

Advanced
**Synthesis &
Catalysis**

Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2008

SUPPORTING INFORMATION

Chiral Bis(*N*-arylamino)phosphine-oxazolines: Synthesis and Application in Iridium-Catalyzed Asymmetric Hydrogenation

Marc Schönleber, Robert Hilgraf, Andreas Pfaltz*

Department of Chemistry, University of Basel, St. Johannis-Ring 19,
4056 Basel, Switzerland

Fax: (+41)-61-267-1103. e-mail: Andreas.Pfaltz@unibas.ch

General Remarks

NMR spectra were recorded on a Bruker Avance DRX 500 (^1H : 500 MHz, ^{31}P : 202.5 MHz, ^{13}C : 125.8 MHz), Bruker Avance DPX 400 (^1H : 400 MHz, ^{31}P : 162.0 MHz, ^{13}C : 100.6 MHz), Varian Gemini 300 (^1H : 300 MHz, ^{31}P : 121.5 MHz, ^{13}C : 75.5 MHz). All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ value in CDCl_3 or C_6D_6). MS was measured on Finnegan MAT 312 (FAB), VG 70-SE (70 eV, EI) in m/z (% of basic peak). IR spectra were obtained with a Perkin Elmer 1600 FTIR-spectrometer. Optical rotation was measured with a Perkin Elmer PE-141 polarimeter. Melting points were obtained on a Büchi 535 apparatus; values are uncorrected. The hydrogenation reactions were performed in a 60 ml autoclave from Premex Reactor AG (Lengnau, Switzerland). GC was measured on CE Instruments GC 8000 Top (FID detector). HPLC was measured on a Shimadzu SCL-10A. Elemental analyses were performed by the Microanalytical Laboratory of the Institut für Organische Chemie, Universität Basel. Column chromatography was conducted on Merck silica gel 60, 0.040–0.063 mm, 230–400 mesh, or on silica gel C-560, 0.035–0.070 mm, available from Uetikon Chemie (Uetikon, Switzerland). TLC was performed with Macherey-Nagel Polygram SIL G/UV₂₅₄ plates, detection by UV or common detecting agents (alkaline KMnO_4 solution) followed by heating. Solvents were dried and distilled shortly before use. All reagents were purchased from Fluka, Aldrich, Acros, Lancaster and Strem and

used without further purification. All reactions were carried out under an atmosphere of argon.

Analytical data of compounds synthesized according to the general procedure for the bis-arylation of chiral diamines

(1*R*,2*R*)-1,2-*N,N'*-Bis(3-methoxyphenylamino)-1,2-diphenylethane (6a): White solid; yield: 80%; mp 146–147 °C; $[\alpha]_D^{20}$: + 107.2 (c 0.96, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.20–7.08 (m, 10H, *H*_{Ar}), 6.94 (t, ³*J* = 8.3 Hz, 2H, *H*_{Ar}), 6.24–6.18 (m, 2H, *H*_{Ar}), 6.13–6.11 (m, 2H, *H*_{Ar}), 6.05 (t, ⁴*J* = 2.0 Hz, 2H, *H*_{Ar}), 4.66 (br s, 2H, NH), 4.52 (s, 2H, CH-N), 3.61 (s, 6H, CH₃-O); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 161.0 (s, 2C, ArC-O), 148.9 (s, 2C, ArC-N), 140.4 (s, 2C, PhC(*ipso*)), 130.2 (s, 2C, ArC-H), 128.8 / 127.9 / 127.8 (s, 10C, PhC-H), 107.5 / 103.8 / 100.5 (s, 6C, ArC-H), 64.4 (s, 2C, CH-N), 55.3 (s, 2C, CH₃-O); IR (NaCl): 3406s, 3079w, 3005m, 2963m, 2937m, 2876m, 2839m, 1962w, 1914w, 1820w, 1614s, 1494s, 1453s, 1413s, 1321s, 1277s, 1209s, 1162s, 1097m, 1071m, 1038s, 990w, 934w, 838s, 756s, 706s, 690s cm⁻¹; MS (FAB): *m/z* = 425 ([M]⁺, 7), 302 (11), 213 (18), 212 (100); anal. calcd. for C₂₈H₂₈N₂O₂: C 79.22, H 6.65, N 6.60, O 7.54; found: C 78.93, H 6.85, N 6.31, O 7.39.

(1*R*,2*R*)-1,2-*N,N'*-Bis(4-methoxyphenylamino)-1,2-diphenylethane (6b): Pale brown solid; yield: 47%; mp 58–60 °C; $[\alpha]_D^{20}$: + 79.2 (c 0.55, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.25–7.12 (m, 10H, *H*_{Ar}); 6.70–6.54 / 6.51–6.45 (m, 8H, *H*_{Ar}); 4.46 (s, 2H, CH-N); 4.40 (br s, 2H, NH); 3.68 (s, 6H, CH₃-O); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 152.4 / 141.2 / 140.3 (s, 6C, ArC-O, ArC-N and PhC(*ipso*)); 128.3 / 127.4 / 127.3 / 115.3 / 114.7 (s, 18C, PhC-H and ArC-H); 64.9 (s, 2C, CH-N); 55.6 (s, 2C, CH₃-O); IR (KBr): 3356w, 3058w, 3026w, 2996w, 2928w, 2902w, 2830w, 1603w, 1508s, 1452m, 1405w, 1293w, 1239s, 1178m, 1035m, 818m, 756m, 700m, 587w, 522w cm⁻¹; MS (FAB): *m/z* = 425 ([M]⁺, 5), 302 (7), 213 (17), 212 (100), 122 (5); anal. calcd. for C₂₈H₂₈N₂O₂: C 79.22, H 6.65, N 6.60; found: C 79.04, H 6.65, N 6.38.

(1R,2R)-1,2-*N,N'*-Bis(4-*tert*-butylphenylamino)-1,2-diphenylethane (6c): White solid; yield: 89%; mp 80–82 °C; $[\alpha]_D^{20}$: + 84.7 (c 0.86, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.32–7.19 (m, 10H, *H*_{Ar}); 7.16 (d, ³*J* = 8.6 Hz, 4H, *H*_{Ar}); 6.63 (d, ³*J* = 8.6 Hz, 4H, *H*_{Ar}); 4.60 (br s, 2H, *NH*); 4.55 (s, 2H, *CH-N*); 1.28 (s, 18H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 144.4 / 140.4 / 140.1 (s, 6H, PhC(*ipso*), ArC-C and ArC-N); 128.1 / 127.1 / 127.0 / 125.5 / 113.4 (s, 18C, ArC-H); 64.1 (s, 2C, CH-N); 33.5 (s, 2C, C(CH₃)₃); 31.1 (s, 6C, C(CH₃)₃); IR (KBr): 3382w, 3059w, 3026m, 2959m, 2900m, 2869m, 1613m, 1517s, 1474m, 1452m, 1403m, 1392w, 1361m, 1318m, 1300m, 1261m, 1194m, 1155w, 1128w, 1094w, 1068w, 1027w, 912w, 886w, 820m, 771m, 752w, 699s, 620w, 549m, 512w cm⁻¹; MS (FAB): *m/z* = 477 ([M]⁺, 7), 328 (6), 239 (20), 238 (100), 57 (13); anal. calcd. for C₃₄H₄₀N₂: C 85.67, H 8.46, N 5.88; found: C 85.63, H 8.35, N 5.79.

(1R,2R)-1,2-*N,N'*-Bis(4-biphenylamino)-1,2-diphenylethane (6d): White solid (recrystallized from CH₂Cl₂/hexane); yield: 29%; mp 216–218 °C; $[\alpha]_D^{20}$: + 126.4 (c 0.95, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.49–7.43 (m, 4H, *H*_{Ar}); 7.39–7.30 (m, 8H, *H*_{Ar}); 7.28–7.15 (m, 12H, *H*_{Ar}); 6.59 (d, ³*J* = 8.6 Hz, 4H, *H*_{Ar}); 4.65 (br s, 2H, *NH*); 4.63 (s, 2H, *CH-N*); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 146.4 / 141.0 / 139.8 / 131.2 (s, 8C, ArC(*ipso*)); 128.6 / 128.5 / 127.8 / 127.7 / 127.4 / 126.3 / 126.2 / 114.4 (s, 28C, ArC-H); 64.0 (s, 2C, CH-N). IR (NaCl): 3387w, 3059w, 3026w, 1610s, 1522s, 1488s, 1453m, 1442m, 1404w, 1319m, 1297m, 1272m, 1190w, 1123w, 1095w, 1071w, 1028w, 908w, 824m, 761s, 732m, 697s cm⁻¹. MS (FAB): *m/z* = 517 ([M]⁺, 3), 348 (7), 259 (24), 258 (100), 257 (10), 153 (12), 152 (15); anal. calcd. for C₃₈H₃₂N₂: C 88.34, H 6.24, N 5.42; found: C 88.01, H 6.16, N 5.25.

(1R,2R)-*N,N'*-Bis(2-naphthyl)-1,2-diphenylethane-1,2-diamine (6e): White solid; yield: 90%; mp 216–217 °C; $[\alpha]_D^{20}$: + 97.6 (c 0.70, CHCl₃); ¹H-NMR (300 MHz, CDCl₃): δ = 7.54 (br d, ³*J* = 8.1 Hz, 2H, *H*_{Ar}); 7.51 (d, ³*J* = 8.8 Hz, 2H, *H*_{Ar}); 7.36 (br d, ³*J* = 8.2 Hz, 2H, *H*_{Ar}); 7.24–7.04 (m, 14H, *H*_{Ar}); 6.83 (dd, ³*J* = 8.8 Hz, ⁴*J* = 2.2 Hz, 2H, *H*_{Ar}); 6.56 (d, ⁴*J* = 2.2 Hz, 2H, *H*_{Ar}); 4.71 (s, 2H, *CH-N*); 4.65 (br s, 2H, *NH*); ¹³C{¹H}-NMR (75

MHz, CDCl₃): δ = 144.4 (s, 2C, ArC-N); 139.5 (s, 2C, PhC(*ipso*)); 134.7 / 127.8 (s, 4C, ArC-C); 128.9 / 128.5 / 127.7 / 127.5 / 127.4 / 126.2 / 126.1 (s, 2C / 4C / 2C / 2C / 4C / 2C / 2C, 8ArC-H and 10PhC-H); 122.4 / 118.3 / 107.0 (s, 6C, ArC-H); 63.8 (s, 2C, CH-N); IR (NaCl): 3386w, 3057w, 2851w, 1628s, 1601s, 1517s, 1472m, 1395m, 908w, 834m, 807m, 746m, 698m cm⁻¹; MS (FAB): m/z = 465 ([M+H]⁺, 1), 233 (21), 232 (100), 131 (49), 115 (17), 103 (16), 91 (24), 43 (21); anal. calcd. for C₃₄H₂₈N₂: C 87.90, H 6.07, N 6.03; found: C 87.74, H 6.27, N 5.87.

1-(Bromomethyl)naphthalene (8): Colorless solid; yield: 2.11 g (95%); mp 50–52 °C; ¹H-NMR (400 MHz, CDCl₃): δ = 8.15 (dd, ³J = 8.6 Hz, ⁴J = 0.8 Hz, 1H, H_{Ar}); 7.90–7.87 (m, 1H, H_{Ar}); 7.84 (d, ³J = 8.3 Hz, 1H, H_{Ar}); 7.61 (ddd, ³J = 8.3 Hz, ³J = 6.8 Hz, ⁴J = 1.3 Hz, 1H, H_{Ar}); 7.54 (dd, ³J = 7.1 Hz, ⁴J = 1.3 Hz, 1H, H_{Ar}); 7.52 (ddd, ³J = 8.1 Hz, ³J = 6.8 Hz, ⁴J = 1.3 Hz, 1H, H_{Ar}); 7.41 (dd, ³J = 8.1 Hz, ³J = 6.8 Hz, 1H, H_{Ar}); 4.96 (s, 2H, CH₂-Br). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 134.0 / 133.3 / 131.1 (s, 3C, ArC-C); 129.8 / 128.8 / 127.7 / 126.6 / 126.2 / 125.4 / 123.7 (s, 7C, ArC-H); 31.7 (s, 1C, CH₂-Br). IR (NaCl): 3063m, 3047m, 3010m, 2971w, 2927w, 2862w, 1944w, 1878w, 1817w, 1724w, 1596m, 1578w, 1511s, 1450m, 1398m, 1378w, 1351m, 1242m, 1207s, 1168m, 1144m, 1119w, 1078w, 1040w, 1017m, 970w, 951w, 910w, 886w, 866w, 799s, 774s, 734m, 706m, 655m, 596s, 575s cm⁻¹. MS (FAB): m/z = 222 (7), 221 ([M]⁺, 7), 141 (100); anal. calcd. for C₁₁H₉Br: C 59.76, H 4.10; found: C 59.57, H 4.01.

