Supporting Information for:

Rhodium-Catalyzed 1,4-Addition of Arylboronic Acids to α,β -Unsaturated Carbonyl Compounds: Large Accelerating Effects of Bases and Ligands

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All reactions were carried out under nitrogen. HPLC analyses were carried out using a chiral stationary phase column; Chiralpak AD, Chiralcel OD-H, or OB-H purchased from Dacel Co., Ltd.

Materials and Reagents: $[\text{RhCl}(\text{cod})]_2$ is commercially available. $[\text{Rh}(\text{cod})_2]\text{BF}_4$,¹ $[\text{Rh}(\text{cod})(\text{MeCN})_2]\text{BF}_4$,² $\text{Rh}(\text{acac})(\text{cod})$,³ $\text{Rh}(\text{acac})(\text{coe})_2$,⁴ and $[\text{RhOH}(\text{cod})]_2$ ⁵ were synthesized by the reported procedures. $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{Ph}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ (dppe), $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dppp), $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb), dppf (1,1'-bis(diphenylphosphino)ferrocene), and (*R*)-binap ((*R*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl) were available from Aldrich. The syntheses of DPFphos (2-(diphenylphosphino)phenyl)ether), Xantphos (9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene), DBEphos (1,8-bis(diphenylphosphino)dibenzofuran) were reported.⁶ Phenylboronic acid, (4-methylphenyl)boronic acid, (4-methoxyphenyl)boronic acid, (3-methoxyphenyl)boronic acid, and (3-chlorophenyl)boronic acid were commercially available from Lancaster or can be synthesized from the corresponding Grignard or lithium reagents and trimethoxyborate or triisopropoxyborate.⁷

Synthesis of $[\text{Rh}((\text{R})\text{-binap})(\text{nbd})]\text{BF}_4$.⁸ In a 25 mL-flask containing a magnetic stirring bar were placed $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (169 mg, 0.452 mmol) and (*R*)-BINAP (310 mg, 0.498 mmol) under argon. CH_2Cl_2 (10 mL) was added and the mixture was then stirred at room temperature for 3 h. THF (10 mL) was slowly added to the resulting orange-red solution which was then allowed to stand in a freezer for 1 day. After being evaporated the solvent, the orange crystal was collected by filtration, washed with THF and ether, and dried. 348 mg (85%); ³¹P NMR (CDCl_3) δ 26.31 (d, $J_{\text{Rh-P}} = 154.1$ Hz); anal. calcd for $\text{C}_{51}\text{H}_{40}\text{BF}_4\text{P}_2\text{Rh}$: C, 67.72; H, 4.46. found C, 66.79; H, 4.66.

General procedure for Table 1. Rhodium complex (0.03 mmol for Rh), a ligand (0–0.09 mmol), and (4-methylphenyl)boronic acid (1.5 mmol) were added to a 25 mL-flask

containing a magnetic stirring bar, a septum inlet. The flask was flashed with argon and charged with 1,4-dioxane/H₂O (6/1, 3 mL). After being stirred for 30 min, 2-cyclohexenone (1.0 mmol) was added. The mixture was then stirred for 6 h at the temperature shown in Table 1. Yields of products were analyzed by GC using pentadecane as an internal standard.

General procedure for Table 2. [RhCl(cod)]₂ (0.000002-0.01 mmol), and (4-methylphenyl)boronic acid (1.5 mmol) were added to a sealed tube containing a magnetic stirring bar. The flask was flashed with argon and charged with 1,4-dioxane/H₂O (6/1, 3 mL). Aqueous NaHCO₃ (0.01 mmol) and 2-cyclohexenone (1.0 mmol) were then added. The resulting mixture was stirred for 16-36 h at the temperature shown in Table 2. Chromatography over silica gel gave the desired product.

