Supplementary Information

Metal-Free Oxidative [2+2+1] Heteroannulation of 1,7-Enynes with Thiocyanates toward Thieno[3,4-c]quinolin-4(5H)-ones

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(A) General Experimental Procedures

Unless otherwise noted, all reactions were carried out under argon, and all starting materials and solvents were commercially available and used without further purification. Substrates **1a-v** were prepared according to the literatures.[1,2] All products were identified by ^{1}H and ^{13}C NMR, LRMS and HRMS. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 500 MHz spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. ^{19}F NMR spectroscopy were recorded on a Bruker Avance III HD 500 MHz spectrometer at room temperature in $CDCl_3$ with TFA as external standard. Low-resolution mass spectra (LRMS) data were measured on a Shimadzu GCMS-QP2010 Ultra spectrometer. High-resolution mass spectra (HRMS) were obtained on a Waters Xevo G2-XS QTOF spectrometer. Melting point was determined by an X-4 microscopic melting point apparatus. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

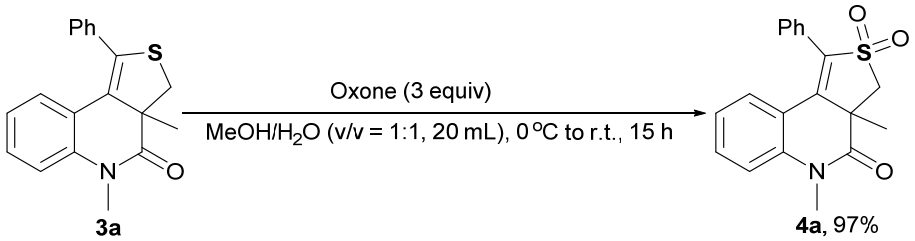
(a) General Procedure for the Cyclization Cascades of 1,7-Eneynes with Sodium Sulfocyanate:

0.2 mmol

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with substrate **1a** (0.2 mmol), NaSCN (2 equiv), BPO (1.5 equiv) and

$MeNO_2$ (2 mL). The tube was evacuated and back-filled with argon for three times and the mixture was stirred at 120 °C (oil bath temperature) for 24 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. A combination of NaSCN (2 equiv) and BPO (1.5 equiv) were added when the mixture was cooled to room temperature, and the resulting mixture was then stirred at 120 °C in argon for 24 h. After the reaction was finished, the reaction mixture was diluted with brine (5 mL), and the resulting solution extracted with ethyl acetate (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **3a**.

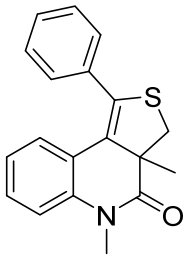
(b) Preparation of 4a[3]:



To a cooled solution (0 °C) containing **3a** in MeOH/H_2O (1:1, 10 ml total volume) was added oxone (3 equiv) and the suspension was stirred for 15 h at room temperature. Subsequently, the reaction mixture was diluted with $CHCl_3$ (3 × 10 ml), and the organics were extracted with H_2O (3 × 10 ml), dried over $MgSO_4$, filtered, and concentrated. Purification by column chromatography afforded **4a** (97% yield).

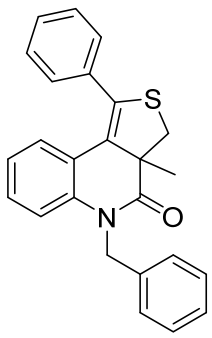
(B) Analytical data

3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3a):



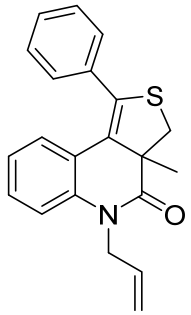
72% yield; white solid, mp 130 - 131 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.26 (m, 5H), 7.18 - 7.15 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.77 - 6.73 (m, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 3.28 (d, *J* = 12.0 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 139.4, 137.7, 135.3, 129.0, 128.6, 128.3, 128.1, 127.5, 125.3, 122.7, 121.1, 115.4, 58.1, 41.4, 30.2, 21.4; LRMS (EI, 70 eV) *m/z* (%): 307 (M^+, 52), 292 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{17}NOS$ $[M+H]^+$ 308.1104, Found 308.1169.

5-benzyl-3a-methyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3b):



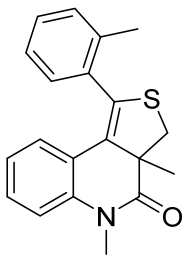
38% yield; white solid, mp 198 - 199 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 7H), 7.27 - 7.23 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 5.60 (d, *J* = 16.0 Hz, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 12.0 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 138.7, 137.9, 137.0, 135.2, 129.0, 128.7, 128.5, 128.1, 127.6, 127.3, 126.3, 125.1, 122.9, 121.2, 116.2, 58.2, 46.8, 41.1, 21.7; LRMS (EI, 70 eV) *m/z* (%): 383 (M^+, 96), 368 (70), 292 (26), 91 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{21}NOS$ $[M+H]^+$ 384.1417, Found 384.1466.

5-allyl-3a-methyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3c):



55% yield; white solid, mp 101 - 102 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 5H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 5.96 - 5.88 (m, 1H), 5.23 - 5.15 (m, 2H), 4.95 - 4.90 (m, 1H), 4.30 - 4.25 (m, 1H), 4.06 (d, *J* = 12.0 Hz, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 138.6, 137.8, 135.3, 132.5, 129.0, 128.6, 128.4, 128.0, 127.6, 125.2, 122.8, 121.2, 116.3, 116.0, 58.1, 45.5, 41.1, 21.6; LRMS (EI, 70 eV) *m/z* (%): 333 (M^+, 75), 318 (100), 277 (28); HRMS *m/z* (ESI) calcd for $C_{21}H_{19}NOS$ $[M+H]^+$ 334.1260, Found 334.1330.

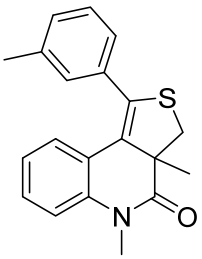
3a,5-dimethyl-1-(*o*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3e):



46% yield; white solid, mp 119 - 120 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.28 (m, 2.3H), 7.26 - 7.10 (m, 2.7H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.73 - 6.68 (m, 1.5H), 6.55 (d, *J* = 7.5 Hz, 0.5H), 4.02 - 3.99 (m, 1H), 3.41 (s, 3H), 3.30 (d, *J* = 11.5 Hz, 1H), 2.42 (s, 1.7H), 2.03 (s, 1.3H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.6, 139.0, 138.6, 137.9, 136.9, 135.7, 134.7, 134.4, 131.0, 130.5, 129.0, 128.9, 128.8, 128.7, 127.9, 127.8, 127.0, 126.3, 126.1, 126.0, 125.8, 123.1, 121.2, 120.9, 115.3, 115.2, 57.6 (2C), 41.6, 41.4, 30.2 (2C), 21.9, 21.7, 19.5, 19.3; LRMS (EI, 70 eV) *m/z* (%): 321 (M^+, 47), 306 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{19}NOS$ $[M+H]^+$

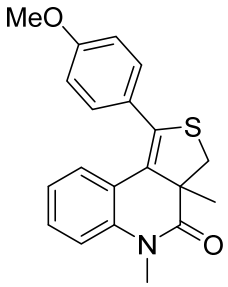
322.1260, Found 322.1344.

3a,5-dimethyl-1-(*m*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3f):



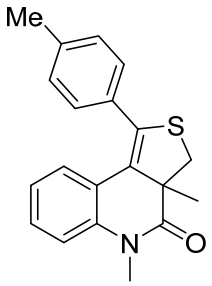
48% yield; white solid, mp 83 - 84 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.18 - 7.11 (m, 4H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 4.00 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 3.27 (d, *J* = 12.0 Hz, 1H), 2.33 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 139.3, 138.7, 137.9, 135.2, 129.4, 128.8, 128.8, 128.0, 127.5, 125.3, 125.1, 122.7, 121.2, 115.3, 58.0, 41.4, 30.2, 21.5, 21.4; LRMS (EI, 70 eV) *m/z* (%): 321 (M^+, 52), 306 (100); HRMS *m*/*z* (ESI) calcd for $C_{20}H_{19}NOS$ $[M+H]^+$ 322.1260, Found 322.1347.

1-(4-methoxyphenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3g):



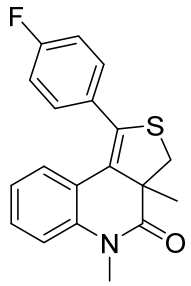
80% yield; pale yellow solid, mp 146 - 147 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 - 7.24 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 8.0 Hz, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.83 (s, 3H), 3.41 (s, 3H), 3.26 (d, *J* = 12.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 159.8, 139.4, 137.5, 129.6, 127.9, 127.4, 127.3, 124.5, 122.7, 121.4, 115.4, 114.3, 58.0, 55.4, 41.3, 30.2, 21.4; LRMS (EI, 70 eV) *m/z* (%): 337 (M^+, 54), 322 (100); HRMS *m*/*z* (ESI) calcd for $C_{20}H_{19}NO_2S$ $[M+H]^+$ 338.1209, Found 338.1251.

3a,5-dimethyl-1-(*p*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-on e (3h):



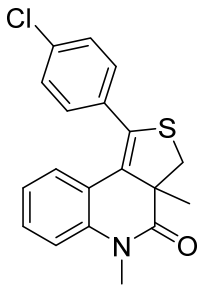
52% yield; white solid, mp 151 - 152 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 - 7.13 (m, 5H), 7.00 - 6.97 (m, 2H), 6.76 (t, *J* = 7.5 Hz, 1H), 4.01 (d, *J* = 12.0 Hz, 1H), 3.41 (s, 3H), 3.26 (d, *J* = 12.0 Hz, 1H), 2.36 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 139.3, 138.5, 137.9, 132.2, 129.6, 128.1, 127.9, 127.5, 124.8, 122.7, 121.3, 115.3, 58.1, 41.3, 30.2, 21.5, 21.4; LRMS (EI, 70 eV) *m/z* (%): 321 (M^+, 55), 306 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{19}NOS$ $[M+H]^+$ 322.1260, Found 322.1349.

1-(4-fluorophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4 (5*H*)-one (3i):



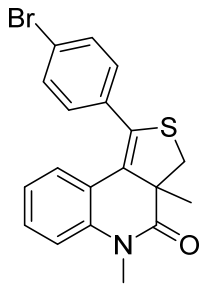
45% yield; white solid, mp 147 - 148 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.0, 5.5 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.05 - 7.00 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 3.28 (d, *J* = 12.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 162.8 (d, J_{C-F} = 247.5 Hz), 139.5, 136.5, 131.2 (d, J_{C-F} = 3.8 Hz), 130.2 (d, J_{C-F} = 7.5 Hz), 128.2, 127.4, 125.7, 122.8, 121.00, 116.2, 115.7 (d, J_{C-F} = 66.3 Hz), 58.1, 41.4, 30.2, 21.5; ^{19}F NMR (470 MHz, $CDCl_3$) δ -35.8; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 49), 310 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{16}FNOS$ $[M+H]^+$ 326.1009, Found 326.1065.

1-(4-chlorophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3j):



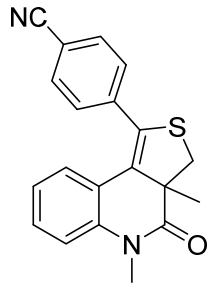
34% yield; white solid, mp 130 - 131 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.30 (m, 2H), 7.28 - 7.25 (m, 2H), 7.21 - 7.17 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.78 (td, *J* = 7.5, 1.0 Hz, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.41 (s, 3H), 3.28 (d, *J* = 12.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 139.4, 136.2, 134.4, 133.7, 129.8, 129.2, 128.4, 127.4, 126.0, 122.9, 120.8, 115.5, 58.1, 41.4, 30.2, 21.4; LRMS (EI, 70 eV) *m/z* (%): 343 (M^++2, 19), 341 (M^+, 49). 328 (38), 326 (100); HRMS *m*/*z* (ESI) calcd for $C_{19}H_{16}ClNOS$ $[M+H]^+$ 342.0714, Found 342.0763.

1-(4-bromophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3k):



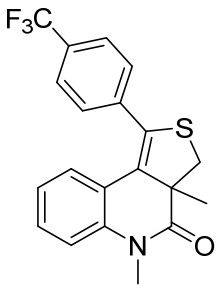
48% yield; pale yellow solid, mp 119 - 120 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.18 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.41 (s, 3H), 3.28 (d, *J* = 12.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 139.4, 136.2, 134.2, 132.2, 130.0, 128.4, 127.4, 126.1, 122.9, 122.6, 120.8, 115.5, 58.2, 41.4, 30.2, 21.4; LRMS (EI, 70 eV) *m/z* (%): 387 (M^++2, 46), 385 (M^+, 46), 372 (100), 370 (92); HRMS *m*/*z* (ESI) calcd for $C_{19}H_{16}BrNOS$ $[M+H]^+$ 386.0209, Found 386.0229.

4-(3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydrothieno[3,4-*c*]quinolin-1-yl) benzonitrile (3l):



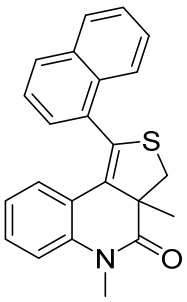
61% yield; yellow solid, mp 168 - 169 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.84 - 6.77 (m, 2H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 3.32 (d, *J* = 12.0 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 140.4, 139.7, 135.2, 132.7, 129.3, 128.9, 127.9, 127.5, 123.0, 120.3, 118.6, 115.7, 112.3, 58.4, 41.5, 30.3, 21.3; LRMS (EI, 70 eV) *m/z* (%): 332 (M^+, 42), 317 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{16}N_2OS$ $[M+H]^+$ 333.1056, Found 333.1077.

3a,5-dimethyl-1-(4-(trifluoromethyl)phenyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3m):



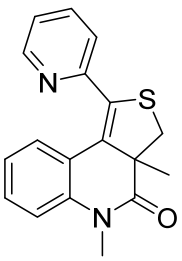
42% yield; white solid, mp 155 - 156 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.22 - 7.19 (m, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.43 (s, 3H), 3.31 (d, *J* = 12.0 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 139.5, 139.2, 135.7, 130.5 (q, $J_{C\text{-}F}$ = 31.3 Hz), 128.8, 128.6, 127.5, 127.0, 125.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $J_{C\text{-}F}$ = 271.3 Hz), 122.9, 120.5, 115.6, 58.2, 41.5, 30.2, 21.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ 13.9; LRMS (EI, 70 eV) *m/z* (%): 375 (M^+, 43), 360 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{16}F_3NOS$ $[M+H]^+$ 376.0977, Found 376.1073.

3a,5-dimethyl-1-(naphthalen-1-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3n):



63% yield; pale yellow solid, mp 160 - 161 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 - 8.10 (m, 1.7H), 7.93 - 7.91 (m, 1.7H), 7.87 (d, *J* = 8.0 Hz, 2.7H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.52 (m, 5.4H), 7.44 - 7.40 (m, 2.7H), 7.35 - 7.30 (m, 2.7H), 7.08 (t, *J* = 8.0 Hz, 1.7H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.98 - 6.94 (m, 2.7H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.51 (t, *J* = 7.5 Hz, 1.7H), 6.46 (t, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1.7H), 4.14 - 4.10 (m, 2.7H), 3.45 - 3.37 (m, 10.8H), 1.61 (s, 5.1H), 1.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 173.7, 139.1, 138.7, 136.6, 135.4, 134.1, 133.9, 132.7, 132.7, 131.8, 129.8, 129.1, 129.0, 128.8, 128.4, 128.1, 127.9, 127.0, 127.0, 126.9, 126.8, 126.5, 126.4, 126.3, 126.3, 125.5, 125.4, 125.3, 122.9, 122.9, 120.8, 120.6, 115.2, 115.1, 58.1, 57.8, 41.9, 41.8, 30.2 (2C), 21.9, 21.8; LRMS (EI, 70 eV) *m/z* (%): 357 (M^+, 52), 342 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{19}NOS$ $[M+H]^+$ 358.1260, Found 358.1312.

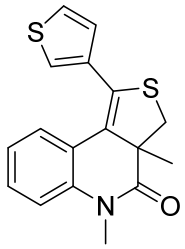
3a,5-dimethyl-1-(pyridin-2-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3o):



28% yield; yellow solid, mp 31 - 32 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 4.0 Hz, 1H), 7.60 (td, *J* = 8.0, 2.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.25 - 7.21 (m, 2H), 7.07 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (td, *J* = 7.5, 0.5 Hz, 1H), 3.97 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 3.30 (d, *J* = 12.0 Hz, 1H), 1.43 (s, 3H); ^{13}C

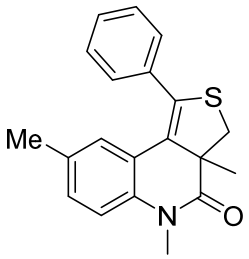
NMR (125 MHz, $CDCl_3$) δ 173.9, 154.0, 150.1, 139.7, 137.5, 136.4, 128.9, 128.0, 127.9, 123.4, 123.2, 122.8, 120.6, 115.6, 58.5, 41.0, 30.2, 20.7; LRMS (EI, 70 eV) *m/z* (%): 308 (M^+, 54), 293 (49), 275 (20), 262 (100), 230 (30); HRMS *m*/*z* (ESI) calcd for $C_{18}H_{16}N_2OS$ $[M+H]^+$ 309.1056, Found 309.1123.

3a,5-dimethyl-1-(thiophen-3-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3p):



67% yield; yellow solid, mp 110 - 111 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 - 7.28 (m, 2H), 7.22 - 7.19 (m, 1H), 7.13 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.03 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.02 - 7.01 (m, 1H), 6.84 (td, *J* = 7.5, 1.0 Hz, 1H), 4.03 (d, *J* = 12.0 Hz, 1H), 3.41 (s, 3H), 3.26 (d, *J* = 12.0 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 139.3, 134.9, 132.0, 128.3, 127.5, 127.3, 126.1, 125.6, 124.4, 122.8, 121.3, 115.4, 58.1, 41.3, 30.2, 21.5; LRMS (EI, 70 eV) *m/z* (%): 313 (M^+, 57), 298 (100); HRMS *m*/*z* (ESI) calcd for $C_{17}H_{15}NOS_2$ $[M+H]^+$ 314.0668, Found 314.0702.

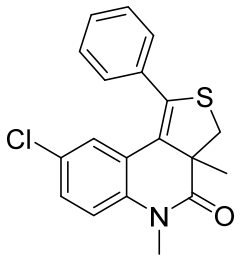
3a,5,8-trimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3r):



50% yield; pale yellow solid, mp 163 - 164 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 - 7.32 (m, 5H), 6.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 1.5 Hz, 1H), 4.01 (d, *J* = 12.0 Hz, 1H), 3.39 (s, 3H), 3.27 (d, *J* = 12.0 Hz, 1H), 2.01 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 137.3, 137.1, 135.3, 132.1, 128.8, 128.7, 128.6, 128.3, 128.0, 125.6, 120.9, 115.2, 58.1, 41.4, 30.2, 21.4,

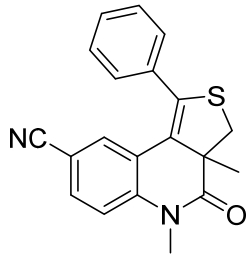
20.6; LRMS (EI, 70 eV) *m/z* (%): 321 (M^+, 52), 306 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{19}NOS$ $[M+H]^+$ 322.1260, Found 322.1346.

8-chloro-3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3s):



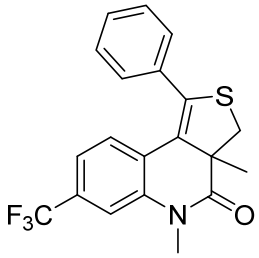
61% yield; yellow solid, mp 181 - 182 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.36 (m, 3H), 7.32 - 7.30 (m, 2H), 7.11 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.39 (s, 3H), 3.28 (d, *J* = 12.0 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 139.9, 137.9, 134.5, 129.1, 129.1, 128.1, 127.7, 127.1, 123.9, 122.5, 116.6, 57.8, 41.4, 30.4, 21.5; LRMS (EI, 70 eV) *m/z* (%): 343 (M^++2, 20), 341 (M^+, 51), 328 (40), 326 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{16}ClNOS$ $[M+H]^+$ 342.0714, Found 342.0776.

