A New Type of Catalytic Tandem 1,4-Addition-Aldol Reaction Which Proceeds through an (Oxa- π -allyl)rhodium Intermediate

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Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform-*d* (δ 77.05) for ^{13}C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. DMF was dried over P_2O_5 , distilled under nitrogen, and stored in a glass flask with a Teflon stopcock under nitrogen. Rhodium complexes, $[\text{Rh}(\text{OMe})(\text{cod})]_2$,¹ $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$,² $[\text{RhCl}(\text{cod})]_2$,³ and $[\text{Rh}(\text{OH})((S)\text{-binap})]_2$ ⁴ were prepared according to the reported procedures. *tert*-Butyl vinyl ketone (**1a**)⁵ and phenyl vinyl ketone (**1b**)⁶ were prepared according to the reported procedures. Methyl vinyl ketone (**1c**) and propionaldehyde (**3y**) were purchased from Wako Pure Chemical Industries and distilled before use. 9-Phenyl-9-borabicyclo[3.3.1]nonane (*B*-Ph-9BBN) (**2n**) was prepared according to the reported procedure.⁷ 9-(4-Fluorophenyl)-9-borabicyclo[3.3.1]nonane (**2m**) and 9-(4-methoxyphenyl)-9-borabicyclo[3.3.1]nonane (**2o**) were prepared in a similar manner to **2n**. **2m**; ^1H NMR (CDCl_3) δ 1.26-1.35 (m, 2H), 1.76-1.83 (m, 4H), 1.93-2.04 (m, 6H), 2.22-2.29 (br m, 2H), 7.13 (t, J = 8.7 Hz, 2H), 7.98 (dd, J = 8.7, 6.4 Hz, 2H). **2o**; ^1H NMR (CDCl_3) δ 1.29-1.35 (m, 2H), 1.76-1.82 (m, 4H), 1.93-2.02 (m, 6H), 2.23-2.28 (br m, 2H), 3.87 (s, 3H), 6.99 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6

Hz, 2H). 9-(*E*)-1-Heptenyl-9-borabicyclo[3.3.1]nonane (**2p**) was prepared in a similar manner to the reported procedure.⁸ **2p**; ¹H NMR (CDCl₃) δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.22-1.40 (m, 6H), 1.48 (quint, *J* = 7.5 Hz, 2H), 1.66-1.93 (m, 12H), 2.24-2.28 (m, 2H), 6.23 (dt, *J* = 17.4, 1.4 Hz, 1H), 6.84 (dt, *J* = 17.4, 6.5 Hz, 1H). Benzaldehyde (**3x**) was purchased from Aldrich Chemical Co. and distilled before use. Isobutyraldehyde (**3z**) was purchased from Nacalai Tesque and distilled before use. Pyridine and *N,N*-diisopropylethylamine were purchased from Wako Pure Chemical Industries and used as received. (+)- α -Methoxy- α -(trifluoromethyl)phenylacetyl chloride ((+)-MTPA chloride) was prepared from (*R*)-(+)-MTPA acid according to the reported procedure.⁹

Rhodium-Catalyzed Tandem 1,4-Addition-Aldol Reaction of α,β -Unsaturated Ketones, 9-Aryl- and 9-Alkenyl-9-borabicyclo[3.3.1]nonanes (*B-R-9BBN*), and Aldehydes. To a solution of [Rh(OMe)(cod)]₂ (1.5 mg, 3.0 μ mol), α,β -unsaturated ketone **1** (0.22 mmol), and aldehyde **3** (0.20 mmol) in toluene (0.7 mL) was added *B-R-9-BBN* **2** (0.220 mmol) at 0 °C under argon. The flask was immersed in a bath maintained at 20 °C for 2 h. The resulting mixture was cooled to 0 °C and treated with 3*N* NaOH (ca. 0.2 mL) and 30% H₂O₂ (ca. 0.2 mL). For complete oxidation of organoboranes, the mixture was heated at 50 °C for 1 h. The organic layer was diluted with AcOEt, washed with saturated K₂CO₃ and dried over MgSO₄. The residue was purified by PTLC on silica gel to give three-components coupling product **4** as a mixture of diastereomers. The separation of *syn* and *anti*-**4** for the NMR analyses was accomplished by further PTLC.

