

# A New, Mild Synthesis of *N*-Sulfonyl Ketimines via the Palladium-Catalyzed Isomerization of Aziridines

John P. Wolfe\* and Joshua E. Ney

*Department of Chemistry, University of Michigan, 930 N. University Avenue, Ann Arbor, MI 48109-1055*

## Supporting Information

Experimental procedures and characterization data for new compounds shown in Table 2 and eqs 2–3 (9 pages).

**General** All reactions were carried out under an argon atmosphere in oven or flame dried glassware. Bis(tricyclohexylphosphine)palladium (0), copper(II) triflate, triphenylphosphine and (dppf)PdCl<sub>2</sub> were purchased from Strem Chemical Co. and used without further purification. Styrene, 1-hexene, 1,5-hexadiene, 1,7-octadiene, anhydrous acetonitrile, and anhydrous DMF were purchased from Acros chemical company and were used as obtained. Methylmagnesium bromide (1.4 M in 3:1 toluene:THF) and 9-BBN (0.5 M in THF) were purchased from Aldrich Chemical company and was used as received. Toluene was purified with a GlassContour solvent purification system. PhINTs,<sup>1</sup> *N*-(4-toluenesulfonyl)-2-phenylaziridine,<sup>2</sup> *N*-(4-toluenesulfonyl)-2-*n*-butylaziridine (**1**),<sup>2</sup> *N*-benzoyl-2-methylaziridine (**8**),<sup>3</sup> and diethyl diallylmalonate<sup>4</sup> were prepared according to published procedures. Aziridine substrates were degassed under vacuum immediately prior to use. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by <sup>1</sup>H NMR, and either capillary GC (known compounds) or combustion analysis

(new compounds). The yields reported in the supporting information describe the result of a single experiment, whereas the yields reported in Table 2 are average yields of two or more experiments. Thus, the yields reported in the supporting information may differ from those shown in Table 2.

**General procedure for the synthesis of sulfonylaziridines.**<sup>2</sup> An oven or flame-dried flask was purged with argon and charged with Cu(OTf)<sub>2</sub> (5 mol %), the appropriate olefin (5.0 equiv), and acetonitrile (3 mL/mmol PhINTs). Solid PhINTs (1.0 equiv) was added in a single portion and the mixture was stirred at room temperature until all PhINTs had dissolved (ca 30 min). The reaction mixture was diluted with ethyl acetate (100 mL), filtered through a pad of silica gel, and eluted with additional ethyl acetate (50 mL). The resulting solution was concentrated *in vacuo* and the crude material was purified by flash chromatography on silica gel.

**2-Allyl-2-[1-(toluene-4-sulfonyl)aziridin-2-ylmethyl]malonic acid diethyl ester** (Table 2, Entry 3 substrate). Reaction of diethyl diallylmalonate (2.3 g, 9.0 mmol) with PhINTs (1.1 g, 3.0 mmol) following the general procedure afforded 610 mg (50 %) of the title compound as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 8.5 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 5.60–5.50 (m, 1 H), 5.10–5.04 (m, 2 H), 4.21–4.11 (m, 4 H), 2.74 (p, *J* = 5.0 Hz, 1 H), 2.64 (dd, *J* = 7.0, 1.0 Hz, 2 H), 2.56 (d, *J* = 6.5 Hz, 1H), 2.42 (s, 3 H), 2.14 (dd, *J* = 14.5, 5.5 Hz, 1 H), 2.00 (d, *J* = 4.5 Hz, 1 H), 1.88 (dd, *J* = 14.5, 7.5 Hz, 1 H), 1.25–1.19 (m, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.22, 170.18, 144.6, 134.7, 131.9, 129.7, 128.0, 119.6, 61.6, 61.5, 37.1, 36.1, 34.1, 33.6, 21.6, 14.01, 13.99; IR (film) 1732, 1327, 1163 cm<sup>-1</sup>. Anal calcd for C<sub>20</sub>H<sub>27</sub>NO<sub>6</sub>S: C, 58.66; H, 6.65; N, 3.42. Found: C, 58.66; H, 6.64, N, 3.16.