3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydrothieno[3,4-*c*]quinoline-8-carbonitrile (3t):



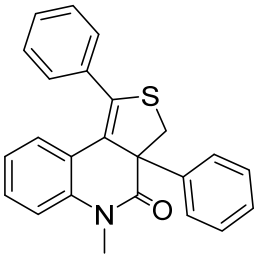
55% yield; white solid, mp 216 - 217 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.40 - 7.38 (m, 3H), 7.29 - 7.27 (m, 2H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 4.04 (d, *J* = 12.0 Hz, 1H), 3.43 (s, 3H), 3.30 (d, *J* = 12.0 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 142.5, 141.7, 133.9, 131.5, 130.9, 129.5, 129.4, 127.9, 122.5, 121.9, 118.5, 115.9, 106.1, 57.6, 41.3, 30.4, 21.7; LRMS (EI, 70 eV) *m/z* (%): 332 (M^+, 44), 317 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{16}N_2OS$ $[M+H]^+$ 333.1056, Found 333.1079.

3a,5-dimethyl-1-phenyl-7-(trifluoromethyl)-3,3a-dihydrothieno[3,4-*c*] quinolin-4(5*H*)-one (3u):



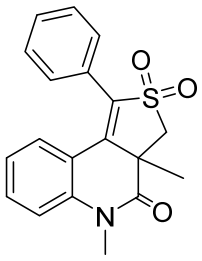
81% yield; white solid, mp 125 - 126 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.36 (m, 3H), 7.31 - 7.29 (m, 2H), 7.20 (s, 1H), 6.99 (s, 1H), 4.06 (d, *J* = 12.0 Hz, 1H), 3.45 (s, 3H), 3.31 (d, *J* = 12.0 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 141.3, 139.6, 134.6, 129.6 (q, J_{C-F} = 32.5 Hz), 129.2, 129.1, 128.2, 127.7, 124.3, 124.0 (q, J_{C-F} = 270.0 Hz), 123.8, 119.4 (q, J_{C-F} = 3.8 Hz), 112.2 (q, J_{C-F} = 3.8 Hz), 57.7, 41.5, 30.3, 21.7; ^{19}F NMR (470 MHz, $CDCl_3$) δ 13.9; LRMS (EI, 70 eV) *m/z* (%): 375 (M^+, 44), 360 (100); HRMS *m/z* (ESI) calcd for $C_{20}H_{16}F_3NOS$ $[M+H]^+$ 376.0977, Found 376.1022.

5-methyl-1,3a-diphenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3v):



46% yield; white solid, mp 179 - 180 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.42 (m, 4H), 7.40 - 7.37 (m, 3H), 7.27 - 7.25 (m, 1H), 7.25 - 7.24 (m, 1H), 7.21 - 7.18 (m, 1H), 7.06 - 7.03 (m, 1H), 7.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.71 (td, *J* = 7.5, 1.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.44 - 3.41 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 141.9, 139.3, 139.2, 135.0, 129.0, 128.9, 128.4, 128.0, 127.8, 127.3, 126.5, 123.2, 122.8, 122.1, 115.6, 65.6, 43.7, 30.6; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+, 71), 292 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{19}NOS$ $[M+H]^+$ 370.1260, Found 370.1348.

3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one 2,2-dioxide (4a):



97% yield; white solid, mp 204 - 205 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 - 7.39 (m, 6H), 7.15 - 7.12 (m, 2H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.53 (d, *J* = 14.0 Hz, 1H), 3.47 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 140.5, 140.0, 137.2, 132.1, 130.1, 129.5, 129.4, 129.3, 127.0, 123.5, 117.2, 115.8, 57.5, 47.6, 30.6, 25.7; LRMS (EI, 70 eV) *m/z* (%): 339 (M^+, 74), 274 (57), 260 (100); HRMS *m/z* (ESI) calcd for $C_{19}H_{17}NO_3S$ $[M+H]^+$ 340.1002, Found 340.1107.

(C) References

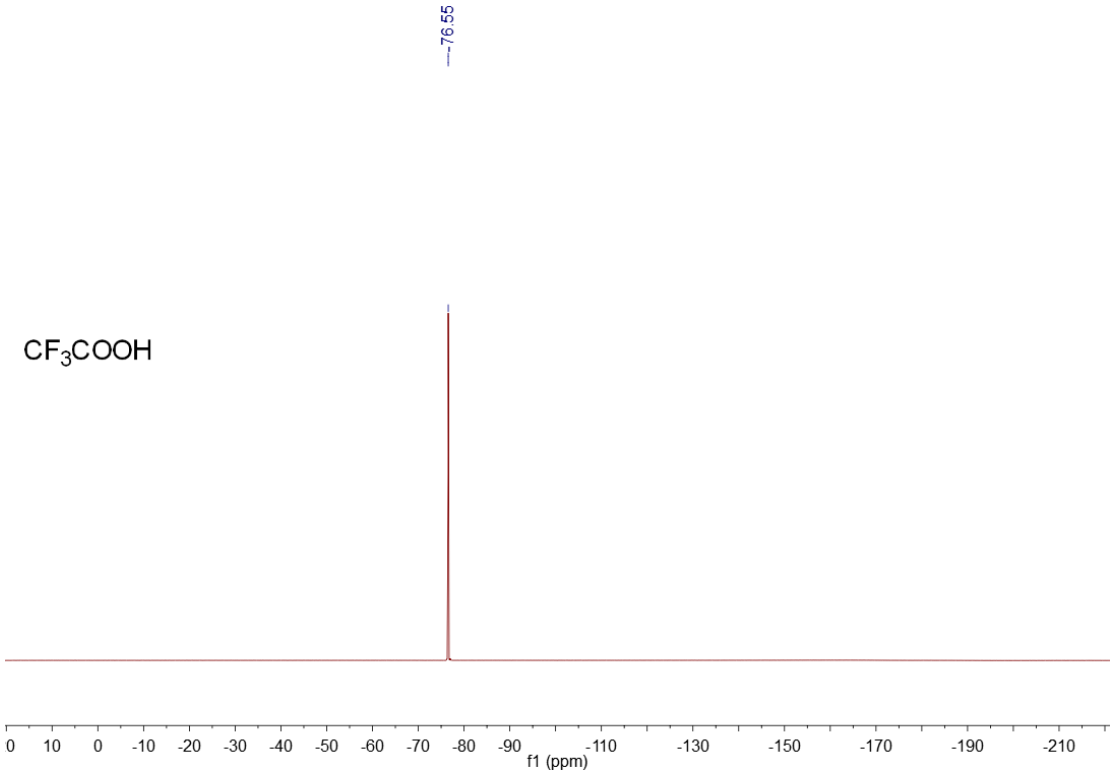
(1) X. Mu, T. Wu, H.-y. Wang, Y.-l. Guo and G. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 878.

(2) N. Sakiyama, K. Noguchi and K. Tanaka, *Angew. Chem. Int. Ed.*,, 2012, **51**, 5976.

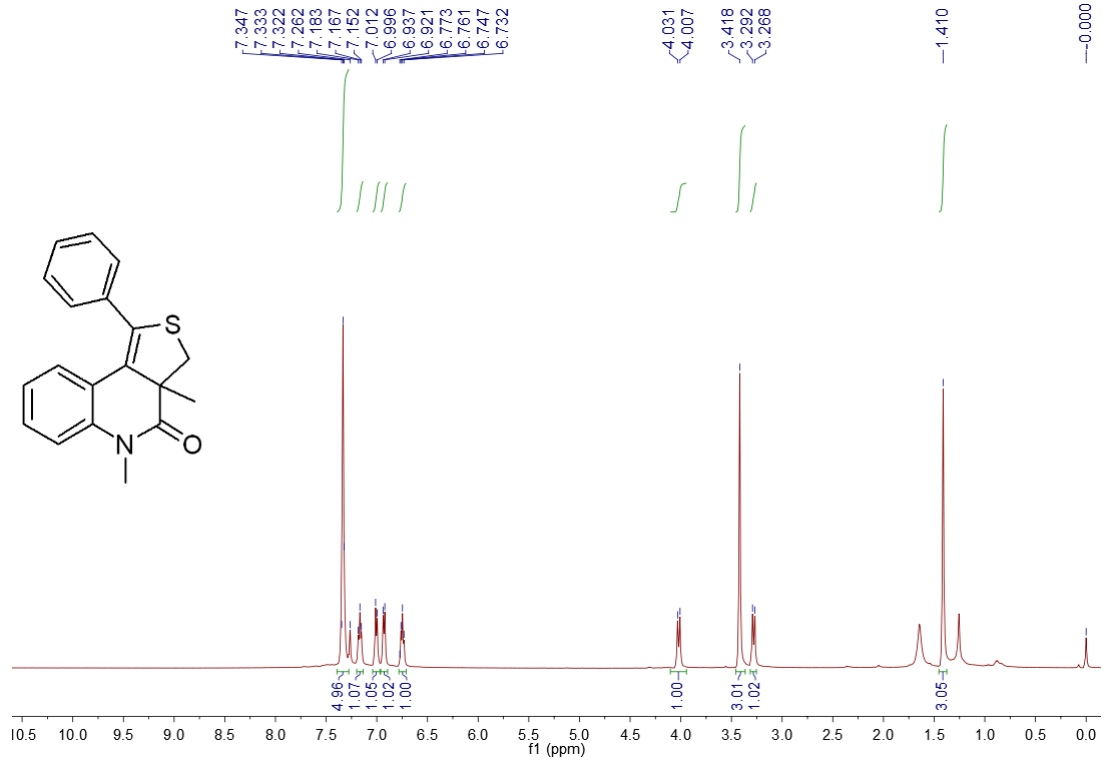
(3) C. D. McCune, M. L. Beio, J. M. Sturdivant, R. de la Salud-Bea, B. M. Darnell and D. B. Berkowitz, *J. Am. Chem. Soc.*, 2017, **139**, 14077.

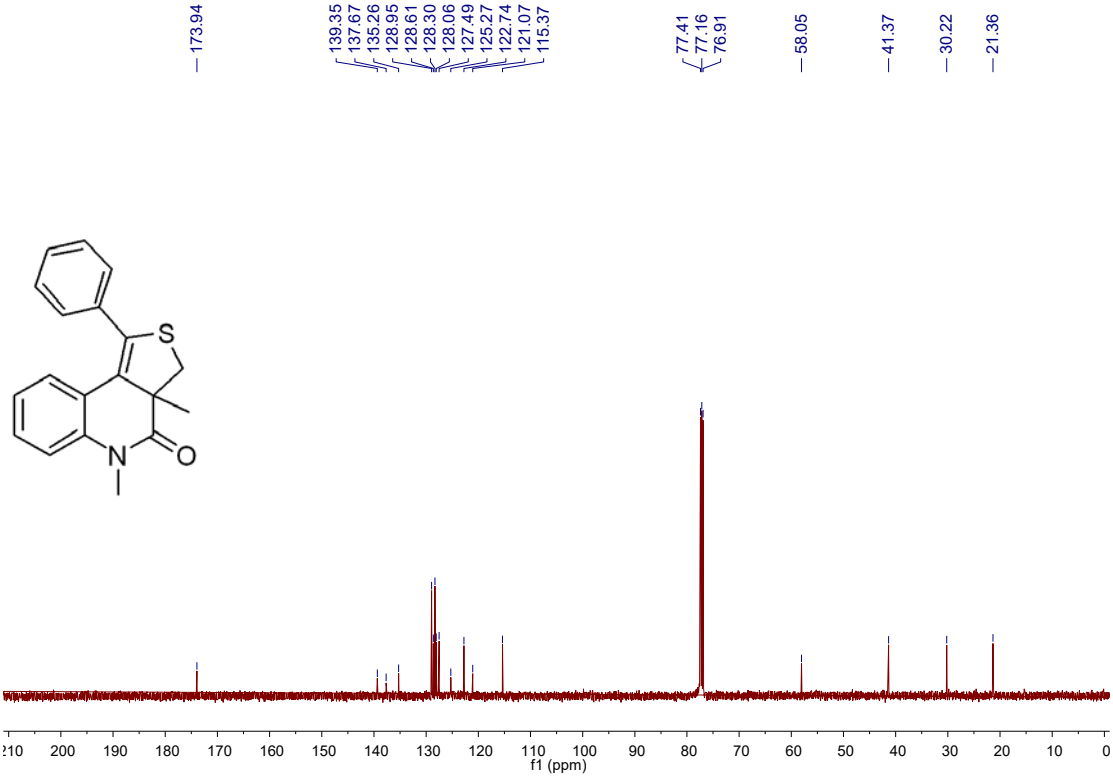
(D) Spectra

trifluoroacetic acid (TFA)

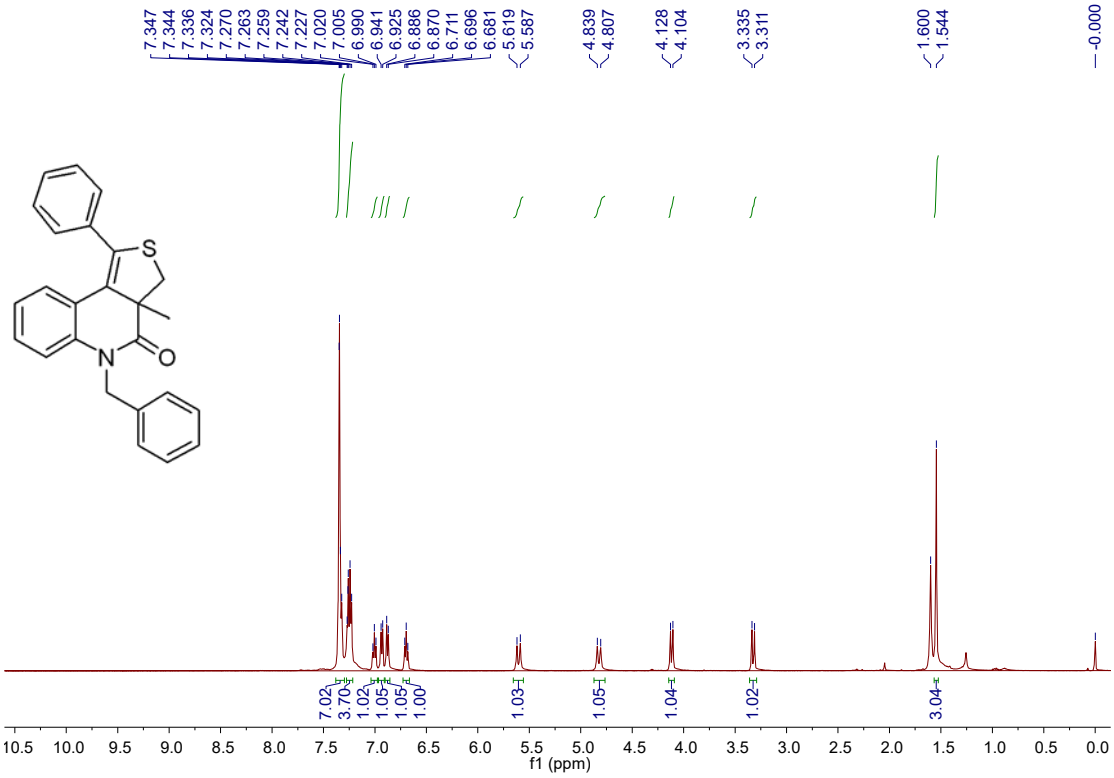


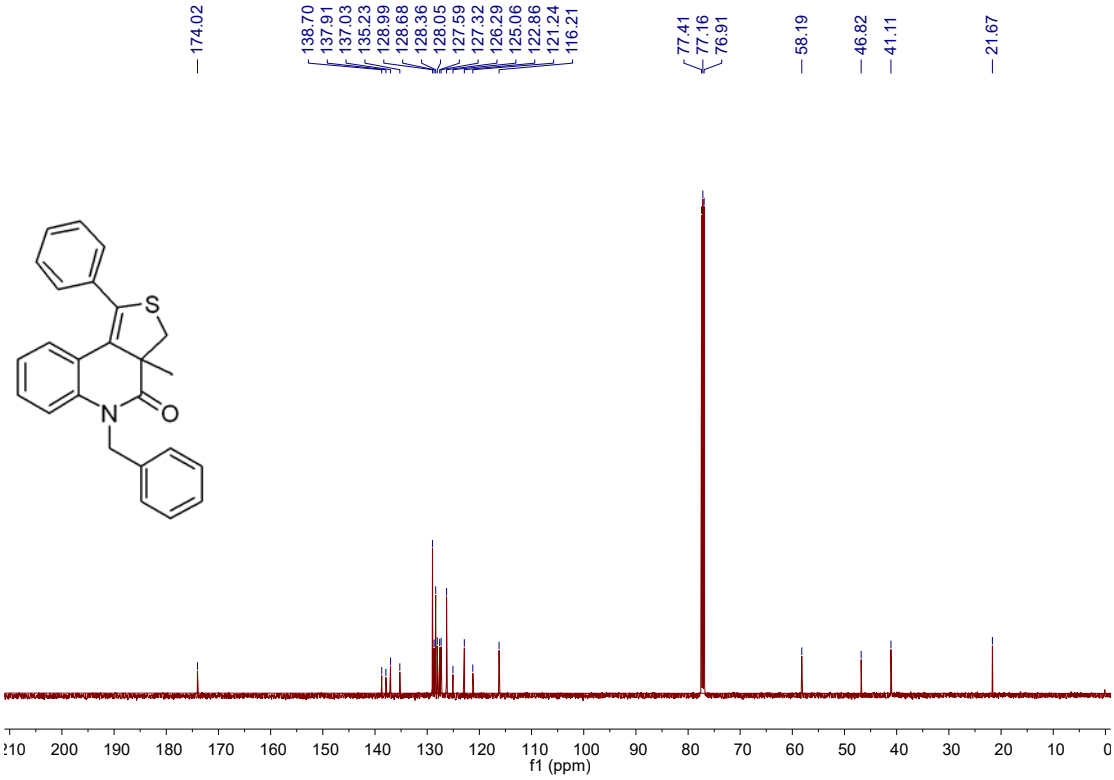
3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3a):