(1R,2R)-N,N'-Bis((1-naphthyl)methyl)-1,2-diphenylethane-1,2-diamine (6f): Yellow solid; yield: 39%; mp 45–46 °C; [α]_D²⁰: + 1.2 (c 1.06, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.91 (d, ³J = 8.6 Hz, 2H, H_{Ar}); 7.81 (d, ³J = 8.1 Hz, 2H, H_{Ar}); 7.72 (d, ³J = 8.1 Hz, 2H, H_{Ar}); 7.40 (t, ³J = 7.2 Hz, 2H, H_{Ar}); 7.33 (t, ³J = 7.6 Hz, 2H, H_{Ar}); 7.30–7.07 (m, 14H, H_{Ar}); 4.03 / 3.89 (d, ²J = 14.9 Hz, 4H, CH₂); 3.78 (s, 2H, CH-N); 2.47 (br s, 2H, NH); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 141.3 / 136.1 / 133.8 / 131.9 (s, 8C, ArC-C und PhC(*ipso*)); 128.4 / 128.0 / 127.6 / 127.0 / 126.1 / 125.8 / 125.5 / 125.2 / 124.0 (s, 24C, 14ArC-H and 10PhC-H); 69.1 (s, 2C, CH-N); 49.5 (s, 2C, CH₂); IR (NaCl): 3310m, 3059s, 3027s, 2899m, 2845m, 1738m, 1597m, 1509m, 1493m, 1454s, 1397m, 1372m, 1348m, 1264s, 1242m, 1199m, 1166m, 1109s, 1071s, 1027m, 1017m, 968w, 914w,

880m, 858m, 791s, 736s, 699s cm^{-1} ; MS (FAB): $m/z = 493$ ($[\text{M}]^+$, 23), 246 (43), 142 (14), 141 (100); anal. calcd. for $\text{C}_{36}\text{H}_{32}\text{N}_2$: C 87.77, H 6.55, N 5.69; found: C 87.47, H 6.86, N 5.31.

(1R,2R)-N,N'-Di-*p*-tolylcyclohexane-1,2-diamine (6g): Orange-brown oil; yield: 76%; $[\alpha]_D^{20}$: + 46.6 (c 0.56, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.00$ (d, $^3J = 8.0$ Hz, 4H, H_{Ar}); 6.56 (d, $^3J = 8.0$ Hz, 4H, H_{Ar}); 3.70 (br s, 2H, NH); 3.19–3.12 (m, 2H, CH-N); 2.38–2.28 (m, 2H, CH_2); 2.26 (s, 6H, CH_3); 1.84–1.72 / 1.49–1.35 / 1.31–1.18 (m, 6H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 145.5$ (s, 2C, ArC-N); 129.8 (s, 4C, ArC-H); 126.9 (s, 2C, ArC- CH_3); 113.8 (s, 4C, ArC-H); 57.7 (s, 2C, CH-N); 32.6 / 24.6 (s, 4C, CH_2); 20.3 (s, 2C, ArC- CH_3); IR (NaCl): 3375m, 3018m, 2928s, 2856s, 1616s, 1584m, 1517s, 1484m, 1449m, 1406m, 1357m, 1301s, 1253s, 1202w, 1182m, 1137m, 1102m, 954w, 876w, 855w, 807s, 702w cm^{-1} ; MS (FAB): $m/z = 295$ (25), 294 ($[\text{M}]^+$, 29), 189 (14), 188 (100), 91 (9); (AMM): calcd. for $\text{C}_{20}\text{H}_{26}\text{N}_2$: 294.20960; found: 294.20996.

Analytical data of compounds synthesized according to the general procedure for the synthesis of ligands 10a-g

(4R,5R)-1,3-Bis(3-methoxyphenyl)-2-(2-((S)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10a): White solid; yield: 61%; mp 55–57 °C; $[\alpha]_D^{20}$: + 72.0 (c 0.98, CHCl_3); $^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 7.36$ (dd, $^3J = 8.1$ Hz, $^4J = 1.6$ Hz, 2H, PhC-*H*(*ortho*)); 7.29–7.18 (m, 6H, PhC-*H*(*meta* and *para*)); 7.13 (dd, $^3J = 7.9$ Hz, $^4J = 1.9$ Hz, 2H, PhC-*H*(*ortho*)); 7.01 (t, $^3J = 8.2$ Hz, 1H, H_{Ar}); 7.00 (t, $^3J = 8.1$ Hz, 1H, H_{Ar}); 6.67–6.62 (m, 1H, H_{Ar}); 6.60–6.57 (m, 2H, H_{Ar}); 6.52–6.48 (m, 1H, H_{Ar}); 6.41–6.38 (m, 1H, H_{Ar}); 6.34 (dd, $^3J = 8.2$ Hz, $^4J = 2.2$ Hz, 1H, H_{Ar}); 5.10 (d, $^3J = 7.8$ Hz, 1H, CH-N); 4.84 (dd, $^3J = 7.8$ Hz, $^3J_{\text{HP}} = 2.5$ Hz, 1H, CH-N); 4.13–4.07 (m, 2H, $\text{CH}_2\text{-Ox.}$); 3.82 (dd, $^3J = 9.4$ Hz, $^3J = 8.3$ Hz, 1H, CH-Ox.); 3.66 / 3.63 (s, 6H, $\text{CH}_3\text{-O}$); 1.45 / 1.42 (s, 6H, $\text{C}(\text{CH}_3)_2$); 0.88 (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 168.7$ (s, 1C, C=N); 160.5 / 160.4 (s, 2C, ArC-O); 146.5 (d, $^2J_{\text{CP}} = 22.8$ Hz, 1C, ArC-N); 144.3 (d, $^2J_{\text{CP}} = 11.0$ Hz, 1C, ArC-N); 141.2 / 139.9 (s, 2C, PhC(*ipso*));

128.9 / 128.8 / 128.1 / 128.0 / 127.9 / 127.8 (s, 10C, PhC-H(*ortho*, *meta* and *para*)); 129.7 / 129.6 (s, 2C, ArC-H); 115.1 (d, $J_{CP} = 10.0$ Hz, 1C, ArC-H); 109.8 (d, $J_{CP} = 16.9$ Hz, 1C, ArC-H); 108.2 (d, $J_{CP} = 9.2$ Hz, 1C, ArC-H); 108.0 / 105.3 (s, 2C, ArC-H); 103.4 (d, $J_{CP} = 16.1$ Hz, 1C, ArC-H); 76.0 (s, 1C, CH-Ox.); 74.4 (d, $^2J_{CP} = 8.7$ Hz, 1C, CH-N); 74.2 (s, 1C, C(CH₃)₂); 71.5 (d, $^2J_{CP} = 6.9$ Hz, 1C, CH-N); 69.2 (s, 1C, CH₂-Ox.); 55.4 / 55.3 (s, 2C, CH₃-O); 34.1 (s, 1C, C(CH₃)₃); 28.9 (d, $^3J_{CP} = 4.9$ Hz, 1C, C(CH₃)₂); 28.2 (d, $^3J_{CP} = 10.2$ Hz, 1C, C(CH₃)₂); 26.2 (s, 3C, C(CH₃)₃); ³¹P{¹H}-NMR (242 MHz, CDCl₃): $\delta = 117.4$ (s); IR (NaCl): 3443s, 3062m, 3020m, 2957s, 2903m, 2834m, 1667s, 1599s, 1493s, 1454s, 1365m, 1294m, 1266m, 1204s, 1163s, 1132m, 1049m, 978m, 949m, 873m, 834m, 769m, 717m, 688m cm⁻¹; MS (FAB): $m/z = 638$ ([M]⁺, 21), 637 (23), 469 (54), 468 (38), 454 (31), 453 (100), 212 (58), 210 (38), 169 (31), 168 (75), 152 (49), 69 (67), 57 (28), 55 (64), 53 (39), 43 (50), 41 (32); anal. calcd. for C₃₈H₄₄N₃O₄P: C 71.57, H 6.95, N 6.59, O 10.04; found: C 71.22, H 7.15, N 6.35, O 10.21.

(4*R*,5*R*)-1,3-Bis(4-methoxyphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10b): Pale yellow solid; yield: 64%; mp 66–68 °C; $[\alpha]_D^{20}$: + 71.3 (c 0.84, CHCl₃); ¹H-NMR (300 MHz, CDCl₃): $\delta = 7.39$ – 7.09 (m, 10H, H_{Ar}); 7.05–6.97 / 6.96–6.88 (m, 4H, H_{Ar}); 6.72–6.64 (m, 4H, H_{Ar}); 5.10 (br d, $^3J = 8.4$ Hz, 1H, CH-N); 4.81 (dd, $^3J = 8.4$ Hz, $^3J_{HP} = 2.5$ Hz, 1H, CH-N); 4.14 (dd, $^3J = 10.1$ Hz, $^2J = 8.7$ Hz, 1H, CH₂-Ox.); 4.09 (dd, $^2J = 8.7$ Hz, $^3J = 7.5$ Hz, 1H, CH₂-Ox.); 3.86 (dd, $^3J = 10.1$ Hz, $^3J = 7.5$ Hz, 1H, CH-Ox.); 3.69 / 3.68 (s, 6H, CH₃-O); 1.42 / 1.38 (s, 6H, C(CH₃)₂); 0.91 (s, 9H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, C₆D₆): $\delta = 169.1$ (s, 1C, C=N); 155.5 (d, $^5J_{CP} = 3.1$ Hz, 1C, ArC-O); 154.4 (s, 1C, ArC-O); 141.6 (s, 1C, ArC-N or PhC(*ipso*)); 139.9 (d, $J_{CP} = 3.8$ Hz, 1C, ArC-N oder PhC(*ipso*)); 138.8 (d, $J_{CP} = 23$ Hz, 1C, ArC-N or PhC(*ipso*)); 136.2 (d, $J_{CP} = 9.2$ Hz, 1C, ArC-N or PhC(*ipso*)); 128.8 / 128.7 / 128.5 / 128.4 / 127.9 / 127.6 (s, 10C, PhC-H); 124.3 (d, $J_{CP} = 7.7$ Hz, 2C, ArC-H); 119.1 (d, $J_{CP} = 14$ Hz, 2C, ArC-H); 114.6 / 114.4 (s, 4C, ArC-H); 76.1 (s, 1C, CH-Ox.); 75.2 (d, $^2J_{CP} = 8.4$ Hz, 1C, CH-N); 73.9 (d, $^2J_{CP} = 11$ Hz, 1C, C(CH₃)₂); 72.2 (d, $^2J_{CP} = 6.9$ Hz, 1C, CH-N); 68.9 (s, 1C, CH₂-Ox.); 55.0 / 54.7 (s, 2C, CH₃-O); 33.7 (s, 1C, C(CH₃)₃); 29.2 (d, $^3J_{CP} = 3.8$ Hz, 1C, C(CH₃)₂); 28.2 (d, $^3J_{CP} = 11$ Hz, 1C, C(CH₃)₂); 26.0 (s, 3C, C(CH₃)₃); ³¹P{¹H}-NMR (162 MHz, C₆D₆): $\delta = 118.4$ (s); IR (KBr): 3028w,

2953m, 2902m, 2867m, 1665m, 1507s, 1454m, 1364w, 1286m, 1237s, 1179m, 1157m, 1128m, 1060m, 1036m, 977m, 943m, 917m, 871m, 820m, 771m, 708m cm^{-1} ; MS (FAB): $m/z = 638$ ($[\text{M}]^+$, 14), 637 (25), 470 (31), 469 (100), 468 (58), 454 (28), 453 (87), 215 (23), 212 (89), 211 (40), 210 (41), 169 (23), 168 (95), 158 (25), 152 (93); anal. calcd. for $\text{C}_{38}\text{H}_{44}\text{N}_3\text{O}_4\text{P}$: C 71.57, H 6.95, N 6.59; found: C 71.42, H 7.08, N 6.41.

