Supporting information

The use of a [4+2] cycloaddition reaction for the preparation of a series of 'tethered' Ru(II)/diamine and aminoalcohol complexes.

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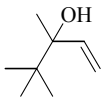
Contents:

i) Preparation of reagents for synthetic processes and ketone reductions.

General Experimental Details

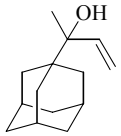
All reactions, unless otherwise stated, were run under an atmosphere of nitrogen at ambient temperature (18-22 ^{o}C). 0 ^{o}C refers to an ice slush bath and –78 ^{o}C refers to a dry ice-acetone bath. Heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by TLC using aluminium backed silica gel 60 (F254) plates, visualised using UV 254 nm and phosphomolybdic acid, ninhydrin, potassium permanganate or vanillin dips as appropriate. Flash column chromatography was carried out routinely using 60 Å silica gel (Merck). Reagents were used as received from commercial sources unless otherwise stated. NMR spectra were recorded on a Bruker DPX (300 or 400 MHz) spectrometer. Chemical shifts are reported in δ units, parts per million downfield from TMS. Coupling constants (*J*) are measured in hertz. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Golden Gate. Mass spectra were recorded on a 7070E VG mass spectrometer. Melting points were recorded on a Stuart Scientific SMP 1 instrument and are uncorrected. Optical rotations were measured with an AA1000 polarimeter and are given in 10^{-1} deg cm^2 g^{-1}. Determination of enantiomeric excesses by HPLC analysis was achieved using a Merck-Hitachi L-6200A HPLC pump, Merck-Hitachi L-4000 UV absorbance detector, Axiomm 727 data module and a Daicel Chiralcel OD, OD-H or AD 4.6 x 25 cm column. Determination of enantiomeric excesses by GC analysis was achieved using a Chrompac cyclodextrin-β-236M-19 50m or Chiracel β-DEX-120 25m column.

Synthesis of 3,4,4-trimethylpent-1-en-3-ol.



To a stirred solution of 1 M vinylmagnesium bromide in THF (36 cm^3, 36.0 mmol) was added a solution of pinacolone (3.005 g, 30.0 mmol) in THF (9 cm^3) at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred overnight at reflux, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm^3), diluted with water (20 cm^3) and extracted with DCM (2 x 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered and concentrated under vacuum at room tempaerature to give the crude product. The residue was purified by distillation to give the alcohol[1] (2.25 g, 59%) as a colourless oil; bp 61-63 ^oC / 50 mbar; ν_{max}/cm^{-1} (thin film) 3485 (OH), 1642 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.94 (9 H, s, $C(CH_3)_3$), 1.24 (3 H, s, CH_3), 1.40 (1 H, s, OH), 5.09 (1 H, dd, *J* 11.1 and 1.5, =C*H*H *trans* to =CR), 5.22 (1 H, dd, *J* 17.3 and 1.5, =CH*H cis* to =CR), 6.08 (1 H, dd, *J* 17.3 and 11.1, =CHR); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 23.3 (q), 25.3 (q), 37.1 (s), 77.3 (s), 112.3 (t), 143.3 (d).

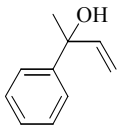
Synthesis of 2-adamantan-1-ylbut-3-en-2-ol.



To a stirred solution of 1 M vinylmagnesium bromide in THF (14.5 cm^3, 14.5 mmol) was added a solution of 1-adamantylmethyl ketone (2.150 g, 30.0 mmol) in THF (5 cm^3) at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred overnight at reflux, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm^3), diluted with water (20 cm^3) and extracted with DCM (2 x 30

cm^3). The combined extracts were dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (2.5% EtOAc/hexane to 10% EtOAc/hexane) to give the alcohol[2] (1.36 g, 55%) as a colourless oil; ν_{max}/cm^{-1} (thin film) 3489 (OH), 1640 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.19 (3 H, s, CH_3), 1.36 (1 H, s, OH), 1.58-1.82 (12 H, m, adamantyl 6 x CH_2), 1.96-2.02 (3 H, m, adamantyl 3 x CH), 5.09 (1 H, dd, *J* 11.1 and 1.6, =C*H*H *trans* to =CR), 5.18 (1 H, dd, *J* 17.3 and 1.6, =CH*H cis* to =CR), 6.03 (1 H, dd, *J* 17.3 and 11.1, =CHR); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 22.1 (q), 28.6 (3 x d), 36.3 (3 x t), 37.1 (3 x t), 38.3 (s), 77.2 (s), 112.3 (t), 142.9 (d); Found (EI) 206.1652 $[M]^+$, $C_{14}H_{22}O$ requires 206.1671 (1.9 mDa error); *m/z* (EI) 188 ($M-OH_2^+$, 10%), 135 (100), 107 (15), 93 (30), 79 (30).

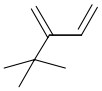
Synthesis of 2-phenylbut-3-en-2-ol.



To a stirred solution of 1 M vinylmagnesium bromide in THF (36 cm^3, 36.0 mmol) was added a solution of acetopheneone (3.60 g, 30.0 mmol) in THF at a rate to maintain gentle reflux without external heating. The reaction mixture was stirred at reflux for 1 hour, cooled, quenched with the addition of saturated ammonium chloride solution (aq.) (10 cm^3), diluted with water (20 cm^3) and extracted with DCM (2 x 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (5% EtOAc/hexane to 10% EtOAc/hexane) to give the alcohol[3] (2.73 g, 61%) as a colourless

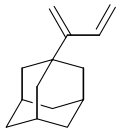
oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.65 (3 H, s, CH_3), 1.96 (1 H, s, OH), 5.13 (1 H, dd, *J* 10.8 and 1.3, =C*H*H *trans* to =CR), 5.29 (1 H, dd, *J* 17.3 and 1.3, =C*H*H *cis* to =CR), 6.16 (1 H, dd, *J* 17.3 and 10.8, =CHR), 7.22-7.27 (1 H, m, Ph), 7.31-7.36 (2 H, m, Ph), 7.44-7.48 (2 H, m, Ph); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 29.4 (q), 74.8 (s), 112.4 (t), 125.2 (2 x d), 127.0 (d), 128.3 (2 x d), 144.9 (d), 146.5 (s).

Synthesis of 4,4-dimethyl-3-methylenepent-1-ene.



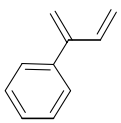
To a stirred solution of tetrabutylammonium perrhenate (0.531 g, 1.08 mmol) and *para*-toluenesulphonic acid mono-hydrate (0.103 g, 0.54 mmol) in DCM (40 cm^3) was added a solution of 3,4,4-trimethylpent-1-en-3-ol (1.015 g, 4.92 mmol) in DCM (20 cm^3). The reaction mixture was stirred overnight, diluted with diethyl ether (75 cm^3) and saturated $NaHCO_3$ (75 cm^3) added. The layers were separated and the organic layer was dried ($MgSO_4$), filtered and concentrated to a small volume by distillation at ambient pressure. The residue was filtered (silica) and washed with pentane (50 cm^3) and again concentrated to a small volume by distillation at ambient pressure. The residue was then distilled under reduced pressure (30 mbar) at room temperature, collecting the product in a trap at -78 ^oC to give the diene[4] (0.163 g, 14%) as a colourless oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.09 (9 H, s, $C(CH_3)_3$), 4.79 (1 H, d, *J* 1.8, $CH_aH_bCR_2$), 5.01 (1 H, dd, *J* 10.8 and 2.3, CHR=C*H*H *trans* to CR), 5.06 (1 H, m, $CH_aH_bCR_2$), 5.39 (1 H, dd, *J* 17.1 and 2.3, CHR=CH*H cis* to CR), 6.42 (1 H, dd, *J* 17.1 and 10.8, C*H*R=CH_2); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 29.3 (3 x q), 35.0 (s), 107.1 (t), 114.6 (t), 137.0 (d), 156.7 (s).

Synthesis of 1-(1-methyleneallyl)-adamantane.



To a stirred solution of tetrabutylammonium perrhenate (0.242 g, 0.49 mmol) and *para*-toluenesulphonic acid mono-hydrate (0.047 g, 0.25 mmol) in DCM (30 cm^3) was added a solution of 2-adamantan-1-ylbut-3-en-2-ol (1.015 g, 4.92 mmol) in DCM (20 cm^3). The reaction mixture was stirred overnight, diluted with diethyl ether (20 cm^3) and saturated $NaHCO_3$ (50 cm^3) added. The layers were separated and the organic layer was dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (pentane) to give the diene[5] (1.36 g, 55%) as a colourless oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.62-1.76 (12 H, m, adamantyl 6 x CH_2), 1.97-2.05 (3 H, m, adamantyl 3 x CH), 4.72 (1 H, d, *J* 1.5, CH_aH$_b$CR_2), 5.00 (1 H, dd, *J* 10.8 and 2.3, CHR=C*H*H *trans* to CR), 5.08 (1 H, m, C$H_a$$H_bCR_2$), 5.37 (1 H, dd, *J* 17.1 and 2.3, CHR=CH*H cis* to CR), 6.44 (1 H, dd, *J* 17.1 and 10.8, C*H*R=CH_2); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 28.7 (3 x d), 36.9 (3 x t), 40.5 (s), 41.2 (3 x t), 107.1 (t), 114.7 (t), 136.4 (d), 157.1 (s).

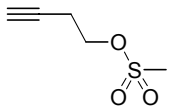
Synthesis of (1-methyleneallyl)-benzene.



To a stirred solution of 2-phenylbut-3-en-2-ol (1.870 g, 12.6 mmol) in THF (30 cm^3) was added *para*-toluenesulphonic acid mono-hydrate (0.480 g, 2.5 mmol). The reaction

mixture was stirred overnight at 60 ^{o}C, diluted with saturated $NaHCO_3$ (50 cm^3) and extracted with DCM (2 x 50 cm^3). The combined extracts were dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash column chromatography (pentane) to give the product[6] (0.528 g, 33%) as a colourless oil; δ_H (400 MHz; $CDCl_3$; Me_4Si) 5.16-5.23 (3 H, m, CHR=CH_2 and CH_aH$_b$CR$_2$), 5.29-5.31 (1 H, m, CH$_a$$H_bCR_2$), 6.62 (1 H, dd, *J* 17.1 and 10.8, C*H*R=CH$_2$), 7.27-7.38 (5 H, m, Ph); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 116.9 (t), 117.2 (t), 127.5 (d), 128.1 (2 x d), 128.3 (2 x d), 138.2 (d), 139.8 (s), 148.3 (s).

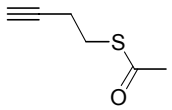
Synthesis of methanesulfonic acid but-3-ynyl ester.



To a stirred solution of 3-butyn-1-ol (4.63 g, 66.1 mmol) and triethylamine (10.01 g, 99.1 mmol) in DCM (60 cm^3) was added a solution of methanesulphonyl chloride (11.36 g, 99.1 mmol) in DCM (30 cm^3). The reaction mixture was stirred overnight, diluted with 2M HCl solution (30 cm^3) and extracted with DCM (30 cm^3). The combined extracts were washed with 1M HCl solution (30 cm^3), saturated sodium hydrogen carbonate solution (30 cm^3), and brine (30 cm^3) and then dried ($MgSO_4$), filtered and concentrated under vacuum to give the product (9.64 g, 98%) as a clear oil; ν_{max}/cm^{-1} (thin film) 3286 (≡CH), 1333 and 1168 (SO_2O); δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.08 (1 H, t, *J* 2.7, ≡CH), 2.67 (2 H, dt, *J* 6.8 and 2.7, ≡CCH_2), 3.07 (3 H, s, CH_3), 4.32 (2 H, t, *J* 6.8, CH_2OSO_2); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 19.5 (t), 37.5 (q), 66.9 (t), 70.7 (d), 78.4 (s). Found (EI)

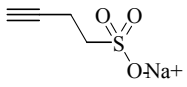
149.0257 $[MH]^+$, $C_5H_9O_3S$ requires 149.0272 (1.5 mDa error); *m/z* (EI) 149 (MH^+, 50%), 109 (50), 79 (100), 70 (45).

Synthesis of thioacetic acid *S*-but-3-ynyl ester.



