Electronic Supplementary Information

Asymmetric Olefin Aziridination Using a Newly Designed Ru(CO)(salen) Complex as Catalyst

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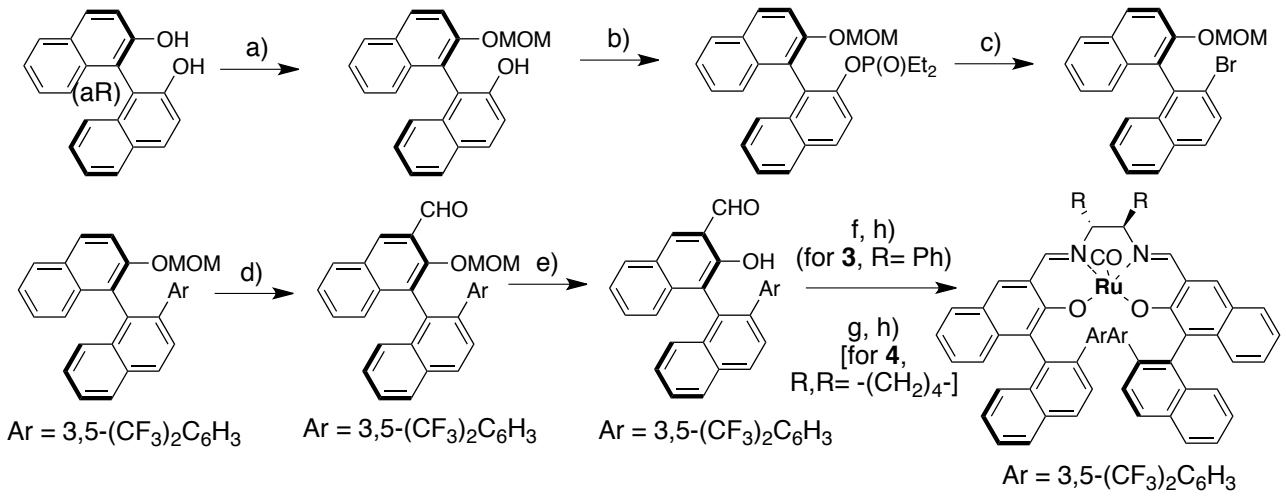
1. General

^{1}H and ^{13}C NMR spectra were recorded at JEOL JNM–AL–400 spectrometer at 400 and 270 MHz, respectively. All signals were expressed as ppm downfield from tetramethylsilane used as an internal standard (δ–value in $CDCl_3$). Optical rotations were measured with a JASCO P–1020 polarimeter. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC–10AT–VP equipped with a chiral stationary phase. Column chromatography was conducted on a silica gel 60N (spherical, neutral), 63-210 mm, available from Kanto Chemical Co., Inc., or a Chromatorex® NH (spherical, basic), 100-200 mm, available from Fuji Silysia Chemical LTD. Ru(CO)(salen) complex **3**,[1)] and 2-(trimethylsilyl)ethanesulfonyl azide ($SESN_3$)[1,2)] were prepared according to the literatures.

1.1. Scheme for the synthesis of Ru(CO)(salen) complexes[1)]



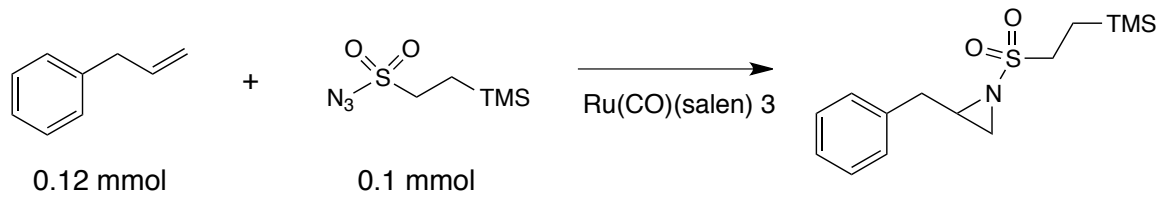
a) diisopropylethylamine, MOMCl, CH_2Cl_2, 0°C, 82%; b) *n*-BuLi, THF, -78°C; $ClP(O)(OEt)_2$, 76%; c) Li/naphthalene, THF, -78°C, 1,2-dibromoethane, THF, -78°C to r.t., 60%; d) $Pd(PPh_3)_4$ (5 mol %), 3,5-bis(trifluoromethyl)phenylboronic acid, 1M Na_2CO_3, toluene, reflux, 70%; e) TMEDA, *n*-BuLi, -78°C, DMF, THF, 65%; e) HCl/*i*PrOH (20%, *w/w*), THF, 99%; f) (1*R*, 2*R*)-diphyenyl-1,2-diamine, EtOH, reflux, 95%; g) (1*R*, 2*R*)-1,2-diaminocyclohexane, EtOH, reflux, 95%; h) $Ru_3(CO)_{12}$, EtOH, N_2, 65%.

1.2 Synthesis of (a*R*, *R*)-Ru(CO)(salen) complex 3 [1b)]

A solution of salen ligand (170 mg, 0.14 mmol) and triruthenium dodecacarbonyl ($Ru_3(CO)_{12}$, 180 mg, 2 eq) in dehydrated EtOH (6 mL) was refluxed under argon atmosphere for 48 h. The mixture was evaporated and subjected to chromatography on silica gel (hexanes/ethyl acetate = 4:1) to give **3** as a reddish-brown solid (122 mg, 65 % yield); IR (KBr) 3423, 3055, 1944, 1658, 1608, 1577,

1546, 1494, 1479, 1425, 1384, 1324, 1278, 1180, 1132, 1091, 954, 894, 815, 748, 705, 680, 536 cm^{-1}; HRMS (ESI-TOF): Ru(CO)(salen) *m/z* $[M+H]^+$ Calcd for $[C_{73}H_{43}F_{12}N_2O_3Ru_1]^+$: 1324.2062; Found: 1324.2046; elemental analysis: Calcd (%) for $C_{73}H_{42}F_{12}N_2O_3Ru \bullet 1.5H_2O$: C 64.04, H 3.46, N 2.05; Found: C 64.00, H 3.59, N 1.97

2. Solvent screening

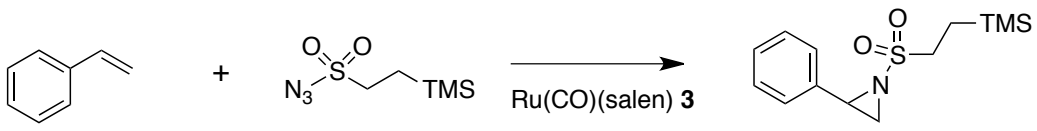


0.12 mmol 0.1 mmol

condition: M.S. 4A (50 mg), solvent (0.4 mL), r.t. to 40oC, 3 mol% catalyst roading

solvents	yield	ee
$CHCl_3$	54 %	88%
EtOAc	51 %	88 %
Toluene	54 %	90 %
DCM	81 %	90%

3. Ru(CO)(salen) 3 – catalyst loading



0.12 mmol 0.1 mmol

condition: M.S. 4A (30 mg), DCM (0.2 mL), r.t., 6 hr

catalyst amount	yield[a]	ee
3 mol %	99 %	90 %
2 mol %	99 %	90 %
1 mol %	99 %	90 %
0.5 mol %	99 %	90 %
0.1 mol %	57 %	90 %

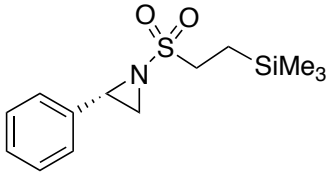
[a] Isolated yield.

4. Asymmetric aziridination of alkenes

4.1. Typical experiment for asymmetric aziridination of alkenes using a combination of Ru(CO)(salen) complex 3 with $SESN_3$.

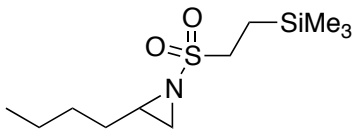
A dried Schlenk tube was charged with 4Å MS (50 mg) and then additionally dried with a heat gun for 10 min. The Schlenk tube was then evacuated, backfilled with nitrogen and equipped with a magnetic stir bar. To the Schrenlk tube, were added Ru(CO)(salen) complex **3** (0.5 ~ 3 mol%) and 0.4 ml of solvent, followed by olefins (0.36 ~ 0.9 mmol) and the azide (0.3 mmol) at room temperature. After stirred for another 6 ~ 24 h, the mixture was filtered through a Celite pad. Evaporation of the resulting solution and chromatographic separation on silica gel (Hexane/AcOEt=10/1 ~ 5/1) gave the corresponding aziridination compounds.

4.2. (2*S*)-2-(Phenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 1, entry 2)



Colorless oil (99%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0mL/min), t_r (Major)=15.0 min, t_r (Minor)=21.4 min].; $[\alpha]_D^{27.1}$ = +124.1 (*c* = 1.35, $CDCl_3$); {$[\alpha]_D^{25}$= + 115 (*c* = 1.3, $CDCl_3$)};[1a)] ^1H NMR ($CDCl_3$, 400 MHz): δ 7.21-7.32 (m, 5H), 3.65 (dd, *J*=4.4, 4.4 Hz, 1H), 3.05-3.10 (m, 2H), 2.92 (d, *J*=6.8 Hz, 1H), 2.37 (d, *J*=4.4 Hz, 1H), 1.06-1.11 (m, 2H), -0.017 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.2, 128.7, 128.4, 126.5, 49.1, 40.5, 35.1, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{13}H_{21}NO_2SSi$: 306.0954; Found: 306.0960.

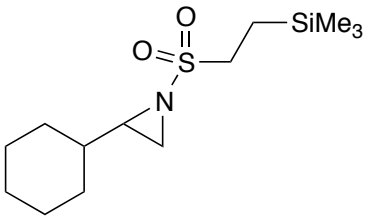
4.3. 2-Butyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 1)



Colorless oil (74%); >99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=10.6].; $[\alpha]_D^{23}$ = +20.0 (*c* 0.83, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 3.03-3.08 (m, 2H), 2.70-2.72 (m, 1H), 2.58 (d, *J*=6.8 Hz, 1H), 2.05 (d, *J*=5.2 Hz, 1H), 1.33-1.57 (m, 6H), 1.11-1.14 (m,

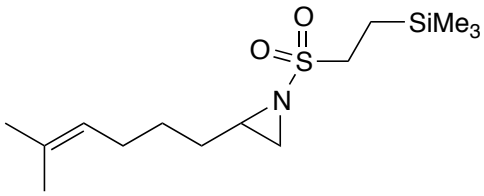
2H), 0.91 (t, *J*=6.8 Hz, 3H), 0.05 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 45.8, 39.1, 33.6, 31.2, 28.9, 22.8, 14.0, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{11}H_{25}NO_2SSi$: 286.1267; Found: 286.1266.

4.4. 2-Cyclohexyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 2)



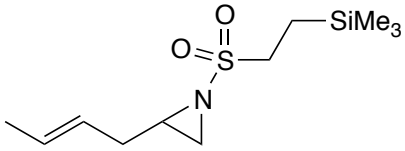
Colorless oil (45%); >99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/*i*-PrOH=99/01, 1.0 mL/min), t_r (Major)=13.8 min].; $[\alpha]_D^{22}$ = +18.47 (*c* 1.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.00-3.06 (m, 2H), 2.50-2.54 (m, 2H), 2.21 (d, *J*=4.4 Hz, 1H), 1.63-1.80 (m, 5H), 1.11-1.23 (m, 8H), 0.04 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 48.6, 43.8, 39.4, 32.3, 30.4, 29.7, 26.0, 25.6, 25.4, 9.7, -2.0 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{13}H_{27}NO_2SSi$: 312.1426; Found: 312.1460.

4.5. 2-(5-Methylhex-4-en-1-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 3)



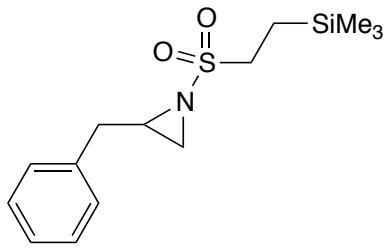
Colorless oil (54%); 89% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=6.3 min, t_r (Minor)=7.4 min].; $[\alpha]_D^{22}$ = + 8.94 (*c* 0.96, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.99-5.05 (m, 1H), 2.96-3.03 (m, 2H), 2.63-2.67 (m, 1H), 2.52 (d *J*=10.4 Hz, 1H), 2.00 (d, *J*=4.28 Hz, 1H), 1.61 (s, 3H), 1.53 (s, 3H), 1.38-1.51 (m, 6H), 1.04-1.11 (m, 2H), 0.00 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.2, 123.8, 48.4, 39.0, 33.4, 30.9, 27.4, 26.9, 25.7, 17.7, 9.8, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{29}NO_2SSi$: 325.1580; Found: 326.1238.

