Supporting Information

Highly Stereo- and Regioselective Ni-Catalyzed Homoallylation of Aldimines with Conjugated Dienes Promoted by Diethylzinc

Masanari Kimura [†], Atsuko Miyachi, Keisuke Kojima, Shuji Tanaka, and Yoshinao Tamaru*
*Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-
machi, Nagasaki 852-8521, Japan*

[†] *Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi,
Nagasaki 852-8521, Japan*

e-mail; tamaru@net.nagasaki-u.ac.jp

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel 60F254). Flash chromatography columns were packed with silica gel (FUJI SILYSIA NH, 100-200 mesh) as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents. Tetrahydrofuran was distilled from a blue solution of sodium benzophenone ketyl under N₂ immediately prior to use. Ni(acac)₂ (Aldrich), diethylzinc (1.0 M solution in hexanes) (Kanto Kagaku Kogyo, Co., Ltd.), *p*-chlorobenzaldehyde, *p*-anisidine, and *p*-bromoaniline (Tokyo Kasei Kogyo Co., Ltd.) were purchased and used without further purification. Benzylamine, benzaldehyde, *p*-tolualdehyde, furfural, and 2-

methylpropionaldehyde were purchased from Tokyo Kasei Kogyo Co., Ltd., and purified by distillation prior to use. Paraformaldehyde was dried overnight over P₂O₅ at room temperature beforehand. Isoprene, 1,3-dimethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, myrcene, 1,3-cyclohexadiene were purchased from Tokyo Kasei Kogyo Co., Ltd., and purified by distillation prior to use. 2-Trimethylsilylmethyl-1,3-butadiene was prepared according to the literature.¹

General Procedure (Table 2, run 3): Into a N₂ purged two-necked round bottom flask containing *p*-anisidine (246 mg, 2.0 mmol) and furfural (96 mg, 1.0 mmol) was added THF (2.0 mL) via a syringe. The mixture was stirred at room temperature for 20 h to form an aldimine, which was detected by TLC (hexane:ethyl acetate = 2:1, v/v, *R_f* = 0.58). A solution of Ni(acac)₂ (25.7 mg, 0.1 mmol) dissolved in THF (3.0 mL) was introduced to the aldimine solution via a cannula, and 2,3-dimethyl-1,3-butadiene (450 μL, 4 mmol) and diethylzinc (3.6 mL, 1 M hexane, 3.6 mmol) were successively added via syringe. The reaction mixture was stirred at room temperature for 30 min and monitored by means of TLC. After completion of reaction, the reaction mixture was poured into 20 mL of ice-water. The mixture was diluted with 30 mL of ether, washed with 2M HCl (25 mL), and separated. The aqueous phase was alkalified with KOH (5 g, 89 mmol) and extracted with ether (3 x 20 mL). Combined organic phase and extracts with ether were dried (K₂CO₃) and concentrated *in vacuo*, and the residue was subjected to column chromatography over silica gel (eluent; hexane:ethyl acetate = 64:1, v/v) to give **2i** in 94% yield (268 mg). *R_f*(**2i**) = 0.76 (hexane:ethyl acetate = 2:1, v/v).

5-(*p*-Anisidyl)-3-methyl-5-phenyl-1-pentene (2a): a mixture of *syn* and *anti*-**2a** in a 10:1 ratio containing a minor regioisomer **5-(*p*-anisidyl)-2-methyl-5-phenyl-1-pentene (3a)**: IR (neat) 3406 (m), 2907 (m), 1512 (s), 1238 (s), 1038 (m), 818 (s), 702 (s) cm⁻¹; ¹H NMR (400

MHz, CDCl₃) *syn-2a*: δ 1.05 (d, J = 7.0 Hz, 3 H), 1.72 – 1.78 (m, 2 H), 2.33 (dqm, J = 8.1, 7.0 Hz, 1 H), 3.68 (s, 3 H), 4.31 (m, 1 H), 4.96 (dd, J = 10.1, 1.1 Hz, 1 H), 4.98 (dd, J = 17.3, 1.1 Hz, 1H), 5.71 (ddd, J = 17.3, 10.1, 8.1 Hz, 1 H), 6.43 – 6.56 (m, 2 H), 6.62 – 6.69 (m, 2 H), 7.20 (m, 1 H), 7.26 – 7.35 (m, 4 H); ¹H NMR (400 MHz, CDCl₃) *anti-2a* and a minor regioisomer (**3a**) are partially assigned: δ 0.98 (d, J = 7.0 Hz, 3 H of *anti-2a*), 4.67 (br s, 1 H of **3a**), 4.73 (br s, 1 H of **3a**); ¹³C NMR (100 MHz, CDCl₃) *syn-2a*: δ 20.6, 34.9, 46.2, 55.7, 56.9, 113.8, 114.6, 114.8, 128.6, 141.7, 143.7, 144.8, 151.9; HRMS, calcd for C₁₉H₂₃NO: 281.1780, found m/z (relative intensity) 281.1797 (M⁺, 40), 212 (100).

