Supporting Information

Base-catalyzed bicyclization of dialkyl glutaconates with cinnamoylacetamides: a synthetic strategy for isoquinolinedione derivatives

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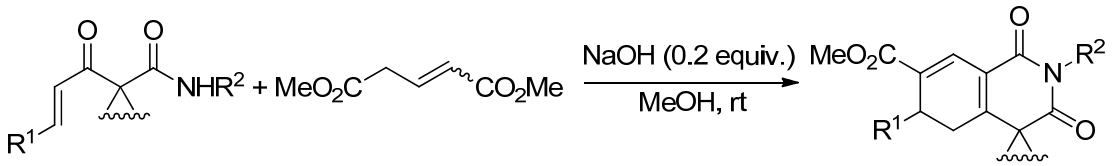
I. General Information

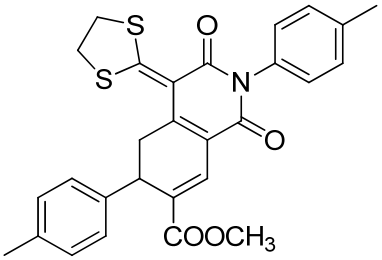
All reagents were commercial and were used without further purification. Chromatography was carried on flash aluminium oxide, basic (200-300 mesh) or silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). Melting points were uncorrected. Unless noted, the ^{1}H NMR spectra were recorded at 500 or 300 MHz in $CDCl_3$ and the ^{13}C NMR spectra were recorded at 125 or 75 MHz in $CDCl_3$ or DMSO with TMS as internal standard. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound **4c** with dimension 0.15 x 0.12 x 0.11 mm was glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo Kα radiation (λ = 0.71073Å) and IP technique in the range $2.19^\circ < \theta < 27.48^\circ$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 4 (4a as Example):



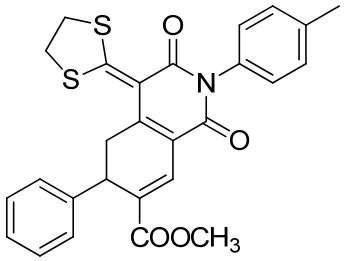
To a solution of **1a** (0.5 mmol, 198 mg) and dimethyl glutaconate **2** (1.0 mmol, 0.14 mL) in MeOH (4.0 mL) was added NaOH (20% mmol, 4 mg) in one portion. The reaction mixture was stired at r.t. for 18 min. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by aluminium oxide, basic (200-300 mesh) chromatography (petroleum ether/acetone = 10/4, v/v) to give **4a** (214 mg, 85%) as a yellow solid.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2,6-di-*p*-tolyl-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4a):



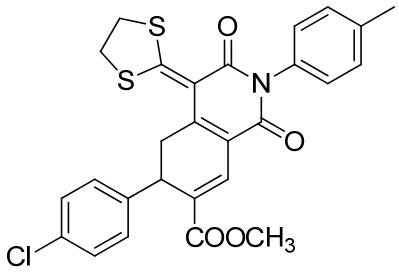
Yellow solid; m.p. 191-193 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.30 (s, 3H), 2.40 (s, 3H), 3.28-3.42 (m, 3H), 3.54 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H), 3.97 (d, *J* = 17.0 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 7.05-7.11 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 2H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.9, 21.2, 36.2, 36.3, 37.6, 38.6, 51.7, 115.3, 118.7, 127.0 (2C), 127.4, 128.0 (2C), 129.3 (2C), 129.9 (2C), 131.3, 132.7, 136.6, 138.2, 138.3, 144.1, 161.6, 163.7, 166.6, 178.4. HRMS (ESI-TOF) calcd for $C_{28}H_{26}NO_4S_2^+$ ([M + H]$^+$): 504.1298, found: 504.1294.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-phenyl-2-(*p*-tolyl)-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4b):



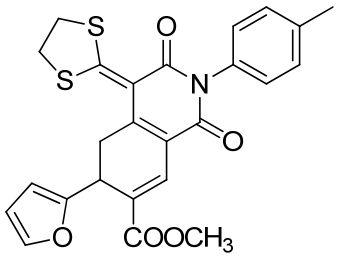
Yellow solid; m.p. 242-244 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.40 (s, 3H), 3.29-3.44 (m, 3H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 3.99 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.33 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.21-7.28 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 36.1, 36.7, 37.6, 38.6, 51.8, 115.4, 118.9, 127.0, 127.1 (2C), 127.3, 128.1 (2C), 128.6 (2C), 130.1 (2C), 131.5, 132.7, 138.4, 141.2, 144.1, 161.6, 163.8, 166.7, 178.3. HRMS (ESI-TOF) calcd for $C_{27}H_{24}NO_4S_2^+$ ([M + H]$^+$): 490.1141, found: 490.1149.

Methyl 6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2-(*p*-tolyl)-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4c):



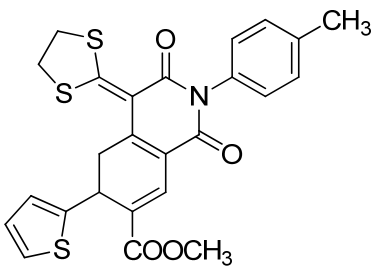
Yellow solid; m.p. 193-195 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.40 (s, 3H), 3.30-3.42 (m, 3H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 3.96 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 36.0, 36.2, 37.6, 38.6, 51.8, 115.3, 118.8, 126.9, 128.0 (2C), 128.5 (2C), 128.8 (2C), 130.0 (2C), 131.7, 132.6, 132.8, 138.4, 139.7, 143.8, 161.5, 163.7, 166.5, 178.3. HRMS (ESI-TOF) calcd for $C_{27}H_{23}ClNO_4S_2^+$ ([M + H]$^+$): 524.0752, found: 524.0752.

Methyl 4-(1,3-dithiolan-2-ylidene)-6-(furan-2-yl)-1,3-dioxo-2-(*p*-tolyl)-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4d):



Yellow solid; m.p. 233-235 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.39 (s, 3H), 3.17 (dd, *J* = 17.0, 9.0 Hz, 1H), 3.32-3.43 (m, 2H), 3.60 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 4.17 (dd, *J* = 17.0, 1.0 Hz, 1H), 4.41 (d, *J* = 8.5 Hz, 1H), 5.95 (d, *J* = 3.0 Hz, 1H), 6.21 (t, *J* = 3.0 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.28 (t, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 30.9, 32.8, 37.7, 38.7, 52.0, 106.1, 110.1, 115.4, 118.6, 124.9, 128.0 (2C), 130.1 (2C), 132.2, 132.6, 138.4, 141.9, 144.4, 153.6, 161.6, 163.8, 166.4, 178.2. HRMS (ESI-TOF) calcd for $C_{25}H_{22}NO_5S_2^+$ ([M + H]$^+$): 480.0934, found: 480.0937.

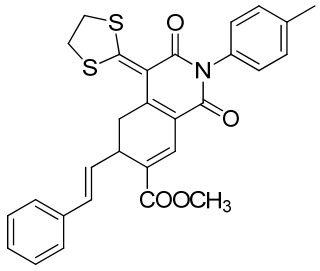
Methyl4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-(thiophen-2-yl)-2-(p-tolyl)-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4e):



Yellow solid; m. p. 230-232 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.39 (s, 3H), 3.27-3.36 (m, 3H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 4.11 (d, *J* = 17.5, 1H), 4.59 (d, *J* = 8.5 Hz, 1H), 6.82 (s, 1H), 6.84 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 3H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 32.4, 36.0, 37.7, 38.7, 52.0, 115.4, 118.7, 123.9, 124.6,

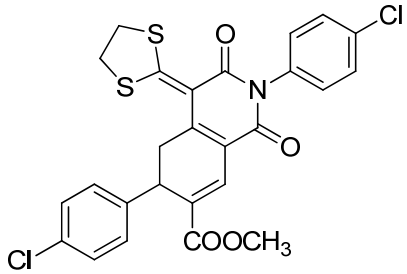
126.6, 127.7, 128.1 (2C), 130.1 (2C), 131.1, 132.7, 138.4, 144.2, 144.3, 161.6, 163.8, 166.4, 178.6. HRMS (ESI-TOF) calcd for $C_{25}H_{22}NO_4S_3^+$ ([M + H]$^+$): 496.0705, found: 496.0713.

(*E*)-methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-styryl-2-(*p*-tolyl)-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4f):



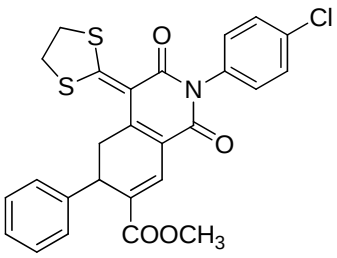
Yellow solid; m.p. 276-278 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.39 (s, 3H), 3.16 (dd, *J* = 17.5, 8.5 Hz, 1H), 3.31-3.42 (m, 2H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 3.84-3.95 (m, 2H), 6.10 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.27-7.32 (m, 6H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 33.8, 34.8, 37.7, 38.6, 51.8, 115.6, 118.9, 126.4 (2C), 127.1, 127.4, 128.0, 128.1 (2C), 128.4 (2C), 130.0 (2C), 130.7, 130.8, 132.7, 136.8, 138.4, 144.1, 161.6, 163.8, 166.5, 177.8. HRMS (ESI-TOF) calcd for $C_{29}H_{26}NO_4S_2^+$ ([M + H]$^+$): 516.1298, found: 516.1294.

Methyl 2,6-bis(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4g):



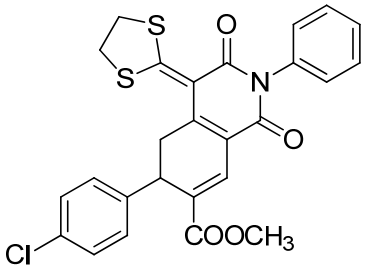
Yellow solid; m.p.181-183 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.34-3.42 (m, 3H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 3.96 (d, *J* = 17.0, 1H), 4.32 (d, *J* = 11.0 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 2H), 7.15 (d, *J* = 3.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.1, 36.2, 37.7, 38.8, 52.0, 115.1, 118.5, 127.1, 128.5 (2C), 128.8 (2C), 129.5 (2C), 129.9 (2C), 131.6, 132.9, 133.8, 134.5, 139.6, 144.2, 161.3, 163.4, 166.4, 179.4. HRMS (ESI-TOF) calcd for $C_{26}H_{20}Cl_2NO_4S_2^+$ ([M + H]$^+$): 544.0205, found: 544.0201.

Methyl 2-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-phenyl-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4h):



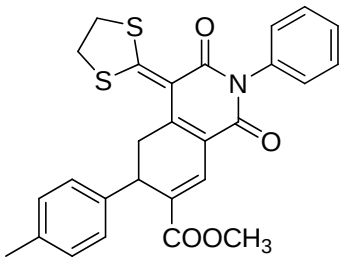
Yellow solid; m.p. 187-189 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.32-3.38 (m, 2H), 3.41 (dd, *J* = 17.5, 10.0 Hz , 1H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 4.00 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.34 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 6.5 Hz, 2H), 7.20-7.28 (m, 5H), 7.46 (d, *J* = 8.5 Hz, 2H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.2, 36.7, 37.7, 38.7, 51.9, 115.2, 118.7, 127.0 (2C), 127.1, 127.5, 128.7 (2C), 129.5 (2C), 129.9 (2C), 131.3, 133.8, 134.4, 141.1, 144.4, 161.3, 163.5, 166.6, 179.0. HRMS (ESI-TOF) calcd for $C_{26}H_{21}ClNO_4S_2^+$ ([M + H]$^+$): 510.0595, found: 510.0593.

Methyl 6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2-phenyl-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4i):



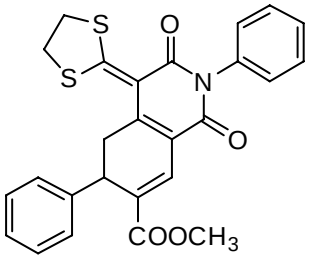
Yellow solid; m.p. 187-189 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.31-3.43 (m, 3H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 3.96 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.31 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.17-7.24 (m, 4H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 2H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.0, 36.2, 37.6, 38.6, 51.9, 115.3, 118.7, 126.9, 128.4 (2C), 128.5, 128.6 (2C), 128.8 (2C), 129.3 (2C), 131.7, 132.8, 135.3, 139.6, 143.9, 161.4, 163.6, 166.5, 178.6. HRMS (ESI-TOF) calcd for $C_{26}H_{21}ClNO_4S_2^+$ ([M + H]$^+$): 510.0595, found: 510.0597.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2-phenyl-6-(*p*-tolyl)-1,2,3,4,5,6- hexahydroisoquinoline-7-carboxylate (4j):



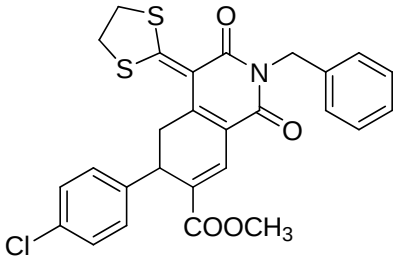
Yellow solid; m.p. 165-167 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.30 (s, 3H), 3.31-3.36 (m, 2H), 3.40 (dd, *J* = 17.0, 9.5 Hz, 1H), 3.55 (t, *J* = 5.5 Hz, 2H), 3.73 (s, 3H), 3.97 (d, *J* = 17.5 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.0, 36.3, 36.4, 37.7, 38.6, 51.8, 115.5, 119.0, 127.1 (2C), 127.6, 128.4 (2C), 128.5, 129.3 (2C), 129.4 (2C), 131.3, 135.4, 136.7, 138.2, 144.2, 161.6, 163.7, 166.7, 178.2. HRMS (ESI-TOF) calcd for $C_{27}H_{24}NO_4S_2^+$ ([M + H]$^+$): 490.1141, found: 490.1146.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2,6-diphenyl-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4k):



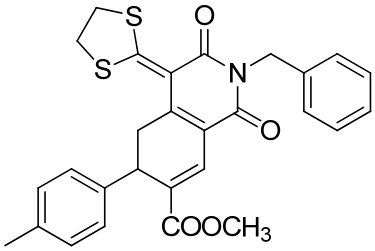
Yellow solid; m.p. 197-199 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.30-3.37 (m, 2H), 3.42 (dd, *J* = 17.5, 10.0 Hz, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 4.00 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.34 (d, *J* = 9.0 Hz, 1H), 7.20-7.28 (m, 7H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.2, 36.7, 37.7, 38.7, 51.9, 115.4, 118.9, 127.1, 127.2 (2C), 127.4, 128.5 (2C), 128.6, 128.7 (2C), 129.3 (2C), 131.5, 135.4, 141.2, 144.2, 161.6, 163.7, 166.7, 178.3. HRMS (ESI-TOF) calcd for $C_{26}H_{22}NO_4S_2^+$ ([M + H]$^+$): 476.0985, found: 476.1001.

Methyl2-benzyl-6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4l):



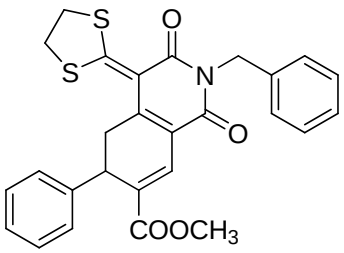
Yellow solid; m.p. 280-282 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.29-3.39 (m, 3H), 3.54 (t, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 3.86 (d, *J* = 17.5 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 5.21 (dd, *J* = 14.0, 14.0 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 7.24-7.31 (m, 3H), 7.44 (d, *J* = 7.0 Hz, 2H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 35.9, 36.2, 37.6, 38.6, 43.8, 51.9, 115.4, 118.6, 127.0, 127.4 (2C), 128.4 (2C), 128.6 (2C), 128.8 (3C), 131.9, 132.8, 137.1, 139.7, 143.4, 161.5, 163.3, 166.5, 177.9. HRMS (ESI-TOF) calcd for $C_{27}H_{23}ClNO_4S_2^+$ ([M + H]$^+$): 524.0752, found: 524.0749.

Methyl 2-benzyl-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-(*p*-tolyl)-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4m):



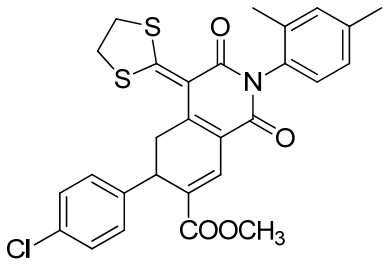
Yellow solid; m. p. 263-265 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.27 (s, 3H), 3.29-3.38 (m, 3H), 3.52 (t, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 3.88 (d, *J* = 16.5, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 5.21 (dd, *J* = 14.0, 13.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.0, 36.2, 36.4, 37.5, 38.5, 43.7, 51.8, 115.5, 118.7, 127.0 (2C), 127.3, 127.5, 128.3 (2C), 128.7 (2C), 129.3 (2C), 131.5, 136.6, 137.2, 138.2, 143.7, 161.6, 163.4, 166.7, 177.6. HRMS (ESI-TOF) calcd for $C_{28}H_{26}NO_4S_2^+$ ([M + H]$^+$): 504.1298, found: 504.1291.

Methyl 2-benzyl-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-phenyl-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4n):



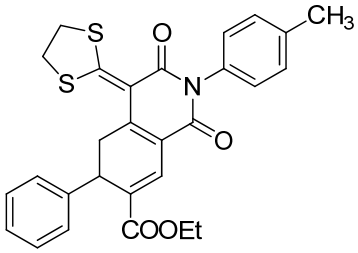
Yellow solid; m. p. 253-255 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.29-3.38 (m, 3H), 3.52 (t, *J* = 6.0 Hz, 2H), 3.73 (s, 3H), 3.91 (d, *J* = 16.5 Hz, 1H), 4.28 (d, *J* = 9.0 Hz, 1H), 5.21 (dd, *J* = 14.5, 14.0 Hz, 2H), 7.15-7.30 (m, 8H), 7.43 (d, *J* = 6.5 Hz, 2H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.1, 36.7, 37.5, 38.5, 43.7, 51.8, 115.5, 118.7, 127.0, 127.1 (3C), 127.3, 128.3 (2C), 128.6 (2C), 128.7 (2C), 131.6, 137.1, 141.2, 143.6, 161.5, 163.4, 166.6, 177.6. HRMS (ESI-TOF) calcd for $C_{27}H_{24}NO_4S_2^+$ ($[M + H]^+$): 490.1141, found: 490.1130.

Methyl 6-(4-chlorophenyl)-2-(2,4-dimethylphenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4o):



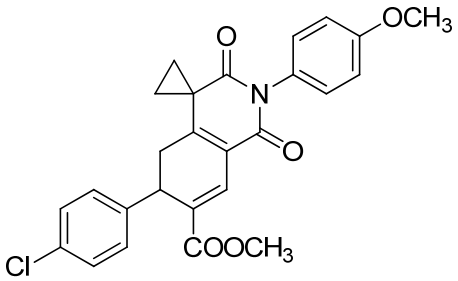
Yellow solid; m.p. 278-280 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.00 (s, 3H), 2.36 (s, 3H), 3.29-3.42 (m, 3H), 3.53-3.58 (m, 2H), 3.74 (s, 3H), 3.89 (d, *J* = 17.0 Hz, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 6.5 Hz, 2H), 7.15 (d, *J* = 6.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 17.2, 21.2, 36.1, 36.3, 37.7, 38.6, 51.9, 115.4, 119.0, 127.1, 127.8, 128.1, 128.5 (2C), 128.7 (2C), 131.8 (2C), 132.0, 132.9, 135.0, 138.8, 139.4, 144.0, 161.2, 163.4, 166.5, 178.0. HRMS (ESI-TOF) calcd for $C_{28}H_{25}ClNO_4S_2^+$ ($[M + H]^+$): 538.0908, found: 538.0916.

Ethyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-phenyl-2-(*p*-tolyl)-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4p):



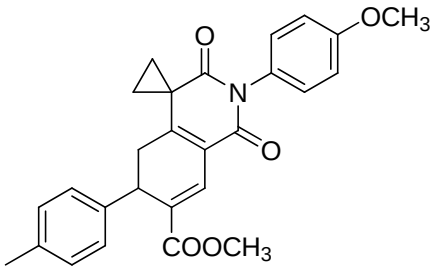
Yellow solid; m. p. 144-146 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27 (t, *J* = 9.0 Hz, 3H), 2.41 (s, 3H), 3.33-3.47 (m, 3H), 3.56 (t, *J* = 6.0 Hz, 2H), 4.00 (d, *J* = 15.0 Hz, 1H), 4.20 (q, *J* = 9.0 Hz, 2H), 4.35 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.24-7.32 (m, 7H), 8.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.6, 20.7, 35.6, 36.2, 37.0, 38.1, 60.1, 114.9, 118.4, 126.4, 126.6 (2C), 127.2, 127.6 (2C), 128.1 (2C), 129.4 (2C), 130.6, 132.1, 137.8, 140.9, 143.5, 161.1, 163.2, 165.6, 177.6. HRMS (ESI-TOF) calcd for $C_{28}H_{26}NO_4S_2^+$ ($[M + H]^+$): 504.1298, found: 504.1299.

Methyl 6'-(4-chlorophenyl)-2'-(4-methoxyphenyl)-1',3'-dioxo-2',3',5',6'-tetrahydro-1'H-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4q):



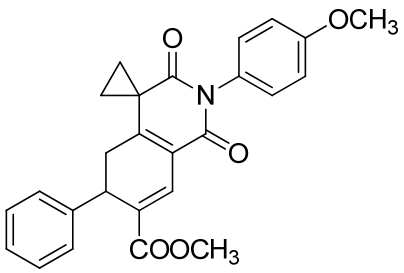
Green solid; m.p. 186-187 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.26 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.74 (tt, *J* = 9.0, 4.0 Hz, 1H), 1.83 (tt, *J* = 8.0, 5.0 Hz, 1H), 2.04 (tt, *J* = 9.0, 4.0 Hz, 1H), 2.23 (d, *J* = 17.5 Hz, 1H), 2.86 (dd, *J* = 9.5, 17.0 Hz, 1H), 3.74 (s, 3H), 3.84 (s, 3H), 4.17 (d, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.26-7.28 (m, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.7, 25.4, 29.7, 32.4, 35.6, 52.0, 55.4, 114.6 (2C), 122.9, 127.3, 128.2 (2C), 128.4, 129.0 (2C), 129.2 (2C), 130.4, 133.1, 138.8, 153.2, 159.4, 163.2, 166.5, 171.8. HRMS (ESI-TOF) calcd for $C_{26}H_{23}ClNO_5^+$ ($[M + H]^+$): 464.1259, found: 464.1253.

