Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Catalytic Asymmetric Formation of δ-Lactones by [4+2]-Cycloaddition of Zwitterionic Dienolates Generated from α,β-Unsaturated Acid Chlorides

Supporting Information

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Experimental

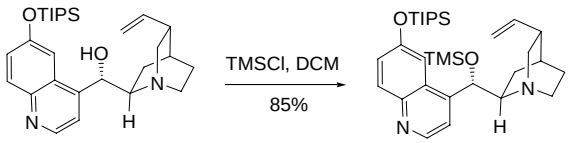
Except as otherwise indicated, all reactions were carried out in oven dried glassware under a positive pressure of nitrogen. 1,2-dimethoxyethane (Fluka, >99.5%), DMF (Fluka, >99.5%) and benzene (Fluka, >99.5%) were stored in crown-capped bottles under argon over 4Å molecular sieves. Dichloromethane, toluene, diethyl ether and THF were purified by distillation and dried by a passage over activated alumina under nitrogen atmosphere. Methanol (Fluka, HPLC grade), *n*-pentane (J.T. Baker, UV quality), *n*-hexane (Fluka, UV quality), cyclohexane (Thommen & Furler), ethyl acetate (Thommen & Furler) and triethylamine (Fluka, >99.5%) were used as purchased. N-ethyl-diisopropylamine was distilled over CaH_2. Catalyst **3a** was prepared according to literature.[1] All other laboratory chemicals were purchased from *ABCR*, *Aldrich*, *Fluka*, *J.T. Baker* or *Merck* and were used without purification. For work-up procedures and flash chromatography, distilled technical grade solvents were used. Unless otherwise indicated, all liquids were added via syringe, solids were added neat against an argon flow. Solvents were removed at a heating bath temperature of 40 °C and 600 - 30 mbar pressure by rotary evaporation. Non-volatile compounds were dried *in vacuo* at 0.01 mbar. Yields refer to purified compounds and are calculated in mol% of the used starting material. Except as otherwise indicated, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using silica gel plates from *Merck* (silica gel 60 F_{254}). Visualization occurred by fluorescence quenching under UV light and by staining with $KMnO_4$ / NaOH. Purification by flash chromatography was performed on silica gel 60 Å, 32-62, provided by *Fluka,* using a forced flow of eluent at 0.2-0.4 bar pressure. NMR-spectra were recorded on a *Varian Gemini 300* and a *Varian Mercury 300* spectrometer operating at 300 MHz (^{1}H), 75 MHz (^{13}C) or by the NMR service of the Laboratory of Organic Chemistry at ETHZ on a *Bruker DRX400* spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C). Chemical shifts δ are referred in terms of ppm and *J*-coupling constants are given in Hz. Abbreviations for multiplicity are as follows: *s* (singulet), *d* (doublet), *t* (triplet), *q* (quadruplet), *m* (multiplet), *b* (broad signal). IR-spectra were recorded on a *Perkin Elmer Spectrum One FT-IR* with a *Universal ATR Sampling Accessory* and the signals are given by wave numbers (cm^{-1}). Optical rotation was measured on a *Jasco DIP-100 digital Polarimeter* operating at the sodium D line with a 100 mm path length cell. Melting points were measured using a *Büchi 535* melting point apparatus in open glass capillaries and are uncorrected. Mass spectra were obtained from the ETH Zürich MS Service. High resolution EI mass spectra were performed on a *Micromass AutoSpec Ultima* and were calibrated with perfluorotributylamine (PFTBA) prior to data acquisition. High resolution ESI mass spectra were

performed on an *Ion Spec Ultima 2 FTICR*. ESI mass spectra were performed on a *Finnigan TSQ7000*. Combustion analysis was performed by the Mikroelementaranalytisches Laboratorium at ETH Zürich.

Activation of metal triflate salts

All metal triflate salts employed were dried using a *Büchi* Kugelrohr oven. The salts were placed in a flame dried round bottomed flask and heated to 140 °C at 0.01 mbar until weight constancy (usually overnight). The activated Lewis acids were stored and handled in a glove box.

Preparation of catalyst 3b

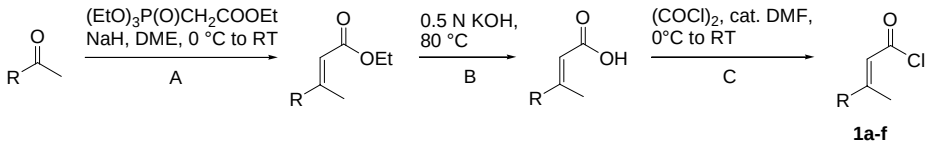


3b

To a solution of 6'-OTIPS quinidine[2] (1.00 g, 2.14 mmol) in DCM (15 mL), chlorotrimethylsilane (271 μL, 2.14 mmol) was added under nitrogen. After 24 h the reaction mixture was partitioned between DCM (10 mL) and saturated aqueous $NaHCO_3$ (20 mL) and the aqueous layer was extracted with DCM (3x5 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (ethyl acetate / MeOH / NH_3 100:1:1, R_f = 0.56) to afford the desired product as a colorless oil (0.98 g, 1.82 mmol, 85% yield).

$C_{31}H_{50}N_2O_2Si_2$, MW: 538.93 g/mol. **$[\alpha]_D^{20.7°C}$** (c = 0.97, $CHCl_3$) = +144.70. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 8.71 (*br*, 1H); 7.98 (*d*, 1H, *J* = 9.0 Hz); 7.61-7.25 (*m*, 3H); 6.04 (*m*, 1H); 5.07 (*m*, 2H); 3.30 (*br*, 1H); 3.01-2.57 (*m*, 4H); 2.21 (*m*, 1H, 2.18-1.65 (*m*, 4H); 1.55-1.45 (*m*, 2H); 1.35 (*sept*, 3H, *J* = 7.5 Hz); 1.14 (*d*, *J* = 7.5, 18H); 0.01 (*s*, 9H). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 154.2, 147.8, 147.6, 144.2, 140.8, 131.6, 126.6, 124.7, 118.6, 114.2, 109.3, 72.8, 60.6, 50.3, 49.7, 40.1, 28.2, 26.5, 20.8, 17.9, 12.7, –0.08. **IR (neat):** ν = 2943, 2866, 1750, 1616, 1501, 1458, 1250, 956, 881, 835. **HRMS (ESI) *m/z*:** Calc. for $[M+H^+]^+$: 539.3484. Found: 539.3471. **Anal. Calcd. for $C_{31}H_{50}N_2O_2Si_2$:** C, 69.09; H, 9.35. Found: C, 68.96; H, 9.19.

General procedure for the synthesis of disubstituted α,β-unsaturated acid chlorides 1a-f (GP1)



Reaction A:

To a suspension of sodium hydride (5.55 g, 138.7 mmol, 60% in mineral oil) in 1,2-dimethoxyethane (150 mL), triethylphosphonoacetate (27.8 mL, 138.7 mmol) was added dropwise under nitrogen at 0 °C. After 30 minutes the ice bath was removed and the mixture was allowed to warm to room temperature over 30 minutes. Then a solution of the corresponding alkyl or aryl methyl ketone (138.7 mmol) in 1,2-dimethoxyethane (50 mL) was added dropwise to the reaction flask. After 24 h the reaction mixture was cooled to 0 °C and diluted cautiously with water (100 mL). The mixture was extracted with diethyl ether (3x100 mL) and the combined organic phase was washed with brine (200 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes / ethyl acetate) to afford the desired product as a clear oil.

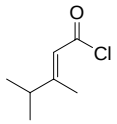
Reaction B:

The corresponding ethyl ester (70.3 mmol) was treated with 0.5 N aqueous KOH (160 mL) and the reaction mixture was stirred at 80 °C until the oil layer disappeared. The reaction mixture was cooled to 0 °C and 0.5 N aqueous H_2SO_4 solution was added (200 mL). The reaction mixture was extracted with diethyl ether (3x200 mL), then the combined organic phase was washed with brine (200 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure to afford the desired product as a white solid.

Reaction C:

The corresponding acid (43.8 mmol) was dissolved in DCM (60 mL) under nitrogen and the reaction mixture was cooled to 0 °C. Oxalyl chloride (11.5 mL, 131.4 mmol) was added dropwise followed by one drop of DMF. After 1 h the ice bath was removed and the reaction mixture was allowed to stir at rt for 17 h. The oxalyl chloride excess was removed under reduced pressure by subsequent additions of benzene and evaporation.

3,4-Dimethylpent-2-enoyl chloride (1a)

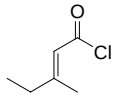


1a

3,4-Dimethylpent-2-enoyl chloride **1a** (*E*/*Z* 6.1:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1a** as a colorless oil (5.39 g, 36.8 mmol, yield: 84%).

$C_7H_{11}ClO$, **MW:** 146.61 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 6.04 (*m*, 1H, C*H*CO); 2.43 (*sept*, 1H, *J* = 6.9, C*H*$(CH_3)_2$; 2.11 (*d*, 3H, *J* = 1.2, CH_3); 1.10 (*d*, 6H, *J* = 6.9, CH(CH_3)$_2$). *Z* isomer δ: 5.97 (*m*, 1H, C*H*CO); 2.43 (*sept*, 1H, *J* = 6.9, C*H*$(CH_3)_2$); 1.87 (*d*, 3H, *J* =1.2, CH_3); 1.04 (*d*, 6H, *J* = 6.9, CH(CH_3)$_2$). The other analytical data are in accordance with literature precedence.[3]

3-Methylpent-2-enoyl chloride (1b)

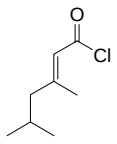


1b

3-Methylpent-2-enoyl chloride **1b** (*E*/*Z* 2.7:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1b** as a colorless oil (3.54 g, 26.7 mmol, yield: 61%).

C_6H_9ClO, **MW:** 132.59 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 6.02 (*m*, 1H, C*H*CO); 2.24 (*q*, 2H, *J* = 7.5, CH_2CH$_3$); 2.14 (*d*, 3H, *J* =1.2, CH_3); 1.11 (*t*, 3H, *J* = 7.5, CH$_2$CH_3). *Z* isomer δ: 6.02 (*m*, 1H, C*H*CO); 2.54 (*q*, 2H, *J* =7.5, CH_2CH$_3$); 1.96 (*d*, 3H, *J* = 1.2, CH_3); 1.08 (*t*, 3H, *J* = 7.5, CH$_2$CH_3). The other analytical data are in accordance with literature precedence.[4]

3,5-Dimethylhex-2-enoyl chloride (1c)

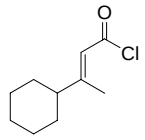


1c

3,5-Dimethylhex-2-enoyl chloride **1c** (*E*/*Z* 4.7:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1c** as a colorless oil (4.81 g, 32.9 mmol, yield: 75%).

$C_7H_{12}ClO$, **MW:** 146.61 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 6.01 (*m*, 1H, C*H*CO); 2.12 (*d*, 3H, *J* = 1.2, CH_3); 2.06 (*d*, 2H, *J* = 7.5, CH_2CH); 1.90 (m, 1H, C*H*(CH$_3$)$_2$); 0.91 (*d*, 6H, *J* = 6.5, CH(CH_3)$_2$). *Z* isomer δ: 6.08 (*m*, 1H, C*H*CO); 2.47 (*d*, 2H, *J* = 7.5, CH_2CH); 1.95 (*d*, 3H, *J* = 1.2, CH_3); 1.90 (m, 1H, C*H*(CH$_3$)$_2$); 0.92 (*d*, 6H, *J* = 6.5, CH(CH_3)$_2$). The other analytical data are in accordance with literature precedence.[5]

3-Cyclohexylbut-2-enoyl chloride (1d)

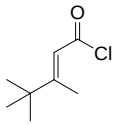


1d

3-Cyclohexylbut-2-enoyl chloride **1d** (*E*/*Z* 7.4:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1d** as a colorless oil (6.62 g, 35.5 mmol, yield: 81%).

$C_{10}H_{15}ClO$, **MW:** 186.68 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 6.02 (*m*, 1H, C*H*CO); 2.13 (*d*, 3H, *J* =1.2, CH_3); 1.78 (*m*, 6H, Cy ring); 1.27 (*m*, 5H, Cy ring). *Z* isomer δ: 5.96 (*m*, 1H, C*H*CO); 1.89 (*d*, 3H, *J* =1.2, CH_3); 1.78 (*m*, 6H, Cy ring); 1.27 (*m*, 5H, Cy ring). The other analytical data are in accordance with literature precedence.[6]

3,4,4-Trimethylpent-2-enoyl chloride (1e)

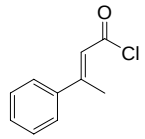


1e

3,4,4-trimethylpent-2-enoyl chloride **1e** (*E*/*Z* >99:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1e** as a colorless oil (5.49 g, 34.2 mmol, yield: 78%).

$C_8H_{13}ClO$, **MW:** 160.64 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 6.08 (*m*, 1H, C*H*CO); 2.13 (*d*, 3H, *J* =1.2, CH_3); 1.14 (*s*, 9H, C(CH_3)$_3$). The other analytical data are in accordance with literature precedence.[7]

3-Phenylbut-2-enoyl chloride (1f)

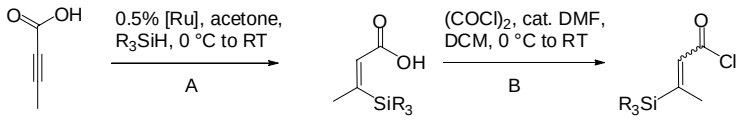


1f

3-Phenylbut-2-enoyl chloride **1f** (*E*/*Z* 12.0:1) was prepared according to GP1 and purified by Kugelrohr distillation to furnish **1f** as a colorless oil (6.80 g, 37.7 mmol, yield: 86%).

$C_{10}H_9ClO$, **MW:** 180.63 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** *E* isomer δ: 7.58-7.48 (*m*, 2H, Ph ring); 7.47-7.37 (*m*, 3H, Ph ring); 6.48 (*m*, 1H, C*H*CO); 2.57 (*d*, 3H, *J* = 1.2, CH_3). *Z* isomer δ: 7.58-7.48 (*m*, 2H, Ph ring); 7.47-7.37 (*m*, 3H, Ph ring); 6.25 (*m*, 1H, C*H*CO); 2.25 (*d*, 3H, *J* = 1.2, CH_3). The other analytical data are in accordance with literature precedence.[8]

General procedure for the synthesis of silyl-substituted but-2-enoyl acid chlorides 1g-k (GP2)



1g-k

[Ru] = [Cp*Ru(MeCN)$_3$]PF$_6$

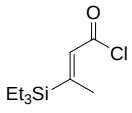
Reaction A:[9]

To a solution of [Cp*Ru(MeCN)$_3$]PF$_6$ (25.2 mg, 0.05 mmol) in acetone (5 mL), a solution of tetrolic acid (840.7 mg, 10.0 mmol) in acetone (4 mL) and a solution of the corresponding silane (12.0 mmol) in acetone (4 mL) were simultaneously added dropwise under nitrogen at 0 °C. After 2 minutes the ice bath was removed and the mixture was allowed to warm to room temperature. After 2 h the solvent was removed under reduced pressure.

Reaction B:

The crude material of reaction A was dissolved in DCM (60 mL) under nitrogen and the reaction mixture was cooled to 0 °C. Oxalyl chloride (2.6 mL, 30 mmol) was added dropwise followed by one drop of DMF. After 1 h the ice bath was removed and the reaction mixture was allowed to stir at room temperature for 17 h. The excess of oxalyl chloride was removed under reduced pressure by subsequent additions of benzene and evaporation. The residue was purified by Kugelrohr distillation to afford the desired product as a colorless oil.

3-(Triethylsilyl)but-2-enoyl chloride (1g)

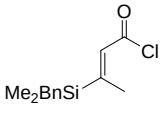


1g

3-(Triethylsilyl)but-2-enoyl chloride **1g** (mixture of geometrical isomers 1.1:1) was prepared according to GP2 and purified by Kugelrohr distillation to furnish **1g** as a colorless oil (2.06 g, 9.4 mmol, yield: 94%).

$C_{10}H_{19}ClOSi$, **MW:** 218.80 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.67 (q, *J* = 2.1, 1H, C*H*CO, major isomer); 6.30 (q, *J* = 2.1, 1H, C*H*CO, minor isomer); 2.18 (d, 3H, *J* = 2.1, CH_3, minor isomer); 2.06 (d, 3H, *J* = 2.1, CH_3, major isomer); 0.95 (*t*, 9H, Si(CH_2CH_3)$_3$, minor isomer); 0.92 (*t*, 9H, Si(CH_2CH_3)$_3$, major isomer); 0.75 (q, 6H, Si(CH_2CH_3)$_3$, minor isomer); 0.68 (q, 6H, Si(CH_2CH_3)$_3$, major isomer). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 170.1, 169.5, 164.6, 161.9, 136.6, 132.1, 27.5, 19.4, 7.4, 7.0, 2.3, 2.0. **IR (neat):** ν = 2955, 1770, 1566, 1238, 1004, 720. **Anal. Calcd. for $C_{10}H_{19}ClOSi$**: C, 54.90; H, 8.75. Found: C, 54.89; H, 8.98.

3-(Benzyldimethylsilyl)but-2-enoyl chloride (1h)

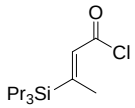


1h

3-(Benzyldimethylsilyl)but-2-enoyl chloride (**1h**) (mixture of geometrical isomers 5.1:1) was prepared according to GP2 and purified by Kugelrohr distillation to furnish **1h** as a colorless oil (2.48 g, 9.8 mmol, yield: 98%).

$C_{13}H_{17}ClOSi$, **MW:** 252.81 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 7.25-6.96 (*m*, 5H, *Ph*); 6.65 (q, *J* = 1.6, 1H, C*H*CO, minor isomer); 6.27 (q, *J* = 1.6, 1H, C*H*CO, major isomer); 2.33 (s, 2H, CH_2Ph, minor isomer); 2.22 (s, 2H, CH_2Ph, major isomer); 2.16 (d, 3H, *J* = 1.6, CH_3, major isomer); 1.90 (d, 3H, *J* =1.6, CH_3, minor isomer); 0.39 (s, 6H, Si(CH_3)$_2$, minor isomer); 0.15 (s, 6H, Si(CH_3)$_2$, major isomer). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 170.8, 169.0, 162.1, 138.1, 136.4, 131.9, 128.4, 128.2, 128.0, 124.6, 28.8, 26.9, 24.0, 19.1, -3.59, -4.75. **IR (neat):** ν = 2959, 1770, 1569, 1250, 1027, 793. **Anal. Calcd. for $C_{13}H_{17}ClOSi$**: a satisfactory microanalysis could not be obtained due to hygroscopicity.

3-(Tripropylsilyl)but-2-enoyl chloride (1i)

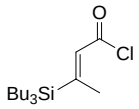


1i

3-(Tripropylsilyl)but-2-enoyl chloride **1i** (mixture of geometrical isomers 3.1:1) was prepared according to GP2, but using 0.07 mmol of [Ru] catalyst. The product was purified by Kugelrohr distillation to furnish **1i** as a colorless oil (2.40 g, 9.2 mmol, yield: 92%).

$C_{13}H_{25}ClOSi$, **MW:** 260.88 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.64 (q, *J* = 1.8, 1H, C*H*CO, major isomer); 6.29 (q, *J* = 1.8, 1H, C*H*CO, minor isomer); 2.18 (d, 3H, *J* = 1.8, CH_3, minor isomer); 2.06 (d, 3H, *J* = 1.8, CH_3, major isomer); 1.34-1.24 (m, 6H, Si(CH_2CH_2CH_3)$_3$, both isomers); 1.05-0.93 (*m*, 9H, Si(CH_2CH_2CH_3)$_3$, both isomers); 0.80-0.68 (*m*, 6H, SiCH_2CH_2CH_3)$_3$, both isomers). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 170.9, 170.4, 164.6, 161.9, 136.4, 131.8, 27.4, 19.5, 18.3, 18.3, 17.4, 17.1, 14.0, 13.6. **IR (neat):** ν = 2956, 1770, 1566, 1454, 1055, 803. **Anal. Calcd. for $C_{13}H_{25}ClOSi$**: a satisfactory microanalysis could not be obtained due to hygroscopicity.

3-(Tributylsilyl)but-2-enoyl chloride (1k)

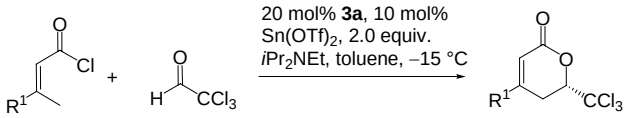


1k

3-(Tributylsilyl)but-2-enoyl chloride **1k** (mixture of geometrical isomers 1.4:1) was prepared according to GP2, but using 0.15 mmol of [Ru] catalyst. The product was purified by Kugelrohr distillation to furnish **1k** as a clear oil (2.91 g, 9.6 mmol, yield: 96%).

$C_{16}H_{31}ClOSi$, **MW:** 302.96 g/mol. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.64 (q, *J* = 1.8, 1H, C*H*CO, minor isomer); 6.29 (q, *J* = 1.8, 1H, C*H*CO, major isomer); 2.18 (d, 3H, *J* = 1.8, C*H*$_3$, major isomer); 2.06 (d, 3H, *J* = 1.8, C*H*$_3$, minor isomer); 1.40-1.12 (m, 12H, Si($CH_2CH_2CH_2CH_3$)$_3$, both isomers); 0.92-0.84 (*m*, 9H, Si($CH_2CH_2CH_2CH_3$)$_3$, both isomers); 0.80-0.62 (*m*, 6H, Si$CH_2CH_2CH_2CH_3$)$_3$, both isomers). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 170.8, 170.4, 164.6, 161.9, 136.4, 131.9, 27.5, 26.5, 26.5, 26.1, 25.7, 19.5, 13.6, 13.6, 10.9, 10.6. **IR (neat):** ν = 2956, 1770, 1567, 1464, 1055, 804. **Anal. Calcd. for $C_{16}H_{31}ClOSi$**: a satisfactory microanalysis could not be obtained due to hygroscopicity.

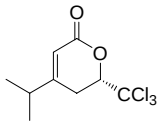
General procedure for the formation of α,β-unsaturated δ-lactones 6 (GP3)



1a-h **5a** **6a-k**

In a glove-box the reaction flask was charged with $Sn(OTf)_2$ (41.7 mg, 0.1 mmol). Subsequently toluene (3.6 mL), a solution of trimethylsilylquinidine (**3a**, 79.3 mg, 0.2 mmol) in toluene (2.4 mL) and N-ethyl-diisopropylamine (331 μL, 2.0 mmol) were successively added. After cooling to −15 °C, a solution of chloral **5a** (97 μL, 1 mmol) in toluene (2 mL) was added. After additional 10 minutes a solution of the corresponding acid chloride **1a-k** (1 mmol) in toluene (2 mL) was added over 120 minutes using a syringe pump. The reaction was allowed to stir for additional 3 h, then 1 N aqueous HCl (6 mL) was added to quench the reaction. Methyl *tert*-butyl ether (20 mL) was added and the organic phase was washed with 0.1 N aqueous HCl (2x10 mL) and with brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure.

(*S*)-4-Isopropyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6a)

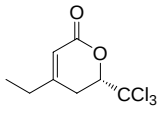


6a

(*S*)-4-Isopropyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6a**) was prepared according to GP1 and purified by flash chromatography on silica gel (hexanes / ethyl acetate 4:1, R_f = 0.39) to furnish **6a** as a white solid (200.9 mg, 0.78 mmol, yield: 78%, *ee* = 82%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25 cm, hexane / *i*PrOH 98:2, flow 1 mL / min, λ = 220 nm).

$C_9H_{11}Cl_3O_2$, MW: 257.54 g/mol. **Mp:** 56.8 – 57.9 °C. **[α]** $_D^{24.2°C}$ (c = 1.21, $CHCl_3$) = –55.4. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.88 (*m*, 1H, C*H*CO); 4.79 (*m*, 1H, C*H*CCl_3); 2.79 (*m*, 2H, CH_2); 2.53 (*sept*, 1H, *J* = 6.9, C*H*$(CH_3)_2$); 1.17 (*d*, 6H, *J* = 6.9, CH$(CH_3)_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 164.5, 162.5, 113.1, 97.7, 84.5, 34.7, 27.8, 20.2, 19.7. **IR (neat):** ν = 2970, 1727, 1639, 1242, 1082, 773. **HRMS (ESI) *m/z*:** Calc. for [M+Na] $^+$: 278.9717. Found: 278.9719. **Anal. Calcd. for $C_9H_{11}Cl_3O_2$**: C, 41.97; H, 4.30. Found: C, 41.88; H, 4.32.

(*S*)-4-Ethyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6b)



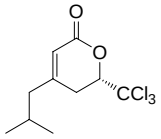
6b

(*S*)-4-Ethyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6b**) was prepared according to GP1 and purified by flash chromatography on silica gel (hexanes / ethyl acetate 4:1, R_f = 0.30) to furnish **6b** as a white solid (146.1 mg, 0.60 mmol, yield: 60%, *ee* = 54%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25 cm, hexane / *i*PrOH 98:2, flow 1 mL / min, λ = 220 nm).

