NeoPHOX – an Easily Accessible P,N Ligand for Iridium-Catalyzed Asymmetric Hydrogenation: Preparation, Scope and Application in the Synthesis of Demethyl Methoxycalamenene

Marcus G. Schrems and Andreas Pfaltz*

Department of Chemistry,
University of Basel
St. Johanns-Ring 19
CH 4056 Basel

email: andreas.pfaltz@unibas.ch

Supporting Information

General: For general information regarding instrumentation refer to our previous publications.[1] All chemicals were purchased from Acros Organics, Aldrich, Fluka, Lancaster Synthesis, Merck, Molecula and Strem Chemicals. NMR-shifts (1H, 13C) are referenced to the corresponding (residual) solvent peak (CDCl3: 7.26 (CHCl3) for 1H-NMR; 77.0 (CDCl3) for 13C-NMR; CD2Cl2: 5.32 (CDCl3) for 1H-NMR; 53.1 (CD2Cl2) for 13C-NMR).

Content:

a) Synthesis of the amides 3a-e (pages 2-3)
b) Synthesis of the oxazolines 2a-e (pages 4-5)
c) Synthesis of NeoPHOX-ligands 1a-e (pages 6-9)
d) Synthesis of NeoPHOX-iridium complexes Ir-1a-e (pages 10-14)
e) Synthesis of 13, 14, 15 and (R)-(+)7-Demethyl-2-methoxycalamenene (16) (pages 15-18)
f) General asymmetric hydrogenation procedure (page 19)
g) References (page 20)
a) Synthesis of the amides 3a-c:

\[
\text{Cl} - \text{COCl} \quad \text{H} \quad \text{N} \quad \text{O} \quad \text{Cl} - \text{OH} \\
3a: R = \text{iPr} \\
3b: R = \text{tBu} \\
3c: R = \text{CH}_2\text{Ph}
\]

3a:
L-valinol (1.00 g, 9.68 mmol, 1.00 eq) and triethylamine (4.60 mL, 32.4 mmol, 3.30 eq) were dissolved in 60 mL of ether. To this mixture a solution of chloropivaloyl chloride (1.50 g, 9.68 mmol, 1.00 eq) in 10 mL of ether was added dropwise at 0 °C, leading to a precipitation of HCl·NEt$_3$. After addition of chloropivaloyl chloride the solution was stirred for 75 minutes at room temperature. A saturated NaHCO$_3$ solution (50 mL) was added and the phases were separated. The aqueous phase was extracted three times with 50 mL of ether. The combined organic phases were washed with brine (50 mL), dried over MgSO$_4$ and concentrated on a rotavap leaving a brown oil. Kugelrohr-distillation (150 °C, 9×10$^{-2}$ mbar) afforded the title compound as a colorless solid. The solid was dissolved in CH$_2$Cl$_2$ (5 mL) and added dropwise to 150 mL of ice-cold pentane. The colorless precipitate was collected by filtration. After drying at 1×10$^{-1}$ mbar 1.65 g (7.44 mmol, 77%) of the title compound were obtained.

**Elemental Analysis** for C$_{10}$H$_{20}$ClNO$_2$ (221.72), calc.: C, 54.17; H, 9.09; N, 6.32; found: C, 54.04; H, 8.82; N, 6.22; **M.p.**: 74 °C; [α]$_D^{20}$ $-$33.5 (c 1.00, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): δ(ppm) 5.95 (s, 1H, NH), 3.75-3.63 (m, 5H, C$_2$H$_5$Cl, NC$_2$H$_3$, C$_2$H$_5$OH), 2.54 (s, 1H, OH), 1.97-1.85 (m, 1H, C$_2$H$_5$(CH$_3$)$_2$), 1.31 (s, 6H, C(C$_2$H$_3$)$_2$), 0.97 (d, 3H, J = 6.8 Hz, CH(C$_2$H$_3$)$_2$), 0.94 (d, 3H, J = 6.8 Hz, CH(C$_2$H$_3$)$_2$); $^{13}$C{$_1$H}-NMR (100.6 MHz, CDCl$_3$, 300 K): δ(ppm) 175.6 (C=O), 64.0 (C$_2$H$_5$OH), 57.2 (CH), 52.8 (C$_2$H$_5$Cl), 44.4 (C(CH$_3$)$_2$), 29.0 (CH(C$_2$H$_3$)$_2$), 23.5 (C(CH$_3$)$_2$), 19.6 (CH(CH$_3$)$_2$), 18.8 (CH(CH$_3$)$_2$); MS (FAB) m/z (%): 224 (32), 223 (12), 222 ([M+H]$^+$, 100), 204 (8), 190 (9), 136 (8), 91 (26), 89 (8), 77 (10), 69 (8), 55 (14), 41 (10); IR (ν [cm$^{-1}$]) 3308s, 3250s, 2961s, 2930m, 1620s, 1549s, 1471s, 1446s, 1389s, 1352m, 1315m, 1280m, 1237m, 1165w, 1122w, 1095m, 1034s, 1027s, 975m, 908s, 882m, 832s, 810m, 732s, 674s.

3b:
L-tert.-leucinol (1.17 g, 10.0 mmol, 1.00 eq) and triethylamine (3.39 g, 33.0 mmol, 3.30 eq) were dissolved in 60 mL of ether. To this mixture a solution of chloropivaloyl chloride (1.55 g, 10.0 mmol, 1.00 eq) in 10 mL of ether was added dropwise at 0 °C, leading to a precipitation of HCl·NEt$_3$. After addition of chloropivaloyl chloride the solution was stirred for 2 h at room temperature. A saturated NaHCO$_3$ solution (50 mL) was added and the phases were separated. The aqueous phase was extracted 1×with 50 mL and 2×with 25 mL of ether. The combined organic phases were washed with brine (50 mL), dried over MgSO$_4$ and concentrated on a rotavap leaving a colorless solid (2.24 g, 9.50 mmol, 95%), which needed no further purification.

**Elemental Analysis** for C$_{11}$H$_{22}$ClNO$_2$ (235.75), calc.: C, 56.04; H, 9.41; N, 5.94; found: C, 56.07; H, 9.26, N, 5.81; **M.p.**: 126-127 °C; [α]$_D^{20}$ $-$11.7 (c 0.99, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): δ(ppm) 5.95 (d,
3c: L-phenylalaninol (2.44 g, 16.1 mmol, 1.00 eq) was suspended in 90 mL of ether. Triethylamine (7.60 mL, 54.0 mmol, 3.30 eq) dissolved in 20 mL of dichloromethane was added in one portion. To this mixture a solution of chloropivaloyl chloride (2.50 g, 16.1 mmol, 1.00 eq) in 10 mL of ether was added dropwise at 0 °C, leading to a precipitation of HCl·NEt$_3$. After addition of the acid chloride, the solution was stirred for 75 minutes at room temperature. A saturated NaHCO$_3$ solution (50 mL) was added and the phases were separated. The aqueous phase was extracted with 50 mL of ether (3×). The combined organic phases were washed with brine (50 mL), dried over MgSO$_4$ and concentrated on a rotavap leaving a brown oil. Kugelrohr-distillation (175 °C, 1×10$^{-1}$ mbar) afforded the title compound as a yellow oil (4.31 g, 16.0 mmol, 99%), which solidified in the fridge.

**Elemental Analysis** for C$_{14}$H$_{20}$ClNO$_2$ (269.77), calc.: C, 62.33; H, 7.47; N, 5.19; found: C, 62.07; H, 7.47; N, 5.08; M.p. 80 °C; [α]$_D^{20}$ $-12.8$ (c 0.99, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) 7.33-7.21 (m, 5H, H$_{Ar}$), 5.96 (d, 1H, J = 6.2 Hz, NH), 4.22-4.15 (m, 1H, CH$_3$), 3.70-3.51 (m, 4H, C$_2$H$_5$Cl, C$_2$H$_5$OH), 2.96-2.83 (m, 2H, C$_6$H$_5$CH$_2$), 2.69 (s, 1H, OH), 1.22 (s, 3H, CH$_3$), 1.17 (s, 3H, CH$_3$); $^{13}$C$[^1]$H-NMR (100.6 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) 175.3 (C=O), 137.4 (C$_{Ar}$), 129.2 (HC$_{Ar}$), 128.66 (HC$_{Ar}$), 126.74 (HC$_{Ar}$), 64.1 (C$_2$H$_5$OH), 52.9 (CH), 52.7 (CH$_2$Cl), 44.2 (C(CH$_3$)$_2$), 36.8 (C$_6$H$_5$CH$_2$), 23.3 (CH$_3$); MS (FAB) m/z (%) 272 (32), 271 (18), 270 (M$^+$, 100), 252 (12), 194 (12), 178 (14), 137 (11), 117 (14), 91 (55), 77 (13), 65 (8), 55 (22), 51 (8), 39 (16); IR (V [cm$^{-1}$]) 3368m, 3027w, 2866m, 1733m, 1635s, 1516s, 1496m, 1472m, 1454m, 1391m, 1366m, 1286w, 1242m, 1157w, 1039m, 733s. 

