# Aminals as substrates for sulfur ylides: A synthesis of functionalised aziridines and *N*-heterocycles

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## Supplementary Information

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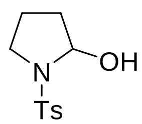
## General Methods

All chemicals were purchased from Aldrich, Fluka or Lancaster. Anhydrous THF, $CH_2Cl_2$ were obtained from a purification column composed of activated alumina (A-2). Chromatography: Flash chromatography was performed on silica gel (Merck Kieselgel 60 $F_{254}$ 230-400 mesh). TLC was performed on aluminum backed silica plates (0.2 mm, 60 $F_{254}$) which were developed using standard visualising agents: UV fluorescence (254 & 366 nm), phosphomolybdic acid / Δ, anisaldehyde / Δ, potassium permanganate / Δ. Melting points were determined on a Khofler hot stage apparatus. Infra red spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. Only selected absorbencies ($\nu_{max}$) are reported. $^1$H NMR spectra were recorded at either 270 or 400 MHz on Delta GX/270 or Delta GX/400 instruments respectively. Chemical shifts ($\delta_H$) are quoted in parts per million (ppm), referenced to TMS. $^{13}$C NMR spectra were recorded at either 68 or 100 MHz on Delta GX/270 or Delta GX/400 instruments respectively. Chemical shifts ($\delta_c$) are quoted in parts per million (ppm), referenced to the appropriate solvent peak and are assigned as s, d, t, q for C, CH, $CH_2$, $CH_3$ respectively. Low resolution mass spectra (m/z) were recorded on a Micromass Analytical Autospec spectrometer, with only molecular ions ($M^+$ or $MH^+$) and major peaks being reported with intensities quoted as percentages of the base peak. High-resolution mass spectra were recorded on a Micromass Analytical Autospec Spectrometer. All GC-MS experiments were performed using an Agilent

6890 apparatus and the following conditions: column: HP190915-433 HP-5MS 5% Phenyl Methyl Siloxane, capillary 30 m x 250 μm x 0.25 μm nominal, carrier gas: helium 1 mL/min (constant flow mode), injector: 250 $^{o}$C (split less mode), detector: agilent MSD 5973 (EI mode), Oven: 70 $^{o}$ C (3 min), 15 $^{o}$ C/min (15.3 min), 300 $^{o}$ C (8 min).

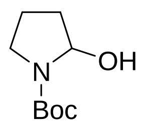
## Experimental procedures

**_N_-[(4-Methylphenyl)sulfonyl]pyrrolidin-2-ol**




For the synthesis see: Kokotos, C. G.; Aggarwal, V. K. *Chem. Comm.*, **2006**, 2156.

***tert*-Butyl 2-hydroxy-1-pyrrolidinecarboxylate**

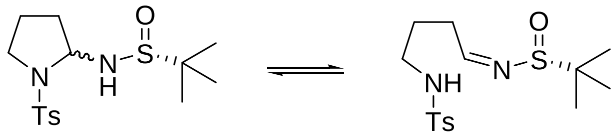



For the synthesis see: Dieter, R. K.; Sharma, R. R. *J. Org. Chem.*, **1996**, *61*, 4180.

**General procedure for chiral imine synthesis**

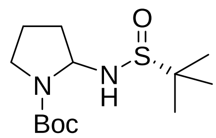
To a stirred solution of *N*-[(4-Methylphenyl)sulfonyl]pyrrolidin-2-ol or *tert*-Butyl 2-hydroxy-1-pyrrolidinecarboxylate (1 eq.) in $CH_2Cl_2$ (15 mL), $Ti(OEt)_4$ (20 % solution in ethanol) (2 eq.) was added under argon at room temperature. The solution was treated with (*R*)-2-methyl-2-propanesulfinamide (1.1 eq.) in one portion and the reaction mixture was then heated at reflux for 7 h under argon. The reaction mixture was allowed to cool to room temperature before quenching with an equal amount of brine (15 mL). The resulting slurry was then filtered through Celite, washed with an excess of $CH_2Cl_2$ (100 mL) and the filtrate partitioned between brine (80 mL) and $CH_2Cl_2$ (80 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 75 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was then purified by flash chromatography eluting with 1:1 EtOAc:pet. ether followed by EtOAc to give the product.

**(R)$_s$-N2-1-[(4-Methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide 4**[1]



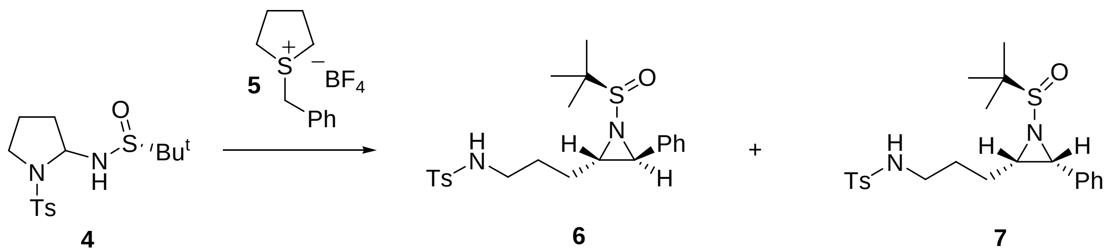
Colourless gum (81%) as a mixture of ring opened and ring closed form; $R_f$ (EtOAc:pet.ether, 1:1) 0.1/0.15/0.3; IR (film) 2957 (NH), 2925 (NH), 2870 (NH), 1597 (HC=N), 1335 (S=O), 1155 ($SO_2$), 1091 (S=O), 1033 (S=O) cm$^{-1}$; <u>open form</u> $\delta_H$ (400 MHz, $CDCl_3$) 8.01 (1H, t, *J* 4.0 Hz, N=CH), 7.72 (2H, d, *J* 8.3 Hz, Ar), 7.29 (2H, d, *J* 8.3 Hz, ArH), 4.74 (1H, t, *J* 6.3 Hz, NH), 3.04-2.97 (2H, m, $NCH_2$), 2.53 (2H, td, *J* 7.1 and 4.0 Hz, $CH_2C$=N), 2.42 (3H, s, $CH_3$) 1.81 (2H, m, $NCH_2CH_2$), 1.15 [9H, s, $C(CH_3)_3$]; <u>closed form two diastereomers (1:1)</u> $\delta_H$ (400 MHz, $CDCl_3$) 7.80-7.70 (4H, d, *J* 8.3 Hz, Ar), 7.33-7.27 (4H, d, *J* 8.3 Hz, ArH), 5.18 (1H, td, *J* 6.8 and 2.6 Hz, NCH), 5.05 (1H, dt, *J* 6.3 and 2.4 Hz, NCH), 4.16 (1H, d, *J* 2.4 Hz, NH), 3.89 (1H, d, *J* 6.8 Hz, NH), 3.59 (1H, ddd, *J* 10.3, 7.5 and 3.1 Hz, NC*H*H), 3.42 (1H, ddd, *J* 11.3, 6.2 and 2.5 Hz, NC*H*H), 3.15-3.07 (2H, m, 2 x NC*H*H), 2.72-2.55 (4H, m, 2 x $CH_2$CHN), 2.41 (6H, s, 2 x $CH_3$) 2.20-1.61 (4H, m, 2 x $CH_2CH_2$), 1.23 [9H, s, $C(CH_3)_3$], 1.23 [9H, s, $C(CH_3)_3$]; <u>ring-open and ring closed forms</u> $\delta_c$ (100.5 MHz, $CDCl_3$) 168.4 (d), 144.0 (s), 143.8 (s), 143.3 (s), 137.3 (s), 137.2 (s), 137.1 (s), 130.0 (d), 129.8 (d), 129.7 (d), 127.7 (d), 127.5 (d), 127.1 (d), 72.8 (d), 70.6 (d), 56.7 (s), 56.3 (s), 56.0 (s), 48.6 (t), 48.1 (t), 42.6 (t), 34.1 (t), 33.2 (t), 32.2 (t), 25.3 (t), 23.6 (t), 23.2 (t), 22.6 (q), 22.5 (q), 22.4 (q), 21.6 (q), 21.5 (q), 21.1 (q); MS (ESI) *m/z* (%) 367 (M+Na$^+$, 25%) and 345 (MH$^+$, 23%); HRMS (ESI) found 367.1121. $C_{15}H_{24}N_2O_3S_2Na$ requires 367.1115.

**(R)$_s$-2-(2-Methyl-propane-2-sulfinylamino)-pyrrolidine-1-carboxylic acid *tert*-butyl ester**



Colourless oil (39%); $R_f$ (EtOAc:pet.ether, 1:1) 0.05; IR (film) 2952 (NH), 1641 (OCONH), 1335 (S=O) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 5.20-5.16 (1H, m, NCH), 3.80-3.78 (1H, m, NH), 3.49-3.47 (1H, m, NC*H*H), 3.29-3.25 (1H, m, NCH*H*), 2.10-1.80 (4H, m, $CH_2CH_2$), 1.44 [9H, s, $C(CH_3)_3$], 1.18 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.7 (s), 83.2 (d), 79.9 (s), 56.7 (s), 45.2 (t), 28.4 (q), 28.3 (t), 22.4 (q), 22.3 (t). MS (CI) *m/z* (%) 291 ($MH^+$, 100%) and 186 ($MH^+$-SOBu$^t$, 45%); (Found: C, 53.92%; H, 8.89%; N, 9.43%. $C_{13}H_{26}N_2O_3S$ requires C, 53.76%; H, 9.02%; N, 9.65%); $[\alpha]_D^{23}$ –104 (*c* 1.0, $CH_2Cl_2$).

**Reaction of aminal 4 with achiral sulfonium salt 5**

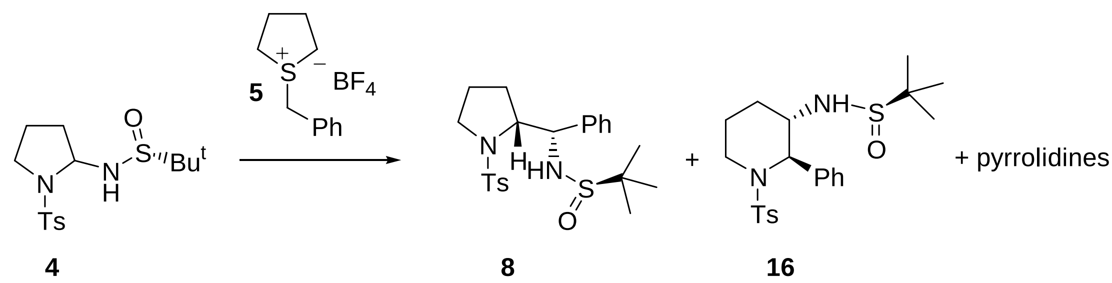


To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 °C was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-Benzyltetrahydrothiophenium tetrafluoroborate **5** (0.12 g, 0.44 mmol) was added at 0 °C followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was then stirred for 3.5 hours at 0 °C, diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

*(R)<sub>s</sub>-(2S)-(3R)*-4-methyl-*N*-{3-[3-phenyl-1-(propane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **(6)** (major trans) as a colourless oil (63 mg, 50%); $R_f$ (EtOAc:pet. ether, 1:1) 0.50; IR (film) 3063 (NH), 1599 (Ar), 1338 ($SO_2$), 1159 ($SO_2$), 1058 (SO) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.3 Hz, ArH), 7.31-7.25 (5H, m, ArH), 7.19 (2H, d, *J* 8.3 Hz, ArH), 5.24 (1H, t, *J* 6.1 Hz, NH), 3.11 (1H, d, *J* 3.9 Hz, NCHPh), 3.05-2.91 (2H, m, $NCH_2$), 2.51 (1H, td, *J* 6.4 and 3.9 Hz, C*H*NCHPh), 2.41 (3H, s, $CH_3$), 2.21-2.13 (1H, m, C*H*H$CH_2$), 2.04-1.96 (1H, m, CHHC*H*H), 1.79-1.63 (2H, m, C*H*HC*H*H), 1.19 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.3 (s), 143.2 (s), 136.8 (s), 129.7 (d), 128.7 (d), 128.0 (d), 127.2 (d), 126.3 (d), 57.1 (s), 50.2 (d), 46.1 (d), 42.5 (t), 28.2 (t), 25.8 (t), 22.3 (q), 21.4 (q); MS (CI): *m/z* (%) 435 ($MH^+$, 87%), 378 ($MH^+$-$Bu^t$, 17%) and 224 ($M^+$-$NSOBu^t$-$CH_2Ph$, 100%); HRMS (CI) found 435.1776. $C_{22}H_{30}N_2O_3S_2$ requires 435.1772 (Found: C, 61.02%; H, 6.73%; N, 6.21%. $C_{22}H_{30}N_2O_3S_2$ requires C, 60.80%; H, 6.96%; N, 6.45%); $[\alpha]_D^{23}$ -36 (*c* 1.0, $CH_2Cl_2$).

4-methyl-*N*-{3-[3-phenyl-1-(propane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **(6** minor**:7)** (minor *trans:cis* 5:1) as a colourless oil (32 mg, 27%); $R_f$ (EtOAc:pet. ether, 1:1) 0.55; IR (film) 3063 (NCH), 1599 (Ar), 1330 ($SO_2$), 1158 ($SO_2$), 1093 (SO) $cm^{-1}$; minor *trans* $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.3 Hz, ArH), 7.33-7.24 (7H, m, ArH), 4.87 (1H, t, *J* 6.2 Hz, NH), 3.33 (1H, d, *J* 3.9 Hz, NCHPh), 2.98 (2H, q, *J* 6.2 Hz, $NCH_2$), 2.43-2.34 (4H, m, $CH_3$ and C*H*NCHPh), 1.96-1.83 (1H, m, C*H*H$CH_2$), 1.82-1.60 (3H, m, C*HH*C*H*H), 1.12 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.4 (s), 143.2 (s), 137.6 (s), 129.8 (d), 128.0 (d), 128.6 (d), 127.2 (d), 127.1 (d), 57.4 (s), 50.9 (d), 47.4 (d), 42.8 (t), 28.3 (t), 25.9 (t), 22.8 (q), 21.5 (q); *cis* $\delta_H$ (400 MHz, $CDCl_3$) 7.70 (2H, d, *J* 8.3 Hz, ArH), 7.33-7.24 (5H, m, ArH), 7.17 (2H, d, *J* 8.3 Hz, ArH), 4.41 (1H, t, *J* 6.3 Hz, NH), 3.79 (1H, d, *J* 7.0 Hz, NCHPh), 2.88-2.77 (2H, m, $NCH_2$), 2.43-2.34 (4H, m, $CH_3$ and C*H*NCHPh), 1.96-1.83 (1H, m, C*H*H$CH_2$), 1.82-1.60 (3H, m, C*HH*C*H*H), 1.17 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.6 (s), 143.4 (s), 137.3 (s), 129.7 (d), 128.4 (d), 128.1 (d), 127.6 (d), 126.6 (d), 57.0 (s), 48.0 (d), 46.7 (d), 42.5 (t), 28.2 (t), 24.8 (t), 22.7 (q), 21.5 (q); MS (CI): *m/z* (%) 435 ($MH^+$, 67%), 330 ($MH^+$-$SOBu^t$, 15%) and 224 ($M^+$-$NSOBu^t$-$CH_2Ph$, 100%).

## Reaction of aminal 4 with achiral sulfonium salt 5 leading to pyrrolidines and piperidine

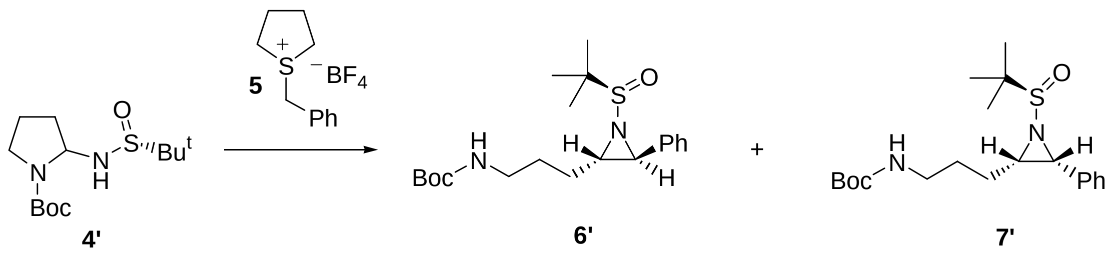


To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 $^{o}$C was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-Benzyltetrahydrothiophenium tetrafluoroborate **5** (0.12 g, 0.44 mmol) was added at 0 $^{o}$C followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was stirred for 5 hours at 0 $^{o}$C and then heated to reflux for 15 h. The reaction was diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

*(R)$_S$-(R)-α-(2R)*-2-Methylpropane-2-sulfinic acid {phenyl-[1-(toluene-4-sulfonyl)-pyrrolodin-2-yl]-methyl}amide **(8)** (major) as a white solid (58 mg, 46%) mp 72-75 °C (pet. ether); $R_f$ (EtOAc:pet. ether, 1:1) 0.30; IR (film) 1599 (Ar), 1341 ($SO_2$), 1159 ($SO_2$), 1058 (SO) cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.78 (2H, d, *J* 8.3 Hz, ArH), 7.43-7.21 (7H, m, ArH), 5.55 (1H, d, *J* 3.5 Hz, NH), 4.44 [1H, t (ap), *J* 3.5 Hz, NCHPh], 4.20 (1H, m, NC*H*CHPh), 3.09 (1H, dt, *J* 10.9 and 7.4 Hz, NC*H*H), 2.80 (1H, ddd, *J* 10.9, 7.4 and 5.7 Hz, NC*H*H), 2.41 (3H, s, $CH_3$), 1.79-1.71 (1H, m, C*H*H$CH_2$), 1.63-1.58 (1H, m, CHHC*H*H), 1.56-1.42 (2H, m, C*H*HC*H*H), 1.24 [9H, s, C($CH_3$)$_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.9 (s), 138.8 (s), 134.1 (s), 129.7 (d), 128.6 (d), 128.0 (d), 127.3 (d), 127.0 (d), 65.0 (d), 61.8 (d), 55.9 (s), 50.1 (t), 29.1 (t), 22.8 (t), 22.7 (q), 21.5 (q); MS (CI): *m*/*z* (%) 435 ($MH^+$, 85%) and 224 ($M^+$-NSOBu$^t$-$CH_2$Ph, 100%); HRMS (CI) found 435.1776. $C_{22}H_{30}N_2O_3S_2$ requires 435.1772; $[\alpha]_D^{23}$ -76 (*c* 1.0, $CH_2Cl_2$).

