Supporting Information for

Novel C_2-Symmetric Planar Chiral Diphosphine Ligands and Their Application in Pd-Catalyzed Asymmetric Allylic Substitutions

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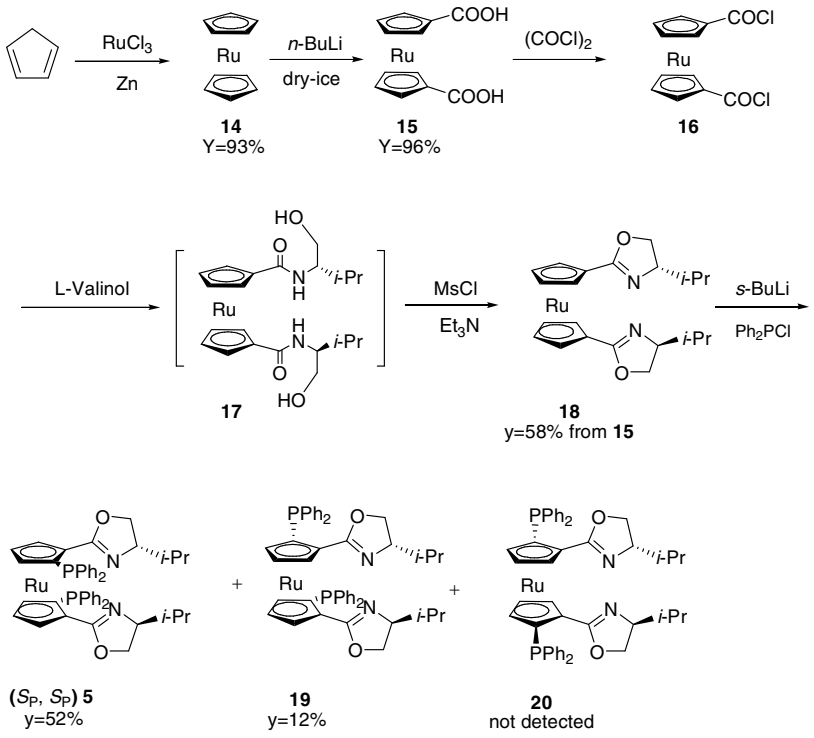
General Experimental Conditions. All reactions were performed under a nitrogen atmosphere, and the workup was carried out in air. The reaction solvents were distilled prior to used (Tetrahydrofuran was distilled from sodium-benzophenone ketyl. Methanol and Ethanol were dried with magnesium. Dichloromethane was distilled from CaH_2). The commercially available reagents were used without further purification. The substrate of asymmetric allylic substitutions **9** was prepared by literature procedure.[1] Melting points were determined on a XT-5 microscopic melting point apparatus without uncorrected. ^{1}H NMR (400 MHz) spectra, ^{13}C NMR (100 MHz) spectra and ^{31}P NMR (162 MHz) were recorded on a Varian MERCURY plus-400 spectrometer. The *ee* values were determined by HPLC using a Daicel Chiralcel OD-H, OJ-H and AD-H column.



Ruthenocene [Ru(η^5-C_5H_5)$_2$] (14)

To a mixture of ruthenium trichloride (10.52 g, 0.040 mol) and absolute ethanol (160 mL) was added cyclopentadiene (50 mL, 0.60 mol) following by zinc dust (26 g, 0.40 mol). The reaction mixture turned rapidly dark blue, and then, more slowly, dark grey. After stirring for 2 hours at room temperature, the mixture was filtered in air. The filtrate was concentrated and followed by another filtration to afford light green

crystalline solid (1.6 g). The metallic grey solid was washed with toluene (8×50 mL) and the filtrate was evaporated to obtain another 7.0 g. Total yield: 93.0%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (s).

1,1'-Dicarboxylic ruthenocene (15)

Ruthenocene (4.62 g, 20 mmol) was placed in a 500 mL flask followed by adding *n*-hexane (150 mL). Another 250 mL flask were charged with *n*-hexane (100 mL) followed by adding *n*- butyllithium (32 mL, 2.5 M, 80 mmol) and TMEDA (8.3 mL, 52 mmoL). The solution was then transferred into the cloudy ruthenocene solution. This mixture was stirred at room temperature for 19 h to give lithiated compound, which was then poured into a mixture of dry-ice and *n*-hexane (100 mL). The mixture was placed for 3 h before concentrated hydrochloric acid was added until pH=2. After filtered and dried in vacuum, 1,1'-dicarboxylic ruthenocene **13** was obtained as a light brown solid (6.13 g; 96.0%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.77 (t, *J*=1.6 Hz, 4H), 5.03 (t, *J*=1.6 Hz, 4H), 12.3 (br, 2H).

