2-Aryl-*N*-tosylazetidines as formal 1,4 dipoles for [4+2] cycloaddition reactions with nitriles: An easy access to the tetrahydropyrimidine derivatives

B. A. Bhanu Prasad, Alakesh Bisai, and Vinod K. Singh*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

vinodks@iitk.ac.in

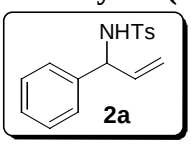
Experimental Section

General

^{1}H and ^{13}C NMR spectra were recorded on Joel PMX (400 MHz) NMR spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as internal standard (0 ppm) for ^{1}H NMR and $CDCl_3$ was used as internal standard (77.0 ppm) for ^{13}C NMR. Chemical shifts were reported in ppm and coupling constants were reported in Hz. IR spectra were measured with Bruker FT/IR Vector 22 spectrometer. Elemental (C, H, N) analyses were done on Perkin-Elmer 240-C automatic elemental analyzer. Routine monitoring of reactions were performed using precoated silicagel tlc plates from E-Merck. All the chromatographic separations were carried out by using silica gel (Acme's, 100–200 mesh). Petroleum ether used was of boiling range 60–80^{o}C. Melting points were determined by using Perfit apparatus and are uncorrected. Dichloromethane (CH_2Cl_2) was distilled in presence of calcium hydride. All the nitriles were purchased from Lancaster and used as received. $BF_3{\cdot}Et_2O$ was obtained from Fluka and used after freshly distilling. All the reactions were carried out under argon atmosphere in dried glassware.

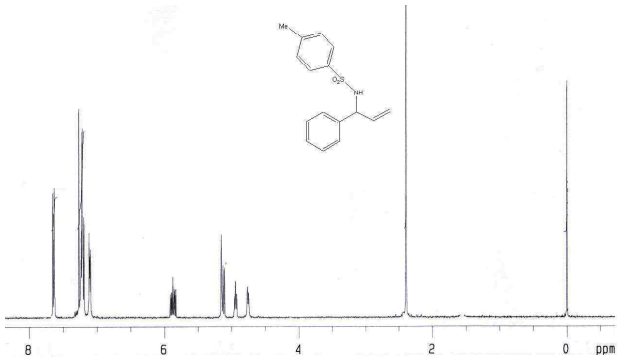
General experimental procedure for the synthesis of 2-aryl-*N*-tosylazetidines:

4-Methyl-*N*-(1-phenyl-allyl)-benzenesulphonamide (2a):



The *N*-tosylimine (1.81 g, 7 mmol) was taken in 1:1 mixture of THF:ether solvent (30 mL) and vinylmagnesium chloride (5.69 mL, 1.6 M in THF) was added slowly at rt and continued stirring for 12 h. The reaction mixture was quenched with addition of saturated NH_4Cl and extracted into ether. The combined organic layer was washed with water, brine and dried over *anhydrous* Na_2SO_4 and concentrated to give the crude product. Purification by column chromatography gave the pure Product (1.85 g, 92% yield).

Colourless Solid, Melting point 85-88 ^{0}C, R_f = 0.6 (30% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.67- 7.69 (d, *J*= 8.4 Hz, 2H), 7.13-7.30 (m, 7H), 5.86-5.94 (m, 1H), 5.32-5.34 (m, 1H), 5.12-5.17 (m, 2H), 4.96-4.99 (m, 1H), 2.42 (S, 3H); Anal. calcd for $C_{16}H_{17}NO_2S$. C, 66.87; H, 5.96; N, 4.87. Found: C, 66.69; H, 5.86; N, 4.99.

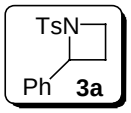


^{1}H NMR (400 MHz) Spectrum of Compound **2a**

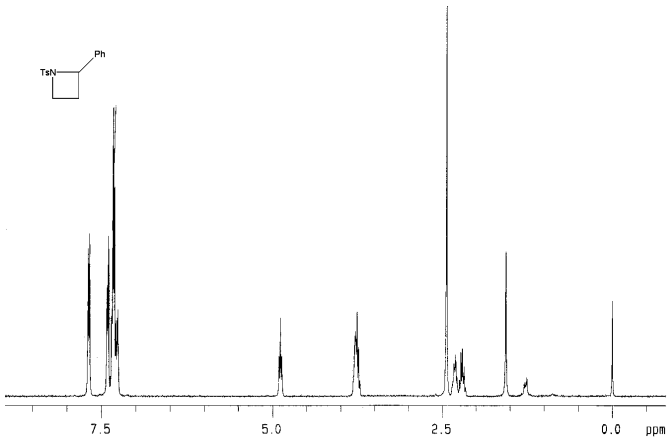
2-phenyl-1-(toluene-4-sulphonyl)-azetidine (3a):

1.85 g of (6.44 mmol) corresponding allylamine **(2a)** was taken in an oven dried rb, flushed with N_2, then it was evacuated and purged with N_2, this process was repeated three times. Then dry THF (25 mL) was added followed by dropwise addition of BH_3.DMS (1.53 mL, 16.10 mmol) and the reaction was allowed to proceed for 12 h at rt. Excess borane was destroyed by addition of 6 mL EtOH. Then to this 3M NaOH (2.2 mL) was added in one portion followed by dropwise addition of 30% H_2O_2 (2.2 mL) and stirred for 2 h at rt. Solvent was evaporated in vacuo and the residue was taken in water and extracted with EtOAc. The combined organic layer was dried over *anhydrous* Na_2SO_4, concentrated and directly set up for next step.

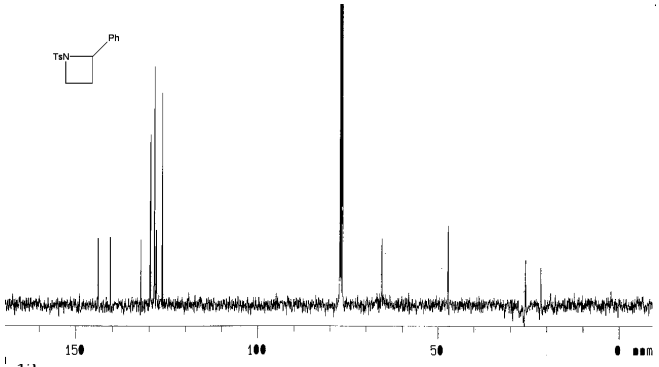
To an oven dried roundbottom flask, crude 1,3 *N*-tosylaminoalcohol (1.96 g, 6.44 mmol) was taken in dry THF (20 mL) and the solution was brought to 0 °C, then DIAD (1.90 mL, 9.66 mmol) was added slowly and stirring was continued overnight with gradual warming to rt. The solvent was evaporated under reduced pressure then directly chromatographed over silicagel to give the pure azetidine (1.39 g, 75% yield). Overall yield starting from *N*-tosylaldimine 70%, as colourless solid. For all the other azetidine synthesis, we followed same procedures (same mmol scale).



