Supporting information for: Synthesis, Structure and Catalytic Studies of Palladium and Platinum Bissulfoxide Complexes

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Experimental section

All reactions were carried out using standard Schlenk or glovebox (Mecaplex or Innovative Technology) techniques under nitrogen. NMR spectra were collected on an AV2 400 MHz Bruker spectrometer. Solvents were purchased in the best quality

available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). $Pt(PhCN)_2Cl_2$[S1], $[Pt(\mu\text{-}SMe_2)Me_2]_2$[S2], $PtCODCl_2$[S3] and the ligands[S4] were prepared according to literature procedures. $Pd(PhCN)_2Cl_2$, silver salts, boranes, diboranes, cyclohexenone and *p*-tolylsulfonamide were purchased from Aldrich or Strem and used as received. Styrene was purchased from Aldrich, distilled and stored in the refrigerator inside the glovebox. All measurements for crystal-strucutre determinations were made on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Elemental analyses were performed at the Institute of Organic Chemistry, University of Zurich or at the ETH, Zurich (hygroscopic compounds were corrected for water content).

$Pd(II)Cl_2$.(M,S_S,S_S)-*p*-tolyl-binaso (4): A vial was charged with 49 mg (0.188 mmol) $Pd(PhCN)_2Cl_2$ and 100 mg (0.188 mmol) (M,S_S,S_S)-*p*-tolyl-binaso. 5 mL CH_2Cl_2 was added and the mixture was left stirring for 1 hour. The red solution was then concentrated to roughly 1 mL volume, and diethyl ether (20 mL) was slowly added with vigorous stirring. A red solid precipitated out of solution. The vial was centrifuged for 10 minutes, and then the supernatant solvent was decanted off *via* Pasteur pipette. The remaining solid was washed twice more with diethyl ether, and then dried thoroughly under high vacuum, to obtain 111 mg (83% yield) of product. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.09 (s, 6H), 6.20-6.22 (d, J = 8.5 Hz, 2H), 6.61-6.69 (m, 8H), 6.81-6.85 (t, J = 7.4 Hz, 2H),

7.40-7.43 (t, J = 7.6 Hz, 2H), 7.92-7.94 (d, J = 8.2 Hz, 2H), 8.30-8.32 (d, J = 8.8 Hz, 2H), 8.43-8.46 (d, J = 8.7 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.46, 120.21, 126.23, 126.46, 127.65, 127.81, 128.85, 129.71, 129.84, 131.07, 131.55, 132.74, 132.83, 133.35, 134.81 ppm. Elemental analysis: Calculated for $PdC_{34}H_{26}Cl_2O_2S_2$: C = 57.67%, H = 3.70%; Found: C = 57.45%, H = 3.63%.

Pt(II)(*M*,*S*$_S$,*S*$_S$)*p*-tolyl-binasoCl$_2$ (5a): A 100 mL Schlenk tube was charged with 533.8 mg (1.13 mmol) $Pt(PhCN)_2Cl_2$ and 600 mg (1.13 mmol) (*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso. 30 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 795 mg (88% yield) of product. Yellow needle-like crystals, suitable for an X-ray crystal structure analysis, could be grown by diffusion of THF into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.96 (s, 6H), 6.48-6.51 (d, J = 8.6 Hz, 2H), 6.56-6.58 (d, J = 7.8 Hz, 4H), 7.11-7.15 (t, J = 7.4 Hz, 2H), 7.47-7.51 (m, 6H), 7.77-7.79 (d, J = 7.9 Hz, 2H), 8.16-8.18 (d, J = 9.0 Hz, 2H), 8.52-8.54 (d, J = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.54, 122.00, 127.68, 127.81, 128.54, 128.81, 129.04, 129.09, 129.56, 129.62, 129.75, 130.27, 132.06, 132.33, 135.70, 139.84, 145.03 ppm. Elemental analysis: Calculated for $PtC_{34}H_{26}Cl_2O_2S_2$: C = 51.26%, H = 3.29%; Found: C = 51.32%, H = 3.43%.

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

was filtered off over celite to leave a yellow solution. Solvent was removed to leave a volume of about 1 mL, and diethyl ether (20 mL) was added dropwise, with stirring, to precipitate a yellow solid. The vial was centrifuged for 5 minutes, so the supernatant solvent could be decanted off *via* Pasteur pipette. The remaining orange solid was washed twice more with diethyl ether (2 x 5 mL), and then dried thoroughly under high vacuum, to give 140 mg (86% yield) of the product. Orange crystals suitable for an X-ray crystal structure analysis could be grown by slow diffusion of diethyl ether into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.99 (s, 6H), 6.43-6.46 (d, *J* = 8.6 Hz, 2H), 6.64-6.66 (d, *J* = 8.3 Hz, 2H), 7.13-7.17 (t, *J* = 7.4 Hz, 2H), 7.53-7.57 (t, *J* = 7.5 Hz, 2H), 7.75-7.77 (d, *J* = 7.0 Hz, 2H), 7.80-7.82 (d, *J* = 8.3 Hz, 2H), 8.22-8.24 (d, *J* = 9.0 Hz, 2H), 8.50-8.52 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.50, 122.03, 127.37, 127.72, 128.78, 129.14, 129.71, 130.13, 130.63, 131.95, 132.75, 134.28, 135.94, 138.03, 145.69 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -74.14 (s) ppm. Elemental Analysis: Calculated for $PdC_{38}H_{26}F_6O_6S_2.0.5H_2O$: C = 52.33%, H = 3.12%; Found: C = 52.22%, H = 3.51%.

Pd(II)((*P*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso)$_2$(BF$_4$)$_2$ (7): A vial was charged with 49 mg (0.188 mmol) $Pd(PhCN)_2Cl_2$, 200 mg (0.376 mmol) (*P*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso and 73 mg (0.376 mmol) $AgBF_4$. 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 was filtered off over celite to leave a deep red solution. Solvent was removed to leave a volume of about 1 mL, and diethyl ether (20 mL) was added dropwise, with stirring, to precipitate a red solid. The vial was centrifuged for 5 minutes, so the supernatant solvent could be

decanted off *via* Pasteur pipette. The remaining red solid was washed twice more with diethyl ether (2 x 5 mL), and then dried thoroughly under high vacuum, to give 214 mg (85% yield) of the product. Red crystals suitable for an X-ray crystal structure analysis could be grown by slow diffusion of a 1:1 pentane/diethyl ether mixture into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.99 (s, 6H), 2.51 (s, 6H), 5.84-5.86 (d, *J* = 8.7 Hz, 2H), 6.59-6.71 (m, 12H), 6.82-6-86 (t, *J* = 7.8 Hz, 2H), 7.22-7.43 (m, 12H), 7.72-7.78 (m, 4H), 7.88-7.91 (d, *J* = 9.2 Hz, 2H), 8.37-8.39 (d, *J* = 8.4 Hz, 2H), 8.70-8.72 (d, *J* = 8.4 Hz, 2H), 8.94-8.96 (d, *J* = 8.5 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 20.74, 21.95, 120.79, 123.44, 126.58, 126.82, 127.20, 127.41, 127.56, 128.26, 128.85, 128.93, 129.16, 129.45, 129.99, 130.29, 131.68, 132.59, 132.69, 133.76, 133.79, 134.9, 135.46, 136.41, 138.52, 139.50, 143.14, 147.35 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -152.11 (s, 4F), -152.06 (s, 1F) ppm. Elemental Analysis: Calculated for $PdC_{68}H_{52}B_2F_8O_4S_4.3H_2O$: C = 58.53%, H = 4.18%; Found: C = 58.57%, H = 3.95%.

Pt(II)(*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso(OC(O)CF$_3$)$_2$ (8): A vial was charged with 100 mg (0.126 mmol) of **5** and 56 mg (0.252 mmol) $Ag(OC(O)CF_3)$. 5 mL CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for four hours, after this time it was filtered over celite to remove the precipitated AgCl. The resulting colourless solution was concentrated to a volume of about 1 mL, and diethyl ether (20 mL) was added dropwise to the stirred solution to precipitate a white solid. The vial was centrifuged for five minutes, so that the supernatant solvent could be decanted off *via* Pasteur pipette. The solid was washed twice with diethyl ether (2 x 5 mL) and then dried

thoroughly under high vacuum to give 97 mg (81% yield) of the complex. Colorless crystals suitable for an X-ray crystal structure analysis could be grown by diffusion of diethyl ether into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.96 (s, 6H), 6.44-6.46 (d, *J* = 8.6 Hz, 2H), 6.59-6.61 (d, *J* = 8.2 Hz, 4H), 7.12-7.16 (t, *J* = 7.7 Hz, 2H), 7.50-7.53 (t, *J* = 7.6, 2H), 7.65 (br s, 4H), 7.79-7.81 (d, *J* = 8.3 Hz, 2H), 8.21-8.23 (d, *J* = 9.0 Hz, 2H), 8.51-8.53 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 21.40, 121.52, 127.55, 128.54, 129.06, 129.46, 129.91, 130.15, 131.75, 132.47, 134.70, 135.80, 137.64, 145.33, 145.34 ppm. ^{19}F-NMR (400 MHz, CD_2Cl_2): δ = -74.46 (s) ppm. Elemental Analysis: Calculated for $PtC_{38}H_{26}F_6O_6S_2$: C = 47.95%, H = 2.75%; Found: C = 47.92%, H = 3.01%.

Pt(II)(*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso(OC(O)CF$_3$)Cl (9): A vial was charged with 50 mg (0.063 mmol) **5** and 14 mg (0.063 mmol) $AgOC(O)CF_3$. 3 mL CH_2Cl_2 was added and the vial was covered. The reaction was left stirring in the dark for 4 hours and was then filtered over celite. The clear, colorless solution obtained was concentrated to a volume of about 1 mL and 20 mL diethyl ether was added dropwise to the stirred solution so that a white precipitate appeared. The vial was centrifuged for 10 minutes, so the supernatant solvent could be removed by Pasteur pipette. The white solid was then dried thoroughly under high vacuum to give 45 mg (82% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3H), 1.94 (s, 3H), 6.38-6.54 (m, 6H), 7.04-7.17 (m, 2H), 7.43-7.79 (m, 8H), 8.06-8.22 (m, 2H), 8.53-8.56 (m, 2H) ppm. ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 21.33, 21.35, 21.39, 21.41, 66.07, 68.20, 121.50, 121.65, 121.73, 121.82, 127.18, 127.23, 127.28, 127.30, 127.52, 127.74, 127.86, 127.97, 128.00, 128.10, 128.21, 128.62, 128.65, 128.72, 128.77,

129.10, 129.13, 129.40, 129.59, 129.67, 129.77, 129.82, 130.06, 131.44, 131.47, 131.63, 131.70, 131.78, 131.85, 132.01, 132.10, 134.29, 134.63, 135.18, 135.24, 135.31, 135.42, 136.14, 137.81, 138.38, 139.10, 144.31, 144.65 ppm. Elemental Analysis: Calculated for $PtC_{36}H_{26}O_4F_3S_2Cl$: C = 49.46%, H = 3.00%; Found: C = 49.16%, H = 3.14%.

Pt(II)(*M*,*S*$_S$,*S*$_S$)*p*-tolyl-binasoI$_2$ (10): A vial was charged with 100 mg (0.126 mmol) **5** and 38 mg (0.252 mmol) NaI. 3 mL Acetone was added to the stirred mixture and the solution instantly became red. The reaction was left for 30 minutes, after which time an orange-red precipitate had appeared. The vial was centrifuged for 5 minutes and the supernatant solvent was decanted off, to leave the solid. The solid was redissolved in CH_2Cl_2 (2 mL) and filtered over celite, to give a clear red solution. Diethyl ether (20 mL) was added dropwise to the solution to precipitate the complex. The vial was centrifuged and the supernatant solvent was decanted off *via* Pasteur pipette. The deep orange solid was washed twice more with diethyl ether (2 x 5 mL) and dried thoroughly under high vacuum to give 91 mg (74% yield) of the product. Orange crystals suitable for an X-ray crystal structure analysis were grown by slow diffusion of hexane into a concentrated solution of the complex in CH_2Cl_2. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.95 (s, 6H), 6.46-6.49 (d, *J* = 9.0 Hz, 2H), 6.53-6.55 (d, *J* = 7.3 Hz, 4H), 7.08-7.12 (t, *J* = 7.7 Hz, 2H), 7.38 (br s, 4H), 7.47-7.51 (t, *J* = 7.1 Hz, 2H), 7.75-7.79 (d, *J* = 8.1 Hz, 2H), 8.12-8.16 (d, *J* = 9.1 Hz, 2H), 8.53-8.55 (d, *J* = 9 Hz, 2H) ppm. ^{13}C-NMR (400 MHz, CD_2Cl_2): δ = 120.16, 122.31, 126.24, 126.45, 127.62, 128.32, 129.00, 129.48, 129.77, 131.39, 131.99, 132.08, 135.57, 136.26, 140.44, 144.53 ppm. Elemental Analysis: Calculated for $PtC_{34}H_{26}I_2S_2O_2.H_2O$: C = 38.83%, H = 2.79%; Found: C = 38.35%, H = 2.74%.