*(2S)-(3S)*-2-Methylpropane-2-sulfinic acid [2-phenyl-1-(toluene-4-sulfonyl)-piperidin-3-yl]-amide **(16)** as a white solid (15 mg, 12%) mp 79-82 °C (pet. ether); $R_f$ (EtOAc:pet. ether, 1:1) 0.25; IR (film) 1599 (Ar), 1326 ($SO_2$), 1159 ($SO_2$), 1058 (SO) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (2H, d, *J* 8.3 Hz, ArH), 7.30-7.19 (5H, m, ArH), 7.04 (2H, d, *J* 8.3 Hz, ArH), 5.21 (1H, br s, NCHPh), 4.17 (1H, d, *J* 8.2 Hz, NH), 3.84 (1H, ddd, *J* 9.8, 8.2 and 2.0 Hz, NHC*H*CHPh), 3.05 (1H, td, *J* 13.1 and 2.5 Hz, NC*H*H), 2.87 (1H, dt, *J* 13.1 and 6.9 Hz, NC*H*H), 2.41 (3H, s, $CH_3$), 1.92-1.75 (3H, m, C*H*HC*H₂*), 1.64-1.52 (1H, m, CHHC*H*H), 1.24 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.3 (s), 138.2 (s), 136.5 (s), 129.8 (d), 128.8 (d), 127.4 (d), 127.0 (d), 126.8 (d), 61.2 (d), 59.1 (d), 56.0 (s), 50.6 (t), 24.3 (t), 23.8 (t), 22.8 (q), 21.5 (q); MS (CI): *m/z* (%) 435 ($MH^+$, 89%) and 224 ($M^+$-$NSOBu^t$-$CH_2Ph$, 100%); HRMS (CI) found 435.1776. $C_{22}H_{30}N_2O_3S_2$ requires 435.1769; $[\alpha]_D^{23}$ -32 (*c* 1.0, $CH_2Cl_2$).

**Reaction of Boc aminal 4' with achiral sulfonium salt 5**

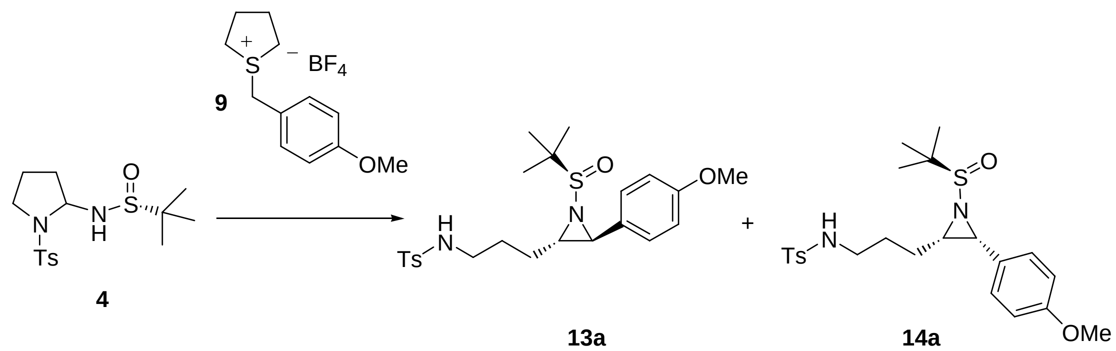



To a solution of 2-(2-methylpropane-2-sulfinylamino)-pyrrolidine-1-carboxylic acid *tert*-butyl ester **4'** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 °C was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-Benzyltetrahydrothiophenium tetrafluoroborate **5** (0.12 g, 0.44 mmol) was added at 0 °C followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was stirred for 3.5 hours at 0 °C, diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were washed with brine (20 mL), and dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

{3-[1-(2-Methylpropane-2-sulfinyl)-3-phenylaziridin-2-yl]-propyl}-carbamic acid *tert*-butyl ester **(6':7')** (*trans:cis*) as a colourless oil (15:1) (23 mg, 39%); $R_f$ (EtOAc:pet. ether, 1:1) 0.25; IR (film) 3350 (NH), 2926 (Me), 1693 (OCONH), 1056

(SO) $cm^{-1}$; <u>*trans*</u> $\delta_H$ (400 MHz, $CDCl_3$) 7.38-7.21 (5H, m, ArH), 4.61 (1H, br s, NH), 3.42 (1H, d, *J* 3.9 Hz, NCHPh), 3.22-3.12 (2H, m, $NCH_2$), 2.97-2.93 (1H, br m, C*H*NCHPh), 2.00-1.95 (1H, m, C*H*$HCH_2$), 1.83-1.62 (3H, m, C*HH*C*H*H), 1.43 [9H, s, $C(CH_3)_3$], 1.11 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.3 (s), 132.5 (s), 129.0 (d), 128.7 (d), 125.6 (d), 82.3 (s), 58.6 (s), 48.5 (d), 44.7 (d), 40.5 (t), 31.0 (t), 28.5 (q), 24.8 (t), 22.8 (q); <u>*cis*</u> $\delta_H$ (400 MHz, $CDCl_3$) 7.38-7.21 (5H, m, ArH), 4.32 (1H, br s, NH), 3.84 (1H, d, *J* 7.0 Hz, NCHPh), 3.12-2.98 (2H, m, $NCH_2$), 2.47-2.41 (1H, br m, C*H*NCHPh), 2.00-1.95 (1H, m, C*H*$HCH_2$), 1.83-1.62 (3H, m, C*HH*C*H*H), 1.45 [9H, s, $C(CH_3)_3$], 1.19 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.3 (s), 132.5 (s), 129.0 (d), 128.7 (d), 125.6 (d), 82.4 (s), 57.4 (s), 40.5 (t), 38.7 (d), 36.5 (d), 31.0 (t), 28.5 (q), 24.8 (t), 22.8 (q); MS (CI): *m/z* (%) 381 ($MH^+$, 100); HRMS (CI) found 381.2212. $C_{20}H_{33}N_2O_3S$ requires 381.2210..

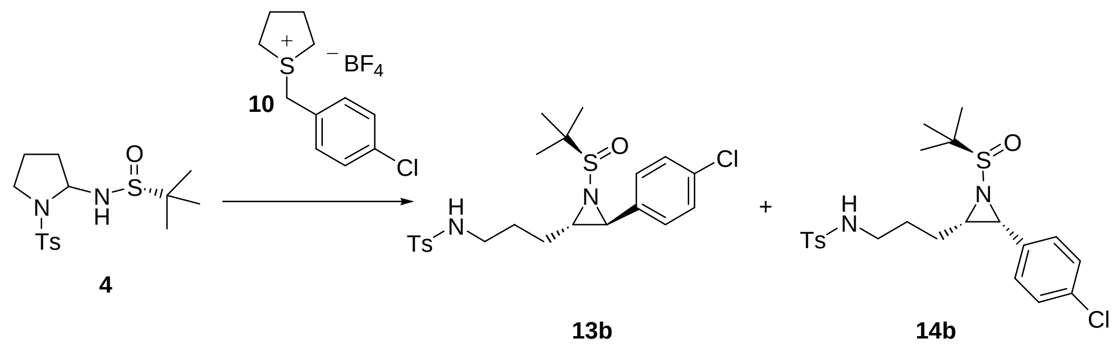
**Reaction of aminal 4 with achiral sulfonium salt 9**




To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 °C was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-4-Methoxybenzyltetrahydrothiophenium tetrafluoroborate **9** (0.13 g, 0.44 mmol) was added at 0 °C followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was then stirred for 3.5 hours at 0 °C, diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were washed with brine (20 mL), and dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

*N*-{3-[3-(4-Methoxyphenyl)-1-(2-methylpropane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **(13a** major**:13a** minor**:14a)** (major *trans*: minor *trans*:*cis*) as a colourless oil (2.9:1.6:1) (58 mg, 43%); $R_f$ (EtOAc:pet. ether, 1:1) 0.45; IR (film), 2868 (O-Me), 1598 (Ar), 1327 ($SO_2$), 1155 ($SO_2$), 1092 (SO), 813 (*p*-substitution) $cm^{-1}$; major *trans* $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.6 Hz, ArH), 7.31 (2H, d, *J* 8.4 Hz, ArH), 7.29 (2H, d, *J* 8.4 Hz, ArH), 6.85 (2H, d, *J* 8.6 Hz, ArH), 5.42 (1H, dd, *J* 5.5 and 1.6 Hz, NH), 3.80 (3H, s, $OCH_3$), 3.31 (1H, d, *J* 3.9 Hz, NCHPh), 3.10-3.01 (1H, m, NC*H*H), 2.99-2.93 (1H, m, NC*H*H), 2.89-2.85 (1H, m, C*H*NCHPh), 2.41 (3H, s, $CH_3$), 1.93-1.87 (1H, m, C*H*H$CH_2$), 1.80-1.63 (3H, m, C*HH*C*H*H), 1.12 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.2 (s), 143.4 (s), 136.2 (s), 132.0 (s), 129.8 (d), 129.7 (d), 127.6 (d), 127.1 (d), 83.9 (q), 57.9 (s), 56.2 (d), 47.9 (d), 42.5 (t), 34.4 (t), 24.6 (t), 22.3 (q), 21.5 (q); minor *trans* $\delta_H$ (400 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.8 Hz, ArH), 7.62 (2H, d, *J* 8.3 Hz, ArH), 7.30 (2H, d, *J* 8.3 Hz, ArH), 7.15 (2H, d, *J* 8.8 Hz, ArH), 4.83 (1H, br m, NH), 3.83 (3H, s, $OCH_3$), 3.35 (1H, d, *J* 4.0 Hz, NCHPh), 3.10-3.01 (1H, m, NC*H*H), 2.99-2.93 (1H, m, NC*H*H), 2.41-2.35 (4H, m, $CH_3$ and NC*H*$CH_2$), 1.93-1.87 (1H, m, C*H*H$CH_2$), 1.80-1.63 (3H, m, C*HH*C*H*H), 1.12 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.2 (s), 143.4 (s), 136.2 (s), 132.0 (s), 129.8 (d), 129.7 (d), 127.6 (d), 127.1 (d), 83.9 (q), 57.9 (s), 53.3 (d), 47.4 (d), 42.5 (t), 34.4 (t), 24.6 (t), 22.3 (q), 21.5 (q); *cis* $\delta_H$ (400 MHz, $CDCl_3$) 7.84 (2H, d, *J* 8.3 Hz, ArH), 7.69 (2H, d, *J* 8.4 Hz, ArH), 7.17 (2H, d, *J* 8.4 Hz, ArH), 6.99 (2H, d, *J* 8.3 Hz, ArH), 4.80 (1H, t, *J* 6.2 Hz, NH), 3.81 (3H, s, $OCH_3$), 3.75 (1H, d, *J* 6.9 Hz, NCHPh), 3.10-3.01 (1H, m, NC*H*H), 2.99-2.93 (1H, m, NC*H*H), 2.71-2.63 (1H, m, C*H*NCHPh), 2.41 (3H, s, $CH_3$), 1.93-1.87 (1H, m, C*H*H$CH_2$), 1.80-1.63 (3H, m, C*HH*C*H*H), 1.12 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 154.2 (s), 143.4 (s), 136.2 (s), 132.0 (s), 129.8 (d), 129.7 (d), 127.6 (d), 127.1 (d), 83.8 (q), 54.2 (s), 44.2 (d), 43.4 (d), 42.5 (t), 28.1 (t), 24.6 (t), 22.3 (q), 21.5 (q); MS (ESI): *m/z* (%) 487 ($M+Na^+$, 28%), 465 ($MH^+$, 49%) and 391 ($M^+$-$Bu^t$-O, 100%); HRMS (ESI) found 487.1695. $C_{23}H_{32}N_2O_4S_2Na$ requires 487.1696.

**Reaction of aminal 4 with achiral sulfonium salt 10**

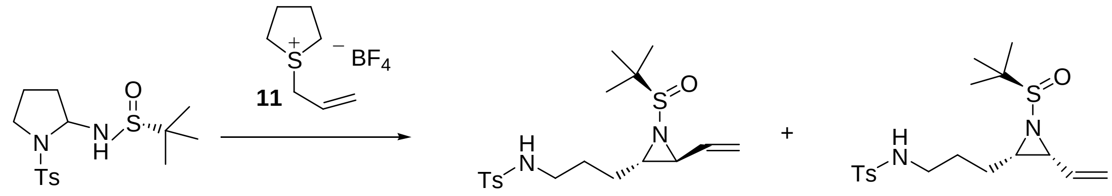


To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 $^{o}$C was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-4-Chlorobenzyltetrahydrothiophenium tetrafluoroborate **11** (0.13 g, 0.44 mmol) was added at 0 $^{o}$C followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was stirred for 3.5 hours at 0 $^{o}$C, diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (3 × 20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were washed with brine (20 mL), and dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

*(R)$_S$-(2S)-(3R)-N-*{3-[3-(4-Chlorophenyl)-1-(2-methylpropane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **(13b)** as a white solid (60 mg, 50%) mp 59-61 °C (pet. ether); $R_f$ (EtOAc:pet. ether, 1:1) 0.35; IR (film), 1598 (Ar), 1327 ($SO_2$), 1158 ($SO_2$), 1089 (SO), 815 (*p*-substitution), 663 (C-Cl) cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.3 Hz, ArH), 7.33-7.26 (4H, m, ArH), 7.12 (2H, d, *J* 8.3 Hz, ArH), 5.28 (1H, t, *J* 6.2 Hz, NH), 3.11 (1H, d, *J* 3.9 Hz, NCHPh), 3.01-2.89 (2H, m, $NCH_2$), 2.47 (1H, td, *J* 6.4 and 3.9 Hz, C*H*NCHPh), 2.41 (3H, s, $CH_3$), 2.21-2.13 (1H, m, C*H*H$CH_2$), 2.04-1.95 (1H, m, CHHC*H*H), 1.83-1.63 (2H, m, C*H*HC*H*H), 1.19 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.3 (s), 137.0 (s), 135.4 (s), 133.9 (s), 129.8 (d), 128.9 (d), 127.6 (d), 127.2 (d), 57.2 (s), 50.3 (d), 45.5 (d), 42.4 (t), 28.0 (t), 25.6 (t), 22.3 (q), 21.6 (q); MS (ESI): *m*/*z* (%) 491 (M + $Na^+$, 17%) and 469 ($MH^+$, 100%); HRMS (ESI) found 469.1384 $C_{22}H_{29}N_2O_3S_2Cl$ requires 469.1380 (Found: C, 56.68%; H, 6.00%; N, 5.74%. $C_{22}H_{29}N_2O_3S_2Cl$ requires C, 56.33%; H, 6.23%; N, 5.97%); $[\alpha]_D^{23}$ -133 (*c* 0.75, $CH_2Cl_2$).

*N*-{3-[3-(4-Chlorophenyl)-1-(2-methylpropane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **(13b** minor**:14b)** (*trans:cis*) as a colourless oil (2:1) (19 mg, 16%); $R_f$ (EtOAc:pet. ether, 1:1) 0.50; IR (film), 1599 (Ar), 1329 ($SO_2$), 1161 ($SO_2$), 1091 (SO), 815 (*p*-substitution), 661 (C-Cl) $cm^{-1}$; *trans* $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.3 Hz, ArH), 7.33-7.26 (4H, m, ArH), 7.12 (2H, d, *J* 8.3 Hz, ArH), 4.86 (1H, t, *J* 6.2 Hz, NH), 3.34 (1H, d, *J* 3.7 Hz, NCHPh), 2.99-2.93 (2H, m, $NCH_2$), 2.41-2.35 (4H, m, $CH_3$ and NC*H*$CH_2$), 1.94-1.88 (1H, m, C*H*H$CH_2$), 1.71-1.68 (3H, m, C*HH*C*H*H), 1.19 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.5 (s), 136.9 (s), 135.4 (s), 132.5 (s), 129.8 (d), 128.9 (d), 127.6 (d), 127.2 (d), 57.7 (s), 48.2 (d), 42.7 (d), 42.6 (t), 28.1 (t), 25.2 (t), 22.3 (q), 21.6 (q); *cis* $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (2H, d, *J* 8.3 Hz, ArH), 7.33-7.26 (4H, m, ArH), 7.19 (2H, d, *J* 8.3 Hz, ArH), 4.52 (1H, t, *J* 6.3 Hz, NH), 3.75 (1H, d, *J* 7.0 Hz, NCHPh), 2.87-2.79 (2H, m, $NCH_2$), 2.41-2.35 (4H, m, $CH_3$ and NC*H*$CH_2$), 1.94-1.88 (1H, m, C*H*H$CH_2$), 1.71-1.68 (3H, m, C*HH*C*H*H), 1.19 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.5 (s), 136.9 (s), 135.4 (s), 132.5 (s), 129.8 (d), 128.9 (d), 127.6 (d), 127.2 (d), 58.1 (s), 48.0 (d), 42.6 (t), 39.9 (d), 28.0 (t), 25.2 (t), 22.3 (q), 21.6 (q); MS (CI): *m/z* (%) 469 ($MH^+$, 62%) and 224 ($M^+$-NHSOBu$^t$-CHPhCl, 100%); HRMS (CI) found 469.1385 $C_{22}H_{29}N_2O_3S_2Cl$ requires 469.1380.

