Supporting Information for:

Ruthenium Complexes of Tetradentate Bipyridine Ligands: Highly Efficient Catalysts for the Hydrogenation of Carboxylic Esters and Lactones

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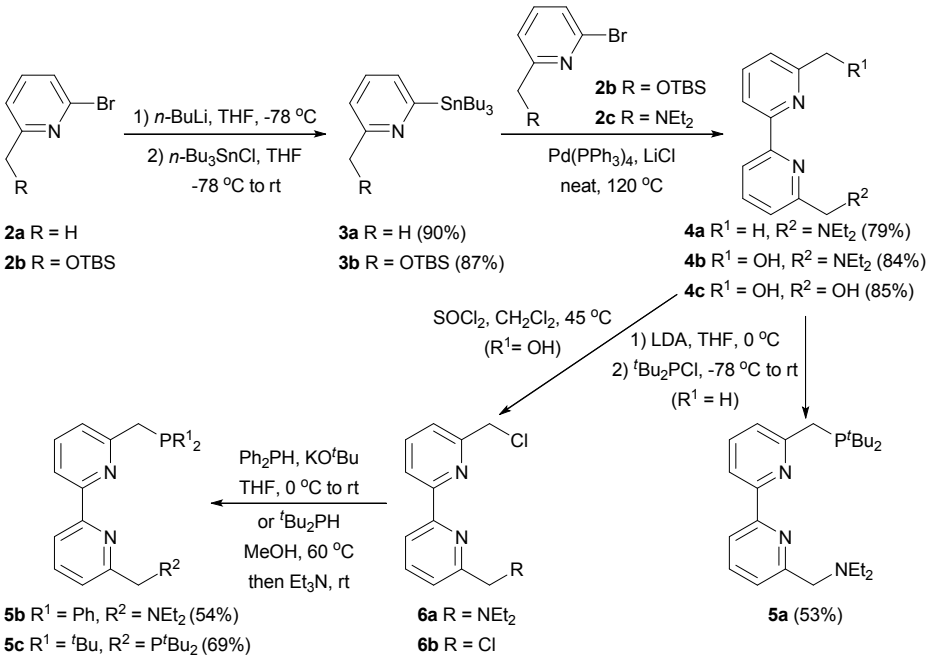
CONTENTS:

General: Unless mentioned otherwise, all manipulations were performed in an argon-filled glove box MBRAUN LABstar or using standard Schlenk techniques. NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR) and 162 MHz (^{31}P NMR). Chemical shifts were reported in ppm relative to internal TMS for ^{1}H NMR data, deuterated solvent for ^{13}C NMR data, and external 85% H_3PO_4 for ^{31}P NMR data, respectively. Data are presented in the following space: chemical shift, multiplicity, coupling constant in hertz (Hz), and signal area integration in natural numbers. High-resolution mass spectra were recorded on an IonSpec FT-ICR mass spectrometer with ESI resource. Elemental analysis was performed on Elementar Vario EL elemental analyzer. GC analysis were performed using a Agilent Technologies 7890A GC System.

Hydrogen gas (99.999%) was purchased from Boc Gas Inc., Tianjin. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent. $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ was purchased from Strem Chemicals, Inc. Other commercially available reagents were purchased from Acros, Aldrich and Alfa Aesar Chemical Company. $Pd(PPh_3)_4$ was prepared according to the literature procedure and kept in a refrigerator under argon.[1] $HPPh_2$ and HP^tBu_2 were synthesized according to the literature procedure.[2] All of the liquid substrates for hydrogenation were distilled before use. All of the solid substrates except for long chain fatty esters and triglycerides for hydrogenation were recrystallized before use.

(A) Preparation and Analytical Data of Ligands 5



1. Preparation and Analytical Data of Ligand 5a

2-Bromo-6-diethylamminomethylpyridine (2c):

(1) 2-Bromo-6-(((4-methylphenyl)sulfonyl)oxy)methylpyridine

To a 500 mL round-bottom flask were added 2-bromo-6-hydroxymethylpyridine (11.2 g, 59.6 mmol) and THF (200 mL). A solution of NaOH (7.2 g, 180 mmol)) in H_2O (50 ml) was added in one portion with stirring and the mixture was cooled to 0 °C. To the mixture, a solution of TsCl (12.6 g, 66.1 mmol) in THF (50 mL) was added dropwise over 30 min. The mixture was allowed to slowly warm up to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was diluted with CH_2Cl_2 (300 mL) and washed with water and brine. The CH_2Cl_2 solution was dried over Na_2SO_4, filtered and concentrated, yielding crude title compound as a pale-yellow solid. It was pure enough for the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 5.09 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.18 (s), 145.38 (s), 141.47 (s), 139.36 (s), 132.48 (s), 130.06 (s), 128.12 (s), 127.82 (s), 120.61 (s), 70.73 (s), 21.73 (s). HRMS (ESI) calcd for $C_{13}H_{13}BrNO_3S^+$ ([M+H]$^+$): 341.9794; Found: 341.9789.

(2) 2-Bromo-6-diethylamminomethylpyridine (**2c**)

To a 250 mL 2-neck round-bottom flask were added the above compound, diethylamine (43.9 g, 600 mmol) and THF (120 mL). The mixture was stirred at room temperature overnight. After removal of the solvent, the residue was diluted with CH_2Cl_2 (300 mL), washed with saturated $NaHCO_3$, water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was distilled under vaccum, yielding 2-bromo-6-diethylamminomethylpyridine as a pale yellow oil (14.0 g, 96% for two steps). B.p.: 56 °C/0.1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 4.9 Hz, 2H), 7.32 (t, J = 4.8 Hz, 1H), 3.70 (s, 2H), 2.56 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.09 (s), 141.04 (s), 138.73 (s), 125.85 (s), 121.37 (s),

59.09 (s), 47.51 (s), 12.08 (s). HRMS (ESI) calcd for $C_{10}H_{16}BrN_2^+$ ([M+H]$^+$): 243.0491; Found: 243.0487.

2-Tri-*n*-butylstannyl-6-methylpyridine (3a)[3]:

To an oven-dried 500 mL 2-neck round-bottom flask under an argon atmosphere were added 2-bromo-6-methylpyridine (20.0 g, 116.3 mmol) and dry THF (200 mL). The solution was cooled to -78 ºC and a solution of *n*-BuLi in hexane (2.4 M, 56 mL, 134.4 mmol) was added with a syringe during 30 min. The deep reddish brown solution was stirred at -78 ºC for 2 hrs and tributyltin chloride (45.4 g, 139.5 mmol) was added dropwise with a syringe during 30 min. The mixture was stirred at -78 ºC for 30 min then was slowly warm up to room temperature and stirred overnight. Thereafter, the mixture was evaporated to dryness and the residue was diluted with Et_2O (300 mL), washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was distilled under vacuum, yielding the title compound as a colorless oil (40.0 g, 90%). B.p.: 145 ^{o}C/0.4 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 2.54 (s, 3H), 1.69 – 0.76 (m, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.11 (s), 158.70 (s), 133.40 (s), 129.48 (s), 121.62 (s), 29.22 (s), 27.47 (s), 24.98 (s), 13.82 (s), 9.95 (s). HRMS (ESI) calcd for $C_{18}H_{34}NSn^+$ ([M+H]$^+$): 384.1708; Found: 384.1712.

6-Diethylamminomethyl-6'-methyl-2,2'-bipyridine (4a):

To an oven-dried 100 mL Schlenk flask were added $Pd(PPh_3)_4$ (1.28 g, 1.1 mmol), anhydrous LiCl (4.1 g, 96.7 mmol), 2-tri-*n*-butylstannyl-6-methylpyridine (14.5 g, 37.9 mmol) and 2-bromo-6-diethylamminomethylpyridine (7.7 g, 31.7 mmol). The mixture was degassed, followed by the introduction of highly pure argon and then heated at 120 ^{o}C for 16 hrs with stirring, at which time a black precipitate was formed. GC analysis showed a full conversion of 2-bromo-6-diethylamminomethylpyridine. After cooling to room temperature, the mixture was diluted with ethyl acetate (100 mL) and filtered to remove unsolved material and then acidified with 6N HCl (aq). The organic layer was washed with water and the combined aqueous layer was made alkaline with 6N NaOH (aq) and extracted with ethyl ether (3 × 100 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was distilled under vaccum, yielding the title compound as a pale yellow oil (6.4 g, 79%). B.p.: 130 ^{o}C/0.1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 2H), 2.65 – 2.58 (m, 7H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.10 (s), 157.87 (s), 156.07 (s), 155.64 (s), 137.12 (s), 137.05 (s), 123.09 (s), 122.73 (s), 119.15 (s), 118.27 (s), 59.53 (s), 47.51 (s), 24.77 (s), 12.18 (s). HRMS (ESI) calcd for $C_{16}H_{22}N_3^+$ ([M+H]$^+$): 256.1808; Found: 256.1807.

6-Di-*tert*-butylphosphinomethyl-6'-diethylamminomethyl-2,2'-bipyridine (5a):

To an oven-dried 100 mL Schlenk flask was added a degassed solution of 6-diethylamminomethyl-6'-methyl-2,2'-bipyridine (4.0 g, 15.7 mmol) in dry THF (10 mL) under an argon atmosphere. The solution was cooled to 0 ºC and a solution of freshly prepared LDA (20 mL, 1.2 M) in THF was added with a syringe during 30 min. The mixture was stirred for 2 hrs at 0 ^{o}C and then cooled to -78 ^{o}C, and a degassed solution of di-*tert*-butylchlorophosphine (5.7 g, 31.5 mmol) in dry THF (10 mL) was added dropwise with a syringe during 30 min. The mixture was

allowed slowly warm up to room temperature and stirred overnight. The solvent was removed under vaccum. To the residue was added degassed water (30 mL) and degassed ethyl ether (30 mL). The ether phase was separated under an argon atmosphere. The aqueous phase was extracted with degassed ethyl ether (2 × 10 mL). The combined ether solutions were dried over Na_2SO_4, filtered, and the solvent was removed under vacuum. The residue was distilled under vacuum, yielding the title compound as a viscous pale-yellow oil (3.3 g, 53%), which was gradually solidified upon standing at room temperature in the glove box. B.p.: 180 °C /0.1 mmHg. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 37.12 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.7 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 3.82 (s, 2H), 3.14 (d, *J* = 2.4 Hz, 2H), 2.62 (q, *J* = 7.0 Hz, 4H), 1.18 (d, *J* = 11.0 Hz, 18H), 1.09 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.46 (d, *J* = 13.7 Hz), 159.88 (s), 155.70 (s), 155.49 (s), 137.16 (s), 137.00 (s), 123.82 (d, *J* = 8.5 Hz), 122.75 (s), 119.14 (s), 117.99 (s), 59.46 (s), 47.53 (s), 32.09 (d, *J* = 21.6 Hz), 31.97 (d, *J* = 23.9 Hz), 29.86 (d, *J* = 13.2 Hz), 12.18 (s). HRMS (ESI) calcd for $C_{24}H_{39}N_3P^+$([M+H]$^+$): 400.2876; Found: 400.2867.

2. Preparation and Analytical Data of Ligand 5b

2-((*tert*-Butyldimethylsilyloxy)methyl)-6-(tributylstannyl)pyridine (3b):

(1) 2-Bromo-6-((*tert*-butyldimethylsilyloxy)methyl)pyridine (**2b**)[4]

To an oven-dried 100 mL Schlenk flask were added TBSCl (10.2 g, 67.7 mmol), 2-bromo-6-hydroxymethylpyridine (10.6 g, 56.4 mmol), imidazole (15.4 g, 226.1 mmol) and anhydrous DMF (50 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature until TLC showed complete conversion of the starting alcohol (1 hr). Water (50 mL) was added and then the mixture was extracted with Et_2O (100 mL ×3). The combined ethereal phases were washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The resulting yellow oily residue was distilled under vaccum, yielding the title compound as a colorless oil (15.3 g, 90%). B.p.: 92 °C/0.1 mmHg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.33 (dd, *J* = 7.8, 0.7 Hz, 1H), 4.80 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H).

(2) 2-((*tert*-Butyldimethylsilyloxy)methyl)-6-(tributylstannyl)pyridine (**3b**)

To an oven-dried 250 mL 2-neck round-bottom flask were added the above silyl ether (15.5 g, 51.3 mmol) and dry THF (150 mL) under an argon atmosphere. The solution was cooled to -78 ºC and a solution of *n*-BuLi in hexane (2.4 M, 25 mL, 60 mmol) was added with a syringe during 30 min. The deep reddish brown solution was stirred at -78 ºC for 2 hrs and a solution of tributyltin chloride (20.0 g, 61.4 mmol) in dry THF (30 mL) was added dropwise with a syringe during 30 min. The mixture was stirred at -78 ºC for 30 min then allowed slowly warm up to room temperature and stirred overnight. Thereafter, the mixture was evaporated to dryness and the residue was diluted with Et_2O (200 mL), washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was distilled under vacuum, yielding the title compound as a colorless oil (23.0 g, 87%). B.p.: 170 °C/0.1 mmHg. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 1.60 – 1.49 (m, 6H), 1.36 – 1.28 (m, 6H), 1.12 – 1.05 (m, 6H), 0.95 (s, 9H), 0.87 (t, *J* = 7.3 Hz, 9H), 0.12 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.63 (s), 161.56 (s), 133.78 (s), 130.57 (s), 118.49 (s), 66.77 (s), 29.22 (s), 27.46 (s), 26.10 (s), 18.52 (s), 13.84 (s), 9.98 (s), -5.16 (s). HRMS (ESI) calcd for $C_{24}H_{48}NOSiSn^+$

([M+H]$^+$): 514.2522; Found: 514.2530.

6-Diethylamminomethyl-6'-Diphenylphosphinomethyl-2,2'-bipyridine (5b):

(1) 6-Diethylamminomethyl-6'-Hydroxymethyl-2,2'-bipyridine (**4b**)

To an oven-dried 100 mL Schlenk flask were added $Pd(PPh_3)_4$ (1.42 g, 1.2 mmol), anhydrous LiCl (4.5 g, 106 mmol), 2-bromo-6-diethylamminomethylpyridine (8.5 g, 35.0 mmol) and the tributyltin derivative **3b** (21.5 g, 42.0 mmol). The mixture was degassed, followed by the introduction of highly pure argon and then heated at 120 ^{o}C for 10 hrs with stirring, at which time a black precipitate was formed. GC analysis showed a full conversion of 2-bromo-6-diethylamminomethylpyridine. After cooling to room temperature, the mixture was diluted with ethyl acetate (100 mL) and filtered to remove unsolved material and then acidified with 6N HCl (aq). The organic layer was washed with water and the combined aqueous layer was made alkaline with 6N NaOH (aq) and extracted with ethyl ether (3 × 100 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was distilled under vaccum, yielding the title compound as a pale yellow oil (8.0 g, 84%). B.p.: 150 ^{o}C/0.1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.81, 7.79 (2t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 4.83 (s, 2H), 4.06 (s, 1H), 3.84 (s, 2H), 2.63 (q, *J* = 7.1 Hz, 4H), 1.10 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.26 (s), 158.22 (s), 155.30 (s), 154.76 (s), 137.67 (s), 137.23 (s), 123.19 (s), 120.29 (s), 119.89 (s), 119.06 (s), 64.05 (s), 59.46 (s), 47.53 (s), 12.16 (s). HRMS (ESI) calcd for $C_{16}H_{22}N_3O^+$ ([M+H]$^+$): 272.1757; Found: 272.1762.

(2) 6-Chloromethyl-6'-diethylamminomethyl-2,2'-bipyridine (**6a**)

To a 250 mL 2-neck round-bottom flask were added the above compound (5.8 g, 21.4 mmol) and dry CH_2Cl_2 (80 mL). The solution was cooled to 0 ºC and a solution of $SOCl_2$ (13.0 g, 109 mmol) in CH_2Cl_2 (20 mL) was added with a syringe during 30 min. The reaction solution was allowed to warm up to room temperature and stirred at 45 ^{o}C for 3 hrs. The reaction mixture was cooled and then poured into ice-water, made alkaline with 6N NaOH (aq) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo, yielding crude title compound as a pale-brown oil. Due to the instability of the product, it was used without purification for the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.50, 7.48 (2d, *J* = 8.8 Hz and 8.4 Hz, 2H), 4.75 (s, 2H), 3.83 (s, 2H), 2.62 (q, *J* = 7.0 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.19 (s), 156.25 (s), 156.07 (s), 154.86 (s), 137.93 (s), 137.25 (s), 123.20 (s), 122.56 (s), 120.49 (s), 119.33 (s), 59.47 (s), 47.54 (s), 47.13 (s), 12.18 (s). HRMS (ESI) calcd for $C_{16}H_{21}ClN_3^+$ ([M+H]$^+$): 290.1419; Found: 290.1427.