Colourless solid, Melting point 104-108 ^{0}C, R_f 0.48 (30% EtOAc in Petroleum ether), ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.64-7.66 (d, J = 8.04 Hz, 2H), 6.85-7.31 (m, 7H), 4.84 (t, J = 8.32 Hz, 1H), 3.76 (m, 2H), 2.45 (s, 3H), 2.29 (m, 2H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 159.41, 143.82, 132.67, 132.27, 129.57, 128.38, 127.75, 113.85, 65.47, 47.02, 25.93, 21.55; Anal. calcd for $C_{16}H_{17}NO_2S$. C, 66.87; H, 5.96; N, 4.87. Found: C, 66.85; H, 6.43; N, 4.38.

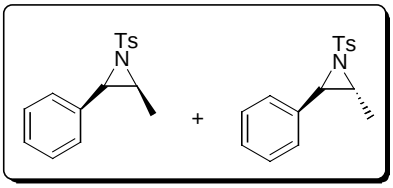


^{1}H NMR (400 MHz) Spectrum of Compound **3a**

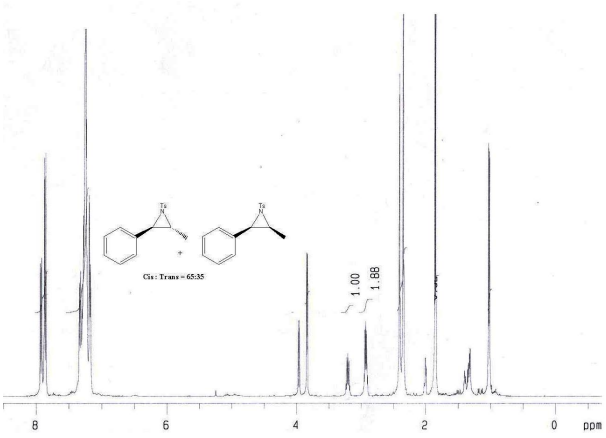


^{13}C NMR (100 MHz) Spectrum of Compound **3a**

1-phenyl-2-methyl (toluene-4-sulphonyl)-aziridine:

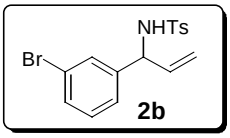


0.271 g, 15% yield, Colourless gel, (cis: trans = 65:35), R_f = 0.4 (30% EtOAc in Petroleum ether), ^{1}H NMR ($CDCl_3$, 400 MHz) δ:7.90–7.92 (d, *J*= 8.32 Hz, 2H, for trans product), 7.84-7.87 (d, *J*= 12.00Hz, 2H, for cis product), 7.16-7.33 (m, 7H, for cis and trans), 3.95-3.97 (d, *J*= 7.32, 2H, for trans), 3.83-3.84 (d, *J*= 4.36, 2H, for cis), 3.18-3.22 (m, 1H, for trans), 2.91-2.94 (m, 1H, for cis), 2.40 (s, 3H, for trans), 2.34 (s, 3H, for cis), 1.84-1.86 (d, *J*= 8.00Hz, 3H. for cis), 1.02-1.03 (d, *J*= 5.84, 2H, for trans); Anal. calcd for $C_{16}H_{17}NO_2S$. C, 66.87; H, 5.96; N, 4.87. Found: C, 66.69; H, 5.87; N, 4.99.



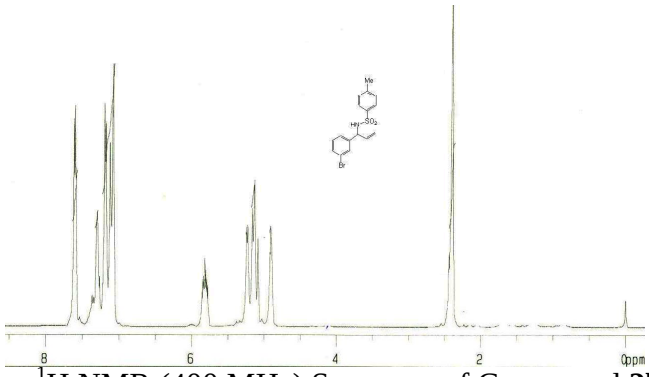
^{1}H NMR (400 MHz) Spectrum of (Cis+Trans) mixture of 1-phenyl-2- (toluene-4-sulphonyl)-aziridine

4-Methyl-*N*-(1-(3-Bromo)-phenyl-allyl)-benzenesulphonamide (2b):

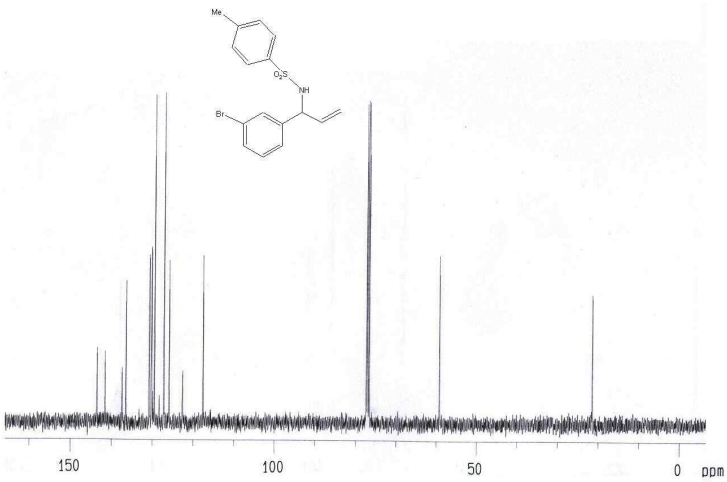


90% yield, Colourless gel, R_f = 0.6 (30% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.58-7.60 (m, 2H), 7.06-7.30 (m, 6H), 5.77-5.85 (m, 1H), 5.08-5.23 (m, 2H), 4.90-4.91 (m, 1H), 2.39 (bs, 3H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 143.45, 141.46, 137.33, 136.33, 130.69, 130.22, 130.08, 129.86, 129.44, 127.08, 125.80, 122.53,