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b) Synthesis of the oxazolines 2a-c:

2a:
Amide 3a (510 mg, 2.30 mmol, 1.00 eq) and Burgess’ reagent (714 mg, 2.99 mmol, 1.30 eq) were dissolved in 25 mL of THF. The mixture was heated to reflux for 4 h. The solvent was removed on a rotavap and the crude product was extracted with ether (10×2 mL). After removal of the ether on a rotavap the crude product was purified by Kugelrohr distillation (70 °C, 7.6×10⁻² mbar). The title compound was obtained as a colorless oil (440 mg, 2.16 mmol, 94%).

Elemental Analysis for C₁₀H₁₆ClNO (203.71), calc.: C, 58.96; H, 8.91; N, 6.88; found: C, 58.89; H, 8.72; N, 6.88; [α]D²⁰ −77.4 (c 1.16, CHCl₃); ¹H-NMR (400.1 MHz, CDCl₃, 300 K): δ(ppm) 4.23-4.15 (m, 1H, NCH), 1.79 (q, 1H, J = 10.1 Hz, OCCH₃), 1.30 (s, 6H, C(CH₃)₃), 0.92 (d, 3H, J = 6.8 Hz, CH(CH₃)₂), 0.86 (d, 3H, J = 6.8 Hz, CH(CH₃)₂); ¹³C[¹H]-NMR (100.6 MHz, CDCl₃, 300 K): δ(ppm) 168.7 (C≡N), 71.7 (NCH), 69.6 (OCH₃), 52.6 (CH₂Cl), 38.8 (C(CH₃)₂), 32.2 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 18.6 (C(CH₃)₂), 17.5 (C(CH₃)₂); MS (EI) m/z (%) 203 (M⁺, 1), 188 (1), 168 (6), 160 (100), 132 (16), 110 (20), 91 (11), 70 (78), 55 (63), 41 (74); IR (ν [cm⁻¹]) 2973m, 2957s, 2904m, 2873m, 1732m, 1663vs, 1477m, 1447m, 1387m, 1364m, 1351m, 1177w, 1116s, 1045w, 1015w, 981m, 920s, 834m, 755m.

2b:
Amide 3b (4.62 g, 19.6 mmol, 1.00 eq) and Burgess’ reagent (6.07 mg, 25.5 mmol, 1.30 eq) were dissolved in 200 mL of THF. The mixture was heated to reflux for 4 h. The solvent was removed on a rotavap. To the crude product was added ether (100 mL) to dissolve the soluble components of the reaction mixture. The ether containing the product was decanted and the solvent was removed on a rotavap. Kugelrohr distillation (100 °C, 0.15 mbar) gave a colorless oil which was filtered through a plug of silica (h×d: 4.5 cm×3.5 cm) eluting with pentane/ether (10/1). The title compound was obtained as a colorless oil (4.18 g, 19.2 mmol, 98%).

Elemental Analysis for C₁₀H₁₆ClNO (217.74), calc.: C, 60.68; H, 9.26; N, 6.43; found: C, 60.86; H, 9.12; N, 6.41; [α]D²⁰ −80.5 (c 1.17, CHCl₃); ¹H-NMR (400.1 MHz, CDCl₃, 300 K): δ(ppm) 4.14 (dd, 1H, J = 8.6 Hz, J = 10.1 Hz, NCH), 4.08 (dd, 1H, J = 7.2 Hz, J = 8.6 Hz, OCH₃), 3.83 (dd, 1H, J = 7.2 Hz, J = 10.1 Hz, OCH₂), 3.62 (s, 2H, CH₂Cl), 1.30 (s, 6H, C(CH₃)₃), 0.88 (s, 9H, C(CH₃)₂); ¹³C[¹H]-NMR (100.6 MHz, CDCl₃, 300 K): δ(ppm) 169.7 (C≡N), 75.5 (NCH), 68.7 (OCH₃), 52.6 (CH₂Cl), 38.8 (C(CH₃)₂), 33.7 (C(CH₃)₂), 25.7 (C(CH₃)₂), 23.9 (C(CH₃)₂), 23.8 (C(CH₃)₂); MS (EI) m/z (%) 217 (M⁺, 1), 202 (4), 182 (2), 160 (100), 132 (15), 110 (36), 91 (45), 70 (79), 55 (72), 41 (97); IR (ν [cm⁻¹]) 2973m, 2953s, 2903m, 2870m, 1778w, 1743m, 1732m, 1663vs, 1477m, 1447m, 1387m, 1364m, 1351m, 1339m, 1177w, 1116s, 980s, 920s, 834m, 755m.
Amide 3c (1.01 g, 3.76 mmol, 1.00 eq) and Burgess' reagent (1.21 g, 5.05 mmol, 1.30 eq) were dissolved in 40 mL of THF. The mixture was heated to reflux for 4 h. The solvent was removed on a rotavap and the crude was dissolved in 20 mL of CH$_2$Cl$_2$. After extraction with water (2×20 mL) and brine (1×20 mL) the organic phase was dried over MgSO$_4$. After removal of the solvent on a rotavap the crude product was purified by Kugelrohr distillation (150 °C, 0.2 mbar). The title compound was obtained as a colorless oil (679 mg, 2.70 mmol, 72%).

C$_{14}$H$_{18}$ClNO (251.75); HRMS (+ESI-TOF) for [C$_{14}$H$_{18}$ClNO+H]$^+$, calc.: 252.1155; found: 252.1152; $\left[\alpha\right]_{\mathrm{D}}^{20}$ −29.7 (c 1.00, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): $\delta$(ppm) 7.27-7.31 (m, 2H, H$_{\text{Ar}}$), 7.19-7.24 (m, 3H, H$_{\text{Ar}}$), 4.39 (dddd, 1H, $J = 4.8$ Hz, $J = 6.8$ Hz, $J = 8.7$ Hz, $J = 8.9$ Hz, NCH), 4.16 (dd, 1H, $J = 8.4$ Hz, $J = 8.9$ Hz, OCH$_2$), 4.00 (dd, 1H, $J = 6.8$ Hz, $J = 8.4$ Hz, OCH$_2$), 3.59 (s, 2H, ClCH$_2$), 3.09 (dd, 1H, $J = 8.4$ Hz, $J = 13.7$ Hz, CH$_2$C$_6$H$_5$), 2.65 (dd, 1H, $J = 8.6$ Hz, $J = 13.7$ Hz, CH$_2$C$_6$H$_5$), 1.28 (s, 3H, C(CH$_3$)$_2$), 1.27 (s, 3H, C(CH$_3$)$_2$); $^{13}$C{$^1$H}-NMR (100.6 MHz, CDCl$_3$, 300 K): $\delta$(ppm) 170.5 (C=N), 137.7 (C$_{\text{Ar}}$), 129.4 (HC$_{\text{Ar}}$), 128.4 (HC$_{\text{Ar}}$), 126.5 (HC$_{\text{Ar}}$), 71.6 (OCH$_2$), 67.1 (NCH), 52.5 (ClCH$_2$), 41.5 (CH$_2$C$_6$H$_5$), 38.7 (C(CH$_3$)$_2$), 23.6 (C(CH$_3$)$_2$); MS (FAB) m/z (%) 254 ([M+H]$^+$, 32), 252 ([M+H]$^+$, 100), 160 (17), 117 (16), 91 (25), 55 (15); IR (v [cm$^{-1}$]) 2976m, 1718m, 1656s, 1494m, 1453m, 1445m, 1387m, 1349s, 1290m, 1179m, 1115s, 1074m, 980s, 927m, 828m, 751s, 729m.
c) Synthesis of NeoPHOX-ligands 1a-e:

1a:

A Schlenk tube with a magnetic stirrer was dried in an oven overnight, cooled under vacuum and charged with argon. After another two vacuum/argon cycles, oxazoline 2a (392 mg, 1.92 mmol, 1.05 eq) was added followed by 3.65 mL of a 0.5 M solution of KPPh$_2$ in THF (1.00 eq, 1.83 mmol). The red solution was heated to reflux for fourteen hours resulting in a colorless suspension. The solvent was removed in vacuo and 25 mL of MTBE and 15 mL of a saturated NH$_4$Cl solution were added. The phases were separated; the aqueous phase was diluted with 2 mL of water and extracted with 2×25 mL of MTBE. The combined organic phases were washed with brine (10 mL) and dried over Na$_2$SO$_4$. The solvent was removed on a rotavap. The crude product still contained some PHPh$_2$Cl-solution. This mixture was extracted with MTBE (3×20 mL), the combined organic phases were washed with brine (10 mL) and dried over Na$_2$SO$_4$. The solvent was removed on a rotavap. After filtration over silica gel (hex: 11 cm×2.5 cm, pentane/ethyl acetate, 5/1) the product was obtained as a colorless oil (595 mg, 1.68 mmol, 92%).

