Supporting Information

Tandem Michael addition/intramolecular isocyanide [3 + 2] cycloaddition: highly diastereoselective one pot synthesis of fused oxazolines

Lingjuan Zhang, Xianxiu Xu,* Jing Tan, Ling Pan, Wenming Xia, and Qun liu*
Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China
xuxx677@nenu.edu.cn

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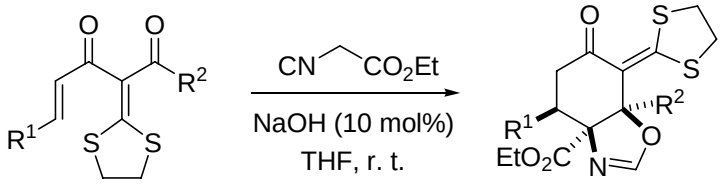
I. General information

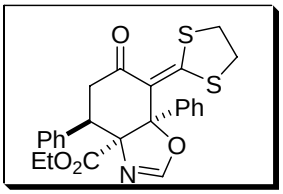
All reagents were commercial and used without further purification, unless otherwise indicated. Chromatography was carried on flash silica gel (300−400 mesh). All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). Melting points were uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were determined at 25ºC on a 500 MHz and 125 MHz, respectively, and TMS as internal standard. All shifts are given in ppm. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400-4000 cm^{-1}. Mass spectra were obtained on Agilent 1100 LCMSD mass spectrometer using the ESI method. Elemental analyses were measured on a GmbH VarioEL analyzer (Elementar Analysensysteme). The compound **2a** and **6b** was glued on a glass fiber. Data were collected at 273K using graphite-monochromated Mo Kα radiation (λ = 0.71073Å) and Bruker APEX CCD area-detector in the range 1.70° < θ < 26.07°. Substrates **1** were prepared by the similar method as our previously reported papers[1].

II. Synthetic procedures/analytical data of compounds **2**, **4**, **6** and **8.**

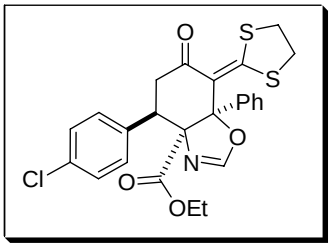


1 **2**

General procedure for the synthesis of 2, 4, 6 and 8 (taking 2a as an example): To the mixture of **1a** (352.5 mg, 1.0 mmol) and ethyl isocyanoacetate **2** (0.132 mL, 1.2 mmol) in THF (5 mL) was added NaOH (4.0 mg, 0.1 mmol) in one portion at room temperature. The reaction mixture was stirred at room temperature, and the reaction mixture was monitored by TLC. After the substrate **1a** was consumed, the resulting mixture was poured into ice-water (30 mL) under stirring. The precipitated solid was collected by filtration, washed with water (3 × 10 mL), and dried in vacuo to afford the product **2a** (428.4 mg, 92 %) as a white solid.

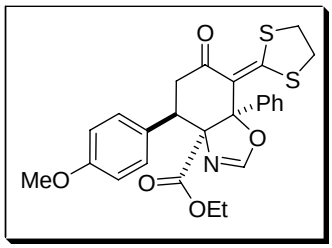


2a, ethyl 7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxo-4,7a-diphenylbenzo[*d*]oxazole-3a-carboxylate. White solid, m.p. 201-203°C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.60 (t, *J* = 7.0 Hz, 3H), 2.76 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.84-3.18 (m, 1H), 3.13-3.18 (m, 4H), 3.23-3.27 (m, 1H), 3.35-3.39 (m, 1H), 3.89 (dd, *J* = 14.0, 3.5 Hz, 1H), 7.19-7.25 (m, 4H), 7.27-7.34 (m, 3H), 7.43 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.8, 37.2, 37.5, 40.0, 41.1, 61.0, 84.1, 94.0, 122.4, 126.7, 127.1, 127.6, 127.8, 128.1, 128.8, 137.7, 139.8, 157.5, 168.3, 176.7, 190.8. IR (KBr, cm^{-1}) 3734, 3623, 2924, 1741, 1692, 1564, 1512, 1483, 1111, 676. ES-MS: m/z = 466.0 $[M + H]^+$. Anal. Calcd for $C_{25}H_{23}NO_4S_2$: C, 64.49; H, 4.98; N, 3.01; Found: C, 64.40; H, 5.03; N, 2.93.

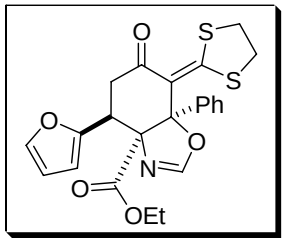


1. (a) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. *J. Am. Chem. Soc.,* 2005, **127**, 4578; (b) Liu, J.; Wang, M.; Li, B.; Liu, Q.; Zhao, Y. *J. Org. Chem.,* 2007, **72**, 4401.

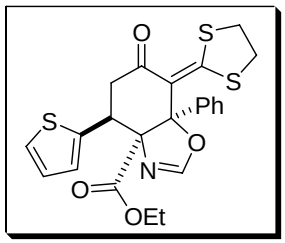
2b, ethyl 4-(4-chlorophenyl)-7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxo-7a-phenylbenzo [*d*]oxazole-3a-carboxylate. White solid, m.p. 212-213 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.64 (t, *J* = 7.5 Hz, 3H), 2.72 (dd, *J* = 17.5, 3.0 Hz, 1H), 3.00-3.17 (m 5H), 3.18-3.26 (m, 1H), 3.36-3.41 (m, 1H), 3.85 (dd, *J* = 11.0, 3.0 Hz, 1H), 7.20-7.48 (m, 9H), 7.57 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.9, 37.2, 37.5, 39.4, 40.9, 61.1, 83.9, 94.0, 122.2, 127.4, 127.7, 127.8, 128.0, 130.2, 132.5, 137.5, 138.4, 157.7, 168.1, 177.0, 190.4. IR (KBr, cm^{-1}) 3064, 1728, 1611, 1129. ES-MS: m/z = 500.0 $[M + H]^+$. Anal. Calcd for $C_{25}H_{22}ClNO_4S_2$: C, 60.05; H, 4.43; N, 2.80; Found: C, 59.97; H, 4.47; N, 2.73.



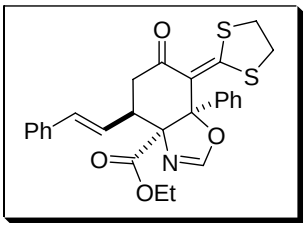
2c, ethyl 7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-4-(4-methoxyphenyl)-6-oxo-7a-phenylbenzo [d]oxazole-3a-carboxylate. White solid, m.p. 213-214^{o}C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.64 (t, *J* = 7.0 Hz, 3H), 2.72 (dd, *J* = 17.5, 3.5 Hz, 1H), 2.95-3.01 (m, 1H), 3.06-3.25 (m, 5H), 3.30-3.41 (m, 1H), 3.74 (s, 3H), 3.84 (dd, *J* = 14.5, 3.5 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 7.18-7.33 (m, 4H), 7.43 (d, J = 9.0 Hz, 2H), 7.40 (s, 1H), 7.57 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.9, 37.2, 37.5, 39.2, 41.2, 54.8, 61.0, 84.3, 94.0, 113.1, 122.5, 126.3, 127.8, 128.0, 130.0, 131.8, 137.8, 157.4, 158.2, 168.4, 176.4, 191.0. IR (KBr, cm^{-1}) 3034, 1728, 1631, 1488, 1395, 1281, 1127, 1074. ES-MS: m/z = 496.0 $[M + H]^+$. Anal. Calcd for $C_{26}H_{25}NO_5S_2$: C, 63.01; H, 5.08; N, 2.83; Found: C, 62.96; H, 5.10; N, 2.79.



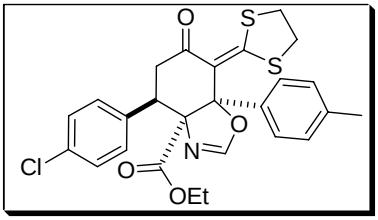
2d, ethyl 7-(1,3-dithiolan-2-ylidene)-4-(furan-2-yl)-3a,4,5,6,7,7a-hexahydro-6-oxo-7a-phenylbenzo[*d*]oxazole-3a-carboxylate. White solid, m.p.189-190^{o}C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.74 (t, *J* = 7.5 Hz, 3H), 2.91 (dd, *J* = 17.0, 4.0 Hz, 1H), 3.03-3.24 (m, 6H), 3.45-3.58 (m, 1H), 4.14 (dd, *J* = 13.5, 4.0 Hz, 1H), 6.26 (d, J = 1.5 Hz, 1H), 6.29 (d, J = 2.5 Hz, 1H), 7.29 (s, 1H), 7.33 (s, 3H), 7.39 (s, 1H), 7.58-7.62 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 13.6, 35.0, 37.7, 38.0, 38.9, 61.7, 83.8, 94.2, 107.5, 110.5, 122.7, 127.5, 128.2, 128.7, 138.1, 141.5, 153.7, 158.2, 168.8, 177.4, 190.6. IR (KBr, cm^{-1}) 3044, 1729, 1625, 1395, 1275, 1249, 1118, 892, 691. ES-MS: m/z = 456.0 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}NO_5S_2$: C, 60.64; H, 4.65; N, 3.07; Found: C, 60.50; H, 4.58; N, 3.11.



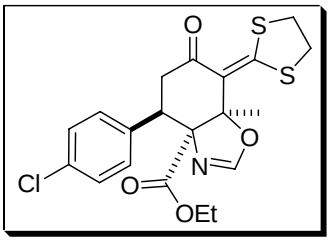
2e, ethyl 7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxo-7a-phenyl-4-(thiophen-2-yl)benzo[*d*]oxazole -3a-carboxylate. White solid, m.p. 200-202^{o}C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.71 (t, *J* = 7.0 Hz, 3H), 2.86 (dd, *J* = 17.5, 4.0 Hz, 1H), 2.97-3.27 (m, 6H), 3.41-3.48 (m, 1H), 4.28 (dd, *J* = 14.0, 4.0 Hz, 1H), 6.87(t, J = 4.0 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 7.13 (d, J = 4.0 Hz, 1H), 7.25 (s, 1H), 7.33 (s, 3H), 7.41 (s, 1H), 7.59 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.9, 36.1, 37.2, 37.5, 42.0, 61.2, 84.2, 93.8, 122.2, 124.2, 125.9, 126.2, 126.5, 127.8, 128.1, 137.7, 141.9, 157.6, 168.1, 176.9, 189.9. IR (KBr, cm^{-1}) 3044, 1737, 1626, 1400, 1246, 1113, 678. ES-MS: m/z = 472.0 $[M + H]^+$. Anal. Calcd for $C_{23}H_{21}NO_4S_3$: C, 58.57; H, 4.49; N, 2.97; Found: C,58.69; H, 4.53; N, 3.07.



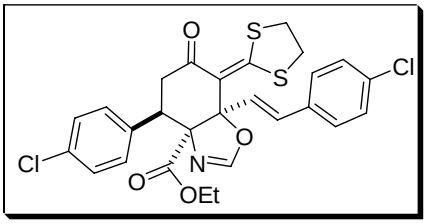
2f, ethyl 7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxo-7a-phenyl-4-styrylbenzo[*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 1:1). Yellowish solid, m. p. 146-148 ^oC. ^1H NMR ($CDCl_3$, 500 Hz) δ 0.83 (t, *J* = 7.5 Hz, 3H), 2.68 (dd, *J* = 17.5, 4.5 Hz, 1H), 2.86 (dd, *J* = 17.5, 13.5 Hz, 1H), 3.08-3.23 (m, 5H), 3.56-3.61 (m, 1H), 6.29 (dd, *J* = 15.5, 8.5 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.24-7.27 (m, 3H), 7.31-7.33 (m, 5H), 7.37 (s, 1H), 7.58 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 13.5, 37.5, 37.8, 38.8, 39.2, 61.5, 84.1, 93.8, 122.6, 126.3, 127.4, 127.5, 127.9, 128.3, 128.4, 133.2, 136.7, 138.1, 157.8, 168.8, 176.6, 190.9. ES-MS: m/z = 492.1 $[M + H]^+$. Anal. Calcd for $C_{27}H_{25}NO_4S_2$: C, 65.96; H, 5.13; N, 2.85; Found: C, 65.81; H, 5.02; N, 2.97.



2h, ethyl 4-(4-chlorophenyl)-7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxo-7a-*p*-tolylbenzo [*d*]oxazole-3a-carboxylate. White solid, m. p. 210-212 ^oC. ^1H NMR ($CDCl_3$, 500 Hz) δ 0.66 (t, *J* = 7.5 Hz, 3H), 2.36 (s, 3H), 2.70 (dd, *J* = 17.5, 4.0 Hz, 1H), 3.03-3.17 (m, 5H), 3.21-3.27 (m, 1H), 3.35-3.41 (m, 1H), 3.85 (dd, *J* = 14.0, 4.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 3H), 7.21 (d, J = 8.5 Hz, 2H), 7.40 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 13.0, 21.0, 37.3, 37.6, 39.5, 41.0, 61.2, 83.9, 94.2, 122.3, 126.3, 127.1, 128.0, 128.4, 128.8, 130.3, 132.5, 134.5, 138.2, 138.6, 157.9, 168.3, 177.1, 190.5. IR (KBr, cm^{-1}) 3047, 1736, 1627, 1491, 1395, 1281, 1129, 1073, 874, 605. ES-MS: m/z = 514.0 $[M + H]^+$. Anal. Calcd for $C_{26}H_{24}ClNO_4S_2$: C, 60.75; H, 4.71; N, 2.72; Found: C, 60.49; H, 4.69; N, 2.76.

