Supplementary Material (ESI) for Chemical Communications

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

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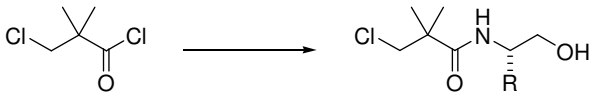
Supporting Information

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 (^{1}H, ^{13}C) are referenced to the corresponding (residual) solvent peak ($CDCl_3$: 7.26 ($CHCl_3$) for ^{1}H-NMR; 77.0 ($CDCl_3$) for ^{13}C-NMR; CD_2Cl_2: 5.32 ($CHDCl_2$) for ^{1}H-NMR; 53.1 (CD_2Cl_2) for ^{13}C-NMR).

Content:

a) Synthesis of the amides 3a-c:



3a: R = *i*Pr
3b: R = *t*Bu
3c: R = CH_2Ph

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 $HCl{\cdot}NEt_3$. 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_2Cl_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; $[\alpha]_D^{20}$ −33.5 (*c* 1.00, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 5.95 (s, 1H, N*H*), 3.75-3.63 (m, 5H, CH_2Cl, NC*H*, CH_2OH), 2.54 (s, 1H, O*H*), 1.97-1.85 (m, 1H, C*H*$(CH_3)_2$), 1.31 (s, 6H, C(C$H_3)_2$), 0.97 (d, 3H, *J* = 6.8 Hz, CH(C$H_3)_2$), 0.94 (d, 3H, *J* = 6.8 Hz, CH(C$H_3)_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 175.6 (*C*=O), 64.0 (*C*H_2OH), 57.2 (*C*H), 52.8 (*C*H_2Cl), 44.4 (*C*$(CH_3)_2$), 29.0 (*C*H$(CH_3)_2$), 23.5 (C(*C*$H_3)_2$), 19.6 (CH(*C*$H_3)_2$), 18.8 (CH(*C*$H_3)_2$); **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** ($\tilde{\nu}$ [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 $HCl{\cdot}NEt_3$. 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; $[\alpha]_D^{20}$ −11.7 (*c* 0.99, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 5.95 (d,

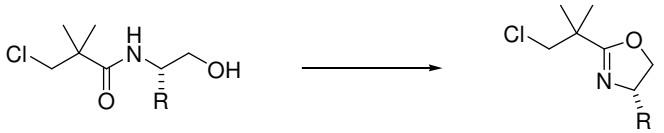
1H, J = 5.8 Hz, N*H*), 3.82-3.88 (m, 2H), 3.64 (s, 2H, CH_2Cl), 3.55-3.61 (m, 1H), 2.38 (dd, 1H, J = 5.0 Hz, J = 6.1 Hz, O*H*), 1.33 (s, 6H, C(CH_3)$_2$), 0.97 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 175.9 (*C*=O), 63.3 (*C*H_2OH), 59.7 (*C*H), 52.8 (*C*H_2Cl), 44.5 (*C*(CH$_3$)$_2$), 33.5 (*C*(CH$_3$)$_3$), 26.9 (C(*C*H$_3$)$_3$), 23.6 (C(*C*H$_3$)$_2$); **MS** (FAB) m/z (%) 238 (48), 237 (19), 236 ([M+H]$^+$, 100), 204 (9), 178 (7), 137 (10), 119 (7), 93 (10), 91 (27), 83 (12), 77 (10), 65 (6), 57 (12), 55 (16); **IR** ($\tilde{\nu}$ [cm^{-1}]) 3289m, 2952m, 2910w, 2867w, 1622s, 1544s, 1479m, 1447m, 1394w, 1366m, 1348w, 1309w, 1282w, 1244m, 1216w, 1089w, 1053s, 907m, 880m, 733s.

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; $[\alpha]_D^{20}$ −12.8 (*c* 0.99, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 7.33-7.21 (m, 5H, H_{Ar}), 5.96 (d, 1H, J = 6.2 Hz, N*H*), 4.22-4.15 (m, 1H, C*H*), 3.70-3.51 (m, 4H, CH_2Cl, CH_2OH), 2.96-2.83 (m, 2H, C$_6$H$_5$CH_2), 2.69 (s, 1H, O*H*), 1.22 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 175.3 (*C*=O), 137.4 (C_{Ar}), 129.2 (HC_{Ar}), 128.66 (HC_{Ar}), 126.74 (HC_{Ar}), 64.1 (*C*H_2OH), 52.9 (*C*H), 52.7 (*C*H_2Cl), 44.2 (*C*(CH$_3$)$_2$), 36.8 (C$_6$H$_5$*C*H$_2$), 23.3 (*C*H$_3$); **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** ($\tilde{\nu}$ [cm^{-1}]) 3368m, 3027w, 2866m, 1733m, 1635s, 1516s, 1496m, 1472m, 1454m, 1391m, 1366m, 1286w, 1242m, 1157w, 1039m, 701s, 632s.

b) Synthesis of the oxazolines 2a-c:



3a: R = *i*Pr
3b: R = *t*Bu
3c: R = CH_2Ph

2a: R = *i*Pr
2b: R = *t*Bu
2c: R = CH_2Ph

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 $C_{10}H_{18}ClNO$ (203.71), calc.: C, 58.96; H, 8.91; N, 6.88; found: C, 58.89; H, 8.72; N, 6.88; $[\alpha]_D^{20}$ −77.4 (*c* 1.16, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 4.23-4.15 (m, 1H, NCH), 4.01-3.92 (m, 2H, O*C*H_2), 3.61 (s, 2H, *C*H_2Cl), 1.79 (qd, 1H, *J* = 6.8 Hz, *J* = 12.1 Hz, *C*H(CH_3)$_2$), 1.30 (s, 6H, C(*C*H_3)$_2$), 0.92 (d, 3H, *J* = 6.8 Hz, CH(*C*H_3)$_2$), 0.86 (d, 3H, *J* = 6.8 Hz, CH(*C*H_3)$_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 169.7 (*C*=N), 71.7 (N*C*H), 69.6 (O*C*H_2), 52.6 (*C*H_2Cl), 38.8 (*C*(CH_3)$_2$), 32.2 (*C*H(CH_3)$_2$), 23.8 (CH(*C*H_3)$_2$), 18.6 (C(*C*H_3)$_2$), 17.5 (C(*C*H_3)$_2$); **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** ($\tilde{\nu}$ [cm^{-1}]) 2957s, 2904m, 2873m, 1732m, 1662s, 1470m, 1442m, 1386m, 1366m, 1351m, 1311w, 1265w, 1242w, 1180w, 1113s, 1045w, 1015w, 981m, 923m, 835w, 754w.

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 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%).

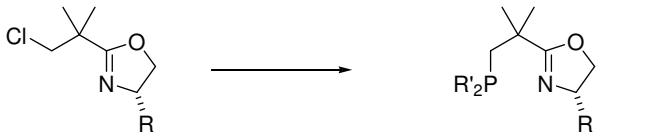
Elemental Analysis for $C_{11}H_{20}ClNO$ (217.74), calc.: C, 60.68; H, 9.26; N, 6.43; found: C, 60.86; H, 9.12; N, 6.41; $[\alpha]_D^{20}$ −80.5 (*c* 1.17, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 4.14 (dd, 1H, *J* = 8.6 Hz, *J* = 10.1 Hz, NC*H*), 4.08 (dd, 1H, *J* = 7.2 Hz, *J* = 8.6 Hz, O*C*H_2), 3.83 (dd, 1H, *J* = 7.2 Hz, *J* = 10.1 Hz, O*C*H_2), 3.62 (s, 2H, *C*H_2Cl), 1.30 (s, 6H, C(*C*H_3)$_2$), 0.88 (s, 9H, C(*C*H_3)$_3$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 169.7 (*C*=N), 75.5 (N*C*H), 68.7 (O*C*H_2), 52.6 (*C*H_2Cl), 38.8 (*C*(CH_3)$_2$), 33.7 (*C*(CH_3)$_3$), 25.7 (C(*C*H_3)$_3$), 23.9 (C(*C*H_3)$_2$), 23.8 (C(*C*H_3)$_2$); **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** ($\tilde{\nu}$ [cm^{-1}]) 2973m, 2953s, 2903m, 2870m, 1778w, 1743m, 1732m, 1663vs, 1477m, 1447m, 1387m, 1364m, 1351m, 1339m, 1177w, 1116s, 980s, 920s, 834m, 755m.

