Intermolecular, Markovnikov Hydroamination of Vinylarenes with Alkylamines

Supporting Information

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General comments. All reactions were performed under a nitrogen atmosphere using standard Schlenk and drybox techniques. Toluene, diethyl ether, and pentane were distilled from sodium and benzophenone under nitrogen. Vinylarenes, amines, ligands, triflic acid, and nonafluorobutane sulfonic acid were purchased from commercial sources and were used without further purification. $Pd(DPPF)(OTf)_2$[1] and $Pd(DPPF)_2$[2] were synthesized by literature procedures. NMR spectra were recorded on Bruker DPX 400 and 500 MHz instruments. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

General Procedure for the Hydroamination of Vinylarenes with Alkyl Amines (Table 2). In a drybox, $Pd(O_2CCF_3)_2$ and 1,1'-Bis(diphenylphosphino)ferrocene were suspended in 0.25 mL of dioxane in a screw-capped vial. Vinylarenes (2.00 mmol) and amines (1.00 mmol) were placed into a second small vial and dissolved in 0.25 mL of 1,4-dioxane. The vials were sealed with a cap containing a PTFE septum and removed from the drybox. Triflic acid (0.20 mmol) was added to the catalyst suspension. The solution of vinylarenes and amines was then added to the catalyst suspension. The reaction mixture was stirred at 120 ˚C for 24 h. After heating, the reaction mixture was directly adsorbed onto silica gel and purified by flash column chromatography.

***N*-(1-Phenethyl)morpholine (Table 2, Entry 1).**[3] The general procedure was followed with styrene (229 μl, 2.00 mmol) and morpholine (87.2 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 144 mg (75%) of the hydroamination product: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.45 (d, *J* = 6.7 Hz, 3H), 2.35 (m, 2H), 2.47 (m, 2H), 3.29 (q, *J* = 6.7 Hz, 1H), 3.68 (t, J = 4.9 Hz, 4H), 7.23 (m, 1H), 7.31 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.8, 51.2, 65.3, 67.2, 126.9, 127.6, 128.2, 143.9.

***N*-[1-(2,4-Dimethylphenyl)ethyl]morpholine (Table 2, Entry 2).** The general procedure was followed with 2,4-dimethylstyrene (584 μl, 4.00 mmol) and morpholine (86.8 mg, 1.00 mmol). The reaction mixture was stirred at 120 ˚C for 48 h. The reaction mixture was purified by flash column chromatography (5% EtOAc in hexane) to give 111 mg (51%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (d, *J* = 6.6 Hz, 3H), 2.28 (s, 3H), 2.32 (s, 3H), 2.31-2.41 (m, 2H), 2.43-2.54 (m, 2H), 3.49 (q, *J* = 6.6 Hz, 1H), 3.60-3.74 (m, 4H), 6.94 (s, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 18.6, 19.4, 20.9, 51.3, 60.6, 67.3, 126.7, 126.7, 131.1, 135.6, 135.8, 139.5; Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.59; H, 9.70; N, 6.25.

***N*-[1-(4-Methoxyphenyl)ethyl]morpholine (Table 2, Entry 3).** The general procedure was followed with 4-methoxystyrene (266 μl, 2.00 mmol) and morpholine (87.5 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 168 mg (76%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.33 (d, *J* = 6.8 Hz, 3H), 2.29-2.39 (m, 2H), 2.40-2.52 (m, 2H), 3.26 (q, *J* = 6.8 Hz, 1H), 3.68 (t, *J* = 4.7 Hz, 4H) 3.79 (s, 3H), 6.78-6.88 (m, 2H), 7.16-7.26 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.7, 51.2, 55.1, 64.6, 67.2, 113.5, 128.6, 135.7, 158.4; Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.47; H, 8.44; N, 6.25.