(3) 6-Diethylamminomethyl-6'-Diphenylphosphinomethyl-2,2'-bipyridine (**5b**)

To an oven-dried 250 mL Schlenk flask were added KO^{t}Bu (3.4 g, 30.3 mmol) and degassed dry THF (50 mL) under an argon atmosphere. The solution was cooled to 0 ^{o}C and a solution of $HPPh_2$ (4.7 g, 25.2 mmol) in degassed dry THF (15 mL) was added with a syringe during 15 min. The reddish solution was stirred at 0 ºC for 1 hr and a solution of the above chloride in degassed dry THF (15 mL) was added dropwise with a syringe during 30 min. The mixture was stirred at 0

ºC for 30 min, then allowed slowly to warm up to room temperature and stirred overnight. Degassed water (30 mL) was added and the organic phase was separated, dried over Na_2SO_4, filtered and concentrated. The residue was distilled under vaccum, yielding the title compound as a pale yellow oil (5.0 g, 54%). B.p.: 230 ºC/0.1 mmHg. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ -11.09 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.53 – 7.47 (m, 4H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.28 (m, 6H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 2H), 3.71 (s, 2H), 2.62 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.93 (s), 157.46 (d, *J* = 7.5 Hz), 156.02 (s), 155.49 (s), 138.59 (d, *J* = 14.9 Hz), 137.06 (s, 2C), 133.15 (d, *J* = 19.0 Hz), 128.74 (s), 128.47 (d, *J* = 6.8 Hz), 123.47 (d, *J* = 5.5 Hz), 122.81 (s), 119.42 (s), 118.45 (d, *J* = 1.4 Hz), 59.53 (s), 47.55 (s), 38.72 (d, *J* = 16.3 Hz), 12.23 (s). HRMS (ESI) calcd for $C_{28}H_{31}N_3P^+$ ($[M+H]^+$): 440.2250; Found: 440.2258.

3. Preparation and Analytical Data of Ligand 5c

(1) 6,6'-Dihydroxymethyl-2,2'-bipyridine (**4c**)

To an oven-dried 100 mL Schlenk flask were added $Pd(PPh_3)_4$ (1.14 g, 0.99 mmol), anhydrous LiCl (3.6 g, 84.9 mmol), the tributyltin derivative **3b** (16.9 g, 33.0 mmol) and 2-bromo-6-((*tert*-butyldimethylsilyloxy)methyl)pyridine (8.5 g, 28.1 mmol). The mixture was degassed, followed by the introduction of highly pure argon and then heated at 120 ºC for 12 hrs with stirring, at which time a black precipitate was formed. GC analysis showed a full conversion of 2-bromo-6-((*tert*-butyldimethylsilyloxy)methyl)pyridine. After cooling to room temperature, the mixture was diluted with ethyl acetate (100 mL) and filtered to remove unsolved material and then acidified with 6N HCl (aq). The organic layer was washed with water and the combined aqueous layer was made alkaline with 6N NaOH (aq) and extracted with ethyl ether (3 × 100 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo, yielding the title compound as a white solid (5.2 g, 85%). ^1H NMR (400 MHz, DMSO) δ 8.23 (d, *J* = 7.7 Hz, 2H), 7.93 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 5.48 (t, *J* = 5.8 Hz, 2H), 4.65 (d, *J* = 5.7 Hz, 4H).

(2) 6,6'-Dichloromethyl-2,2'-bipyridine (**6b**)

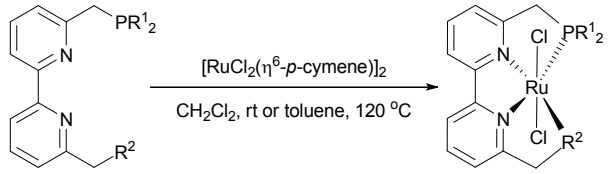
To an oven-dried 100 mL Schlenk flask were added 6,6'-dihydroxymethyl-2,2'-bipyridine (1.7 g, 7.9 mmol) and dry CH_2Cl_2 (40 mL) under an argon atmosphere. The solution was cooled to 0 ºC and a solution of $SOCl_2$ (4.8 g, 40.4 mmol) in CH_2Cl_2 (10 mL) was added with a syringe during 15 min. The reaction solution was allowed to warm up to room temperature and stirred at 45 ºC for 3 hrs. The reaction mixture was cooled and then poured into ice-water, made alkaline with 6N NaOH (aq) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated in vacuo, yielding crude title compound as a pale-yellow solid (1.8 g, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 2H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 4.75 (s, 4H).

(3) 6,6'-Bis((di-*tert*-butylphosphino)methyl)-2,2'-bipyridine (**5c**)

To an oven-dried 50 mL Schlenk flask were added 6,6'-dichloromethyl-2,2'-bipyridine (1.0 g, 4.0 mmol), HP^tBu_2 (2.4 g, 16.4 mmol) and degassed dry MeOH (30 mL) under an argon atmosphere. The reaction solution was stirred at 60 ºC for 48 hrs to give a white suspension. After

cooling to room temperature, degassed triethylamine (2.1 g, 20.8 mmol) was added via a syringe in one portion. The reaction mixture was stirred at room temperature overnight and evaporated to dryness. The residue was diluted with degassed CH_2Cl_2 (50 mL) and washed with degassed water (3 × 10 mL). The CH_2Cl_2 solution was dried over Na_2SO_4, filtered and evaporated in vacuo, yielding the title compound as a white solid (1.3 g, 69%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 37.02 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.7 Hz, 2H), 7.67 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 7.7 Hz, 2H), 3.13 (d, J = 3.2 Hz, 4H), 1.18 (d, J = 11.0 Hz, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.33 (d, J = 13.8 Hz), 155.49 (s), 136.91 (s), 123.67 (d, J = 8.4 Hz), 117.87 (s), 32.03 (d, J = 21.7 Hz), 31.91 (d, J = 23.9 Hz), 29.81 (d, J = 13.2 Hz). HRMS (ESI) calcd for $C_{28}H_{47}N_2P_2^+$ ($[M+H]^+$): 473.3209; Found: 473.3213.

(B) Preparation and Analytical Data of Complexes 1



5a R^1 = ^{t}Bu, R^2 = NEt_2
5b R^1 = Ph, R^2 = NEt_2
5c R^1 = ^{t}Bu, R^2 = P^{t}Bu$_2$

1a R^1 = ^{t}Bu, R^2 = NEt_2 (99%)
1b R^1 = Ph, R^2 = NEt_2 (86%)
1c R^1 = ^{t}Bu, R^2 = P^{t}Bu$_2$ (91%)

1. Preparation and Analytical Data of Complex 1a

To an oven-dried 15 mL Schlenk tube was added PNNN ligand **5a** (600 mg, 1.5 mmol), $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (400 mg, 0.65 mmol), and degassed dry CH_2Cl_2 (5 mL) under argon. The mixture was stirred at room temperature for 4 hrs to give a deep blue violet suspension. The solvent was removed under vaccum. The solid thus obtained was washed with ethyl ether (3 × 10 mL), filtered under air and dried under vacuum to give pure complex **1a** as a deep blue violet solid (740 mg, 99%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 63.21 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.45 – 7.33 (m, 2H), 4.45 (s, 2H), 3.62 (d, J = 8.5 Hz, 2H), 3.57, 3.54 (2q, J = 6.8 Hz and 6.7 Hz, 2H), 3.25, 3.22 (2q, J = 6.6 Hz and 6.6 Hz, 2H), 1.44 (d, J = 11.8 Hz, 18H), 1.18 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.25 (d, J = 3.3 Hz), 161.58 (d, J = 2.0 Hz), 161.00 (s), 158.56 (s), 134.17 (s), 131.69 (s), 121.16 (d, J = 1.9 Hz), 120.56 (s), 120.47 (s), 120.30 (s), 67.79 (s), 51.42 (s), 38.67 (d, J = 14.5 Hz), 38.31 (d, J = 7.1 Hz), 30.78 (d, J = 3.9 Hz), 10.71 (s). Anal. Calcd. for $C_{24}H_{38}Cl_2N_3PRu$: C, 50.44; H, 6.70; N, 7.35. Found: C, 50.34; H, 6.92; N, 7.31.

2. Preparation and Analytical Data of Complex 1b

To an oven-dried 15 mL Schlenk tube was added PNNN ligand **5b** (210 mg, 0.48 mmol), $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (122 mg, 0.2 mmol), and degassed dry toluene (5 mL) under argon. The mixture was stirred at 120 °C for 16 hrs to give a deep blue violet suspension. The solvent was removed under vaccum. The solid thus obtained was washed with ethyl ether (3 × 5 mL) and ethanol (3 × 5 mL), filtered under air and dried under vacuum to give pure complex **1b** as a deep blue violet solid (210 mg, 86%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 45.75 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.80 – 7.70 (m, 4H), 7.57 – 7.47 (m, 3H), 7.41 – 7.31 (m, 6H), 4.54 (s, 2H), 4.27 (d, J = 10.2 Hz, 2H), 3.38, 3.35 (2q, J = 6.8 Hz and

6.7 Hz, 2H), 3.20, 3.17 (2q, J = 6.4 Hz and 6.6 Hz, 2H), 1.08 (t, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93 (d, J = 5.1 Hz), 160.76 (d, J = 3.1 Hz), 160.53 (s), 157.62 (s), 137.24 (d, J = 34.5 Hz), 134.74 (s), 133.61 (d, J = 10.4 Hz), 132.12 (s), 129.27 (s), 127.82 (d, J = 8.9 Hz), 121.45 (d, J = 2.9 Hz), 120.82 (s), 120.69 (s), 120.56 (d, J = 9.3 Hz), 66.63 (s), 51.28 (s), 48.59 (d, J = 25.4 Hz), 10.53 (s). HRMS (ESI) calcd for $C_{28}H_{30}ClN_3PRu^+$ ([M-Cl]$^+$): 576.0904; Found: 576.0897.

Single crystal of complex **1b** was grown by slow diffusion of *n*-hexane into its saturated solution in CH_2Cl_2 at room temperature. Data of X-ray diffraction of single crystal of complex **1b** were collected at 293 K on a Rigaku 007 Saturn 70 CCD diffractometer. Positional disorder is observed in the atoms of one of the pyridine ring and the (diethylamino)methyl substituent (except for the N3 atom). These atoms are disordered over two orientations with a refined site-occupancy ratio of 0.629(5):0.371(5). The dihedral angles between the other pyridine ring and the major and minor components of the disordered pyridine ring are 12.2(5) and -15.2(9)º, respectively.

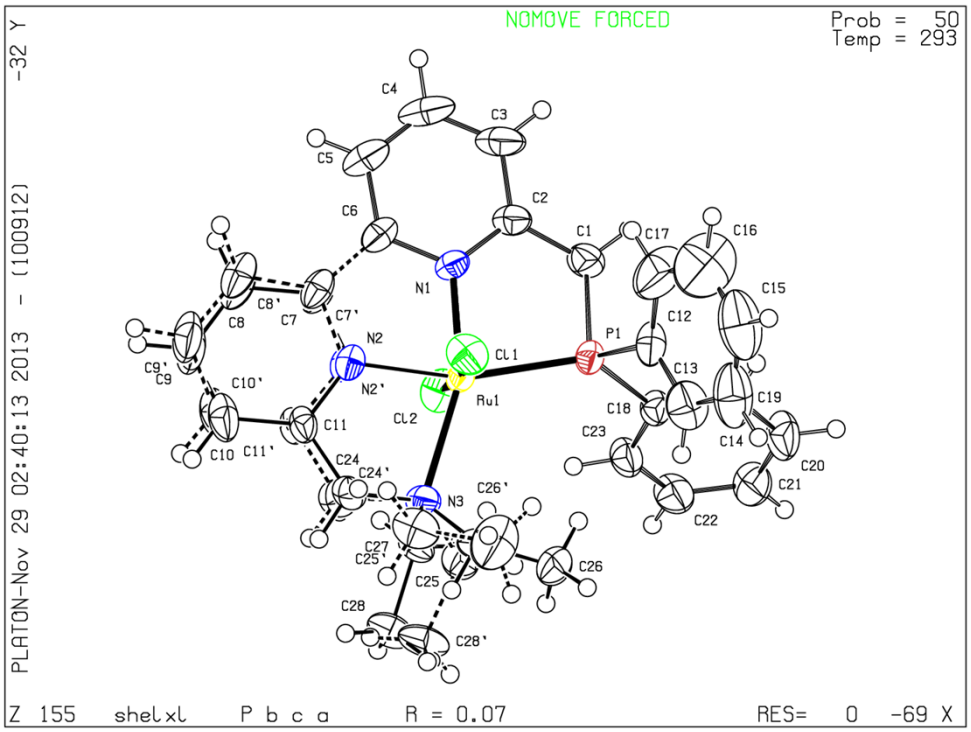


Figure S1 Single-crystal X-ray structure of complex **1b**, showing 50% probability displacement ellipsoids and the atom numbering scheme (H atoms are omitted for clarity). Open bonds indicate the minor disorder component.

Table S1 Crystal data and structure of refinement for complex **1b**

Identification code	shelxl
Empirical formula	$C_{28}H_{30}Cl_2N_3PRu$
Formula weight	611.49
Temperature	293(2) K
Wavelength	0.71075 Å

Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 11.8935(5) Å α = 90 deg. b = 13.1976(6) Å β = 90 deg. c = 33.9681(16) Å γ = 90 deg.
Volume	5331.8(4) $Å^3$
Z, Calculated density	8, 1.524 Mg/m^3
Absorption coefficient	0.871 mm^{-1}
F(000)	2496
Crystal size	0.420 × 0.320 × 0.120 mm
Theta range for data collection	2.090 to 29.499 deg.
Limiting indices	$-16 \le h \le 16$, $-18 \le k \le 17$, $-47 \le l \le 46$
Reflections collected/unique	42309/7351 [R(int) = 0.0397]
Completeness to theta = 25.242	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.840 and 0.691
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7351/49/361
Goodness-of-fit on F^2	1.293
Final R indices [I>2σ(I)]	R1 = 0.0659, wR2 = 0.1255
R indices (all data)	R1 = 0.0705, wR2 = 0.1273
Extinction coefficient	0.0042(2)
Largest diff. peak and hole	0.954 and −1.009 e. $Å^{-3}$

Table S2 Selected bond lengths [Å] and angles [deg] for complex **1b**

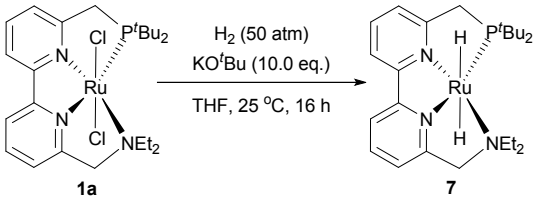
Ru(1)-N(1)	1.992(3)	Ru(1)-N(2)	1.946(5)
Ru(1)-N(2')	2.016(8)	Ru(1)-N(3)	2.262(3)
Ru(1)-P(1)	2.2821(11)	Ru(1)-Cl(1)	2.4196(12)
Ru(1)-Cl(2)	2.4088(12)		
N(1)-Ru(1)-N(2)	79.9(2)	N(2)-Ru(1)-N(3)	79.9(2)
N(1)-Ru(1)-N(3)	159.34(14)	N(1)-Ru(1)-P(1)	84.14(11)
N(2)-Ru(1)-P(1)	163.3(2)	N(3)-Ru(1)-P(1)	116.35(9)
N(1)-Ru(1)-Cl(1)	91.29(11)	N(1)-Ru(1)-Cl(2)	84.12(11)
N(2)-Ru(1)-Cl(1)	83.48(18)	N(2)-Ru(1)-Cl(2)	90.64(18)
N(3)-Ru(1)-Cl(1)	90.64(9)	N(3)-Ru(1)-Cl(2)	91.87(9)

P(1)-Ru(1)-Cl(1)	92.08(4)	P(1)-Ru(1)-Cl(2)	92.56(4)
Cl(1)-Ru(1)-Cl(2)	173.11(5)	N(2')-Ru(1)-N(1)	79.0(4)
N(2')-Ru(1)-N(3)	80.3(4)	N(2')-Ru(1)-P(1)	162.4(4)
N(2')-Ru(1)-Cl(1)	93.4(3)	N(2')-Ru(1)-Cl(2)	80.7(3)

3. Preparation and Analytical Data of Complex 1c

To an oven-dried 15 mL Schlenk tube was added PNNP ligand **5c** (113 mg, 0.24 mmol), $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (61 mg, 0.1 mmol), and degassed dry CH_2Cl_2 (5 mL) under argon. The mixture was stirred at room temperature for 4 hrs to give a deep blue violet suspension. The solvent was removed under vaccum. The solid was washed with ethyl ether (3 × 10 mL), filtered and dried under vacuum to give pure complex **1c** as a deep blue violet solid (117 mg, 91%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 66.25 (s). ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 3.87 (d, J = 8.3 Hz, 4H), 1.45 (d, J = 11.3 Hz, 36H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50 (s), 159.51 (s), 134.04 (s), 122.30 (vt, J = 4.8 Hz), 120.45 (s), 39.25 (dd, J = 11.8, 6.7 Hz), 37.46 (vt, J = 3.8 Hz), 30.70 (s). Anal. Calcd. for $C_{28}H_{46}Cl_2N_2P_2Ru$: C, 52.17; H, 7.19; N, 4.35. Found: C, 52.29; H, 6.91; N, 4.56.

(C) Preliminary Study on the Reaction of 1a with Hydrogen in the Presence of KO^{t}Bu



1a **7**

In a glove box, a hydrogenation vessel was charged with complex **1a** (11.5 mg, 20 μmol) and KO^{t}Bu (23 mg, 0.2 mmol). The vessel was placed into the autoclave and degassed dry THF (5.0 mL) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 50 atm. The reaction mixture was stirred at 25 °C for 16 hrs and then the pressure was released. The reaction mixture was transferred to a Schlenk tube under an argon atmosphere and the solvent was removed under vaccum. The remaining residue was taken back into the glove box, redissolved in degassed C_6D_6 (1.0 mL), passed through a PTFE syringe filter, and transferred into a J-Young NMR tube. Then the sample was submitted to NMR analysis imediately. The preliminary $^{31}P\{^1H\}$ NMR and hydride region ^1H NMR study on the major product is shown in Figure S2 and S3, respectively. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 123.12 (s). ^1H NMR (400 MHz, C_6D_6) δ −11.08 (d, J = 14.4 Hz, 2H). The chemical shift of −11.08 ppm in ^1H NMR for the hydride ligands suggests the coordination of a ligand with a strong *trans* influence (such as a hydride) in the *trans* position. Based on these preliminary results, we tentatively assign the major product to be *trans*-dihydride complex **7**. Attempts to isolate and purify this complex, however, failed due to a lack of sufficient stability. Further studies are needed to fully characterize this complex.