Elemental Analysis for C$_2$H$_2$NO$_2$P (353.44), calc.: C, 74.76; H, 7.99; N, 3.96; found: C, 74.75; H, 8.03; N, 3.95; [α]$_D$$^20$ $-27.5$ (c 1.01, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): δ (ppm) 7.43-7.48 (m, 4H, H$_{Ar}$), 7.28-7.34 (m, 6H, H$_{Ar}$), 3.68-3.78 (m, 3H, OC$_3$H$_7$), 2.44 (dq, 2H, J = 3.5 Hz, J = 14.3 Hz, PCH$_2$), 1.64-1.74 (m, 1H, HC(CH$_3$)$_2$), 1.34 (s, 3H, C(C$_2$H$_5$)$_2$), 1.30 (s, 3H, C(CH$_3$)$_2$), 0.89 (d, 3H, J = 6.8 Hz, HC(CH$_3$)$_2$), 0.80 (d, 3H, J = 6.8 Hz, HC(CH$_3$)$_2$); $^{31}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$, 300 K): δ (ppm) 171.8 (d, J = 3 Hz, C=N), 139.6 (d, J = 13 Hz, C$_{Ar}$), 133.3 (d, J = 20 Hz, H$_{C(A)}$), 132.7 (d, J = 19 Hz, H$_{C(A)}$), 128.3 (d, J = 5 Hz, H$_{C(A)}$), 128.3 (d, J = 2 Hz, H$_{C(A)}$), 128.2 (d, J = 4 Hz, H$_{C(A)}$), 71.6 (NCH), 69.3 (OCH$_3$), 41.0 (d, J = 17 Hz, PCH$_2$), 36.6 (d, J = 17 Hz, C(CH$_3$)$_2$), 32.3 (CH(CH$_3$)$_2$), 27.7 (d, J = 9 Hz, C(CH$_3$)$_2$), 27.3 (d, J = 10 Hz, C(CH$_3$)$_2$), 18.8 (HC(CH$_3$)$_2$), 17.5 (HC(CH$_3$)$_2$); $^{31}$P($^1$H)-NMR (162.0 MHz, CDCl$_3$, 300 K): δ (ppm) $-26.2$; MS (FAB) m/z (%) 370 (33), 354 ([M+H]$^+$, 100), 284 (11), 276 (27), 227 (52), 208 (37), 199 (13), 185 (17), 121 (13), 41 (11); IR (ν [cm$^{-1}$]) 3070w, 3053w, 2959m, 2926w, 2899w, 2870w, 1659s, 1585w, 1479m, 1468m, 1433s, 1383w, 1366w, 1346w, 1308w, 1263w, 1204w, 1182w, 1165w, 1142w, 1121w, 1094m, 1026w, 982m, 920w, 818w, 743m, 696s, 631w; R$_f$ 0.50 (silica gel, hexanes/ethyl acetate, 4/1).

1b:

A Schlenk tube with a magnetic stirrer was dried in an oven overnight, cooled down under vacuum and charged with argon. After another two vacuum/argon cycles oxazoline 2b (795 mg, 3.65 mmol) was added followed by 7.5 mL of a 0.5 M solution of KPPh$_2$ in THF (1.03 eq, 3.75 mmol). The red solution was heated to reflux for seven hours with stirring. To the pale red solution were added 10 mL of a saturated NH$_4$Cl-solution. This mixture was extracted with MTBE (3×20 mL), the combined organic phases were washed with brine (10 mL) and dried over Na$_2$SO$_4$. The solvent was removed on a rotavap. The crude product still contained some PHPh$_2$.
Elemental Analysis for C$_2$H$_4$NOP (367.46), calc.: C, 75.18; H, 8.23; N, 3.81; found: C, 75.02; H, 8.18; N, 3.67; M.p.: 64 °C; [α]$^D_{20}$ = −33.7 (c 1.02, CHCl$_3$); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300 K): δ (ppm) 7.44-7.48 (m, 4H, $H_{Ar}$), 7.28-7.34 (m, 6H, $H_{Ar}$), 3.92 (dd, 1H, $J = 6.6$ Hz, $J = 8.0$ Hz, NCH$_2$), 3.73 (dd, 1H, $J = 8.0$ Hz, $J = 10.0$ Hz, OCH$_2$), 3.66 (dd, 1H, $J = 6.6$ Hz, $J = 10.0$ Hz, OCH$_2$), 2.50 (dd, 1H, $J = 3.9$ Hz, $J = 14.3$ Hz, PCH$_2$), 2.42 (dd, 1H, $J = 3.5$ Hz, $J = 14.3$ Hz, PCH$_2$), 1.34 (s, 3H, C(CH$_3$)$_2$), 1.29 (s, 3H, C(CH$_3$)$_2$), 0.85 (s, 9H, C(CH$_3$)$_3$); $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$, 300 K): δ (ppm) 171.9 (d, $J = 3$ Hz, C=N), 139.8 (d, $J = 3$ Hz, C$_a$), 139.7 (d, $J = 3$ Hz, C$_a$), 133.2 (d, $J = 13.6$ Hz, OCH$_2$), 68.3 (OCH$_2$), 41.0 (d, $J = 17$ Hz, PCH$_2$), 36.7 (d, $J = 17$ Hz, PCH$_2$C(CH$_3$)$_2$), 33.7 (C(CH$_3$)$_3$), 27.7 (d, $J = 9$ Hz, PCH$_2$C(CH$_3$)$_2$), 27.2 (d, $J = 11$ Hz, PCH$_2$C(CH$_3$)$_2$), 25.7 (C(CH$_3$)$_3$); $^{31}$P($^1$H)-NMR (162.0 MHz, CDCl$_3$, 300 K): δ (ppm) −25.9; MS (FAB) m/z (%) 384 (26), 368 ([M+H]$^+$, 100), 310 (33), 290 (43), 227 (64), 183 (19), 168 (11), 121 (15), 41 (13); IR (ν [cm$^{-1}$]) 3070w, 3057w, 2966m, 2947m, 2924m, 2897m, 2866m, 1661s, 1585w, 1477m, 1468m, 1433s, 1383w, 1367m, 1350m, 974s, 922s, 798m, 733s, 694s; R$_f$ 0.37 (silica gel, hexanes/ethyl acetate, 4/1).

1c:
A Schlenk tube with a magnetic stirrer was dried in an oven overnight, cooled down under vacuum and charged with argon. In a glove box 221 mg oTol$_2$PH (1.03 mmol) were added, followed by 81.0 mg (2.02 mmol) of KH. Outside of the glove box, oxazoline 2b (240 mg, 1.10 mmol) and 2 mL of THF were added under inert gas. The red-orange solution was heated to reflux for four hours. A $^{31}$P-NMR spectrum in CD$_2$Cl$_2$ showed full conversion. The NMR-sample was added to the reaction mixture followed by 4 mL of MTBE and 4 mL of a saturated NH$_4$Cl-solution. The phases were separated and the aqueous phase was diluted with 2 mL of water. The aqueous phase was then extracted with MTBE (3×4 mL), the combined organic phases were washed with brine (10 mL) and dried over Na$_2$SO$_4$. To the organic phase was added silica gel (3 g) and the solvent was removed on a rotavap. After filtration over silica gel (hxd: 1 cm×2.5 cm, pentane/ethyl acetate, 50/1→25/1) the product was obtained as a colorless oil (352 mg, 0.89 mmol, 86%).