2c:

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_2Cl_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; $[\alpha]_D^{20}$ −29.7 (*c* 1.00, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 7.27-7.31 (m, 2H, H_{Ar}), 7.19-7.24 (m, 3H, H_{Ar}), 4.39 (dddd, 1H, *J* = 4.8 Hz, *J* = 6.8 Hz, *J* = 8.7 Hz, *J* = 8.9 Hz, NC*H*), 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* = 4.7 Hz, *J* = 13.7 Hz, C$H_2C_6H_5$), 2.65 (dd, 1H, *J* = 8.6 Hz, *J* = 13.7 Hz, C$H_2C_6H_5$), 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): δ(ppm) 170.5 (*C*=N), 137.7 (C_{Ar}), 129.4 (HC_{Ar}), 128.4 (HC_{Ar}), 126.5 (HC_{Ar}), 71.6 (OCH$_2$), 67.1 (NCH), 52.5 (ClCH$_2$), 41.5 (CH$_2C_6H_5$), 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** ($\tilde{\nu}$ [cm^{-1}]) 2976m, 1718m, 1656s, 1494m, 1453m, 1445m, 1387m, 1349s, 1290m, 1179m, 1115s, 1074m, 980s, 927m, 828m, 751s, 729m.

c) Synthesis of *Neo*PHOX-ligands 1a-e:



2a: R = *i*Pr
2b: R = *t*Bu
2c: R = CH_2Ph

1a: R = *i*Pr; R' = Ph
1b: R = *t*Bu; R' = Ph
1c: R = *t*Bu; R' = *o*Tol
1d: R = *t*Bu; R' = Xyl
1e: R = CH_2Ph; R' = Ph

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_4Cl 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 (15 mL) and dried over Na_2SO_4. The solvent was removed on a rotavap. After filtration over silica gel (h×d: 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 $C_{22}H_{28}NOP$ (353.44), calc.: C, 74.76; H, 7.99; N, 3.96; found: C, 74.75; H, 8.03; N, 3.95; $[\alpha]_D^{20}$ −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, OCH_2, NCH), 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, $C(CH_3)_2$), 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, $HC(CH_3)_2$); **^{13}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, HC_{Ar}), 132.7 (d, *J* = 19 Hz, HC_{Ar}), 128.3 (d, *J* = 5 Hz, HC_{Ar}), 128.3 (d, *J* = 2 Hz, HC_{Ar}), 128.2 (d, *J* = 4 Hz, HC_{Ar}), 71.6 (N*C*H), 69.3 (OCH_2), 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** ($\tilde{\nu}$ [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_4Cl-solution. This mixture was extracted with MTBE (3×20 mL), the combined organic phases were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed on a rotavap. The crude product still contained some $PHPh_2$

and O=PHPh$_2$. After filtration over silica gel (h×d: 16 cm×2.5 cm, pentane/ethyl acetate, 5/1) the product was obtained as a colorless solid (807 mg, 2.20 mmol, 60%).

Elemental Analysis for $C_{23}H_{30}NOP$ (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; $[\alpha]_D^{20}$ −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, NC*H*), 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_{Ar}), 139.7 (d, *J* = 3 Hz, C_{Ar}), 133.2 (HC_{Ar}), 133.0 (HC_{Ar}), 132.8 (HC_{Ar}), 132.6 (HC_{Ar}), 128.3 (3×HC_{Ar}), 128.2 (3×HC_{Ar}), 75.3 (N*C*H), 68.3 (O*C*H$_2$), 41.0 (d, *J* = 17 Hz, P*C*H$_2$), 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(*C*H$_3$)$_2$), 27.2 (d, *J* = 11 Hz, PCH$_2$C(*C*H$_3$)$_2$), 25.7 (C(*C*H$_3$)$_3$); **^{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** ($\tilde{\nu}$ [cm^{-1}]) 3070w, 3057w, 2966m, 2947m, 2924m, 2897m, 2866m, 1661s, 1585w, 1477m, 1468m, 1433s, 1383w, 1367m, 1350m, 1128s, 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 *o*Tol$_2$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 C_6D_6 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_4Cl-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_2SO_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×2.5 cm, pentane/ethyl acetate, 50/1→25/1) the product was obtained as a colorless oil (352 mg, 0.89 mmol, 86%).

$C_{25}H_{34}NOP$ (395.52), **HRMS** (+ESI-TOF) for [$C_{25}H_{34}NOP$+H]$^+$, calc.: 396.2456, found: 396.2455; $[\alpha]_D^{20}$ −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, NC*H*, OCH_2), 2.53 (s, 3H, C_{Ar}CH_3), 2.41 (s, 3H, C_{Ar}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_{Ar}CH$_3$), 142.0 (d, *J* = 27 Hz, C_{Ar}CH$_3$), 137.40 (d, *J* = 27 Hz, PC_{Ar}), 137.30 (d, *J* = 28 Hz, PC_{Ar}), 132.1 (HC_{Ar}), 131.0 (HC_{Ar}), 130.0 (d, *J* = 5 Hz, HC_{Ar}), 129.9 (d, *J* = 5 Hz, HC_{Ar}), 128.2 (HC_{Ar}), 128.1 (HC_{Ar}), 125.7 (d, *J* = 7 Hz, HC_{Ar}), 75.2 (N*C*H), 68.2 (O*C*H$_2$), 38.3 (d, *J* = 18 Hz, P*C*H$_2$), 36.5 (d, *J* = 17 Hz, *C*(CH$_3$)$_2$), 33.2 (*C*(CH$_3$)$_3$), 27.2 (d, *J* = 9 Hz, C(*C*H$_3$)$_2$), 27.4 (d, *J* = 10 Hz, C(*C*H$_3$)$_2$), 25.7 (C(*C*H$_3$)$_3$), 21.3 (d, *J* = 18 Hz, C_{Ar}*C*H$_3$), 21.1 (d, *J* = 18 Hz, C_{Ar}*C*H$_3$); **^{13}P-NMR** (162.0 MHz, $CDCl_3$, 300 K): δ(ppm) −54.0; **MS** (+ESI) m/z (%) 396 ([M+H]$^+$, 100);

IR ($\tilde{\nu}$ [cm^{-1}]) 3055w, 2957m, 2901w, 2868w, 1661s, 1466m, 1450m, 1383w, 1364m, 1271w, 1196w, 1163w, 1122m, 1095w, 980s, 920m, 746s, 719w; R_f 0.42 (silica, hexanes/ethyl acetate, 10:1).