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.

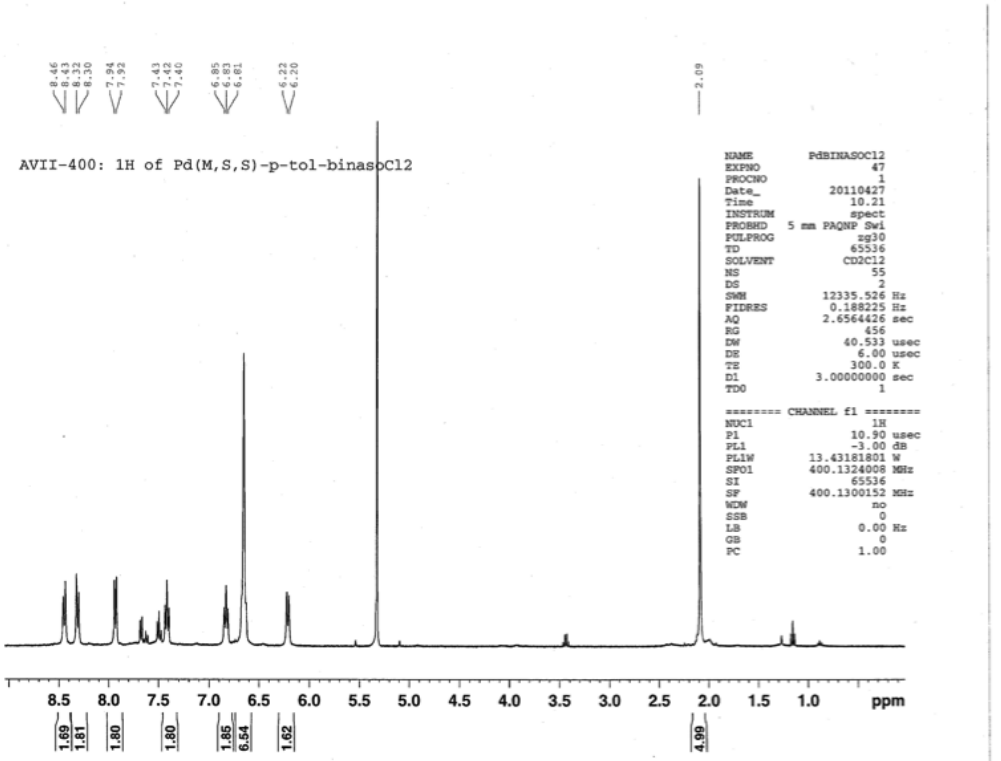
General Procedure for the Hydroboration of Styrene: A vial was charged with the Pt precatalyst (0.01 mmol), to this was added 2 mL CH_2Cl_2. Low temperature reactions were charged in a special vial with a cooling jacket. To the stirred catalyst solution was added 57 μL (0.5 mmol) styrene. The vial was 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

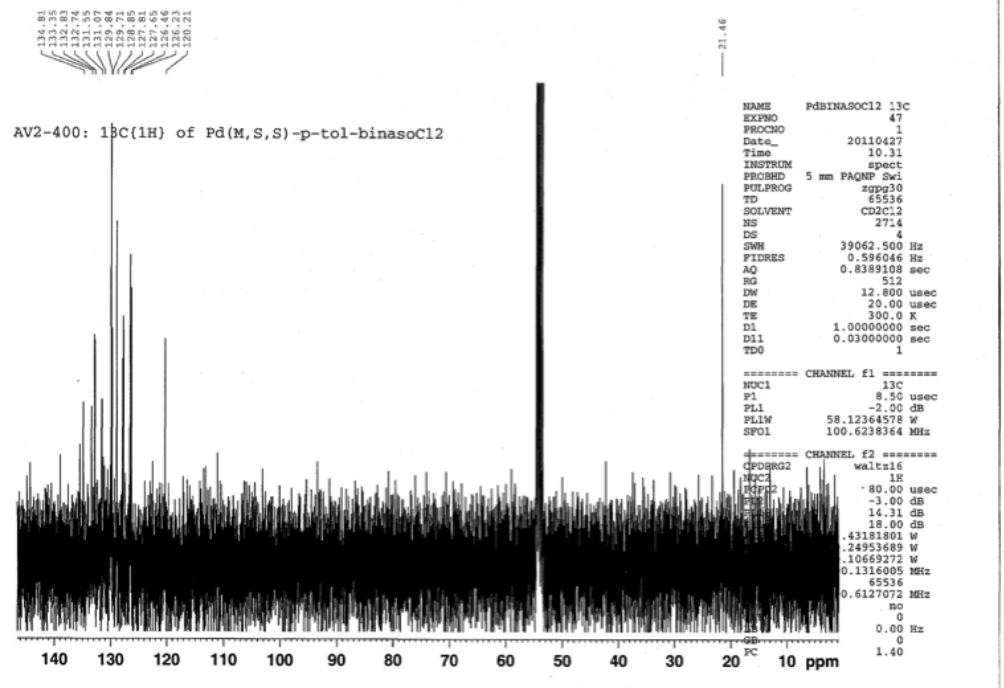
with the neck open. After this time, the reaction was allowed to warm to room temperature; the flask was sealed with a rubber septum with a needle inside, so the system was not completely closed. The reaction was left for 6 hours and then diluted with more diethyl ether (20 mL) and water (20 mL). The phases were separated and the aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by column chromatography using hexane/ethyl acetate 24:1 as the eluent. A white solid was obtained which could be analyzed by chiral GC (Lipodex E, 25m x 0.25 mm) to obtain the ratio of Markovnikov and anti-Markovnikov product, and also the enantiomeric excess of the Markovnikov product.

General Procedure for the Diboration of Styrene: A vial was charged with the Pt precursor (0.01 mmol) and 152 mg (0.6 mmol) $B_2(pin)_2$. 2 mL CH_2Cl_2 was added, and, immediately after, 57 μL (0.5 mmol) styrene was added. The reaction was left stirring at room temperature for 1 hour and then removed from the glovebox. The solution was diluted with 10 mL diethyl ether and quenched in the same way as the hydroboration reactions, except the quenching reaction was left overnight and then worked up. The crude product was purified by column chromatography using hexane/ethyl acetate 7:3 as the eluent. A white solid was obtained, which could be further analyzed by chiral HPLC using chiralcel OD-H column (hexane/^{i}PrOH, 95:5; 1ml/min) to determine its enantiomeric excess.

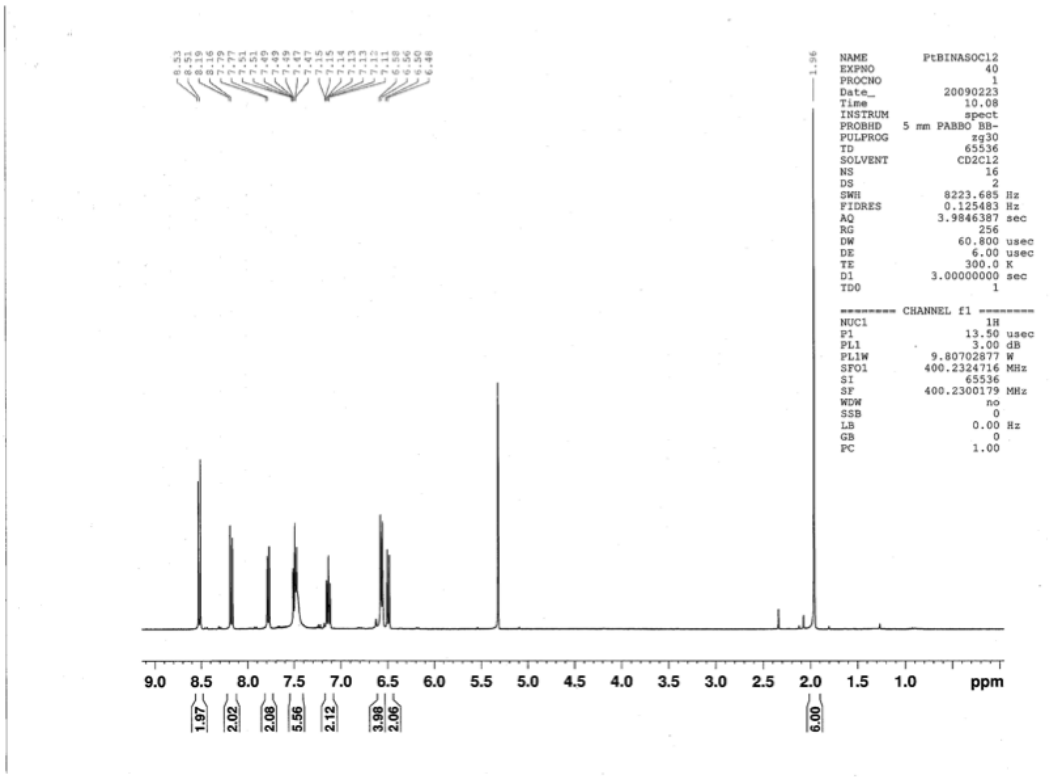
NMR spectra of the Compounds

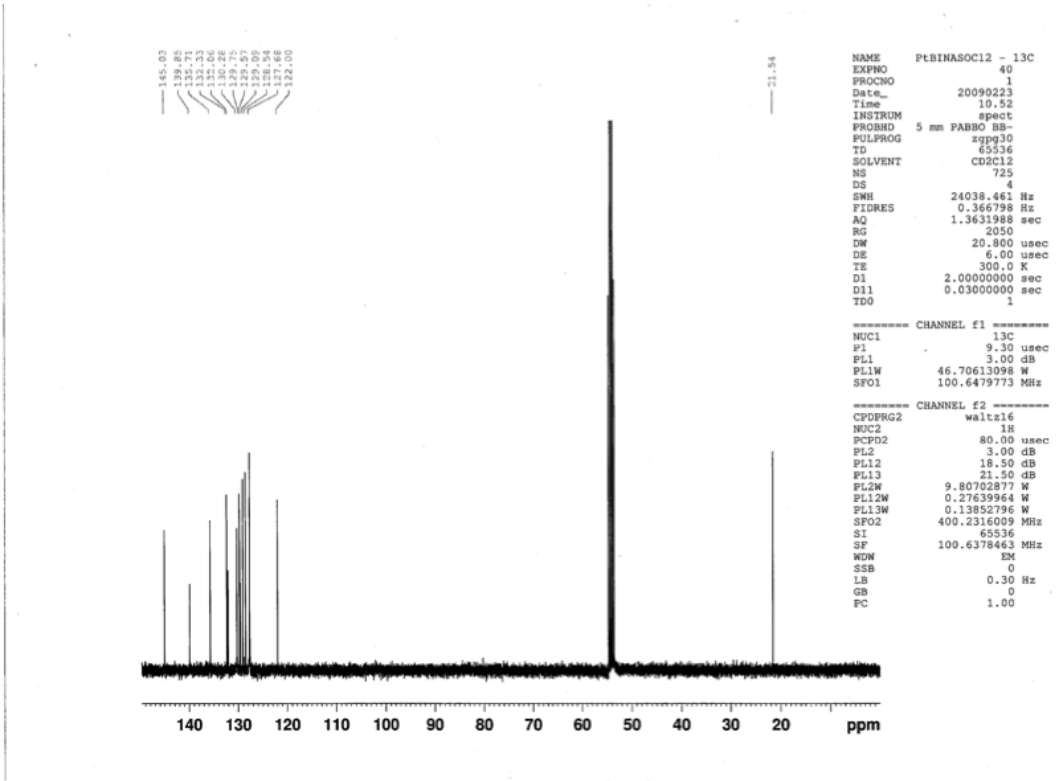
Pd(II)Cl_2.(M,S_S,S_S)-*p*-tolyl-binaso (4):