***syn*- and *anti*-2-(4-Fluorophenyl)methyl-1-hydroxy-4,4-dimethyl-1-phenylpentan-3-one (4amx):** purified by PTLC (hexane/AcOEt = 4/1); Anal. Calcd for C₂₀H₂₃FO₂: C, 76.41; H, 7.37. Found: C, 76.51; H, 7.38.; *syn* ¹H NMR (CDCl₃) δ 0.75 (s, 9H), 2.72 (dd, *J* = 13.6, 3.5 Hz, 1H), 2.99 (dd, *J* = 13.6, 11.0 Hz, 1H), 3.28 (s, 1H), 3.53 (dt, *J* = 11.0, 3.4 Hz, 1H), 4.91 (d, *J* = 3.3 Hz, 1H), 6.83-6.90 (m, 4H), 7.29 (tt, *J* = 7.1, 1.6 Hz, 1H), 7.36-7.42 (m, 4H). ¹³C NMR (CDCl₃) δ 25.60, 32.02, 45.01, 55.25, 73.51, 115.13 (d, *J* = 20.6 Hz), 126.01, 127.65, 128.45, 130.81 (d, *J* = 7.8 Hz), 135.25 (d, *J* = 3.0 Hz), 141.36, 161.58 (d, *J* = 243.1 Hz), 220.15. *anti* ¹H NMR (CDCl₃) δ 0.74 (s,

9H), 2.84 (dd, $J = 13.5, 6.9$ Hz, 1H), 2.89 (dd, $J = 13.5, 8.3$ Hz, 1H), 3.48 (ddd, $J = 8.1, 6.9, 4.8$ Hz, 1H), 4.00 (d, $J = 8.1$ Hz, 1H), 4.68 (dd, $J = 7.9, 4.7$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 7.16-7.20 (m, 4H), 7.23 (tt, $J = 7.4, 1.4$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 25.72, 36.02, 45.03, 54.11, 74.44, 115.45 (d, $J = 21.1$ Hz), 125.95, 127.63, 128.43, 130.81 (d, $J = 7.8$ Hz), 134.41 (d, $J = 3.1$ Hz), 143.19, 161.79 (d, $J = 243.6$ Hz), 221.64.

syn*- and *anti*-2-Benzyl-1-hydroxy-4,4-dimethyl-1-phenylpentan-3-one (4anx):** purified by PTLC (Hexane/AcOEt = 4/1); Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$: C, 81.04; H, 8.16. Found: C, 80.92; H, 8.29.; ***syn ^1H NMR (CDCl_3) δ 0.73 (s, 9H), 2.75 (dd, $J = 13.4, 3.3$ Hz, 1H), 3.00 (dd, $J = 13.3, 11.2$ Hz, 1H), 3.34 (s, 1H), 3.56 (dt, $J = 11.2, 3.3$ Hz, 1H), 4.93 (d, $J = 3.1$ Hz, 1H), 6.93 (d, $J = 7.1$ Hz, 2H), 7.10-7.18 (m, 3H), 7.30 (t, $J = 7.3$ Hz, 1H), 7.37-7.43 (m, 4H). ^{13}C NMR (CDCl_3) δ 25.57, 32.85, 45.01, 55.22, 73.63, 126.04, 126.34, 127.60, 128.36, 128.43, 129.39, 139.58, 141.43, 220.50. ***anti*** ^1H NMR (CDCl_3) δ 0.72 (s, 9H), 2.87 (dd, $J = 13.3, 6.5$ Hz, 1H), 2.95 (dd, $J = 13.3, 8.5$ Hz, 1H), 3.51 (ddd, $J = 8.4, 6.6, 4.7$ Hz, 1H), 4.14 (d, $J = 8.2$ Hz, 1H), 4.71 (dd, $J = 8.1, 4.6$ Hz, 1H), 7.17-7.20 (m, 2H), 7.22-7.24 (m, 4H), 7.27-7.31 (m, 4H). ^{13}C NMR (CDCl_3) δ 25.68, 36.83, 45.03, 54.01, 74.33, 125.91, 127.50, 127.61, 128.36, 128.63, 129.35, 138.73, 143.37, 221.95.

