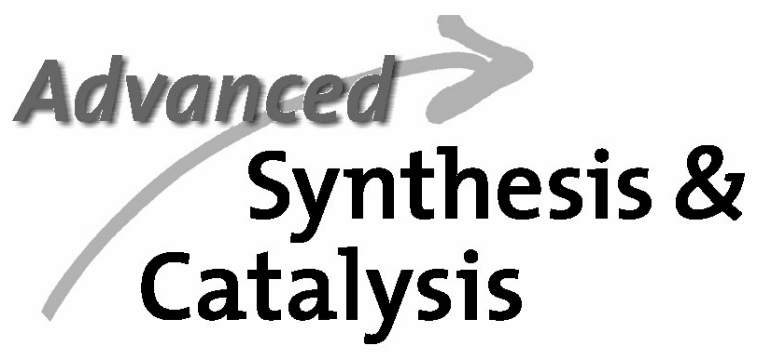


Supporting Information

# Practical Enantioselective Synthesis of β-Lactones Catalyzed by Aluminum Bissulfonamide Complexes

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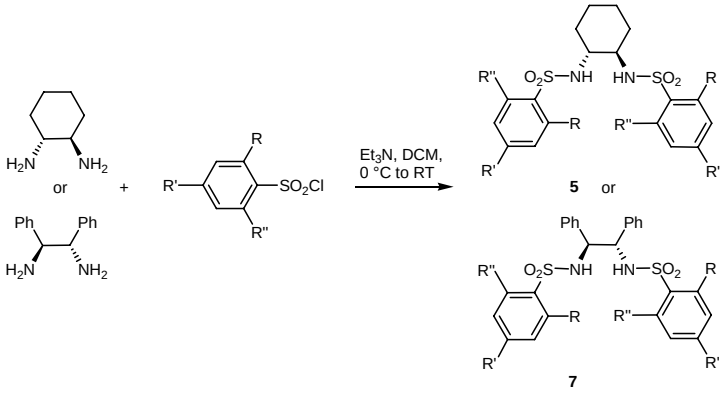
## Experimental

Except as otherwise indicated, all reactions were carried out in oven or flame dried glassware under a positive pressure of argon. Toluene was dried by passage over activated alumina under nitrogen atmosphere. Dichloromethane was purified by distillation and dried by a passage over activated alumina under nitrogen atmosphere. All aldehydes and *N,N*-diisopropylethylamine (Acros, >99.5%) were distilled from $CaH_2$ under nitrogen. Aldehydes **4d** and **4g** were prepared from the commercially available alcohols according to published procedures.[1] Aldehyde **4e** was synthesized from 2-methyl-2-penten-1-ol according to literature procedures.[1,2] Enantiomerically pure 1,2-diaminocyclohexane was generously donated by *Reuter Chemische Apparatebau KG* (RCA; Freiburg, Germany). Enantiomerically pure 1,2-diamino-1,2-diphenylethane was prepared according to literature.[3] (*1S*,*2S*)-1,2-*N*,*N'*-Bis(*p*-toluenesulfonylamino)cyclohexane **5h** (Aldrich, 98%), (*1R*,*2R*)-1,2-*N*,*N'*-bis(trifluoromethylsulfonylamino)cyclohexane **5k** (Aldrich, 97%), methanol (Fluka, HPLC grade), pentane (J.T. Baker, UV quality), *n*-hexane (Fluka, UV quality), cyclohexane (Thommen & Furler), ethyl acetate (Thommen & Furler), diethyl ether (Fluka) and triethylamine (Fluka, >99.5%) were used as purchased. All other laboratory chemicals were purchased from *ABCR*, *Acros*, *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 800 - 30 mbar pressure by rotary evaporation. Non-volatile compounds were dried *in vacuo* at 0.01 mbar. Except as otherwise indicated, reactions were magnetically stirred and monitored either by $^1$H-NMR spectra or 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 aqueous $KMnO_4$ / NaOH. Purification by flash chromatography was

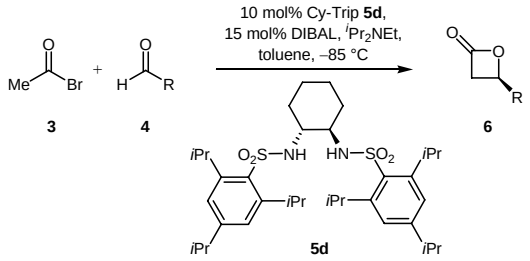
performed on silica gel 60 Å, 32-62, provided by *Fluka,* using a forced flow of eluent at 0.2-0.4 bar pressure. NMR-spectra were recorded on a *Varian Gemini 300* and a *Varian Mercury 300* spectrometer operating at 300 MHz ($^{1}$H) and 75 MHz ($^{13}$C) or by the NMR service of the Laboratory of Organic Chemistry at ETHZ on a *Bruker DRX400* spectrometer operating at 400 MHz ($^{1}$H) and 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. Analytical gas chromatography (GC) was performed on a *Hewlett Packard HP6890 Series gas chromatograph* with a flame ionization detector using a *Supelco GammaDex$^{TM}$ 120 Fused Silica Capillary Column* (30 m x 0.25 mm x 0.25 μm film thickness). Hydrogen was used as the carrier gas at the indicated pressure. Analytical high performance liquid chromatography (HPLC) was performed on a *Hitachi LaChrom Elite liquid chromatograph* equipped with a variable wavelength UV detector (deuterium lamp, 190-600 nm), using a *Daicel Chiralcel$^{TM}$ OD-H column* (25 x 0.46 cm). HPLC grade isopropanol and hexanes were used as the eluting solvents.

**General procedure for the formation of bis(N-sulfonylamino)-1,2-diphenylethane ligands and bis(N-sulfonylamino)cyclohexane-ligands (GP1)[4]**




To a solution of the corresponding diamine (2 mmol, 1 equiv.) in DCM (20 mL) at 0 °C the corresponding sulfonyl chloride (4 mmol, 2 equiv.) and triethylamine (6 mmol, 3 equiv.) were added. The solution was stirred for 30 min at 0 °C. Subsequently, the solution was stirred at ambient temperature until complete conversion as monitored by TLC (typically 20 h). The solvent was removed *in vacuo* and the crude product was purified by flash chromatography (cyclohexane/ethyl acetate).

**General procedure for the formation of β-lactones 6 from α-unbranched aldehydes (GP2)**

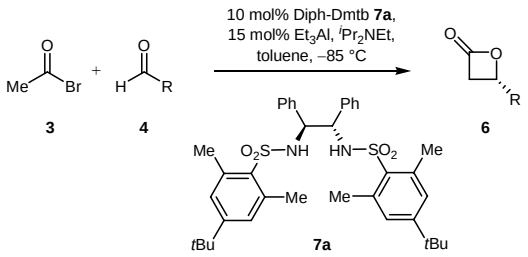



To a mixture of ligand **5d** (0.05 mmol, 0.1 equiv.) in toluene (2 mL) was slowly added at ambient temperature a solution of Dibal (1.0 M in hexane, 0.075 mmol, 0.15 equiv.). The mixture was heated to 80 °C and stirred for 4 h. Subsequently, the solution was stirred for 1 h at ambient temperature. The catalyst solution was then cooled to –85 °C and α-unbranched

aldehyde **4** (0.5 mmol, 1 equiv.), acetyl bromide (**3**, 1.5 mmol, 3 equiv.) and diisopropylethylamine (1.25 mmol, 2.5 equiv.) were successively added. The resulting heterogeneous mixture was stirred at −85 °C until complete conversion as monitored by $^1$H-NMR (24-140 h). The reaction mixture was poured into aqueous 1 M HCl (20 mL) and extracted with diethyl ether (3 x 15 mL). The combined organic phase was dried over $MgSO_4$, filtered and diethyl ether was removed *in vacuo*. The yield was determined by $^1$H-NMR using acetophenone as internal standard.

The crude product mixtures of **6a,f** were purified by flash chromatography (pentane/diethyl ether). The solutions of the crude products were directly added to the column without prior removal of toluene.

**General procedure for the formation of β-lactones 6 from α-branched aldehydes (GP3)**

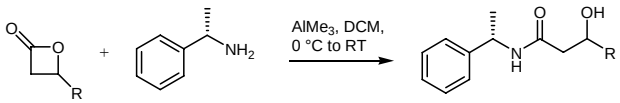



To a mixture of ligand **7a** (0.05 mmol, 0.1 equiv.) in toluene (2 mL) was slowly added at ambient temperature a solution of $Et_3Al$ (1.0 M in hexane, 0.075 mmol, 0.15 equiv.). The mixture was heated to 80 °C and stirred for 4 h. Subsequently, the solution was stirred for 1 h at ambient temperature. The catalyst solution was then cooled to −85 °C and α-branched aldehyde **4** (0.5 mmol, 1 equiv.), acetyl bromide (**3**, 1.5 mmol, 3 equiv.) and diisopropylethylamine (1.25 mmol, 2.5 equiv.) were successively added. The resulting heterogeneous mixture was stirred at −85 °C until complete conversion as monitored by $^1$H-NMR (25-136 h). The reaction mixture was poured into aqueous 1 M HCl (20 mL) and extracted with diethyl ether (3 x 15 mL). The

combined organic phase was dried over $MgSO_4$, filtered and diethyl ether was removed *in vacuo*. The yield was determined by $^1$H-NMR using acetophenone as internal standard.

The crude product mixture of **6b** was purified by flash chromatography (pentane/diethyl ether). The solution of the crude product was directly added to the column without prior removal of toluene.

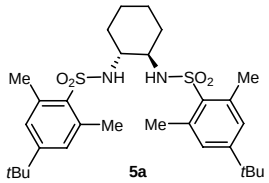
**General procedure for the ring opening of β-lactones 4 (GP4)**




**6** **8**

To a solution of (*S*)-1-phenylethylamine (1.09 mmol, 2 equiv.) in dichloromethane (1.5 mL) at 0 °C was slowly added a solution of trimethylaluminum in hexane (2.0 M, 523 µL, 1.05 mmol, 1.9 equiv.). The mixture was stirred at ambient temperature for 2 h. A solution of the lactone **6** (0.55 mmol) in DCM (1.5 mL) was added dropwise. The reaction was stirred at ambient temperature until complete conversion as monitored by TLC (24 h). The reaction mixture was diluted with dichloromethane (3 mL) and poured into an ice cooled saturated solution of potassium sodium tartrate (10 mL). The mixture was transferred into a separatory funnel and the layers were separated. The aqueous phase was extracted with DCM (5 mL). The combined organic layers were dried over $Na_2SO_4$, filtered and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (cyclohexane/ethyl acetate).

**(*1R*,*2R*)-1,2-*N*,*N*'-Bis(4-*tert*-butyl-2,6-dimethylbenzenesulfonylamino)cyclohexane (5a)**

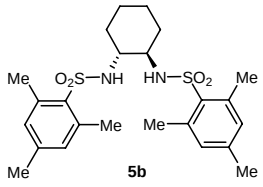



**5a**

Bissulfonamide **5a** was prepared according to GP1 from (*1R,2R*)-cyclohexane-1,2-diamine and 4-*tert*-butyl-2,6-dimethylbenzene-1-sufonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 4:1) gave title compound **5a** as a white solid (1.07 g, 1.89 mmol, yield: 95%).

**$C_{30}H_{46}N_2O_4S_2$**, **MW:** 562.83 g/mol. **Mp:** 157-160 °C. **[α]** $\overset{22.1°C}{D}$ (c = 5.060 , $CHCl_3$) = +4.5 ± 0.2. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 7.12 (*s*, 4 H, C$H_{Ar}$); 4.86 (*d*, *J* = 5.9, 2 H, N*H*); 2.88 (*m*, 2 H, C*H*-N); 2.65 (*s*, 12 H, $C_{Ar}CH_3$); 1.88 (*m*, 2 H, $(CH_2)_{ring}$); 1.55 (*m*, 2 H, $(CH_2)_{ring}$); 1.30 (*s*, 18 H, $C(CH_3)_3$); 1.11 (*m*, 4 H, $(CH_2)_{ring}$). **$^{13}$C NMR (100 MHz, $CDCl_3$, 21 °C):** δ = 155.1, 138.6, 134.3, 128.5, 56.3, 34.6, 33.1, 30.9, 24.2, 23.5. **IR (ATR):** 3287, 2956, 2866, 1595, 1558, 1450, 1406, 1315, 1172, 1143, 1052, 895, 870, 751, 646. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 562.2899. Found: 562.2899. **Anal. Calcd. for $C_{30}H_{46}N_2O_4S_2$:** C, 64.02; H, 8.24; N, 4.98; O, 11.37; S, 11.39. Found: C, 64.10; H, 8.25; N, 4.98.

**(*1R,2R*)-1,2-*N,N*'-Bis(2,4,6-trimethylbenzenesulfonylamino)cyclohexane (5b)**

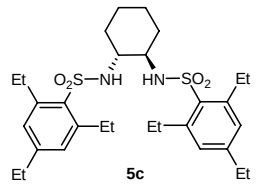


**5b**

Bissulfonamide **5b** was prepared according to GP1 from (*1R,2R*)-cyclohexane-1,2-diamine and 2,4,6-trimethylbenzene-1-sulfonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 8:1) gave title compound **5b** as a white solid (884 mg, 1.85 mmol, yield: 92%).

**$C_{24}H_{34}N_2O_4S_2$**, **MW:** 478.67 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 6.95 (*s*, 4 H, C$H_{Ar}$); 4.90 (*d*, *J* = 5.7, 2 H, N*H*); 2.82 (*m*, 2 H, C*H*-N); 2.61 (*s*, 12 H, $CH_3$); 2.30 (*s*, 6 H, $CH_3$); 1.85 (*m*, 2 H, $(CH_2)_{ring}$); 1.54 (*m*, 2 H, $(CH_2)_{ring}$); 1.08 (*m*, 4 H, $(CH_2)_{ring}$). All other analytical data are in accordance with the literature.[5]

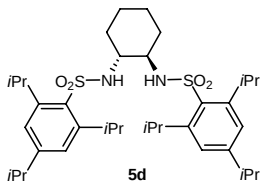
**(*1R*,*2R*)-1,2-*N*,*N*'-Bis(2,4,6-triethylbenzenesulfonylamino)cyclohexane (5c)**




Bissulfonamide **5c** was prepared according to GP1 from (*1R*,*2R*)-cyclohexane-1,2-diamine and 2,4,6-triethylbenzene-1-sulfonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 9:1) gave title compound **5c** as a white solid (913 mg, 1.62 mmol, yield: 81%).