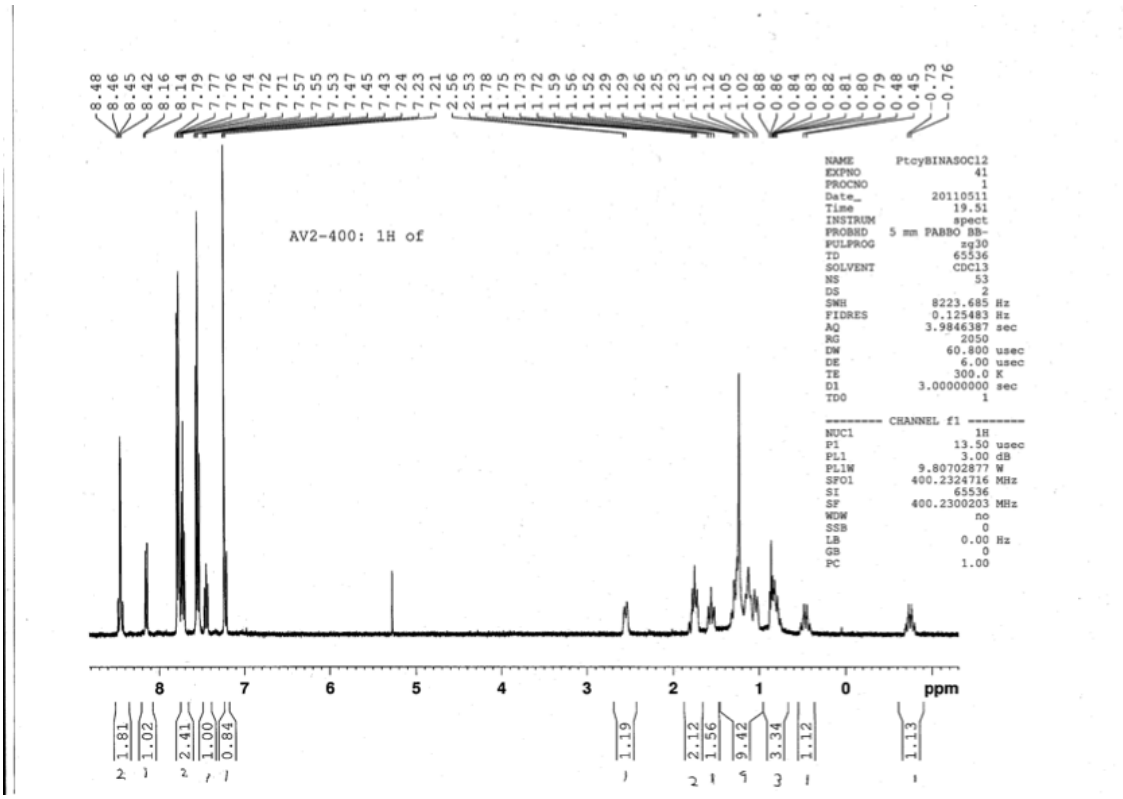


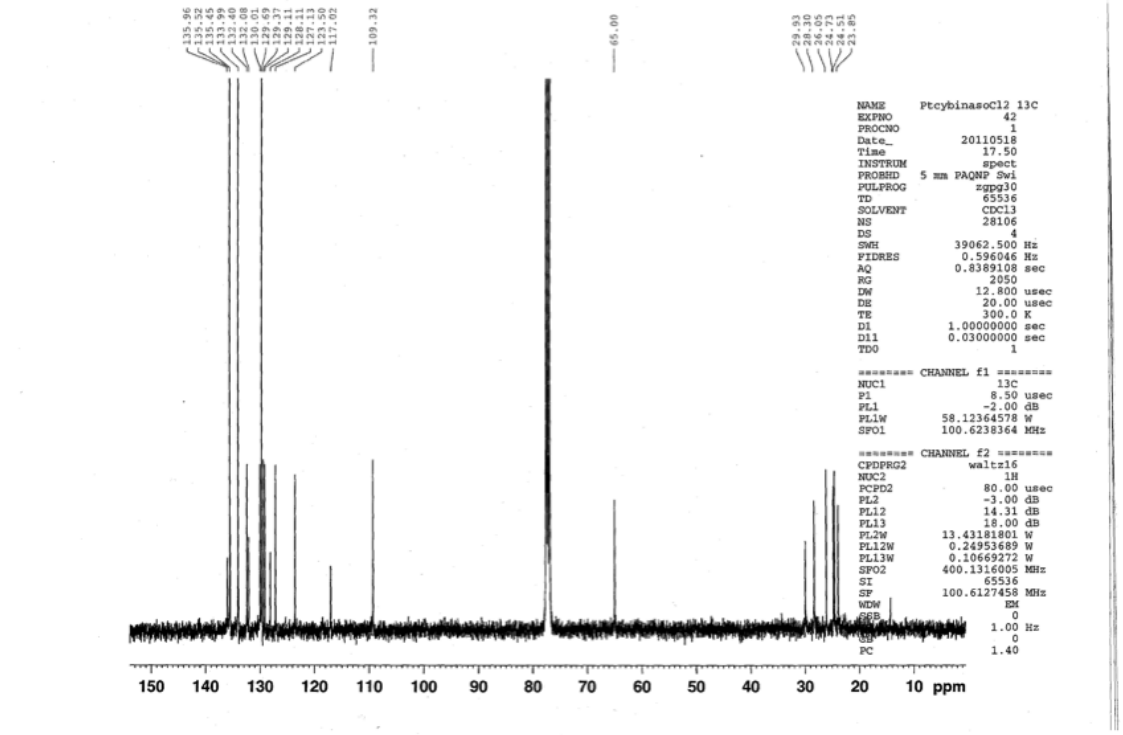
Pt(II)(M,S_S,S_S)*p*-tolyl-binasoCl$_2$ (5a):



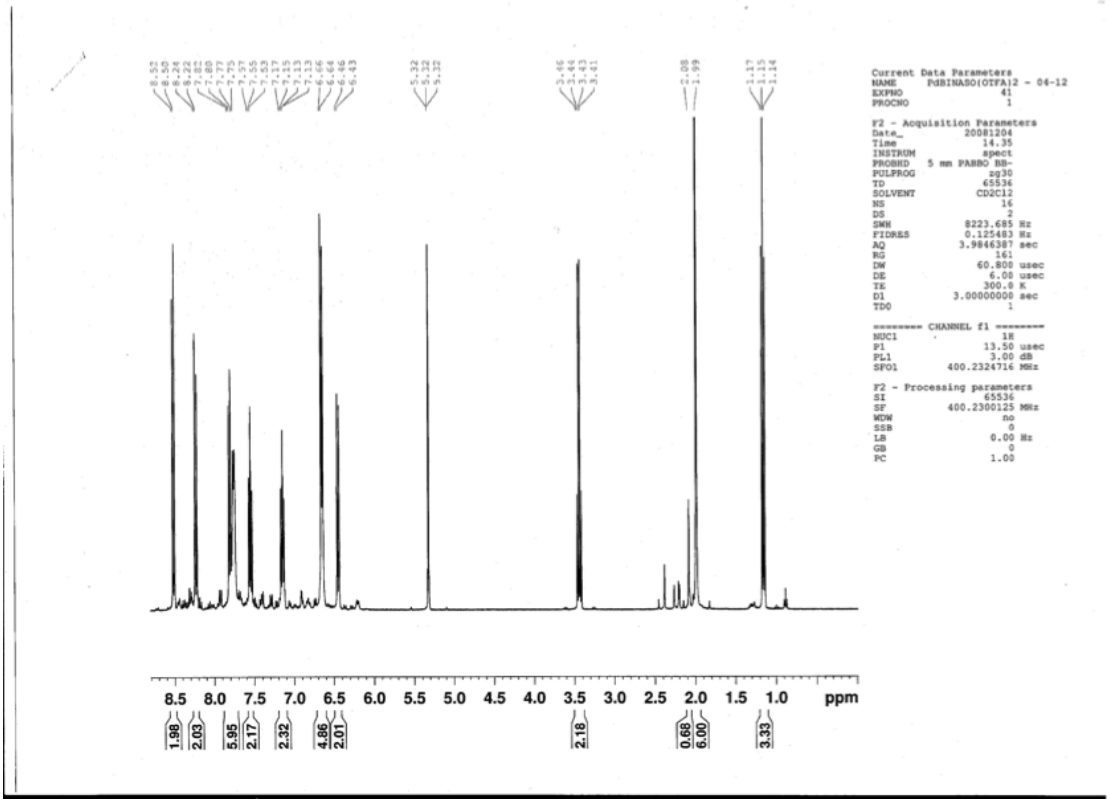


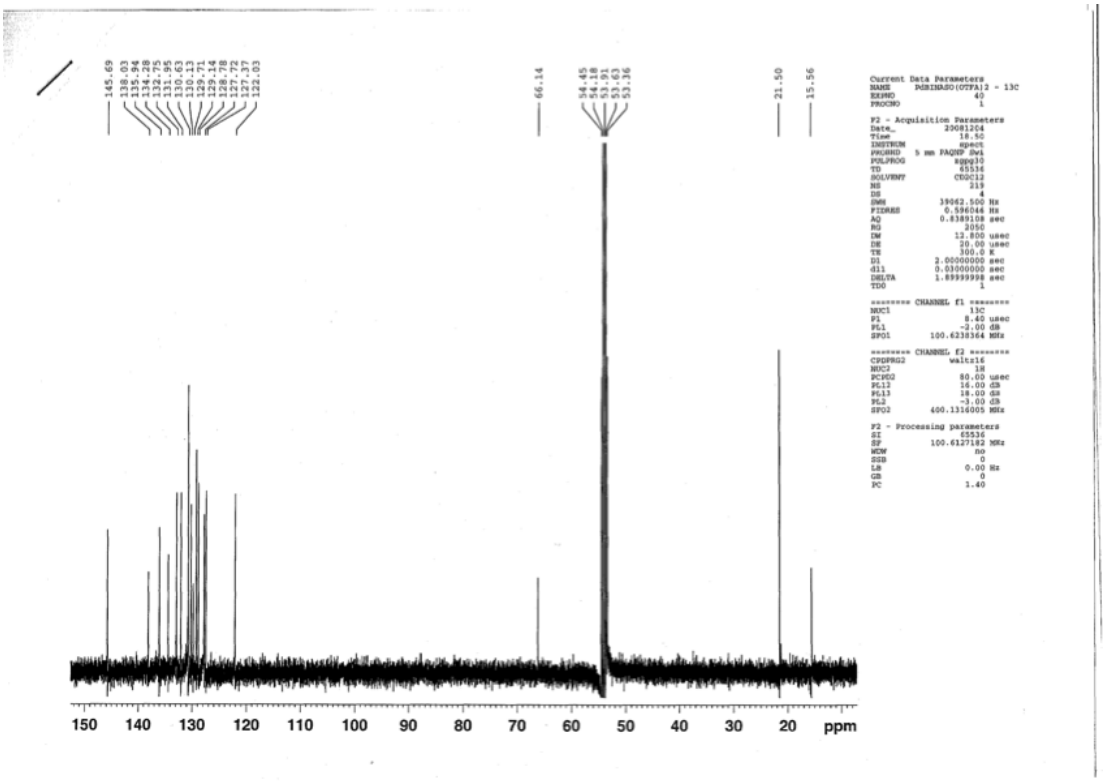
Pt(II)(M,S_S,S_S)-cyclohexyl-binasoCl$_2$ (5b):



