Supporting Information

Tandem [5 + 1] Annulation-Isocyanide Cyclization: Efficient Synthesis of Hydroindolones

He Wang, Yu-Long Zhao, Chuan-Qing Ren, Aboubacar Diallo, and Qun Liu**

Department of Chemistry, Northeast Normal University, Changchun, 130024,

People's Republic of China

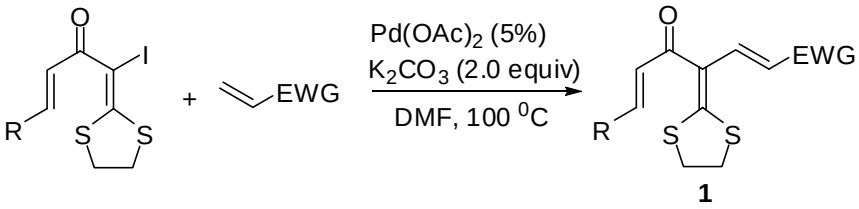
e-mail: zhaoyl351@nenu.edu.cn

Table of contents

I. General Information

All reagents were commercial and were used without further purification. Chromatography was carried on flash 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 600 MHz in $CDCl_3$ and the ^{13}C NMR spectra were recorded at 125 or 150 MHz in $CDCl_3$ 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 **2m** with dimension 0.17 x 0.15 x 0.13 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° < θ < 27.48°. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 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 1 (1a as Example):



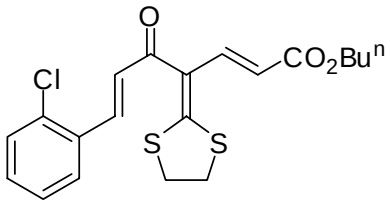
1

entry	R	EWG	time (min)	product	yield (%)[a]
1	4-ClC_6H_4	CO_2Bu^n	35	**1a**	84
2	C_6H_5	CO_2Bu^n	40	**1b**	80
3	4-$MeOC_6H_4$	CO_2Bu^n	50	**1c**	75
4	2-ClC_6H_4	CO_2Bu^n	45	**1d**	72
5	4-BrC_6H_4	CO_2Bu^n	40	**1e**	86
6	4-$NO_2C_6H_4$	CO_2Bu^n	50	**1f**	70
7	4-MeC_6H_4	CO_2Bu^n	40	**1g**	83
8	3,4-$O_2CH_2C_6H_3$	CO_2Bu^n	50	**1h**	71
9	2-furyl	CO_2Bu^n	50	**1i**	82
10	2-thienyl	CO_2Bu^n	50	**1j**	84
11	PhCH=CH	CO_2Bu^n	50	**1k**	65
12	4-ClC_6H_4	CO_2Et	45	**1l**	85
13	4-ClC_6H_4	CN	55	**1m**	76

[a] Isolated yield.

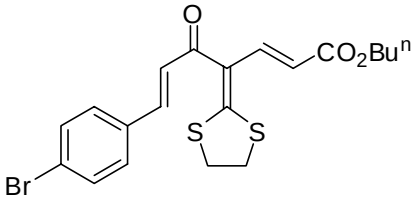
To a solution of (*E*)-4-(4-chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-1-iodobut-3-en-2-one (1.0 mmol, 408 mg), butyl acrylate (2.0 mmol, 0.29 mL) and K_2CO_3 (2.0 mmol, 276 mg) in DMF (5.0 mL) was added $Pd(OAc)_2$ (0.05 mmol, 11.2 mg). The reaction mixture was heated to 100 ^{0}C for 35 min. After completion of the reaction (monitored by TLC), the reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (3×10 mL). 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 chromatography (silica gel, petroleum ether/acetone = 10/1, V/V) to give **1a** (343 mg, 84%) as a yellow solid.

(2*E*,6*E*)-Butyl 7-(2-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxohepta-2,6-dienoate (1d):



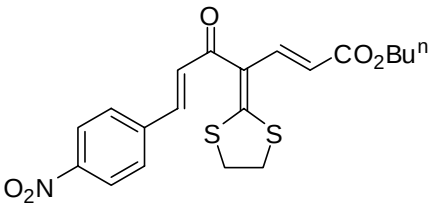
Yellow solid; m. p. 75-77 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.96 (t, *J* = 7.5 Hz, 3H), 1.43 (q, *J* = 7.5 Hz, 2H), 1.68 (t, *J* = 7.5 Hz, 2H), 3.46 (s, 4H), 4.20 (t, *J* = 6.5 Hz, 2H), 6.03 (d, *J* = 16.0 Hz, 1H), 7.13 (d, *J* = 15.5 Hz, 1H), 7.28-7.30 (m, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.62 (q, *J* = 7.00 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 1H), 8.12 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.7, 19.2, 30.7, 36.5, 38.9, 64.5, 120.9, 123.0, 126.2, 127.0, 127.8, 130.2, 130.9, 133.3, 135.4, 139.3, 140.3, 166.9, 169.8, 185.5. HRMS (ESI-TOF) calcd for $C_{20}H_{22}ClO_3S_2^+$ ($[M + H]^+$): 409.0693, found: 409.0690.

(2*E*,6*E*)-Butyl 7-(4-bromophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxohepta-2,6-dienoate (1e):



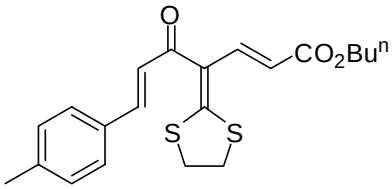
Yellow solid; m. p. 108-110 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.96 (t, *J* = 7.5 Hz, 3H), 1.43 (q, *J* = 7.5 Hz, 2H), 1.68 (t, *J* = 7.5 Hz, 2H), 3.46 (s, 4H), 4.21 (t, *J* = 6.5 Hz, 2H), 6.01 (d, *J* = 16.0 Hz, 1H), 7.12 (d, *J* = 15.0 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 15.5 Hz, 1H), 7.81 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 19.2, 30.7, 36.5, 38.9, 64.6, 120.8, 123.1, 124.3, 124.5, 129.8 (2C), 132.1 (2C), 133.9, 140.2, 142.2, 166.9, 169.4, 185.7.

(2*E*,6*E*)-Butyl 4-(1,3-dithiolan-2-ylidene)-7-(4-nitrophenyl)-5-oxohepta-2,6-dienoate (1f):



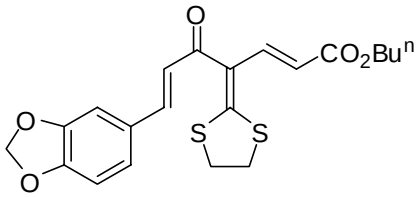
Yellow solid; m. p. 151-152 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.96 (t, *J* = 7.5 Hz, 3H), 1.43 (q, *J* = 7.5 Hz, 2H), 1.68 (q, *J* = 7.5 Hz, 2H), 3.49 (s, 4H), 4.22 (t, *J* = 6.5 Hz, 2H), 6.02 (d, *J* = 16.0 Hz, 1H), 7.25 (d, *J* = 16.0 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.7, 19.2, 30.7, 36.6, 39.0, 64.6, 121.2, 122.8, 124.1 (2C), 127.6, 128.8 (2C), 140.1, 140.2, 141.2, 148.3, 166.8, 171.3, 184.7.

(2*E*,6*E*)-Butyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-*p*-tolylhepta-2,6-dienoate (1g):



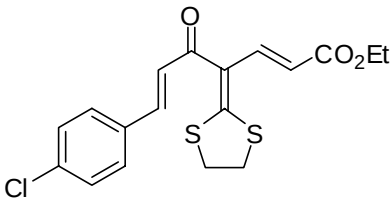
Yellow solid; m. p. 92-94 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.96 (t, *J* = 7.5 Hz, 3H), 1.42 (q, *J* = 7.5 Hz, 2H), 1.68 (t, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 3.44 (s, 4H), 4.20 (t, *J* = 6.5 Hz, 2H), 6.01 (d, *J* = 16.0 Hz, 1H), 7.09 (d, *J* = 16.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 16.0 Hz, 1H), 7.81 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.7, 19.2, 21.5, 30.7, 36.5, 38.8, 64.5, 120.5, 122.8, 123.4, 128.4 (2C), 129.6 (2C), 132.2, 140.3, 140.8, 143.9, 167.0, 168.2, 186.3; HRMS (ESI-TOF) calcd for $C_{21}H_{25}O_3S_2^+$ ([M + H]$^+$): 389.1239, found: 389.1250.

(2*E*,6*E*)-Butyl7-(benzo[d][1,3]dioxol-5-yl)-4-(1,3-dithiolan-2-ylidene)-5-oxohepta-2,6-dienoate (1h):



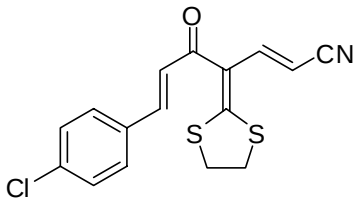
Yellow solid; m. p. 107-109 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.96 (t, *J* = 7.5 Hz, 3H), 1.43 (q, *J* = 7.5 Hz, 2H), 1.68 (t, *J* = 7.0 Hz, 2H), 3.44 (s, 4H), 4.21 (t, *J* = 6.5 Hz, 2H), 6.01 (s, 2H), 6.02 (d, *J* = 16.0 Hz, 1H), 6.82 (q, *J* = 6.0 Hz, 1H), 6.95 (d, *J* = 15.0 Hz, 1H), 7.05 (d, *J* = 6.0 Hz, 1H), 7.06 (s, 1H), 7.64 (d, *J* = 15.0 Hz, 1H), 7.80 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.7, 19.2, 30.7, 36.5, 38.8, 64.5, 101.6, 106.7, 108.6, 120.5, 121.9, 123.5, 125.1, 129.5, 140.4, 143.7, 148.3, 149.7, 167.0, 168.0, 186.2.

(2*E*,6*E*)-Ethyl 7-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxohepta-2,6-dienoate (1l):



Yellow solid; m. p. 113-115 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.33 (t, *J* = 7.0 Hz, 3H), 3.46 (s, 4H), 4.26 (q, *J* = 7.5 Hz, 2H), 6.01 (d, *J* = 15.5 Hz, 1H), 7.09 (d, *J* = 15.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.81 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.3, 36.6, 38.9, 60.6, 120.8, 123.1, 124.2, 129.1 (2C), 129.6 (2C), 133.5, 136.1, 140.3, 142.2, 166.9, 169.3, 185.7; HRMS (ESI-TOF) calcd for $C_{18}H_{18}ClO_3S_2^+$ ($[M + H]^+$): 381.0380, found: 381.0379.

(2*E*,6*E*)-7-(4-Chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxohepta-2,6-dienenitrile (1m):

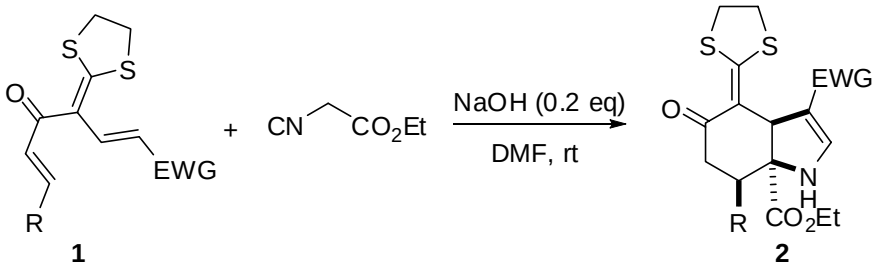


Yellow solid; m. p. 194-196 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.45 (s, 4H), 5.47 (d, *J* = 16.5 Hz, 1H), 7.04 (d, *J* = 16.0 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 15.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.8, 39.0, 98.2, 118.3, 122.8, 123.7, 127.3, 129.3 (2C), 129.6 (2C), 133.1, 136.6, 143.1, 146.0, 185.3; HRMS (ESI-TOF) calcd for $C_{16}H_{13}ClNOS_2^+$ ($[M + H]^+$): 334.0121, found: 334.0123.

Spectral data of compounds **1a-c** and **1i-k** match those previously reported.[1]

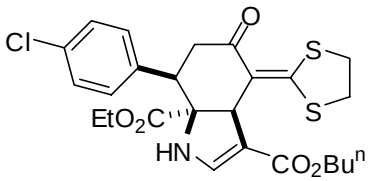
1. H. Yu, W. Jin, C. Sun, J. Chen, W. Du, S. He, Z. Yu, *Angew. Chem., Int. Ed.* **2010**, *49*, 5792

III. General Procedure for the Preparation of 1 (1a as Example):



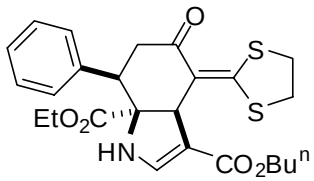
To a solution of 5-oxohepta-2,6-dienoate **1a** (1.0 mmol, 408 mg) and ethyl isocyanoacetate (1.2 mmol, 0.13 mL) in DMF (4.0 mL) was added NaOH (0.2 mmol, 8 mg) in one portion. The reaction mixture was stired for 18 min at room temperature. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into ice-water (45 mL) under stirring. The precipitated solid was collected by filtration, and dried in vacuo to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether/acetone = 5/1, V/V) to give **2a** (469 mg, 90 %) as a white solid.

3-Butyl 7a-ethyl 7-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2a):



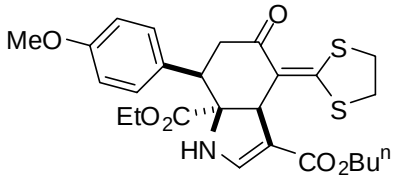
White solid; m. p. 222-224 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.92 (t, J = 7.5 Hz, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.32-1.38 (m, 2H), 1.53-1.59 (m, 2H), 2.45 (d, J = 13.5 Hz, 1H), 3.04 (t, J = 14.5 Hz, 1H), 3.29-3.34 (m, 1H), 3.40-3.56 (m, 4H), 3.96 (tt, J = 14.0, 7.0 Hz, 1H), 4.06 (tt, J = 13.5, 7.0 Hz, 1H), 4.17 (qq, J = 14.0, 7.0 Hz, 1H), 4.28 (qq, J = 14.0, 7.5 Hz, 1H), 4.42 (s, 1H), 4.90 (s, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 30.9, 36.1, 39.0, 39.3, 46.2, 52.8, 62.1, 63.3, 73.7, 104.6, 119.4, 128.7 (2C), 129.5 (2C), 133.8, 135.6, 148.0, 164.5, 164.7, 173.2, 194.9; HRMS (ESI-TOF) calcd for $C_{25}H_{29}ClNO_5S_2^+$ ($[M + H]^+$): 522.1170, found: 522.1176.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-phenyl-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2b):



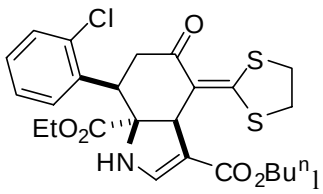
White solid; m. p. 210-212 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.91 (t, *J* = 7.5 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.30-1.38 (m, 2H), 1.53-1.58 (m, 2H), 2.50 (dd, *J* = 15.5, 13.5 Hz, 1H), 3.07 (t, *J* = 15.0 Hz, 1H), 3.30-3.34 (m, 1H), 3.43-3.56 (m, 4H), 3.97 (tt, *J* = 13.5, 6.5 Hz, 1H), 4.06 (tt, *J* = 13.0, 7.0 Hz, 1H), 4.18 (qq, *J* = 14.0, 7.0 Hz, 1H), 4.29 (qq, *J* = 14.5, 7.0 Hz, 1H), 4.48 (s, 1H), 4.90 (s, 1H), 7.06 (d, *J* = 6.5 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 6.0 Hz, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 31.0, 36.0, 39.0, 39.3, 46.7, 52.7, 62.0, 63.2, 73.9, 104.1, 119.6, 127.8, 128.2 (2C), 128.6 (2C), 137.0, 148.0, 164.1, 164.9, 173.4, 195.3; HRMS (ESI-TOF) calcd for $C_{25}H_{30}NO_5S_2^+$ ($[M + H]^+$): 488.1559, found: 488.1571.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-7-(4-methoxyphenyl)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2c):



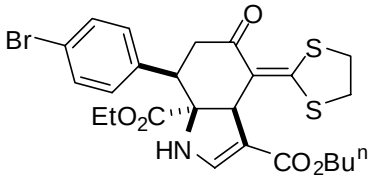
White solid; m. p. 194-196 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.32-1.38 (m, 2H), 1.53-1.59 (m, 2H), 2.46 (dd, *J* = 16.0, 14.0 Hz, 1H), 3.03 (t, *J* = 15.5 Hz, 1H), 3.29-3.33 (m, 1H), 3.42-3.54 (m, 4H), 3.79 (s, 3H), 3.96 (tt, *J* = 13.5, 6.5 Hz, 1H), 4.06 (tt, *J* = 13.5, 7.0 Hz, 1H), 4.18 (qq, *J* = 14.5, 7.0 Hz, 1H), 4.28 (qq, *J* = 14.5, 7.5 Hz, 1H), 4.48 (s, 1H), 4.87 (s, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 30.9, 36.0, 39.0, 39.6, 46.0, 52.5, 55.2, 61.9, 63.2, 74.0, 104.0, 114.0 (2C), 119.6, 128.9, 129.1 (2C), 148.0, 159.1, 163.9, 164.9, 173.5, 195.4; HRMS (ESI-TOF) calcd for $C_{26}H_{32}NO_6S_2^+$ ($[M + H]^+$): 518.1665, found: 518.1660.