syn*- and *anti*-1-Hydroxy-2-(4-methoxyphenyl)methyl-4,4-dimethyl-1-phenylpentan-3-one (4aox):** purified by PTLC (Hexane/AcOEt = 4/1); Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$: C, 77.27; H, 8.03. Found: C, 77.05; H, 7.97.; ***syn ^1H NMR (CDCl_3) δ 0.76 (s, 9H), 2.69 (dd, $J = 13.6, 3.4$ Hz, 1H), 2.96 (dd, $J = 13.6, 11.1$ Hz, 1H), 3.31 (s, 1H), 3.54 (dt, $J = 11.0, 3.5$ Hz, 1H), 3.73 (s, 3H), 4.91 (d, $J = 3.2$ Hz, 1H), 6.71 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 7.29 (tt, $J = 7.1, 1.6$ Hz, 1H), 7.36-7.42 (m, 4H). ^{13}C NMR (CDCl_3) δ 25.66, 31.94, 45.09, 55.23, 55.25, 73.63, 113.74, 126.05, 127.57, 128.41, 130.33, 131.52, 141.50, 158.18, 220.66. ***anti*** ^1H NMR (CDCl_3) δ 0.73 (s, 9H), 2.82 (dd, $J = 13.6, 6.3$ Hz, 1H), 2.90 (dd, $J = 13.7, 8.6$ Hz, 1H), 3.46 (ddd, $J = 8.6, 6.2, 4.4$ Hz, 1H), 3.80 (s, 3H), 4.18 (d, $J = 8.4$ Hz, 1H), 4.70 (dd, $J = 8.2, 4.3$ Hz, 1H), 6.84 (d, $J = 8.6$ Hz,

2H), 7.15 (d, $J = 8.6$ Hz, 2H), 7.18 (d, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 25.70, 35.98, 45.05, 54.22, 55.30, 74.18, 114.02, 125.88, 127.44, 128.34, 130.32, 130.71, 143.49, 158.42, 222.13.

syn*- and *anti*-4-(Hydroxyphenyl)methyl-2,2-dimethyl-dodec-6-en-3-one (4apx):** purified by PTLC (Hexane/AcOEt = 5/1); Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{O}_2$: C, 79.70; H, 10.19. Found: C, 79.65; H, 10.27.; ***syn ^1H NMR (CDCl_3) δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.04 (s, 9H), 1.17-1.30 (m, 6H), 1.88 (q, $J = 6.9$ Hz, 2H), 2.19 (dddd, $J = 14.1, 6.2, 4.4, 1.1$ Hz, 1H), 2.41 (dt, $J = 14.1, 8.3$ Hz, 1H), 3.23 (d, $J = 1.2$ Hz, 1H), 3.34 (dt, $J = 8.9, 4.3$ Hz, 1H), 4.89 (d, $J = 4.2$ Hz, 1H), 5.16 (dddt, $J = 14.9, 8.0, 6.5, 1.4$ Hz, 1H), 5.34 (dt, $J = 14.8, 6.6, 1.2$ Hz, 1H), 7.23-7.27 (m, 1H), 7.31-7.36 (m, 4H). ^{13}C NMR (CDCl_3) δ 14.05, 22.51, 26.10, 28.89, 30.46, 31.42, 32.43, 44.99, 52.66, 73.75, 126.22, 127.09, 127.49, 128.25, 133.23, 141.74, 219.96. ***anti*** ^1H NMR (CDCl_3) δ 0.86 (s, 9H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.22-1.38 (m, 6H), 1.99 (q, $J = 7.1$ Hz, 2H), 2.19 (dt, $J = 14.3, 5.9$ Hz, 1H), 2.38 (dt, $J = 14.1, 8.1$ Hz, 1H), 3.25 (dt, $J = 8.2, 5.2$ Hz, 1H), 4.00 (d, $J = 7.9$ Hz, 1H), 4.85 (dd, $J = 7.8, 4.8$ Hz, 1H), 5.36 (dt, $J = 15.2, 7.2$ Hz, 1H), 5.51 (dt, $J = 15.2, 6.8$ Hz, 1H), 7.21-7.26 (m, 3H), 7.29-7.32 (m, 2H). ^{13}C NMR (CDCl_3) δ 14.09, 22.54, 25.84, 28.99, 31.44, 32.54, 33.63, 44.89, 52.23, 74.46, 126.00, 126.02, 127.45, 128.32, 134.26, 143.58, 221.65.