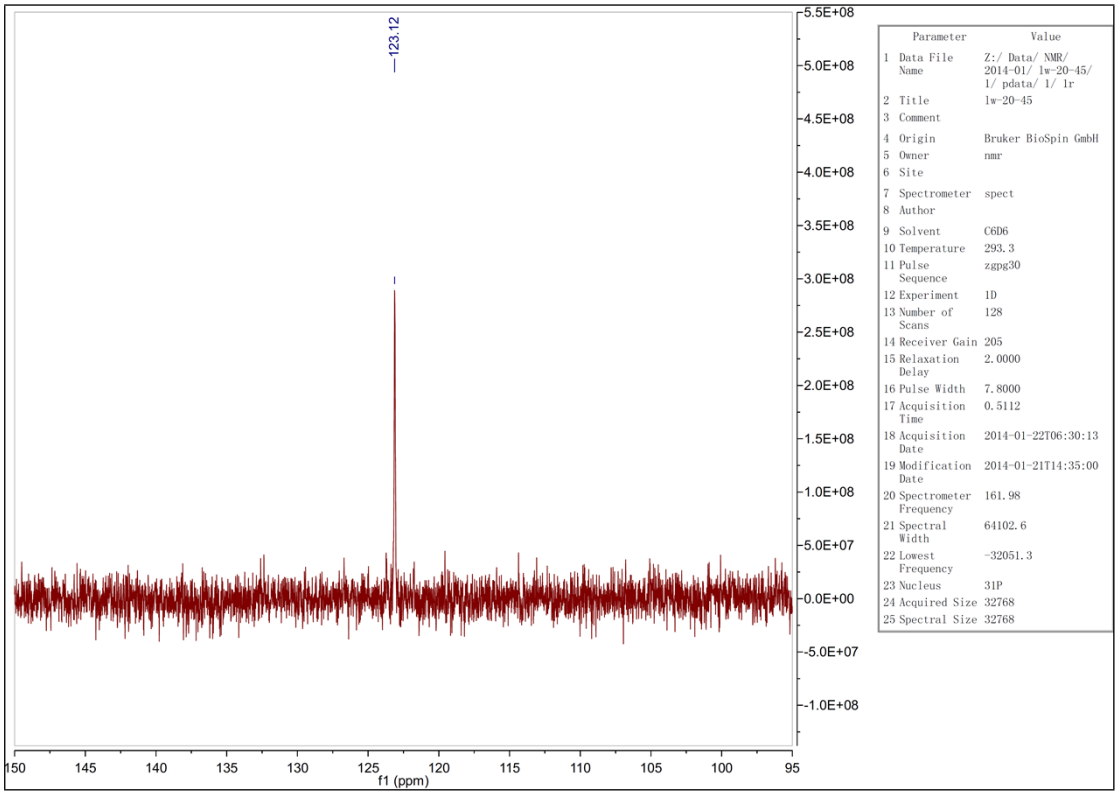


Figure S2 Preliminary $^{31}P\{^{1}H\}$ NMR study of complex **7**.

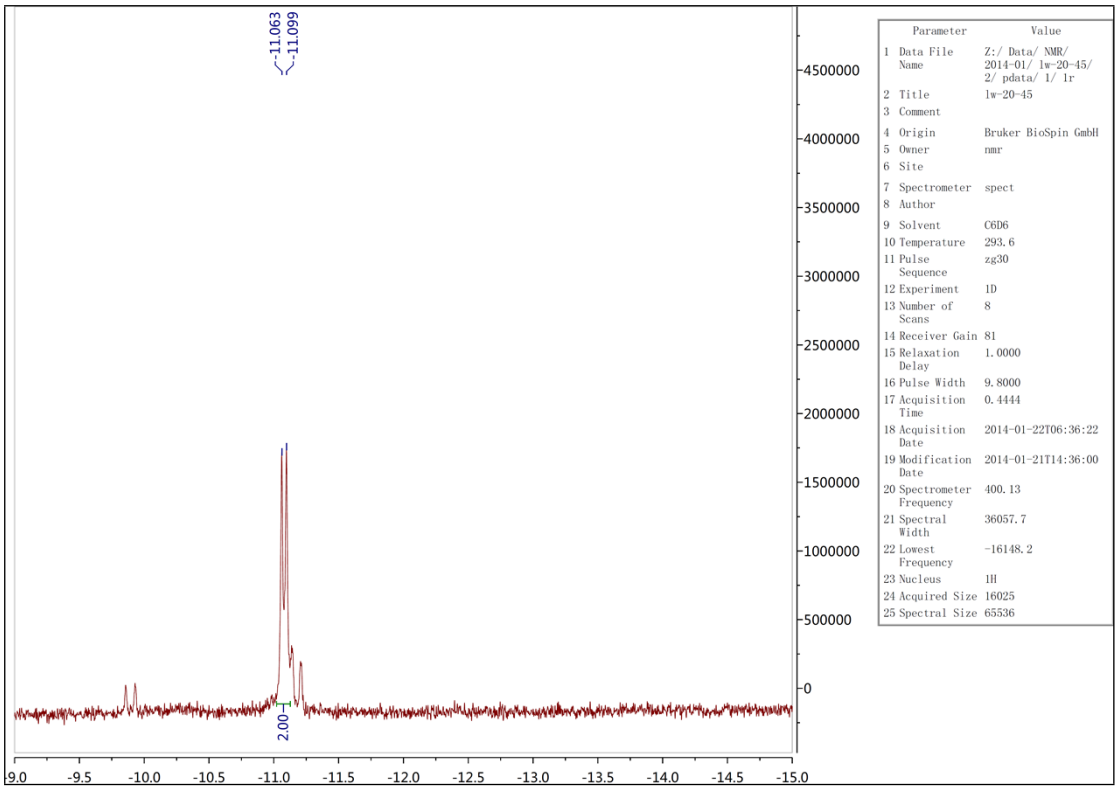


Figure S3 Preliminary hydride region ^{1}H NMR study of complex **7**.

(D) Procedures for Hydrogenation

Hydrogenation of GVL at S/C = 1000. In a glove box, a hydrogenation vessel was charged

with complex **1a** (1.7 mg, 3.0 μmol) and NaOMe (17 mg, 0.3 mmol). The vessel was placed into the autoclave and a degassed solution of GVL (300.3 mg, 3.0 mmol) in dry ^{i}PrOH (5.0 mL) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 50 atm. The reaction mixture was stirred at 25 ^{o}C until no pressure drop was observed (4 hrs) and then the pressure was released. After adding 1,5-pentandiol (1,5-PDO) as an internal standard, an aliquot portion of the mixture was taken and filtered through a short silica column and submitted to analysis of yield of 1,4-PDO by GC (Agilent DB-35, 30 m × 0.32 mm × 0.25 μm) using a flame ionization detector (FID) operating at 250 ^{o}C. Injector temperature was set at 230 ^{o}C. The carrier gas was nitrogen with a flow rate of 1.0 mL/min. The following temperature program was used in the analysis: 50 ^{o}C – 10 ^{o}C/min – 250 ^{o}C (10 min). Using these conditions, the retention times for 1,4-PDO (7.918 min), GVL (8.295 min), and 1,5-PDO (9.035 min) were observed. The GC yield 1,4-PDO is 99%.

Hydrogenation of GVL at S/C = 100,000. A solution of complex **1a** (3.5×10^{-4} mmol/mL) was made by dissolving complex **1a** (1.0 mg, 0.00175 mmol) in degassed dry ^{i}PrOH (5.0 mL). In a glove box, a hydrogenation vessel was charged with NaOMe (195 mg, 3.6 mmol) and then placed into the autoclave. A degassed solution of GVL (3.61 g, 36 mmol) in dry ^{i}PrOH (3.0 mL) and the freshly prepared complex **1a** solution (1.0 mL, 3.5×10^{-4} mmol) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 100 atm. The reaction mixture was stirred at 25 ^{o}C until no pressure drop was observed (48 hrs) and then the pressure was released. An aliquot portion of the mixture was taken and filtered through a short silica column and submitted to GC analysis. The GC yield is 91%. Silica gel was added to the rest of the mixture, the solvent was removed in vacuo and the residue was purified by flash column chromatograph (silica gel, eluents: petroleum ether/ethyl acetate (1:1), then ethyl acetate) to afford 1,4-PDO (3.40 g, 90%) as a colorless oil.

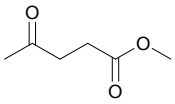
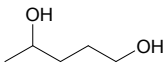
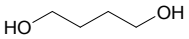
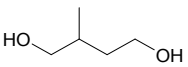
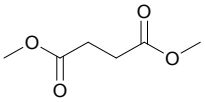
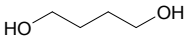
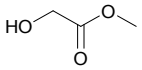
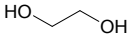
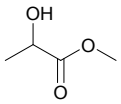
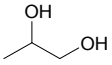
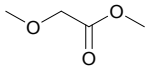
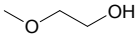
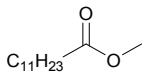
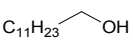
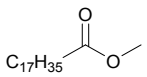
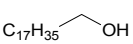
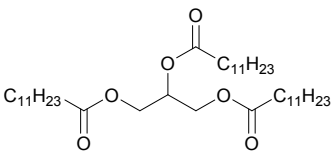
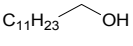
Hydrogenation of Methyl Benzoate at S/C = 100,000. In a glove box, a hydrogenation vessel was charged with complex **1a** (0.5 mg, 1.0 μmol) and NaOMe (540 mg, 10 mmol). The vessel was placed into the autoclave and a degassed solution of methyl benzoate (13.7 g, 100 mmol) in dry ^{i}PrOH (20 mL) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 100 atm. The reaction mixture was stirred at 25 ^{o}C until no pressure drop was observed (64 hrs) and then the pressure was released. An aliquot portion of the mixture was taken and filtered through a short silica column and submitted to GC analysis. The GC yield is 91%. Silica gel was added to the rest of the mixture, the solvent was removed in vacuo and the residue was purified by flash column chromatograph (silica gel, eluents: petroleum ether/ethyl acetate (3:1)) to afford benzyl alcohol (9.4 g, 87%) as a colorless oil.

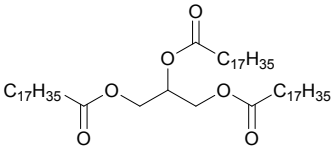
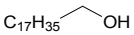
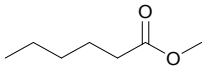
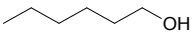
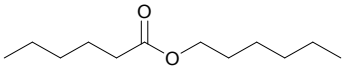
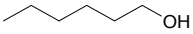
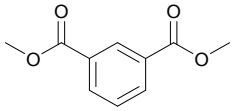
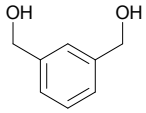
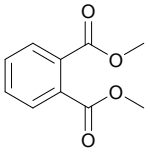
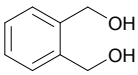
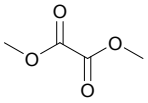
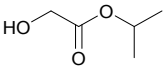
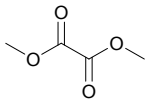
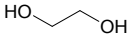
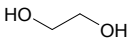
Hydrogenation of Ethyl Acetate at S/C = 100,000. In a glove box, a hydrogenation vessel was charged with complex **1a** (1.1 mg, 2.0 μmol) and NaOEt (1.36 g, 20 mmol). The vessel was placed into the autoclave and degassed ethyl acetate (17.6 g, 200 mmol) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 50 atm. The reaction mixture was

stirred at 40 °C until no pressure drop was observed (48 hrs) and then the pressure was released. After adding toluene as an internal standard, an aliquot portion of the mixture was taken and filtered through a short silica column and submitted to GC analysis. The GC yield is 90%.

General Procedure for the Hydrogenation of Other Substrates at S/C = 1000. In a glove box, a hydrogenation vessel was charged with complex **1a** (1.7 mg, 3.0 μmol) and NaOMe (17 mg, 0.3 mmol). The vessel was placed into the autoclave and a degassed solution of the substrate (3 mmol) in dry ^{i}PrOH (3.0 mL) was added through the injection port. The autoclave was tightened and purged three times with argon and three times with hydrogen before it was finally charged with hydrogen to 50 atm. The reaction mixture was stirred at 25 °C or 100 °C until no pressure drop was observed and then the pressure was released. An aliquot portion of the mixture was taken and filtered through a short silica column and submitted to GC analysis. For nonvolatile product, isolated yield was obtained by flash column chromatography.

Table S3 Hydrogenation of other substrates with complex **1a**[a]

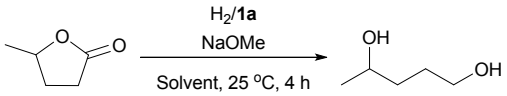
Entry	Substrate	Product	Time (h)	Yield (%)[b]
1[c]			16	95
2			6	99(96)
3			6	99(96)
4			6	99(97)
5[d]			2	99(97)
6[d]			2	99(97)
7			4	99
8			16	99(95)
9[d]			2	99(97)
10[e]			2	99(97)

11[e]			2	99(98)
12[f]			24	97
13[f]			24	96
14[g]			16	99(99)
15[d]			2	99(99)
16			16	99(96)
17[d]			2	99(97)
18[g]			16	99(95) 99[h]

[a] Reaction conditions: 3.0 mmol substrate, 0.1 mol% **1a**, 3.0 mL ^{i}PrOH, 10 mol% NaOMe, P(H_2) = 50 atm, 25 °C. [b] GC yield, isolated yield in the parentheses. The balance of material present was unreacted starting material. [c] The balance of material present was GVL. [d] 100 °C. [e] 100 °C, 0.3 mol% **1a**. [f] S/C = 10,000, 12 mmol substrate, 3.0 mL ^{i}PrOH, 10 mol% NaOMe, P(H_2) = 50 atm, 25 °C. [g] THF as solvent. [h] GC yield of methanol.

(E) Complementary Reaction Optimization Data

Table S4 Effect of solvent on the hydrogenation of GVL into 1,4-PDO with complex **1a**[a]

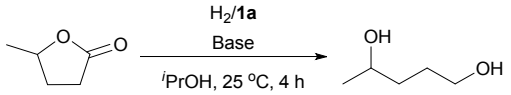


Entry	Solvent	Yield (%)[b]
1	THF	98
2	Et_2O	94
3	2-MeTHF	98
4	CH_2Cl_2	0
5	DMF	0
6	DMSO	0
7	Toluene	78
8	MeOH	0

9	EtOH	20
10	^{i}PrOH	99
11	Neat	95

[a] Reaction conditions: 3.0 mmol GVL, 0.1 mol% **1a**, 5.0 mL solvent, 10 mol% NaOMe, P(H_2) = 50 atm, 25 °C, 4 h. [b] GC yield. The balance of material present was unreacted GVL.

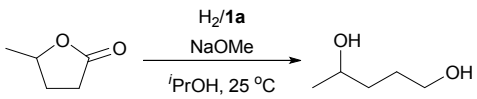
Table S5 Effect of base on the hydrogenation of GVL into 1,4-PDO with complex **1a**[a]



Entry	Base	Yield (%)[b]
1	NaOMe	99
2[c]	NaOMe	62
3[c,d]	NaOMe	95
4[e]	NaOMe	0
5[e,f]	NaOMe	0
6	NaOEt	96
7	NaO^{i}Pr	79
8[f]	NaO^{i}Pr	99
9	NaO^{t}Bu	72
10[f]	NaO^{t}Bu	99
11	KO^{t}Bu	98
12	KOH	0
13	NaOH	0
14	Cs_2CO_3	0
15	K_2CO_3	0
16	DBU	0
17	Et_3N	0

[a] Reaction conditions: 3.0 mmol GVL, 0.1 mol% **1a**, 5.0 mL ^{i}PrOH, 10 mol% Base, P(H_2) = 50 atm, 25 °C, 4 h. [b] GC yield. The balance of material present was unreacted GVL. [c] 5 mol% NaOMe. [d] 10 h. [e] 1 mol% NaOMe. [f] 16 h.

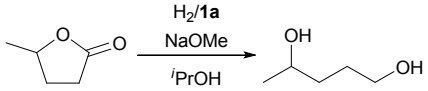
Table S6 Effect of H_2 pressure on the hydrogenation of GVL into 1,4-PDO with complex **1a**[a]



Entry	P(H_2) (atm)	Time (h)	Yield (%)[b]
1	50	4	99
2	30	4	92
3	30	6	98
4	10	4	51
5	10	16	95

[a] Reaction conditions: 3.0 mmol GVL, 0.1 mol% **1a**, 5.0 mL ^{i}PrOH, 10 mol% NaOMe, 25 °C. [b] GC yield. The balance of material present was unreacted GVL.