3-Butyl 7a-ethyl 7-(2-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2d):



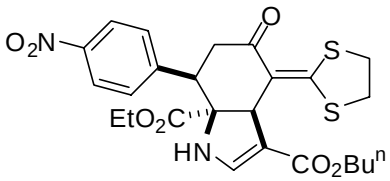
White solid; m. p. 172-174 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.91 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.34 (q, *J* = 7.5 Hz, 2H), 1.55 (*J* = 7.0 Hz, 2H), 2.36 (d, *J* = 15.0 Hz, 1H), 3.09 (t, *J* = 15.0 Hz, 1H), 3.34-3.54 (m, 4H), 3.98 (t, *J* = 7.0 Hz, 2H), 4.08 (tt, *J* = 17.5, 7.0 Hz, 2H), 4.29 (dd, *J* = 11.0, 7.0 Hz, 1H), 4.59 (s, 1H), 5.10 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.25-7.27 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 13.9, 19.2, 31.0, 36.0, 39.1, 40.4, 43.0, 52.4, 62.2, 63.2, 72.4, 104.6, 119.1, 126.6, 128.8, 129.8, 129.9, 134.4, 134.7, 147.5, 164.8, 164.9, 172.9, 194.5. HRMS (ESI-TOF) calcd for $C_{25}H_{29}ClNO_5S_2^+$ ($[M + H]^+$): 522.1170, found: 522.1181.

3-Butyl 7a-ethyl 7-(4-bromophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2e):



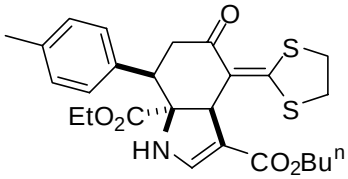
White solid; m. p. 192-194 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.91 (t, *J* = 7.5 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.31-1.36 (m, 2H), 1.53-1.57 (m, 2H), 2.44 (d, *J* = 14.0 Hz, 1H), 3.03 (t, *J* = 15.0 Hz, 1H), 3.32 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.40-3.53 (m, 4H), 3.96 (tt, *J* = 13.0, 6.5 Hz, 1H), 4.05 (tt, *J* = 13.5, 6.5 Hz, 1H), 4.17 (tt, *J* = 18.0, 7.0 Hz, 1H), 4.28 (tt, *J* = 18.0, 7.5 Hz, 1H), 4.47 (s, 1H), 4.90 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 7.35 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 30.9, 36.0, 39.0, 39.2, 46.2, 52.8, 62.1, 63.2, 73.6, 104.6, 119.3, 121.9, 129.8 (2C), 131.6 (2C), 136.1, 148.0, 164.5, 164.7, 173.1, 194.8; HRMS (ESI-TOF) calcd for $C_{25}H_{29}BrNO_5S_2^+$ ($[M + H]^+$): 566.0665, found: 566.0666.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-7-(4-nitrophenyl)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2f):



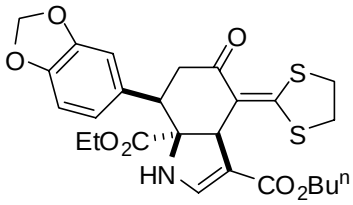
White solid; m. p. 249-251 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.92 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.31-1.38 (m, 2H), 1.54-1.63 (m, 2H), 2.49 (d, *J* = 15.5 Hz, 1H), 3.11 (t, *J* = 15.5 Hz, 1H), 3.3s (dd, *J* = 12.5, 9.0 Hz, 1H), 3.42-3.64 (m, 4H), 3.97 (tt, *J* = 14.0, 6.5 Hz, 1H), 4.07 (tt, *J* = 13.0, 7.0 Hz, 1H), 4.19 (qq, *J* = 13.0, 7.0 Hz, 1H), 4.30 (dd, *J* = 13.5, 7.0 Hz, 1H), 4.38 (s, 1H), 4.95 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 8.17 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.3, 19.2, 30.9, 36.1, 39.1 (2C), 46.8, 53.2, 62.4, 63.4, 73.4, 105.6, 119.0, 123.6 (2C), 129.3 (2C), 144.8, 147.5, 147.9, 164.6, 165.4, 172.9, 194.2; HRMS (ESI-TOF) calcd for $C_{25}H_{29}N_2O_7S_2^+$ ($[M + H]^+$): 533.1410, found: 533.1426.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-*p*-tolyl-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2g):



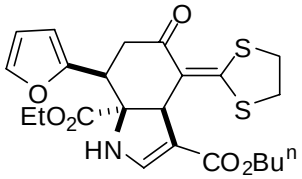
White solid; m. p. 121-123 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.91 (t, *J* = 7.5 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.30-1.36 (m, 2H), 1.53-1.57 (m, 2H), 2.32 (s, 3H), 2.47 (d, *J* = 15.0 Hz, 1H), 3.04 (t, *J* = 15.0 Hz, 1H), 3.32 (dd, *J* = 10.5, 6.5 Hz, 1H), 3.42-3.53 (m, 4H), 3.96 (dd, *J* = 12.5, 7.0 Hz, 1H), 4.05 (dd, *J* = 13.0, 6.5 Hz, 1H), 4.18 (dd, *J* = 17.5, 7.0 Hz, 1H), 4.28 (dd, *J* = 18.0, 7.5 Hz, 1H), 4.49 (s, 1H), 4.88 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 21.0, 31.0, 36.0, 39.0, 39.4, 46.3, 52.8, 61.9, 63.2, 74.0, 104.0, 119.7, 128.0 (2C), 129.3 (2C), 133.9, 137.5, 148.0, 164.0, 164.9, 173.4, 195.5; HRMS (ESI-TOF) calcd for $C_{26}H_{32}NO_5S_2^+$ ($[M + H]^+$): 502.1716, found: 502.1713.

3-Butyl 7a-ethyl 7-(benzo[d][1,3]dioxol-5-yl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2h):



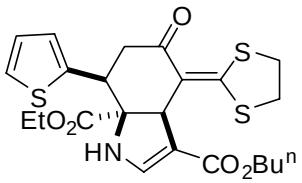
White solid; m. p. 230-232 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.31-1.37 (m, 2H), 1.53-1.58 (m, 2H), 2.44 (t, *J* = 16.0 Hz, 1H), 2.98 (t, *J* = 15.5 Hz, 1H), 3.28-3.33 (m, 1H), 3.41-3.54 (m, 4H), 3.96 (tt, *J* = 14.0, 6.5 Hz, 1H), 4.06 (tt, *J* = 13.5, 7.0 Hz, 1H), 4.17 (tt, *J* = 14.0, 7.5 Hz, 1H), 4.29 (qq, *J* = 14.5, 7.5 Hz, 1H), 4.53 (s, 1H), 4.87 (s, 1H), 5.95 (s, 2H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 7.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 30.9, 36.0, 39.0, 39.7, 46.4, 52.6, 62.0, 63.2, 74.0, 101.1, 104.1, 108.3, 108.4, 119.6, 121.4, 130.7, 147.1, 147.8, 148.1, 164.1, 164.8, 173.4, 195.2; HRMS (ESI-TOF) calcd for $C_{26}H_{30}NO_7S_2^+$ ($[M + H]^+$): 532.1458, found: 532.1449.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-7-(furan-2-yl)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2i):



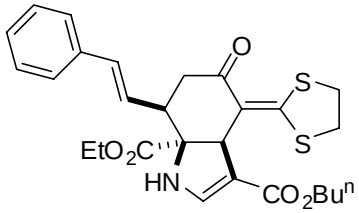
White solid; m. p. 158-160 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.32-1.37 (m, 2H), 1.52-1.61 (m, 2H), 2.56 (dd, *J* = 16.0, 14.0 Hz, 1H), 2.89 (t, *J* = 15.5 Hz, 1H), 3.27-3.32 (m, 1H), 3.40-3.54 (m, 3H), 3.68 (d, *J* = 12.5 Hz, 1H), 3.94 (tt, *J* = 13.5, 6.5 Hz, 1H), 4.05 (tt, *J* = 13.0, 6.5 Hz, 1H), 4.25 (tt, *J* = 14.5, 7.5 Hz, 1H), 4.32 (tt, *J* = 14.5, 7.0 Hz, 1H), 4.69 (s, 1H), 4.83 (s, 1H), 6.07 (d, *J* = 3.0 Hz, 1H), 6.31 (s, 1H),7.32 (s, 1H), 7.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.1, 19.2, 30.9, 36.1, 38.0, 39.0, 41.3, 52.5, 62.1, 63.2, 72.8, 103.7, 107.9, 110.4, 119.4, 142.5, 148.0, 151.6, 164.3, 164.8, 173.2, 194.4; HRMS (ESI-TOF) calcd for $C_{23}H_{28}NO_6S_2^+$ ($[M + H]^+$): 478.1352, found: 478.1355.

3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-(thiophen-2-yl)-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2j):



White solid; m. p. 173-175 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.33-1.36 (m, 2H), 1.53-1.58 (m, 2H), 2.60 (dd, *J* = 16.0, 14.0 Hz, 1H), 2.99 (t, *J* = 16.0 Hz, 1H), 3.29-3.32 (m, 1H), 3.42-3.52 (m, 3H), 3.89 (d, *J* = 12.5 Hz, 1H), 3.96 (tt, *J* = 13.5, 7.0 Hz, 1H), 4.05 (tt, *J* = 13.5, 7.0 Hz, 1H), 4.21 (dd, *J* = 18.0, 7.5 Hz, 1H), 4.31 (tt, *J* = 18.0, 7.0 Hz, 1H), 4.70 (s, 1H), 4.86 (s, 1H), 6.78 (d, *J* = 3.0 Hz, 1H), 6.95 (t, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 5.0 Hz, 1H), 7.37 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 14.2, 19.2, 30.9, 36.1, 39.0, 40.8, 42.8, 52.6, 62.2, 63.3, 73.7, 104.5, 119.3, 125.1, 125.8, 126.9, 139.6, 148.0, 164.4, 164.7, 173.0, 194.4; HRMS (ESI-TOF) calcd for $C_{23}H_{28}NO_5S_3^+$ ($[M + H]^+$): 494.1124, found: 494.1140.

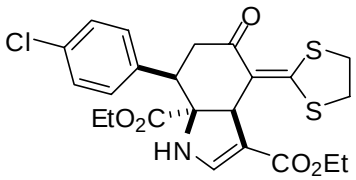
3-Butyl 7a-ethyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-styryl-3a,4,5,6,7,7a-hexahydro-1*H*-indole-3,7a-dicarboxylate (2k):



Yellow solid; m. p. 154-156 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.33-1.36 (m, 2H), 1.53-1.59 (m, 2H), 2.45 (dd, *J* = 16.0, 14.0 Hz, 1H), 2.72 (t, *J* = 16.0 Hz, 1H), 3.08 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.28-3.31 (m, 1H), 3.41-3.53 (m, 3H), 3.96 (tt, *J* = 13.5, 7.0 Hz, 1H), 4.06 (tt, *J* = 13.5, 7.5 Hz, 1H), 4.23 (dd, *J* = 18.0, 7.0 Hz, 1H), 4.32 (dd, *J* = 17.5, 7.0 Hz, 1H), 4.86 (s, 1H), 4.87 (s, 1H), 6.02 (dd, *J* = 16.0, 7.5 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 7.24-7.32 (m, 5H), 7.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.9, 14.3, 19.2, 31.0, 36.0, 39.0, 39.1, 45.1, 52.4, 62.1, 63.3, 73.3, 104.8, 119.6, 124.9, 126.4 (2C), 128.0, 128.4, 128.6, 133.5, 136.3, 148.1, 163.9, 164.8, 173.5, 195.0; HRMS (ESI-TOF) calcd for $C_{27}H_{32}NO_5S_2^+$ ($[M + H]^+$): 514.1716, found: 514.1712.

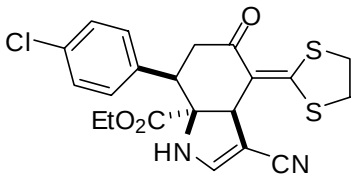
Diethyl 7-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-

indole-3,7a-dicarboxylate (2l):



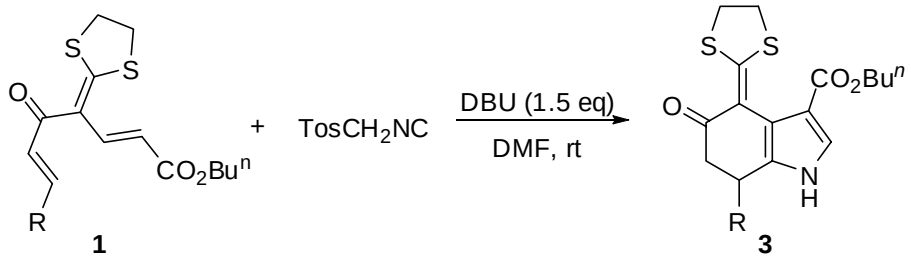
White solid; m. p. 226-228 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.20 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.5 Hz, 3H), 2.45 (d, *J* = 15.5 Hz, 1H), 3.03 (t, *J* = 15.0 Hz, 1H), 3.34 (qq, *J* = 10.0, 6.0 Hz, 1H), 3.44-3.53 (m, 4H), 4.03 (dd, *J* = 17.5, 7.5 Hz, 1H), 4.10 (dd, *J* = 17.5, 7.5 Hz, 1H), 4.18 (tt, *J* = 17.5, 7.0 Hz, 1H), 4.28 (tt, *J* = 17.0, 7.0 Hz, 1H), 4.47 (s, 1H), 4.90 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.2, 14.5, 36.0, 39.1, 39.3, 46.2, 52.8, 59.2, 62.1, 73.6, 104.7, 119.3, 128.7 (2C), 129.5 (2C), 133.8, 135.6, 148.0, 164.6, 164.7, 173.2, 194.9; HRMS (ESI-TOF) calcd for $C_{23}H_{25}ClNO_5S_2^+$ ([M + H]$^+$): 494.0857, found: 494.0858.

Ethyl 7-(4-chlorophenyl)-3-cyano-4-(1,3-dithiolan-2-ylidene)-5-oxo-3a,4,5,6,7,7a-hexahydro-1*H*-indole-7a-carboxylate (2m):



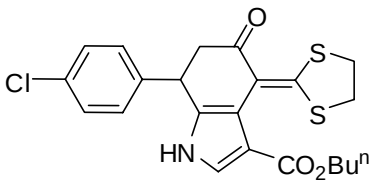
White solid; m. p. 271-273 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.26 (t, *J* = 7.5 Hz, 3H), 2.48 (dd, *J* = 15.5, 13.5 Hz, 1H), 3.02 (t, *J* = 15.5 Hz, 1H), 3.39-3.57 (m, 5H), 4.19 (qq, *J* = 18.0, 7.0 Hz, 1H), 4.25 (qq, *J* = 17.5, 7.0 Hz, 1H), 4.55 (s, 1H), 4.88 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.2, 36.5, 39.0, 39.3, 45.0, 52.6, 62.6, 72.8, 84.3, 117.0, 117.1, 128.9 (2C), 129.3 (2C), 134.1, 135.4, 149.8, 166.9, 173.0, 193.0; HRMS (ESI-TOF) calcd for $C_{21}H_{20}ClN_2O_3S_2^+$ ([M + H]$^+$): 447.0598, found: 447.0601.

IV. General Procedure for the Preparation of 3 (3a as Example):



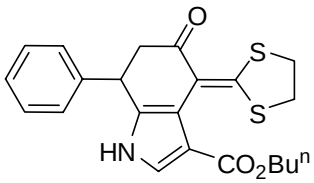
To a solution of 5-oxohepta-2,6-dienoate **1a** (1.0 mmol, 408 mg) and tosylmethyl isocyanide (1.2 mmol, 234 mg) in DMF (4.0 mL) was added DBU (1.5 mmol, 0.22 mL) in one portion. The reaction mixture was stired for 1 h at room temperature. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into ice-water (45 mL) under stirring. The precipitated solid was collected by filtration, and dried in vacuo to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether/acetone = 5/2, V/V) to give **3a** (358 mg, 80 %) as a yellow solid.

Butyl 7-(4-chlorophenyl)-4-(1,3-dithiolan-2-ylidene)-5-oxo-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3a):



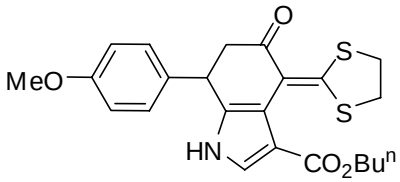
Yellow solid; m. p. 150-152 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.94 (t, J = 7.5 Hz, 3H), 1.39-1.43 (m, 2H), 1.63-1.69 (m, 2H), 2.83 (dd, J = 6.5, 16.0 Hz, 1H), 2.90 (dd, J = 6.0, 16.0 Hz, 1H), 3.20-3.25 (m, 1H), 3.30-3.44 (m, 3H), 4.19 (q, J = 7.0 Hz, 2H), 4.22 (t, J = 7.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 8.20 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.9, 19.3, 30.8, 36.3, 38.1, 38.9, 45.8, 64.2, 115.7, 118.7, 118.9, 122.9, 129.3 (2C), 129.4 (2C), 130.9, 133.5, 138.0, 157.5, 165.5, 194.2; HRMS (ESI-TOF) calcd for $C_{22}H_{23}ClNO_3S_2^+$ ($[M + H]^+$): 448.0802, found: 448.0812.