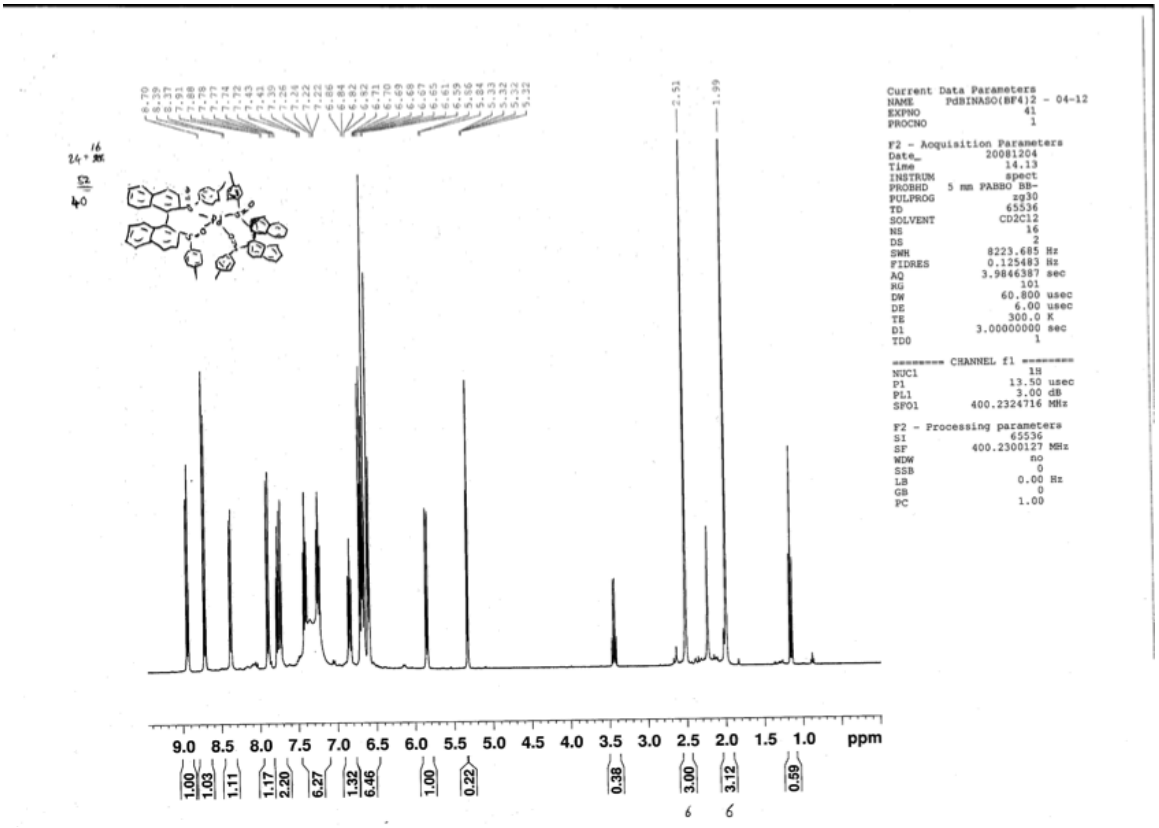


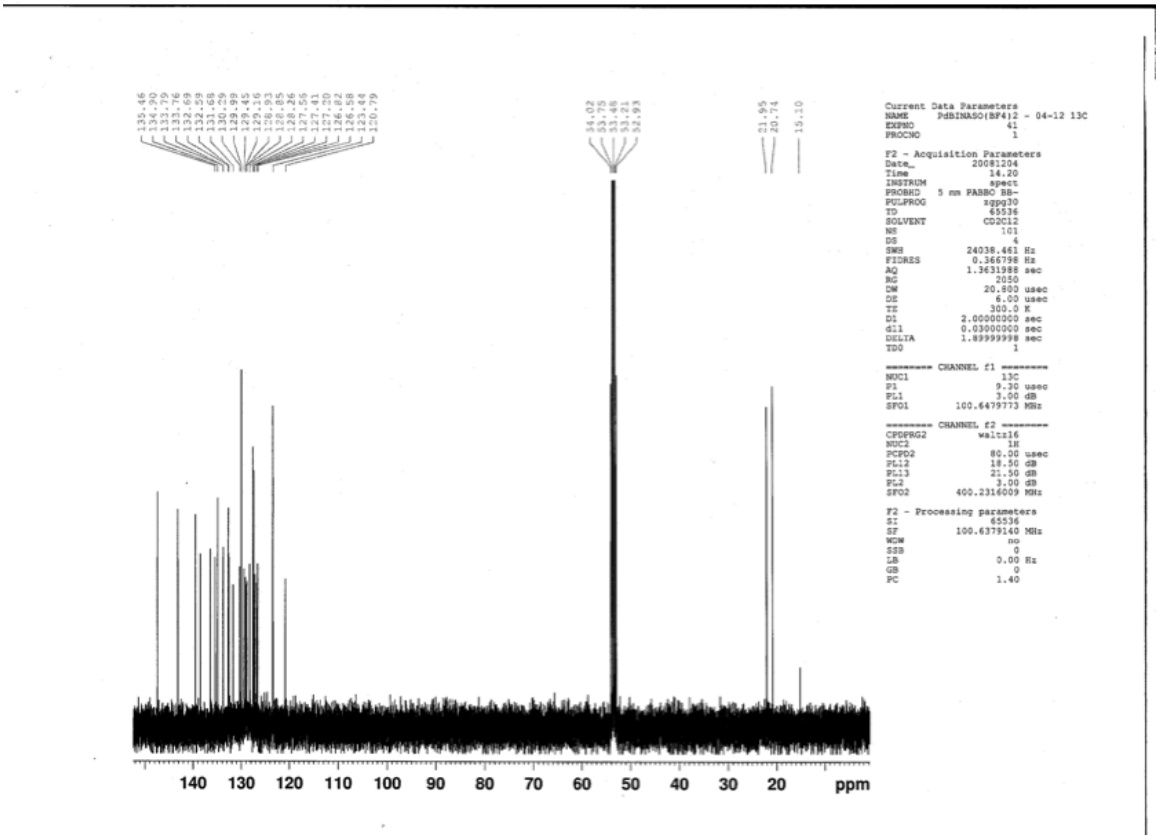
Pd(II)(M,S_S,S_S)-*p*-tolyl-binaso(OC(O)CF_3)$_2$ (6):



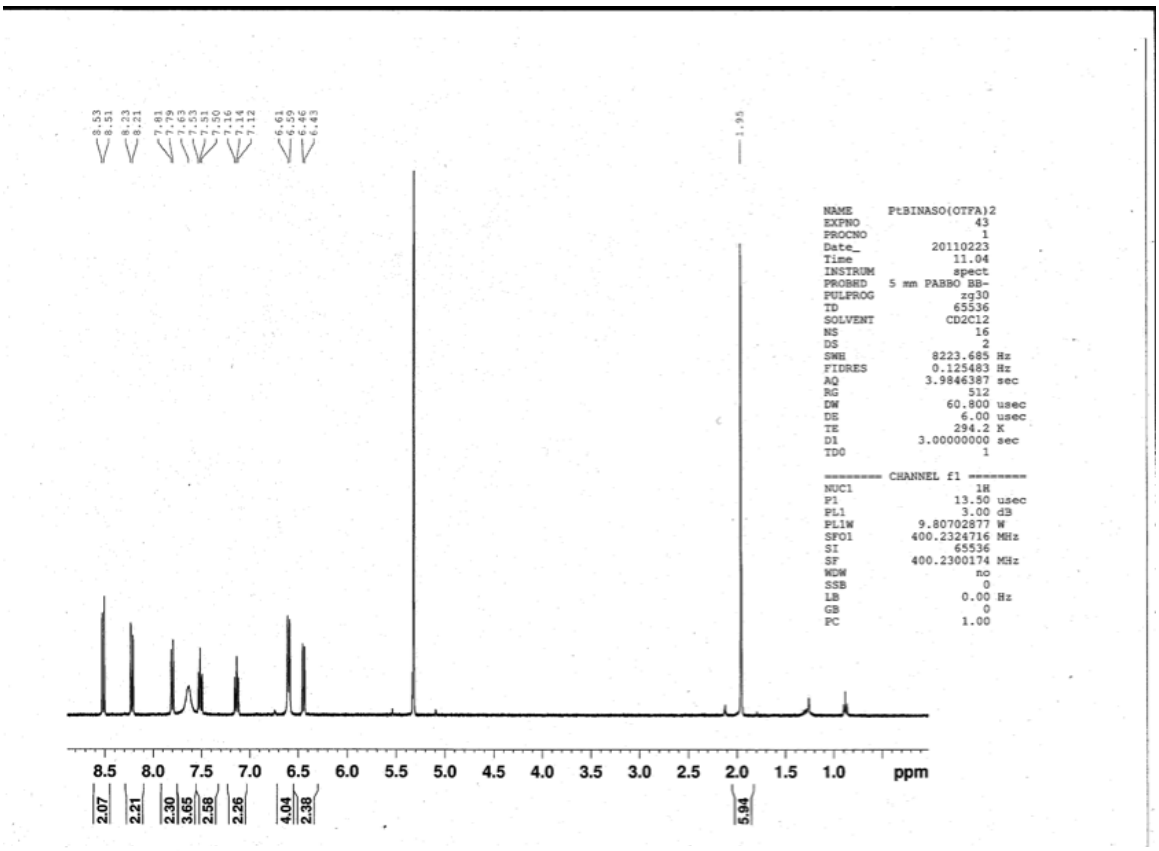


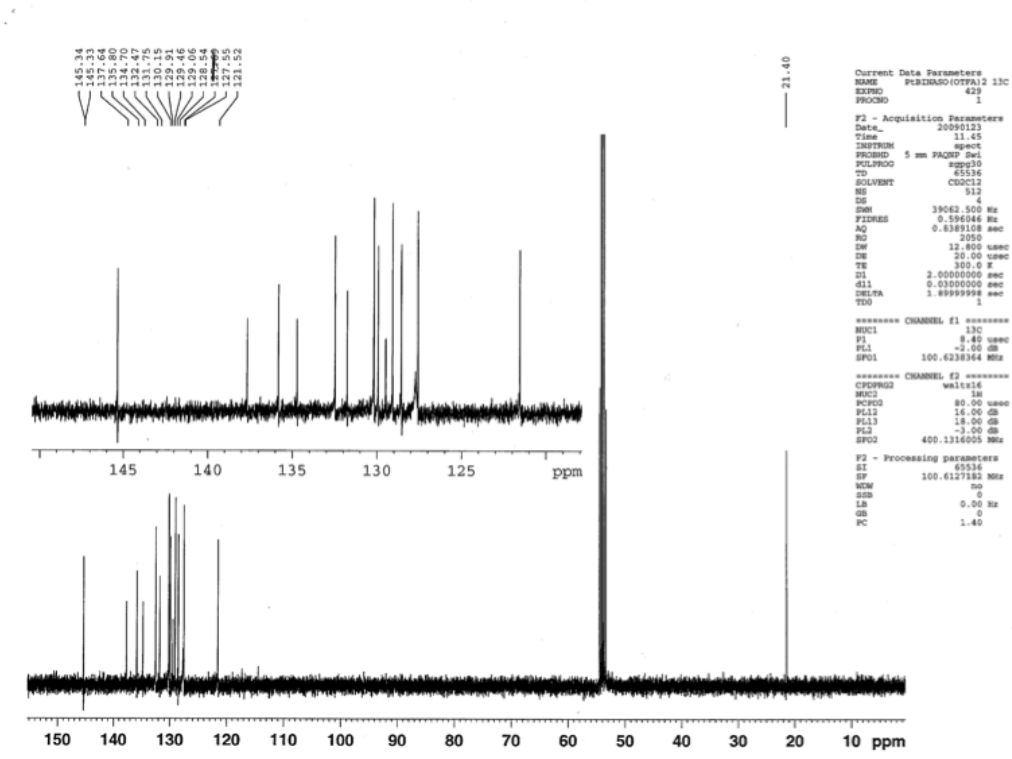
Pd(II)((*P*,S_S,S_S)-*p*-tolyl-binaso)$_2$(BF_4)$_2$ (7):