1, l'-Bis[(S)-4-isopropyloxazolin-2-yl]-ruthenocene (18)

1,1'-Dicarboxylic ruthenocene (4.25 g, 13.3 mmol) was suspended in dichloromethane (70 mL) followed by adding oxalyl chloride (11.0 mL, 106 mmol) and pyridine (0.1 mL). This mixture was refluxed for 2 h and then evaporated to dryness. The residue was washed with ethyl ether and the organic phase was evaporated to offer 1,1'-dichlorocarbonylruthenocene as a yellow-green solid. The product was directly used in the next step without any purification.

To a solution of (S)-(+)-valinol (3.20 g, 26.6 mmol) and triethylamine (11.2 ml, 58.5 mmol) in 30 ml of dichloromethane was added dropwise the above 1,1'-dichlorocarbonylruthenocence in 40 ml of dichloromethane under nitrogen atmosphere in ice-water bath. The reaction mixture was stirred at room temperature for 24 h. To this solution was added dropwise methanesulfonyl chloride (2.80 mL, 34.6 mmol) for a period of 30 min at 0°C, and then the solution was stirred at room

temperature for 2 h. The resulting solution was washed with chilled water (5 °C) and then brine. The organic layer was dried over Na_2SO_4 and then the solvent was evaporated in vacuum. The residue was purified on silica gel column chromatography with petrol ether-ethyl acetate (2:1) to afford pure product **18** (3.5 g, 58%) as a light yellow solid.

^{1}H NMR(400 MHz, $CDCl_3$): δ 0.87 (d, *J*=6.4 Hz, 6H), 0.95 (d, *J*=6.4 Hz, 6H), 1.84-1.79 (m, 2H), 3.95-3.91 (m, 2H), 3.99 (t, *J*=7.6 Hz, 2H), 4.22 (t, *J*=9.2 Hz , 4H), 5.09 (brs, 2H), 5.14 (brs, 2H).

2,2'-Bis[(S)-4-isopropyloxazolin-2-yl]-(S)-(S)-1,1'-bis(diphenylphosphino)-ruthenocene (5)

To a solution of **18** (1.0 g, 2.2 mmol) in 40 ml of THF was added dropwise a solution of *sec*-butyllithium in cyclohexane (7.0 mL, 0.98 M, 6.6 mmol) at -78°C under nitrogen atmosphere. The reaction solution was stirred at the temperature for 3 h and then at 0°C for 10 min. Chlorodiphenylphosphine (1.23 mL, 6.6 mmol) was dropped at 0°C to the solution containing dilithiated species generated from **16**, and then the solution was stirred at room temperature for 3 h. After the solvent was evaporated in vacuum, the residue was isolated directly by silica gel column chromatography eluted with degassed petrol ether-ethyl acetate (8:1) to give **5** (0.93 g, 51.4%); mp 178-180°C; $[\alpha]^D_{27}$=-263.6 (c 0.61, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.60 (d, *J*=6.8 Hz, 6H), 0.86 (d, *J*=6.8 Hz, 6H), 1.65-1.71 (m, 2H), 3.67 (t, *J*=8 Hz, 2H), 3.82 (brs, 2H), 3.89-3.91 (m, 2H), 4.23-4.27 (dd, *J*=8, 9.6 Hz, 2H), 4.67 (brs, 2H), 5.41 (brs, 2H), 7.17-7.32 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.4, 19.1, 32.1, 69.6, 72.2, 75.8, 77.4, 78.0, 78.1, 81.9, 82.1, 84.5, 84.8, 128.21, 128.28, 128.30, 128.33, 128.4, 128.9, 132.8, 133.0, 134.4, 134.6, 137.9, 138.0, 139.2, 139.3, 163.37, 163.39. ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ -16.85; MS (MALDI): *m/z* 823 [M+1$^+$] (100); HRMS calcd for $C_{46}H_{47}N_2O_2P_2Ru$ 823.2151, found 823.2154.

The diastereomeric compound **19** was also obtained as by-product with the yield of 12%. mp 87-88°C; $[\alpha]^D_{27}$= -62.9 (c 0.44, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Hz): δ 0.49-0.54 (m, 9H), 0.71 (d, *J*=6.8 Hz, 3H), 1.36-1.43 (m, 1H), 1.48-1.56 (m, 1H), 3.38

(t, *J*=8.4 Hz, 1H), 3.70-3.72 (m, 1H), 3.76-3.80 (m, 1H), 3.85-3.94 (m, 2H), 3.96-4.02 (m, 1H), 4.16 (brs, 2H), 4.78-4.80 (q, *J*=2.8 Hz, 2H), 5.26 (brs, 1H), 5.29 (brs, 1H), 7.59-7.43 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.4, 18.0, 18.0, 18.9, 31.9, 32.7, 69.5, 69.6, 72.1, 72.3, 76.4, 76.7, 77.3, 77.8, 78.6, 78.7, 78.8, 78.9, 128.1, 128.21, 128.25, 128.27, 128.32, 128.38, 128.42, 128.49, 128.5, 128.8, 128.9, 132.6, 132.84, 132.87, 133.0, 134.6, 134.8, 134.9, 135.1, 162.92, 162.95; ^{31}P NMR ($CDCl_3$, 162 Hz, 85% H_3PO_4): δ -16.77, -15.72; MS (MALDI): *m/z* 823 [M+1$^+$] (100); HRMS calcd for $C_{46}H_{47}N_2O_2P_2Ru$ 823.2151, found 823.2159.