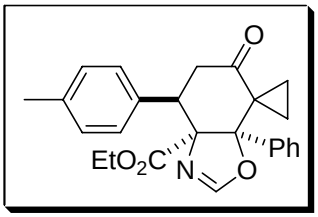


2i, ethyl 4-(4-chlorophenyl)-7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-7a-methyl-6-oxobenzo [*d*]oxazole-3a-carboxylate. White solid, m.p. 175-177 ^oC. ^1H NMR ($CDCl_3$, 500 Hz) δ 1.07 (t, *J* = 7.5 Hz, 3H), 1.92 (s, 3H), 2.59 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.91 (dd, *J* = 19.0, 15.0 Hz, 1H), 3.14-3.19 (m, 1H), 3.30-3.38 (m, 2H), 3.44-3.47 (m, 1H), 3.73 (dd, *J* = 14.0, 3.5 Hz, 1H), 4.02 (m, 2H), 7.18 (s, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 13.8, 20.2, 36.9, 37.4, 40.8, 41.4, 61.9, 81.9, 90.3, 123.3, 128.4, 130.5, 132.9, 138.4, 158.0, 169.5, 191.2. IR (KBr, cm^{-1}) 3034, 1719, 1705, 1618, 1256, 1114. ES-MS: m/z = 438.0 $[M + H]^+$. Anal. Calcd for $C_{20}H_{20}ClNO_4S_2$: C, 54.85; H, 4.60; N, 3.20; Found: C, 54.77; H, 4.53; N, 3.32.

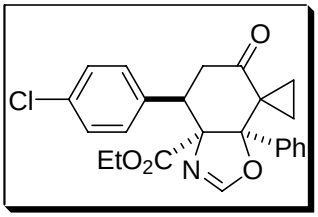


2j, ethyl 7a-(4-chlorostyryl)-4-(4-chlorophenyl)-7-(1,3-dithiolan-2-ylidene)-3a,4,5,6,7,7a-hexahydro-6-oxobenzo [*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 3:1). Yellowish solid, m.p. 114-116 ^oC. m.p. 175-177 ^oC. ^1H NMR ($CDCl_3$, 500 Hz) δ 0.87 (t, *J* = 7.0 Hz, 3H), 2.64 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.98 (dd, *J* = 17.0, 15.0 Hz, 1H), 3.22-3.33 (m, 4H), 3.65-3.68 (m, 1H), 3.75-3.79 (m, 1H), 3.88 (dd, *J* = 14.5, 3.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.32 (s, 5H), 7.45 (d, *J*

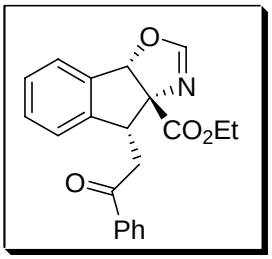
= 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 13.7, 37.7, 37.8, 40.6, 40.8, 61.8, 84.3, 91.4, 120.6, 126.5, 127.8, 128.3, 129.0, 130.5, 131.1, 133.0, 134.1, 138.1, 157.5, 168.9, 176.3, 191.0. ES-MS: m/z = 560.0 $[M + H]^+$. Anal. Calcd for $C_{27}H_{23}Cl_2NO_4S_2$: C, 57.86; H, 4.14; N, 3.32; Found: C, 57.97; H, 4.00; N, 3.51.



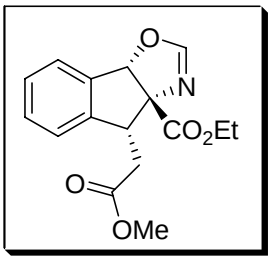
4a, ethyl 3a,4,5,6,7,7a-hexahydro-7-cyclopropyl-6-oxo-7a-phenyl-4-p-tolylbenzo[*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 9:1). Purified by flash chromatography (silica gel. PE-Et_2O, 9:1). Yellowish viscous liquid. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.60 (t, *J* = 7.5 Hz, 3H), 0.62-0.65 (m, 1H), 1.12-1.16 (m, 1H), 1.19-1.25 (m, 1H), 1.57-1.61 (m, 1H), 2.29(s, 3H), 2.65 (dd, *J* = 18.0, 3.0 Hz, 1H), 2.92 (dd, *J* = 18.0, 14.5 Hz, 1H), 3.31-3.35 (m, 1H), 3.38-3.43 (m, 1H), 4.27 (dd, *J* = 14.5, 3.0 Hz, 1H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.24-7.33 (m, 3H), 7.37 (s, 2H), 7.39 (s, 1H), 7.41(d, *J* = 9.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.7, 13.1, 21.0, 21.3, 35.7, 42.2, 42.9, 61.3, 84.7, 94.3, 126.6, 127.4, 128.3, 128.8, 129.3, 135.7, 136.4, 136.6, 155.2, 168.9, 207.3. ES-MS: m/z = 404.2 $[M + H]^+$. Anal. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47; Found: C, 74.63; H, 6.12; N, 3.58.



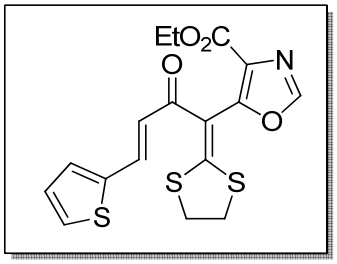
4b, ethyl 3a,4,5,6,7,7a-hexahydro-7-cyclopropyl-6-oxo-7a-phenyl-4-(4-chlorophenyl)benzo[*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 9:1). Purified by flash chromatography (silica gel. PE-Et_2O, 9:1). Yellowish viscous liquid. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 0.60 (t, *J* = 7.5 Hz, 3H), 0.62-0.64 (m, 1H), 1.12-1.16 (m, 1H), 1.21-1.25 (m, 1H), 1.55-1.61 (m, 1H), 2.65 (dd, *J* = 18.0, 3.5 Hz, 1H), 2.92 (dd, *J* = 18.0, 14.5 Hz, 1H), 3.31-3.35 (m, 1H), 3.38-3.43 (m, 1H), 4.27 (dd, *J* = 14.5, 3.0 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.30-7.33 (m, 3H), 7.37 (s, 1H), 7.39 (s, 1H), 7.49 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 12.6, 13.1, 21.6, 35.7, 42.0, 42.8, 61.5, 84.4, 94.5, 126.5, 127.4, 128.2, 128.4, 130.9, 132.9, 135.5, 138.1, 155.5, 168.8, 206.7. ES-MS: m/z = 424.1 $[M + H]^+$. Anal. Calcd for $C_{24}H_{22}ClNO_4$: C, 68.00; H, 5.23; N, 3.30; Found: C, 68.21; H, 5.11; N, 3.48.



6a, ethyl 4-(2-oxo-2-phenylethyl)-4,8b-dihydro-3aH-indeno[2,1-*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 6:1). Yellowish solid, m.p. 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.33 (t, *J* = 7.5 Hz, 3H), 3.39 (dd, *J* = 18.5, 6.0 Hz, 1H), 3.76 (dd, *J* = 18.5, 8.0 Hz, 1H), 4.32-4.35 (m, 2H), 4.68 (dd, *J* = 8.0, 6.0 Hz, 1H), 6.06 (s, 1H), 6.89 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.34-7.38 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 3H), 7.55 (t, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 14.1, 40.8, 47.5, 61.9, 83.9, 88.4, 124.3, 125.9, 128.1, 128.2, 128.5, 130.4, 133.1, 136.6, 137.6, 144.1, 155.1, 172.4, 198.3. ES-MS: m/z = 350.1 $[M + H]^+$. Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01; Found: C, 72.32; H, 5.61; N, 4.26.



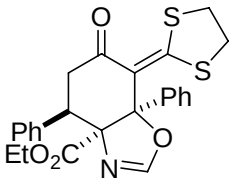
6b, ethyl 4-(2-methoxy-2-oxoethyl)-4,8b-dihydro-3aH-indeno[2,1-*d*]oxazole-3a-carboxylate. Purified by flash chromatography (silica gel. PE-Et_2O, 9:1). White solid, m.p. 88-90 °C. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.33 (t, *J* = 7.0 Hz, 3H), 2.79 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.96 (dd, *J* = 17.0, 8.5 Hz, 1H), 3.76 (s, 3H), 4.31 (q, *J* = 7.0 Hz, 2H), 4.42 (dd, *J* = 8.5, 6.0 Hz, 1H), 5.98 (s, 1H), 6.90 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 14.1, 35.7, 48.3, 51.8, 61.9, 83.7, 88.5, 124.0, 126.0, 128.3, 130.4, 137.4, 143.3, 155.3, 172.2, 172.7. ES-MS: m/z = 304.1 $[M + H]^+$. Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62; Found: C, 63.21; H, 5.46; N, 4.83.



8, (*E*)-ethyl 2-(1-(1,3-dithiolan-2-ylidene)-2-oxo-4-(thiophen-2-yl)but-3-en-1-yl)furan-3-carboxylate. ^{1}H NMR ($CDCl_3$, 500 Hz) δ 1.25 (t, *J* = 7.0 Hz, 3h), 3.36 (t, *J* = 6.5 Hz, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 4.29 (q, *J* = 7.0 Hz, 2H), 6.24 (d, *J* = 15.0 Hz, 1H), 7.00 (t, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 3.0 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.83 (d, *J* = 15.0 Hz, 1H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 Hz), δ 14.3, 36.3, 39.8, 61.6, 112.7, 121.4, 128.4, 128.8, 130.7, 131.7, 136.2, 140.5, 151.2, 153.3, 160.9, 174.8, 182.2. ES-MS: m/z = 394.1 $[M + H]^+$. Anal. Calcd for $C_{17}H_{15}NO_4S_3$: C, 51.89; H, 3.84; N, 3.56; Found: C, 51.97; H, 3.68; N, 3.72.

III. Crystal data and ORTEP drawing of compound 2a and 6b

2a: $C_{100}H_{92}N_4O_{16}S_8$, *M* = 1862.26, orthorhombic, space group *Fdd*2, *a* = 24.784(5), *b* = 15.750(5), *c* = 23.149(5) Å, *V* = 9036(4) Å^3, α = 90.000(5), β = 90.000(5), γ = 90.000(5), Z = 4, *T* = 273(2) K, *F*000 = 3904, 3965 reflections collected, 2710 unique, R_1 = 0.0510, wR_2 = 0.0883 ($I > 2\sigma(I)$).



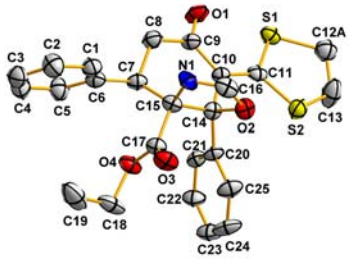
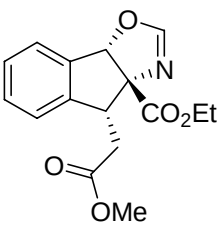


Fig 1. ORTEP diagram of **2a** (30% probability displacement ellipsoids and all hydrogen atoms are omitted).

6b: $C_{16}H_{17}NO_5$, *M* = 303.31, orthorhombic, space group *P*212121, *a* = 7.5750(8), *b* = 12.0480(12), *c* = 16.6840(17) Å, *V* = 1522.6(3) Å^3, α = 90.00, β = 90.00, γ = 90.00, Z = 4, *T* = 273(2) K, *F*000 = 640, 3225 reflections collected, 2175 unique, R_1 = 0.0523, wR_2 = 0.1323 ($I > 2\sigma(I)$).



