

Supporting Information

Aerobic, copper-catalyzed desulfitative C–C bond-forming reaction of ketene dithioacetals/vinylogous thioesters and arylboronic acids

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I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 25°C on a Varian 500 MHz and 125 MHz or a Bruker 100 MHz, respectively, and using TMS as internal standard. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400~4000 cm^{-1} . High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Melting points were uncorrected. The substrates, **1a–i**,^{1a} **1j** and **1k**,^{1b} were prepared according to the procedures in our previously reported papers.

II. Preparation of ketene dithioacetals **1a–k**

General procedure for the synthesis of ketene dithioacetals **1a–i** (taking **1a** as example): To a well-stirred suspension of diethyl malonate (15.2 mL, 100 mmol), K_2CO_3 (30.4 g, 220 mmol) and DMF (40 mL) at room temperature was added CS_2 (6.6 mL, 110 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 0.5 h, PhCH_2Br (26.2 mL, 220 mmol) was added dropwise within 15 min. The mixture was allowed to warm to room temperature and stirred for 8.0 h, and then poured into ice-water (200 mL) under stirring and neutralized with dilute HCl. The resulting mixture was extracted with CH_2Cl_2 (3×80 mL). The combined organic phase was washed with water (5×80 mL), dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/diethyl ether 20/1, V/V) to give diethyl 2-(bis(benzylthio)methylene)malonate **1a** (38.9 g, 93%) as a yellow crystal.

General procedure for the synthesis of ketene dithioacetals **1j and **1k**** (taking **1j** as an example): To a solution of 3-(bis(methylthio)methylene)pentane-2,4-dione (1.02 g, 5.0 mmol) in 50 mL of CH_2Cl_2 was added concentrated H_2SO_4 (1.1 mL, 20 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 10 h, and then poured onto saturated NaCl ice-water (50 mL) under stirring. The mixture was neutralized with aqueous Na_2CO_3 , and extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with water (3×15 mL), dried over MgSO_4 and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether/diethyl ether 30/1, V/V) to give 4,4-bis(methylthio)but-3-en-2-one **1j** (770 mg, 95%) as a white solid.

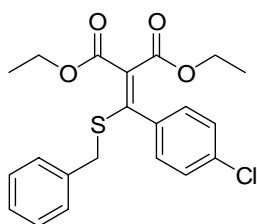
III. Synthesis and analytical data of **3a–o**

General Procedure for the reaction of ketene dithioacetals **1a–e and boronic acids **2** leading to**

3a–l (taking the reaction of **1a** and **2a** as an example): To a solution of **1a** (208 mg, 0.5 mmol) and 4-chlorophenylboronic acid **2a** (234 mg, 1.5 mmol) in DMF (4.0 mL) was added Cu(OAc)₂ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at 130°C for 60 h and monitored by TLC. Then the mixture was cooled to room temperature and poured into the saturated aqueous NaCl solution (50 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (100:1, V/V) as eluent to give diethyl 2-(benzylthio(4-chlorophenyl)methylene)malonate **3a** (142 mg, 70%), benzyl(4-chlorophenyl)sulfane (83 mg, 71%) and 4,4'-dichlorobiphenyl (42 mg).

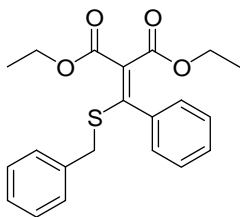
General Procedure for the reaction of ketene dithioacetals 1f–h with boronic acid 2a leading to 3m–o (taking the reaction of **1f** and **2a** as an example): To a solution of **1f** (117 mg, 0.5 mmol) and PhB(OH)₂ **2b** (183 mg, 1.5 mmol) in DMF (4.0 mL) was added Cu(OAc)₂ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at 110°C for 50 h and monitored by TLC. Then the mixture was cooled to room temperature and poured into the saturated aqueous NaCl solutions (50 mL). The resulting mixture was extracted with dichloromethane (3 × 20 mL). The combined organic phase was dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (50:1, V/V) as eluent to give **3m** as a mixture of two isomers (79 mg, 60% yield, The molar ratio of two isomers were 3.5 to 1 based on ¹H NMR).

Diethyl 2-(benzylthio(4-chlorophenyl)methylene)malonate (**3a**)



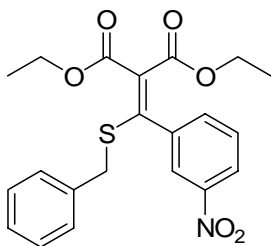
Yellowish viscous liquid; ¹H NMR (500 Hz, CDCl₃) δ 0.96 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 3.49 (s, 2H), 3.91 (q, *J* = 7.0 Hz, 2H), 4.28 (q, *J* = 7.0 Hz, 2H), 7.02–7.04 (m, 2H), 7.11–7.12 (m, 2H), 7.21 (d, *J* = 6.5 Hz, 3H), 7.32–7.33 (m, 2H); ¹³C NMR (125 Hz, CDCl₃) δ 13.8, 14.3, 37.6, 61.4, 61.5, 122.7, 127.6, 128.6 (2C), 128.7 (2C), 129.0 (2C), 129.8 (2C), 134.1, 135.2, 135.9, 159.5, 164.0, 164.8; IR (KBr): 3061, 2924, 2854, 1728, 1245 cm⁻¹; HRMS (ESI-TOF) calcd for C₂₁H₂₁ClO₄SN⁺ ([M+Na]⁺) 427.0741, found 427.0730; Anal. calcd for C₂₁H₂₁ClO₄S: C, 62.29; H, 5.23. Found: C, 62.18; H, 5.29.

Diethyl 2-(benzylthio(phenyl)methylene)malonate (3b)



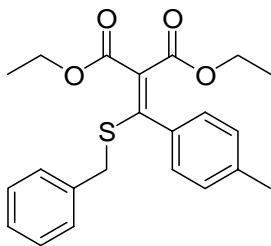
Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 3.47 (s, 2H), 3.86 (q, $J = 7.0$ Hz, 2H), 4.28 (q, $J = 7.0$ Hz, 2H), 7.01-7.03 (m, 2H), 7.18-7.21 (m, 5H), 7.34-7.37 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.5, 14.1, 37.4, 61.0, 61.1, 121.8, 127.2, 128.1 (2C), 128.2 (2C), 128.3 (2C), 128.8 (2C), 128.9, 135.5, 135.9, 161.1, 163.9, 165.0; IR (KBr): 3084, 3028, 2989, 1720, 1285 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 393.1131, found 393.1125.

Diethyl 2-(benzylthio(3-nitrophenyl)methylene)malonate (3c)



Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.96 (t, $J = 7.0$ Hz, 3H), 1.34 (t, $J = 7.0$ Hz, 3H), 3.52 (s, 2H), 3.90 (q, $J = 7.0$ Hz, 2H), 4.33 (q, $J = 7.0$ Hz, 2H), 6.97 (t, $J = 4.0$ Hz, 2H), 7.18-7.19 (m, 3H), 7.48-7.55 (m, 2H), 7.94 (s, 1H), 8.20 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.7, 14.1, 37.3, 61.3, 61.6, 123.5, 123.6, 123.8, 127.6, 128.5 (2C), 128.6 (2C), 129.2, 134.2, 135.4, 136.9, 147.7, 156.9, 163.7, 163.8; IR (KBr): 3055, 2980, 1726, 1245 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_6\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 438.0982, found 438.0973; Anal. calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_6\text{S}$: C, 60.71; H, 5.09; N, 3.37. Found: C, 60.80; H, 5.01; N, 3.39.

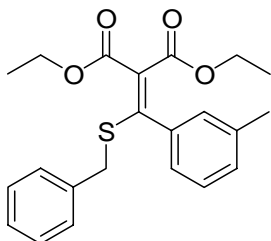
Diethyl 2-(benzylthio(p-tolyl)methylene)malonate (3d)



White semi-solid; ^1H NMR (500 Hz, CDCl_3) δ 0.93 (t, $J = 7.0$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H), 2.37 (s, 3H), 3.48 (s, 2H), 3.89 (q, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.0$ Hz, 2H), 7.04-7.05 (m, 2H),

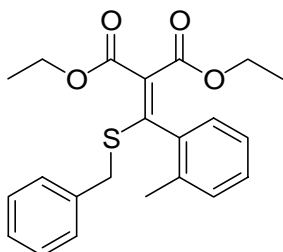
7.09 (d, $J = 8.5$ Hz, 2H), 7.16-7.20 (m, 5H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.6, 14.2, 21.3, 37.5, 61.0, 61.1, 121.7, 127.3, 128.1 (2C), 128.4 (2C), 128.9 (2C), 129.0 (2C), 132.7, 136.0, 138.9, 161.5, 164.0, 165.1; IR (KBr): 3064, 2923, 2854, 1728, 1244, 1079 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 407.1288, found 407.1302.

Diethyl 2-(benzylthio(m-tolyl)methylene)malonate (3e)



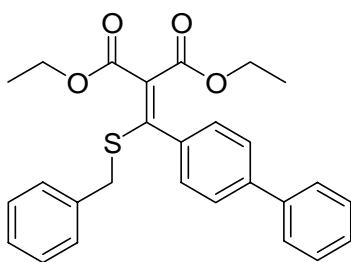
Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.30 (t, $J = 7.0$ Hz, 3H), 2.31 (s, 3H), 3.48 (s, 2H), 3.87 (q, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.0$ Hz, 2H), 6.93 (s, 1H), 6.99-7.02 (m, 3H), 7.14-7.20 (m, 4H), 7.24-7.26 (m, 1H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.5, 14.1, 21.2, 37.4, 60.8, 61.0, 121.8, 125.3, 127.2, 128.1, 128.3 (2C), 128.9 (3C), 129.5, 135.5, 136.2, 137.9, 161.2, 163.9, 164.9; IR (KBr): 3032, 2926, 2856, 1728, 1245 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 407.1288, found 407.1293.

Diethyl 2-(benzylthio(o-tolyl)methylene)malonate (3f)



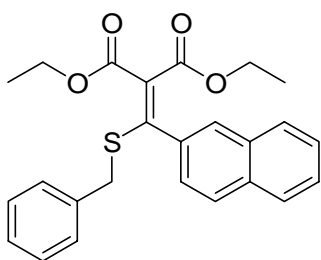
Yellow semi-solid; ^1H NMR (500 Hz, CDCl_3) δ 0.93 (t, $J = 7.0$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H), 2.37 (s, 3H), 3.48 (s, 2H), 3.89 (q, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.0$ Hz, 2H), 7.04-7.05 (m, 2H), 7.09 (d, $J = 8.5$ Hz, 2H), 7.16-7.20 (m, 5H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.6, 14.1, 21.3, 37.5, 60.9, 61.0, 127.2, 127.7, 128.2 (2C), 128.4 (2C), 129.0 (4C), 132.8, 136.2, 138.9, 161.2, 164.0, 165.0; IR (KBr): 3028, 2925, 1727, 1690, 1243, cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 407.1288, found 407.1296.

Diethyl 2-(benzylthio(biphenyl-4-yl)methylene)malonate (3g)



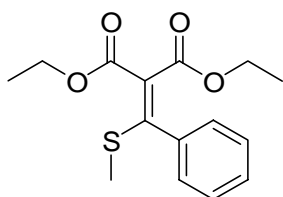
Yellowish viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.31 (t, $J = 7.0$ Hz, 3H), 3.55 (s, 2H), 3.90 (q, $J = 7.0$ Hz, 2H), 4.29 (q, $J = 7.0$ Hz, 2H), 7.03-7.05 (m, 2H), 7.18-7.20 (m, 3H), 7.25-7.26 (m, 2H), 7.38 (t, $J = 7.0$ Hz, 1H), 7.45-7.48 (m, 2H), 7.59 (t, $J = 9.0$ Hz, 4H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.6, 14.2, 37.5, 61.1, 61.2, 122.0, 126.8 (2C), 127.0 (2C), 127.3, 127.8, 128.4 (2C), 128.7 (2C), 128.8 (2C), 128.9 (2C), 134.4, 136.0, 140.1, 141.7, 160.9, 163.9, 165.0; IR (KBr): 3029, 2926, 2855, 1725, 1245, 1083 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{27}\text{H}_{27}\text{O}_4\text{S}^+$ ($[\text{M}+\text{H}]^+$) 447.1625, found 447.1630; Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{S}$: C, 72.62; H, 5.87. Found: C, 72.73; H, 5.84.

Diethyl 2-(benzylthio(naphthalen-2-yl)methylene)malonate (3h)



Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.75 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 3.47 (s, 2H), 3.79 (q, $J = 7.0$ Hz, 2H), 4.30 (q, $J = 7.0$ Hz, 2H), 6.94-6.96 (m, 2H), 7.13-7.14 (m, 3H), 7.36 (d, $J = 8.5$ Hz, 1H), 7.51-7.54 (m, 2H), 7.60 (s, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.5, 14.2, 37.5, 61.0, 61.2, 122.2, 125.8, 126.7, 127.0, 127.3, 127.5, 127.7, 128.1, 128.3 (2C), 128.8, 128.9 (2C), 130.9, 132.6, 133.0, 135.9, 161.1, 163.9, 165.0; IR (KBr): 3058, 2928, 1725, 1232 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 443.1288, found 443.1297.

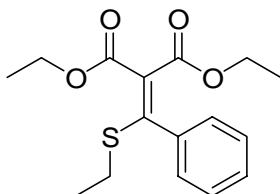
Diethyl 2-(methylthio(phenyl)methylene)malonate (3i)



Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H),

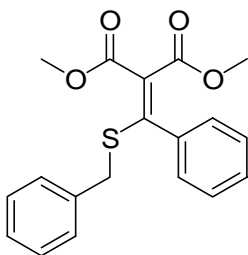
1.80 (s, 3H), 3.87 (q, $J = 7.0$ Hz, 2H), 4.30 (q, $J = 7.0$ Hz, 2H), 7.19 (d, $J = 7.0$ Hz, 2H), 7.35-7.30 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.5, 14.2, 16.1, 61.0, 61.1, 121.4, 127.9 (2C), 128.3 (2C), 128.7, 135.4, 162.7, 163.9, 165.2; IR (KBr): 3056, 2927, 1727, 1242 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 317.0818, found 317.0830.

Diethyl 2-(ethylthio(phenyl)methylene)malonate (3j)



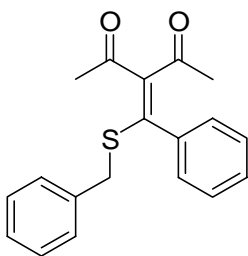
Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 0.90 (t, $J = 7.0$ Hz, 3H), 1.07 (t, $J = 7.5$ Hz, 3H), 1.32 (t, $J = 7.0$ Hz, 3H), 2.24 (q, $J = 7.5$ Hz, 2H), 3.87 (q, $J = 7.0$ Hz, 2H), 4.30 (q, $J = 7.0$ Hz, 2H), 7.24 (d, $J = 7.0$ Hz, 2H), 7.36 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.5, 14.0, 14.1, 26.9, 60.9, 61.0, 121.7, 128.0 (2C), 128.1 (2C), 128.7, 135.7, 161.7, 164.0, 165.1; IR (KBr): 3010, 2925, 1731, 1235 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 331.0975, found 331.0991.