To a stirred solution of methanesulfonic acid but-3-ynyl ester (18.73 g, 126.5 mmol) in acetonitrile (400 cm^3) was added potassium thioacetate (28.88 g, 253.0 mmol). The reaction mixture was stirred for 2 days, diluted with water (100 cm^3) and extracted with diethyl ether (3 x 200 cm^3). The combined extracts were dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by distillation to give the thioester (8.70 g, 54%) as a clear oil; bp 76-78^oC / 30 mm Hg; ν_{max}/cm^{-1} (thin film) 3291 (≡C-H), 2938 (CH_2), 1686 (C=O); δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.03 (1 H, t, *J* 2.6, ≡CH), 2.35 (3 H, s, CH3), 2.49 (2 H, dt, *J* 7.0 and 2.6, ≡CCH2), 3.04 (2 H, t, *J* 7.0, CH2S); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 17.6 (t), 26.2 (t), 28.7 (q), 67.8 (d), 80.2 (s), 193.4 (s). Found (EI) 127.0202 $[M-H]^+$, C_6H_7OS requires 127.0218 (1.5 mDa error); *m/z* (EI) 129 (MH^+, 5%), 128 (M^+, 5), 127 (10), 113 (35), 79 (70), 78 (100), 63 (55), 61 (15).

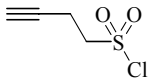
Synthesis of but-3-yne-1-sulfonic acid sodium salt.



To a stirred solution of thioacetic acid *S*-but-3-ynyl ester (5.00 g, 39.1 mmol) in acetic acid (65 cm^3) at 60 ^oC was added dropwise 30% hydrogen peroxide solution in water (25 cm^3, 196.0 mmol) and the reaction mixture was stirred for 3 hours, cooled and concentrated under vacuum to give the crude product, using heptane to azeotropically

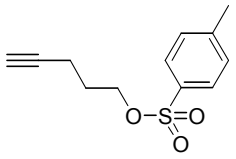
remove any traces of acetic acid. The residue was dissolved in water (50 cm^3) and neutralized with 2M sodium hydroxide solution. The solution was then concentrated under vacuum to give the sulfonate ester (5.98 g, 99%) as an off-white solid; mp >320 ^oC; ν_{max}/cm^{-1} (solid) 3307 (≡CH), 1321 and 1155 (SO_2O); δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.31 (1 H, t, *J* 2.6, ≡CH), 2.54 (2 H, dt, *J* 7.3 and 2.6, ≡CCH_2), 2.99 (2 H, t, *J* 7.3, CH_2SO_3Na); δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 14.5 (t). 49.6 (t), 70.8 (d), 82.7 (s). Found (LSIMS) 132.9967 $[M]^-$, $C_4H_5O_3S$ requires 132.9959 (0.8 mDa error); *m/z* (LSIMS) 133 (M^-, 100%).

Synthesis of but-3-yne-1-sulfonyl chloride 15.



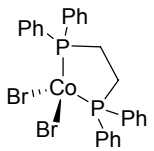
To a suspension of but-3-yne-1-sulfonic acid sodium salt (7.05 g, 45.5 mmol) in DCM (15 cm^3) and thionyl chloride (23 cm^3) was added dimethylformamide (15 drops). The reaction mixture was refluxed for 5 hours, cooled to room temperature and concentrated under vacuum to give the crude product. The residue was purified by distillation to give **15** (2.38 g, 34%) as a pale yellow oil; bp 44-45 ^oC / 0.5 mm Hg; ν_{max}/cm^{-1} (thin film) 3295 (≡C-H), 2994 and 2930 (CH_2), 1368 and 1166 (SO_2Cl); δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.17 (1 H, t, *J* 2.5, ≡CH), 2.93-2.98 (2 H, m, ≡CCH_2), 3.85 (2 H, t, *J* 7.5, CH_2SO_2Cl); δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 14.6 (t), 62.6 (t), 71.8 (d), 77.3 (s). Found (EI) 149 (5%), 78 (75), 63 (100).

Synthesis of pent-4-ynyl 4-methylbenzenesulfonate 26.



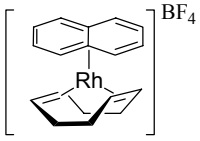
To a solution of 4-penty-1-ol (8.52 g, 101 mmol) and triethylamine (11.25 g, 111 mmol) in acetonitrile (85 cm^3) was added para-toluene sulphonyl chloride (18.68 g, 98 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred overnight, filtered and concentrated under vacuum. The residue was dissolved in dichoromethane (200 cm^3), washed with 2 M HCl (200 cm^3), sat. $NaHCO_3$ solution (200 cm^3) and sat. NaCl solution (200 cm^3), dried ($MgSO_4$), filtered and concentrated under vacuum to give the crude product. The residue was purified by flash chromatography (5 % EtOAc/hexane to 30 % EtOAc/hexane) to give **26** (17.34 g, 74%) as a colourless oil. (Found: C, 60.11; H, 5.92. $C_{12}H_{14}O_3S$ requires C, 60.48; H, 5.92%); ν_{max}/cm^{-1} (thin film) 3289 (≡CH), 1356 and 1173 (SO_2O), 812 (disubstituted benzene); δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.82-1.91 (3 H, m, C*H*$_2$CH$_2$C≡CH and ≡C*H*), 2.26 (2 H, dt, *J* 7.0 and 2.6, C*H*$_2$C≡CH), 2.45 (3 H, s, CH_3), 4.15 (2 H, t, *J* 6.2, CH_2OSO_2), 7.35 (2 H, d, *J* 8.2, ArH *o* to CH_3), 7.80 (2 H, d, *J* 8.2, ArH *o* to SO_2); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 14.3 (t), 21.3 (q), 27.4 (t), 68.6 (t), 69.4 (d), 81.9 (s), 127.6 (2 x d), 129.7 (2 x d), 132.5 (s), 144.7 (s). Found (LSIMS): 239.0737 $[MH]^+$, $C_{12}H_{15}O_3S$ requires 239.0742 (2.2 ppm error); *m/z* (CI) 256 (MNH_4^+, 100%), 239 (MH^+, 5), 174 (10), 91 (5).

Synthesis of cobalt cycloaddition catalyst 18.



To a stirred solution of 1,2-bis(diphenylphosphino)ethane (2.000 g, 5.02 mmol) in THF (60 cm^3) was added cobalt(II) bromide (1.098 g, 5.02 mmol). The resulting brown solution was stirred overnight to give a green precipitate, which was collected by vacuum filtration to give **18**[7] (2.870 g) as a green solid, which was used in the cycloaddition reactions without further purification or characterisation.

Synthesis of rhodium cycloaddition catalyst 19.



To a suspension of $[Rh(cyclooctadiene)Cl]_2$ (0.098 g, 0.20 mmol) in acetone (15 cm^3) was added naphthalene (0.102 g, 0.80 mmol) followed by silver tetrafluoroborate (0.077 g, 0.40 mmol). The reaction mixture was stirred for 1 hour, filtered (celite) and concentrated under vacuum to give **19**[8] (0.182 g) as a yellow/orange solid which was used in the cycloaddition reactions without further purification or characterisation.

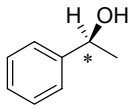
Reduction of ketones in isopropyl alcohol using tethered ruthenium aminoalcohol chiral ligands, typical procedure:

To a suspension of ruthenium dimer (0.00425 mmol) in isopropanol (15 cm^3) was added a 0.1 M solution of potassium hydroxide (0.85 cm^3, 0.085 mmol) and the solution stirred at 28 ^oC for 20 minutes. Substrate (1.70 mmol) was added and the reaction mixture stirred at 28 ^oC for 2 hours, diluted with hexane (30 cm^3), filtered (silica), washed (50% EtOAc/hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash chromatography where necessary.

Reduction of ketones in formic acid/triethylamine using tethered ruthenium diamine chiral ligands, typical procedure:

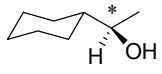
A solution of ruthenium dimer (0.0075 mmol) or pre-formed ruthenium monomer (0.015 mmol) in formic acid : triethylamine 5 : 2 azeotrope (1.5 cm^3) was stirred in a flame dried Schlenk tube at 28 ^oC for 30 minutes. Substrate (3.00 mmol) was added and the reaction mixture was stirred at 28 ^oC for 22 hours. The reaction mixture was filtered (silica), washed (50% EtOAc/hexane) and concentrated under vacuum to give the reduction product. The residue was purified by flash chromatography where necessary.

1-Phenylethanol KPA.



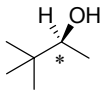
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 115 ^oC, P = 7 psi, ketone 13.2 min., *R* isomer 19.3 min., *S* isomer 20.3 min.); $[\alpha]_D^{22}$ +49.0 (c 1.0 in $CHCl_3$) 98% ee (*R*) (lit.[9] $[\alpha]_D^{23}$ +48.6 (c 1.0 in CH_2Cl_2) 96% ee (*R*)); δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.47 (3 H, d, *J* 6.4, CH_3), 2.04 (1 H, br s, OH), 4.86 (1 H, q, *J* 6.4, PhC*H*CH_3), 7.33-7.35 (5 H, m, Ph); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 24.9 (q), 70.2 (d), 125.2 (2 x d), 127.2 (d), 128.3 (2 x d), 145.6 (s).

1-Cyclohexylethanol.



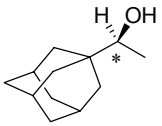
Method A: Enantiomeric excess by HPLC of 2-naptholate ester derivative (Chialcel OD-H, 4% iso-propanol/hexane (0.7 mL min^{-1}), *R* isomer 8.3 min., *S* isomer 9.6 min.), conversion by ^{1}H-NMR; Method B: Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 100 ^{o}C, P = 7 psi, ketone 17.6 min., *R* isomer 26.3 min., *S* isomer 26.9 min.); $[\alpha]_D^{18}$ -1.61 (c 1.80 in $CHCl_3$) 19% ee (*R*) (lit.[10] $[\alpha]_D$ +3.51 (c 3.1 in $CHCl_3$) 95% ee (*S*)); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.92-1.32 (6 H, m, cyclohexyl), 1.15 (3 H, d, *J* 6.3, CH_3),1.46 (1 H, br s, OH), 1.63-1.88 (5 H, m, cyclohexyl), 3.54 (1 H, dt, *J* 6.3 and 6.3, $CH(OH)CH_3$); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 20.4 (q), 26.2 (2 x overlapping t), 26.5 (t), 28.4 (t), 28.7 (t), 45.1 (d), 72.2 (d).

3,3-Dimethylbutan-2-ol.



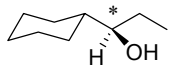
Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 80 ^{o}C, P = 7 psi, ketone 5.5 min., *R* isomer 8.7 min., *S* isomer 8.9 min.); $[\alpha]_D^{23}$ +2.0 (c 0.9 in CCl_4) 63% ee (*S*) (lit.[11] $[\alpha]_D^{29}$ -43.0 (c 1.5 in CCl_4) 99% ee (*R*)); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.89 (9 H, s, $C(CH_3)_3$), 1.12 (3 H, d, *J* 6.5, CH_3), 1.58-1.82 (1 H, br s, OH), 3.44-3.52 (1 H, m, C*H*OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 17.8 (q), 25.4 (3 x q), 34.9 (s), 75.6 (d).

1-Adamantanylethanol.



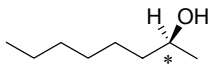
Enantiomeric excess by GC analysis (Chiracel β-DEX-120 25m, T = 115 ^{o}C, P = 48 psi, *R* isomer 57.1 min., *S* isomer 58.4 min.), conversion by ^{1}H-NMR; $[\alpha]_D^{18}$ +0.4 (c 1.5 in $CHCl_3$) 12% ee (*R*) (lit.[12] $[\alpha]_D^{25}$ -1.6 (c 2.2 in $CHCl_3$) 99.8% ee (*S*)); δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.10 (3 H, d, *J* 6.5, CH_3), 1.32 (1 H, br s, OH), 1.45-1.75 (12 H, m, adamantyl 6 x CH_2), 1.96-2.02 (3 H, m, adamantyl 3 x CH), 3.28 (1 H, q, *J* 6.5, C*H*OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 16.5 (q), 28.4 (3 x d), 36.6 (s), 37.3 (3 x t), 37.7 (3 x t), 75.8 (d).

1-Cyclohexylpropan-1-ol.