$C_8H_9Cl_3O_2$, MW: 243.51 g/mol. **Mp:** 63.6 – 64.8 °C. **[α]** $_D^{21.9°C}$ (c = 1.00, $CHCl_3$) = –36.0. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.89 (*m*, 1H, C*H*CO); 4.80 (*m*, 1H, C*H*CCl_3); 2.78 (*m*, 2H, CH_2); 2.35 (*m*, 2H, CH_2CH_3); 1.17 (*t*, 3H, *J* = 7.5, CH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 162.2, 160.7, 114.0, 97.7, 84.3, 29.6, 29.6, 10.6. **IR (neat):** ν = 2978, 1723, 1640, 1241,

1064, 778. **HRMS (ESI) *m/z*:** Calc. for [M+Na] $^{+}$: 264.9560. Found: 264.9560. **Anal. Calcd. for $C_8H_9Cl_3O_2$**: C, 39.46; H, 3.73. Found: C, 39.71; H, 3.70.

(*S*)-4-Isobutyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6c)

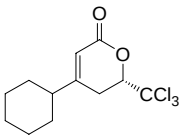


6c

(*S*)-4-Isobutyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6c**) was prepared according to GP1 but using 0.2 mmol of $Sn(OTf)_2$ and 0.4 mmol of catalyst **3b**. The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 85:15, R_f = 0.40) to furnish **6c** as a white solid (198.2 mg, 0.73 mmol, yield: 73%, *ee* = 70%). The *ee* value was determined by HPLC (Chiralcel OD-H columns 25+15 cm, hexane / *i*PrOH 98:2, flow 0.7 mL / min, λ = 220 nm).

$C_{10}H_{13}Cl_3O_2$, **MW:** 271.57 g/mol. **Mp:** 54.2 – 55.8 °C. **[α]** $^{22.4°C}_{D}$ (c = 1.00, $CHCl_3$) = –47.7. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.87 (*m*, 1H, C*H*CO); 4.81 (*m*, 1H, C*H*CCl_3); 2.76 (*m*, 2H, CH_2); 2.20 (*m*, 2H, CH_2CH$(CH_3)_2$); 1.92 (*m*, 1H, C*H*$(CH_3)_2$); 0.97 (*m*, 6H, CH(C$H_3)_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 162.0, 158.5, 116.1, 97.6, 84.4, 46.0, 29.4, 26.0, 22.5, 22.1. **IR (neat):** ν = 2944, 1725, 1643, 1237, 1072, 773. **HRMS (ESI) *m/z*:** Calc. for [M+Na] $^{+}$: 292.9873. Found: 292.9866. **Anal. Calcd. for $C_{10}H_{13}Cl_3O_2$**: C, 44.23; H, 4.82. Found: C, 44.52; H, 4.94.

(*S*)-4-Cyclohexyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6d)



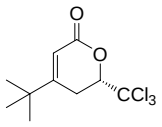
6d

(*S*)-4-Cyclohexyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6d**) was prepared according to GP1 and purified by flash chromatography on silica gel (hexanes / ethyl acetate 9:1, R_f = 0.24) to furnish **6d** as a white solid (223.2 mg, 0.75 mmol, yield: 75%, *ee* = 83%). The *ee* value

was determined by HPLC (Chiralcel OD-H column 25 cm, hexane / *i*PrOH 98:2, flow 1 mL / min, λ = 220 nm).

$C_{12}H_{15}Cl_3O_2$, MW: 297.61 g/mol. **Mp:** 57.6 – 58.6 °C. **[α]** $_D^{21.1°C}$ (c = 1.00, $CHCl_3$) = –48.6. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 5.86 (*m*, 1H, C*H*CO); 4.78 (*m*, 1H, C*H*CCl_3); 2.79 (*m*, 2H, CH_2); 2.17 (*m*, 1H, Cy ring); 1.90-1.68 (*m*, 5H, Cy ring); 1.44-1.09 (*m*, 5H, Cy ring). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 163.8, 162.6, 113.3, 97.7, 84.5, 44.7, 30.7, 30.1, 28.2, 25.9, 25.7, 25.7. **IR (neat):** ν = 2927, 1721, 1632, 1242, 1100, 777. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 319.0030. Found: 319.0029. **Anal. Calcd. for $C_{12}H_{15}Cl_3O_2$**: C, 48.43; H, 5.08. Found: C, 48.70; H, 5.08.

(*S*)-4-*tert*-Butyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6e)

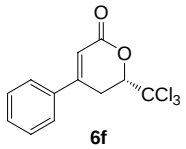


6e

(*S*)-4-*tert*-Butyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6e**) was prepared according to GP1 but using 0.2 mmol of $Sn(OTf)_2$ and 0.4 mmol of TMS-quinidine (**3a**). The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 9:1, R_f = 0.27) to furnish **6e** as a white solid (217.2 mg, 0.80 mmol, yield: 80%, *ee* = 95%). The *ee* value was determined by HPLC (Chiralcel OD-H columns 25+15 cm, hexane / *i*PrOH 98:2, flow 0.7 mL / min, λ = 220 nm).

$C_{10}H_{13}Cl_3O_2$, MW: 271.57 g/mol. **Mp:** 82.7 – 83.5 °C. **[α]** $_D^{21.4°C}$ (c = 1.00, $CHCl_3$) = –56.2 **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.93 (*d*, 1H, *J* = 2.5, C*H*CO); 4.74 (*dd*, 1H, *J* = 11.8, *J* = 3.6, C*H*CCl_3); 2.96 (*dd*, 1H, *J* = 17.1, *J* = 3.6, CH_2); 2.66 (*ddd*, 1H, *J* = 17.1, *J* = 11.8, *J* = 2.5, CH_2); 1.19 (s, 9H, (CH_3)$_3$). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 166.7, 162.7, 112.7, 97.8, 84.9, 36.7, 27.9, 26.2. **IR (neat):** ν = 2972, 1729, 1634, 1245, 1092, 771. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 292.9873. Found: 292.9872. **Anal. Calcd. for $C_{10}H_{13}Cl_3O_2$**: C, 44.23; H, 4.82. Found: C, 44.31; H, 4.75.

(*S*)-4-Phenyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6f)

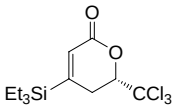


6f

(*S*)-4-Phenyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6f**) was prepared according to GP1 and purified by flash chromatography on silica gel (hexanes / ethyl acetate 85:15, R_f = 0.33) to furnish **6f** as a white solid (212.8 mg, 0.73 mmol, yield: 73%, *ee* = 81%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25 cm, hexane / *i*PrOH 95:5, flow 1 mL / min, λ = 270 nm).

$C_{12}H_9Cl_3O_2$, **MW:** 291.56 g/mol. **Mp:** 132.4 – 134.1 °C. **[α]** $_D^{20.5°C}$ (c = 1.00, $CHCl_3$) = –73.2. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 7.57 (*m*, 2H, *Ph*); 7.49 (*m*, 3H, *Ph*); 6.43 (*d*, *J* = 2.7, 1H, C*H*CO); 4.98 (*dd*, 1H, *J* = 11.8, *J* = 3.8, C*H*CCl_3); 3.39 (*dd*, 1H, *J* = 17.6, *J* = 3.8, CH_2); 3.18 (*ddd*, 1H, *J* = 17.6, *J* = 11.8, *J* = 2.5, CH_2). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 162.4, 153.3, 135.3, 131.2, 129.1, 126.0, 114.1, 97.7, 84.5, 28.0. **IR (neat):** ν = 2928, 1718, 1623, 1253, 1236, 1103, 762. **HRMS (ESI) *m/z*:** Calc. for [M+Na] $^+$: 312.9560. Found: 312.9557. **Anal. Calcd. for $C_{12}H_9Cl_3O_2$**: C, 49.43; H, 3.11. Found: C, 49.71; H, 3.19.

(*S*)-6-(Trichloromethyl)-4-(triethylsilyl)-5,6-dihydro-2*H*-pyran-2-one (6g)



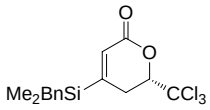
6g

(*S*)-6-(Trichloromethyl)-4-(triethylsilyl)-5,6-dihydro-2*H*-pyran-2-one (**6g**) was prepared according to GP1, but using 0.3 mmol of $Sn(OTf)_2$ and 1 mmol of TMS-quinidine (**3a**). The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 95:5, R_f = 0.32) to furnish **6g** as a colorless oil (178.1 mg, 0.54 mmol, yield: 54%, *ee* = 96%). The *ee* value was determined by HPLC (Chiralcel AD-H column 25cm, hexane / EtOH 99.5:0.5, flow 1mL / min, λ = 220 nm).

$C_{12}H_{19}Cl_3O_2Si$, **MW:** 329.73 g/mol. **[α]** $_D^{20.5°C}$ (c = 1.16, $CHCl_3$) = –61.7. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.25 (*d*, *J* = 2.7, 1H, C*H*CO); 4.76 (*dd*, 1H, *J* = 11.8, *J* = 4.4, C*H*CCl_3); 2.92 (*dd*, 1H, *J* = 17.9, *J* = 4.4, CH_2); 2.64 (*ddd*, 1H, *J* = 17.9, *J* = 11.8, *J* = 2.7, CH_2); 0.98 (*t*, 9H, *J* =

8.0, CH_3); 0.73 (*q*, 6H, *J* = 8.0, SiCH_2). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 160.3, 159.4, 127.3, 97.5, 84.9, 28.2, 7.06, 1.8. **IR (neat):** ν = 2955, 1731, 1238, 1089, 1013, 774. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 351.0112. Found: 351.0114. **Anal. Calcd. for $C_{12}H_{19}Cl_3O_2Si$**: C, 43.71; H, 5.81. Found: C, 44.15; H, 5.80.

(*S*)-4-(Benzyldimethylsilyl)-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6h)

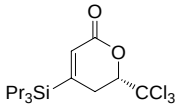


6h

(*S*)-4-(Benzyldimethylsilyl)-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6h**) was prepared according to GP1, but using 0.3 mmol of $Sn(OTf)_2$ and 1 mmol of TMS-quinidine (**3a**). The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 9:1, R_f = 0.30) to furnish **6h** as a colorless oil (170.8 mg, 0.47 mmol, yield: 47%, *ee* = 92%). The *ee* value was determined by HPLC (Chiralcel OD-H columns 25 cm, hexane / *i*PrOH 99:1, flow 1mL / min, λ = 220 nm).

$C_{15}H_{17}Cl_3O_2Si$, MW: 363.75 g/mol. **$[\alpha]_D^{21.2°C}$** (c = 0.83, $CHCl_3$) = –64.1. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 7.24 (*m*, 2H, *Ph*); 7.11 (*m*, 1H, *Ph*); 6.98 (*m*, 2H, *Ph*); 6.22 (*d*, 1H, *J* = 2.8, C*H*CO); 4.59 (*dd*, 1H, *J* = 11.8, *J* = 3.9, C*H*CCl$_3$); 2.62 (*dd*, 1H, *J* = 17.9, *J* = 3.9, CH_2); 2.46 (*ddd*, 1H, *J* = 17.9, *J* = 11.8, *J* =2.8, CH_2); 2.26 (*s*, 2H, CH_2Ph); 0.26 (*s*, 3H, Si(CH_3)$_2$); 0.23 (*s*, 3H, Si(CH_3)$_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 160.2, 159.7, 137.7, 128.6, 127.8, 127.0, 125.0, 97.4, 84.8, 27.9, 24.3, –4.6, –4.9. **IR (film):** ν = 2928, 1728, 1493, 1240, 1088, 831, 772. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 384.9956. Found: 384.9945. **Anal. Calcd. for $C_{15}H_{17}Cl_3O_2$**: C, 49.53; H, 4.71. Found: C, 49.82; H, 4.75.

(*S*)-6-(Trichloromethyl)-4-(tripropylsilyl)-5,6-dihydro-2*H*-pyran-2-one (6i)

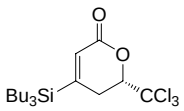


6i

(*S*)-6-(trichloromethyl)-4-(tripropylsilyl)-5,6-dihydro-2*H*-pyran-2-one (**6i**) was prepared according to GP1 but using 0.3 mmol of $Sn(OTf)_2$ and 1 mmol of TMS-quinidine (**3a**). The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 95:5, R_f = 0.33) to furnish **6i** as a colorless oil (189.6 mg, 0.51 mmol, yield: 51%, *ee* = 97%). The *ee* value was determined by HPLC (Chiralcel OD-H columns 25+15cm, hexane / *i*PrOH 99:1, flow 0.6mL / min, λ = 220 nm).

$C_{15}H_{25}Cl_3O_2Si$, **MW:** 371.81 g/mol. **$[\alpha]_D^{21.0°C}$** (c = 0.95, $CHCl_3$) = –58.5. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.24 (*d*, *J* = 2.8, 1H, C*H*CO); 4.75 (*dd*, 1H, *J* = 11.8, *J* = 3.7, C*H*CCl_3); 2.92 (*dd*, 1H, *J* = 17.7, *J* = 3.7, CH_2); 2.62 (*ddd*, 1H, *J* = 17.7, *J* = 11.8, *J* = 2.8, CH_2); 1.34 (*m*, 6H, $SiCH_2CH_2CH_3$); 0.99 (*t*, 9H, *J* = 7.2, CH_3); 0.71 (*m*, 6H, SiCH_2). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 160.3, 160.2, 127.1, 97.5, 85.0, 28.2, 18.2, 17.1, 13.5. **IR (neat):** ν = 2959, 1729, 1639, 1238, 1086, 775. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 393.0582. Found: 393.0576. **Anal. Calcd. for $C_{15}H_{25}C_3O_2Si$**: a satisfactory microanalysis could not be obtained due to solvent inclusion.

(*S*)-4-(Tributylsilyl)-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (6k)



6k

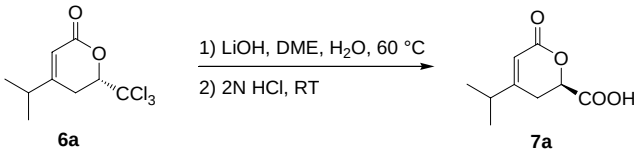
(*S*)-4-(Tributylsilyl)-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**6k**) was prepared according to GP1, but using 0.3 mmol of $Sn(OTf)_2$ and 1 mmol of TMS-quinidine (**3a**). The product was purified by flash chromatography on silica gel (hexanes / ethyl acetate 95:5, R_f = 0.38) to furnish **6k** as a colorless oil (252.5 mg, 0.61 mmol, yield: 61%, *ee* = 97%). The *ee* value was determined by HPLC (Chiralcel OD-H columns 25+15cm, hexane / *i*PrOH 99.8:0.2, flow 0.6 mL / min, λ = 220 nm).

$C_{18}H_{31}Cl_3O_2Si$, **MW:** 413.89 g/mol. **$[\alpha]_D^{21.6°C}$** (c = 1.015, $CHCl_3$) = –50.9. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 6.24 (*d*, *J* = 2.8, 1H, C*H*CO); 4.75 (*dd*, 1H, *J* = 11.8, *J* = 3.4, C*H*CCl_3); 2.92 (*dd*, 1H, *J* = 17.7, *J* = 3.4, CH_2); 2.62 (*ddd*, 1H, *J* = 17.7, *J* = 11.8, *J* = 2.8, CH_2); 1.32 (*m*, 12H, $SiCH_2CH_2CH_2CH_3$); 0.90 (*t*, 9H, *J* = 7.2, CH_3); 0.70 (*m*, 6H, SiCH_2). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 160.4, 160.2, 127.1, 97.6, 85.0, 28.2, 26.4, 25.7, 13.6, 10.4. **IR (neat):** ν = 2956, 1733, 1237, 1088, 1012, 774. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 435.1051. Found:

435.1054. **Anal. Calcd. for $C_{18}H_{31}Cl_3O_2Si$**: a satisfactory microanalysis could not be obtained due to solvent inclusion.

Modifications of the trichloromethyl group

(*R*)-4-Isopropyl-6-oxo-3,6-dihydro-2*H*-pyran-2-carboxylic acid (7a)

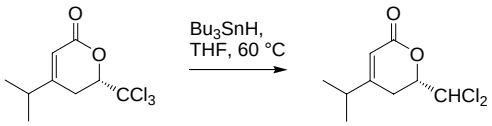


6a **7a**

To a solution of lactone **6a** (128.8 mg, 0.5 mmol) in DME (4.0 mL) water was added (2 mL) followed by 1N aqueous LiOH (2.5 mL, 2.5 mmol) and the reaction mixture was warmed up to 60 °C. After 17 h the mixture was cooled down to room temperature and 2N aqueous HCl was added till acidic. The reaction was allowed to stir for 3 h, then methyl *tert*-butyl ether (5 mL) was added and the organic phase was washed with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. Flash column chromatography on silica gel (DCM / MeOH / acetic acid 9:1:0.1, R_f = 0.35) furnished pure carboxylic acid **7a** as a colorless oil (57.1 mg, 0.31 mmol, yield: 62%, *ee* = 79%). The *ee* value was determined by HPLC (Chiralcel AD-H column 25 cm, 0.1% TFA in hexane / 0.1% TFA in *i*PrOH 93:7, flow 1 mL / min, λ = 220 nm).

$C_9H_{12}O_4$, **MW:** 184.19 g/mol. **$[\alpha]_D^{23.3°C}$** (c = 0.905, $CHCl_3$) = +22.2. **^{1}H NMR (300 MHz, $(CD_3)_2SO$, 21 °C):** δ = 5.61 (*m*, 1H, C*H*CO); 4.73 (*m*, 1H, C*H*COOH); 2.65 (*m*, 2H, CH_2), 2.39 (*sept*, 1H, *J* = 6.6, C*H*(CH_3)$_2$); 1.02 (*d*, 6H, *J* = 6.6, CH(CH_3)$_2$). **^{13}C NMR (75 MHz, $(CD_3)_2SO$, 21 °C):** δ = 172.0, 163.9, 163.9, 113.3, 75.0, 33.6, 28.6, 19.9, 19.7. **IR (neat):** ν = 3406, 2965, 1699, 1590, 1247, 1086, 864. **HRMS (EI) *m/z*:** Calc. for $[M+Na]^+$: 207.0628. Found: 207.0630. **Anal. Calcd. for $C_9H_{12}O_4$**: a satisfactory microanalysis could not be obtained due to hygroscopicity.

(*S*)-6-(Dichloromethyl)-4-(isopropyl)-5,6-dihydro-2*H*-pyran-2-one (8a)

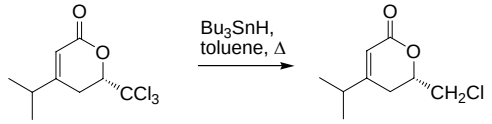


6a **8a**

To a solution of lactone **6a** (128.8 mg, 0.5 mmol) in THF (5 mL) under nitrogen tributyltin hydride (398 μL, 1.5 mmol) was added at room temperature. The reaction mixture was then warmed up to 60 °C. After 17 h the mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in MeCN and washed with hexane (6x5 mL) to remove all tin compounds. Flash column chromatography on silica (cyclohexane / ethylacetate 8:2, R_f = 0.28) furnished pure dichloro lactone **8a** as a colorless oil (98.2 mg, 0.44 mmol, yield: 88%, *ee* = 82%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25cm, hexane / *i*PrOH 98:2, flow 1mL / min, λ = 220 nm).

$C_9H_{12}Cl_2O_2$, **MW:** 223.10 g/mol. **$[\alpha]_D^{23.6°C}$** (c = 0.84, $CHCl_3$) = –98.1. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.91 (*d*, 1H, *J* = 3.8, C*H*Cl_2); 5.84 (*m*, 1H, C*H*CO); 4.68 (*m*, 1H, C*H*$CHCl_2$); 2.74 (*ddd*, 1H, *J* = 17.6, *J* = 11.3, *J* = 1.9, CH_2); 2.55 (*dd*, 1H, *J* = 17.6, *J* = 4.4, CH_2); 2.53 (*sept*, 1H, *J* = 6.9, C*H*$(CH_3)_2$); 1.16 (*d*, 6H, *J* = 6.9, CH$(CH_3)_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 165.3, 163.0, 113.2, 79.2, 71.1, 34.8, 25.7, 20.2, 19.7. **IR (neat):** ν = 3070, 1718, 1622, 1374, 1253, 1235, 1102, 763. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 245.0107. Found: 245.0103. **Anal. Calcd. for $C_9H_{12}Cl_2O_2$**: C, 48.45; H, 5.42. Found: C, 48.69; H, 5.48.

(*S*)-6-(Chloromethyl)-4-(isopropyl)-5,6-dihydro-2*H*-pyran-2-one (9a)



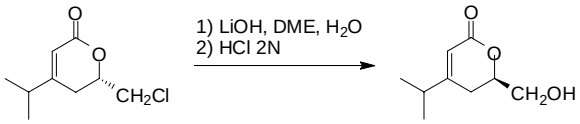
6a **9a**

To a solution of lactone **6a** (128.8 mg, 0.5 mmol) in toluene (5 mL) under nitrogen tributyltin hydride (795 μL, 3 mmol) was added at room temperature. The reaction mixture was then heated to reflux. After 17 h the mixture was cooled to room temperature and the solvent was removed *in vacuo*. The residue was dissolved in MeCN and washed with hexane (6x5 mL) to remove all tin compounds. Flash column chromatography on silica gel (cyclohexane / ethylacetate 7:3, R_f = 0.28) furnished pure monochloro lactone **9a** as a colorless oil (83.9 mg, 0.45 mmol, yield: 89%,

ee = 82%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25cm, hexane / *i*PrOH 98:2, flow 1mL / min, λ = 220 nm).

$C_9H_{13}ClO_2$, MW: 188.66 g/mol. **$[\alpha]_D^{20.2°C}$** (c = 0.805, $CHCl_3$) = –103.8. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.81 (*m*, 1H, C*H*CO); 4.56 (*m*, 1H, C*H*CH_2Cl); 3.72 (*m*, 2H, CH_2Cl), 2.49 (*m*, 3H, CH_2 + C*H*$(CH_3)_2$); 1.13 (*d*, 6H, *J* = 6.9, CH(CH_3)$_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 165.4, 164.1, 113.3, 75.8, 44.5, 34.6, 28.7, 20.2, 19.7. **IR (neat):** ν = 2962, 1755, 1704, 1226, 1065, 776. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 211.0496. Found: 211.0494. **Anal. Calcd. for $C_9H_{13}ClO_2$**: C, 57.30; H, 6.95. Found: C, 57.40; H, 6.91.

(*R*)-6-(Hydroxymethyl)-4-(isopropyl)-5,6-dihydro-2*H*-pyran-2-one (10a)

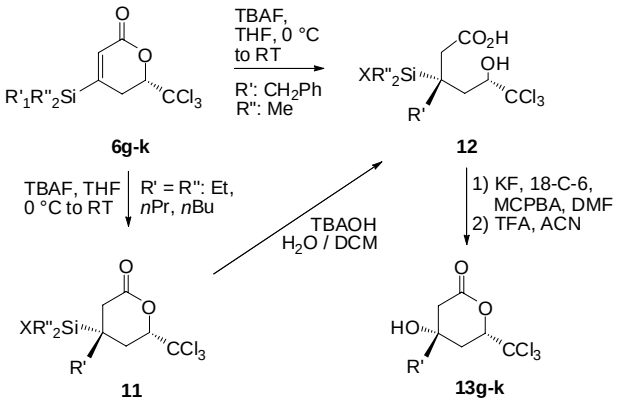


9a **10a**

To a solution of monochloro lactone **9a** (56.6 mg, 0.30 mmol) in DME (3 mL) water was added (1 mL). 1N aqueous LiOH (0.9 mL, 0.9 mmol) was added. After 17 h 2N aqueous HCl was added till acidic. The reaction was allowed to stir for 3 h, then methyl *tert*-butyl ether (5 mL) was added and the organic phase was washed with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. Flash column chromatography on silica (DCM / MeOH 20:1, R_f = 0.46) furnished pure hydroxymethyl lactone **10a** as a colorless oil (35.7 mg, 0.21 mmol, yield: 71%, *ee* = 82%). The *ee* value was determined by HPLC (Chiralcel OD-H column 25cm, hexane / *i*PrOH 95:5, flow 1mL / min, λ = 220 nm). For the determination of the absolute configuration see S28.

