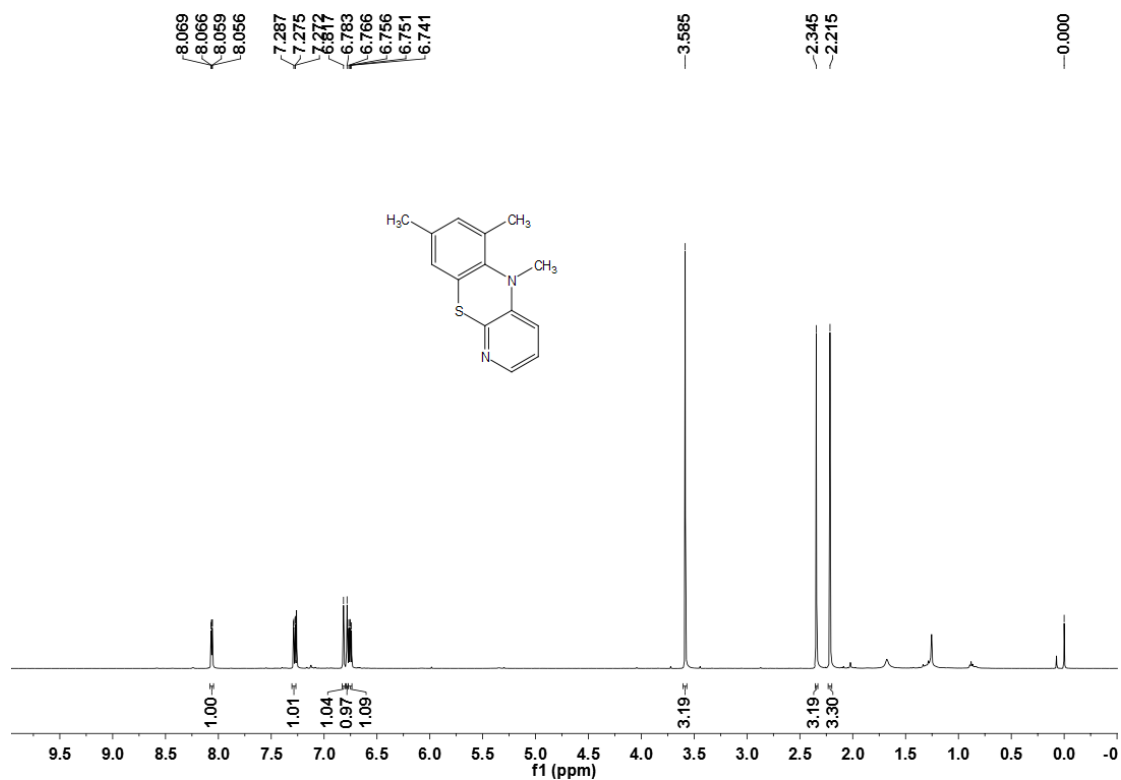
5-ethyl-8-methyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3i)



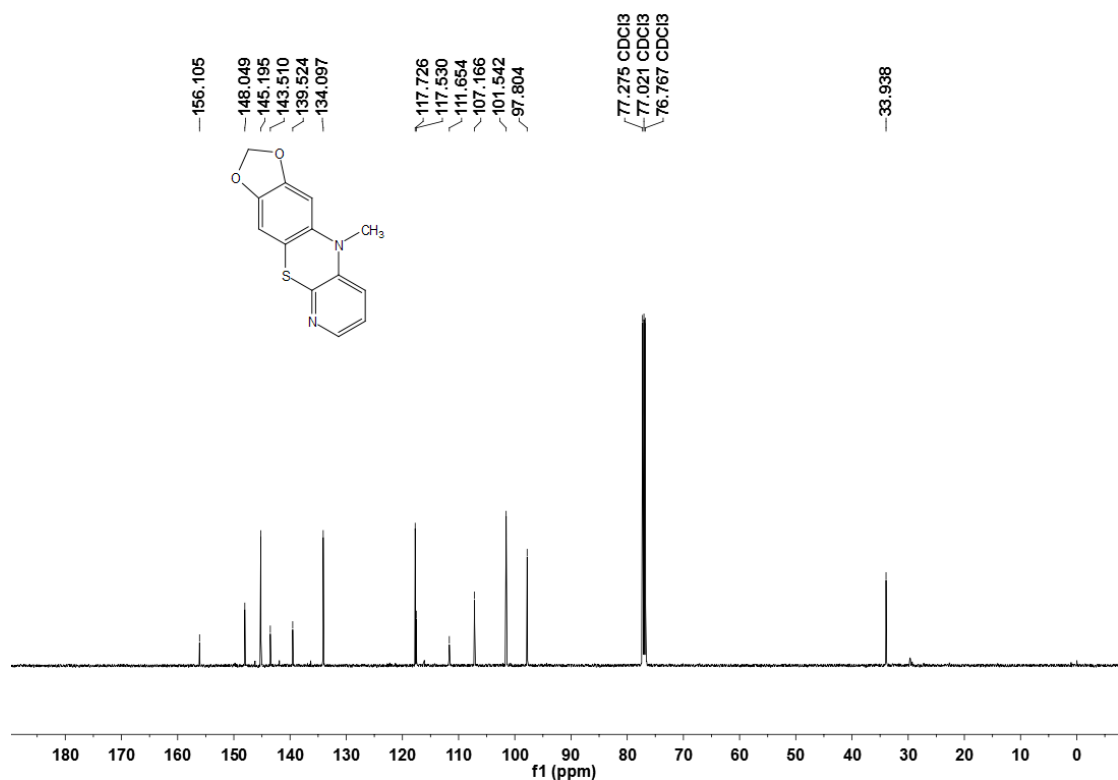
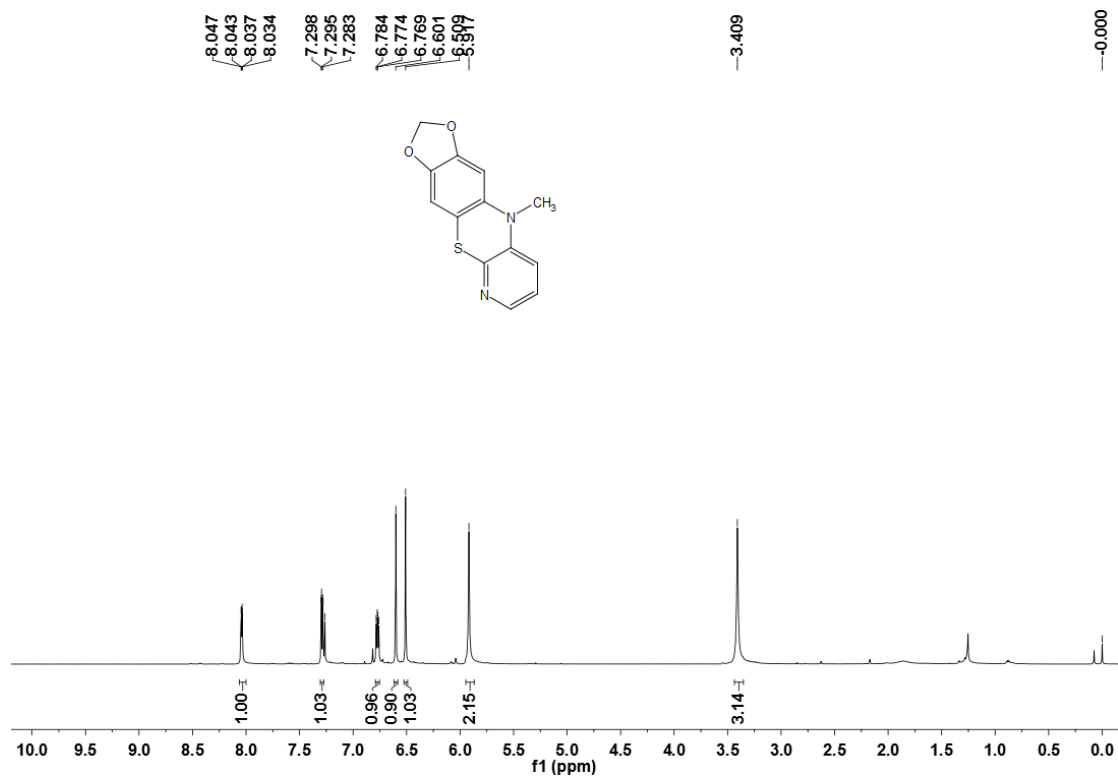