**2-(5,5-Diethoxypentyl)-1-(toluene-4-sulfonyl)aziridine** (Table 2, Entry 4 substrate). Reaction of 1,7-octadiene (5.2 mL g, 35.1 mmol) with PhINTs (4.35 g, 11.7 mmol) following the

general procedure afforded 1.82 g (57 %) of 2-Hex-5-enyl-1-(toluene-4-sulfonyl)aziridine as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J$  = 8.0 Hz, 2 H), 7.33 (d,  $J$  = 8.0 Hz, 2 H), 5.76–5.68 (m, 1 H), 4.98–4.90 (m, 2 H), 2.74–2.68 (m, 1 H), 2.64 (d,  $J$  = 7.5 Hz, 1 H), 2.45 (s, 3 H), 2.06 (d,  $J$  = 5.0 Hz, 1H), 1.94 (q,  $J$  = 7.0 Hz, 2 H), 1.59–1.50 (m, 1 H), 1.38–1.28 (m, 3 H), 1.27–1.20 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 138.3, 135.0, 129.5, 127.9, 114.4, 40.2, 33.6, 33.4, 31.0, 28.1, 26.1, 21.5; IR (film) 1324, 1162  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_2\text{S}$ : C, 64.48; H, 7.58; N, 5.01. Found: C, 64.20; H, 7.49, N, 4.79.

A solution of 2-Hex-5-enyl-1-(toluene-4-sulfonyl)aziridine (1.3 g, 4.9 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) was cooled to  $-78^\circ\text{C}$  and  $\text{O}_3$  was bubbled through the solution until a blue color persisted. The solution was sparged with  $\text{N}_2$  until the blue color was discharged, and  $\text{PPh}_3$  (1.6 g, 5.9 mmol) was added. The mixture was warmed to rt with stirring until the intermediate ozonide had been completely consumed as judged by TLC analysis. The mixture was concentrated *in vacuo*, and a solution of 2:1 hexanes:ethyl acetate (80 mL) was added. The resulting suspension was filtered through a plug of silica gel and the solution was concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 690 mg (50%) of 5-[1-toluene-4-sulfonyl)aziridin-2-yl]pentanal as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.71 (t,  $J$  = 1.5 Hz, 1 H), 7.82 (d,  $J$  = 8.5 Hz, 2 H), 7.33 (d,  $J$  = 8.5 Hz, 2 H), 2.76–2.70 (m, 1 H), 2.62 (d,  $J$  = 7.5 Hz, 1 H), 2.45 (s, 3 H), 2.35 (td,  $J$  = 1.5, 7.5 Hz, 2 H), 2.06 (d,  $J$  = 4.5 Hz, 1 H), 1.66–1.56 (m, 3 H), 1.38–1.24 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.1, 144.5, 134.9, 129.6, 127.9, 43.5, 39.8, 33.7, 30.9, 26.2, 21.5, 21.3; IR (film) 1722, 1322, 1161  $\text{cm}^{-1}$ .

To a solution of 5-[1-toluene-4-sulfonyl)aziridin-2-yl]pentanal (304 mg, 1.1 mmol) in ethanol (5 mL) was added triethylorthoformate (0.36 mL, 2.2 mmol) and PPTS (28 mg, 0.11 mmol). The mixture was stirred at room temperature until the starting material had been

consumed as judged by TLC analysis. The mixture was concentrated *in vacuo* and the crude product was purified by flash chromatography on silica gel to afford 306 mg (80%) of the title compound as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.4 Hz, 2 H), 7.33 (d,  $J$  = 8.7 Hz, 2 H), 4.41 (t,  $J$  = 5.7 Hz, 1 H), 3.68–3.54 (m, 2 H), 3.51–3.40 (m, 2 H), 2.76–2.67 (m, 1 H), 2.63 (d,  $J$  = 6.9 Hz, 1 H), 2.45 (s, 3 H), 2.05 (d,  $J$  = 4.5 Hz, 1 H), 1.59–1.46 (m, 3 H), 1.40–1.24 (m, 5 H), 1.19 (t,  $J$  = 6.6 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 135.1, 129.6, 127.9, 102.6, 61.0, 60.9, 40.2, 33.7, 33.3, 31.2, 26.6, 24.1, 21.6, 15.3; IR (film) 1325, 1162  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{18}\text{H}_{29}\text{NO}_4\text{S}$ : C, 60.81; H, 8.22; N, 3.94. Found: C, 60.45; H, 8.15, N, 3.90.