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 100 ^{o}C, P = 15 psi, ketone 19.9 min., *S* isomer 31.5 min., *R* isomer 32.1 min.); $[\alpha]_D^{23}$ -1.92 (c 0.65 in $CHCl_3$) 28% ee (*S*) (lit.[13] $[\alpha]_D^{25}$ -3.9 (c 3.05 in $CHCl_3$) 99% ee (*S*)); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.95 (3 H, t, *J* 7.4, CH_2CH_3), 0.99-1.82 (14 H, m, CH_2CH_3, OH and cyclohexyl), 3.25-3.30 (1 H, m, C*H*OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 10.2 (q), 26.2 (t), 26.4 (t), 26.6 (t), 26.8 (t), 27.7 (t), 29.3 (t), 77.6 (d).

Octan-2-ol.



Enantiomeric excess and conversion by GC analysis (Chrompac cyclodextrin-β-236M-19 50m, T = 70 ^{o}C, P = 10 psi, ketone 29.3 min., *R* isomer 54.1 min., *S* isomer 55.1 min.); $[\alpha]_D^{23}$ +3.31 (c 0.65 in $CHCl_3$) 24% ee (*S*) (lit.[14] $[\alpha]_D^{25}$ +9.0 (c 1.23 in $CHCl_3$) 99% ee

(*S*)); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.89 (3 H, t, *J* 6.8, CH_2CH_3), 1.18 (3 H, d, *J* 6.3, CH_3CHOH), 1.27-1.47 (10 H, m, 5 x CH_2), 1.57 (1 H, br s, OH), 3.78 (1 H, m, C*H*OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 14.1 (q), 22.6 (t), 23.4 (q), 25.7 (t), 29.3 (t), 31.8 (t), 39.4 (t), 68.1 (d).

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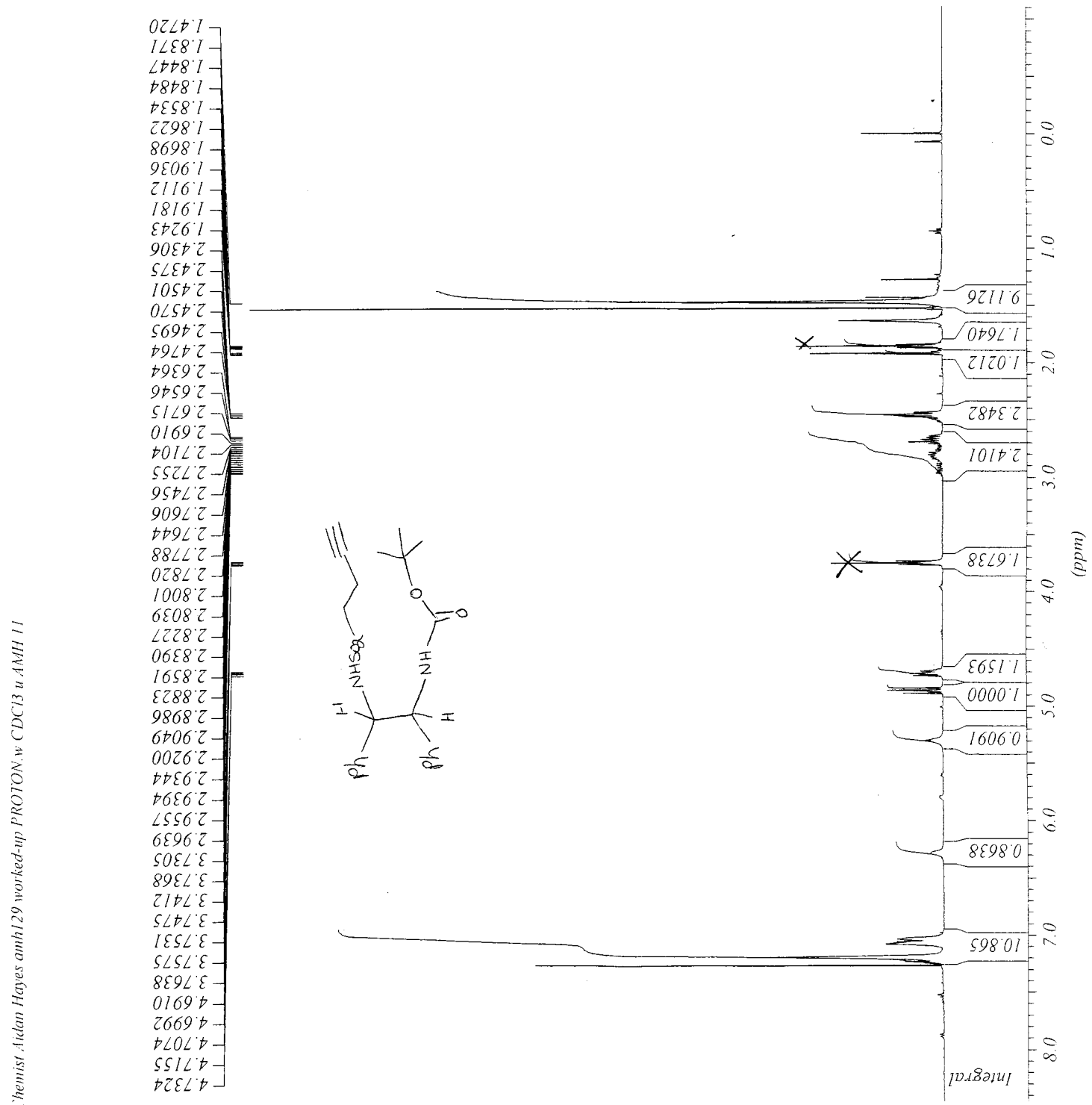
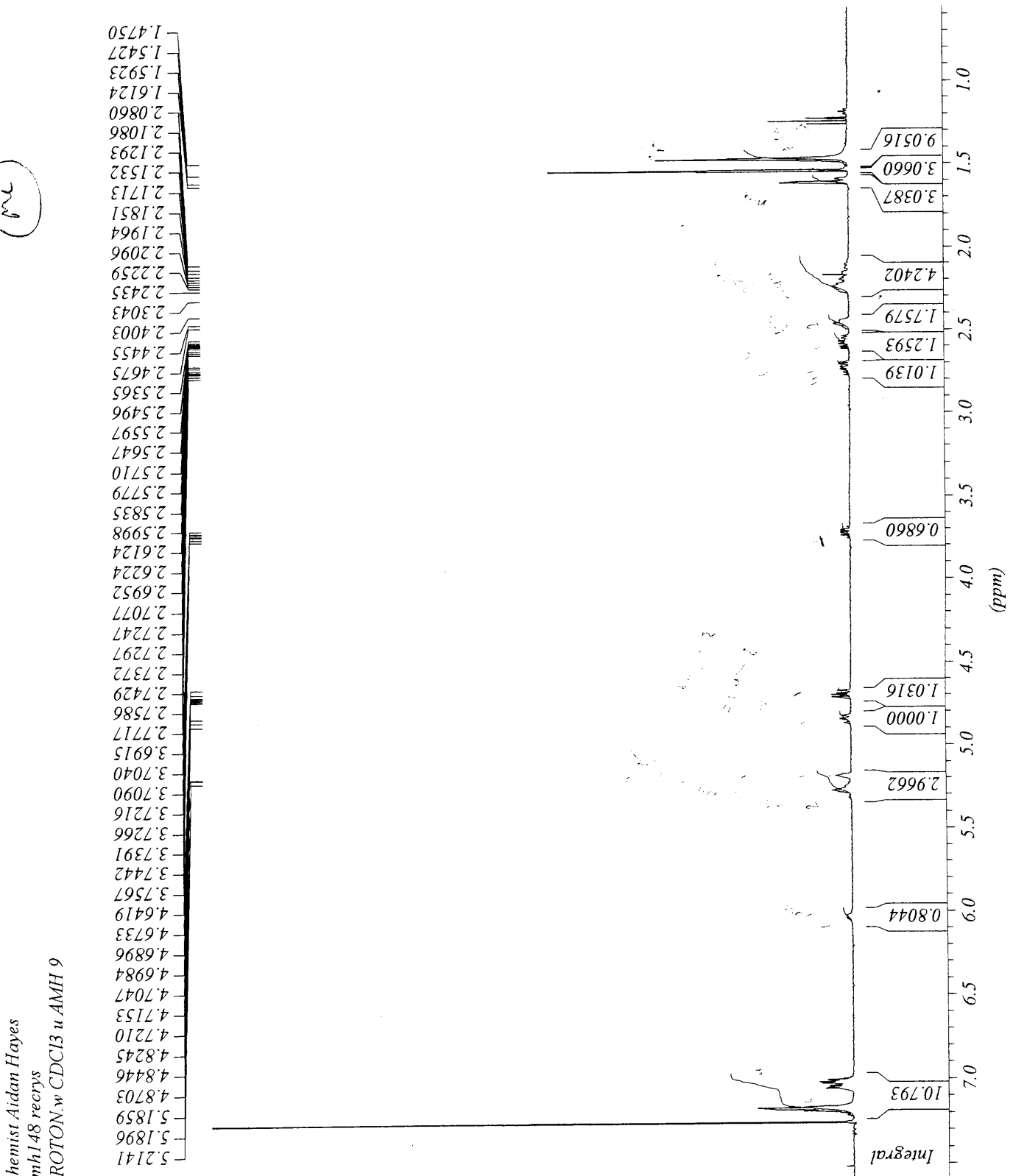
ii) 1H-NMR spectra of compounds lacking CHN analyses.

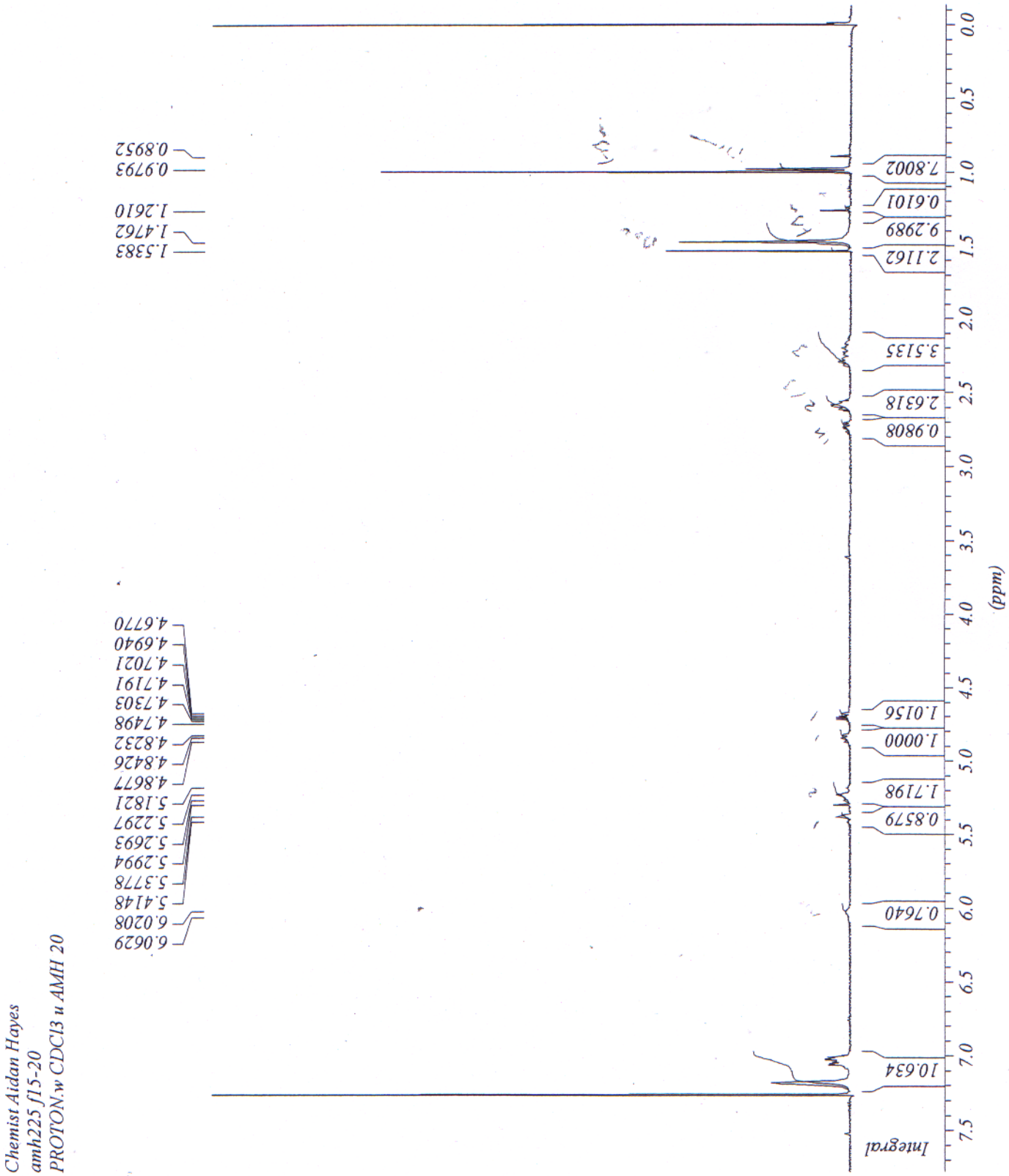
[(*R*,*R*)-2-(but-3-yne-1-sulfonylamino)-1,2-diphenylethyl]-carbamic acid *tert*-butyl ester 17.