C$_2$H$_4$NOP (395.52), HRMS (+ESI-TOF) for [C$_2$H$_4$NOP+H]$^+$, calc.: 396.2456, found: 396.2455; [α]$^D_{20}$ = −28.0 (c 0.61, CHCl$_3$); $^1$H-NMR (500.1 MHz, CDCl$_3$, 300 K): δ (ppm) 7.33-7.35 (m, 1H, $H_{Ar}$), 7.24-7.26 (m, 1H, $H_{Ar}$), 7.11-7.21 (m, 6H, $H_{Ar}$), 3.87-3.92 (dd, 1H, $J = 12.1$ Hz, $J = 13.6$ Hz, OCH$_2$), 3.60-3.65 (m, 2H, NCH$_2$), 2.53 (s, 3H, C$_a$CH$_3$), 2.41 (s, 3H, C$_a$CH$_3$), 2.39 (dd, 1H, $J = 2.4$ Hz, $J = 14.8$ Hz, PCH$_2$), 2.34 (dd, 1H, $J = 1.6$ Hz, $J = 14.5$ Hz, PCH$_2$), 1.40 (s, 3H, C(CH$_3$)$_2$), 1.33 (s, 3H, C(CH$_3$)$_2$), 0.85 (s, 9H, C(CH$_3$)$_3$), $^{13}$C($^1$H)-NMR (125.8 MHz, CDCl$_3$, 300 K): δ (ppm) 171.8 (d, $J = 3$ Hz, C=N), 142.4 (d, $J = 28$ Hz, C$_a$CH$_3$), 142.0 (d, $J = 27$ Hz, C$_a$CH$_3$), 137.40 (d, $J = 27$ Hz, PC$_a$), 137.30 (d, $J = 28$ Hz, PC$_a$), 132.1 (d, $J = 13.6$ Hz, NCH$_2$), 131.0 (d, $J = 5$ Hz, H$_2$Ar), 129.9 (d, $J = 5$ Hz, H$_2$Ar), 128.2 (d, $J = 13.6$ Hz, H$_2$Ar), 128.1 (d, $J = 7$ Hz, H$_2$Ar), 75.2 (NCH), 68.2 (OCH$_2$), 38.3 (d, $J = 18$ Hz, PCH$_2$), 36.5 (d, $J = 17$ Hz, C(CH$_3$)$_2$), 33.2 (C(CH$_3$)$_3$), 27.2 (d, $J = 9$ Hz, C(CH$_3$)$_2$), 27.4 (d, $J = 10$ Hz, C(CH$_3$)$_2$), 25.7 (C(CH$_3$)$_3$), 21.3 (d, $J = 18$ Hz, C$_a$CH$_3$), 21.1 (d, $J = 18$ Hz, C$_a$CH$_3$); $^{31}$P-NMR (162.0 MHz, CDCl$_3$, 300 K): δ (ppm) −54.0; MS (+ESI) m/z (%) 396 ([M+H]$^+$, 100);
Id:
A Schlenk tube with a magnetic stirrer was dried in an oven overnight, cooled down under vacuum and charged with argon. In a glove box 250 mg Xyl\(\cdot\)PH (1.03 mmol) were added, followed by 81.0 mg (2.02 mmol) of KH. Outside the glove box oxazoline \(\textbf{2b}\) (240 mg, 1.10 mmol) and 2 mL of THF were added under inert gas. The orange solution was heated to reflux for six hours. The solvent was removed in vacuo and 10 mL of MTBE followed by 5 mL of a saturated NH\(_4\)Cl-solution were added. The phases were separated and the aqueous phase was diluted with 2 mL of water. The aqueous phase was then extracted with MTBE (2×10 mL), the combined organic phases were washed with brine (10 mL) and dried over Na\(_2\)SO\(_4\). To the organic phase was added silica gel (3 g) and the solvent was removed on a rotavap. After filtration over silica gel (h×d: 11 cm×3.5 cm, pentane/ethyl acetate, 5/1) the product was obtained as a colorless oil (360 mg, 0.85 mmol, 83%).

**Elemental Analysis** for C\(_2\)H\(_6\)NOP (423.57), calc.: C, 76.56; H, 9.04; N, 3.31; found: C, 76.38; H, 9.05; N, 3.42; \([\alpha]_D^\text{27}^{\text{C}}\) −29.0 (c 0.95, CHCl\(_3\)); \(\textbf{1H-NMR}\) (400.1 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) 7.09 (s, 2H, \(H_{\text{Ar}}\), 7.07 (s, 2H, \(H_{\text{Ar}}\)), 6.91 (s, 2H, \(H_{\text{Ar}}\)), 3.93 (dd, 1H, \(J = 6.8\ Hz, J = 8.2\ Hz, \text{NCH}\)), 3.75 (dd, 1H, \(J = 8.2\ Hz, J = 10.0\ Hz, \text{OCH}_2\)), 3.67 (dd, 1H, \(J = 6.8\ Hz, J = 10.0\ Hz, \text{OCH}_2\)), 2.42 (ddd, 2H, \(J = 3.7\ Hz, J = 14.3\ Hz, J = 33.6\ Hz, \text{PCH}_2\)), 2.28 (s, 12H, \(C(C\text{H}_3)_2\)), 1.33 (s, 3H, \(C(C\text{H}_3)_2\)), 1.29 (s, 3H, \(C(C\text{H}_3)_2\)), 0.86 (s, 9H, \(C(C\text{H}_3)_2\)); \(\textbf{13C\({}^\text{1H}\)}\)-NMR (100.6 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) 172.1 (d, \(J = 3\ Hz, C=\text{N}\)), 139.5 (d, \(J = 5\ Hz, C_{\text{Ar}}\)), 139.4 (d, \(J = 4\ Hz, C_{\text{Ar}}\)), 137.5 (d, \(J = 5\ Hz, C_{\text{Ar}}\)), 137.5 (d, \(J = 5\ Hz, C_{\text{Ar}}\)), 130.8 (d, \(J = 20\ Hz, \text{HC}_{\text{Ar}}\)), 130.5 (d, \(J = 20\ Hz, \text{HC}_{\text{Ar}}\)), 130.0 (d, \(J = 11\ Hz, \text{HC}_{\text{Ar}}\)), 75.4 (NCH), 68.2 (OCH\(_2\)), 40.8 (d, \(J = 17\ Hz, \text{PCH}_2\)), 36.7 (d, \(J = 17\ Hz, \text{PCH}_2\)), 33.7 (C(\text{CH}_3)), 27.7 (d, \(J = 10\ Hz, \text{PCH}_2\)C(\text{CH}_3)), 27.2 (d, \(J = 11\ Hz, \text{PCH}_2\)C(\text{CH}_3)), 25.8 C(\text{CH}_3), 21.3 (2×C\(_{\text{Ar}}\)CH\(_3\)); \(\textbf{31P\({}^\text{1H}\)}\)-NMR (162.0 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) −26.5; MS (EI) m/z (%) 423 (M\(^+\), 3), 408 (5), 366 (33), 318 (26), 283 (100), 241 (7), 149 (5); \(\textbf{IR}\) (\(\bar{\nu}\) [cm\(^{-1}\)]) 3020w, 2955m, 2903m, 2866m, 1661s, 1598m, 1582m, 1478m, 1364m, 1269w, 1196m, 1122s, 11092m, 978s, 918m, 843s, 802w, 725w, 690s, \(R_f\) 0.62 (silica gel, hexanes/ethyl acetate, 4/1).

Ie:
A Schlenk tube with a magnetic stirrer was dried in an oven overnight, cooled down under vacuum and charged with argon. After another two vacuum/argon cycles oxazoline \(\textbf{2c}\) (184 mg, 0.73 mmol) was added followed by 1.4 mL of a 0.5 M solution of KPPH\(_2\) in THF (0.96 eq, 0.70 mmol). The red solution was heated to reflux for 14 h. To the resulting pale yellow solution were added 5 mL of a saturated NH\(_4\)Cl-solution. This mixture was extracted with MTBE (3×10 mL), the combined organic phases were washed with brine (10 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed on a rotavap. After filtration over silica gel (hxd: 16 cm×2.5 cm, pentane/ethyl acetate, 5/1) the product was obtained as a colorless oil (807 mg, 2.20 mmol, 60%). The product decomposes slowly on silica.

**Elemental Analysis** for C\(_{28}\)H\(_{32}\)NOP (401.48), calc.: C, 77.78; H, 7.03; N, 3.49; found: C, 77.57; H, 7.11; N, 3.51; \([\alpha]_D^\text{20}^{\text{C}}\) −16.5 (c 0.92, CHCl\(_3\)); \(\textbf{1H-NMR}\) (400.1 MHz, CDCl\(_3\), 300 K): \(\delta\) (ppm) 7.43-7.47 (m, 4H, \(H_{\text{Ar}}\)), 7.12-
7.33 (m, 11H, $H_A$), 4.15 (ddt, 1H, $J = 4.5$ Hz, $J = 7.6$ Hz, $J = 8.9$ Hz), 3.69 (dd, 2H, $J = 3.3$ Hz, $J = 8.2$ Hz), 3.03 (dd, 1H, $J = 4.5$ Hz, $J = 13.7$ Hz), 2.47 (dd, 1H, $J = 8.8$ Hz, $J = 13.7$ Hz), 2.41 (dd, 2H, $J = 3.3$ Hz, $J = 5.4$ Hz), 1.35 (s, 3H, C(C(H$_3$)$_2$)$_3$), 1.28 (s, 3H, C(C(H$_3$)$_2$)$_3$); $^{1}$H-NMR (100.6 MHz, CDCl$_3$, 300 K): $\delta$(ppm) 172.5 (d, $J = 3$ Hz, NC=O), 139.4 (d, $J = 13$ Hz, $C_A$), 139.3 (d, $J = 12$ Hz, $C_A$), 138.0 ($C_A$), 133.1 (d, $J = 20$ Hz, 2x$H_A$), 132.8 (d, $J = 20$ Hz, 2x$H_A$), 129.3 ($H_A$), 128.4 (d, $J = 14$ Hz, 2x$H_A$), 128.3 ($H_A$), 128.3 (d, $J = 13$ Hz, 2x$H_A$), 128.3 (d, $J = 5$ Hz, 4x$H_A$), 126.3 ($H_A$), 71.2 (OCH$_3$), 66.9 (NCH), 41.4 (CH$_2$C$_6$H$_5$), 40.9 (d, $J = 17$ Hz, PCH$_2$), 36.4 (d, $J = 16$ Hz, C(CH$_3$)$_2$), 27.5 (d, $J = 9$ Hz, C(CH$_3$)$_2$), 27.3 (d, $J = 10$ Hz, C(CH$_3$)$_2$); $^{31}$P-NMR (162.0 MHz, CDCl$_3$, 300 K): $\delta$(ppm) $-26.7$; MS (FAB) m/z (%) 418 ([M+OH]$^+$, 22), 402 ([M+H]$^+$, 100), 324 (29), 310 (51), 284 (17), 227 (81), 165 (8), 91 (43), 41 (9); IR ($\nu$ [cm$^{-1}$]) 3053w, 2966w, 2920w, 1653s, 1472m, 1454m, 1433s, 1200w, 1164w, 1094m, 1068w, 980m, 926w, 743m, 696s; $R_f$ 0.40 (silica gel, hexanes/ethyl acetate, 4/1).
d) Synthesis of NeoPHOX-iridium complexes Ir-1a-e:

