Supporting Information

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Supporting Information

for

An Unprecedented Rhodium-Catalyzed Asymmetric Intermolecular Hydroacylation Reaction with Salicylaldehydes

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(−)-exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxyphenyl)methanone [(−)-exo-3a].[S1] Colorless oil; \([\alpha]_D^{21} = -19.6\ (c = 1.40, \text{CHCl}_3)\); \(^1\)H NMR (300 MHz) \(\delta = 1.16–1.39\ (m, 2H), 1.42–1.68\ (m, 5H), 2.04\ (dddd, \(J = 12.2, 5.6, 4.3, 2.6\ \text{Hz}, 1H)), 2.37\ (br s, 1H), 2.55\ (br s, 1H), 3.25\ (dd, \(J = 8.8, 5.6\ \text{Hz}, 1H)), 6.89\ (ddd, \(J = 8.4, 7.2, 1.2\ \text{Hz}, 1H)), 6.98\ (dd, \(J = 8.4, 1.2\ \text{Hz}, 1H)), 7.45\ (ddd, \(J = 8.4, 7.2, 1.7\ \text{Hz}, 1H)), 7.78\ (ddd, \(J = 8.1, 1.6, 0.4\ \text{Hz}, 1H)), 12.49\ (s, 1H); \(^{13}\)C NMR (75 MHz) \(\delta = 27.9\ (\text{CH}_2), 28.7\ (\text{CH}_2), 32.8\ (\text{CH}_2), 35.2\ (\text{CH}), 35.3\ (\text{CH}_2), 40.5\ (\text{CH}), 48.2\ (\text{CH}), 117.6\ (\text{CH}), 117.7\ (\text{CH}), 129.0\ (\text{CH}), 134.8\ (\text{CH}), 136.3\ (\text{C}), 161.9\ (\text{C}), 206.9\ (\text{C});\) IR (neat) \(\nu = 3049, 2955, 2871, 1636, 1581, 1486, 1448, 1352, 1311, 1276, 1239, 1202, 1158, 1033, 993, 943, 805, 757, 653, 529;\) MS (EI) \(m/z\ (\%) = 216\ (M^+ , 50), 187\ (14), 149\ [(M+1–C_5H_8)^{+}, 20], 121\ [(M–C_7H_{11})^{+}, 100].\) Anal. calcd. for C_{14}H_{16}O_2: C, 77.75; H, 7.46. Found: C, 78.15; H, 7.22. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 230 nm, 20 °C, 22.0 min (+), 25.9 min (−): 62% ee.

(−)-exo-Bicyclo[2.2.1]heptan-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [(−)-exo-3b]. Mp 87–89°C; \([\alpha]_D^{22} = -1.6\ (c = 0.21, \text{CHCl}_3);\) \(^1\)H NMR (300 MHz) \(\delta = 1.14–1.75\ (m, 7H), 1.91–2.03\ (m, 1H), 2.39\ (s, 1H), 2.54\ (s, 1H), 3.17\ (dd, \(J = 8.9, 5.7\ \text{Hz}, 1H)), 7.55\ (d, \(J = 2.4\ \text{Hz}, 1H)), 7.65\ (d, \(J = 2.4\ \text{Hz}, 1H)), 12.99\ (s, 1H);\) \(^{13}\)C NMR (75 MHz) \(\delta = 28.8\ (\text{CH}_2), 29.6\ (\text{CH}_2), 34.1\ (\text{CH}_2), 36.2\ (\text{CH}), 36.4\ (\text{CH}_2), 41.3\ (\text{CH}), 49.5\ (\text{CH}), 119.7\ (\text{C}), 123.1\ (\text{C}), 124.1\ (\text{C}), 127.8\ (\text{CH}), 135.4\ (\text{CH}), 157.4\ (\text{C}), 207.0\ (\text{C});\) IR (KBr) \(\nu = 3780, 3714, 3432, 3064, 2949, 2870, 2289, 1639, 1440, 1382, 1269, 1215, 1167, 1024, 945, 805, 735, 551;\) MS (EI) \(m/z\ (\%) = 286\ [(M+1)^{+}, 31], 284\ [(M–1)^{+}, 48], 257\ (18), 255\ (28), 219\ (20), 217\ (35), 191\ [(M+1–C_7H_{11})^{+}, 42], 189\ [(M–1–C_7H_{11})^{+}, 42], 95\ (C_7H_{11}^{+}, 100], 67\ (C_3H_7^{+}, 28).\) Anal. calcd.
for C$_{14}$H$_{14}$Cl$_2$O$_2$: C, 58.97; H, 4.95. Found: C, 58.96; H, 4.72. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane, 1.0 mL/min, 230 nm, 20 °C, 22.2 min (+), 26.0 min (−): 7% ee.