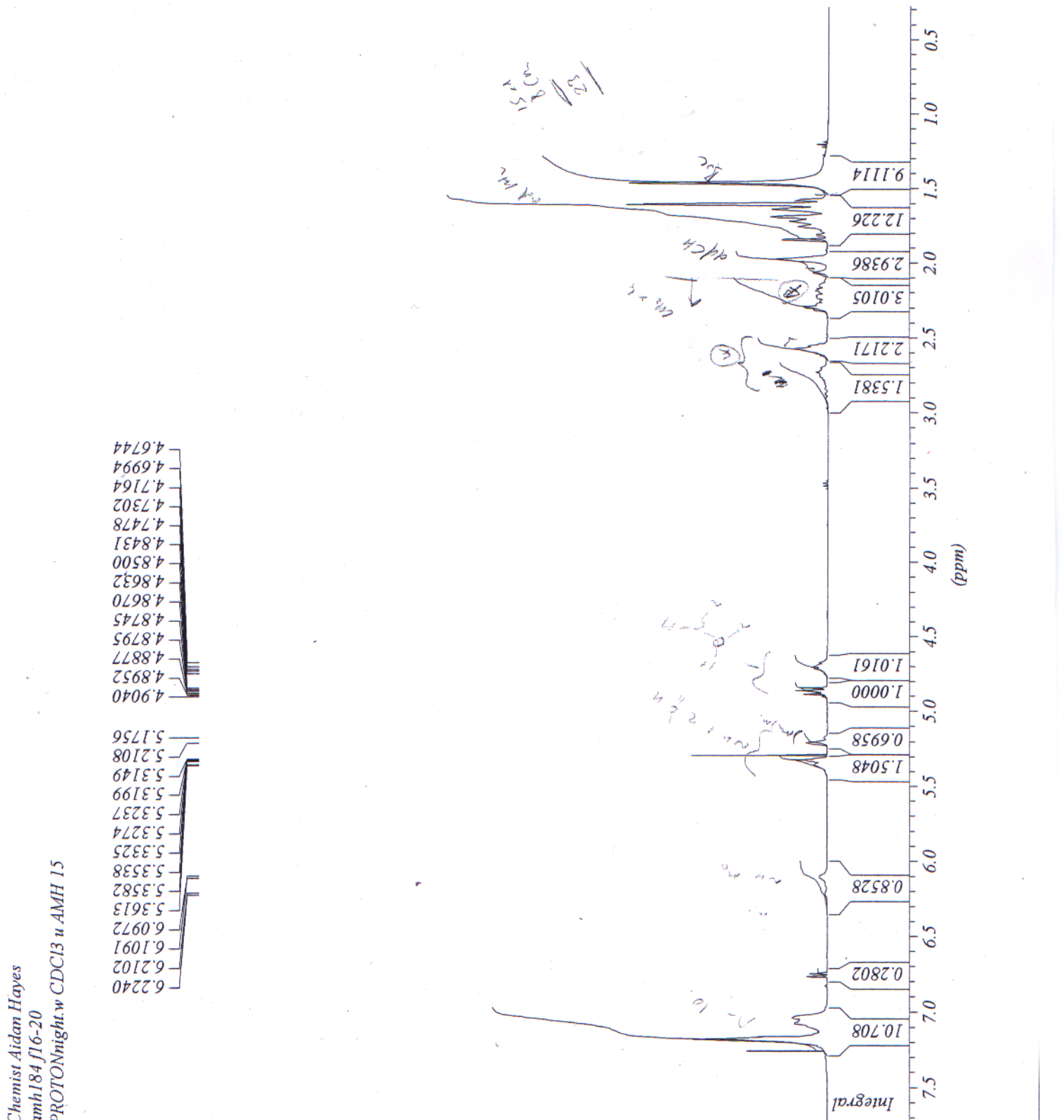
{(*R*,*R*)-2-[2-(4-methylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-1,2-diphenylethyl}-carbamic acid *tert*-butyl ester 20a.



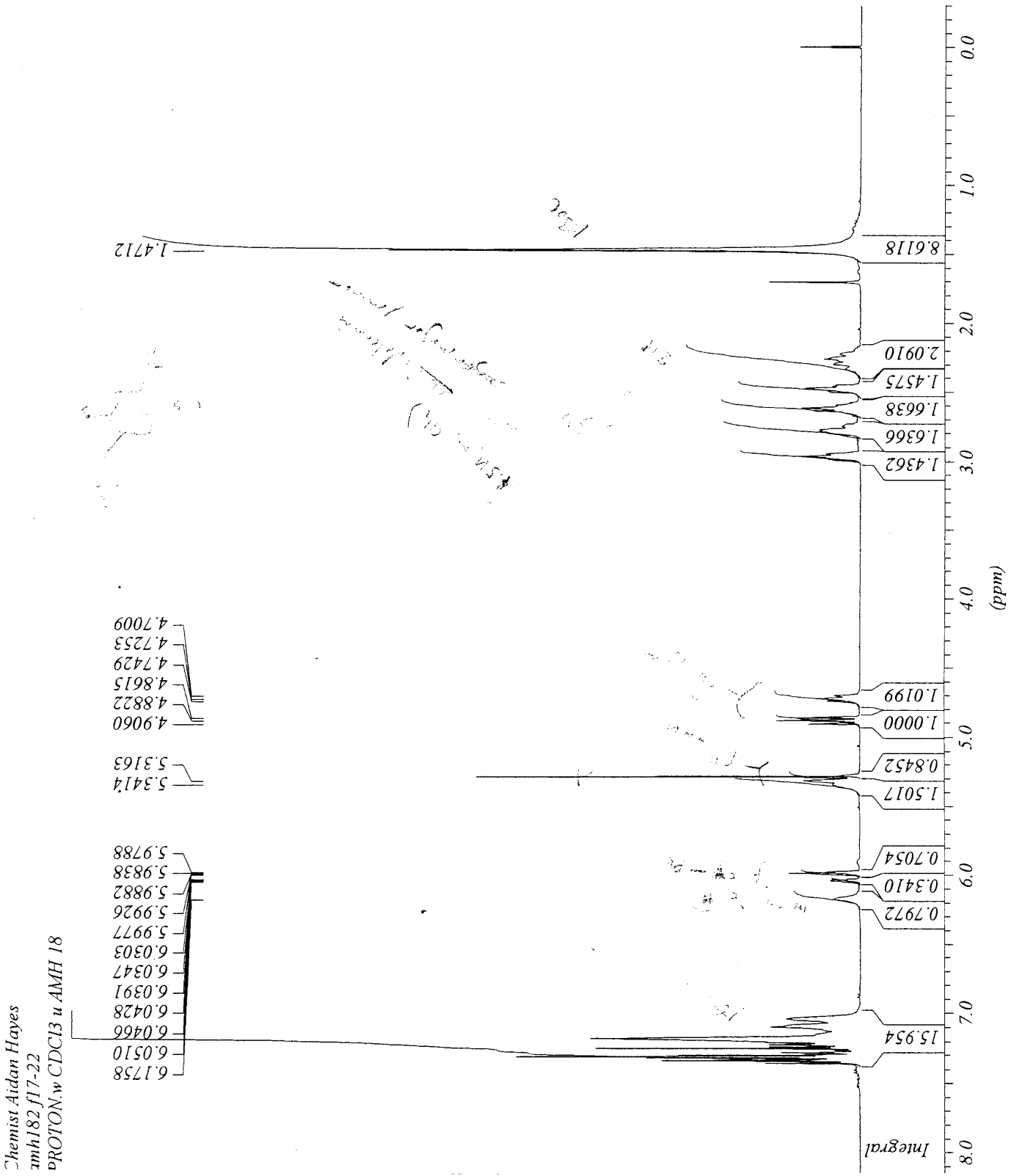
{(*R*,*R*)-2-[2-(4-*tert*-butylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-1,2-diphenylethyl}-carbamic acid *tert*-butyl ester 20b.



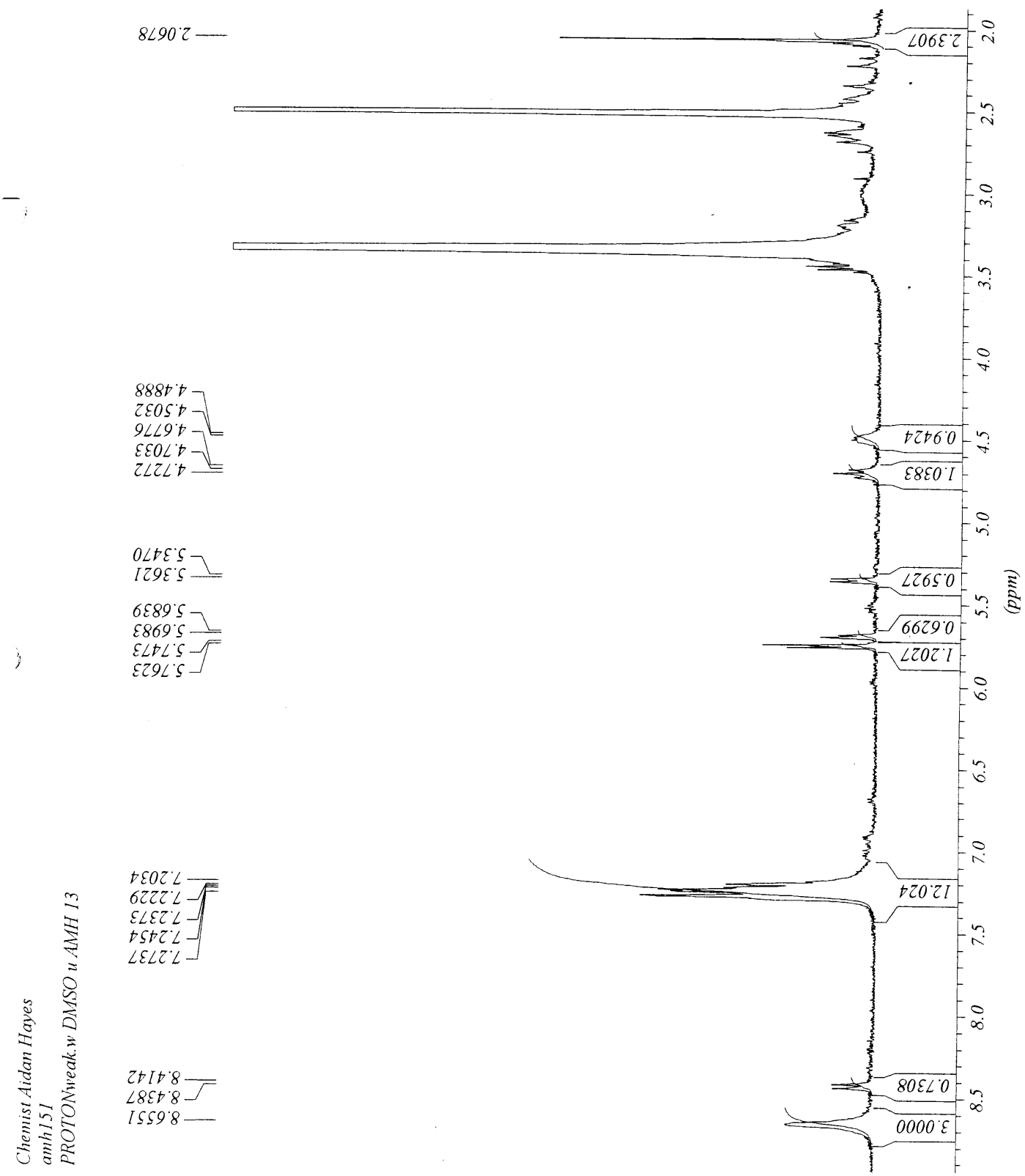
{(*R*,*R*)-2-[2-(4-adamantan-1-ylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-1,2-diphenylethyl}-carbamic acid *tert*-butyl ester 20c.