(4*R*,5*R*)-1,3-Bis(4-*tert*-butylphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10c): Pale yellow solid; yield: 54%; mp 119–122 °C; $[\alpha]_D^{20}$: + 18.1 (c 0.76, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 7.42\text{--}7.39$ (m, 2H, H_{Ar}); 7.31–7.17 (m, 6H, H_{Ar}); 7.16–7.12 (m, 4H, H_{Ar}); 7.12–7.08 (m, 2H, H_{Ar}); 7.01–6.96 (m, 2H, H_{Ar}); 6.91–6.87 (m, 2H, H_{Ar}); 5.12 (d, $^3J = 7.7$ Hz, 1H, CH-N); 4.82 (dd, $^3J = 7.7$ Hz, $^3J_{\text{HP}} = 2.8$ Hz, 1H, CH-N); 4.02 (dd, $^2J = 8.6$ Hz, $^3J = 7.6$ Hz, 1H, $\text{CH}_2\text{-Ox.}$); 3.94 (dd, $^3J = 9.9$ Hz, $^2J = 8.6$ Hz, 1H, $\text{CH}_2\text{-Ox.}$); 3.80 (dd, $^3J = 9.9$ Hz, $^3J = 7.6$ Hz, 1H, CH-Ox.); 1.48 / 1.39 (s, 6H, $\text{C}(\text{CH}_3)_2$); 1.24 / 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$); 0.87 (s, 9H, $\text{C}(\text{CH}_3)_3\text{-Ox.}$); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3): $\delta = 169.2$ (s, 1C, C=N); 144.0 (d, $^5J_{\text{CP}} = 3.0$ Hz, 1C, $\text{ArC}(ipso)$); 142.4 (d, $^2J_{\text{CP}} = 23.0$ Hz, 1C, $\text{ArC}(ipso)$); 141.9 (d, $^5J_{\text{CP}} = 1.0$ Hz, 1C, $\text{ArC}(ipso)$); 141.2 (s, 1C, $\text{PhC}(ipso)$); 140.1 (d, $^2J_{\text{CP}} = 10.3$ Hz, 1C, $\text{ArC}(ipso)$); 140.0 (d, $^3J_{\text{CP}} = 3.4$ Hz, 1C, $\text{PhC}(ipso)$); 128.5 / 128.4 / 127.9 / 127.7 (s, 8C, PhC-H); 127.4 / 127.3 (s, 2C, PhC-H); 125.5 / 125.4 (s, 4C, ArC-H); 121.3 (d, $^3J_{\text{CP}} = 9.6$ Hz, 2C, ArC-H); 115.8 (d, $^3J_{\text{CP}} = 16.0$ Hz, 2C, ArC-H); 75.5 (s, 1C, CH-Ox.); 74.2 (d, $^2J_{\text{CP}} = 8.0$ Hz, 1C, CH-N); 73.6 (d, $^2J_{\text{CP}} = 10.6$ Hz, 1C, $\text{C}(\text{CH}_3)_2$); 71.2 (d, $^2J_{\text{CP}} = 7.0$ Hz, 1C, CH-N); 68.8 (s, 1C, $\text{CH}_2\text{-Ox.}$); 34.0 / 33.9 (s, 2C, $\text{C}(\text{CH}_3)_3$); 33.8 (s, 1C, $\text{C}(\text{CH}_3)_3\text{-Ox.}$); 31.5 / 31.4 (s, 6C, $\text{C}(\text{CH}_3)_3$); 28.3 (d, $^3J_{\text{CP}} = 6.0$ Hz, 1C, $\text{C}(\text{CH}_3)_2$); 27.8 (d, $^3J_{\text{CP}} = 9.6$ Hz, 1C, $\text{C}(\text{CH}_3)_2$); 25.8 (s, 3C, $\text{C}(\text{CH}_3)_3\text{-Ox.}$); $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (162 MHz, CDCl_3): $\delta = 117.8$ (s); IR (KBr): 3415w, 3062w, 3032w, 2962m, 2903m, 2868m, 1664m, 1514s, 1364m, 1259m, 1237m, 1201m, 1155w, 1069w, 1015w, 983m cm^{-1} ; MS (FAB): $m/z = 690$ ($[\text{M}]^+$, 1), 505 (51), 238 (53), 222 (15), 186 (100), 91 (15), 57 (91); anal. calcd. for $\text{C}_{44}\text{H}_{56}\text{N}_3\text{O}_2\text{P}$: C 76.60, H 8.18, N 6.09; found: C 76.74, H 8.30, N 5.98.

(4*R*,5*R*)-1,3-Bis(4-biphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10d): White solid; yield: 38%; mp 98–100

°C; $[\alpha]_D^{20}$: + 76.2 (c 0.91, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.50–7.45 (m, 4H, H_{Ar}); 7.44–7.39 (m, 2H, H_{Ar}); 7.39–7.20 (m, 16H, H_{Ar}); 7.20–7.16 (m, 2H, H_{Ar}); 7.15–7.10 (m, 2H, H_{Ar}); 7.06–7.01 (m, 2H, H_{Ar}); 5.19 (d, ³J = 7.8 Hz, 1H, CH-N); 4.91 (dd, ³J = 7.8 Hz, ³J_{HP} = 2.8 Hz, 1H, CH-N); 4.05 (d, ³J = 9.6 Hz, 1H, CH₂-Ox.); 4.04 (d, ³J = 8.2 Hz, 1H, CH₂-Ox.); 3.80 (dd, ³J = 9.6 Hz, ³J = 8.2 Hz, 1H, CH-Ox.); 1.49 / 1.42 (s, 6H, C(CH₃)₂); 0.86 (s, 9H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 168.6 (s, 1C, C=N); 143.9 (d, ²J_{CP} = 20 Hz, 1C, ArC(*ipso*)); 141.7 (d, ²J_{CP} = 13 Hz, 1C, ArC(*ipso*)); 140.7 / 140.4 / 140.3 / 139.1 / 133.9 / 132.0 (s, 6C, ArC(*ipso*)); 128.7 / 128.6 / 128.5 / 128.4 / 127.8 / 127.7 / 127.6 / 127.4 (s, 14C, ArC-H); 127.3 / 127.1 (br s, 4C, ArC-H); 126.6 / 126.5 / 126.4 / 126.3 (s, 1C / 2C / 2C / 1C, ArC-H); 122.2 (d, ³J_{CP} = 9.6 Hz, 2C, ArC-H); 116.6 (d, ³J_{CP} = 17 Hz, 2C, ArC-H); 75.6 (s, 1C, CH-Ox.); 73.8 (d, ²J_{CP} = 8.8 Hz, 1C, CH-N); 73.2 (d, ²J_{CP} = 10 Hz, 1C, C(CH₃)₂); 70.8 (d, ²J_{CP} = 7.3 Hz, 1C, CH-N); 68.8 (s, 1C, CH₂-Ox.); 33.4 (s, 1C, C(CH₃)₃); 28.5 (d, ³J_{CP} = 5.8 Hz, 1C, C(CH₃)₂); 27.8 (d, ³J_{CP} = 10 Hz, 1C, C(CH₃)₂); 25.5 (s, 3C, C(CH₃)₃); ³¹P{¹H}-NMR (162 MHz, CDCl₃): δ = 117.4 (s); IR (KBr): 3415w, 3058w, 3028w, 2956m, 2926m, 2867w, 1607m, 1518s, 1485s, 1452m, 1379w, 1270m, 1254s, 1155w, 1093w, 1025w, 974m, 939m, 824m, 761m, 752m, 709m, 696s cm⁻¹; MS (FAB): *m/z* = 730 ([M]⁺, 28), 561 (54), 560 (38), 545 (31), 453 (97), 212 (58), 211 (29), 210 (38), 198 (32), 184 (100), 168 (75); anal. calcd. for C₄₈H₄₈N₃O₂P: C 78.99, H 6.63, N 5.76; found: C 78.78, H 6.65, N 5.47.

(4*R*,5*R*)-1,3-Bis(2-naphthyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10e): White solid; yield: 11%; mp 88–91 °C; $[\alpha]_D^{20}$: + 38.0 (c 0.24, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.67–7.61 / 7.51–7.40 / 7.32–7.12 (m, 6H / 6H / 12H, 24 H_{Ar}); 5.31 (d, ³J = 7.8 Hz, 1H, CH-N); 5.06 (dd, ³J = 7.8 Hz, ³J_{HP} = 2.5 Hz, 1H, CH-N); 3.98 (d, ³J = 8.6 Hz, 1H, CH₂-Ox.); 3.97 (d, ³J = 9.2 Hz, 1H, CH₂-Ox.); 3.68 (t, ³J = 8.9 Hz, 1H, CH-Ox.); 1.44 / 1.36 (s, 6H, C(CH₃)₂); 0.82 (s, 9H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 168.8 (s, 1C, C=N); 142.3 (d, ²J_{CP} = 9.2 Hz, 1C, ArC(*ipso*)); 140.3 (s, 1C, PhC(*ipso*)); 139.0 (s, 1C, PhC(*ipso*)); 138.7 (d, ²J_{CP} = 1.8 Hz, 1C, ArC(*ipso*)); 133.6 / 133.3 / 131.8 / 131.2 / 128.3 / 127.7 / 127.6 / 127.3 / 127.2 / 126.9 / 126.7 / 126.4 / 126.3 / 125.3 / 124.8 / 122.3 / 121.4 / 120.1 / 119.7 (s, 28C, ArC(*ipso*), ArC-H and PhC-H); 75.6 (s, 1C, CH-Ox.); 74.0 (d, ²J_{CP} = 8.3

Hz, 1C, CH-N); 73.6 (d, $^2J_{CP} = 9.5$ Hz, 1C, C(CH₃)₂); 70.4 (d, $^2J_{CP} = 6.8$ Hz, 1C, CH-N); 68.8 (s, 1C, CH₂-Ox.); 33.8 (s, 1C, C(CH₃)₃); 28.7 (d, $^3J_{CP} = 6.2$ Hz, 1C, C(CH₃)₂); 27.6 (d, $^3J_{CP} = 9.6$ Hz, 1C, C(CH₃)₂); 25.6 (s, 3C, C(CH₃)₃); $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = 117.1$ (s); IR (KBr): 3044m, 3033w, 2956m, 2867m, 1661m, 1622s, 1594s, 1505s, 1455m, 1378m, 1356m, 1261s, 1217s, 1183s, 1150m, 1122m, 1094m, 1061m, 1022m, 977s, 944m, 866m, 806s, 767m, 700m cm⁻¹; MS (FAB): $m/z = 677$ ([M]⁺, 18), 509 (48), 493 (71), 232 (81), 231 (45), 230 (53), 172 (85), 168 (100), 127 (65), 57 (62), 41 (67).

(4R,5R)-1,3-Bis((1-naphthyl)methyl)-2-(2-((S)-4-tert-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine (10f): White solid; yield: 60%; mp 66–67 °C; $[\alpha]_D^{20}$: + 5.5 (c 0.96, CHCl₃); ^1H -NMR (400 MHz, CDCl₃): $\delta = 8.16$ –8.08 (m, 2H, H_{Ar}); 7.87–7.78 (m, 2H, H_{Ar}); 7.72 (d, $^3J = 8.3$ Hz, 1H, H_{Ar}); 7.67 (d, $^3J = 8.3$ Hz, 1H, H_{Ar}); 7.63 (d, $^3J = 7.0$ Hz, 1H, H_{Ar}); 7.53–7.42 (m, 4H, H_{Ar}); 7.38–7.28 (m, 2H, H_{Ar}); 7.28–7.16 (m, 6H, H_{Ar}); 7.05–6.94 (m, 3H, H_{Ar}); 6.94–6.87 (m, 2H, H_{Ar}); 5.00 (dd, $^2J = 15.4$ Hz, $^3J_{HP} = 9.4$ Hz, 1H, CH₂); 4.54 (dd, $^2J = 14.8$ Hz, $^3J_{HP} = 11.6$ Hz, 1H, CH₂); 4.43 (dd, $^3J = 8.1$ Hz, $^3J_{HP} = 2.0$ Hz, 1H, CH-N); 4.17 (dd, $^2J = 15.4$ Hz, $^3J_{HP} = 9.6$ Hz, 1H, CH₂); 3.97 (dd, $^3J_{HP} = 17.4$ Hz, $^2J = 14.8$ Hz, 1H, CH₂); 3.92 (dd, $^3J = 8.1$ Hz, $^3J_{HP} = 4.3$ Hz, 1H, CH-N); 3.89–3.83 (m, 1H, CH₂-Ox.); 3.82–3.75 (m, 2H, CH₂-Ox. and CH); 1.71 / 1.56 (s, 6H, C(CH₃)₂); 0.84 (s, 9H, C(CH₃)₃); $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl₃): $\delta = 169.7$ (s, 1C, C=N); 141.0 / 140.5 / 135.3 / 134.1 / 134.0 / 133.8 / 133.5 / 131.8 (s, 8C, 6ArC(*ipso*) and 2PhC(*ipso*)); 128.6 / 128.5 / 128.4 / 128.1 / 128.0 / 127.9 / 127.8 / 127.3 / 127.1 / 127.0 / 126.6 / 126.5 / 125.8 / 125.5 / 125.4 / 125.2 / 125.0 / 124.1 (s, 24C, 14ArC-H and 10PhC-H); 75.5 (s, 1C, CH); 73.4 (d, $^2J_{CP} = 9.2$ Hz, 1C, CH-N); 73.2 (d, $^2J_{CP} = 10$ Hz, 1C, C(CH₃)₂); 72.6 (d, $^2J_{CP} = 9.2$ Hz, 1C, CH-N); 68.6 (s, 1C, CH₂-Ox.); 48.1–47.0 (m, 2C, CH₂); 33.8 (s, 1C, C(CH₃)₃); 29.0 (d, $^3J_{CP} = 5.8$ Hz, 1C, C(CH₃)₂); 28.5 (d, $^3J_{CP} = 9.0$ Hz, 1C, C(CH₃)₂); 25.7 (s, 3C, C(CH₃)₃); $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = 124.0$ (s); IR (NaCl): 3059w, 2956m, 2901m, 2866m, 1666s, 1597w, 1509m, 1491w, 1477m, 1454m, 1395w, 1378m, 1364m, 1261m, 1206m, 1161s, 1128s, 1100s, 1066m, 1043m, 1028m, 975s, 953s, 867m, 829w, 792s, 774s, 720s, 700s cm⁻¹; MS

(FAB): $m/z = 705$ ($[M]^+$, 2), 537 (12), 521 (17), 168 (17), 141 (100); anal. calcd. for $C_{46}H_{48}N_3O_2P$: C 78.27, H 6.85, N 5.95, O 4.53; found: C 77.99, H 6.84, N 5.70, O 4.67.

