Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Catalyst Free Aziridination and Unespected Homologation of Aziridines from Imines

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General methods and experimental procedures

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated were used, respectively. The spots were visualized using UV light and a DNP solution followed by heating. Medium performance liquid chromatography and flash column chromatography were performed using Merck, Kieselgel 60 with (0.063–0.200 mm) and (0.040–0.063 mm), respectively. Infrared spectra were recorded on a Perkin Elmer spectrum 1000. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer at 400 and 100.62, respectively. ^{1}H shifts are reported relative to internal TMS. Carbon shifts are given relative to the ^{13}C signal of $CDCl_3$ (δ 77.0 ppm). Mass spectra were recorded at the Mass Spectrometry Unit at the University of Santiago de Compostela, Spain. The electron impact mass spectra were recorded using a magnetic Micromass Autospec apparatus. For electrospray ionization it was used athe apparatus Bruker Microtof ESI – TOF.

General procedure for aziridination: To a solution of *N*-tosylimine (0.2 mmol) in dry THF (10mL) cooled to -5 to 0ºC under nitrogen atmosphere it was added 3 ml (nearly 5 equivalents) of a diazomethane solution in ethyl ether prepared according to Vogel's procedure[1]. The reaction complete in 10-30 min, depending on substrate. The reaction mixture was concentrated and purified by flash column chromatography (5% ethyl acetate in hexane as eluent).

***N*-(Benzenesulfonyl)-2-(4-bromophenyl)aziridine (2e):** oil, obtained in 71% yield. IR(film) ν_{max}: 1324 (S=O), 1163 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.98 (2H, d, *J*=7.4 Hz, $ArH_{2',6'}$), 7,65 (1H, t, *J*=7.2 Hz, $ArH_{4'}$), 7,55 (2H, t, *J*=7.2 Hz, $ArH_{3',5'}$), 7.42 (2H, d, *J*=8.0 Hz, ArH_{3+5}), 7.09 (2H, d, *J*=8.0 Hz, ArH_{2+6}), 3.75 (1H, dd, *J*=7.1 and 4.3 Hz, H_2), 3.01 (1H, d, *J*=7.1 Hz, H_{3b}), 2.36 (1H, d, *J*=4.3 Hz, H_{3a}). MSEI(+) m/z: 338 $[M^{81}Br+H]^+$ (21.92), 340 $[M^{79}Br+H]^+$ (21.77), 196 $[M\text{-}Bs]^+$ (71.2). HRMSEI(+) calcd for $C_{14}H_{12}BrNO_2S$ $[M]^+$ 338.9990 found 338.9985.

***N*-(*p*-Toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxyphenyl)aziridine (2v):** oil, obtained in 30% yield. IR(film) ν_{max}: 1321 (S=O), 1160 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.88 (2H, d, *J*=8.0 Hz, $ArH_{2',6'}$), 7,35 (2H, d, *J*=8.0 Hz, $ArH_{3',5'}$), 6.94 (1H, s, ArH_3), 6.64 (1H, s, ArH_6), 5.93 (2H, s, OCH_2O), 3.91 (1H, dd, *J*=7.0 and 4.4 Hz, H_2), 2.98 (1H, d, *J*=7 Hz, H_{3a}), 2.45 (3H, s, $ArCH_3$), 2.20 (1H, d, *J*=4 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 148.2, 147.5, 144.9, 134.6, 129.8, 129.5, 128.1, 113.9, 112.5, 107.6 (ArC), 101.9 (OCH_2O), 41.2 (C_2), 35.9 (C_3), 21.7 ($ArCH_3$). MSEI(+) *m/z*: 397 $[M^{81}Br]^+$ (4.34), 395 $[M^{79}Br]^+$ (4.0), 240 $[M^{79}Br\text{-}Ts]^+$ (55.6), 161 $[M\text{-}Ts\text{-}Br]^+$ (100). HRMSEI(+) calcd for $C_{16}H_{14}NO_4S^{79}Br$ $[M]^+$ 394.9827 found 394.9827.

***N*-(*p*-Toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (3k):** white solid (108-109ºC, ethyl acetate/hexane), obtained in 72% yield. IR(film) ν_{max}: 1321 (S=O), 1160 (S=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.67 (2H, d, *J*=8.0 Hz, $ArH_{2',6'}$), 7,21 (2H, d, *J*=8.0 Hz, $ArH_{3',5'}$), 6.95 (2H, d, *J*=8.3 Hz, ArH_{2+6}), 6.68 (2H, d, *J*=8.0 Hz, ArH_{3+5}), 3.77 (3H, s, OCH_3), 2.94-2.88 (1H, m, H_2), 2.77 (1H, dd, *J*=14.5 and 4.9 Hz, $H_{1'a}$), 2.70 (1H, d, *J*=6.8 Hz, H_{3a}), 2.60 (1H, dd, *J*=14.5 and 7.2Hz, $H_{1'b}$), 2.43 (3H, s, $ArCH_3$), 2.14 (1H, d, *J*=4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.3 (ArC_4), 144.3 ($ArC_{4'}$), 134.8 ($ArC_{1'}$), 129.6 (ArC_{2+6}), 129.5

($ArC_{3'+5'}$), 129.0 (ArC_1), 127.8 ($ArC_{2'+6'}$), 113.8 (ArC_{3+5}), 55.1 (OCH_3), 41.4 (C_2), 36.5 ($C_{1'}$), 32.7 (C_3), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 317 $[M]^+$ (14.6), 162 $[M\text{-}Ts)]^+$ (98.5), 121 $[MeOC_6H_4CH_2]^+$ (100). HRMSEI(+) calcd for $C_{17}H_{19}NO_3S$ $[M]^+$ 317,10856 found 317.1081.

***N*-(Benzenesulfonyl)-2-(4-methoxybenzyl)aziridine (3l):** oil, obtained in 68% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.81 (2H, d, *J*=7.7 Hz, $ArH_{2'+6'}$), 7.58 (1H, t, *J*=7.4 Hz, $ArH_{4'}$), 7,44 (2H, t, *J*=7,7 Hz, $ArH_{3'+5'}$), 6.95 (2H, d, *J*=8.4 Hz, ArH_{2+6}), 6.68 (2H, d, *J*=8.4 Hz, ArH_{3+5}), 3.77 (3H, s, OCH_3), 2.99-2.93 (1H, m, H_2), 2.77 (1H, dd, *J*=14.7 and 5 Hz, $H_{1'a}$), 2.72 (1H, d, *J*=6.9 Hz, H_{3a}), 2.62 (1H, dd, *J*=14.5 and 7.2Hz, $H_{1'b}$), 2.16 (1H, d, *J*=4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.3 (ArC_4), 138.0 ($ArC_{1'}$), 133.3 ($ArC_{4'}$), 129.6 (ArC_{2+6}), 128.9 ($ArC_{3'+5'}$+ ArC_1), 127.8 ($ArC_{2'+6'}$), 113.8 (ArC_{3+5}), 55.2 (OCH_3), 41.6 (C_2), 36.5 ($C_{1'}$), 32.8 (C_3). MSEI(+) *m/z*: 303 $[M]^+$ (11), 162 $[M\text{-}Bs]^+$ (96.5), 160 $[M\text{-}Bs\text{-}H_2]^+$ (100). HRMSEI(+) calcd for $C_{16}H_{17}NO_3S$ $[M]^+$ 303.0929 found 303.0924.

***N*-(*p*-Nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (3m):** oil, obtained in 78% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 8.17 (2H, d, *J*=8.8, $ArH_{3'+5'}$), 7.88 (2H, d, *J*=8.8, $ArH_{2'+6'}$), 6.87 (2H, d, *J*=8.6, ArH_{2+6}), 6.59 (2H, d, *J*=8.6, ArH_{3+5}), 3.71 (3H, s, OCH_3), 3.01-2.90 (2H, m, H_2 + $H_{1'a}$), 2.88 (1H, d, *J*=6.8, H_{3a}), 2.39 (1H, dd, *J*=14.2 and 8.2 Hz, $H_{1'b}$), 2.30 (1H, d, *J*=4.5 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 158.5 (ArC_4), 150.2 ($ArC_{1'/4'}$), 143.4 ($ArC_{1'/4'}$), 129.6 (ArC_{2+6}), 129.0 ($ArC_{2'+6'}$), 128.7 (ArC_1), 123.9 ($ArC_{3'+5'}$), 113.6 (ArC_{3+5}), 55.0 (OCH_3), 43.1 (C_2), 36.5 ($C_{1'}$), 33.5 (C_3). MSEI(+) *m/z*: 348 $[M]^+$ (26.7), 162 $[M\text{-}Nz]^+$ (100), 121 $[MeOC_6H_4CH_2]^+$ (83.9). HRMSEI(+) calcd for $C_{16}H_{16}N_2O_5S$ $[M]^+$ 348.0780 found 348.0778.

***N*-(*p*-Toluenesulfonyl)-2-(2,4-dimethoxybenzyl)aziridine (3n):** oil, obtained in 74% yield. IR(film) ν_{max}: 1321 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.66 (2H, d, *J*=8.0 Hz, $ArH_{2'+6'}$), 7,19 (2H, d, *J*=8.0 Hz, $ArH_{3'+5'}$), 6.82 (1H, d, *J*=8.2 Hz, ArH_6), 6.32 (1H, d, *J*=2.0 Hz, ArH_3), 6.24 (1H, dd, *J*=8.2 and 2.0 Hz, ArH_5), 3.77 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.03-2.97 (1H, m, H_2), 2.78 (1H, dd, *J*=14.1 and 5.4 Hz, $H_{1'a}$), 2.68 (1H, d, *J*=6.9 Hz, H_{3a}), 2.54 (1H, dd, *J*=14.1 and 6.9Hz, $H_{1'b}$), 2.41 (3H, s, $ArCH_3$), 2.16 (1H, d, *J*=4.5 Hz, H_{3b}); ^{13}C NMR ($CDCl_3$) δ: 159.9 (ArC_4), 158.1 (ArC_2), 144.0 ($ArC_{4'}$), 135.1 ($ArC_{1'}$), 130.7 (ArC_6), 129.4 ($ArC_{3'+5'}$), 127.8 ($ArC_{2'+6'}$), 117.8 (ArC_1), 103.9 (ArC_5), 98.3 (ArC_3), 55.2 (OCH_3), 40.5 (C_2), 33.3 (C_3), 31.8 ($C_{1'}$), 21.5 ($ArCH_3$); MSEI(+) *m/z*: 347 $[M]^+$ (29.1), 192 $[M\text{-}Ts]^+$ (100), 151 $[(MeO)_2C_6H_4CH_2]^+$ (64.2). HRMSEI calcd for $C_{18}H_{21}NO_4S$ $[M]^+$ 347,1191 found 347,1196.

***N*-(*p*-Toluenesulfonyl)-2-(2-methylbenzyl)aziridine (3o):** white solid (128-129ºC ethyl acetate/hexane), obtained in 74% yield. IR(film) ν_{max}: 1320 (S=O), 1159 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.58 (2H, d, *J*=8.0 Hz, $ArH_{2'+6'}$), 7,12 (2H, d, *J*=8.0 Hz, $ArH_{3'+5'}$), 6.99-6.90 (4H, m, ArH), 2.90-2.84 (1H, m, H_2), 2.75 (1H, dd, *J*=14.7 and 5 Hz, $H_{1'a}$), 2.65-2.60 (2H, m, $H_{1'b}$ + H_{3a}), 2.34 (3H, s, $ArCH_3$), 2.12 (3H, s, $ArCH_3$), 2.06 (1H, d, *J*=4.4 Hz, H_{3b}). ^{13}C NMR ($CDCl_3$) δ: 144.2, 136.0, 135.2, 134.7, 130.1, 129.4, 129.3, 127.7, 126.6, 125.9 (ArC), 40.4 (C_2), 34.4, 32.7 ($C_{1'}$/C_3), 21.5 ($ArCH_3$), 19.4 ($ArCH_3$). MSEI(+) *m/z*: 301 $[M]^+$ (9.1), 146 $[M\text{-}Ts]^+$ (70.4), 130 $[M\text{-}TsN\text{-}2H]^+$ (100); HRMSEI calcd for $C_{17}H_{19}NO_2S$ $[M]^+$ 301,11365 obtained 301.1132.

***N*-(Benzenesulfonyl)-2-(2-methylbenzyl)aziridine (3p):** oil, obtained in 73% yield. IR(film) ν_{max}: 1322 (S=O), 1163 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, *J*=7.8 Hz, $ArH_{2',+6'}$), 7.57 (1H, t, *J*=6.9 Hz, $ArH_{4'}$), 7,43 (2H,m, $ArH_{3',+5'}$), 7.11-7.00 (4H, m, $ArH_{3+4+5+6}$), 3.04-2.98 (1H, m, H_2), 2.85 (1H, dd, *J*=14.7 and 5.5 Hz, $H_{1',a}$), 2.73 (1H, d, *J*=6.7 Hz, H_{3a}), 2.36 (1H, dd, *J*=14.5 and 4.7 Hz, $H_{1',b}$), 2.19 (3H, s, $ArCH_3$), 2.16 (1H, d, *J*=4.5 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 137.8, 136.0, 135.1, 133.3, 130.2, 129.3, 128.8, 127.6, 126.8, 125.9 (ArC), 40.6 (C_2), 34.3, 32.8 ($C_{1'}$/C_3), 19.4 ($ArCH_3$). MS(EI): 387 $[M]^+$ (3.61), 146 $[M^+$-Bs] (43.9), 132 $[M^+$-TsN] (79.6), 130 $[M^+$-TsN-2H] (100); HRMSEI calcd for $C_{16}H_{17}NO_2S$ $[M]^+$ 287,0980 obtained 287.10979.

***N*-(*p*-Toluenesulfonyl)-2-(2-furanyl)methylaziridine (3q):** oil, obtained in 77% yield. IR(film) ν_{max}: 1322 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.77 (2H, d, *J*=8.1 Hz, $ArH_{2',+6'}$), 7,30 (2H, d, *J*=8.1 Hz, $ArH_{3',+5'}$), 7.18 (1H, s, $FuranylH_4$), 6.21-6.20 (1H, m, $FuranylH_3$), 6.01 (1H, d, *J*=3Hz, $FuranylH_2$), 3.04-2.98 (1H, m, H_2), 2.80 (2H, d, *J*=6 Hz, $H_{1'}$), 2.70 (1H, d, *J*=7 Hz, H_{3a}), 2.44 (3H, s, $ArCH_3$), 2.17 (1H, d, *J*=4.4 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 150.7 ($FuranylC_1$), 144.4 ($ArC_{4'}$), 141.6 ($FuranylC_4$), 134.9 ($ArC_{1'}$), 129.6 ($ArC_{3',+5'}$), 127.9 ($ArC_{2',+6'}$), 110.2 (FuranylC3), 106.7 ($FuranylC_2$), 38.4 (C_2), 32.9 (C_3), 30.2 ($C_{1'}$), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 278 $[M+H]^+$ (1), 171 $[Ts]^+$ (25.4), 155 $[Ts]^+$ (31.2), 91 $[C_7H_7]^+$ (100). HRMSEI calcd for $C_{14}H_{15}NaNO_3S$ $[M+Na]^+$ 300,06703 found 300.0664.

***N*-(*p*-Toluenesulfonyl)-2-(2-phenylethenyl)aziridine (3r):** white solid (90-91ºC ethyl acetate/hexane), obtained in 68% yield. IR(film) ν_{max}: 1322 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, *J*=7.9 Hz, $ArH_{2',+6'}$), 7,28-7.14 (7H, m, PhH + $ArH_{3',+5'}$), 6.32 (1H, d, *J*=15.9 Hz, $H_{3'}$), 5.81 (1H, dt, *J*=15.9 and 7.5 Hz, $H_{2'}$), 2.81-2.78 (1H, m, H_2), 2.73 (1H, d, *J*=6.8 Hz, H_3), 2.51-2.43 (1H, m, $H_{1',a}$), 2.32 (3H, s, $ArCH_3$), 2.22-2.14 (1H, d, $H_{1',b}$), 2.17 (1H, d, *J*=4.8 Hz, H_{3b}); ^{13}C ($CDCl_3$) δ: 144.5 ($ArC_{4'}$), 136.8 (ArC_1), 132.6 ($C_{3'}$), 129.6 ($ArC_{3',+5'}$), 128.4 (ArC_{3+5}), 128.0 ($ArC_{2',+6'}$), 127.3 (ArC_4), 126.1 (ArC_{2+6}), 124.5 ($C_{2'}$), 41.3 (C_2), 34.6 ($C_{1'}$), 32.9 (C_3), 21.5 ($ArCH_3$); MSEI(+) *m/z*: 313 $[M]^+$ (3.1), 222 $[M-C_7H_7]^+$ (100), 91 $[C_7H_7]^+$ (97.4). HRMSEI calcd for $C_{18}H_{19}NO_2S$ $[M]^+$ 313.1137 found 313.1133.

***N*-(*p*-Toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (3s):** oil, obtained in 76% yield. IR(film) ν_{max}: 1320 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.67 (2H, d, *J*=8.0 Hz, $ArH_{2',+6'}$), 7,22 (2H, d, *J*=8.0 Hz, $ArH_{3',+5'}$), 6.57 (1H, d, *J*=8.3 Hz, ArH_6), 6.48-6.46 (2H, m, ArH_{2+5}), 5.88 (2H, dd, *J*=1.4 Hz, OCH_2O), 2.89-2.97 (1H, m, H_2), 2.76 (1H, dd, *J*=14.5 and 4.7 Hz, $H_{1',a}$), 2.71 (1H, d, *J*=6.8 Hz, H_{3a}), 2.50 (1H, dd, *J*=14.1 and 7.5 Hz, $H_{1',b}$), 2.42 (3H, s, $ArCH_3$), 2.14 (1H, d, *J*=4.4 Hz, H_{3b}); ^{13}C ($CDCl_3$) δ: 147.4 (ArC_4), 146.2 (ArC_3), 144.3 ($ArC_{4'}$), 134.7 ($ArC_{1'}$), 130.7 (ArC_1), 129.4 ($ArC_{3',+5'}$), 127.8 ($ArC_{2',+6'}$), 121.6 (ArC_2), 109.1 (ArC_5), 108.1 (ArC_6), 100.8 (OCH_2O), 41.2 (C_2), 37.2($C_{1'}$), 32.6 (C_3), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 331 $[M]^+$ (24.3), 176 $[M-Ts]^+$ (100), 91 $[C_7H_7]^+$ (46.8). HRMSEI calcd for $C_{17}H_{17}NO_4S$ $[M]^+$ 331.0878 found 331.0875.

***N*-(*p*-Benzenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (3t):** oil, obtained in 72% yield. IR(film) ν_{max}: 1321 (S=O), 1159 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.80 (2H, d, *J*=7.6 Hz, $ArH_{2',+6'}$), 7,58 (1H, t, *J*=7.2 Hz, $ArH_{4'}$), 7,44 (2H, t, *J*=7.2 Hz, $ArH_{3',+5'}$), 6.58 (1H, d, *J*=7.8 Hz, ArH_6), 6.49-6.46 (2H, m, ArH_{2+5}), 5.89 (2H, s, OCH_2O), 2.94-2.88 (1H, m, H_2), 2.79-2.73 (2H, m, $H_{1',a+3a}$), 2.51 (1H, dd, *J*=14.4 and

7.5 Hz, $H_{1'b}$), 2.17 (1H, d, *J*=4.5 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 147.4 ($ArC_{3/4}$), 146.3 ($ArC_{3/4}$), 137.8 ($ArC_{1'}$), 133.3, 130.6, 128.8, 127.8, 121.6, 109.1, 108.2 (ArC), 100.8 (OCH_2O), 41.6 (C_2), 37.1, 32.8 ($C_{3/1'}$). MSEI(+) *m/z*: 317 $[M]^+$ (18.6), 176 $[M\text{-}Bs]^+$ (51.7), 77 $[C_6H_5]^+$ (100). HRMSEI(+) calcd for $C_{16}H_{15}NO_4S$ $[M]^+$ 317.0725 found 317.0722.

***N*-(*p*-Toluenesulfonyl)-2-(anthracen-9-ylmethylene)aziridine (3u):** oil, obtained in 65% yield. IR(film) ν_{max}: 1321 (S=O), 1161 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 8.24 (1H, s, ArH_{10}), 8.07-8.05 (2H, m, ArH_{8+1}), 7.93-7.91 (2H, m, ArH_{4+5}), 7.44-742 (4H, m, $ArH_{2+3+6+7}$), 7.04 (2H, d, *J*=8 Hz, $ArH_{2'+6'}$), 6.50 (2H, d, *J*=8 Hz, $ArH_{3'+5'}$), 3.92 (1H, dd, *J*=15.1 and 3.1 Hz, $H_{1'a}$), 3.47 (1H, dd, *J*=15.1 and 8.5 Hz, $H_{1'b}$), 3.10-3.08 (1H, m, H_2), 2.89 (1H, d, *J*=6.8 Hz, $H_{3'a}$), 2.42 (1H, d, *J*=4.4 Hz, $H_{3'b}$), 2.21 (3H, s, $ArCH_3$). ^{13}C ($CDCl_3$) δ: 143.5 ($ArC_{4'}$), 133.6 ($ArC_{1'}$), 131.3 (ArC_9), 129.9 (ArC_{12+13}), 128.8 (ArC_{4+5}), 128.5 ($ArC_{3'+5'}$), 126.9 ($ArC_{2'+6'}$), 126.3 (ArC_{11+14}), 125.8, 124.8 ($ArC_{2/3/6/7}$), 124.3 (ArC_{8+1}), 41.2 (C_2), 32.6, 28.8 ($C_{1'/3}$), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 387 $[M]^+$ (38.4), 210 $[M\text{-}Anthr.]^+$ (75.6), 91 $[C_7H_7]^+$ (100). HRMSEI(+) calcd for $C_{24}H_{21}NO_2S$ $[M]^+$ 387.1293 found 387.1293.

***N*-(*p*-Toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxybenzyl)aziridine (3v):** oil, obtained in 50% yield. IR(film) ν_{max}: 1320 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.65 (2H, d, *J*=8.0 Hz, $ArH_{2'+6'}$), 7,20 (2H, d, *J*=8.0 Hz, $ArH_{3'+5'}$), 6.85 (1H, s, ArH_3), 6.44 (1H, s, ArH_6), 5.93 (1H, s, OCH_2O), 5.88 (1H, s, OCH_2O), 3.04 (1H, dd, *J*=14.2 and 4.2 Hz, $H_{1'a}$), 2.97-2.92 (1H, m, H_2), 2.78 (1H, d, *J*=6.8 Hz, H_{3a}), 2.46 (1H, dd, *J*=14.5 and 7.7 Hz, $H_{1'b}$), 2.42 (3H, s, $ArCH_3$), 2.20 (1H, d, *J*=4.3 Hz, H_{3b}). ^{13}C ($CDCl_3$) δ: 147.2, 147.0, 144.2, 134.6, 129.6, 129.4, 127.9, 114.2, 112.4, 110.8 (ArC), 101.5 (OCH_2O), 39.9 (C_2), 37.4, 32.8 ($C_{3/1'}$), 21.5 ($ArCH_3$). MSEI(+) *m/z*: 411 $[M^{81}Br]^+$ (4.83), 409 $[M^{79}Br]^+$ (4.62), 330 $[M\text{-}Br]^+$ (23.6), 175 $[M\text{-}Ts\text{-}Br]^+$ (67.34), 175 $[M\text{-}Ts\text{-}Br+H]^+$ (100). HRMSEI(+) calcd for $C_{17}H_{16}NO_4S^{81}Br$ $[M]^+$ 410.9963 found 410.9967.