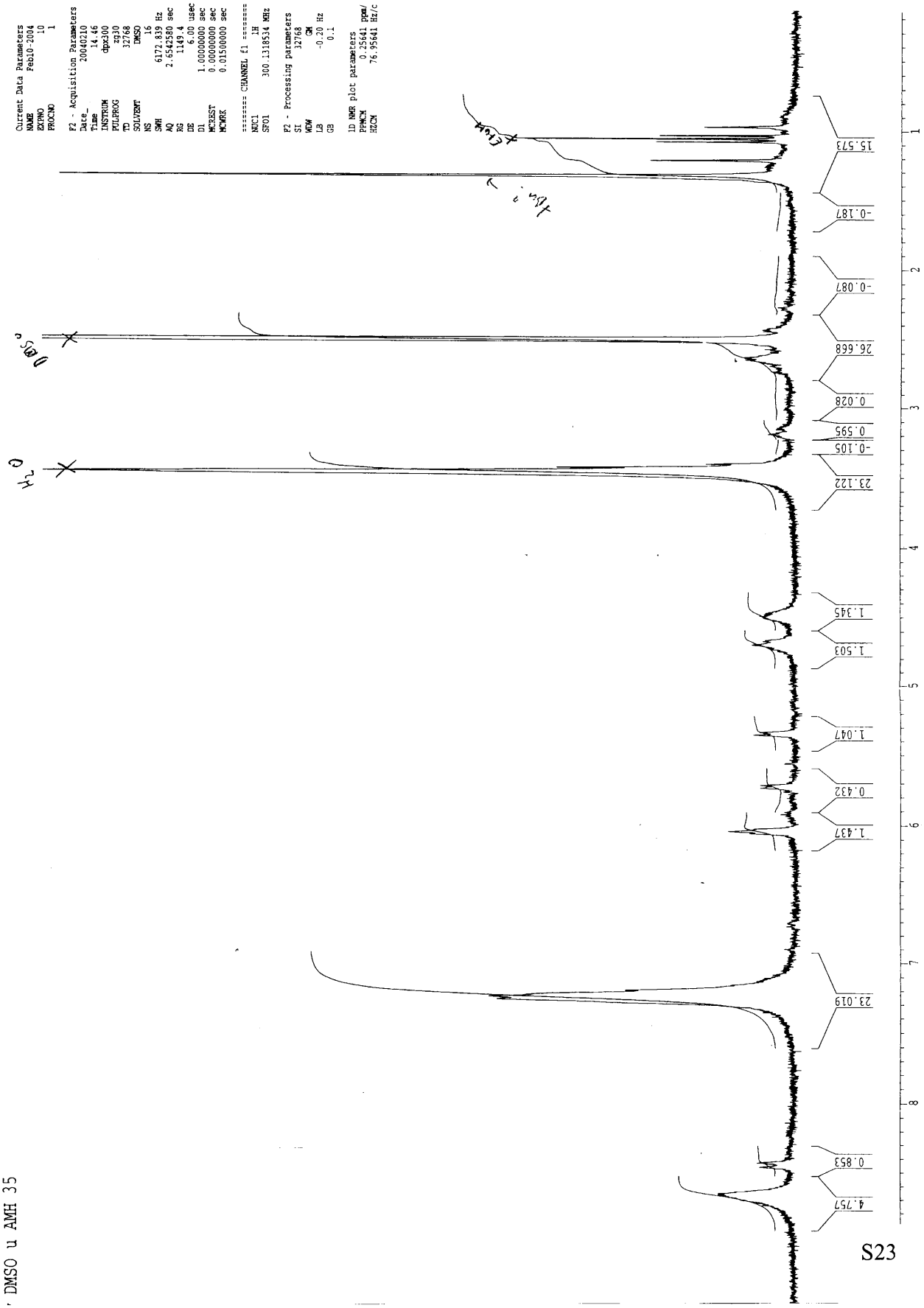
{(*R*,*R*)-1,2-diphenyl-2-[2-(4-phenylcyclohexa-1,4-dienyl)-ethanesulfonylamino]-ethyl}-carbamic acid *tert*-butyl ester 20d.



2-*p*-tolyl-ethanesulfonic acid ((*R*,*R*)-2-amino-1,2-diphenylethyl)-amide ammonium chloride ruthenium dimer 21a.

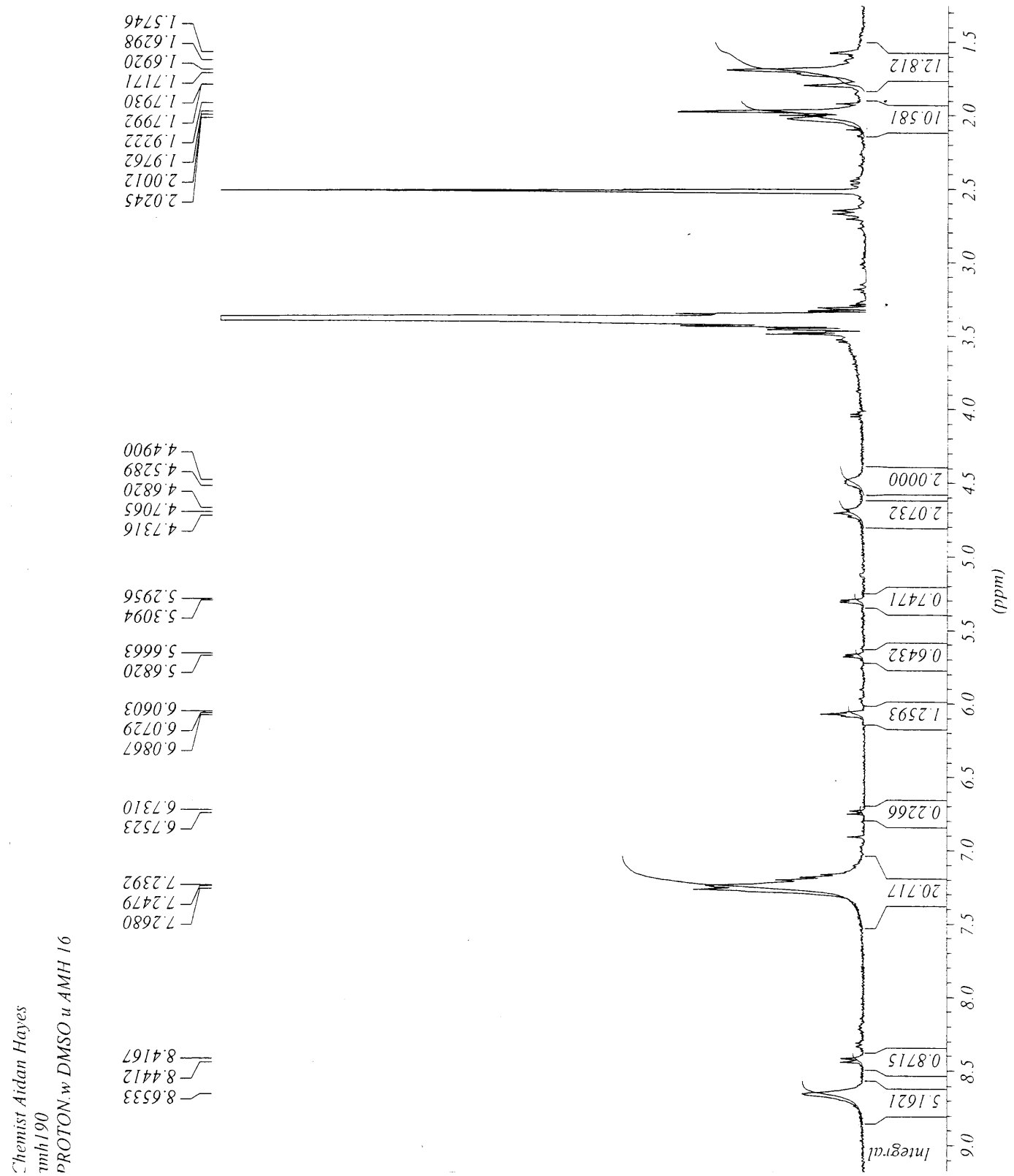


2-(4-*tert*-butyl-phenyl)-ethanesulfonic acid ((*R*,*R*)-2-amino-1,2-diphenylethyl)-amide ammonium chloride ruthenium dimer 21b.