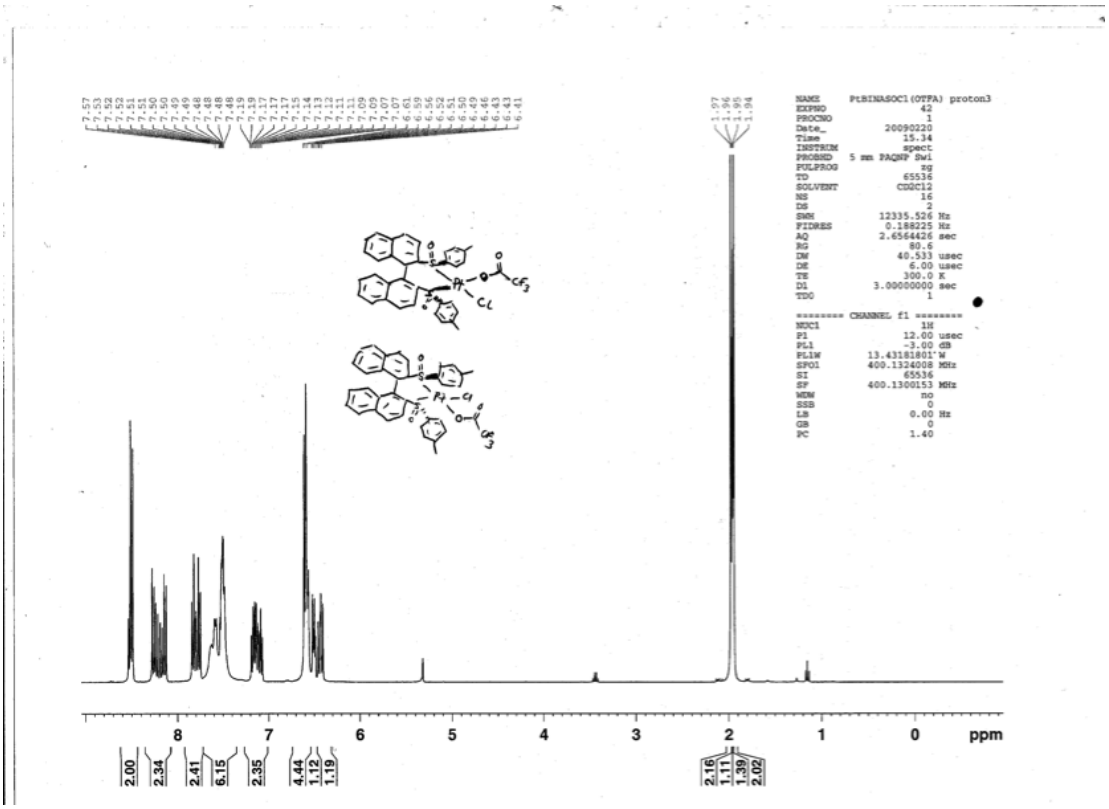


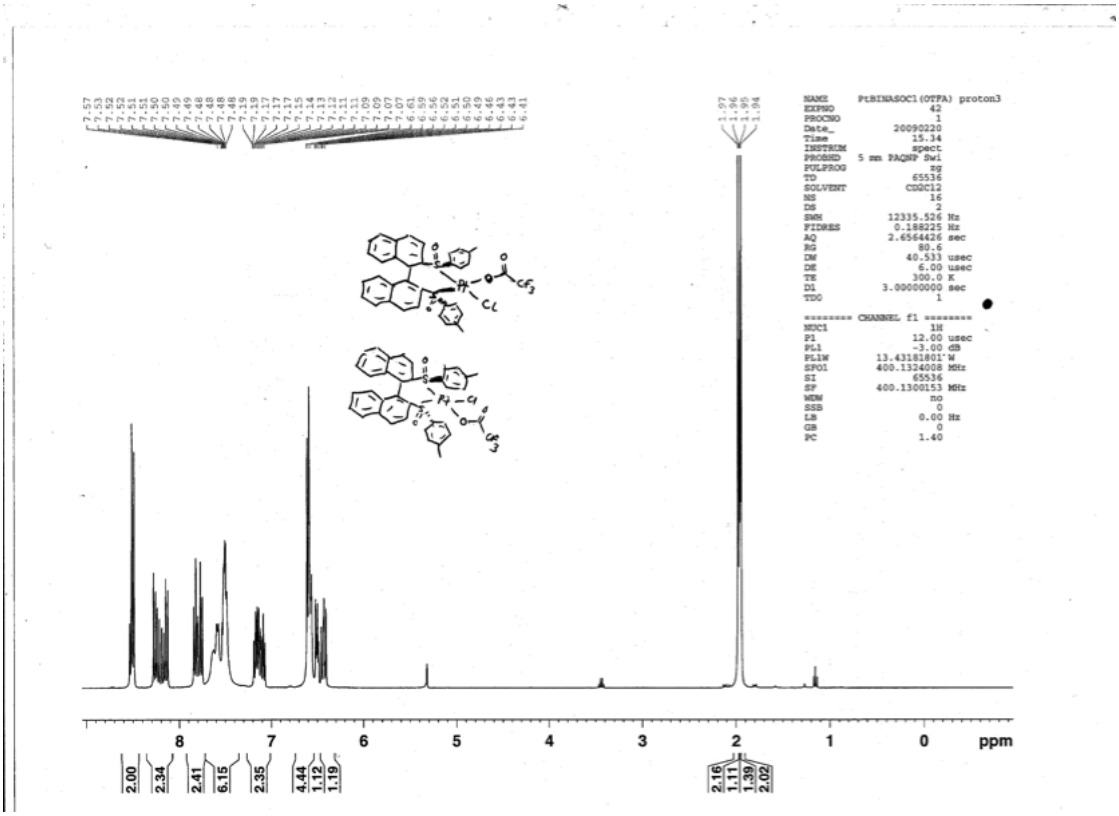
Pt(II)(M,S_S,S_S)-*p*-tolyl-binaso(OC(O)CF_3)$_2$ (8):



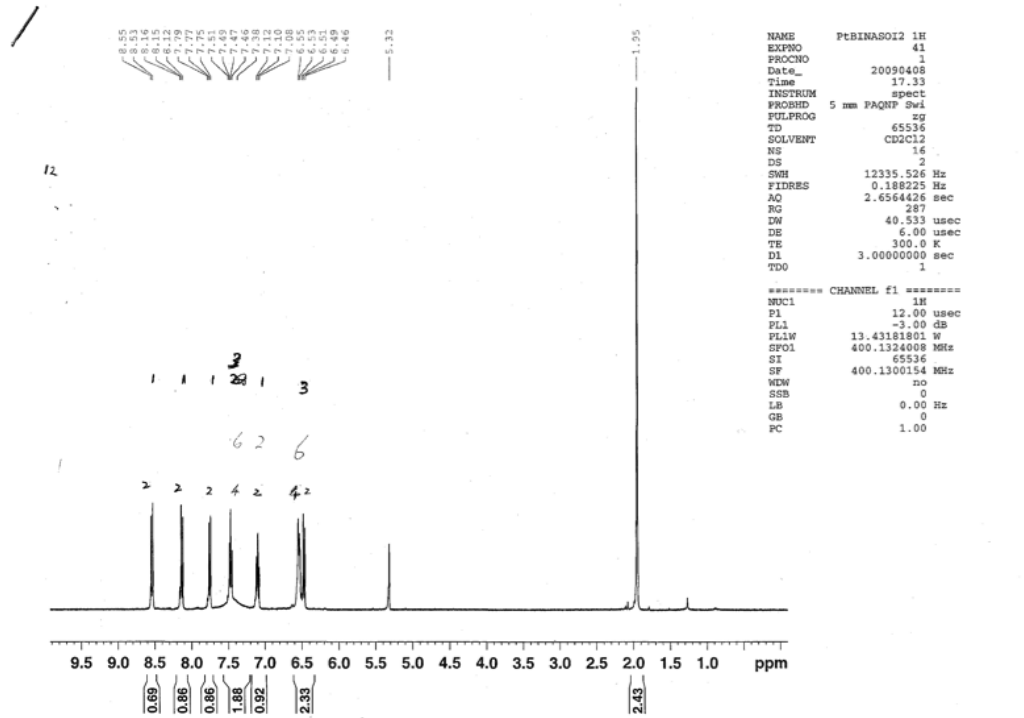


Pt(II)(M,S_S,S_S)-*p*-tolyl-binaso(OC(O)CF_3)Cl (9):





Pt(II)(M,S_S,S_S)*p*-tolyl-binasoI$_2$ (10):

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PROCNO                 1
Date_           20090408
Time               17.33
INSTRUM            spect
PROBHD   5 mm PAQNP Swi
PULPROG               zg
TD                 65536
SOLVENT           CD2Cl2
NS                    16
DS                     2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ             2.6564426 sec
RG                   287
DW                40.533 usec
DE                 6.00 usec
TE                300.0 K
D1           3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W          13.43181801 W
SFO1          400.1324008 MHz
SI                 65536
SF            400.1300154 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
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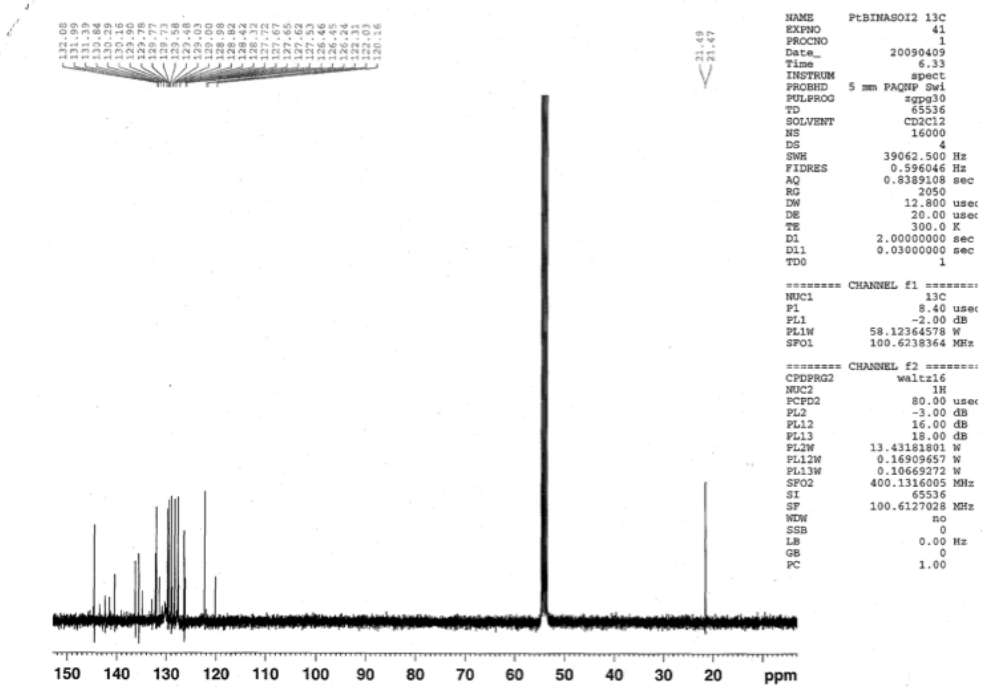


