

### General procedure for the olefin aziridination reaction

PhINTs (0.5 m mol) was filled in a dry Schlenk filled with argon, followed by the olefin (2.5 m mol). The catalyst (0.005 – 0.015 m mol) was dissolved in dry acetonitrile (2 ml) and the solution was injected into the Schlenk tube by syringe. The mixture was stirred for the time shown in table 2, 3, 4 and 5, until the reaction mixture turned clear. Then the solution was concentrated under high vacuum, affording the crude product. The product was purified by silica gel column chromatography (n-hexane / ethyl acetate) and the yield was determined by weighting the isolated product. The structure of pure product was established by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

**ethyl 3-phenyl-1-tosylaziridine-2-carboxylate (2a):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 (d,  $J$ =8.3, 2H), 7.27 (dt,  $J$ =3.7, 12.7, 7H), 4.44 (d,  $J$ =4.0, 1H), 4.31 (ddq,  $J$ =3.6, 7.3, 14.5, 2H), 3.51 (d,  $J$ =4.0, 1H), 2.39 (s, 3H), 1.33 (t,  $J$ =7.1, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 165.77, 144.34, 137.23, 132.73, 129.60, 128.93, 128.61, 127.50, 127.37, 62.45, 47.70, 47.15, 21.61, 14.00.

**ethyl 3-(4-bromophenyl)-1-tosylaziridine-2-carboxylate (2b):** White oily solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.76 (d,  $J$ =8.3, 2H), 7.40 (d,  $J$ =8.4, 2H), 7.26 (d,  $J$ =8.1, 2H), 7.11 (d,  $J$ =8.4, 2H), 4.37 (d,  $J$ =3.9, 1H), 4.29 (pd,  $J$ =3.6, 7.6, 2H), 3.47 (d,  $J$ =3.9, 1H), 2.40 (s, 3H), 1.32 (t,  $J$ =7.1, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 165.56, 144.61, 137.10, 131.92, 131.85, 129.74, 129.12, 127.55, 123.13, 62.62, 47.21, 46.99, 21.70, 14.05

**ethyl 3-(4-methoxyphenyl)-1-tosylaziridine-2-carboxylate (2c):** White oily solid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 7.90 (d,  $J$ =8.1, 2H), 7.32 (d,  $J$ =8.1, 2H), 7.21 (d,  $J$ =8.6, 2H), 6.77 (d,  $J$ =8.6, 2H), 4.05 (d,  $J$ =7.5, 1H), 3.94 (m, 2H), 3.72 (s, 3H), 3.63 (d,  $J$ =7.5, 1H), 2.40 (s, 3H), 0.98 (t,  $J$ =7.1, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz)  $\delta$  = 164.60, 159.87, 145.21, 134.26, 129.97, 128.86, 128.17, 123.21, 113.72, 61.59, 55.29, 55.27, 45.15, 43.65, 21.75, 13.93, 1.10.

**ethyl 3-propyl-1-tosylaziridine-2-carboxylate (2d):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.84 (d,  $J$ =8.2, 2H), 7.30 (d,  $J$ =8.3, 2H), 4.15 (q,  $J$ =7.1, 2H), 3.27 (d,  $J$ =4.0, 1H), 3.08 (m, 1H), 2.42 (s, 3H), 1.22 (dd,  $J$ =6.4, 13.5, 7H), 0.97 (t,  $J$ =7.4, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 167.06, 144.42, 137.15, 129.67, 127.58, 61.92, 49.00, 44.13, 30.16, 21.70, 21.05, 14.04, 13.67.

**2-(4-bromophenyl)-1-tosylaziridine (2e):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.85 (d,  $J$ =8.2, 2H), 7.38 (d,  $J$ =8.4, 2H), 7.32 (d,  $J$ =8.1, 2H), 7.08 (d,  $J$ =8.4, 2H), 3.72 (dd, 1H), 2.96 (d,  $J$ =7.2, 1H), 2.41 (s,

3H), 2.33 (d,  $J=4.4$ , 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 144.95, 134.83, 134.30, 131.80, 129.95, 128.35, 128.05, 122.40, 40.39, 36.15, 21.79.