## Reaction of aminal 4 with achiral sulfonium salt 11




**4** **13c** **14c**

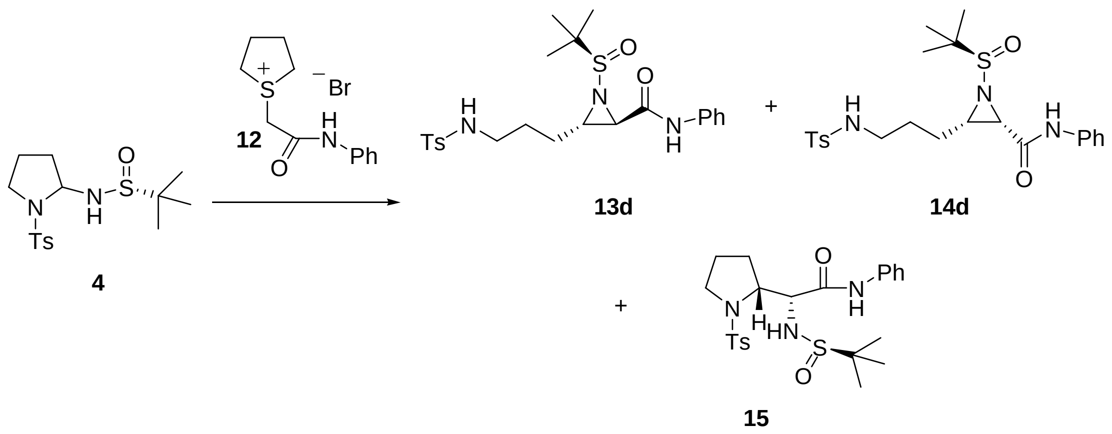
To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 $^oC$ was added $P_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-Allyltetrahydrothiophenium tetrafluoroborate **12** (0.09 g, 0.44 mmol) was added at 0 $^oC$ followed by $P_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was then stirred for 3.5 hours at 0 $^oC$, diluted with $CH_2Cl_2$ (20 mL) and $H_2O$ (20 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were dried ($MgSO_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give:

*(R)$_S$-(2S)-(3R)*-4-methyl-*N*-{3-[1-(2-methyl-propane-2-sulfinyl)-3-vinyl-aziridin-2-yl]-propyl}-benzenesulfonamide **(13c)** as a colourless oil (45 mg, 41%); $R_f$ (EtOAc:pet. ether, 1:1) 0.45; IR (film) 3054 (NH), 1161 ($SO_2$), 1093 (SO), 903 (C=$CH_2$), 896 (C=$CH_2$) cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.79 (2H, d, *J* 8.3 Hz, ArH), 7.32 (2H, d, *J* 8.3 Hz, ArH), 5.79 (1H, ddd, *J* 17.1, 10.2 and 7.9 Hz, C*H*=$CH_2$), 5.38 (1H, d, *J* 17.1 Hz, CH=C*H*H), 5.20 (1H, d, *J* 10.2 Hz, CH=C*H*H), 4.81 (1H, t, *J* 6.2 Hz, NH), 3.05-2.97 (2H, m, $NCH_2$), 2.78 (1H, dd, *J* 7.9 and 3.9 Hz, NC*H*C=C), 2.41-2.35 (4H, m, $CH_3$ and NC*H*$CH_2$), 1.77-1.58 (4H, m, $CH_2CH_2$), 1.23 [9H, s, C$(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 149.7 (d), 143.5 (s), 135.8 (s), 129.8 (d), 127.2 (d), 120.2 (t), 57.4 (s), 50.2 (d), 42.7 (t), 41.9 (d), 28.8 (t), 26.2 (t), 22.6 (q), 21.6 (q); MS (CI): *m/z* (%) 385 ($MH^+$, 59%) and 224 ($M^+$-HNSOBu$^t$-CHCH=$CH_2$, 100%); HRMS (CI) found 385.1619. $C_{18}H_{28}N_2O_3S_2$ requires 385.1613; $[\alpha]_D^{23}$ -160 (*c* 0.1, $CH_2Cl_2$).

*(R)$_S$-(2S)-(3S)*-4-methyl-*N*-{3-[1-(2-methyl-propane-2-sulfinyl)-3-vinyl-aziridin-2-yl]-propyl}-benzenesulfonamide **(14c)** as a colourless oil ( always obtained as a mixture with *trans*) (35 mg, 32%); $R_f$ (EtOAc:pet. ether, 1:1) 0.50; IR (film) 1163 ($SO_2$), 903

(C=CH$_2$), 896 (C=CH$_2$) cm$^{-1}$; $\delta_H$ (400 MHz, CDCl$_3$) 7.73 (2H, d, *J* 8.3 Hz, ArH), 7.27 (2H, d, *J* 8.3 Hz, ArH), 5.79 (1H, ddd, *J* 17.2, 10.3 and 7.4 Hz, C*H*=CH$_2$), 5.37 (1H, d, *J* 17.2 Hz, CH=C*H*H), 5.31 (1H, d, *J* 10.3 Hz, CH=C*H*H), 4.68 (1H, t, *J* 6.3 Hz, NH), 3.16 (1H, t, J 7.4 Hz, NCHC=C), 3.01-2.92 (2H, m, NCH$_2$), 2.41 (3H, s, CH$_3$), 2.20 (1H, td, *J* 7.4 and 5.5 Hz, NC*H*CH$_2$), 1.62-1.42 (4H, m, CH$_2$CH$_2$), 1.17 [9H, s, C(CH$_3$)$_3$]; $\delta_c$ (100.5 MHz, CDCl$_3$) 143.4 (d), 135.9 (s), 131.5 (s), 129.8 (d), 127.1 (d), 120.9 (t), 56.8 (s), 42.6 (t), 38.6 (d), 35.9 (d), 27.2 (t), 24.3 (t), 22.7 (q), 21.5 (q); MS (ESI): *m*/*z* (%) 407 (M+ Na$^+$, 42%) and 385 (MH$^+$, 100%); HRMS (ESI) found 407.1435. $C_{18}H_{28}N_2O_3S_2Na$ requires 407.1434.

**Reaction of sulfinylimine 4 with achiral sulfonium salt 12**

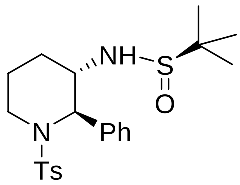



To a solution of *N*2-1-[(4-methylphenyl)sulfonyl]tetrahydro-1H-2-pyrrolyl-2-methyl-2-propanesulfinamide **4** (0.10 g, 0.29 mmol) in THF (4 mL) at 0 °C was added P$_2$ base (0.10 mL, 0.3 mmol) and the reaction mixture was left stirring for 30 min. 1-Phenylcarbamoylmethyltetrahydrothiophenium bromide **12** (0.13 g, 0.44 mmol) was added at 0 °C followed by P$_2$ base (0.10 mL, 0.3 mmol). The reaction mixture was stirred for 3.5 hours at 0 °C. If the reaction is stopped and quenched, a mixture of all three compounds is obtained (aziridines 63% 1:4 *trans:cis* and 29% pyrrolidine **15**). The reaction was diluted with CH$_2$Cl$_2$ (20 mL) and H$_2$O (20 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic layers were washed with brine (20 mL), and dried (MgSO$_4$). The solvents were removed in vacuo and the resultant residue was purified by column chromatography, eluting with 1:1 pet. ether:EtOAc.

1-(2-Methyl-propane-2-sulfinyl)-3-[3-(toluene-4-sulfonylamino)propyl]-aziridine-2-carboxylic acid phenylamide **(13d:14d)** (trans:cis) (1:4) as a colourless oil (87 mg, 63%); $R_f$ (EtOAc:pet. ether, 1:1) 0.30; IR (film) 3055 (NH), 1693 (NHCO), 1600 (Ar), 1526 (NHCO), 1327 ($SO_2$), 1160 ($SO_2$), 1027 (SO) $cm^{-1}$; *trans* $\delta_H$ (400 MHz, $CDCl_3$) 8.66 (1H, s, NHCO), 7.73 (2H, d, *J* 8.3 Hz, ArH), 7.50 (2H, dd, *J* 7.8 and 1.6 Hz, ArH), 7.35-7.21 (4H, m, ArH), 7.07 (1H, tt, *J* 7.8 and 1.6 Hz, ArH), 5.25 (1H, t, *J* 6.3 Hz, NH), 3.23 (1H, d, *J* 3.7 Hz, NCHCO), 3.02-2.91 (2H, m, $NCH_2$), 2.82 (1H, ddd, *J* 6.9, 5.5 and 3.7 Hz, C*H*NCHCO), 2.39 (3H, s, $CH_3$), 1.91-1.82 (1H, m, C*H*$HCH_2$), 1.78-1.69 (3H, m, C*HH*C*H*H), 1.30 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 165.1 (s), 143.5 (s), 137.2 (s), 136.9 (s), 129.8 (d), 129.2 (d), 127.1 (d), 124.9 (d), 119.9 (d), 57.6 (s), 46.1 (d), 44.0 (d), 42.3 (t), 27.4 (t), 24.4 (t), 22.5 (q), 21.6 (q); *cis* $\delta_H$ (400 MHz, $CDCl_3$) 8.36 (1H, s, NHCO), 7.68 (2H, d, *J* 8.3 Hz, ArH), 7.56 (2H, dd, *J* 8.6 and 1.1 Hz, ArH), 7.33 (2H, t , *J* 8.6 Hz, ArH), 7.24 (2H, d, *J* 8.3 Hz, ArH), 7.14 (1H, tt, *J* 8.6 and 1.1 Hz, ArH), 5.08 (1H, t, *J* 6.3 Hz, NH), 3.42 (1H, d, *J* 7.3 Hz, NCHCO), 3.08-2.95 (2H, m, $NCH_2$), 2.43 (1H, ddd, *J* 7.3, 6.8 and 4.9 Hz, C*H*NCHCO), 2.39 (3H, s, $CH_3$), 1.75-1.63 (4H, m, C*HH*C*H*H), 1.28 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 164.5 (s), 143.5 (s), 137.0 (s), 136.9 (s), 129.8 (d), 129.2 (d), 127.1 (d), 125.0 (d), 119.9 (d), 57.6 (s), 42.3 (t), 39.5 (d), 35.8 (d), 27.2 (t), 23.9 (t), 22.6 (q), 21.6 (q); MS (CI): *m/z* (%) 478 ($MH^+$, 20%), 253 ($MH^+$-$TsNHCH_2CH_2CH_2CH$, 48%), 224 ($M^+$-$HNSOBu^t$-CHCONHPh, 71%) and 57 ($Bu^{t+}$, 100%); *cis* isomer: HRMS (CI) found 478.1834 $C_{23}H_{31}N_3O_4S_2$ requires 478.1833; $[\alpha]_D^{23}$ -110 (*c* 0.1, $CH_2Cl_2$).

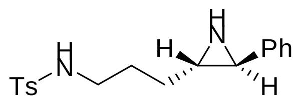
If the reaction is left stirring for 2 more days, then a mixture of *cis* aziridine **14d** and pyrrolidine **15** is obtained (*cis* aziridine 45% and 47% pyrrolidine **15**): *(R)$_S$-(R)-α-(2R)*-2-(2-Methyl-propane-2-sulfinylamino)-N_phenyl-2-[1-(toluene-4-sulfonyl)-pyrrolodon-2-yl]-acetamide **(15)** as a yellow oil (65 mg, 47%); $R_f$ (EtOAc:pet. ether, 1:1) 0.30; IR (film) 3055 (NH), 1693 (NHCO), 1600 (Ar), 1526 (NHCO), 1327 ($SO_2$), 1160 ($SO_2$), 1027 (SO) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 8.53 (1H, s, NHCO), 7.73 (2H, d, *J* 8.3 Hz, ArH), 7.50 (2H, dd, *J* 7.8 and 1.6 Hz, ArH), 7.35-7.21 (4H, m, ArH), 7.14 (1H, tt, *J* 7.8 and 1.6 Hz, ArH), 5.84 (1H, d, *J* 6.4 Hz, NH), 4.20 (1H, dd, *J* 6.4 and 2.1 Hz, NCHCO), 3.41-3.27 (2H, m, $NCH_2$), 2.45-2.41 (4H, m, NC*H*CHCO and $CH_3$), 1.91-1.69 (4H, m, $CH_2CH_2$), 1.39 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 168.2 (s), 144.4 (s), 137.3 (s), 133.7 (s), 129.8 (d), 129.0 (d), 127.8 (d), 124.7 (d), 119.7 (d), 64.7 (d), 62.9 (d), 56.7 (s), 51.3 (t), 30.1 (t), 26.0 (t), 22.9 (q), 21.7 (q); MS (CI): *m*/*z* (%) 478 ($MH^+$, 20%), 253 ($MH^+$-$TsNHCH_2CH_2CH_2CH$, 48%), 224 ($M^+$-$HNSOBu^t$-CHCONHPh, 71%) and 57 ($Bu^{t+}$, 100%). HRMS (CI) found 478.1838 $C_{23}H_{31}N_3O_4S_2$ requires 478.1833; $[\alpha]_D^{23}$ -40 (*c* 1.0, $CH_2Cl_2$).

## (*R*)$_s$-(2*S*)-(3*S*)-2-Methylpropane-2-sulfinic acid [2-phenyl-1-(toluene-4-sulfonyl)-piperidin-3-yl]-amide (16)



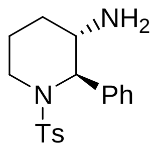

To a solution of 4-methyl-*N*-{3-[3-phenyl-1-(propane-2-sulfinyl)-aziridin-2-yl]propyl}benzenesulfonamide **7** (30 mg, 0.07 mmol) in $CH_2Cl_2$ (2 mL) at room temperature was added $Yb(OTf)_3$ (50 mg, 0.02 mmol). After 48 h the reaction was diluted with $CH_2Cl_2$ (10 mL) and $H_2O$ (10 mL). The aqueous layer was washed with $CH_2Cl_2$ (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$) and the solvents were removed in vacuo. The crude product purified by column chromatography, eluting with 1:1 pet. ether:EtOAc to give the product as a white solid (25 mg, 93%) mp 79-82 °C (pet. ether); $R_f$ (EtOAc:pet. ether, 1:1) 0.25; IR (film) 1599 (Ar), 1326 ($SO_2$), 1159 ($SO_2$), 1058 (SO) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 (2H, d, *J* 8.3 Hz, ArH), 7.30-7.19 (5H, m, ArH), 7.04 (2H, d, *J* 8.3 Hz, ArH), 5.21 (1H, br s, NCHPh), 4.17 (1H, d, *J* 8.2 Hz, NH), 3.84 (1H, ddd, *J* 9.8, 8.2 and 2.0 Hz, NHC*H*CHPh), 3.05 (1H, td, *J* 13.1 and 2.5 Hz, NC*H*H), 2.87 (1H, dt, *J* 13.1 and 6.9 Hz, NC*H*H), 2.41 (3H, s, $CH_3$), 1.92-1.75 (3H, m, C*H*HC*H*$_2$), 1.64-1.52 (1H, m, CHHC*H*H), 1.24 [9H, s, $C(CH_3)_3$]; $\delta_c$ (100.5 MHz, $CDCl_3$) 143.3 (s), 138.2 (s), 136.5 (s), 129.8 (d), 128.8 (d), 127.4 (d), 127.0 (d), 126.8 (d), 61.2 (d), 59.1 (d), 56.0 (s), 50.6 (t), 24.3 (t), 23.8 (t), 22.8 (q), 21.5 (q); MS (CI): *m*/*z* (%) 435 ($MH^+$, 89%) and 224 ($M^+$-$NSOBu^t$-$CH_2Ph$, 100%); HRMS (CI) found 435.1776. $C_{22}H_{30}N_2O_3S_2$ requires 435.1769; $[\alpha]_D^{23}$ -32 (*c* 1.0, $CH_2Cl_2$).

**_(2R)-(3S)-trans_ 4-Methyl-_N_-[3-(3-phenylaziridin-2-yl)-propyl] benzenesulfonamide (17)**



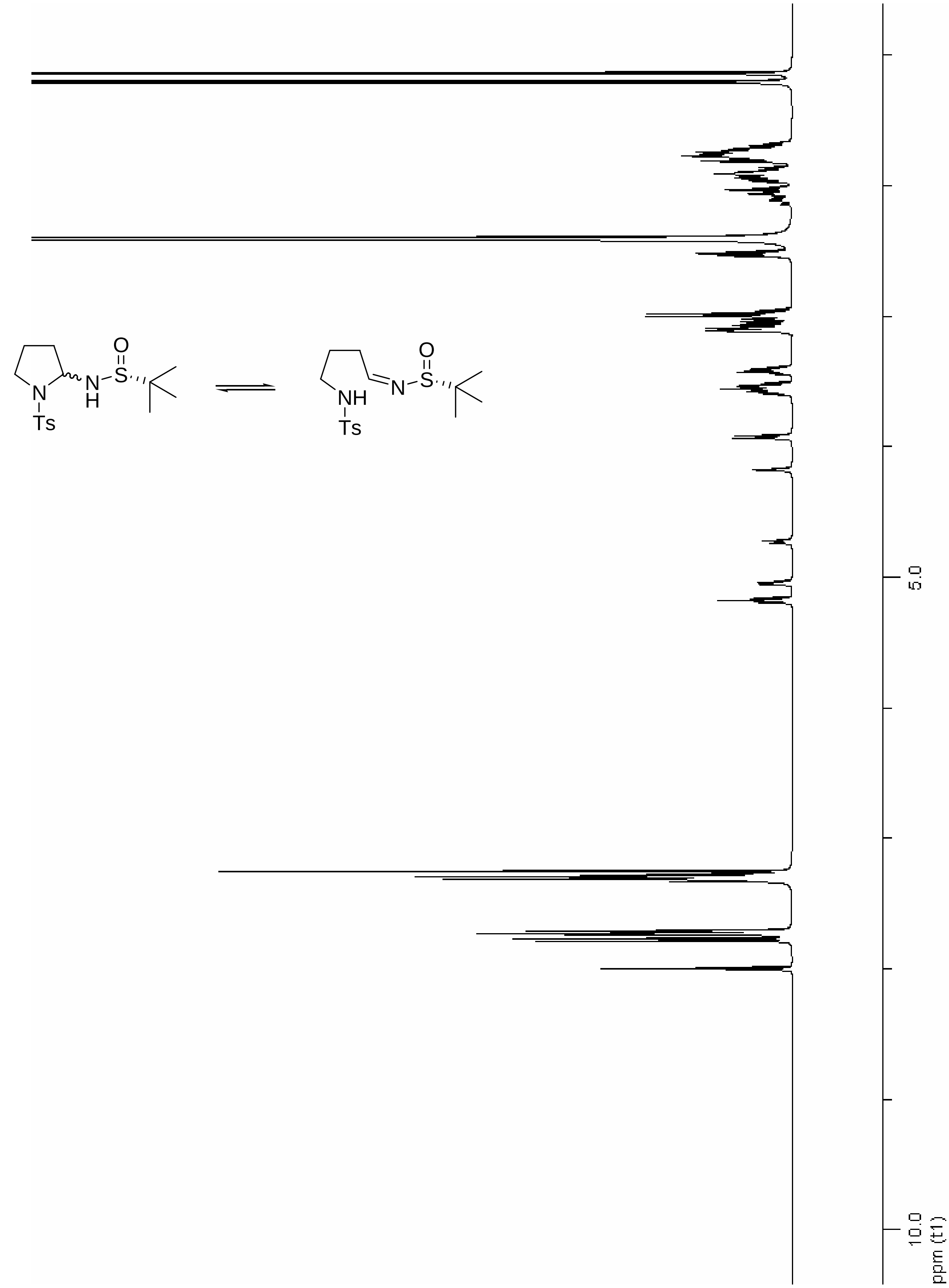
To a solution of 4-methyl-*N*-{3-[3-phenyl-1-(propane-2-sulfinyl)-aziridin-2-yl]-propyl}-benzenesulfonamide **6** (20 mg, 0.04 mmol) in anhydrous 1,4-dioxane (1 mL) at r.t. was added a solution of HCl (1.25 M) in EtOH. The reaction was monitored by TLC and the amount of HCl was determined by the reaction progress. Once all starting material was consumed, the reaction mixture was concentrated. The reaction mixture was diluted with $Et_2O$ (4 mL) and washed with $H_2O$ (3 × 4 mL). The combined aqueous layers were basified with $NH_3$ (1 N, 30 mL), extracted with $Et_2O$ (3 × 25 mL) and dried ($MgSO_4$). The solvents were removed in vacuo to afford the product as a white solid (11 mg, 81%) mp 122-124 °C ($CH_2Cl_2$); $R_f$ ($CH_2Cl_2$:MeOH, 9:1) 0.10; IR (film) 3379 (NH), 3324 (NH), 1597 (Ar), 1330 ($SO_2$), 1163 ($SO_2$) cm$^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.68 (2H, d, *J* 8.3 Hz, ArH), 7.28-7.19 (5H, m, ArH), 7.17 (2H, d, *J* 8.3 Hz, ArH), 4.91 (1H, d, *J* 2.9 Hz, NCHPh), 3.69 (1H, dt, *J* 13.3 and 3.9 Hz, NC*H*H), 3.54 (1H, dd, *J* 7.6 and 2.9 Hz, NC*H*$CH_2$), 3.19 (1H, ddd, *J* 13.3, 11.8 and 3.4 Hz, NC*H*H), 2.41 (3H, s, $CH_3$), 1.85-1.74 (1H, m, C*H*H$CH_2$), 1.68-1.57 (3H, m, CHHC*H*H and 2 x NH), 1.53-1.47 (1H, m, C*H*HCHH), 1.43-1.39 (1H, m, C*H*HCHH); $\delta_c$ (100.5 MHz, $CDCl_3$) 143.3 (s), 143.2 (s), 132.8 (s), 129.7 (d), 128.7 (d), 128.0 (d), 127.2 (d), 126.3 (d), 53.2 (d), 50.4 (d), 42.5 (t), 28.2 (t), 25.8 (t), 21.4 (q); MS (CI): *m/z* (%) 331 ($MH^+$, 98%), 314 ($MH^+$-$NH_3$, 100%) and 175 ($M^+$-Ts, 75%); HRMS (CI) found 331.1480. $C_{18}H_{22}N_2O_2S$ requires 331.1473; (Found: C, 65.51%; H, 6.61%; N, 8.34%. $C_{18}H_{22}N_2O_2S$ requires C, 65.42%; H, 6.71%; N, 8.48%) $[\alpha]_D^{23}$ +40 (*c* 0.1, $CH_2Cl_2$).