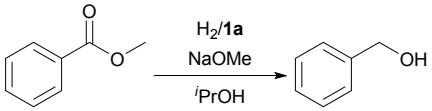
Table S7 Hydrogenation of GVL at low catalyst loading with complex **1a**[a]



Entry	$P(H_2)$ (atm)	Temp. (°C)	Time (h)	Yield (%)[b]
1[c]	50	25	10	98
2	50	25	64	50
3	50	40	48	76
4	100	25	48	91(90)
5[d]	100	25	48	67
6[e]	100	25	48	30

[a] Reaction conditions: 36 mmol GVL, 0.001 mol% **1a**, 4.0 mL ^{i}PrOH, 10 mol% NaOMe. [b] GC yield, isolated yield in the parentheses. The balance of material present was unreacted GVL. [c] 12 mmol GVL, 0.01 mol% **1a**, 1.0 mL ^{i}PrOH, 10 mol% NaOMe. [d] 5 mol% NaOMe. [e] 1 mol% NaOMe.

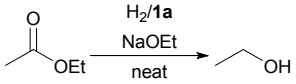
Table S8 Hydrogenation of methyl benzoate at low catalyst loading with complex **1a**[a]



Entry	$P(H_2)$ (atm)	Temp. (°C)	Time (h)	Yield (%)[b]
1[c]	50	25	16	99(97)
2	50	25	64	47
3	50	40	64	60
4	100	25	48	58
5	100	25	64	91(87)

[a] Reaction conditions: 100 mmol methyl benzoate, 0.001 mol% **1a**, 20 mL ^{i}PrOH, 10 mol% NaOMe. [b] GC yield, isolated yield in the parentheses. The balance of material present was unreacted methyl benzoate. [c] 12 mmol methyl benzoate, 0.01 mol% **1a**, 3.0 mL ^{i}PrOH, 10 mol% NaOMe.

Table S9 Hydrogenation of ethyl acetate at low catalyst loading with complex **1a**[a]

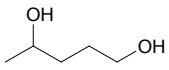


Entry	$P(H_2)$ (atm)	Temp. (°C)	Time (h)	Yield (%)[b]
1	50	25	64	79
2	50	40	21	55
3	50	40	48	90
4	100	25	48	88

[a] Reaction conditions: 200 mmol ethyl acetate, 0.001 mol% **1a**, 10 mol% NaOEt. [b] GC yield. The balance of material present was unreacted ethyl acetate.

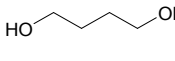
(F) Analytical Data of the Hydrogenation Products

Pentane-1,4-diol[5]



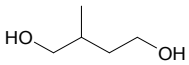
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 – 3.81 (m, 1H), 3.76 – 3.62 (m, 2H), 2.06 (br s, 2H), 1.78 – 1.45 (m, 4H), 1.22 (d, *J* = 6.2 Hz, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 89(5), 71(100), 58(16), 45(82), 31(16).

Butane-1,4-diol[6]



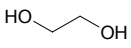
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 – 3.58 (m, 4H), 2.57 (br s, 2H), 1.93 – 1.59 (m, 4H). GC-MS (EI, 70 eV): *m/z* (%) = 71(42), 57(31), 42(100), 31(71).

2-Methylbutane-1,4-diol[7]



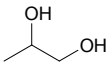
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 – 3.35 (m, 4H), 2.86 (br s, 2H), 1.94 – 1.73 (m, 1H), 1.75 – 1.49 (m, 2H), 0.93 (d, *J* = 6.9 Hz, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 86(3), 71(30), 58(34), 56(100), 55(43), 43(30), 41(46), 31(36).

Ethane-1,2-diol[8]



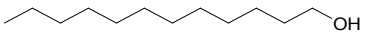
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 – 3.53 (m, 4H), 2.23 – 1.85 (m, 2H). GC-MS (EI, 70 eV): *m/z* (%) = 62([M^+], 7), 43(18), 31(100).

Propane-1,2-diol[9]



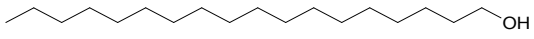
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 – 3.85 (m, 1H), 3.70 – 3.59 (m, 1H), 3.47 – 3.33 (m, 1H), 2.00 (d, *J* = 3.9 Hz, 1H), 1.83 (t, *J* = 5.8 Hz, 1H), 1.17 (d, *J* = 6.4 Hz, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 76([M^+], 1), 61(8), 45(100), 43(20), 31(12), 15(2).

Dodecan-1-ol[10]



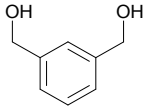
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 1.61 – 1.50 (m, 2H), 1.40 – 1.18 (m, 19H), 0.87 (t, *J* = 6.8 Hz, 3H). GC-MS (EI, 70 eV): *m/z* (%) = 168(3), 140(18), 125(13), 111(42), 97(74), 83(94), 69(98), 55(100), 43(64), 31(38).

Octadecan-1-ol[10]



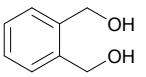
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.6 Hz, 2H), 1.76 (br s, 1H), 1.63 – 1.50 (m, 2H), 1.39 – 1.16 (m, 30H), 0.87 (t, *J* = 6.8 Hz, 3H) GC-MS (EI, 70 eV): *m/z* (%) = 252(3), 224(6), 196(3), 182(3), 168(4), 153(6), 139(11), 125(29), 111(54), 97(92), 83(100), 69(89), 55(93), 43(75), 31(22).

1,3-Phenylenedimethanol[11]



White solid. ^{1}H NMR (400 MHz, DMSO) δ 7.33 – 7.15 (m, 4H), 5.21 (t, *J* = 5.7 Hz, 2H), 4.51 (d, *J* = 5.7 Hz, 4H). GC-MS (EI, 70 eV): *m/z* (%) = 138([M^+], 67), 120(22), 107(63), 91(85), 79(100), 77(64), 65(13), 51(15), 39(9), 31(7).

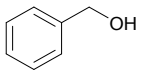
1,2-Phenylenedimethanol[12]



White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 4.75 (s, 4H), 2.79 (s, 2H). GC-MS (EI, 70 eV): *m/z* (%) = 120(100), 91(83), 77(29), 65(16), 51(9),

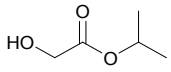
39(7), 29(3).

Phenylmethanol[13]



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 4.71 (d, *J* = 6.0 Hz, 2H), 1.62 (t, *J* = 6.0 Hz, 1H). GC-MS (EI, 70 eV): *m/z* (%) = 108([M^+], 79), 91(16), 79(100), 77(62), 65(7), 51(23), 39(9), 29(3).

Isopropyl glycolate[14]



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (hept, *J* = 6.3 Hz, 1H), 4.10 (d, *J* = 5.2 Hz, 2H), 2.50 (t, *J* = 5.3 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 6H). GC-MS (EI, 70 eV): *m/z* (%) = 75(20), 59(9), 45(64), 43(100), 41(44), 39(11), 31(21), 27(14).

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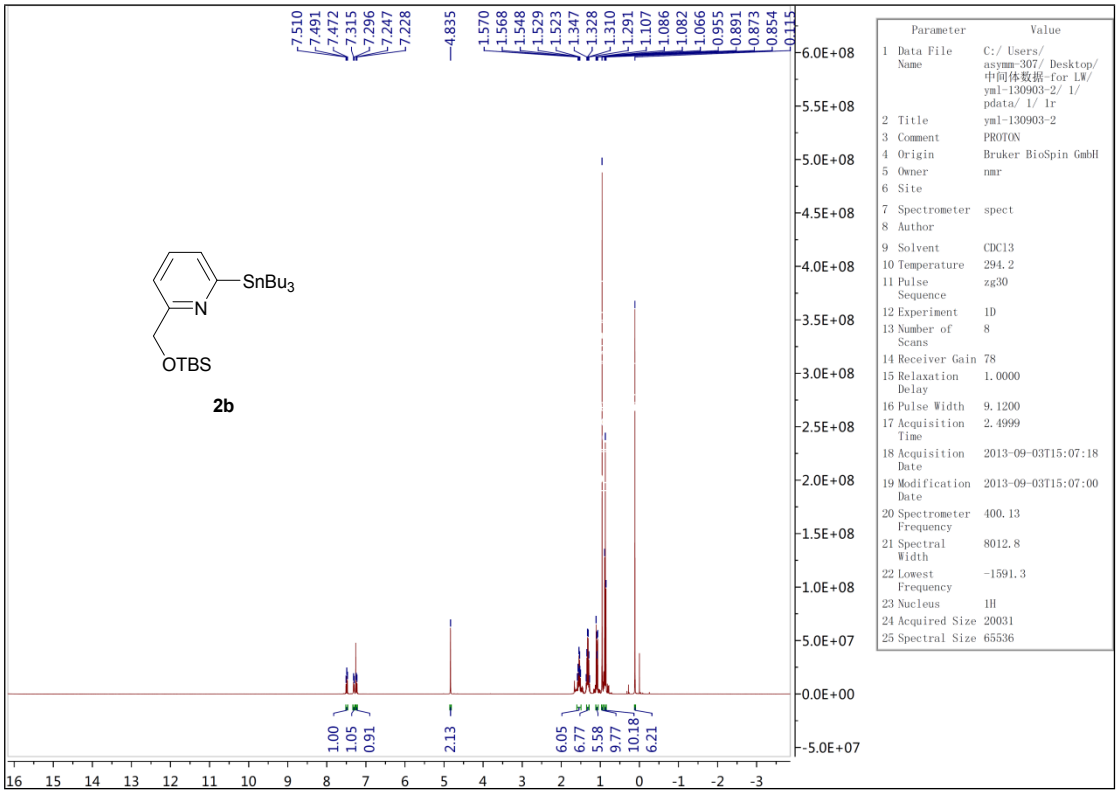
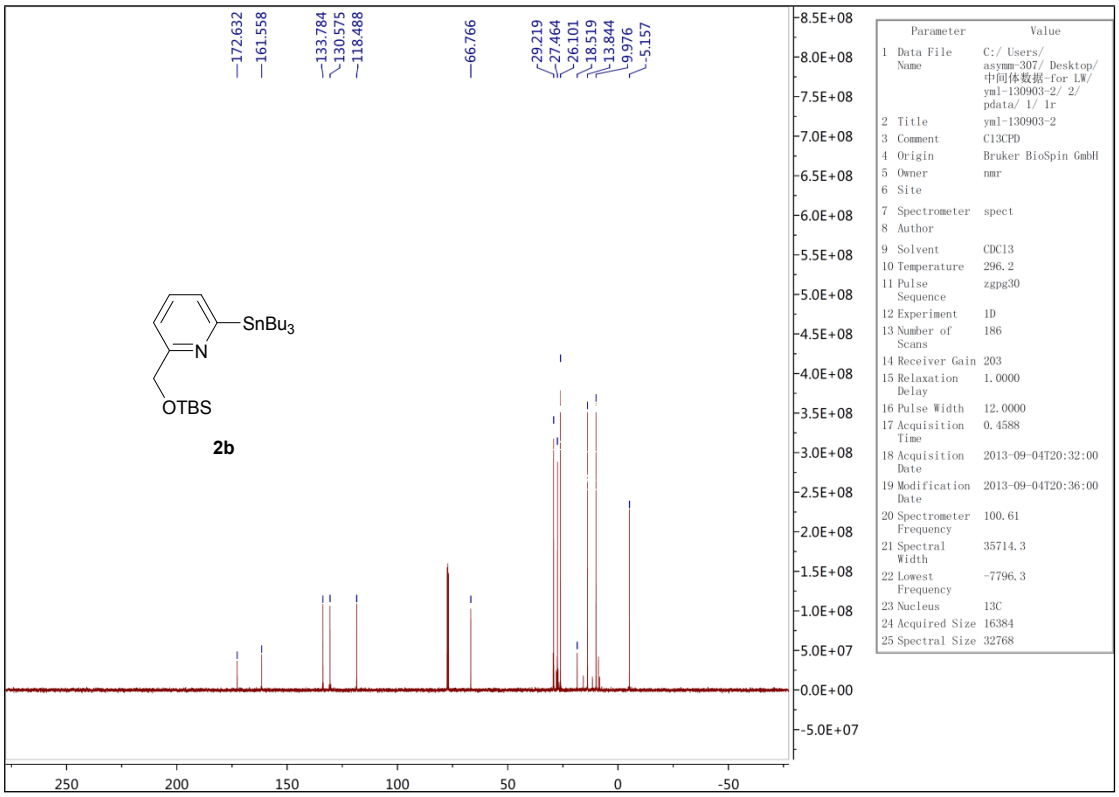
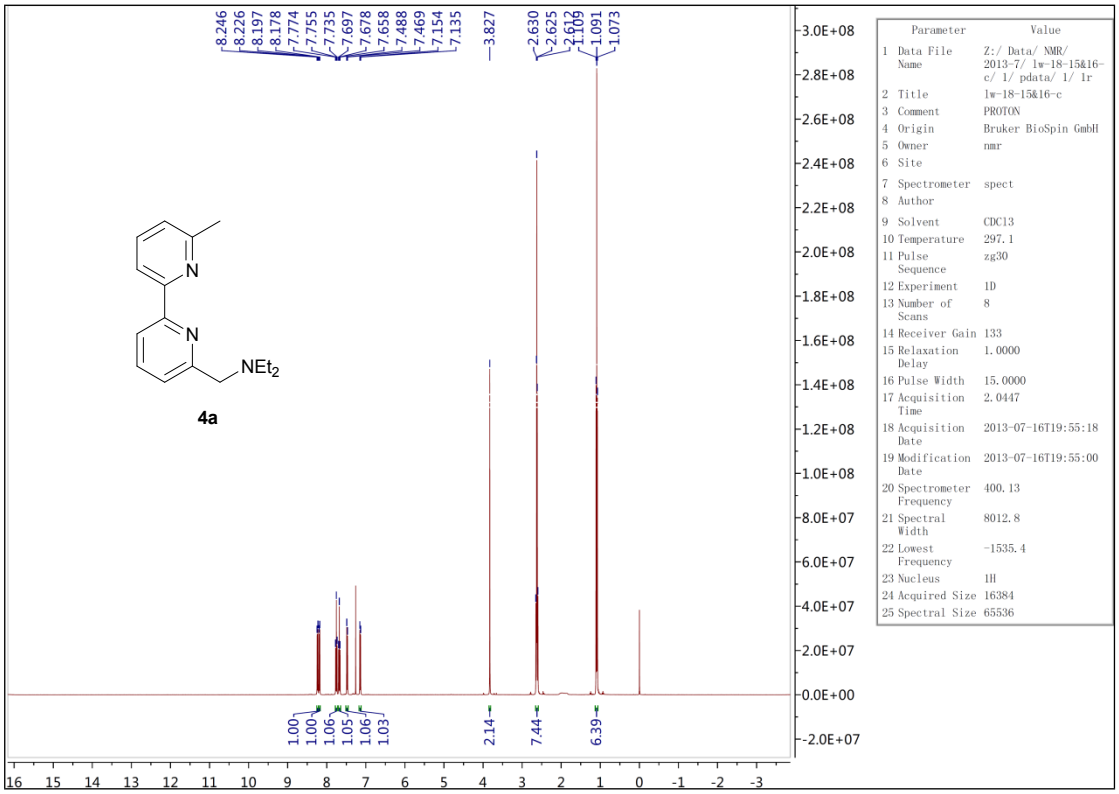
(G) NMR Spectra of New Compounds







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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.1
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	133
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
18	Acquisition Date	2013-07-16T19:55:18
19	Modification Date	2013-07-16T19:55:00
20	Spectrometer Frequency	400.13
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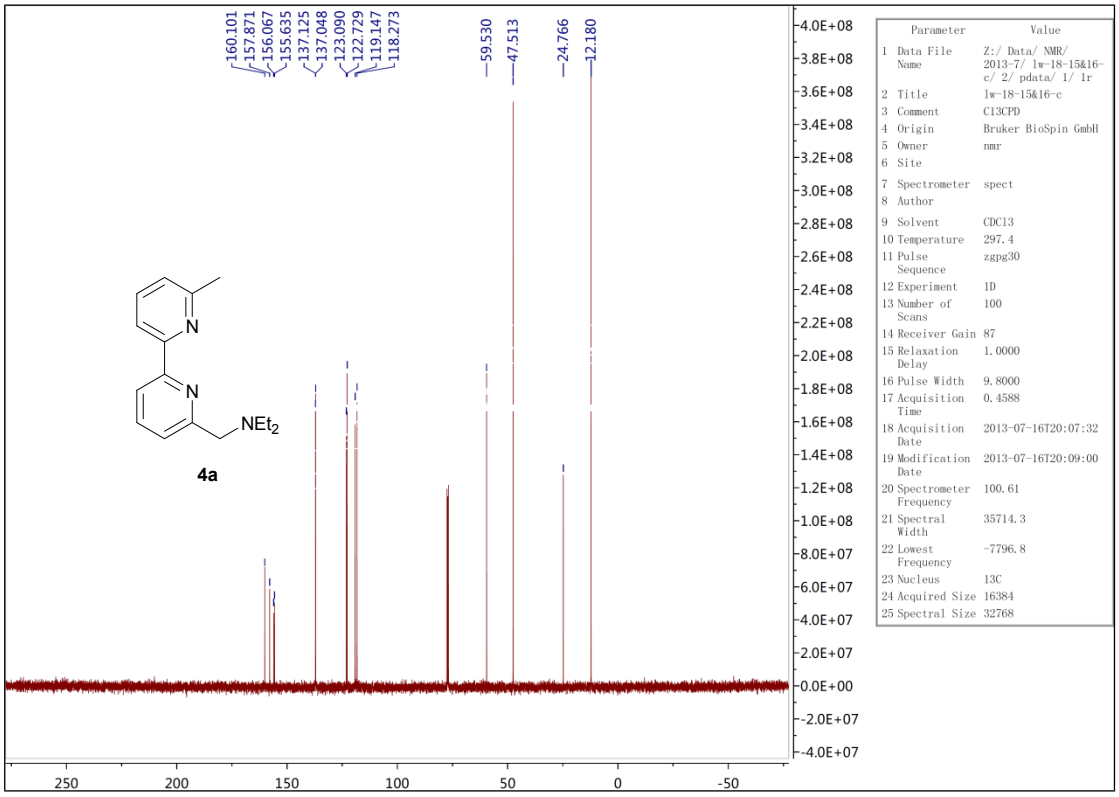
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	65536