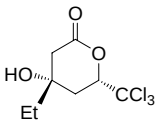
$C_9H_{14}O_3$, MW: 170.21 g/mol. **$[\alpha]_D^{22.4°C}$** (c = 0.635, $CHCl_3$) = +106.1. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 5.80 (*m*, 1H, C*H*CO); 4.45 (*m*, 1H, C*H*CH_2OH); 3.89 (*dd*, 1H, *J* = 12.1, *J* = 3.0, CH_2OH); 3.74 (*dd*, 1H, *J* = 12.1, *J* = 4.4, CH_2OH); 2.58 (*ddd*, 1H, *J* = 17.6, *J* = 12.6, *J* = 2.2, CH_2); 2.48 (*sept*, 1H, *J* = 6.6, C*H*$(CH_3)_2$); 2.30 (*br*, 1H, OH); 2.20 (*dd*, 1H, *J* = 17.6, *J* = 3.8, CH_2); 1.12 (*d*, 6H, *J* = 6.6, CH(CH_3)$_2$). **^{13}C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 166.5, 165.1, 113.0, 77.8, 63.8, 34.7, 27.3, 20.2, 19.7. **IR (neat):** ν = 3476, 2971, 1737, 1417, 1260, 1095, 766. **HRMS (ESI) *m/z*:** Calc. for [M+Na]$^+$: 193.0835. Found: 193.0833. **Anal. Calcd. for $C_9H_{14}O_3$**: C, 63.51; H, 8.29. Found: C, 63.13; H, 8.29.

General procedure for the synthesis of β-hydroxy-δ-lactones 13 (GP4)



To a solution of the corresponding δ-lactone **6g-k** (0.5 mmol) in THF (10 mL), TBAF (1M solution in THF, 1 mL, 1 mmol) was added dropwise at 0 °C. The reaction was monitored by TLC. After disappearance of the starting material the reaction mixture was diluted with saturated aqueous KH_2PO_4 (10 mL) to adjust pH 6. The mixture was extracted with MTBE (2x10 mL) and the combined organic phase was washed with saturated aqueous KH_2PO_4 (5 mL) and brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. Crude **11** was dissolved in DCM (5 mL), then water (5 mL) and TBAOH (1.62 mL, 2.5 mmol, 40% solution in water) were added. After 19h the reaction mixture was diluted with saturated aqueous KH_2PO_4 (10 mL) to adjust pH 6. The mixture was extracted with MTBE (2x10 mL) and the combined organic phase was washed with saturated aqueous KH_2PO_4 (5 mL) and brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure.
Crude **12** was dissolved in DMF (2.5 mL) under nitrogen. KF (58.1 mg, 1 mmol), 18-crown-6 (264.3 mg, 1 mmol) and MCPBA (271.2 mg, 1.1 mmol, 70% MCPBA / 30% water) were subsequently added to the reaction mixture. After 19h the mixture was diluted with saturated aqueous KH_2PO_4 (10 mL) to adjust pH 6. The mixture was extracted with MTBE (2x10 mL) and the combined organic phase was washed with saturated aqueous KH_2PO_4 (5 mL) and brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure.
The crude material was dissolved in acetonitrile (3 mL), then TFA (2 mL, 17.54 mmol) was added. After 17 h the solvent and TFA were removed under reduced pressure.

(4*S*,6*S*)-4-Ethyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (13g)

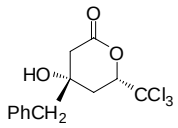


13g

(4*S*,6*S*)-4-ethyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (**13g**) was prepared according to GP1 (reaction with TBAF was complete after 30 min at 0 °C) and purified by flash chromatography on silica gel (hexanes / ethyl acetate 65:35, R_f = 0.29) to furnish **13g** as a colorless oil (41.8 mg, 0.16 mmol, overall yield: 31%, *dr* = >99 : 1). The *dr* value was determined by ^{1}H-NMR.

$C_8H_{11}Cl_3O_3$, MW: 261.53 g/mol. **$[\alpha]_D^{23.7°C}$** (c = 0.655, $CHCl_3$) = +21.5. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 4.68 (*dd*, 1H, *J* = 11.3, *J* = 4.7, C*H*CCl_3); δ = 2.72 (*dd*, 1H, *J* = 16.2, *J* = 1.1, C*H*$_2$CO); δ = 2.63 (*d*, 1H, *J* = 16.2, C*H*$_2$CO); 2.58 (*ddd*, 1H, *J* = 14.0, *J* = 4.7, *J* = 1.4, C*H*$_2$); 2.12 (*dd*, 1H, *J* = 14.0, *J* = 11.3, C*H*$_2$); 1.85 (*br*, 1H, OH); 1.70 (q, 2H, *J* = 7.4, C*H*$_2$$CH_3$); 1.00 (t, 3H, *J* = 7.4, CH_2C*H*$_3$). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 167.9, 98.2, 83.9, 70.3, 42.8, 36.6, 33.4, 7.2. **IR (neat):** ν = 3475, 2923, 1737, 1417, 1260, 1184, 766. **HRMS (ESI) *m/z*:** Calc. for [M+Na] $^+$: 282.9666. Found: 282.9662. **Anal. Calcd. for $C_8H_{11}Cl_3O_3$**: a satisfactory microanalysis could not be obtained due to solvent inclusion.

(4*S*,6*S*)-4-Benzyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (13h)



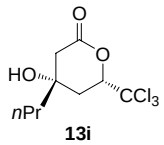
13h

(4*S*,6*S*)-4-Benzyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (**13h**) was prepared according to GP1 (reaction with TBAF was complete after 1 h 30 min at 0 °C and 1 h 30 min at rt), but without the TBAOH promoted hydrolysis step. The final product was purified by flash

chromatography on silica gel (hexanes / ethyl acetate 7:3, R_f = 0.33) to furnish **6a** as a white solid (135.9 mg, 0.42 mmol, overall yield: 78%, *dr* = 25:1). The *dr* value was determined by ^{1}H-NMR.

$C_{13}H_{13}Cl_3O_3$, MW: 323.61 g/mol. **Mp:** 85.2 – 86.3 °C. **$[\alpha]_D^{22.8°C}$** (c = 0.94, $CHCl_3$) = +6.3. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ: 7.37 (*m*, 3H, Ph ring); 7.22 (*m*, 2H, Ph ring); 5.08 (*m*, 1H, C*H*CCl_3, minor diastereomer); δ = 4.79 (*dd*, 1H, *J* = 11.0, *J* = 4.9, C*H*CCl_3, major diastereomer); δ = 2.94 (*app s*, 2H, CH_2CO); 2.75 (*dd*, 1H, *J* = 16.5, *J* = 1.4, CH_2Ph); 2.60 (*d*, 1H, *J* = 16.5, CH_2Ph); 2.60 (*ddd*, 1H, *J* = 14.0, *J* = 4.9, *J* = 1.4, CH_2); 2.16 (*dd*, 1H, *J* = 14.0, *J* = 11.0, CH_2); 2.03 (*br*, 1H, OH). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 167.6, 134.0, 130.2, 129.1, 127.8, 98.3, 83.8, 69.8, 46.3, 42.4, 36.9. **IR (neat):** ν = 3471, 2937, 1757, 1232, 1091, 772. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 344.9822. Found: 344.9817. **Anal. Calcd. for $C_{13}H_{13}Cl_3O_3$**: C, 48.25; H, 4.05. Found: C, 48.17; H, 3.99.

(4*S*,6*S*)-4-Hydroxy-4-propyl-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (13i)



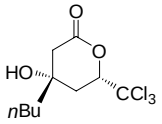
13i

(4*S*,6*S*)-4-Hydroxy-4-propyl-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (**13i**) was prepared according to GP1 (reaction with TBAF was complete after 2 h 30 min at 0 °C) and purified by flash chromatography on silica gel (hexanes / ethyl acetate 65:35, R_f = 0.32) to furnish **13i** as a colorless oil (34.4 mg, 0.125 mmol, overall yield: 25%, *dr* = >99:1). The *dr* value was determined by ^{1}H-NMR.

$C_9H_{13}Cl_3O_3$, MW: 275.56 g/mol. **$[\alpha]_D^{22.0°C}$** (c = 0.923, $CHCl_3$) = +19.5. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 4.67 (*dd*, 1H, *J* = 11.2, *J* = 4.7, C*H*CCl_3); 2.73 (*dd*, 1H, *J* = 16.2, *J* = 0.9, CH_2CO); 2.63 (*d*, 1H, *J* = 16.2, CH_2CO); 2.60 (*ddd*, 1H, *J* = 14.0, *J* = 4.7, *J* = 1.6, CH_2); 2.12 (*dd*, 1H, *J* = 14.0, *J* = 11.2, CH_2); 1.87 (*br*, 1H, OH); 1.64 (m, 2H, C$H_2$$CH_2CH_3$); 1.47 (m, 2H, CH_2CH_2CH_3); 1.00 (*t*, 3H, *J* = 7.5, CH_2CH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 167.9, 98.2, 83.9, 70.2, 43.1, 42.9, 37.1, 16.3, 14.1. **IR (neat):** ν = 3441, 2963, 1749, 1693, 1225,

1088, 776. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 296.9822. Found: 296.9822. **Anal. Calcd. for $C_9H_{13}Cl_3O_3$**: a satisfactory microanalysis could not be obtained due to solvent inclusion.

(4*S*,6*S*)-4-Butyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (13k)

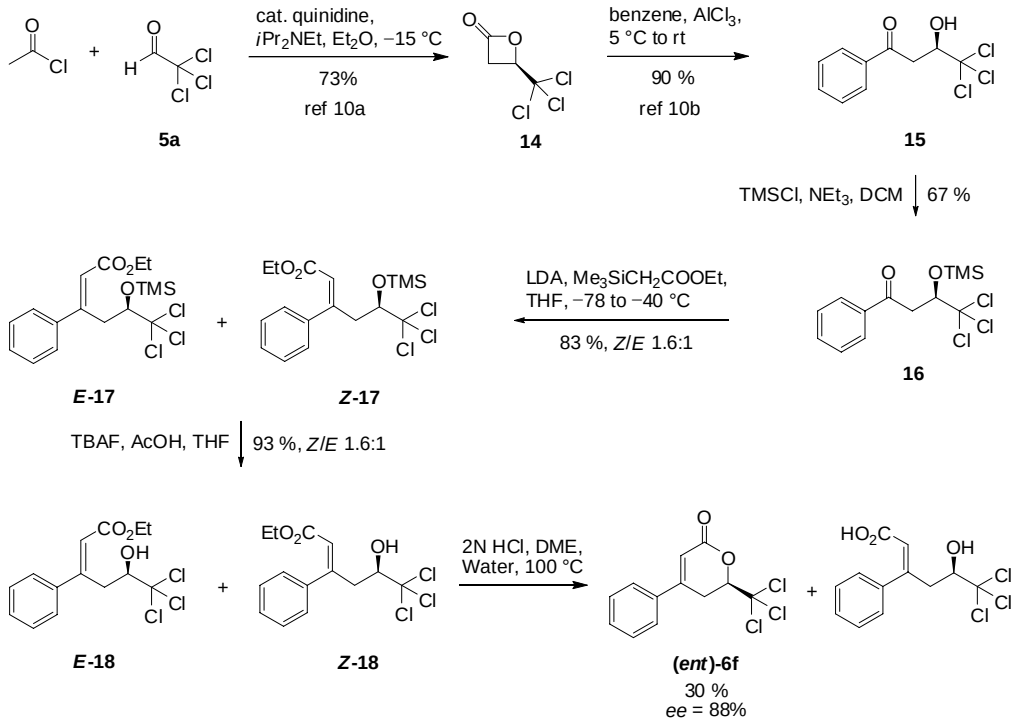


13k

(4*S*,6*S*)-4-Butyl-4-hydroxy-6-(trichloromethyl)tetrahydro-2*H*-pyran-2-one (**13k**) was prepared according to GP1 (reaction with TBAF was complete after 3 h 30 min at 0 °C and additional 1 h at rt) and purified by flash chromatography on silica gel (hexanes / ethyl acetate 65:35, R_f = 0.37) to furnish **13k** as a colorless oil (36.2 mg, 0.125 mmol, overall yield: 25%, *dr* = >99:1). The *dr* value was determined by ^{1}H-NMR.

$C_{10}H_{15}Cl_3O_3$, MW: 289.59 g/mol. **$[\alpha]_D^{22.8°C}$** (c = 1.44, $CHCl_3$) = +17.5. **^{1}H NMR (300 MHz, $CDCl_3$, 22 °C):** δ = 4.68 (*dd*, 1H, *J* = 11.3, *J* = 4.9, C*H*CCl_3); 2.73 (*dd*, 1H, *J* =16.2, *J* =1.1, CH_2CO); 2.63 (*d*, 1H, *J* = 16.2, CH_2CO); 2.58 (*ddd*, 1H, *J* = 14.1, *J* = 4.9, *J* = 1.1, CH_2); 2.12 (*dd*, 1H, *J* = 14.1, *J* = 11.3, CH_2); 2.00 (*br*, 1H, OH); 1.65 (*m*, 2H, C$H_2$$CH_2CH_2CH_3$); 1.40 (*m*, 4H, CH_2CH_2C$H_2$$CH_3$); 0.95 (*m*, 3H, CH_2CH_2CH_3). **^{13}C NMR (75 MHz, $CDCl_3$, 22 °C):** δ = 168.1, 98.2, 83.9, 70.1, 43.1, 40.4, 37.0, 25.0, 22.7, 13.9. **IR (neat):** ν = 3441, 2963, 1749, 1693, 1225, 1088, 776. **IR (neat):** ν = 3442, 2959, 1748, 1224, 1090, 775. **HRMS (ESI) *m/z*:** Calc. for $[M+Na]^+$: 310.9979. Found: 310.9974. **Anal. Calcd. for $C_{10}H_{15}Cl_3O_3$**: a satisfactory microanalysis could not be obtained due to solvent inclusion.

Determination of the absolute configuration: synthesis of enantiomerically enriched (*R*)-4-phenyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (*ent*-6f)



To a solution of (*R*)-4,4,4-trichloro-3-hydroxy-1-phenylbutan-1-one[10a,b] **15** (802.5 mg, 3 mmol) in DCM (2 mL) chlorotrimethylsilane (417 μL, 3.3 mmol) and triethylamine (459 μL, 3.3 mmol) were added. After 4 h 0.1 N aqueous HCl was added (5 mL) and the organic phase was washed with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes / ethyl acetate 98:2, R_f = 0.27) to afford **16** as a colorless oil (684 mg, 2.01 mmol, 67 % yield).

To a solution of diisopropylamine (247 μL, 1.89 mmol) in THF (5 mL) *n*BuLi (1.18 mL, 1.89 mmol, 1.6 M in hexane) was added dropwise at –78 °C. The reaction mixture was stirred for 15 minutes, then ethyl(trimethylsilyl)acetate (348 μL, 1.89 mmol) was added dropwise. After 15 minutes a solution of compound **16** (493 mg, 1.45 mmol) in THF (6 mL) was added to the reaction flask by syringe pump over 30 minutes. The reaction mixture was allowed to warm up to –40 °C over 3 h, then saturated aqueous NH_4Cl was added (10 mL) to quench the reaction. The reaction mixture was extracted with MTBE (2x10 mL) and the combined organic extracts

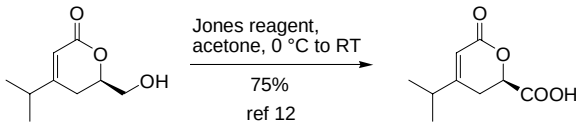
were washed with brine (10 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes / ethyl acetate 95:5, R_f = 0.29+0.52) to afford **17** as a colorless oil (643 mg, 1.57 mmol, 83 % yield, *Z*/*E* 1.6:1).

To a solution of compound **17** (50 mg, 0.12 mmol) in THF (1.5 mL) acetic acid (14 μL, 0.24 mmol) was added. The reaction mixture was then cooled to 0 °C and TBAF (183 μl, 0.183 mmol, 1M solution in THF) was added. After 1h the ice bath was removed and the reaction mixture was allowed to stir at room temperature. After 3 h saturated aqueous NH_4Cl was added (5 mL) to quench the reaction. The mixture was extracted with MTBE (5 mL) and the organic phase was washed with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure to provide **18** as a colorless oil (37.7 mg, 0.11 mmol, 93 % yield, *Z*/*E* 1.6:1).

To a solution of compound **18** (10 mg, 0.03 mmol) in DME (1 mL) 2N aqueous HCl (1 mL, 2.0 mmol) was added and the reaction mixture was heated to 100 °C. After 17 h the mixture was cooled to room temperature and MTBE was added (5 mL) and the organic phase was washed with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes / ethyl acetate 85:15, R_f = 0.33) to afford **(*ent*)-6f** as a white solid (2.6 mg, 0.009 mmol, 30 % yield).

The configuration of **(*ent*)-6f** was assigned as *R* according to literature precedence for the formation of 4-trichloromethyl)oxetan-2-one **14**[11] and assuming that no epimerisation occurred in the next synthetic steps. (*R*)-4-phenyl-6-(trichloromethyl)-5,6-dihydro-2*H*-pyran-2-one (**(*ent*)-6f)** obtained by the depicted synthesis showed to be identical to compound **6f** obtained by GP3 except for the configuration of the stereocenter, as determined by chiral HPLC analysis (Chiralcel OD-H column 25 cm, hexane / *i*PrOH 95:5, flow 1 mL / min, λ = 220 nm).

Determination of the absolute configuration of compound 10a: conversion to 7a



10a **7a**

To a solution of (*R*)-6-(hydroxymethyl)-4-(isopropyl)-5,6-dihydro-2H-pyran-2-one **10a** (8.0 mg, 0,047 mmol) in acetone (1.3 mL) at 0 °C, Jones reagent (CrO_3 in 8 N aqueous H_2SO_4, 53 μL, 0.14 mmol) was added. After 30 min the ice bath was removed and the reaction mixture was allowed to stir at room temperature for 1 h. Isopropanol (500 μL) was added in order to quench the reaction, then MTBE (5 mL) was added. The organic phase was washed with 0.1 N aqueous HCl (5 mL) and with brine (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (DCM / MeOH / acetic acid 9:1:0.1, R_f = 0.35) to afford **7a** as a colorless oil (6.5 mg, 0.035 mmol, 75 % yield).

(*R*)-4-Isopropyl-6-oxo-3,6-dihydro-2*H*-pyran-2-carboxylic acid (**7a**) obtained by the depicted reaction showed to be identical to compound **7a** obtained by hydrolysis of compound **6a** (S19) including HPLC retention times (Chiralcel AD-H column 25 cm, 0.1% TFA in hexane / 0.1% TFA in *i*PrOH 93:7, flow 1 mL / min, λ = 220 nm).

References

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[10] Preparation of compound **14**: a) B. G. Jackson, *Patent* CH 681302A5; Preparation of compound **15**: b) T. Fujisawa, T. Ito, K. Fujimoto, M. Shimizu, H. Wynberg, E.G. J. Staring, *Tetrahedron Lett.* **1997**, 38, 1593.

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LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:32:35 USER:rtisen GROUP:peters SAMPLE:PTiPr1HFP

STANDARD 1H OBSERVE

Sample directory: PTiPr1HFP

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Ambient temperature
User: rtisen
File: PTiPr1HFP
INOVA-500 "nmroc"

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Pulse 30.2 degrees
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DATA PROCESSING
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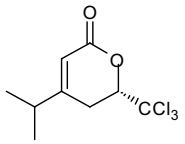
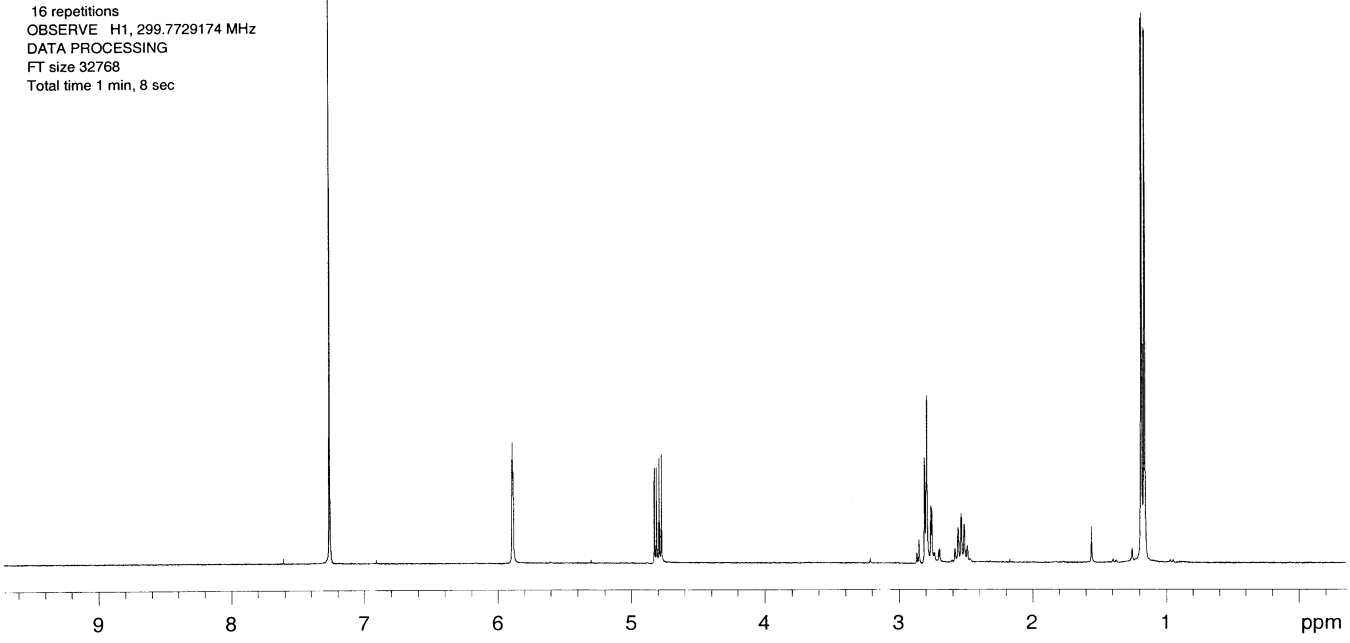
Total time 1 min, 8 sec



6a



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13C OBSERVE

Sample directory: pt2-566C13FP

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Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT2-566C13FP
INOVA-500 "nmroc"

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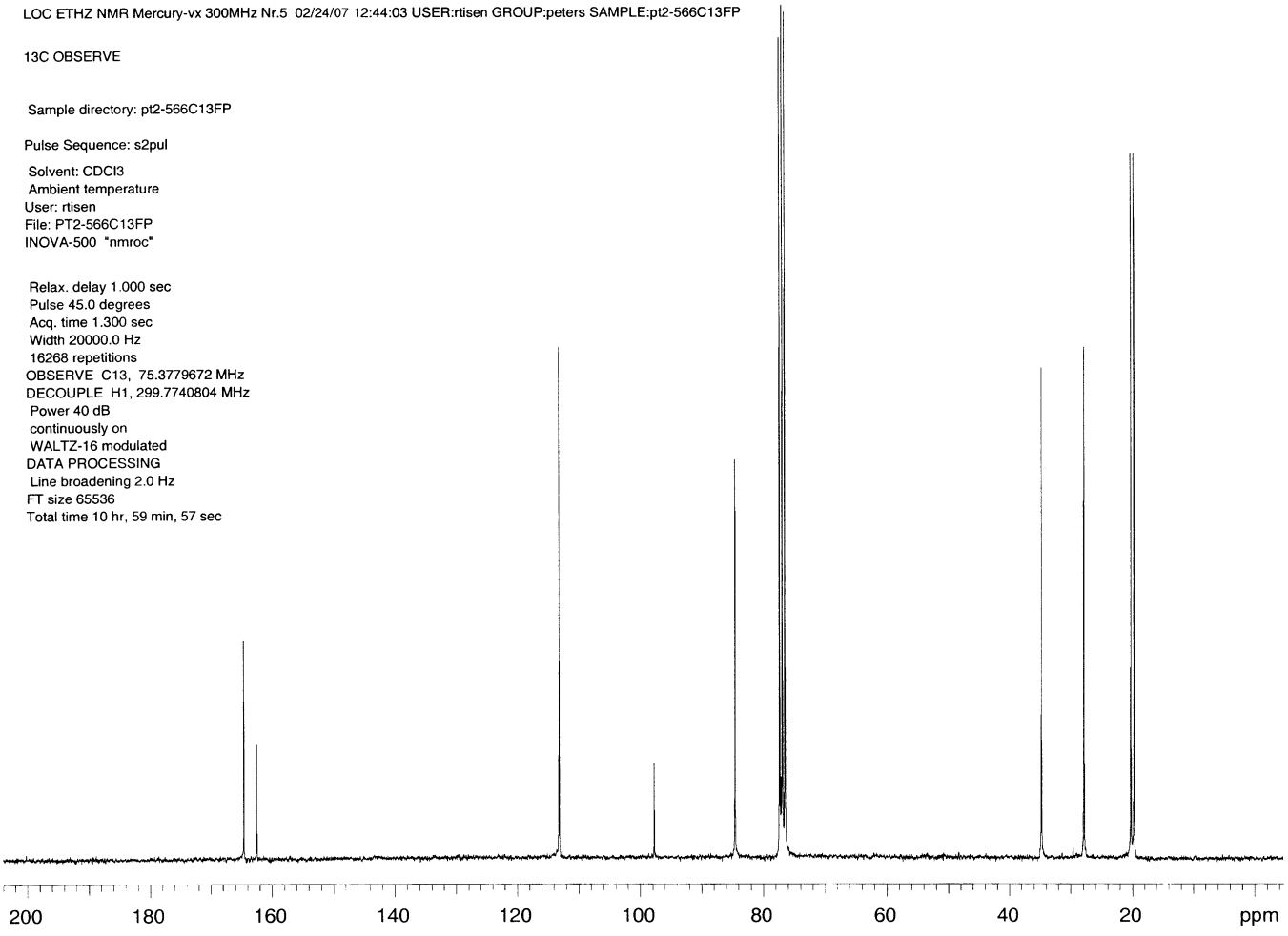
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