Methyl 2'-(4-methoxyphenyl)-1',3'-dioxo-6'-(*p*-tolyl)-2',3',5',6'-tetrahydro-1'H-spiro [cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4r):



Green solid; m.p. 163-165 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.28 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.72 (tt, *J* = 8.5, 4.0 Hz , 1H), 1.78 (tt, *J* = 8.0, 4.5 Hz, 1H), 2.01 (tt, *J* = 8.5, 5.0 Hz, 1H), 2.22 (d, *J* = 18.0 Hz, 1H), 2.31 (s, 3H), 2.83 (dd, *J* = 10.0, 17.5 Hz, 1H), 3.73 (s, 3H), 3.83 (s, 3H), 4.16 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.04-7.10 (m, 6H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.6, 21.0, 25.3, 29.7, 32.6, 35.7, 51.9, 55.4, 114.6 (2C), 122.8, 126.7 (2C), 127.5, 129.0, 129.2 (2C), 129.5 (2C), 130.0, 136.9, 137.3, 153.4, 159.4, 163.3, 166.6, 172.0. HRMS (ESI-TOF) calcd for $C_{27}H_{26}NO_5^+$ ($[M + H]^+$): 444.1805, found: 444.1802.

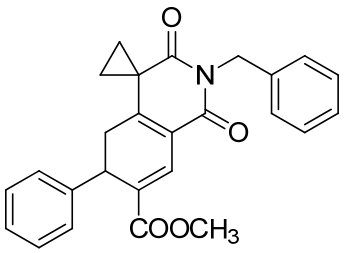
Methyl 2'-(4-methoxyphenyl)-1',3'-dioxo-6'-phenyl-2',3',5',6'-tetrahydro-1'H-spiro [cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4s):



Green solid; m.p. 137-139 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.25 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.74 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.78 (tt, *J* = 8.0, 5.0 Hz, 1H), 2.02 (tt, *J* = 8.0, 2.5 Hz, 1H), 2.23 (d, *J* = 17.5 Hz, 1H), 2.86 (dd, *J* = 9.0, 17.0 Hz, 1H), 3.73 (s, 3H), 3.83 (s, 3H), 4.20 (d, *J* = 9.5 Hz, 1H), 6.99 (d, *J* = 9.5 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.22-7.30 (m, 3H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.6, 25.3, 29.7, 32.6, 36.1, 52.0, 55.4, 114.6 (2C), 122.9, 126.8 (2C), 126.9,

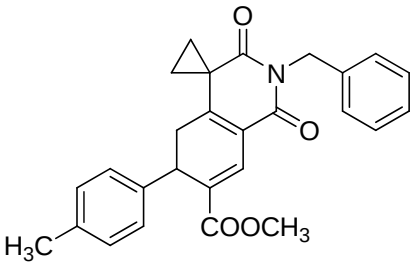
127.3, 127.4, 128.8 (2C), 129.2 (2C), 130.1, 140.3, 153.4, 159.4, 163.3, 166.6, 172.0. HRMS (ESI-TOF) calcd for $C_{26}H_{24}NO_5^+$ ($[M + H]^+$): 430.1649, found: 430.1647.

Methyl 2'-benzyl-1',3'-dioxo-6'-phenyl-2',3',5',6'-tetrahydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4t):



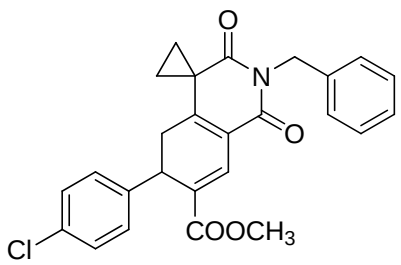
Green solid; m. p. 170-172 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.17 (tt, *J* = 8.5, 3.5 Hz, 1H), 1.64-1.68 (m, 1H), 1.74 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.93 (tt, *J* = 8.5, 4.0 Hz, 1H), 2.15 (d, *J* = 17.5 Hz, 1H), 2.77 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.72 (s, 3H), 4.15 (d, *J* = 9.5 Hz, 1H), 5.08 (dd, *J* = 14.0, 14.0 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.18-7.27 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.5, 25.2, 29.4, 32.4, 36.1, 43.6, 52.0, 122.6, 126.8 (2C), 127.3, 127.6, 128.4 (2C), 128.7, 128.8 (2C), 129.2 (2C), 130.2, 137.0, 140.4, 153.2, 163.0, 166.6, 171.8. HRMS (ESI-TOF) calcd for $C_{26}H_{24}NO_4^+$ ($[M + H]^+$): 414.1700, found: 414.1709.

Methyl 2'-benzyl-1',3'-dioxo-6'-(*p*-tolyl)-2',3',5',6'-tetrahydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4u):



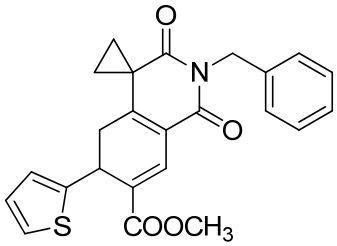
Green solid; m. p. 72-74 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.20 (tt, *J* = 8.5, 3.5 Hz, 1H), 1.66 (tt, *J* = 9.0, 4.0 Hz, 1H), 1.75 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.97 (tt, *J* = 9.0, 3.5 Hz, 1H), 2.23 (d, *J* = 17.0 Hz, 1H), 2.28 (s, 3H), 2.75 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.72 (s, 3H), 4.11 (d, *J* = 9.5 Hz, 1H), 5.08 (dd, *J* = 14.0, 14.0 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.24-2.27(m, 1H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.5, 21.0, 25.2, 29.4, 32.5, 35.7, 43.5, 51.9, 122.6, 126.6 (2C), 127.5, 128.4 (2C), 129.0, 129.2 (2C), 129.5 (2C), 129.9, 136.8, 137.0, 137.4, 153.2, 163.1, 166.6, 171.8. HRMS (ESI-TOF) calcd for $C_{27}H_{26}NO_4^+$ ($[M + H]^+$): 428.1856, found: 428.1868.

Methyl 2'-benzyl-6'-(4-chlorophenyl)-1',3'-dioxo-2',3',5',6'-tetrahydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4v):



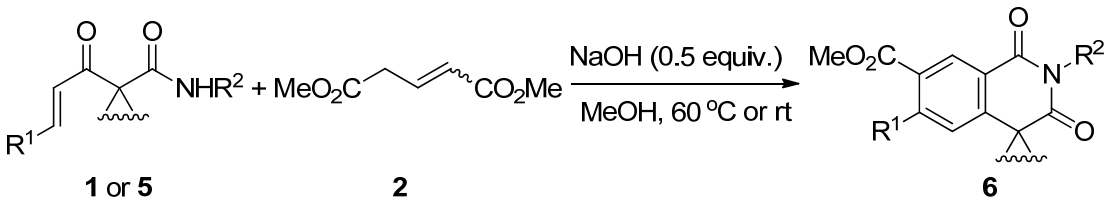
Green solid; m. p. 75-77 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.18 (tt, *J* = 8.5, 3.5 Hz, 1H), 1.66 (tt, *J* = 9.0, 4.0 Hz, 1H), 1.78 (tt, *J* = 9.0, 4.0 Hz, 1H), 1.99 (tt, *J* = 9.0, 4.0 Hz, 1H), 2.11 (d, *J* = 17.5 Hz, 1H), 2.77 (dd, *J* = 18.0, 9.5 Hz, 1H), 3.73 (s, 3H), 4.12 (d, *J* = 9.5 Hz, 1H), 5.08 (dd, *J* = 14.0, 13.5 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.26-2.28 (m, 1H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.6, 25.3, 29.4, 32.3, 35.6, 43.6, 52.0, 122.6, 127.6, 128.2 (2C), 128.3 (2C), 128.4, 129.0 (2C), 129.2 (2C), 130.3, 133.0, 136.9, 138.9, 152.9, 162.9, 166.4, 171.6. HRMS (ESI-TOF) calcd for $C_{26}H_{23}ClNO_4^+$ ([M + H]$^+$): 448.1310, found: 448.1316.

Methyl 2'-benzyl-1',3'-dioxo-6'-(thiophen-2-yl)-2',3',5',6'-tetrahydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4w):



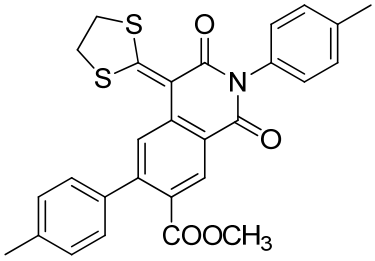
Green solid; m. p. 133-135 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.52-1.54 (m, 1H), 1.69-1.72 (m, 1H), 1.90-1.92 (m, 1H), 1.99-2.01 (m, 1H), 2.28 (d, *J* = 17.5 Hz, 1H), 2.71 (dd, *J* = 17.5, 8.5 Hz, 1H), 3.77 (s, 3H), 4.43 (d, *J* = 8.5 Hz, 1H), 5.08 (s, 2H) , 6.77 (d, *J* = 3.0 Hz, 1H), 6.84 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 5.0 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.8, 25.7, 29.5, 31.6, 32.3, 43.5, 52.0, 122.4, 123.8, 124.7, 126.6, 127.5, 128.3 (2C), 128.8, 129.0 (2C), 129.6, 136.9, 143.4, 153.3, 162.9, 166.3, 171.6. HRMS (ESI-TOF) calcd for $C_{24}H_{22}NO_4S^+$ ([M + H]$^+$): 420.1264, found: 420.1266.

III. General Procedure for the Preparation of 6 (6a as Example):



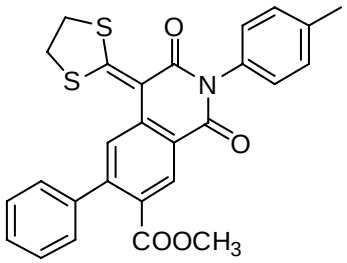
To a solution of (E)-2-(1,3-dithiolan-2-ylidene)-3-oxo-N,5-di-p-tolylpent-4-enamide **1a** (0.5 mmol, 198 mg) and dimethyl glutaconate **2** (1.0 mmol, 0.14 mL) in MeOH (4.0 mL) was added NaOH (50% mmol, 10 mg) in one portion. The reaction mixture was stired at 60℃ for 4 h. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to yield the corresponding crude product, which was purified by aluminium oxide, basic (200-300 mesh) chromatography (petroleum ether/acetone = 10/4, v/v) to give **6a** (226 mg, 90%) as a yellow solid.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2,6-di-*p*-tolyl-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (6a):



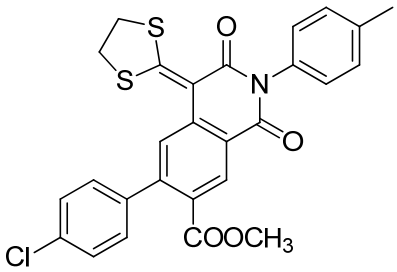
Yellow solid; m.p. 286-298 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 2.43 (s, 3H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.58 (t, *J* =6.0 Hz, 2H), 3.75 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 8.31 (s, 1H), 8.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3 (2C), 38.0, 38.2, 52.3, 112.6, 122.1 128.2 (2C), 128.3 (2C), 128.4, 129.1 (2C), 130.1 (2C), 131.5, 132.8, 136.5, 137.3, 138.0, 138.5, 143.0, 146.8, 162.8, 163.9, 167.6, 172.7. HRMS (ESI-TOF) calcd for $C_{28}H_{24}NS_2O_4^+$ ($[M + H]^+$): 502.1141, found: 502.1140.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-phenyl-2-(*p*-tolyl)-1,2,3,4- tetrahydroisoquinoline-7-carboxylate (6b):



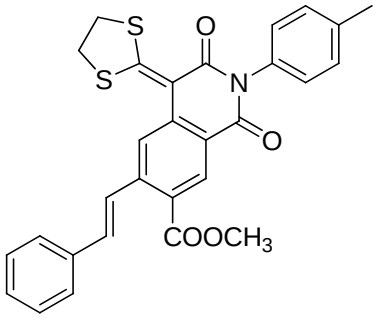
Yellow solid; m.p. 184-186 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.72 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.43-7.47 (m, 5H), 8.32 (s, 1H), 8.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 38.0, 38.2, 52.3, 112.5, 122.3 128.1, 128.2 (2C), 128.2 (2C), 128.3 (3C), 128.4, 130.0 (2C), 131.5, 132.8, 136.6, 138.5, 140.3, 146.7, 162.7, 163.8, 167.5, 173.0. HRMS (ESI-TOF) calcd for $C_{27}H_{22}NS_2O_4^+$ ($[M + H]^+$): 488.0985, found: 488.0983.

Methyl 6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2-(*p*-tolyl)-1,2,3,4- tetrahydroisoquinoline-7-carboxylate (6c):



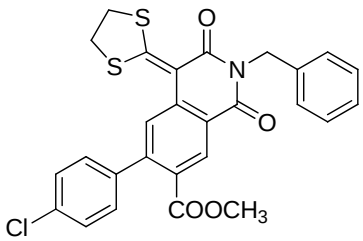
Yellow solid; m.p. 186-188 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 3.43 (t, *J* = 6.5 Hz, 2H), 3.59 (t, *J* = 5.5 Hz, 2H), 3.75 (s, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 8.28 (s, 1H) , 8.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 38.0, 38.2, 52.3, 112.4, 122.6, 127.8, 128.2 (2C), 128.4, 128.5 (2C), 129.7 (2C), 130.1 (2C), 131.8, 132.7, 134.3, 136.7, 138.6, 138.8, 145.7, 162.6, 163.8, 167.1, 173.2. HRMS (ESI-TOF) calcd for $C_{27}H_{21}ClNS_2O_4^+$ ($[M + H]^+$): 522.0595, found: 522.0594.

(E)-methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-styryl-2-(*p*-tolyl)-1,2,3,4- tetrahydroisoquinoline-7-carboxylate (6d):



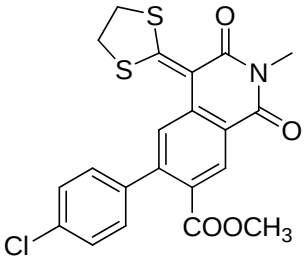
Yellow solid; m.p. 292-294 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 3.46 (t, *J* = 7.0 Hz, 2H), 3.63 (t, *J* = 6.0 Hz, 2H), 3.95 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 16.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 3H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 8.17 (d, *J* = 16.0 Hz, 1H), 8.61 (s, 1H), 8.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 38.0, 38.3, 52.3, 112.8, 122.2, 124.4, 125.9, 127.0, 127.2 (2C), 128.2 (2C), 128.5, 128.7 (2C), 130.0 (2C), 132.5, 132.8, 134.1, 136.9, 137.1, 138.5, 143.6, 162.7, 163.9, 166.6, 172.6. HRMS (ESI-TOF) calcd for $C_{29}H_{24}NO_4S_2^+$($[M + H]^+$): 514.1141, found: 514.1149.

Methyl 2-benzyl-6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (6e):



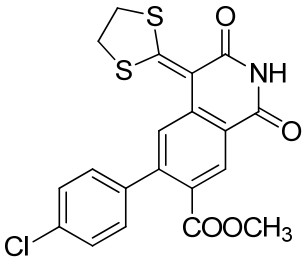
Yellow solid; m.p. 111-113 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.43 (t, *J* = 7.0 Hz, 2H), 3.57 (t, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 5.32 (s, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.26-7.33 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.0 Hz, 2H), 8.19 (s, 1H), 8.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 37.8, 38.2, 43.9, 52.3, 112.4, 122.4, 127.4, 127.7, 128.4 (3C), 128.5 (2C), 128.9 (2C), 129.7 (2C), 131.8, 134.2, 136.5, 137.1, 138.8, 145.6, 162.5, 163.4, 166.9, 172.4. HRMS (ESI-TOF) calcd for $C_{27}H_{21}NClS_2O_4^+$ ($[M + H]^+$): 522.0595, found: 522.0609.

Methyl 6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-2-methyl-1,3-dioxo-1,2,3,4-tetrahydro-isoquinoline-7-carboxylate (6f):



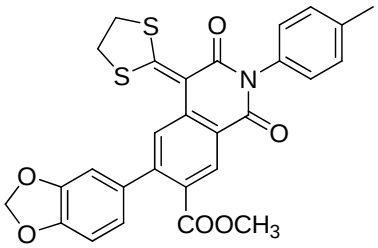
Yellow solid; m.p. 176-178 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.44 (t, *J* = 5.5 Hz, 2H), 3.50 (s, 3H), 3.58 (t, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 8.22 (s, 1H), 8.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 27.5, 37.8, 38.1, 52.2, 112.4, 122.3 127.7, 128.3, 128.4 (2C), 128.9, 129.6 (2C), 131.5, 134.2, 136.3, 138.9, 145.5, 162.7, 163.7, 167.0. HRMS (ESI-TOF) calcd for $C_{21}H_{17}ClNS_2O_4^+$ ([M + H]$^+$): 446.0282, found: 446.0277.

Methyl 6-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (6g):



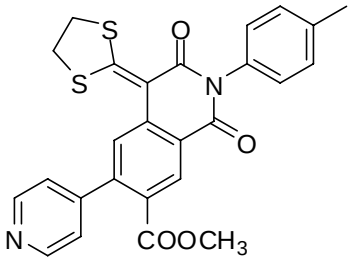
Yellow solid; m. p. 243-245 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.48 (t, *J* = 7.0 Hz, 2H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.76 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 8.23 (s, 1H), 8.27 (s, 1H), 8.81 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 38.2, 38.8, 52.8, 111.5, 122.7, 127.4, 128.7, 128.9 (2C), 130.4, 130.5 (2C), 133.5, 137.9, 139.2, 145.0, 162.7, 163.7, 166.9, 174.2. HRMS (ESI-TOF) calcd for $C_{20}H_{15}ClNO_4S_2^+$ ([M + H]$^+$): 432.0126, found: 432.0125.

Methyl 6-(benzo[d][1,3]dioxol-5-yl)-4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-2-(*p*-tolyl)-1,2,3,4-tetrahydro-isoquinoline-7-carboxylate (6h):



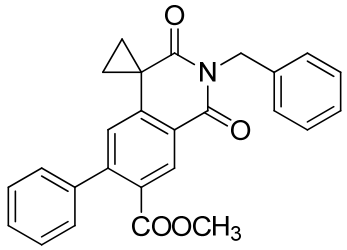
Yellow solid; m.p. 293-195 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 3.43 (t, *J* = 6.0 Hz, 2H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 6.05 (s, 2H), 6.90 (s, 2H), 6.94 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 8.28 (s, 1H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 37.7, 37.9, 38.2, 52.3, 101.0, 101.3, 108.3, 108.9, 112.5, 122.2, 128.2 (2C), 128.3, 130.0 (2C), 131.4, 132.8, 134.1, 136.5, 138.4, 146.2, 147.6, 147.7, 162.7, 163.8, 167.6, 172.8. HRMS (ESI-TOF) calcd for $C_{28}H_{22}NS_2O_6^+$ ([M + H]$^+$): 532.0883, found: 532.0905.

Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-(pyridin-4-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (6i):



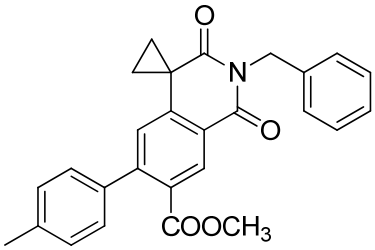
Yellow solid; m. p. 277-279 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.42 (s, 3H), 3.43 (t, *J* = 6.0, Hz, 2H), 3.59 (t, *J* = 6.0 Hz, 2H), 3.77 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 8.68 (d, *J* =4.0 Hz, 1H), 8.71 (s, 1H), 8.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 38.0, 38.3, 52.4, 112.1, 122.8, 123.0, 127.5, 128.2 (2C), 128.8, 130.1 (2C), 132.3, 132.7, 135.9, 136.3, 137.1, 138.6, 143.5, 148.9, 149.2, 162.6, 163,8, 166.6, 174.0. HRMS (ESI-TOF) calcd for $C_{26}H_{21}N_2O_4S_2^+$ ($[M + H]^+$): 489.0937, found: 489.0950.

Methyl 2'-benzyl-1',3'-dioxo-6'-phenyl-2',3'-dihydro-1'H-spiro[cyclopropane-1,4'-Isoquinoline]-7'-carboxylate (6j):



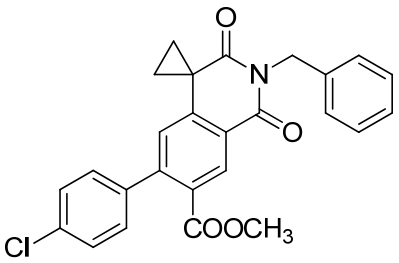
White solid; m.p. 169-171 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.69 (q, *J* = 4.0 Hz , 2H), 2.22 (q, *J* = 4.0 Hz, 2H), 3.69 (s, 3H), 5.24 (s, 2H), 6.74 (s, 1H), 7.25-7.32 (m, 5H), 7.42 (*J* = 6.5 Hz, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 8.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 25.7, 27.9 (2C), 43.9, 52.2, 123.2, 124.3, 127.5, 128.0 (2C), 128.1, 128.2 (2C), 128.4 (2C), 128.9 (2C), 129.1, 131.3, 137.0, 140.0, 143.9, 148.1, 163.7, 167.2, 171.9. HRMS (ESI-TOF) calcd for $C_{26}H_{22}NO_4^+$ ($[M + H]^+$): 412.1543, found: 412.1547.