Dimethyl 2-(benzylthio(phenyl)methylene)malonate (3k)



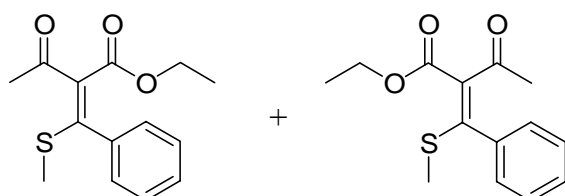
Yellow viscous liquid; ^1H NMR (500 Hz, CDCl_3) δ 3.38 (s, 3H), 3.48 (s, 2H), 3.81 (s, 3H), 7.01-7.03 (m, 2H), 7.19 (t, $J = 6.5$ Hz, 5H), 7.37 (d, $J = 4.5$ Hz, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 37.5, 52.0, 52.1, 121.1, 127.3, 128.0 (2C), 128.3 (2C), 128.4 (2C), 128.9 (3C), 135.5, 135.8, 162.2, 164.2, 165.5; IR (KBr): 3026, 2950, 2852, 1735, 1247, 1085 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}]^+$) 365.0818, found 365.0826; Anal. calcd for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{S}$: C, 66.65; H, 5.30. Found: C, 66.73; H, 5.25.

3-(Benzylthio(phenyl)methylene)pentane-2,4-dione (3l)



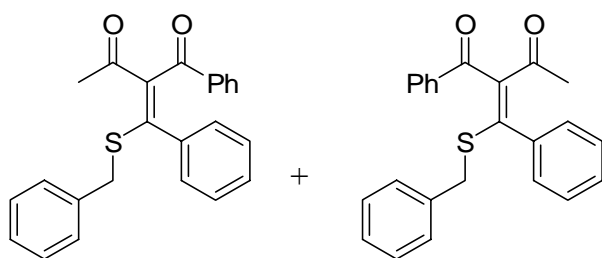
Yellow solid, mp 75-76 °C; ^1H NMR (500 Hz, CDCl_3) δ 1.69 (s, 3H), 2.28 (s, 3H), 3.50 (s, 2H), 6.98 (d, $J = 6.0$ Hz, 2H), 7.21 (d, $J = 6.0$ Hz, 3H), 7.25-7.26 (m, 2H), 7.42-7.44 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 30.1, 31.1, 37.6, 127.3, 128.4 (2C), 128.8 (2C), 128.9 (2C), 129.2 (2C), 129.8, 135.5, 136.3, 140.6, 155.3, 197.1, 210.7; IR (KBr): 3058, 2961, 2855, 1680, 1474, 1233 cm^{-1} . HRMS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{19}\text{O}_2\text{S}^+$ ($[\text{M}+\text{H}]^+$) 311.1100, found 311.1117.

(E) and (Z)-Ethyl 2-(benzylthio(phenyl)methylene)-3-oxobutanoate (3m)



Yellow solid; **One of two isomers:** ^1H NMR (500 Hz, CDCl_3) δ 0.83 (t, $J = 7.0$ Hz, 3H), 1.77 (s, 3H), 2.35 (s, 3H), 3.83 (q, $J = 7.0$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 2H), 7.30-7.43 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.4, 16.4, 29.1, 60.9, 127.8 (2C), 128.3 (2C), 128.6, 129.0, 135.9, 164.0, 167.2, 193.8; **The other one:** ^1H NMR (500 Hz, CDCl_3) δ 1.32 (t, $J = 7.0$ Hz, 3H), 1.81 (s, 3H), 1.96 (s, 3H), 4.30 (q, $J = 7.0$ Hz, 2H), 7.17 (t, $J = 7.5$ Hz, 2H), 7.30-7.43 (m, 3H); ^{13}C NMR (125 Hz, CDCl_3) δ 14.1, 15.9, 30.9, 60.9, 127.8 (2C), 128.3 (2C), 128.6, 129.9, 135.1, 159.8, 164.3, 198.9; HRMS: calcd. For $\text{C}_{14}\text{H}_{17}\text{O}_3\text{S}^+$ ($[\text{M}+\text{H}]^+$) 265.0893, found 265.0911.

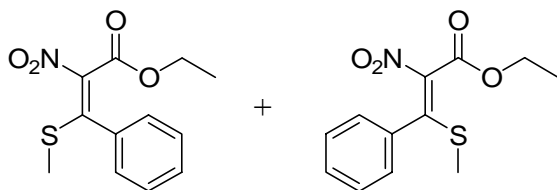
(E) and (Z)-2-(Benzylthio(phenyl)methylene)-1-phenylbutane-1,3-dione (3n)



Yellow viscous liquid; **One of two isomers:** ^1H NMR (500 Hz, CDCl_3) δ 2.23 (s, 3H), 3.46 (s, 2H), 7.00-7.02 (m, 2H), 7.07-7.15 (m, 2H), 7.20-7.22 (m, 2H), 7.23-7.26 (m, 1H), 7.38-7.43 (m, 2H), 7.47-7.49 (m, 2H), 7.56-7.59 (m, 2H), 7.90 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 Hz, CDCl_3) δ 29.7, 37.8, 127.3, 128.2 (2C), 128.4 (2C), 128.6 (2C), 128.8 (2C), 129.0 (2C), 129.1 (2C), 129.4, 130.2, 133.1, 133.3, 135.1, 136.1, 137.8, 194.5, 196.5; **The other one:** ^1H NMR (500 Hz, CDCl_3) δ 1.80 (s, 3H), 3.46 (s, 2H), 6.69 (d, $J = 4.5$ Hz, 2H), 7.00-7.02 (m, 2H), 7.07-7.15 (m, 2H), 7.20-7.22 (m, 2H), 7.23-7.26 (m, 2H), 7.38-7.43 (m, 2H), 7.56-7.59 (m, 1H), 7.90 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 Hz, CDCl_3) δ 29.6, 37.2, 127.2, 128.1 (2C), 128.3 (2C), 128.6 (2C), 128.8 (2C), 129.0 (2C), 129.1 (2C), 129.4, 130.2, 133.1, 133.3, 135.1, 136.1, 137.8, 194.5, 196.5; HRMS (ESI-TOF)

calcd for $C_{24}H_{21}O_2S^+$ ($[M+H]^+$) 373.1257, found 373.1273.

(E) and (Z)-Ethyl 3-(methylthio)-2-nitro-3-phenylacrylate (3o)

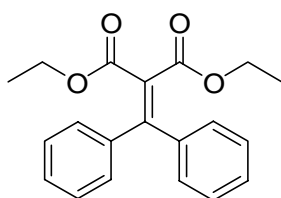


Yellow liquid; **One of two isomers:** 1H NMR (500 Hz, $CDCl_3$) δ 0.93 (t, $J = 7.0$ Hz, 3H), 1.88 (s, 3H), 3.97 (q, $J = 7.0$ Hz, 2H), 7.18-7.23 (m, 2H), 7.43-7.48 (m, 3H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 13.4, 16.6, 62.2, 121.0, 128.4 (2C), 128.8 (2C), 129.3, 132.2, 159.5, 160.6. **The other one:** 1H NMR (500 Hz, $CDCl_3$) δ 1.34 (t, $J = 7.0$ Hz, 3H), 1.84 (s, 3H), 4.35 (q, $J = 7.0$ Hz, 2H), 7.18-7.23 (m, 2H), 7.43-7.48 (m, 3H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 14.0, 16.3, 62.3, 122.0, 127.8, 128.6 (2C), 128.9 (2C), 131.9, 159.4, 160.1; HRMS (ESI-TOF) calcd for $C_{12}H_{13}NO_4SNa^+$ ($[M+Na]^+$) 290.0457, found 290.0470.

IV. Synthesis and analytical data of 4a–e

General Procedure for the synthesis of Compound 4a–e (taking **4a** as an example): To a solution of **3b** (185 mg, 0.5 mmol) and $PhB(OH)_2$ (183 mg, 1.5 mmol) in DMF (4.0 mL) was added $Cu(OAc)_2$ (27 mg, 0.15 mmol). The reaction mixture was allowed to stir at $130^\circ C$ for 30 h and monitored by TLC. Then, the reaction mixture was cooled to room temperature and poured into saturated NaCl solution (50 mL). The resulting mixture was extracted with dichloromethane (3×20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification was carried out by flash silica gel chromatography using petroleum ether/diethyl ether (50:1, V/V) as eluent to give diethyl 2-(diphenylmethylene)malonate **4a** (76 mg, 47%), benzyl(phenyl)sulfane (45 mg, 45%) and biphenyl (62 mg).

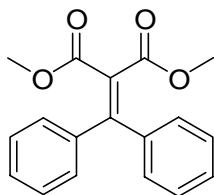
Diethyl 2-(diphenylmethylene)malonate (4a)²



White solid, mp: $69-71^\circ C$ (lit. $41-41.5^\circ C$); 1H NMR (500 Hz, $CDCl_3$) δ 1.02 (t, $J = 7.0$ Hz, 6H), 4.07 (q, $J = 7.0$ Hz, 4H), 7.18-7.20 (m, 4H), 7.31-7.36 (m, 6H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 13.6 (2C), 61.2 (2C), 128.1 (4C), 129.1 (7C), 140.2 (2C), 155.6, 165.9 (2C); IR (KBr): 3050, 2925, 2853,

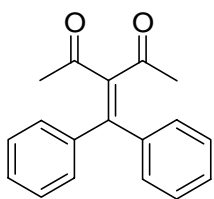
1723, 1302, 1285 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 347.1254, found 347.1261.

Dimethyl 2-(diphenylmethylene)malonate (4b)³



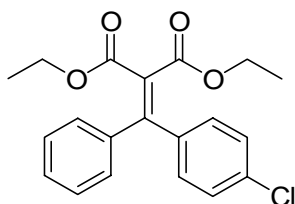
White solid, mp: 115-116 °C (lit. 119-121 °C); ^1H NMR (500 Hz, CDCl_3) δ 3.61 (s, 6H), 7.18 (d, J = 6.5 Hz, 4H), 7.32-7.37 (m, 6H); ^{13}C NMR (125 Hz, CDCl_3) δ 52.2 (2C), 128.2 (5C), 129.0 (4C), 129.3 (2C), 139.9 (2C), 156.5, 166.4 (2C); IR (KBr): 3028, 2950, 1735, 1247 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 319.0941, found 319.0949.

3-(Diphenylmethylene)pentane-2,4-dione (4c)⁴



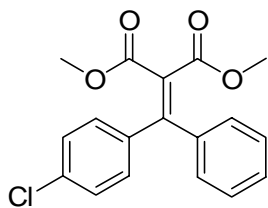
White solid, mp: 116-118 °C (lit. 120-121 °C); ^1H NMR (500 Hz, CDCl_3) δ 1.94 (s, 6H), 7.18-7.20 (m, 4H), 7.35-7.38 (m, 4H), 7.40-7.42 (m, 2H); ^{13}C NMR (125 Hz, CDCl_3) δ 31.3 (2C), 128.6 (4C), 129.8 (2C), 130.0 (4C), 139.3 (2C), 143.1, 149.2, 203.6 (2C); IR (KBr): 3061, 3028, 2923, 2852, 1695, 12873 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 287.1043, found 287.1046.

Diethyl 2-((4-chlorophenyl)(phenyl)methylene)malonate (4d)



White solid, mp: 89-90 °C; ^1H NMR (500 Hz, CDCl_3) δ 1.02 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H), 4.05-4.13 (m, 4H), 7.12-7.18 (m, 4H), 7.30-7.37 (m, 5H); ^{13}C NMR (125 Hz, CDCl_3) δ 13.6, 13.7, 61.3, 61.4, 126.9, 128.2 (2C), 128.4 (2C), 129.1 (2C), 129.3, 130.5 (2C), 135.4, 138.5, 139.7, 154.2, 165.6, 165.7; IR (KBr): 3021, 2980, 29312, 1725, 1296 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{20}\text{H}_{19}\text{ClO}_4\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 381.0864, found 381.0869; Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{ClO}_4$: C, 66.95; H, 5.34. Found: C, 66.81; H, 5.39.

Dimethyl 2-((4-chlorophenyl)(phenyl)methylene)malonate (4e)



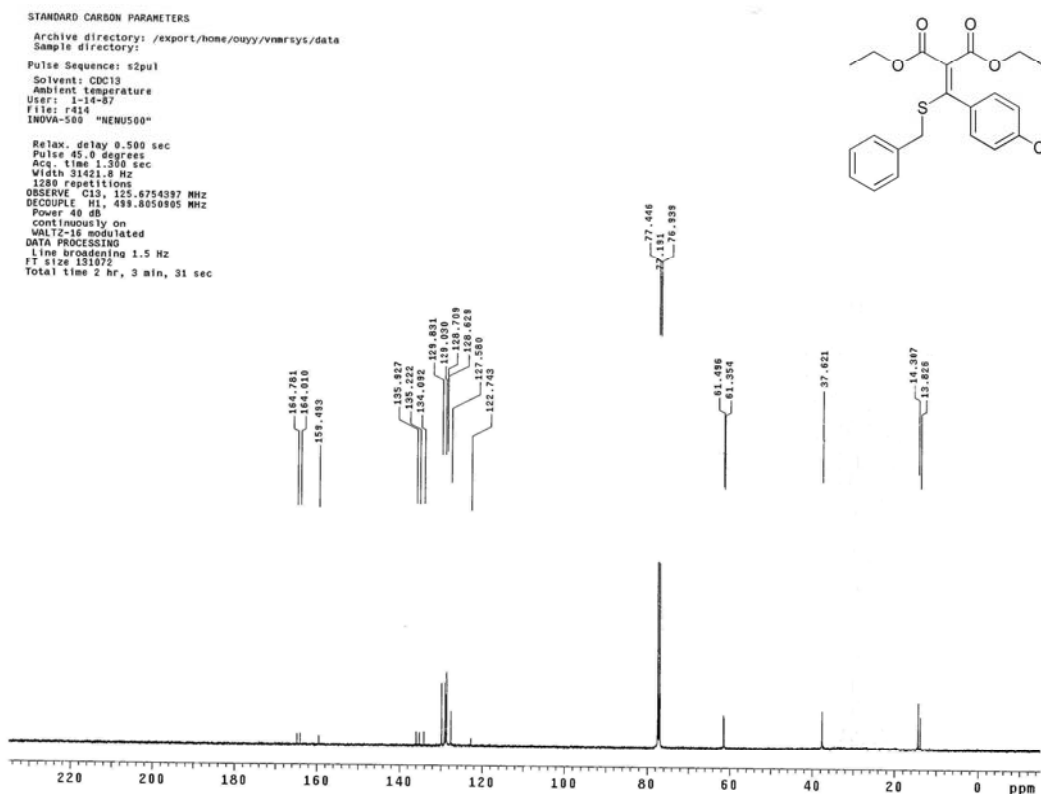
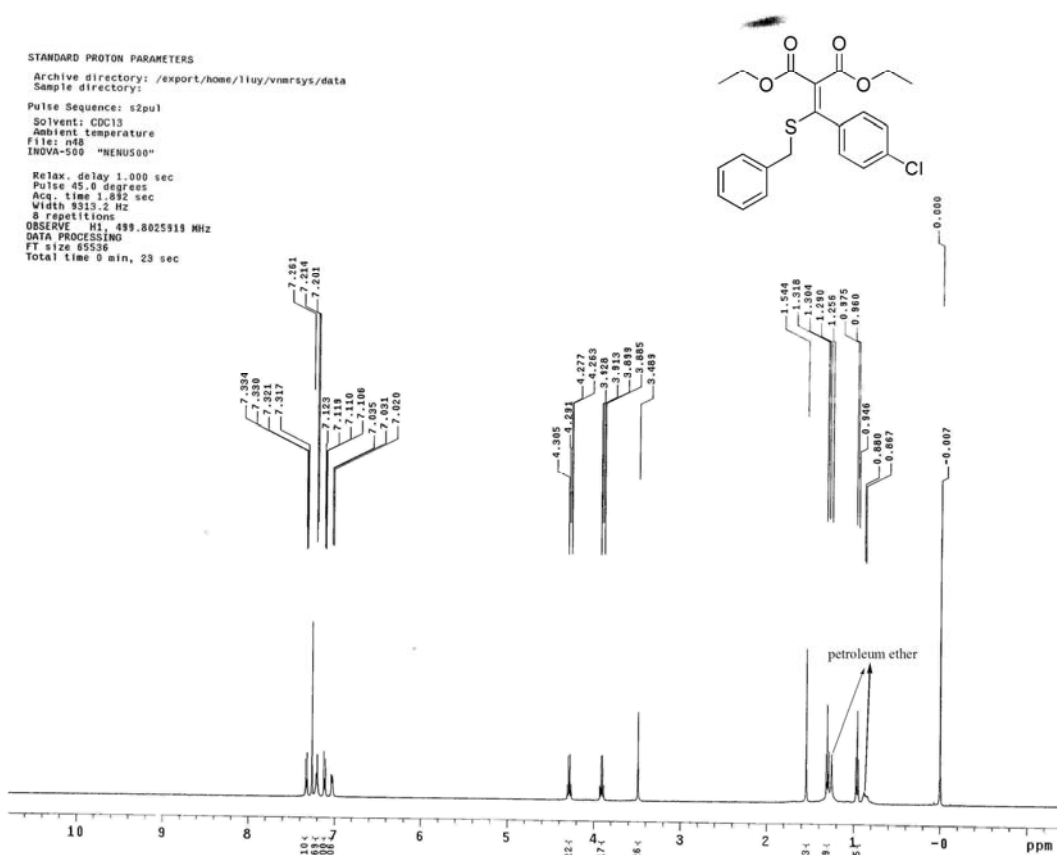
White solid, mp: 82-83 °C; ^1H NMR (500 Hz, CDCl_3) δ 3.61 (s, 3H), 3.65 (s, 3H), 7.11-7.16 (m, 4H), 7.30-7.37 (m, 5H); ^{13}C NMR (125 Hz, CDCl_3) δ 52.2, 52.3, 127.3, 128.3 (2C), 128.5 (2C), 129.0 (2C), 129.5, 130.4 (2C), 135.5, 138.3, 139.6, 155.1, 166.0, 166.1; IR (KBr): 3025, 2946, 1746, 1285 cm^{-1} ; HRMS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{16}\text{ClO}_4^+$ ($[\text{M}+\text{H}]^+$) 331.0732, found 331.0735; Anal. calcd for $\text{C}_{18}\text{H}_{15}\text{ClO}_4$: C, 65.36; H, 4.57. Found: C, 65.43; H, 4.47.

