Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

SUPPLEMENTARY INFORMATION (PART 1)

Asymmetric synthesis of carbocycles: use of intramolecular conjugate displacement

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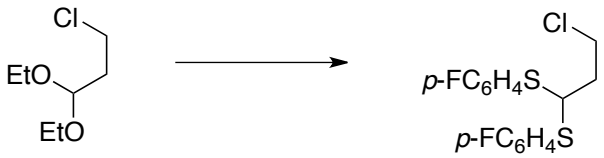
1-({3-Chloro-1-[(4-fluorophenyl)sulfanyl]propyl}sulfanyl)-4-fluorobenzene (3.2)

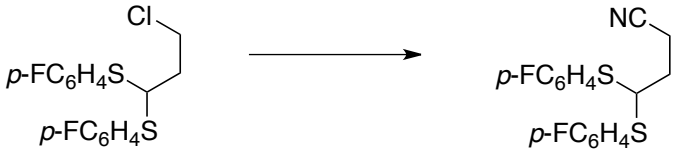


3.1 **3.2**

4-Fluorothiophenol (3.6 g, 28.15 mmol) and CF_3CO_2H (2.38 g, 21.11 mmol) were added to a stirred solution of **3.1** (1.17 g, 7.03 mmol) in CH_2Cl_2 (30 mL) at room temperature and stirring was continued for 24 h. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic extracts were washed with aqueous NaOH (10w/v) 2 x 10 mL) and brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the

residue over silica gel (4 x 15 cm), using 8% Et_2O-hexane, gave **3.2** which was used directly for the next step.

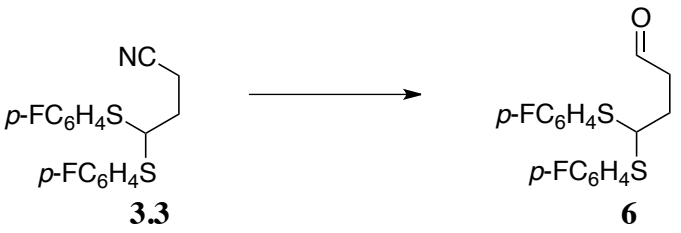
4,4-Bis[(4-fluorophenyl)sulfanyl]butanenitrile (3.3)



3.2 **3.3**

A solution of **3.2** (2.13 g, 6.44 mmol) in DMSO (2.5 mL) was added to a stirred mixture of NaCN (1.58 g, 32.23 mmol) and Bu_4NI (475 mg, 1.28 mmol) in DMSO (25 mL), and the resulting mixture was stirred at 50 °C for 24 h, cooled to room temperature, diluted with water (20 mL) and extracted with Et_2O (2 x 100 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 20% Et_2O-hexane, gave **3.3** (1.37 g, 61% over two steps) as an oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3094, 3067, 2856, 2248, 1589, 1489, 1443, 1420; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.45 (m, 4 H), 7.07-7.02 (m, 4 H), 4.27 (t, J = 7.1 Hz, 1 H), 2.68 (t, J = 7.1 Hz, 2 H), 2.10 (q, J = 7.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (**C**F, d, $^1J_{CF}$ = 249.9 Hz), 136.1 (**C**CCF, d, $^3J_{CF}$ = 8.4 Hz), 127.5 (**C**CCCF, d, $^4J_{CF}$ = 3.5 Hz), 118.4 (s), 116.4 (**C**CF, d, $^2J_{CF}$ = 21.9 Hz), 58.5 (d), 31.0 (t), 15.2 (t); exact mass (electrospray) m/z calcd for $C_{16}H_{13}F_2NNaS_2$ (M + Na) 344.0350, found 344.0358.

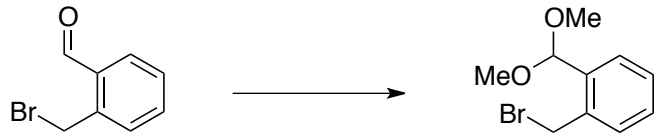
4,4-Bis[(4-fluorophenyl)sulfanyl]butanal (6)



3.3 **6**

DIBAL-H (1 M in PhMe, 3.1 mL, 3.11 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of **3.3** (500 mg, 1.55 mmol) in CH_2Cl_2 (16 mL). After the addition, stirring at -78 °C was continued for 1 h and then the cold bath was replaced by an ice bath. Stirring at 0 °C was continued for 30 min and the mixture was quenched with water (0.56 mL, 31 mmol) and NaF[24] (1.34 g, 31 mmol). The ice bath was removed, the mixture was diluted with Et_2O (50 mL), stirred vigorously for 1 h and then filtered through a pad of Celite (1 x 3 cm diameter) using Et_2O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (2 x 15 cm), using 20% Et_2O-hexane, gave **6** (359 mg, 72%) as an oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3067, 2927, 2249, 2726, 1724, 1589, 1490, 1443, 1443; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1 H), 7.49-7.45 (m, 4 H), 7.07-7.02 (m, 4 H), 4.30 (t, J = 6.8 Hz, 1 H), 2.83 (td, J = 7.1, 1.0 Hz, 2 H), 2.14 (q, J = 7.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6 (s), 162.9 (**C**F, $^1J_{CF}$ = 249.0 Hz), 135.7 (**C**CCF, $^3J_{CF}$ = 8.3 Hz), 128.3 (**C**CCCF, $^4J_{CF}$ = 3.5 Hz), 116.2 (**C**CF, $^2J_{CF}$ = 21.9 Hz), 59.2 (d), 41.1 (t), 27.9 (t); exact mass (electrospray) m/z calcd for $C_{16}H_{14}F_2NaOS_2$ (M + Na) 347.0346, found 347.0346.

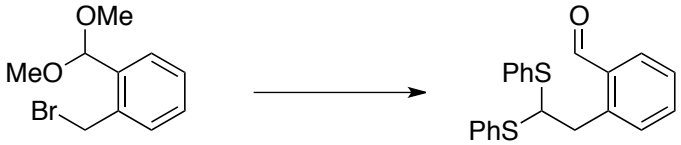
1-(Bromomethyl)-2-(dimethoxymethyl)benzene (4.3)



4.2 **4.3**

$CH(OMe)_3$ (2.54 mL, 23.23 mmol) was added to a solution of **4.2**[11] (925 mg, 4.65 mmol) and $TsOH.H_2O$ (88 mg, 0.46 mmol) in anhydrous MeOH (23 mL), and the mixture was heated at 50 °C for 12 h., cooled, and quenched with Et_3N (3 mL). The MeOH was evaporated under reduced pressure and the residue was diluted with water (20 mL) and extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 6% Et_2O-hexane, gave **4.3** (1.10 g, 100%) as a colorless oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3064, 2991, 2953, 2904, 2829, 1488, 1455; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60-7.56 (m, 1 H), 7.40-7.37 (m, 1 H), 7.34-7.30 (m, 2 H), 5.64 (s, 1 H), 4.69 (s, 2 H), 3.35 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2 (s), 135.7 (s), 131.1 (d), 129.0 (d), 128.4 (d), 127.4 (d), 101.1 (d), 53.3 (q), 30.7 (t); exact mass (electrospray) *m/z* calcd for $C_{10}H_{13}{}^{79}BrNaO_2$ (M + Na) 266.9991, found 266.9989.

2-[2,2-Bis(phenylsulfanyl)ethyl]benzaldehyde (8)

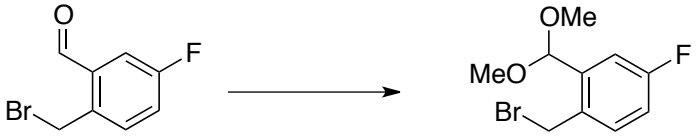


4.3 **8**

BuLi (2.5 in hexane, 0.63 mL, 1.57 mmol) was added dropwise to a stirred and cooled (0 °C) solution of $(PhS)_2CH_2$ (335 mg, 1.45 mmol) in THF (4 mL). Stirring at 0 °C was continued for

10 min and the mixture was then cooled to -78 °C. A solution of **4.3** (300 mg, 1.20 mmol) in THF (6 mL) was added rapidly in one portion and stirring at -78 °C was continued for 30 min and then at 0 °C (ice bath) for 10 min. Hydrochloric acid (4 M, 3 mL) was added, the cold bath was removed and stirring was continued for 3 h. The mixture was diluted with water (20 mL) and extracted with Et_2O (50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 8% Et_2O-hexane, gave **8** (289 mg, 69%) as a colorless oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3055, 2861, 2832, 2742, 1699, 1598, 1574, 1480, 1451; ^1H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1 H), 7.76 (dd, *J* = 7.6, 1.4 Hz, 1 H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.41 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.36-7.34 (m, 4 H), 7.31-7.24 (m, 7 H), 4.71 (t, *J* = 7.5 Hz, 1 H), 3.60 (d, *J* = 7.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4 (d), 139.9 (s), 134.2 (s), 134.1 (d), 133.5 (d), 133.0 (d), 132.9 (d), 132.9 (d), 128.9 (d), 127.9 (d), 127.6 (d), 59.5 (d), 39.7 (t); exact mass (EI) *m/z* calcd for $C_{21}H_{18}OS_2$ 350.0799, found 350.0796.

1-(Bromomethyl)-2-(dimethoxymethyl)-4-fluorobenzene (5.4)

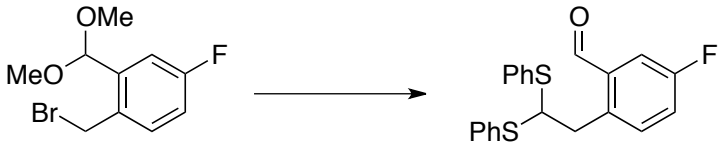


5.3 **5.4**

$CH(OMe)_3$ (4.2 mL, 38.35 mmol) was added to a solution of **5.3**[12,13] (1.67 g, 7.67 mmol) and $TsOH.H_2O$ (146 mg, 0.77 mmol) in anhydrous MeOH (30 mL) and the mixture was heated at 50 °C for 1 h. The reaction mixture quenched with Et_3N (3 mL) and the MeOH was evaporated under reduced pressure. The residue was partitioned between water (20 mL) and Et_2O (50 mL),

and the organic phase was washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 5% Et_2O-hexane, gave **5.4** (1.75 g, 86%) as a colorless oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3081, 2993, 2956, 2936, 2907, 2831, 1611, 1595, 1495, 1447, 1423; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2 H), 7.01 (td, J = 8.2, 2.8 Hz, 1 H), 5.63 (s, 1 H), 4.64 (s, 2 H), 3.35 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (**C**F, $^1J_{CF}$ = 248.5 Hz), 139.0 (**C**CCF, $^3J_{CF}$ = 7.3 Hz), 132.8 (**C**CCF, $^3J_{CF}$ = 8.3 Hz), 131.6 (**C**CCCF, $^4J_{CF}$ = 3.6 Hz), 115.8 (**C**CF, $^2J_{CF}$ = 21.7 Hz), 114.9 (**C**CF, $^2J_{CF}$ = 23.4 Hz), 99.9 (d, J = 1.8 Hz), 53.1 (q), 29.8 (t); exact mass (electrospray) m/z calcd for $C_{10}H_{12}BrFNaO_2$ (M + Na) 284.9897, found 284.9896.

2-[2,2-Bis(phenylsulfanyl)ethyl]-5-fluorobenzaldehyde (9)

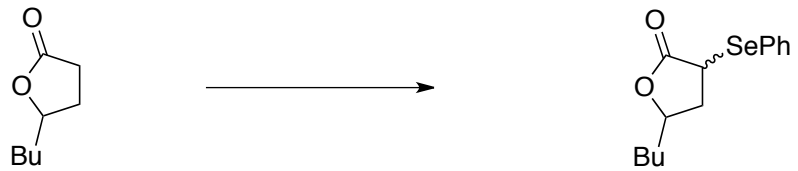


5.4 **9**

BuLi (2.5 M in hexane, 1.2 mL, 2.84 mmol) was added dropwise to a stirred and cooled (0 °C) solution of $(PhS)_2CH_2$ (660 mg, 2.84 mmol) in THF (20 mL). Stirring at 0 °C was continued for 10 min and the mixture was then cooled to -78 °C. A solution of **5.4** (630 mg, 2.36 mmol) in THF (6 mL) was added rapidly in one portion and stirring at -78 °C was continued for another 30 min and then at 0 °C (ice bath) for 10 min. Hydrochloric acid (4 M, 3 mL) was added, the cold bath was removed and stirring was continued for 3 h. The mixture was diluted with water (20 mL) and extracted with Et_2O (50 mL). The combined organic extracts were washed with brine,

dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 10% Et_2O-hexane, gave **9** (839 mg, 96%) as a colorless oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3059, 3019, 2923, 2866, 2736, 1695, 1609, 1582, 1494, 1479, 1439, 1419; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.00 (d, *J* = 1.7 Hz, 1 H), 7.49 (dd, *J* = 8.7, 2.8 Hz, 1 H), 7.40-7.37 (m, 4 H), 7.32-7.29 (m, 7 H), 7.23 (td, *J* = 8.1, 2.8 Hz, 1 H), 4.63 (t, *J* = 7.4 Hz, 1 H), 3.58 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5 (d), 161.9 (**C**F, $^1J_{CF}$ = 248.7 Hz), 135.8 (s), 135.8 (s), 135.8 (s), 134.6 (**C**CCF, $^3J_{CF}$ = 7.3 Hz), 133.9 (s), 133.0 (d), 129.0 (d), 128.0 (d), 120.6 (**C**CF, $^2J_{CF}$ = 21.4 Hz), 117.7 (**C**CF, $^2J_{CF}$ = 22.0 Hz), 60.0 (s), 38.5 (t); exact mass (electrospray) *m/z* calcd for $C_{21}H_{17}FNaOS_2$ (M + Na) 391.0597, found 391.0590.

5-Butyl-3-(phenylselanyl)oxolan-2-one (2).



4 **2**

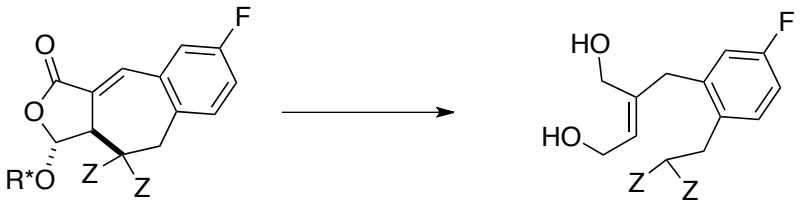
$(Me_3Si)_2NK$ (0.5 M in PhMe, 1.29 mL, 0.65 mmol) was added dropwise to a stirred and cooled (-78 °C) solution 5-butyloxolane-2-one[10,25] **(4)** (92 mg, 0.64 mmol) in THF (4 mL). Stirring at -78 °C was continued for 45 min. Then a solution of PhSeCl (62 mg, 0.324 mmol) in THF (1 mL) was injected rapidly in ONE PORTION (this mode of addition is important) and stirring at -78 °C was continued for 20 min. Saturated aqueous NH_4Cl (ca 3 mL) was added and the mixture was extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 14% Et_2O-hexane, gave **2**

as a mixture of diastereomers which was separated into three fractions (more polar, 24 mg, 25%; less polar, 28 mg, 29%; mixture, 20.2 mg, 21%).

The more polar selenide had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3057, 2956, 2933, 2862, 1764, 1578, 1478, 1466, 1438; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2 H), 7.38-7.30 (m, 3 H), 4.41-4.35 (m, 1 H), 4.01 (t, *J* = 9.6 Hz, 1 H), 2.71 (ddd, *J* = 13.5, 9.4, 6.5 Hz, 1 H), 1.93 (ddd, *J* = 13.5, 9.8, 8.6 Hz, 1 H), 1.63-1.56 (m, 1 H), 1.49-1.42 (m, 1 H), 1.36-1.21 (m, 4 H), 0.87 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8 (s), 135.6 (d), 129.3 (d), 128.8 (d), 127.1 (s), 79.3 (d), 37.6 (d), 36.0 (t), 35.1 (t), 27.1 (t), 22.3 (t), 13.8 (q); exact mass (electrospray) calcd for $C_{14}H_{18}NaO_2{}^{80}Se$ (M + Na) 319.0375, found 319.0374.

The less polar selenide had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3057, 2956, 2932, 2862, 1770, 1578, 1478, 1467, 1438; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2 H), 7.40-7.31 (m, 3 H), 4.35-4.29 (m, 1 H), 3.95 (dd, *J* = 7.8, 3.1 Hz, 1 H), 2.37-2.27 (m, 2 H), 1.73-1.66 (m, 1 H), 1.58-1.51 (m, 1 H), 1.42-1.26 (m, 4 H), 0.89 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7 (s), 135.7 (d), 129.4 (d), 129.1 (d), 126.9 (s), 79.5 (d), 37.2 (d), 36.7 (t), 34.9 (t), 27.2 (t), 22.3 (t), 13.9 (q); exact mass (electrospray) *m/z* calcd for $C_{14}H_{18}NaO_2{}^{80}Se$ (M + Na) 319.0375, found 319.0375.

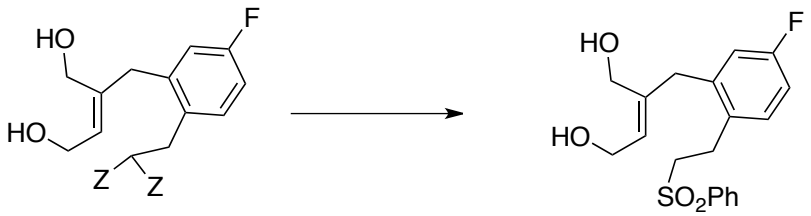
(2*Z*)-2-({2-[2,2-Bis(benzenesulfonyl)ethyl]-5-fluorophenyl}methyl)but-2-ene-1,4-diol (9.1)



9g **9.1**, Z = SO_2Ph

DIBAL-H (1 M solution in PhMe, 0.61 mL, 0.61 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of **9g** (40 mg, 0.061 mmol) in PhMe. After the addition, stirring at -78 °C was continued for 1 h. The cold bath was replaced by an ice bath and stirring at 0 °C was continued for 1 h. Finally the ice bath was removed and stirring was continued for 2 h. The reaction mixture was quenched with water (1.226 mmol, 0.022 mL) and NaF[24] (51 mg, 1.2 mmol), diluted with Et_2O (50 mL), stirred vigorously for 1 h at room temperature, and then filtered through a pad of Celite (1 x 1 cm), using Et_2O as a rinse. Evaporation o the filtrate and flash chromatography of the residue over silica gel (1 x 15 cm), using 80% EtOAc-hexane, gave **9.1** (21 mg, 68%) as an oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3524, 3378, 3069, 2858, 2926, 2855, 1588, 1498, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.4, 1.1 Hz, 4 H), 7.67-7.64 (m, 2 H), 7.52-7.49 (m, 4 H), 7.23 (dd, *J* = 8.5, 5.8 Hz, 1 H), 6.84-6.79 (m, 2 H), 5.28 (t, *J* = 6.8 Hz, 1 H), 5.10 (t, *J* = 6.3 Hz, 1 H), 4.18 (d, *J* = 6.7 Hz, 2 H), 4.13 (s, 2 H), 3.59 (d, *J* = 6.3 Hz, 2 H), 3.51 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (**C**F, $^1J_{CF}$ = 246.8 Hz), 141.7 (s), 139.5 (s), 139.4 (s), 138.1 (s), 134.6 (d), 133.0 (d), 133.0 (d), 129.7 (s), 129.7 (s), 129.4 (d), 129.1 (d), 128.7 (d), 117.4 (**C**CF, $^2J_{CF}$ = 21.3 Hz), 113.7 (**C**CF, $^2J_{CF}$ = 21.2 Hz), 83.7 (d), 60.5 (t), 58.4 (t), 37.9 (t), 28.4 (t); exact mass (electrospray) *m*/*z* calcd for $C_{25}H_{25}FNaO_6S_2$ (M + Na) 527.0969, found 527.0958.

(2*Z*)-2-({2-[2-(Benzenesulfonyl)ethyl]-5-fluorophenyl}methyl)but-2-ene-1,4-diol (9.2)

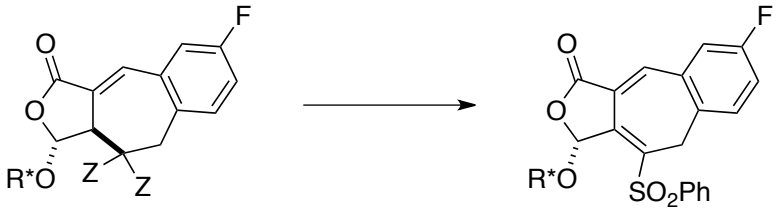


9.1, Z = SO_2Ph **9.2**

6% Na(Hg) (80 mg) was added to a stirred and cooled (0 °C) solution of **9.1** (5 mg, 0.009 mmol) and Na_2HPO_4 (14 mg, 0.099 mmol) in MeOH (2 mL). Stirring at 0 °C was continued for 30 min. The ice bath was removed and stirring was continued for 2 h. The reaction mixture was quenched with water (2 mL) and the MeOH was evaporated under reduced pressure. The residue was extracted with EtOAc (20 mL) and the combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 100% EtOAc, gave **9.2** (2.3 mg, 64%) as a solid: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3415, 3064, 2926, 2855, 1611, 1590, 1499, 1477; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.3, 1.6 Hz, 2 H), 7.68 (tt, *J* = 7.5, 1.5 Hz, 1 H), 7.60-7.57 (m, 2 H), 7.04 (dd, *J* = 8.3, 5.8 Hz, 1 H), 6.89-6.84 (m, 2 H), 5.30 (t, *J* = 6.8 Hz, 1 H), 4.21 (d, *J* = 6.9 Hz, 2 H), 4.16 (s, 2 H), 3.48 (s, 2 H), 3.32-3.28 (m, 2 H), 3.03 (dt, *J* = 7.9, 4.2 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7 (**C**F, $^1J_{CF}$ = 246.1 Hz), 141.7 (s), 139.2 (s), 139.1 (s), 138.9 (s), 134.0 (d), 132.0 (s), 132.0 (s), 131.0 (d), 130.9 (d), 129.5 (d), 128.5 (d), 128.0 (d), 117.9 (**C**CF, $^2J_{CF}$ = 21.2 Hz), 114.0 (**C**CF, $^2J_{CF}$ = 21.1 Hz), 60.4 (t), 58.4 (t), 56.9 (t), 38.4 (t), 24.5 (t); exact mass (electrospray) *m/z* calcd for $C_{19}H_{21}FNaO_4S$ (M + Na) 387.1037, found 387.1028.

For X-ray analysis crystals of **9.2** were grown by slow vapor diffusion of hexanes into a solution of the compound in Et_2O.

(6*R*)-8-(Benzenesulfonyl)-13-fluoro-6-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]-oxy}-5-oxatricyclo[8.4.0.0^{3,7}]tetradeca-1(14),2,7,10,12-pentaen-4-one (9.3)

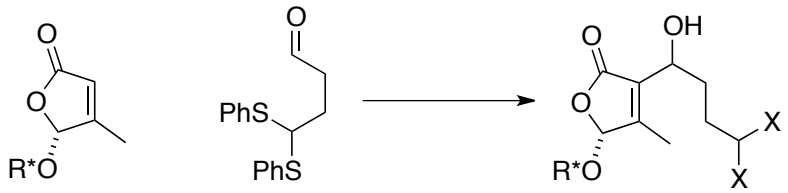


9g, Z = SO_2Ph **9.3**

6% Na(Hg) (100 mg) and Na_2HPO_4 (37 mg, 0.026 mmol) were added to a stirred and cooled (0 °C) solution of **9g** (17 mg, 0.026 mmol) in MeOH (1 mL), and stirring at 0 °C was continued for 30 min. The ice bath was removed and stirring was continued for 2 h. The mixture was quenched with water (2 mL) and the MeOH was evaporated under reduced pressure. The residue was extracted with EtOAc (10 mL) and the organic layer was washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% EtOAc, gave **9.3** (6 mg, 45%) as an oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3065, 2955, 2925, 2869, 1776, 1644, 1613, 1571, 1494, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1 H), 8.01 (d, *J* = 7.2 Hz, 2 H), 7.61 (t, *J* = 7.4 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 2 H), 7.17 (dd, *J* = 8.8, 2.6 Hz, 1 H), 7.07 (td, *J* = 8.2, 2.7 Hz, 1 H), 6.95 (s, 1 H), 6.70 (dd, *J* = 8.4, 5.2 Hz, 1 H), 3.77 (td, *J* = 10.7, 4.2 Hz, 1 H), 3.69 (d, *J* = 15.0 Hz, 1 H), 3.13 (d, *J* = 14.8 Hz, 1 H), 2.47 (d, *J* = 13.8 Hz, 1 H), 2.00-1.94 (m, 1 H), 1.67-1.63 (m, 2 H), 1.41-1.38 (m, 1 H), 1.24-1.20 (m, 1 H), 1.08-0.77 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3 (s), 161.6 (**C**F, $^1J_{CF}$ = 246.3 Hz), 142.4 (d), 140.1 (s), 140.0 (s), 135.0 (s), 134.9 (s), 134.0 (d), 131.6 (s), 130.4 (d), 130.3 (d), 129.3 (d), 128.9 (s), 128.4 (d), 125.3 (d), 120.6 (**C**CF, $^2J_{CF}$ = 21.8 Hz), 116.7 (**C**CF, $^2J_{CF}$ = 21.9 Hz), 96.4 (d), 77.9 (d), 48.0 (d), 38.8 (t), 34.3 (t), 34.1 (t), 31.6 (d), 25.3 (d), 23.3 (t), 22.3 (q), 21.0 (q),

15.6 (q); exact mass (electrospray) *m/z* calcd for $C_{29}H_{31}NaO_5S$ (M + Na) 533.1768, found 533.1767.

(5*R*)-3-[1-Hydroxy-4,4-bis(phenylsulfanyl)butyl]-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (5i, 5i')



3 **5** **5i, 5i'**, X = SPh

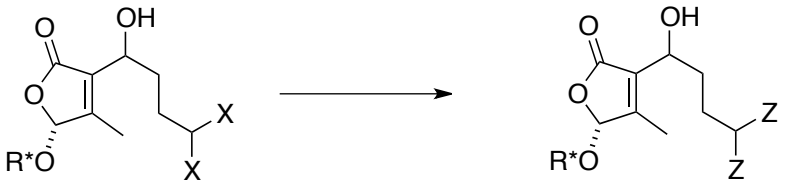
BuLi (2.5 M in hexanes, 0.38 mL, 0.95 mmol) was added to a stirred and cooled (-78 °C) solution of *i*-Pr_2NH (0.15 mL, 1.11 mmol) in THF (3 mL), and stirring was continued for 30 min at -78 °C. A solution of **3**[9,26] (200 mg, 0.79 mmol) in THF (2 mL) was then added dropwise and stirring at -78 °C was continued for 50 min. A solution of aldehyde **5**[4] (274 mg, 0.95 mmol) in THF (2 mL) was added at a fast dropwise rate and stirring at -78 °C was continued for 30 min. Saturated aqueous NH_4Cl (ca 3 mL) was added and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine (10 mL), dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 50% Et_2O-hexane, gave an oil, which was separated into three fractions: less polar alcohol **5i'** (41 mg, 10 %), more polar alcohol **5i** (52 mg, 12%), and a mixture of both isomers (172 mg, 40%).

The more polar alcohol **5i** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3476, 3058, 2954, 2923, 2869, 1756, 1686, 1583, 1480, 1455, 1439; ^1H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 4 H), 7.33-7.26 (m, 6 H), 5.63 (s, 1 H), 4.46-4.41 (m, 2 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.84 (d, *J* =

9.1 Hz, 1 H), 2.15-1.81 (m, 9 H), 1.70-1.64 (m, 2 H), 1.44-1.39 (m, 1 H), 1.27-1.21 (m, 1 H), 1.03-0.78 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 (s), 155.6 (s), 133.9 (s), 133.9 (s), 132.9 (d), 132.9 (d), 130.2 (s), 129.0 (d), 129.0 (d), 127.9 (d), 127.9 (d), 100.8 (d), 79.6 (d), 66.4 (d), 58.0 (d), 47.8 (d), 40.5 (t), 34.2 (t), 33.8 (t), 31.7 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.5 (q); exact mass (electrospray) *m*/*z* calcd for $C_{31}H_{40}NaO_4S_2$ (M + Na) 563.2260, found 563.2251.

The less polar alcohol **5i'** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3477, 3058, 2954, 2923, 2869, 1755, 1687, 1583, 1480, 1455, 1439; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.48 (m, 4 H), 7.36-7.29 (m, 6 H), 5.68 (s, 1 H), 4.49-4.44 (m, 2 H), 3.64 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.84 (d, *J* = 9.2 Hz, 1 H), 2.18-1.88 (m, 9 H), 1.73-1.67 (m, 2 H), 1.46-1.41 (m, 1 H), 1.30-1.25 (m, 1 H), 1.08-0.82 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4 (s), 155.6 (s), 133.9 (s), 133.9 (s), 132.9 (d), 132.9 (d), 130.3 (s), 129.0 (d), 129.0 (d), 127.9 (d), 127.9 (d), 101.1 (d), 79.8 (d), 66.6 (d), 58.1 (d), 47.7 (d), 40.6 (t), 34.2 (t), 33.9 (t), 31.8 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.6 (q); exact mass (electrospray) *m*/*z* calcd for $C_{31}H_{40}NaO_4S_2$ (M + Na) 563.2260, found 563.2255.

(5*R*)-3-[4,4-Bis(benzenesulfonyl)-1-hydroxybutyl]-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (5j, 5j')



5i, 5i', X = SPh **5j, 5j'**, Z = SO_2Ph

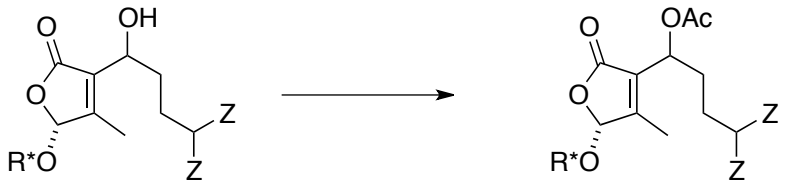
MCPBA (70%, 1.18 g, 4.77 mmol) was added to a stirred and cooled (0 °C) solution of a mixture of **5i** and **5i'** (172 mg, 0.318 mmol) in CH_2Cl_2 (4 mL). The ice bath was removed and stirring was continued for 3 h. The mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (3 mL) and saturated aqueous $Na_2S_2O_3$ (3 mL), and extracted with CH_2Cl_2 (2 x 30 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et_2O-hexane, gave a separable mixture of isomers (140 mg, 73%): more polar sulfone alcohol **5j** (74 mg, 39%) and the less polar sulfone alcohol **5j'** (66 mg, 34%).

The more polar alcohol **5j** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3517, 3065, 2955, 2924, 2870, 1753, 1687, 1585, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.94 (m, 4 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.9 Hz, 4 H), 5.69 (s, 1 H), 4.65 (t, *J* = 5.8 Hz, 1 H), 4.48 (td, *J* = 8.4, 3.8 Hz, 1 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.89 (d, *J* = 8.2 Hz, 1 H), 2.46-2.25 (m, 2 H), 2.14-1.91 (m, 7 H), 1.70-1.64 (m, 2 H), 1.44-1.38 (m, 1 H), 1.27-1.21 (m, 1 H), 1.06-0.78 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 (s), 156.3 (s), 137.9 (s), 137.7 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.5 (d), 129.2 (d), 129.2 (d), 101.0 (d), 82.8 (d), 79.8 (d), 66.3 (d), 47.8 (d), 40.5 (t), 34.2 (t), 33.8 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.3 (t), 22.3 (q), 20.9 (q), 15.8 (q), 11.6 (q); exact mass (electrospray) *m/z* calcd for $C_{31}H_{40}NaO_8S_2$ (M + Na) 627.2057, found 627.2050.

The less polar alcohol **5j'** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3514, 3066, 2955, 2924, 2870, 1754, 1686, 1585, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.94 (m, 4 H), 7.72-7.68 (m, 2 H), 7.60-7.56 (m, 4 H), 5.69 (s, 1 H), 4.66 (t, *J* = 5.8 Hz, 1 H), 4.47 (td, *J* = 9.0, 3.9 Hz, 1 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.85 (d, *J* = 8.6 Hz, 1 H), 2.39 (ddt, *J* = 15.2, 9.2, 5.8 Hz, 1 H), 2.29 (ddt, *J* = 15.3, 9.0, 6.3 Hz, 1 H), 2.14-1.91 (m, 7 H), 1.70-1.64 (m, 2 H), 1.45-1.36 (m, 1 H), 1.28-1.22 (m, 1 H), 1.06-0.76 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 (s), 156.3 (s),

137.9 (s), 137.7 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.2 (d), 101.2 (d), 82.8 (d), 79.9 (d), 66.5 (d), 47.7 (d), 40.6 (t), 34.2 (t), 34.1 (t), 31.5 (d), 25.2 (d), 23.1 (t), 22.4 (t), 22.3 (q), 21.0 (q), 15.7 (q), 11.7 (q); exact mass (electrospray) *m/z* calcd for $C_{31}H_{40}NaO_8S_2$ (M + Na) 627.2057, found 627.2050.

4,4-Bis(benzenesulfonyl)-1-[(5*R*)-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]butyl acetate (5k, 5k'). Use of 5j'



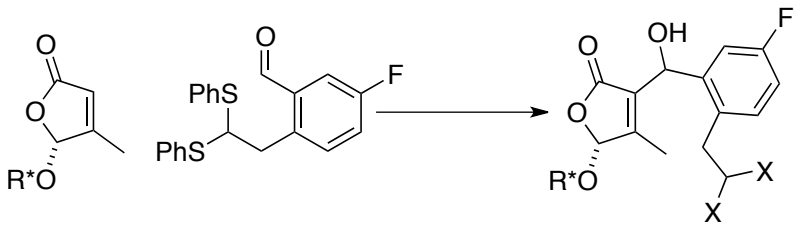
5j, 5j', Z = SO_2Ph **5k, 5k'**

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of **5j'** (12 mg, 0.0198 mmol) in CH_2Cl_2 (1 mL). The mixture was then cooled to 0 °C, and AcCl (8.5 μL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et_2O-hexane, gave **5k'** (10.1 mg, 79%) as a colorless foam: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3065, 3023, 2955, 2925, 2870, 1760, 1670, 1584, 1448; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 4 H), 7.76-7.73 (m, 2 H), 7.62 (t, *J* = 7.8 Hz, 4 H), 5.72 (s, 1 H), 5.58 (dd, *J* = 8.9, 4.5 Hz, 1 H), 4.54 (t, *J* = 5.8 Hz, 1 H), 3.64 (td, *J* = 10.6, 4.2 Hz, 1 H),

2.46-2.39 (m, 1 H), 2.29-2.10 (m, 11 H), 1.73-1.69 (m, 2 H), 1.48-1.42 (m, 1 H), 1.32-1.26 (m, 1 H), 1.10-0.84 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2 (s), 169.4 (s), 159.5 (s), 137.8 (s), 137.6 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.2 (d), 126.8 (s), 100.6 (d), 82.6 (d), 79.8 (d), 66.6 (d), 47.7 (d), 40.5 (t), 34.2 (t), 31.5 (q), 30.1 (t), 25.1 (d), 23.1 (t), 22.3 (d), 21.6 (t), 20.9 (q), 20.8 (q), 15.7 (q), 12 (q); exact mass (electrospray) *m/z* calcd for $C_{33}H_{42}NaO_9S_2$ (M + Na) 669.2162, found 669.2156.