**6-[1-(Toluene-4-sulfonyl)aziridin-2-yl]-hexan-2-one** (Table 2, Entry 5 Substrate)

Reaction of 1,5-hexadiene (4.50 mL, 37.5 mmol) with PhINTs (2.66 g, 7.49 mmol) following the general procedure afforded 1.07 g (59%) of 2-but-3-enyl-1-(toluene-4-sulfonyl)aziridine<sup>5</sup> as a colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.7 Hz, 2 H), 7.33 (d,  $J$  = 8.7 Hz, 2 H), 5.79–5.66 (m, 1 H), 5.00–4.93 (m, 2 H), 2.81–2.72 (m, 1 H), 2.63 (d,  $J$  = 7.2 Hz, 1 H), 2.45 (s, 3 H), 2.08–1.99 (m, 3 H), 1.71–1.59 (m, 1 H), 1.51–1.40 (m, 1 H).

A solution of 2-but-3-enyl-1-(toluene-4-sulfonyl)aziridine (1.07 g, 4.4 mmol) in THF (15 mL) was cooled to 0 °C and 9-BBN (10 mL, 5.0 mmol, 0.5 M in THF) was added dropwise. The mixture was warmed to rt and stirred for 4h, then 2-bromo-2-butene (0.54 mL, 5.3 mmol), aqueous  $\text{K}_3\text{PO}_4$  (3.1 mL, 9.3 mmol, 3 M), (dppf) $\text{PdCl}_2$  (172 mg, 0.22 mmol), and DMF (10 mL) were added. The flask was purged with argon and the mixture was stirred at rt for 18 h until the starting material had been consumed as judged by TLC analysis. Water (20 mL) was added and the resulting mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were washed with brine and dried over  $\text{MgSO}_4$ . The crude material was purified by flash chromatography on silica gel to afford 476 mg (35%) of 2-(5-methylhept-5-enyl)-1-(toluene-4-

sulfonyl)aziridine as a colorless oil. The product was determined to be a ~1:1 mixture of olefin isomers as judged by  $^1\text{H}$  NMR analysis. Data are for the mixture of isomers.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J$  = 8.4 Hz, 2 H), 7.33 (d,  $J$  = 8.7 Hz, 2 H), 5.21–5.09 (m, 1 H), 2.76–2.67 (m, 1 H), 2.63 (d,  $J$  = 6.9 Hz, 1 H), 2.45 (s, 3 H), 2.05 (d,  $J$  = 4.5 Hz, 1 H), 1.96–1.81 (m, 2 H), 1.59–1.46 (m, 7 H), 1.40–1.16 (m, 5 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 135.6, 135.4, 135.1, 129.57, 129.55, 127.9, 119.0, 118.3, 40.4, 40.3, 39.2, 33.7, 31.2, 31.1, 30.9, 27.2, 27.1, 26.5, 26.3, 23.2, 21.6, 15.4, 13.25, 13.15; IR (film) 1325, 1162  $\text{cm}^{-1}$ . MS (ESI)  $m/z$  330.1504 (330.1504 calcd for  $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$ ,  $\text{M} + \text{Na}^+$ ).