(−)-exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxy-5-nitrophenyl)methanone [(−)-exo-3c]. Mp 87–90°C; [α]$_D^{22}$ = −1.0 (c = 0.53, CHCl$_3$); $^1$H NMR (300 MHz) δ = 1.25 (dtd, J = 9.9, 2.8, 1.4 Hz, 1H), 1.31–1.57 (m, 3H), 1.57–1.77 (m, 3H), 1.99 (dddd, J = 12.3, 5.8, 4.1, 2.6 Hz, 1H), 2.41 (s, 1H), 2.57 (s, 1H), 3.30 (dd, J = 9.1, 5.7 Hz, 1H), 7.08 (d, J = 9.2 Hz, 1H), 8.33 (dd, J = 9.2, 2.7 Hz, 1H), 8.73 (d, J = 2.7 Hz, 1H), 13.11 (s, 1H); $^{13}$C NMR (75 MHz) δ = 28.7 (CH$_2$), 29.5 (CH$_2$), 34.3 (CH$_2$), 36.3 (CH), 36.5 (CH$_2$), 41.2 (CH), 49.4 (CH), 117.5 (C), 119.6 (CH), 126.5 (CH), 130.5 (CH), 139.4 (C), 167.8 (C), 207.5 (C); IR (KBr) ν = 2953, 2871, 1648, 1583, 1516, 1473, 1340, 1291, 1264, 1182, 1111, 1023, 947, 804, 747, 705, 639; MS (EI) m/z (%) = 261 (M$^+$, 51), 232 (16), 194 [(M+1–C$_3$H$_8$)$^+$, 66], 166 [(M–C$_7$H$_11$)$^+$, 34], 120 (18), 95 (C$_7$H$_{11}^+$, 100), 67 (30). HRMS calcd. for C$_{14}$H$_{15}$NO$_2$ 261.1001, found 261.1001. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OJ, heptane/2-PrOH 99:1, 0.7 mL/min, 230 nm, 20 °C, 18.8 min (−), 23.0 min (+): 6% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone [(+)-endo-5a]. Mp 42–44 °C; [α]$_D^{22}$ = +96.7 (c = 0.65, CHCl$_3$); $^1$H NMR (400 MHz) δ = 1.45–1.57 (m, 2H), 1.63 (ddd, J = 11.6, 4.5, 2.3 Hz, 1H), 1.98 (ddd, J = 11.6, 9.1, 3.7 Hz, 1H), 2.99 (s, 1H), 3.29 (s, 1H), 3.90 (ddd, J = 9.0, 4.2, 3.7 Hz, 1H), 5.86 (dd, J = 5.6, 2.9 Hz, 1H), 6.22 (dd, J = 5.6, 3.1 Hz, 1H), 6.91 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 6.97 (dd, J = 8.4, 1.2 Hz, 1H), 7.45 (ddd, J =
8.5, 7.2, 1.7 Hz, 1H), 7.92 (dd, J = 8.1, 1.7 Hz, 1H), 12.39 (s, 1H); $^{13}$C NMR (100 MHz) δ = 29.3 (CH$_2$), 43.0 (CH), 47.0 (CH), 48.1 (CH), 50.1 (CH$_2$), 118.4 (CH), 118.6 (CH), 119.2 (C), 129.9 (CH), 131.6 (CH), 135.7 (CH), 137.2 (CH), 162.4 (C), 206.7 (C); IR (KBr) ν = 3058, 2974, 2871, 1636, 1487, 1447, 1352, 1282, 1237, 1203, 1158, 757, 717; MS (EI) m/z (%) = 214 (M$^+$, 34), 149 [(M+H–C$_5$H$_6$)$^+$, 56], 148 (42), 147 (100), 121 [(M–C$_7$H$_9$)$^+$, 95], 66 (49). Anal. calcd. for C$_{14}$H$_{14}$O$_2$: C, 78.48; H, 6.59. Found: C, 78.40; H, 6.75. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 98:2, 0.5 mL/min, 254 nm, 20 °C, 10.8 min (+), 11.7 min (–): 41% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone  [(+)

endo-5b]. Mp 54–56 °C; [α]$_D^{22}$ = +54.4 (c = 0.40, CHCl$_3$); $^1$H NMR (400 MHz) δ = 1.48–1.57 (m, 2H), 1.62 (ddd, J = 11.6, 4.4, 2.5 Hz, 1H), 2.00 (ddd, J = 11.7, 9.1, 3.7 Hz, 1H), 3.02 (s, 1H), 3.29 (s, 1H), 3.83 (ddd, J = 9.0, 4.1, 3.7 Hz, 1H), 5.83 (dd, J = 5.7, 2.9 Hz, 1H), 6.24 (dd, J = 5.6, 3.1 Hz, 1H), 7.56 (dd, J = 2.5, 0.4 Hz, 1H), 7.81 (d, J = 2.5 Hz, 1H), 12.88 (s, 1H); $^{13}$C NMR (100 MHz) δ = 29.5 (CH$_2$), 43.0 (CH), 47.5 (CH), 48.3 (CH), 50.2 (CH$_2$), 120.3 (C), 123.1 (C), 124.0 (C), 127.8 (CH), 131.3 (CH), 135.3 (CH), 137.7 (CH), 156.9 (C), 205.9 (C); IR (KBr) ν = 2988, 2935, 2861, 1646, 1592, 1441, 1371, 1336, 1274, 1218, 1171, 1142, 1101, 811, 739, 709; MS (EI) m/z (%) = 284 [(M+1)$^+$, 26], 282 [(M–1)$^+$, 49], 219 (40), 218 (55), 217 [(M–C$_5$H$_6$)$^+$, 100], 216 (82), 215 (85), 191 (28), 189 [(M–C$_7$H$_9$)$^+$, 58], 66 (C$_5$H$_6$$^+$, 74). Anal. calcd. for C$_{14}$H$_{12}$Cl$_2$O$_2$: C, 59.39; H, 4.27. Found: C, 59.45; H, 4.17. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 230 nm, 20 °C, 27.6 min (–), 30.5 min (+): 42% ee.
(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone [(+)-endo-5c].
Mp 133–136 °C; [α]D 22 = +91.2 (c = 0.49, CHCl3); 1H NMR (300 MHz) δ = 1.57 (d, J = 1.3 Hz, 2H), 1.63 (dd, J = 11.8, 4.3 Hz, 1H), 2.08 (ddd, J = 11.4, 9.1, 3.6 Hz, 1H), 3.04 (s, 1H), 3.34 (s, 1H), 3.95 (dt, J = 8.8, 3.9 Hz, 1H), 5.85 (dd, J = 5.6, 2.8 Hz, 1H), 6.24 (dd, J = 5.6, 3.1 Hz, 1H), 7.07 (d, J = 9.2 Hz, 1H), 8.33 (dd, J = 9.2, 2.7 Hz, 1H), 8.88 (d, J = 2.7 Hz, 1H), 13.02 (s, 1H); 13C NMR (75 MHz) δ = 29.4 (CH2), 43.0 (CH), 47.4 (CH), 48.2 (CH), 50.2 (CH2), 118.1 (C), 119.6 (CH), 126.5 (CH), 130.5 (CH), 131.4 (CH), 137.9 (CH), 139.5 (C), 167.5 (C), 206.6 (C); IR (KBr) ν = 3462, 2968, 2946, 1638, 1583, 1516, 1476, 1369, 1338, 1288, 1245, 1190, 1112, 910, 840, 737, 700, 640; MS (EI) m/z (%) = 259 (M+1, 28), 194 [(M+1–C5H6)+, 64], 166 [(M–C7H8)+, 20], 148 (11), 120 (12), 93 [(M–C7H4NO4)+, 18], 66 (C5H6+, 100). Anal. calcd. for C14H13NO4: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.58; H, 5.17; N, 5.37. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane/2-PrOH 95:5, 1.0 mL/min, 220 nm, 20 °C, 10.9 min (+), 17.7 min (–): 40% ee.