Butyl 4-(1,3-dithiolan-2-ylidene)-5-oxo-7-phenyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3b):



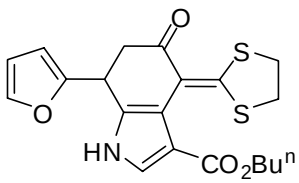
Yellow solid; m. p. 234-235 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.94 (t, J = 7.5 Hz, 3H), 1.39-1.43 (m, 2H), 1.64-1.69 (m, 2H), 2.92 (t, J = 6.5 Hz, 2H), 3.18-3.23 (m, 1H), 3.32-3.47 (m, 3H), 4.19 (q, J = 7.5 Hz, 2H), 4.24 (t, J = 6.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.25 (s, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.9, 19.3, 30.8, 36.2, 38.7, 38.9, 45.8, 64.1, 115.7, 118.6, 118.9, 122.7, 127.8, 128.0 (2C), 129.3 (2C), 131.7, 139.2, 157.0, 165.5, 194.7; HRMS (ESI-TOF) calcd for $C_{22}H_{24}NO_3S_2^+$ ([M + H]$^+$): 414.1192, found: 414.1195.

Butyl 4-(1,3-dithiolan-2-ylidene)-7-(4-methoxyphenyl)-5-oxo-4,5,6,7-tetrahydro-1H-indole-3-carboxylate (3c):



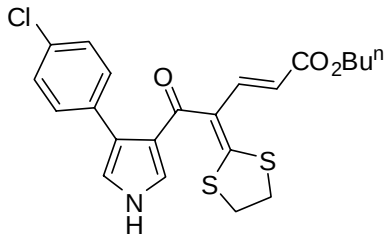
Yellow solid; m. p. 117-119 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.93 (t, J = 7.5 Hz, 3H), 1.38-1.43 (m, 2H), 1.63-1.68 (m, 2H), 2.85 (d, J = 8.0 Hz, 2H), 3.17-3.21 (m, 1H), 3.32-3.44 (m, 3H), 3.79 (s, 3H), 4.17 (t, J = 8.0 Hz, 1H), 4.21 (q, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.24 (s, 1H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.9, 19.3, 30.8, 36.2, 37.8, 38.9, 46.0, 55.3, 64.1, 114.5 (2C), 115.5, 118.3, 119.0, 122.7, 129.0 (2C), 131.1, 132.2, 156.7, 159.0, 165.6, 195.0; HRMS (ESI-TOF) calcd for $C_{23}H_{26}NO_4S_2^+$ ([M + H]$^+$): 444.1297, found: 444.1290.

Butyl 4-(1,3-dithiolan-2-ylidene)-7-(furan-2-yl)-5-oxo-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (3i):



Yellow solid; m. p. 88-89 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.93 (t, *J* = 7.5 Hz, 3H), 1.38-1.42 (m, 2H), 1.62-1.68 (m, 2H), 2.93 (dd, *J* = 5.5, 16.0 Hz, 1H), 2.97 (dd, *J* = 9.5, 15.5 Hz, 1H), 3.18-3.23 (m, 1H), 3.29-3.44 (m, 3H), 4.20 (q, *J* = 6.5 Hz, 2H), 4.35 (dd, *J* = 5.5, 9.5 Hz, 1H), 6.11 (d, *J* = 3.0 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.40 (s, 1H), 8.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.9, 19.3, 30.8, 32.0, 36.2, 38.9, 42.4, 64.1, 106.5, 110.6, 115.2, 118.4, 118.5, 123.1, 129.1, 142.3, 152.9, 157.3, 165.6, 194.2; HRMS (ESI-TOF) calcd for $C_{20}H_{22}NO_4S_2^+$ ($[M + H]^+$): 404.0984, found: 404.0986.

(E)-Butyl 5-(4-(4-chlorophenyl)-1H-pyrrol-3-yl)-4-(1,3-dithiolan-2-ylidene)-5-oxopent-2 -enoate (4a):



Red liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.93 (t, *J* = 7.5 Hz, 3H), 1.35-1.40 (m, 2H), 1.58-1.64 (m, 2H), 3.36-3.45 (m, 4H), 4.10 (t, *J* = 6.5 Hz, 2H), 5.71 (d, *J* = 15.5 Hz, 1H), 6.79 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.29 (s, 1H), 7.46 (d, *J* = 16.0 Hz, 1H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.8, 19.2, 30.7, 37.2, 38.5, 64.2, 117.4, 118.6, 122.2, 124.9, 125.2, 126.9, 128.0 (2C), 129.9 (2C), 132.3, 133.0, 140.8, 161.1, 167.6, 188.4.

V. Crystal data and ORTEP drawing of compound 2m

$C_{21}H_{19}ClN_2O_3S_2$, white crystal, M = 446.82, Monoclinic, C2/c, a = 40.139(6) Å, b = 9.4559(13) Å, c = 11.1246(14) Å, α = 90.00 º, β = 100.587(2) º, γ = 90.00 º, V = 4150.5(10) Å^3, Z = 8, T = 293(2), F_{000} = 1856, R_1 = 0.0486, wR_2 = 0.1252. CCDC 824546.

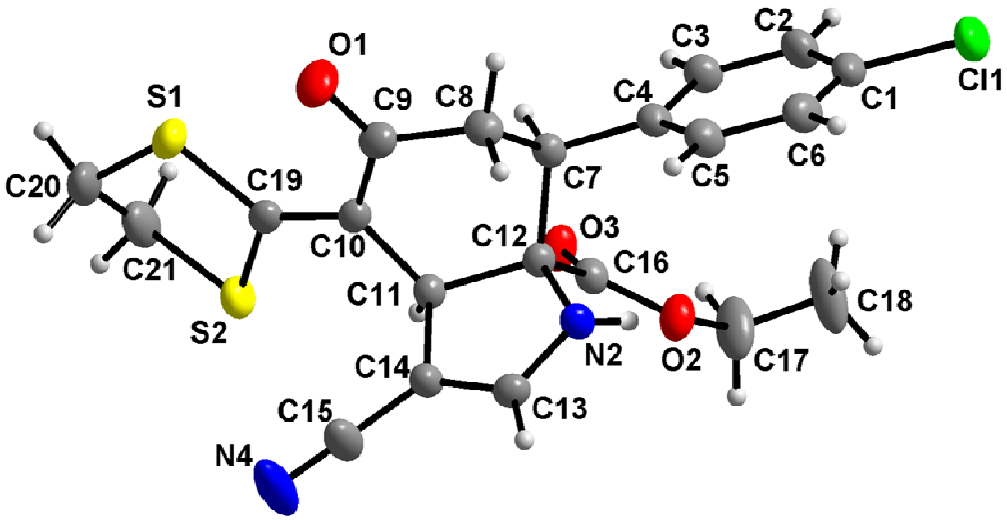


Figure 1. ORTEP drawing of **2m**

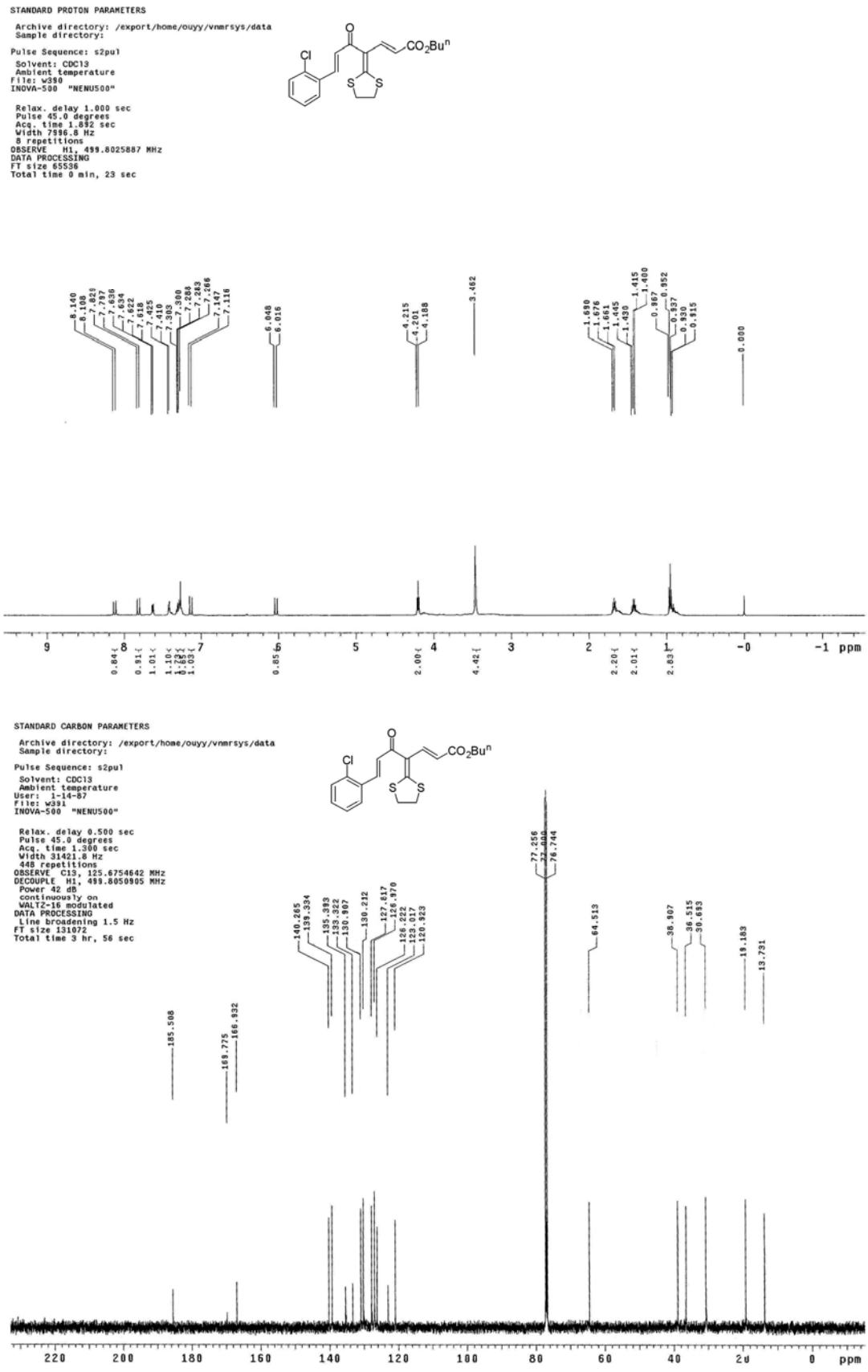


Figure 1. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1d**.

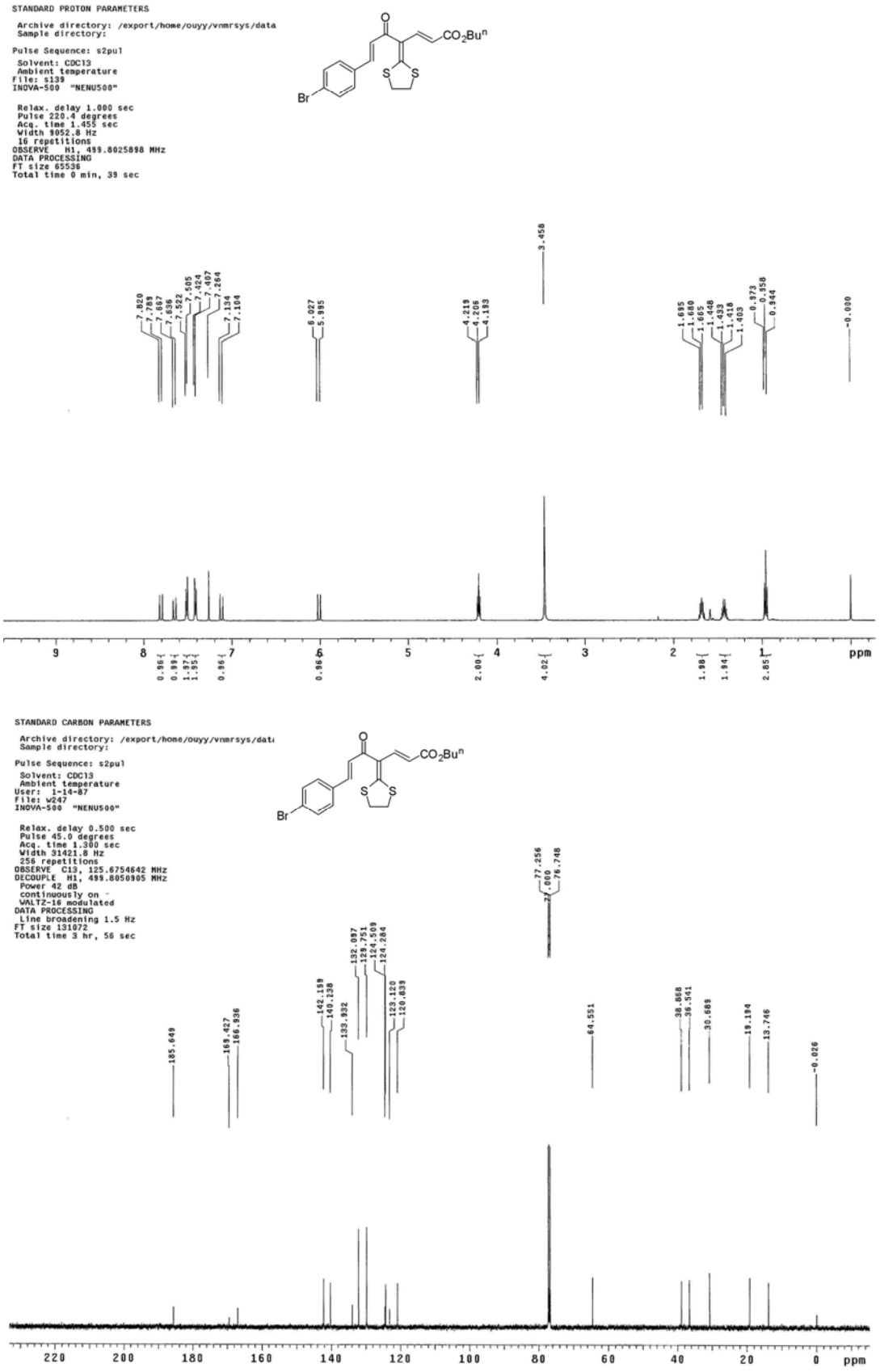


Figure 2. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1e**.

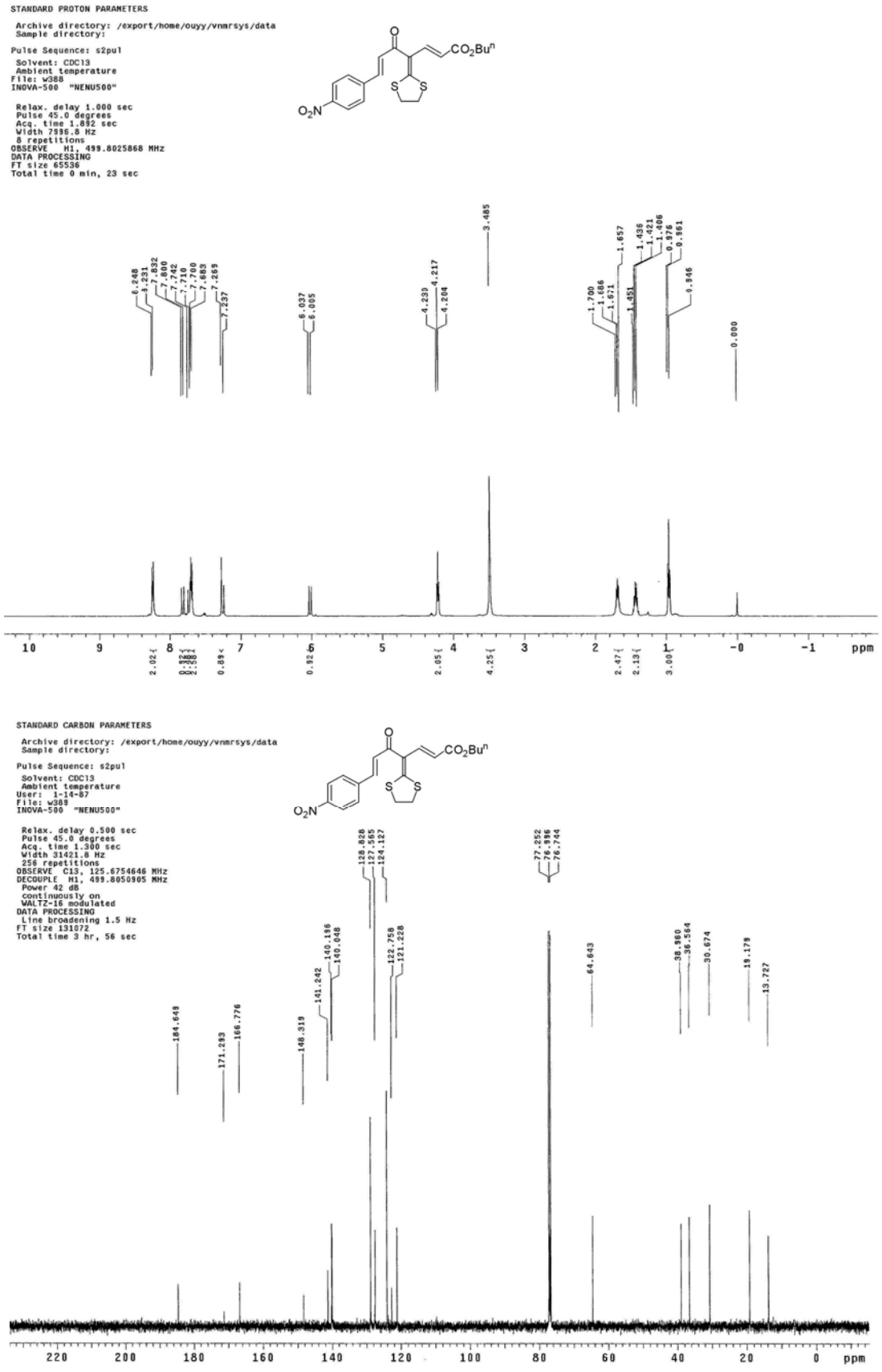


Figure 3. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1f**.

