A Facile Highly Regio- and Stereo-selective Preparation of *N*-Tosyl Allylic Amines from Allylic Alcohols and Tosyl Isocyanate via Palladium(II)-Catalyzed Aminopalladation-β-Heteroatom Elimination

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General procedure for the synthesis of *N*-tosyl Allylic amines from allylic *N*-tosyl carbamates

Allylic *N*-tosyl carbamate (1.0 mmol) was reacted with $Pd(OAc)_2$ (0.05 mmol) and LiBr (4.0 mmol) in DMF (5 mL) at rt or $100^{O}C$. After the reaction was complete as monitored by TLC, diethyl ether (100 mL) was added and the organic layer was washed successively with H_2O (3 X 20 mL) and brine (3 X 20 mL), dried and concentrated. The crude product was purified by column chromatography on silica gel to give the product.

General procedure for the synthesis of Allylic sulfonamides from allylic alcohol

Allylic alcohol (1.0 mmol) was reacted with TsNCO (1.1 mmol) in THF (5mL) for 10 min at rt under N_2; the THF solvent was removed and the residue was dissloved in DMF (5 mL), then $Pd(OAc)_2$ (0.05 mmol) and LiBr (4.0 mmol) were added and the reaction was stirred at rt or $100^{O}C$. After the reaction was complete as monitored by TLC, diethyl ether (100 mL) was added and the organic layer was washed successively with H_2O (3 X 20 mL) and brine (3 X 20 mL), dried and concentrated. The crude product was purified by column chromatography on silica gel to give product.

3a: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3Hz, 2H), 7.24 (d, *J* = 8.3Hz, 2H), 5.65- 5.59 (m, 1H), 5.12-4.98 (m, 2H), 4.93 (br, 1H), 3.52-3.47 (m, 2H), 2.35 (s, 3H); IR (neat): 3250, 1596, 1494, 1425, 1331, 1321, 1161 cm^{-1}; MS m/e: 211 (M^+), 149, 139, 120, 92, 91, 65, 56.

3b: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3Hz, 2H), 7.27 (d, *J* = 8.3Hz, 2H), 5.65- 5.56 (m, 1H), 5.06-4.91 (m, 3H), 3.89-3.83 (m, 1H), 2.35 (s, 3H), 1.14 (d, *J* = 6.8Hz, 3H); IR (neat): 3278, 2980, 1598, 1428, 1328, 1159, 1093 cm^{-1}; MS m/e: 226 (M^+), 210, 198, 172, 155, 139, 91, 65

3c: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3Hz, 2H), 7.20 (d, *J* = 8.3Hz, 2H), 5.50- 5.42 (m, 1H), 4.95-4.86 (m, 2H), 4.46 (d, *J* = 7.7Hz, 1H), 3.72-3.63 (m, 1H), 2.35 (s, 3H), 1.37-1.35 (m, 2H), 1.19-1.12 (m, 4H), 0.75 (t, *J* = 6.9Hz, 3H); IR (neat): 3279, 2998, 2922, 1599, 1496, 1429, 1328, 1306, 1289, 1162, 1095, 1042, 923, 815, 668, 577, 550 cm^{-1}; MS m/e: 268 (M^+ +1), 210, 184, 172, 155, 112, 97, 91, 65.

3d: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3Hz, 2H), 7.22-7.11 (m, 7H), 6.35 (d, *J* = 15.9, 1H), 5.93 (td, *J* = 6.3, 15.9Hz, 1H), 4.73 (t, *J* = 6.1Hz, 1H), 3.66 (ddd, *J* = 1.4, 6.3, 6.1Hz, 2H), 2.33 (s, 3H); IR (neat) 3283, 1597, 1494, 1446, 1421, 1307, 1292, 1162, 1154, 1092, 1047, 817, 747, 689, 670, 59, 547 cm^{-1}; MS m/e: 287 (M^+), 184, 155, 132, 130, 117, 105, 91, 77, 65.