V. References

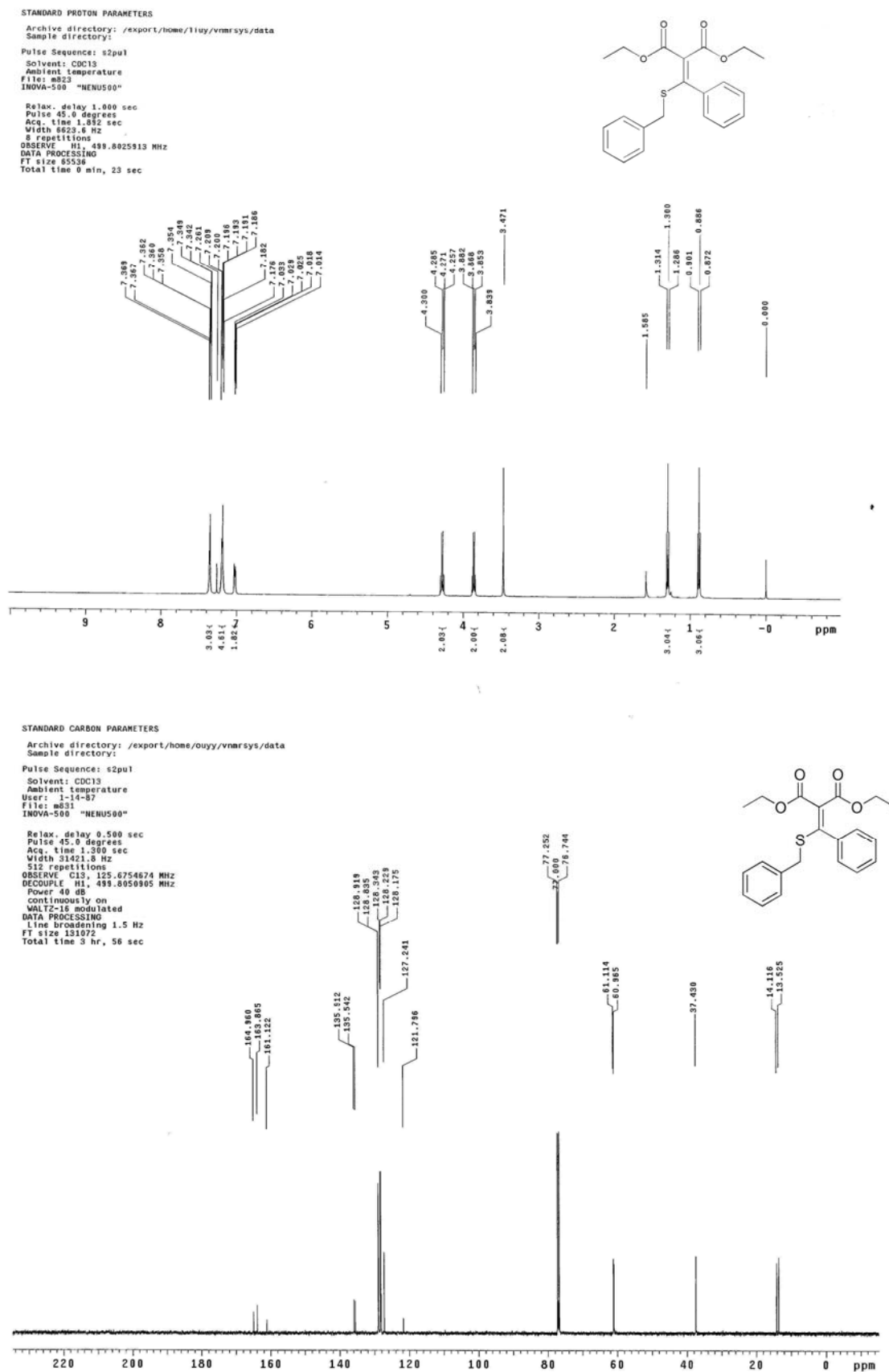
- 1 (a) M. Wang, L. Ai, J. Zhang, Q. Liu, L. Gao. *Chin. J. Chem.* **2002**, 20, 1591; (b) Y. Liu, M. Wang, H. Yuan, Q. Liu, Q. *Adv. Synth. Catal.* **2010**, 352, 884.
- 2 X. L. Liu, X. Yang, M. Sun, X. H. Liu, R. Zhao, F. M. Liao, *Acta Chim. Sinica* **2002**, 60, 487.
- 3 G. Mlostón, H. Heimgartner, *Helv. Chim. Acta.* **1996**, 79, 1785.
- 4 S. Motoki, C. Urakawa, A. Kano, Y. Fushimi, T. Hirano, K. Murata, *Bull. Chem. Soc. Japan* **1970**, 43, 809.

VI. Copies of NMR spectra for compounds 3a–l and 4a–e

3a



3b



3c

STANDARD PROTON PARAMETERS

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

Pulse Sequence: s2pu1

Solvent: CDCl₃

Ambient temperature

File: r556

INOVA-500 "NENUS00"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.052 sec

Width 8988.8 Hz

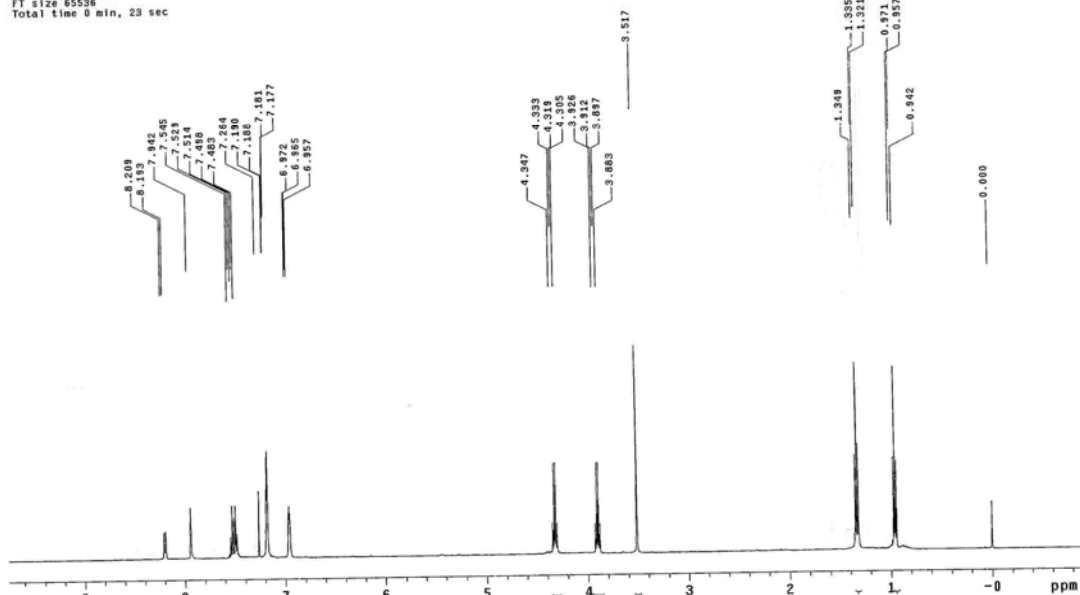
8 repetitions

OBSERVE H1, 499.8025898 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: s2pu1

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: r561

INOVA-500 "NENUS00"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

784 repetitions

OBSERVE C13, 125.6754642 MHz

DECOUPLE H1, 499.8050905 MHz

Power 40 dB

continuously on

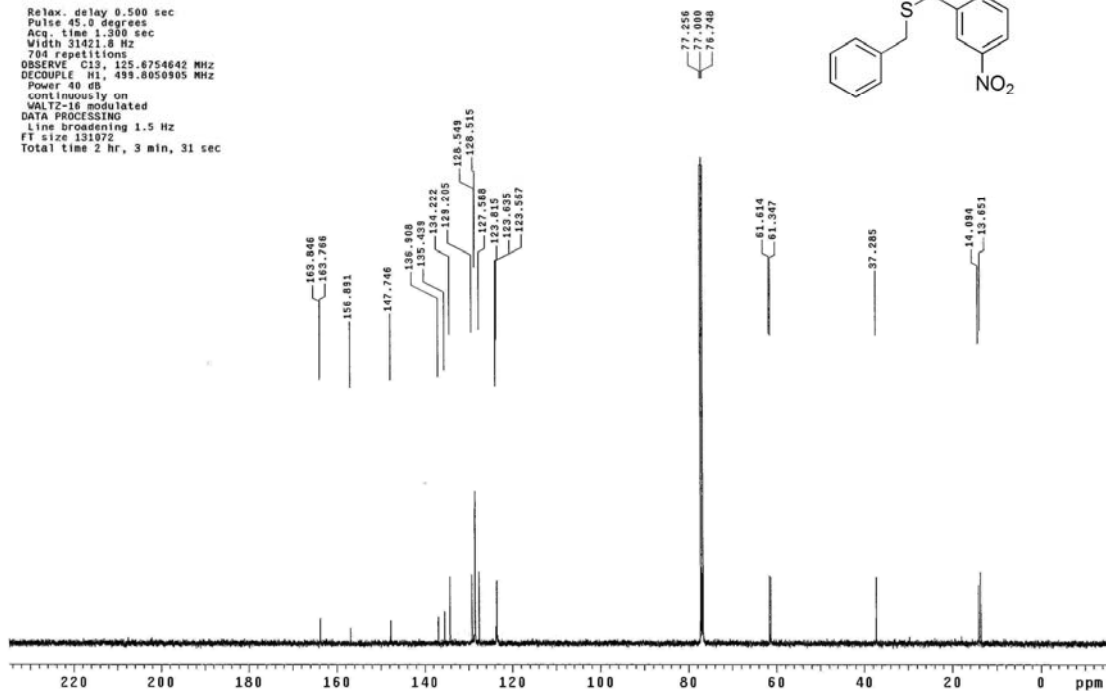
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 2 hr, 3 min, 31 sec



3d

STANDARD PROTON PARAMETERS

Archive directory: /export/home/liuy/vnmr/sys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: n35

INOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.852 sec

Width 9315.2 Hz

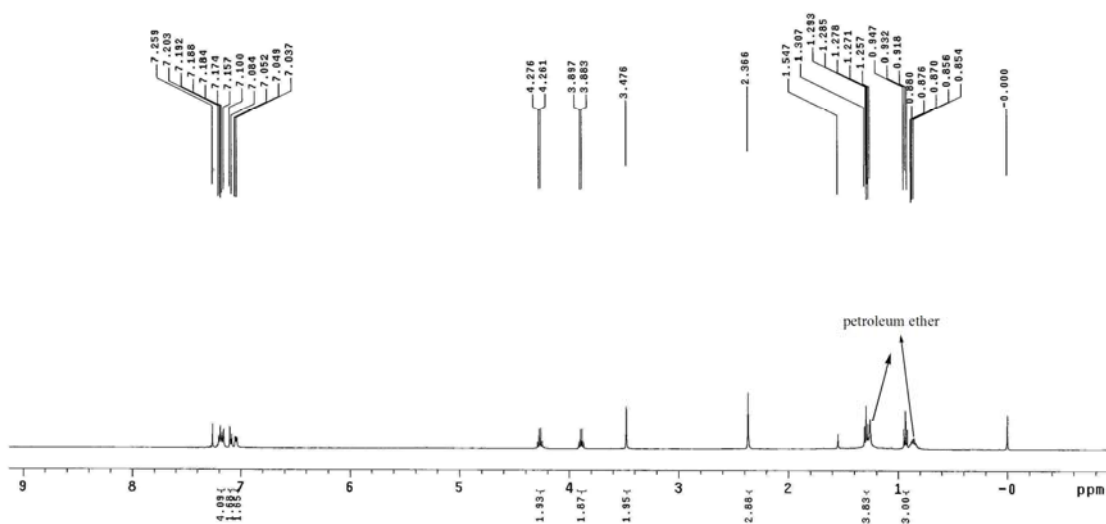
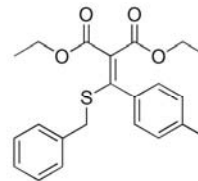
8 repetitions

OBSERVE N1, 499.8025922 MHz

DATA PROCESSING

FT size 45536

Total time 0 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmr/sys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: r415

INOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.389 sec

Width 31421.8 Hz

640 repetitions

OBSERVE C13, 125.6754627 MHz

DECOUPLE N1, 499.8050905 MHz

Power 40 dB

continuously on

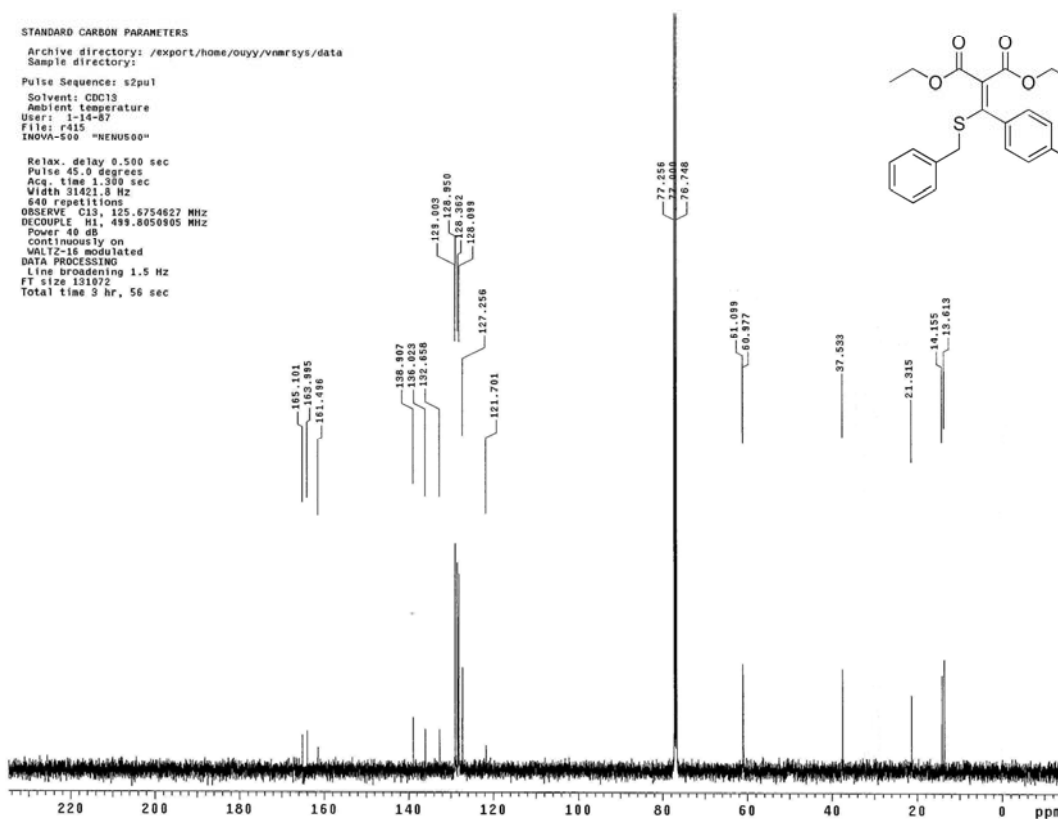
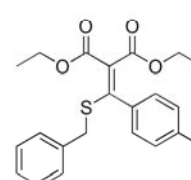
WALTZ-16 modulated

DATA PROCESSING

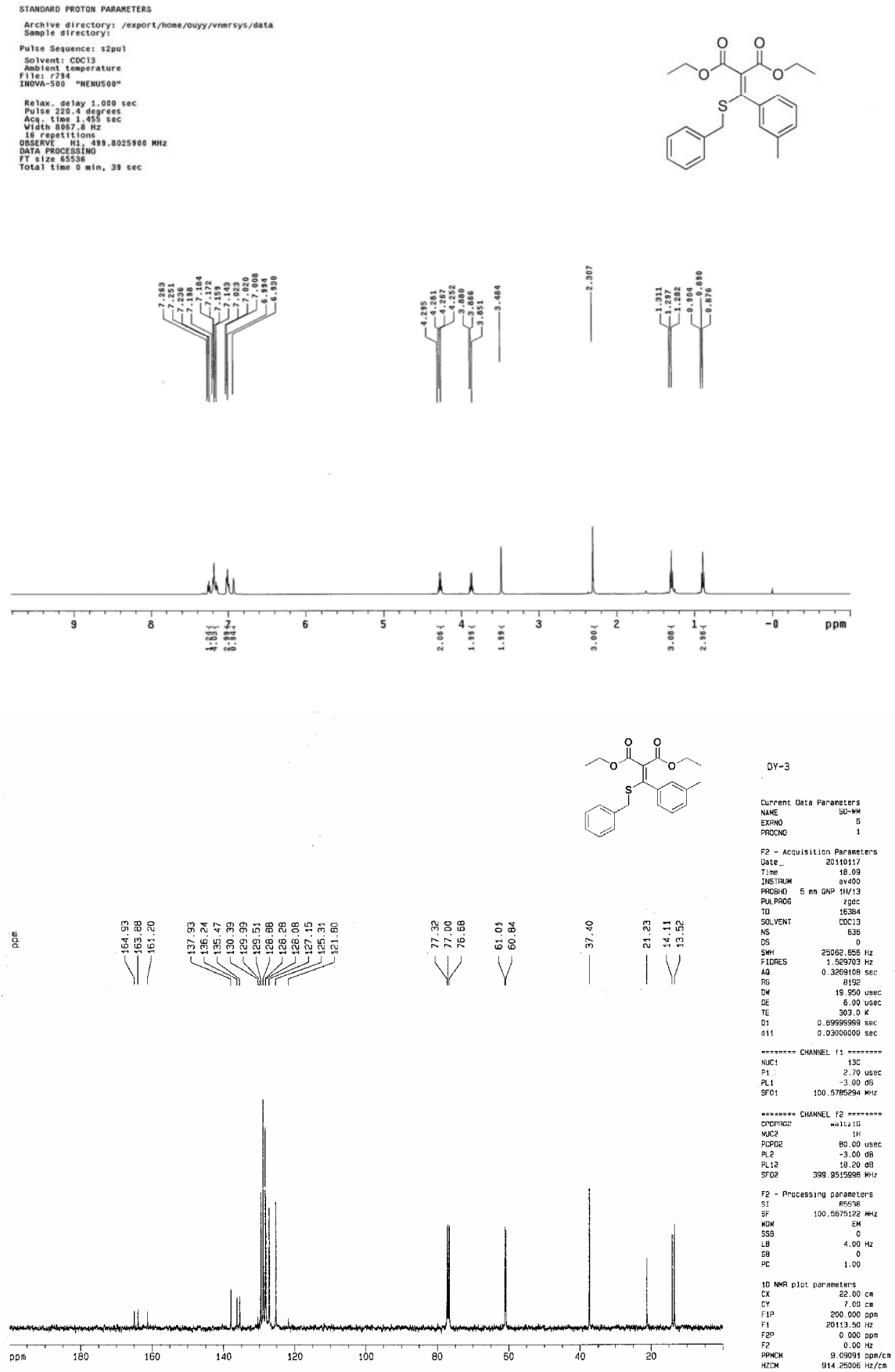
Line broadening 1.5 Hz

FT size 131072

Total time 3 hr, 56 sec



3e



3f

STANDARD PROTON PARAMETERS

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

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

File: r707

INOVA-500 "HENU500"

Relax. delay 1.000 sec

Pulse 220.4 degrees

Acq. time 1.092 sec

Width 7996.8 Hz

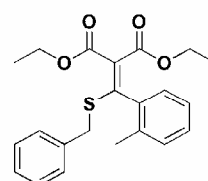
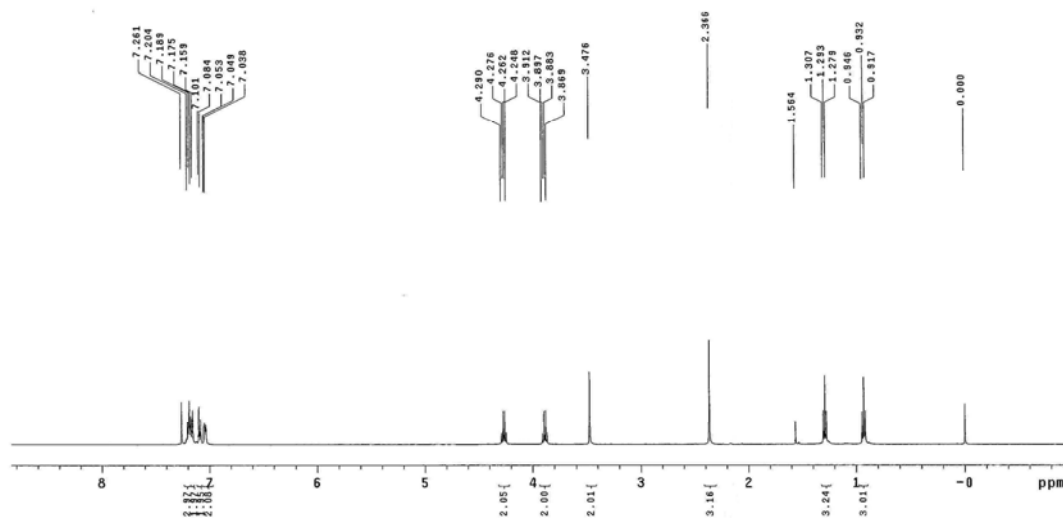
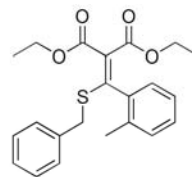
16 repetitions

OBSERVE H1, 499.8025914 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 46 sec



DY-2

Current Data Parameters
NAME SD-NM
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters

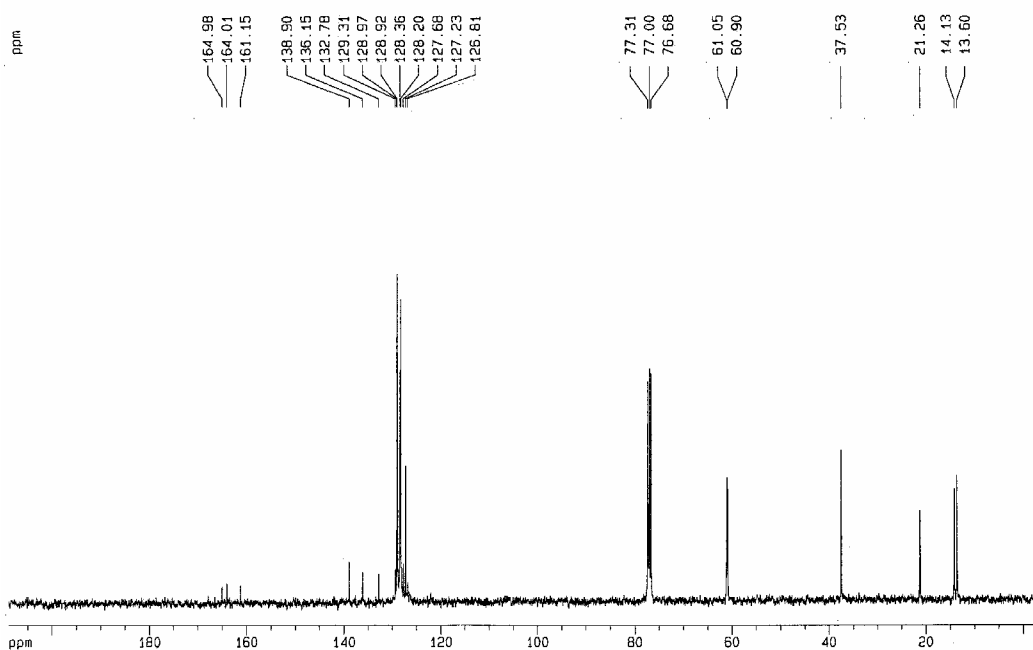
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SOLVENT CDCl3
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DS 0
SWH 25062.656 Hz
FIDRES 1.529703 Hz
AQ 0.3268108 sec
RG 6132
DW 19.950 usec
DE 5.00 usec
TE 303.0 K
d1 0.69999999 sec
d11 0.03000000 sec

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NUC1 13C
P1 2.70 usec
PL1 -3.00 dB
SF01 100.5785294 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 18.20 dB
SF02 399.9515998 MHz

F2 - Processing parameters
SI 65536
SF 100.5676087 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
CY 7.00 cm
F1P 209.012 ppm
F1 21019.79 Hz
F2P -3.400 ppm
F2 -341.91 Hz
PPMCM 9.65507 ppm/cm
HZCM 970.98621 Hz/cm



3g

STANDARD PROTON PARAMETERS

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

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: r571

INOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8889.8 Hz

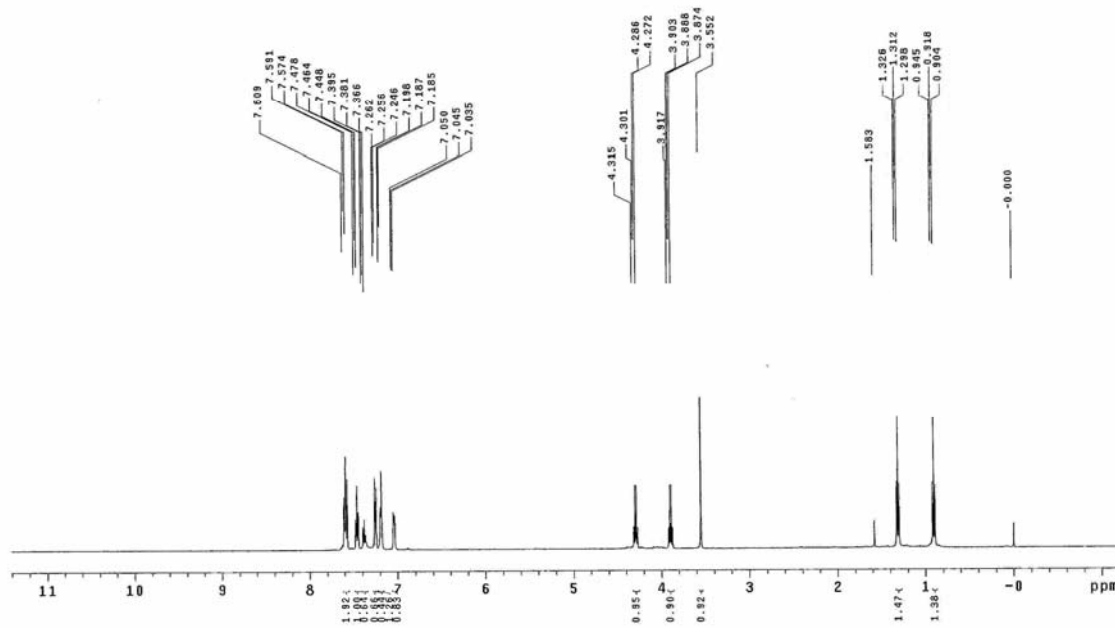
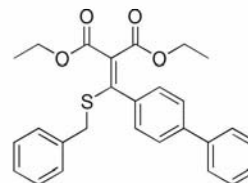
8 repetitions

OBSERVE H1, 499.8025939 MHz

DATA PROCESSING

FT size 65536

Total time 8 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: r578

INOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

256 repetitions

OBSERVE C13, 125.8754661 MHz

DECOUPLE H1, 499.8050905 MHz

Power 40 dB

continuously on

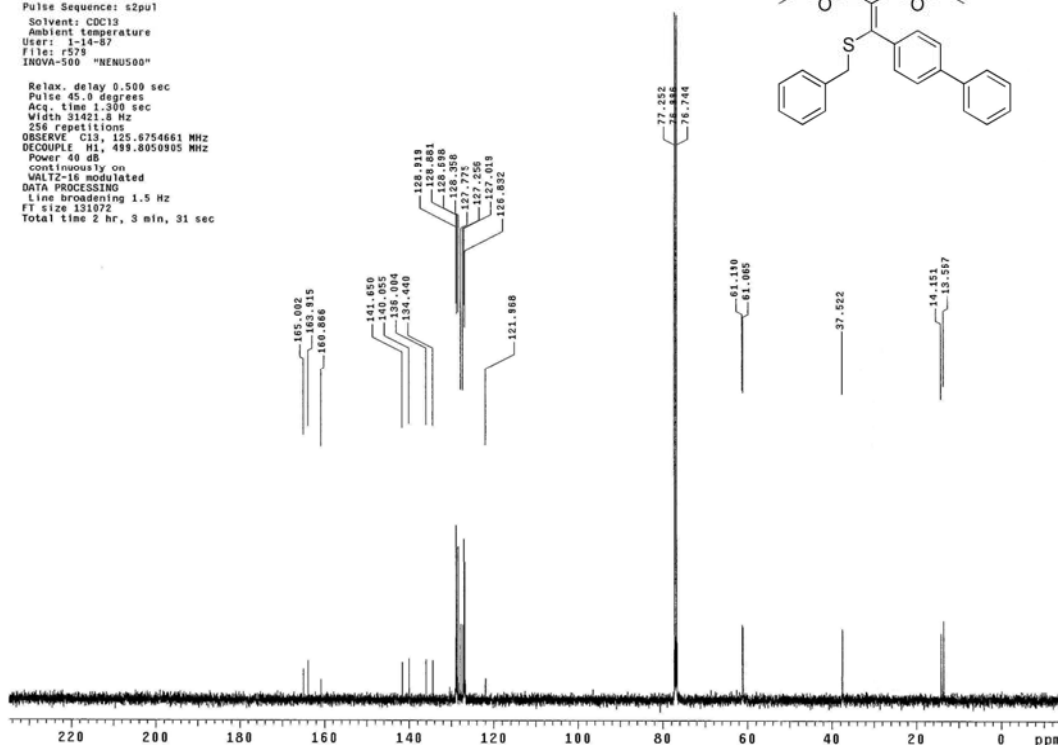
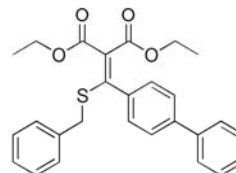
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 2 hr, 3 min, 31 sec