Methyl 2'-benzyl-1',3'-dioxo-6'-(*p*-tolyl)-2',3'-dihydro-1'H-spiro[cyclopropane-1,4'-Isoquinoline]-7'-carboxylate (6k):



White solid; m.p. 163-165 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.68 (q, *J* = 4.0 Hz, 2H), 2.21 (q, *J* = 4.0 Hz, 2H), 2.41 (s, 3H), 3.72 (s, 3H), 5.24 (s, 2H), 6.73 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.22-7.25 (m, 3H), 7.26-7.32 (m, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 8.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.3, 25.7, 27.9 (2C), 43.9, 52.2, 123.2, 124.1, 127.5, 128.0 (2C), 128.4 (2C), 128.9 (3C), 129.0 (2C), 129.1, 131.2, 137.0, 138.1, 143.9, 148.2, 163.8, 167.3, 172.0. HRMS (ESI-TOF) calcd for $C_{27}H_{24}NO_4^+$ ($[M + H]^+$): 426.1700, found: 426.1708.

Methyl 2'-benzyl-6'-(4-chlorophenyl)-1',3'-dioxo-2',3'-dihydro-1'H-spiro[cyclopropane-1,4'-isoquinoline]-7'-carboxylate (6l):



White solid; m.p. 165-167 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.68 (q, *J* = 4.0 Hz, 2H), 2.23 (q, *J* = 4.0 Hz, 2H), 3.73 (s, 3H), 5.24 (s, 2H), 6.69 (s, 1H), 7.19 (d, *J* = 6.5 Hz, 2H), 7.25-7.29 (m, 1H), 7.30-7.32 (m, 2H), 7.39 (d, *J* = 6.5 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 8.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 25.8, 28.1 (2C), 44.0, 52.3, 123.2, 124.7, 127.6, 128.5 (4C), 128.7, 129.0 (2C), 129.4 (2C), 131.6, 134.4, 136.9, 138.4, 144.2, 147.1, 163.6, 166.8, 171.8. HRMS (ESI-TOF) calcd for $C_{26}H_{21}NClO_4^+$ ($[M + H]^+$): 446.1154, found: 446.1152.

IV. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 4 and 6:

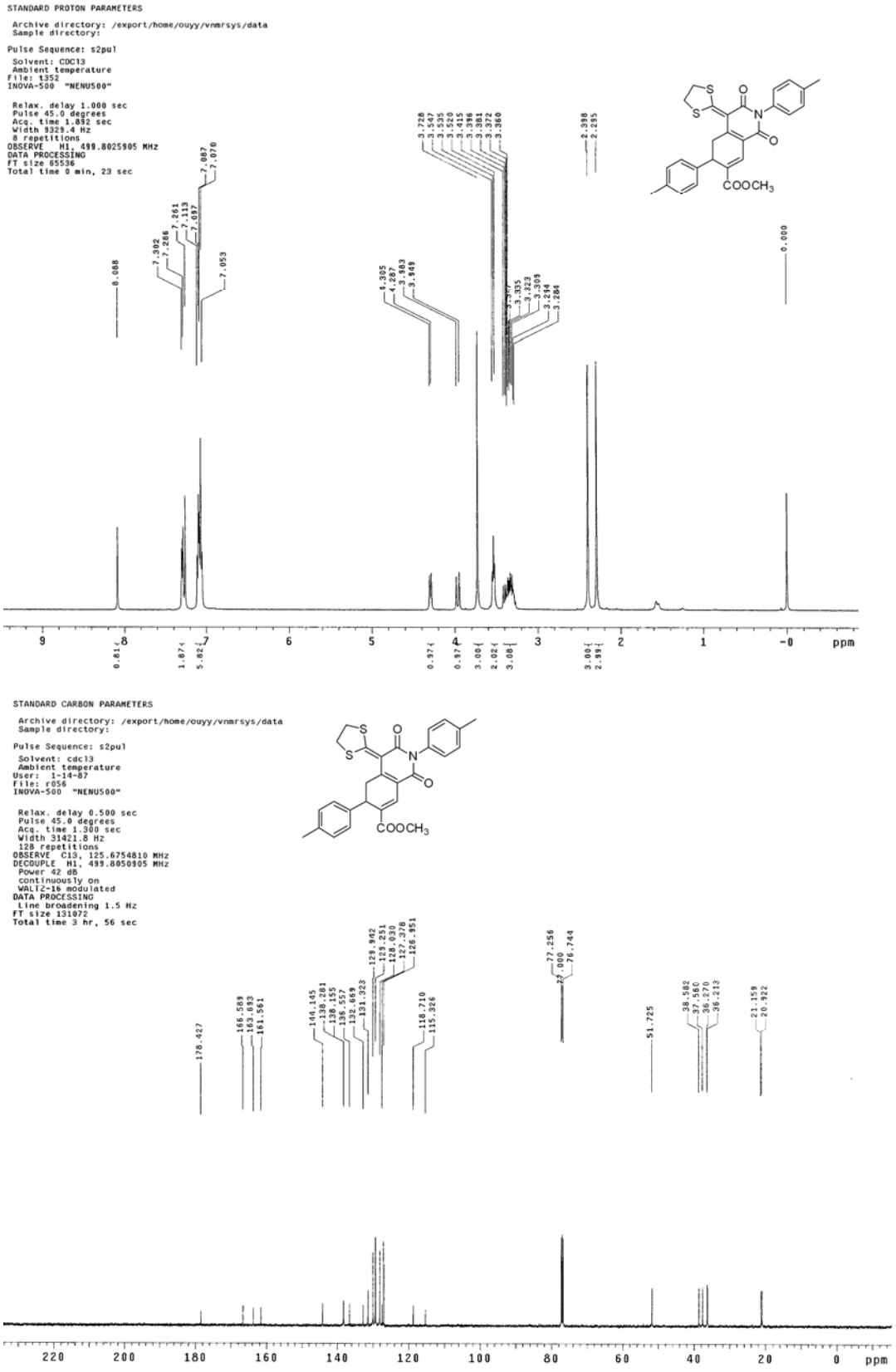


Figure 1. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4a**.

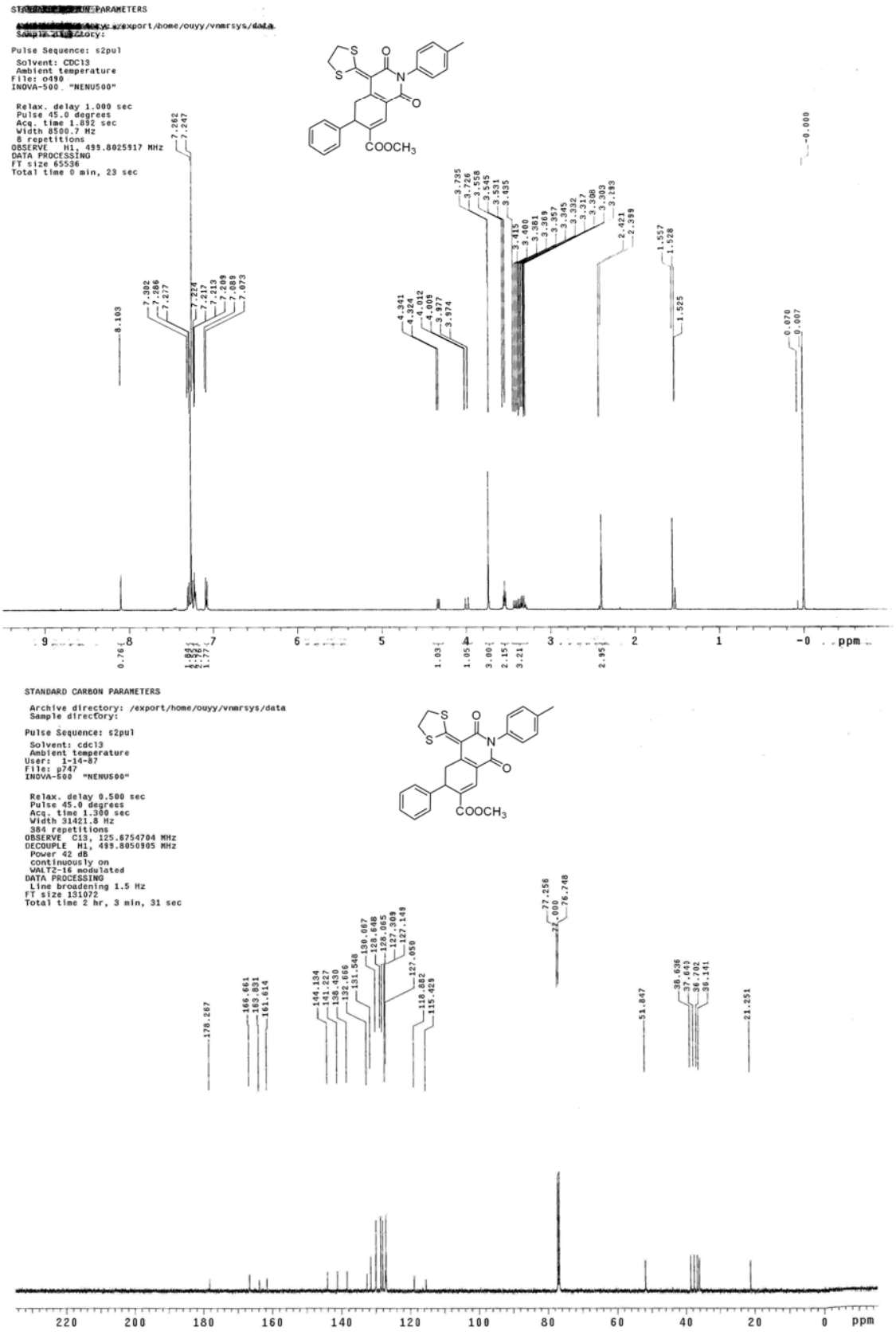


Figure 2. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4b**.

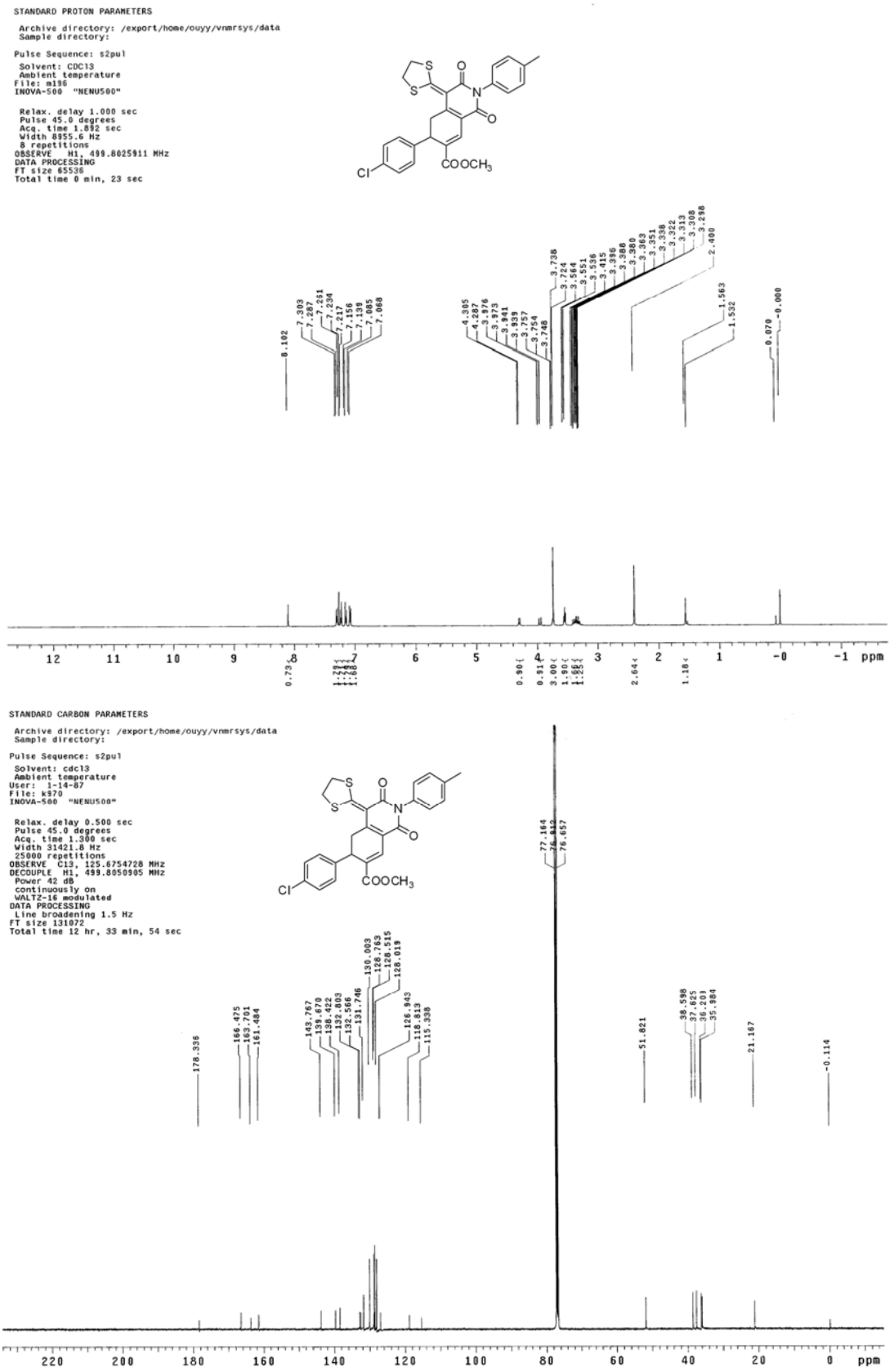


Figure 3. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4c**.

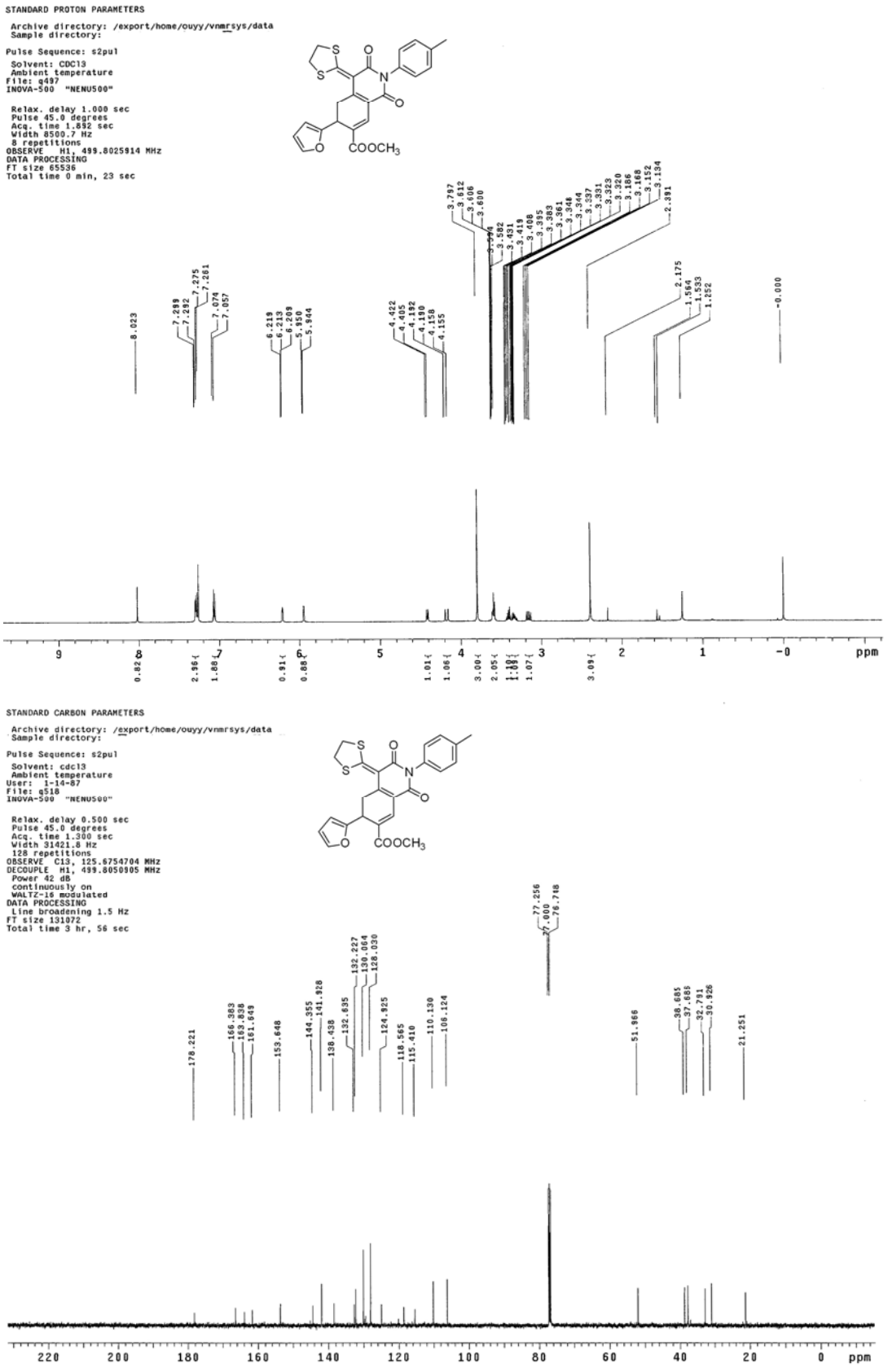


Figure 4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4d**.

Figure 4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4e**.

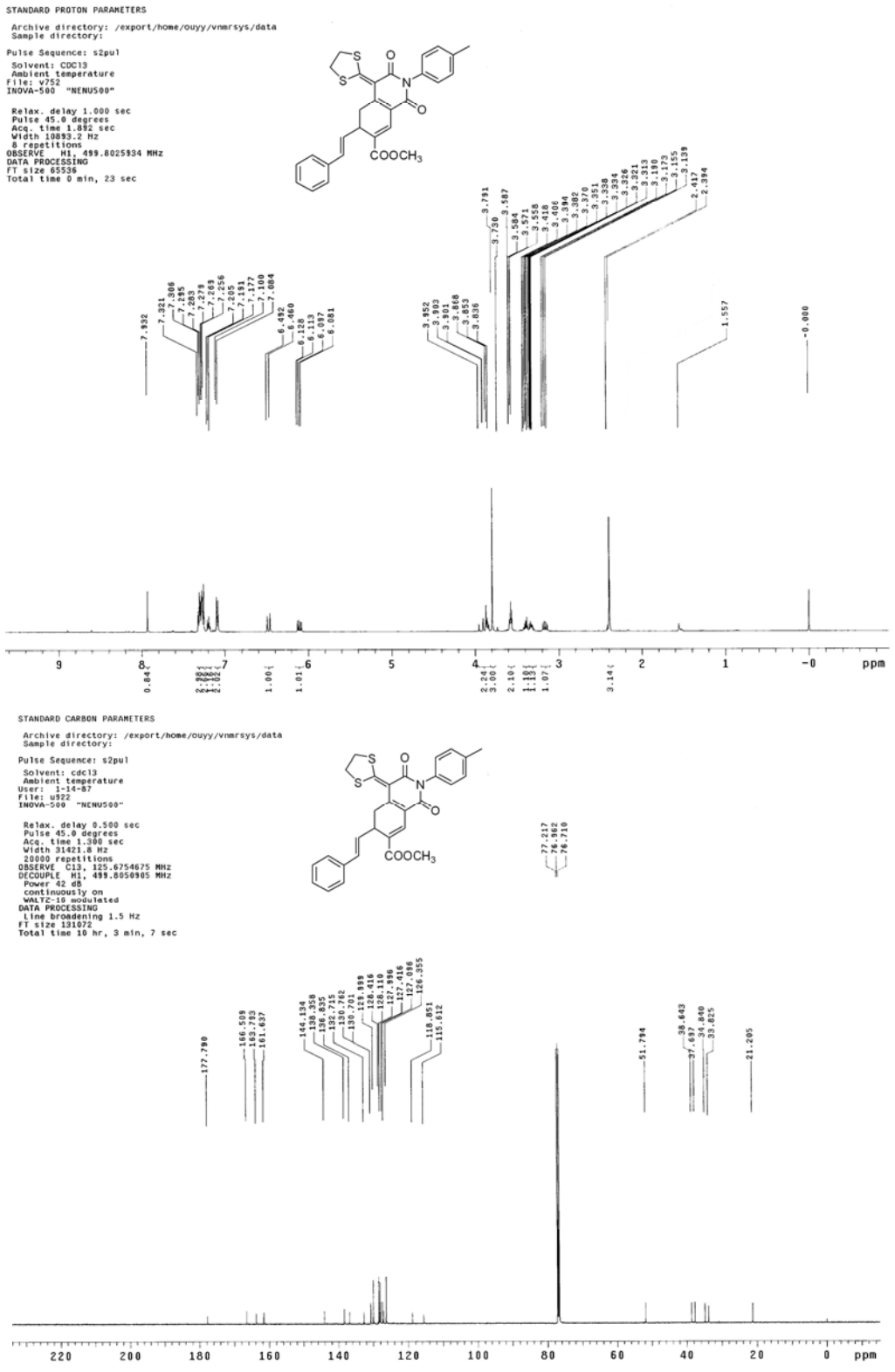


Figure 6. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4f**.

