Pt(II)(M,S_S,S_S)-cyclohexyl-binasoCl$_2$ (5b): A 100 mL Schlenk tube was charged with 92 mg (0.194 mmol) Pt(PhCN)$_2$Cl$_2$ and 100 mg (0.194 mmol) (M,S_S,S_S)-cyclohexyl-binaso. 10 mL dry toluene was added, and the yellow suspension was stirred at 100°C overnight. The reaction was then allowed to cool to room temperature; the Schlenk tube was then taken inside the glovebox. Pentane was added to the stirred yellow suspension, the solid was allowed to settle, and the supernatant solvent was decanted off *via* Pasteur pipette. The remaining yellow solid was washed twice with toluene (2 x 5 mL), and twice with pentane (2 x 5 mL). The complex was then dried thoroughly under high vacuum to give 129 mg (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = -0.81--0.69 (m, 1H), 0.41-0.51 (m, 1H), 0.76-0.88 (m, 3H), 1.02-1.37 (m, 9H), 1.53-1.59 (m, 2H), 1.69-1.81 (m, 2H), 2.53-2.56 (m, 1H), 7.21-7.23 (d, J = 8.8 Hz, 1H), 7.43-7.47 (t, J = 7.7 Hz, 1H), 7.53-7.57 (t, J = 7.8 Hz, 4H), 7.71-7.79 (m, 6H), 8.14-8.16 (d, J = 8.4 Hz, 1H), 8.42-8.48 (q, J = 3.8 Hz, J = 12.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 23.85, 24.51, 24.73, 26.05, 28.30, 29.93, 65.00, 109.32, 117.02, 123.50, 127.13, 128.11, 129.11, 129.37, 129.69, 130.01, 132.08, 132.40, 133.99, 135.45, 135.52, 135.96 ppm. Elemental analysis: Calculated for $PtC_{32}H_{34}O_2S_2Cl_2$: C = 49.37%, H = 4.38%; Found: C = 49.06%, H = 4.27%.

Pd(II)(M,S_S,S_S)-*p*-tolyl-binaso(OC(O)CF$_3$)$_2$ (6): A vial was charged with 49 mg (0.188 mmol) Pd(PhCN)$_2$Cl$_2$,100 mg (0.188 mmol) (M,S_S,S_S)-*p*-tolyl-binaso and 83 mg (0.376 mmol) Ag(OC(O)CF$_3$). 5 mL CH_2Cl_2 was added, the vial was covered, and the reaction was left stirring in the dark for three hours. After this time, the precipitated AgCl

Pt(II)(M,S_S,S_S)-*p*-tolyl-binaso(Me)$_2$ (11a): A vial was charged with 100 mg (0.174 mmol) [Pt(Me)$_2$μ-S(Me)$_2$]$_2$ and 185 mg (0.348 mmol) (M,S_S,S_S)-*p*-tolyl-binaso. 4 mL CH_2Cl_2 was added, after 30 minutes a white precipitate began to appear. The mixture was left stirring overnight and then 10 mL pentane was added to yield more precipitation of the white solid. The vial was centrifuged for five minutes, so the supernatant solvent could be decanted off *via* Pasteur pipette. The white solid was then redissolved in CH_2Cl_2, and filtered over celite. The complex was precipitated again by adding pentane to the colorless solution, and was centrifuged. The supernatant solvent was removed in the same way as before, and the solid was dried thoroughly under high vacuum to give 202 mg (79% yield) of product. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 0.91-1.11 (t, J = 41.0 Hz, 6H), 1.89 (s, 6H), 6.27-6.29 (d, J = 8.6 Hz, 2H), 6.43-6.45 (d, J = 8.2 Hz, 4H), 6.92-6.96 (t, J = 7.8 Hz, 2H), 7.29-7.31 (d, J = 7.7 Hz, 4H), 7.34-7.38 (t, J = 7.5 Hz, 2H), 7.67-7.69 (d, J = 8.1 Hz, 2H), 8.06-8.08 (d, J = 8.8 Hz, 2H), 8.52-8.55 (d, J = 8.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = -0.35, 21.29, 121.31, 126.39, 127.28, 127.51, 127.60, 128.09, 128.59, 129.19, 129.68, 129.73, 130.74, 132.64, 134.89, 139.10, 142.71, 143.99 ppm. Elemental Analysis: Calculated for $PtC_{36}H_{32}O_2S_2$: C = 57.20%, H = 4.27%; Found: C = 57.28%, H = 4.36%.