3h

STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmr/sys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: r272

INNOVA-500 "NENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8989.8 Hz

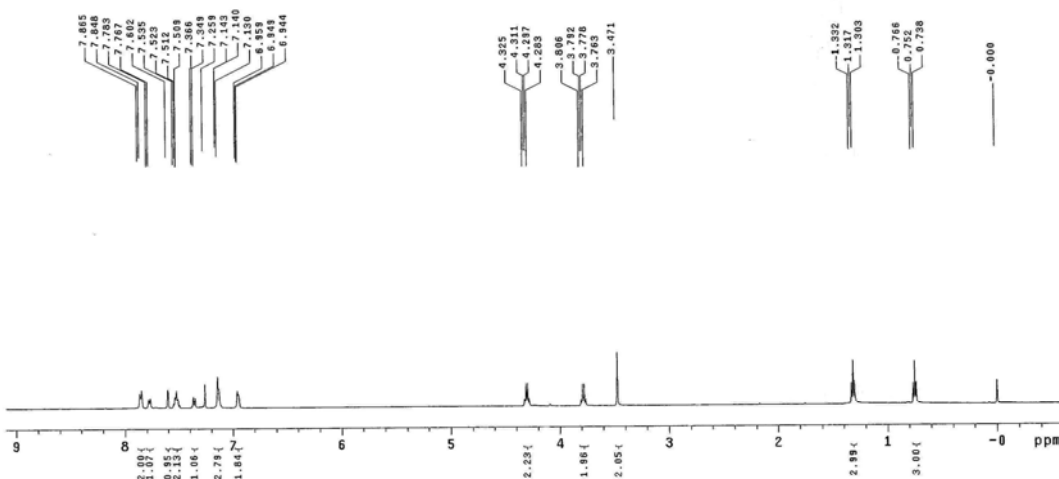
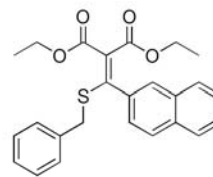
8 repetitions

OBSERVE H1, 499.8025925 MHz

DATA PROCESSING

FT size 65536

Total time 8 min, 23 sec



STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmr/sys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

User: 1-14-87

File: r294

INNOVA-500 "NENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

1624 repetitions

OBSERVE C13, 125.6754646 MHz

DECOUPLE H1, 499.8050305 MHz

Power 40 dB

continuously on

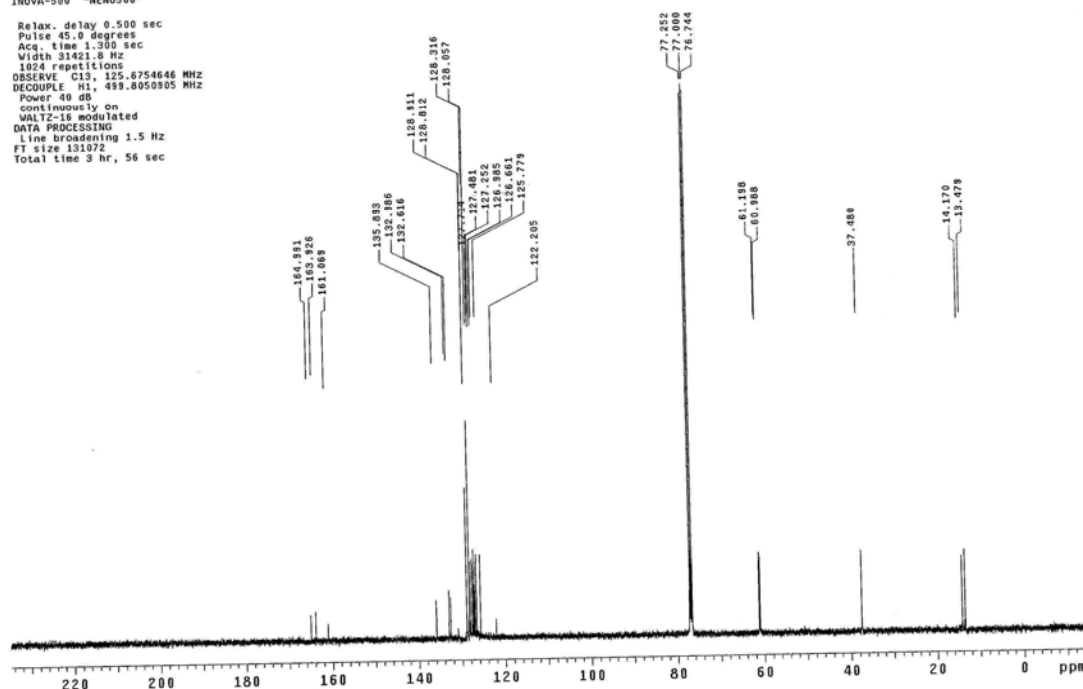
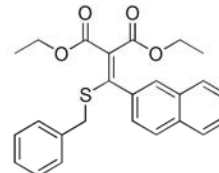
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 3 hr, 56 sec



3i

STANDARD PROTON PARAMETERS

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

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: t051

INNOVA-500 "MENU500"

Relax. delay 1.000 sec

Pulse 220.4 degrees

Acq. time 1.455 sec

Width 1052.0 Hz

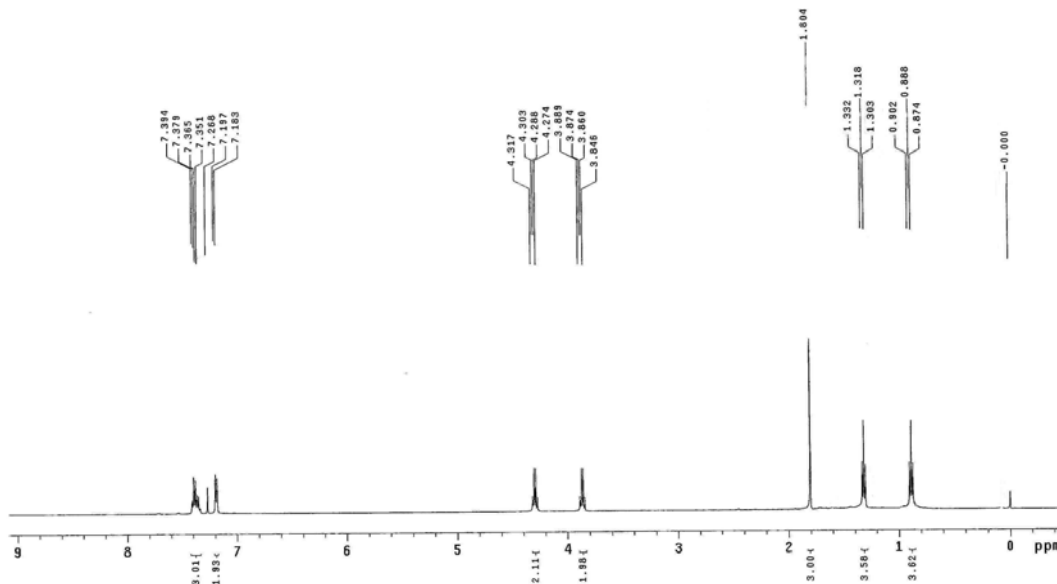
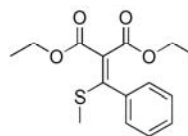
8 repetitions

OBSERVE R1, 499.8025873 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 19 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: t057

INNOVA-500 "MENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.360 sec

Width 31421.0 Hz

320 repetitions

OBSERVE C13, 125.6754661 MHz

DECOUPLE R1, 499.8050905 MHz

Power 40 dB

continuously on

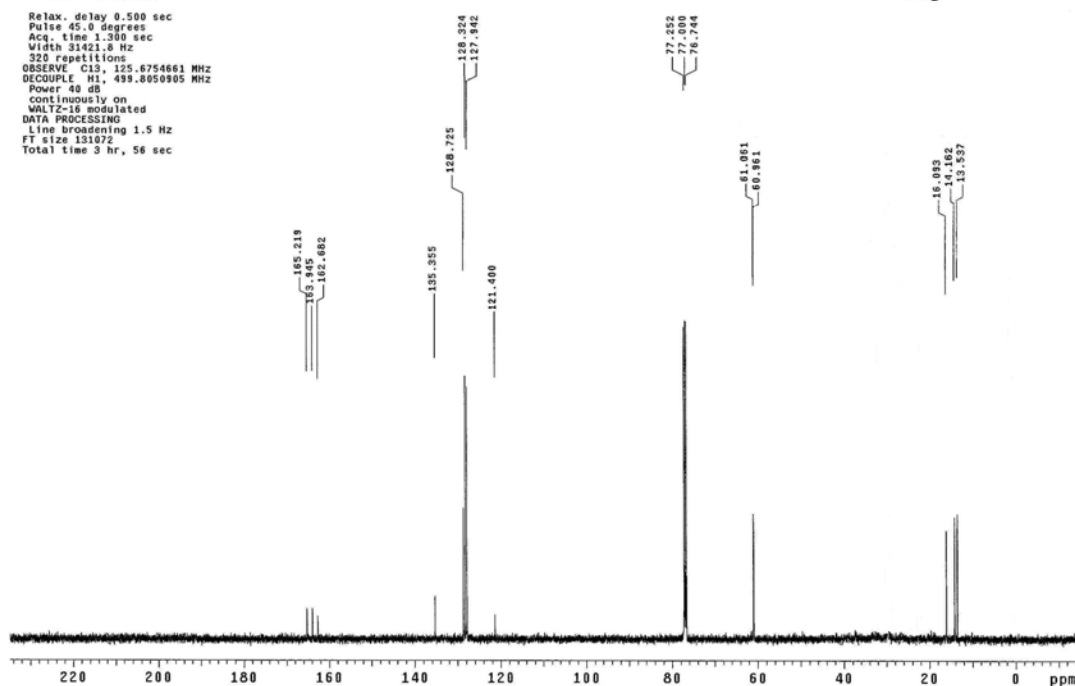
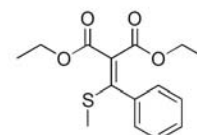
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 131072

Total time 3 hr, 56 sec



3j

STANDARD PROTON PARAMETERS

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

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: r154-1

INOVA-500 "MENU500"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.852 sec

Width 8888.8 Hz

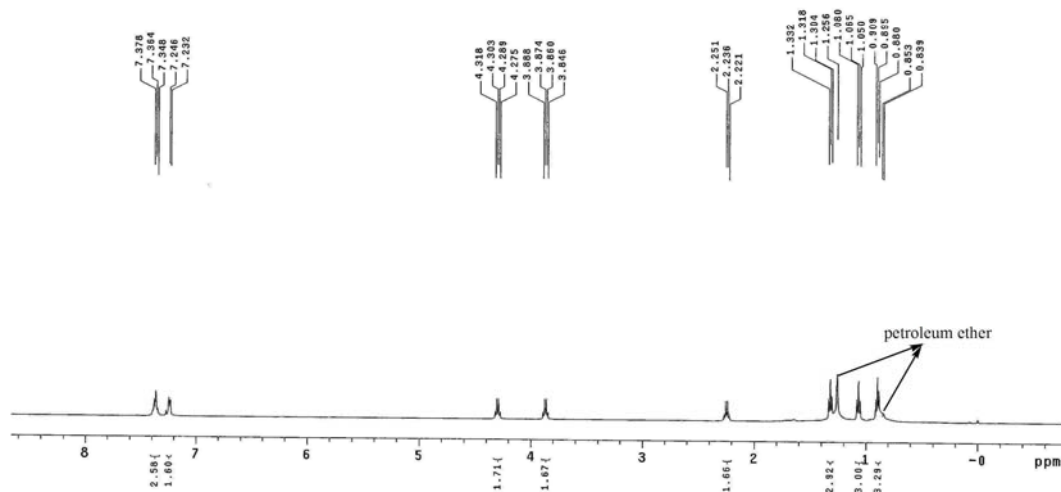
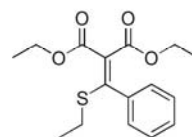
Single scan

OBSERVE H1, 499.8025859 MHz

DATA PROCESSING

FT size 85538

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

Upors: 1-14.87

File: r154

INOVA-500 "MENU500"

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 31421.8 Hz

256 repetitions

OBSERVE C13, 125.6754670 MHz

DECOUPLE H1, 499.8050905 MHz

Power 40 dB

continuously on

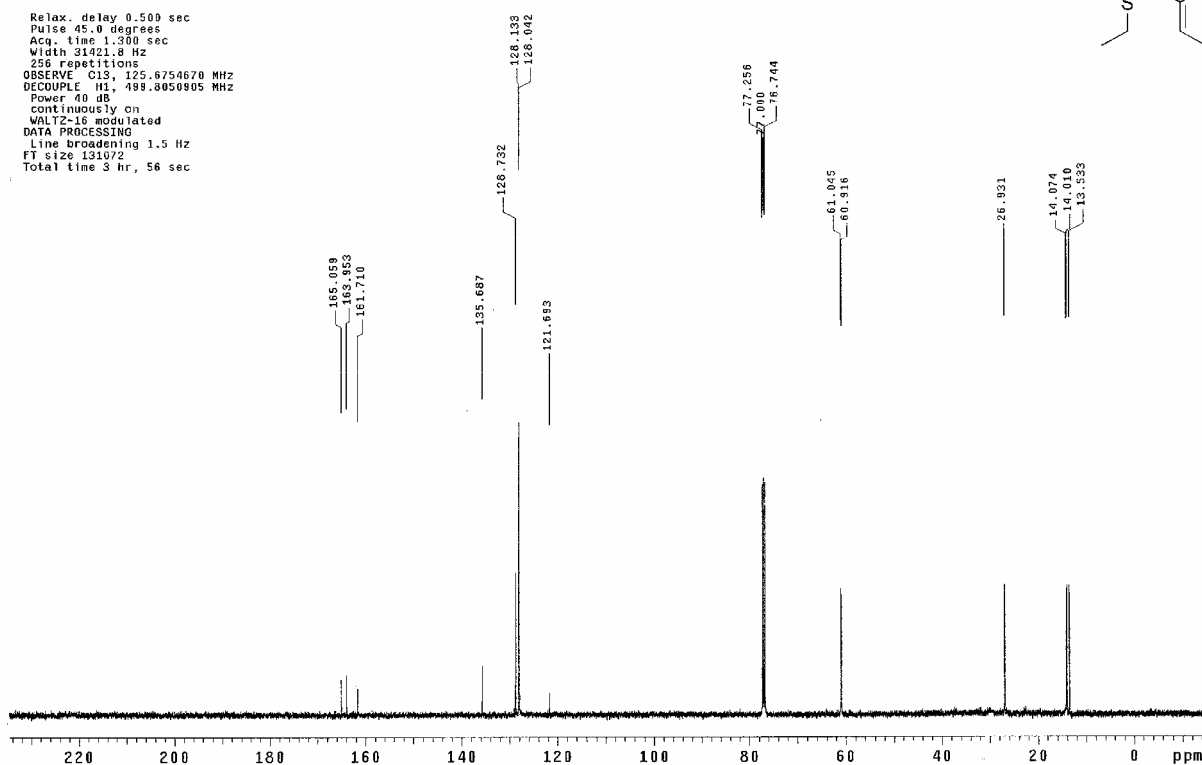
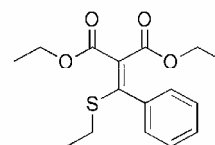
WALTZ-16 modulated

