Supporting Information

Tin-free Intermolecular Addition of Primary Alkyls to Imines via Dimethylzinc–Air Radical Process

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Experimental Section

General. Silica gel was used for column chromatography. NMR (500 MHz for ^{1}H and 125 MHz for ^{13}C) was measured in $CDCl_3$, and chemical shifts and coupling constants were presented in ppm δ and Hz, respectively. The wavenumbers of maximum absorption peaks of IR spectroscopy were presented in cm^{-1}.

Materials. *N*-Tosylimines **1** were prepared according to the known procedure described in the literatures: B. E. Love, P. D. Raje, T. C. Williams II, *Synlett* **1994**, 493–494 for **1a**–**e**, F. Chemla, V. Hebbe, J.-F. Normant, *Synthesis* **2000**, 75–77 for **1f** and **1g**. Copper(II) triflate was purified by recrystallization from acetonitrile–ether and dried by heating in vacuo prior to use.

The General Procedure for Addition of Alkyls to Aromatic Imines. *N*-(1-Phenylpentyl)-4-toluenesulfonamide (4a): A stirrer bar, dried $Cu(OTf)_2$ (36 mg, 0.10 mmol), and imine **1a** (259 mg, 1.00 mmol) were placed in a dried 10 mL round-bottom flask, which was capped with an argon balloon. CH_2Cl_2 (1.0 mL) was added to the flask and the mixture was stirred for 5 min before cooling in an ice-water bath. To the mixture were added BuI (0.57 mL, 5.0 mmol), BF_3•OEt_2 (0.25 mL, 2.0 mmol), and 1.0 M solution of Me_2Zn in hexane (1.0 mL, 1.0 mmol) at the same temperature. The argon balloon was replaced with a $CaCl_2$ drying tube and the mixture was stirred for 45 min at the same temperature. Another portion of 1.0 M solution of Me_2Zn in hexane (1.0 mL, 1.0 mmol) was added at the same temperature and the mixture was further stirred for 45 min before quenching with sat. aq. NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. Purification of the resulting crude material by column chromatography (hexane/EtOAc 85/15) gave the titled compound (254 mg, 80%) as a white solid, whose recrystallization from hexane gave colorless prisms of mp 78.5–79.5 °C: ^{1}H NMR: 0.80 (t, *J* = 7.3, 3H), 1.07 (m, 1H), 1.20–1.26 (m, 3H), 1.68 (m, 1H), 1.76 (m, 1H), 2.35 (s, 3H), 4.25 (dt,

J = 7.0, 7.5, 1H), 4.70 (d, *J* = 7.0, 1H), 6.99–7.01 (m, 2H), 7.11 (d, *J* = 8.6, 2H), 7.14–7.16 (m, 3H), 7.52 (d, *J* = 8.6, 2H). ^{13}C NMR: 13.7, 21.3, 22.1, 27.9, 37.3, 58.3, 126.5, 127.0, 127.1, 128.3, 129.2, 137.7, 141.1, 142.8. IR (KBr): 3260, 2951, 2928, 2858, 1319, 1165. EIMS (*m*/*z*): 317 (M), 260 (M – C_4H_9), 155 (tosyl), 104, 91. Anal. Calcd. for $C_{18}H_{23}NO_2S$: C, 68.10; H, 7.30; N, 4.41. Found: C, 68.10; H, 7.25; N, 4.37. CAS [124070-43-5].

***N*-(1-Phenylheptyl)-4-toluenesulfonamide (2):** Purified by column chromatography (hexane/EtOAc 9/1). Colorless prisms of mp 68–69 °C (hexane). ^{1}H NMR: 0.82 (t, *J* = 7.0, 3H), 1.04–1.27 (m, 8H), 1.65 (m, 1H), 1.72 (m, 1H), 2.34 (s, 3H), 4.24 (dt, *J* = 7.3, 7.3, 1H), 5.53 (brs, 1H), 7.02 (m, 2H), 7.07–7.14 (m, 5H), 7.55 (d, *J* = 8.3, 2H). ^{13}C NMR: 13.9, 21.3, 22.4, 25.7, 28.7, 31.5, 37.6, 58.3, 126.5, 127.1, 127.2, 128.4, 129.2, 137.7, 141.2, 142.9. IR (KBr): 3260, 2951, 2924, 2854, 1323, 1157. EIMS (*m*/*z*): 260 (M – C_6H_{13}), 190 (M – tosyl), 155 (tosyl), 104, 91. Anal. Calcd. for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.67; H, 7.91; N, 4.05.