***N*-[1-(2-naphthyl)ethyl]morpholine (Table 2, Entry 4).** The general procedure was followed with 2-vinylnapthalene (308 mg, 2.00 mmol) and morpholine (87.0 mg, 0.99 mmol). The reaction mixture was stirred at 100 ˚C for 24 h and was then purified by flash column chromatography (10% EtOAc in hexane) to give 190 mg (79%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.41 (d, *J* = 6.6 Hz, 3H), 2.32-2.44 (m, 2H), 2.46-2.60 (m, 2H), 3.43 (q, *J* = 6.6 Hz, 1H), 3.62-3.78 (m, 4H), 7.39-7.54 (m, 3H), 7.7 (s, 1H), 7.74-7.88 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.8, 51.4, 65.5, 67.1, 125.5, 125.7, 125.9, 126.1, 127.5, 127.6, 128.0, 132.7, 133.3, 141.6; Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.91; H, 7.77; N, 5.50.

***N*-[1-(3-Trifluoromethylphenyl)ethyl]morpholine (Table 2, Entry 5).** The general procedure was followed with 3-trifluoromethylstyrene (593 μl, 4.00 mmol) and morpholine (87.0 mg, 0.99 mmol), and 0.20 mL of 1,4-dioxane. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 132 mg (51%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.35 (d, *J* = 6.6 Hz, 3H), 2.27-2.39 (m, 2H), 2.42-2.55 (m, 2H), 3.37 (q, *J* = 6.6 Hz, 1H), 3.62-3.77 (m, 4H), 7.39-7.46 (m, 1H), 7.47-7.55 (m, 2H), 7.59 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.7, 51.2, 64.9, 67.1, 123.8 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.1 Hz), 128.8, 130.6 (q, *J* = 32.1 Hz), 130.9, 145.3; Anal. Calcd for $C_{13}H_{16}F_3NO$: C, 60.22; H, 6.22; N, 5.40. Found: C, 59.95; H, 6.34; N, 5.66.

***N*-[1-(4-Trifluoromethylphenyl)ethyl]morpholine (Table 2, Entry 6).** The general procedure was followed with 4-trifluoromethylstyrene (591 μl, 4.00 mmol), morpholine (87.1 mg, 1.00 mmol) and 0.20 mL of 1,4-dioxane. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 126 mg (48%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.34 (d, *J* = 6.8 Hz, 3H), 2.27-2.39 (m, 2H), 2.42-2.57 (m,

2H), 3.36 (q, *J* = 6.8 Hz, 1H), 3.62-3.77 (m, 4H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 19.8, 51.2, 65.0, 67.1, 124.2 (q, *J* = 272.6 Hz), 125.3 (q, *J* = 4.0 Hz), 127.8, 129.2 (q, *J* = 31.8 Hz), 148.4; Anal. Calcd for $C_{13}H_{16}F_3NO$: C, 60.22; H, 6.22; N, 5.40. Found: C, 60.38; H, 6.04; N, 5.11.

***N*-(1-Phenylethyl)-4-phenylpiperazine (Table 2, Entry 7).** The general procedure was followed with styrene (229 l, 2.00 mmol) and 4-phenylpiperazine (163 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (5% EtOAc in hexane) to give 192 mg (72%) of the hydroamination product as an oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 1.39 (d, *J* = 6.8 Hz, 3H), 2.47-2.57 (m, 2H), 2.58-2.68 (m, 2H), 3.15 (t, *J* = 5.0 Hz, 4H), 3.38 (q, *J* = 6.8 Hz, 1H), 6.78-6.86 (m, 1H), 6.87-6.93 (m, 2H), 7.17-7.28 (m, 3H), 7.27-7.37 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 20.0, 49.2, 50.6, 64.9, 115.8, 119.5, 126.9, 127.6, 128.2, 129.0, 143.9, 151.3; Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 80.93; H, 8.41; N, 10.22.

***N*-(1-Phenylethyl)-4-*t*butylcarboxypiperazine (Table 2, Entry 8).** The general procedure was followed with styrene (229 l, 2.00 mmol) and 4-*tert*-butyl carboxypiperazine (189 mg, 1.02 mmol). The reaction mixture was stirred at 110 ˚C for 24 h. The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 187 mg (63%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 1.36 (d, *J* = 6.6 Hz, 3H), 1.43 (s, 9H), 2.24-2.38 (m, 2H), 2.34-2.48 (m, 2H), 3.37 (q, *J* = 6.6 Hz, 1H), 3.37-3.43 (m, 4H), 7.20-7.28 (m, 1H), 7.27-7.33 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 19.6. 28.3, 43.6 (br), 50.2, 64.6, 79.3, 126.9, 127.5, 128.2, 143.5. 154.6.