117.46, 59.26, 21.48; Anal. calcd for $C_{16}H_{16}BrNO_2S$. C, 52.47; H, 4.40; N, 3.82. Found: C, 51.99; H, 4.37; N, 4.02

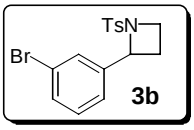


^{1}H NMR (400 MHz) Spectrum of Compound **2b**



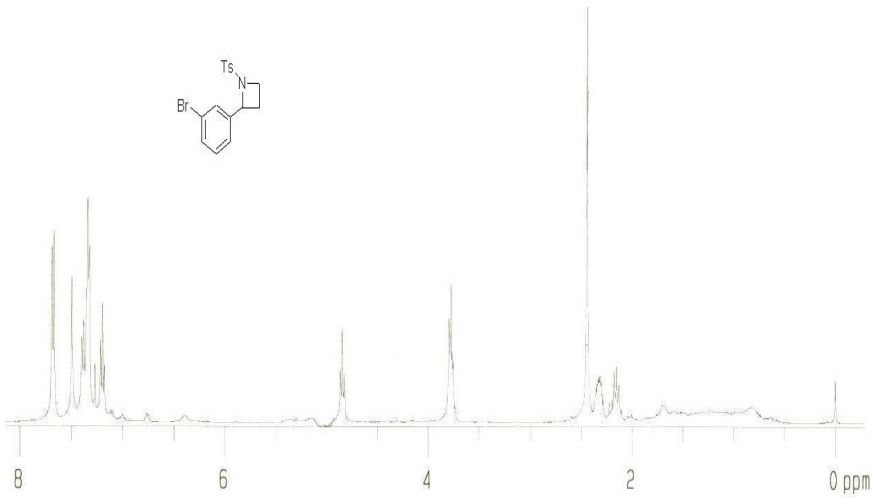
^{13}C NMR (100 MHz) Spectrum of Compound **2b**

2-(3-Bromo-phenyl)-1-(toluene-4-sulphonyl)-azetidine (3b):

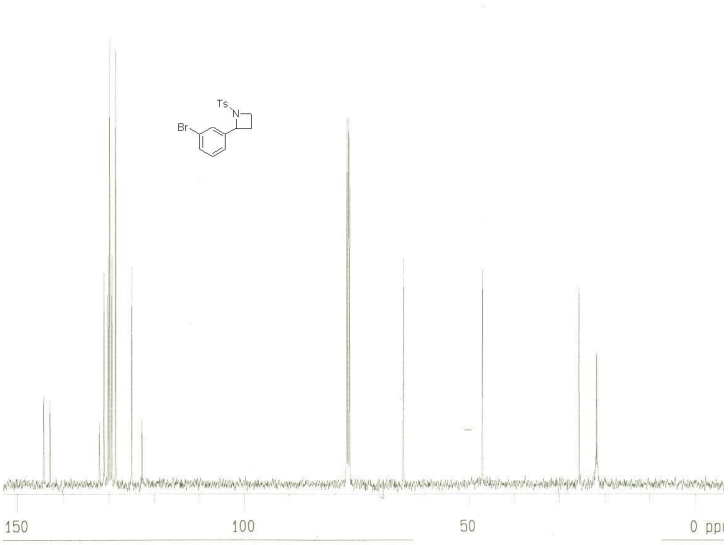


70% yield, Overall yield starting from *N*-tosylaldimine 63% as colourless Solid, Melting point 125-130 ^{0}C, R_f 0.39 (30% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66–7.68 (d, *J*= 8.00 Hz, 2H), 7.17-7.49 (m, 6H), 4.82-4.86 (t, *J*= 8.28 Hz, 1H), 3.75-3.79 (m, 2H), 2.44 (s, 3H); 2.29-2.35 (m, 1H); 2.13-2.17 (m, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz)

δ: 144.19, 142.82, 131.96, 130.94, 130.05, 129.68, 129.25, 128.35, 124.87, 122.50, 64.69 , 47.12, 25.47, 21.89; Anal. calcd for $C_{16}H_{16}BrNO_2S$. C, 52.47; H, 4.40; N, 3.82. Found: C, 52.43; H, 4.38; N, 4.39.

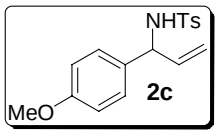


^{1}H NMR (400 MHz) Spectrum of Compound **3b**

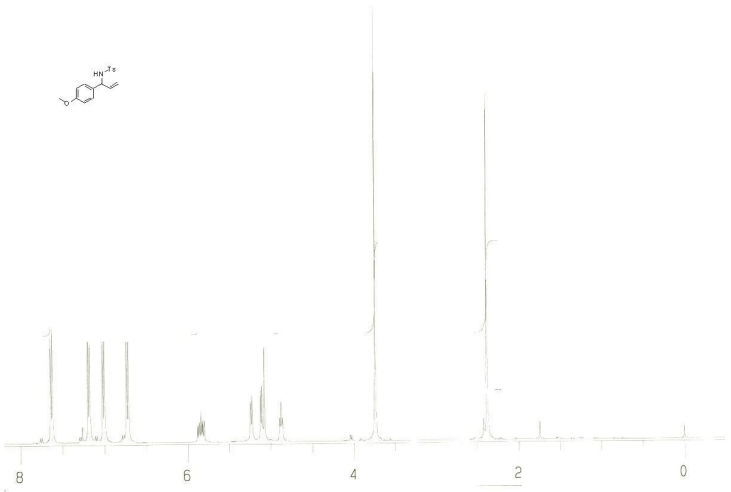


^{13}C NMR (100 MHz) Spectrum of Compound **3b**

4-Methyl-*N*-(1-(4-methoxy)-phenyl-allyl)-benzenesulphonamide (2c):