(3aR,7aR)-2-(2-((S)-4-tert-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-octahydro-1,3-di-*p*-tolyl-1H-benzo[*d*][1,3,2]diazaphosphole (10g): Pale yellow solid; yield: 60%; mp 51–53 °C; $[\alpha]_D^{20}$: +43.2 (c 0.95, $CHCl_3$); 1H -NMR (400 MHz, $CDCl_3$): $\delta = 7.04$ – 6.97 (m, 6H, H_{Ar}); 6.93–6.86 (m, 2H, H_{Ar}); 4.02 (dd, $^3J = 10.1$ Hz, $^2J = 8.6$ Hz, 1H, CH_2 -Ox.); 3.92 (dd, $^2J = 8.6$ Hz, $^3J = 7.8$ Hz, 1H, CH_2 -Ox.); 3.70 (dd, $^3J = 10.1$ Hz, $^3J = 7.8$ Hz, 1H, CH -Ox.); 3.72–3.64 / 3.27–3.18 (m, 2H, CH -N); 3.32–2.20 (m, 2H, CH_2); 2.22 (s, 6H, $ArC-CH_3$); 1.80–1.65 / 1.40–1.20 (m, 5H, CH_2); 1.17 / 1.06 (s, 6H, $C(CH_3)_2$); 1.10–1.00 (m, 1H, CH_2); 0.77 (s, 9H, $C(CH_3)_3$); $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): $\delta = 173.1$ (s, 1C, $C=N$); 142.7 / 139.8 / 132.2 / 130.5 (s, 4C, $ArC-N$ and $ArC-CH_3$); 129.8 / 129.3 / 123.9 / 119.8 (s, 8C, $ArC-H$); 75.6 (s, 1C, CH -Ox.); 73.2 (s, 1C, $C(CH_3)_2$); 68.6 (s, 1C, CH_2 -Ox.); 65.7 (d, $^2J_{CP} = 6.9$ Hz, 1C, CH -N); 61.4 (d, $^2J_{CP} = 6.1$ Hz, 1C, CH -N); 33.7 (s, 1C, $C(CH_3)_3$); 28.7 / 27.6 (s, 2C, $C(CH_3)_2$); 28.6 / 28.0 / 24.6 / 24.5 (s, 4C, CH_2); 25.9 (s, 3C, $C(CH_3)_3$); 20.8 / 20.7 (s, 2C, $ArC-CH_3$); $^{31}P\{^1H\}$ -NMR (162 MHz, $CDCl_3$): $\delta = 126.8$ (s); IR (KBr): 3419m, 3064w, 3018w, 2957m, 2834m, 1667s, 1599m, 1493s, 1454s, 1365m, 1266m, 1204m, 1163s, 1131m, 1049m, 978m, 950m, 872m, 716m cm^{-1} ; MS (FAB): $m/z = 508$ ($[M]^+$, 25), 339 (42), 324 (34), 168 (100); anal. calcd. for $C_{30}H_{42}N_3O_2P$: C 70.98, H 8.35, N 8.28; found: C 70.65, H 8.47, N 8.01.

Analytical data of rhodium complex 11

$[(\eta^4-1,5\text{-Cyclooctadiene})-\{(3aR,7aR)-2-(2-((S)-4\text{-tert-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-octahydro-1,3-di-}p\text{-tolyl-1H-benzo}[d][1,3,2]\text{diazaphosphole}\}-\text{rhodium(I)}\text{-hexafluorophosphate (11):}$ 1H -NMR (400 MHz, $CDCl_3$): 1.42–2.36 (m, 6 H, 3 x $H_2C(COD)$), 1.43 (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 2.21 (s, 3 H, $C_6H_5-CH_3$), 2.25 (s, 3 H, $C_6H_5-CH_3$), 2.64–2.86 (m, 2 H, 1 x $H_2C(COD)$), 4.24 (br m, 1 H, $HC(COD)$), 4.43 (m, 1 H, $H_{2a}C(5')$), 4.43 (br m, 1 H, $HC(COD)$), 4.78 (m, 1 H, CH), 4.96–5.04 (m, 2 H, $H_{2b}C(5') + H_2C(4')$), 5.07 (br m, 1 H, $HC(COD)$), 5.38 (m, 1 H, CH), 6.12 (br m, 1 H,

HC(COD)), 6.14 (br m, 1 H, *HC(COD)*), 6.83-7.68 (m, 23 H, H_{Ar}); ^{31}P -NMR (121.5 MHz, $CDCl_3$): -160.4, -156.0, -151.6, -147.2, -142.8, -138.4, -134.0, 106.1, 107.5. MS (FAB): 836; IR (NaCl): 3420m, 3032w, 2922w, 2884w, 2360w, 2340w, 1611m, 1510s, 1455m, 1369w, 1286w, 1260m, 1229m, 1148w, 1060m, 1018m, 962m, 842s, 751s, 718w, 704m, 667w, 631w, 558w; $[\alpha]^{589} = 221.7$ (c = 0.31, $CHCl_3$, 20 °C).

Analytical data of compounds synthesized according to the general procedure for the synthesis of iridium complexes of ligands 12a-g

[(η^4 -1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis(3-methoxyphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine)}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12a): Orange solid; yield: 89%; mp 66–68 °C; $[\alpha]_D^{20}$: + 141.8 (c 0.94, $CHCl_3$); 1H -NMR (400 MHz, $CDCl_3$): δ = 7.74–7.67 (m, 8H, $H_{Ar}(BAr_F)$); 7.52 (br s, 4H, $H_{Ar}(BAr_F)$); 7.42–7.38 (m, 1H, H_{Ar}); 7.25–7.05 (m, 9H, 6PhC-*H*(*meta* and *para*) and 3 H_{Ar}); 7.01–6.97 (m, 2H, PhC-*H*(*ortho*)); 6.95–6.90 (m, 2H, PhC-*H*(*ortho*)); 6.71–6.67 (m, 1H, H_{Ar}); 6.61–6.53 (m, 3H, H_{Ar}); 5.74–5.67 / 4.80–4.73 / 4.34–4.28 / 4.07–3.98 (m, 4H, *CH*(COD)); 5.08 (d, $^3J = 9.1$ Hz, 1H, *CH*-N); 4.78 (dd, $^3J = 9.1$ Hz, $^3J_{HP} = 2.5$ Hz, 1H, *CH*-N); 4.57 (dd, $^2J = 9.9$ Hz, $^3J = 2.0$ Hz, 1H, *CH*₂-Ox.); 4.18 (dd, $^2J = 9.9$ Hz, $^3J = 8.6$ Hz, 1H, *CH*₂-Ox.); 3.75 (dd, $^3J = 8.6$ Hz, $^3J = 2.0$ Hz, 1H, *CH*-Ox.); 3.67 / 3.65 (s, 6H, *CH*₃-O); 2.83-2.70 / 2.60-2.40 / 2.14-2.02 / 1.93-1.73 (m, 8H, *CH*₂(COD)); 1.72 / 1.01 (s, 6H, C(*CH*₃)₂); 0.73 (s, 9H, C(*CH*₃)₃); $^{13}C\{^1H\}$ -NMR (125 MHz, $CDCl_3$): δ = 175.4 (d, $^3J_{CP} = 5.7$ Hz, 1C, C=N); 161.7 (q, $^1J_{CB} = 50$ Hz, 4C, ArC(*BAr*_F)); 160.4 (d, $^2J_{CP} = 1.7$ Hz, 1C, ArC-O); 160.3 (s, 1C, ArC-O); 140.8-140.5 (m, 2C, ArC-N); 136.7 (d, $^3J_{CP} = 8.1$ Hz, 1C, PhC(*ipso*)); 135.8 (d, $^3J_{CP} = 1.9$ Hz, 1C, PhC(*ipso*)); 134.8 (s, 8C, ArC(*BAr*_F)); 130.5 / 130.0 (s, 2C, ArC-H); 128.9 (qq, $^2J_{CF} = 30$ Hz, $^3J_{CB} = 2.9$ Hz, 8C, ArC(*BAr*_F)); 128.9 / 128.7 / 128.6 / 128.0 / 127.1 (s, 10C, PhC-H(*ortho*, *meta* and *para*)); 124.5 (q, $^1J_{CF} = 273$ Hz, 8C, CF₃); 117.4 (sept, $^3J_{CF} = 4.1$ Hz, 4C, ArC(*BAr*_F)); 115.2 (d, $J_{CP} = 4.5$ Hz, 1C, ArC-H); 112.6 (d, $J_{CP} = 4.6$ Hz, 1C, ArC-H); 111.2 (d, $J_{CP} = 4.8$ Hz, 1C, ArC-H); 109.8 / 108.1 (s, 2C / 1C, ArC-

H); 104.7 (d, $J_{CP} = 12$ Hz, 1C, CH(COD)); 97.8 (d, $J_{CP} = 19$ Hz, 1C, CH(COD)); 78.2 (d, $^2J_{CP} = 5.8$ Hz, 1C, C(CH₃)₂); 73.7 / 69.5 (s, 2C, CH-N); 73.6 (s, 1C, CH-Ox.); 71.8 (s, 1C, CH₂-Ox.); 67.1 / 62.3 (s, 2C, CH(COD)); 55.2 / 55.0 (s, 2C, CH₃-O); 36.4 (d, $J_{CP} = 5.8$ Hz, 1C, CH₂(COD)); 34.4 (s, 1C, C(CH₃)₃); 34.0 (s, 1C, CH₂(COD)); 29.7 (s, 1C, C(CH₃)₂); 28.3 (d, $^3J_{CP} = 6.3$ Hz, 1C, C(CH₃)₂); 27.9 (s, 1C, CH₂(COD)); 25.0 (s, 3C, C(CH₃)₃); 24.3 (d, $J_{CP} = 3.0$ Hz, 1C, CH₂(COD)); $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = 87.7$ (s); IR (NaCl): 3442m, 2962w, 2921w, 2849w, 1603m, 1492m, 1467w, 1438w, 1355s, 1278s, 1162s, 1126s, 1048m, 1005m, 964w, 887m, 839m, 744m, 714m, 682m, 670m, 613m cm⁻¹; MS (FAB): $m/z = 939$ (51), 938 ([M-BAr_F]⁺, 100), 937 (32), 936 (58), 830 ([M-BAr_F-COD]⁺, 26), 828 (22), 210 (28), 168 (39), 152 (29), 77 (36); anal. calcd. for C₇₈H₆₈BF₂₄IrN₃O₄P: C 52.01, H 3.81, N 2.33, O 3.55; found: C 51.81, H 4.10, N 2.11, O 3.83.