Procedure for homologation of 4-bromoaziridine: To a solution of *N*-(4-bromobenzylidene)-4-methyl-benzenesulfonamide (**1e**, 0.417 mmol) in dry THF (10mL) cooled to -5 to 0ºC under nitrogen atmosphere it was added 3 ml (nearly 5 equivalents) of a diazomethane solution in ethyl ether prepared according to Vogel's procedure[1].The reaction was monitored by TLC (30 % ethyl acetate in hexane as eluent). Once the reaction was complete BF_3-etherate (10 mol %) was added and the reaction allowed to come to room temperature and stirred for plus 2 hours. The reaction mixture was then neutralised with solid sodium bicarbonate, cooled to 0ºC and added more 3 ml of diazomethane. The reaction mixture was allowed to stir for 30 min and then filtered through celite cake concentrated and purified by flash column chromatography. (5% ethyl acetate in hexane as eluent).

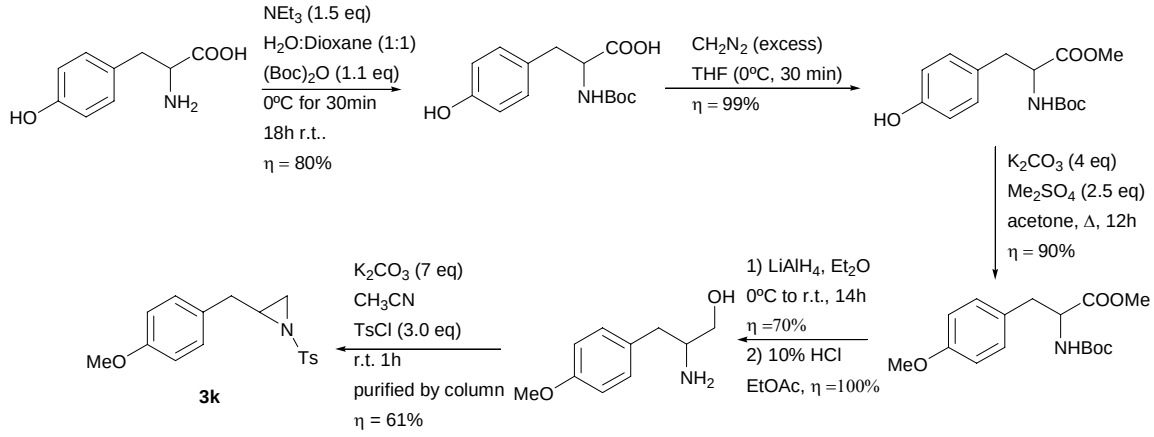
***N*-(*p*-Benzenesulfonyl)-2-(4-bromobenzyl)aziridine (3e):** oil, obtained in 35% yield. IR(film) ν_{max}: 1318 (S=O), 1160 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.74 (2H, d, *J*=8.0 Hz, $ArH_{2'+6'}$), 7.61 (1H, t, *J*=7.5 Hz, $ArH_{4'}$), 7,41 (2H, t, *J*=7.6 Hz, $ArH_{3'+5'}$), 7.20 (2H, d, *J*=8.1 Hz, ArH_{3+5}), 6.87 (2H, d, *J*=8.1 Hz, ArH_{2+6}), 2.94-2.84 (2H, m, $H_{1'+2a}$), 2.77 (1H, d, *J*=6.7 Hz, H_{3b}), 2.48 (1H, dd, *J*=14 and 8Hz, $H_{1'b}$), 2.19 (1H, d, *J*=4.4 Hz, H_{3a}). ^{13}C NMR ($CDCl_3$) δ: 137.66, 135.93, 133.35, 131.47, 130.33, 128.92, 127.76, 120.65

(ArC), 41.34 (C_{2a}), 36.83 ($C_{1'/3a}$), 32.72 ($C_{1'/3a}$). HRMSEI(+) calcd for $C_{15}H_{14}BrNO_2S$ $[M]^+$ 350.9929 found 350.9923.

***N*-(Benzenesulfonyl)-2-(4-chlorobenzyl)aziridine (3f):** in this case 50 μl of H_2SO_4 were used for the rearrangement instead of BF_3. Obtained in 18,3%. IR (film): νmax: 1323 (S=O), 1162 (S=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.79 (2H, d, *J*=7.8 Hz, $ArH_{2'+6'}$), 7.57 (1H, t, *J*=7.4 Hz, $ArH_{4'}$), 7.44 (2H, t, *J*=7.8 Hz, $ArH_{3'+5'}$), 7.09 (2H, m, ArH_{4+5}), 7.00 (1H, s, ArH_2), 6.93 (1H, d, *J*=7.2 Hz, ArH_6), 2.95 (1H, m, H_{2a}), 2.86 (1H, dd, *J*=4.6 e 14.4 Hz, $H_{1'a}$), 2.77 (1H, d, J=6.8, H_{3a}), 2.56 (1H, dd, *J*=7.6 e 14.4 Hz, $H_{1'b}$), 2.18 (1H, d, *J*=4.36 Hz, H_{3b}), ^{13}C-RMN ($CDCl_3$) δ: 138.94, 137.63, 134.16, 133.56, 129.70, 128.93, 127.72, 126.97, 126.85 (ArC), 41.01, 37.11, 32.74 (C1'a+2a+3a). MSEI(+) m/z: 307 [M]+ (8.1), 166 [M-Bs]+ (100). HRMSEI(+) calcd for C15H14ClNO2S [M]+ 307.0434 found 307.0431.

Synthesis of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (3k) starting from tyrosine:

The synthesis of compound **3i** was accomplished by a different procedure starting from tyrosine and the structure was confirmed (Scheme 1). The synthesis started with the amino group protection with t-Boc followed by methylation of the carboxylic acid with diazomethane. Methylation of the hydroxylic aromatic goup was subsequently achieved using $K_2CO_3/(MeO)_2SO_2$. After Boc removal,[2] the reduction with $LiAlH_4$ lead to the 1,2 aminoalcohol. The final step of cyclization to the aziridine ring was carried out by tosyl cholride and potassium carbonate[3] and compound **3i** was obtained in 30 % overall yield.



Scheme 1 – Schematic representation of the synthesis of *N*-(*p*-Toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3k**) from tyrosine.

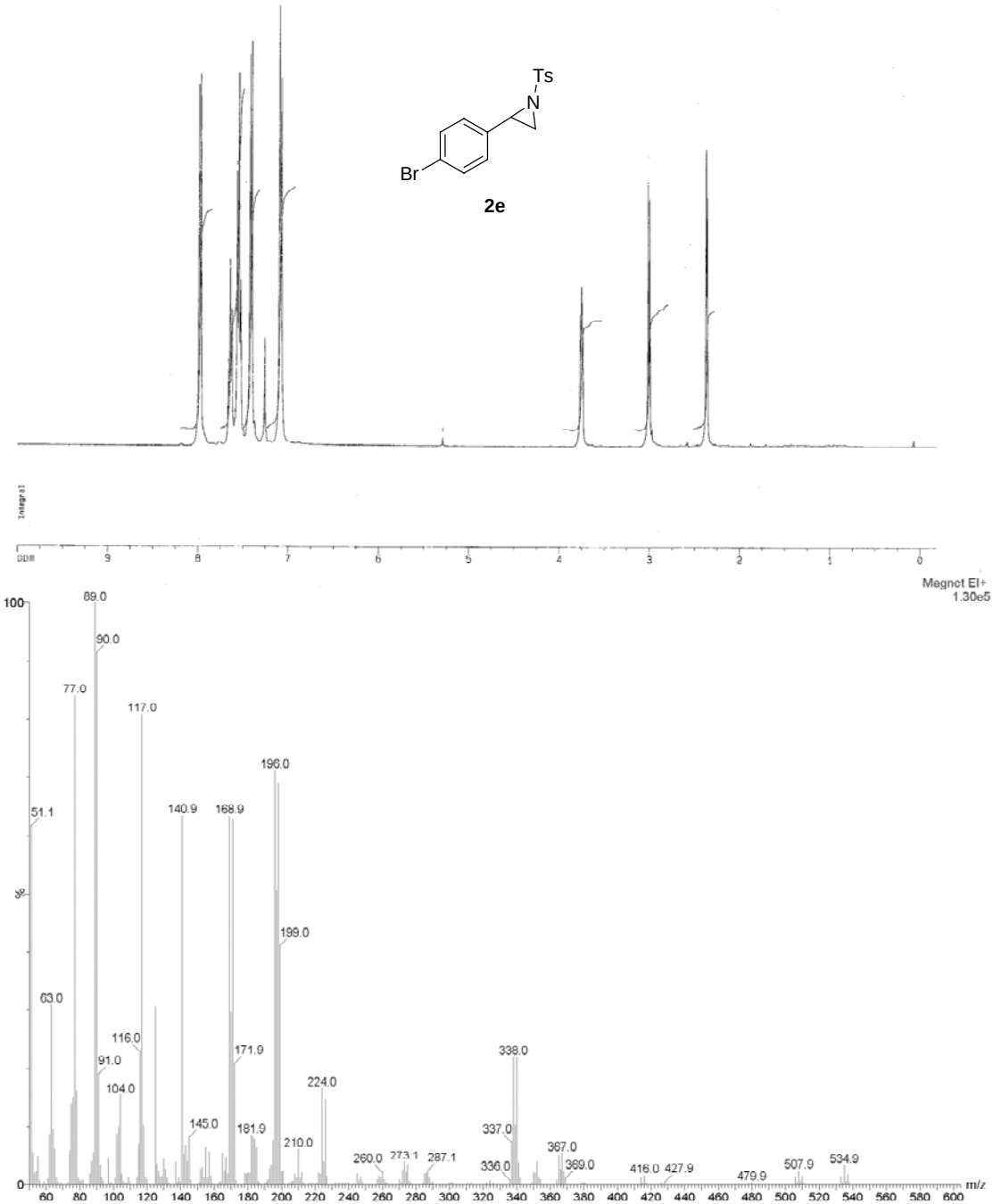
References

1 A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford, P. W. G. Smith in *Vogel's Textbook of Practical Organic Chemistry*, ed by Prentice Hall, England, 5th edn, 1989.

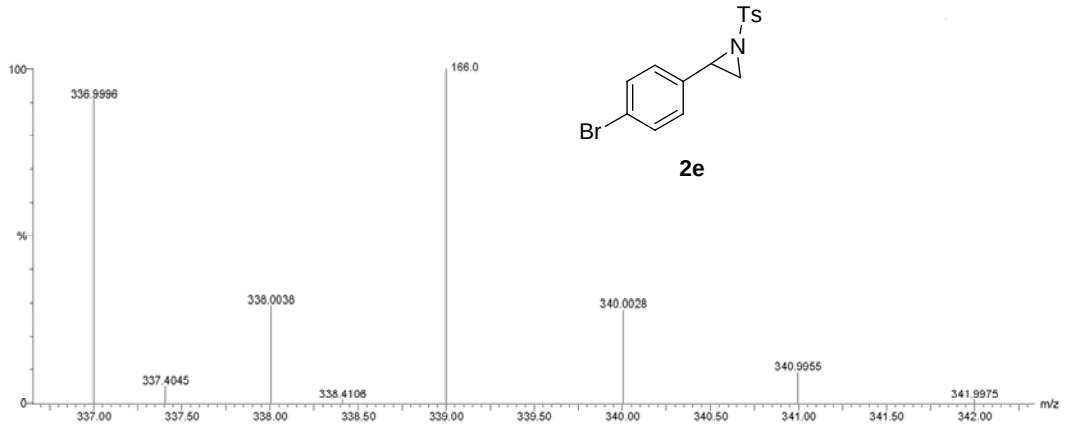
2 M. K. Gurjar, S. Karmakar, D. K. Mohapatra, U. D. Phalgune, *Tetrahedron Lett.* 2002, ***43***, 1897

3 L. W. Bieber, M. C. F. de Araujo, *Molecules* 2002, ***7***, 902.

NMR and Massa spectra

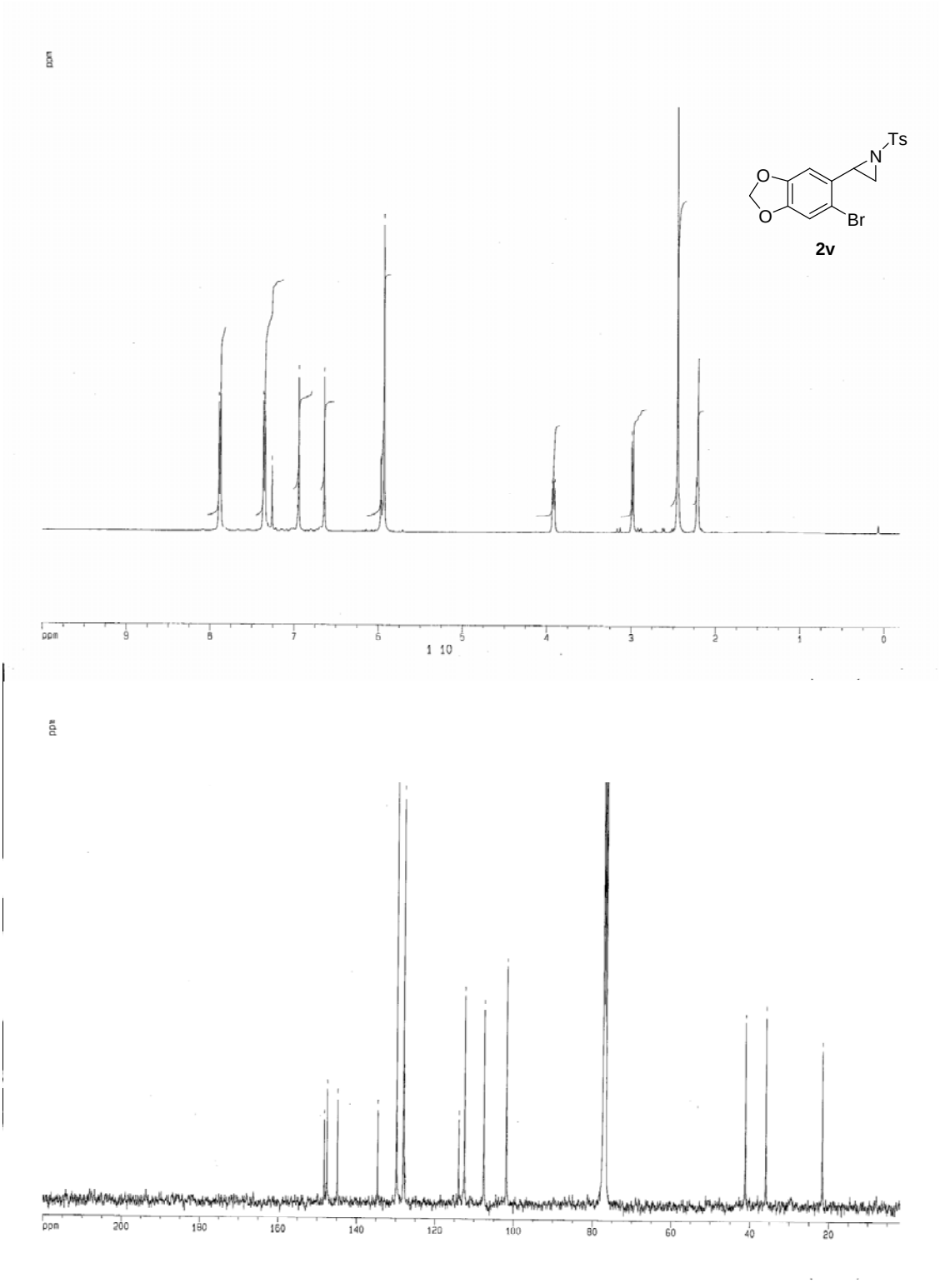


^{1}H NMR and Mass spectra of *N*-(benzenesulfonyl)-2-(4-bromophenyl)aziridine (**3e**).

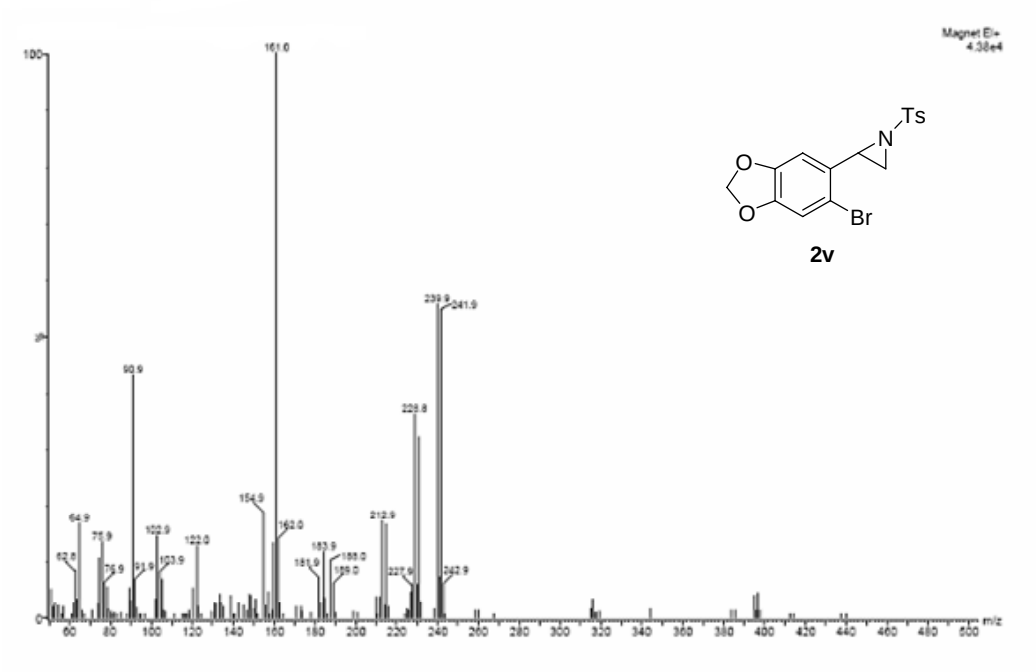


2e

Minimum:	0.30				-1.5		
Maximum:	100.00		5.0	5.0	90.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
		338.0029	0.9	2.7	9.5	181.8	12C13 13C3 H14 O S 81Br
		338.0050	-1.2	-3.6	15.5	217.5	12C14 13C3 H7 N2 O2 S2
338.9985	100.00	338.9990	-0.5	-1.5	8.5	8.9	12C14 H14 N2 O S 81Br
		338.9981	0.4	1.2	9.5	20.2	12C12 13C3 H13 N O S 81Br
		338.9999	-1.4	-4.1	14.0	35.7	12C14 13C3 H9 N2 O 79Br

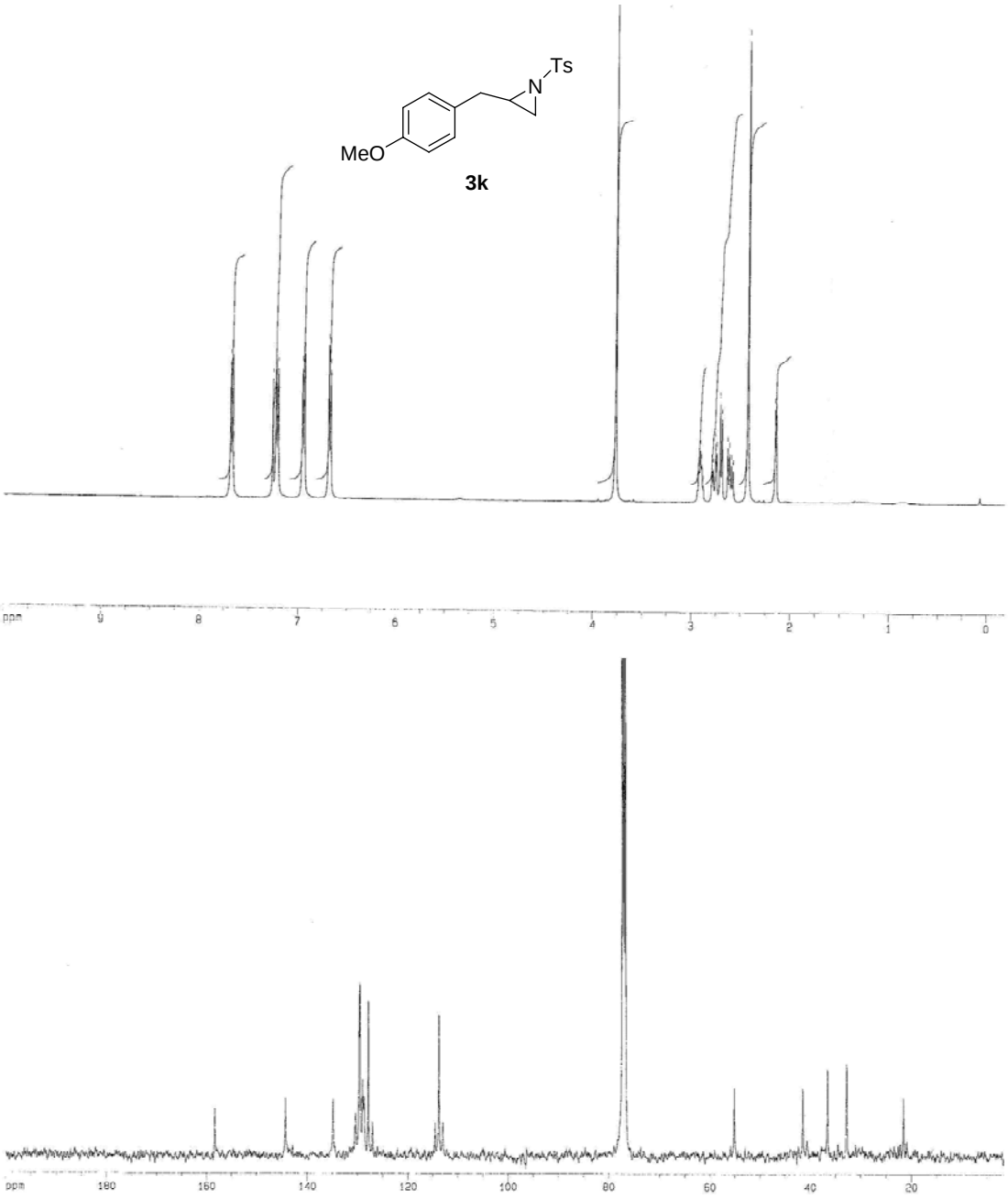


^{1}H and ^{13}C RMN spectra of *N*-(*p*-toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxyphenyl)aziridine (**2v**).