91% yield, colourless solid, Melting point 98-101 ^{0}C, R_f 0.39 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61- 7.63 (d, *J*= 8.28 Hz, 2H), 7.17-7.19 (d, *J*= 8.08 Hz, 2H), 6.99-7.01 (d, *J*= 8.52 Hz, 2H), 6.71-7.73 (d, *J*= 8.56 Hz, 2H), 5.81-5.88 (m, 1H), 5.22-5.24 (d, *J*= 7.32 Hz, 1H), 5.10-5.11 (m, 1H), 4.85-4.89 (t, *J*= 6.36 Hz, 2H), 3.74(s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$ 100 MHz)

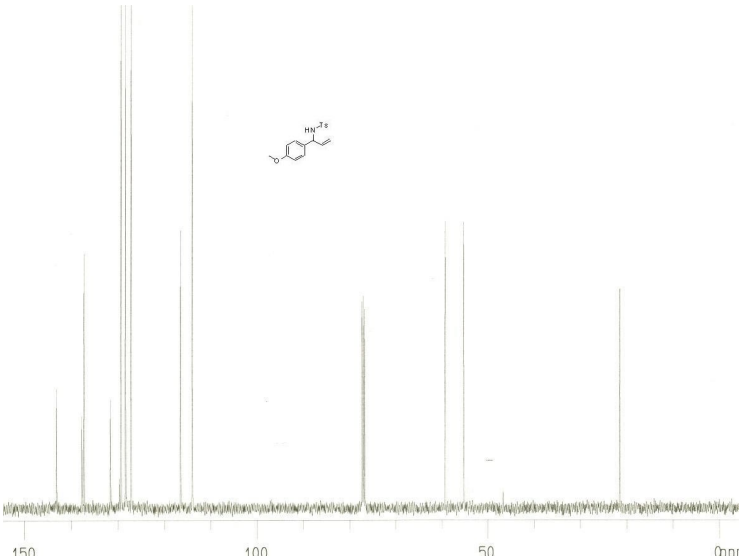


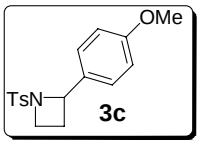
δ: 159.00, 143.02, 137.65, 137.21, 131.51, 129.30, 128.25, 127.14, 116.37, 113.84, 59.27 , 55.18, 21.42; Anal. calcd for $C_{17}H_{19}NO_3S$. C, 64.33; H, 6.03; N, 4.41. Found: C, 64.28; H, 5.99; N, 4.63.

^{1}H NMR (400 MHz) Spectrum of Compound **2c**

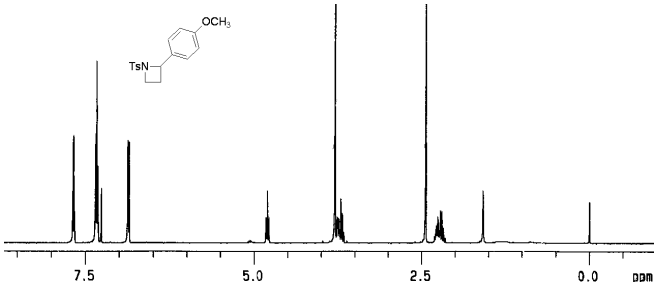
^{13}C NMR (100 MHz) Spectrum of Compound **2c**

2-(4-Methoxy-phenyl)-1-(toluene-4-sulphonyl)-azetidine (3c):

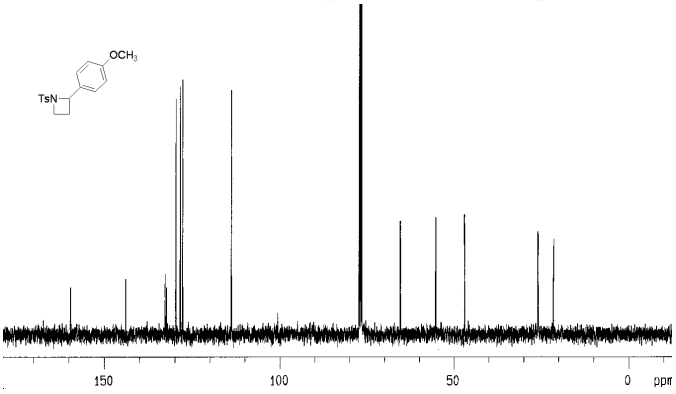




71% yield, Overall yield starting from *N*-tosylaldimine 65%, as colourless solid, Melting point 68-72 ^{0}C, R_f 0.40 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.67 (d, *J* = 8.04 Hz, 2H), 7.32 (m, 4H), 6.86 (m, 2H), 4.80 (t, *J* = 8.32 Hz, 1H), 3.80 (s, 3H), 3.73 (m, 2H), 2.44 (s, 3H), 2.23 (m, 2H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 159.41, 143.82, 132.67, 132.27, 129.57, 128.38, 127.75, 113.85, 65.47, 55.28, 47.02, 25.93, 21.55; Anal. calcd for $C_{17}H_{19}NO_3S$. C, 64.33; H, 6.03; N, 4.41. Found: C, 64.29; H, 6.01; N, 4.46.

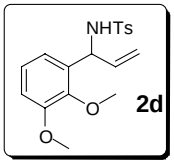


^{1}H NMR (400 MHz) Spectrum of Compound **3c**

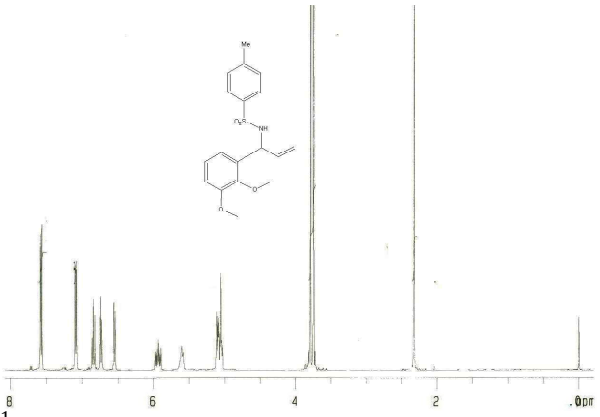


^{13}C NMR (100 MHz) Spectrum of Compound **3c**

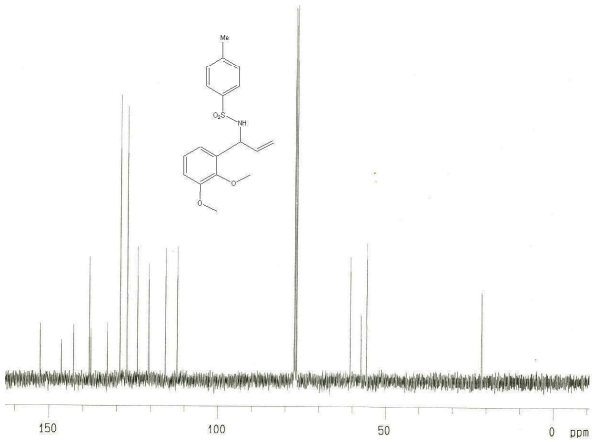
4-Methyl-*N*-(1-(2,3-dimethoxy)-phenyl-allyl)-benzenesulphonamide (2d):