5-ethyl-8-methoxy-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3j)



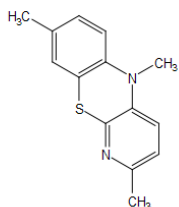
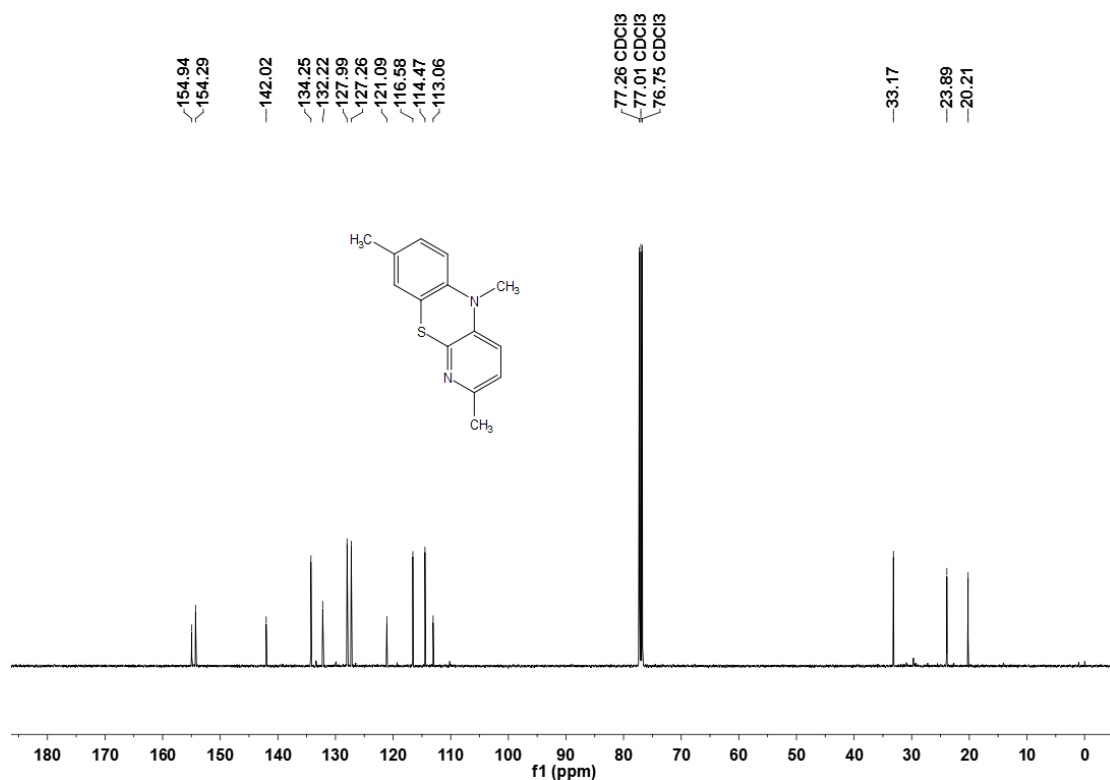
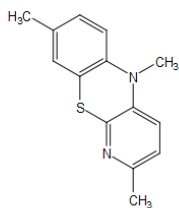
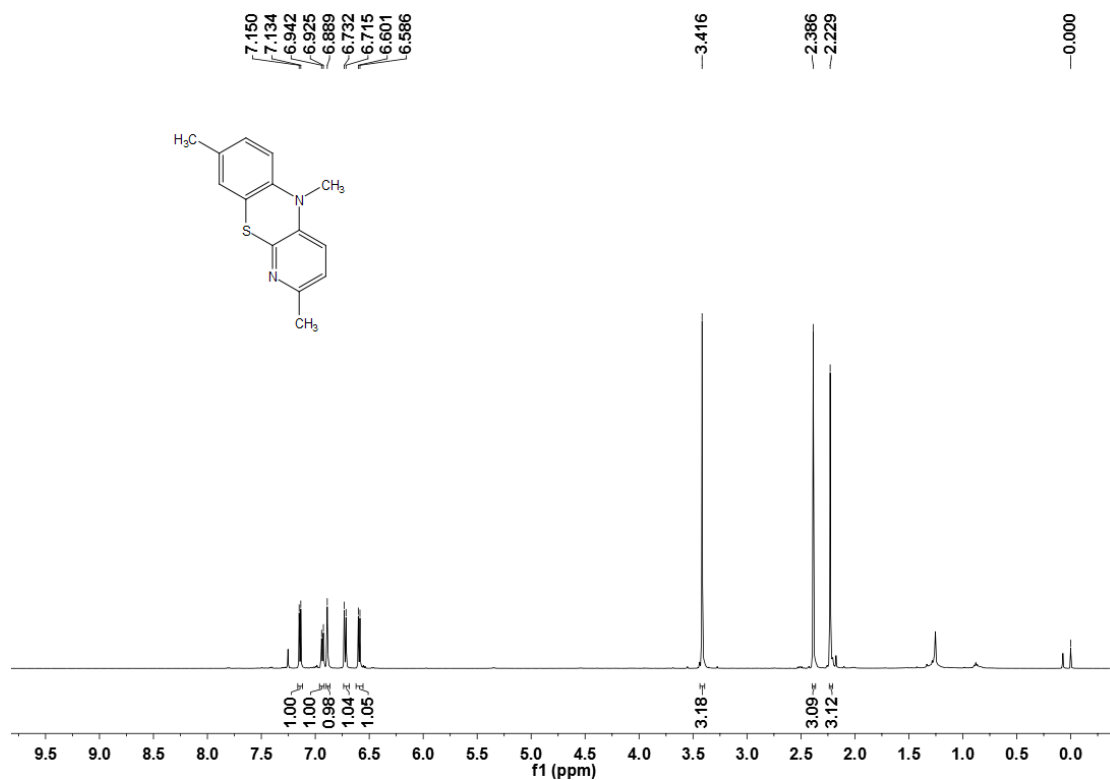
