

Supporting Information

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

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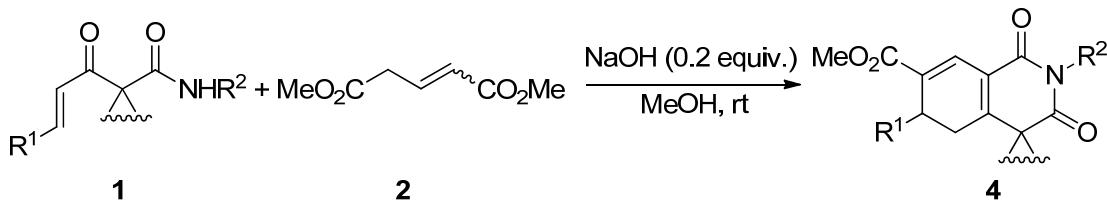
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I. General Information

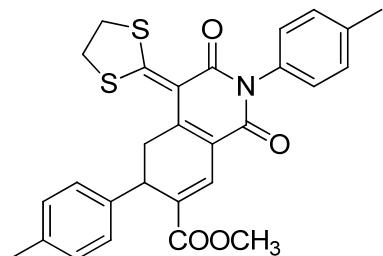
All reagents were commercial and were used without further purification. Chromatography was carried on flash aluminium oxide, basic (200-300 mesh) or silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). Melting points were uncorrected. Unless noted, the ^1H 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 K α radiation ($\lambda = 0.71073\text{\AA}$) 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):



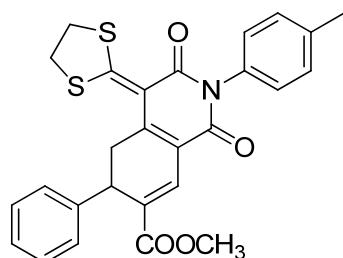
To a solution of **1a** (0.5 mmol, 198 mg) and dimethyl glutaconate **2** (1.0 mmol, 0.14 mL) in MeOH (4.0 mL) was added NaOH (20% mmol, 4 mg) in one portion. The reaction mixture was stirred at r.t. for 18 min. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, 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**):



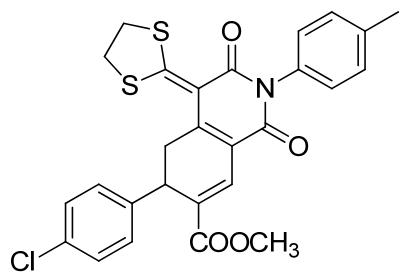
Yellow solid; m.p. 191-193 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.30 (s, 3H), 2.40 (s, 3H), 3.28-3.42 (m, 3H), 3.54 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H), 3.97 (d, *J* = 17.0 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 7.05-7.11 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 2H), 8.09 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ: 20.9, 21.2, 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 C₂₈H₂₆NO₄S₂⁺ ([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**):



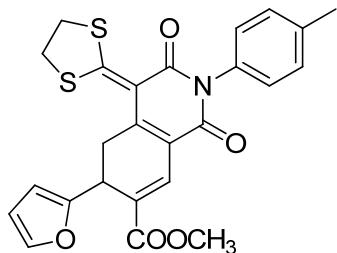
Yellow solid; m.p. 242-244 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.40 (s, 3H), 3.29-3.44 (m, 3H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 3.99 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.33 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.21-7.28 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 8.10 (s, 1H); ¹³C NMR (CDCl₃, 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 C₂₇H₂₄NO₄S₂⁺ ([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):



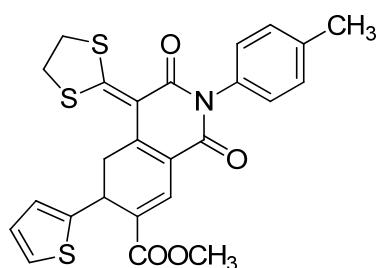
Yellow solid; m.p. 193-195 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.40 (s, 3H), 3.30-3.42 (m, 3H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.74 (s, 3H), 3.96 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.30 (d, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 8.10 (s, 1H); ¹³C NMR (CDCl₃, 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 C₂₇H₂₃ClNO₄S₂⁺ ([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 °C; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₂₅H₂₂NO₅S₂⁺ ([M + H]⁺): 480.0934, found: 480.0937.

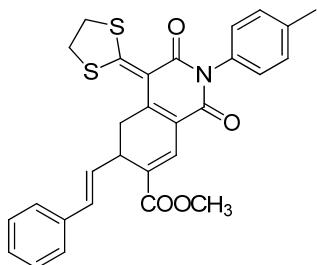
Methyl 4-(1,3-dithiolan-2-ylidene)-1,3-dioxo-6-(thiophen-2-yl)-2-(*p*-tolyl)-1,2,3,4,5,6-hexahydroisoquinoline-7-carboxylate (4e):



Yellow solid; m.p. 230-232 °C; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 125 MHz) δ: 21.3, 32.4, 36.0, 37.7, 38.7, 52.0, 115.4, 118.7, 123.9, 124.6,

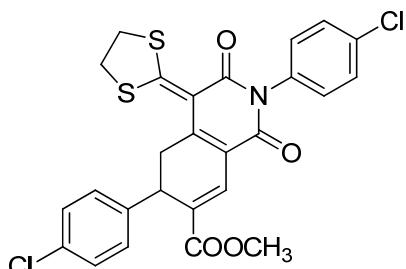
126.6, 127.7, 128.1 (2C), 130.1 (2C), 131.1, 132.7, 138.4, 144.2, 144.3, 161.6, 163.8, 166.4, 178.6. HRMS (ESI-TOF) calcd for $C_{25}H_{22}NO_4S_3^+ ([M + H]^+)$: 496.0705, found: 496.0713.

(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):



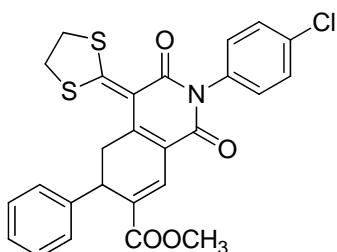
Yellow solid; m.p. 276-278 °C; 1H NMR ($CDCl_3$, 500 MHz) δ: 2.39 (s, 3H), 3.16 (dd, $J = 17.5, 8.5$ Hz, 1H), 3.31-3.42 (m, 2H), 3.57 (t, $J = 6.5$ Hz, 2H), 3.79 (s, 3H), 3.84-3.95 (m, 2H), 6.10 (dd, $J = 16.0, 7.5$ Hz, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 7.0$ 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):



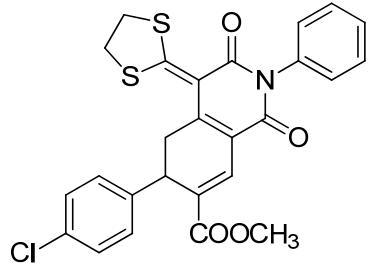
Yellow solid; m.p. 181-183 °C; 1H NMR ($CDCl_3$, 500 MHz) δ: 3.34-3.42 (m, 3H), 3.58 (t, $J = 6.5$ Hz, 2H), 3.75 (s, 3H), 3.96 (d, $J = 17.0$, 1H), 4.32 (d, $J = 11.0$ Hz, 1H), 7.14 (d, $J = 2.5$ Hz, 2H), 7.15 (d, $J = 3.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 9.0$ Hz, 2H), 8.09 (s, 1H); ^{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):



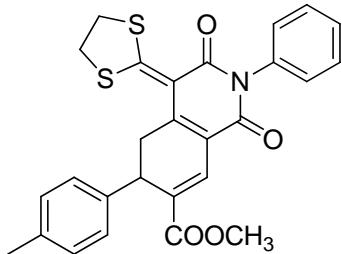
Yellow solid; m.p. 187-189 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 3.32-3.38 (m, 2H), 3.41 (dd, $J = 17.5, 10.0$ Hz, 1H), 3.56 (t, $J = 6.0$ Hz, 2H), 3.74 (s, 3H), 4.00 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.34 (d, $J = 8.5$ Hz, 1H), 7.15 (d, $J = 6.5$ Hz, 2H), 7.20-7.28 (m, 5H), 7.46 (d, $J = 8.5$ Hz, 2H), 8.09 (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 $\text{C}_{26}\text{H}_{21}\text{ClNO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



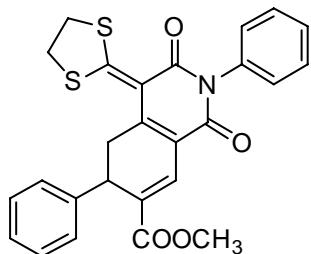
Yellow solid; m.p. 187-189 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 3.31-3.43 (m, 3H), 3.56 (t, $J = 6.0$ Hz, 2H), 3.74 (s, 3H), 3.96 (dd, $J = 17.0, 1.5$ Hz, 1H), 4.31 (d, $J = 8.5$ Hz, 1H), 7.15 (d, $J = 8.5$ Hz, 2H), 7.17-7.24 (m, 4H), 7.43 (t, $J = 7.0$ Hz, 1H), 7.50 (t, $J = 7.0$ Hz, 2H), 8.11 (s, 1H); ^{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 $\text{C}_{26}\text{H}_{21}\text{ClNO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



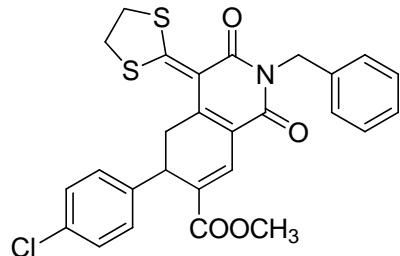
Yellow solid; m.p. 165-167 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 2.30 (s, 3H), 3.31-3.36 (m, 2H), 3.40 (dd, $J = 17.0, 9.5$ Hz, 1H), 3.55 (t, $J = 5.5$ Hz, 2H), 3.73 (s, 3H), 3.97 (d, $J = 17.5$ Hz, 1H), 4.30 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.0$ 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 $\text{C}_{27}\text{H}_{24}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



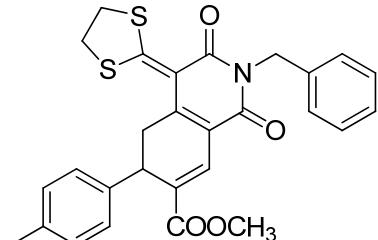
Yellow solid; m.p. 197-199 °C; ^1H NMR (CDCl_3 , 500 MHz) δ: 3.30-3.37 (m, 2H), 3.42 (dd, $J = 17.5, 10.0$ Hz, 1H), 3.55 (t, $J = 6.5$ Hz, 2H), 3.74 (s, 3H), 4.00 (dd, $J = 17.5, 1.5$ Hz, 1H), 4.34 (d, $J = 9.0$ Hz, 1H), 7.20-7.28 (m, 7H), 7.42 (t, $J = 7.0$ Hz, 1H), 7.50 (t, $J = 8.0$ Hz, 2H), 8.11 (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 $\text{C}_{26}\text{H}_{22}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 476.0985, found: 476.1001.

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



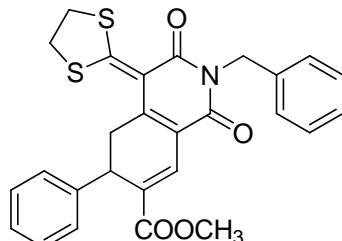
Yellow solid; m.p. 280-282 °C; ^1H NMR (CDCl_3 , 500 MHz) δ: 3.29-3.39 (m, 3H), 3.54 (t, $J = 7.0$ Hz, 2H), 3.73 (s, 3H), 3.86 (d, $J = 17.5$ Hz, 1H), 4.25 (d, $J = 9.0$ Hz, 1H), 5.21 (dd, $J = 14.0, 14.0$ Hz, 2H), 7.08 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 9.0$ Hz, 2H), 7.24-7.31 (m, 3H), 7.44 (d, $J = 7.0$ 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 $\text{C}_{27}\text{H}_{23}\text{ClNO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



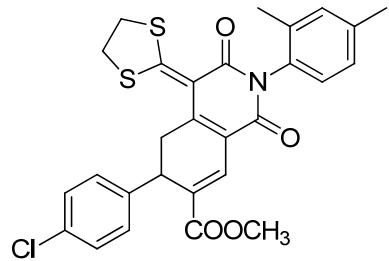
Yellow solid; m.p. 263-265 °C; ^1H NMR (CDCl_3 , 500 MHz) δ: 2.27 (s, 3H), 3.29-3.38 (m, 3H), 3.52 (t, $J = 6.0$ Hz, 2H), 3.72 (s, 3H), 3.88 (d, $J = 16.5$, 1H), 4.25 (d, $J = 9.0$ Hz, 1H), 5.21 (dd, $J = 14.0, 13.5$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 7.5$ 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 $\text{C}_{28}\text{H}_{26}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



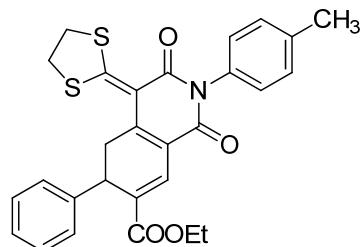
Yellow solid; m. p. 253-255 °C; ^1H NMR (CDCl_3 , 500 MHz) δ: 3.29-3.38 (m, 3H), 3.52 (t, $J = 6.0$ Hz, 2H), 3.73 (s, 3H), 3.91 (d, $J = 16.5$ Hz, 1H), 4.28 (d, $J = 9.0$ Hz, 1H), 5.21 (dd, $J = 14.5, 14.0$ Hz, 2H), 7.15-7.30 (m, 8H), 7.43 (d, $J = 6.5$ Hz, 2H), 8.12 (s, 1H); ^{13}C NMR (CDCl_3 , 125 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 $\text{C}_{27}\text{H}_{24}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



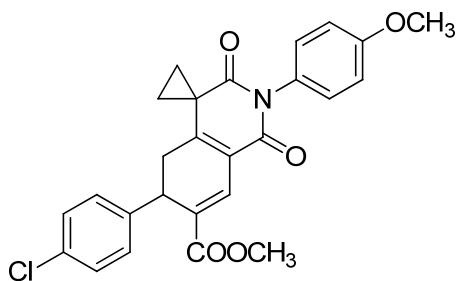
Yellow solid; m.p. 278-280 °C; ^1H NMR (CDCl_3 , 500 MHz) δ: 2.00 (s, 3H), 2.36 (s, 3H), 3.29-3.42 (m, 3H), 3.53-3.58 (m, 2H), 3.74 (s, 3H), 3.89 (d, $J = 17.0$ Hz, 1H), 4.30 (d, $J = 9.5$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 6.5$ Hz, 2H), 7.15 (d, $J = 6.5$ Hz, 2H), 7.20 (d, $J = 8.0$ 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 $\text{C}_{28}\text{H}_{25}\text{ClNO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



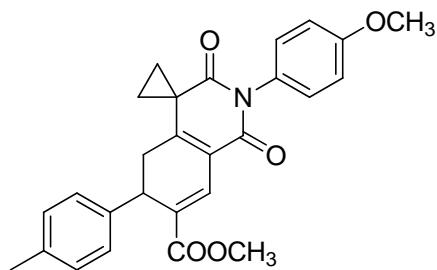
Yellow solid; m. p. 144-146 °C; ^1H NMR (CDCl_3 , 300 MHz) δ: 1.27 (t, $J = 9.0$ Hz, 3H), 2.41 (s, 3H), 3.33-3.47 (m, 3H), 3.56 (t, $J = 6.0$ Hz, 2H), 4.00 (d, $J = 15.0$ Hz, 1H), 4.20 (q, $J = 9.0$ Hz, 2H), 4.35 (d, $J = 9.0$ Hz, 1H), 7.10 (d, $J = 9.0$ Hz, 2H), 7.24-7.32 (m, 7H), 8.11 (s, 1H); ^{13}C 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 $\text{C}_{28}\text{H}_{26}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



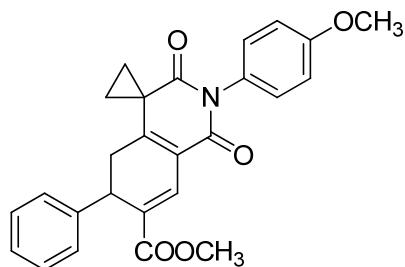
Green solid; m.p. 186-187 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 1.26 (tt, $J = 9.0, 3.5$ Hz, 1H), 1.74 (tt, $J = 9.0, 4.0$ Hz, 1H), 1.83 (tt, $J = 8.0, 5.0$ Hz, 1H), 2.04 (tt, $J = 9.0, 4.0$ Hz, 1H), 2.23 (d, $J = 17.5$ Hz, 1H), 2.86 (dd, $J = 9.5, 17.0$ Hz, 1H), 3.74 (s, 3H), 3.84 (s, 3H), 4.17 (d, $J = 9.0$ 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 $\text{C}_{26}\text{H}_{23}\text{ClNO}_5^+$ ($[\text{M} + \text{H}]^+$): 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; ^1H 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 $\text{C}_{27}\text{H}_{26}\text{NO}_5^+$ ($[\text{M} + \text{H}]^+$): 444.1805, found: 444.1802.

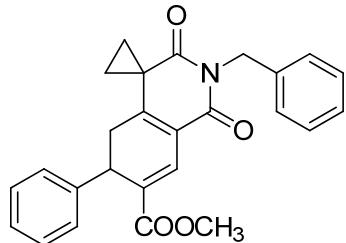
Methyl 2'-(4-methoxyphenyl)-1',3'-dioxo-6'-phenyl-2',3',5',6'-tetrahydro-1'H-spiro [cyclopropane-1,4'-isoquinoline]-7'-carboxylate (4s):



Green solid; m.p. 137-139 °C; ^1H 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,

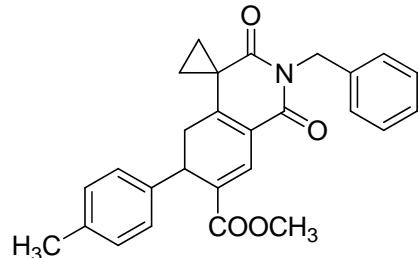
127.3, 127.4, 128.8 (2C), 129.2 (2C), 130.1, 140.3, 153.4, 159.4, 163.3, 166.6, 172.0. HRMS (ESI-TOF) calcd for $C_{26}H_{24}NO_5^+$ ($[M + H]^+$): 430.1649, found: 430.1647.

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



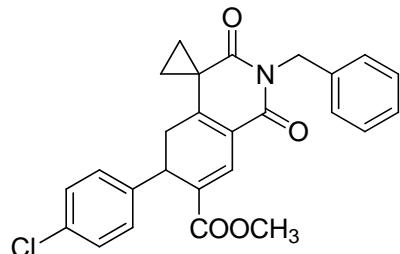
Green solid; m. p. 170-172 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 1.17 (tt, *J* = 8.5, 3.5 Hz, 1H), 1.64-1.68 (m, 1H), 1.74 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.93 (tt, *J* = 8.5, 4.0 Hz, 1H), 2.15 (d, *J* = 17.5 Hz, 1H), 2.77 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.72 (s, 3H), 4.15 (d, *J* = 9.5 Hz, 1H), 5.08 (dd, *J* = 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); ¹³C NMR (CDCl₃, 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):



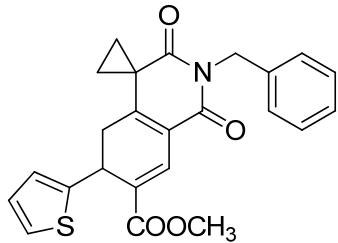
Green solid; m. p. 72-74 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 1.20 (tt, *J* = 8.5, 3.5 Hz, 1H), 1.66 (tt, *J* = 9.0, 4.0 Hz, 1H), 1.75 (tt, *J* = 9.0, 3.5 Hz, 1H), 1.97 (tt, *J* = 9.0, 3.5 Hz, 1H), 2.23 (d, *J* = 17.0 Hz, 1H), 2.28 (s, 3H), 2.75 (dd, *J* = 17.5, 9.5 Hz, 1H), 3.72 (s, 3H), 4.11 (d, *J* = 9.5 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); ¹³C NMR (CDCl₃, 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):



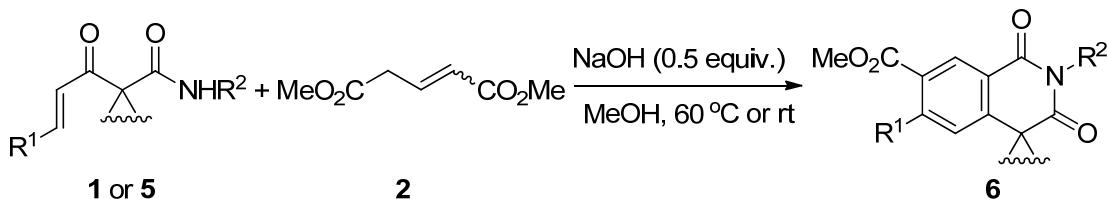
Green solid; m. p. 75-77 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 1.18 (tt, $J = 8.5, 3.5$ Hz, 1H), 1.66 (tt, $J = 9.0, 4.0$ Hz, 1H), 1.78 (tt, $J = 9.0, 4.0$ Hz, 1H), 1.99 (tt, $J = 9.0, 4.0$ Hz, 1H), 2.11 (d, $J = 17.5$ Hz, 1H), 2.77 (dd, $J = 18.0, 9.5$ Hz, 1H), 3.73 (s, 3H), 4.12 (d, $J = 9.5$ Hz, 1H), 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 $\text{C}_{26}\text{H}_{23}\text{ClNO}_4^+$ ($[\text{M} + \text{H}]^+$): 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):



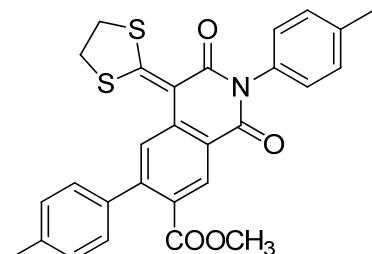
Green solid; m. p. 133-135 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 1.52-1.54 (m, 1H), 1.69-1.72 (m, 1H), 1.90-1.92 (m, 1H), 1.99-2.01 (m, 1H), 2.28 (d, $J = 17.5$ Hz, 1H), 2.71 (dd, $J = 17.5, 8.5$ Hz, 1H), 3.77 (s, 3H), 4.43 (d, $J = 8.5$ Hz, 1H), 5.08 (s, 2H), 6.77 (d, $J = 3.0$ Hz, 1H), 6.84 (d, $J = 4.0$ 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 $\text{C}_{24}\text{H}_{22}\text{NO}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 420.1264, found: 420.1266.