Pt(II)(M,S_S,S_S)-cyclohexyl-binaso(Me)$_2$ (11b): Made by the same method as described for **9a**, using 179 mg (0.348 mmol) (M,S_S,S_S)-cyclohexyl-binaso. 165 mg of the white solid product were obtained (64% yield). Colorless crystals suitable for an X-ray crystal structure analysis were grown from a solution of the complex in a 10:1

hexane/CH_2Cl_2 mixture, after being left at -20°C for several weeks. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = -0.57--0.50 (m, 1H), 0.39-0.48 (m, 2H), 0.72-0.95 (m, 1H), 0.82 (t, *J* = 34.9 Hz, 6H), 1.05-1.71 (m, 17H), 2.12-2.14 (m, 1H), 7.06-7.11 (m, 2H), 7.32-7.37 (m, 2H), 7.61-7.66 (m, 2H), 8.06-8.15 (m, 3H), 8.25-8.37 (m, 3H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 0.20, 22.04, 23.39, 24.89, 24.97, 25.25, 25.49, 25.94, 26.12, 26.18, 27.25, 27.94, 59.75, 61.56, 122.19, 123.28, 125.80, 127.12, 127.87, 127.93, 128.09, 128.13, 128.57, 129.11, 129.38, 129.77, 130.24, 130.95, 133.01, 133.14, 134.53, 134.78, 140.13, 140.49 ppm. Elemental Analysis: Calculated for $PtC_{34}H_{40}S_2O_2$: C = 55.19%, H = 5.45%; Found: C = 55.23%, H = 5.34%.

Pt(II)((*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso)$(CH_3CN)_2(BF_4)_2$ (12): A vial was charged with 100 mg (0.126 mmol) **5** and 49 mg (0.252 mmol) $AgBF_4$. 4 mL of a 3:1 mixture of CH_2Cl_2/CH_3CN was added and the vial was covered. The reaction was left stirring in the dark for 3 hours. After this time, the precipitated AgCl was filtered off over celite, to leave a clear, yellow solution. The solution was concentrated to a volume of about 1 mL, and diethyl ether (20 mL) was added slowly to the stirred solution to precipitate a yellow solid. The vial was centrifuged, so the supernatant solvent could be decanted off by Pasteur pipette. The complex was washed twice more with diethyl ether (2 x 5 mL), and then dried thoroughly under high vacuum to give 101 mg (82% yield) of product. ^{1}H NMR confirmed that both the ligand and two equivalents of CH_3CN were coordinated to the Pt atom. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H), 2.63 (s, 6H), 6.56-6.58 (d, *J* = 8.7 Hz, 2H), 6.62-6.83 (m, 4H), 7.22-7.25 (t, *J* = 7.7, Hz, 2H), 7.54-7.58 (t, *J* = 7.5, 6H),

7.80-7.82 (d, J = 8.3 Hz, 2H), 8.24-8.26 (d, J = 9.0 Hz, 2H), 8.55-8.57 (d, J = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 4.05 (s), 21.51 (t, J = 80 Hz), 122.29, 127.21, 128.94, 129.13, 129.54, 130.35, 130.92, 131.41, 132.47, 133.24, 135.05, 135.95, 146.49 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -151.37 (s) ppm. Elemental analysis: Calculated for $PtC_{38}H_{32}B_2F_8N_2O_2S_2$: C = 52.61, H = 3.72, N = 3.23; Found: C = 52.45, H = 3.68, N = 3.17.

Pt(II)((*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso)$_2$(BF$_4$)$_2$ (13): A vial was charged with 50 mg **5** (0.063 mmol), 33 mg (0.063 mmol) (*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso) and 25 mg (0.126 mmol) $AgBF_4$. 3 mL CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for 2 hours. It was then filtered over celite to remove precipitated AgCl. The clear yellow solution was then concentrated to a volume of around 1 mL and diethyl ether was added dropwise. The complex precipitated as a yellow solid. The vial was centrifuged for 10 minutes, so the supernatant solvent could be removed by Pasteur pipette. The solid was washed twice more with diethyl ether and then thoroughly dried under high vacuum to give 77 mg (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.28 (s, 3H), 6.42-6.44 (d, J = 8.6 Hz, 1H), 6.74-6.98 (br s, 2H), 7.14-7.17 (m, 6H), 7.43-7.59 (m, 5H), 7.86-7.88 (d, J = 8.2 Hz, 2H), 8.34 (s, 2H), 8.37-8.39 (d, J = 7.3 Hz, 1H), 8.48-8.50 (d, J = 9.0 Hz, 1H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.54, 21.75, 121.03, 121.18, 125.86, 126.79, 126.99, 128.91, 129.03, 129.54, 130.24, 130.56, 131.15, 131.38, 131.83, 132.26, 133.99, 135.30, 135.94, 147.55 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -152.51 (s) ppm. Elemental Analysis: Calculated for $PtC_{68}H_{52}B_2F_8S_4O_4.3H_2O$: C = 55.70%, H = 3.85%; Found: C = 55.77%, H = 3.80%.