DATA PROCESSING

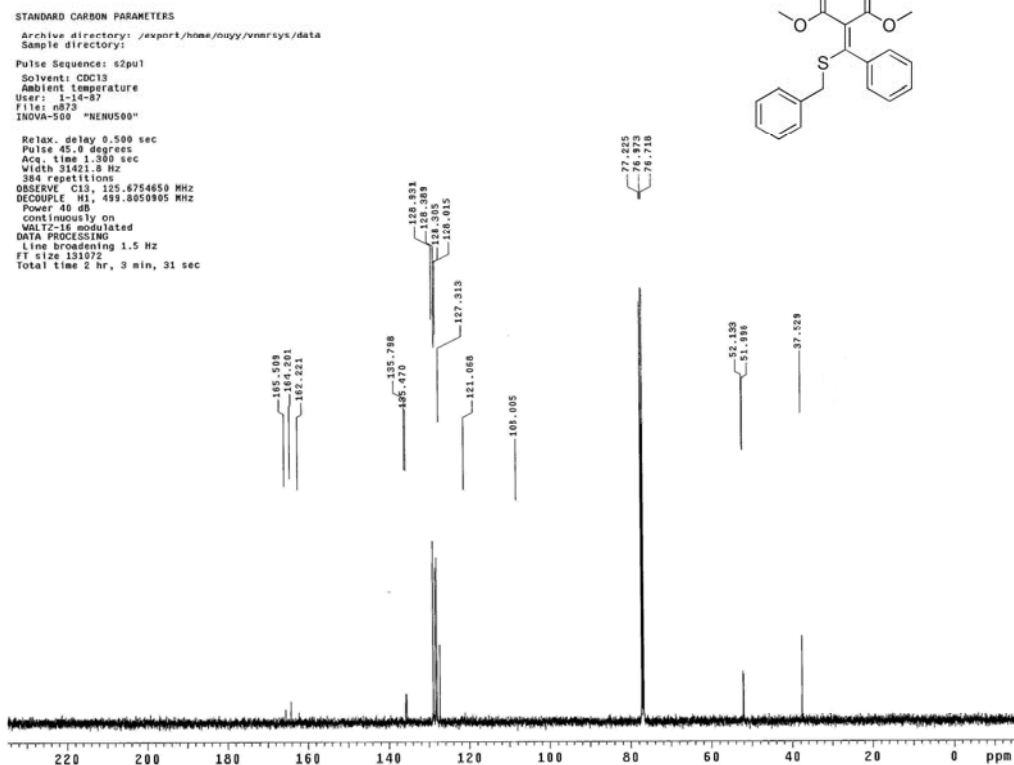
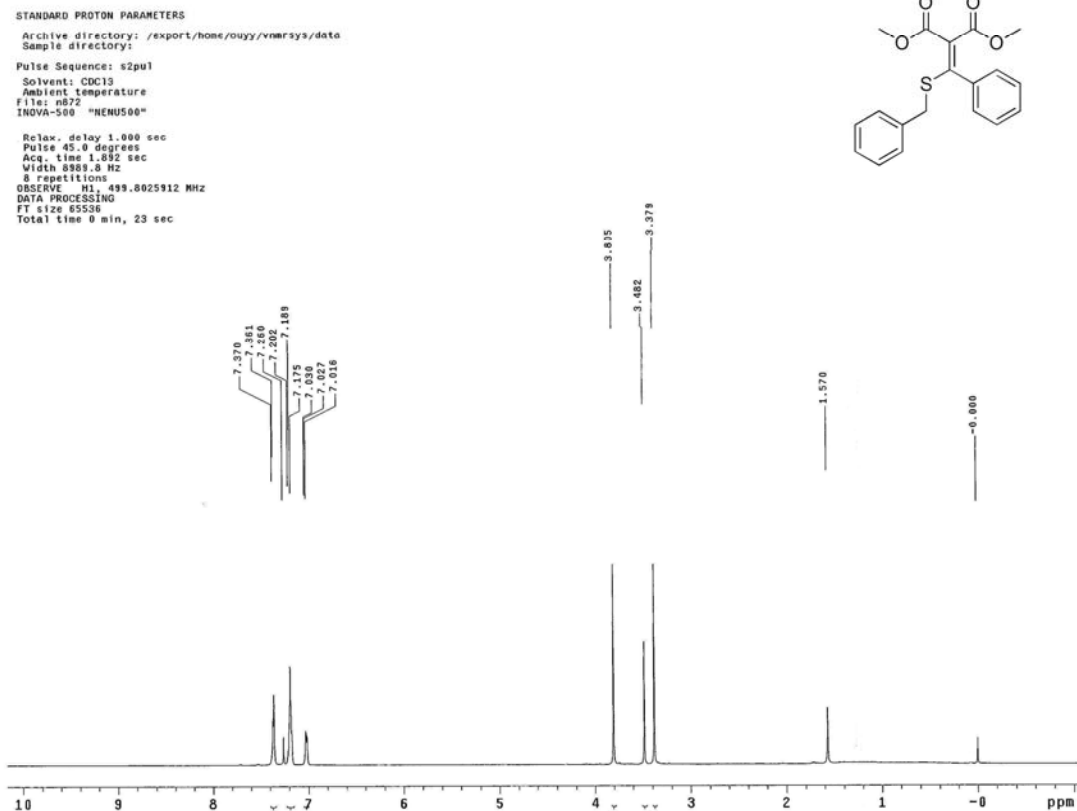
Line broadening 1.5 Hz

FT size 131072

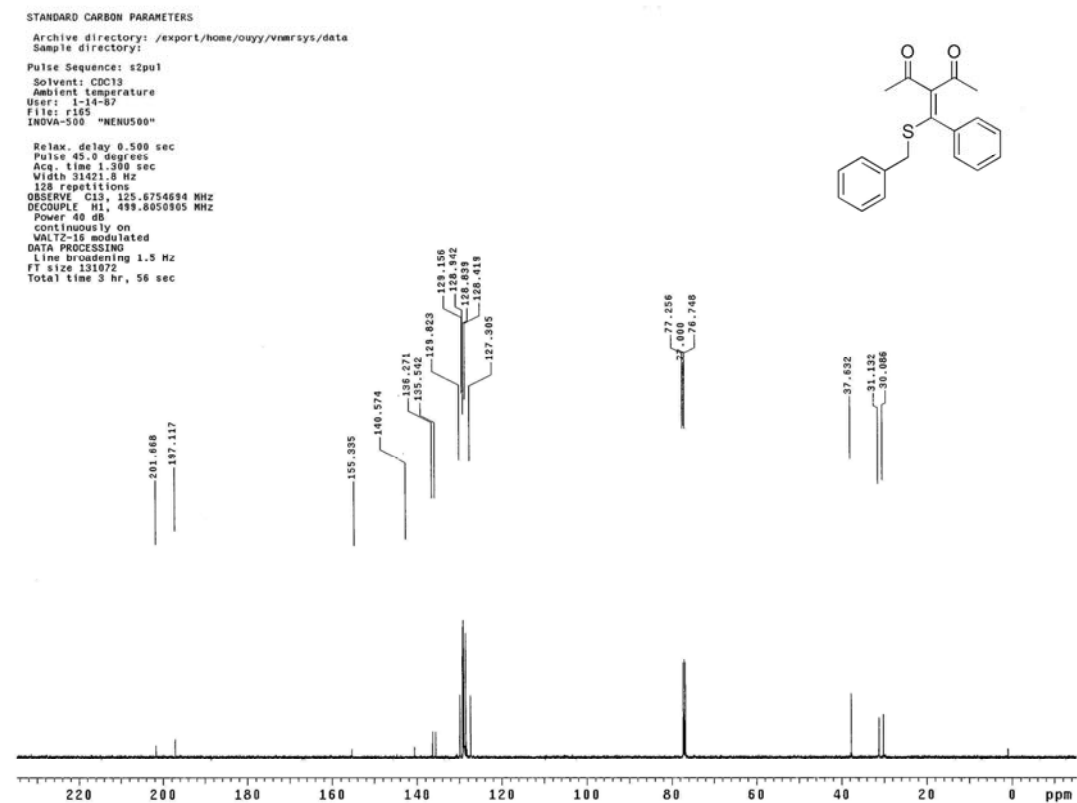
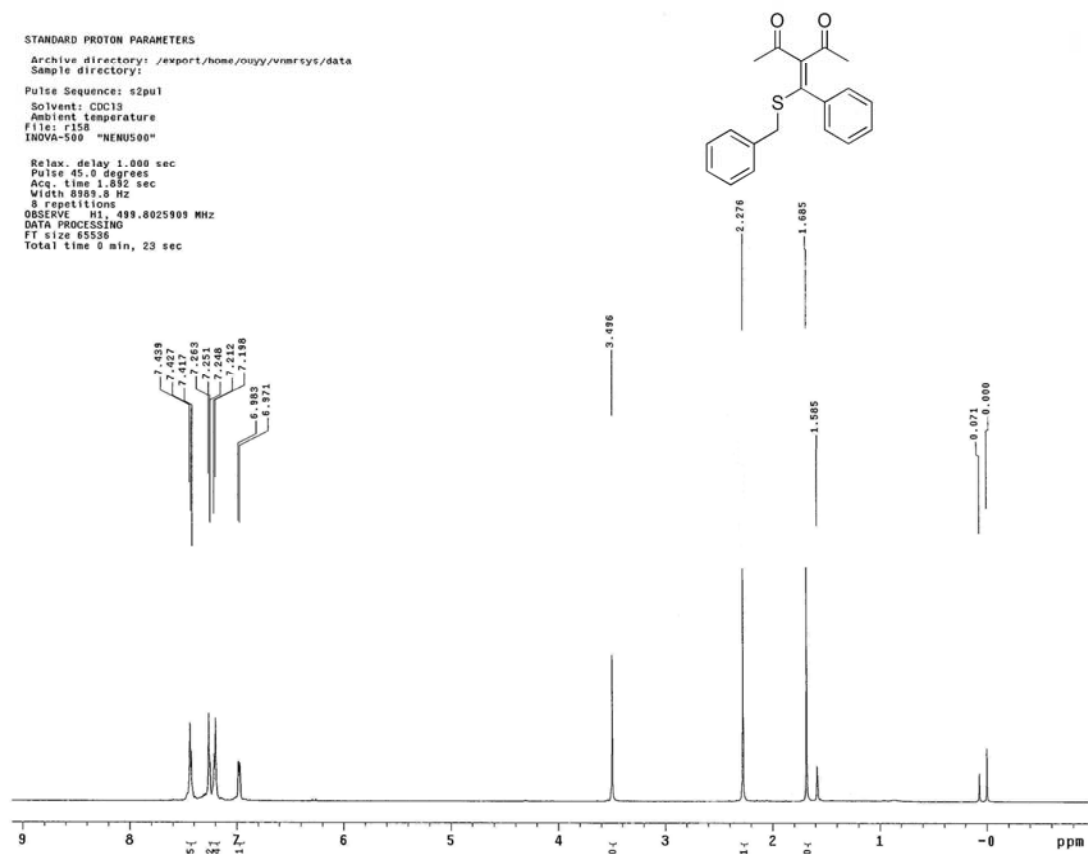
Total time 3 hr, 56 sec



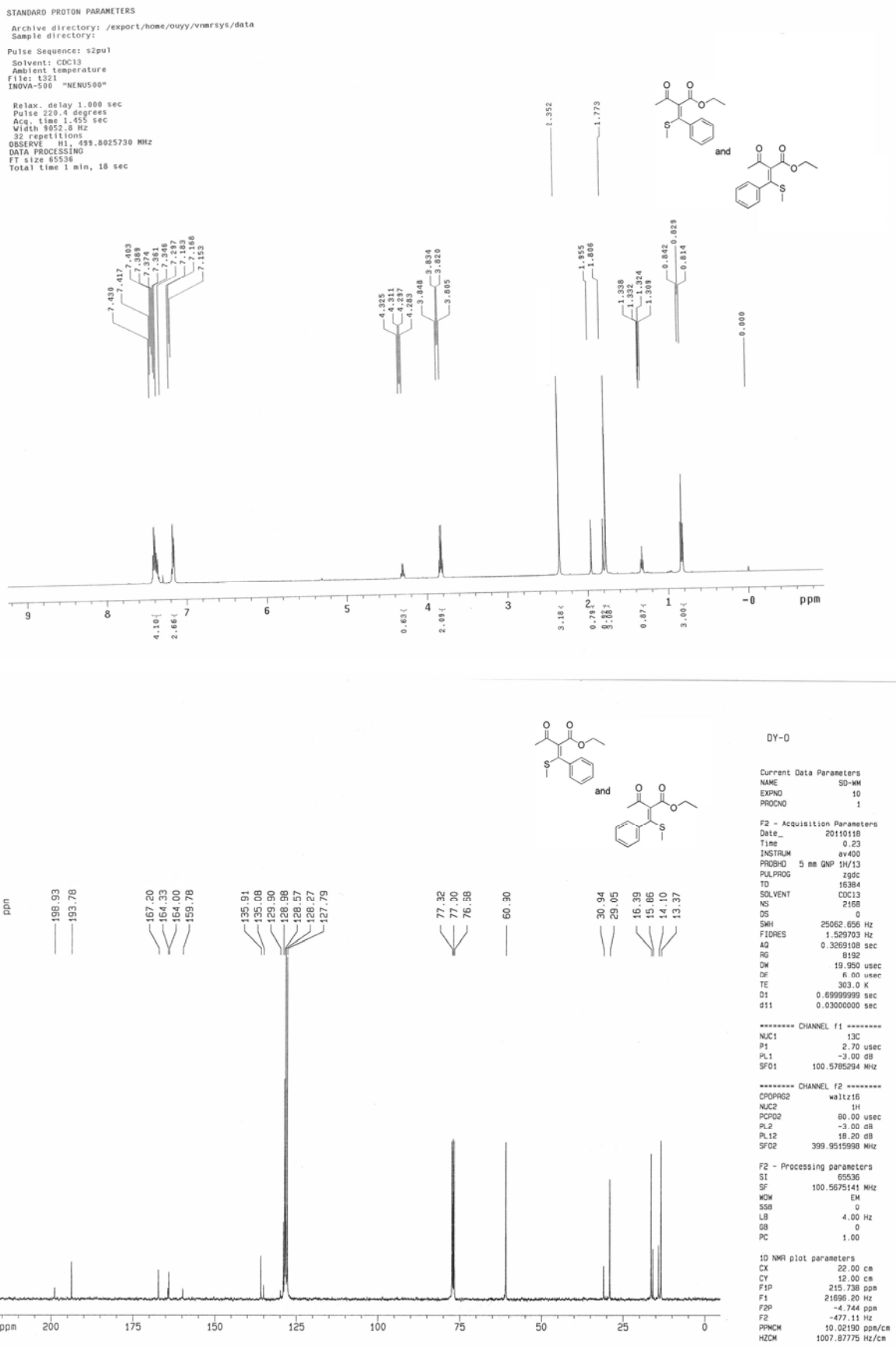
3k

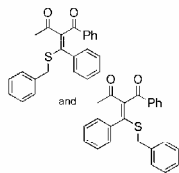
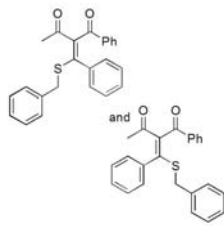


