Supporting Information for

Ruthenium-Catalyzed Hydroamination of Unactivated Terminal Alkenes with Stoichiometric Amounts of Alkene and an Ammonia Surrogate by Sequential Oxidation and Reduction

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1. General Information

All manipulations were performed in a nitrogen-filled glovebox or on a Schlenk manifold unless otherwise noted. Glassware was dried at 150 °C for at least 4 hours before use. Pentane, Et_2O, THF and hexane were collected from a solvent purification system containing a 0.33 m column of activated alumina under nitrogen. Diisopropyl ether, 1,2-dichlorobenzene and olefin substrates were degassed and subjected to 4 Å molecular sieves for at least 12 hours prior to use. Anhydrous methanol was purchased from a commercial source, degassed and stored in the glovebox before use. *cis*-$[Ru(DMSO)_4Cl_2]$[1] and $[Ru_2(PEt_3)_6(OTf)_3](OTf)$[2] were prepared following published procedures. All other reagents were purchased from commercial suppliers, stored in the glove box and used as received.

^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker 400, 500 or 600 MHz spectrometer. ^1H chemical shifts are reported in parts per million relative residual protiated solvent as a reference ($CHCl_3$ in $CDCl_3$: δ 7.27 ppm; CH_nD_{2-n} in $CDCl_2$: δ 5.32 ppm). ^{13}C chemical shifts are reported in parts per million relative to the deuterated solvent as a reference. ^{31}P chemical shifts were reported in parts per million relative to an 85% H_3PO_4 external standard. ^{19}F chemical shifts were reported in parts per million relative to an external standard of $CFCl_3$. Elemental analyses were performed at the Microanalytical Facility at the University of California, Berkeley. X-ray crystal structures were obtained at the Small Molecule X-ray Crystallography Facility at the University of California, Berkeley. High-resolution mass spectra were obtained on a high-resolution mass spectrometer at the QB3/Chemistry Mass Spectrometry Facility at UC Berkeley and on the Perkin Elmer AxION2 TOF MS operated by the LBNL Catalysis Facility.

2. Procedures for the Synthesis of Ruthenium Complexes

cis-$Ru(PMe_3)_4Cl_2$

cis-$[Ru(DMSO)_4Cl_2]$ (0.24 g, 0.50 mmol), PMe_3 (1.0M in toluene, 2.2 mL, 2.2 mmol, 4.4 equiv), and trifluoroethanol (2.0 mL) were combined and heated at 100 ˚C for 2 hours with stirring. Over this period, all the material dissolved, and the supernatant turned bright orange. The reaction was allowed to cool to room temperature, and the solvent was removed under vacuum. The resulting powder was recrystallized using DCM and $^iPr_2O$ to yield light yellow crystals. The resulting crystals were rinsed with $^iPr_2O$ (2 x 5.0 mL) and pentane (5.0 mL) and dried under high vacuum. Yield = 0.21 g (87%). ^1H NMR (600 MHz, chloroform-*d*) δ 1.56 (t, *J* = 3.2 Hz, 36H), 1.47 (m, 36H). ^{31}P NMR (243 MHz, chloroform-d) δ 20.05. Anal. Calc'd C:30.26 H:7.62 Found C:30.45 H:7.84.

$[Ru_2(PEt_3)_6Cl_3][Cl]$

cis-[Ru(DMSO)$_4$Cl$_2$] (3.0 g, 6.2 mmol), PEt$_3$ (3.0 mL, 20 mmol, 3.3 equiv), and MeOH (10 mL) were combined and heated at 65 ˚C for 90 minutes with stirring. Over this period, all the material dissolved, and the supernatant turned green and then bright orange. The reaction was allowed to cool to room temperature and the solvent was removed under vacuum. The resulting powder was recrystallized using DCM and Et$_2$O to yield light yellow crystals. The resulting crystals were rinsed with Et$_2$O (2 x 10 mL) and pentane (10 mL) and dried under high vacuum. Yield = 2.9 g (88%). ^{1}H NMR (400 MHz, chloroform-*d*) δ 1.92 (m, 36H), 1.21 (m, 54H). ^{31}P NMR (162 MHz, chloroform-*d*) δ 34.06. Anal. Calc'd C:41.07 H:8.62 Found C:41.13 H:8.46.

[Ru$_2$(P^{n}Pr$_3$)$_6$Cl$_3$][Cl]

cis-[Ru(DMSO)$_4$Cl$_2$] (0.24 g, 0.50 mmol), PPr$_3$ (0.31 mL, 0.25 g, 1.6 mmol, 3.1 equiv), and a magnetic stir bar were added to a Schlenk flask in a N$_2$ filled glove box. Outside the glove box, degassed H$_2$O (0.80 mL) was added via syringe under nitrogen pressure. The Schlenk flask was sealed and heated at 100 ˚C for 2 hours with vigorous stirring. The reaction turned green and the product precipitated as a yellow solid. The reaction was allowed to cool to room temperature, and the yellow precipitation was collected by filtration. The yellow solid was rinsed with H$_2$O (3 x 5.0 mL) and hexanes (3 x 5.0 mL) and dried under high vacuum. Yield = 0.28 g (86%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 1.76 (m, 36H), 1.57 (m, 36H), 0.99 (t, *J* = 7.2 Hz, 54H). ^{31}P NMR (243 MHz, chloroform-*d*) δ 29.16. Anal. Calc'd C:49.69 H:9.73. Found C:49.87 H:9.60.

[Ru$_2$(PMePh$_2$)$_6$Cl$_3$][Cl]

cis-[Ru(DMSO)$_4$Cl$_2$] (0.63 g, 1.3 mmol), PPh$_2$Me (0.80 mL, 0.86 g, 4.3 mmol, 3.3 equiv), and MeOH (1.0 mL) were combined and stirred at room temperature for 90 minutes. The mixture was then placed in the freezer (-30 ˚C) overnight and the precipitation was collected by filtration, rinsed with Et$_2$O (2 x 5.0 mL), and dried under vacuum. Combined yield = 0.83 g (83%). ^{1}H NMR (600 MHz, chloroform-d_1) δ 7.27 (t, J = 7.5 Hz, 12H), 7.07 (m, 24H), 7.02 (m, 24H), 1.82 (m, 18H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 136.70 (m), 132.93, 129.58, 127.95, 19.88 (m). ^{31}P NMR (243 MHz, chloroform-*d*) δ 18.93. Anal. Calc'd C:60.63 H:5.09 Found C:60.34 H:5.18.

***cis*-Ru(Et$_2$P(CH$_2$)$_4$PEt$_2$)$_2$Cl$_2$**

cis-[Ru(DMSO)$_4$Cl$_2$] (0.15 g, 0.31 mmol), Et$_2$P(CH$_2$)$_4$PEt$_2$ (0.16 g 0.68 mmol, 2.2 equiv), and MeOH (1.0 mL) were combined and heated at 65 ˚C for 14 hours with stirring. Over this period, all the material dissolved, and the reaction turned bright red and then orange. The mixture was allowed to cool to room temperature and layered with ^{i}Pr$_2$O (19 mL) to yield yellow crystals. The crystals were collected by filtration, rinsed with ^{i}Pr$_2$O (2 x 5.0 mL) and pentane (1 mL), and dried under high vacuum. Yield = 0.17 g (83%). ^{1}H NMR (600 MHz, methylene chloride-d_2) δ 2.20-2.75 (m, 8H), 1.45-2.05 (m, 20H), 0.95-1.35 (m, 28H). ^{31}P NMR (243 MHz, CD$_2$Cl$_2$) δ 32.27 (t, J = 29 Hz), 4.62 (t, J = 29 Hz). Anal. Calc'd C:45.00 H:8.81 Found C:45.33 H:9.05.

[Ru$_2$(N(CH$_2$PEt$_2$)$_3$)$_2$Cl$_3$][Cl]

cis-[Ru(DMSO)$_4$Cl$_2$] (0.17 g, 0.35 mmol), N(CH$_2$PEt$_2$)$_3$ (0.11 g, 0.35 mmol, 1.0 equiv), MeOH (1 mL), and a magnetic stir bar were combined and heated at 65 ˚C for 5 hours with stirring. The mixture was allowed to cool to room temperature and layered with ^{i}Pr$_2$O (12 mL). The yellow microcrystalline precipitation was collected by filtration, rinsed with ^{i}Pr$_2$O (2 x 5.0 mL) and dried under high vacuum. Yield = 83 mg (71%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 2.87 (s,

12H), 2.19 (h, *J* = 9.8, 9.1 Hz, 12H), 1.80 (dt, *J* = 15.1, 7.5 Hz, 12H), 1.18 (p, *J* = 7.2 Hz, 36H). ^{31}P NMR (243 MHz, chloroform-*d*) δ 28.08. Anal. Calc'd C:36.37 H:7.33 N:2.83 Found C:36.53 H:7.19 N:2.64.

$Ru(PEt_3)_3(NTf_2)_2$ (Ru-1)
$[Ru_2Cl_3(PEt_3)_6][Cl]$ (0.38 g, 0.36 mmol), $AgNTf_2$ (0.56 g, 1.4 mmol, 4.0 equiv) and DCM (5.0 mL) were combined and stirred at room temperature for 3 hours. The mixture turned red and orange precipitation was formed during the reaction. The mixture was then filtered, and the solvent was removed under vacuum. The resulting orange solid was recrystallized with DCM and $^{i}Pr_2O$ at -35 ˚C, washed with $^{i}Pr_2O$ (2 x 5.0 mL) and dried under high vacuum. Yield = 0.65 g (89%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 1.91 (m, 18H), 1.24 (m, 27H). ^{31}P NMR (162 MHz, Methylene Chloride-d_2) δ 50.83. Anal. Calc'd C:26.01 H:4.47 N:2.76 Found C:25.91 H:4.49 N:2.70. The identity of the product was confirmed by x-ray crystallography.

3. Development of Reaction Conditions

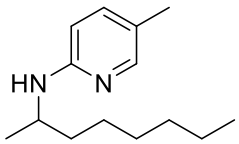
Preparation of ruthenium complexes for *in situ* examination of catalytic activity

The complexes **Ru-1** to **Ru-6** were generated for in situ for the examination of catalytic activity for convenience. To generate the ruthenium triflimide complex from the corresponding ruthenium chloride precursor *in situ*, ruthenium chloride complex (0.020 mmol for dimeric complex or 0.040 mmol for monomeric complex), $AgNTf_2$ (31 mg, 0.080 mmol, 2.0 equiv relative to [Ru]), trifluoroethanol (0.50 mL), and a magnetic stir bar were combined in a 1 dram vial. The vial was capped and heated at 80 ˚C for 2 h with stirring and then allowed to cool to room temperature. The solution was filtered, and the volatile materials were evaporated using high vacuum to form a residue. This residue was then triturated with $^{i}Pr_2O$ and dried. The purity and identity of the ruthenium triflimide complex was verified by NMR spectroscopy.

Conditions for the examination of catalysts for hydroamination of alkenes

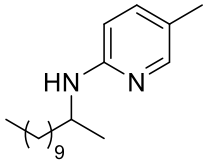
1-dodecene (0.20 mmol, 44 µL, 34 mg), 2-amino-5-methylpyridine (0.20 mmol, 22 mg), ruthenium complex (0.010 mmol, 5.0 mol % [Ru]), and solvent (60 µL) were combined with a magnetic stir bar in a one-dram vial to form a solution. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool to room temperature, and yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

4. Procedures for the Catalytic Hydroamination Reactions



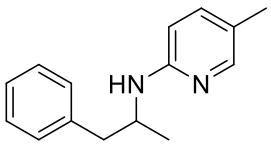
5-methyl-*N*-(octan-2-yl)pyridine-2-amine (2a)

1-Octene (31 μL, 23 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 28 mg (62%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.88 (s, 1H), 7.23 (dd, J = 8.4, 2.2 Hz, 1H), 6.28 (d, J = 8.4 Hz, 1H), 4.16 (d, J = 8.1 Hz, 1H), 3.67 (m, 1H), 2.16 (s, 3H), 1.57 – 1.24 (m, 10H), 1.17 (d, J = 6.4 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 156.8, 147.8, 138.58, 121.2, 106.4, 47.5, 37.4, 32.0, 29.5, 26.2, 22.8, 21.1, 17.5, 14.2. GC-MS (EI+): 220 (M), 205 (M-CH_3), 135 ([N-ethyl-5-methylpyridin-2-amine]$^•$).



5-methyl-*N*-(dodecan-2-yl)pyridine-2-amine (3a)

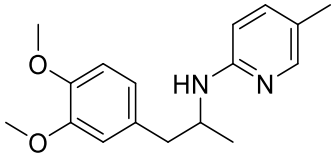
1-Dodecene (44 μL, 34 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 35 mg (63%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.87 (m, 1H), 7.21 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.27 (d, *J* = 8.4 Hz, 1H), 4.21 (d, *J* = 8.6 Hz, 1H), 3.66 (dh, *J* = 8.5, 6.4 Hz, 1H), 2.14 (s, 3H), 1.51 (dddd, *J* = 12.9, 10.0, 6.5, 5.2 Hz, 1H), 1.44 (ddt, *J* = 12.9, 9.5, 6.0 Hz, 1H), 1.39 – 1.31 (m, 2H), 1.30 – 1.22 (m, 14H), 1.16 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.8, 147.9, 138.4, 138.4, 121.0, 106.3, 47.4, 37.4, 32.0, 29.8, 29.7, 29.4, 26.2, 22.8, 21.1, 17.4, 14.2, 14.20. GC-MS (EI+): 276 (M), 261 (M-CH_3), 135 ([N-ethyl-5-methylpyridin-2-amine]$^•$).



5-methyl-*N*-(1-phenylpropan-2-yl)pyridine-2-amine (4a)

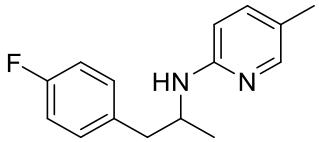
Allylbenzene (27 μL, 24 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 30 mg (66%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.92 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.23 – 7.17 (m, 3H), 6.32 (d, *J* = 8.4 Hz, 1H), 4.24 (d, *J* = 8.6 Hz, 1H), 4.03 (dq, *J* = 8.7, 6.7 Hz, 1H), 2.92 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.75 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.17 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.4, 148.1, 138.7, 138.5, 129.7, 128.4,

126.4, 121.6, 106.9, 48.3, 42.7, 20.3, 17.5. GC-MS (EI+): 226 (M), 211 (M-CH_3), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



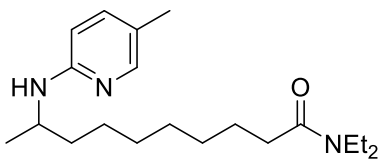
***N*-(1-(3,4-dimethoxyphenyl)propan-2-yl)-5-methylpyridin-2-amine (5a)**

3,4-Dimethoxy-allylbenzene (36 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) were combined along with a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 30 mg (52%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.91 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.72 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 4.23 (d, *J* = 8.6 Hz, 1H), 4.01 (hept, *J* = 6.5 Hz, 1H), 3.85 (d, *J* = 10.2 Hz, 6H), 2.83 (dd, *J* = 13.5, 5.3 Hz, 1H), 2.72 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.17 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.5, 148.9, 148.0, 147.7, 138.5, 131.2, 121.7, 121.6, 113.0, 111.3, 107.1, 56.1, 56.0, 48.4, 42.3, 20.5, 17.5. GC-MS (EI+): 286 (M), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



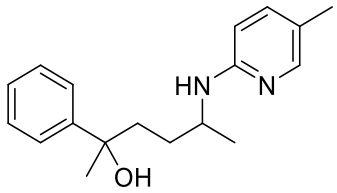
5-methyl-*N*-(1-(4-fluoro-phenyl)propan-2-yl)pyridine-2-amine (6a)

p-Fluoro-allylbenzene (27 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 28 mg (56%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.92 (s, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.14 (dd, J = 8.0, 5.8 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 6.29 (d, J = 8.4 Hz, 1H), 4.14 (d, J = 7.8 Hz, 1H), 4.01 (m, 1H), 2.87 (dd, J = 13.7, 5.2 Hz, 1H), 2.74 (dd, J = 13.6, 6.9 Hz, 1H), 2.17 (s, 3H), 1.14 (d, J = 6.4 Hz, 3H). 13C NMR (101 MHz, chloroform-*d*) δ 162.9, 160.5, 156.3, 148.0, 138.5, 134.3 (d, *J* = 3.2 Hz), 131.1 (d, *J* = 7.7 Hz), 121.7, 115.2 (d, *J* = 21.1 Hz), 107.0, 48.3, 41.8, 20.3, 17.5. GC-MS (EI+): 244 (M), 229 (M-CH_3), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



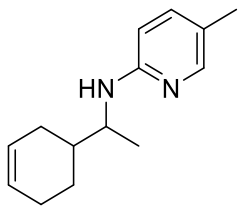
***N*,*N*-diethyl-9-((5-methylpyridin-2-yl)amino)decanamide (7a)**

9-decenoic acid diethyl amide (45 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 44 mg (66%). ^{1}H NMR (600 MHz, chloroform-d) δ 7.86 (s, 1H), 7.21 (dd, J = 8.4, 2.4 Hz, 1H), 6.27 (d, J = 8.4 Hz, 1H), 4.18 (d, J = 8.6 Hz, 1H), 3.65 (dq, J = 8.3, 6.2 Hz, 1H), 3.34 (q, J = 7.1 Hz, 2H), 3.27 (q, J = 7.1 Hz, 2H), 2.26 (d, J = 8.5 Hz, 1H), 2.24 (d, J = 8.5 Hz, 1H), 2.14 (s, 3H), 1.60 (p, J = 7.5 Hz, 2H), 1.50 (m, 1H), 1.43 (m, 1H), 1.39 – 1.21 (m, 8H), 1.14 (t, J = 6.5 Hz, 6H, 2 methyl groups), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 172.4, 156.8, 147.9, 138.5, 121.1, 106.4, 47.5, 42.1, 40.1, 37.3, 33.2, 29.6, 29.5, 29.5, 26.1, 25.6, 21.1, 17.6, 14.5, 13.2. GC-MS (EI+): 333 (M), 318 (M – Me), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



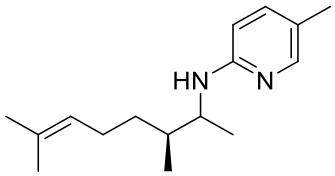
5-((5-methylpyridin-2-yl)amino)-2-phenylhexan-2-ol (8a)

2-phenylhex-5-en-2-ol (35 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.020 mmol, 10 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 24 mg (42%, 52:48 dr). The peaks derived from diastereomer 1 are labelled and those derived from diastereomer 2 are given without labels. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (s, 1H), 7.87 (s, 1H, diastereomer 1), 7.47 (d, *J* = 8.1 Hz, 4H, both diastereomers), 7.34 (d, *J* = 7.7 Hz, 2H, diastereomer 1), 7.32 (d, J = 7.7 Hz, 2H), 7.22 (m, 4H, both diastereomers), 6.26 (d, *J* = 8.5 Hz, 2H, both diastereomers), 4.11 (s, 2H, both diastereomers), 3.89 (h, *J* = 6.0 Hz, 2H, both diastereomers), 2.16 (s, 6H, both diastereomers), 1.91 (t, J = 7.5 Hz, 4H, both diastereomers) 1.52 (s, 6H, both diastereomers), 1.50 – 1.38 (m, 4H, both diastereomers), 1.25 (s, 2H, both diastereomers), 1.10 (d, *J* = 6.4 Hz, 6H, both diastereomers). ^{13}C NMR (101 MHz, chloroform-*d*) δ 156.3 (diastereomer 1), 156.1, 148.8, 148.4 (diastereomer 1), 146.6 (diastereomer 1), 146.6, 139.0 (diastereomer 1), 138.9, 128.2 (diastereomer 1), 128.2, 126.4 (diastereomer 1), 126.4, 125.0, 125.0 (diastereomer 1), 121.35, 121.30 (diastereomer 1), 107.90, 107.71 (diastereomer 1), 74.87, 74.62 (diastereomer 1), 48.1, 47.5 (diastereomer 1), 39.8 (diastereomer 1), 39.7, 32.6 (diastereomer 1), 32.1, 31.4 (diastereomer 1), 31.1, 29.9, 21.7, 21.4 (diastereomer 1), 17.5 (diastereomer 1). GC-MS (EI+): 284 (M), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



***N*-(1-(cyclohex-3-en-1-yl)ethyl)-5-methylpyridin-2-amine (9a)**

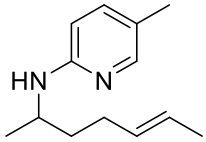
4-ethenyl-cyclohexene (26 μL, 22 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.020 mmol, 10 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 27 mg (61%). ^{1}H NMR (600 MHz, chloroform-*d*) δ Major isomer: 7.88 (s, 1H, major), 7.22 (dd, *J* = 8.5, 2.4 Hz, 1H, major), 6.30 (d, *J* = 8.4 Hz, 1H, major), 5.67 (m, 2H, major), 4.19 (d, *J* = 9.3 Hz, 1H, major), 3.67 (h, J = 7 Hz, 1H, major), 2.20 – 1.98 (m, 3H, major), 2.16 (s, 3H, major), 1.88 – 1.83 (m, 2H, major), 1.69 (m, 1H, major), 1.28 (m, 1H, major), 1.16 (t, *J* = 6.4 Hz, 3H, major). Minor isomer: 7.88 (s, 1H), 7.22 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 5.67 (m, 2H), 4.24 (d, *J* = 9.3 Hz, 1H), 3.67 (h, J = 7 Hz, 1H), 2.20 – 1.98 (m, 3H), 2.16 (s, 3H), 1.90 (m, 1H), 1.78 (m, 1H), 1.71 (m, 1H), 1.36 (m, 1H), 1.16 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 157.0, 156.9 (major), 147.8 (major), 147.8, 138.5 (major), 138.5, 127.2, 127.1 (major), 126.4 (major), 126.4, 121.1, 121.1 (major), 106.5, 106.4 (major), 51.3, 51.1 (major), 39.7, 39.5 (major), 28.3 (major), 28.0, 25.8, 25.5 (major), 25.4, 25.0 (major), 18.1, 18.0 (major), 17.4, 17.4(major). GC-MS (EI+): 216 (M), 201 (M – Me), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



***N*-((*3S*)-3,7-dimethyloct-6-en-2-yl)-5-methylpyridin-2-amine (10a)**

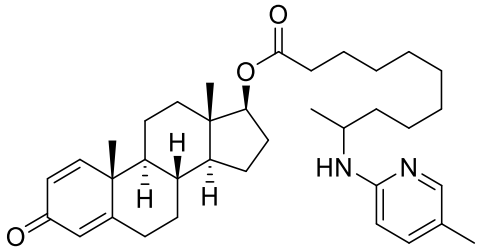
(+)-β-Citronellene (28 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.020 mmol, 10 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 20% ethyl acetate in hexanes. Yield = 27 mg (54%, 7:4 dr). ^{1}H NMR (600 MHz, chloroform-*d*) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H, major), 7.87 (s, 1H, minor), 7.22 (d, *J* = 8.2 Hz, 1H, major), 7.22 (d, *J* = 8.2 Hz, 1H, minor), 6.28 (d, *J* = 8.5 Hz, 1H, major), 6.27 (d, J = 8.4 Hz, 1H, minor), 5.10 (ddt, *J* = 7.1, 5.7, 1.5 Hz, 1H, minor), 5.05 (tt, *J* = 7.2, 1.5 Hz, 1H, major), 4.31 (d, *J* = 9.1 Hz, 1H, minor), 4.27 (d, *J* = 9.1 Hz, 1H, major), 3.68 (dtd, *J* = 13.1, 6.6, 3.2 Hz, 1H, major), 3.63 (ddd, *J* = 8.9, 6.8, 5.0 Hz, 1H, minor), 2.15 (s, 3H, major), 2.15 (s, 3H, minor), 2.06 (m, 1H, minor), 2.04 (m, 1H, major), 1.96 (m, 1H, minor), 1.92 (m, 1H, major), 1.68 (s, 3H, minor), 1.67 (m, 1H, minor), 1.65 (m, 1H, major), 1.65 (s, 3H, major), 1.60 (s, 3H, minor), 1.57 (s, 3H, major), 1.48 (m, 1H, minor), 1.46 (m, 1H, major), 1.19 (m, 1H, minor), 1.18 (m, 1H, major), 1.12 (d, *J* = 6.6 Hz, 3H, major), 1.09 (d, *J* = 6.6 Hz, 3H, minor), 0.95 (d, *J* = 6.9 Hz, 3H, major), 0.89 (d, *J* = 6.8 Hz, 3H, minor). ^{13}C NMR (151 MHz, chloroform-*d*) δ 157.0 (major), 156.8 (minor), 148.0 (minor), 147.9 (major), 138.5 (minor), 138.5 (major), 131.6 (minor), 131.5 (major), 124.8 (major), 124.7 (minor), 121.1 (minor), 121.1 (major), 106.3 (major), 106.3 (minor), 51.2 (minor), 51.1 (major), 37.5 (major), 36.9 (minor), 33.8 (minor), 32.8 (major), 26.0 (minor), 26.0 (major), 25.8 (minor), 25.8 (major),

17.8 (major), 17.8 (minor), 17.5 (major), 16.4 (minor), 15.5 (major), 14.5 (minor). GC-MS (EI+): 246 (M), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



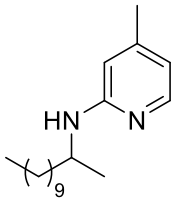
(*E*)-*N*-(hept-5-en-2-yl)-5-methylpyridin-2-amine (11a)

1,5-heptadiene (19 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 27 mg (67%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.88 (s, 1H), 7.23 (d, J = 8.5 Hz, 1H), 6.28 (d, J = 8.3 Hz, 1H), 5.50 – 5.30 (m, 2H), 4.19 (bs, 1H), 3.69 (dt, J = 13.8, 7.0 Hz, 1H), 2.16 (s, 3H), 2.14 – 2.00 (m, 2H), 1.71 – 1.43 (m, 5H), 1.18 (d, J = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.6, 147.7, 138.3, 130.6, 125.2, 121.0, 106.2, 46.9, 37.0, 29.1, 20.8, 17.8, 17.3. GC-MS (EI+): 204 (M), 149 (M-butene), 135 ([N-ethyl-5-methylpyridin-2-amine]•).



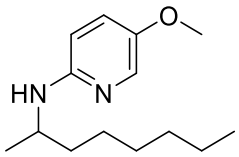
Aminopyridyl boldenone undecylenate (12a)

Boldenone undecylenate (91 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (30 mg, 0.030 mmol, 15 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with a gradient of 20% to 60% ethyl acetate in hexanes. Yield = 38 mg (34%). Both diastereomers gave identical NMR and mass spectra. ^{1}H NMR (500 MHz, chloroform-*d*) δ 7.87 (s, 1H), 7.23 (dd, 1H), 7.03 (d, *J* = 10.2 Hz, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 6.22 (dd, *J* = 10.1, 1.5 Hz, 1H), 6.06 (s, 1H), 4.58 (t, *J* = 8.5 Hz, 1H), 4.18 (d, *J* = 8.4 Hz, 1H), 3.66 (hept, *J* = 6.6 Hz, 1H), 2.46 (td, *J* = 13.4, 4.7 Hz, 1H), 2.36 (d, *J* = 12.6 Hz, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 1.94 (d, *J* = 14.2 Hz, 2H), 1.86 – 1.54 (m, 9H), 1.54 – 1.41 (m, 4H), 1.38-1.32 (m, 2H), 1.31 – 1.24 (m, 6H), 1.22 (s, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.10 – 0.98 (m, 4H), 0.85 (s, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 186.4, 173.9, 168.9, 156.2, 155.8, 146.5, 139.3, 127.6, 124.0, 121.2, 106.8, 82.1, 52.3, 50.0, 47.6, 43.6, 42.8, 37.2, 36.6, 35.4, 34.6, 33.1, 32.8, 29.6, 29.4, 29.2, 29.2, 27.5, 26.1, 25.1, 23.8, 22.4, 20.9, 18.8, 17.4, 12.2. ESI-MS (+): Calc. for $C_{36}H_{53}O_3N_2$: 561.4051. Found: 563.4048.



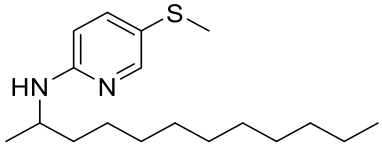
4-methyl-*N*-(dodecan-2-yl)pyridine-2-amine (13a)

1-Dodecene (44 μL, 34 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 15% ethyl acetate in hexanes. Yield = 35 mg (63%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 5.2 Hz, 1H), 6.39 (d, *J* = 5.2 Hz, 1H), 6.18 (s, 1H), 4.29 (d, *J* = 8.5 Hz, 1H), 3.72 (dq, *J* = 8.4, 6.3 Hz, 1H), 2.24 (s, 3H), 1.60 – 1.50 (m, 1H), 1.51 – 1.43 (m, 1H), 1.43 – 1.35 (m, 2H), 1.20-1.30 (m, 14H), 1.20 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.6, 148.2, 147.9, 113.9, 106.7, 47.1, 37.3, 31.9, 29.6, 29.6, 29.3, 26.0, 22.7, 21.2, 21.0, 14.1. GC-MS (EI+): 276 (M), 261 (M-CH_3), 135 ([N-ethyl-5-methylpyridin-2-amine]$^\bullet$).



5-methoxy-*N*-(octan-2-yl)pyridin-2-amine (14a)

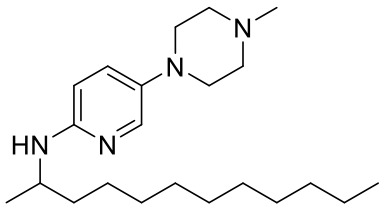
1-octene (31 μL, 23 mg, 0.20 mmol), 5-methoxypyridin-2-amine (25 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 25% ethyl acetate in hexanes. Yield = 32 mg (68%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.80 (d, *J* = 3.0 Hz, 1H), 7.09 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.33 (d, *J* = 9.0 Hz, 1H), 4.05 (s, 1H), 3.77 (s, 3H), 3.64 (dt, *J* = 11.2, 5.1 Hz, 2H), 1.53 (dddd, *J* = 12.8, 9.9, 6.3, 5.1 Hz, 1H), 1.49 – 1.40 (m, 1H), 1.41 – 1.31 (m, 2H), 1.33 – 1.21 (m, 6H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 153.8, 148.5, 133.8, 125.8, 107.3, 56.7, 48.0, 37.4, 31.9, 29.5, 26.2, 22.7, 21.1, 14.2. GC-MS (EI+): 236 (M), 221 (M-CH_3), 151 ([N-ethyl-5-methoxypyridin-2-amine]$^\bullet$).



***N*-(dodecan-2-yl)-5-(methylthio)pyridin-2-amine (15a)**

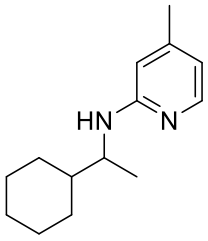
1-dodecene (34 mg, 0.20 mmol), 5-(methylthio)pyridin-2-amine (28 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape

and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 26 mg (42%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.12 (d, *J* = 2.2 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.29 (d, *J* = 8.7 Hz, 1H), 4.44 (d, *J* = 8.3 Hz, 1H), 3.73 – 3.66 (m, 1H), 2.35 (s, 3H), 1.49 (dtdd, *J* = 25.4, 13.2, 9.7, 5.9 Hz, 2H), 1.34 (dtt, *J* = 18.8, 8.4, 4.9 Hz, 2H), 1.29 – 1.22 (m, 14H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 157.6, 151.4, 141.3, 119.9, 106.9, 47.4, 37.3, 32.0, 29.7, 29.7, 29.7, 29.4, 26.1, 22.7, 21.0, 20.4, 14.2. GC-MS (EI+): 308 (M), 292 (M-CH_4), 167 ([N-ethyl-5-(methylthio)pyridin-2-amine]$^{\bullet}$).



***N*-(dodecan-2-yl)-5-(4-methylpiperazin-1-yl)pyridin-2-amine (16a)**

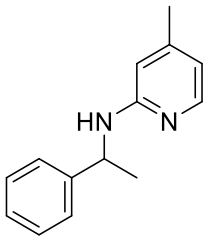
1-dodecene (34 mg, 0.20 mmol), 5-(4-methylpiperazin-1-yl)pyridin-2-amine (39 mg, 0.20 mmol), and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 5% MeOH in DCM. Yield = 34 mg (47%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.78 (d, *J* = 2.8 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.33 (d, *J* = 8.9 Hz, 1H), 4.18 (s, 1H), 3.63 (h, *J* = 6.4 Hz, 1H), 3.06 – 3.01 (m, 4H), 2.60 – 2.55 (m, 4H), 2.35 (s, 3H), 1.52 (ddd, *J* = 16.1, 12.2, 5.7 Hz, 1H), 1.44 (ddd, *J* = 13.0, 6.4, 4.2 Hz, 1H), 1.41 – 1.31 (m, 2H), 1.30 – 1.23 (m, 14H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 153.9, 139.4, 137.5, 129.3, 107.1, 55.3, 51.1, 47.8, 46.2, 37.4, 32.0, 29.8, 29.7, 29.4, 26.2, 22.8, 21.1, 14.2. GC-MS (EI+): 360 (M), 345 (M-CH_3), 219 ([N-ethyl-5-(4-methylpiperazin-1-yl)pyridin-2-amine]$^{\bullet}$).



***N*-(1-cyclohexylethyl)-4-methylpyridin-2-amine (17a)**

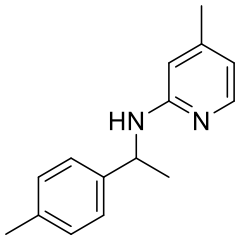
Vinylcyclohexane (27 μL, 22 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 μL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 20% ethyl acetate in hexanes. Yield = 28 mg (63%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 5.2 Hz, 1H), 6.40 (dd, *J* = 5.2, 1.4 Hz, 1H), 6.20 (s, 1H), 4.38 (d, *J* = 9.1 Hz, 1H), 3.64 (dt, *J* = 9.1, 6.3 Hz, 1H), 2.27 (s, 3H), 1.95 – 1.65 (m,

5H), 1.46 (ddp, *J* = 14.6, 8.6, 3.0 Hz, 1H), 1.35 – 0.99 (m, 9H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 148.6, 148.2, 114.2, 107.1, 51.9, 43.8, 29.9, 29.2, 26.9, 26.8, 26.7, 21.67, 18.2. GC-MS (EI+): 218 (M), 203 (M-CH_3).



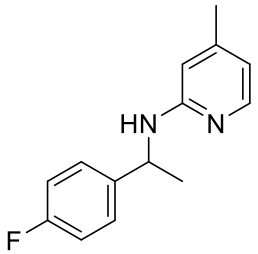
4-methyl-*N*-(1-phenylethyl)pyridin-2-amine (18a)

Styrene (23 µL, 21 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 27 mg (62%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 (m, *J* = 8.5, 6.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.39 (ddd, *J* = 5.1, 1.4, 0.7 Hz, 1H), 6.03 (dt, *J* = 1.6, 0.8 Hz, 1H), 4.92 (d, *J* = 6.4 Hz, 1H), 4.74 (p, *J* = 6.71 Hz, 1H), 2.13 (d, *J* = 0.7 Hz, 3H), 1.54 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 148.5, 147.9, 144.9, 128.75, 127.0, 125.9, 114.7, 107.1, 51.9, 24.4, 21.3. GC-MS (EI+): 212 (M), 197 (M-CH_3).



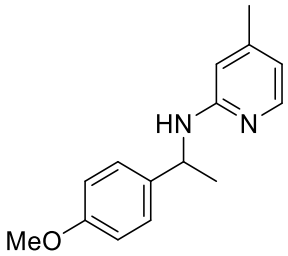
4-methyl-N-(1-(p-tolyl)ethyl)pyridin-2-amine (19a)

4-Methylstyrene (26 µL, 24 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 27 mg (59%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 5.2 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.39 (dd, *J* = 5.2, 1.4 Hz, 1H), 6.05 (s, 1H), 5.07 (d, *J* = 6.5 Hz, 1H), 4.72 (p, *J* = 6.6 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 148.7, 147.7, 141.9, 136.6, 129.4, 125.9, 114.7, 107.1, 51.6, 24.5, 21.4, 21.1. GC-MS (EI+): 226 (M), 211 (M-CH_3).



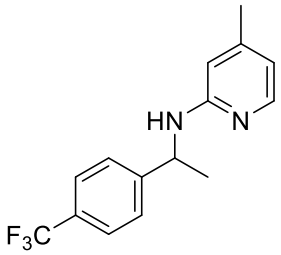
N-(1-(4-fluorophenyl)ethyl)-4-methylpyridin-2-amine (20a)

4-Fluorostyrene (24 µL, 25 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 120 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 26 mg (57%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 5.1, 0.7 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.03 – 6.95 (m, 2H), 6.40 (ddd, *J* = 5.2, 1.4, 0.7 Hz, 1H), 6.00 (dt, *J* = 1.6, 0.8 Hz, 1H), 4.91 (d, *J* = 6.4 Hz, 1H), 4.73 (p, *J* = 6.7 Hz, 1H), 2.14 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 161.1, 158.2, 148.6, 148.0, 140.7 (d, *J* = 3.0 Hz), 127.4 (d, *J* = 7.9 Hz), 115.5 (d, *J* = 21.4 Hz), 114.9, 107.1, 51.2, 24.5, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.18. GC-MS (EI+): 230 (M), 215 (M-CH_3).



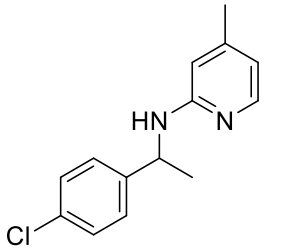
N-(1-(4-methoxyphenyl)ethyl)-4-methylpyridin-2-amine (21a)

4-Methoxystyrene (27 µL, 27 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 30 mg (61%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 6.88 – 6.82 (m, 2H), 6.38 (ddd, *J* = 5.2, 1.5, 0.7 Hz, 1H), 6.03 (dt, *J* = 1.6, 0.8 Hz, 1H), 4.91 (d, *J* = 6.5 Hz, 1H), 4.69 (p, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 2.14 (d, *J* = 0.7 Hz, 3H), 1.51 (d, *J* = 6.7 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 158.4, 148.5, 147.9, 137.0, 127.0, 114.6, 114.0, 107.1, 55.3, 51.3, 24.4, 21.3. GC-MS (EI+): 242 (M), 227 (M-CH_3).



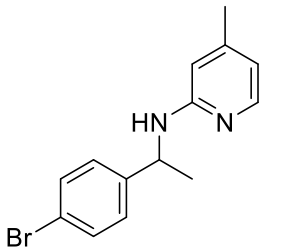
4-methyl-N-(1-(4-(trifluoromethyl)phenyl)ethyl)pyridin-2-amine (22a)

4-Trifluoromethylstyrene (30 µL, 34 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 120 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 33 mg (60%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.44 – 6.37 (m, 1H), 4.95 (b, 1H), 4.88 – 4.77 (p, *J* = 6.8 Hz, 1H), 2.14 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.0, 149.3, 148.7, 148.0, 129.3 (q, *J* = 32.1 Hz), 124.3 (q, *J* = 272.0 Hz), 126.3, 125.7, 115.1, 107.2, 51.5, 24.4, 21.3. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.37. GC-MS (EI+): 280 (M), 265 (M-CH_3).



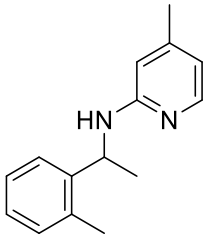
N-(1-(4-chlorophenyl)ethyl)-4-methylpyridin-2-amine (23a)

4-Chlorostyrene (24 µL, 28 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 120 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 24 mg (49%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 5.2 Hz, 1H), 7.35 – 7.21 (m, 4H), 6.39 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.99 (s, 1H), 4.99 (d, *J* = 6.4 Hz, 1H), 4.72 (p, *J* = 6.7 Hz, 1H), 2.13 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 148.6, 147.9, 143.6, 132.6, 128.8, 127.3, 114.9, 107.1, 51.3, 24.4, 21.3. GC-MS (EI+): 248 (M+2), 246 (M), 231 (M-CH_3).



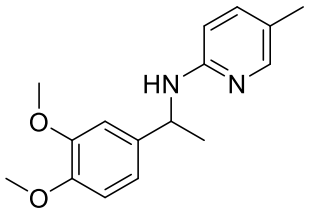
N-(1-(4-bromophenyl)ethyl)-4-methylpyridin-2-amine (24a)

4-Bromostyrene (26 µL, 37 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 120 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 20% ethyl acetate in hexanes. Yield = 27 mg (46%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 5.2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.30 – 7.19 (m, 2H), 6.41 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.99 (s, 1H), 4.89 (d, *J* = 6.2 Hz, 1H), 4.70 (p, *J* = 6.7 Hz, 1H), 2.14 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.1, 148.6, 148.0, 144.1, 131.8, 127.7, 120.7, 115.0, 107.1, 51.4, 24.4, 21.3. GC-MS (EI+): 292 (M+2), 290 (M), 275 (M-CH_3).



4-methyl-N-(1-(o-tolyl)ethyl)pyridin-2-amine (25a)

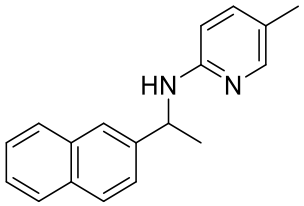
2-Methylstyrene (26 µL, 24 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 120 ˚C with stirring for 48 hours. The mixture was allowed to cool, and all of the volatile materials were removed. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 18 mg (40%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 5.1 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.20 – 7.11 (m, 3H), 6.38 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.92 (d, *J* = 1.5 Hz, 1H), 4.97 – 4.89 (m, 1H), 4.82 (d, *J* = 6.5 Hz, 1H), 2.44 (s, 3H), 2.13 (s, 3H), 1.50 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 148.5, 148.0, 142.6, 135.0, 130.7, 126.9, 126.6, 124.8, 114.7, 106.8, 48.3, 22.6, 21.4, 19.2. GC-MS (EI+): 226 (M), 211 (M-CH_3).



***N*-(1-(3,4-dimethoxyphenyl)ethyl)-5-methylpyridine-2-amine (26a)**

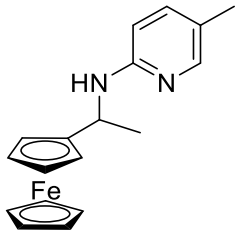
3,4-dimethoxy-vinylbenzene (33 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 µL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 30% ethyl acetate in hexanes. Yield = 35 mg (64%).

^{1}H NMR (600 MHz, chloroform-*d*) δ 7.90 (s, 1H), 7.16 (d, J = 10.0 Hz, 1H), 6.90 (d, J = 10.7 Hz, 2H), 6.81 (d, J = 8.1 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 4.76 (d, J = 5.5 Hz, 1H), 4.61 (p, J = 6.5 Hz, 1H), 3.85 (s, 6H), 2.14 (s, 3H), 1.52 (d, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.1, 149.1, 147.8, 147.4, 138.5, 137.4, 121.8, 117.7, 111.1, 109.0, 106.4, 55.8, 55.8, 51.9, 24.4, 17.3. GC-MS (EI+): 272 (M), 267 (M-CH_3), 165 (M-[p-Me-aminopyridine]•).



***N*-(ethyl-naphthalene-2-yl)-5-methylpyridin-2-amine (27a)**

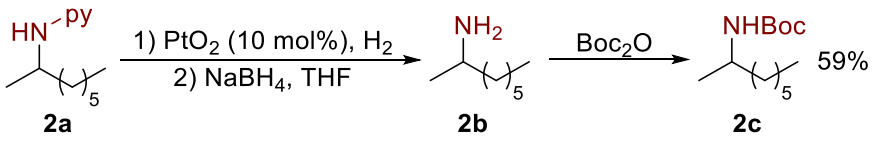
Vinyl naphthalene (31 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 μL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 34 mg (65%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.93 – 7.90 (m, 1H), 7.84 – 7.77 (m, 4H), 7.50 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.45 (pd, *J* = 6.8, 1.5 Hz, 2H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.16 (d, *J* = 8.5 Hz, 1H), 4.95 (d, *J* = 5.9 Hz, 1H), 4.83 (p, *J* = 6.6 Hz, 1H), 2.12 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.4, 148.0, 142.5, 138.5, 133.6, 132.8, 128.6, 127.9, 127.7, 126.1, 125.6, 124.5, 124.3, 122.0, 106.5, 52.4, 24.6, 17.4. GC-MS (EI+): 262 (M), 155 (M-[p-Me-aminopyridine]•).



N-(ethylferrocene-2-yl)-5-methylpyridin-2-amine (28a)

Vinyl ferrocene (42 mg, 0.20 mmol), 2-amino-5-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3(NTf_2)_2$ (20 mg, 0.010 mmol, 10 mol%), 1,2-DCB (60 μL) and a magnetic stir bar were combined in a one dram vial. The vial threads were wrapped with 1 layer of Teflon tape and the resulting mixture was heated at 100 ˚C with stirring for 48 hours. The reaction was allowed to cool, and all of the volatile materials were evaporated. The crude product was purified by silica gel chromatography, eluting with 40% ethyl acetate in hexanes. Yield = 39 mg (61%). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.95 (s, 1H), 7.27 – 7.24 (m, *J* = 2.0 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 4.66 (m, 1H), 4.55 (d, *J* = 8.2 Hz, 1H), 4.20 (s, 5H), 4.18 (m, 2H), 4.13 (dt, *J* = 7.7, 1.7 Hz, 2H), 2.18 (s, 3H), 1.52 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 156.4, 147.9, 138.5, 121.5, 107.0, 93.3, 68.5, 67.8, 67.6, 67.0, 66.1, 45.7, 21.3, 17.5. GCMS: (EI+): 320 (M), 305 (M-CH_3), 213 (M-[p-Me-aminopyridine]•).

5. Removal of Pyridyl Group from the Hydroamination Product



5-methyl-*N*-(octan-2-yl)pyridine-2-amine **2a** (44 mg, 0.20 mmol), HCl in dioxane (4.0 M, 0.10 mL, 2.0 equiv), ethanol (2.0 mL) and a stir bar were combined in a reaction tube. The tube was capped with a septum-cap and stirred for 15 minutes. PtO_2 (4.6 mg, 10 mol%) was added to the tube and the tube was capped and sealed. The tube was purged with H_2 for 10 minutes using a hydrogen balloon and placed in a cold bath set at 0 ℃. After 15 hours, the mixture was filtered through celite and the solvent was removed *in vacuo*. The residue was dissolved in 1.0 mL of THF and 0.2 mL of EtOH and placed in in a cold bath set at 0 ℃. Sodium borohydride (76 mg, 2.0 mmol, 10 equiv) was added to the mixture and the mixture was allowed to stir for 2 hours. Water (10 mL) was added to the mixture and the mixture was extracted with DCM (10 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was then removed *in vacuo* and the residue was dissolved in 2.0 mL of THF. Boc_2O (87 mg, 0.40 mmol, 2.0 equiv) and 4-Dimethylaminopyridine (2.4 mg, 0.020 mmol, 0.10 equiv) was added to the mixture and the mixture was stirred overnight. The solvent was removed and the crude Boc-protected amine product **2c** was purified by column chromatography, eluting with 10% ethyl acetate in hexanes. Yield = 27 mg (59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 (s, 1H), 3.64 (s, 1H), 1.46 (s, 9H), 1.37-1.42 (m, 2H), 1.35 – 1.23 (m, 8H), 1.11 (d, J = 6.6 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H).

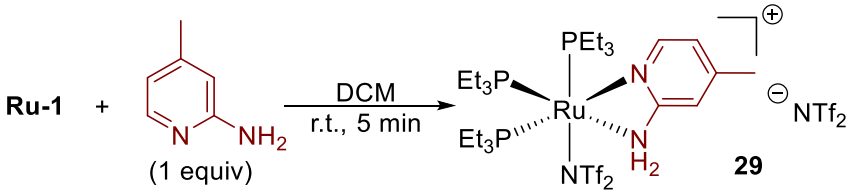
6. Determination of the Catalyst Resting State

Initial Investigation of the Catalyst Resting State

$Ru(PEt_3)_3(NTf_2)_2$ (**Ru-1**) (10 mg, 0.010 mmol) were combined with D_4-DCB (0.50 mL) and appropriate amount of 2-amino-4-methylpyridine **(1b)** and dodecane in a J-young tube. The tube was heated at 80 ˚C for 4 hours and a ^{31}P NMR spectrum of the mixture was taken at 80 ˚C.

Independent Synthesis of the Catalyst Resting State

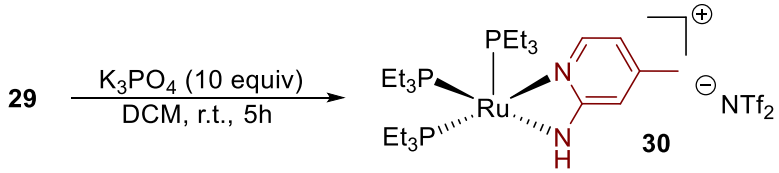
$Ru(PEt_3)_3$(amine)$(NTf_2)_2$ (29)



$Ru(PEt_3)_3(NTf_2)_2$ (**Ru-1**) (51 mg, 0.050 mmol), 2-amino-5-methylpyridine (5.4 mg, 0.050 mmol) and DCM (2.0 mL) were combined in a 20-mL vial and stirred at room temperature for 5 minutes. The mixture turned bright yellow. The solvent was removed under vacuum and the resulting yellow solid was washed with cold diethyl ether three times. Single crystals suitable for x-ray crystallography analysis was obtained by cooling a DCM/^{i}Pr$_2$O saturated solution of $Ru(PEt_3)_3$(amine)$(NTf_2)_2$ (**29**). Yield = 46 mg (82%). ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 8.16 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 5.14 (s, 2H), 2.44 (s, 3H),

2.00 – 1.80 (m, 18H), 1.15 (m, 24H). ^{31}P NMR (162 MHz, Methylene Chloride-d_2) δ 38.33. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -78.19. The identity of the product was confirmed by x-ray crystallography. Anal. Calc'd C:28.64 H:4.44 N:4.99 Found C:28.51 H:4.46 N:4.61.

Ru(PEt$_3$)$_3$(amido)(NTf$_2$) (30)



Ru(PEt$_3$)$_3$(amine)(NTf$_2$)$_2$ (**29**) (56 mg, 0.050 mmol), anhydrous K_3PO_4 (0.11 g, 0.50 mmol, 10 equiv) and DCM (3.0 mL) were combined in a 20-mL vial and stirred at room temperature for 5 hours. The black mixture was then filtered, and the solvent was removed under vacuum. The resulting black oil was triturated with cold ^{i}Pr$_2$O three times to afford black powder. Single crystals suitable for x-ray crystallography analysis was obtained by cooling a DCM/^{i}Pr$_2$O saturated solution of Ru(PEt$_3$)$_3$(amido)(NTf$_2$) (**30**). Yield = 36 mg (85%). ^{1}H NMR (600 MHz, Methylene Chloride-d_2) δ 7.34 (d, J = 5.6 Hz, 1H), 6.06 (d, J = 5.6 Hz, 1H), 5.56 (s, 1H), 4.64 (s, 1H), 2.05 (s, 3H), 1.79 (m, 18H), 1.17 (m, 24H). ^{31}P NMR (243 MHz, Methylene Chloride-d_2) δ 51.95. ^{19}F NMR (376 MHz, Methylene Chloride-d_2) δ -78.76. The identity of the product was confirmed by x-ray crystallography. Anal. Calc'd C:36.60 H:5.94 N:5.09 Found C:36.87 H:6.11 N:5.03.

Examination of the kinetic Competence of Ru(PEt$_3$)$_3$(amido)(NTf$_2$)

1-Dodecene (44 μL, 34 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), and Ru(PEt$_3$)$_3$(amido)(NTf$_2$) (**30**) (8.4 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial was capped, and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The mixture was allowed to cool to room temperature and an NMR yield (65%) of this reaction was obtained using 1,3,5-trimethoxybenzene as the internal standard.

Variable Temperature NMR Spectroscopy Analysis of the Mixture of Ru(PEt$_3$)$_3$(amido)(NTf$_2$) and 2-amino-4-methylpyridine

Ru(PEt$_3$)$_3$(amido)(NTf$_2$) (**30**) (8.4 mg, 0.010 mmol) and 2-amino-4-methylpyridine (22 mg, 0.20 mmol) and were combined with D$_4$-DCB (0.50 mL) in a J-young tube. The mixture turned black and ^{1}H (Figure S1) and ^{31}P NMR spectra of the mixture were taken at 80 ˚C, 60 ˚C, 40 ˚C and 25 ˚C. Ru(PEt$_3$)$_3$(amido)(NTf$_2$) (**30**) (8.4 mg, 0.010 mmol) and 2-amino-4-methylpyridine (22 mg, 0.20 mmol) and were combined with D$_2$-DCM (0.50 mL) in a J-young tube. The mixture turned black and ^{31}P NMR spectra of the mixture was taken at 0 ˚C, -20 ˚C, and -40 ˚C.