(+)-endo-(2-Amino-3,5-dibromophenyl)(bicyclo[2.2.1]hept-5-en-2-yl)methanone [(+)-endo-5d]. Yellow oil; [α]D 22 = +51.9 (c = 0.34, CHCl3); 1H NMR (400 MHz) δ = 1.37–1.52 (m, 2H), 1.57 (ddd, J = 11.3, 4.3, 2.1 Hz, 1H), 1.96 (ddd, J = 11.7, 9.2, 3.7 Hz, 1H), 2.96 (s, 1H), 3.22 (s, 1H), 3.79 (dt, J = 8.8, 4.0 Hz, 1H), 5.84 (dd, J = 5.6, 2.9 Hz, 1H), 6.19 (dd, J = 5.6, 3.1 Hz, 1H), 6.80 (br s, 2H), 7.67 (d, J = 2.2 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H); 13C NMR (100 MHz) δ = 29.8 (CH2), 43.0 (CH), 47.8 (CH), 47.9 (CH), 50.0 (CH2), 105.8 (C), 111.8 (C), 119.7 (C), 131.8 (CH), 132.7 (CH), 137.0 (CH), 138.6 (CH), 146.2 (C), 201.5 (C); IR (CHCl3) ν = 3471, 3327, 3064, 2971, 2870, 1651, 1598, 1563, 1526, 1436, 1340, 1204, 1070, 874, 835, 755, 696, 542; MS (EI) m/z (%) = 373 [(M+2)+, 24], 371 (M+, 50), 369 [(M–2)+,
25], 307 (45), 306 (62), 305 [(M–C₅H₆)+, 97], 304 (100), 303 (50), 302 (48), 280 (14), 278 (30), 276 (16). Anal. calcd. for C₁₄H₁₃Br₂NO: C, 45.32; H, 3.53; N, 3.77. Found: C, 45.46; H, 3.54; N, 4.04. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane/2-PrOH 99:1, 0.5 mL/min, 254 nm, 20 °C, 15.5 min (−), 16.8 min (+): 41% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxynaphthalen-1-yl)methanone [(+)-endo-5e]. Colorless oil; [α]D²² = +40.9 (c = 0.46, CHCl₃); ¹H NMR (300 MHz) δ = 1.32–1.46 (m, 2H), 1.52 (ddd, J = 11.6, 4.6, 2.5 Hz, 1H), 2.06 (ddd, J = 12.0, 9.2, 3.8 Hz, 1H), 2.92 (s, 1H), 3.14 (s, 1H), 4.11–4.21 (m, 1H), 5.81 (dd, J = 5.6, 2.8 Hz, 1H), 6.20 (dd, J = 5.7, 3.1 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.38 (dd, J = 8.0, 7.0 Hz, 1H), 7.54 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 11.26 (s, 1H); ¹³C NMR (75 MHz) δ = 31.2 (CH₂), 43.0 (CH), 47.3 (CH), 49.8 (CH₂), 52.4 (CH), 116.9 (C), 119.4 (CH), 123.7 (CH), 124.5 (CH), 127.6 (CH), 128.6 (C), 129.1 (CH), 131.4 (C), 132.5 (CH), 135.4 (CH), 137.7 (CH), 159.7 (C), 209.6 (C); IR (CHCl₃) ν = 3360, 2972, 2872, 1744, 1673, 1625, 1578, 1512, 1463, 1435, 1349, 1272, 1241, 1183, 1100, 916, 819, 754, 716; MS (EI) m/z (%) = 264 (M⁺, 44), 198 [(M–C₅H₆)+, 36], 197 (37), 171 [(M–C₇H₉)+, 100], 170 (41), 144 [(M+H–C₈H₉O)⁺, 21], 115 (29). HRMS calcd. for C₁₈H₁₆O₂ 264.1150, found 264.1152. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 90:10, 0.5 mL/min, 254 nm, 20 °C, 20.1 min (+), 26.9 min (−); 32% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-methylphenyl)methanone [(+)-endo-5f]. Colorless oil; [α]D²³ = +74.5 (c = 0.37, CHCl₃); ¹H NMR (300 MHz) δ = 1.49–1.54 (m,
2H), 1.59–1.69 (m, 1H), 1.97 (ddd, J = 11.5, 9.1, 3.7 Hz, 1H), 2.34 (s, 3H), 3.00 (br s, 1H), 3.30 (br s, 1H), 3.89 (ddd, J = 9.1, 4.4, 3.5 Hz, 1H), 5.86 (dd, J = 5.6, 2.9 Hz, 1H), 6.22 (dd, J = 5.6, 3.1 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 7.24–7.31 (m, 1H), 7.69 (d, J = 1.5 Hz, 1H), 12.20 (s, 1H); 13C NMR (75 MHz) δ = 20.7 (CH3), 29.3 (CH2), 43.0 (CH), 46.9 (CH), 48.1 (CH), 50.2 (CH2), 118.3 (CH), 119.0 (C), 127.7 (C), 129.7 (CH), 131.7 (CH), 136.9 (CH), 137.3 (CH), 160.5 (C), 206.8 (C); IR (CHCl3) ν = 2973, 2868, 1639, 1613, 1486, 1353, 1285, 1214, 1189, 825, 802, 775, 714, 670, 537; MS (EI) m/z (%) = 228 (M+; 41), 161 [(M–1-C5H6)+, 100], 135 [(M–C7H9)+, 66], 77 (15). HRMS calcd. for C15H16O2 228.1150, found 228.1151. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 98:2, 0.5 mL/min, 254 nm, 20 °C, 11.3 min (+), 14.1 min (−): 11% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-di-tert-butyl-2-hydroxyphenyl)methanone [(+)-endo-5g]. Mp 68–70 °C; [α]D23 = +66.7 (c = 0.27, CHCl3); 1H NMR (300 MHz) δ = 1.35 (s, 9H), 1.42 (s, 9H), 1.52 (m, 2H), 1.62 (dd, J = 11.5, 4.6 Hz, 1H), 2.02 (dd, J = 11.4, 9.2, 3.7 Hz, 1H), 2.98 (br s, 1H), 3.29 (br s, 1H), 3.91 (dd, J = 9.2, 4.4, 3.6 Hz, 1H), 5.93 (dd, J = 5.6, 3.0 Hz, 1H), 6.20 (dd, J = 5.6, 3.1 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.76 (d, J = 2.1 Hz, 1H), 13.06 (d, J = 0.5 Hz, 1H); 13C NMR (75 MHz) δ = 29.4 (CH3, 3C), 29.9 (CH2), 31.4 (CH3, 3C), 34.3 (C), 35.2 (C), 42.9 (CH), 47.4 (CH), 47.9 (CH), 50.0 (CH2), 118.3 (C), 123.8 (CH), 130.7 (CH), 132.3 (CH), 137.0 (CH), 138.0 (C), 139.6 (C), 160.2 (C), 207.6 (C); IR (KBr) ν = 2959, 2909, 2870, 1624, 1437, 1390, 1270, 1246, 1201, 1173, 821, 684; MS (EI) m/z (%) = 326 (M+, 32), 260 [(M–C5H6)+, 69], 245 (100), 233 [(M–C7H9)+, 71], 189 (19), 57 (19). HRMS calcd. for C22H30O2 326.2246, found 326.2245. The enantiomer ratio was
determined by HPLC using a chiral stationary phase: Daicel Chiralcel OG, heptane, 0.7 mL/min, 254 nm, 10 °C, 7.2 min (+), 8.1 min (−): 35% ee.