94% yield, colourless solid, Melting point 95-99 ^{0}C, R_f 0.29 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ; 7.56-7.58 (d, *J* = 8.03 Hz, 2H), 7.07-7.09 (d, *J* = 8.04, 2H), 6.82-6.86 (m, 1H), 6.72-7.74 (m, 1H), 6.53-6.55 (m, 1H), 5.89-5.97 (m, 1H), 5.57-5.59 (m, 1H), 5.02-5.11 (m, 3H), 3.79 (S, 3H), 3.74 (S, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 152.59, 146.28, 142.70, 138.17, 137.66, 132.79, 129.10, 126.96, 123.88, 120.56, 115.56, 112.10, 60.62, 57.43, 55.72, 21.38; Anal. calcd for $C_{18}H_{21}NO_4S$. C, 62.23; H, 6.09; N, 4.03. Found: C, 62.19; H, 6.18; N, 4.23.

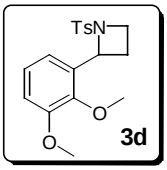


^{1}H NMR (400 MHz) Spectrum of Compound **2d**

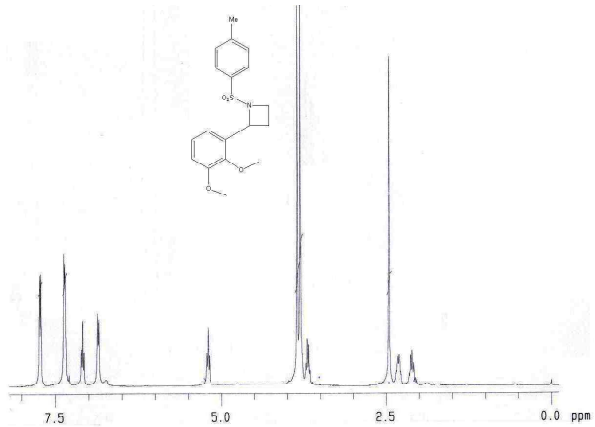


^{13}C NMR (100 MHz) Spectrum of Compound **2d**

2-(2,3-dimethoxy-phenyl)-1-(toluene-4-sulphonyl)-azetidine (3d):



73% yield, Overall yield starting from *N*-tosylaldimine 69%, as colourless Solid, Melting point 99-112 ^{0}C, R_f 0.29 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71–7.73 (d, *J* = 8.00Hz, 2H), 7.34–7.36 (m, 3H), 7.06-7.10 (t, *J*= 8.01 Hz,1H), 6.84-6.86 (d, *J*= Hz, 1H), 5.17-5.21 (t, *J*= 8.00 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.65-3.72 (m, 2H), 2.45 (s, 3H), 2.28-2.35 (m, 1H), 2.08-2.15 (m, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz)δ: 154.74, 151.98, 145.47, 143.83, 134.40, 131.55, 129.50, 128.40, 124.11, 119.23, 111.71, 72.00, 70.04, 55.60, 47.53, 25.50, 21.74; Anal. calcd for $C_{18}H_{21}NO_4S$. C, 62.23; H, 6.09; N, 4.03. Found: C, 62.17; H, 5.97; N, 4.33.

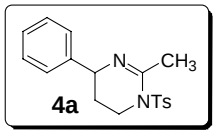


^{1}H NMR (400 MHz) Spectrum of Compound **3d**

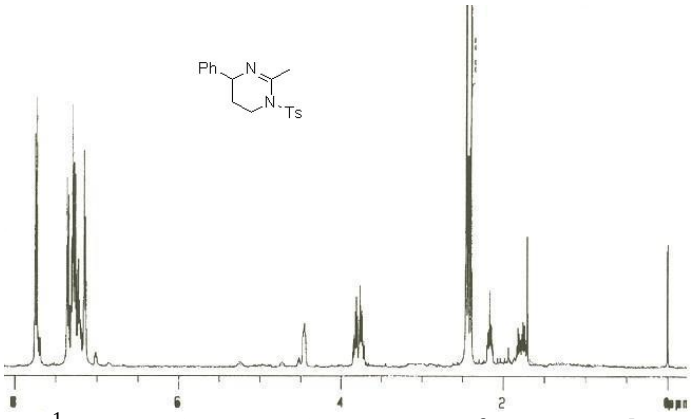
General procedure for [4+2] cycloaddition reaction of azetidines with nitriles:

A 10 mL round-bottom flask was charged with *N*-tosyl azetidine (1 mmol) in *anhydrous* dichloromethane (3 mL) under argon at rt. To this nitrile (1 mmol) was added followed by slow addition of freshly distilled $BF_3{\cdot}Et_2O$ (0.2 mmol). After 3-6 h saturated *aqueous* $NaHCO_3$ solution (2 mL) was added. Organic layer was separated and the *aqueous* layer was extracted with dichloromethane (2 x 5 mL). The combined organic layer were washed with water, brine and dried over *anhydrous* Na_2SO_4 and concentrated to give the crude product. Purification by column chromatography (30% EtOAc in petroleum ether) gave the substituted pyrimidines.