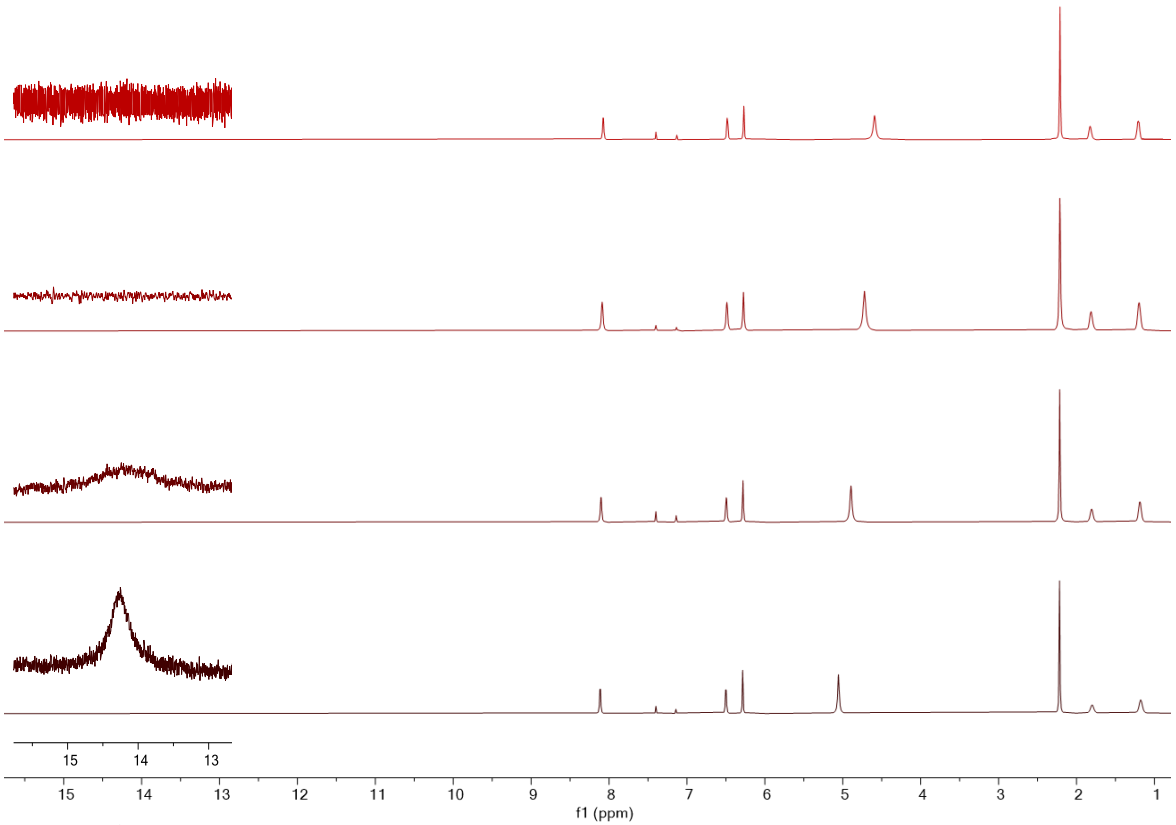
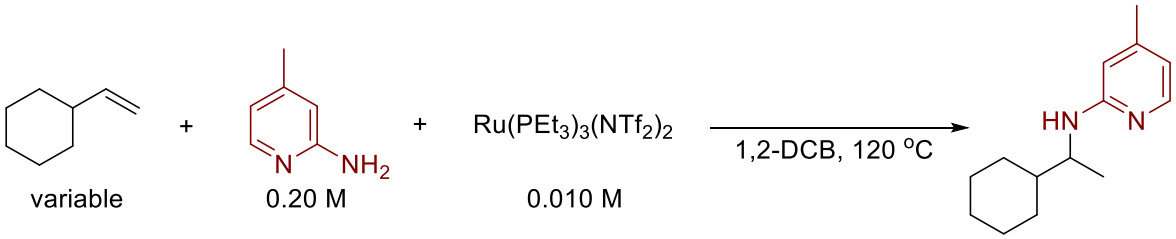


Figure S1. ^{1}H NMR spectra of the mixture of complex **30** and aminopyridine **1b** (20 equiv) at 80 ˚C, 60 ˚C, 40 ˚C and 25 ˚C (from top to bottom).

7. Kinetic Studies of Catalytic Hydroamination

All samples for kinetic experiments were prepared and analyzed according to the following procedures. In a nitrogen-filled glovebox, an appropriate amount of vinylcyclohexane, 2-amino-4-methylpyridine, $Ru(PEt_3)_3(NTf_2)_2$ and 1,3,5-trimethoxybenzene (internal standard) were mixed in a 1.0 mL volumetric flask. Then, 1,2-dichlorobenzene was added to prepare a 1.0 mL solution. The mixture was then transferred into a Schlenk tube equipped with a magnetic stir bar. A t_0 aliquot was then taken and the tube was sealed and heated in an oil bath at 120 ˚C outside the glovebox. The Schlenk tube was removed from the oil bath after a certain amount of time of heating and rapidly cooled. The mixture was then taken into the glovebox, and a 50 µL aliquot was removed from the mixture. The tube was resealed and returned to the oil bath. The aliquots were analyzed by ^{1}H NMR spectroscopy and concentrations were determined by integration relative to the 1,3,5-trimethoxybenzene internal standard. Initial reaction rates were subsequently determined by measuring product formation at low conversion (<10%).

Order in vinylcyclohexane (Figure S2-S5)



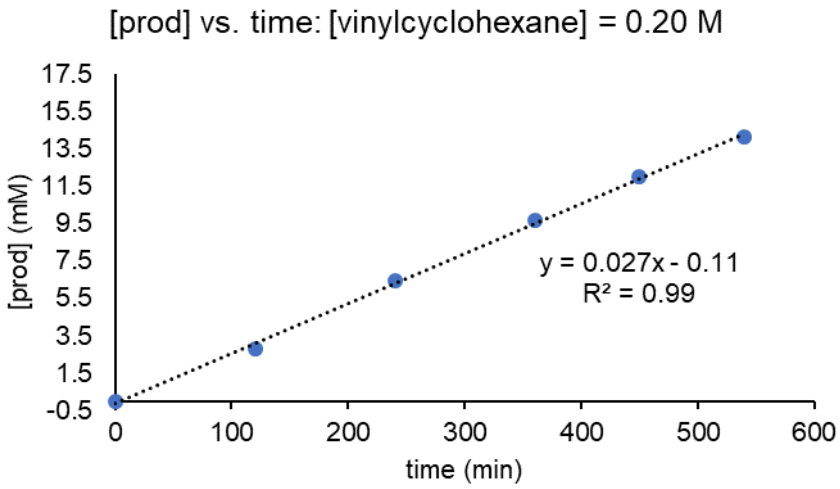


Figure S2. Rate of product formation as a function of time when [vinylcyclohexane] = 0.20 M.

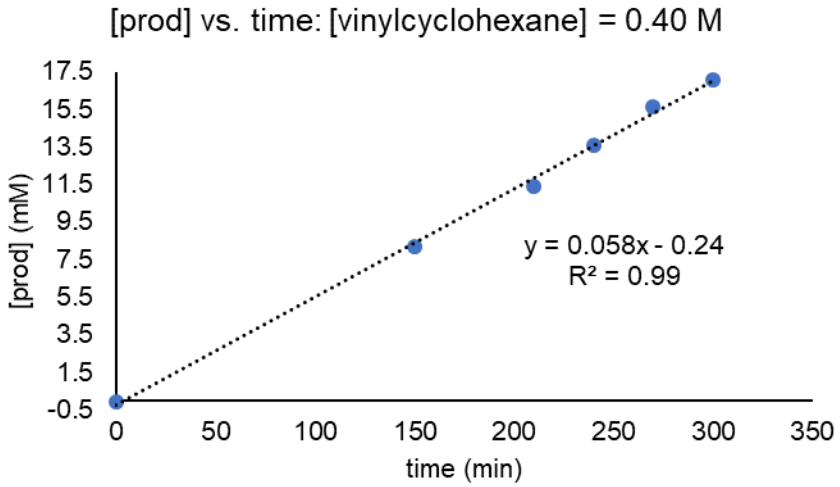


Figure S3. Rate of product formation as a function of time when [vinylcyclohexane] = 0.40 M.

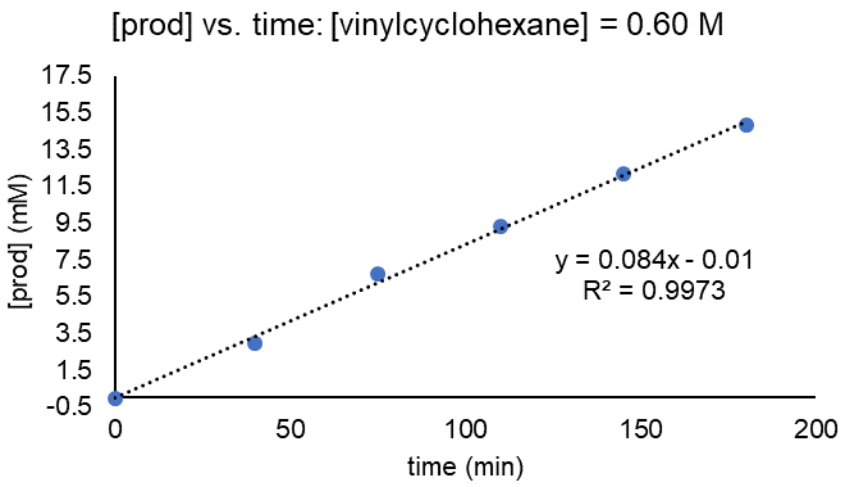


Figure S4. Rate of product formation as a function of time when [vinylcyclohexane] = 0.60 M.

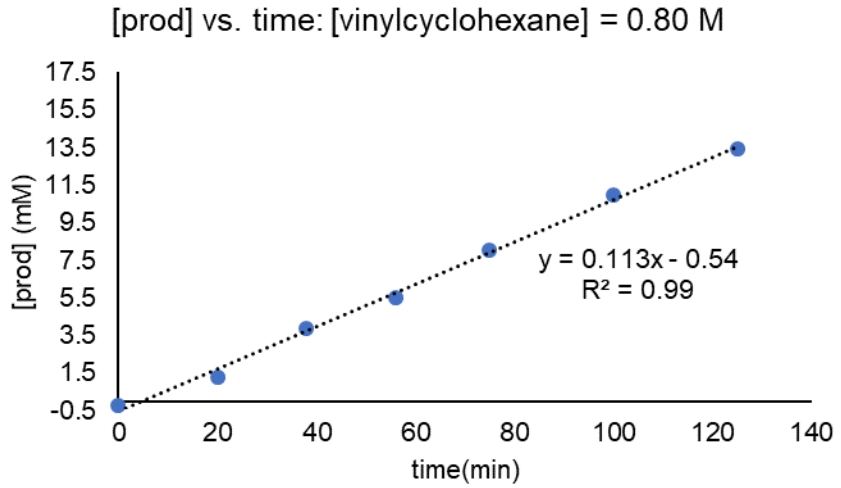
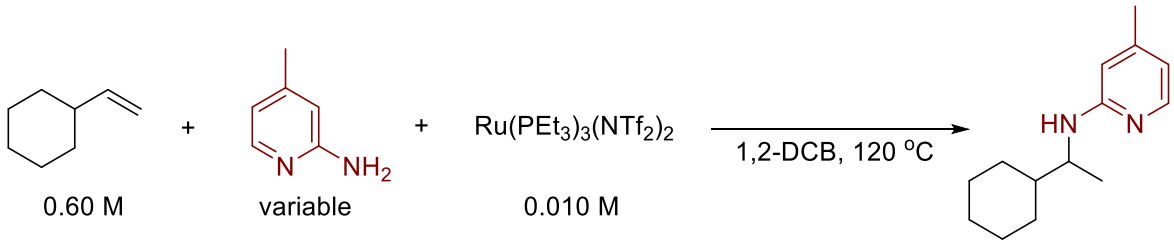


Figure S5. Rate of product formation as a function of time when [vinylcyclohexane] = 0.80 M.

Order in 2-amino-4-methylpyridine (1b) (Figure S6-S9)



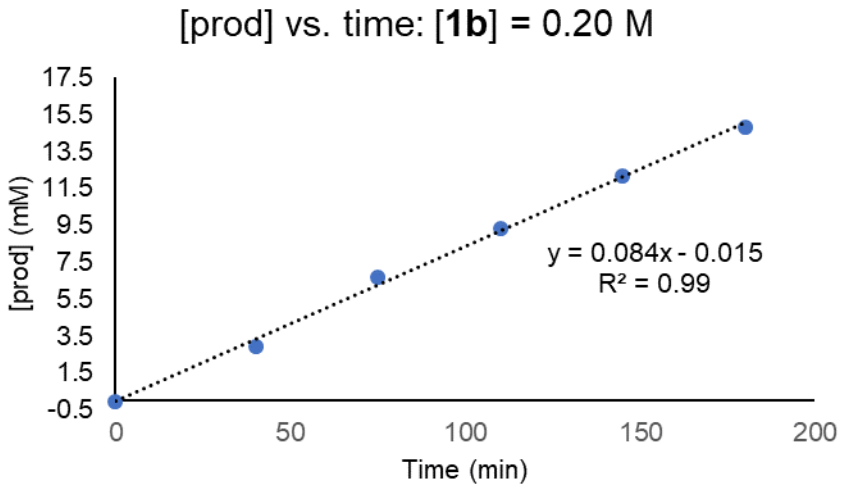


Figure S6. Rate of product formation as a function of time when [**1b**] = 0.20 M.

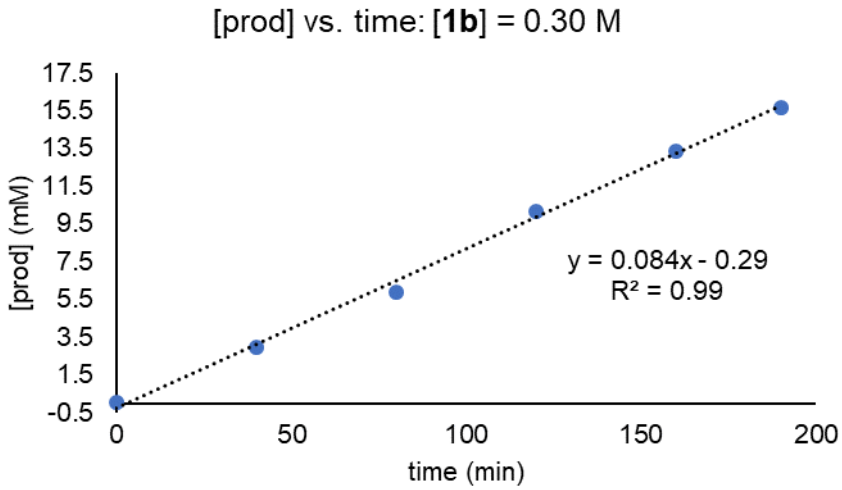


Figure S7. Rate of product formation as a function of time when [**1b**] = 0.30 M.

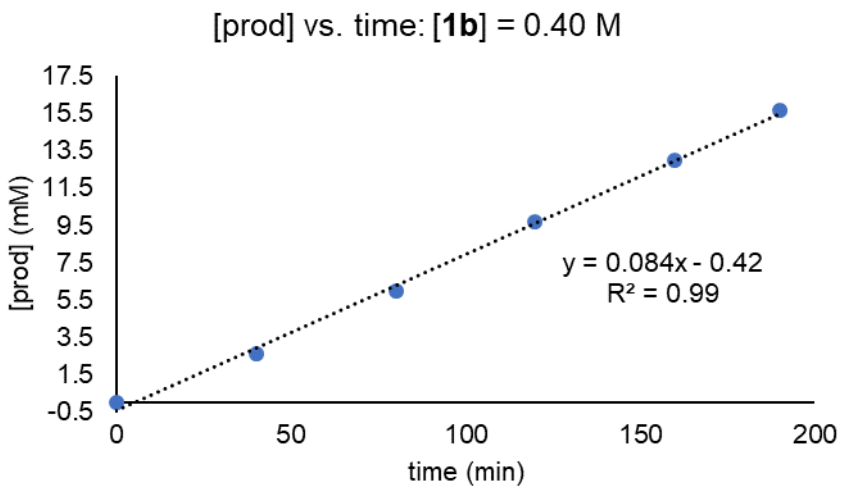


Figure S8. Rate of product formation as a function of time when [**1b**] = 0.40 M.

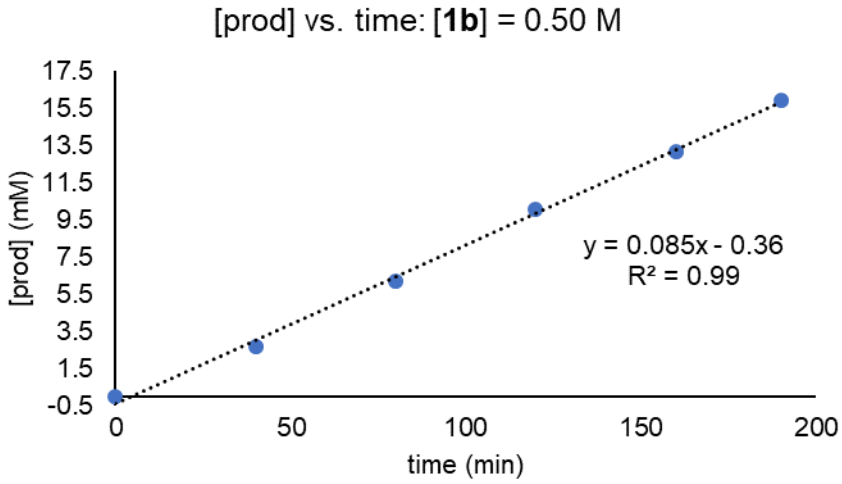
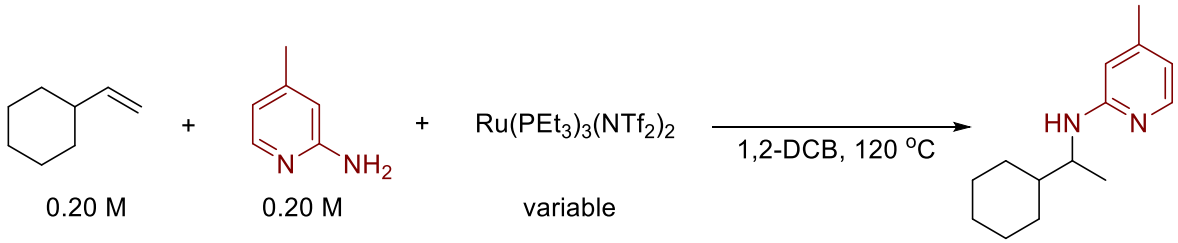


Figure S9. Rate of product formation as a function of time when [**1b**] = 0.50 M.

Order in $Ru(PEt_3)_3(NTf_2)_2$ (Ru-1) (Figure S10-S13)



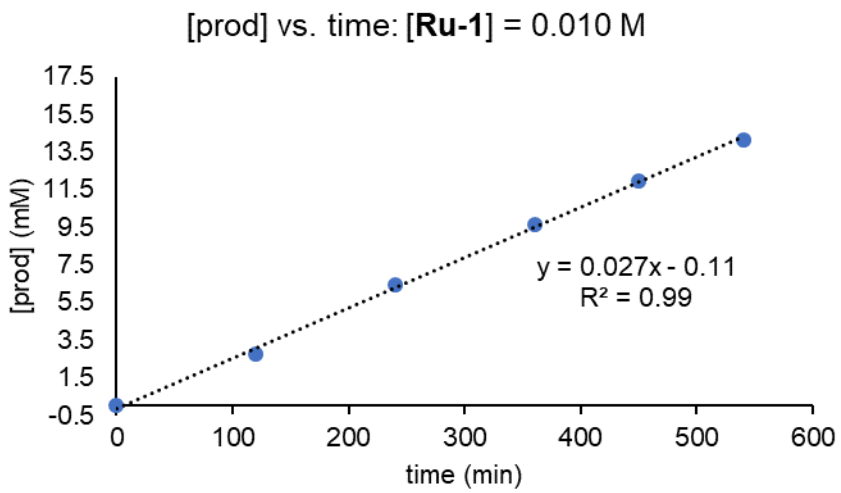


Figure S10. Rate of product formation as a function of time when [**Ru-1**] = 0.010 M.

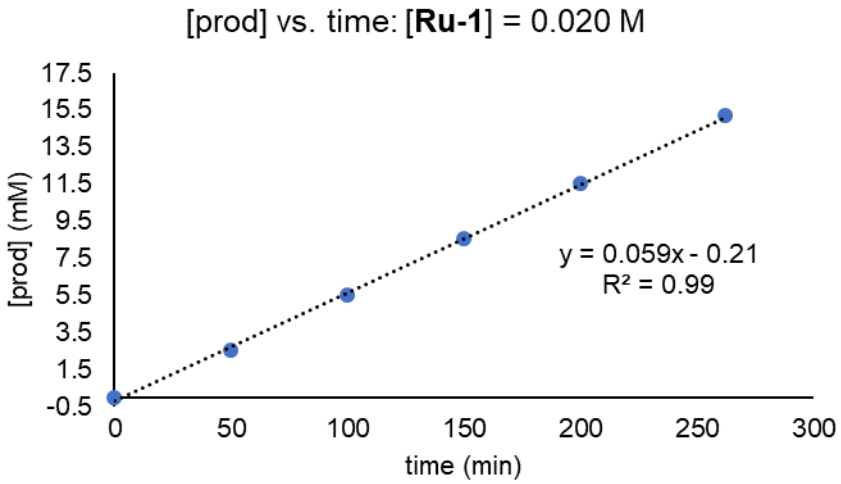


Figure S11. Rate of product formation as a function of time when [**Ru-1**] = 0.020 M.

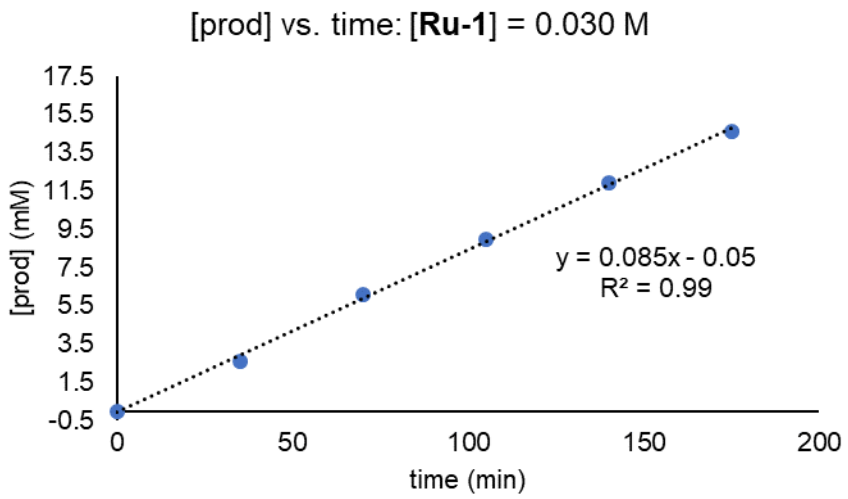


Figure S12. Rate of product formation as a function of time when [**Ru-1**] = 0.030 M.

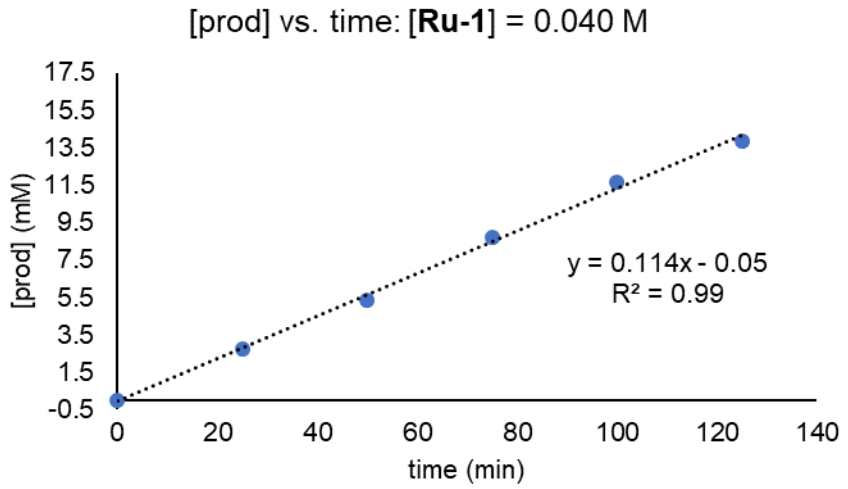
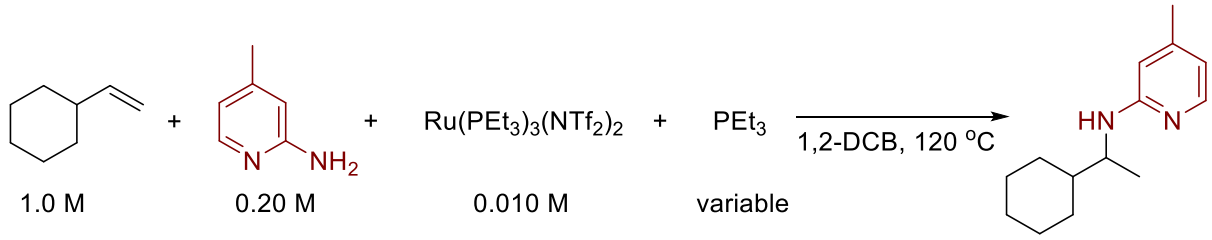


Figure S13. Rate of product formation as a function of time when [**Ru-1**] = 0.040 M.

Order in PEt_3 (Figure S14-S17)



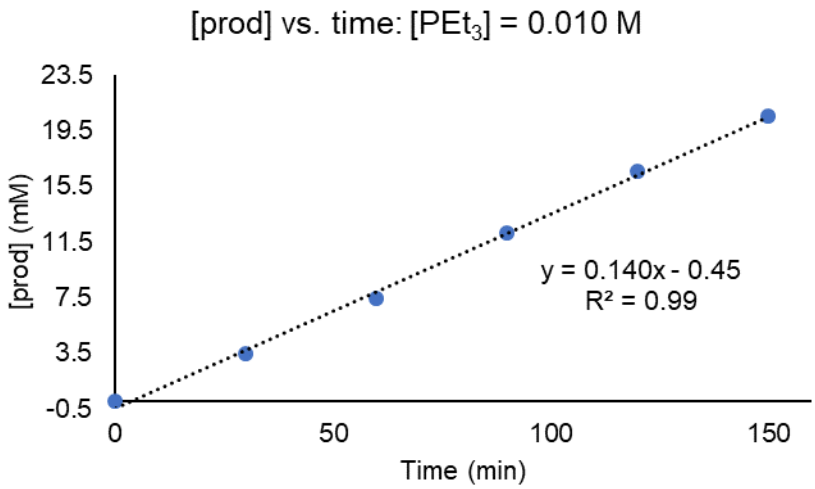


Figure S14. Rate of product formation as a function of time when [PEt_3] = 0.010 M.

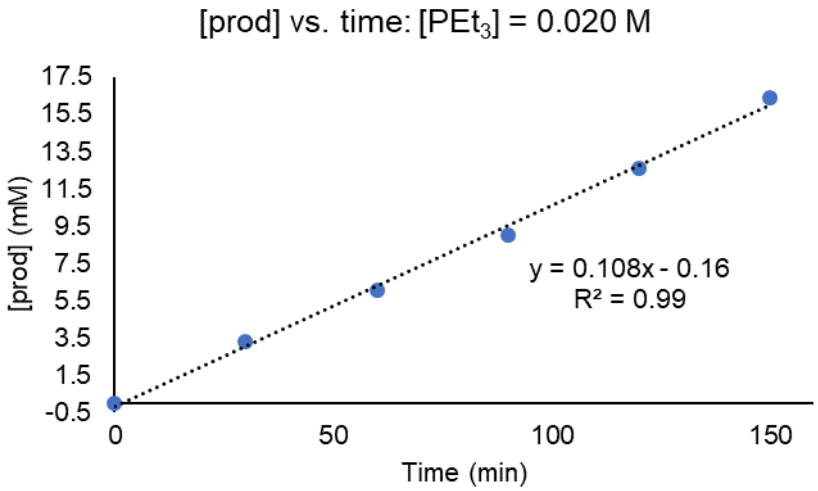


Figure S15. Rate of product formation as a function of time when [PEt_3] = 0.020 M.

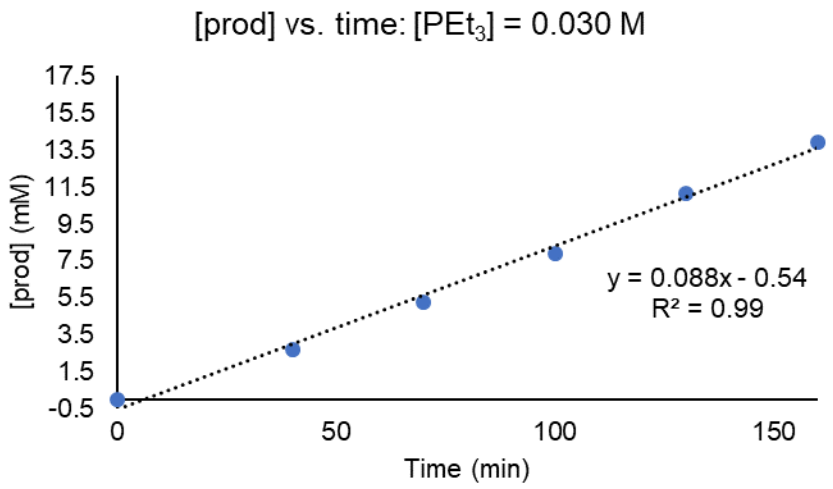


Figure S16. Rate of product formation as a function of time when [PEt_3] = 0.030 M.

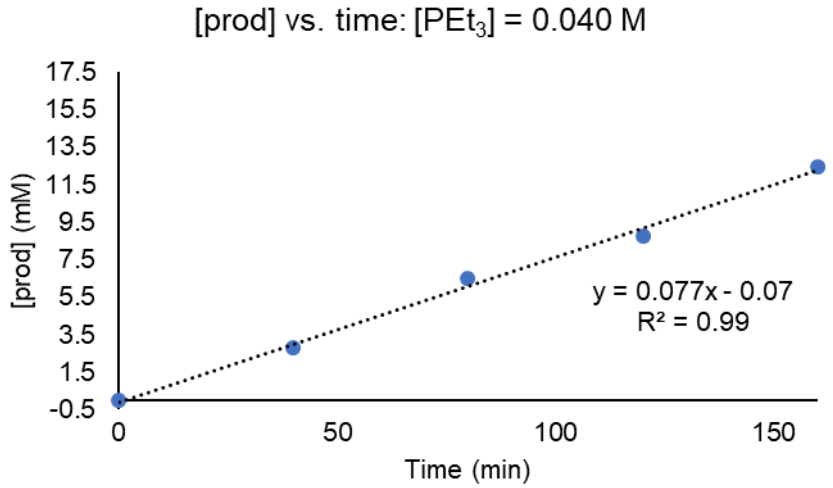
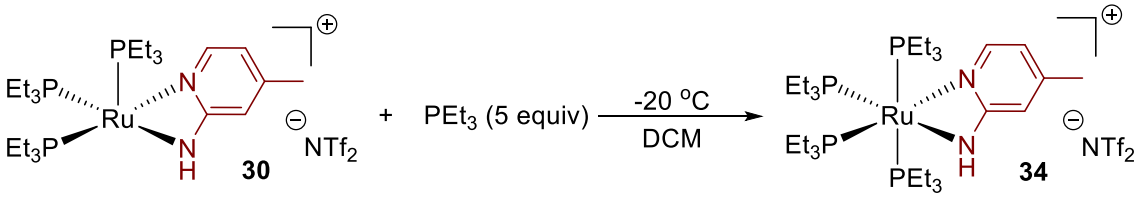


Figure S17. Rate of product formation as a function of time when [PEt_3] = 0.040 M.

8. Studies on the Origin of PEt_3 Inhibition

Low Temperature NMR Spectroscopy



$Ru(PEt_3)_3$(amido)(NTf_2) (**30**) (8.4 mg, 0.010 mmol), PEt_3 (5.9 mg, 7.4 µL, 0.050 mmol) were combined with CD_2Cl_2 (0.50 mL) in a J-young tube and ^{31}P NMR spectrum of this mixture was acquired at -20 ˚C (Figure S18).

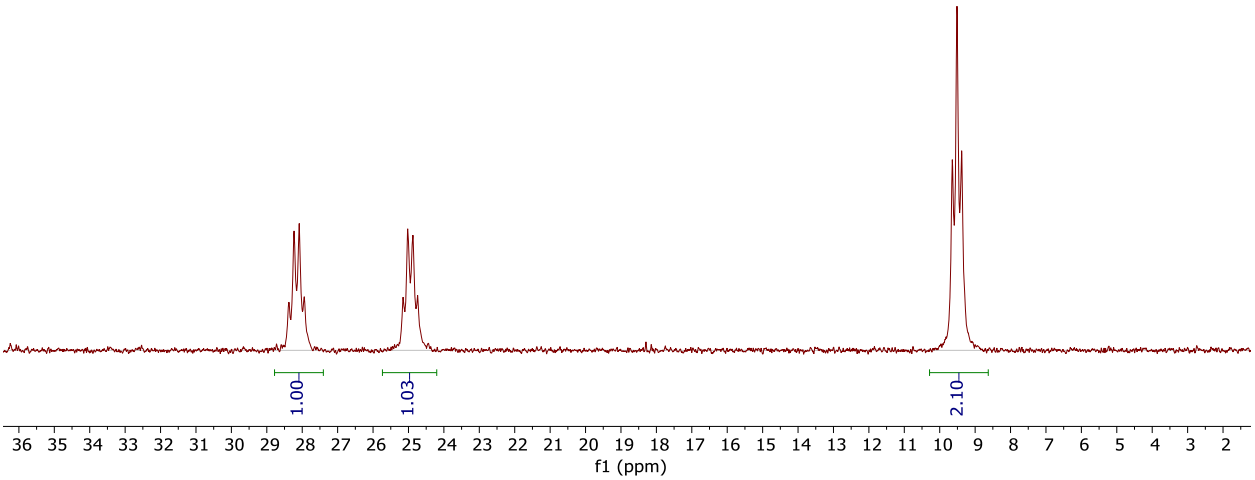
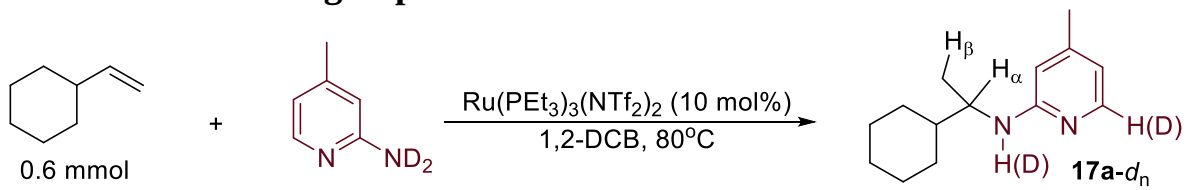


Figure S18. Low T NMR spectrum of Ru-amido complex with excess PEt_3 (the PEt_3 peak is not shown for clarity).

9. Deuterium Labelling Experiment

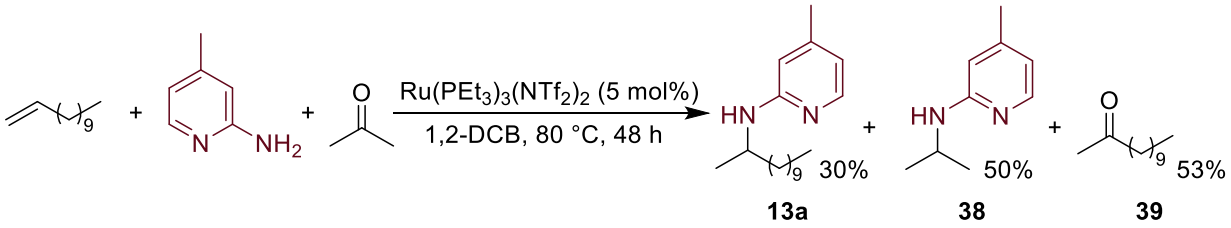


In a nitrogen-filled glovebox, vinylcyclohexane (66 µL, 53 mg, 0.48 mmol), 2-amino-4-methylpyridine-D_2 (66 mg, 0.60 mmol, 80% deuteration), $Ru(PEt_3)_3(NTf_2)_2$ (49 mg, 0.050 mmol, 10 mol%), 1,3,5-trimethoxybenzene (11 mg, 0.060 mmol) and DCB-D_4 (11 mg, 0.070 mmol) were dissolved in DCB (0.32 mL) in a 4 mL vial. After all the solid material was dissolved, the mixture was evenly distributed into 4 vials equipped with a stir bar. The mixture in each vial was heated at 80 ˚C for 0, 24, 36 and 48 hours respectively and analyzed by ^1H and ^2H NMR spectroscopy (Table S1).

Reaction Time	% Yield	%D at H_α position	%D at H_β position
24h	13%	29%	29%
36h	18%	31%	32%
48h	25%	29%	28%

Table S1. % Yield and % D incorporation at H_α and H_β position at 24, 36 and 48h of the reaction between vinylcyclohexane and 2-amino-4-methylpyridine-D_2.

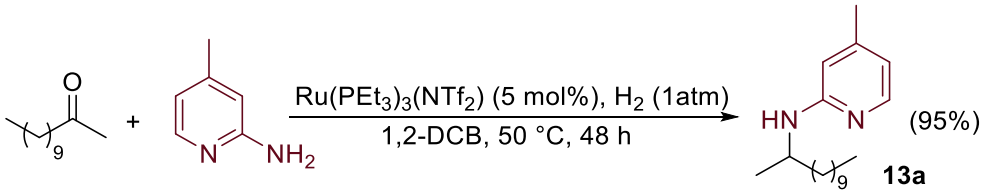
10. Catalytic Hydroamination with Acetone as an Additive



1-Dodecene (44 μL, 34 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), acetone (15 μL, 0.20 mmol) and $Ru(PEt_3)_3(NTf_2)_2$ (10 mg, 0.010 mmol, 5.0 mol%) were combined with DCB (60 μL) and a magnetic stir bar in a one dram vial. The vial was capped, and the resulting mixture was heated at 80 ˚C with stirring for 48 hours. The mixture was allowed to cool and analyzed by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard and gas chromatography.

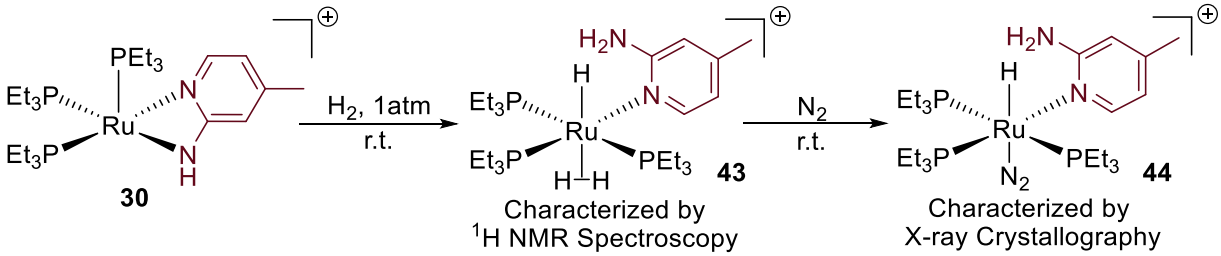
11. Synthesis, Characterization, and Reactivity of the Hydridoruthenium Intermediate

Catalytic Imine Hydrogenation with $Ru(PEt_3)_3(NTf_2)_2$



2-dodecanone (37 mg, 0.20 mmol), 2-amino-4-methylpyridine (22 mg, 0.20 mmol), $Ru(PEt_3)_3$(amido)(NTf_2) (8.4 mg, 0.010 mmol, 5.0 mol%), 1,2-DCB (0.20 mL) and a magnetic stir bar were combined in a sealed tube equipped with a H_2 balloon. The flask was heated at 50 ˚C with stirring for 48 hours. The mixture was allowed to cool and analyzed by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

Synthesis of the Potential Intermediate for Imine Hydrogenation



$Ru(PEt_3)_3$(amido)$(NTf_2)_2$ (**30**) (17 mg, 0.020 mmol) was dissolved in DCB-D_4 (0.50 mL) in a J-young tube. The tube was then sealed and connected to a Schlenk manifold and the N_2 atmosphere in the tube was removed by freeze-pump-thaw. H_2 (1.0 atm) was added to the tube and the mixture was allowed to warm to room temperature. The mixture turned yellow, and was analyzed by NMR spectroscopy (88% NMR yield before crystallization). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, J = 5.5 Hz, 1H), 6.38 (s, 1H), 6.20 (d, J = 5.5 Hz, 1H), 5.91-6.68 (s, 2H), 2.19 (s, 3H), 1.55 – 1.21 (m, 18H), 1.02 (dp, J = 22.2, 7.7 Hz, 27H), -2.98 (s, 2H), -9.22 (q, J = 21.7

Hz, 1H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 39.45, 28.16. Single crystals suitable for x-ray crystallography analysis was obtained by layering $^{i}Pr_2O$ and pentane onto the mixture. Due to the instability of this hydridoruthenium aminopyridyl complex **44**, we were unable to obtain high quality NMR spectroscopic data.

12. DFT Computational Studies

Initial conformational search and preoptimization of all reported structures were conducted using the (Geometry, Frequency, Noncovalent, eXtended Tight Binding") GFN-xTB method to account for the conformational flexibility of the triethylphosphine ligands.[3] The GFN2-xTB implementation of DFT tight binding was used and CREST was used for conformational search.[4-6] The ten GFN2-xTB optimized structures that was found by CREST with the lowest energies were then used as inputs for subsequent DFT optimization.

All DFT calculations were performed with the Gaussian 16 software package. Geometry optimization for all reported structures were performed in the gas-phase using the B3LYP-D3BJ /[6-31G+(d) + Lanl2dz (for Ru)] level of theory with the corresponding Hay-Wadt effective core potential for Ru and Grimme's empirical dispersion correction with Becke-Johnson damping for B3LYP.[7] Frequency calculations were performed on all reported structures to ensure that each minimum-energy structure has no imaginary frequencies and each transition state (TS) structure has precisely one imaginary frequency. Thermal corrections for Gibbs free energy (G) and enthalpy (H) were calculated at the same level of theory and the free energies were corrected at 353.15 K.[8] The electronic energy of every optimized structure was further recalculated under the B3LYP-D3BJ/[6-311+G(d,p) + SDD (for Ru)] level of theory. Bulk solvent effects were taken into consideration for single point energy calculations using the self-consistent reaction field SMD model (IEF-SMD) with chlorobenzene as the solvent.[9] The thermal corrections were applied to the recalculated electronic energies to give the final Gibbs free energy and enthalpy values.

Energy Data for all Reported Structures

Structures	E (Hartree)	ZPE (Hartree)	H (Hartree)	qh-G (Hartree)	Imaginary Frequency (cm^{-1})
Propene	-117.954319	-117.839391	-117.834906	-117.9012	-
1b	-343.108724	-342.876285	-342.867932	-343.01048	-
Enamine	-459.863233	-459.541634	-459.529619	-459.70979	-
Imine	-459.866639	-459.551747	-459.539461	-459.71122	-
Product	-461.093957	-460.749437	-460.736895	-460.91768	-
30	-2175.003901	-2172.772013	-2172.728276	-2174.3525	-
32	-2292.961218	-2290.616426	-2290.569029	-2292.2278	-
TS1	-2292.941595	-2290.601895	-2290.555350	-2292.2079	-317.14
33	-2292.97462	-2290.634056	-2290.586816	-2292.2408	-
TS2	-2292.954251	-2290.611982	-2290.565490	-2292.2229	-675.89
45	-2292.971315	-2290.629788	-2290.581564	-2292.2443	-
46	-2176.216361	-2173.964766	-2173.920112	-2175.5462	-

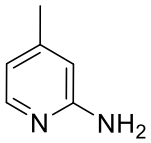
Table S2. Electronic energies (E), zero-point energy corrections (ZPE), enthalpies (H), quasi-harmonic Gibbs free energies calculated at T = 353.15 K (qh-G), and imaginary frequencies of all reported structures.

Cartesian Coordinates (Å) of Optimized Structures

Propene

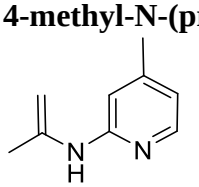
C	-1.28406500	-0.22563000	-0.00001400
H	-1.29932000	-1.31508800	-0.00005000
H	-2.24911000	0.27458000	-0.00000100
C	-0.13787900	0.46174400	0.00001200
H	-0.18438100	1.55116000	0.00004700
C	1.24131500	-0.15856800	0.00000200
H	1.39546000	-0.79065500	-0.88371300
H	2.02560000	0.60527300	-0.00007300
H	1.39552300	-0.79054300	0.88378700

2-amino-4-methylpyridine (1b)



C	-0.17223800	1.73587100	0.00297100
C	1.09708300	1.17006600	0.00476600
C	1.20812700	-0.23240400	0.00135600
C	0.03309600	-0.97481300	-0.00708600
C	-1.20890700	-0.30551500	-0.00701700
N	-1.31276700	1.03013600	0.00176900
H	-0.29218300	2.81770900	0.00712400
H	1.98143600	1.80094200	0.01027000
H	0.06601300	-2.06170800	-0.02373000
C	2.55914800	-0.90161200	0.00244200
H	3.14255100	-0.60542100	-0.87791900
H	3.13889600	-0.61176000	0.88735800
H	2.46819300	-1.99236300	-0.00197500
N	-2.39959600	-1.01293700	-0.06880600
H	-2.39936500	-1.95095600	0.30905100
H	-3.21685800	-0.46639700	0.17449100

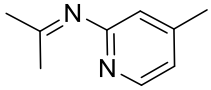
4-methyl-N-(prop-1-en-2-yl)pyridin-2-amine (Enamine)



C	-1.31701700	1.76455800	0.00032300

C	-2.47834100	1.00608800	0.00021900
C	-2.36369200	-0.39833300	-0.00004200
C	-1.08688600	-0.93843700	-0.00015200
C	0.03903700	-0.07882700	0.00003500
N	-0.07482100	1.25303200	0.00023400
H	-1.37078300	2.85180200	0.00049800
H	-3.45221200	1.48742200	0.00032900
H	-0.94829400	-2.01788400	-0.00037900
C	-3.58991100	-1.27504800	-0.00021900
H	-4.21077900	-1.07872500	0.88247000
H	-4.21078700	-1.07835500	-0.88281900
H	-3.32600300	-2.33732800	-0.00044100
N	1.29728200	-0.65695000	-0.00001000
H	1.28553800	-1.66711800	-0.00023400
C	3.65415200	-1.14870100	0.00048500
H	3.57812200	-1.79252000	0.88800200
H	3.57739500	-1.79446100	-0.88556300
H	4.64614600	-0.69188700	-0.00045300
C	2.58059300	-0.08624500	-0.00018500
C	2.87098200	1.22688700	-0.00068100
H	3.91408700	1.52592400	-0.00070000
H	2.10682700	1.98890700	-0.00097200

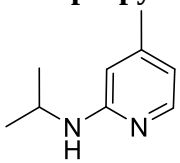
N-(4-methylpyridin-2-yl)propan-2-imine (Imine)



C	1.30737900	1.72942400	-0.35818100
C	2.43384200	0.96695000	-0.06674200
C	2.29078100	-0.42129900	0.09666500
C	1.01288100	-0.95302300	-0.05259100
C	-0.07222300	-0.09889500	-0.32239300
N	0.06926500	1.22692900	-0.47834600
H	1.39457600	2.80504200	-0.50226900
H	3.40777800	1.44135100	0.02130600
H	0.83258200	-2.02055900	0.03121100
C	3.47926900	-1.29552200	0.40695100
H	4.25717500	-1.18688700	-0.35849700
H	3.92940400	-1.01784700	1.36815500
H	3.19671200	-2.35149100	0.45757600
N	-1.33190100	-0.67931200	-0.52111800
C	-2.38935000	-0.23799400	0.05165900
C	-2.45443800	0.86636500	1.08272200
H	-2.71942100	1.81184000	0.59377000
H	-3.23148900	0.64401900	1.82310300
H	-1.49839200	1.02015900	1.58632400
C	-3.70625600	-0.87301100	-0.31167900

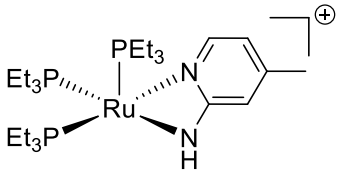
H	-4.15272500	-1.35941500	0.56611700
H	-4.41859900	-0.10609900	-0.64435400
H	-3.57046300	-1.61140600	-1.10465500

N-isopropyl-4-methylpyridin-2-amine (Product)



C	-1.33402500	1.73458400	-0.33785000
N	-0.10699300	1.18980700	-0.34158200
C	-0.02051100	-0.13596000	-0.15371300
C	-1.16241100	-0.94645300	0.05939100
C	-2.42310000	-0.36896500	0.06477400
C	-2.50921900	1.02225700	-0.14348200
H	-3.47003100	1.52914900	-0.14836500
C	-3.66508200	-1.19486700	0.28513400
H	-4.34070200	-1.12157400	-0.57600000
H	-4.22013300	-0.84082400	1.16257500
H	-3.42427900	-2.25159000	0.43862500
H	-1.04569600	-2.01795300	0.20846400
N	1.23087000	-0.71107000	-0.20851600
H	1.29215000	-1.65358500	0.15618800
C	2.46694200	0.07156600	-0.14800300
C	3.62131000	-0.79669400	-0.65042400
H	3.43224100	-1.14890200	-1.67011600
H	4.55785600	-0.22862000	-0.64535400
H	3.76503800	-1.67395500	-0.00382500
C	2.73107900	0.62250700	1.26008400
H	2.87374300	-0.19747100	1.97648700
H	1.88853300	1.23588200	1.59269900
H	3.63476700	1.24436700	1.27044800
H	2.32448800	0.91477800	-0.82956400
H	-1.36500900	2.81128900	-0.49703200

Ru-amido Complex (30)

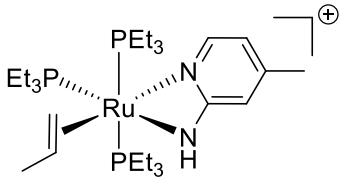


Ru	-0.07138200	0.15865700	0.25365000
P	1.98491600	1.10000900	0.74982600
P	0.06219400	0.43212600	-1.97919300
P	0.59690500	-2.09083500	0.32812900
N	-2.30716200	-0.03759400	0.32122600

N	-1.19644900	1.81014100	0.84771500
C	-3.40275800	-0.80707600	0.24402200
H	-3.25958800	-1.82580600	-0.10167300
C	-4.66839200	-0.34715600	0.56838200
H	-5.52607900	-1.00511300	0.47486200
C	-4.82074300	0.98579600	1.01532000
C	-6.18543300	1.51572100	1.36788700
H	-6.14284100	2.55854800	1.69446900
H	-6.63535500	0.92221500	2.17290200
H	-6.86085300	1.45308800	0.50617800
C	-3.68656100	1.78263100	1.12576900
H	-3.75561500	2.80651500	1.48236400
C	-2.42582100	1.24841800	0.78415900
C	1.85185800	2.95274800	0.81181500
H	1.37312100	3.27062500	-0.11753700
H	1.12405000	3.15638900	1.60473900
C	3.12965100	3.76459900	1.04886000
H	3.83682200	3.66077800	0.22013400
H	3.64075300	3.47471900	1.97256300
H	2.88075500	4.82822500	1.13390200
C	3.49644800	0.75593000	-0.28248800
H	3.36091100	-0.24614700	-0.69719800
H	3.45010500	1.44548400	-1.13476000
C	4.87038700	0.84545400	0.39631100
H	5.65711900	0.62630800	-0.33408300
H	4.96765100	0.11902000	1.20848300
H	5.06823500	1.83647000	0.80968400
C	2.48158000	0.69129400	2.49267300
H	2.82067300	-0.34844900	2.50967800
H	3.34343700	1.30625900	2.77322900
C	1.33609000	0.88399200	3.49491900
H	0.46736200	0.26785900	3.24188300
H	0.99603100	1.92316900	3.53242000
H	1.66340500	0.60520900	4.50214000
C	-1.57702100	0.28434100	-2.83364900
H	-2.28935500	0.85432500	-2.23045300
H	-1.48349900	0.79978500	-3.79764600
C	-2.08652200	-1.14206500	-3.04341500
H	-3.06975100	-1.12097300	-3.52497200
H	-2.19214700	-1.66588100	-2.09412700
H	-1.41850800	-1.72796100	-3.68334500
C	1.18345400	-0.67504600	-2.95880100
H	2.18532800	-0.55966800	-2.53337900
H	0.87098500	-1.70015100	-2.73657800
C	1.22678700	-0.46051400	-4.47787300
H	0.23218200	-0.51685200	-4.93073900

H	1.84419200	-1.23693400	-4.94285300
H	1.66546400	0.50554700	-4.74341700
C	0.58785300	2.12797300	-2.52011200
H	1.56785700	2.33153500	-2.07709000
H	0.73954000	2.09036100	-3.60438700
C	-0.41249600	3.23728600	-2.17602200
H	-1.32876000	3.13993300	-2.76651200
H	0.01916500	4.21909300	-2.39872200
H	-0.69621500	3.20554400	-1.12150900
C	0.46357700	-2.60157700	2.11116900
H	0.72642800	-3.66162900	2.20326100
H	1.21979600	-2.04182600	2.67072200
C	-0.92834400	-2.33698000	2.70077400
H	-1.70538600	-2.90472400	2.17900000
H	-1.20563400	-1.27971000	2.63500300
H	-0.95596400	-2.62690000	3.75636100
C	-0.56504800	-3.27557500	-0.51754600
H	-1.57074300	-2.87376500	-0.37813200
H	-0.35702100	-3.20289100	-1.59132500
C	-0.52743500	-4.74107300	-0.06890900
H	-1.19845200	-5.33883500	-0.69560500
H	-0.85861400	-4.85590300	0.96749700
H	0.47169500	-5.18095400	-0.15240500
C	2.24590900	-2.79891200	-0.19589900
H	2.08068300	-3.84668400	-0.46823100
H	2.53686700	-2.28657400	-1.11736100
C	3.38012600	-2.72495700	0.83144400
H	4.30324500	-3.12556100	0.39868000
H	3.15448200	-3.31224900	1.72627700
H	3.58649600	-1.70035800	1.14627200
H	-1.14145300	2.78574500	1.11397100

Ru-alkene Complex (32)

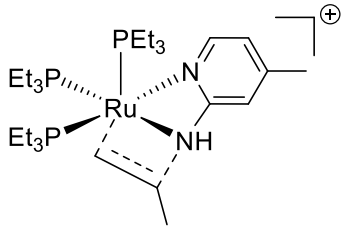


Ru	0.03345800	-0.16157800	-0.56441800
P	0.93189200	-1.76775000	0.97999000
C	0.80642200	-1.05241600	2.70460900
H	0.82384500	0.03041200	2.57591500
H	-0.20198900	-1.30384400	3.05533000
C	1.83758200	-1.44061300	3.77176400
H	2.84033200	-1.08519400	3.51377200
H	1.56426300	-0.97334000	4.72460400