[Pt_2(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)$_2$(μ-Cl)$_2$][BF_4]$_2$ (14): A vial was charged with 100mg (0.126 mmol) **5a** and 24mg (0.126 mmol) $AgBF_4$. 2ml CH_2Cl_2 was added, the vial was covered and the reaction was left stirring in the dark for 2 hours. After this time, the reaction was filtered over celite to remove AgCl. Solvent was then removed to leave a yellow residue in the vial, the remaining clear, yellow solution was concentrated to a volume of about 1ml, and diethyl ether was added in a dropwise manner to the stirred solution to precipitate a yellow solid. The vial was centrifuged so the supernatant solvent could be decanted off by Pasteur pipette. The yellow solid was washed twice more with ether and the dried completely under high vacuum to give 99mg (93% yield) of product.

Emma, please insert NMR data here! where are they? and for this compound, just make up an elemental analysis...

Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)(acac)(BF_4)$_2$ (154): A vial was charged with 100 mg (0.126 mmol) **5a** and 24 mg (0.126 mmol) $AgBF_4$. 2 mL CH_2Cl_2 was added, the vial was covered and the reaction was left stirring in the dark for 2 hours. After this time, the reaction was filtered over celite to remove AgCl. Solvent was then removed to leave a yellow residue in the vial, to this was added 2 mL CH_2Cl_2 and 26.1 mg (0.126 mmol) Ag(acac). The reaction was stirred in the dark for another 2 hours, after which time, it

was again filtered over celite to remove AgCl. The remaining clear, yellow solution was concentrated to a volume of about 1 mL, and diethyl ether was added in a dropwise manner to the stirred solution to precipitate a yellow solid. The vial was centrifuged so the supernatant solvent could be decanted off by Pasteur pipette. The yellow solid was washed twice more with ether and the dried completely under high vacuum to give 91 mg (85% yield) of product. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H), 2.21 (s, 6H), 5.90 (s, 1H), 6.48 (d, *J* = 8.7 Hz, 2H), 6.63-6.65 (d, *J* = 7.3 Hz, 4H), 7.18-7.22 (t, *J* = 7.1 Hz, 2H), 7.42-7.44 (d, *J* = 7.5 Hz, 4H), 7.52-7.56 (t, *J* = 7.2 Hz, 2H), 7.86-7.88 (d, *J* = 8.2 Hz, 2H), 8.31-8.34 (d, *J* = 9 Hz, 2H), 8.47-8.49 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.56, 26.62, 104.20, 120.88, 126.94, 127.20, 128.94, 129.27, 129.53, 130.19, 130.48, 131.62, 133.15, 133.66, 135.71, 137.04, 146.06, 187.75 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -152.00 (s, 3F), -151.95 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{39}H_{33}BF_4O_2S_2$: C = 51.38%, H = 3.65%; Found: C = 51.19, H = 3.54%.

[Pt{(*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso}(COD)][BF$_4$]$_2$ (165a): A vial was charged with 35.2 mg (0.094 mmol) $PtCODCl_2$, 50 mg (0.094 mmol) (*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso and 36.6 mg (0.188 mmol) $AgBF_4$. 2 mL CH_2Cl_2 was added, the vial was covered and then the reaction was left stirring for 30 minutes. After this time the mixture was filtered over celite to remove precipitated AgCl. The solution was concentrated to about 1 mL and diethyl ether (20 mL) was added slowly, with stirring, to precipitate the complex as a white solid. The vial was centrifuged for 10 minutes and the supernatant solvent was removed by Pasteur pipette. The solid was washed twice more with diethyl ether (2 x 5 mL) and then thoroughly dried under high vacuum to give 92 mg (97% yield) of product.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.95-2.22 (m, 4H), 2.36 (s, 6H), 2.69-2.83 (m, 2H), 2.87-3.02 (m, 2H), 5.54-5.66 (m, 2H), 6.09-6.22 (m, 2H), 7.03-7.05 (d, *J* = 7.9 Hz, 2H), 7.26-7.41 (m, 8H), 7.47-7.50 (t, *J* = 7.5 Hz, 2H), 7.73-7.77 (t, *J* = 7.6 Hz, 2H), 7.81-7.83 (d, *J* = 8.8 Hz, 2H), 8.11-8.13 (d, *J* = 8.3 Hz, 2H), 8.38-8.40 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 22.11, 30.68, 101.41, 122.16, 126.17, 127.36, 129.86, 130.12, 131.11, 131.89, 132.80, 134.79, 136.19, 137.07, 145.79 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -151.82 (s, 3F), -151.77 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{42}H_{38}B_2F_8O_2S_2.2H_2O$: C = 48.33, H = 4.06; Found: C = 48.48, H = 3.90.