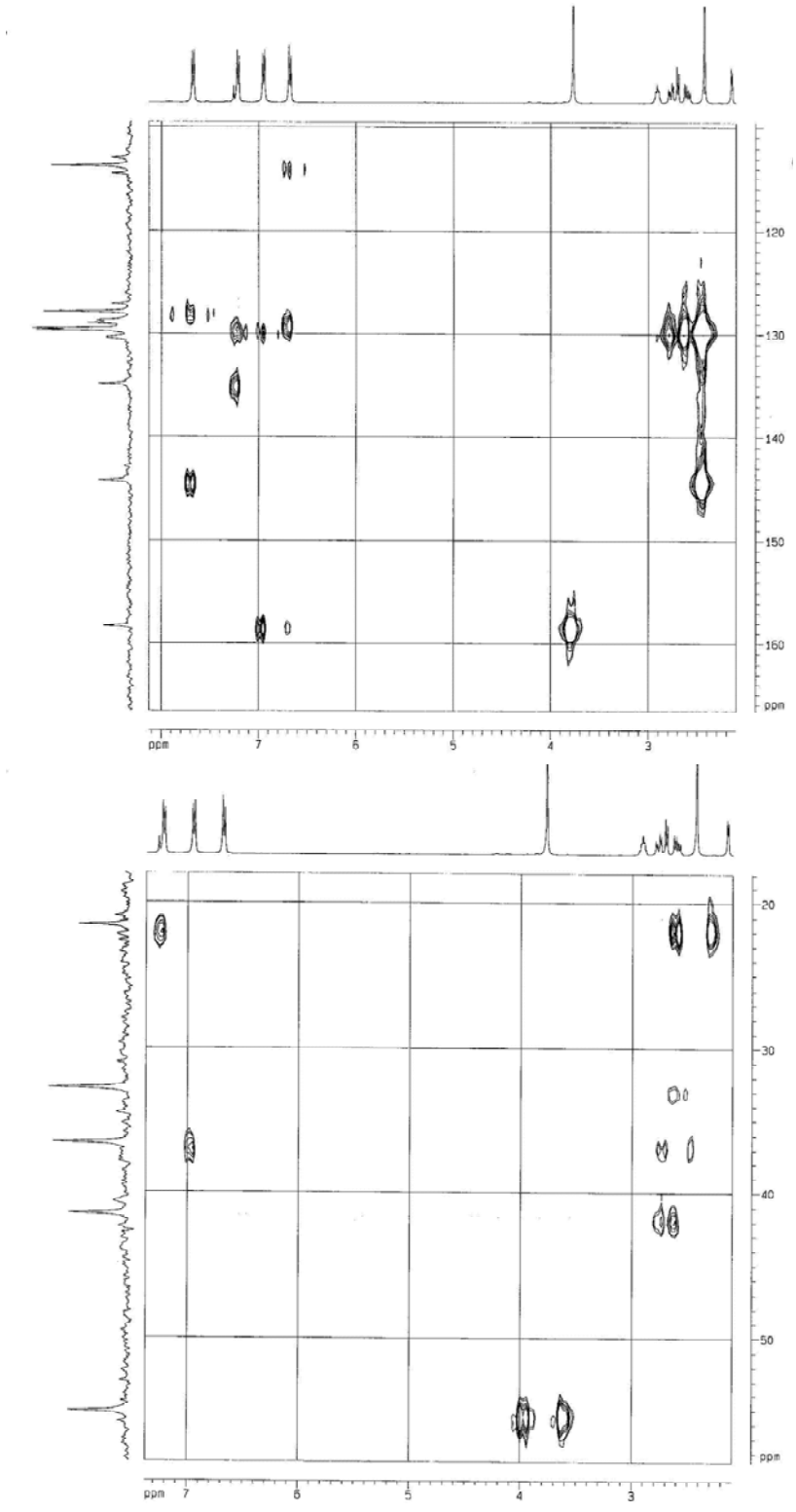


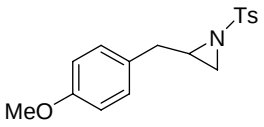
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
394.9827	93.78	394.9827	0.0	0.0	10.0	60.3	12C16 H14 N O4 S 79Br
395.9859	26.98	395.9860	-0.1	-0.3	10.0	82.8	12C15 13C H14 N O4 S 79Br
396.9805	100.00	396.9806	-0.1	-0.3	10.0	42.0	12C16 H14 N O4 S 81Br
397.9849	26.12	397.9840	0.9	2.3	10.0	2773551.8	12C15 13C H14 N O4 S 81Br
398.9878	8.03	398.9874	0.4	1.0	10.0	5546184.5	12C14 13C2 H14 N O4 S 81Br

Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxyphenyl)aziridine (**2v**)



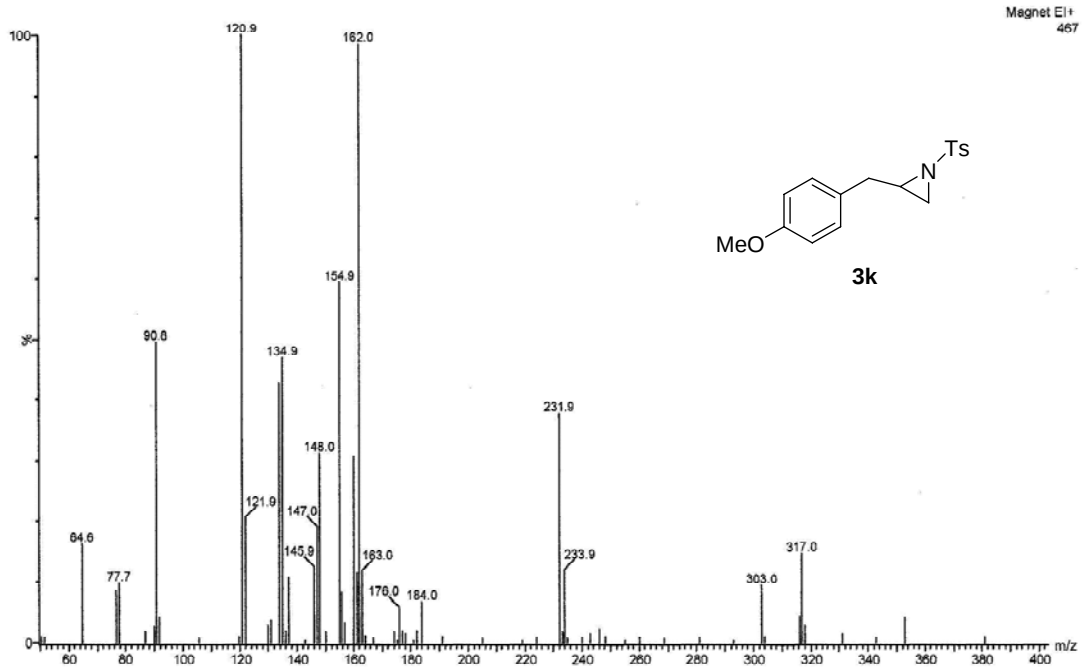
^{1}H NMR and ^{13}C NMR spectra of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3k**).

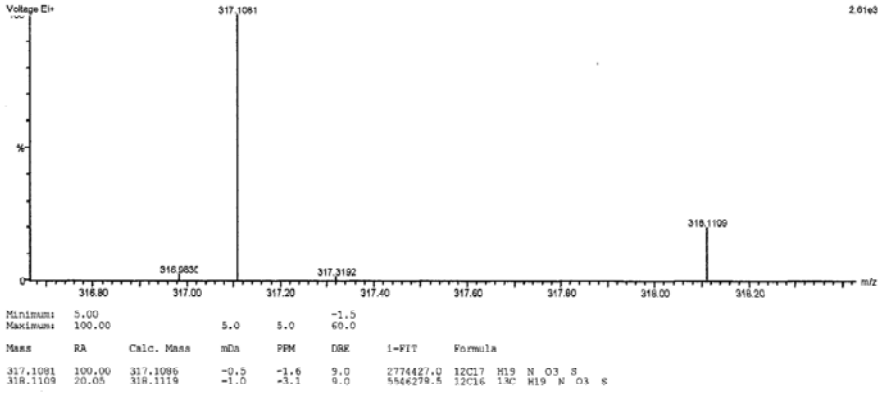




3k

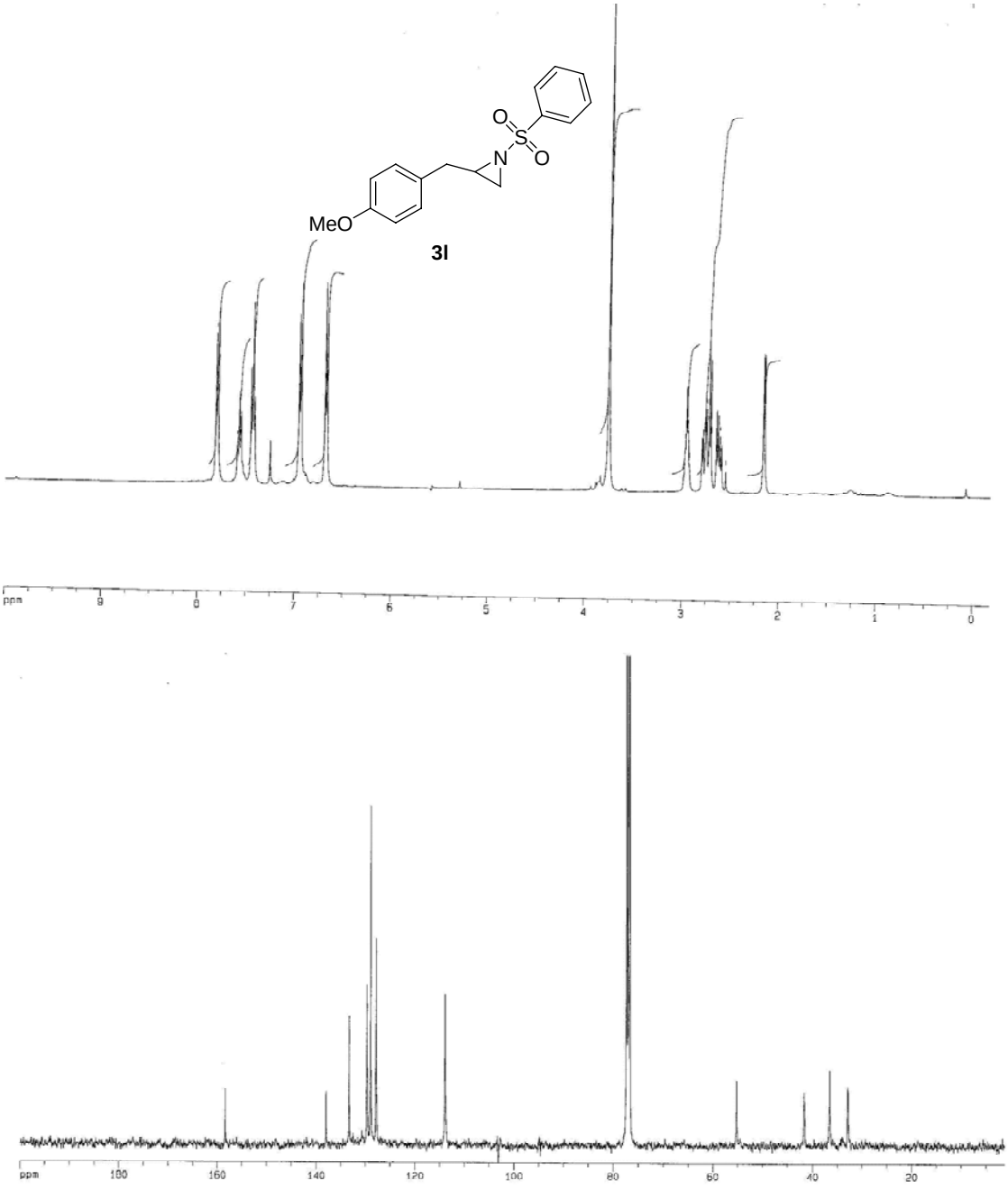
HMBC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3k**).



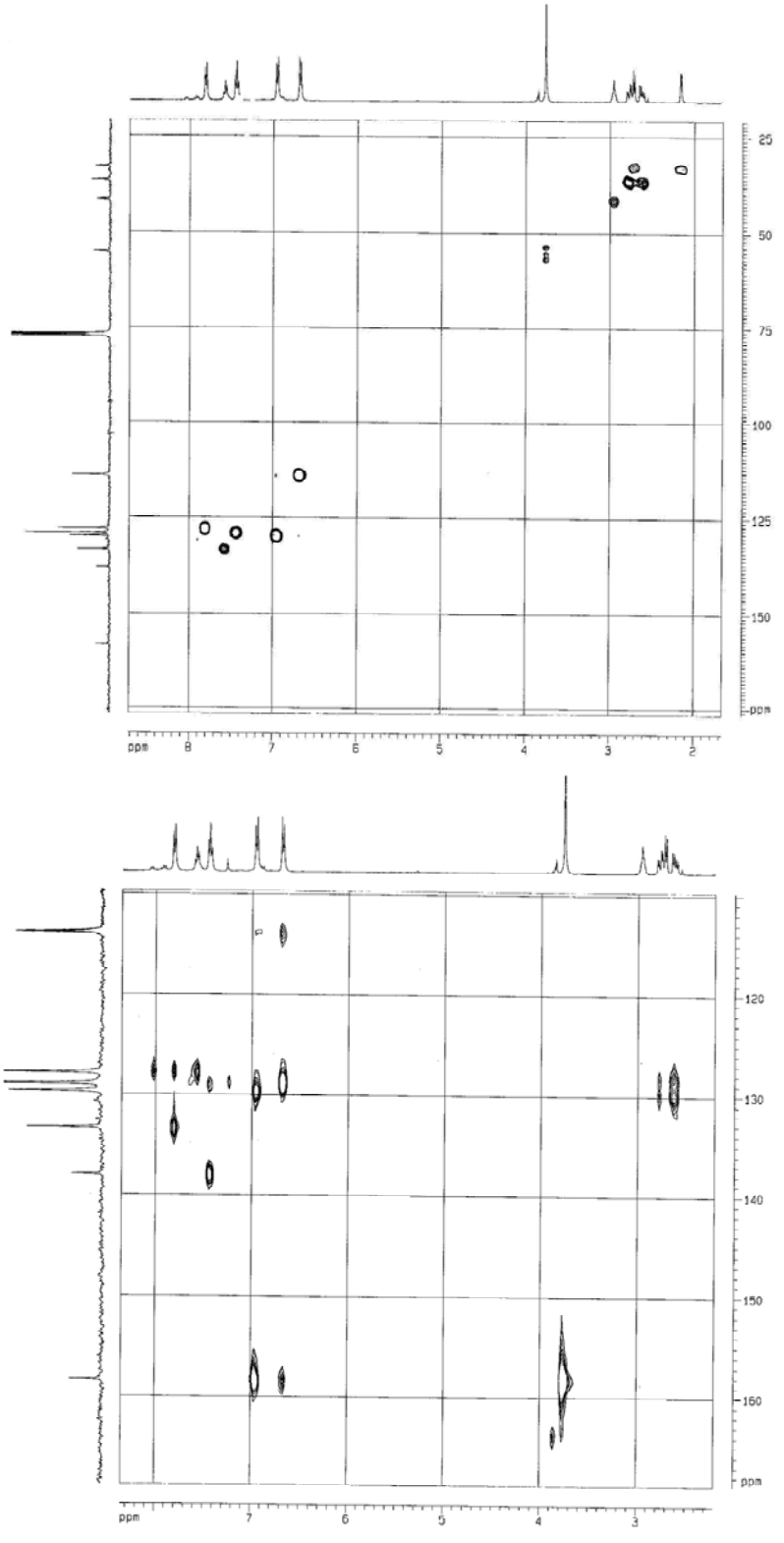


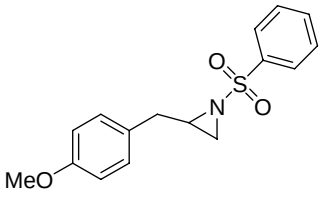
Minimum:	5.00			-1.5			
Maximum:	100.00		5.0	5.0	60.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
317.1081	100.00	317.1086	-0.5	-1.6	9.0	27764Z7.0	12C17 H19 N O3 S
318.1109	20.05	318.1119	-1.0	-3.1	9.0	5546279.5	12C16 13C H19 N O3 S

Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3k**).



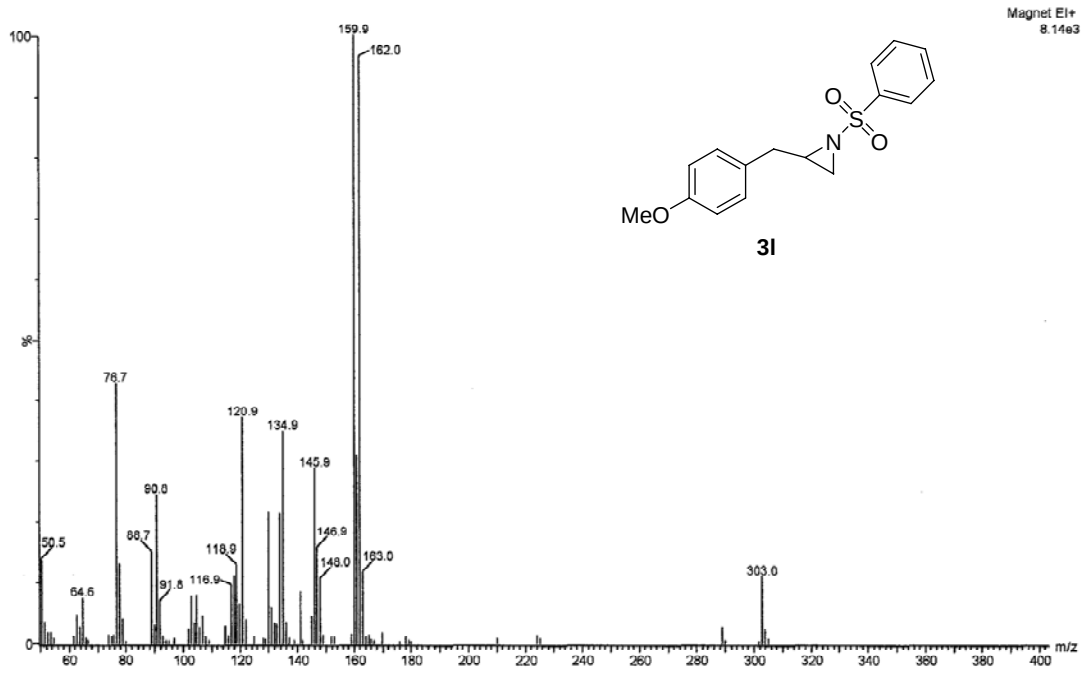
^{1}H NMR and ^{13}C NMR spectra of *N*-(benzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3l**).

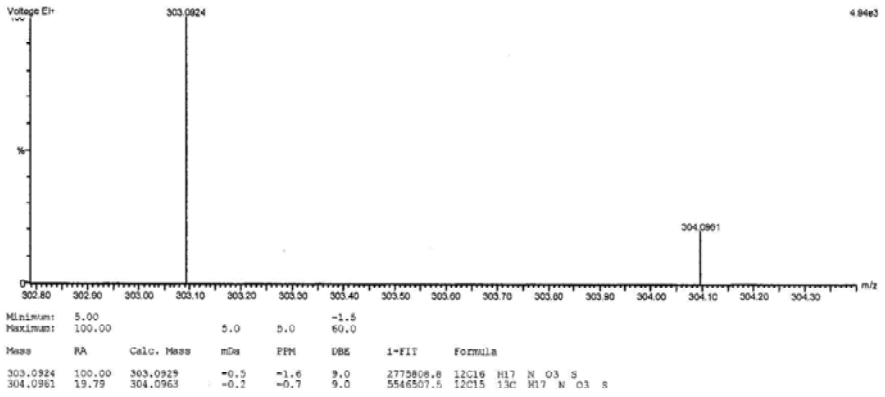




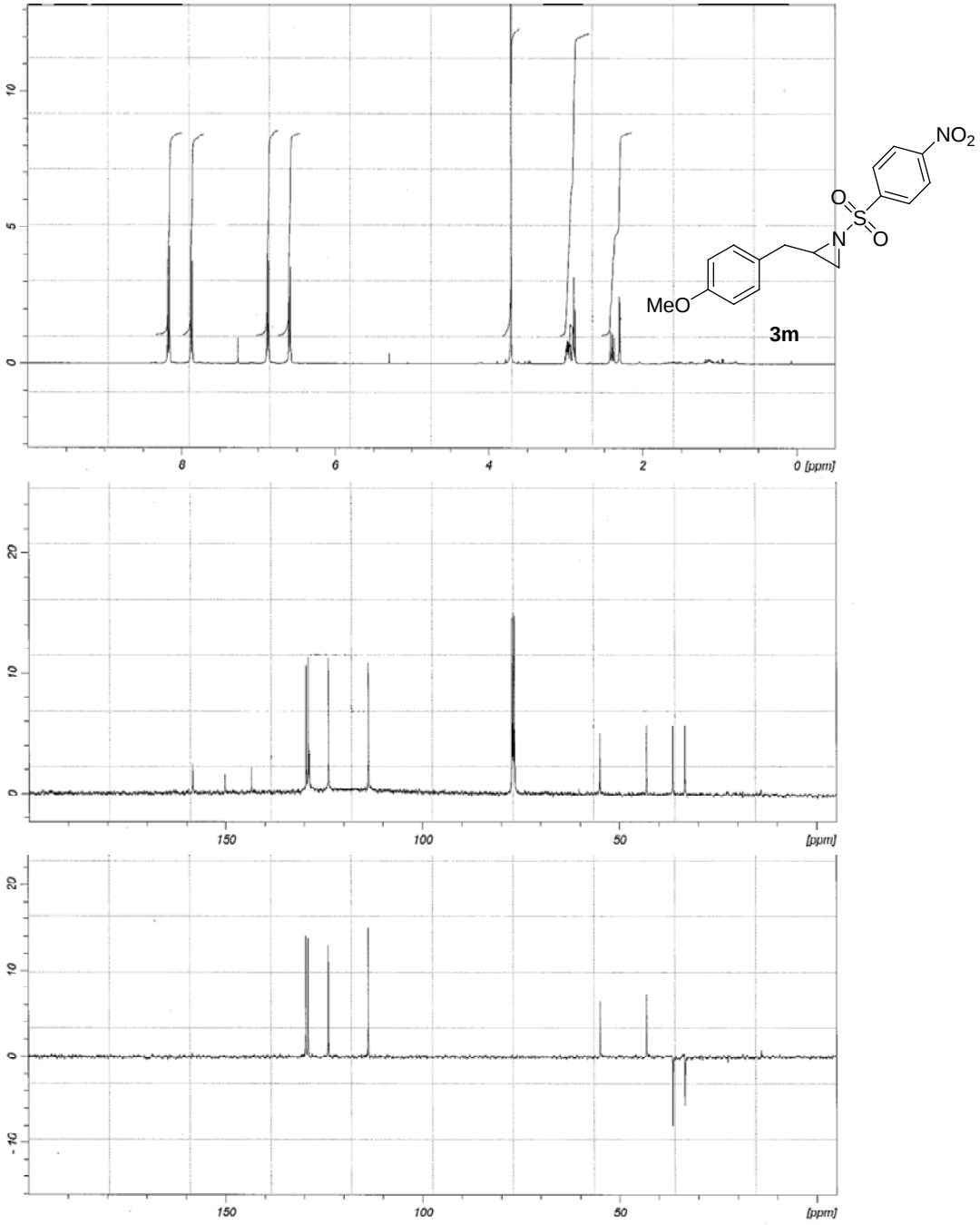
3l

HMQC and HMBC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3l**).