To a dry Schlenk tube was added a solution of 211 mg (1.03 mmol, 1.00 eq) oxazoline 2a in 2 mL of THF. To this solution were added dropwise at 0 °C 2.0 mL of a 0.5 M KPh solution in THF (1.00 mmol, 0.97 eq). The red solution was heated to reflux for 5 h, causing a color change to yellow. The solvent was removed in vacuo and to the residue was added toluene (5 mL) and 0.3 mL methanol. The solution was passed through a plug of silica gel (0.7 cm×2.0 cm) followed by 5×2 mL of toluene. The solvent was removed on a rotavap and the immobilized complex was put on top of a silica gel column (10 cm×4 cm) and eluted with 300 mL MTBE (discarded) followed by 200 mL CHCl₃ (collected). The solvent was removed on a rotavap and the product was dried under vacuum (1×10⁻¹ mbar). The product was obtained as an orange crystalline solid (644 mg, 425 μmol) in 72% yield.

**Elemental Analysis** for C₆₂H₅₂BF₄IrNOP (1517.05), calc.: C, 49.09; H, 3.45; N, 0.92; found: C, 49.21; H, 3.42; N, 0.74; ▰By 178.0 (d, 2H, J = 7.6 Hz, J = 11.2 Hz, H₁a), 7.73 (s, 8H, H₄f⁻), 7.87 (dd, 2H, J = 11 Hz, H₄p), 7.62-7.51 (m, 3H, H₃a), 7.57 (s, 4H, H₃bf⁻), 7.48-7.38 (m, 3H, H₃b), 7.13-7.08 (m, 2H, H₂a), 4.95 (br s, 1H, COD-CH), 4.89-4.76 (m, 1H, COD-CH), 4.44-4.39 (m, 1H, OCH₂), 4.35 (dd, 1H, J = 14.6 Hz, J = 5.1 Hz, OCH₂), 4.09-3.99 (m, 1H, NCH), 3.51 (br s, 1H, COD-CH), 2.65-2.47 (m, 5H, COD-CH, COD-CH₂, PCH₂), 2.44-2.33 (m, 2H, COD-CH₂), 2.18 (s, 3H, C(CH₃)₂), 2.17-2.10 (m, 1H, COD-CH₂), 2.06-1.97 (m, 1H, CH(CH₃)₂), 1.95-1.86 (m, 1H, COD-CH₂), 1.74-1.60 (m, 1H, COD-CH₂), 1.49 (d, 3H, J = 2.7 Hz, C(CH₃)₂), 1.48-1.42 (m, 1H, COD-CH₂), 0.84 (d, 3H, J = 7.1 Hz, CH(CH₃)₂), 0.06 (d, 3H, J = 6.7Hz, CH(CH₃)₂); ¹³C[¹H]-NMR (125.8 MHz, CDCl₃, 300 K): δ (ppm) 178.0 (d, J = 4 Hz, C=N), 161.4 (q, J = 51 Hz, C₆H₁₂⁻), 153.5 (d, J = 13 Hz, HC₆F₅), 134.5 (HC₆F₇⁻), 132.2 (d, J = 3 Hz, HC₆F₅), 132.0 (d, J = 56 Hz, C₆H₁₂⁻), 131.1 (d, J = 10 Hz, HC₆F₇⁻), 130.7 (d, J = 3 Hz, HC₆F₅), 129.2 (d, J = 11 Hz, HC₆F₅), 128.6 (d, J = 10 Hz, HC₆F₅), 128.5 (qq, J = 3 Hz, J = 32 Hz, C₆H₁₂⁻), 128.0 (d, J = 54 Hz, C₆H₁₂⁻), 124.3 (q, J = 273 Hz, CF₃), 117.2 (sept, J = 4 Hz, HC₆F₇⁻), 92.1 (d, J = 11 Hz, COD-CH), 91.5 (d, J = 13 Hz, COD-CH), 69.3 (NCH), 69.2 (OCH₂), 63.7
**Ir-1b:**

To a solution of [Ir(COD)Cl]₂ (343 mg, 0.51 mmol, 0.51 eq) in 5 mL of CH₂Cl₂ was added a solution of ligand 1b (376 mg, 1.00 mmol) in 5 mL of CH₂Cl₂ under argon atmosphere. The mixture was refluxed for 30 min and then cooled to room temperature. NaBArF₃ (930 mg, 1.05 mmol, 1.05 eq) was added as a solid followed by 2 mL of CH₂Cl₂. The mixture was stirred for 30 min and 5 g of silica gel were added. The solvent was removed in vacuo and the immobilized complex was put on top of a silica gel column (h×d, 10 cm×4 cm). The column was eluted with 300 mL of MTBE, followed by 300 mL of CH₂Cl₂. The latter fraction containing the product was concentrated on a rotavap. The concentrated solution was filtered over a glass-wool filter (hexane was added until the mixture became turbid. The solvent was removed on a rotavap and the product crystallized. The product was dried under vacuum. The iridium complex was obtained as a yellow-orange solid (1.45 g, 0.95 mmol) in 95% yield.

**Elemental Analysis** for C₆₅H₅₃BF₃IrNOP (1531.07), calc.: C, 49.42; H, 3.55; N, 0.91; found: C, 49.47; H, 3.46; N, 0.68: [α]¹⁹D +17 (c 0.21, CHCl₃).

**¹H-NMR** (500.1 MHz, CD₂Cl₂, 300 K): δ (ppm) 7.78-7.83 (m, 2H, Hₐ), 7.74 (s, 8H, Hₐ,₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋˓→vrond

**IR** (ν [cm⁻¹]) 2972w, 2893w, 1604m, 1485w, 1439w, 1350s, 1271s, 1157s, 1105s, 1045w, 999w, 896m, 885m, 837m, 734m, 715s, 694m, 680s, 672s.
Ir-1c:

[Ir(COD)Cl]2 (205 mg, 0.31 mmol, 0.55 eq) was added as a solid to a solution of ligand 1c (218 mg, 0.55 mmol, 1.00 eq.) in 4 mL of CH2Cl2 under argon atmosphere. The mixture was refluxed for 10 min and then cooled to room temperature. NaBArF (575 mg, 0.65 mmol, 1.18 eq) was added as a solid followed by 2 mL of CH2Cl2. The mixture was stirred for 30 min and 5 g of silica gel were added. The solvent was removed in vacuo and the immobilized complex was put on top of a silica gel column (hxd, 16 cm×3 cm). The column was eluted with 300 mL of MTBE, followed by 300 mL of CH2Cl2. The latter fraction containing the product was concentrated on a rotavap and the product was dried under vacuum. The iridium complex was obtained as a yellow solid (747 mg, 0.50 mmol) in 91% yield.