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



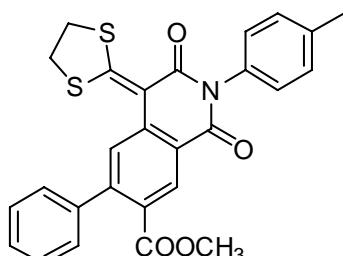
To a solution of (E)-2-(1,3-dithiolan-2-ylidene)-3-oxo-N,5-di-p-tolylpent-4-enamide **1a** (0.5 mmol, 198 mg) and dimethyl glutaconate **2** (1.0 mmol, 0.14 mL) in MeOH (4.0 mL) was added NaOH (50% mmol, 10 mg) in one portion. The reaction mixture was stirred at 60 °C for 4 h. After **1a** was consumed (monitored by TLC), the reaction mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄, 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**):



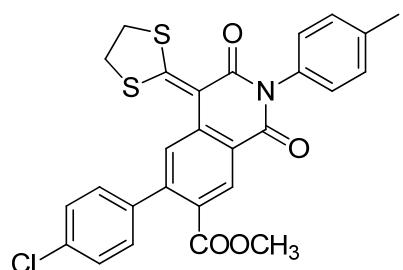
Yellow solid; m.p. 286-298 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.42 (s, 3H), 2.43 (s, 3H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 8.31 (s, 1H), 8.79 (s, 1H); ¹³C NMR (CDCl₃, 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 C₂₈H₂₄NS₂O₄⁺ ([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**):



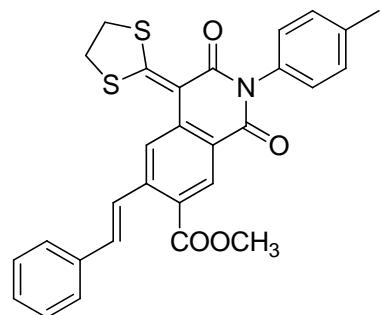
Yellow solid; m.p. 184-186 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.42 (s, 3H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.72 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.43-7.47 (m, 5H), 8.32 (s, 1H), 8.81 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ: 21.3, 38.0, 38.2, 52.3, 112.5, 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 C₂₇H₂₂NS₂O₄⁺ ([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):



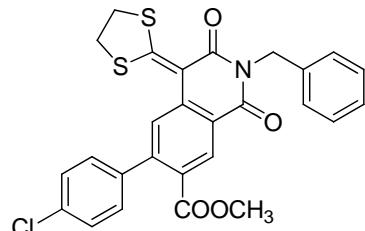
Yellow solid; m.p. 186-188 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 2.42 (s, 3H), 3.43 (t, J = 6.5 Hz, 2H), 3.59 (t, J = 5.5 Hz, 2H), 3.75 (s, 3H), 7.14 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 9.0 Hz, 2H), 8.28 (s, 1H), 8.84 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) 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 $\text{C}_{27}\text{H}_{21}\text{ClNS}_2\text{O}_4^+ ([\text{M} + \text{H}]^+)$: 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):



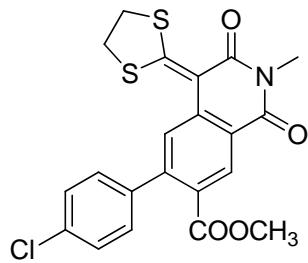
Yellow solid; m.p. 292-294 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 2.42 (s, 3H), 3.46 (t, J = 7.0 Hz, 2H), 3.63 (t, J = 6.0 Hz, 2H), 3.95 (s, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 16.5 Hz, 1H), 7.33 (t, J = 8.0 Hz, 3H), 7.40 (t, J = 8.0 Hz, 2H), 7.63 (d, J = 7.5 Hz, 2H), 8.17 (d, J = 16.0 Hz, 1H), 8.61 (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 $\text{C}_{29}\text{H}_{24}\text{NO}_4\text{S}_2^+ ([\text{M} + \text{H}]^+)$: 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):



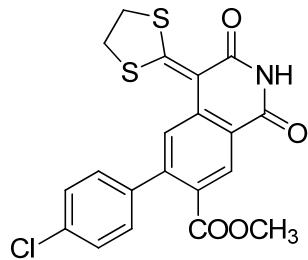
Yellow solid; m.p. 111-113 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 3.43 (t, J = 7.0 Hz, 2H), 3.57 (t, J = 6.0 Hz, 2H), 3.75 (s, 3H), 5.32 (s, 2H), 7.24 (d, J = 7.5 Hz, 1H), 7.26-7.33 (m, 4H), 7.41 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 8.19 (s, 1H), 8.84 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 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 $\text{C}_{27}\text{H}_{21}\text{NClS}_2\text{O}_4^+ ([\text{M} + \text{H}]^+)$: 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):



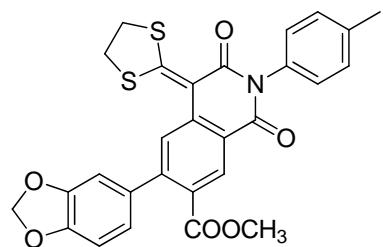
Yellow solid; m.p. 176-178 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 3.44 (t, *J* = 5.5 Hz, 2H), 3.50 (s, 3H), 3.58 (t, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 8.22 (s, 1H), 8.83 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ: 27.5, 37.8, 38.1, 52.2, 112.4, 122.3, 127.7, 128.3, 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 C₂₁H₁₇ClNS₂O₄⁺ ([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):



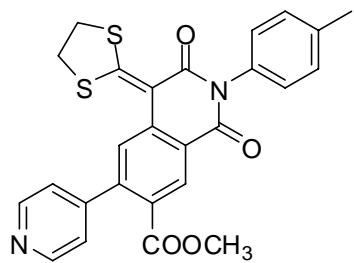
Yellow solid; m.p. 243-245 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 3.48 (t, *J* = 7.0 Hz, 2H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.76 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 8.23 (s, 1H), 8.27 (s, 1H), 8.81 (s, 1H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ: 38.2, 38.8, 52.8, 111.5, 122.7, 127.4, 128.7, 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 C₂₀H₁₅ClNO₄S₂⁺ ([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):



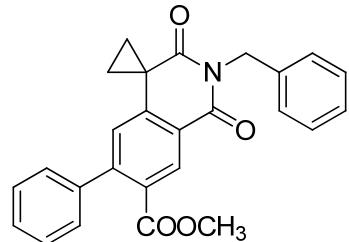
Yellow solid; m.p. 293-195 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 2.42 (s, 3H), 3.43 (t, *J* = 6.0 Hz, 2H), 3.59 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 6.05 (s, 2H), 6.90 (s, 2H), 6.94 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 8.28 (s, 1H), 8.76 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ: 21.2, 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 C₂₈H₂₂NS₂O₆⁺ ([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):



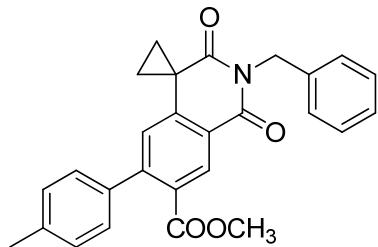
Yellow solid; m. p. 277-279 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 2.42 (s, 3H), 3.43 (t, $J = 6.0$ Hz, 2H), 3.59 (t, $J = 6.0$ Hz, 2H), 3.77 (s, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 8.31 (s, 1H), 8.68 (d, $J = 4.0$ Hz, 1H), 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 $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}_4\text{S}_2^+$ ($[\text{M} + \text{H}]^+$): 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):



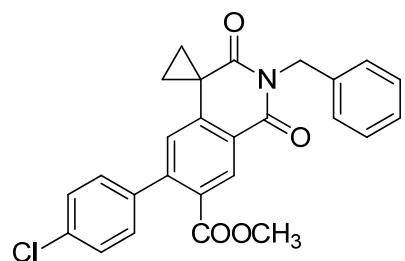
White solid; m.p. 169-171 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 1.69 (q, $J = 4.0$ Hz, 2H), 2.22 (q, $J = 4.0$ Hz, 2H), 3.69 (s, 3H), 5.24 (s, 2H), 6.74 (s, 1H), 7.25-7.32 (m, 5H), 7.42 ($J = 6.5$ Hz, 3H), 7.46 (t, $J = 7.5$ Hz, 2H), 8.76 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ : 25.7, 27.9 (2C), 43.9, 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 $\text{C}_{26}\text{H}_{22}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$): 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):



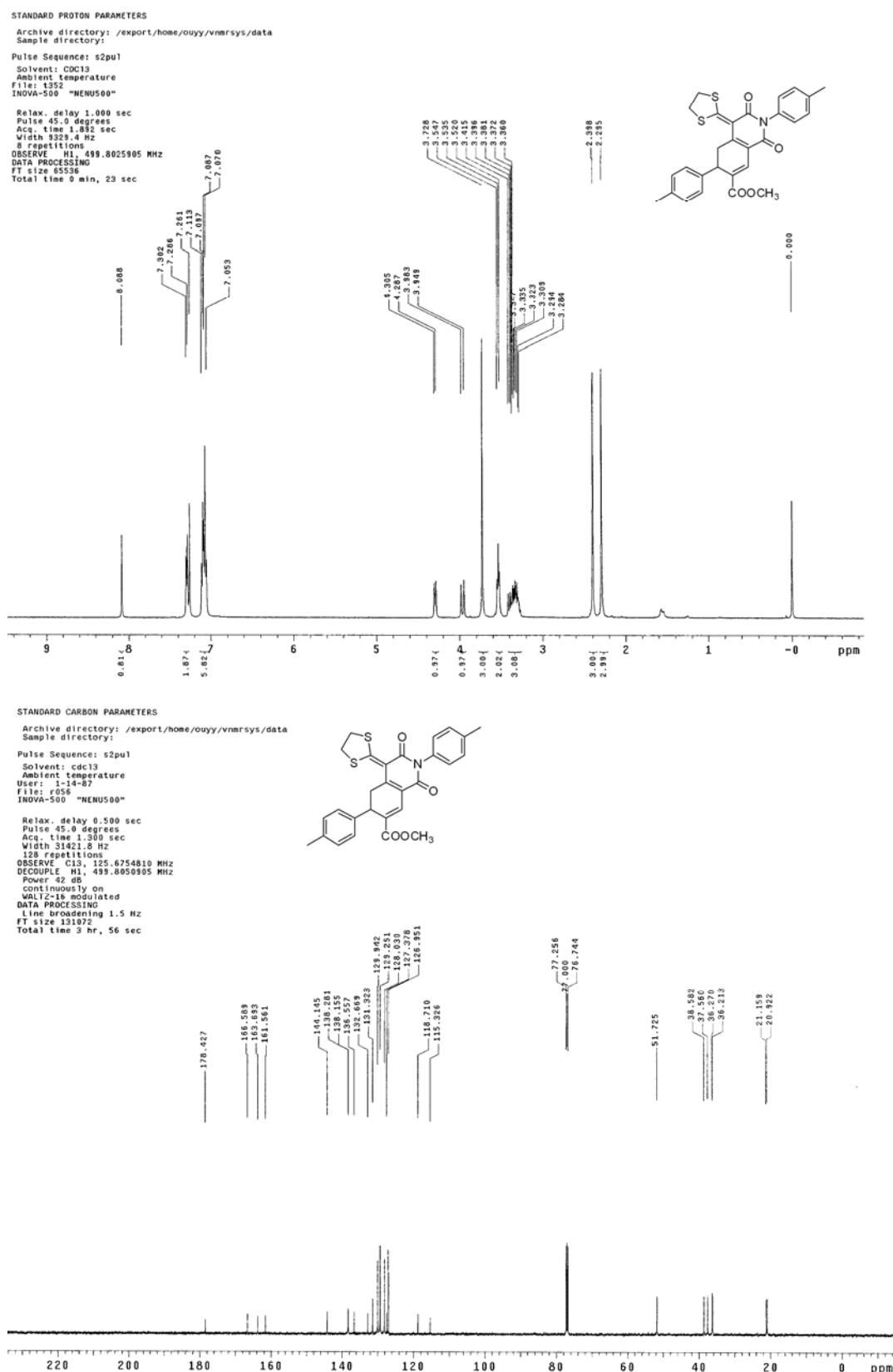
White solid; m.p. 163-165 °C; ^1H NMR (CDCl_3 , 500 MHz) δ : 1.68 (q, $J = 4.0$ Hz, 2H), 2.21 (q, $J = 4.0$ Hz, 2H), 2.41 (s, 3H), 3.72 (s, 3H), 5.24 (s, 2H), 6.73 (s, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.22-7.25 (m, 3H), 7.26-7.32 (m, 2H), 7.47 (d, $J = 9.0$ Hz, 2H), 8.74 (s, 1H); ^{13}C NMR (CDCl_3 , 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 $\text{C}_{27}\text{H}_{24}\text{NO}_4^+$ ($[\text{M} + \text{H}]^+$): 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 °C; ^1H 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 $\text{C}_{26}\text{H}_{21}\text{NClO}_4^+ ([\text{M} + \text{H}]^+)$: 446.1154, found: 446.1152.

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



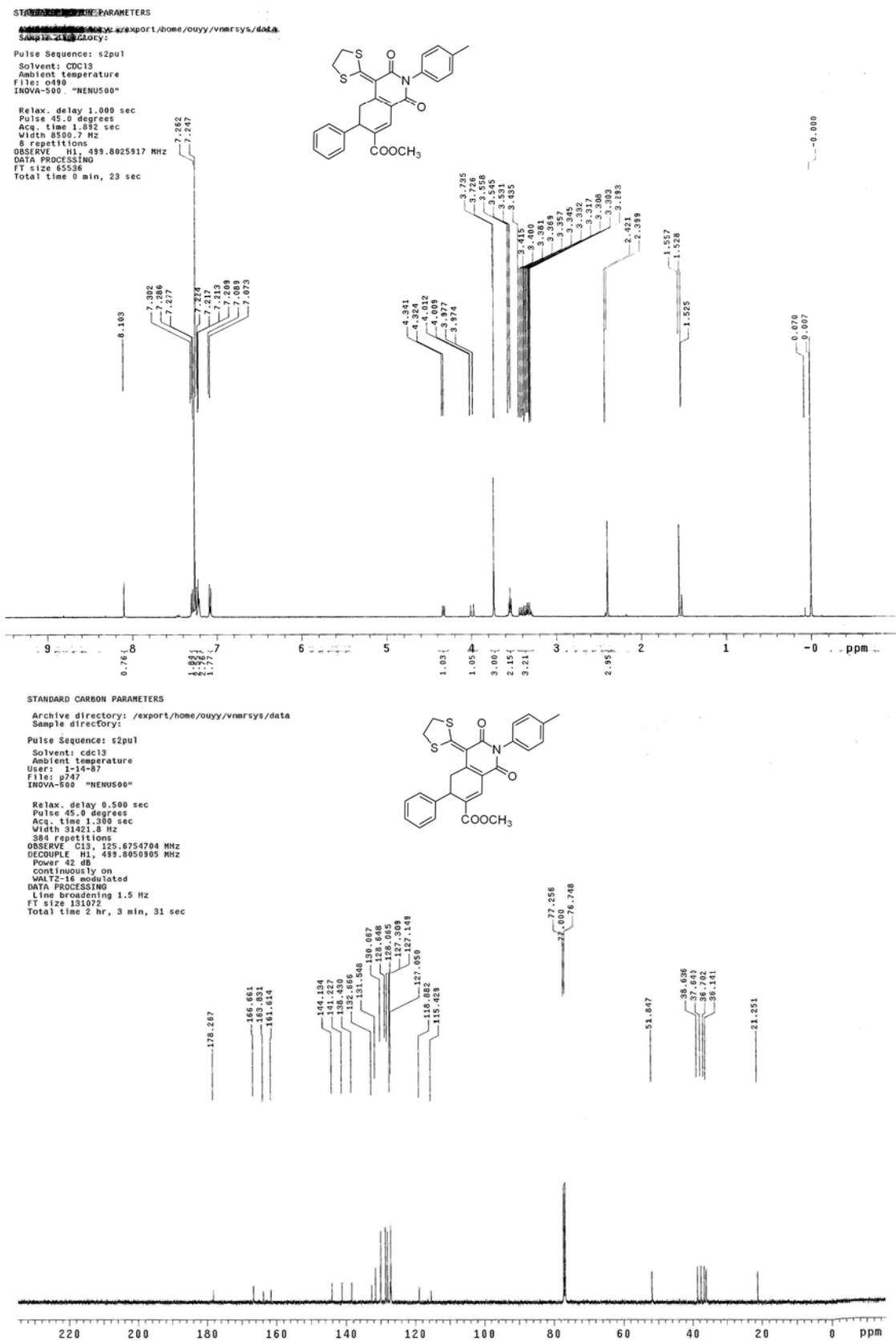


Figure 2. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **4b**.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: m196

INOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.882 sec

Width 8355.6 Hz

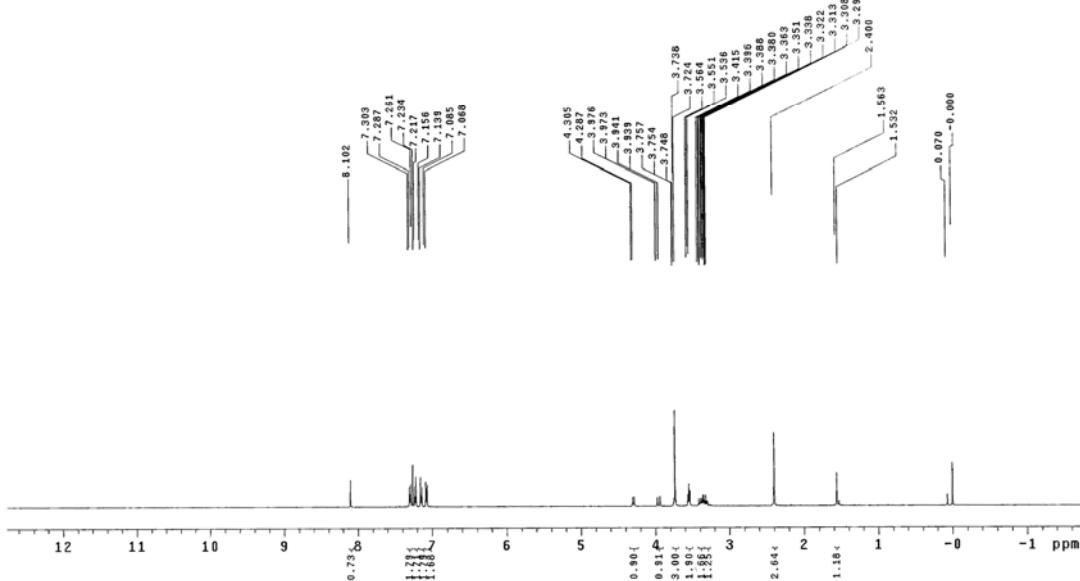
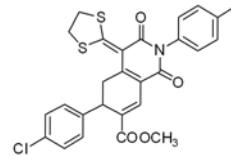
5 points

OBSERVE H1, 499.8025911 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: x370

File: x370

INOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

256 points

OBSERVE C13, 123.6754728 MHz

DECOPPLE H1, 499.8050905 MHz

PROBLEMS

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 12 hr, 33 min, 54 sec

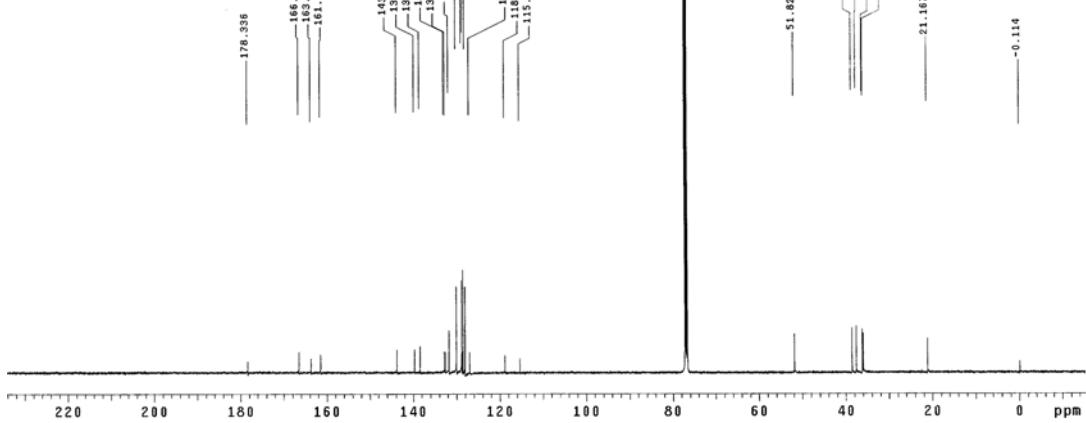
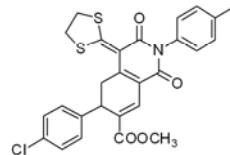
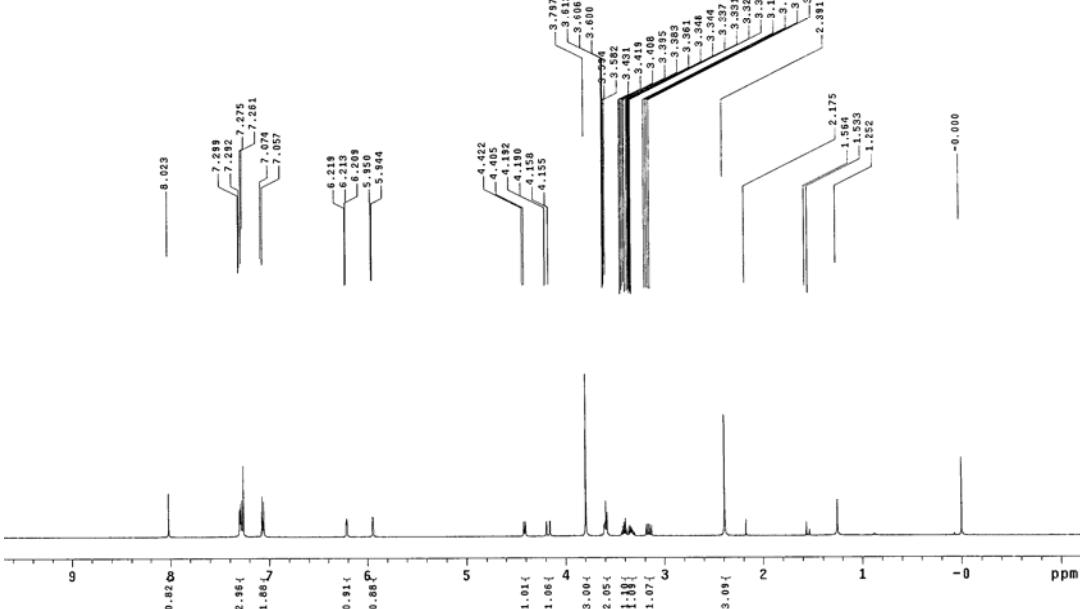
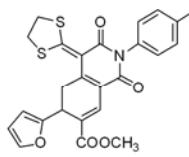


Figure 3. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4c.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: g518 "NENUESO0"
INOVA-500 "NENUESO0"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 1.892 sec
Width 8500.7 Hz
8 repetitions
OBSERVE FID 493.8025914 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: g518 "NENUESO0"
INOVA-500 "NENUESO0"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acc. time 1.892 sec
Width 81421.8 Hz
128 repetitions
OBSERVE C13, 125.6754704 MHz
DQCPMG 125.6754704 MHz
Power 42 dB
continuously on
WALTZ-13 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

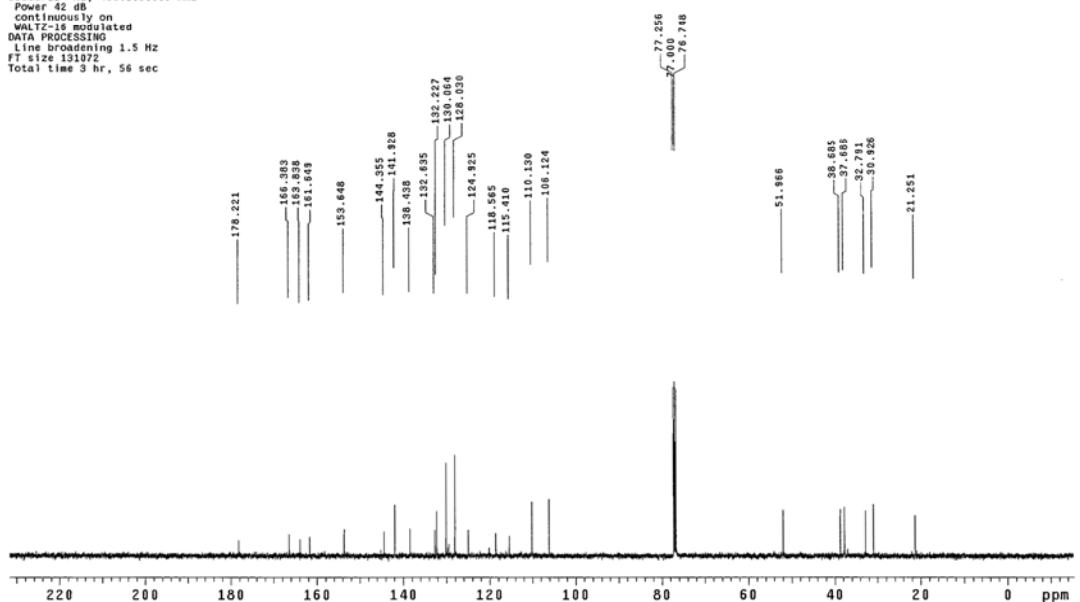
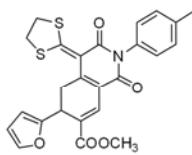
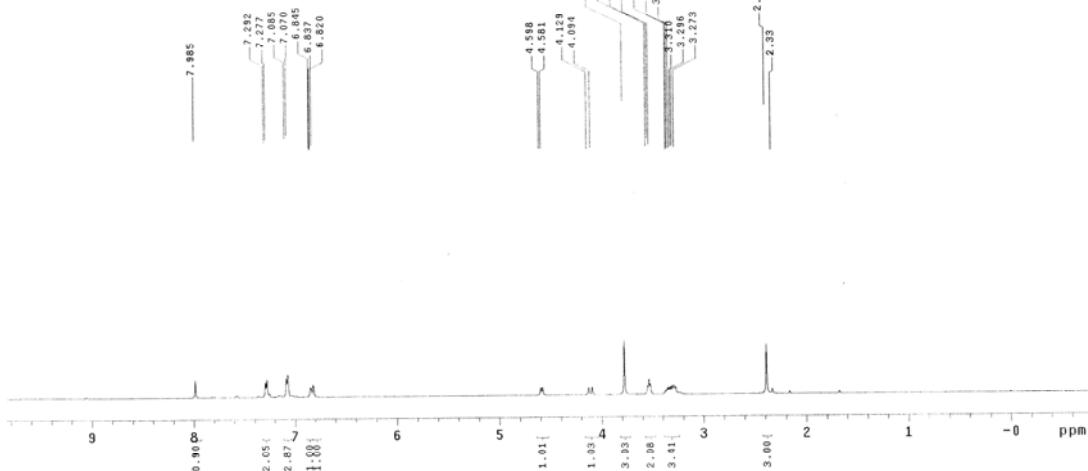
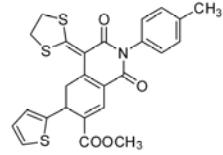