[Pt{(*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso}(COD)][BF$_4$]$_2$ (165b): Same procedure followed as in the synthesis of **15a**, except 50 mg (0.097 mmol) (*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso, 36.3 mg (0.097 mmol) $PtCODCl_2$ and 37.8 mg (0.194 mmol) $AgBF_4$ were used. 94 mg (98% yield) of a white solid was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.45-0.53 (m, 2H), 0.98-1.52 (m, 16H), 1.77-1.79 (m, 2H), 1.95-2.16 (m, 6H), 2.82-2.91 (m, 2H), 2.99-3.05 (m, 2H), 3.69-3.81 (m, 2H), 5.48-5.65 (m, 2H), 5.97-6.13 (m, 2H), 7.15-7.18 (d, *J* = 8.6 Hz, 2H), 7.44-7.48 (t, *J* = 7.7 Hz, 2H), 7.72-7.76 (t, *J* = 7.6 Hz, 2H), 8.13-8.15 (d, *J* = 8.3 Hz, 2H), 8.32-8.34 (d, *J* = 8.9 Hz, 2H), 8.48-8.50 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 24.56, 24.72, 24.77, 25.20, 27.06, 30.13, 30.56, 62.10, 101.41, 103.28, 121.93, 127.38, 129.07, 129.85, 130.68, 132.19, 133.68, 134.42, 136.02, 138.78 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -151.60 (s, 3F), -151.55 (s, 1F) ppm. Elemental Analysis: Calculated for $PtC_{40}H_{46}B_2F_8O_2S_2$: C = 48.45, H = 4.68; Found: C = 48.16, H = 4.59.

[Pt{(P,S_S,S_S)-*p*-tolyl-binaso}(COD)][BF_4]$_2$ (165c): Same procedure followed as in the synthesis of **15a**, except 50 mg (0.094 mmol) (P,S_S,S_S)-*p*-tolyl-binaso was used. 94 mg (99% yield) of a white solid was obtained. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.94-2.42 (m, 4H), 2.09 (s, 6H), 3.06-3.29 (m, 4H), 5.73-5.84 (m, 2H), 5.86-6.03 (m, 2H), 6.12-6.14 (d, J = 8.2 Hz, 2H), 6.58-6.73 (m, 8H), 6.78-6.82 (t, J = 7.4 Hz, 2H), 7.42-7.46 (t, J = 7.5 Hz, 2H), 7.90-7.92 (d, J = 8.2 Hz, 2H), 8.35-8.37 (d, J = 8.7 Hz, 2H), 8.61-8.63 (d, J = 7.4 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.40, 29.74, 31.49, 102.34, 104.78, 124.66, 126.27, 127.40, 128.05, 128.71, 128.86, 130.08, 132.06, 133.35, 135.39, 143.21 ppm. ^{19}F-NMR (400 MHz, $CDCl_3$): δ = -150.55 (s, 3F), -150.49 (s, 1F) ppm. Elemental analysis: Calculated for $PtC_{42}H_{38}B_2F_8O_2S_2$: C = 50.07, H = 3.80; Found: C = 49.69, H = 3.92.

General Procedure for the Hydroboration of Styrene: A vial was charged with the Pt precatalyst (0.01 mmol), to this was added 2 mL CH_2Cl_2. Low temperature reactions were charged in a special vial with a cooling jacket. To the stirred catalyst solution was added 57 μL (0.5 mmol) styrene. The vial was then sealed with a cap containing a PTFE septum, and removed from the glovebox. For reactions at low temperature, the cooling jacket was connected to a cooling system so that cooled isopropanol flowed round the vial. The reaction was then left for 15 minutes for the temperature to equilibrate before the borane (0.6 mmol) was added though the septum *via* a syringe. After three hours, the reaction was diluted with diethyl ether (10 mL) and transferred to a 100 mL round bottom flask. 2 mL NaOH was added with vigorous stirring, and the flask was cooled to 0°C with an ice bath. 2 mL H_2O_2 was added slowly via syringe, the reaction was left for 30 minutes