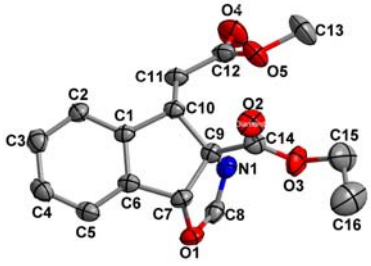
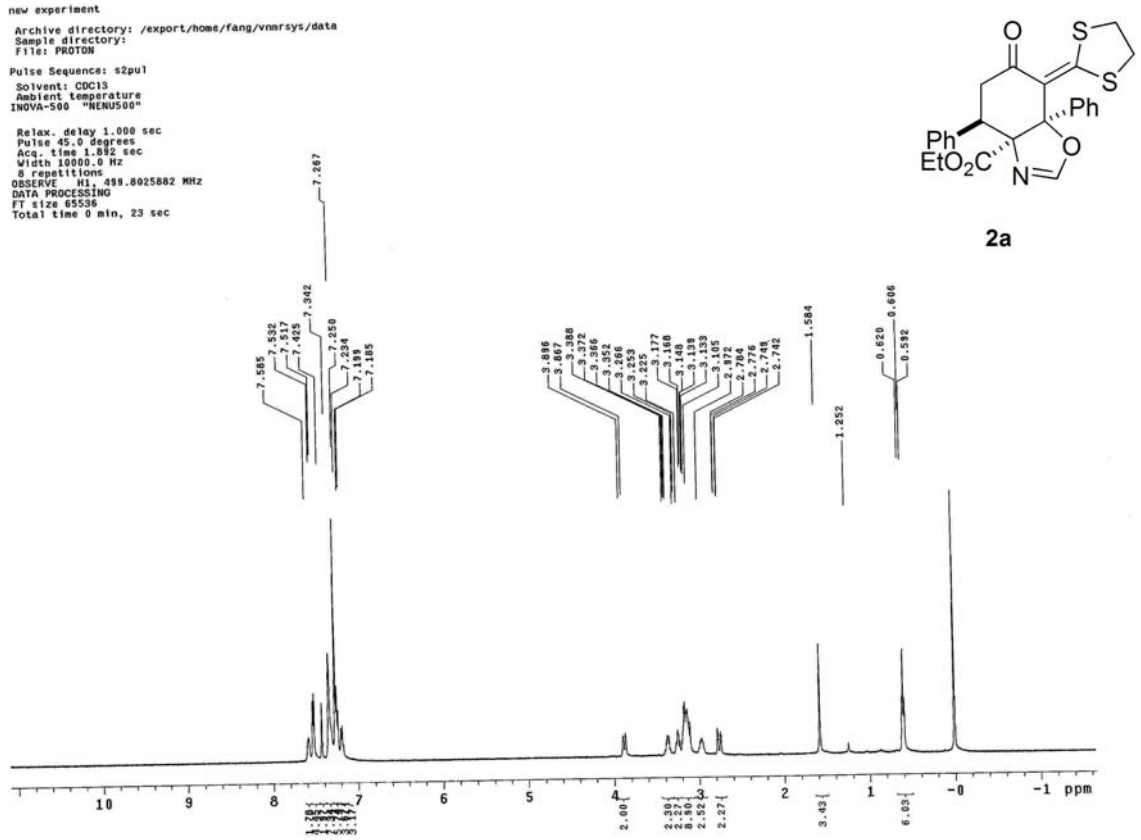
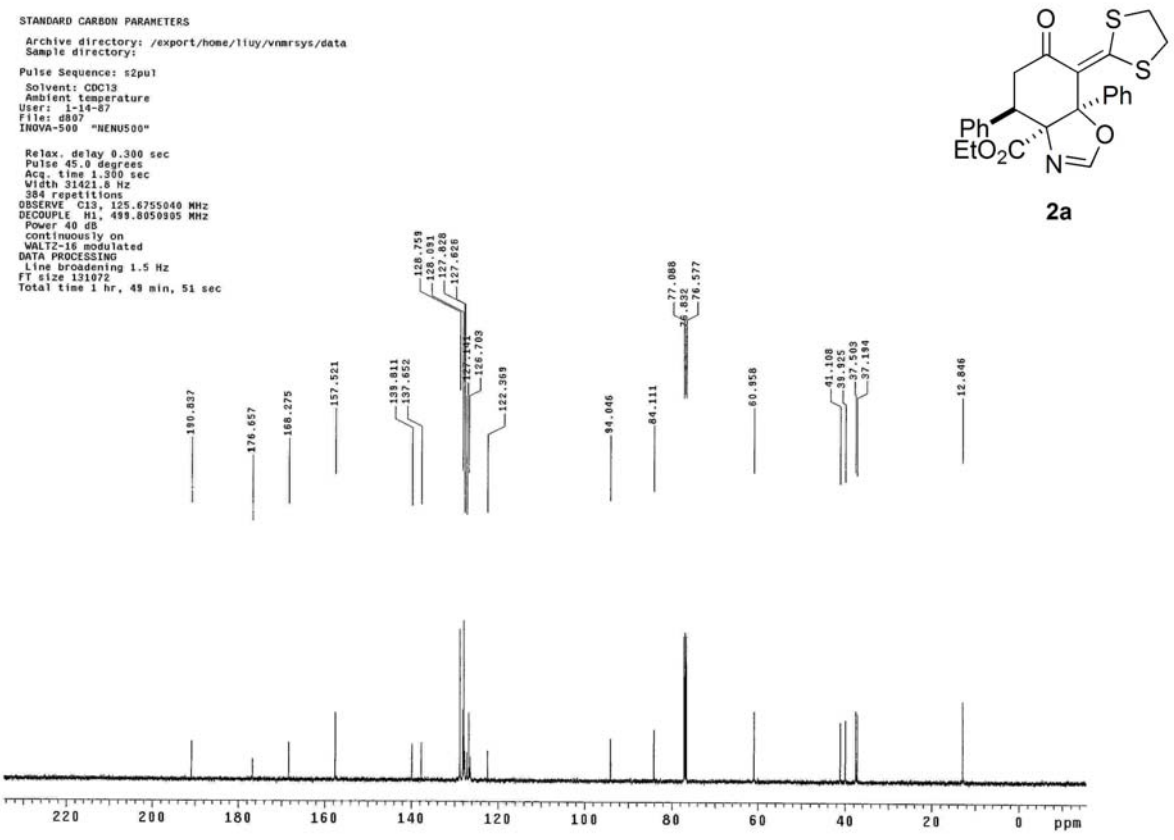
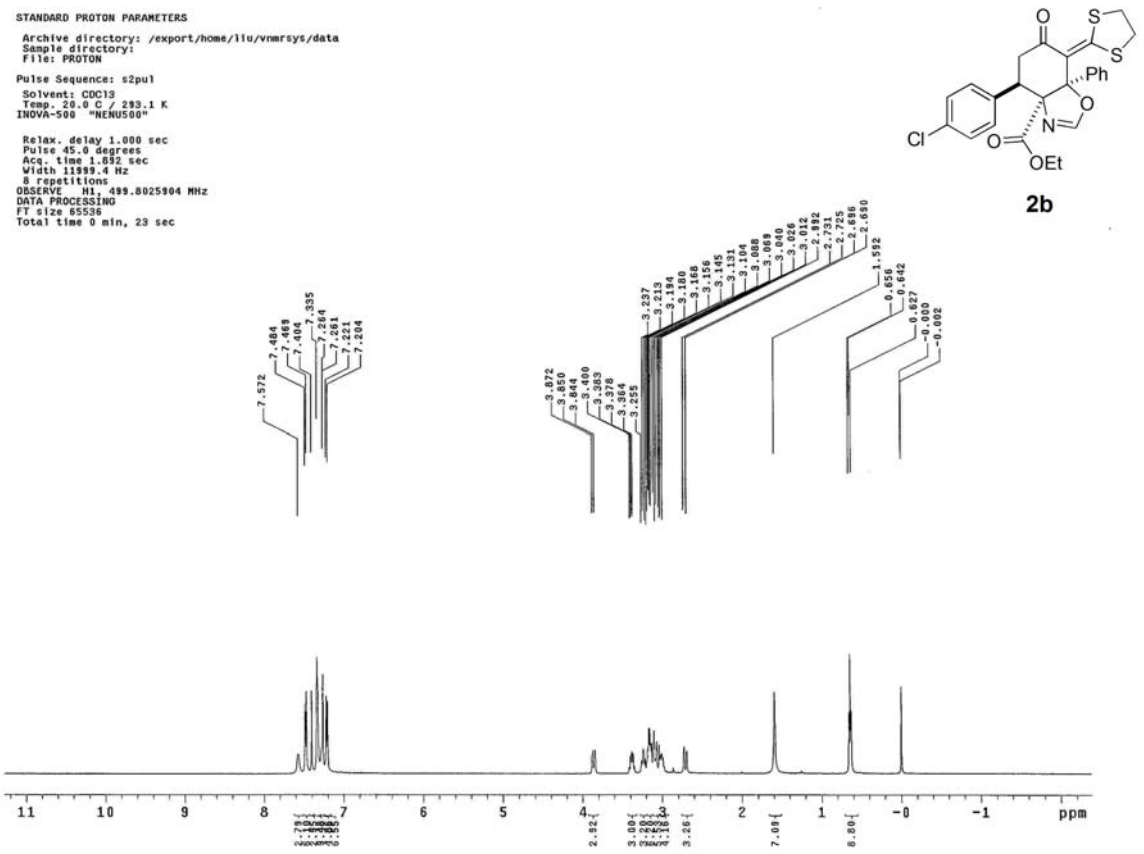


Fig 2. ORTEP diagram of **6b** (30% probability displacement ellipsoids and all hydrogen atoms are omitted).