Figure 4. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4d.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: f728
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 90 degrees
Acc. time 1.892 sec
Width 10311.9 Hz
4 repetitions
OBSERVE H1, 499.8025962 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 11 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 34-07
File: f728
INOVA-500 "NENUS00"
Relax. delay 0.500 sec
Pulse 90 degrees
Acc. time 1.300 sec
Width 31421.8 Hz
4096 points
OBSERVE C13, 125.6754693 MHz
DECOPPLE H1, 499.8050905 MHz
Power 42 dB
coupling on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

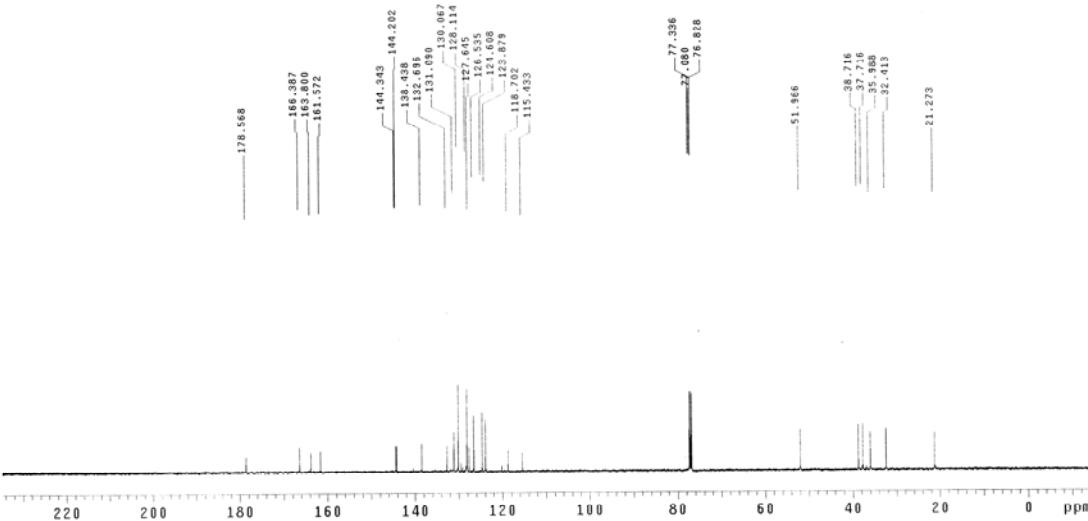
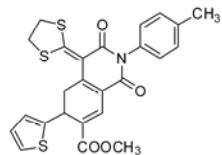
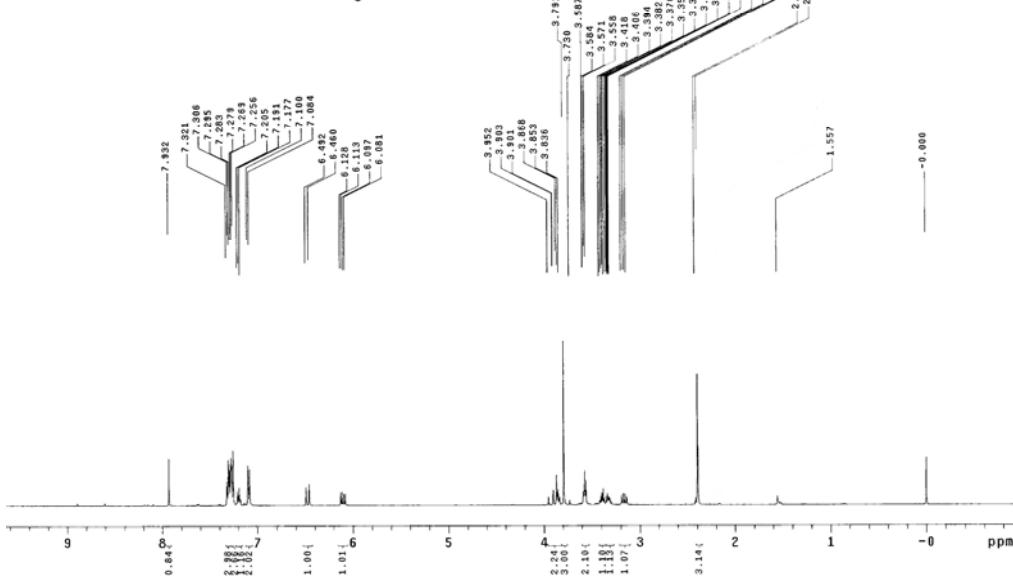
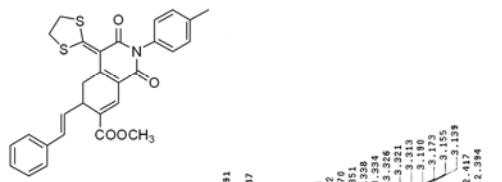


Figure 4. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4e.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: v252
INOVA-500 "NEMUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 1.892 sec
Width 31421.0 Hz
8 repetitions
OBSERVE H1, 499.8025934 MHz
DECOUPLE H1, 499.8056905 MHz
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: v252
INOVA-500 "NEMUS00"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acc. time 1.300 sec
Width 31421.0 Hz
2000 acquisitions
OBSERVE C13, 125.6754675 MHz
DECOUPLE H1, 499.8056905 MHz
Power 52 dB
continuously on
WALTZ-16 modulated
Data points 65536
Line broadening 1.5 Hz
FT size 131072
Total time 10 hr, 3 min, 7 sec

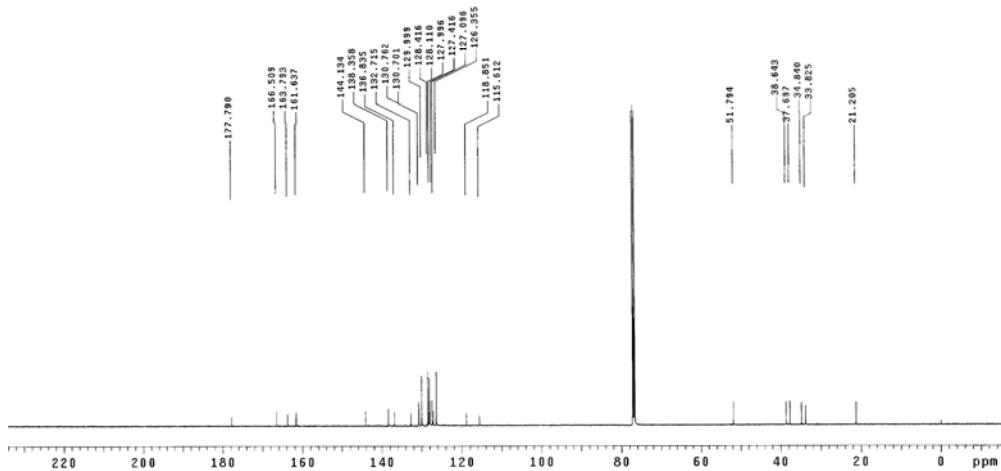
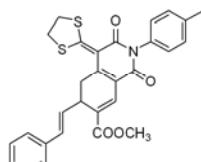
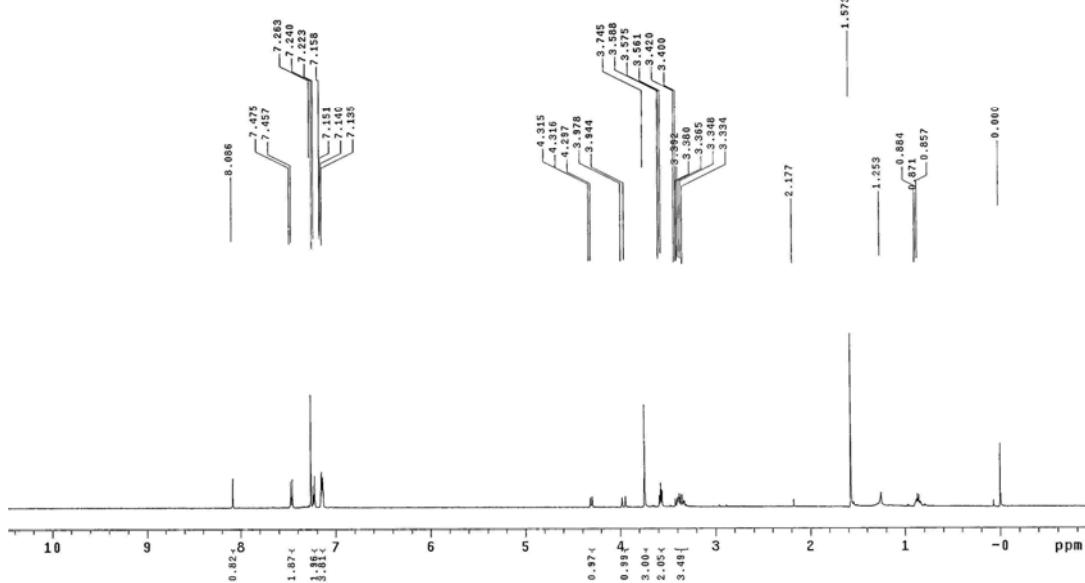
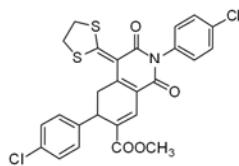


Figure 6. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4f.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: n750
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse width 90°
Acc. time 1.892 sec
Width 8990.6 Hz
8 repetitions
DECOUPLE H-1 499.8025912 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: p022 "NENUS00"
INOVA-500
Relax. delay 0.500 sec
Pulse width 90°
Acc. time 1.890 sec
Width 31421.8 Hz
128 repetitions
DECOUPLE H-1 499.8050905 MHz
DECOUPLE H-1 125.6754680 MHz
DECUPPLE H-1 499.8050905 MHz
Power 42 dB
continues on
WIDENING modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

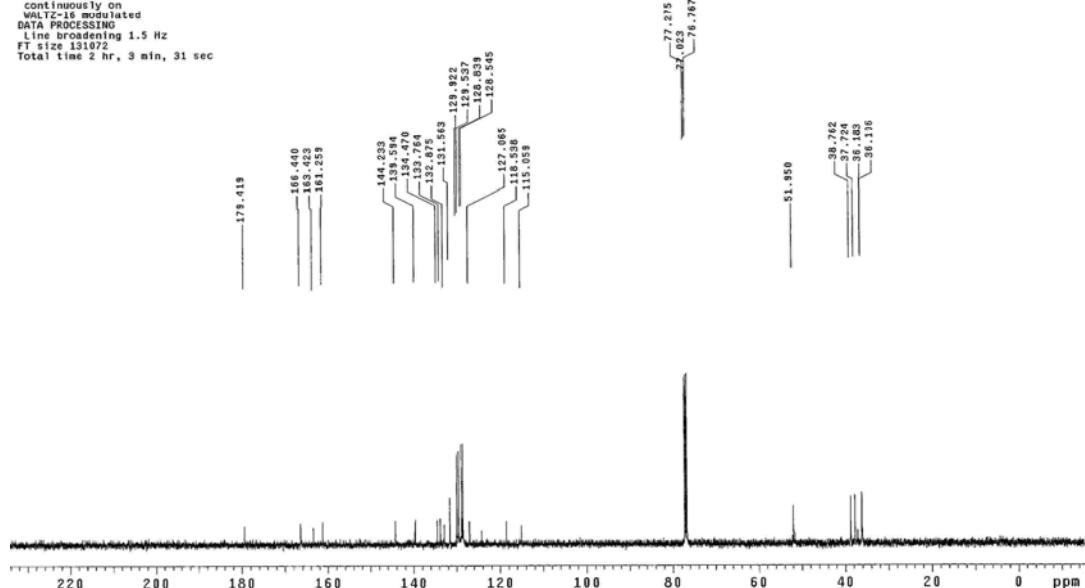
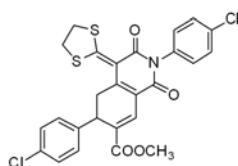
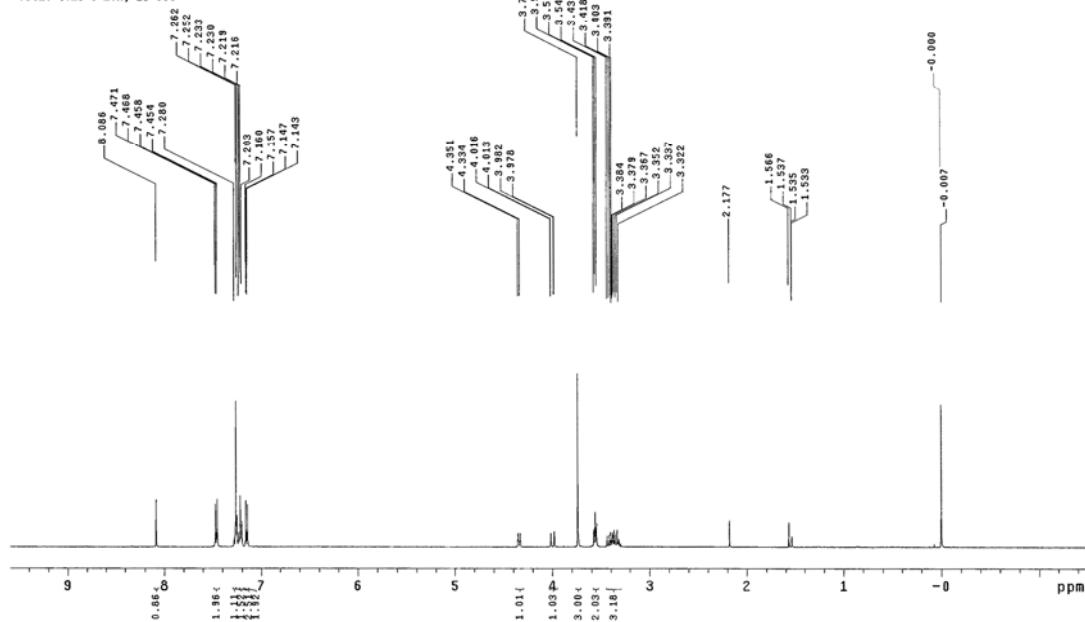
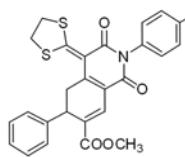


Figure 7. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4g.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: g865
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Aca. time 1.892 sec
Width 1000.0 Hz
8 repetitions
OBSERVE H1, 499.8025909 MHz
DATA PROCESSING
FT size 45536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: g873
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Aca. time 1.300 sec
Width 31421.8 Hz
891 repetitions
OBSERVE C13, 125.6754718 MHz
DECUPLE H1, 499.8050905 MHz
POPPING 16.0 Hz
continuously on
VALTZ-16 modulated
DATA PROCESSING
LINEAR SMOOTHING 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

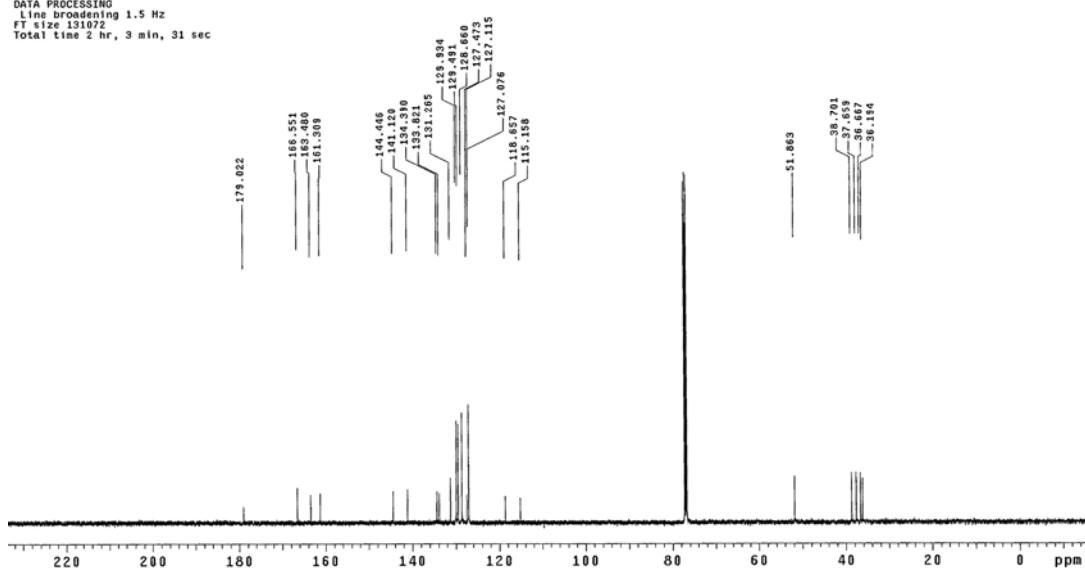
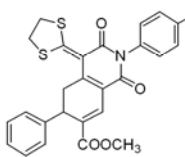
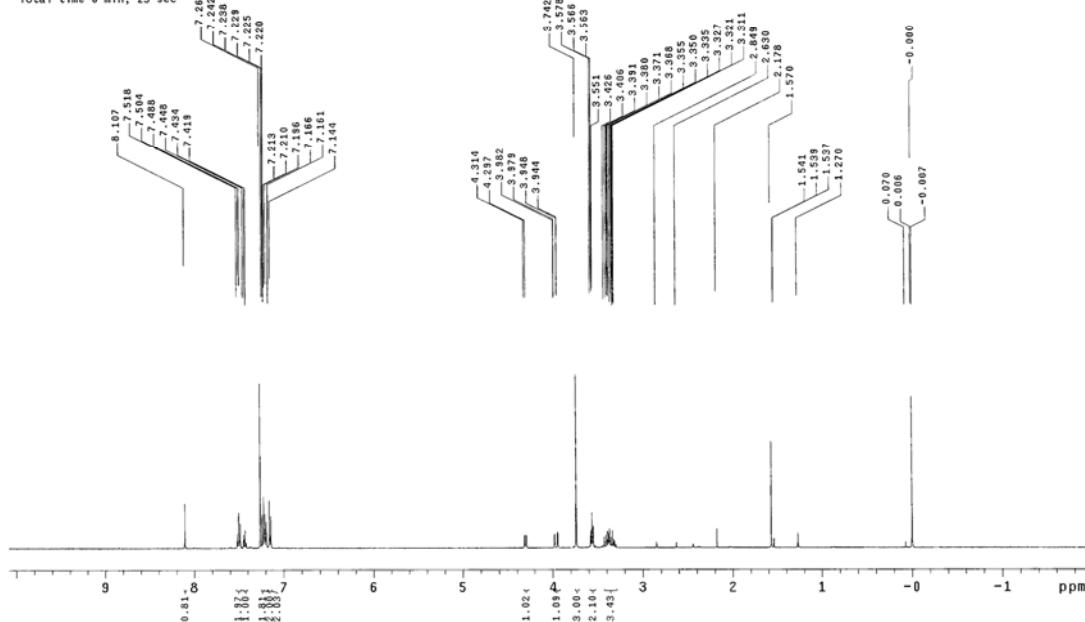
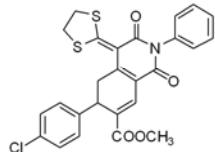


Figure 8. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4h.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: o788
INOVA-500 "NENUS500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 0.02 sec
Width 8500.7 Hz
8 repetitions
OBSERVE H1 499.8025899 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: ouyy-B7
File: o787
INOVA-500 "NENUS500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acc. time 1.300 sec
Width 31421.8 Hz
4996 repetitions
OBSERVE C13, 125.8754718 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
Contrast on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

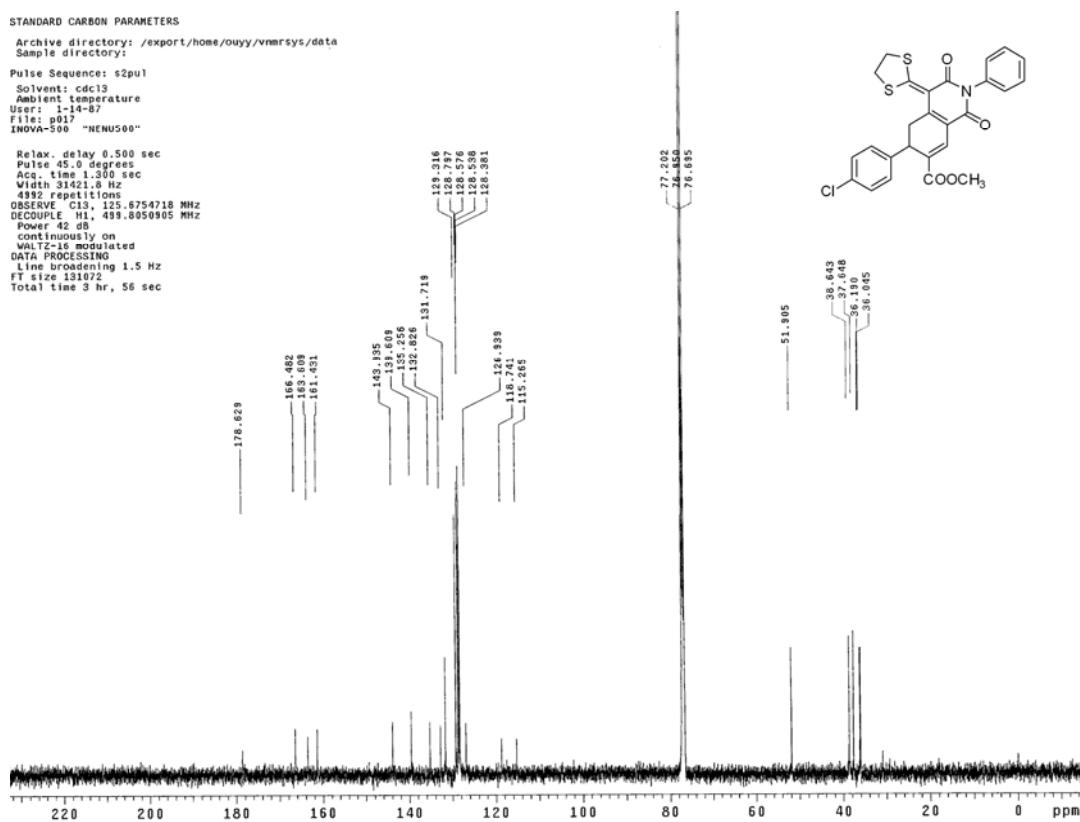
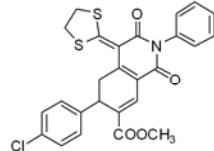


Figure 9. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4i.