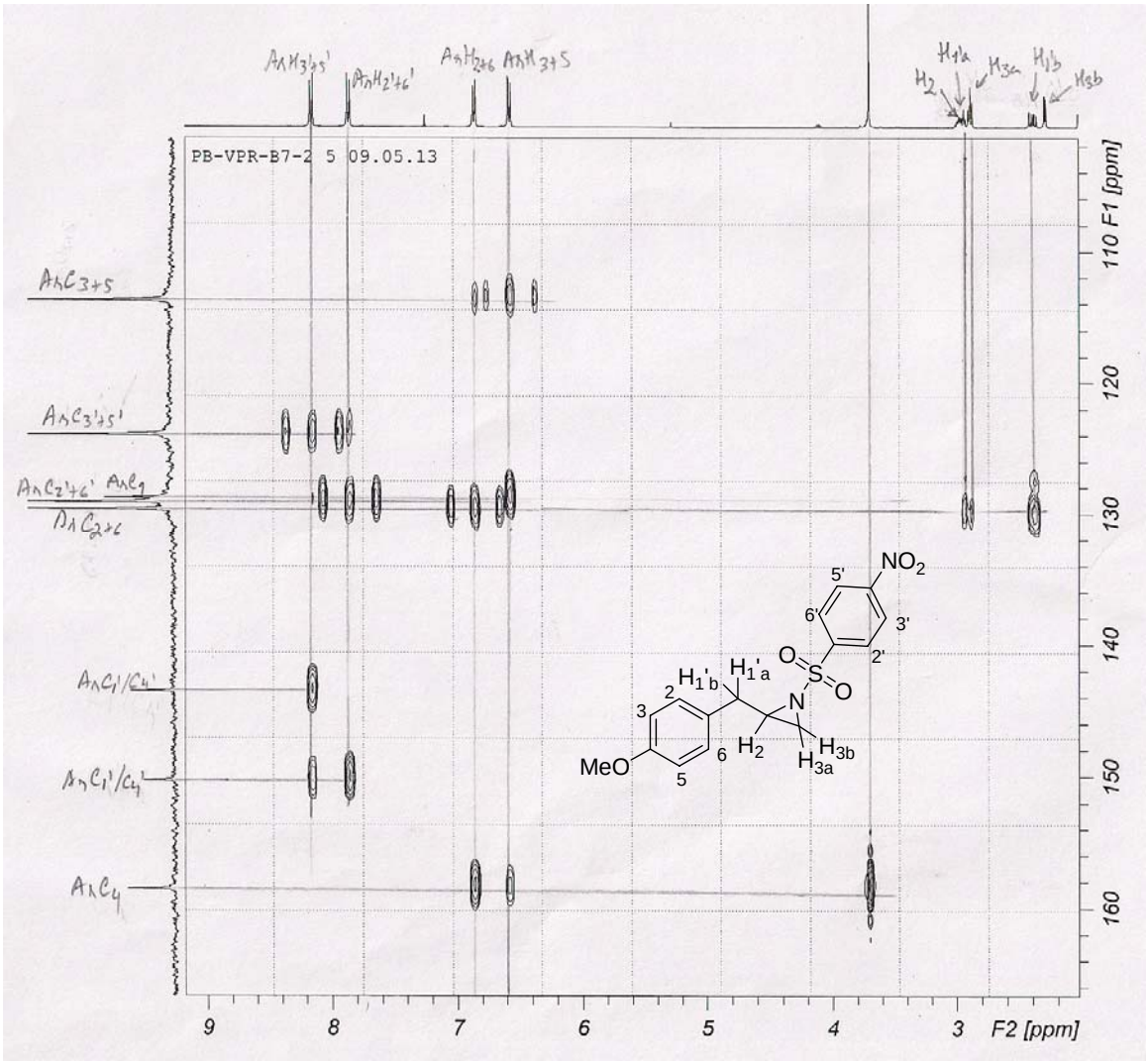




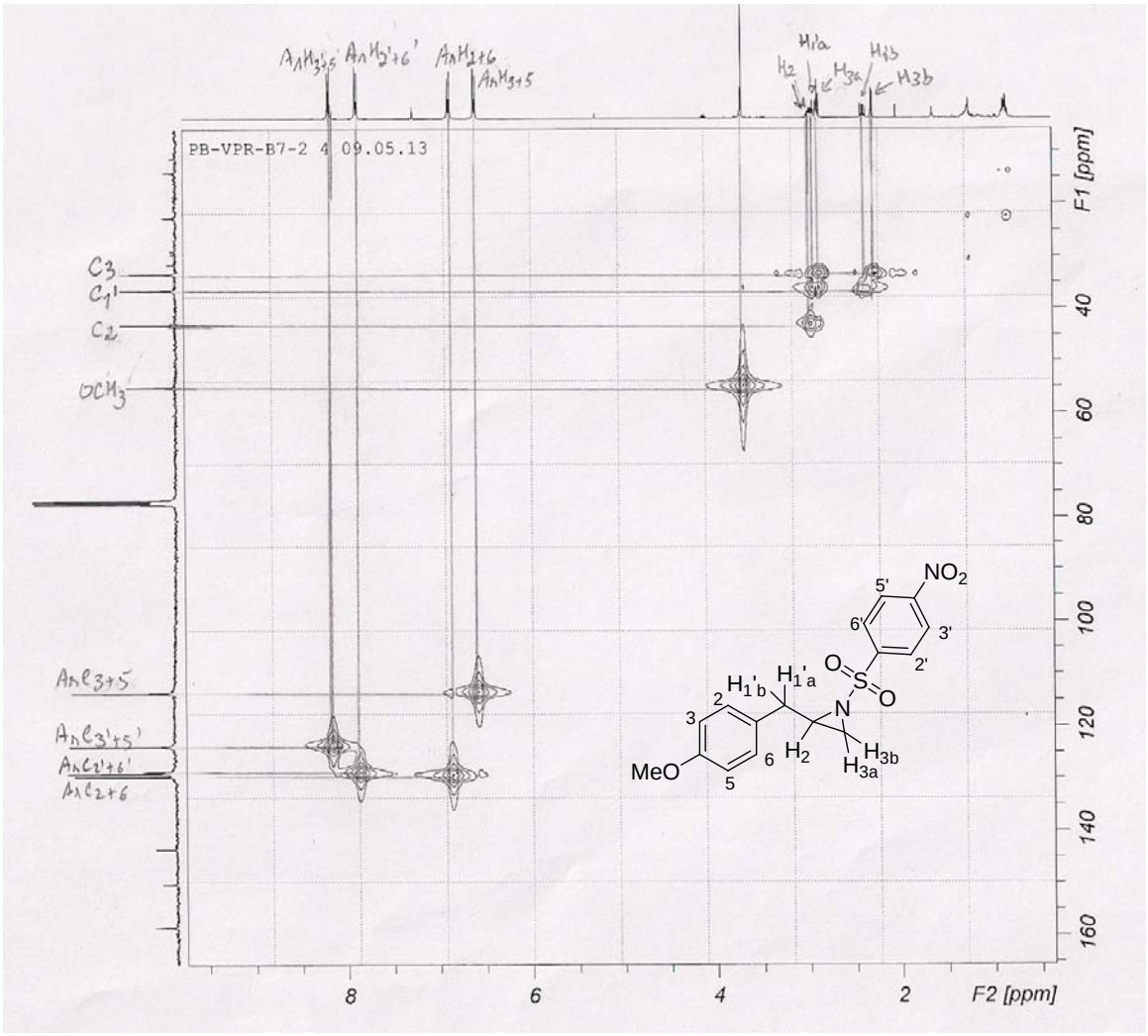
Mass spectra and HRMS of *N*-(benzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3l**).



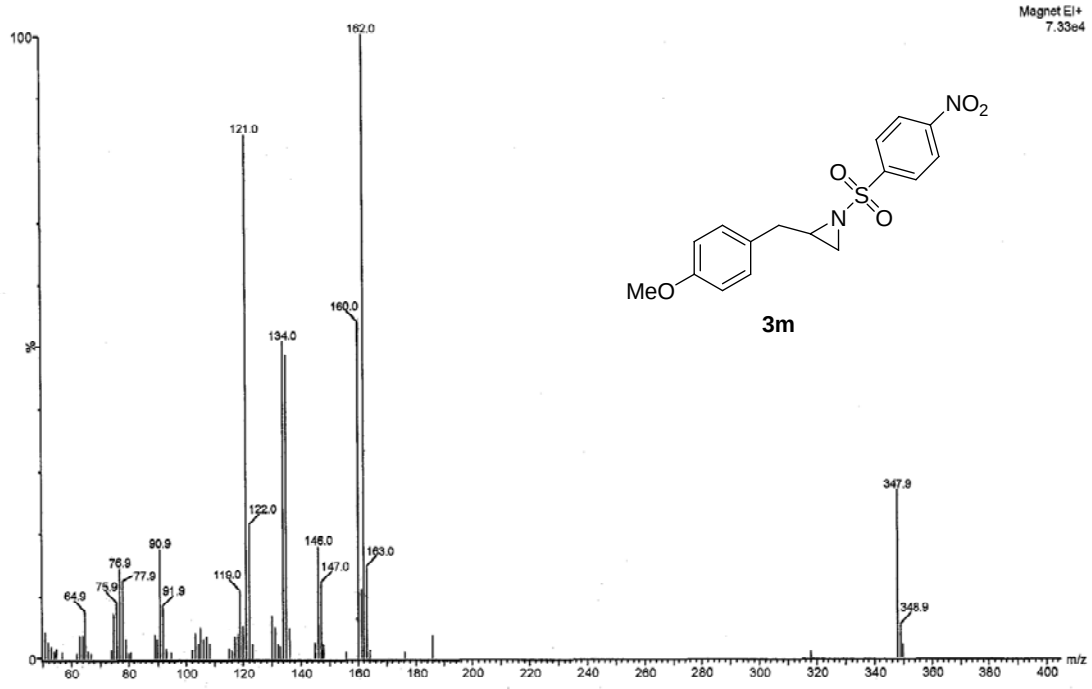
^{1}H NMR ,^{13}C NMR,and DEPT spectra of *N*-(*p*-nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3m**).

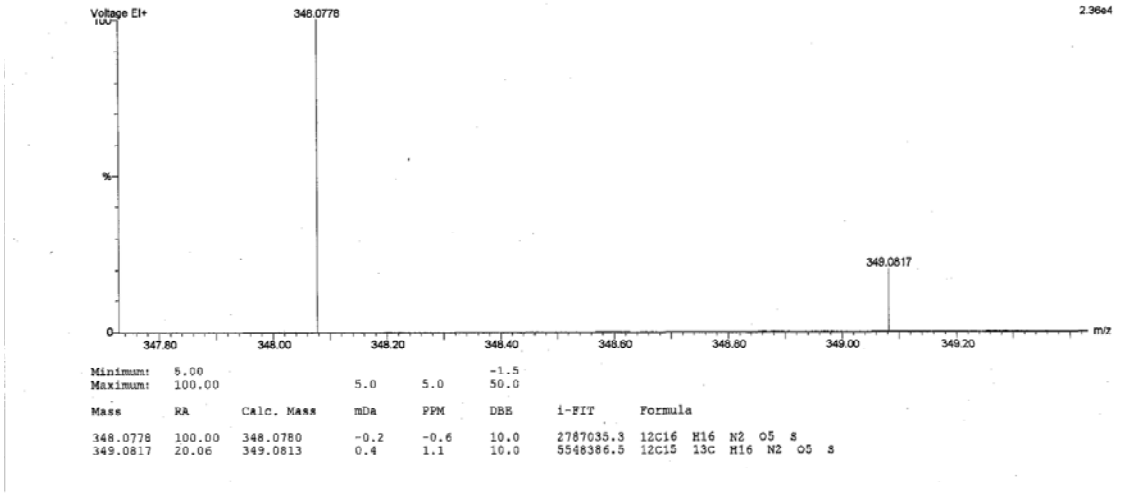


HMBC correlation spectra of *N*-(*p*-nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3m**).



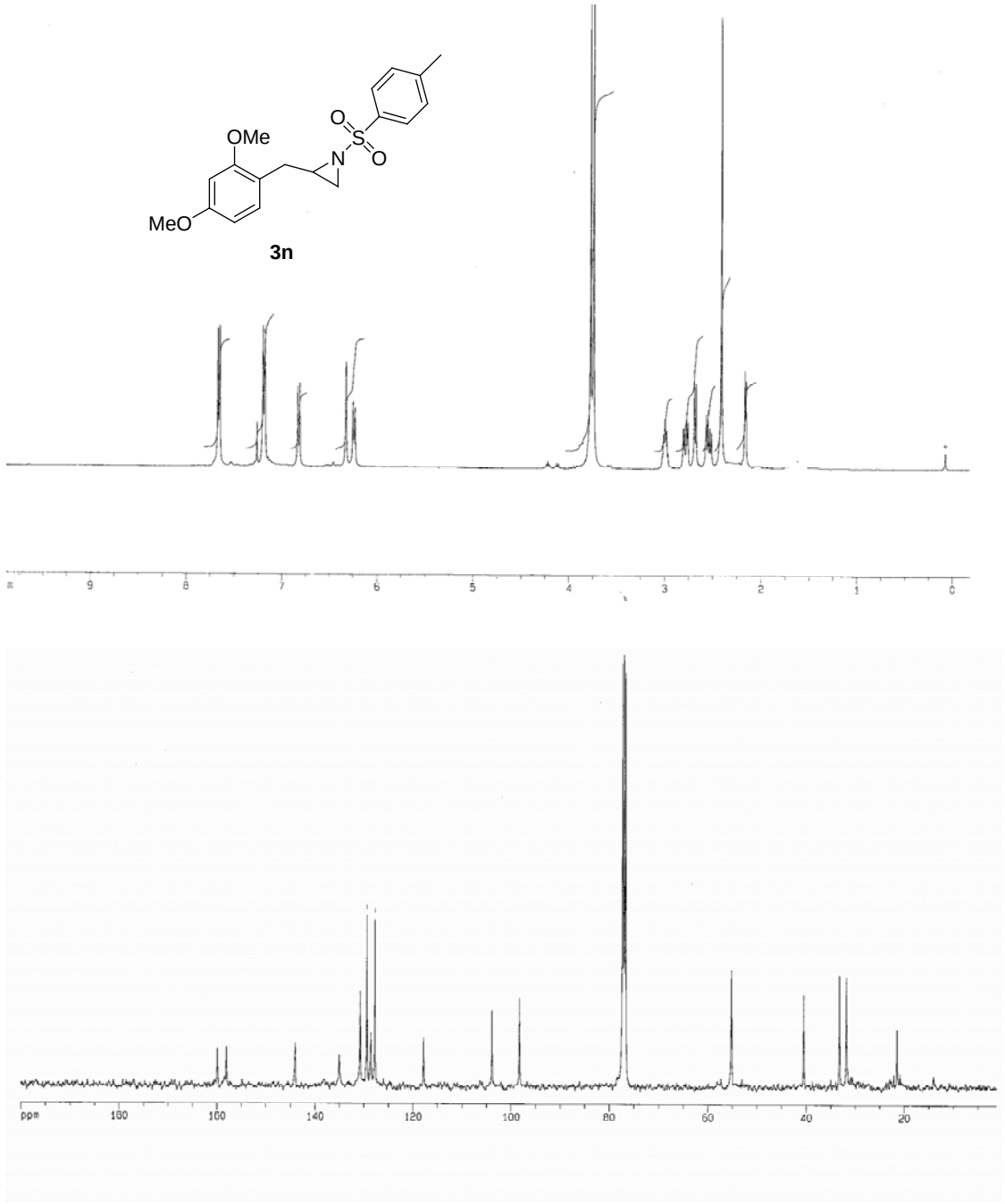
HMQC correlation spectra of *N*-(*p*-nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3m**).



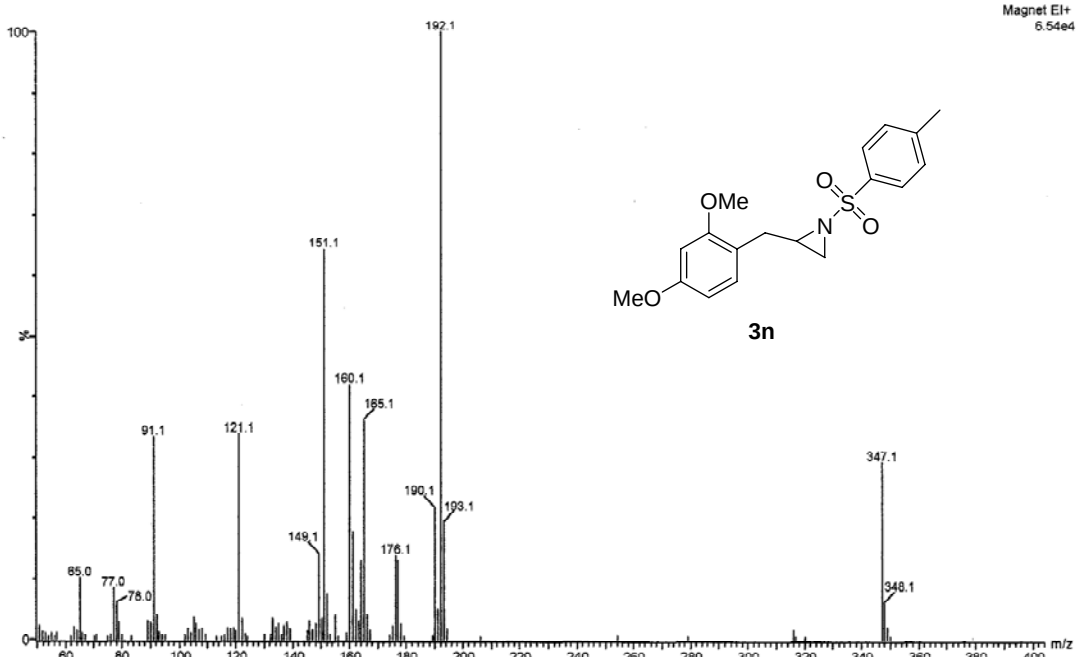


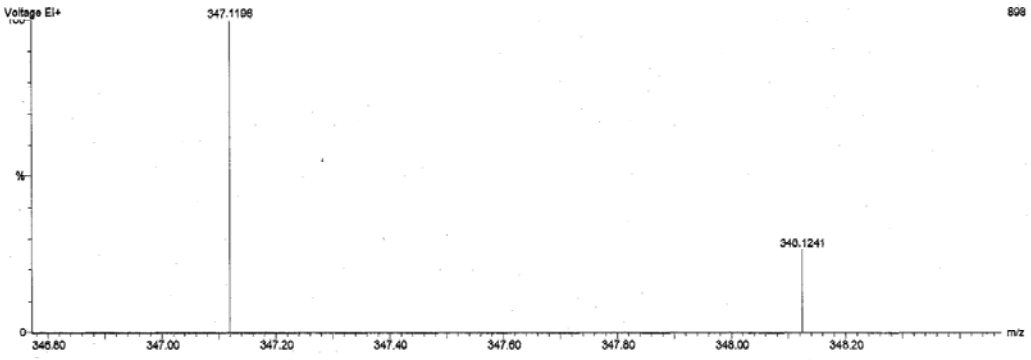
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
348.0778	100.00	348.0780	-0.2	-0.6	10.0	2787035.3	12C16 H16 N2 O5 S
349.0817	20.06	349.0813	0.4	1.1	10.0	5548386.5	12C15 13C H16 N2 O5 S

Mass spectra and HRMS of *N*-(*p*-nitrobenzenesulfonyl)-2-(4-methoxybenzyl)aziridine (**3m**).



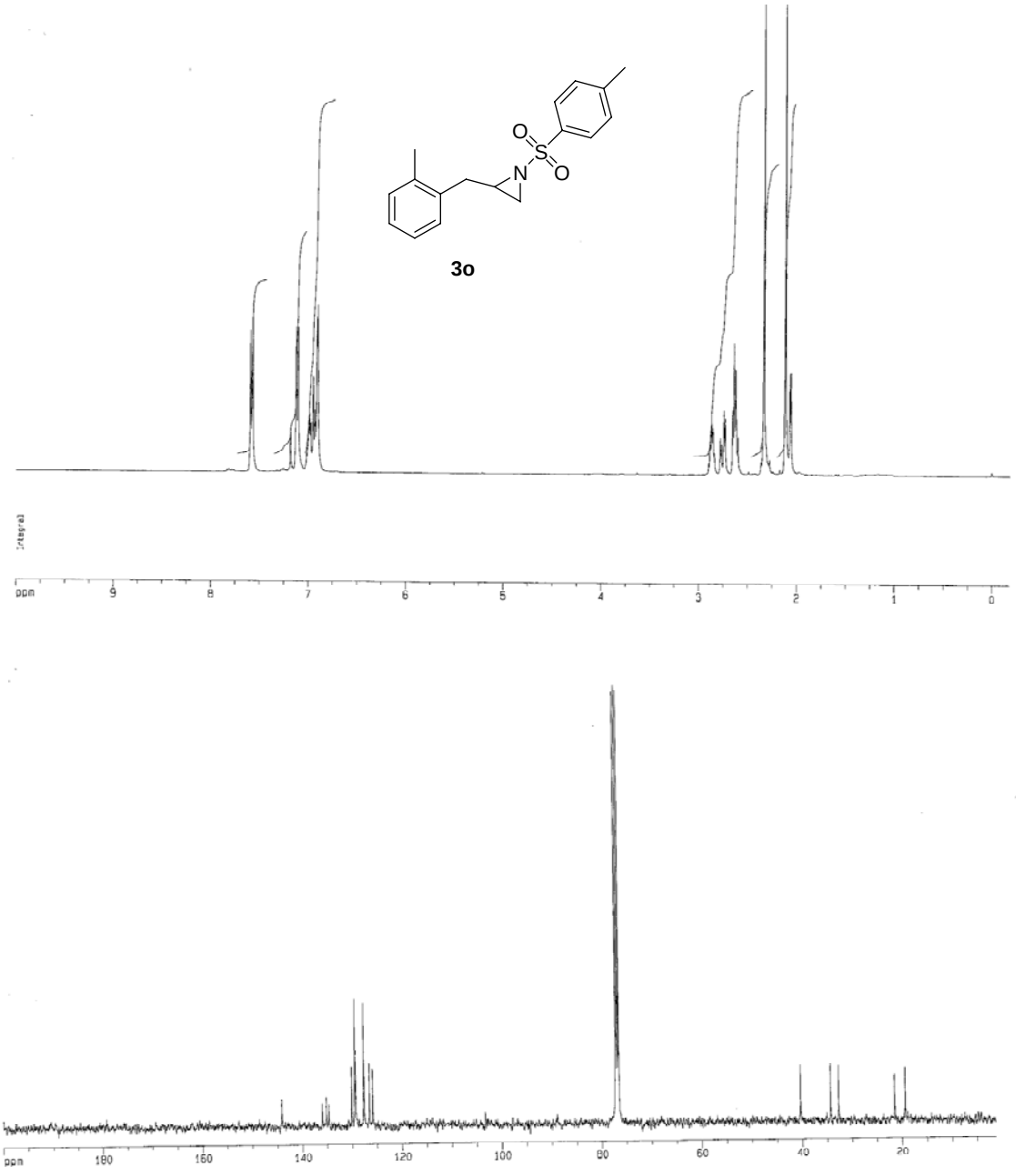
^{1}H NMR and ^{13}C NMR spectra of *N*-(*p*-toluenesulfonyl)-2-(2,4-dimethoxybenzyl)aziridine (**3n**).



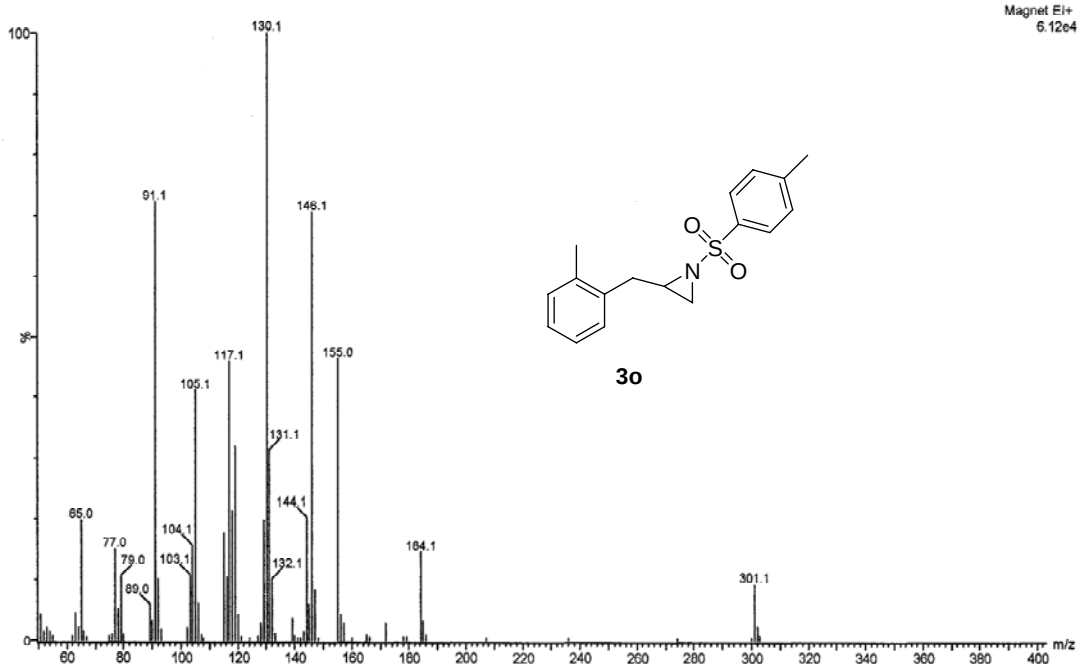


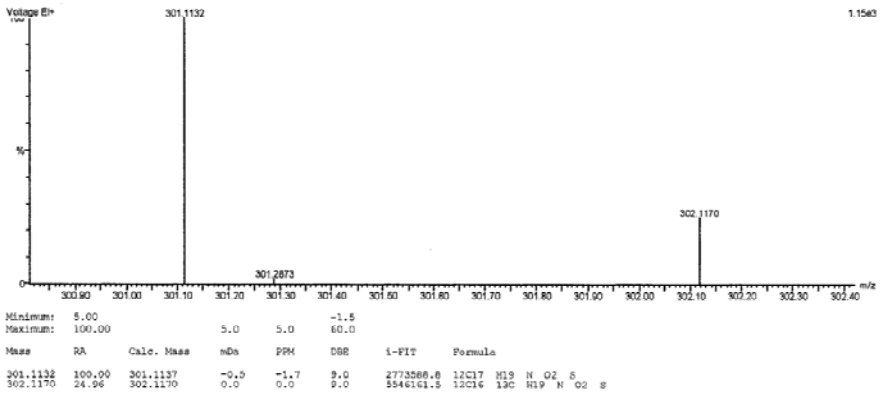
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
347.1196	100.00	347.1191	0.5	1.4	9.0	2773459.3	12C18 H21 N 04 S
348.1241	26.39	348.1225	1.6	4.6	9.0	5546136.5	12C17 13C H21 N 04 S

Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(2,4-dimethoxybenzyl)aziridine (**3n**).