### *(2S)-(3S)*-2-Phenyl-1-(toluene-4-sulfonyl)-piperidin-3-ylamine (18)

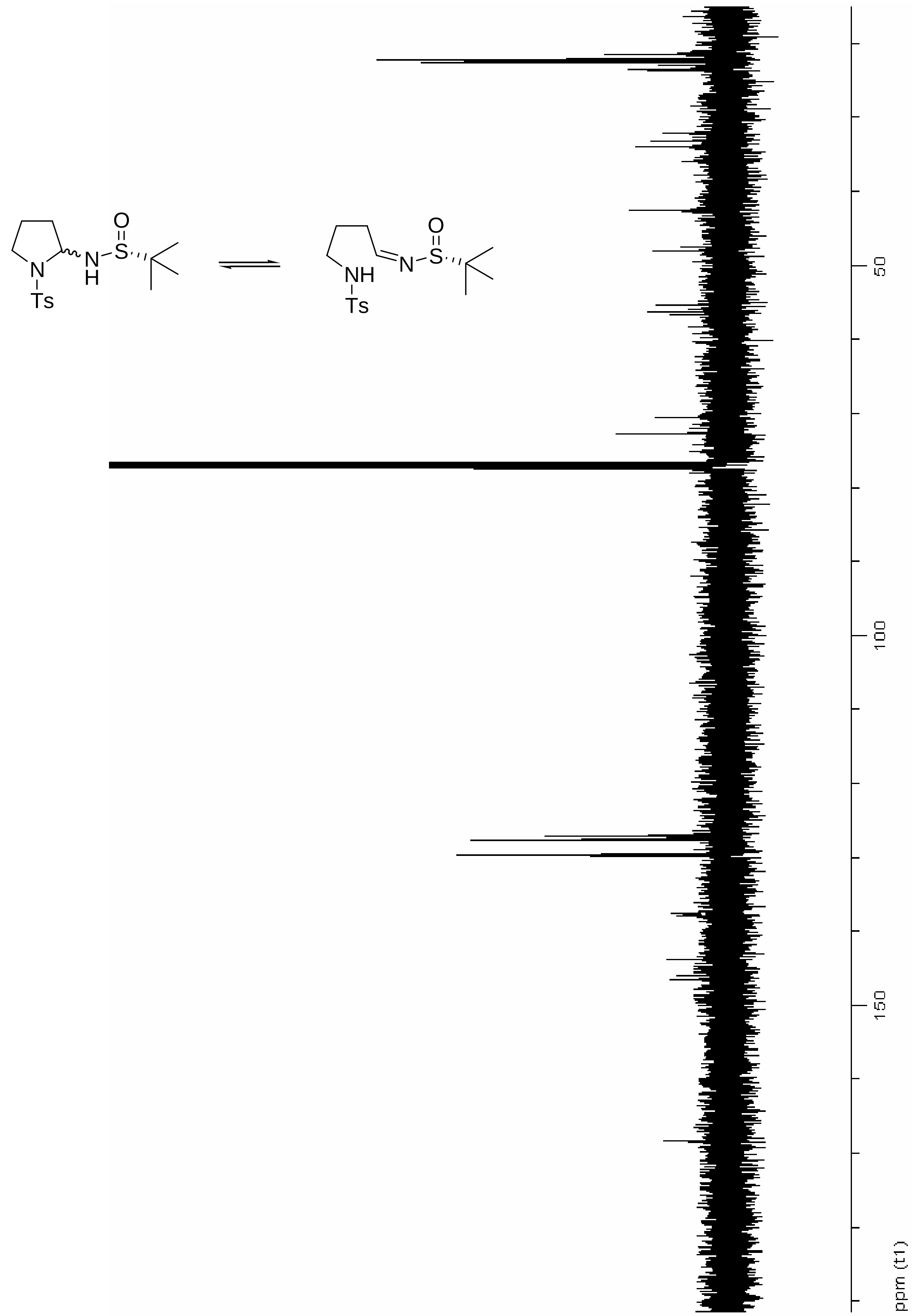


To a solution of 2-methylpropane-2-sulfinic acid [2-phenyl-1-(toluene-4-sulfonyl)-piperidin-3-yl]-amide **16** (10 mg, 0.02 mmol) in anhydrous 1,4-dioxane (1 mL) at room temperature was added a solution of HCl (1.25 M) in EtOH. The reaction was monitored by TLC and the amount of HCl was determined by the reaction progress. Once all starting material was consumed, the reaction mixture was concentrated. The reaction mixture was diluted with $Et_2O$ (4 mL) and washed with $H_2O$ (3 × 4 mL). The combined aqueous layers were basified with $NH_3$ (1 N, 30 mL), extracted with $Et_2O$ (3 × 25 mL) and dried ($MgSO_4$). The solvents were removed in vacuo to afford the product as a colourless oil (6 mg, 88%); $R_f$ ($CH_2Cl_2$:MeOH, 9:1) 0.15; IR (film) 3496 (NH), 1387 ($SO_2$), 1160 ($SO_2$) $cm^{-1}$; $\delta_H$ (400 MHz, $CDCl_3$) 7.68 (2H, d, *J* 8.2 Hz, ArH), 7.43-7.19 (7H, m, ArH), 4.89 (1H, d, *J* 2.6 Hz, NCHPh), 3.84 (1H, ddd, *J* 7.7, 7.6 and 2.6 Hz, $NH_2CH$),3.26-3.18 (2H, m, $NCH_2$), 2.41 (3H, s, $CH_3$), 1.78-1.52 (6H, m, $CH_2CH_2$ and $NH_2$); $\delta_c$ (100.5 MHz, $CDCl_3$) 145.0 (s), 136.9 (s), 136.8 (s), 129.8 (d), 128.7 (d), 127.5 (d), 127.4 (d), 127.2 (d), 60.4 (d), 57.9 (d), 41.9 (t), 29.8 (t), 25.2 (t), 21.6 (q); MS (ESI): *m*/*z* (%) 331 ($MH^+$, 100%); HRMS (ESI) found 331.1476 $C_{18}H_{22}N_2O_2S$ requires 331.1474; (Found: C, 65.53%; H, 6.62%; N, 8.34%. $C_{18}H_{22}N_2O_2S$ requires C, 65.42%; H, 6.71%; N, 8.48%); $[\alpha]_D^{23}$ +40 (*c* 0.2, $CH_2Cl_2$).

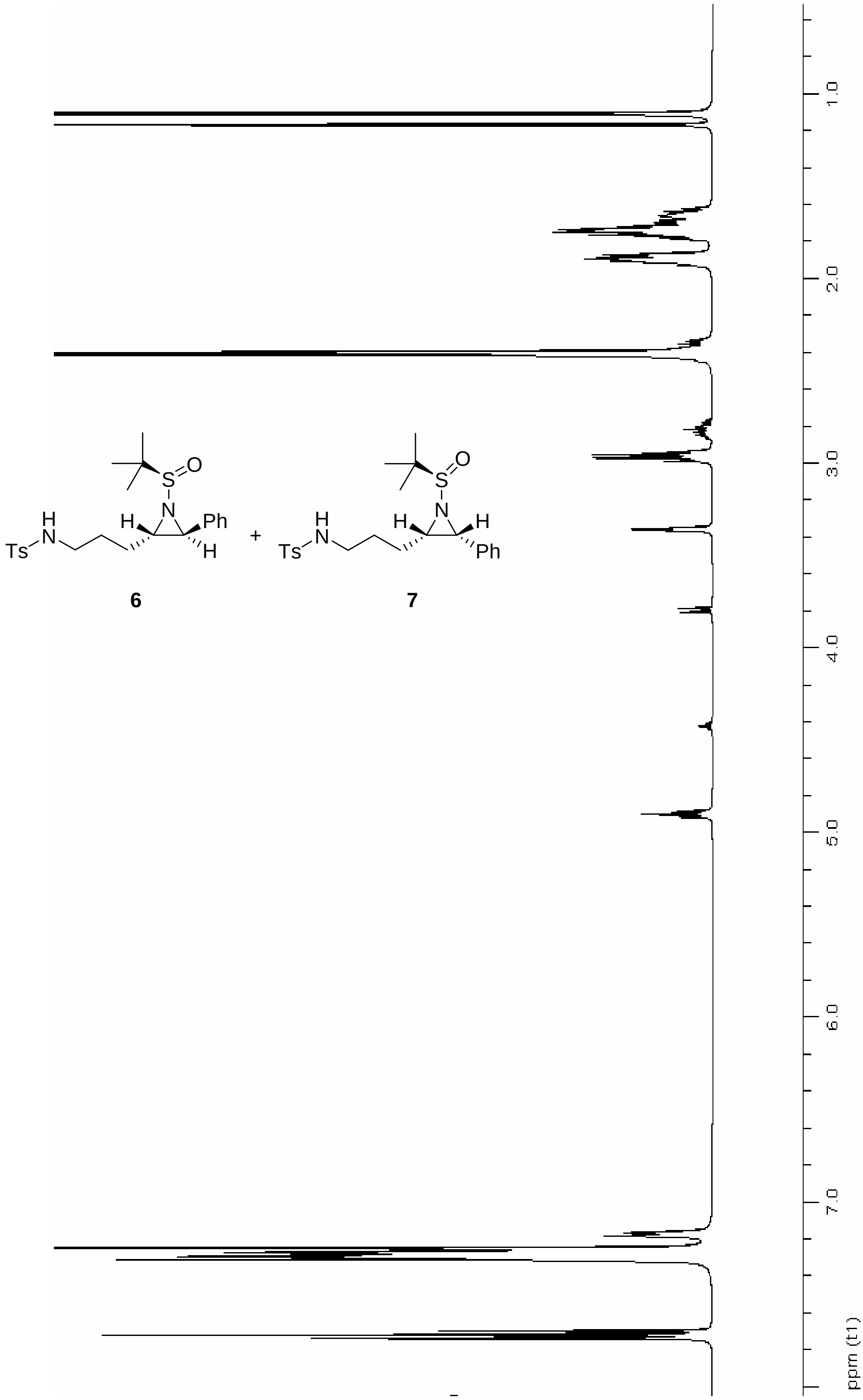
# $^{1}$H NMR ($CDCl_3$) Aminal 4



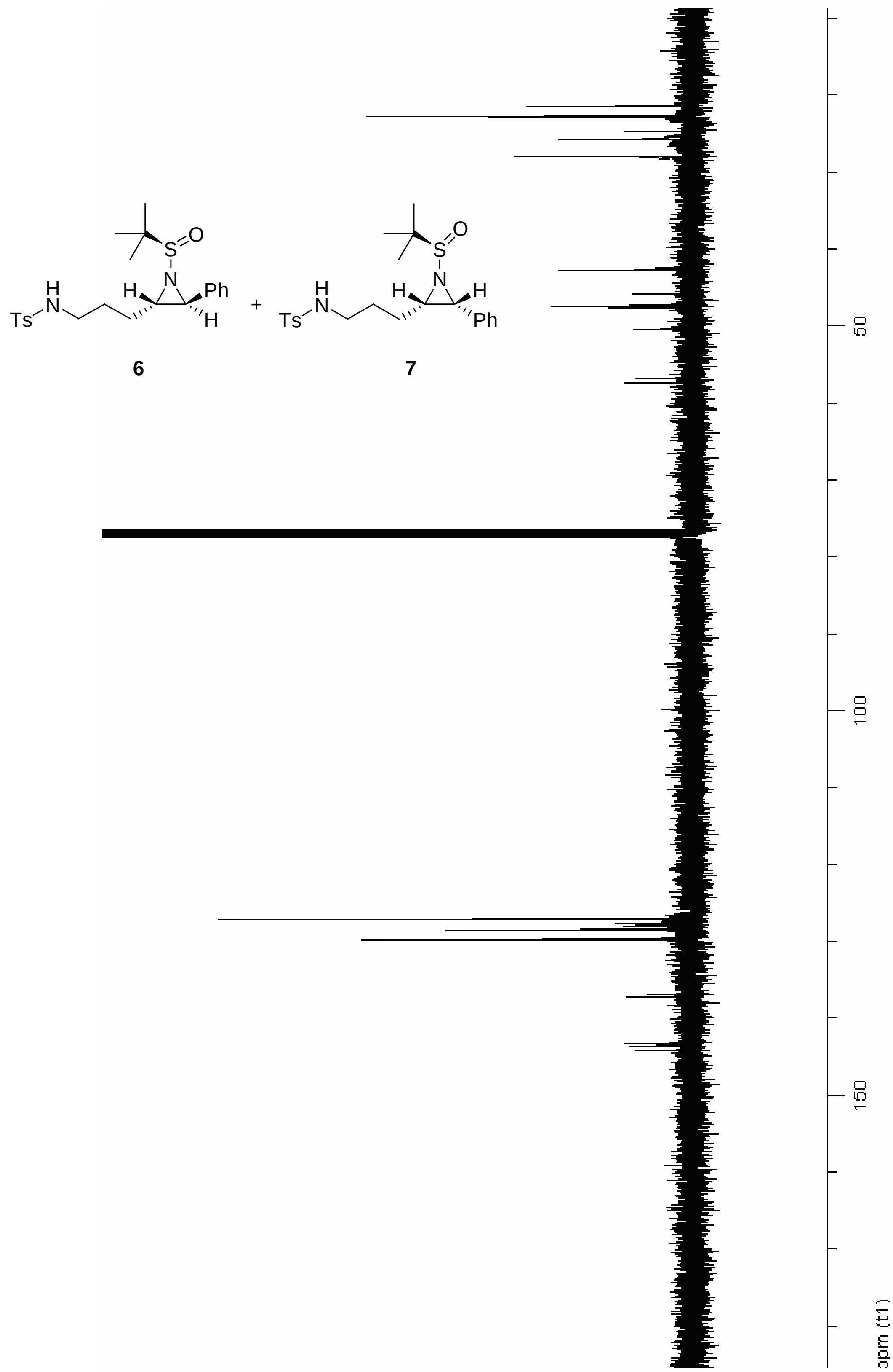
# $^{13}$C NMR ($CDCl_3$) Aminal 4



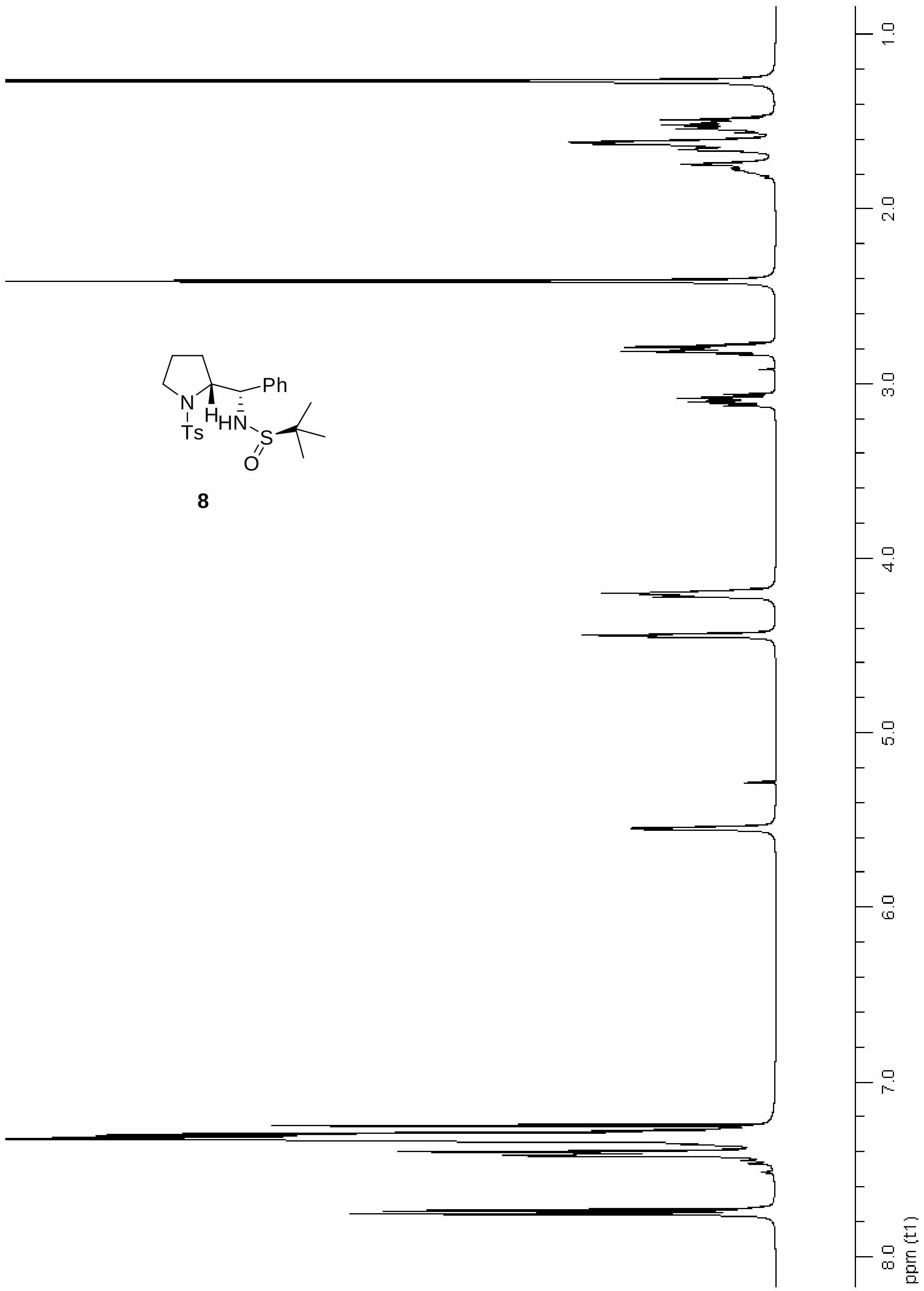
$^{1}$H NMR ($CDCl_3$) aziridines **6** minor: aziridine **7**