***N*-[1-Phenylpropyl]-4-toluenesulfonamide (3):** Purified by column chromatography (hexane/EtOAc 85/15). Colorless prisms of mp 107–108 °C (EtOAc–hexane). CAS [70197-09-0].

5-Phenyl-5-(4-toluenesulfonamido)pentyl acetate (5): Purified by column chromatography (hexane/EtOAc 80/20). Pale-yellow oil. ^{1}H NMR: 1.17 (m, 1H), 1.32 (m, 1H), 1.52 (m, 2H), 1.68 (m, 1H), 1.78 (m, 1H), 1.99 (s, 3H), 2.33 (s, 3H), 3.97 (t, *J* = 6.6, 2H), 4.25 (dt, *J* = 7.5, 7.5, 1H), 5.73 (brd, *J* = 7.5, 1H), 7.01 (m, 2H), 7.08 (d, *J* = 8.3, 2H), 7.11 (m, 3H), 7.54 (d, *J* = 8.3, 2H). ^{13}C NMR: 20.7, 21.2, 22.1, 27.8, 36.9, 58.1, 63.9, 126.4, 126.9, 127.2, 128.3, 129.2, 137.7, 140.8, 142.8, 171.1. IR (KBr): 3279, 2947, 1736, 1323, 1157. EIMS (*m*/*z*): 376 (M+1), 315 (M – HOAc), 260 (M – $AcOC_4H_8$), 155 (tosyl), 104, 91. HRMS–EI: $[M + H]^+$ calcd for $C_{20}H_{26}NO_4S$, 376.1583; found, 376.1577.

***N*-(5-Chloro-1-phenylpentyl)-4-toluenesulfonamide (6):** Purified by column chromatography (hexane/EtOAc 85/15). Colorless prisms of mp 66–68 °C (EtOAc–hexane). ^{1}H NMR: 1.25 (m, 1H), 1.41 (m, 1H), 1.65–1.74 (m, 3H), 1.80 (m, 1H), 2.36 (s, 3H), 3.41 (t, *J* = 6.6, 2H), 4.25 (dt, *J* = 7.3, 7.4, 1H), 5.05 (d, *J* = 7.3, 1H), 6.99–7.01 (m, 2H), 7.12 (d, *J* = 8.3, 2H), 7.14–7.17 (m, 3H), 7.54 (d, *J* = 8.3,

2H). ^{13}C NMR: 21.1, 23.0, 31.7, 36.4, 44.3, 57.9, 126.3, 126.7, 126.9, 128.1, 129.0, 137.5, 140.7, 142.7. IR (KBr): 3236, 2928, 2862, 1319, 1161. EIMS (*m*/*z*): 260 (M – ClC_4H_8), 155 (tosyl), 139, 104, 91. Anal. Calcd. for $C_{18}H_{22}ClNO_2S$: C, 61.44; H, 6.30; N, 3.98. Found: C, 61.20; H, 6.16; N, 3.87.

***N*-(4-Chloro-1-phenylbutyl)-4-toluenesulfonamide (7):** Purified by column chromatography (hexane/EtOAc 85/15). White powder of mp 102–103.5 °C (hexane). ^{1}H NMR: 1.65 (m, 1H), 1.79 (m, 1H), 1.87 (m, 1H), 1.92 (m, 1H), 2.35 (s, 3H), 3.47 (t, *J* = 6.4, 2H), 4.29 (dt, *J* = 7.7, 7.5, 1H), 4.95 (d, *J* = 7.7, 1H), 6.99 (m, 2H), 7.11 (d, *J* = 8.3, 2H), 7.15–7.16 (m, 3H), 7.53 (d, *J* = 8.3, 2H). ^{13}C NMR: 21.3, 28.8, 34.6, 44.2, 57.7, 126.4, 127.0, 127.4, 128.5, 129.3, 137.5, 140.5, 143.0. IR (KBr): 3244, 2928, 1327, 1157. EIMS (*m*/*z*): 301 (M – HCl), 260 (M – ClC_3H_6), 155 (tosyl), 104, 91. Anal. Calcd. for $C_{17}H_{20}ClNO_2S$: C, 60.43; H, 5.97; N, 4.15. Found: C, 60.44; H, 6.01; N, 4.13.