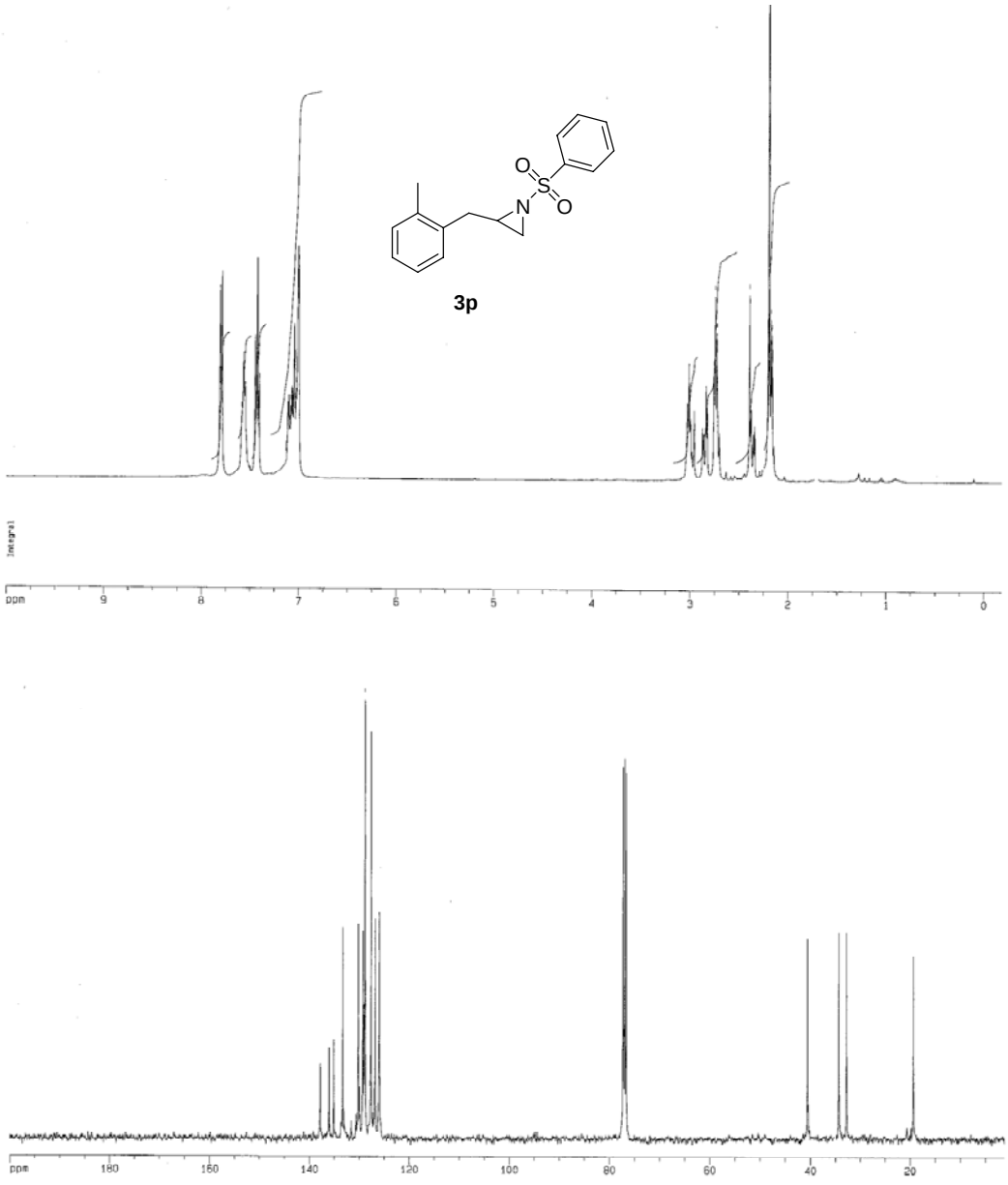
^{1}H NMR and ^{13}C NMR spectra of *N*-(*p*-toluenesulfonyl)-2-(2-methylbenzyl)aziridine (**3o**).



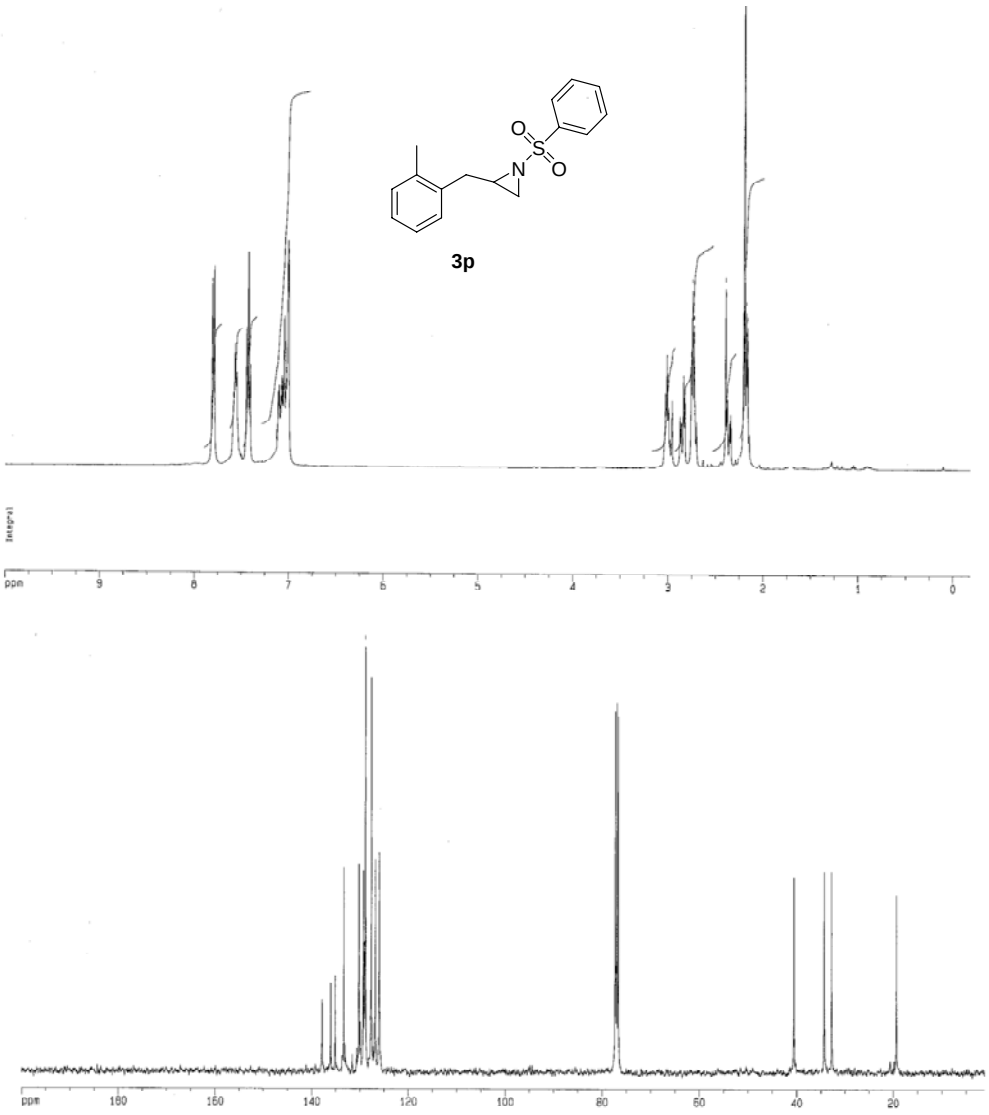


Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	60.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.1132	100.00	301.1137	-0.5	-1.7	9.0	2773566.8	12C17 H19 N O2 S
302.1170	24.96	302.1170	0.0	0.0	9.0	5546161.5	12C16 13C H19 N O2 S

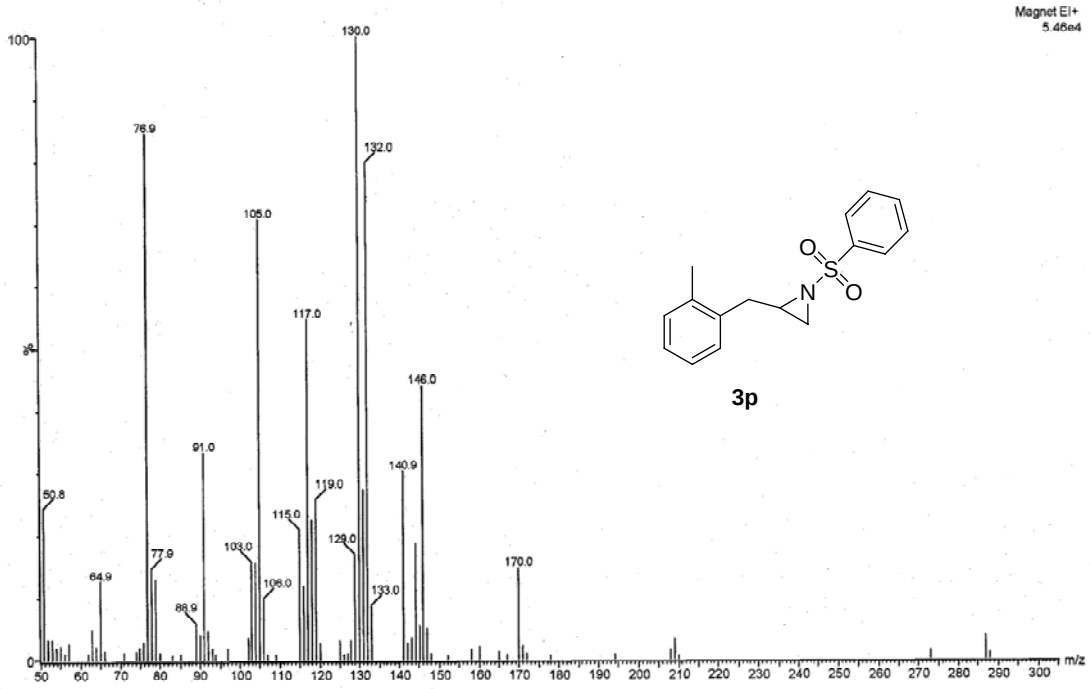
Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(2-methylbenzyl)aziridine (**3o**).



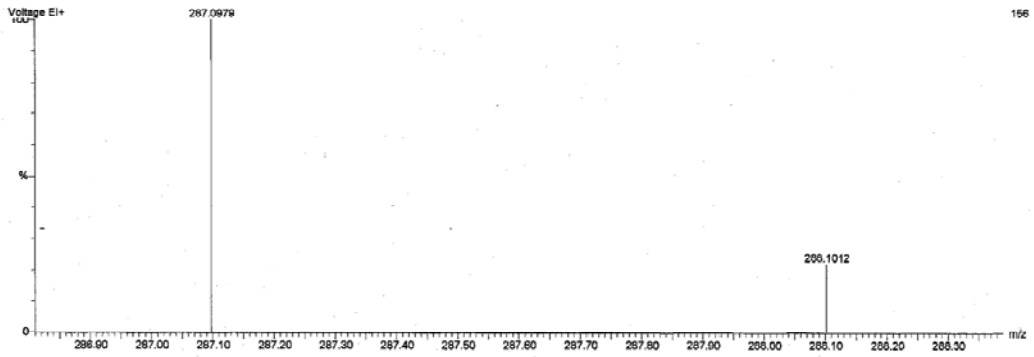
^{1}H and ^{13}C NMR of *N*-(benzenesulfonyl)-2-(2-methylbenzyl)aziridine (**3p**).



^{1}H NMR and ^{13}C NMR spectra of *N*-(benzenesulfonyl)-2-(2-methylbenzyl)aziridine (**3p**).

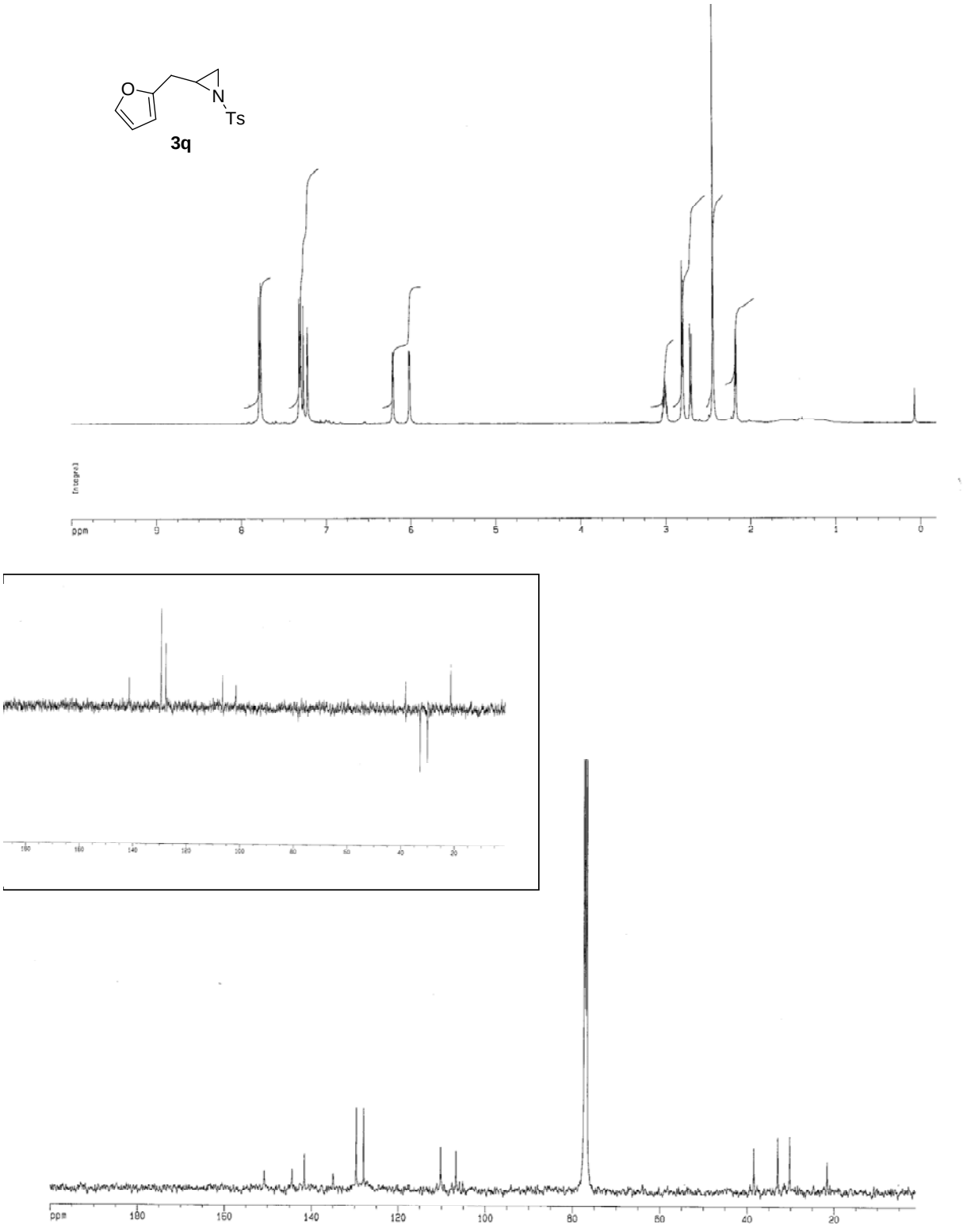


3p

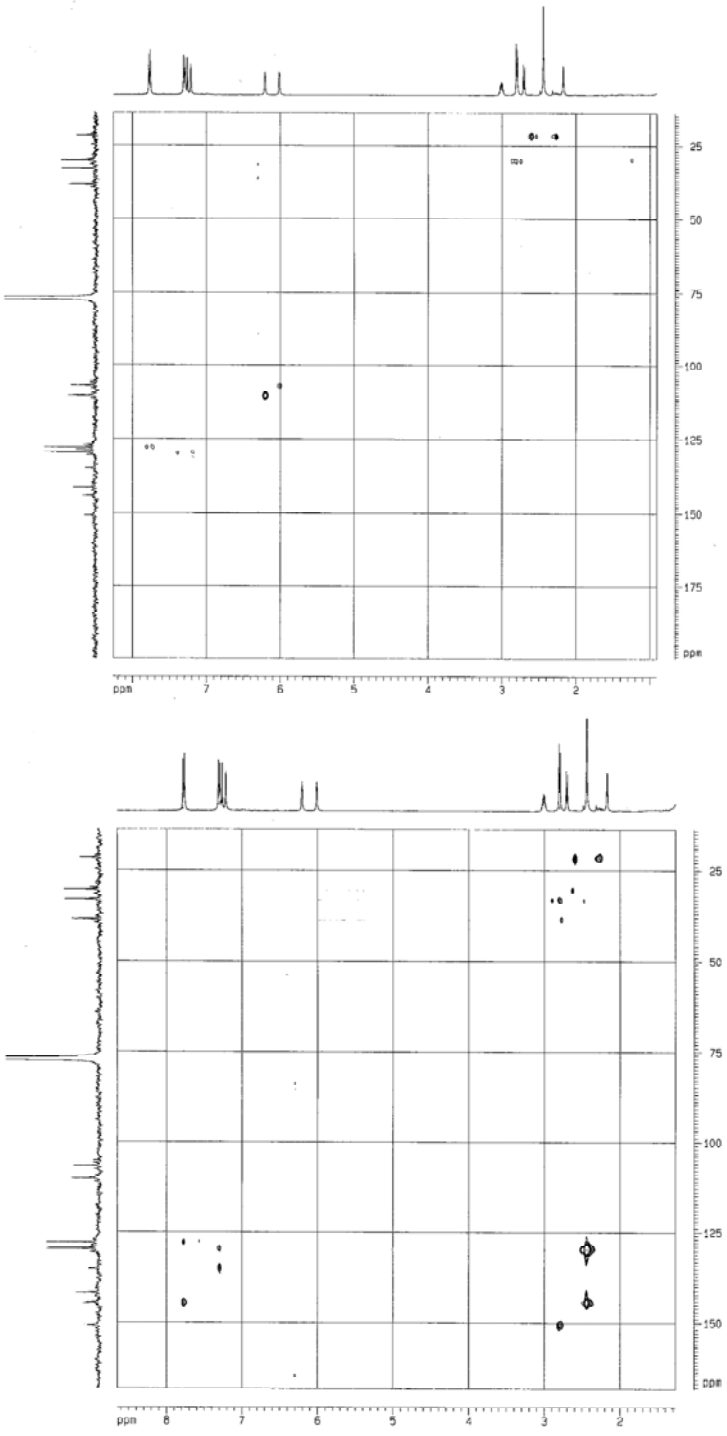


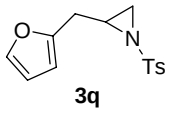
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
287.0979	100.00	287.0980	-0.1	-0.3	9.0	2773041.0	12C16 H17 N O2 S
288.1012	21.78	288.1014	-0.2	-0.7	9.0	5546036.5	12C15 13C H17 N O2 S

Mass spectra and HRMS of *N*-benzenesulfonyl)-2-(2-methylbenzyl)aziridine (**3p**).



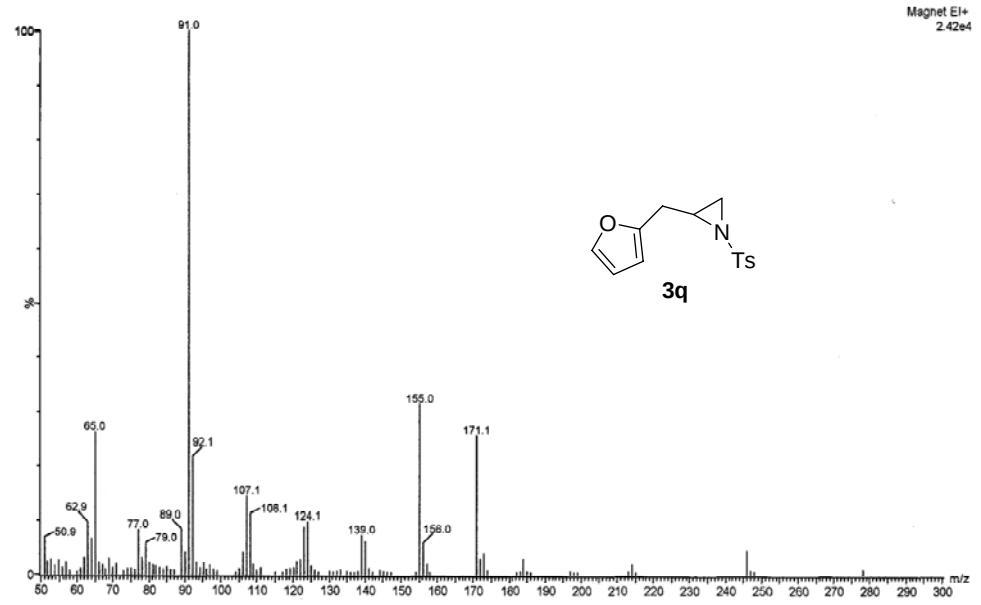
^{1}H NMR, ^{13}C NMR and DEPT spectra of *N*-(*p*-toluenesulfonyl)-2-(furanyllmrethyll)aziridine (**3q**).