VI. Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 2, 4, 6 and 8



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Solvent: CDCl3
Temp. 20.0 C / 293.1 K
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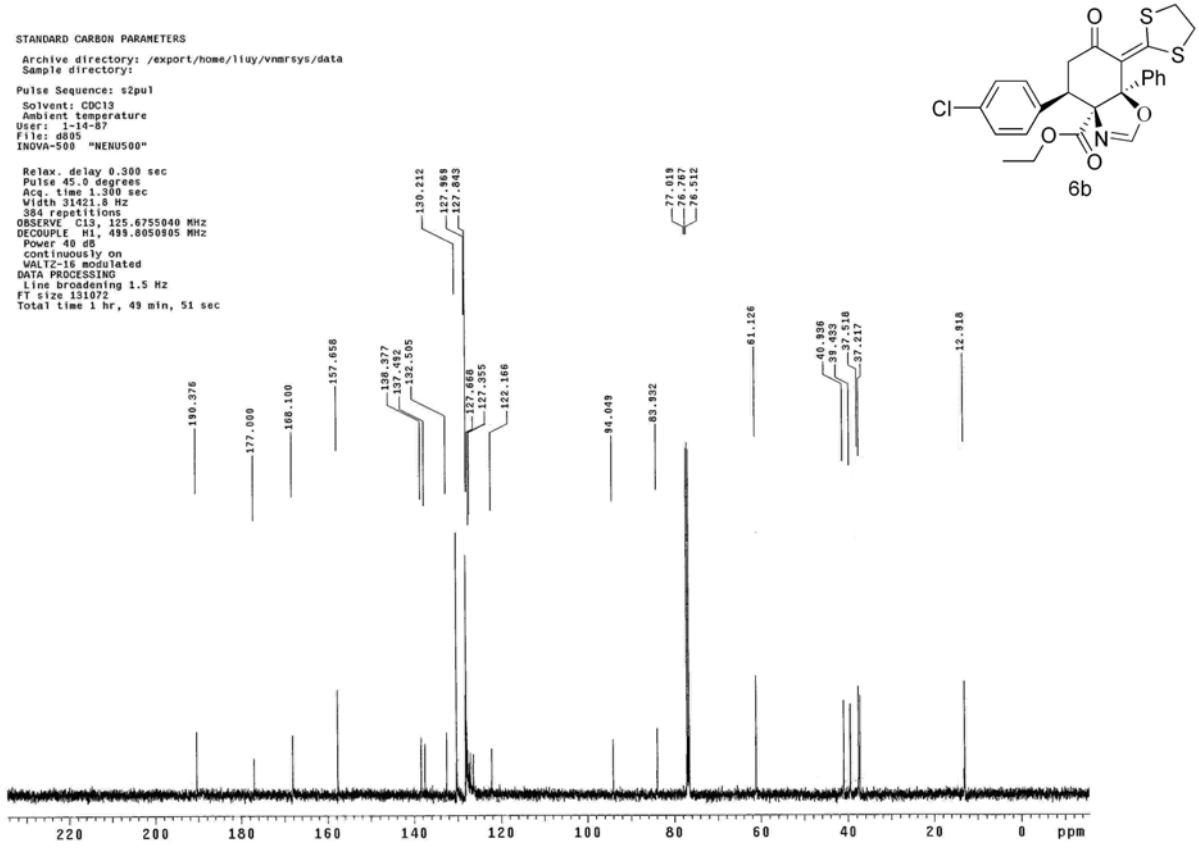
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 11999.4 Hz
8 repetitions
OBSERVE H1, 499.8025304 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2b
ppm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Sample directory:
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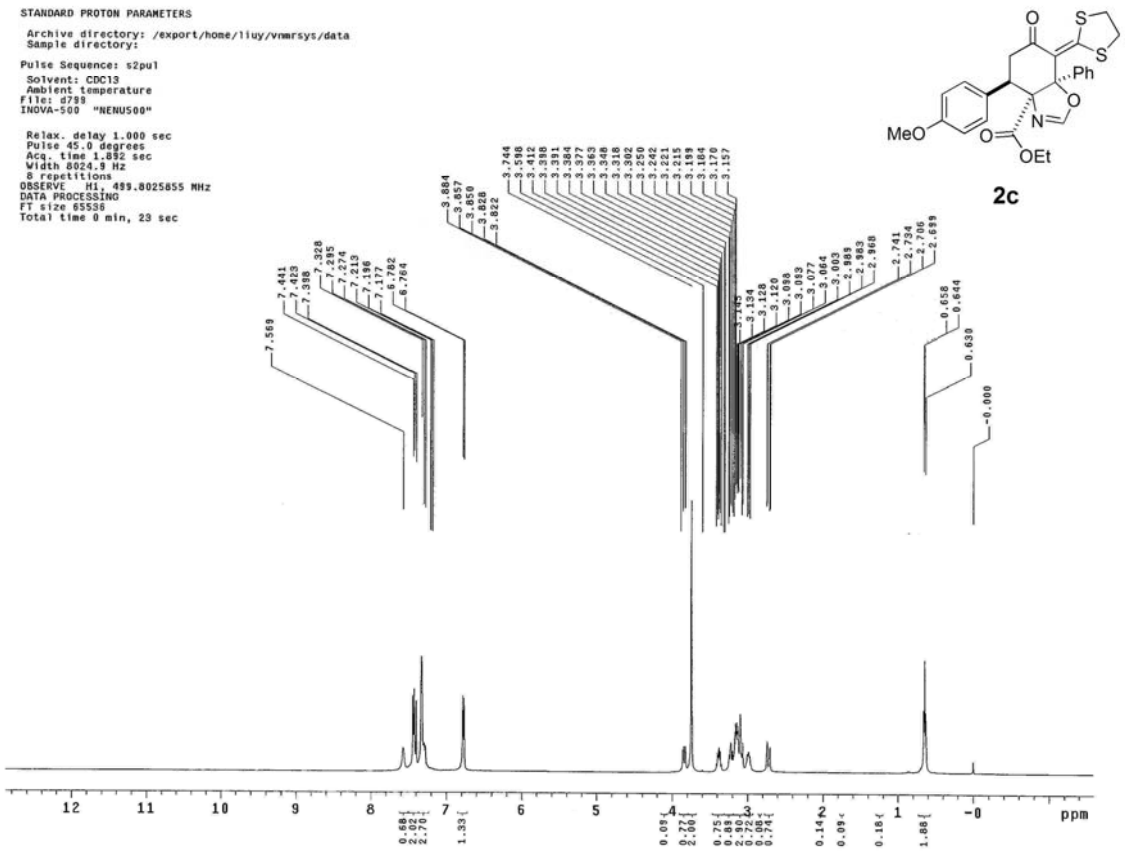
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: d805
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6755040 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
6b
ppm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Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
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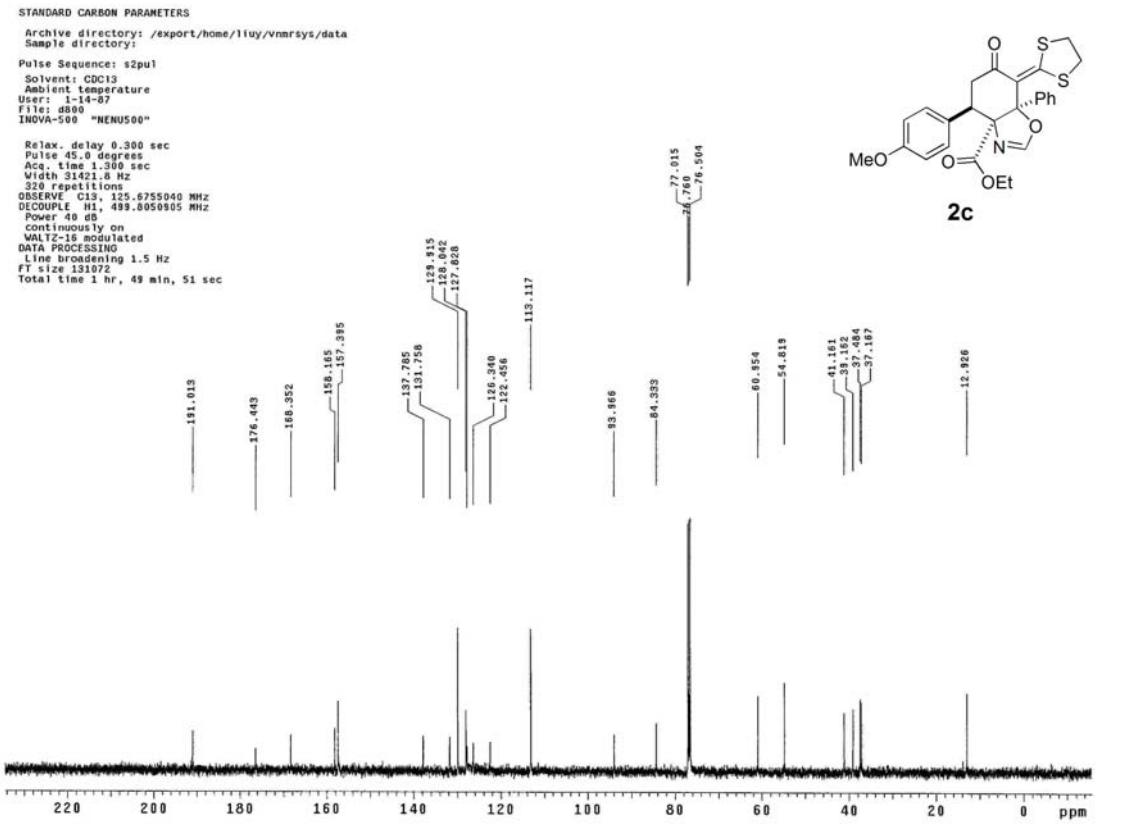
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8024.9 Hz
8 repetitions
OBSERVE H1, 499.8025855 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
MeO
Ph
OEt
2c
ppm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Sample directory:
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Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: d800
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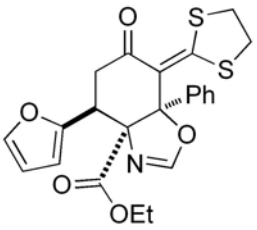
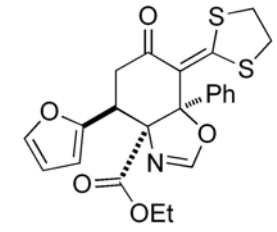
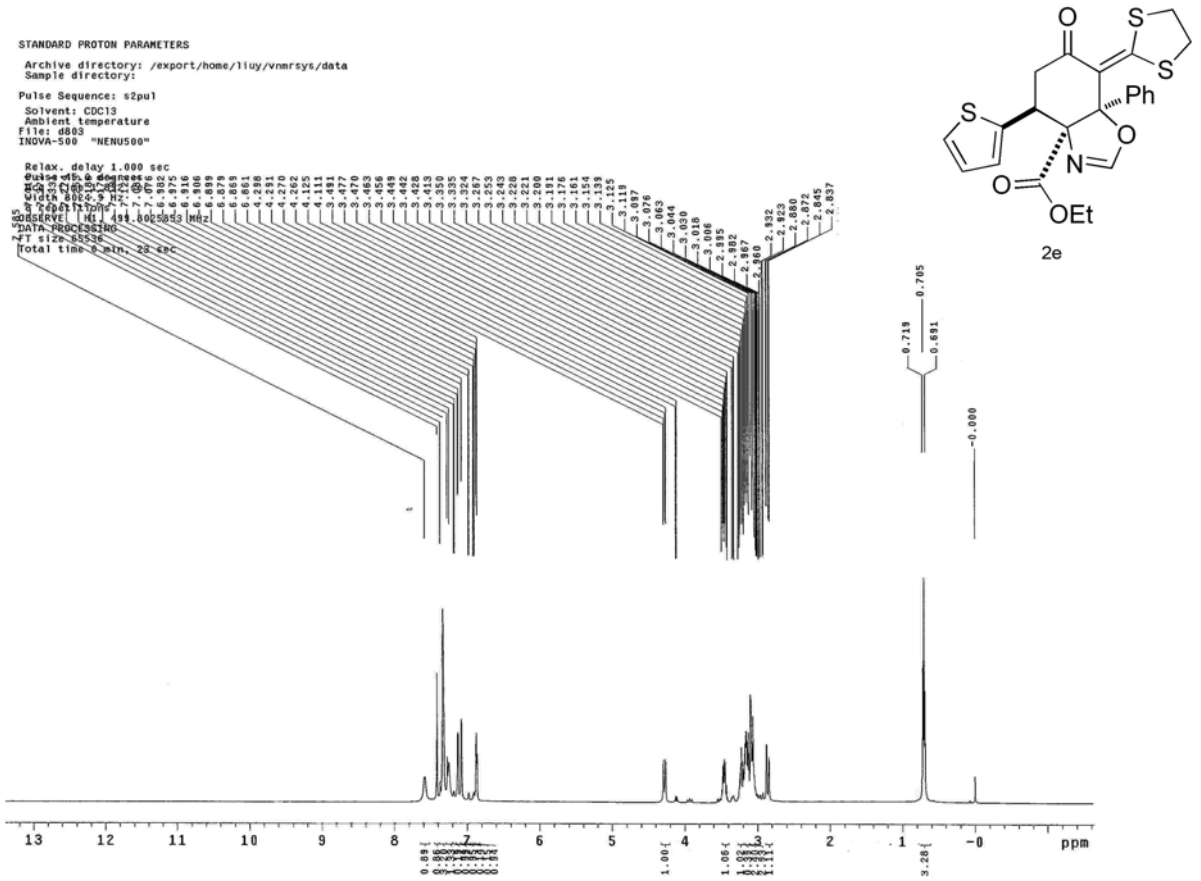
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6755040 MHz
DECOUPLE H1, 499.8050805 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
MeO
Ph
OEt
2c
ppm