5-(*p*-Anisidyl)-3-methyl-5-(*p*-tolyl)-1-pentene (2b): a mixture of *syn* and *anti-2b* in a 8:1 ratio containing a minor regioisomer **5-(*p*-anisidyl)-2-methyl-5-(*p*-tolyl)-1-pentene (3b)**: IR (neat) 3404 (m), 2925 (m), 1514 (s), 1238 (s), 1039 (m), 817 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) *syn-2b*: δ 1.05 (d, J = 6.9 Hz, 3 H), 1.50 – 1.60 (br s, 1 H), 1.64 - 1.77 (m, 2 H), 2.30 (s, 3 H), 2.32 (m, 1 H), 3.68 (s, 3 H), 4.27 (m, 1 H), 4.96 (br d, J = 11.5 Hz, 1 H), 4.97 (br d, J = 15.7 Hz, 1 H), 5.72 (ddm, J = 15.7, 11.5 Hz, 1 H), 6.42 - 6.52 (m, 2 H), 6.62 - 6.69 (m, 2 H), 7.04 - 7.14 (m, 2 H), 7.15 - 7.23 (m, 2 H); ¹H NMR (300 MHz, CDCl₃) *anti-2b* and minor regioisomer (**3b**) are partially assigned: δ 1.00 (d, J = 6.9 Hz, 3 H of *anti-2b*), 4.70 (br s, 1 H of **3b**), 4.73 (br s, 1 H of **3b**); ¹³C NMR(75 MHz, CDCl₃) *syn-2b*: δ 19.6, 20.0, 33.9, 45.2, 54.6, 55.4, 112.8, 113.4, 113.7, 125.4, 128.2, 135.2, 140.7, 142.7, 150.7; HRMS, calcd for C₂₀H₂₅NO: 295.1936, found m/z (relative intensity) 295.1896 (M⁺, 100), 267 (12).

5-(*p*-Anisidyl)-3-methyl-5-(*p*-chlorophenyl)-1-pentene (2c): a mixture of *syn* and *anti-2c* in a 7:1 ratio containing a minor regioisomer **5-(*p*-anisidyl)-2-methyl-5-(*p*-chlorophenyl)-1-pentene (3c)**: IR (neat) 3408 (m), 2908 (m), 1514 (s), 1238 (s), 1037 (m), 817 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) *syn-2c*: δ 0.95 (d, J = 7.0 Hz, 3 H), 1.50 – 1.64 (ddm, J = 8.3, 5.5

Hz, 2 H), 2.21 (dqm, $J = 7.9, 7.0$ Hz, 1 H), 3.58 (s, 3 H), 4.17 (dd, $J = 8.3, 5.5$ Hz, 1 H), 4.86 (br d, $J = 15.6$ Hz, 1 H), 4.87 (br d, $J = 9.7$ Hz, 1 H), 5.59 (ddd, $J = 15.6, 9.7, 7.9$ Hz, 1 H), 6.25 - 6.40 (m, 2 H), 6.50 - 6.60 (m, 2 H), 7.04 - 7.22 (m, 4 H); ^1H NMR (400 MHz, CDCl_3) a minor stereoisomer *anti*-**2c** and regioisomer (**3c**) are partially assigned: δ 0.78 (d, $J = 7.0$ Hz, 3H of *anti*-**2c**), 4.47 (br s, 1 H of **3c**), 4.54 (br s 1 H of **3c**); ^{13}C NMR (100 MHz, CDCl_3) *syn*-**2c**: δ 20.6, 34.9, 45.9, 55.6, 56.5, 114.0, 114.8, 127.7, 128.6, 132.3, 141.0, 143.1, 143.3, 152.2; HRMS, calcd for $\text{C}_{19}\text{H}_{22}\text{ClNO}$: 315.1390, found m/z (relative intensity) 315.1356 (M^+ , 100), 248 (70).