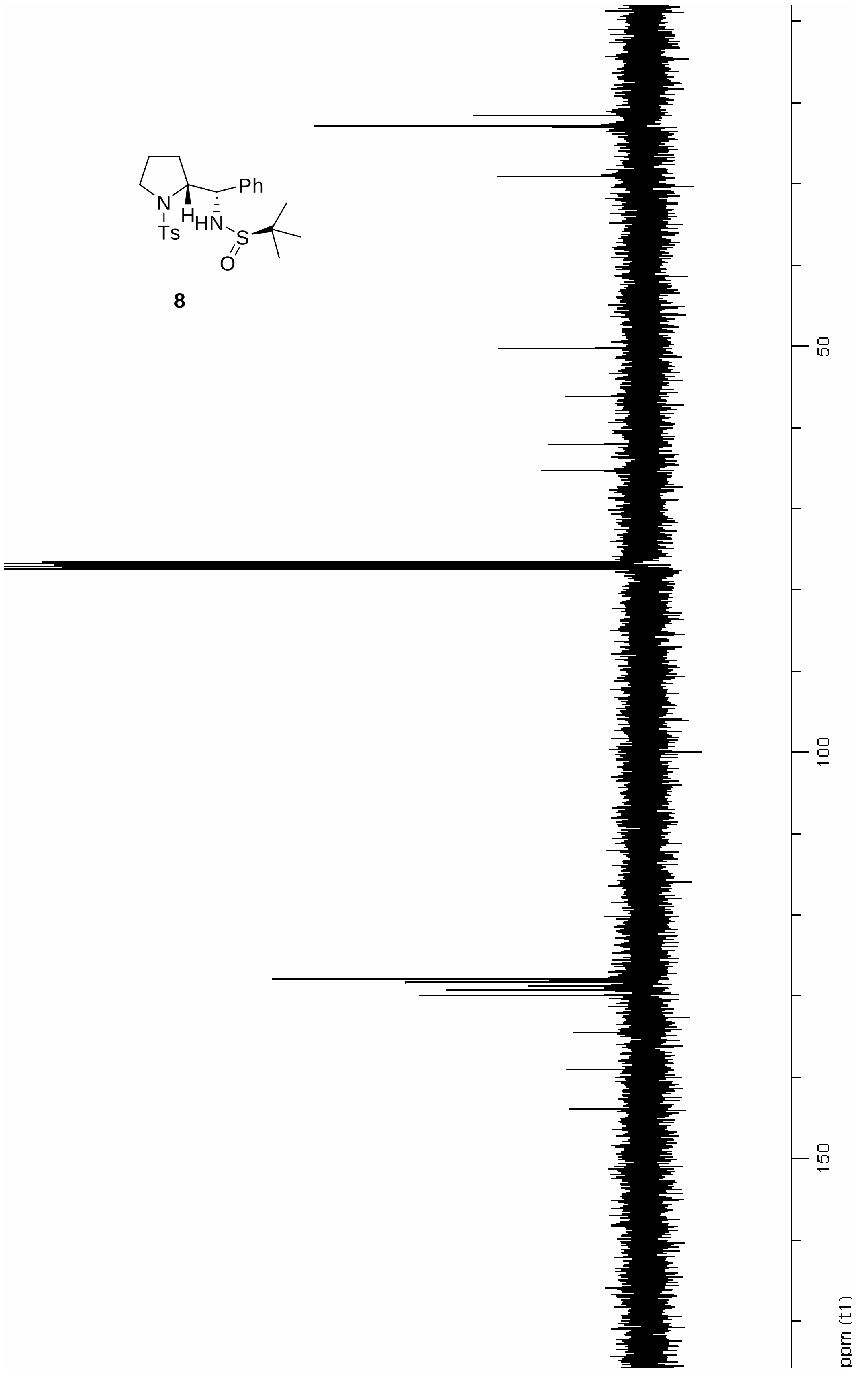
$^{13}$C NMR ($CDCl_3$) aziridines **6** minor: aziridine **7**



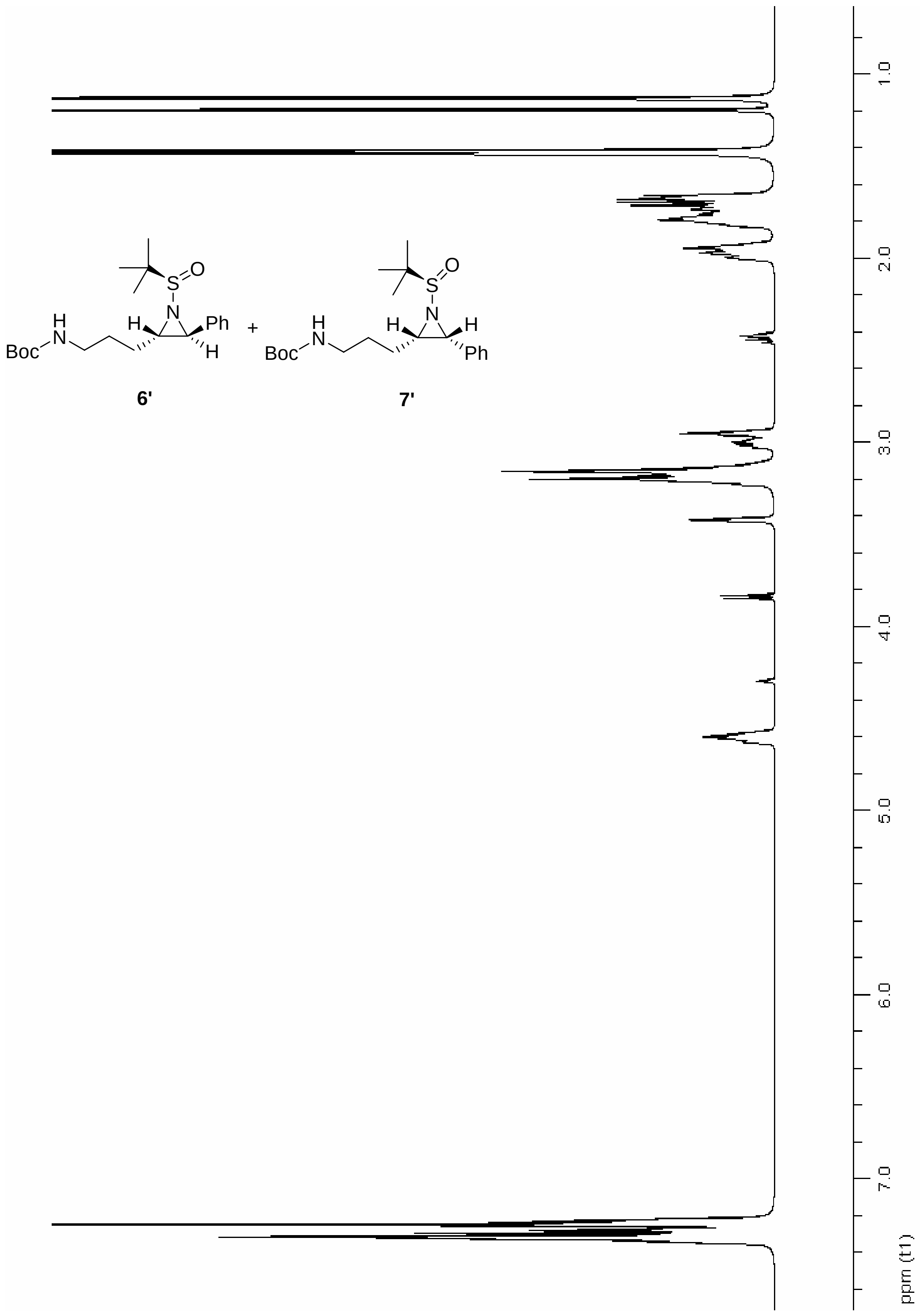
$^{1}H$ NMR ($CDCl_3$) pyrrolidine **8**



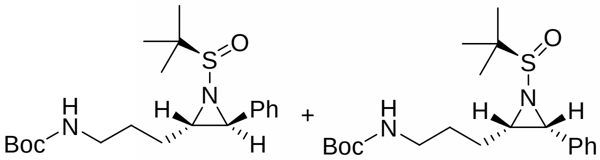
$^{13}C$ NMR ($CDCl_3$) pyrrolidine **8**



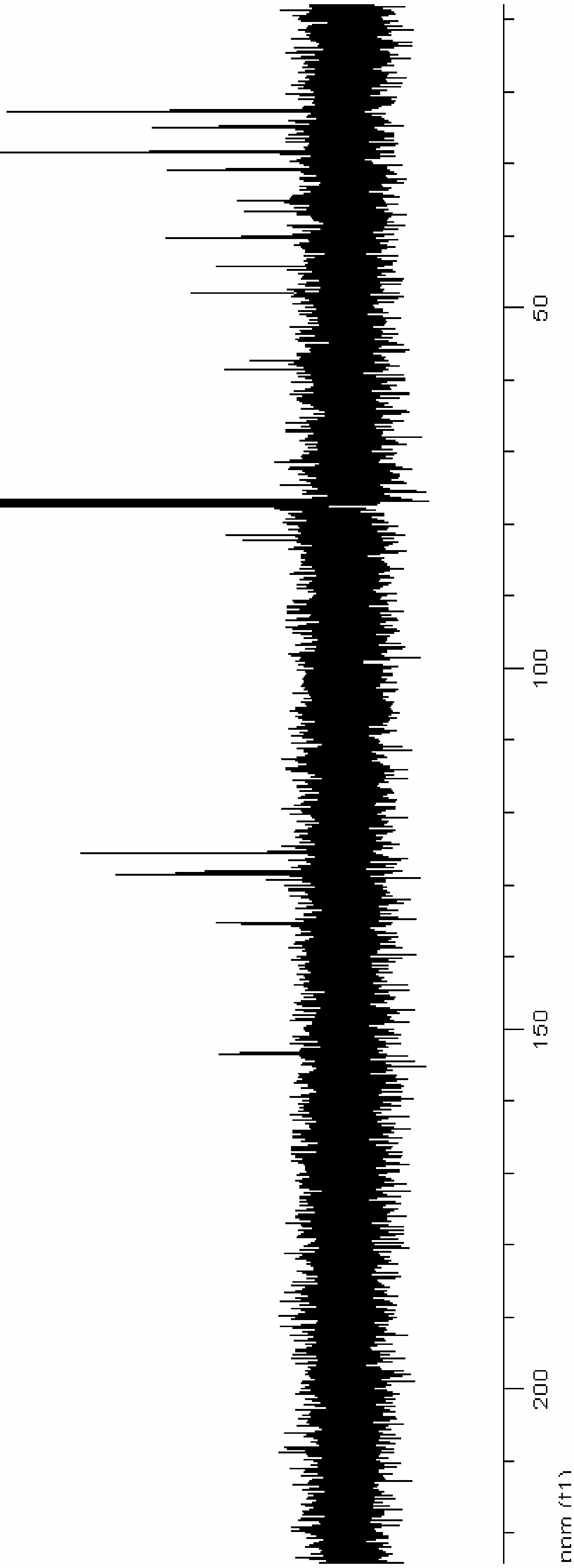
# $^{1}$H NMR ($CDCl_3$) aziridines **6’**:**7’**



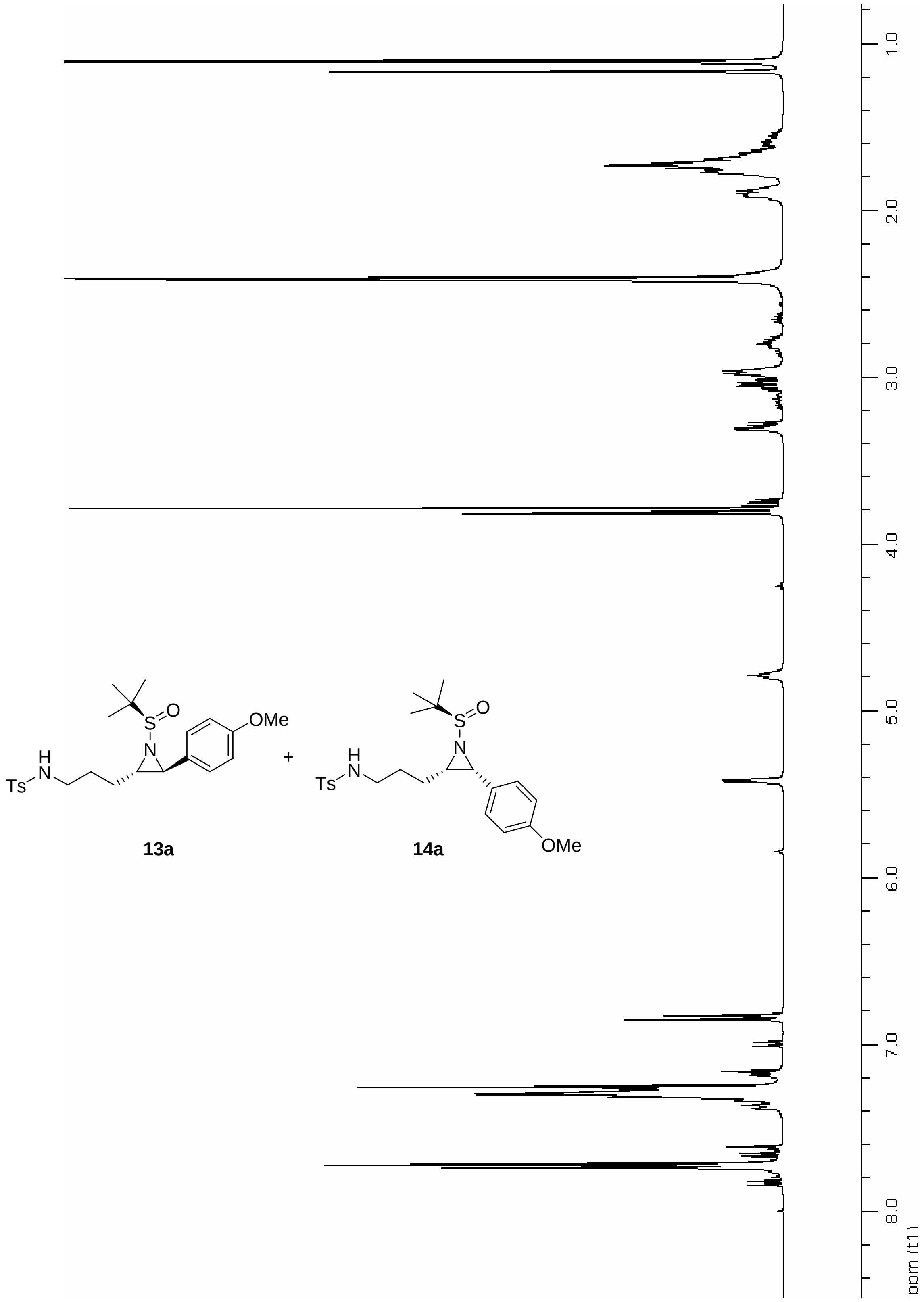
## $^{13}C$ NMR ($CDCl_3$) aziridines **6’**:**7’**