***N*-(2-Methyl-1-phenylpropyl)-4-toluenesulfonamide (8):** Purified by column chromatography (hexane/EtOAc 4/1). Colorless prisms of mp 144–144.5 °C (EtOAc–hexane). CAS [110871-37-9].

***N*-(1-Cyclohexyl-1-phenylmethyl)-4-toluenesulfonamide (9):** Purified by column chromatography (hexane/EtOAc 85/15). White powder of mp 146–146.5 °C (EtOAc–hexane). ^{1}H NMR: 0.84 (m, 1H), 0.94 (m, 1H), 1.06 (m, 2H), 1.13 (m, 1H), 1.27 (m, 1H), 1.51–1.61 (m, 3H), 1.71 (m, 1H), 1.95 (m, 1H), 2.31 (s, 3H), 4.03 (dd, *J* = 8.3, 8.3, 1H), 5.47 (brs, 1H), 6.92 (m, 2H), 7.02 (d, *J* = 8.3, 2H), 7.08 (m, 3H), 7.48 (d, *J* = 8.3, 2H). ^{13}C NMR: 21.3, 25.8, 26.1, 29.4, 29.6, 43.7, 63.4, 126.9, 127.0, 128.0, 129.1, 137.8, 140.0, 142.7. IR (KBr): 3256, 2936, 2855, 1323, 1161. EIMS (*m*/*z*): 260 (M – C_6H_{11}), 188 (M – tosyl), 173 (M – tosylNH), 155 (tosyl), 104, 91. Anal. Calcd. for $C_{20}H_{25}NO_2S$: C, 69.93; H, 7.34; N, 4.08. Found: C, 69.92; H, 7.24; N, 4.10. CAS [318242-27-2].

***N*-[1-(4-Chlorophenyl)pentyl]-4-toluenesulfonamide (4b):** Purified by column chromatography (hexane/EtOAc 85/15). Colorless prisms of mp 142.5–144 °C (hexane). ^{1}H NMR: 0.77 (t, *J* = 7.3, 3H), 1.06 (m, 1H), 1.15–1.27 (m, 3H), 1.60 (m, 1H), 1.71 (m, 1H), 2.37 (s, 3H), 4.24 (dt, *J* = 7.4, 7.4, 1H), 5.58 (brs, 1H), 6.94 (d, *J* = 8.3, 2H), 7.07 (d, *J* = 8.3, 2H), 7.11 (d, *J* = 8.3, 2H), 7.52 (d, *J* = 8.3, 2H). ^{13}C NMR: 13.7, 21.4, 22.1, 27.8, 37.1, 57.6, 127.1, 128.0, 128.5, 129.3, 133.1, 137.6, 139.6, 143.2. IR

(KBr): 3248, 2955, 2928, 2870, 1319, 1165. EIMS (*m*/*z*): 296 (M+2 – C_4H_9), 294 (M – C_4H_9), 155 (tosyl), 138, 91. Anal. Calcd. for $C_{18}H_{22}ClNO_2S$: C, 61.44; H, 6.30; N, 3.98. Found: C, 61.29; H, 6.17; N, 3.91.

***N*-[1-(4-Methoxyphenyl)pentyl]-4-toluenesulfonamide (4c):** Purified by column chromatography (hexane/EtOAc 80/20). Colorless prisms of mp 130.5–132 °C (hexane). ^{1}H NMR: 0.78 (t, *J* = 7.2, 3H), 1.05 (m, 1H), 1.15–1.27 (m, 3H), 1.63 (m, 1H), 1.75 (m, 1H), 2.35 (s, 3H), 3.73 (s, 3H), 4.19 (dt, *J* = 7.4, 7.4, 1H), 5.30 (brs, 1H), 6.66 (d, *J* = 8.6, 2H), 6.92 (d, *J* = 8.6, 2H), 7.11 (d, *J* = 8.3, 2H), 7.54 (d, *J* = 8.3, 2H). ^{13}C NMR: 13.7, 21.3, 22.1, 27.9, 37.2, 55.2, 57.8, 113.7, 127.1, 127.7, 129.2, 133.2, 137.9, 142.8, 158.8. IR (KBr): 3256, 2955, 2928, 2866, 1319, 1161. EIMS (*m*/*z*): 290 (M – C_4H_9), 155 (tosyl), 134, 91. Anal. Calcd. for $C_{19}H_{25}NO_3S$: C, 65.68; H, 7.25; N, 4.03. Found: C, 65.39; H, 7.31; N, 3.97. CAS [79807-48-0].