**$C_{30}H_{46}N_2O_4S_2$**, **MW:** 562.83 g/mol. **Mp:** 136-137 °C. **[α]** $[\alpha]_D^{22.1°C}$ (c = 5.115 , $CHCl_3$) = –6.3 ± 0.1. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 7.01 (*s*, 4 H, C$H_{Ar}$); 4.75 (*d*, *J* = 5.8, 2 H, N*H*); 3.02 (*m*, 8 H, $C_{Ar}CH_2$); 2.86 (*m*, 2 H, C*H*-N); 2.63 (*m*, 4 H, $C_{Ar}CH_2$); 1.85 (*m*, 2 H, $(CH_2)_{ring}$); 1.53 (*m*, 2 H; $(CH_2)_{ring}$); 1.27 (*m*, 18 H, $CH_3$); 1.07 (*m*, 4 H, $(CH_2)_{ring}$). **$^{13}$C NMR (100 MHz, $CDCl_3$, 21 °C):** δ = 148.6, 145.5, 133.6, 129.4, 56.4, 33.4, 28.5, 28.4, 24.3, 16.9, 14.9. **IR (ATR):** 3289, 2966, 2934, 2874, 1600, 1562, 1452, 1419, 1312, 1151, 1071, 1048, 954, 903, 875, 658, 632. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 562.2899. Found: 562.2901. **Anal. Calcd. for $C_{30}H_{46}N_2O_4S_2$:** C, 64.02; H, 8.24; N, 4.98; O, 11.37; S, 11.39. Found: C, 64.14; H, 8.01; N, 5.07.

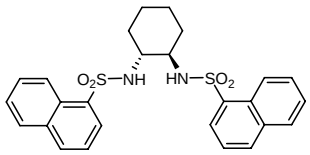
**(*1R*,*2R*)-1,2-*N*,*N*'-Bis(2,4,6-triisopropylbenzenesulfonylamino)cyclohexane (5d)**




Bissulfonamide **5d** was prepared according to GP1 from (*1R*,*2R*)-cyclohexane-1,2-diamine and 2,4,6-triisopropylbenzene-1-sulfonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 12:1) gave title compound **5d** as a white solid (1.23 g, 1.90 mmol, yield: 95%).

**$C_{36}H_{58}N_2O_4S_2$**, **MW:** 646.99 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 7.15 (*s*, 4 H, C*H*$_{Ar}$); 5.03 (*d*, *J* = 5.7, 2 H, N*H*); 4.16 (*m*, 4 H, C*H*$(CH_3)_2$); 3.13 (*m*, 2 H, C*H*-N); 2.90 (*m*, 2 H, C*H*$(CH_3)_2$); 1.85 (*m*, 2 H, $(CH_2)_{ring}$); 1.56 (*m*, 2 H, $(CH_2)_{ring}$); 1.27 (*d*, *J* = 6.8, 24 H, C*H*$_3$); 1.25 (*d*, *J* = 6.9, 12 H, C*H*$_3$); 1.10 (*m*, 4 H, $(CH_2)_{ring}$). All other analytical data are in accordance with the literature.[5]

**(*1R,2R*)-1,2-*N,N'*-Bis(1-naphthylsulfonylamino)cyclohexane (5e)**

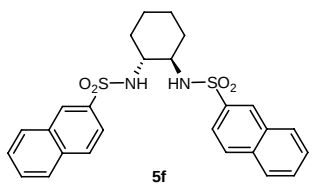



**5e**

Bissulfonamide **5e** was prepared according to GP1 using naphthalene-1-sulfonyl chloride, but using 2.50 mmol of (*1R,2R*)-cyclohexane-1,2-diamine in 30 mL DCM. Purification by flash chromatography (cyclohexane/ethyl acetate 2:1) gave title compound **5e** as a white solid (1.14 g, 2.31 mmol, yield: 92%).

**$C_{26}H_{26}N_2O_4S_2$**, **MW:** 494.63 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 8.52 (*dd*, *J* = 8.5, 0.9, 2 H, C*H*$_{Ar}$); 8.25 (*dd*, *J* = 7.4, 1.3, 2 H, C*H*$_{Ar}$); 8.08 (*d*, *J* = 8.3, 2 H, C*H*$_{Ar}$); 7.96-7.94 (*m*, 2 H, C*H*$_{Ar}$); 7.70-7.66 (*m*, 2 H, C*H*$_{Ar}$); 7.63-7.59 (*m*, 2 H, C*H*$_{Ar}$); 7.56-7.52 (*m*, 2 H, C*H*$_{Ar}$); 5.07 (*d*, *J* = 5.4, 2 H, N*H*); 2.79 (*m*, 2 H, C*H*-N); 1.58 (*m*, 2 H, $(CH_2)_{ring}$); 1.36 (*m*, 2 H, $(CH_2)_{ring}$); 0.99-0.86 (*m*, 4 H, $(CH_2)_{ring}$). All other analytical data are in accordance with the literature.[5]

**(*1R,2R*)-1,2-*N,N'*-Bis(2-naphthylsulfonylamino)cyclohexane (5f)**

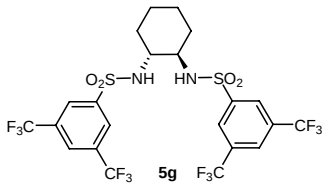



**5f**

Bissulfonamide **5f** was prepared according to GP1 using naphthalene-2-sulfonyl chloride, but using 2.50 mmol of (*1R,2R*)-cyclohexane-1,2-diamine in 30 mL DCM. Purification by flash-chromatography (cyclohexane/ethyl acetate 3:1) gave title compound **5f** as a white solid (1.06 g, 2.15 mmol, yield: 86%).

**$C_{26}H_{26}N_2O_4S_2$, MW:** 494.63 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 8.45 (*m*, 2 H, C*H*$_{Ar}$); 7.91 (*m*, 8 H, C*H*$_{Ar}$); 7.63 (*m*, 4 H, C*H*$_{Ar}$); 4.98 (*d*, *J* = 6.2, 2 H, N*H*); 2.82 (*m*, 2 H, C*H*-N); 1.85 (*m*, 2 H, (C$H_2$)$_{ring}$); 1.50 (*m*, 2 H, (C$H_2$)$_{ring}$); 1.17-0.97 (*m*, 4 H, (C$H_2$)$_{ring}$). All other analytical data are in accordance with the literature.[5]

**(*1R,2R*)-1,2-*N,N'*-Bis(3,5-trifluoromethylbenzenesulfonylamino)cyclohexane (5g)**

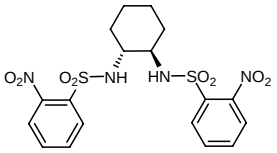


**5g**

Bissulfonamide **5g** was prepared according to GP1 from (*1R,2R*)-cyclohexane-1,2-diamine and 3,5-bis(trifluoromethyl)benzene-1-sulfonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 2:1) gave title compound **5g** as a white solid (1.09 g, 1.64 mmol, yield: 82%).

**$C_{22}H_{18}F_{12}N_2O_4S_2$, MW:** 666.50 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 8.31 (*s*, 4 H, C*H*$_{Ar}$); 8.08 (*m*, 2 H, C*H*$_{Ar}$); 5.06 (*s*, 2 H, N*H*); 2.98 (*m*, 2 H, C*H*-N); 1.81 (*m*, 2 H, (C$H_2$)$_{ring}$); 1.67 (*m*, 2 H, (C$H_2$)$_{ring}$); 1.30-1.15 (*m*, 4 H, (C$H_2$)$_{ring}$). All other analytical data are in accordance with the literature.[6]

**(*1R,2R*)-1,2-*N,N'*-Bis(2-nitrobenzenesulfonylamino)cyclohexane (5i)**

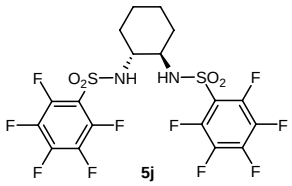



**5i**

Bissulfonamide **5i** was prepared according to GP1 from (*1R,2R*)-cyclohexane-1,2-diamine and 2-nitrobenzene-1-sulfonyl chloride. Purification by flash-chromatography (cyclohexane/ethyl acetate 1:1) gave title compound **5i** as a white solid (1.12 g, 2.30 mmol, yield: 92%).

**$C_{18}H_{20}N_4O_8S_2$, MW:** 484.51 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 8.12 (*m*, 2 H, C*H*$_{Ar}$); 7.84 (*m*, 2 H, C*H*$_{Ar}$); 7.34 (*m*, 4 H, C*H*$_{Ar}$); 5.38 (*m*, 2 H, N*H*); 3.27 (*m*, 2 H, C*H*-N); 1.90 (*m*, 2 H, (C*H*$_2$)$_{ring}$); 1.61 (*m*, 2 H, (C*H*$_2$)$_{ring}$); 1.36-1.20 (*m*, 4 H, (C*H*$_2$)$_{ring}$). All other analytical data are in accordance with the literature.[6]

**(*1R,2R*)-1,2-*N,N'*-Bis(pentafluorobenzenesulfonylamino)cyclohexane (5j)**

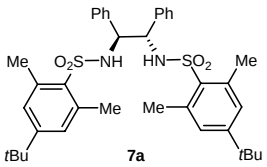



**5j**

Bissulfonamide **5j** was prepared according to GP1 using pentafluorobenzene-1-sulfonyl chloride, but using 2.50 mmol (*1R,2R*)-cyclohexane-1,2-diamine in 30 mL DCM. Purification by flash-chromatography (cyclohexane/ethyl acetate 8:1) gave title compound **5j** as a white solid (863 mg, 1.50 mmol, yield: 75%).

**$C_{18}H_{12}F_{10}N_2O_4S_2$, MW:** 574.41 g/mol. **$^1$H NMR (400 MHz, $CDCl_3$, 21 °C):** δ = 5.46 (*m*, 2 H, N*H*); 3.32 (*m*, 2 H, C*H*-N); 1.92 (*m*, 2 H, (C*H*$_2$)$_{ring}$); 1.72 (*m*, 2 H, (C*H*$_2$)$_{ring}$); 1.44-1.21 (*m*, 4 H, (C*H*$_2$)$_{ring}$). All other analytical data are in accordance with the literature.[5]

**(*1S*,*2S*)-1,2,-*N*,*N*'-Bis(4-*tert*-butyl-2,6-dimethylbenzenesulfonylamino)-1,2-diphenylethylendiamine (7a)**

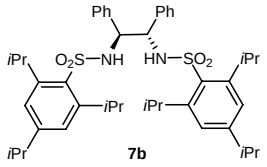


**7a**

Bissulfonamide **7a** was prepared according to GP1 from (*1S*,*2S*)-1,2-diphenylethane-1,2-diamine and 4-*tert*-butyl-2,6-dimethylbenzene-1-sulfonyl chloride. Purification by flash chromatography (cyclohexane/ethyl acetate 8:1) gave title compound **7a** as a white solid (1.17 g, 1.78 mmol, yield: 89%).

**$C_{38}H_{48}N_2O_4S_2$, MW:** 660.93 g/mol. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 6.94-6.79 (*m*, 10 H, C*H*$_{Ar}$); 6.58 (*m*, 4 H, C*H*$_{Ar}$); 5.78 (*m*, 2 H, N*H*); 4.36 (*m*, 2 H, C*H*-N); 2.48 (*s*, 12 H, C*H*$_3$); 1.23 (*m*, 18 H, C*H*$_3$). All other analytical data are in accordance with the literature.[7]

**(*1S*,*2S*)-1,2-*N*,*N*'-Bis(2,4,6-triisopropylbenzenesulfonylamino)-1,2-diphenylethylendiamine (7b)**



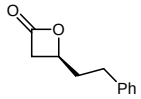
**7b**

Bissulfonamide **7b** was prepared according to GP1 from (*1S*,*2S*)-1,2-diphenylethane-1,2-diamine and 2,4,6-triisopropylbenzene-1-sulfonyl chloride. Purification by flash-chromatography (cyclohexane/ethyl acetate 10:1) gave title compound **7b** as a white solid (1.15 g, 1.55 mmol, yield: 78%).

**$C_{44}H_{60}N_2O_4S_2$, MW:** 745.09 g/mol. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 6.99-6.87 (*m*, 10 H, C*H*$_{Ar}$); 6.58 (*m*, 4 H, C*H*$_{Ar}$); 5.71 (*m*, 2 H, N*H*); 4.47 (*m*, 2 H, C*H*-N); 4.00 (*m*, 4 H,

C*H*($CH_3$)$_2$); 2.83 (*m*, 4 H, C*H*($CH_3$)$_2$); 1.18 (*m*, 24 H, C$H_3$); 1.05 (*d*, *J* = 6.7, 12 H, C$H_3$). All other analytical data are in accordance with the literature.[8]

**(*S*)-4-Phenylethyl-oxetan-2-one (6a)**



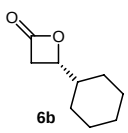

**6a**

β-Lactone **6a** was prepared according to GP2 using aldehyde **4a** (reaction time: 48 h) and was furnished as solution in toluene (0.47 mmol, yield: 93%, *ee* = 88%). The *ee* value was determined by HPLC (Chiralcel OD-H, 97:3 *n*-hexane/*i*PrOH, 1.0 mL/min, 210 nm).

To determine the isolated yield, **6a** was prepared according to GP2, but using 1.50 mmol aldehyde **4a** in 6 mL toluene. Purification by flash chromatography (pentane → pentane/ diethyl ether 4:1) gave **6a** as colorless oil (230 mg, 1.30 mmol, 87%, *ee* = 88%).