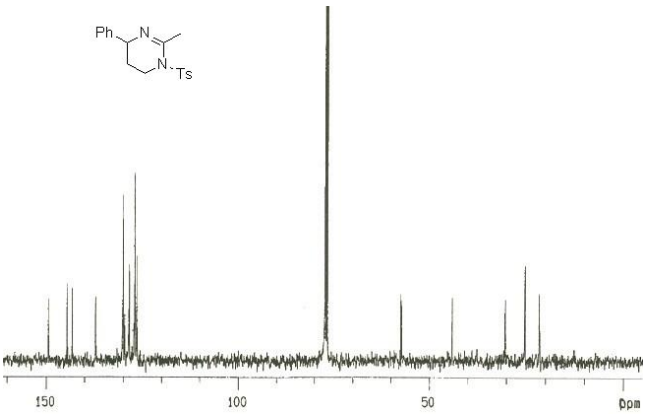
2-Methyl-4-phenyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (4a):



60% yield, Colourless paste; R_f 0.42 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.73 (d, *J* = 8.32 Hz, 2H), 7.36-7.13 (m, 7H), 4.45 (m, 1H), 3.82 (m, 1H), 3.74 (m, 1H), 2.45 (s, 3H), 2.40 (d, *J* = 1.72 Hz, 3H), 2.16 (m, 1H), 1.77 (m, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 149.32, 144.45, 143.13, 129.98, 128.46, 126.82, 126.46, 57.51, 57.24, 44.00, 30.27, 25.27, 21.56; LCMS (EI, *m/z*) 328 (M^+); Anal. calcd for $C_{18}H_{20}N_2O_2S$. C, 65.83; H, 6.14; N, 8.53. Found: C, 64.93; H, 6.76; N, 8.64.

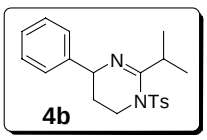


^{1}H NMR (400 MHz) Spectrum of Compound **4a**



^{13}C NMR (100 MHz) Spectrum of Compound **4a**

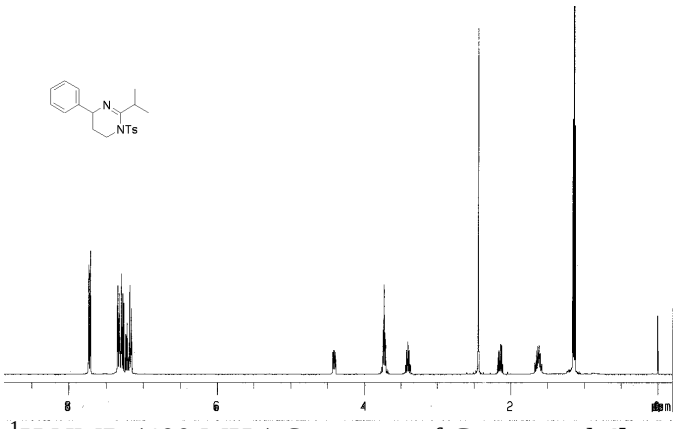
2-Isopropyl-4-phenyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (4b):



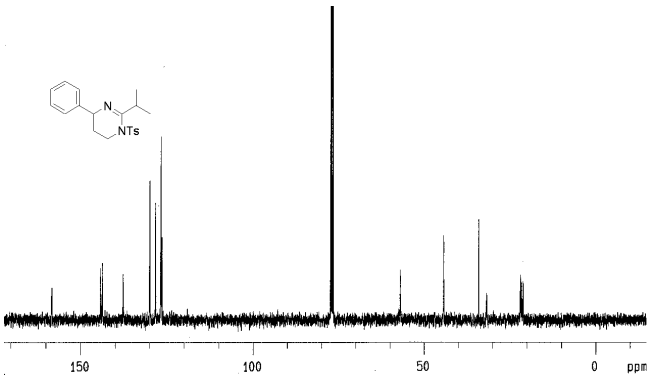
4b

61% yield, Colourless solid, Melting point 113-117 ^{0}C, R_f 0.43 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72 (m, 2H), 7.34-7.15 (m, 7H), 4.41

(dd, *J* = 8.32, 4.88 Hz, 1H), 3.73 (m, 2H), 3.40 (heptet, *J* = 6.84 Hz, 1H), 2.44 (s, 3H), 2.14 (m, 1H), 1.61 (m, 1H), 1.13 (t, *J* = 6.84 Hz, 6H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ: 158.61, 144.10, 143.66, 137.61, 129.91, 128.30, 126.75, 126.39, 57.01, 56.93, 44.22, 33.96, 31.65, 21.81, 21.52, 21.08; LCMS (EI, *m/z*) 356 (M^+); Anal. calcd for $C_{20}H_{24}N_2O_2S$. C, 67.38; H, 6.79; N, 7.86. Found: C, 67.93; H, 6.76; N, 8.04.

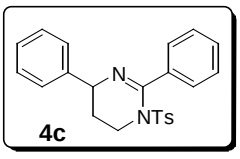


^{1}H NMR (400 MHz) Spectrum of Compound **4b**



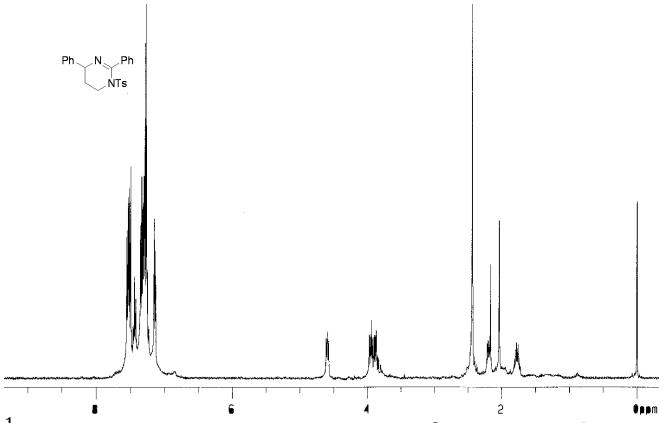
^{13}C NMR (100 MHz) Spectrum of Compound **4b**

2,4-Diphenyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (4c):



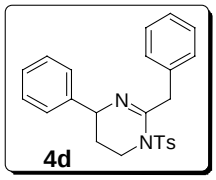
72% yield, Colourless paste, R_f 0.43 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (m, 4H), 7.43 (m, 1H), 7.34-7.24 (m, 7H), 7.13 (m, 2H), 4.59

(dd, *J* = 8.56, 5.4 Hz, 1H), 3.95 (m, 1H), 3.87 (m, 1H), 2.43 (s, 3H), 2.19 (m, 1H), 1.78 (m, 1H); LCMS (EI, *m/z*) 390 (M^+); Anal. calcd for $C_{23}H_{22}N_2O_2S$. C, 70.74; H, 5.68; N, 7.17. Found: C, 70.03; H, 5.76; N, 7.81.