Effect of Bases (Figure 1). Rhodium complex (0.03 mmol) and (4-methylphenyl)boronic acid (1.5 mmol) were added to a 10 mL-tube containing a magnetic stirring bar, a septum inlet. The tube was flashed with argon and charged with aqueous DME (6/1, 3 mL) at 5 °C. Aqueous KOH (1.0 mmol) and 2-cyclohexenone (1.0 mmol) were then added. The mixture was stirred for 1-3 h at 5 °C. The reaction was quenched with 1N HCl for 0.5 h. The product was extracted with benzene, washed with water and brine, and dried over anhydrous magnesium sulfate. Isolated yields by chromatography.

General procedure for Table 3. Rhodium complex (0.03 mmol) and (4-methylphenyl)boronic acid (1.5 mmol) were added to a 25 mL-flask. The flask was flashed with argon and charged with aqueous 1,4-dioxane or aqueous DME (6/1, 3 mL). A base (0.1-1.0 mmol) and α,β -unsaturated carbonyl compound (1.0 mmol) were added. The mixture was then stirred for 6 or 16 h at 0-90 °C. Chromatography over silica gel gave the desired product.

The above procedure gave the following compounds shown in Table 3.

4-(4-Methylphenyl)-4-phenyl-2-butanone (3a, entries 1 and 2). IR (nujol) 1723, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 2.07 (s, 3H), 2.28 (s, 3H), 3.16 (d, J = 7.6 Hz, 2H), 4.54 (t, J = 7.6 Hz, 1H), 7.06-7.28 (m, 9H); ¹³C NMR (CDCl₃) δ 20.94, 30.63, 45.64, 49.71, 126.34, 127.51, 127.60, 128.54, 129.24, 135.95, 140.78, 144.04, 207.04; MS (m/z) 77 (20), 91 (11), 103 (28), 115 (7), 131 (32), 166 (26), 181 (100), 194 (34), 254 (19, M⁺); exact mass calcd for C₁₇H₁₈O₂: 254.1307; found 254.1301.

1,3-Diphenyl-3-(4-methylphenyl)propan-1-one (3b, entry 3). IR (nujol) 1678, 822 cm⁻¹; ¹H NMR (CDCl₃) δ 2.28 (s, 3H), 3.72 (d, J = 7.3 Hz, 2H), 4.79 (t, J = 7.3 Hz, 1H), 7.06-7.08 (m, 2H), 7.17-7.79 (m, 3H), 7.23-7.26 (m, 4H), 7.41-7.45 (m, 2H), 7.52-7.55 (m, 1H), 7.92-7.94 (m, 2H); ¹³C NMR (CDCl₃) δ 20.95, 44.77, 45.52, 126.26, 127.65, 127.75, 128.03, 128.51, 128.55, 129.23, 133.00, 135.85, 137.06, 141.11, 144.36, 198.04; MS (m/z) 77 (36), 91

(6), 105 (98), 117 (10), 165 (27), 181 (100), 195 (23), 300 (35, M⁺); exact mass calcd for C₂₂H₂₀O: 300.1514; found 300.1517.

4-(4-Methylphenyl)-4-(2,6,6-trimethyl-1-cyclohexenyl)-2-butanone (3c, entries 4-6). IR (neat) 1716, 810 cm⁻¹; ¹H NMR (CDCl₃) δ 1.03 (s, 3H), 1.06 (s, 3H), 1.28 (s, 3H), 1.44-1.70 (m, 4H), 1.88-1.99 (m, 2H), 2.24 (s, 3H), 2.28 (s, 3H), 2.79 (dd, *J* = 18.6 and 2.2 Hz), 3.29 (dd, *J* = 18.6 and 8.5 Hz), 4.32 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H); ¹³C NMR (CDCl₃) δ 19.44, 20.83, 22.36, 28.16, 28.45, 30.06, 33.59, 36.07, 36.44, 39.97, 51.78, 126.77, 128.68, 130.21, 134.46, 140.85, 142.09, 207.53; MS (*m/z*) 81 (20), 91 (27), 105 (40), 123 (45), 143 (20), 157 (41), 199 (17), 211 (54), 226 (38), 241 (13), 251 (13), 266 (18), 284 (36, M⁺); exact mass calcd for C₂₆H₂₈O: 284.2140; found 284.2132.