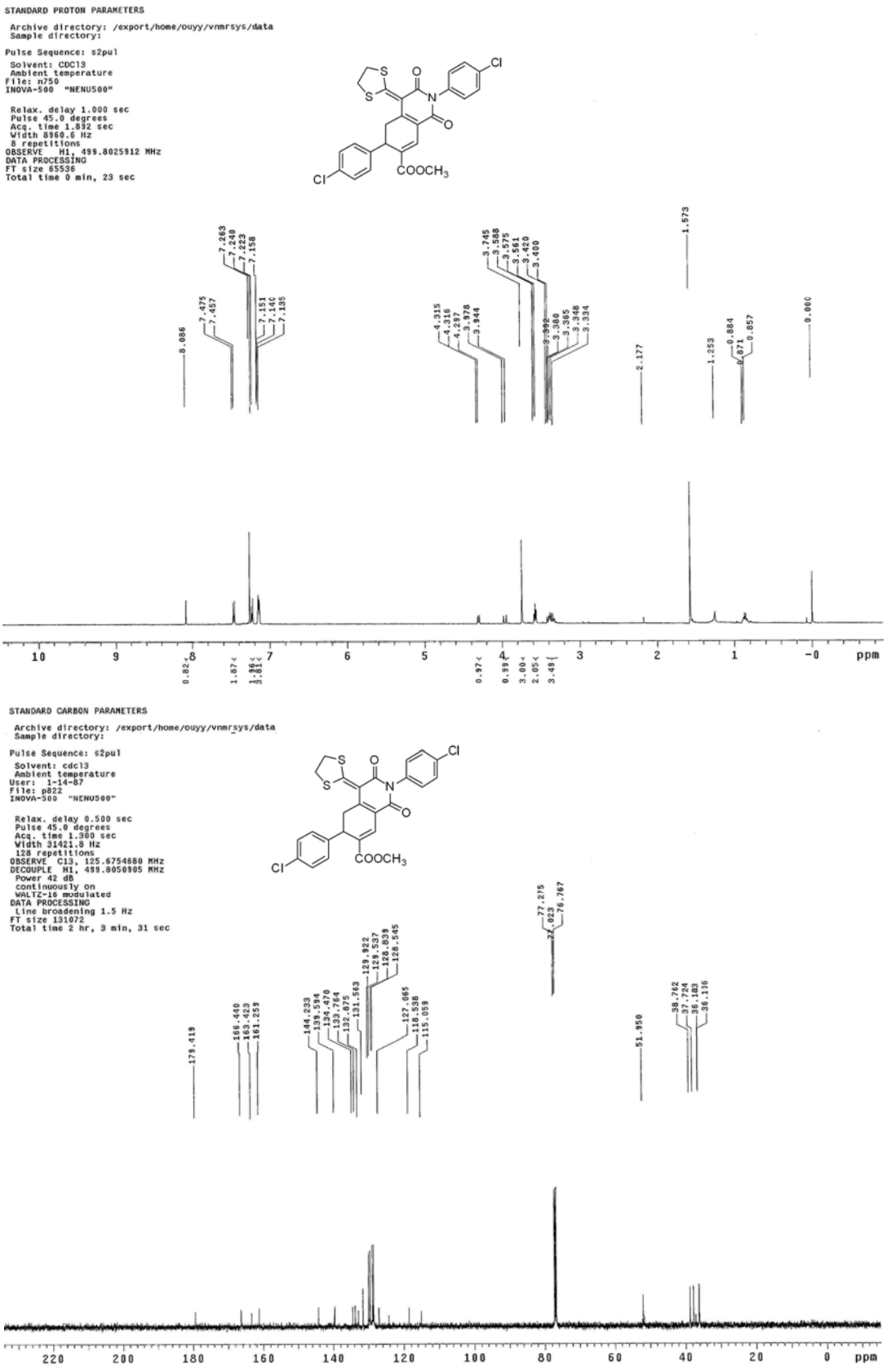


Figure 7. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4g**.

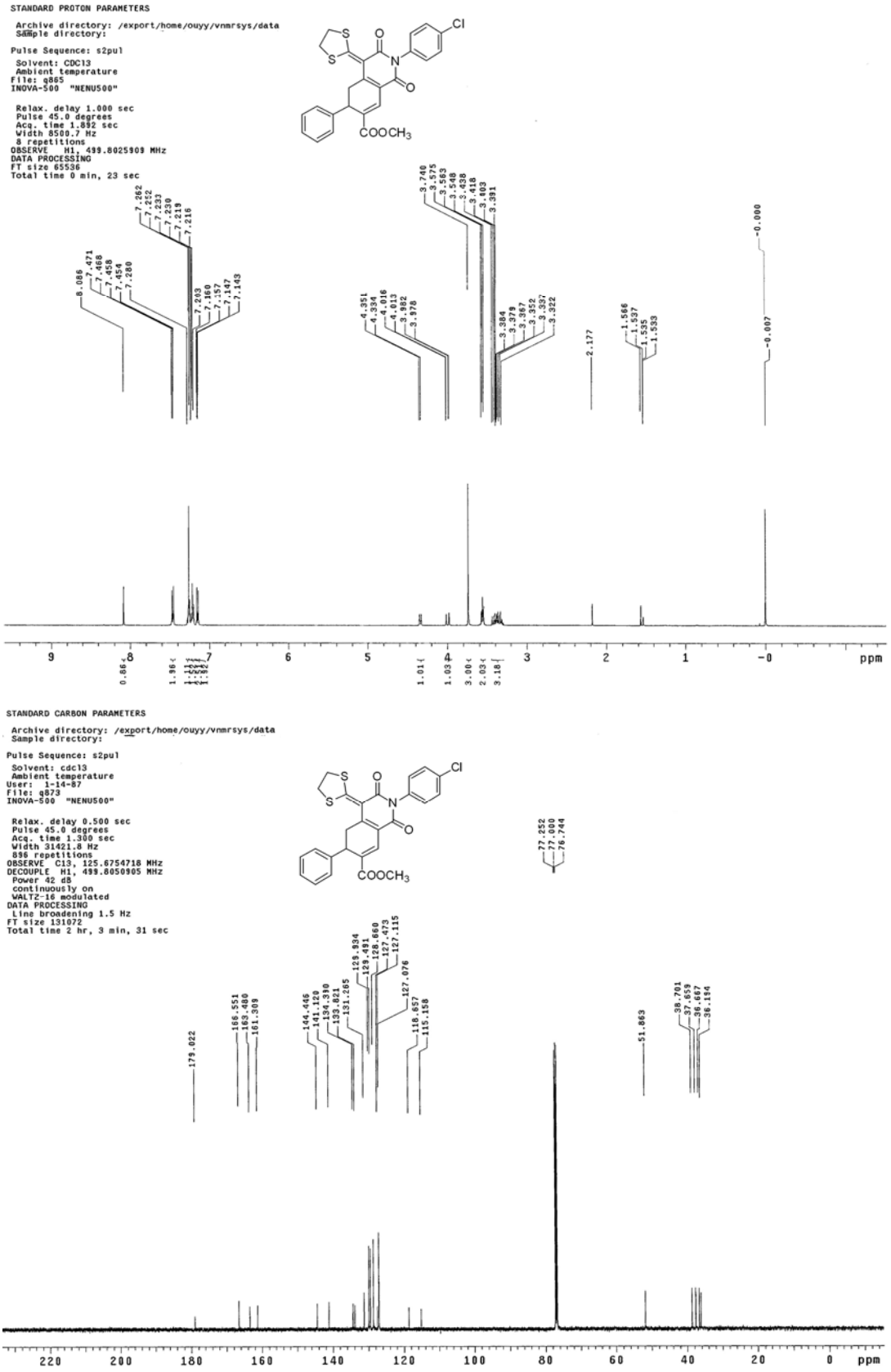


Figure 8. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4h**.

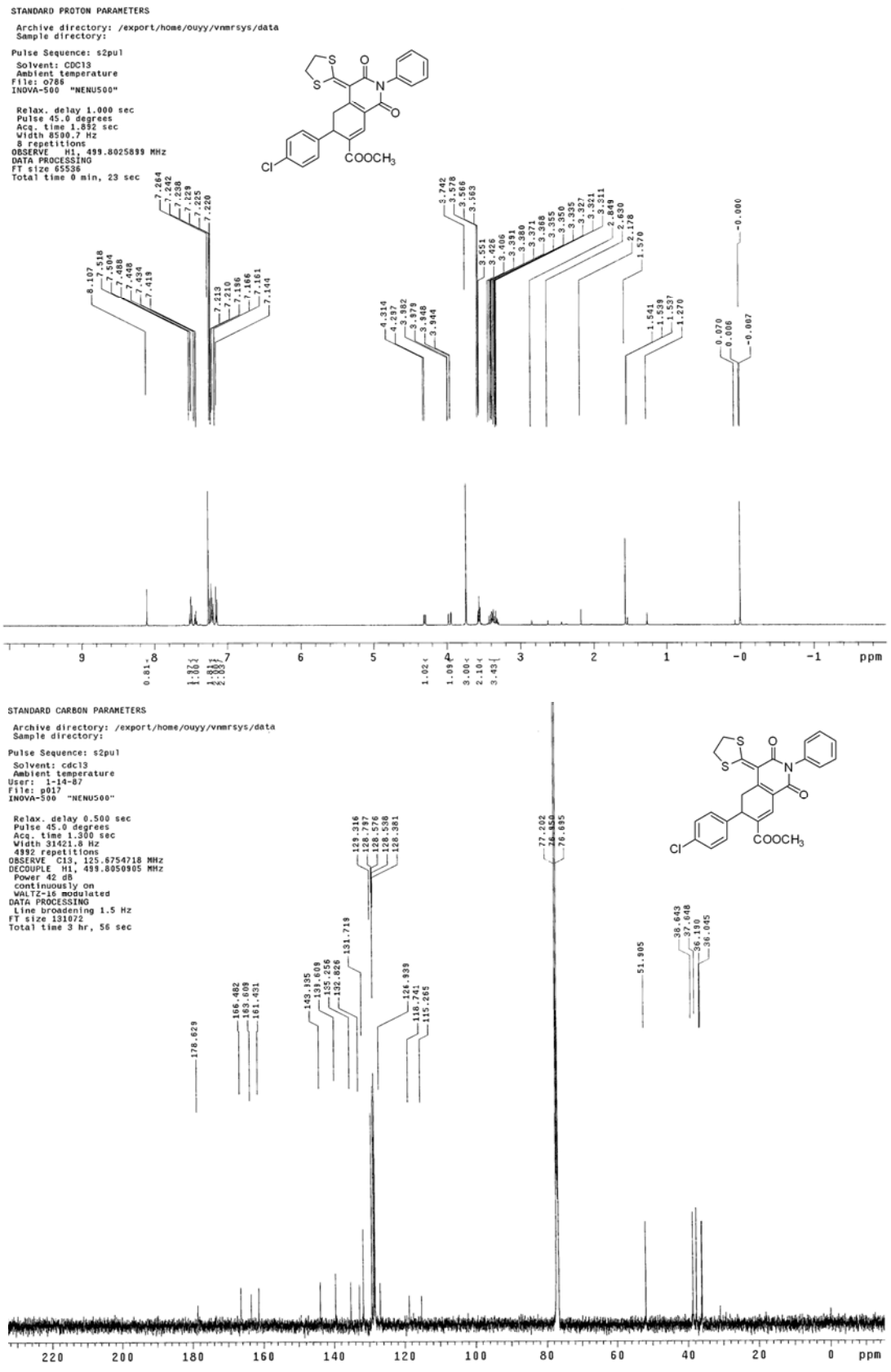


Figure 9. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4i**.

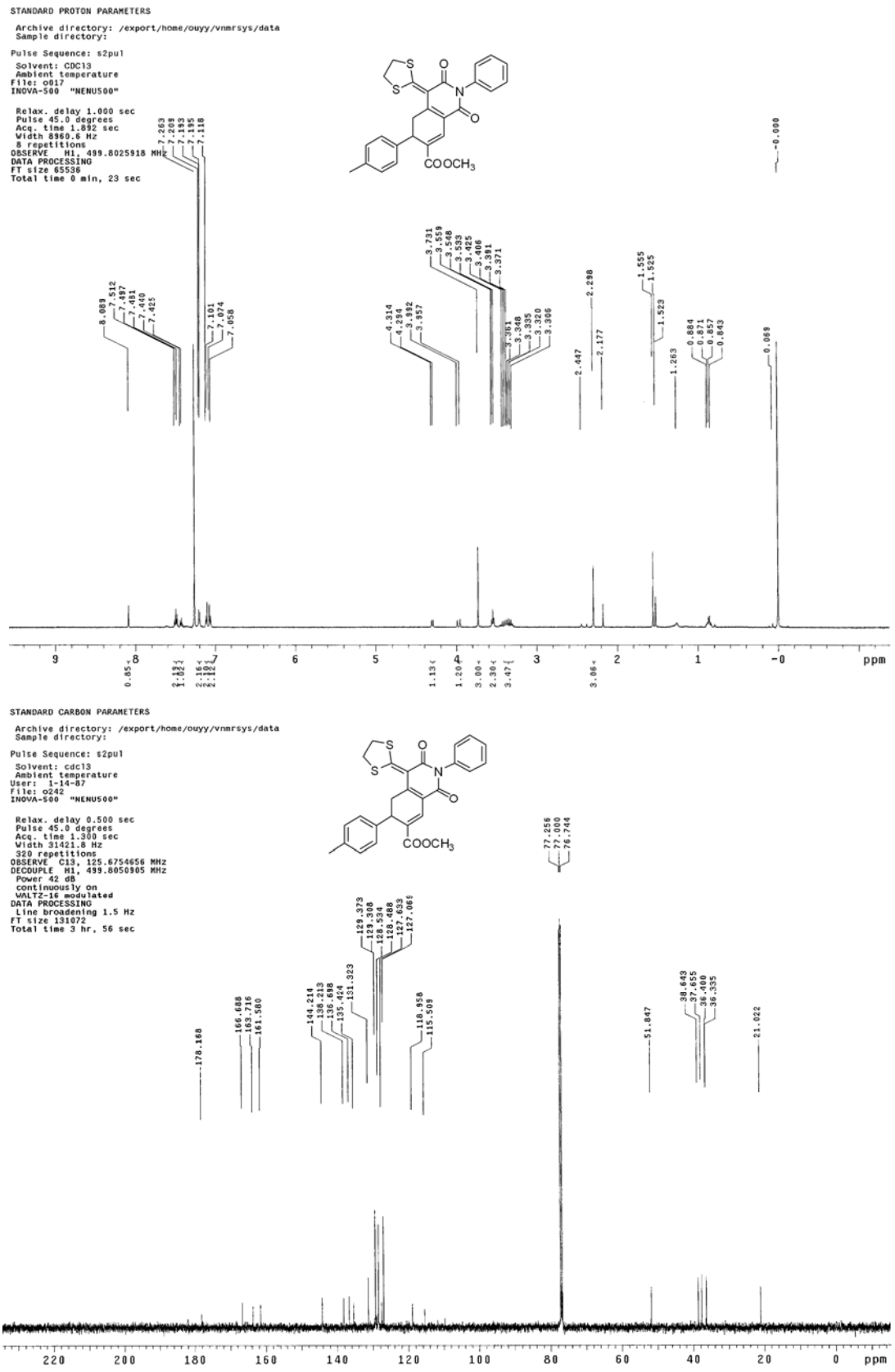


Figure 10. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4j**.

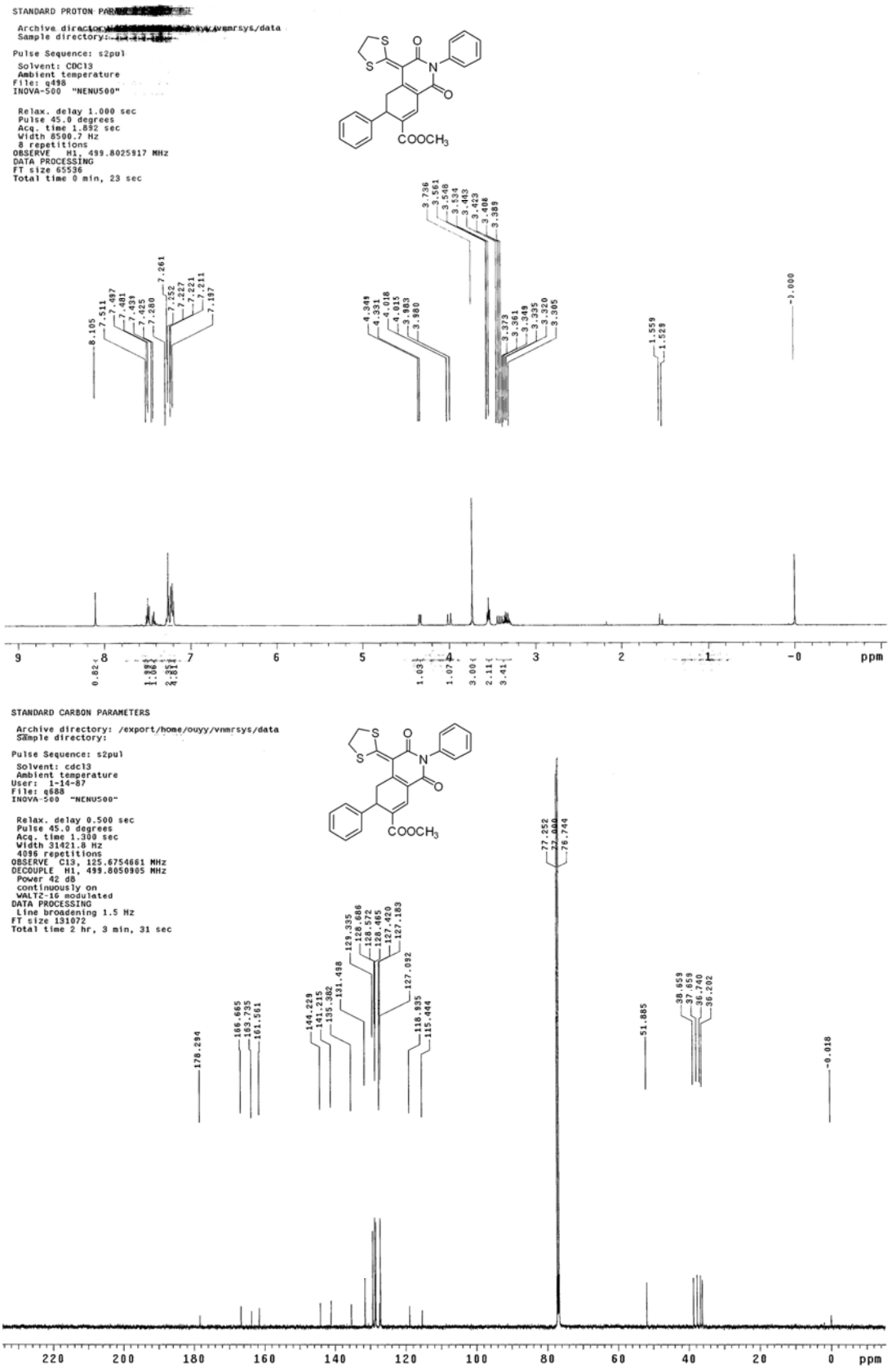


Figure11. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4k**.

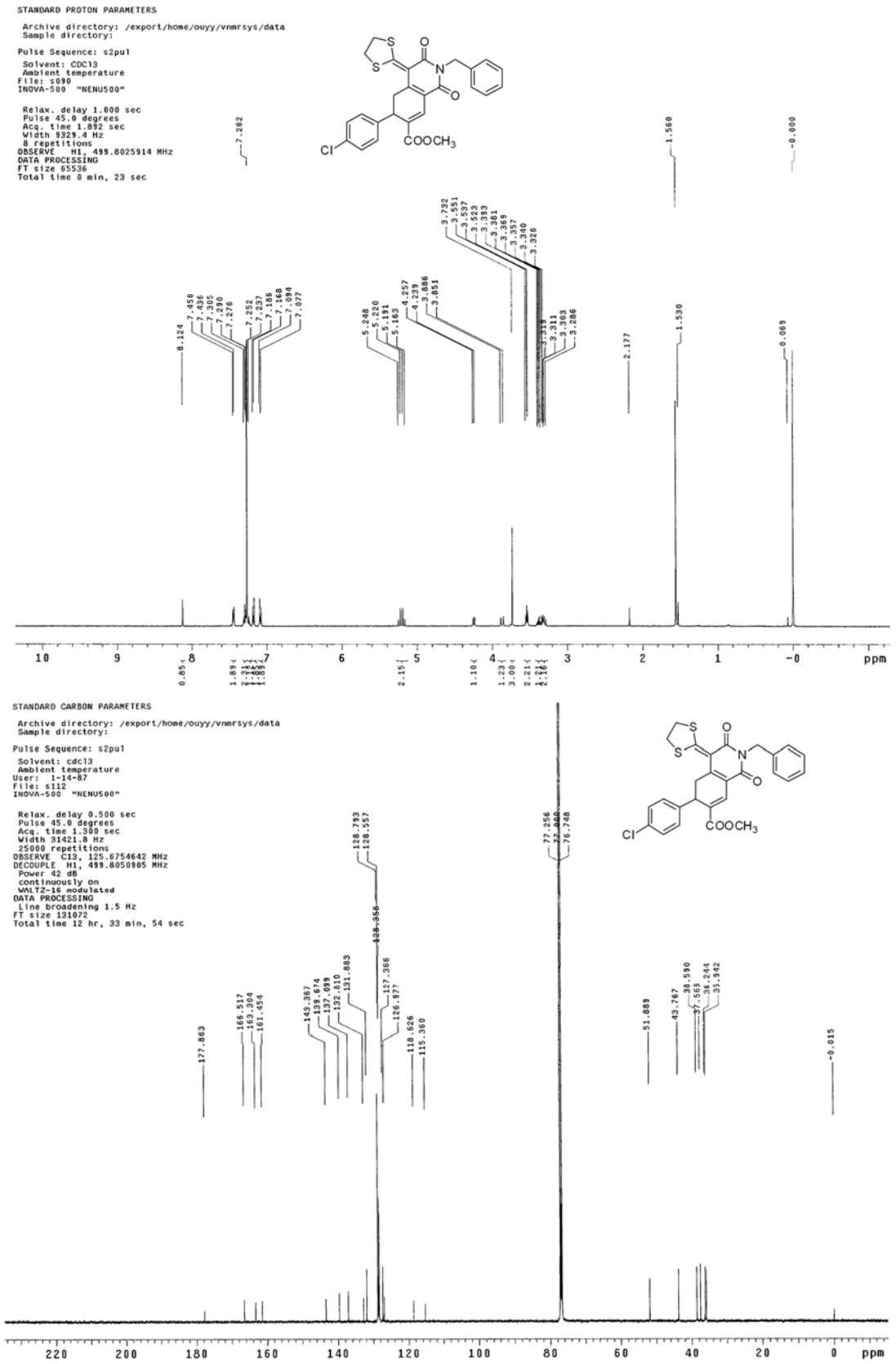


Figure 12. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4l**.