(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone [(+) -endo -5h].

Mp 91–94 °C; \([\alpha]_D^{22} = +115 \ (c = 0.43, \text{CHCl}_3); \) \(^1\)H NMR (400 MHz) \( \delta = 1.45–1.56 \) (m, 2H), 1.63 (ddd, \( J = 11.6, 4.5, 2.4 \) Hz, 1H), 1.97 (ddd, \( J = 11.6, 9.1, 3.7 \) Hz, 1H), 3.00 (s, 1H), 3.31 (s, 1H), 3.90 (ddd, \( J = 9.0, 4.3, 3.6 \) Hz, 1H), 5.75 (br s, 1H), 5.85 (dd, \( J = 5.6, 2.9 \) Hz, 1H), 6.23 (dd, \( J = 5.6, 3.1 \) Hz, 1H), 6.89–6.79 (m, 1H), 7.11 (dd, \( J = 7.9, 1.4 \) Hz, 1H), 7.47 (dd, \( J = 8.2, 1.4 \) Hz, 1H), 12.63 (s, 1H); \(^{13}\)C NMR (100 MHz) \( \delta = 29.3 \) (CH\(_2\)), 43.1 (CH), 47.2 (CH), 48.3 (CH), 50.2 (CH\(_2\)), 118.6 (CH), 119.1 (C), 119.6 (CH), 120.7 (CH), 131.5 (CH), 137.4 (CH), 145.4 (C), 149.6 (C), 207.2 (C); IR (KBr) \( \nu = 3488, 2967, 2864, 1631, 1449, 1366, 1327, 1269, 1197, 1064, 1044, 905, 846, 765, 708, 570, 529, 490; \) MS (EI) \( m/z \) (%) = 230 (M\(^+\), 35), 212 (9), 164 [(M–C\(_5\)H\(_6\))\(^+\), 100], 146 (9), 137 [(M–C\(_7\)H\(_9\))\(^+\), 40]; Anal. calcd. for C\(_{14}\)H\(_{14}\)O\(_3\): C, 73.03; H, 6.13. Found: C, 73.04; H, 6.21. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 99:1, 0.5 mL/min, 230 nm, 20 °C, 47.2 min (+), 48.8 min (−): 54% ee.

(−)-exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone [(−)-exo -5a]. Colorless oil; \([\alpha]_D^{21} = -43.4 \ (c = 0.15, \text{CHCl}_3); \) \(^1\)H NMR (400 MHz) \( \delta = 1.39–1.47 \) (m, 1H), 1.47–1.58 (m, 2H), 2.01 (ddd, \( J = 11.6, 4.9, 3.6 \) Hz, 1H), 2.99 (s, 1H), 3.11 (s, 1H), 3.16 (ddd, \( J = 9.1, 4.9, 1.0 \) Hz, 1H), 6.19–6.32 (m, 2H), 6.89 (ddd, \( J = 8.3, 7.2, 1.2 \) Hz, 1H), 6.98 (dd, \( J = 8.4, 1.1 \) Hz, 1H), 7.45 (ddd, \( J = 8.5, 7.2, 1.7 \) Hz, 1H), 7.77 (dd, \( J = 8.1, 1.7 \) Hz, 1H), 12.49 (s, 1H); \(^{13}\)C NMR (100 MHz) \( \delta = 31.2 \) (CH\(_2\)), 42.1 (CH), 46.3 (CH), 46.3 (CH), 46.5 (CH\(_2\)), 207.2 (C); IR (KBr) \( \nu = 3488, 2967, 2864, 1631, 1449, 1366, 1327, 1269, 1197, 1064, 1044, 905, 846, 765, 708, 570, 529, 490; \) MS (EI) \( m/z \) (%) = 230 (M\(^+\), 35), 212 (9), 164 [(M–C\(_5\)H\(_6\))\(^+\), 100], 146 (9), 137 [(M–C\(_7\)H\(_9\))\(^+\), 40]; Anal. calcd. for C\(_{14}\)H\(_{14}\)O\(_3\): C, 73.03; H, 6.13. Found: C, 73.04; H, 6.21. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 99:1, 0.5 mL/min, 230 nm, 20 °C, 47.2 min (+), 48.8 min (−): 54% ee.
118.4 (CH), 118.7 (CH), 119.2 (C), 130.0 (CH), 135.7 (CH), 135.8 (CH), 138.6 (CH), 162.5 (C), 208.7 (C); IR (CHCl₃) \( \nu = 3059, 2976, 2872, 2362, 2335, 1636, 1579, 1487, 1447, 1350, 1287, 1237, 1203, 1157, 756, 714, 662 \); MS (EI) \( m/z \) (%) = 214 (M⁺, 35), 149 [(M+H–C₅H₆)⁺, 70], 148 (47), 147 (100), 121 [(M–C₇H₉)⁺, 79], 66 (C₅H₆⁺, 31). HRMS calcd. for C₁₄H₁₄O₂ 214.0994, found 214.0994. The enantiomer ratio was determined after hydrogenation to \( \text{exo-3a}. \)