2d



2d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Ambient temperature
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OBSERVE H1, 499.8025853 MHz
DATA PROCESSING
FT size 65536
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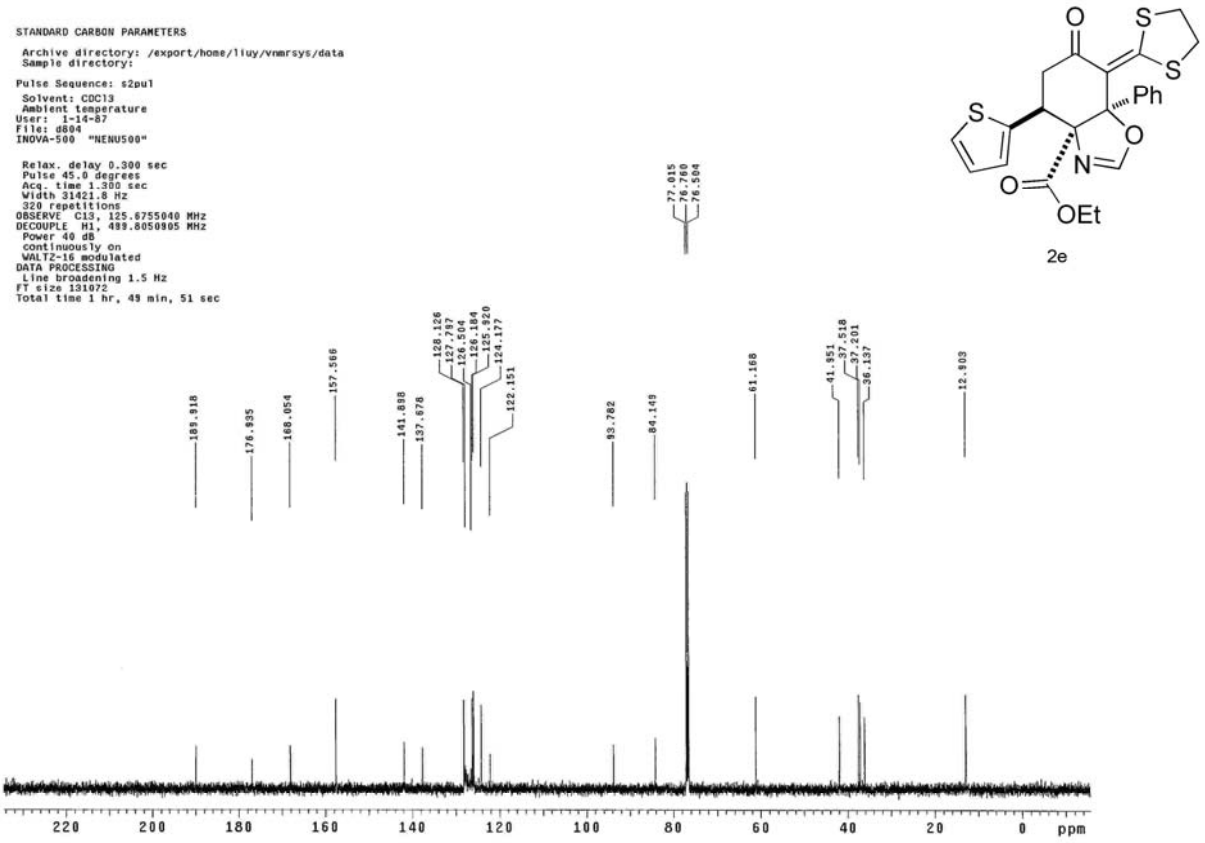
ppm
2e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Sample directory:
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Ambient temperature
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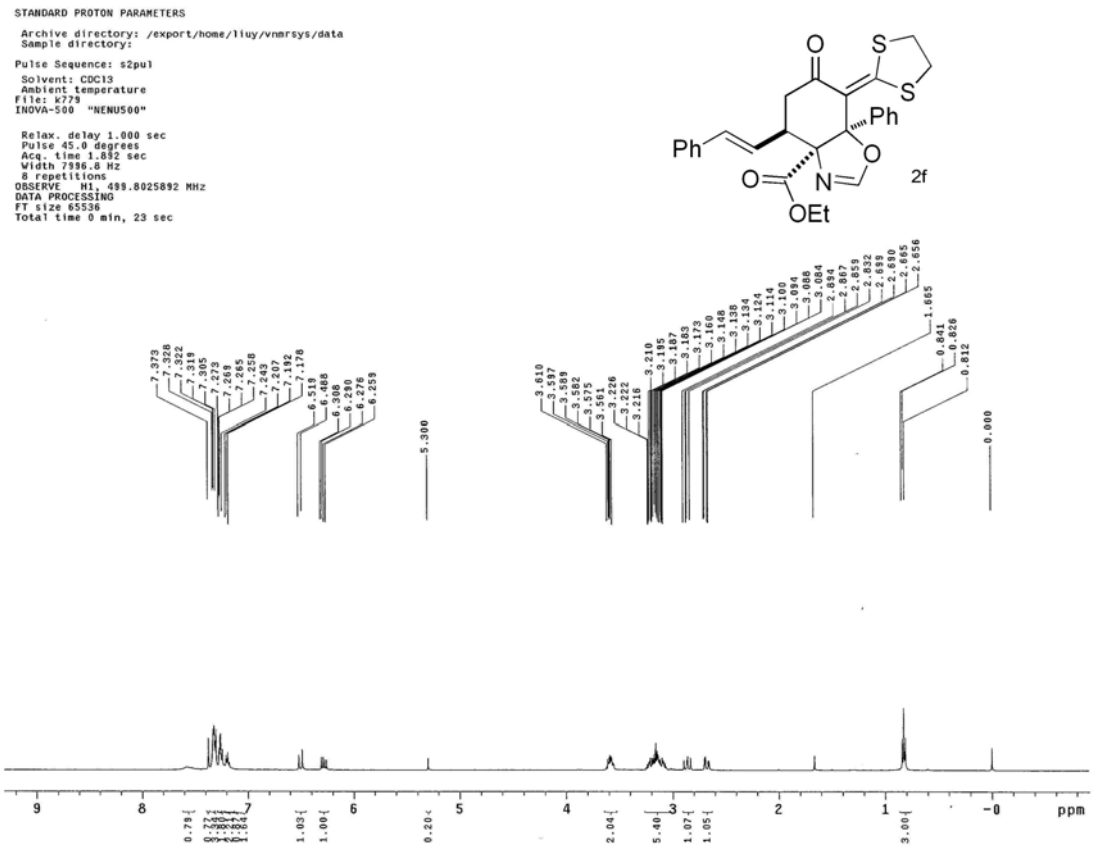
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6755040 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 45 min, 51 sec
ppm
2e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Solvent: CDCl3
Ambient temperature
File: k779
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Pulse 45.0 degrees
Acq. time 1.892 sec
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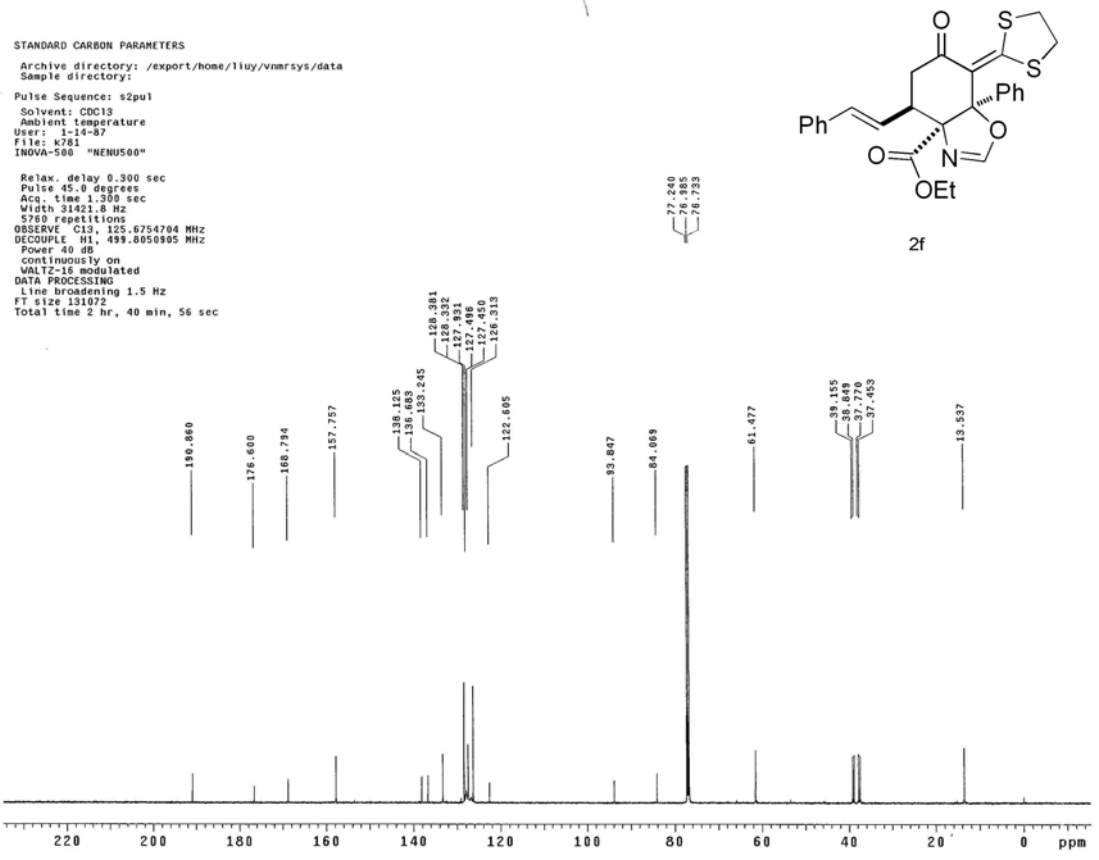
8 repetitions
OBSERVE H1, 499.8025892 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2f
ppm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Sample directory:
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Ambient temperature
User: 1-14-87
File: k781