1d:

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_2PH (1.03 mmol) were added, followed by 81.0 mg (2.02 mmol) of KH. Outside the glove box oxazoline **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_4Cl-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_2SO_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 $C_{27}H_{38}NOP$ (423.57), calc.: C, 76.56; H, 9.04; N, 3.31; found: C, 76.38; H, 9.05; N, 3.42; $[\alpha]_D^{20}$ −29.0 (*c* 0.95, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 7.09 (s, 2H, H_{Ar}), 7.07 (s, 2H, H_{Ar}), 6.91 (s, 2H, H_{Ar}), 3.93 (dd, 1H, *J* = 6.8 Hz, *J* = 8.2 Hz, NC*H*), 3.75 (dd, 1H, *J* = 8.2 Hz, *J* = 10.0 Hz, OCH_2), 3.67 (dd, 1H, *J* = 6.8 Hz, *J* = 10.0 Hz, OCH_2), 2.42 (ddd, 2H, *J* = 3.7 Hz, *J* = 14.3 Hz, *J* = 33.6 Hz, PCH_2), 2.28 (s, 12H, CH_3C_{Ar}), 1.33 (s, 3H, C(CH_3)$_2$), 1.29 (s, 3H, C(CH_3)$_2$), 0.86 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 172.1 (d, *J* = 3 Hz, *C*=N), 139.5 (d, *J* = 5 Hz, C_{Ar}), 139.4 (d, *J* = 4 Hz, C_{Ar}), 137.5 (d, *J* = 5 Hz, C_{Ar}), 137.5 (d, *J* = 5 Hz, C_{Ar}), 130.8 (d, *J* = 20 Hz, HC_{Ar}), 130.5 (d, *J* = 20 Hz, HC_{Ar}), 130.0 (d, *J* = 11 Hz, HC_{Ar}), 75.4 (N*C*H), 68.2 (O*C*H$_2$), 40.8 (d, *J* = 17 Hz, P*C*H$_2$), 36.7 (d, *J* = 17 Hz, PCH$_2$*C*(CH$_3$)$_2$), 33.7 (*C*(CH$_3$)$_3$), 27.7 (d, *J* = 10 Hz, PCH$_2$C(*C*H$_3$)$_2$), 27.2 (d, *J* = 11 Hz, PCH$_2$C(*C*H$_3$)$_2$), 25.8 (C(*C*H$_3$)$_2$), 21.3 (2×C_{Ar}*C*H$_3$); **^{31}P{^{1}H}-NMR** (162.0 MHz, $CDCl_3$, 300 K): δ(ppm) −26.5; **MS** (EI) m/z (%) 423 (M^+, 3), 408 (5), 366 (33), 318 (26), 283 (100), 241 (7), 149 (5); **IR** ($\tilde{\nu}$ [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).

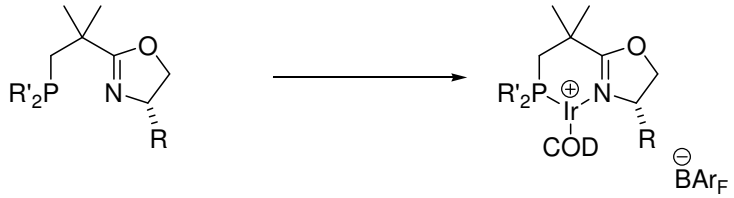
1e:

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 **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_4Cl-solution. This mixture was extracted with MTBE (3×10 mL), the combined organic phases were washed with brine (10 mL) and dried over Na_2SO_4. The solvent was removed on a rotavap. After filtration over silica gel (h×d: 16 cm×2.5 cm, pentane/ethyl acetate, 5/1 → 4/1) the product was obtained as a colorless oil (807 mg, 2.20 mmol, 60%). The product decomposes slowly on silica.

Elemental Analysis for $C_{26}H_{28}NOP$ (401.48), calc.: C, 77.78; H, 7.03; N, 3.49; found: C, 77.57; H, 7.11; N, 3.51; $[\alpha]_D^{20}$ −16.5 (*c* 0.92, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 7.43-7.47 (m, 4H, H_{Ar}), 7.12-

7.33 (m, 11H, H_{Ar}), 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(CH_3)$_2$), 1.28 (s, 3H, C(CH_3)$_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 172.5 (d, J = 3 Hz, N*C*=O), 139.4 (d, J = 13 Hz, C_{Ar}), 139.3 (d, J = 12 Hz, C_{Ar}), 138.0 (C_{Ar}), 133.1 (d, J = 20 Hz, 2×HC_{Ar}), 132.8 (d, J = 20 Hz, 2×HC_{Ar}), 129.3 (HC_{Ar}), 128.4 (d, J = 14 Hz, 2×HC_{Ar}), 128.3 (HC_{Ar}), 128.3 (d, J = 13 Hz, 2×HC_{Ar}), 128.3 (d, J = 5 Hz, 4×HC_{Ar}),126.3 (HC_{Ar}), 71.2 (O*C*H$_2$), 66.9 (N*C*H), 41.4 (*C*H$_2$C$_6$H$_5$), 40.9 (d, J = 17 Hz, P*C*H$_2$), 36.4 (d, J = 16 Hz, *C*(CH$_3$)$_2$), 27.5 (d, J = 9 Hz, C(*C*H$_3$)$_2$), 27.3 (d, J = 10 Hz, C(*C*H$_3$)$_2$); **^{31}P{^{1}H}-NMR** (162.0 MHz, $CDCl_3$, 300 K): δ(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** ($\tilde{\nu}$ [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 *Neo*PHOX-iridium complexes Ir-1a-e:



1a: R = *i*Pr; R' = Ph
1b: R = *t*Bu; R' = Ph
1c: R = *t*Bu; R' = *o*Tol
1d: R = *t*Bu; R' = Xyl
1e: R = CH_2Ph; R' = Ph

Ir-1a: R = *i*Pr; R' = Ph
Ir-1b: R = *t*Bu; R' = Ph
Ir-1c: R = *t*Bu; R' = *o*Tol
Ir-1d: R = *t*Bu; R' = Xyl
Ir-1e: R = CH_2Ph; R' = Ph

Ir-1a:

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 $KPPh_2$ 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 *in vacuo* and 386 mg (1.09 mmol, 106%) of the crude ligand (**1a**) were obtained with sufficient purity (judged from the ^{31}P-NMR spectrum) for complexation.