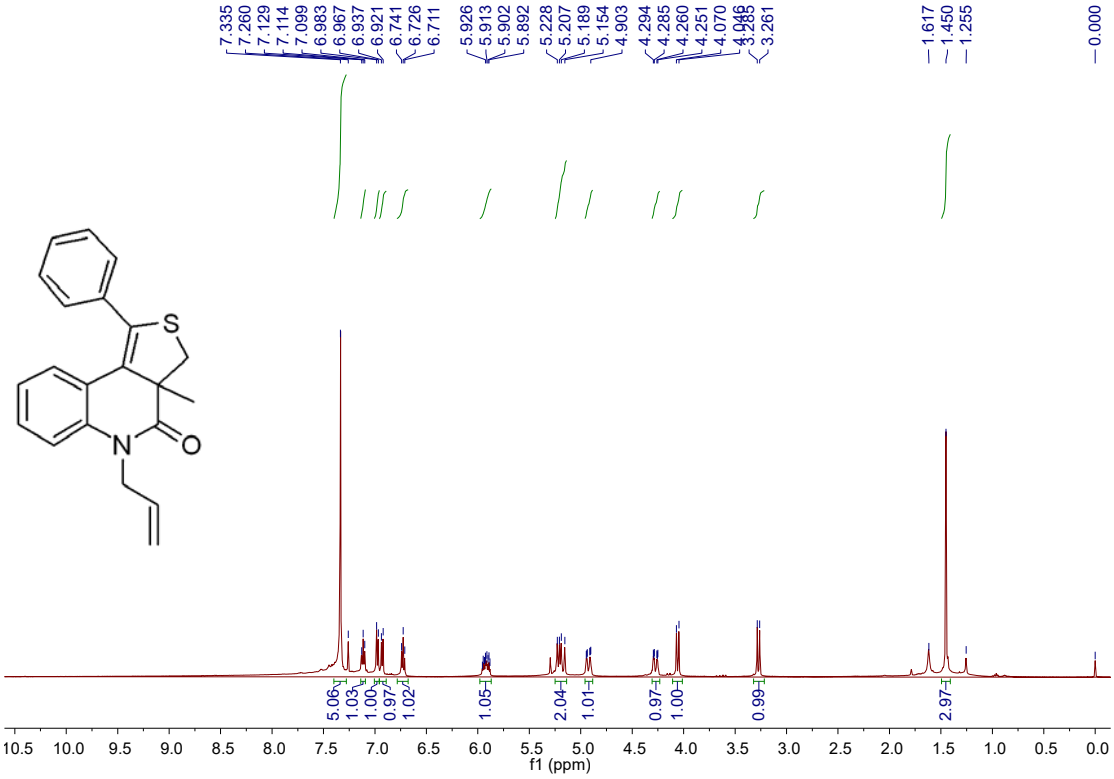


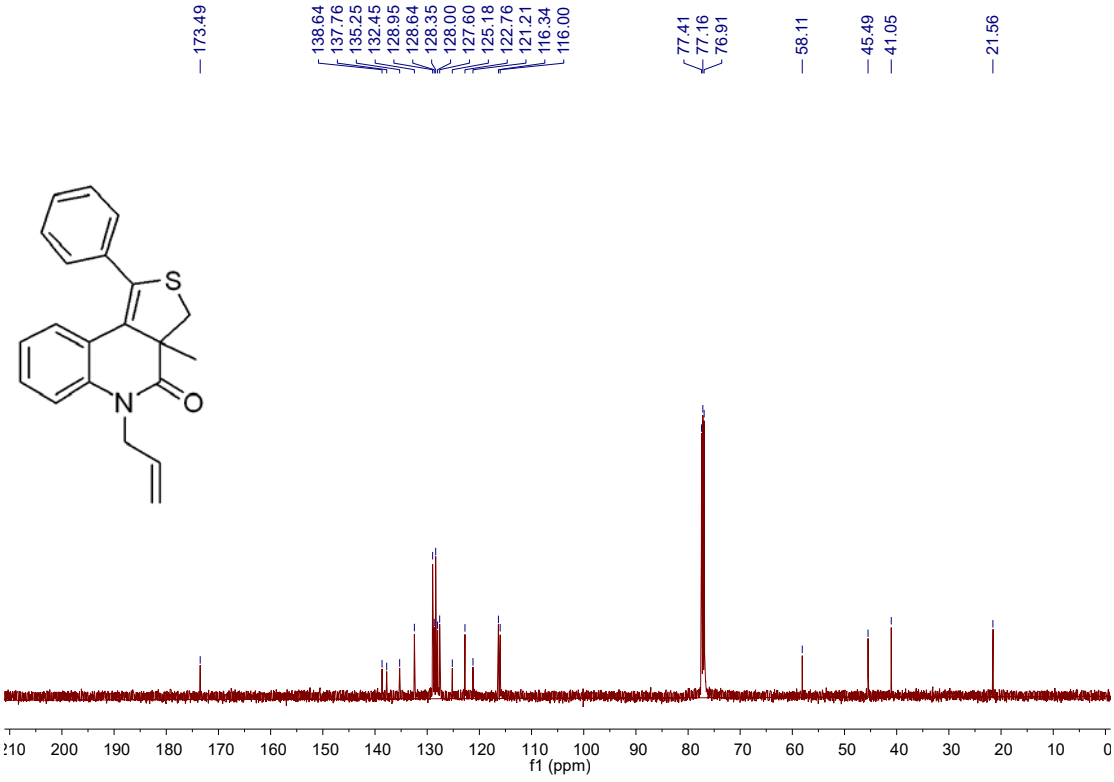
5-benzyl-3a-methyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3b):





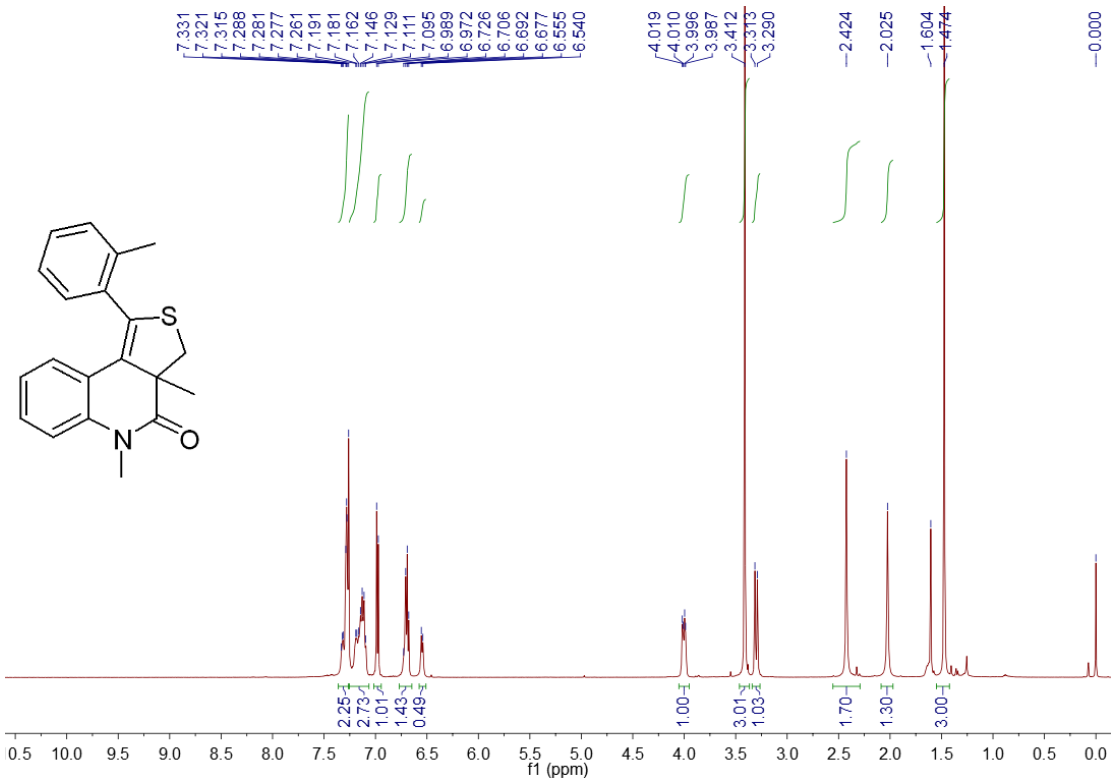
5-allyl-3a-methyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3c):

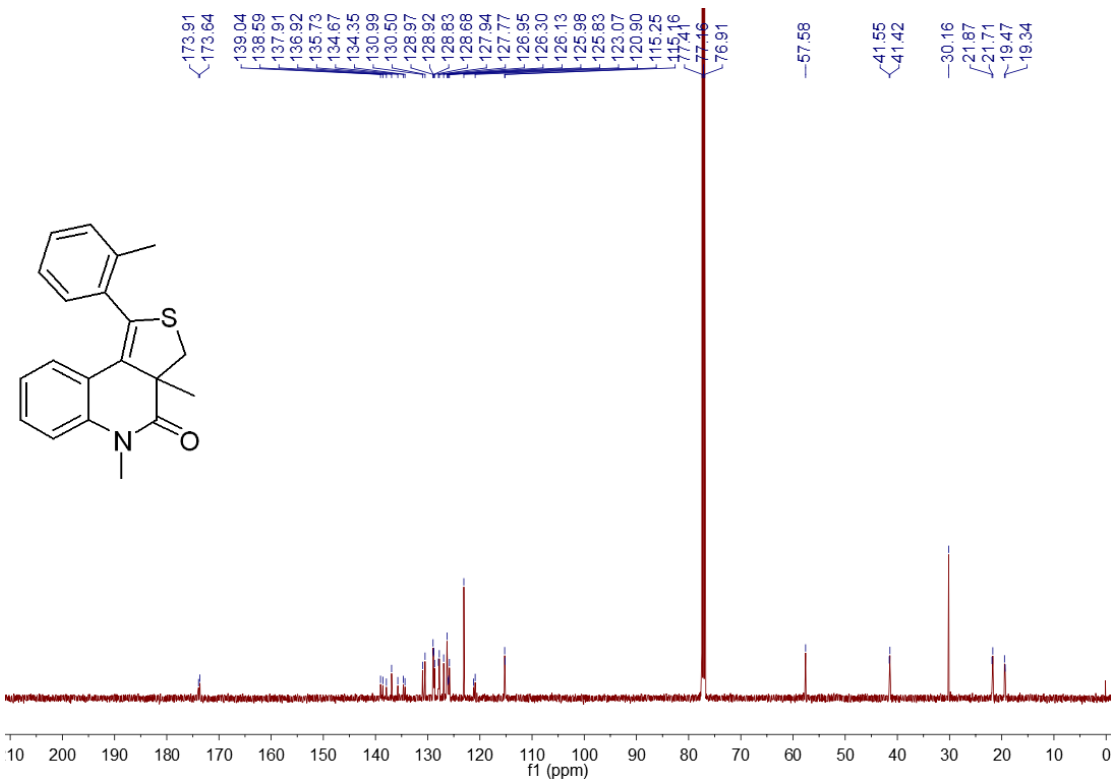




3a,5-dimethyl-1-(*o*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-on

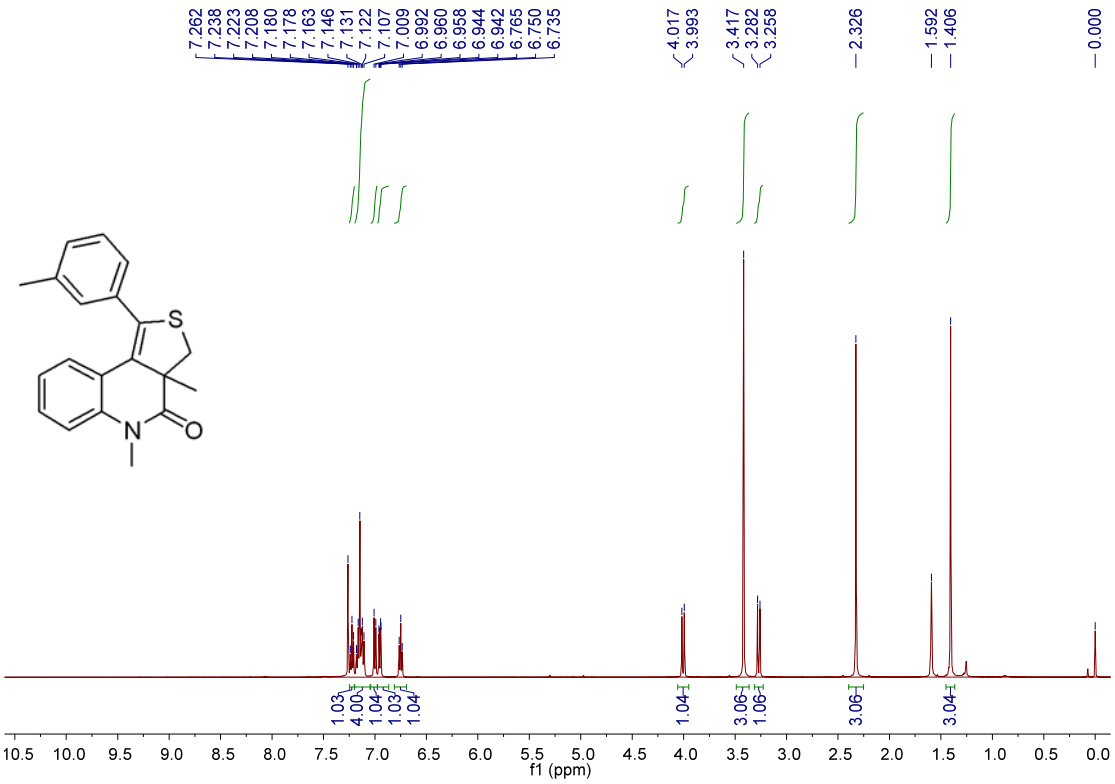
e (3e):

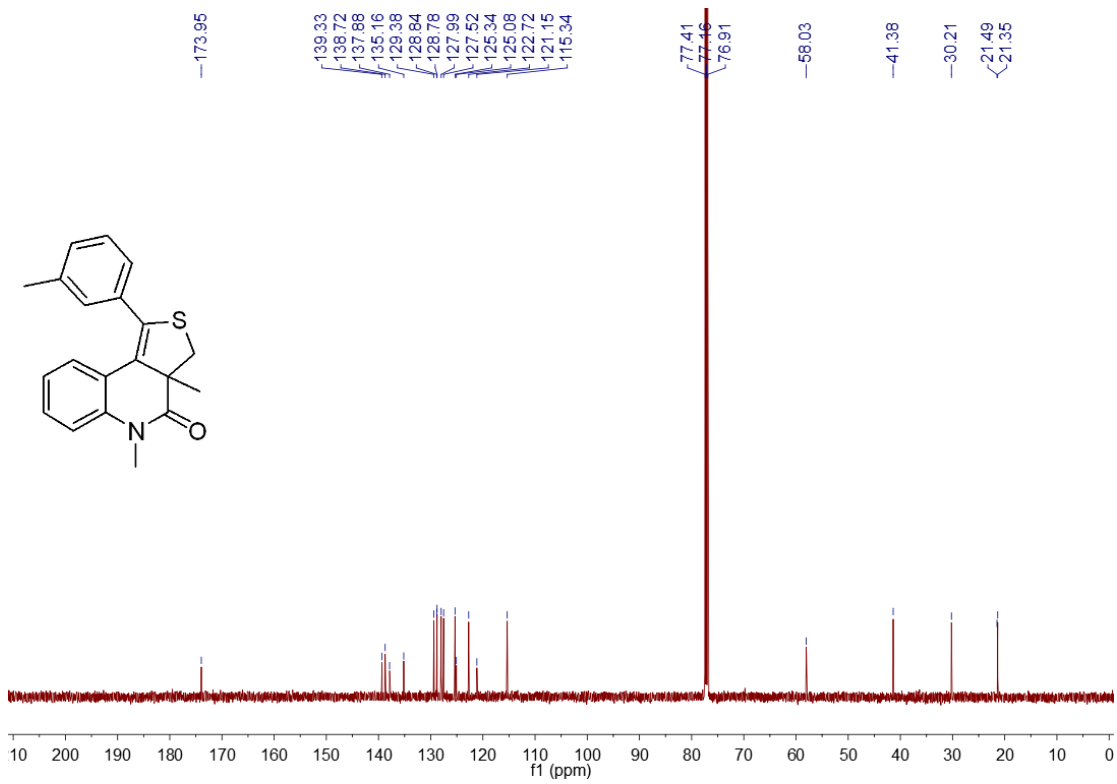




3a,5-dimethyl-1-(*m*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-on

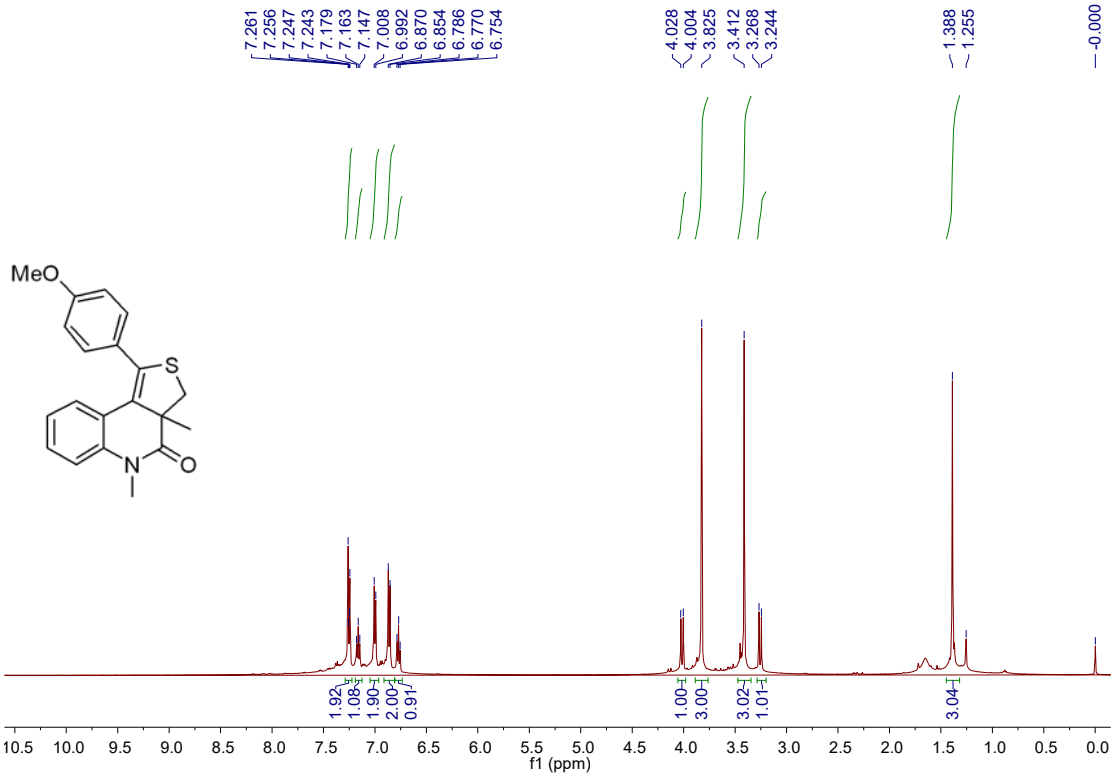
e (3f):

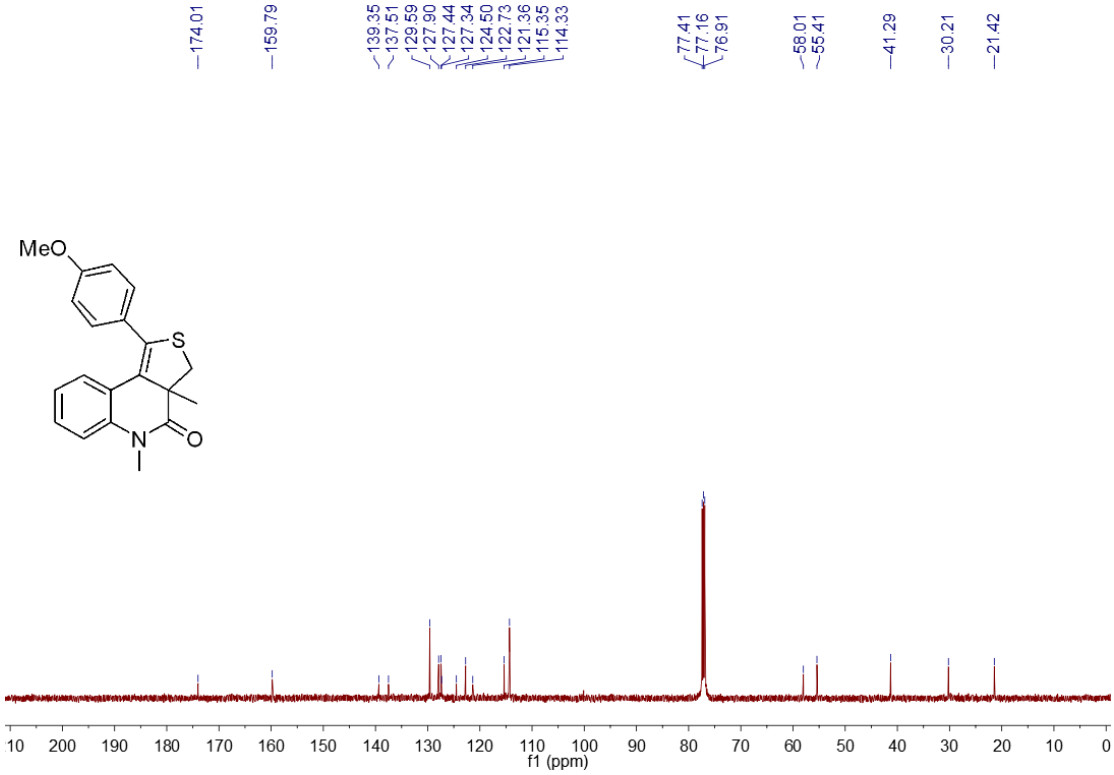




1-(4-methoxyphenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinoli

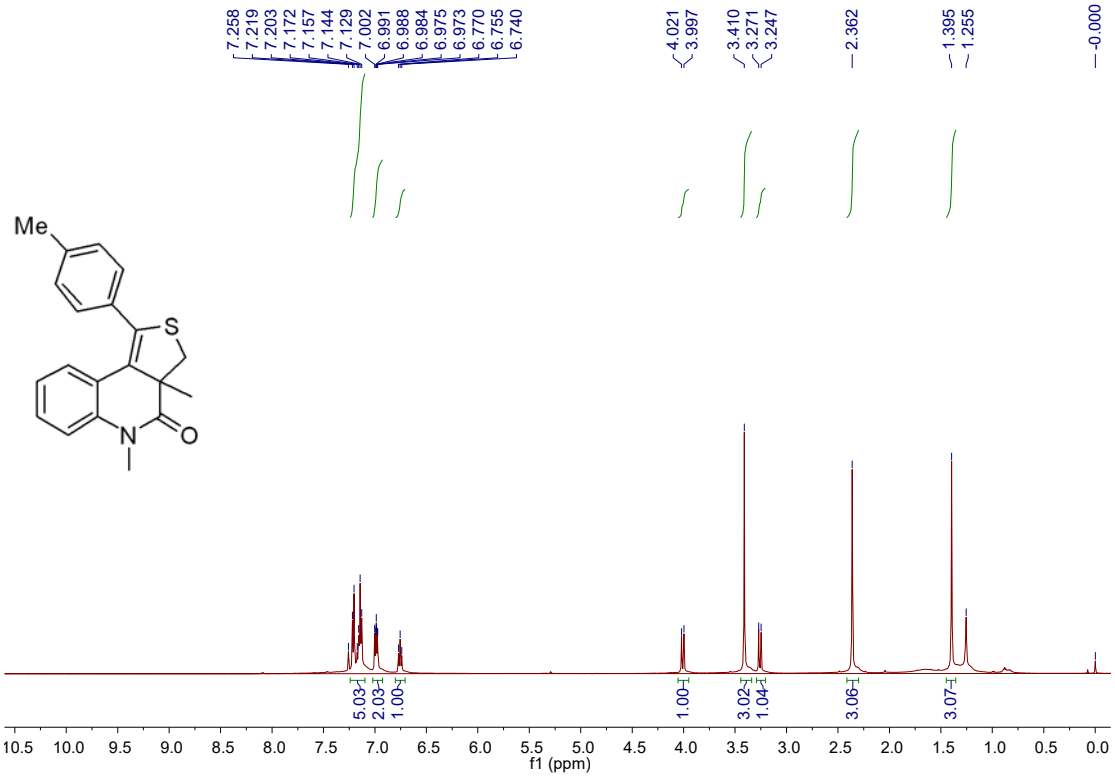
n-4(5*H*)-one (3g):