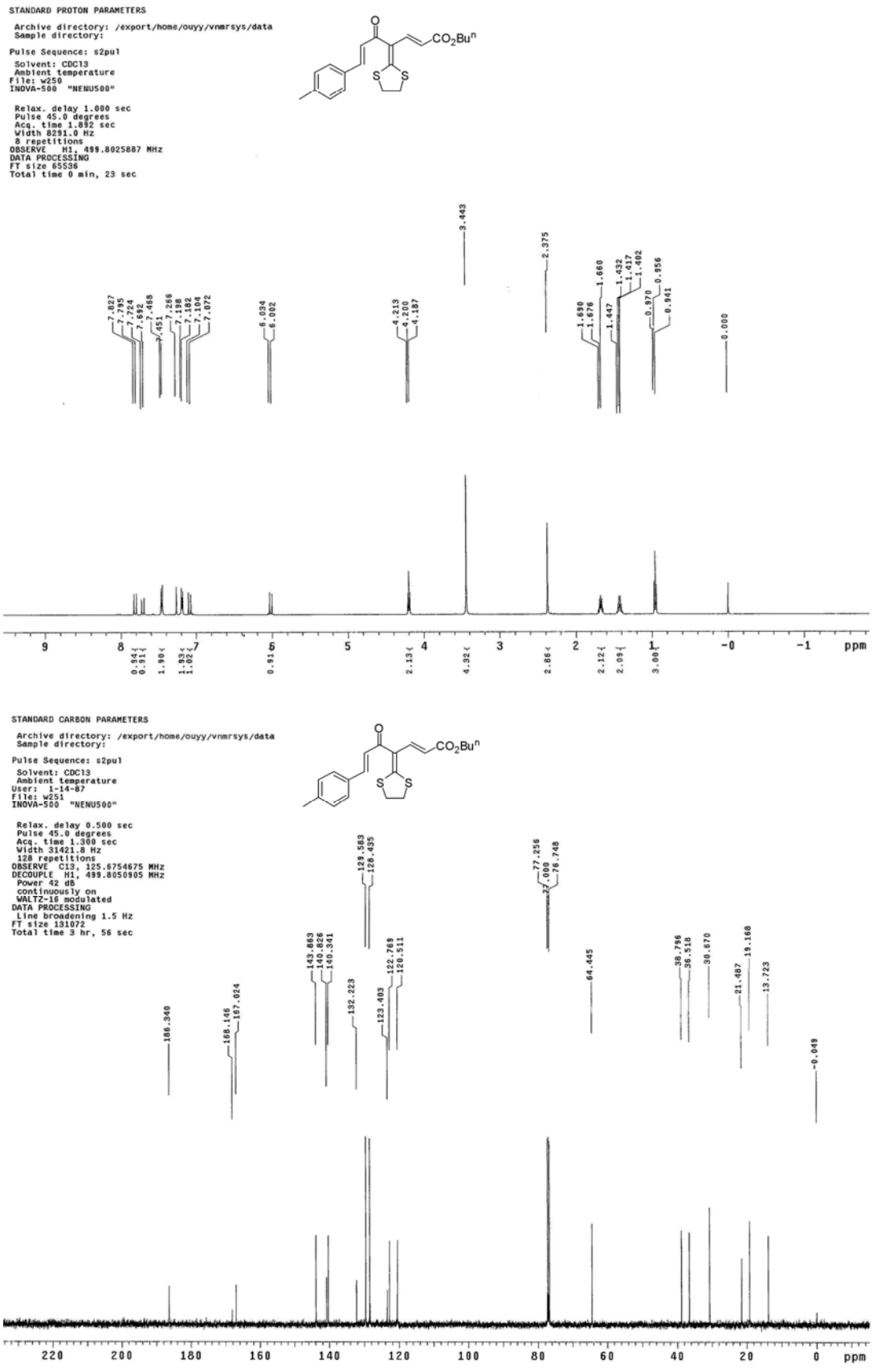


Figure 4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1g**.

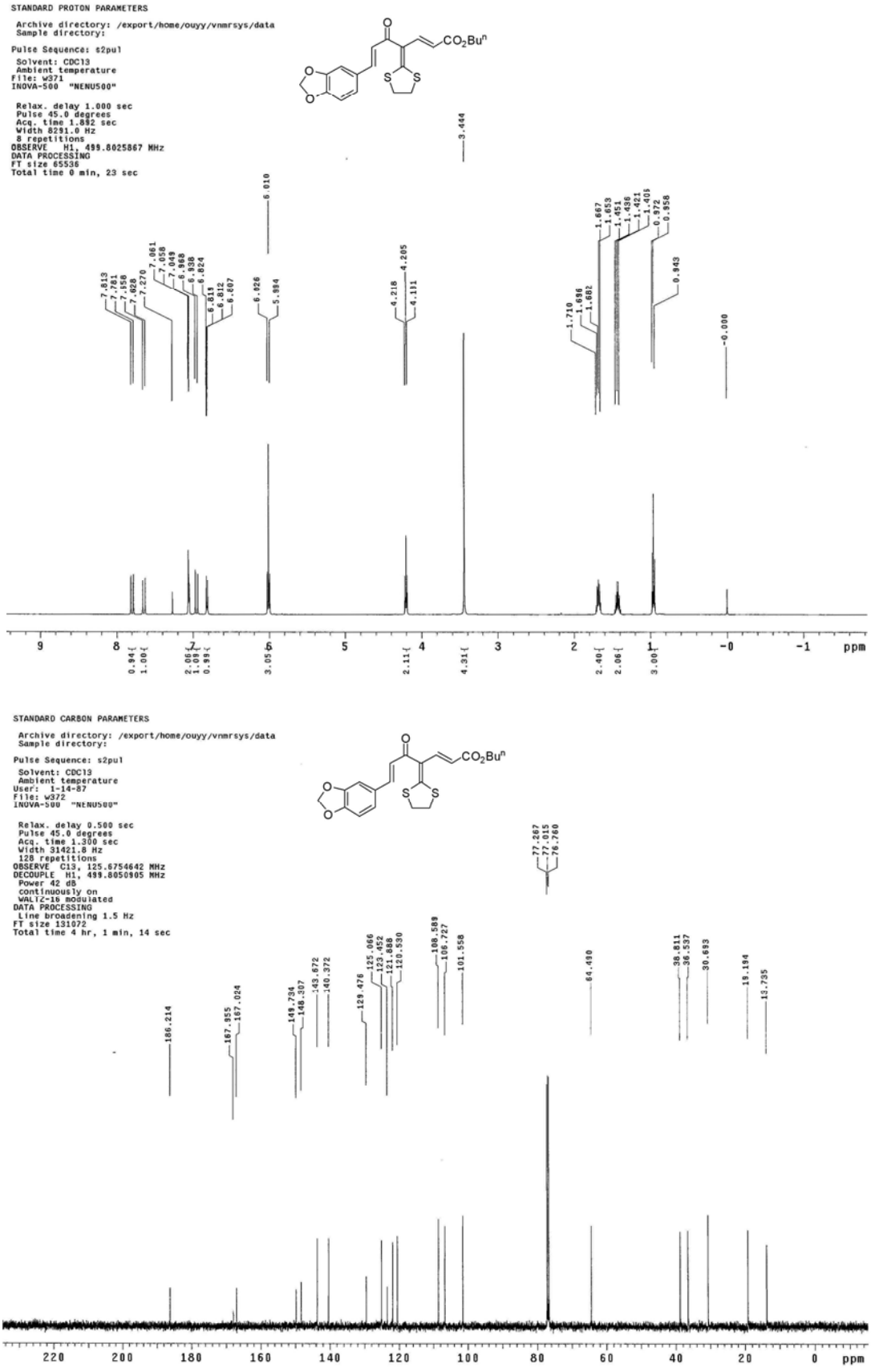


Figure 5. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1h**.

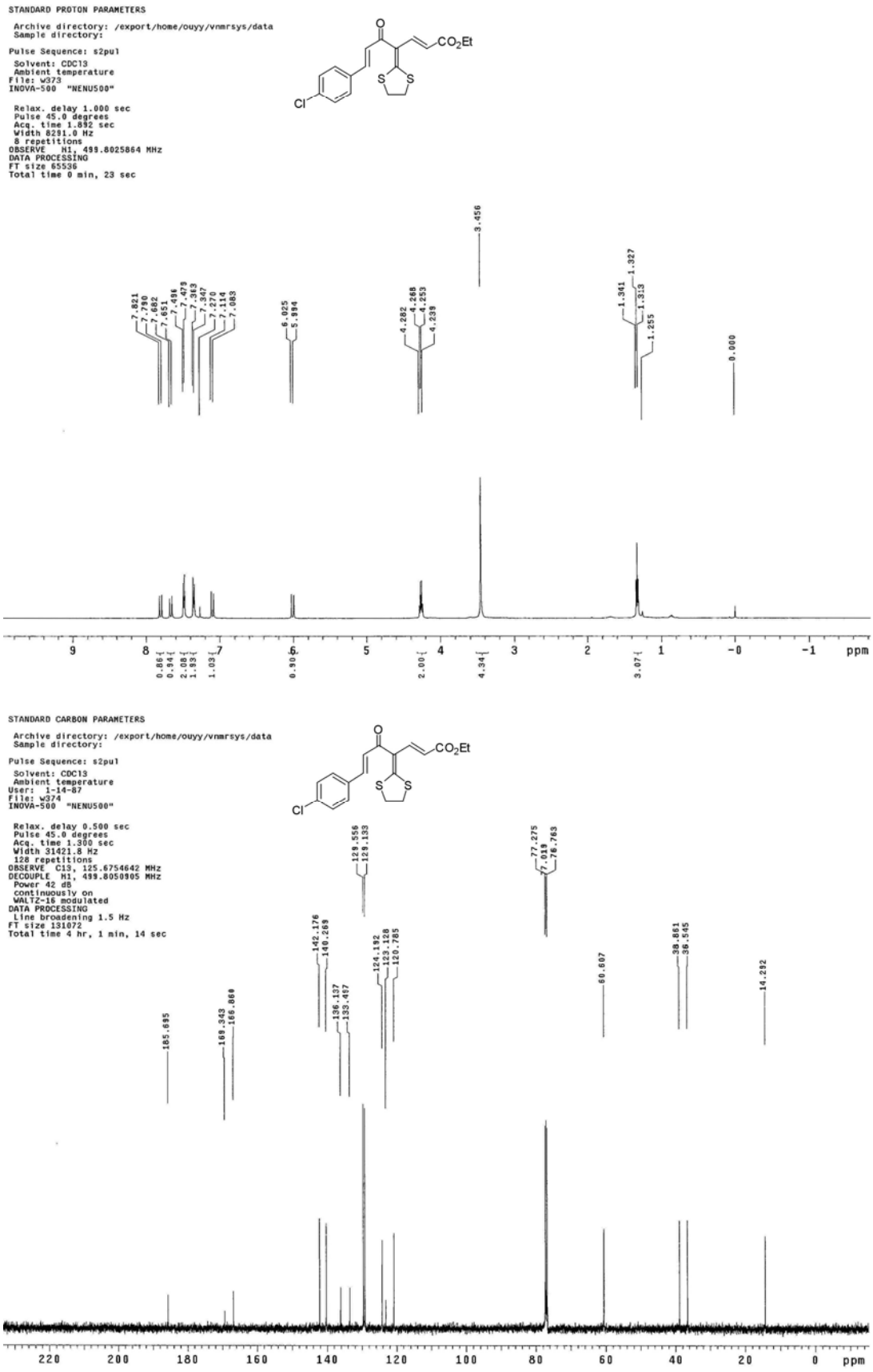


Figure 6. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1l**.

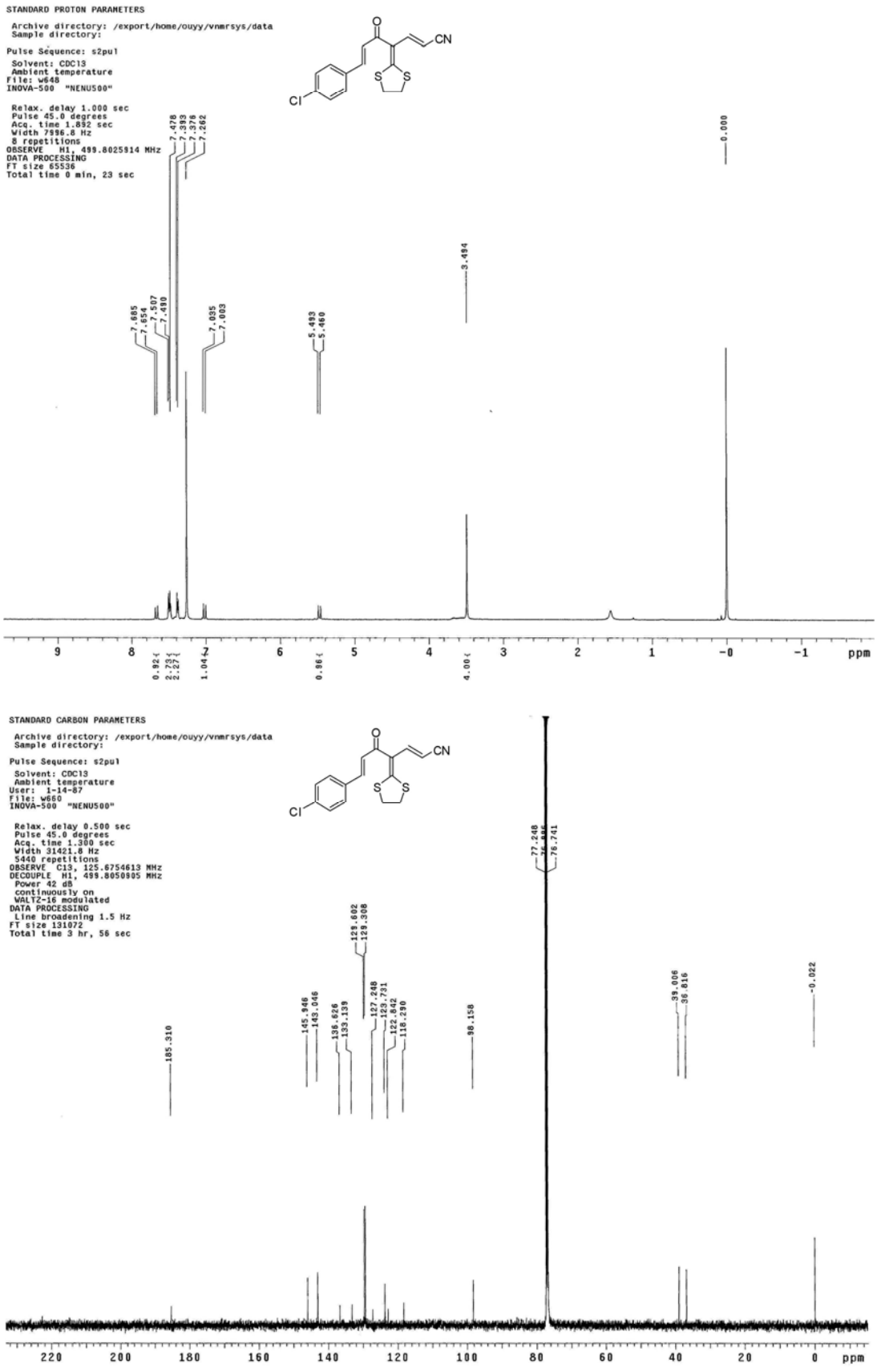


Figure 7. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **1m**.