***N*-[1-(Naphth-1-yl)pentyl]-4-toluenesulfonamide (4d):** Purified by column chromatography (hexane/EtOAc 85/15). Colorless prisms of mp 100–101 °C (EtOAc–hexane). ^{1}H NMR: 0.80 (t, *J* = 7.2, 3H), 1.13–1.36 (m, 4H), 1.88–1.95 (m, 2H), 2.24 (s, 3H), 5.01 (brd *J* = 7.1, 1H), 5.12 (dt, *J* = 7.1, 7.2, 1H), 6.90 (d, *J* = 7.9, 2H), 7.25–7.28 (m, 2H), 7.41 (d, *J* = 7.9, 2H), 7.43–7.46 (m, 2H), 7.64 (dd, *J* = 2.5, 7.0, 1H), 7.78 (m, 1H), 7.89 (m, 1H). ^{13}C NMR: 13.8, 21.2, 22.2, 28.2, 37.2, 54.1, 122.6, 123.9, 125.2, 125.4, 126.1, 126.9, 127.7, 128.7, 128.9, 130.5, 133.7, 137.1, 137.3, 142.7. IR (KBr): 3267, 3951, 3938, 3866, 1450, 1331, 1161, 1092. EIMS (*m*/*z*): 367 (M), 310 (M – C_6H_{13}), 155 (tosyl), 127, 91. Anal. Calcd. for $C_{22}H_{25}NO_2S$: C, 71.90; H, 6.86; N, 3.81. Found: C, 71.76; H, 6.75; N, 3.80.

***N*-[1-(Naphth-2-yl)pentyl]-4-toluenesulfonamide (4e):** Purified by column chromatography (hexane/EtOAc 85/15). White powder of mp 102–103 °C (EtOAc–hexane). ^{1}H NMR: 0.80 (t, *J* = 7.2, 3H), 1.11 (m, 1H), 1.21–1.31 (m, 3H), 1.78 (m, 1H), 1.84 (m, 1H), 2.16 (s, 3H), 4.43 (dt, *J* = 7.0, 7.3, 1H), 4.89 (brd, *J* = 7.0, 1H), 6.91 (d, *J* = 8.3, 2H), 7.13 (dd, *J* = 1.6, 8.6, 1H), 7.35 (brs, 1H), 7.41–7.47 (m, 4H), 7.62 (d, *J* = 8.0, 2H), 7.74 (m, 1H). ^{13}C NMR: 13.7, 21.1, 22.1, 27.9, 37.0, 58.5, 124.1, 125.8, 125.9, 126.0, 127.0, 127.5, 127.8, 128.3, 129.0, 132.6, 133.0, 137.6, 138.0, 142.8. IR (KBr): 3260, 2955,

2928, 2870, 1423, 1327, 1161, 1092. EIMS (*m*/*z*): 310 (M – C_6H_{13}), 154, 127, 91. Anal. Calcd. for $C_{22}H_{25}NO_2S$: C, 71.90; H, 6.86; N, 3.81. Found: C, 72.15; H, 7.05; N, 3.75.