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PROCNO                 1
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Time               6.33
INSTRUM            spect
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PULPROG          zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                 16000
DS                     4
SWH           39062.500 Hz
FIDRES         0.596046 Hz
AQ             0.8389108 sec
RG                  2050
DW                12.800 usec
DE                 20.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.40 usec
PL1                -2.00 dB
PL1W          58.12364578 W
SFO1          100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               16.00 dB
PL13               18.00 dB
PL2W          13.43181801 W
PL12W          0.16909657 W
PL13W          0.10669272 W
SFO2          400.1316005 MHz
SI                 65536
SF            100.6127028 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
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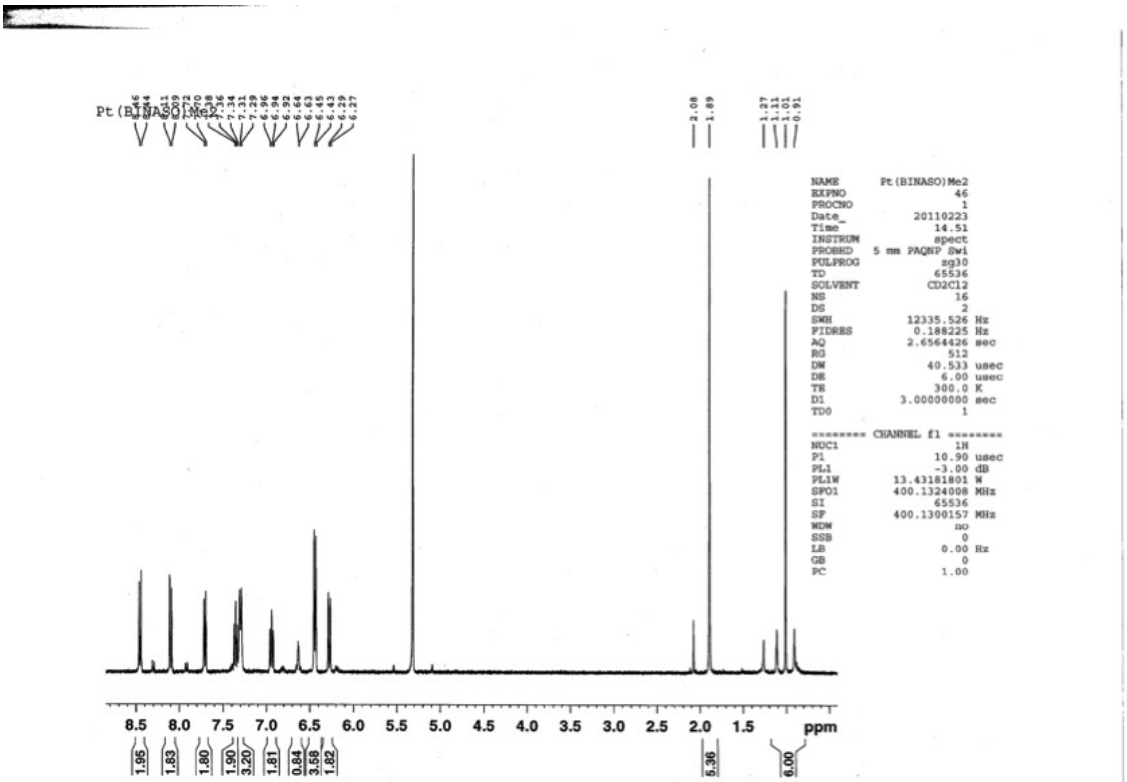
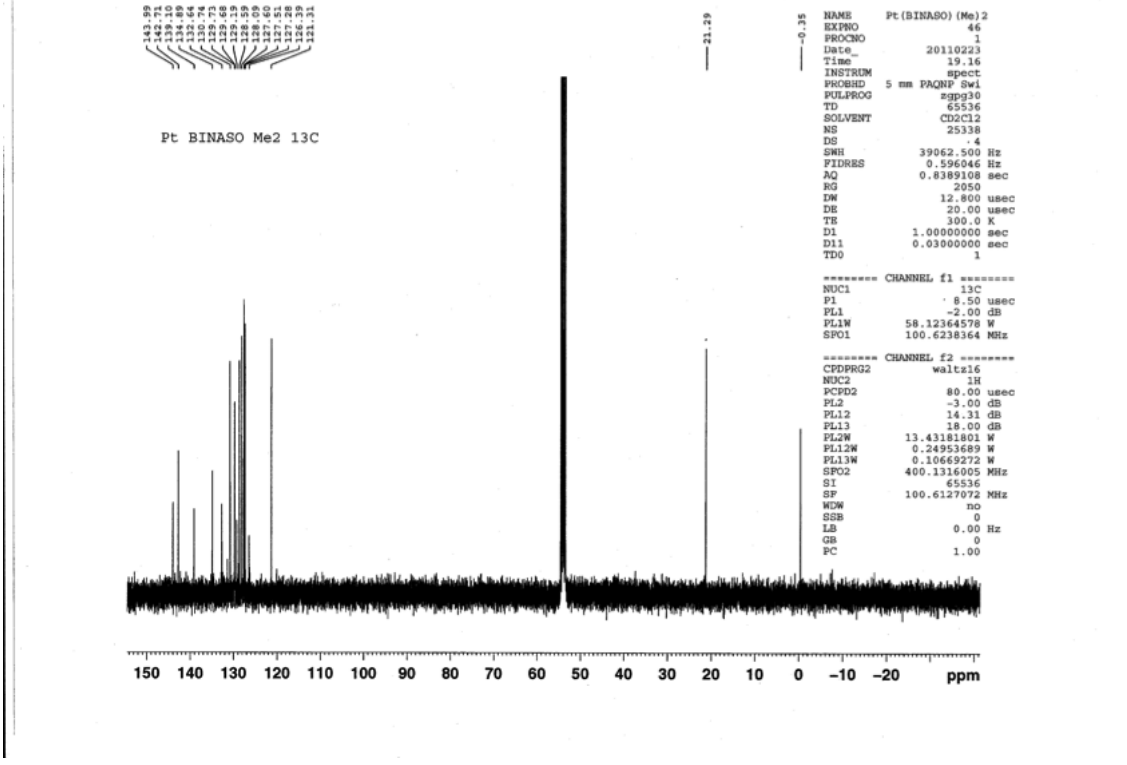
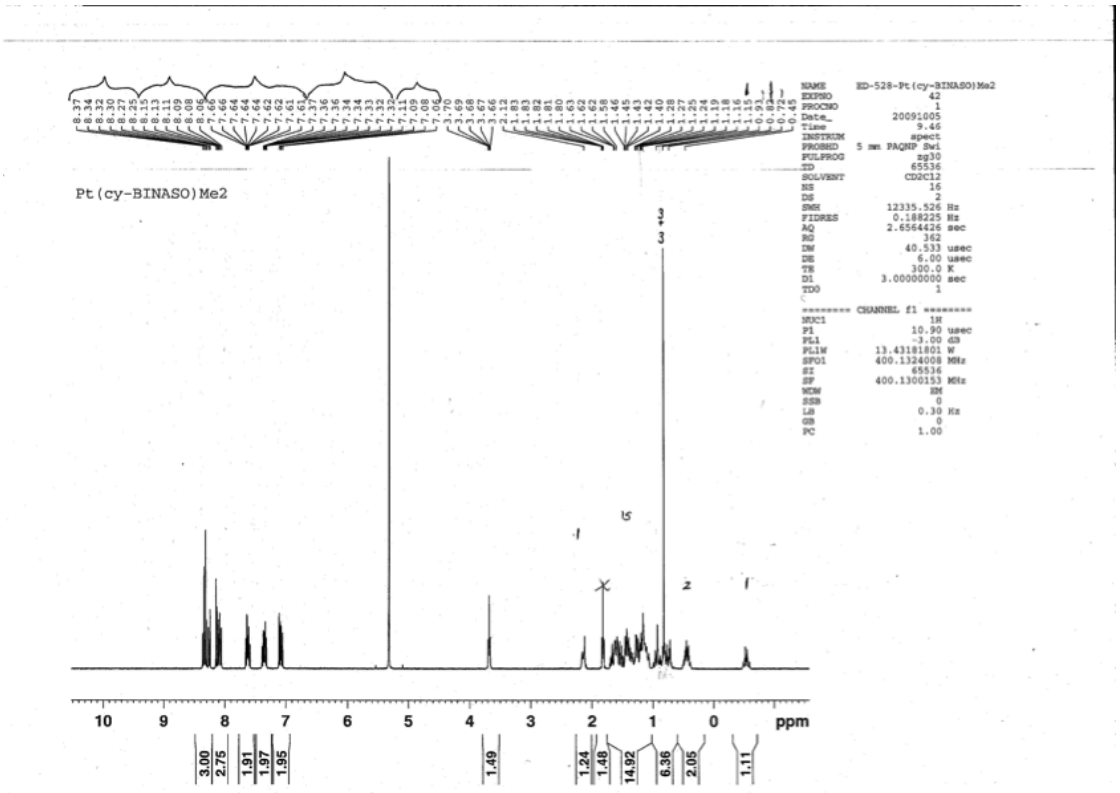
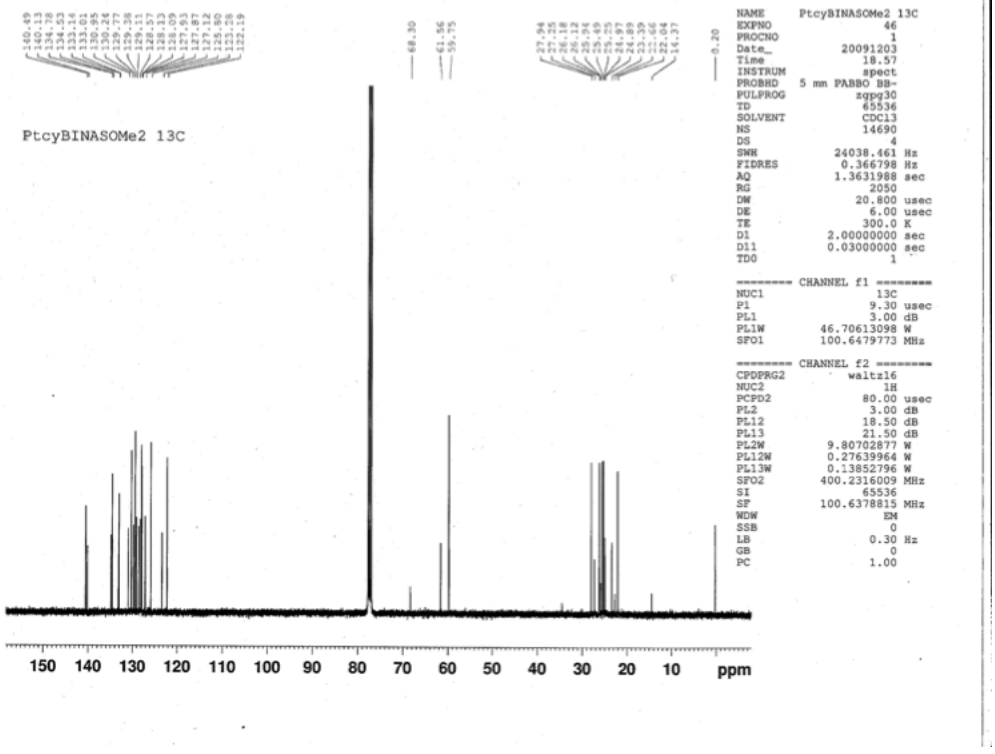
Pt(II)(M,S_S,S_S)-*p*-tolyl-binaso(Me)$_2$ (11a):



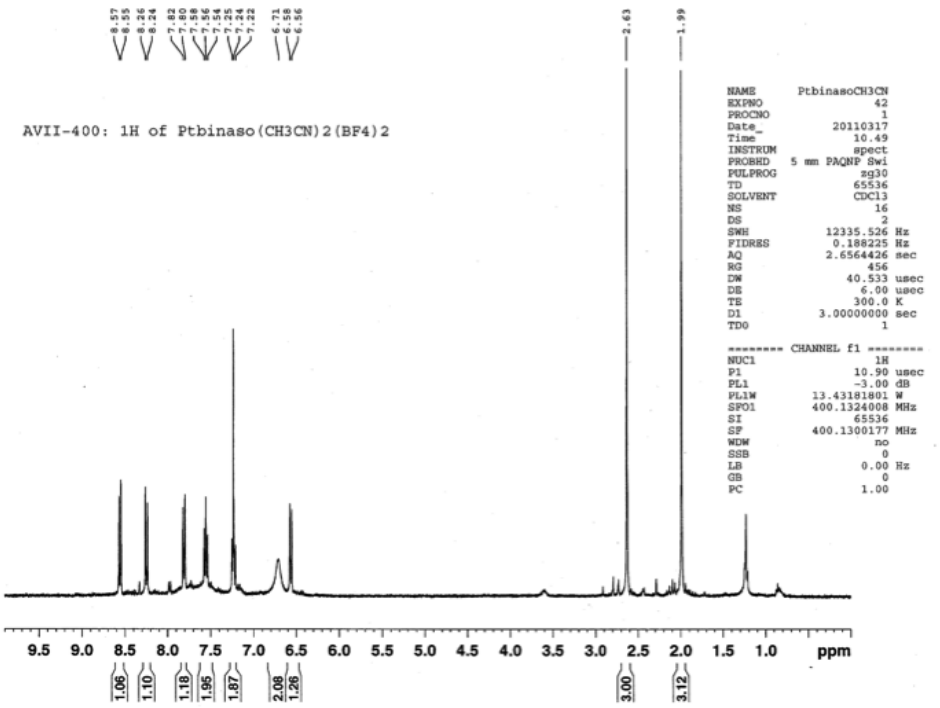


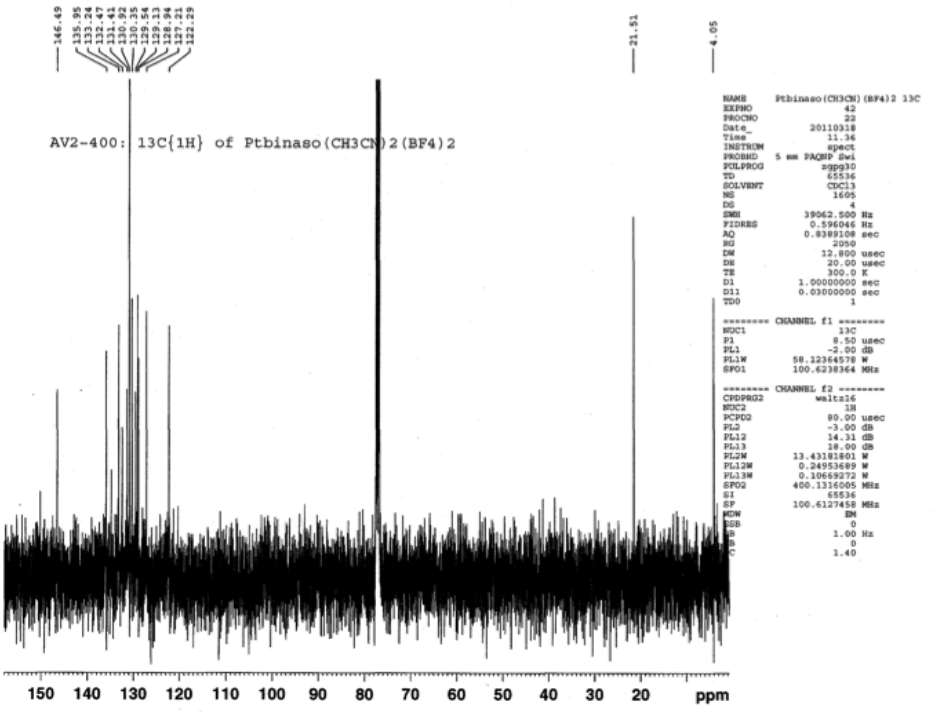
Pt(II)(M,S_S,S_S)-cyclohexyl-binaso(Me)$_2$ (11b):