***syn*-5-(*p*-Anisidyl)-3-methyl-5-(2-furanyl)-1-pentene (2d)**: a mixture of *syn*-**2d** and a minor regioisomer **5-(*p*-anisidyl)-2-methyl-5-(2-furanyl)-1-pentene (3d)** in a 20:1 ratio; IR (neat) 3392 (m), 2910 (m), 1514 (s), 1240 (s), 1039 (m), 819 (s), 734 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) *syn*-**2d**: δ 1.04 (d, $J = 6.6$ Hz, 3 H), 1.80 (dm, $J = 8.1$ Hz, 1 H), 1.82 (dm, $J = 6.2$ Hz, 1 H), 2.32 (qdm, $J = 6.6, 7.6$ Hz, 1 H), 3.72 (s, 3 H), 4.44 (dd, $J = 8.1, 6.2$ Hz, 1 H), 4.96 (br d, $J = 10.2$ Hz, 1 H), 4.98 (br d, $J = 17.2$ Hz, 1 H), 5.70 (ddd, $J = 17.2, 10.2, 7.6$ Hz, 1 H), 6.12 (br d, $J = 2.8$ Hz, 1 H), 6.26 (dm, $J = 2.8$ Hz, 1 H), 6.59 (d, $J = 9.1$ Hz, 2 H), 6.72 (d, $J = 9.1$ Hz, 2 H), 7.31 (m, 1 H); ^1H NMR (400 MHz, CDCl_3) a minor regioisomer **3d** is partially assigned: δ 4.69 (br s, 1 H of **3d**), 4.75 (br s, 1 H of **3d**); ^{13}C NMR (75 MHz, CDCl_3) *syn*-**2d**: δ 20.5, 34.7, 41.9, 51.2, 55.5, 105.6, 109.9, 113.7, 114.6, 115.1, 141.2, 143.5, 152.3, 156.6; HRMS, calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$: 271.1572, found m/z (relative intensity) 271.1604 (M^+ , 61), 202 (100).

5-(*p*-Anisidyl)-3-methyl-1-pentene (2e): a mixture of **2e** and minor regioisomer **5-(*p*-anisidyl)-2-methyl-1-pentene (3e)** in a 78:1 ratio; IR (neat) 3392 (m), 2927 (m), 1514 (s), 1234 (s), 1039 (m), 817 (s) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) **2e**: δ 1.04 (d, $J = 6.6$ Hz, 3 H), 1.59 (q, $J = 7.4$ Hz, 2 H), 2.28 (qm, $J = 6.6$ Hz, 1 H), 3.07 (br t, $J = 7.4$ Hz, 2 H), 3.74 (s,

3 H), 4.96 (d, $J = 10.4$ Hz, 1 H), 4.97 (d, $J = 17.4$ Hz, 1 H), 5.72 (ddd, $J = 17.4, 10.0, 7.4$ Hz, 1 H), 6.58 (d, $J = 9.1$ Hz, 2 H), 6.77 (d, $J = 9.1$ Hz, 2 H); ^1H NMR (400 MHz, CDCl_3) minor regioisomer **3e** is partially assigned: δ 4.72 (br s, 1 H of **3e**), 4.74 (br s 1 H of **3e**); ^{13}C NMR (75 MHz, CDCl_3) **2e**: δ 20.1, 35.7, 35.9, 42.7, 55.4, 112.9, 113.8, 114.6, 142.4, 143.7, 151.7 ; HRMS, calcd for $\text{C}_{13}\text{H}_{19}\text{NO}$: 205.1467, found m/z (relative intensity) 205.1467 (M^+ , 100), 190 (5).