4.6. 2-Butyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry4)



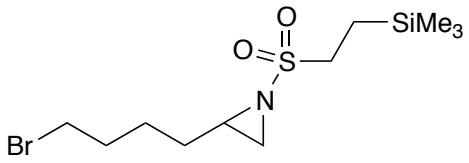
Colorless oil (58%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=6.41 min, t_r (Minor)=7.1 min].; $[\alpha]_D^{24}$ = +25.8 (*c* 1.72, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.56-5.62 (m, 1H), 5.40-5.46 (m, 1H), 3.03-3.08 (m, 2H), 2.71-2.76 (m, 1H), 2.60 (d, *J*=8.0 Hz, 1H), 2.18-2.28 (m, 2H), 2.10 (d, *J*=4 Hz, 1H), 1.68 (dd, *J*=8.0 Hz, 3H), 1.11-1.15 (m, 2H), 0.07 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.8, 125.4, 48.3, 39.2, 34.3, 32.3, 18.0, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{11}H_{23}NO_2SSi$: 284.1111; Found: 284.1164.

4.7. 2-Benzyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 6)



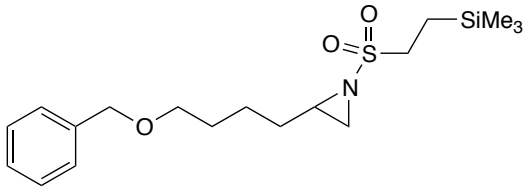
Colorless oil (91%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=16.9 min, t_r (Minor)=24.1 min].; $[\alpha]_D^{22}$ = +19.2 (*c* 0.76, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22-7.30 (m, 5H), 2.70-2.98 (m, 3H), 2.60-2.68 (m, 3H), 2.17 (d *J*=4.4 Hz, 1H), 0.85-1.02 (m, 2H), -0.05 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.2, 128.9, 128.7, 127.1, 48.4, 40.9, 37.7, 32.3, 8.9, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{23}NO_2SSi$: 320.1111; Found: 320.1122.

4.8. 2-(4-Bromobutyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 6)



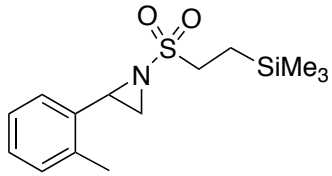
Colorless oil (95%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL WHELK-O1 (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=35.5 min, t_r (Minor)=42.4 min].; $[\alpha]_D^{22}$ = +14.7 (*c* 0.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.42 (t, *J*=8.0 Hz, 3H), 3.04-3.09 (m, 2H), 2.73 (m, 1H), 2.59 (d, *J*=8.0 Hz, 1H), 2.10 (d, *J*=4.4 Hz, 1H), 1.91-1.93 (m, 2H), 1.61-1.65 (m, 4H), 1.11-1.16 (m, 2H), 0.07 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 48.9, 38.3, 33.6, 33.2, 31.9, 30.5, 25.4, 9.7, -2.04 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{11}H_{24}BrNO_2SSi$: 364.0373; Found: 364.0384.

4.9. 2-[3-(Benzyloxy)propyl]-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 7)



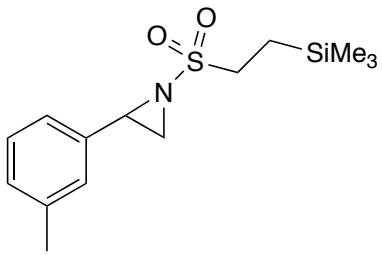
Colorless oil (65%); 87% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=95/05, 1.0 mL/min), t_r (Major)=25.8 min, t_r (Minor)=29.3 min].; $[\alpha]_D^{22}$ = +17.64 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.23-7.32 (m, 5H), 4.46 (s, 2H), 3.45 (t, *J*=6.0 Hz, 2H), 2.99-3.06 (m, 2H), 2.67 (m, 1H), 2.55 (d, *J*=6.8 Hz, 1H), 2.04 (d, *J*=4.3 Hz, 1H), 1.49-2.05 (m, 6H), 1.07-1.14 (m, 2H), 0.03 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 128.4, 127.6, 127.5, 72.9, 69.9, 48.8, 38.8, 33.5, 31.2, 29.3, 23.6, 9.7 -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{18}H_{31}NO_3SSi$: 392.1686; Found: 392.1714.

4.10. 2-(*o*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 1)



Colorless oil (99%); 97% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0mL/min), t_r (Major)=10.1 min, t_r (Minor)=11.3 min].; $[\alpha]_D^{20.0}$ = +126.2 (*c* = 0.9, $CDCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 -7.22 (m, 4H), 3.77 (dd, *J*=4.4, 5.2 Hz, 1H), 3.09-3.14 (m, 2H), 2.93 (d, *J*=7.2 Hz, 1H), 2.40 (s, 3H), 2.29 (d, *J*=4.4 Hz, 1H), 1.11-1.16 (m, 2H), 0.03 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 111.4, 130.1, 128.1, 126.2, 125.5, 49.1, 38.3, 34.9, 19.1, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{23}NO_2SSi$: 320.1111; Found: 320.1271.

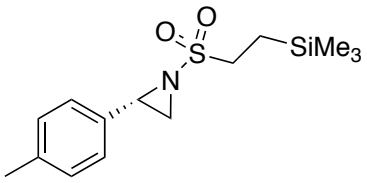
4.11. 2-(*m*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 2)



Colorless oil (99%); >90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=11.6 min, t_r

(Minor)=16.9 min].; $[\alpha]_D^{20}$ = +115.8 (*c* = 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.05-7.22 (m, 4H), 3.62 (dd, *J*=4.4, 4.4 Hz, 1H), 3.05-3.10 (m, 2H), 2.91 (d, *J*=7.2 Hz, 1H), 2.37 (d, *J*=5.2 Hz, 1H), 2.3 (s, 3H), 1.07-1.12 (m, 2H), -0.01 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4, 135.0, 129.2, 128.6, 127.1, 123.6, 49.1, 40.5, 35.0, 21.3, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{23}NO_2SSi$: 320.1111; Found: 320.1117.

4.12. (2*S*)-2-(*p*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 3)



White solid (99%); 89% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=90/10, 1.0 mL/min), t_r (Major)=12.3 min, t_r (Minor)=19.4 min].; $[\alpha]_D^{20}$ = +125.1 (*c* = 0.96, $CHCl_3$).; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.11-7.23 (m, 4H), 3.64 (dd, *J*=6.8, 6.8 Hz, 1H), 3.05-3.11 (m, 2H), 2.92 (d, *J*=10.8 Hz, 1H), 2.37 (d, *J*=6.8 Hz, 1H), 2.32 (s, 3H), 1.07-1.14 (m, 2H), 0.00 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.3, 129,3, 126.4, 49.1, 40.5, 34.9 21.2, 9.6, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{23}NO_2SSi$: 320.1111 Found: 320.1113.

4.12.1. Crystal structure analysis of (2*S*)-2-(*p*-tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine

Single crystals of the aziridine product [**Table 3** (entry 3)] for X-ray diffraction experiments were obtained by recrystallization from Et_2O. The data were collected at 100 K on a Bruker SMART APEX II diffractometer equipped with APEX II 4K CCD area detector, a graphite monochromator and a rotating-anode X-ray tube (Mo-*Kα* radiation, l = 0.71073) focused with Helios multilayer optics for Mo-*Ka* radiation operating at 50 kV and 24 mA. The data collection was performed by APEX2 software program.[4] The cell refinement and the data reduction were carried out using SAINT-NT.[5] The absorption correction was carried out using SADABS.[6] The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 with SHELXLTL.[7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3.[8] Crystallographic data for **Table 3** (entry 3): $C_{17}H_{23}NO_2SSi$, colorless block, 0.15x0.08x0.08 mm^3, monoclinic, $P2_1$, a = 10.8858(17), b = 5.9432(9), c = 12.636(2) Å, V = 808.8(2) $Å^3$, Z = 2, *Flack* = 0.04(6), R = 0.0325 and Rw = 0.0735.

CCDC 870579 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

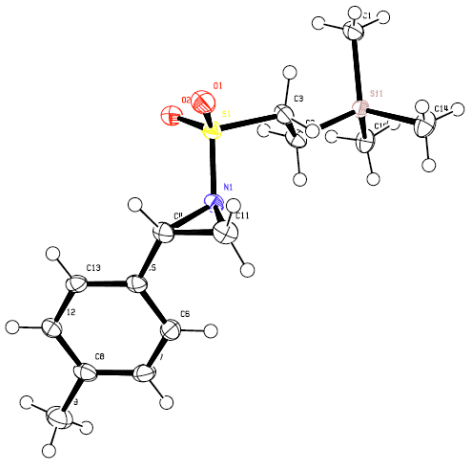
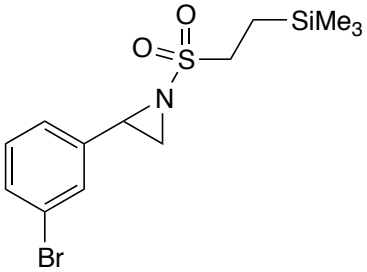


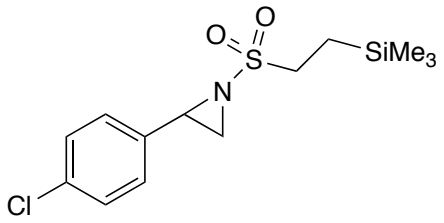
Figure S1. ORTEP view (50% probability) of (2*S*)-2-(*p*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine.

4.13. 2-(3-Bromophenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 4)



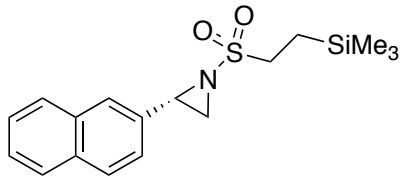
Colorless oil (95 %); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=23.1 min, t_r (Minor)=29.7 min]; $[\alpha]_D^{21}$ = +115.4 (*c* = 0.94, $CHCl_3$).; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.42 (m, 4H), 3.62 (dd, *J*=4.4, 4.4 Hz, 1H), 3.06-3.11 (m, 2H), 2.91 (d, *J*=7.2 Hz, 1H), 2.32 (d, *J*=5.2 Hz, 1H), 1.02-1.16 (m, 2H), 0.00 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.6, 131.6, 130.2, 129.4, 125.4, 122.8, 49.2, 39.3, 34.5, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{13}H_{20}BrNO_2SSi$: 384.0060; Found: 384.0082.

4.14. 2-(4-chlorophenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 5)



Colorless oil (96%); 90% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1 mL/min), t_r (Major)=15.8 min, t_r (Minor)=24.8 min].; $[\alpha]_D^{21}$ = +121.2 (*c* = 1.12, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28 (d, *J*=8.8 Hz, 2H), 7.19(d, *J*=8.79 Hz, 2H), 3.62 (dd, *J*=4.4, 4.4 Hz, 1H), 3.04-3.10 (m, 2H), 2.91 (d, *J*=7.6 Hz 2H), 2.32 (d, *J*=8.4 Hz, 1H), 1.05-1.10 (m, 2H), -0.01 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.4, 133.8, 128.9, 127.9, 49.1, 39.4, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{13}H_{20}ClNO_2SSi$: 340.0565; Found: 340.0573.

4.15. (2*S*)-2-(naphthalen-2-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 6)



White solid (99%); 91% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=54.8 min, t_r (Minor)=126.3 min].; $[\alpha]_D^{21}$ = +125.1 (*c* = 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81 (m, 4H), 7.22-7.49 (m, 3H), 3.84-3.87 (dd, *J*=4.4, 4.4 Hz, 1H), 3.11-3.16 (m, 2H), 3.02 (d, *J*=6.8 Hz, 1H), 1.12-1.16 (m, 2H), 0.00 (s, 9H).; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.2, 132.5, 128.6, 127.8, 126.6, 126.2, 123.6, 49.1, 40.7 35.2, 9.7, -2.0 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{17}H_{23}NO_2SSi$: 356.1111; Found: 356.1127.