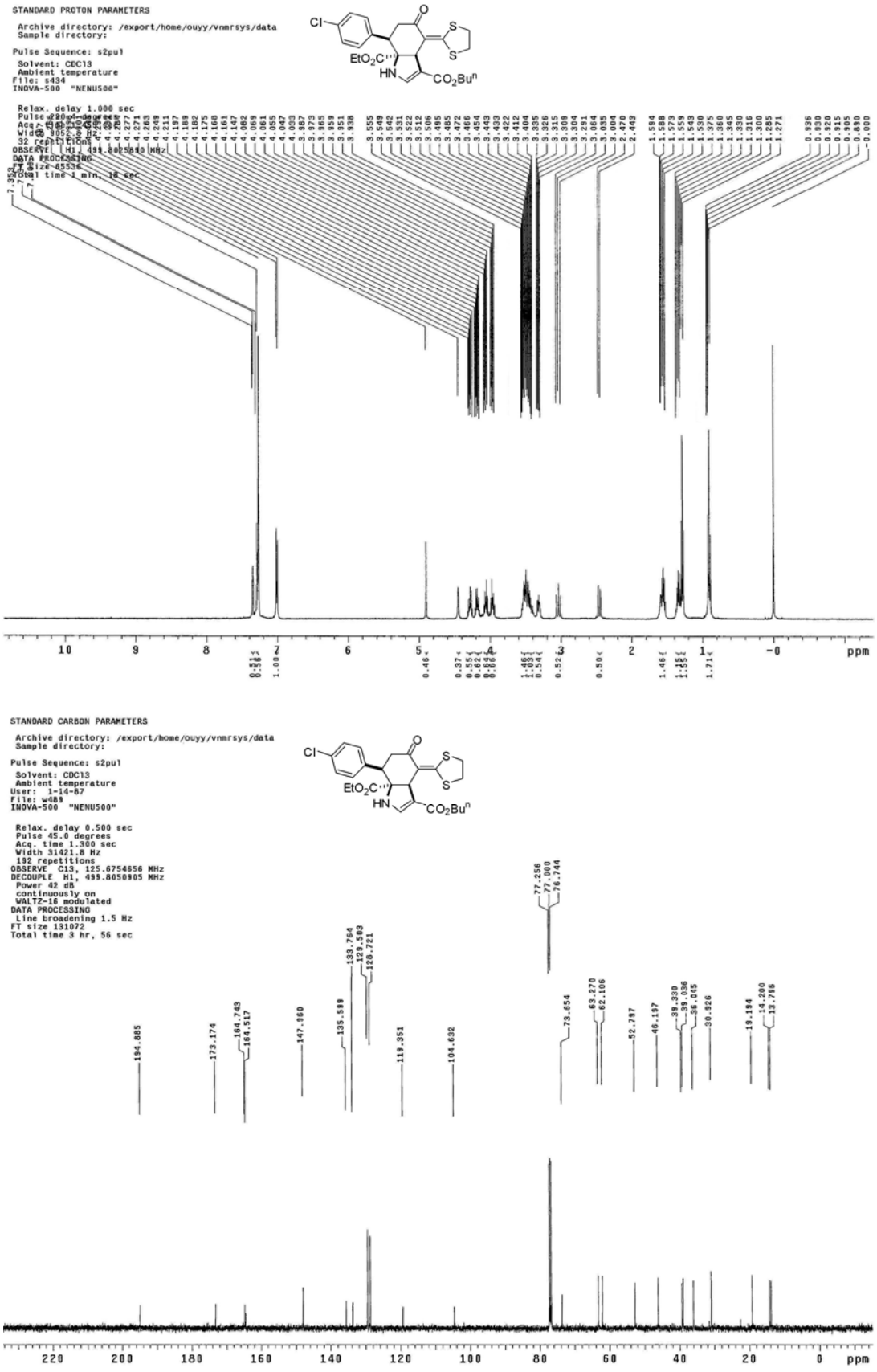


Figure 8. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2a**.

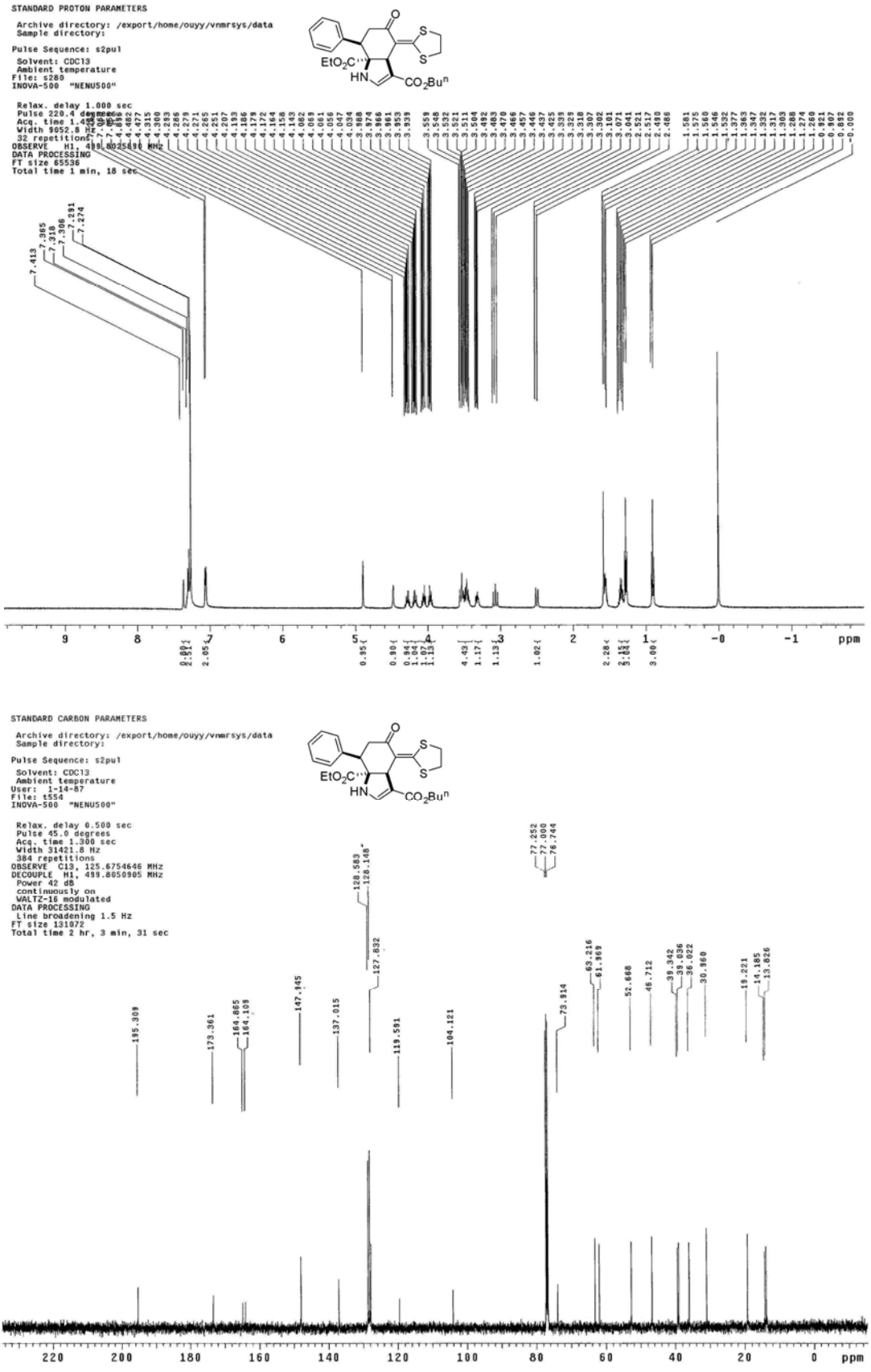


Figure 9. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2b**.

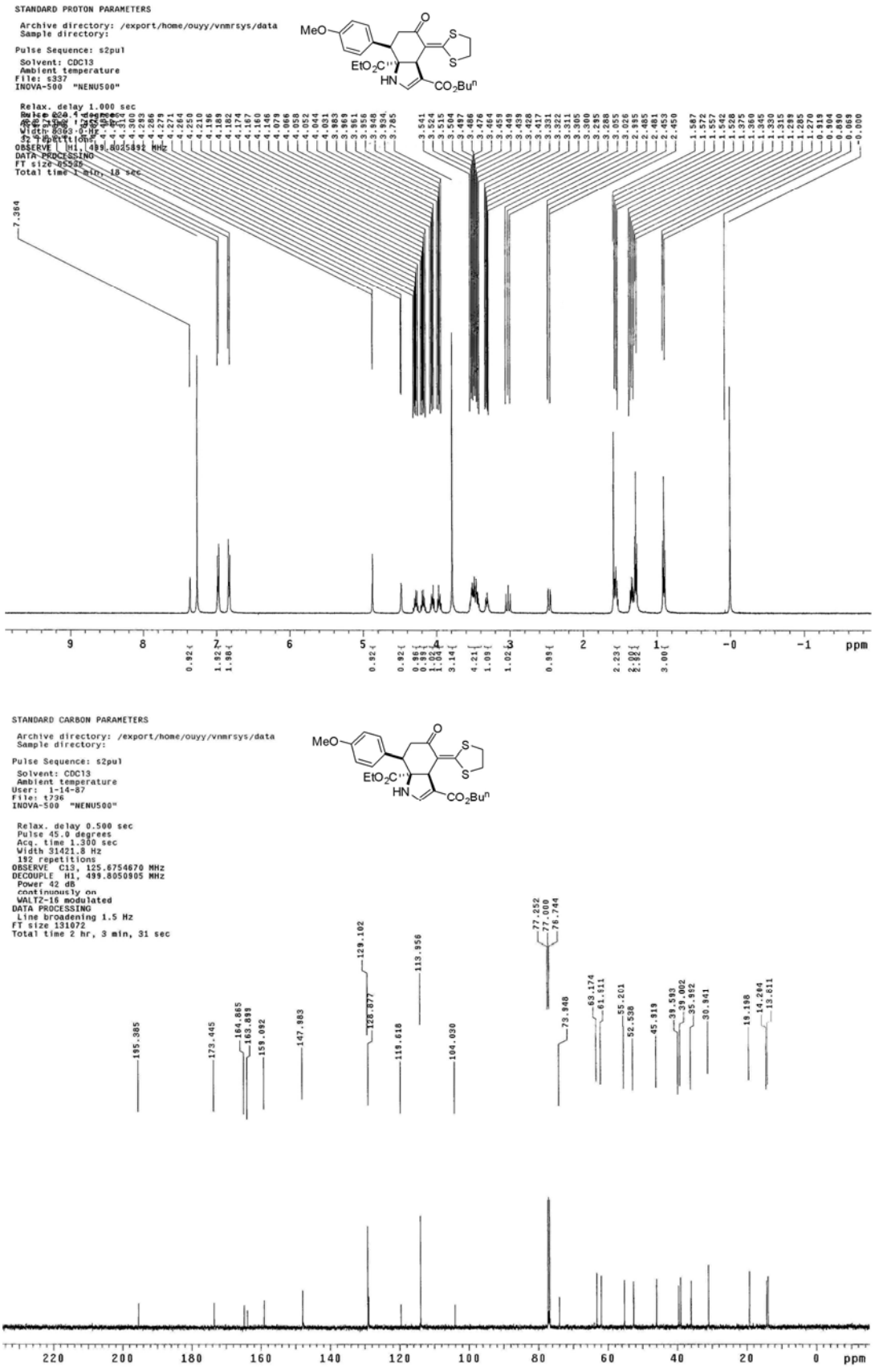


Figure 10. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2c**.

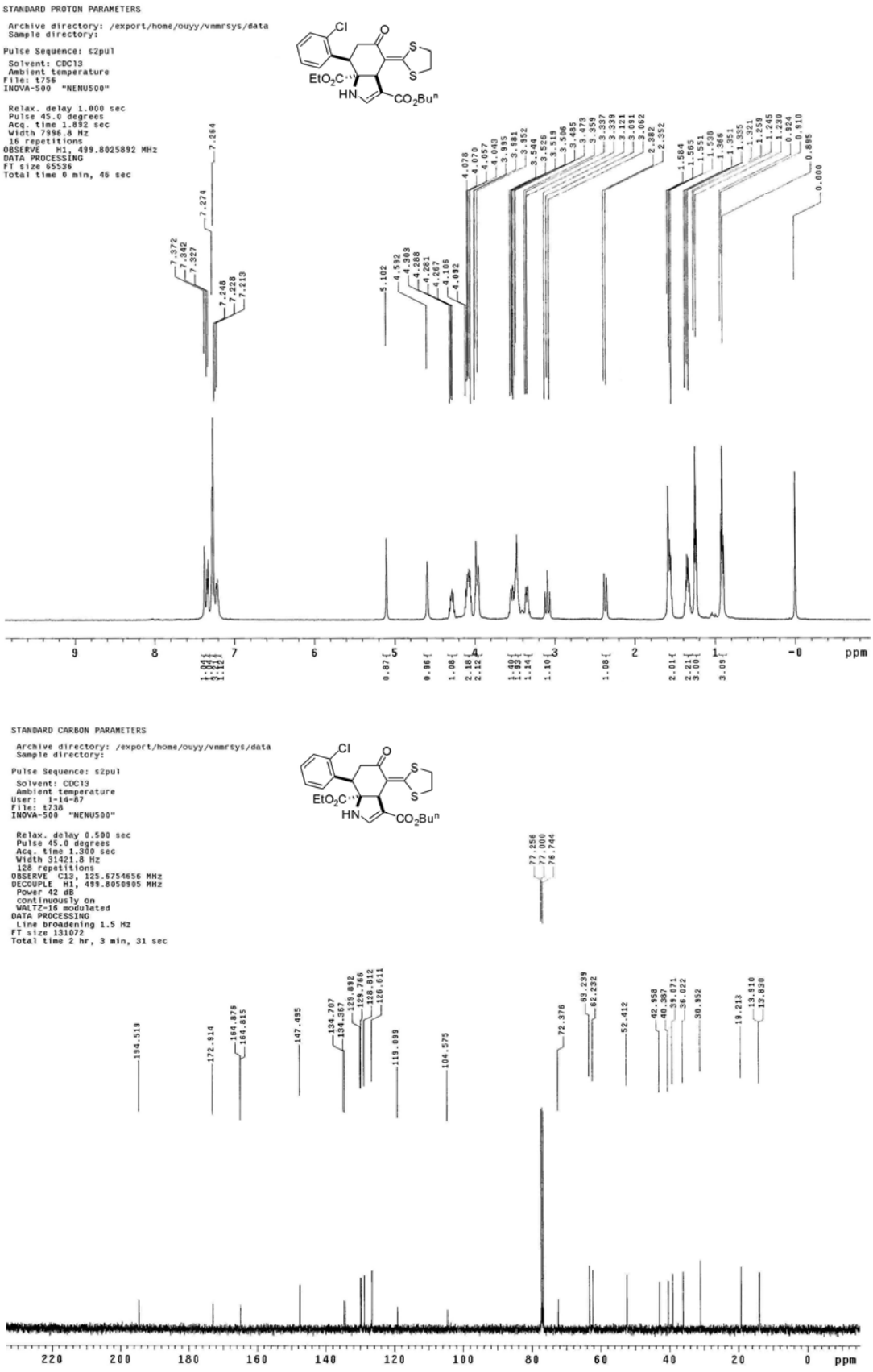


Figure 11. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2d**.

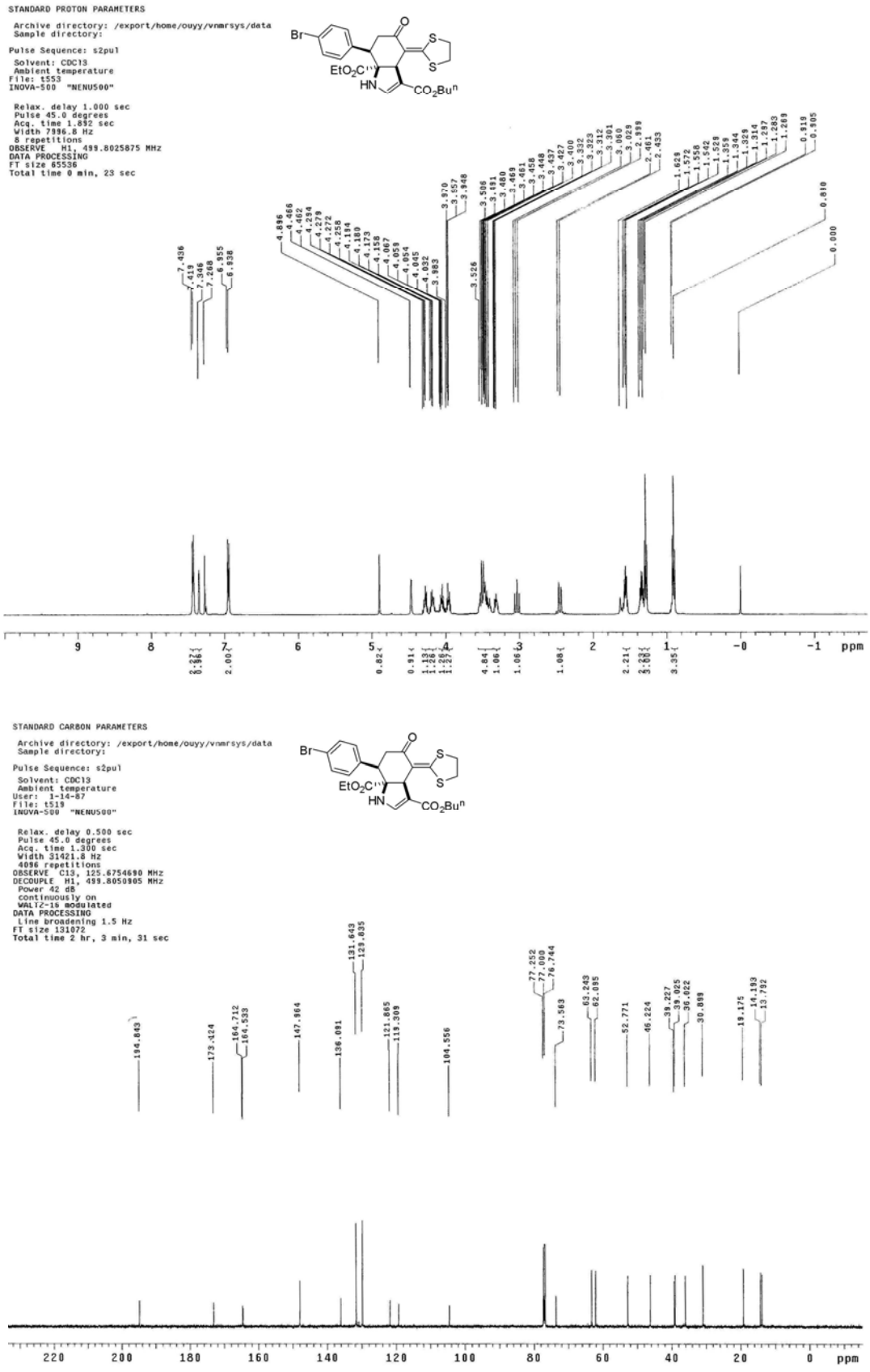


Figure 12. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2e**.