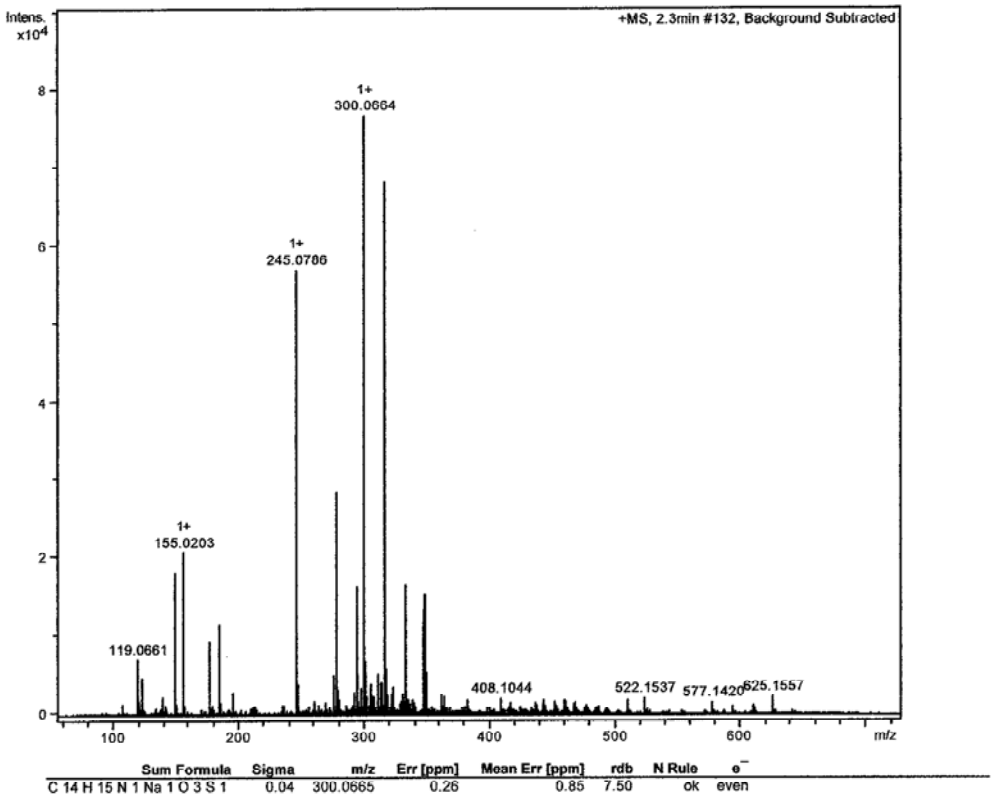




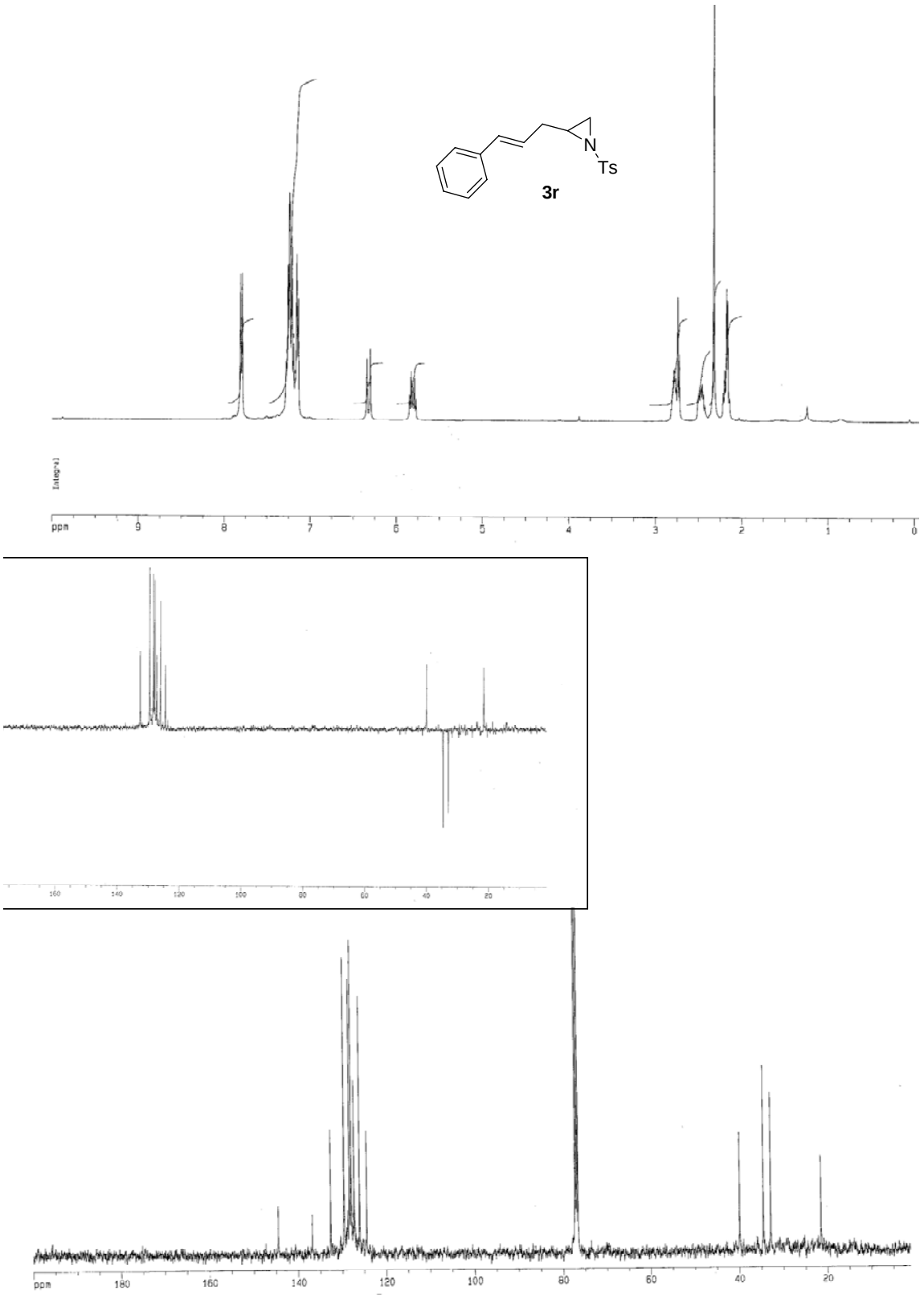
3q

HMQC and HMBC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(furanyllmrethyll)aziridine (**3q**).

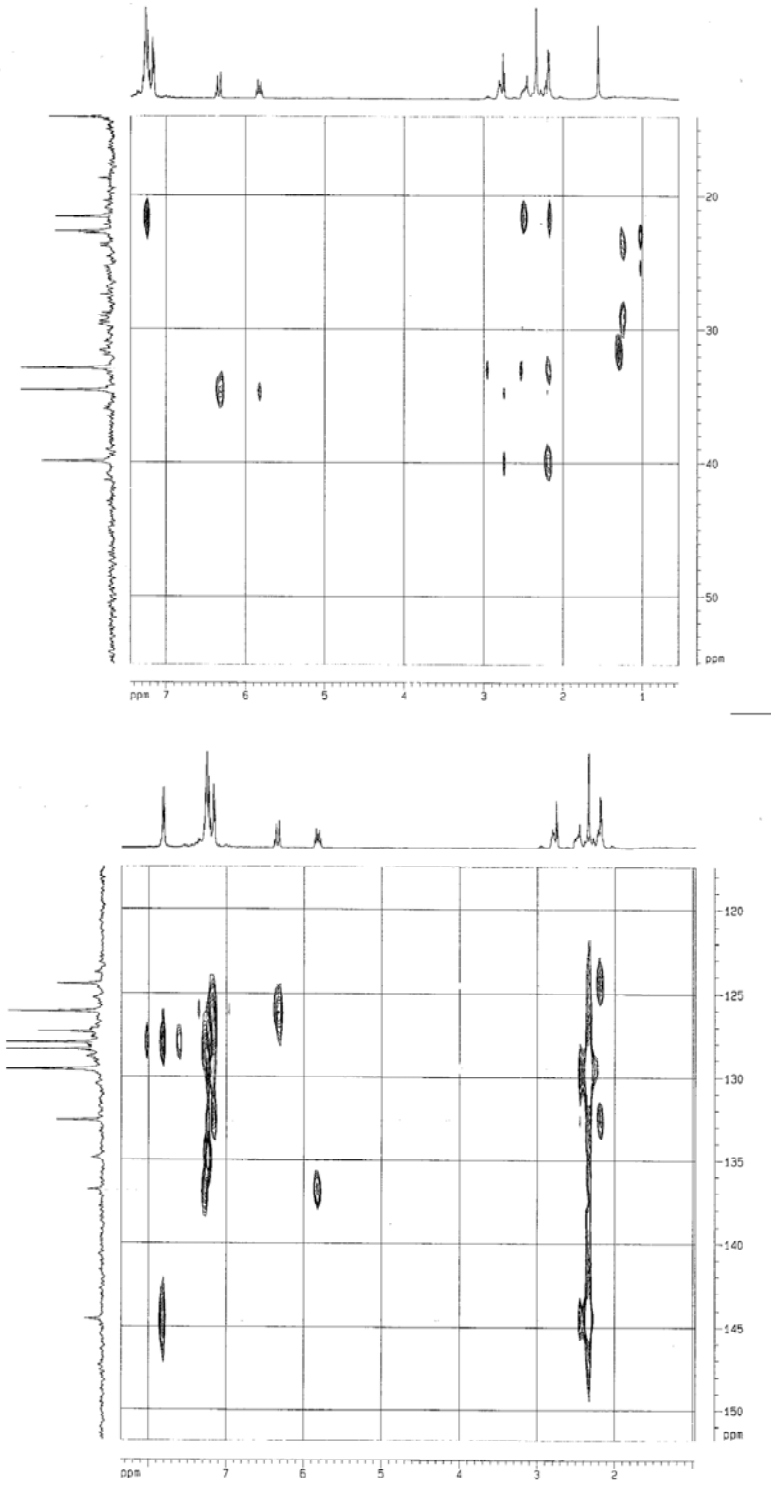


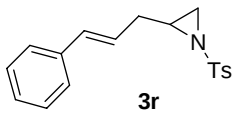


Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(furanyllmrethyl)aziridine (**3q**).



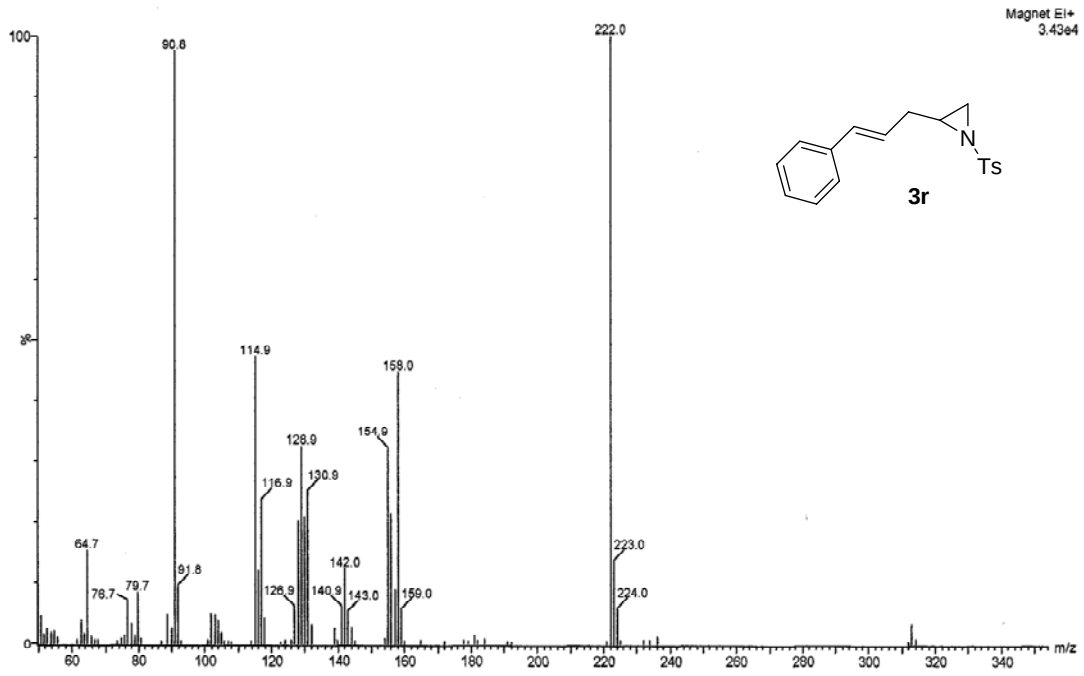
^{1}H NMR, ^{13}C NMR and DEPT spectra of *N*-(*p*-toluenesulfonyl)-2-(2-phenylethenyl)aziridine (**3r**).

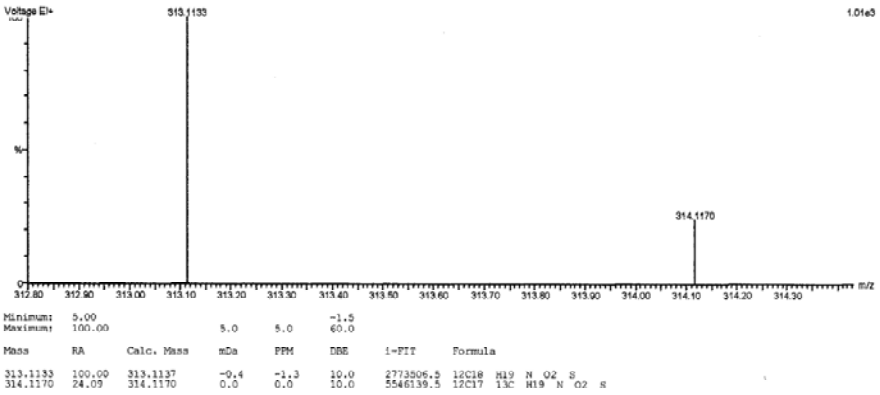




3r

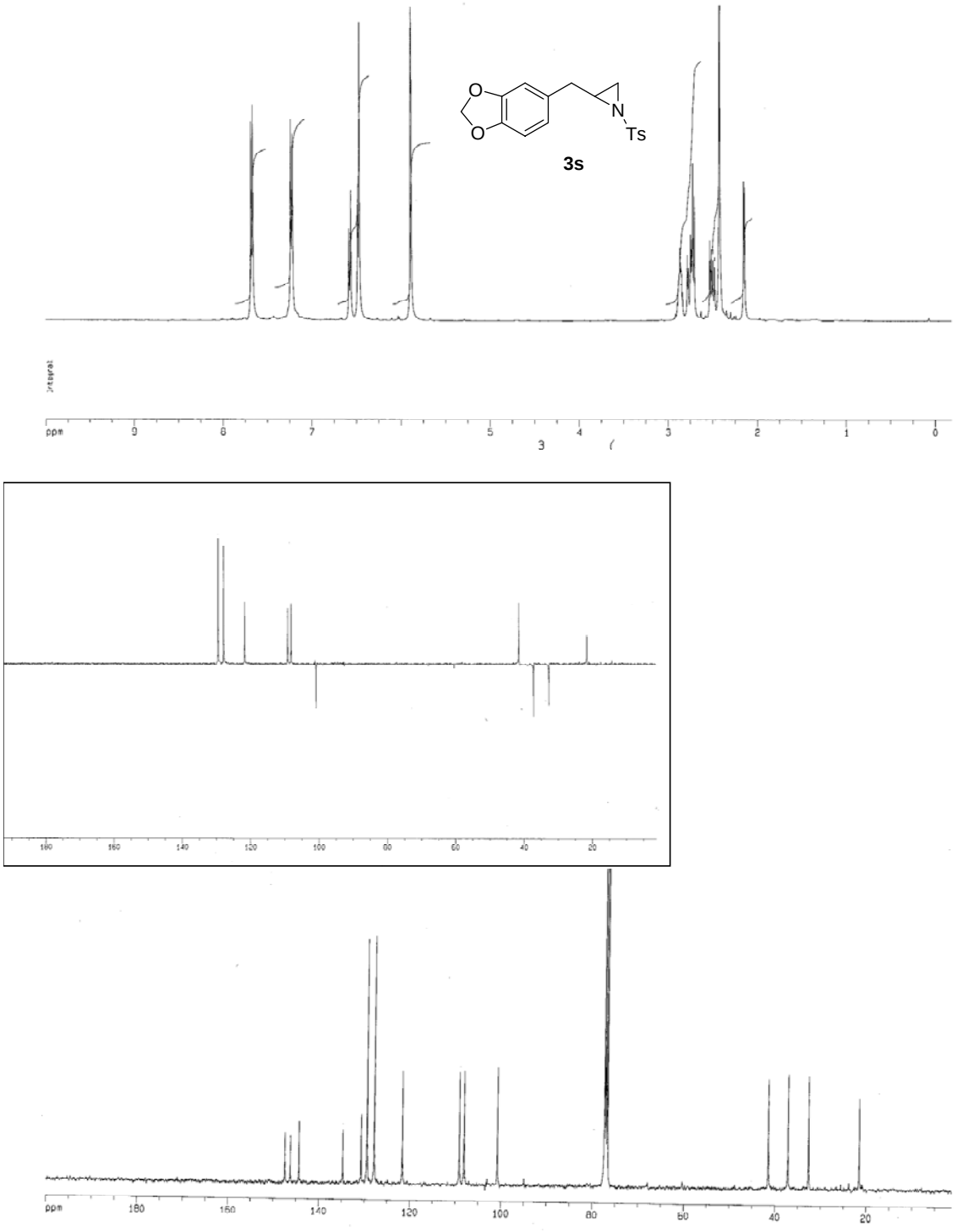
HMBC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(2-phenylethenyl)aziridine (**3r**).



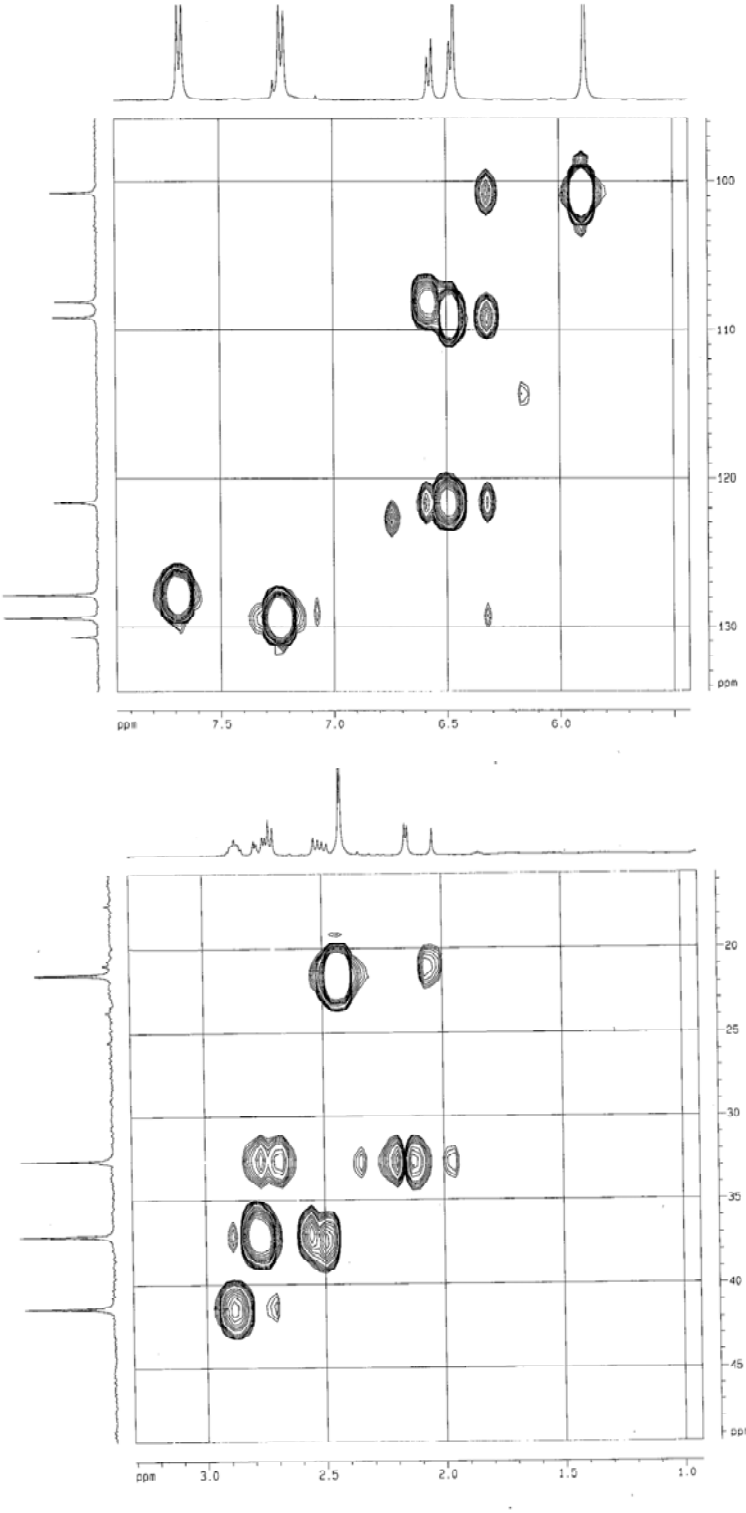


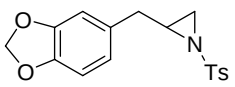
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	60.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
313.1133	100.00	313.1137	-0.4	-1.3	10.0	2773506.5	12C18 H19 N O2 S
314.1170	24.09	314.1170	0.0	0.0	10.0	5546139.5	12C17 13C H19 N O2 S

Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(2-phenylethenyl)aziridine (**3r**).



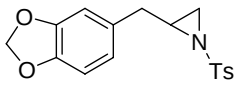
^{1}H NMR, ^{13}C NMR and DEPT spectra of *N*-(*p*-toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3s**).



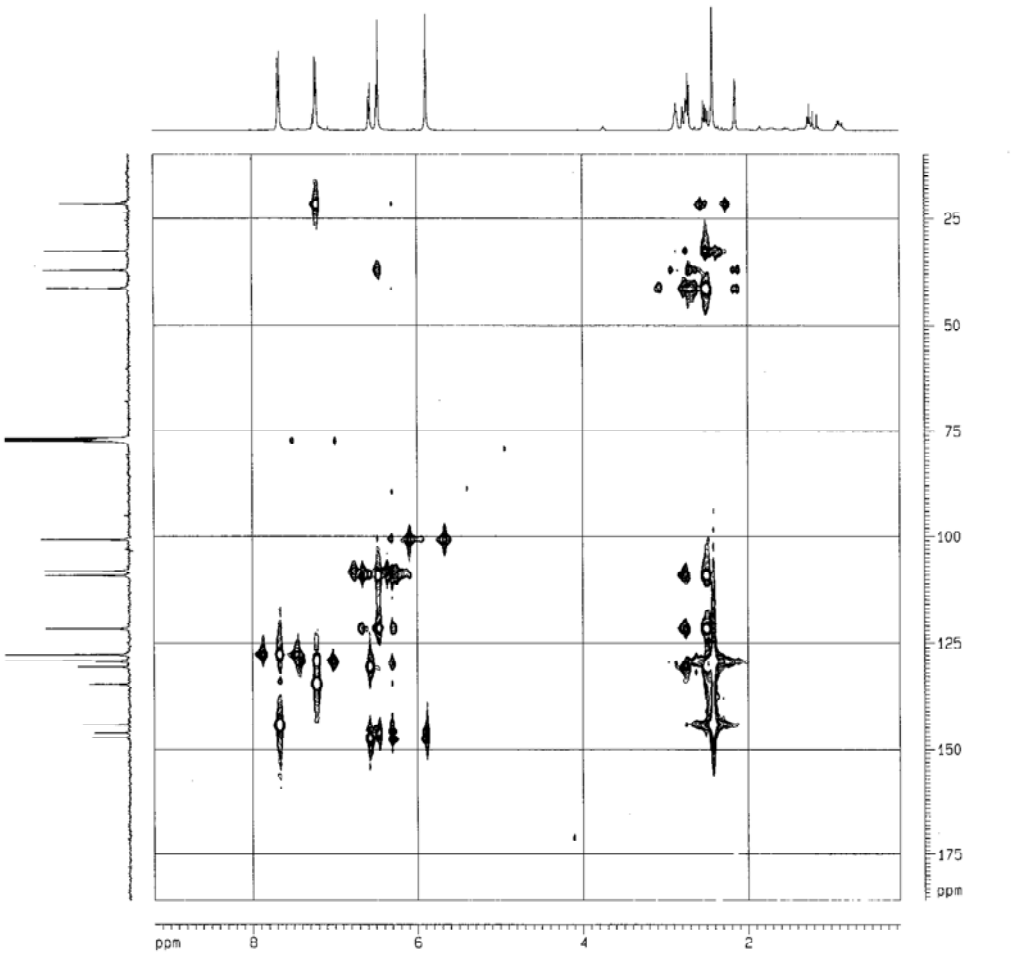


3s

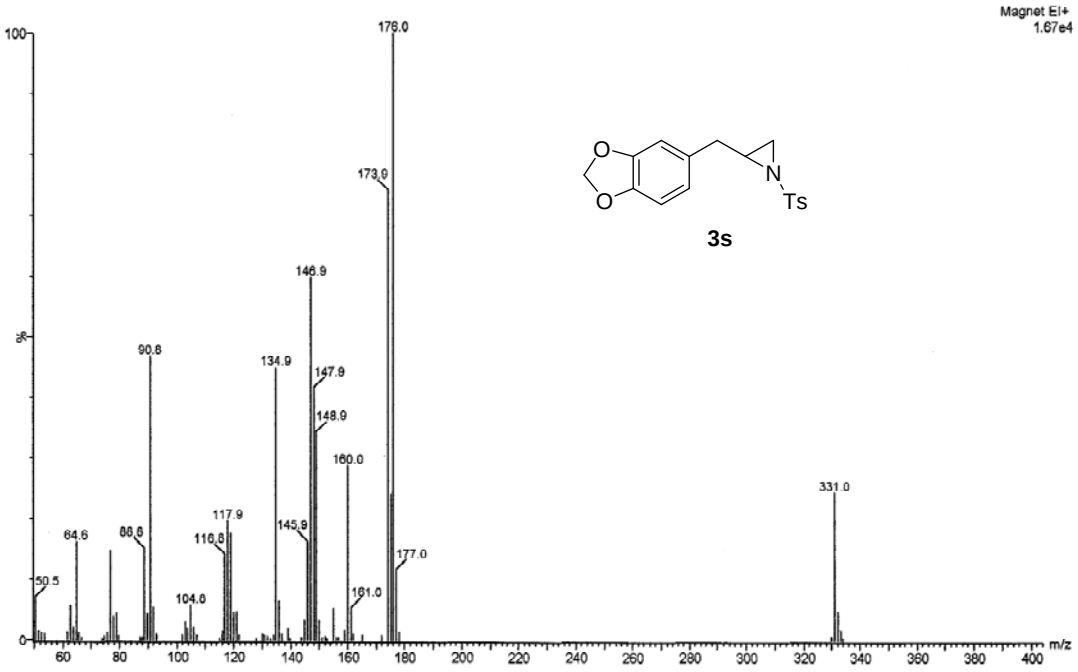
HMQC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3s**).