Use of 5j. DMAP (1.2 mg, 0.01 mmol) was added to a stirred solution of **5j** (12 mg, 0.0198 mmol) in CH_2Cl_2 (1 mL). The mixture was then cooled to 0 °C, and AcCl (8.5 μL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 80% Et_2O-hexane, gave **5k** (10.3 mg, 81%) as a colorless foam: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3067, 3025, 2955, 2925, 2870, 1761, 1690, 1584, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 4 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.6 Hz, 4 H), 5.66 (s, 1 H), 5.55 (dt, *J* = 8.8, 4.5 Hz, 1 H), 4.53 (t, *J* = 5.8 Hz, 1 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.34-2.04 (m, 12 H), 1.69-1.65 (m, 2 H), 1.44-1.37 (m, 1 H), 1.29-1.23 (m, 1 H), 1.07-0.80 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1 (s), 169.4 (s), 158.9 (s), 137.8 (s), 137.6 (s), 134.7 (d), 134.7 (d), 129.7 (d), 129.6 (d), 129.2 (d), 129.2 (d), 127.0 (s), 100.6 (d), 82.5 (d), 80.0 (d), 66.6 (d), 47.7 (d), 40.6 (t), 34.2 (t), 31.5 (q), 30.1 (t), 25.2 (d), 23.1 (t), 22.3 (d), 21.6 (t), 20.9 (q), 20.8 (q), 15.8 (q), 11.8 (q); exact mass (electrospray) *m/z* calcd for $C_{33}H_{42}NaO_9S_2$ (M + Na) 669.2162, found 669.2150.

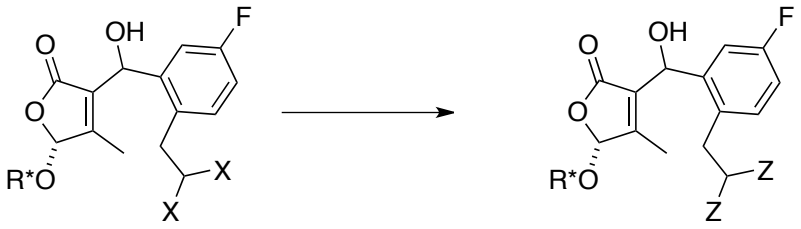
(5*R*)-3-({2-[2,2-Bis(phenylsulfanyl)ethyl]-5-fluorophenyl}(hydroxy)methyl)-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (9d)



3 **9** **9d**, X = SPh

BuLi (2.5 M in hexanes, 0.46 mL, 1.14 mmol) was added to a stirred and cooled (-78 °C) solution of *i*-Pr_2NH (0.18 mL, 1.30 mmol) in THF (5 mL), and stirring was continued for 30 min. A solution of **3** (273 mg, 1.08 mmol) in THF (3 mL) was then added dropwise and stirring at -78 °C was continued for 50 min. A solution of aldehyde **9** (200 mg, 0.54 mmol) in THF (2 mL) was added at a fast dropwise rate and stirring at -78 °C was continued for 30 min. Then saturated aqueous NH_4Cl (ca 5 mL) was added and the mixture was extracted with Et_2O. The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 50% Et_2O-hexane, gave crude **9d** (171 mg, 51%) which could not be purified by flash chromatography and was used directly for next step.

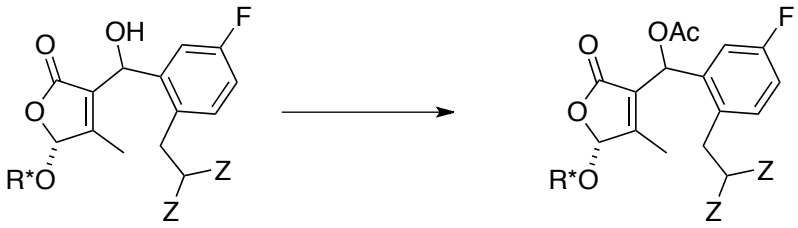
(5*R*)-3-({2-[2,2-Bis(benzenesulfonyl)ethyl]-5-fluorophenyl}(hydroxy)methyl)-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (9e)



9d, X = SPh **9e**, Z = SO_2Ph

MCPBA (70%, 465 mg, 1.88 mmol) was added to a stirred and cooled (0 °C) solution of crude **9d** (117 mg, ca 0.188 mmol) in CH_2Cl_2 (5 mL). The ice bath was removed and stirring was continued for 4 h. The mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (3 mL) and saturated aqueous $Na_2S_2O_3$ (3 mL), and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et_2O-hexane, gave **9e** (81 mg, 63%) as an inseparable mixture of diastereomers: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3502, 3066, 3021, 2956, 2924, 2871, 1749, 1689, 1613, 1592, 1501, 1499, 1479, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2 H), 7.77-7.73 (m, 2 H), 7.66-7.61 (m, 2 H), 7.52-7.46 (m, 4 H), 7.30-7.26 (m, 1 H), 6.96-6.88 (m, 2 H), 5.96 (s, 1 H), 5.80 (s, 1 H), 5.55 (t, *J* = 6.1 Hz, 1 H), 3.95 (dd, *J* = 15.8, 6.1 Hz, 1 H), 3.75 (dd, *J* = 15.8, 6.2 Hz, 1 H), 3.67 (td, *J* = 10.7, 4.3 Hz, 1 H), 3.61 (s, 1 H), 2.15-2.04 (m, 5 H), 1.73-1.69 (m, 2 H), 1.47-1.26 (m, 2 H), 1.12-0.82 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6 (s), 162.2 (**C**F, $^1J_{CF}$ = 247.6 Hz), 157.6 (s), 141.6 (s), 141.6 (s), 138.4 (s), 138.2 (s), 134.4 (d), 134.4 (d), 133.5 (d), 133.5 (d), 129.9 (s), 129.9 (d), 129.2 (d), 129.2 (d), 129.0 (d), 129.0 (d), 128.8 (s), 115.5 (**C**CF, $^2J_{CF}$ = 21.3 Hz), 114.6 (**C**CF, $^2J_{CF}$ = 22.5 Hz), 101.3 (d), 83.7 (d), 79.8 (d), 66.1 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.5 (d), 27.7 (t), 25.4 (d), 23.3 (t), 22.3 (q), 20.8 (q), 15.9 (q), 12 (q); exact mass (electrospray) *m/z* calcd for $C_{36}H_{41}FNaO_8S_2$ (M + Na) 707.2119, found 707.2111.

{2-[2,2-Bis(benzenesulfonyl)ethyl]-5-fluorophenyl}[(5*R*)-4-methyl-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (9f)

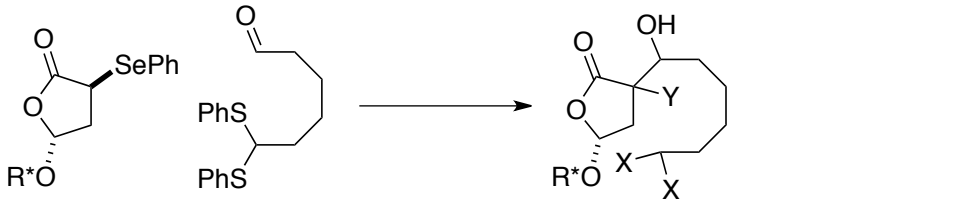


9e **9f**, Z = SO_2Ph

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of **9e** (13.5 mg, 0.0197 mmol) in CH_2Cl_2 (1 mL). The mixture was then cooled to 0 °C, and AcCl (0.0084 mL, 0.11 mmol) and pyridine (0.0128 mL, 0.16 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 50% Et_2O-hexane, gave **9f** (12.7 mg, 89%) as a colorless foam: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3068, 2956, 2926, 2871, 1759, 1685, 1613, 1592, 1501, 1448; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92-7.89 (m, 3 H), 7.63-7.35 (m, 7 H), 7.01 (dd, *J* = 9.6, 2.7 Hz, 1 H), 6.91-6.84 (m, 2 H), 6.16-6.11 (m, 1 H), 5.70 (s, 1 H), 3.93 (d, *J* = 6.1 Hz, 2 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.34-2.01 (m, 9 H), 1.71-1.65 (m, 2 H), 1.43-1.39 (m, 1 H), 1.31-1.24 (m, 1 H), 1.05-0.73 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6 (s), 169.2 (s), 162.2 (**C**F, $^1J_{CF}$ = 247.1 Hz), 157.4 (s), 138.4 (s), 138.2 (s), 134.8 (d), 134.8 (d), 134.1 (d), 129.6 (d), 128.8 (d),

127.4 (s), 115.7 (**C**CF, $^2J_{CF}$ = 21.3 Hz), 114.8 (**C**CF, $^2J_{CF}$ = 22.5 Hz), 101.1 (d), 81.6 (d), 79.9 (d), 68.1 (d), 47.7 (d), 40.5 (t), 34.2 (t), 31.5 (q), 27.8 (t), 25.4 (d), 23.3 (t), 22.3 (d), 20.9 (q), 20.8 (q), 15.9 (q), 12.5 (q); exact mass (electrospray) *m/z* calcd for $C_{38}H_{43}FNaO_9S_2$ (M + Na) 749.2225, found 749.2218.

(5*R*)-3-[1-Hydroxy-6,6-bis(phenylsulfanyl)hexyl]-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-3-(phenylselanyl)oxolan-2-one (10a, 10a')



2.1 **10** **10a, 10a'**, X = SPh, Y = SePh

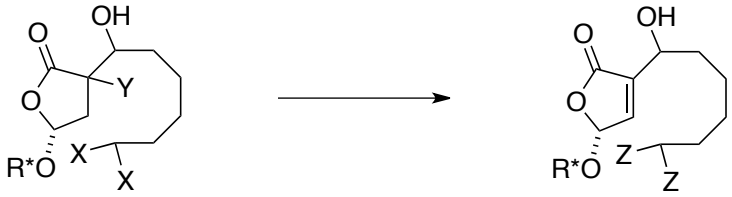
A solution of LDA was prepared as follows: BuLi (2.5 M in hexanes, 0.625 mL, 1.57 mmol) was added to a stirred and cooled (-78 °C) solution of *i*-Pr_2NH (0.25 mL, 1.76 mmol) in THF (5 mL), and stirring was continued for 30 min at -78 °C. A portion (1.18 mL, 0.32 mmol) of this stock solution was then taken up into a syringe and added manually dropwise over ca 10 min, to a stirred and cooled (-78 °C) solution of lactone **2.1** (100 mg, 0.25 mmol) in THF (2 mL). Stirring at -78 °C was continued for 45 min and then HMPA (0.5 mL) was added dropwise. Stirring was continued for 5 min and then a solution of aldehyde **10**[4] (127 mg, 0.55 mmol) in THF (2 mL) was added at a fast dropwise rate. Stirring at -78 °C was continued for 20-30 min (tlc control, silica, Et_2O-hexane, disappearance of aldehyde monitored). Then saturated aqueous NH_4Cl (3 mL) was added and the mixture were extracted with Et_2O. The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the

residue over silica gel (2 x 15 cm), using 30% Et_2O-hexane, gave **10a** (more polar isomer, 98 mg, 55%) and **10a'** (less polar isomer, 40 mg, 22%) as oils.

The more polar alcohol **10a** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3452, 3073, 3058, 2949, 2925, 2866, 1764, 1582, 1478, 1455, 1438; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2 H), 7.47-7.43 (m, 5 H), 7.40-7.37 (m, 1 H), 7.33-7.26 (m, 7 H), 5.67 (d, *J* = 5.8 Hz, 1 H), 4.39 (t, *J* = 6.6 Hz, 1 H), 3.65 (dd, *J* = 10.1, 3.9 Hz, 1 H), 3.58 (td, *J* = 10.7, 4.1 Hz, 1 H), 2.88 (dd, *J* = 14.6, 6.4 Hz, 1 H), 2.54-2.47 (m, 1 H), 2.17-2.10 (m, 2 H), 1.95-1.92 (m, 2 H), 1.87-1.83 (m, 2 H), 1.70-1.56 (m, 5 H), 1.51-1.35 (m, 3 H), 1.30-0.80 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2 (s), 138.2 (d), 134.6 (s), 134.5 (s), 133.0 (d), 132.9 (d), 130.0 (d), 129.2 (d), 129.2 (d), 129.1 (d), 129.1 (d), 127.9 (s), 127.9 (d), 125.9 (d), 98.1 (d), 71.8 (d), 58.6 (d), 50.5 (s), 48.0 (d), 39.7 (t), 36.0 (t), 35.2 (t), 34.6 (t), 31.7 (d), 30.7 (t), 27.0 (t), 26.0 (t), 25.2 (d), 23.0 (t), 22.5 (d), 21.4 (t), 15.7 (q); exact mass (electrospray) *m/z* calcd for $C_{38}H_{48}NaO_4S_2{}^{80}Se$ (M + Na) 735.2051, found 735.2050.

The less polar alcohol **10a'** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3500, 3073, 3058, 2951, 2925, 2867, 1764, 1582, 1477, 1455, 1438; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.1, 1.2 Hz, 2 H), 7.43-7.23 (m, 13 H), 5.66 (dd, *J* = 6.3, 1.2 Hz, 1 H), 4.34 (t, *J* = 6.7 Hz, 1 H), 3.59-3.54 (m, 2 H), 2.81 (s, 1 H), 2.70 (dd, *J* = 15.3, 6.5 Hz, 1 H), 2.46-2.39 (m, 1 H), 2.11-2.07 (m, 1 H), 1.98 (dd, *J* = 15.3, 1.5 Hz, 1 H), 1.82-1.78 (m, 2 H), 1.69-1.65 (m, 2 H), 1.60-1.46 (m, 4 H), 1.43-1.34 (m, 1 H), 1.30-1.21 (m, 3 H), 1.03-0.77 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1 (s), 138.1 (d), 134.2 (s), 132.7 (d), 129.9 (d), 129.1 (d), 128.8 (d), 127.6 (d), 125.8 (s), 97.7 (d), 77.3 (d), 71.9 (d), 58.2 (d), 53.4 (s), 47.8 (d), 39.5 (t), 36.6 (t), 35.6 (t), 34.3 (t), 31.4 (d), 31.1 (t), 26.9 (t), 26.0 (t), 25.0 (d), 22.8 (t), 22.3 (q), 21.1 (q), 15.6 (q); exact mass (electrospray) *m/z* calcd for $C_{38}H_{48}NaO_4S_2{}^{80}Se$ (M + Na) 735.2051, found 735.2047.

(5*R*)-3-[6,6-Bis(benzenesulfonyl)-1-hydroxyhexyl]-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (10b, 10b'). Use of 10a'

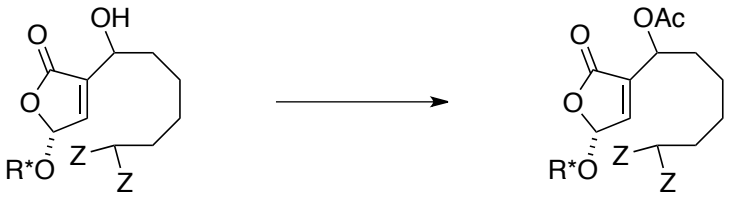


10a, 10a', X = SPh **10b, 10b'**, Z = SO_2Ph

MCPBA (70%, 276 mg, 1.12 mmol) was added to a stirred and cooled (0 °C) solution of **10a'** (40 mg, 0.056 mmol) in CH_2Cl_2 (4 mL). The ice bath was left in place but not recharged and stirring was continued for 3 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (2 mL) and saturated aqueous $Na_2S_2O_3$ (2 mL), and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave **10b'** (29.7 mg, 86%) as a colorless oil: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3525, 3020, 2953, 2925, 2869, 2848, 1761, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 4 H), 7.70 (t, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.9 Hz, 4 H), 6.91 (t, *J* = 1.3 Hz, 1 H), 6.01 (s, 1 H), 4.46 (dd, *J* = 8.4, 3.5 Hz, 1 H), 4.39 (t, *J* = 5.6 Hz, 1 H), 3.64 (td, *J* = 10.7, 4.2 Hz, 1 H), 2.41 (br s, 1 H), 2.19-2.07 (m, 4 H), 1.76-1.55 (m, 6 H), 1.49-1.32 (m, 3 H), 1.29-1.23 (m, 1 H), 1.07-0.80 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4 (s), 143.2 (d), 139.9 (s), 137.8 (s), 134.6 (d), 129.6 (d), 129.1 (d), 99.2 (d), 83.5 (d), 79.2 (d), 66.7 (d), 47.7 (d), 40.4 (t), 34.4 (t), 34.2 (t), 31.5 (d), 27.6 (t), 25.4 (t), 25.3 (d), 24.5 (t), 23.1 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) *m*/*z* calcd for $C_{32}H_{42}NaO_8S_2$ (M + Na) 641.2213, found 641.2206.

Use of 10a. MCPBA (70%, 678 mg, 2.75 mmol) was added to a stirred and cooled (0 °C) solution of **10a** (98 mg, 0.14 mmol) in CH_2Cl_2 (5 mL). The ice bath was left in place but not recharged and stirring was continued for 2 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (2 mL) and saturated aqueous $Na_2S_2O_3$ (2 mL), and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave **10b** (74 mg, 88%) as a colorless oil: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3526, 3065, 2954, 2920, 2869, 2848, 1761, 1455, 1448, 1438; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96-7.93 (m, 4 H), 7.71-7.68 (m, 2 H), 7.59-7.55 (m, 4 H), 6.88 (t, *J* = 1.4 Hz, 1 H), 5.99 (t, *J* = 1.2 Hz, 1 H), 4.44-4.43 (m, 1 H), 4.39 (t, *J* = 5.6 Hz, 1 H), 3.63 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.58 (br s, 1 H), 2.18-2.07 (m, 4 H), 1.74-1.56 (m, 6 H), 1.49-1.34 (m, 3 H), 1.28-1.23 (m, 1 H), 1.06-0.82 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5 (s), 143.0 (d), 139.7 (s), 137.8 (s), 134.6 (d), 129.6 (d), 129.1 (s), 99.3 (d), 83.5 (d), 79.4 (d), 66.4 (d), 47.7 (d), 40.4 (t), 34.4 (t), 34.2 (t), 31.5 (d), 27.6 (t), 25.4 (t), 25.3 (d), 24.5 (t), 23.2 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) *m/z* calcd for $C_{32}H_{42}NaO_8S_2$ (M + Na) 641.2213, found 641.2204.

6,6-Bis(benzenesulfonyl)-1-[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]hexyl acetate (10c, 10c'). Use of 10b'



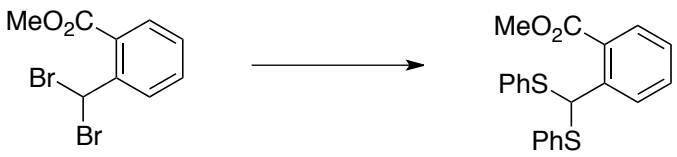
10b, 10b', Z = SO_2Ph **10c, 10c'**

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of **10b'** (27 mg, 0.044 mmol) in CH_2Cl_2 (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.016 mL, 0.22 mmol) and pyridine (0.28 mL, 0.35 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave **10c'** (25.8 mg, 90%) as a colorless foam: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3065, 2954, 2926, 2870, 1766, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 4 H), 7.72-7.69 (m, 2 H), 7.60-7.56 (m, 4 H), 6.91 (t, *J* = 1.3 Hz, 1 H), 6.01 (s, 1 H), 5.60-5.58 (m, 1 H), 4.35 (t, *J* = 5.6 Hz, 1 H), 3.62 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.17-2.09 (m, 7 H), 1.85-1.64 (m, 4 H), 1.62-1.55 (m, 2 H), 1.44-1.37 (m, 1 H), 1.31-1.22 (m, 3 H), 1.06-0.79 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (s), 168.9 (s), 144.5 (d), 137.9 (s), 137.8 (s), 136.8 (s), 134.6 (d), 129.6 (d), 129.6 (d), 129.1 (d), 98.9 (d), 83.6 (d), 79.2 (d), 68.2 (d), 47.7 (d), 40.5 (t), 34.2 (t), 32.0 (t), 31.5 (q), 27.7 (t), 25.4 (t), 25.2 (d), 24.4 (t), 23.1 (t), 22.2 (q), 20.9 (q), 20.9 (q), 15.7 (q); exact mass (electrospray) *m/z* calcd for $C_{34}H_{44}NaO_9S_2$ (M + Na) 683.2319, found 683.2312.

Use of 10b. DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of **10b** (57 mg, 0.092 mmol) in CH_2Cl_2 (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.033 mL, 0.46 mmol) and pyridine (0.060 mL, 0.74 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was then quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic

extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 30% EtOAc-hexane, gave **10c** (55 mg, 91%) as a colorless foam: FTIR ν_{max} (neat)/cm^{-1} 3096, 3067, 2954, 2926, 2870, 1767, 1448; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96-7.94 (m, 4 H), 7.72-7.68 (m, 2 H), 7.59-7.56 (m, 4 H), 6.85 (t, *J* = 1.4 Hz, 1 H), 5.97 (t, *J* = 1.4 Hz, 1 H), 5.51 (tdd, *J* = 5.6, 2.6, 1.5 Hz, 1 H), 4.36 (t, *J* = 5.6 Hz, 1 H), 3.63 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.16-2.07 (m, 7 H), 1.84-1.54 (m, 6 H), 1.44-1.22 (m, 4 H), 1.06-0.80 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8 (s), 168.9 (s), 144.0 (d), 137.9 (s), 137.8 (s), 137.0 (s), 134.6 (d), 129.6 (d), 129.6 (d), 129.1 (d), 129.1 (d), 98.9 (d), 83.6 (d), 79.5 (d), 68.2 (d), 47.7 (d), 40.5 (t), 34.2 (t), 32.3 (t), 31.5 (q), 27.7 (t), 25.4 (t), 25.4 (d), 24.6 (t), 23.2 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) *m/z* calcd for $C_{34}H_{44}NaO_9S_2$ (M + Na) 683.2319, found 683.2310.

Methyl 2-[bis(phenylsulfanyl)methyl]benzoate (6.3)

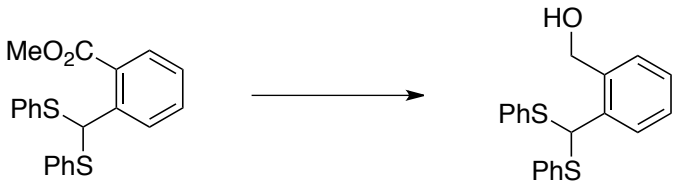


6.2 **6.3**

NaH (60%, 1.58 g, 39.32 mmol) was added slowly to a stirred and cooled (0 °C) solution of PhSH (3.9 mL, 38.04 mmol) in DMF (60 mL). Stirring was continued for 10 min, a solution of **6.2**[14] (4.68 g, 15.21 mmol) in DMF (10 mL) was then added, and stirring was continued for 12 h. The mixture was quenched with hydrochloric acid (1 M, 5 mL) and extracted with Et_2O (2 x 100 mL). The combined organic extracts were washed with aqueous NaOH (10%, 20 mL) to remove

unreacted PhSH, and the organic phase was washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (4 x 15 cm), using 5% Et_2O-hexane, gave **6.3** (3.5 g, 65%) as an oil: FTIR ν_{max} (cast film)/cm^{-1} 3057, 3019, 2948, 2926, 1715, 1598, 1581, 1480, 1438; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87-7.83 (m, 2 H), 7.47 (dddd, *J* = 7.9, 7.4, 1.5, 0.4 Hz, 1 H), 7.39-7.36 (m, 4 H), 7.30-7.21 (m, 7 H), 7.06 (s, 1 H), 3.82 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4 (s), 141.2 (s), 134.4 (d), 132.4 (d), 132.3 (d), 130.4 (d), 129.7 (d), 128.8 (d), 128.1 (s), 127.6 (d), 127.6 (d), 54.7 (q), 52.2 (d); exact mass (electrospray) *m/z* calcd for $C_{21}H_{18}NaO_2S_2$ (M + Na) 389.0640, found 389.0642.

{2-[Bis(phenylsulfanyl)methyl]phenyl}methanol (6.4)

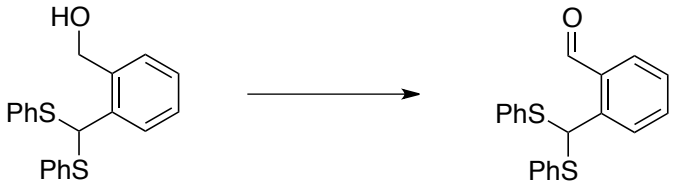


6.3 **6.4**

DIBAL-H (1 M solution in PhMe, 24.6 mL, 24.6 mmol) was added by syringe pump over 20 min to a stirred and cooled (-78 °C) solution of **6.3** (3.49 g, 9.85 mmol) in CH_2Cl_2 (100 mL). After the addition stirring at -78 °C was continued for 1 h and then the cold bath was replaced by an ice bath and stirring was continued for 1 h. The reaction was quenched with water (3.5 mL, 197 mmol) and NaF[24] (8.27 g, 197 mmol) at 0 °C, diluted with Et_2O (100 mL), stirred vigorously for 1 h at room temperature, and filtered through a pad of Celite using Et_2O. Evaporation of the filtrate and flash chromatography of the residue over silica gel (4 x 15 cm), using 40% Et_2O-hexane, gave **6.4** (3.13 g, 94%) as an oil: FTIR ν_{max} (neat)/cm^{-1} 3396, 3059, 3016, 3003, 2922,

2883, 1602, 1582, 1480, 1452, 1439; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 1 H), 7.40-7.22 (m, 13 H), 5.94 (s, 1 H), 4.66 (s, 2 H), 1.70 (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0 (s), 137.4 (s), 134.2 (s), 132.8 (d), 129.1 (d), 129.0 (d), 128.9 (d), 128.6 (d), 128.3 (d), 128.0 (d), 63.4 (t), 56.8 (d); exact mass (electrospray) *m/z* calcd for $C_{20}H_{18}NaOS_2$ (M + Na) 361.0691, found 361.0697.

2-[Bis(phenylsulfanyl)methyl]benzaldehyde (11)

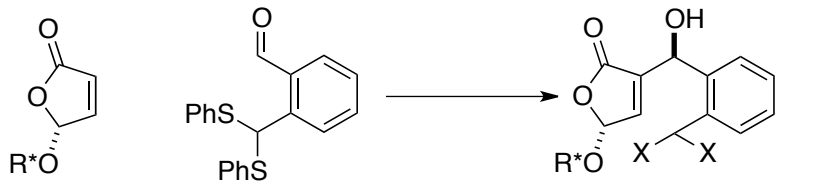


6.4 **11**

Et_3N (4.2 mL, 30 mmol) and DMSO (4.2 mL, 60 mmol) were added to a stirred and cooled (0 °C) solution of **6.4** (1.01 g, 3 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 5 min and then SO_3.py (1.4 g, 9 mmol) was added and stirring was continued for 12 h, the ice bath being left in place but not recharged. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 20% Et_2O-hexane, gave **11** (798 mg, 79%) as an oil: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3057, 3017, 2834, 2745, 1696, 1597, 1581, 1573, 1480, 1449, 1438; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1 H), 7.85 (d, *J* = 7.7 Hz, 1 H), 7.71 (dd, *J* = 7.6, 1.5 Hz, 1 H), 7.55-7.51 (m, 1 H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.39-7.35 (m, 4 H), 7.24-7.21 (m, 6 H), 6.97 (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7 (d), 141.5 (s), 134.1 (d), 134.0 (s), 133.9 (d), 132.6 (d), 132.3 (s),

129.9 (d), 128.9 (d), 128.3 (d), 127.9 (d), 54.1 (d); exact mass (electrospray) *m*/*z* calcd for $C_{20}H_{16}NaOS_2$ (M + Na) 359.0535, found 359.0538.

(5*R*)-3-[(*S*)-{2-[Bis(phenylsulfanyl)methyl]phenyl}(hydroxy)methyl]-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (11a)

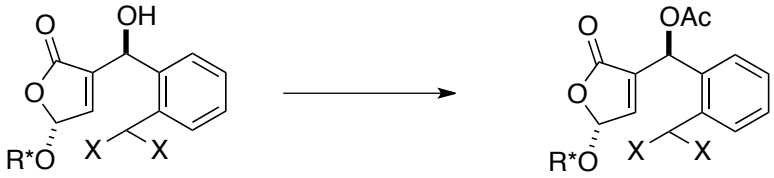


1.1 **11** **11a**, X = SPh

BuLi (2.5 M in hexane, 0.52 mL, 1.29 mmol) was added dropwise to a stirred and cooled (-20 °C) solution of PhSeSePh (367 mg, 1.17 mmol) in THF (5 mL). After 10 min, the mixture was cooled to -45 °C, a mixture of **1.1** (140 mg, 0.59 mmol) and **11** (198 mg, 0.59 mmol) in THF (4 mL) was added dropwise, and stirring was continued for 8 h at -45 °C. Then BnBr (0.18 mL, 1.47 mmol) and Bu_4NI (217 mg, 0.589 mmol) were added and stirring was continued for 8 h at -45 °C to -20 °C. The mixture was quenched with saturated aqueous NH_4Cl (5 mL) and extracted with Et_2O (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et_2O-hexanes, gave **11a** [183 mg, 55 %, 83% after correction for recovered **1.1** (75 mg)]: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3423, 3060, 3020, 2955, 2925, 2869, 1766, 1582, 1480, 1453, 1439; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.2 Hz, 1 H), 7.43-7.22 (m, 13 H), 6.71 (dd, *J* = 1.6, 1.3 Hz, 1 H), 5.90 (s, 1 H), 5.88 (t, *J* = 1.2 Hz, 1 H), 5.79 (s, 1 H), 3.60 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.09-2.04 (m, 2 H), 1.69-1.61 (m, 2 H), 1.34-1.18 (m, 2 H), 1.02-0.75 (m, 13 H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 170.3 (s), 145.2 (d), 138.4 (s), 137.2 (s), 134.1 (s), 133.6 (s), 133.2 (d), 132.8 (d), 129.3 (d), 128.9 (d), 128.9 (d), 128.9 (d), 128.5 (d), 128.3 (d), 128.0 (d), 99.4 (d), 79.3 (d), 66.1 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.4 (d), 25.3 (d), 23.1 (t), 22.2 (d), 20.8 (q), 15.8 (q); exact mass (electrospray) *m*/*z* calcd for $C_{34}H_{38}NaO_4S_2$ (M + Na) 597.2104, found 597.2102.

(*S*)-{2-[Bis(phenylsulfanyl)methyl]phenyl}[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (11b)

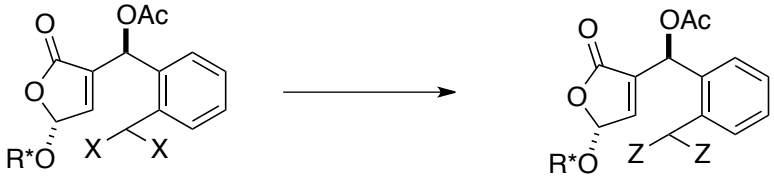


11a **11b**, X = SPh

DMAP (0.5 mg, 0.005 mmol) was added to a stirred solution of **11a** (28 mg, 0.049 mmol) in CH_2Cl_2 (2 mL). The mixture was then cooled to 0 °C, and AcCl (0.0104 mL, 0.146 mmol) and pyridine (0.0196 mL, 0.24 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was then quenched with saturated aqueous $CuSO_4$ (2 mL) and water (2 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% Et_2O-hexane, gave **11b** (23 mg, 76%): FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3060, 3022, 2955, 2924, 2869, 1774, 1745, 1582, 1481, 1454, 1439; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.38-7.21 (m, 13 H), 6.94 (s, 1 H), 6.65 (t, *J* = 1.4 Hz, 1 H), 5.96 (s, 1 H), 5.87 (t, *J* = 1.1 Hz, 1 H), 3.59 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.07-1.99 (m, 5 H), 1.67-

1.60 (m, 2 H), 1.39-1.33 (m, 1 H), 1.22-1.15 (m, 1 H), 1.01-0.69 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4 (s), 168.4 (s), 146.7 (d), 137.1 (s), 136.3 (s), 134.1 (s), 133.8 (s), 133.4 (s), 132.7 (d), 132.4 (d), 129.6 (d), 129.2 (d), 128.9 (d), 128.9 (d), 128.4 (d), 128.1 (d), 128.0 (d), 127.7 (d), 98.7 (d), 79.0 (d), 66.3 (d), 55.9 (d), 47.7 (d), 40.4 (t), 34.2 (t), 31.4 (q), 25.2 (d), 23.1 (t), 22.2 (d), 20.8 (q), 15.7 (q); exact mass (electrospray) *m/z* calcd for $C_{36}H_{40}NaO_5S_2$ (M + Na) 639.2209, found 639.2214.

(*S*)-{2-[Bis(benzenesulfonyl)methyl]phenyl}[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (11c)

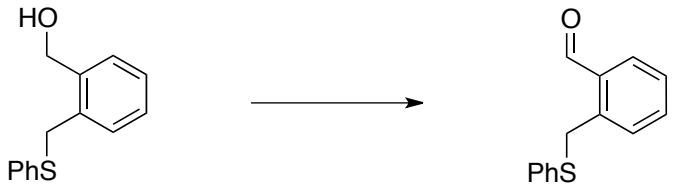


11b, X = SPh **11c**, Z = SO_2Ph

MCPBA (70%, 58 mg, 0.26 mmol) was added to a stirred and cooled (0 °C) solution of **11b** (16 mg, 0.026 mmol) in CH_2Cl_2 (3 mL). The ice bath was left in place but not recharged and stirring was continued for 6 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (2 mL) and saturated aqueous $Na_2S_2O_3$ (2 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 40% EtOAc-hexane, gave **11c** (14 mg, 82%) as a colorless oil: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3067, 3024, 2955, 2926, 2870, 1768, 1584, 1478, 1446; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.79 (m, 5 H), 7.65-7.60 (m, 2 H), 7.52-7.44 (m, 6 H), 7.34-7.30 (m, 1 H), 6.86 (t, *J* = 1.4 Hz, 1 H), 6.68 (s, 1

H), 6.43 (s, 1 H), 6.01 (t, *J* = 1.2 Hz, 1 H), 3.62 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.13-2.07 (m, 5 H), 1.67-1.61 (m, 2 H), 1.40-1.35 (m, 1 H), 1.26-1.19 (m, 1 H), 1.00-0.74 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6 (s), 168.4 (s), 146.7 (d), 138.2 (s), 137.6 (s), 137.6 (s), 136.1 (s), 134.6 (d), 134.4 (d), 133.7 (d), 131.6 (d), 130.8 (d), 130.2 (d), 130.1 (d), 130.0 (d), 129.8 (d), 129.1 (d), 128.9 (d), 128.8 (d), 128.8 (d), 128.3 (d), 124.0 (s), 99.1 (d), 82.6 (d), 79.5 (d), 65.7 (d), 47.7 (d), 40.6 (t), 34.1 (t), 31.4 (q), 30.9 (d), 25.2 (d), 23.1 (t), 22.2 (q), 20.9 (q), 15.8 (q); exact mass (electrospray) *m/z* calcd for $C_{36}H_{40}NaO_5S_2$ (M + Na) 703.2006, found 703.2001.