4.15.1. Crystal structure analysis of (2*S*)-2-(Naphthalen-2-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 6)

Single crystals of the aziridine product [**Table 3** (entry 6)] for X-ray diffraction experiments were obtained by recrystallization from CH_2Cl_2/Hexane. The data were collected at 100 K on a Bruker SMART APEX II diffractometer equipped with APEX II 4K CCD area detector, a graphite monochromator and a rotating-anode X-ray tube (Mo-*Ka* radiation, l = 0.71073) focused with Helios multilayer optics for Mo-*Kα* radiation operating at 50 kV and 24 mA. The data collection

was performed by APEX2 software program.[3] The cell refinement and the data reduction were carried out using SAINT-NT.[4] The absorption correction was carried out using SADABS.[5] The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 with SHELXLTL.[6] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed from the difference map and refined with geometrical and isotropic displacement parameters. Molecular plot was obtained with ORTEP-3.[7] Crystallographic data for **Table 3** (entry 6): $C_{17}H_{23}NO_2SSi$, colorless block, 0.15x0.10x0.05 mm^3, orthorhombic, $P2_12_12_1$, a = 6.0186(10), b = 11.5512(18), c = 24.941(4) Å, V = 1733.9(5) $Å^3$, Z = 4, *Flack* = 0.05(6), R = 0.0281 and Rw = 0.0682. CCDC 870052 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

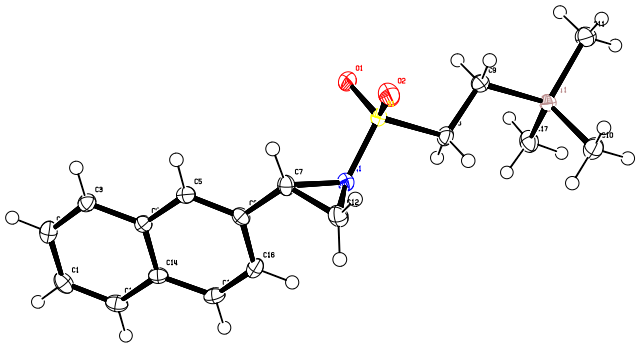
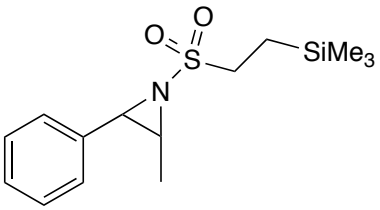


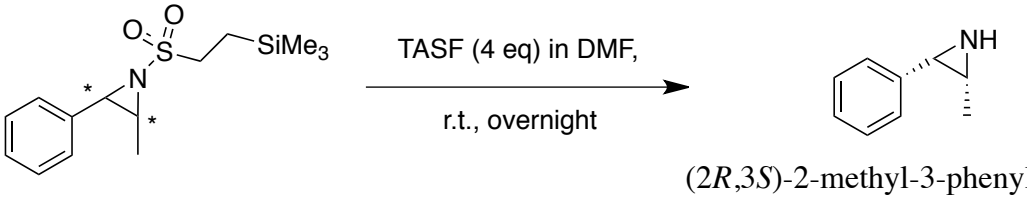
Figure S2. ORTEP view (50% probability) of (2*S*)-2-(naphthalen-2-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine.

4.16. 2-Methyl-3-phenyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 7)



Colorless oil (72%); 99% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=8.4 min, t_r (Minor)=12.2 min].; $[\alpha]_D^{22}$ = +124.1 (c = 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26-7.38 (m, 4H), 3.90 (d, J=8.0 Hz, 1H), 3.10-3.17 (m, 3H), 1.13-1.19 (m, 2H), 1.10 (d, J=8.0 Hz, 3H), 0.05 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.4, 127.9, 127.5, 49.1, 45.7, 40.9, 11.8, 9.8, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{23}NO_2SSi$: 320.1111; Found: 320.1118.

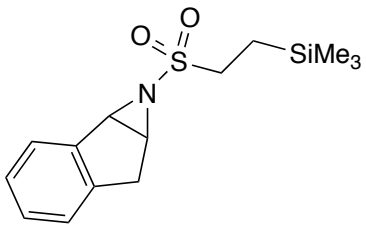
4.16.1 Deprotection of the 2-Methyl-3-phenyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine and determination of its configuration



(2*R*,3*S*)-2-methyl-3-phenylaziridine

A solution of 2-methyl-3-phenyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (38 mg, 0.12 mmol) and TASF (150 mg, 4 equiv.) in DMF (0.5 mL) was stirred at room temperature overnight, and chromatographed on silica gel (hexanes : ethyl acetate = 1:2) to obtain the deprotected aziridine product (11.4 mg, 67%) as a white solid.[8a)] Its spectroscopic data were identical to those previously reported: $[\alpha]_D^{24}$ = +68.5 (*c* = 0.7, $CHCl_3$), {lit.[8b)] $[\alpha]_D^{22}$ = +69.1 (*c* 4.43 × 10^{-3}, $CHCl_3$) for (2*R*,3*S*)-2-methyl-3-phenylaziridine}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17-7.30 (m, 3H), 3.21 (d, *J*=8.0 Hz, 1H), 2.37 (m, 1H), 0.87 (d, *J*=8.0 Hz, 3H) HRMS [ESI-TOF] ($[M + H]^+$) Calcd for $C_9H_{12}N$: 134.0964; Found: 134.1082.

4.17. 1-{[2-(Trimethylsilyl)ethane]sulfonyl}-1,1a,6,6a-tetrahydroindeno[1,2-*b*]aziridine (Table 3, entry 8)



Colorless oil (66%); 97% ee [determined by HPLC analysis using a chiral stationary phase column, DICEL CHIRALCEL OJ-H (Hexane/*i*-PrOH=97/03, 1.0 mL/min), t_r (Major)=15.2 min, t_r (Minor)=18.1 min].; $[\alpha]_D^{22}$ = +26.5 (*c* = 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, *J*=6.8 Hz, 1H), 7.21-7.26 (m, 3H), 4.20 (d, *J*=4.8 Hz, 1H), 3.88 (m, 1H), 3.21 (m, 1H), 3.05-3.09 (m, 2H), 1.07- 1.12 (m, 2H), 0.02 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 127.8, 126.8, 125.7, 124.9, 49.6, 49.5, 43.5, 34.8, 9.7, -2.1 ppm.; HRMS [ESI-TOF] ($[M + Na]^+$) Calcd for $C_{14}H_{21}NO_2SSi$: 318.0954; Found: 318.0963.

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1) a) H. Kawabata, K. Omura and T. Katsuki, *Tetrahedron Lett.,* 2006, **47**, 1571; (*b*) H. Kawabata,

K. Omura, T. Uchida and T. Katsuki, *Chem. Asian J.* 2007, **2**, 248

2) a) S. M. Weinreb, D. M. Demko, T. A. Lessen, J. P. Demers, *Tetrahedron Lett.,* 1986, **27**, 2099. b) L. L. Parker, N. D. Gowans, S. W. Jones, and D. J. Robins, *Tetrahedron*, 2003, **59**, 10165.

3) Bruker APEX2, Version 2008.5-0; Bruker AXS Inc.: Madison, WI (USA), 2005.

4) Bruker SAINT-NT (includes XPREP and SADABS), Version 6.0; Madison, WI (USA), 2005.

5) G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen (Germany), 1996.

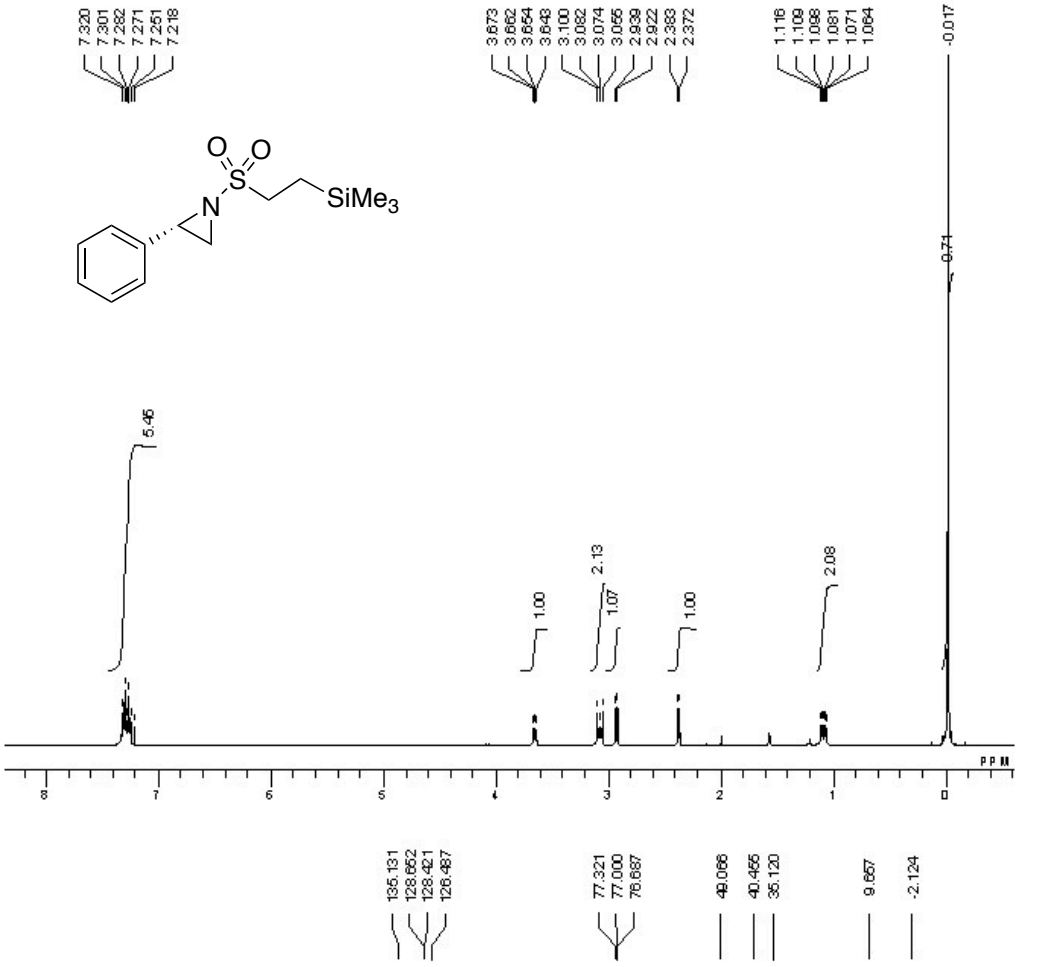
6) a) Bruker SHELXTL (includes XS, XL, XP, and XShell), Version 5.1; Madison, WI (USA), 1997. b) G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112-122.

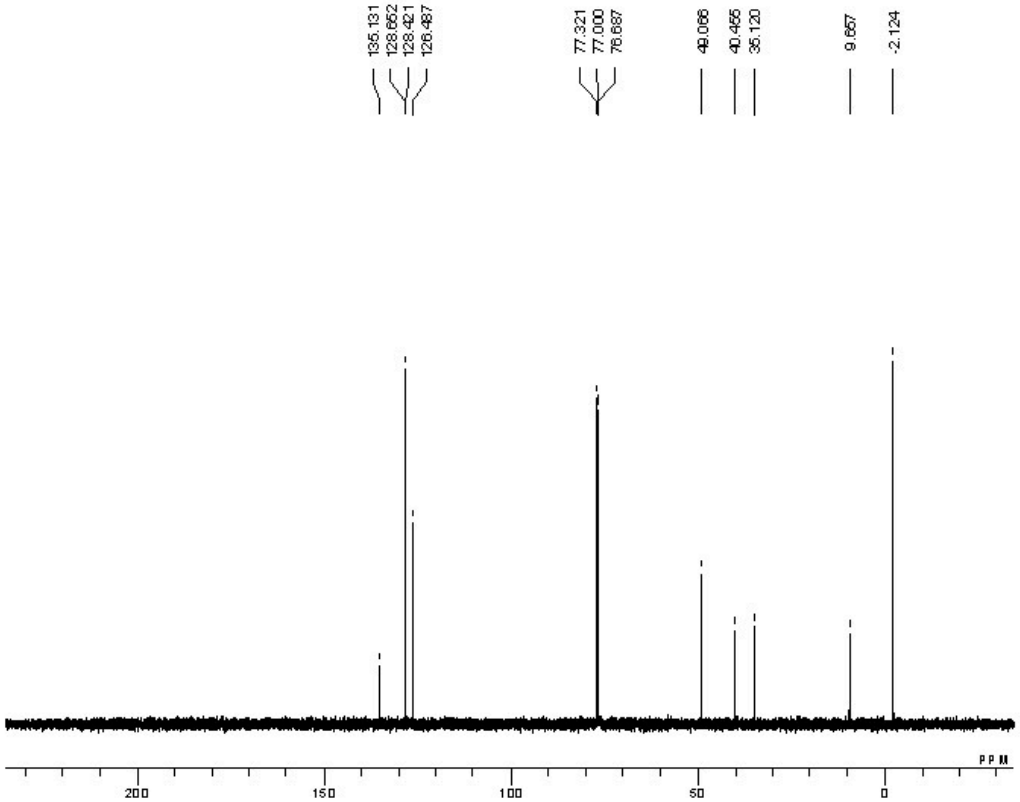
7) L. J. Farrugia, *J. Appl. Crystallogr.,* 1997, **30**, 565.