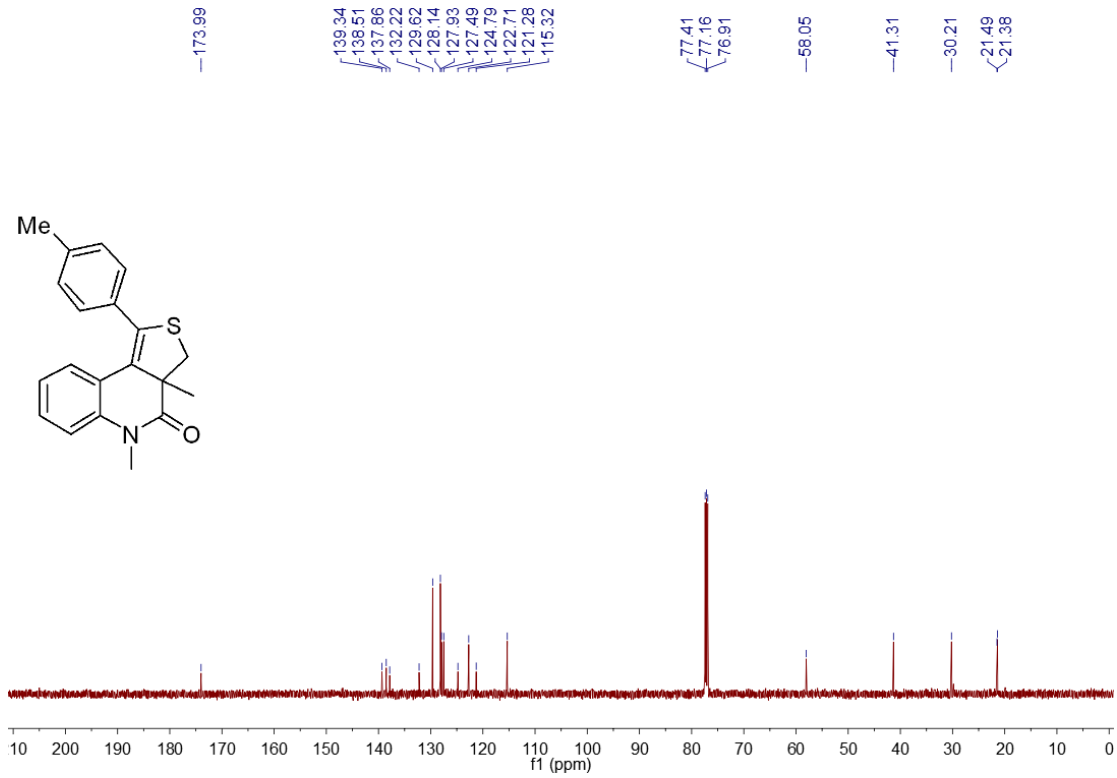




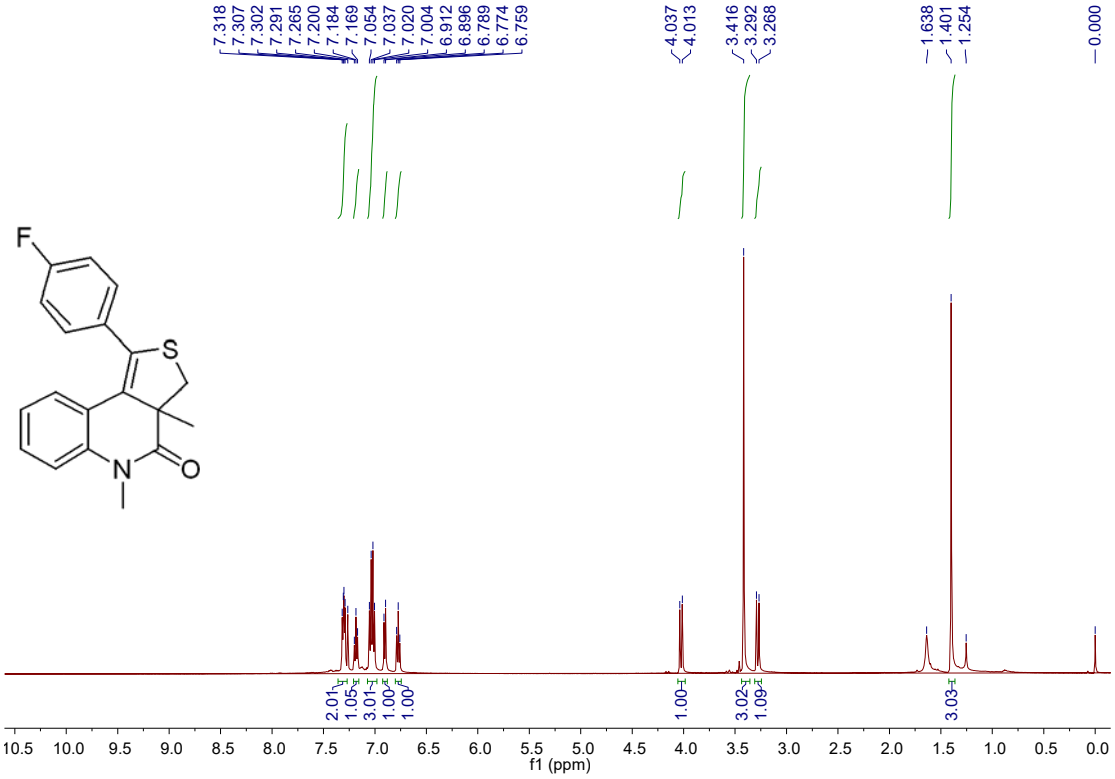
3a,5-dimethyl-1-(*p*-tolyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-on

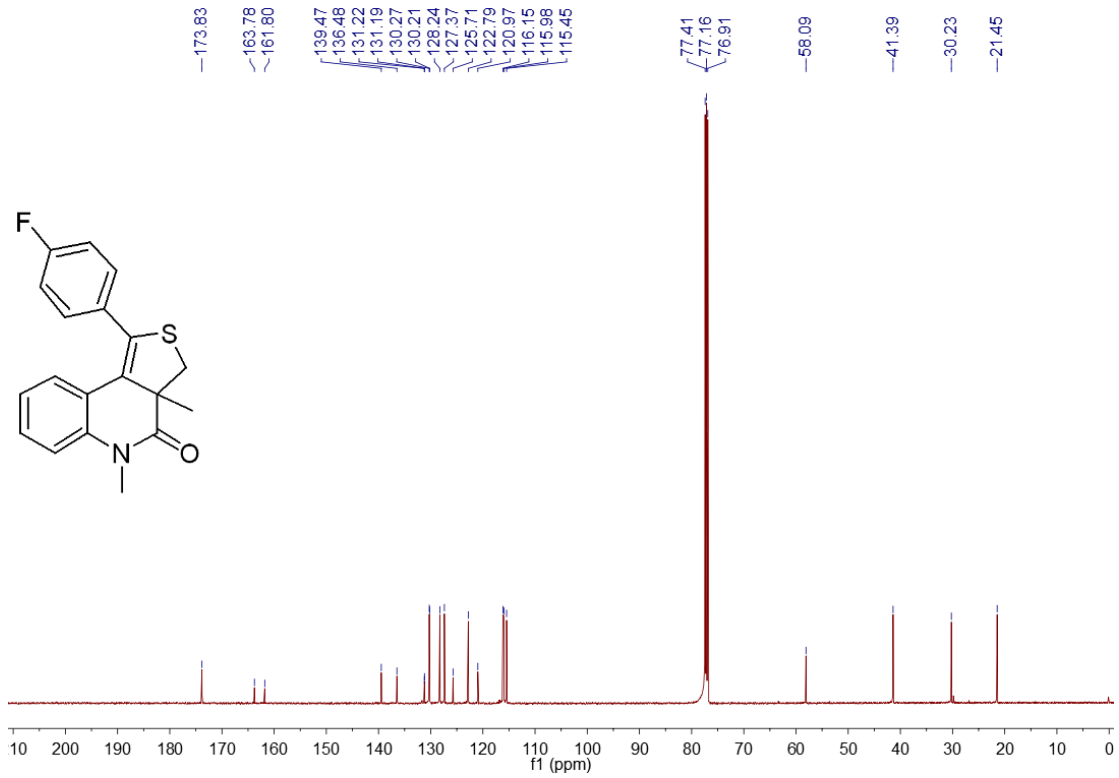
e (3h):

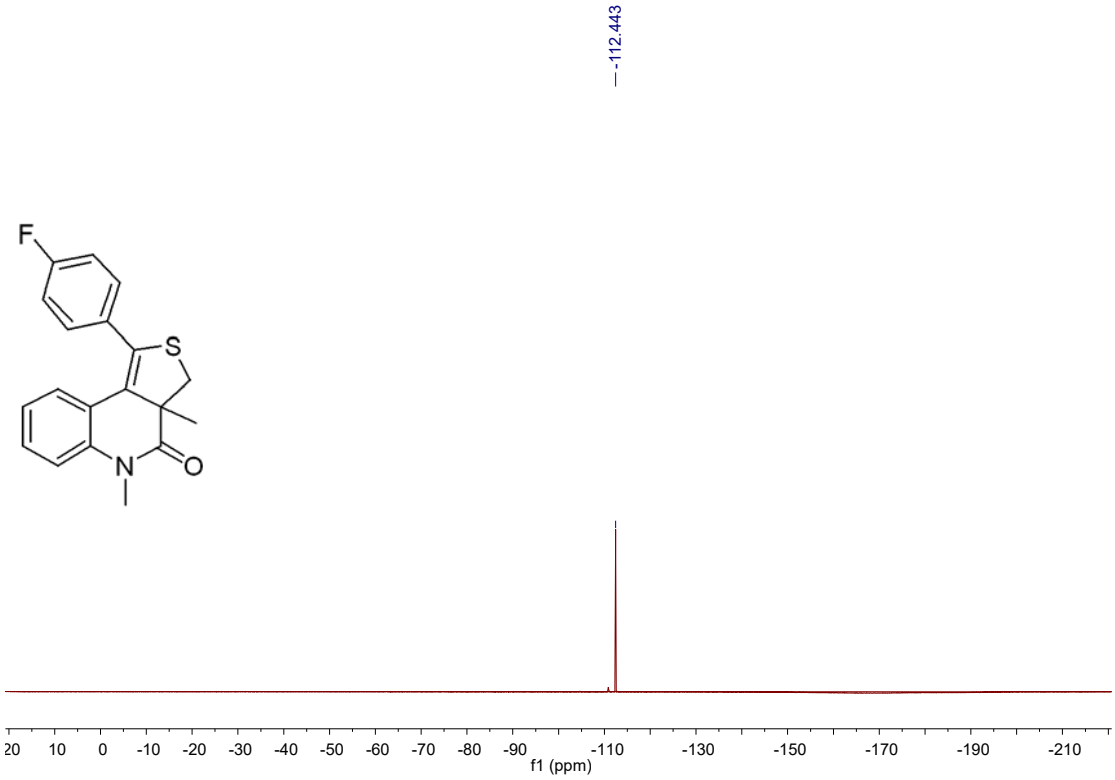




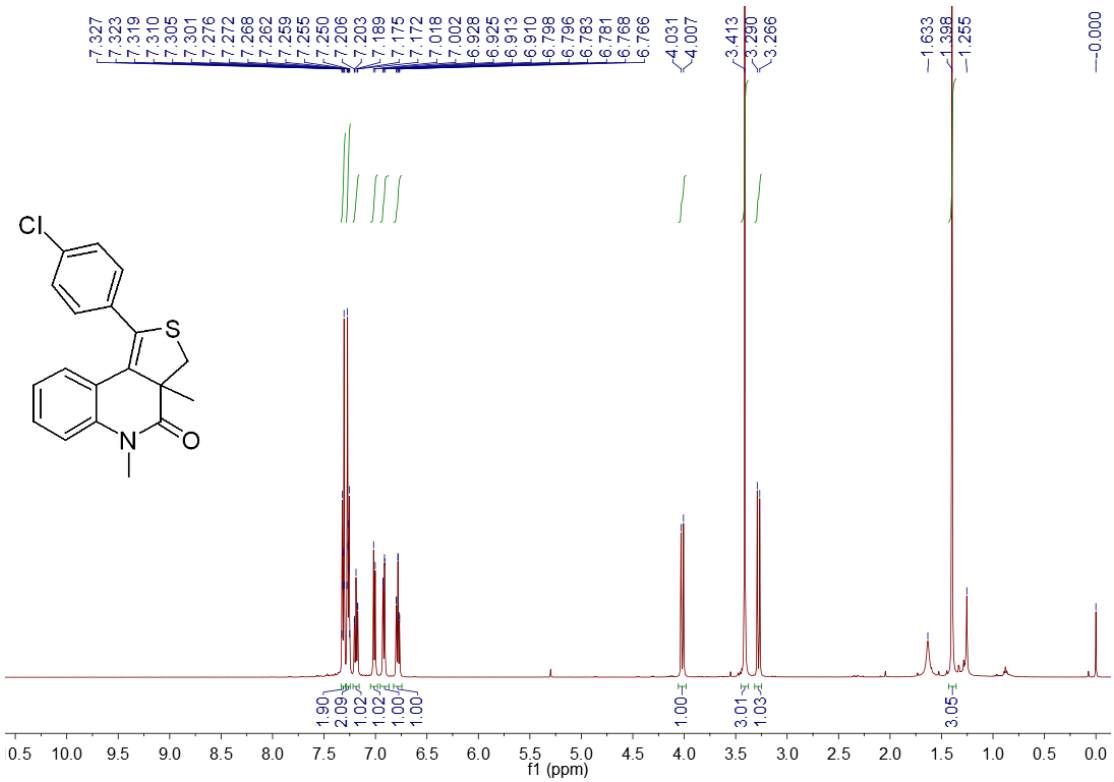
1-(4-fluorophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3i):