The General Procedure for Addition of Alkyls to Aliphatic Imines. *N*-[1-(2-Phenylethyl)pentyl]-4-toluenesulfonamide (4f): A stirrer bar and dried $Cu(OTf)_2$ (36 mg, 0.10 mmol) were placed in a dried 10 mL round-bottom flask, which was capped with an argon balloon. CH_2Cl_2 (0.5 mL) was added to the flask and the mixture was cooled in an ice-water bath. To the mixture were added BuI (0.57 mL, 5.0 mmol), BF_3•OEt_2 (0.38 mL, 3.0 mmol), and 1.0 M solution of Me_2Zn in hexane (1.0 mL, 1.0 mmol) at the same temperature. Imine **1f** was transferred into the flask as a solution in CH_2Cl_2 (0.5 mL and 0.25 mL x 2 for wash). The argon balloon was replaced with a $CaCl_2$ drying tube and the mixture was stirred for 1 h at the same temperature. Another portion of 1.0 M solution of Me_2Zn in hexane (1.0 mL, 1.0 mmol) was added at the same temperature and the mixture was further stirred for 1 h before quenching with sat. aq. NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers was washed with brine, dried over Na_2SO_4 and concentrated. Purification of the resulting crude material by column chromatography (hexane/EtOAc 85/15) gave the titled compound (231 mg, 67%) as a white solid, whose recrystallization from hexane gave colorless prisms of mp 70.5–71 °C. ^{1}H NMR: 0.77 (t, *J* = 7.0, 3H), 1.06–1.20 (m, 4H), 1.33 (m, 1H), 1.42 (m, 1H), 1.62 (m, 1H), 1.72 (m, 1H), 2.42 (s, 3H), 2.48 (m, 1H), 2.56 (m, 1H), 3.26 (dtt, *J* = 6.6, 6.6, 6.6, 1H), 5.47 (brm, 1H), 7.03 (d, *J* = 7.0, 2H), 7.17 (t, *J* = 7.3, 1H), 7.24 (dd, *J* = 7.0, 7.3, 2H), 7.28 (d, *J* = 8.3, 2H), 7.74 (d, *J* = 8.3, 2H). ^{13}C NMR: 13.8, 21.4, 22.3, 27.2, 31.6, 34.5, 36.7, 53.7, 125.9, 127.1, 128.3, 128.4, 129.6, 138.4, 141.5, 143.2. (KBr): 3275, 2936, 2858, 1327, 1157. EIMS (*m*/*z*): 345, 288 (M – C_4H_9), 240 (M – $PhCH_2CH_2$), 174, 155, 117, 104, 91 ($PhCH_2$). Anal. Calcd. for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.39; H, 7.90; N, 4.03.

***N*-[1-Cyclohexylpentyl]-4-toluenesulfonamide (4g):** The 3rd portion of Me_2Zn was added and the mixture was stirred for additional 1 h before quenching. The crude material was purified by column

chromatography (hexane/EtOAc 85/15) to give a white solid, whose recrystallization from hexane gave colorless prisms of mp 90–92 °C. ^{1}H NMR: 0.75 (t, *J* = 7.2, 3H), 0.86 (m, 1H), 0.93–1.41 (m, 12H), 1.49 (brd, *J* = 12.6, 1H), 1.55–1.62 (m, 2H), 1.66–1.72 (m, 1H), 2.42 (s, 3H), 3.06 (m, 1H), 4.24 (d, *J* = 8.9, 1H), 7.28 (d, *J* = 7.6, 2H), 7.74 (d, *J* = 7.6, 2H). ^{13}C NMR: 13.7, 21.3, 22.3, 26.11, 26.14, 26.2, 27.6, 28.1, 28.7, 31.2, 41.2, 58.8, 127.0, 129.4, 138.8, 142.9. IR (KBr): 3287, 2928, 2846, 1323, 1161. EIMS (*m*/z): 324, 266, 240, 184, 155, 91. Anal. Calcd. for $C_{18}H_{29}NO_2S$: C, 66.83; H, 9.04; N, 4.33. Found: C, 66.59; H, 8.87; N, 4.36.

Cyclization of Chlorides. 2-Phenyl-1-(4-toluenesulfonyl)-piperidine (10): To a solution of chloride **5** (35 mg, 0.10 mmol) in DMF (1 mL) was added K_2CO_3 (69 mg, 0.50 mmol). The reaction mixture was stirred for 1 h at rt and diluted with EtOAc. The mixture was washed three times with water and with brine, dried over Na_2SO_4 and concentrated to give a crude mixture (32.7 mg) as colorless oil. The mixture was purified by column chromatography (hexane/EtOAc 85/15) to give the titled compound (30.3 mg, 96%) as a white solid, whose recrystallization from EtOAc–hexane gave colorless prisms of mp 138–139.5 °C. CAS [176650-38-7].

2-Phenyl-1-(4-toluenesulfonyl)-pyrrolidine (11): Purified by column chromatography (hexane/EtOAc 80/20). Colorless prisms of mp 109–109.5 °C (EtOAc–hexane). CAS [24517-59-7].

Supporting Information