5,6,8-trimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3k)



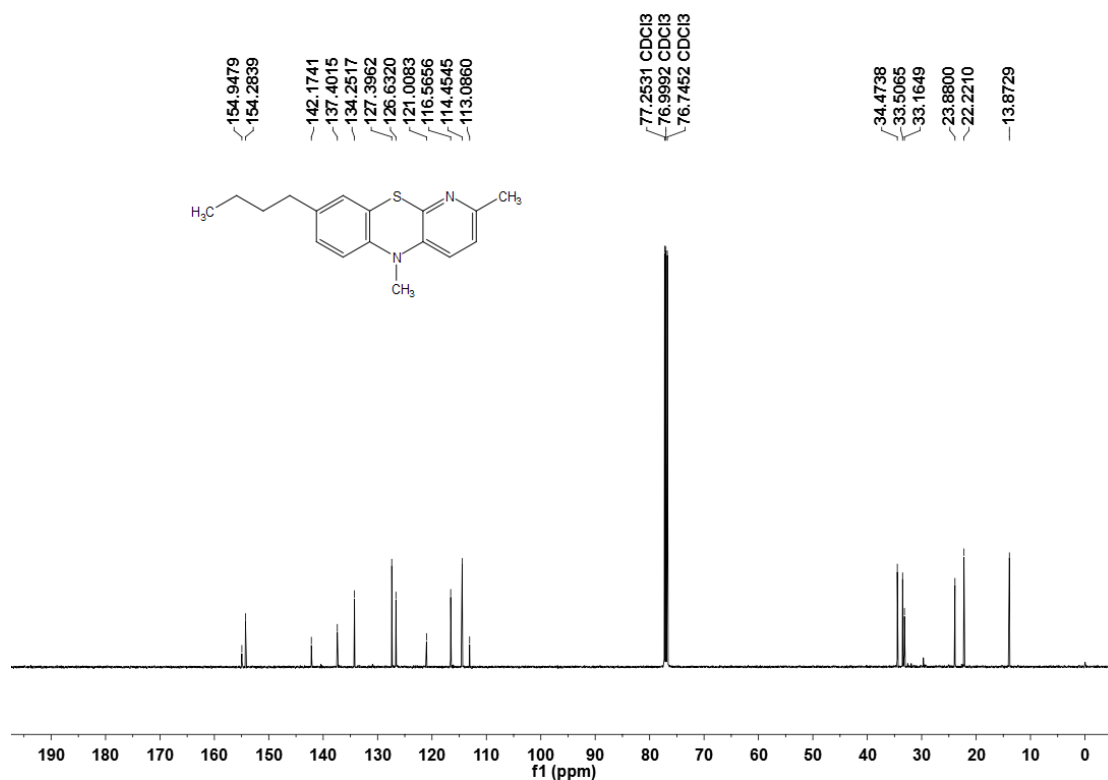
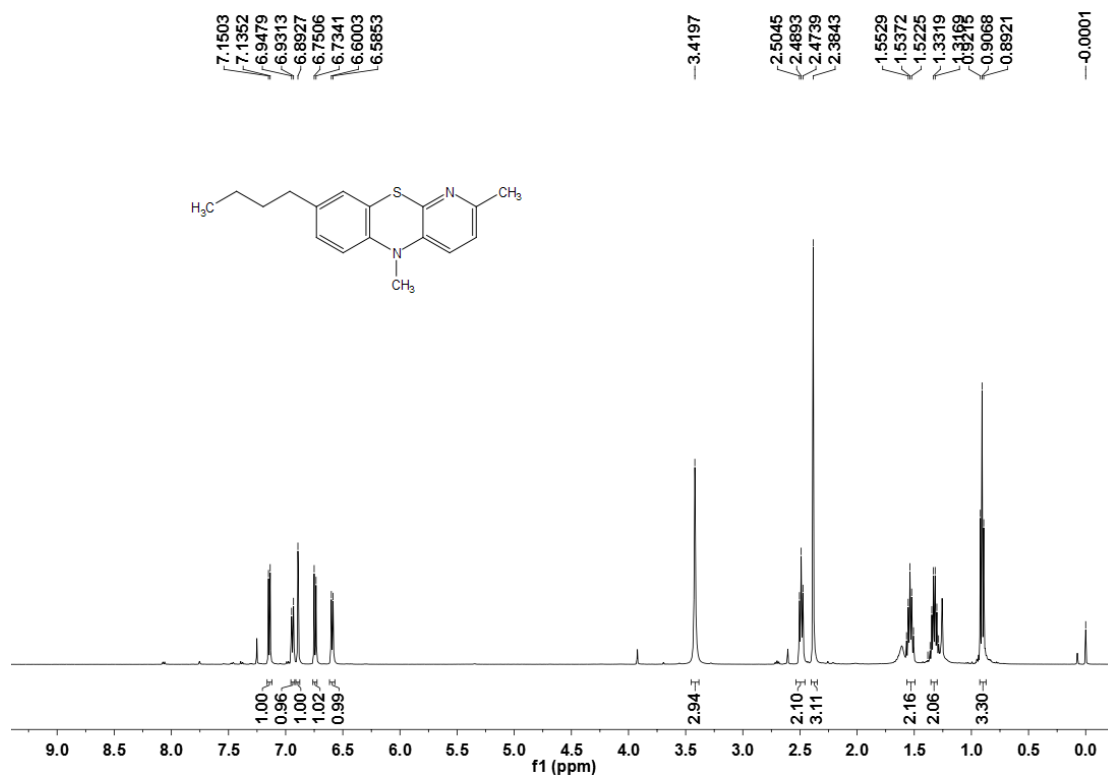
10-methyl-10H-[1,3]dioxolo[4',5':4,5]benzo[1,2-b]pyrido[3,2-e][1,4]thiazine (3l)