(*S*)-{2-[(benzenesulfonyl)methyl]phenyl}[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (14) (a) 2-[(Phenyl-sulfanyl)methyl]benzaldehyde (12)

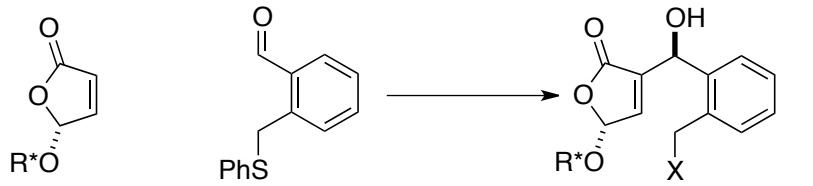


7.3 **12**

Et_3N (2.16 mL, 15.5 mmol) and DMSO (2.2 mL, 31.04 mmol) were added to a stirred and cooled (0 °C) solution of **7.3**[16] (388 mg, 1.55 mmol) in CH_2Cl_2 (11 mL). Stirring was continued for 5 min and then SO_3.py (988 mg, 6.21 mmol) was added. Stirring was continued for 12 h, the ice bath being left in place but not recharged. The reaction mixture was then quenched with water (5 mL) and extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 15% Et_2O-hexane, gave **12** (343 mg, 89%) as an oil: FTIR ν_{max}

($CDCl_3$, cast)/cm^{-1} 3059, 3019, 2932, 2836, 2744, 1696, 1598, 1575, 1481, 1451, 1439, 1402; ^1H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1 H), 7.85-7.83 (m, 1 H), 7.49-7.41 (m, 2 H), 7.34-7.21 (m, 6 H), 4.53 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0 (d), 139.8 (s), 135.3 (s), 133.7 (s), 133.6 (d), 132.8 (d), 131.3 (d), 131.2 (d), 128.9 (d), 127.8 (d), 127.1 (d), 36.3 (t); exact mass (EI) *m/z* calcd for $C_{14}H_{12}OS$ (M) 228.0608, found 228.0610.

(b) (5*R*)-3-[(*S*)-Hydroxy({2-[(phenylsulfanyl)methyl]phenyl})methyl]-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2,5-dihydrofuran-2-one (12a)

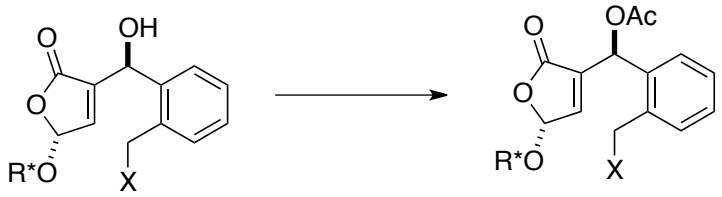


1.1 **12** **12a**, X = SPh

BuLi (2.5 M in hexane, 80 μL, 0.20 mmol) was added dropwise to a stirred and cooled (-20 °C) solution of PhSeSePh (63 mg, 0.20 mmol) in THF (2 mL). After 10 min, the mixture was cooled to -45 °C, a mixture of **1.1** (78 mg, 0.33 mmol) and **12** (90 mg, 0.39 mmol) in THF (2 mL) was added dropwise, and stirring was continued for 8 h at -45 °C. Then BnBr (44 μL, 0.36 mmol) and Bu_4NI (12 mg, 0.036 mmol) were added and stirring was continued for 8 h at -45 °C to -20 °C. The mixture was quenched with saturated aqueous NH_4Cl (5 mL) and extracted with Et_2O (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et_2O-hexanes, gave **12a** [78 mg, 56%, 87% after correction for recovered **1.1** (32 mg)]: FTIR ν_{max} (microscope)/cm^{-1} 3452, 3060, 2954, 2924, 2869, 1768, 1584, 1481, 1454, 1439; ^1H NMR (400

MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.34-7.17 (m, 8 H), 6.88 (t, *J* = 1.5 Hz, 1 H), 6.02 (t, *J* = 1.3 Hz, 1 H), 5.93 (s, 1 H), 4.36 (d, *J* = 12.6 Hz, 1 H), 4.15 (d, *J* = 12.7 Hz, 1 H), 3.64 (td, *J* = 10.7, 4.3 Hz, 1 H), 3.16 (s, 1 H), 2.14-2.04 (m, 2 H), 1.70-1.63 (m, 2 H), 1.44-1.21 (m, 2 H), 1.07-0.76 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2 (s), 144.5 (d), 139.2 (s), 138.3 (s), 135.2 (s), 134.7 (s), 130.9 (d), 130.8 (d), 129.0 (d), 128.5 (d), 128.2 (d), 127.6 (d), 127.1 (d), 99.3 (d), 79.2 (d), 65.8 (d), 47.7 (d), 40.4 (t), 37.1 (t), 34.2 (t), 31.5 (d), 25.5 (d), 23.3 (t), 22.2 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) *m/z* calcd for $C_{28}H_{34}NaO_4S$ (M + Na) 489.207, found 489.2070.

(c) (*S*)-[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]({2-[(phenylsulfanyl)methyl]phenyl})methyl acetate (12b)

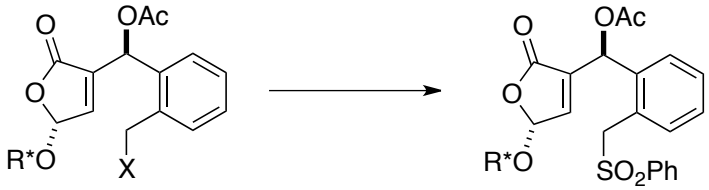


12a **12b**, X = SPh

DMAP (1.2 mg, 0.01 mmol) was added to a stirred solution of **12a** (20 mg, 0.043 mmol) in CH_2Cl_2 (2 mL). The mixture was then cooled to 0 °C, and AcCl (9.1 μL, 0.13 mmol) and pyridine (21 μL, 0.25 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over

silica gel (1 x 15 cm), using 40% Et_2O-hexane, gave **12b** (21 mg, 96%) as a colorless oil: FTIR ν_{max} ($CHCl_3$, cast)/cm^{-1} 3060, 2955, 2925, 2869, 1771, 1748, 1659, 1600, 1584, 1481, 1455, 1439; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.36-7.18 (m, 8 H), 6.94 (t, *J* = 1.3 Hz, 1 H), 6.83 (t, *J* = 1.4 Hz, 1 H), 6.03 (t, *J* = 1.2 Hz, 1 H), 4.36 (d, *J* = 13.0 Hz, 1 H), 4.31 (d, *J* = 13.0 Hz, 1 H), 3.64 (td, *J* = 10.7, 4.2 Hz, 1 H), 2.12-2.03 (m, 5 H), 1.69-1.62 (m, 2 H), 1.43-1.36 (m, 1 H), 1.26-1.20 (m, 1 H), 1.02-0.73 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5 (s), 168.6 (s), 146.0 (d), 137.0 (s), 135.8 (s), 135.3 (s), 135.0 (s), 130.7 (d), 130.4 (d), 128.9 (d), 128.9 (d), 128.1 (d), 127.9 (d), 126.6 (d), 98.7 (d), 79.0 (d), 66.4 (d), 47.8 (d), 40.4 (t), 36.7 (t), 34.2 (t), 31.5 (q), 25.4 (d), 23.3 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.9 (q); exact mass (electrospray) *m*/*z* calcd for $C_{30}H_{36}NaO_5S$ (M + Na) 531.2175, found 531.2172.

(d) (*S*)-{2-[(benzenesulfonyl)methyl]phenyl}[(5*R*)-5-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-oxo-2,5-dihydrofuran-3-yl]methyl acetate (14)

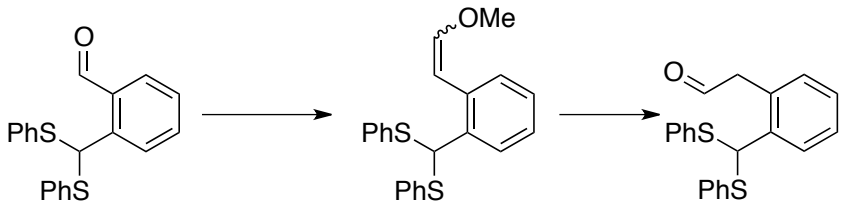


12b, X = SPh **14**, Z = SO_2Ph

MCPBA (70%, 102 mg, 0.41 mmol) was added to a stirred and cooled (0 °C) solution of **12b** (21 mg, 0.041 mmol) in CH_2Cl_2 (3 mL). The ice bath was left in place but not recharged and stirring was continued for 4 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (2 mL) and saturated aqueous $Na_2S_2O_3$ (2 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and

evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et_2O-hexane, gave **14** (22 mg, 100%) as a colorless oil: FTIR ν_{max} (CH_2Cl_2, cast)/cm^{-1} 3065, 2955, 2926, 2870, 1768, 1585, 1496, 1448; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2 H), 7.67-7.52 (m, 4 H), 7.41 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.31 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.21 (dd, *J* = 7.8, 1.3 Hz, 1 H), 6.93 (t, *J* = 1.4 Hz, 1 H), 6.78 (t, *J* = 1.4 Hz, 1 H), 6.04 (t, *J* = 1.3 Hz, 1 H), 4.69 (d, *J* = 14.1 Hz, 1 H), 4.62 (d, *J* = 14.1 Hz, 1 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.12-2.01 (m, 5 H), 1.68-1.60 (m, 2 H), 1.43-1.32 (m, 1 H), 1.26-1.19 (m, 1 H), 1.01-0.70 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8 (s), 168.8 (s), 145.1 (d), 139.1 (s), 137.0 (s), 136.8 (s), 133.8 (d), 133.0 (d), 129.5 (d), 129.2 (d), 129.1 (d), 129.0 (d), 128.4 (d), 126.4 (s), 99.2 (d), 79.2 (d), 66.7 (d), 59.4 (t), 47.7 (d), 40.6 (t), 34.2 (t), 31.4 (q), 25.3 (d), 23.2 (t), 22.2 (d), 20.9 (q), 20.8 (q), 15.8 (q); exact mass (electrospray) *m/z* calcd for $C_{30}H_{36}NaO_7S$ (M + Na) 563.2074, found 563.2074.

(1*S*)-2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-[(3*R*)-3-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-5-oxocyclopent-1-en-1-yl]ethyl acetate (15) (a) 2-{2-[Bis(phenyl-sulfanyl)methyl]phenyl}acetaldehyde (13)



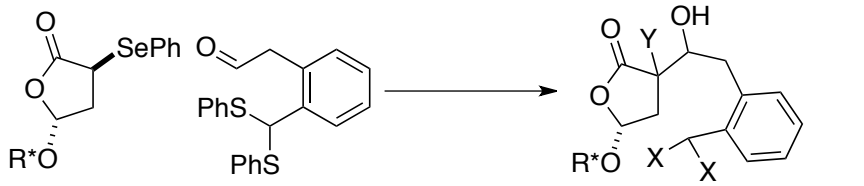
11 **8.1** **13**

$(Me_3Si)_2NNa$ (1 M in THF, 7.13 mL, 7.13 mmol) was added dropwise over 5 min to a stirred and cooled (-78 °C) solution of (methoxymethyl)triphenylphosphonium chloride (3.26 g, 9.5 mmol) in THF (20 mL). The resulting slurry was stirred for 90 min at -78 °C and then a solution of **11**

(798 mg, 2.38 mmol) was added dropwise over 5 min. The cold bath was left in place but not recharged and stirring was continued for 12 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (ca 10 mL) and extracted with Et_2O. The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 5% Et_2O-hexane, gave **8.1**, which was used for the next step.

Hydrochloric acid (4 M, 4 mL) was added to a solution of **8.1** in THF (15 mL) and the mixture was refluxed at 66 °C for 3 h, cooled, quenched with saturated aqueous $NaHCO_3$ (ca 5 mL), diluted with water (20 mL) and extracted with Et_2O (50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 x 15 cm), using 10% Et_2O-hexane, gave **13** (464 mg, 56% over two steps) as an oil: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3058, 3019, 2822, 2724, 1721, 1581, 1480, 1448, 1438, 1415; ^1H NMR (500 MHz, $CDCl_3$) δ 9.53 (t, *J* = 2.3 Hz, 1 H), 7.71 (d, *J* = 6.9 Hz, 1 H), 7.37-7.24 (m, 12 H), 7.15 (dd, *J* = 7.2, 1.8 Hz, 1 H), 5.54 (s, 1 H), 3.71 (d, *J* = 1.9 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0 (d), 138.5 (s), 133.9 (s), 133.0 (d), 131.2 (d), 129.7 (s), 129.5 (d), 129.0 (d), 128.5 (d), 128.2 (d), 128.2 (d), 57.9 (d), 47.9 (t); exact mass (electrospray) *m/z* calcd for $C_{21}H_{18}NaOS_2$ (M + Na) 373.0691, found 373.0695.

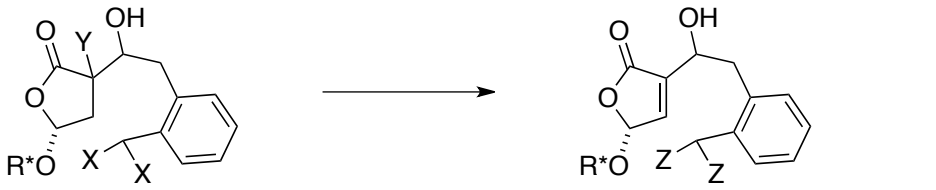
(b) (4*R*)-2-(2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-hydroxyethyl)-4-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-2-(phenylselanyl)cyclopentan-1-one (13a, 13a')



2.1 **13** **13a, 13a'**, X = SPh

$(Me_3Si)_2NK$ (0.5 M in PhMe, 0.92 mL, 0.46 mmol) was added dropwise (over ca 10 min) to a stirred and cooled (-78 °C) solution of lactone **2.1** (166 mg, 0.42 mmol) in THF (5 mL). Stirring at -78 °C was continued for 45 min and then a solution of aldehyde **13** (165 mg, 0.47 mmol) in THF (2 mL) was added. Stirring at -78 °C was continued for 20-30 min (tlc control, silica, 40% Et_2O-hexane, disappearance of aldehyde monitored). Then saturated aqueous NH_4Cl (3 mL) was added and the mixture was extracted with Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 40% Et_2O-hexane gave **13a** and **13a'** as an oil. This mixture of diastereoisomers was used directly for next step.

(c) (4*R*)-2-[2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-hydroxyethyl]-4-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}cyclopent-2-en-1-one (13b, 13b')



13a, 13a', X = SPh **13b, 13b'**, Z = SO_2Ph

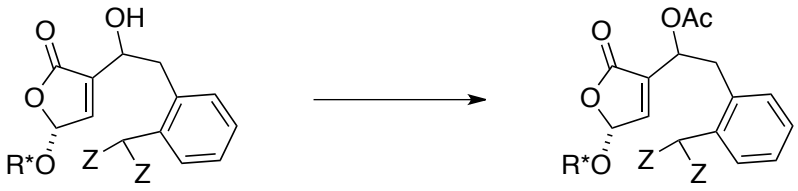
MCPBA (70%, 1.27 g, 5.1 mmol) was added to a stirred and cooled (0 °C) solution of **13a** and **13a'** (192 mg, 0.26 mmol) in CH_2Cl_2 (5 mL). The ice bath was left in place but not recharged

and stirring was continued for 12 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ (2 mL) and saturated aqueous $Na_2S_2O_3$ (2 mL) and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, dried (Na_2SO_4) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 60% Et_2O-hexane, gave a mixture of diastereomers which was separated into three fractions (more polar, 13 mg, 5%; less polar, 10 mg, 4%; mixture, 73 mg, 27%). The more polar alcohol **13b** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3508, 3067, 2954, 2928, 2871, 1754, 1584, 1493, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.84-7.78 (m, 4 H), 7.66-7.62 (m, 2 H), 7.47 (t, *J* = 7.5 Hz, 4 H), 7.38 (td, *J* = 7.5, 1.4 Hz, 1 H), 7.31 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.15 (dd, *J* = 7.6, 1.3 Hz, 1 H), 6.95 (t, *J* = 1.4 Hz, 1 H), 6.31 (s, 1 H), 6.02 (t, *J* = 1.4 Hz, 1 H), 4.60-4.58 (m, 1 H), 3.65 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.77 (dd, *J* = 14.5, 2.6 Hz, 1 H), 2.42 (dd, *J* = 14.5, 9.0 Hz, 1 H), 2.16-2.10 (m, 2 H), 1.71-1.66 (m, 2 H), 1.41-1.37 (m, 1 H), 1.30-1.21 (m, 2 H), 1.05-0.82 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1 (s), 143.8 (s), 139.1 (s), 139.0 (s), 138.5 (s), 138.0 (s), 134.7 (s), 134.5 (s), 131.8 (s), 131.5 (s), 130.9 (s), 130.0 (s), 129.6 (s), 128.9 (s), 128.9 (s), 127.6 (s), 124.6 (s), 99.4 (s), 82.7 (s), 79.3 (s), 68.6 (s), 47.8 (s), 40.4 (s), 39.0 (s), 34.2 (s), 31.6 (s), 25.4 (s), 23.2 (s), 22.3 (s), 21.0 (s), 15.9 (q); exact mass (electrospray) *m/z* calcd for $C_{35}H_{40}NaO_8S_2$ (M + Na) 675.2057, found 675.2046.

The less polar alcohol **13b'** had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3503, 3067, 2955, 2928, 2870, 1753, 1599, 1584, 1493, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.94 (m, 1 H), 7.85-7.77 (m, 4 H), 7.66-7.57 (m, 3 H), 7.49-7.28 (m, 5 H), 7.14 (dd, *J* = 7.6, 1.3 Hz, 1 H), 6.96 (t, *J* = 1.4 Hz, 1 H), 6.39 (s, 1 H), 6.00 (s, 1 H), 4.61-4.59 (m, 1 H), 3.66 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.84 (dd, *J* = 14.5, 2.7 Hz, 1 H), 2.43 (dd, *J* = 14.5, 9.1 Hz, 1 H), 2.16-2.11 (m, 2 H), 1.71-1.66 (m, 2 H), 1.42-1.38 (m, 1 H), 1.29-1.19 (m, 2 H), 1.08-0.81 (m, 12 H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 13C NMR ($CDCl_3$, 126 MHz) δ 170.1 (s), 144.1 (d), 139.1 (s), 139.0 (s), 138.5 (s), 137.9 (s), 135.4 (d), 134.6 (d), 134.5 (d), 133.7 (d), 131.7 (d), 131.5 (d), 130.8 (d), 130.0 (d), 129.6 (d), 128.9 (d), 128.9 (d), 128.8 (d), 128.3 (d), 127.5 (d), 124.6 (s), 99.3 (d), 82.7 (d), 79.2 (d), 68.6 (d), 47.8 (d), 40.3 (d), 38.5 (d), 34.2 (d), 31.5 (d), 25.4 (d), 23.2 (t), 22.2 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) *m/z* calcd for $C_{35}H_{40}NaO_8S_2$ (M + Na) 675.2057, found 675.2058.

(d) (1*S*)-2-{2-[Bis(benzenesulfonyl)methyl]phenyl}-1-[(3*R*)-3-{[(1*R*,2*S*,5*R*)-5-methyl-2-(propan-2-yl)cyclohexyl]oxy}-5-oxocyclopent-1-en-1-yl]ethyl acetate (15)



13b, 13b' **15**, Z = SO_2Ph

DMAP (ca 1 mg, 0.01 mmol) was added to a stirred solution of **13b** and **13b'** (73 mg, 0.11 mmol) in CH_2Cl_2 (3 mL). The mixture was then cooled to 0 °C, and AcCl (0.048 mL, 0.67 mmol) and pyridine (0.072 mL, 0.89 mmol) were added sequentially. The ice bath was left in place but not recharged and stirring was continued for 3 h, during which time the cold bath reached room temperature. The reaction mixture was quenched with saturated aqueous $CuSO_4$ (2 mL) and water (5 mL), and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 x 15 cm), using 50% EtOAc-hexane, gave **15** as a mixture of diastereomers which was separated into two fractions (less polar, 22 mg, 28%; mixture, 42 mg,

55%). The less polar isomer had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3066, 2954, 2928, 2870, 1758, 1748, 1584, 1491, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.3 Hz, 1 H), 7.94 (dd, *J* = 8.3, 1.0 Hz, 2 H), 7.71-7.64 (m, 3 H), 7.59-7.49 (m, 3 H), 7.40-7.28 (m, 4 H), 6.98 (dd, *J* = 7.5, 1.3 Hz, 1 H), 6.81 (t, *J* = 0.9 Hz, 1 H), 6.35 (s, 1 H), 5.86 (s, 1 H), 5.62 (t, *J* = 7.3 Hz, 1 H), 3.61 (td, *J* = 10.7, 4.3 Hz, 1 H), 2.87 (dd, *J* = 14.3, 7.3 Hz, 1 H), 2.50 (dd, *J* = 14.3, 7.4 Hz, 1 H), 2.12-2.04 (m, 5 H), 1.68-1.64 (m, 2 H), 1.41-1.34 (m, 1 H), 1.25-1.19 (m, 1 H), 1.00-0.75 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2 (s), 169.2 (s), 147.0 (d), 138.7 (s), 138.1 (s), 137.7 (s), 134.5 (d), 134.4 (d), 134.1 (s), 132.0 (d), 131.2 (d), 130.5 (d), 129.9 (d), 129.6 (d), 128.9 (d), 128.8 (d), 127.7 (d), 124.4 (s), 99.1 (d), 82.0 (d), 79.8 (d), 69.3 (d), 47.7 (d), 40.4 (t), 35.0 (t), 34.1 (t), 31.5 (q), 25.4 (d), 23.1 (t), 22.2 (d), 20.9 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) *m/z* calcd for $C_{37}H_{42}NaO_9S_2$ (M + Na) 717.2162, found 717.2162.

The mixture of isomers (containing mainly the more polar) had: FTIR ν_{max} ($CDCl_3$, cast)/cm^{-1} 3067, 2955, 2928, 2870, 1807, 1758, 1748, 1584, 1492, 1448; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-7.97 (m, 3 H), 7.75-7.64 (m, 3 H), 7.62-7.31 (m, 7 H), 7.03-6.99 (m, 1 H), 6.85-6.83 (m, 1 H), 6.42-6.39 (m, 1 H), 5.99-5.90 (m, 1 H), 5.73-5.65 (m, 1 H), 3.67-3.57 (m, 1 H), 2.91 (dd, *J* = 14.2, 7.6 Hz, 1 H), 2.64-2.51 (m, 1 H), 2.15-2.04 (m, 5 H), 1.72-1.66 (m, 2 H), 1.45-1.37 (m, 1 H), 1.29-1.20 (m, 1 H), 1.06-0.78 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2 (s), 169.3 (s), 147.5 (d), 139.0 (s), 138.8 (s), 138.1 (s), 137.8 (s), 137.7 (s), 137.5 (s), 135.4 (d), 134.6 (d), 134.5 (d), 134.5 (d), 134.4 (d), 134.2 (d), 133.9 (s), 132.0 (d), 131.9 (d), 131.3 (d), 131.3 (d), 130.8 (d), 130.5 (d), 130.5 (d), 130.0 (d), 129.9 (d), 129.9 (d), 129.7 (d), 129.7 (d), 129.6 (d), 128.9 (d), 128.9 (d), 128.9 (d), 128.8 (d), 128.8 (d), 128.7 (d), 128.7 (d), 128.7 (d), 128.7 (d), 127.7 (d), 127.7 (d), 124.4 (s), 124.4 (s), 99.1 (d), 98.7 (d), 82.1 (d), 82.0 (d), 79.8 (d), 78.5 (d), 69.4 (d), 69.4 (d), 47.7 (d), 47.7 (d), 40.5 (t), 40.1 (t), 35.0 (t), 34.9 (t), 34.2 (t), 34.2 (t),

31.5 (q), 31.5 (q), 25.4 (d), 25.3 (d), 23.1 (t), 22.2 (t), 22.2 (d), 21.0 (q), 21.0 (q), 20.9 (q), 20.9 (q), 15.9 (q); exact mass (electrospray) *m*/*z* calcd for $C_{37}H_{42}NaO_9S_2$ (M + Na) 717.2162, found 717.2163.

Notes and references

25 Made by hydrogenation of 5-butyl-2,5-dihydrofuran-2-one: K. Iwai, M. Kawai, Kosugi and H. Uda, *Chem. Lett.*, 1974, 385-388.

26 J. J. Bourguignon and C. G. Wermuth, *J. Org. Chem.*, 1981, **46**, 4889-4894.

X-ray Structure Determination For X-ray analysis, crystals were grown via slow vapor diffusion of a poor solvent into a solution of the compound in a good solvent, as indicated for the individual compounds below. Data were collected using a three-circle (fixed-chi) diffractometer equipped with an CCD-based area detector.[a] All data were collected using Mo K*a* radiation (*l* = 0.71073 Å) and with the crystal cooled to –100 °C. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using direct methods with dual-space recycling (*SHELXd*[b]), and least-squares refinements were completed using the program *SHELXL-97*.[b] Hydrogen atoms attached to carbons were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbons, and were given thermal parameters 20% greater than those of their parent atoms.

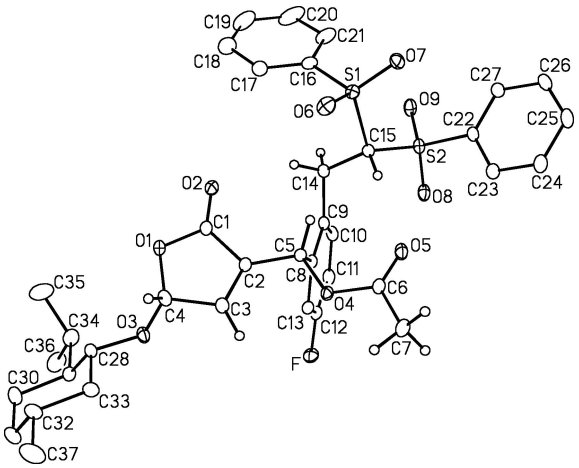


Figure 1. ORTEP diagram of **9c**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of **9c** in Et_2O.

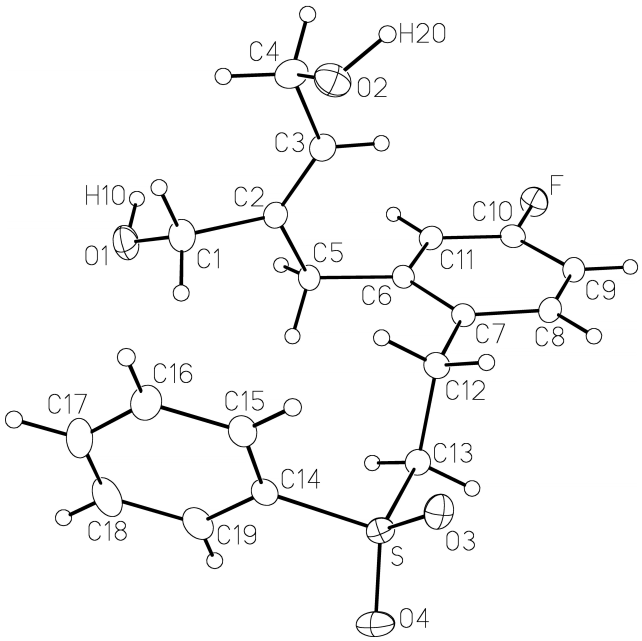


Figure 2. ORTEP diagram of **9.2**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of **9.1** in Et_2O.

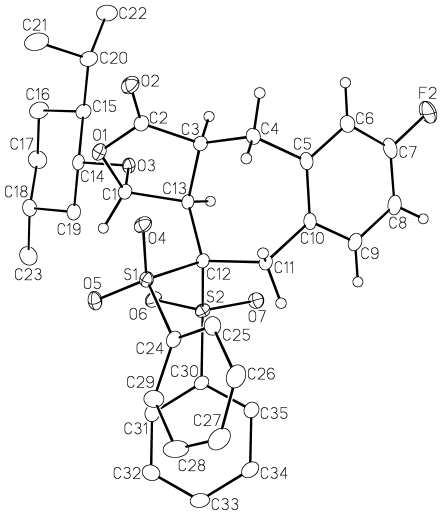


Figure 3. ORTEP diagram of **9.4** Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization Crystallization by vapor diffusion of hexanes into a solution of **9.3** in *i*-Pr_2O.

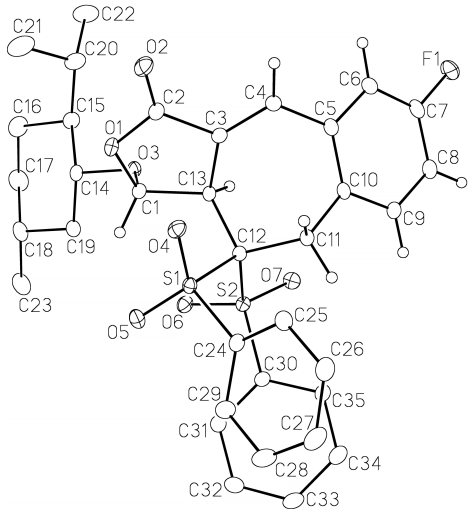


Figure 4. ORTEP diagram of **9g**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of **9g** in Et_2O.