***N*-1-(Phenylethyl)isoindoline (Table 2, Entry 9).[4]** The general procedure was followed with styrene (458 l, 4.00 mmol) and isoindoline (119 mg, 1.00 mmol). The reaction mixture was purified by flash column chromatography (2% EtOAc in hexane) to give 158 mg (71%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 1.49 (d, J = 6.5 Hz, 3H), 3.63 (q, J = 6.5 Hz, 1H), 3.75-3.84 (m, 2H), 3.89-3.98 (m, 2H), 7.16 (s, 4H), 7.24-7.31 (m, 1H), 7.32-7.38 (m, 2H), 7.28-7.44 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) 23.3, 58.0, 65.4, 122.3, 126.6, 127.1, 127.2, 128.5, 140.1, 145.2.

***N*-1-(Phenylethyl)tetrahydroisoquinoline (Table 2, Entry 10).** The general procedure was followed with styrene (229 l, 2.00 mmol) and 1,2,3,4-tetrahydroisoquinoline (136 mg, 1.02 mmol). The reaction mixture was purified by flash column chromatography (2% EtOAc in

hexane) to give 139 mg (58%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.47 (d, J = 6.8 Hz, 3H), 2.54-2.66 (m, 1H), 2.71-2.94 (m, 3H), 3.55 (q, J = 6.8 Hz, 1H), 3.56 (d, J =14.6 Hz, 1H), 3.82 (d, J = 15.1 Hz, 1H), 6.95-7.02 (m, 1H), 7.03-7.14 (m, 3H), 7.22-7.28 (m, 1H), 7.29-7.36 (m, 2H), 7.35-7.41 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 20.2, 29.3, 48.0, 53.6, 64.4, 125.5, 126.0, 126.8, 126.9, 127.5, 128.3, 128.6, 134.6, 135.1, 144.2; Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.81; H, 8.13; N, 5.79.

***N*-[1-(2-Naphthyl)ethyl]piperidine (Table 2, Entry 11).** The general procedure was followed with vinylnaphthalene (308 mg, 2.00 mmol) and piperidine (84.5 mg, 0.992 mmol). The reaction mixture was stirred at 110 ˚C for 24 h. The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 124 mg (52%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.33-1.42 (m 2H), 1.43 (d, J = 6.6 Hz, 3H), 1.49-1.59 (m, 4H), 2.26-2.43 (m, 2H), 2.36-2.52 (m, 2H), 3.52 (q, J = 6.6 Hz, 1H), 7.28-7.48 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.79 (t, J = 7.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 19.4, 24.6, 26.2, 51.7, 65.3, 125.3, 125.7, 126.1, 126.2, 127.5, 127.6, 127.7, 132.6, 133.2, 141.8; Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85. Found: C, 85.62; H, 8.65; N, 5.64.

***N*-[1-(2-naphthyl)ethyl]benzylmethylamine (Table 2, Entry 12).** The general procedure was followed with 2-vinylnaphtalene (308 mg, 2.00 mmol) and *N*-benzyl methylamine (122 mg, 1.00 mmol). The reaction mixture was stirred at 80 ˚C for 24 h. The reaction mixture was purified by flash column chromatography (4% EtOAc in hexane) to give 175 mg (63%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.49 (d, J = 6.7 Hz, 3H), 2.16 (s, 3H), 3.34 (d, J = 13.6 Hz, 1H), 3.59 (d, J = 13.6 Hz, 1H), 3.77 (q, J = 6.7 Hz, 1H), 7.15-7.23 (m, 1H), 7.24-7.34 (m, 4H), 7.37-7.46 (m, 2H), 7.58-7.66 (m, 1H), 7.74-7.84 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 18.2, 38.4, 58.9, 63.3, 125.4, 125.8, 125.9, 126.2, 126.7, 127.6, 127.8, 127.8, 128.1, 128.7, 132.7, 133.3, 139.9, 142.0; Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.08; H, 7.92; N, 5.04.