8) a) P. Dauban and R. H. Dodd, *J. Org. Chem*., 1999, **64**, 5304. b) A. Cruz, I. I. Padilla-Martinez and E. V. Garcia-Baez, *Tetrahedron: Asymmetry*, 2010, **21**, 909.

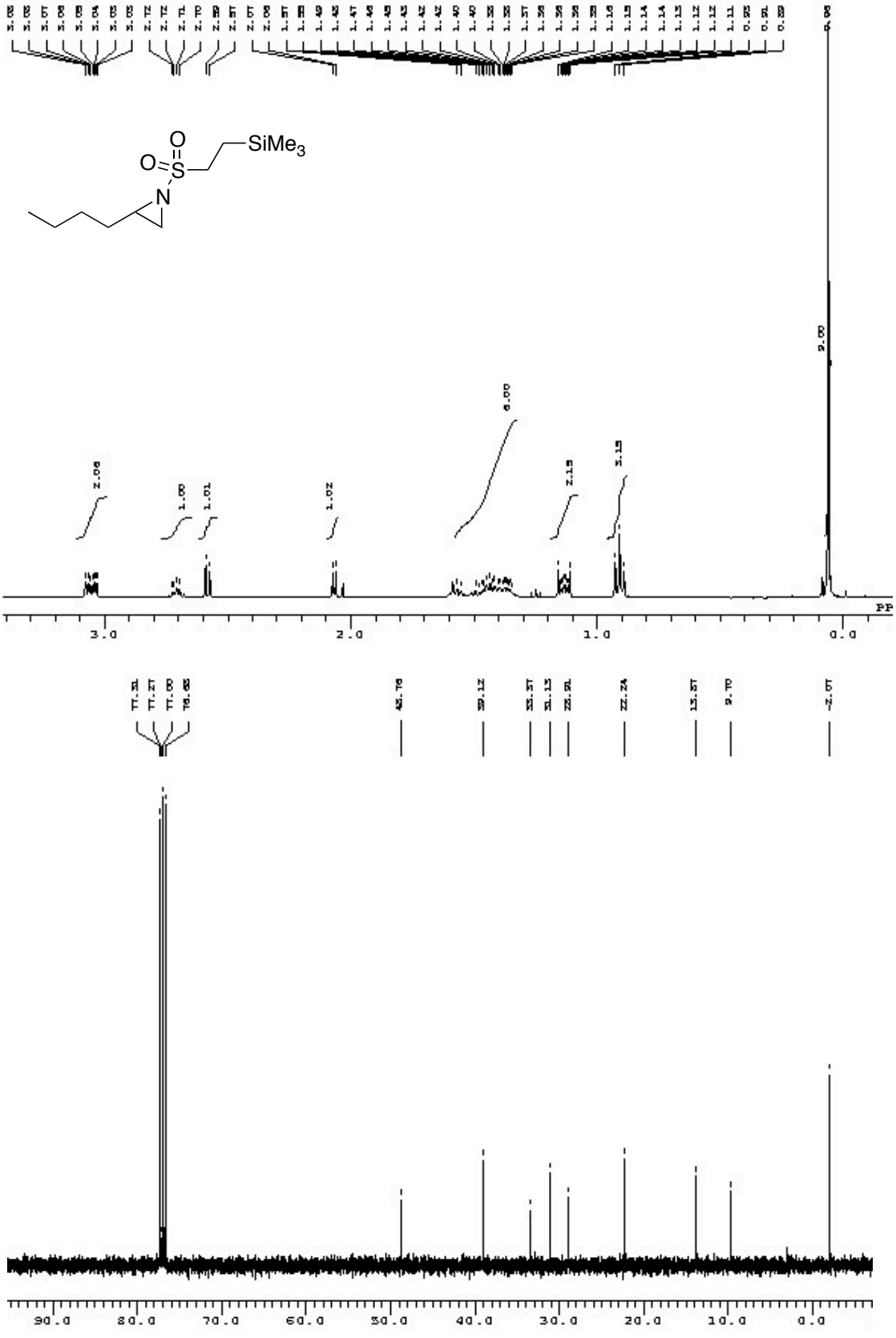
5. ^{1}H and ^{13}C NMR spectra

5.1. (2*S*)-2-(Phenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 1, entry 2)

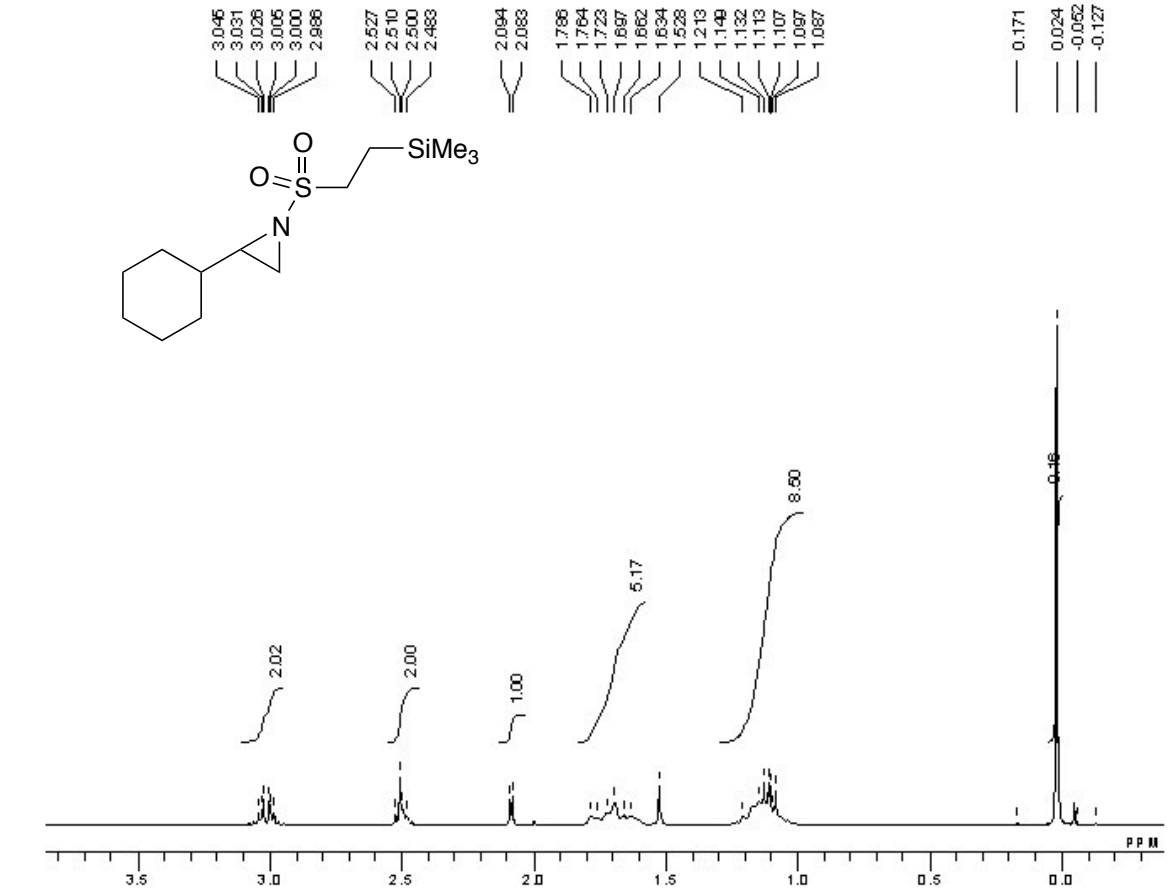


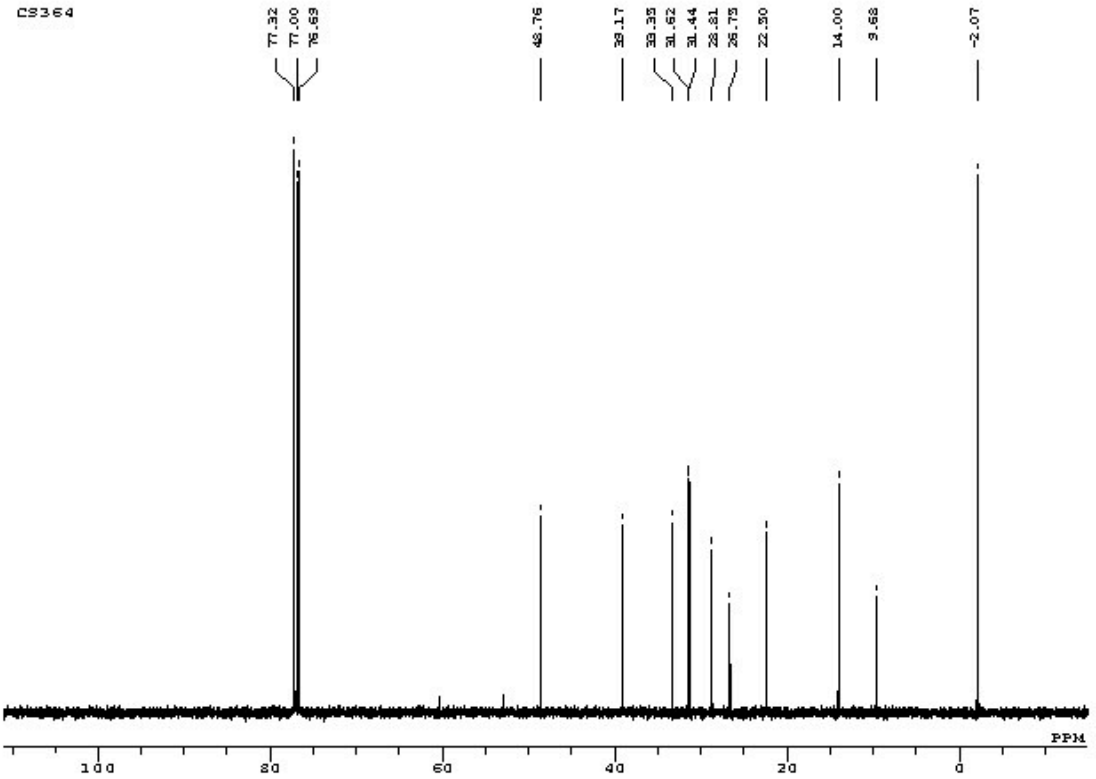


5.2. 2-Butyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry1)