[(η^4 -1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis(4-methoxyphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12b**):** Orange solid; yield: 91%; mp 167–168 °C; $[\alpha]_D^{20}$: + 138.2 (c 0.74, CHCl₃); ^1H -NMR (500 MHz, CDCl₃): $\delta = 7.74$ – 7.70 (m, 8H, $H_{Ar}(\text{BAr}_F)$); 7.53 (br s, 4H, $H_{Ar}(\text{BAr}_F)$); 7.50–7.45 (m, 2H, H_{Ar}); 7.22–7.16 (m, 6H, PhC-*H*(*meta* and *para*)); 7.06–7.03 (m, 2H, H_{Ar}); 7.03–7.00 / 6.95–6.91 (m, 4H, PhC-*H*(*ortho*)); 6.80–6.76 / 6.71–6.67 (m, 4H, H_{Ar}); 5.51–5.45 / 4.74–4.66 / 4.43–4.38 / 4.20–4.14 (m, 4H, CH(COD)); 5.04 (d, $^3J = 9.0$ Hz, 1H, CH-N); 4.76 (dd, $^3J = 9.0$ Hz, $^3J_{HP} = 2.0$ Hz, 1H, CH-N); 4.55 (dd, $^2J = 10.0$ Hz, $^3J = 2.1$ Hz, 1H, CH₂-Ox.); 4.18 (dd, $^2J = 10.0$ Hz, $^3J = 8.8$ Hz, 1H, CH₂-Ox.); 3.69 (s, 6H, CH₃-O); 3.67 (dd, $^3J = 8.8$ Hz, $^3J = 2.1$ Hz, 1H, CH-Ox.); 2.65 (dd, $J = 15.8$ Hz, $J = 7.0$ Hz, 1H, CH₂(COD)); 2.55–2.32 / 2.30–2.20 / 1.98–1.90 / 1.87–1.77 (m, 7H, CH₂(COD)); 1.67 / 1.03 (s, 6H, C(CH₃)₂); 0.62 (s, 9H, C(CH₃)₃); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl₃): $\delta = 175.8$ (d, $^3J_{CP} = 5.0$ Hz, 1C, C=N); 161.7 (q, $^1J_{CB} = 50$ Hz, 4C, ArC(BAr_F)); 157.8 (s, 1C, ArC-O); 157.3 (d, $^5J_{CP} = 1.8$ Hz, 1C, ArC-O); 136.7 (d, $^3J_{CP} = 8.4$ Hz, 1C, PhC(*ipso*)); 135.9 (d, $^3J_{CP} = 2.0$ Hz, 1C, PhC(*ipso*)); 134.8 (s, 8C, ArC(BAr_F)); 132.4 (d, $^2J_{CP} = 1.9$ Hz, 1C, ArC-N); 131.6 (d, $^2J_{CP} = 11$ Hz, 1C, ArC-N); 128.9 (qq, $^2J_{CF} = 31$ Hz, $^3J_{CB} = 2.8$ Hz, 8C, ArC(BAr_F)); 128.8 / 128.7 / 128.6 / 128.5 / 128.2 / 127.3 (s, 10C, PhC-*H*(*ortho*, *meta* and *para*)); 128.1 (d,

$J_{CP} = 3.4$ Hz, 2C, ArC-H); 125.9 (d, $J_{CP} = 4.0$ Hz, 2C, ArC-H); 123.4 (q, $^1J_{CF} = 273$ Hz, 8C, CF_3); 117.5 (sept, $^3J_{CF} = 3.8$ Hz, 4C, ArC(BAr_F)); 115.0 / 114.5 (s, 4C, ArC-H); 103.0 (d, $J_{CP} = 12$ Hz, 1C, CH(COD)); 97.1 (d, $J_{CP} = 19$ Hz, 1C, CH(COD)); 78.1 (d, $^2J_{CP} = 5.5$ Hz, 1C, C(CH₃)₂); 74.5 (d, $^2J_{CP} = 2.1$ Hz, 1C, CH-N); 73.3 (s, 1C, CH-Ox.); 71.9 (s, 1C, CH₂-Ox.); 71.6 (s, 1C, CH-N); 65.9 / 61.9 (s, 2C, CH(COD)); 55.3 / 55.2 (s, 2C, CH₃-O); 36.5 (d, $J_{CP} = 5.7$ Hz, 1C, CH₂(COD)); 34.1 (s, 1C, CH₂(COD)); 34.0 (s, 1C, C(CH₃)₃); 30.9 (s, 1C, C(CH₃)₂); 27.8 (s, 1C, CH₂(COD)); 27.4 (d, $^3J_{CP} = 6.0$ Hz, 1C, C(CH₃)₂); 24.9 (s, 3C, C(CH₃)₃); 24.4 (d, $J_{CP} = 2.6$ Hz, 1C, CH₂(COD)); $^{31}P\{^1H\}$ -NMR (162 MHz, CDCl₃): $\delta = 88.4$ (s); IR (NaCl): 2961w, 2926w, 2841w, 1509s, 1356s, 1277s, 1248m, 1223m, 1125s, 1036w, 886w, 838m, 773w, 712m, 682m cm⁻¹; MS (FAB): $m/z = 939$ (49), 938 ([M-BAr_F]⁺, 100), 937 (34), 936 (59), 830 ([M-BAr_F-COD]⁺, 32), 828 (27), 212 (39), 210 (69), 168 (57), 152 (55), 91 (31), 77 (66); anal. calcd. for C₇₈H₆₈BF₂₄IrN₃O₄P: C 52.01, H 3.81, N 2.33, O 3.55; found: C 52.17, H 4.02, N 2.08, O 3.62.

[(η^4 -1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis(4-*tert*-butylphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12c**): Orange solid; yield: 52%; mp 86–88 °C; $[\alpha]_D^{20}$: + 95.8 (c 0.80, CHCl₃); 1H -NMR (400 MHz, CDCl₃): $\delta = 7.74$ – 7.68 (m, 8H, H_{Ar} (BAr_F)); 7.58–7.53 (m, 2H, ArC-H); 7.52 (br s, 4H, H_{Ar} (BAr_F)); 7.28–7.14 (m, 10H, H_{Ar}); 7.02–6.91 (m, 6H, H_{Ar}); 5.67–5.60 / 4.77–4.67 / 4.34–4.27 / 4.17–4.07 (m, 4H, CH(COD)); 5.10 (d, $^3J = 9.1$ Hz, 1H, CH-N); 4.81 (dd, $^3J = 9.1$ Hz, $^3J_{HP} = 2.6$ Hz, 1H, CH-N); 4.54 (dd, $^2J = 10.1$ Hz, $^3J = 2.0$ Hz, 1H, CH₂-Ox.); 4.13 (dd, $^2J = 10.1$ Hz, $^3J = 8.6$ Hz, 1H, CH₂-Ox.); 3.72 (dd, $^3J = 8.6$ Hz, $^3J = 2.0$ Hz, 1H, CH-Ox.); 2.67–2.40 / 2.05–1.73 (m, 8H, CH₂(COD)); 1.68 / 1.26 (s, 6H, C(CH₃)₂); 1.22 / 1.20 (s, 18H, C(CH₃)₃); 0.74 (s, 9H, C(CH₃)₃-Ox.); $^{13}C\{^1H\}$ -NMR (100 MHz, CDCl₃): $\delta = 175.9$ (s, 1C, C=N); 161.8 (q, $^1J_{CB} = 51$ Hz, 4C, ArC(BAr_F)); 146.8 / 145.7 (s, 2C, ArC-C); 137.3 (d, $^3J_{CP} = 7.8$ Hz, 1C, PhC(*ipso*)); 137.2 (d, $^2J_{CP} = 2.0$ Hz, 1C, ArC-N); 136.5 (d, $^3J_{CP} = 1.9$ Hz, 1C, PhC(*ipso*)); 135.1 (d, $^2J_{CP} = 10$ Hz, 1C, ArC-N); 134.9 (s, 8C, ArC(BAr_F)); 133.8 / 131.2 (s, 4C, ArC-H); 129.0 (qq, $^2J_{CF} = 30$ Hz, $^3J_{CB} = 2.8$ Hz, 8C, ArC(BAr_F)); 128.6 / 128.5 / 128.3 / 127.9 / 127.3 (s, 10C, PhC-H(*ortho*, *meta* and *para*));**

124.5 (q, $^1J_{CF} = 272$ Hz, 8C, CF₃); 121.5 (s, 2C, ArC-H); 117.5 (sept, $^3J_{CF} = 4.1$ Hz, 4C, ArC(BAr_F)); 116.2 (s, 2C, ArC-H); 104.8 (d, $J_{CP} = 12$ Hz, 1C, CH(COD)); 97.8 (d, $J_{CP} = 18$ Hz, 1C, CH(COD)); 78.3 (d, $^2J_{CP} = 5.6$ Hz, 1C, C(CH₃)₂); 74.3 / 70.9 (s, 2C, CH-N); 73.4 (s, 1C, CH-Ox.); 72.0 (s, 1C, CH₂-Ox.); 67.2 / 62.3 (s, 2C, CH(COD)); 36.4 (d, $J_{CP} = 5.4$ Hz, 1C, CH₂(COD)); 34.2 (s, 1C, C(CH₃)₃-Ox.); 34.1 (s, 1C, CH₂(COD)); 33.9 / 33.7 (s, 2C, C(CH₃)₃); 31.5 / 31.3 (s, 6C, C(CH₃)₃); 30.6 (s, 1C, C(CH₃)₂); 28.0 (s, 1C, CH₂(COD)); 27.3 (d, $^3J_{CP} = 6.3$ Hz, 1C, C(CH₃)₂); 25.3 (s, 3C, C(CH₃)₃-Ox.); 24.5 (d, $J_{CP} = 3.2$ Hz, 1C, CH₂(COD)); $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = 87.9$ (s); IR (KBr): 3067w, 3028w, 2960w, 2929w, 1609w, 1560w, 1520m, 1487m, 1355s, 1277s, 1124s, 1002m, 961m, 885w, 838m, 752w, 711m, 699m, 682m, 669m cm⁻¹; MS (FAB): $m/z = 991$ (52), 990 ([M-BAr_F]⁺, 100), 989 (29), 988 (54), 882 ([M-BAr_F-COD]⁺, 29), 880 (25), 168 (49), 133 (43), 77 (28), 57 (72); anal. calcd. for C₈₄H₈₀BF₂₄IrN₃O₂P: C 54.43, H 4.35, N 2.27; found: C 54.10, H 4.09, N 2.15.

[(η^4 -1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis(4-biphenyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12d**):** Orange solid; yield: 95%; mp 107–109 °C; $[\alpha]_D^{20}$: + 131.1 (c 1.04, CHCl₃); ^1H -NMR (400 MHz, CDCl₃): $\delta = 7.77$ – 7.72 (m, 2H, H_{Ar}); 7.72 – 7.67 (m, 8H, H_{Ar} (BAr_F)); 7.50 (br s, 4H, H_{Ar} (BAr_F)); 7.48 – 7.25 (m, 14H, H_{Ar}); 7.23 – 7.12 (m, 8H, H_{Ar}); 7.06 – 6.99 (m, 2H, H_{Ar}); 6.98 – 6.93 (m, 2H, H_{Ar}); 5.70 – 5.62 / 4.84 – 4.73 / 4.40 – 4.32 / 4.15 – 4.06 (m, 4H, CH(COD)); 5.18 (d, $^3J = 8.9$ Hz, 1H, CH-N); 4.88 (dd, $^3J = 8.9$ Hz, $^3J_{HP} = 2.5$ Hz, 1H, CH-N); 4.57 (dd, $^2J = 9.8$ Hz, $^3J = 1.9$ Hz, 1H, CH₂-Ox.); 4.17 (dd, $^2J = 9.8$ Hz, $^3J = 8.5$ Hz, 1H, CH₂-Ox.); 3.73 (dd, $^3J = 8.5$ Hz, $^3J = 1.9$ Hz, 1H, CH-Ox.); 2.70 – 2.40 / 2.15 – 2.00 / 1.95 – 1.75 (m, 8H, CH₂(COD)); 1.71 / 1.03 (s, 6H, C(CH₃)₂); 0.73 (s, 9H, C(CH₃)₃); $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl₃): $\delta = 176.0$ (s, 1C, C=N); 162.1 (q, $^1J_{CB} = 50$ Hz, 4C, ArC(BAr_F)); 139.9 / 139.7 (s, 2C, ArC-C); 139.1 (d, $^3J_{CP} = 9.2$ Hz, 1C, ArC-C); 136.8 (d, $^3J_{CP} = 8.0$ Hz, 1C, ArC-C); 135.2 (s, 8C, ArC(BAr_F)); 129.4 / 129.3 / 129.1 / 128.7 / 128.5 / 128.2 / 128.0 / 127.6 / 127.0 / 126.9 (s, 30C, ArC-H, PhC-H, ArC-C and PhC-C); 129.1 (mc, 8C, ArC(BAr_F)); 126.0 (d, $J_{CP} = 4.6$ Hz, 1C, ArC-H); 125.0 (q, $^1J_{CF} = 272$ Hz, 8C, CF₃); 124.0 (d, $J_{CP} = 4.0$ Hz, 1C, ArC-H); 117.8 (mc, 4C, ArC(BAr_F)); 105.1 (d, $J_{CP} = 12$ Hz,