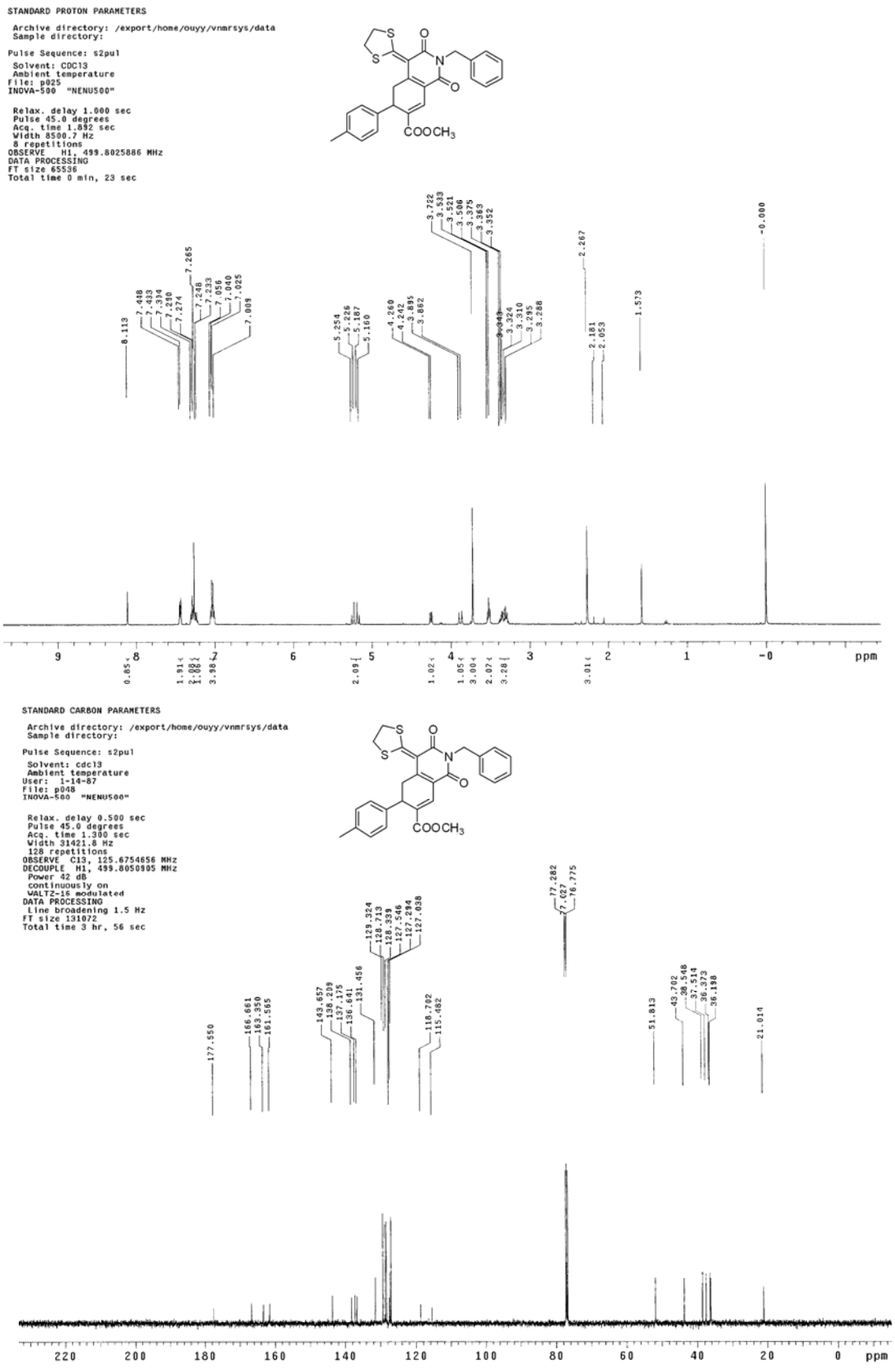


Figure 13. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4m**.

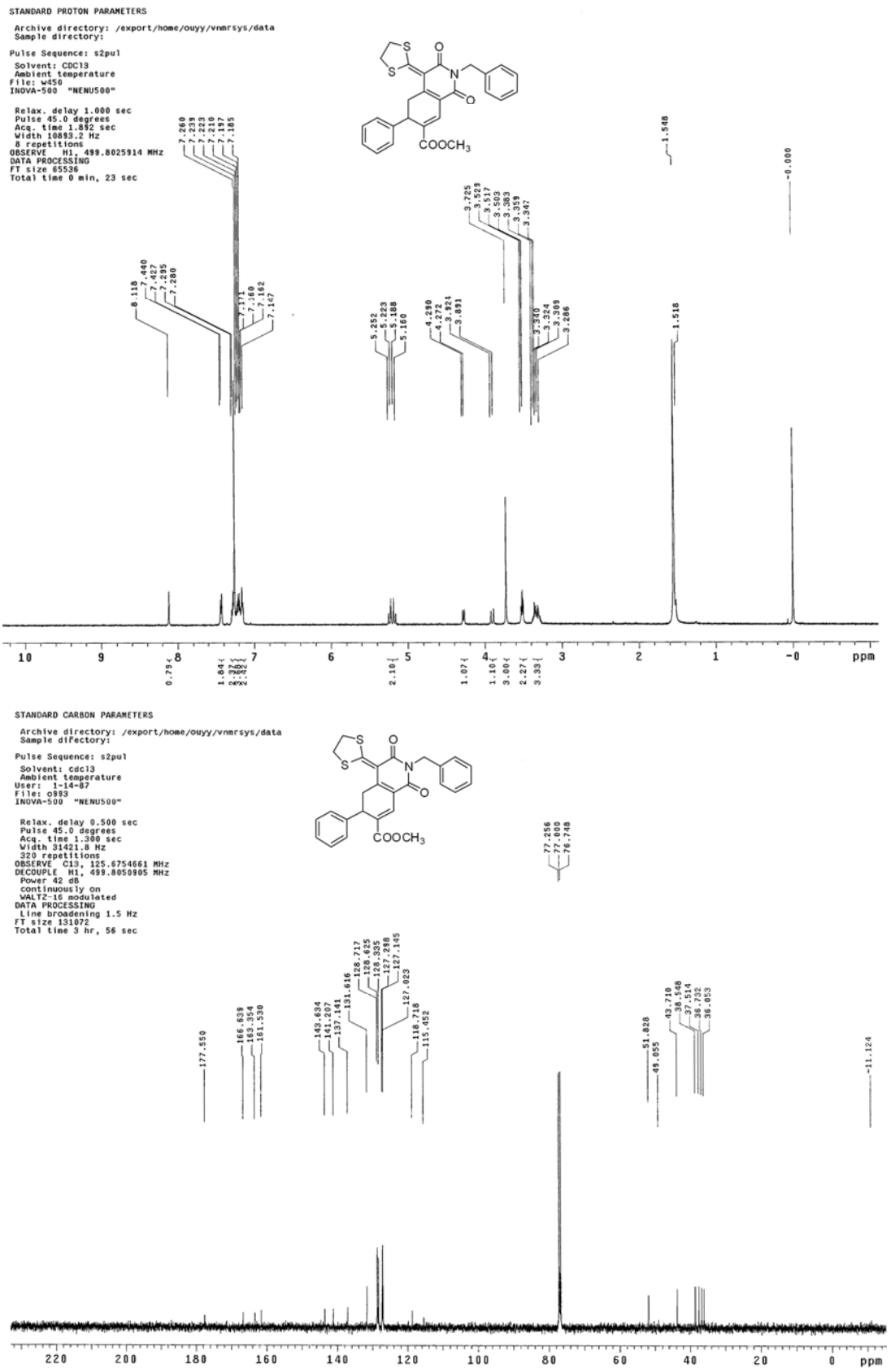


Figure 14. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4n**.

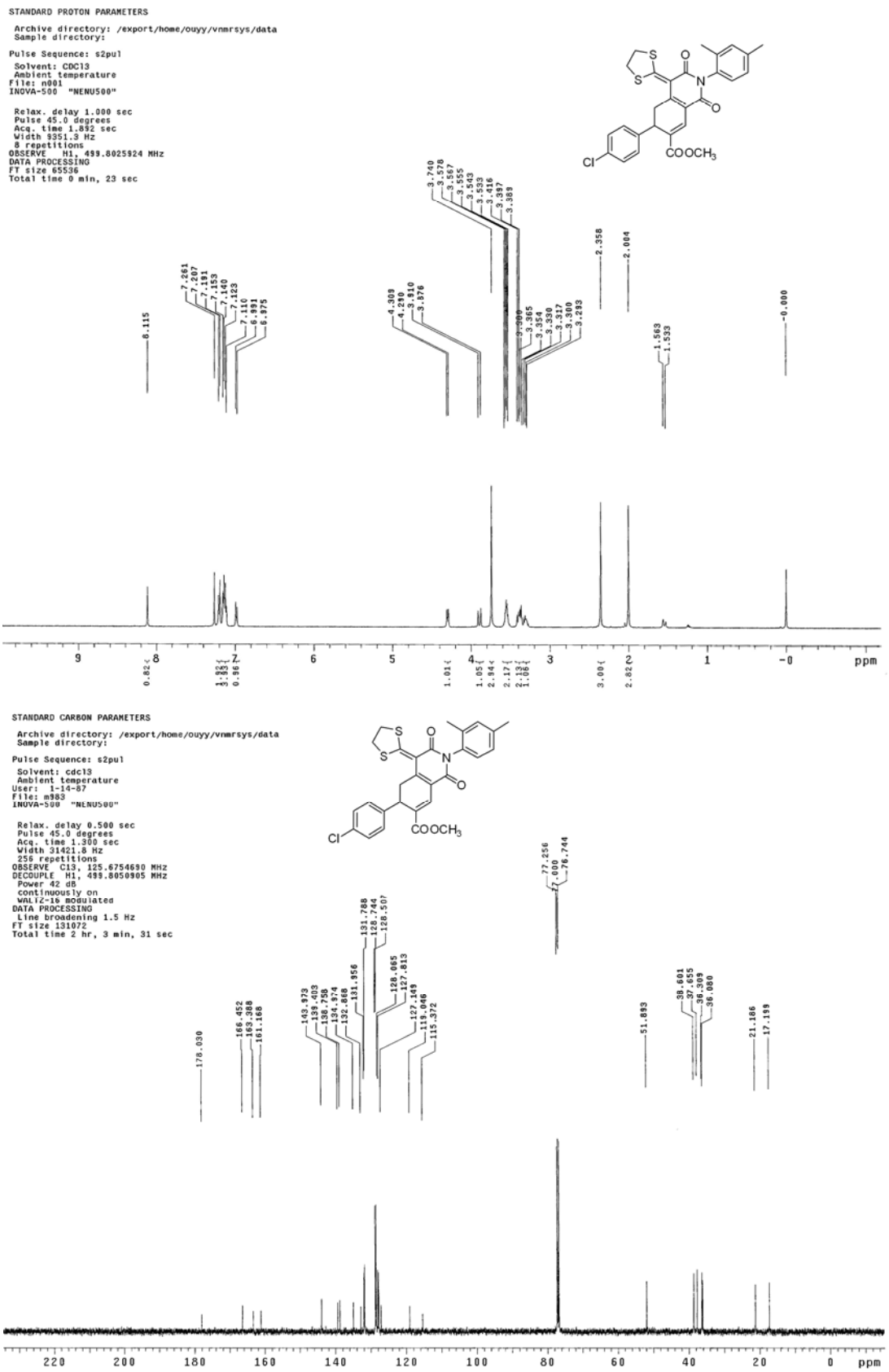


Figure 15. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4o**.

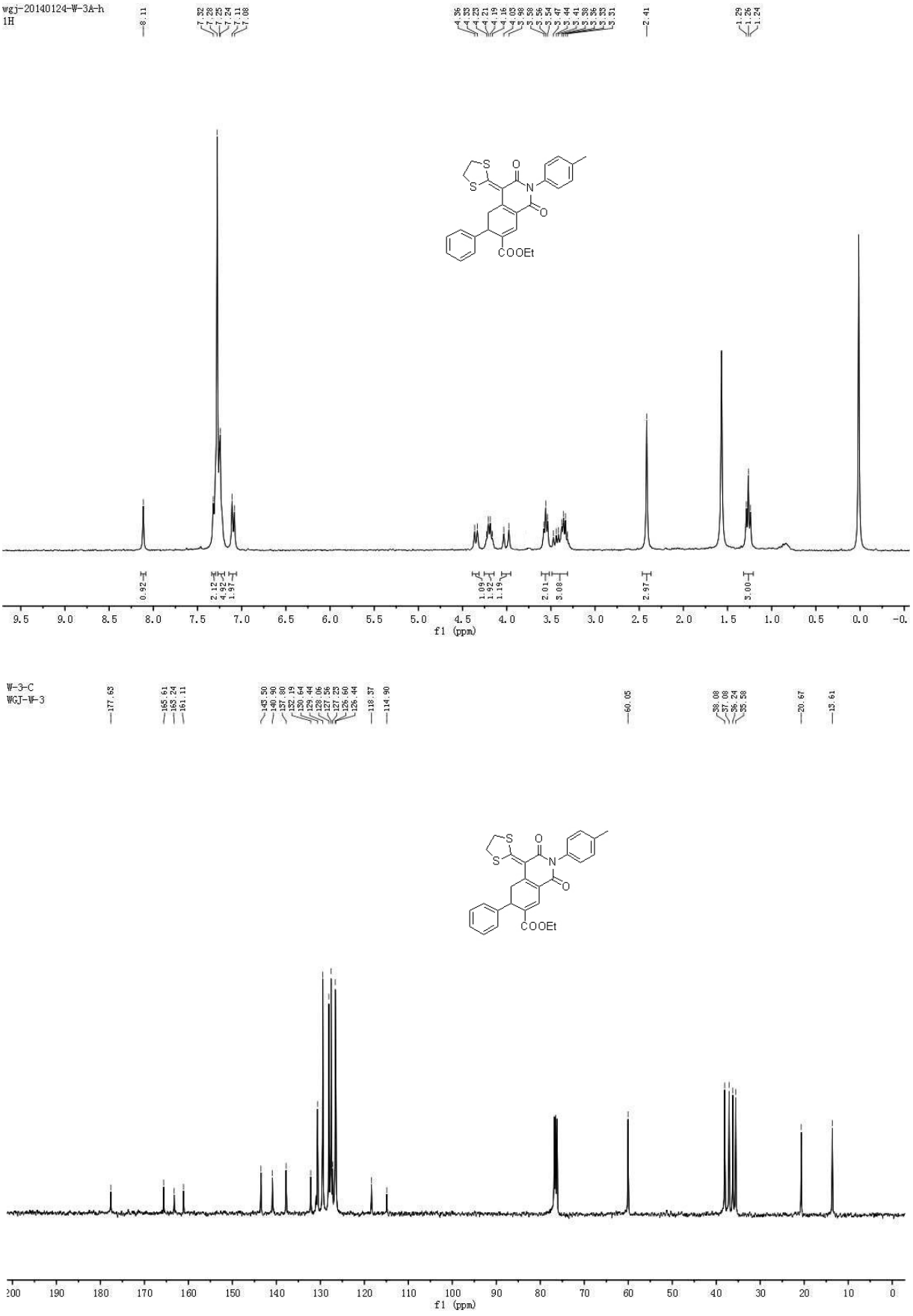


Figure 16. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4p**.

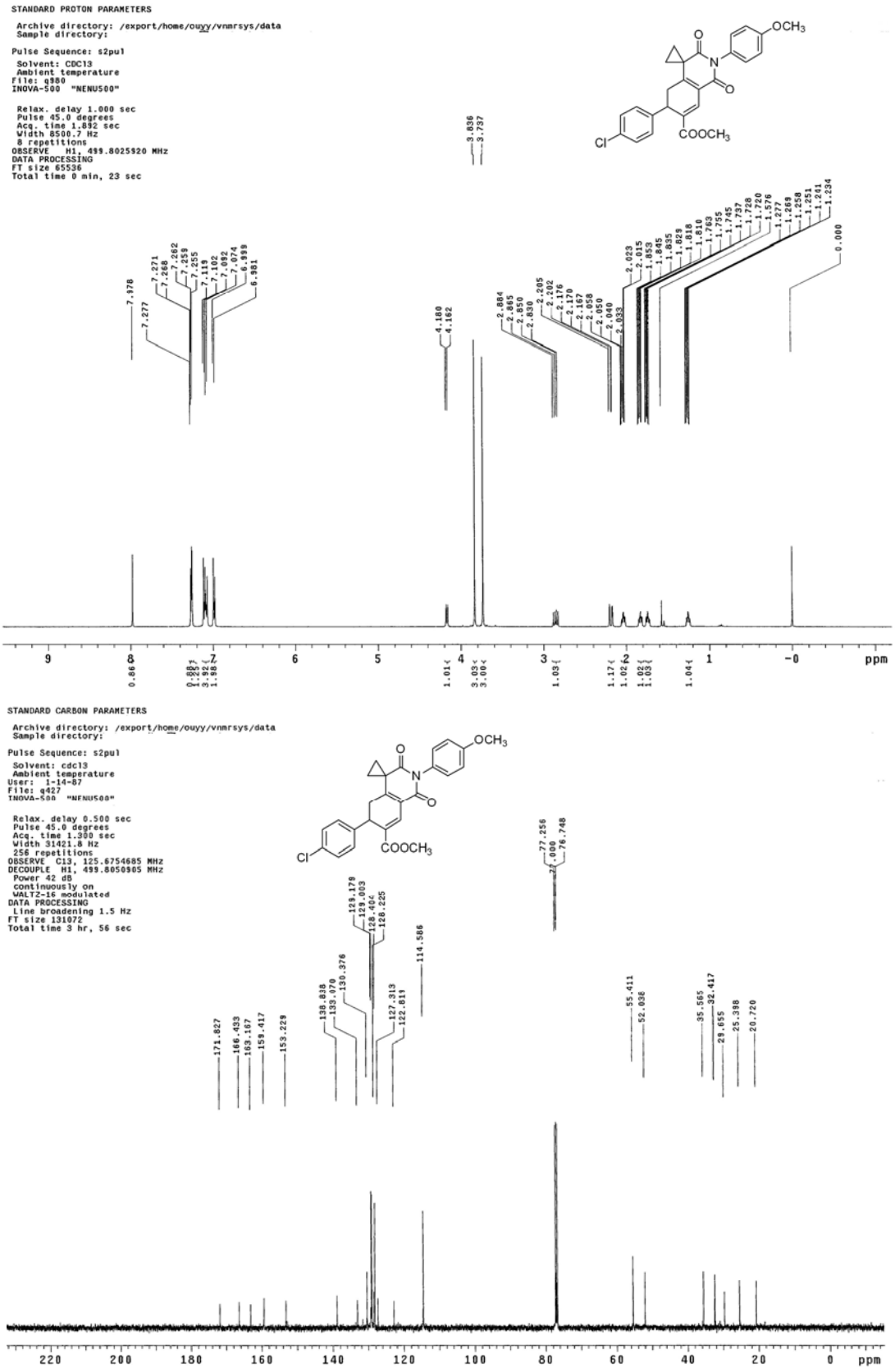


Figure 17. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4q**.

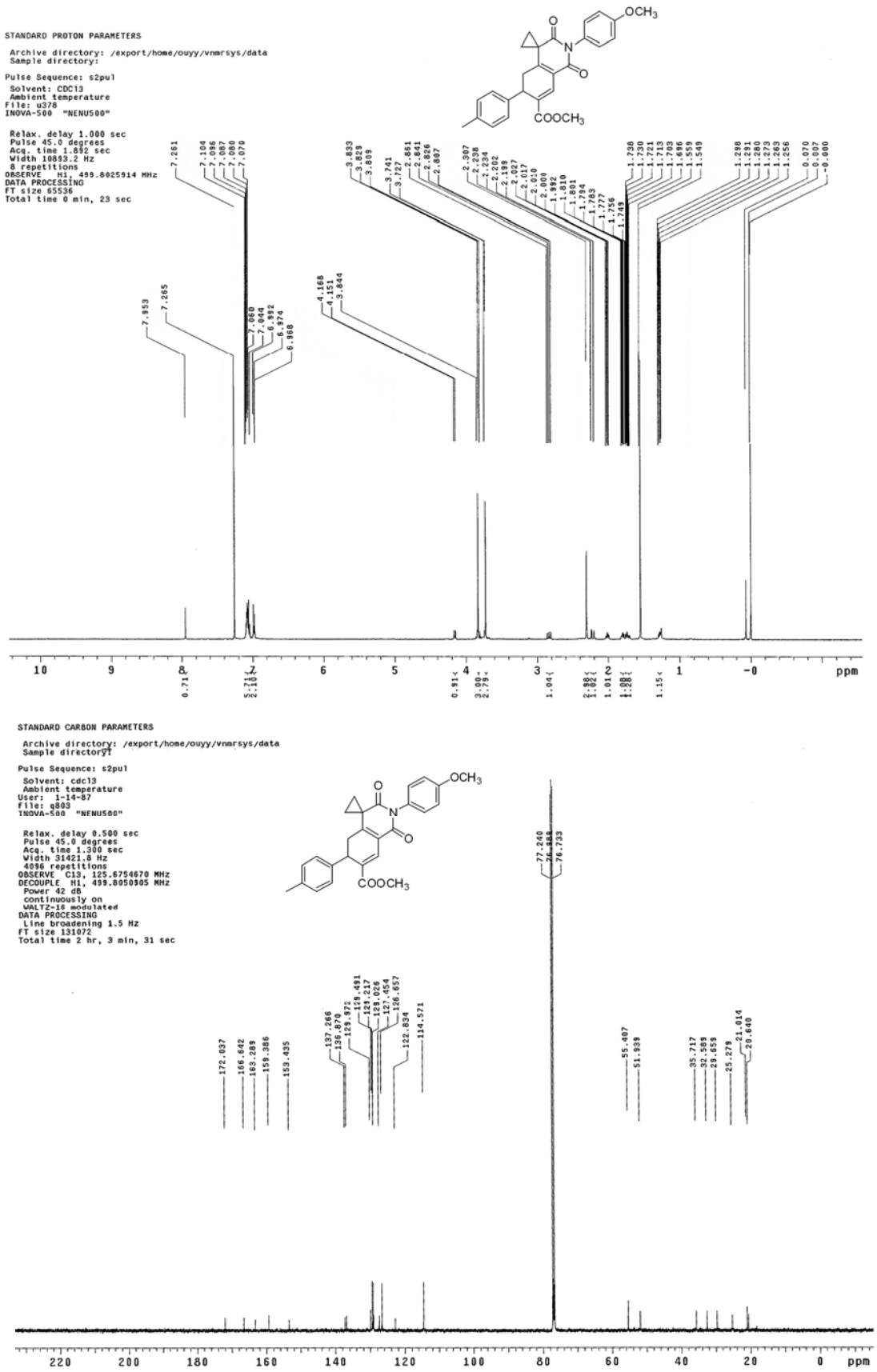


Figure 18. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4r**.