**$C_{11}H_{12}O_2$**, **MW:** 176.21 g/mol. **[α]** $[\alpha]_D^{21.1°C}$ (c = 0.915, $CHCl_3$) = −48.8 ± 0.3. Spectral data including the specific optical rotation have been reported earlier for the (*R*)-enantiomer.[9] **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 7.25 (*m*, 5 H, C$H_{Ar}$); 4.50 (*m*, 1 H, C*H*-O); 3.48 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.03 (*dd*, *J* = 16.3, 4.3, 1 H, CH*H*-C(O)); 2.77 (*m*, 2 H, $CH_2CH_2C_{Ar}$); 2.13 (*m*, 2 H, $CH_2CH_2C_{Ar}$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 167.9, 139.9, 128.5, 128.2, 126.3, 70.4, 42.9, 36.4, 31.3. **IR (ATR):** ν = 3028, 2933, 1817, 1603, 1131, 1110 827, 748, 699. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 176.0832. Found: 176.0833. **Anal. Calcd. for $C_{11}H_{12}O_2$**: C, 74.98; H, 6.86; O, 18.16. Found: C, 74.84; H, 6.95.

**(*S*)-4-Cyclohexyl-oxetan-2-one (6b)**



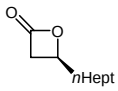

**6b**

β-Lactone **6b** was prepared according to GP3 using aldehyde **4b** (reaction time: 25 h) and was furnished as solution in toluene (0.44 mmol, yield: 88%, *ee* = 90%). The *ee* value was determined by GC (GammaDex$^{TM}$, 145 °C, 2.0 mL/min).

To determine the isolated yield **6b** was prepared according to GP3, but using 1.50 mmol of aldehyde **4b** in 6 mL toluene. Purification by flash chromatography (pentane → pentane/diethyl ether 8:1) gave **6b** as colorless oil (209 mg, 1.35 mmol, yield: 90%, *ee* = 90%).

**$C_9H_{14}O_2$, MW:** 154.21 g/mol. **[α]** $_D^{25.0°C}$ (c = 0.605, $CHCl_3$) = +18.8 ± 1.0. Spectral data including the specific optical rotation have been reported earlier for the (*S*)-enantiomer.[10] **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.19 (*ddd*, *J* = 8.2, 5.8, 4.4, 1 H, C*H*-O); 3.42 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.10 (*dd*, *J* = 16.3, 4.4, 1 H, CH*H*-C(O)); 1.93 (*m*, 1 H, C*H*$(CH_2)_2$); 1.82-1.54 & 1.23 & 1.00 (3 x *m*, 10 H, 5 x $(CH_2)_{ring}$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.4, 74.8, 42.0, 41.0, 28.2, 27.1, 26.0, 25.4, 25.2. **IR (ATR):** ν = 2926, 2854, 1818, 1450, 1275, 1117, 948, 866, 853, 833. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 154.0988. Found: 154.0992. **Anal. Calcd. for $C_9H_{14}O_2$**: C, 70.10; H, 9.15; O, 20.75. Found: C, 70.15; H, 9.40.

**(*S*)-4-*n*-Heptyl-oxetan-2-one (6c)**

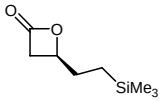



**6c**

β-Lactone **6c** was prepared according to GP2 using aldehyde 4c (reaction time: 63 h), but using 1.00 mmol of aldehyde **4c** in 4 mL toluene. **6c** was furnished as solution in toluene (0.82 mmol, yield: 86%, *ee* = 84%). The *ee* value was determined by HPLC (Chiralcel OD-H, 95:5 *n*-hexane/*i*PrOH, 1.0 mL/min, 210 nm) after ring opening with (*S*)-1-phenylethylamine (*vide infra*).

**$C_{10}H_{18}O_2$**, **MW:** 170.25 g/mol. **$[\alpha]_D^{23.8°C}$** (c = 1.660, $CHCl_3$) = –24.8 ± 0.7. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.50 (*m*, 1 H, C*H*-O); 3.50 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.05 (*dd*, *J* = 16.3, 4.3, 1 H, CH*H*-C(O)); 1.93-1.68 (*m*, 2 H, $CH_2CH_2CH$); 1.50-1.28 (*m*, 10 H, $(CH_2)_5CH_3$); 0.88 (*m*, 3 H, $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.2, 71.3, 42.9, 34.7, 31.7, 29.2, 29.1, 25.0, 22.7, 14.2. **IR (ATR):** ν = 2926, 2856, 1822, 1464, 1124, 946, 860, 813. **MS (EI) *m/z*:** 43.0 (100), 128.1 [$M^+$-$C_3H_7$] (10). **Anal. Calcd. for $C_{10}H_{18}O_2$**: C, 70.55; H, 10.66; O, 18.80. Found: C, 70.62; H, 10.67.

**(*R*)-4-(2-Trimethylsilanyl-ethyl)-oxetan-2-one (6d)**

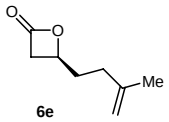



**6d**

β-Lactone **6d** was prepared according to GP2 using aldehyde **4d** (reaction time: 62 h) and was furnished as solution in toluene (0.41 mmol, yield: 82%, *ee* = 84%). The *ee* value was determined by GC (GammaDex™, 100 °C, 2.0 mL/min).

**$C_8H_{16}O_2Si$**, **MW:** 172.30 g/mol. **$[\alpha]_D^{25.4°C}$** (c = 1.140, $CHCl_3$) = –13.3 ± 0.4. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.45 (*m*, 1 H, C*H*-O); 3.47 (*dd*, *J* = 16.3, 5.7, 1 H, C*H*H-C(O)); 3.03 (*dd*, *J* = 16.3, 4.3, 1 H, CH*H*-C(O)); 1.92-1.64 (*m*, 2 H, $CHCH_2$); 0.64-0.41 (*m*, 2 H, $CH_2Si$); 0.02 (*s*, 9 H, 3 x $CH_3Si$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.3, 73.0, 42.3, 29.2, 11.1, –1.8. **IR (ATR):** ν = 2954, 2898, 1824, 1739, 1414, 1248, 1124, 834, 762, 691. **HRMS (EI) *m/z*:** Calc. for [$MH^+$]: 173.0998. Found: 173.0993. **Anal. Calcd. for $C_8H_{16}O_2Si$**: C, 55.77; H, 9.36; O, 18.57; Si, 16.30. Found: C, 55.81; H, 9.34.

**(*S*)-4-(3-Methyl-but-3-enyl)oxetan-2-one (6e)**

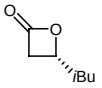



**6e**

β-Lactone **6e** was prepared according to GP2 using aldehyde **4e** (reaction time: 140 h) and was furnished as solution in toluene (0.46 mmol, yield: 92%, *ee* = 88%). The *ee* value was determined by GC (GammaDex$^{TM}$, 90 °C, 2.0 mL/min).

**$C_8H_{12}O_2$, MW:** 140.18 g/mol. **[α]** $_D^{24.2°C}$ (c = 1.450, $CHCl_3$) = –23.4 ± 0.7. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.75 (*d*, *J* = 18.3, 2 H, C*H*$_2$-C); 4.52 (*m*, 1 H, C*H*-O); 3.52 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.08 (*dd*, *J* = 16.3, 4.3, 1 H, CH*H*-C(O)); 2.23-1.84 (*m*, 4 H, C$H_2$C$H_2$); 1.75 (*s*, 3 H, C$H_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.0, 143.5, 111.0, 70.8, 42.9, 33.0, 32.7, 22.4. **IR (ATR):** ν = 2970, 2938, 1819, 1650, 1444, 1132, 1111, 885, 830. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 140.0832. Found: 140.0831. **Anal. Calcd. for $C_8H_{12}O_2$**: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.72; H, 8.85.

**(*R*)-4-Isobutyl-oxetan-2-one (6f)**



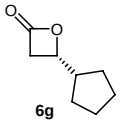

**6f**

β-Lactone **6f** was prepared according to GP3 using aldehyde **4f** (reaction time: 26 h), but using Dibal instead of $Et_3Al$ and ligand **7b**. **6f** was furnished as solution in toluene (0.49 mmol, yield: 98%, *ee* = 85%). The *ee* value was determined by GC (GammaDex$^{TM}$, 100 °C, 2.0 mL/min).

To determine the isolated yield the crude product was purified by flash chromatography (pentane → pentane/ diethyl ether 4:1) giving **6f** as colorless oil (57 mg, 0.43 mmol, yield: 85%, *ee* = 85%).

**$C_7H_{12}O_2$**, **MW:** 128.17 g/mol. **$[\alpha]_D^{25.9°C}$** (c = 0.920, $CHCl_3$) = +19.3 ± 0.8. Spectral data including the specific optical rotation have been reported earlier for the (*S*)-enantiomer.[9] **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.58 (*m*, 1 H, C*H*-O); 3.54 (*dd*, *J* = 16.2, 5.6, 1 H, C*H*H-C(O)); 3.05 (*dd*, *J* = 16.5, 4.2, 1 H, CH*H*-C(O)); 1.79 & 1.58 (2 x *m*, 3 H, $CH_2CH(CH_3)_2$); 0.95 (*d*, *J* = 6.6, 6 H, 2 x $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.2, 70.2, 43.6, 43.4, 25.4, 22.8, 22.2. **IR (ATR):** ν = 2960, 2874, 1820, 1118, 881, 805. **MS (EI) *m/z*:** 128.1 [$M^+$] (6), 43.1 (100). **Anal. Calcd. for $C_7H_{12}O_2$**: C, 65.60; H, 9.44; O, 24.96. Found: C, 65.50; H, 9.45.

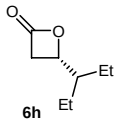
**(*S*)-4-Cyclopentyl-oxetan-2-one (6g)**




β-Lactone **6g** was prepared according to GP3 using aldehyde **4g** (reaction time: 84 h) and was furnished as solution in toluene (0.41 mmol, yield: 90%, *ee* = 80%). The *ee* value was determined by GC (GammaDex™, 100 °C, 2.0 mL/min).

**$C_8H_{12}O_2$**, **MW:** 140.18 g/mol. **$[\alpha]_D^{23.3°C}$** (c = 1.770, $CHCl_3$) = +27.7 ± 0.5. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.37 (*ddd*, *J* = 8.0, 5.8, 4.3, 1 H, C*H*-O); 3.47 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.07 (*dd*, *J* = 16.3, 4.3, 1 H, CH*H*-C(O)); 2.23 (*m*, 1 H, $CH(CH_2)_2$); 1.72 & 1.45 & 1.26 (3 x *m*, 8 H, 4 x $(CH_2)_{ring}$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.3, 74.2, 43.5, 41.8, 28.4, 27.7, 25.7, 25.6. **IR (ATR):** ν = 2954, 2869, 1816, 1277, 1123, 857. **MS (EI) *m/z*:** 140.1 [$M^+$] (3), 67.1 (100). **Anal. Calcd. for $C_8H_{12}O_2$**: C, 68.55; H, 8.63; O, 22.83. Found: C, 68.72; H, 8.79.

**(*S*)-4-(1-Ethyl-propyl)-oxetan-2-one (6h)**

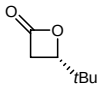


**6h**

β-Lactone **6h** was prepared according to GP3 using aldehyde **4b** (reaction time: 136 h) and was furnished as solution in toluene (0.47 mmol, yield: 94%, *ee* = 80%). The *ee* value was determined by GC (GammaDex$^{TM}$, 100 °C, 2.0 mL/min).

**$C_8H_{14}O_2$, MW:** 142.20 g/mol. **$[\alpha]_D^{26.0°C}$** (c = 1.000, $CHCl_3$) = +13.7 ± 0.7. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.37 (*ddd*, *J* = 8.3, 5.7, 4.5, 1 H, C*H*-O); 3.47 (*dd*, *J* = 16.3, 5.8, 1 H, C*H*H-C(O)); 3.12 (*dd*, *J* = 16.3, 4.4, 1 H, CH*H*-C(O)); 1.55 + 1.36 (2 x *m*, 5 H, C*H*($CH_2$)$_2$); 0.93 (*m*, 6 H, 2 x $CH_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.3, 73.8, 44.7, 41.7, 21.6, 21.0, 11.1, 10.4. **IR (ATR):** ν = 2965, 2878, 1825, 1462, 1277, 1119, 862. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 142.0988. Found: 142.0987. **Anal. Calcd. for $C_8H_{14}O_2$**: C, 67.57; H, 9.92; O, 22.50. Found: C, 67.52; H, 9.68.

**(*S*)-4-*tert*-Butyl-oxetan-2-one (6i)**



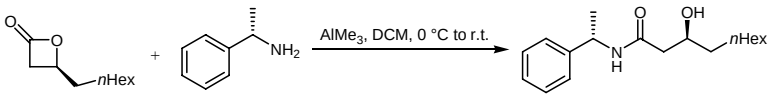
**6i**

β-Lactone **6i** was prepared according to GP3 using aldehyde **4i** (reaction time: 135 h) and was furnished as solution in toluene (0.42 mmol, yield: 83%, *ee* = 78%) The *ee* value was determined by HPLC (Chiralcel OD-H, 97:3 *n*-hexane/*i*PrOH, 1.0 mL/min, 210 nm) after ring opening with (*S*)-1-phenylethylamine (*vide infra*).

**$C_7H_{12}O_2$, MW:** 128.17 g/mol. **$[\alpha]_D^{24.4°C}$** (c = 0.825, $CHCl_3$) = +18.3 ± 0.8. Spectral data including the specific optical rotation have been reported earlier for the (*S*)-enantiomer.[10] **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C):** δ = 4.25 (*dd*, *J* = 6.0, 4.5, 1 H, C*H*-O); 3.32 (*dd*, *J* = 16.5, 6.0, 1 H, C*H*H-

C(O)); 3.16 (*dd*, *J* = 16.5, 4.5, 1 H, CH*H*-C(O)); 1.00 (*s*, 9 H, 3 x C$H_3$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 168.2, 77.9, 38.2, 32.9, 24.1. **IR (ATR):** ν = 2963, 2875, 1823, 1129, 944, 866. **HRMS (EI) *m/z*:** Calc. for [$M^+$]: 128.0832. Found: 128.0828. **Anal. Calcd. for $C_7H_{12}O_2$**: C, 65.60; H, 9.44; O, 24.97. Found: C, 65.49; H, 9.29.