***syn*-5-(*p*-Anisidyl)-3-methyl-5-isopropyl-1-pentene (2f)**: a mixture of *syn*-**2f** and a minor regioisomer **5-(*p*-anisidyl)-2-methyl-5-isopropyl-1-pentene (3f)** in a 67:25 ratio: IR (neat) 3396 (s), 2957 (m), 1512 (s), 1463 (s), 1236 (s), 1041 (s), 912 (s), 818 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) *syn*-**2f**: δ 0.86 (d, $J = 7.1$ Hz, 3 H), 0.89 (d, $J = 7.1$ Hz, 3 H), 1.00 (d, $J = 6.9$ Hz, 3 H), 1.23 (dm, $J = 11.0$, 1 H), 1.40 (dm, $J = 11.0$, 1 H), 1.59 (m, 1 H), 1.87 (qm, $J = 7.1$ Hz, 1 H), 2.33 (dqm, $J = 8.3, 6.9$ Hz, 1 H), 3.19 (m, 1 H), 3.73 (s, 3 H), 4.89 (dd, $J = 15.1, 1.3$ Hz, 1 H), 4.93 (dd, $J = 10.2, 1.3$ Hz, 1 H), 5.60 (ddd, $J = 15.1, 10.2, 8.3$ Hz, 1 H), 6.42 – 6.60 (m, 2 H), 6.70 – 6.79 (m, 2 H); minor regioisomer **3f**: δ 0.90 (d, $J = 7.0$ Hz, 6 H), 1.20 – 2.20 (m, 6 H), 1.70 (s, 3 H), 3.12 (m, 1 H), 3.73 (s, 3 H), 4.65 (br s, 1 H), 4.70 (br s, 1 H), 6.40 – 6.80 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3) *syn*-**2f**: δ 17.8, 18.6, 21.6, 31.1, 35.2, 38.8, 55.8, 57.1, 113.9, 114.5, 114.9, 142.7, 144.3, 151.6; minor regioisomer **3f**: δ 18.3, 18.5, 22.6, 29.5, 31.1, 34.7, 55.8, 59.0, 110.0, 114.4, 114.9, 115.0, 144.9, 145.8; HRMS, calcd for $\text{C}_{16}\text{H}_{25}\text{NO}$: 247.1936, found m/z (relative intensity) 247.1911 (M^+ , 100), 178(11).

***syn*-5-(*p*-Anisidyl)-3-trimethylsilylmethyl-5-(2-furanyl)-1-pentene (2g)**; IR (neat) 3392 (s), 2950 (s), 1512 (s), 1240 (s), 1039 (m), 820 (m), 732 (s), 692 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.05 (s, 9 H), 0.69 (dd, $J = 8.5, 14.5$ Hz, 1 H), 0.75 (dd, $J = 5.5, 14.5$ Hz, 1 H), 1.82 (t, $J = 6.9$ Hz, 2 H), 2.45 (dddt, $J = 5.5, 8.5, 9.3, 6.9$ Hz, 1 H), 3.56 (br s, 1 H), 3.73 (s, 3 H), 4.43 (br t, $J = 6.9$ Hz, 1 H), 4.96 (dd, $J = 17.4, 1.7$ Hz, 1 H), 4.97 (dd, $J = 10.3, 1.7$ Hz, 1

H), 5.61 (ddd, $J = 17.4, 10.3, 9.3$ Hz, 1 H), 6.07 (br d, $J = 3.0$ Hz, 1 H), 6.25 (br d, $J = 3.0$ Hz, 1 H), 6.56 (d, $J = 9.0$ Hz, 2 H), 6.73 (d, $J = 9.0$ Hz, 2 H), 7.31 (br s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ -0.6, 23.5, 37.2, 44.0, 51.2, 55.5, 105.4, 109.9, 114.3, 114.6, 115.3, 141.1, 144.1, 152.3, 156.9; HRMS, calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{Si}$: 343.1968, found m/z (relative intensity) 343.1980 (M^+ , 100), 220 (6), 202 (13).

***syn*-6-(*p*-Anisidyl)-4-methyl-6-(2-furanyl)-2-pentene (2h)**: IR (neat) 3392 (s), 2932 (s), 1514 (s), 1238 (s), 1040 (m), 820 (s), 735 (s) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.00 (d, $J = 6.6$ Hz, 3 H), 1.63 (br d, $J = 5.5$ Hz, 3 H), 1.72 – 1.85 (ddm, $J = 5.9, 8.1$ Hz, 2 H), 2.28 (dm, $J = 6.6$ Hz, 1 H), 3.72 (s, 3 H), 4.41 (dd, $J = 5.9, 8.1$ Hz, 1 H), 5.27 (dm, $J = 15.4$ Hz, 1H), 5.38 (dqm, $J = 15.4, 5.5$ Hz, 1 H), 6.10 (d, $J = 3.0$ Hz, 1 H), 6.24 (br d, $J = 3.0$ Hz, 1 H), 6.56 (d, $J = 8.8$ Hz, 2 H), 6.72 (d, $J = 8.8$ Hz, 2 H), 7.30 (br s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.9, 21.1, 33.7, 42.3, 51.3, 55.6, 105.6, 110.0, 114.6, 115.2, 124.3, 136.2, 141.1, 141.2, 152.3, 156.8; ; HRMS, calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$: 285.1729, found m/z (relative intensity) 285.1712 (M^+ , 100), 216 (10), 203 (4), 202 (22).