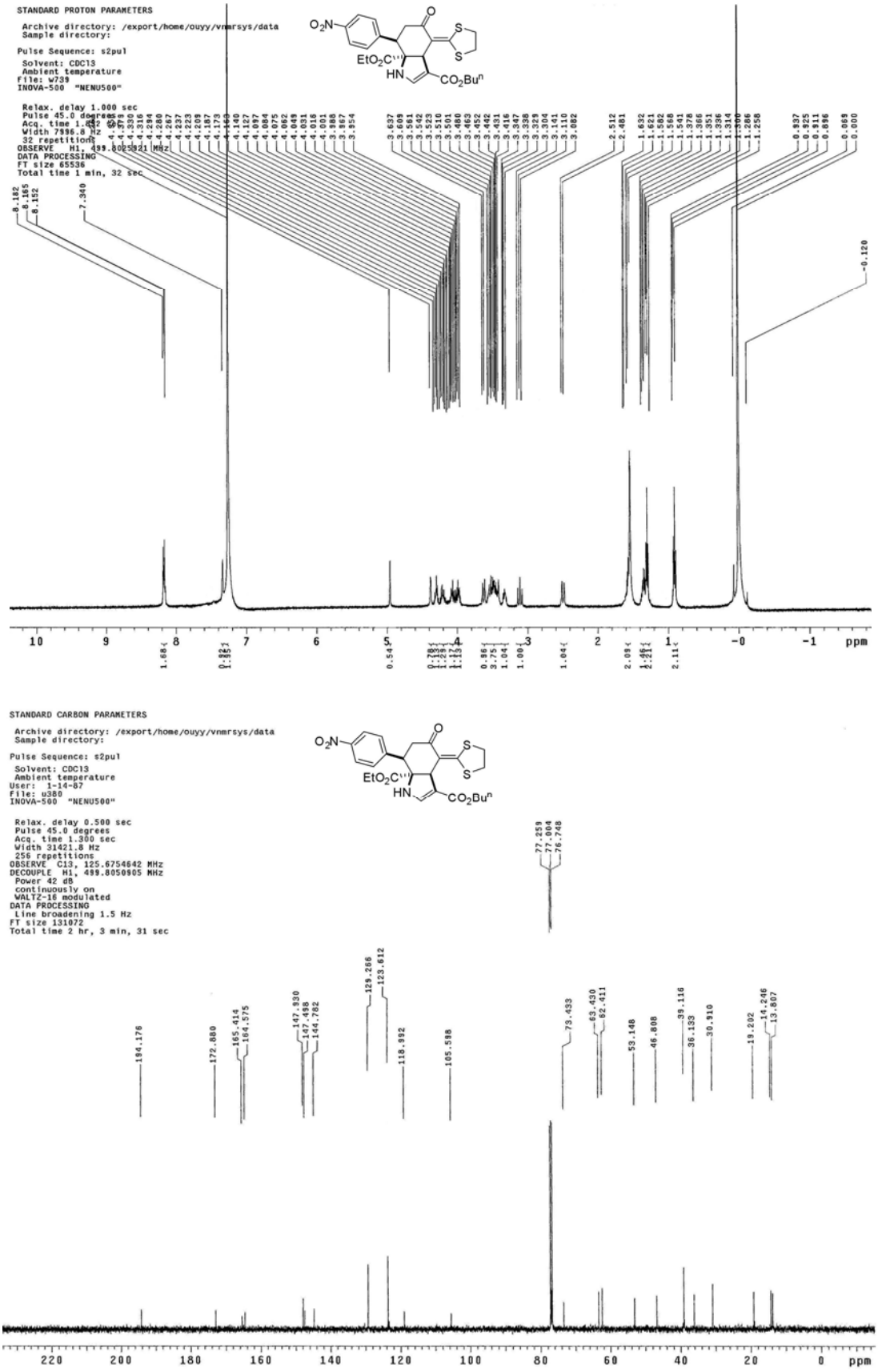


Figure 13. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2f**.

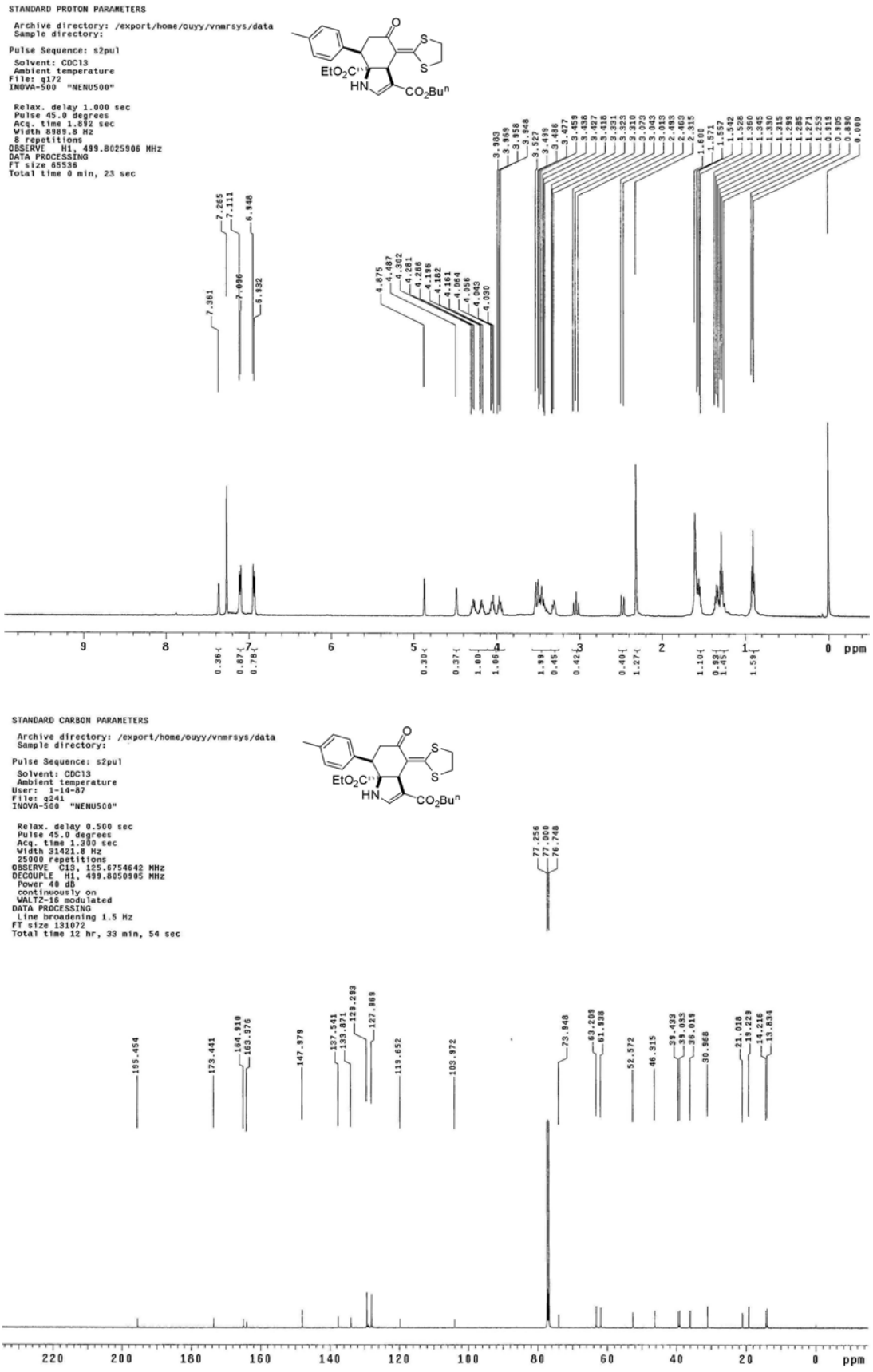


Figure 14. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2g**.

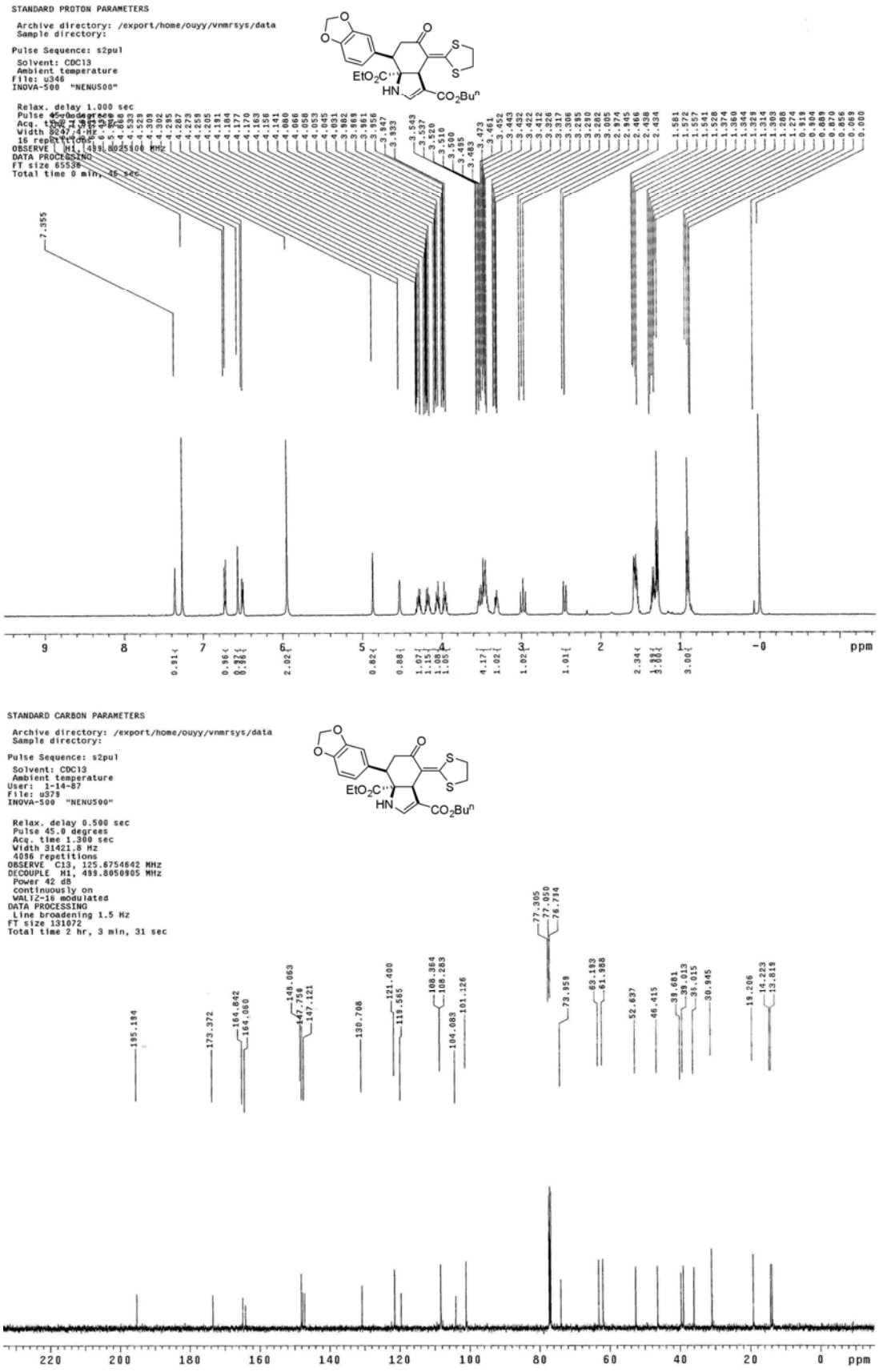


Figure 15. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2h**.

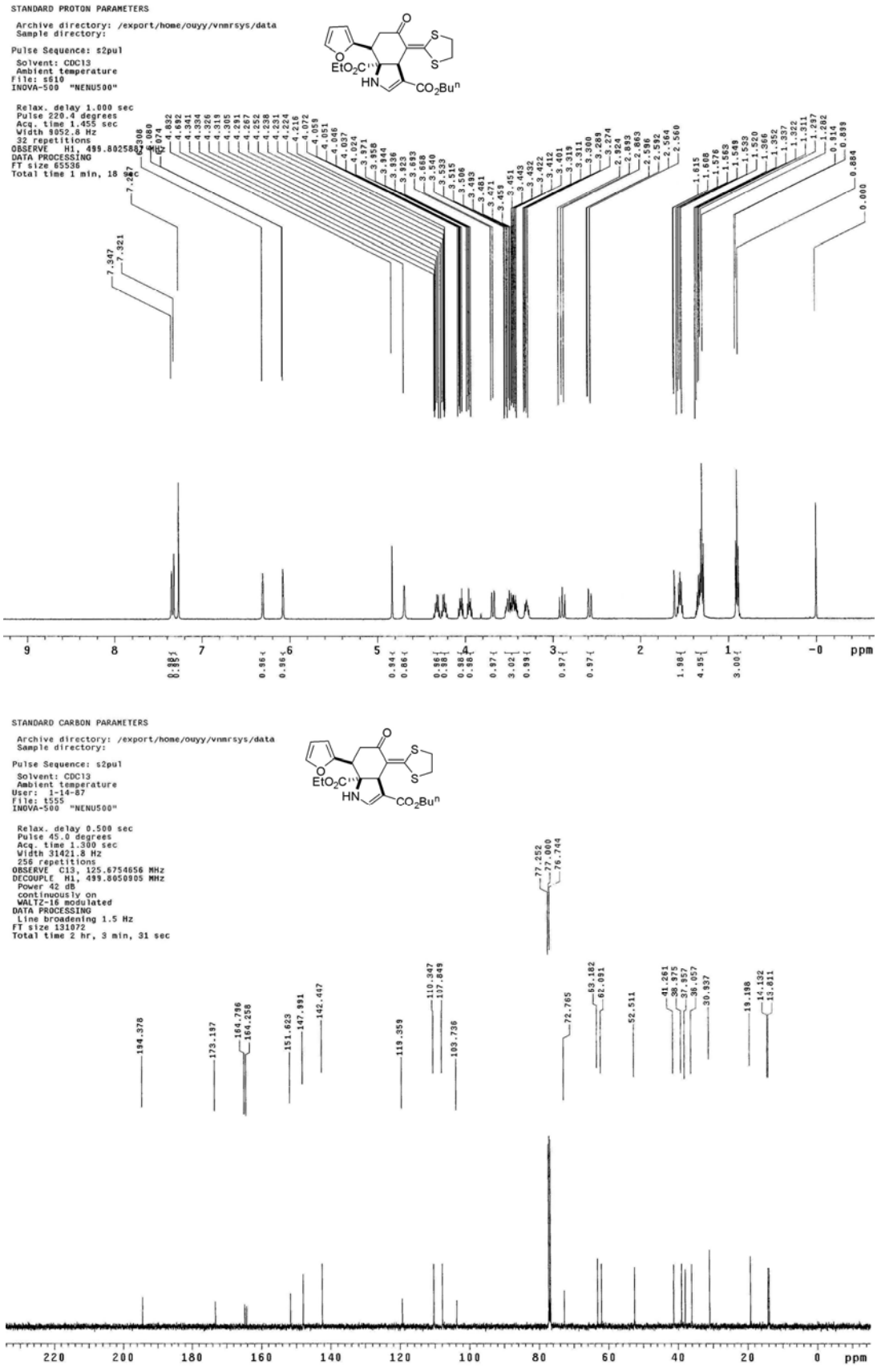


Figure 16. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2i**.