H	1.89510500	-2.51904700	3.93814100
C	2.72086500	-2.30283700	0.89214000
C	3.08841300	-3.40476000	-0.11041300
H	4.14571600	-3.66428600	0.01183600
H	2.94408300	-3.10608400	-1.14926600
H	2.50989700	-4.31826800	0.05564100
H	3.32876500	-1.41333400	0.71201200
H	2.98832600	-2.65075200	1.89337100
C	0.07681900	-3.41260100	1.12765800
H	-0.98904500	-3.20076200	1.23277700
C	0.51892200	-4.34463500	2.26244600
H	1.59181000	-4.55695900	2.23770600
H	0.27927500	-3.92272600	3.24280800
H	-0.00711900	-5.30243400	2.18180700
H	0.19593100	-3.91114200	0.15911600
P	2.16788100	1.05852300	-0.50793600
C	2.85823100	1.47733700	1.17506600
H	2.88794500	0.55595700	1.76384100
C	2.09630500	2.56778300	1.93711100
H	2.16364800	3.53364900	1.42749600
H	1.03883200	2.33275000	2.05520500
H	2.53180400	2.69404700	2.93463800
H	3.89823800	1.78956700	1.04881900
C	2.06992900	2.73492800	-1.29989300
C	3.36654700	3.55074200	-1.35020200
H	4.13187200	3.06352600	-1.96235900
H	3.78855700	3.72167700	-0.35468900
H	3.17055800	4.53273900	-1.79528800
H	1.68512100	2.57466800	-2.31158800
H	1.28815900	3.28362600	-0.76636000
C	3.63582500	0.28098600	-1.38988300
C	5.03623600	0.44380000	-0.78508100
H	5.33047100	1.49204200	-0.68675100
H	5.11341200	-0.02068000	0.20348400
H	5.77098100	-0.04585700	-1.43413600
H	3.42403400	-0.78398000	-1.50376700
H	3.62981000	0.69626400	-2.40392800
H	0.30984700	1.18484700	-3.72579500
C	0.79240500	0.20400600	-3.68911200
H	0.74440600	-0.21331200	-4.70466700
H	1.84606900	0.34180900	-3.44213900
C	0.10289500	-0.74398100	-2.74602800
C	0.76610000	-1.73052400	-2.02403300
H	0.27610800	-2.67133500	-1.80016100
H	1.84480500	-1.77723500	-2.08220900
H	-0.93848700	-0.91231400	-2.99641600

P	-2.20956300	-1.06475400	-0.51818800
C	-3.50243900	0.02594800	-1.28522100
C	-3.40586100	0.17850700	-2.80617000
H	-3.47232500	-0.78430900	-3.32482600
H	-4.23260400	0.79947700	-3.16845600
H	-2.47172100	0.66350500	-3.09518000
H	-4.48199700	-0.38038000	-1.01711300
H	-3.42417500	1.00543000	-0.80707000
C	-2.85809800	-1.36855300	1.21672000
H	-2.03233500	-1.14307500	1.89403400
C	-4.09547100	-0.57790200	1.65888800
H	-3.94397500	0.50076500	1.56206900
H	-4.98582500	-0.85362700	1.08665900
H	-4.30531600	-0.78912500	2.71356000
H	-3.05791100	-2.44199800	1.31269300
C	-2.51903900	-2.69652600	-1.35932900
H	-1.89288300	-3.43620400	-0.85041600
C	-3.97759900	-3.17096300	-1.38448400
H	-4.03999000	-4.17218800	-1.82480800
H	-4.60993800	-2.50912700	-1.98332700
H	-4.40824400	-3.22734000	-0.37884500
H	-2.13241400	-2.62632100	-2.38210000
N	-0.81091400	1.64388600	-1.33611100
C	-1.18931700	2.18079200	-0.18090000
N	-0.89783500	1.29122200	0.82957600
C	-1.31052900	1.56712400	2.08141800
C	-1.96149900	2.73931100	2.41214700
C	-2.20860600	3.70651300	1.40269200
C	-1.81777500	3.42140800	0.10541800
H	-2.00414000	4.12127700	-0.70470800
C	-2.88990900	5.00335200	1.75178400
H	-3.02393500	5.63952300	0.87229000
H	-2.30499100	5.56157500	2.49287300
H	-3.87594800	4.81813300	2.19483700
H	-2.26864200	2.91562700	3.43772800
H	-1.10002500	0.82331500	2.84033200
H	-0.86423100	2.19640300	-2.18154000

Migratory Insertion TS (TS1)

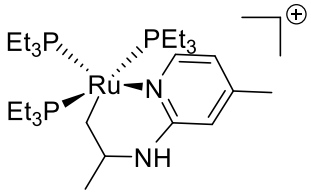


Ru	0.07116900	-0.06715500	-0.42929400

P	2.10440500	-1.22477700	-0.37085200
P	-0.40697100	-0.31733700	1.88365700
P	1.06451100	2.02978400	-0.25046100
N	-2.08425100	0.42635200	-0.56575500
C	-3.02086100	1.35290600	-0.29386700
H	-2.66261700	2.34916900	-0.06291100
C	-4.37639600	1.07204700	-0.29752600
H	-5.09022000	1.85805900	-0.07232000
C	-4.81601900	-0.23693300	-0.60005800
C	-6.28529800	-0.56622200	-0.61237800
H	-6.81155000	0.03630000	-1.36250400
H	-6.74350900	-0.34315300	0.35851900
H	-6.46066800	-1.62163700	-0.83912400
C	-3.85276300	-1.19640400	-0.88905100
H	-4.13505000	-2.21900700	-1.12437900
C	-2.48787200	-0.84481200	-0.85848000
C	1.94797900	-3.01170800	0.12987500
H	2.94391000	-3.40725700	0.34768000
H	1.38729000	-3.03706600	1.06751000
C	1.26266500	-3.90138500	-0.91226100
H	1.11096300	-4.90847200	-0.50901600
H	1.86657200	-4.00034200	-1.81988000
H	0.28790000	-3.50382700	-1.19988700
C	3.45059300	-0.56455500	0.75369300
H	4.07090400	0.08985800	0.12822800
H	2.95889400	0.08744800	1.47332600
C	4.34040800	-1.55722800	1.51182600
H	4.88097900	-2.23468300	0.84595200
H	3.75824500	-2.16613400	2.21086500
H	5.08528200	-1.00797500	2.09896000
C	3.01724600	-1.38264300	-1.98981900
H	2.32574900	-1.84420900	-2.70300100
H	3.19058800	-0.36436700	-2.35448000
C	4.34263600	-2.15315500	-1.97630500
H	4.74922000	-2.21199900	-2.99216200
H	4.22296300	-3.17826800	-1.61162100
H	5.09337600	-1.65805700	-1.35326500
C	-1.09741400	1.26029900	2.63491800
H	-0.30572600	1.69137300	3.25889000
H	-1.23990600	1.95333800	1.80365600
C	-2.40075500	1.17045100	3.43727800
H	-2.29942400	0.54080900	4.32600300
H	-3.21940700	0.77263700	2.82973500
H	-2.69487500	2.17095800	3.77494900
C	0.89535800	-0.78892600	3.13278200
H	1.37590300	-1.70643900	2.77857400

H	1.66750900	-0.01399300	3.09516200
C	0.42259900	-0.96696400	4.58038500
H	-0.04524200	-0.05703000	4.96964400
H	1.27538800	-1.19985400	5.22789300
H	-0.29712200	-1.78503700	4.67900100
C	-1.72364000	-1.58381000	2.23271000
H	-2.06467300	-1.46117400	3.26437300
H	-2.57866500	-1.34964100	1.59380200
C	-1.27273300	-3.02936500	2.00277800
H	-2.11286800	-3.71592300	2.15575000
H	-0.48185600	-3.32428800	2.70117300
H	-0.89835600	-3.17167000	0.98711400
C	2.37092400	2.38142400	-1.52967000
H	3.16228200	1.64173300	-1.36515100
H	1.93415000	2.14667100	-2.50525300
C	2.97551000	3.78980400	-1.54563000
H	2.22291400	4.55634100	-1.75499500
H	3.73910300	3.86024400	-2.32834300
H	3.45816100	4.03917700	-0.59534300
C	-0.11628400	3.44494200	-0.51994200
H	-0.87698400	3.38953600	0.26571900
H	0.42676600	4.37755900	-0.34403600
C	-0.77461100	3.48867800	-1.90170600
H	-1.37222200	2.59612400	-2.09330200
H	-0.02986500	3.57481900	-2.69984700
H	-1.43380000	4.36086500	-1.97474300
C	1.94799800	2.52821100	1.33238100
H	1.65517900	1.80497700	2.09476100
H	3.01682800	2.36451800	1.15398700
C	1.72785300	3.94222500	1.88412400
H	0.67506900	4.12754900	2.11974600
H	2.05926900	4.71837900	1.18873200
H	2.29924300	4.06643100	2.81110000
N	-1.40232200	-1.62694800	-1.08694300
H	-1.59325100	-2.62208600	-1.14613900
C	-0.62186800	-1.09985600	-2.97141800
H	-0.05967200	-2.03090300	-3.00551600
C	-1.90563100	-1.09516400	-3.74469200
H	-1.65290100	-1.02124800	-4.81230900
H	-2.49452900	-2.00559500	-3.60005500
H	-2.52120600	-0.22588100	-3.49453800
C	0.10438200	0.08363800	-2.72471100
H	-0.37249300	1.00741000	-3.04066500
H	1.16942500	0.04592000	-2.91475700

Ru-alkyl Complex (33)

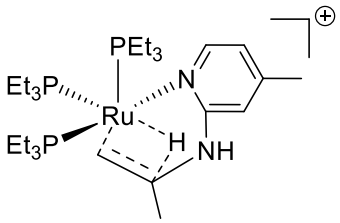


Ru	-0.16285900	-0.00105500	-0.04158900
P	-2.46903900	-0.38545800	0.09894800
C	-3.29195100	-1.05758100	-1.42954300
H	-2.74728800	-1.95730000	-1.72806300
H	-4.31167300	-1.37352300	-1.19057500
C	-3.30924400	-0.05599400	-2.58955500
H	-3.92349100	0.82018800	-2.35673100
H	-2.30305700	0.29543100	-2.83407500
H	-3.72810700	-0.51959400	-3.48916000
C	-3.57810800	1.05471200	0.51273400
C	-5.08651700	0.79451700	0.58975000
H	-5.61454000	1.72700200	0.81949900
H	-5.33580500	0.07742900	1.37718500
H	-5.48920500	0.41492700	-0.35467700
H	-3.22447400	1.43039400	1.47829600
H	-3.37644800	1.84729800	-0.21197800
C	-2.94885300	-1.56512000	1.47711400
H	-2.03854300	-2.08514600	1.77909300
C	-4.06499700	-2.58193100	1.21203700
H	-3.80844400	-3.26548800	0.39688000
H	-4.23279300	-3.18960100	2.10870100
H	-5.01446100	-2.10356700	0.95735000
H	-3.21830700	-0.92979600	2.32970800
P	-0.32990300	2.37791200	-0.13988600
C	-1.18071600	2.97795700	-1.68285600
H	-2.19794200	2.57853100	-1.68319300
C	-0.44788900	2.51699200	-2.94865100
H	0.54313400	2.97435400	-3.03361800
H	-0.31554700	1.42881700	-2.96024000
H	-1.01602200	2.78884400	-3.84445100
H	-1.26795300	4.06830600	-1.67221600
C	1.31088500	3.25686700	-0.26642100
C	1.26560300	4.78004700	-0.42772600
H	0.75155200	5.08054400	-1.34654700
H	2.28439400	5.18074000	-0.47864900
H	0.76504100	5.26945100	0.41363500
H	1.87343900	2.99002300	0.63519500
H	1.86376600	2.81085000	-1.09741400
C	-1.11192700	3.31414400	1.28381800
C	-2.09051700	4.44375900	0.94269200
H	-1.61619400	5.23736600	0.35836000

H	-2.95088900	4.07795100	0.37346100
H	-2.47412200	4.89574900	1.86435600
H	-1.60491200	2.57796200	1.92209400
H	-0.27919400	3.71055900	1.87720900
P	0.37256900	-2.35707800	-0.32009900
C	1.85535800	-3.06468900	0.55141100
C	1.63734600	-3.39135100	2.03201800
H	0.84006200	-4.12887500	2.17521200
H	2.55190900	-3.81284000	2.46415300
H	1.38435600	-2.49351600	2.60020400
H	2.16275800	-3.96426700	0.00467300
H	2.66739300	-2.34140200	0.43945500
C	0.93363300	-2.53177300	-2.08519500
H	1.11802400	-3.58741800	-2.31079900
C	-0.04263900	-1.92333600	-3.09568700
H	-0.25572900	-0.87265500	-2.86260900
H	0.36561600	-1.96376700	-4.11144000
H	-1.00082100	-2.45267500	-3.10386900
H	1.90479000	-2.02988100	-2.14769800
C	-0.86658900	-3.73750800	-0.13460400
H	-1.75851900	-3.44342800	-0.69506100
C	-0.42615400	-5.14346900	-0.55729500
H	-1.23831300	-5.85658900	-0.37651200
H	0.44375600	-5.48920200	0.00948500
H	-0.17907100	-5.19558600	-1.62212600
H	-1.16736000	-3.74883800	0.91761800
C	-0.10531400	0.01980300	2.04238500
C	1.13555600	0.68159500	2.62198000
N	2.38522400	0.05751200	2.14725700
C	2.86555400	0.15030400	0.86849500
N	1.99995800	0.24902900	-0.16238400
C	2.51364300	0.35490700	-1.41239400
C	3.85893300	0.31742400	-1.70363200
C	4.77981700	0.16680500	-0.64124400
C	4.26299800	0.09309300	0.64037200
H	4.92842800	0.00072000	1.49478800
C	6.26004300	0.11230900	-0.90520000
H	6.83216400	-0.00138800	0.01970800
H	6.59871800	1.02608800	-1.40790700
H	6.50509000	-0.72815700	-1.56555400
H	4.19610000	0.40229500	-2.73165700
H	1.77880300	0.46647400	-2.20407300
H	3.12004300	0.04430900	2.84364900
C	1.14652200	0.61529100	4.15416900
H	2.01591400	1.13562600	4.57740200
H	0.24706700	1.09171600	4.55463300

H	1.16026200	-0.42600900	4.49675700
H	1.14603400	1.74182900	2.33102000
H	-0.97364500	0.55971500	2.44181200
H	-0.16747600	-1.00764200	2.41685600

BHE TS (TS2)

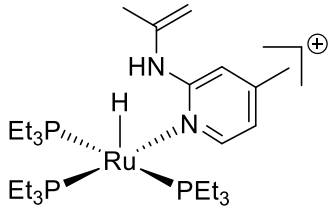


Ru	-0.04283900	-0.19725900	-0.40840600
P	-2.37676400	-0.46095000	-0.62340700
C	-3.45019900	0.61561200	0.47526300
H	-2.82962200	0.89899600	1.32412900
H	-3.63449200	1.53796900	-0.08743000
C	-4.78164200	0.06026900	0.99828400
H	-5.46137400	-0.23732300	0.19635500
H	-4.63326800	-0.80658900	1.64963300
H	-5.28815200	0.82992900	1.59186000
C	-3.06148300	-2.16056300	-0.27319600
C	-2.54040500	-3.29246400	-1.15790500
H	-2.81281200	-3.14754300	-2.20810200
H	-2.97472500	-4.24596200	-0.83767500
H	-1.45289600	-3.37986200	-1.09532100
H	-2.84022500	-2.38831800	0.77320900
H	-4.15115100	-2.10741700	-0.34854300
C	-3.07519100	-0.10674900	-2.31508300
H	-2.72251800	0.89308100	-2.58826500
C	-4.59486400	-0.18890700	-2.49603300
H	-5.11786700	0.55796700	-1.89159100
H	-4.85382000	0.00032500	-3.54386400
H	-4.99039700	-1.17577000	-2.23533900
H	-2.58632500	-0.79296800	-3.01246300
P	-0.08552100	-1.16270200	1.80376900
C	-1.56384900	-0.93556000	2.92723400
H	-1.65139200	0.14160000	3.10565200
C	-1.57269400	-1.68221100	4.26647400
H	-0.71708800	-1.41814400	4.89532200
H	-2.47965800	-1.42746700	4.82658200
H	-1.56843200	-2.76779300	4.13026200
H	-2.45345200	-1.21047600	2.35652700
C	1.28919800	-0.79646600	3.01130100
C	1.23778500	0.59570400	3.64858900
H	2.12829600	0.77152300	4.26217300

H	0.36482400	0.71054200	4.29919800
H	1.18605900	1.39215500	2.89961600
H	1.25120400	-1.56331800	3.79354100
H	2.23744400	-0.94533700	2.48943400
C	0.06648800	-3.01826400	1.73356200
C	1.33528700	-3.50693300	1.02626600
H	1.38485800	-3.13578500	-0.00174800
H	2.24137000	-3.17767200	1.54654800
H	1.35339400	-4.60192900	0.99482600
H	0.03695300	-3.41284500	2.75501600
H	-0.81920800	-3.39886800	1.21363200
P	-0.20971700	2.17516200	0.00797900
C	1.35118500	3.19768800	-0.07717000
C	2.12310200	3.10371600	-1.39641800
H	2.98172800	3.78396100	-1.37386400
H	2.50141400	2.09555900	-1.57390900
H	1.50127500	3.38942300	-2.25134800
H	1.06586100	4.23713300	0.10512900
H	2.00003100	2.91964700	0.75706500
C	-1.00558300	2.80422500	1.59463500
H	-1.01141800	1.96042600	2.28825100
C	-0.39757800	4.02420000	2.29776300
H	-0.42718300	4.92222100	1.67434400
H	-0.96280800	4.23965200	3.21178100
H	0.64338500	3.85330200	2.59016800
H	-2.05489300	3.00879800	1.35517800
C	-1.23168300	3.03163800	-1.29668900
H	-2.22418200	2.57443500	-1.25420000
C	-1.36877100	4.55520200	-1.21190400
H	-2.02843200	4.91626200	-2.00921800
H	-0.40708300	5.06322900	-1.33195700
H	-1.80401200	4.87388000	-0.25909800
H	-0.80862000	2.73753300	-2.26263300
C	0.29958000	0.17391400	-2.53473100
C	0.62381800	-1.21707400	-2.37592000
N	2.00440800	-1.55489300	-2.17529000
C	2.80333100	-0.89572100	-1.28831600
N	2.17150700	-0.18181100	-0.32771800
C	2.95217000	0.44243900	0.58070700
C	4.33048600	0.38530800	0.58971600
C	4.99583900	-0.35585900	-0.40956700
C	4.20785400	-0.99329600	-1.35555200
H	4.66141500	-1.56560800	-2.15977800
C	6.49769800	-0.43431800	-0.44556600
H	6.88478800	-0.86976800	0.48335000
H	6.93618000	0.56620700	-0.54008800

H	6.85142200	-1.04331400	-1.28202100
H	4.88595000	0.91169200	1.35932100
H	2.42146300	1.00515300	1.33114000
H	2.44341800	-2.15323200	-2.86168900
C	-0.04331200	-2.26792400	-3.24159300
H	-1.10670400	-2.06929800	-3.35508900
H	0.40555100	-2.22625700	-4.24297200
H	0.08457600	-3.27729000	-2.84022500
H	0.04674800	-1.77551600	-0.98211200
H	-0.58020900	0.41081900	-3.12265700
H	1.12895800	0.85633100	-2.68515100

Ru-hydridoenamine Complex (45)

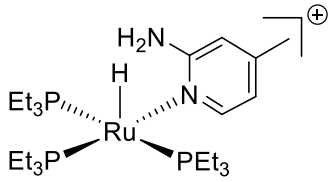


Ru	-0.48232700	-0.02642500	-0.21907300
P	-0.59065900	2.35840000	-0.04750700
P	-2.77935100	-0.37103300	0.05581000
P	0.00787000	-2.37610100	-0.20840600
N	1.63747200	0.26047800	-0.69989000
N	2.27938600	0.27130500	1.49540600
C	1.90065100	0.37413000	-2.01666600
H	1.03749900	0.29927000	-2.67331200
C	3.16450900	0.57046600	-2.53365800
H	3.31140700	0.64422400	-3.60609700
C	4.24510800	0.69038600	-1.63496300
C	5.64122700	0.93542800	-2.14112500
H	5.97154800	0.10761000	-2.78014300
H	6.35667100	1.03920300	-1.32074900
H	5.68069100	1.84687800	-2.74913000
C	3.97867800	0.59310200	-0.27566700
H	4.78319100	0.72463700	0.43188300
C	2.66522900	0.35953300	0.18405000
C	1.07467700	3.19457000	-0.13034400
H	1.69965500	2.72338200	0.63321400
H	1.51844000	2.92269600	-1.09397100
C	1.10185000	4.71676300	0.04813800
H	2.13371600	5.07788500	-0.02878900
H	0.72197600	5.02480300	1.02711600
H	0.51975900	5.23866400	-0.71773900
C	-1.51029800	3.22325400	-1.41393700
H	-2.57671200	3.20128300	-1.17732800
H	-1.22012600	4.27860300	-1.43848600

C	-1.25098100	2.55837800	-2.77098200
H	-1.55900500	1.50483100	-2.75656900
H	-0.18878300	2.59394600	-3.03899500
H	-1.80863200	3.05978400	-3.56935300
C	-1.30533000	3.09866800	1.49655300
H	-1.42335600	4.17857800	1.34886500
H	-2.30897100	2.68568600	1.62819300
C	-0.46281000	2.81333900	2.74474400
H	0.52744500	3.27526200	2.68452400
H	-0.31851100	1.73804300	2.88571600
H	-0.95857800	3.20586500	3.63881500
C	-3.93662600	1.04112500	-0.32438700
H	-3.64099400	1.87864600	0.31221600
H	-3.71521300	1.34720500	-1.35206500
C	-5.44008500	0.78638900	-0.16779900
H	-5.79758000	-0.00344900	-0.83536700
H	-5.99816100	1.69669900	-0.41408500
H	-5.70497300	0.50929800	0.85730500
C	-3.38128500	-0.92819900	1.72111200
H	-4.43890200	-1.20045200	1.63079500
H	-2.84193900	-1.84521200	1.96825300
C	-3.18448800	0.10317700	2.83497900
H	-2.13181000	0.38384700	2.92815700
H	-3.51282400	-0.30554000	3.79657400
H	-3.76393300	1.01476200	2.65200500
C	-3.49070000	-1.68795200	-1.04657900
H	-3.01409800	-2.63448900	-0.77634000
H	-4.55627100	-1.80903100	-0.82408900
C	-3.28201300	-1.38549400	-2.53420100
H	-2.22686600	-1.19019100	-2.75682200
H	-3.85565400	-0.50729500	-2.84874800
H	-3.60468000	-2.22754200	-3.15602000
C	-0.79213900	-3.44213100	1.08242000
H	-1.87487500	-3.39551500	0.92960300
H	-0.50383300	-4.48392600	0.90233600
C	-0.43092500	-3.02435300	2.51239200
H	0.63713800	-3.15624200	2.71262800
H	-0.98176800	-3.62871600	3.24124600
H	-0.66810400	-1.97109700	2.69126600
C	1.81346700	-2.74110400	0.07689700
H	2.36842000	-2.23567200	-0.71887500
H	2.08592700	-2.23301700	1.00632800
C	2.22675200	-4.21491000	0.14682100
H	2.00450100	-4.75291400	-0.78012200
H	1.73711700	-4.74320300	0.97076100
H	3.30778200	-4.28757700	0.31203100

C	-0.33119000	-3.34674300	-1.76064100
H	-0.00860100	-4.38190800	-1.60298300
H	-1.41423000	-3.37931300	-1.90776700
C	0.34621500	-2.75820800	-3.00240500
H	0.12654000	-3.36616200	-3.88642100
H	1.43480600	-2.71346800	-2.89160600
H	-0.00972200	-1.74194300	-3.20428300
H	-0.44356700	-0.08614500	1.34867700
H	1.25988300	0.21067400	1.55972600
C	2.94979200	-0.10148300	2.67664900
C	2.21842300	-0.26464100	3.79445700
H	1.14462800	-0.10110000	3.80858400
H	2.68881000	-0.55967400	4.72420000
C	4.43569700	-0.33238700	2.65878400
H	4.72873000	-1.04329900	1.87792400
H	4.99444500	0.59722300	2.49910600
H	4.74659200	-0.74079100	3.62251300

Ru-hydrido-aminopyridine Complex (46)



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P	-0.40299400	2.35215300	-0.04174200
P	-2.54745000	-0.41287700	-0.15369000
P	0.26743400	-2.37265400	0.14498100
N	1.92490100	0.26871300	-0.07798900
N	2.15029200	0.53993700	2.21423600
C	2.48350400	0.25037500	-1.30965200
H	1.78861400	0.11302500	-2.13348800
C	3.83504900	0.38499200	-1.54246400
H	4.21831900	0.35573300	-2.55716900
C	4.70180300	0.55831400	-0.43907500
C	6.18536100	0.70502600	-0.64273100
H	6.59548300	-0.17395500	-1.15410300
H	6.71415500	0.82671100	0.30652700
H	6.40559800	1.57561400	-1.27196800
C	4.13233500	0.59361300	0.82376200
H	4.75188800	0.73815300	1.70427100
C	2.73694600	0.45172900	0.98436600
C	1.23728500	3.22465000	0.11283100
H	1.71213500	2.83446100	1.01691800
H	1.85559600	2.88614500	-0.72564200
C	1.21038400	4.75666900	0.15942600

H	2.23372800	5.14074400	0.23936100
H	0.65343600	5.13406500	1.02262800
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H	-2.14639200	3.03735800	-1.60039500
H	-0.77134700	4.11828900	-1.70850000
C	-0.53707600	2.27432500	-2.84126300
H	-0.83296700	1.21892300	-2.77502500
H	0.55633900	2.31293800	-2.90719200
H	-0.93776900	2.67595500	-3.77827600
C	-1.40756200	3.19932800	1.26799900
H	-1.50838100	4.25925300	1.00649000
H	-2.41281400	2.77040900	1.24478100
C	-0.81372000	3.04345700	2.67244100
H	0.15960000	3.53603500	2.75960000
H	-0.67556700	1.98782900	2.92586600
H	-1.47993300	3.48648100	3.42028100
C	-3.64321900	0.94749400	-0.80864700
H	-3.46181700	1.83215000	-0.19375000
H	-3.26385900	1.18884300	-1.80708800
C	-5.14972800	0.67222700	-0.87520200
H	-5.38857700	-0.16641600	-1.53616100
H	-5.67088900	1.55287400	-1.26720600
H	-5.57139800	0.45655000	0.11144000
C	-3.40624900	-0.88096500	1.42471700
H	-4.42775500	-1.19564000	1.18297400
H	-2.89184900	-1.76007100	1.82024000
C	-3.41986500	0.22722600	2.48062400
H	-2.40340700	0.54828800	2.72376000
H	-3.89362100	-0.12809400	3.40201500
H	-3.98130300	1.10477400	2.14171400
C	-3.06276200	-1.80748100	-1.27036300
H	-2.62134000	-2.72554800	-0.87338400
H	-4.14807400	-1.93916700	-1.20475100
C	-2.63492800	-1.58976800	-2.72539600
H	-1.56221500	-1.37917600	-2.79860800
H	-3.16973600	-0.74845900	-3.17843300
H	-2.84427000	-2.47641000	-3.33362900
C	-0.71641300	-3.40542900	1.33292100
H	-1.76236000	-3.37498900	1.01250900
H	-0.39768800	-4.44959200	1.23766600
C	-0.58831900	-2.93534400	2.78612700
H	0.43452300	-3.06065900	3.15728200
H	-1.24829500	-3.51577300	3.43982100
H	-0.85206700	-1.87743300	2.88589100
C	2.01140800	-2.69463400	0.72209100

H	2.67804000	-2.23535900	-0.01373900
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C	2.41562600	-4.15491500	0.95081200
H	2.32977300	-4.75547700	0.03973000
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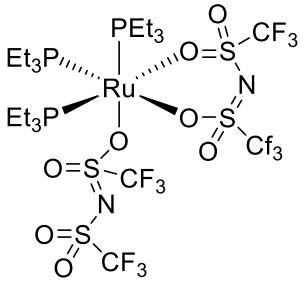
H	3.46223100	-4.20301600	1.27242000
C	0.19094300	-3.40979000	-1.40026300
H	0.50573700	-4.42971900	-1.15286900
H	-0.85571000	-3.47576600	-1.70930700
C	1.03868600	-2.85259800	-2.54839200
H	0.96202600	-3.49577800	-3.43144200
H	2.09774100	-2.78411800	-2.27826000
H	0.70313100	-1.85111800	-2.84027100
H	-0.46250300	-0.01980400	1.51787900
H	1.17339600	0.26374500	2.26636400
H	2.71861200	0.42639100	3.04126600

13. X-ray Structure of Ruthenium Complexes

$Ru(PEt_3)_3(NTf_2)_2$



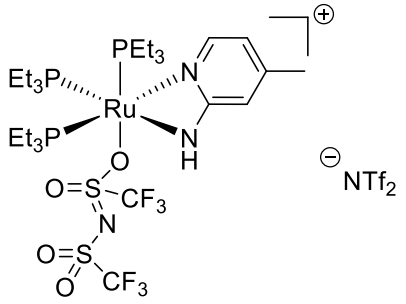
A yellow prism 0.060 x 0.050 x 0.050 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 50 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 100.0% complete to 25.000° in θ. A total of 122543 reflections were collected covering the indices, -13<=*h*<=13, -22<=*k*<=22, -21<=*l*<=21. 7199 reflections were found to be symmetry independent, with an R_{int} of 0.0671. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2016). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2016.

Table 1. Crystal data and structure refinement for $Ru(PEt_3)_3(NTf_2)_2$.

Empirical formula	C22 H45.25 F12 N2 O8.25 P3 Ru S4
Formula weight	1020.14

Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.433(3) Å	α = 90°.
	b = 18.944(5) Å	β = 91.423(5)°.
	c = 18.126(5) Å	γ = 90°.
Volume	3924.6(18) $Å^3$	
Z	4	
Density (calculated)	1.727 Mg/m^3	
Absorption coefficient	0.836 mm^{-1}	
F(000)	2073	
Crystal size	0.060 x 0.050 x 0.050 mm^3	
Theta range for data collection	1.555 to 25.384°.	
Index ranges	-13<=h<=13, -22<=k<=22, -21<=l<=21	
Reflections collected	122543	
Independent reflections	7199 [R(int) = 0.0671]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.928 and 0.836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7199 / 4 / 468	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0933	
R indices (all data)	R1 = 0.0468, wR2 = 0.0965	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.150 and -0.993 $e.Å^{-3}$	

$Ru(PEt_3)_3(Amine)(NTf_2)_2$ (29)



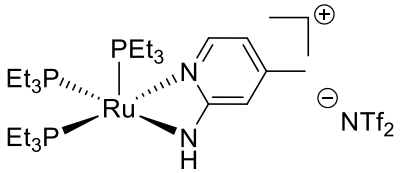
A yellow block 0.24 x 0.10 x 0.09 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 35 mm and exposure time was 6.00 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.372° in θ. A total of 72140 reflections were collected covering the indices -13<=h<=13, -22<=k<=23, -28<=l<=30. 9834 reflections were founded to be symmetry independent, with an R_{int} of 0.0536. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.40.44a software program and scaled using the SCALE3

ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 1. Crystal data and structure refinement for $Ru(PEt_3)_3(Amine)(NTf_2)_2$.

Empirical formula	C29 H55 Cl2 F12 N4 O8 P3 Ru S4	
Formula weight	1208.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.5702(2) Å	α = 90°.
	b = 18.7348(4) Å	β = 92.934(2)°.
	c = 24.3472(5) Å	γ = 90°.
Volume	4815.17(17) $Å^3$	
Z	4	
Density (calculated)	1.668 Mg/m^3	
Absorption coefficient	0.804 mm^{-1}	
F(000)	2464	
Crystal size	0.240 x 0.100 x 0.090 mm^3	
Theta range for data collection	2.738 to 26.372°.	
Index ranges	-13<=h<=13, -22<=k<=23, -28<=l<=30	
Reflections collected	72140	
Independent reflections	9834 [R(int) = 0.0536]	
Completeness to theta = 26.372°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.55675	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9834 / 2 / 632	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0730	
R indices (all data)	R1 = 0.0378, wR2 = 0.0754	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.617 and -1.025 $e.Å^{-3}$	

$Ru(PEt_3)_3$(Amido)(NTf_2) (30)



A red block 0.25 x 0.11 x 0.09 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector

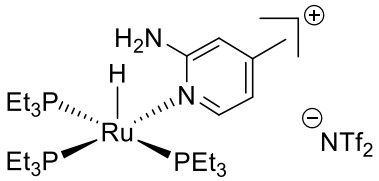
distance was 35 mm and exposure time was 2.00 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.369° in θ. A total of 49254 reflections were collected covering the indices -15<=h<=15, -17<=k<=17, -25<=l<=25. 7366 reflections were founded to be symmetry independent, with an R_{int} of 0.0659. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/n (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.40.44a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 1. Crystal data and structure refinement for $Ru(PEt_3)_3(Amido)(NTf_2)$.

Empirical formula	C26 H52 F6 N3 O4 P3 Ru S2	
Formula weight	842.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.6581(4) Å	α = 90°.
	b = 14.3288(4) Å	β = 106.345(3)°.
	c = 20.7537(6) Å	γ = 90°.
Volume	3612.08(19) $Å^3$	
Z	4	
Density (calculated)	1.550 Mg/m^3	
Absorption coefficient	0.749 mm^{-1}	
F(000)	1744	
Crystal size	0.250 x 0.110 x 0.090 mm^3	
Theta range for data collection	2.843 to 26.369°.	
Index ranges	-15<=h<=15, -17<=k<=17, -25<=l<=25	
Reflections collected	49254	
Independent reflections	7366 [R(int) = 0.0659]	
Completeness to theta = 26.369°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.28562	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7366 / 6 / 440	
Goodness-of-fit on F^2	1.033	

Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0794
R indices (all data)	R1 = 0.0401, wR2 = 0.0819
Extinction coefficient	n/a
Largest diff. peak and hole	0.719 and -0.511 e.Å^{-3}

Ru(H)(PEt$_3$)$_3$(Amine)(NTf$_2$)$_2$ (44)



A colorless block 0.31 x 0.17 x 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 4.00 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 30.500° in θ. A total of 60357 reflections were collected covering the indices -14<=h<=14, -16<=k<=16, -23<=l<=23. 11552 reflections were found to be symmetry independent, with an R_{int} of 0.0955. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the CrysAlis^{Pro} 1.171.40.54a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table 1. Crystal data and structure refinement for Ru(H)(PEt$_3$)$_3$(Amine)(NTf$_2$)$_2$.

Empirical formula	C26 H54 F6 N3.80 O4 P3 Ru S2	
Formula weight	856.03	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.2586(2) Å	α = 79.6870(10)°.
	b = 11.4779(2) Å	β = 82.7900(10)°.
	c = 16.7535(2) Å	γ = 78.3830(10)°.
Volume	1892.84(6) Å^3	
Z	2	
Density (calculated)	1.502 Mg/m^3	
Absorption coefficient	0.716 mm^{-1}	
F(000)	887	

Crystal size	0.310 x 0.170 x 0.100 mm^3
Theta range for data collection	2.979 to 30.508°.
Index ranges	-14<=h<=14, -16<=k<=16, -23<=l<=23
Reflections collected	60357
Independent reflections	11552 [R(int) = 0.0955]
Completeness to theta = 30.500°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.78072
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11552 / 1 / 555
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0310, wR2 = 0.0736
R indices (all data)	R1 = 0.0392, wR2 = 0.0765
Extinction coefficient	n/a
Largest diff. peak and hole	0.684 and -0.750 $e.Å^{-3}$

14. References

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Rendell, J. C. Burant, S. S. Iyengar,; J. Tomasi, M. C., J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L.; Martin, K. M., O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03. **2016**.
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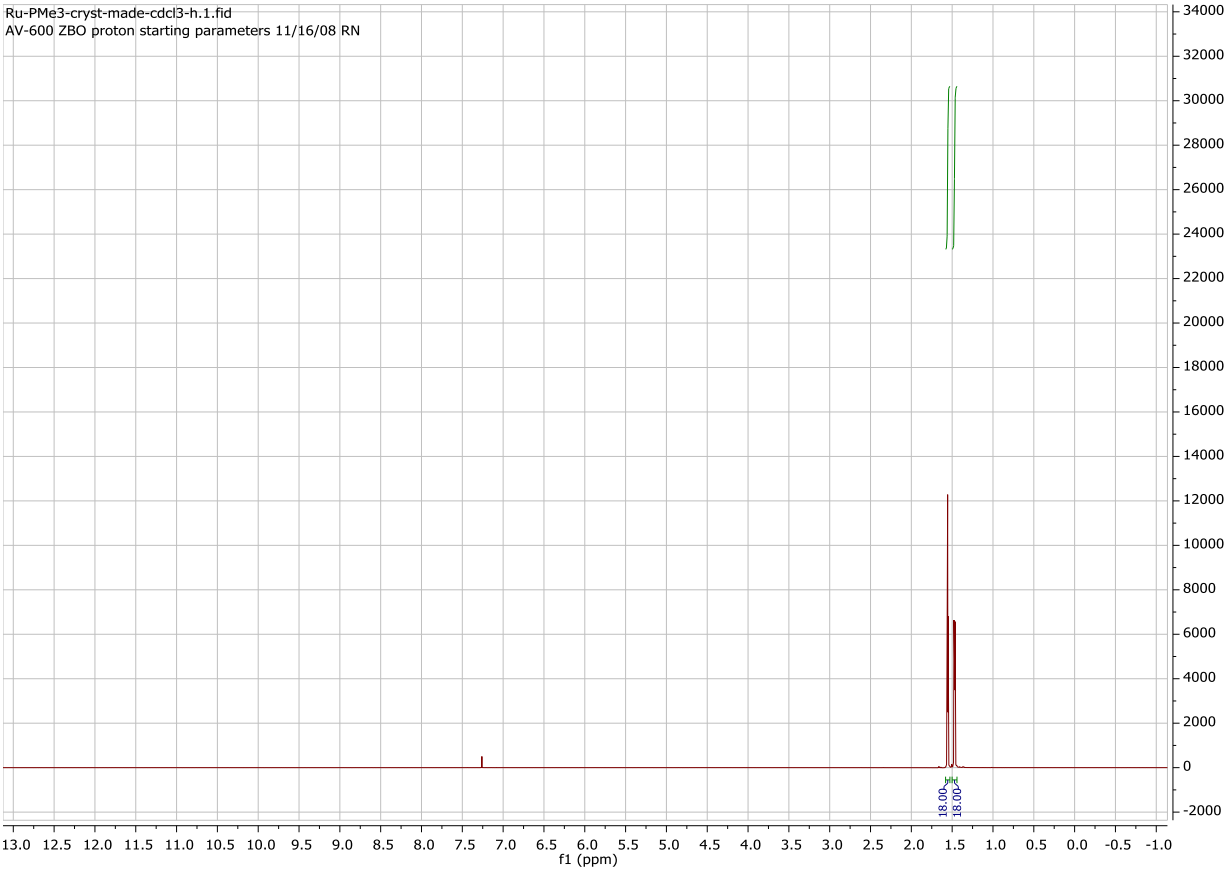
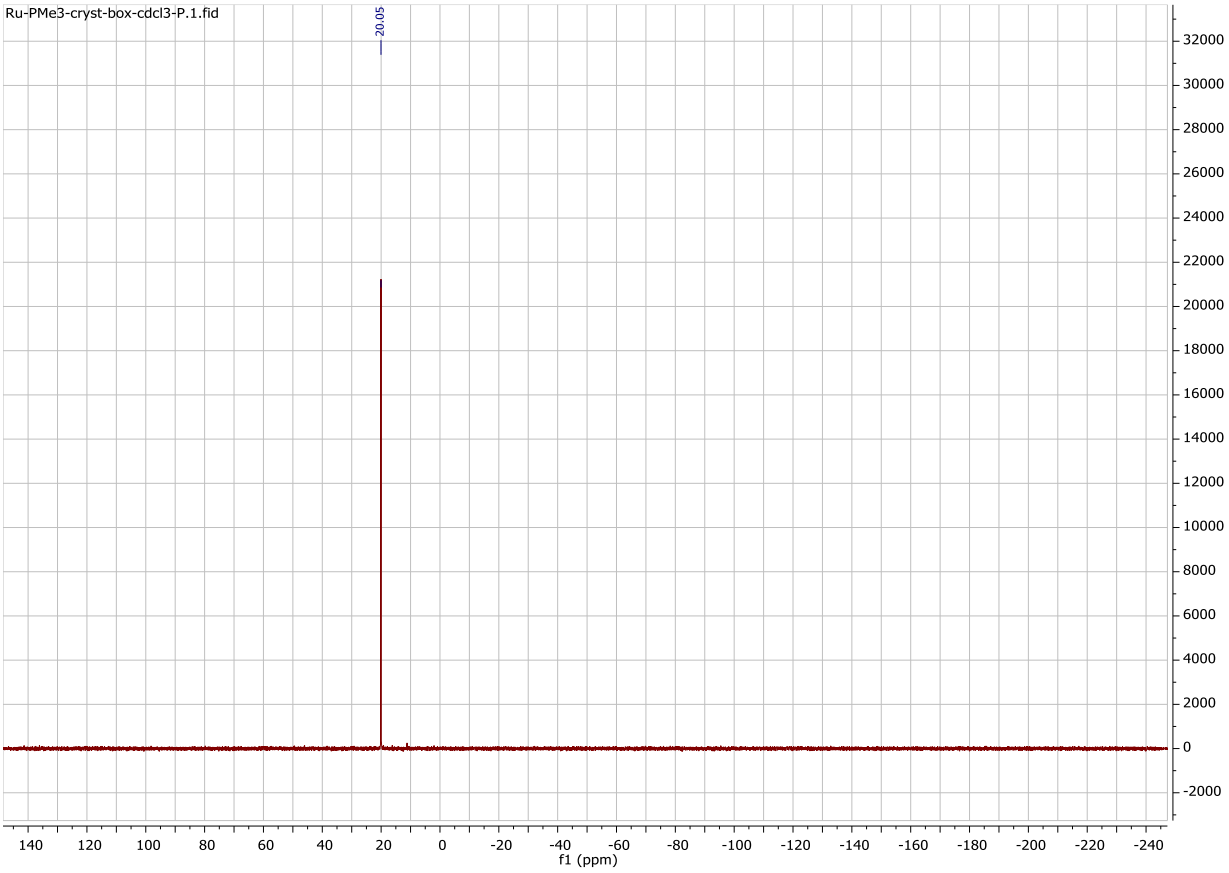
15. Copies of Spectroscopy Data

***cis*-Ru(PMe$_3$)$_4$Cl$_2$**

^{1}H



^{31}P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120
100
80
60
40
20
0
-20
-40
-60
-80
-100
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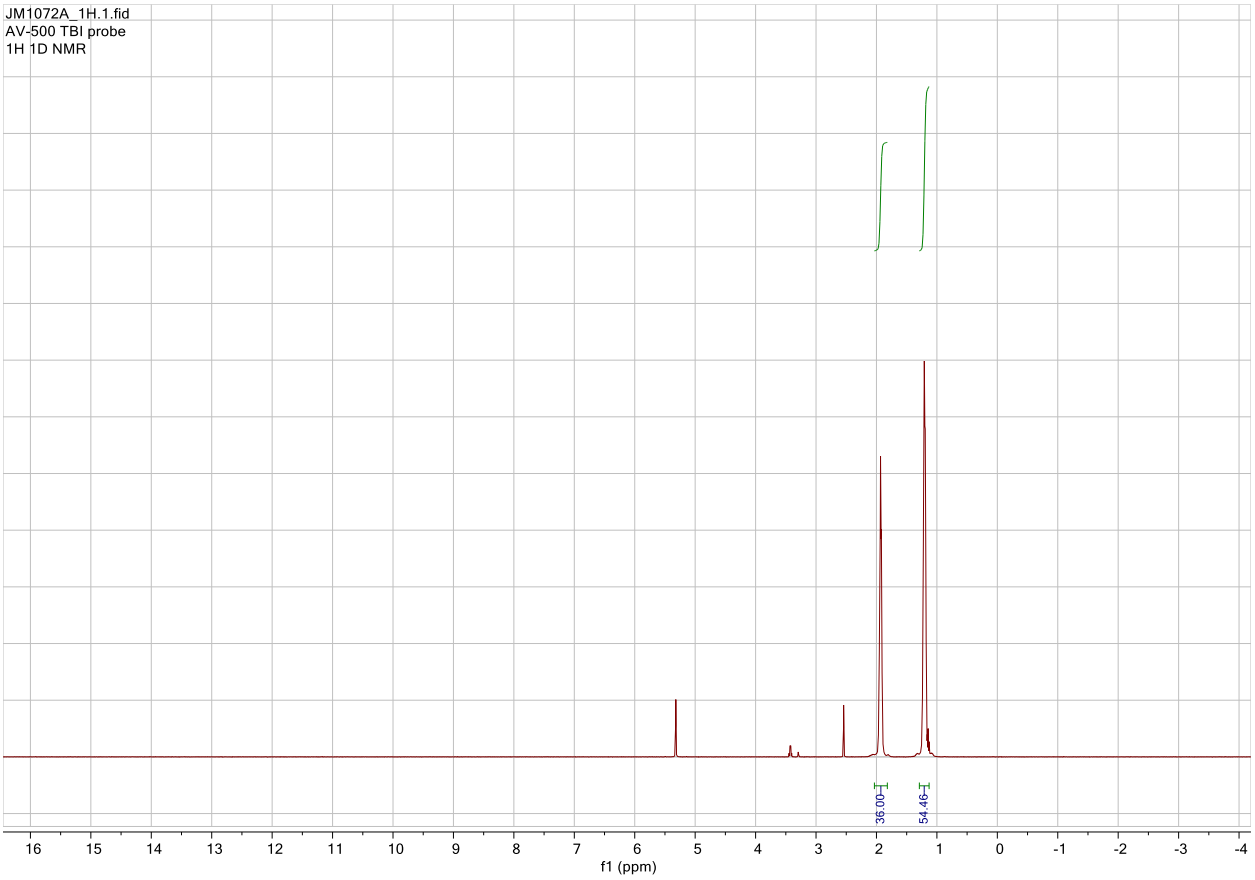
f1 (ppm)

[$Ru_2(PEt_3)_6Cl_3$][Cl]

^1H



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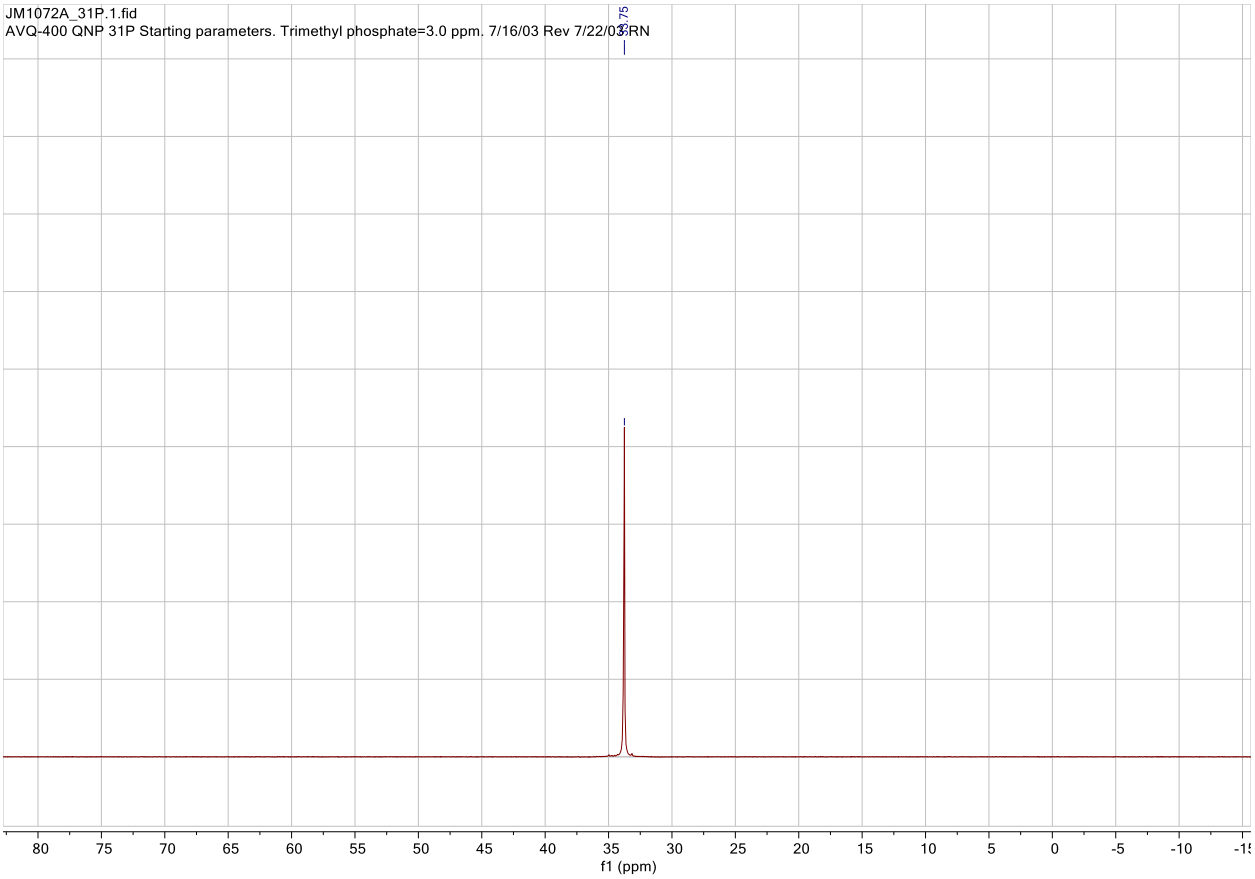
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35.75
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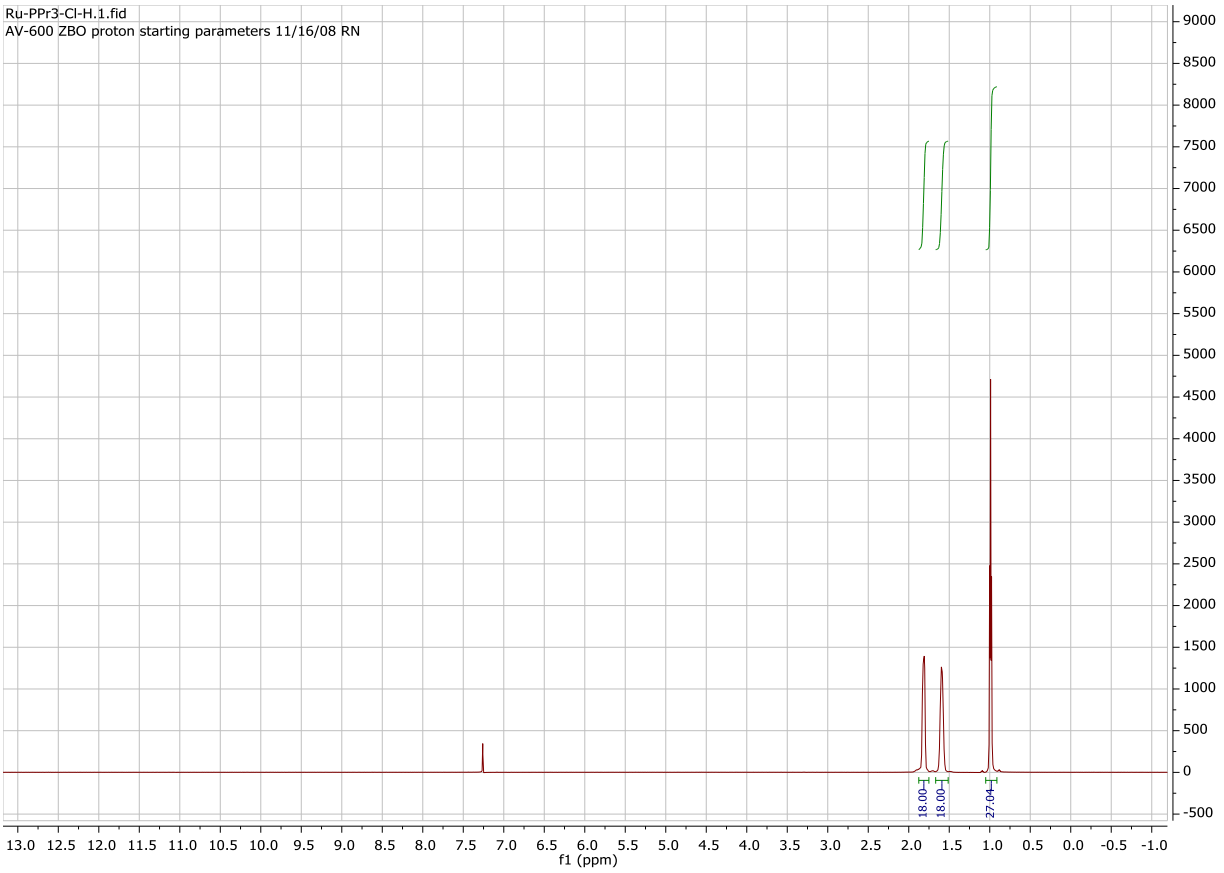
f1 (ppm)

[Ru(P^{n}Pr$_3$)$_6$Cl$_3$][Cl]