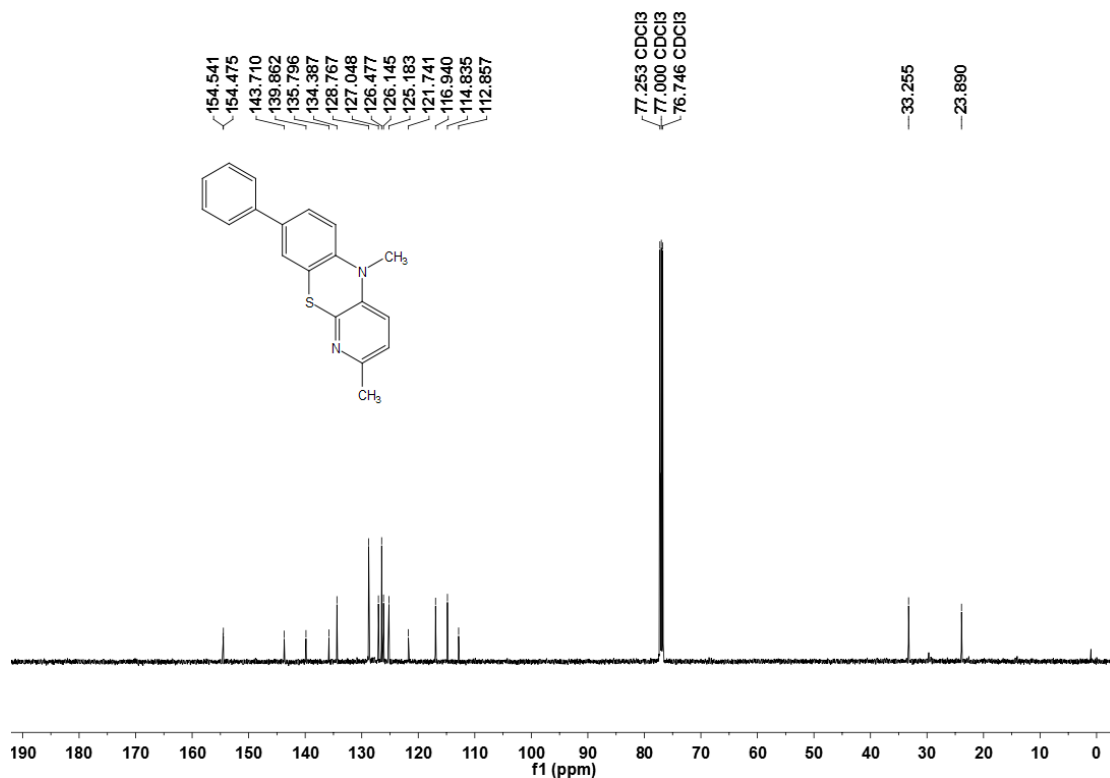
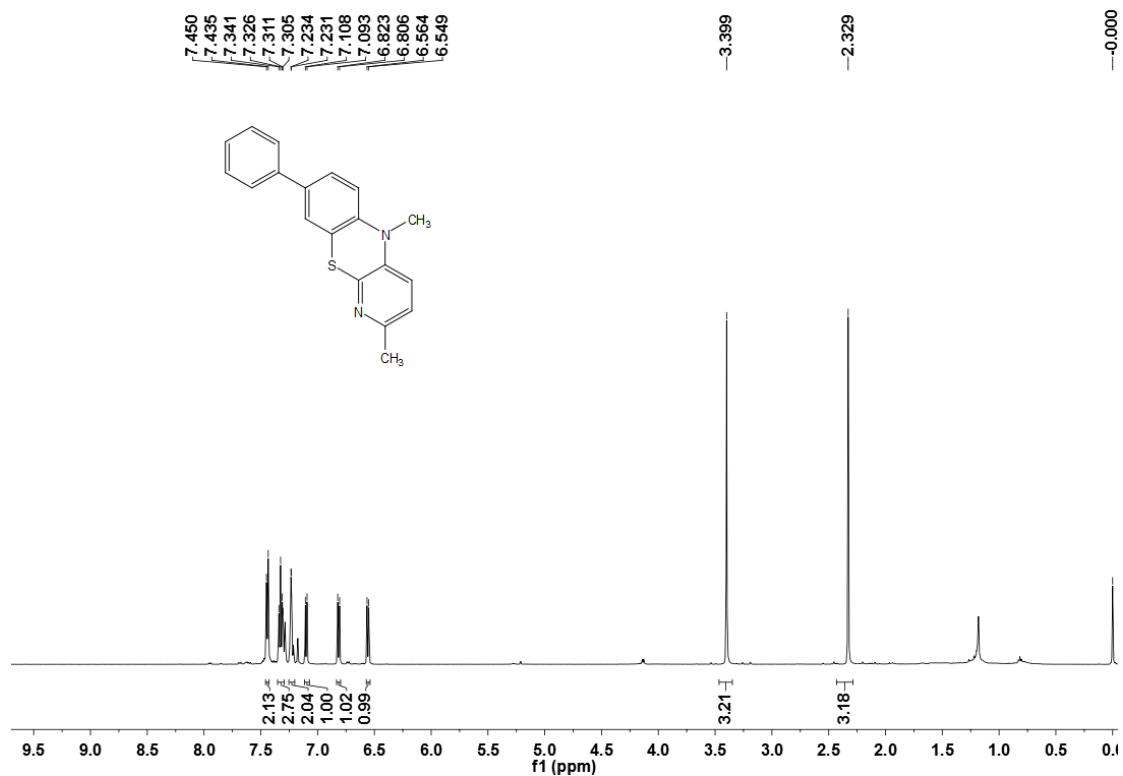
2,5,8-trimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3m)



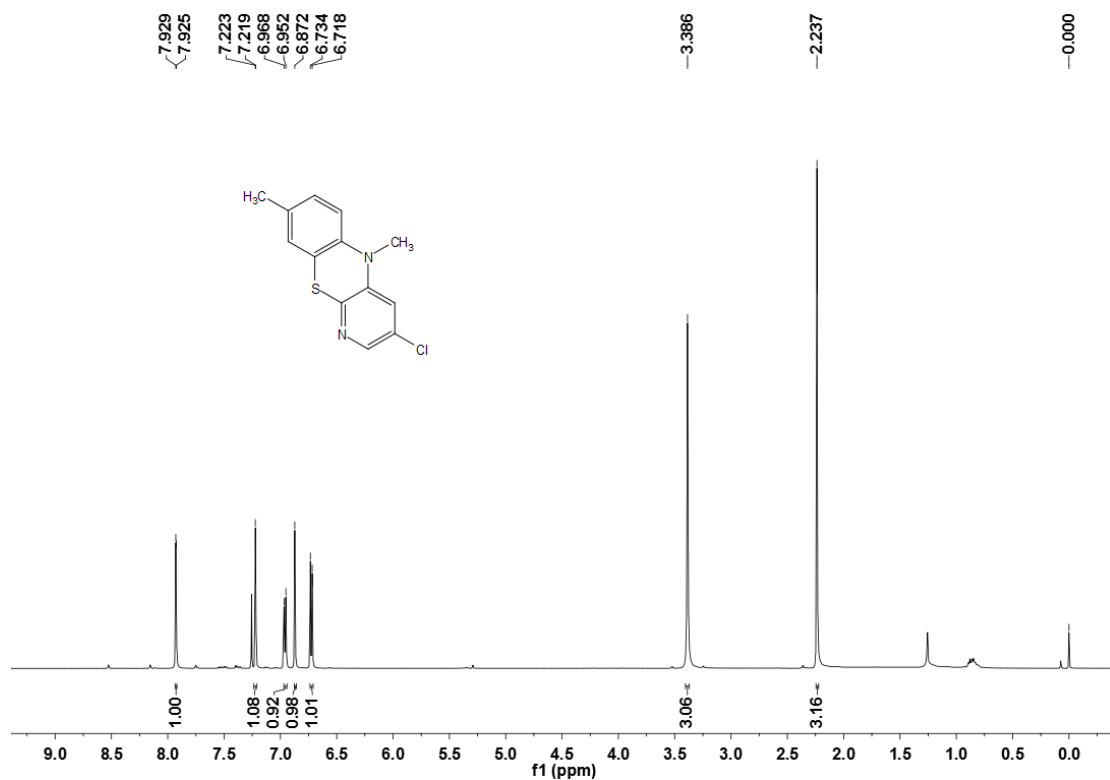
8-butyl-2,5-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3n)