syn*- and *anti*-4-(4-Fluorophenyl)methyl-5-hydroxy-2,2-dimethylheptan-3-one (4amy):** purified by PTLC (hexane/AcOEt = 3/1); Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{FO}_2$: C, 72.15; H, 8.70. Found: C, 72.06; H, 8.73.; ***syn ^1H NMR (CDCl_3) δ 0.82 (s, 9H), 1.02 (t, $J = 7.5$ Hz, 3H), 1.52 (d quint, $J = 15.0, 7.0$ Hz, 1H), 1.71 (d quint, $J = 15.2, 7.1$ Hz, 1H), 2.82 (dd, $J = 13.6, 3.8$ Hz, 1H), 2.95 (br s, 1H), 2.98 (dd, $J = 13.6, 11.0$ Hz, 1H), 3.33 (ddd, $J = 10.9, 3.8, 1.8$ Hz, 1H), 3.61 (td, $J = 7.6, 1.7$ Hz, 1H), 6.93 (t, $J = 8.7$ Hz, 2H), 7.06 (dd, $J = 8.6, 5.7$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 10.64, 25.67, 27.29, 31.30, 44.90, 51.59, 72.93, 115.26 (d, $J = 21.1$ Hz), 130.82 (d, $J = 7.6$ Hz), 135.62 (d, $J = 3.6$ Hz), 161.60 (d, $J = 243.6$ Hz), 220.55. ***anti*** ^1H NMR (CDCl_3) δ 0.94 (t, $J = 7.4$ Hz, 3H), 1.08 (s, 9H), 1.29-1.43 (m, 2H), 2.80 (dd, $J = 13.6, 5.8$ Hz, 1H), 2.97 (dd, $J = 13.5, 9.1$ Hz,

1H), 3.17 (br d, $J = 9.4$ Hz, 1H), 3.20 (ddd, $J = 9.2, 5.8, 3.7$ Hz, 1H), 3.38 (br tt, $J = 8.9, 3.7$ Hz, 1H), 6.98 (t, $J = 8.7$ Hz, 2H), 7.19 (dd, $J = 8.6, 5.5$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 10.80, 26.34, 29.38, 35.25, 45.24, 51.76, 73.25, 115.34 (d, $J = 21.1$ Hz), 130.79 (d, $J = 7.6$ Hz), 134.66 (d, $J = 3.1$ Hz), 161.67 (d, $J = 243.6$ Hz), 222.02.