3-(4-Methylphenyl)cyclohexanone (3d, entries 7 and 8). IR (nujol) 1718, 806 cm⁻¹; ¹H NMR (CDCl₃) δ 1.70-1.88 (m, 2H), 2.01-2.19 (m, 2H), 2.33 (s, 3H), 2.36-2.60 (m, 4H), 2.97 (tt, *J* = 11.6 and 4.0 Hz, 1H), 7.10-7.15 (m, 4H); ¹³C NMR (CDCl₃) δ 20.93, 25.50, 32.84, 41.14, 44.34, 49.02, 126.38, 129.28, 136.19, 141.36, 211.22; MS (*m/z*) 77 (9), 83 (10), 94 (38), 105 (19), 118 (39), 131 (100), 145 (26), 173 (5), 188 (57, M⁺); exact mass calcd for C₁₃H₁₆O: 188.1201; found 188.1201.

Methyl 3-(4-methylphenyl)butanoate (3f, entries 10 and 11). IR (neat) 1736, 1266, 1163, 815 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (d, *J* = 6.9 Hz, 3H), 2.31 (s, 3H), 2.53 (dd, *J* = 15.1 and 8.2 Hz, 1H), 2.591 (dd, *J* = 15.1 and 7.1 Hz, 1H), 3.24 (ddq, *J* = 8.2, 7.1 and 6.9 Hz, 1H), 3.62 (s, 3H), 7.11 (s, 4H); ¹³C NMR (CDCl₃) δ 20.98, 21.85, 35.99, 42.79, 51.48, 126.54, 129.16, 135.87, 142.68, 172.92; MS (*m/z*) 77 (6), 91 (18), 105 (7), 132 (35), 192 (23, M⁺); exact mass calcd for C₁₂H₁₆O₂: 192.1150; found 192.1143.

Methyl 3-(4-methylphenyl)-3-phenylpropionate (3g, entry 12). IR (nujol) 1747, 1254, 1158, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 2.33 (s, 3H), 3.04 (d, *J* = 8.1 Hz, 2H), 3.57 (s, 3H), 4.52 (t, *J* = 8.1 Hz, 1H), 7.07-7.28 (m, 9H); ¹³C NMR (CDCl₃) δ 20.94, 40.57, 46.53, 51.60, 126.41, 127.44, 127.54, 128.50, 129.22, 136.01, 140.44, 143.67, 172.29; MS (*m/z*) 77 (20), 91 (11), 103 (28), 115 (7), 131 (32), 166 (26), 151 (100), 194 (34), 254 (19, M⁺); exact mass calcd for C₁₇H₁₈O₂: 254.1307; found 254.1301.

Diethyl 2-(1-4'-methylphenyl-ethyl)malonate (3h, entries 13 and 14). IR (neat) 1731, 1751, 1175, 817 cm⁻¹; ¹H NMR (CDCl₃) δ 1.00 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.8 Hz, 3H), 2.30 (s, 3H), 3.45-3.53 (m, 1H), 3.57 (d, *J* = 10.7 Hz, 1H), 3.88-3.94 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 7.07-7.13 (m, 4H); ¹³C NMR (CDCl₃) δ 13.75, 14.10, 20.29, 21.00, 39.62, 59.38, 61.07, 61.41, 127.27, 129.05, 136.29, 140.11, 168.01, 168.51; MS (*m/z*) 77 (3), 91 (14), 105 (3), 119 (100), 132 (14), 145 (6), 159 (34), 175 (4), 187 (12), 204

(64), 233 (5), 278 (28, M^+); exact mass calcd for $C_{16}H_{22}O_4$: 278.1518; found 278.1522.

General procedure for Table 4. $[Rh((R)\text{-binap})(nbd)]BF_4$ (0.03 mmol) and phenylboronic acid (1.5 mmol) were added to a 25 mL-flask containing a magnetic stirring bar and a septum inlet. The flask was flashed with argon and charged with aqueous 1,4-dioxane or aqueous DME (6/1, 3 mL). A base (0.1-1.5) and 2-cyclohexenone (1.0 mmol) were added. The mixture was stirred for 6 h at 25 °C. Benzene, brine and 1N HCl were added and the resulting mixture was stirred at room temperature. The product was extracted with benzene, washed with water and brine, and dried over anhydrous magnesium sulfate. Chromatography over silica gel gave the desired product. The enantiomer excess was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD) with hexane/2-propanol = 98/2.