^{1}H



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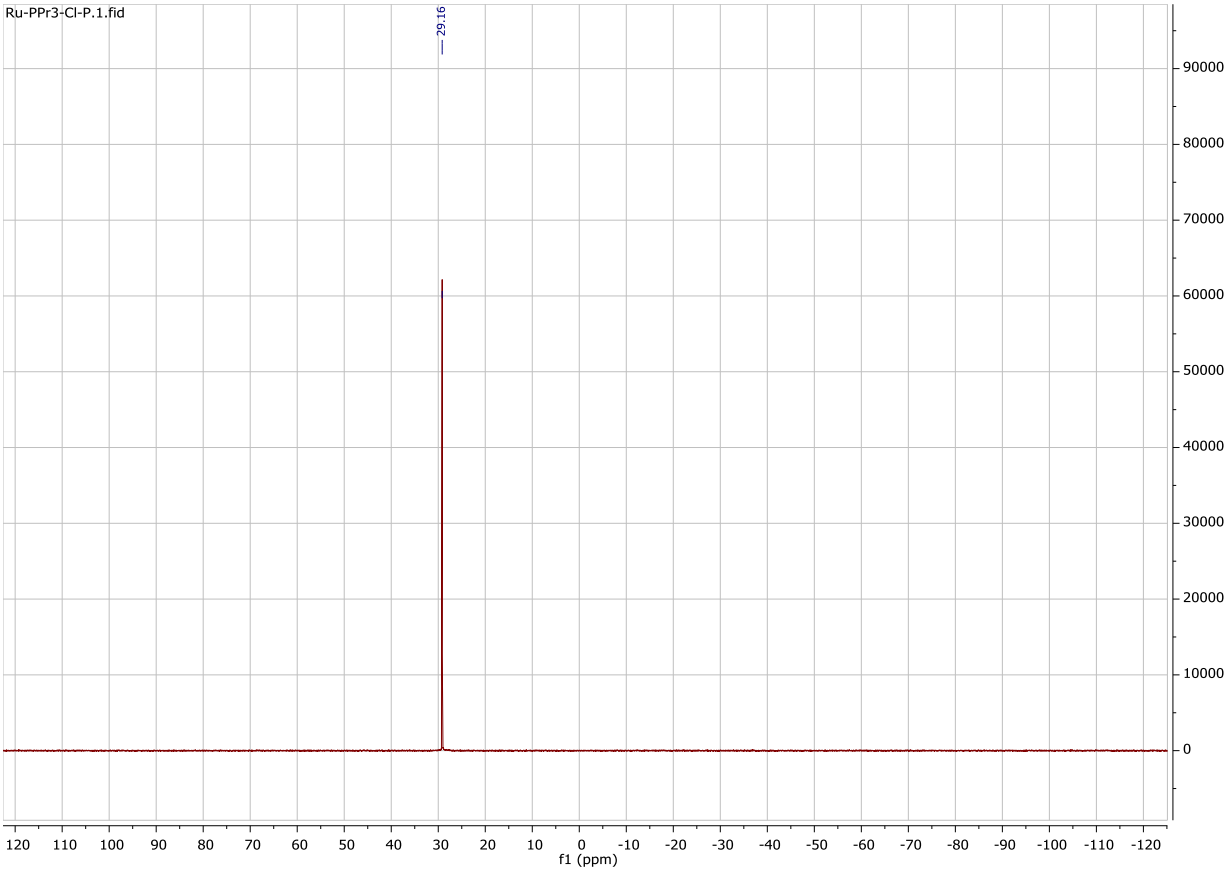
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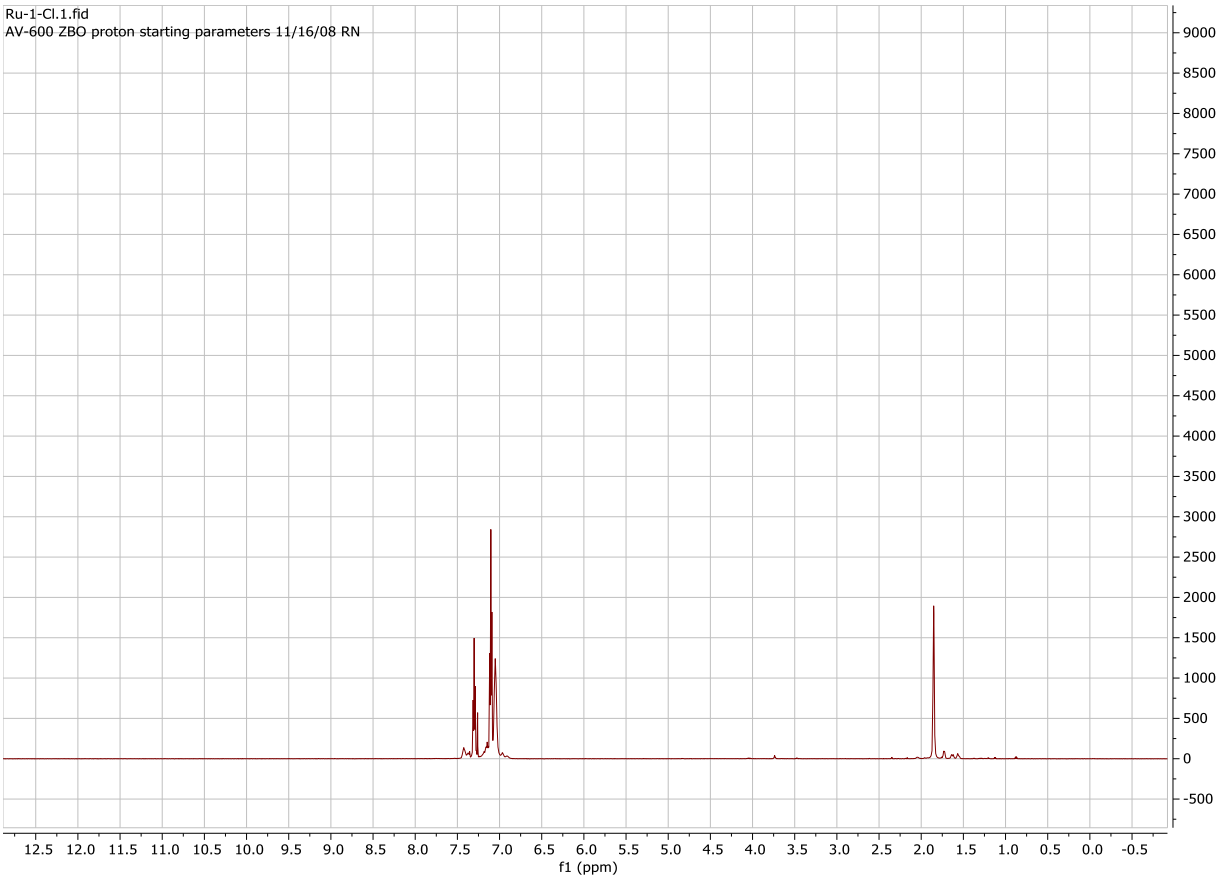
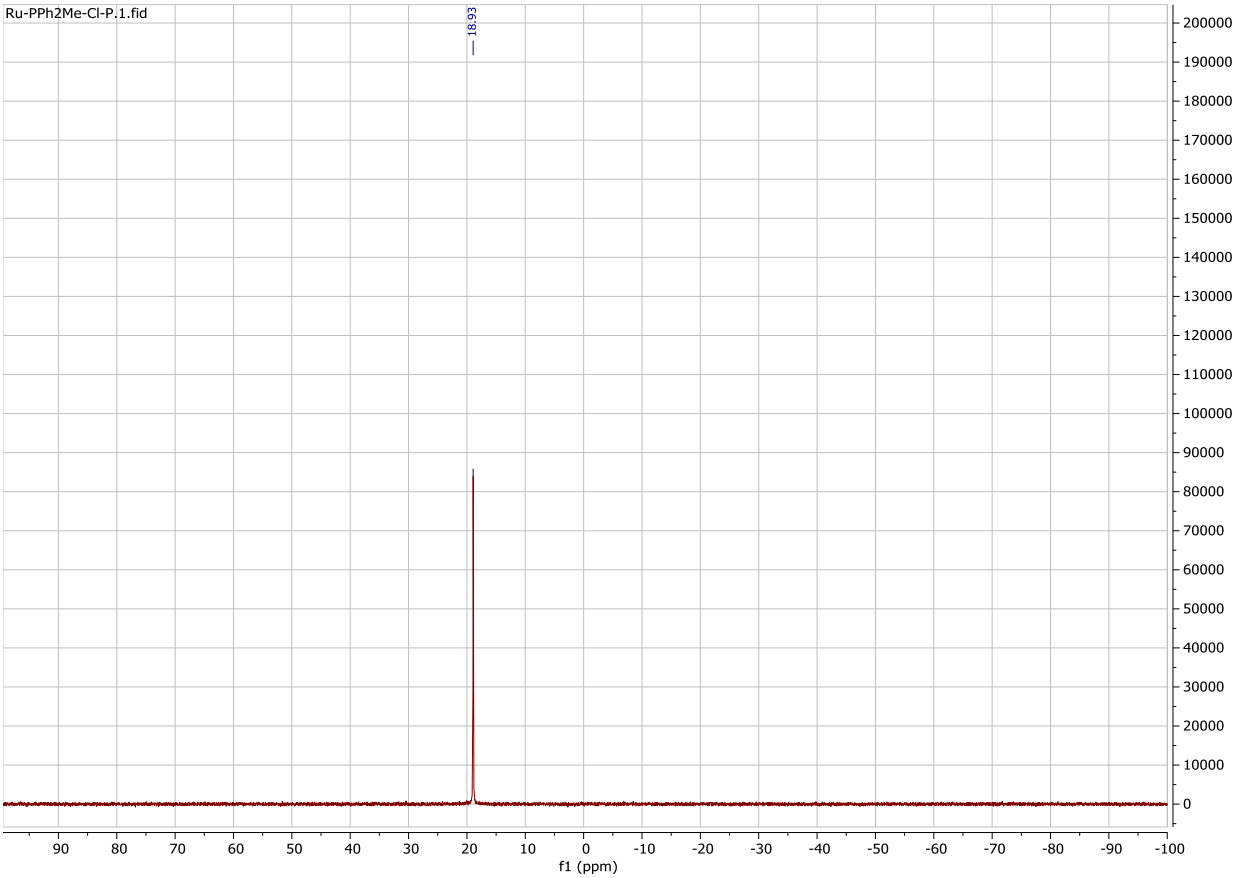
f1 (ppm)

$[Ru_2(PMePh_2)_6Cl_3][Cl]$

^1H

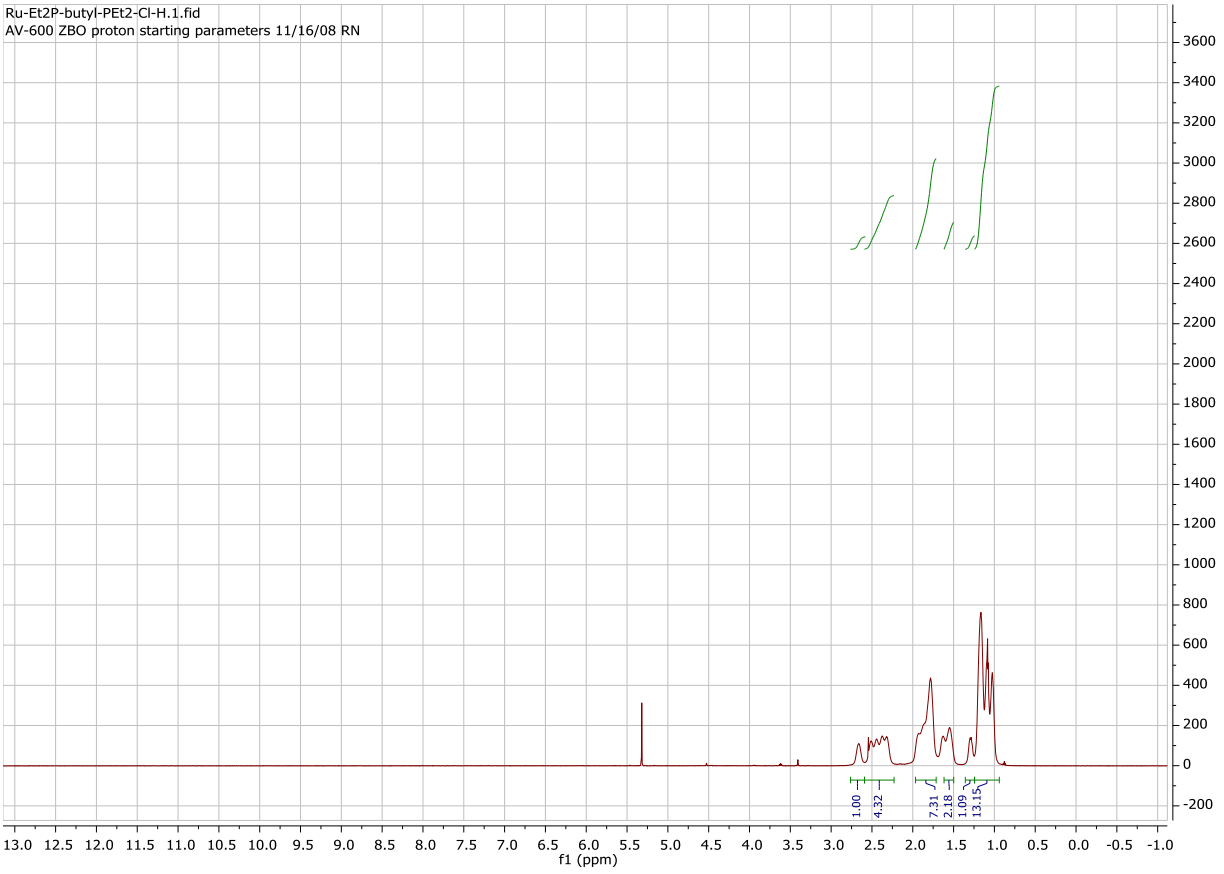


^{31}P

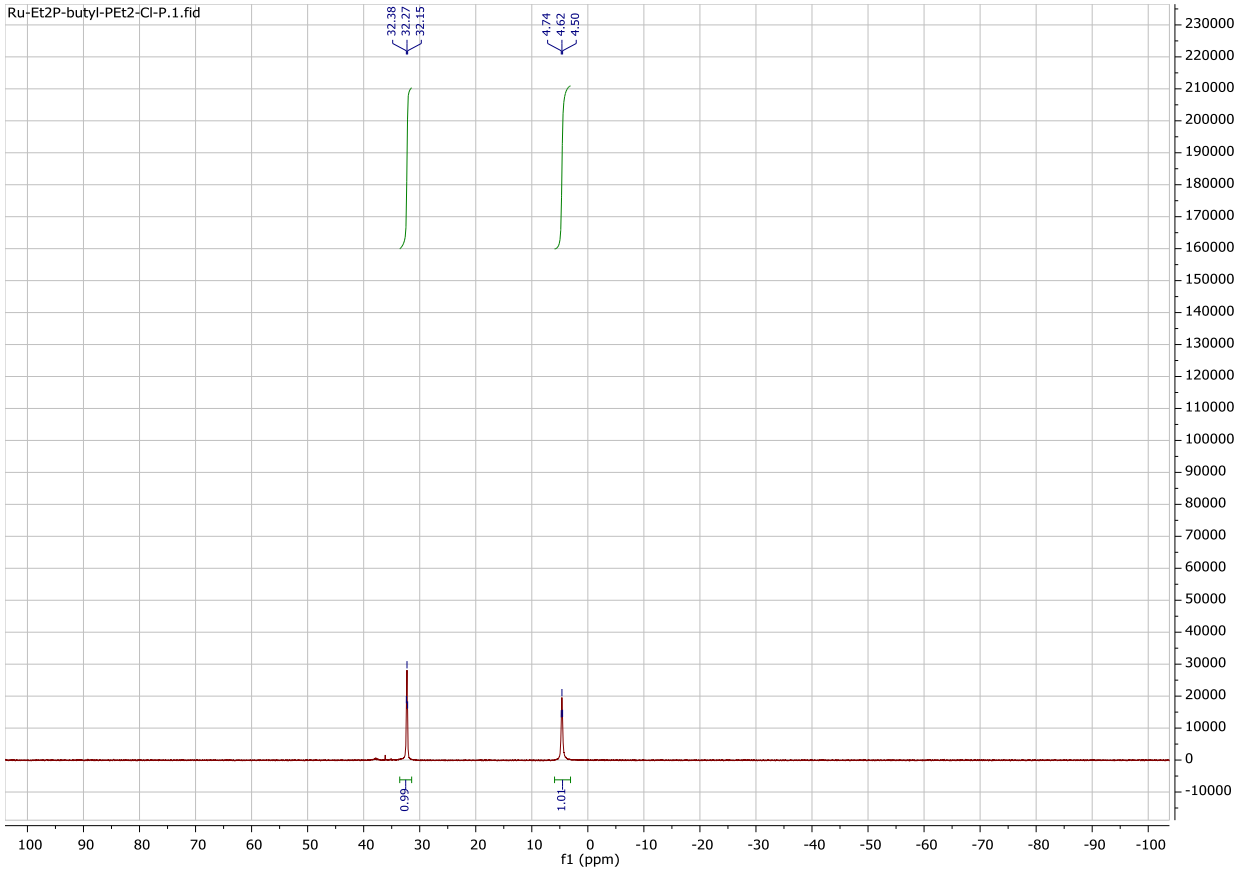

Ru-PPh2Me-Cl-P.1.fid
18.93
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

cis-$Ru(Et_2P(CH_2)_4PEt_2)_2Cl_2$

^1H

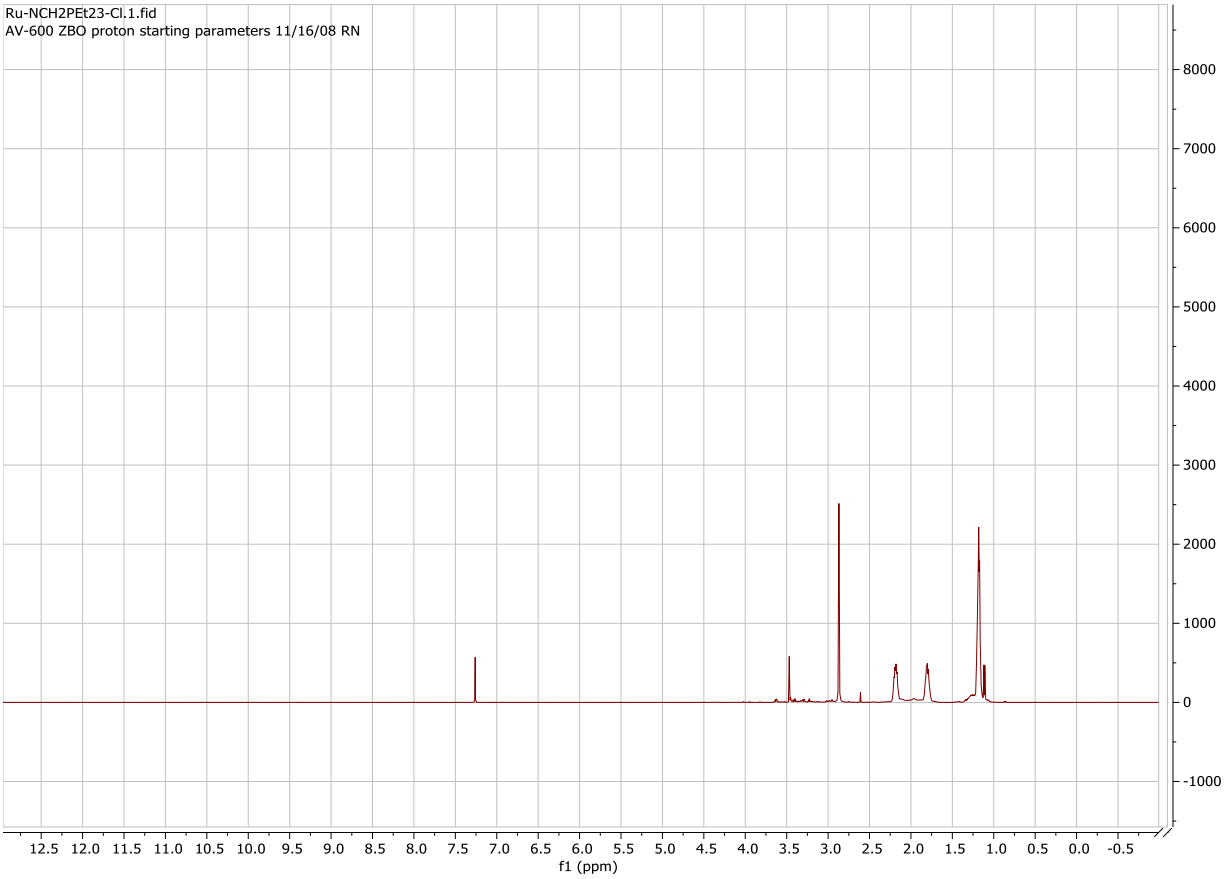


^{31}P

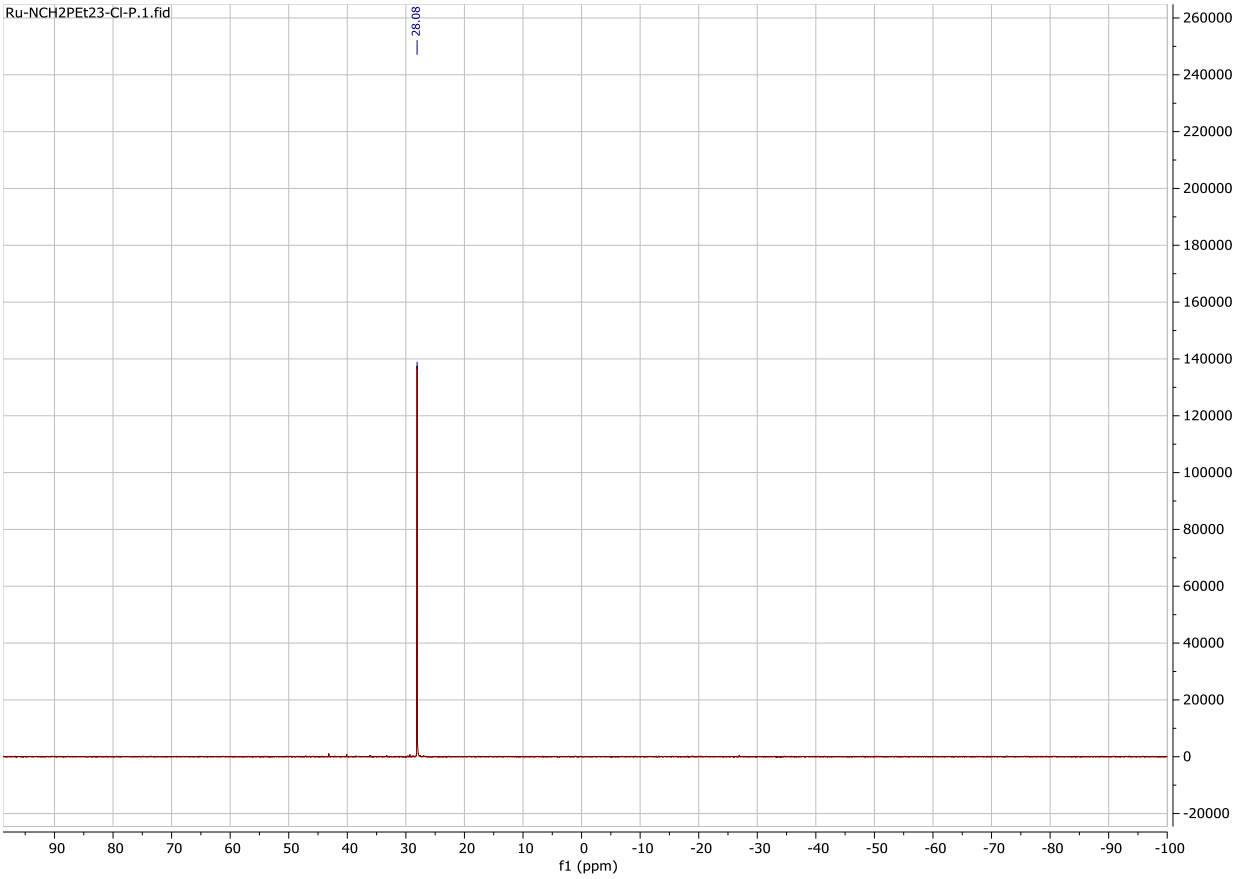

Ru-Et2P-butyl-PEt2-Cl-P.1.fid
32.38
32.27
32.15
4.74
4.62
4.50
0.99
1.01
f1 (ppm)

[$Ru_2(N(CH_2PEt_2)_3)_2Cl_3$][Cl]

^1H

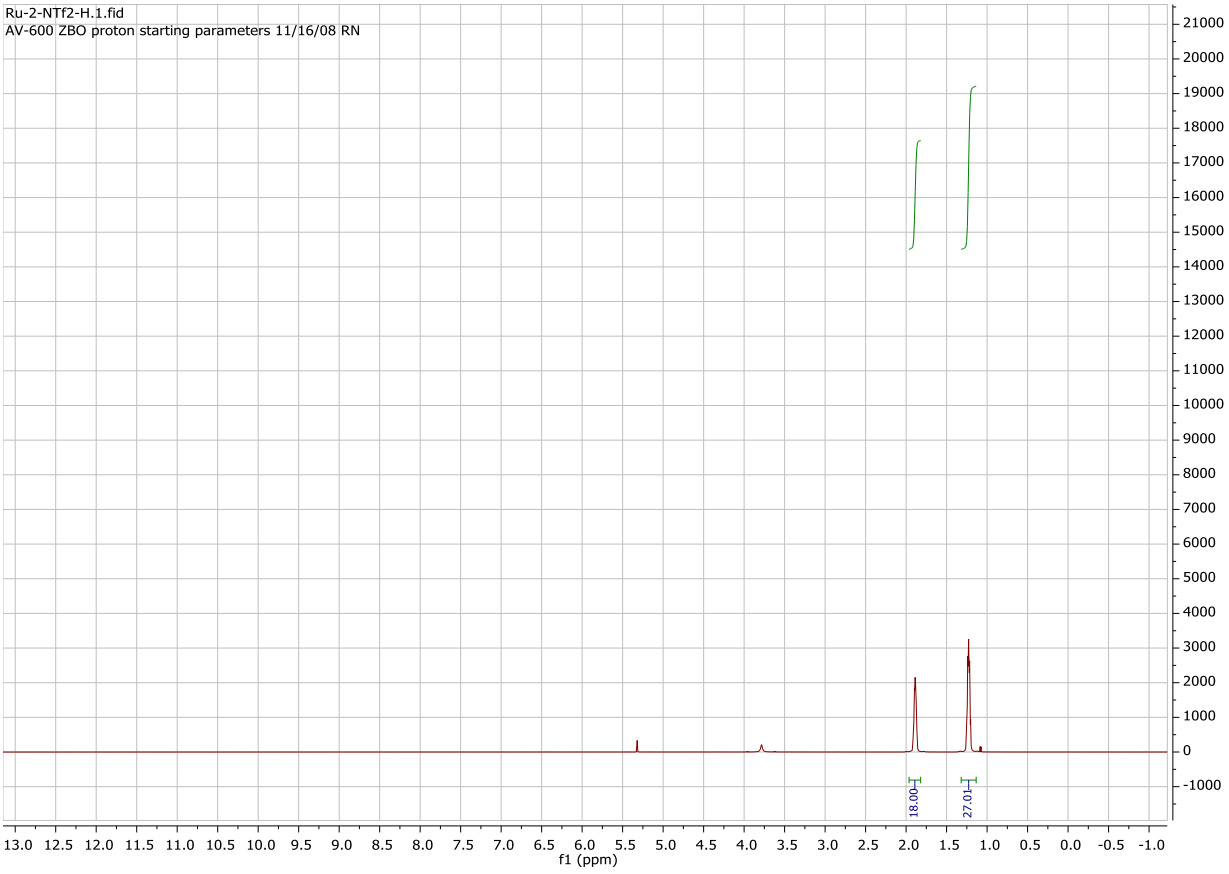


^{31}P

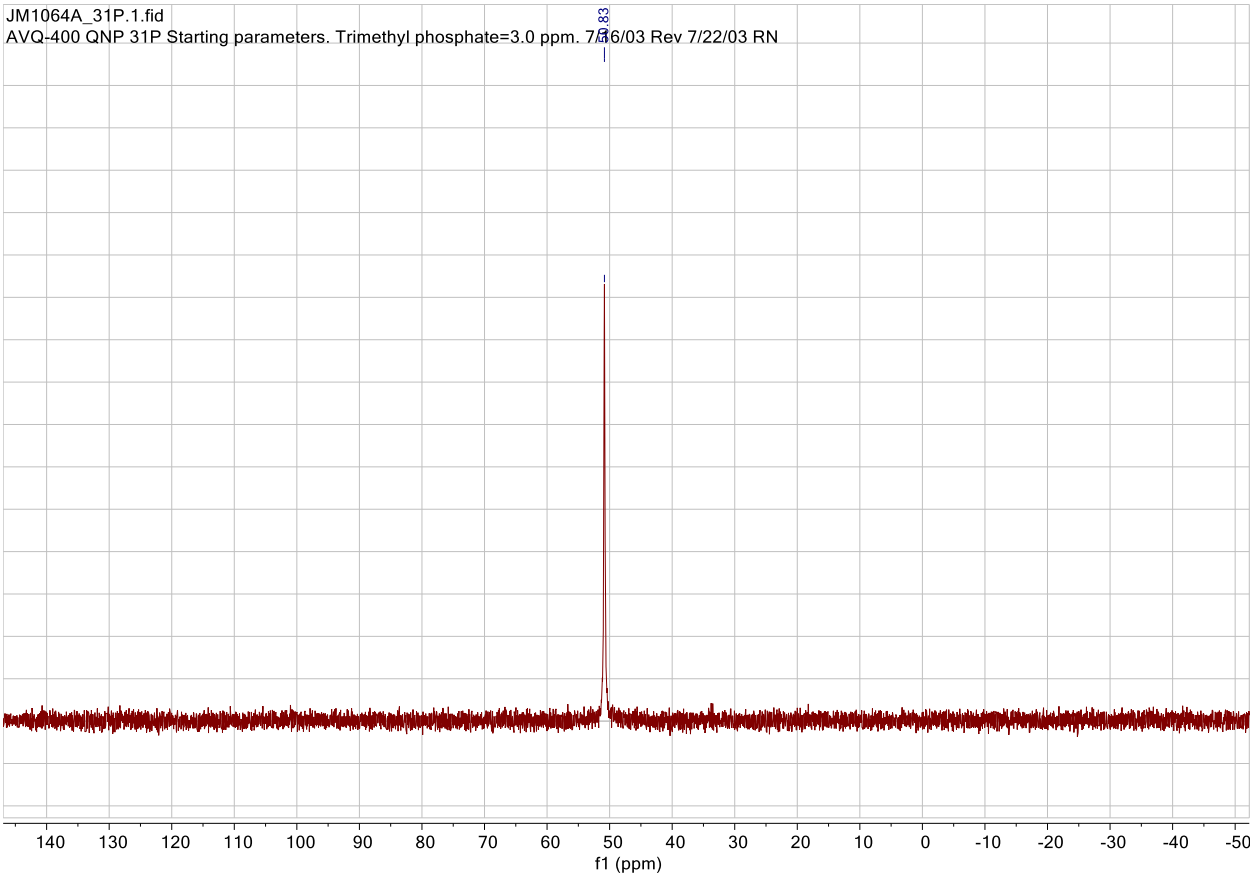

Ru-NCH2PEt23-Cl-P.1.fid
28.08
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

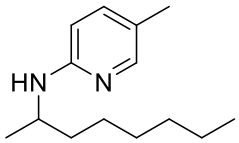
$Ru(PEt_3)_3(NTf_2)_2$ (Ru-1)

^1H



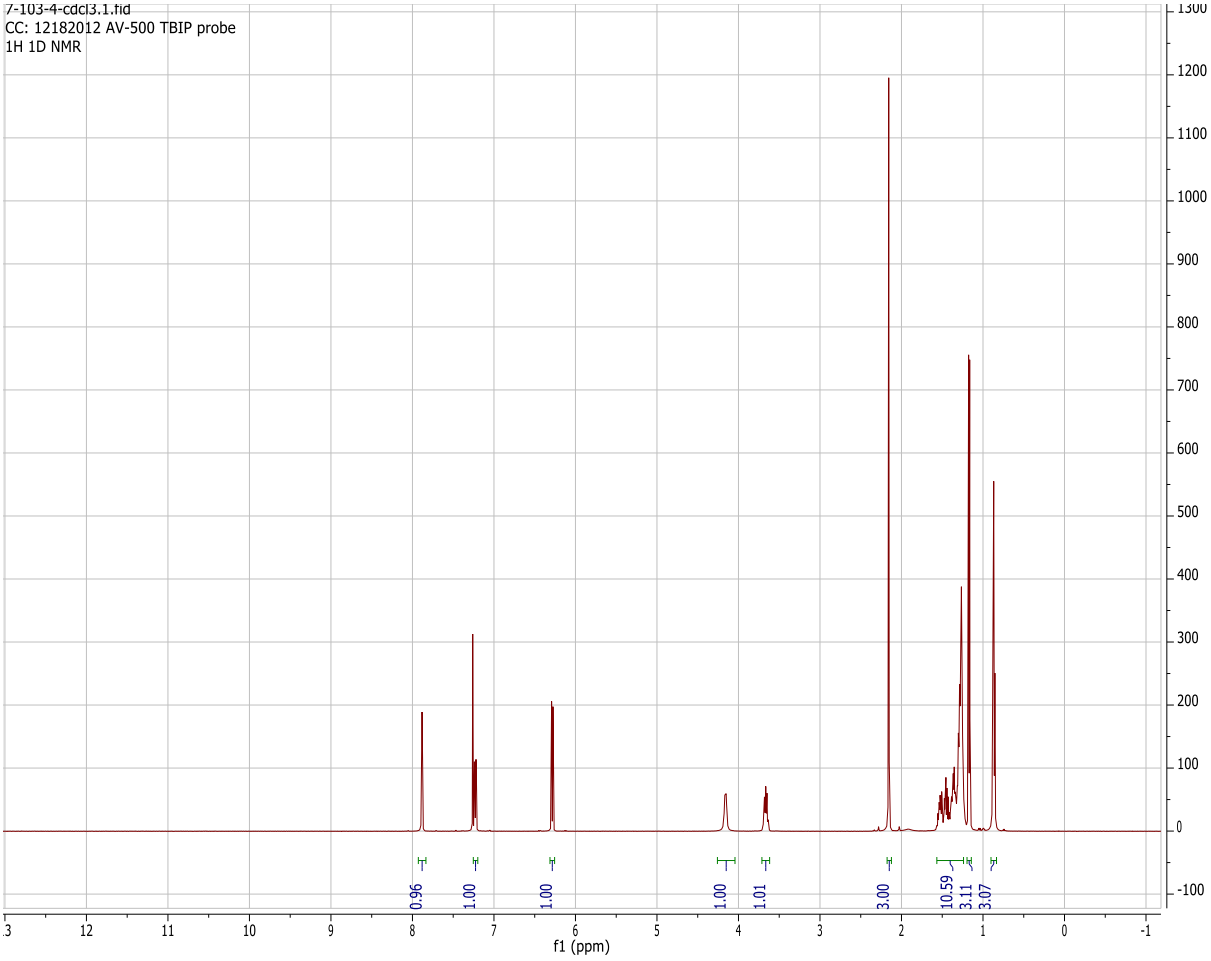
^{31}P


JM1064A_31P.1.fid
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
49.83
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

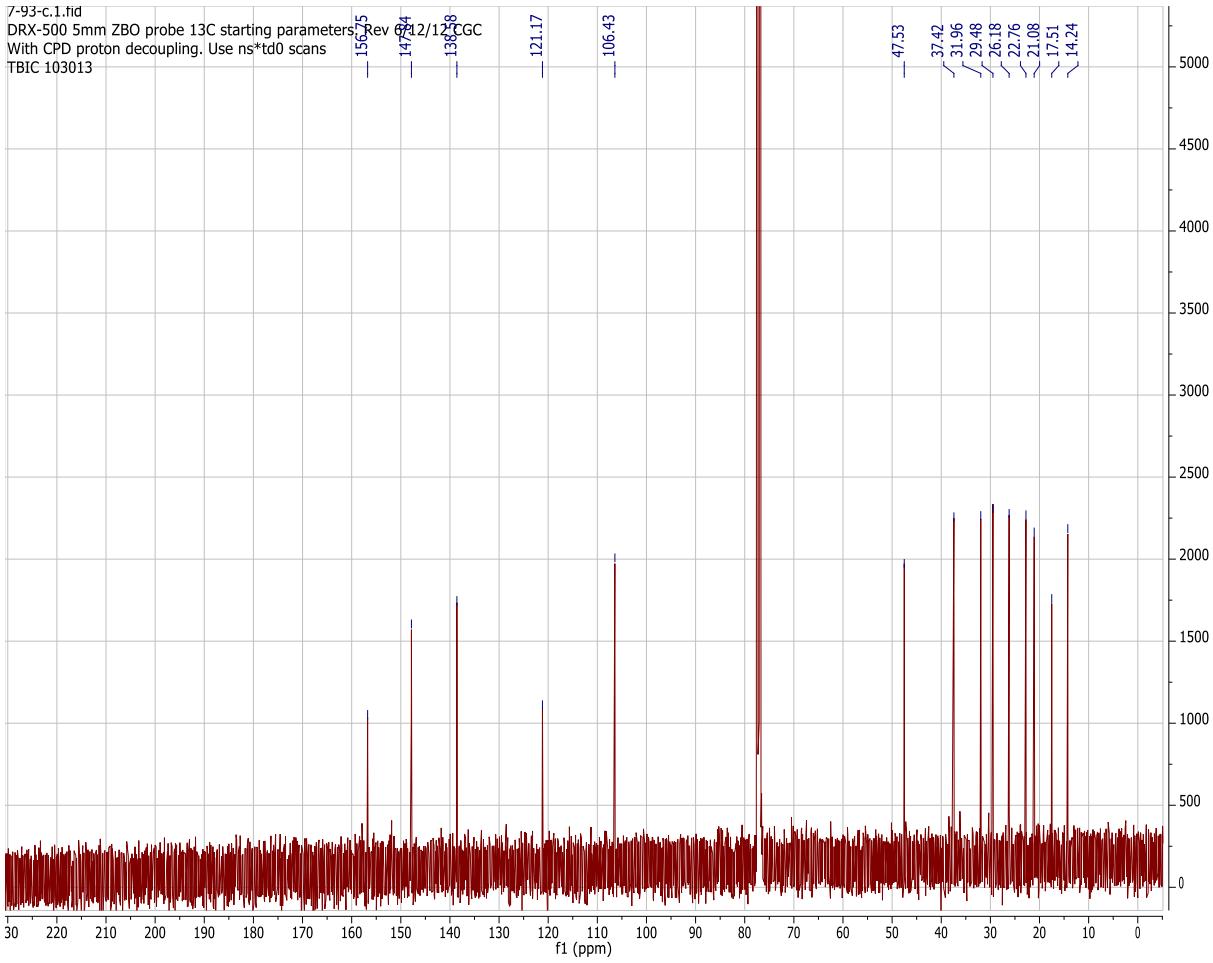


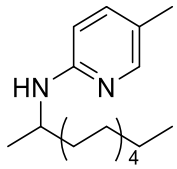
5-methyl-*N*-(octan-2-yl)pyridine-2-amine (2a)

^{1}H



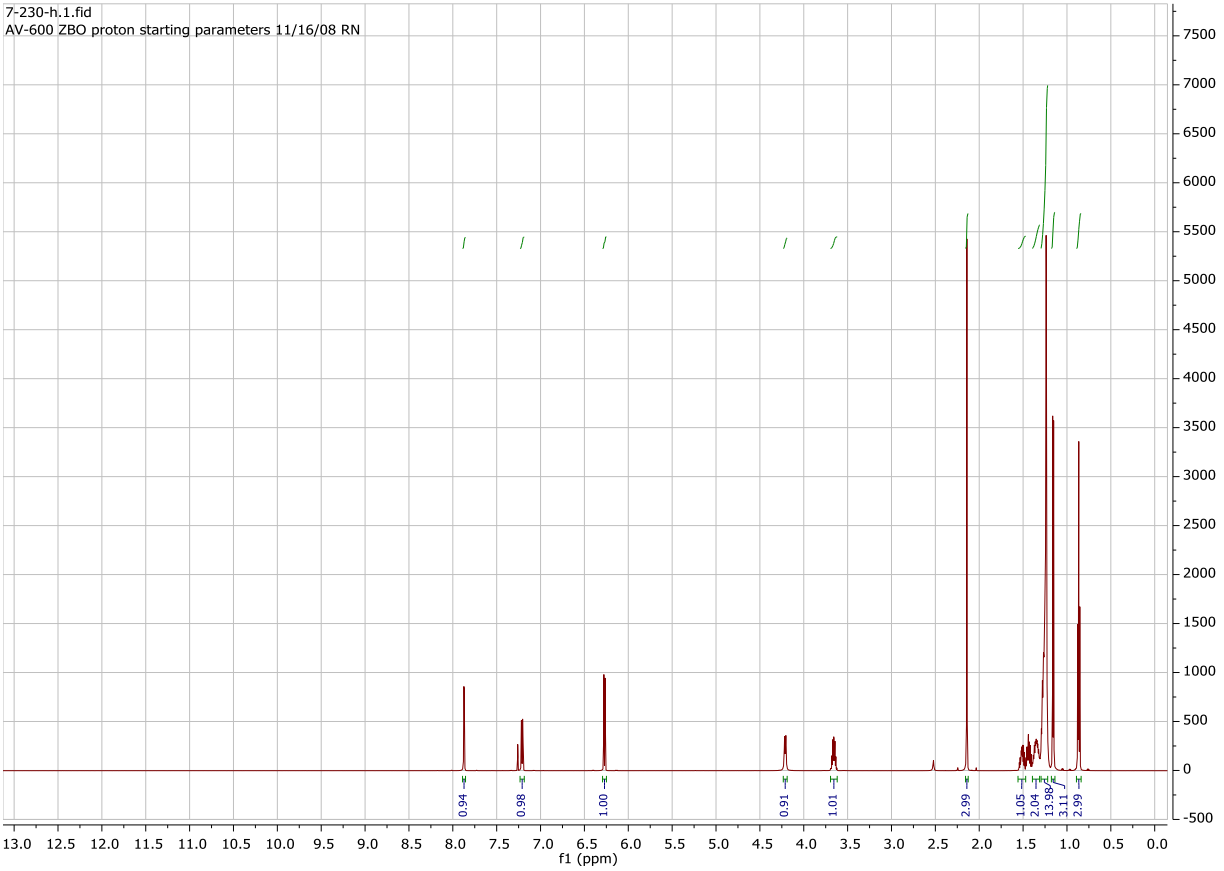
^{13}C


7-93-c.1.fid
DRX-500 5mm ZBO probe 13C starting parameters Rev 6.2 12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
TBIC 103013
156.55
147.24
138.58
121.17
106.43
47.53
37.42
31.96
29.48
26.18
22.76
21.08
17.51
14.24
f1 (ppm)

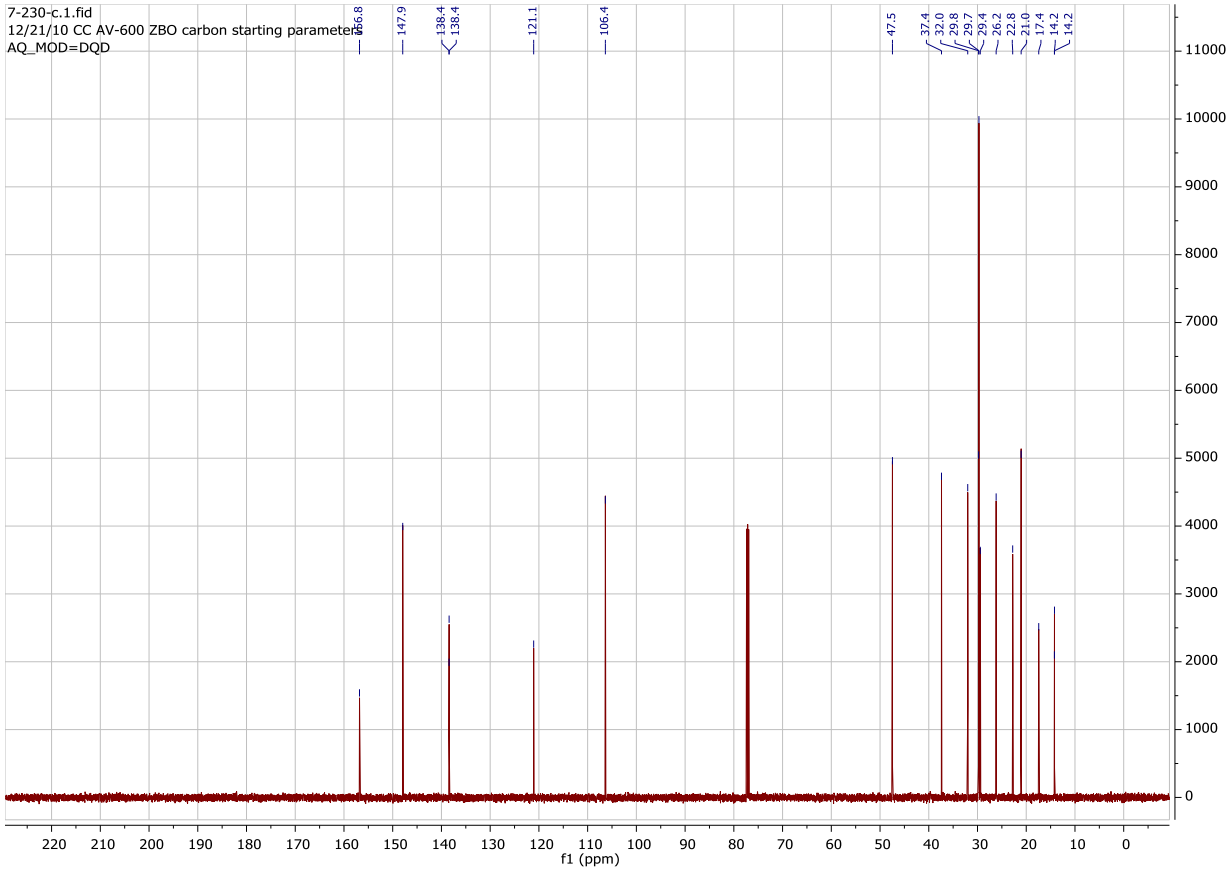


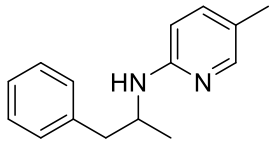
5-methyl-N-(dodecan-2-yl)pyridine-2-amine (3a)

^{1}H



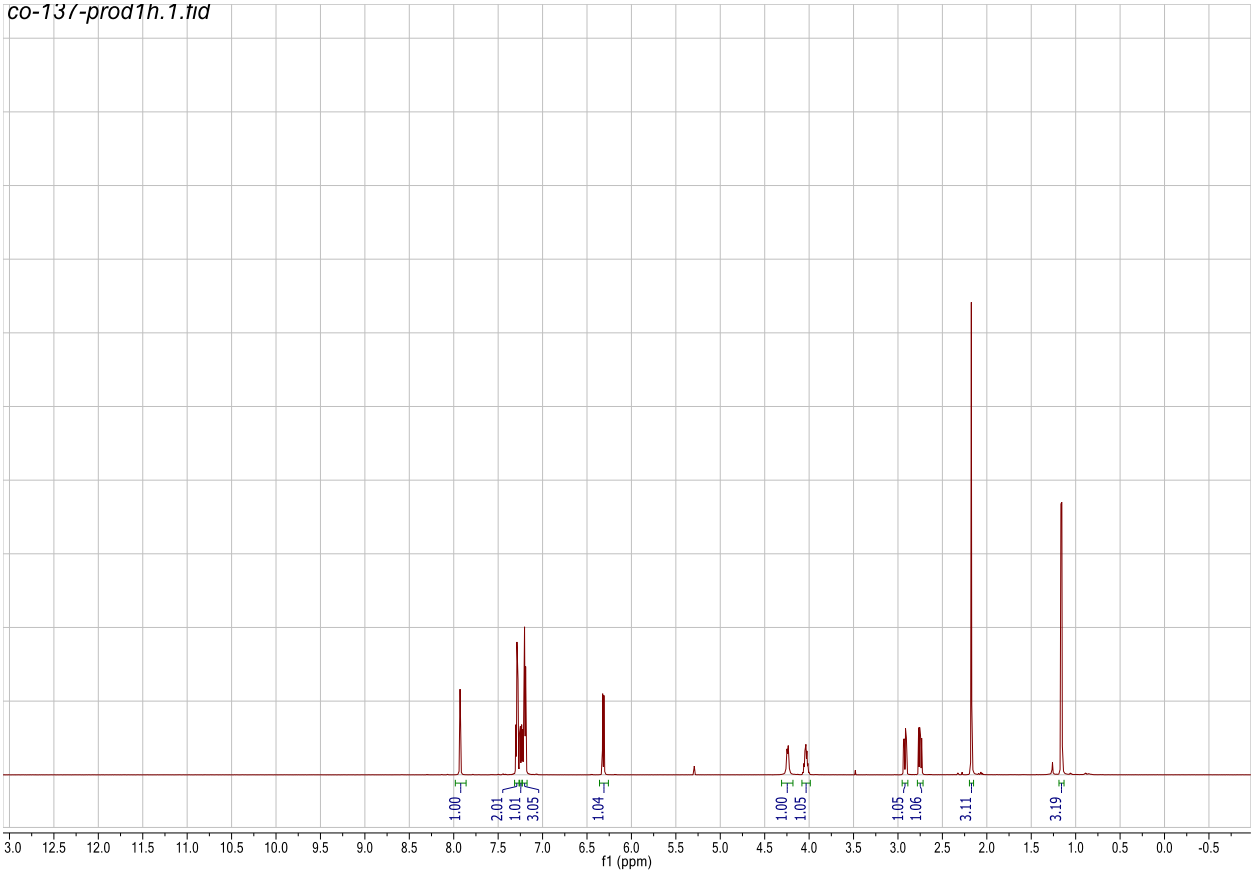
^{13}C


7-230-c.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
166.8
147.9
138.4
138.4
121.1
106.4
47.5
37.4
32.0
29.8
29.7
29.4
26.2
22.8
21.0
17.4
14.2
14.2
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

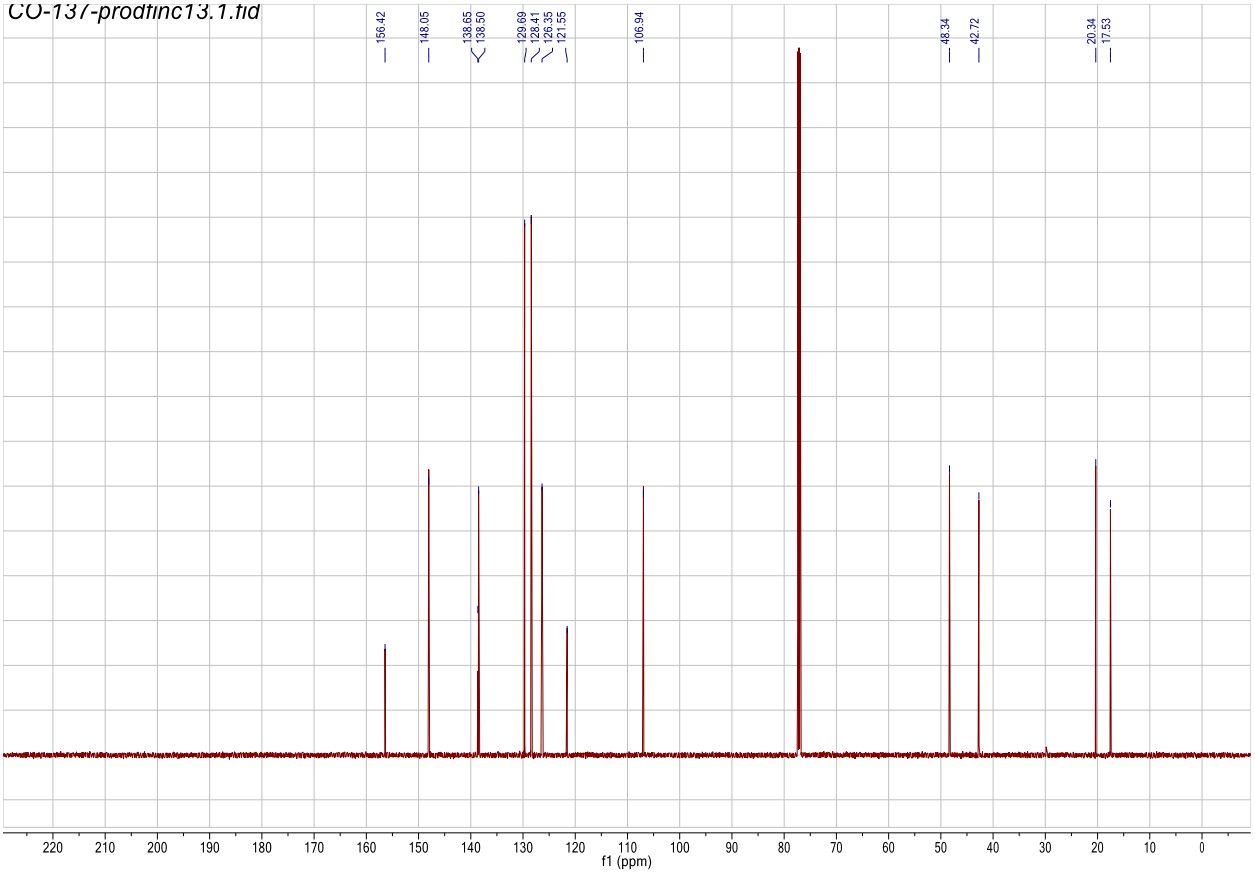


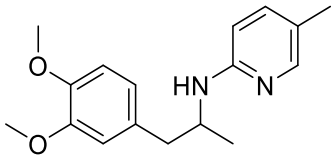
5-methyl-*N*-(1-phenylpropan-2-yl)pyridine-2-amine (4a)

^{1}H



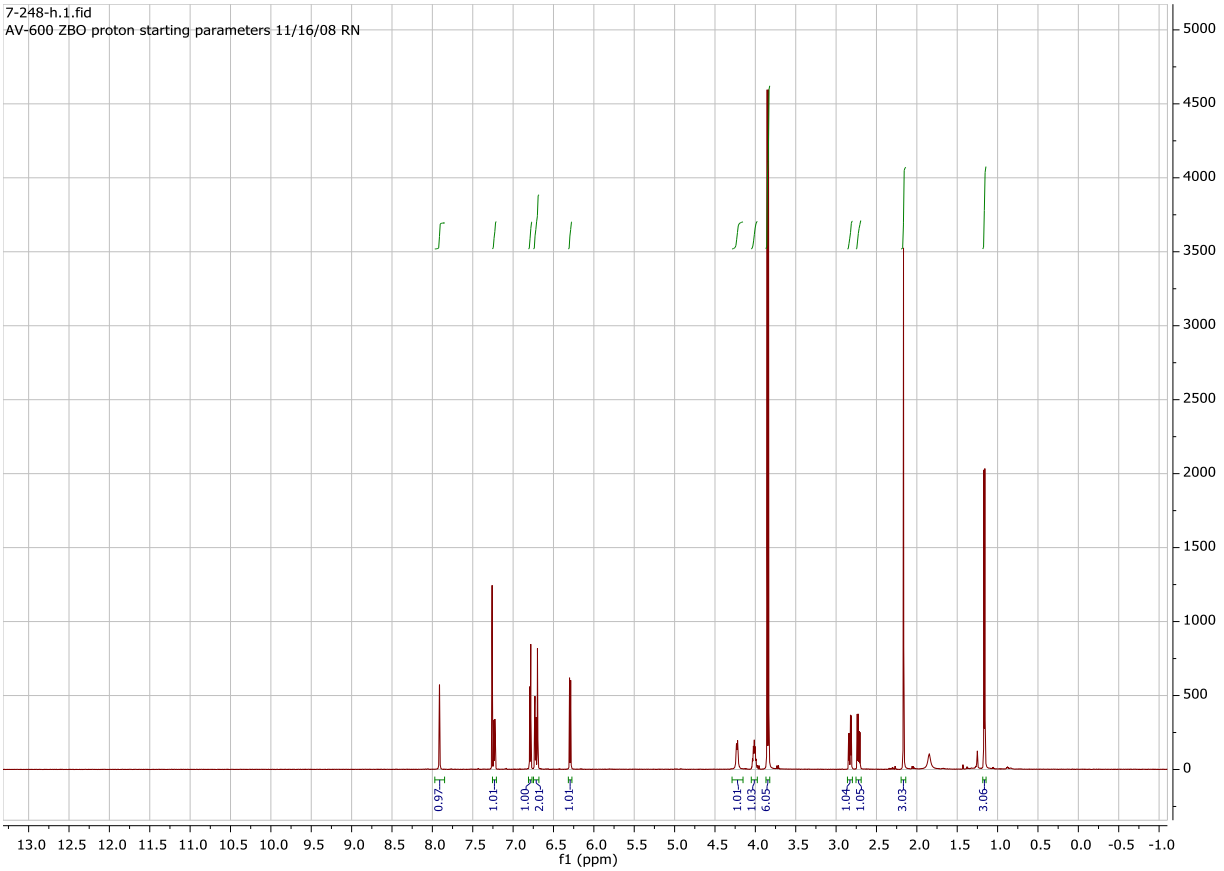
^{13}C


CO-137-prodtinc13.1.fid
156.42
148.05
138.65
138.50
129.69
128.41
126.35
121.55
106.94
48.34
42.72
20.34
17.53
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