A solution of 2-(5-methylhept-5-enyl)-1-(toluene-4-sulfonyl)aziridine (476 mg, 1.55 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was cooled to  $-78^\circ\text{C}$  and  $\text{O}_3$  was bubbled through the solution until a blue color persisted. The solution was sparged with  $\text{N}_2$  until the blue color was discharged, and  $\text{PPh}_3$  (609 mg, 2.32 mmol) was added. The mixture was warmed to rt with stirring until the intermediate ozonide had been completely consumed as judged by TLC analysis. The mixture was concentrated *in vacuo*, and a solution of 2:1 hexanes:ethyl acetate (40 mL) was added. The resulting suspension was filtered through a plug of silica gel and the solution was concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 259 mg (57%) of the title compound as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J$  = 8.5 Hz, 2 H), 7.33 (d,  $J$  = 8.5 Hz, 2 H), 2.75–2.70 (m, 1 H), 2.61 (d,  $J$  = 7.0 Hz, 1 H), 2.45 (s, 3 H), 2.34 (t,  $J$  = 7.5 Hz, 2 H), 2.10 (s, 3 H), 2.05 (d,  $J$  = 5.0 Hz, 1 H), 1.62–1.50 (m, 3 H), 1.35–1.24 (m, 3 H),  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  208.5, 144.4, 134.9, 129.5, 127.7, 43.2, 39.9, 33.7, 30.9, 29.8, 26.2, 22.9, 21.5; IR (film) 1714, 1322, 1161  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{S}$ : C, 60.99; H, 7.17; N, 4.74. Found: C, 61.16; H, 7.32; N, 4.68.

**General procedure for the palladium-catalyzed isomerization of sulfonyl aziridines to sulfonyl imines.** An oven or flame-dried Schlenk tube was charged with Pd[PCy<sub>3</sub>]<sub>2</sub> (2 mol %) in a nitrogen-filled glovebox. The tube was removed from the glovebox and a toluene solution of the aziridine (0.25 M) was added. The mixture was heated to 70 °C with stirring until the starting material had been consumed as judged by GC or <sup>1</sup>H NMR analysis. The mixture was cooled to room temperature and concentrate *in vacuo*. The crude material was purified by flash chromatography on silica gel.

**4-Methyl-*N*-(1-methylpentylidene)benzenesulfonamide** (Table 2, Entry 1 product). Reaction of 101 mg (0.4 mmol) of *N*-(4-toluenesulfonyl)-2-*n*-butylaziridine<sup>2</sup> following the general procedure afforded 75 mg (74 %) of the title compound as a colorless oil. This material was obtained as a ~5/1 mixture of E/Z isomers. Data are for the major isomer. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 8.5 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 2.54 (s, 3 H), 2.43–2.41 (m, 5 H), 1.57–1.51 (m, 2 H), 1.34–1.28 (m, 2 H), 0.88 (t, *J* = 7.0 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.1, 143.4, 138.3, 129.4, 127.0, 43.3, 27.5, 24.0, 22.0, 21.5, 13.7; IR (film) 1622 cm<sup>-1</sup>. Anal calcd for C<sub>13</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.63; H, 7.54, N, 5.44.

**4-Methyl-*N*-(1-phenylethylidene)benzenesulfonamide** (Table 2, Entry 2 product).<sup>6</sup> Reaction of 108 mg (0.4 mmol) of *N*-(4-toluenesulfonyl)-2-phenylaziridine following the general procedure afforded 82 mg (76 %) of the title compound as a white solid, m.p. 84–86 °C (lit<sup>6</sup> m.p. 88–89 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 7.5 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.41 (t, *J* = 7.5 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 2.99 (s, 3 H), 2.45 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.8, 143.5, 138.6, 137.5, 133.1, 129.4, 128.6, 128.2, 127.0, 21.5, 21.1; IR (film) 1591, 1287 cm<sup>-1</sup>.