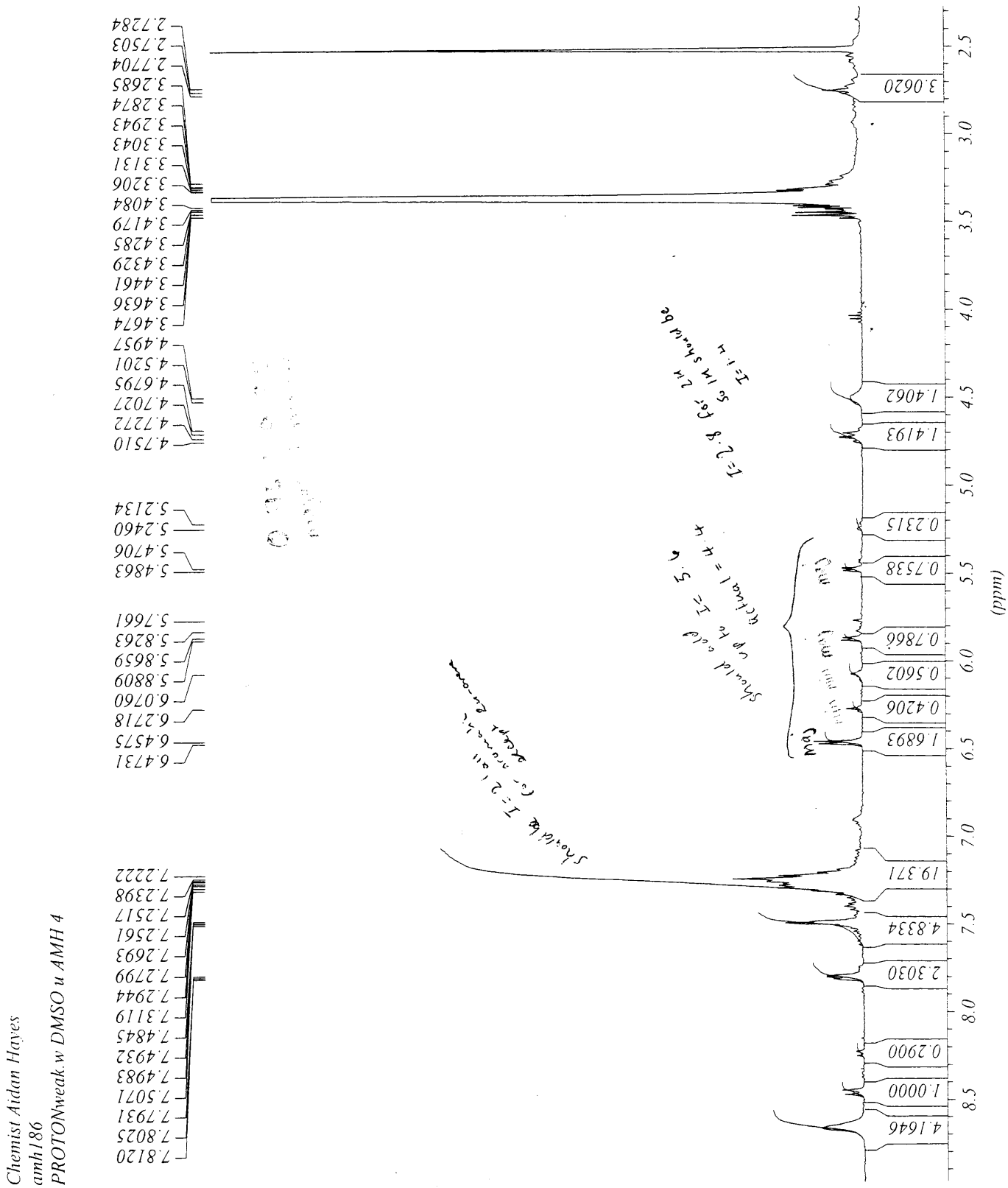


Aidan Hayes
DMSO u AMH 35

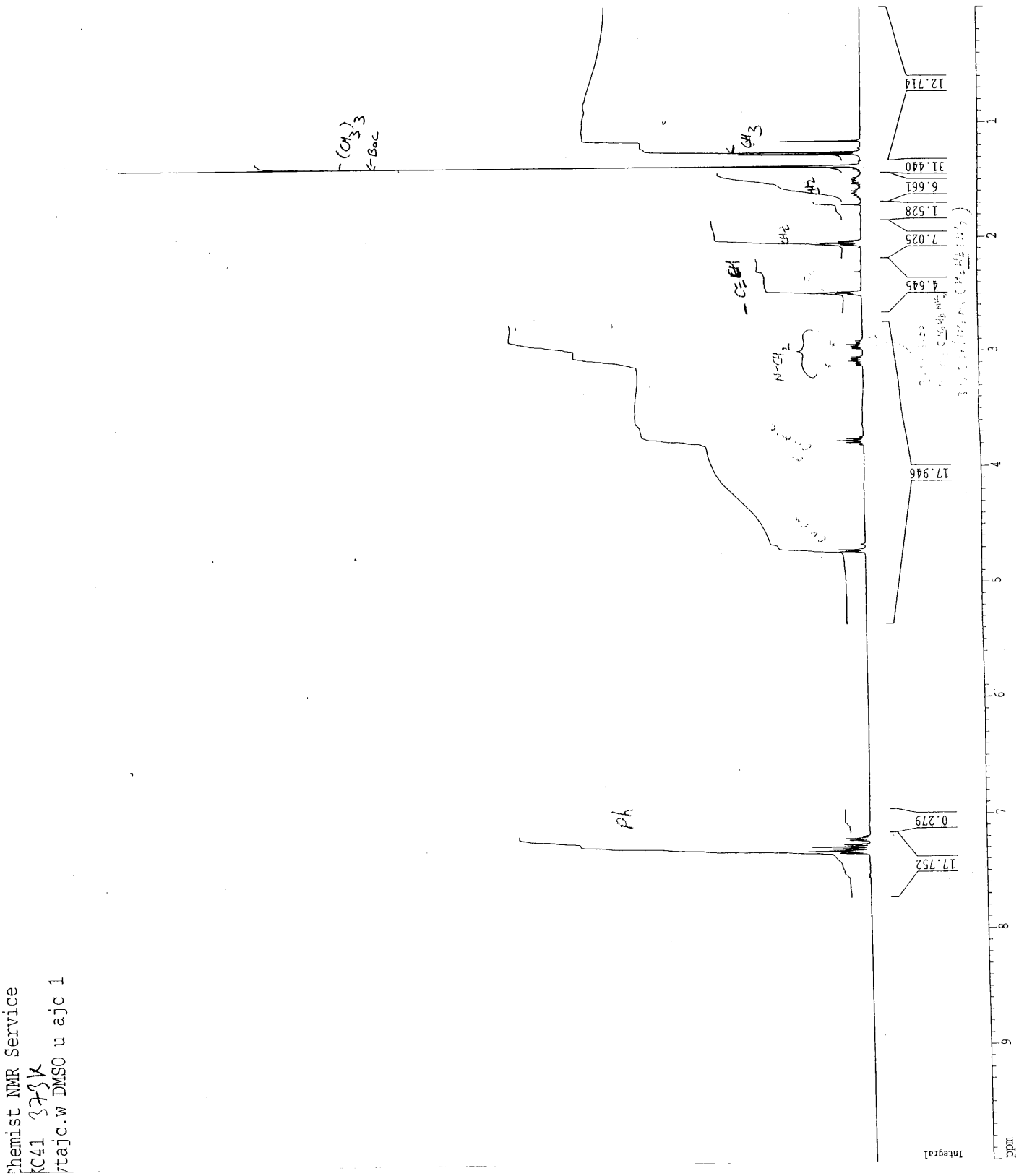
2-(4-adamantan-1-yl-phenyl)-ethanesulfonic acid ((*R*,*R*)-2-amino-1,2-diphenylethyl)-amide ammonium chloride ruthenium dimer 21c.



2-biphenyl-4-yl-ethanesulfonic acid ((*R*,*R*)-2-amino-1,2-diphenylethyl)-amide ammonium chloride ruthenium dimer 21d.

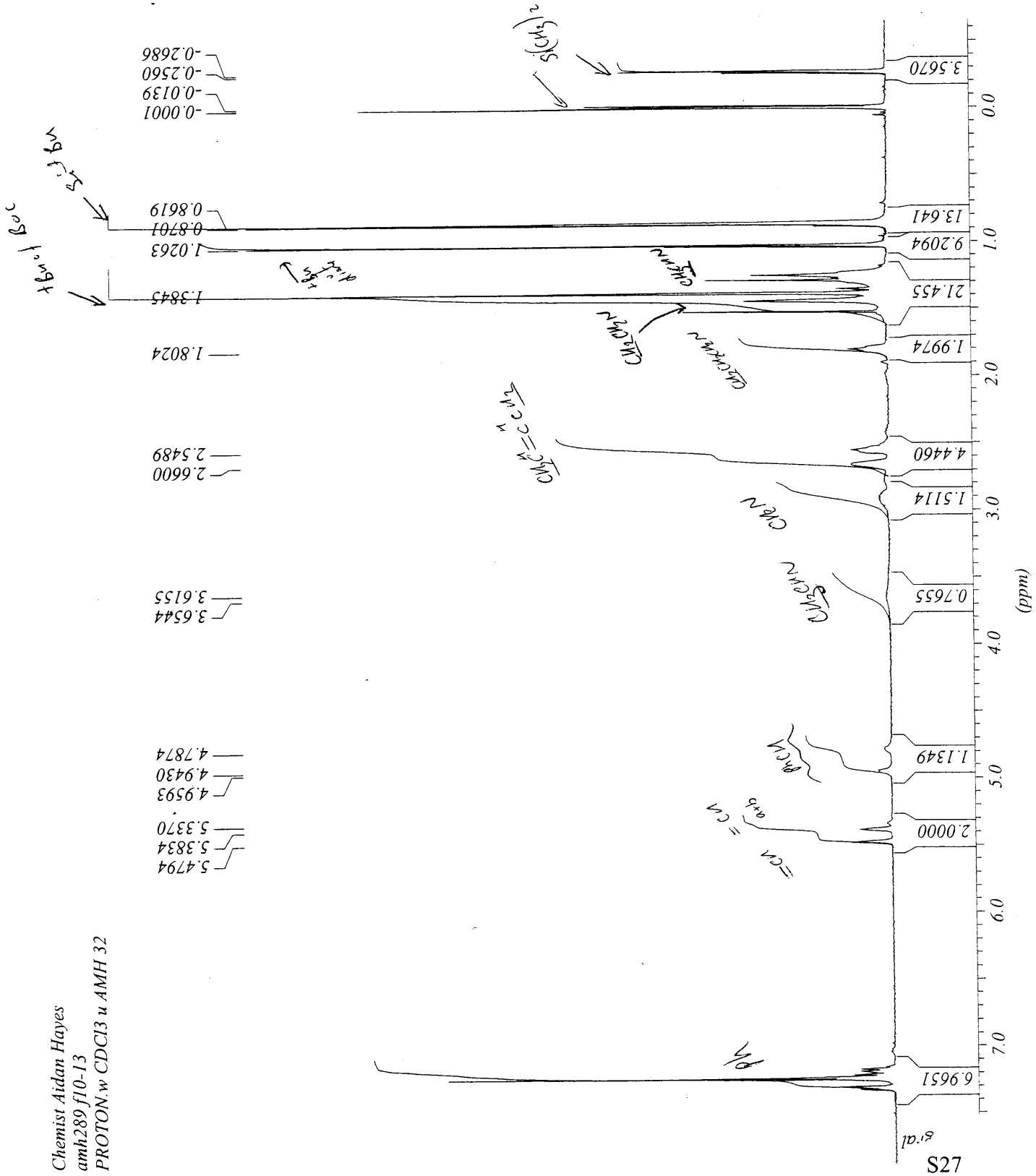


tert-butyl (1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl(pent-4-ynyl) carbamate 25.