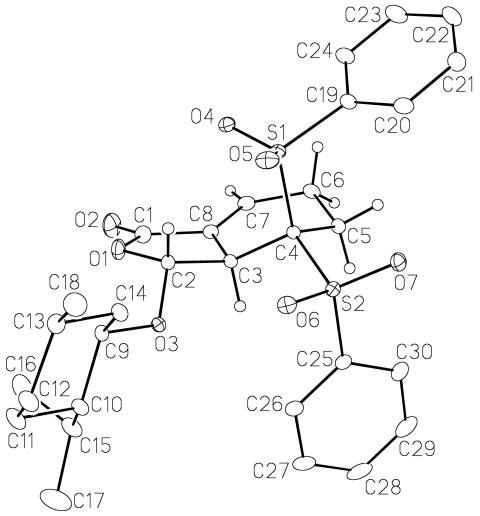
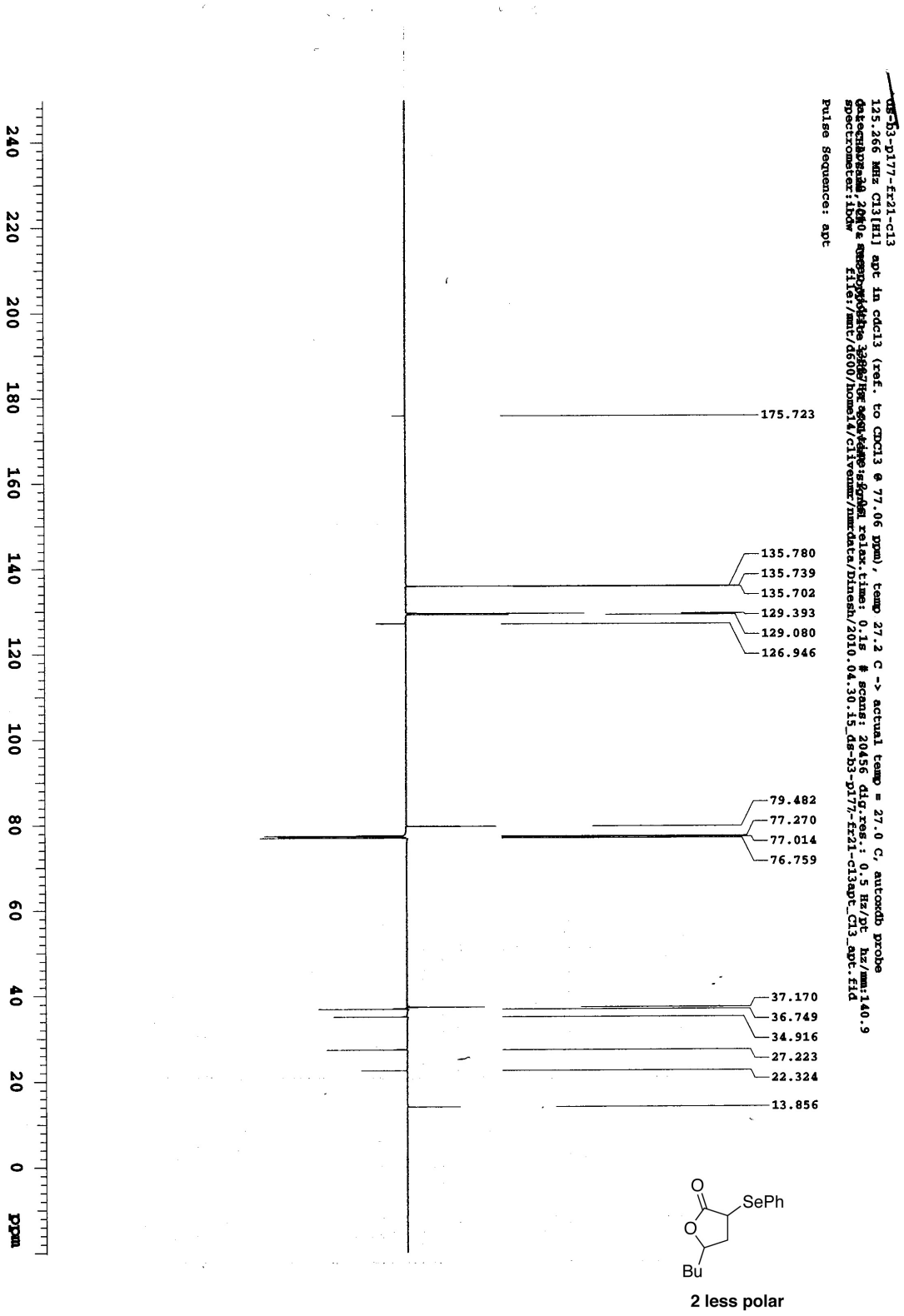
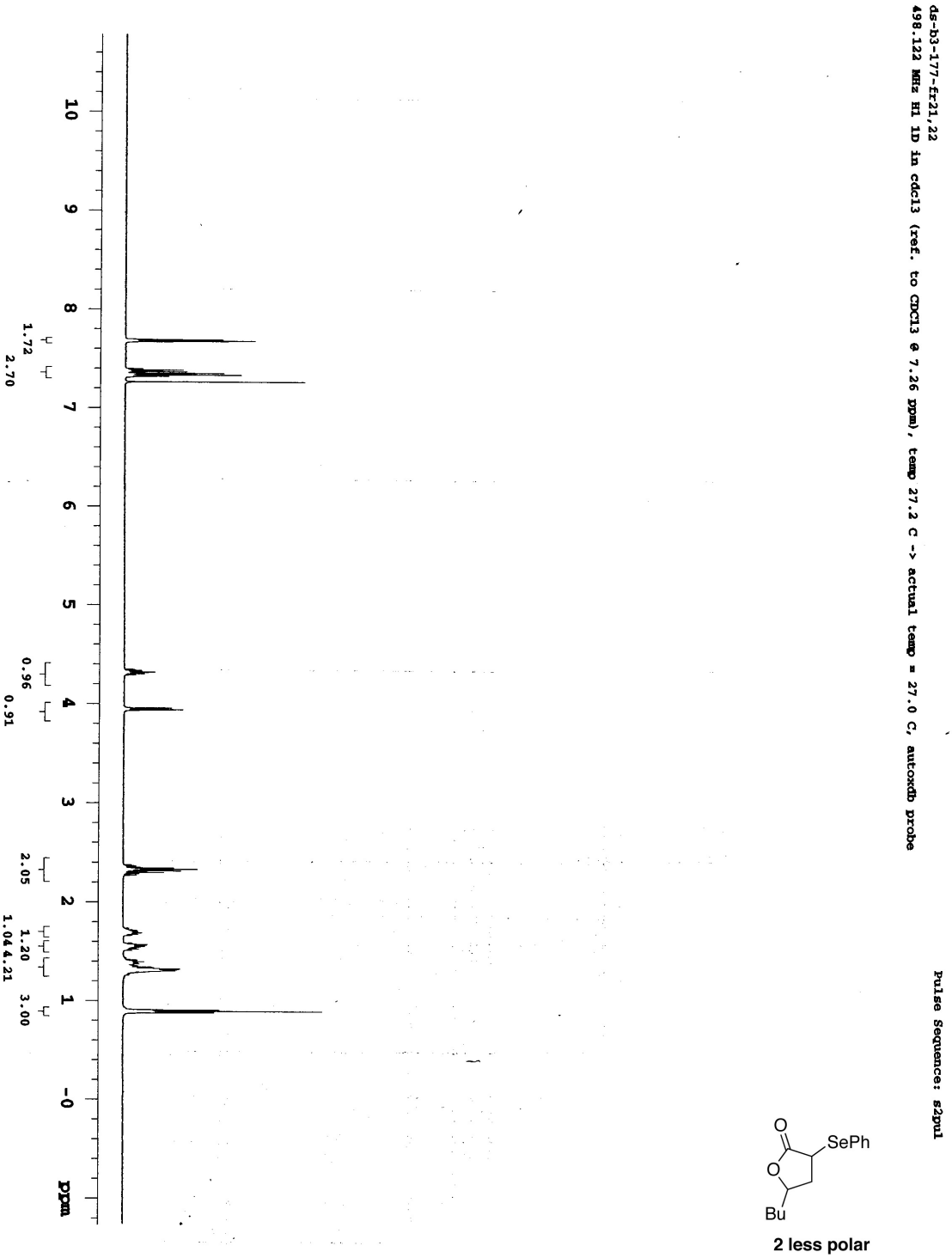
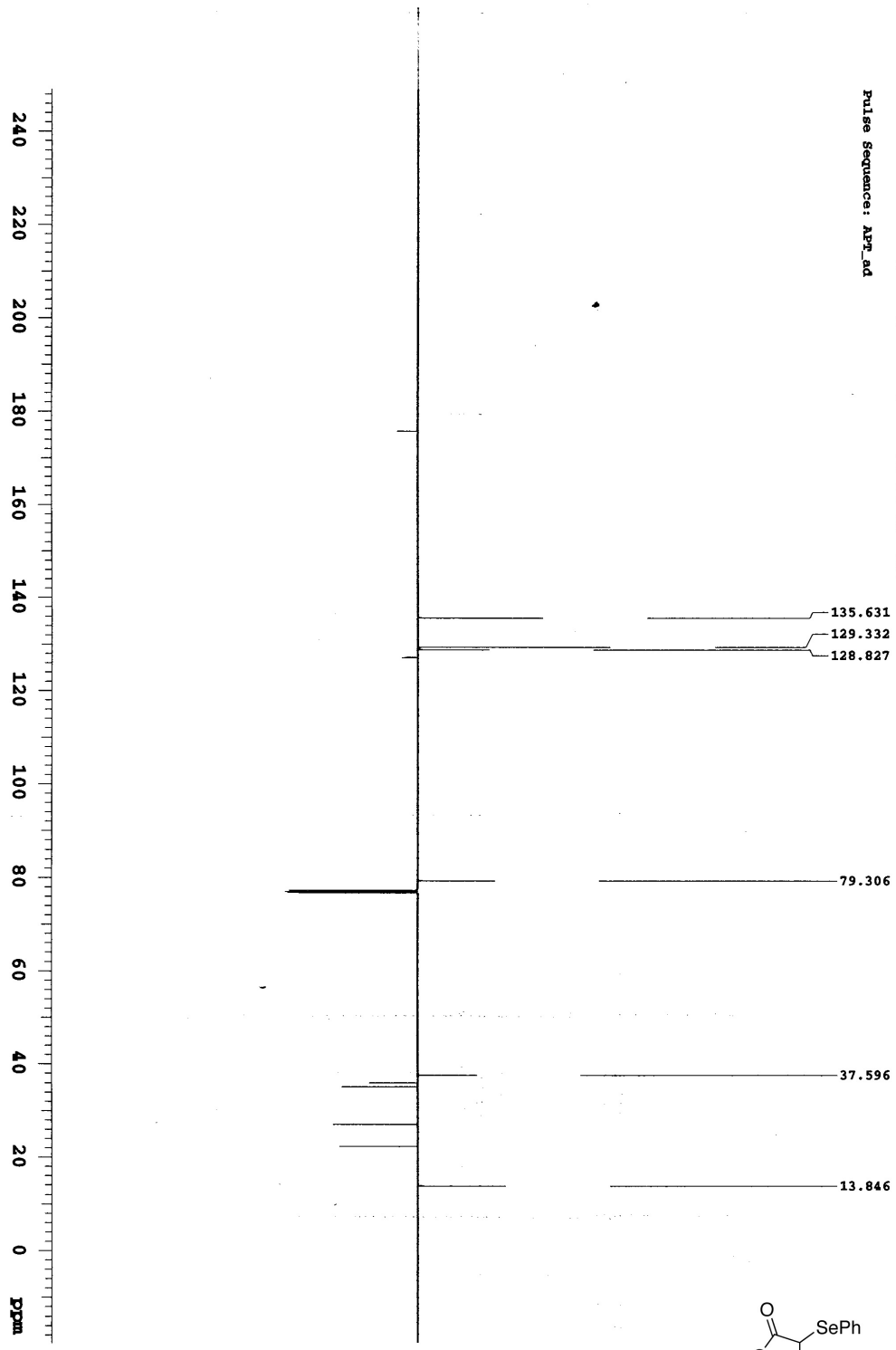


Figure 5. ORTEP diagram of **5l**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Crystallization by vapor diffusion of hexanes into a solution of **5l** in CH_2Cl_2.

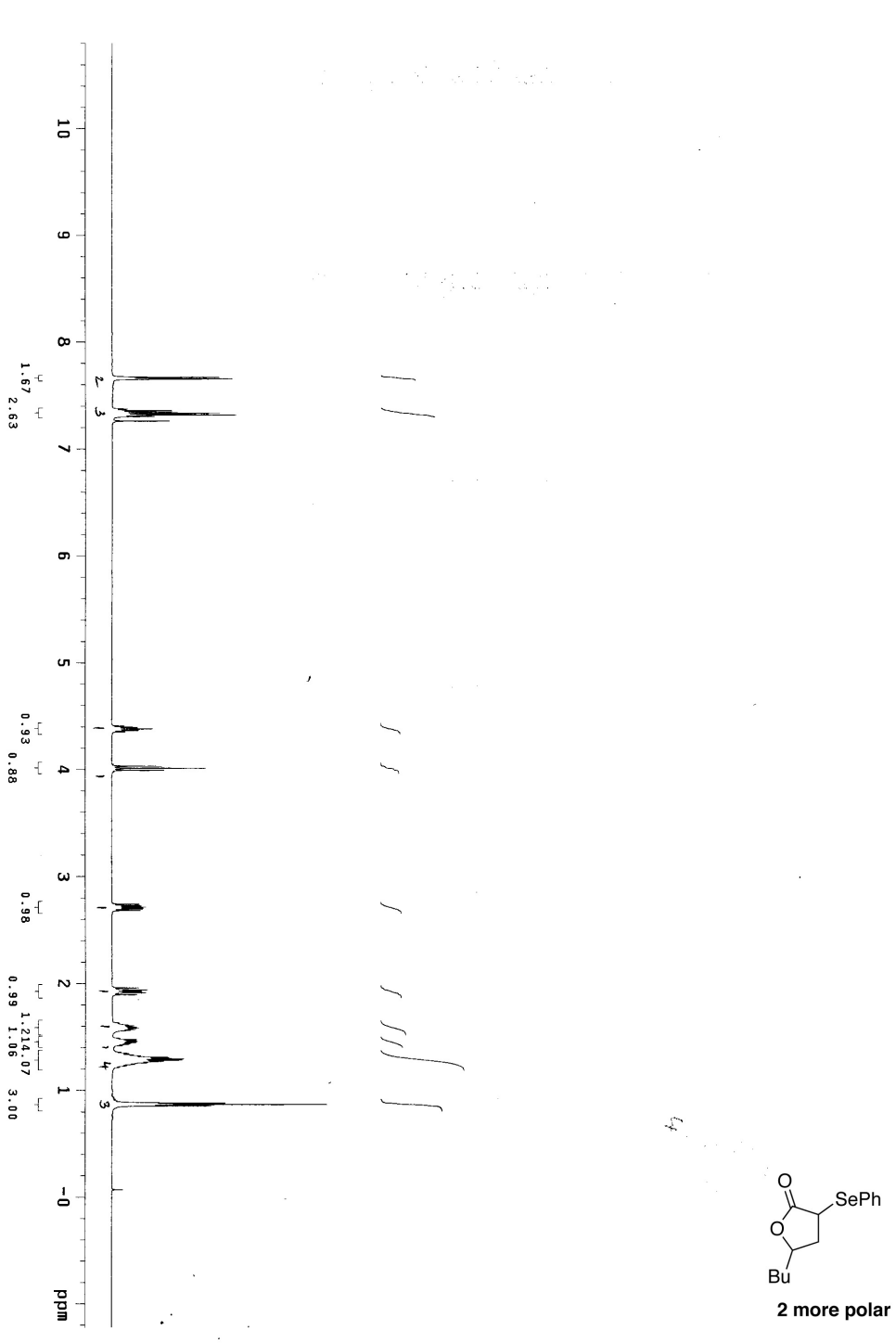

ds-b3-p177-fr21-c13
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
Pulse Sequence: apt
175.723
135.780
135.739
135.702
129.393
129.080
126.946
79.482
77.270
77.014
76.759
37.170
36.749
34.916
27.223
22.324
13.856
O
SePh
O
Bu
2 less polar
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

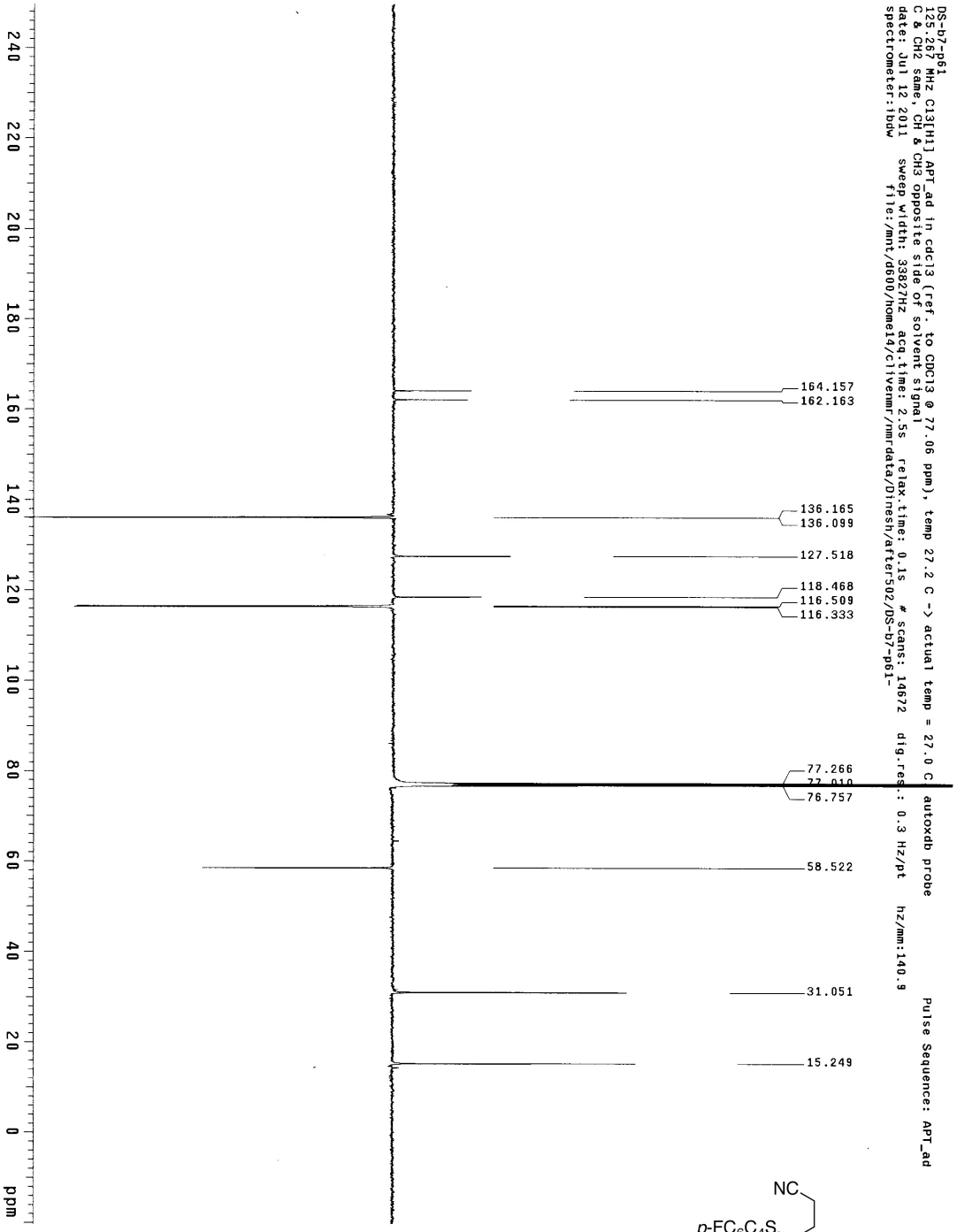


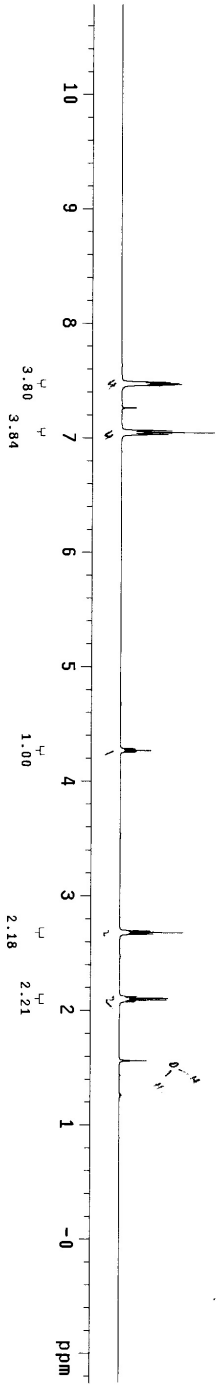
2 less polar



2 more polar

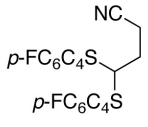



DS-b7-p61
125.267 MHz C13[H1]_APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jul 12 2011 sweep width: 33827Hz acq.time: 2.5s relax.time: 0.1s # scans: 14672 dig.res.: 0.3 Hz/pt
spectrometer:ibdw file:/mnt/d600/home14/clivenmr/nmrdata/Dinesh/after502/DS-b7-p61- autoxdb probe
Pulse Sequence: APT_ad hz/mm:140.9
164.157
162.163
136.165
136.099
127.518
118.468
116.509
116.333
77.266
77.010
76.757
58.522
31.051
15.249
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm
NC
p-FC6C4S
p-FC6C4S
3.3

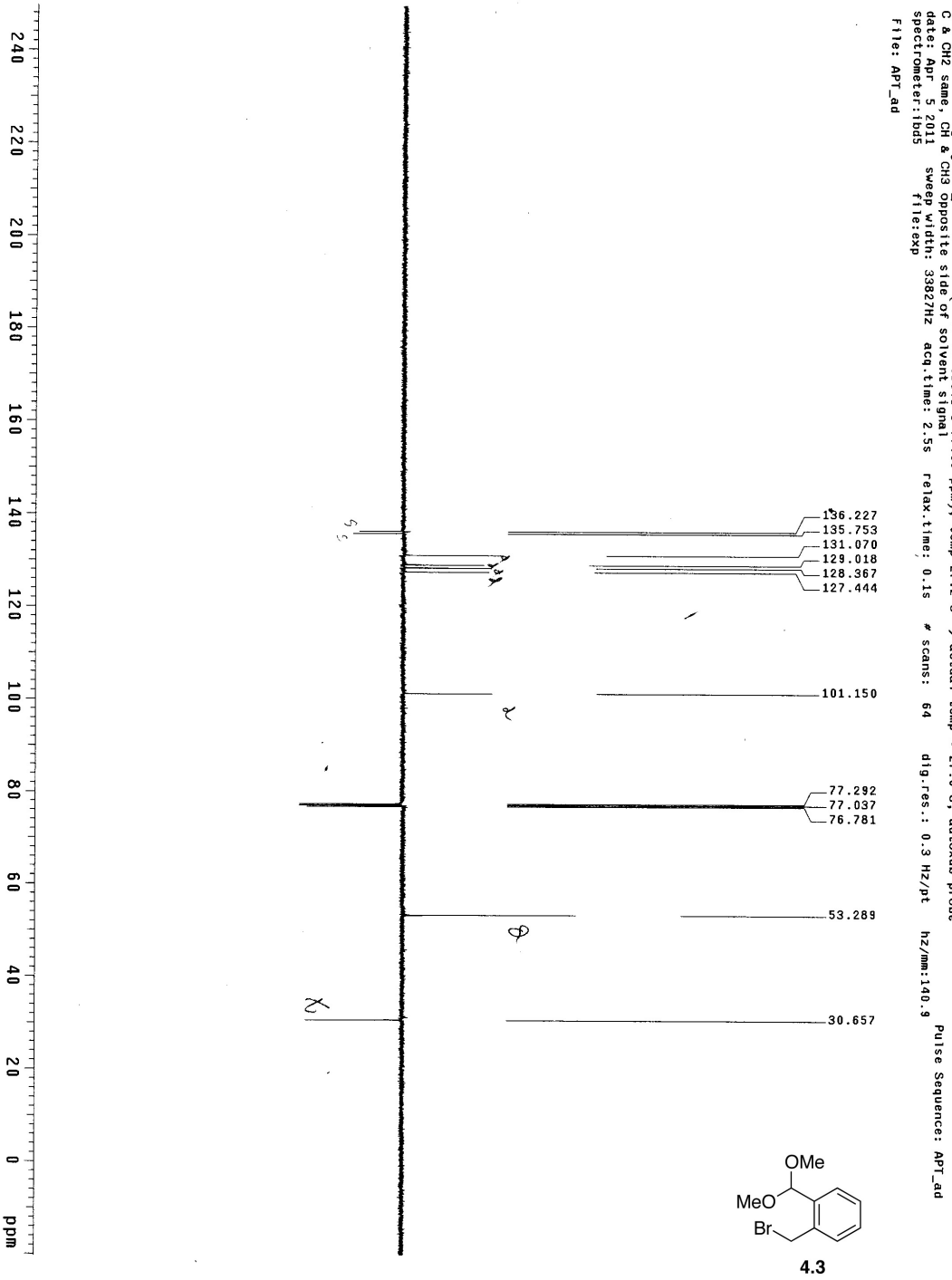


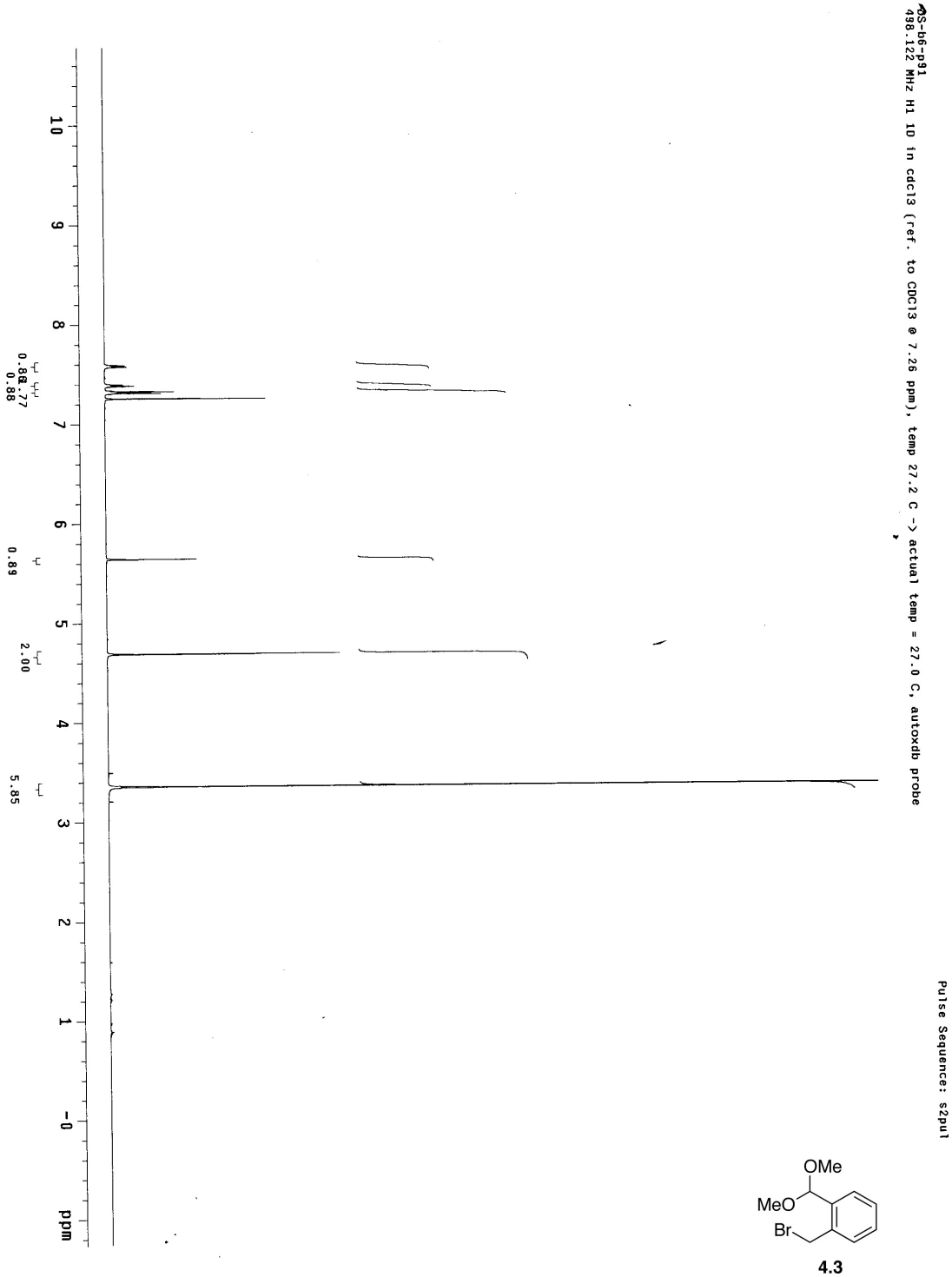
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

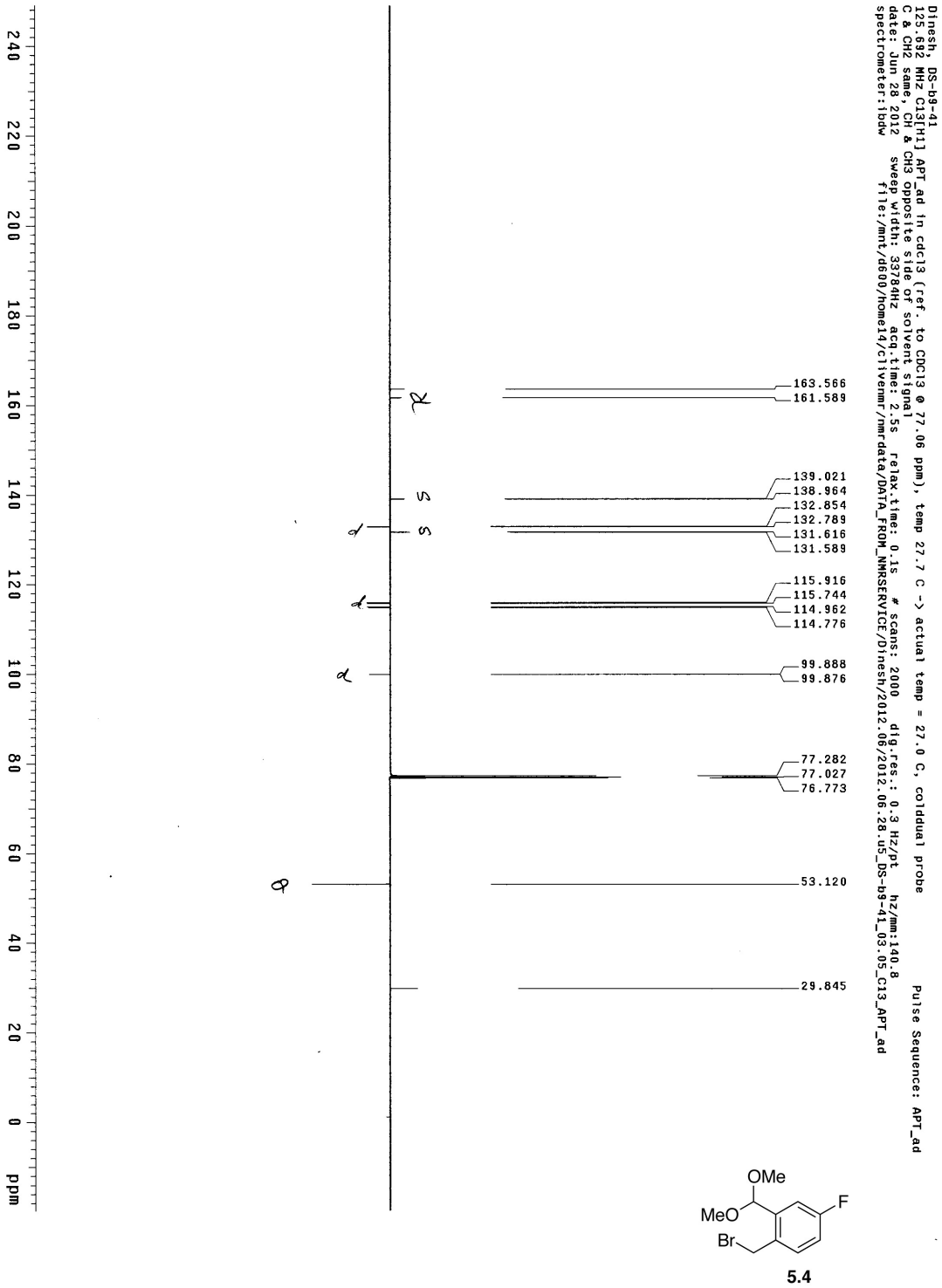
Pulse Sequence: s2pul

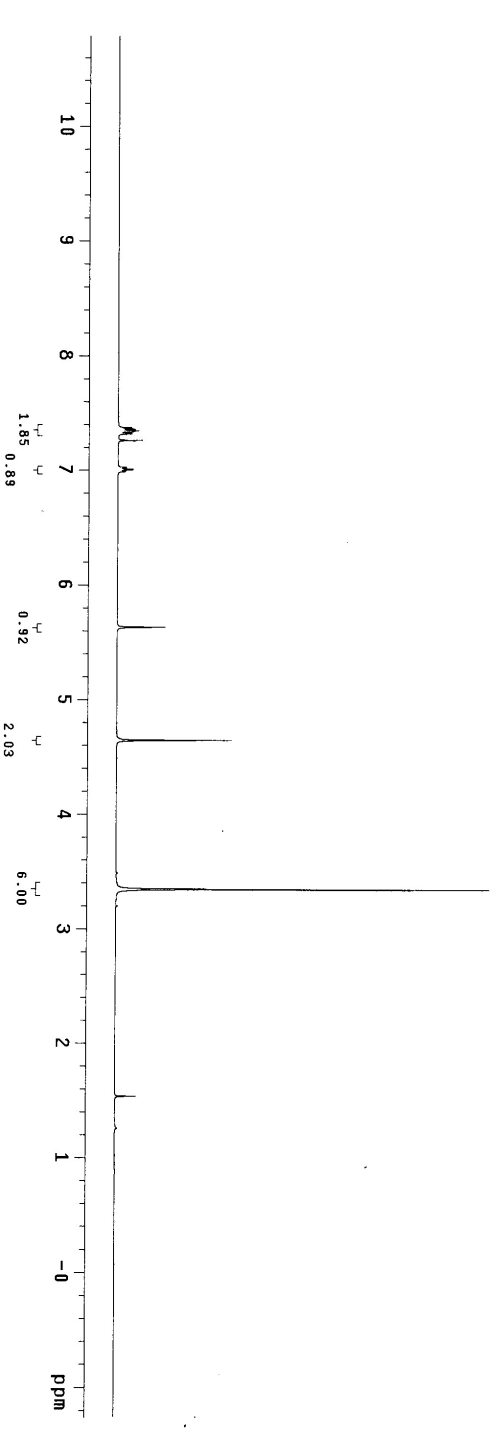


3.3



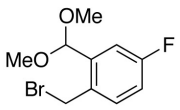



Dinesh, DS-b9-41
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: APT_ad
date: Jun 28 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 2000 dig.res.: 0.3 Hz/pt hz/mm:140.8
spectrometer:ibdw file:/mnt/d600/home14/clivenmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2012.06/2012.06.28.u5_DS-b9-41_03.05_C13_APT_ad
163.566
161.589
139.021
138.964
132.854
132.789
131.616
131.589
115.916
115.744
114.962
114.776
99.888
99.876
77.282
77.027
76.773
53.120
29.845
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
OMe
MeO
Br
F
5.4

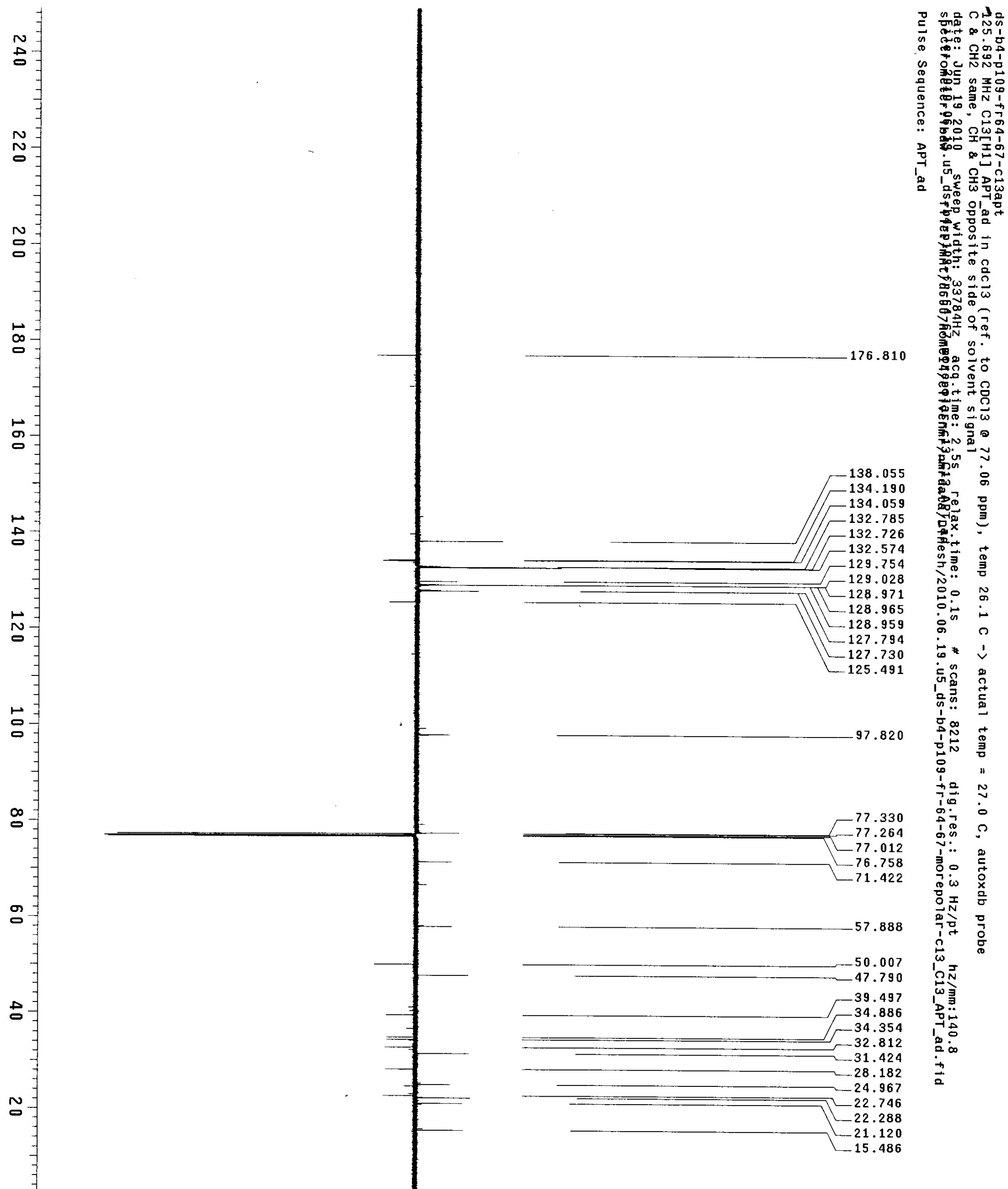


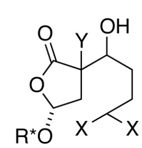
DS-bg-p41-acetal
496.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul



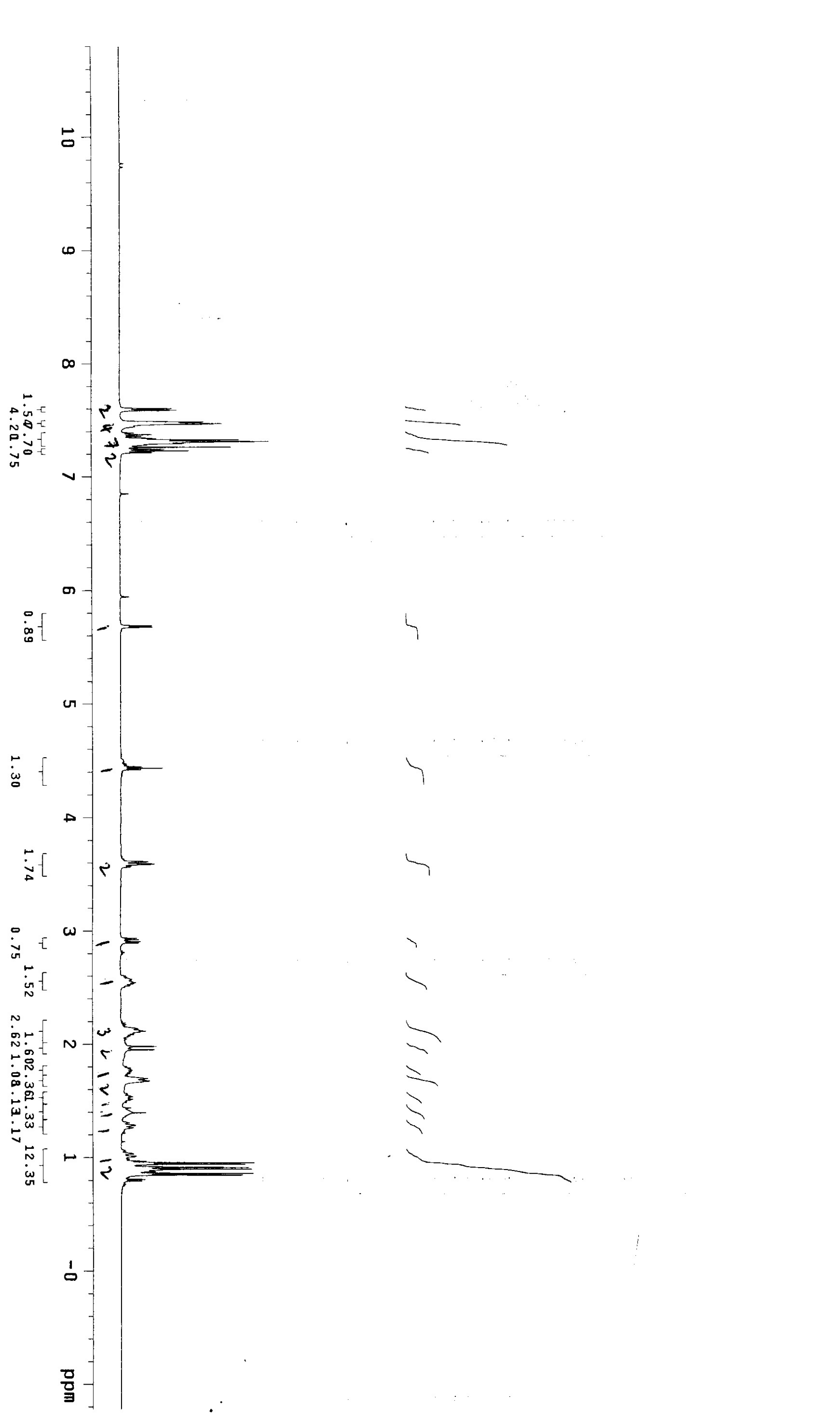
5.4

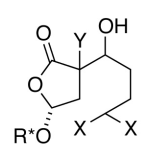

ds-b4-p109-fr64-67-c13apt
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 19 2010 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 8212 dig.res.: 0.3 Hz/pt hz/mm:140.8
Pulse Sequence: APT_ad
176.810
138.055
134.190
134.059
132.785
132.726
132.574
129.754
129.028
128.971
128.965
128.959
127.794
127.730
125.491
97.820
77.330
77.264
77.012
76.758
71.422
57.888
50.007
47.790
39.497
34.886
34.354
32.812
31.424
28.182
24.967
22.746
22.288
21.120
15.486
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Y
OH
O
R*O
X
X

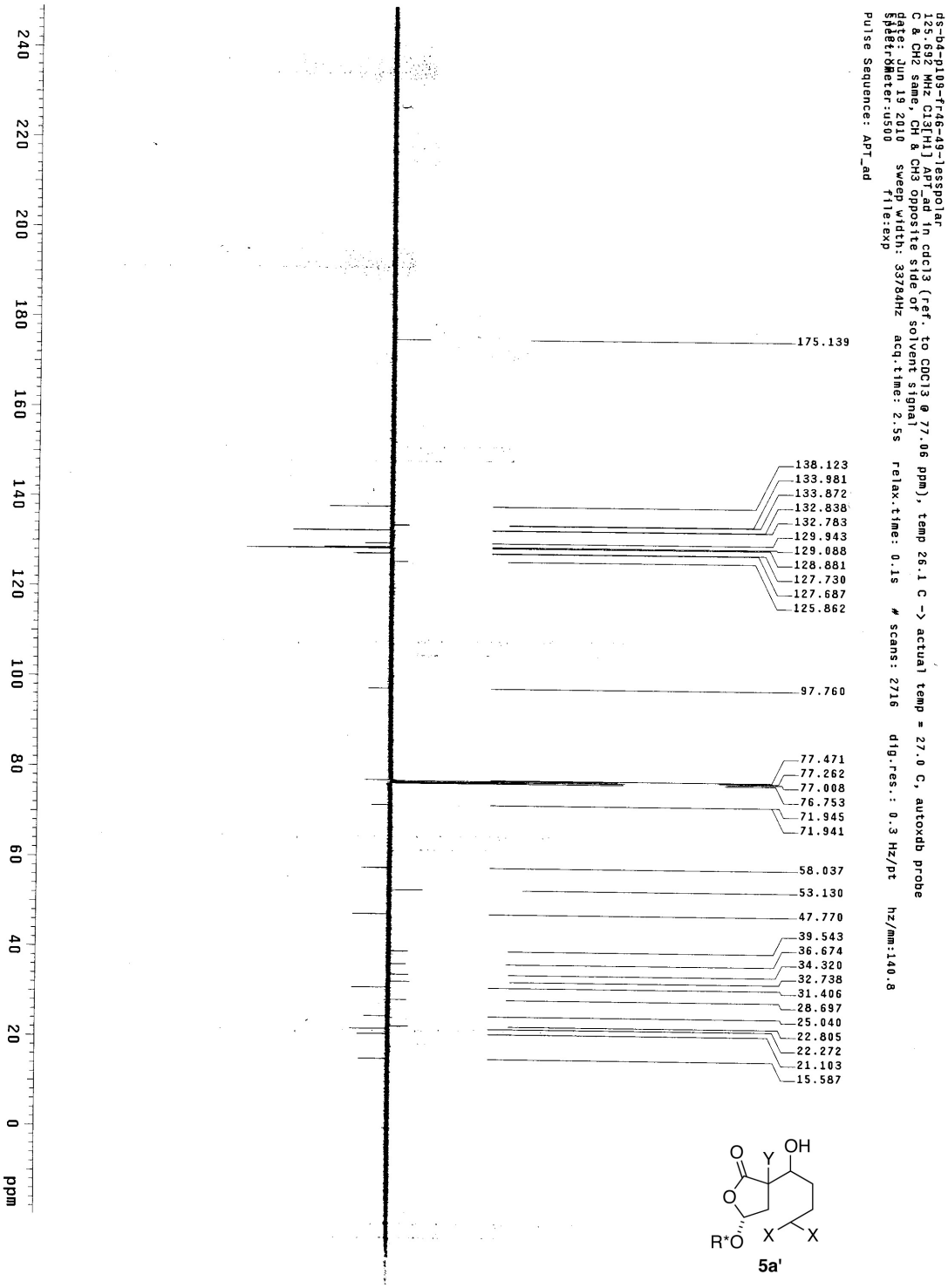
5a

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

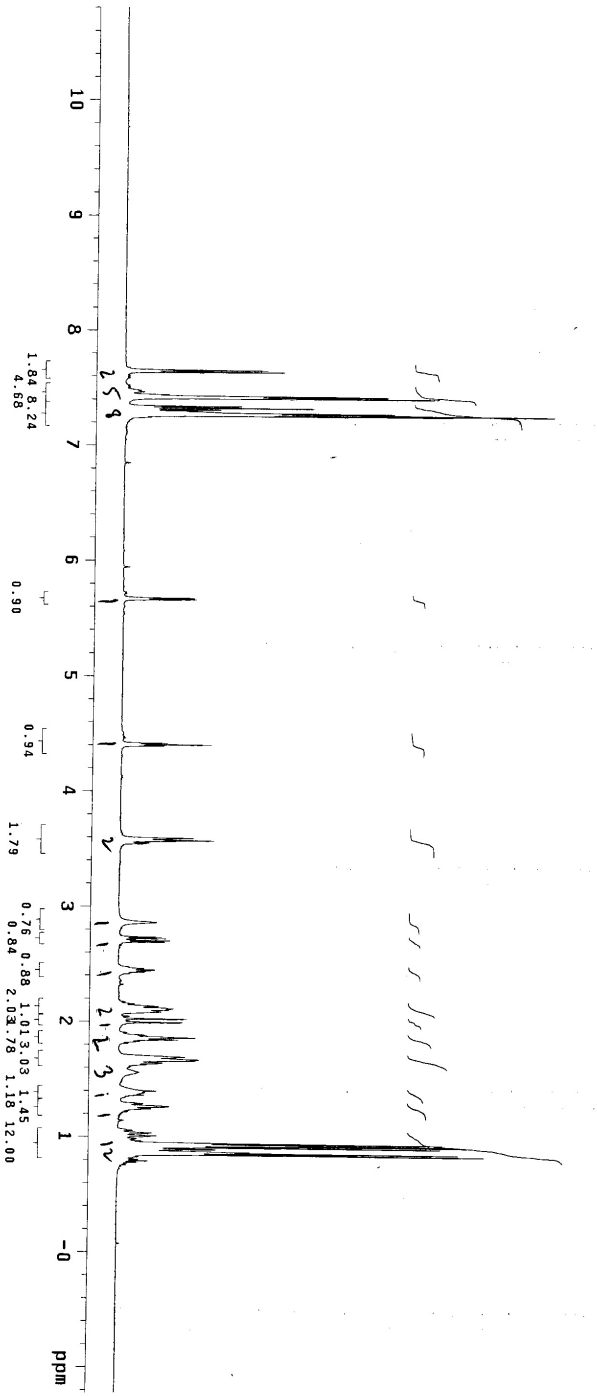


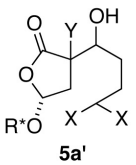


5a

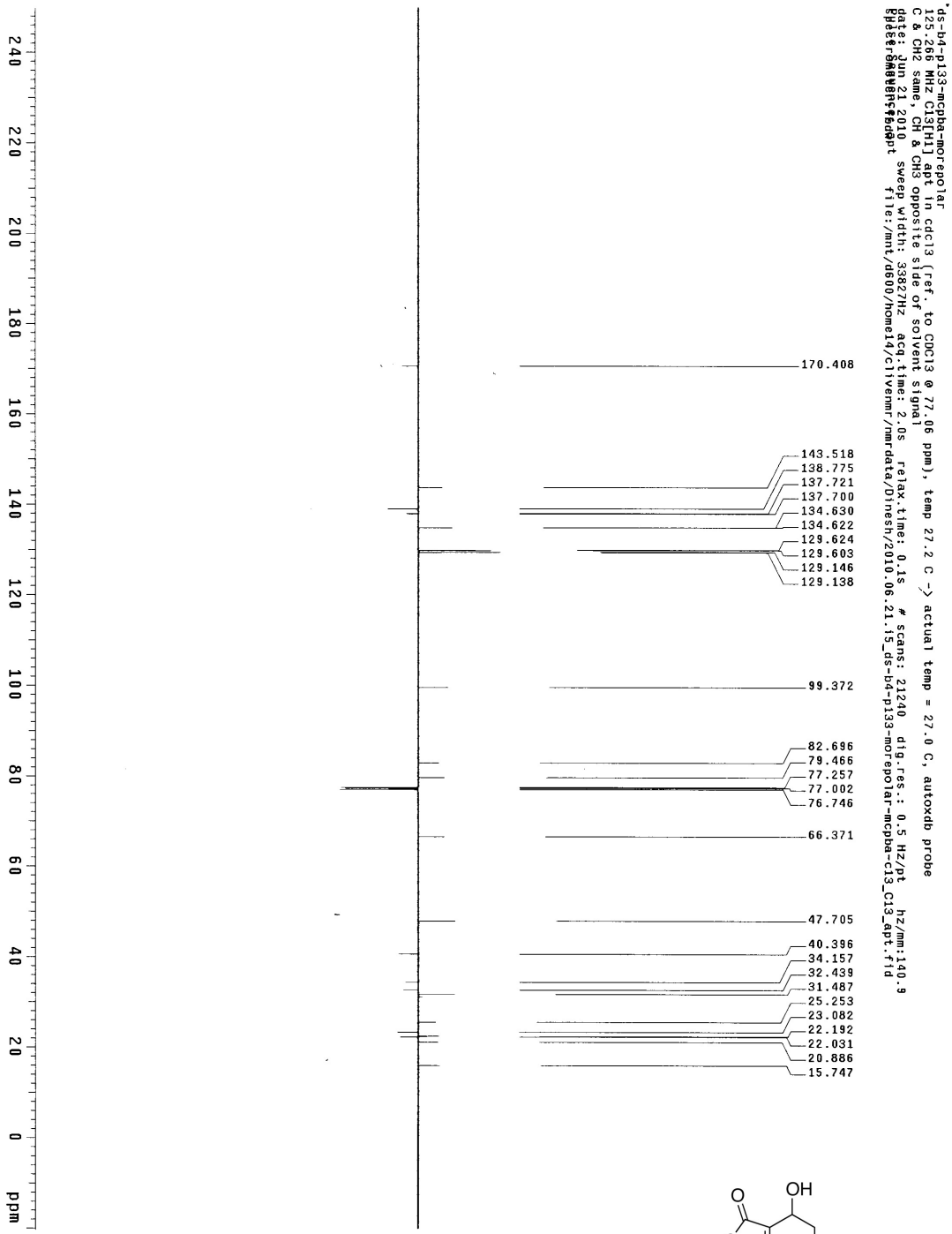


ds-b4-p109-fr46-49
499.815 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
File: xp
Pulse Sequence: s2pul



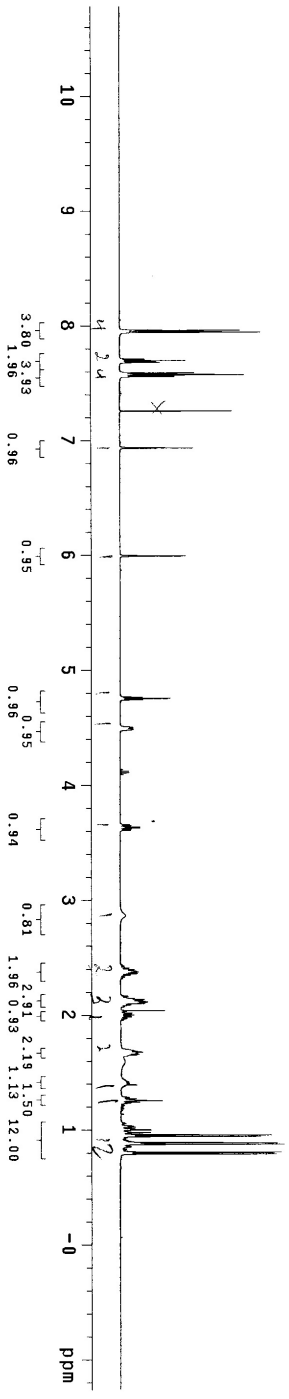


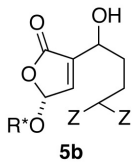
5a'


ds-b4-p133-mcpba-morepolar
125.266 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 21 2010 sweep width: 33827Hz acq.time: 2.0s relax.time: 0.1s # scans: 21240 dig.res.: 0.5 Hz/pt hz/mm:140.9
file:/mnt/d600/home14/clivenmr/nmrdata/Dinesh/2010.06.21.15_ds-b4-p133-morepolar-mcpba-c13_C13_apt.fid
170.408
143.518
138.775
137.721
137.700
134.630
134.622
129.624
129.603
129.146
129.138
99.372
82.696
79.466
77.257
77.002
76.746
66.371
47.705
40.396
34.157
32.439
31.487
25.253
23.082
22.192
22.031
20.886
15.747
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OH
O
R*O
Z
Z

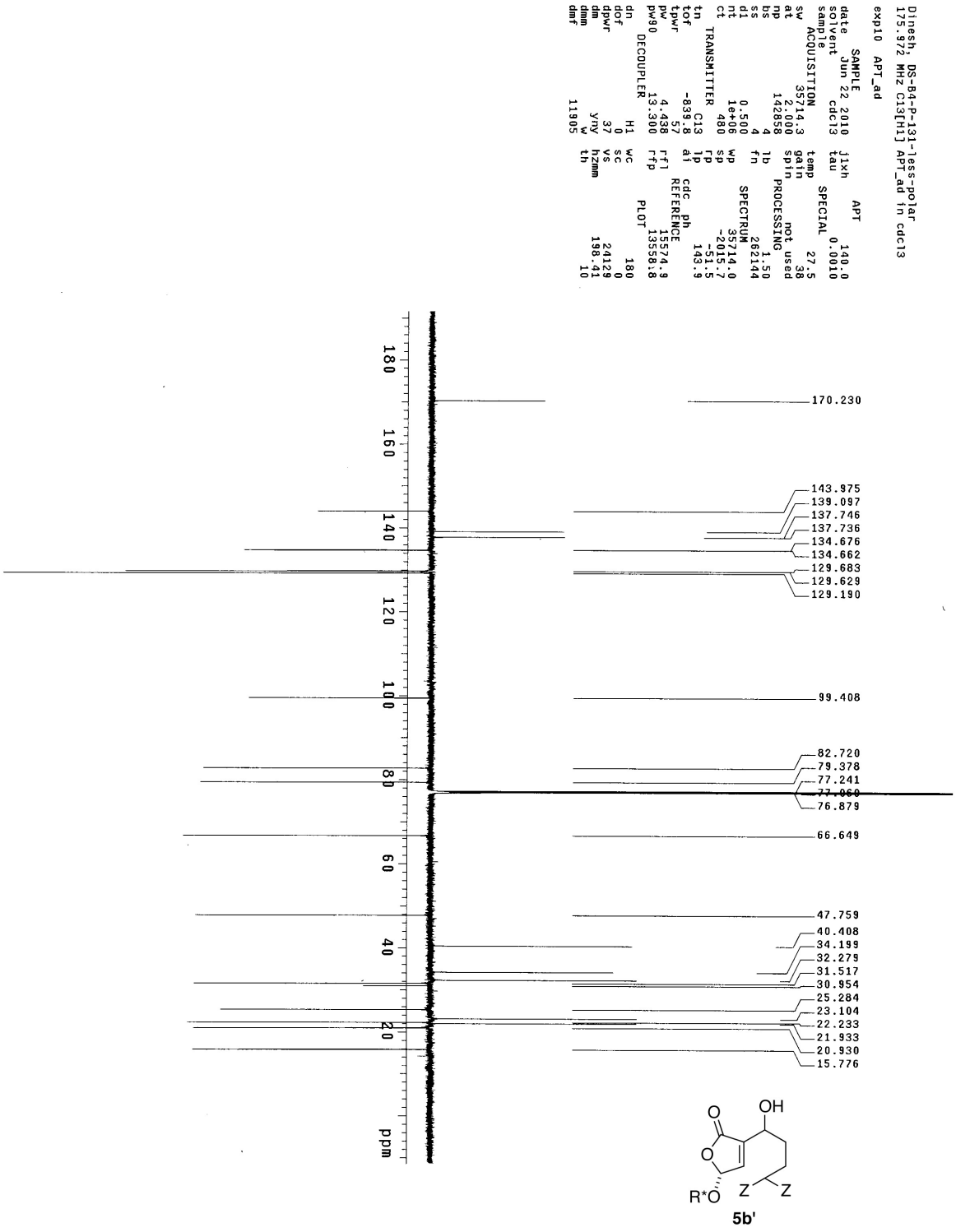
5b

ds-b4-p133-mcpba-morepolar-h1
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
File: xp
Pulse Sequence: s2pul

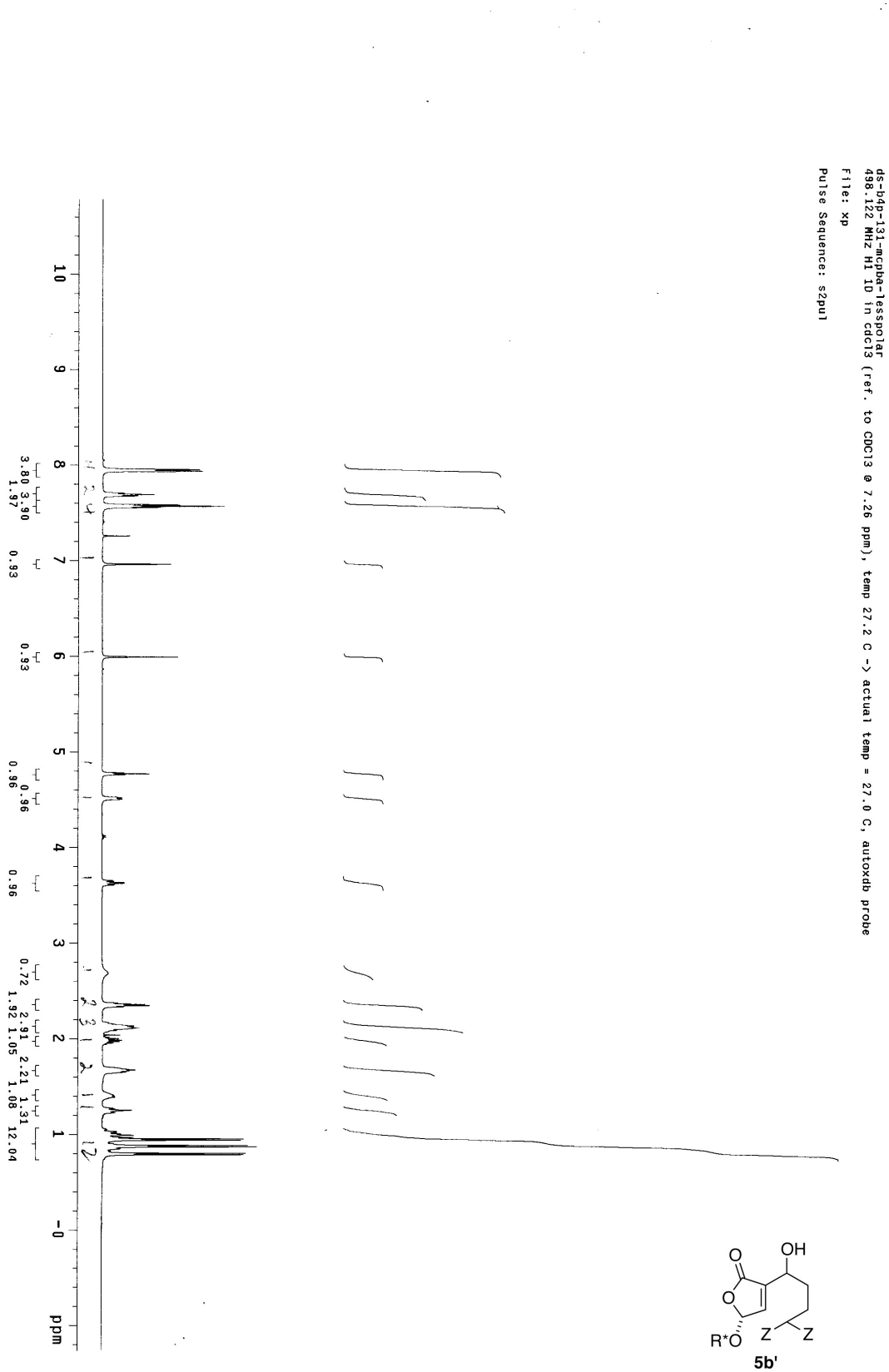


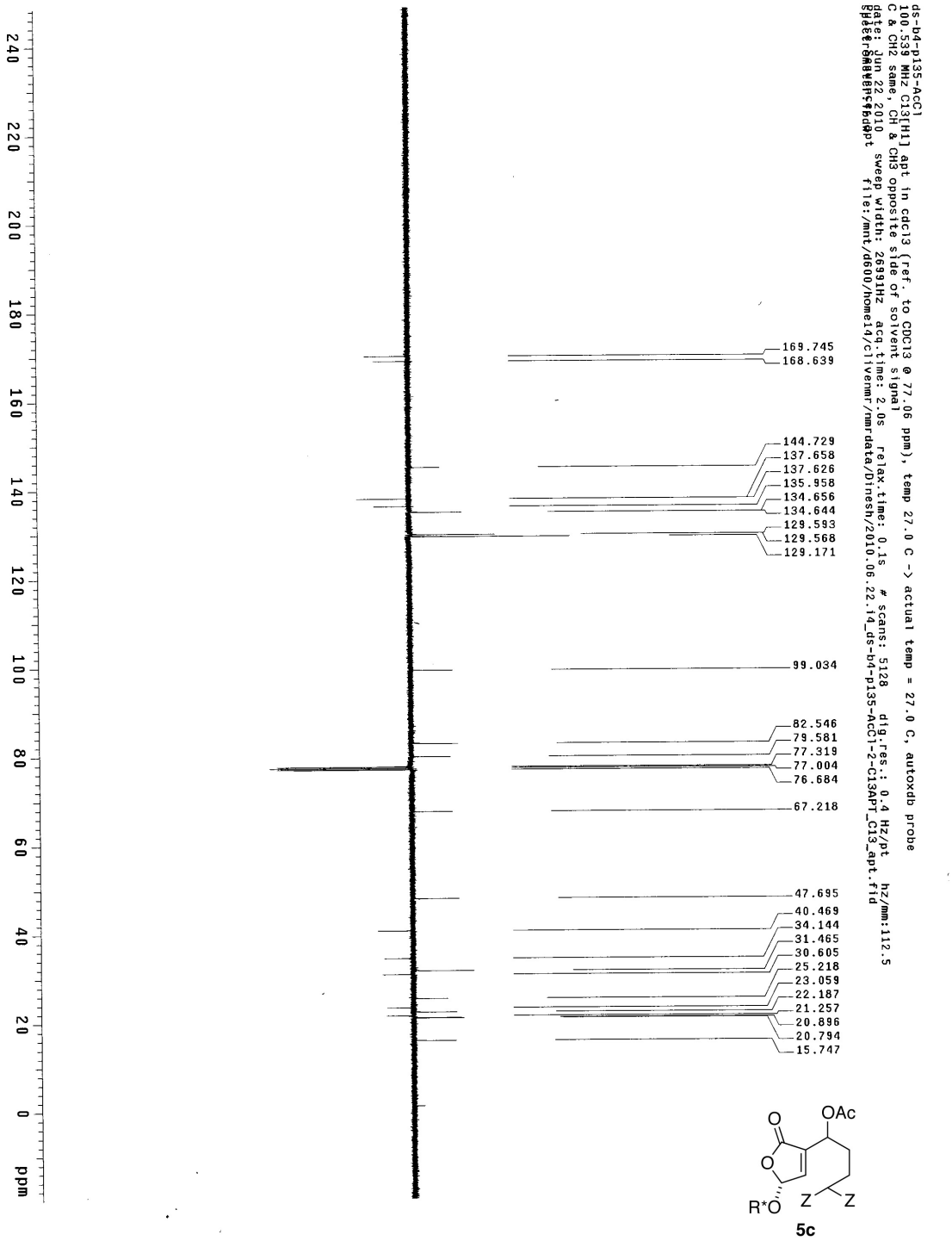


5b

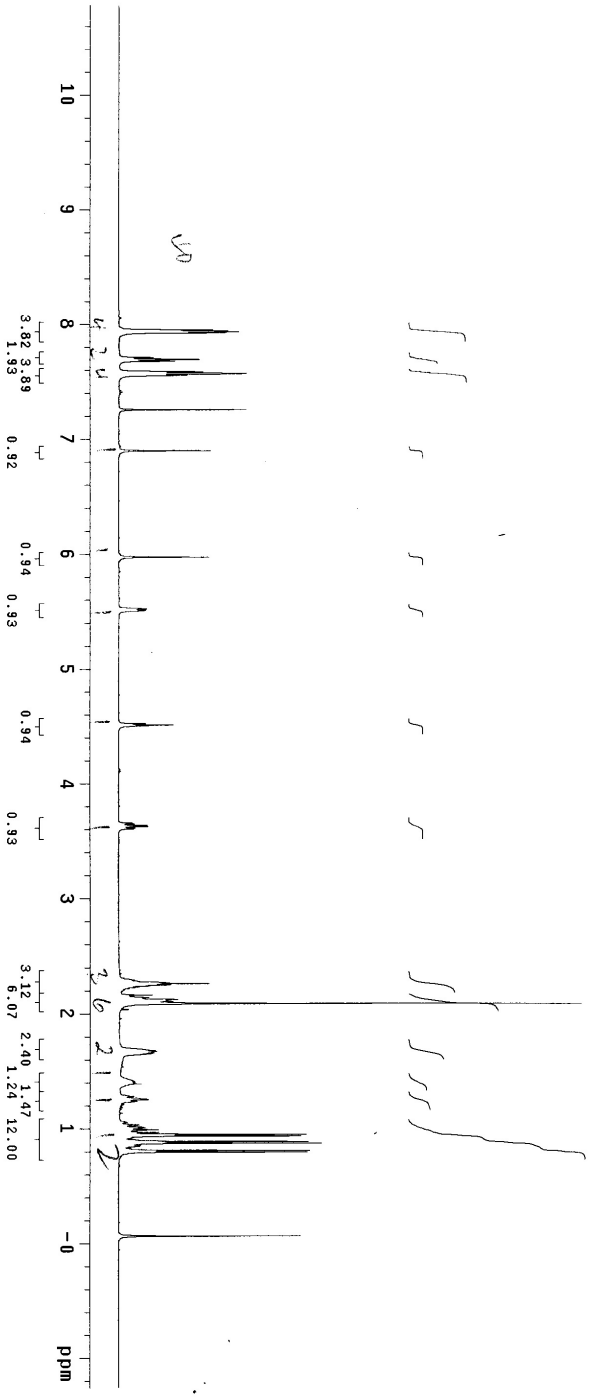


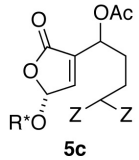
5b'



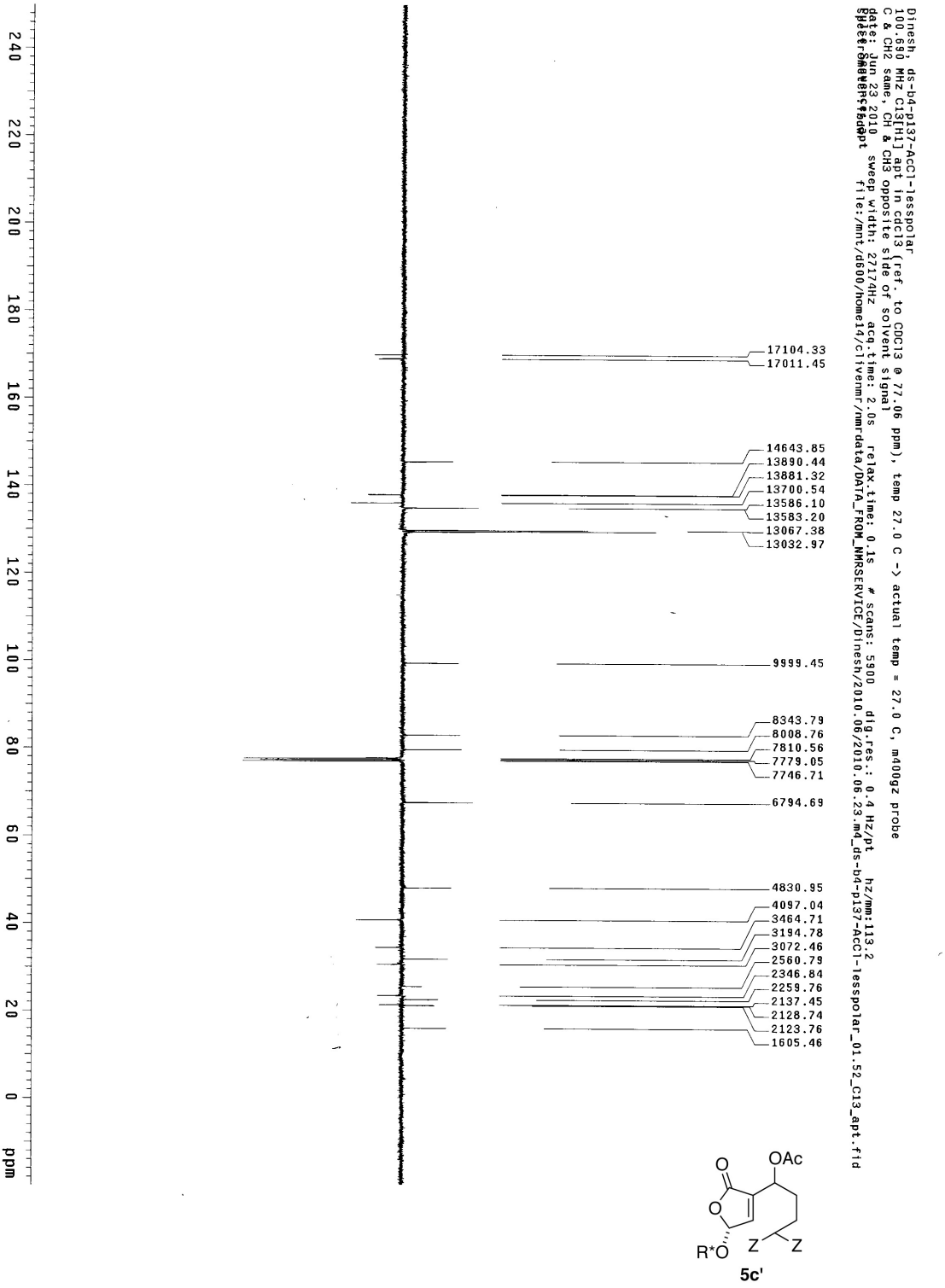

ds-b4-p135-AcCl
100.539 MHz C13{H1} apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.0 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 22 2010 sweep width: 26991Hz acq.time: 2.0s relax.time: 0.1s # scans: 5128 dig.res.: 0.4 Hz/pt hz/mm:112.5
file:/mnt/d600/home14/clivenmr/nmrdata/Dinesh/2010.06.22.14_ds-b4-p135-AcCl-2-C13APT_C13_apt.fid
169.745
168.639
144.729
137.658
137.626
135.958
134.656
134.644
129.593
129.568
129.171
99.034
82.546
79.581
77.319
77.004
76.684
67.218
47.695
40.469
34.144
31.465
30.605
25.218
23.059
22.187
21.257
20.896
20.794
15.747
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OAc
O
R*O
Z
Z