To a solution of 208 mg (310 µmol, 0.53 eq) of $[Ir(COD)Cl]_2$ in 5 mL of CH_2Cl_2 were added 207 mg (586 µmol, 1.0 eq) of the crude ligand (**1a**, see above). The solution was heated to reflux for 30 min and the solution was cooled to RT followed by addition of 675 mg (762 µmol, 1.30 eq) of $NaBAr_F$ as a solid. After 30 min, 20 mL of water were added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried over $MgSO_4$, 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 CH_2Cl_2 (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 $C_{62}H_{52}BF_{24}IrNOP$ (1517.05), calc.: C, 49.09; H, 3.45; N, 0.92; found: C, 49.21; H, 3.42; N, 0.74; $[\alpha]_D^{20}$ −11 (*c* 0.21, $CHCl_3$); **^{1}H-NMR** (500.1 MHz, CD_2Cl_2, 300 K): δ(ppm) 7.87 (dd, 2H, *J* = 7.6 Hz, *J* = 11.2 Hz, H_{Ar}), 7.73 (s, 8H, $H_{ArF\text{-}o}$), 7.62-7.51 (m, 3H, H_{Ar}), 7.57 (s, 4H, $H_{ArF\text{-}p}$), 7.48-7.38 (m, 3H, H_{Ar}), 7.13-7.08 (m, 2H, H_{Ar}), 4.95 (br s, 1H, COD-C*H*), 4.89-4.76 (m, 1H, COD-C*H*), 4.44-4.39 (m, 1H, OCH_2), 4.35 (dd, 1H, *J* = 14.6 Hz, *J* = 5.1 Hz, OCH_2), 4.09-3.99 (m, 1H, NC*H*), 3.51 (br s, 1H, COD-C*H*), 2.65-2.47 (m, 5H, COD-C*H*, COD-CH_2, PCH_2), 2.44-2.33 (m, 2H, COD-CH_2), 2.18 (s, 3H, C(CH_3)$_2$), 2.17-2.10 (m, 1H, COD-CH_2), 2.06-1.97 (m, 1H, C*H*(CH_3)$_2$), 1.95-1.86 (m, 1H, COD-CH_2), 1.74-1.60 (m, 1H, COD-CH_2), 1.49 (d, 3H, *J* = 2.7 Hz, C(CH_3)$_2$), 1.48-1.42 (m, 1H, COD-CH_2), 0.84 (d, 3H, *J* = 7.1 Hz, CH(CH_3)$_2$), 0.06 (d, 3H, *J* = 6.7Hz, CH(CH_3)$_2$); **^{13}C{^{1}H}-NMR** (125.8 MHz, CD_2Cl_2, 300 K): δ(ppm) 178.0 (d, *J* = 4 Hz, *C*=N), 161.4 (q, *J* = 51 Hz, $C_{ArF\text{-}i}$), 135.1 (d, *J* = 13 Hz, HC_{Ar}), 134.5 (H$C_{ArF\text{-}o}$), 132.2 (d, *J* = 3 Hz, HC_{Ar}), 132.0 (d, *J* = 56 Hz, C_{Ar}), 131.1 (d, *J* = 10 Hz, HC_{Ar}), 130.7 (d, *J* = 3 Hz, HC_{Ar}), 129.2 (d, *J* = 11 Hz, HC_{Ar}), 128.6 (d, *J* = 10 Hz, HC_{Ar}), 128.5 (qq, *J* = 3 Hz, *J* = 32 Hz, $C_{ArF\text{-}m}$), 128.0 (d, *J* = 54 Hz, C_{Ar}), 124.3 (q, *J* = 273 Hz, *C*F_3), 117.2 (sept, *J* = 4 Hz, H$C_{ArF\text{-}p}$), 92.1 (d, *J* = 11 Hz, COD-*C*H), 91.5 (d, *J* = 13 Hz, COD-*C*H), 69.3 (N*C*H), 69.2 (OCH_2), 63.7

(COD-*C*H), 61.2 (COD-*C*H), 38.2 (d, *J* = 3 Hz, *C*(CH_3)$_2$), 35.6 (d, *J* = 5 Hz, COD-*C*H_2), 34.4 (d, *J* = 33 Hz, P*C*H_2), 33.0 (d, *J* = 6 Hz, C(*C*H_3)$_2$), 31.9 (d, *J* = 1 Hz, COD-*C*H_2), 31.7 (*C*H(CH_3)$_2$), 28.1 (d, *J* = 2 Hz, COD-*C*H_2), 26.3 (d, *J* = 11 Hz, C(*C*H_3)$_2$), 26.2 (d, *J* = 1 Hz, COD-*C*H_2), 18.2 (CH(*C*H_3)$_2$), 12.7 (CH(*C*H_3)$_2$); **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2, 300 K): δ(ppm) 7.3; **^{19}F{^{1}H}-NMR** (376.5 MHz, CD_2Cl_2, 300 K): δ(ppm) −64.0; **MS** (+ESI) m/z (%) 654 ([M−BAr_F]$^+$, 100); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2972w, 2893w, 1604m, 1485w, 1439w, 1350s, 1271s, 1157s, 1119s, 1105s, 1045w, 999w, 960w, 899m, 885m, 837m, 734m, 715s, 694m, 680s, 667s.

Ir-1b:

To a solution of $[Ir(COD)Cl]_2$ (343 mg, 0.51 mmol, 0.51 eq) in 5 mL of CH_2Cl_2 was added a solution of ligand **1b** (376 mg, 1.00 mmol) in 5 mL of CH_2Cl_2 under argon atmosphere. The mixture was refluxed for 30 min and then cooled to room temperature. $NaBAr_F$ (930 mg, 1.05 mmol, 1.05 eq) was added as a solid followed by 2 mL of CH_2Cl_2. 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 CH_2Cl_2. The latter fraction containing the product was concentrated on a rotavap. The concentrated solution was filtered over a glass-wool filter (*Whatman*®) and 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 $C_{63}H_{54}BF_{24}IrNOP$ (1531.07), calc.: C, 49.42; H, 3.55; N, 0.91; found: C, 49.47; H, 3.46; N, 0.68; $[\alpha]_D^{20}$ +17 (*c* 0.21, $CHCl_3$); **^{1}H-NMR** (500.1 MHz, CD_2Cl_2, 300 K): δ(ppm) 7.78-7.83 (m, 2H, H_{Ar}), 7.74 (s, 8H, $H_{Ar,F\text{-}o}$), 7.53-6.63 (m 3H, H_{Ar}), 7.57 (s, 4H, $H_{Ar,F\text{-}p}$), 7.40-7.42 (m, 3H, H_{Ar}), 7.06-7.10 (m, 2H, H_{Ar}), 4.82-4.92 (m, 2H, COD-C*H*), 4.58 (dd, 1H, *J* = 4.0 Hz, *J* = 10.0 Hz, OCH_2), 4.36 (dd, 1H, *J* = 9.9 Hz, *J* = 10.0 Hz, OCH_2), 3.82 (dd, 1H, *J* = 4.0 Hz, *J* = 9.9 Hz, NC*H*), 3.69-3.74 (m, 1H, COD-C*H*), 2.47-2.72 (m, 5H, COD-CH_2, PCH_2, COD-C*H*), 2.33-2.37 (m, 2H, COD-CH_2), 2.30 (s, 3H, C(CH_3)$_2$), 2.06-2.14 (m, 1H COD-CH_2), 1.83-1.92 (m, 1H, COD-CH_2), 1.60-1.68 (m, 1H, COD-CH_2), 1.55 (d, *J* = 2.5 Hz, 3H, C(CH_3)$_2$), 1.37-1.47 (m, 1H, COD-CH_2), 0.73 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (125.8 MHz, CD_2Cl_2, 300 K): δ(ppm) 178.4 (d, *J* = 3 Hz, *C*=N), 161.4 (q, *J* = 50 Hz, $C_{ArF\text{-}i}$), 134.8 (d, *J* = 12 Hz, HC_{Ar}), 134.5 (H$C_{ArF\text{-}o}$), 132.1 (d, *J* = 2 Hz, HC_{Ar}), 131.8 (d, *J* = 54 Hz, C_{Ar}), 130.9 (d, *J* = 10 Hz, HC_{Ar}), 130.6 (d, *J* = 3 Hz, HC_{Ar}), 129.1 (d, *J* = 11 Hz, HC_{Ar}), 128.6 (d, *J* = 53 Hz, C_{Ar}), 128.6 (d, *J* = 10 Hz, HC_{Ar}), 128.5 (qq, *J* = 3 Hz, *J* = 32 Hz, $C_{ArF\text{-}m}$), 124.3 (q, *J* = 272 Hz, *C*F_3), 117.1 (sept, *J* = 4 Hz, H$C_{ArF\text{-}p}$), 93.7 (d, *J* = 10 Hz, COD-*C*H), 91.5 (d, *J* = 13 Hz, COD-*C*H), 73.6 (N*C*H), 70.7 (O*C*H_2), 63.2 (COD-*C*H), 60.0 (COD-*C*H), 38.6 (d, *J* = 2 Hz, *C*(CH_3)$_2$), 36.2 (d, *J* = 5 Hz, COD-*C*H_2), 33.3 (s, *C*(CH_3)$_3$), 33.1 (d, *J* = 6 Hz, C(*C*H_3)$_2$), 32.9 (d, *J* = 33 Hz, P*C*H_2), 32.2 (d, *J* = 2 Hz, COD-*C*H_2), 27.8 (d, *J* = 2 Hz, COD-*C*H_2), 26.7 (d, *J* = 12 Hz, C(*C*H_3)$_2$), 25.1 (d, *J* = 2 Hz, COD-*C*H_2), 24.8 (C(*C*H_3)$_3$); **^{31}P{^{1}H}-NMR** (162.0 MHz, $CDCl_3$, 300 K): δ(ppm) 5.9; **^{19}F{^{1}H}-NMR** (376.5 MHz, $CDCl_3$, 300 K): δ(ppm) −64.0; **MS** (+ESI) m/z (%) (668 [M−BAr_F]$^+$, 100); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2974w, 2890w, 2840w, 1600m, 1438w, 1351s, 1269s, 1158s, 1119s, 1106s, 897m, 883s, 838s, 745m, 734m.