syn*- and *anti*-2-(4-Fluorophenyl)methyl-3-hydroxy-1,3-diphenylpropan-1-one (4bm_x):** purified by PTLC (hexane/AcOEt = 3/1); Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{FO}_2$: C, 79.02; H, 5.73. Found: C, 79.18; H, 5.70.; ***syn ^1H NMR (CDCl_3) δ 3.03 (dd, $J = 13.7, 3.6$ Hz, 1H), 3.17 (dd, $J = 13.7, 10.5$ Hz, 1H), 3.21 (br s, 1H), 4.00 (dt, $J = 10.6, 4.2$ Hz, 1H), 5.10 (d, $J = 4.4$ Hz, 1H), 6.76 (t, $J = 8.6$ Hz, 2H), 6.91 (dd, $J = 8.5, 5.5$ Hz, 2H), 7.23-7.34 (m, 5H), 7.41-7.46 (m, 3H), 7.55 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 32.62, 55.58, 73.87, 115.09 (d, $J = 21.1$ Hz), 126.18, 127.74, 128.21, 128.44, 128.47, 130.46 (d, $J = 7.8$ Hz), 133.28, 134.94 (d, $J = 3.6$ Hz), 137.21, 141.51, 161.36 (d, $J = 243.1$ Hz), 204.68. ***anti*** ^1H NMR (CDCl_3) δ 2.83 (dd, $J = 13.6, 6.1$ Hz, 1H), 3.01 (dd, $J = 13.6, 8.8$ Hz, 1H), 3.33 (d, $J = 6.5$ Hz, 1H), 4.06 (dt, $J = 8.8, 6.3$ Hz, 1H), 4.96 (t, $J = 6.3$ Hz, 1H), 6.84 (t, $J = 8.7$ Hz, 2H), 7.05 (dd, $J = 8.7, 5.5$ Hz, 2H), 7.24 (tt, $J = 7.2, 1.5$ Hz, 1H), 7.30-7.37 (m, 6H), 7.46 (tt, $J = 7.4, 1.3$ Hz, 1H), 7.65 (dd, $J = 8.4, 1.4$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 35.85, 54.86, 75.57, 115.27 (d, $J = 21.1$ Hz), 126.20, 127.91, 128.14, 128.45, 128.59, 130.47 (d, $J = 7.8$ Hz), 133.23, 134.24 (d, $J = 3.1$ Hz), 137.99, 142.50, 161.53 (d, $J = 243.6$ Hz), 205.37.

syn*- and *anti*-2-(4-Fluorophenyl)methyl-3-hydroxy-4-methyl-1-phenylpentan-1-one (4bm_z):** purified by PTLC (hexane/AcOEt = 3/1); Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{FO}_2$: C, 75.98; H, 7.05. Found: C, 76.00; H, 7.10.; ***syn ^1H NMR (CDCl_3) δ 0.98 (d, $J = 6.6$ Hz, 3H), 1.02 (d, $J = 6.8$ Hz, 3H), 1.84 (octet, $J = 6.7$ Hz, 1H), 2.74 (d, $J = 3.1$ Hz, 1H), 3.06 (dd, $J = 13.7, 3.7$ Hz, 1H), 3.17 (dd, $J = 13.7, 10.5$ Hz, 1H), 3.59 (dt, $J = 6.9, 3.7$ Hz, 1H), 3.95 (dt, $J = 10.6, 4.0$ Hz, 1H), 6.83 (t, $J = 8.8$ Hz, 2H), 7.08 (dd, $J = 8.6, 5.4$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.49 (tt, $J = 7.5, 1.3$ Hz, 1H), 7.66 (dd, $J = 7.3, 1.3$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 18.24, 19.57, 31.07, 32.43, 50.79 (d, $J = 1.0$ Hz), 77.07, 115.17 (d, $J = 21.1$ Hz), 128.20, 128.60, 130.45 (d, $J = 7.8$ Hz), 133.32, 135.37 (d,

$J = 3.1$ Hz), 137.14, 161.37 (d, $J = 243.1$ Hz), 204.83. **anti** ^1H NMR (CDCl_3) δ 0.77 (d, $J = 6.7$ Hz, 3H), 0.97 (d, $J = 6.6$ Hz, 3H), 1.66 (octet, $J = 7.0$ Hz, 1H), 3.05 (dd, $J = 13.6$, 7.4 Hz, 1H), 3.08 (dd, $J = 13.7$, 7.8 Hz, 1H), 3.33 (ddd, $J = 9.9$, 7.7, 3.7 Hz, 1H), 3.40 (d, $J = 9.8$ Hz, 1H), 3.87 (td, $J = 7.7$, 3.6 Hz, 1H), 6.92 (t, $J = 8.7$ Hz, 2H), 7.18 (dd, $J = 8.6$, 5.4 Hz, 2H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.56 (tt, $J = 7.3$, 1.1 Hz, 1H), 7.81 (dd, $J = 7.3$, 1.3 Hz, 2H). ^{13}C NMR (CDCl_3) δ 18.89, 19.67, 32.78, 36.24, 49.16, 78.20, 115.37 (d, $J = 21.1$ Hz), 128.19, 128.81, 130.59 (d, $J = 7.8$ Hz), 133.65, 134.55 (d, $J = 3.1$ Hz), 137.31, 161.61 (d, $J = 243.6$ Hz), 206.62.