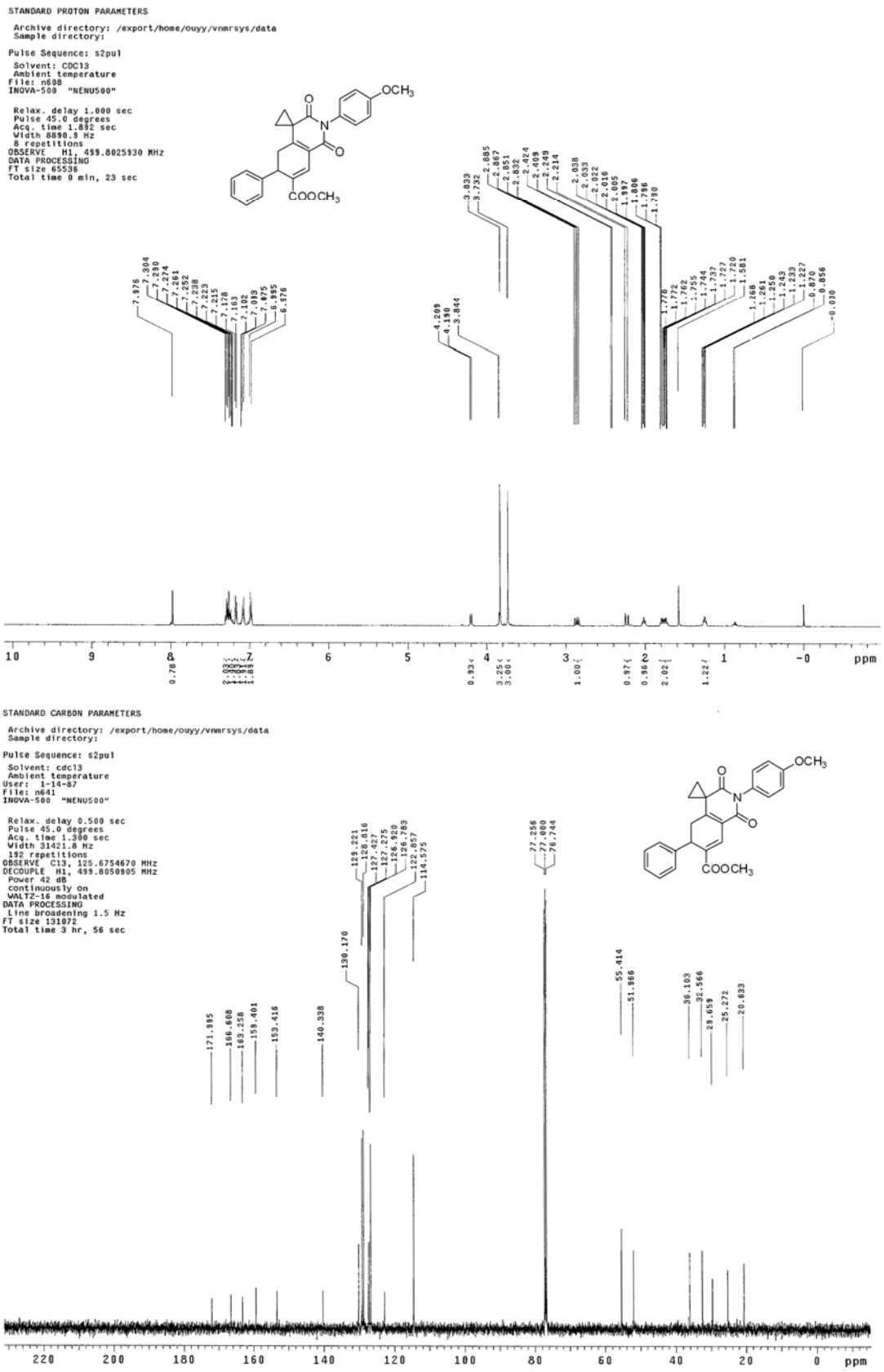


Figure 19. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4s**.

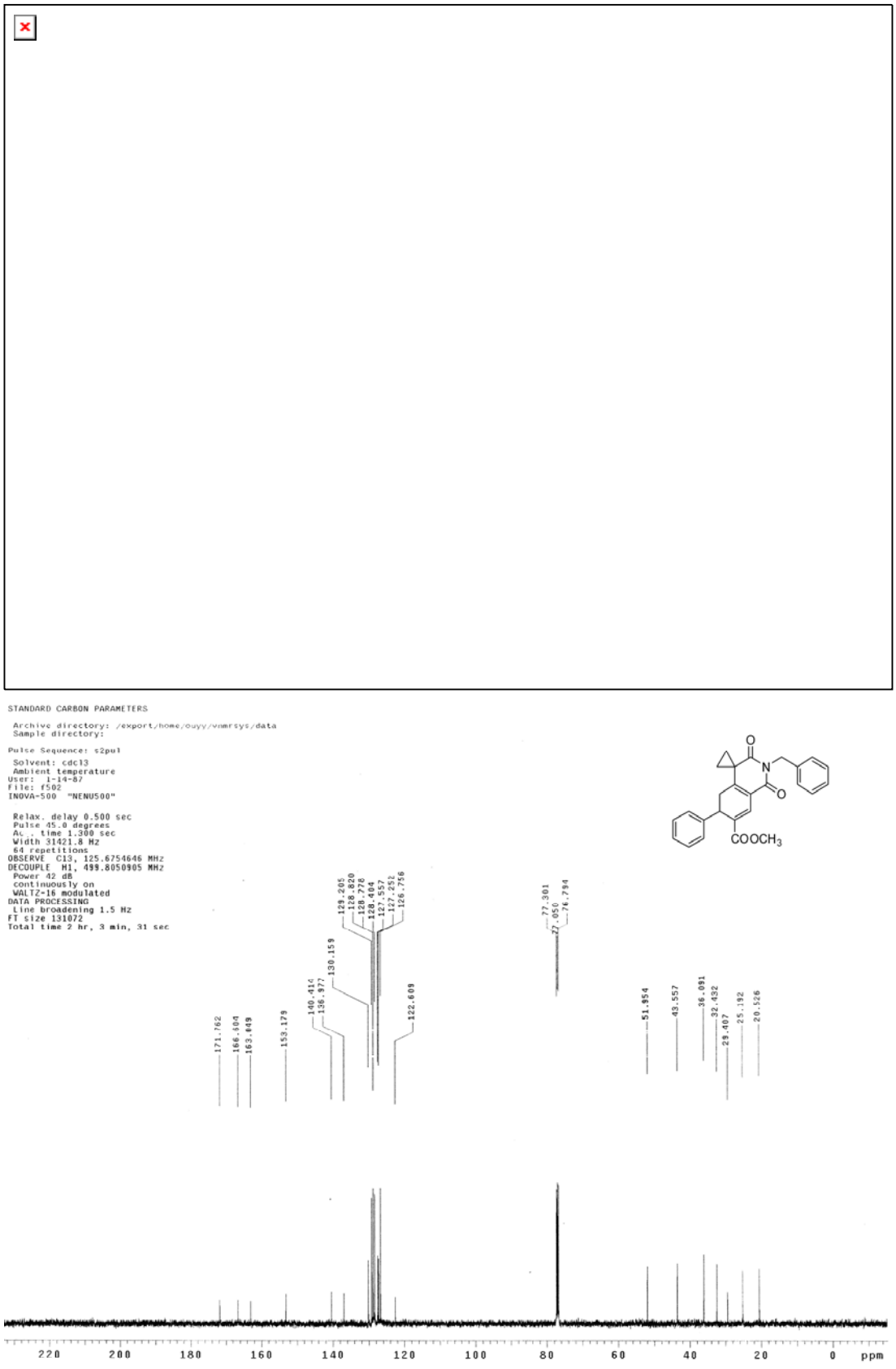


Figure 20. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4t**.

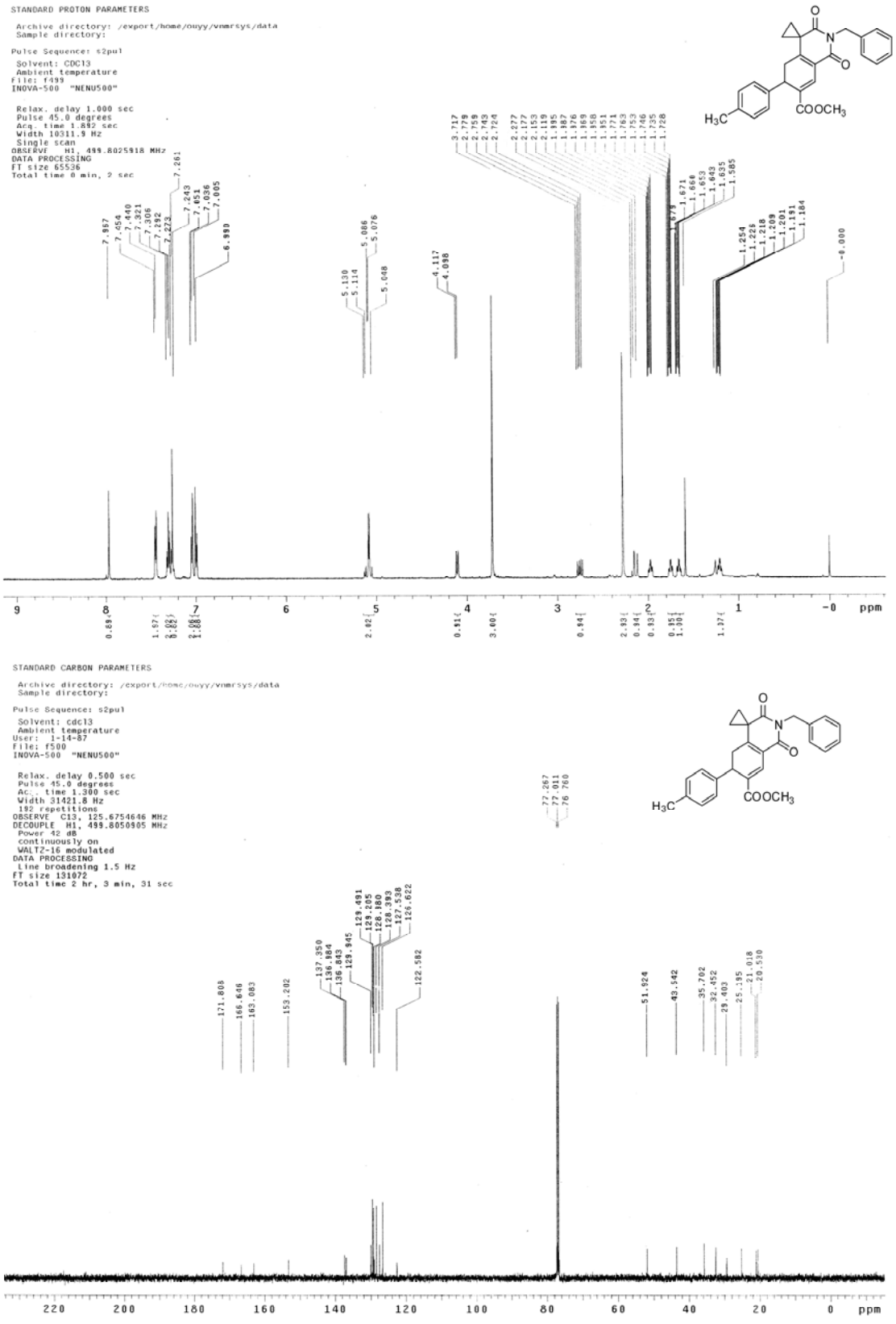


Figure 21. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4u**.

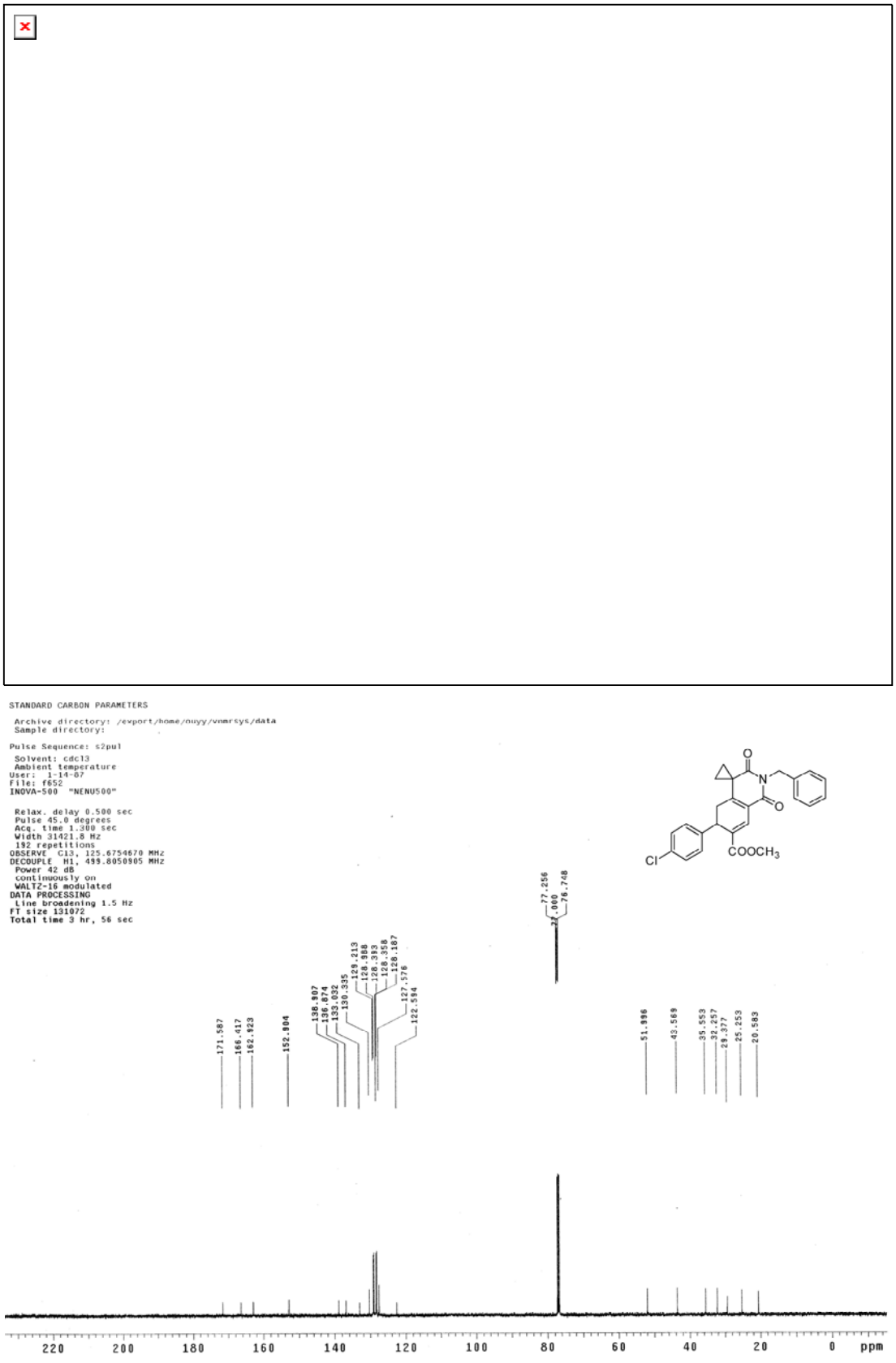


Figure 22. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4v**.

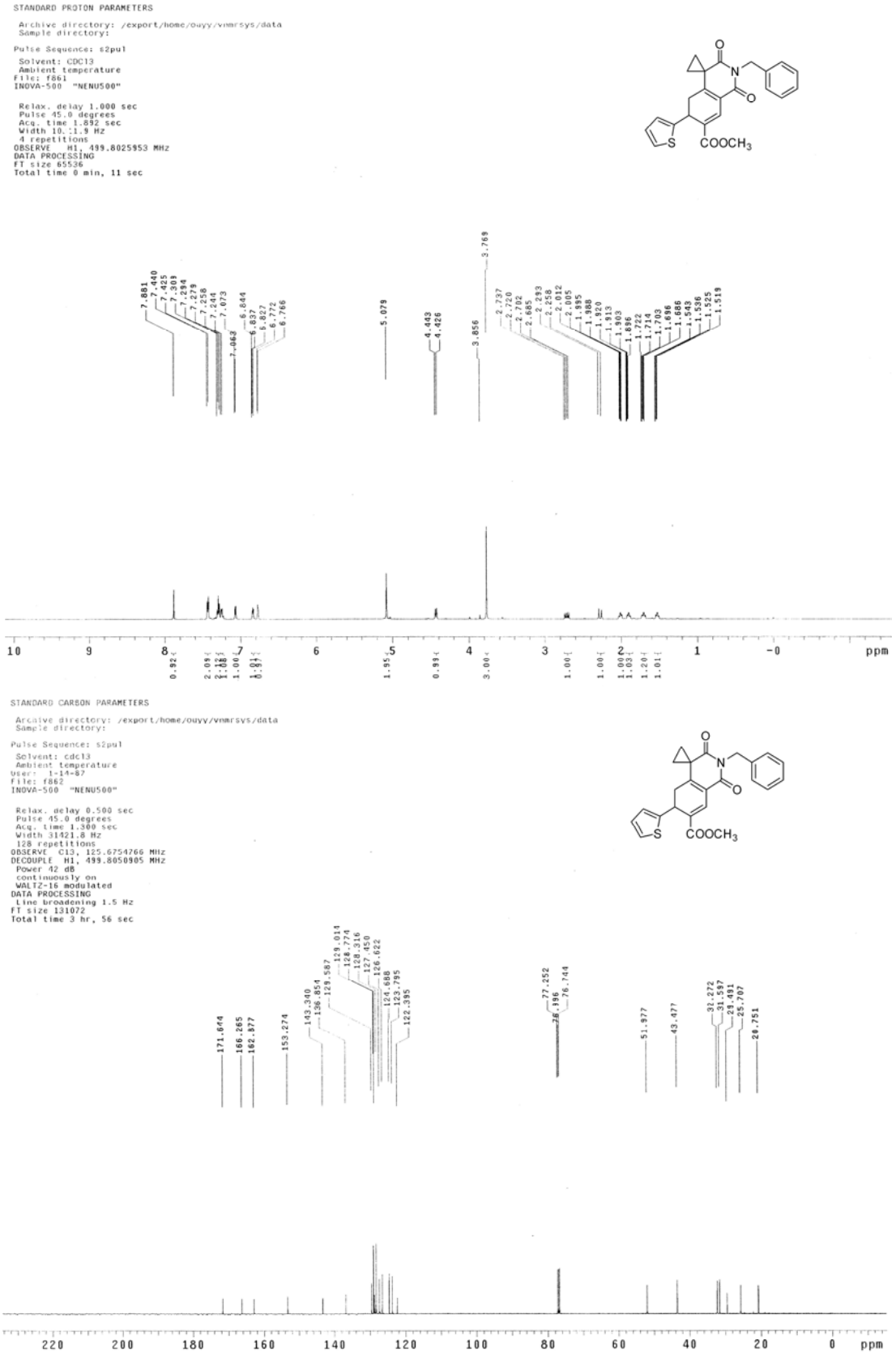


Figure 23. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4w**.

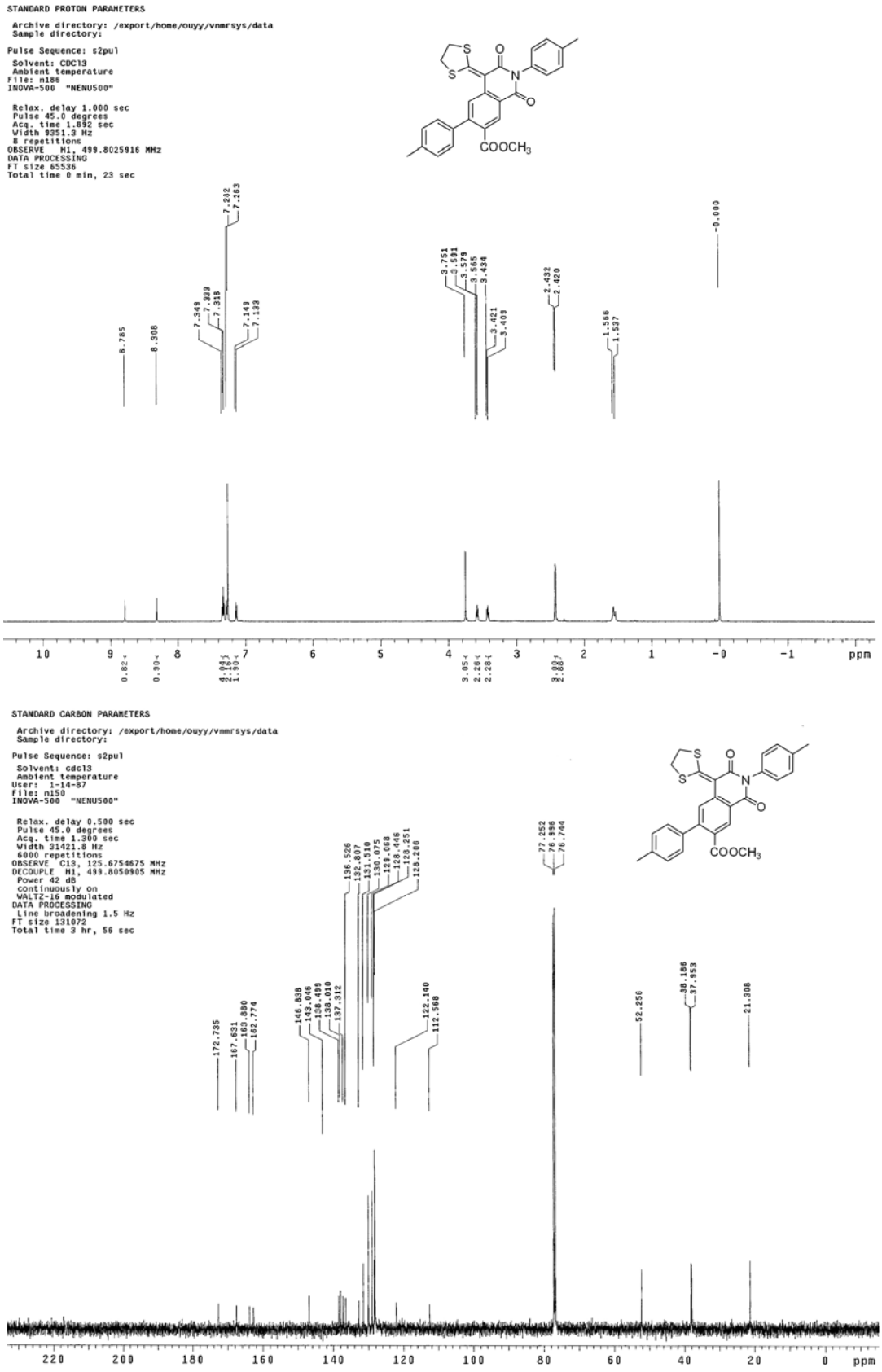


Figure 24. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6a**.