**(*S*)-3-Hydroxy-decanoic acid ((*S*)-1-phenyl-ethyl)amide (8c)**



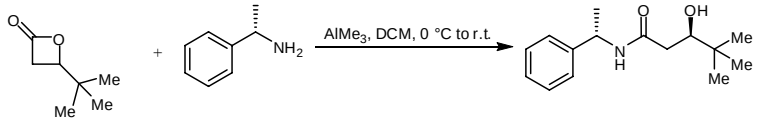

**6c** **8c**

Amide **8c** was prepared according to GP4 using 4-*n*heptyl-oxetan-2-one **6c** (0.21 mmol) in DCM (1.2 mL). Purification by flash chromatography (cyclohexane/ethyl acetate 2:1) gave title compound **8c** as a white solid (54 mg, 0.19 mmol, yield: 89%). The *dr* value of the crude product was determined by HPLC (Chiralcel OD-H, 97:3 *n*-hexane/*i*PrOH, 1.0 mL/min, 210 nm).

**$C_{18}H_{29}NO_2$**, **MW:** 291.43 g/mol. **MP:** 87-88 °C ((*S*)-3-hydroxy isomer). **$[\alpha]_D^{25.9°C}$** ((*S*)-3-hydroxy isomer, c = 0.875, $CHCl_3$) = 57.5 ± 0.5. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C, mixture of (*S*)- and (*R*)-3-hydroxy isomers):** δ = 7.37-7.23 (*m*, 5 H, C$H_{Ar}$); 6.03 (*m*, 1 H, N*H*); 5.14 (*m*, 1 H, C*H*-N); 3.98 (*m*, 1 H, C*H*-O); 3.53 (*m*, 1 H, O*H*); 2.40-2.21 (*m*, 2 H, C$H_2$-C(O)); 1.49 (*d*, *J* = 6.8, 3 H, C$H_3$-CH); 1.42-1.26 (*m*, 12 H, C$H_2$); 0.87 (*m*, 3 H, C$H_3$-$CH_2$). **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C, (*S*)-3-hydroxy isomer):** δ = 7.36-7.23 (*m*, 5 H, C$H_{Ar}$); 6.17 (*d*, *J* = 7.4, 1 H, N*H*); 5.12 (*m*, 1 H, C*H*-N); 3.97 (*m*, 1 H, C*H*-O); 3.58 (*d*, *J* = 3.6, 1 H, O*H*); 2.36 (*dd*, *J* = 15.3, 2.9, 1 H, C*H*H-C(O)); 2.24 (*dd*, *J* = 15.3, 8.9, 1 H, CH*H*-C(O)); 1.48 (*d*, *J* = 6.9, 3 H, C$H_3$-CH); 1.42-1.26 (*m*, 12 H, C$H_2$); 0.87 (*m*, 3 H, C$H_3$-$CH_2$). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C):** δ = 171.5, 143.0, 128.7, 127.4, 126.0, 68.7, 48.7, 42.5, 36.9, 31.7, 29.5, 29.2, 25.4, 22.6, 21.9, 14.1. **IR (ATR):** ν = 3292, 3204, 2921, 2851, 1635, 1540, 1470, 1453, 1376, 1129, 1085, 1019, 694. **HRMS (ESI)**

***m/z*:** Calc. for [$MNa^+$]: 314.2091. Found: 314.2087. **Anal. Calcd. for $C_{18}H_{29}NO_2$**: C, 74.18; H, 10.03; N, 4.81; O, 10.98. Found: C, 74.42; H, 10.07; N, 4.81.

**(*S*)-3-Hydroxy-4,4-dimethyl-pentanoic acid ((*S*)-1-phenyl-ethyl)amide (8i)**




**6i** **8i**

Amide **8i** was prepared according to GP4 using 4-*tert*-butyl-oxetan-2-one (0.55 mmol) **6i** in DCM (3 mL). Purification by flash chromatography (cyclohexane/ethyl acetate 2:1) gave title compound **8i** as an amorphous colorless solid (102 mg, 0.41 mmol, yield: 75%, *ee* = 79%). The *dr* value of the crude product was determined by HPLC (Chiralcel OD-H, 97:3 *n*-hexane/*i*PrOH, 1.0 mL/min, 210 nm).

**$C_{15}H_{23}NO_2$**, **MW:** 249.35 g/mol. **MP:** 66-67 °C ((*S*)-3-hydroxy isomer). **$[\alpha]_D^{25.7°C}$** ((*S*)-3-hydroxy isomer, c = 0.995, $CHCl_3$) = 87.3 ± 0.4. **$^1$H NMR (300 MHz, $CDCl_3$, 21 °C, (*S*)-3-hydroxy isomer):** δ = 7.37-7.23 (*m*, 5 H, C$H_{Ar}$); 6.18 (*m*, 1 H, N*H*); 5.13 (*m*, 1 H, C*H*-N); 3.66 (*m*, 1 H, C*H*-O); 3.57 (*d*, *J* = 3.1, 1 H, O*H*); 2.34 (*dd*, *J* = 15.3, 2.2, 1 H, C*H*H-C(O)); 2.21 (*dd*, *J* = 14.9, 10.3, 1 H, CH*H*-C(O)); 1.49 (*d*, *J* = 6.9, 3 H, C$H_3$-CH); 0.90 (*s*, 9 H, C$H_3$-C). **$^{13}$C NMR (75 MHz, $CDCl_3$, 21 °C, (*S*)-3-hydroxy isomer):** δ = 172.0, 142.8, 128.6, 127.3, 126.0, 76.1, 48.8, 37.7, 34.5, 25.7, 21.9. **IR (ATR):** ν = 3466, 3283, 3066, 2962, 2871, 1641, 1623, 1539, 1387, 1375, 1362, 1078, 1013, 761, 697. **HRMS (ESI) *m/z*:** Calc. for [$MNa^+$]: 272.1621. Found: 272.1627. **Anal. Calcd. for $C_{15}H_{23}NO_2$**: C, 72.25; H, 9.30; N, 5.62;O, 12.83. Found: C, 72.09; H, 9.33; N, 5.56.

## References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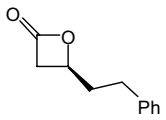
LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 13:19:18 USER:rkull GROUP:peters SAMPLE:Lacton-Zimt

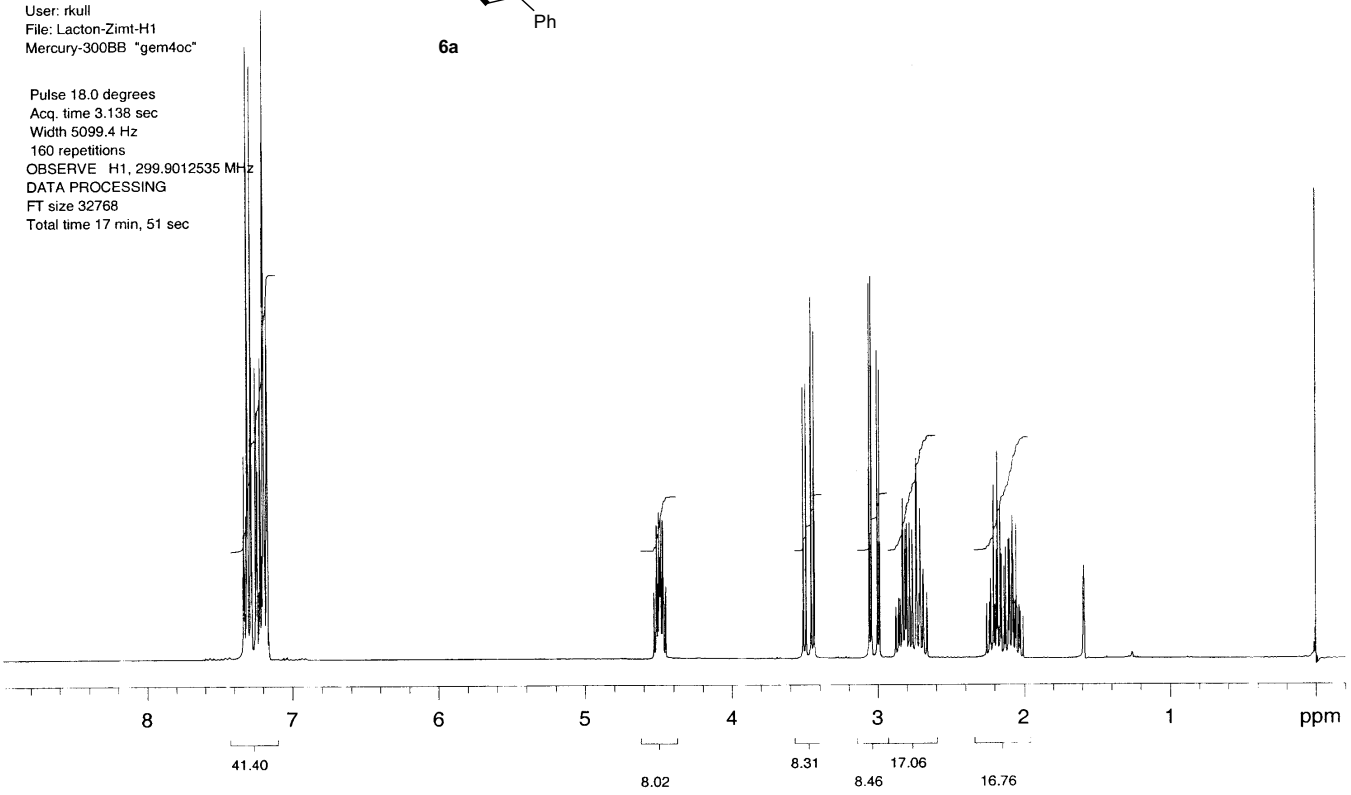
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: Lacton-Zimt-H1
Mercury-300BB "gem4oc"

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
160 repetitions
OBSERVE H1, 299.9012535 MHz
DATA PROCESSING
FT size 32768
Total time 17 min, 51 sec




**6a**

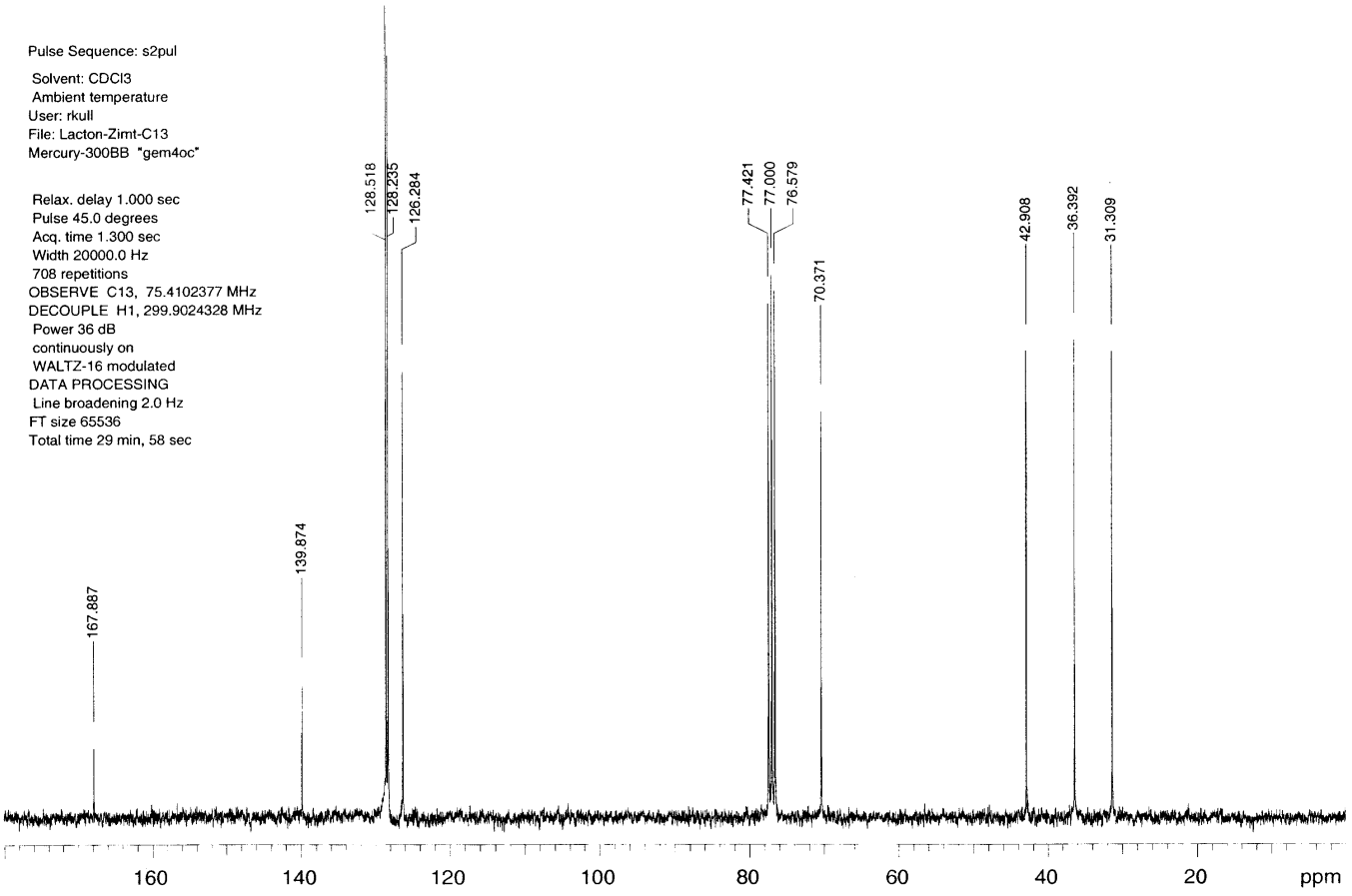



LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 13:16:45 USER:rkull GROUP:peters SAMPLE:Lacton-Zimt

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: Lacton-Zimt-C13
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
708 repetitions
OBSERVE C13, 75.4102377 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 58 sec