General procedure for Table 5. $[Rh((R)\text{-binap})(nbd)]BF_4$ (0.03 mmol) and arylboronic acid (1.5 mmol) were added to the 25 mL-flask containing a magnetic stirring bar, a septum inlet. The flask was flashed with argon and charged with aqueous 1,4-dioxane (6/1, 3 mL). Triethylamine (1.0 mmol) and α,β -unsaturated carbonyl compound (1.0 mmol) were then added. The mixture was stirred for 6 h at 25 °C. Benzene, brine and 1N HCl were added at room temperature. Chromatography over silica gel gave the desired product.

The above procedure gave the following compounds shown in Table 5.

(*R*)-3-Phenylcyclohexanone (5a, entry 1). $[\alpha]_D^{20} +21.4$ (c 0.95, $CHCl_3$); IR (neat) 1708, 700 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.72-1.91 (m, 2H), 2.05-2.19 (m, 2H), 2.34-2.63 (m, 4H), 3.01 (tt, $J = 11.7$ and 4.0 Hz, 1H), 7.22-7.26 (m, 3H), 7.32-7.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.52, 32.75, 41.17, 44.73, 48.93, 126.54, 126.67, 128.66, 144.31, 211.09; MS (m/z) 77 (13), 83 (14), 91 (26), 96 (3), 104 (60), 117 (88), 131 (68), 146 (6), 156 (1), 174 (100, M^+); exact mass calcd for $C_{12}H_{14}O$: 174.1045; found 174.1042.

3-(3-Methoxyphenyl)cyclohexanone (5b, entry 2). $[\alpha]_D^{20} +12.7$ (c 0.91, $CHCl_3$); IR (neat) 1708, 1600, 1261, 780, 697 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.71-1.90 (m, 2H), 2.07-2.18 (m, 2H), 2.34-2.62 (m, 4H), 2.98 (tt, $J = 11.8$ and 3.9 Hz, 1H), 3.81 (s, 3H), 6.76-6.83 (m, 3H), 7.23-7.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.52, 32.68, 41.19, 44.76, 48.93, 55.19, 111.62, 112.69, 118.89, 129.67, 146.02, 159.81, 211.03; MS (m/z) 77 (14), 83 (11), 91 (31), 96 (8), 105 (12), 108 (6), 115 (10), 121 (28), 134 (57), 147 (45), 163 (38), 175 (5), 186 (2), 204 (100, M^+); exact mass calcd for $C_{13}H_{16}O_2$: 204.1150; found 204.1154.

3-(3-Chlorophenyl)cyclohexanone (5c, entry 3). $[\alpha]_D^{20} +11.6$ (c 1.13, $CHCl_3$); IR (neat) 1708, 782, 693 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.72-1.89 (m, 2H), 2.05-2.19 (m, 2H), 2.34-2.61 (m, 4H), 2.95-3.03 (m, 1H), 7.01-7.11 (m, 1H), 7.21-7.28 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.38, 32.55, 41.07, 44.36, 48.63, 124.85, 126.78, 126.87, 129.96, 134.46, 146.27, 210.39; MS (m/z)

77 (12), 83 (16), 91 (6), 103 (24), 115 (18), 125 (13), 138 (46), 145 (17), 151 (35), 165 (98), 173 (6), 179 (2), 208 (100, M^+); exact mass calcd for $C_{12}H_{13}OCl$: 208.0655; found 208.0653.