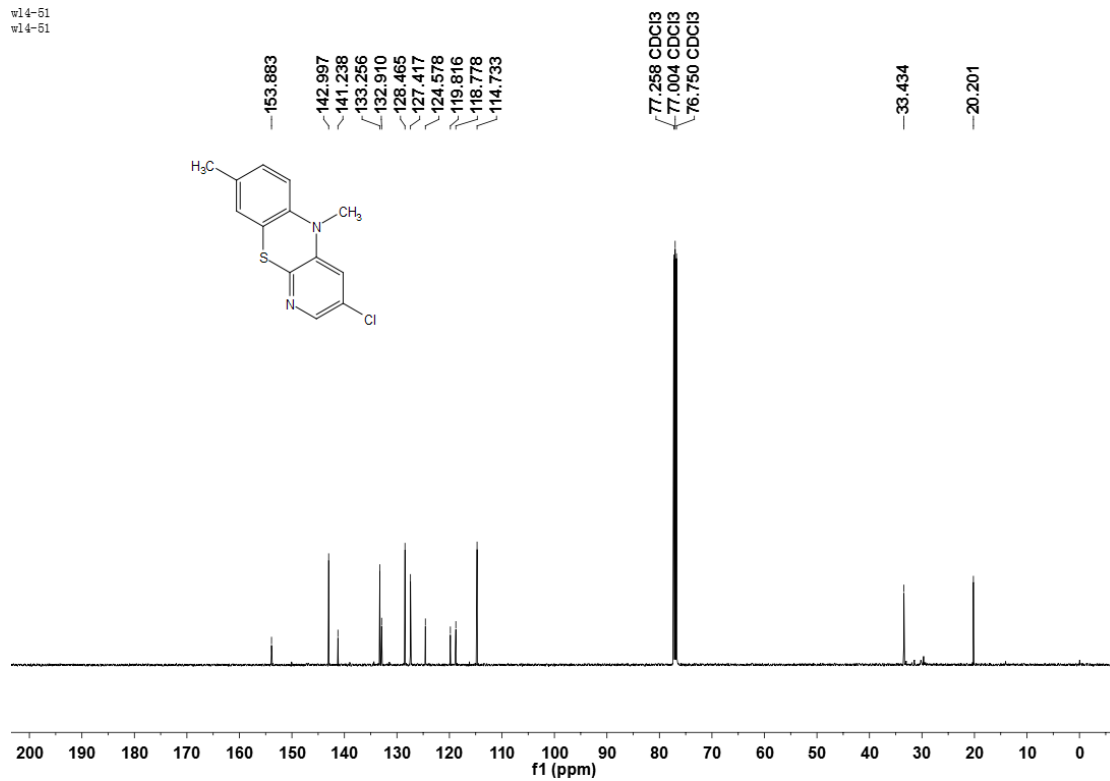
2,5-dimethyl-8-phenyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3o)



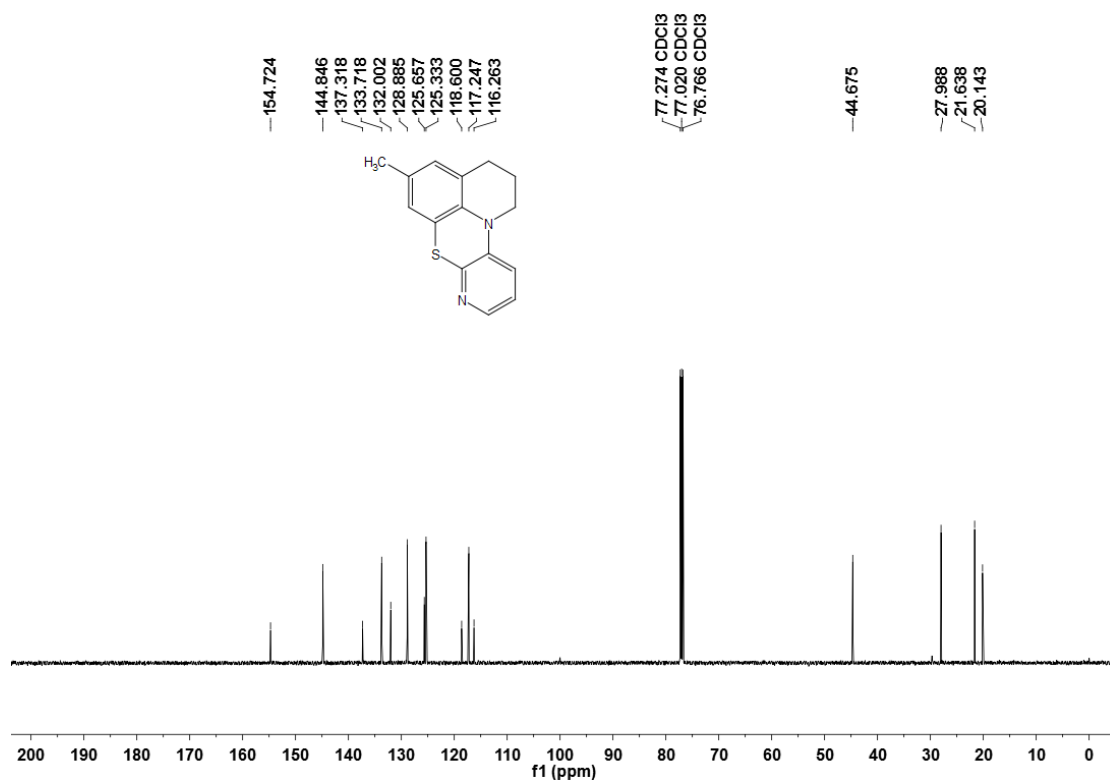
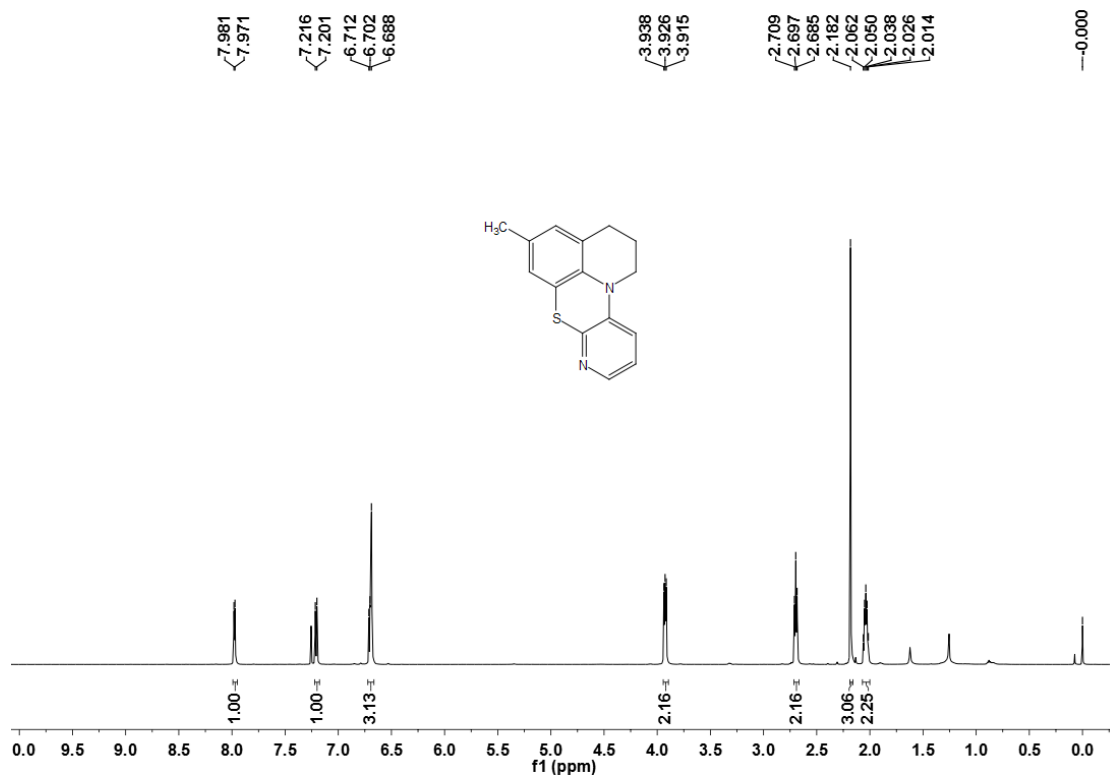
