

Supporting information.

Characterization data

CDA **1a**: m.p. 145-148 °C; ^1H NMR (300 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 1.93 (d, 6H, Me, $J_{\text{H-H}}=7.02$ Hz), 4.00 (m, 2H, CH), 4.71 (bs, 4H, C_2H_4 , $J_{\text{H-Pt}}=32$ Hz), 7.44-7.55 (m, 10H, Ph), 8.79 (bs, 2H, NH_2); ^{13}C NMR (75 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 21.8, 57.9, 69.4, 127.7, 129.5, 129.6; ^{195}Pt NMR (64 MHz, CDCl_3 , 25° C, δ/ppm , Na_2PtCl_6 external standard): -2738.4. Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{NCl}_3\text{Pt}$: C 38.89, H 4.35, N 2.52, Cl 19.13. Found: C 38.94, H 4.12, N 2.38, Cl 19.20 %.

CDA **1b**: ^1H NMR (300 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 1.73 (d, 3H, Me, $J_{\text{H-H}}=6.7$ Hz), 4.38 (bs, 4H, C_2H_4 , $J_{\text{H-Pt}}=31$ Hz), 4.62 (m, 1H, CH), 7.29-7.54 (m, 8H, Ph+ NH_3), ^{13}C NMR (75 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 20.5, 52.7, 70.0, 127.3, 129.2, 129.3, 136.9; ^{195}Pt NMR (64 MHz, CDCl_3 , 25° C, δ/ppm , Na_2PtCl_6 external standard): -2779.8. Anal. Calc. for $\text{C}_{10}\text{H}_{16}\text{NCl}_3\text{Pt}$: C 26.59, H 3.57, N 3.10, Cl 23.55. Found: C 26.65, H 3.68, N 3.07, Cl 23.48 %.

CDA **2a**: m.p. 166-168 °C; ^1H NMR (300 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 1.33 (d, 3H, Me, $J_{\text{H-H}}=7.1$ Hz), 2.03 (d, 3H, Me, $J_{\text{H-H}}=7.1$ Hz), 4.25 (bs, 4H, C_2H_4 , $J_{\text{H-Pt}}=32$ Hz), 4.54 (m, 2H, CH), 5.29 (bs, 1H, NH), 7.25-7.48 (m, 10H, Ph); ^{13}C NMR (75 MHz, CDCl_3 , 25° C, δ/ppm , TMS external standard): 22.1, 24.3, 61.5, 62.5, 71.4, 127.0, 127.1, 128.1, 128.5, 129.2, 129.4, 140.0, 142.2; ^{195}Pt NMR (64 MHz, CDCl_3 , 25° C, δ/ppm , Na_2PtCl_6 external standard): -2847.5. Anal. Calc. for

$C_{18}H_{23}NCl_2Pt$: C 41.63, H 4.46, N 2.69, Cl 13.65. Found: C 40.56, H 4.17, N 2.52, Cl 11.30 %.

CDA **2b**: 1H NMR (300 MHz, $CDCl_3$, 25° C, δ/ppm , TMS external standard): 1.80 (d, 3H, Me, $J_{H-H}=6.61$ Hz), 4.16 (bs, 2H, NH_2), 4.40 (m, 1H, CH), 4.63 (bs, 4H, C_2H_4 , $J_{H-Pt}=32$ Hz), 7.20-7.58 (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$, 25° C, δ/ppm , TMS external standard): 22.8, 55.6, 75.0, 126.4, 128.7, 129.1, 141.7; ^{195}Pt NMR (64 MHz, $CDCl_3$, 25° C, δ/ppm , Na_2PtCl_6 external standard): -3017.4. Anal. Calc. for $C_{10}H_{15}NCl_2Pt$: C 28.93, H 3.64, N 3.37, Cl 17.08. Found: C 28.82, H 3.70, N 3.45, Cl 17.15 %.

Amine hydrochloride **a**: 1H NMR (300 MHz, $CDCl_3$, 25° C, δ/ppm , TMS external standard): 1.89 (d, 6H, Me, $J_{H-H}=6.91$ Hz), 3.84 (m, 2H, CH), 7.33-7.52 (m, 10H, Ph), 10.48 (bs, 2H, NH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25° C, δ/ppm , TMS external standard): 21.4, 57.1, 128.2, 129.0, 129.1, 136.3.

d=doublet, bs=broad singlet, m=multiplet

Experimental procedure involved in the use of the CDAs.

The chiral substrate was added (substrate:CDA 0.8:1) to a solution containing 50-100 mg of CDA in 0.5 mL of deuterated solvent and the ^{195}Pt NMR spectra of the reaction mixtures were analyzed by using a standard pulse sequence and a spectral window of 50000 Hz. All ^{195}Pt NMR chemical shifts were referenced to Na_2PtCl_6 as external standard and the ^{195}Pt resonances of the small excess of CDAs were at lower

frequencies (see characterization data) than the absorptions due to the diastereoisomeric mixtures.

Gas chromatographic analyses

The enantiomeric compositions of the samples of the allene **3b** have been determined by gas chromatographic analyses on CYDEX-B (25 m, i.d. 0.33 mm, film thickness 0.25 μm) and helium as carrier gas (10 psig).