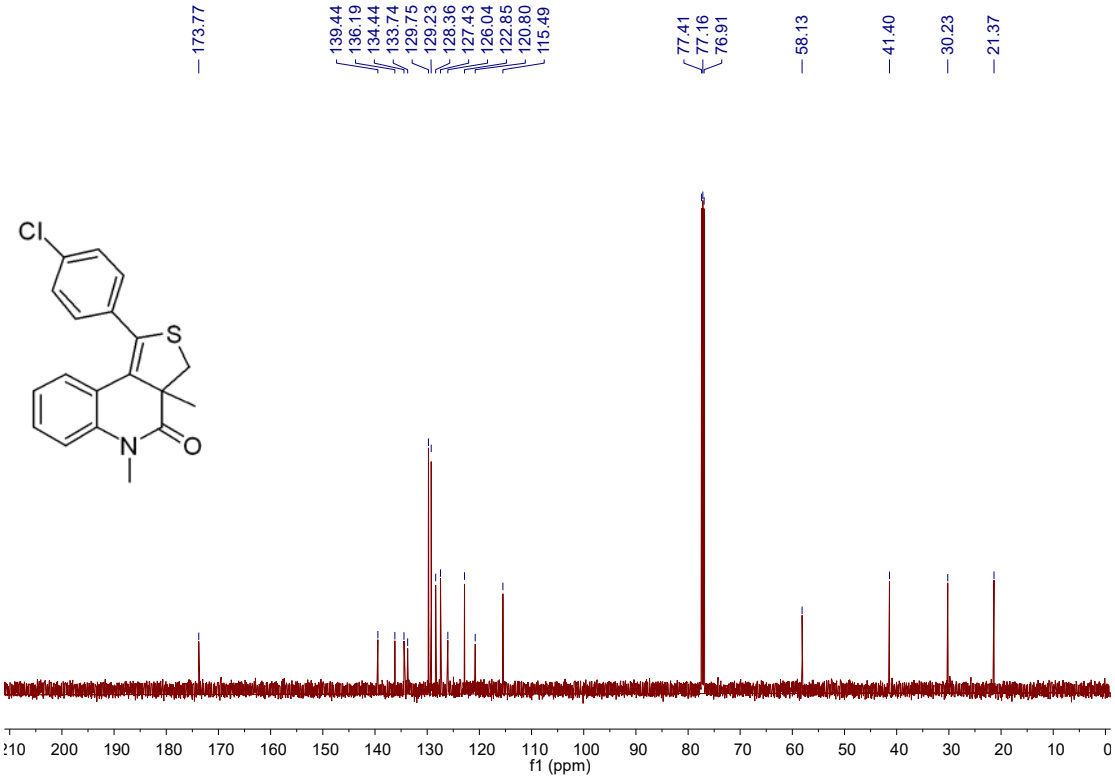




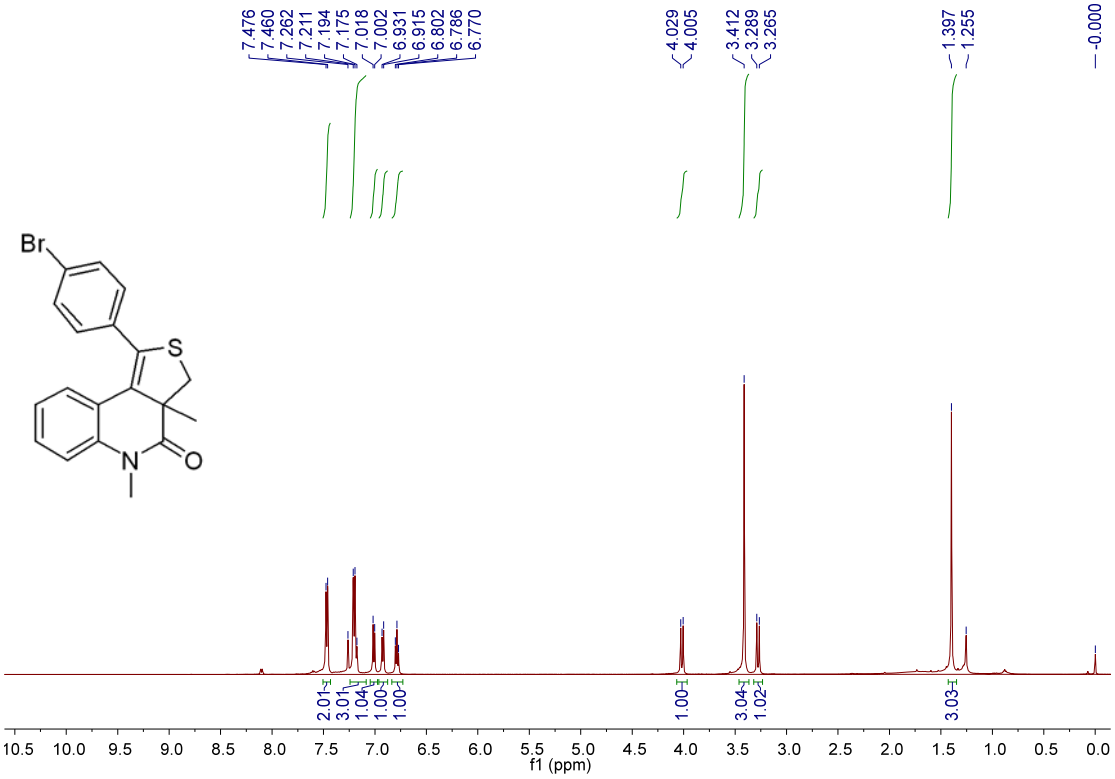

-112.443
F
S
N
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

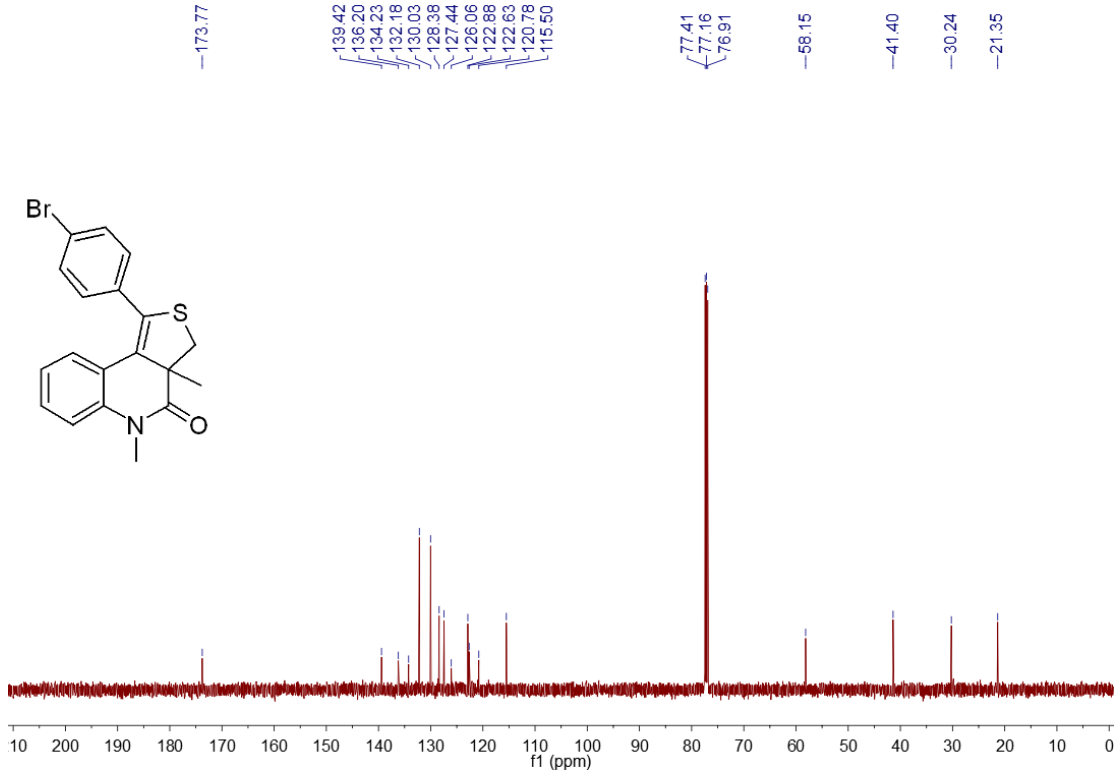
1-(4-chlorophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3j):



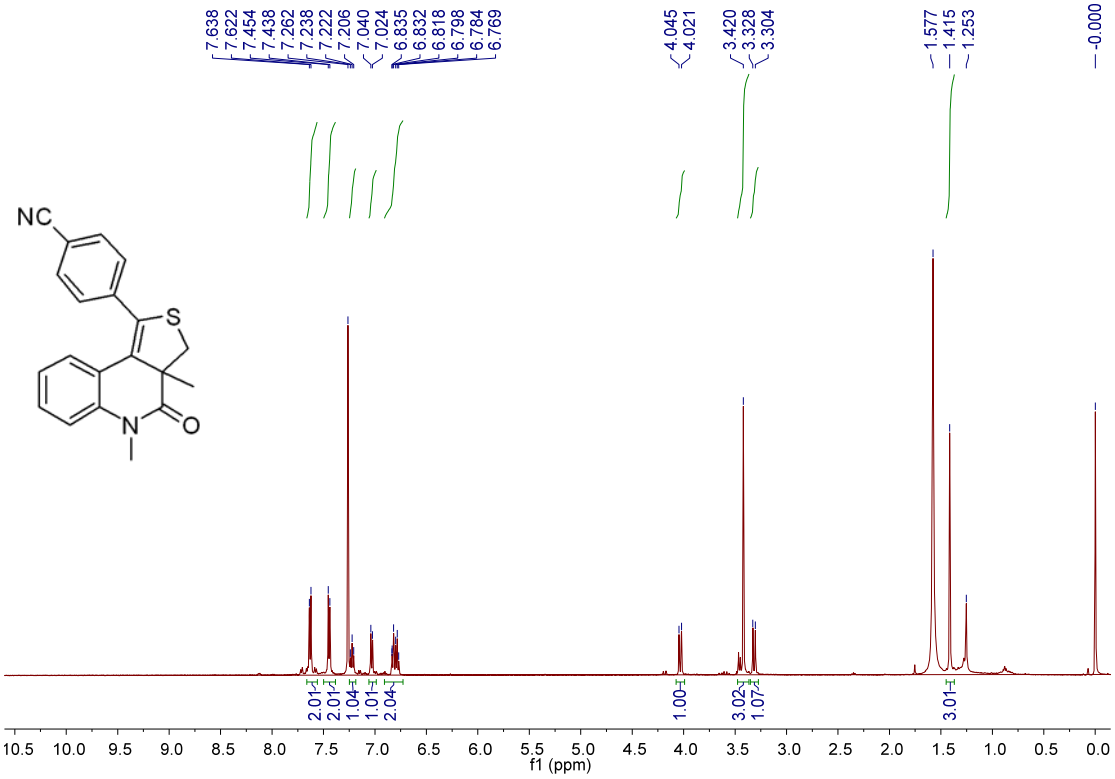


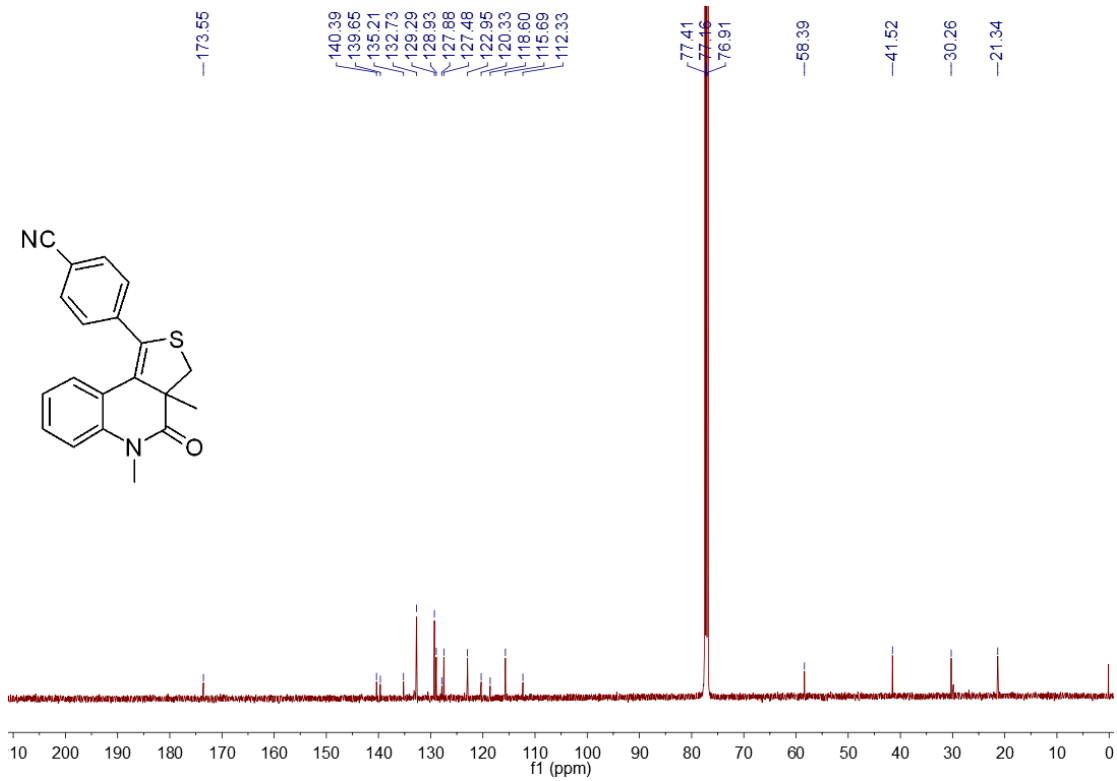
1-(4-bromophenyl)-3a,5-dimethyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3k):



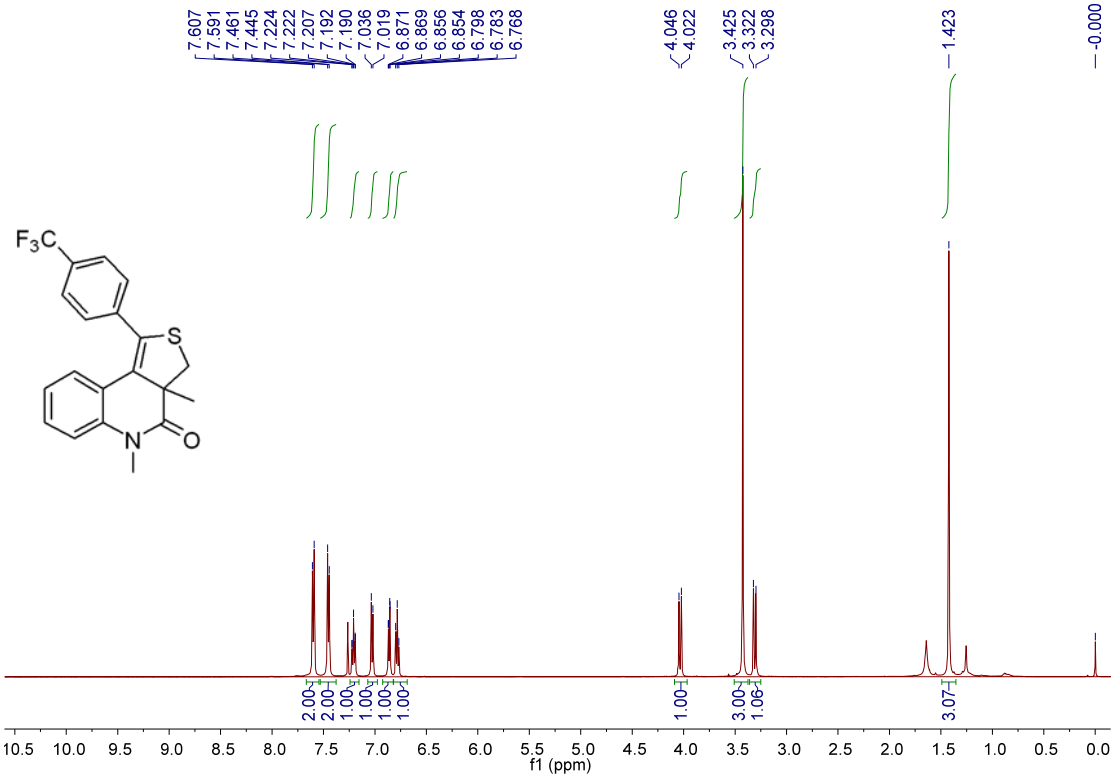


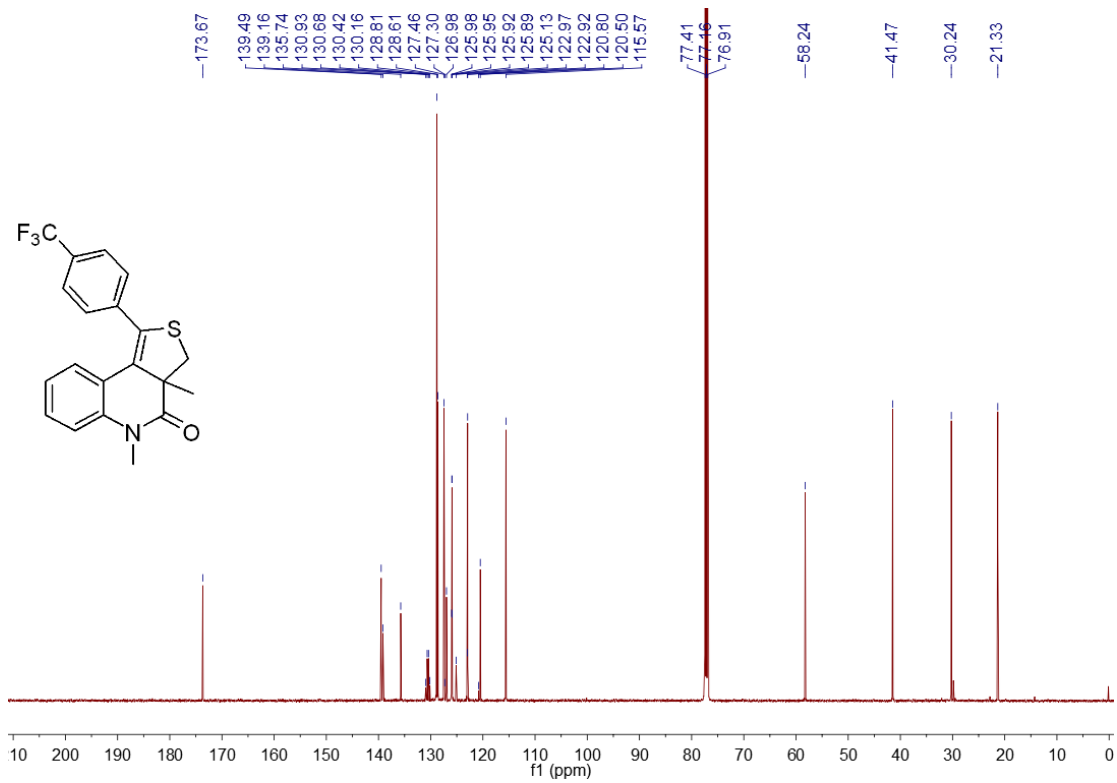
4-(3a,5-dimethyl-4-oxo-3,3a,4,5-tetrahydrothieno[3,4-*c*]quinolin-1-yl) benzonitrile (3l):

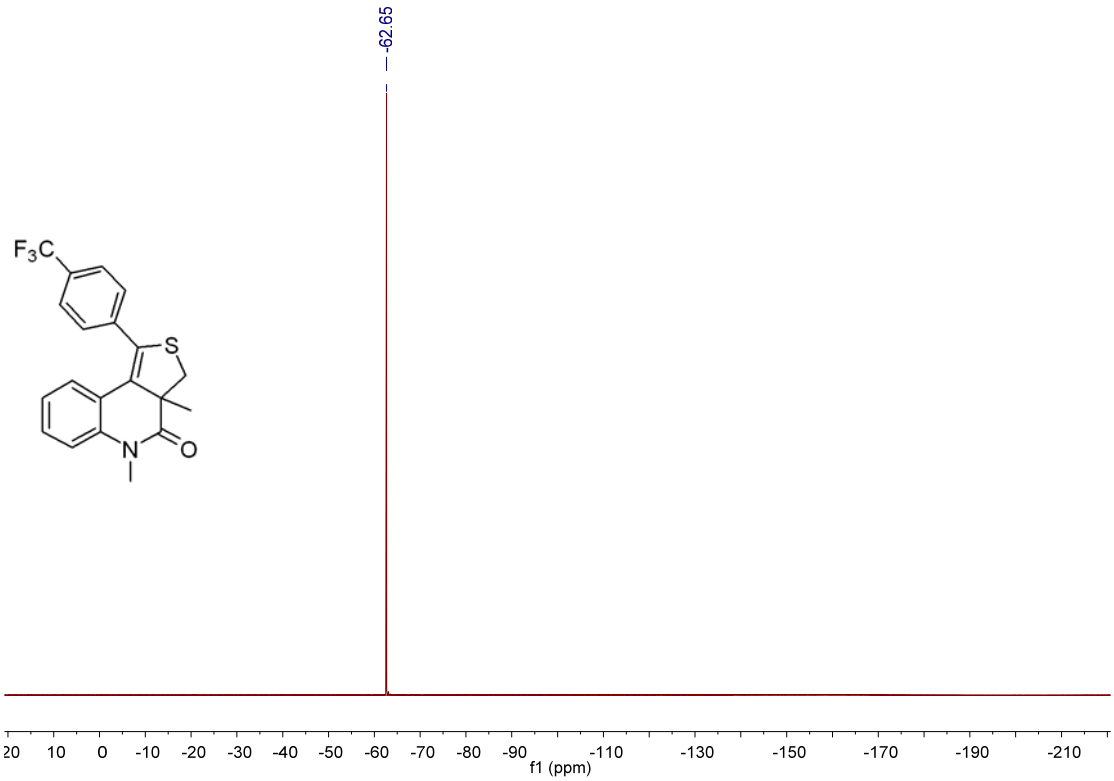




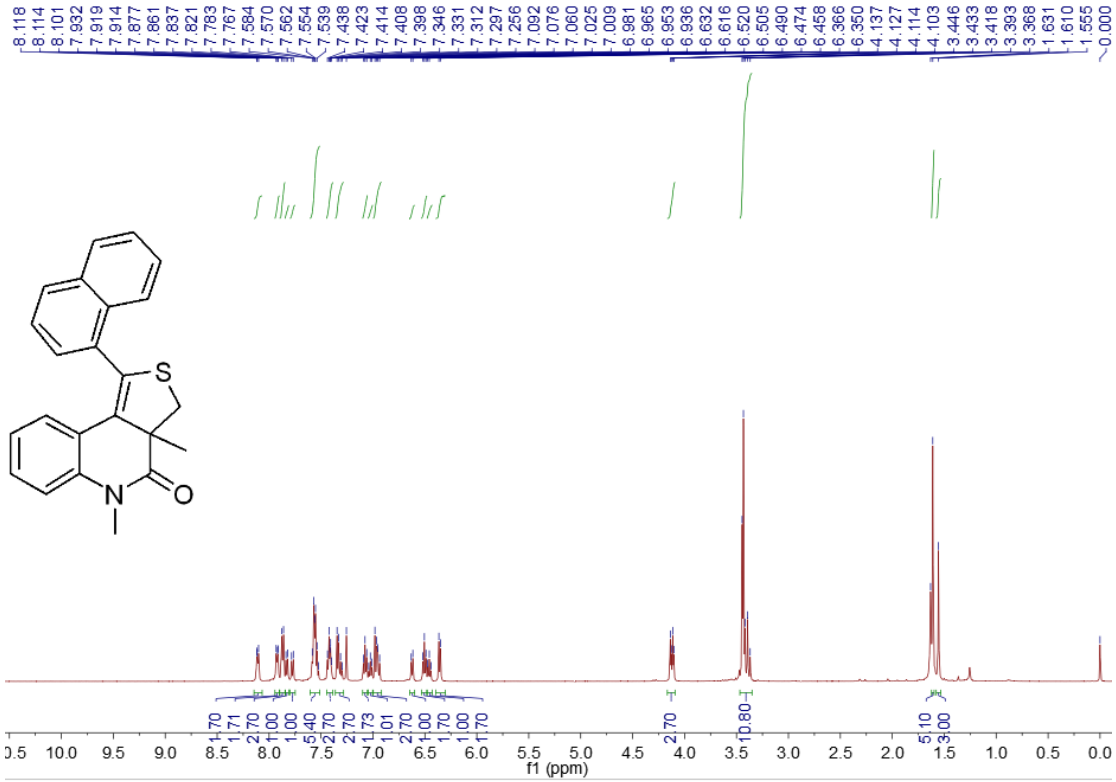
3a,5-dimethyl-1-(4-(trifluoromethyl)phenyl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3m):