**2-(4-methoxyphenyl)-1-tosylaziridine (2f):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.71 (d,  $J=8.2$ , 2H), 7.28 (m, 2H), 7.11 (d,  $J=8.5$ , 2H), 6.83 (d,  $J=8.7$ , 2H), 3.76 (m, 3H), 3.33 (m, 1H), 3.17 (m, 2H), 2.94 (m, 1H), 2.42 (d,  $J=11.0$ , 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.66, 143.52, 137.03, 130.97, 129.82, 127.88, 127.18, 114.08, 64.23, 55.38, 49.47, 21.64.

**2-octyl-1-tosylaziridine (2g):**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.80 (d,  $J=8.2$ , 2H), 7.31 (d,  $J=8.1$ , 2H), 2.69 (m, 1H), 2.61 (d,  $J=7.0$ , 1H), 2.42 (s, 3H), 2.04 (d,  $J=4.5$ , 1H), 1.20 (m, 14H), 0.85 (t,  $J=7.0$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 144.50, 135.22, 129.70, 128.07, 40.58, 33.85, 31.92, 31.39, 29.46, 29.19, 29.10, 26.85, 22.73, 21.70, 14.20.

**7-tosyl-3-vinyl-7-azabicyclo[4.1.0]heptanes (2h):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 (d,  $J=7.8$ , 2H), 7.30 (d,  $J=7.8$ , 2H), 5.62 (m, 1H), 4.90 (m, 2H), 2.97 (m, 2H), 2.41 (s, 3H), 2.00 (m, 1H), 1.69 (m, 1H), 1.45 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 144.19, 142.37, 135.85, 129.70, 127.69, 113.30, 40.69, 40.19, 39.08, 36.78, 33.55, 26.50, 21.66.

**trans-2,3-diethyl-1-tosylaziridine (3a):** White oily solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.81 (d,  $J=8.3$ , 2H), 7.28 (d,  $J=8.0$ , 2H), 2.59 (m, 2H), 2.40 (s, 3H), 1.72 (m, 4H), 0.91 (t,  $J=7.5$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 143.80, 138.10, 129.48, 127.51, 51.01, 23.30, 21.63, 11.82.

**cis-2,3-diethyl-1-tosylaziridine (3b):** White oily solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.80 (d,  $J=8.2$ , 2H), 7.29 (d,  $J=8.0$ , 2H), 2.71 (m, 2H), 2.41 (s, 3H), 1.42 (m, 4H), 0.84 (t,  $J=7.4$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 144.26, 135.50, 129.55, 128.11, 46.80, 21.65, 20.11, 11.62.

**trans-2,3-dipropyl-1-tosylaziridine (3c):** Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.82 (d,  $J=8.1$ , 2H), 7.28 (d,  $J=7.9$ , 2H), 2.63 (m, 2H), 2.41 (s, 3H), 1.68 (m, 4H), 1.34 (m, 4H), 0.89 (t,  $J=7.4$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 143.77, 138.16, 129.46, 127.48, 49.70, 31.96, 21.62, 20.81, 13.77.

**cis-2,3-dipropyl-1-tosylaziridine (3d):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 (d,  $J=8.0$ , 2H), 7.28 (d,  $J=8.0$ , 2H), 2.75 (m, 2H), 2.40 (s, 3H), 1.29 (m, 8H), 0.84 (t,  $J=7.2$ , 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 144.08, 135.23, 129.37, 127.87, 44.85, 28.62, 21.48, 20.46, 13.63.

**cis-2-methyl-3-phenyl-1-tosylaziridine (3e):**  $^{13}\text{C}$  White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ (ppm)) 1.00 (d, 3H), 2.42 (s, 3H), 3.18 (dq, 1H), 3.91 (d, 1H), 7.25-7.33 (m, 7H), 7.87 (d, 2H).

***trans*-2-methyl-3-phenyl-1-tosylaziridine (3f):** <sup>[1]</sup> White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ(ppm))  
1.83 (d, 3H), 2.38 (s, 3H), 2.90 (dq, 1H), 3.78 (d, 1H), 7.12-7.26 (m, 7H), 7.80 (d, 2H).

**2,3-diphenyl-1-tosylaziridine:** <sup>[1]</sup> White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ(ppm)) For *cis* – isomer:  
2.45 (s, 3H), 4.22 (s, 2H), 7.02-7.12(m, 10H), 7.33(d, 2H), 7.96 (d, 2H); for *trans* – isomer: 2.39 (s,  
3H), 4.26 (s, 2H), 7.20 (d, 2H), 7.34-7.43 (m, 10H), 7.63 (d, 2H).

[1] R. Vyas, G. Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2004**, *6*, 1907.