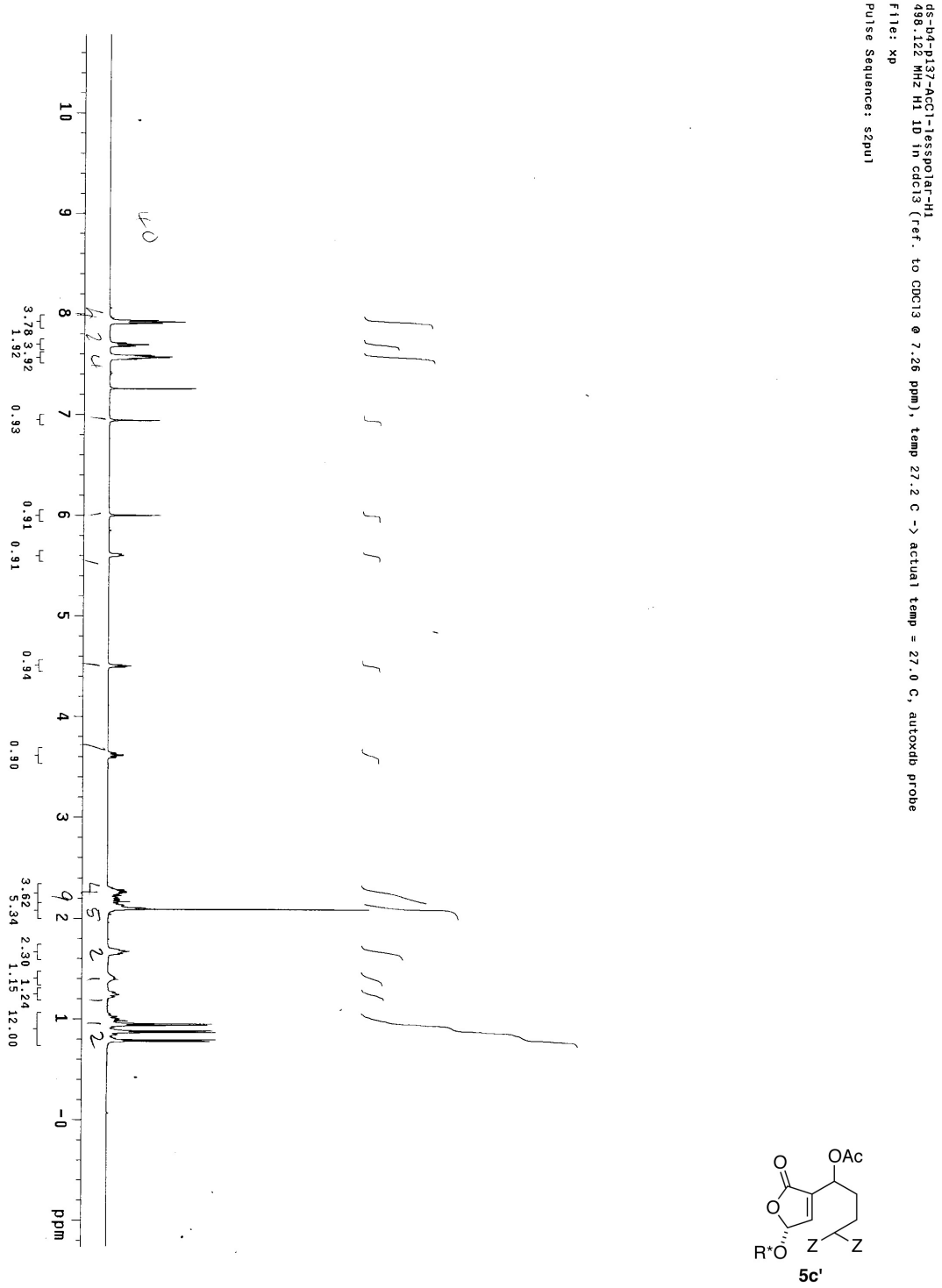
5c



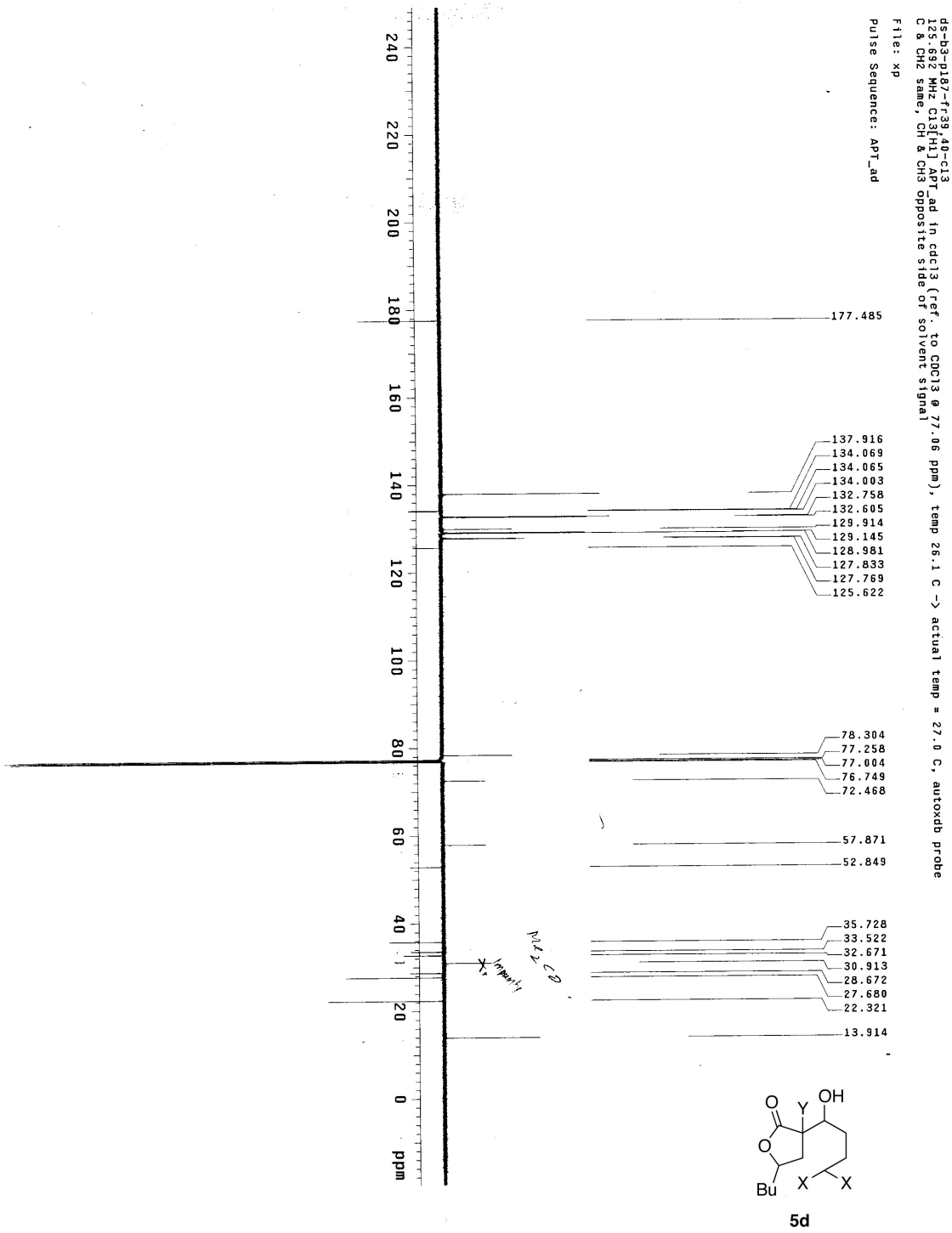


5c

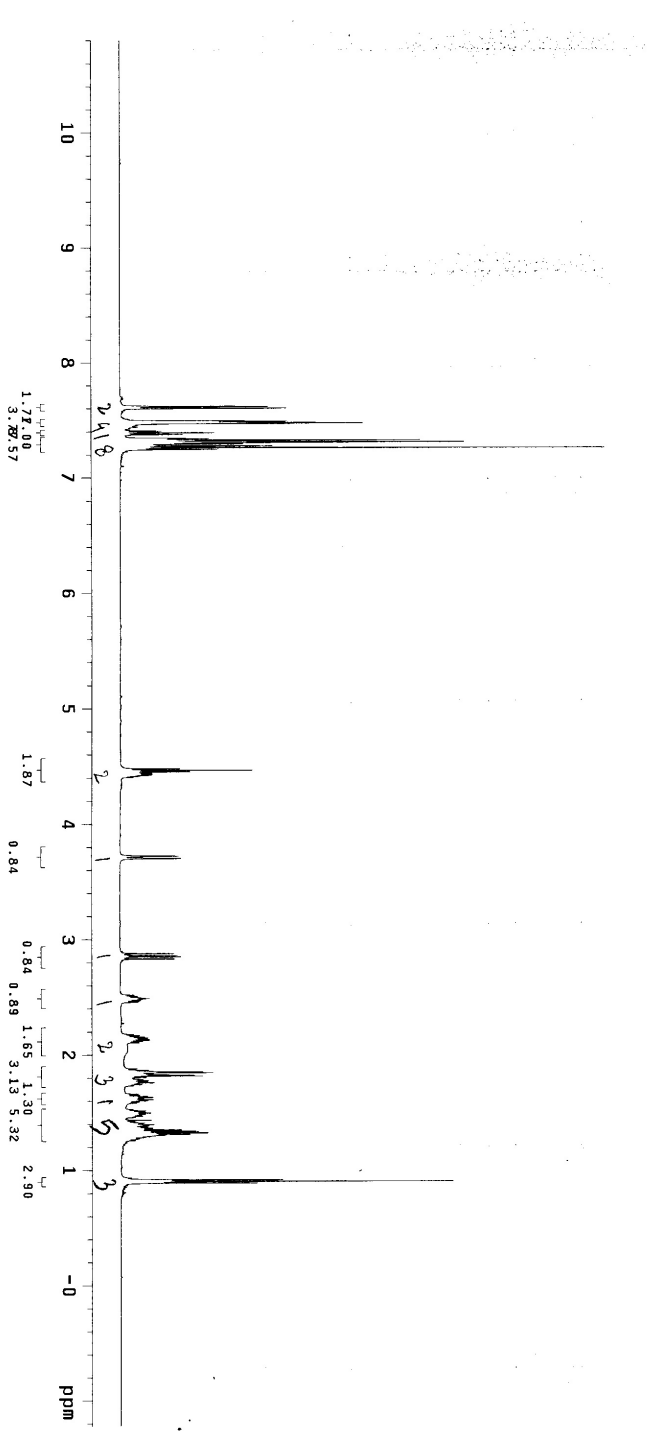

Dinesh, ds-b4-p137-AcCl-lesspolar
100.690 MHz C13[H1] apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 23 2010 sweep width: 27174Hz acq.time: 2.0s relax.time: 0.1s # scans: 5900 dig.res.: 0.4 Hz/pt hz/mm:113.2
file:/mnt/d600/home14/clivenmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2010.06/2010.06.23.m4_ds-b4-p137-AcCl-lesspolar_01.52_C13_apt.fid
17104.33
17011.45
14643.85
13890.44
13881.32
13700.54
13586.10
13583.20
13067.38
13032.97
9999.45
8343.79
8008.76
7810.56
7779.05
7746.71
6794.69
4830.95
4097.04
3464.71
3194.78
3072.46
2560.79
2346.84
2259.76
2137.45
2128.74
2123.76
1605.46
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
OAc
O
O
R*O
Z
Z
5c'

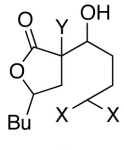


5c'

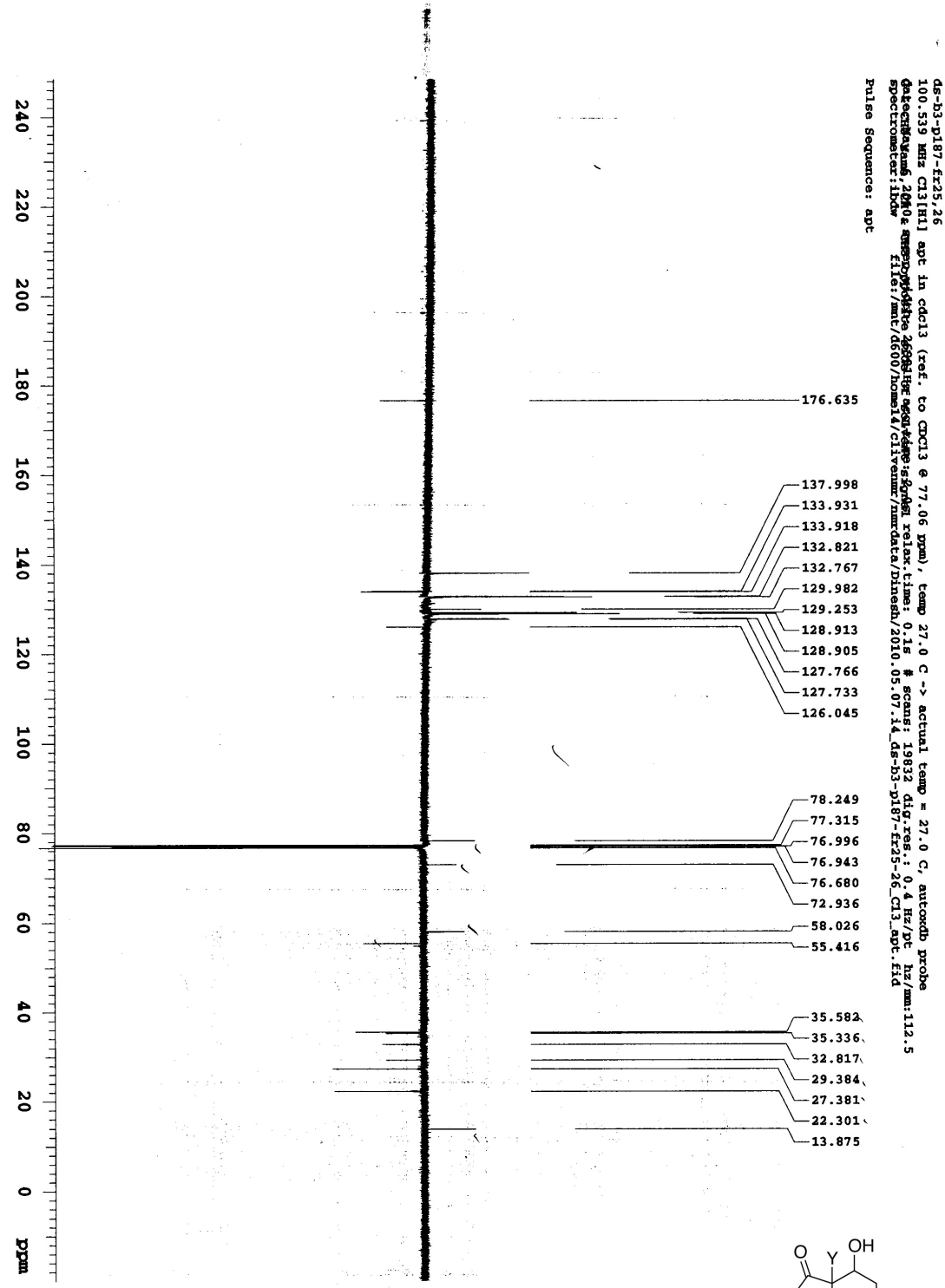

ds-b3-p187-fr39_40-c13
125.692 MHz C13{H1} APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
File: xp
Pulse Sequence: APT_ad
177.485
137.916
134.069
134.065
134.003
132.758
132.605
129.914
129.145
128.981
127.833
127.769
125.622
78.304
77.258
77.004
76.749
72.468
57.871
52.849
35.728
33.522
32.671
30.913
28.672
27.680
22.321
13.914
impurity
Me2 CO
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
Y
OH
O
Bu
X
X

5d

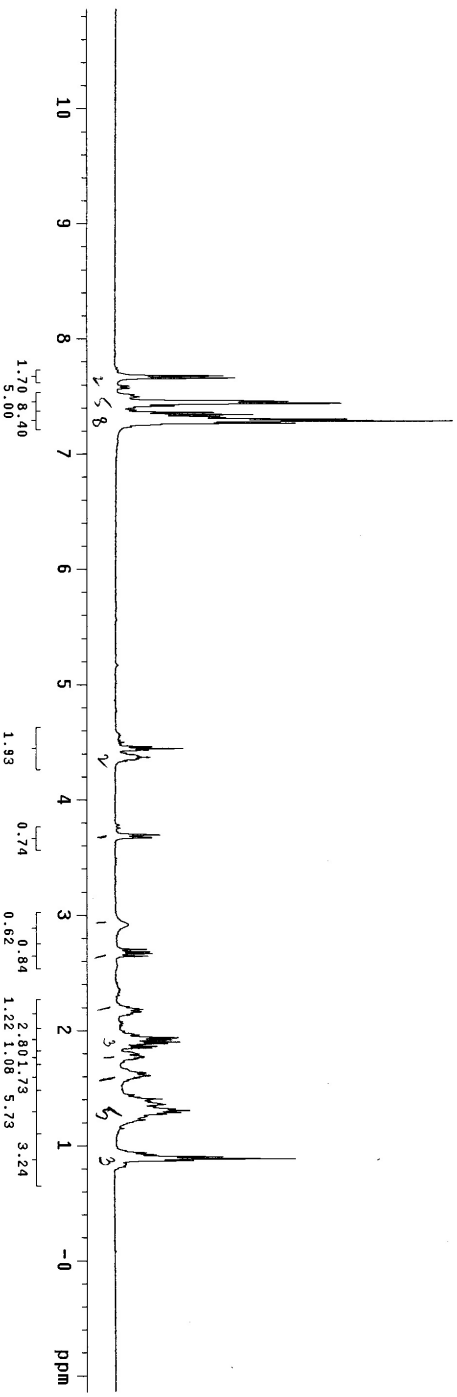




5d

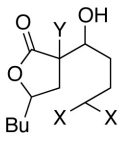


5d'

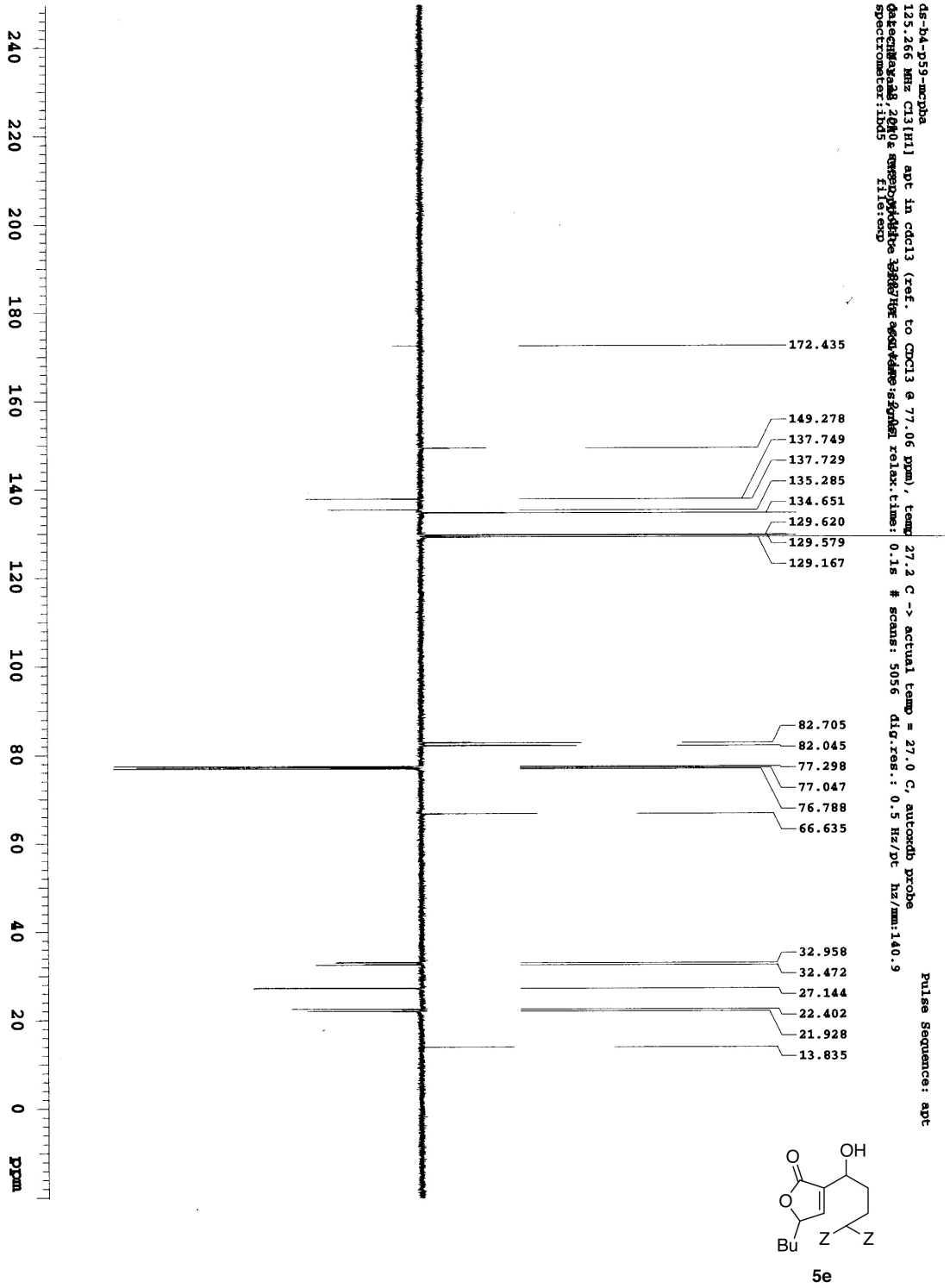


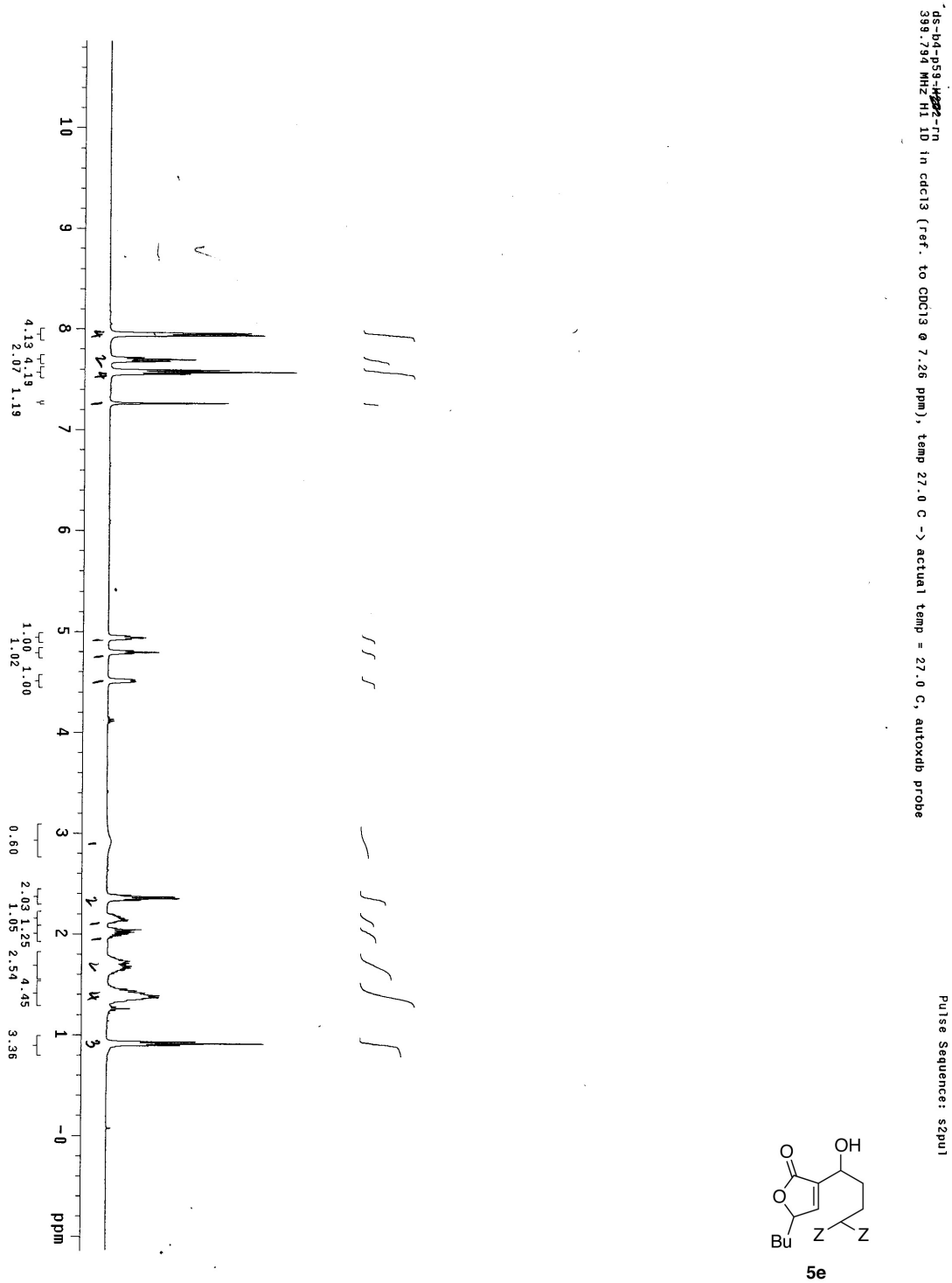
ds-b3-187-fr25,26
399.794 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, autoxdb probe

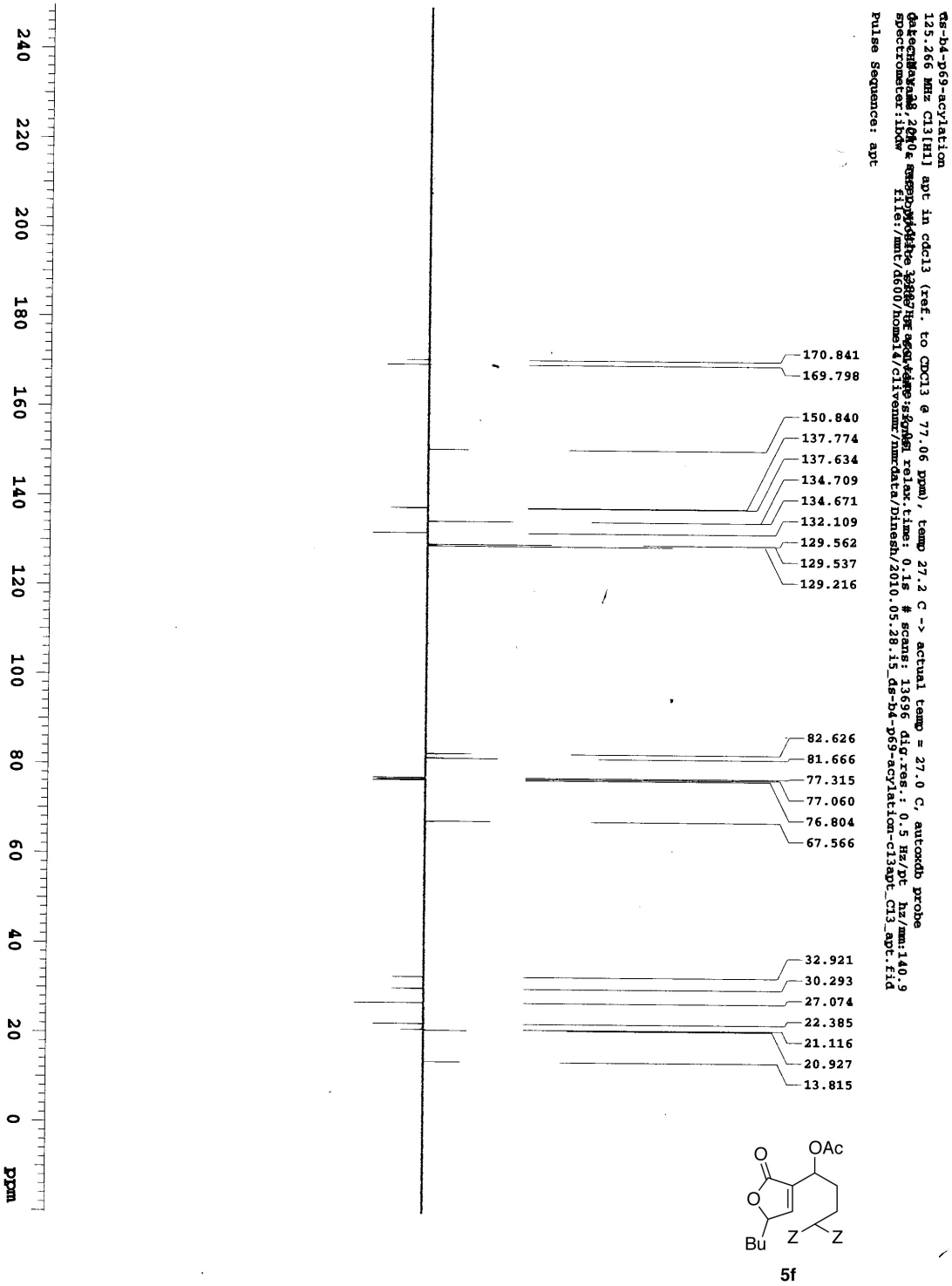
Pulse Sequence: s2pul



5d'


ds-b4-p59-mcpba
125.266 MHz C13{H1} apt in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe
spectrometer:ibd5 file:exp
relax.time: 0.1s # scans: 5056 dig.res.: 0.5 Hz/pt hz/mm:140.9
Pulse Sequence: apt
172.435
149.278
137.749
137.729
135.285
134.651
129.620
129.579
129.167
82.705
82.045
77.298
77.047
76.788
66.635
32.958
32.472
27.144
22.402
21.928
13.835
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm
O
OH
O
Bu
Z
Z
5e

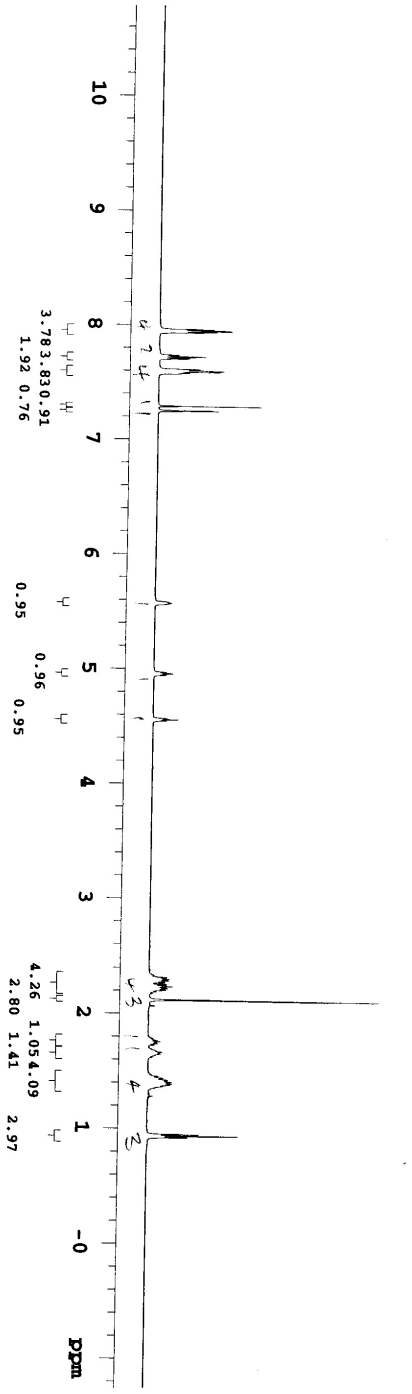


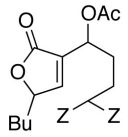


5f

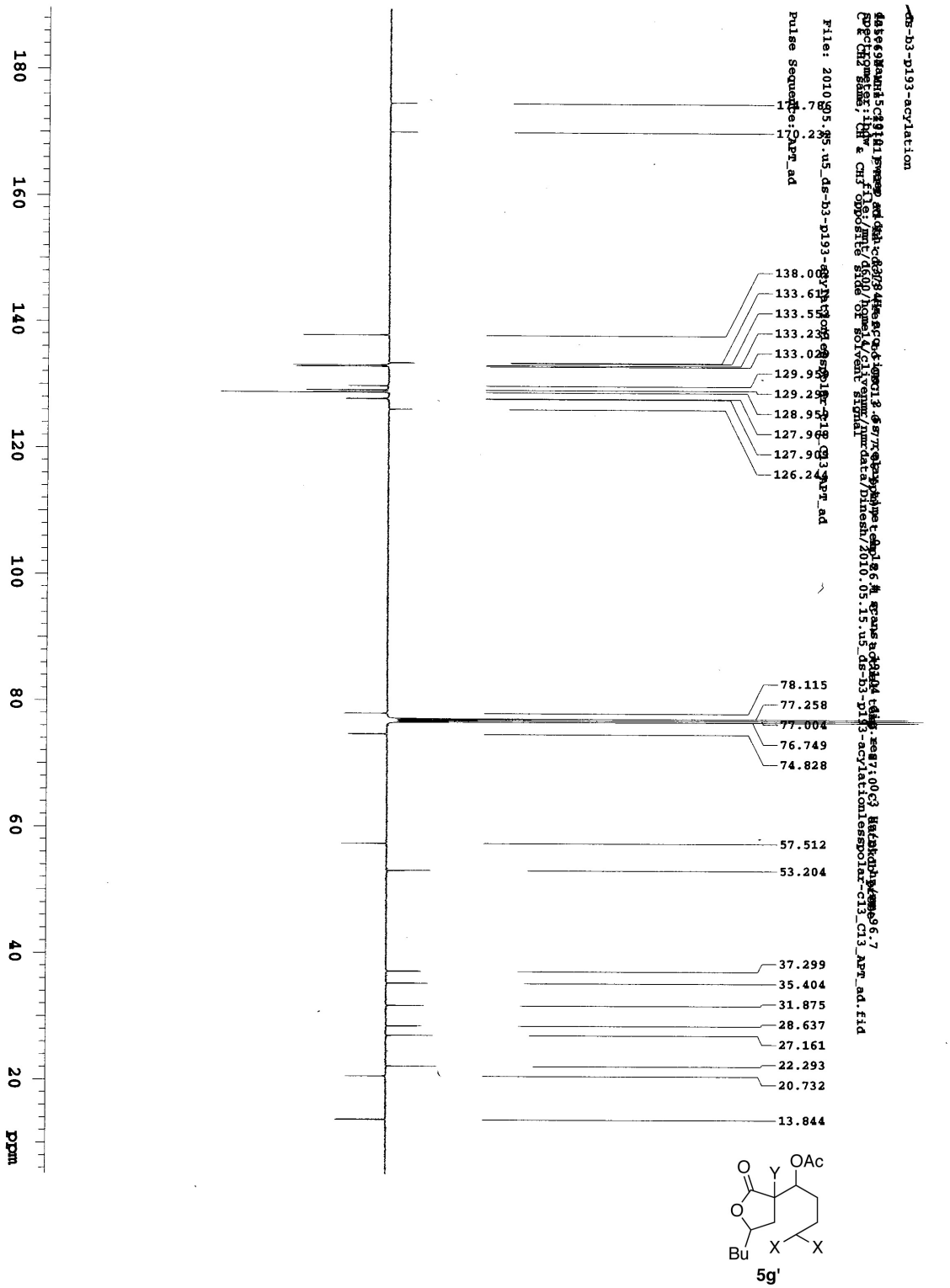
ds-b4-p69-Acylation
498.122 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