1C, CH(COD)); 98.6 (d, $J_{CP} = 19$ Hz, 1C, CH(COD)); 78.7 (d, $^2J_{CP} = 6.1$ Hz, 1C, C(CH₃)₂); 74.2 / 70.3 (s, 2C, CH-N); 73.9 (s, 1C, CH-Ox.); 72.3 (s, 1C, CH₂-Ox.); 67.5 / 62.6 (s, 2C, CH(COD)); 36.7 (d, $J_{CP} = 5.8$ Hz, 1C, CH₂(COD)); 34.9 (s, 1C, C(CH₃)₃); 34.6 (s, 1C, CH₂(COD)); 30.1 (s, 1C, C(CH₃)₂); 28.6 (d, $^3J_{CP} = 6.5$ Hz, 1C, C(CH₃)₂); 28.3 (s, 1C, CH₂(COD)); 25.5 (s, 3C, C(CH₃)₃); 24.7 (d, $J_{CP} = 3.1$ Hz, 1C, CH₂(COD)); ³¹P{¹H}-NMR (162 MHz, CDCl₃): δ = 87.7 (s); IR (KBr): 3065w, 3033w, 2964w, 2925w, 1609m, 1560w, 1520m, 1487m, 1355s, 1278s, 1124s, 1002m, 961m, 885w, 838m, 755w, 744w, 712m, 698m, 681m, 669m, 641w cm⁻¹; MS (FAB): *m/z* = 1031 (58), 1030 ([M-BAr_F]⁺, 100), 1029 (37), 1028 (54), 922 (34), 921 (25), 920 (28), 256 (39), 168 (34), 152 (30), 77 (34); anal. calcd. for C₈₈H₇₂BF₂₄IrN₃O₂P: C 55.82, H 3.83, N 2.22; found: C 56.08, H 4.12, N 2.15.

[(η⁴-1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis(2-naphthyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12e): Orange solid; yield: 72%; mp 96–98 °C; [α]_D²⁰: + 156.6 (c 0.98, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 8.07–8.04 (m, 1H, H_{Ar}); 7.91–7.87 (m, 1H, H_{Ar}); 7.77–7.66 / 7.65–7.59 / 7.54–7.48 (m, 7H, H_{Ar}); 7.72–7.68 (m, 8H, H_{Ar}(BAr_F)); 7.51 (br s, 4H, H_{Ar}(BAr_F)); 7.48–7.38 (m, 4H, H_{Ar}); 7.32 (dd, $^3J = 8.7$ Hz, $^4J = 1.8$ Hz, 1H, H_{Ar}); 7.23–7.14 (m, 6H, PhC-*H*(*meta* and *para*)); 7.13–7.07 / 7.04–6.98 (m, 4H, PhC-*H*(*ortho*)); 5.64–5.55 / 4.76–4.66 / 4.58–4.51 / 4.29–4.19 (m, 4H, CH(COD)); 5.34 (d, $^3J = 8.9$ Hz, 1H, CH-N); 5.00 (dd, $^3J = 8.9$ Hz, $^3J_{HP} = 1.8$ Hz, 1H, CH-N); 4.47 (dd, $^2J = 9.1$ Hz, $^3J = 1.8$ Hz, 1H, CH₂-Ox.); 4.10 (dd, $^3J = 9.1$ Hz, $^2J = 9.1$ Hz, 1H, CH₂-Ox.); 3.60 (dd, $^3J = 9.1$ Hz, $^3J = 1.8$ Hz, 1H, CH-Ox.); 2.80–2.63 / 2.62–2.47 / 2.25–2.10 / 1.95–1.80 (m, 8H, CH₂(COD)); 1.73 / 0.87 (s, 6H, C(CH₃)₂); 0.35 (s, 9H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 175.5 (d, $^3J_{CP} = 6.1$ Hz, 1C, C=N); 161.7 (q, $^1J_{CB} = 50$ Hz, 4C, ArC(BAr_F)); 137.2 (d, $J_{CP} = 3.1$ Hz, 1C, ArC-C / ArC-N / PhC(*ipso*)); 136.6 / 133.6 / 133.4 / 131.7 (s, 4C, ArC-C, ArC-N and PhC(*ipso*)); 136.5 (d, $J_{CP} = 3.8$ Hz, 1C, ArC-C / ArC-N / PhC(*ipso*)); 135.6 (d, $J_{CP} = 2.3$ Hz, 1C, ArC-C / ArC-N / PhC(*ipso*)); 134.8 (s, 8C, ArC(BAr_F)); 130.6 (d, $J_{CP} = 1.5$ Hz, 1C, ArC-C / ArC-N / PhC(*ipso*)); 130.0 / 129.2 / 128.9 / 128.7 / 128.2 / 127.7 / 127.6 / 127.2 / 127.1 / 127.0 / 126.6 / 126.0 (s, 20C, 10ArC-H and 10PhC-H); 129.3 (qq, $^2J_{CF} = 32$ Hz,

$^3J_{\text{CB}} = 1.5$ Hz, 8C, ArC(BAr_F)); 125.5 (d, $^3J_{\text{CP}} = 4.6$ Hz, 1C, ArC-H); 124.6 (q, $^1J_{\text{CF}} = 272$ Hz, 8C, CF₃); 124.2 (d, $^3J_{\text{CP}} = 3.1$ Hz, 1C, ArC-H); 122.1 (d, $^3J_{\text{CP}} = 3.8$ Hz, 1C, ArC-H); 121.2 (d, $^3J_{\text{CP}} = 6.1$ Hz, 1C, ArC-H); 117.4 (sept, $^3J_{\text{CF}} = 3.8$ Hz, 4C, ArC(BAr_F)); 104.2 (d, $J_{\text{CP}} = 12$ Hz, 1C, CH(COD)); 98.5 (d, $J_{\text{CP}} = 18$ Hz, 1C, CH(COD)); 78.2 (d, $^2J_{\text{CP}} = 6.3$ Hz, 1C, C(CH₃)₂); 74.4 / 70.2 (s, 2C, CH-N); 73.4 (s, 1C, CH-Ox.); 71.9 (s, 1C, CH₂-Ox.); 66.5 / 62.4 (s, 2C, CH(COD)); 36.4 (d, $J_{\text{CP}} = 6.1$ Hz, 1C, CH₂(COD)); 34.2 / 28.1 / 24.4 (s, 3C, CH₂(COD)); 33.9 (s, 1C, C(CH₃)₃); 30.4 / 28.0 (s, 2C, C(CH₃)₂); 24.5 (s, 3C, C(CH₃)₃); $^31\text{P}\{^1\text{H}\}$ -NMR (162 MHz, CDCl₃): $\delta = 88.1$ (s); IR (NaCl): 3064w, 3033w, 2964w, 2924m, 2851w, 1632m, 1599m, 1509m, 1469m, 1456m, 1355s, 1278s, 1217m, 1125s, 1017m, 1003m, 966m, 933w, 887m, 839m, 746m, 731w, 682m, 648m cm⁻¹; MS (FAB): $m/z = 979$ (54), 978 ([M-BAr_F]⁺, 100), 977 (33), 976 (53), 870 ([M-BAr_F-COD]⁺, 23), 868 (21), 232 (36), 230 (61), 172 (39), 168 (66), 128 (24), 127 (78), 115 (27); anal. calcd. for C₈₄H₆₈BF₂₄IrN₃O₂P: C 54.79, H 3.72, N 2.28, O 1.74; found: C 54.84, H 4.09, N 2.09, O 1.86.

[(η^4 -1,5-Cyclooctadiene)-{(4*R*,5*R*)-1,3-bis((1-naphthyl)methyl)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-diphenyl[1,3,2]diazaphospholidine)}-iridium(I)]-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12f**): Orange solid; yield: 73%; mp 86–87 °C; [α]_D²⁰: + 100.5 (c 1.03, CHCl₃); ^1H -NMR (500 MHz, CDCl₃): $\delta = 7.88$ – 7.77 (m, 4H, H_{Ar}); 7.76–7.72 (m, 2H, H_{Ar}); 7.71–7.68 (m, 8H, H_{Ar} (BAr_F)); 7.56–7.43 (m, 6H, H_{Ar}); 7.51 (br s, 4H, H_{Ar} (BAr_F)); 7.40 (dd, $^3J = 6.9$ Hz, $^4J = 1.3$ Hz, 1H, H_{Ar}); 7.36 (dd, $^3J = 7.8$ Hz, $^3J = 7.4$ Hz, 1H, H_{Ar}); 7.21–7.13 (m, 6H, H_{Ar}); 7.09 (t, $^3J = 7.6$ Hz, 2H, H_{Ar}); 6.72 (d, $^3J = 7.2$ Hz, 2H, H_{Ar}); 5.43–5.38 (m, 1H, CH(COD)); 4.94 (dd, $^2J = 16.2$ Hz, $^3J_{\text{HP}} = 8.4$ Hz, 1H, CH₂); 4.90–4.80 (m, 2H, CH(COD) and CH₂); 4.78 (d, $^3J = 6.6$ Hz, 1H, CH-N); 4.74 (dd, $^2J = 16.2$ Hz, $^3J_{\text{HP}} = 12.9$ Hz, 1H, CH₂); 4.66–4.54 (m, 3H, CH(COD), CH₂ and CH₂-Ox.); 4.46 (dd, $^3J_{\text{HP}} = 9.0$ Hz, $^3J = 6.6$ Hz, 1H, CH-N); 4.22 (dd, $^2J = 9.6$ Hz, $^3J = 9.2$ Hz, 1H, CH₂-Ox.); 3.77 (dd, $^3J = 9.2$ Hz, $^3J = 3.0$ Hz, 1H, CH-Ox.); 3.57–3.50 (m, 1H, CH(COD)); 2.93–2.86 / 2.75–2.65 / 2.40–2.25 / 2.14–2.05 / 1.93–1.80 (m, 8H, CH₂(COD)); 1.76 / 1.73 (s, 6H, C(CH₃)₂); 0.57 (s, 9H, C(CH₃)₃-Ox.); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl₃): $\delta = 176.5$ (d, $^3J_{\text{CP}} = 3.4$ Hz, 1C, C=N); 161.7 (q, $^1J_{\text{CB}} = 50$ Hz, 4C, ArC(BAr_F)); 137.6 (s, 1C, PhC(*ipso*)); 137.2 (d, $^3J_{\text{CP}} = 5.7$ Hz, 1C,**

PhC(*ipso*)); 134.8 (br s, 8C, ArC(BAr_F)); 133.9 / 133.7 (s, 2C, ArC-H); 131.2 (d, $J_{CP} = 6.2$ Hz, 1C, ArC-H); 130.9 (d, $J_{CP} = 8.4$ Hz, 1C, ArC-H); 129.6 / 128.6 (s, 2C, ArC-H); 129.2 / 129.1 / 129.0 / 128.9 (s, 5C, ArC-H); 128.8 (qq, $^2J_{CF} = 30$ Hz, $^3J_{CB} = 2.9$ Hz, 8C, ArC(BAr_F)); 128.7 / 128.6 / 128.5 / 127.6 / 127.3 / 126.6 / 126.1 / 126.0 / 125.7 / 124.8 / 124.6 / 124.5 (s, 17C, ArC-H); 124.4 (q, $^1J_{CF} = 273$ Hz, 8C, CF₃); 122.3 / 121.4 (s, 2C, ArC-H); 117.5 (sept, $^3J_{CF} = 3.9$ Hz, 4C, ArC(BAr_F)); 102.5 (d, $J_{CP} = 12$ Hz, 1C, CH(COD)); 97.7 (d, $J_{CP} = 19$ Hz, 1C, CH(COD)); 77.4 (d, $^2J_{CP} = 4.4$ Hz, 1C, C(CH₃)₂); 73.7 (s, 1C, CH-Ox.); 73.1 / 69.2 (s, 2C, CH-N); 72.3 (s, 1C, CH₂-Ox.); 65.4 / 61.3 (s, 2C, CH(COD)); 46.6 (d, $^2J_{CP} = 16.1$ Hz, 1C, CH₂); 43.5 (d, $^2J_{CP} = 9.3$ Hz, 1C, CH₂); 37.2 (d, $J_{CP} = 5.4$ Hz, 1C, CH₂(COD)); 33.7 (s, 1C, C(CH₃)₃); 33.4 (s, 1C, CH₂(COD)); 32.2 (d, $^3J_{CP} = 4.7$ Hz, 1C, C(CH₃)₂); 29.7 (s, 1C, CH₂(COD)); 28.5 (s, 1C, CH₂(COD)); 25.6 (d, $^3J_{CP} = 5.5$ Hz, 1C, C(CH₃)₂); 24.8 (s, 3C, C(CH₃)₃); ³¹P{¹H}-NMR (162 MHz, CDCl₃): δ = 99.7 (s); IR (NaCl): 3067w, 2966w, 2926w, 1609m, 1485w, 1458w, 1433w, 1354s, 1277s, 1125s, 1002w, 909m, 886m, 839m, 796m, 771m, 744m, 713m, 699m, 682m, 670m, 650w cm⁻¹; MS (FAB): *m/z* = 1006 ([M-BAr_F]⁺, 21), 898 (5), 521 (10), 168 (11), 141 (100); anal. calcd. for C₈₆H₇₂BF₂₄IrN₃O₂P: C 55.25, H 3.88, N 2.25; found: C 55.41, H 4.06, N 2.08.