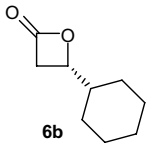
LOC ETHZ NMR Mercury 300MHz Nr.4 03/04/06 15:57:58 USER:rkull GROUP:peters SAMPLE:TK2b-4rac-dest

STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"



**6b**

Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
360 repetitions
OBSERVE H1, 299.9012457 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 49 sec




LOC ETHZ NMR Mercury 300MHz Nr.4 03/04/06 15:55:45 USER:rkull GROUP:peters SAMPLE:TK2b-4rac-dest-C13

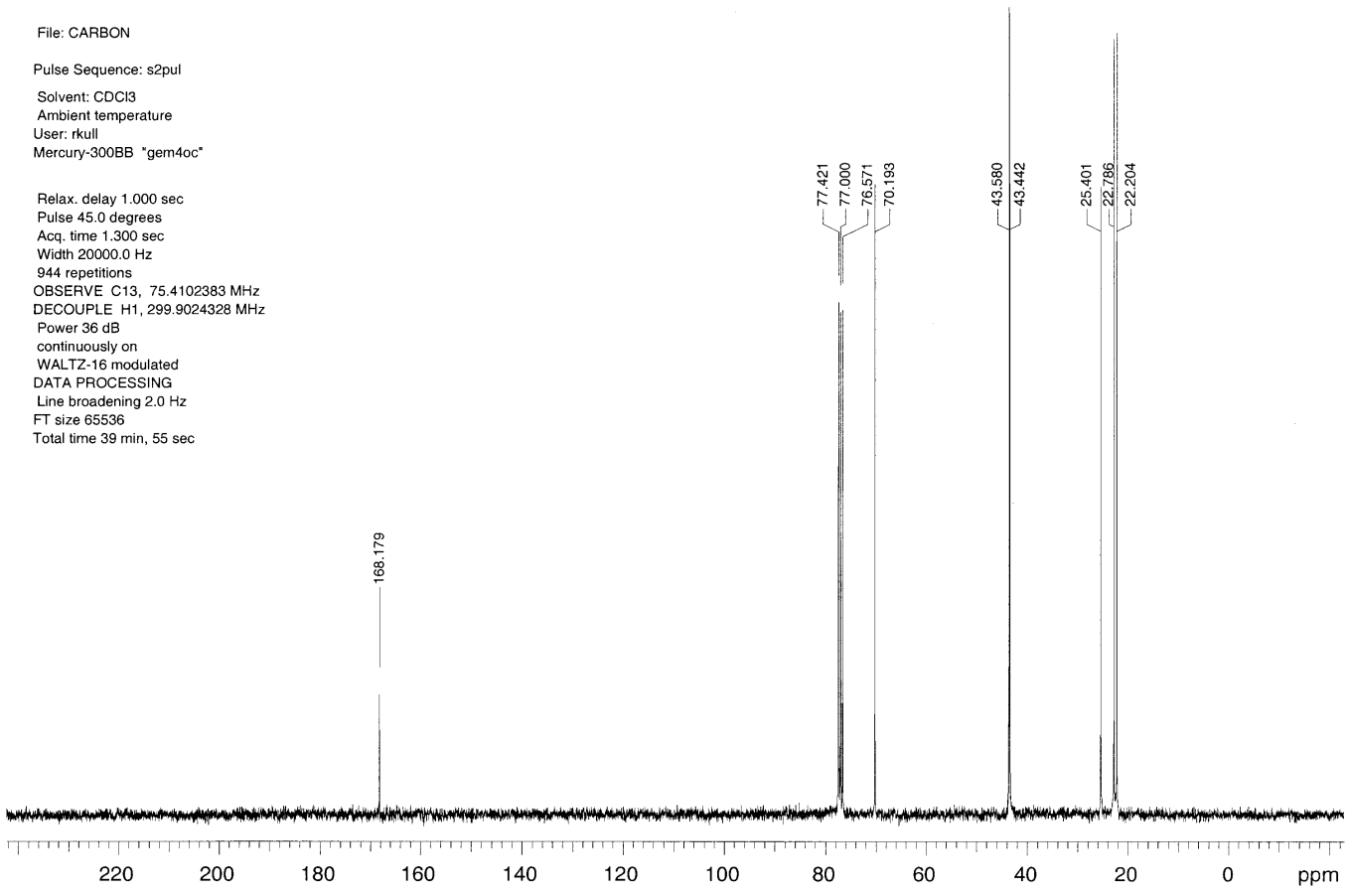
13C OBSERVE

File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
944 repetitions
OBSERVE C13, 75.4102383 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 39 min, 55 sec



LOC ETHZ NMR Mercury 300MHz Nr.4 11/10/06 16:27:20 USER:rkull GROUP:peters SAMPLE:TK2h-11Chrom

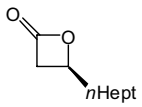
STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
384 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 24 min, 53 sec




**6c**




LOC ETHZ NMR Mercury-vx 300MHz Nr.6 11/13/06 13:52:06 USER:rkull GROUP:peters SAMPLE:TK2h-11ChromC13

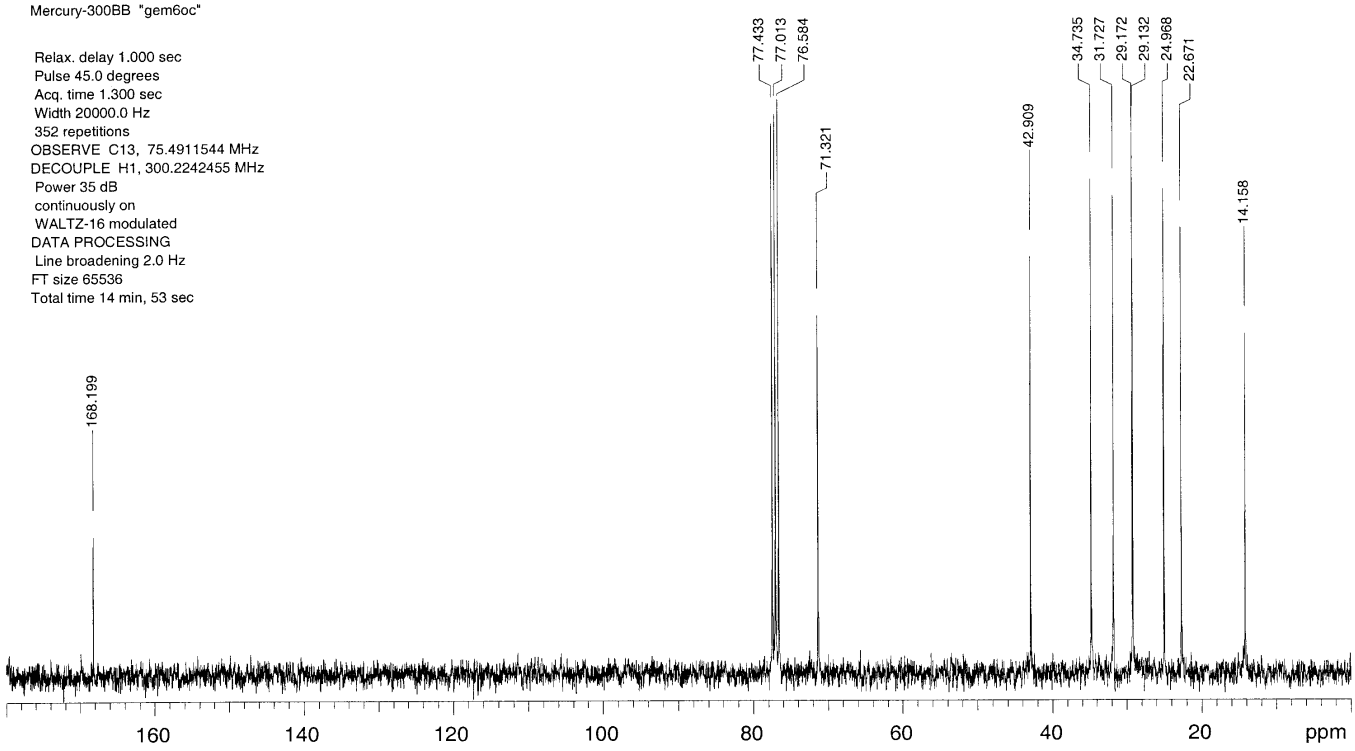
13C OBSERVE

File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem6oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
352 repetitions
OBSERVE C13, 75.4911544 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 14 min, 53 sec



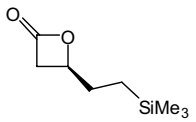
LOC ETHZ NMR Gemini 300 MHz Nr.3 11/27/06 14:18:08 USER:rkull GROUP:peters SAMPLE:TK2k-8Fr6

STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
GEMINI-300BB "gem3oc"




**6d**

Pulse 29.5 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
256 repetitions
OBSERVE H1, 300.0836333 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 49 sec



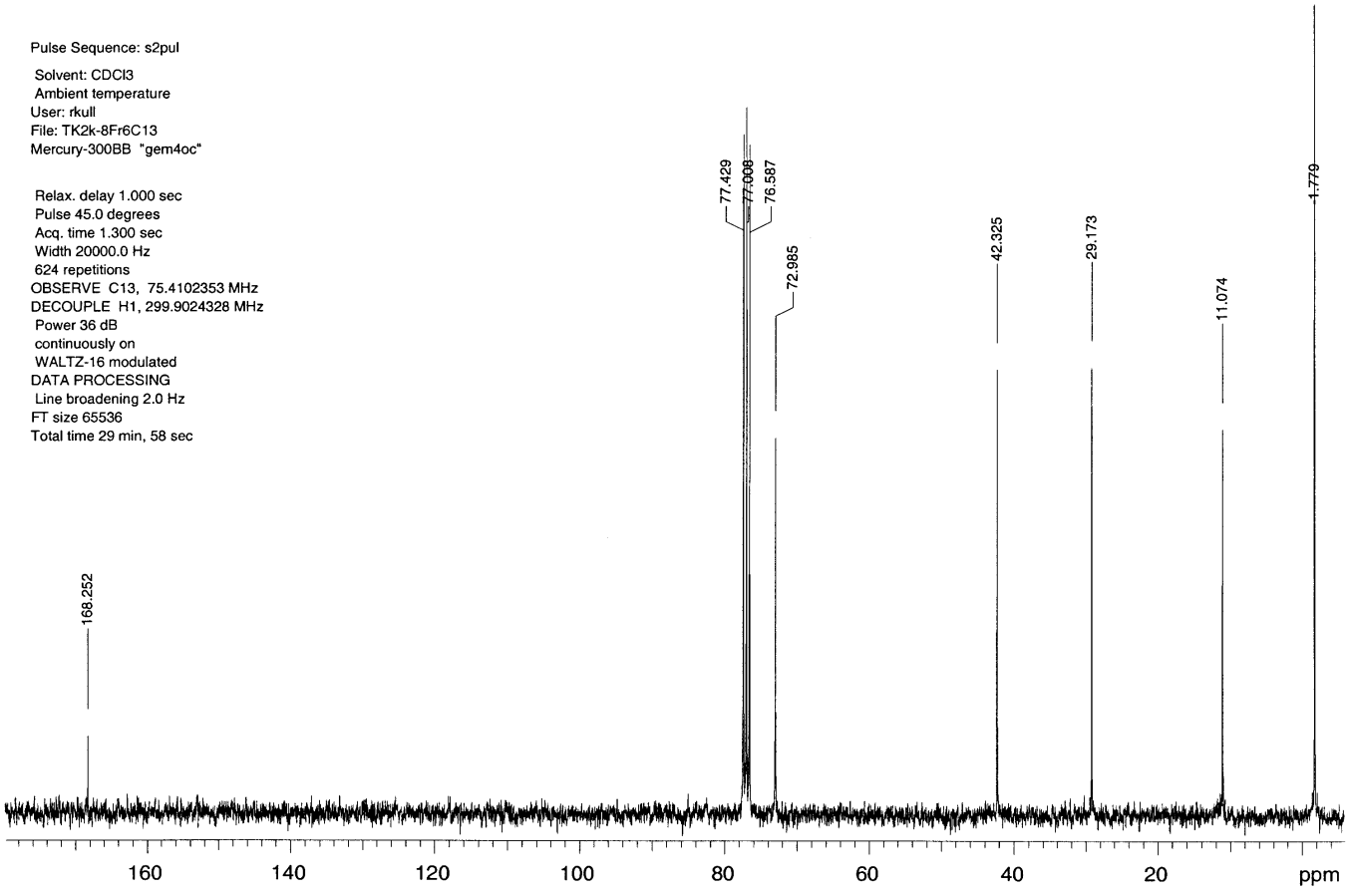

LOC ETHZ NMR Mercury 300MHz Nr.4 11/27/06 13:56:16 USER:rkull GROUP:peters SAMPLE:TK2k-8Fr6

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2k-8Fr6C13
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
624 repetitions
OBSERVE C13, 75.4102353 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 58 sec



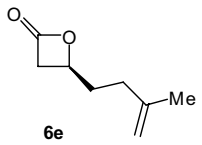
LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 15:54:10 USER:rkull GROUP:peters SAMPLE:TK2m-7Chrom

STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"




**6e**

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
192 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 16 min, 58 sec