31

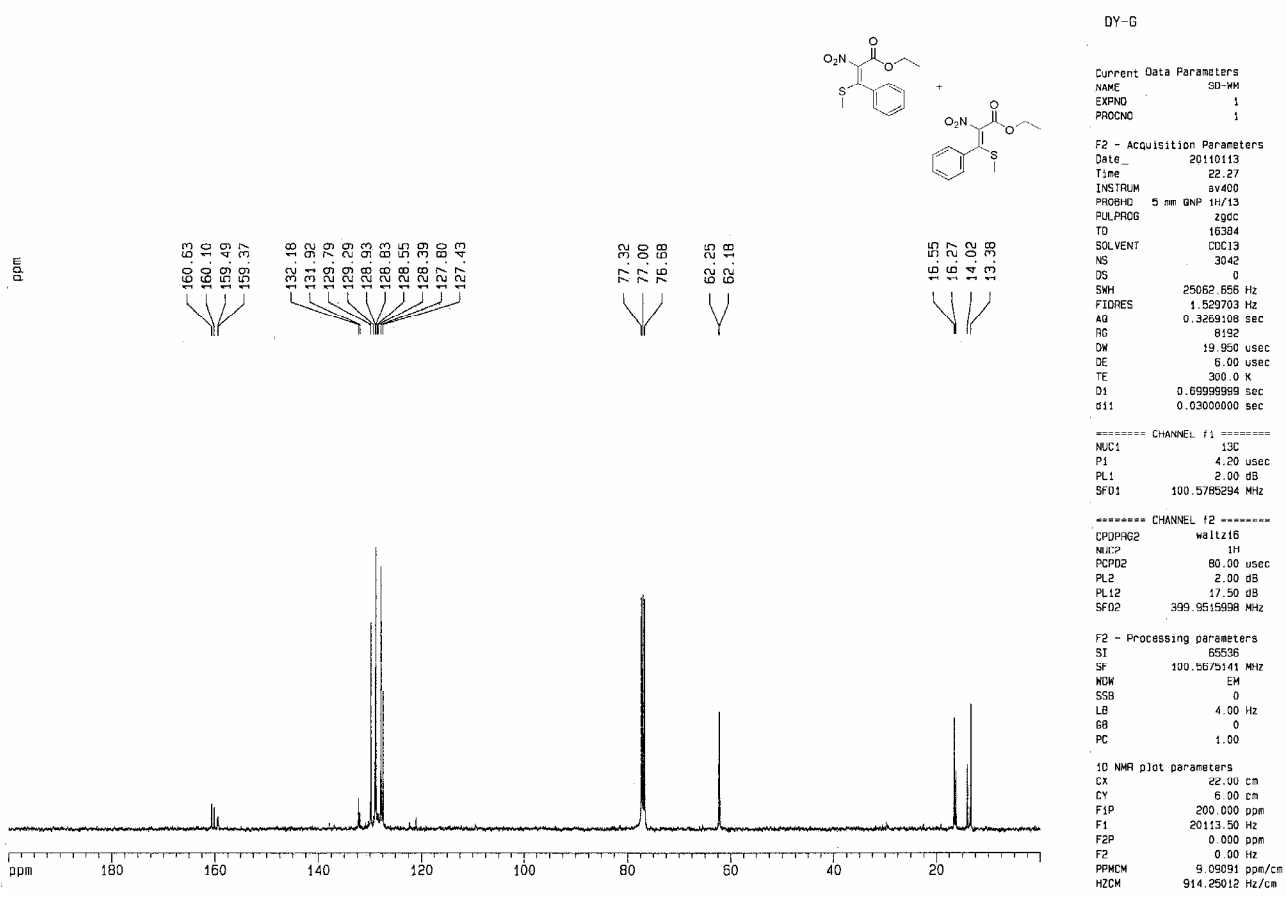
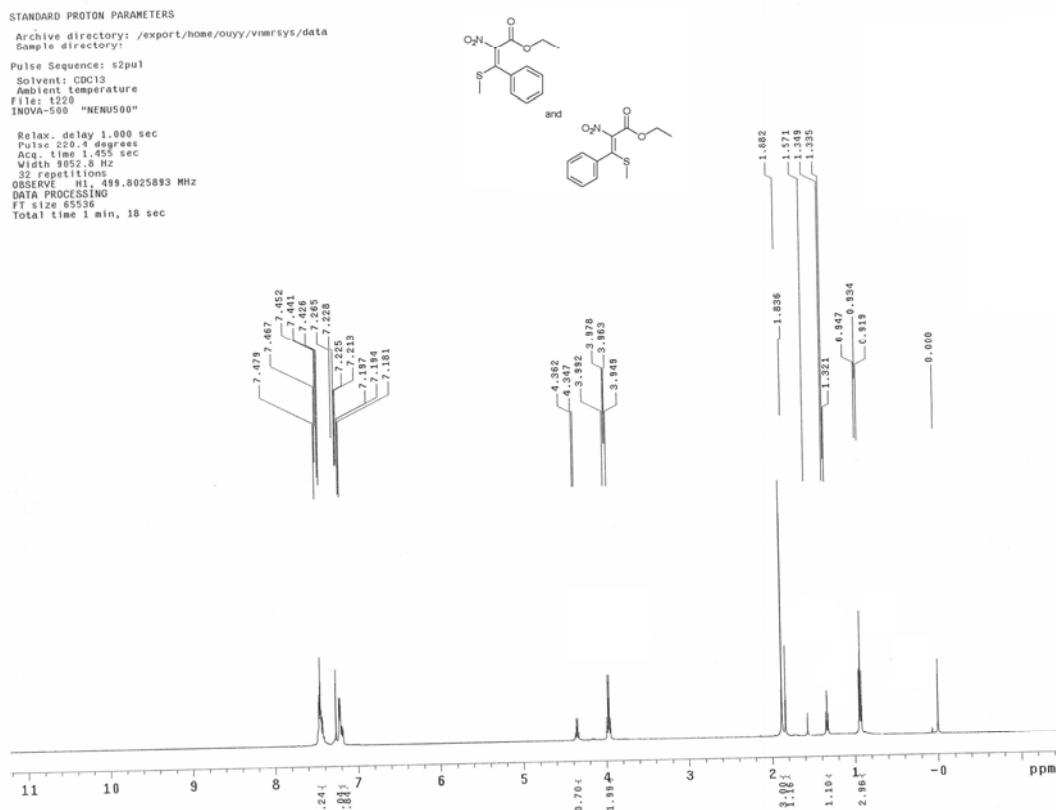


3m





30

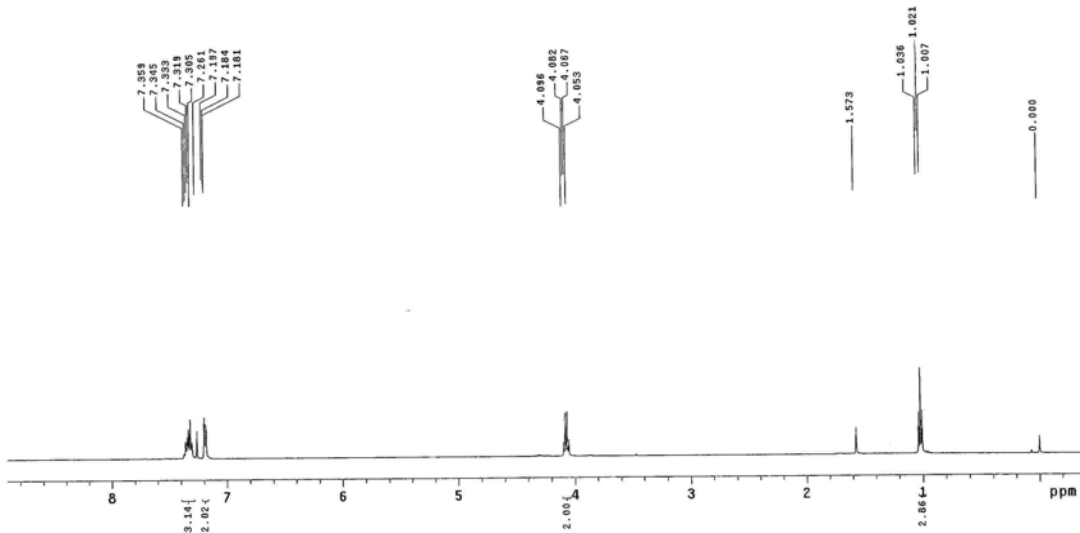
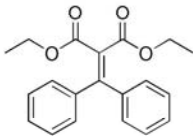


4a

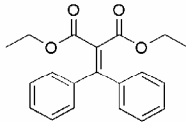
STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Files: r749
INNOVA-500 "NMR500"

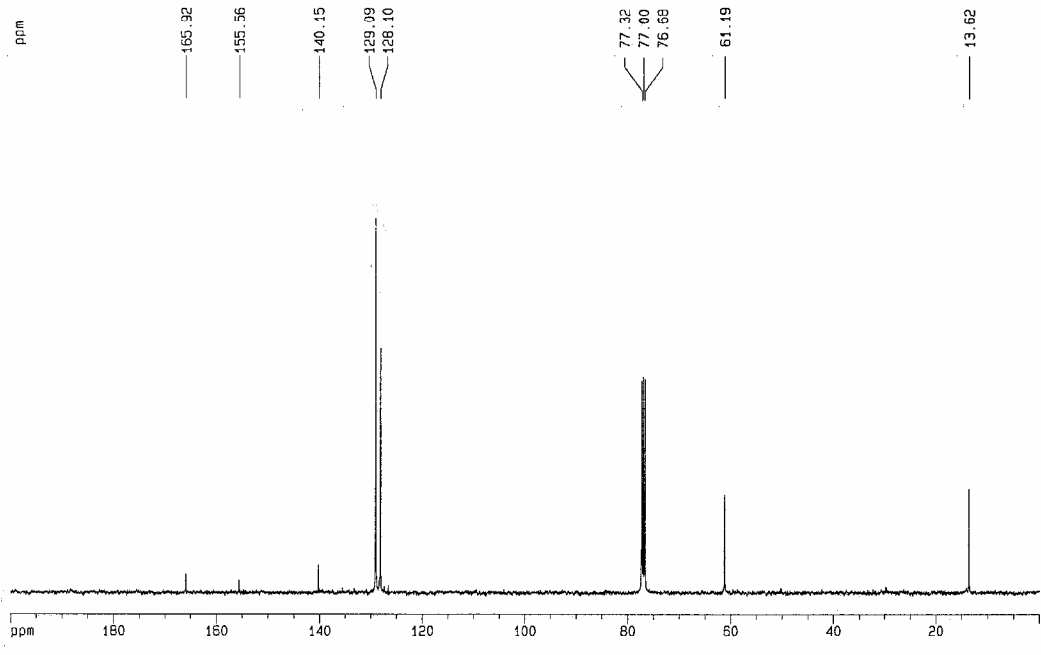
Relax. delay 1.000 sec
Pulse 220.4 degrees
Acq. time 1.892 sec
Width 7856.6 Hz
16 repetitions
OBSERVE H1, 499.8025909 MHz
DATA PROCESSING
FT size 65536
Total time 8 min, 46 sec



OY-A



Current Data Parameters
NAME SD-WM
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110117
Time 15.40
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 16384
SOLVENT CDCl3
NS 4208
DS 0
SWH 25062.656 Hz
FIDRES 1.529703 Hz
AQ 0.3263108 sec
RG 8192
DW 19.950 usec
DE 6.00 usec
TE 303.0 K
D1 0.63999999 sec
d11 0.03000000 sec



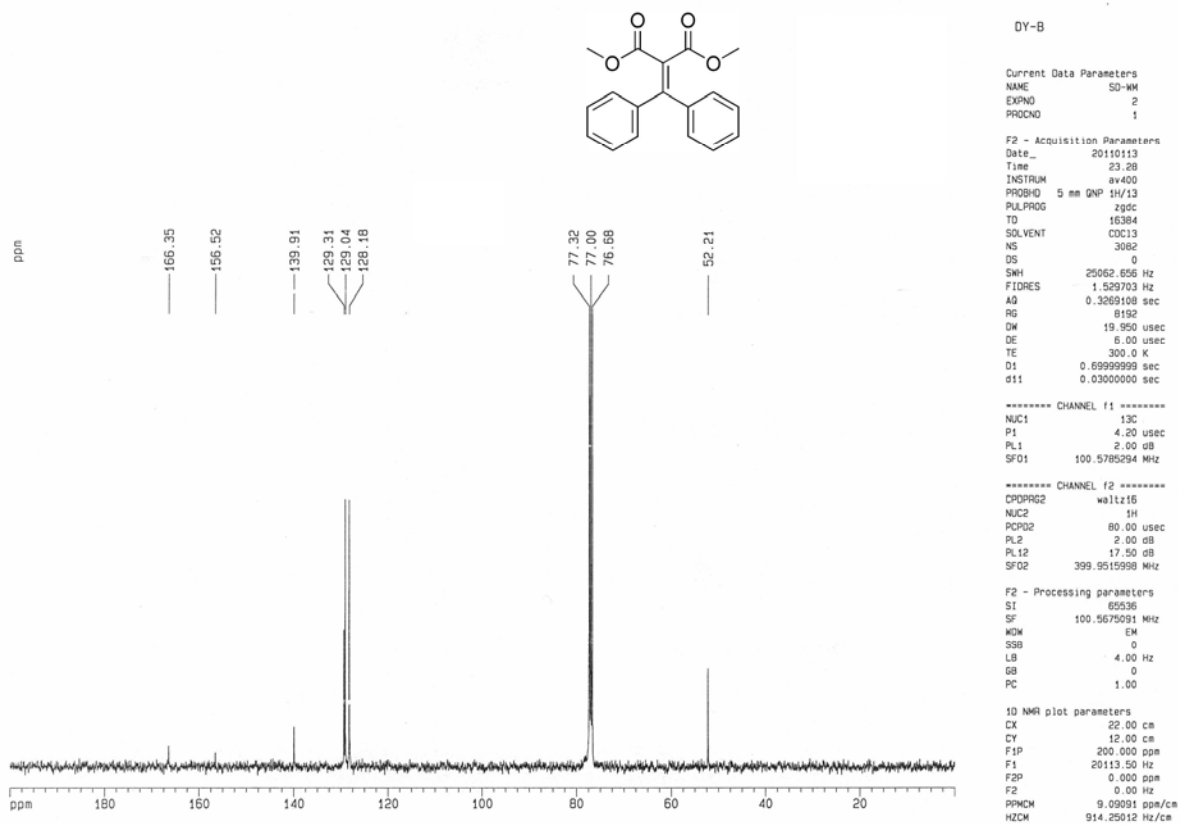
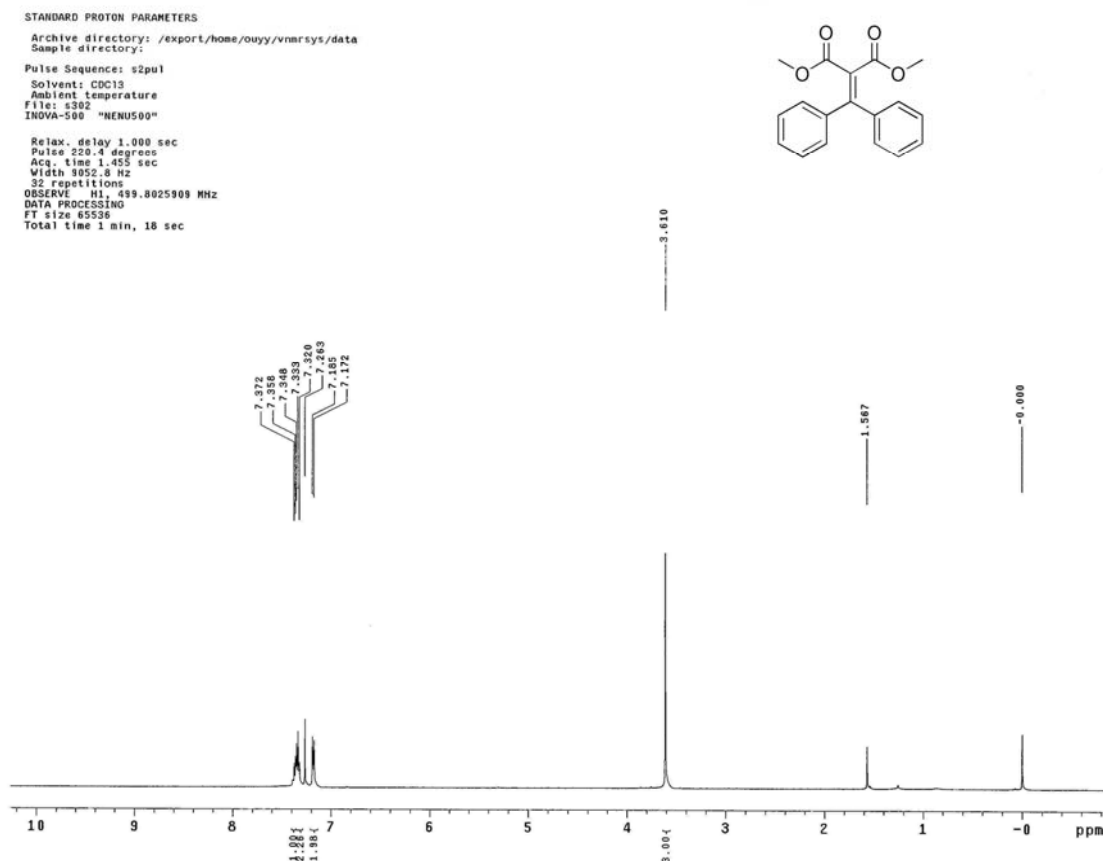
===== CHANNEL f1 =====
NUC1 13C
P1 2.70 usec
PL1 -3.00 dB
SF01 100.5785294 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 18.20 dB
SF02 399.9615998 MHz