\((\pm)\text{-exo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone} \ [\text{(+)-exo-5b}]. \) Mp 86–88°C; \([\alpha]_D^{22} = +65.3 \ (c = 0.35, \text{CHCl₃}); \] \(^1\)H NMR (400 MHz) \( \delta = 1.44–1.60 \) (m, 3H), 1.98 (ddd, \( J = 11.6, 4.9, 3.6 \) Hz, 1H), 3.02 (br s, 1H), 3.07 (ddd, \( J = 9.2, 5.0, 0.8 \) Hz, 1H), 3.11 (br s, 1H), 6.27 (dq, \( J = 5.6, 3.0 \) Hz, 1H), 7.56 (d, \( J = 2.5 \) Hz, 1H), 7.64 (d, \( J = 2.5 \) Hz, 1H), 12.99 (s, 1H); \(^{13}\)C NMR (100 MHz) \( \delta = 31.6 \) (CH₂), 42.2 (CH), 46.3 (CH), 46.6 (CH₂), 46.8 (CH), 120.3 (C), 123.2 (C), 127.9 (CH), 135.4 (CH), 138.9 (CH), 157.1 (C), 208.1 (C); IR (KBr) \( \nu = 3063, 2977, 2948, 2875, 1644, 1594, 1563, 1439, 1367, 1334, 1283, 1213, 1171, 1017, 900, 856, 800, 742, 721, 574, 558 \); MS (EI) \( m/z \) (%) = 284 [(M+2)⁺, 22], 283 [(M+1)⁺, 11], 282 (M⁺, 49), 219 (42), 218 [(M+2–C₃H₆)⁺, 68], 217 [(M+1–C₃H₆)⁺, 100], 216 [(M–C₃H₆)⁺, 98], 215 [(M–1–C₃H₆)⁺, 80], 191 [(M+2–C₇H₉)⁺, 27], 189 [(M–C₇H₉)⁺, 42], 66 (C₃H₆⁺, 63). Anal. calcd. for C₁₄H₁₂Cl₂O₂: C, 59.39; H, 4.27. Found: C, 59.49; H, 4.18. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 254 nm, 20 °C, 25.9 min (–), 28.5 min (+): 80% ee.

\((\pm)\text{-exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone} \ [\text{(+)-exo-5c}]. \) Mp 86–88°C; \([\alpha]_D^{22} = -95.6 \ (c = 0.11, \text{CHCl₃}); \] \(^1\)H NMR (400 MHz) \( \delta = 1.45–1.51 \) (m, 1H), 1.54 (br d, \( J = 9.4 \) Hz, 1H), 1.65 (ddd, \( J = 11.6, 9.3, 2.5 \) Hz, 1H), 1.99 (ddd, \( J = 11.6, 4.9, 3.5 \) Hz, 1H), 2.27 (t, \( J = 7.5 \) Hz, 2H), 2.99 (ddd, \( J = 13.5, 11.4, 2.5 \) Hz, 1H), 3.04 (ddd, \( J = 9.3, 6.7, 0.8 \) Hz, 1H), 3.07 (dd, \( J = 9.3, 6.3 \) Hz, 1H), 3.11 (br s, 1H), 6.29 (dq, \( J = 5.2, 3.0 \) Hz, 1H), 7.56 (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.64 (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.67 (s, 1H), 12.98 (s, 1H); \(^ {13}\)C NMR (100 MHz) \( \delta = 31.6 \) (CH₂), 42.2 (CH), 46.3 (CH), 46.7 (CH₂), 46.8 (CH), 120.3 (C), 123.2 (C), 127.9 (CH), 135.4 (CH), 138.9 (CH), 157.1 (C), 208.1 (C); IR (KBr) \( \nu = 3063, 2977, 2948, 2875, 1644, 1594, 1563, 1439, 1367, 1334, 1283, 1213, 1171, 1017, 900, 856, 800, 742, 721, 574, 558 \); MS (EI) \( m/z \) (%) = 284 [(M+2)⁺, 22], 283 [(M+1)⁺, 11], 282 (M⁺, 49), 219 (42), 218 [(M+2–C₃H₆)⁺, 68], 217 [(M+1–C₃H₆)⁺, 100], 216 [(M–C₃H₆)⁺, 98], 215 [(M–1–C₃H₆)⁺, 80], 191 [(M+2–C₇H₉)⁺, 27], 189 [(M–C₇H₉)⁺, 42], 66 (C₃H₆⁺, 63). Anal. calcd. for C₁₄H₁₂Cl₂O₂: C, 59.39; H, 4.27. Found: C, 59.49; H, 4.18. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 254 nm, 20 °C, 25.9 min (–), 28.5 min (+): 80% ee.
Hz, 1H), 3.05 (br s, 1H), 3.14 (br s, 1H), 3.20 (ddd, J = 9.3, 4.9, 0.9 Hz, 1H), 6.23–6.36 (m, 2H), 7.09 (d, J = 9.2 Hz, 1H), 8.34 (dd, J = 9.2, 2.7 Hz, 1H), 8.73 (d, J = 2.7 Hz, 1H), 13.11 (s, 1H); $^{13}$C NMR (100 MHz) δ = 31.6 (CH$_2$), 42.2 (CH), 46.2 (CH), 46.6 (CH$_2$), 46.7 (CH), 118.1 (C), 119.6 (CH), 126.5 (CH), 130.6 (CH), 135.6 (CH), 138.9 (CH), 139.4 (C), 167.4 (C), 208.5 (C); IR (KBr) ν = 2972, 1642, 1581, 1515, 1475, 1337, 1292, 1220, 1183, 1114, 824, 722; MS (EI) m/z (%) = 259 (M$^+$, 22), 194 [(M+1–C$_5$H$_6$)$_+$, 77], 166 (15), 148 (15), 120 (13), 93 (14), 66(C$_7$H$_6^+$, 100). Anal. calcd. for C$_{14}$H$_{13}$NO$_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 65.23; H, 5.17; N, 5.26. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 90:10, 0.5 mL/min, 254 nm, 20 °C, 23.7 min (–), 38.5 min (+): 94% ee.