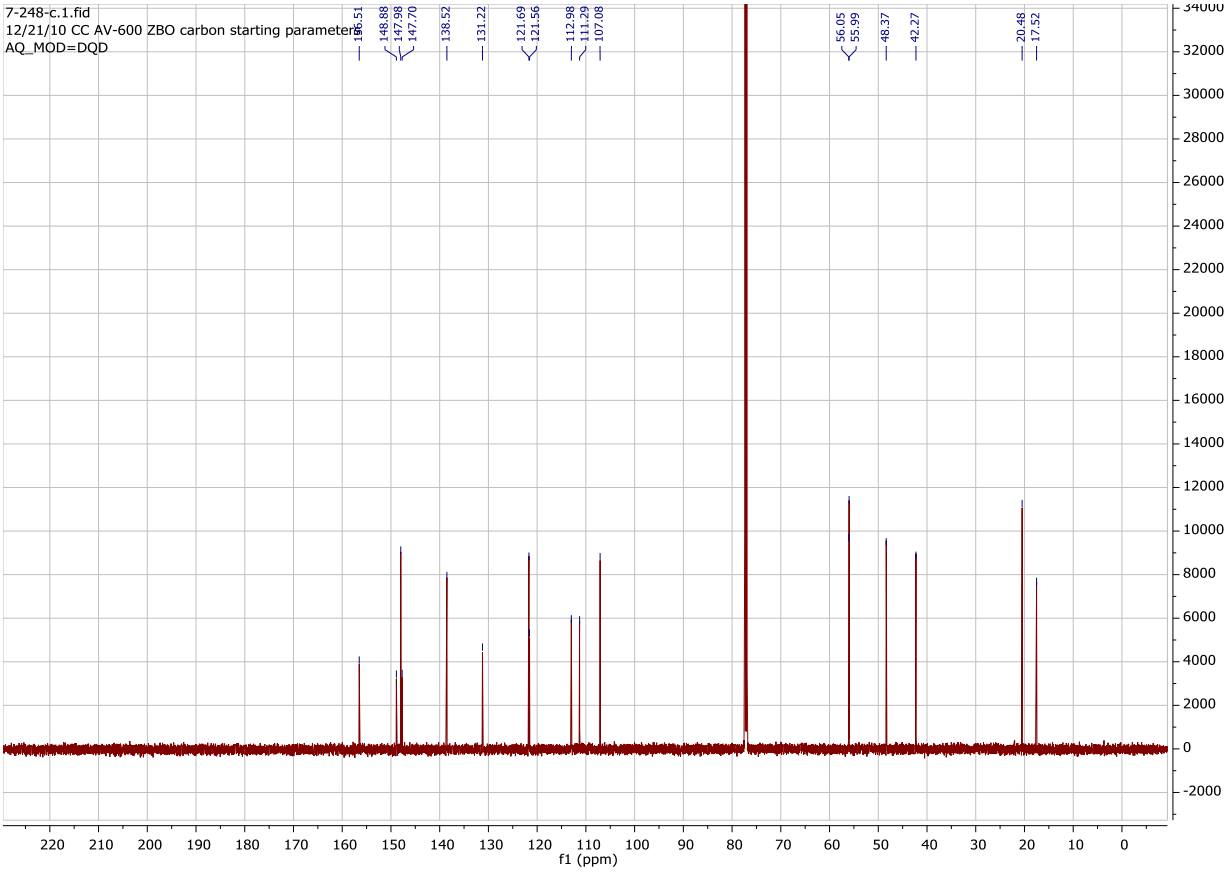


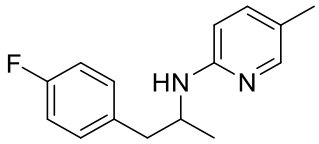
N-(1-(3,4-dimethoxyphenyl)propan-2-yl)-5-methylpyridin-2-amine (5a)

^{1}H



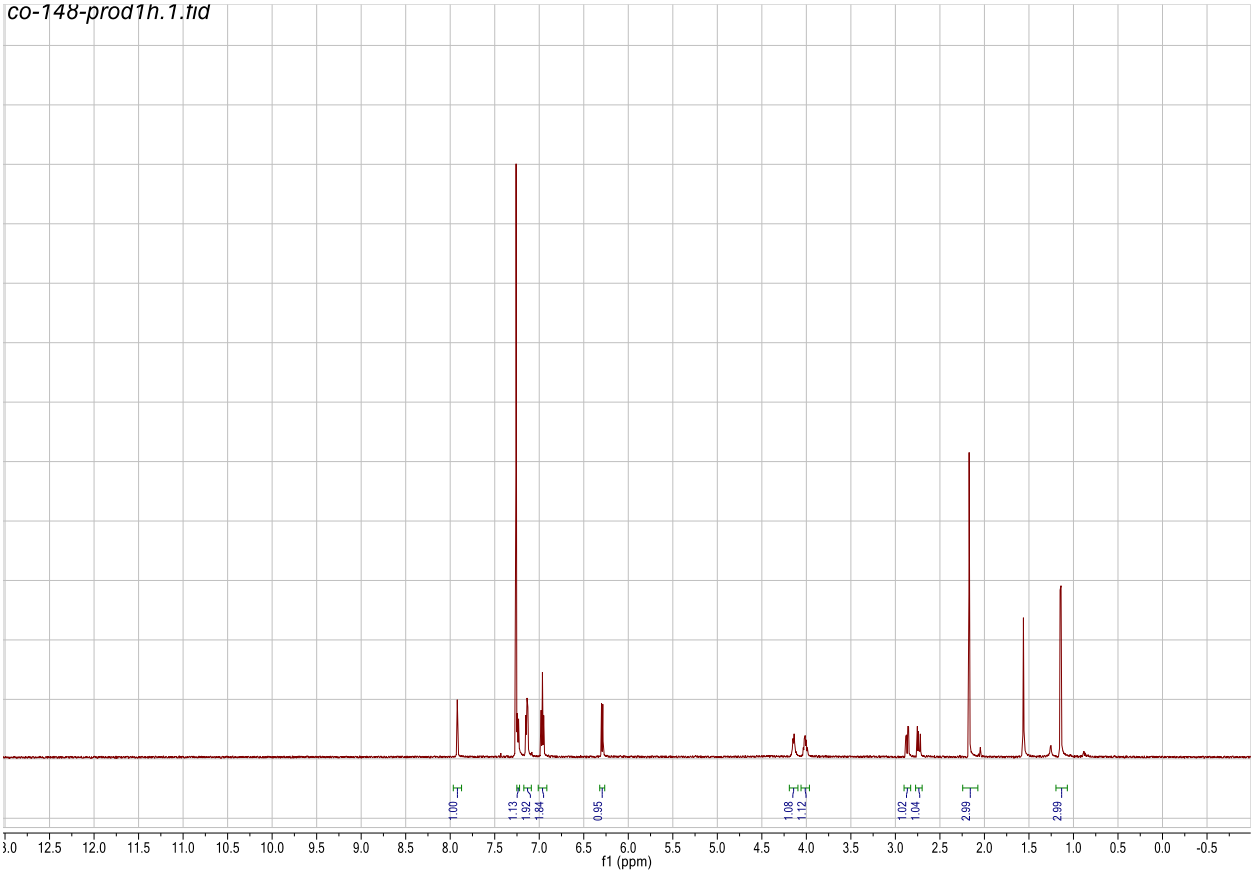
^{13}C


7-248-c.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
196.51
148.88
147.98
147.70
138.52
131.22
121.69
121.56
112.98
111.29
107.08
56.05
55.99
48.37
42.27
20.48
17.52
f1 (ppm)

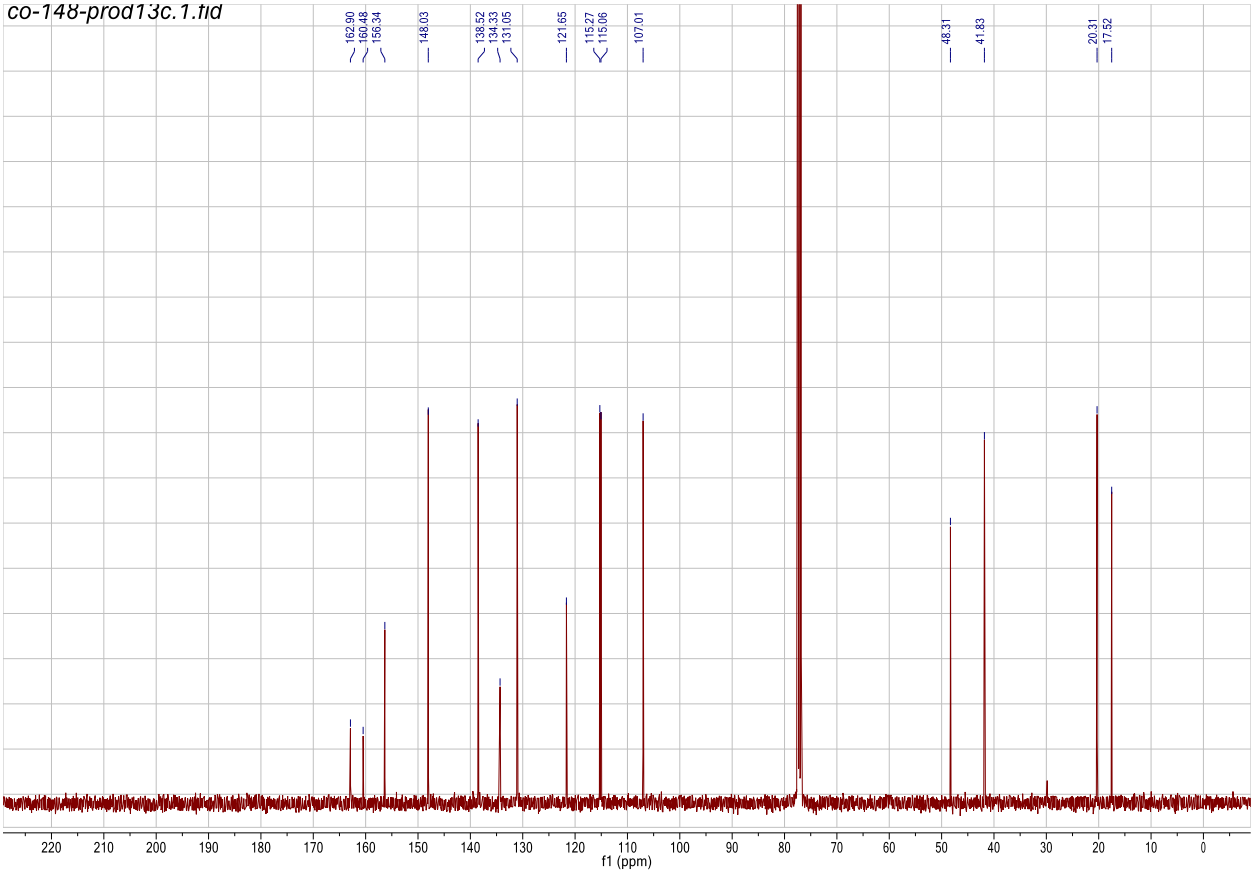


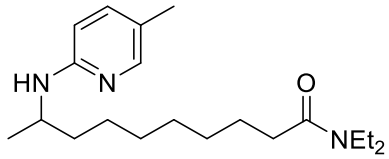
5-methyl-*N*-(1-(4-fluoro-phenyl)propan-2-yl)pyridine-2-amine (6a)

^{1}H



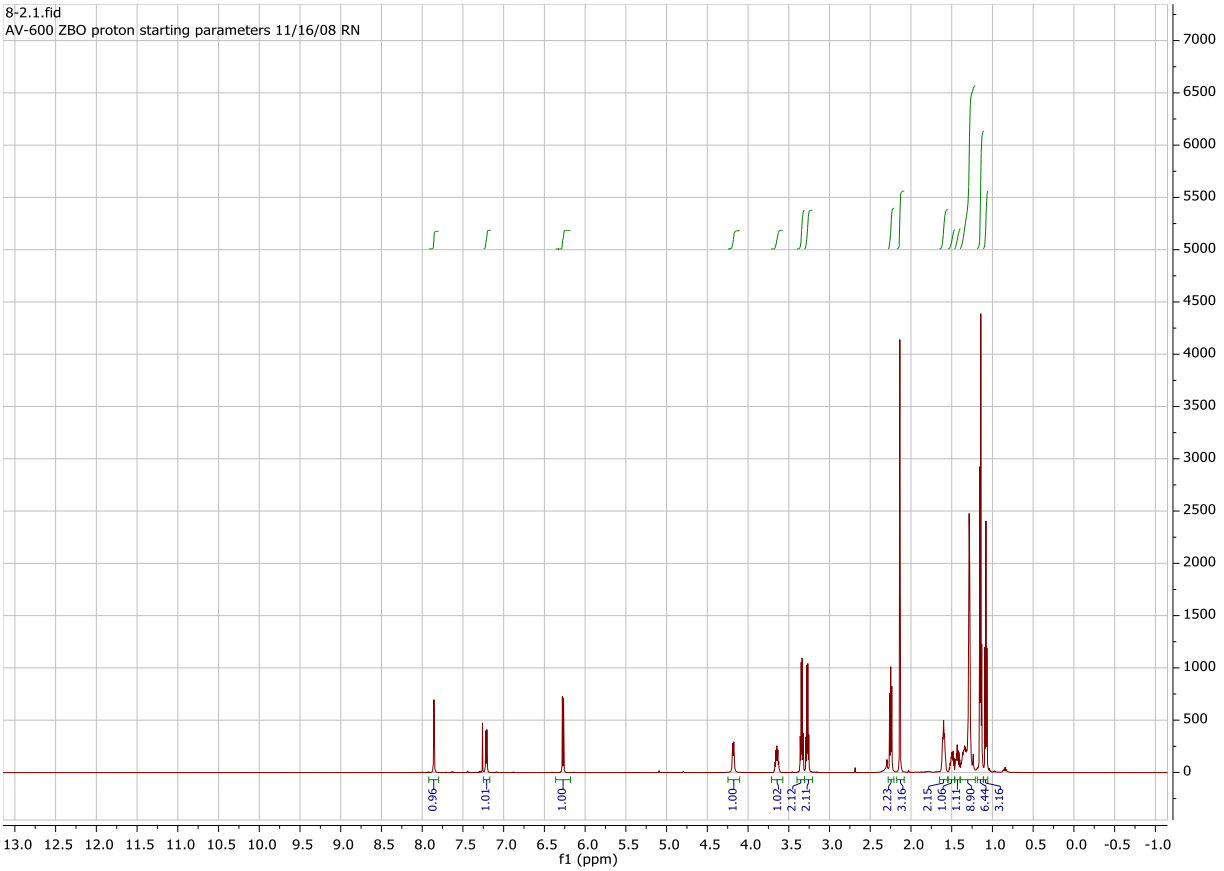
^{13}C


co-148-prod13c.1.fid
162.90
160.48
156.34
148.03
138.52
134.33
131.05
121.65
115.27
115.06
107.01
48.31
41.83
20.31
17.52
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

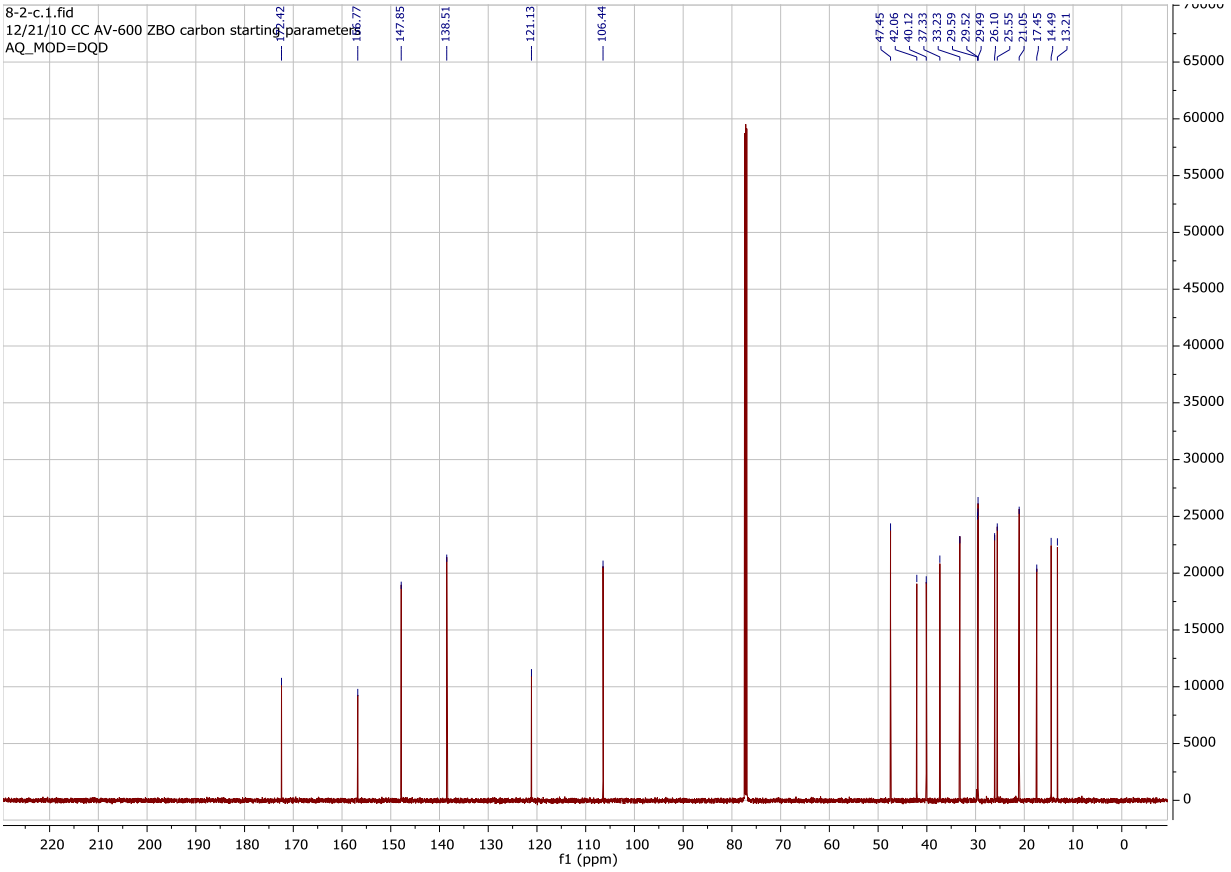


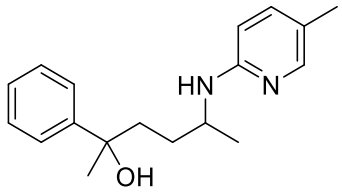
N,N-diethyl-9-((5-methylpyridin-2-yl)amino)decanamide (7a)

^{1}H

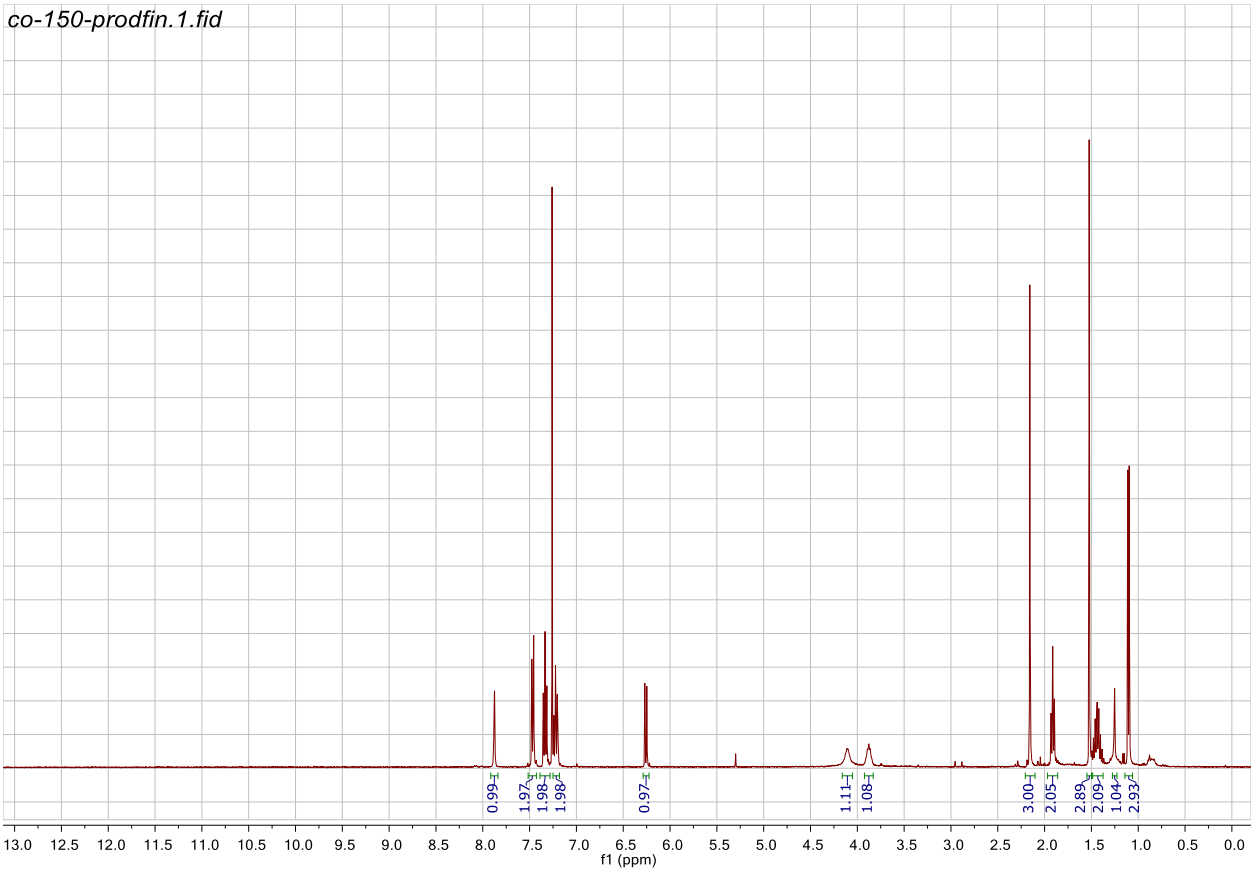


^{13}C

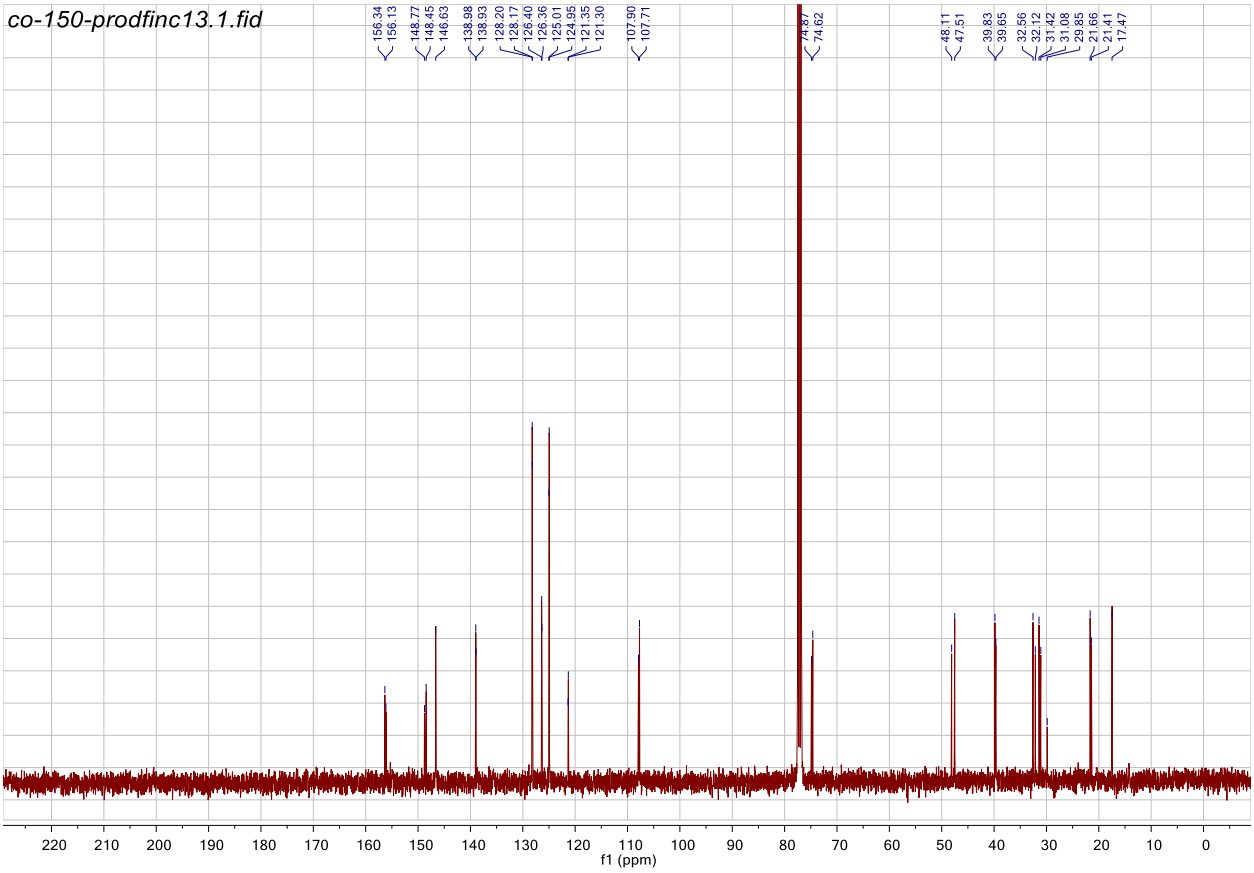

8-2-c.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
172.42
156.77
147.85
138.51
121.13
106.44
47.45
42.06
40.12
37.33
33.23
29.59
29.52
29.49
26.10
25.55
21.05
17.45
14.49
13.21
f1 (ppm)

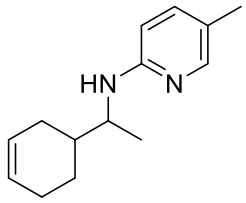


5-((5-methylpyridin-2-yl)amino)-2-phenylhexan-2-ol (8a)
^{1}H



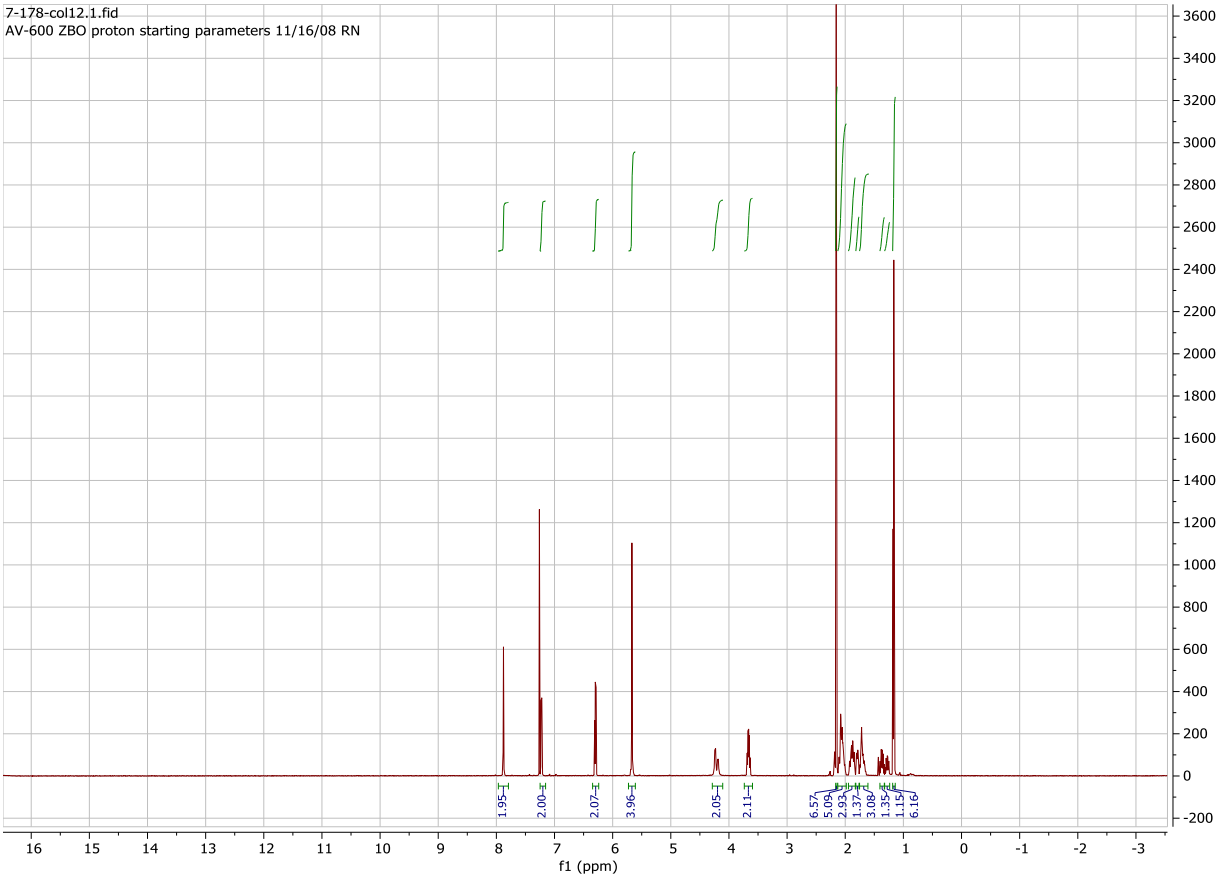
^{13}C


co-150-prodfinc13.1.fid
156.34
156.13
148.77
148.45
146.63
138.98
138.93
128.20
128.17
126.40
126.36
125.01
124.95
121.35
121.30
107.90
107.71
74.87
74.62
48.11
47.51
39.83
39.65
32.56
32.12
31.42
31.08
29.85
21.66
21.41
17.47
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

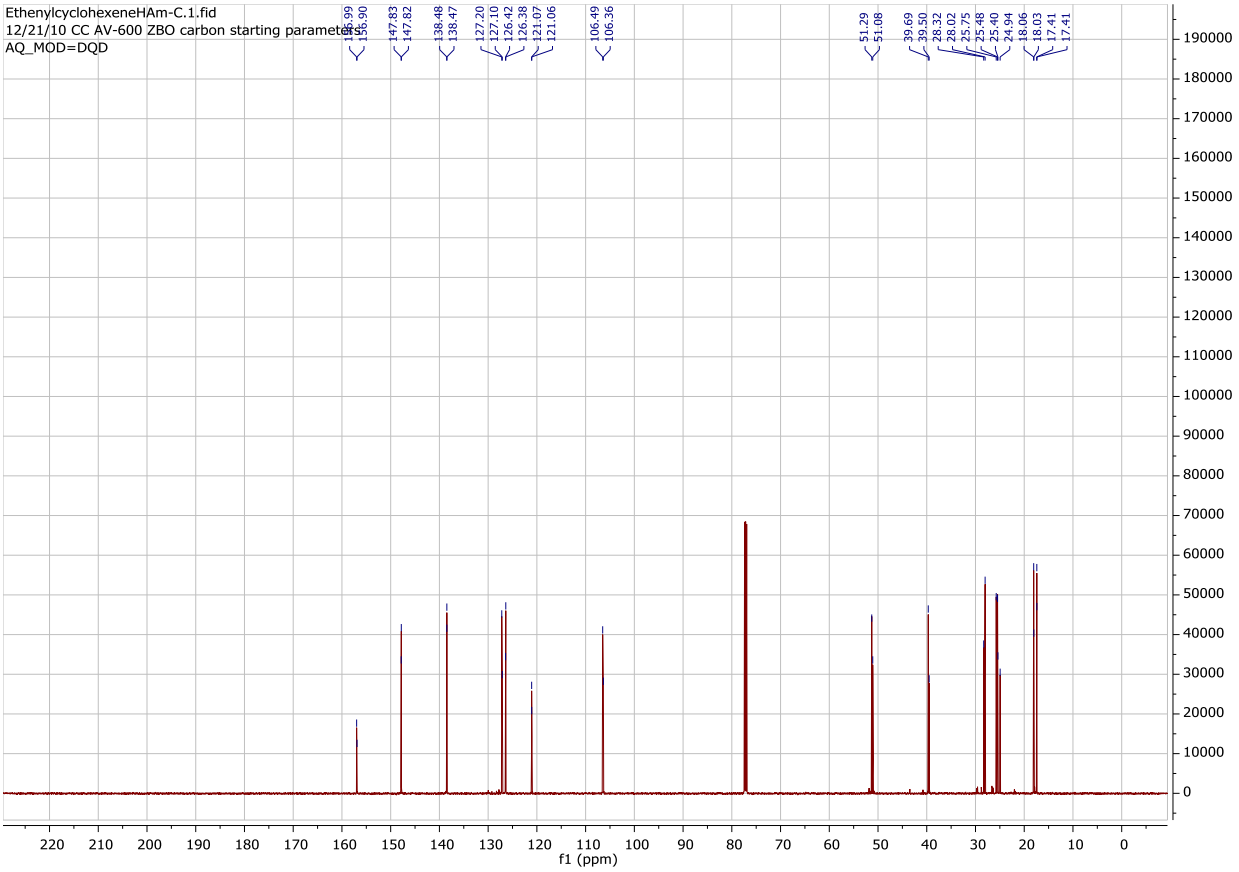


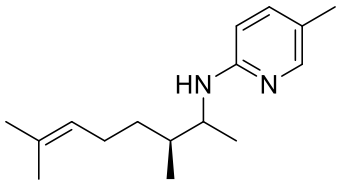
N-(1-(cyclohex-3-en-1-yl)ethyl)-5-methylpyridin-2-amine (9a)

^{1}H



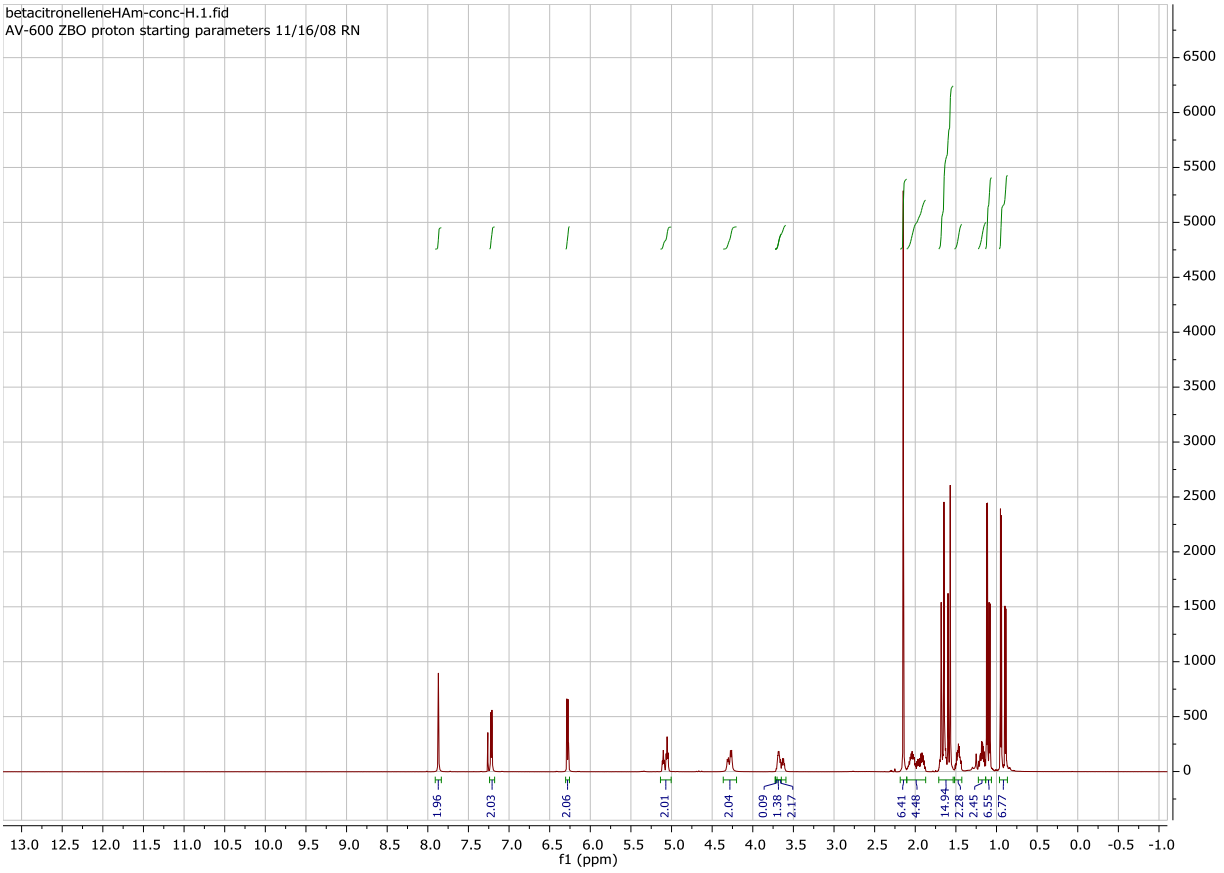
^{13}C


EthenylcyclohexeneHAm-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
156.99
156.90
147.83
147.82
138.48
138.47
127.20
127.10
126.42
126.38
121.07
121.06
106.49
106.36
51.29
51.08
39.69
39.50
28.32
28.02
25.75
25.48
25.40
24.94
18.06
18.03
17.41
17.41
f1 (ppm)

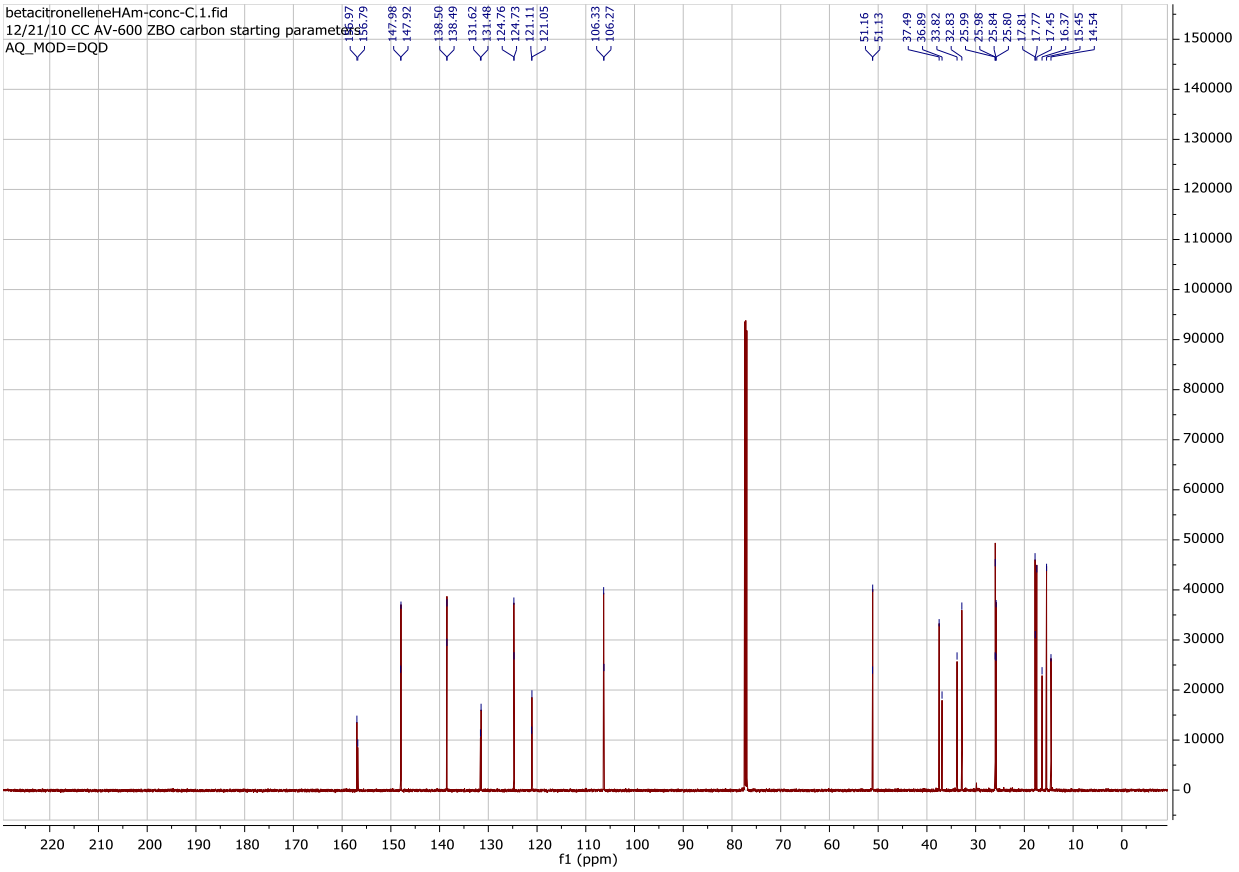


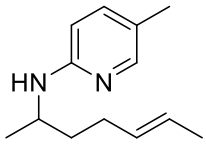
N-((3S)-3,7-dimethyloct-6-en-2-yl)-5-methylpyridin-2-amine (10a)

^{1}H



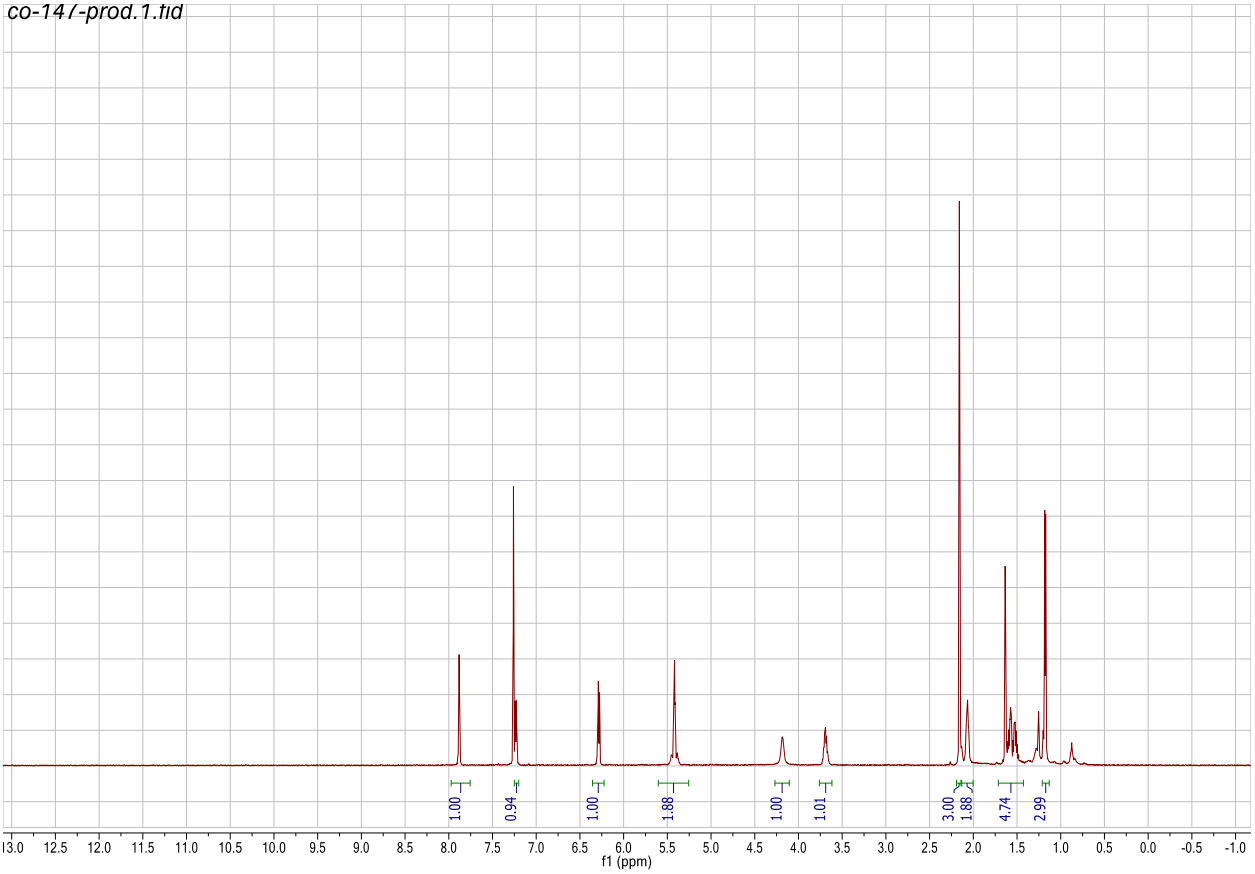
^{13}C


betacitronelleneHAm-conc-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
156.97
156.79
147.98
147.92
138.50
138.49
131.62
131.48
124.76
124.73
121.11
121.05
106.33
106.27
51.16
51.13
37.49
36.89
33.82
32.83
25.99
25.98
25.84
25.80
17.81
17.77
17.45
16.37
15.45
14.54
f1 (ppm)

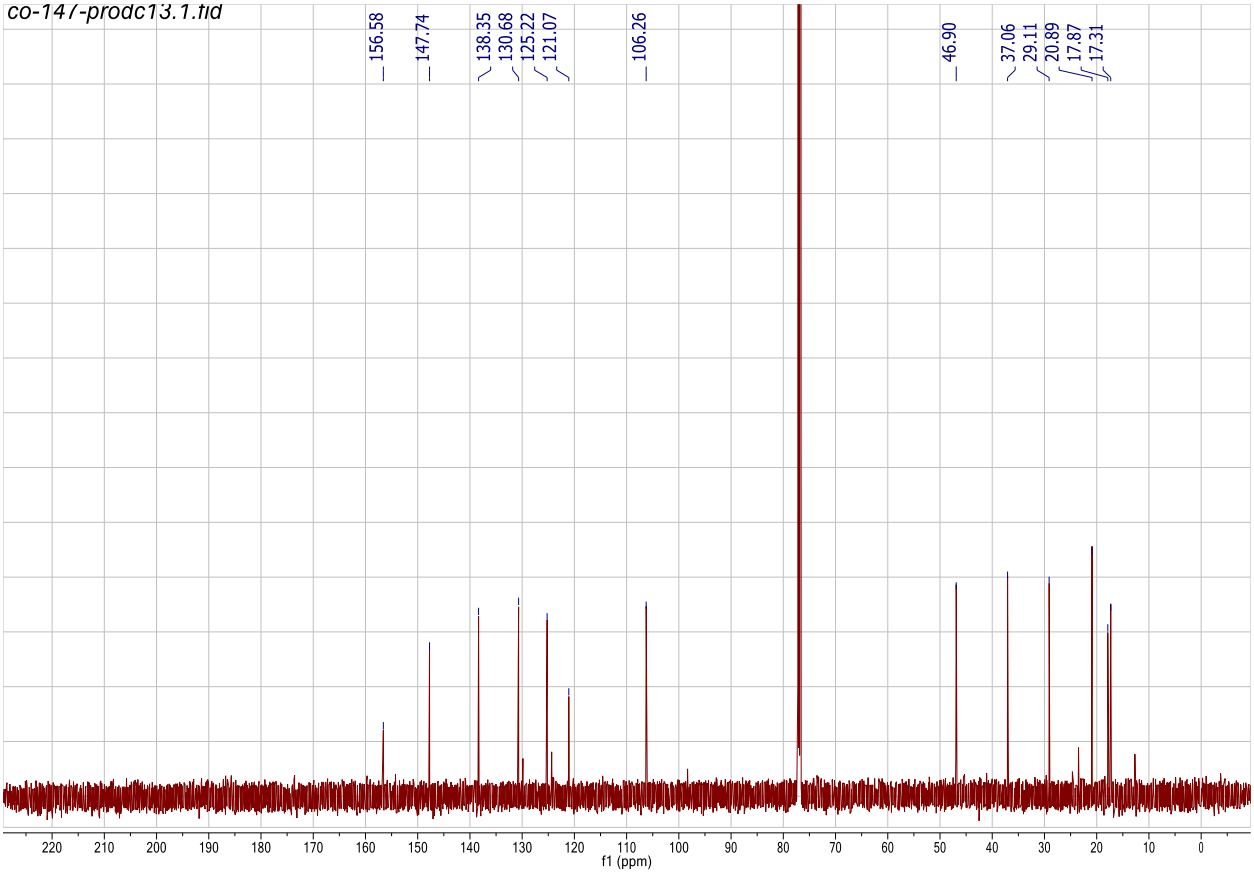


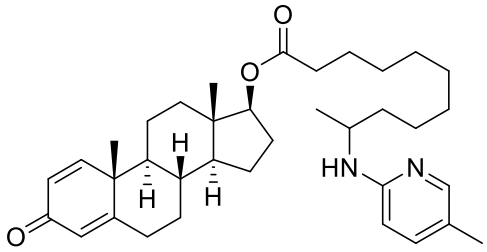
(E)-N-(hept-5-en-2-yl)-5-methylpyridin-2-amine (11a)

^{1}H



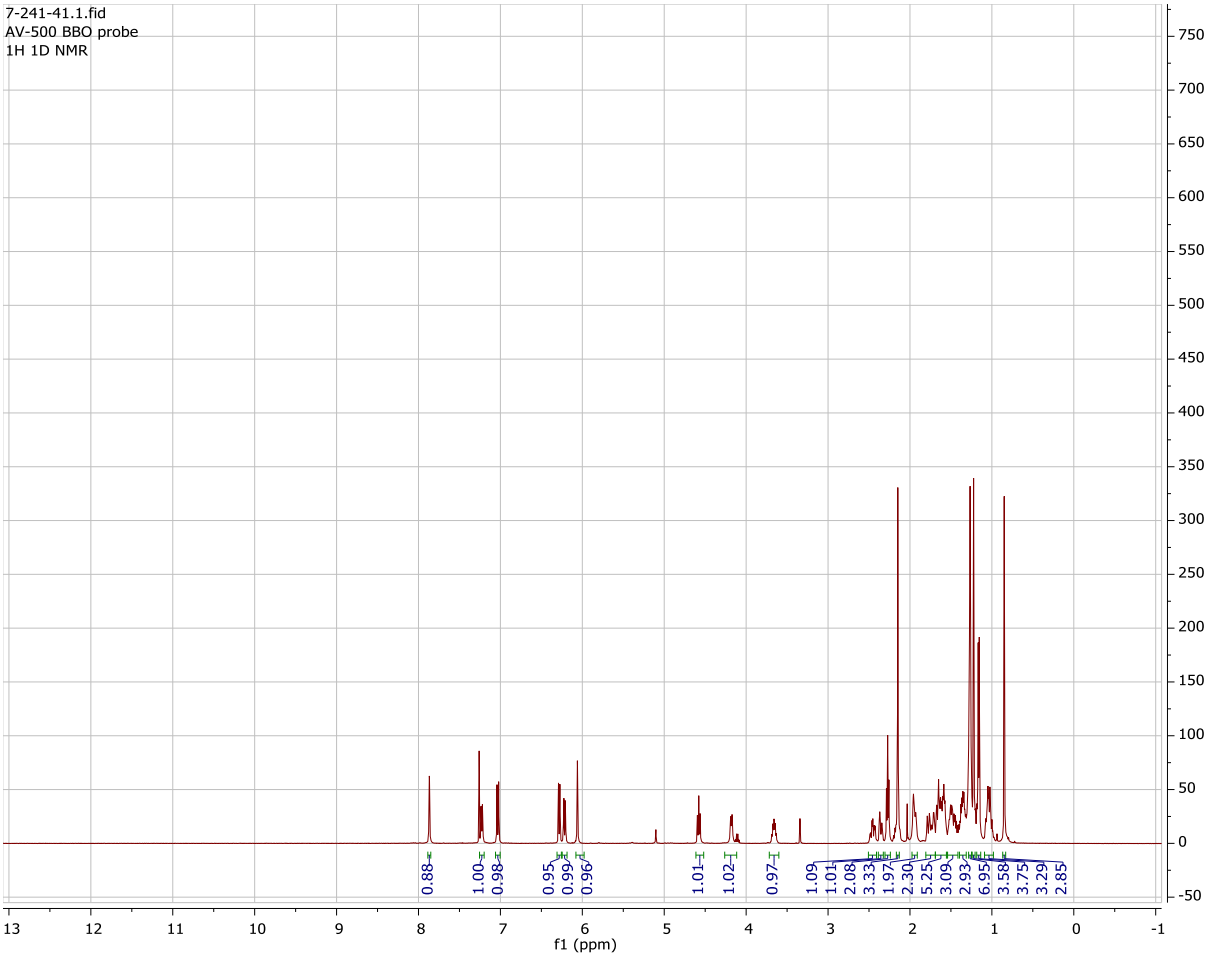
^{13}C


co-147-prodc13.1.fid
156.58
147.74
138.35
130.68
125.22
121.07
106.26
46.90
37.06
29.11
20.89
17.87
17.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