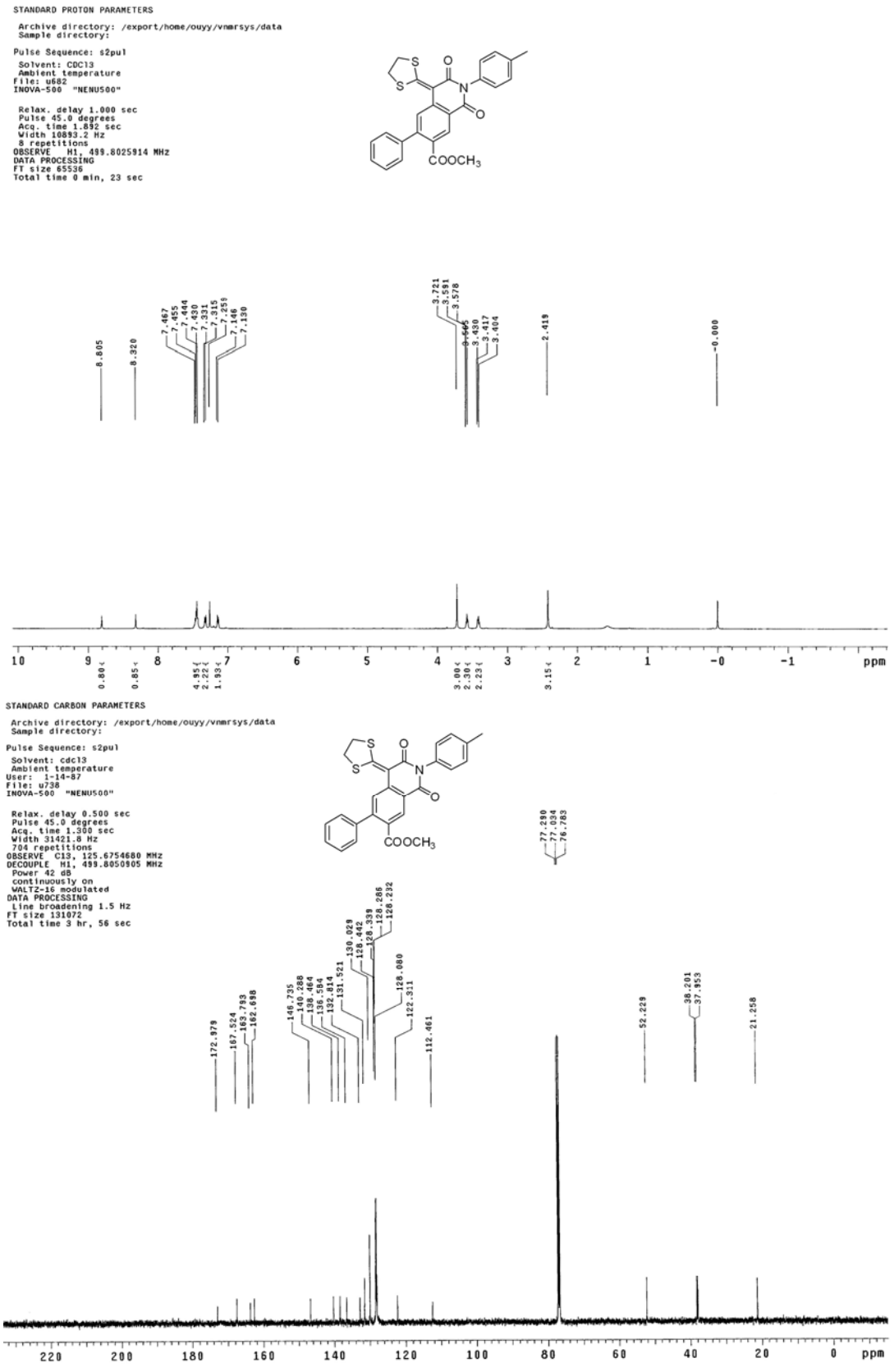


Figure 25. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6b**.

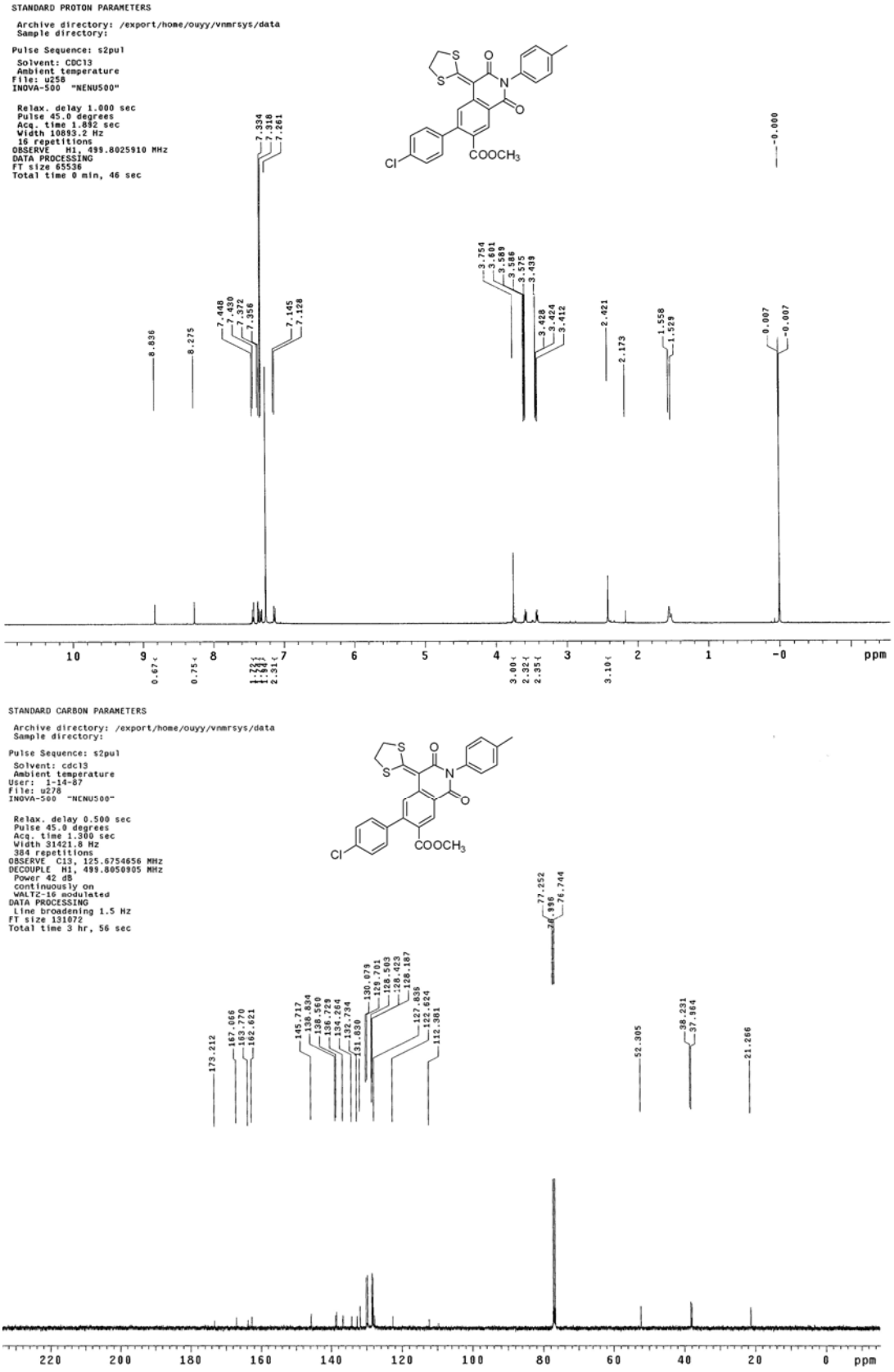


Figure 26. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6c**.

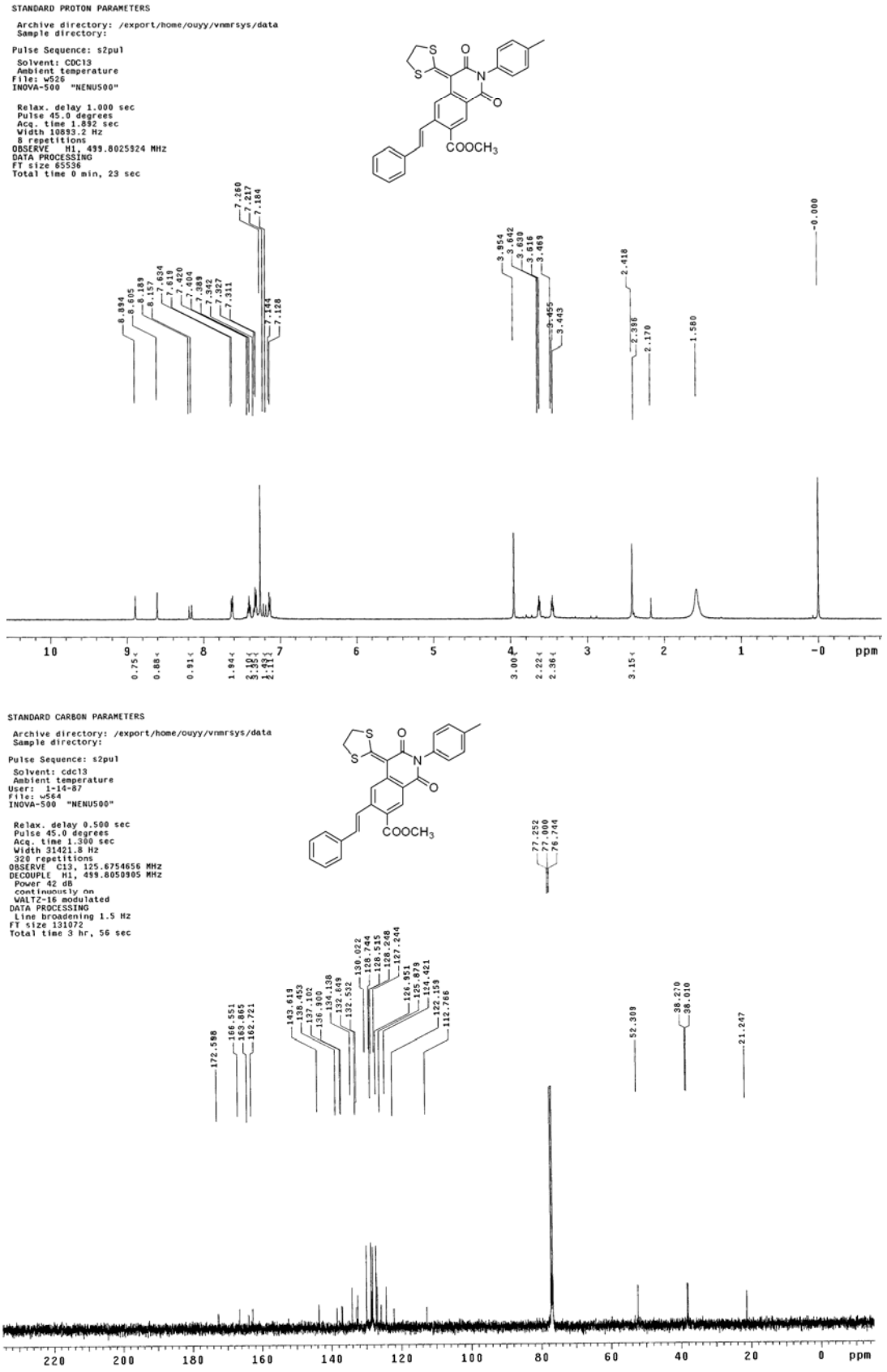


Figure 27. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6d**.

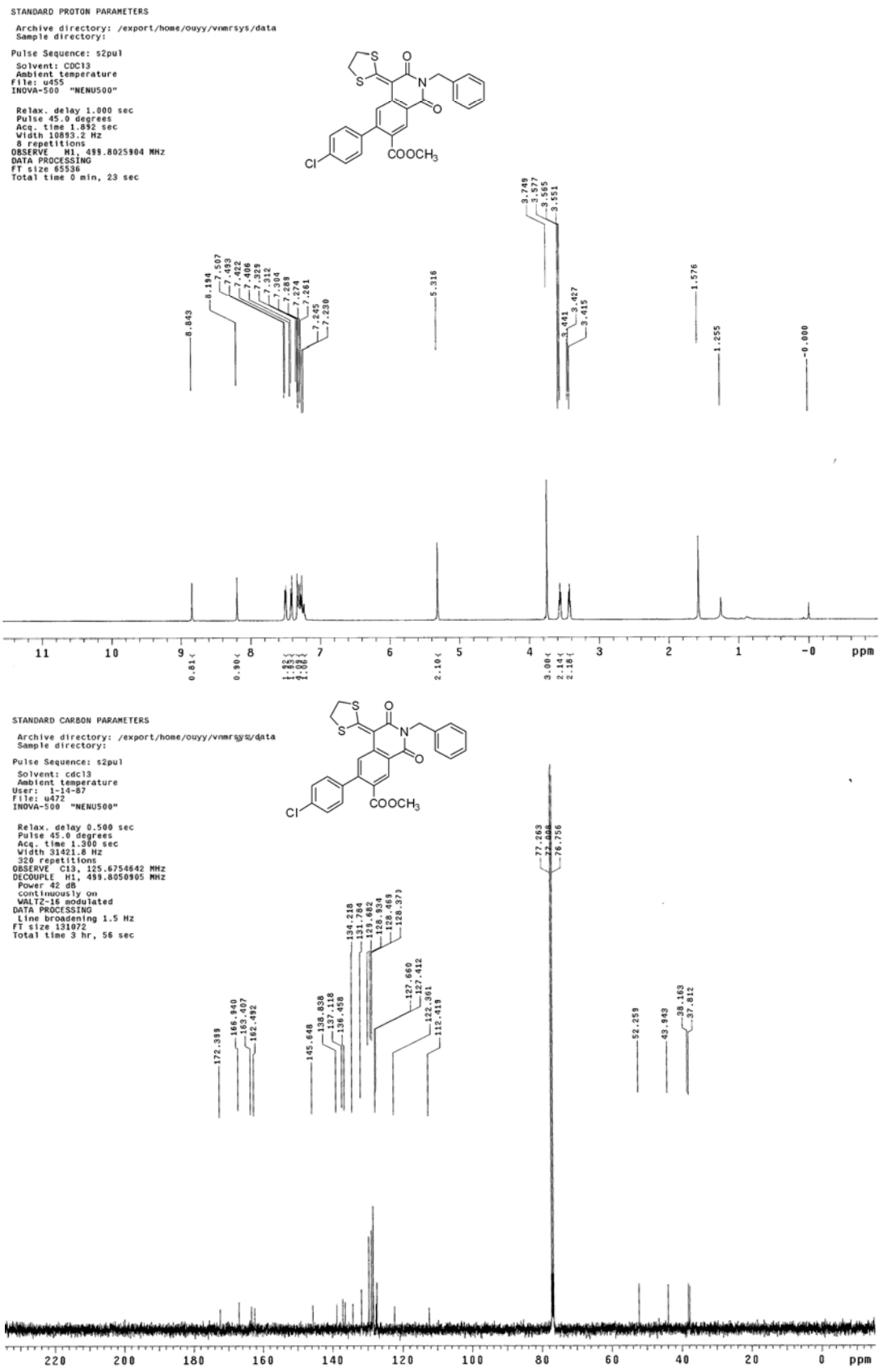


Figure 28. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6e**.

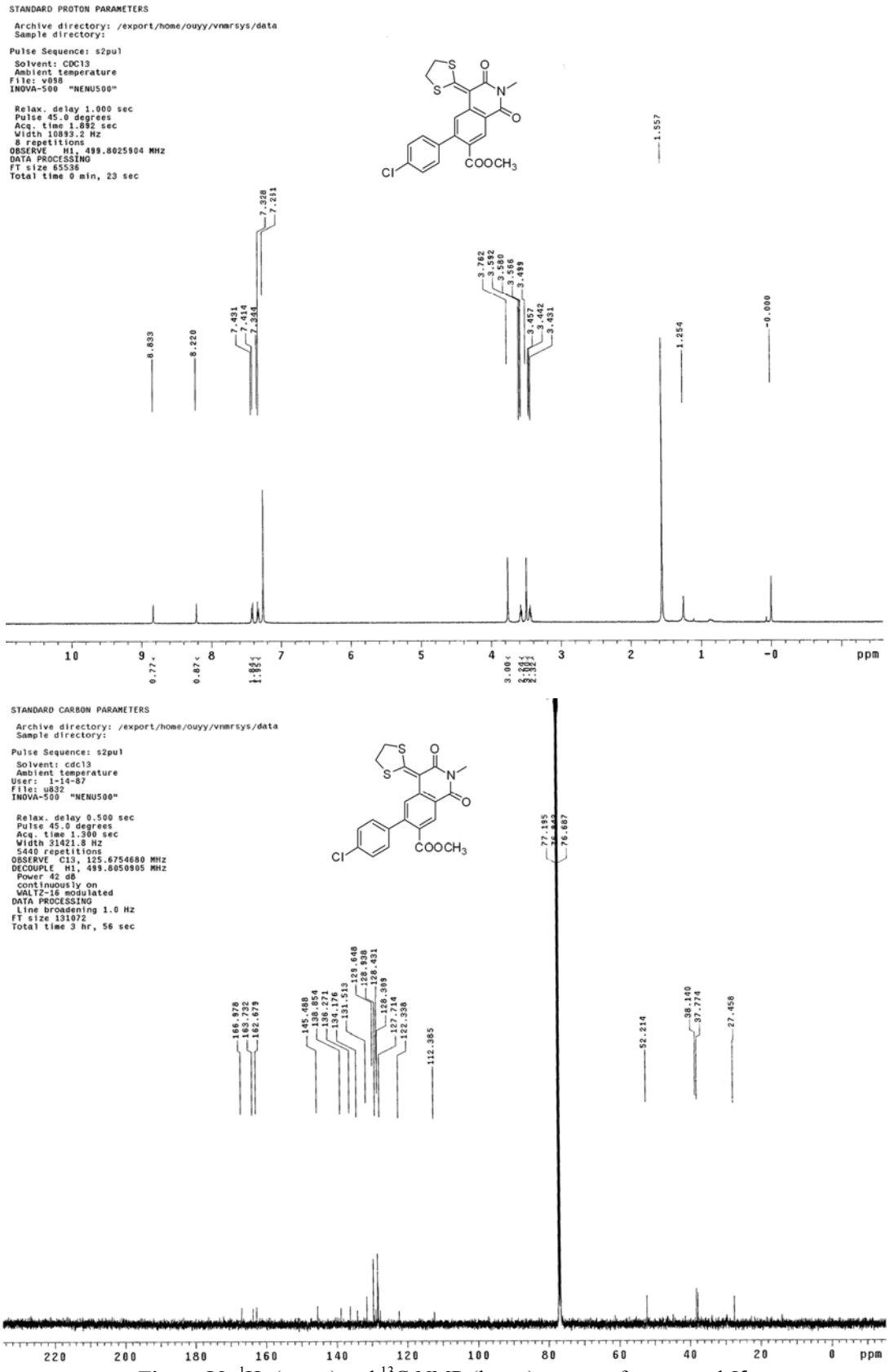


Figure 29. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6f**.