(+)-exo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone [(+)-exo-5h]. Mp 83–85°C; [α]$_D^{22}$ = +43.1 (c = 0.12, CHCl$_3$); $^1$H NMR (400 MHz) δ = 1.40–1.57 (m, 3H), 2.02 (ddd, J = 11.6, 4.6, 3.7 Hz, 1H), 3.00 (s, 1H), 3.11 (s, 1H), 3.15 (dd, J = 9.0, 5.0 Hz, 1H), 5.73 (br s, 1H), 6.21–6.30 (m, 2H), 6.81 (t, J = 8.0, 8.0 Hz, 1H), 7.15-7.08 (m, 1H), 7.28–7.35 (m, 1H), 12.72 (s, 1H); $^{13}$C NMR (100 MHz) δ = 31.1 (CH$_2$), 42.1 (CH), 46.5 (CH), 46.6 (CH, 2C), 118.7 (CH), 119.1 (C), 119.7 (CH), 120.7 (CH), 135.7 (CH), 138.7 (CH), 145.4 (C), 149.7 (C), 209.2 (C); IR (KBr) ν = 3484, 2963, 2874, 1629, 1449, 1328, 1272, 1193, 1060, 908, 748, 714, 570, 528; MS (EI) m/z (%) = 230 (M$^+$, 20), 164[(M–C$_3$H$_6$)$_+$, 100], 146 (7), 137 [(M–C$_7$H$_9$)$_+$, 26]. Anal. calcd. for C$_{14}$H$_{14}$O$_5$: C, 73.03; H, 6.13. Found: C, 73.01; H, 6.16. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OJ, heptane/2-PrOH, 0.7 mL/min, 230 nm, 20 °C, 22.1 min (+), 25.0 min (–): 55% ee.
(11bR)-N,N-Dimethyl-2,6-bis[4-(trifluoromethyl)phenyl]dinaphtho[2,1-d:1',2'-
[1,3,2]dioxaphosphepin-4-amine [((R)-19]. Mp 156–159 °C; [α]_{D}^{22} = −397 (c = 0.16, CHCl₃); ¹H NMR (300 MHz) δ = 1.95 (s, 3H), 1.98 (s, 3H), 7.30-7.52 (m, 6H), 7.67–8.15 (m, 12H); ¹³C NMR (75 MHz) δ = 34.4 (d, ²J_C,P = 20.3 Hz, CH₃, 2C), 124.3 (q, ¹J_C,F = 266 Hz, C, 2C), 125.1 (q, ³J_C,F = 3.7 Hz, CH, 4C), 125.5 (CH, 2C), 126.5 (CH, 2C), 126.7 (CH, 2C), 126.9 (CH, 2C), 128.6 (CH, 2C), 129.4 (q, ²J_C,F = 32.4 Hz, C, 2C), 130.2 (CH, 4C), 130.9 (C, 2C), 131.0 (C, 2C), 132.7 (d, J_C,P = 8.8 Hz, C, 2C), 133.5 (C, 2C), 141.7 (C, 2C), 146.8 (d, J_C,P = 10.0 Hz, C, 2C); IR (KBr) ν = 3487, 3058, 2924, 1497, 1403, 1324, 1121, 1064, 1017, 956, 838, 746, 506; MS (EI) m/z (%) = 647 (M⁺, 100), 601 (13), 583 (18), 556 [(M–C₉H₆NOP)⁺, 28], 278 (17), 91 (22), 85 (35), 83 (42). HRMS calcd. for C₃₆H₂₄F₆NÖ₂P 647.1449, found 647.1448.

exo-(2-Hydroxyphenyl)(1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methanone (exo-29). This compound was prepared in analogy to RP4, using 1,4-epoxy-1,4-
dihydonaphthalene (28) and salicylaldehyde (1a, 3 h, 80 °C); 75% yield; mp 118–120 °C; ¹H NMR (300 MHz) δ = 1.93 (dd, J = 11.6, 9.0 Hz, 1H), 2.49 (dt, J = 11.5, 4.9 Hz, 1H), 3.48 (dd, J = 8.9, 4.7 Hz, 1H), 5.53 (d, J = 4.9 Hz, 1H), 5.70 (s, 1H), 6.89 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 7.19–7.28 (m, 2H), 7.29–7.40 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.64 (dd, J = 8.0, 1.2 Hz, 1H), 12.29 (s, 1H); ¹³C NMR (75 MHz) δ = 32.9 (CH₂), 47.8 (CH), 79.0 (CH), 80.6 (CH), 118.6 (C), 118.9 (CH, 2C), 118.9 (CH), 119.4 (CH), 127.0 (CH), 127.2 (CH), 129.6 (CH), 136.4 (CH), 144.4 (C), 146.0 (C), 162.9 (C), 205.1 (C); IR (KBr) ν = 3026, 3009, 1637, 1612, 1579, 1485, 1446, 1353, 1288, 1261, 1217, 1196, 1159, 1030, 990, 968, 915, 862, 840, 786, 758, 609; MS (EI) m/z (%) = 266 (M⁺, 28), 145 [(M–C₇H₅O₂)⁺, 25], 121 [(M–C₁₀H₉O)⁺, 33], 118 [(M–C₉H₈O₂)⁺, 100]. Anal. calcd. for C₁₇H₁₄O₃: C, 76.68; H, 5.30.
Found: C, 77.09; H, 5.43. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane/2-PrOH 90:10, 1.0 mL/min, 254 nm, 20 °C, 14.4 min, 29.8 min: racemate.