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STANDARD 1H OBSERVE

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Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTEt1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
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Width 4500.5 Hz
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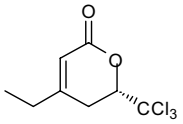
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



6b

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:57:11 USER:rtisen GROUP:peters SAMPLE:PTEtchloralFP

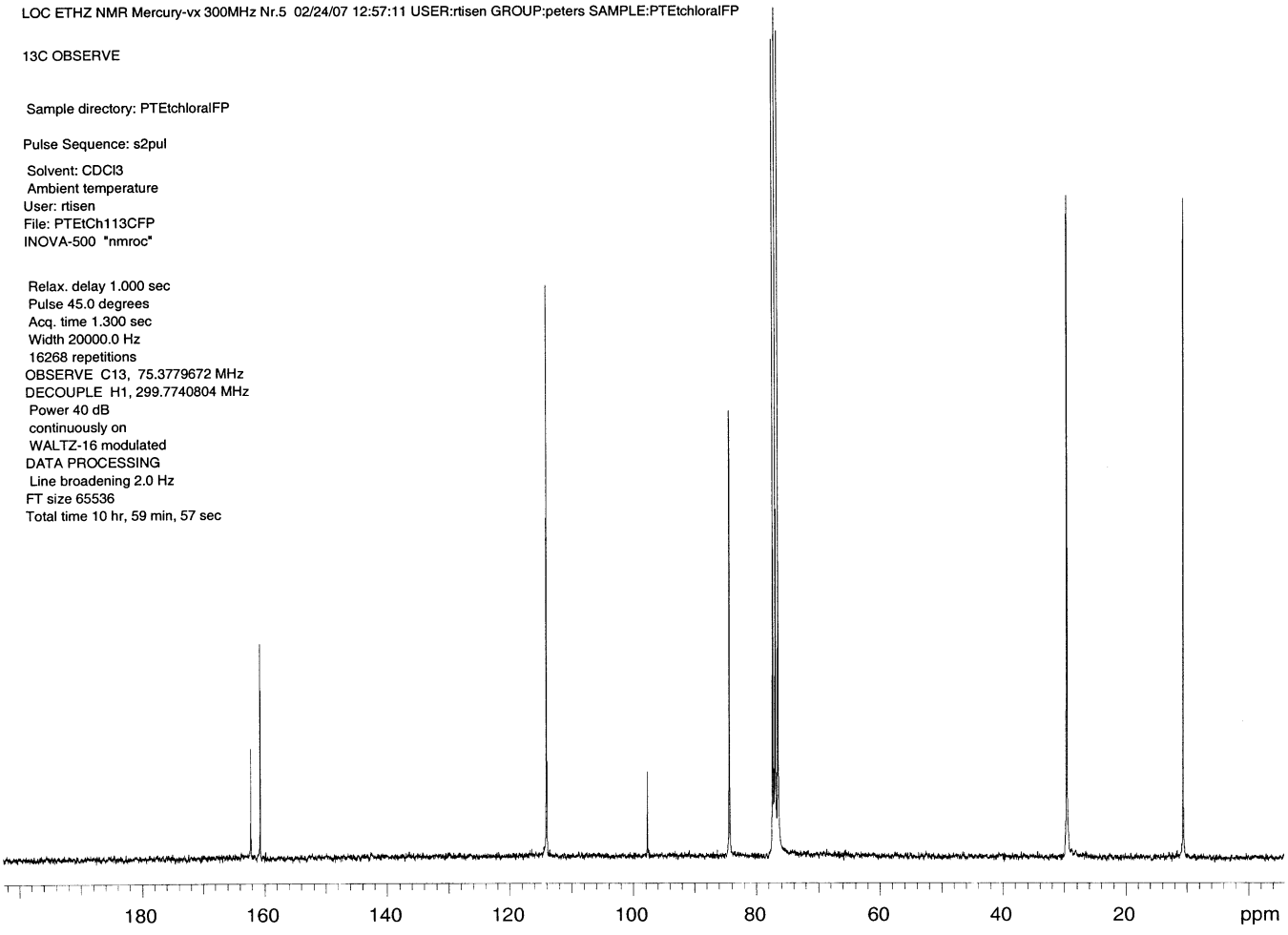
13C OBSERVE

Sample directory: PTEtchloralFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTEtCh113CFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



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STANDARD 1H OBSERVE

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Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: iBuChlFP
INOVA-500 "nmroc"

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Width 5099.4 Hz
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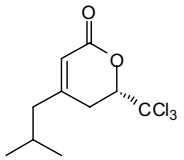
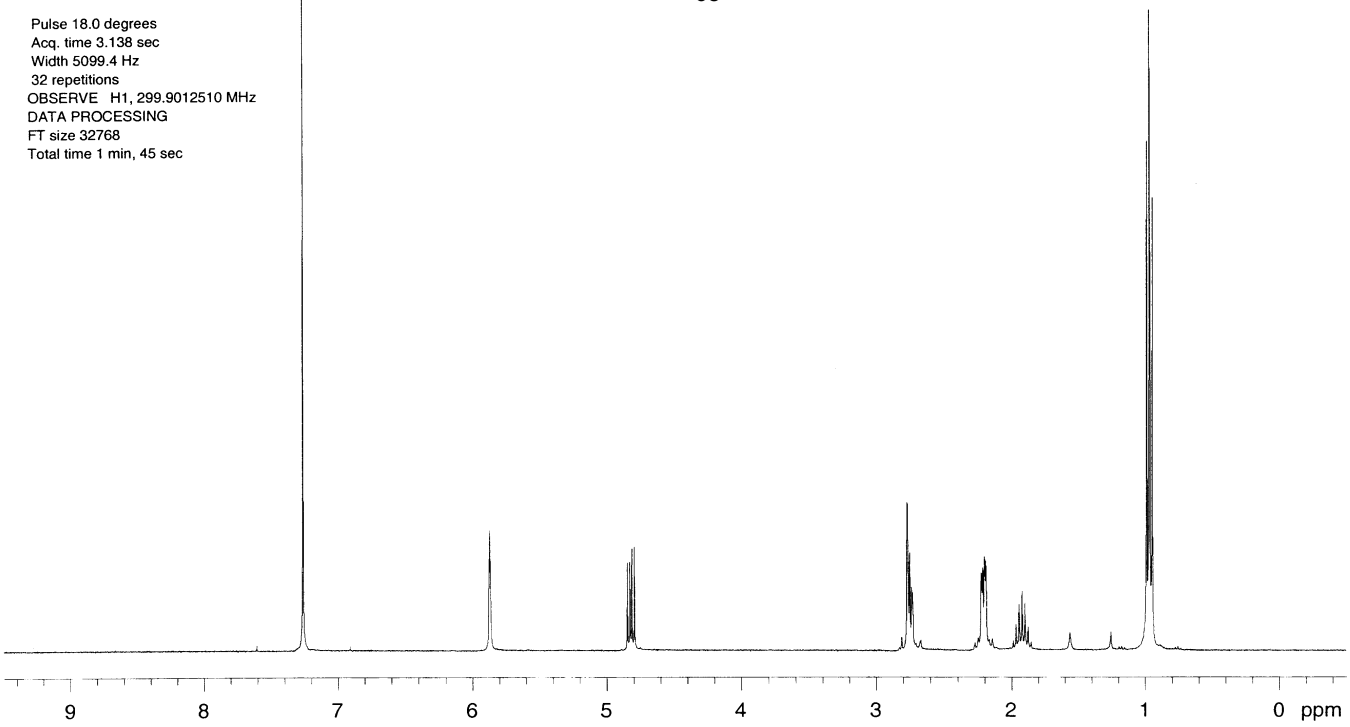
Total time 1 min, 45 sec



6c



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13C OBSERVE

Sample directory: pt2-570C13

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT2-57013C
INOVA-500 "nmroc"

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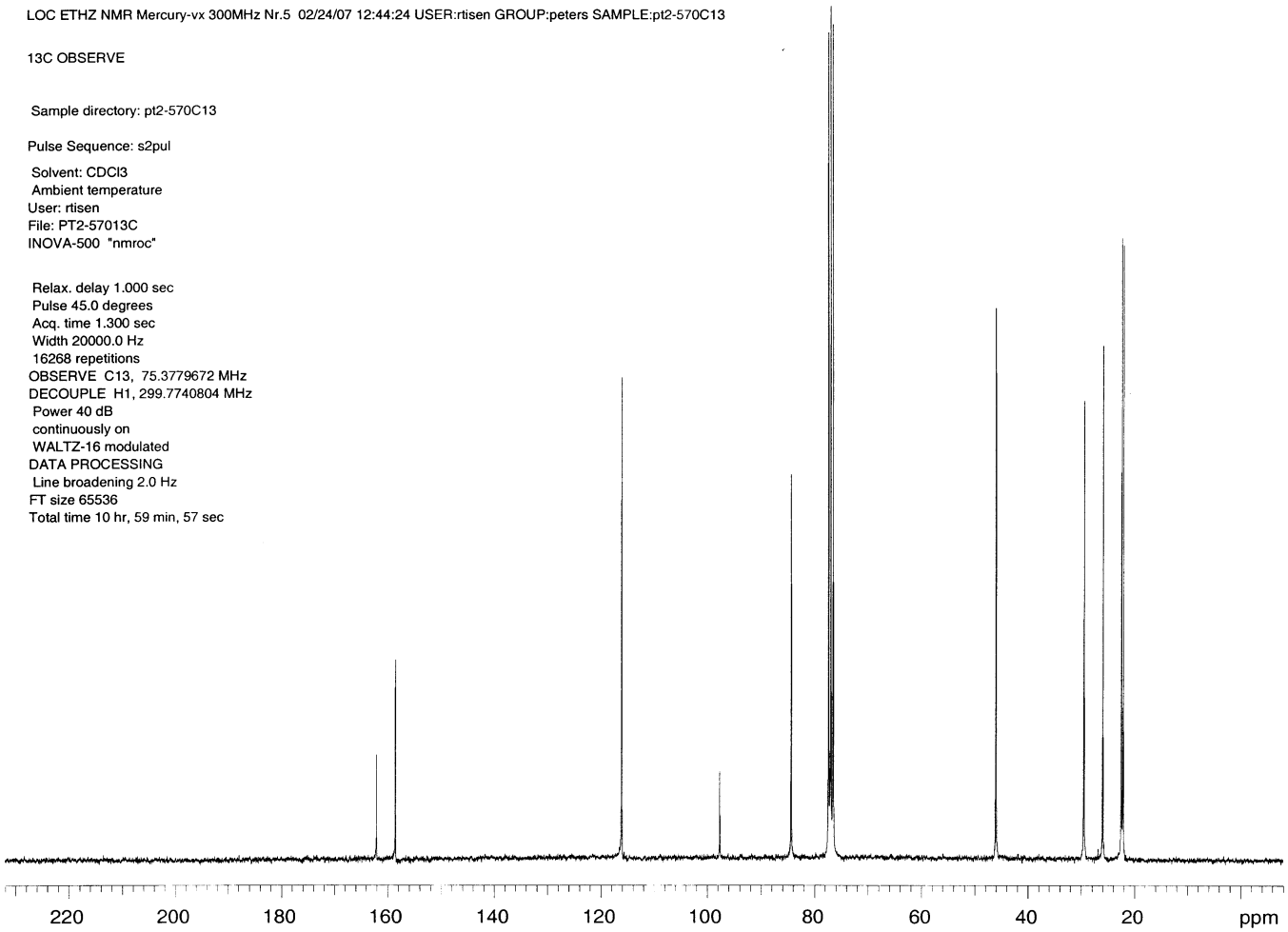
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:25:12 USER:rtisen GROUP:peters SAMPLE:PTCy1HFP

STANDARD 1H OBSERVE

Sample directory: PTCy1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTCy1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
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16 repetitions
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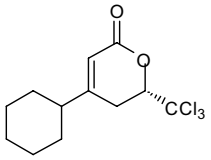
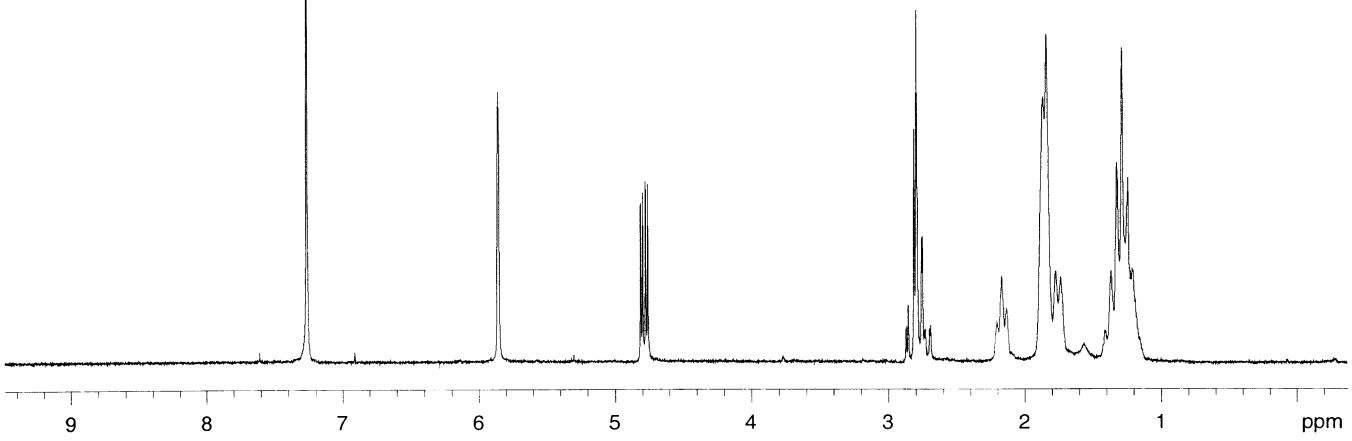
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



6d



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13C OBSERVE

Sample directory: pt3-517C13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
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INOVA-500 "nmroc"

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DECOUPLE H1, 299.7740804 MHz
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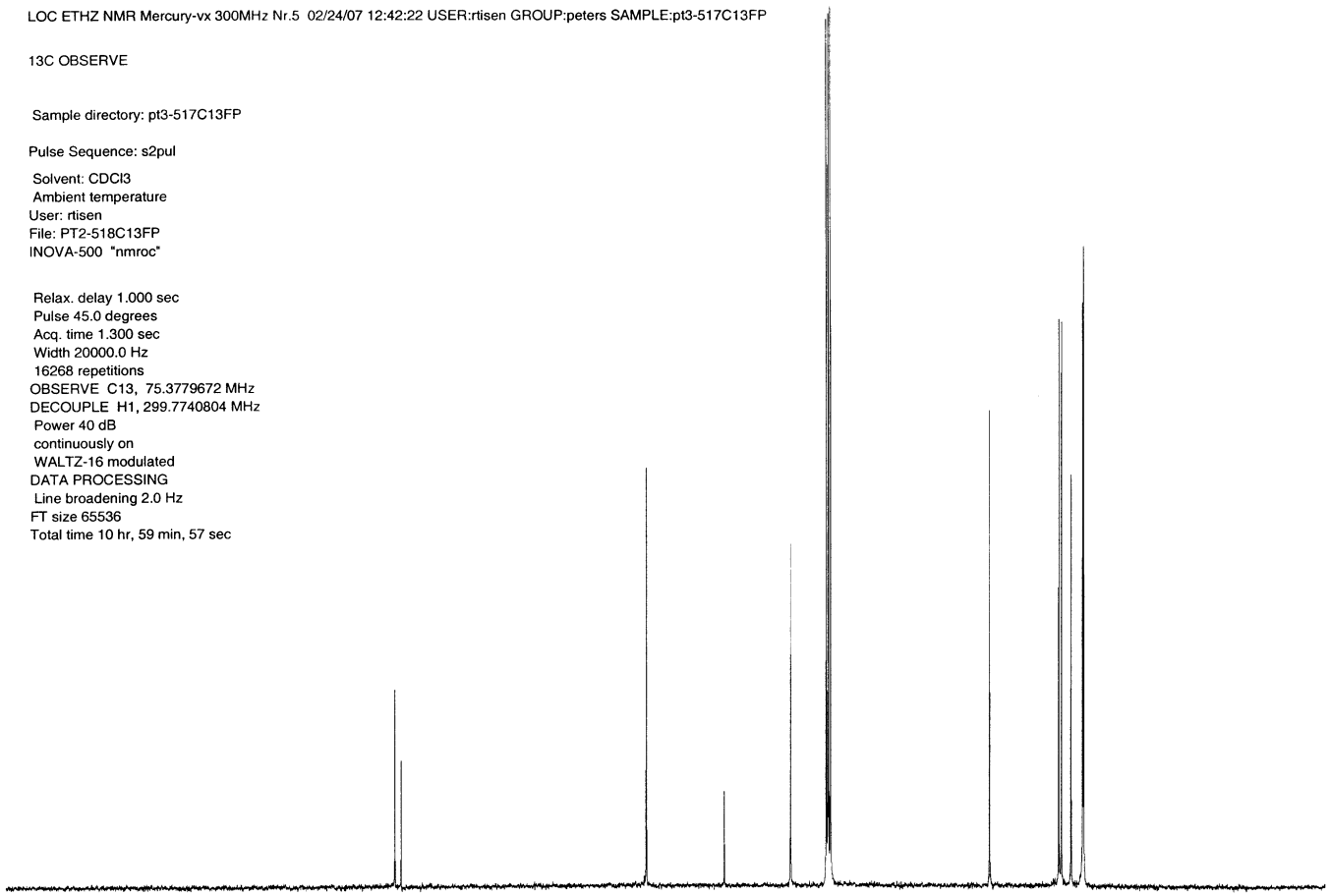

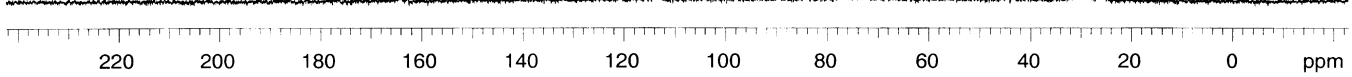

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STANDARD 1H OBSERVE

Sample directory: PTtBu1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTtBu1HFP
INOVA-500 "nmroc"

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Pulse 30.2 degrees
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Width 4500.5 Hz
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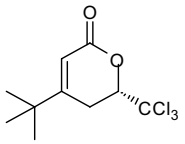
Total time 1 min, 8 sec



6e

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13C OBSERVE

Sample directory: PT2-548_13C_FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT2-517tBu13CFP
INOVA-500 "nmroc"

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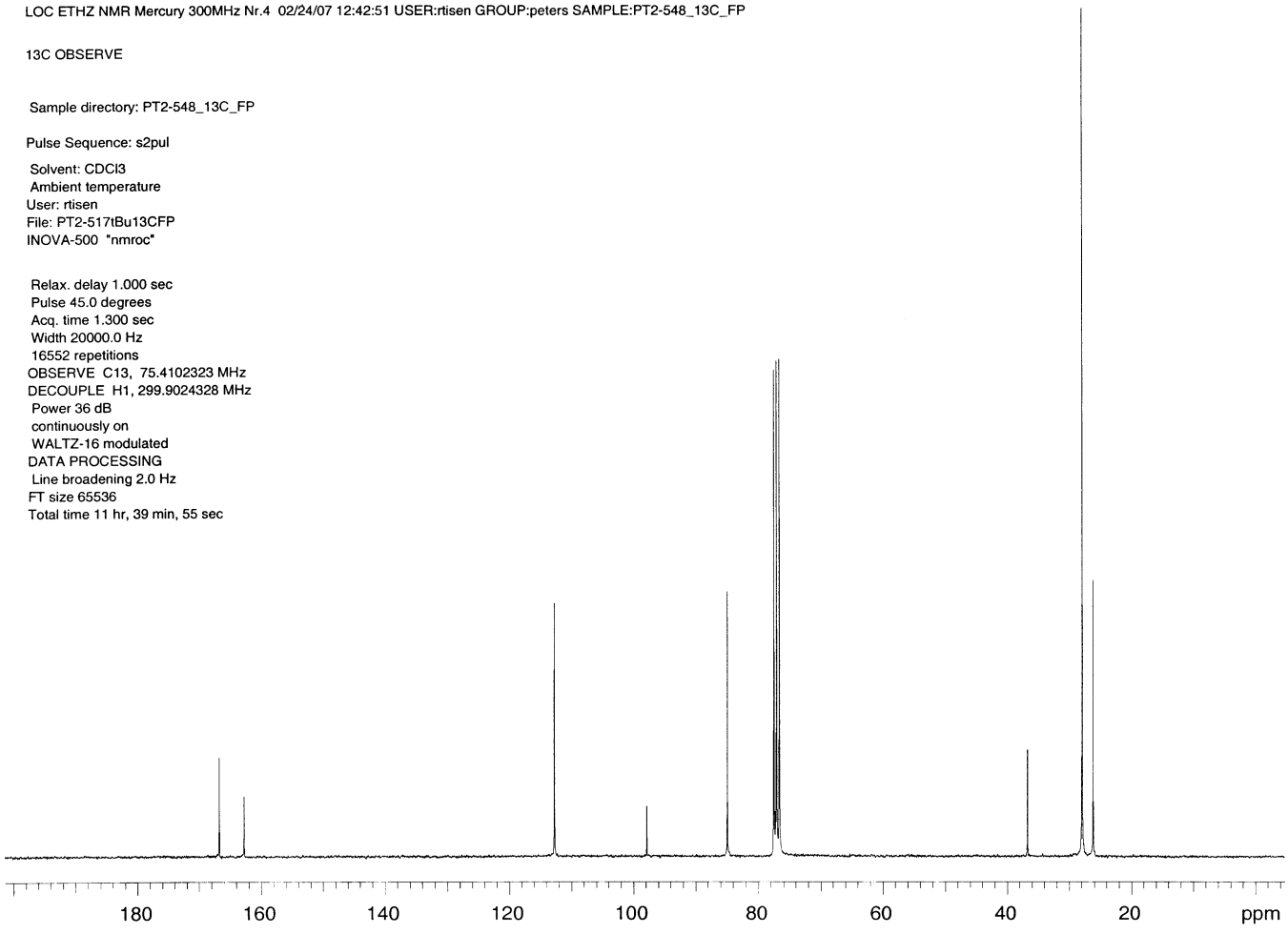

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STANDARD 1H OBSERVE

Sample directory: PTPh1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTPh1HFP
INOVA-500 "nmroc"

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Pulse 30.2 degrees
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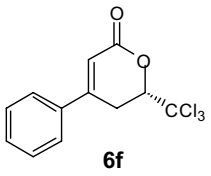
Total time 1 min, 8 sec



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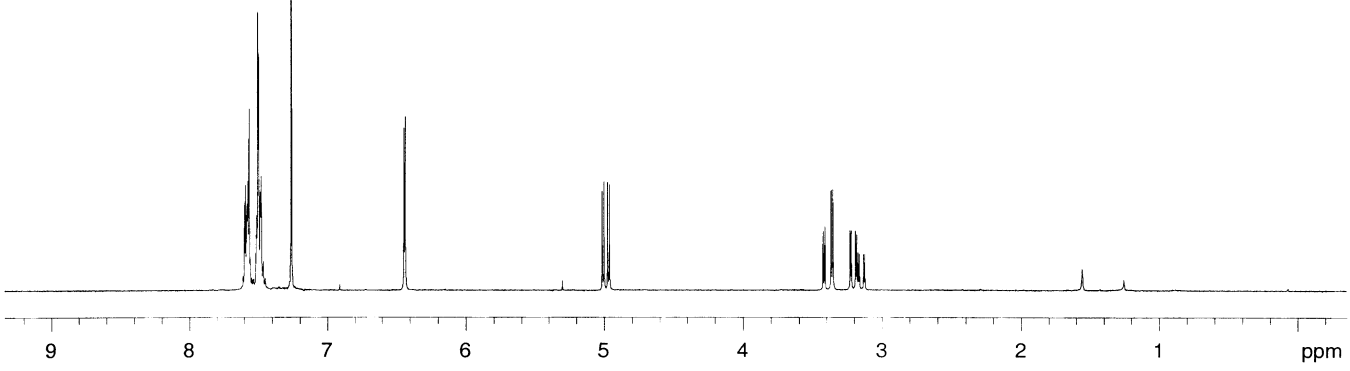

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13C OBSERVE

Sample directory: 2-548_13C

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rfisch
File: PT-2-548_13C
INOVA-500 "nmroc"