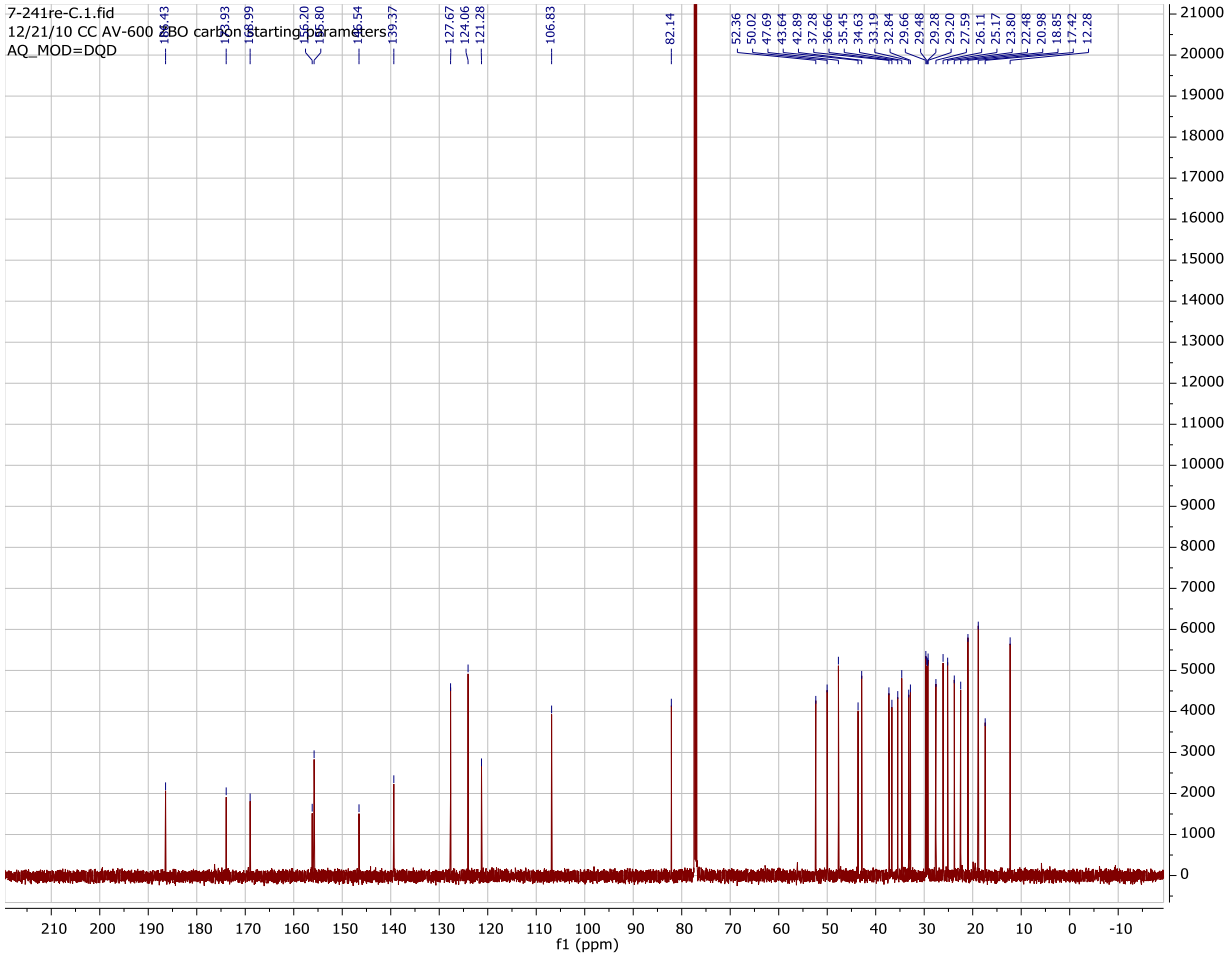


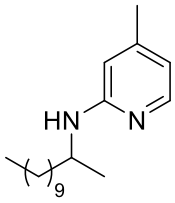
Aminopyridyl boldenone undecylenate (12a)

^{1}H



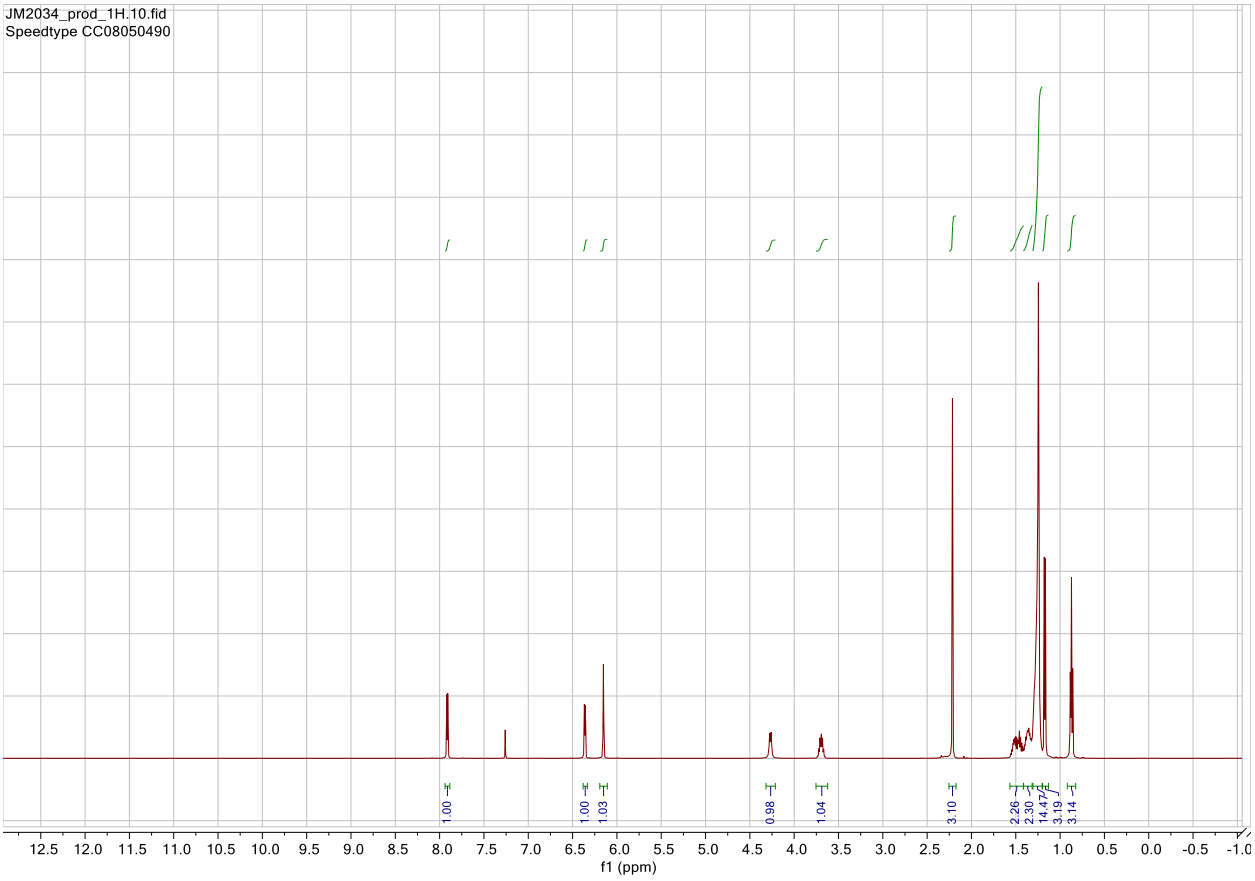
^{13}C


7-241re-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
193.43
173.93
169.99
159.20
158.80
153.54
139.37
127.67
124.06
121.28
106.83
82.14
52.36
50.02
47.69
43.64
42.89
37.28
36.66
35.45
34.63
33.19
32.84
29.66
29.48
29.28
29.20
27.59
26.11
25.17
23.80
22.48
20.98
18.85
17.42
12.28
f1 (ppm)

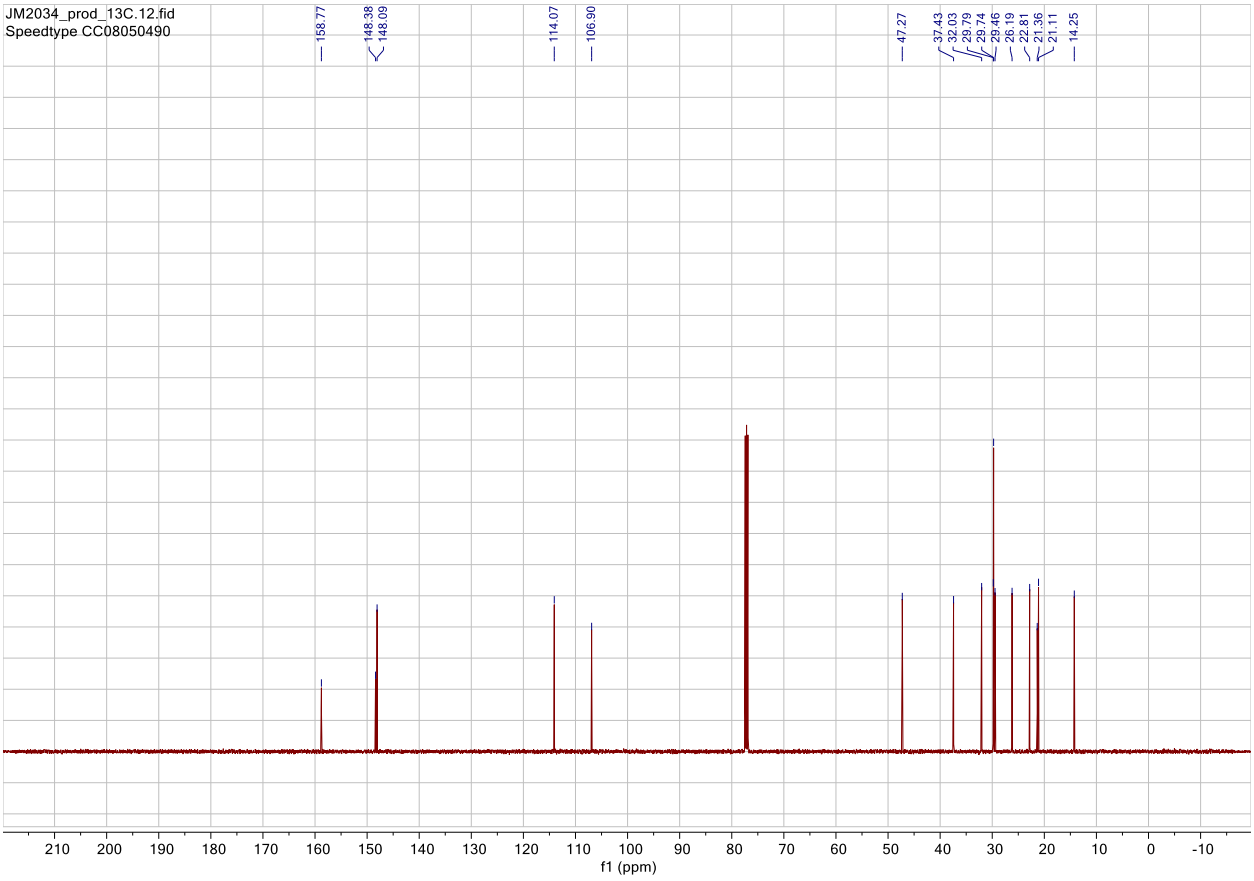


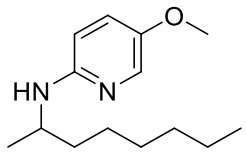
4-methyl-*N*-(dodecan-2-yl)pyridine-2-amine (13a)

^{1}H



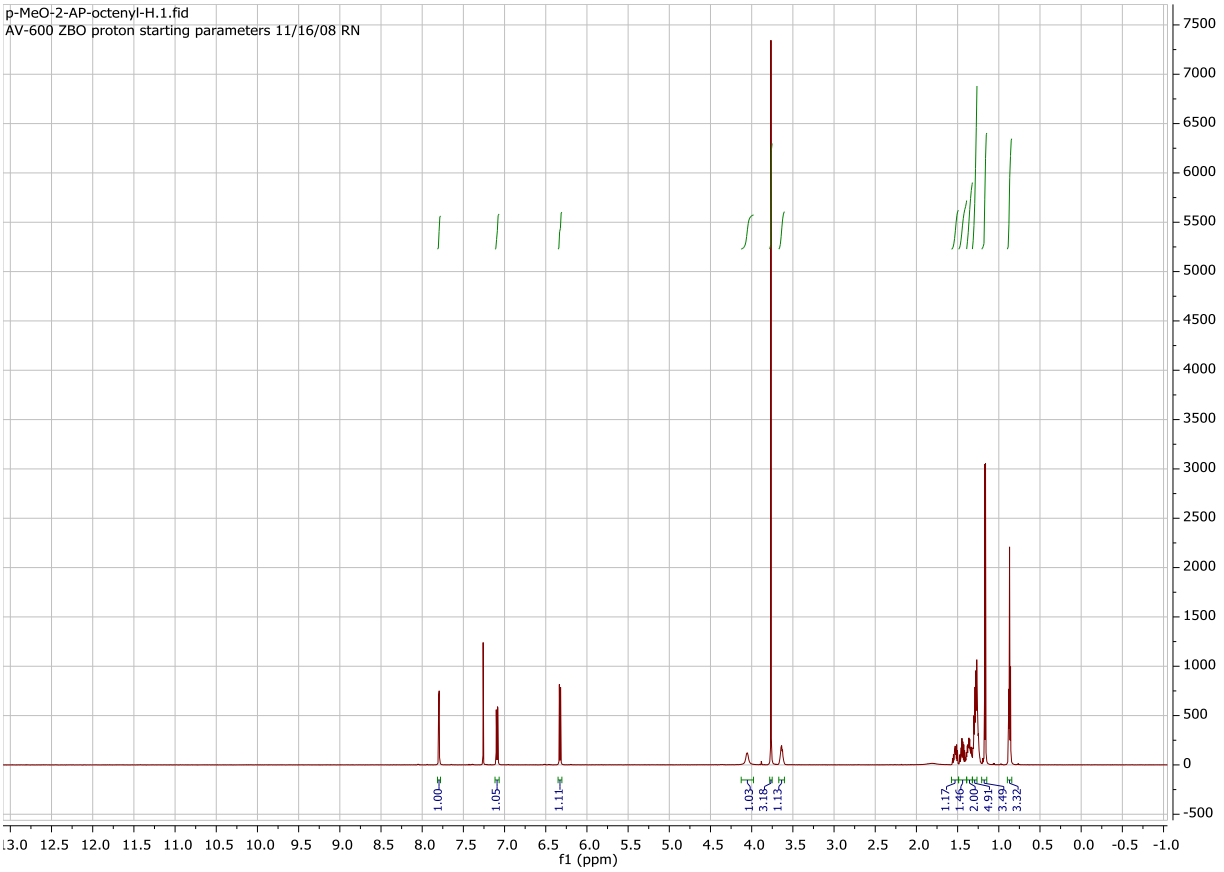
^{13}C


JM2034_prod_13C.12.fid
Speedtype CC08050490
158.77
148.38
148.09
114.07
106.90
47.27
37.43
32.03
29.79
29.74
29.46
26.19
22.81
21.36
21.11
14.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

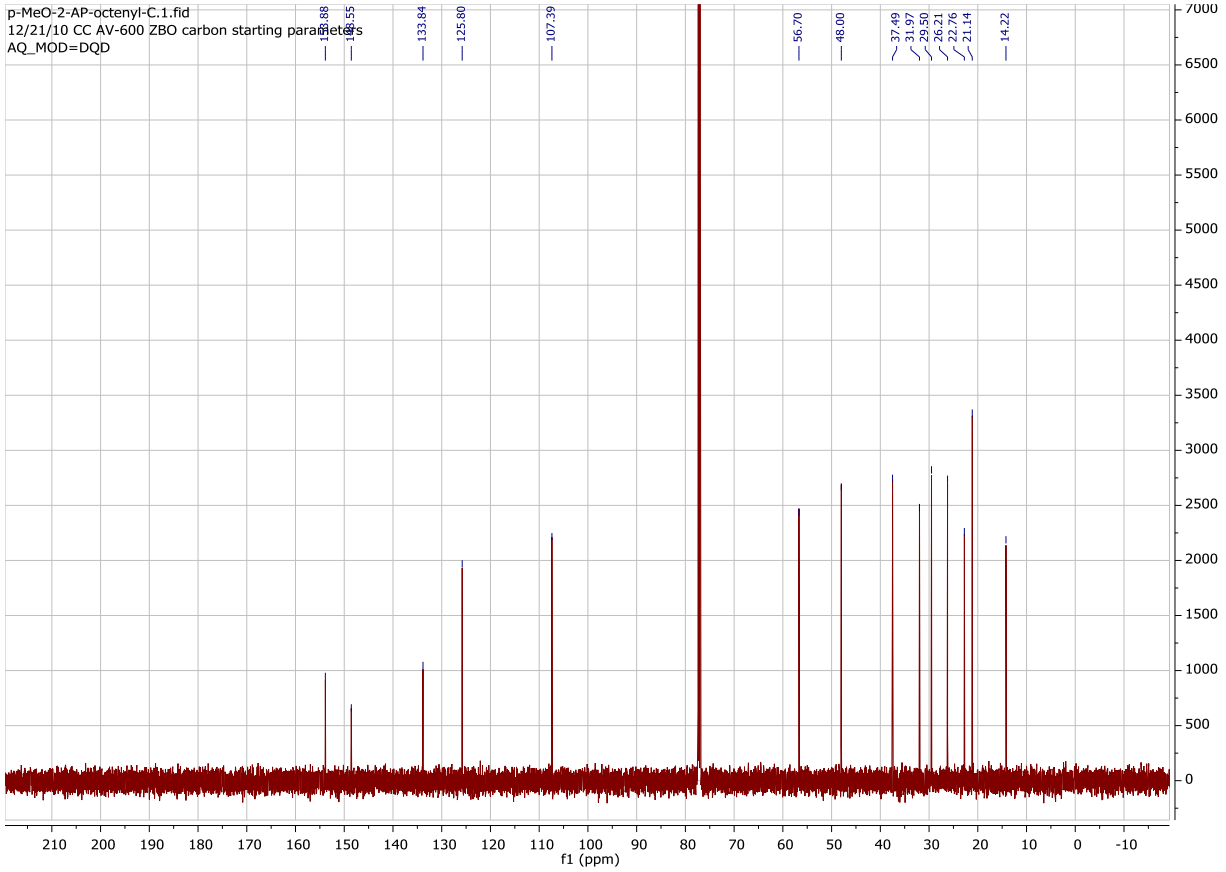


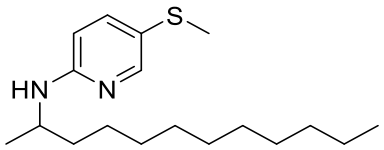
5-methoxy-N-(octan-2-yl)pyridin-2-amine (14a)

^{1}H

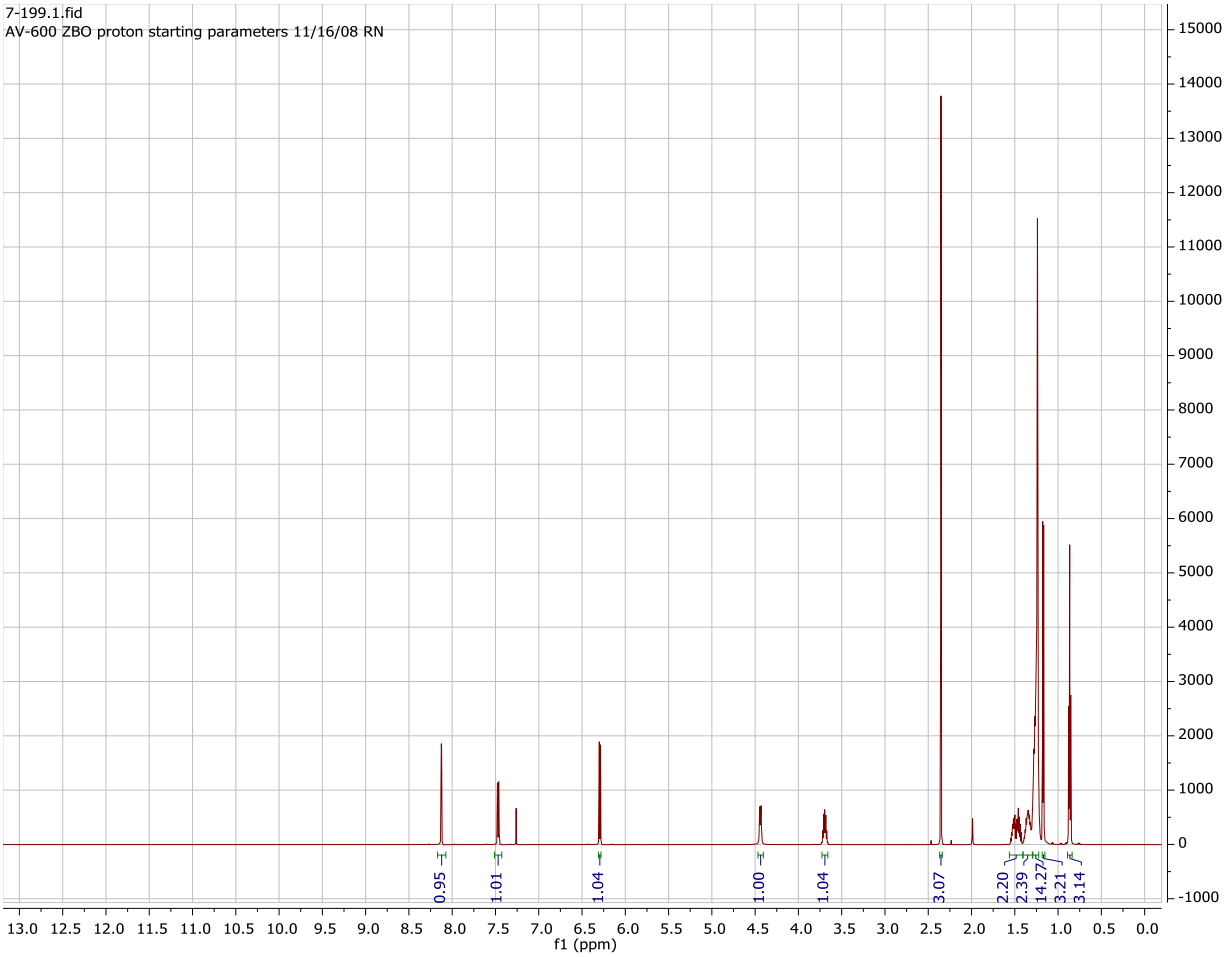


^{13}C

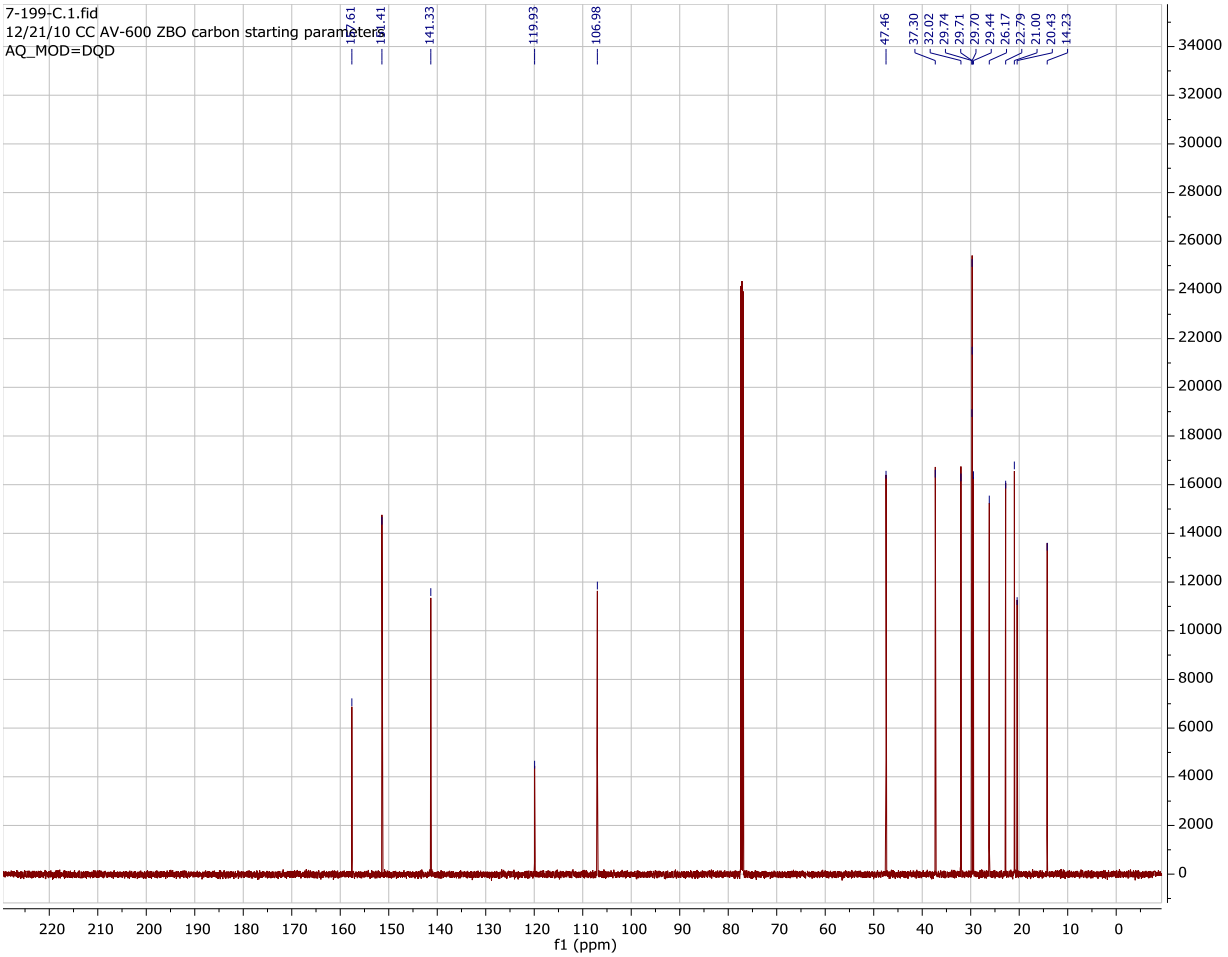

p-MeO-2-AP-octenyl-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
158.88
150.55
133.84
125.80
107.39
56.70
48.00
37.49
31.97
29.50
26.21
22.76
21.14
14.22
f1 (ppm)

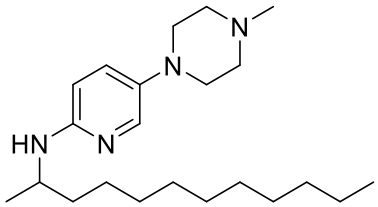


N-(dodecan-2-yl)-5-(methylthio)pyridin-2-amine (15a)
^{1}H

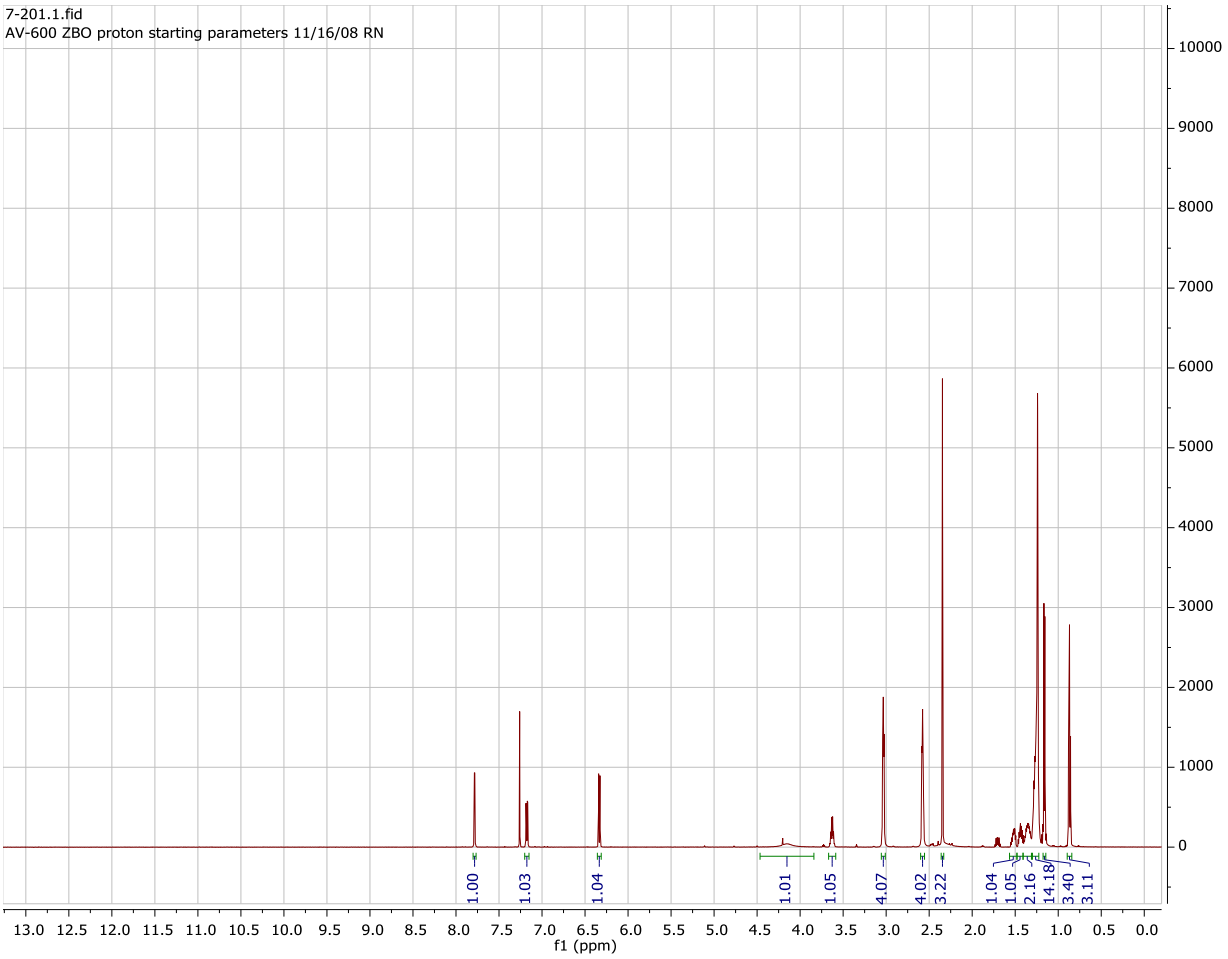


^{13}C

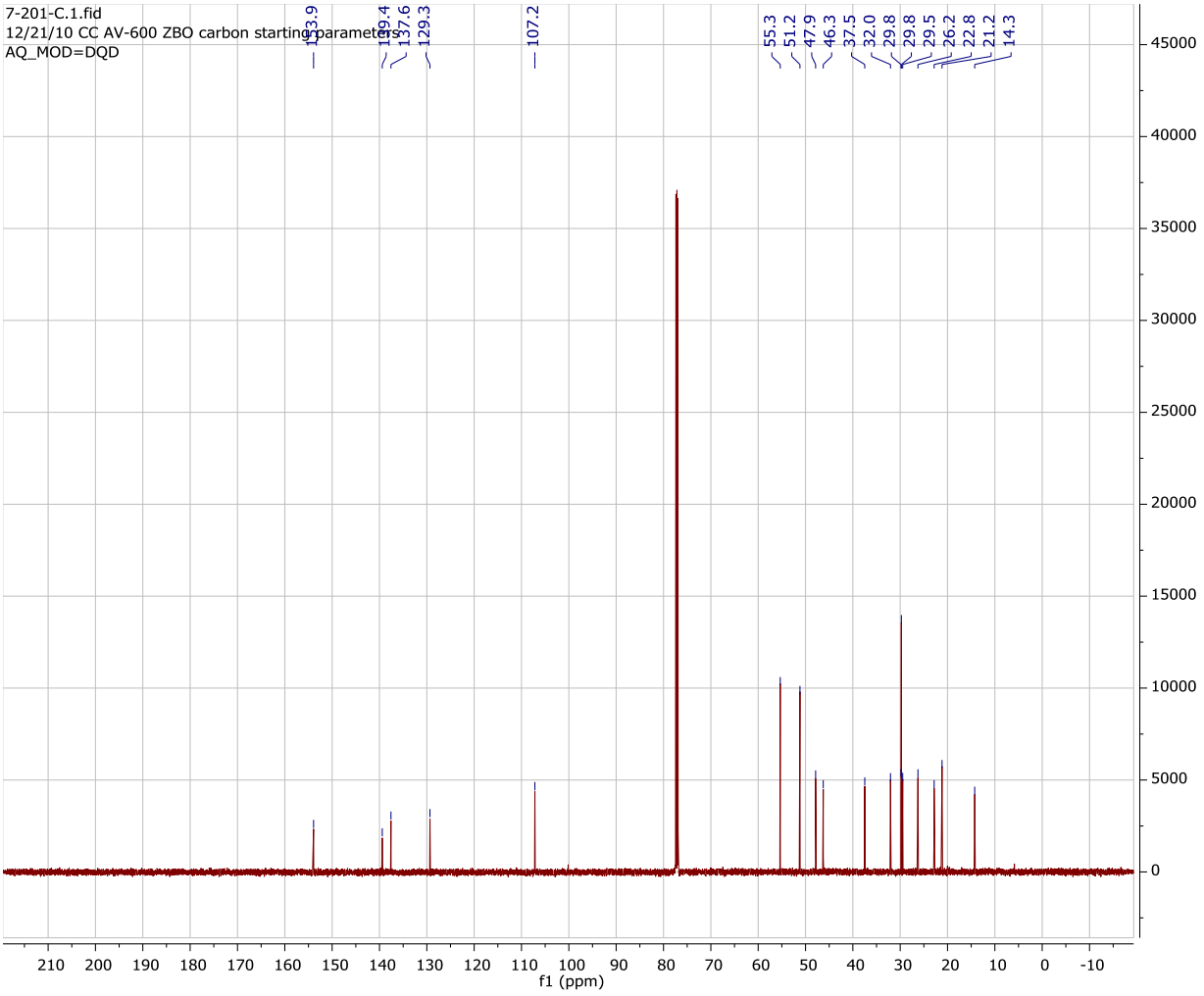

7-199-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
157.61
155.41
141.33
119.93
106.98
47.46
37.30
32.02
29.74
29.71
29.70
29.44
26.17
22.79
21.00
20.43
14.23
f1 (ppm)



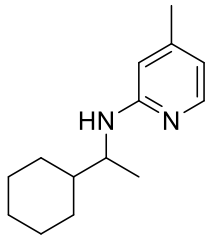
N-(dodecan-2-yl)-5-(4-methylpiperazin-1-yl)pyridin-2-amine (16a)
^{1}H



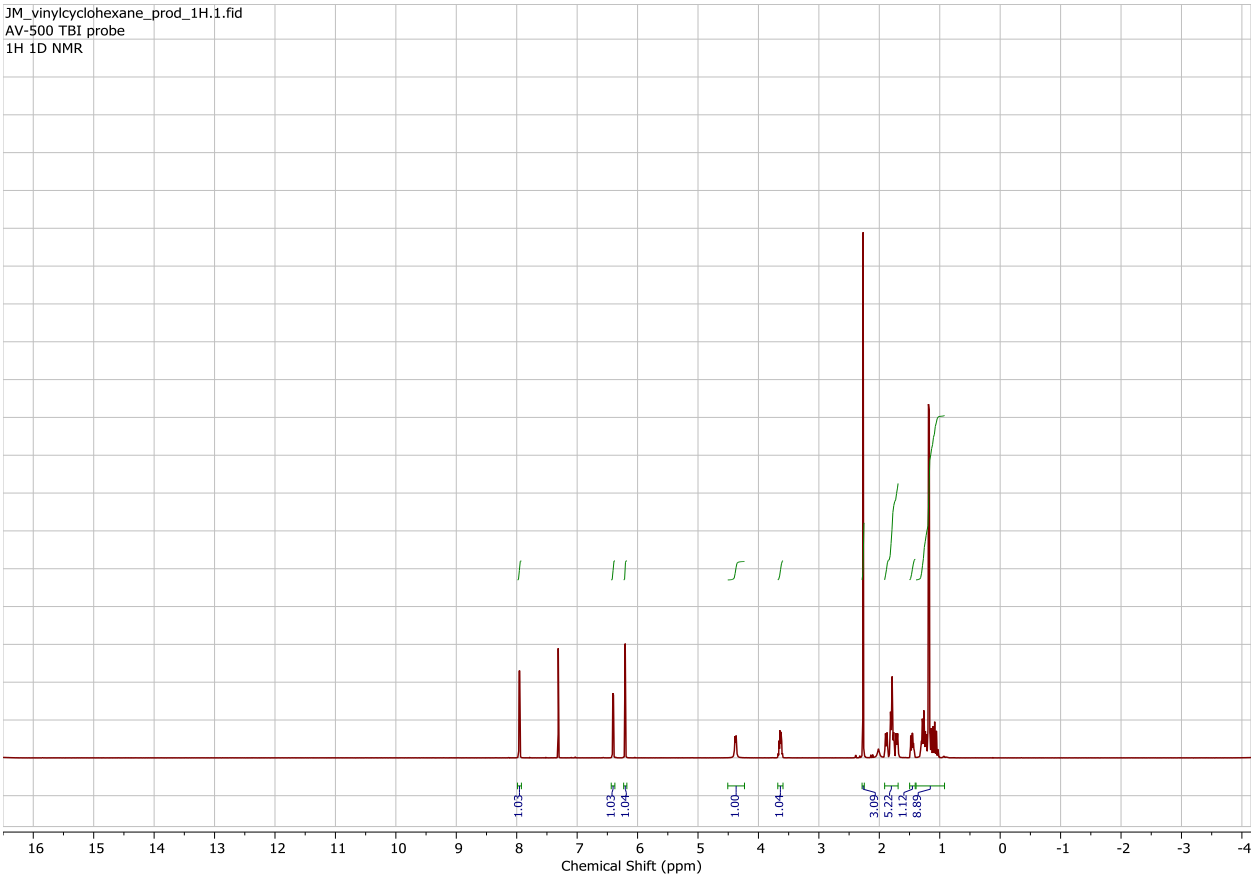
^{13}C


7-201-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
153.9
139.4
137.6
129.3
107.2
55.3
51.2
47.9
46.3
37.5
32.0
29.8
29.8
29.5
26.2
22.8
21.2
14.3
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

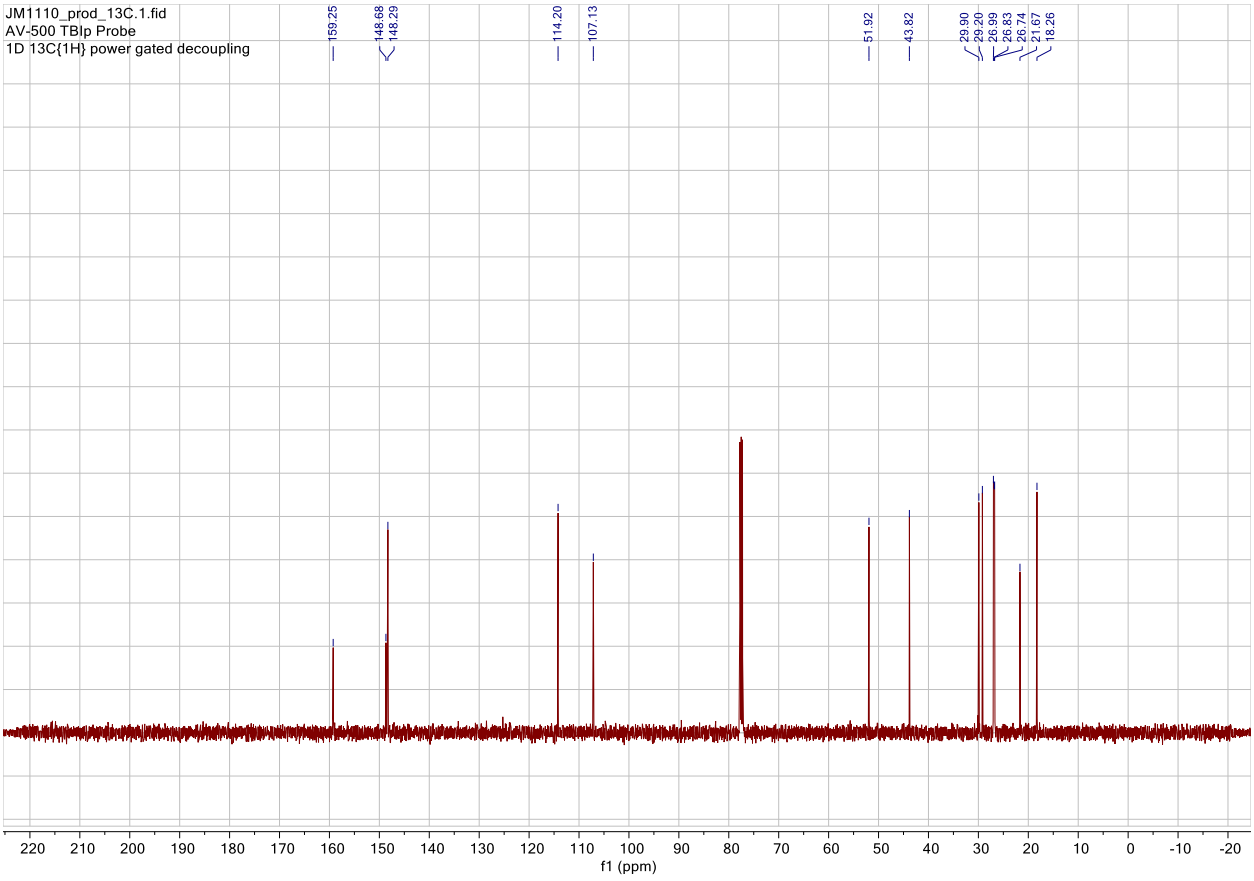
N-(1-cyclohexylethyl)-5-methylpyridin-2-amine (17a)

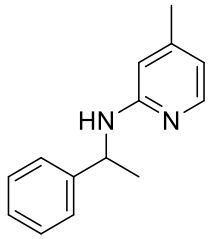


^{1}H



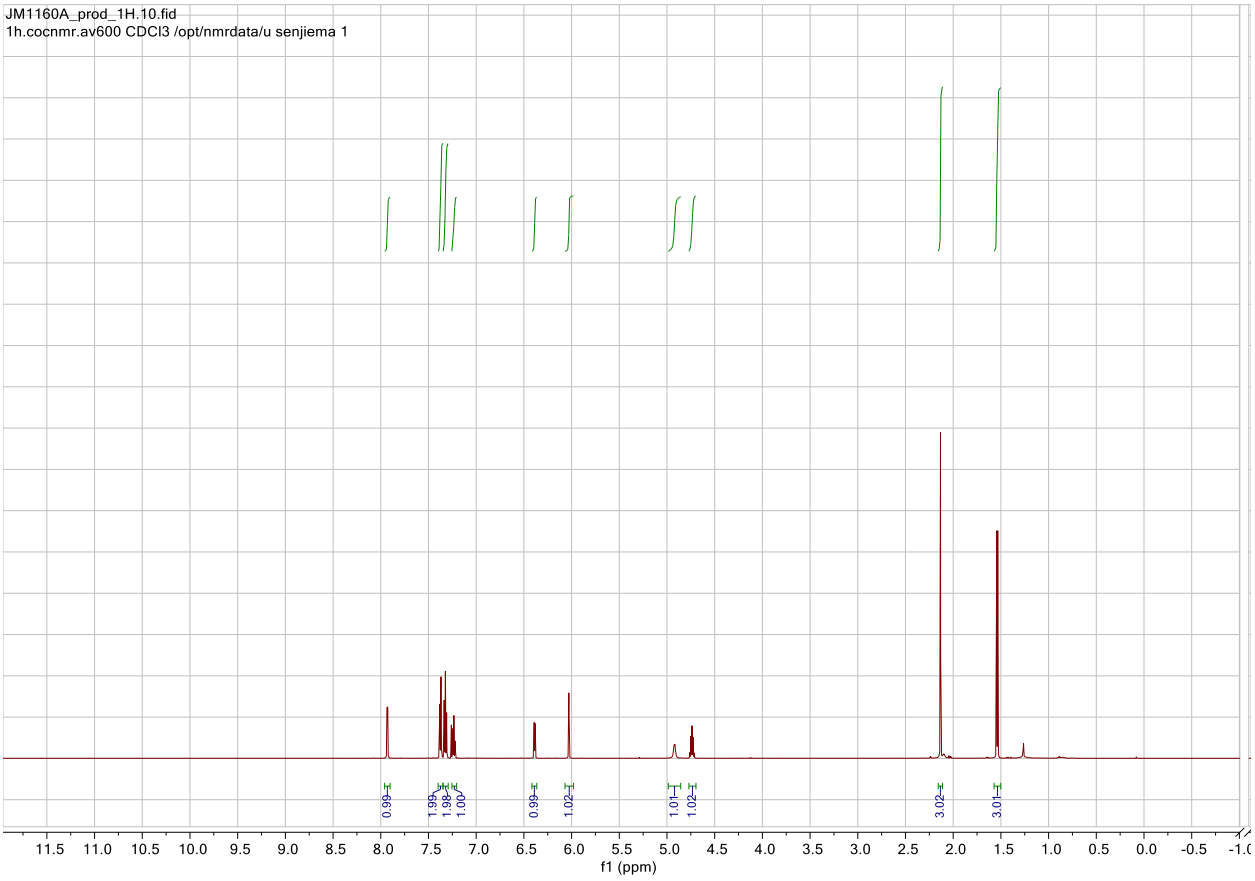
^{13}C


JM1110_prod_13C.1.fid
AV-500 TBIp Probe
1D 13C{1H} power gated decoupling
159.25
148.68
148.29
114.20
107.13
51.92
43.82
29.90
29.20
26.99
26.83
26.74
21.67
18.26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

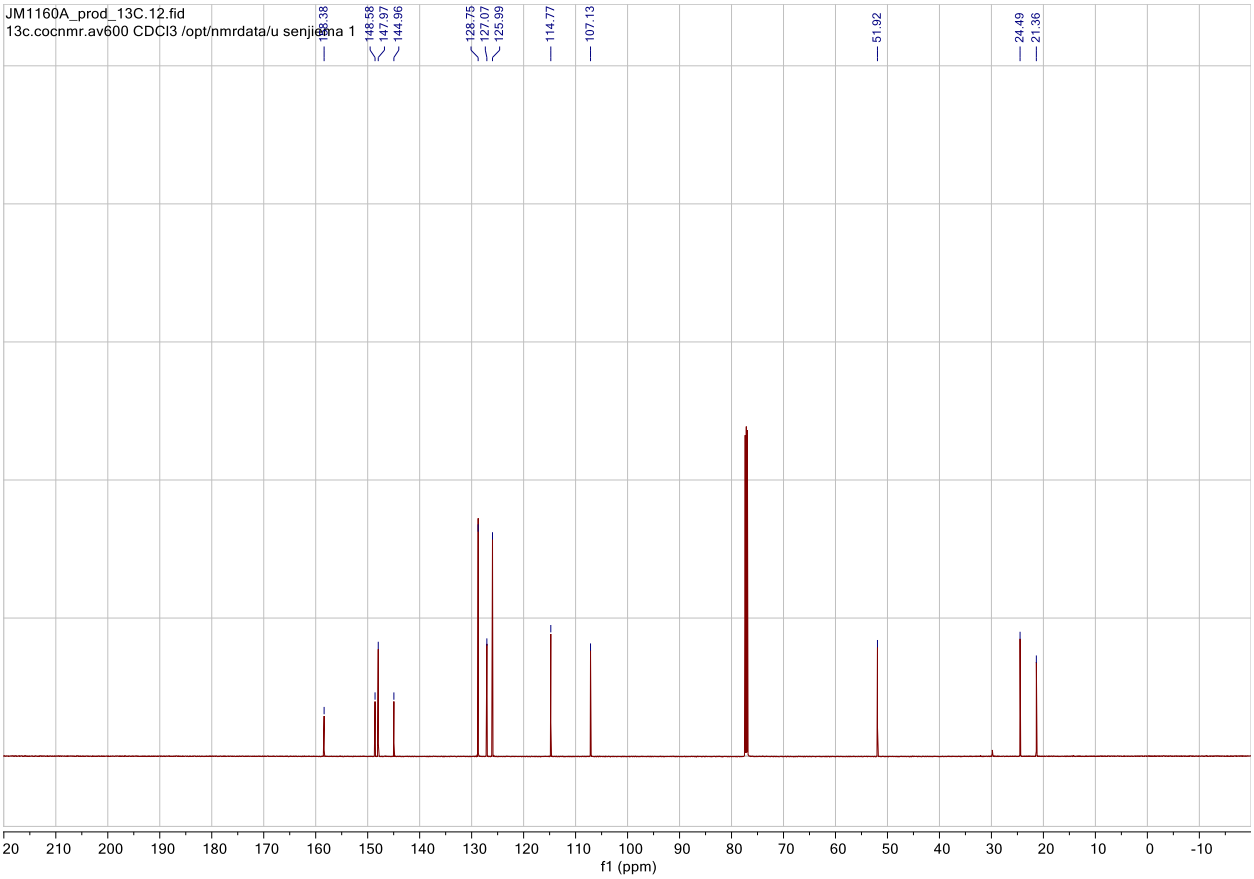


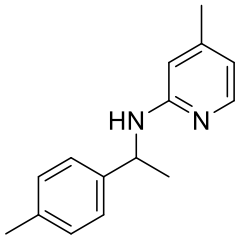
4-methyl-*N*-(1-phenylethyl)pyridin-2-amine (18a)

^{1}H



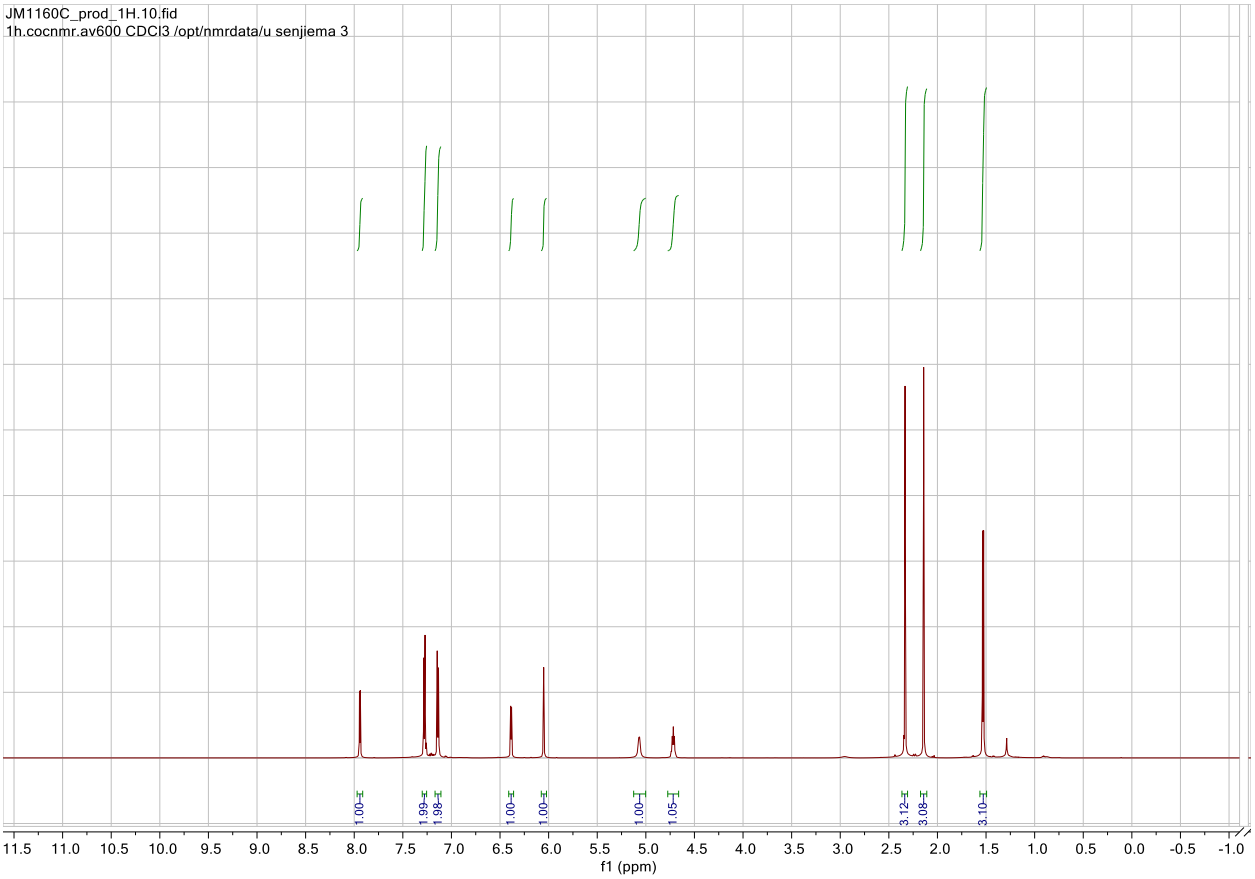
^{13}C


JM1160A_prod_13C.12.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 1
158.38
148.58
147.97
144.96
128.75
127.07
125.99
114.77
107.13
51.92
24.49
21.36
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

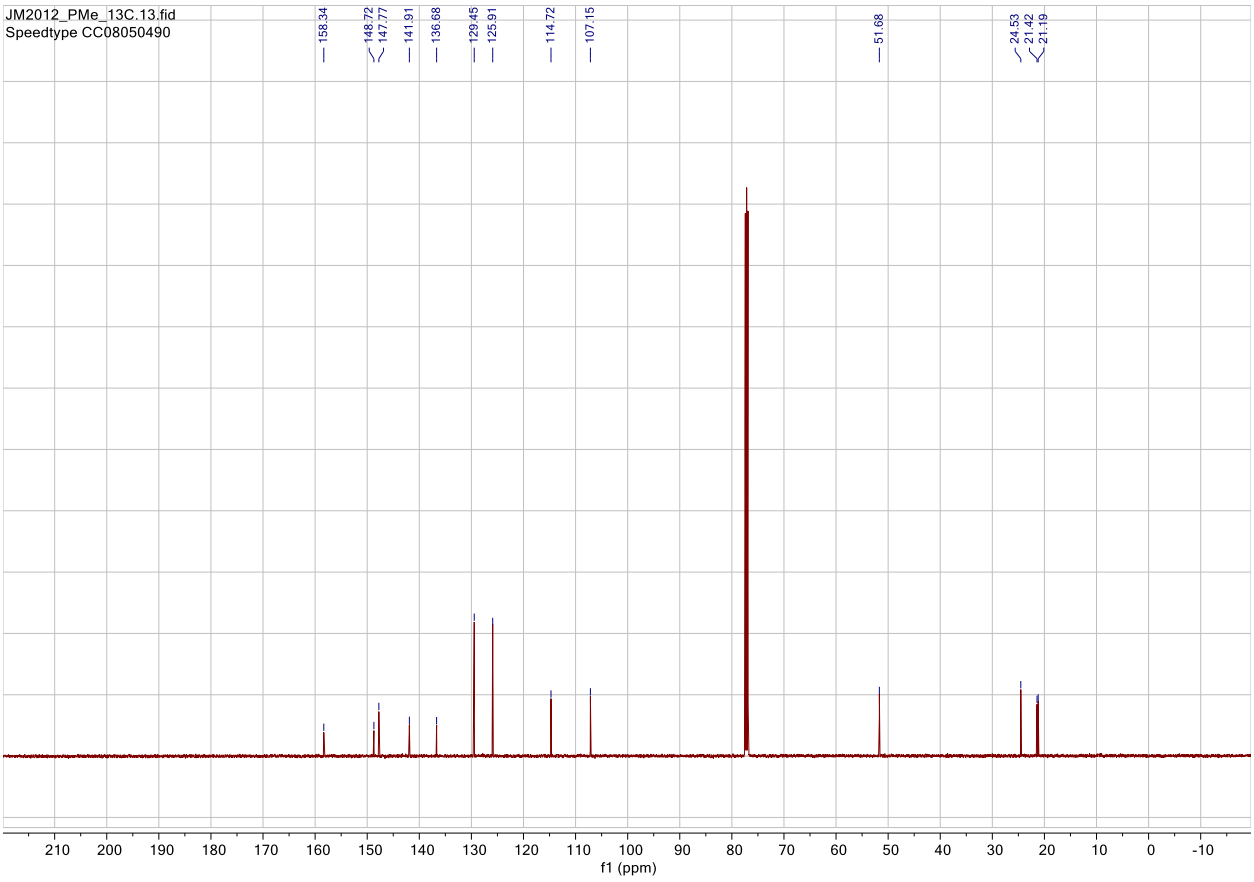


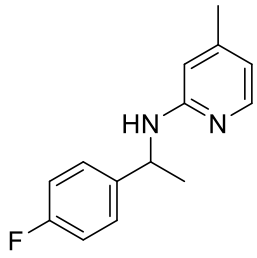
4-methyl-N-(1-(p-tolyl)ethyl)pyridin-2-amine (19a)