**Representative procedure for the synthesis of catalyst precursors 30-32.** These compounds were prepared in analogy to the procedure for the preparation of [Rh(acac)(coe)] by Varshavsky.\[^{[S2]}\] To a solution of \{[Rh(cod)Cl]₂\} (200 mg, 0.509 mmol, 0.5 equiv.) in benzene (30 mL) was added sodium 2,2,6,6-tetramethyl-3,5-heptanedionate (210 mg, 1.02 mmol, 1.0 equiv.) and the reaction mixture was heated to reflux for 80 min. After cooling to rt, the solution was filtered and the filtrate was concentrated in vacuo. The residue was taken up in Et₂O (5 mL) and concentrated again to give (2,2,6,6-tetramethyl-3,5-heptanedionato)-(1,5-cyclooctadiene)rhodium(I) (30) as a yellow crystalline powder (358 mg, 89%).

\[(2,2,6,6\text{-Tetramethyl-3,5-heptanedionato})-(1,5\text{-cyclooctadiene})\text{rhodium(I)} \quad (30).\]

168–171 °C (Lit.\[^{[S3]}\] 185 °C); \(^1\)H NMR (300 MHz) \(\delta = 1.08 \text{ (s, 18H)}, 1.70–1.98 \text{ (m, 4H)}, 2.31-2.63 \text{ (m, 4H)}, 4.07 \text{ (br s, 4H)}, 5.68 \text{ (s, 1H)}; \(^{13}\)C NMR (75 MHz) \(\delta = 28.6 \text{ (CH\textsubscript{3}, 6C)}, 30.2 \text{ (CH\textsubscript{2}, 4C)}, 40.9 \text{ (C, 2C)}, 76.4 \text{ (d, J\textsubscript{C,Rh} = 14.1 Hz, CH, 4C)}, 89.8 \text{ (CH, 1C)}, 196.0 \text{ (C, 2C)}; \text{IR (KBr)} \nu = 2962, 2873, 2833, 1544, 1499, 1457, 1386, 1357, 1225, 1139, 963, 874; MS (EI) \(m/z \% = 394 (M^+, 100), 337 (24), 309 (19), 211 [(M-dpm)^+, 78], 207 (25), 181 (17).\) Anal. calcd. for C\textsubscript{19}H\textsubscript{31}O\textsubscript{2}Rh: C, 57.87; H, 7.92. Found: C, 58.10; H, 8.14.

\[(1,3\text{-Diphenyl-1,3-propanedionato})-(1,5\text{-cyclooctadiene})\text{rhodium(I)} \quad (31).\]

The same procedure as described for the synthesis of 30 was applied using sodium 1,3-diphenyl-1,3-propanedionate (251 mg, 1.02 mmol, 1.0 equiv.). Rhodium complex 31 was obtained in 90%
yield (398 mg). Mp 176–178 °C (dec.); $^1$H NMR (300 MHz) $\delta$ = 1.83–2.03 (m, 4H), 2.40–2.70 (m, 4H), 4.29 (br s, 4H), 6.66 (s, 1H), 7.32–7.50 (m, 6H), 7.78–7.89 (m, 4H); $^{13}$C NMR (75 MHz) $\delta$ = 30.3 (CH$_2$, 4C), 77.0 (d, $J_{C,Rh}$ = 14.0 Hz, 4C), 94.1 (CH, 1C), 127.3 (CH, 4C), 128.2 (CH, 4C), 130.8 (CH, 2C), 139.6 (C, 2C), 181.5 (C, 2C); IR (KBr) $\nu$ = 2829, 1590, 1477, 1452, 1381, 1305, 1263, 1225, 1073, 1023, 755, 694, 652; MS (EI) $m/z$ (%) = 434 (M$^+$, 100), 208 (22), 182 (16), 149 (20). Anal. calcd. for C$_{23}$H$_{23}$O$_2$Rh: C, 63.60; H, 5.38. Found: C, 63.48; H, 5.10.

(1,1,1,5,5,5-Hexafluoroacetylacetonato)-(1,5-cyclooctadiene)rhodium(I) (32). The same procedure as described for the synthesis of 30 was applied using sodium 1,1,1,5,5,5-hexafluoroacetylacetonate (187 mg, 0.811 mmol, 1.0 equiv.). Rhodium complex 32 was obtained in 98% yield (336 mg). Mp 122–124 °C; $^1$H NMR (400 MHz) $\delta$ = 1.87–1.94 (m, 4H, CH$_2$), 2.37–2.63 (m, 4H, CH$_2$), 4.30 (br s, 4H, CH), 6.12 (s, 1H, CH); $^{13}$C NMR (100 MHz) $\delta$ = 30.1 (s, CH$_2$, 4C), 78.2 (s, CH, 2C), 78.4 (s, CH, 2C), 90.1 (s, CH), 117.6 (q, $J_{C,F}$ = 284.0 Hz, CF$_3$, 2C), 174.6 (q, $J_{C,F}$ = 34.3 Hz, CO, 2C) $^{19}$F NMR (376 MHz) $\delta$ = –74.91 (s); IR (KBr) $\nu$ = 2953, 2887, 2843, 1618, 1553, 1463, 1345, 1263, 1200, 1146, 802, 681, 590; MS (EI) $m/z$ (%) = 418 (M$^+$, 100), 211 [(M–hfac)$^+$, 38]. Anal. calcd. for C$_{13}$H$_{13}$F$_6$O$_2$Rh: C, 37.34; H, 3.13. Found: C, 37.24; H, 3.35.