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Acq. time 1.300 sec
Width 20000.0 Hz
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DECOUPLE H1, 299.7740804 MHz
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DATA PROCESSING
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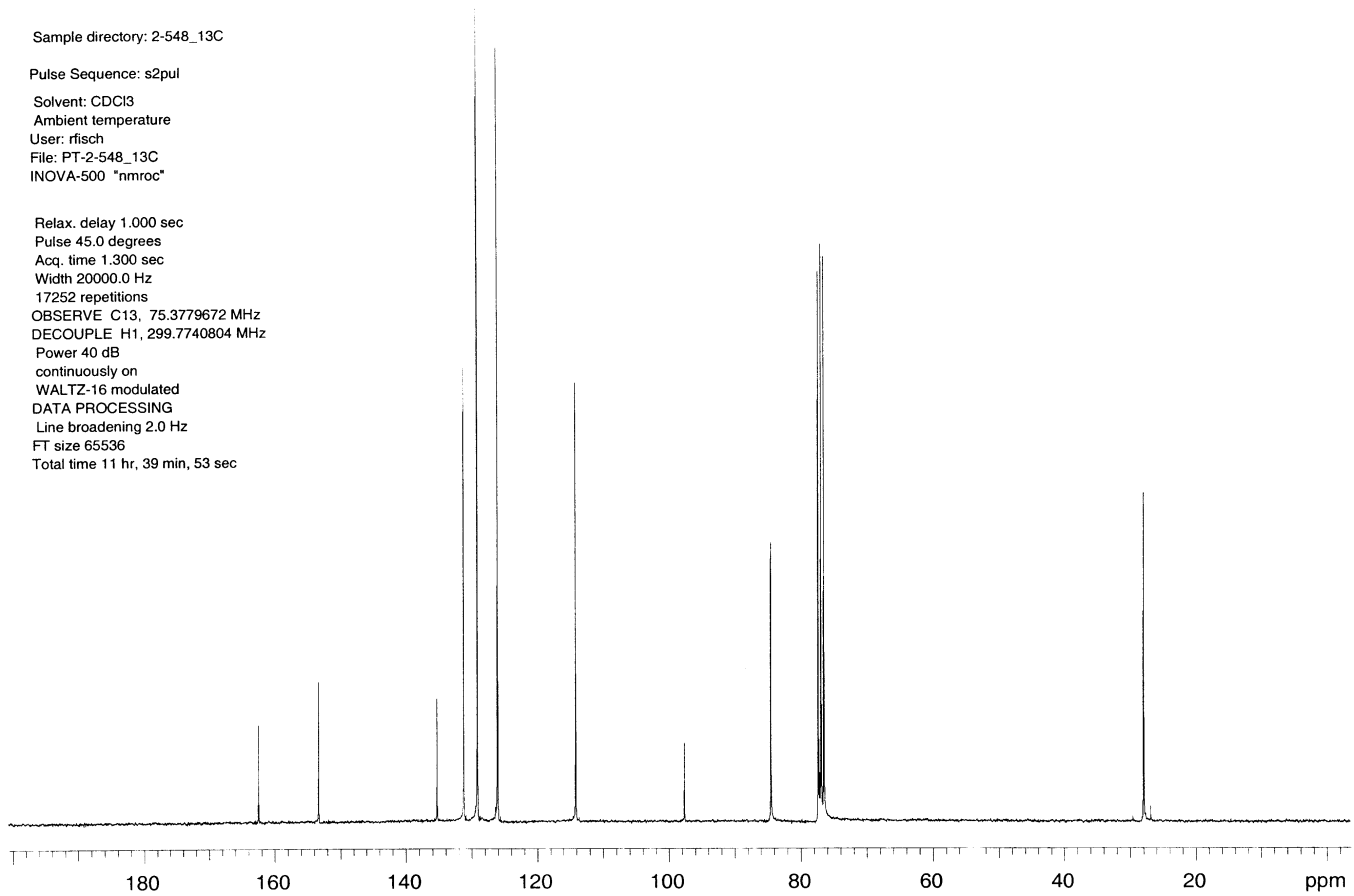


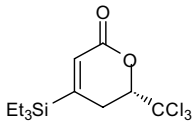
LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:26:13 USER:rtisen GROUP:peters SAMPLE:PTEt3Si1HFP

STANDARD 1H OBSERVE

Sample directory: PTEt3Si1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTEt3Si1HFP
INOVA-500 "nmroc"



6g

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16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:52:22 USER:rtisen GROUP:peters SAMPLE:PTPr3SiC13FP

13C OBSERVE

Sample directory: PTPr3SiC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTPr3SiC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
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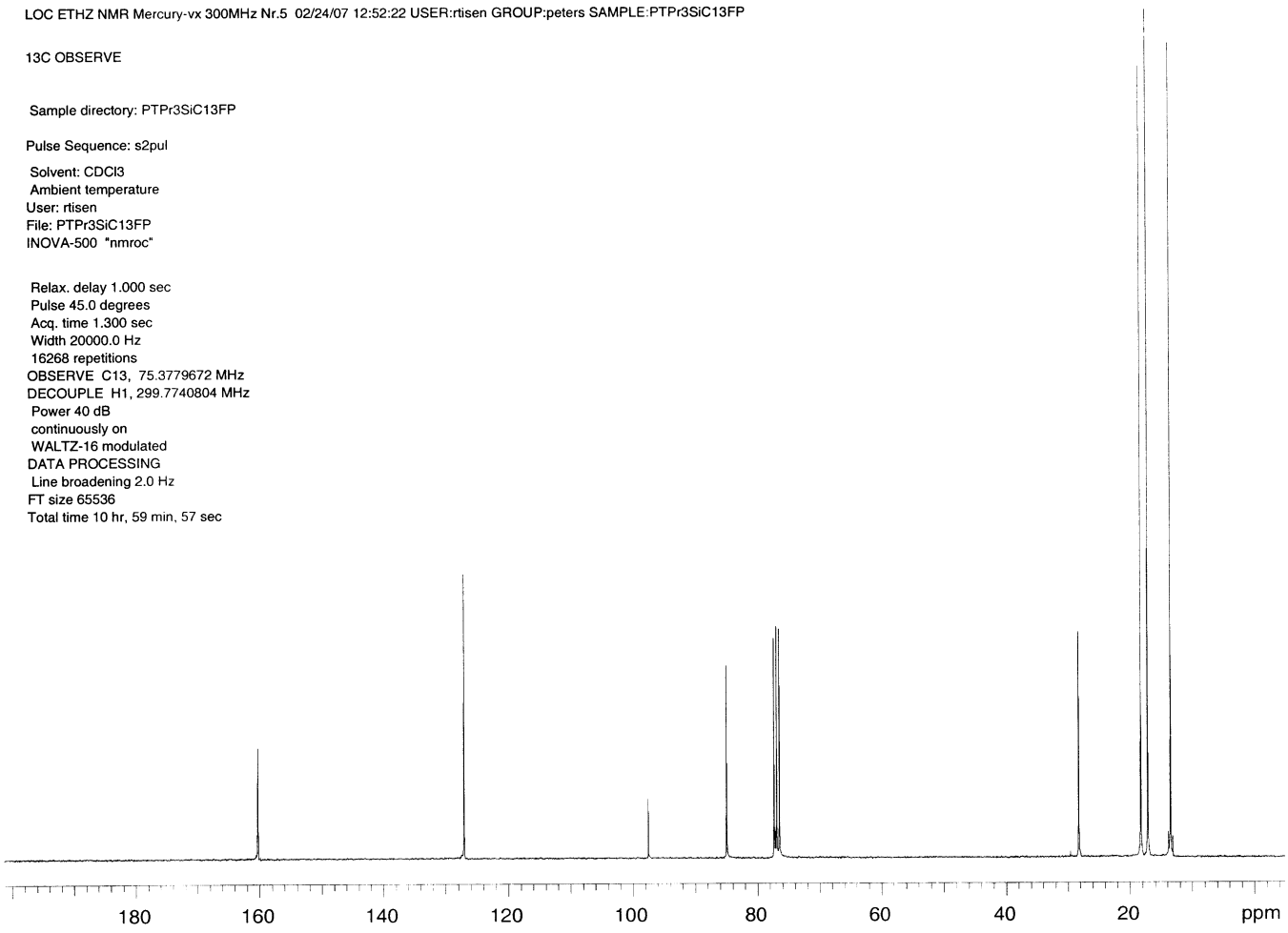

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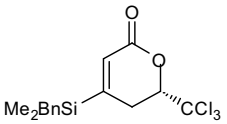
STANDARD 1H OBSERVE

Sample directory: PT-BnMe2Si1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT-BnMe2Si1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



6h

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 13:02:09 USER:rtisen GROUP:peters SAMPLE:PTBnMeSiChlC13FP

13C OBSERVE

Sample directory: PTBnMeSiChlC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBuMeSiChl13CFP
INOVA-500 "nmroc"

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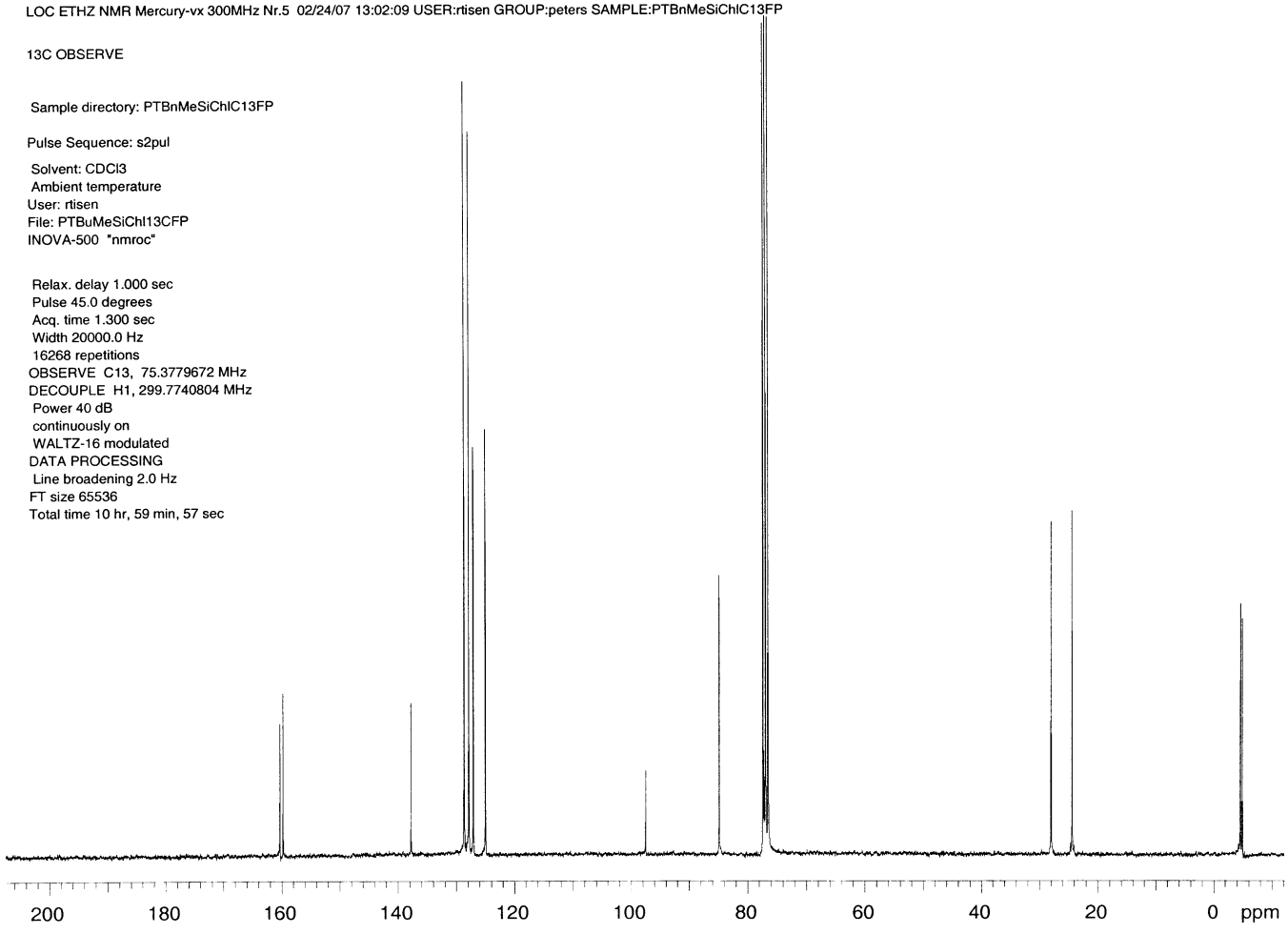
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.6 02/24/07 12:33:45 USER:rtisen GROUP:peters SAMPLE:PTPrSi1HFP

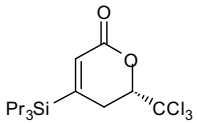
STANDARD 1H OBSERVE

Sample directory: PTPrSi1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PtPr3Si1HFP
INOVA-500 "nmroc"

Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 52 sec



6i

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:52:22 USER:rtisen GROUP:peters SAMPLE:PTPr3SiC13FP

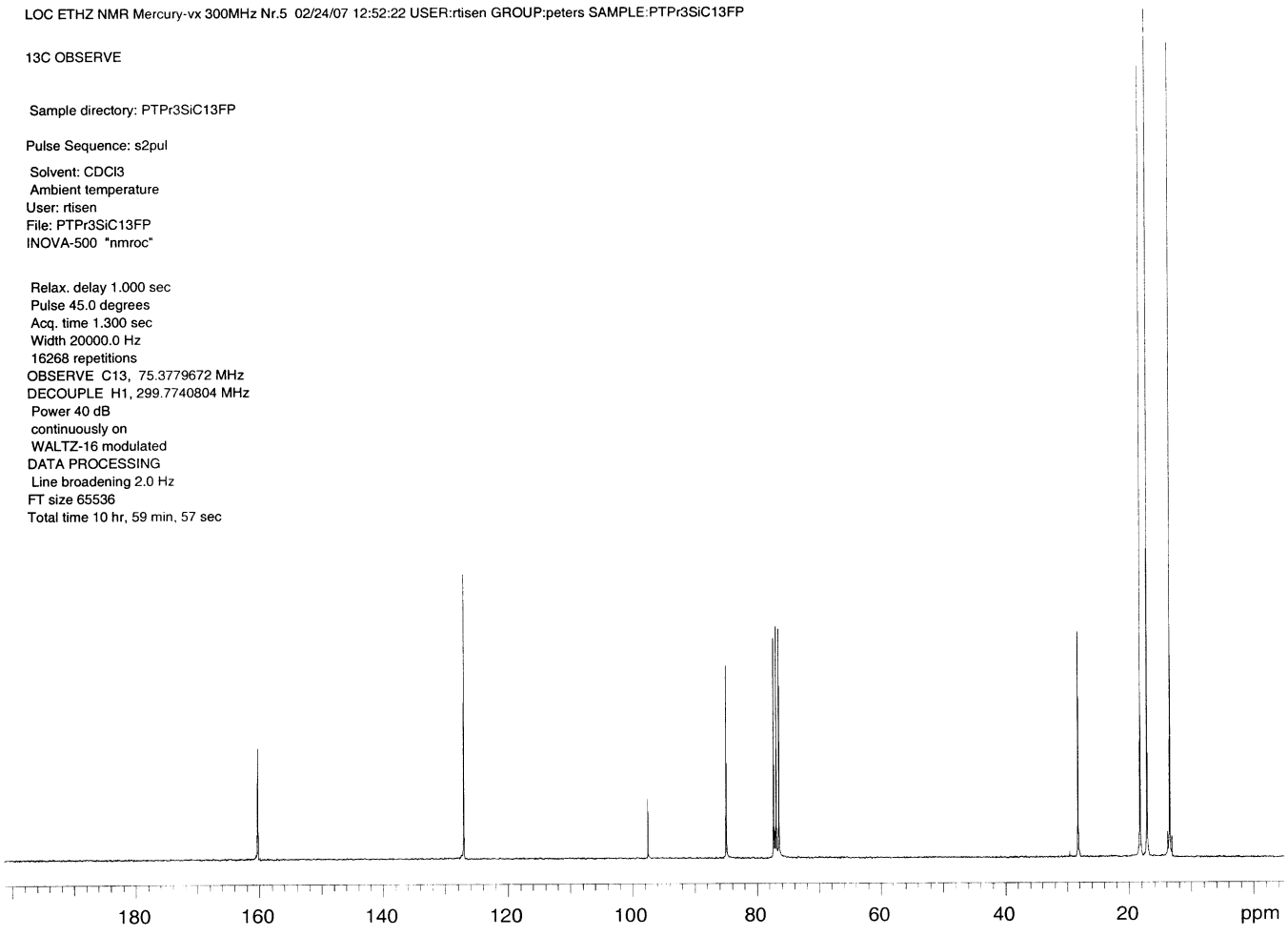
13C OBSERVE

Sample directory: PTPr3SiC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTPr3SiC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.6 02/24/07 12:15:30 USER:rtisen GROUP:peters SAMPLE:PTBu3Si1HFP

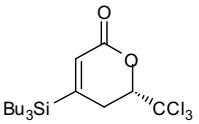
STANDARD 1H OBSERVE

Sample directory: PTBu3Si1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: 3PTBu3Si1HFP
INOVA-500 "nmroc"

Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 52 sec



6k

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:47:18 USER:rtisen GROUP:peters SAMPLE:PTBu3SiC13FP

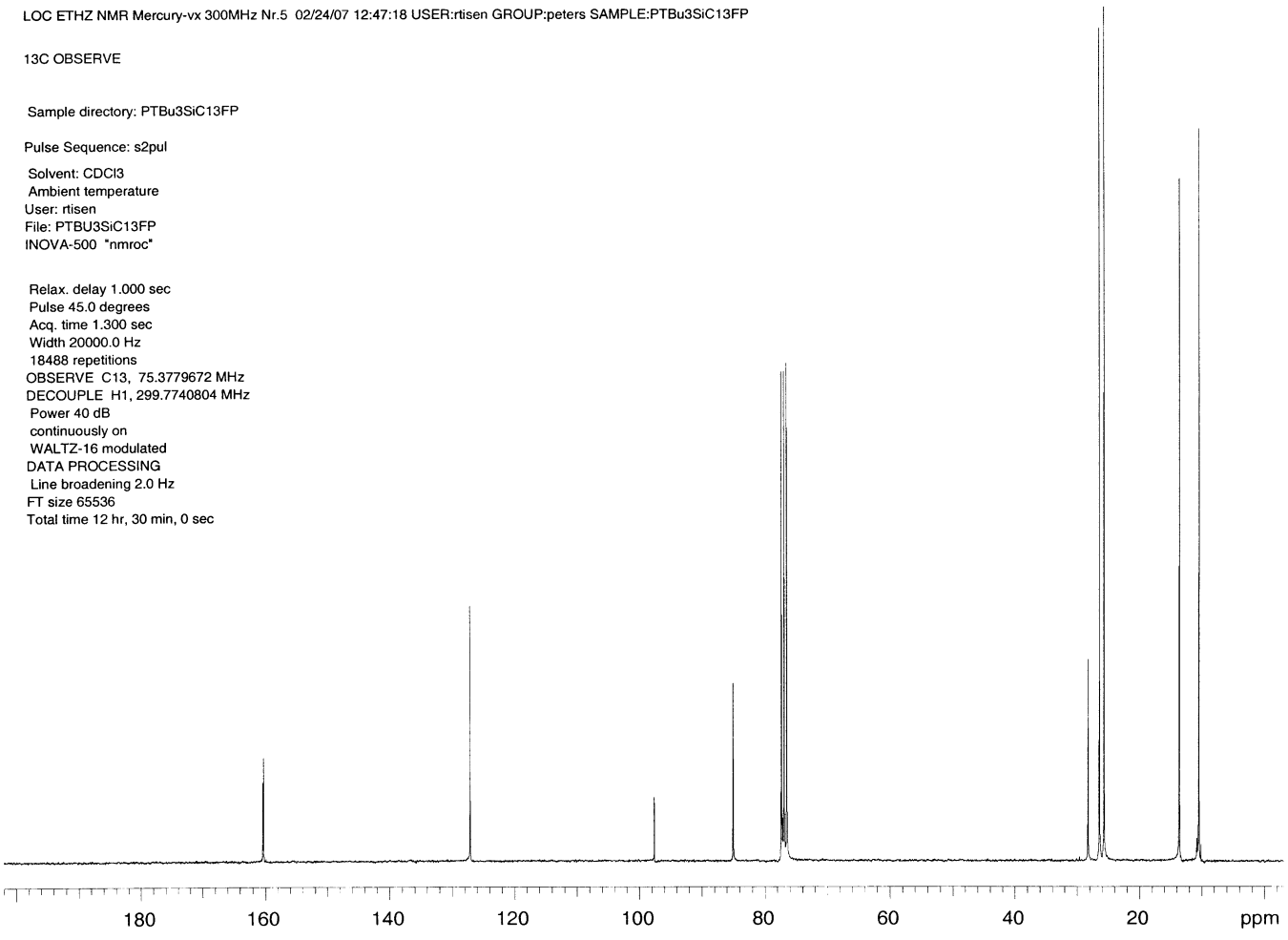
13C OBSERVE

Sample directory: PTBu3SiC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBU3SiC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
18488 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 12 hr, 30 min, 0 sec



LOC ETHZ NMR Mercury 300MHz Nr.4 02/24/07 12:24:23 USER:rtisen GROUP:peters SAMPLE:PTCOOH1HFP

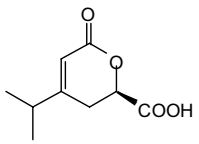
STANDARD 1H OBSERVE

Sample directory: PTCOOH1HFP

Pulse Sequence: s2pul

Solvent: DMSO
Ambient temperature
User: rtisen
File: PTCOOH1HFP
INOVA-500 "nmroc"

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9026712 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 52 sec



7a

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 02/24/07 12:50:16 USER:rtisen GROUP:peters SAMPLE:PTCOOH13CFP

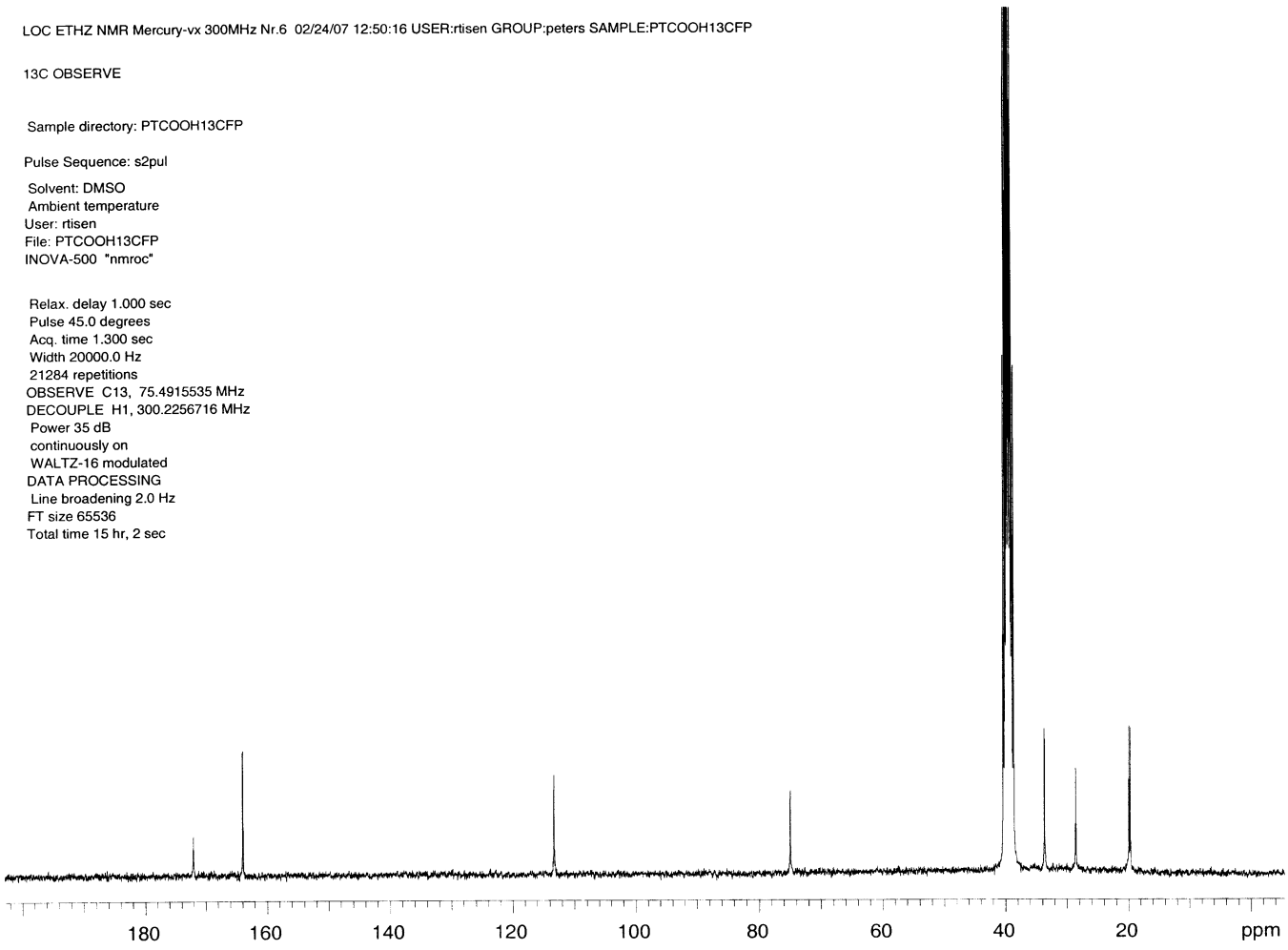
13C OBSERVE

Sample directory: PTCOOH13CFP

Pulse Sequence: s2pul

Solvent: DMSO
Ambient temperature
User: rtisen
File: PTCOOH13CFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
21284 repetitions
OBSERVE C13, 75.4915535 MHz
DECOUPLE H1, 300.2256716 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 15 hr, 2 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:23:12 USER:rtisen GROUP:peters SAMPLE:PTCHCl21HFP