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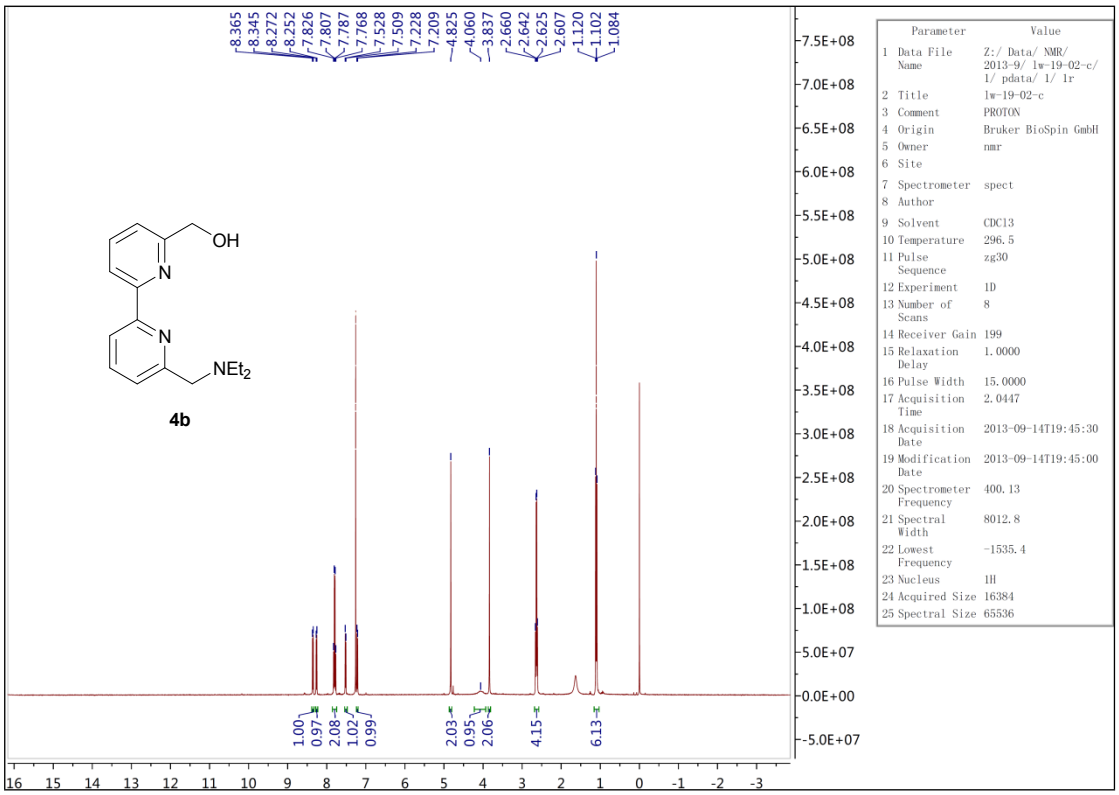
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.4
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	100
14	Receiver Gain	87
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2013-07-16T20:07:32
19	Modification Date	2013-07-16T20:09:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768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8.272
8.252
8.826
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7.787
7.768
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7.509
7.228
7.209
4.825
4.060
3.837
2.660
2.642
2.625
2.607
1.120
1.102
1.084
OH
N
N
NEt2
4b
1.00
0.97
2.08
1.02
0.99
2.03
0.95
2.06
4.15
6.13
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5 Owner nmr
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 296.5
11 Pulse Sequence zg30
12 Experiment 1D
13 Number of Scans 8
14 Receiver Gain 199
15 Relaxation Delay 1.0000
16 Pulse Width 15.0000
17 Acquisition Time 2.0447
18 Acquisition Date 2013-09-14T19:45:30
19 Modification Date 2013-09-14T19:45:00
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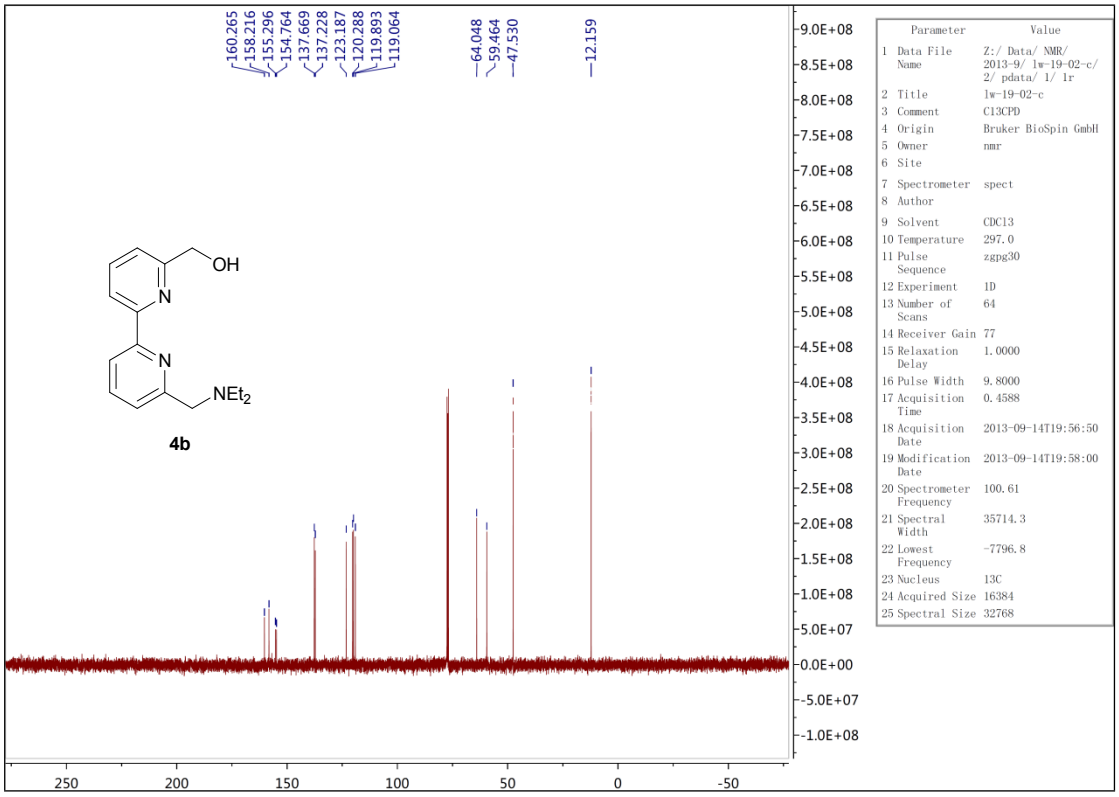
22 Lowest Frequency -1535.4
23 Nucleus 1H
24 Acquired Size 16384
25 Spectral Size 65536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47.530
12.159
OH
N
N
NEt2
4b
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9 Solvent CDCl3
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12 Experiment 1D
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14 Receiver Gain 77
15 Relaxation Delay 1.0000
16 Pulse Width 9.8000
17 Acquisition Time 0.4588
18 Acquisition Date 2013-09-14T19:56:50
19 Modification Date 2013-09-14T19:58:00
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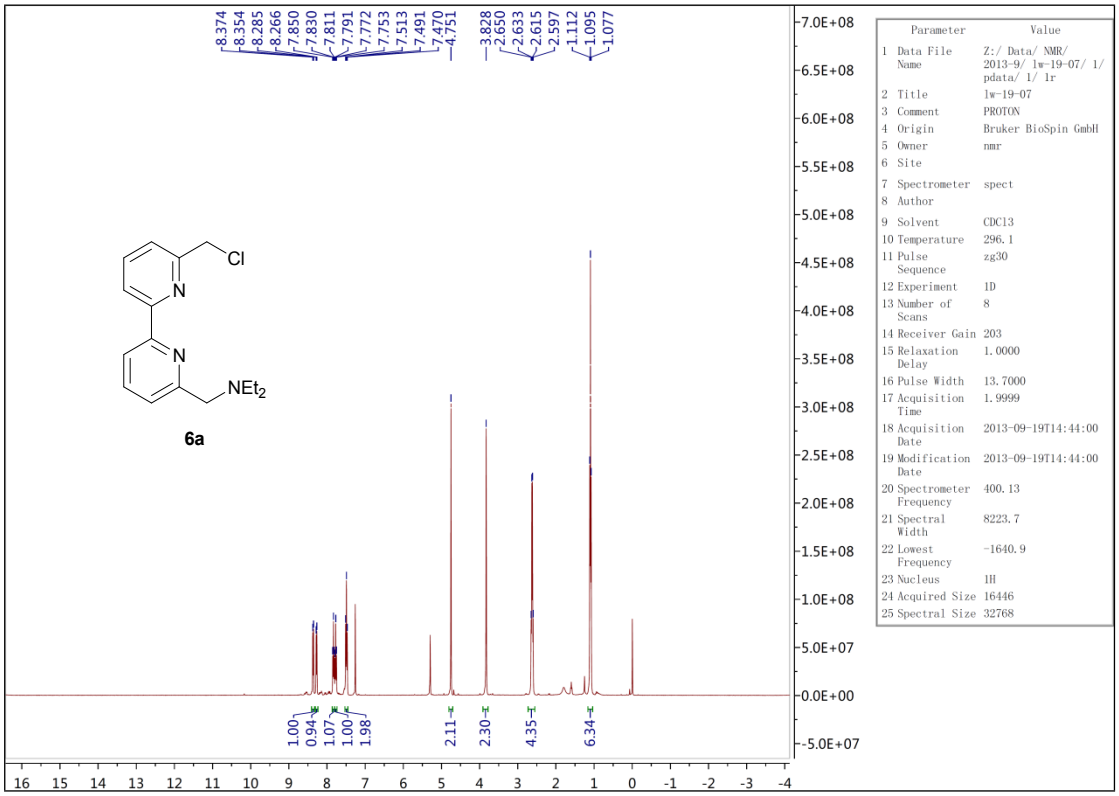
21 Spectral Width 35714.3
22 Lowest Frequency -7796.8
23 Nucleus 13C
24 Acquired Size 16384
25 Spectral Size 32768



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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.1
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12	Experiment	1D
13	Number of Scans	8
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16	Pulse Width	13.7000
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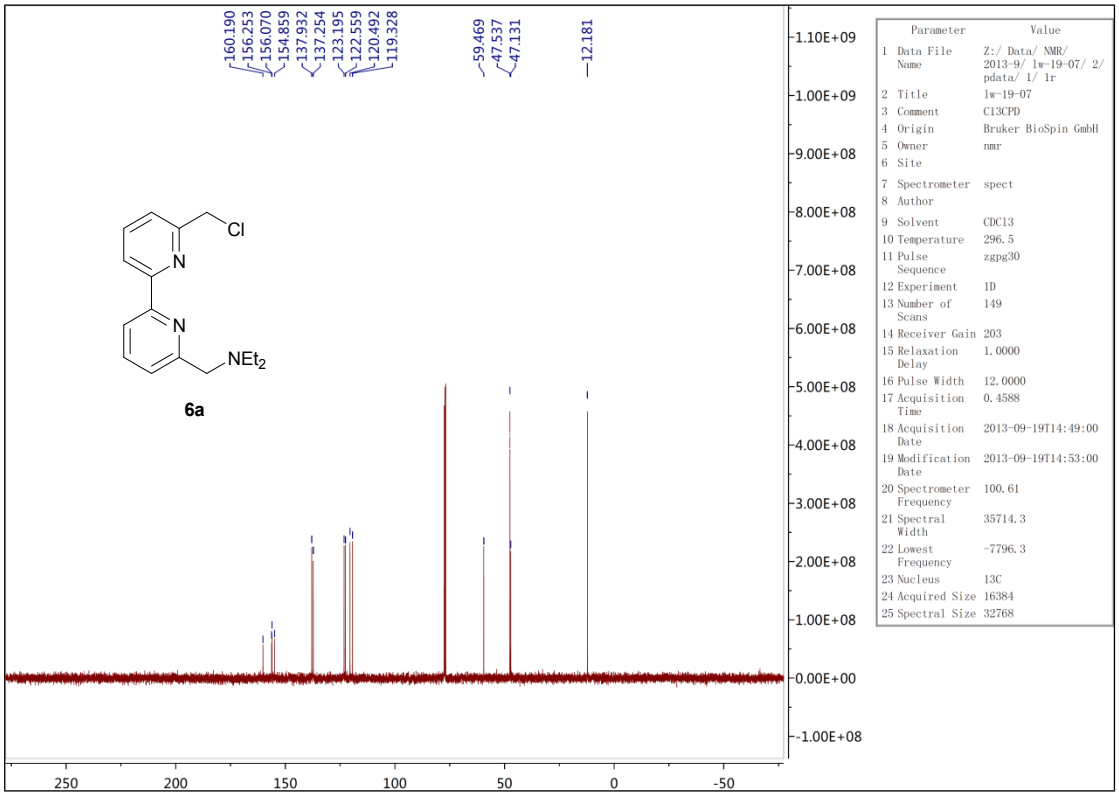
22	Lowest Frequency	-1640.9
23	Nucleus	1H
24	Acquired Size	16446
25	Spectral Size	32768



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7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
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14	Receiver Gain	203
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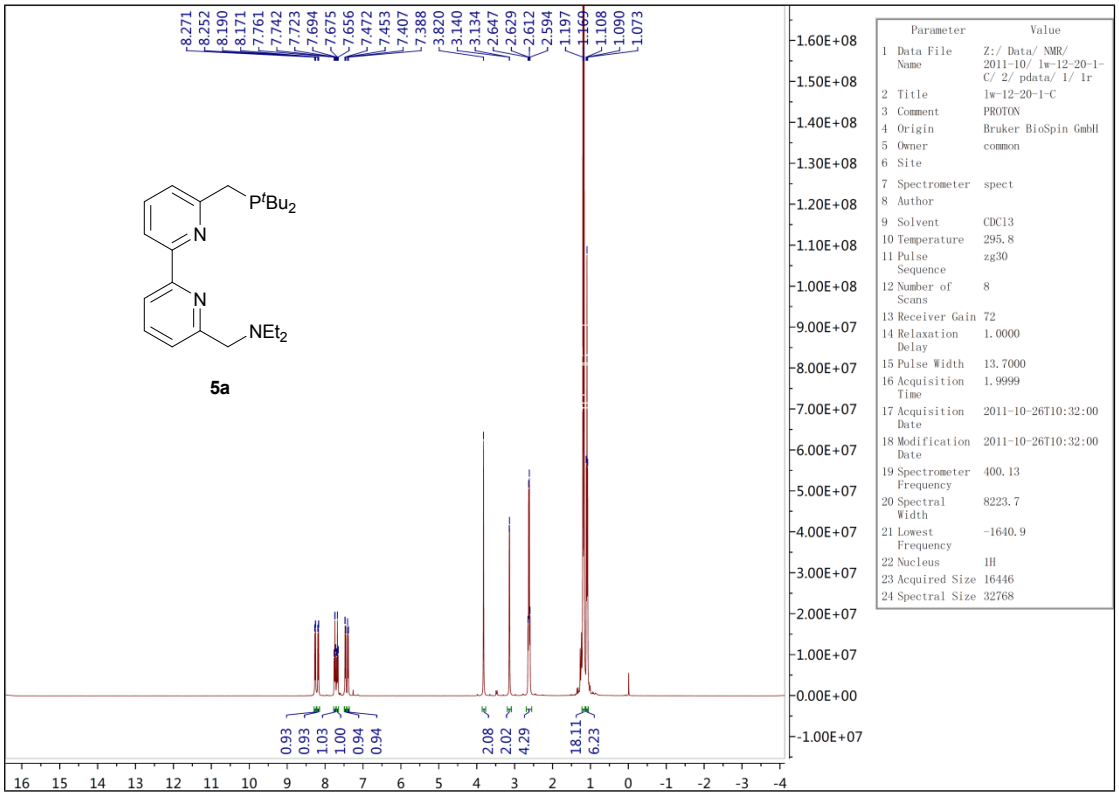
19	Modification Date	2013-09-19T14:53:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.3
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