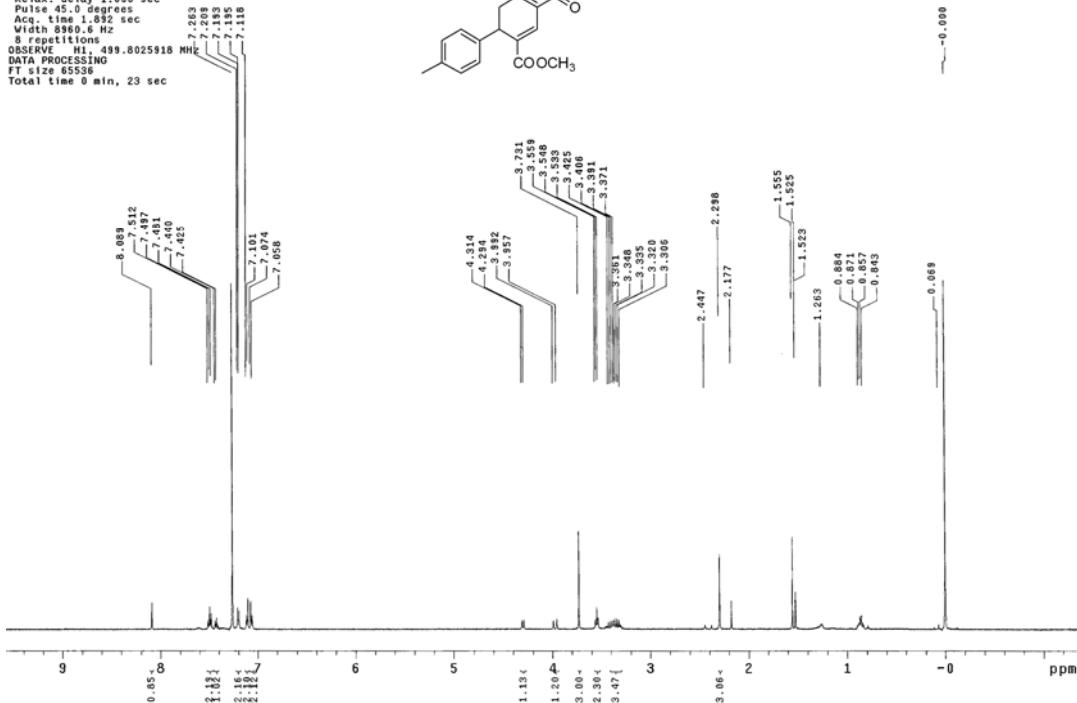
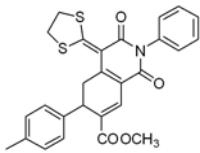
```

STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDC13
ambient temperature
FID抑止: 100
INOVA-500 "NEMUNUS0"
 $\tau$ : 1.000 sec
Relaxation delay: 1.000 sec
Pulse width: 1.000 sec
Acq. time: 1.892 sec
B width: 8960.6 Hz
b repetitions: 1
QSBSS: 1.000 sec, 49.8025918 MHz
DATA PROCESSING
FT size: 65536
Total time: 0 min, 23 sec

```



```

STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: cdc13
Ambient temperature
User temperature: 24-87
File: 0242
INNOVA-500 "NENU500"

Relax, delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31428.8 Hz
32 scans per file
OBSERVE C13 125.674565 MHz
DECOUPLE H1, 49.605095 MHz
Power 42 dB
Continuously on.
WALTZ-16 modulated
DATA PROCESSING
   FID scaling 1.000000 1.5 Hz
   FT size 131024
Total time 3 hr, 56 sec

```

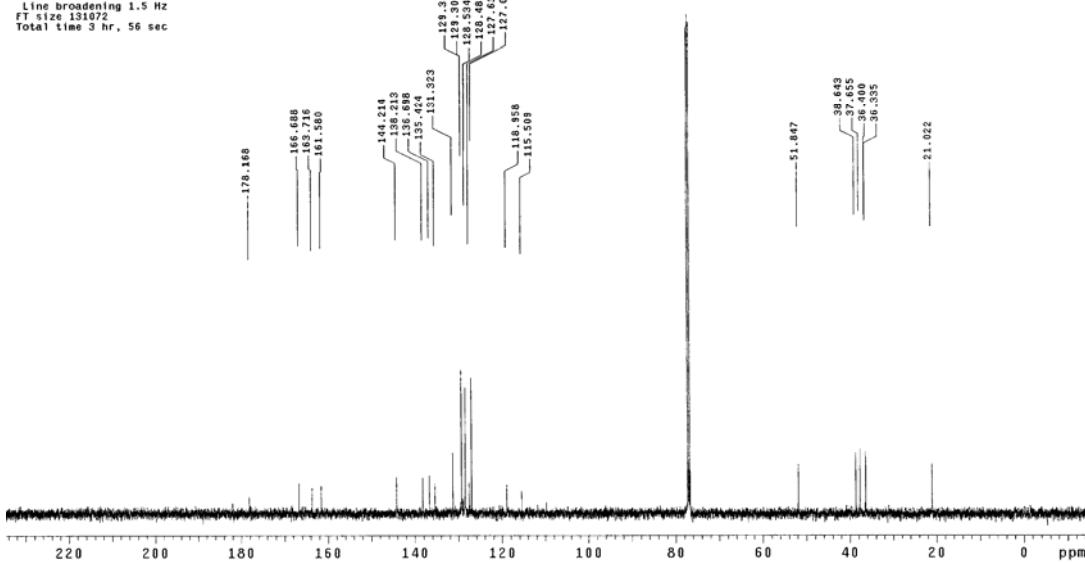
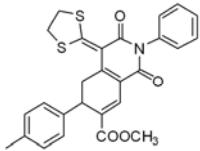


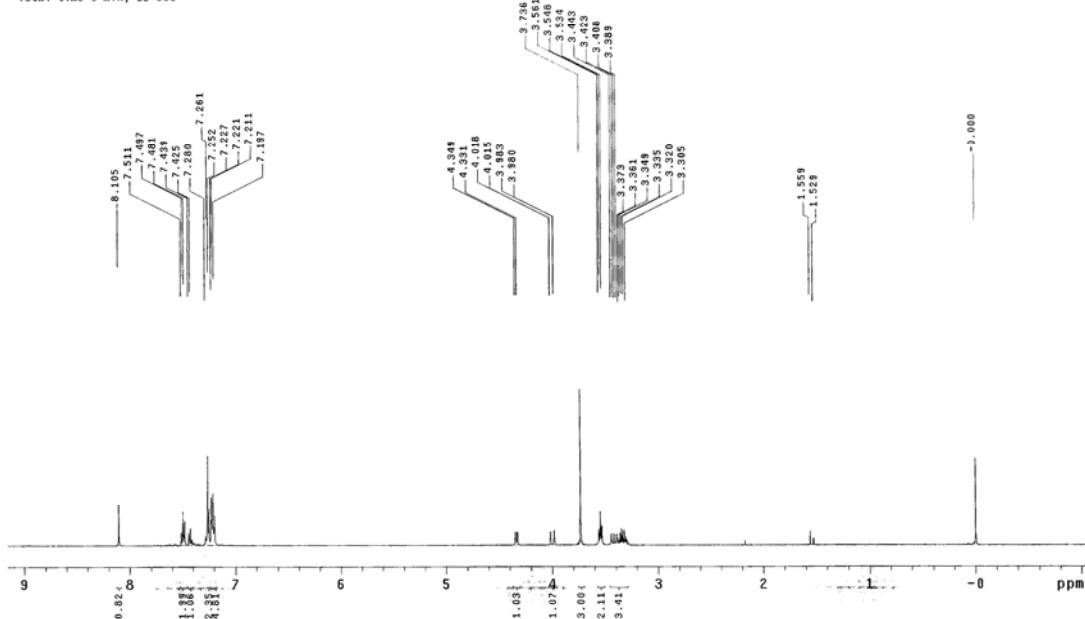
Figure 10. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **4j**.

STANDARD PROTON PARMS

Archive directory: /export/home/ouyy/vnmrsys/data
 Sample directory: /export/home/ouyy/vnmrsys/data

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Ambient temperature
 File: q498
 INOVA-500 "NENU500"

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.02 sec
 Width 8500.7 Hz
 8 repetitions
 OBSERVE: H1, 499.8025917 MHz
 DATA PROCESSING:
 FT size 65536
 Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
 Sample directory:

Pulse Sequence: s2pul
 Solvent: cdcl₃
 Ambient temperature
 User: 1-14-87
 File: q498
 INOVA-500 "NENU500"

Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 1.02 sec
 Width 31421.8 Hz
 4096 repetitions
 OBSERVE: C13, 125.6754661 MHz
 DECOUPLE C13, 499.8050905 MHz
 Power 42 dB
 continuously on
 W1 16 sec integrated
 DATA PROCESSING:
 Line broadening 1.5 Hz
 FT size 131072
 Total time 2 hr, 3 min, 31 sec

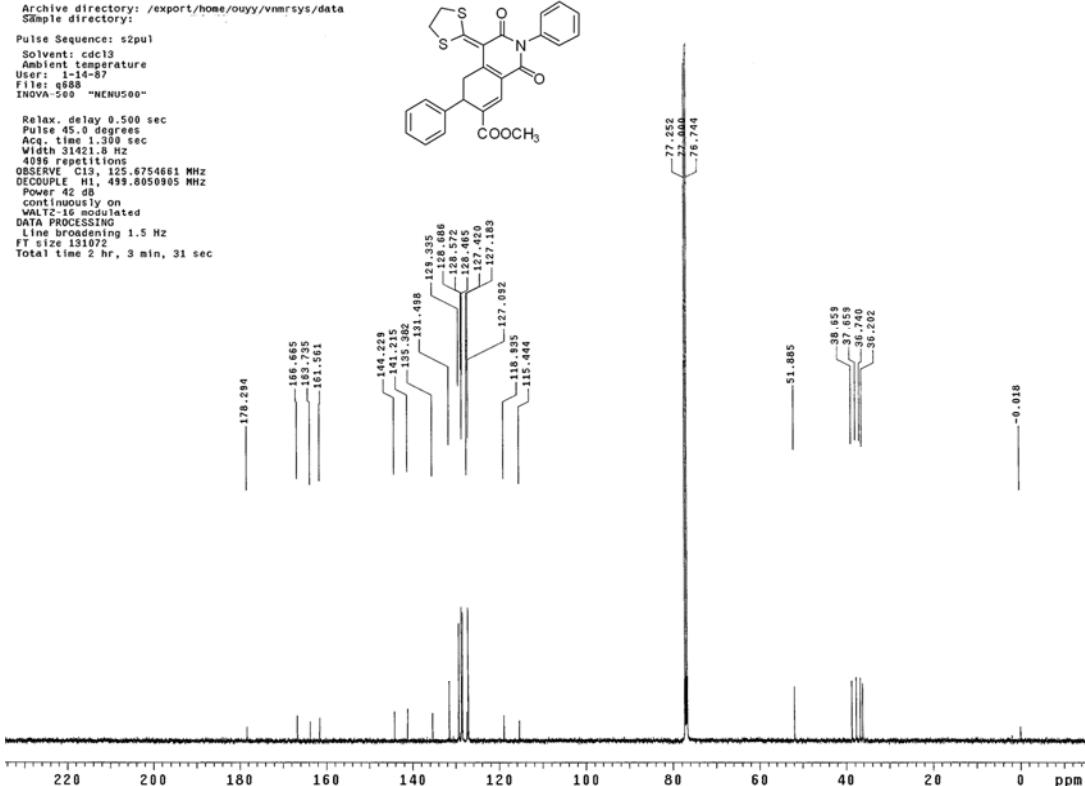
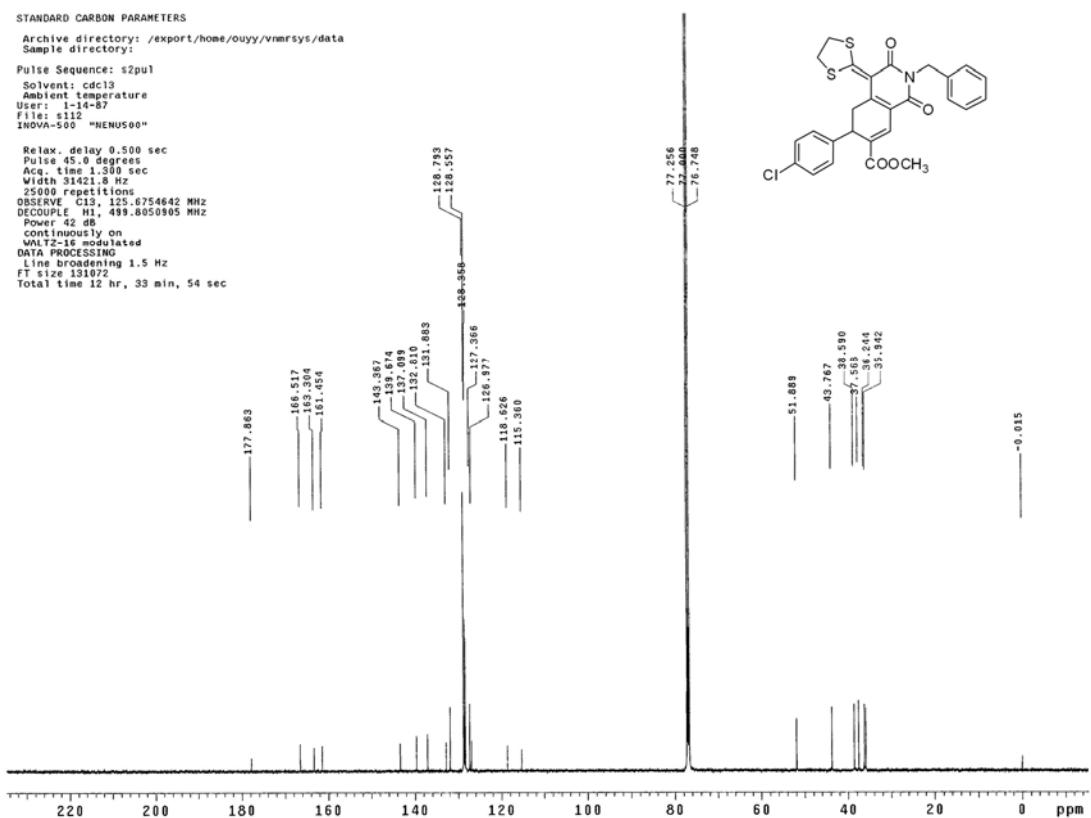
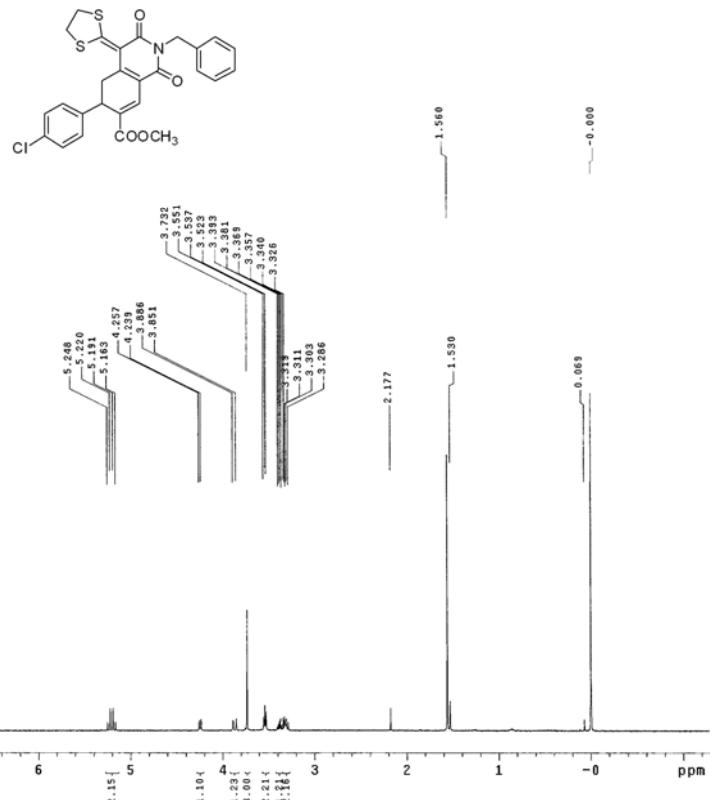
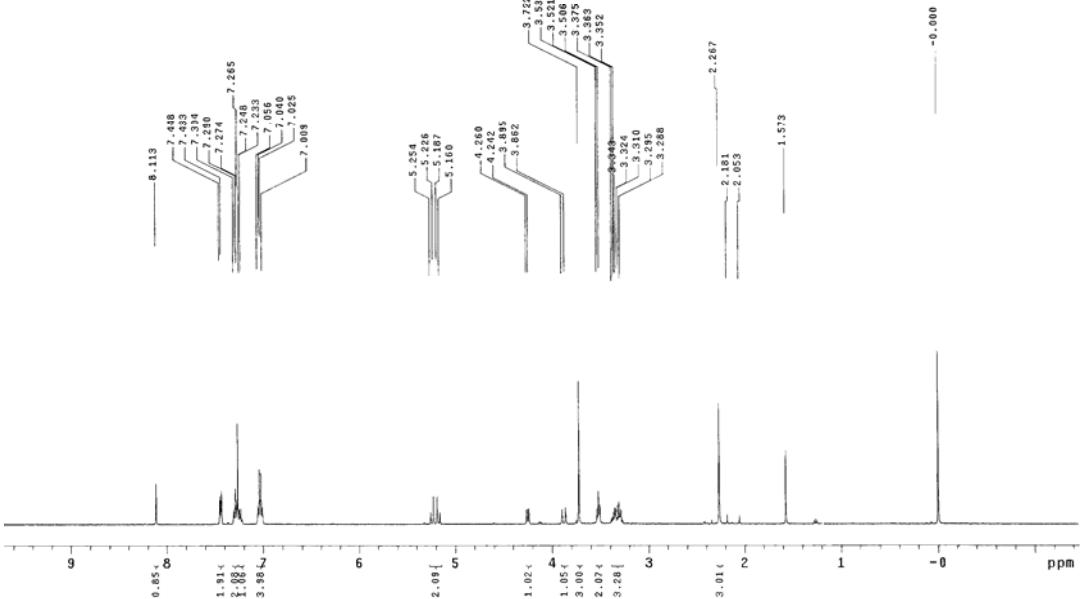


Figure 11. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4k.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: s090
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Aqc. time 1.300 sec
Width 3328.4 Hz
8 repetitions
OBSERVE H1, 499.8025914 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: p025
INNOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Aqc. time 1.300 sec
Width 8500.7 Hz
8 repetitions
OBSERVE: H1 499.8025886 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Width 31421.8 Hz
87 repetitions
File: p048
INNOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Aqc. time 1.300 sec
Width 31421.8 Hz
128 repetitions
DESSCHEM: H1, 125.6754656 MHz
DECOPPLE: H1, 499.8050995 MHz
Power 42 dB
no decoupling on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

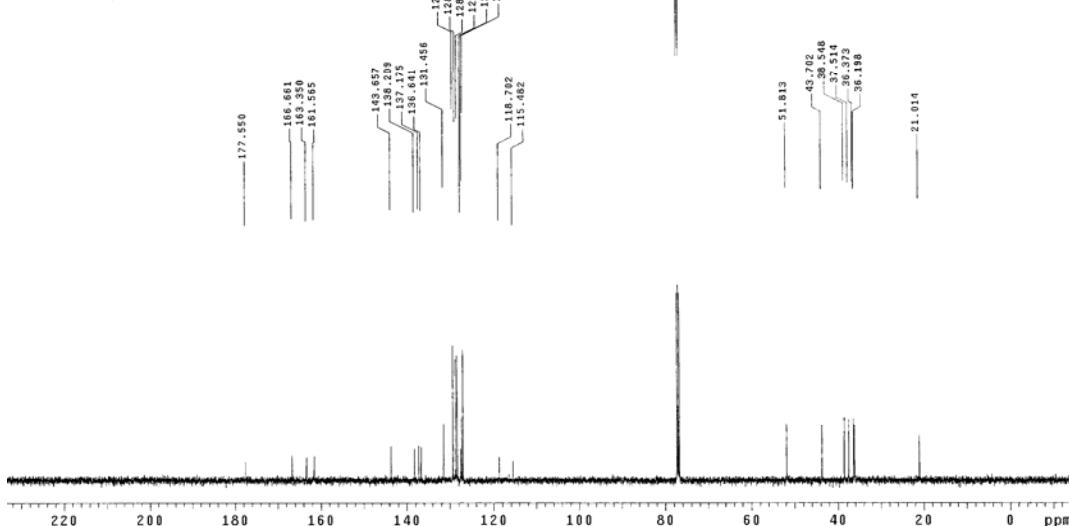
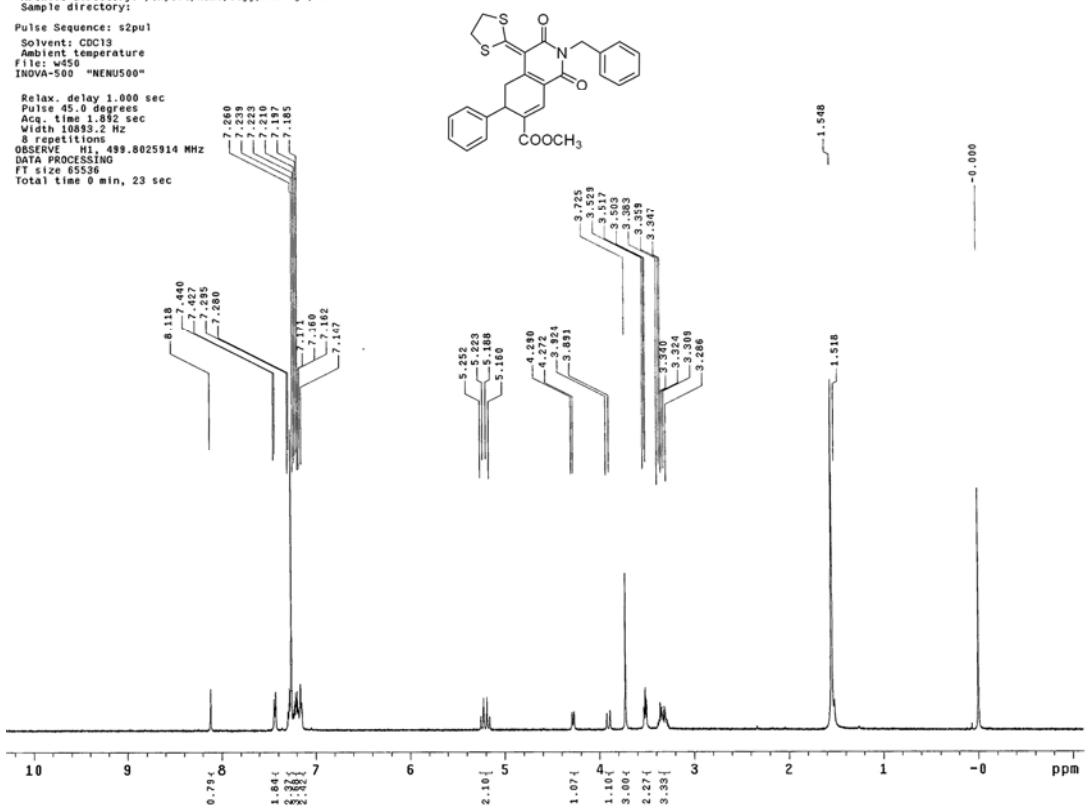


Figure 13. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4m.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: o993 "NENU500"
Relax, delay 1.000 sec
Pulse 45.0 degrees
Ave. time 1.882 sec
Width 10893.2 Hz
8 repetitions
OBSERVE 1H, 499.8025914 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: o993
INOVA-500 "NENU500"
Relax, delay 0.500 sec
Pulse 45.0 degrees
Ave. time 1.882 sec
Width 31424.8 Hz
320 repetitions
OBSERVE C13, 125.6754661 MHz
DECODE C13, 499.8050905 MHz
Power 42 dB
continuously on
WALT 16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

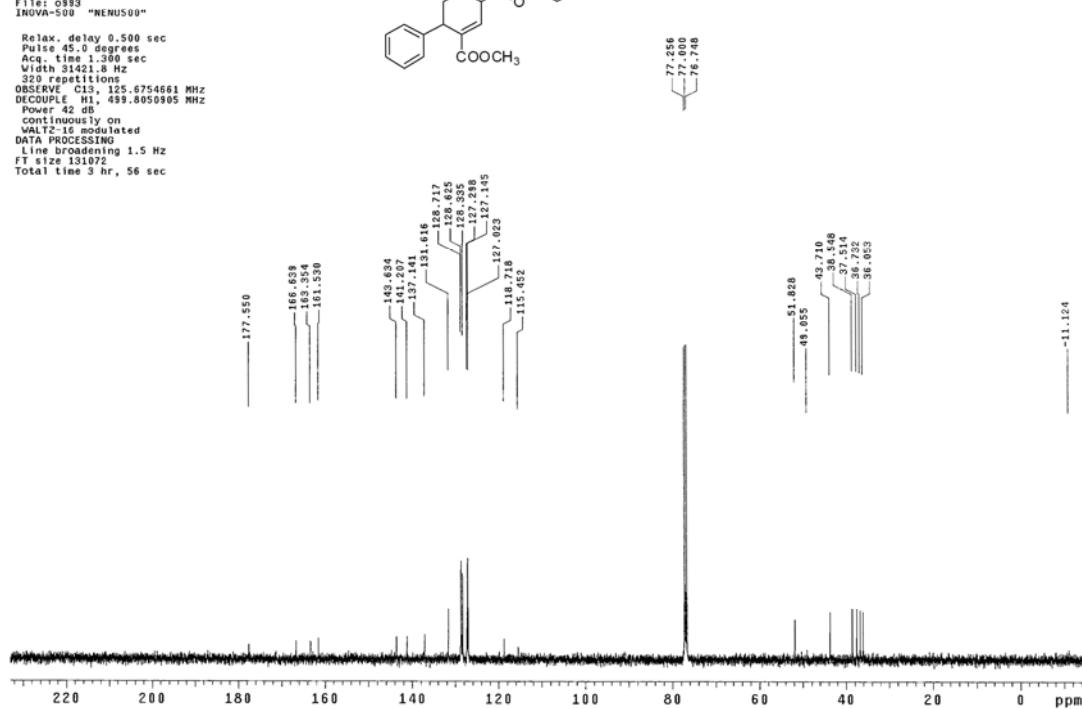
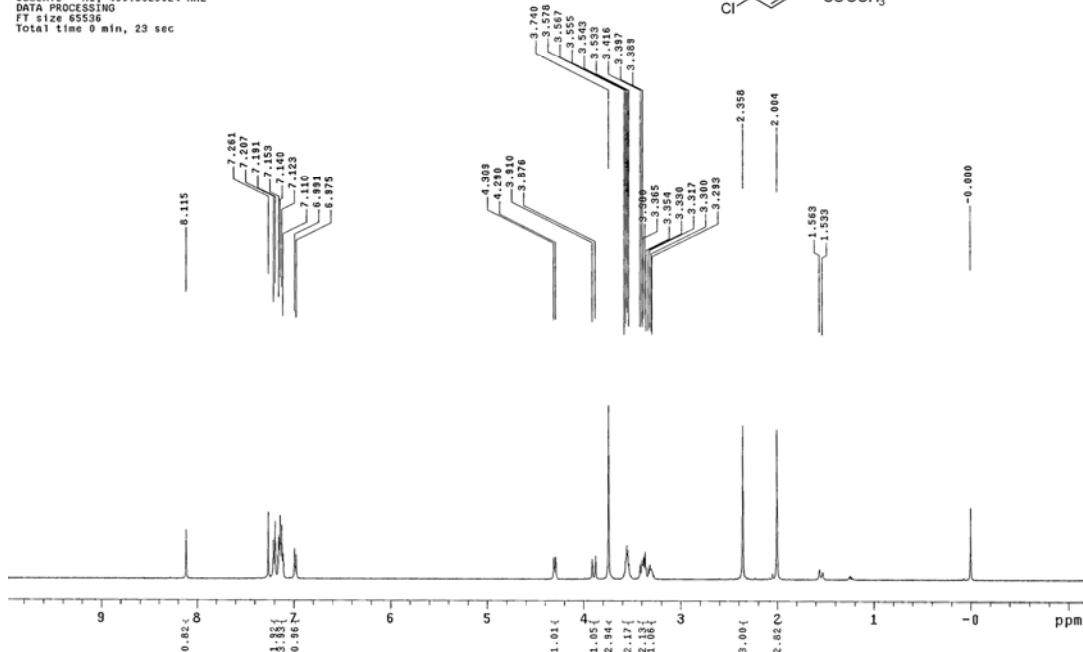
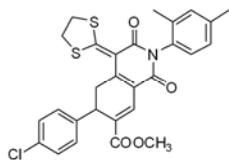