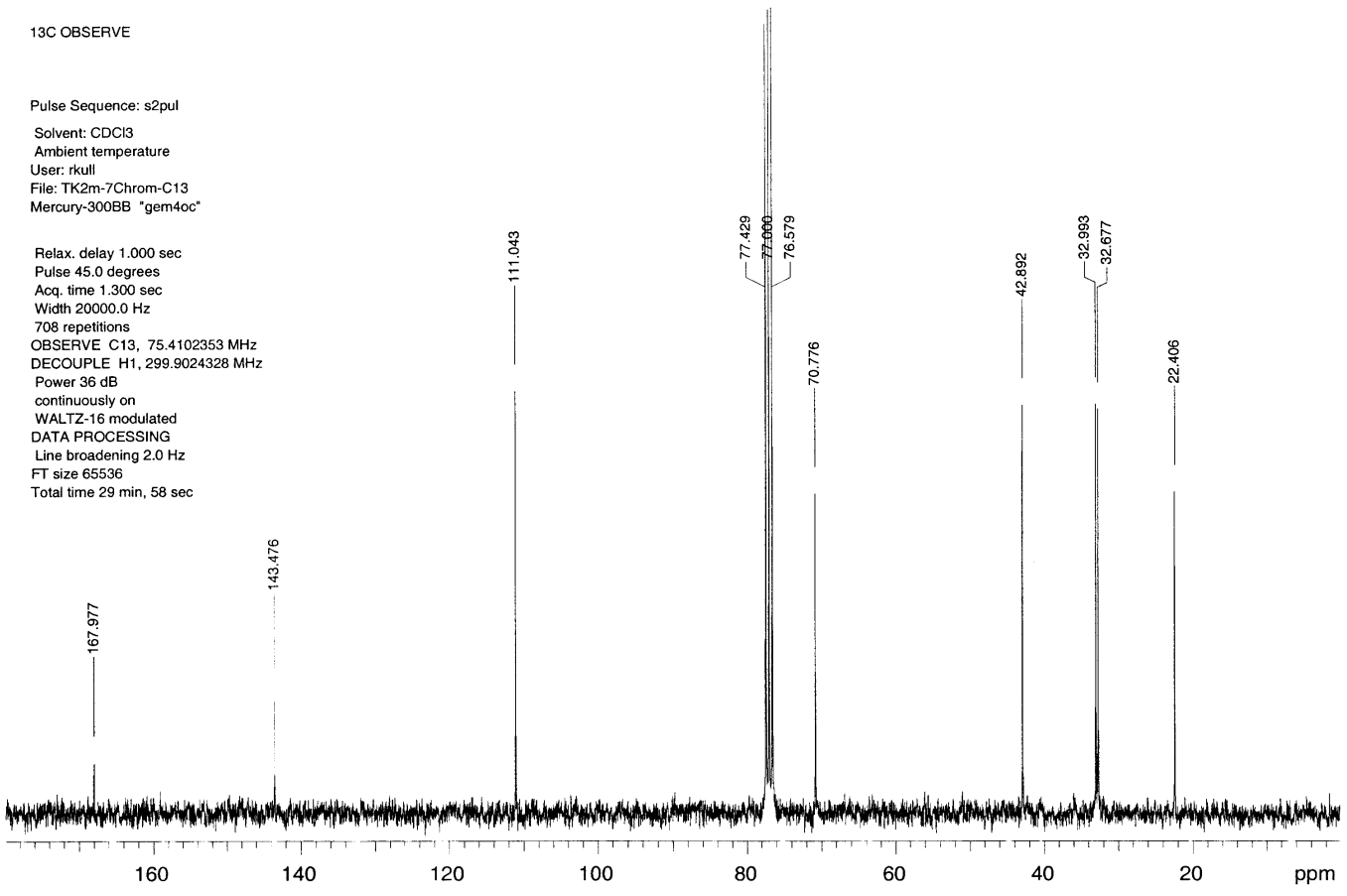

LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 15:49:29 USER:rkull GROUP:peters SAMPLE:TK2m-7Chrom

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2m-7Chrom-C13
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
708 repetitions
OBSERVE C13, 75.4102353 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 58 sec



LOC ETHZ NMR Mercury 300MHz Nr.4 03/04/06 15:57:58 USER:rkull GROUP:peters SAMPLE:TK2b-4rac-dest

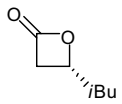
STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
360 repetitions
OBSERVE H1, 299.9012457 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 49 sec




**6f**




LOC ETHZ NMR Mercury 300MHz Nr.4 03/04/06 15:55:45 USER:rkull GROUP:peters SAMPLE:TK2b-4rac-dest-C13

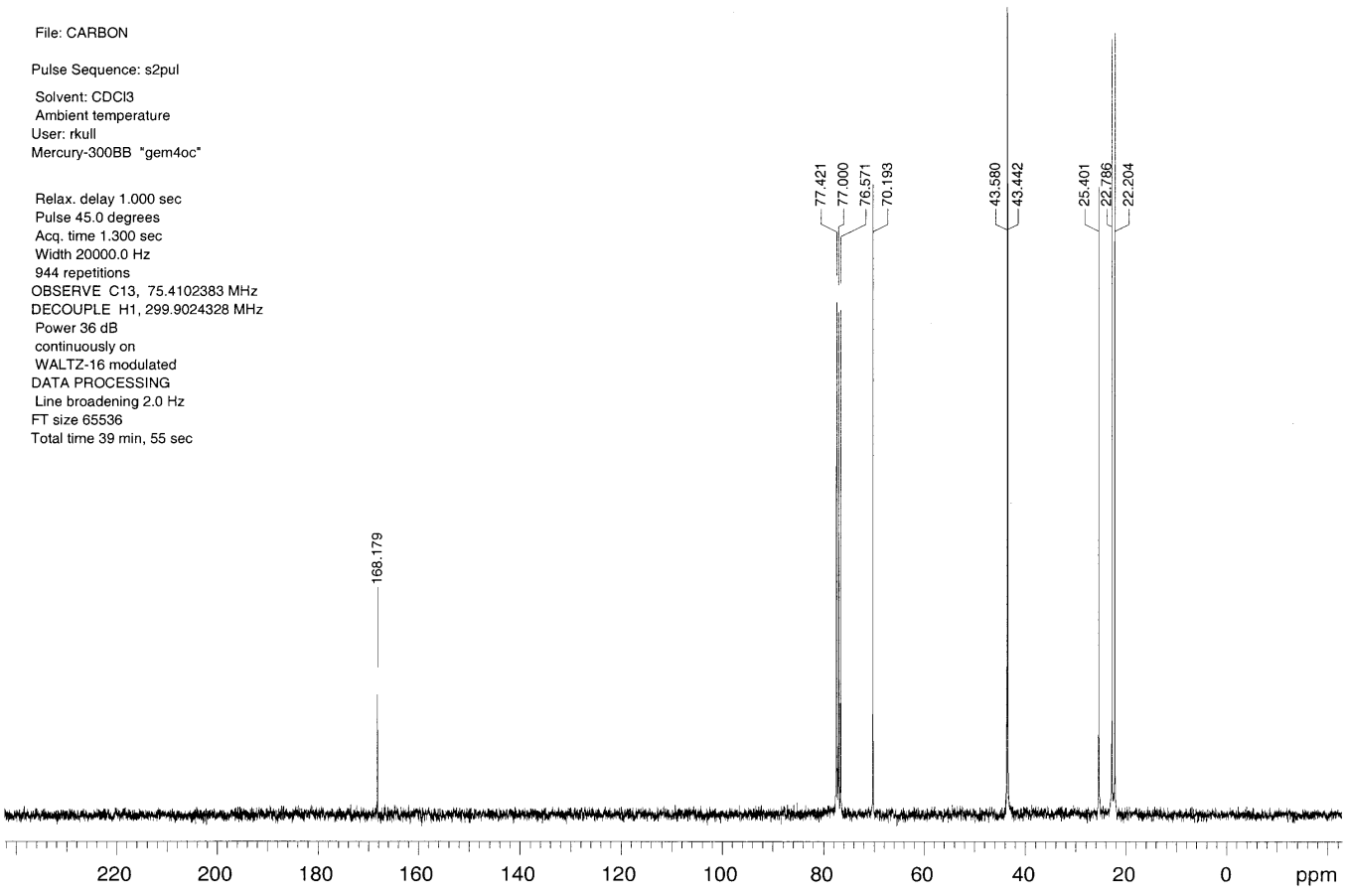
13C OBSERVE

File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
944 repetitions
OBSERVE C13, 75.4102383 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 39 min, 55 sec



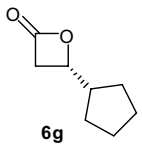
LOC ETHZ NMR Mercury-vx 300MHz Nr.5 11/21/06 15:09:52 USER:rkull GROUP:peters SAMPLE:TK2y-2Chrom

STANDARD 1H OBSERVE

Sample directory: TK2y-2Chrom

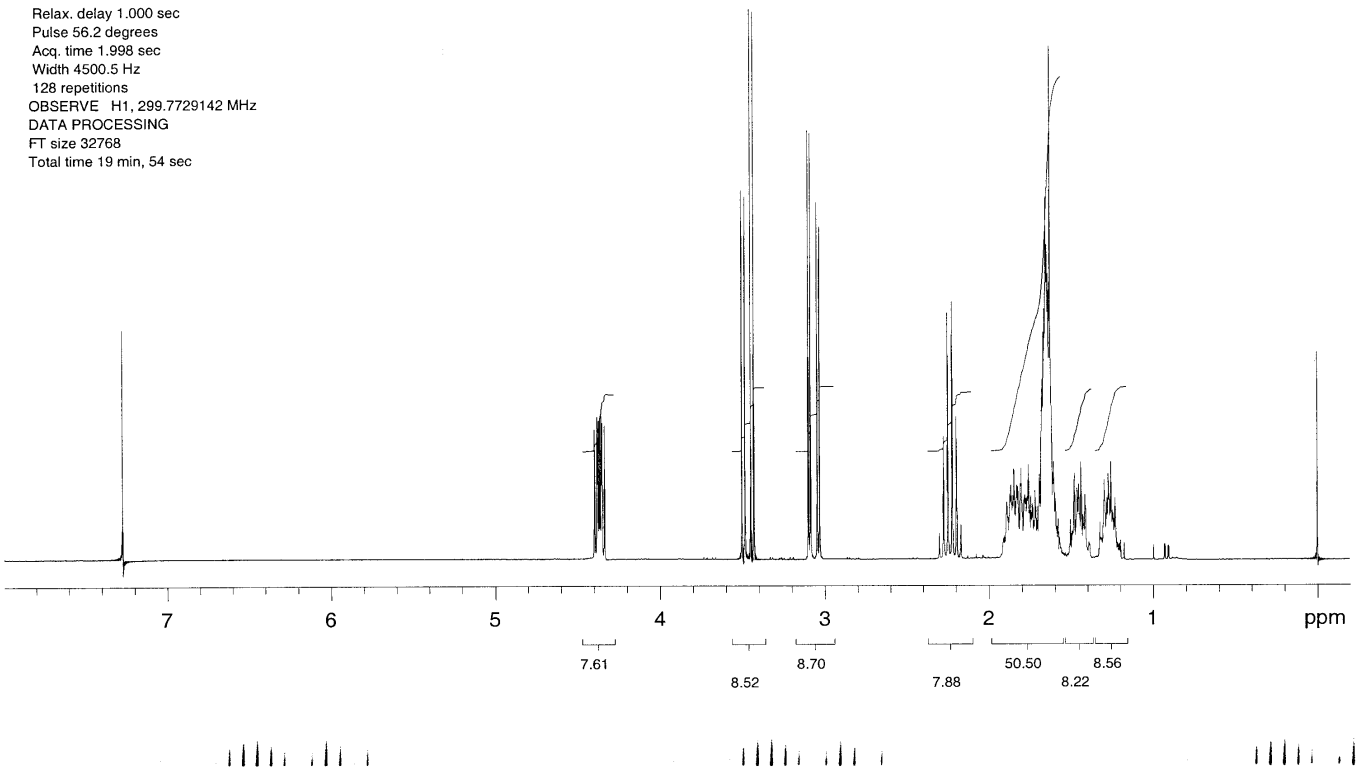
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2y-2Chrom
Mercury-300BB "gem5oc"



**6g**

Relax. delay 1.000 sec
Pulse 56.2 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
128 repetitions
OBSERVE H1, 299.7729142 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 54 sec




LOC ETHZ NMR Mercury 300MHz Nr.4 11/21/06 14:56:16 USER:rkull GROUP:peters SAMPLE:TK2y-2Chrom

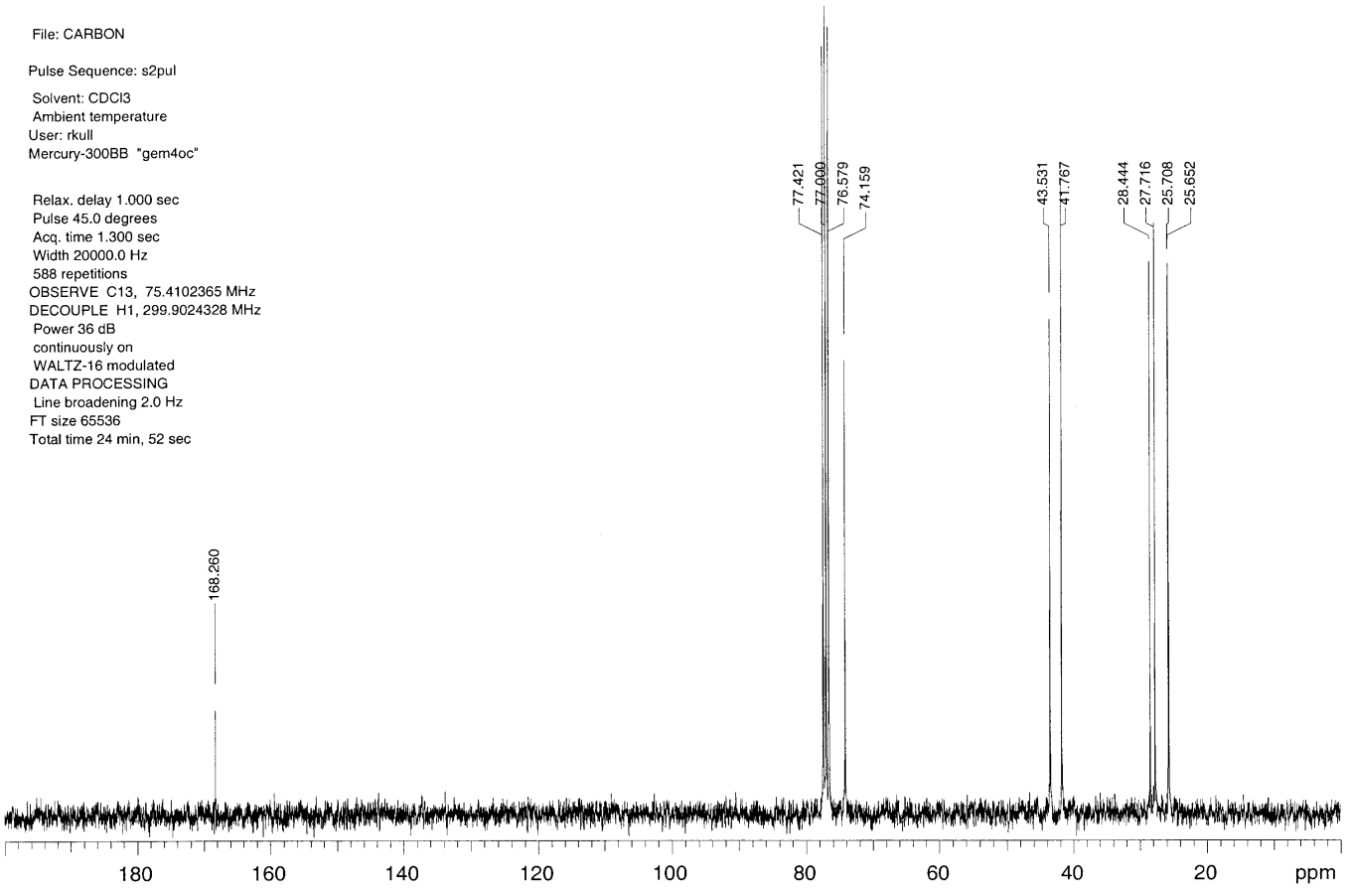
13C OBSERVE

File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

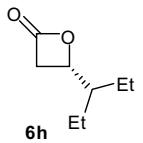
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
588 repetitions
OBSERVE C13, 75.4102365 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 24 min, 52 sec



LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 14:40:15 USER:rkull GROUP:peters SAMPLE:Lacton-Et-butanal

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: Lacton-Et-butanal-1H
Mercury-300BB "gem4oc"




**6h**

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
288 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 15 min, 50 sec

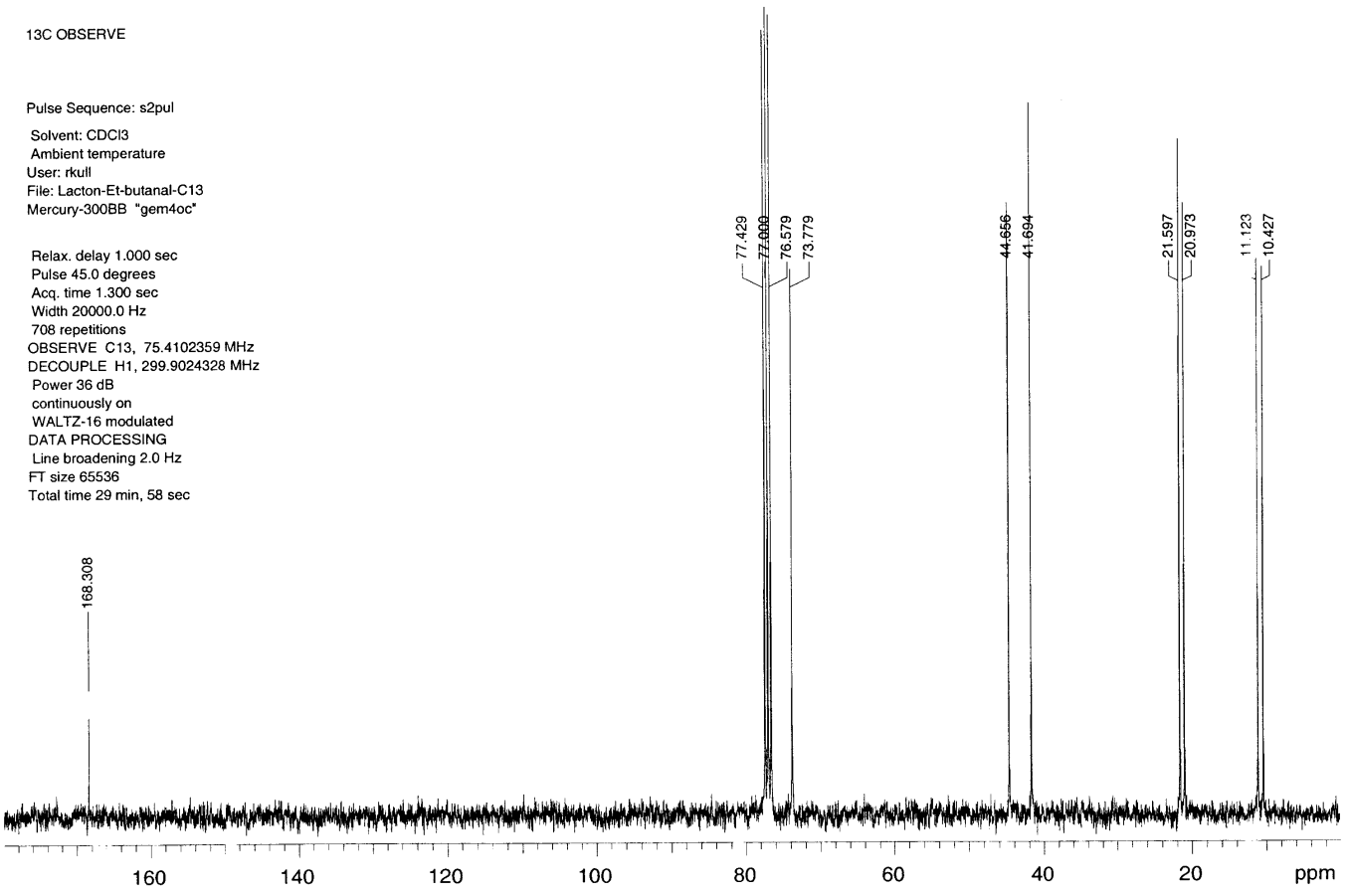



LOC ETHZ NMR Mercury 300MHz Nr.4 12/02/06 14:41:03 USER:rkull GROUP:peters SAMPLE:Lacton-Et-butanal

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: Lacton-Et-butanal-C13
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
708 repetitions
OBSERVE C13, 75.4102359 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 58 sec



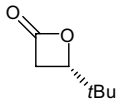
LOC ETHZ NMR Mercury 300MHz Nr.4 09/21/06 18:20:26 USER:rkull GROUP:peters SAMPLE:Lacton-Piv-Dest

STANDARD 1H OBSERVE

File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"




**6i**

Pulse 18.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
96 repetitions
OBSERVE H1, 299.9012510 MHz
DATA PROCESSING
FT size 32768
Total time 14 min, 5 sec




LOC ETHZ NMR Mercury 300MHz Nr.4 11/14/06 13:55:29 USER:rkull GROUP:peters SAMPLE:Lacton-Piv-C13

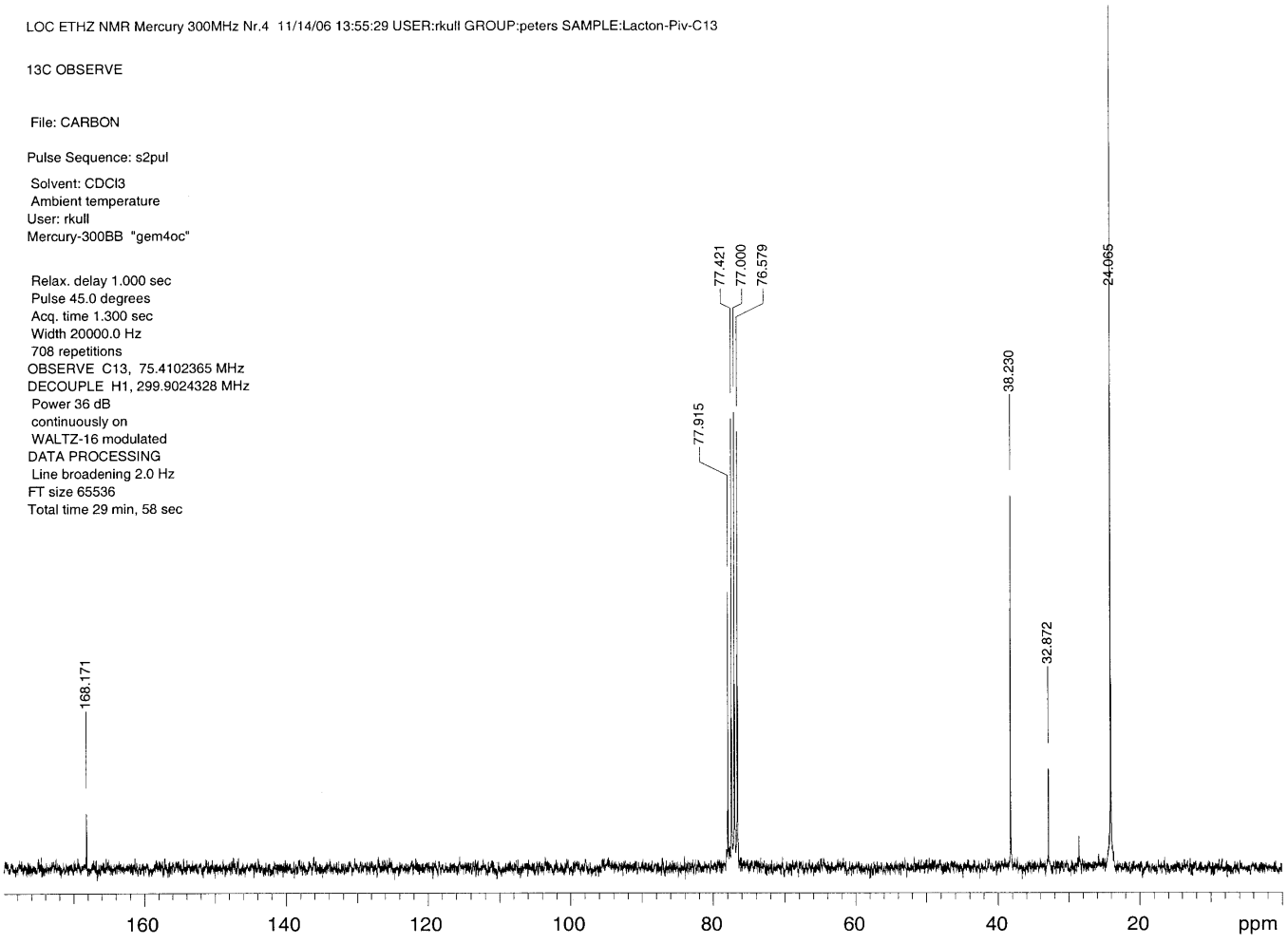
13C OBSERVE

File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: rkull
Mercury-300BB "gem4oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
708 repetitions
OBSERVE C13, 75.4102365 MHz
DECOUPLE H1, 299.9024328 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 58 sec

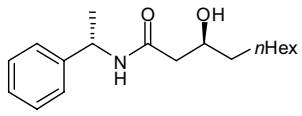


LOC ETHZ NMR Mercury-vx 300MHz Nr.5 01/27/07 12:09:42 USER:rkull GROUP:peters SAMPLE:TK2R-3Fr19-30

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2R-3-1H
GEMINI-300BB "gem3oc"

Relax. delay 1.000 sec
Pulse 30.2 degrees
Acq. time 3.138 sec
Width 4500.5 Hz
112 repetitions
OBSERVE H1, 299.7729179 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 45 sec




**8c**



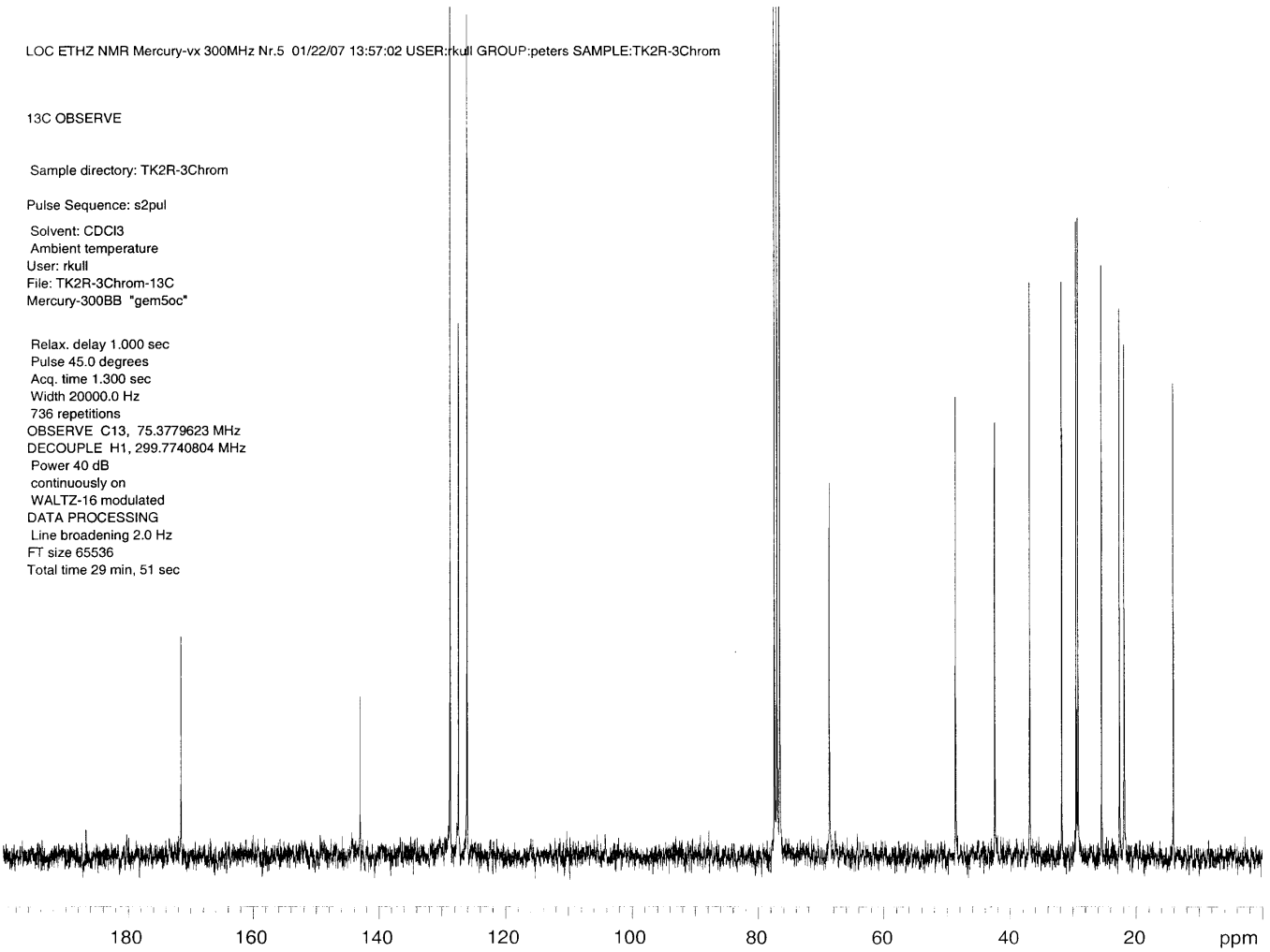

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 01/22/07 13:57:02 USER:rkull GROUP:peters SAMPLE:TK2R-3Chrom