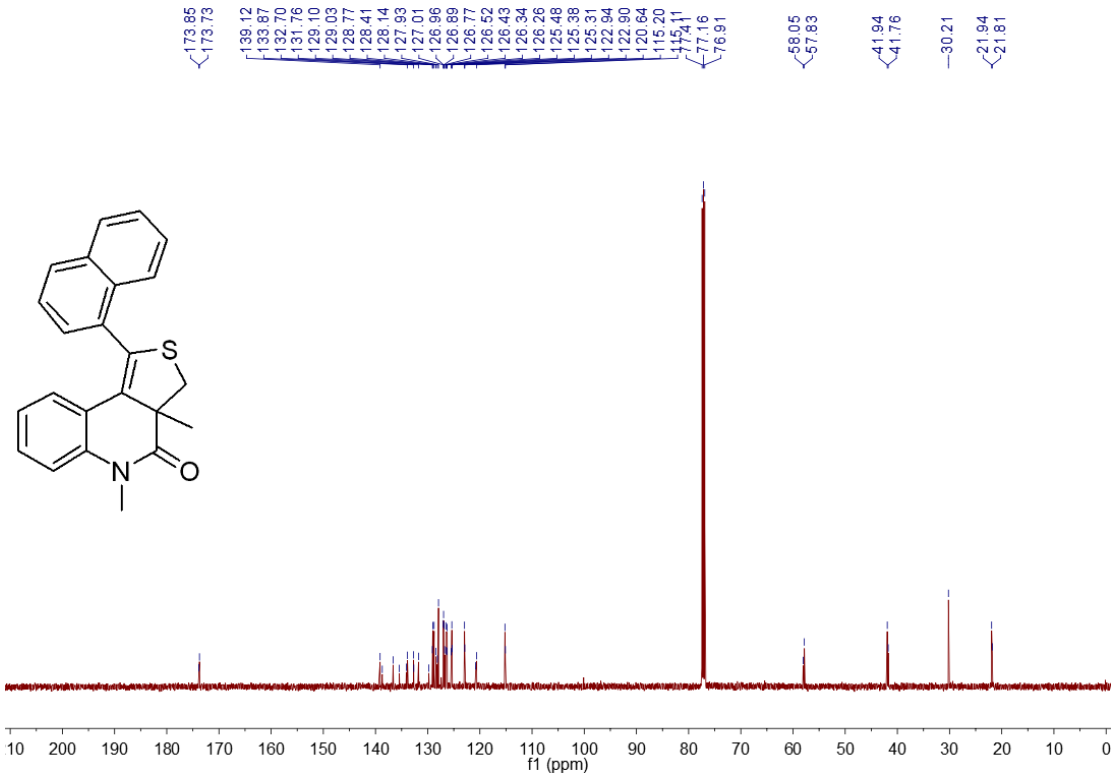




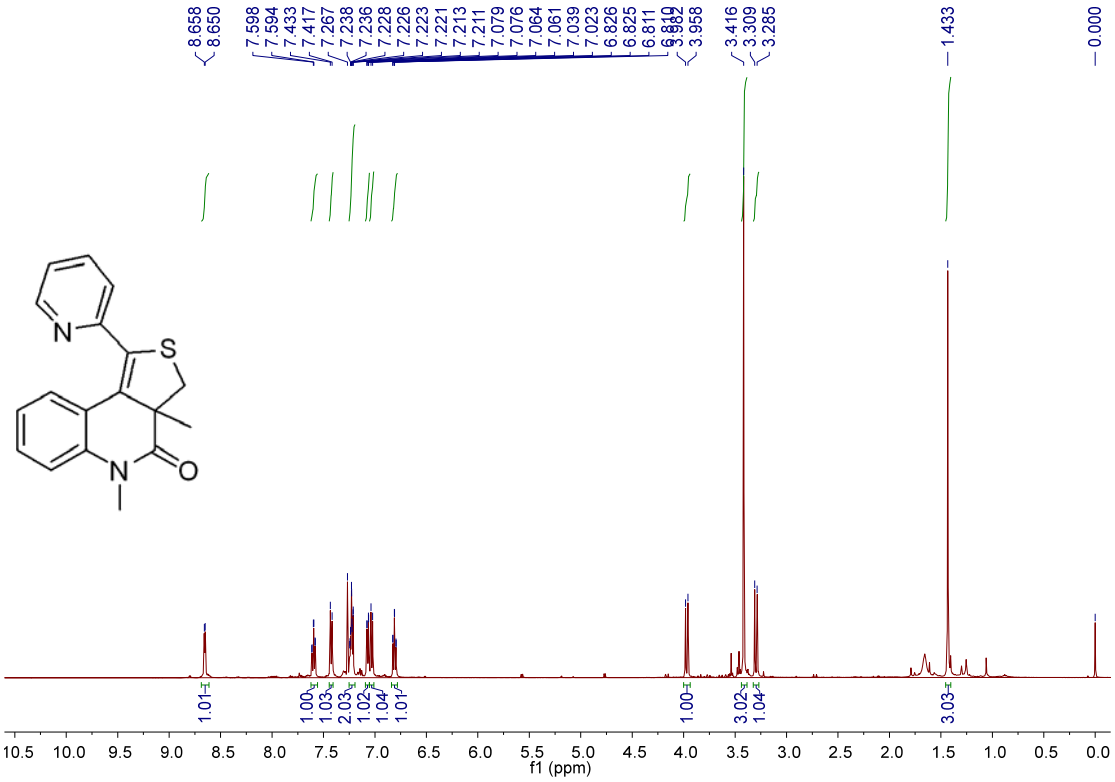

-62.65
F3C
S
N
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

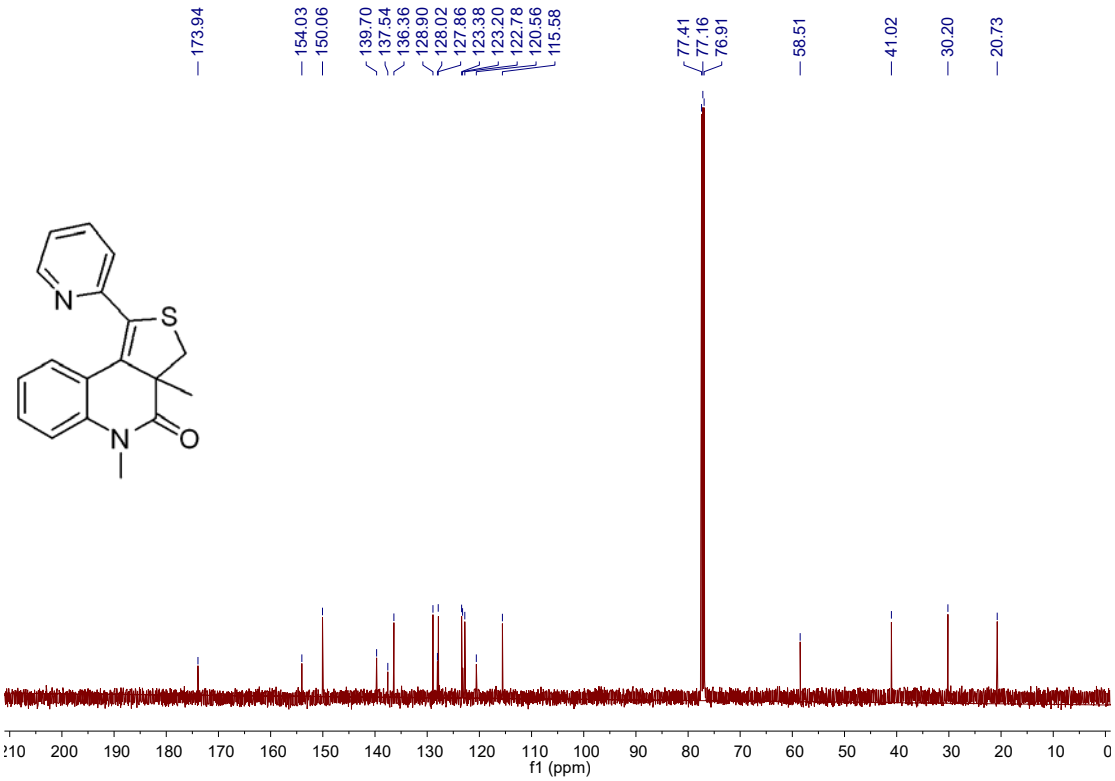
3a,5-dimethyl-1-(naphthalen-1-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3n):



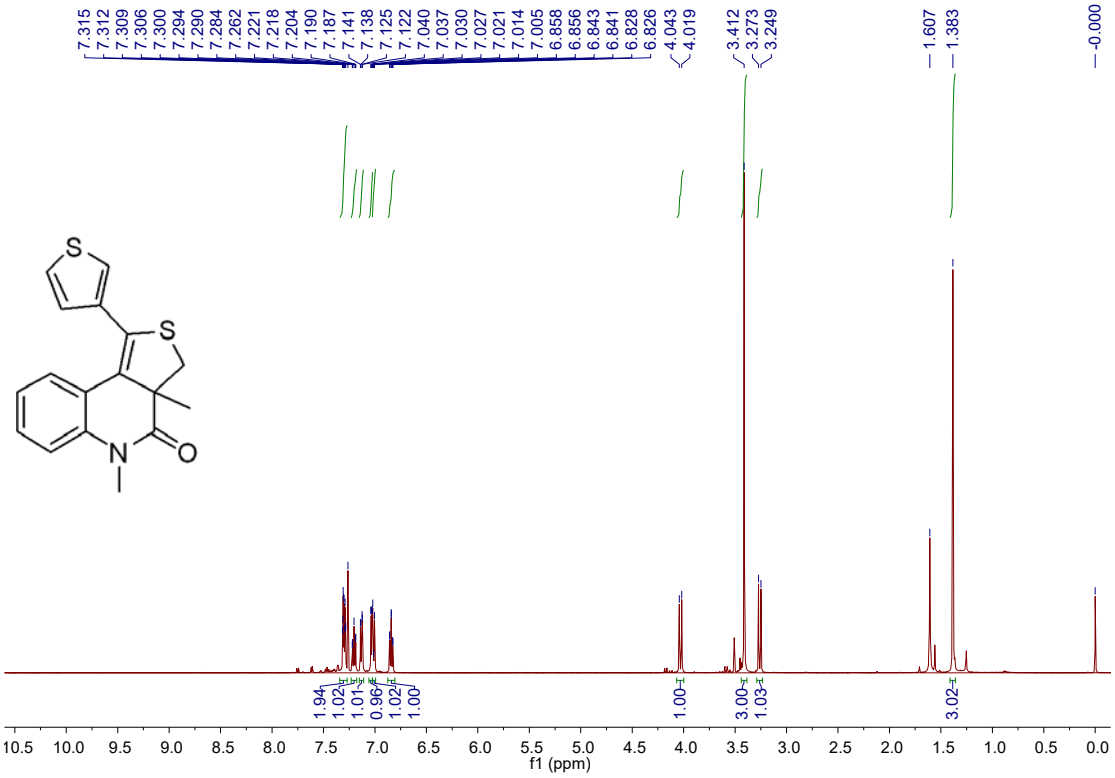


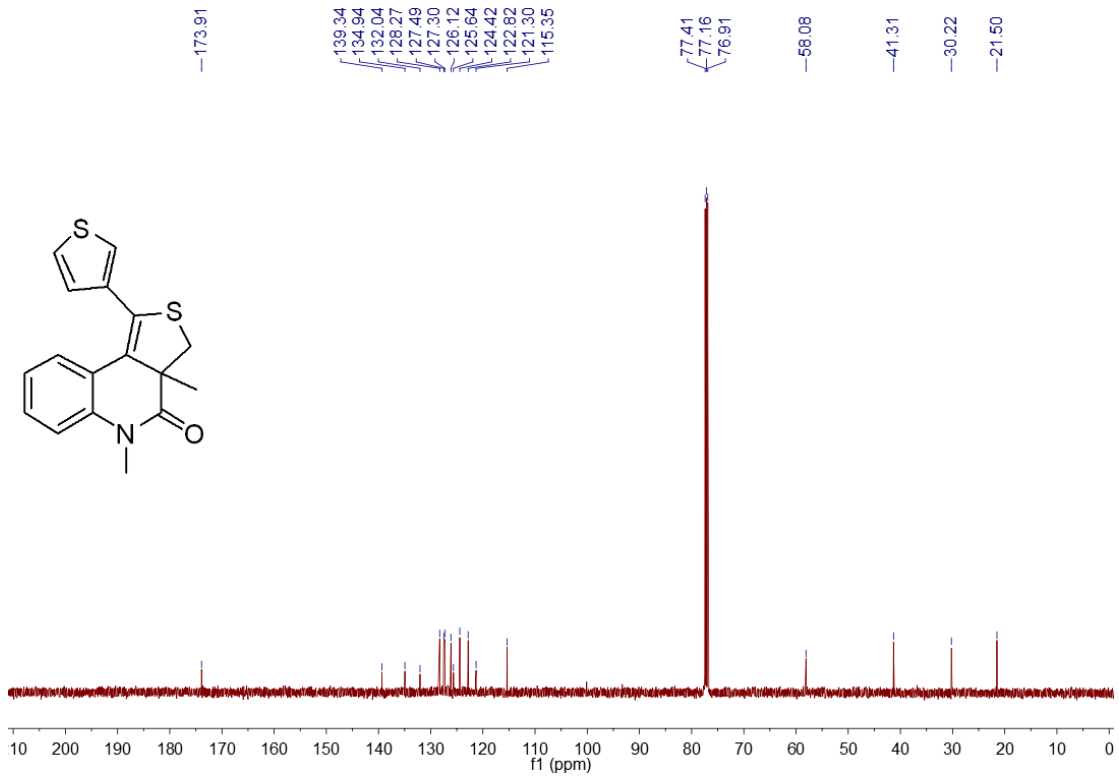
3a,5-dimethyl-1-(pyridin-2-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3o):



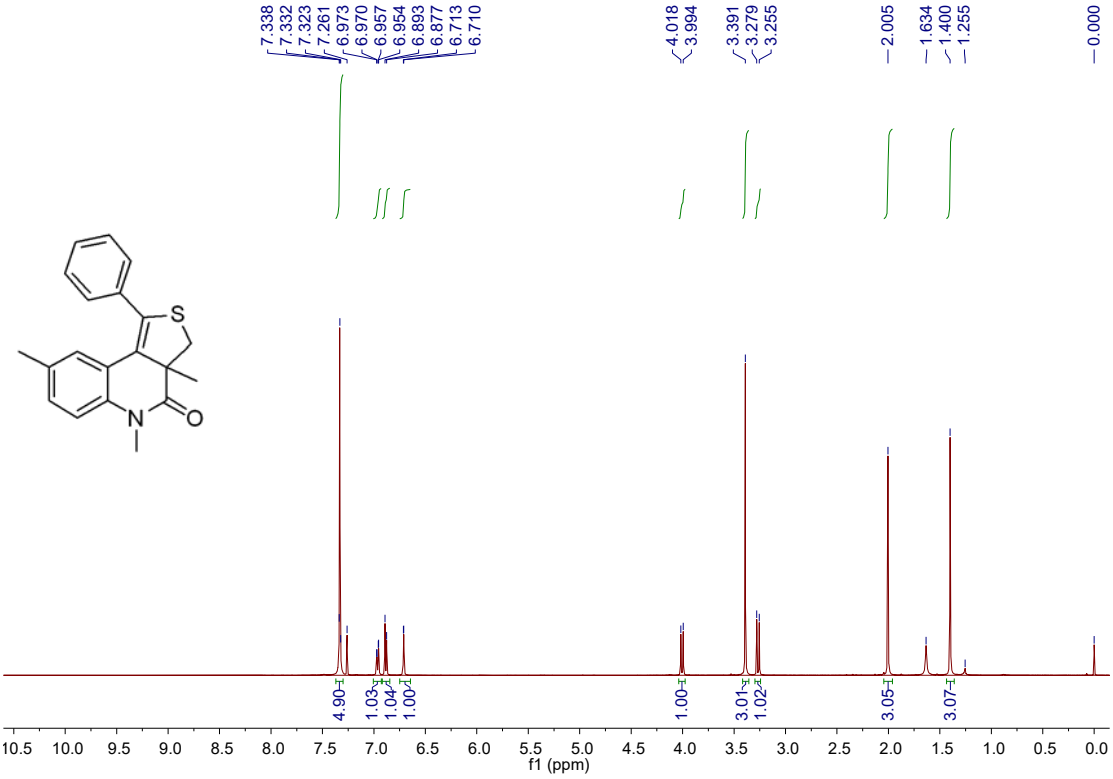


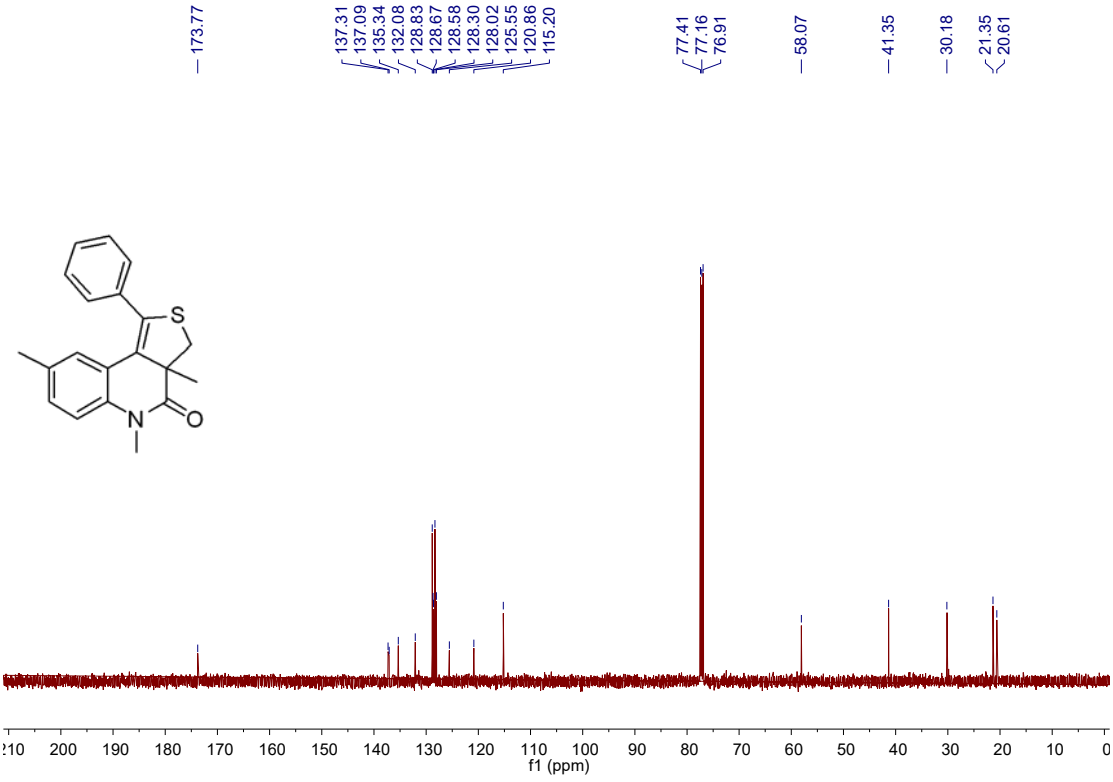
3a,5-dimethyl-1-(thiophen-3-yl)-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3p):