Figure 14. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4n.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: n001
INNOVA-500 "NENNU500"
Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.302 sec
Width 3351.6 Hz
8 repetitions
OBSERVE: H1 499.8025924 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-300-07
File: m003
INNOVA-500 "NENNU500"
Relax, delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 scans
OBSERVE: C13, 125.6754690 MHz
DECOUPLE: H1, 499.8050905 MHz
Power: 42 dB
containing 1% on
WALZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

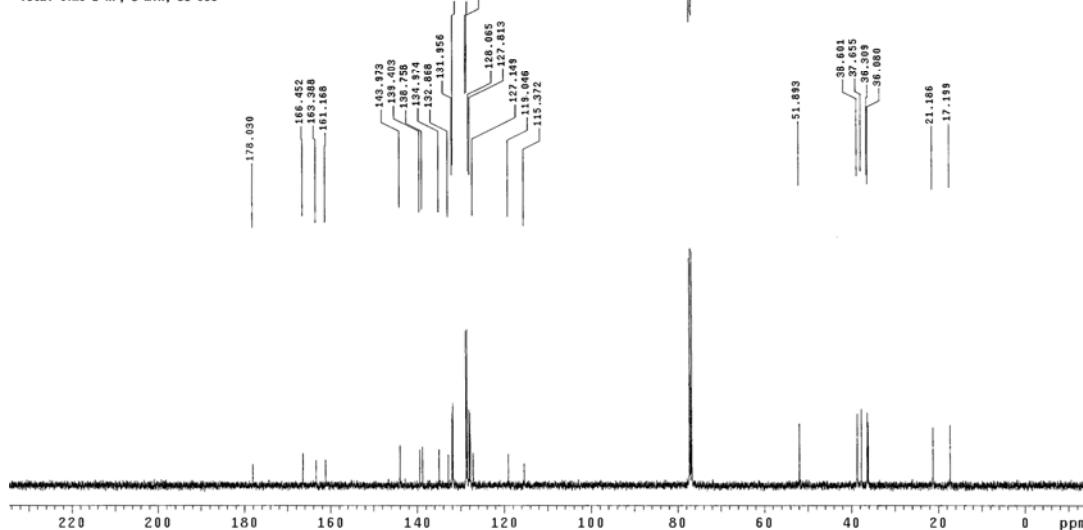
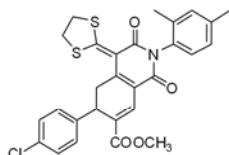
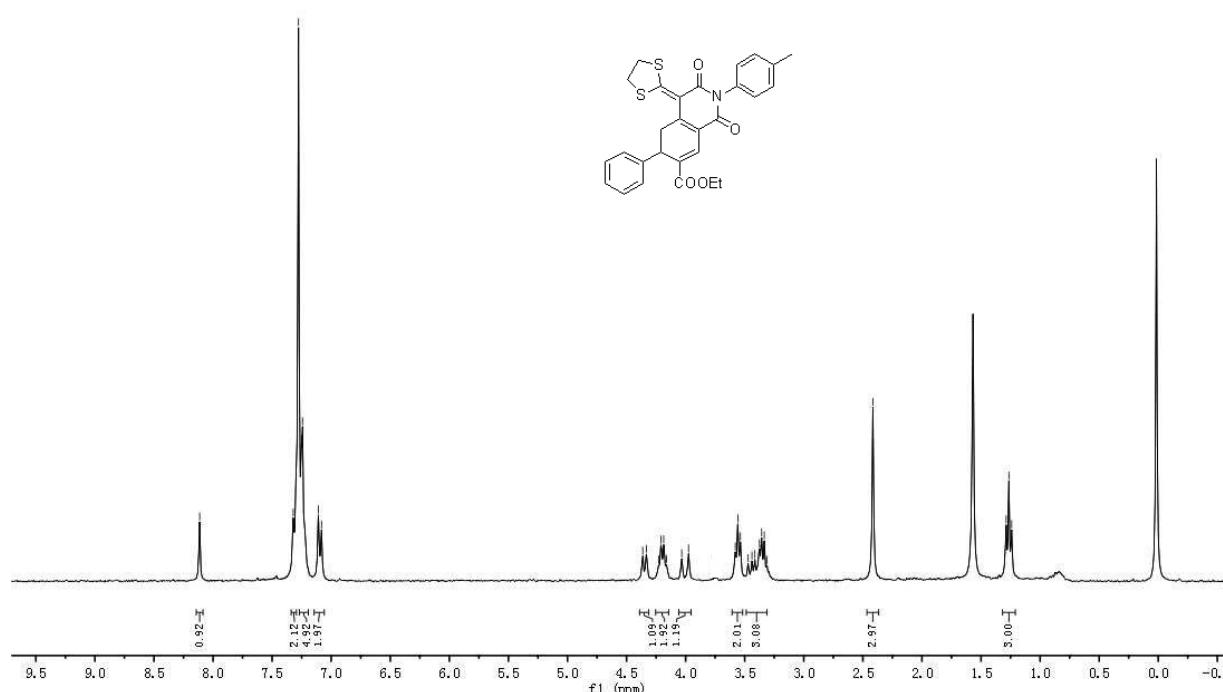


Figure 15. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4o.

wgj-20140124-W-3A-h
¹H



W-3-C
WGJ-W-3

—177.63 —165.61 —163.24 —161.11

—145.30 —137.80 —132.19 —129.44 —128.05 —127.23 —126.60 —126.44

—118.37 —114.90

—60.05

—59.08
—57.09
—56.24
—55.58

—20.67
—15.61

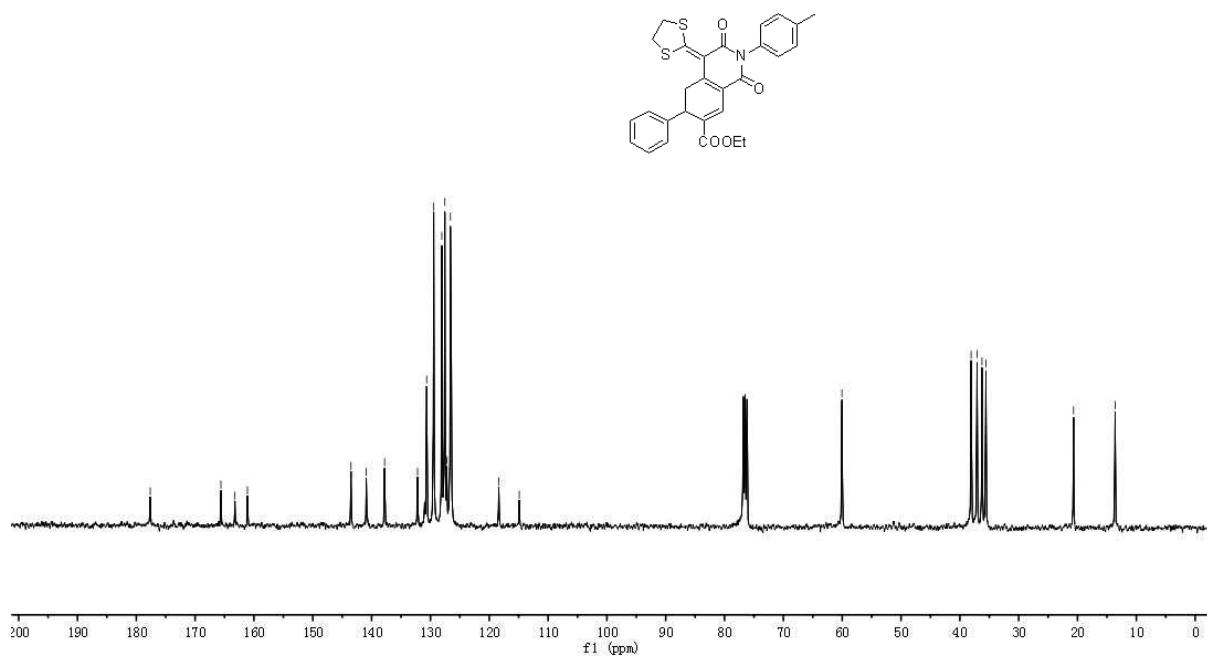
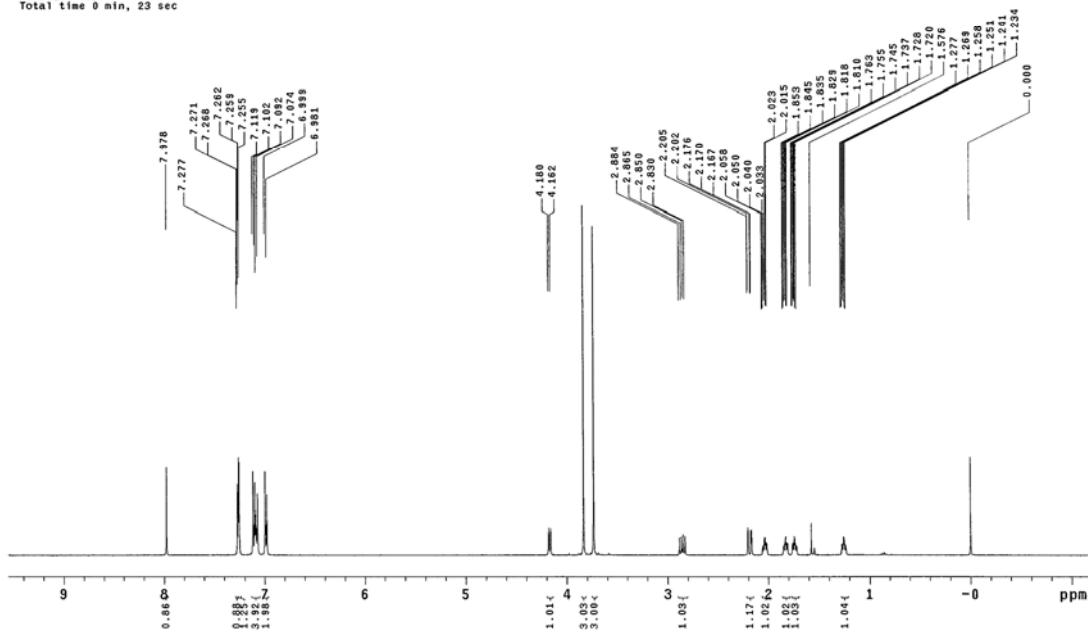


Figure 16. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4p.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: q427
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8500.7 Hz
Sensitivity 1.000
OBSERVE H1, 499.8025920 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: q427
INOVA-500 "INFINIUS00"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 8500.7 Hz
256 repetitions
OBSERVE C13, 125.6754685 MHz
DECOUPLE H1, 499.8050905 MHz
Pulse 45.0 degrees
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

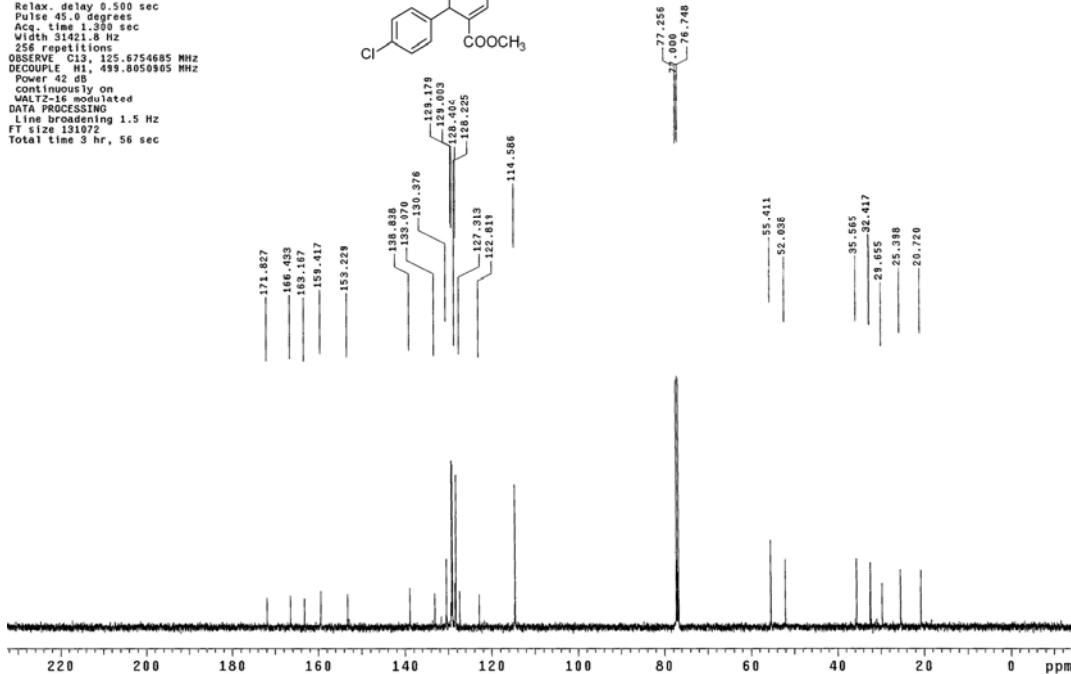


Figure 17. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4q.

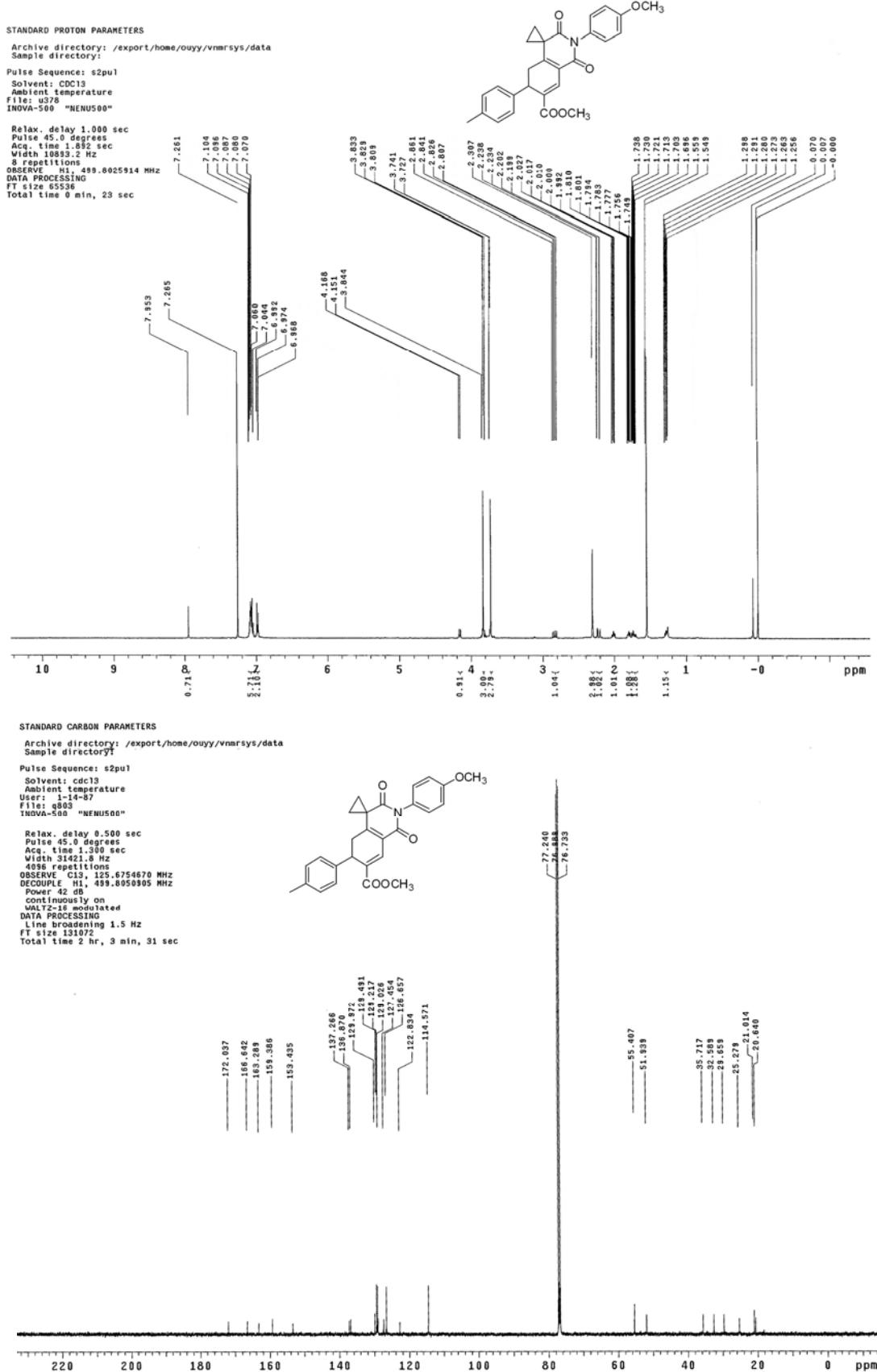


Figure 18. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4r.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: n688

INOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acc. time 1.00 sec

Width 8890.3 Hz

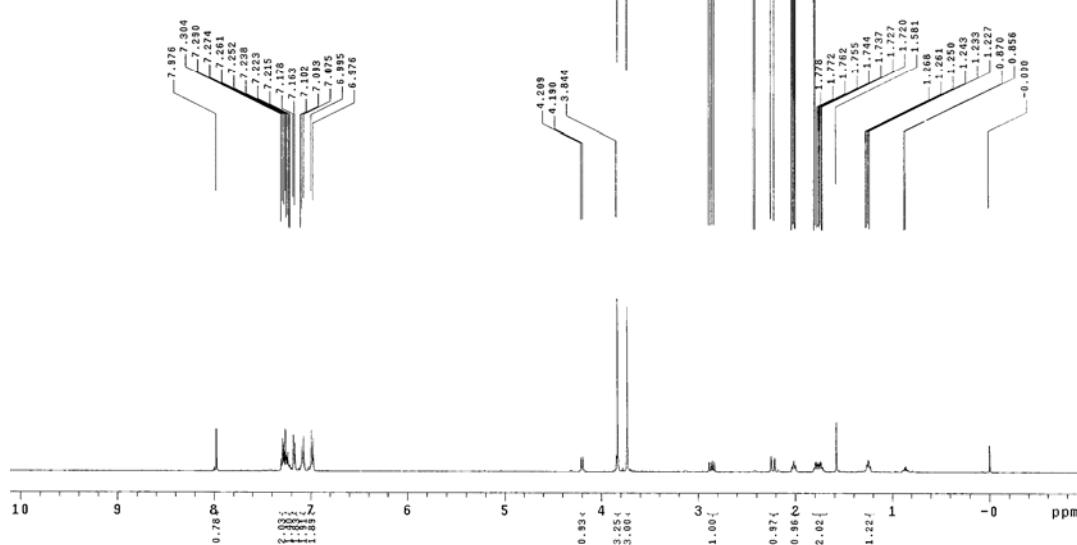
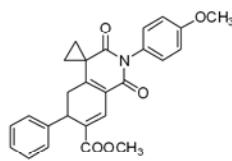
8 repetitions

OBSERVE: H1 499.8025930 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: I-14-B7

File: n688

INOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acc. time 1.00 sec

Width 31421.8 Hz

162 repetitions

OBSERVE: C13, 125.6754670 MHz

DECODE: FID, 499.8050905 MHz

Power 42 dB

continuously on

WAVELENGTH: 1.34000

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 3 hr, 56 sec

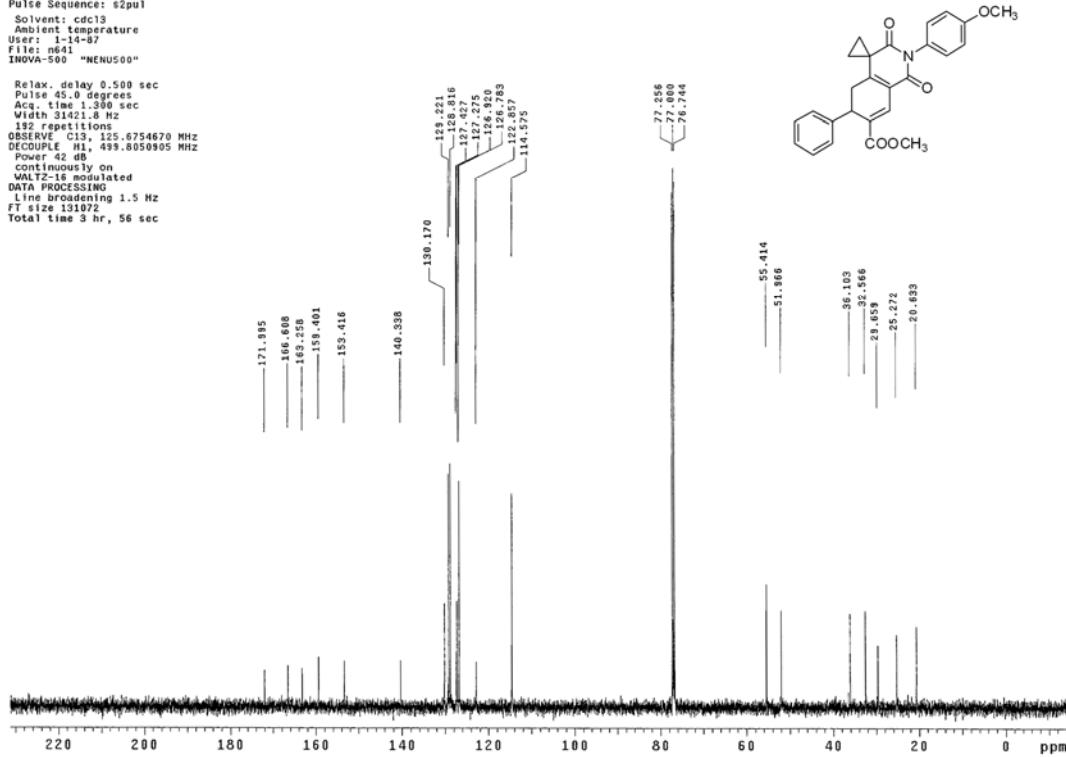
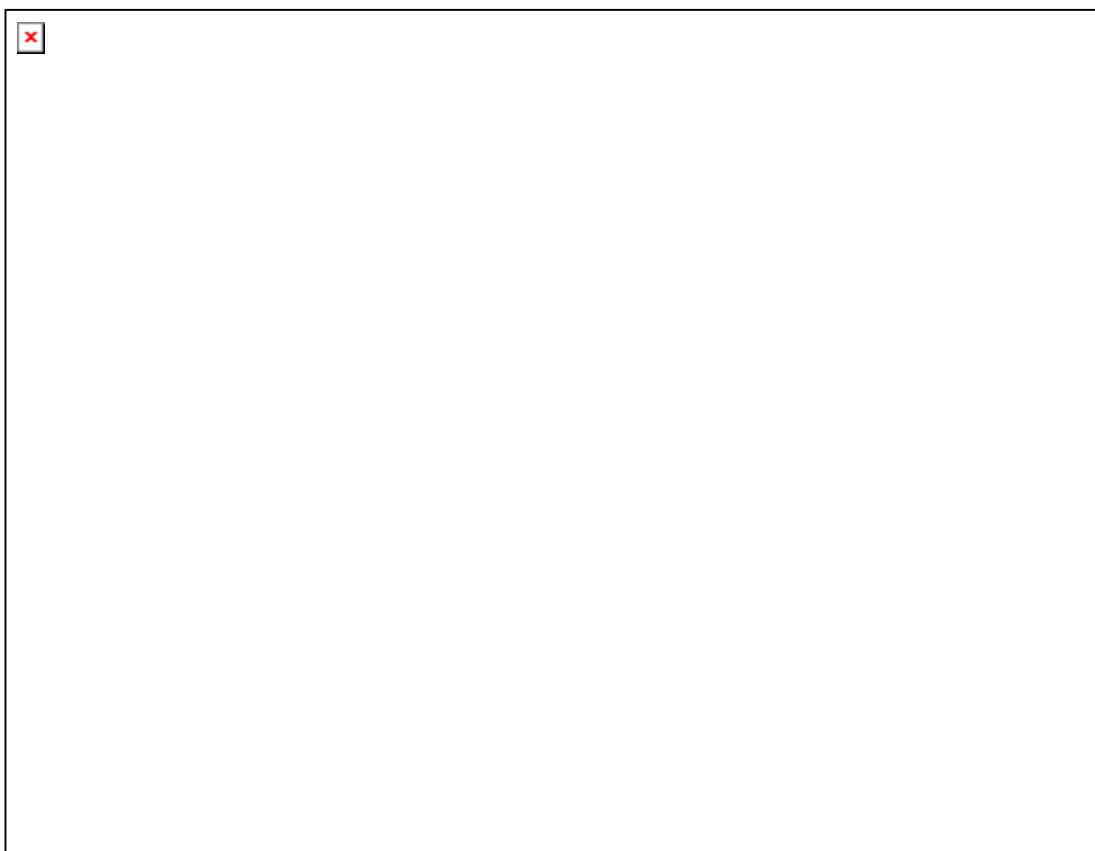


Figure 19. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4s.