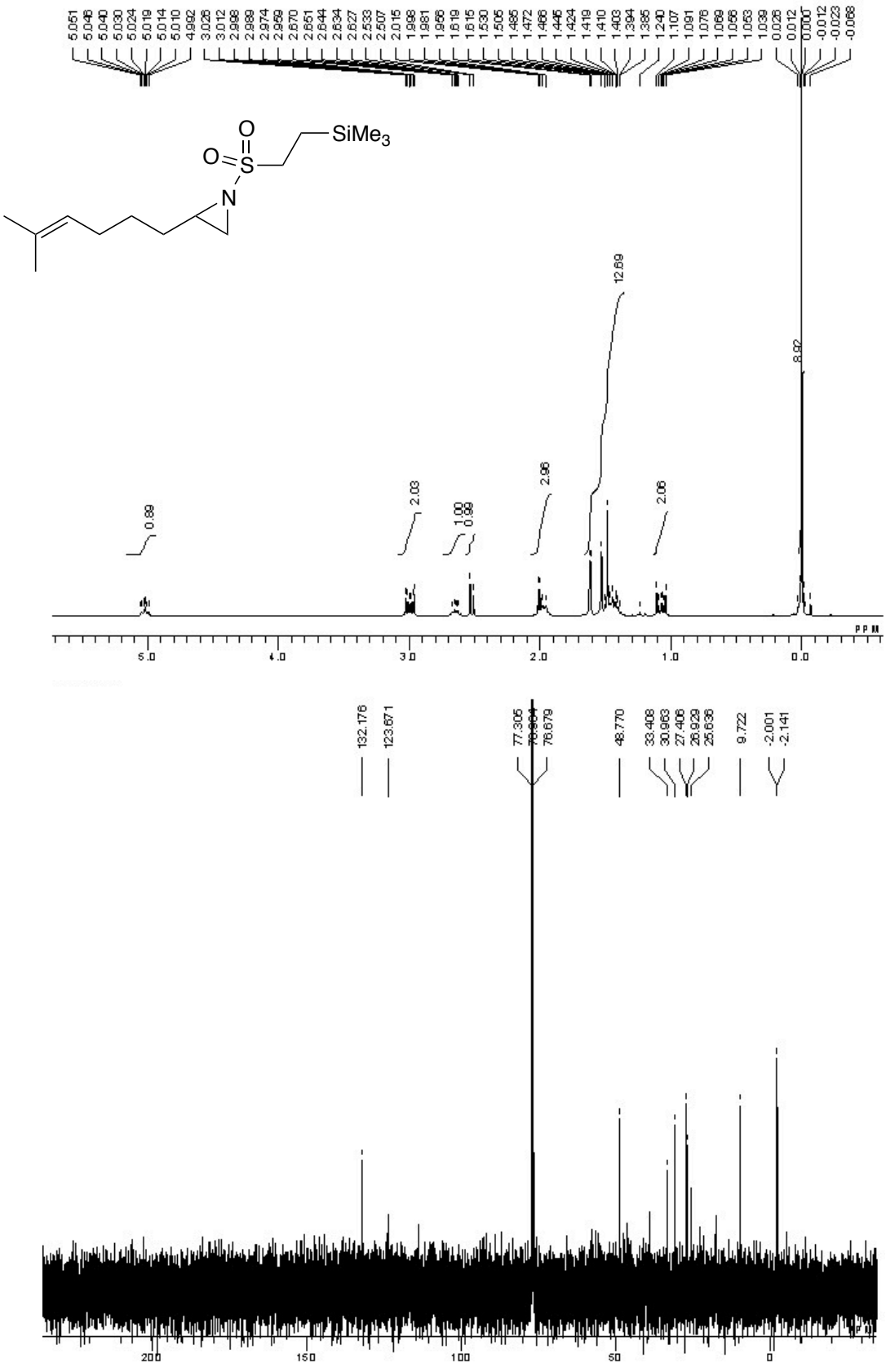


5.3. 2-Cyclohexyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 2)

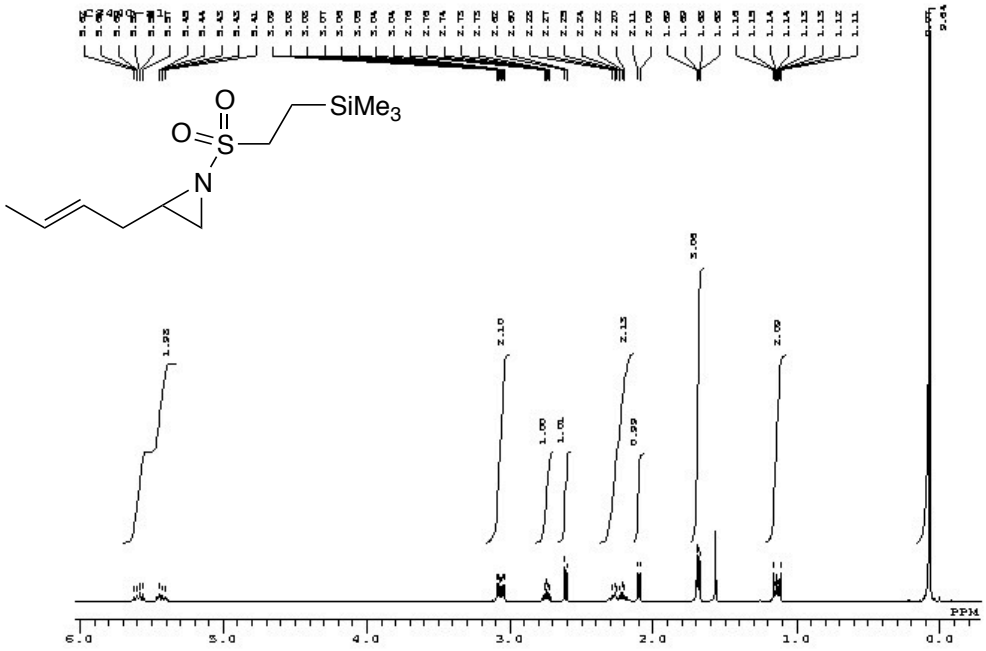


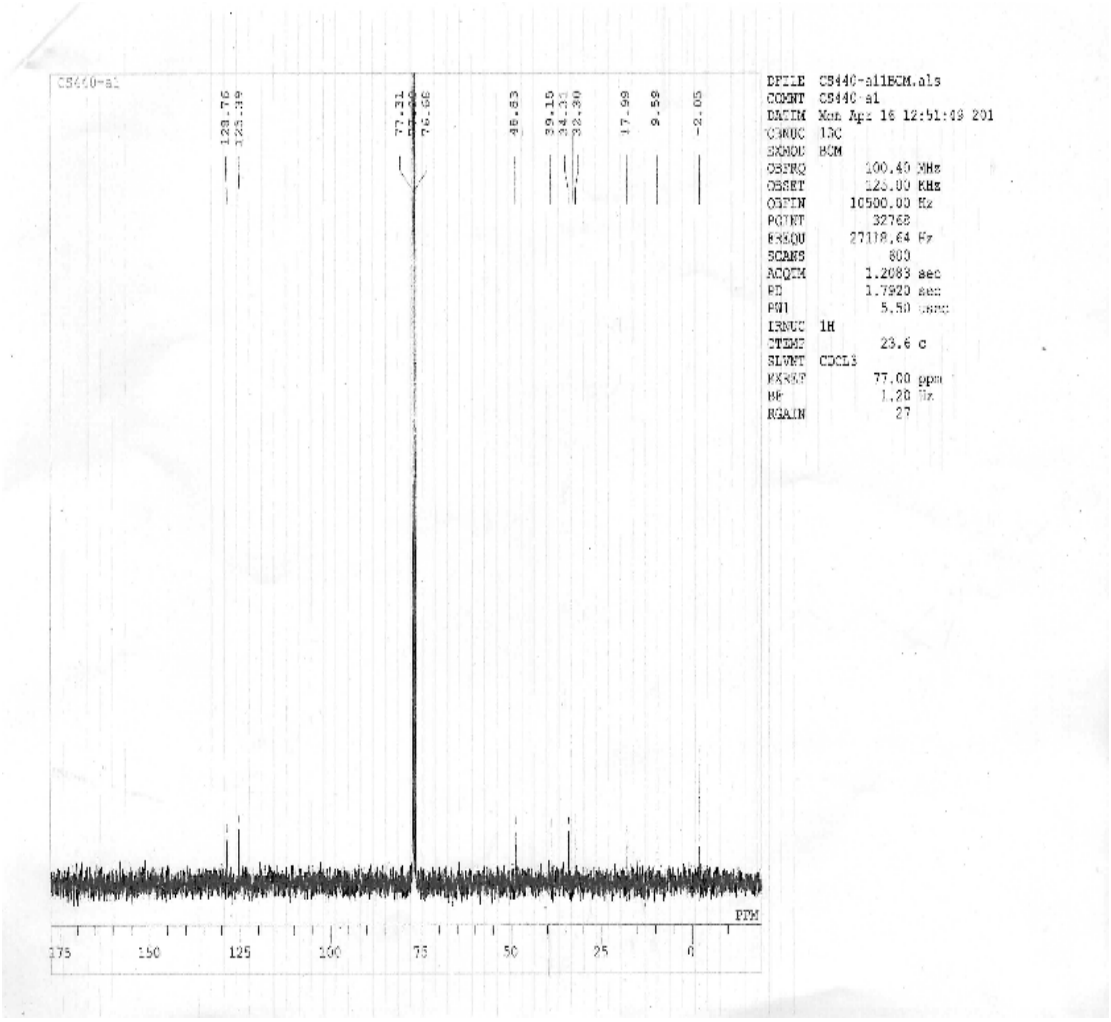


5.4. 2-(5-Methylhex-4-en-1-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 3)

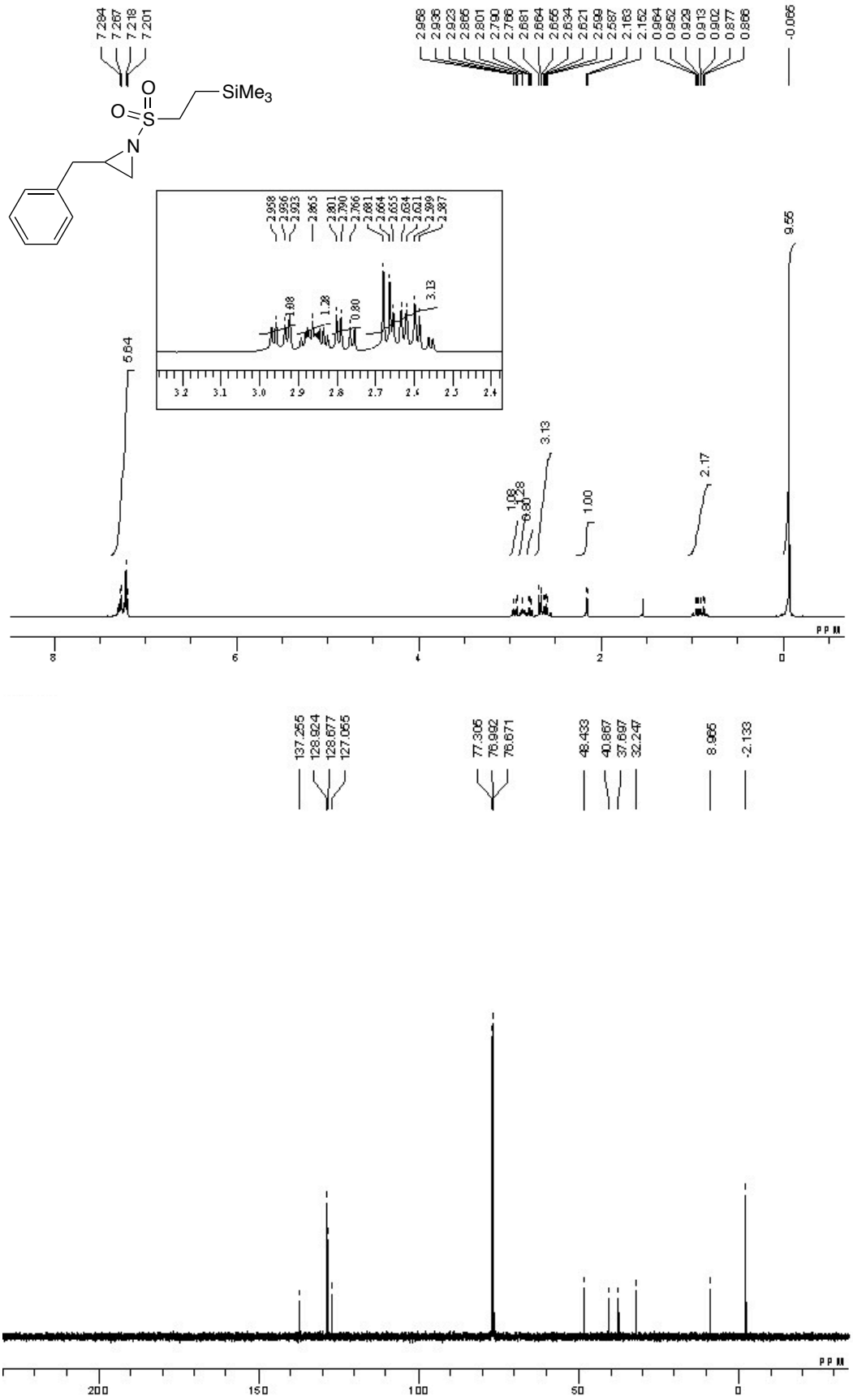


5.5. 2-Butyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry4)