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 CH_2Cl_2 under argon atmosphere. The mixture was refluxed for 10 min and then cooled to room temperature. $NaBAr_F$ (575 mg, 0.65 mmol, 1.18 eq) was added as a solid followed by 2 mL of CH_2Cl_2. 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, 16 cm×3 cm). The column was eluted with 300 mL of MTBE, followed by 300 mL of CH_2Cl_2. 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 (778 mg, 0.50 mmol) in 91% yield.

Elemental Analysis for $C_{65}H_{58}BF_{24}IrNOP$ (1559.13), calc.: C, 50.07; H, 3.75; N, 0.90; found: C, 49.99; H, 3.69; N, 0.70; $[\alpha]_D^{20}$ +4 (*c* 0.20, $CHCl_3$); NMR-analysis was hampered by signal broadening caused by conformational equilibria: **^{1}H-NMR** (500.1 MHz, CD_2Cl_2, 300 K): δ(ppm) 8.57 (dd, 1H, *J* = 6.8 Hz, *J* = 16.5 Hz, H_{Ar}), 7.74 (s, 8H, $H_{Ar,F\text{-}o}$), 7.57 (s, 5H, $HC_{Ar,F\text{-}p}$, H_{Ar}), 7.46-7.49 (m, 2H, HC_{Ar}), 7.36 (t, 2H, *J* = 6.9 Hz, HC_{Ar}), 7.27 (s, 1H, HC_{Ar}), 7.13 (s, 1H, H_{Ar}), 4.75-4.85 (m, 2H, 2×COD-C*H*), 4.57 (dd, 1H, *J* = 4.3 Hz, *J* = 9.7 Hz, OCH_2), 4.36 (t, 1H, *J* = 9.9 Hz, OCH_2), 4.07 (s, 1H, COD-C*H*), 3.94 (dd, 1H, *J* = 4.1 Hz, *J* = 9.9 Hz, NC*H*), 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-*C*H), 2.34-2.41 (m, 1H), 2.26 (s, 3H, $C(CH_3)_2$), 2.14-2.24 (m, 2H), 2.03-2.12 (m, 1H), 2.02 (s, 3H, $CArCH_3$), 1.72-1.84 (m, 1H), 1.67 (s, 3H, $CArCH_3$), 1.54-1.60 (m, 1H), 1.52 (s, 3H, $C(CH_3)_2$), 1.31-1.41 (m, 1H), 0.88 (s, 9H, $C(CH_3)_3$); **^{13}C{^{1}H}-NMR** (125.8 MHz, $CDCl_3$, 300 K): δ(ppm) 178.3 (br s, *C*=N), 161.4 (q, *J* = 50 Hz, $C_{ArF\text{-}i}$), 141.7, 140.1, 134.5 ($HC_{ArF\text{-}o}$), 132.4, 132.0, 130.8, 130.3, 128.5 (qq, *J* = 3 Hz, *J* = 32 Hz, $C_{ArF\text{-}m}$), 125.8 (d, *J* = 16.0 Hz), 127.0, 124.3 (q, *J* = 272 Hz, CF_3), 117.1 (m, $HC_{ArF\text{-}p}$), 92.1 (COD-*C*H), 89.0 (COD-*C*H), 73.6 (N*C*H), 70.5 (OCH_2), 64.4 (COD-*C*H), 60.2 (COD-*C*H), 39.0, 36.7 (d, *J* = 5 Hz), 35.7 (d, *J* = 28 Hz), 33.5, 32.5 (br s, $C(CH_3)_3$), 32.2 (br s, PCH_2), 28.1, 27.1, 25.2 ($C(CH_3)_3$), 24.9, 22.3 ($C_{Ar}CH_3$), 21.1 ($C_{Ar}CH_3$); **^{31}P{^{1}H}-NMR** (202.5 MHz, CD_2Cl_2, 300 K): δ(ppm) 15.2 (minor, s, br), 8.0 (major, s, br); **^{19}F{^{1}H}-NMR** (376.5 MHz, CD_2Cl_2, 300 K): δ(ppm) −64.0; **MS** (+ESI) m/z (%) 696 ([M−BAr_F^+], 100); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2968w, 2935w, 2893w, 1599m, 1454w, 1352s, 1271s, 1161s,sh, 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 CH_2Cl_2 under argon atmosphere. The mixture was refluxed for 30 min and then cooled to room temperature. $NaBAr_F$ (564 mg, 0.64 mmol, 1.20 eq) was added as a solid followed by 2 mL of CH_2Cl_2. 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, 20 cm×3 cm). The column was eluted with 300 mL of MTBE, followed by 300 mL of CH_2Cl_2. 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 $C_{67}H_{62}BF_{24}IrNOP$(1587.18), calc.: C, 50.70; H, 3.94; N, 0.88; found: C, 50.75; H, 3.70; N, 0.75; $[\alpha]_D^{20}$ +10 (*c* 0.10, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 7.74 (s, 8H, $H_{Ar,F\text{-}o}$), 7.58 (s,