Elemental Analysis for C63H56BF24IrNOP (1559.13), calc.: C, 50.07; H, 3.75; N, 0.90; found: C, 49.99; H, 3.69; N, 0.70; [α]D20 +4 (c 0.20, CHCl3); NMR-analysis was hampered by signal broadening caused by conformational equilibria: 1H-NMR (500.1 MHz, CD2Cl2, 300 K): δ(ppm) 8.57 (dd, 1H, J = 6.8 Hz, J = 16.5 Hz, Hα), 7.74 (s, 8H, HAr,F), 7.57 (s, 5H, HAr,F, J = 7.46-7.49 (m, 2H, HCl, 7.36 (t, 2H, J = 6.9 Hz, HCl, 7.27 (s, 1H, HCl, 7.13 (s, 1H, Hα), 4.75-4.85 (m, 2H, 2×COD-CH), 4.57 (dd, 1H, J = 4.3 Hz, J = 9.7 Hz, OCH2), 4.36 (t, HCl, J = 9.9 Hz, OCH2), 4.07 (s, 1H, COD-CH), 3.94 (dd, 1H, J = 4.1 Hz, J = 9.9 Hz, NCH), 2.83 (dd, 1H, J = 11.4 Hz, J = 15.5 Hz), 2.57-2.67 (m, 1H), 2.45-2.53 (m, 2H, 1×COD-CH), 2.34-2.41 (m, 1H), 2.26 (s, 3H, C(CH3)2), 2.14-2.24 (m, 2H), 2.03-2.12 (m, 1H), 2.02 (s, 3H, CArCH3), 1.72-1.84 (m, 1H), 1.67 (s, 3H, CArCH3), 1.54-1.60 (m, 1H), 1.52 (s, 3H, C(CH3)2), 1.31-1.41 (m, 1H), 0.88 (s, 9H, C(CH3)3), 13C[1H]-NMR (125.8 MHz, CDCl3, 300 K): δ(ppm) 178.3 (br s, C≡N), 161.4 (q, J = 50 Hz, CArF), 141.7, 140.1, 134.5 (HCAr-F), 132.4, 132.0, 130.8, 130.3, 128.5 (qq, J = 3 Hz, J = 32 Hz, CAr-F), 125.8 (d, J = 16.0 Hz), 127.0, 124.3 (q, J = 272 Hz, CF3), 117.1 (m, HArF), 92.1 (COD-CH), 89.0 (COD-CH), 73.6 (NCH), 70.5 (OCH2), 64.4 (COD-CH), 60.2 (COD-CH), 39.0, 36.7 (d, J = 5 Hz), 35.7 (d, J = 28 Hz), 33.5, 32.5 (br s, C(CH3)2), 32.2 (br s, PCH2), 28.1, 27.1, 25.2 (C(CH3)2), 24.9, 22.3 (CArCH3), 21.1 (CArCH3), 31P[1H]-NMR (202.5 MHz, CD2Cl2, 300 K): δ(ppm) −64.0; MS (+ESI) m/z (%) 698 [M−BArF]+, 100; IR (υ [cm⁻¹]) 2968w, 2935w, 2893w, 1599m, 1454w, 1352s, 1271s, 1161s, 1121s, 1001w, 885m, 839m, 767m, 715s, 680s.

Ir-1d:

[Ir(COD)Cl]2 (196 mg, 0.29 mmol, 0.55 eq) was added as a solid to a solution of ligand 1d (225 mg, 0.53 mmol) in 4 mL of CH2Cl2 under argon atmosphere. The mixture was refluxed for 30 min and then cooled to room temperature. NaBArF (564 mg, 0.64 mmol, 1.20 eq) was added as a solid followed by 2 mL of CH2Cl2. The mixture was stirred for 30 min and 5 g of silica gel were added. The solvent was removed in vacuo and the immobilized complex was put on top of a silica gel column (hxd, 20 cm×3 cm). The column was eluted with 300 mL of MTBE, followed by 300 mL of CH2Cl2. The latter fraction containing the product was concentrated on a rotavap and the product was dried under vacuum. The iridium complex was obtained as a yellow solid (780 mg, 0.49 mmol) in 93% yield.

Elemental Analysis for C67H58BF34IrNOP (1587.18), calc.: C, 50.70; H, 3.94; N, 0.88; found: C, 50.75; H, 3.70; N, 0.75; [α]D20 +10 (c 0.10, CHCl3); 1H-NMR (400.1 MHz, CDCl3, 300 K): δ(ppm) 7.74 (s, 8H, HAr,F), 7.58 (s,
**Ir-1e:**

To a dry Schlenk tube was added a solution of 246 mg (0.98 mmol, 1.00 eq) oxazoline 2e in 2 mL of THF. To this solution were added dropwise at 0 °C 2.0 mL of a 0.5 M KPPh₂ solution in THF (1.00 mmol, 1.02 eq). The red solution was heated to reflux for 5 h, causing a color change to yellow. The solvent was removed in vacuo and to the residue was added toluene (5 mL) and 0.3 mL methanol. The solution was passed through a plug of silica gel (0.7 cm×2.0 cm) followed by 5×2 mL of toluene. The solvent was removed in vacuo and 409 mg (>100%) of the crude ligand (1e) were obtained with sufficient purity (judged from the 31P-NMR spectrum) for complexation.

To a solution of 120 mg (179 μmol, 0.36 eq) of [Ir(COD)Cl]₂ in 5 mL of CH₂Cl₂ were added 201 mg (500 μmol, 1.0 eq) of the crude ligand (1e, see above). The solution was heated to reflux for 30 min and the solution was cooled to RT followed by addition of 576 mg (650 μmol, 1.3 eq) of NaBARF as a solid. After 30 min, 20 mL of water were added, the phases were separated and the aqueous phase was extracted with CH₂Cl₂ (2×10 mL). The combined organic phases were dried over MgSO₄, silica gel (3 g) was added and the solvent was removed on a rotavap. The immobilized complex was put on top of a silica gel column (10 cm×4 cm) and eluted with 300 mL MTBE (discarded) followed by 200 mL CH₂Cl₂ (collected). The solvent was removed on a rotavap and the product was dried under vacuum (1×10⁻¹ mbar). The product was obtained as an orange crystalline solid (553 mg, 353 μmol) in 71% yield.

**Elemental Analysis** for C₆₆H₅₂BF₂₄IrNOP (1565.09), calc.: C, 50.65; H, 3.35; N, 0.89; found: C, 50.64; H, 3.30; N, 0.74; [IrCl₄]⁺ +12 (c 0.22, CHCl₃); **¹H-NMR** (500.1 MHz, CD₂Cl₂, 300 K): δ (ppm) 7.96-7.92 (m, 2H, H₆), 7.73 (s, 8H, H₆,Ar), 7.64-7.63 (m, 1H, H₅), 7.60-7.59 (m, 2H, H₆), 7.56 (s, 4H, H₆,Ar), 7.46 (s, 3H, H₅), 7.32-7.26 (m, 3H, H₅), 7.17-7.13 (m, 2H, H₆), 7.02-7.01 (m, 2H, H₅), 5.10-5.00 (m, 2H, 2 COD-CH), 4.43-4.30 (m, 3H, NCH, OCH₂), 3.63 (br s, 1H, COD-CH), 3.45 (dd, 1H, J = 2.9 Hz, J = 13.6 Hz, CH₂C₆H₅), 2.67-2.37 (m,
7H, PCH₂, COD-CH₂, 2 COD-CH₂, 2.26-2.17 (m, 2H, COD-CH₂, CH₂C₆H₅), 2.18 (s, 3H, C(CH₃)₂), 1.98-1.91 (m, 1H, COD-CH₂), 1.77-1.69 (m, 1H, COD-CH₂), 1.53-1.42 (m, 1H, COD-CH₂), 1.48 (d, J = 2.5 Hz, 3H, C(CH₃)₂); ¹³C{¹H}-NMR (125 MHz, CD₂Cl₂, 300 K): δ (ppm) 178.6 (d, J = 4 Hz, C=N), 161.4 (q, J = 51 Hz, C₆H₅-), 135.3 (d, J = 13 Hz, HC₆H₅), 134.5 (HC₆H₅-o), 134.1 (C₆H₅), 132.3 (d, J = 2 Hz, HC₆H₅), 131.8 (d, J = 55 Hz, HC₆H₅), 131.1 (d, J = 10 Hz, HC₆H₅), 130.8 (d, J = 3 Hz, HC₆H₅), 129.3 (d, J = 11 Hz, HC₆H₅), 128.8 (HC₆H₅), 128.6 (d, J = 11 Hz, HC₆H₅), 128.5 (qq, J = 3 Hz, J = 11 Hz, HC₆H₅-o), 128.3 (HC₆H₅), 127.8 (d, J = 54 Hz, C₆H₅), 127.4 (HC₆H₅), 124.3 (q, J = 273 Hz, CF₃), 117.2 (sept, J = 4 Hz, HC₆H₅-p), 92.0 (d, J = 10 Hz, COD-CH), 90.8 (d, J = 13 Hz, COD-CH), 73.1 (OCH₂), 65.8 (NCH), 63.8 (COD-CH), 62.1 (COD-CH), 42.9 (CH₃Ph), 38.3 (d, J = 3 Hz, C(CH₃)₂), 35.7 (d, J = 5 Hz, COD-CH₂), 34.4 (d, J = 32 Hz, PCH₂), 33.0 (d, J = 7 Hz, C(CH₃)₂), 32.2 (COD-CH₂), 28.0 (COD-CH₂), 26.2 (COD-CH₂), 26.1 (CH₃); ³¹P{¹H}-NMR (162 MHz, CD₂Cl₂, 300 K): δ (ppm) 8.5; ¹⁹F{¹H}-NMR (376.5 MHz, CD₂Cl₂, 300 K): δ (ppm) −64.0; MS (+ESI) m/z (%) 702 ([M−BArF]⁺, 100); IR (ν [cm⁻¹]) 2970w, 2930w, 2843w, 1603m, 1353s, 1271s, 1114s, 885m, 839m, 737m, 713m, 696m, 681s, 668s.
A three necked round bottom flask with a magnetic stirrer was dried in an oven overnight, cooled under vacuum and charged with argon. A thermometer was added and after another two vacuum/argon cycles a solution of iPrMgCl (22 mL, 2 M in THF from Acros Organics, 44.0 mmol, 1.3 eq) was added. To this solution was added dry ZnCl$_2$ (461 mg, 3.38 mmol, 0.1 eq) as a solid. The mixture was stirred for one hour and was then cooled to 0 °C. Next, 6-methoxytetralone (5.96 g, 33.8 mmol, 1.00 eq) was added as a solid in several portions, keeping the temperature in a range between 0 and 5 °C. The cooling bath was removed and the mixture was stirred for another two hours at room temperature. The mixture was quenched by careful addition of 6 mL of a saturated NH$_4$Cl-solution at 0 °C. MTBE (50 mL) was added, followed by 150 mL of 1 M HCl. The phases were separated and the aqueous phase was extracted with MTBE (2×75 mL). The combined organic phases were washed with brine, dried over MgSO$_4$ and concentrated on a rotavap. This crude product, which is an inseparable mixture of the tertiary alcohol and the starting material, was taken up in 20 mL of toluene. One crystal of iodine and 75 mg of pTsOH were added and the mixture was refluxed overnight. Water was removed by soxhlet extraction with molecular sieves (4 Å). MTBE (40 mL) and a Na$_2$S$_2$O$_3$ solution (0.5 M, 20 mL) were added to the reaction mixture. The phases were separated and the aqueous phase was extracted with 2×10 mL of MTBE. The combined organic phases were washed with 20 mL of NaHCO$_3$ and the phases were separated. The aqueous phase was washed with MTBE (2×20 mL) and the combined organic phases were washed with brine and dried over MgSO$_4$. Silica gel (15 g) was added to the organic phase and the solvent was removed on a rotavap. The compound adsorbed on silica gel was dried on an oil pump, then put on top of a silica gel column (h×d: 9 cm×5 cm) and eluted with 2 liters of pentane. The solvent was then removed on a rotavap, giving 3.15 g of a colorless oil. Recrystallization from pentane (−20 °C) gave 2.97 g of a colorless solid (14.7 mmol, 43%). By elution with ethyl acetate and subsequent crystallization, 1.18 g of starting material could be recovered. Based on this, olefin 13 was obtained in 54% yield.