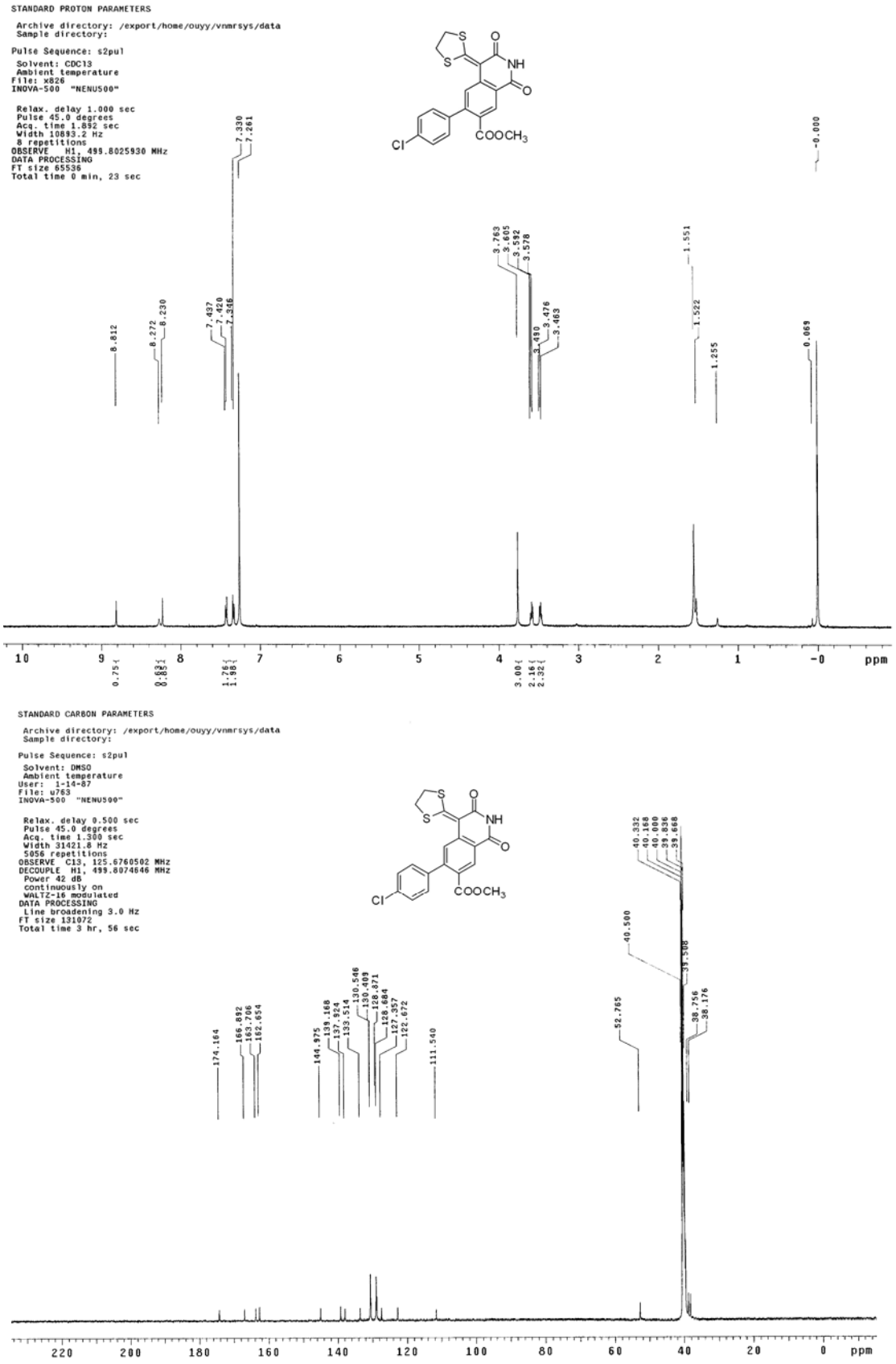


Figure 30. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6g**.

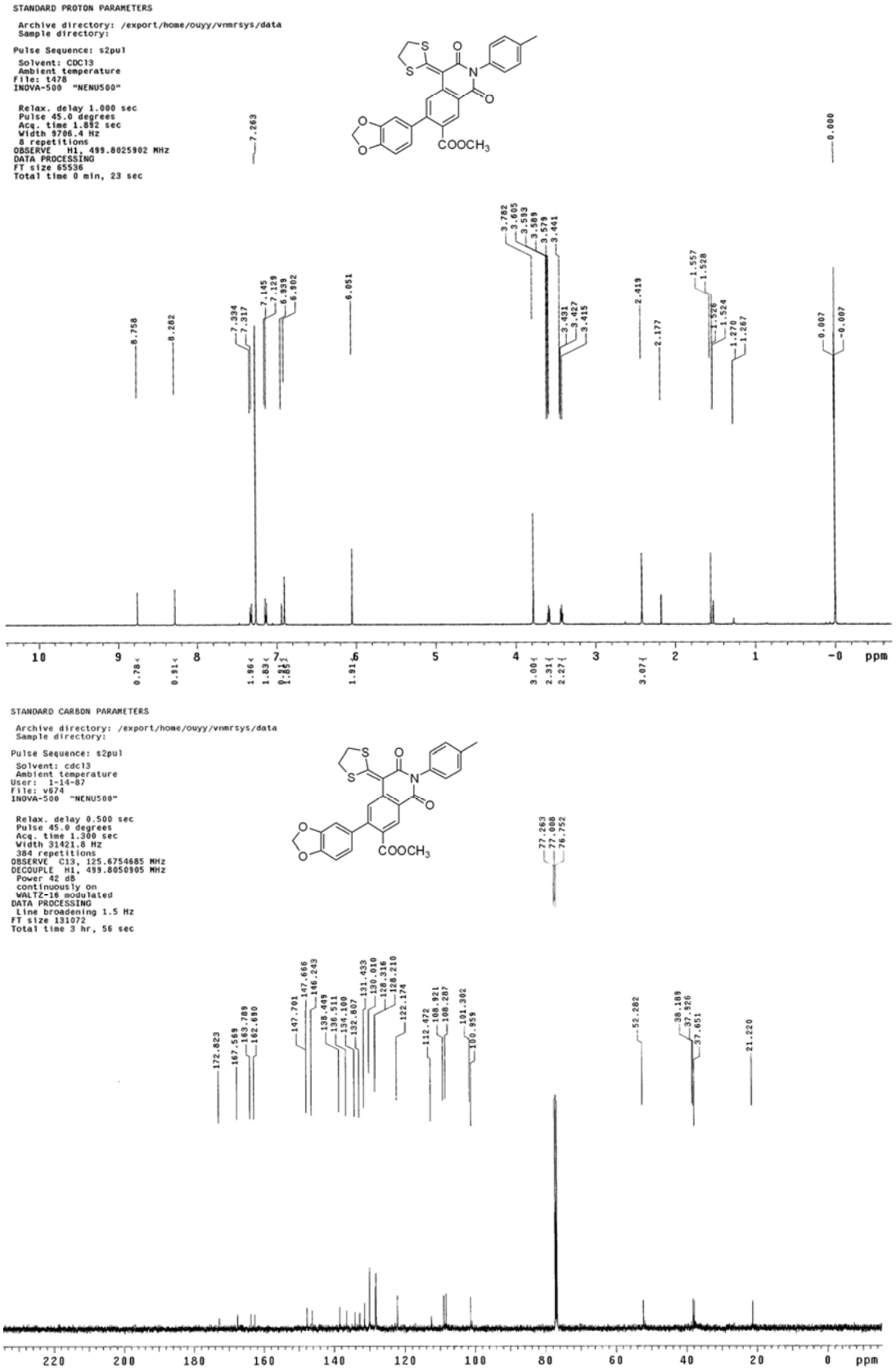


Figure 31. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6h**.

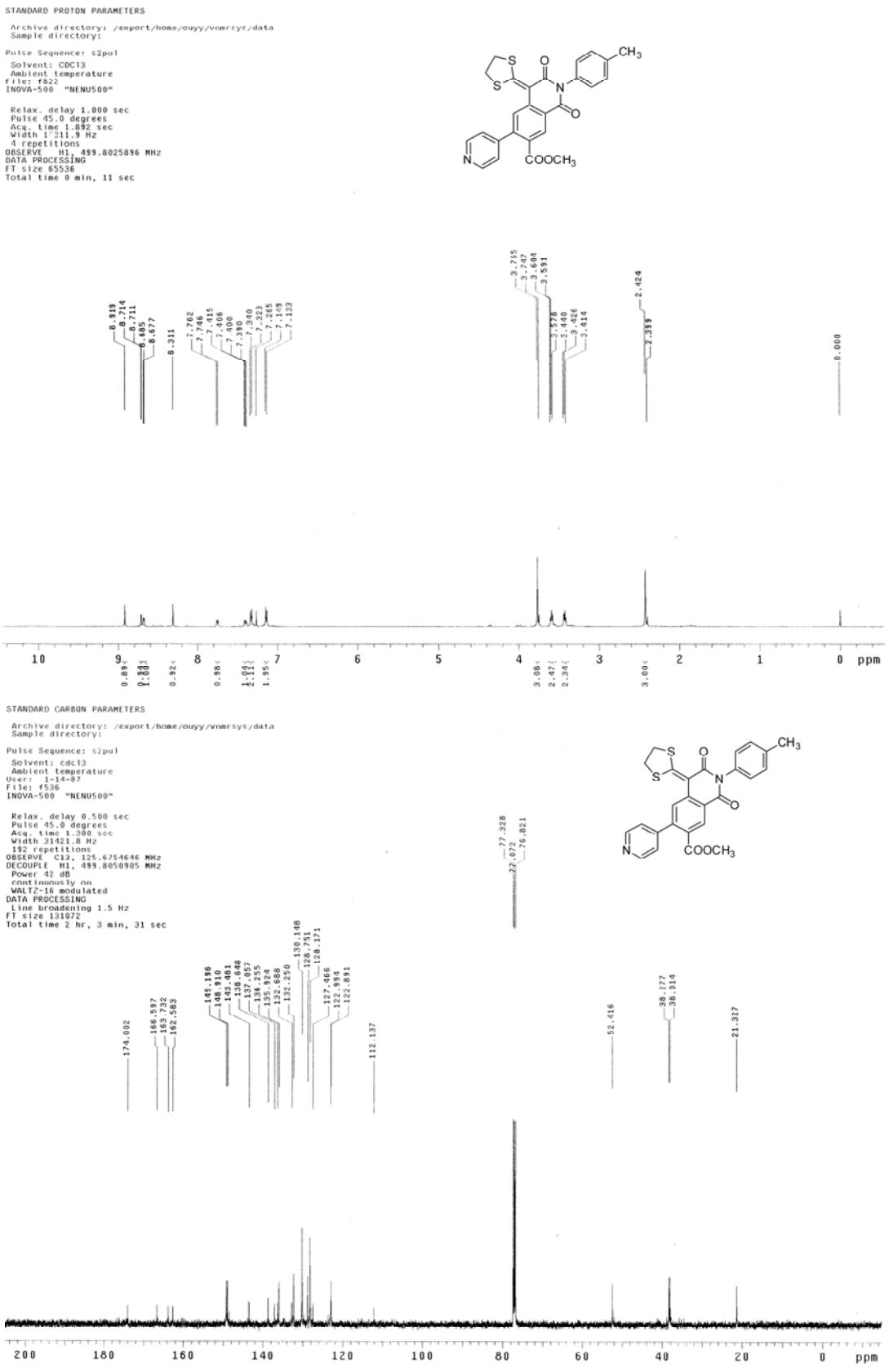


Figure 32. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6i**.

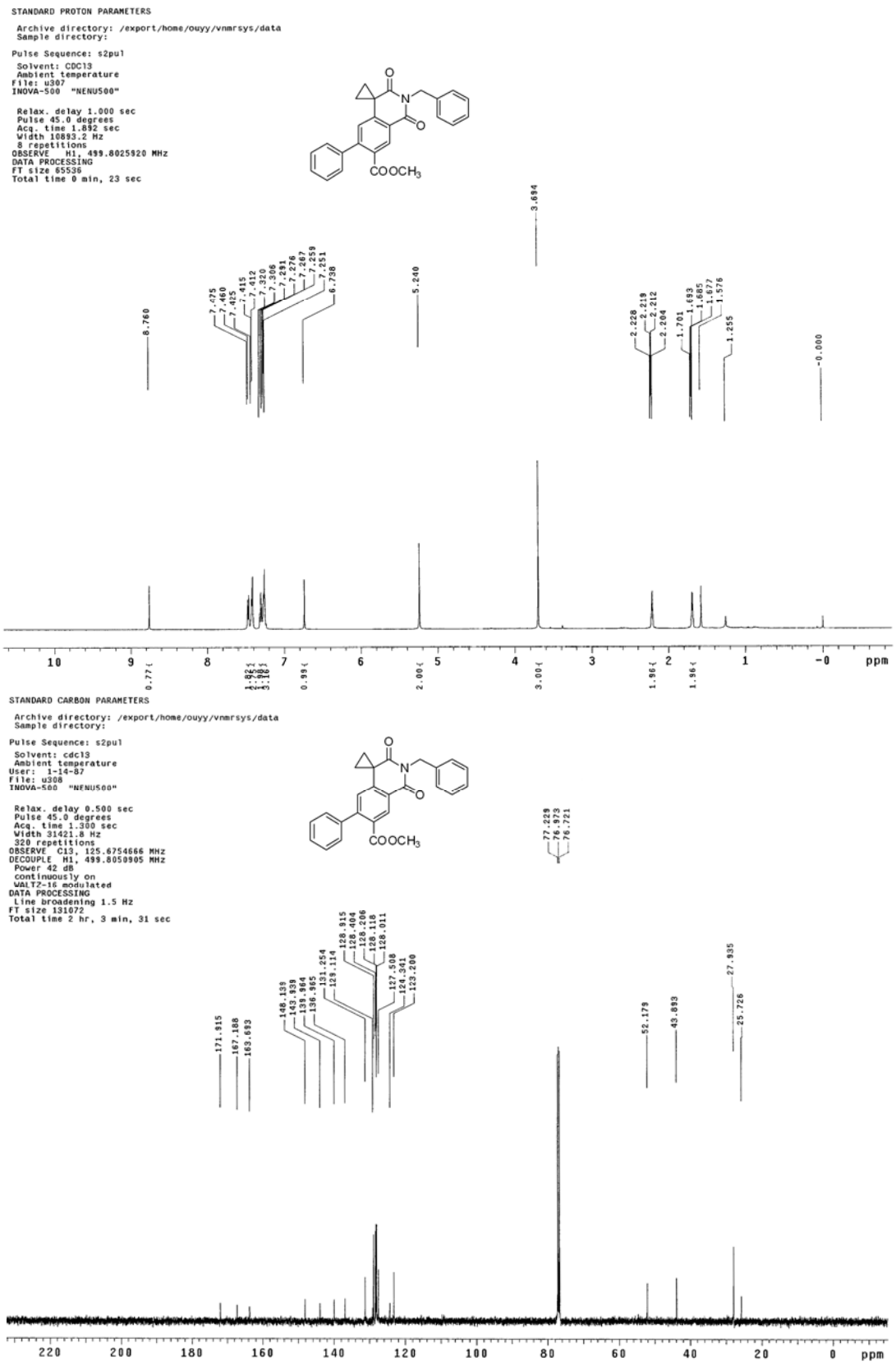


Figure 33. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6j.**

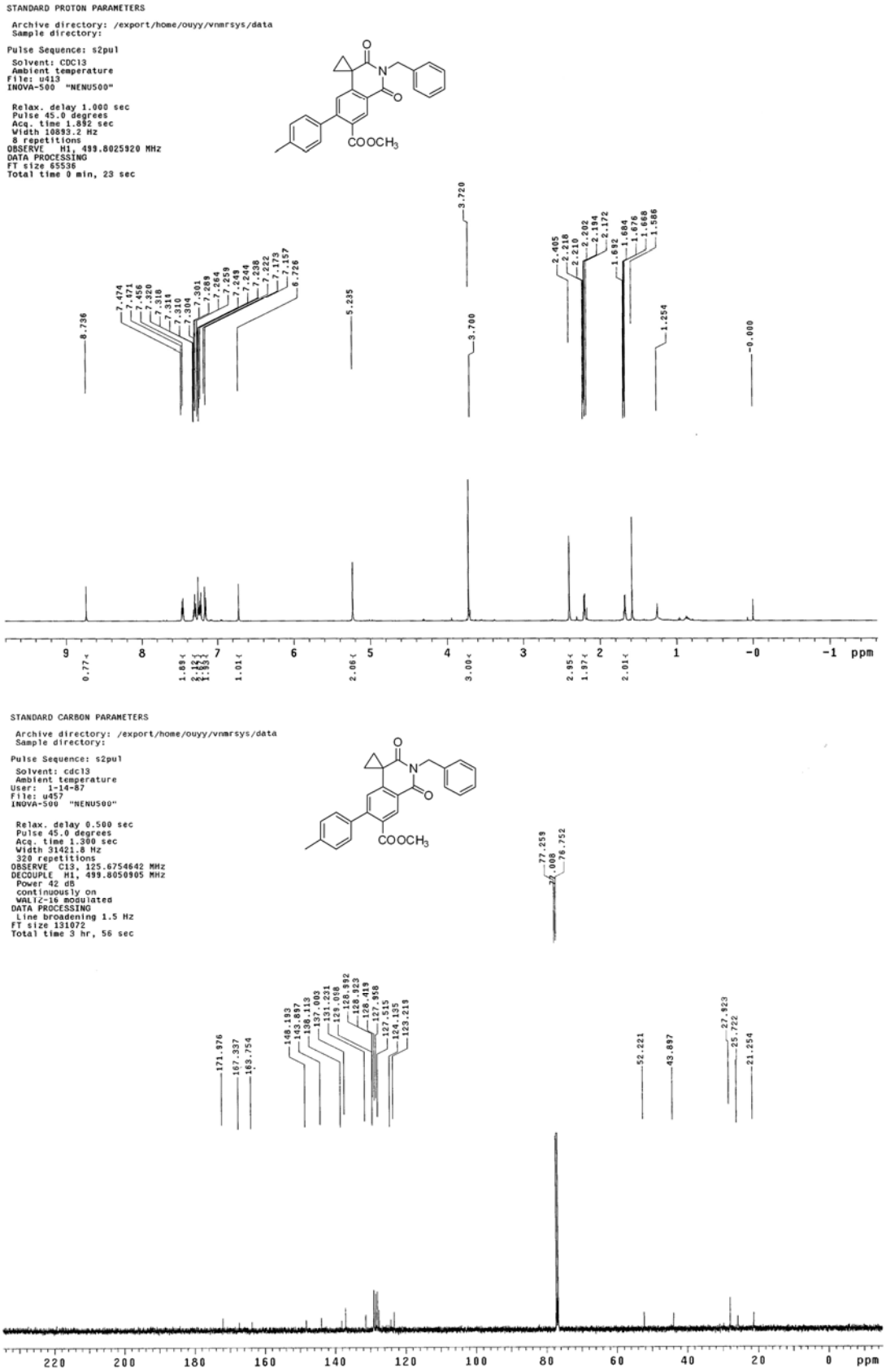


Figure 34. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6k**.

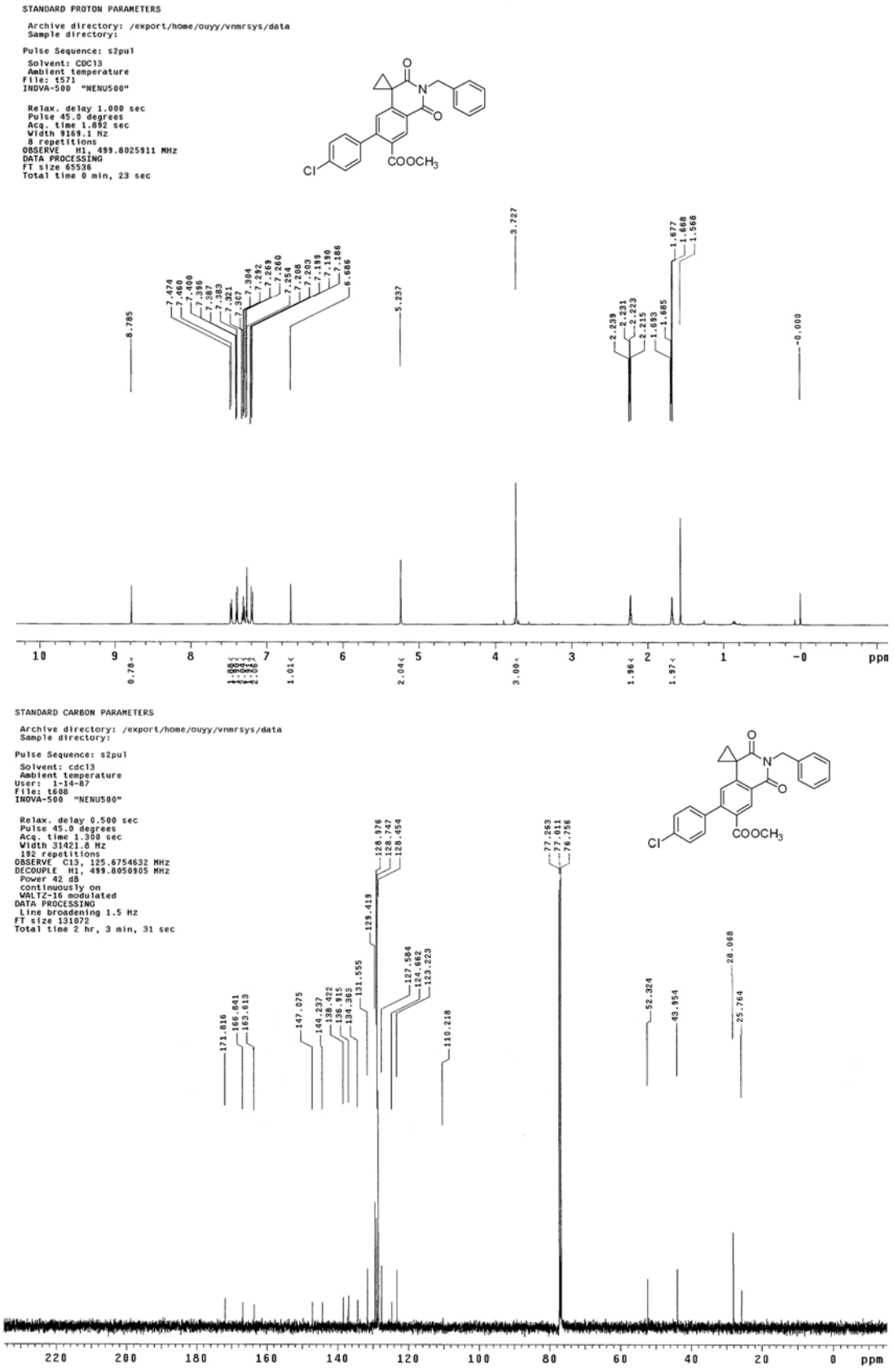


Figure 35. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **6l**.