Pulse Sequence: s2pul

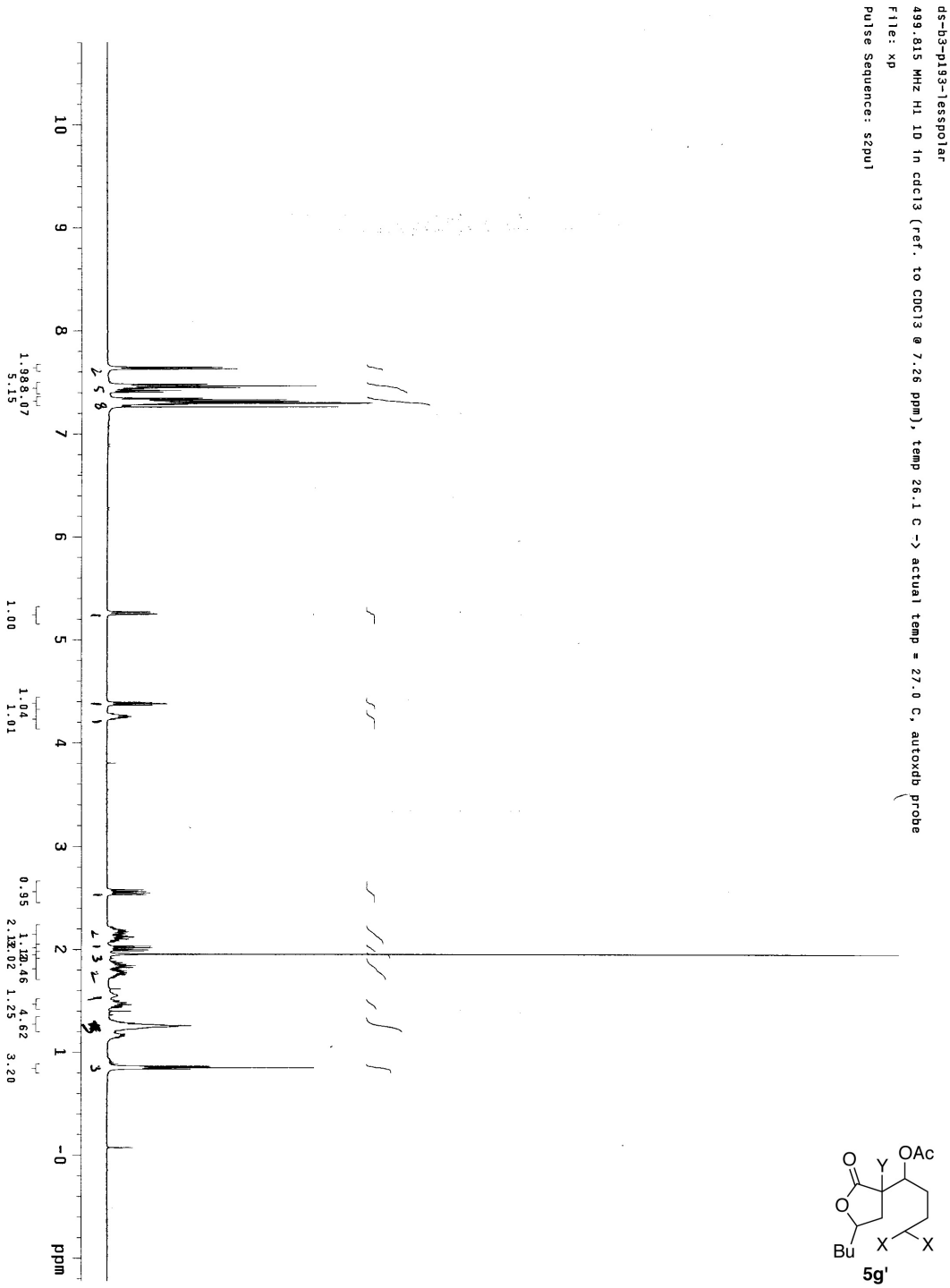




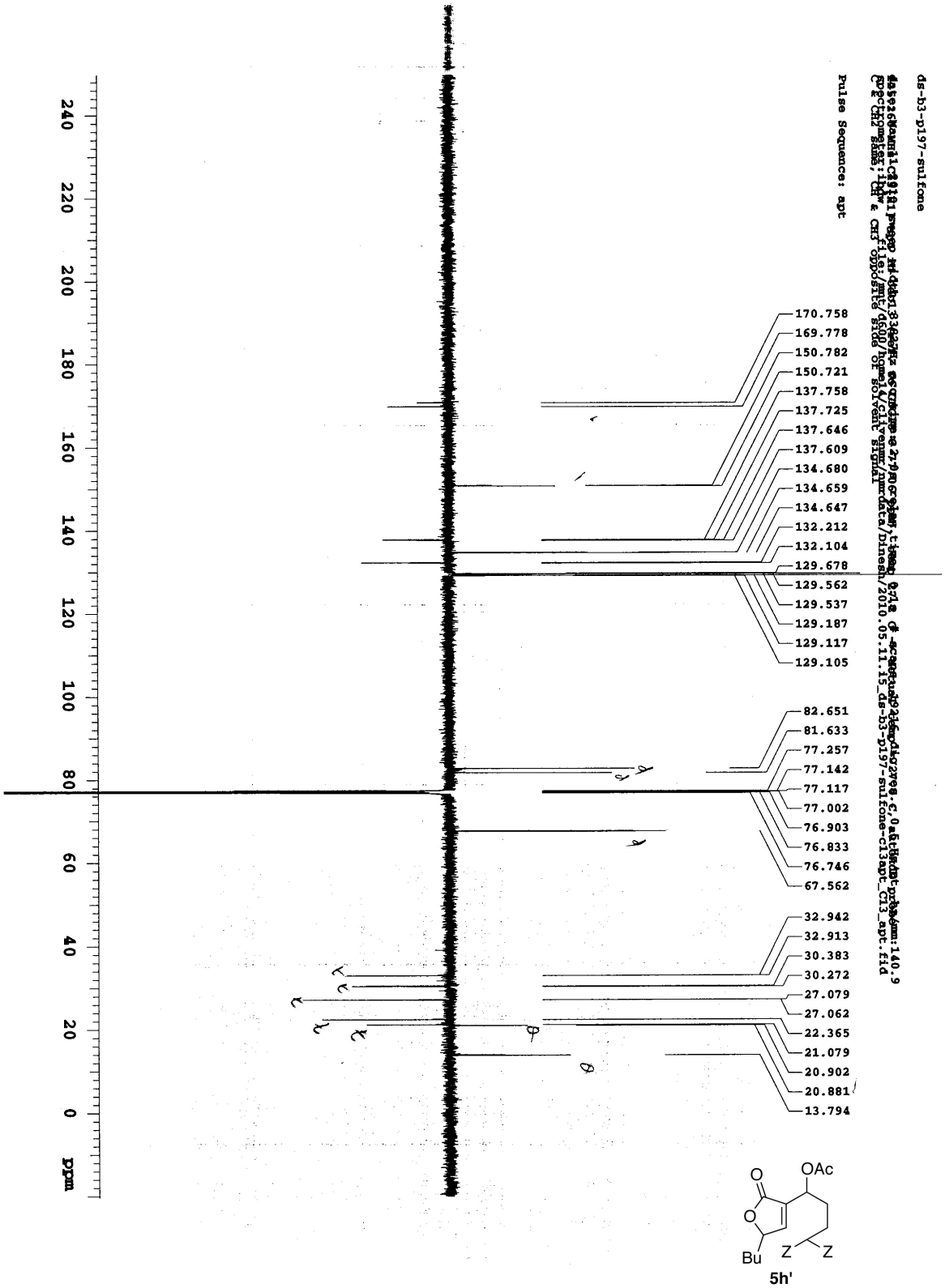
5f

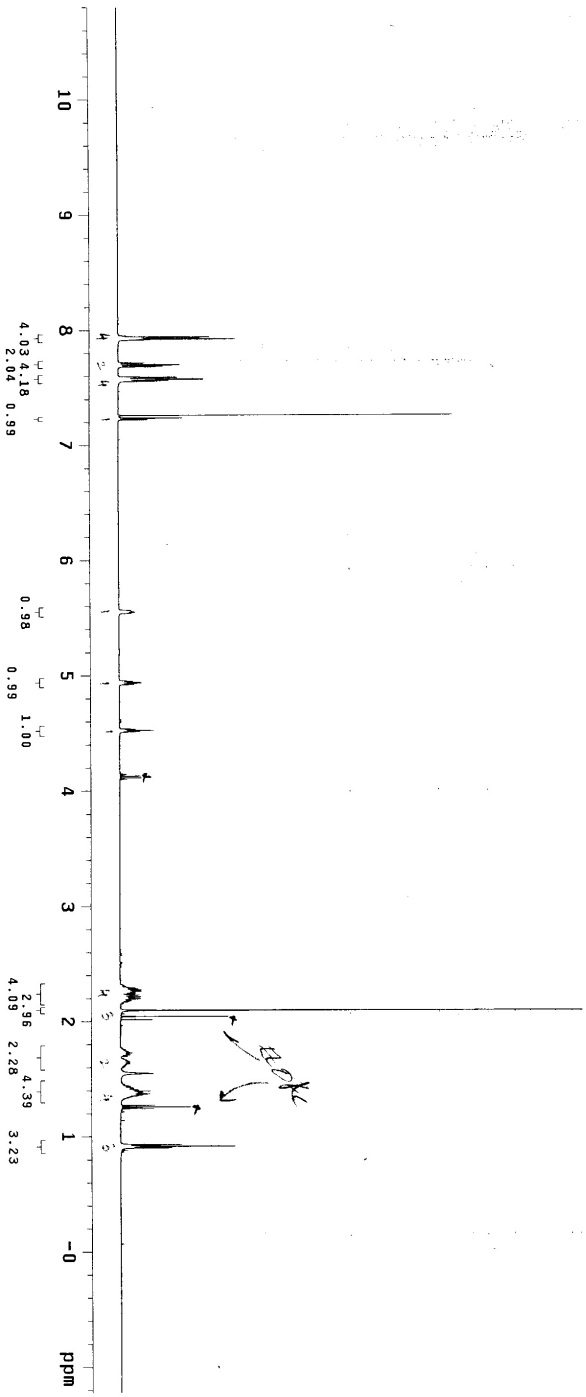

ds-b3-p193-acylation
File: 2010.05.15.u5_ds-b3-p193-acylation
Pulse Sequence: APT_ad
170.78
170.23
138.08
133.61
133.55
133.23
133.02
129.95
129.25
128.95
127.98
127.91
126.27
78.115
77.258
77.004
76.749
74.828
57.512
53.204
37.299
35.404
31.875
28.637
27.161
22.293
20.732
13.844
180
160
140
120
100
80
60
40
20
ppm
O
Y
OAc
O
Bu
X
X

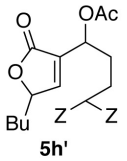
5g'



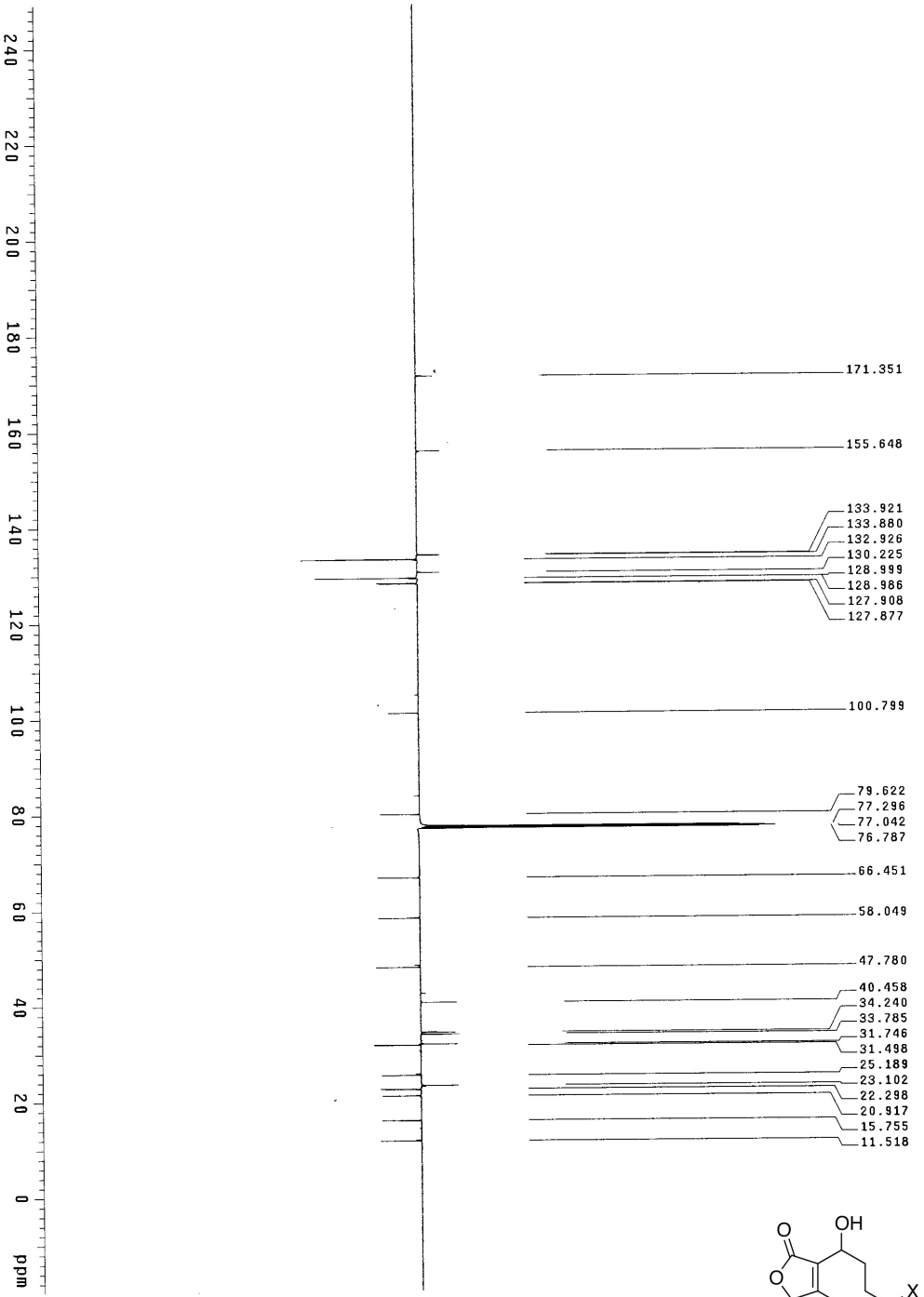
5g'



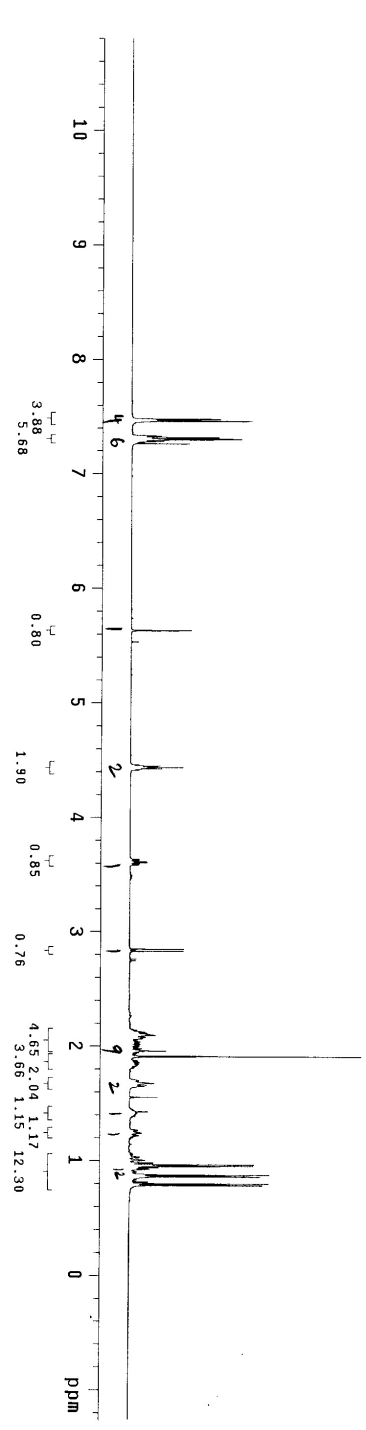


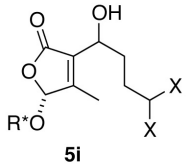


5h'

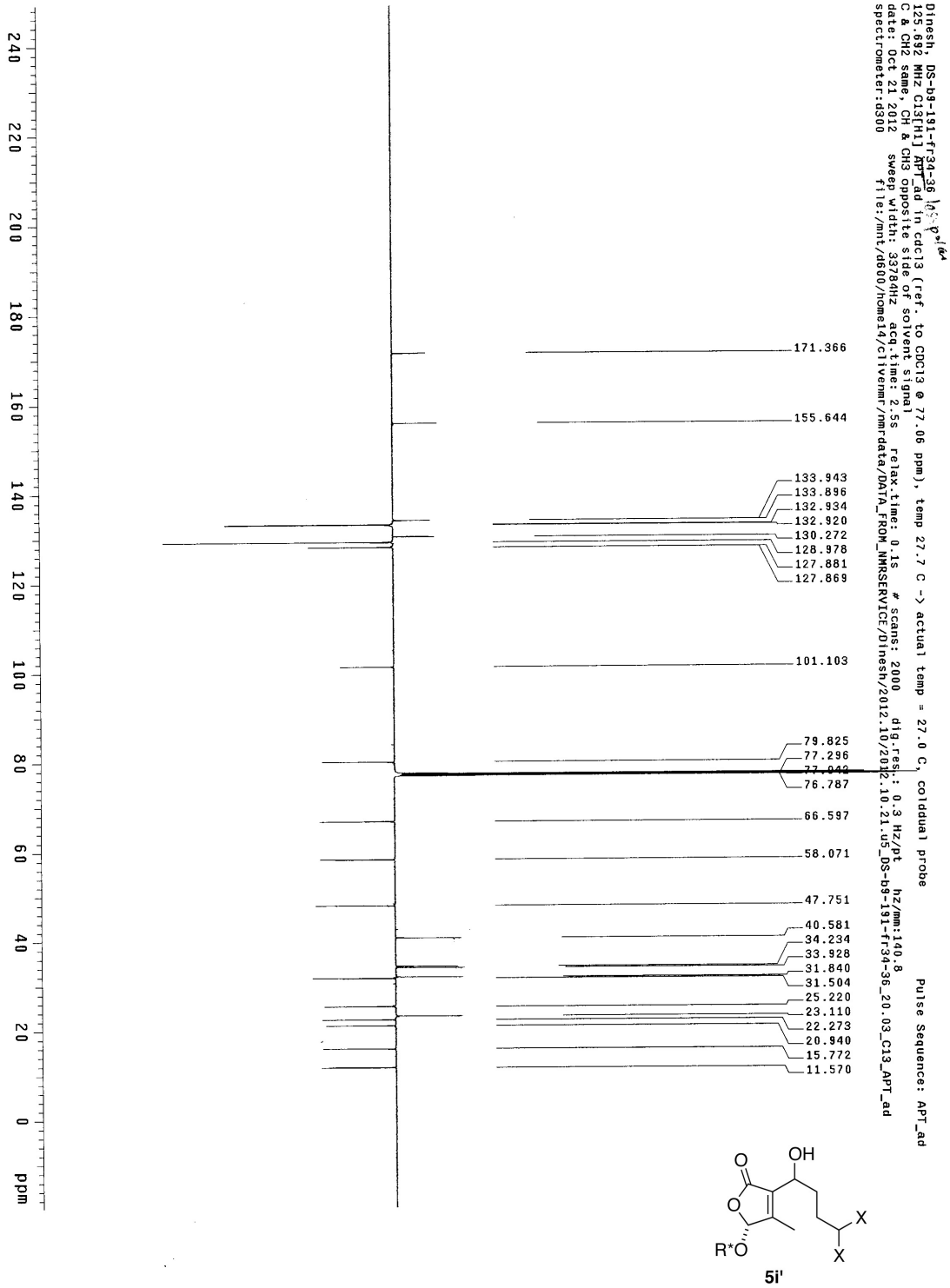

Dinesh, DS-b9-191-fr48-50 more polar diast-1
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe Pulse Sequence: APT_ad
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Oct 21 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 2000 dig.res.: 0.3 Hz/pt hz/mm:140.8
spectrometer:d300 file:/mnt/d600/home14/clivernmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2012.10/2012.10.21.u5_DS-b9-191-fr48-50_23.11_C13_APT_ad
171.351
155.648
133.921
133.880
132.926
130.225
128.999
128.986
127.908
127.877
100.799
79.622
77.296
77.042
76.787
66.451
58.049
47.780
40.458
34.240
33.785
31.746
31.498
25.189
23.102
22.298
20.917
15.755
11.518
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OH
O
X
R*O
X

5i

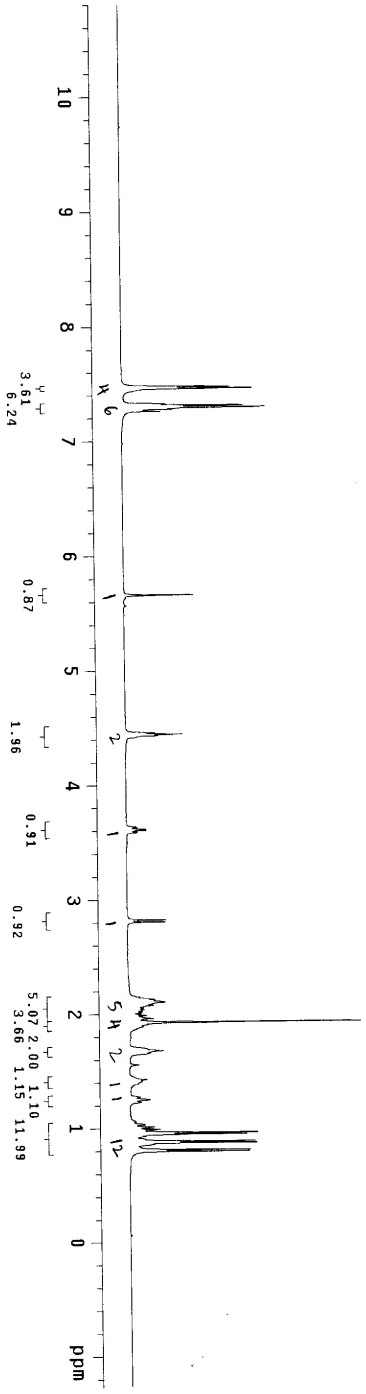




5i


Dinesh, DS-b9-191-fr34-36 APT_ad
125.692 MHz C13{H1} APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Oct 21 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 2000 dig.res.: 0.3 Hz/pt hz/mm:140.8
spectrometer:d300 file:/mnt/d600/home14/cliversmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2012.10/2012.10.21.u5_DS-b9-191-fr34-36_20.03_C13_APT_ad
Pulse Sequence: APT_ad
171.366
155.644
133.943
133.896
132.934
132.920
130.272
128.978
127.881
127.869
101.103
79.825
77.296
77.048
76.787
66.597
58.071
47.751
40.581
34.234
33.928
31.840
31.504
25.220
23.110
22.273
20.940
15.772
11.570
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OH
O
X
R*O
X

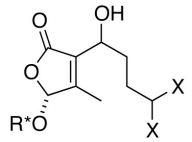
5i'



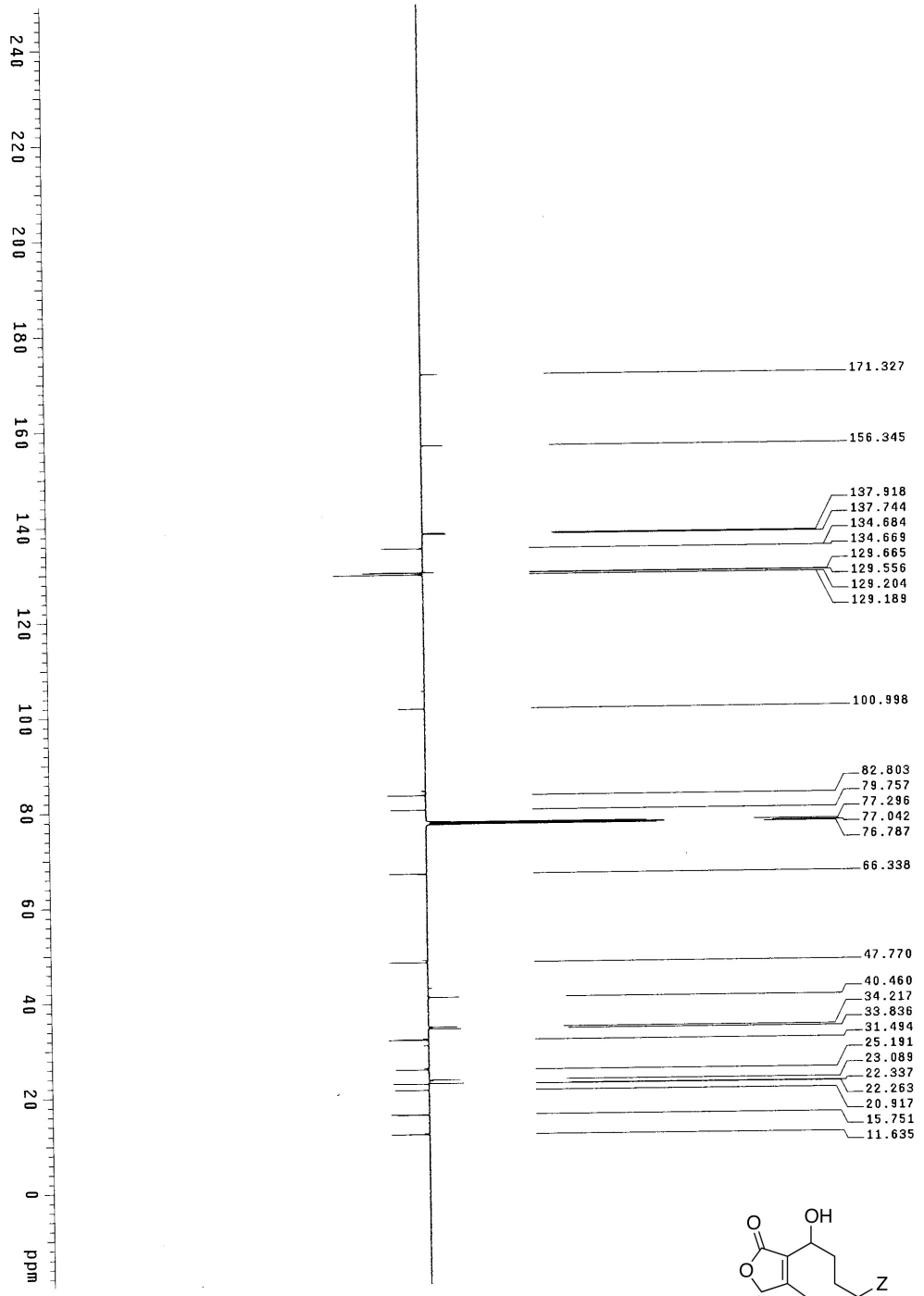
DS-b9-191-fr34-36
498.118 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, autoxdb probe

File: PROTON

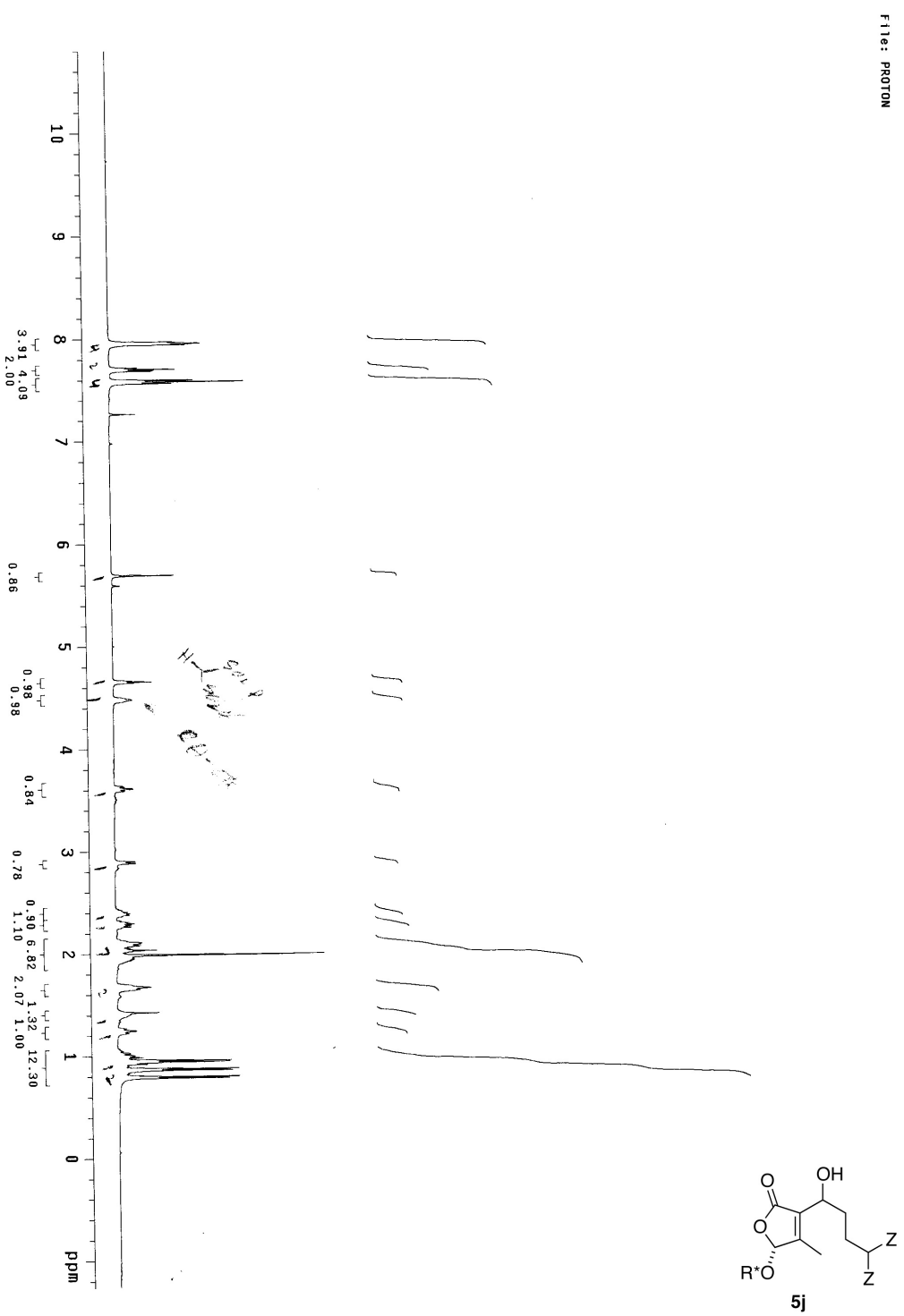
Pulse Sequence: s2pul



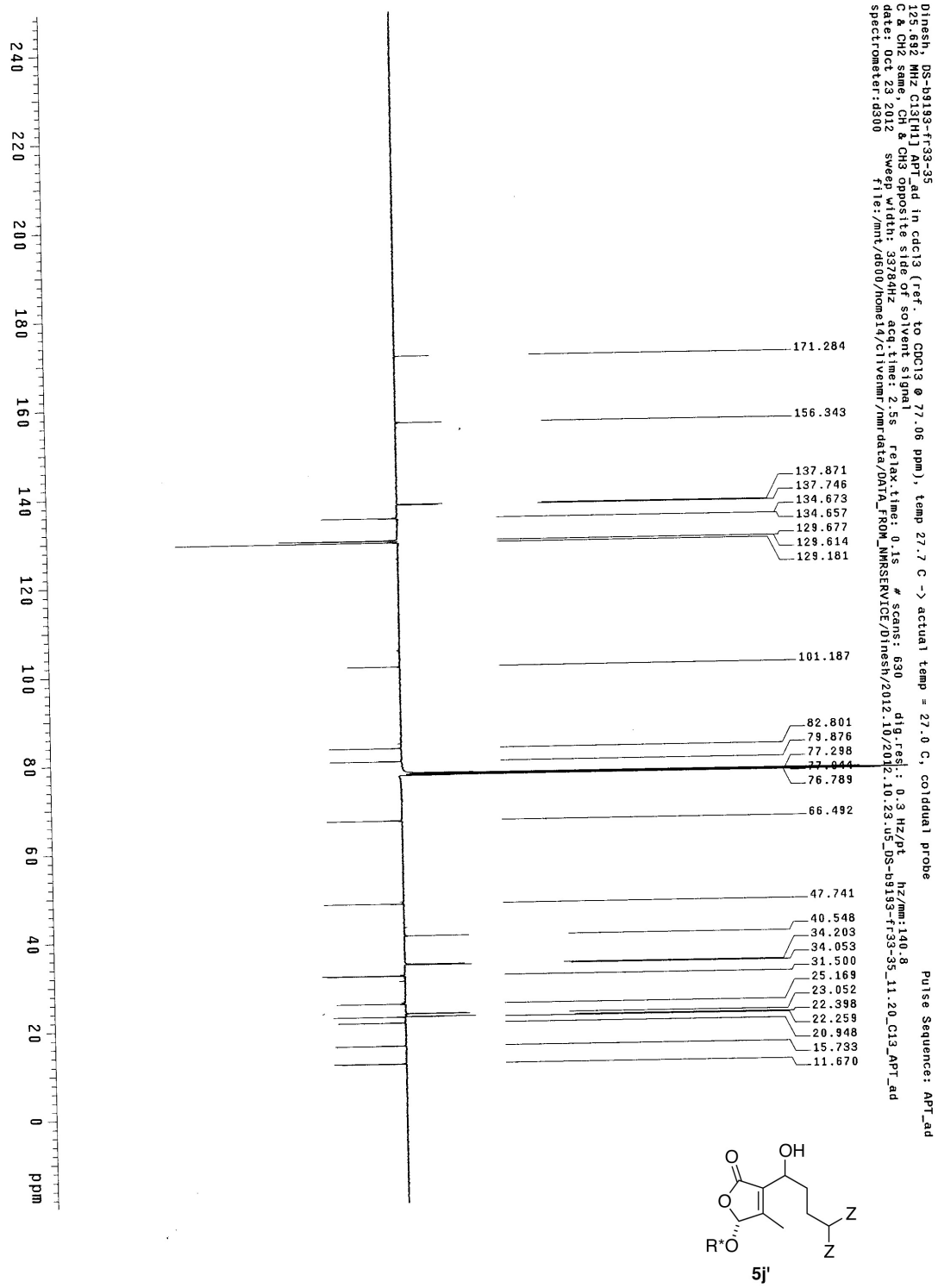
5i'