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: cdc13

Ambient temperature

User: 1-14-87

File: 13C_4t

INOVA-500 "HENUS00"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 0.000 sec

Width 31421.8 Hz

64 repetitions

0.032 sec C13, 125.6754646 MHz

0.032 sec C13, 499.8050905 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

DATA 13C SSNMR

Line broadening 1.5 Hz

FT size 131072

Total time 2 hr, 3 min, 31 sec

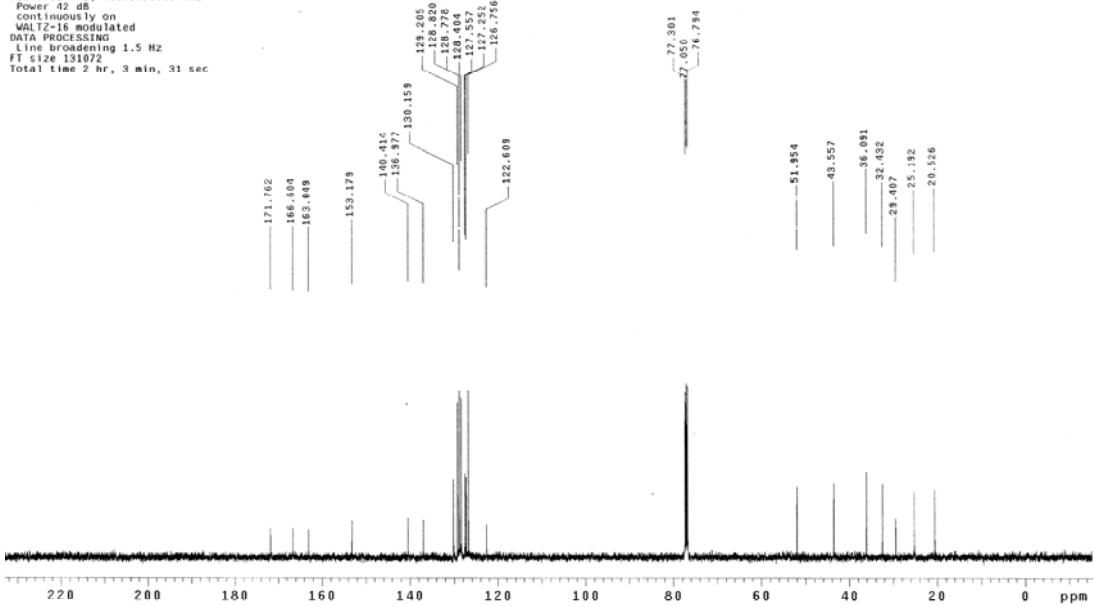
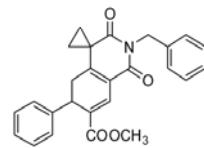
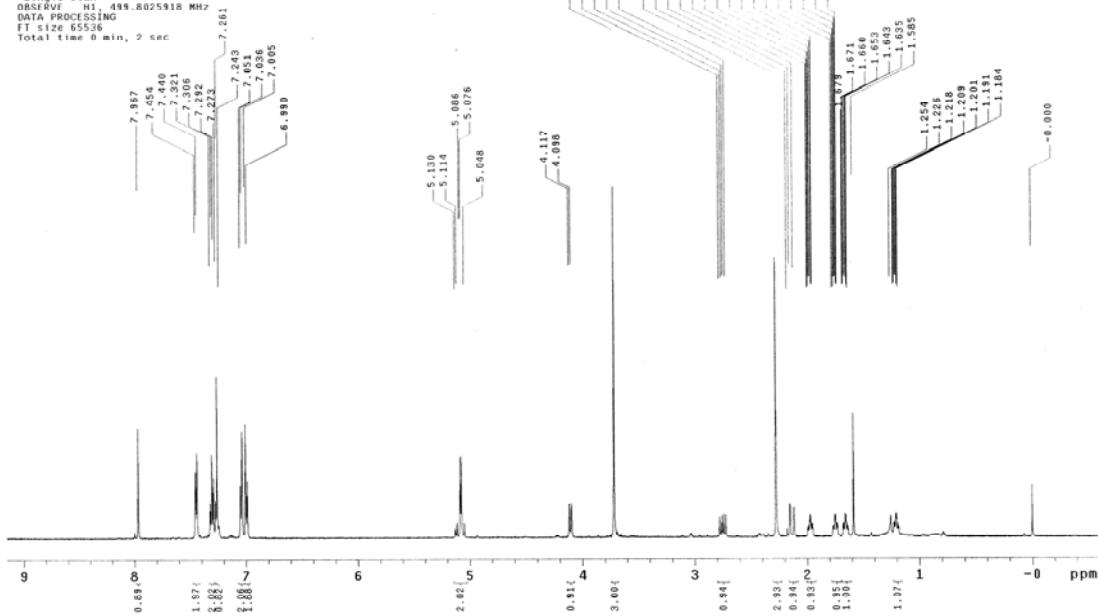


Figure 20. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **4t**.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: f509
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.88 sec
Width 10311.9 Hz
Single scan
ns 1, ws 409.8025518 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 2 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 14-87
File: f500
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 15.0 degrees
Acq. time 1.00 sec
Width 31421.8 Hz
182 repetitions
DESYNCH: C13, 125.6754646 MHz
DECOUPLE: H1, 493.0050905 MHz
Power 42 dB
continuous¹H
contiguous¹C
WALTZ-16
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

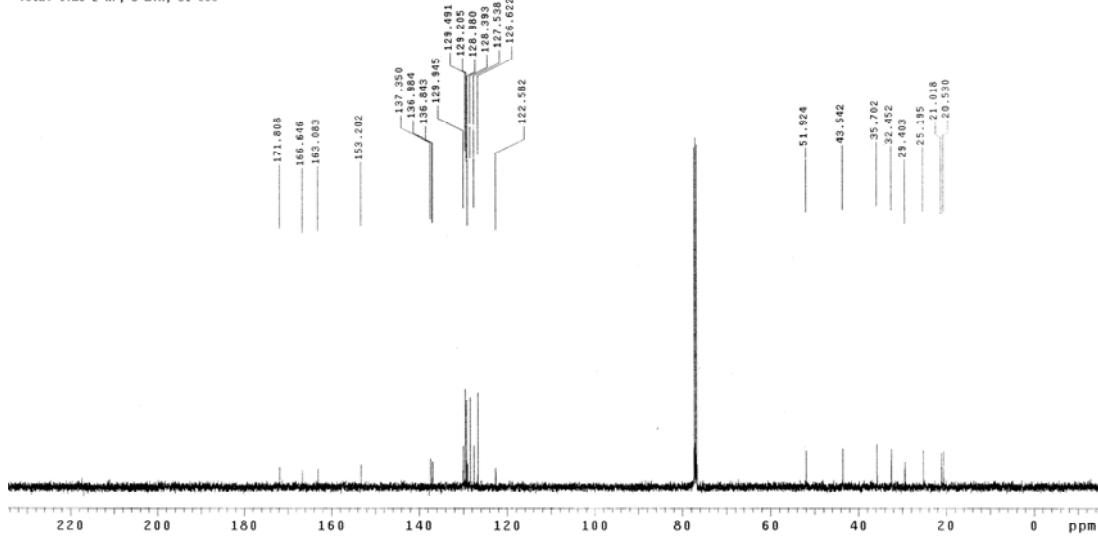
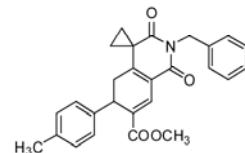
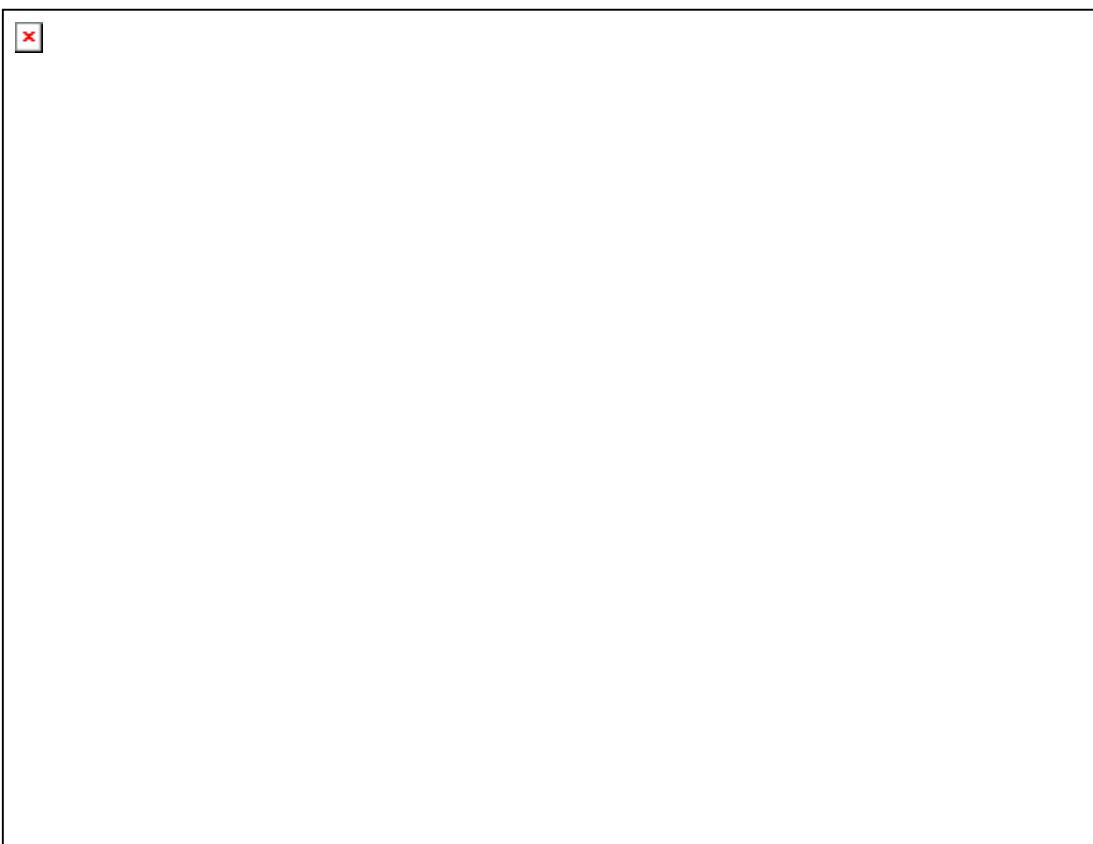


Figure 21. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 4u.





STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnarsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdc13
Ambient temperature
User: 14-07
File: f652
INOVA-500 "NENUS500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
192 scans, 16 points
OBSERVE C13 125.6754670 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
Contact time 1.00 ms
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

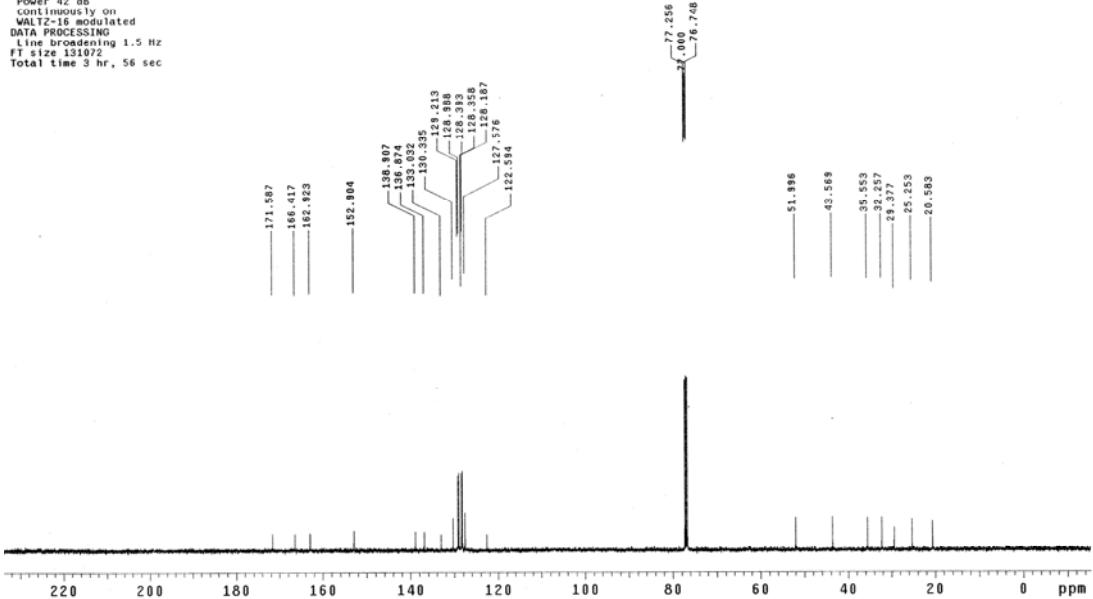
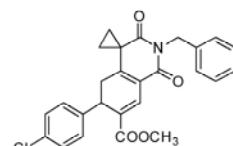


Figure 22. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **4v**.

```

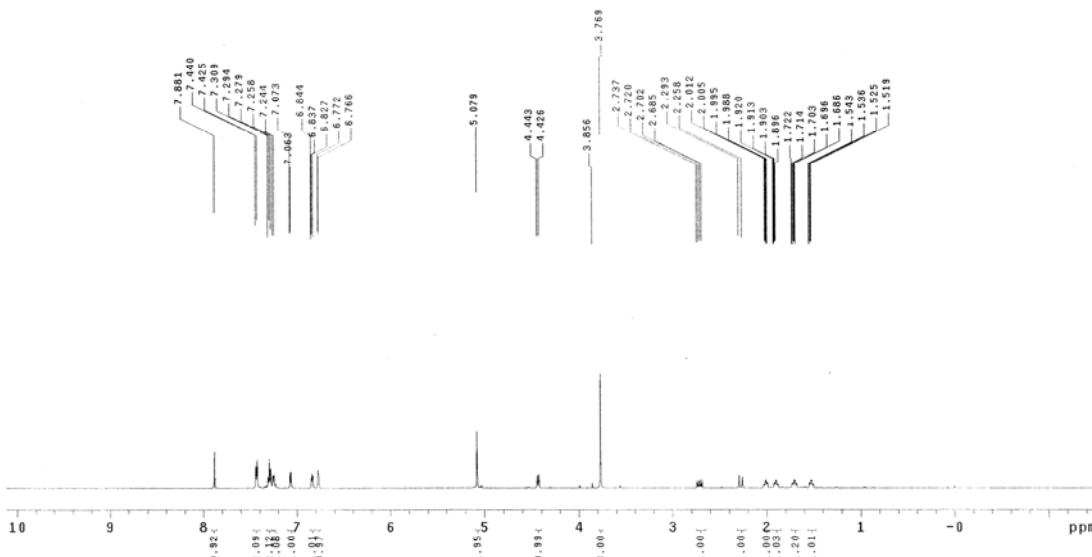
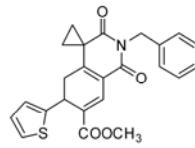
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: zspul
Solvent: CDC13
Ambient temperature
FTC: 1861
INOVN 500 "NENUS006"

Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq time 1.000 sec
Width 10.19 Hz
4 repetitions
OBSERVE_H1 499.8025953 MHz
NOISE PROCESSING
FT size 65536
Total time 0 min, 11 sec

```



```

STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: cdc13
Ambient temperature
User temperature: 87
File: f852
INNOVA-500 "NEUN500"

Relax: delay 0.500 sec
Pulse: 90.0 degrees
Aq.: time 1.300 sec
Width 3142.8 Hz
128 repetitions

QBERDESS: 1.15.6754266 MHz
DECOUPLE: HI, 499.8050905 MHz

Power 42 dB
Cross polarization
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.5 Hz
Filter width 6130 Hz
Total time 3 hr . 56 sec

```

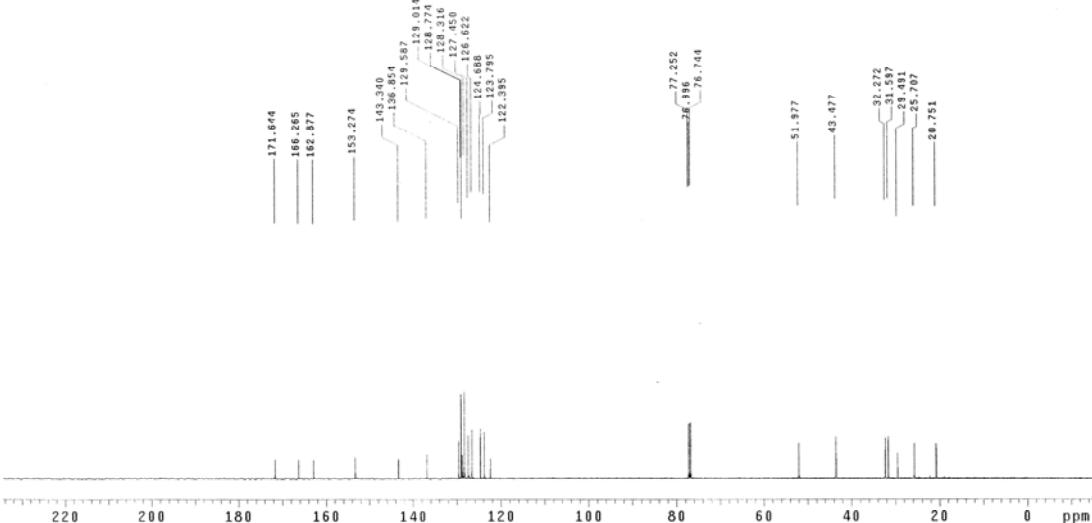
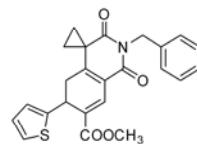
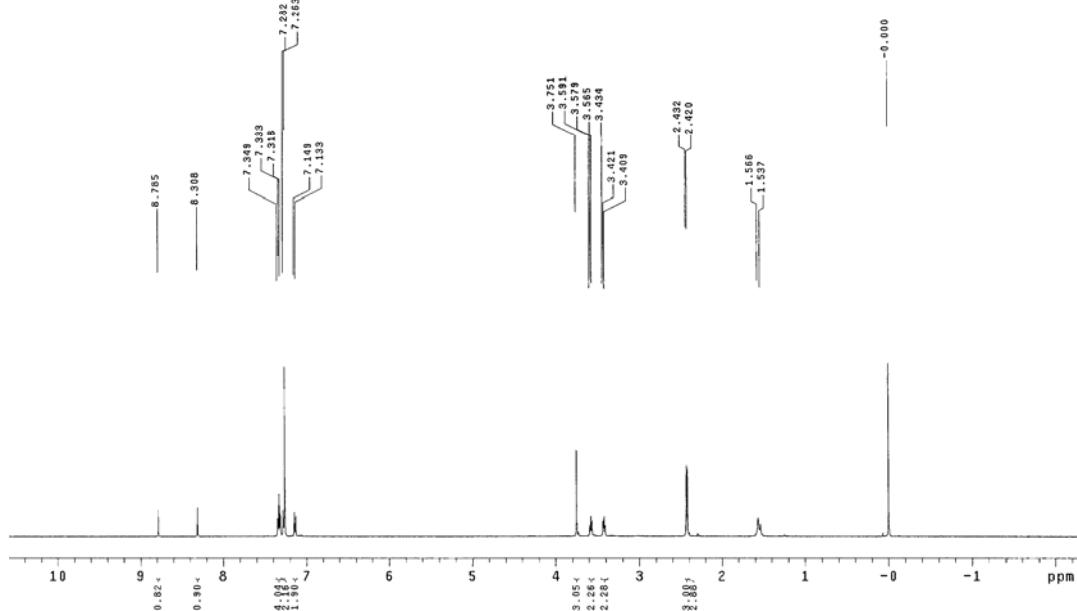
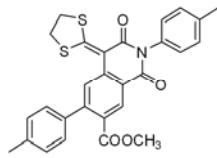


Figure 23. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **4w**.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: n186
INNOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.892 sec
Width 3251.8 Hz
8 repetitions
OBSERVE H1 499.8025916 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
File: n150
INNOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
8000 repetitions
OBSERVE C13, 125.1254625 MHz
DECOPPLE H1, 499.8050905 MHz
Power 42 dB
Control 100% on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 430072
Total time 3 hr, 56 sec

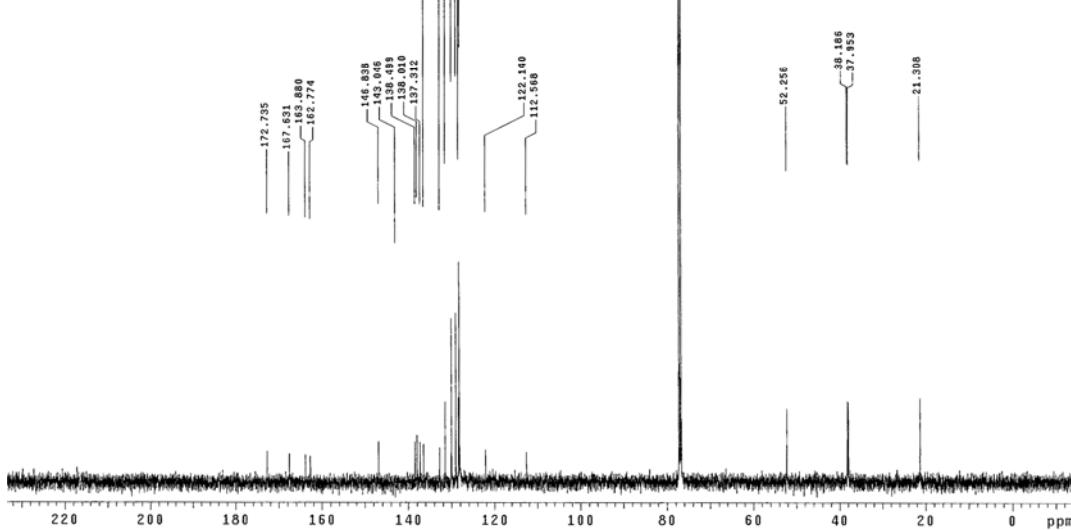
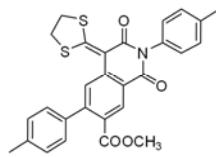


Figure 24. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6a.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: u682
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 100.0 Hz
8 scans/line
OBSERVE H₁, 499.8025914 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec