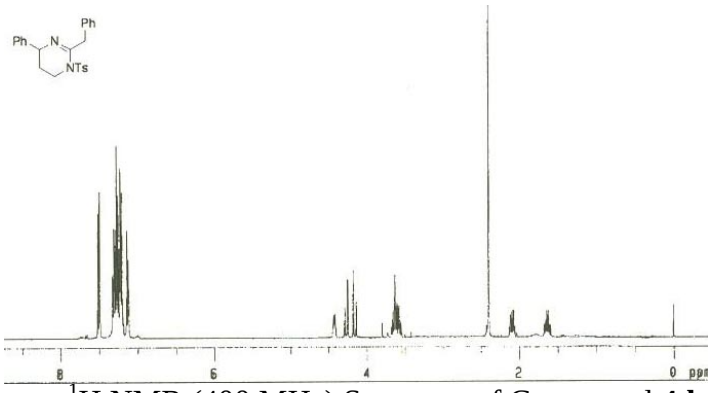


^{1}H NMR (400 MHz) Spectrum of Compound **4c**

2-Benzyl-4-phenyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (4d):

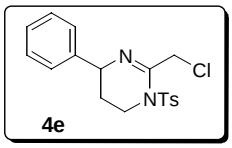


65% yield, Colourless paste; R_f 0.47 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.51 (m, 2H), 7.32-7.12 (m, 7H), 4.43 (dd, *J* = 8.8, 4.88 Hz, 1H), 4.21 (ABq, *J* = 45.88 Hz, 2H), 3.61 (m, 2H), 2.39 (s, 3H), 2.09 (m, 1H), 1.63 (m, 1H); LCMS (EI, *m/z*) 404 (M^+); Anal. calcd for $C_{24}H_{24}N_2O_2S$. C, 71.26; H, 5.98; N, 6.93. Found: C, 71.93; H, 5.76; N, 6.84.

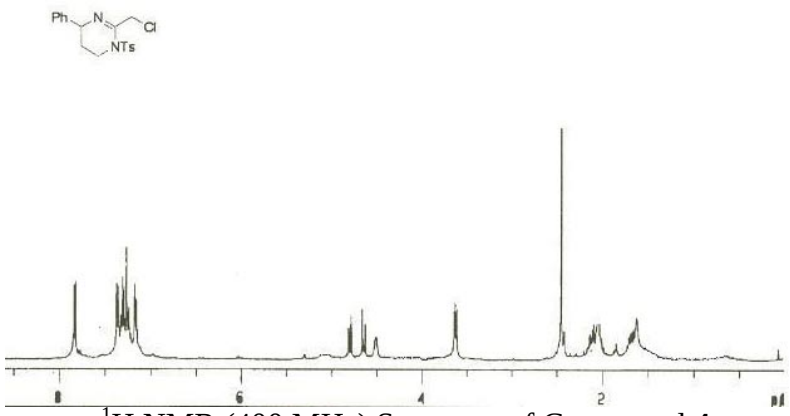


^{1}H NMR (400 MHz) Spectrum of Compound **4d**

4-(3-Bromo-phenyl)-2-chloromethyl-1-(toluene-4-sulfonyl)-1,4,5,6-tetrahydro-pyrimidine (4e):

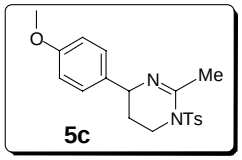


42% yield, Colourless paste; R_f 0.48 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.52 Hz, 2H), 7.37-7.15 (m, 7H), 4.70 (ABq, *J* = 62.24 Hz, 2H), 4.50 (dd, *J* = 8.28, 5.12 Hz, 1H), 3.63 (dd, *J* = 6.84, 4.88 Hz, 2H), 2.45 (s, 3H), 2.11 (m, 1H), 1.67 (m, 1H); LCMS (EI, *m/z*) 362 (M^+); Anal. calcd for $C_{18}H_{19}ClN_2O_2S$. C, 59.58; H, 5.28; N, 7.72. Found: C, 60.03; H, 5.76; N, 7.84.



^{1}H NMR (400 MHz) Spectrum of Compound **4e**

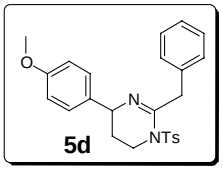
4-(4-Methoxy-phenyl)-2-methyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (5c):



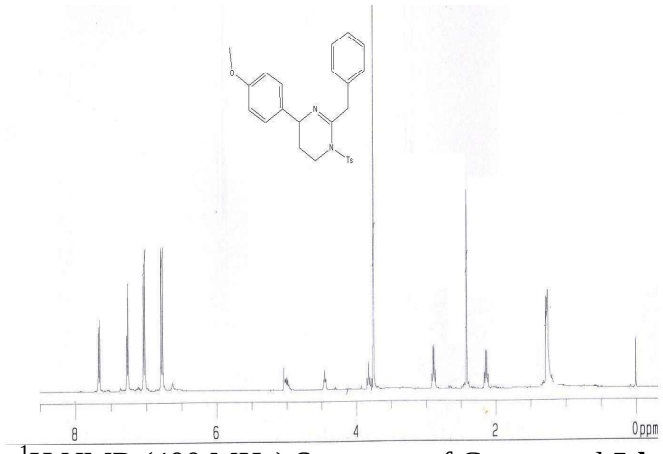
47% yield, Colourless paste; R_f = 0.40 (60% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.76-7.78 (m, 1H), 7.62-7.64 (m, 1H), 7.21-7.25 (m, 2H), 6.97-7.00 (m, 2H), 6.71-6.75 (m, 2H), 5.01-5.26 (m, 1H), 3.69-3.80 (m, 2H), 3.68 (S, 3H), 2.84-2.85 (m, 1H), 2.41 (bS, 3H), 2.38 (bs, 3H), 2.07-2.13 (m, 1H); ^{13}C NMR ($CDCl_3$ 100MHz)δ:157.95, 154.82, 136.86, 136.16, 129.59, 128.47, 127.21, 126.36, 113.87, 72.

28, 70.26, 46.39, 41.64, 35.65; LCMS (EI, *m/z*) 358 (M^+); Anal. calcd for $C_{19}H_{22}N_2O_3S$. C, 63.66; H, 6.19; N, 7.82. Found: C, 63.01; H, 5.99; N, 7.80.