**2-Allyl-2-[2-(toluene-4-sulfonylimino)propyl]malonic acid diethyl ester** (Table 2, Entry 3 product). Reaction of 164 mg (0.4 mmol) of 2-allyl-2-[1-(toluene-4-sulfonyl)aziridin-2-ylmethyl]malonic acid diethyl ester following the general procedure afforded 121 mg (74 %) of the title compound as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 8.0 Hz, 2 H), 7.32 (d,  $J$  = 8.0 Hz, 2 H), 5.61–5.55 (m, 1 H), 5.08–4.98 (m, 2 H), 3.99 (q,  $J$  = 7.0 Hz, 4 H), 3.11 (s, 2 H), 2.72 (d,  $J$  = 7.5 Hz, 2 H), 2.54 (s, 3 H), 2.43 (s, 3 H), 1.13 (t,  $J$  = 7.0 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  184.6, 169.6, 143.6, 137.8, 132.4, 129.3, 127.1, 119.6, 61.5, 55.3, 44.0, 36.8, 24.8, 21.5, 13.8; IR (film) 1732, 1634, 1320, 1092  $\text{cm}^{-1}$ . Anal calcd for  $\text{C}_{20}\text{H}_{27}\text{NO}_6\text{S}$ : C, 58.66; H, 6.65; N, 3.42. Found: C, 58.73; H, 6.69, N, 3.34.

***N*-(6,6-Diethoxy-1-methylhexylidene)-4-methylbenzenesulfonamide** (Table 2, Entry 4 product). Reaction of 45 mg (0.13 mmol) of 2-(5,5-diethoxypentyl)-1-(toluene-4-sulfonyl)aziridine following the general procedure afforded 40 mg (89 %) of the title compound as a colorless oil. This material was obtained as a ~5/1 mixture of E/Z isomers and contained ~15% 7,7-diethoxy-heptan-2-one (resulting from hydrolysis during chromatography) as judged by  $^1\text{H}$  NMR analysis. Data are for the major isomer.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 8.5 Hz, 2 H), 7.31 (d,  $J$  = 8.0 Hz, 2 H), 4.42 (t,  $J$  = 5.5 Hz, 1 H), 3.68–3.54 (m, 2 H), 3.51–3.40 (m, 2 H), 2.54 (s, 3 H), 2.46–2.40 (m, 5 H), 1.60–1.54 (m, 4 H), 1.39–1.31 (m, 2 H), 1.17 (t,  $J$  = 7.0 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.6, 143.5, 138.3, 129.4, 127.0, 102.6, 61.0, 43.5, 33.2, 25.2, 24.1, 24.0, 21.5, 15.3; IR (film) 1620, 1317, 1154  $\text{cm}^{-1}$ . MS (ESI)  $m/z$  378.1704 (378.1715 calcd for  $\text{C}_{18}\text{H}_{29}\text{NO}_4\text{S}$ ,  $\text{M}+\text{Na}^+$ ).

**4-Methyl-*N*-(1-methyl-6-oxoheptylidene)benzenesulfonamide** (Table 2, Entry 5 product). Reaction of 92 mg (0.3 mmol) of 6-[1-(toluene-4-sulfonyl)aziridin-2-yl]-hexan-2-one following the general procedure afforded 59 mg (64 %) of the title compound as a colorless oil.

This material was obtained as a ~5/1 mixture of imine isomers and contained approximately 5% *p*-toluenesulfonamide as judged by  $^1\text{H}$  NMR analysis. Data are for the major isomer.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 8.5 Hz, 2 H), 7.32 (d,  $J$  = 8.5 Hz, 2 H), 2.54 (s, 3 H), 2.46–2.38 (m, 7 H), 2.14–2.18 (m, 2 H), 2.09 (s, 3 H), 1.56–1.52 (m, 2 H)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  208.4, 189.3, 143.6, 138.2, 129.4, 127.0, 43.2, 43.1, 29.8, 24.6, 24.1, 22.8, 21.5; IR (film) 1714, 1621, 1315, 1152  $\text{cm}^{-1}$ . MS (EI)  $m/z$  296.1321 (296.1320 calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{S}$ ,  $\text{M} + \text{H}^+$ )

***N*-Isopropenylbenzamide** (Table 2, Entry 7 product).<sup>7</sup> Reaction of 40 mg (0.25 mmol) of *N*-benzoyl-2-methylaziridine following the general procedure afforded 24 mg (60 %) of the title compound as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76–7.70 (m, 2 H), 7.50–7.44 (m, 1 H), 7.42–7.36 (m, 2 H), 7.17 (s, br, 1H), 5.55 (s, 1 H), 4.56 (s, 1 H), 2.01 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 137.6, 135.1, 131.7, 128.7, 126.8, 99.6, 22.2; IR (film) 3292, 1660, 1537  $\text{cm}^{-1}$ .