^{1}H



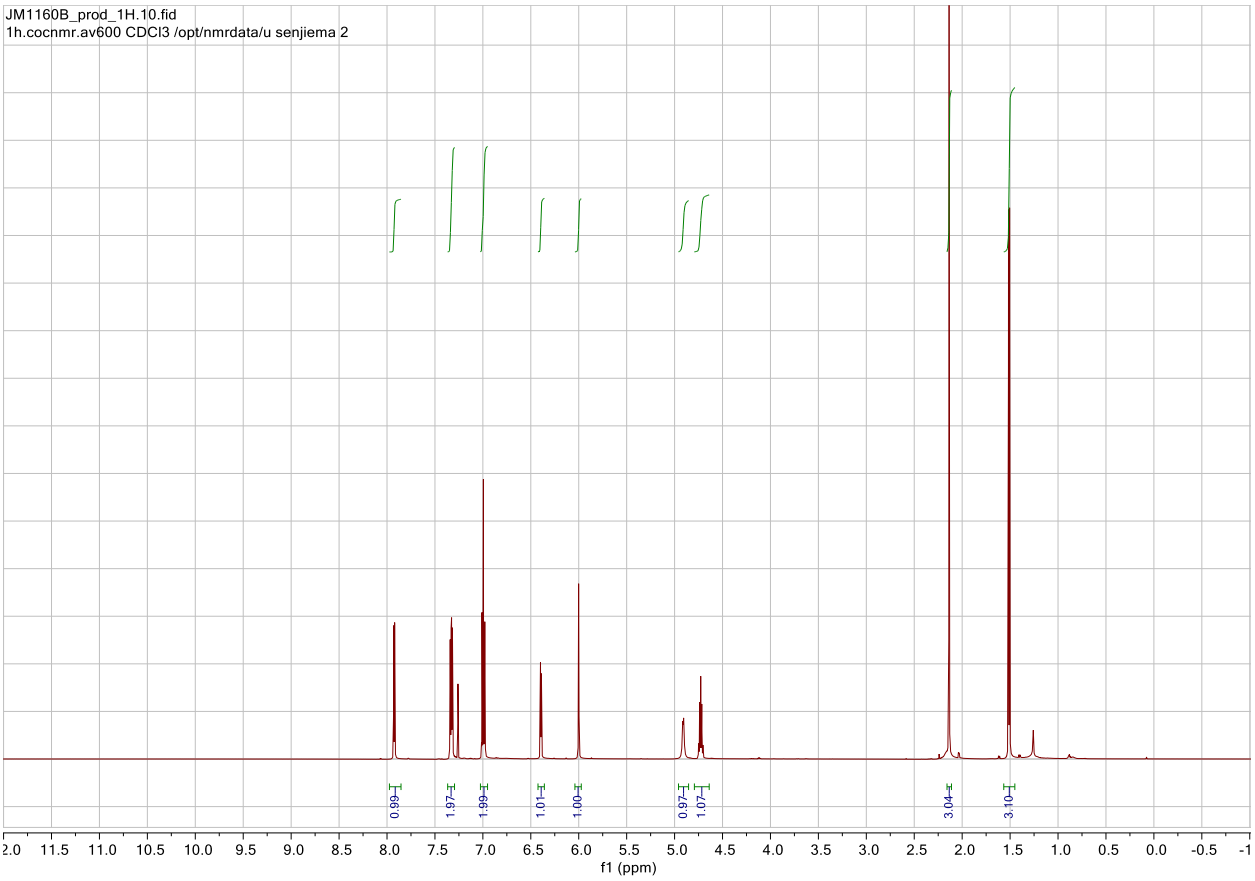
^{13}C


JM2012_PMe_13C.13.fid
Speedtype CC08050490
158.34
148.72
147.77
141.91
136.68
129.45
125.91
114.72
107.15
51.68
24.53
21.42
21.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

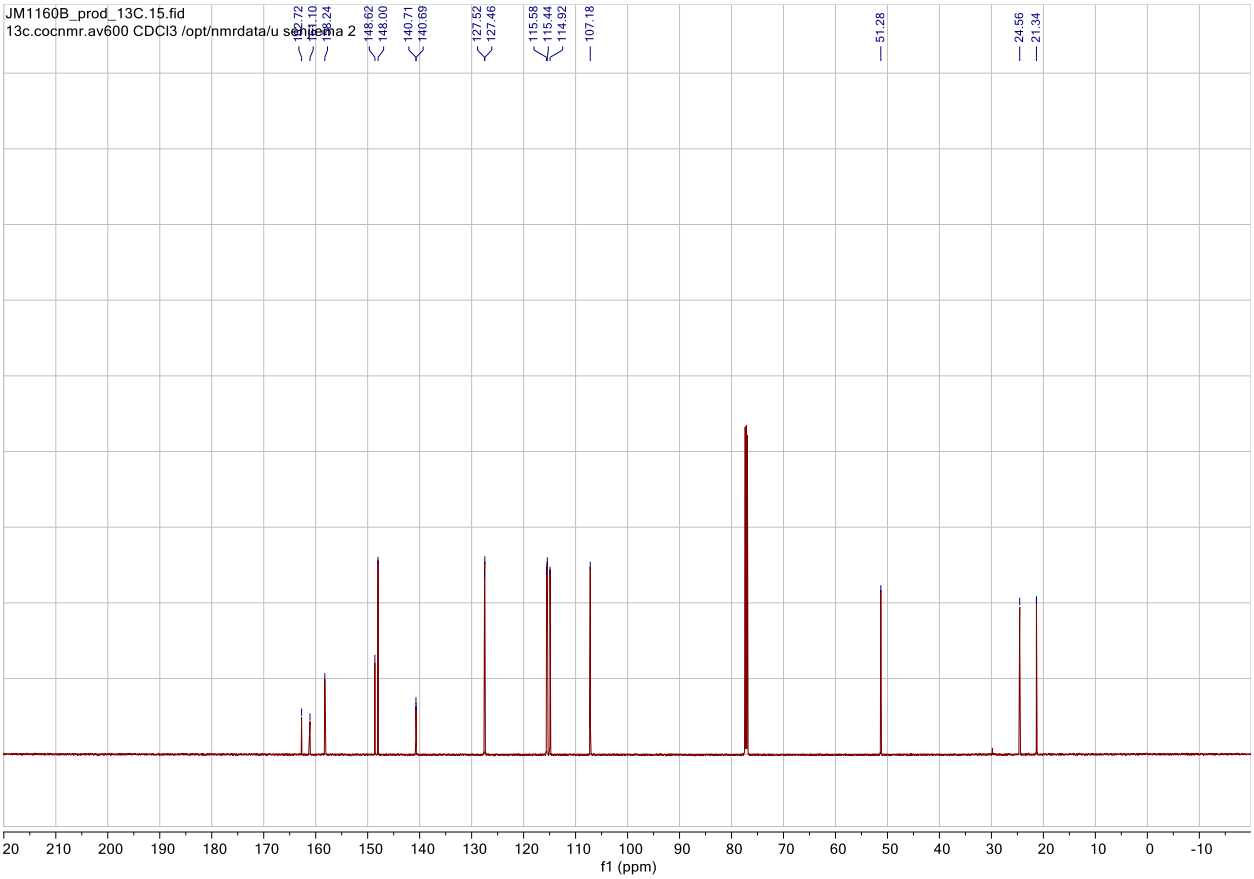


N-(1-(4-fluorophenyl)ethyl)-4-methylpyridin-2-amine (20a)

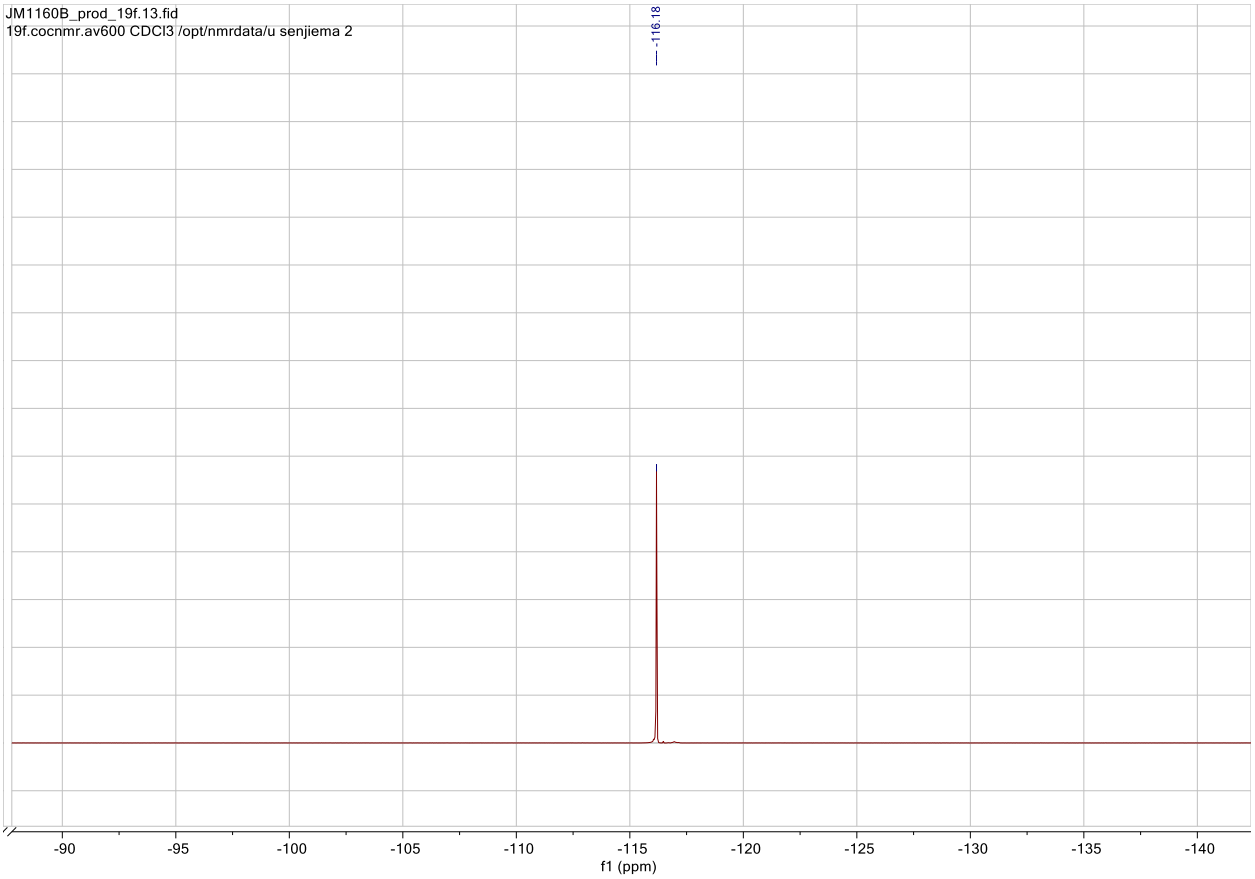
^{1}H

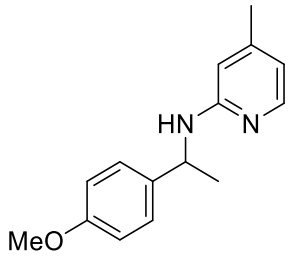


^{13}C


JM1160B_prod_13C.15.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u serhenna 2
157.72
157.10
156.24
148.62
148.00
140.71
140.69
127.52
127.46
115.58
115.44
114.92
107.18
51.28
24.56
21.34
f1 (ppm)

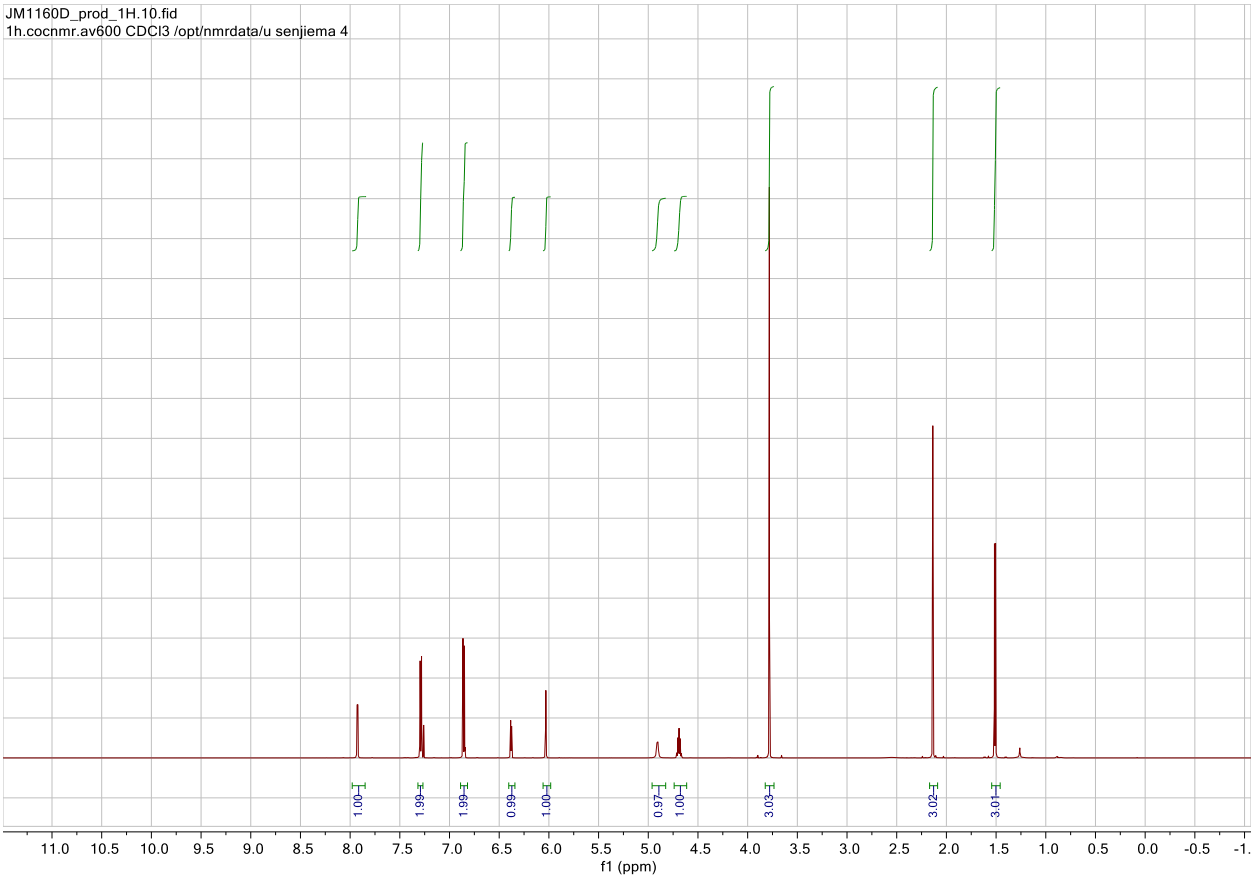
^{19}F


JM1160B_prod_19f.13.fid
19f.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 2
-116.18
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)

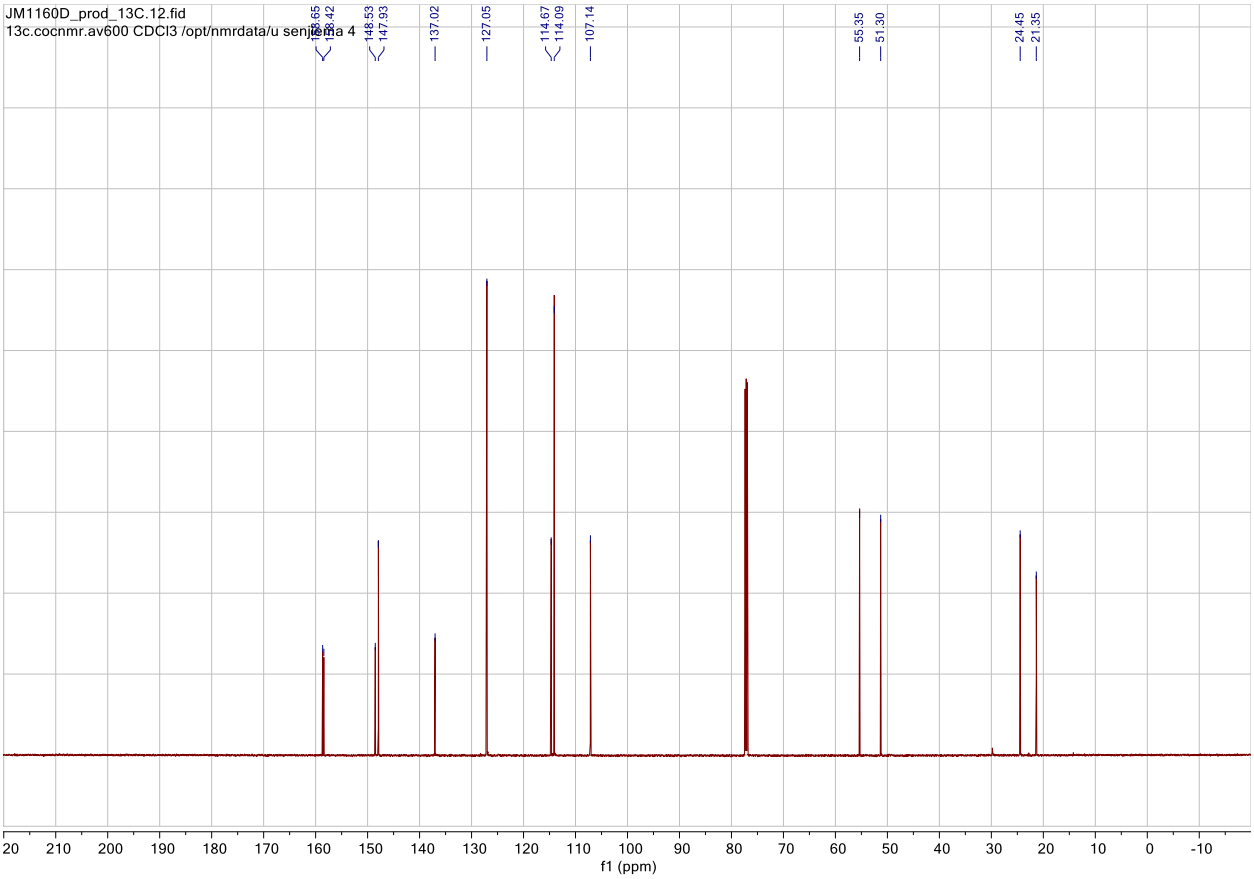


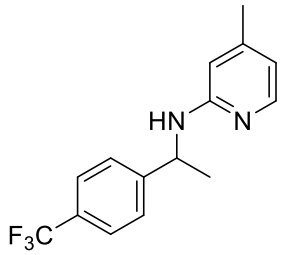
N-(1-(4-methoxyphenyl)ethyl)-4-methylpyridin-2-amine (21a)

^{1}H



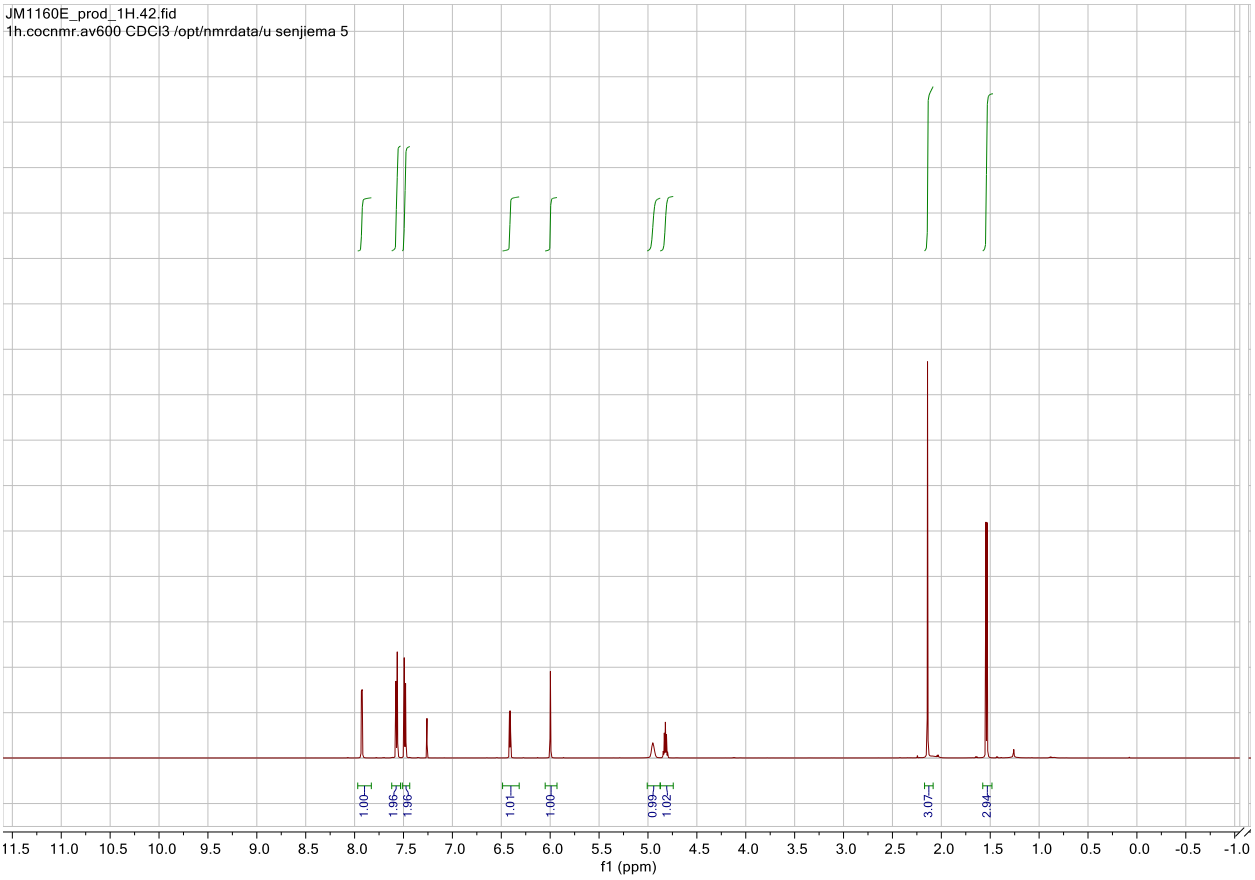
^{13}C


JM1160D_prod_13C.12.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u sen
158.65
158.42
148.53
147.93
137.02
127.05
114.67
114.09
107.14
55.35
51.30
24.45
21.35
f1 (ppm)

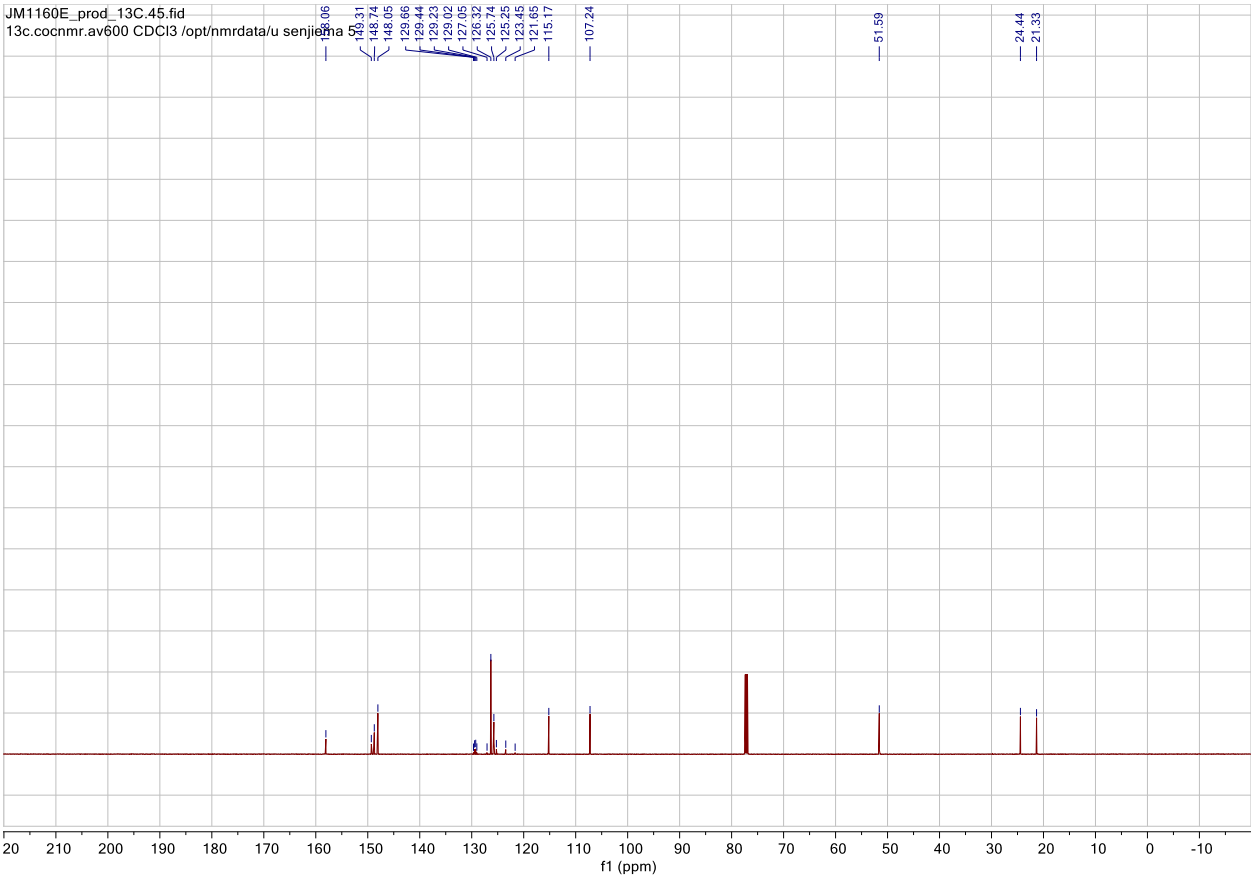


4-methyl-N-(1-(4-(trifluoromethyl)phenyl)ethyl)pyridin-2-amine (22a)

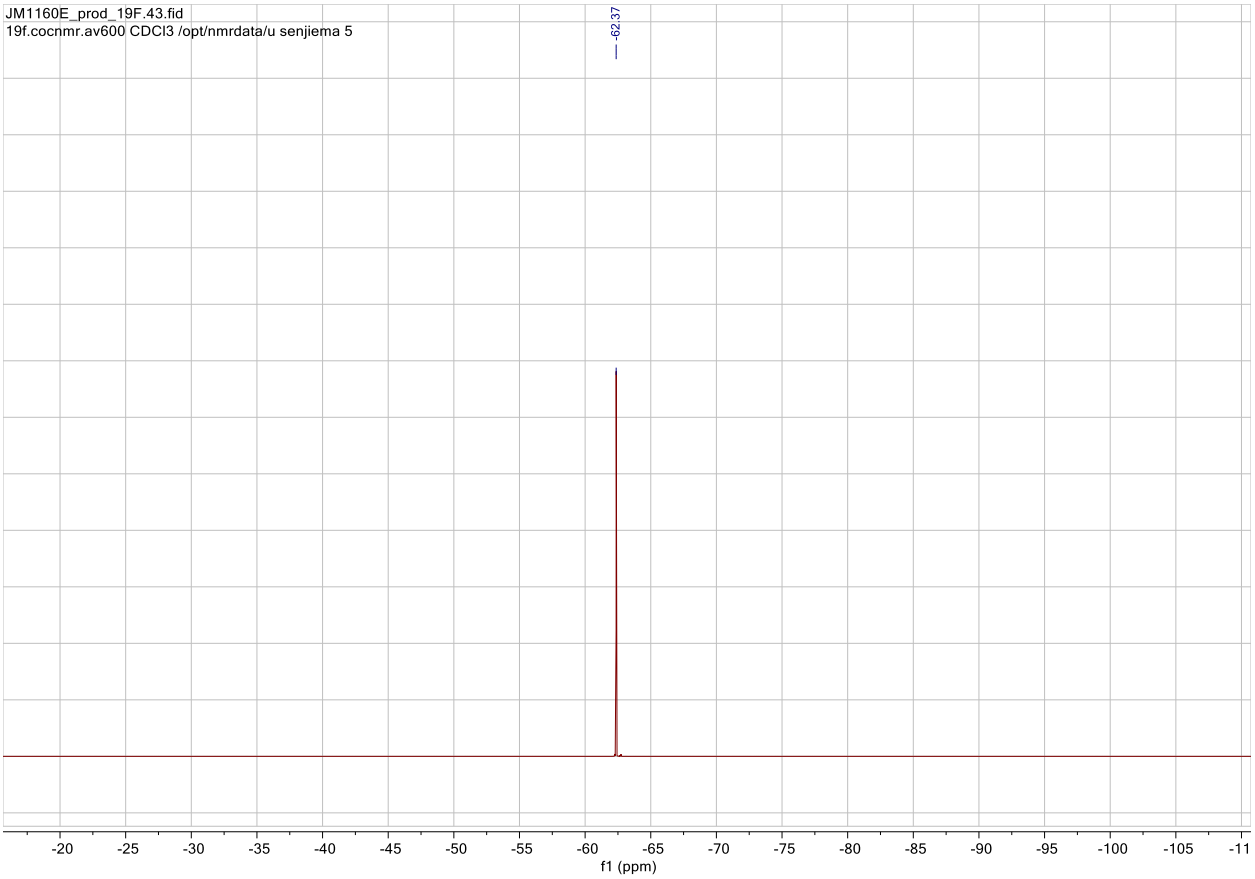
^{1}H

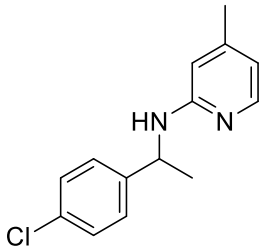


^{13}C


JM1160E_prod_13C.45.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 5
158.06
149.31
148.74
148.05
129.66
129.44
129.23
129.02
127.05
126.32
125.74
125.25
123.45
121.65
115.17
107.24
51.59
24.44
21.33
f1 (ppm)

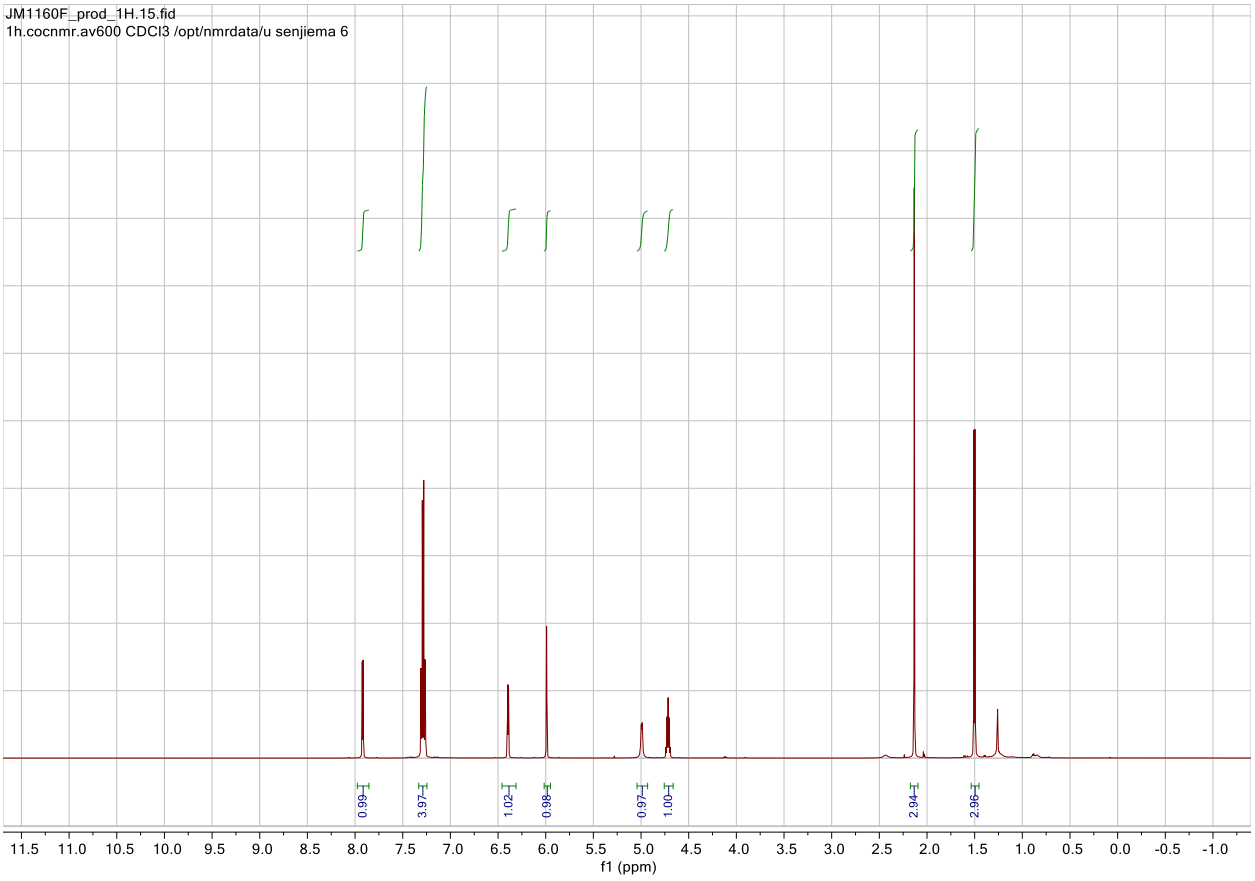
^{19}F


JM1160E_prod_19F.43.fid
19f.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 5
-62.37
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-11
f1 (ppm)

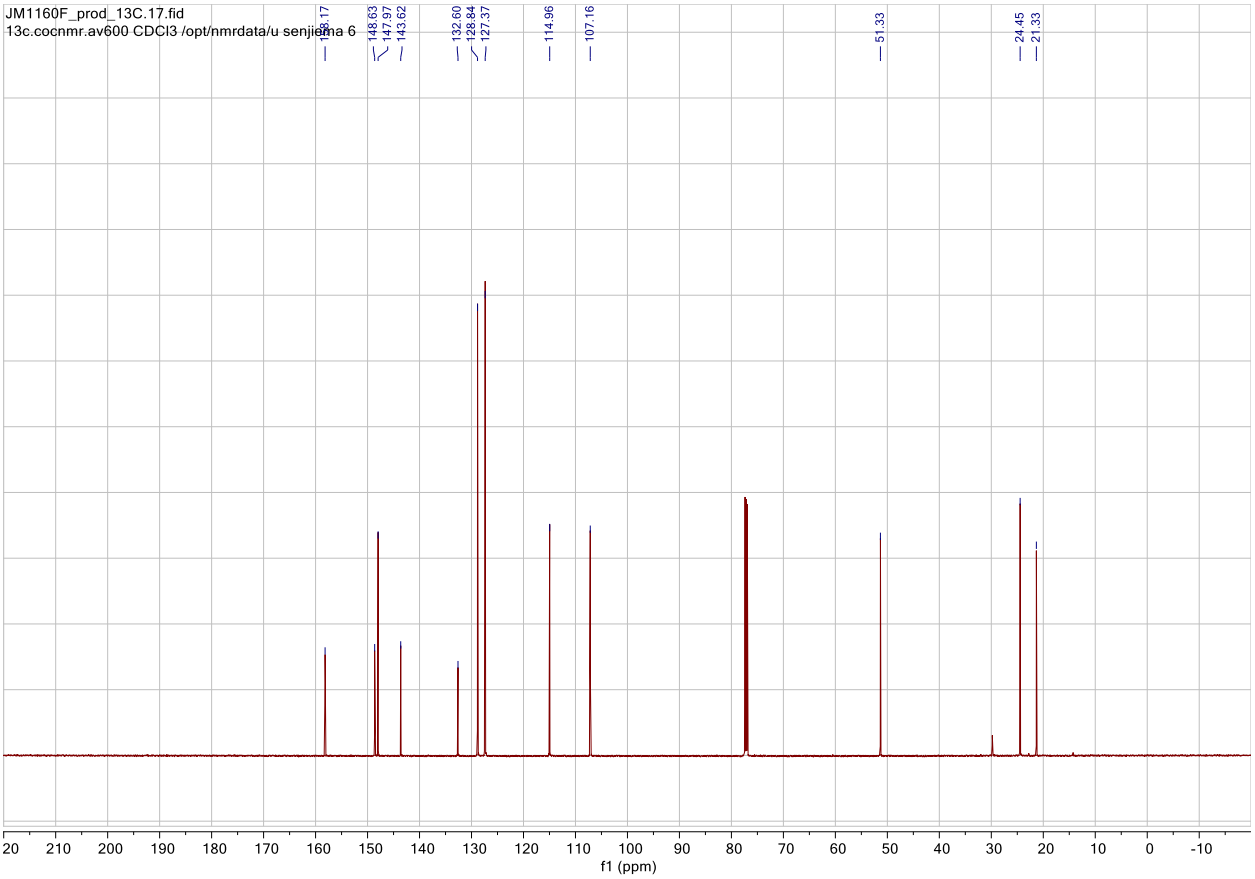


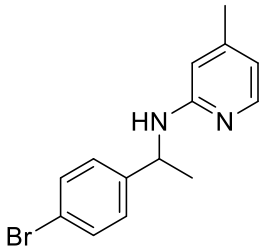
N-(1-(4-chlorophenyl)ethyl)-4-methylpyridin-2-amine (23a)

^{1}H



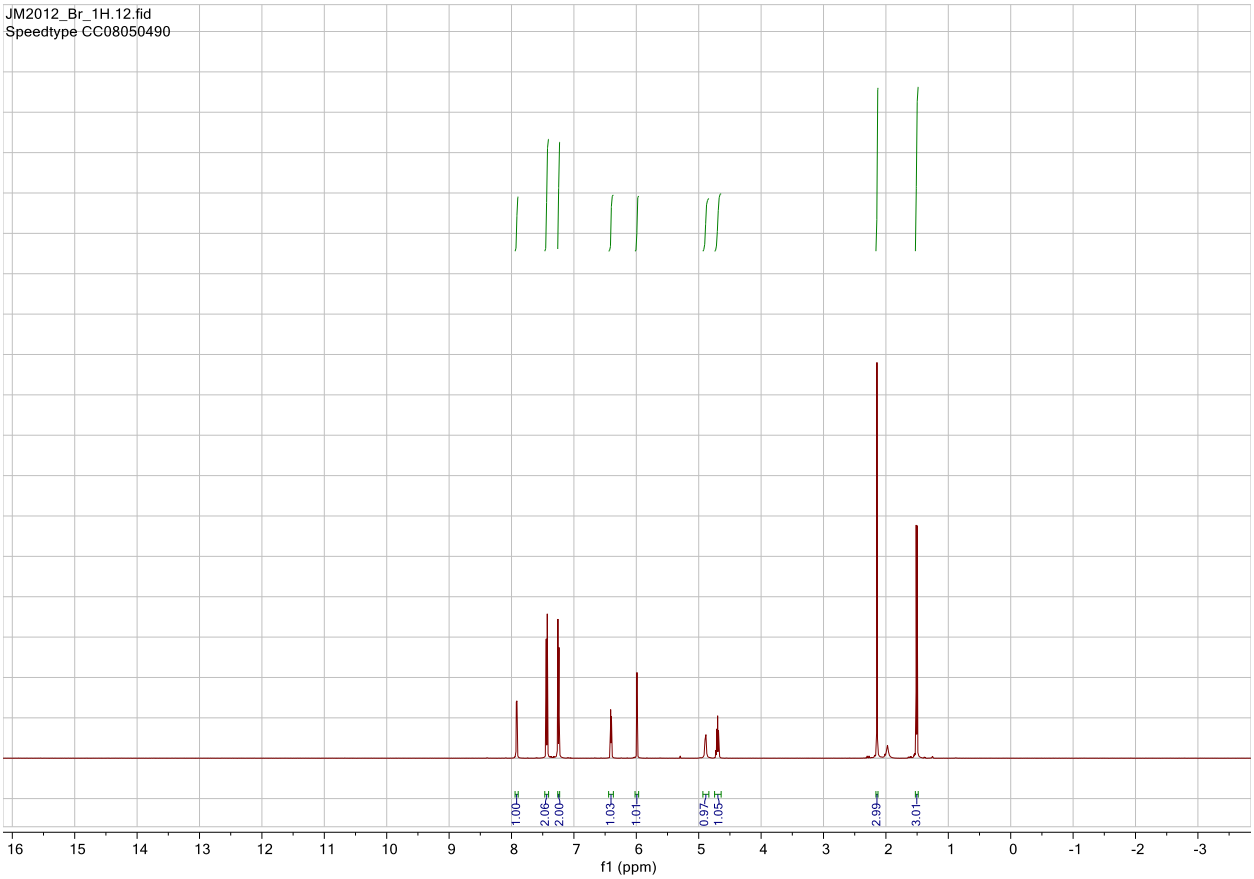
^{13}C


JM1160F_prod_13C.17.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 6
158.17
148.63
147.97
143.62
132.60
128.84
127.37
114.96
107.16
51.33
24.45
21.33
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

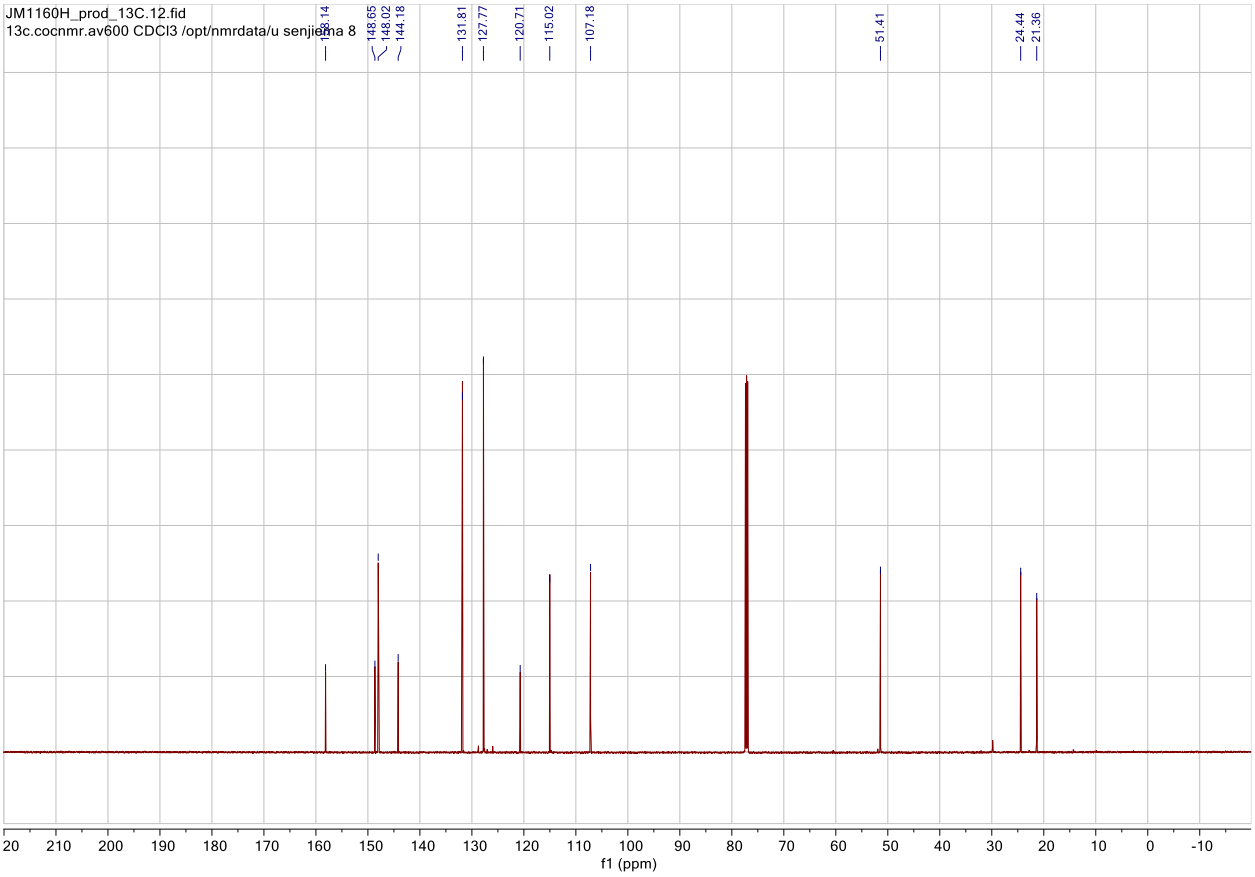


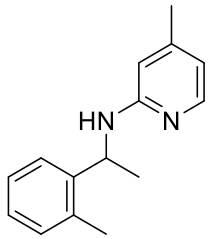
N-(1-(4-bromophenyl)ethyl)-4-methylpyridin-2-amine (24a)

^{1}H



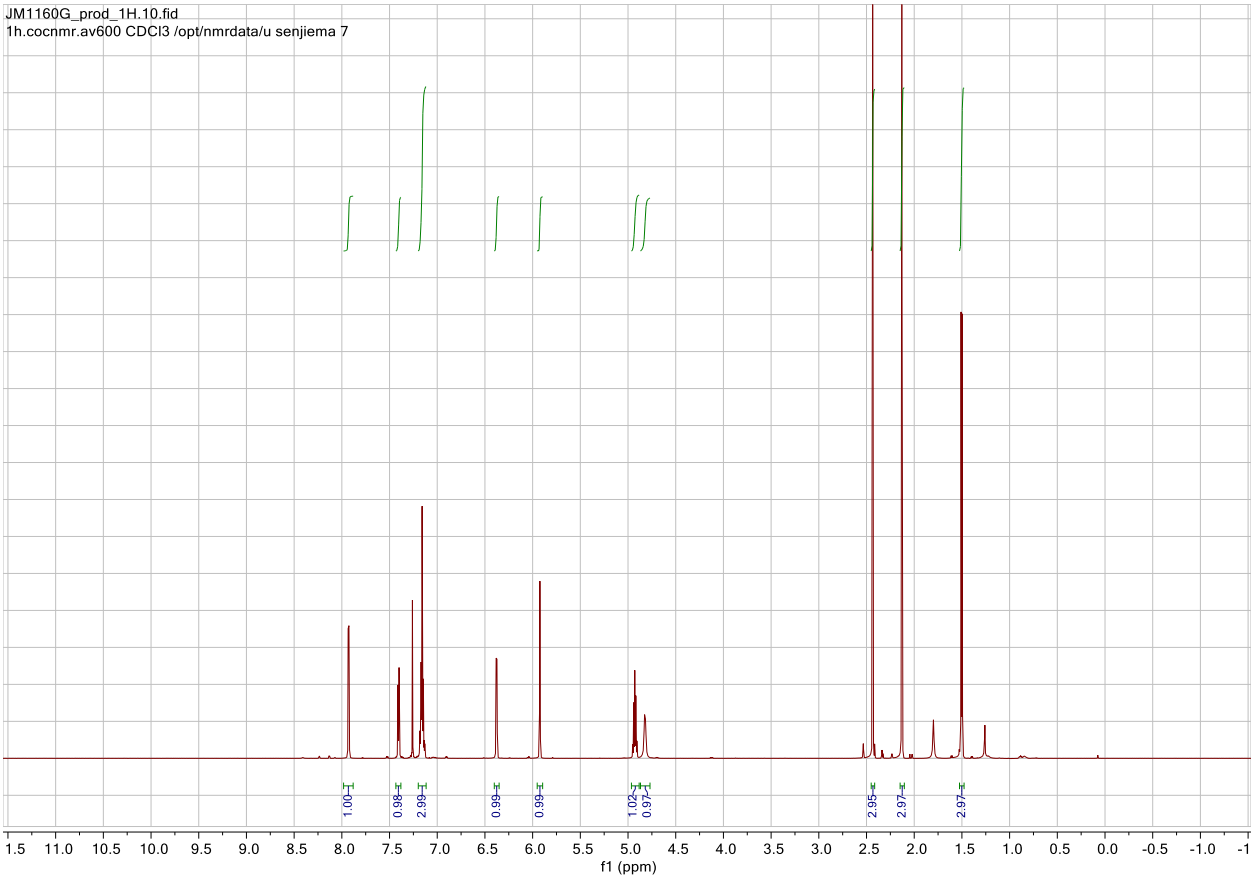
^{13}C


JM1160H_prod_13C.12.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 8
158.14
148.65
148.02
144.18
131.81
127.77
120.71
115.02
107.18
51.41
24.44
21.36
f1 (ppm)

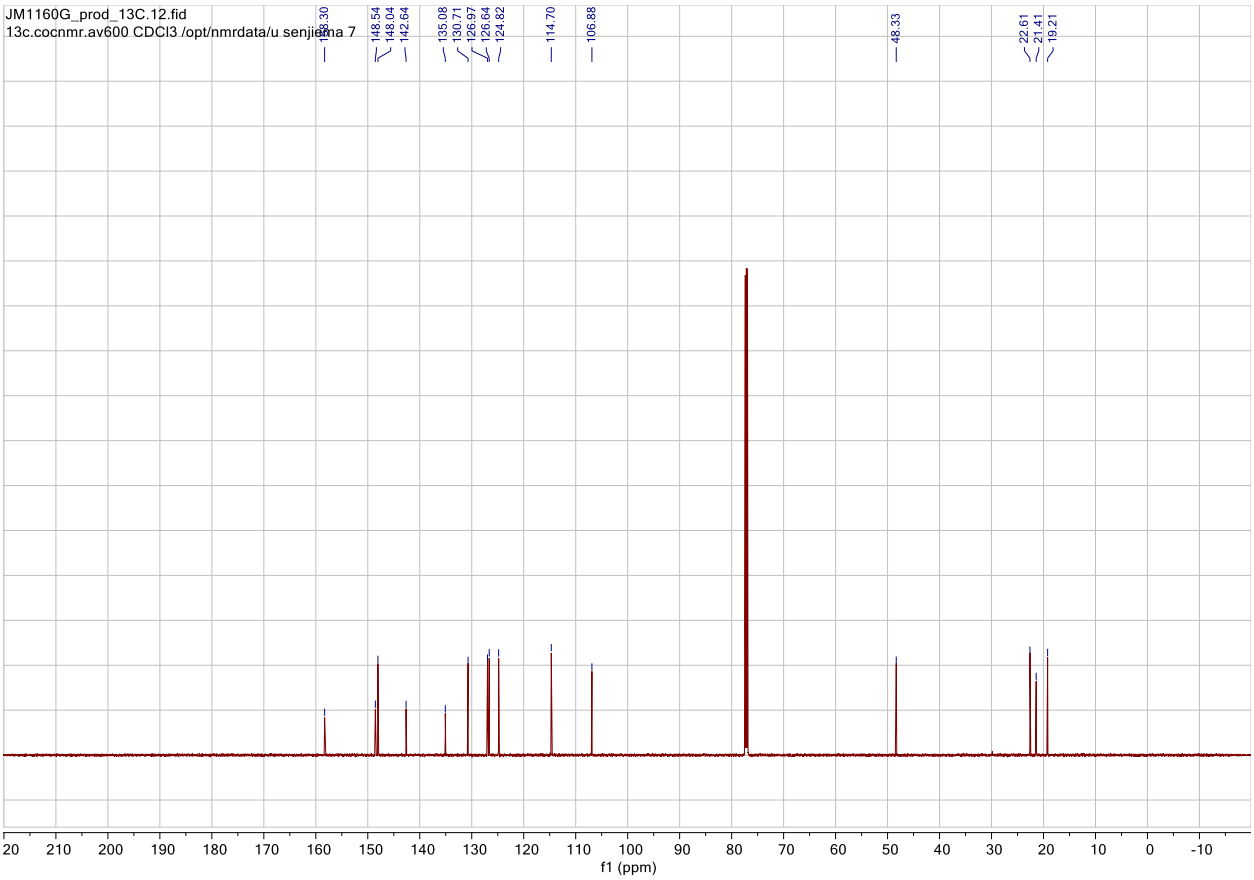


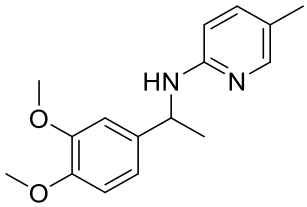
4-methyl-N-(1-(o-tolyl)ethyl)pyridin-2-amine (25a)