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5	Owner	common
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.8
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	72
14	Relaxation Delay	1.0000
15	Pulse Width	13.7000
16	Acquisition Time	1.9999
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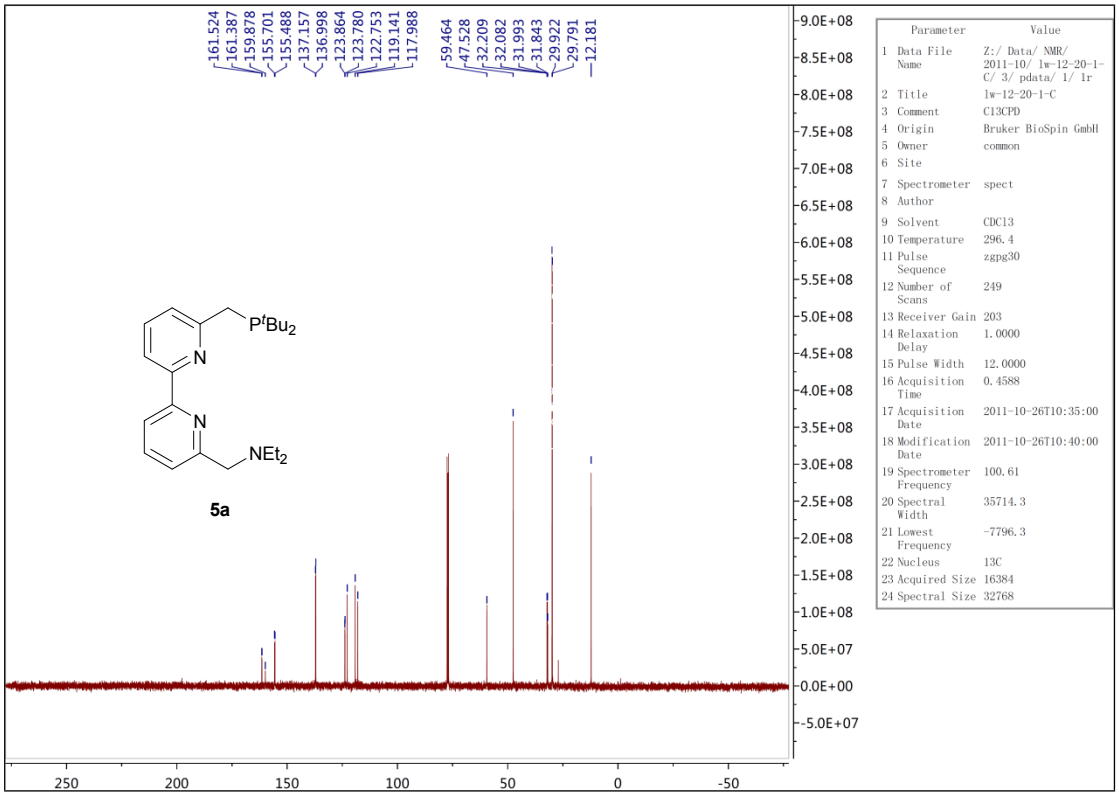
19	Spectrometer Frequency	400.13
20	Spectral Width	8223.7
21	Lowest Frequency	-1640.9
22	Nucleus	1H
23	Acquired Size	16446
24	Spectral Size	32768



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8	Author	
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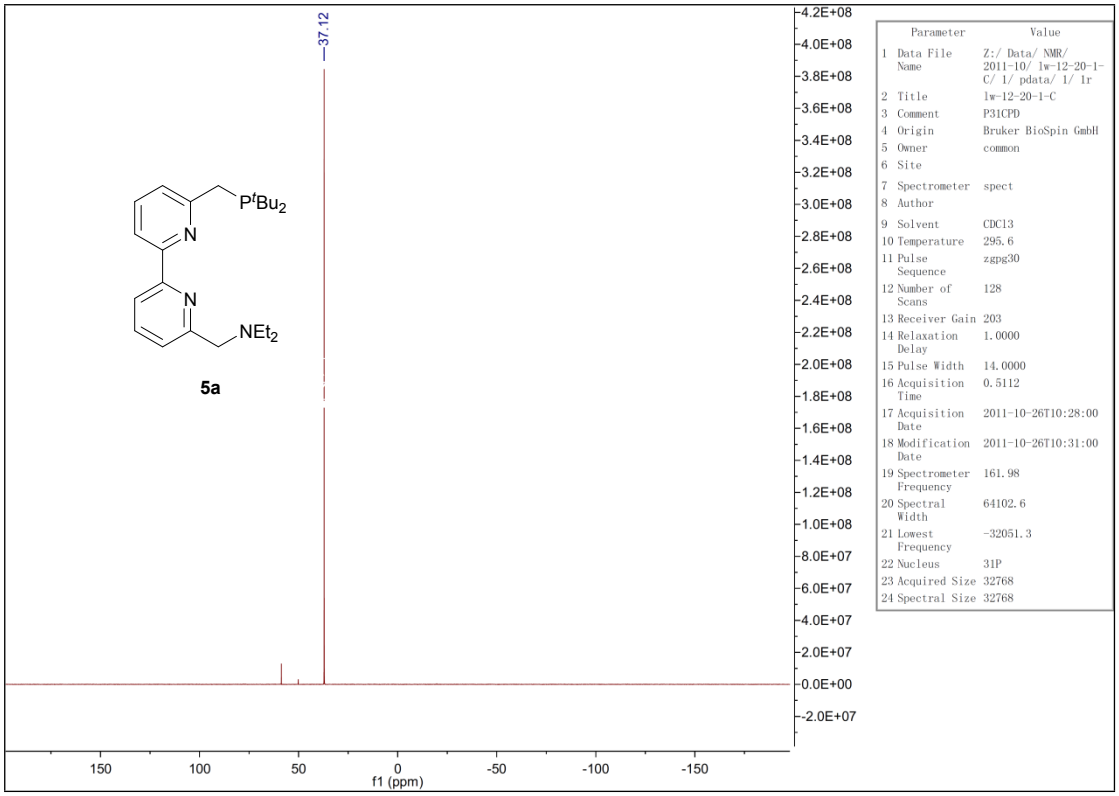
21	Lowest Frequency	-7796.3
22	Nucleus	13C
23	Acquired Size	16384
24	Spectral Size	32768



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8	Author	
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15	Pulse Width	14.0000
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17	Acquisition Date	2011-10-26T10:28:00
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19	Spectrometer Frequency	161.98
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22	Nucleus	31P
23	Acquired Size	32768
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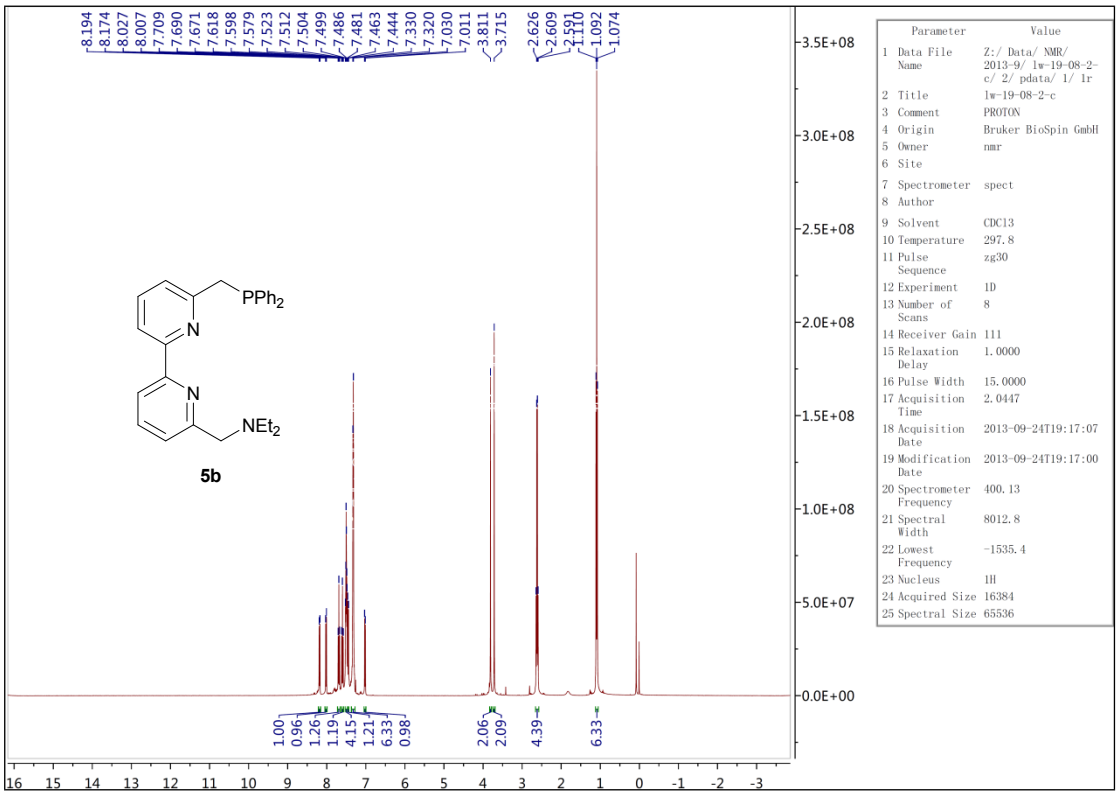

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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.8
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	111
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
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23	Nucleus	1H
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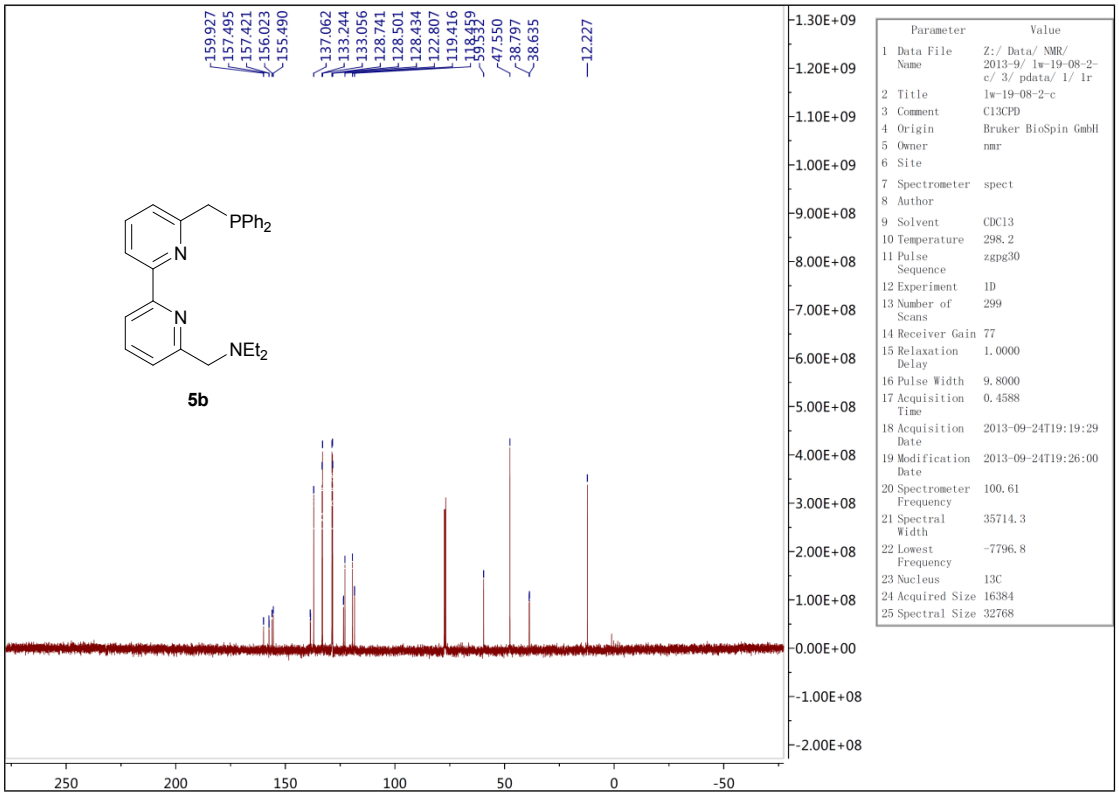

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5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.2
11	Pulse Sequence	zgpg30
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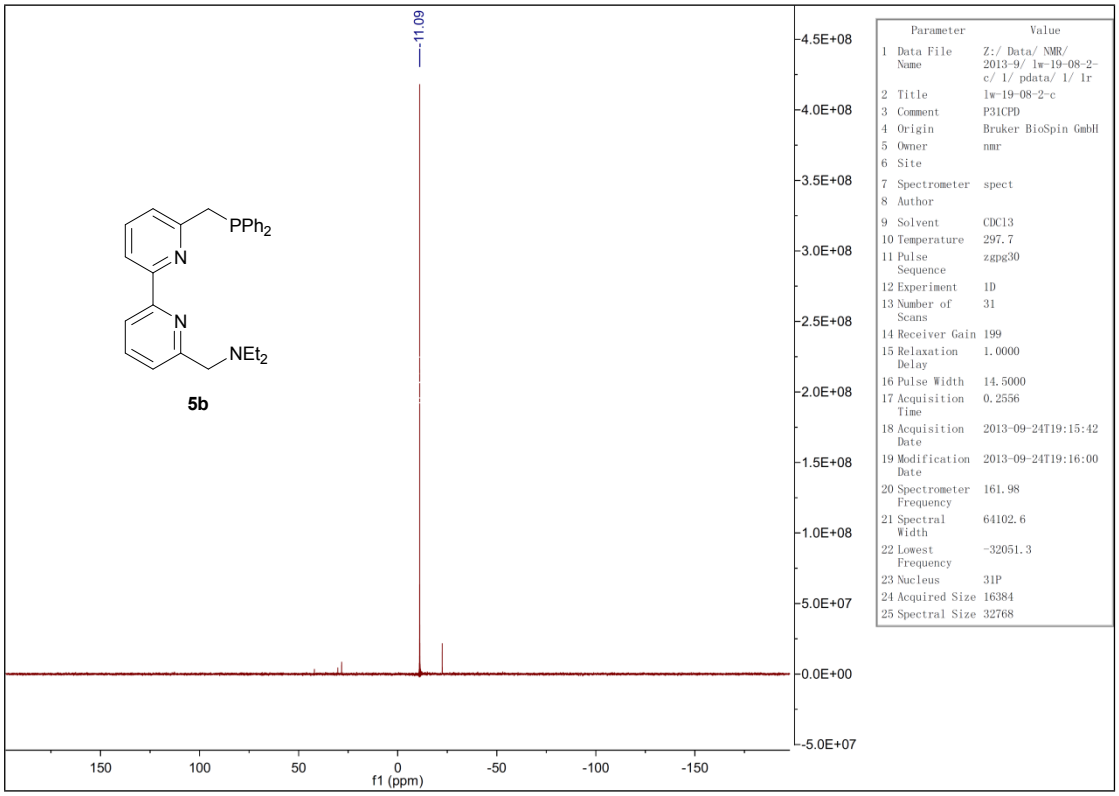

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6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.7
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12	Experiment	1D
13	Number of Scans	31
14	Receiver Gain	199
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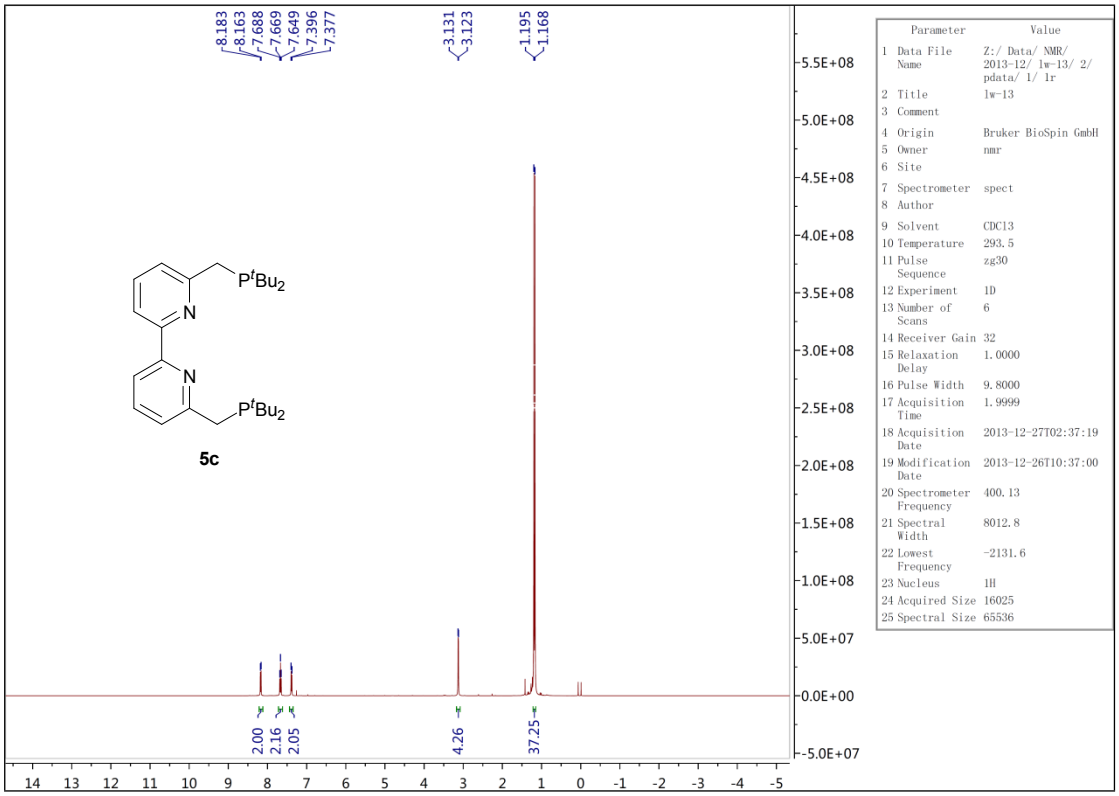
22	Lowest Frequency	-32051.3
23	Nucleus	31P
24	Acquired Size	16384
25	Spectral Size	32768