3-chloro-5,8-dimethyl-5H-benzo[b]pyrido[3,2-e][1,4]thiazine (3p)



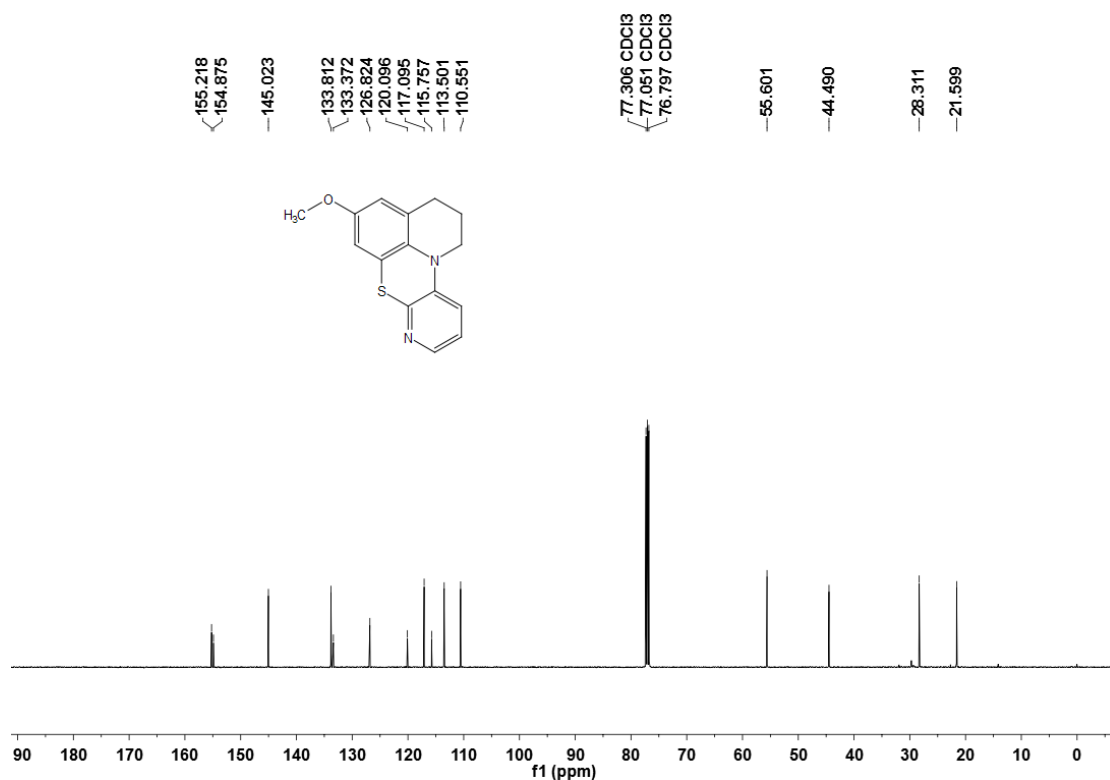
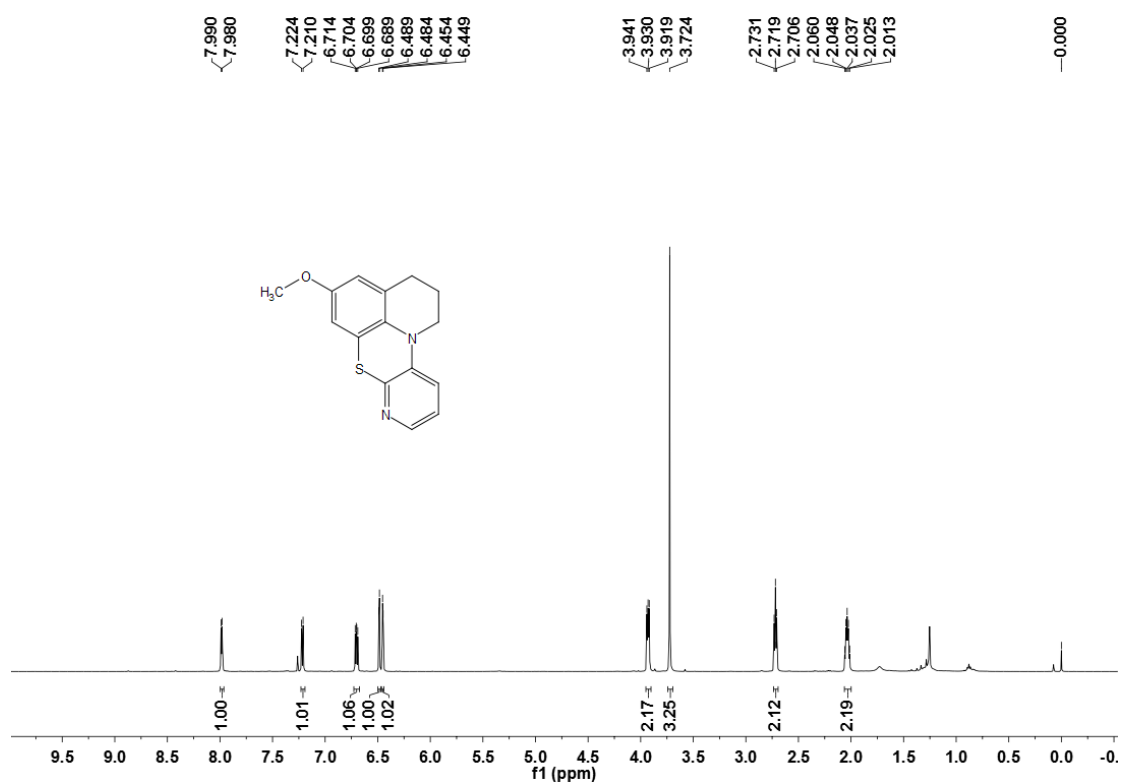
w14-51
w14-51



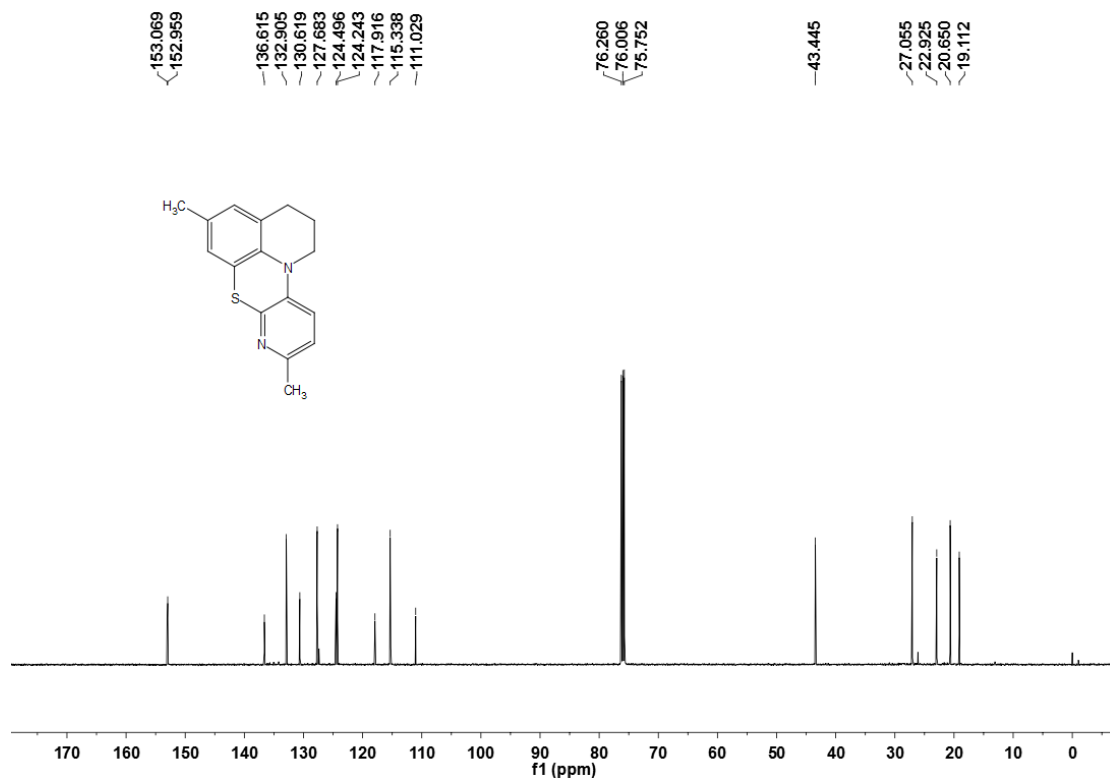