[(η⁴-1,5-Cyclooctadiene)-{(3*aR*,7*aR*)-2-(2-((*S*)-4-*tert*-butyl-4,5-dihydrooxazol-2-yl)propan-2-yl)-octahydro-1,3-di-*p*-tolyl-1*H*-benzo[*d*][1,3,2]diazaphosphole}-iridium(I)-tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (12g): Orange solid; yield: 98%; mp 68–69 °C; [α]_D²⁰: + 88.7 (c 0.61, CHCl₃); ¹H-NMR (400 MHz, CDCl₃): δ = 7.74–7.68 (m, 8H, *H*_{Ar}(BAr_F)); 7.53 (br s, 4H, *H*_{Ar}(BAr_F)); 7.37 (dd, $^3J = 8.6$ Hz, $^4J = 1.8$ Hz, 2H, *H*_{Ar}); 7.22 (d, $^3J = 8.6$ Hz, 2H, *H*_{Ar}); 7.14 (d, $^3J = 8.3$ Hz, 2H, *H*_{Ar}); 7.03 (d, $^3J = 8.3$ Hz, 2H, *H*_{Ar}); 5.37–5.30 / 4.60–4.51 / 4.24–4.18 / 3.97–3.88 (m, 4H, CH(COD)); 4.48 (dd, $^2J = 9.9$ Hz, $^3J = 2.5$ Hz, 1H, CH₂-Ox.); 4.06 (dd, $^2J = 9.9$ Hz, $^3J = 8.8$ Hz, 1H, CH₂-Ox.); 3.61–3.53 (m, 1H, CH-N); 3.59 (dd, $^3J = 8.8$ Hz, $^3J = 2.5$ Hz, 1H, CH-Ox.); 3.34–3.26 (m, 1H, CH-N); 2.63–2.53 (m, 1H, CH₂(COD)); 2.45–2.18 (m, 4H, 2CH₂ and 2CH₂(COD)); 2.34 / 2.33 (s, 6H, ArC-CH₃); 2.00–1.67 (m, 7H, 2CH₂ and 5CH₂(COD)); 1.50 / 0.89 (s, 6H, C(CH₃)₂); 1.40–0.98 (m, 4H, CH₂); 0.52 (s, 9H, C(CH₃)₃); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 175.7 (d, $^3J_{CP} = 4.6$ Hz, 1C, C=N); 161.7 (q, $^1J_{CB} = 50$ Hz,

4C, ArC(BAr_F)); 137.0 (s, 1C, ArC-N / ArC-C); 136.6 (d, $J_{CP} = 2.3$ Hz, 1C, ArC-N / ArC-C); 136.3 (d, $J_{CP} = 3.1$ Hz, 1C, ArC-N / ArC-C); 135.9 (d, $J_{CP} = 10.7$ Hz, 1C, ArC-N / ArC-C); 134.8 (br s, 8C, ArC(BAr_F)); 130.6 / 127.1 (s, 4C, ArC-H); 130.2 (d, $J_{CP} = 2.3$ Hz, 2C, ArC-H); 129.0 (qq, $^2J_{CF} = 35$ Hz, $^3J_{CB} = 2.5$ Hz, 8C, ArC(BAr_F)); 125.5 (d, $J_{CP} = 3.8$ Hz, 2C, ArC-H); 124.6 (q, $^1J_{CF} = 272$ Hz, 8C, CF₃); 117.5 (sept, $^3J_{CF} = 3.8$ Hz, 4C, ArC(BAr_F)); 101.8 (d, $J_{CP} = 12$ Hz, 1C, CH(COD)); 95.8 (d, $J_{CP} = 20$ Hz, 1C, CH(COD)); 77.7 (d, $^2J_{CP} = 5.4$ Hz, 1C, C(CH₃)₂); 73.3 (s, 1C, CH-Ox.); 71.9 (s, 1C, CH₂-Ox.); 65.8 (d, $^2J_{CP} = 3.8$ Hz, 1C, CH-N); 65.2 / 62.6 (s, 2C, CH(COD)); 63.8 (s, 1C, CH-N); 36.7 (d, $J_{CP} = 6.1$ Hz, 1C, CH₂(COD)); 34.0 (s, 1C, CH₂(COD)); 33.7 (s, 1C, C(CH₃)₃); 30.8 (d, $^3J_{CP} = 1.9$ Hz, 1C, C(CH₃)₂); 28.9 (d, $J_{CP} = 2.3$ Hz, 1C, CH₂ / CH₂(COD)); 28.2 (d, $J_{CP} = 7.7$ Hz, 1C, CH₂ / CH₂(COD)); 27.6 / 24.0 / 23.9 (s, 3C, CH₂ / CH₂(COD)); 26.8 (d, $^3J_{CP} = 6.1$ Hz, 1C, C(CH₃)₂); 24.8 (s, 3C, C(CH₃)₃); 24.3 (d, $J_{CP} = 3.1$ Hz, 1C, CH₂(COD)); 20.9 / 20.7 (s, 2C, ArC-CH₃); ³¹P{¹H}-NMR (162 MHz, CDCl₃): δ = 92.3 (s); IR (NaCl): 2928m, 2876w, 1608m, 1512m, 1354s, 1277s, 1241m, 1126s, 1068m, 964m, 887m, 839m, 744w, 713m, 682m, 670m cm⁻¹; MS (FAB): *m/z* = 809 (43), 808 ([M-BAr_F]⁺, 100), 807 (30), 806 (62), 700 (25), 136 (34), 91 (38), 77 (31); anal. calcd. for C₇₀H₆₆BF₂₄IrN₃O₂P: C 50.31, H 3.98, N 2.51; found: C 50.47, H 4.23, N 2.25.

(*E*)-Ethyl 2-methyl-3-phenylacrylate (21)

α-Methyl cinnamic acid (3.83 g, 23 mmol) was dissolved in ethanol (40 mL). Conc. H₂SO₄ (0.6 mL) was added and the mixture heated under reflux for 6 h. After cooling to room temperature the reaction mixture was hydrolyzed with ice water, neutralised with sat. NaHCO₃ and extracted with ethyl acetate. The organic phase was washed with aqueous sat. NaCl solution, dried over MgSO₄ and the solvent evaporated. The residue was purified by column chromatography (hexane/ethyl acetate (15:1)) to give the desired product as colourless oil; yield: 92%; ¹H-NMR (400 MHz, CDCl₃): δ = 7.68 (q, $^4J = 1.5$ Hz, 1H, CH=); 7.42–7.28 (m, 5H, H_{Ar}); 4.27 (q, $^3J = 7.2$ Hz, 2H, CH₃-CH₂-O); 2.12 (d, $^4J = 1.5$ Hz, 3H, CH₃-C=); 1.35 (t, $^3J = 7.2$ Hz, 3H, CH₃-CH₂-O); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 168.7 (s, 1C, C=O); 138.6 (s, 1C, CH=); 136.0 (s, 1C, PhC(*ipso*)); 129.6 / 128.3 / 128.2 (s, 5C, PhC-H); 128.7 (s, 1C, CH₃-C=); 60.9 (s, 1C, CH₃-CH₂-O); 14.3 /

14.0 (s, 2C, CH₃-CH₂-O and CH₃-C=); IR (NaCl): 3058w, 2981m, 2931m, 1713s, 1633m, 1493m, 1446m, 1391m, 1366s, 1295m, 1252s, 1201s, 1172m, 1111s, 1036m, 992m, 765s, 739m, 703s cm⁻¹; MS (FAB): *m/z* = 192 (12), 191 ([M+H]⁺, 100), 190 (42), 145 (54), 117 (34); anal. calcd. for C₁₂H₁₄O₂: C 75.76, H 7.42, O 16.82; found: C 75.41, H 7.48, O 16.98; GC (CE Instruments GC 8000 Top, FID detector, column: Restek RTX-1701 (30 m*0.25 mm*0.25 μm), carrier gas: He): 100 °C for 2 min, with 7 °C min⁻¹ up to 250 °C, 60 kPa, *t_R* = 17.2 min.

Ethyl 2-Methyl-3-phenyl-butanoate

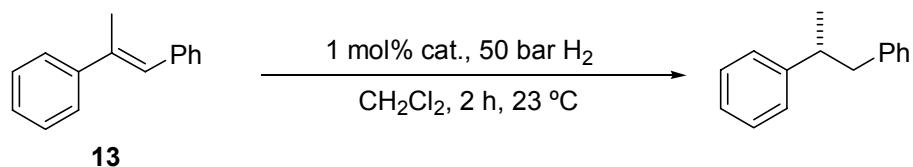
(*E*)-Ethyl 2-methyl-3-phenylacrylate **21** (87 mg, 0.46 mmol) was dissolved in ethanol (1 mL) and a few mg of Pd/C were added. After hydrogenation at 50 bar H₂ for 30 min the reaction mixture filtered and the solvent evaporated to give the desired product as colourless oil; yield: 89%; ¹H-NMR (400 MHz, CDCl₃): δ = 7.30–7.24 (m, 2H, *H_{Ar}*); 7.23–7.14 (m, 3H, *H_{Ar}*); 4.09 (q, ³*J* = 7.1 Hz, 2H, CH₃-CH₂-O); 3.06–2.98 / 2.78–2.62 (m, 3H, Ph-CH₂ and CH₃-CH); 1.19 (t, ³*J* = 7.1 Hz, 3H, CH₃-CH₂-O); 1.15 (d, ³*J* = 6.8 Hz, 3H, CH₃-CH); ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 176.1 (s, 1C, C=O); 139.4 (s, 1C, PhC(*ipso*)); 129.0 / 128.3 / 126.2 (s, 5C, PhC-H); 60.3 (s, 1C, CH₃-CH₂-O); 41.4 / 39.7 (s, 2C, Ph-CH₂ and CH₃-CH); 16.8 / 14.1 (s, 2C, CH₃-CH₂-O and CH₃-CH); IR (NaCl): 3058w, 2981m, 2931m, 1730s, 1497m, 1454m, 1378m, 1371m, 1309m, 1295w, 1265m, 1176w, 1084s, 1029m, 878w cm⁻¹; MS (GC-MS, Hewlett Packard Series II 5890 and Mass Selective Detector Hewlett Packard 5971, column: 25 m dimethyl silicon (OV-101), carrier gas: He, 100 °C for 2 min, with 7 °C min⁻¹ up to 250 °C, 20 kPa): *m/z* = 192 ([M]⁺, 12), 121 (36), 118 (65), 105 (100), 91 (28), 77 (25); anal. calcd. for C₁₂H₁₆O₂: C 74.97, H 8.39, O 16.64; found: C 75.21, H 8.48, O 16.98; GC (CE Instruments GC 8000 Top, FID detector, column: Restek RTX-1701 (30 m*0.25 mm*0.25 μm), carrier gas: He): 100 °C for 2 min, with 7 °C min⁻¹ up to 250 °C, 60 kPa, *t_R* = 14.5 min; HPLC (OB-H, heptane/*iso*-propanol (99.8:0.2), 20 °C, 0.5 ml/min, 220 nm): *t_R* = 15.3 min (-), *t_R* = 16.8 (+).