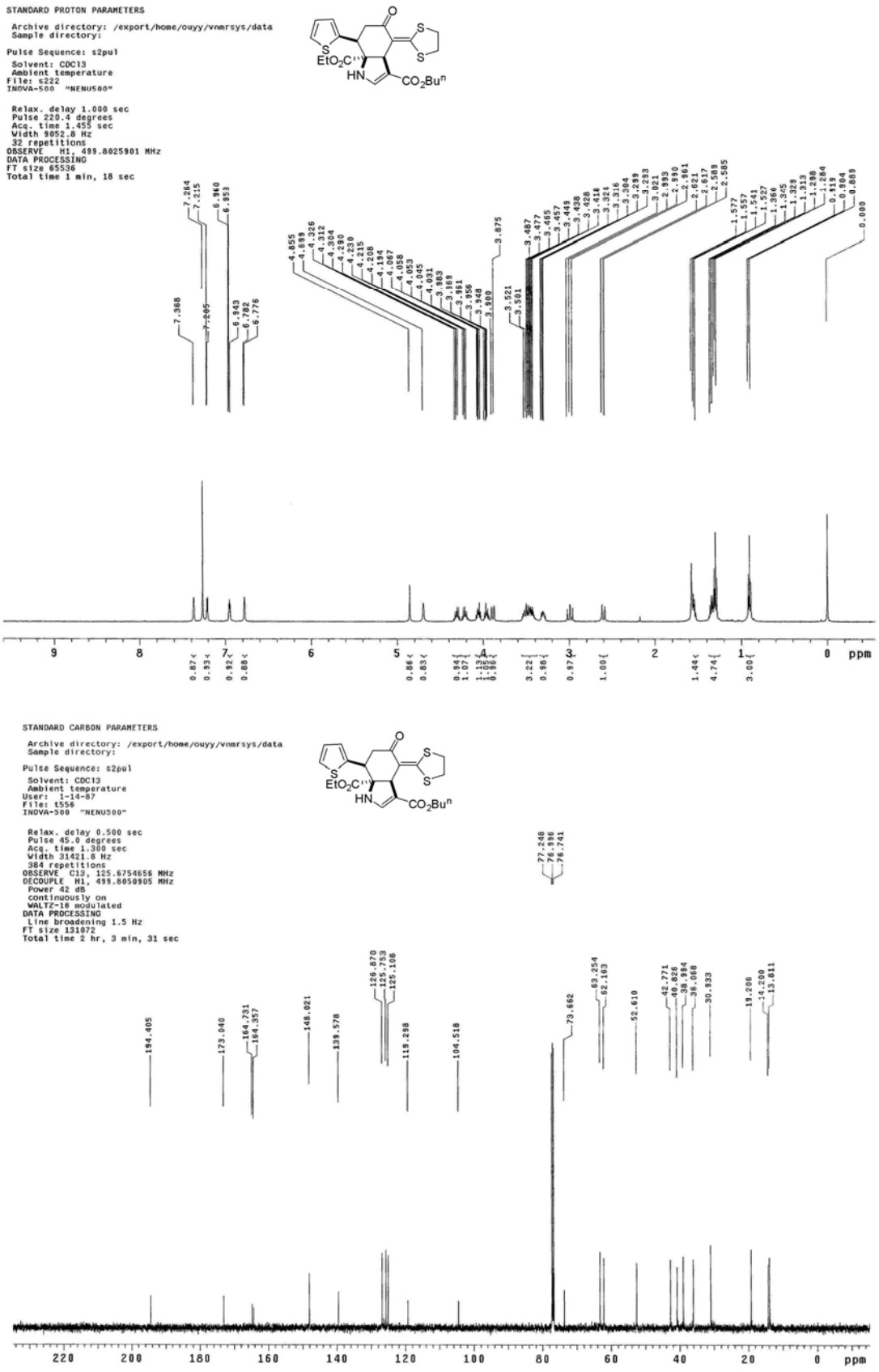


Figure 17. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2j**.

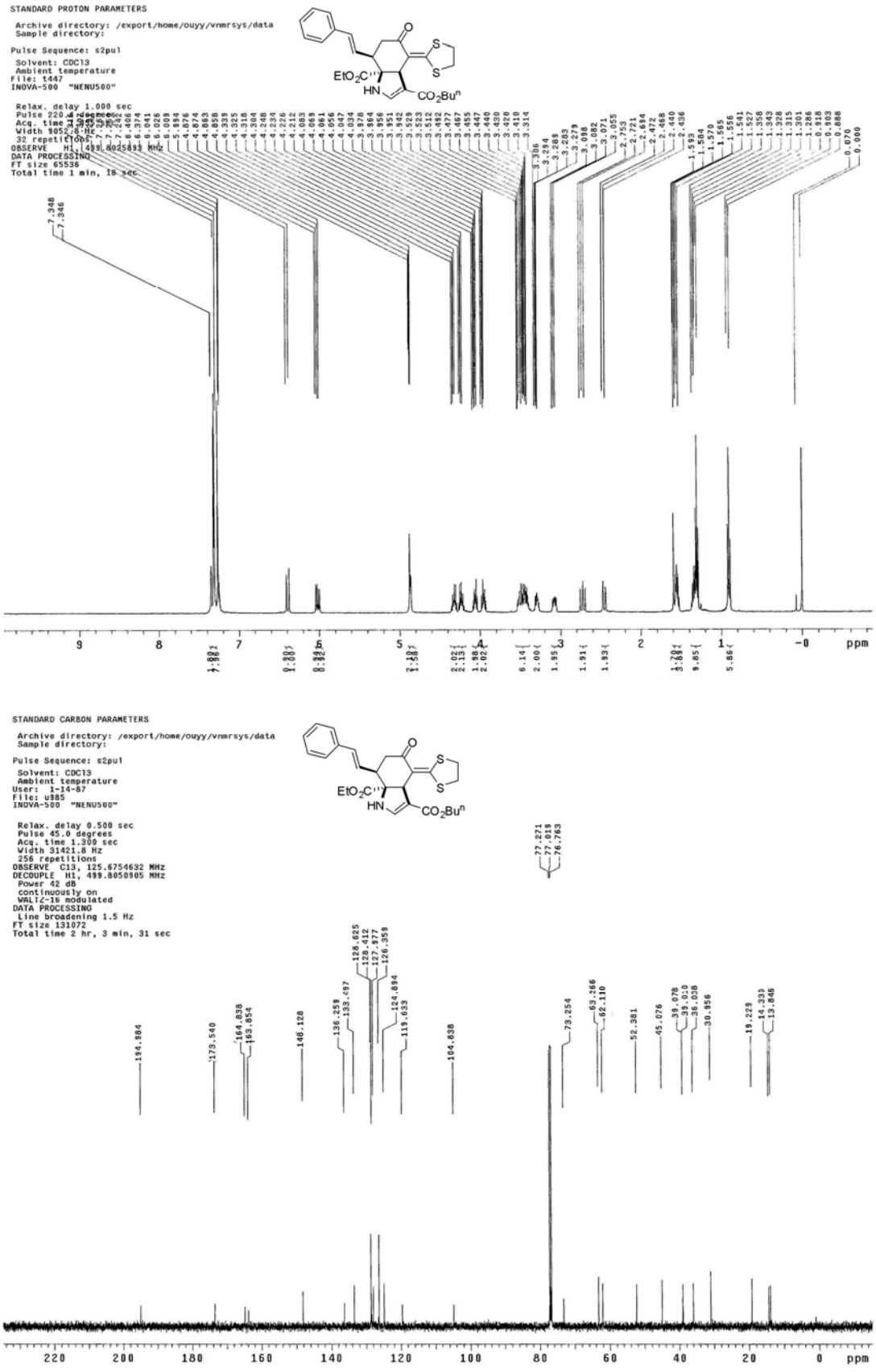


Figure 18. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2k**.

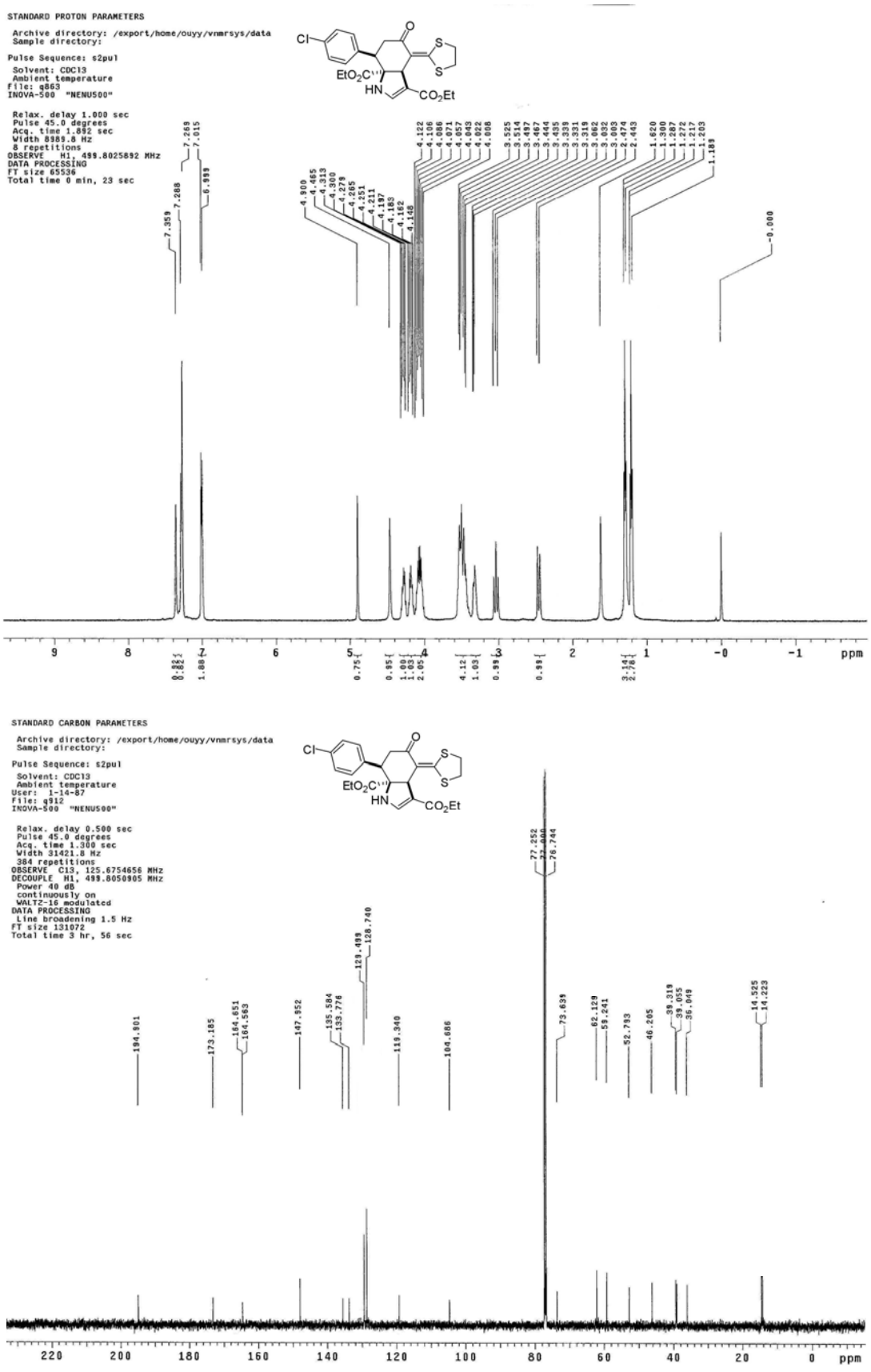


Figure 19. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2l**.

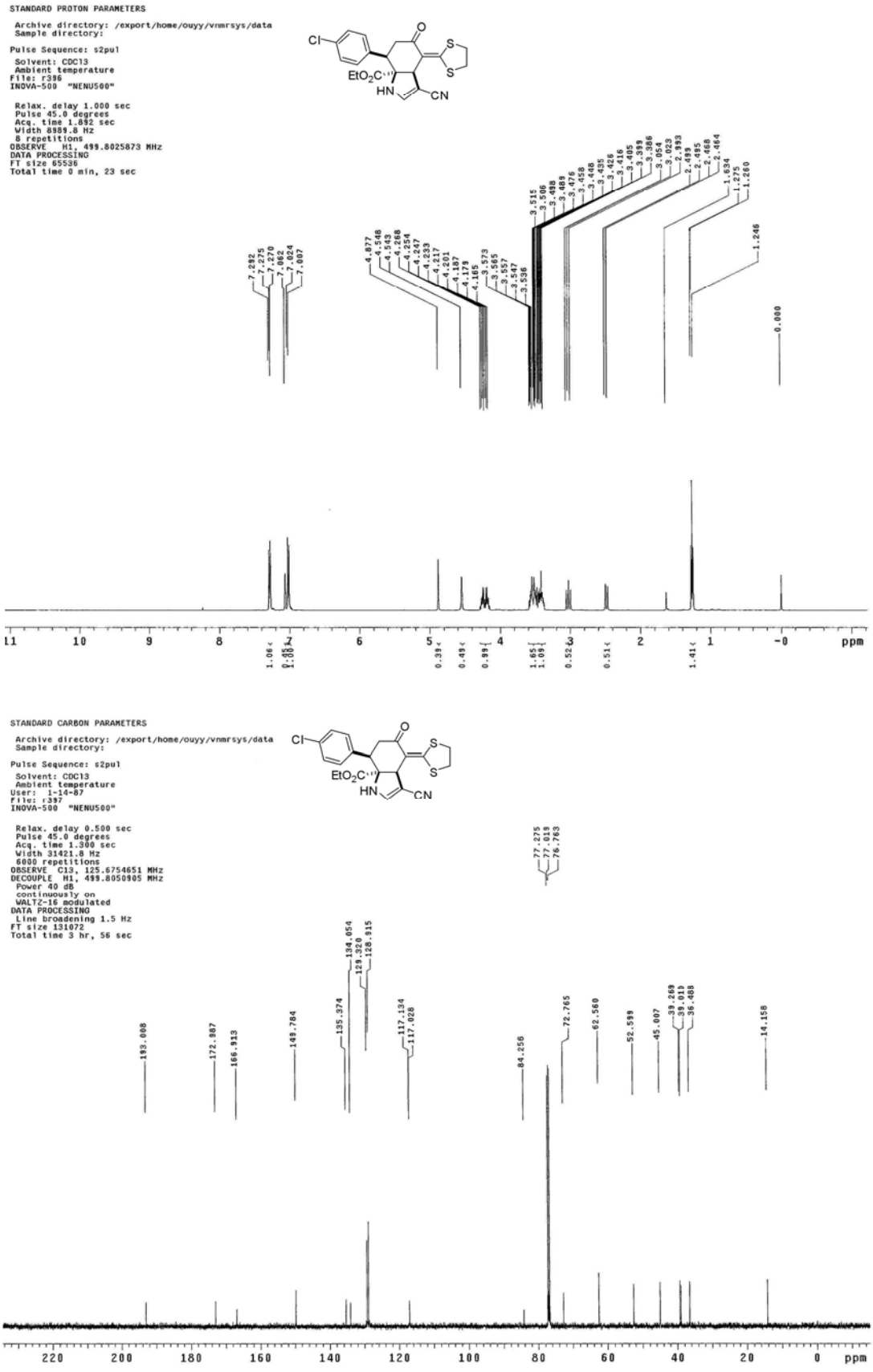


Figure 20. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2m**.

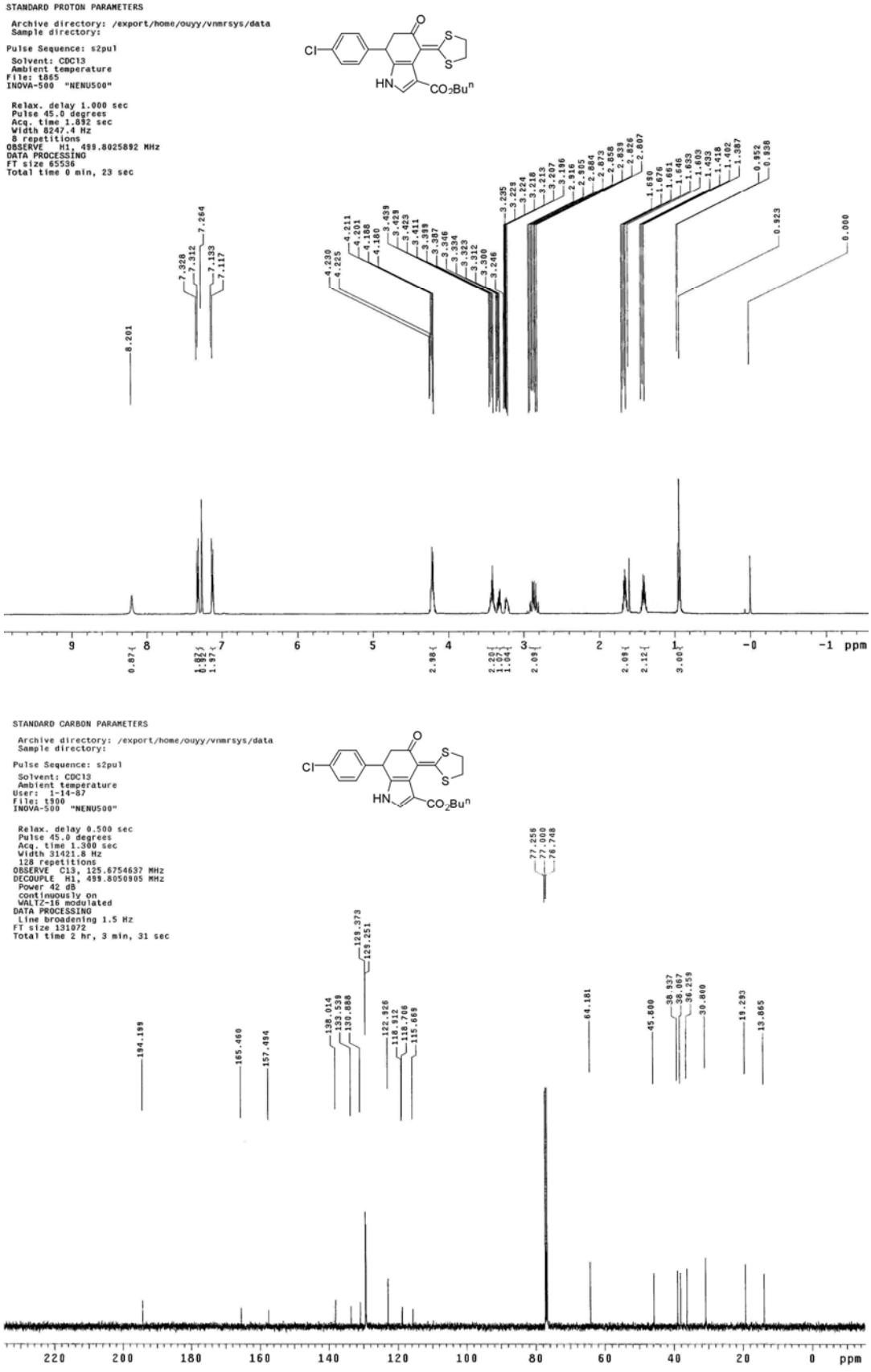


Figure 21. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3a**.