4H, $H_{Ar,F\text{-}p}$), 7.40 (d, 2H, J = 11.7 Hz, H_{Ar}), 7.22 (s, 1H, H_{Ar}), 7.05 (s, 1H, H_{Ar}), 6.67 (d, 2H, J = 11.7 Hz, H_{Ar}), 4.76-4.86 (m, 2H, COD-C*H*), 4.57 (dd, 1H, J = 4.0 Hz, J = 10.0 Hz, OCH_2), 4.35 (dd, 1H, J = 9.9 Hz, J = 10.0 Hz, OCH_2), 3.82 (dd, 1H, J = 4.0 Hz, J = 9.9 Hz, NC*H*), 3.69-3.74 (m, 1H, COD-C*H*), 2.58-2.68 (m, 2H, COD-CH_2), 2.48-2.56 (m, 3H, COD-C*H*, PCH_2), 2.35 (s, 6H, $C_{Ar}CH_3$), 2.31-2.34 (m, 2H, COD-CH_2), 2.28 (s, 3H, C(CH_3)$_2$), 2.25 (s, 6H, $C_{Ar}CH_3$), 2.05-2.11 (m, 1H, COD-CH_2), 1.83-1.90 (m, 1H, COD-CH_2), 1.58-1.64 (m, 1H, COD-CH_2), 1.54 (s, 3H, C(CH_3)$_2$), 1.36-1.43 (m, 1H, COD-CH_2), 0.74 (s, 9H, C(CH_3)$_3$); **^{13}C{^{1}H}-NMR** (125.8 MHz, $CDCl_3$, 300 K): δ(ppm) 178.5 (d, J = 3 Hz, *C*=N), 161.4 (q, J = 50 Hz, $C_{ArF\text{-}i}$), 138.8 (d, J = 11 Hz, C_{Ar}), 138.4 (d, J = 11 Hz, C_{Ar}), 134.5 (H$C_{ArF\text{-}o}$), 133.5 (d, J = 2 Hz, HC_{Ar}), 132.7 (d, J = 12 Hz, HC_{Ar}), 132.3 (d, J = 3 Hz, HC_{Ar}), 131.6 (d, J = 54 Hz, C_{Ar}), 128.5 (d, J = 10 Hz, HC_{Ar}), 128.6 (qq, J = 3 Hz, J = 31 Hz, $C_{ArF\text{-}m}$), 128.5 (d, J = 53 Hz, C_{Ar}), 124.3 (q, J = 273 Hz, *C*F$_3$), 117.2 (septett, J = 4 Hz, H$C_{ArF\text{-}p}$), 92.8 (d, J = 11 Hz, COD-*C*H), 90.4 (d, J = 14 Hz, COD-*C*H), 73.5 (N*C*H), 70.7 (O*C*H$_2$), 62.9 (COD-*C*H), 60.3 (COD-*C*H), 38.6 (d, J = 2 Hz, *C*(CH$_3$)$_2$), 36.4 (d, J = 5 Hz, COD-*C*H$_2$), 33.4 (*C*(CH$_3$)$_3$), 33.2 (d, J = 7 Hz, C(*C*H$_3$)$_2$), 32.8 (d, J = 32 Hz, P*C*H$_2$), 32.3 (COD-CH_2), 27.8 (COD-CH_2), 26.7 (d, J = 12 Hz, C(*C*H$_3$)$_2$), 25.1 (d, J = 2 Hz, COD-CH_2), 24.7 (C(*C*H$_3$)$_3$), 20.8 (C_{Ar}*C*H$_3$), 20.7 (C_{Ar}*C*H$_3$); **^{31}P{^{1}H}-NMR** (162.0 MHz, $CDCl_3$, 300 K): δ(ppm) 5.4; **^{19}F{^{1}H}-NMR** (376.5 MHz, $CDCl_3$, 300 K): δ(ppm) −63.5; **MS** (+ESI) m/z (%) 724 ([M−BAr_F^+], 100); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2966w, 2928w, 2889w, 2841w, 1596m, 1472w, 1353s, 1272s, 1115s, 885s, 839s, 744m, 712s, 691m, 682s, 668s.

Ir-1e:

To a dry Schlenk tube was added a solution of 246 mg (0.98 mmol, 1.00 eq) oxazoline **2c** in 2 mL of THF. To this solution were added dropwise at 0 °C 2.0 mL of a 0.5 M $KPPh_2$ 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 ^{31}P-NMR spectrum) for complexation.

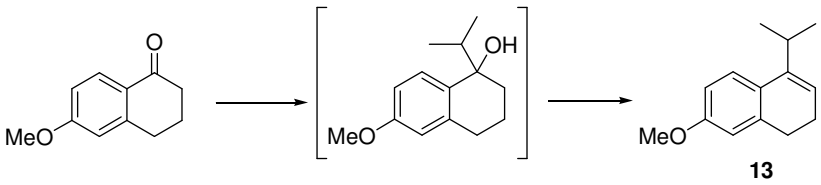
To a solution of 120 mg (179 µmol, 0.36 eq) of $[Ir(COD)Cl]_2$ in 5 mL of CH_2Cl_2 were added 201 mg (500 µmol, 1.0 eq) of the crude ligand (**1e**, see above). The solution was heated to reflux for 30 min and the solution was cooled to RT followed by addition of 576 mg (650 µmol, 1.3 eq) of $NaBAr_F$ as a solid. After 30 min, 20 mL of water were added, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2×10 mL). The combined organic phases were dried over $MgSO_4$, 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 CH_2Cl_2 (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 $C_{66}H_{52}BF_{24}IrNOP$ (1565.09), calc.: C, 50.65; H, 3.35; N, 0.89; found: C, 50.64; H, 3.30; N, 0.74; $[\alpha]_D^{20}$ +12 (*c* 0.22, $CHCl_3$); **^{1}H-NMR** (500.1 MHz, CD_2Cl_2, 300 K): δ(ppm) 7.96-7.92 (m, 2H, H_{Ar}), 7.73 (s, 8H, $H_{Ar,F\text{-}o}$), 7.64-7.63 (m, 1H, H_{Ar}), 7.60-7.59 (m, 2H, H_{Ar}), 7.56 (s, 4H, $H_{Ar,F\text{-}p}$), 7.46 (s, 3H, H_{Ar}), 7.32-7.26 (m, 3H, H_{Ar}), 7.17-7.13 (m, 2H, H_{Ar}), 7.02-7.01 (m, 2H, H_{Ar}), 5.10-5.00 (m, 2H, 2 COD-C*H*), 4.43-4.30 (m, 3H, NC*H*, OCH_2), 3.63 (br s, 1H, COD-C*H*), 3.45 (dd, 1H, J = 2.9 Hz, J = 13.6 Hz, C$H_2C_6H_5$), 2.67-2.37 (m,

7H, PCH_2, COD-CH, 2 COD-CH_2), 2.26-2.17 (m, 2H, COD-CH_2, CH_2C$_6$H$_5$), 2.18 (s, 3H, C(CH_3)$_2$), 1.98-1.91 (m, 1H, COD-CH_2), 1.77-1.69 (m, 1H, COD-CH_2), 1.53-1.42 (m, 1H, COD-CH_2), 1.48 (d, J = 2.5 Hz, 3H, C(CH$_3$)$_2$); **^{13}C{^{1}H}-NMR** (125 MHz, CD_2Cl_2, 300 K): δ(ppm) 178.6 (d, J = 4 Hz, C=N), 161.4 (q, J = 51 Hz, $C_{ArF\text{-}i}$), 135.3 (d, J = 13 Hz, HC_{Ar}), 134.5 (H$C_{ArF\text{-}o}$), 134.1 (C_{Ar}), 132.3 (d, J = 2 Hz, HC_{Ar}), 131.8 (d, J = 55 Hz, HC_{Ar}), 131.1 (d, J = 10 Hz, HC_{Ar}), 130.8 (d, J = 3 Hz, HC_{Ar}), 129.3 (d, J = 11 Hz, HC_{Ar}), 128.8 (HC_{Ar}), 128.6 (d, J = 11 Hz, HC_{Ar}), 128.5 (qq, J = 3 Hz, J = 31 Hz,$C_{ArF\text{-}m}$), 128.3 (HC_{Ar}), 127.8 (d, J = 54 Hz, C_{Ar}), 127.4 (HC_{Ar}), 124.3 (q, J = 273 Hz, CF$_3$), 117.2 (sept, J = 4 Hz, H$C_{ArF\text{-}p}$), 92.0 (d, J = 10 Hz, COD-CH), 90.8 (d, J = 13 Hz, COD-CH), 73.1 (OCH$_2$), 65.8 (NCH), 63.8 (COD-CH), 62.1 (COD-CH), 42.9 (CH$_2$Ph), 38.3 (d, J = 3 Hz, C(CH$_3$)$_2$), 35.7 (d, J = 5 Hz, COD-CH$_2$), 34.4 (d, J = 32 Hz, PCH$_2$), 33.0 (d, J = 7 Hz, C(CH$_3$)$_2$), 32.2 (COD-CH$_2$), 28.0 (COD-CH$_2$), 26.2 (COD-CH$_2$), 26.1 (CH$_3$); **^{31}P{^{1}H}-NMR** (162 MHz, CD_2Cl_2, 300 K): δ(ppm) 8.5; **^{19}F{^{1}H}-NMR** (376.5 MHz, CD_2Cl_2, 300 K): δ(ppm) −64.0; **MS** (+ESI) m/z (%) 702 ([M−BAr_F]$^+$, 100); **IR** ($\tilde{V}$ [cm^{-1}]) 2970w, 2930w, 2843w, 1603m, 1353s, 1271s, 1114s, 885m, 839m, 737m, 713m, 696m, 681s, 668s.