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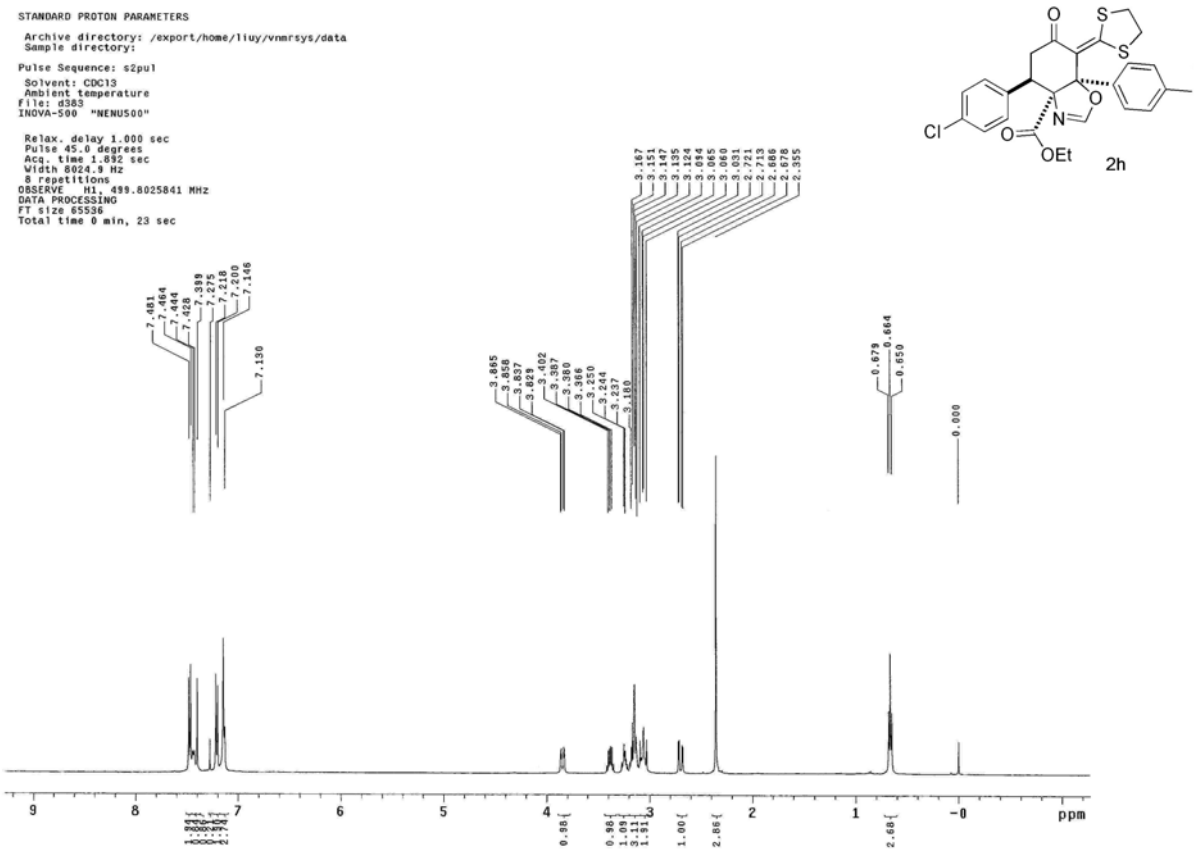
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
5760 repetitions
OBSERVE C13, 125.6754704 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
2f
ppm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Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: d383
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
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8 repetitions
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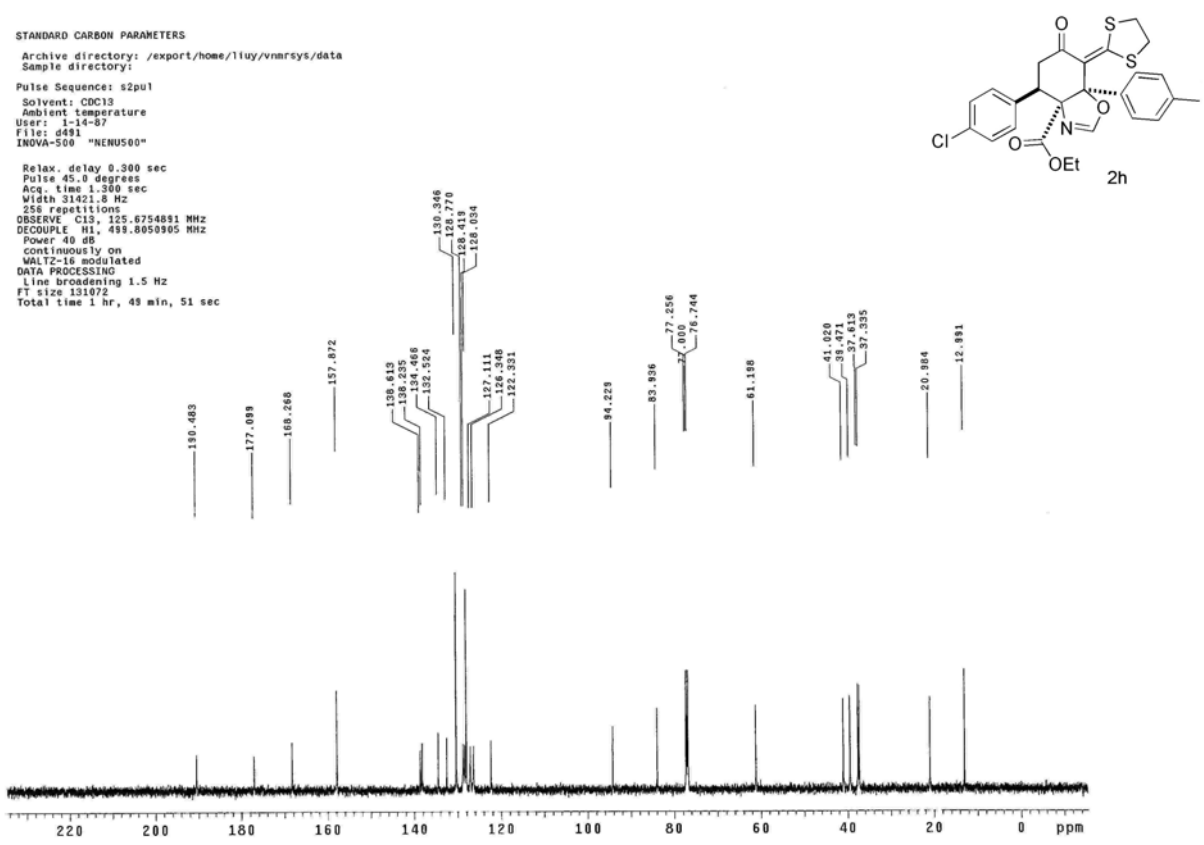
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2h
ppm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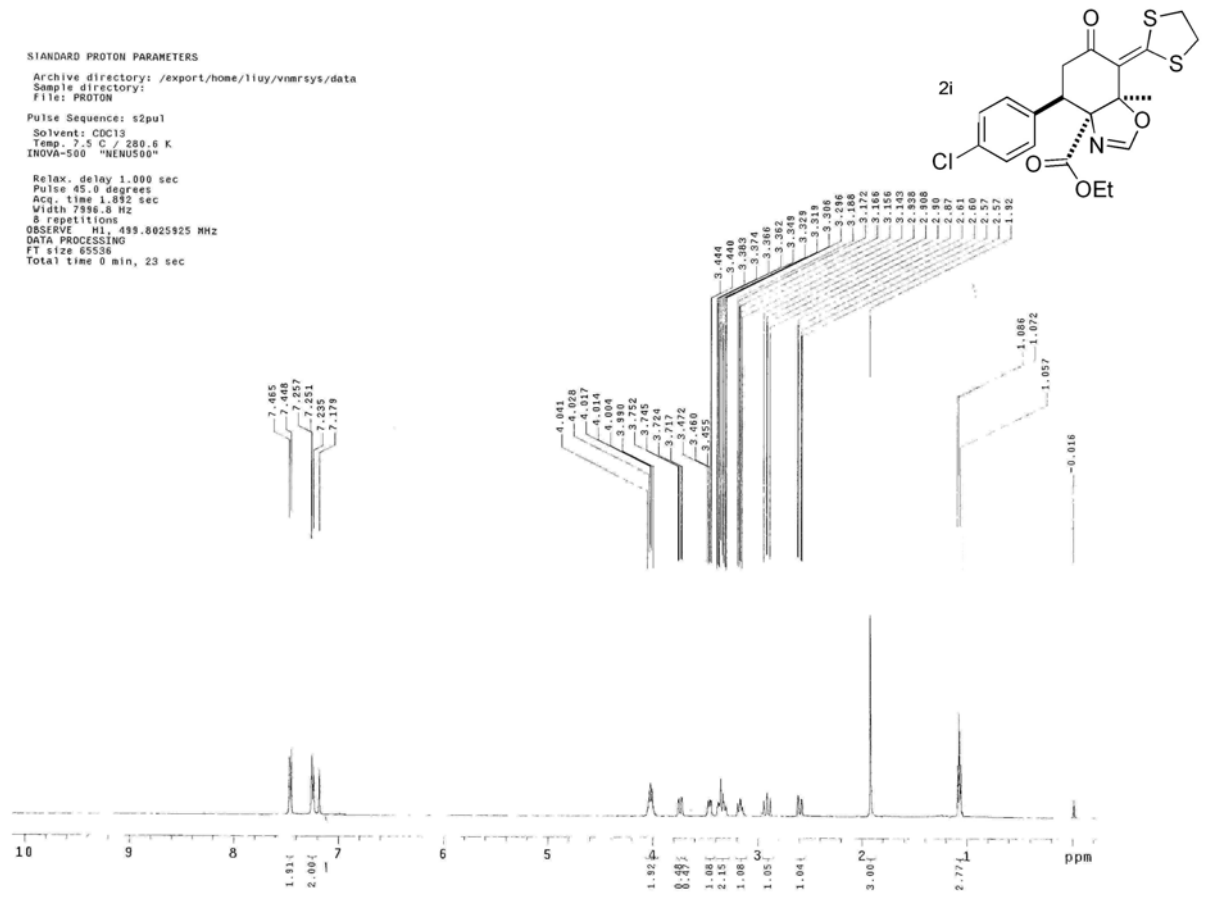
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: d491
INOVA-500 "NENUS00"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754881 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 48 min, 51 sec
2h
ppm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Sample directory:
File: PROTON
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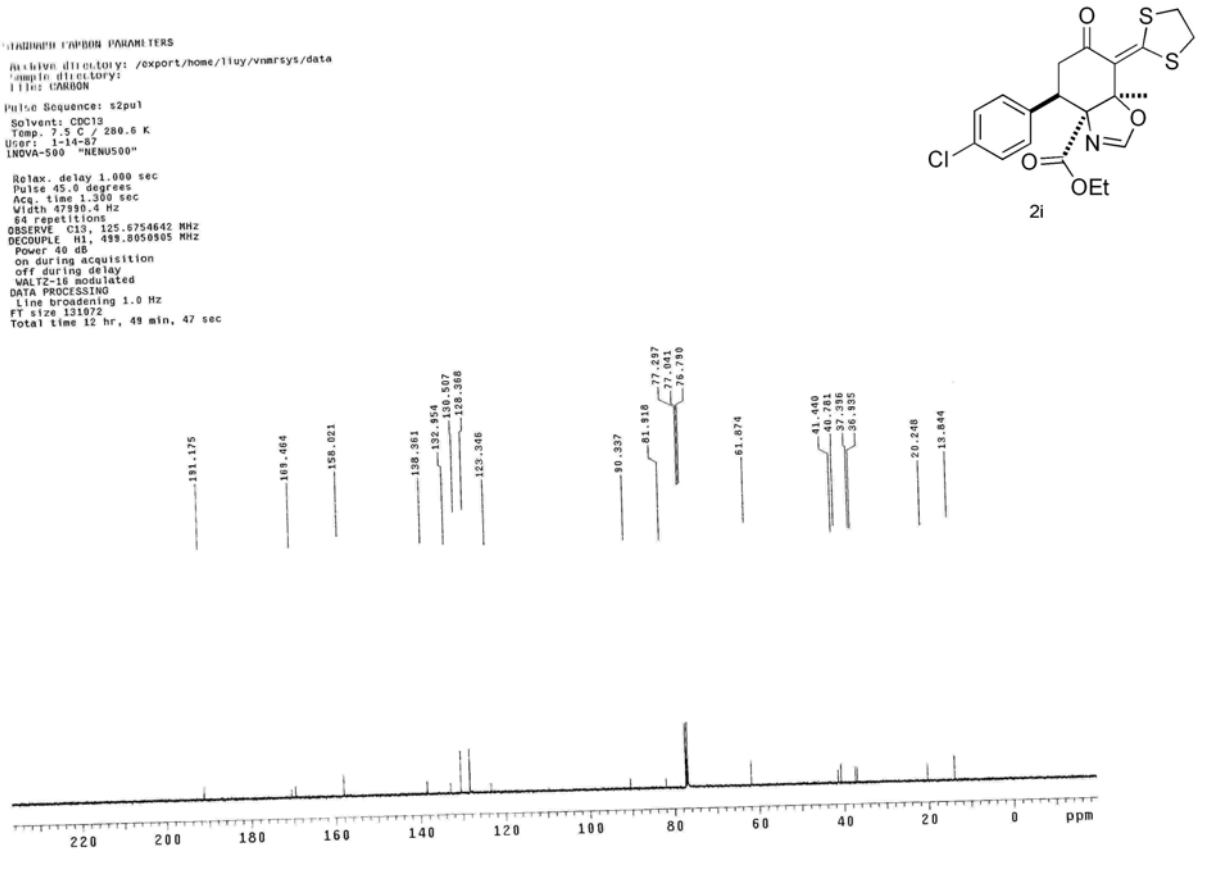
Solvent: CDCl3
Temp. 7.5 C / 280.6 K
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.852 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8025925 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2i