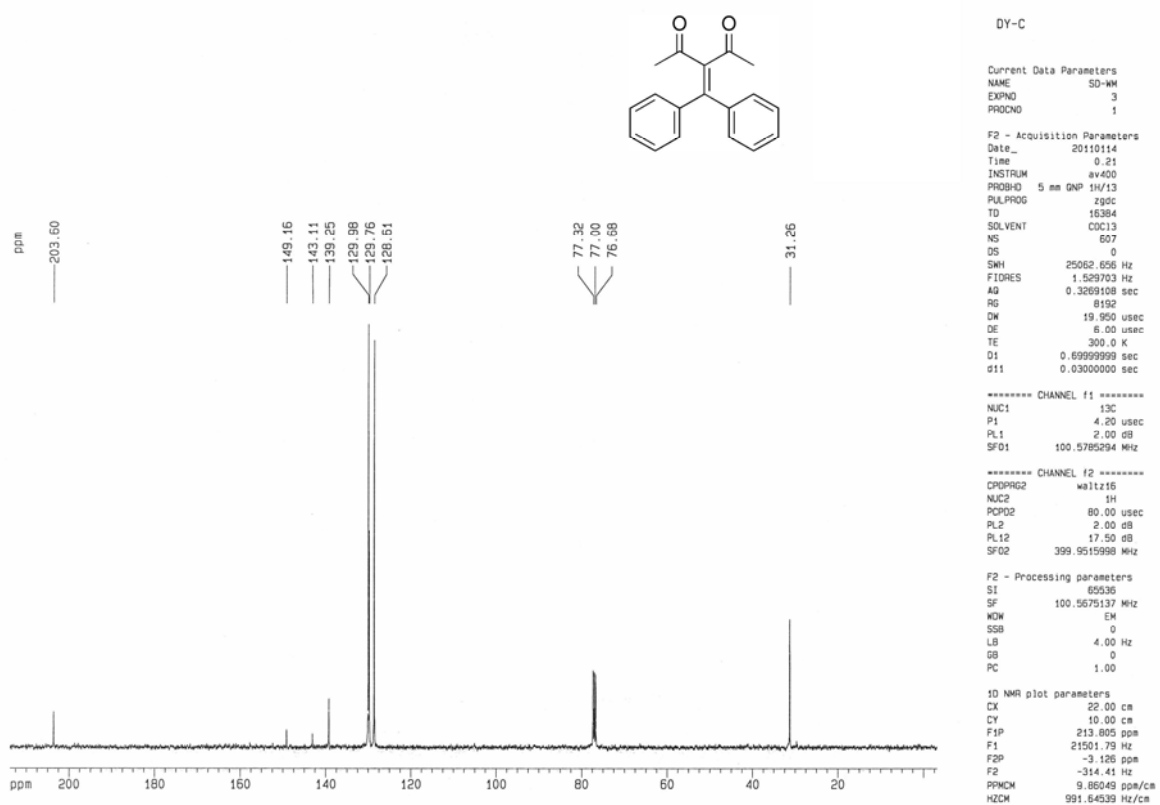
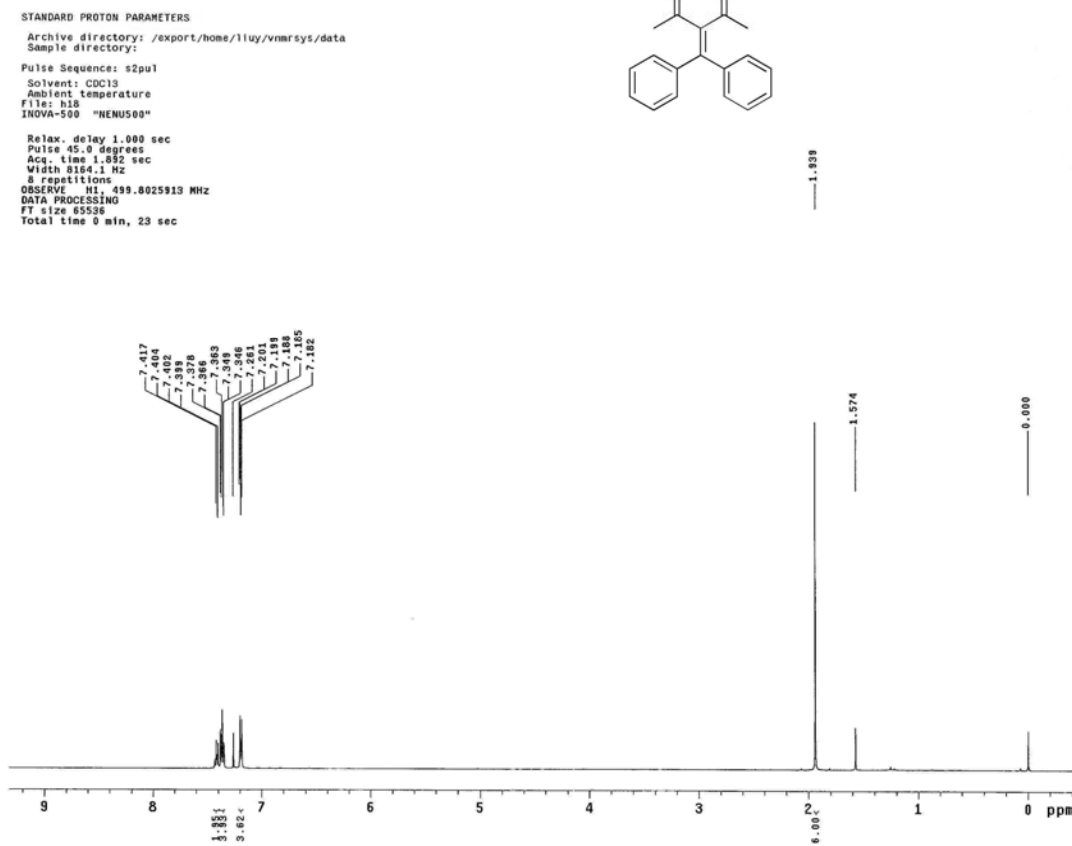
F2 - Processing parameters
SI 65536
SF 100.5675060 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 2.00

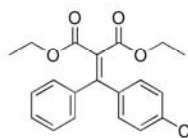
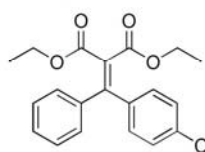
1D NMR plot parameters
CX 22.00 cm
CY 6.00 cm
F1P 200.000 ppm
F1 20113.50 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 9.09091 ppm/cm
HZCM 914.25006 Hz/cm

4b

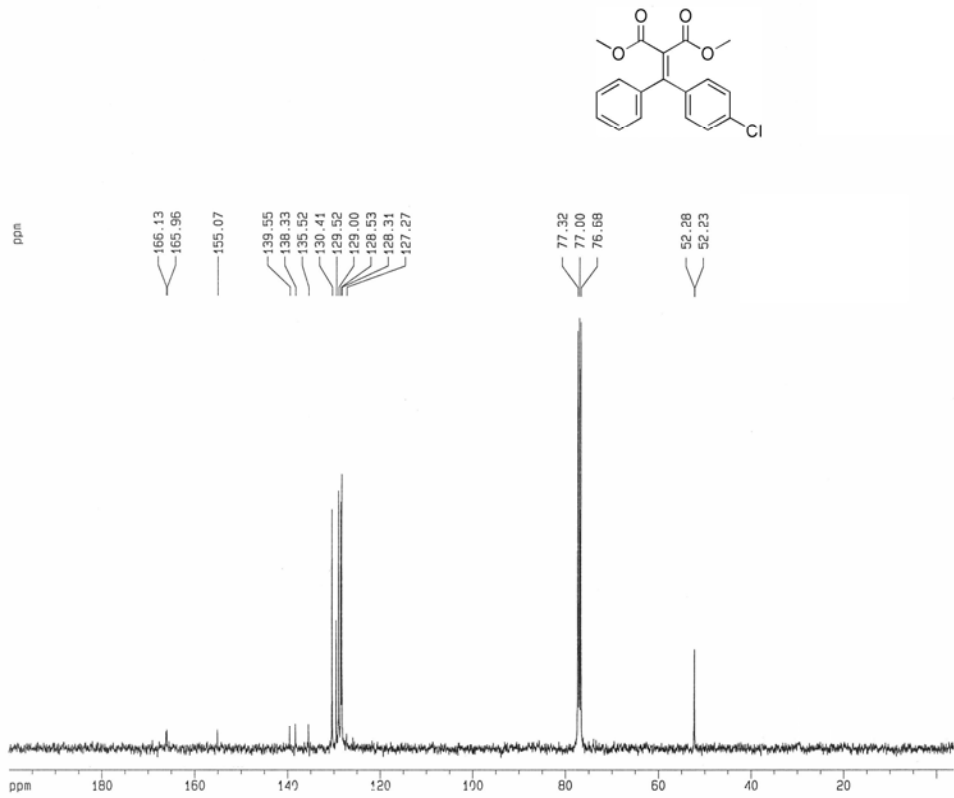
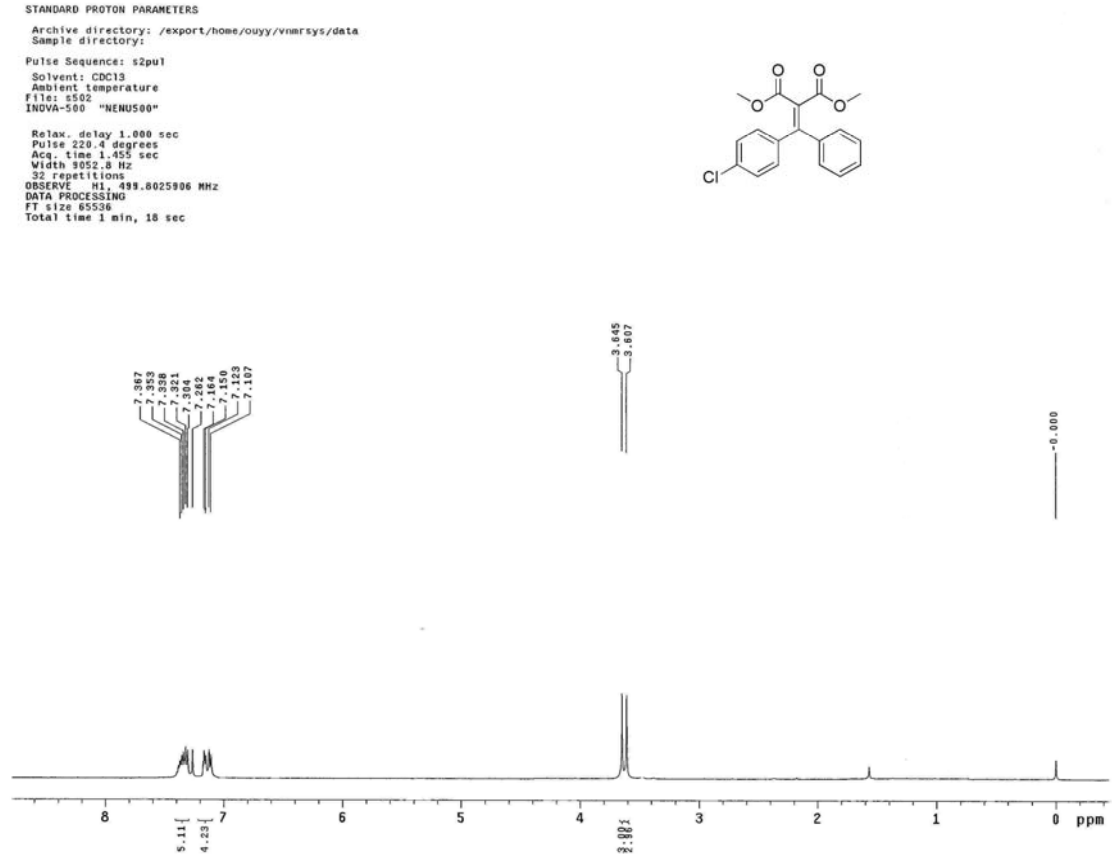


4c





4e



DY-F

Current Data Parameters

NAME SD-MM
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters

Date_ 20110117
Time 19.42
INSTRUM av400
PROBHD 5 mm QNP
PULPROG zgpg
TD 16384
SOLVENT CDCl3
DS 4012
SH 0
FIDRES 25062.656 Hz
AQ 1.529703 Hz
RG 0.3269108 sec
RG 8192
DM 19.950 usec
DE 6.00 usec
TE 303.0 K
d11 0.69999999 sec
d11 0.03000000 sec

***** CHANNEL f1 *****

NUC1 13C
P1 2.70 usec
PL1 -3.00 dB
SF01 100.5785294 MHz

***** CHANNEL f2 *****

CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 18.20 dB
SF02 399.9515998 MHz

F2 - Processing parameters

SI 65536
SF 100.5675060 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 22.00 cm
CY 10.00 cm
F1P 200.000 ppm
F1 20113.46 Hz
F2P -3.696 ppm
F2 -371.69 Hz
RPMCM 9.25889 ppm/cm
HZCM 931.14337 Hz/cm