syn- and anti-3-(4-Fluorophenyl)methyl-4-hydroxy-4-phenylbutan-2-one (4cmx): purified by PTLC (hexane/AcOEt = 2/1); Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{FO}_2$: C, 74.98; H, 6.29. Found: C, 74.93; H, 6.35.; **syn** ^1H NMR (CDCl_3) δ 1.61 (s, 3H), 2.93 (dd, $J = 13.7$, 10.9 Hz, 1H), 2.94 (br s, 1H), 2.99 (dd, $J = 13.7$, 3.8 Hz, 1H), 3.17 (ddd, $J = 10.5$, 6.0, 3.9 Hz, 1H), 4.92 (d, $J = 6.1$ Hz, 1H), 6.91 (t, $J = 8.7$ Hz, 2H), 7.02 (dd, $J = 8.6$, 5.4 Hz, 2H), 7.27-7.31 (m, 1H), 7.36 (d, $J = 4.3$ Hz, 4H). ^{13}C NMR (CDCl_3) δ 32.78, 32.93, 61.78, 73.96, 115.35 (d, $J = 21.1$ Hz), 126.17, 127.96, 128.59, 130.28 (d, $J = 7.6$ Hz), 135.03 (d, $J = 3.1$ Hz), 141.61, 161.47 (d, $J = 243.6$ Hz), 212.72. **anti** ^1H NMR (CDCl_3) δ 1.83 (s, 3H), 2.58 (dd, $J = 13.6$, 5.3 Hz, 1H), 2.82 (dd, $J = 13.6$, 10.3 Hz, 1H), 2.89 (d, $J = 5.6$ Hz, 1H), 3.23 (ddd, $J = 10.4$, 7.0, 5.4 Hz, 1H), 4.79 (dd, $J = 7.0$, 5.6 Hz, 1H), 6.94 (t, $J = 8.7$ Hz, 2H), 7.03 (dd, $J = 8.6$, 5.4 Hz, 2H), 7.31 (tt, $J = 7.0$, 1.6 Hz, 1H), 7.33-7.39 (m, 4H). ^{13}C NMR (CDCl_3) δ 33.59, 35.17, 60.80, 75.64, 115.46 (d, $J = 21.1$ Hz), 126.18, 128.12, 128.73, 130.27 (d, $J = 7.8$ Hz), 134.28 (d, $J = 3.1$ Hz), 142.24, 161.60 (d, $J = 244.1$ Hz), 213.70.

Rhodium-Catalyzed Asymmetric Tandem 1,4-Addition-Aldol Reaction of *tert*-Butyl Vinyl Ketone (1a), 9-(4-Fluorophenyl)-9-borabicyclo[3.3.1]nonane (2m), and Propionaldehyde (3y).

To a solution of $[\text{Rh}(\text{OH})((S)\text{-binap})]_2$ (4.5 mg, 3.0 μmol), *tert*-butyl vinyl ketone (**1a**) (22.4 mg, 0.220 mmol), and propionaldehyde (**3y**) (11.2 mg, 0.193 mmol) in DMF (0.7 mL) was added 9-(4-fluorophenyl)-9-borabicyclo[3.3.1]nonane (**2m**) (47.5mg, 0.220 mmol) at 0

°C under argon. The flask was immersed in a bath maintained at 20 °C for 12 h. The resulting mixture was evaporated under reduced pressure, diluted with toluene, cooled to 0 °C and treated with 3*N* NaOH (ca. 0.2 mL) and 30% H₂O₂ (ca. 0.2 mL). For complete oxidation of organoboranes, the mixture was heated at 50 °C for 1 h. The organic layer was diluted with AcOEt, washed with saturated K₂CO₃ and dried over MgSO₄. The residue was purified by PTLC on silica gel to give three-components coupling product **4amy** as a mixture of diastereomers (22.6 mg, 44% yield). The enantioselectivities of *syn*- and *anti*- **4amy** were determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H) (41% ee (*4S,5R*) of *syn* and 94% ee (*4R,5R*) of *anti*).