Note: The best results were obtained when commercially available anhydrous ZnCl$_2$ was further dried by heating under vacuum until it started to melt.

<table>
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<th>Chemical Name</th>
<th>Formula</th>
<th>Mass</th>
<th>Melting Point</th>
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<tr>
<td>13</td>
<td>C$<em>{14}$H$</em>{18}$O</td>
<td>202</td>
<td>38-39 °C (pentane)</td>
</tr>
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</table>

Elemental Analysis for C$_{14}$H$_{18}$O, (202.29), calc.: C, 83.12; H, 8.97; found: C, 82.86; H, 8.80; M. p.: 38-39 °C (pentane); $^1$H-NMR (400.1 MHz, CDCl$_3$, 300K): $\delta$ (ppm) 7.22 (dd, 1H, $J = 1.0$ Hz, $J = 7.8$ Hz, $H_{Ar}$); 6.76-6.71 (m, 2H, $H_{Ar}$); 5.75 (dt, 1H, $J = 1.1$ Hz, $J = 4.6$ Hz, C=CH); 3.80 (s, 3H, OC$_3$H$_3$); 2.89 (d sept., 1H, $J = 1.1$ Hz, $J = 6.8$ Hz, iPr-CH$_2$); 2.71-2.65 (m, 2H, CH$_2$); 2.25-2.19 (m, 2H, CH$_2$); 1.14 (d, 6H, $J = 6.8$ Hz, iPr-CH$_3$); $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$, 300 K): $\delta$ (ppm) 158.0 (C$_{quat}$), 142.2 (C$_{quat}$), 138.9 (C$_{quat}$), 128.1 (C$_{quat}$), 123.6 (CH), 118.9 (CH), 113.7 (CH), 110.8 (CH), 55.2 (OCH$_3$), 29.1 (CH$_3$), 28.3 (CH), 23.0 (CH$_2$), 22.2 (CH$_3$); MS (+EI) m/z (%) 202 (M$^+$, 49), 187 (14), 159 (100), 144 (34), 128 (21), 115 (26); IR ($\bar{v}$ [cm$^{-1}$]) 2958m, 2929m, 2882m, 2878m, 2871m, 2830m, 1633, 1606s, 1569m, 1493s, 1464m, 1426m, 1379m, 1359w, 1301m, 1276m, 1276m.
Olefin 13 (1.48 g, 7.31 mmol), complex 1c (57.0 mg, 36.5 µmol, 0.50 mol%), a magnetic stir bar and 7.5 mL of dry, degassed CH2Cl2 were added into a glass insert. The glass insert was put into a steel autoclave, which was then sealed. The autoclave was purged five times with 10 bar of hydrogen and a final pressure of 5 bar was applied. The mixture was stirred for 4 h, the hydrogen was carefully released and the solvent was removed on a rotavap. The catalyst was separated by Kugelrohr distillation and tetrahydronaphthalene 14 was obtained as a colorless oil (1.46 g, 7.15 mmol, 98%). The enantiomeric excess was determined to be 93% by chiral GC.

Elemental Analysis for C14H20O, (204.31), calc.: C, 82.30; H, 9.87; found: C, 82.13; H, 9.75; [α]D +64.2 (c 1.03, CHCl3); ¹H-NMR (400.1 MHz, CDCl3, 300K): δ (ppm) 7.13 (d, 1H, J = 8.5 Hz, HAr), 6.70 (dd, 1H, J = 2.7 Hz, J = 8.5 Hz, HAr), 6.61 (d, 1H, J = 2.6 Hz, HAr), 3.78 (s, 3H, OCH3), 2.77-2.61 (m, 3H, ArCH), 1.95-1.86 (m, 1H, CH2), 1.83-1.75 (m, 1H, CH2), 1.65-1.55 (m, 2H, CH2), 1.01 (d, 3H, J = 6.8 Hz, CH(CH3)2), 0.74 (d, 3H, J = 6.8 Hz, CH(CH3)2); ¹³C{¹H}-NMR (100.6 MHz, CDCl3, 300 K): δ (ppm) 157.0 (CAr), 139.2 (CAr), 132.5 (CAr), 129.1 (HCAr), 113.4 (HCAr), 111.5 (HCAr), 55.1 (OCH3), 42.8 (CH), 31.4 (CH), 30.3 (CH2), 23.4 (CH2), 21.4 (CH2), 21.2 (CH), 17.4 (CH); MS (+EI) m/z (%): 204 (8), 161 (100), 146 (7), 128 (6), 115 (1), 91 (10), 41 (11); IR (ν [cm⁻¹]) 2953s, 2932s, 2868s, 2833s, 1609m, 1575w, 1500s, 1463m, 1256s, 1463m, 1256s, 1232m, 1155w, 1043m; GC (chiral, β-Cyclodextrin, DEtButSil [Brechbühler, SE54], 0.25 mm, 0.25 µm, 25 m, 60 kPa H2, 140 °C, 0 min, 2 K/min, 180°C, 5 min): tR(S)-14 = 10.8 min, tR(R)-14 = 11.3 min, tR(13) = 12.5 min, tR(17) = 15.0 min.

To a dry Schlenk tube was added dry CH2Cl2 (6 mL) followed by N-methylformanilide (5.9 mL, 6.43 g, 47.6 mmol, 6.65 eq) and POCl3 (3.0 mL, 5.03 g, 47.6 mmol, 4.58 eq). The mixture was stirred at RT for 1 h (color change from colorless to yellow) and the tetrahydronaphthalene (1.46 g, 7.15 mmol) dissolved in 3 mL of CH2Cl2 was syringed to the solution. The mixture was heated to reflux for 48 h. After cooling to RT the mixture was poured into 20 mL of 1M HCl containing 40 g of ice and stirred for 30 min. The phases were separated and the aqueous phase was extracted with 2x25 mL of CH2Cl2. The combined organic phases were washed with
50 mL of brine and dried over MgSO4. Silica gel (20 g) was added to the organic phase and the solvent was removed on a rotavap. A flash column was prepared from 100 g silica gel (15 cm x 4 cm) and a pentane/ethyl acetate mixture (25/1) and the compound adsorbed on silica gel was loaded on top. Elution with a pentane/ethyl acetate mixture (25/1) afforded the product as a yellowish oil (1.47 g, 6.31 mmol, 88%, 93% ee by HPLC), which solidified in the fridge.