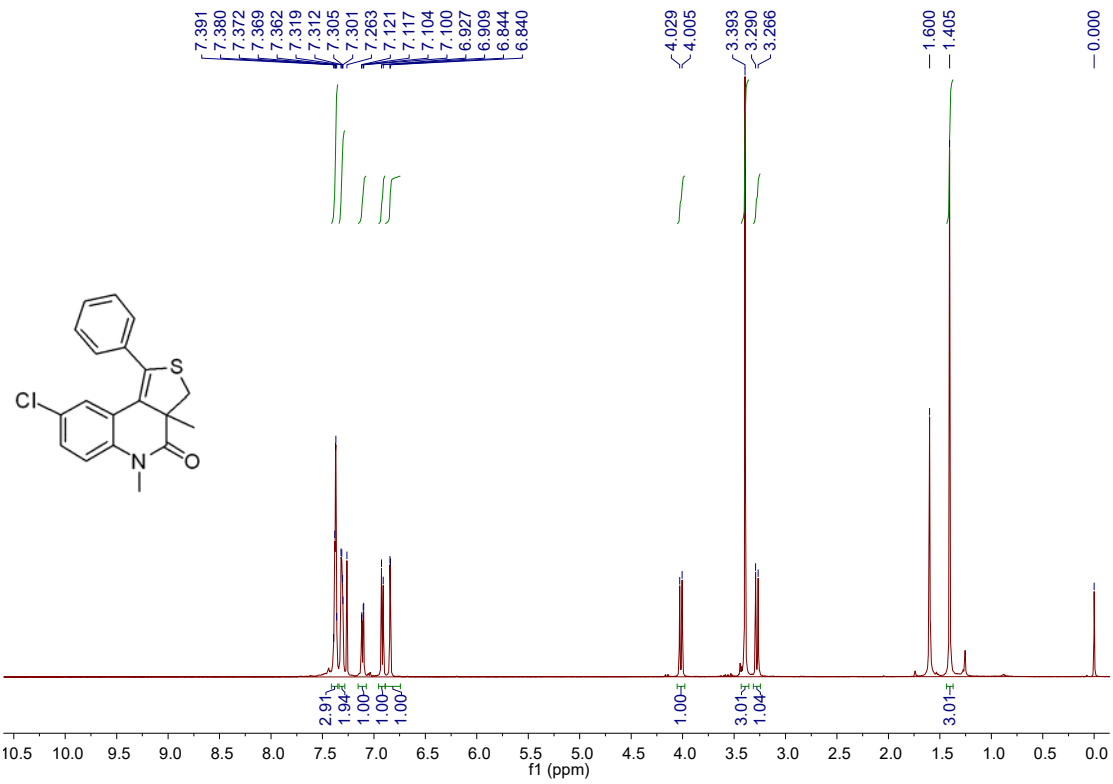


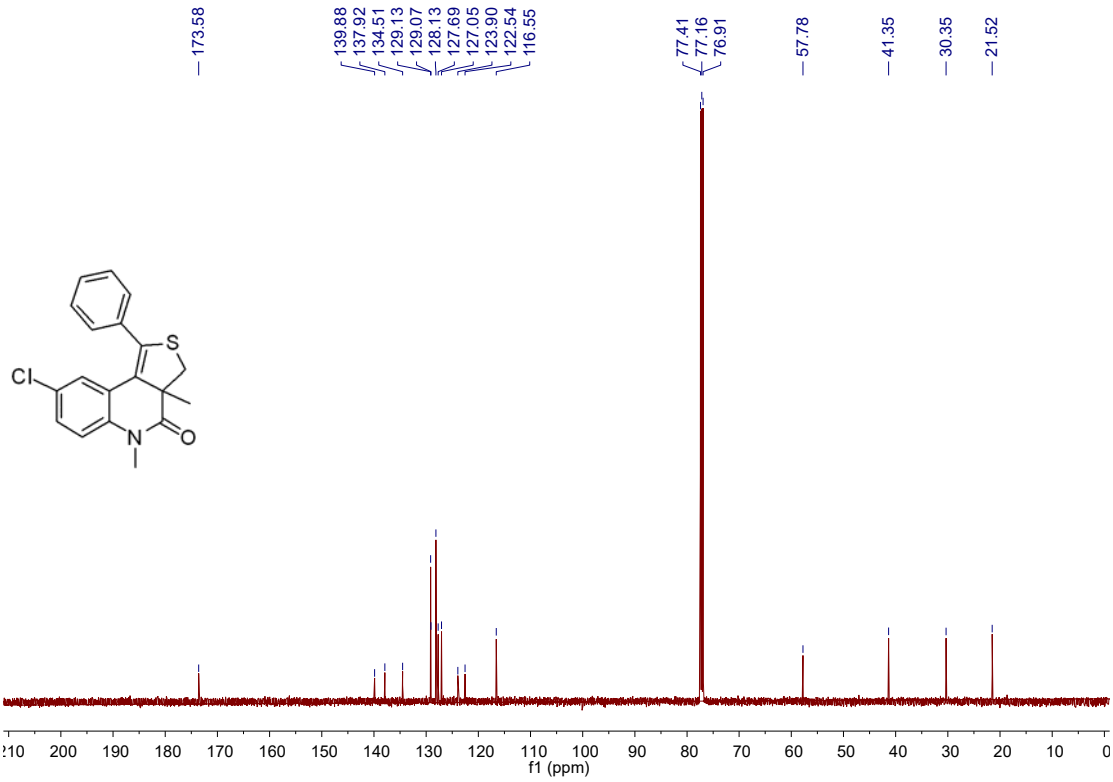
3a,5,8-trimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3r):



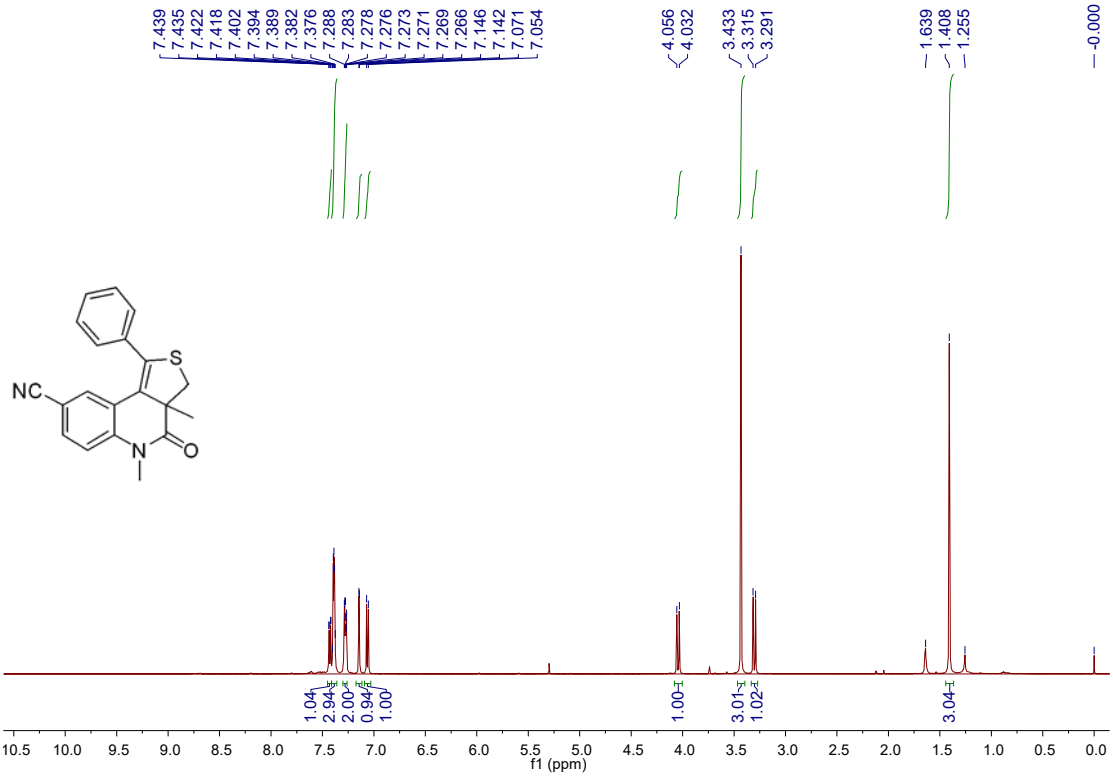


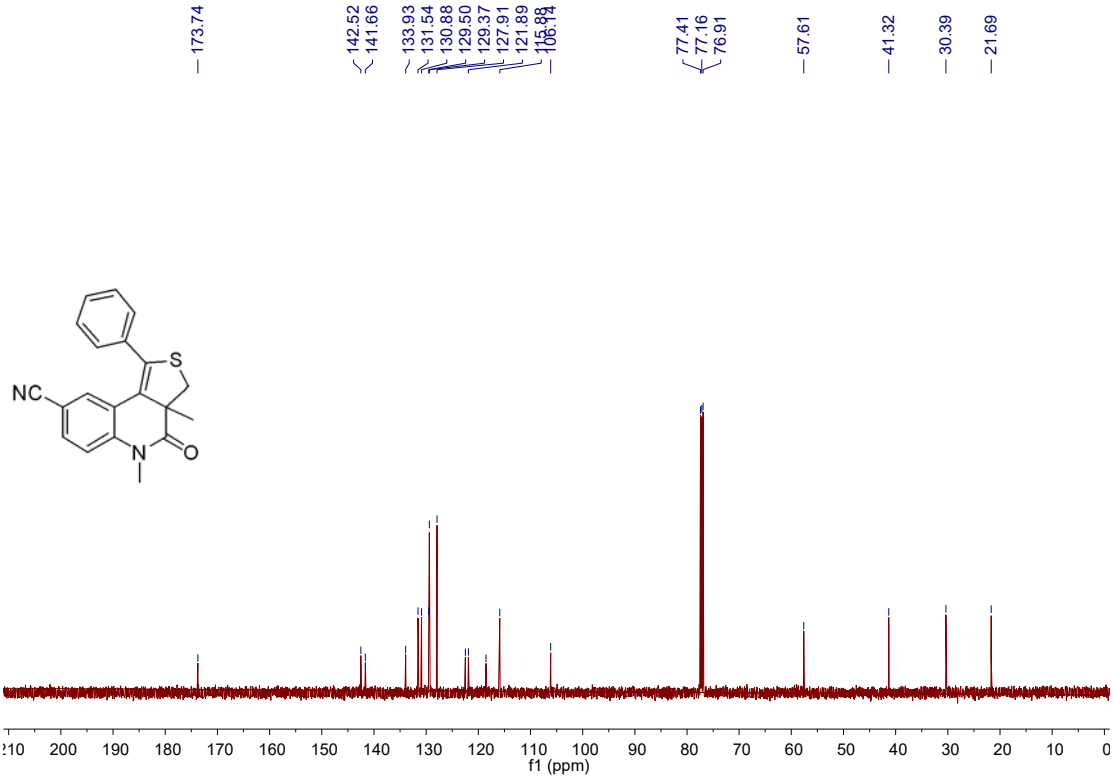
8-chloro-3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3s):



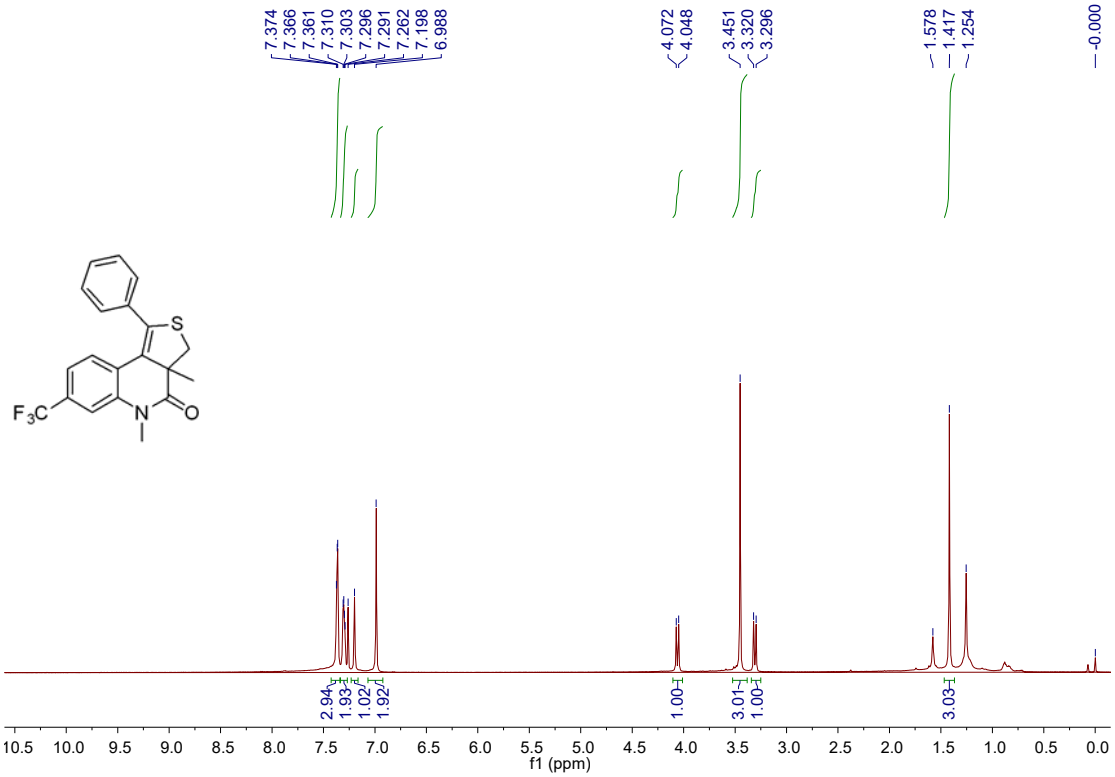


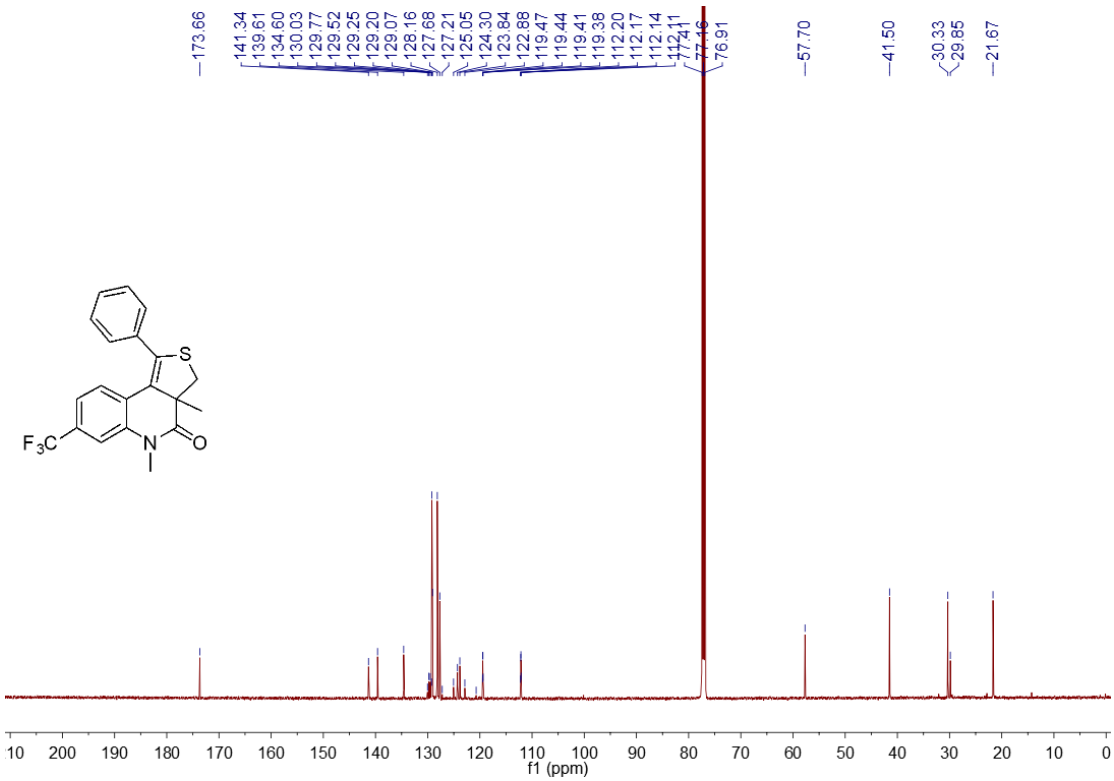
3a,5-dimethyl-4-oxo-1-phenyl-3,3a,4,5-tetrahydrothieno[3,4-*c*]quinoline-8-carbonitrile (3t):

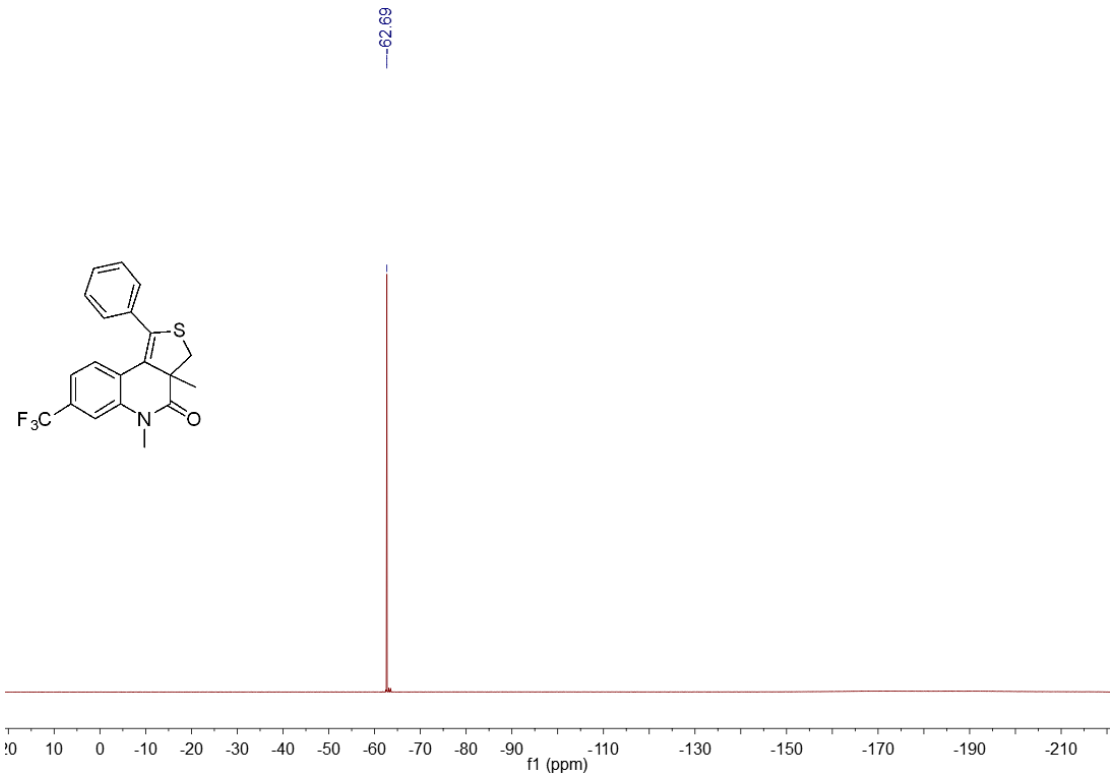




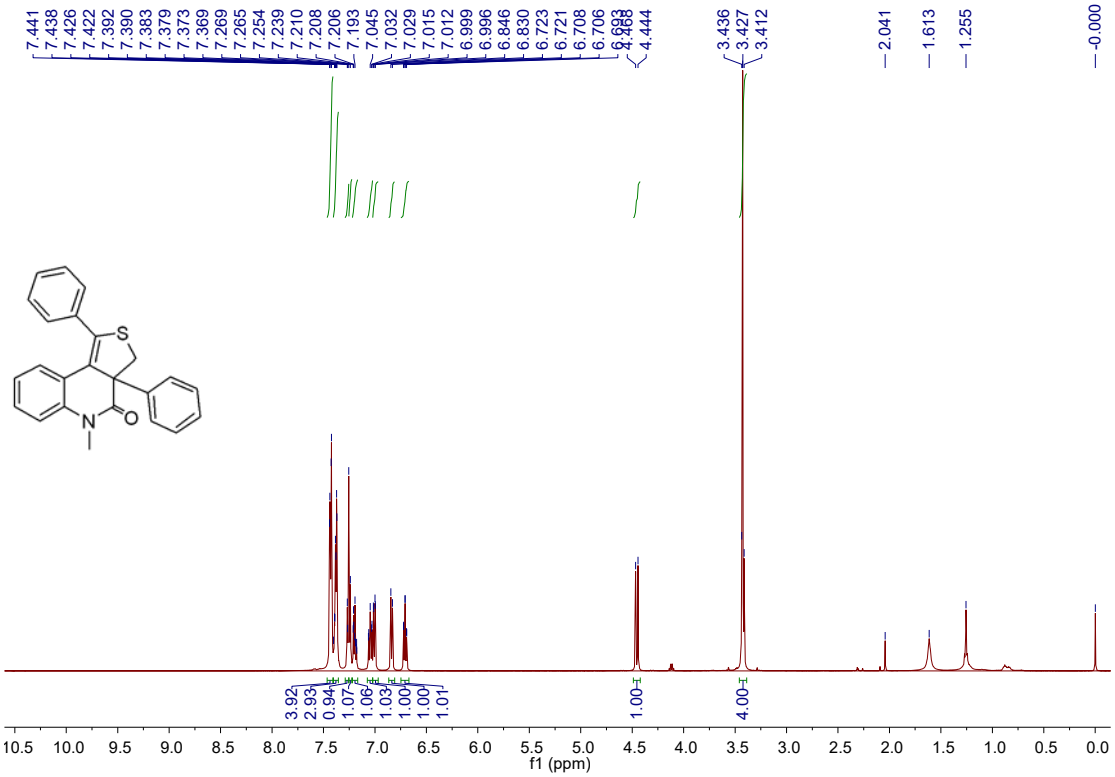
3a,5-dimethyl-1-phenyl-7-(trifluoromethyl)-3,3a-dihydrothieno[3,4-*c*] quinolin-4(5*H*)-one (3u):