5-(*p*-Anisidyl)-2,3-dimethyl-5-(2-furanyl)-1-pentene (2i): a mixture of *syn* and *anti* = 15:1; IR (neat) 3393 (s), 2936 (s), 1512 (s), 1443 (m), 1238 (s), 1040 (s), 820 (s), 735 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) *syn*-**2i**: δ 1.06 (d, $J = 6.9$ Hz, 3 H), 1.67 (s, 3 H), 1.73 (ddd, $J = 5.5, 8.2, 14.1$ Hz, 1 H), 2.00 (ddd, $J = 5.5, 8.2, 14.1$ Hz, 1 H), 2.38 (ddq, $J = 5.5, 8.2, 6.9$ Hz, 1 H), 3.72 (s, 3 H), 4.37 (dd, $J = 5.5, 8.2$ Hz, 1H), 4.71 (br d, $J = 1.4$ Hz, 1 H), 4.73 (br d, $J = 1.4$ Hz, 1 H), 6.10 (m, 1 H), 6.25 (m, 1 H), 6.57 (d, $J = 8.8$ Hz, 2 H), 6.72 (d, $J = 8.8$ Hz, 2 H), 7.30 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) *syn*-**2i**: δ 18.7, 19.8, 37.7, 40.4, 51.2, 55.4, 105.5, 109.9, 110.5, 114.6, 115.0, 141.2, 141.4, 149.9, 152.2, 156.8; HRMS, calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$: 285.1729, found m/z (relative intensity) 285.1752 (M^+ , 72), 216 (21), 203 (18), 202 (100).

***syn*-5-(*p*-Anisidyl)-2-methyl-3-(4-methyl-3-pentenyl)-5-(2-furanyl)-1-pentene (2j):** a mixture of *syn* and *anti* = 15:1; IR (neat) 3396 (s), 2914 (s), 1734 (s), 1512 (s), 1442 (m), 1240 (s), 1041 (s), 914 (s), 820 (s), 733 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) *syn*-**2f**: δ 1.27 – 1.44 (m, 2 H), 1.58 (s, 3 H), 1.68 (s, 3 H), 1.82 (t, *J* = 7.1 Hz, 2 H), 1.85 – 2.08 (m, 2 H), 2.24 (dm, *J* = 8.8 Hz, 1 H), 3.72 (s, 3 H), 4.43 (t, *J* = 7.1 Hz, 1 H), 4.96 (dd, *J* = 17.0, 1.9 Hz, 1 H), 5.04 (dd, *J* = 10.2, 1.9 Hz, 1 H), 5.07 (m, 1 H), 5.57 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1 H), 6.07 (m, 1 H), 6.24 (m, 1 H), 6.56 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 7.29 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) *syn*-**2f**: δ 17.6, 25.5, 25.6, 35.2, 40.3, 40.5, 50.9, 55.5, 105.3, 109.9, 114.5, 115.0, 115.7, 124.2, 131.3, 141.1, 141.3, 142.0, 152.1; HRMS, calcd for C₂₂H₂₉NO₂: 339.2198, found *m/z* (relative intensity) 339.2191 (M⁺, 62), 202 (96), 123 (100).

(*p*-Anisidyl)-(3-cyclohexenyl)-(2-furanyl)methane (2k): IR (neat) 3408 (s), 2931 (s), 1514 (s), 1463 (m), 1242 (s), 1149 (s), 1040 (s), 820 (s), 733 (s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.41 – 1.62 (m, 3 H), 1.63 – 1.73 (m, 2 H), 1.98 – 2.24 (m, 2 H), 2.73 (m, 1 H), 3.71 (s, 3 H), 4.28 (d, *J* = 5.3 Hz, 1 H), 5.68 (br d, *J* = 10.2 Hz, 1 H), 5.87 (dm, *J* = 10.2 Hz, 1 H), 6.11 (m, 1 H), 6.25 (m, 1 H), 6.54 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 7.32 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 21.7, 25.2, 26.5, 40.2, 55.7, 57.0, 106.7, 110.0, 114.6, 114.7, 126.8, 130.6, 141.3, 152.1, 155.5; HRMS, calcd for C₁₈H₂₁NO₂: 283.1572, found *m/z* (relative intensity) 283.1573 (M⁺, 17), 202 (100), 187 (4).

Reference

1. Hosomi, A.; Sakata, Y.; Sakurai, H. *Tetrahedron Lett.* **1979**, 429 - 432.

¹H NMR Spectra of Products **2**

Chem3D Presentation of X-ray structure

3,5-dinitrobenzamide derivative of **2a**

3,5-dinitrobenzamide derivative of **2d**

3,5-dinitrobenzamide derivative of **2f**

3,5-dinitrobenzamide derivative of **2i**