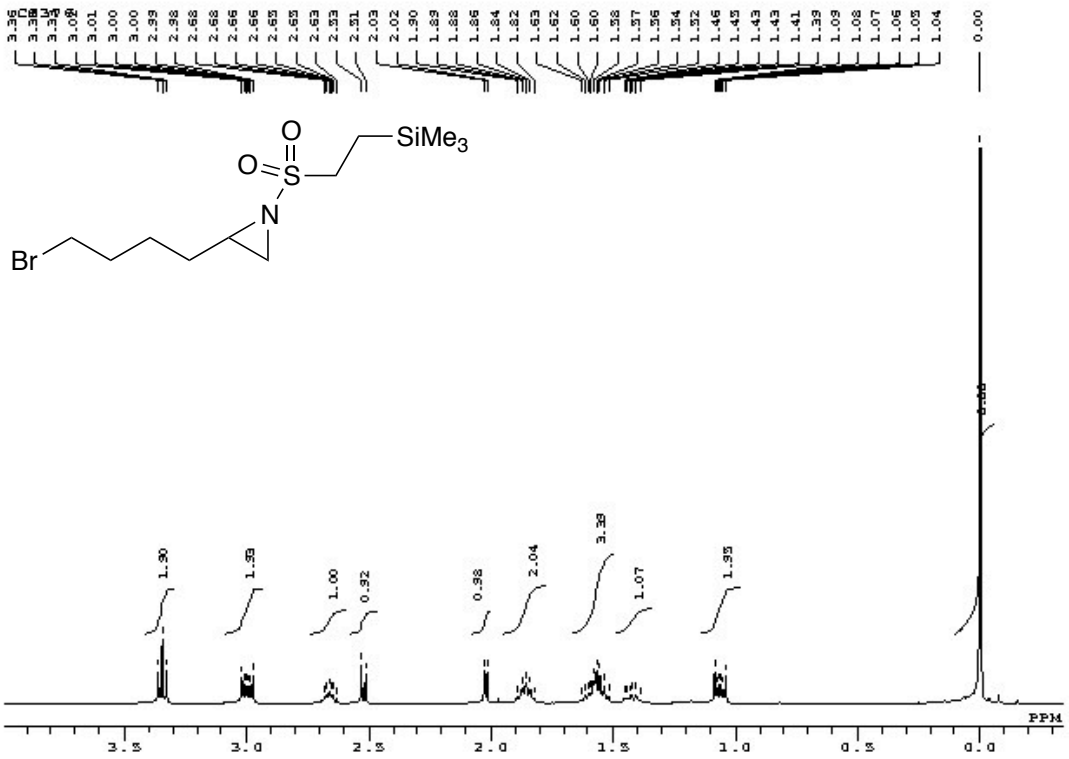


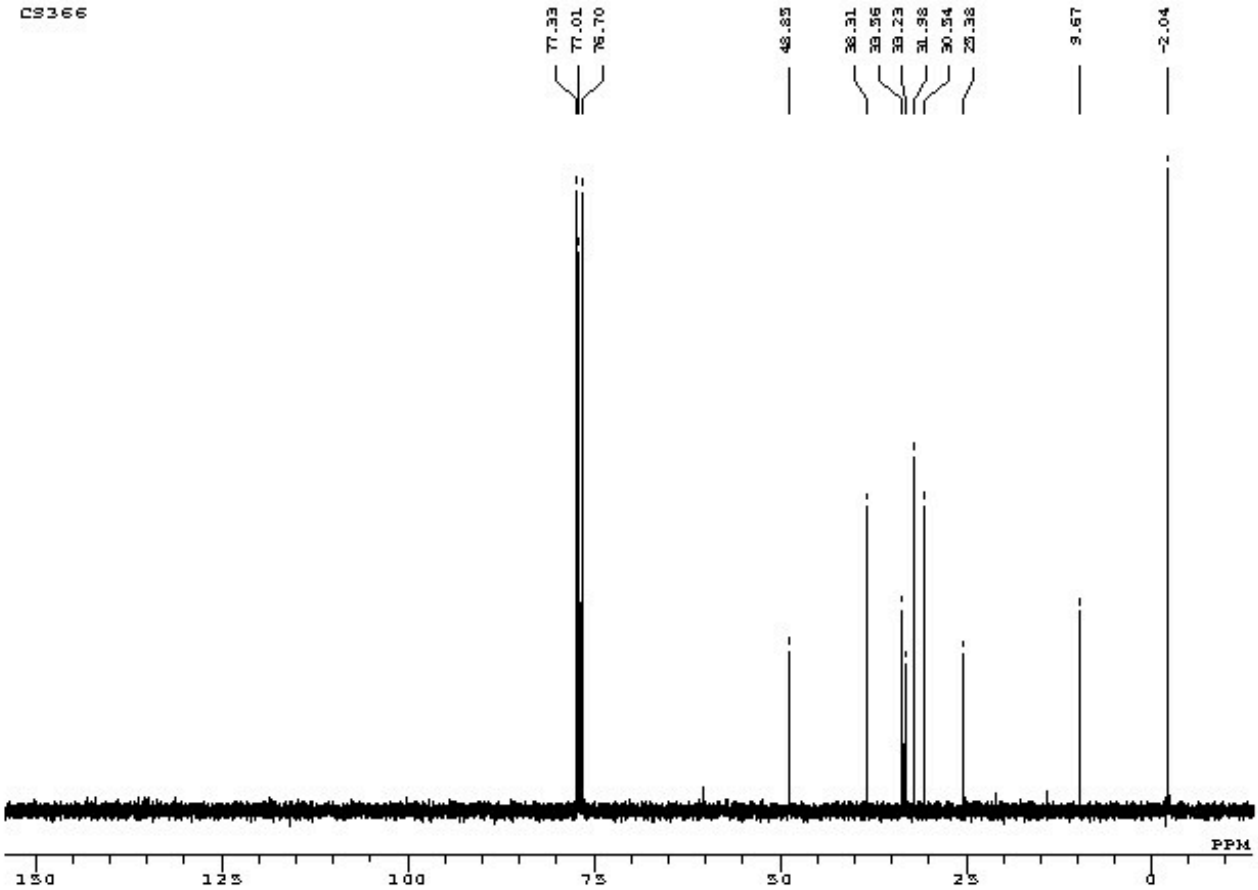


5.6. 2-Benzyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 5)

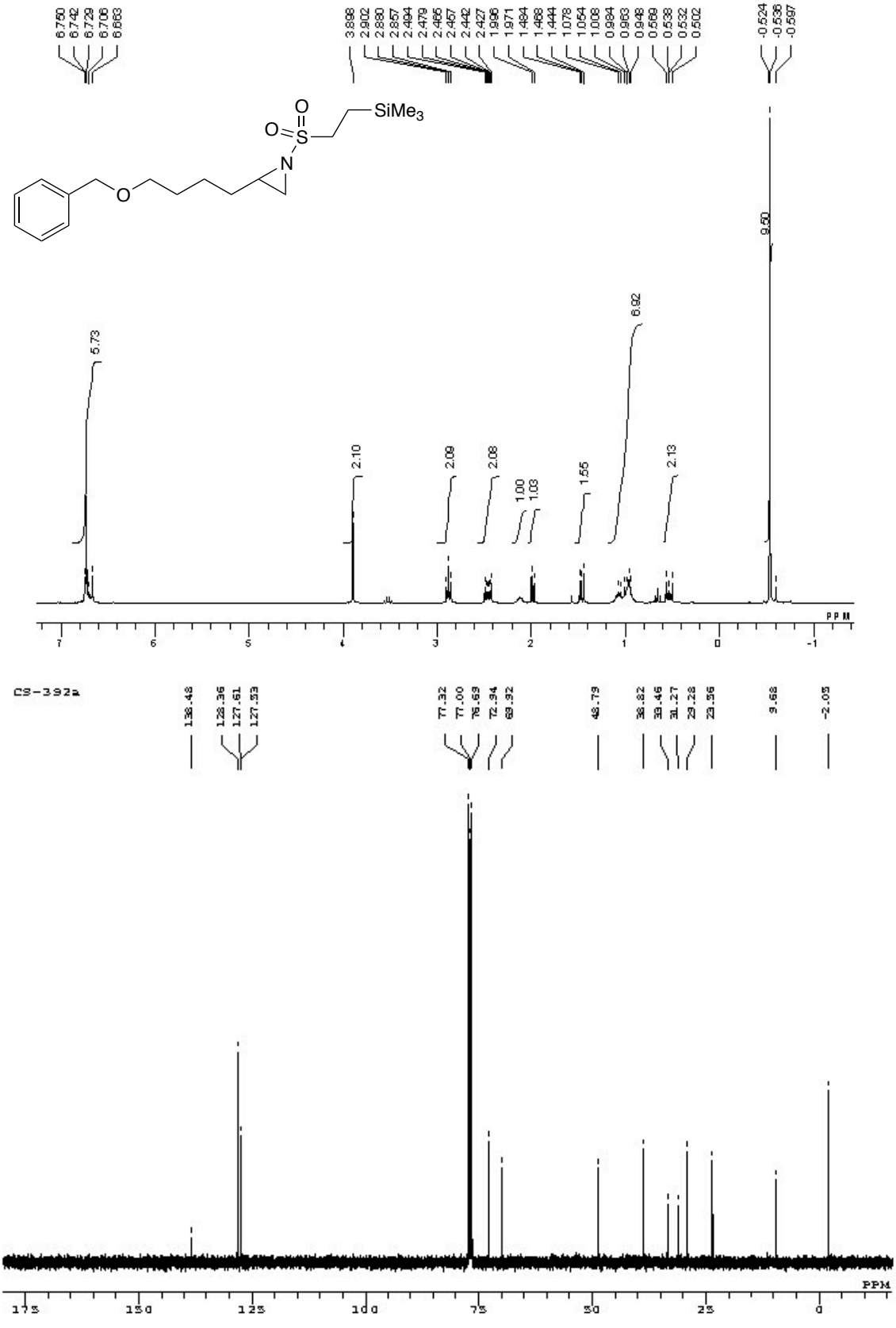


5.7. 2-(4-Bromobutyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 6)