***N*-[1-(4-Methylphenyl)ethyl]benzylmethylamine (Table 2, Entry 13).** The general procedure was followed with 4-methylstyrene (527 μl, 4.00 mmol), *N*-methyl benzylamine (121 mg, 1.00 mmol) and 0.20 mL of 1,4-dioxane. The reaction mixture was stirred at 110 ˚C for 24 h. The reaction mixture was purified by flash column chromatography (10% EtOAc in hexane) to give 129 mg of a mixture of the hydroamination product and dibenzylmethylamine consisting of a 4.3:1 ratio of the hydroamination product to dibenzylmethylamine, as determined by ^{1}H

NMR spectroscopy. These quantities corresponded to a 43% yield of the hydroamination product. *N*-[1-(4-methylphenyl)ethyl]benzylmethylamine was difficult to separate from dibenzylmethylamine in high yield, but 43.1 mg (18%) of a pure sample of *N*-[1-(4-methylphenyl)ethyl]benzylmethylamine was isolated from the reaction mixture by selectively combining fractions collected by flash column chromatography (2% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) □ 1.41 (d, *J* = 6.9 Hz, 3H), 2.12 (s, 3H), 2.34 (s, 3H), 3.27 (d, *J* = 12.9 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H), 3.61 (q, *J* = 6.8 Hz, 1H), 7.15 (d, *J* = 7.8Hz, 2H), 7.18-7.36 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) □ 18.5, 21.1, 38.3, 58.7, 62.9, 126.7, 127.6, 128.1, 128.2, 128.7, 128.8, 128.9, 136.3; Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85. Found: C, 85.39; H, 8.80; N, 5.57.

***N*-[1-(2-naphthyl)ethyl]hexylmethylamine (Table 2, Entry 14).** The general procedure was followed with 2-vinylnaphtalene (308 mg, 2.00 mmol) and *N*-hexyl methylamine (116 mg, 1.01 mmol). The reaction mixture was stirred at 110 ˚C for 18 h and was then purified by flash column chromatography (2% EtOAc in hexane) to give 144 mg (53%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) □ 0.84 (t, J = 6.8 Hz, 3H), 1.17-1.27 (m, 6H), 1.39-1.52 (m, 2H), 1.42 (d, J = 6.7 Hz, 3H), 2.22 (s, 3H), 2.27-2.34 (m, 1H), 2.37-2.48 (m, 1H), 3.68 (q, J = 6.5 Hz, 1H), 7.37-7.48 (m, 2H), 7.49-7.55 (m, 1H), 7.70 (s, 1H), 7.74-7.84 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) □ 14.1, 18.6, 22.6, 27.1, 27.1, 31.8, 38.7, 54.5, 63.5, 125.3, 125.7, 125.9, 126.3, 127.5, 127.7, 127.7, 132.6, 133.3, 142.1; Anal. Calcd for $C_{19}H_{27}N$: C, 84.70; H, 10.10; N, 5.20. Found: C, 84.58; H, 9.96; N, 5.33.

Synthesis of {[DPPF]Pd[1-(4-methylphenyl)ethyl]}triflate (1). In a dry box, $Pd(DPPF)(OTf)_2$ (143 mg, 0.15 mmol) was suspended in 3.0 mL of toluene in a screw-capped vial. 4-Methylstyrene (295 □l, 2.24 mmol) and 4-trifluoromethylaniline (188 □l, 1.50 mmol) were added to the suspension. The vial was sealed with a cap containing a PTFE septum and removed from the dry box. The suspension was stirred at 80 ˚C for 12 h. After heating, the reaction mixture was added to 20 mL of pentane while stirring in a dry box, and an orange precipitate was obtained by filtration. The crude product was washed repeatedly with pentane and diethyl ether, and was recrystallized from toluene at -30 °C. Complex **1** was obtained as an orange solid (29.1 mg, 0.031 mmol) in 21% yield. ^{1}H NMR (400 MHz, acetone-d_6, TMS) □ 0.90 (ddd, *J* = 12.6, 11.3, 6.8 Hz, 3H), 1.87 (dd, *J* = 4.4, 2.3 Hz, 3H), 3.67-3.72 (m, 1H), 3.83-3.88 (m, 1H), 4.85 (br q, *J* = 11.3 Hz, 1H), 4.35-4.42 (m, 2H), 4.63-4.67 (m, 1H), 4.67-4.72 (m, 1H),