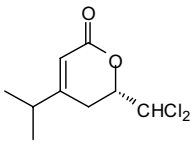
STANDARD 1H OBSERVE

Sample directory: PTCHCl21HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTCHCl21HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



8a

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:45:26 USER:rtisen GROUP:peters SAMPLE:pt3-13413CFP

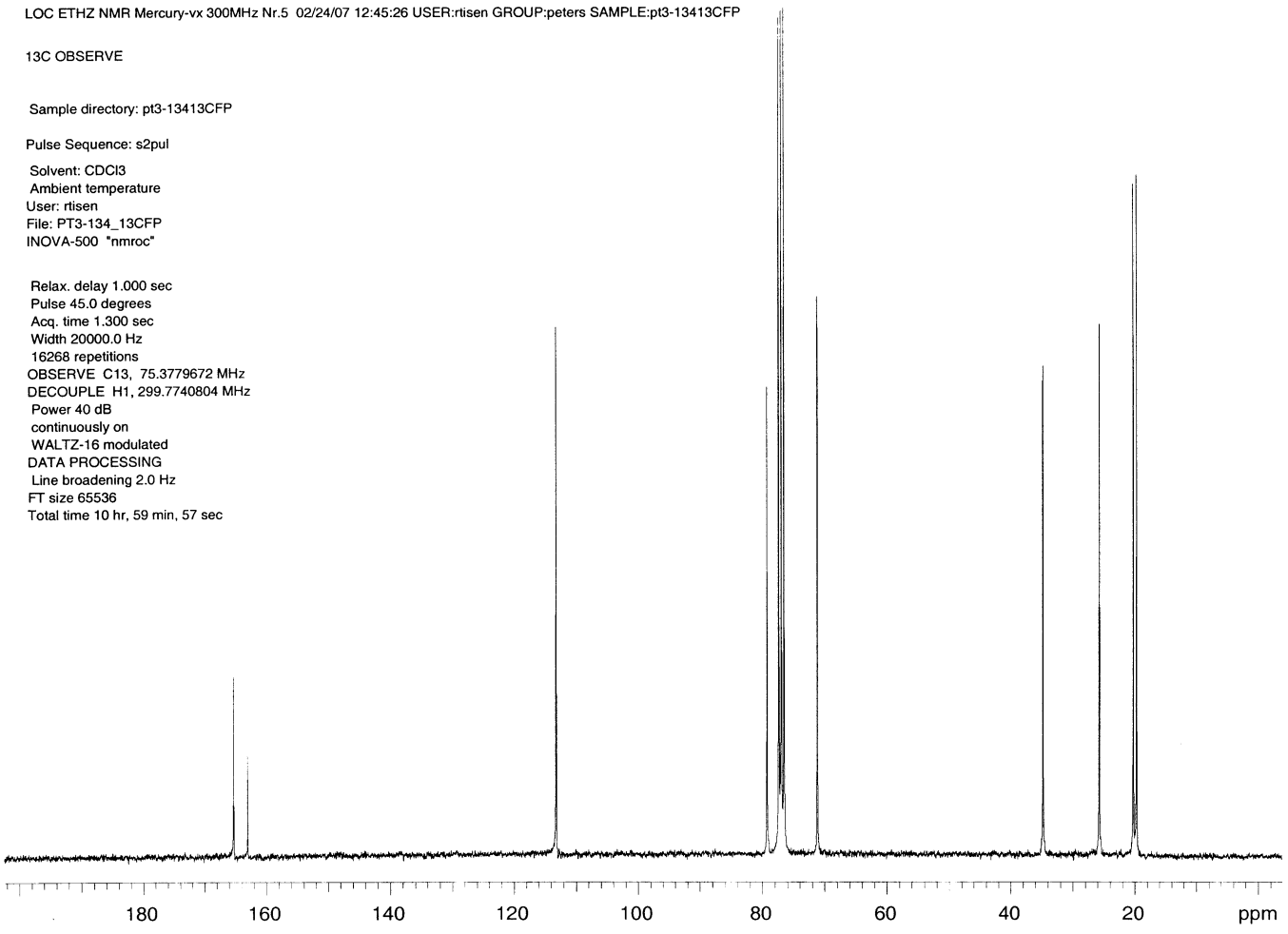
13C OBSERVE

Sample directory: pt3-13413CFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT3-134_13CFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:22:03 USER:rtisen GROUP:peters SAMPLE:PTCH2Cl1HFP

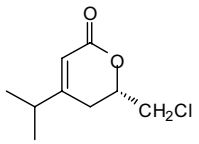
STANDARD 1H OBSERVE

Sample directory: PTCH2Cl1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTCH2Cl1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



9a

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:46:49 USER:rtisen GROUP:peters SAMPLE:pt3-135CH2ClC13FP

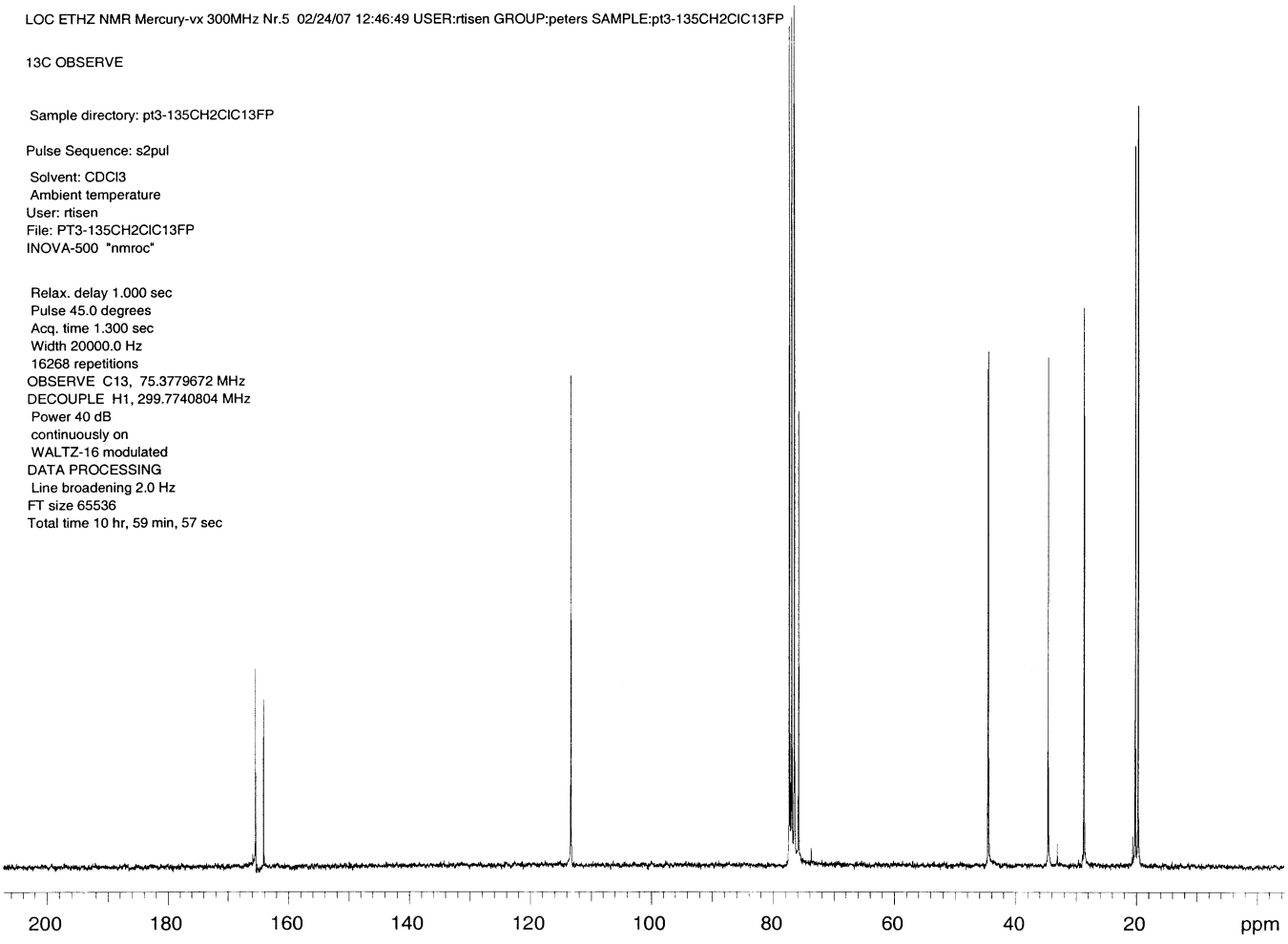
13C OBSERVE

Sample directory: pt3-135CH2ClC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT3-135CH2ClC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:22:43 USER:rtisen GROUP:peters SAMPLE:PTCH2OH1HFP

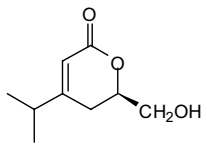
STANDARD 1H OBSERVE

Sample directory: PTCH2OH1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTCH2OH1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



10a

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:48:45 USER:rtisen GROUP:peters SAMPLE:PTCH2OH13CFP

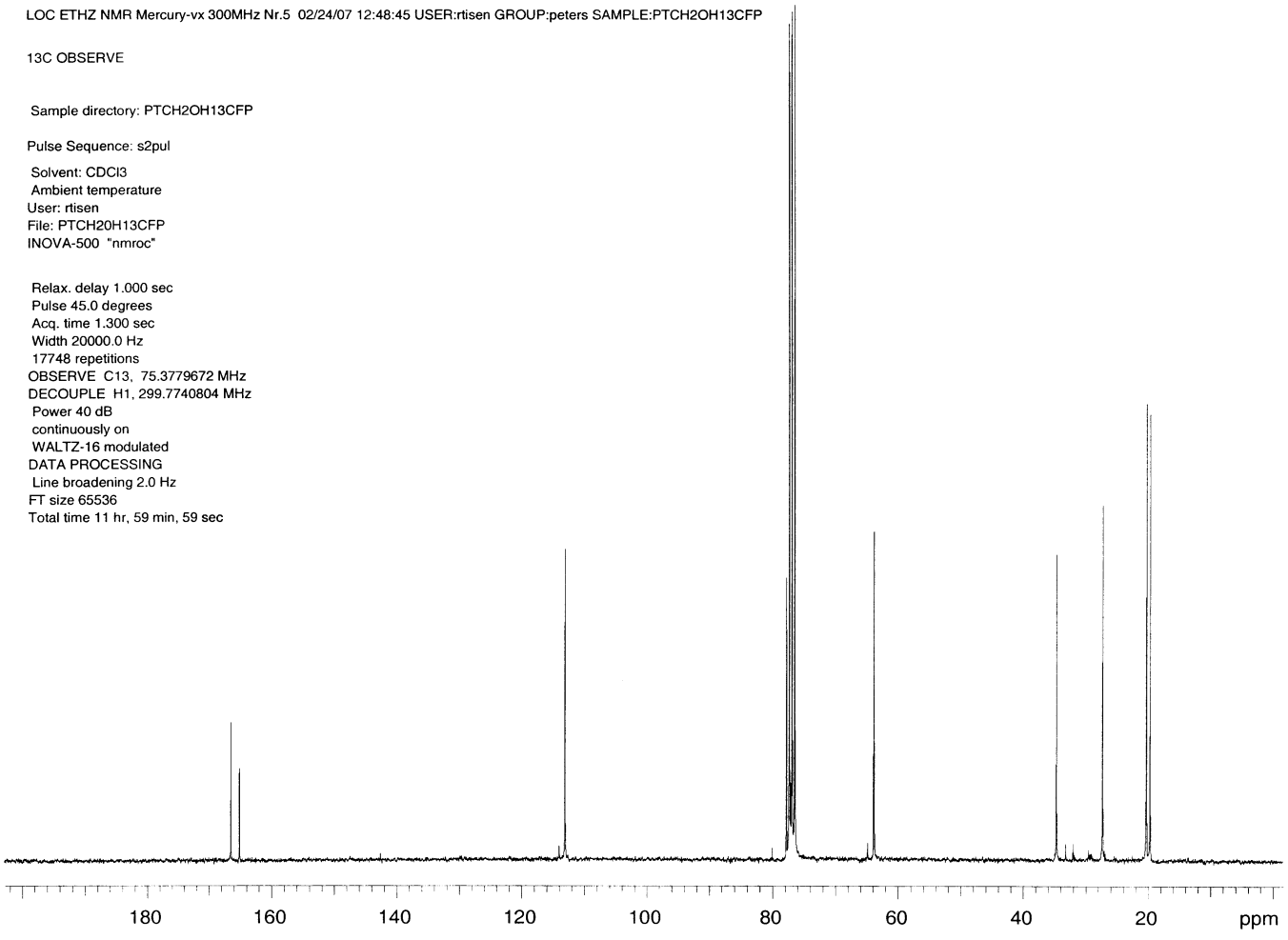
13C OBSERVE

Sample directory: PTCH2OH13CFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTCH20H13CFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
17748 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 11 hr, 59 min, 59 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:30:11 USER:rtisen GROUP:peters SAMPLE:PTEtOH1HFP

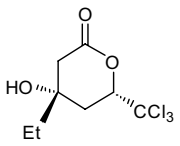
STANDARD 1H OBSERVE

Sample directory: PTEtOH1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTEtOH1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



13g

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 13:02:32 USER:rtisen GROUP:peters SAMPLE:pt3-117EtOHC13FP

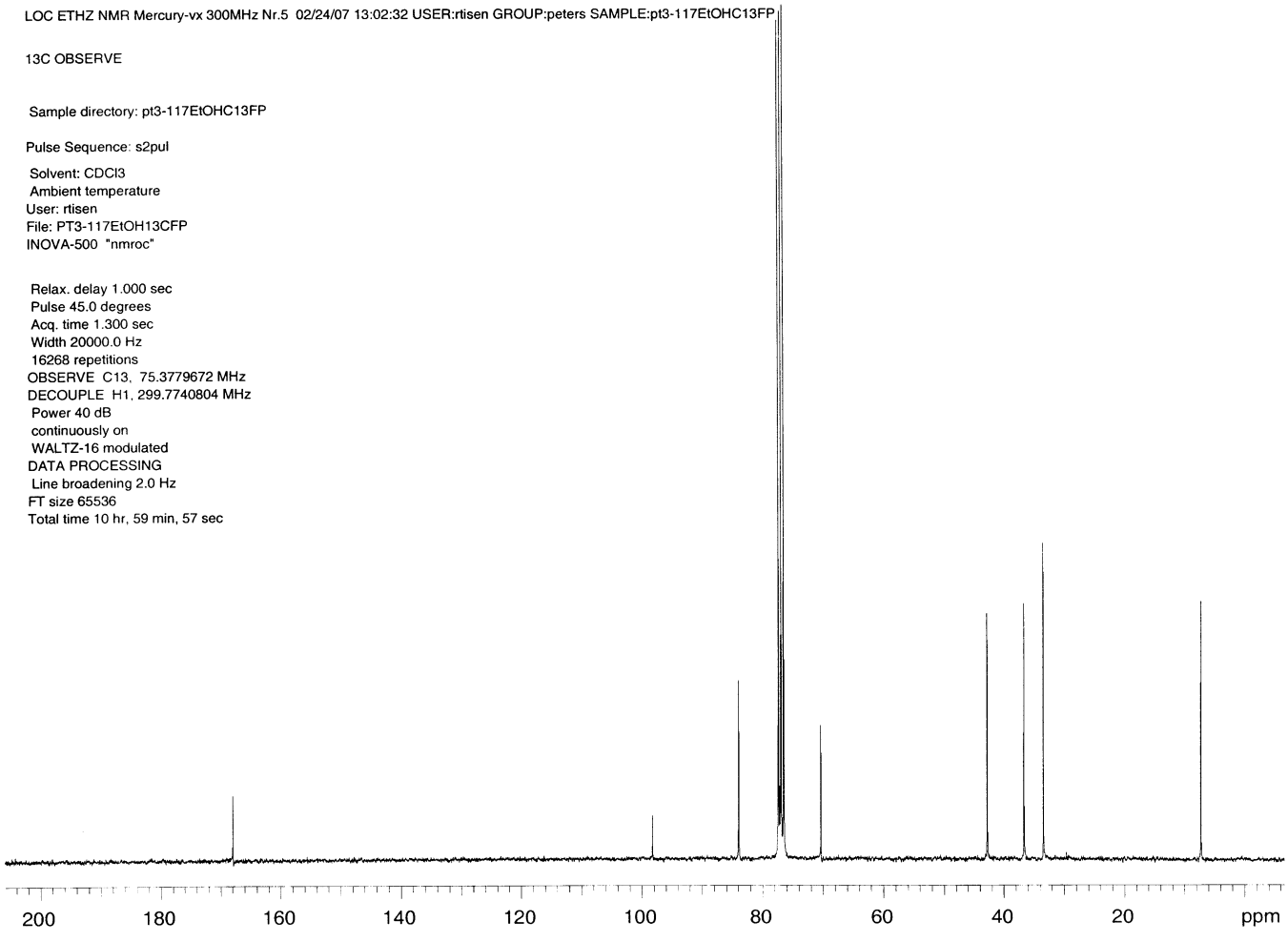
13C OBSERVE

Sample directory: pt3-117EtOHC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PT3-117EtOH13CFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:20:10 USER:rtisen GROUP:peters SAMPLE:PTBnOH1HFP

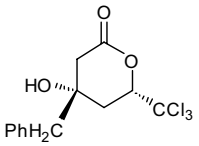
STANDARD 1H OBSERVE

Sample directory: PTBnOH1HFP

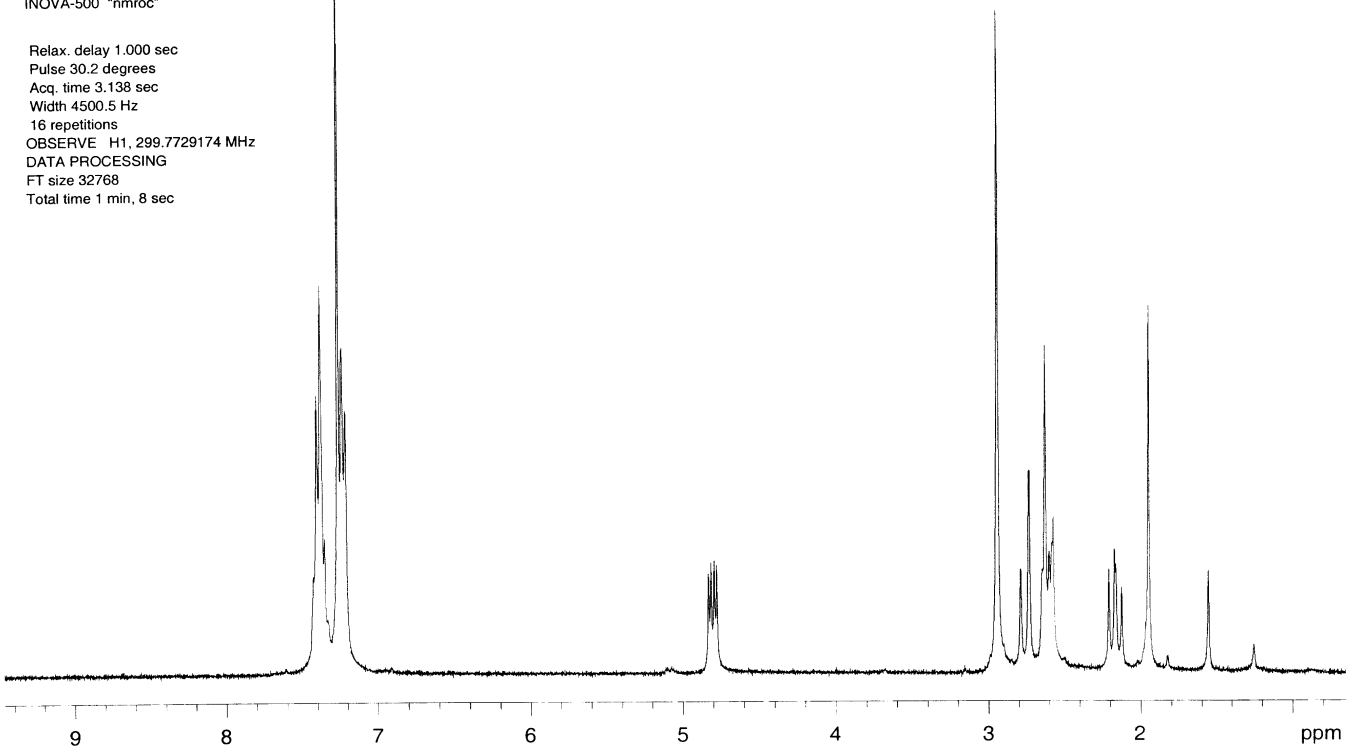
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBnOH1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



13h



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:47:44 USER:rtisen GROUP:peters SAMPLE:ptBnOH13CFP

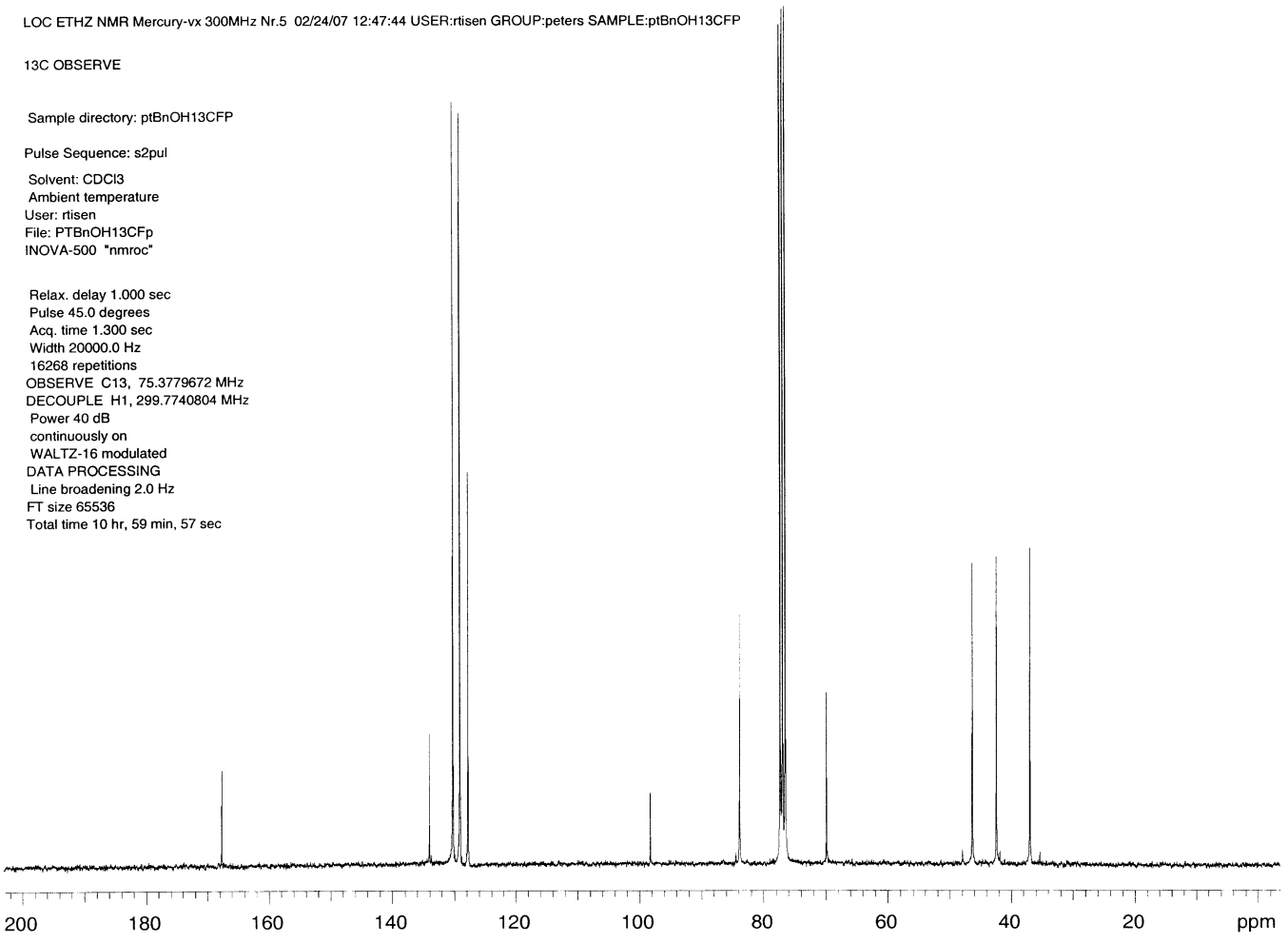
13C OBSERVE

Sample directory: ptBnOH13CFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBnOH13CFp
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury 300MHz Nr.4 02/24/07 12:31:49 USER:rtisen GROUP:peters SAMPLE:PTPrOH1HFP