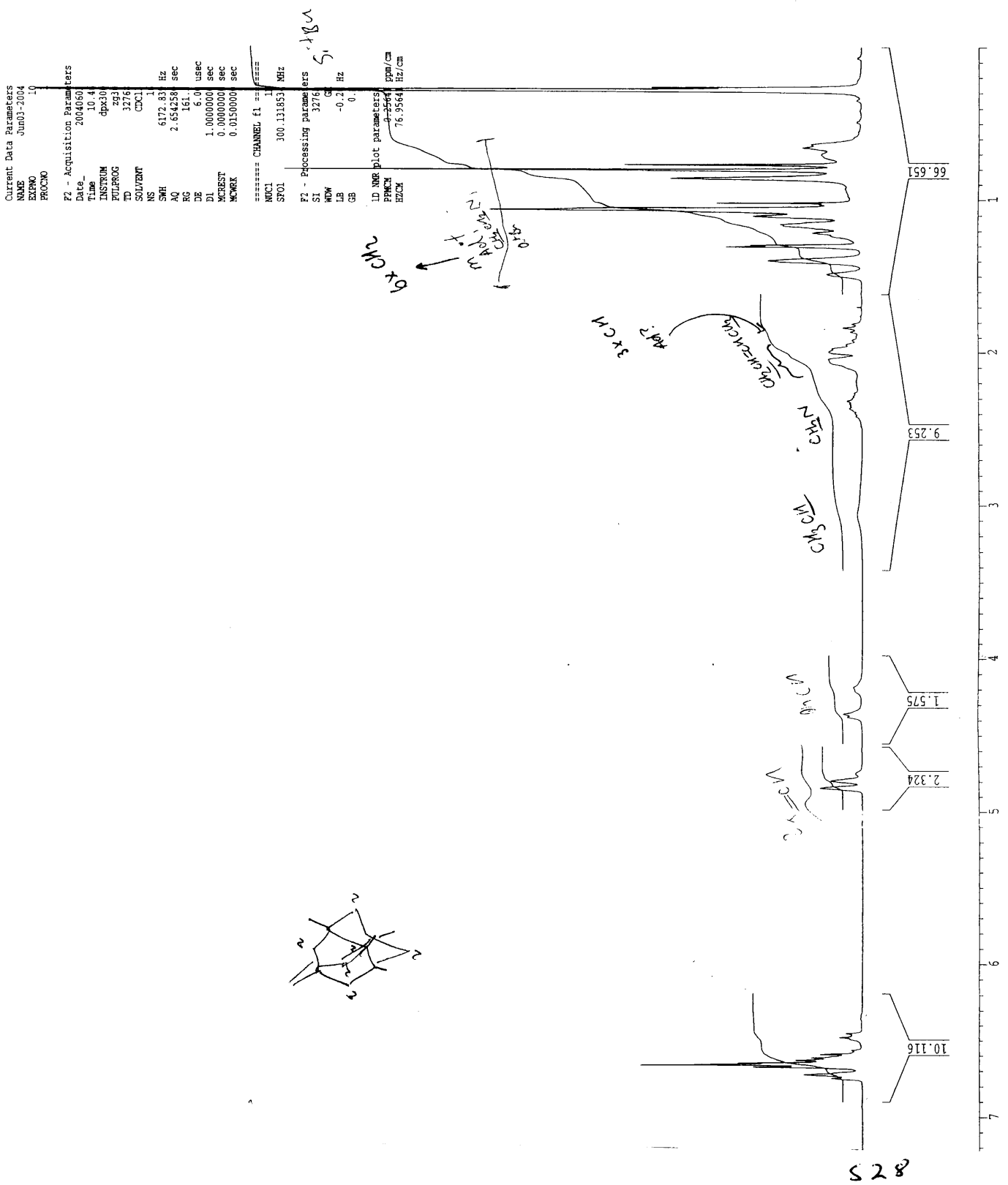


Chemist NMR Service
KC41 373K
ytajc.w DMSO u ajc 1

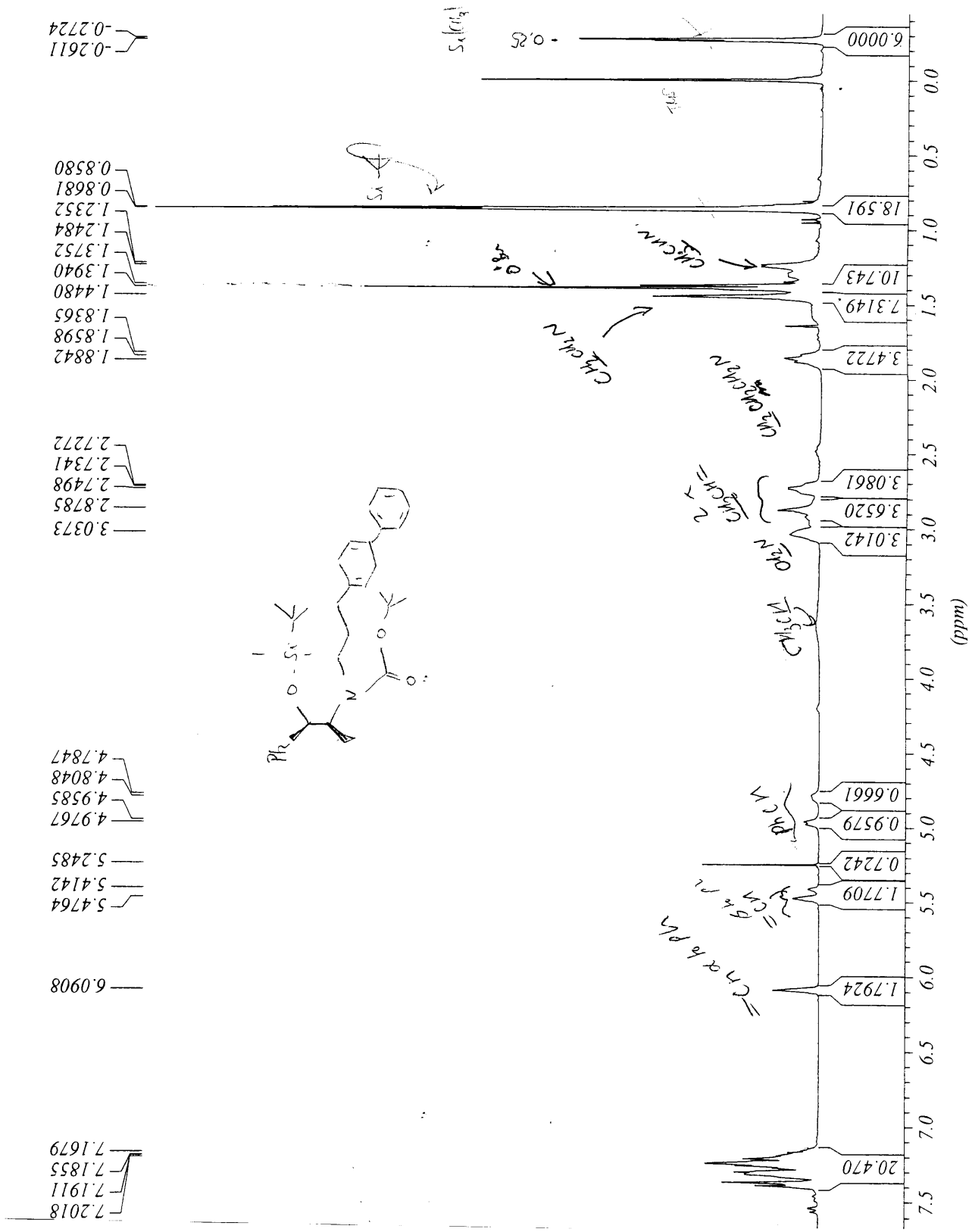
[3-(4-*tert*-butyl-cyclohexa-1,4-dienyl)-propyl]-[(1*S*,2*R*)-2-(*tert*-butyldimethylsilanyloxy)-1-methyl-2-phenylethyl]-carbamic acid *tert*-butyl carbamate 28b.



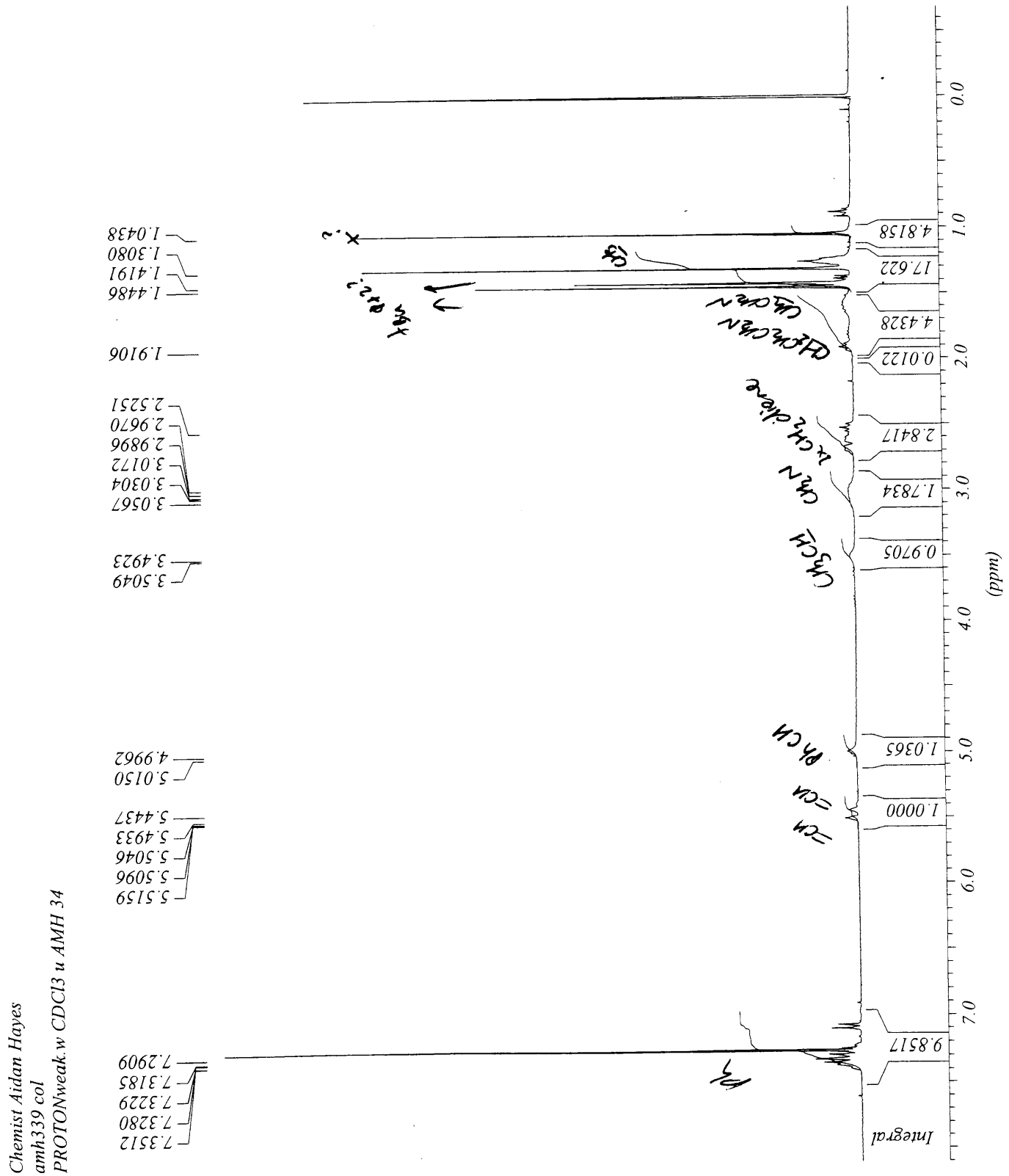
[3-(4-adamantan-1-ylcyclohexa-1,4-dienyl)-propyl]-[(1*S*,2*R*)-2-(*tert*-butyldimethylsilanyloxy)-1-methyl-2-phenylethyl]-carbamic acid *tert*-butyl carbamate 28c.



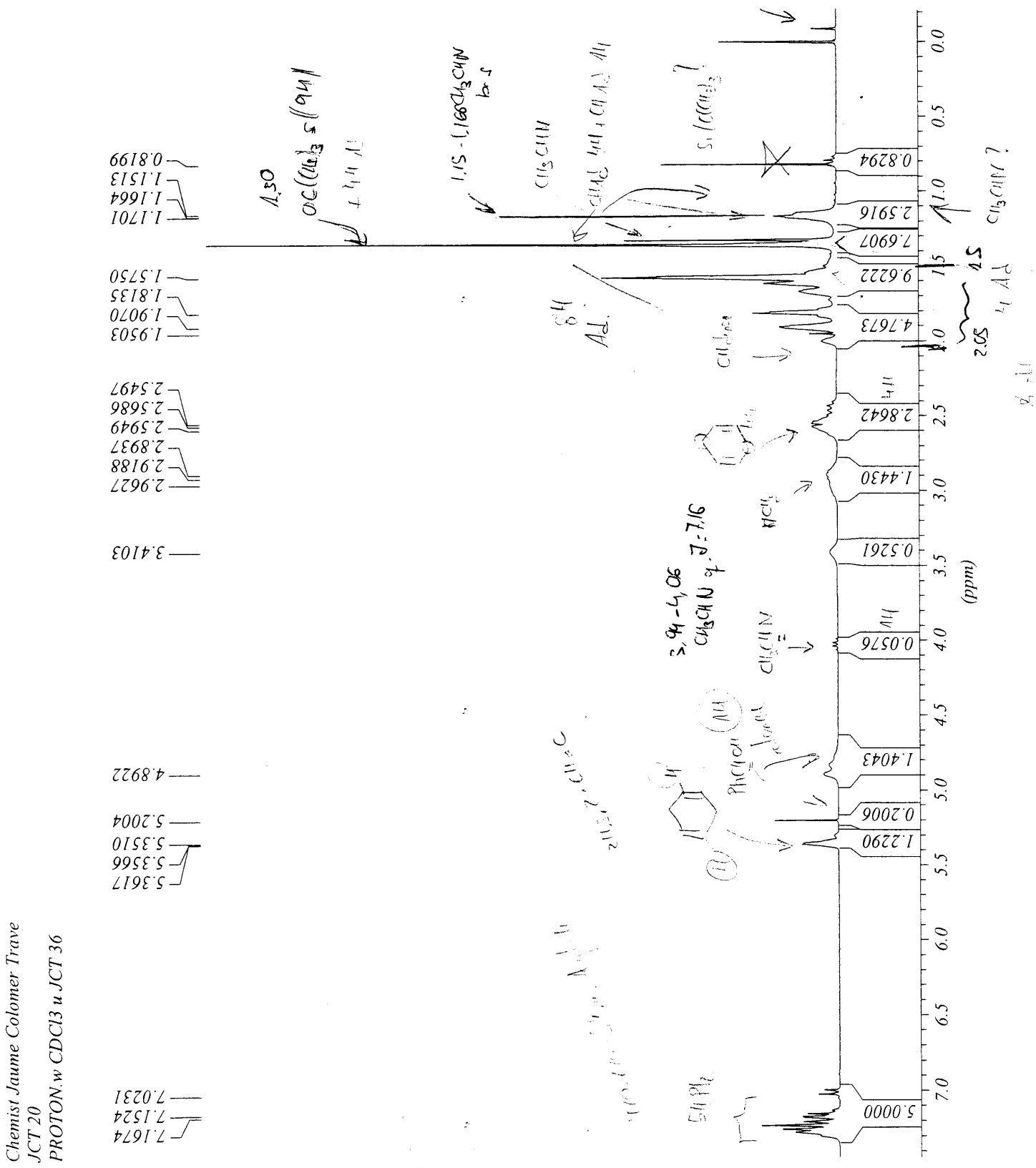
[(1*S*,2*R*)-2-(*tert*-butyldimethylsilanyloxy)-1-methyl-2-phenylethyl]-[3-(4-phenylcyclohexa-1,4-dienyl)-propyl]-carbamic acid *tert*-butyl carbamate 28d.