**General procedure for the palladium-catalyzed isomerization of sulfonyl aziridines to sulfonyl imines with *in situ* Grignard reagent addition.** An oven or flame-dried Schlenk tube was charged with  $\text{Pd}[\text{PCy}_3]_2$  (2 mol %) in a nitrogen-filled glovebox. The tube was removed from the glovebox and a toluene solution of the aziridine (0.25 M) was added. The mixture was heated to 70 °C with stirring until the starting material had been consumed as judged by GC or  $^1\text{H}$  NMR analysis. The mixture was cooled to room temperature and concentrated *in vacuo*. Methylmagnesium bromide (4.0 equiv, 1.4 M in 3:1 toluene/THF) was added and the mixture was heated to 70 °C with stirring until the sulfonyl imine had been consumed as judged by  $^1\text{H}$  NMR analysis. The mixture was quenched with saturated aqueous ammonium chloride and extracted with ether. The combined organic extracts were washed with water, dried with



anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel.

***N*-(1,1-Dimethylpentyl)-4-methylbenzenesulfonamide** (eq 3 product). Reaction of 63 mg (0.25 mmol) of **1** following the general procedure afforded 45 mg (67 %) of the title compound as a white solid, m.p. 68-69 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 4.31 (s, 1 H), 2.42 (s, 3 H), 1.48-1.43 (m, 2 H), 1.23-1.18 (m, 4 H), 1.17 (s, 6 H), 0.85 (t, *J* = 7.0 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.7, 140.6, 129.4, 127.0, 57.1, 42.7, 27.6, 26.0, 22.9, 21.4, 13.9; IR (film) 3276, 1323, 1151 cm<sup>-1</sup>. Anal calcd for C<sub>14</sub>H<sub>23</sub>NO<sub>2</sub>S: C, 62.42; H, 8.61; N, 5.20. Found: C, 62.36; H, 8.39, N, 5.08.

***N*-(6,6-Diethoxy-1,1-dimethylhexyl)-4-methylbenzenesulfonamide** (eq 4 product). Reaction of 44 mg (0.12 mmol) of **7** following the general procedure afforded 33 mg (72 %) of the title compound as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 4.52 (s, 1 H), 4.43 (t, *J* = 5.5 Hz, 1 H), 3.67–3.58 (m, 2 H), 3.52–3.44 (m, 2 H), 2.41 (s, 3 H), 1.59–1.51 (m, 2 H), 1.49–1.44 (m, 2 H), 1.27–1.23 (m, 4 H), 1.20 (t, *J* = 7 Hz, 6 H), 1.16 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.8, 140.6, 129.4, 126.9, 102.8, 60.9, 57.0, 42.9, 33.5, 27.6, 24.9, 23.7, 21.4, 15.3 IR (film) 3276, 1325, 1151 cm<sup>-1</sup>. Anal calcd for C<sub>19</sub>H<sub>33</sub>NO<sub>4</sub>S: C, 61.42; H, 8.95; N, 3.77. Found: C, 61.09; H, 9.09, N, 3.64.

<sup>1</sup> Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361–362.

<sup>2</sup> Evans, D. A.; Bilodeau, M. T.; Faul, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.

<sup>3</sup> Chamchaang, W.; Pinhas, A. R. *J. Org. Chem.* **1990**, *55*, 2943–2950.

<sup>4</sup> Semmelhack, M. F.; Foos, J. S.; Katz, S. *J. Am. Chem. Soc.* **1973**, *95*, 7325–7336.

<sup>5</sup> Lapinsky, D. J.; Bergmeier, S. C. *Tetrahedron Lett.* **2001**, *42*, 8583–8586.

<sup>6</sup> Boger, D. L.; Corbett, W. L. *J. Org. Chem.* **1992**, *57*, 4777–4780.

<sup>7</sup> Jendrzewski, S.; Steglich, W. *Chem. Ber.* **1981**, *114*, 1337–1342.