^{1}H



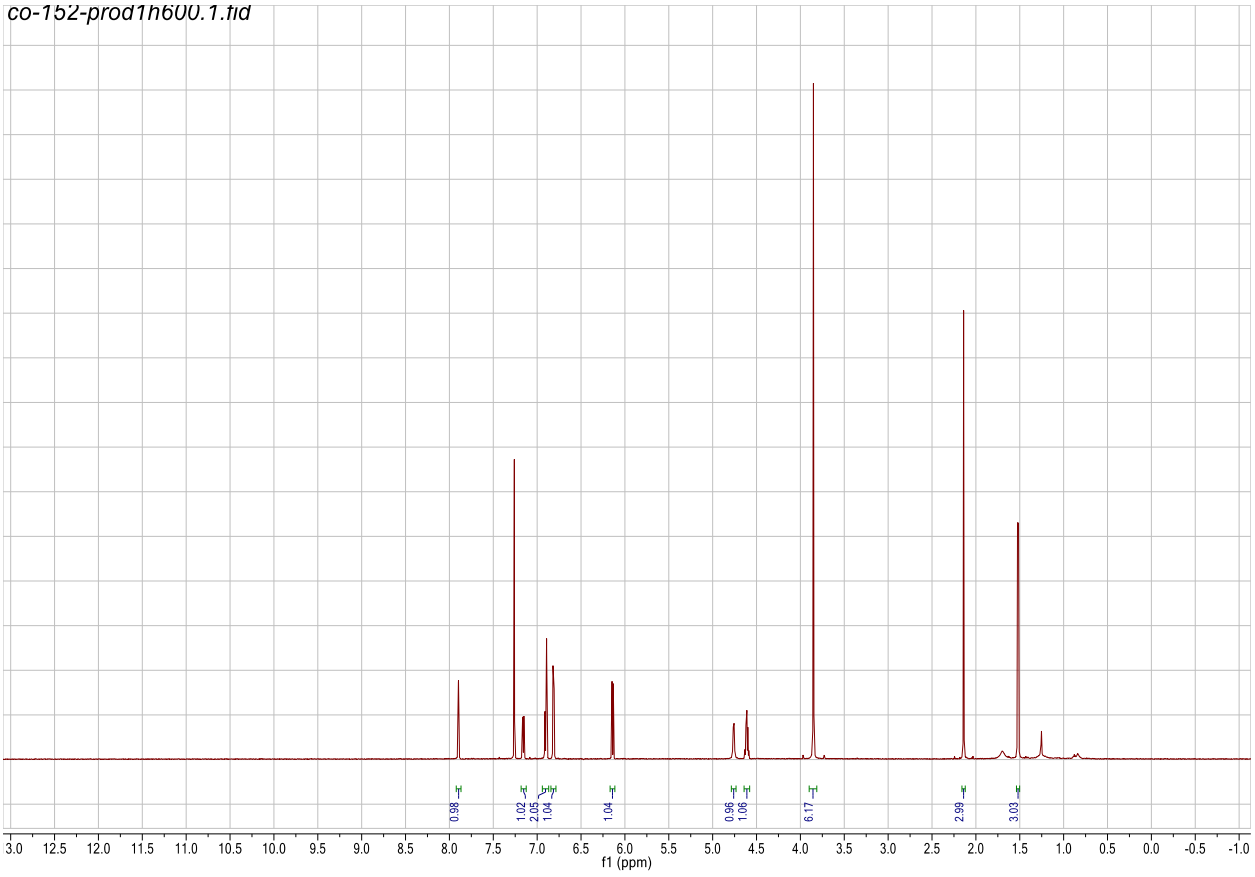
^{13}C


JM1160G_prod_13C.12.fid
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u senjiema 7
161.30
148.54
148.04
142.64
135.08
130.71
126.97
126.64
124.82
114.70
106.88
48.33
22.61
21.41
19.21
f1 (ppm)

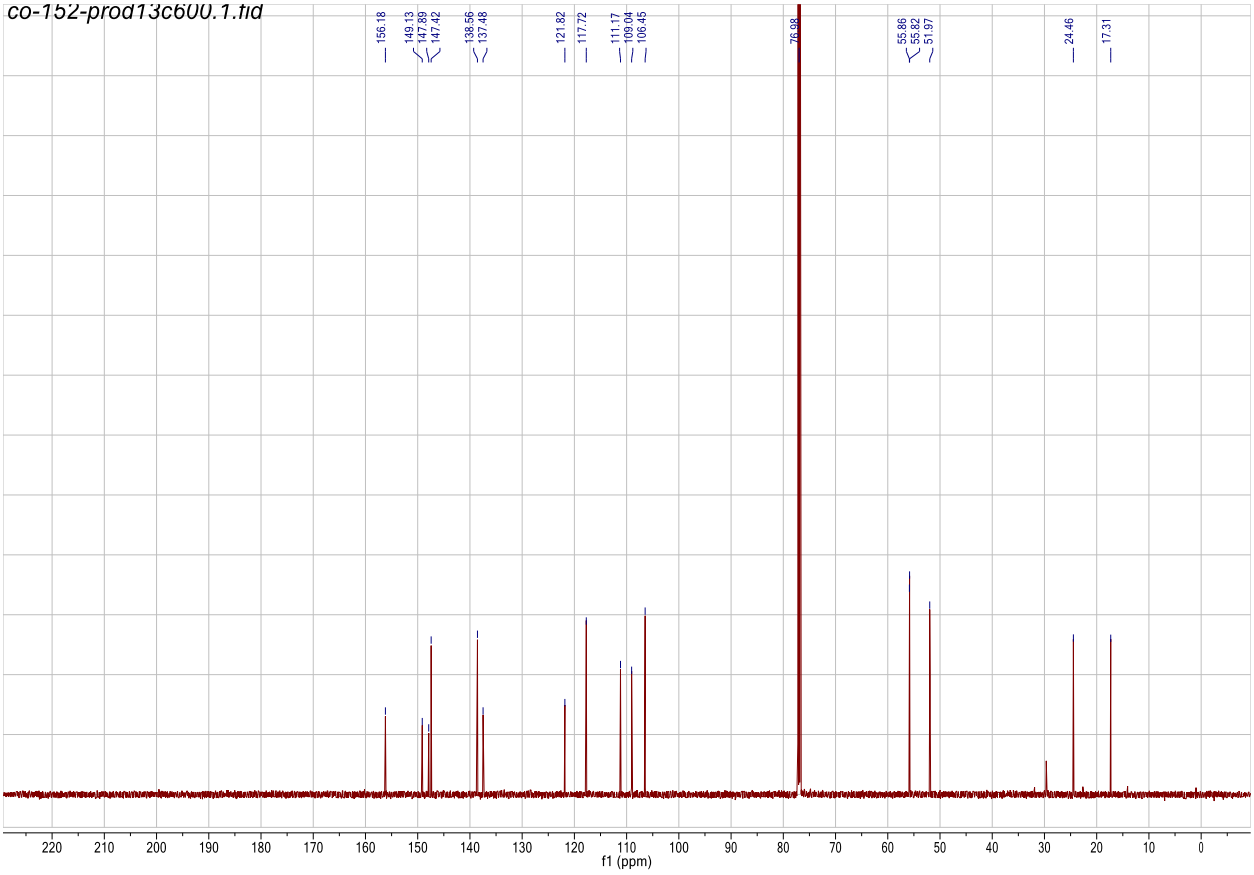


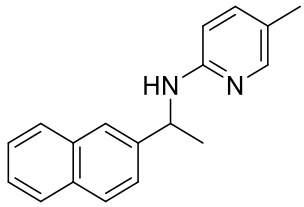
***N*-(1-(3,4-dimethoxyphenyl)ethyl)-5-methylpyridine-2-amine (26a)**

^{1}H



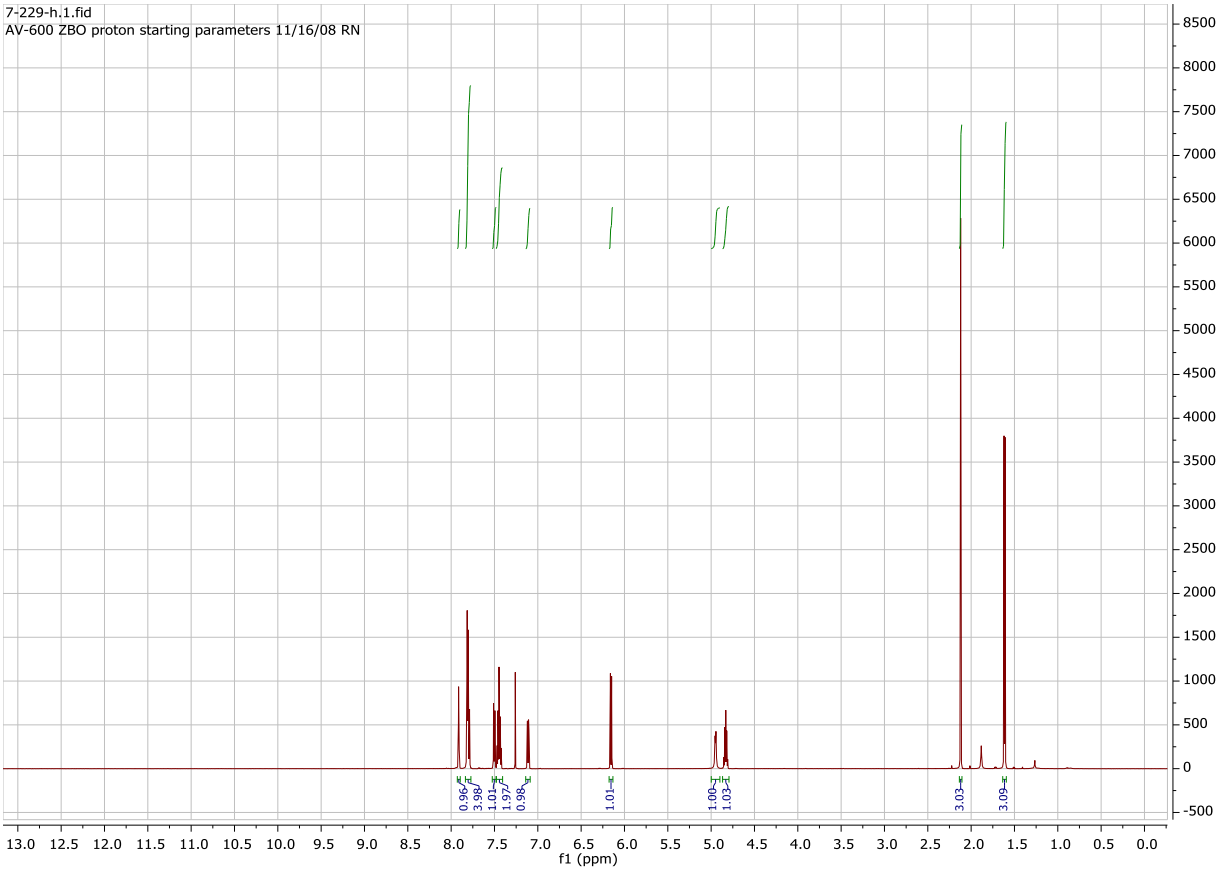
^{13}C


co-152-prod13c600.1.fid
156.18
149.13
147.89
147.42
138.56
137.48
121.82
117.72
111.17
109.04
106.45
76.98
55.86
55.82
51.97
24.46
17.31
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

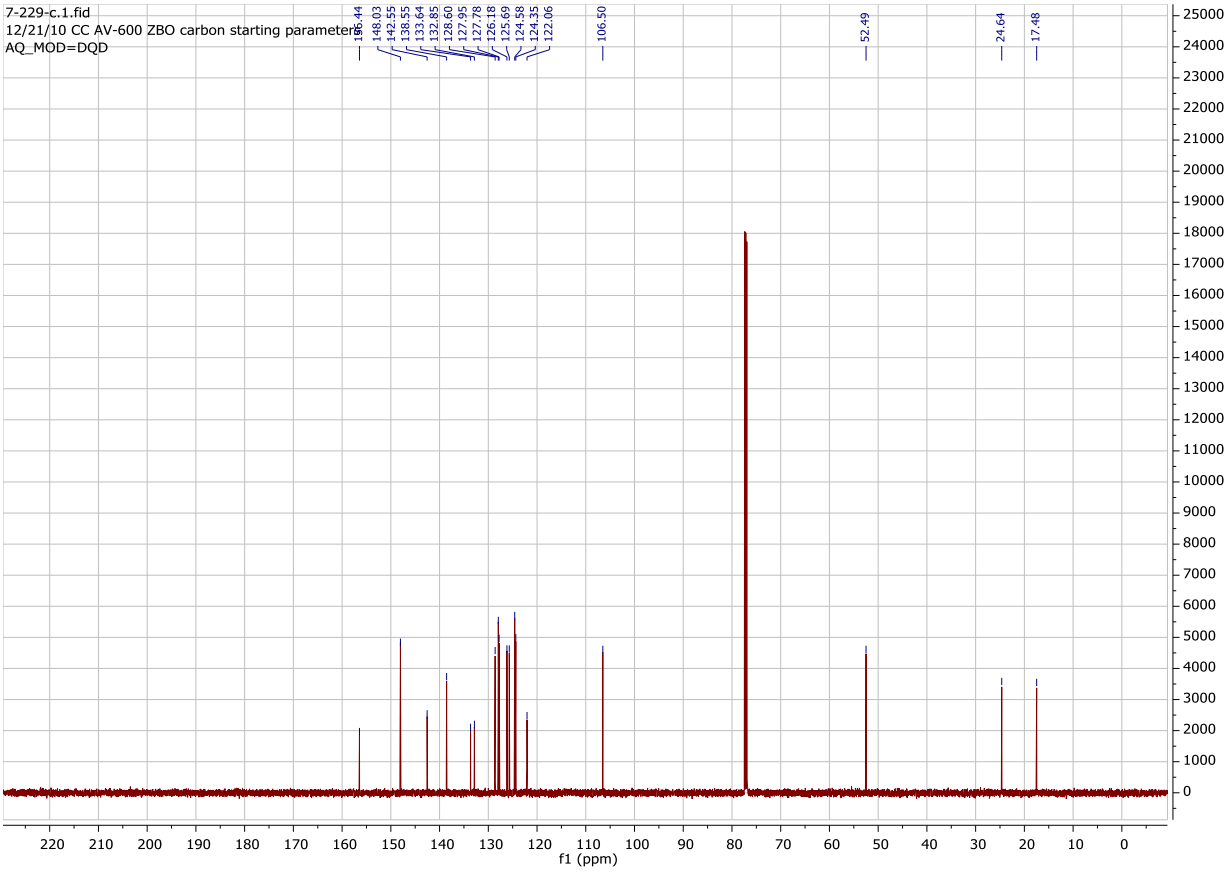


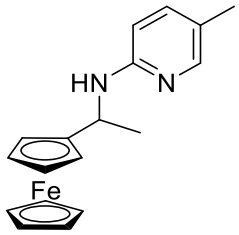
N-(ethyl-naphthalene-2-yl)-5-methylpyridin-2-amine (27a)

^{1}H



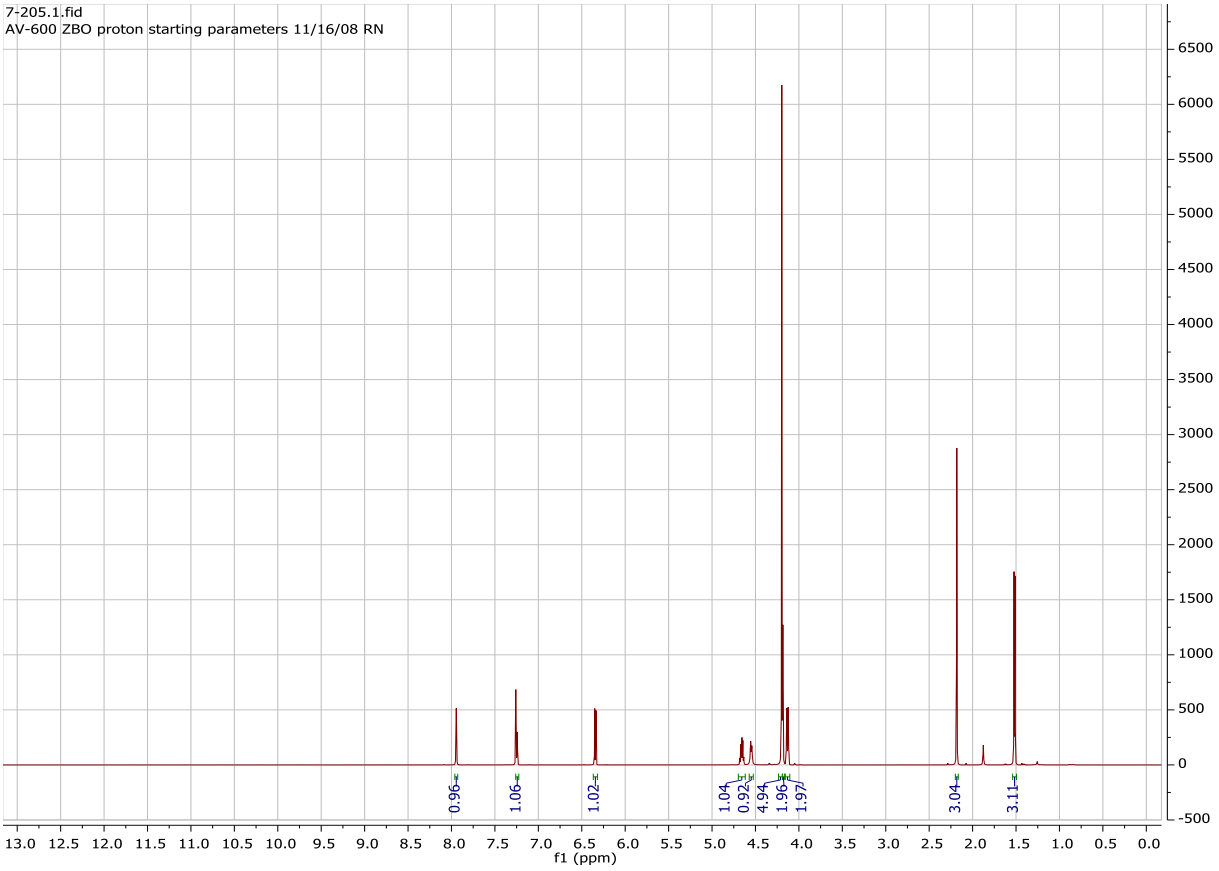
^{13}C


7-229-c.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
196.44
148.03
142.55
138.55
133.64
132.85
128.60
127.95
127.78
126.18
125.69
124.58
124.35
122.06
106.50
52.49
24.64
17.48
f1 (ppm)

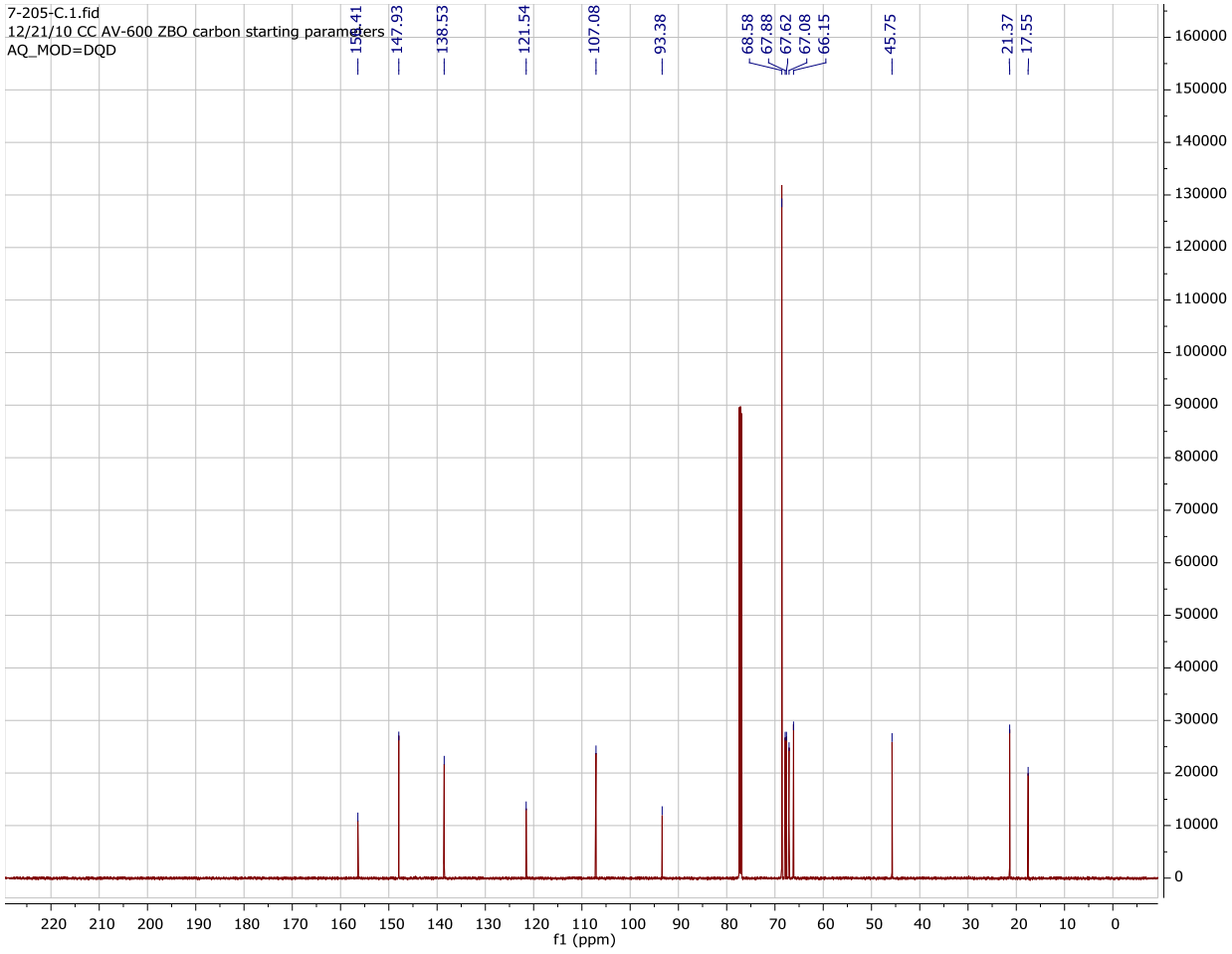


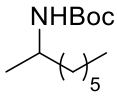
N-(ethylferrocene-2-yl)-5-methylpyridin-2-amine (28a)

^{1}H



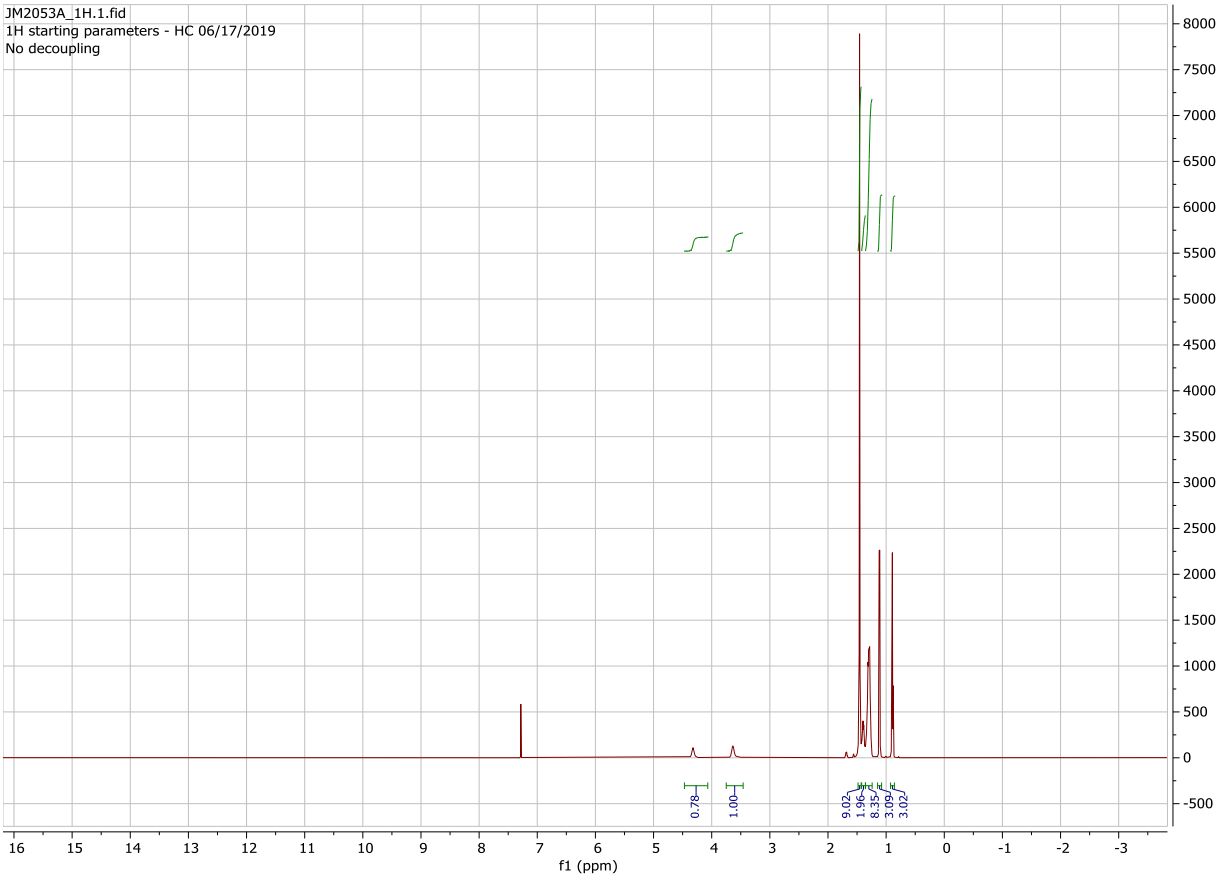
^{13}C

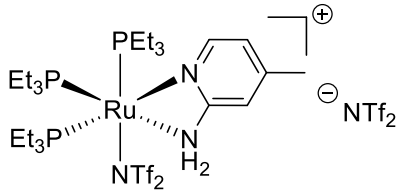

7-205-C.1.fid
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
154.41
147.93
138.53
121.54
107.08
93.38
68.58
67.88
67.62
67.08
66.15
45.75
21.37
17.55
f1 (ppm)



tert-butyl octan-2-ylcarbamate (2c)

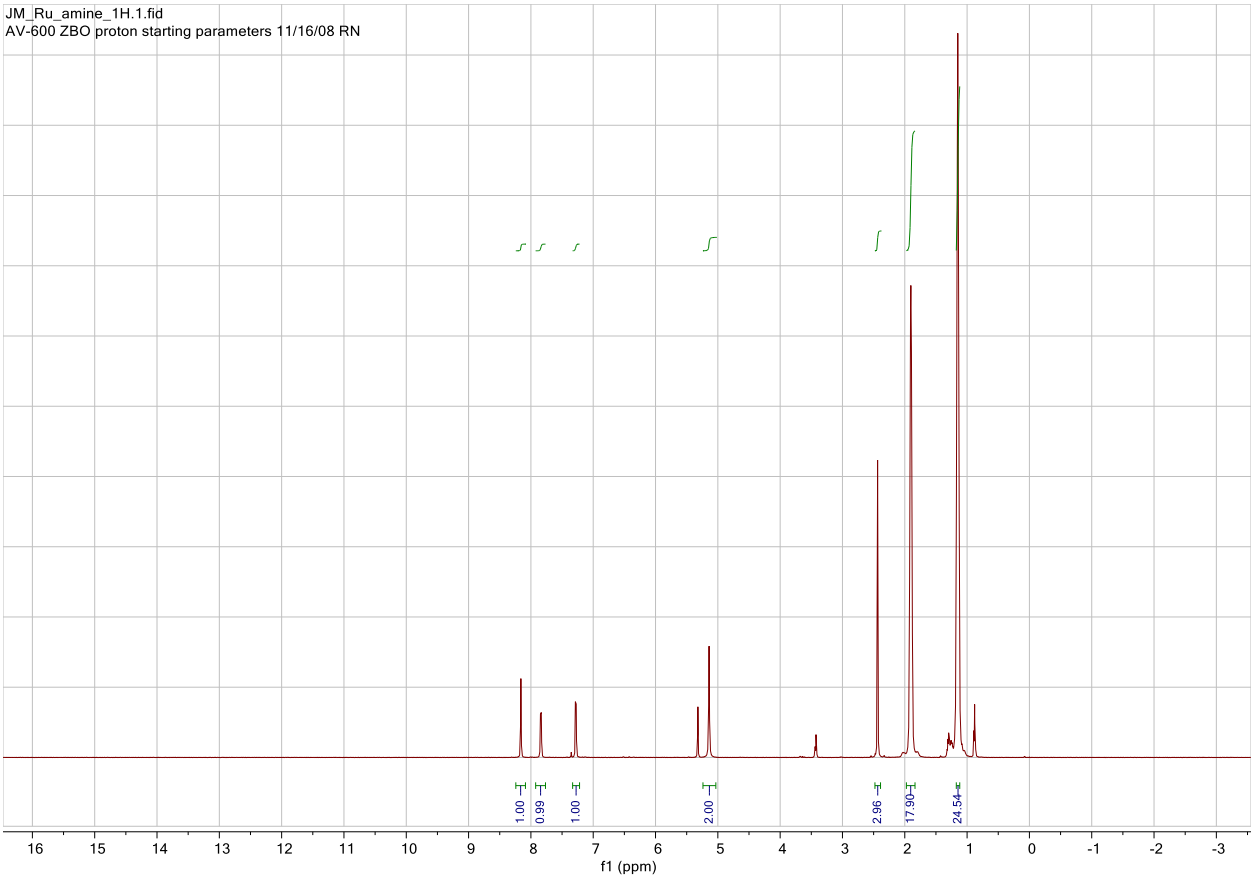
^{1}H



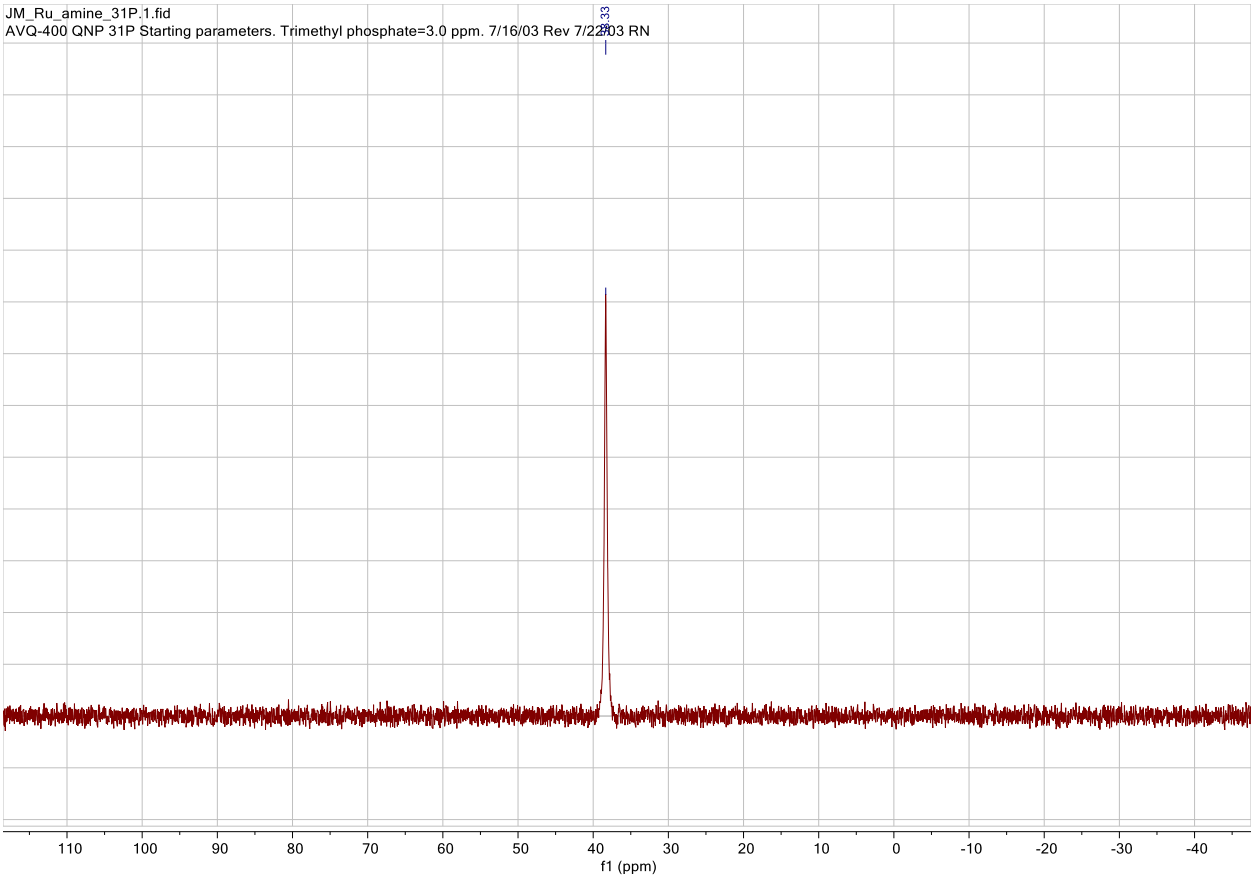


Ru(PEt3)3(amine)(NTf2)2 (29)

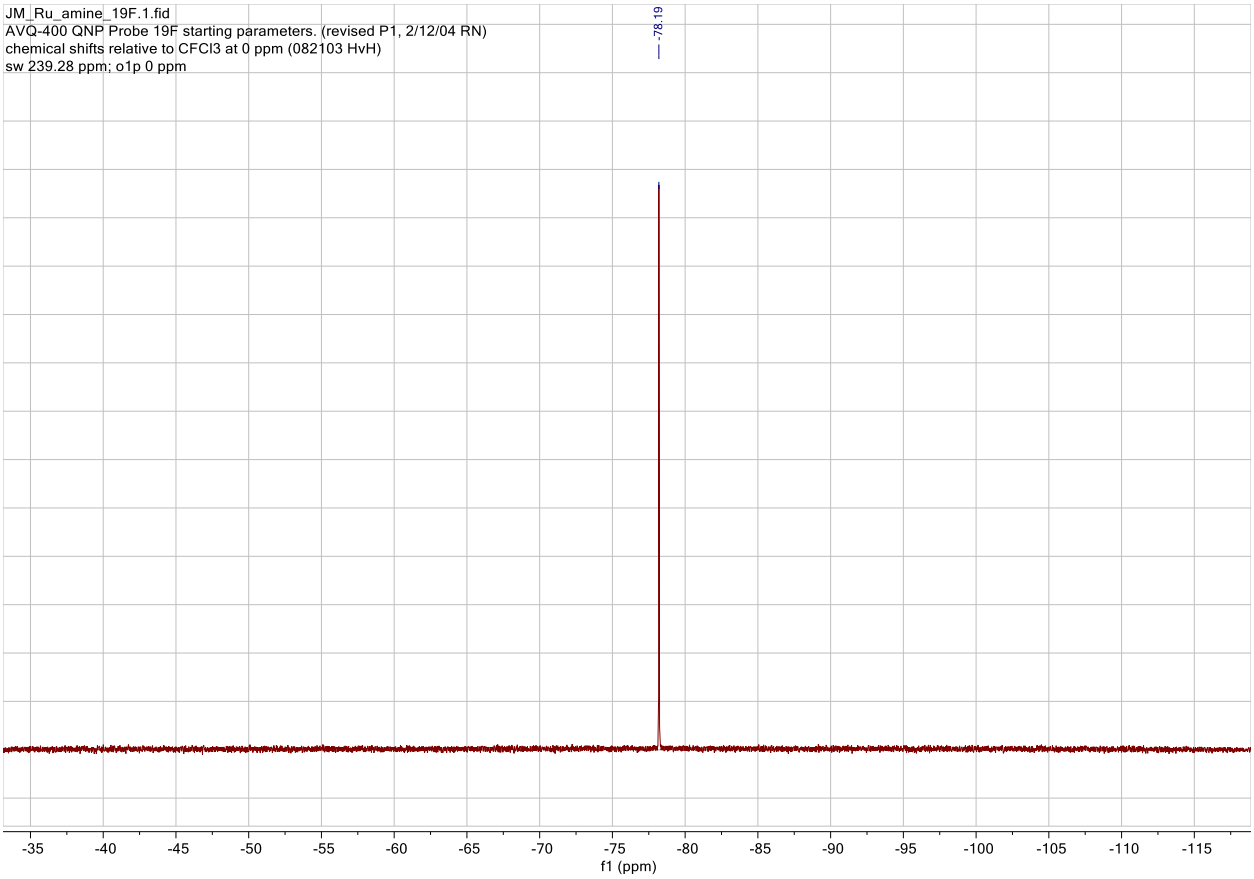
^{1}H

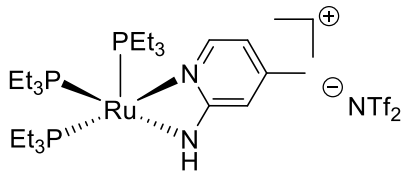


^{31}P


JM_Ru_amine_31P.1.fid
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
33
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

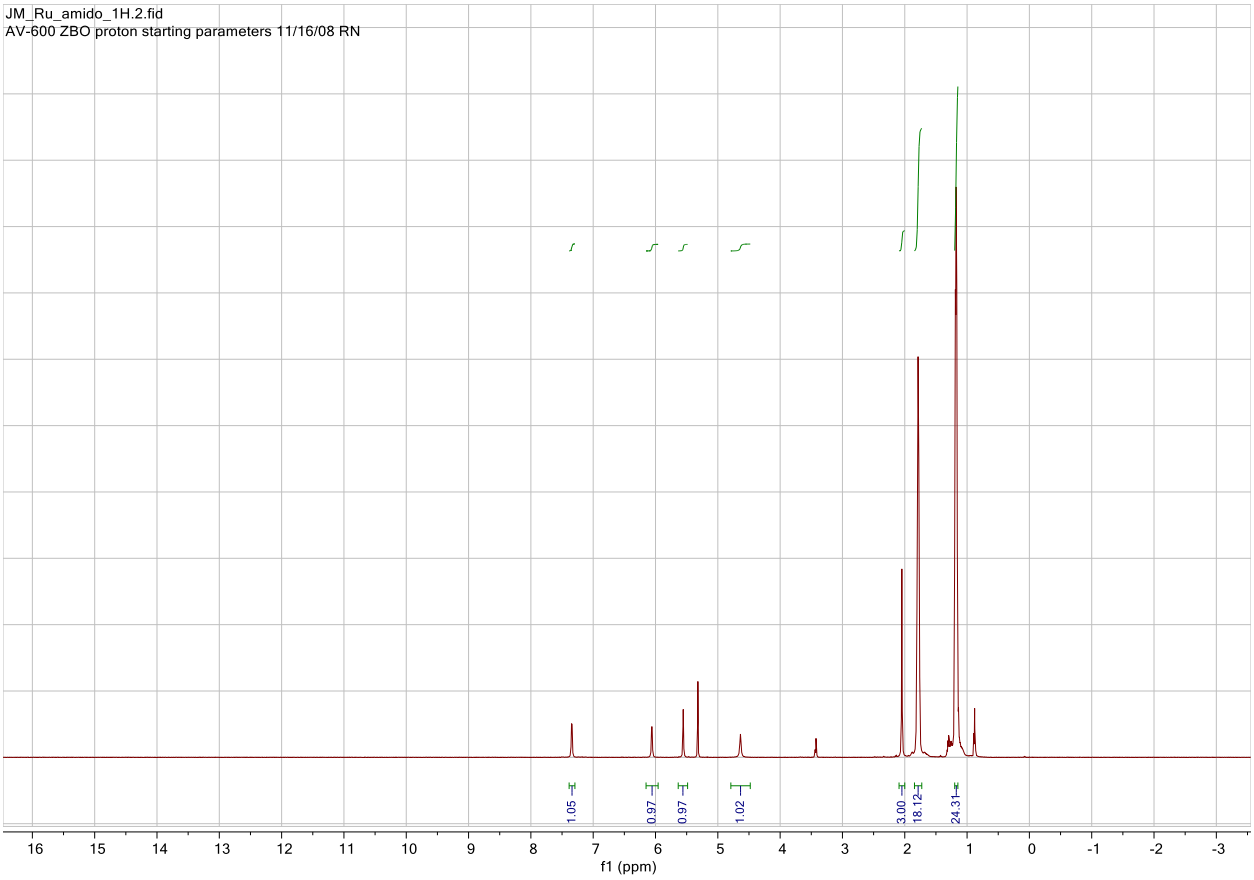
^{19}F


JM_Ru_amine_19F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-78.19
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

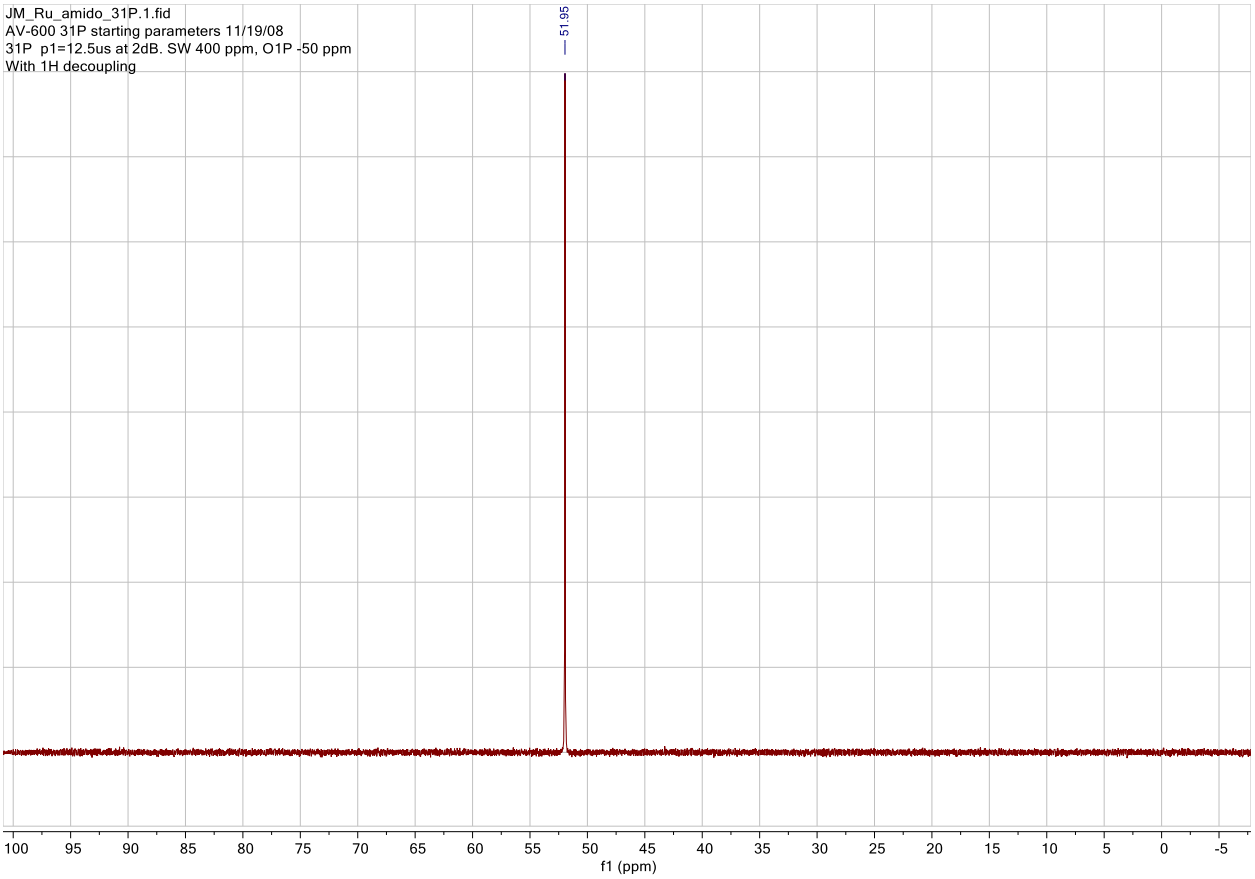


Ru(PEt$_3$)$_3$(amide)(NTf$_2$) (30)

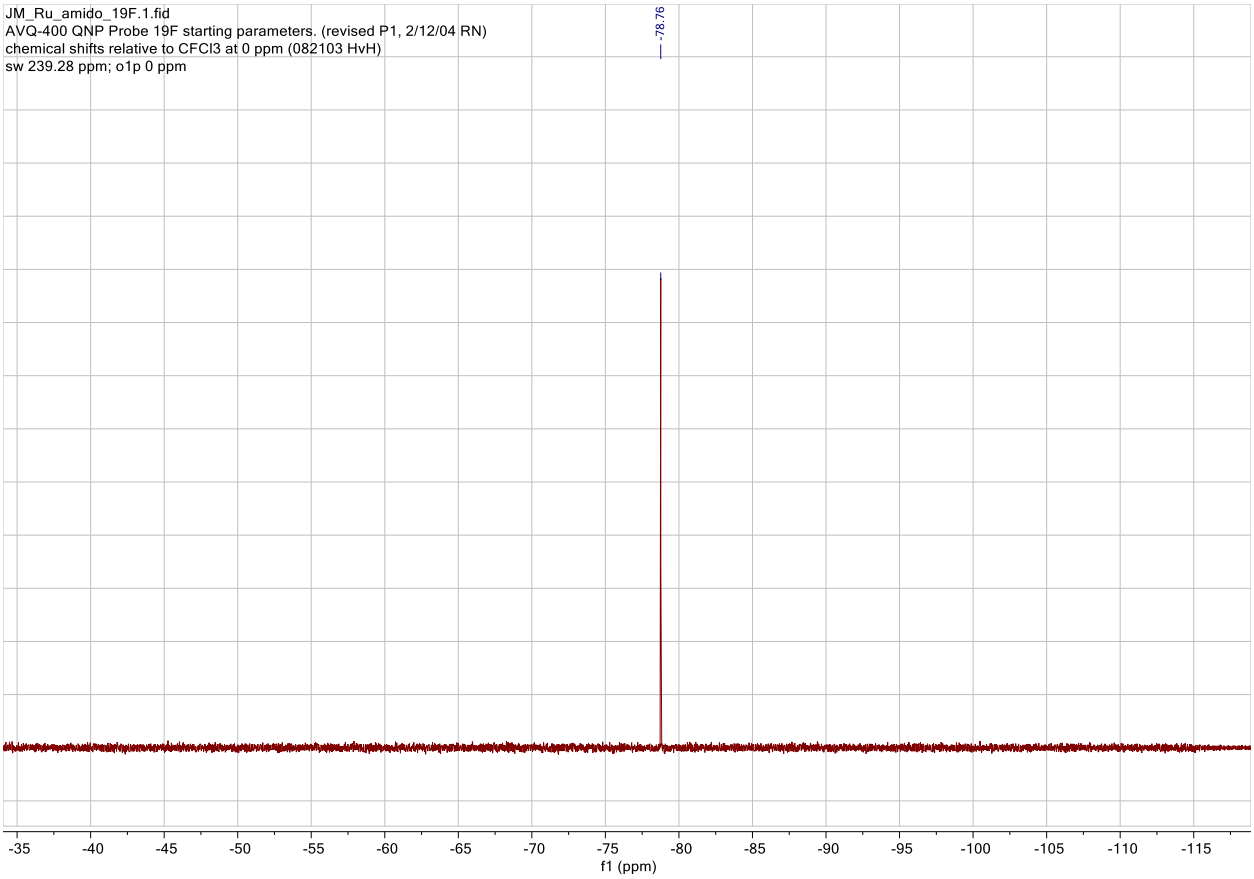
^{1}H

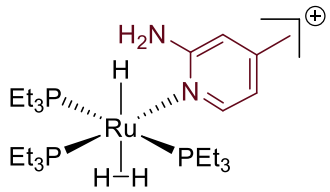


^{31}P


JM_Ru_amido_31P.1.fid
AV-600 31P starting parameters 11/19/08
31P p1=12.5us at 2dB. SW 400 ppm, O1P -50 ppm
With 1H decoupling
51.95
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

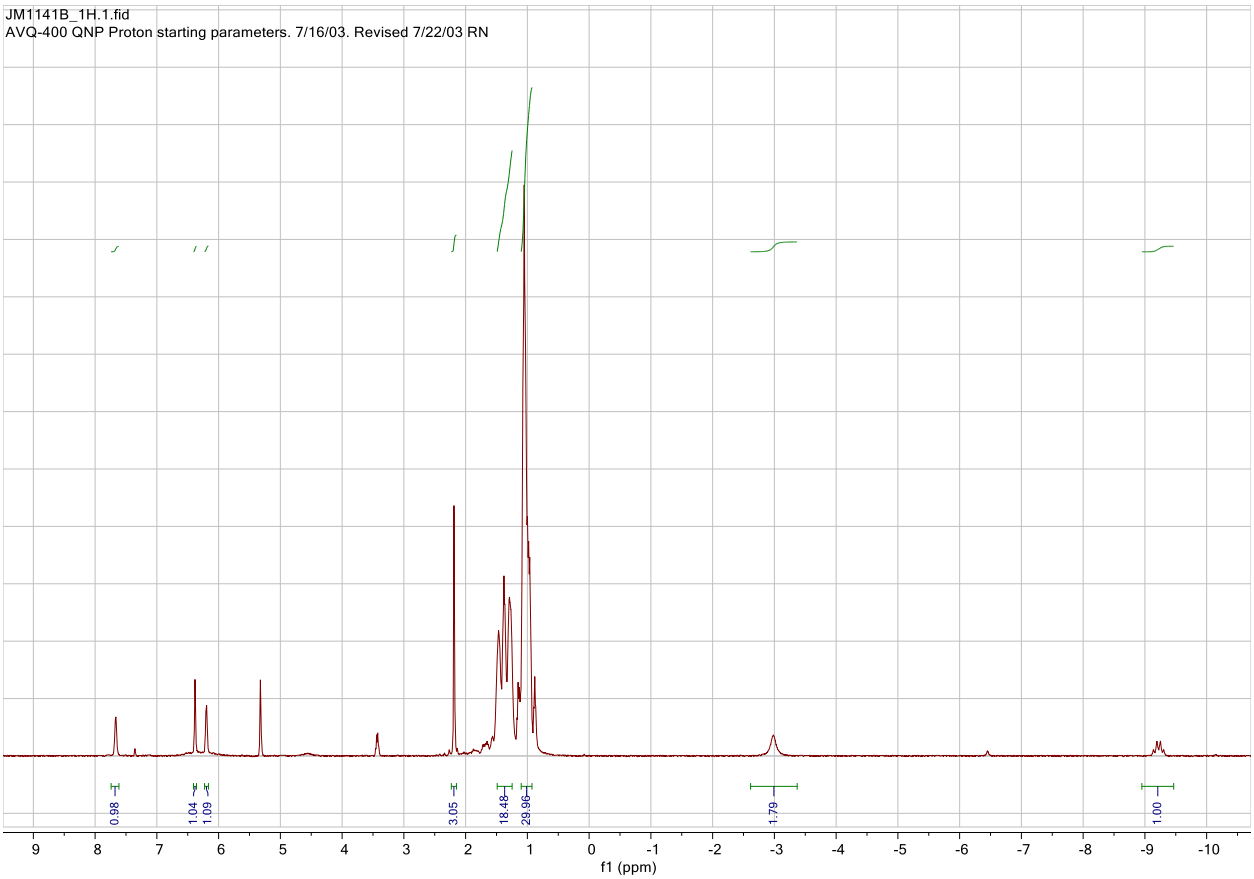
^{19}F


JM_Ru_amido_19F.1.fid
AVQ-400 QNP Probe 19F starting parameters. (revised P1, 2/12/04 RN)
chemical shifts relative to CFCl3 at 0 ppm (082103 HvH)
sw 239.28 ppm; o1p 0 ppm
-78.76
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

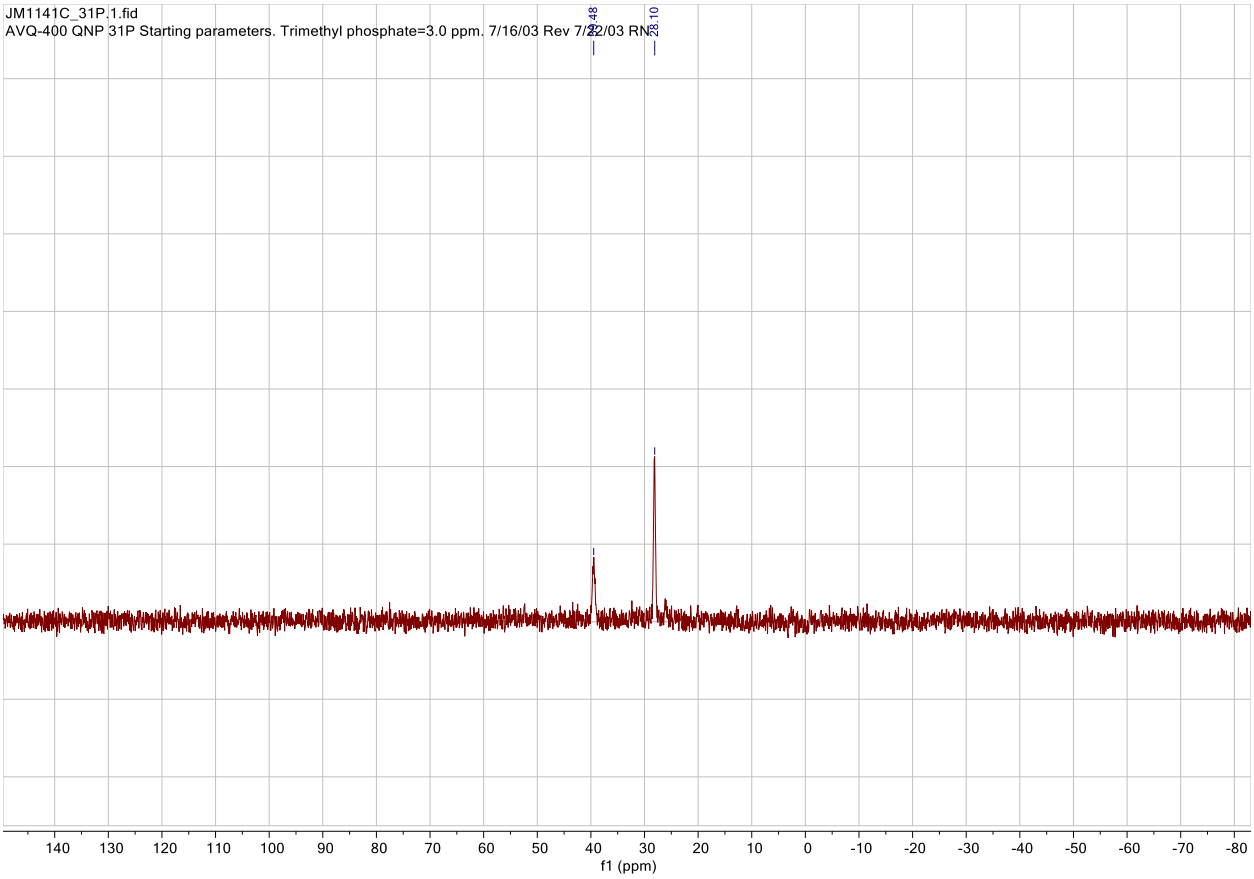


Ru(H)(H_2)(PEt_3)$_3$(amine)(NTf_2) (43)

^{1}H



^{31}P


JM1141C_31P.1.fid
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
28.48
28.10
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)