3-(4-Methoxyphenyl)cyclohexanone (5d, entry 4). $[\alpha]_D^{20} +17.2$ (c 0.96, $CHCl_3$); IR (nujol) 1702, 1611, 829 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.70-1.87 (m, 2H), 2.01-2.20 (m, 2H), 2.33-2.60 (m, 4H), 2.97 (tt, $J = 11.8$ and 3.9 Hz, 1H) 3.80 (s, 3H), 6.87 (dt, $J = 8.7$ and 2.5 Hz, 2H), 7.14 (dt, 2H, $J = 8.7$ and 2.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 25.47, 32.97, 41.15, 43.94, 49.22, 55.24, 113.96, 127.46, 136.53, 158.21, 211.25; MS (m/z) 77 (11), 91 (29), 103 (5), 115 (7), 121 (18), 134 (33), 147 (100), 161 (20), 173 (2), 204 (46, M^+); exact mass calcd for $C_{13}H_{16}O_2$: 204.1150; found 204.1154.

3-(3-Chlorophenyl)cyclopentanone (5e, entry 5). $[\alpha]_D^{20} +75.3$ (c 0.96, $CHCl_3$); IR (neat) 1739, 1135, 784, 690 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.92-2.03 (m, 1H), 2.26-2.36 (m, 2H), 2.41-2.51 (m, 2H), 2.64-2.71 (m, 1H), 3.40 (tt, $J = 11.0$ and 6.8 Hz, 1H), 7.13-7.15 (m, 1H), 7.22-7.30 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 30.95, 38.73, 41.86, 45.52, 124.90, 126.90, 126.98, 129.93, 134.48, 145.06, 217.62; MS (m/z) 77 (12), 91 (5), 103 (24), 117 (47), 125 (8), 131 (7), 138 (82), 152 (26), 159 (5), 165 (16), 179 (2), 194 (100, M^+); exact mass calcd for $C_{11}H_{11}OCl$: 194.0498; found 194.0499.

4-Phenyl-2-nonanone (5f, entry 6). $[\alpha]_D^{20} +17.6$ (c 1.27, $CHCl_3$); IR (neat) 1715, 699 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.62 (t, $J = 6.7$ Hz, 1H), 0.87-1.04 (m, 6H), 1.29-1.44 (m, 2H), 1.81 (s, 3H), 2.48 (dd, $J = 16.1$ and 7.1 Hz, 1H), 2.53 (dd, $J = 16.1$ and 7.3 Hz, 1H), 2.87-2.94 (m, 1H), 6.96-7.00 (m, 3H), 7.06-7.10 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.46, 27.02, 30.62, 31.71, 36.42, 41.32, 50.95, 126.28, 127.45, 128.43, 144.62, 208.02; MS (m/z) 77 (6), 91 (61), 104 (55), 117 (29), 129 (8), 147 (66), 160 (100), 203 (1), 218 (7, M^+); exact mass calcd for $C_{15}H_{22}O$: 218.1671; found 218.1674.

4-(3-Methoxyphenyl)-2-nonanone (5g, entry 7). $[\alpha]_D^{20} +15.9$ (c 1.27, $CHCl_3$); IR (neat) 1714, 1599, 1584, 780, 700 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.83 (t, $J = 6.8$ Hz, 3H), 1.10-1.24 (m, 6H), 1.48-1.60 (m, 2H), 2.03 (s, 3H), 2.67 (dd, $J = 16.1$ and 7.1 Hz, 1H), 2.72 (dd, $J = 16.1$ and 7.3 Hz, 1H), 3.04-3.12 (m, 1H), 3.80 (s, 3H), 6.72-6.78 (m, 3H), 7.20 (t, $J = 7.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.47, 27.03, 30.67, 31.72, 36.33, 41.30, 50.87, 55.11, 111.18, 113.46, 119.85, 129.37, 146.35, 159.58, 208.07; MS (m/z) 77 (8), 91 (17), 109 (25), 121 (84), 135 (84), 147 (19), 161 (8), 177 (63), 190 (63), 205 (98), 214 (3), 233 (2), 248 (100, M^+); exact mass calcd for $C_{16}H_{24}O_2$: 248.1776; found 248.1776.

5-Methyl-4-phenyl-2-hexanone (5h, entry 8). $[\alpha]_D^{20} +33.7$ (c 1.12, $CHCl_3$); IR (neat) 1711, 701 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.74 (d, $J = 6.8$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 1.83 (octet, $J = 6.8$ Hz, 1H), 1.98 (s, 3H), 2.74-2.85 (m, 2H), 2.89-2.94 (m, 1H), 7.13-7.20 (m, 3H).