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7	Spectrometer	spect
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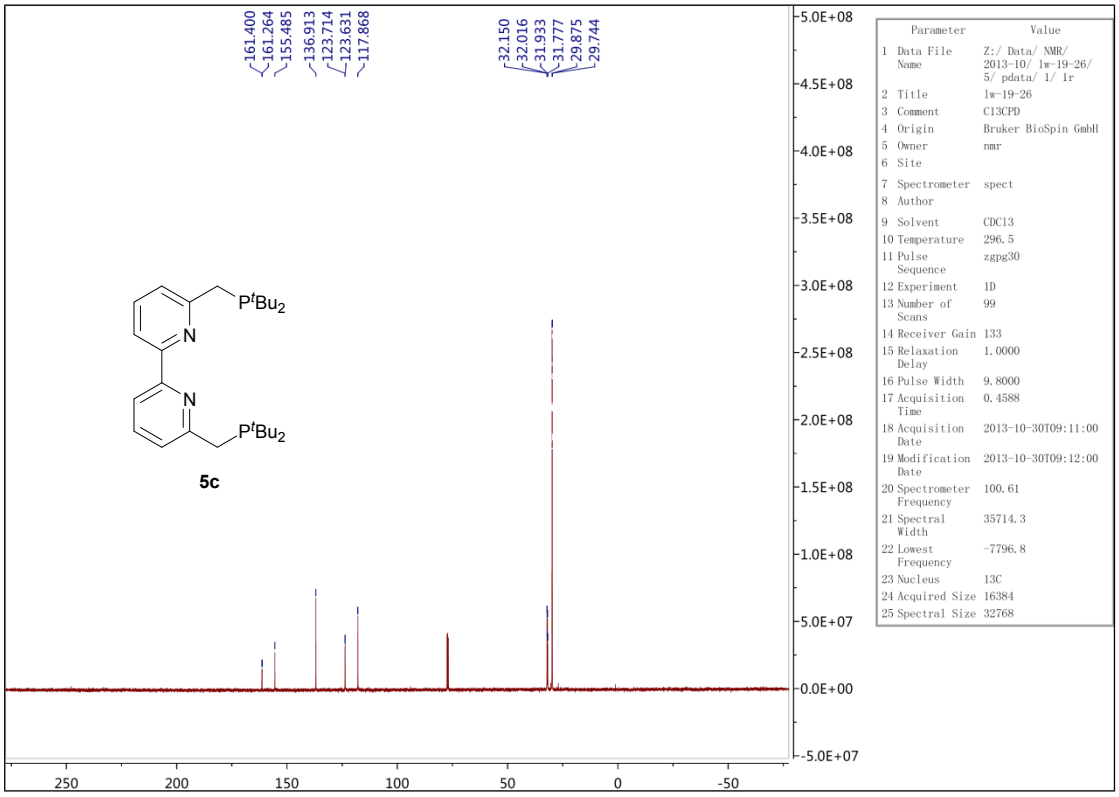

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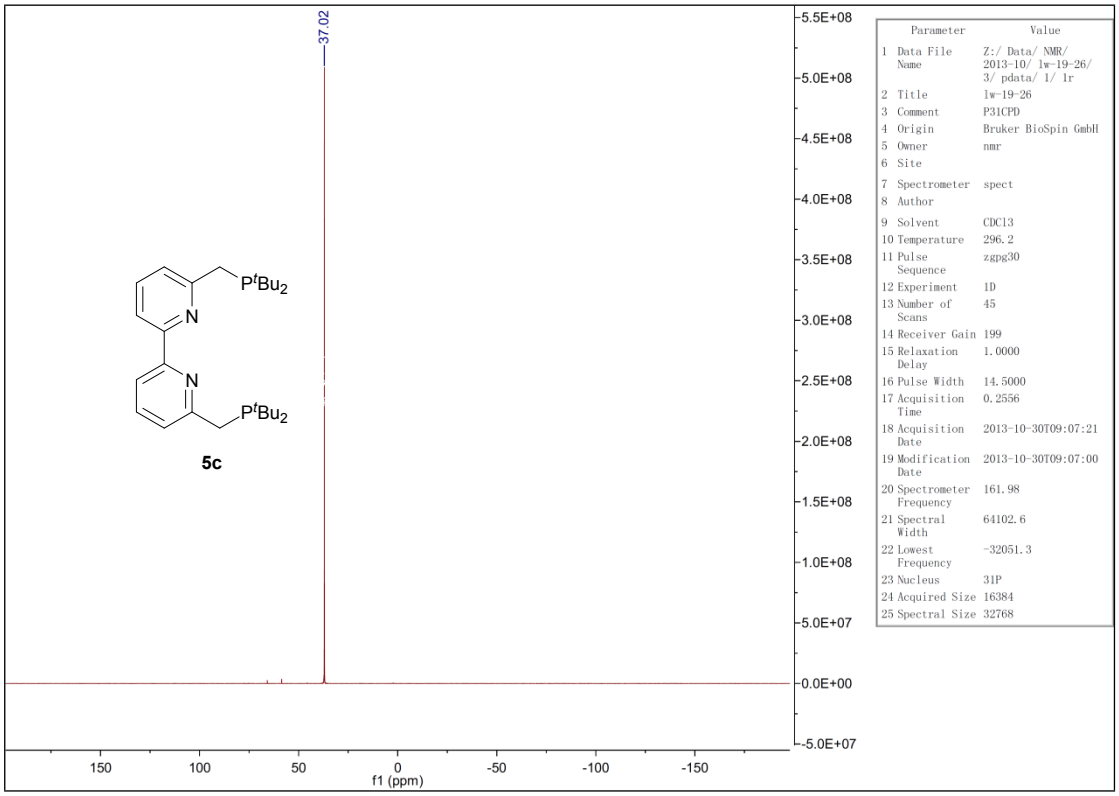

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23	Nucleus	31P
24	Acquired Size	16384
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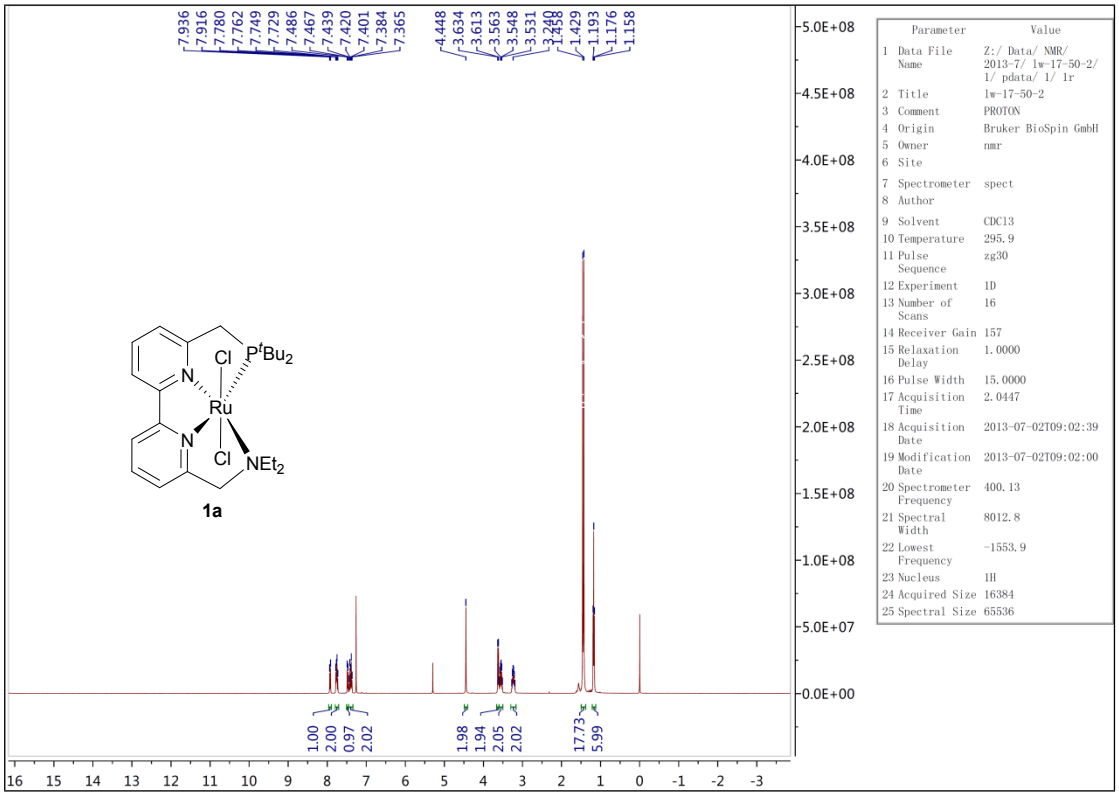

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8	Author	
9	Solvent	CDCl3
10	Temperature	295.9
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	157
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
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19	Modification Date	2013-07-02T09:02:00
20	Spectrometer Frequency	400.13
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22	Lowest Frequency	-1553.9
23	Nucleus	1H
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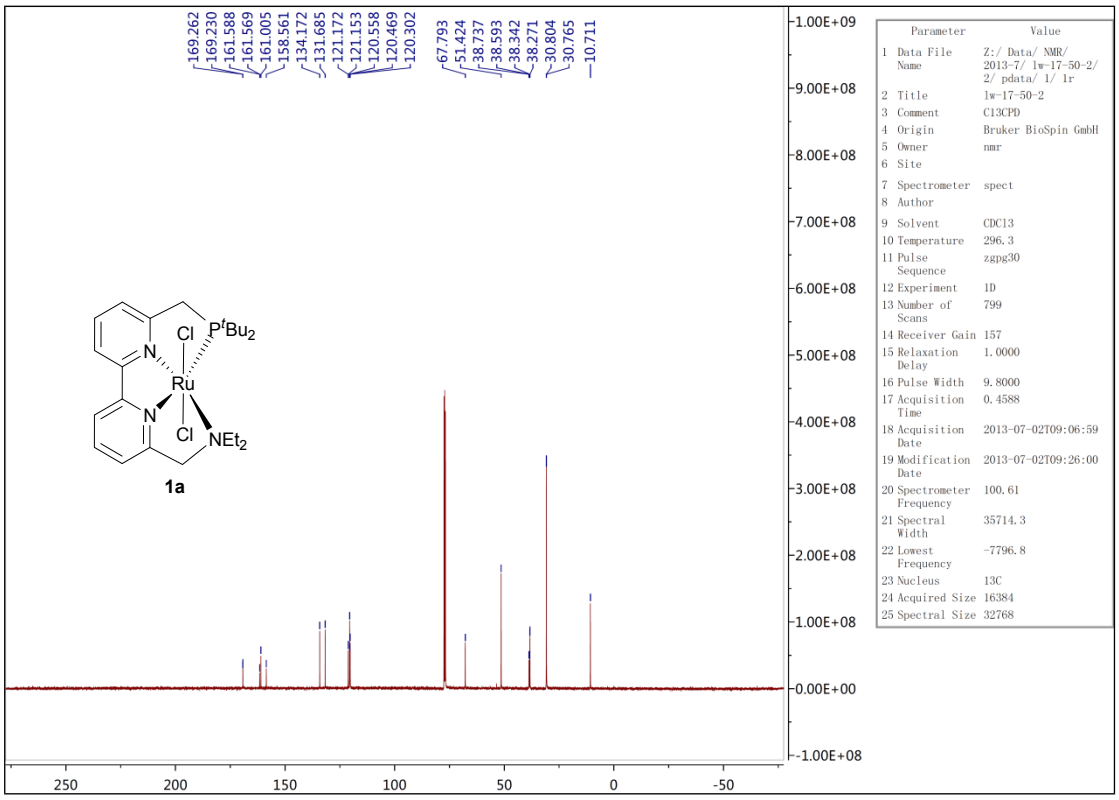

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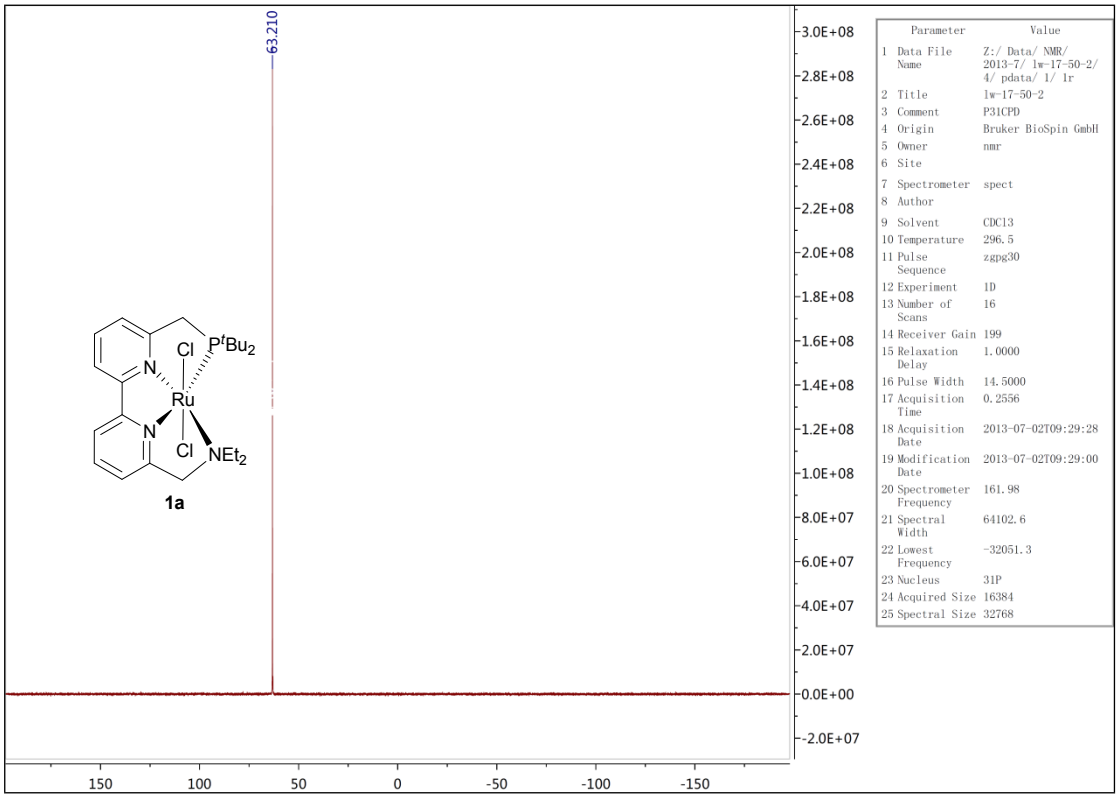
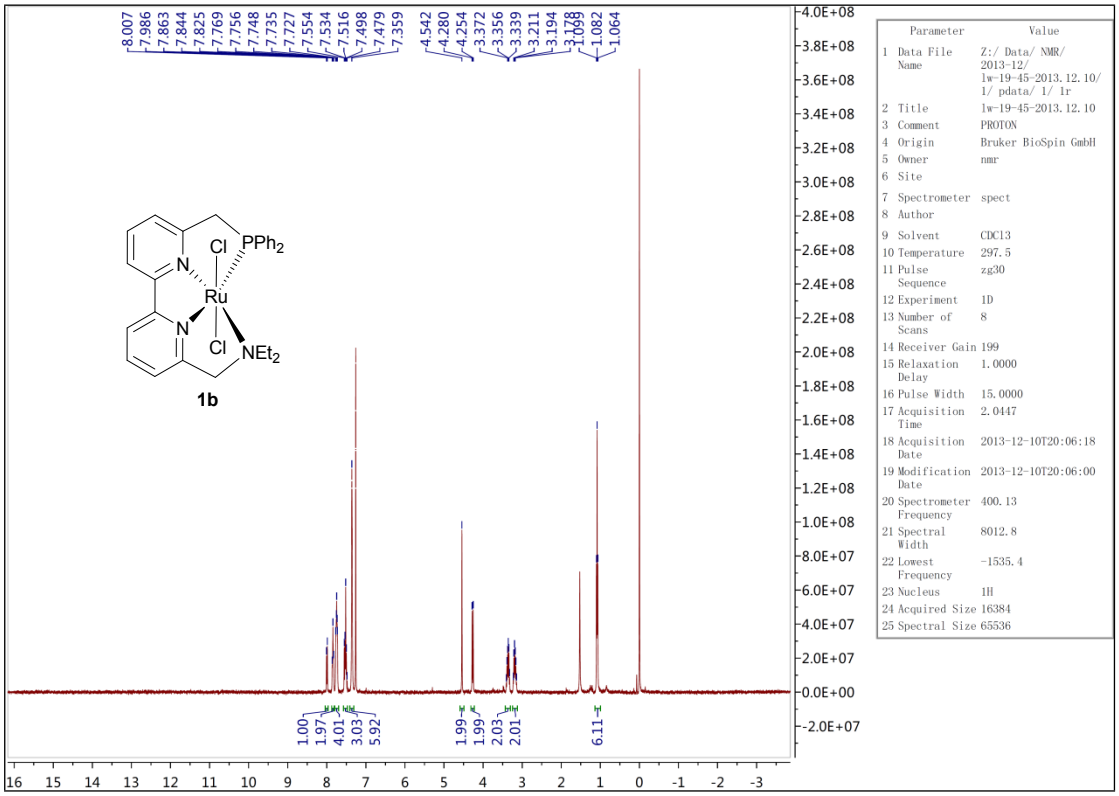
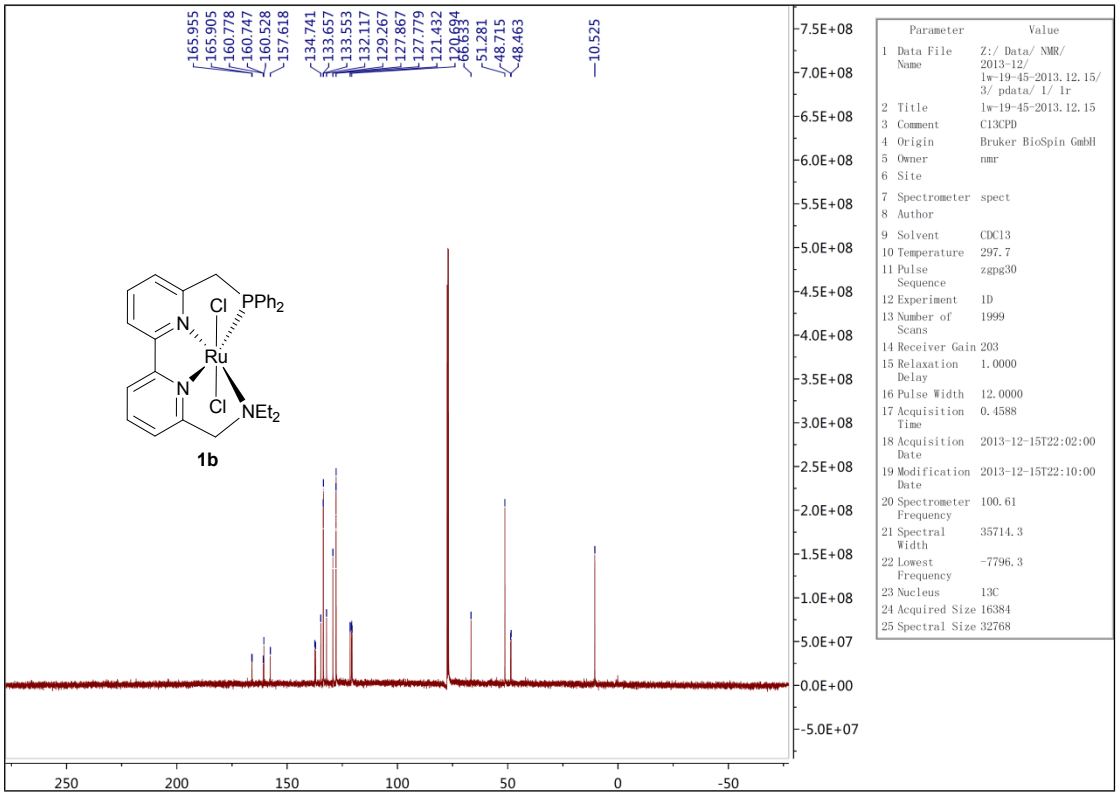
8	Author	
9	Solvent	CDCl3
10	Temperature	296.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	799
14	Receiver Gain	157
15	Relaxation Delay	1.0000
16	Pulse Width	9.8000
17	Acquisition Time	0.4588
18	Acquisition Date	2013-07-02T09:06:59
19	Modification Date	2013-07-02T09:26:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.8
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