Cl
O
S
S
N
OEt
ppm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Sample directory:
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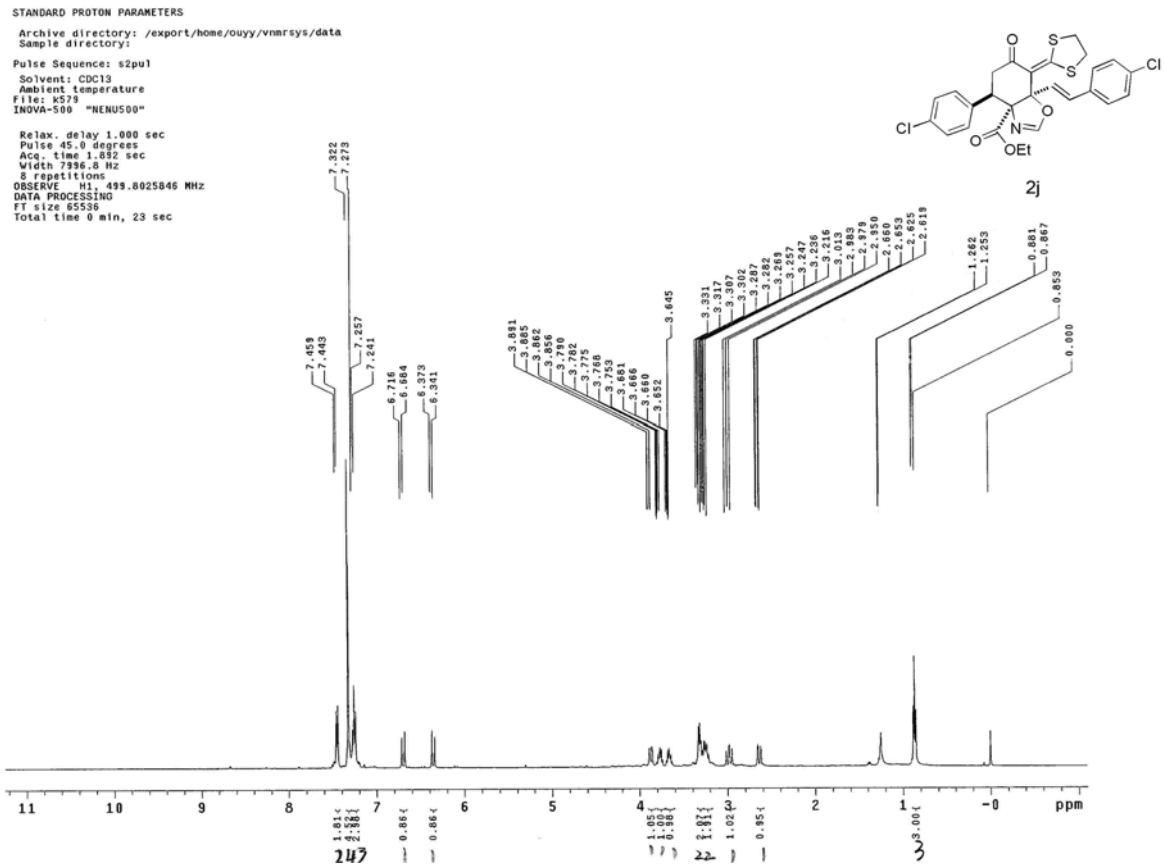
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 7.5 C / 280.6 K
User: 1-14-87
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 47990.4 Hz
64 repetitions
OBSERVE C13, 125.6754642 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 hr, 49 min, 47 sec
2i
Cl
O
S
S
N
OEt
ppm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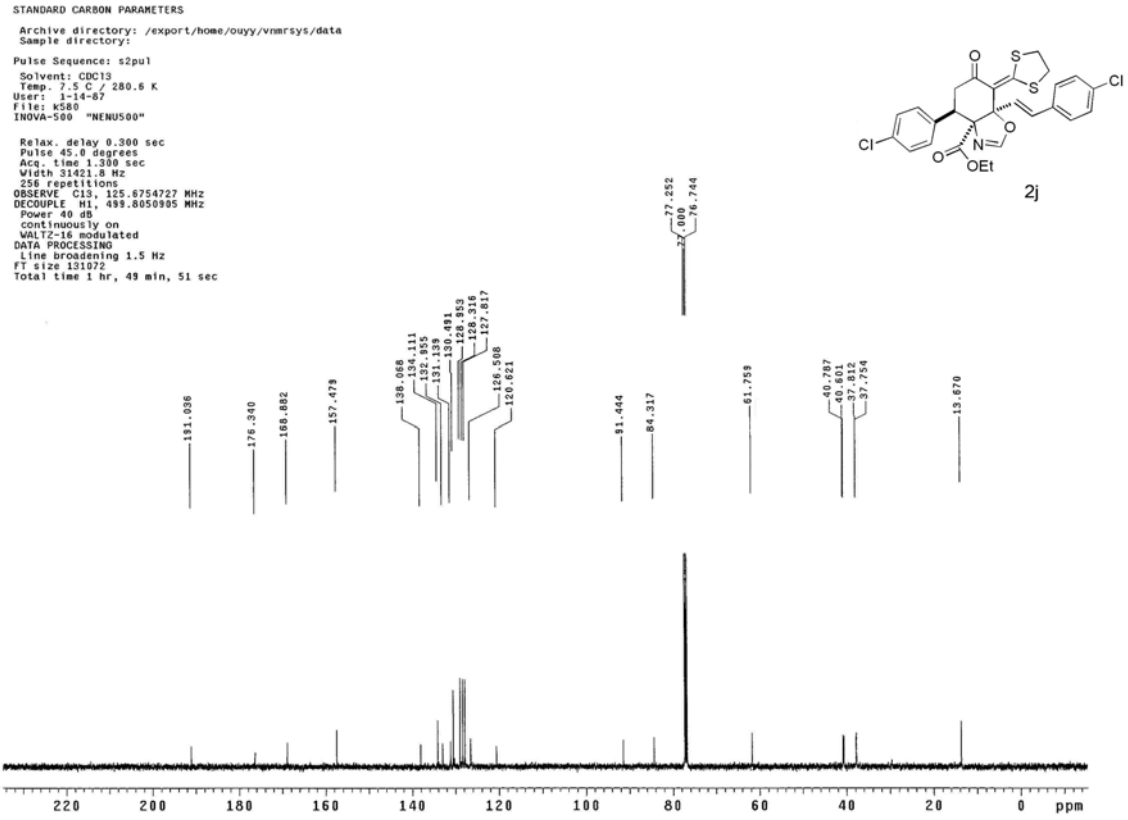
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k579
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8025846 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2j
ppm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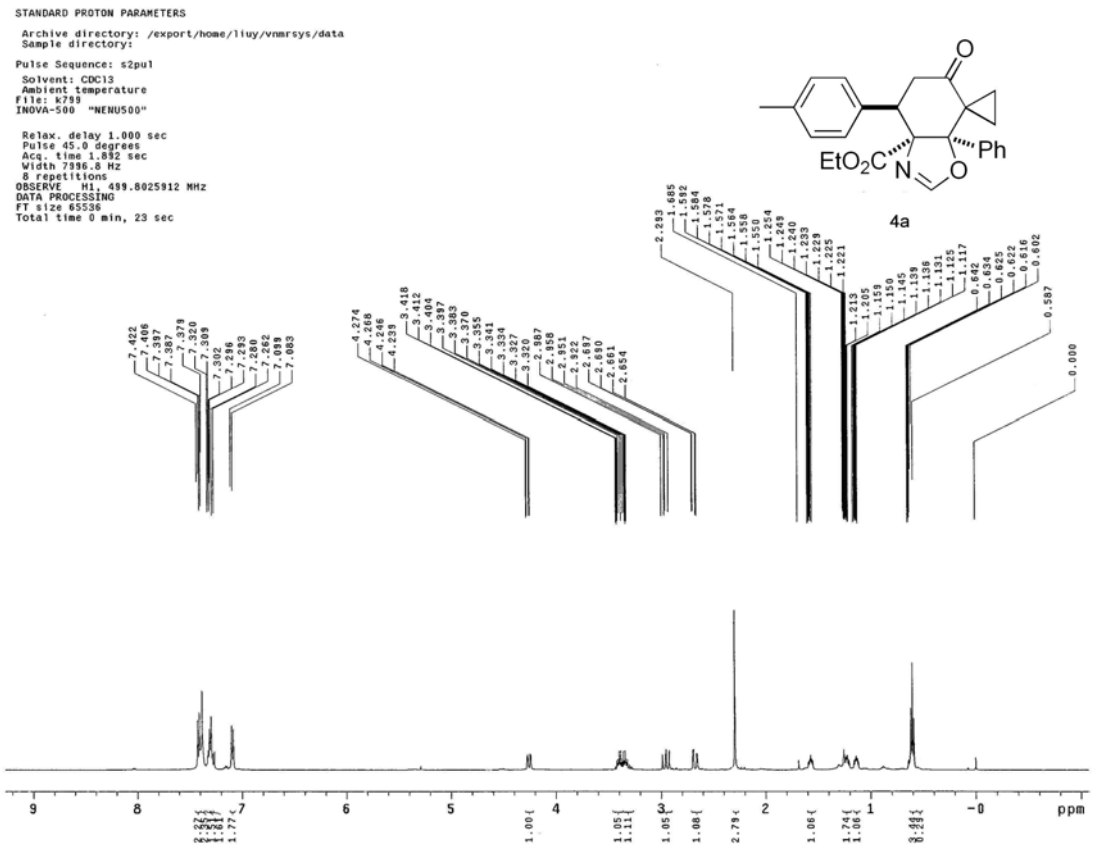
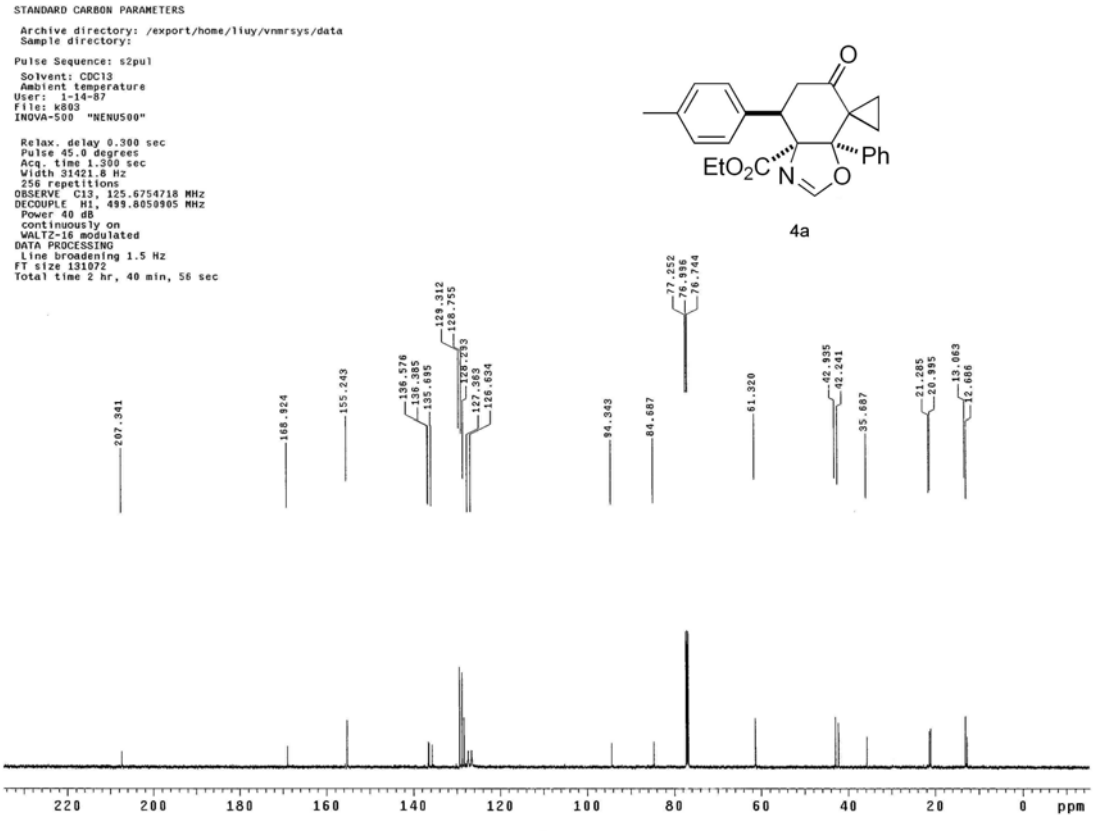
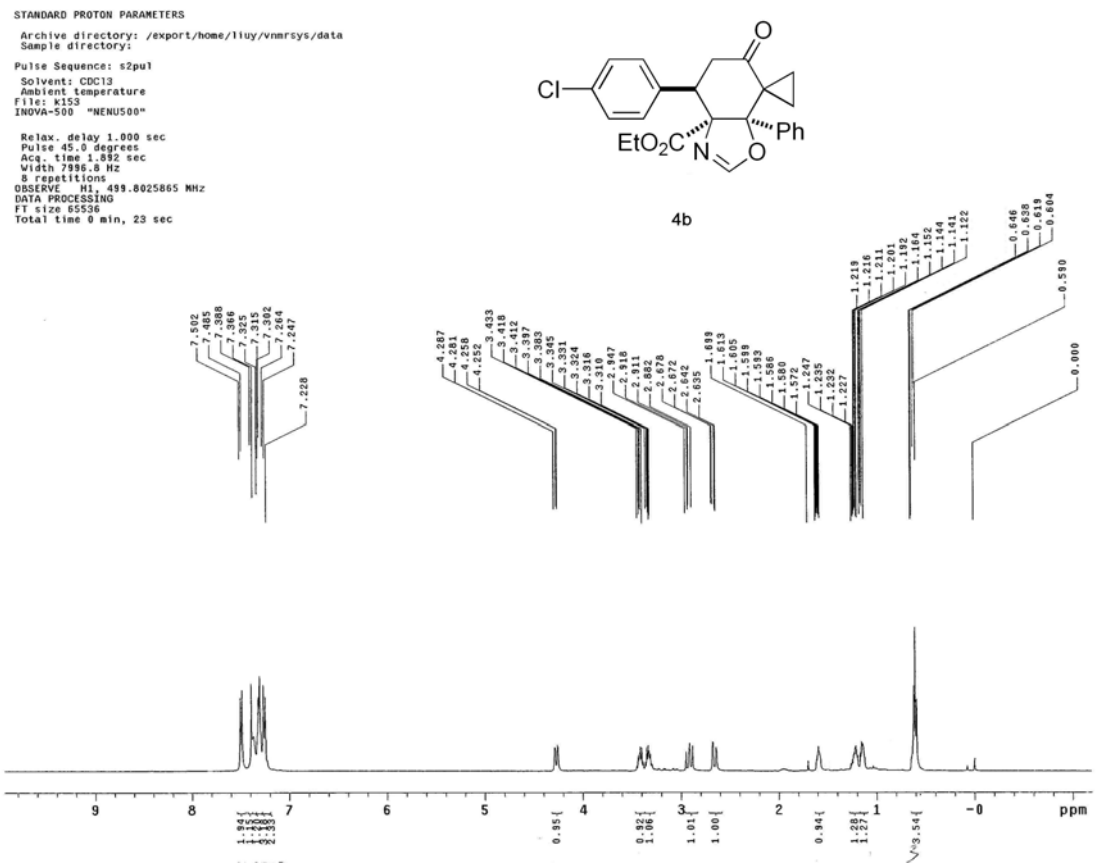
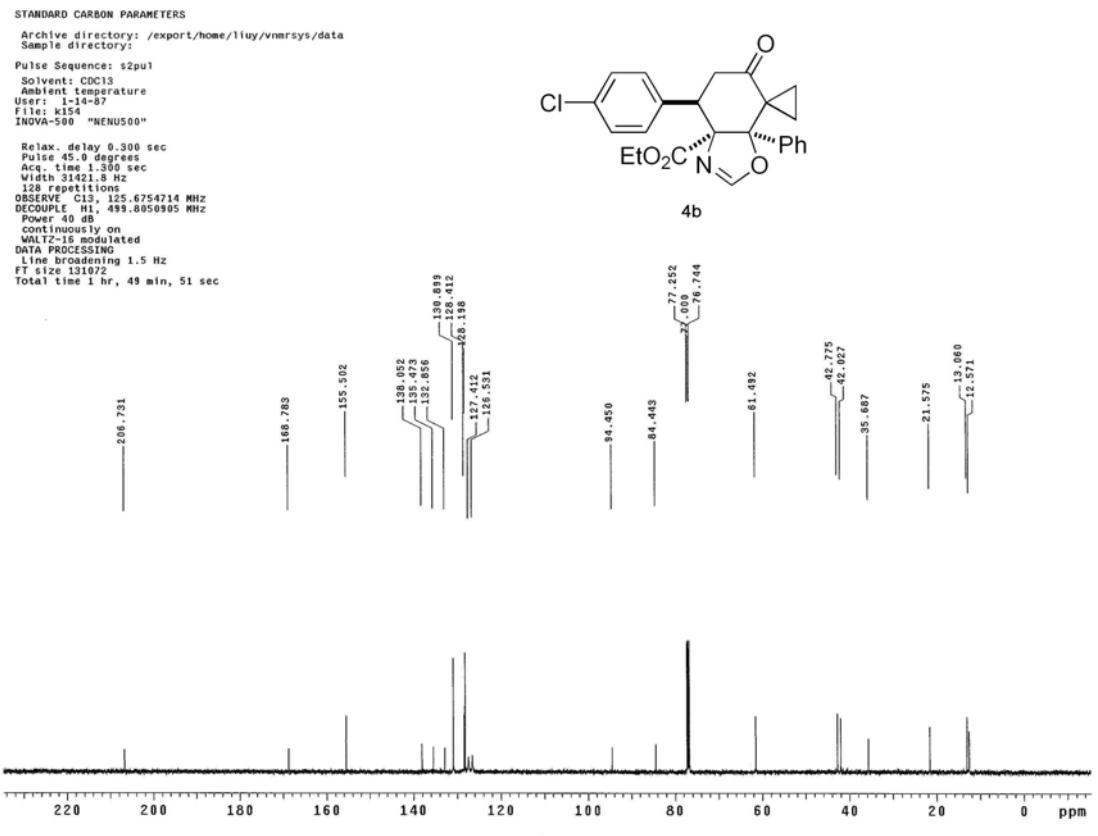
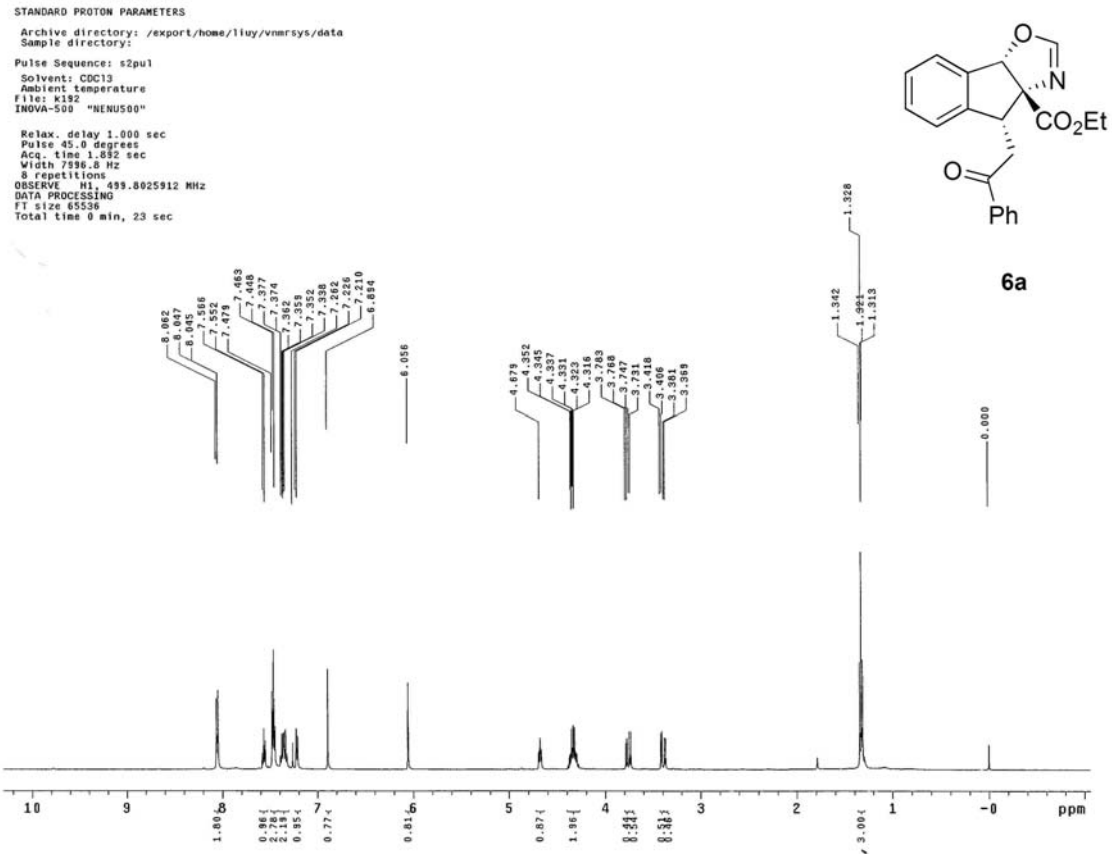
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 7.5 C / 280.6 K
User: 1-14-87
File: k580
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754727 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
2j
ppm