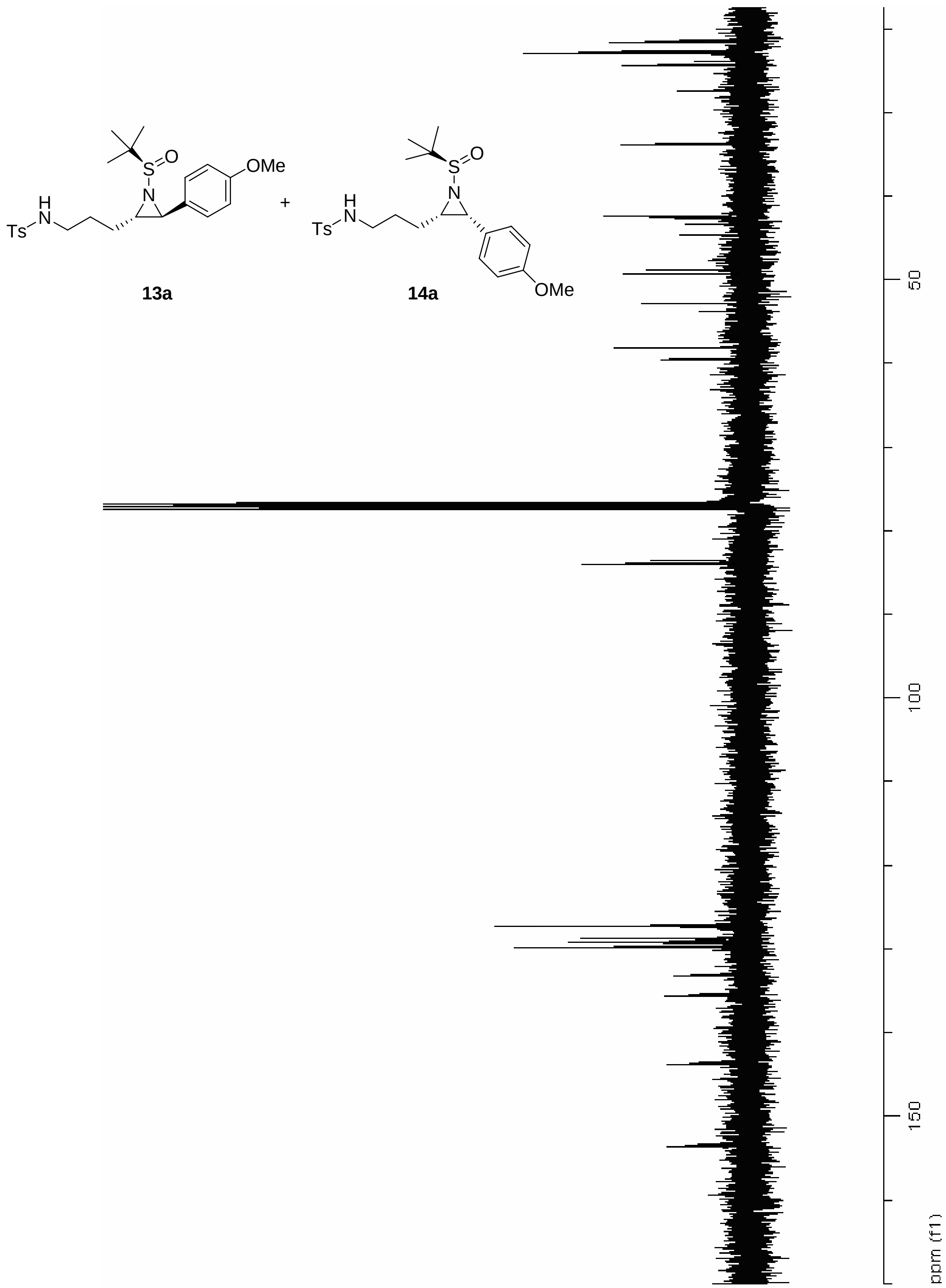
**6'** **7'**



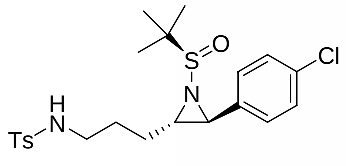
[1]H NMR ($CDCl_3$) aziridines **13a**major:**13a**minor:**14a**



$^{13}$C NMR ($CDCl_3$) aziridines **13a**major:**13a**minor:**14a**

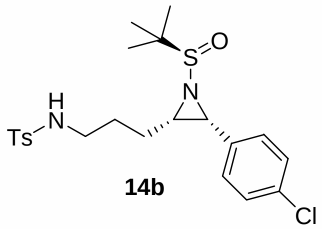


$^{1}H$ NMR ($CDCl_3$) aziridines **13b**minor:**14b**

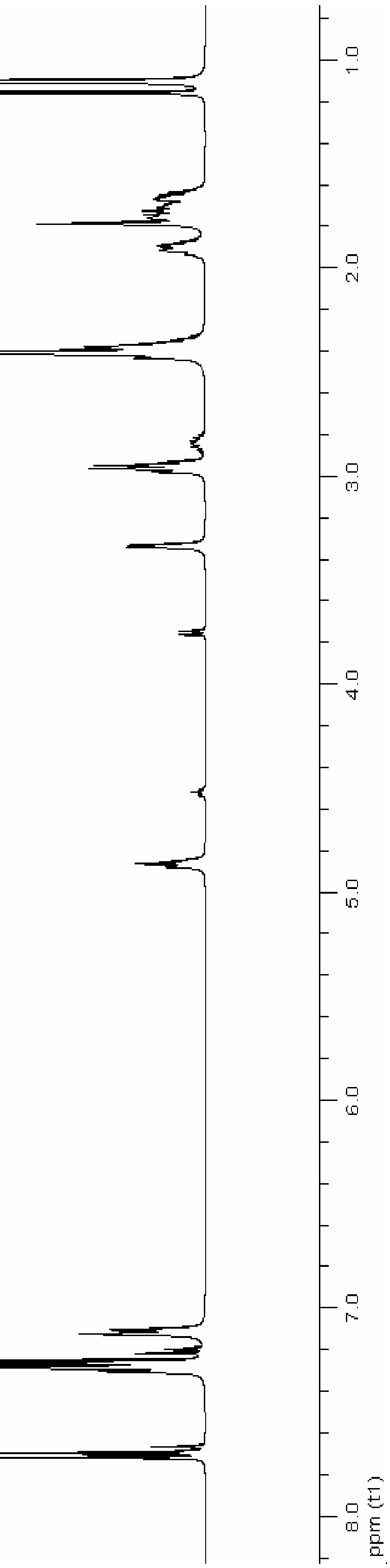


**13b**

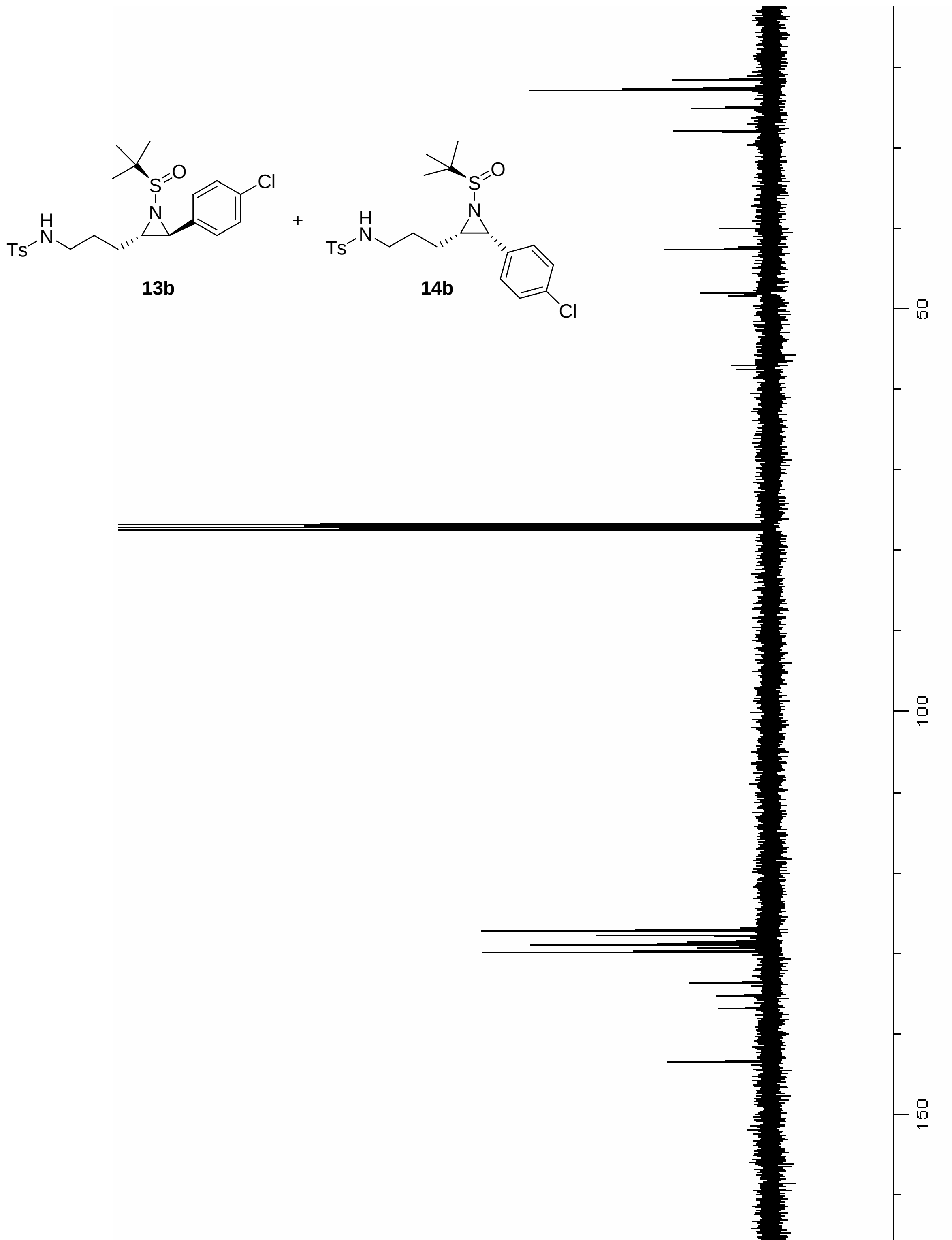
\+



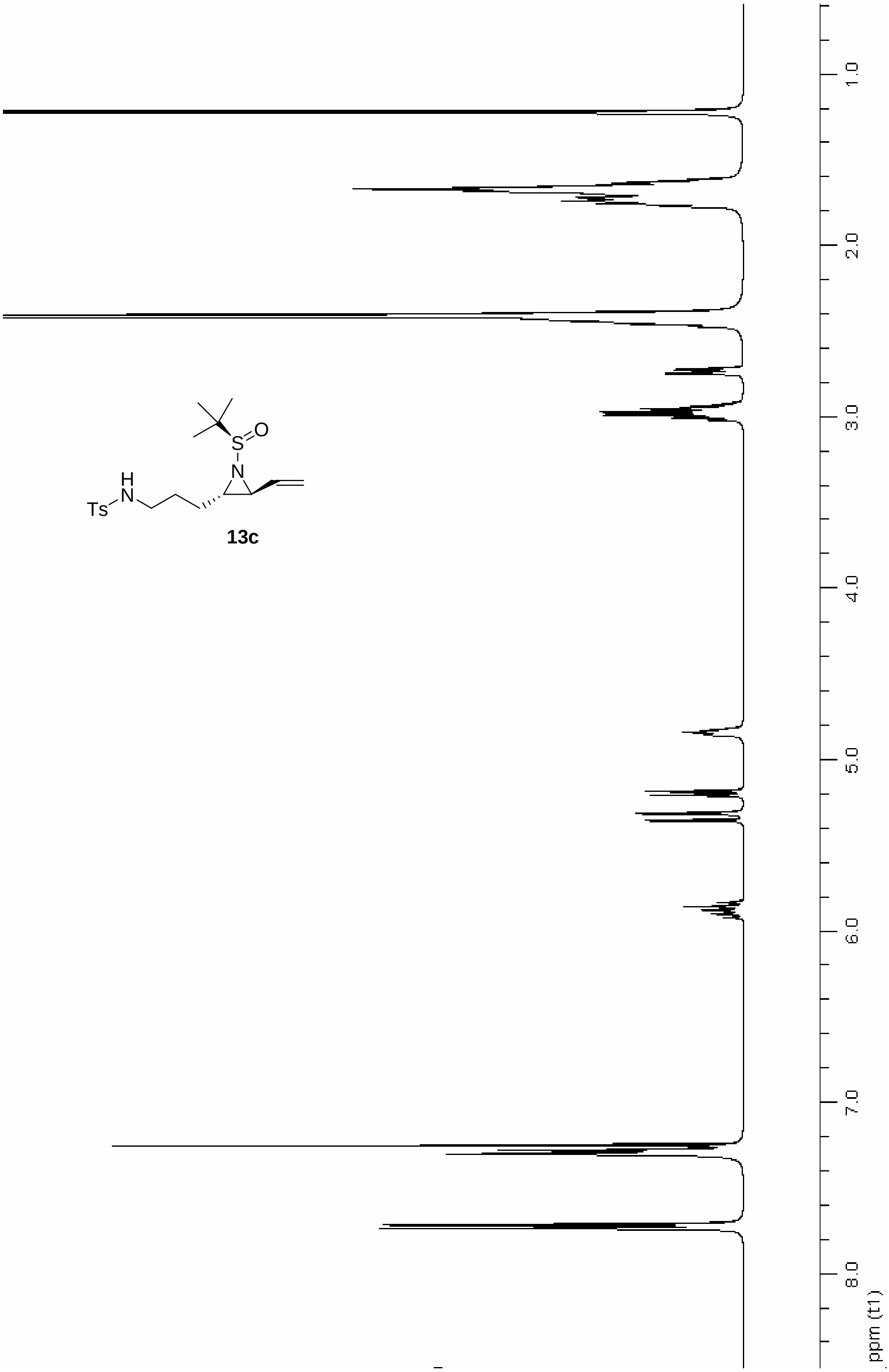
**14b**



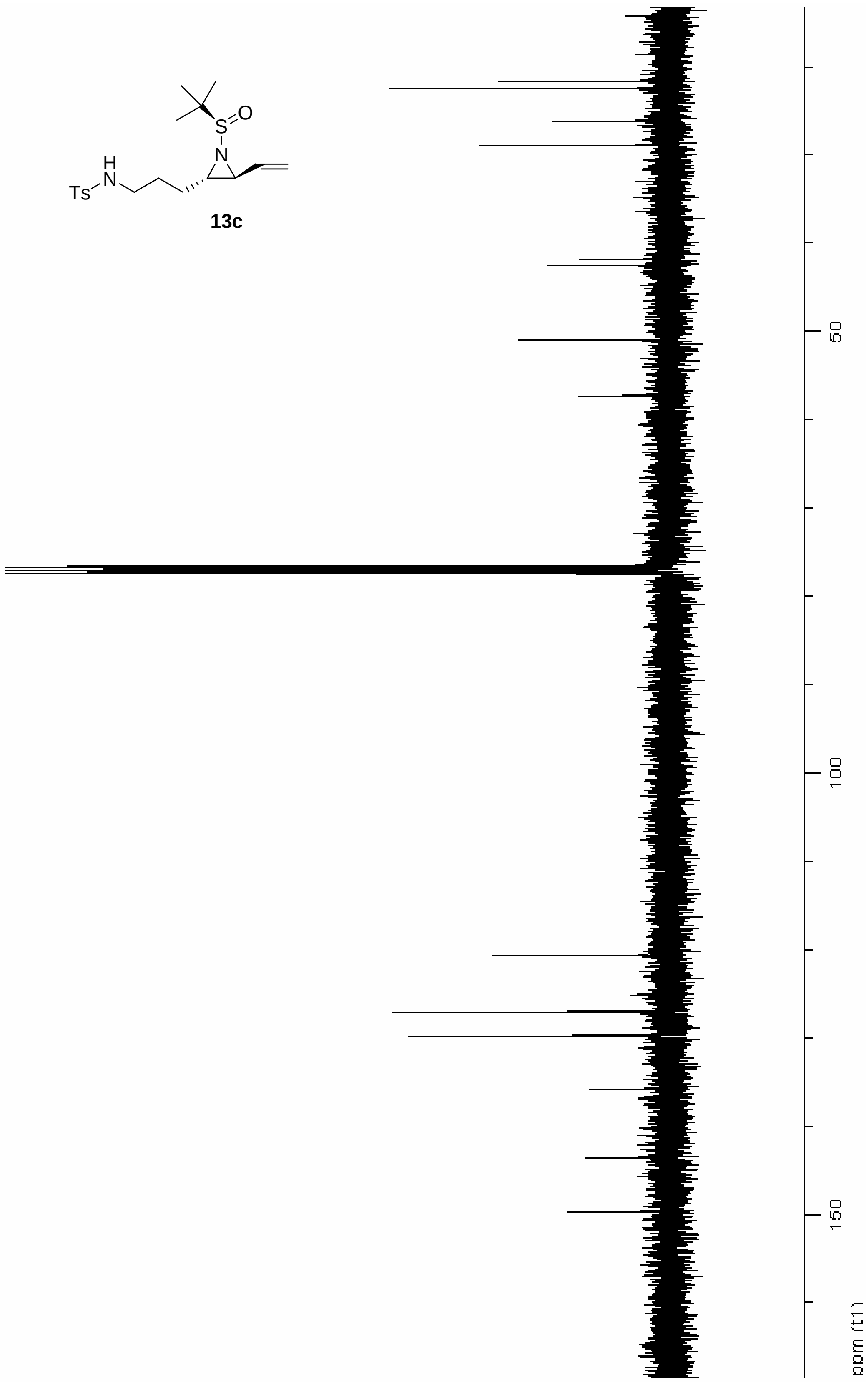
# $^{13}C$ NMR ($CDCl_3$) aziridines **13b**minor:**14b**



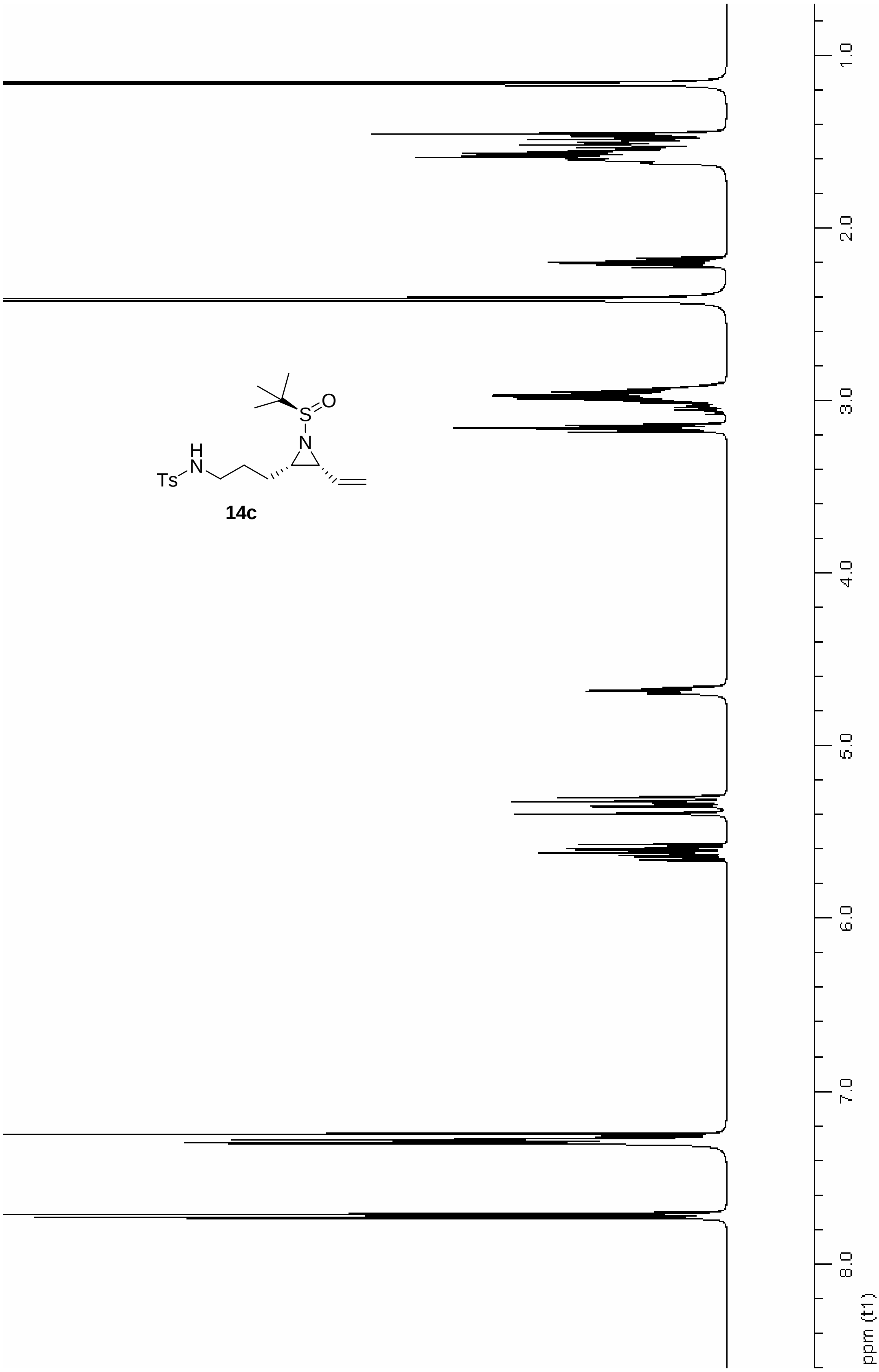
$^{1}$H NMR ($CDCl_3$) aziridine **13c**