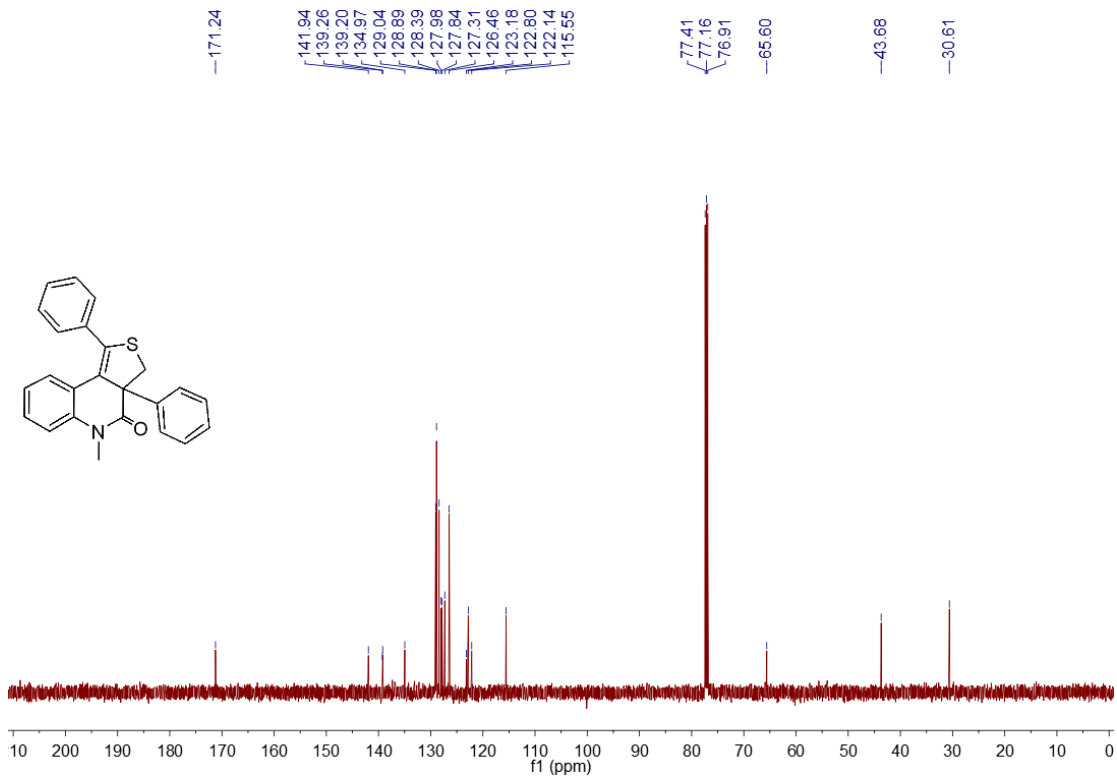




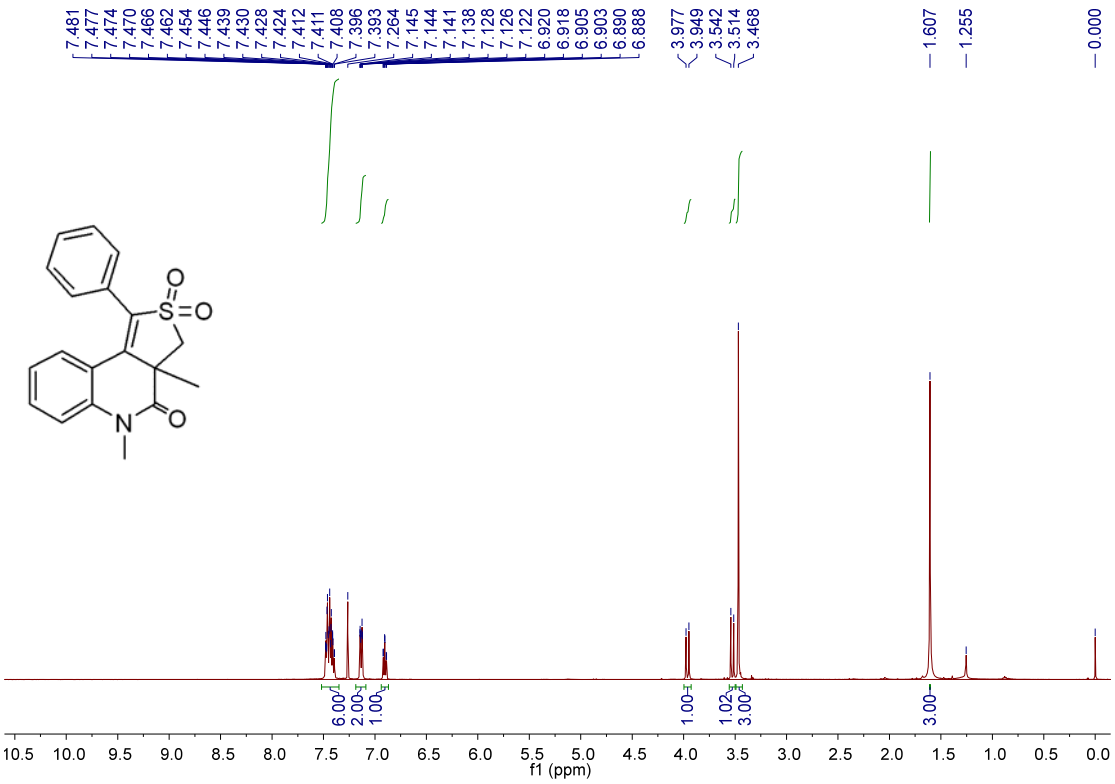

-62.69
S
F3C
N
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

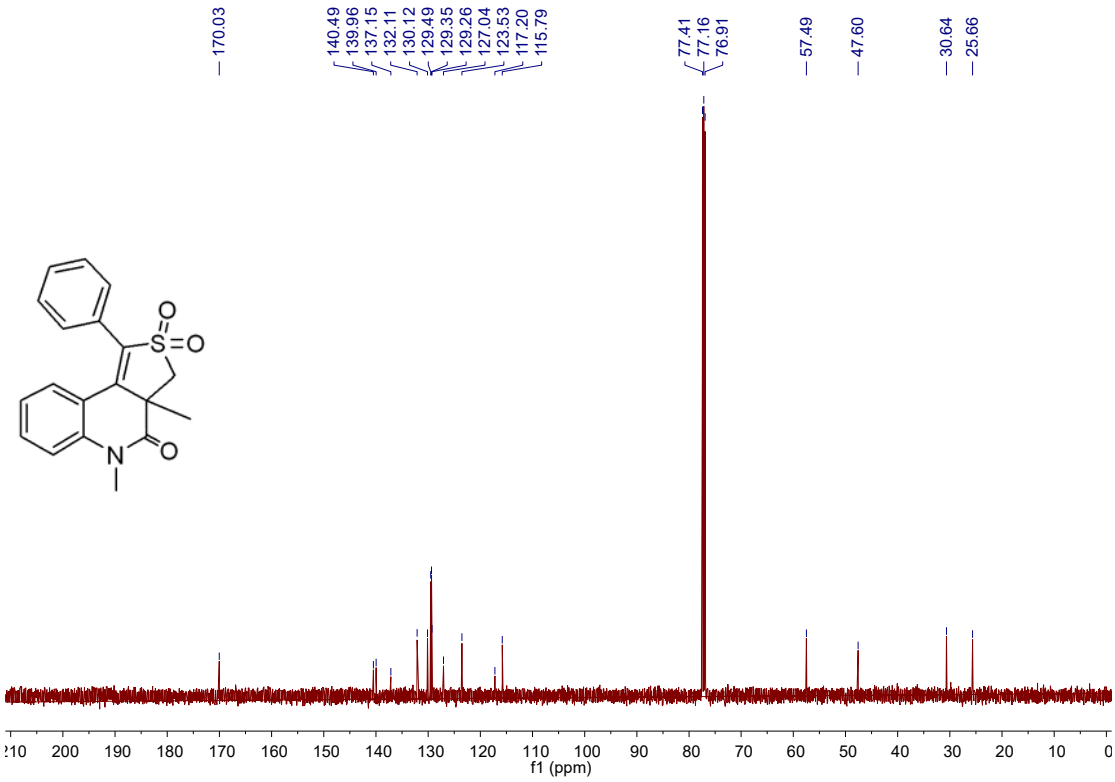
5-methyl-1,3a-diphenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one (3v):



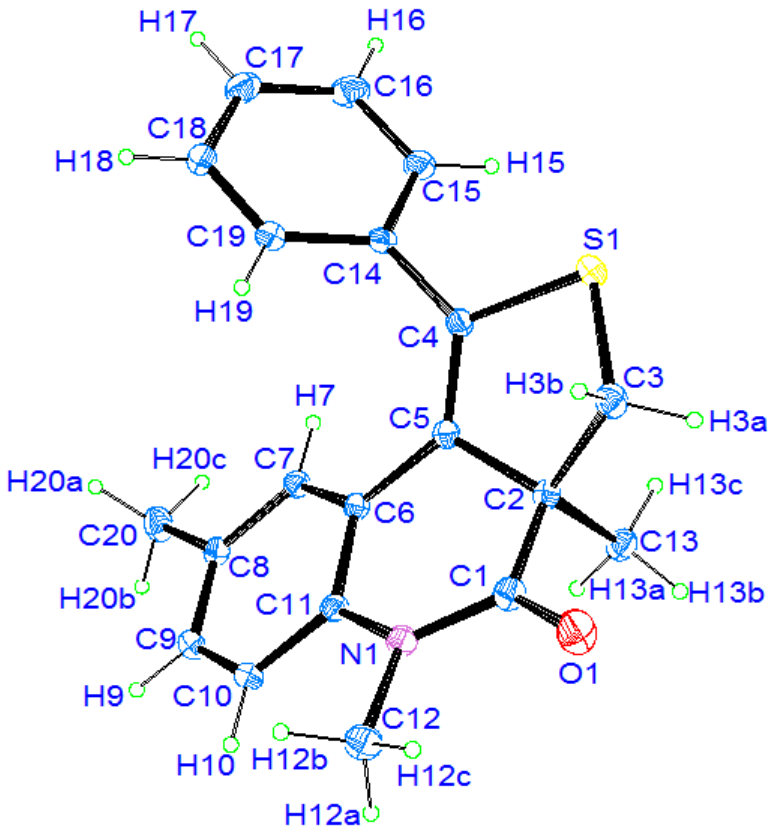


3a,5-dimethyl-1-phenyl-3,3a-dihydrothieno[3,4-*c*]quinolin-4(5*H*)-one 2,2-dioxide (4a):





(E) The X-ray single-crystal diffraction analysis of 3r (CCDC: 1904009)



Molecular structure of 3r with 15% probability ellipsoids.

Table S1. Crystal data and structure refinement for yjx204.

Identification code	yjx204
Empirical formula	$C_{20}H_{19}NOS$
Formula weight	321.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	$P2_1/c$
Unit cell dimensions	a = 12.2921(15) Å α= 90° b = 13.3688(17) Å β= 101.103(2)° c = 10.0405(12) Å γ = 90°
Volume	1619.1(3) $Å^3$
Z	4
Density (calculated)	1.319 Mg/m^3
Absorption coefficient	0.204 mm^{-1}
F(000)	680
Crystal size	0.210 × 0.200 × 0.170 mm^3
Theta range for data collection	1.688 to 26.572°
Index ranges	-13≦h≦15, -16≦k≦15, -12≦l≦12
Reflections collected	9188
Independent reflections	3367 [R(int) = 0.0382]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3367 / 0 / 211
Goodness-of-fit on F^2	1.022
Final R indices [I > 2sigma(I)]	R_1 = 0.0430, wR_2 = 0.1054
R indices (all data)	R_1 = 0.0593, wR_2 = 0.1183
Extinction coefficient	n/a

Largest diff. peak and hole	0.197 and -0.339 e.Å^{-3}

Table S2. Bond lengths [Å] and angles [°] for yjx204.

S(1)-C(4)	1.7709(18)
S(1)-C(3)	1.814(2)
O(1)-C(1)	1.218(2)
N(1)-C(1)	1.364(2)
N(1)-C(11)	1.419(2)
N(1)-C(12)	1.466(2)
C(1)-C(2)	1.522(3)
C(2)-C(5)	1.516(2)
C(2)-C(3)	1.532(3)
C(2)-C(13)	1.538(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.345(2)
C(4)-C(14)	1.480(2)
C(5)-C(6)	1.464(2)
C(6)-C(7)	1.394(2)
C(6)-C(11)	1.410(2)
C(7)-C(8)	1.384(2)
C(7)-H(7)	0.9300

C(8)-C(9)	1.385(3)
C(8)-C(20)	1.504(3)
C(9)-C(10)	1.385(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.387(2)
C(10)-H(10)	0.9300
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.388(3)
C(14)-C(19)	1.390(2)
C(15)-C(16)	1.381(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(3)
C(16)-H(16)	0.9300
C(17)-C(18)	1.381(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.378(3)
C(18)-H(18)	0.9300

C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(4)-S(1)-C(3)	90.25(9)
C(1)-N(1)-C(11)	123.18(15)
C(1)-N(1)-C(12)	117.49(16)
C(11)-N(1)-C(12)	118.96(16)
O(1)-C(1)-N(1)	121.85(18)
O(1)-C(1)-C(2)	120.32(17)
N(1)-C(1)-C(2)	117.82(16)
C(5)-C(2)-C(1)	112.27(15)
C(5)-C(2)-C(3)	105.22(15)
C(1)-C(2)-C(3)	109.36(15)
C(5)-C(2)-C(13)	110.64(15)
C(1)-C(2)-C(13)	108.00(15)
C(3)-C(2)-C(13)	111.37(16)
C(2)-C(3)-S(1)	105.65(13)
C(2)-C(3)-H(3A)	110.6
S(1)-C(3)-H(3A)	110.6
C(2)-C(3)-H(3B)	110.6

S(1)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
C(5)-C(4)-C(14)	129.63(16)
C(5)-C(4)-S(1)	112.94(13)
C(14)-C(4)-S(1)	117.40(12)
C(4)-C(5)-C(6)	129.68(16)
C(4)-C(5)-C(2)	114.35(15)
C(6)-C(5)-C(2)	115.87(14)
C(7)-C(6)-C(11)	118.72(16)
C(7)-C(6)-C(5)	124.19(16)
C(11)-C(6)-C(5)	117.05(15)
C(8)-C(7)-C(6)	122.43(17)
C(8)-C(7)-H(7)	118.8
C(6)-C(7)-H(7)	118.8
C(7)-C(8)-C(9)	117.54(17)
C(7)-C(8)-C(20)	121.33(17)
C(9)-C(8)-C(20)	121.11(17)
C(10)-C(9)-C(8)	121.78(17)
C(10)-C(9)-H(9)	119.1
C(8)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	120.35(17)
C(9)-C(10)-H(10)	119.8

C(11)-C(10)-H(10)	119.8
C(10)-C(11)-C(6)	119.09(17)
C(10)-C(11)-N(1)	120.74(16)
C(6)-C(11)-N(1)	120.17(16)
N(1)-C(12)-H(12A)	109.5
N(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(2)-C(13)-H(13A)	109.5
C(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	118.51(17)
C(15)-C(14)-C(4)	121.03(17)
C(19)-C(14)-C(4)	120.39(17)
C(16)-C(15)-C(14)	120.6(2)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7

C(17)-C(16)-C(15)	120.4(2)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	119.5(2)
C(16)-C(17)-H(17)	120.2
C(18)-C(17)-H(17)	120.2
C(19)-C(18)-C(17)	120.3(2)
C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(14)	120.58(19)
C(18)-C(19)-H(19)	119.7
C(14)-C(19)-H(19)	119.7
C(8)-C(20)-H(20A)	109.5
C(8)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(8)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Table S3. Torsion angles [°] for yjx204.

C(11)-N(1)-C(1)-O(1)	-172.95(18)
C(12)-N(1)-C(1)-O(1)	0.0(3)
C(11)-N(1)-C(1)-C(2)	6.2(3)
C(12)-N(1)-C(1)-C(2)	179.11(17)
O(1)-C(1)-C(2)-C(5)	-157.58(18)
N(1)-C(1)-C(2)-C(5)	23.3(2)
O(1)-C(1)-C(2)-C(3)	-41.2(2)
N(1)-C(1)-C(2)-C(3)	139.67(17)
O(1)-C(1)-C(2)-C(13)	80.2(2)
N(1)-C(1)-C(2)-C(13)	-98.98(19)
C(5)-C(2)-C(3)-S(1)	-33.86(17)
C(1)-C(2)-C(3)-S(1)	-154.66(13)
C(13)-C(2)-C(3)-S(1)	86.05(16)
C(4)-S(1)-C(3)-C(2)	30.06(14)
C(3)-S(1)-C(4)-C(5)	-18.34(16)
C(3)-S(1)-C(4)-C(14)	159.78(15)
C(14)-C(4)-C(5)-C(6)	6.0(3)
S(1)-C(4)-C(5)-C(6)	-176.16(15)
C(14)-C(4)-C(5)-C(2)	-177.78(17)
S(1)-C(4)-C(5)-C(2)	0.1(2)
C(1)-C(2)-C(5)-C(4)	141.49(17)

C(3)-C(2)-C(5)-C(4)	22.6(2)
C(13)-C(2)-C(5)-C(4)	-97.77(19)
C(1)-C(2)-C(5)-C(6)	-41.7(2)
C(3)-C(2)-C(5)-C(6)	-160.61(15)
C(13)-C(2)-C(5)-C(6)	78.99(19)
C(4)-C(5)-C(6)-C(7)	30.1(3)
C(2)-C(5)-C(6)-C(7)	-146.07(17)
C(4)-C(5)-C(6)-C(11)	-152.35(19)
C(2)-C(5)-C(6)-C(11)	31.5(2)
C(11)-C(6)-C(7)-C(8)	2.6(3)
C(5)-C(6)-C(7)-C(8)	-179.87(16)
C(6)-C(7)-C(8)-C(9)	0.0(3)
C(6)-C(7)-C(8)-C(20)	178.83(18)
C(7)-C(8)-C(9)-C(10)	-1.9(3)
C(20)-C(8)-C(9)-C(10)	179.29(18)
C(8)-C(9)-C(10)-C(11)	1.1(3)
C(9)-C(10)-C(11)-C(6)	1.6(3)
C(9)-C(10)-C(11)-N(1)	-178.11(17)
C(7)-C(6)-C(11)-C(10)	-3.4(3)
C(5)-C(6)-C(11)-C(10)	178.90(16)
C(7)-C(6)-C(11)-N(1)	176.35(15)
C(5)-C(6)-C(11)-N(1)	-1.3(2)

C(1)-N(1)-C(11)-C(10)	161.02(18)
C(12)-N(1)-C(11)-C(10)	-11.8(3)
C(1)-N(1)-C(11)-C(6)	-18.7(3)
C(12)-N(1)-C(11)-C(6)	168.45(17)
C(5)-C(4)-C(14)-C(15)	-134.8(2)
S(1)-C(4)-C(14)-C(15)	47.5(2)
C(5)-C(4)-C(14)-C(19)	48.2(3)
S(1)-C(4)-C(14)-C(19)	-129.53(16)
C(19)-C(14)-C(15)-C(16)	-1.3(3)
C(4)-C(14)-C(15)-C(16)	-178.35(19)
C(14)-C(15)-C(16)-C(17)	0.5(4)
C(15)-C(16)-C(17)-C(18)	0.5(4)
C(16)-C(17)-C(18)-C(19)	-0.6(3)
C(17)-C(18)-C(19)-C(14)	-0.2(3)
C(15)-C(14)-C(19)-C(18)	1.1(3)
C(4)-C(14)-C(19)-C(18)	178.21(18)

Table S4. Hydrogen bonds for yjx204 [Å and °].

D-H...A	*d*(D-H)	*d*(H...A)	*d*(D...A)	∠(DHA)
C(12)-H(12B)...O(1)$^{\#1}$	0.96	2.36	3.229(3)	149.6

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, -y+3/2, z+1/2.