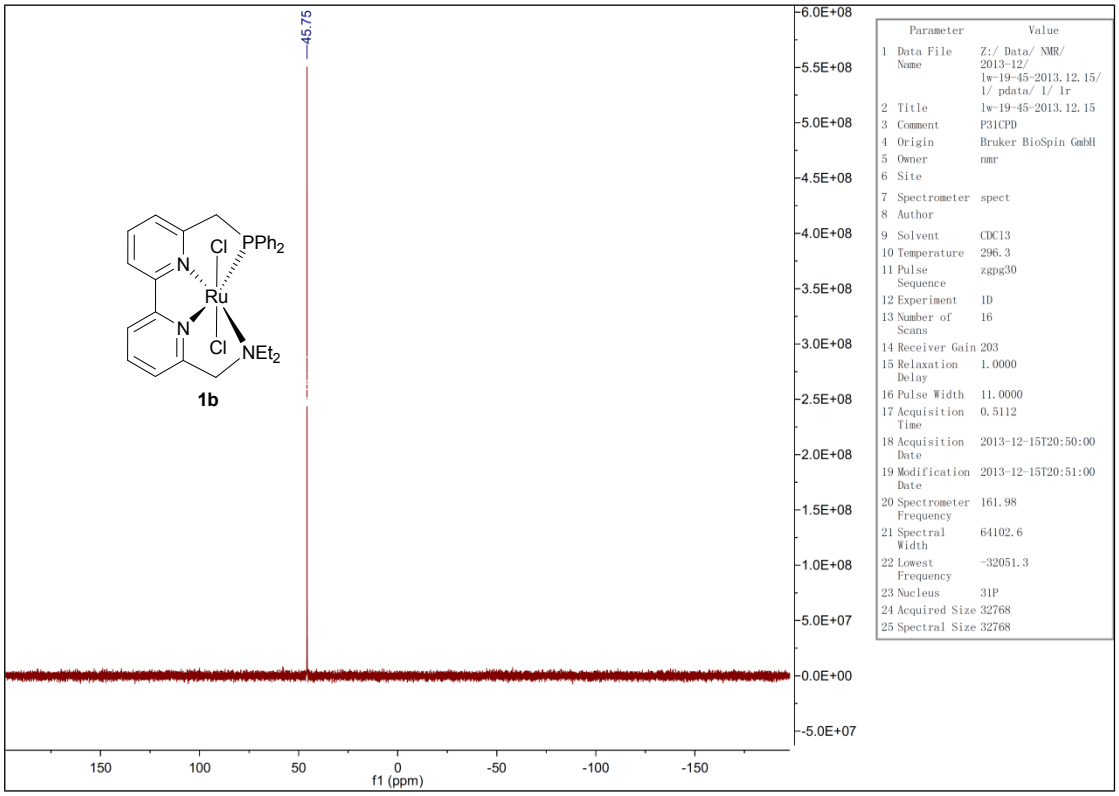
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-7/ lw-17-50-2/ 4/ pdata/ 1/ 1r
2	Title	lw-17-50-2
3	Comment	P31CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.5
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	199
15	Relaxation Delay	1.0000
16	Pulse Width	14.5000
17	Acquisition Time	0.2556
18	Acquisition Date	2013-07-02T09:29:28
19	Modification Date	2013-07-02T09:29:00
20	Spectrometer Frequency	161.98
21	Spectral Width	64102.6
22	Lowest Frequency	-32051.3
23	Nucleus	31P
24	Acquired Size	16384
25	Spectral Size	32768



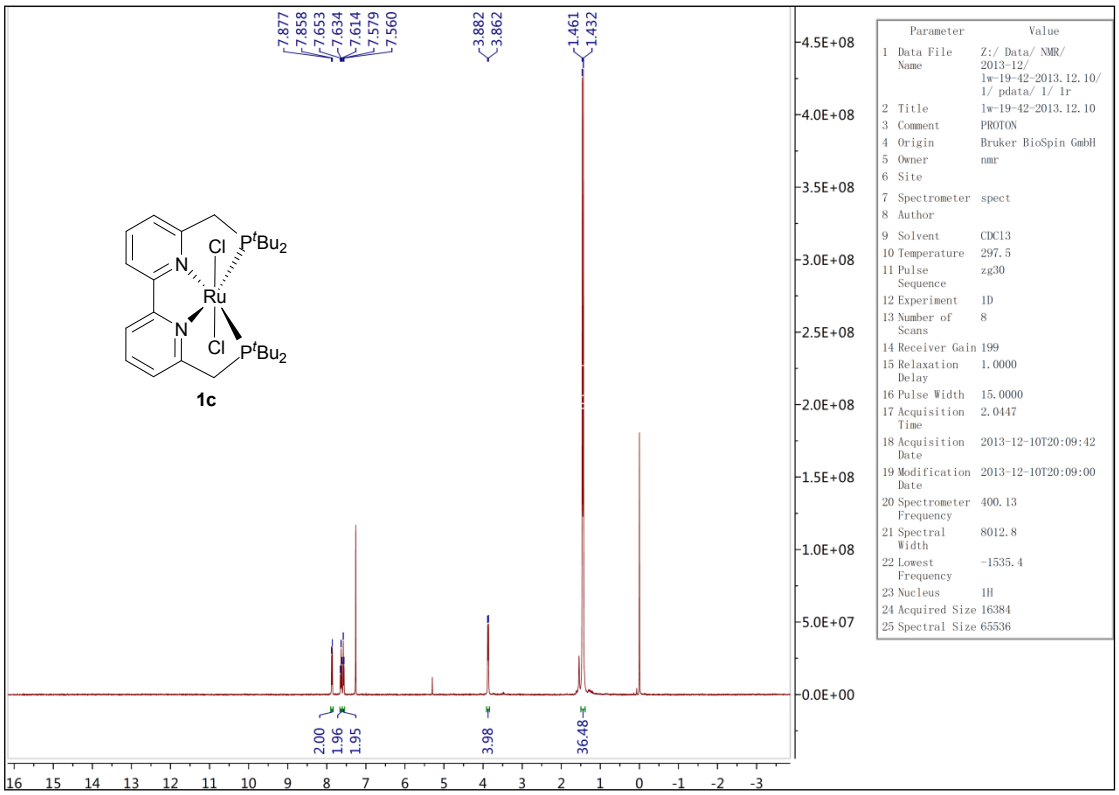
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ 1w-19-45-2013.12.10/ 1/ pdata/ 1/ 1r
2	Title	1w-19-45-2013.12.10
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.5
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	199
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
18	Acquisition Date	2013-12-10T20:06:18
19	Modification Date	2013-12-10T20:06:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	65536



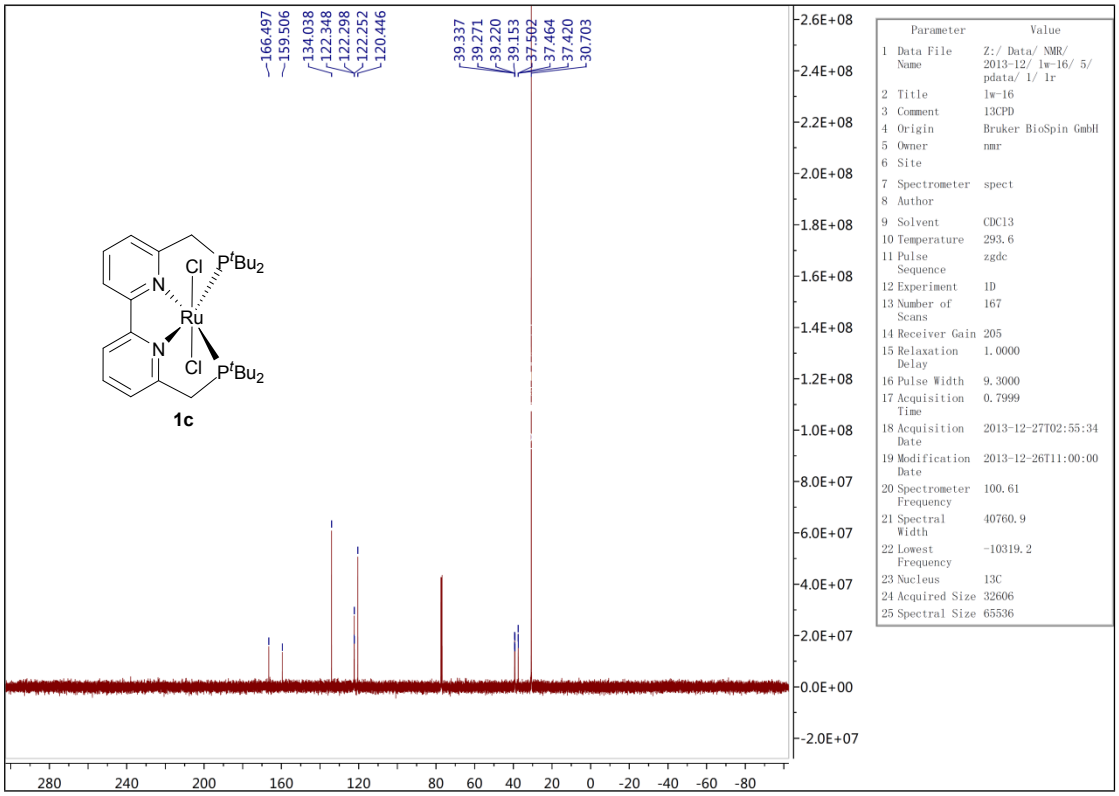
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ 1w-19-45-2013.12.15/ 3/ pdata/ 1/ 1r
2	Title	1w-19-45-2013.12.15
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.7
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	1999
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	12.0000
17	Acquisition Time	0.4588
18	Acquisition Date	2013-12-15T22:02:00
19	Modification Date	2013-12-15T22:10:00
20	Spectrometer Frequency	100.61
21	Spectral Width	35714.3
22	Lowest Frequency	-7796.3
23	Nucleus	13C
24	Acquired Size	16384
25	Spectral Size	32768



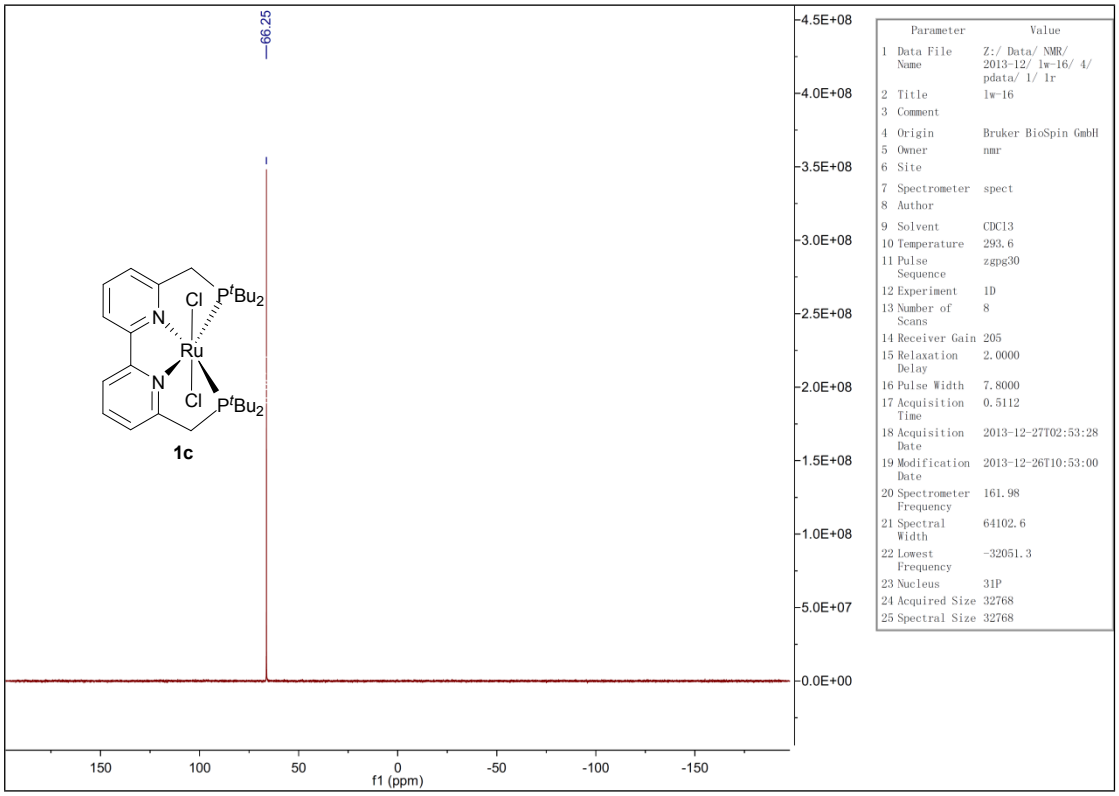
	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ lw-19-45-2013.12.15/ 1/ pdata/ 1/ 1r
2	Title	lw-19-45-2013.12.15
3	Comment	P31CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	296.3
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	16
14	Receiver Gain	203
15	Relaxation Delay	1.0000
16	Pulse Width	11.0000
17	Acquisition Time	0.5112
18	Acquisition Date	2013-12-15T20:50:00
19	Modification Date	2013-12-15T20:51:00
20	Spectrometer Frequency	161.98
21	Spectral Width	64102.6
22	Lowest Frequency	-32051.3
23	Nucleus	31P
24	Acquired Size	32768
25	Spectral Size	32768



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ lw-19-42-2013.12.10/ 1/ pdata/ 1/ 1r
2	Title	lw-19-42-2013.12.10
3	Comment	PROTON
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.5
11	Pulse Sequence	zg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	199
15	Relaxation Delay	1.0000
16	Pulse Width	15.0000
17	Acquisition Time	2.0447
18	Acquisition Date	2013-12-10T20:09:42
19	Modification Date	2013-12-10T20:09:00
20	Spectrometer Frequency	400.13
21	Spectral Width	8012.8
22	Lowest Frequency	-1535.4
23	Nucleus	1H
24	Acquired Size	16384
25	Spectral Size	65536



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ lw-16/ 5/ pdata/ 1/ 1r
2	Title	lw-16
3	Comment	13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.6
11	Pulse Sequence	zgdc
12	Experiment	1D
13	Number of Scans	167
14	Receiver Gain	205
15	Relaxation Delay	1.0000
16	Pulse Width	9.3000
17	Acquisition Time	0.7999
18	Acquisition Date	2013-12-27T02:55:34
19	Modification Date	2013-12-26T11:00:00
20	Spectrometer Frequency	100.61
21	Spectral Width	40760.9
22	Lowest Frequency	-10319.2
23	Nucleus	13C
24	Acquired Size	32606
25	Spectral Size	65536



	Parameter	Value
1	Data File Name	Z:/ Data/ NMR/ 2013-12/ lw-16/ 4/ pdata/ 1/ 1r
2	Title	lw-16
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.6
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	8
14	Receiver Gain	205
15	Relaxation Delay	2.0000
16	Pulse Width	7.8000
17	Acquisition Time	0.5112
18	Acquisition Date	2013-12-27T02:53:28
19	Modification Date	2013-12-26T10:53:00
20	Spectrometer Frequency	161.98
21	Spectral Width	64102.6
22	Lowest Frequency	-32051.3
23	Nucleus	31P
24	Acquired Size	32768
25	Spectral Size	32768