2-benzyl-4-(4-Methoxy-phenyl)-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (5d):

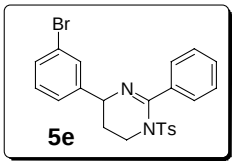


48% yield, Colourless paste; R_f = 0.42 (60% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.65–7.67 (d, *J*=8.0 Hz, 2H), 7.25-7.27 (m, 3H), 7.00-7.03 (m, 4H), 6.76-6.79 (m, 4H), 4.97-5.08 (m, 1H), 4.40-4.47 (t, *J*= 6.12 Hz, 1H), 3.78-3.85 (m, 1H), 3.75 (s, 3H), 2.86-2.91 (m, 2H), 2.41 (S, 3H), 2.10-2.16 (m, 2H); LCMS (EI, *m/z*) 434 (M^+); Anal. calcd for $C_{19}H_{22}N_2O_3S$. C, 69.10; H, 6.03; N, 6.45. Found: C, 68.98; H, 5.98; N, 6.51.



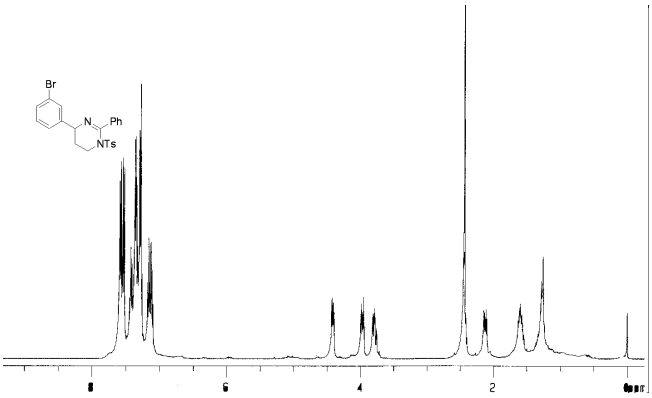
^{1}H NMR (400 MHz) Spectrum of Compound **5d**

4-(3-Bromo-phenyl)-2-phenyl-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (5e):

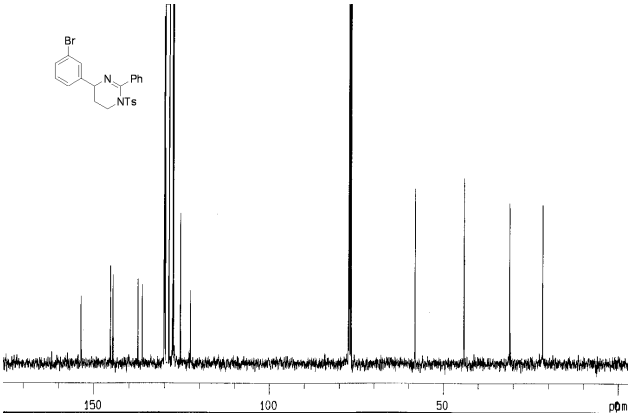


49% yield, Colourless paste; R_f 0.49 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56 (m, 4H), 7.42-7.25 (m, 7H), 7.13 (m, 2H), 4.14 (dd, *J* = 9.24,

5.12 Hz, 1H), 3.97 (dt, *J* = 12.92, 4.4 Hz, 1H), 3.78 (m, 1H), 2.43 (s, 3H), 2.11 (m, 1H), 1.58 (m, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 153.54, 145.31, 144.52, 137.55, 136.26, 130.04, 129.97, 129.82, 129.58, 128.65, 127.43, 125.31, 122.53, 58.25, 44.15, 31.11, 29.65, 21.62; LCMS (EI, *m/z*) 469 (M^+); Anal. calcd for $C_{23}H_{21}BrN_2O_2S$. C, 58.85; H, 4.51; N, 5.97. Found: C, 59.03; H, 4.96; N, 5.81.

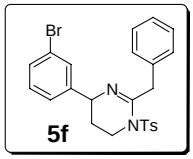


^{1}H NMR (400 MHz) Spectrum of Compound **5e**



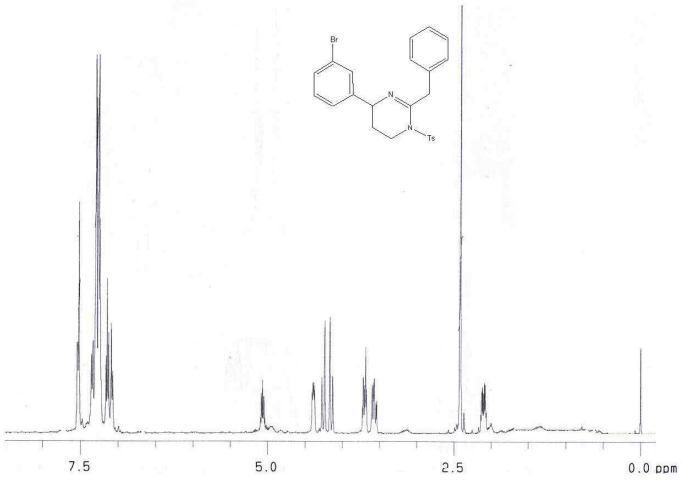
^{13}C NMR (100 MHz) Spectrum of Compound **5e**

2-benzyl-4-(3-bromo-phenyl)-1-(toluene-4-sulphonyl)-1,4,5,6-tetrahydro-pyrimidine (5f):



48% yield, Colourless paste; R_f 0.44 (40% EtOAc in Petroleum ether); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52 (m, 2H), 7.43-6.98 (m, 11H), 5.01-5.14 (m, 1H), 4.13-4.40 (m, 3H), 3.53-3.72 (m, 2H), 2.41 (s, 3H), 2.06-2.13 (m, 1H); ^{13}C NMR ($CDCl_3$ 100 MHz)

δ: 152.21, 145.59, 137.15, 130.09, 130.01, 129.94, 129.63, 129.54, 129.12, 128.30, 126.97, 126.51, 126.45, 125.13, 122.57, 72.20, 44.37, 43.31, 30.63; LCMS (EI, *m/z*) 482 (M^+); Anal. calcd for $C_{24}H_{23}BrN_2O_2S$. C, 59.63; H, 4.80; N, 5.79. Found: C, 59.03; H, 4.96; N, 5.81.



^{1}H NMR (400 MHz) Spectrum of Compound **5f**