(S)-Benzyl 2-methylbutanoate

Phenylmethanol (160 μ L, 1.6 mmol) was dissolved in dichloromethane (5 mL) and DMAP (52 mg, 390 μ mol) as well as (*S*)-(+)-2-methyl butyric acid (160 μ L, 1.5 mmol) were added. After 10 min at room temperature DCC (409 mg, 2.0 mmol) was added and the reaction mixture stirred for 10 h at room temperature. Filtration, evaporation of the solvent and column chromatography (hexane/ethyl acetate (4:1)) gave the desired product as colourless oil; yield: 45%; $[\alpha]_D^{20}$: + 11.5 (c 2.21, CHCl_3); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.40–7.28 (m, 5H, H_{Ar}); 5.12 (s, 2H, $\text{CH}_2\text{-O}$); 2.42 (sext, $^3J = 7.2$ Hz, 1H, $\text{CH}_3\text{-CH}$); 1.71 / 1.49 (dq, $^2J = 13.7$ Hz, $^3J = 7.2$ Hz, 2H, $\text{CH}_3\text{-CH}_2$); 1.16 (d, $^3J = 7.2$ Hz, 3H, $\text{CH}_3\text{-CH}$); 0.90 (t, $^3J = 7.2$ Hz, 3H, $\text{CH}_3\text{-CH}_2$); $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3): δ = 176.5 (s, 1C, C=O); 136.3 (s, 1C, $\text{PhC}(ipso)$); 128.5 / 128.1 / 128.0 (s, 5C, PhC-H); 66.0 (s, 1C, $\text{CH}_2\text{-O}$); 41.1 (s, 1C, $\text{CH}_3\text{-CH}$); 26.8 (s, 1C, $\text{CH}_2\text{-CH}$); 16.6 / 11.6 (s, 2C, $\text{CH}_3\text{-CH}_2$ and $\text{CH}_3\text{-CH}$); IR (NaCl): 3034w, 2968s, 2936m, 2877m, 1732s, 1456m, 1383m, 1354m, 1262m, 1234m, 1183s, 1147s, 1078m, 1012m, 973w, 748m, 698m cm^{-1} ; MS (FAB): m/z = 193 ($[\text{M}+\text{H}]^+$, 12), 91 (100), 85 (15), 57 (59), 43 (24); anal. calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C 74.97, H 8.39, O 16.64; found: C 74.96, H 8.34, O 16.64; GC (Restek RTX-1701, carrier gas: H_2): 100 $^\circ\text{C}$ for 2 min, with 7 $^\circ\text{C min}^{-1}$ up to 250 $^\circ\text{C}$, 60 kPa, $t_{\text{R}} = 10.5$ min; (β -CD DiEtTBuSil SE54 (25 m*0.25 mm*0.25 μm), carrier gas: H_2): 85 $^\circ\text{C}$ for 110 min, 50 kPa, $t_{\text{R}} = 95.9$ min (*S*), $t_{\text{R}} = 99.4$ min (*R*).

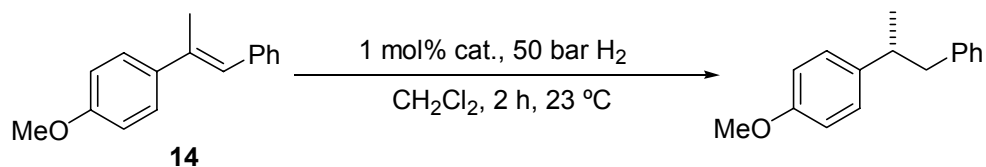
Ethyl 3-methyl-5-phenylpentanoate

GC (CE Instruments GC 8000 Top, FID detector, column: Restek RTX-1701 (30 m*0.25 mm*0.25 μm), carrier gas: He): 100 $^\circ\text{C}$ for 2 min, with 7 $^\circ\text{C min}^{-1}$ up to 250 $^\circ\text{C}$, 60 kPa, $t_{\text{R}} = 18.8$ min; HPLC (OB-H, heptane/*iso*-propanol (99.8:0.2), 20 $^\circ\text{C}$, 0.5 ml/min, 220 nm): $t_{\text{R}} = 23.8$ min (*S*), $t_{\text{R}} = 26.6$ min (*R*). Assignment of abs. configuration according to ref. [1].



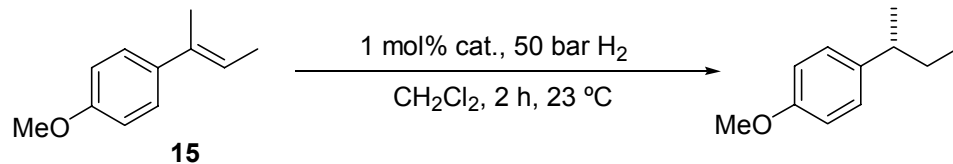
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	89	95 (<i>R</i>)
2	12b	> 99	> 99 (<i>R</i>)
3	12c	> 99	98 (<i>R</i>)
4	12d	> 99	99 (<i>R</i>)
5	12e	> 99	99 (<i>R</i>)
6	12f	> 99	88 (<i>R</i>)
7	12g	> 99	> 99 (<i>R</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [2]); abs. configuration: assigned by optical rotation according to ref. [3].



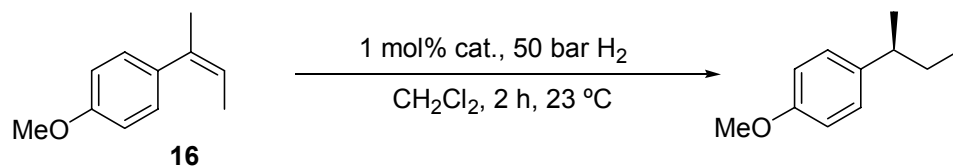
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	91	97 (<i>R</i>)
2	12b	> 99	> 99 (<i>R</i>)
3	12c	> 99	98 (<i>R</i>)
4	12d	> 99	98 (<i>R</i>)
5	12e	> 99	98 (<i>R</i>)
6	12f	> 99	75 (<i>R</i>)
7	12g	> 99	> 99 (<i>R</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [2]); abs. configuration: assigned by analogy with the hydrogenation product of **13**.



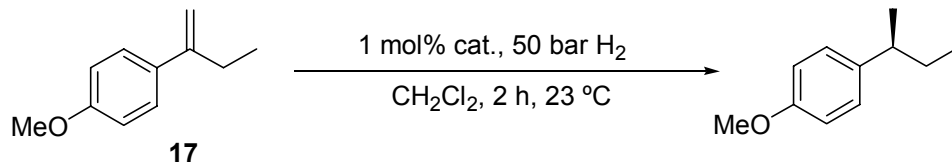
Entry	Catalyst	Conversion [%] ^[b]	<i>ee</i> [%] ^[c]
1	12a	50	84 (<i>R</i>)
2	12b	> 99	75 (<i>R</i>)
3	12c	> 99	93 (<i>R</i>)
4	12d	> 99	94 (<i>R</i>)
5	12e	78	78 (<i>R</i>)
6	12f	> 99	68 (<i>R</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [2]); abs. configuration: assigned by optical rotation according to ref. [3].



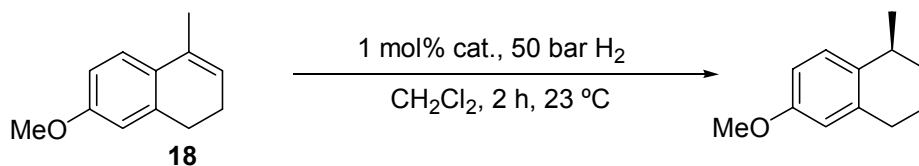
Entry	Catalyst	Conversion [%] ^[b]	<i>ee</i> [%] ^[c]
1	12a	87	52 (<i>S</i>)
2	12b	94	79 (<i>S</i>)
3	12c	> 99	73 (<i>S</i>)
4	12d	> 99	53 (<i>S</i>)
5	12e	95	78 (<i>S</i>)
6	12f	> 99	88 (<i>S</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [2]); abs. configuration: assigned by optical rotation according to ref. [3].



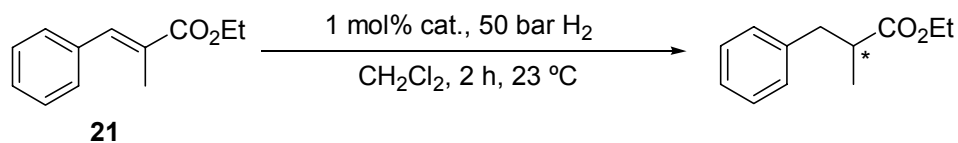
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	> 99	49 (<i>S</i>)
2	12b	> 99	30 (<i>S</i>)
3	12c	> 99	64 (<i>S</i>)
4	12d	> 99	55 (<i>S</i>)
5	12e	> 99	48 (<i>S</i>)
6	12f	> 99	70 (<i>S</i>)
7	12g	> 99	14 (<i>S</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [2]); abs. configuration: assigned by optical rotation according to ref. [3].



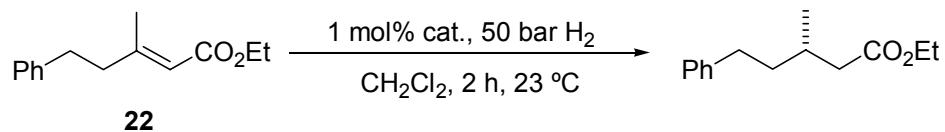
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	> 99	82 (<i>S</i>)
2	12b	> 99	82 (<i>S</i>)
3	12e	> 99	83 (<i>S</i>)
4	12f	> 99	82 (<i>S</i>)
5	12g	> 99	72 (<i>S</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see ref. [4]); abs. configuration: assigned by optical rotation according to ref. [3].



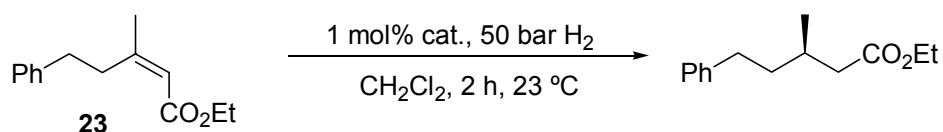
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	71	88 (S)
2	12b	95	88 (S)
3	12c	66	86 (S)
4	12e	48	71 (S)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see page 14); abs. configuration: assigned by optical rotation according to ref. [5].



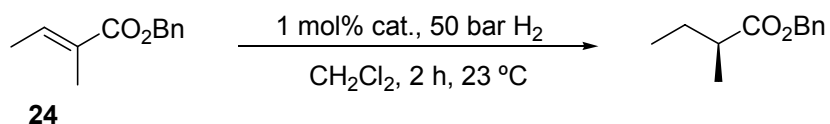
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	> 99	88 (S)
2	12b	> 99	87 (S)
3	12c	> 99	88 (S)
4	12d	> 99	84 (S)
5	12e	> 99	88 (S)
6	12f	90	67 (S)
7	12g	> 99	88 (S)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Determined by HPLC on a chiral stationary phase (see page 15); abs. configuration: assigned by optical rotation according to ref. [1].



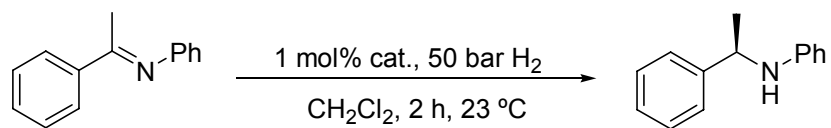
Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	> 99	76 (<i>R</i>)
2	12b	> 99	90 (<i>R</i>)
3	12d	> 99	83 (<i>R</i>)
4	12f	> 99	78 (<i>R</i>)
5	12g	> 99	86 (<i>R</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by HPLC on a chiral stationary phase (see page 15); abs. configuration: assigned by optical rotation according to ref. [1].



Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	> 99	66 (<i>S</i>)
2	12b	> 99	65 (<i>S</i>)
3	12c	> 99	65 (<i>S</i>)
4	12e	> 99	72 (<i>S</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Abs. configuration and ee values were determined by GC on a chiral stationary phase (see page 15).



Entry	Catalyst	Conversion [%] ^[b]	ee [%] ^[c]
1	12a	86	21 (<i>R</i>)
2	12e	93	30 (<i>R</i>)

^[a] All reactions were carried out with 1 mol % of catalyst in CH₂Cl₂ at 50 bar H₂ at 23 °C for 2 h. ^[b] Determined by GC. ^[c] Abs. configuration and ee values were determined by HPLC on a chiral stationary phase according to ref. [6].

References

- [1] U. Leutenegger, A. Madin, A. Pfaltz, *Angew. Chem.* **1989**, *101*, 61–62; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 60–61.
- [2] A. Lightfoot, P. Schnider, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 3047–3050; *Angew. Chem. Int. Ed.* **1998**, *37*, 2897–2899.
- [3] R. D. Broene, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 12569–12570.
- [4] J. Blankenstein, A. Pfaltz, *Angew. Chem.* **2001**, *113*, 4577–4579; *Angew. Chem. Int. Ed.* **2001**, *40*, 4445–4447.
- [5] A. R. Colwell, L. R. Duckwall, R. Brooks, S. P. McManus, *J. Org. Chem.* **1981**, *46*, 3097–3102.
- [6] P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz, *Chemistry Eur. J.* **1997**, *3*, 887–892.