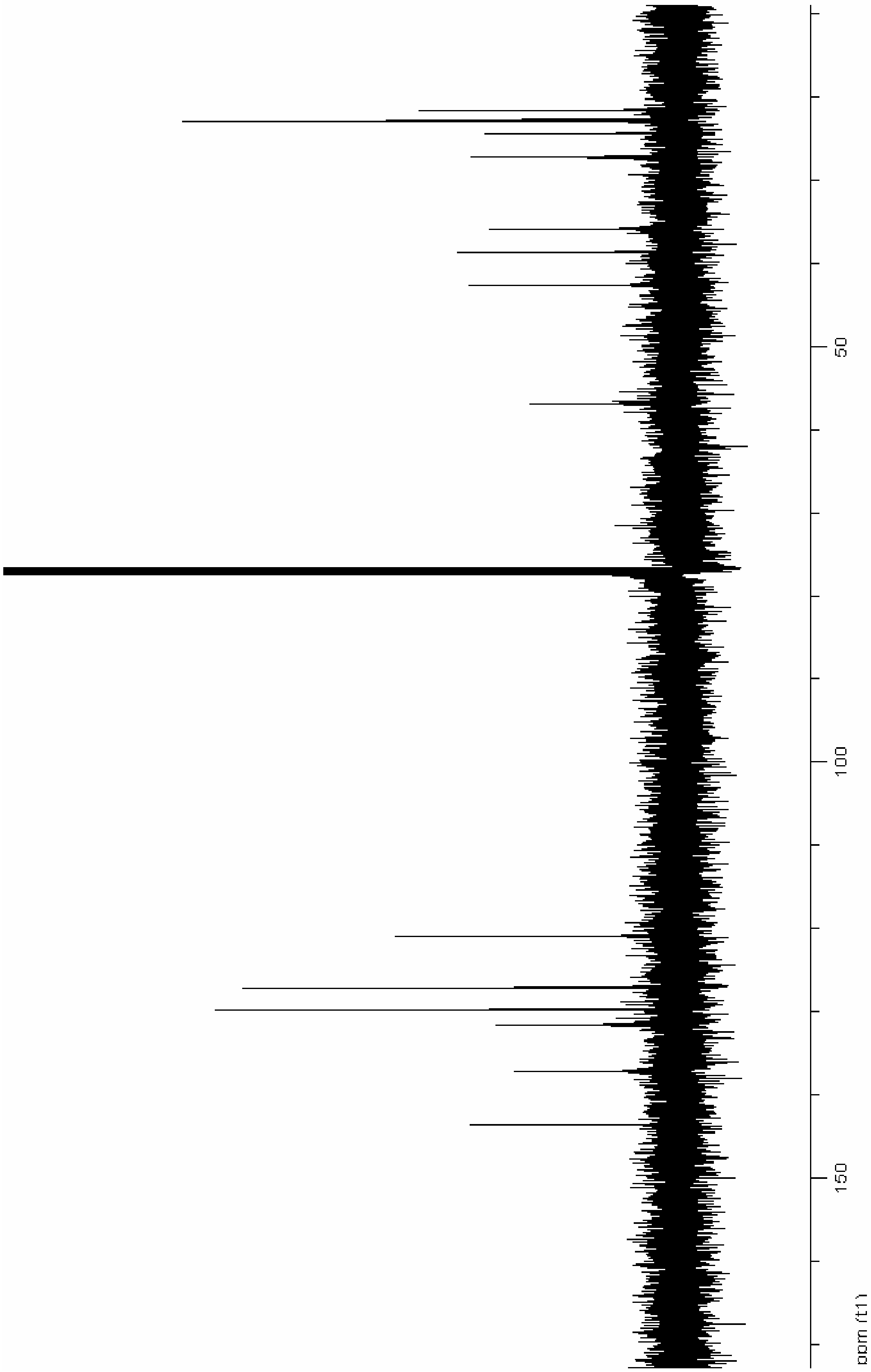
$^{13}C$ NMR ($CDCl_3$) aziridine **13c**



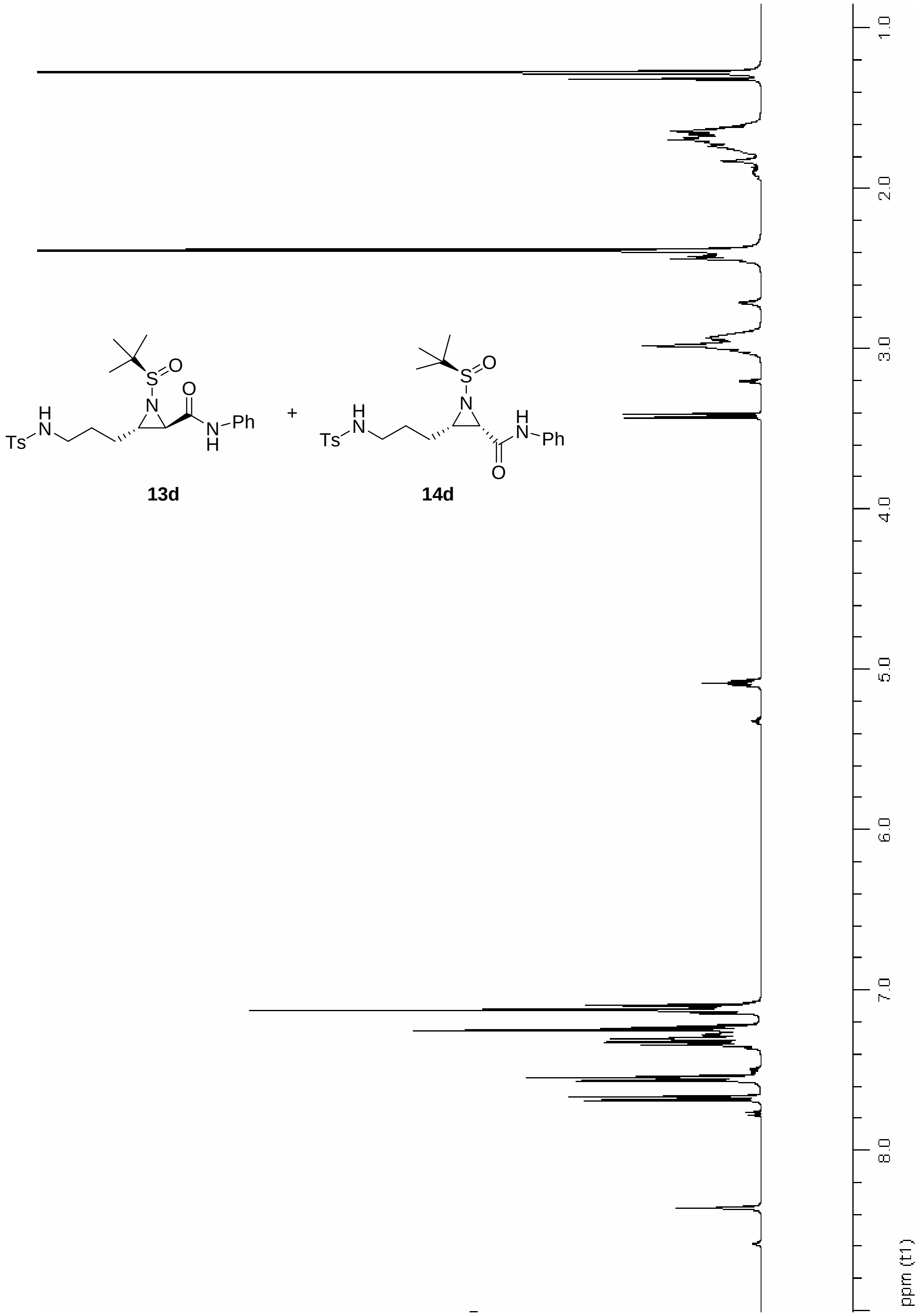
# $^{1}$H NMR ($CDCl_3$) aziridine **14c**



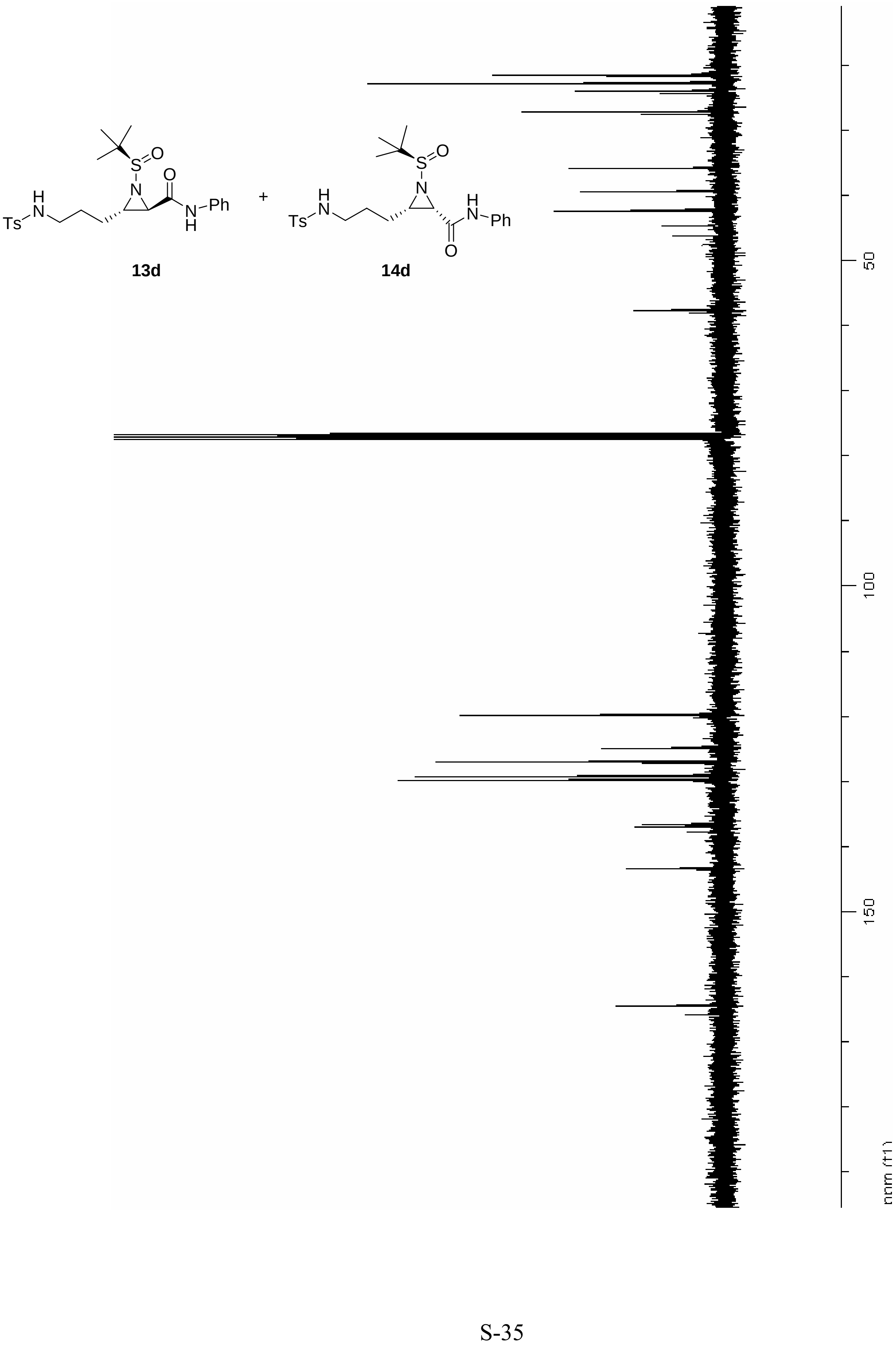
$^{13}C$ NMR ($CDCl_3$) aziridine **14c**