Dinesh, DS-b9-193-fr48-50
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: APT_ad
date: Oct 23 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 630 dig.res.: 0.3 Hz/pt hz/mm:140.8
file:/mnt/d600/home14/clivenmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2012.10/2012.10.23.u5_DS-b9-193-fr48-50_11.52_C13_APT_ad
spectrometer:d300
171.327
156.345
137.918
137.744
134.684
134.669
129.665
129.556
129.204
129.189
100.998
82.803
79.757
77.296
77.042
76.787
66.338
47.770
40.460
34.217
33.836
31.494
25.191
23.089
22.337
22.263
20.917
15.751
11.635
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OH
O
Z
R*O
Z

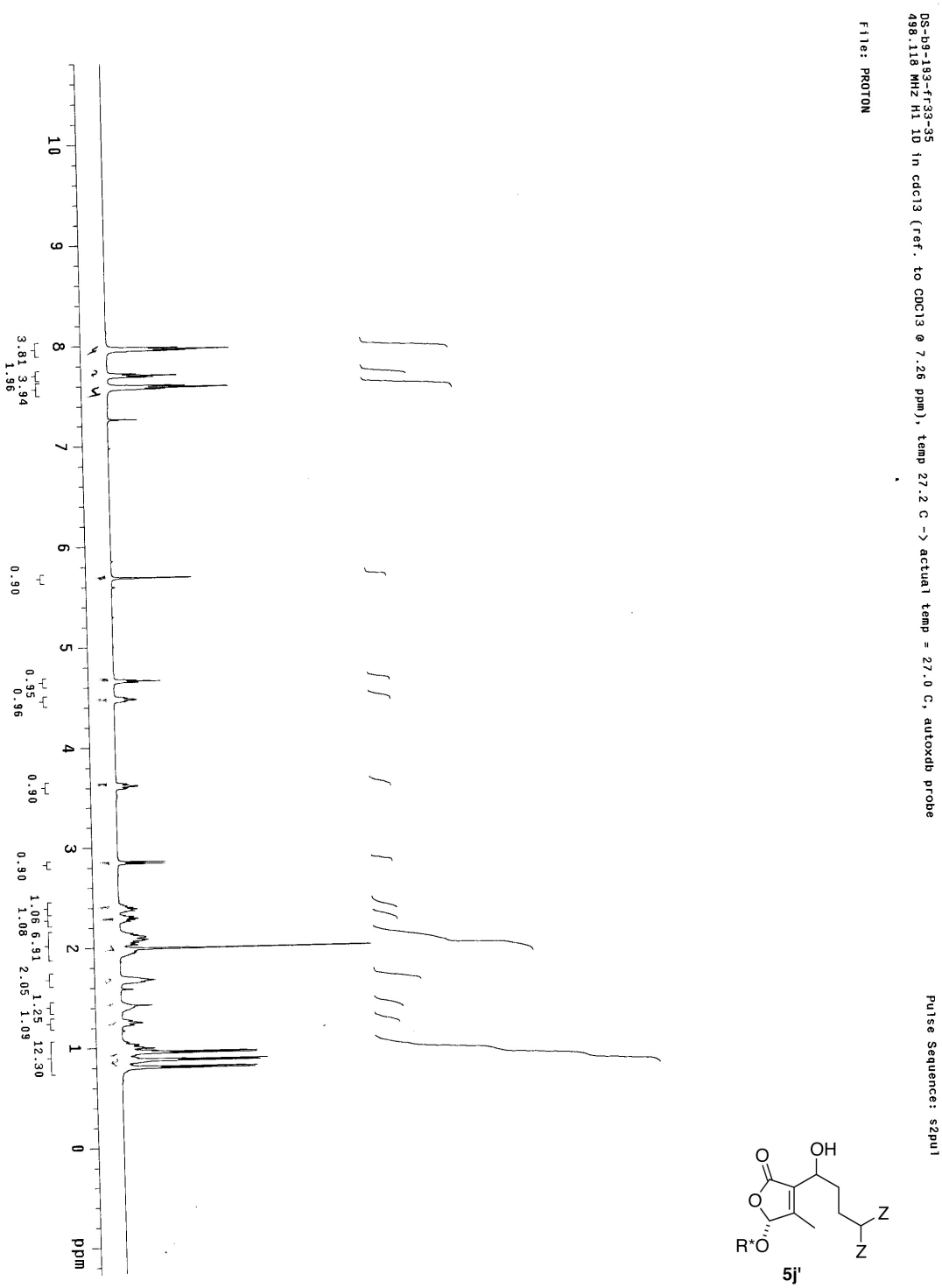
5j

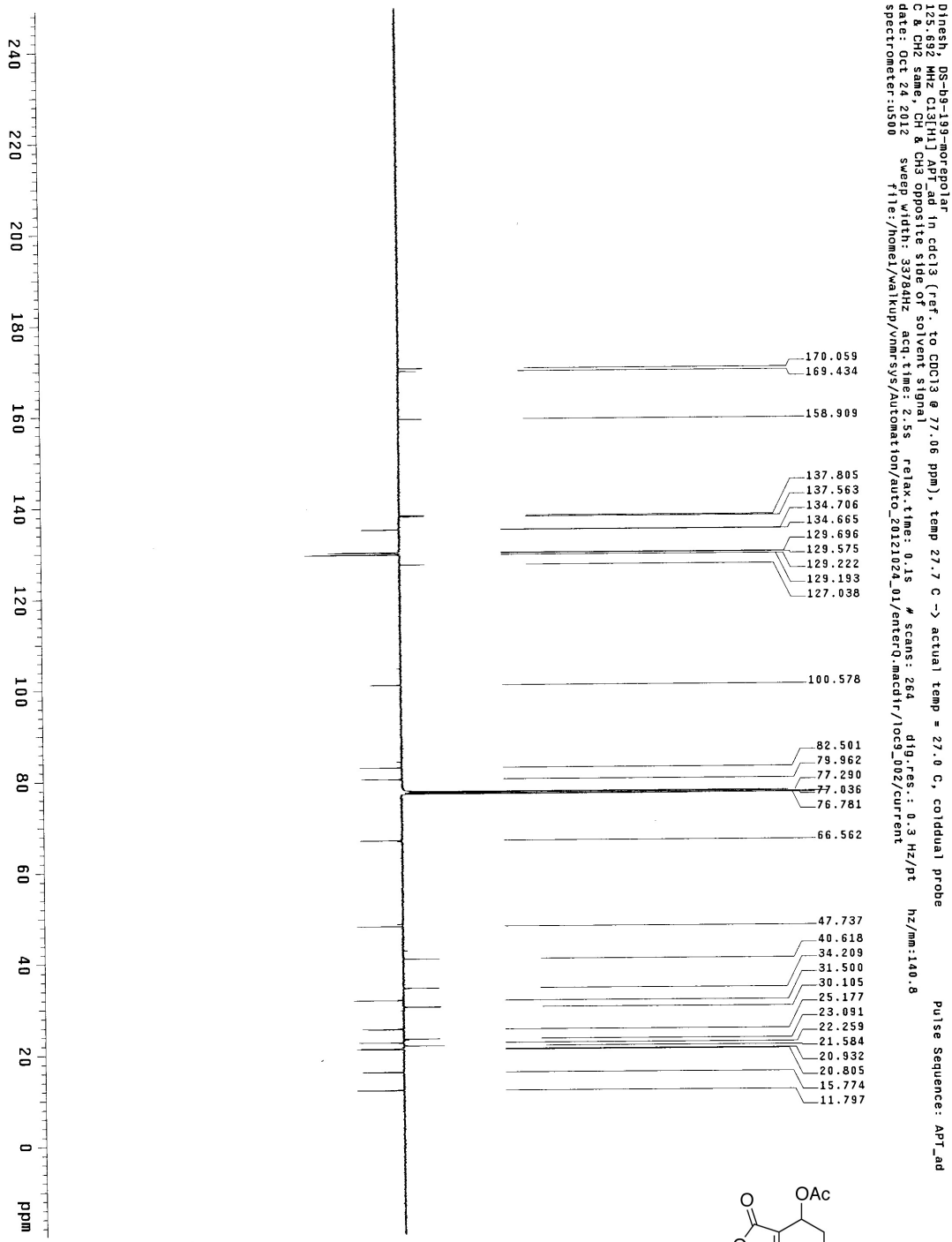


5j

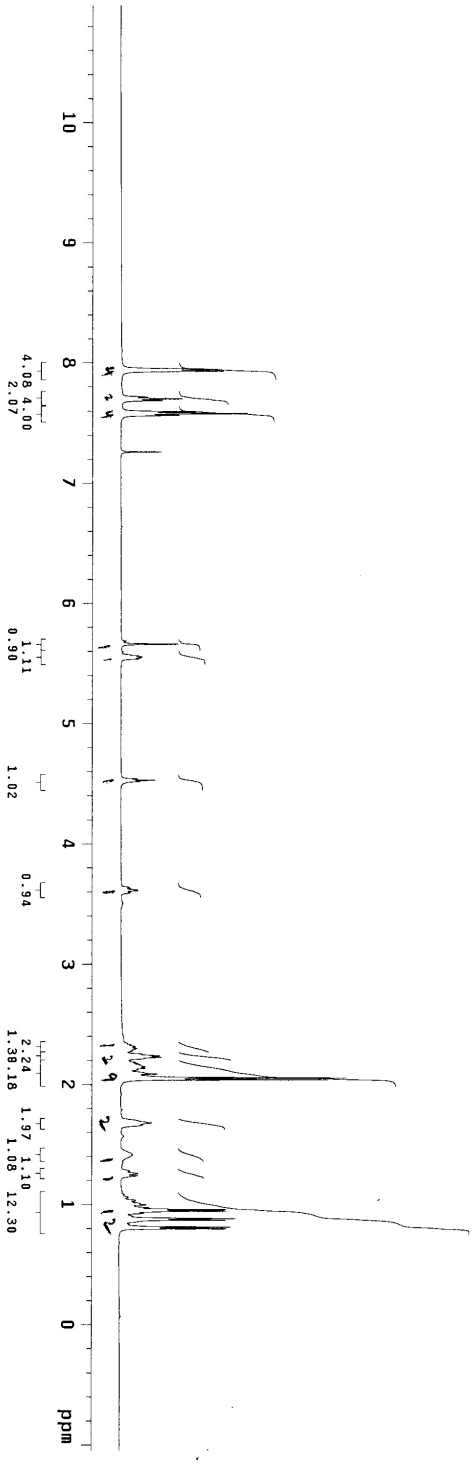

Dinesh DS-b9193-fr33-35
125.682 MHz C13{H1} APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Oct 23 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 630 dig.resl: 0.3 Hz/pt hz/mm:140.8
spectrometer:d300 file:/mnt/d600/home14/clivenmr/nmrdata/DATA_FROM_NMRSERVICE/Dinesh/2012.10/2012.10.23.US_DS-b9193-fr33-35_11.20_C13_APT_ad
Pulse Sequence: APT_ad
171.284
156.343
137.871
137.746
134.673
134.657
129.677
129.614
129.181
101.187
82.801
79.876
77.298
77.044
76.789
66.492
47.741
40.548
34.203
34.053
31.500
25.169
23.052
22.398
22.259
20.948
15.733
11.670
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OH
O
Z
Z
R*O

5j'



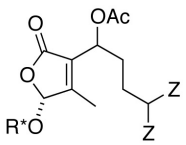

Dinesh, DS-b9-199-morepolar
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: APT_ad
date: Oct 24 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 264 dig.res.: 0.3 Hz/pt hz/mm:140.8
file:/home1/walkup/vnmrsys/Automation/auto_20121024_01/enterQ.macd1r/loc9_002/current
spectrometer:u500
170.059
169.434
158.909
137.805
137.563
134.706
134.665
129.696
129.575
129.222
129.193
127.038
100.578
82.501
79.962
77.290
77.036
76.781
66.562
47.737
40.618
34.209
31.500
30.105
25.177
23.091
22.259
21.584
20.932
20.805
15.774
11.797
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
OAc
O
O
R*O
Z
Z

5k

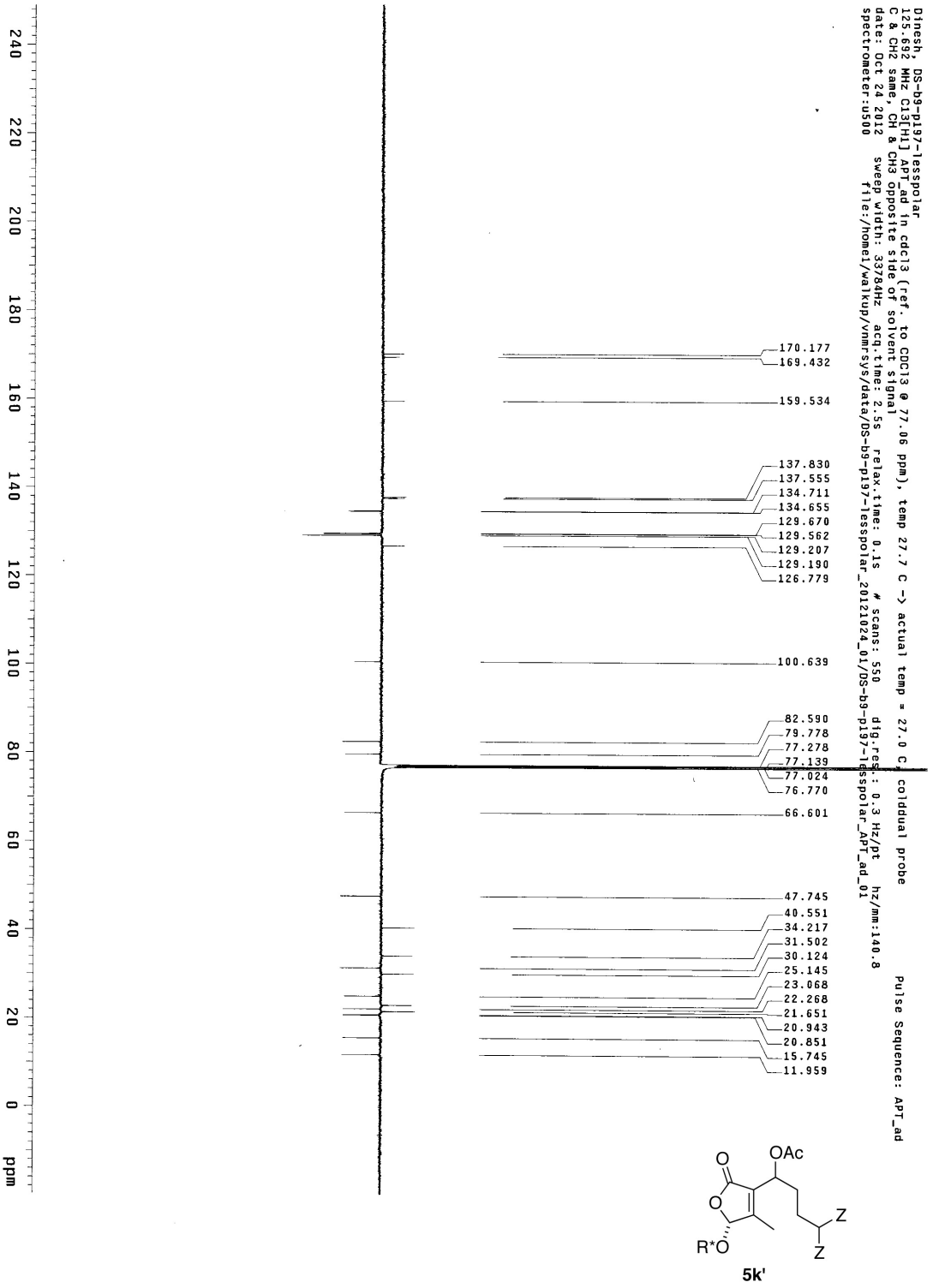


Dinesh, DS-b9-199-morepolar
499.815 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

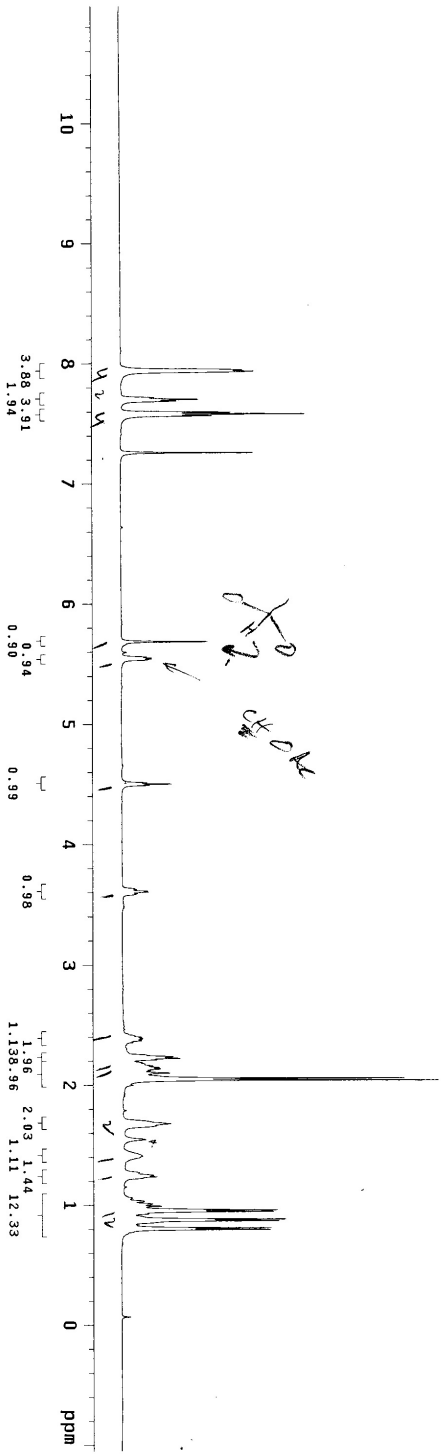
Pulse Sequence: PRESAT



5k

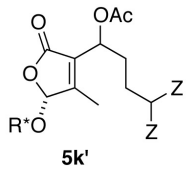

Dinesh, DS-b9-p197-lesspolar
125.692 MHz C13[H1] APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Oct 24 2012 sweep width: 33784Hz acq.time: 2.5s relax.time: 0.1s # scans: 550 dig.res: 0.3 Hz/pt hz/mm:140.8
spectrometer:us500 file:/home1/walkup/vnmrsys/data/DS-b9-p197-lesspolar_20121024_01/DS-b9-p197-lesspolar_APT_ad_01 Pulse Sequence: APT_ad
170.177
169.432
159.534
137.830
137.555
134.711
134.655
129.670
129.562
129.207
129.190
126.779
100.639
82.590
79.778
77.278
77.139
77.024
76.770
66.601
47.745
40.551
34.217
31.502
30.124
25.145
23.068
22.268
21.651
20.943
20.851
15.745
11.959
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
OAc
O
Z
R*O
Z

5k'

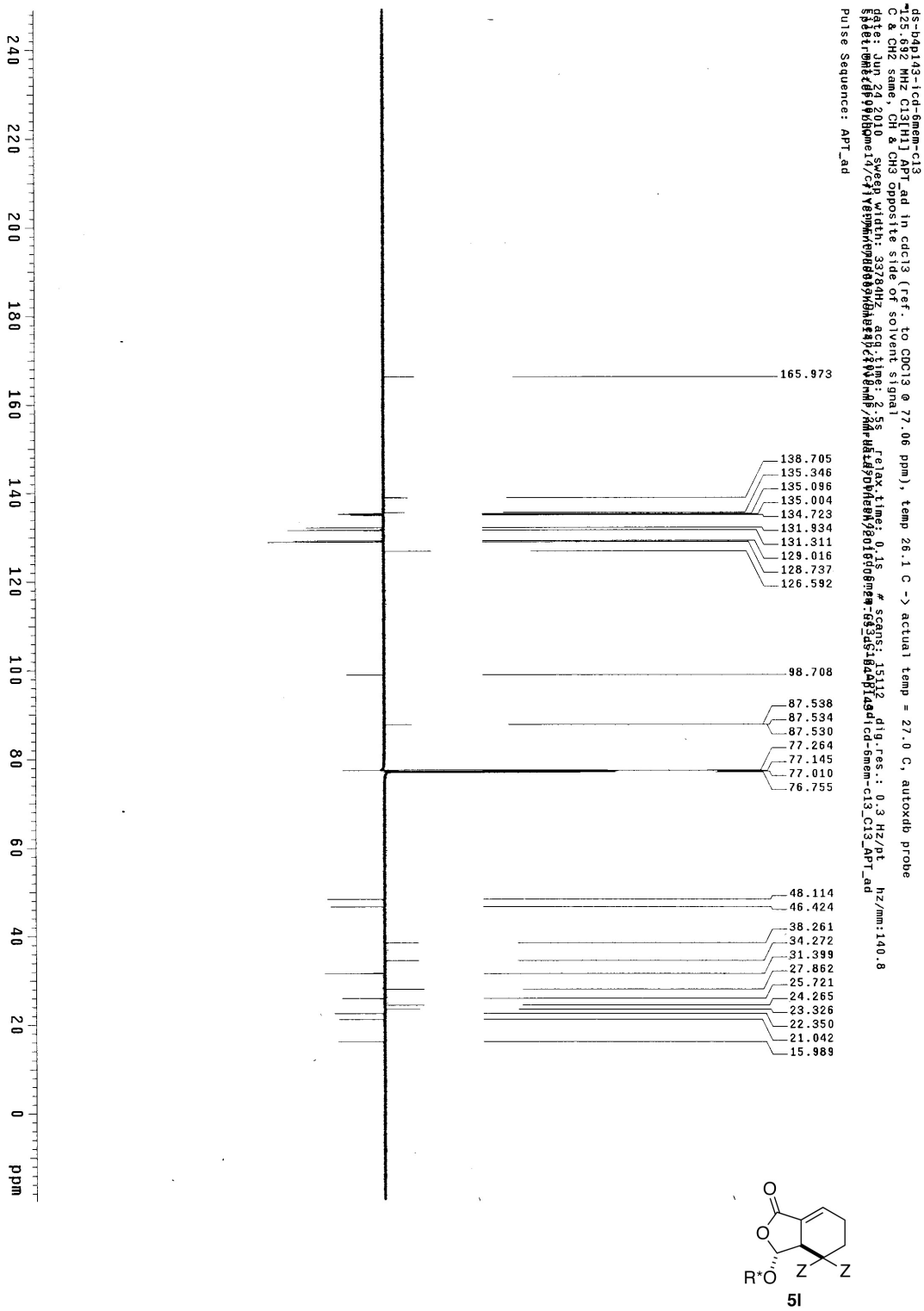


Dinesh, DS-bs-p197-lesspolar
499.815 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, coldDual probe

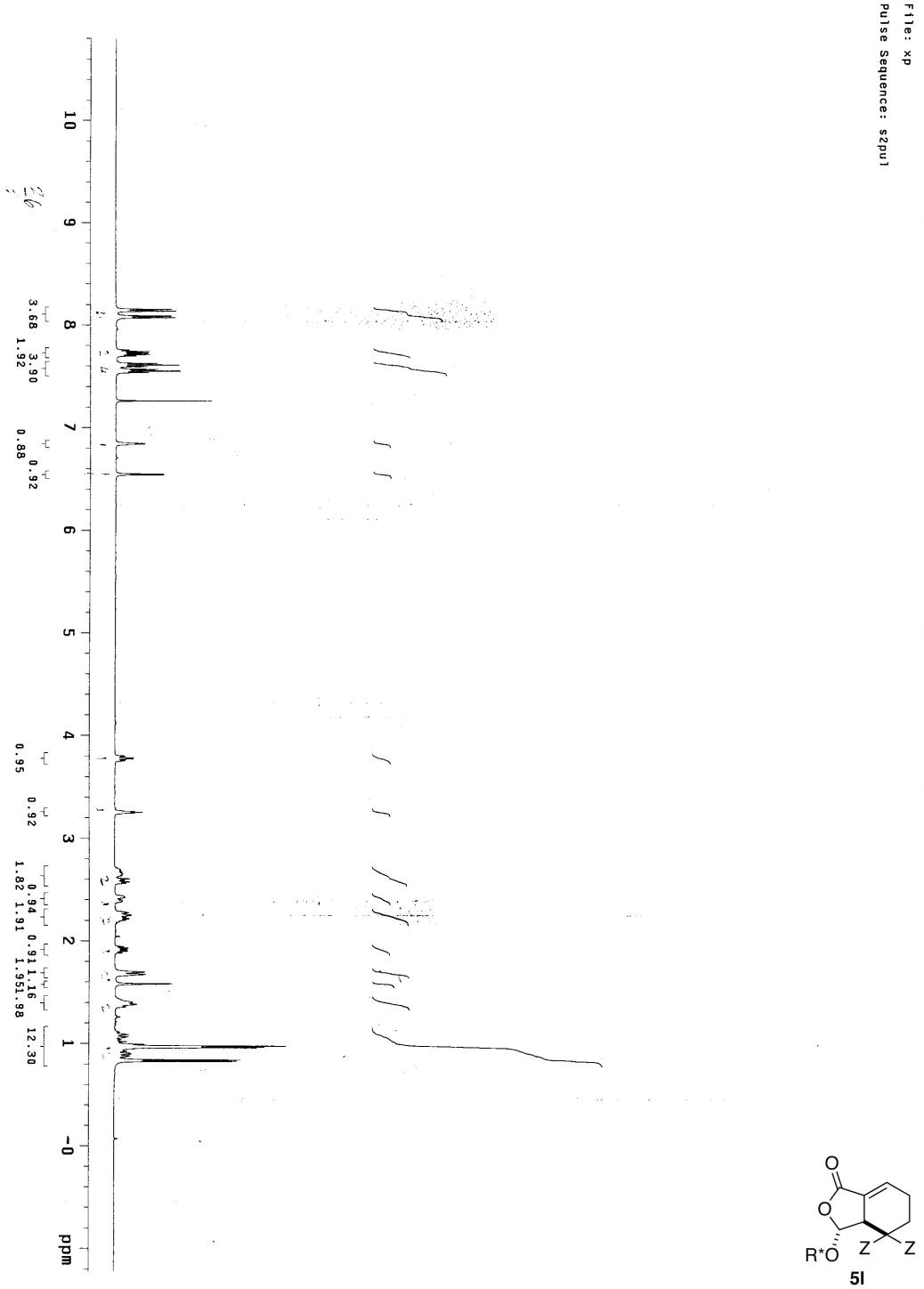
Pulse Sequence: PRESAT



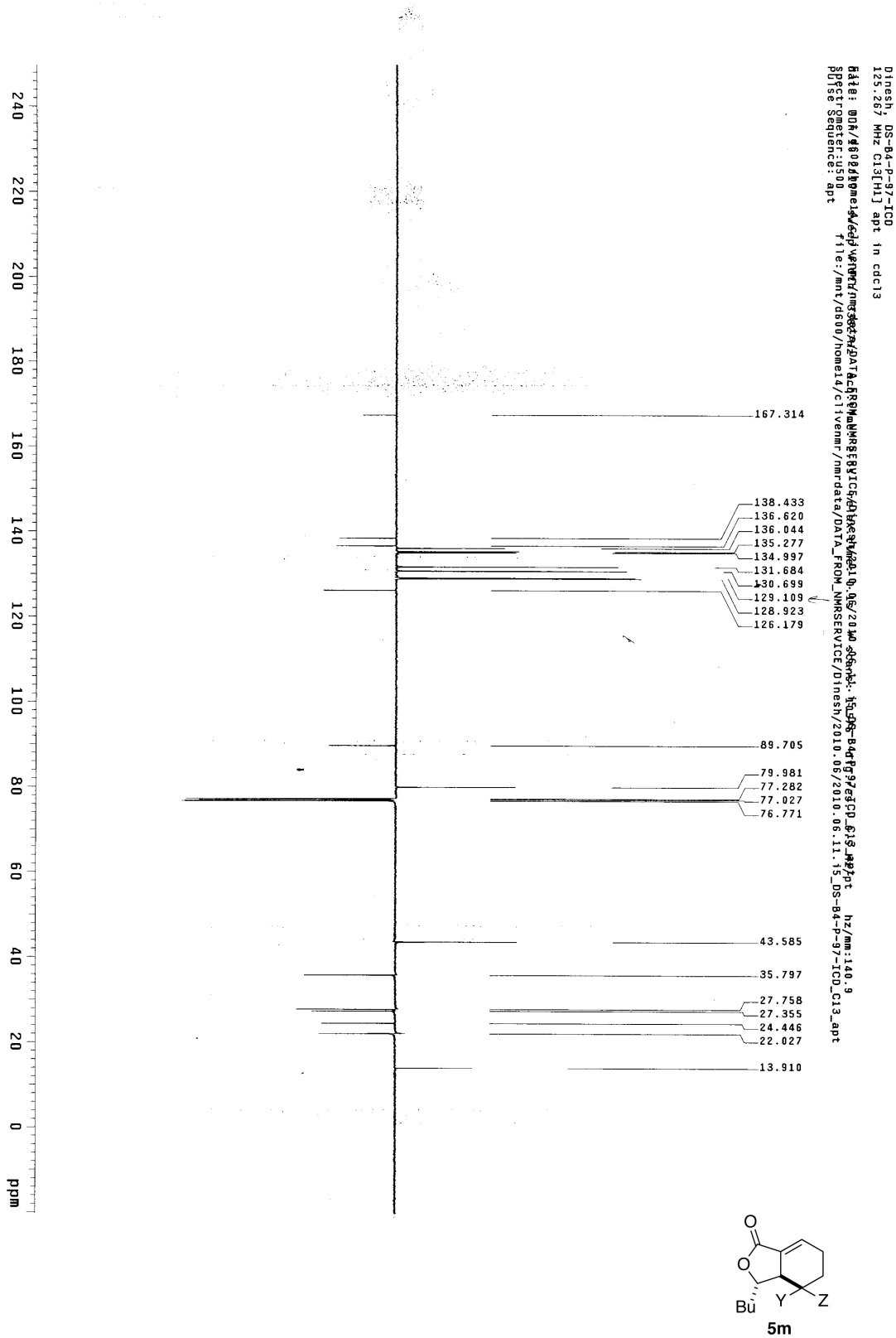
5k'


ds-bdp143-icd-6mem-c13
125.692 MHz C13{H1} APT_ad in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: APT_ad
165.973
138.705
135.346
135.096
135.004
134.723
131.934
131.311
129.016
128.737
126.592
98.708
87.538
87.534
87.530
77.264
77.145
77.010
76.755
48.114
46.424
38.261
34.272
31.399
27.862
25.721
24.265
23.326
22.350
21.042
15.989
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
O
O
R*O
Z
Z

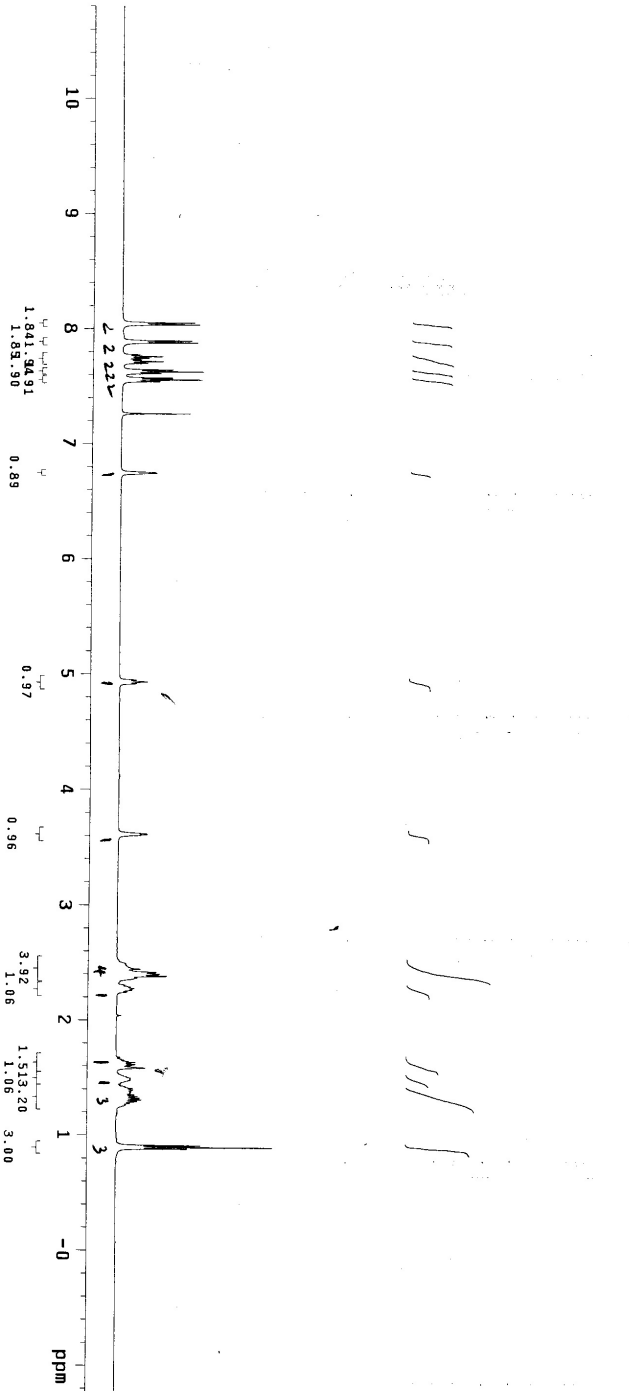
5l

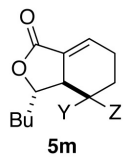


5l



5m





5m