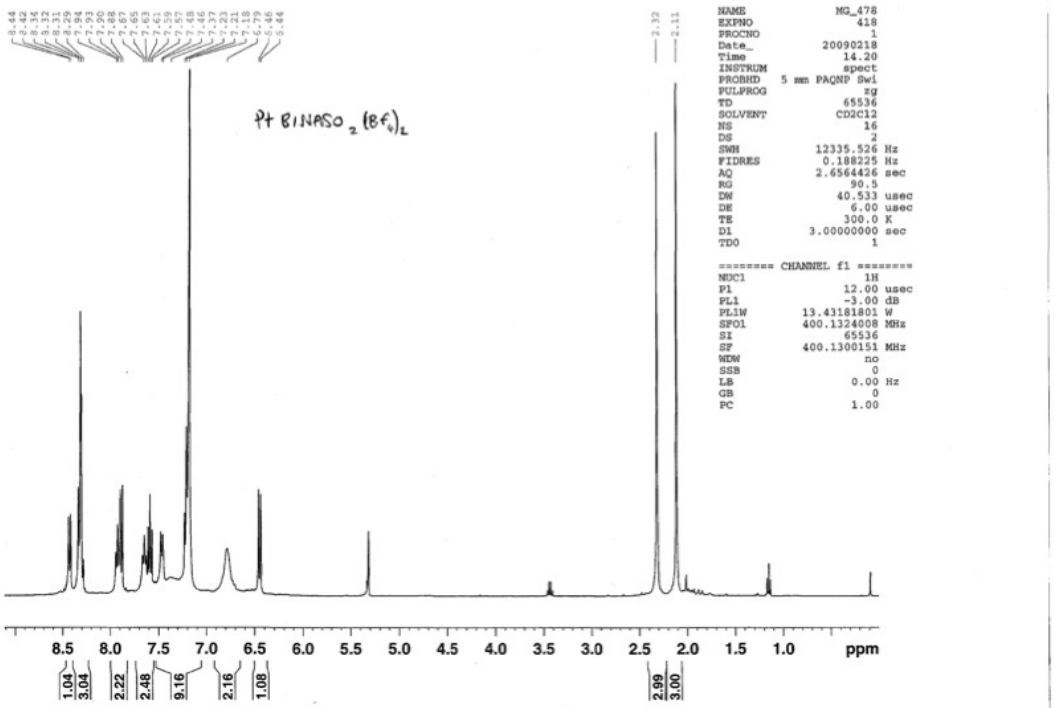


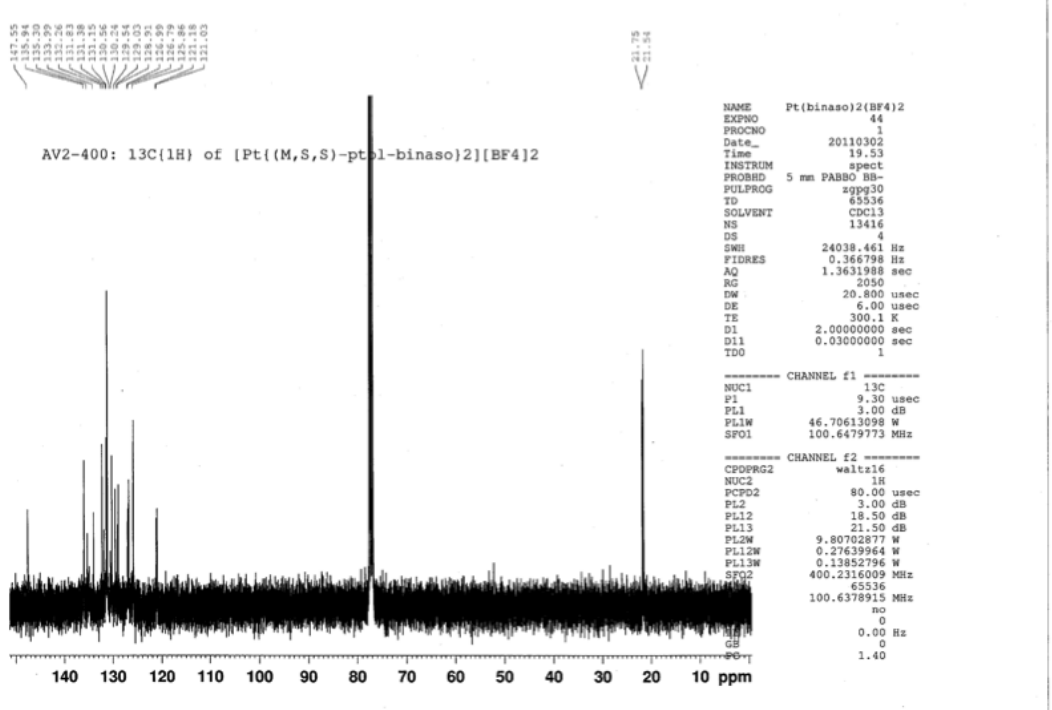
Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)$(CH_3CN)_2(BF_4)_2$ (12):





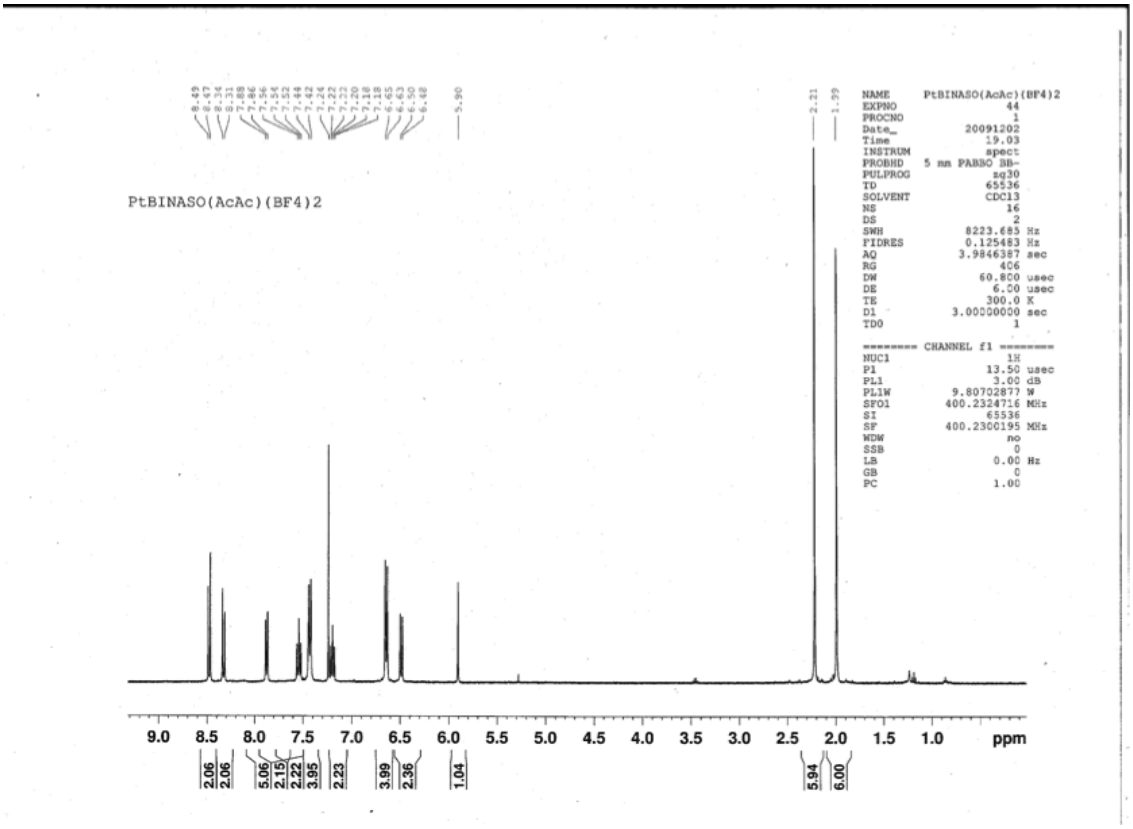
Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)$_2$(BF_4)$_2$ (13):

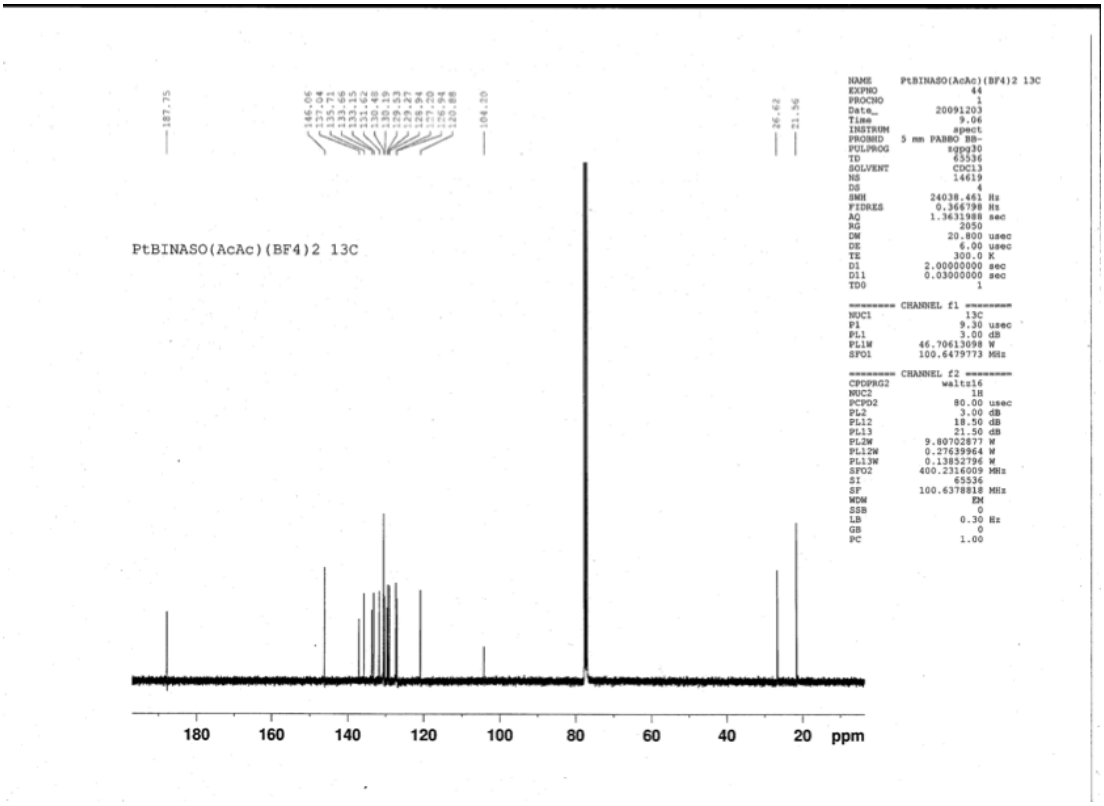




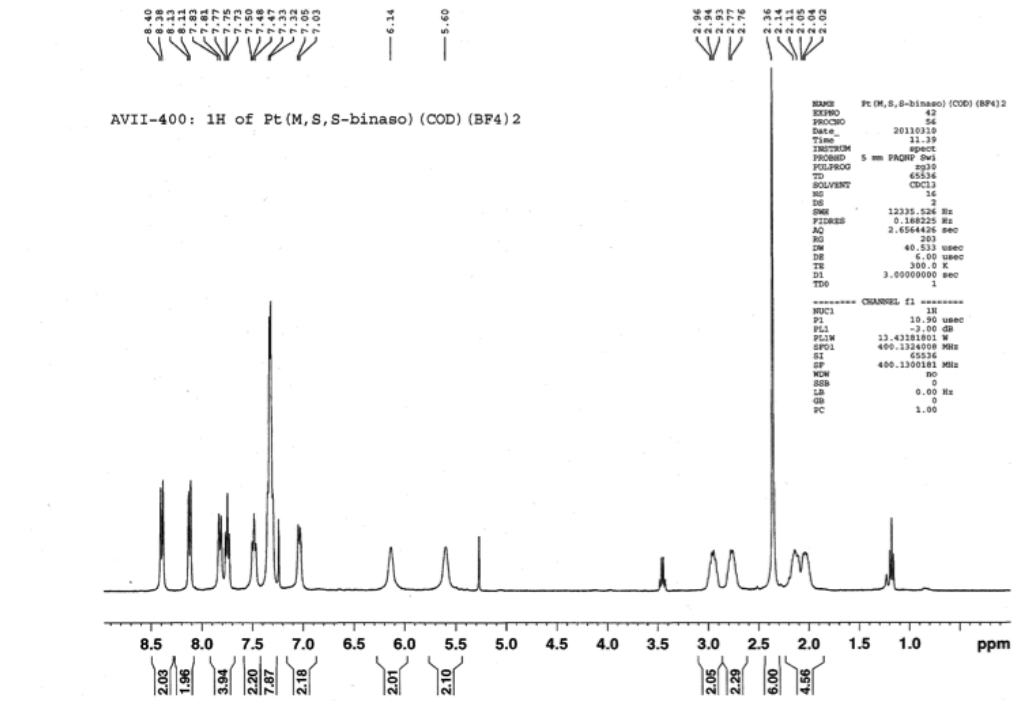
[Pt_2(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)$_2$(μ-Cl)$_2$][BF_4]$_2$ (14):