$^{1}$H NMR ($CDCl_3$) aziridines **13d**:**14d**

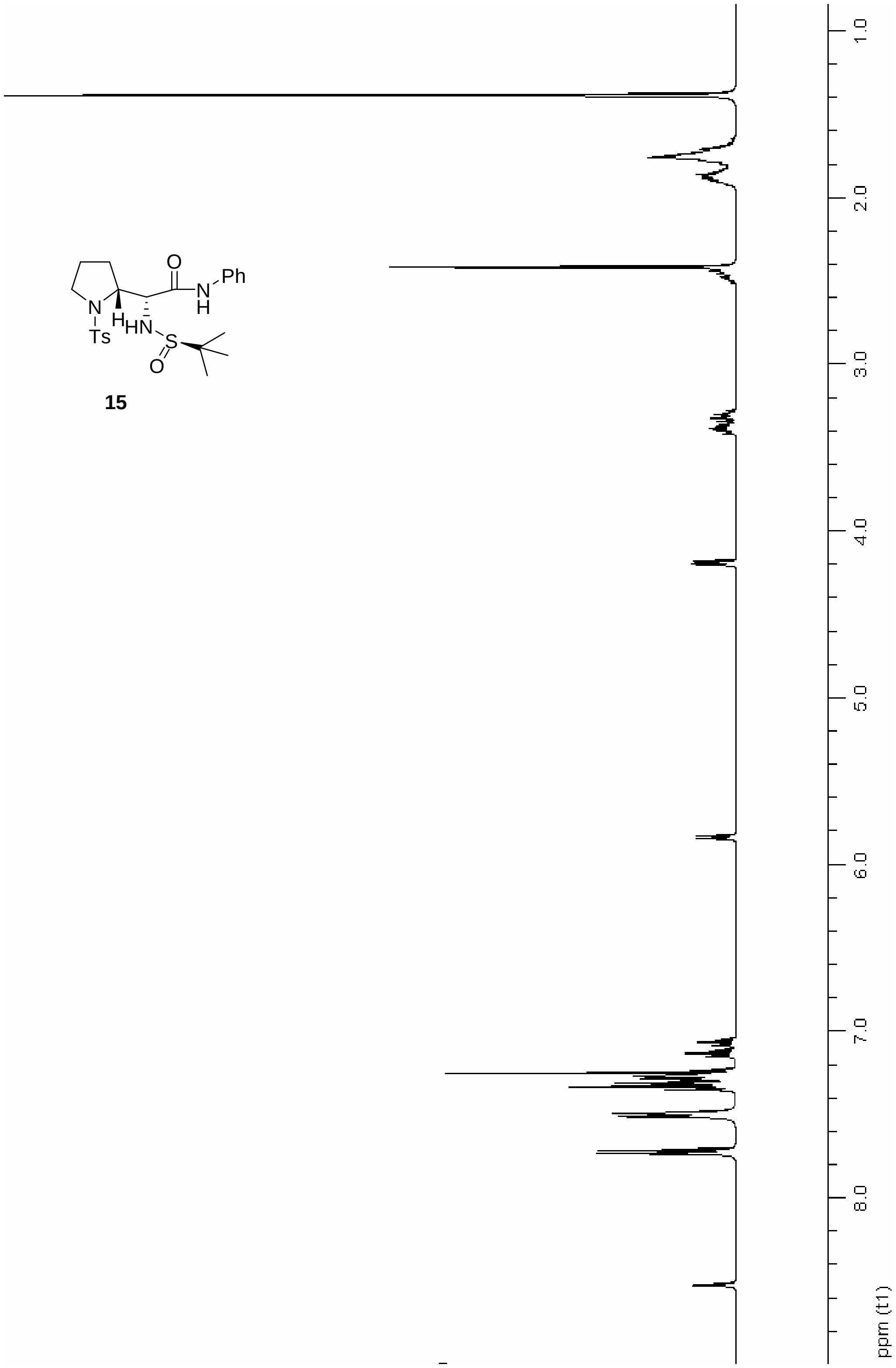


# $^{13}C$ NMR ($CDCl_3$) aziridines **13d**:**14d**

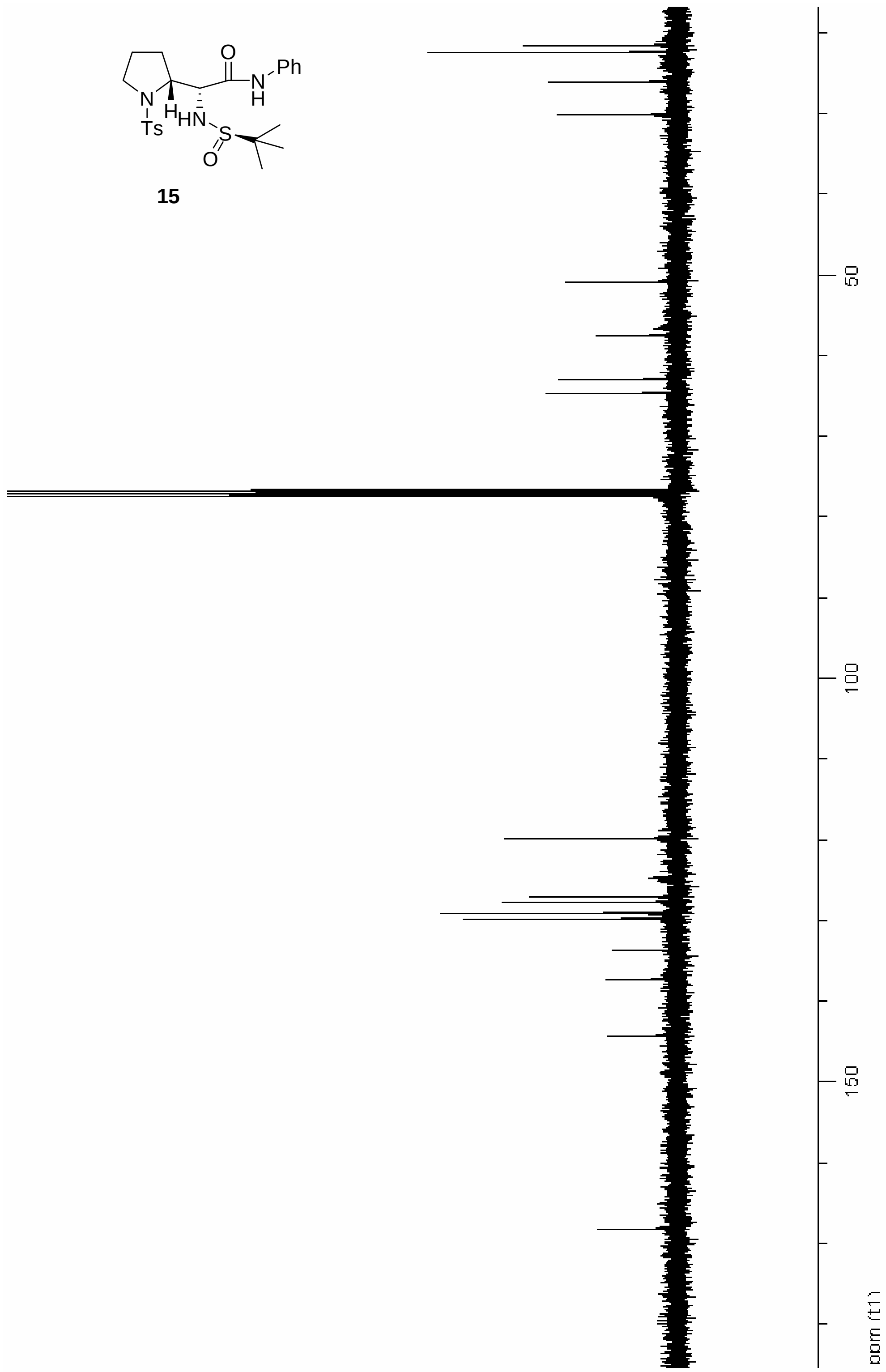


**13d** **14d**

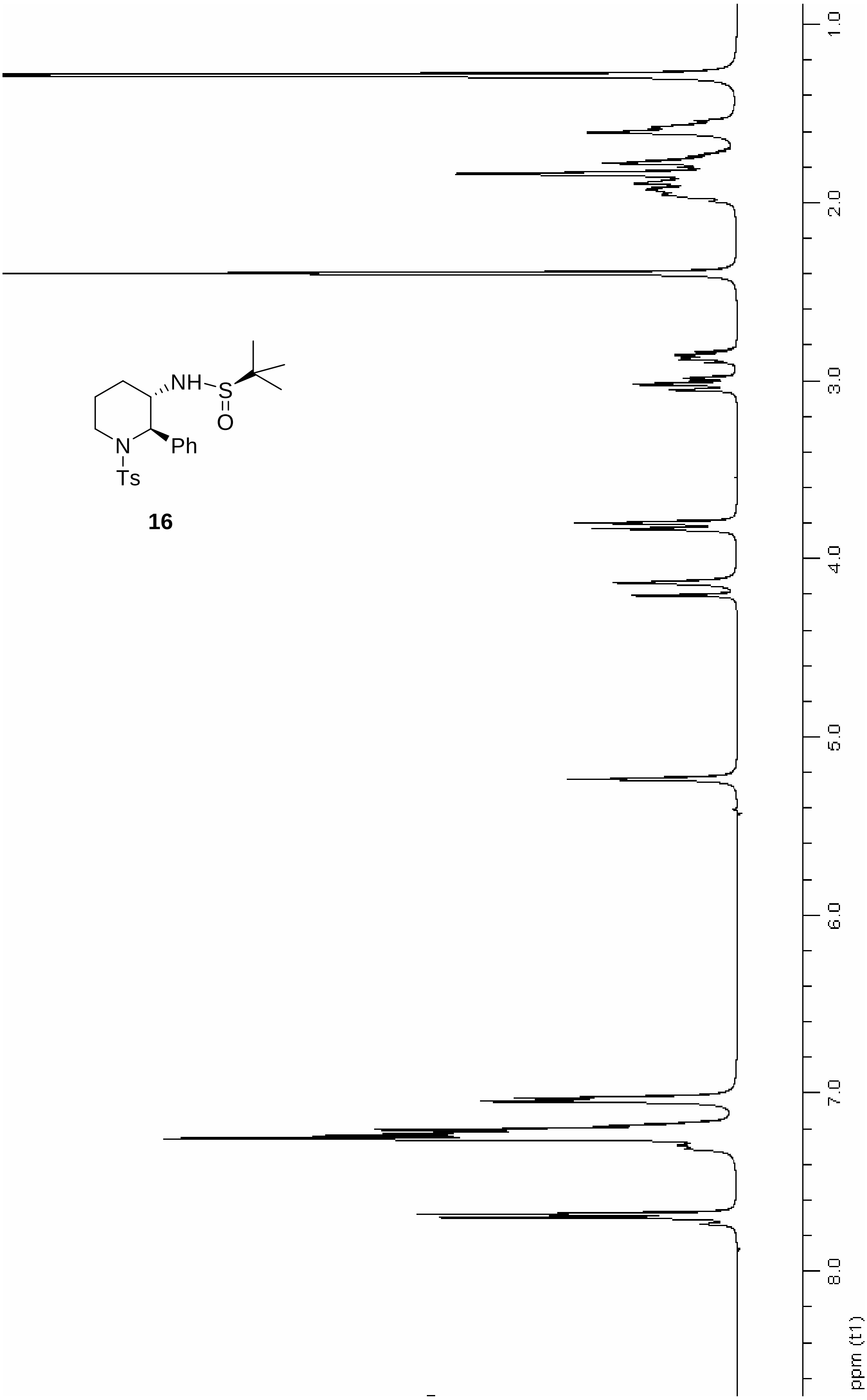
# $^{1}H$ NMR ($CDCl_3$) pyrrolidine **15**



$^{13}$C NMR ($CDCl_3$) pyrrolidine **15**

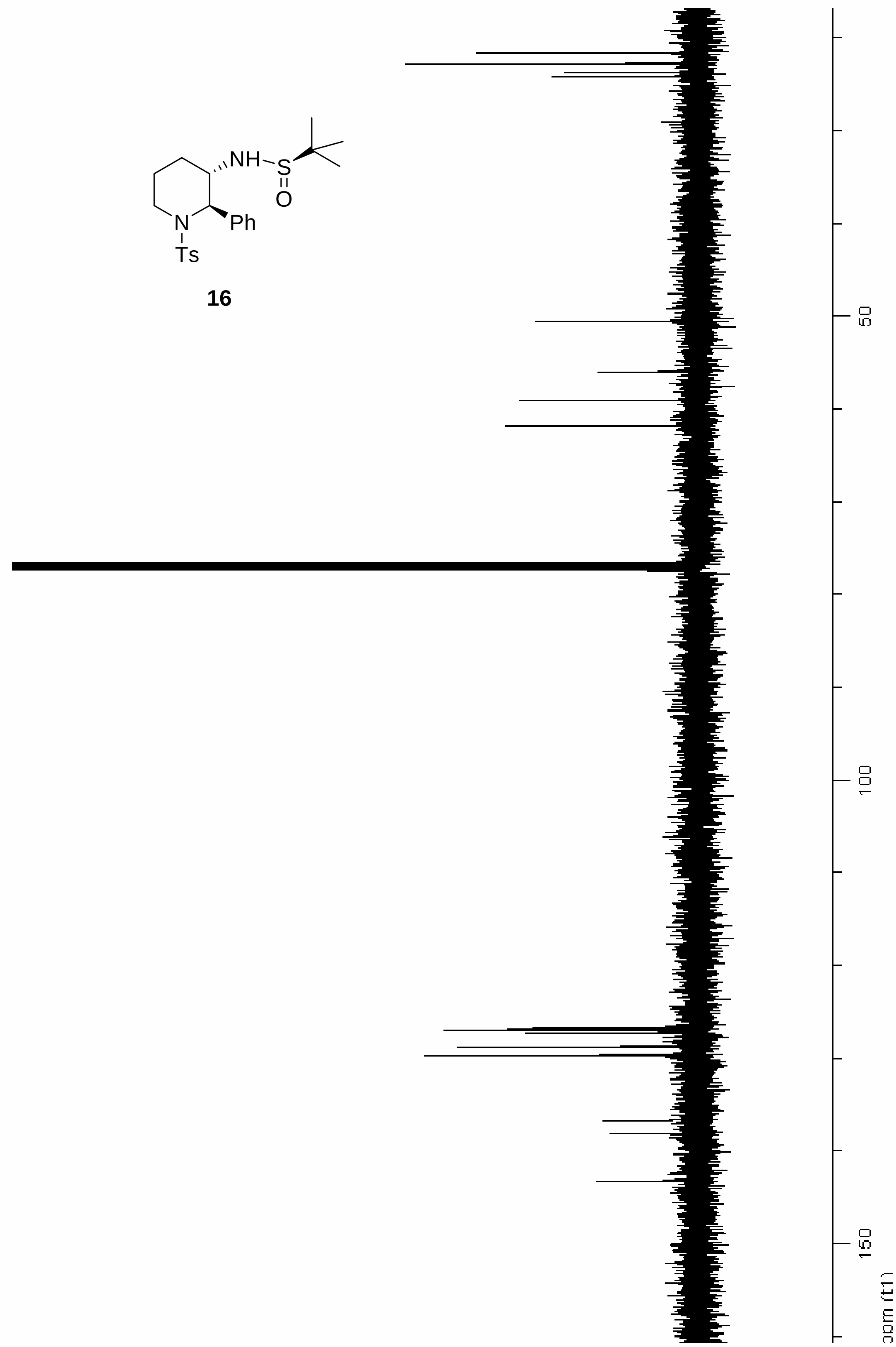


# [1]H NMR ($CDCl_3$) piperidine **16**

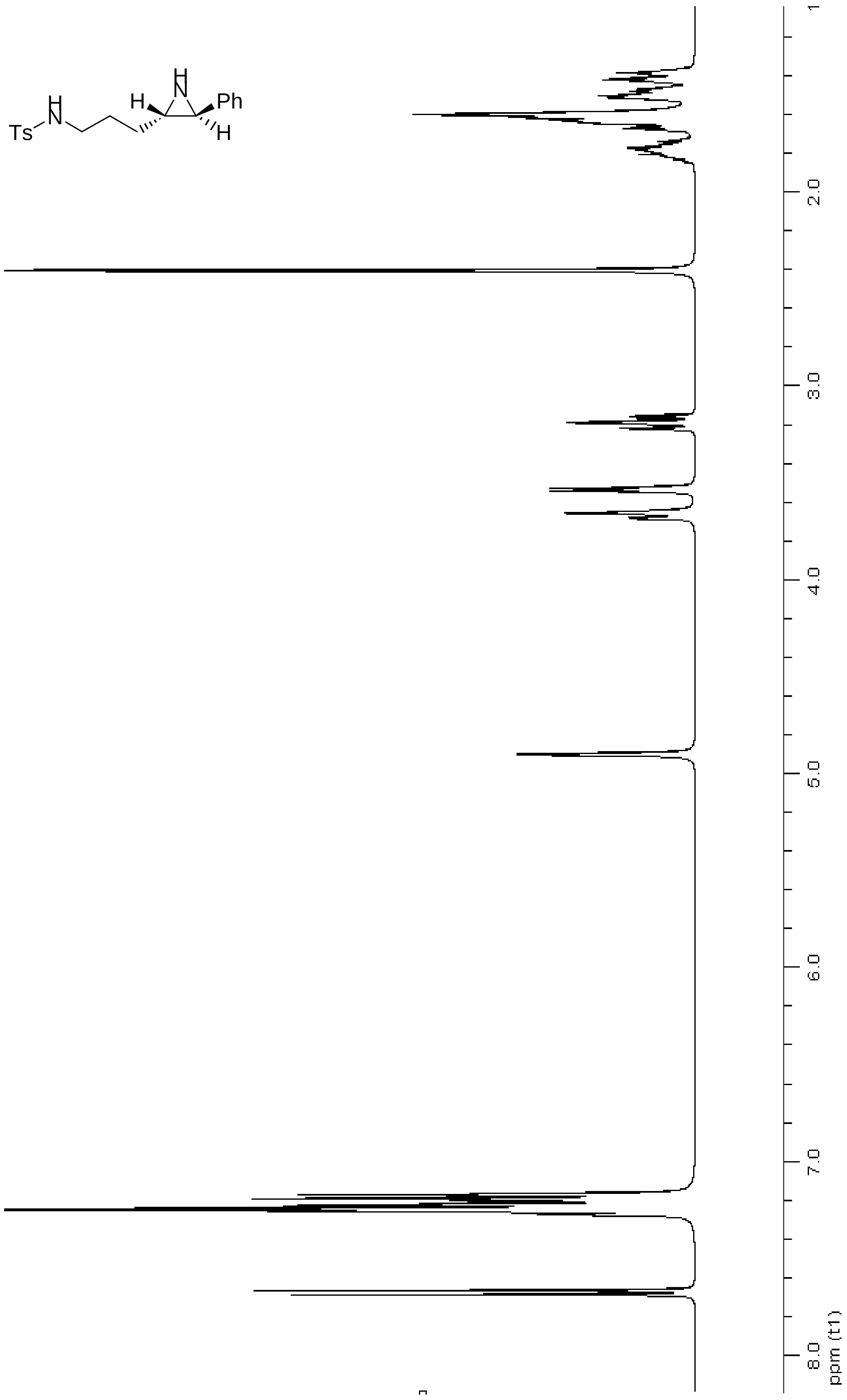



**16**

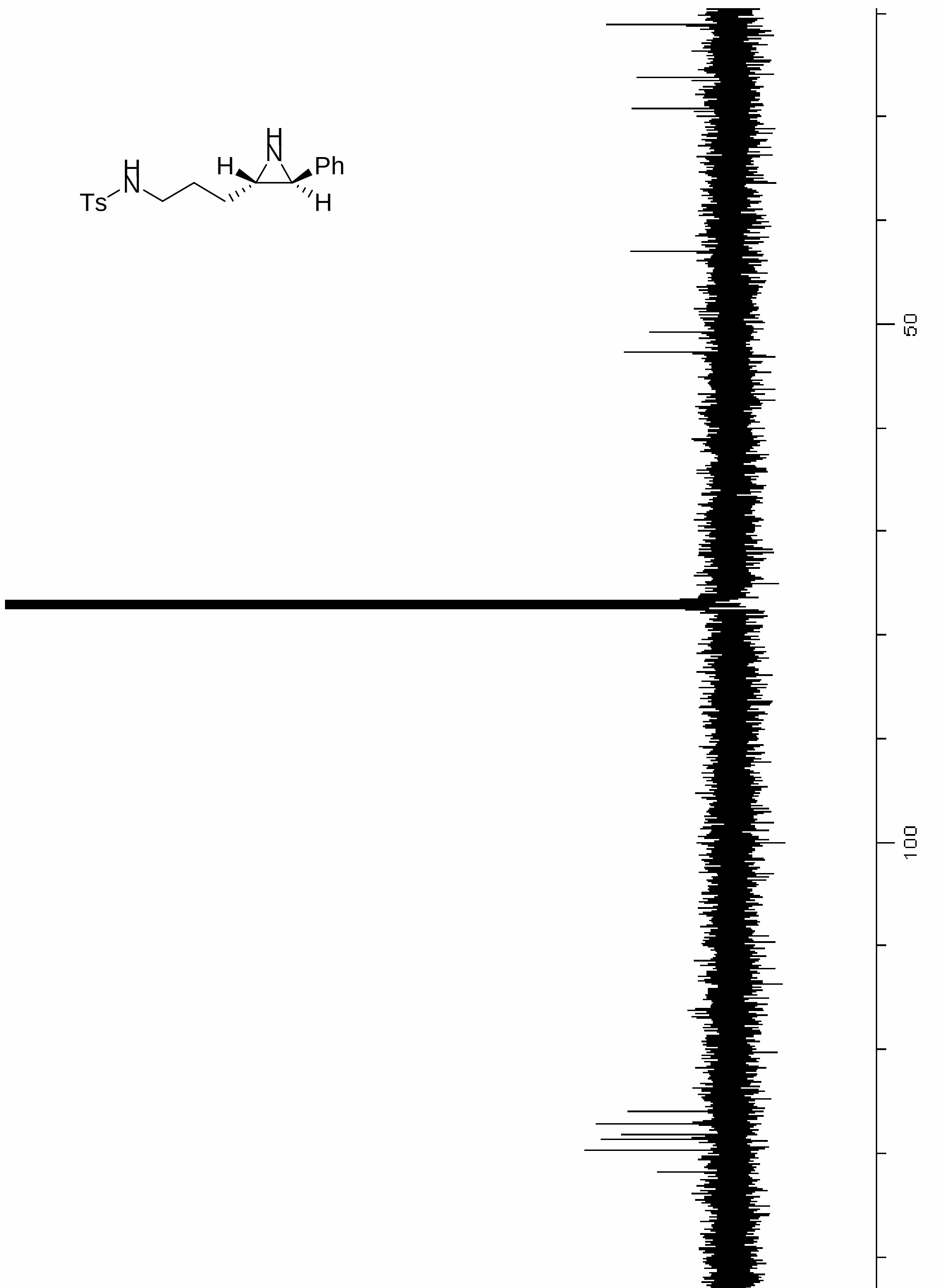
$^{13}C$ NMR ($CDCl_3$) piperidine **16**



$^{1}$H NMR ($CDCl_3$) aziridine **17**



$^{13}$C NMR ($CDCl_3$) aziridine **17**



## References

(1) Unthank, M. G.; Husain, N.; Aggarwal, V. K. *Angew. Chem. Int. Ed.*, **2006**, *45*, 7066.