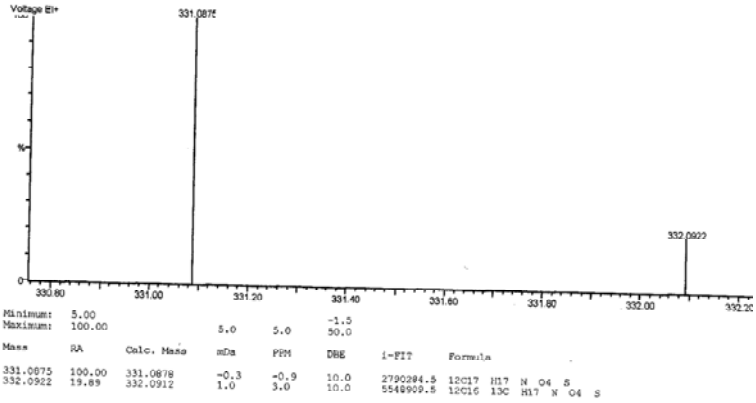


3s

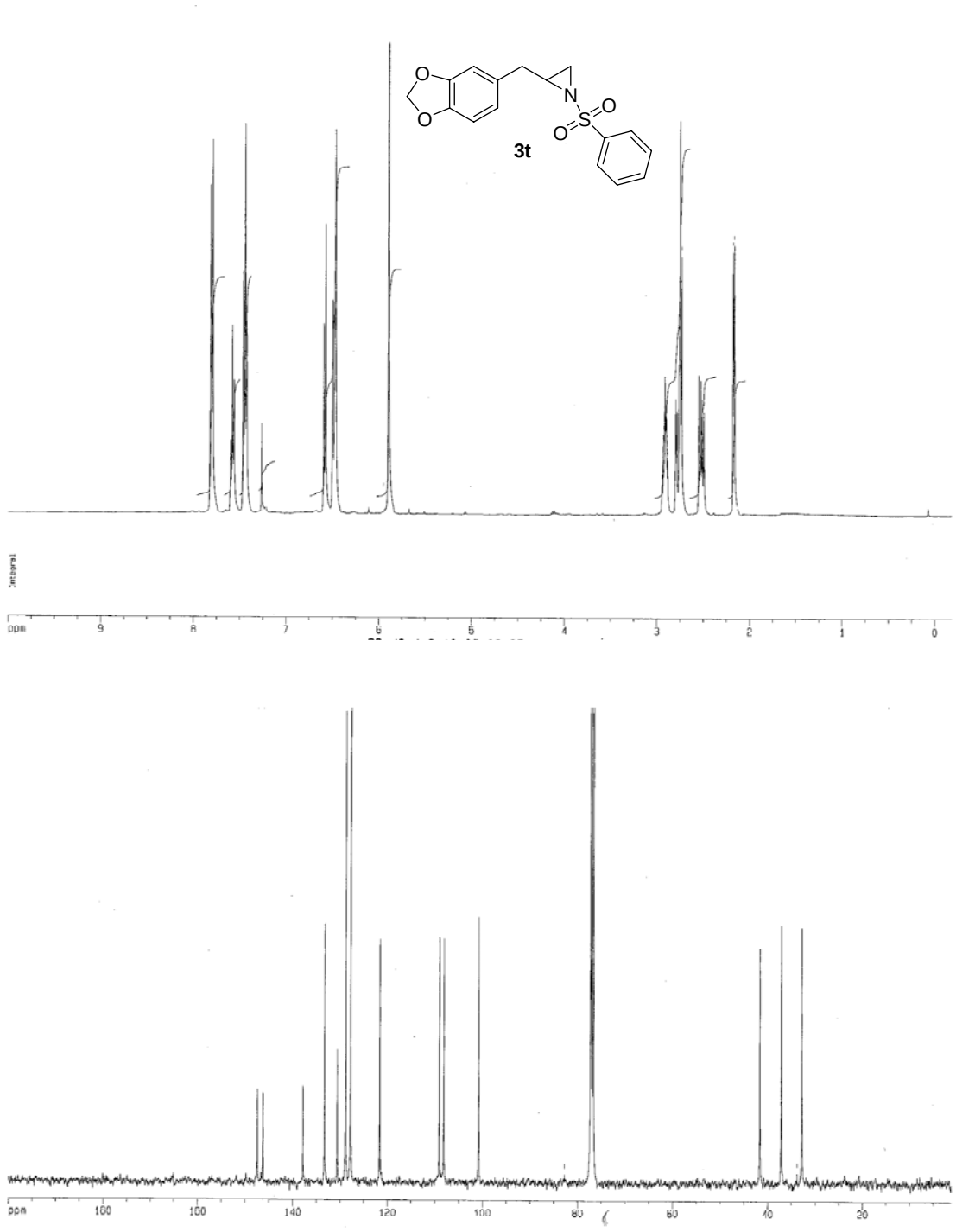


HMBC correlation spectra of *N*-(*p*-toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3s**).

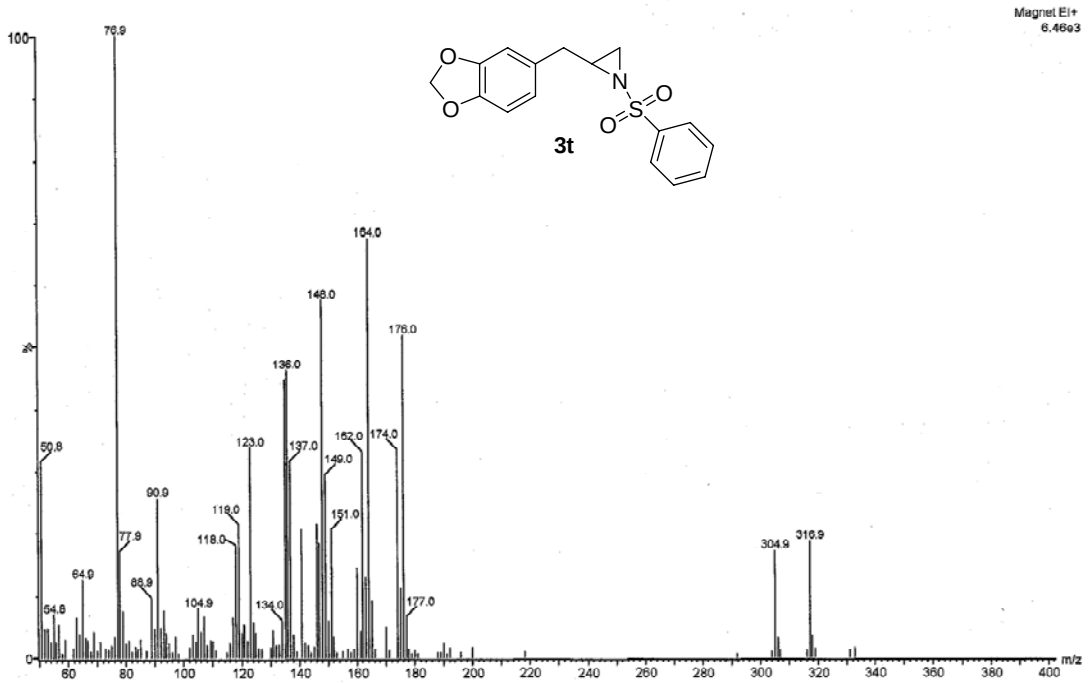


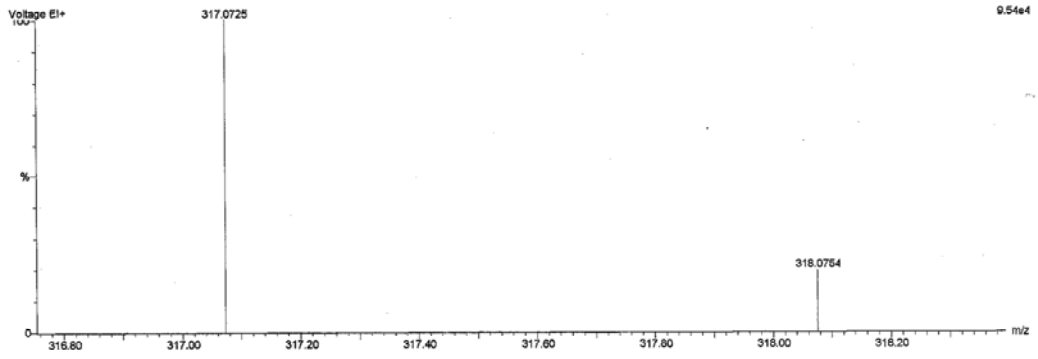


Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3s**).



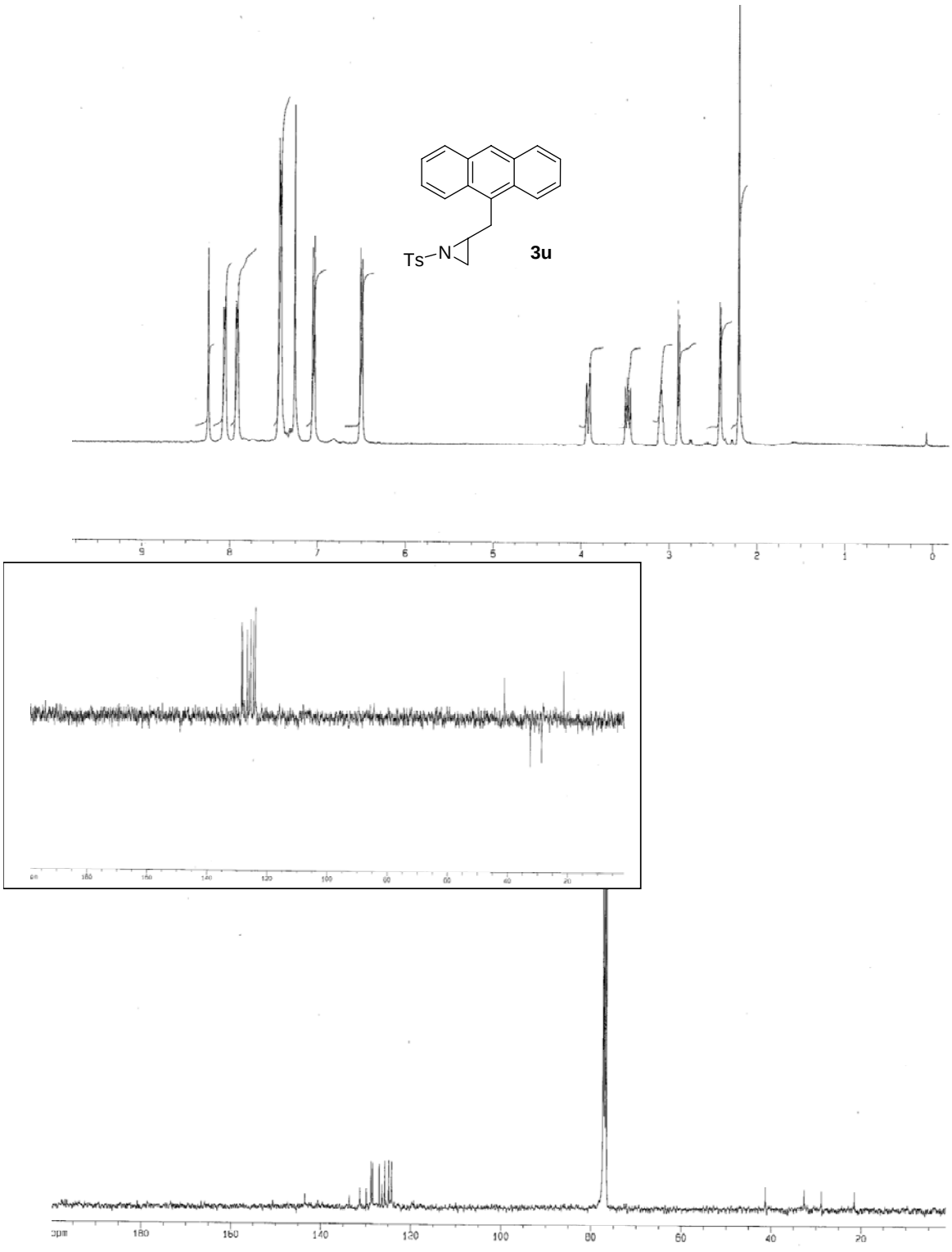
^{1}H NMR and ^{13}C NMR spectra of *N*-(*p*-benzenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3t**).



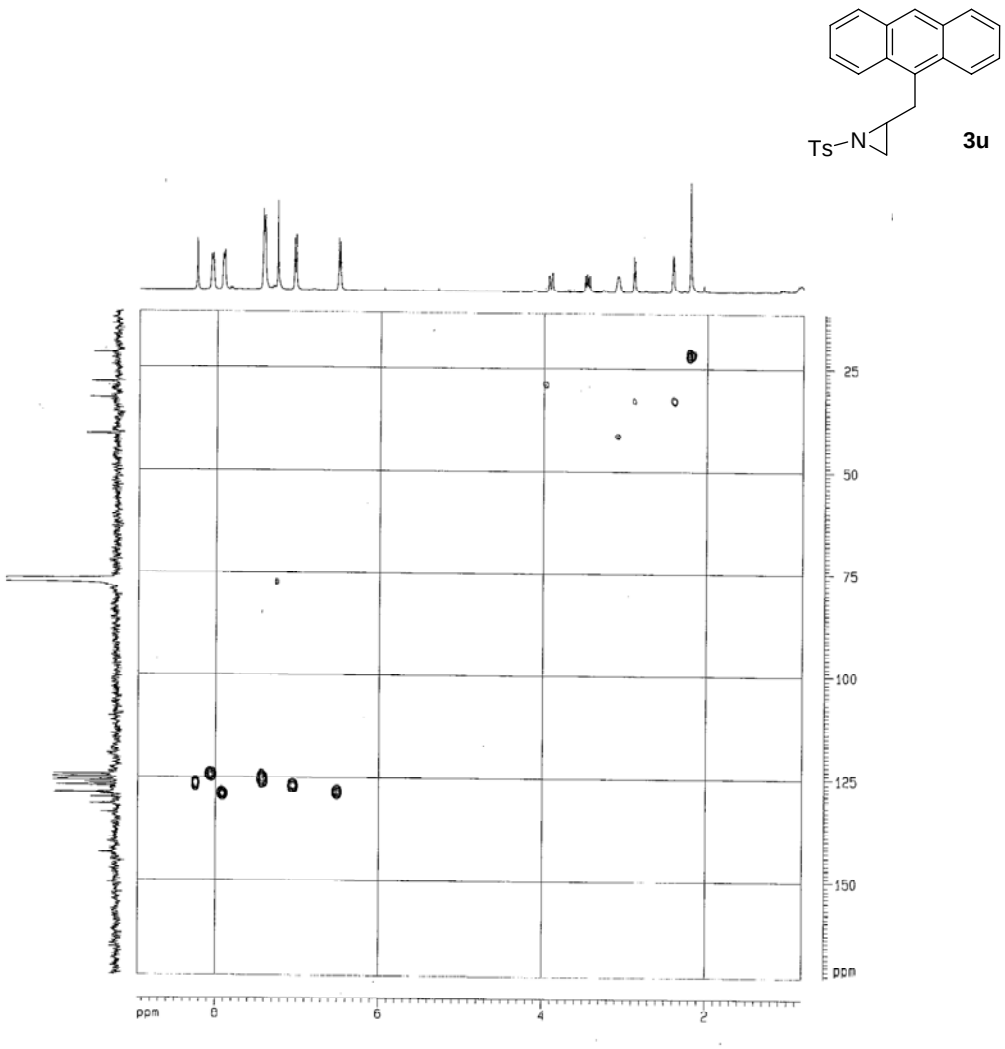


Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
317.0725	100.00	317.0722	0.3	0.9	10.0	2829865.8	12C16 H15 N O4 S
318.0754	19.58	318.0755	-0.1	-0.3	10.0	5555353.5	12C15 13C H15 N O4 S

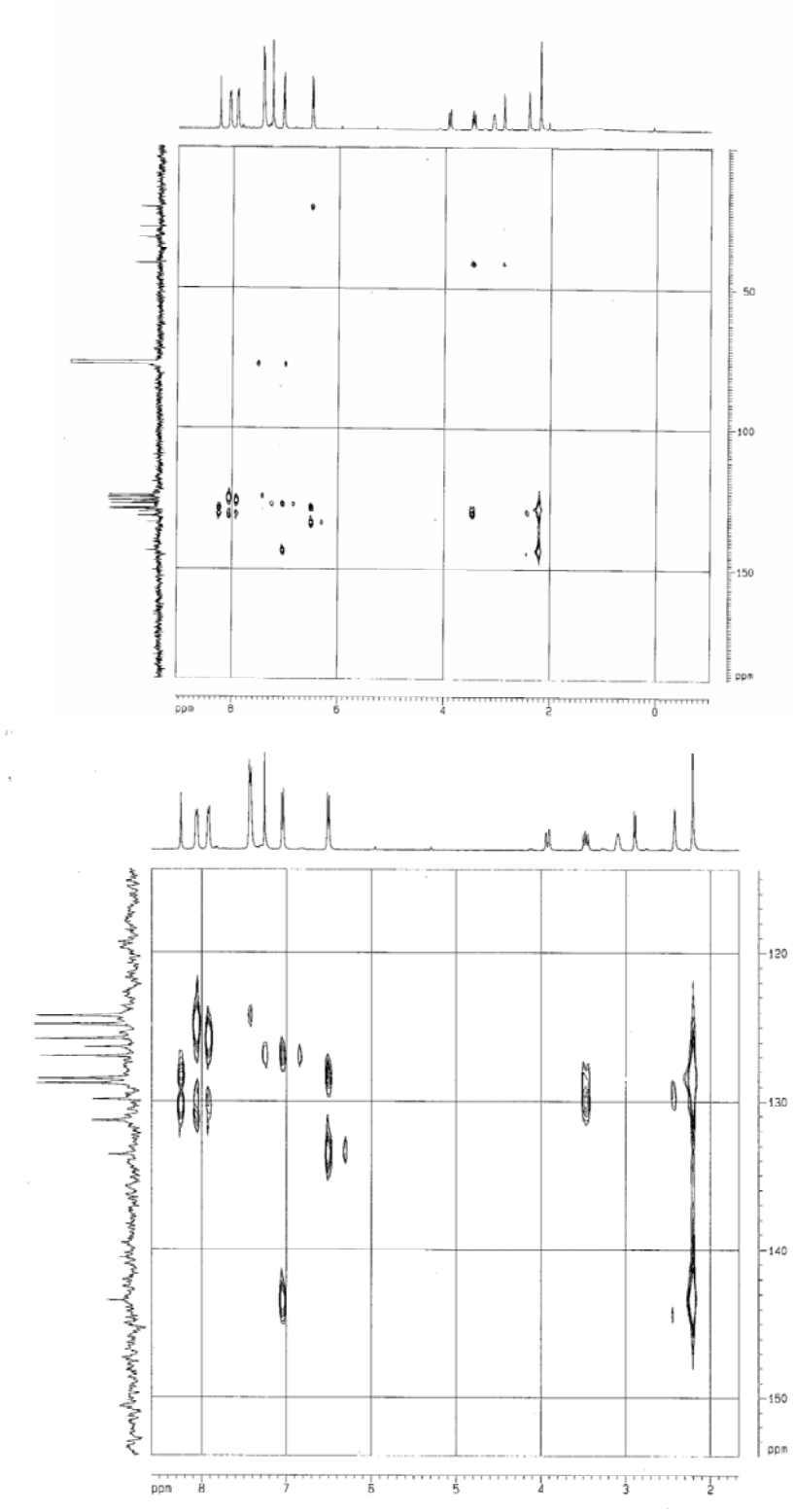
Mass spectra and HRMS of *N*-(*p*-benzenesulfonyl)-2-(3,4-methylenedioxybenzyl)aziridine (**3t**).



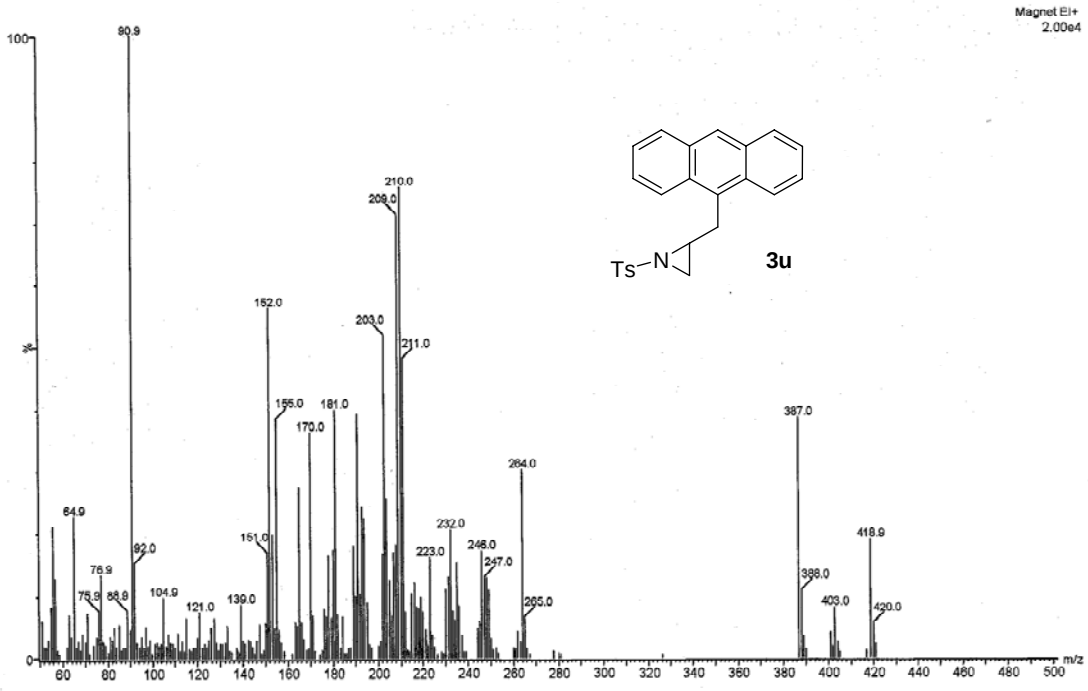
^{1}H NMR, ^{13}C NMR and DEPT spectra of *N*-(*p*-toluenesulfonyl)-2-(anthracen-9-ylmethylene)aziridine (**3u**).