(4*S,5R*)-*syn*- and (4*R,5R*)-*anti*-4-(4-Fluorophenyl)methyl-5-hydroxy-2,2-dimethylheptan-3-one (4amy): purified by PTLC (hexane/AcOEt = 3/1); *syn* [α]_D²⁰ -4.74 (*c* 1.00, CHCl₃) for (*4S,5R*)-**4amy** of 41% ee. *anti* [α]_D²⁰ +55.9 (*c* 1.00, CHCl₃) for (*4R,5R*)-**4amy** of 94% ee.

Preparation of (*R*)-MTPA ester of *syn*-4-(4-Fluorophenyl)methyl-5-hydroxy-2,2-dimethylheptan-3-one (4amy).

To a solution of *syn*-**4amy** (26.6 mg, 0.100 mmol) in pyridine (0.25 mL) was added (+)-MTPA chloride (75.8 mg, 0.300 mmol) and the resulting suspension was allowed to stirred for 3 h at r.t. *N,N*-diisopropylethylamine (25.9 mg, 0.200 mmol) was added, and after 10 min all volatiles were evaporated under reduced pressure. The residue was purified by PTLC (Hexane/EtOAc = 5/1) to give desired (*R*)-MTPA ester (39.0 mg, 81% yield). major isomer: ¹H NMR (CDCl₃) δ 0.82 (s, 9H), 1.01 (t, *J* = 7.5 Hz, 3H), 1.77-1.84 (m, 2H), 2.73 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.95 (dd, *J* = 13.7, 11.1 Hz, 1H), 3.37-3.41 (m, 1H), 3.62 (s, 3H), 5.32 (ddd, *J* = 8.0, 6.1, 3.4 Hz, 1H), 6.88-6.92 (m, 2H), 6.97-7.02 (m, 2H), 7.41-7.45 (m, 3H), 7.61-7.65 (m, 2H). minor isomer: ¹H NMR (CDCl₃) δ 0.86 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 3H), 1.62-1.77 (m, 2H), 2.75 (dd, *J* = 13.3, 3.7 Hz, 1H), 2.98 (dd, *J* = 13.7, 11.3 Hz, 1H), 3.37-3.41 (m, 1H), 3.69 (s, 3H), 5.27 (ddd, *J* = 8.0, 5.6, 2.5 Hz, 1H), 6.88-6.92 (m, 2H), 6.97-7.02 (m, 2H), 7.41-7.45 (m, 3H), 7.61-7.65 (m, 2H).

Preparation of (*R*)-MTPA ester of *anti*-4-(4-Fluorophenyl)methyl-5-hydroxy-2,2-dimethylheptan-3-one (4amy).

This compound was prepared from *anti*-4amy (21.3 mg, 0.0800 mmol) in a similar manner as above. (*R*)-MTPA ester (28.2 mg, 73% yield). major isomer: ^1H NMR (CDCl_3) δ 0.79 (s, 9H), 0.90 (t, J = 7.5 Hz, 3H), 1.65-1.73 (m, 1H), 1.77-1.85 (m, 1H), 2.55 (dd, J = 12.8, 2.7 Hz, 1H), 2.92 (t, J = 12.4 Hz, 1H), 3.47 (dt, J = 12.1, 3.1 Hz, 1H), 3.60 (s, 3H), 5.09 (m, 1H), 6.74 (dd, J = 8.5, 5.5 Hz, 2H), 6.85 (t, J = 8.7 Hz, 2H), 7.42-7.47 (m, 3H), 7.59-7.61 (m, 2H). minor isomer: ^1H NMR (CDCl_3) δ 0.80 (t, J = 7.5 Hz, 3H), 0.82 (s, 9H), 1.65-1.73 (m, 1H), 1.77-1.85 (m, 1H), 2.68 (dd, J = 13.0, 2.7 Hz, 1H), 3.00 (dd, J = 13.1, 11.5 Hz, 1H), 3.56 (s, 3H), 3.56-3.60 (m, 1H), 5.09 (m, 1H), 6.89 (d, J = 7.1 Hz, 4H), 7.44-7.47 (m, 3H), 7.59-7.61(m, 2H).

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