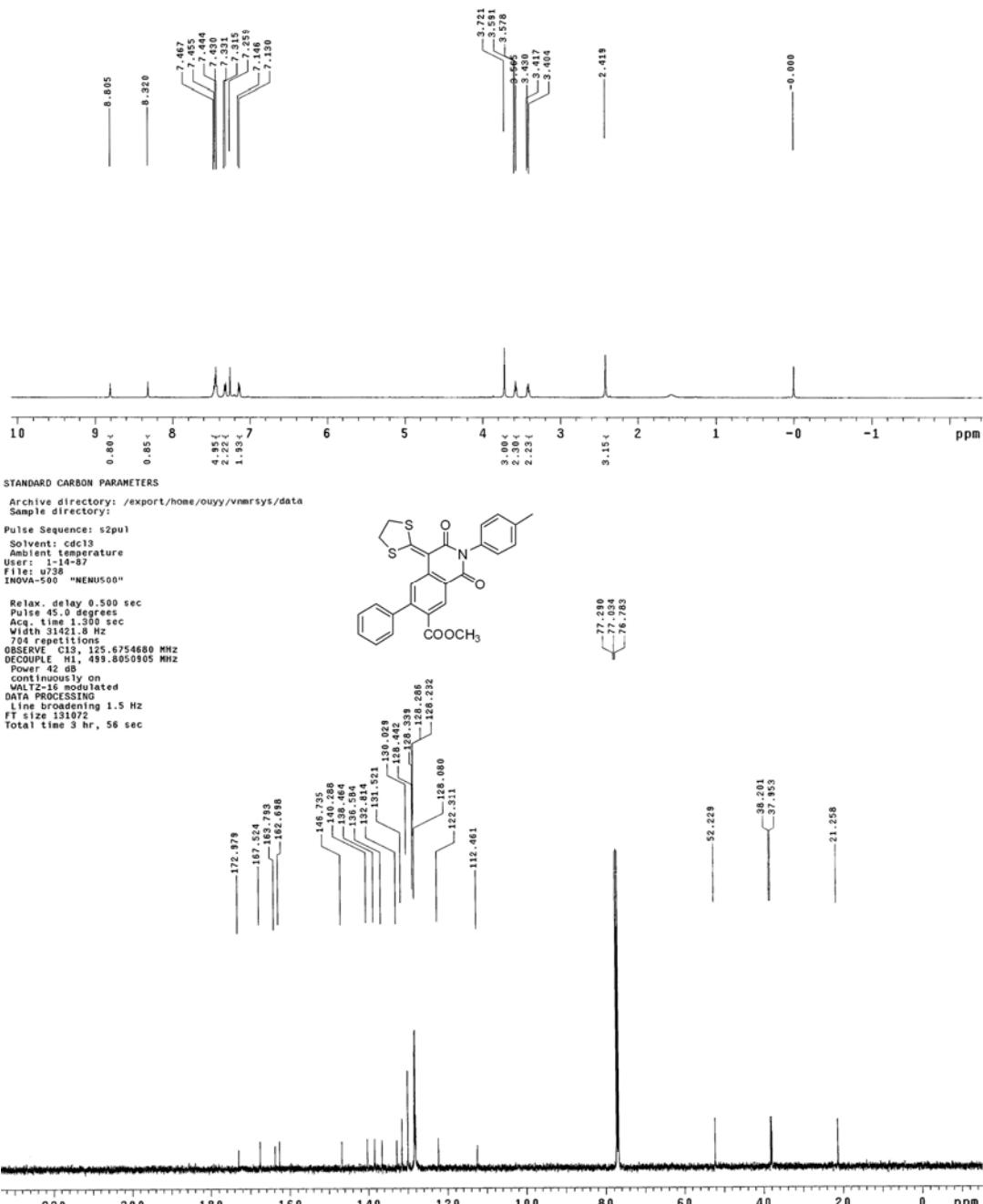
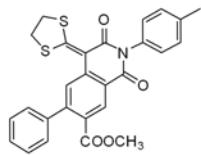
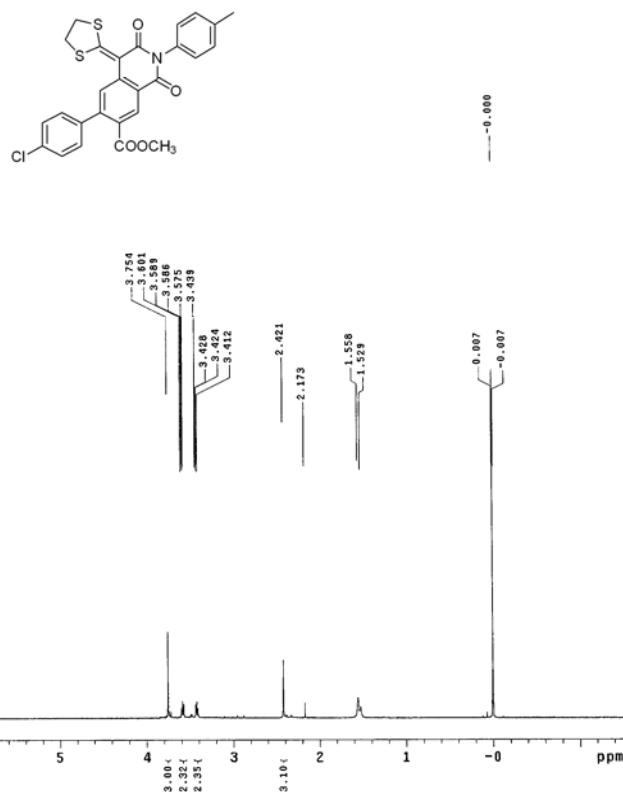


Figure 25. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6b.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: u258
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 10893.2 Hz
16 repetitions
OBSERVE H1, 499.8025910 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: u276
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6754656 MHz
DCOUPLE 13C, 499.8059095 MHz
Power 42 dB
continuously on
WATER SUPPRESS
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

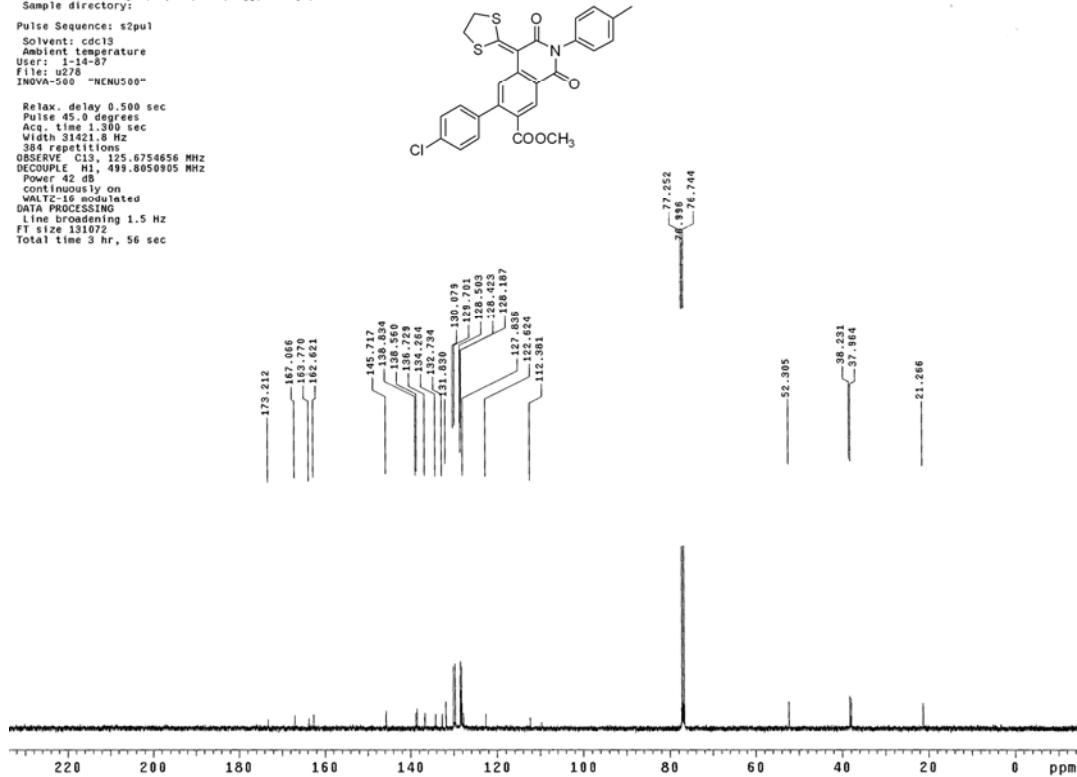
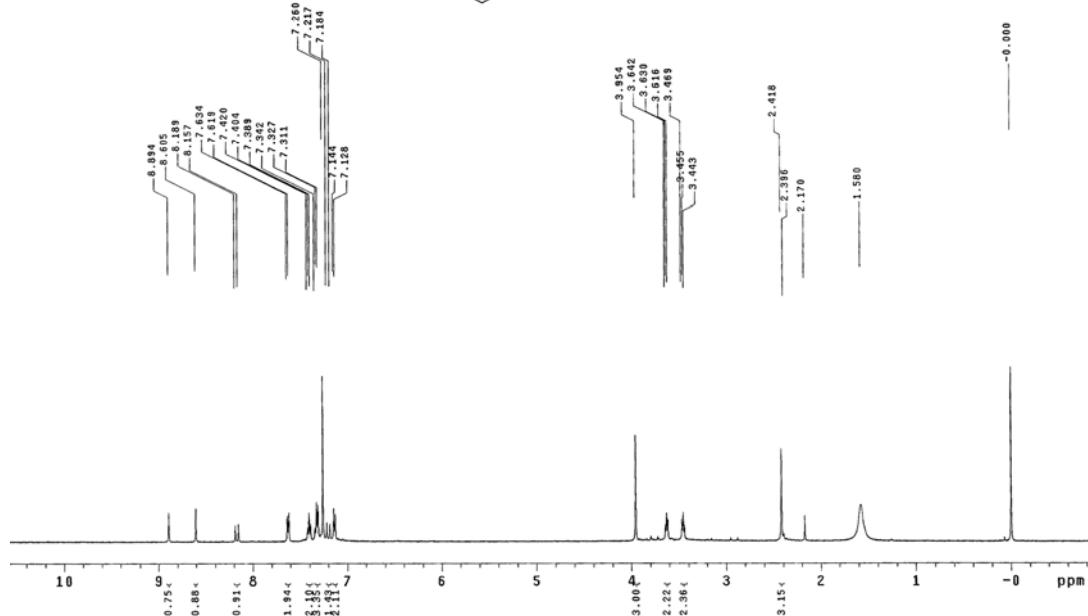
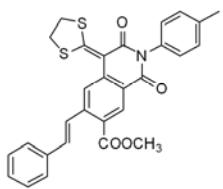


Figure 26. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6c.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: w526
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 1.352 sec
Width 10893.2 Hz
8 repetitions
OBSERVE H1, 499.8025524 MHz
DATA 100000000 NG
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-14-87
File: w564 "NENU500"
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acc. time 1.35 sec
Width 1021.1 Hz
320 repetitions
OBSERVE C13, 125.6754656 MHz
DATA 100000000 NG
Power 42 dB
continuously on
WALTZ-16 modulated
Data 131072
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

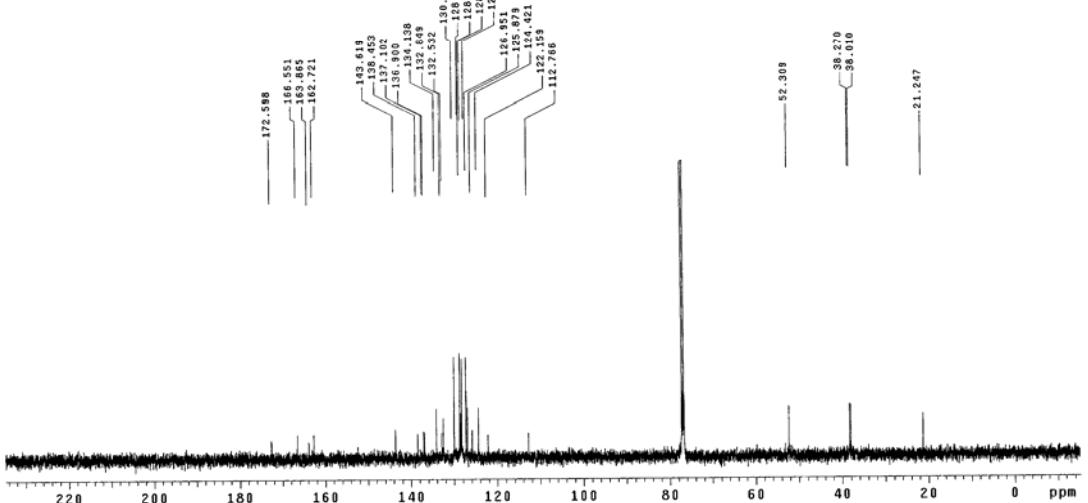
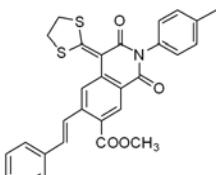
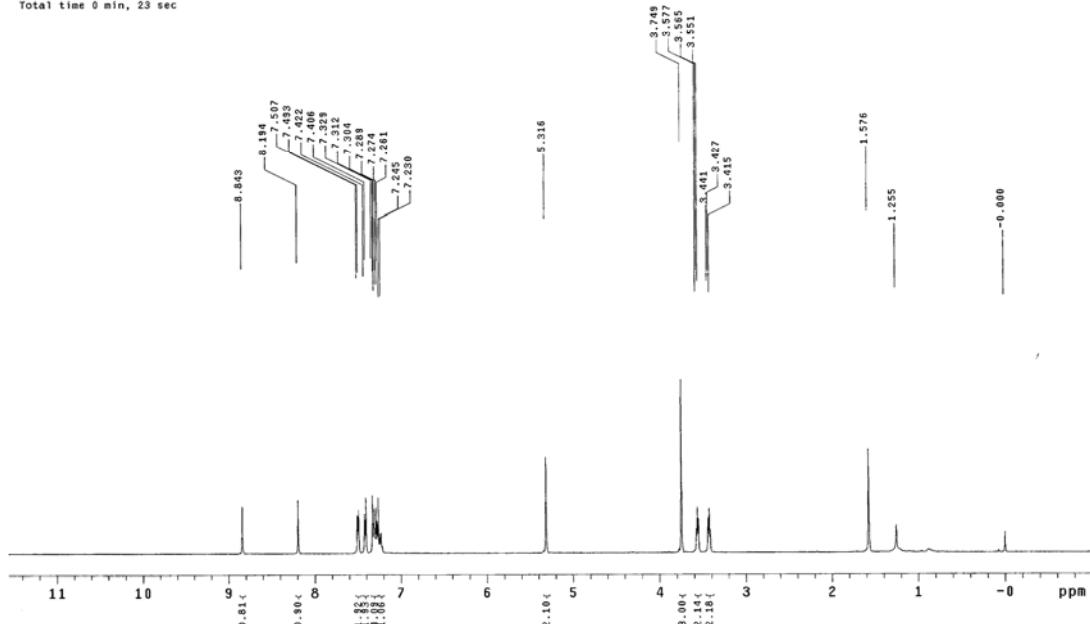
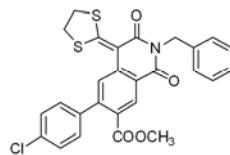


Figure 27. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6d.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: u455
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.200 sec
Width 10893.2 Hz
8 repetitions
OBSERVE MT 499.8025904 MHz
DATA PROCESSING
FT size 45536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: u472
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 10893.2 Hz
320 repetitions
OBSERVE C13, 125.6754642 MHz
DATA PROCESSING
FT size 131072
Power 42 dB
continuously on
WALTZ-16 modulated
Data 131072 points
Line broadening 1.5 Hz
Total time 3 hr, 56 sec

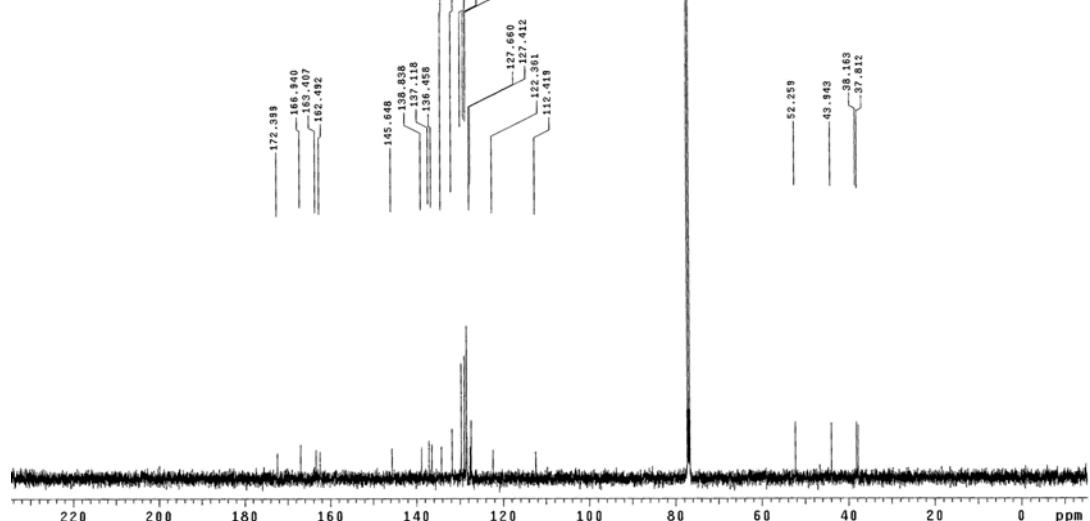
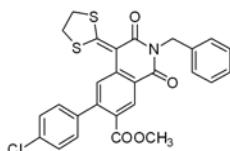
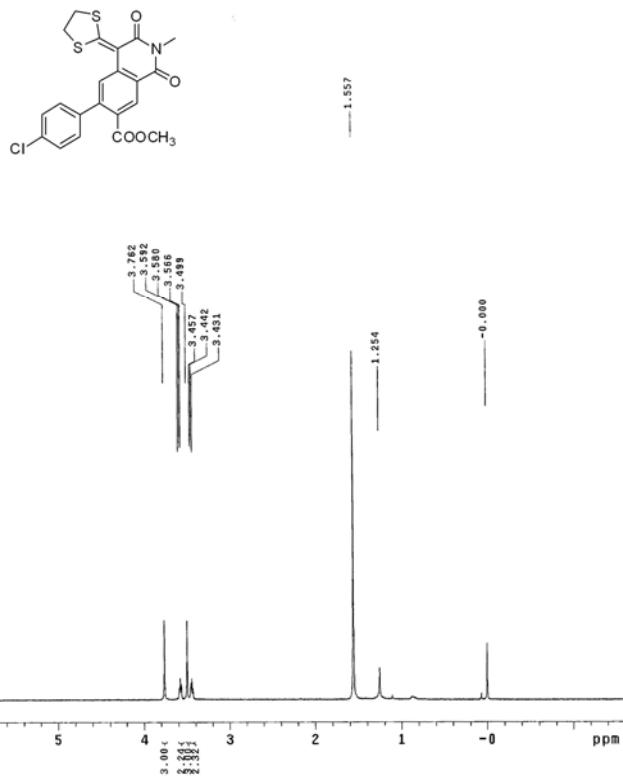


Figure 28. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6e.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: v058 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acc. time 1.882 sec
Width 31421.8 Hz
8 repetitions
OBSERVE H1, 499.8025904 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: u832 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acc. time 1.882 sec
Width 31421.8 Hz
5440 repetitions
OBSERVE C13, 125.6754680 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 hr, 56 sec

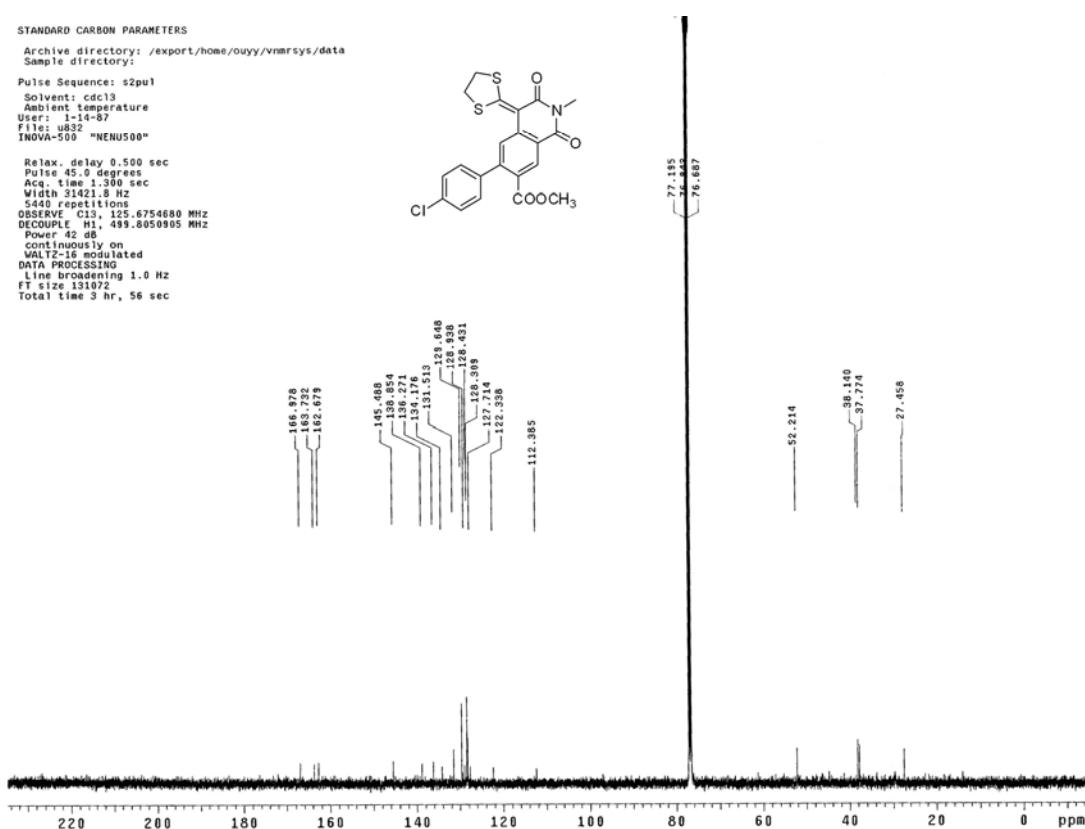
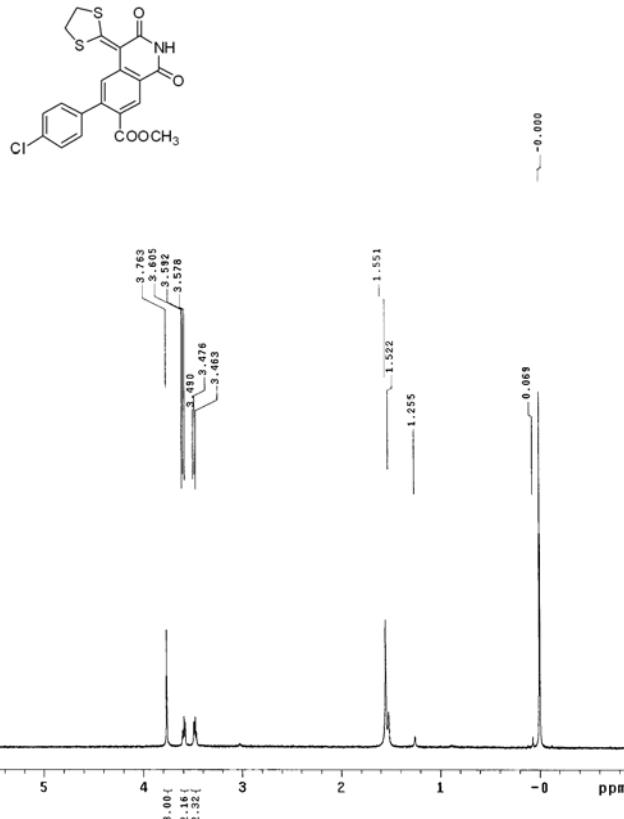


Figure 29. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6f.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: x826
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 10893.2 Hz
8 scans
OBSERVE = H1, 499.8025930 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
User: 1-10-07
File: u763
INOVA-500 "NENUS00"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
5656 points
OBSERVE = C13, 125.6760502 MHz
DECUPLE = H1, 499.8074646 MHz
Power 32 dB
containing 0 on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total time 3 hr, 56 sec