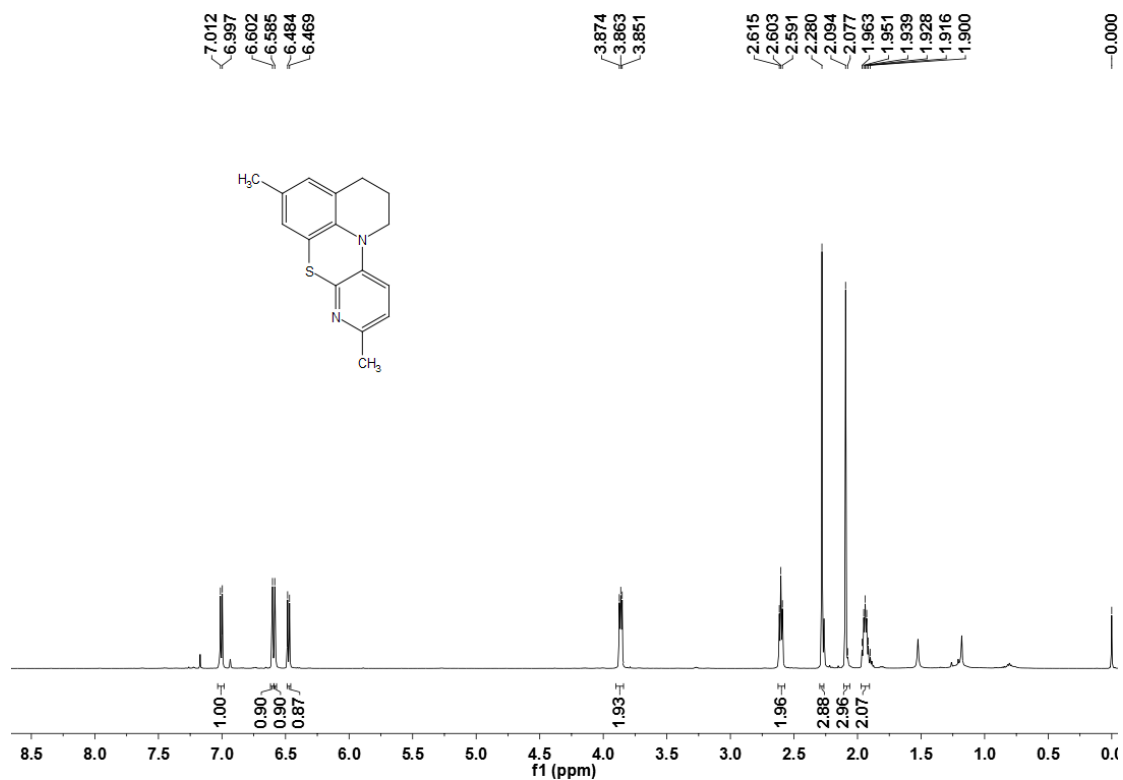
5-methyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3q)



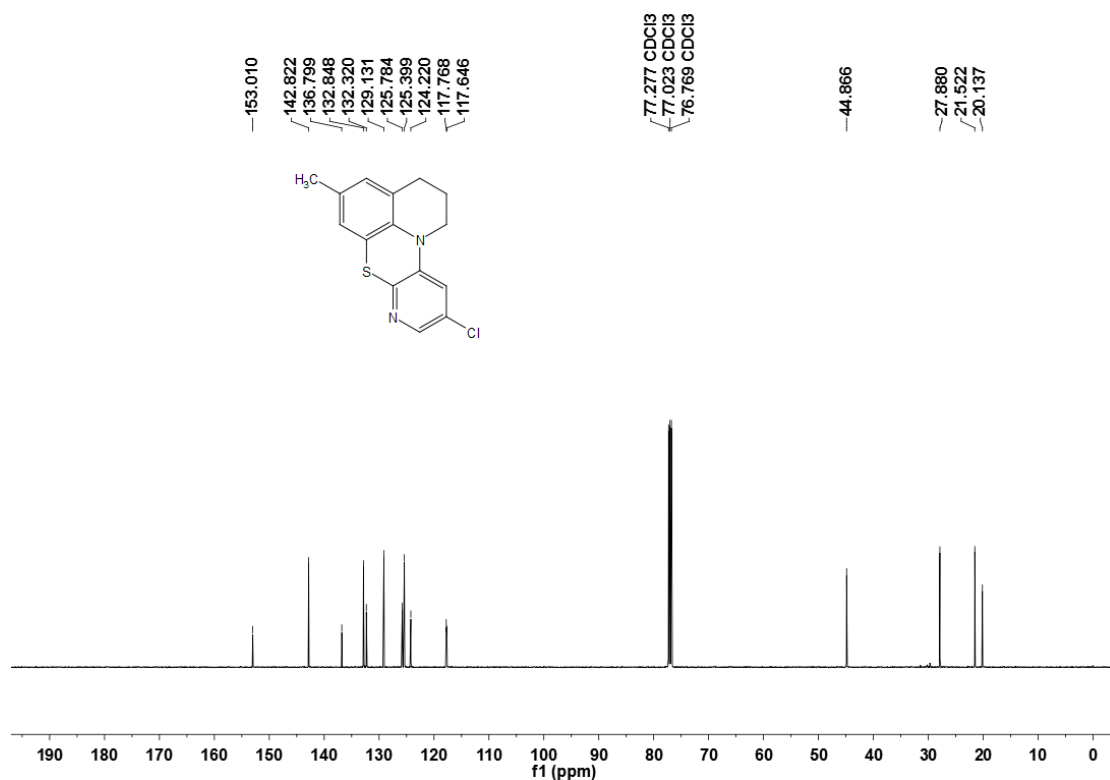
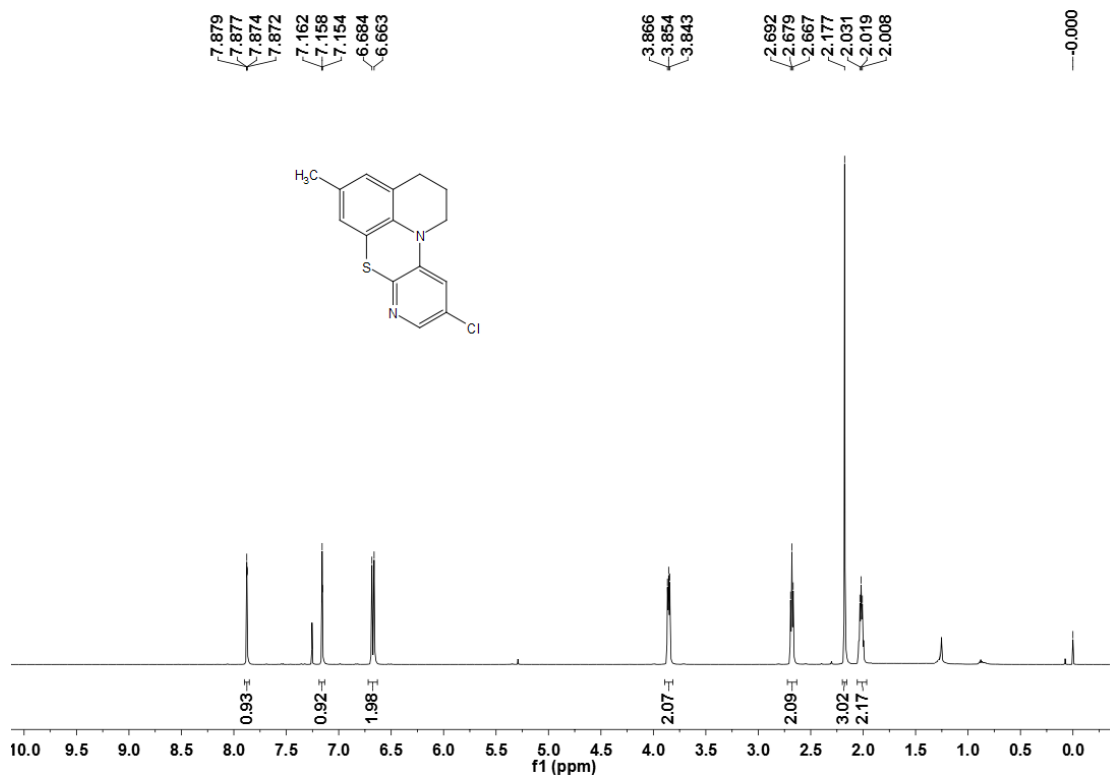
5-methoxy-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3r)



5,9-dimethyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3s)



10-chloro-5-methyl-2,3-dihydro-1H-pyrido[3',2':5,6][1,4]thiazino[2,3,4-ij]quinoline (3t)



***N*,4-dimethyl-2-(pyridin-2-ylthio)aniline (B)**