e) Synthesis of 13, 14, 15 and (*R*)-(+)-7-Demethyl-2-methoxycalamenene (16):

13:



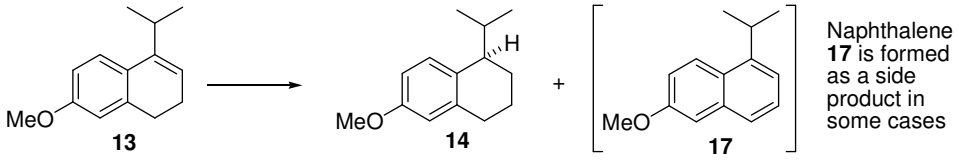
13

A three necked round bottom flask with a magnetic stirrer was dried in an oven over night, cooled under vacuum and charged with argon. A thermometer was added and after another two vacuum/argon cycles a solution of *i*PrMgCl (22 mL, 2M 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_4Cl-solution at 0 °C. MTBE (50 mL) was added, followed by 150 mL of 1M 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 *p*TsOH were added and the mixture was refluxed overnight. Water was removed by soxhlet extraction with molecular sieves (4 Å). MTBE (40 mL) and a $Na_2S_2O_3$ solution (0.5M, 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.

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): δ(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=C*H*), 3.80 (s, 3H, OCH_3), 2.89 (d sept., 1H, J = 1.1 Hz, J = 6.8 Hz, *i*Pr-C*H*), 2.71-2.65 (m, 2H, CH_2), 2.25-2.19 (m, 2H, CH_2), 1.14 (d, 6H, J = 6.8 Hz, *i*Pr-CH_3); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 158.0 (C_{quart}), 142.2 (C_{quart}), 138.9 (C_{quart}), 128.1 (C_{quart}), 123.6 (*C*H), 118.9 (*C*H), 113.7 (*C*H), 110.8 (*C*H), 55.2 (O*C*H_3), 29.1 (*C*H_2), 28.3 (*C*H), 23.0 (*C*H_2), 22.2 (*C*H_3); **MS** (+EI) m/z (%) 202 (M^+, 49), 187 (14), 159 (100), 144 (34), 128 (21), 115 (26); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2958m, 2929m, 2882m, 2878m, 2871m, 2830m, 1633, 1606s, 1569m, 1493s, 1464m, 1426m, 1379m, 1359w, 1301m, 1276m,

1248vs, 1203w, 1187w, 1165m, 1152m, 1134s, 1103m, 1047s, 1005m, 1022w, 1006, 932w, 904w, 886w, 882w, 868w, 843m, 818s, 683m, 634m, 586m. R_f 0.32 (silica gel, hexanes/ethyl acetate 50:1).

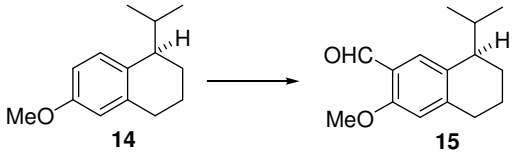
14:



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 CH_2Cl_2 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 $C_{14}H_{20}O$, (204.31), calc.: C, 82.30; H, 9.87; found: C, 82.13; H, 9.75; $[\alpha]_D^{20}$ +64.2 (*c* 1.03, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ(ppm) 7.13 (d, 1H, *J* = 8.5 Hz, H_{Ar}), 6.70 (dd, 1H, *J* = 2.7 Hz, *J* = 8.5 Hz, H_{Ar}), 6.61 (d, 1H, *J* = 2.6 Hz, H_{Ar}), 3.78 (s, 3H, OCH_3), 2.77-2.61 (m, 3H, ArC*H*), 2.21 (sept, 1H, *J* = 6.7 Hz, *J* = 13.6 Hz, $CH(CH_3)_2$), 1.95-1.86 (m, 1H, CH_2), 1.83-1.75 (m, 1H, CH_2), 1.65-1.55 (m, 2H, CH_2), 1.01 (d, 3H, *J* = 6.8 Hz, $CH(CH_3)_2$), 0.74 (d, 3H, *J* = 6.8 Hz, $CH(CH_3)_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 157.0 (C_{Ar}), 139.2 (C_{Ar}), 132.5 (C_{Ar}), 129.1 (HC_{Ar}), 113.4 (HC_{Ar}), 111.5 (HC_{Ar}), 55.1 (OCH_3), 42.8 (*C*H), 31.4 (*C*H), 30.3 (CH_2), 23.4 (CH_2), 21.4 (CH_2), 21.2 (CH_3), 17.4 (CH_3); **MS** (+EI) m/z (%) 204 (8), 161 (100), 146 (7), 128 (6), 115 (11), 91 (10), 41 (11); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2953s, 2932s, 2868s, 2833m, 1609m, 1575w, 1500s, 1463m, 1256s, 1463m, 1256s, 1232m, 1155w, 1043m; **GC** (chiral, β-Cyclodextrin, DEtTButSil (Brechbühler, SE54), 0.25 mm, 0.25 μm, 25 m, 60 kPa H_2, 140 °C, 0 min, 2 K/min, 180°C, 5 min): $t_{R[(S)\text{-}\mathbf{14}]}$ = 10.8 min, $t_{R[(R)\text{-}\mathbf{14}]}$ = 11.3 min, $t_{R(\mathbf{13})}$ = 12.5 min, $t_{R(\mathbf{17})}$ = 15.0 min.

15:



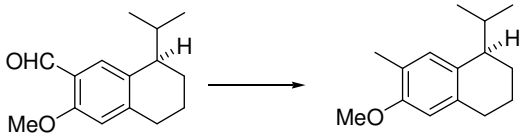
To a dry Schlenk tube was added dry CH_2Cl_2 (6 mL) followed by *N*-methylformanilide (5.9 mL, 6.43 g, 47.6 mmol, 6.65 eq) and $POCl_3$ (3.0 mL, 5.03 g, 47.6 mmol, 4.58 eq). The mixture was stirred at RT for 1 h (color change from colorless to yellow) and the tetrahydronaphthaline (1.46 g, 7.15 mmol) dissolved in 3 mL of CH_2Cl_2 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 2×25 mL of CH_2Cl_2. The combined organic phases were washed with