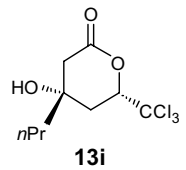
STANDARD 1H OBSERVE

Sample directory: PTPrOH1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTPrOH1HFP
INOVA-500 "nmroc"

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
16 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 52 sec



13i

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:52:49 USER:rtisen GROUP:peters SAMPLE:PTPrOHC13FP

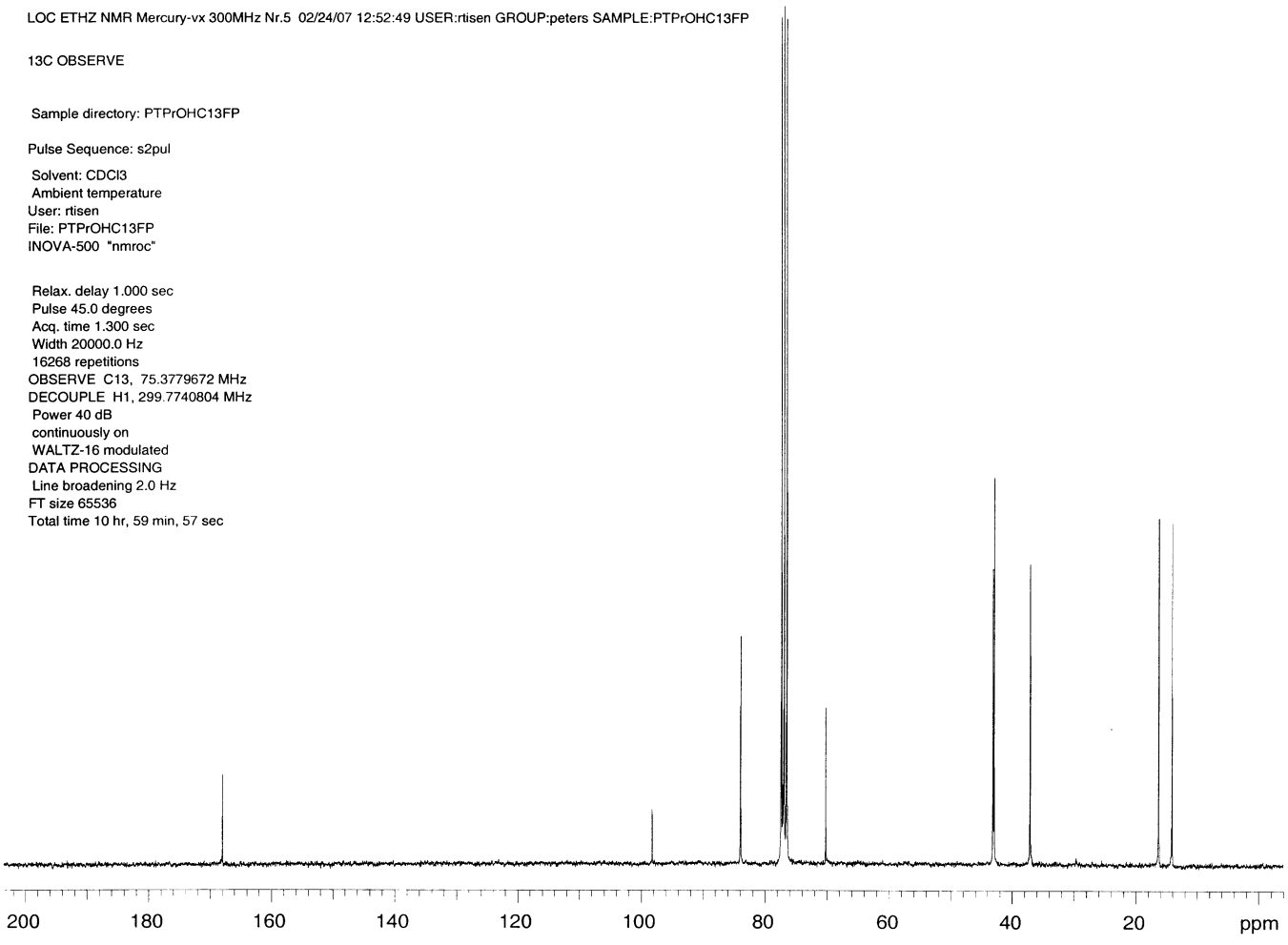
13C OBSERVE

Sample directory: PTPrOHC13FP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTPrOHC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:21:21 USER:rtisen GROUP:peters SAMPLE:PTBuOH1HFP

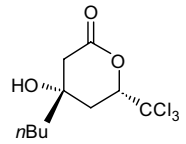
STANDARD 1H OBSERVE

Sample directory: PTBuOH1HFP

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBuOH1HFP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729174 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 8 sec



13k

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 02/24/07 12:48:19 USER:rtisen GROUP:peters SAMPLE:PTBuOH13CFP

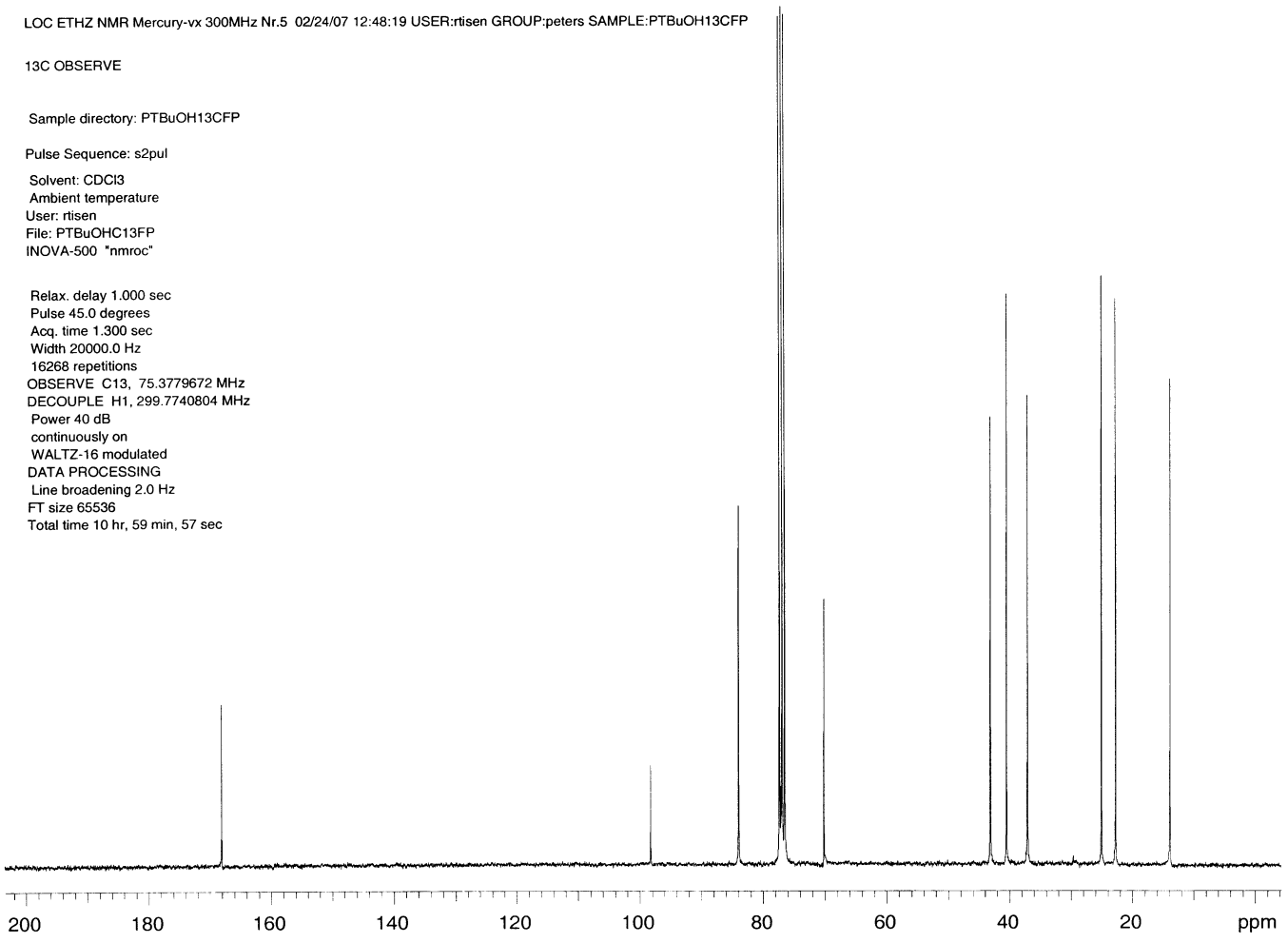
13C OBSERVE

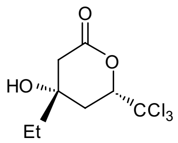
Sample directory: PTBuOH13CFP

Pulse Sequence: s2pul

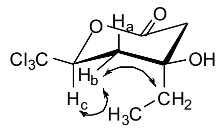
Solvent: CDCl3
Ambient temperature
User: rtisen
File: PTBuOHC13FP
INOVA-500 "nmroc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
16268 repetitions
OBSERVE C13, 75.3779672 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 hr, 59 min, 57 sec





13g



Current Data Parameters
NAME d1186
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
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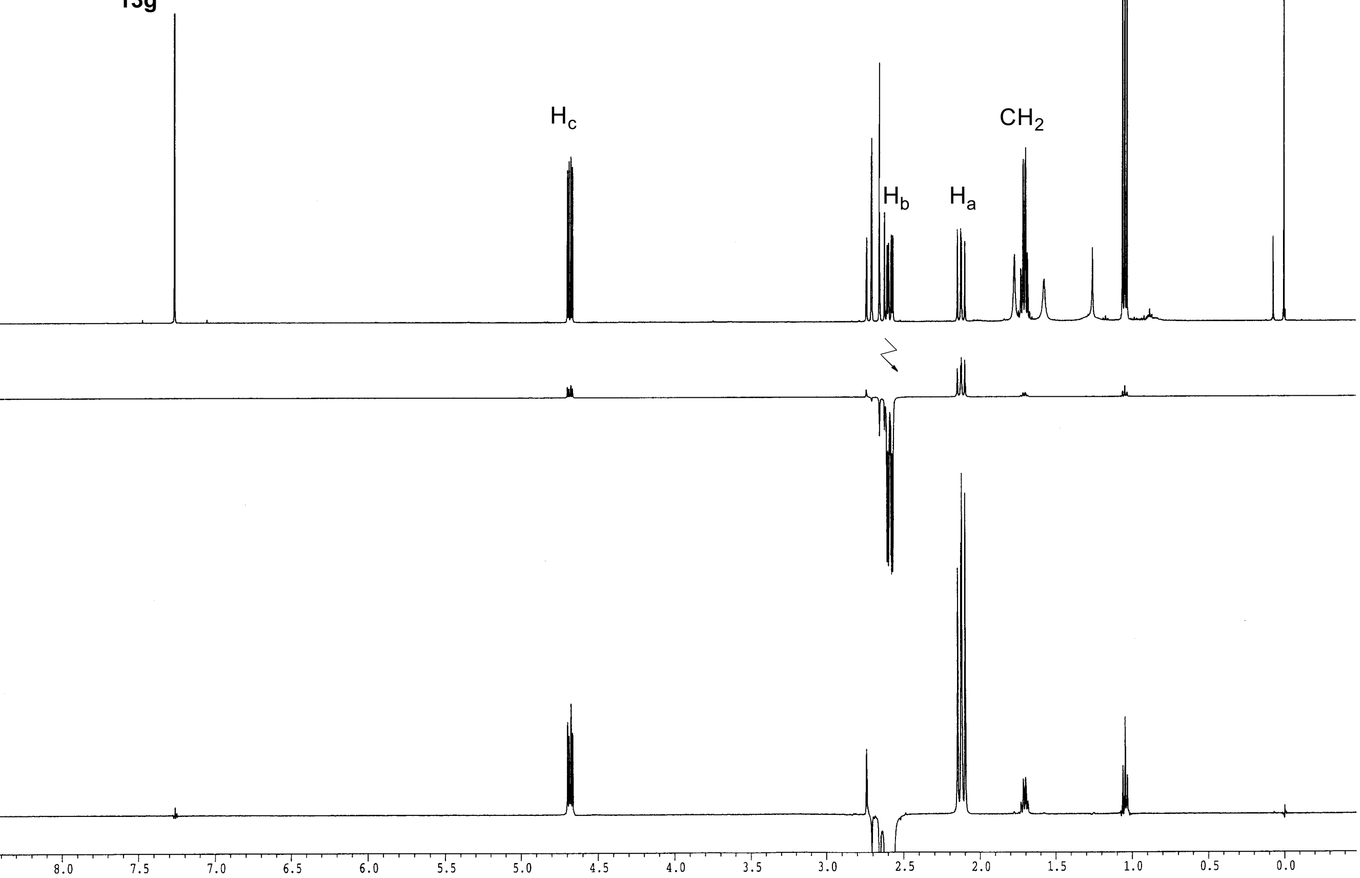
Time 10.48
INSTRUM DRX500
PROBHD 5 mm BBI 1H-
PULPROG noemul
TD 90112
SOLVENT CDCl3
NS 320
DS 4
SWH 8090.615 Hz
FIDRES 0.089784 Hz
AQ 5.5689716 sec
RG 300
DW 61.800 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
D20 0.07000000 sec
L4 30
NUC1 1H
P1 7.10 usec
PL1 -4.00 dB
SFO1 500.0332000 MHz
FQ2LIST f21list.2
NUC2 1H
PL2 120.00 dB
PL14 76.00 dB
SFO2 500.0332000 MHz

F2 - Processing parameters
SI 65536
SF 500.0300101 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 40.00 cm
F1P 9.500 ppm
F1 4750.29 Hz
F2P -0.500 ppm
F2 -250.01 Hz
PPMCM 0.25000 ppm/cm
HZCM 125.00750 Hz/cm



Current Data Parameters
NAME d1186
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
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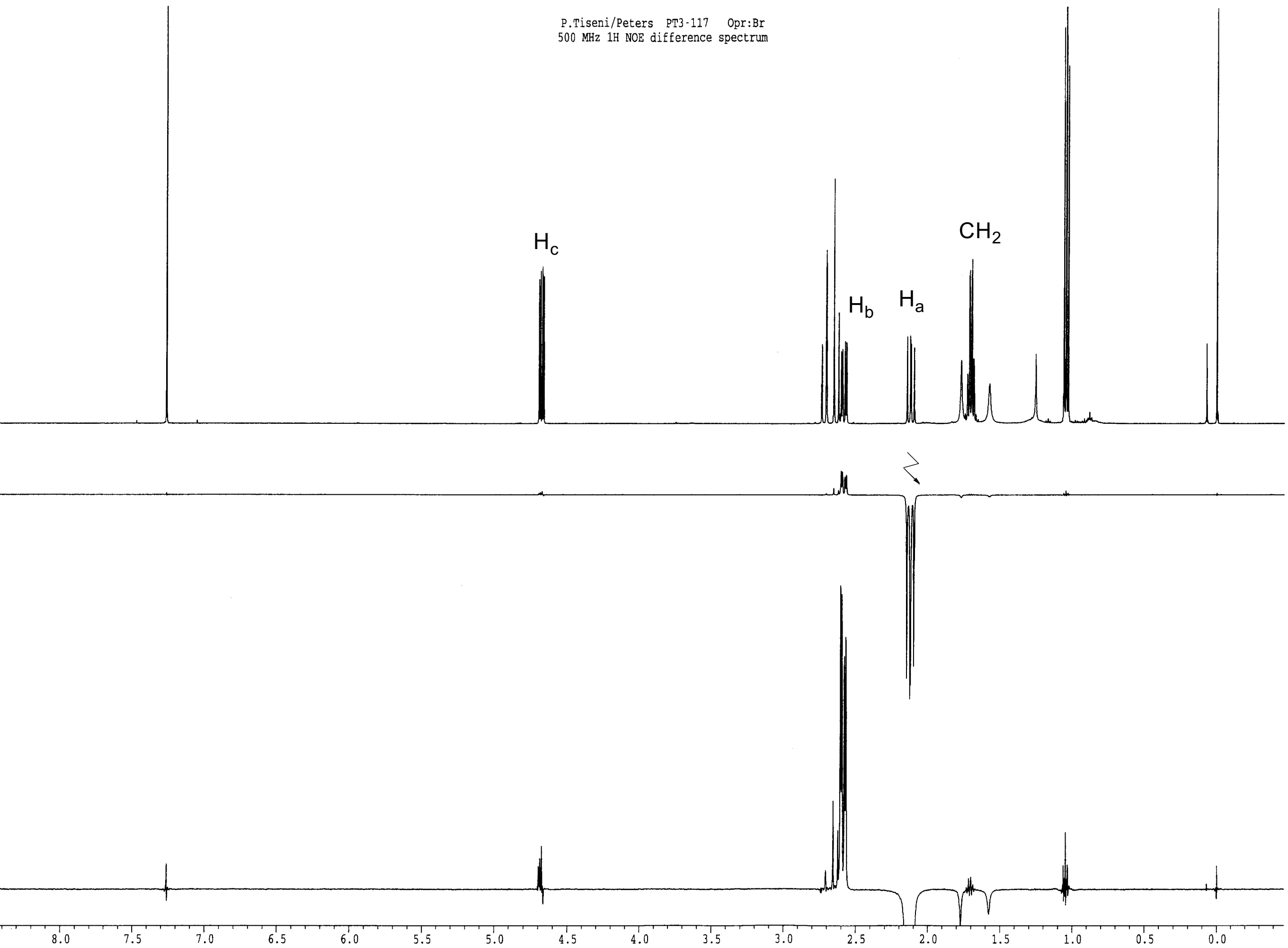
Time 10.51
INSTRUM DRX500
PROBHD 5 mm BBI 1H-
PULPROG noemul
TD 90112
SOLVENT CDCl3
NS 320
DS 4
SWH 8090.615 Hz
FIDRES 0.089784 Hz
AQ 5.5689716 sec
RG 300
DW 61.800 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
D20 0.07000000 sec
L4 30
NUC1 1H
P1 7.10 usec
PL1 -4.00 dB
SFO1 500.0332000 MHz
FQ2LIST f21list.3
NUC2 1H
PL2 120.00 dB
PL14 76.00 dB
SFO2 500.0332000 MHz

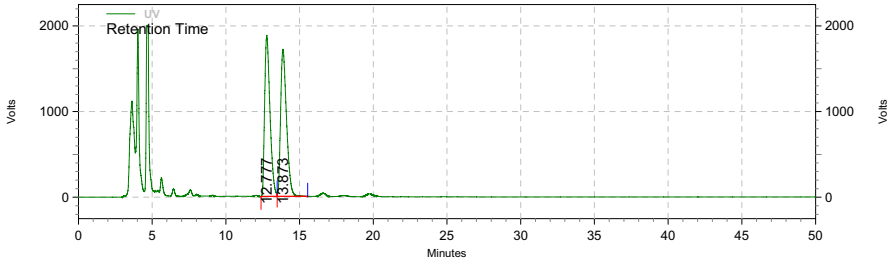
F2 - Processing parameters
SI 65536
SF 500.0300101 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 40.00 cm
F1P 9.500 ppm
F1 4750.29 Hz
F2P -0.500 ppm
F2 -250.01 Hz
PPMCM 0.25000 ppm/cm
HZCM 125.00750 Hz/cm



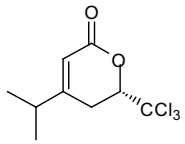
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-201.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 10/24/2005 8:40:31 AM
Printed: 2/26/2007 3:06:07 PM



UV Results

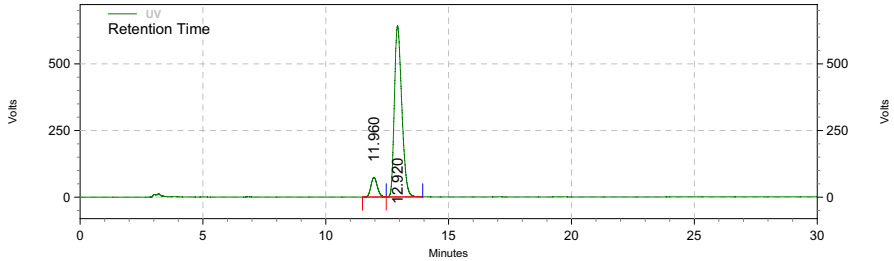
Retention Time	Area	Area %	Height	Height %
12.777	188224294	49.58	7524509	52.28
13.873	191409367	50.42	6867827	47.72
Totals	379633661	100.00	14392336	100.00



6a

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPiPrChl
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 9:44:21 AM
Printed: 2/24/2007 3:26:02 PM

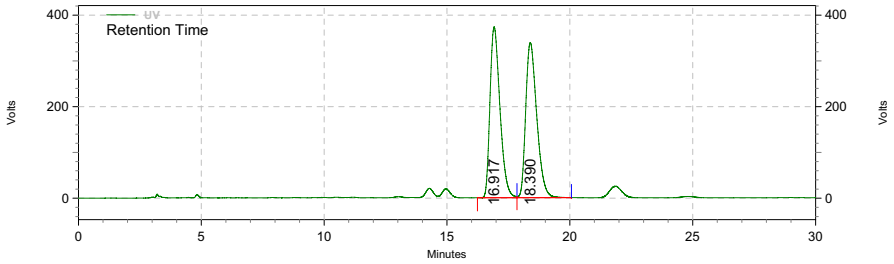


UV Results

Retention Time	Area	Area %	Height	Height %
11.960	5349322	9.06	294982	10.32
12.920	53697185	90.94	2563132	89.68
Totals	59046507	100.00	2858114	100.00

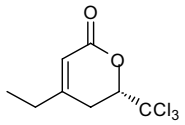
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPEtrac
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 10:15:29 AM
Printed: 2/24/2007 3:24:11 PM



UV Results

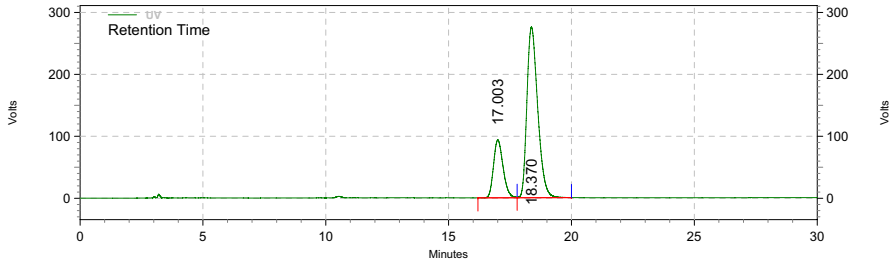
Retention Time	Area	Area %	Height	Height %
16.917	42006145	49.86	1492568	52.42
18.390	42238982	50.14	1354769	47.58
Totals	84245127	100.00	2847337	100.00



6b

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPEtChl
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 10:46:41 AM
Printed: 2/24/2007 3:23:48 PM

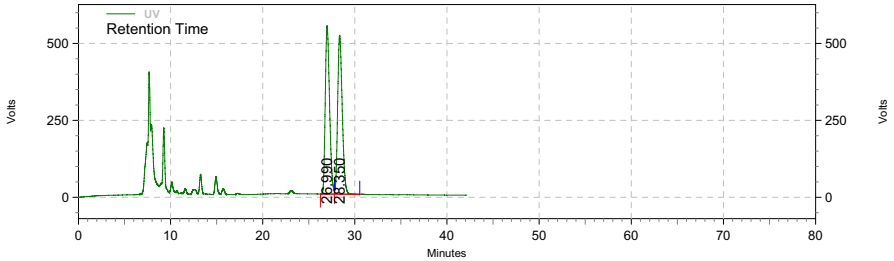


UV Results

Retention Time	Area	Area %	Height	Height %
17.003	10090835	23.08	374038	25.33
18.370	33637012	76.92	1102657	74.67
Totals	43727847	100.00	1476695	100.00

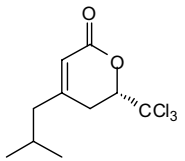
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-2782col.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 1/13/2006 1:31:11 PM
Printed: 2/24/2007 3:31:57 PM