7.25-7.29 (m, 2H); ^{13}C NMR (CDCl_3) δ 20.31, 20.70, 30.59, 33.27, 47.63, 48.04, 126.24, 128.14, 128.21, 143.21, 208.46; MS (m/z) 77 (8), 91 (25), 105 (22), 117 (11), 132 (100), 147 (15), 190 (2, M^+); exact mass calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: 190.1358; found 190.1654.

4-(3-Methoxyphenyl)-5-methyl-2-hexanone (5i, entry 9). $[\alpha]_{\text{D}}^{20} +27.8$ (c 1.14, CHCl_3); IR (neat) 1711, 1583, 779, 701 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.75 (d, $J = 6.8$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 2H), 1.81 (octet, $J = 6.8$ Hz, 1H), 1.99 (s, 3H), 2.73-2.81 (m, 2H), 2.86-2.91 (m, 1H), 3.79 (s, 3H), 6.68-6.75 (m, 3H), 7.19 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 20.41, 20.69, 30.62, 33.27, 47.59, 48.06, 55.08, 111.10, 114.31, 120.65, 129.06, 145.05, 159.35, 208.40; MS (m/z) 77 (7), 91 (11), 105 (7), 121 (16), 135 (60), 147 (7), 162 (72), 177 (24), 205 (1), 220 (37, M^+); exact mass calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: 220.1463; found 220.1467.

3-(3-Methoxyphenyl)butanal (5j, entry 10). $[\alpha]_{\text{D}}^{20}$ 27.63 (c 1.01, CHCl_3). The enantioselectivity was analyzed by OD-H (hexane/2-propanol=98/2) after conversion into the corresponding alcohol; IR (neat) 2835, 2724, 1721, 781, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.31 (d, $J = 6.83$ Hz, 3H), 2.65 (ddd, $J = 16.7, 7.7$ and 2.0 Hz, 1H), 2.75 (ddd, $J = 16.7, 6.8$ and 2.0 Hz, 1H), 3.34 (sextet, $J = 7.1$ Hz, 2H), 3.80 (s, 3H), 6.74-6.83 (m, 3H), 7.23 (dt, $J = 7.5$ and 1.3 Hz, 1H), 9.71 (t, $J = 2.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 22.08, 34.29, 51.62, 55.14, 111.41, 112.84, 119.07, 129.66, 147.13, 159.76, 201.86; MS (m/z) 77 (27), 91 (34), 105 (45), 109 (14), 121 (70), 135 (100), 150 (76), 178 (94, M^+); exact mass calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: 178.0994; found 178.1005.

3-Phenylhexanal (5k, entry 11). $[\alpha]_{\text{D}}^{20}$ 13.3 (c 1.02, CHCl_3). The enantioselectivity was analyzed by OD-H (hexane/2-propanol=98/2) after conversion into the corresponding alcohol; IR (neat) 2720, 1722, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86 (t, $J = 7.3$ Hz, 3H), 1.19 (m, 2H), 1.62 (m, 2H), 2.69 (ddd, $J = 6.6, 7.2$ and 2.1 Hz, 1H), 2.73 (ddd, $J = 16.6, 7.4$ and 2.1 Hz, 1H), 3.18 (quintet, $J = 7.4$ Hz, 1H), 7.17-7.23 (m, 3H), 7.28-7.32 (m, 2H), 9.66 (t, $J = 2.1$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.91, 20.41, 38.76, 39.82, 50.57, 126.53, 127.44, 128.58, 143.89, 202.13; MS (m/z) 77 (19), 91 (97), 105 (75), 117 (11), 133 (100), 176 (50, M^+); exact mass calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: 176.1201; found 176.1207.

The synthesis and analysis of isopropyl 3-(4-methoxyphenyl)butanoate (**5l**, entry 12)⁹ and N-benzyl 3-phenylbutanamide (**5m**, entry 13)¹⁰ were previously reported.

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