(R)-2,2'-Bis(methoxymethoxy)-3,3'-bis(4-(trifluoromethyl)phenyl)-1,1'-binaphthyl [(R)-40]. Mp 79–82 °C; [$\alpha$]$_D^{22}$ = –103 (c = 0.37, CHCl$_3$); $^1$H NMR (300 MHz) $\delta$ = 2.38 (s, 6H), 4.36 (d, $J_{gem}$ = 5.9 Hz, 2H), 4.41 (d, $J_{gem}$ = 5.9 Hz, 2H), 7.28–7.39 (m, 4H), 7.47 (ddd, $J$ = 8.1, 5.7, 2.3 Hz, 2H), 7.71–7.80 (m, 4H), 7.89–7.94 (m, 6H), 7.99 (s, 2H); $^{13}$C NMR (75
MHz) δ = 55.9 (CH₃, 2C), 98.8 (CH₂, 2C), 124.3 (q, ¹JC,F = 272 Hz, C, 2C), 125.2 (q, ³JC,F = 3.6 Hz, CH, 4C), 125.5 (CH, 2C), 126.3 (CH, 2C), 126.5 (C, 2C), 126.9 (CH, 2C), 128.1 (CH, 2C), 129.4 (q, ²JC,F = 32.4 Hz, C, 2C), 130.0 (CH, 4C), 130.8 (C, 2C), 130.8 (CH, 2C), 133.9 (C, 2C), 134.1 (C, 2C), 142.7 (C, 2C), 151.1 (C, 2C); ¹⁹F NMR (282 MHz) δ = −62.38 (s); IR (KBr) ν = 3854, 3743, 3060, 2942, 2361, 2341, 1737, 1718, 1502, 1455, 1398, 1124, 1070, 969, 917, 842, 749, 666, 606; MS (EI) m/z (%) = 662 (M⁺, 16), 586 [(M–C₃H₈O₂)⁺, 100], 558 (58), 413 (10). Anal. calcd. for C₃₈H₂₈O₄F₆: C, 68.88; H, 4.26. Found: C, 68.61; H, 4.49.

(R)-3,3’-Bis[4-(trifluoromethyl)phenyl]-1,1’-binaphthyl-2,2’-diol [(R)-41]. Mp 102–105 °C; [α]D²² = +50.2 (c = 0.21, CHCl₃); ¹H NMR (400 MHz) δ = 5.35 (s, 2H), 7.38 (ddd, J = 8.0, 6.9, 1.1 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.44 (ddd, J = 8.0, 6.9, 0.9 Hz, 2H), 7.75 (d, J = 8.2 Hz, 4H), 7.88 (d, J = 8.1 Hz, 4H), 7.97 (d, J = 8.0 Hz, 2H), 8.07 (s, 2H); ¹³C NMR (100 MHz) δ = 111.9 (C, 2C), 124.0 (CH, 2C), 124.2 (q, ¹JC,F = 272 Hz, C, 2C), 127.7 (CH, 2C), 125.2 (q, ³JC,F = 3.5 Hz, CH, 4C), 128.0 (CH, 2C), 128.6 (CH, 2C), 129.4 (C, 2C), 129.5 (C, 2C), 129.7 (q, ²JC,F = 32.9 Hz, C, 2C), 129.9 (CH, 4C), 132.0 (CH, 2C), 133.0 (C, 2C), 141.0 (C, 2C), 150.0 (C, 2C); IR (KBr) ν = 3854, 3742, 3513, 2361, 2341, 1714, 1619, 1510, 1325, 1122, 1068, 841; MS (EI) m/z (%) = 574 (M⁺, 100), 555(7), 259 (23). Anal. calcd. for C₃₄H₂₀O₂F₆: C, 71.08; H, 3.51. Found: C, 71.02; H, 3.78.
References


exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxyphenyl)methanone (exo-3a)
exo-Bicyclo[2.2.1]heptan-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [exo-3b]
exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxy-5-nitrophenyl)methanone (exo-3c)
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone (exo-5a)
(+)-endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone (endo-5a)
exo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone (exo-5b)
endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone (endo-5b)
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone (exo-5c)
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone (endo-5c)
endo-(2-Amino-3,5-dibromophenyl)(bicyclo[2.2.1]hept-5-en-2-yl)methanone (endo-5d)
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxynaphthalen-1-yl)methanone (endo-5e)
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-methylphenyl)methanone (endo-5f)
endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-di-tert-butyl-2-hydroxyphenyl)methanone (endo-5g)
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone (exo-5h)
**endo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone (endo-5h)**
(11bR)-N,N-dimethyl-2,6-bis[4-(trifluoromethyl)phenyl]dinaphtho[2,1-\textit{d}:1',2'-\textit{f}][1,3,2]dioxaphosphepin-4-amine [(\textit{R})-\textbf{19}]
exo-(2-Hydroxyphenyl)(1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methanone (exo-29)
(2,2,6,6-Tetramethyl-3,5-heptanedionato)-(1,5-cyclooctadiene)rhodium(I) (30)
(1,3-Diphenyl-1,3-propanedionato)-(1,5-cyclooctadiene)rhodium(I) \( \text{31} \)
(1,1,1,5,5,5-Hexafluoroacetylacetonato)-(1,5-cyclooctadiene)rhodium(I) (32)
(R)-2,2'-Bis(methoxymethoxy)-3,3'-bis(4-(trifluoromethyl)phenyl)-1,1'-binaphthyl [(R)-40]
(R)-3,3'-Bis[4-(trifluoromethyl)phenyl]-1,1'-binaphthyl-2,2'-diol [(R)-41]