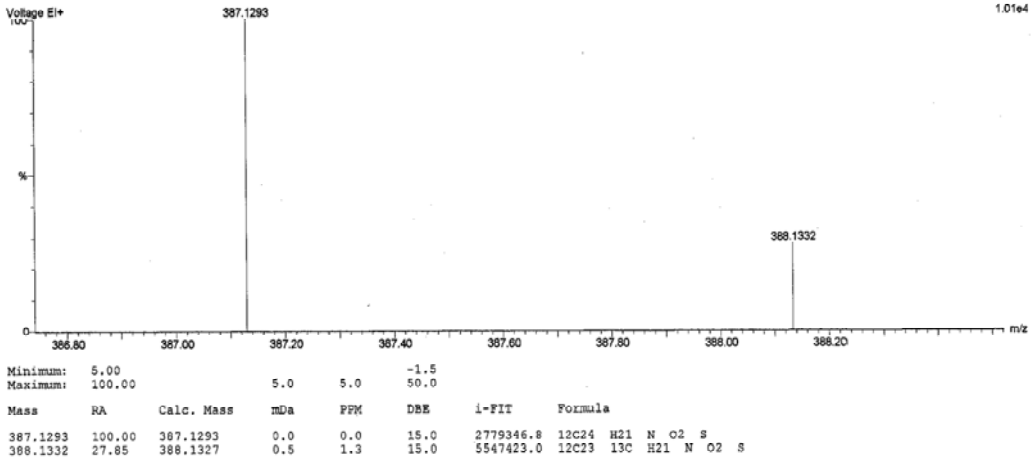


HMQC of *N*-(*p*-toluenesulfonyl)-2-(anthracen-9-ylmethylene)aziridine (**3u**).



HMBC of *N*-(*p*-toluenesulfonyl)-2-(anthracen-9-ylmethylene)aziridine (**3u**).

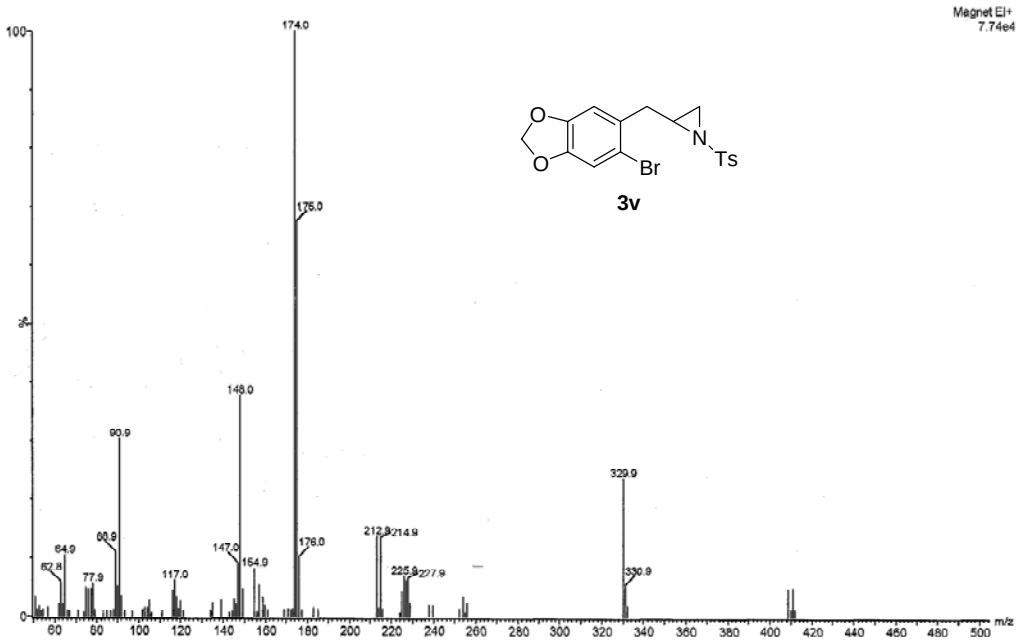




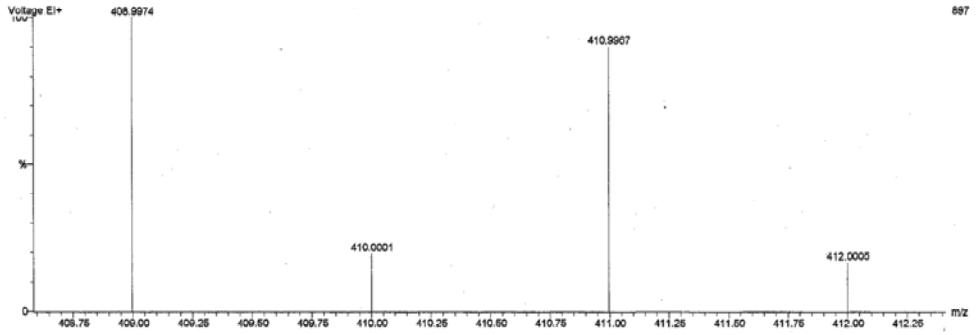
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
387.1293	100.00	387.1293	0.0	0.0	15.0	2779346.8	12C24 H21 N O2 S
388.1332	27.85	388.1327	0.5	1.3	15.0	5547423.0	12C23 13C H21 N O2 S

Mass Spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(anthracen-9-ylmethylene)aziridine (**3u**).

^{1}H NMR and ^{13}C NMR spectra of *N*-(*p*-toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxybenzyl)aziridine (**3v**).

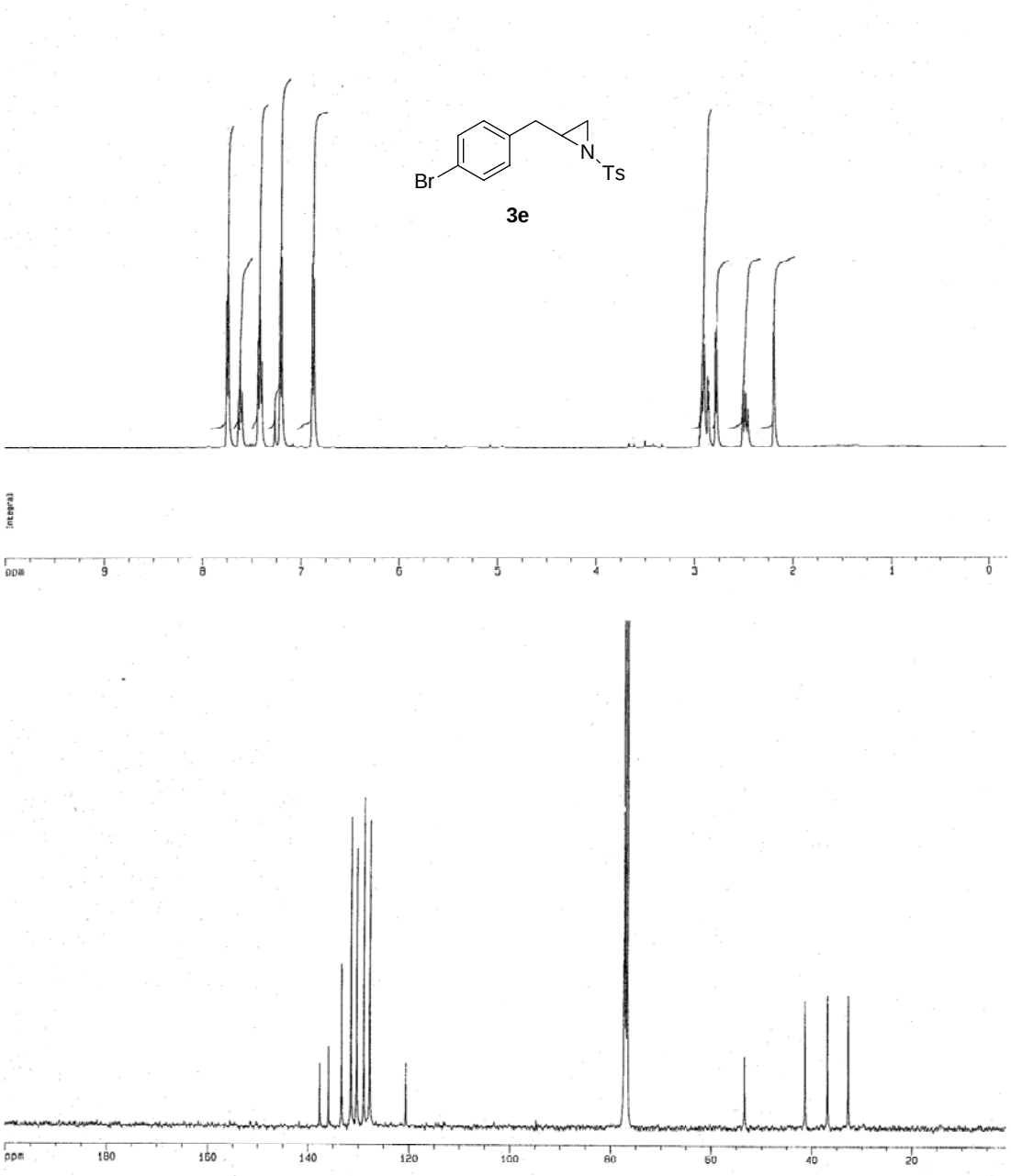


3v

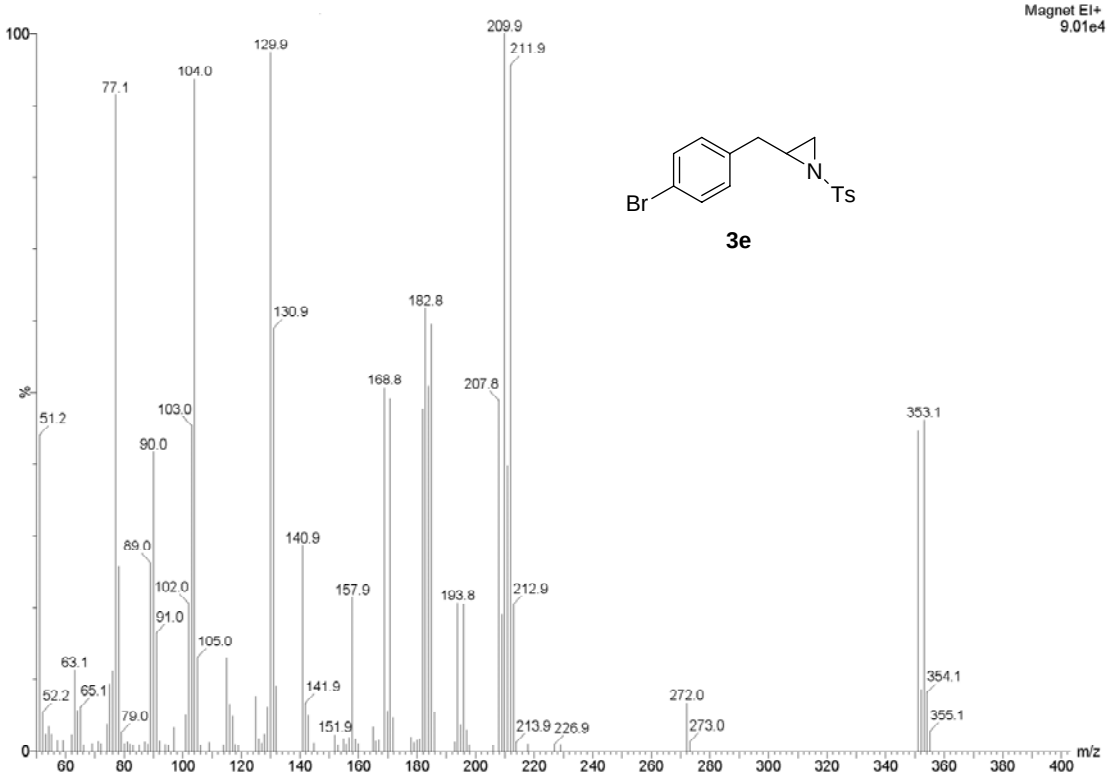


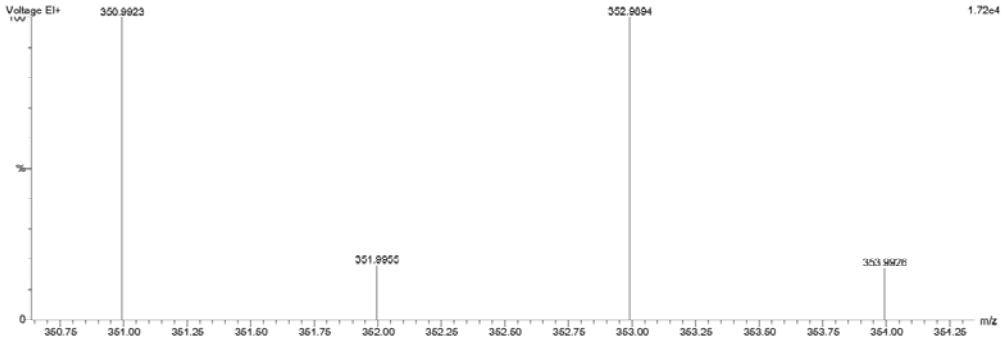
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
408.9974	100.00	408.9983	-0.9	-2.2	10.0	4.7	12C17 H16 N O4 S 79Br
410.0001	19.62	410.0017	-1.6	-3.9	10.0	1.5	12C16 13C H16 N O4 S 79Br
410.9967	90.19	410.9963	0.4	1.0	10.0	2773362.5	12C17 H16 N O4 S 81Br
412.0005	16.61	411.9996	0.9	2.2	10.0	5546093.0	12C16 13C H16 N O4 S 81Br

Mass spectra and HRMS of *N*-(*p*-toluenesulfonyl)-2-(2-bromo-4,5-methylenedioxybenzyl)aziridine (**3v**).



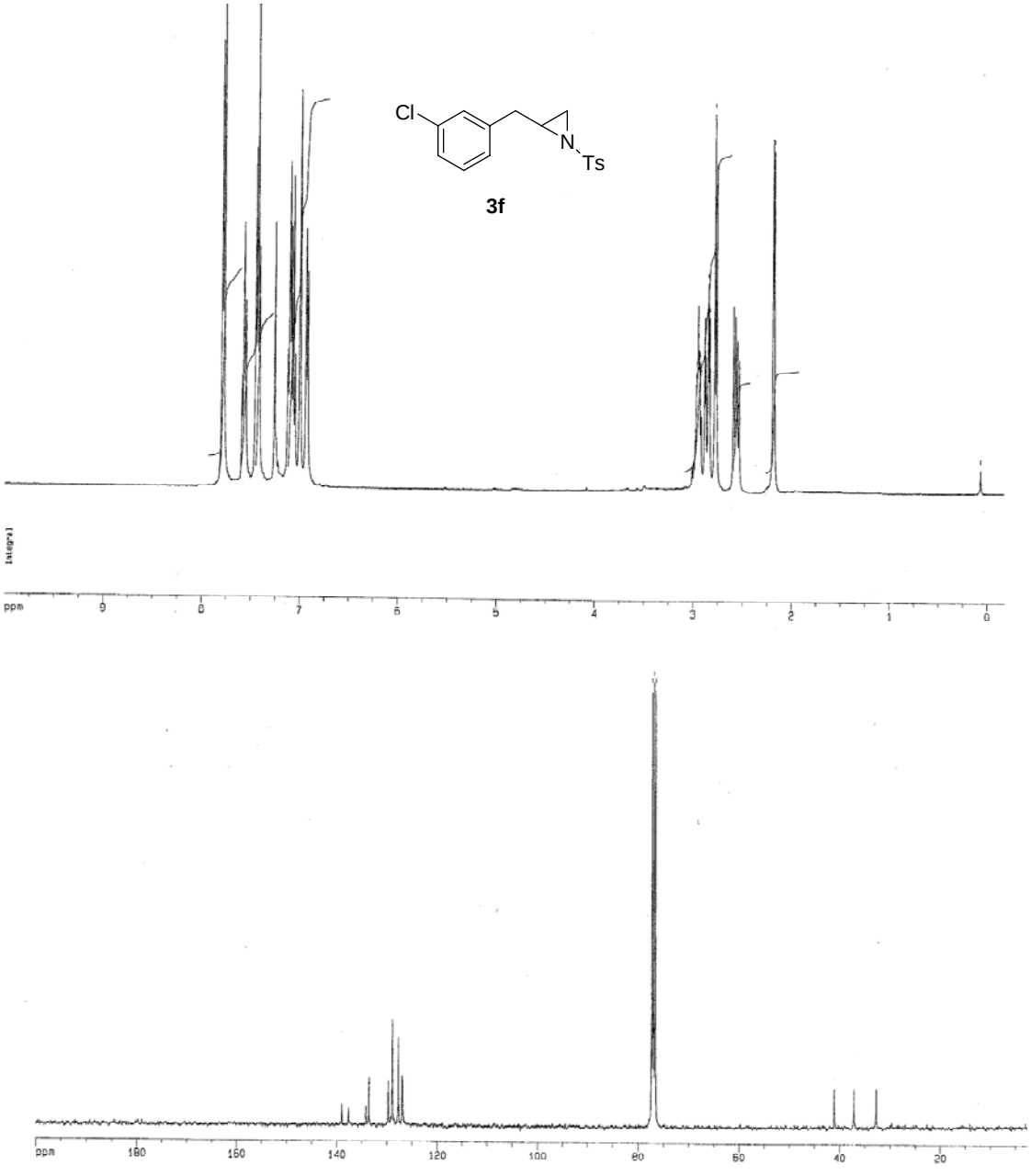
^{1}H NMR and ^{13}C NMR spectra of *N*-(benzenesulfonyl)-2-(4-bromobenzyl)aziridine (**3e**).



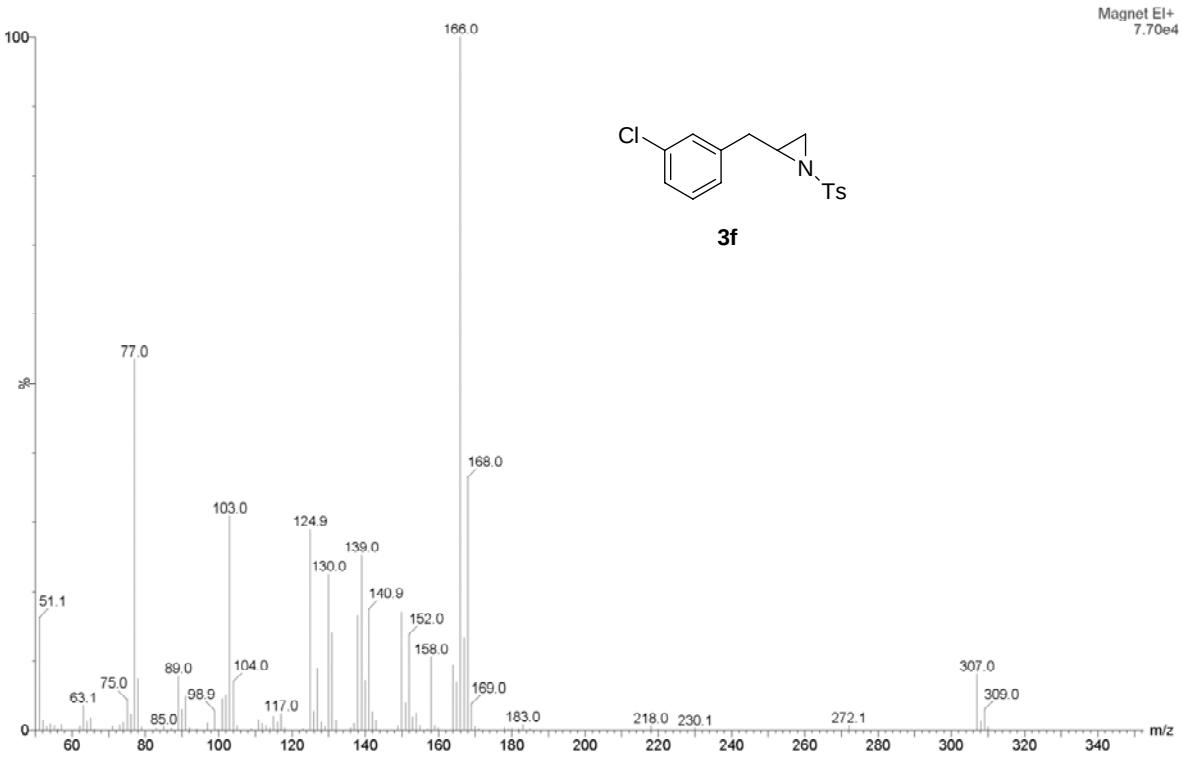


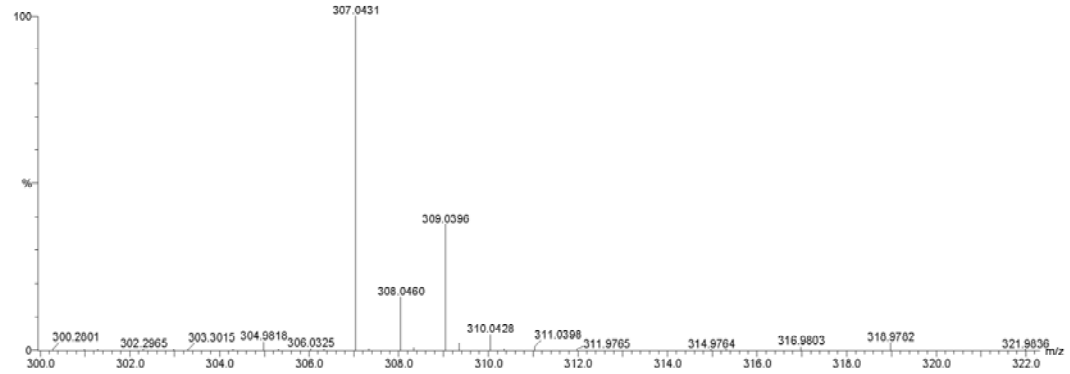
Minimum:	5.00				-1.5		
Maximum:	100.00		5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
350.9923	99.83	350.9929	-0.6	-1.7	9.0	6.0	12C15 H14 N O2 S 79Br
351.9955	17.05	351.9962	-0.7	-2.0	9.0	7.7	12C14 13C H14 N O2 S 79Br
352.9894	100.00	352.9908	-1.4	-4.0	9.0	2782853.3	12C15 H14 N O2 S 81Br
353.9926	16.77	353.9942	-1.6	-4.5	9.0	5547460.5	12C14 13C H14 N O2 S 81Br

Mass spectraand HRMS of *N*-(benzenesulfonyl)-2-(4-bromobenzyl)aziridine (**3e**).



^{1}H NMR and ^{13}C NMR spectra of *N*-(benzenesulfonyl)-2-(3-chlorobenzyl)aziridine (**3f**).





Minimum:	0.30			-1.5			
Maximum:	100.00		5.0	5.0	90.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
307.0431	100.00	307.0434	-0.3	-1.0	9.0	4.2	12C15 H14 N O2 S 35Cl
308.0460	15.86	308.0467	-0.7	-2.3	9.0	12.0	12C14 13C H14 N O2 S 35Cl
309.0396	37.52	309.0404	-0.8	-2.6	9.0	28.2	12C15 H14 N O2 S 37Cl
310.0428	4.50	310.0438	-1.0	-3.2	9.0	2773024.0	12C14 13C H14 N O2 S 37Cl

Mass spectraand HRMS of *N*-(benzenesulfonyl)-2-(3-chlorobenzyl)aziridine (**3f**).