50 mL of brine and dried over $MgSO_4$. 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×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 $C_{15}H_{20}O_2$ (232.32), calc.: C, 77.55; H, 8.68; found: C, 77.41; H, 8.68; **M.p.**: 47-48 °C (hexanes); $[\alpha]_D^{20}$ +76.3 (*c* 1.00, $CHCl_3$); **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300K): δ(ppm) 10.39 (s, 1H, C*H*O), 7.68 (s, 1H, H_{Ar}), 6.65 (s, 1H, H_{Ar}), 3.88 (s, 3H, OCH_3), 2.74-2.77 (m, 2H, C_{Ar}C*H*/CH_2), 2.66 (dd, 1H, *J* = 6.3 Hz, *J* = 12.6 Hz, C_{Ar}C*H*/CH_2), 2.22-2.32 (m, 1H, C*H*(CH_3)$_2$), 1.88-1.97 (m, 1H, CH_2), 1.77-1.83 (m, 1H, CH_2), 1.55-1.67 (m, 2H, CH_2), 0.99 (d, 3H, *J* = 6.8 Hz, CH(CH_3)$_2$), 0.72 (d, 3H, *J* = 6.8 Hz, CH(CH_3)$_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 189.8 (*C*HO), 159.3 (C_{Ar}), 147.6 (C_{Ar}), 132.9 (C_{Ar}), 128.3 (HC_{Ar}), 122.7 (C_{Ar}), 111.6 (HC_{Ar}), 55.5 (O*C*H$_3$), 42.6 (C_{Ar}*C*H), 31.3 (*C*H(CH_3)$_2$), 31.0 (*C*H$_2$), 23.0 (*C*H$_2$), 21.1 (*C*H$_2$), 17.2 (CH(*C*H$_3$)$_2$); **MS** (EI) m/z (%) 232 (M^+, 10), 189 (100), 161 (14), 146 (13), 128 (11), 115 (12), 91 (10), 77 (6), 41 (13); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2953m, 2933m, 2900m, 2892m, 2866m, 2844m, 1680s, 1608s, 1569w, 1493m, 1464m, 1414m, 1394m, 1299m, 1263s, 1205w, 1194w, 1167w, 1156w, 1099m, 1023w, 953w, 839w, 633w; R_f 0.29 (silica gel, hexanes/ethyl acetate, 10/1); **HPLC**, AD-H, heptane/*iso*-propanol (99/1), 0.5 mL/min, 20 °C, $t_{R[(S)\text{-}\mathbf{15}]}$:15.9 min, $t_{R[(R)\text{-}\mathbf{15}]}$: 17.9 min.

16:



15 **16**

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-methoxycalamenene 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]

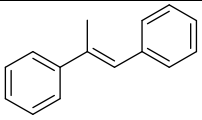
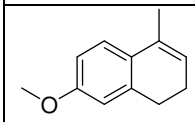
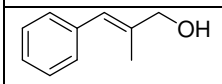
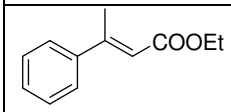
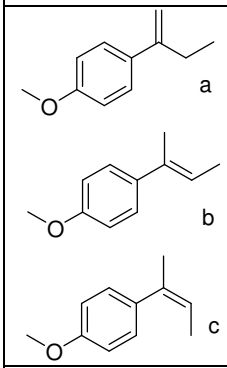
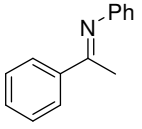
Elemental Analysis for $C_{15}H_{22}O$ (218.33), calc.: C, 82.52; H, 10.16; found: C, 82.65; H, 10.07; $[\alpha]_D^{20}$ +62.1 (*c* 1.06, $CHCl_3$) {Lit[2]: $[\alpha]_D^{20}$ +53.9 (*c* 1.32, $CHCl_3$) }; **^{1}H-NMR** (400.1 MHz, $CDCl_3$, 300 K): δ(ppm) 6.97 (s, 1H, H_{Ar}), 6.52 (s, 1H, H_{Ar}), 3.80 (s, 3H, OCH_3), 2.60-2.75 (m, 3H, C_{Ar}C*H*, C_{Ar}CH_2), 2.17-2.28 (m, 4H, C_{Ar}CH_3, C*H*(CH_3)$_2$), 1.87-1.95 (m, 1H, CH_2), 1.75-1.81 (m, 1H, CH_2), 1.54-1.67 (m, 2H, CH_2), 1.01 (d, 3H, *J* = 6.9 Hz, CH(CH_3)$_2$), 0.74 (d, 3H, *J* = 6.8 Hz, CH(CH_3)$_2$); **^{13}C{^{1}H}-NMR** (100.6 MHz, $CDCl_3$, 300 K): δ(ppm) 155.3

(C_{Ar}), 136.2 (C_{Ar}), 131.8 (C_{Ar}), 130.3 (HC_{Ar}), 123.4 (C_{Ar}), 110.1 (HC_{Ar}), 55.2 (OCH$_3$), 42.7 ($C_{Ar}C$H), 31.4 (CH(CH$_3$)$_2$), 30.2 (CH$_2$), 23.4 (CH$_2$), 21.7 (CH$_2$), 21.3 (CH(CH$_3$)$_2$), 17.3 (CH(CH$_3$)$_2$), 16.0 ($C_{Ar}C$H$_3$); **MS** (EI) m/z (%) 218 (M^+, 10), 175 (100), 160 (9), 145 (6), 128 (7), 115 (7), 41 (8); **IR** ($\tilde{\nu}$ [cm^{-1}]) 2927s, 2856m, 1616m, 1506s, 1464m, 1405w, 1383w, 1365w, 1319w, 1252s, 1208m, 1155w, 1103s, 1027m, 885m, 837m; R_f 0.64 (silica gel, hexanes/ethyl acetate, 20/1), R_f 0.23 (silica gel, hexanes). **GC** (chiral, β-Cyclodextrin, DiMe*t*BuSil (OV1701) from Brechbühler, 0.25 mm, 0.25 µm, 25 m, 60 kPa H_2, 100 °C, 0 min, 2 K/min, 160 °C, 10 min): $t_{R[(S)\text{-}\mathbf{16}]}$: 29.7 min, $t_{R[(R)\text{-}\mathbf{16}]}$: 30.6 min.

f) General asymmetric hydrogenation procedure

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 0.2M 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 H_2. The autoclave was sealed under the appropriate H_2 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 H_2 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:

Substrate	Conversion	*ee*
	GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin^{-1}-250 °C, 10 min, 60 kPa He Substrate: 21.0 min Product: 18.2 min	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)
	GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin^{-1}-250 °C, 10 min, 60 kPa He Substrate: 18.0 min Product: 16.7 min	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)
	GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin^{-1}-250 °C, 10 min, 60 kPa He Substrate: 15.7 min Product: 14.0 min	HPLC with UV-detector Column: Chiralcel ODH Heptane:*i*-Propanol: 95:5 0.5 mL min^{-1}, 40 °C Substrate: 18.5 min Product: 114.8 min (+), 16.8 min (–)
	GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin^{-1}-250 °C, 10 min, 60 kPa He Substrate: 17.2 min Product: 15.0 min	HPLC with UV-detector Column: Chiralcel OBH 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)
	GC: achiral column, Restek Rtx-1701, 30 m, T-Program: 100 °C, 2 min, 7 °Cmin^{-1}-250 °C, 10 min, 60 kPa He Substrate a: 13.0 min Substrate b: 14.2 min Substrate c: 11.8 min Product: 11.9 min	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)
	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 Substrate: 36.0 min Product: 35.3 min	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)

g) References

[1] Asymmetric Hydrogenation, see: a) A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem.* 1998, **110**, 3047; *Angew. Chem. Int. Ed.* 1998, **37**, 2897; b) A. Pfaltz, J. Blankenstein, R. Hilgraf, E. Hörmann, S. McIntyre, F. Menges, M. Schönleber, S. P. Smidt, B. Wüstenberg and N. Zimmermann, *Adv. Synth. Catal.* 2003, **345**, 33; c) G. H. Bernardinelli, E. P. Kündig, P. Meier, A. Pfaltz, K. Radkowski, N. Zimmermann and M. Neuburger-Zehnder, *Helv. Chim. Acta* 2001, **84**, 3233.

[2] F. Bohlmann, C. Zdero, H. Robinson and R. King, *Phytochemistry*, 1979, **18**, 1675.