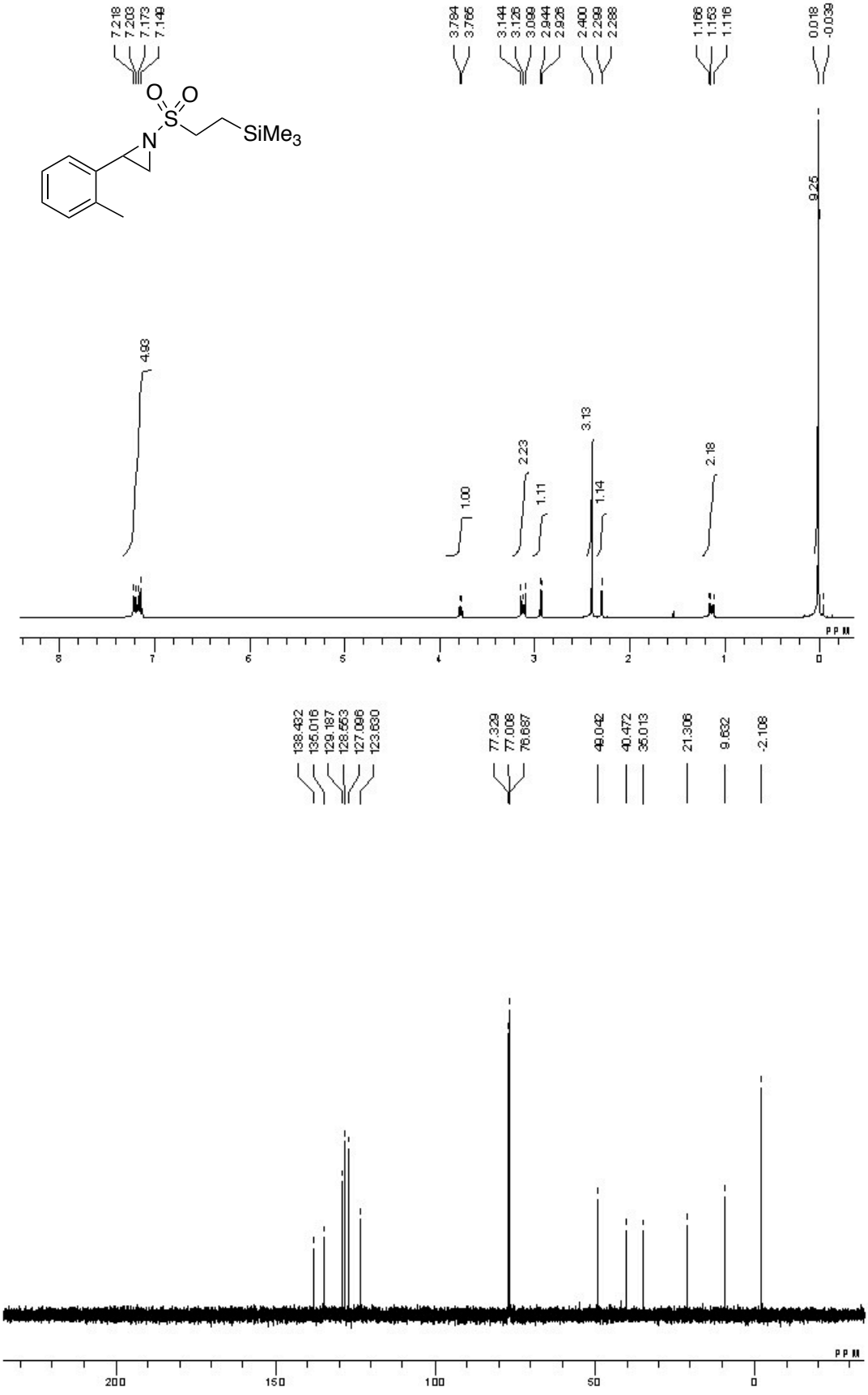




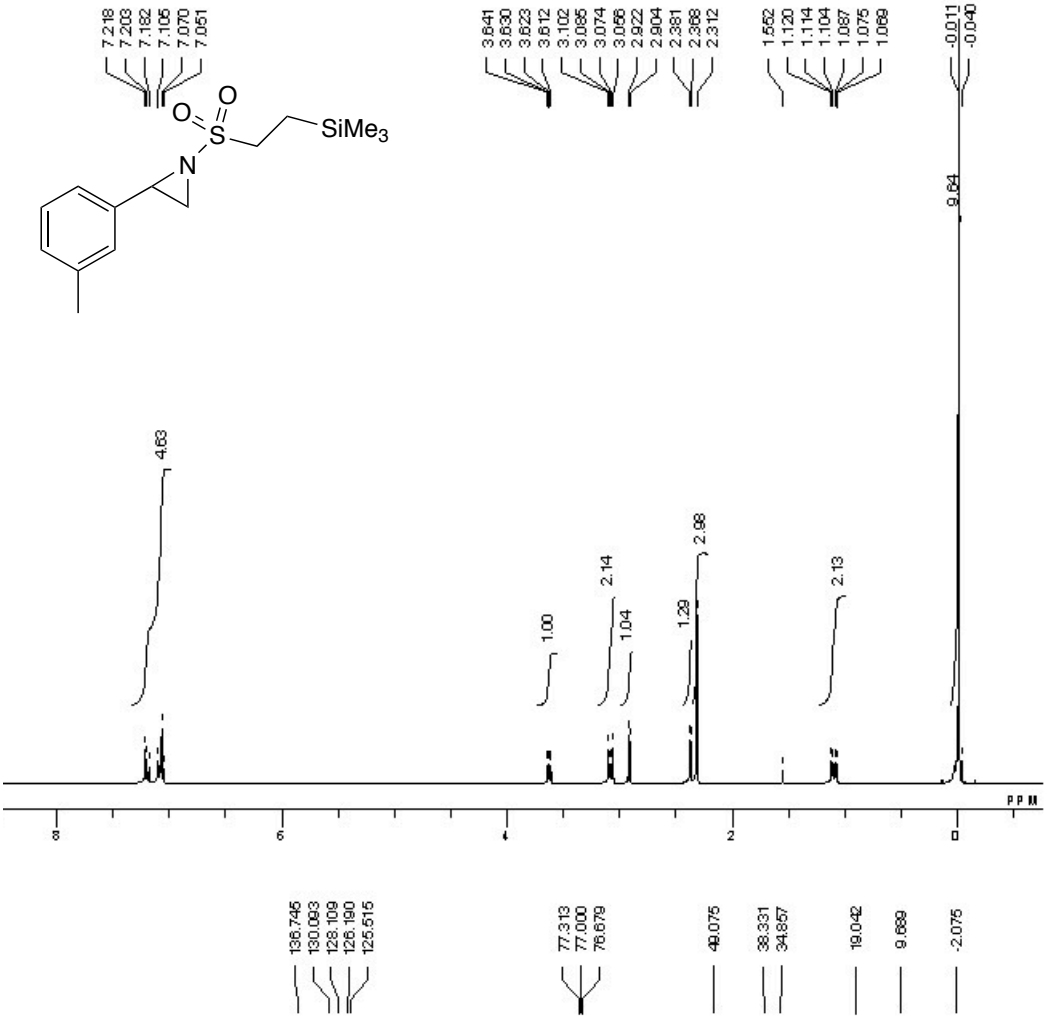
5.8. 2-[3-(Benzyloxy)propyl]-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 2, entry 7)

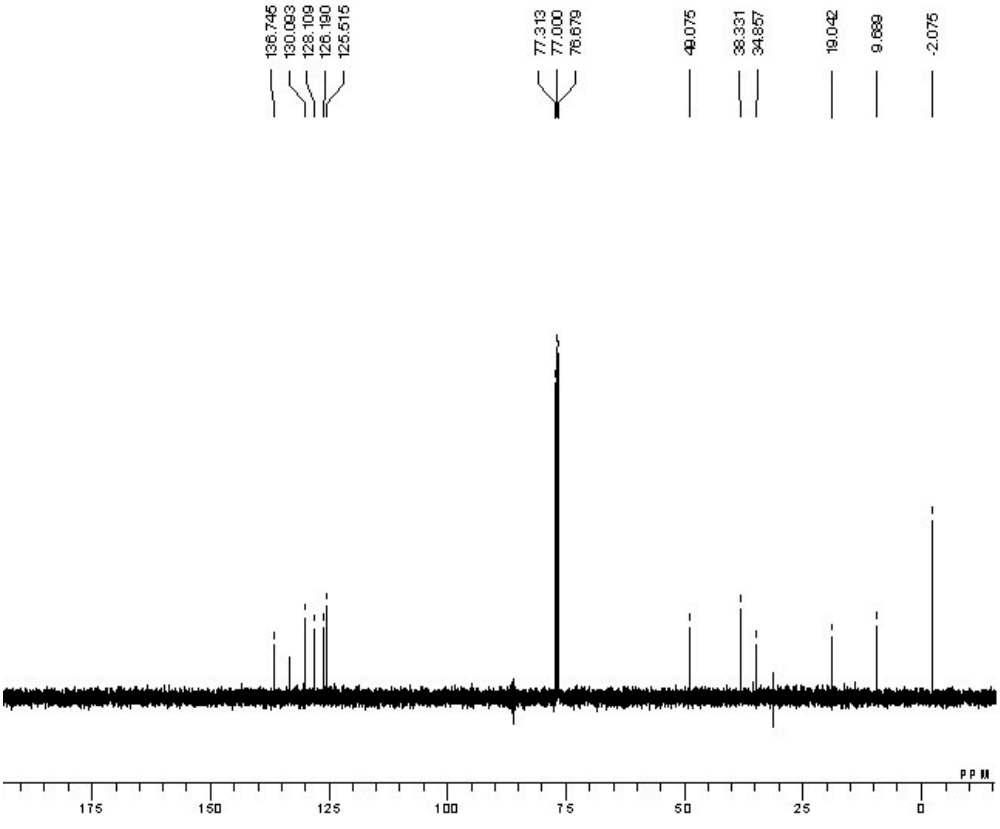


5.9. 2-(*o*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 1)

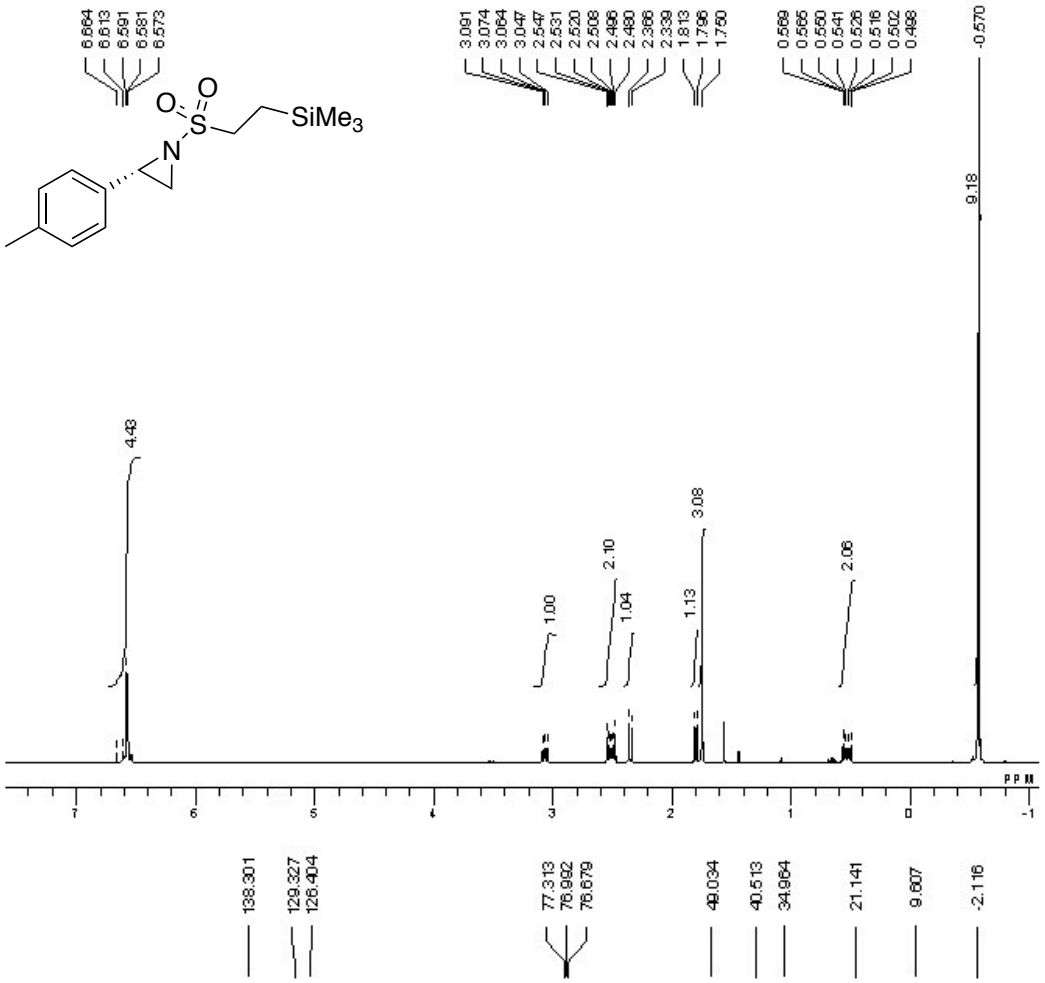


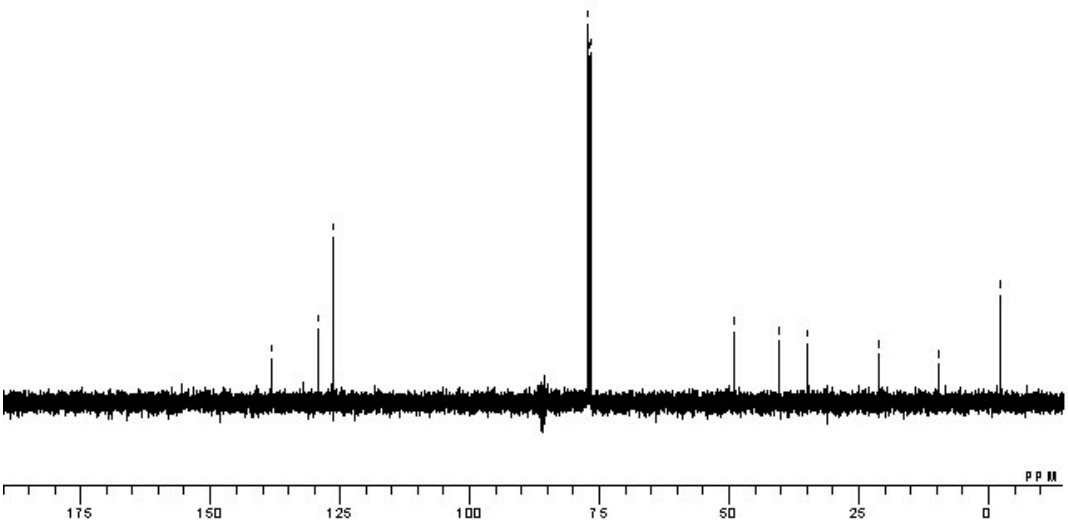
5.10. 2-(*m*-Tolyl)-1-{[2-(trimethylsilyl)ethyl]sulfonyl}aziridine (Table 3, entry 2)