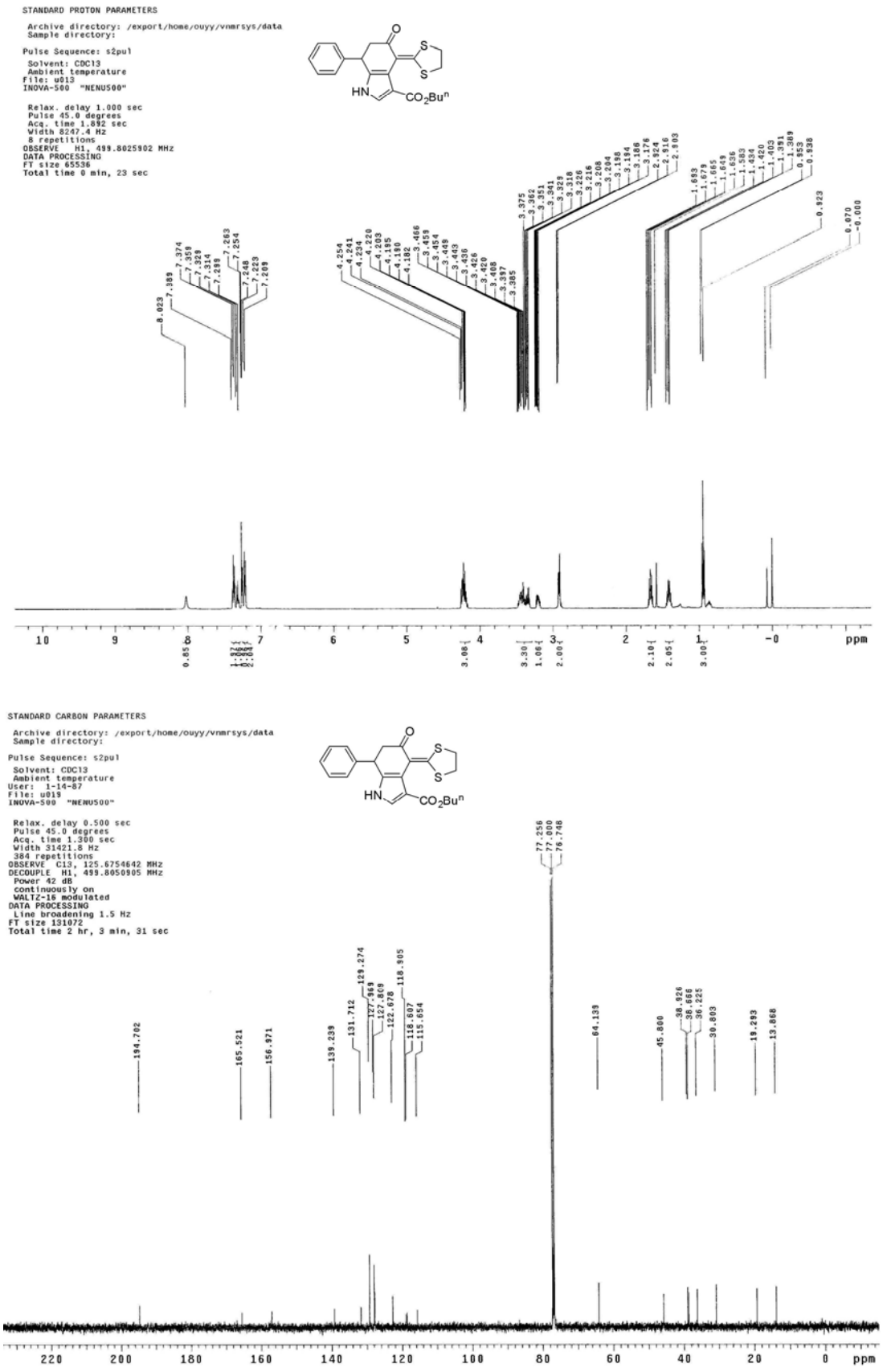


Figure 22. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3b**.

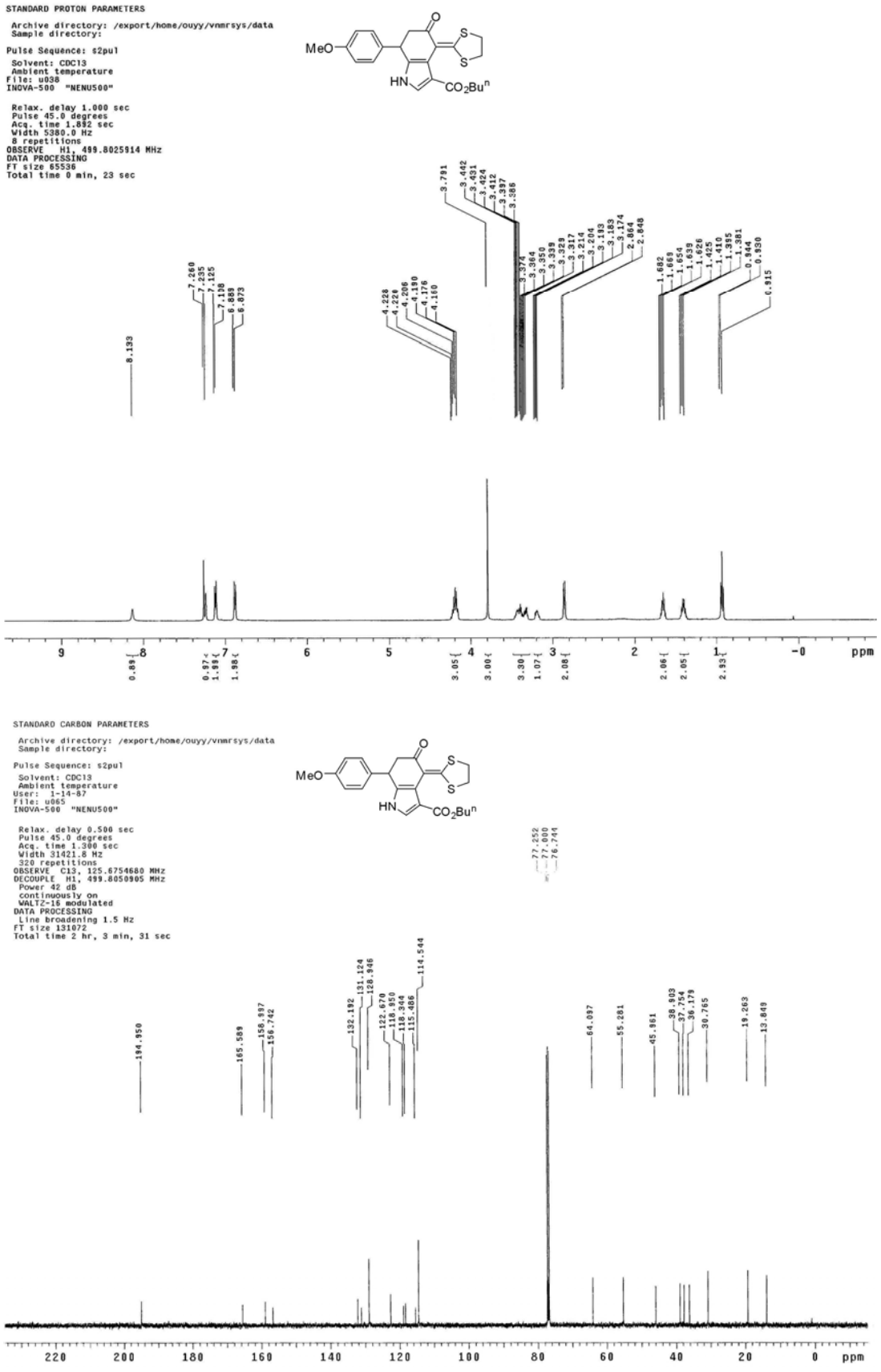


Figure 23. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3c**.

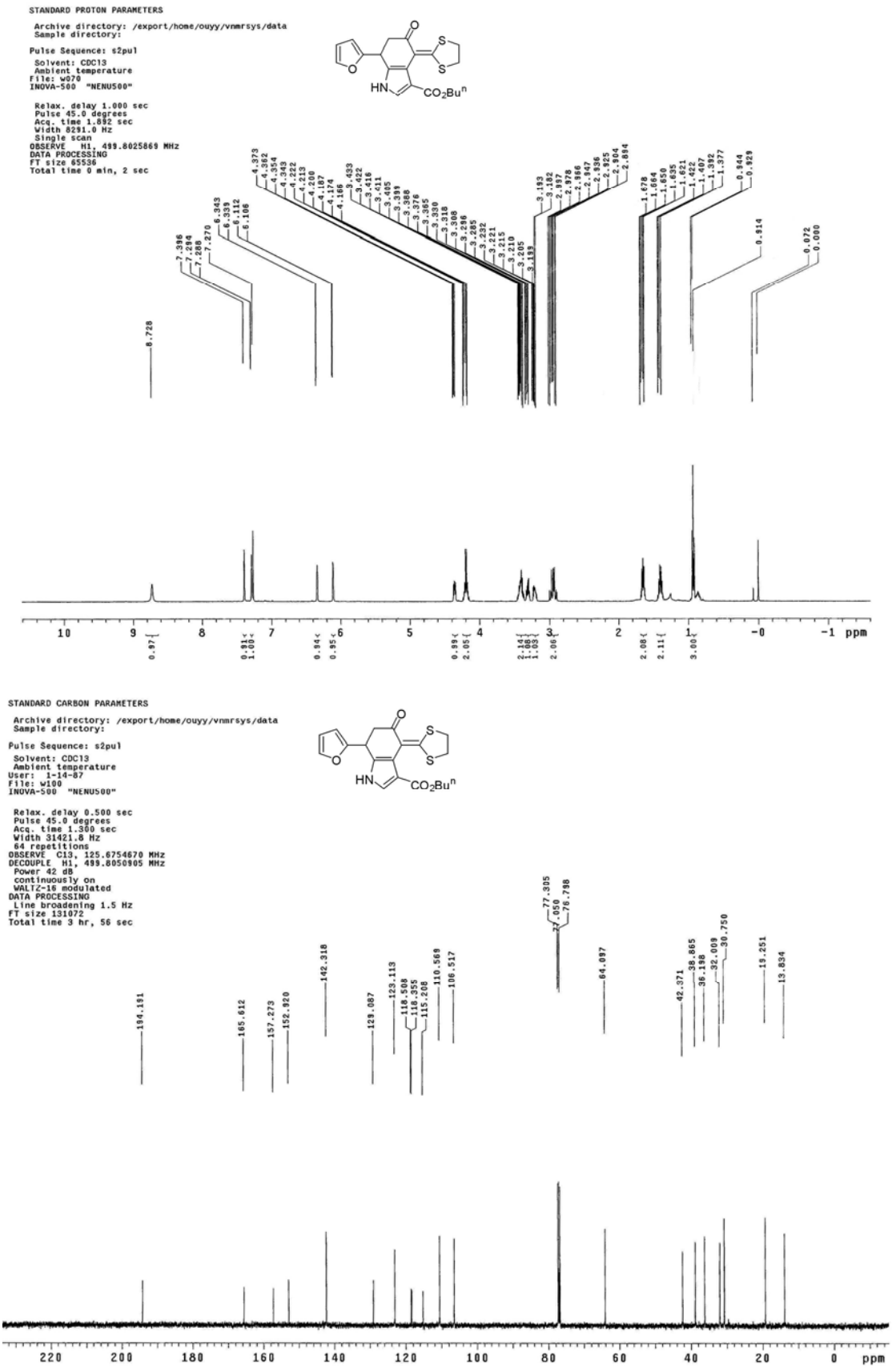


Figure 24. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3i**.

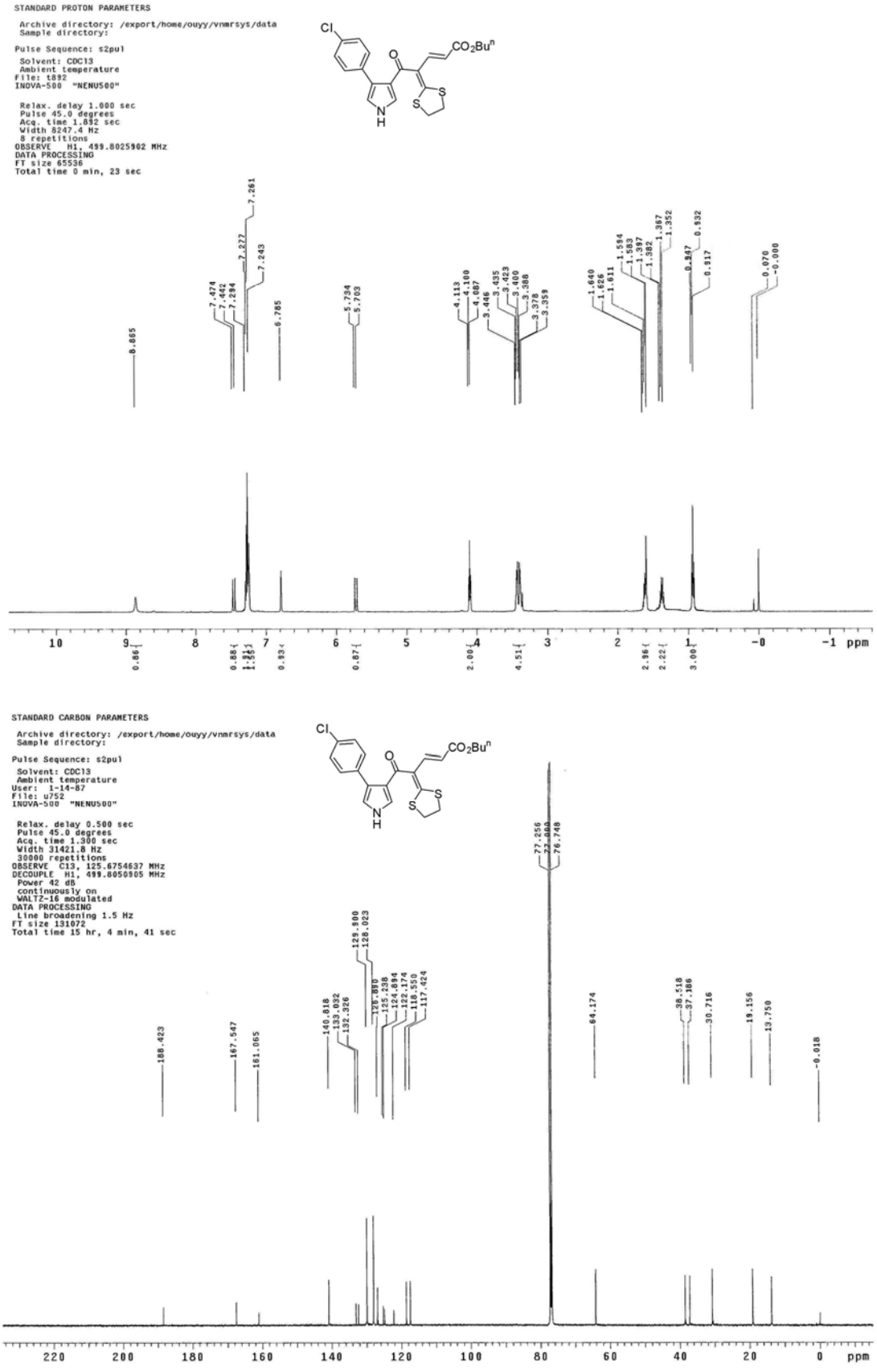


Figure 25. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4a**.