UV Results

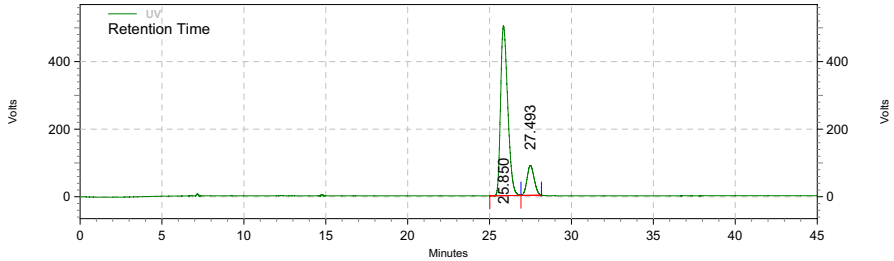
Retention Time	Area	Area %	Height	Height %
26.990	70806033	49.79	2185998	51.42
28.350	71407678	50.21	2065129	48.58
Totals	142213711	100.00	4251127	100.00



6c

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPiBu
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 4:00:22 PM
Printed: 2/23/2007 11:21:08 AM

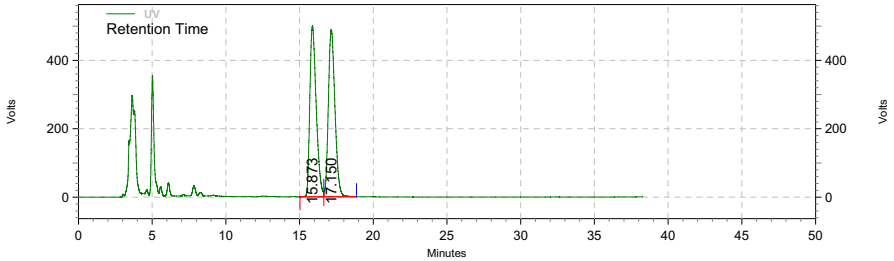


UV Results

Retention Time	Area	Area %	Height	Height %
25.850	60805180	85.10	2008879	85.02
27.493	10646263	14.90	353833	14.98
Totals	71451443	100.00	2362712	100.00

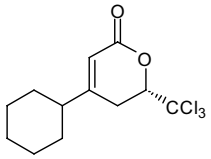
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-285.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 1/18/2006 12:43:05 PM
Printed: 2/24/2007 3:32:42 PM



UV Results

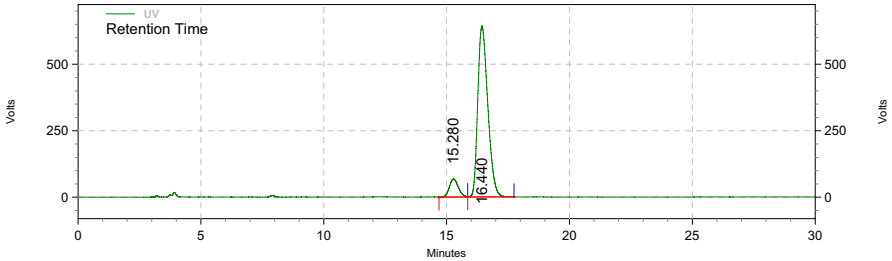
Retention Time	Area	Area %	Height	Height %
15.873	59941078	49.70	1997286	50.53
17.150	60670700	50.30	1955373	49.47
Totals	120611778	100.00	3952659	100.00



6d

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPCyChl
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 11:17:49 AM
Printed: 2/24/2007 3:22:53 PM

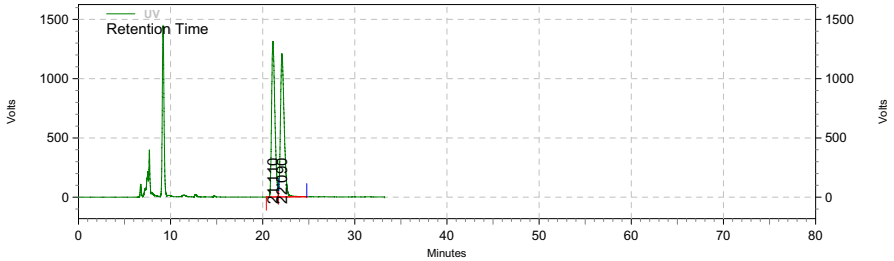


UV Results

Retention Time	Area	Area %	Height	Height %
15.280	6830796	8.56	271179	9.54
16.440	72967526	91.44	2571747	90.46
Totals	79798322	100.00	2842926	100.00

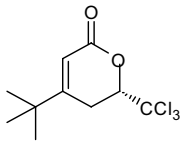
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-260a982col.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 12/19/2005 11:59:20 AM
Printed: 2/26/2007 3:07:32 PM



UV Results

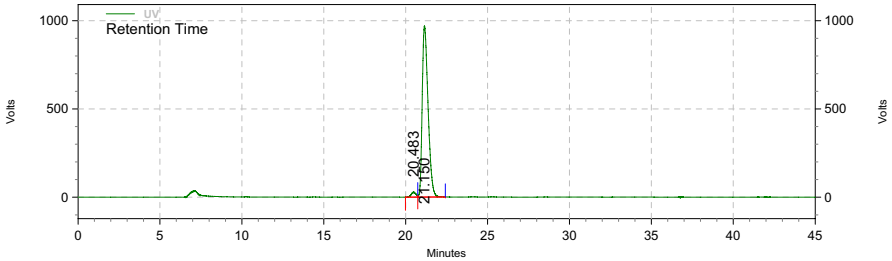
Retention Time	Area	Area %	Height	Height %
21.110	130473915	49.21	5243566	52.06
22.090	134642096	50.79	4827994	47.94
Totals	265116011	100.00	10071560	100.00



6e

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPtBu
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 4:46:29 PM
Printed: 2/24/2007 3:27:15 PM

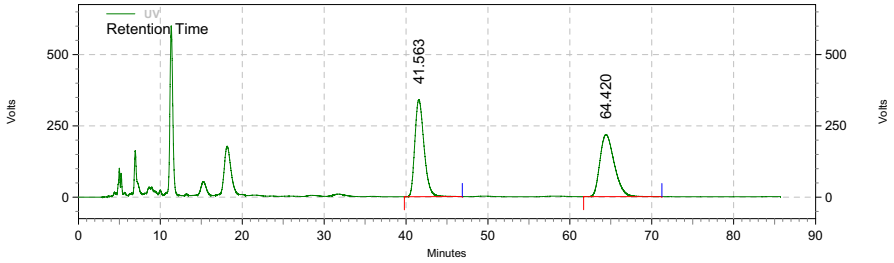


UV Results

Retention Time	Area	Area %	Height	Height %
20.483	2297448	2.34	113318	2.84
21.150	96020484	97.66	3876808	97.16
Totals	98317932	100.00	3990126	100.00

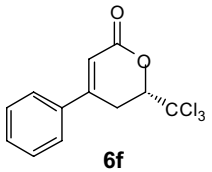
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-237.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 11/28/2005 9:35:50 AM
Printed: 2/24/2007 3:33:12 PM



UV Results

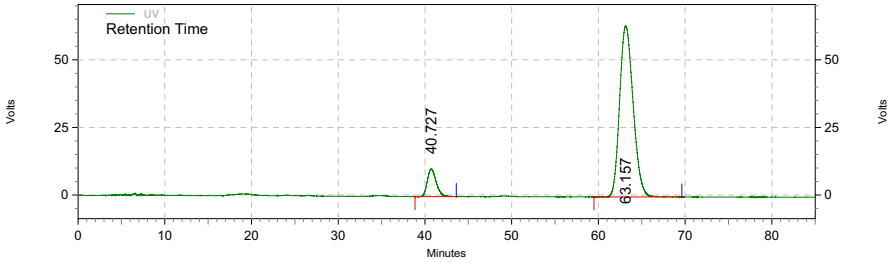
Retention Time	Area	Area %	Height	Height %
41.563	106139649	49.96	1364053	61.01
64.420	106302620	50.04	871726	38.99
Totals	212442269	100.00	2235779	100.00



6f

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\Phlactone
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 1/12/2007 3:53:15 PM
Printed: 2/24/2007 3:44:28 PM

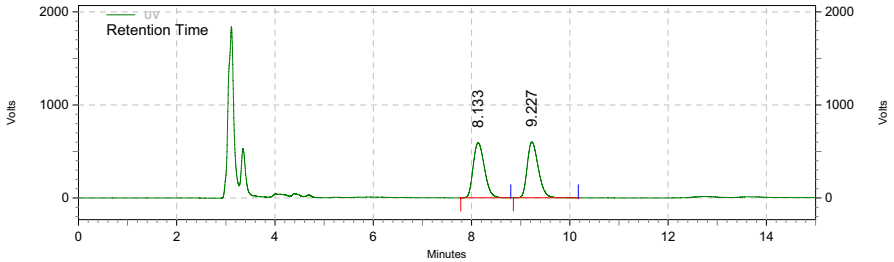


UV Results

Retention Time	Area	Area %	Height	Height %
40.727	2919964	9.63	40708	13.86
63.157	27410494	90.37	252902	86.14
Totals	30330458	100.00	293610	100.00

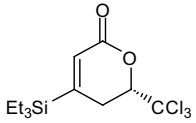
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2340.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 3/2/2006 4:22:12 PM
Printed: 2/24/2007 3:48:58 PM



UV Results

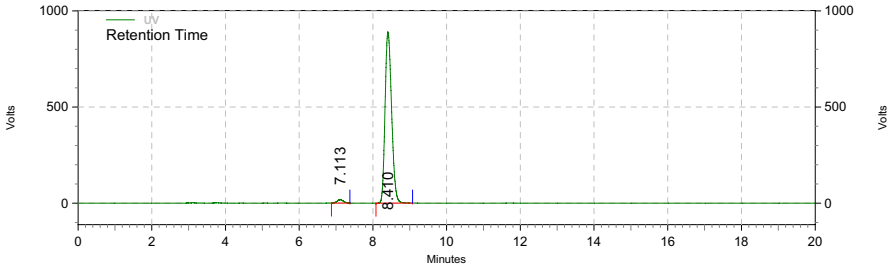
Retention Time	Area	Area %	Height	Height %
8.133	37602109	49.92	2366097	49.65
9.227	37724581	50.08	2399017	50.35
Totals	75326690	100.00	4765114	100.00



6g

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPEt3Si
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/19/2007 9:31:46 AM
Printed: 2/24/2007 3:23:22 PM

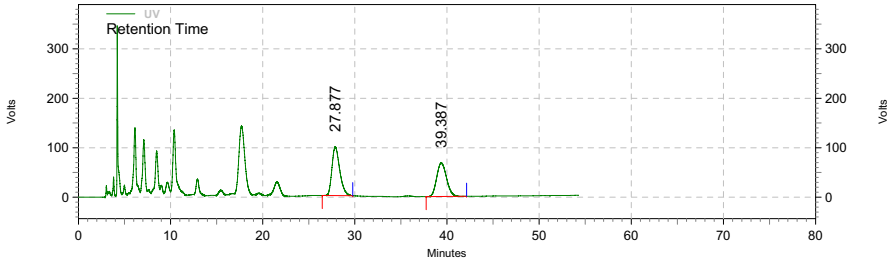


UV Results

Retention Time	Area	Area %	Height	Height %
7.113	816899	1.83	70093	1.93
8.410	43874606	98.17	3561041	98.07
Totals	44691505	100.00	3631134	100.00

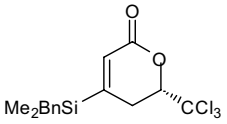
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-316a99.dat
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/11/2006 3:36:25 PM
Printed: 2/24/2007 3:50:16 PM



UV Results

Retention Time	Area	Area %	Height	Height %
27.877	23240980	53.43	394857	59.16
39.387	20258560	46.57	272581	40.84
Totals	43499540	100.00	667438	100.00

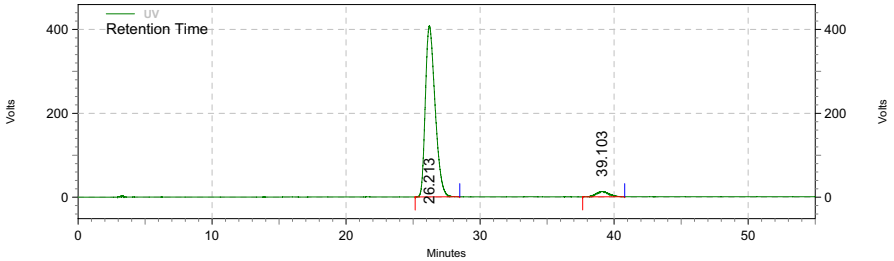


6h

Page 1 of 1

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPBnMeSi
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 12:41:03 PM
Printed: 2/24/2007 3:20:31 PM

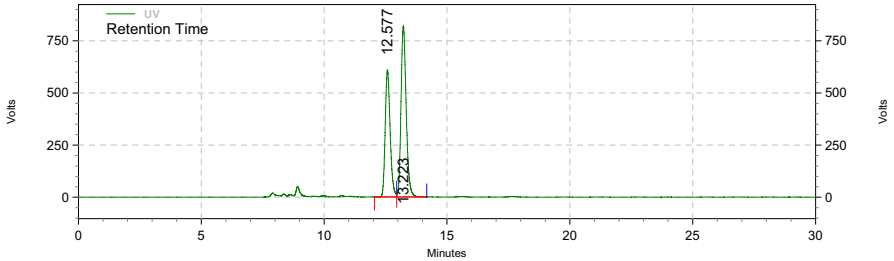


UV Results

Retention Time	Area	Area %	Height	Height %
26.213	82165682	95.98	1630238	97.06
39.103	3445821	4.02	49442	2.94
Totals	85611503	100.00	1679680	100.00

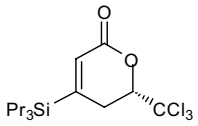
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPPr3Sirac
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 7:52:06 PM
Printed: 2/24/2007 3:26:48 PM



UV Results

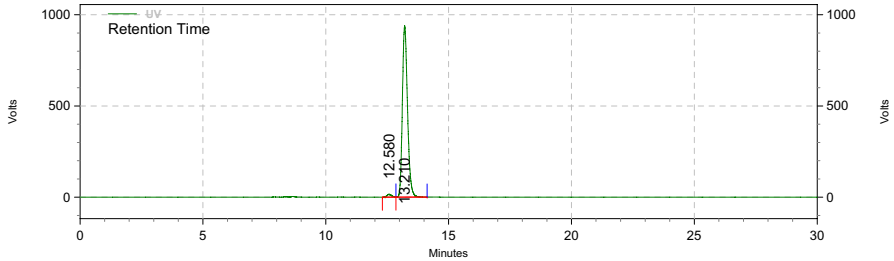
Retention Time	Area	Area %	Height	Height %
12.577	33939976	41.40	2435118	42.61
13.223	48030827	58.60	3279535	57.39
Totals	81970803	100.00	5714653	100.00



6i

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPPr3Si
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 7:20:58 PM
Printed: 2/24/2007 3:26:25 PM

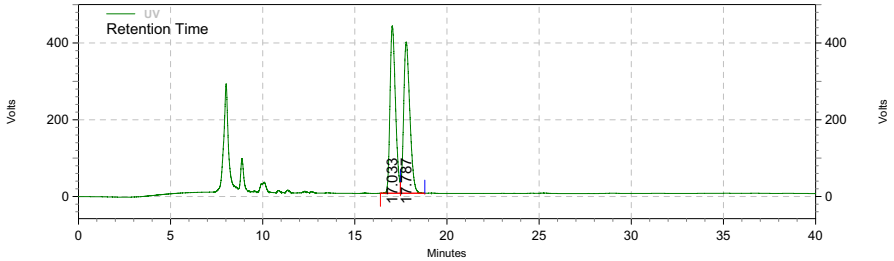


UV Results

Retention Time	Area	Area %	Height	Height %
12.580	849020	1.53	63310	1.66
13.210	54595221	98.47	3752176	98.34
Totals	55444241	100.00	3815486	100.00

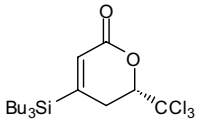
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-5629982col
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 11/8/2006 11:17:28 AM
Printed: 2/24/2007 3:51:14 PM



UV Results

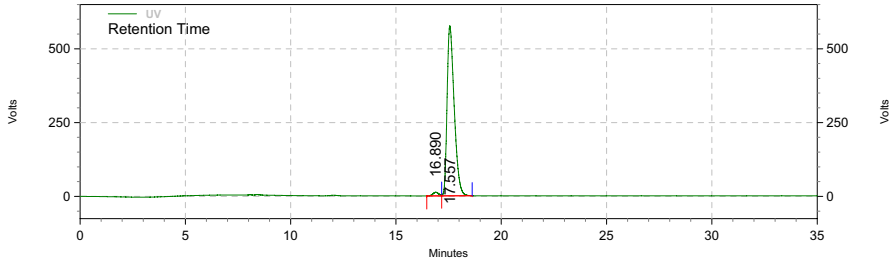
Retention Time	Area	Area %	Height	Height %
17.033	35945660	49.56	1744176	52.52
17.787	36587621	50.44	1576858	47.48
Totals	72533281	100.00	3321034	100.00



6k

Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPBu3Si
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 8:44:17 PM
Printed: 2/24/2007 3:20:56 PM

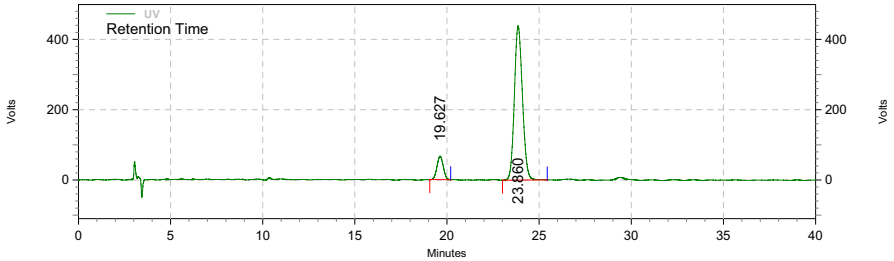


UV Results

Retention Time	Area	Area %	Height	Height %
16.890	931376	1.70	48728	2.07
17.557	53951236	98.30	2302598	97.93
Totals	54882612	100.00	2351326	100.00

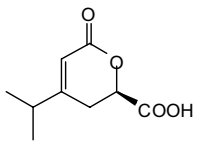
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPCOOH
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/19/2007 10:36:24 AM
Printed: 2/24/2007 3:19:59 PM



UV Results

Retention Time	Area	Area %	Height	Height %
19.627	6330460	10.59	266978	13.21
23.860	53458578	89.41	1754487	86.79
Totals	59789038	100.00	2021465	100.00

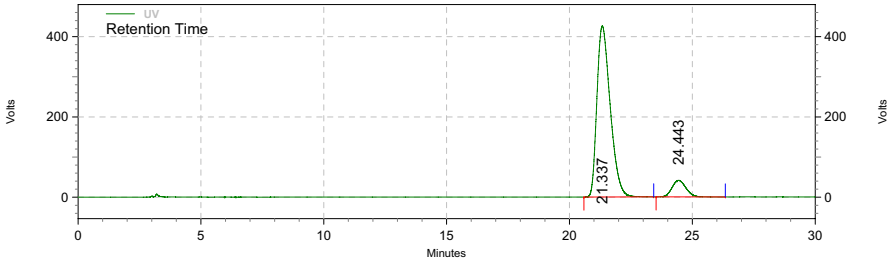


7a

Page 1 of 1

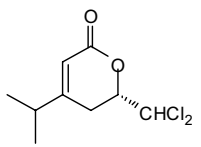
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPCHCl2B
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 2:55:26 PM
Printed: 2/24/2007 3:22:04 PM



UV Results

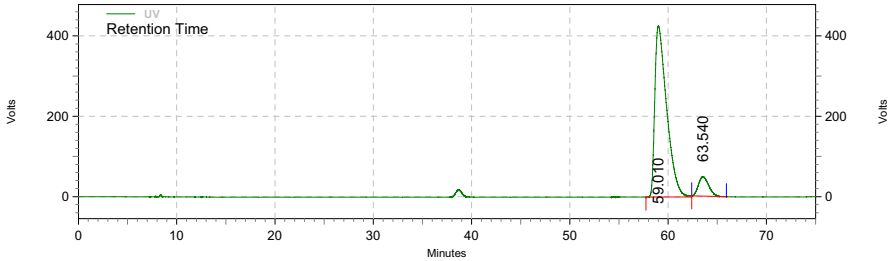
Retention Time	Area	Area %	Height	Height %
21.337	64126839	90.82	1704039	91.15
24.443	6479444	9.18	165392	8.85
Totals	70606283	100.00	1869431	100.00



8a

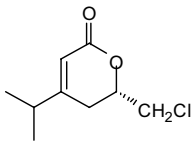
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPCH2Cl
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 5:43:44 PM
Printed: 2/24/2007 3:21:16 PM



UV Results

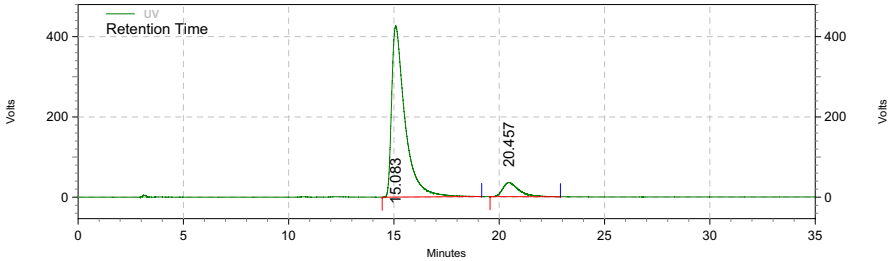
Retention Time	Area	Area %	Height	Height %
59.010	142656428	90.91	1703054	89.76
63.540	14266404	9.09	194217	10.24
Totals	156922832	100.00	1897271	100.00



9a

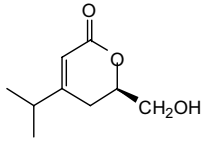
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\FPCH2OH
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 2/17/2007 1:58:17 PM
Printed: 2/24/2007 3:21:38 PM



UV Results

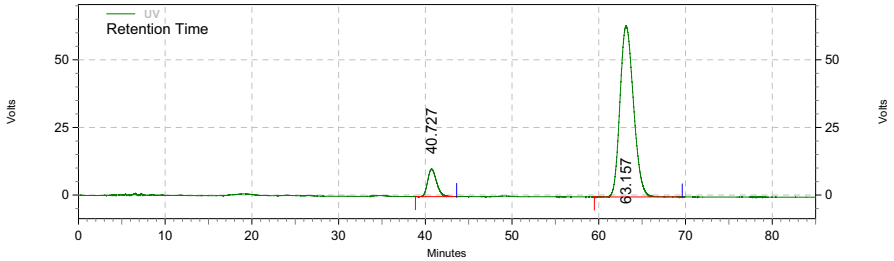
Retention Time	Area	Area %	Height	Height %
15.083	74891093	90.88	1705595	92.41
20.457	7516080	9.12	140127	7.59
Totals	82407173	100.00	1845722	100.00



10a

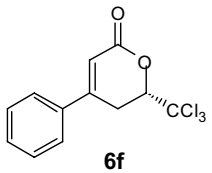
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\Phlactone
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 1/12/2007 3:53:15 PM
Printed: 2/24/2007 3:44:28 PM



UV Results

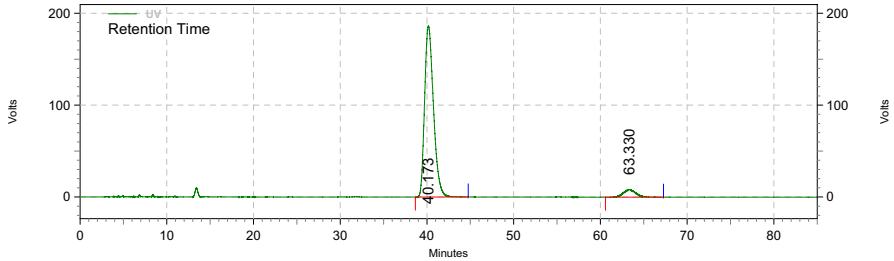
Retention Time	Area	Area %	Height	Height %
40.727	2919964	9.63	40708	13.86
63.157	27410494	90.37	252902	86.14
Totals	30330458	100.00	293610	100.00



6f

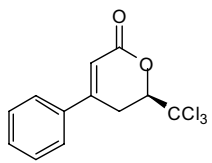
Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Data\pt2-597fr7-9
Method: C:\EZChrom Elite\Enterprise\Projects\diels_alder\Method\pt4.met
Acquired: 1/12/2007 5:19:25 PM
Printed: 2/24/2007 3:43:51 PM



UV Results

Retention Time	Area	Area %	Height	Height %
40.173	52932878	93.92	744893	95.83
63.330	3425741	6.08	32416	4.17
Totals	56358619	100.00	777309	100.00



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Prepared according to the procedure described in the Supporting Information