4.73-4.78 (m, 1H), 4.83-4.87 (m, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 7.06-7.21 (m, 5H), 7.36-7.51 (m, 4H), 7.51-7.75 (m, 14H); ^{31}P NMR (121.6 MHz, d^6-acetone) 32.4 (d, *J* = 51.3 Hz), 21.9 (d, *J* = 51.3 Hz); Anal. Calcd for $C_{44}H_{39}F_3FeO_3P_2PdS$: C, 56.88; H, 4.23. Found: C, 57.13; H, 4.21.

***N*-[1-(4-Methylphenyl)ethyl]morpholine (equation 2).** An authentic sample of the organic product from eq. 2 was synthesised according to the general procedure used to prepare the products in Table 2. The general procedure was followed with 4-methylstyrene (264 l, 2.00 mmol) and morpholine (87.3 mg, 1.00 mmol). The reaction mixture was stirred at 110 ˚C for 24 h. The reaction mixture was purified by flash column chromatography (20% EtOAc in hexane) to give 159 mg (77%) of the hydroamination product. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) 1.34 (d, *J* = 6.8 Hz, 3H), 2.33 (s, 3H), 2.35 (m, 2H), 2.47 (m, 2H), 3.26 (q, *J* = 6.8 Hz, 1H), 3.68 (t, *J* = 4.7 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 19.8, 21.0, 51.2, 65.0, 67.2, 127.5, 128.9, 136.5, 140.7; Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.85; H, 9.56; N, 7.03.

Reaction of complex 1 with morpholine in the presence of styrene. In a dry box, complex **1** (18.6 mg, 20 mol), styrene (4.6 l, 40 mol), morpholine (3.5 l, 40 mol) and dodecane (7.1 mg, 42 mol) as internal standard were suspended in 0.20 mL of dioxane in a screw-capped vial. The vial was sealed with a cap containing a PTFE septum and removed from the dry box. The reaction mixture was stirred at 110 ˚C, and the formation of product was monitored by GC analysis. The data are summarised in Table 1.

Table 1. Product distribution from the reaction of complex **1** with morpholine in the presence of styrene.

Time / min	N-[1-(4-methylphenyl)ethyl]morpholine x 10^2 M	N-1-(phenethyl)morpholine x 10^2 M
1	1.1	0.0
5	1.1	0.4
10	1.5	0.9
15	1.6	1.2
20	1.6	1.4

Enantioselective hydroaminaton (eq. 3). In a dry box, $Pd(O_2CCF_3)_2$ (35.4 mg, 0.080 mmol) and R, R-Et-FerroTANE (35.4 mg, 0.080 mmol) were suspended in 0.10 mL of dioxane in a screw-capped vial. 2-Vinylnaphthalene (493 mg, 3.20 mmol) and *N*-benzylmethylamine (97.8 mg, 0.81 mmol) were added to into another small vial and dissolved in 0.20 mL of 1,4-dioxane. The vials were sealed with a cap containing a PTFE septum and removed from the dry

box. Triflic acid (35.5 μl, 0.40 mmol) was added to the catalyst suspension, followed by the solution of vinylarenes and amines. The reaction mixture was stirred at 50 ˚C for 48 h. After heating, the reaction mixture was purified by flash column chromatography (2% EtOAc in hexane) to give 80.0 mg (36%) of the hydroamination product. The enantiomeric excess was determined to be 63% by HPLC analysis with a Daicel CHIRALCEL OJ column (hexanes/*i*-propanol = 99.5/0.5).

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