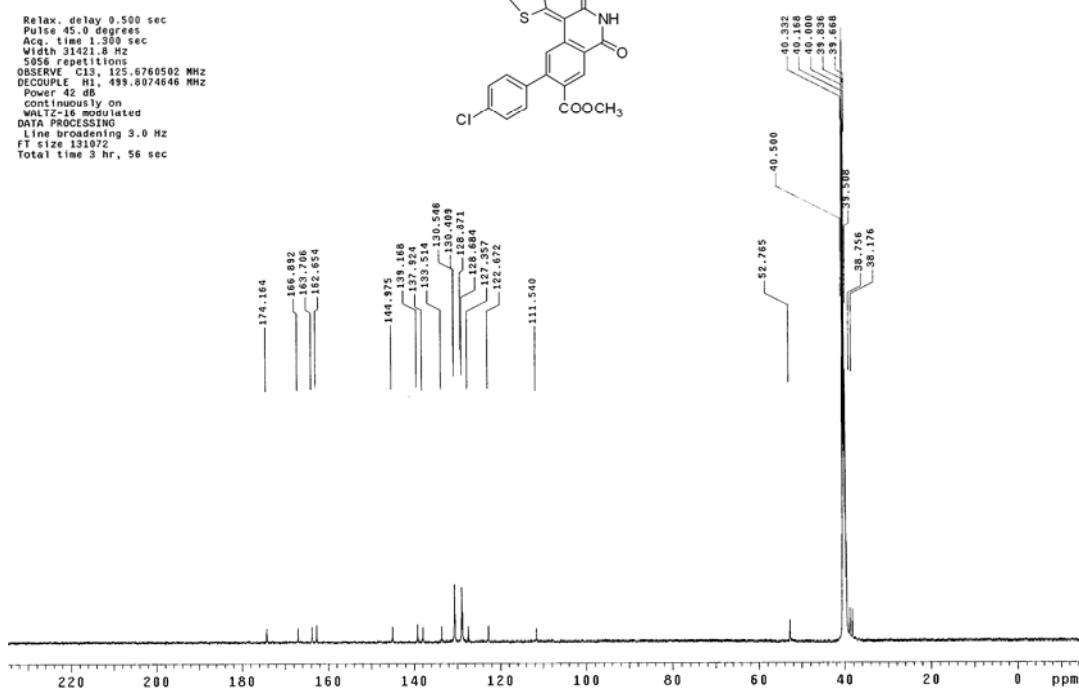
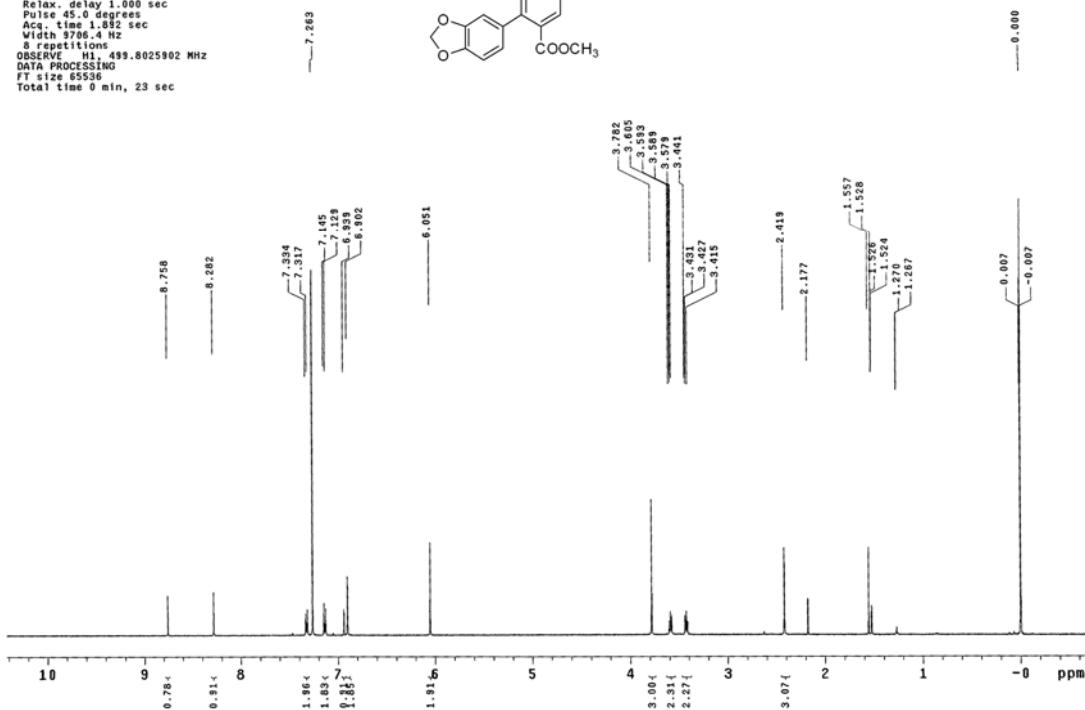


Figure 30. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6g.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: t478
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 37.614 Hz
S resolution 0.001 Hz
OBSERVE H₁, 499.8025902 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
File: v674
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 12.000 Hz
384 repetitions
OBSERVE C13, 125.6754685 MHz
DECUPLE H₁, 499.8050505 MHz
Pulse 45 degrees
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

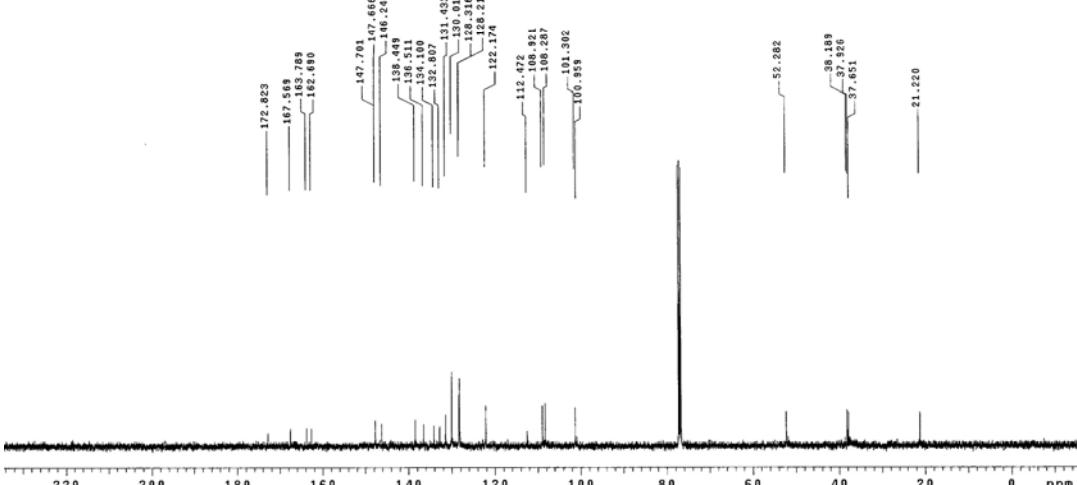
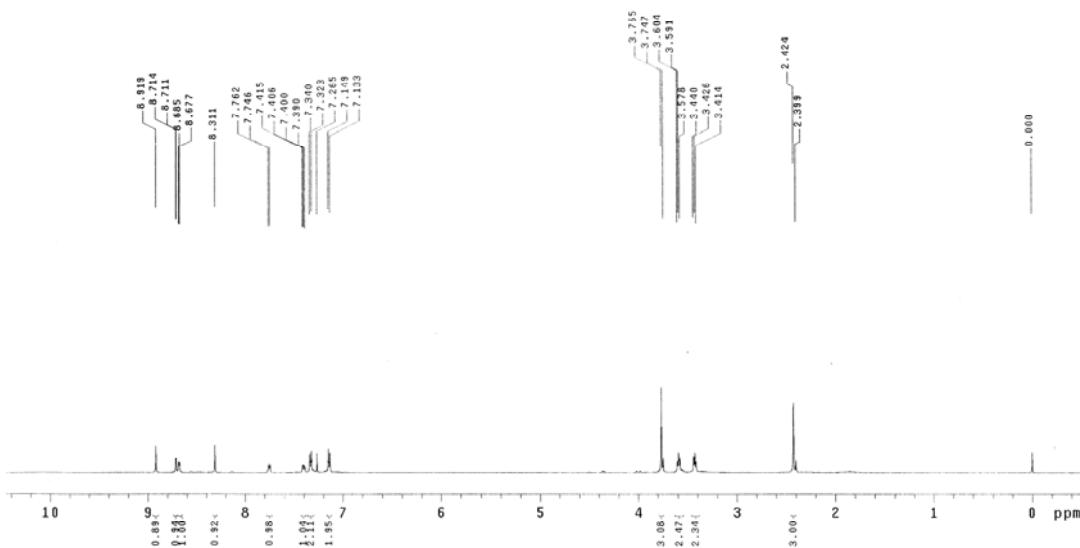
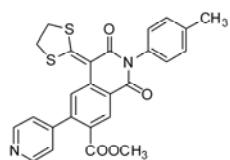


Figure 31. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6h.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnernsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: f822
INOVA-500 "NENNU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 1.311.9 Hz
4 repetitions
observed frequency 499.8025896 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 11 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnernsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User temperature 24.87
File: f536
INOVA-500 "NENNU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
13C evolution time 1.0 sec
OBSERVE C13: 125.6754646 MHz
DECOUPLE M1: 499.8050905 MHz
Power 42 dB
coupling on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

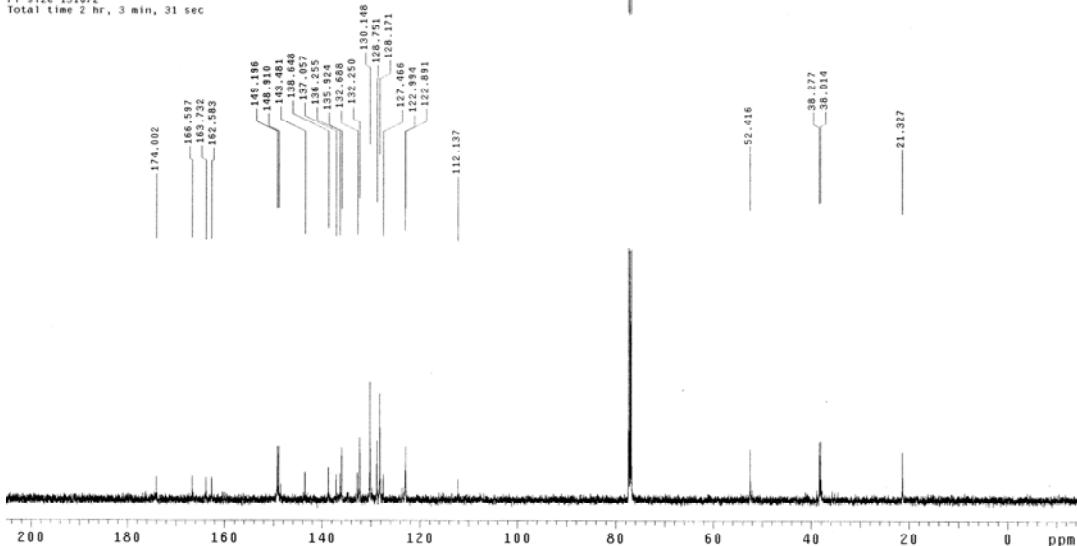
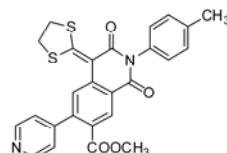
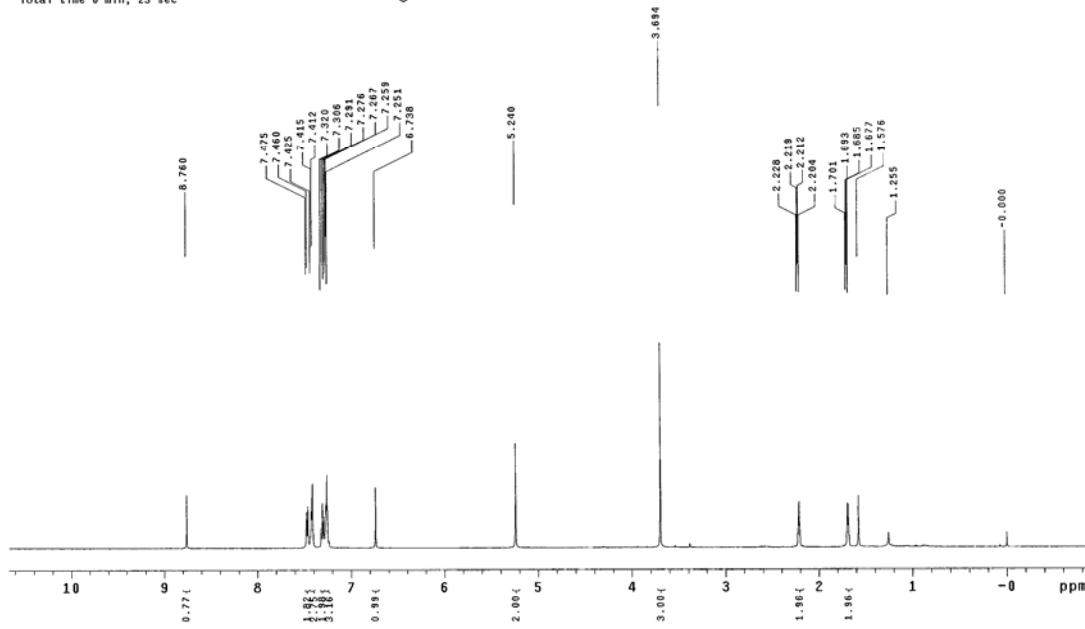
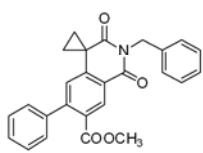


Figure 32. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6i.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: u307
INNOVA-500 "NENU500"
Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 10893.2 Hz
8 repetitions
OBSERVE FID: 499.8025520 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl₃
Ambient temperature
User: 1-t-87
File: u308
INNOVA-500 "NENU500"
Relax, delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6754666 MHz
DECOPPLE H1, 499.8050905 MHz
Power 42 dB
continuity on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

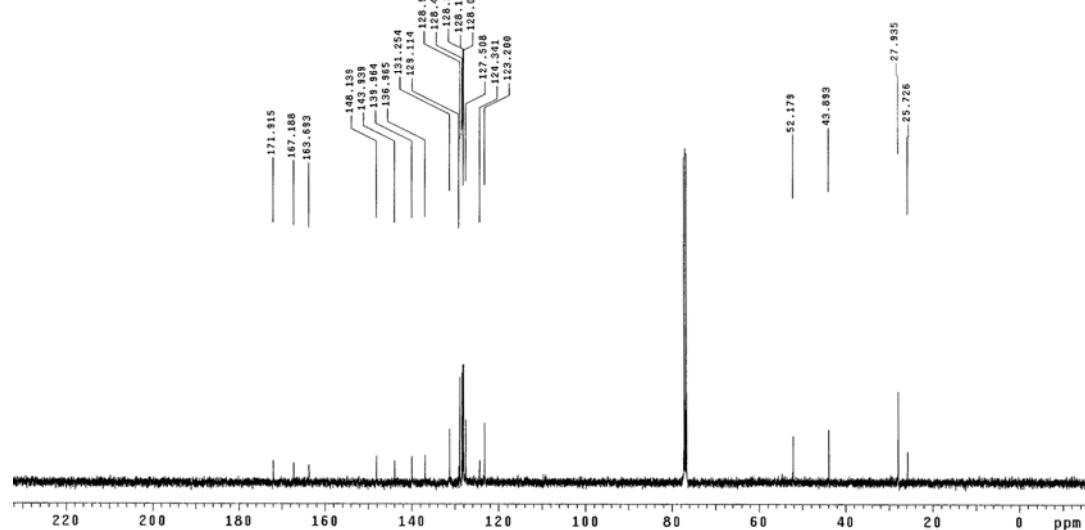
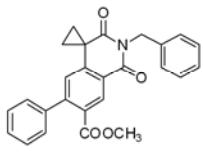


Figure 33. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6j.

```

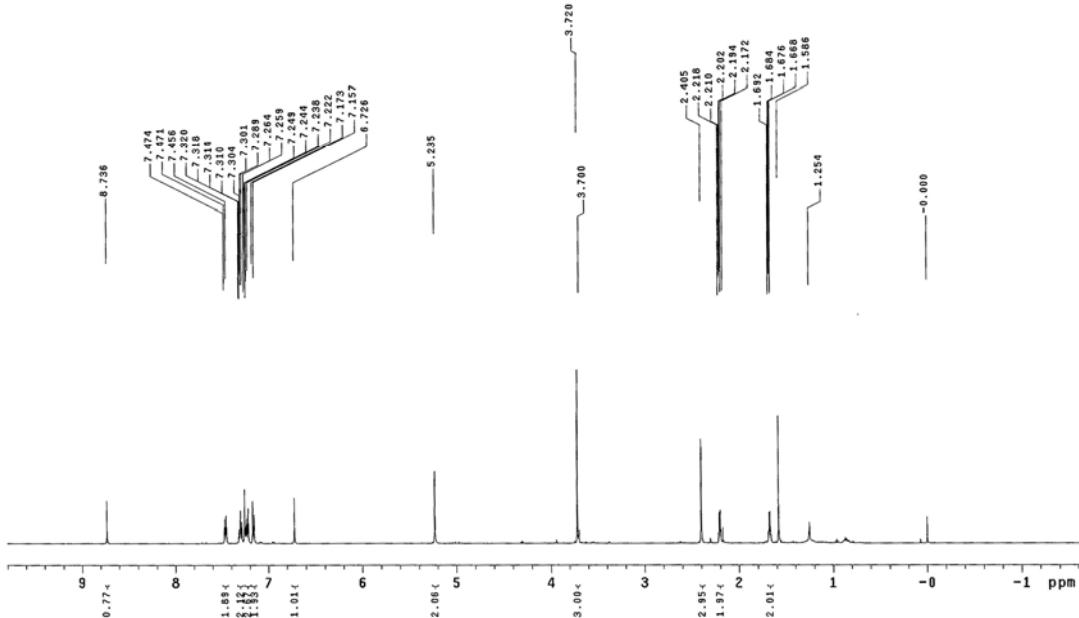
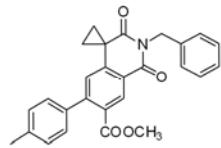
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: $2pul
Solvent: CDC13
Analyte: temperature
Model: US12
INNOVA-500 "NENU500"

Relaxation delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 10893.2 Hz
S value 1111111111111111
OBSERVE F1 49.8025920 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec

```



```

STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: cdc13
Ambient temperature
User temperature -87
File: u457
INDOVN-500 "NENDSU00"

Relax, delay 0.500 sec
Pulse 45.0 degrees
Aco. time 1.300 sec
Width 31428.8 Hz
32 scans

OBSERVE C13, 125.6754642 MHz
DECOUPLE H1, 810.850905 MHz
Power 42 dB
Quadrature on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT Tilt 0.000
Total time 3 hr, 56 sec
Total time 3 hr, 56 sec

```

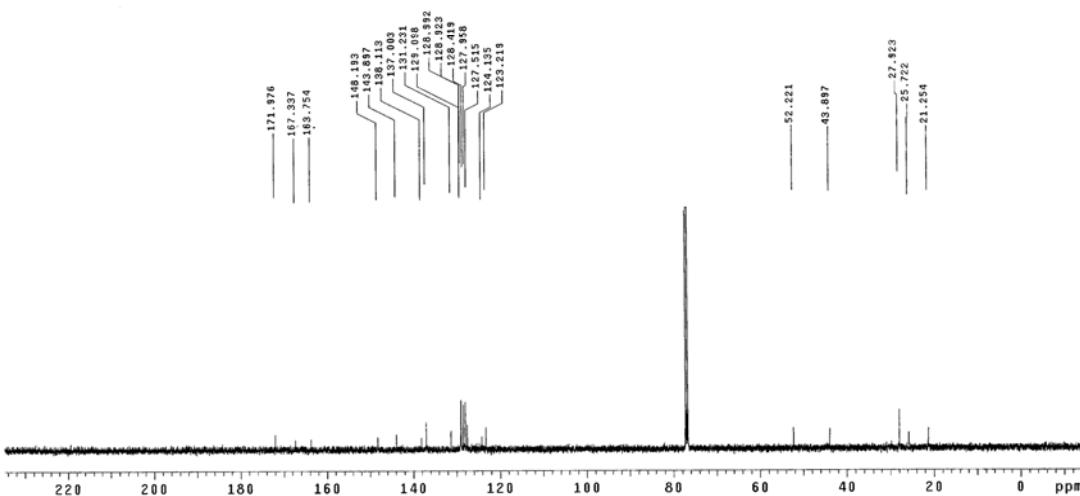
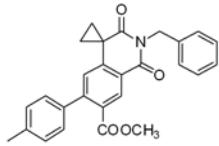
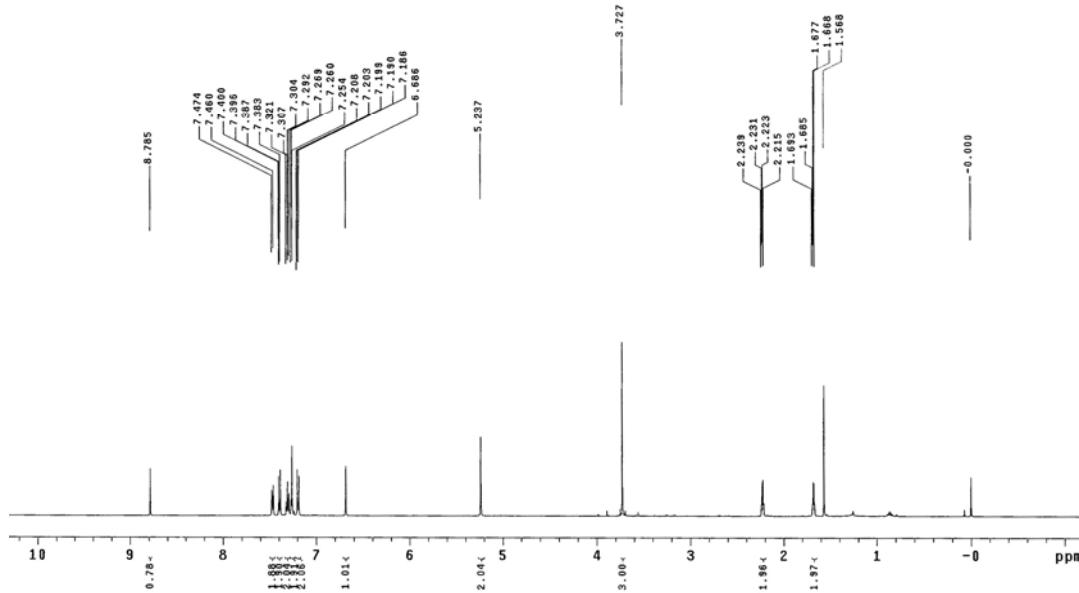
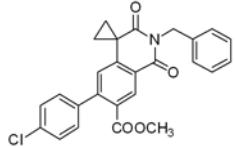


Figure 34. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **6k**.

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Filter: 1571 "NENUS00"
INOVA-500 "NENUS00"
Relax, delay 1.000 sec
Pulse 45.0 degrees
Acq time 1.68 sec
Width 9169.1 Hz
8 repetitions
OBSERVE FID 499.8025911 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
User: 1-14-87
Filter: t600 "NENUS00"
INOVA-500 "NENUS00"
Relax, delay 0.500 sec
Pulse 45.0 degrees
Acq time 1.68 sec
Width 31421.8 Hz
192 repetitions
OBSERVE C13, 125.6754632 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

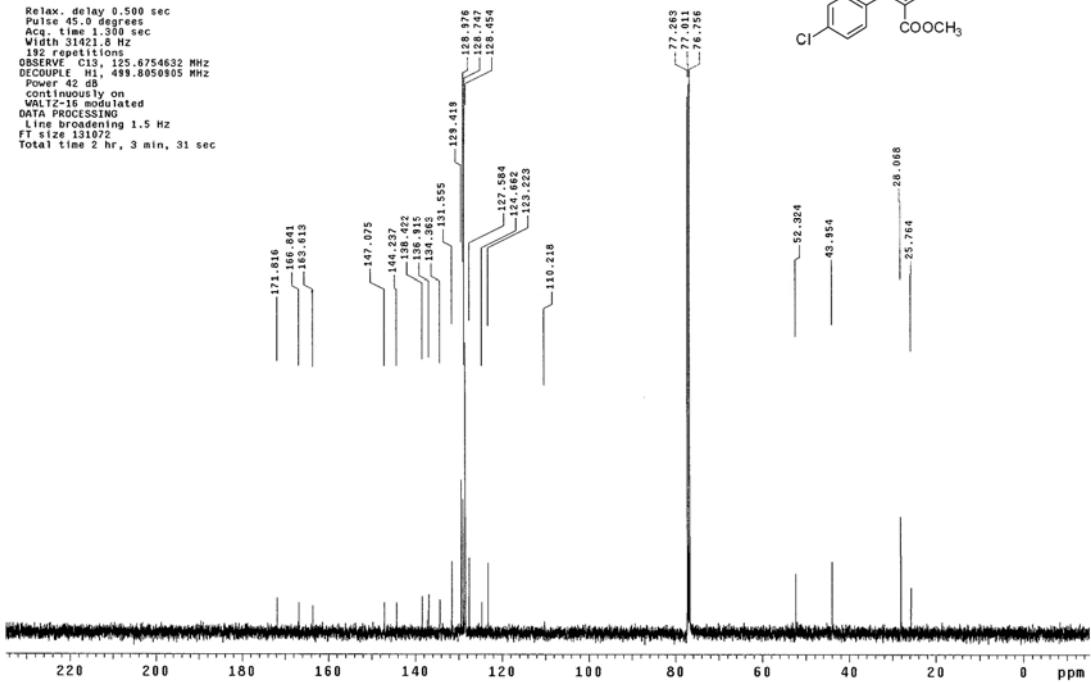
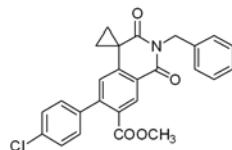


Figure 35. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 6l.