13C OBSERVE

Sample directory: TK2R-3Chrom

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2R-3Chrom-13C
Mercury-300BB "gem5oc"

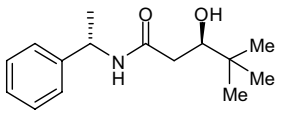
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
736 repetitions
OBSERVE C13, 75.3779623 MHz
DECOUPLE H1, 299.7740804 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 29 min, 51 sec



LOC ETHZ NMR Mercury-vx 300MHz Nr.6 01/27/07 14:11:40 USER:rkull GROUP:peters SAMPLE:TK2R-17-1H

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2R-17-1H
Mercury-300BB "gem6oc"




**8i**

Pulse 30.0 degrees
Acq. time 3.138 sec
Width 5099.4 Hz
336 repetitions
OBSERVE H1, 300.2230602 MHz
DATA PROCESSING
FT size 32768
Total time 19 min, 49 sec

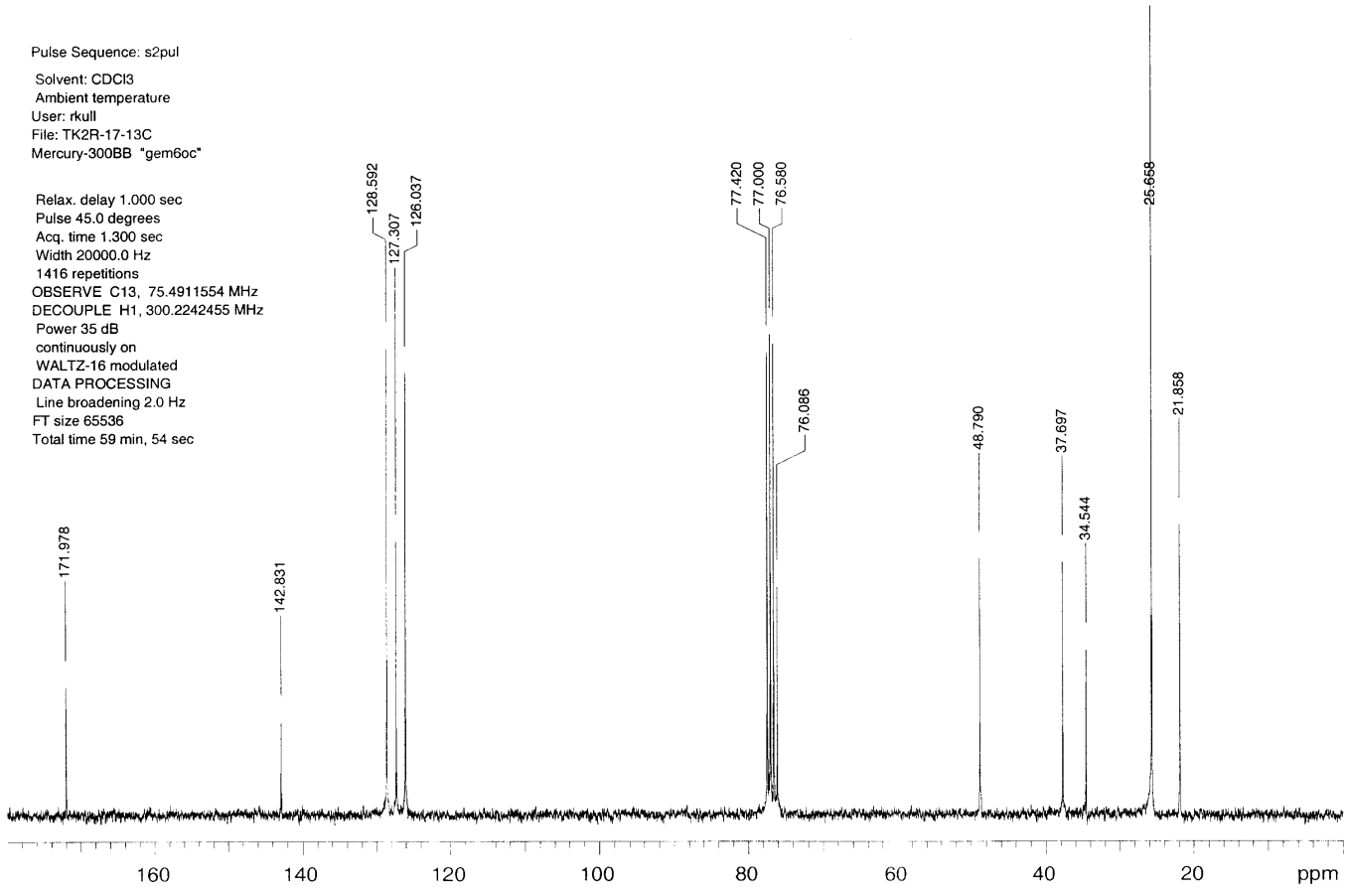



LOC ETHZ NMR Mercury-vx 300MHz Nr.6 01/27/07 14:08:36 USER:rkull GROUP:peters SAMPLE:TK2R-17-13C

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: rkull
File: TK2R-17-13C
Mercury-300BB "gem6oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 20000.0 Hz
1416 repetitions
OBSERVE C13, 75.4911554 MHz
DECOUPLE H1, 300.2242455 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 59 min, 54 sec



Current Data Parameters
NAME g1135
EXPNO 1
PROCNO 1

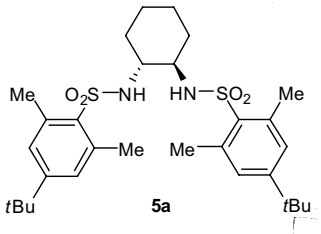
F2 - Acquisition Parameters
Date_ 20050712
Time 10.24
INSTRUM DRX400
PROBHD 5 mm BBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 0
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

============ CHANNEL f1 =============
NUC1 1H
P1 8.20 usec
PL1 -4.00 dB
SFO1 400.1325608 MHz

F2 - Processing parameters
SI 65536
SF 400.1300093 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 40.00 cm
F1P 9.500 ppm
F1 3801.23 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.25000 ppm/cm
HZCM 100.03250 Hz/cm

Th.Kull/Peters TK-2-106L OPR:PZ
400 MHz 1H-NMR




**5a**




Current Data Parameters
NAME g1135
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050712
Time 10.50
INSTRUM DRX400
PROBHD 5 mm BBO BB-
PULPROG zg45_cpd
TD 68804
SOLVENT CDCl3
NS 905
DS 0
SWH 26246.719 Hz
FIDRES 0.381471 Hz
AQ 1.3107662 sec
RG 16384
DW 19.050 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

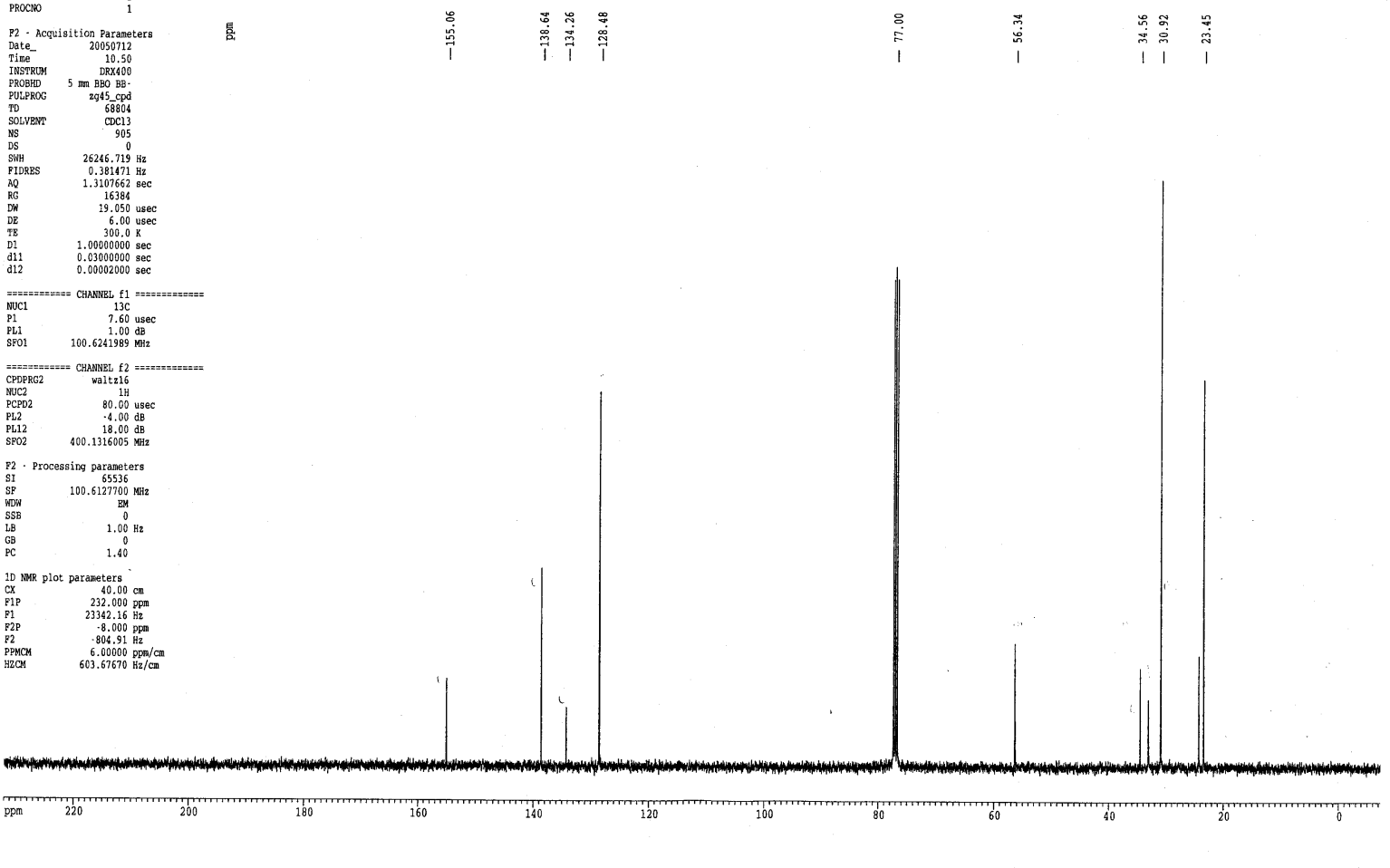
============ CHANNEL f1 =============
NUC1 13C
P1 7.60 usec
PL1 1.00 dB
SFO1 100.6241989 MHz

============ CHANNEL f2 =============
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 18.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 65536
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 40.00 cm
F1P 232.000 ppm
F1 23342.16 Hz
F2P -8.000 ppm
F2 -804.91 Hz
PPMCM 6.00000 ppm/cm
HZCM 603.67670 Hz/cm

Th.Kull/Peters TK-2-106L OPR:PZ
100MHz 13C-BB-NMR



Th.Kull/Peters TK-2-72L OPR:PZ
400 MHz 1H-NMR

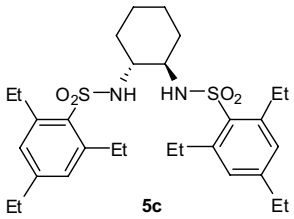
```
Current Data Parameters
NAME                  gl155
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20050811
Time                  9.36
INSTRUM             DRX400
PROBHD     5 mm BBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              CDCl3
NS                      64
DS                       0
SWH               6410.256 Hz
FIDRES               0.097813 Hz
AQ                5.1118579 sec
RG                      128
DW                   78.000 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec

============ CHANNEL f1 =============
NUC1                    1H
P1                    8.20 usec
PL1                  -4.00 dB
SFO1           400.1325608 MHz

F2 - Processing parameters
SI                    65536
SF             400.1300091 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                    40.00 cm
F1P                    9.500 ppm
F1                  3801.23 Hz
F2P                   -0.500 ppm
F2                  -200.07 Hz
PPMCM                0.25000 ppm/cm
HZCM               100.03250 Hz/cm
```




**5c**




Th.Kull/Peters TK-2-72L OPR:PZ
100MHz 13C-BB-NMR

```
Current Data Parameters
NAME                  gl155
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20050811
Time                 11.39
INSTRUM             DRX400
PROBHD     5 mm BBO BB-
PULPROG           zg45_cpd
TD                  68804
SOLVENT              CDCl3
NS                    3200
DS                       0
SWH              26246.719 Hz
FIDRES               0.381471 Hz
AQ                1.3107662 sec
RG                   11585.2
DW                   19.050 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec

============ CHANNEL f1 =============
NUC1                   13C
P1                    7.60 usec
PL1                   1.00 dB
SFO1           100.6241989 MHz

============ CHANNEL f2 =============
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                    65536
SF             100.6127676 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                    40.00 cm
F1P                  232.000 ppm
F1                 23342.16 Hz
F2P                   -8.000 ppm
F2                  -804.91 Hz
PPMCM                6.00000 ppm/cm
HZCM               603.67670 Hz/cm
```