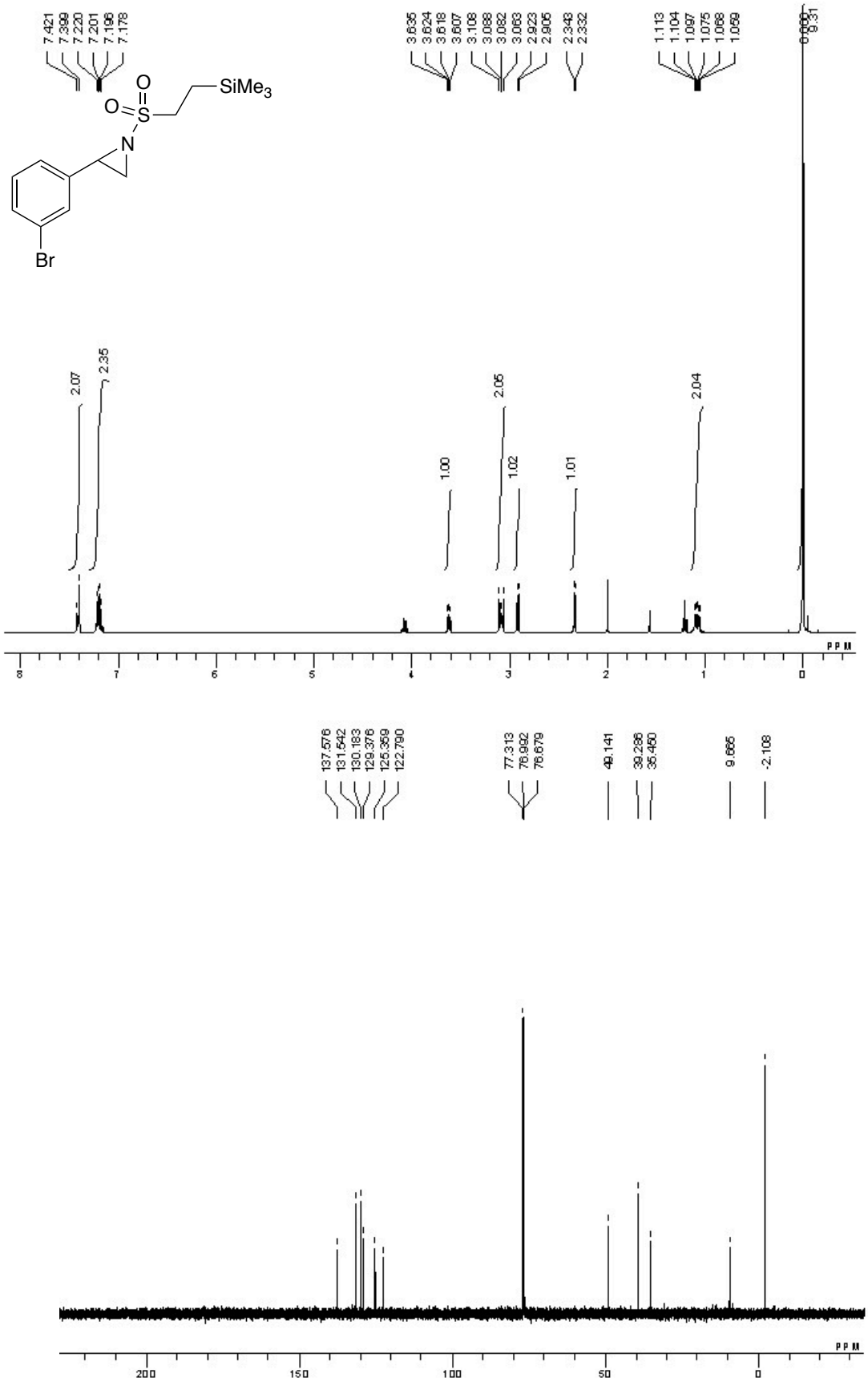


5.11. (2*S*)-2-(*p*-Tolyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 3)

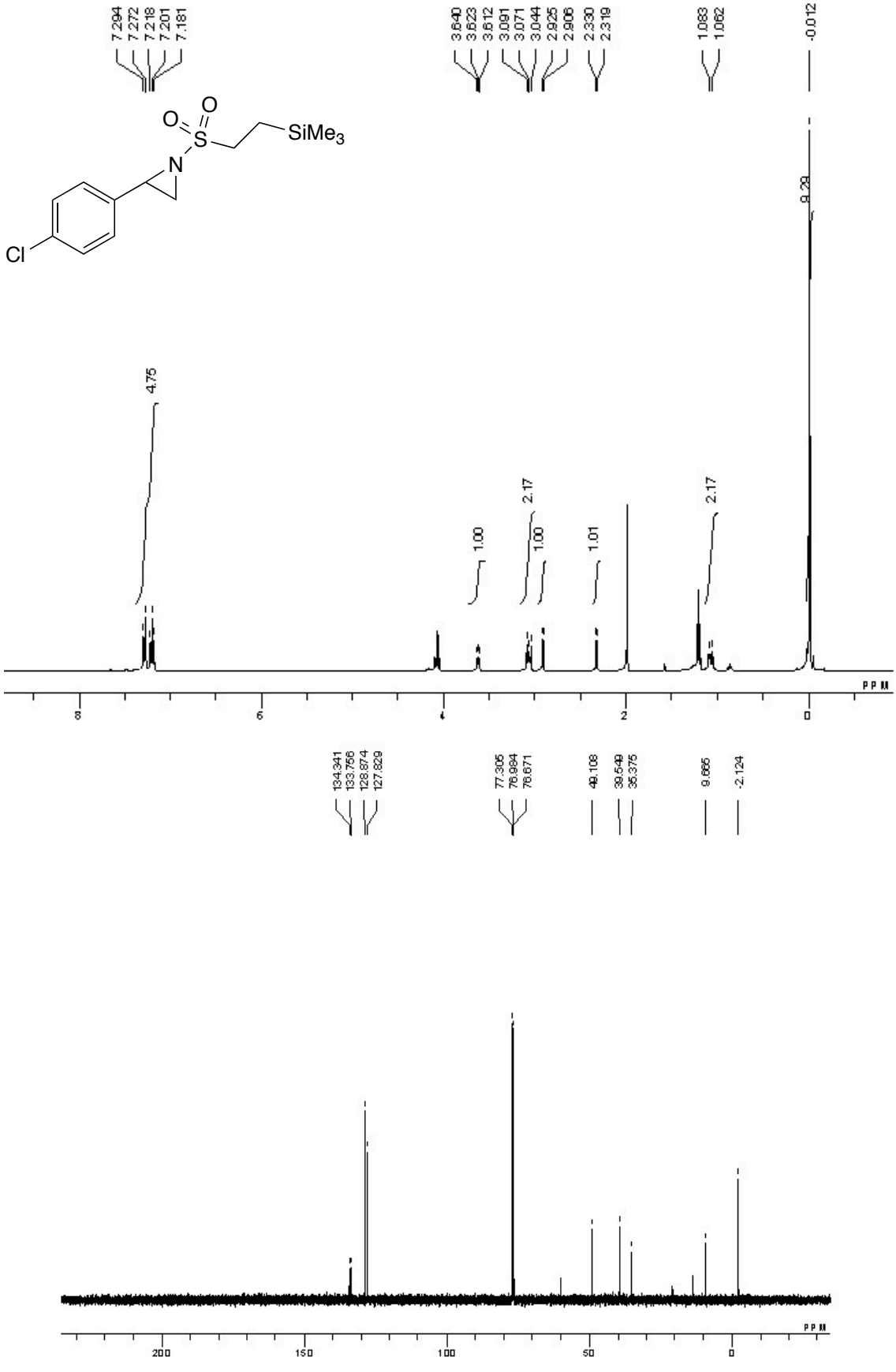




5.12. 2-(3-Bromophenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 4)

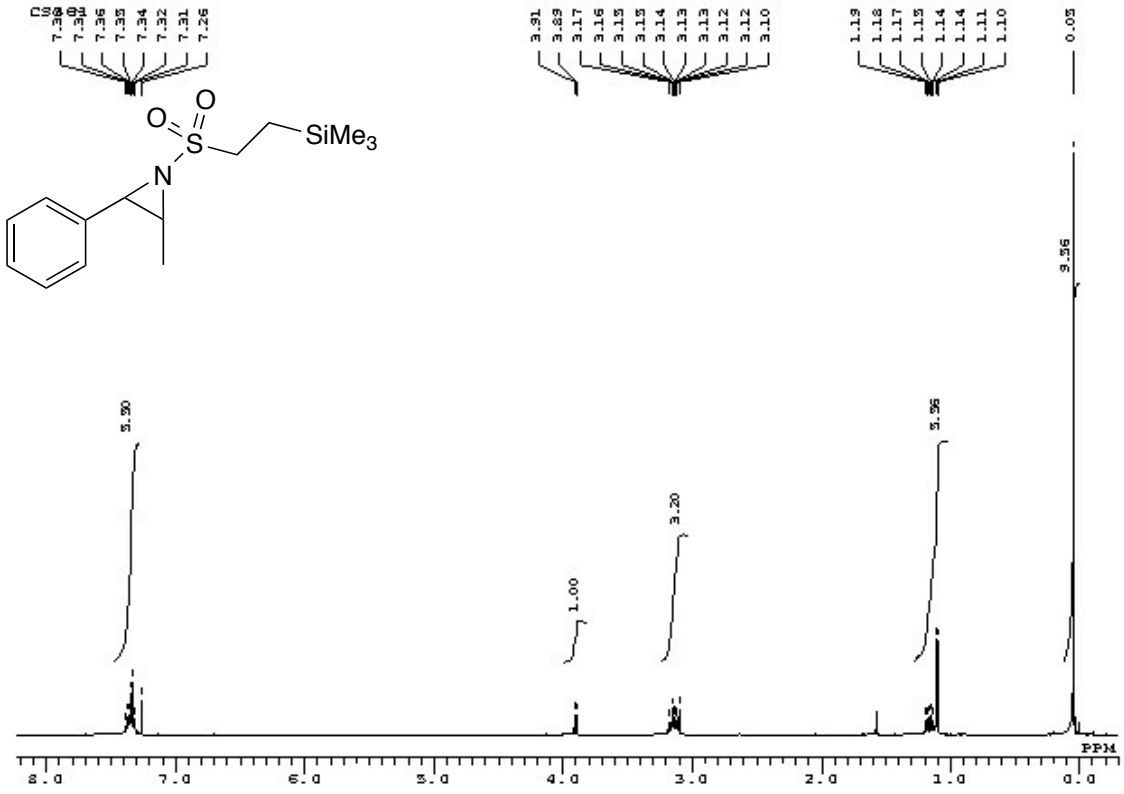


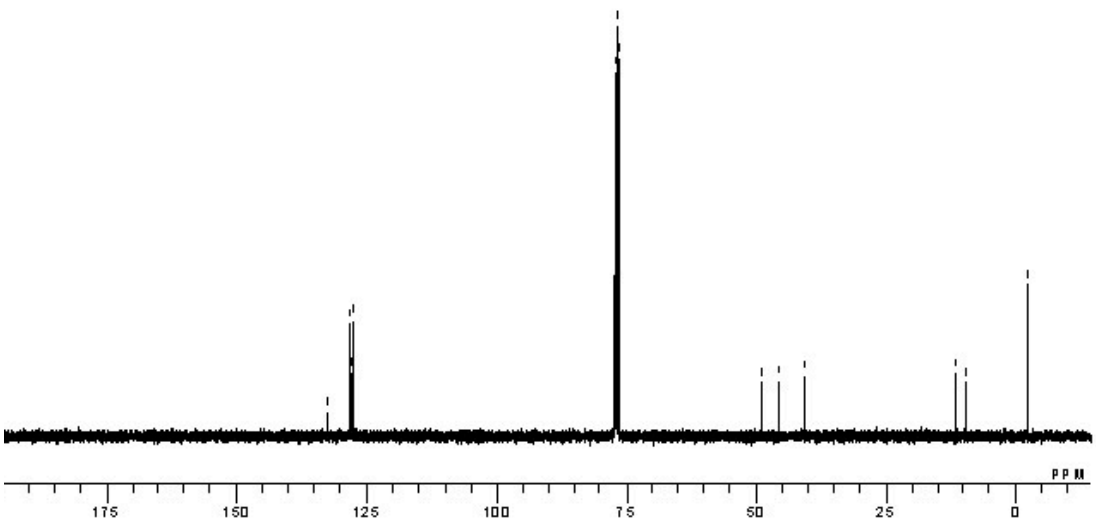
5.13. 2-(4-Chlorophenyl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 5)



5.14. (2*S*)-2-(Naphthalen-2-yl)-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 6)

5.15. 2-Methyl-3-phenyl-1-{[2-(trimethylsilyl)ethane]sulfonyl}aziridine (Table 3, entry 7)





5.16. 1-{[2-(Trimethylsilyl)ethane]sulfonyl}-1,1a,6,6a-tetrahydroindeno[1,2-*b*]aziridine (Table 3, entry 8)