3e: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2Hz, 2H), 7.23 (d, *J* = 8.2Hz, 2H), 5.53-5.44 (m, 1H), 5.30-5.21 (m, 1H), 4.48 (br, 1H), 3.43 (t, *J* = 6.2Hz, 2H), 2.35 (s, 3H), 1.53 (dd, *J* = 1.1, 6.5Hz, 3H); IR (neat): 3250, 3044, 2947, 2922, 2856, 1677, 1650, 1597, 1495, 1421, 1342, 1324, 1290, 1161, 1093, 1048, 971, 933, 869, 811, 708, 670, 552, 520 cm^{-1}; MS m/e: 225 (M^+), 210, 184, 155, 139, 91, 70, 65.

3f: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3Hz, 2H), 7.23 (d, *J* = 8.3Hz, 2H), 5.50- 5.40 (m, 1H), 5.26-5.16 (m, 1H), 4.83 (br, 1H), 3.43 (t, *J* = 6.2, 2H), 2.35 (s, 3H), 1.83-1.79 (m, 2H), 1.17-1.13 (m, 6H), 0.77 (t, *J* = 7.0, 3H); IR (neat): 3282, 2926, 2956, 2858, 1598, 1428, 1327, 1160 cm^{-1}; MS m/e: 281 (M^+), 266, 238, 210, 184, 155, 126, 110, 91, 56.

3g: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3Hz, 2H), 7.28-7.14 (m, 12H), 6.36 (d, *J* = 15.8, 1H), 6.07 (dd, *J* = 6.7, 15.8Hz, 1H), 5.12 (dd, *J* = 6.7, 6.9Hz, 1H), 4.89 (d, *J* = 6.9Hz, 1H), 2.33 (s, 3H); IR (neat): 3271, 3062, 3030, 2958, 2926, 1599, 1495, 1455, 1327, 1160, 1093, 968, 747, 699, 564 cm^{-1}; MS m/e: 363 (M^+), 208, 206, 193, 178, 155, 130, 115, 104, 91.

3h: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2Hz, 2H), 7.21 (d, *J* = 8.2Hz, 2H), 4.99-4,94 (m, 1H), 4.58 (br, 1H), 3.44 (t, *J* = 6.5Hz, 2H), 2.34 (s, 3H), 1.53 (s, 3H), 1.44 (s, 3H); IR (neat): 3277, 1630, 1599, 1430, 1328, 1160, 1093, 1051, 908, 815, 660, 554 cm^{-1}; MS m/e: 239 (M^+), 224, 184, 171, 155, 91, 84, 65.

14: ^{1}H NMR (300MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5Hz, 2H), 7.23 (d, *J* = 8.5Hz, 2H), 6.18-5.98 (m, 2H), 5.51-5.42 (m, 1H), 5.11- 4.99 (m, 2H), 4.57 (br, 1H), 3.55 (t, *J* = 6.3Hz, 2H), 2.35 (s, 3H); IR (neat): 3265, 3093, 2858, 1656, 1604, 1496, 1451, 1422, 1325, 1289, 1162, 1093, 1014, 977, 920, 873, 814, 707, 663, 610, 550, 503 cm^{-1}; MS m/e: 237 (M^+), 210, 184, 172, 155, 139, 91, 82, 65.

The reaction of 1b under $Pd(OAc)_2/PPh_3$

1b (1.0 mmol) was reacted with $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.2 mmol) in DMF (5 mL) at rt under Ar. After the reaction was complete as monitored by TLC, diethyl ether (100 mL) was added and the organic layer was washed successively with H_2O (3 X 20 mL) and brine (3 X 20 mL), dried and concentrated. The crude product was purified by column chromatography on silica gel to give products.

(3b, (*E*)-3e): ^{1}H NMR (300MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.33-7.27 (m, 2H), 5.65- 5.54 (m, 1H), 5.36-5.30 (m, 0.56H), 5.09-4.95 (m, 1.32H), 4.84(br, 0.56H), 3.53-3.48(m, 1.56H), 2.44(s, 3H), 1.60 (dd, *J* = 6.5, 1.2Hz, 1.68H), 1.19 (d, *J* = 6.9Hz, 1.32H);

As compared with standard sample, the experiments of HPLC showed that the area percent of **3b** and (*E*)-**3e** was 37% and 51%, respectively.