For crystallization, the product was taken up in 30 mL of hexanes and crystallized at −20 °C in a freezer. The product was separated by decanting the mother liquor. The aldehyde (855 mg, 3.68 mmol) was obtained as a colorless solid in 58% recovery (98% ee by HPLC).

**Elemental Analysis** for C15H20O2 (232.32), calc.: C, 77.55; H, 8.68; found: C, 77.41; H, 8.68; M.p.: 47-48 °C (hexanes); [α]20D +76.3 (c 1.00, CHCl3); 1H-NMR (400.1 MHz, CDCl3, 300 K): δ (ppm) 10.39 (s, 1H, CHO), 7.68 (s, 1H, HAr), 6.65 (s, 1H, HAr), 3.88 (s, 3H, OCH3), 2.74-2.77 (m, 2H, CArCH/CH2), 2.66 (dd, 1H, J = 6.3 Hz, J = 12.6 Hz, CArCH/CH2), 2.22-2.32 (m, 1H, CH(CH3)2), 1.88-1.97 (m, 1H, CH2), 1.77-1.83 (m, 1H, CH2), 1.55-1.67 (m, 2H, CH2), 0.99 (d, 3H, J = 6.8 Hz, CH(CH3)2), 0.72 (d, 3H, J = 6.8 Hz, CH(CH3)2): 13C[1H]-NMR (100.6 MHz, CDCl3, 300 K): δ (ppm) 189.8 (CHO), 159.3 (CAr), 147.6 (CAr), 132.9 (CAr), 128.3 (HCAr), 122.7 (CAr), 111.6 (HCAr), 55.5 (OCH3), 42.6 (CArCH), 31.3 (CH(CH3)2), 31.0 (CH3), 23.0 (CH3), 21.1 (CH3), 17.2 (CH(CH3)2); MS (EI) m/z (%) 232 (M+, 10), 189 (100), 161 (14), 146 (13), 128 (11), 115 (12), 91 (10), 77 (6), 41 (13); IR (ν [cm⁻¹]) 2953m, 2933m, 2900m, 2892m, 2866m, 2844m, 1680s, 1608s, 1569w, 1493m, 1464m, 1414m, 1394m, 1263s, 1205w, 1194w, 1167w, 1156w, 1099m, 1023w, 953w, 839w, 633w; Rf 0.29 (silica gel, hexanes/ethyl acetate, 10/1); HPLC, AD-H, heptane/isopropanol (99/1), 0.5 mL/min, 20 °C, tR(HPLC): 15.9 min, tR([R]-15): 17.9 min.

Aldehyde 15 (807 mg, 3.47 mmol), Pd/C (10% w/w, 50.0 mg), a magnetic stirbar and 5 mL of MeOH were added into a glass insert. The glass insert was put into a steel autoclave, which was then sealed. The autoclave was purged two times with 50 bar of hydrogen and a final pressure of 100 bar was applied. The mixture was stirred for 24 h, the hydrogen was carefully released. The catalyst was removed by filtration over Celite® and the solvent was removed on a rotavap. (R)-(+) -7-demethyl-2-methoxycalamene was obtained as a colorless oil (752 mg, 3.44 mmol, 99%). The enantiomeric excess was determined to be 98% by chiral GC. The spectroscopic data of the product closely matched published data.[2]

**Elemental Analysis** for C54H82O7 (218.33), calc.: C, 82.52; H, 10.16; found: C, 82.65; H, 10.07; [α]20D +62.1 (c 1.06, CHCl3) [Lit[3]]; [α]20D +53.9 (c 1.32, CHCl3); 1H-NMR (400.1 MHz, CDCl3, 300 K): δ (ppm) 6.97 (s, 1H, HAr), 6.52 (s, 1H, HAr), 3.80 (s, 3H, OCH3), 2.60-2.75 (m, 3H, CArCH, CArCH2), 2.17-2.28 (m, 4H, CArCH3, CH(CH3)2), 1.87-1.95 (m, 1H, CH2), 1.75-1.81 (m, 1H, CH2), 1.54-1.67 (m, 2H, CH2), 1.01 (d, 3H, J = 6.9 Hz, CH(CH3)2), 0.74 (d, 3H, J = 6.8 Hz, CH(CH3)2); 13C[1H]-NMR (100.6 MHz, CDCl3, 300 K): δ (ppm) 155.3
(C₆H), 136.2 (C₆H), 131.8 (H₃C₆H), 123.4 (C₆H), 110.1 (H₃C₆H), 55.2 (OCH₃), 42.7 (C₆H₅CH), 31.4 (CH(CH₃)₂), 30.2 (CH₂), 23.4 (CH₂), 21.7 (CH₂), 21.3 (CH(CH₃)₂), 17.3 (CH(CH₃)₂), 16.0 (C₆H₅CH); MS (EI) m/z (%) 218 (M⁺, 10), 175 (100), 160 (9), 145 (6), 128 (7), 115 (7), 41 (8); IR (ν [cm⁻¹]) 2927s, 2856m, 1616m, 1506s, 1464m, 1405w, 1383w, 1365w, 1319w, 1252s, 1208m, 1155w, 1103s, 1027m, 885m, 837m; Rf 0.64 (silica gel, hexanes/ethyl acetate, 20/1), Rf 0.23 (silica gel, hexanes). GC (chiral, β-Cyclodextrin, DiMeBuSil (OV1701) from Brechbühler, 0.25 mm, 0.25 µm, 25 m, 60 kPa H₂, 100 °C, 0 min, 2 K/min, 160 °C, 10 min): tₛ[R(15)-16]: 29.7 min, tₘ[R(15)-16]: 30.6 min.
A high pressure steel autoclave (Premex Reactor AG; Lengnau, Switzerland; Model HPM-005) with a dry glass insert and a magnetic stir bar was loaded with the appropriate catalyst (0.001 mmol) and 0.5 ml of a 0.2 M degassed substrate solution freshly prepared from the corresponding substrate and dichloromethane. The hydrogenation vessel was sealed and attached to a high pressure hydrogen line and purged with H₂. The autoclave was sealed under the appropriate H₂ pressure (olefins 5, 6, 7, 9, 10, 11: 50 bar; olefin 8: 5 bar) and the mixture was stirred for 2 h (olefin 8: 75 min) at the appropriate pressure at room temperature. After release of H₂ the solution was concentrated in a stream of nitrogen, diluted with 5 ml of hexane, passed through a Chromafil O-20/15 organic stable syringe filter (0.2 µm pore size), and the filtrate directly analyzed for conversion (GC) and ee (GC or HPLC). Alternatively, the solution was passed through a small plug of silica (h×d: 2 mm×1 mm) and the filtrate analyzed directly for conversion (GC) and ee (GC or HPLC).

Analytical information for determination of conversion and enantiomeric exess:

<table>
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<tr>
<th>Substrate</th>
<th>Conversion</th>
<th>ee</th>
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</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Substrate A" /></td>
<td>GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel OJ Heptane:i-Propanol: 99:1 0.5 mL min⁻¹, 20 °C Substrate: 28 min Product: 14 min (R), 24 min (S)</td>
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<tr>
<td><img src="image2.png" alt="Substrate B" /></td>
<td>GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel ODH Heptane:i-Propanol: 99.8:0.2 0.5 mL min⁻¹, 20 °C Substrate: 17.7 min Product: 12.6 min (R), 14.8 min (S)</td>
</tr>
<tr>
<td><img src="image3.png" alt="Substrate C" /></td>
<td>GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel ODH Heptane:i-Propanol: 95:5 0.5 mL min⁻¹, 40 °C Substrate: 18.5 min Product: 11.48 min (+), 16.8 min (−)</td>
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<tr>
<td><img src="image4.png" alt="Substrate D" /></td>
<td>GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel ODH Heptane:i-Propanol: 99.5:0.5 0.5 mL min⁻¹, 20 °C Substrate: 23.6 min Product: 14.8 min (R), 17.3 min (S)</td>
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<tr>
<td><img src="image5.png" alt="Substrate E" /></td>
<td>GC: achiral column, Macherey-Nagel Optima 5-Amin, 30 m, T-Program: 100 °C, 8 min, 5 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel ODH Heptane 0.5 mL min⁻¹, 20 °C Substrates: 17.7 min Product: 12.9 min (S), 14.3 min (R)</td>
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<tr>
<td><img src="image6.png" alt="Substrate F" /></td>
<td>GC: achiral column, Macherey-Nagel Optima 5-Amin, 30 m, T-Program: 100 °C, 8 min, 5 °Cmin⁻¹-250 °C, 10 min, 60 kPa He</td>
<td>HPLC with UV-detector Column: Chiralcel ODH Heptane:i-Propanol: 99:1 0.5 mL min⁻¹, 20 °C Substrate: 23 min Product: 18.8 min (S), 22 min (R)</td>
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Supplementary Material (ESI) for Chemical Communications

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g) References