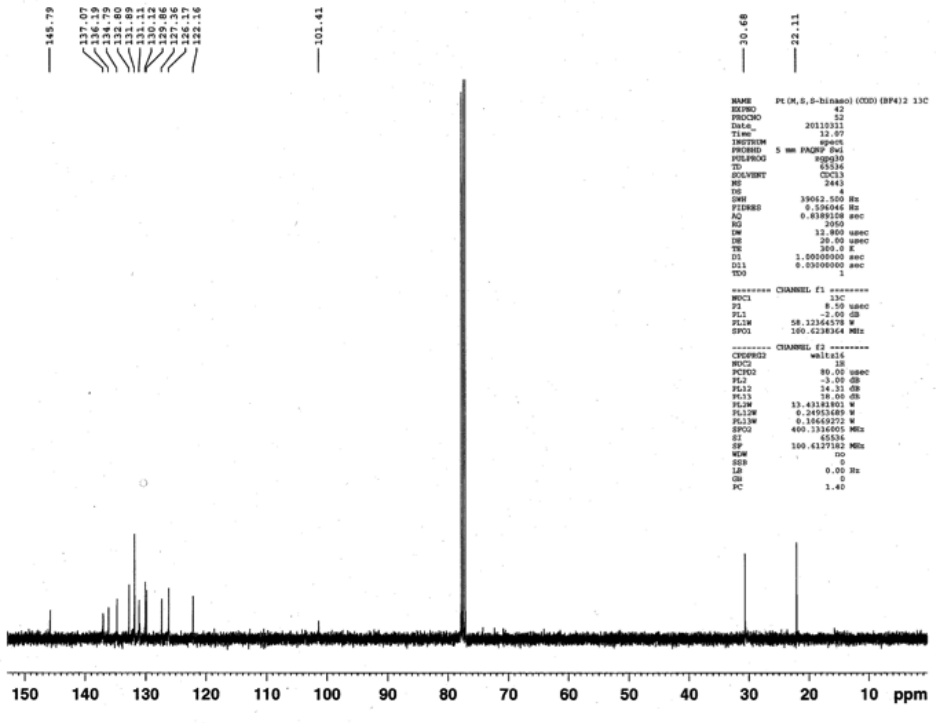
Pt(II)((*M*,S_S,S_S)-*p*-tolyl-binaso)(acac)(BF_4)$_2$ (154):



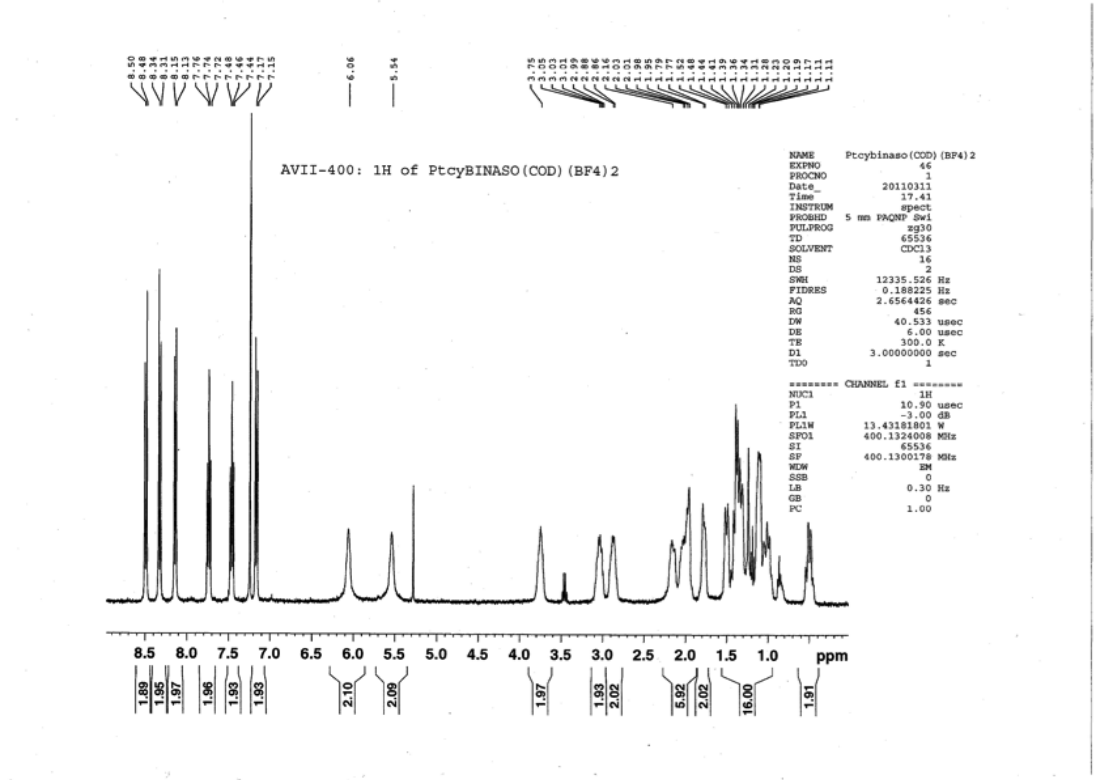


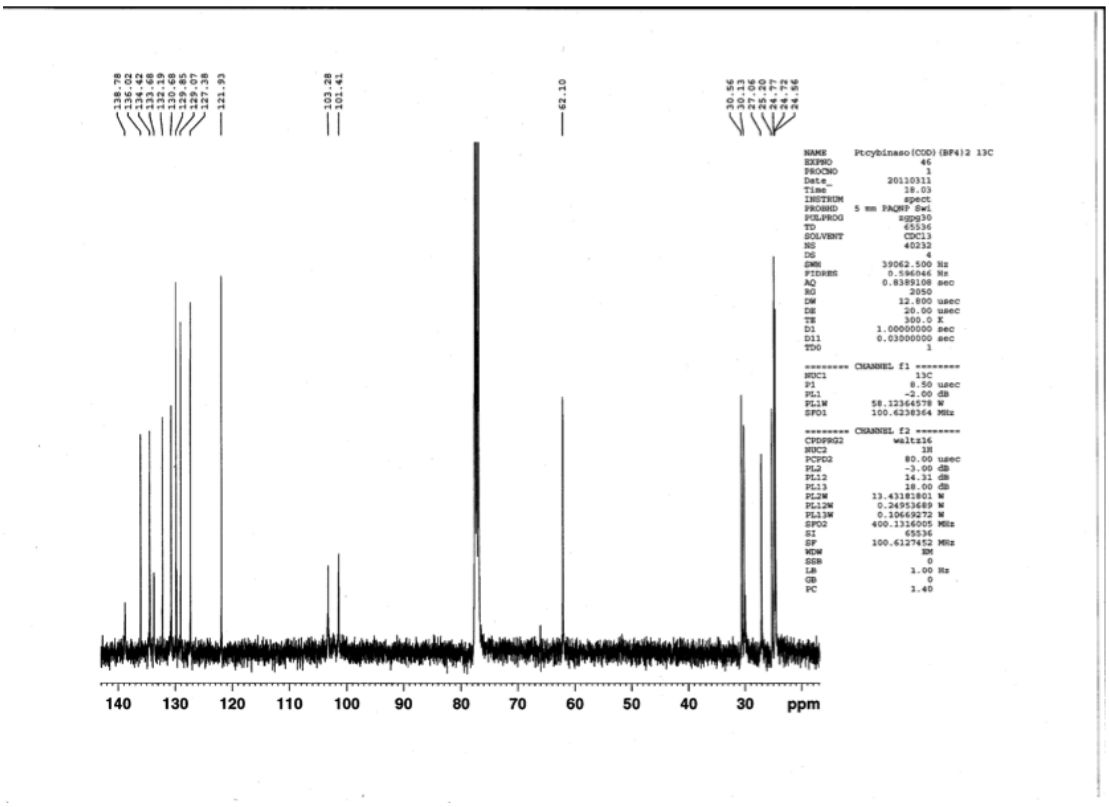
[Pt{(*M*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso}(COD)][BF$_4$]$_2$ (165a):



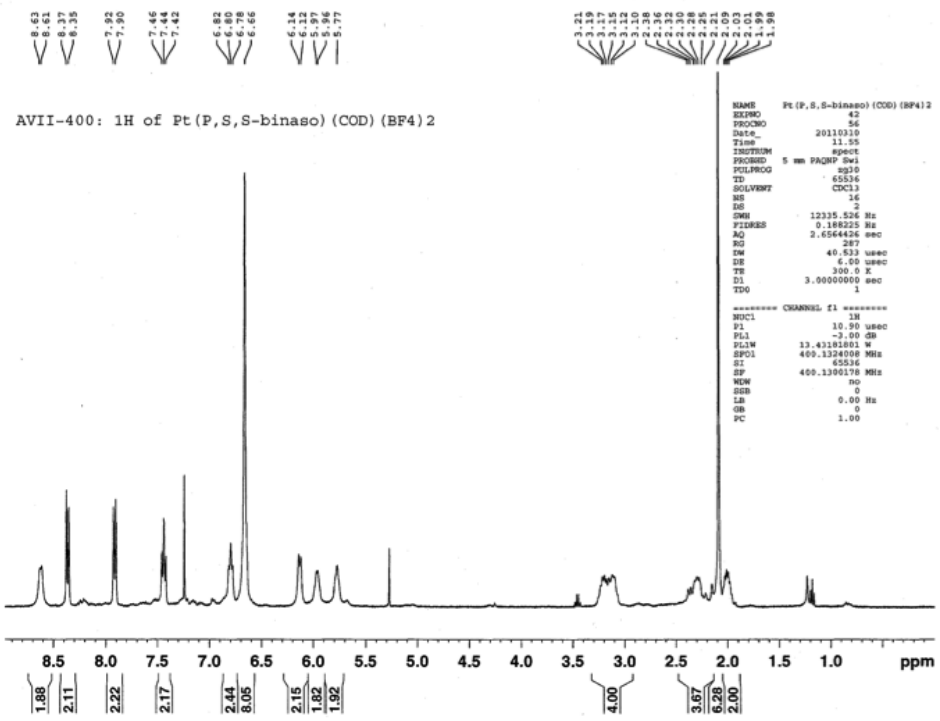


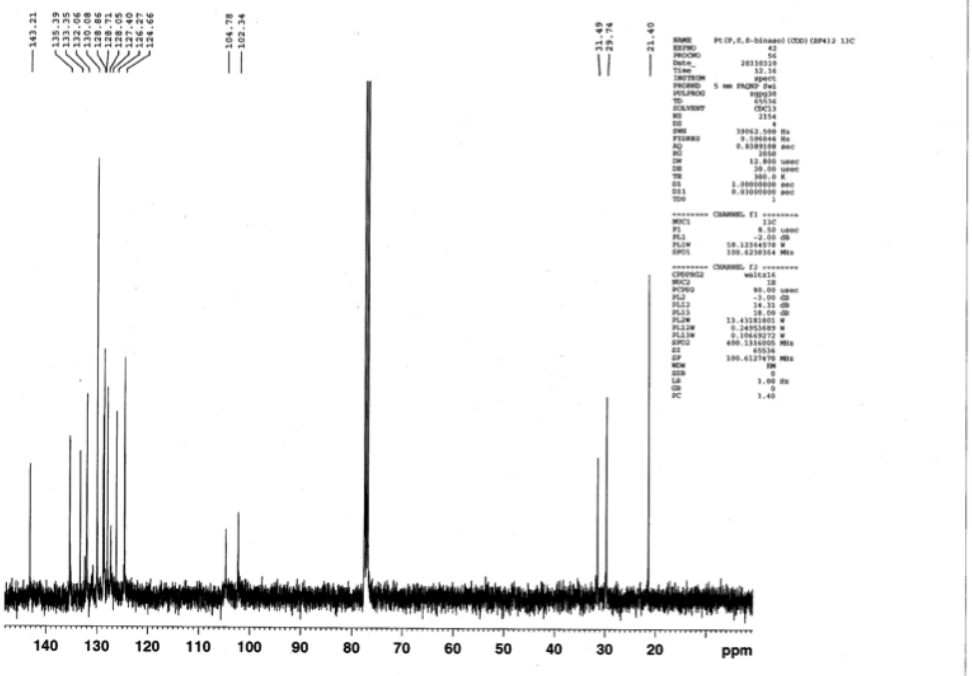
[Pt{(*M*,*S*$_S$,*S*$_S$)-cyclohexyl-binaso}(COD)][BF$_4$]$_2$ (165b):





[Pt{(*P*,*S*$_S$,*S*$_S$)-*p*-tolyl-binaso}(COD)][BF$_4$]$_2$ (165c):


AVII-400: 1H of Pt(P,S,S-binaso)(COD)(BF4)2
8.63
8.61
8.37
8.35
7.92
7.90
7.46
7.44
7.42
6.82
6.80
6.78
6.66
6.14
6.12
5.97
5.96
5.77
3.21
3.19
3.17
3.15
3.12
3.10
2.38
2.36
2.32
2.30
2.28
2.25
2.21
2.09
2.03
2.01
1.99
1.98
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.88
2.11
2.22
2.17
2.44
8.05
2.15
1.82
1.92
4.00
3.67
6.28
2.00


143.21
135.39
133.35
132.06
131.08
128.86
128.71
128.05
127.60
126.27
124.66
104.78
102.34
31.49
29.74
21.40
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

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S4. Mariz, R.; Poater, A.; Gatti, M.; Drinkel, E.; Burgi, J. J.; Luan, X. J.; Blumentritt, S.; Linden, A.; Cavallo, L.; Dorta, R. *Chem.-Eur. J.* **2010,** *16*, 14335.