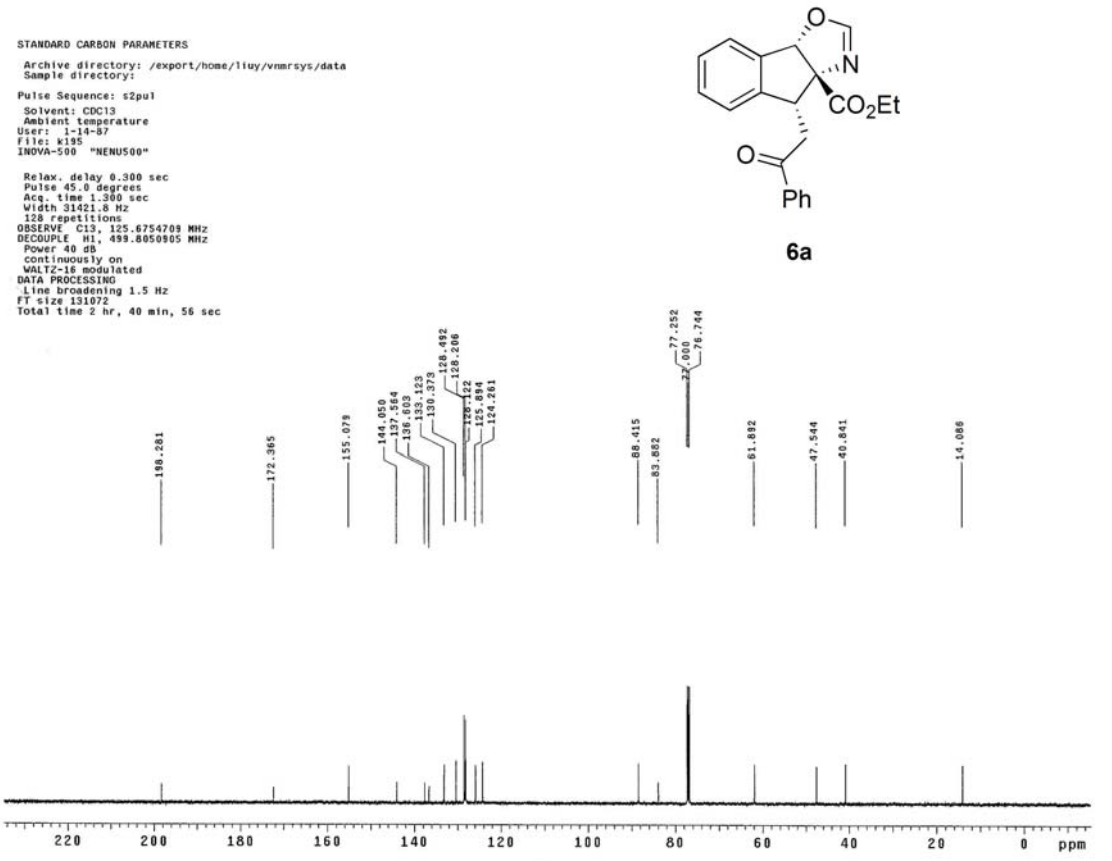

STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k799
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8025912 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
4a
ppm

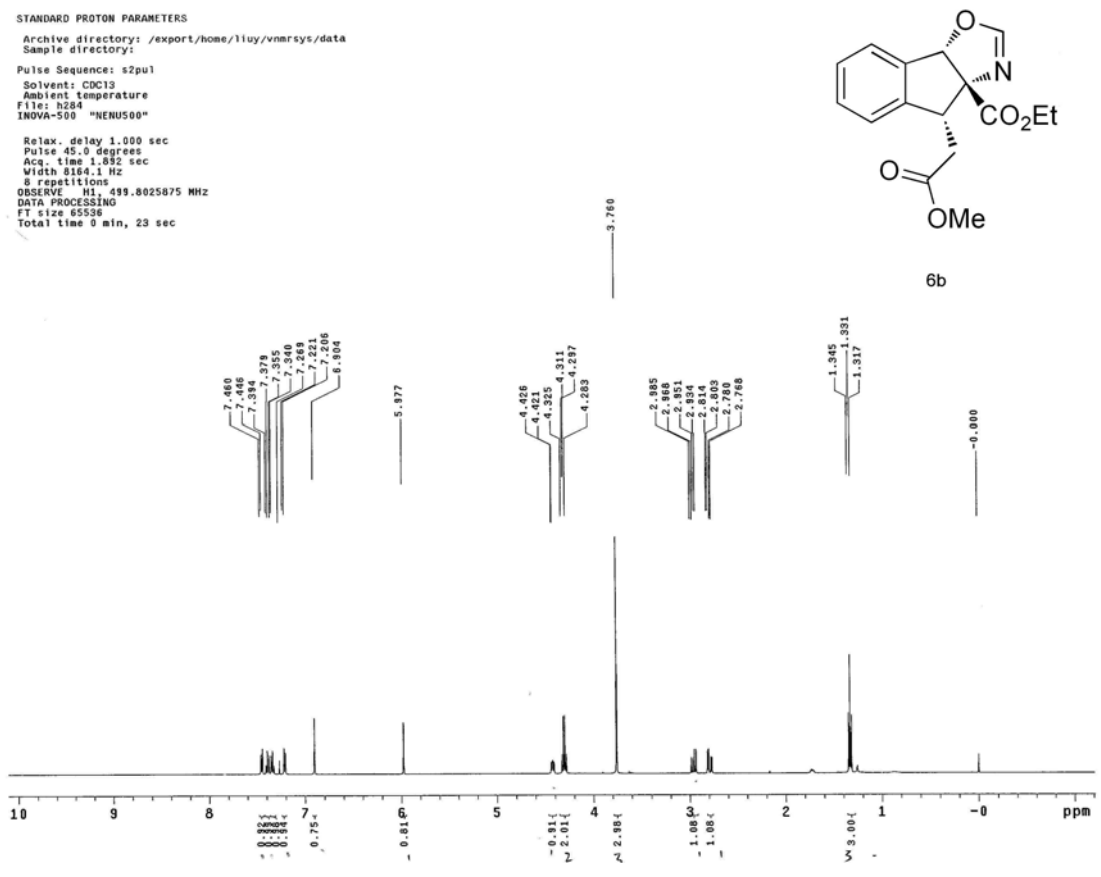

STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k803
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754718 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
4a
ppm

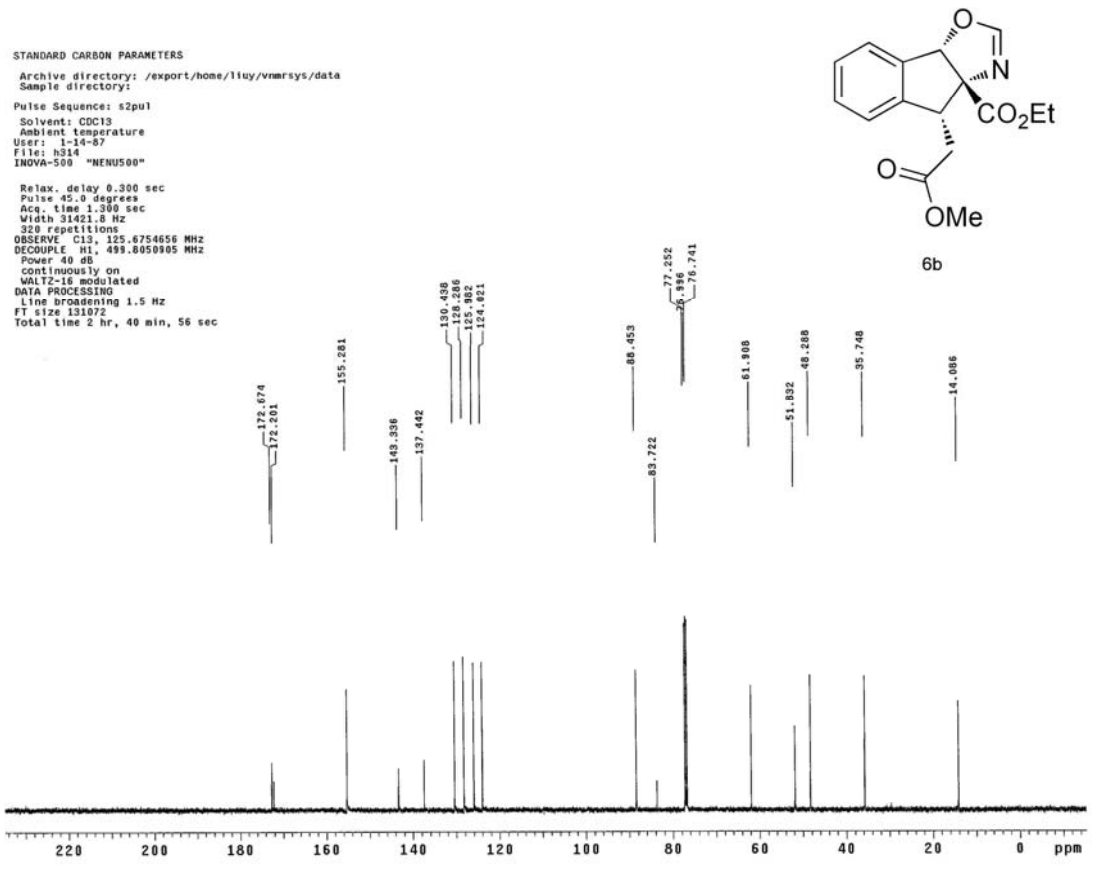

STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k153
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7986.8 Hz
8 repetitions
OBSERVE H1, 499.8025865 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
Cl
O
EtO2C
N
O
Ph
4b
ppm


STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k154
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754714 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 49 min, 51 sec
Cl
O
EtO2C
N
O
Ph
4b
ppm


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: k192
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7596.8 Hz
8 repetitions
OBSERVE H1, 499.8025912 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
6a
ppm


STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: k195
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754709 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
6a
ppm


STANDARD PROTON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: h284
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8164.1 Hz
8 repetitions
OBSERVE H1, 499.8025875 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
O
N
CO2Et
O
OMe
6b
7.460
7.446
7.394
7.379
7.355
7.340
7.269
7.221
7.206
6.904
5.977
4.426
4.421
4.325
4.311
4.297
4.263
3.760
2.985
2.968
2.951
2.934
2.814
2.803
2.788
2.768
1.345
1.331
1.317
-0.000
10
9
8
7
6
5
4
3
2
1
-0
ppm


STANDARD CARBON PARAMETERS
Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: h314
INOVA-500 "NENU500"
Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.6754656 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 40 min, 56 sec
O
N
CO2Et
O
OMe
6b
172.674
172.201
155.281
143.336
137.442
130.438
128.286
125.982
124.021
88.453
83.722
77.252
76.996
76.741
61.908
51.832
48.288
35.748
14.086
220
200
180
160
140
120
100
80
60
40
20
0
ppm

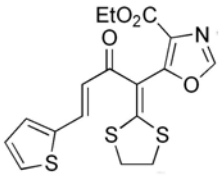
STANDARD PROTON PARAMETERS

Archive directory: /export/home/liu/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 20.0 C / 293.1 K
INOVA-500 "NENU500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 11999.4 Hz
8 repetitions
OBSERVE H1, 499.8025900 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec



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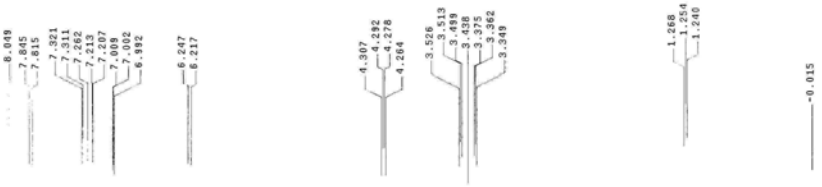
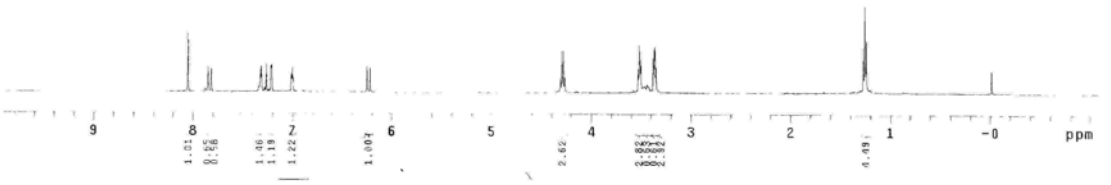




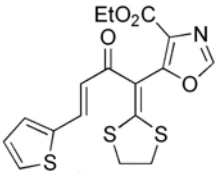
STANDARD CARBON PARAMETERS

Archive directory: /export/home/liuy/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 7.5 C / 280.6 K
User: 1-14-87
INOVA-500 "NENU500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 47990.4 Hz
64 repetitions
OBSERVE C13, 125.6754364 MHz
DECOUPLE H1, 499.8050905 MHz
Power 40 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 hr, 24 min, 53 sec



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