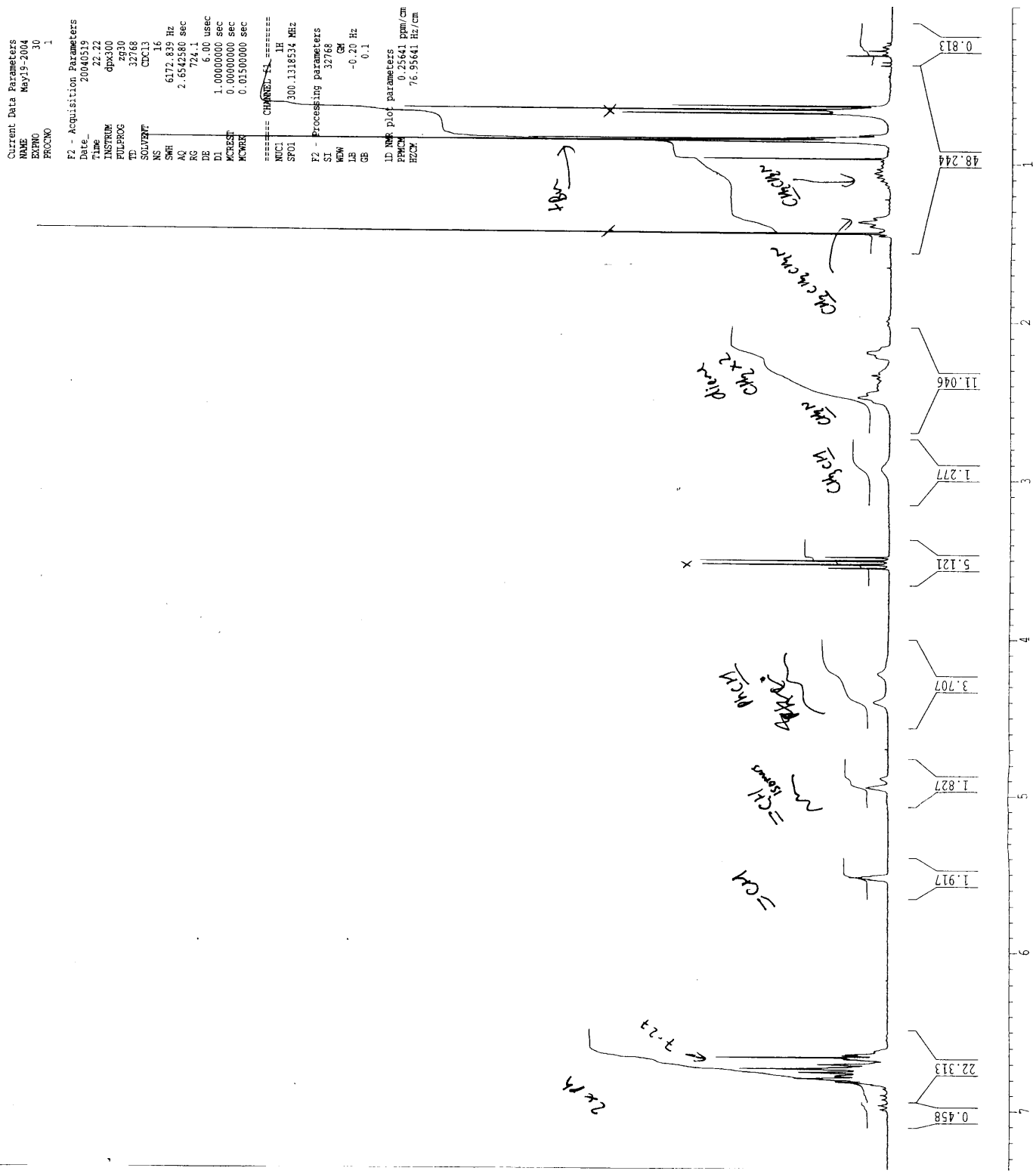
[3-(4-*tert*-butylcyclohexa-1,4-dienyl)-propyl]-((1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl)-carbamic acid *tert*-butyl carbamate.



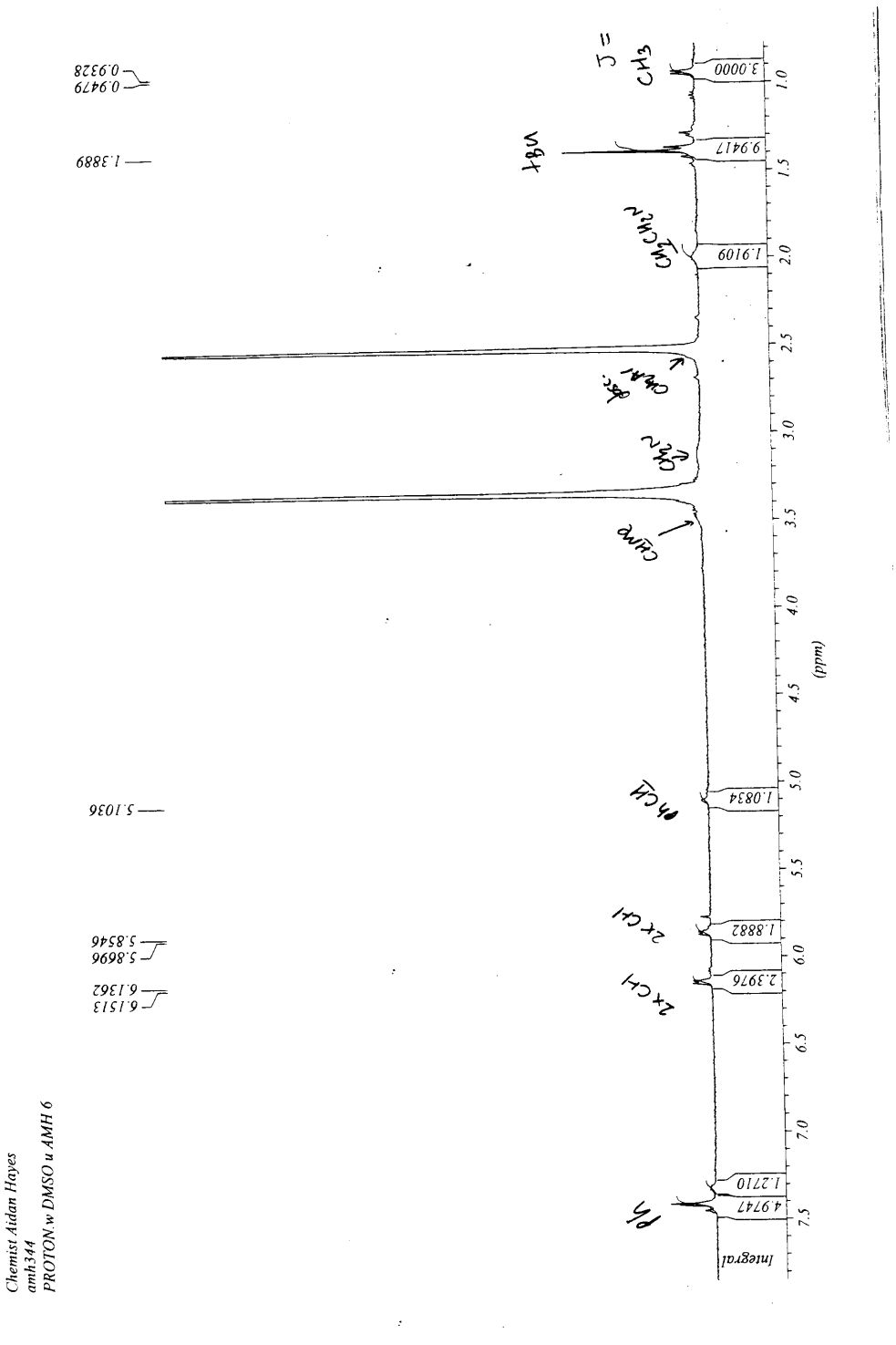
[3-(4-adamantan-1-yl-cyclohexa-1,4-dienyl)-propyl]-((1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl)-carbamic acid *tert*-butyl carbamate.



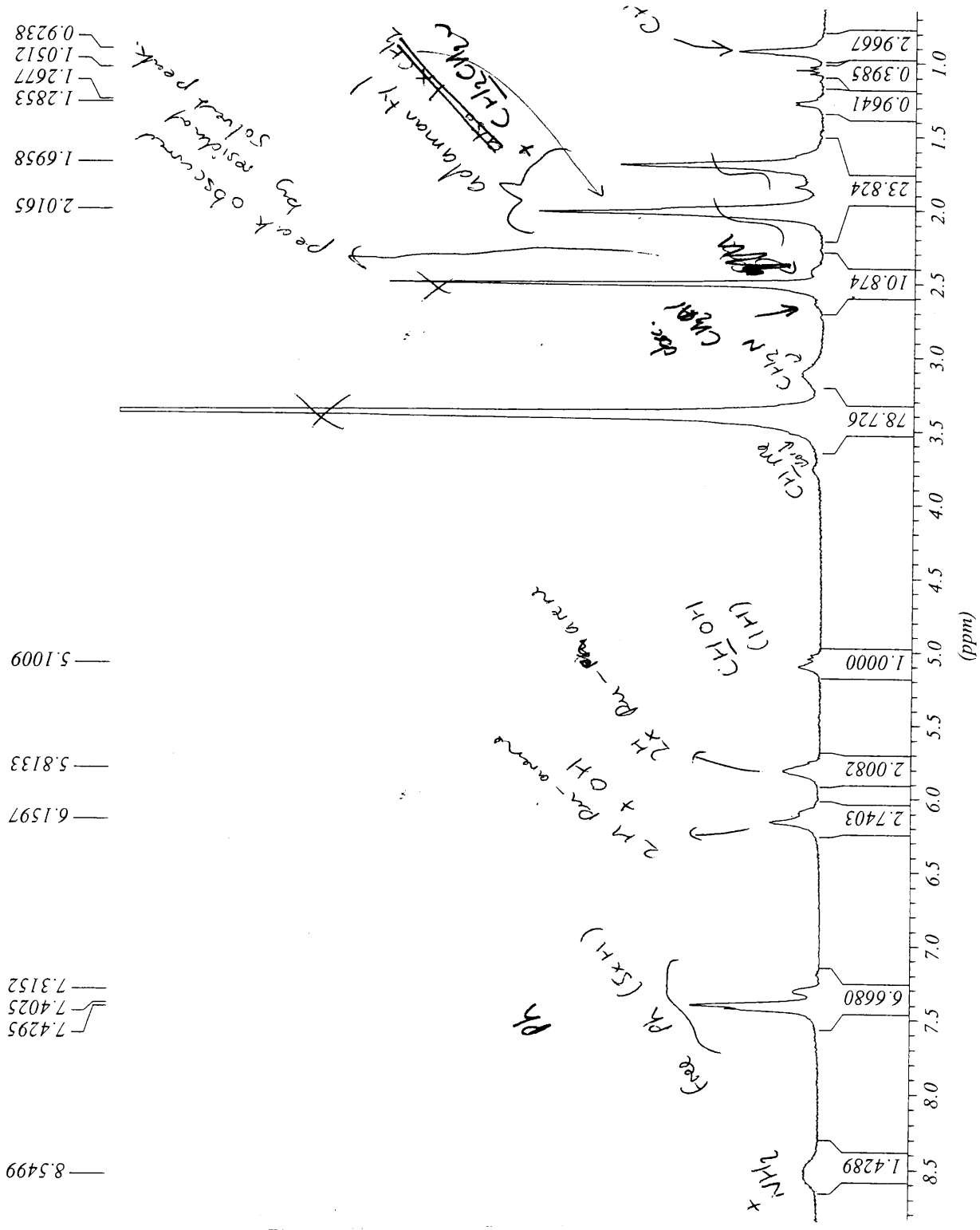
((1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl)-[3-(4-phenylcyclohexa-1,4-dienyl)-propyl]-carbamic acid *tert*-butyl carbamate.



(1*R*,2*S*)-2-[3-(4-*tert*-butylphenyl)-propylamino]-1-phenylpropan-1-ol ruthenium dimer 29b.



(1*R*,2*S*)-2-[3-(4-adamantan-1-yl-phenyl)-propylamino]-1-phenylpropan-1-ol ruthenium dimer 29c.



(1*R*,2*S*)-2-(3-biphenyl-4-yl-propylamino)-1-phenylpropan-1-ol ruthenium dimer

29d.