Complexation Behavior of 4a with Dichlorobis(acetonitrile)palladium.

Compound **4a** (6.9 mg, 0.01 mmol) was dissolved in acetonitrile-d_3 (0.40 mL) to give solution A, and dichlorobis(acetonitrile)palladium (8.0 mg, 0.03 mmol) was dissolved in acetonitrile-d_3 (1.50 mL) to give solution B. Addition of 0.25 mL of solution B (0.005 mmol) to solution A gave a solution containing **4a** and a C_2-symmetric 1:1 complex, **7a** ([**4a**]$PdCl_2$), judging from the ^{1}H NMR analysis. When 0.50 mL of solution B (0.01 mmol) was added, compound **4a** disappeared, and only complex **7a** was formed as determined by ^{1}H NMR analysis. The addition of more than 0.5 mL of solution B gave the same result as above and did not produce a new complex.

Ref.

1. Watson, L. D. G.; Styler, S. A.; Yudin, A. K. *J. Am. Chem. Soc*. **2004**, *126*, 5086.
2. Zhang, W.; Shimanuki, T.; Kida, T,; Nakatsuji, Y.; Ikeda, I., *J. Org. Chem*. **1999**, *64*, 6247.

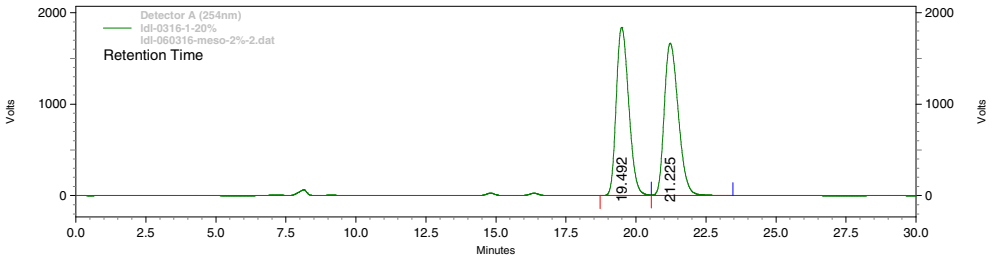


Figure S1. HPLC chromatograms showing the separation **10** using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min). Product from asymmetric allylic alkylation using PPh_3 at 25°C, racemic isomer.

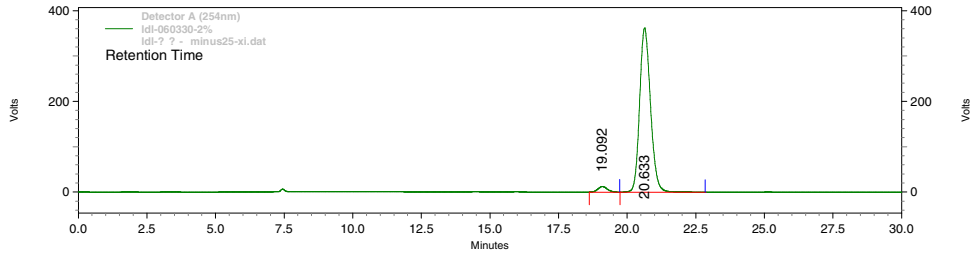


Figure S2. HPLC chromatograms showing the separation **10** using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min). Product from asymmetric allylic alkylation using **4a** as ligand at -25°C (Table 1, entry 8), 95.7% *ee*.

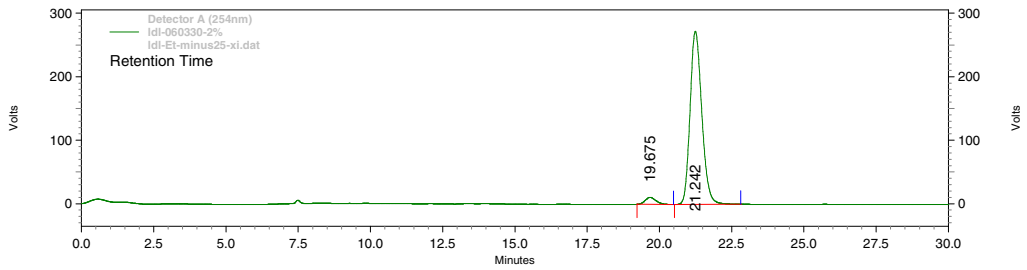


Figure S3. HPLC chromatograms showing the separation **10** using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min). Product from asymmetric allylic alkylation using **4b** as ligand at -25°C (Table 1, entry 10), 92.9% *ee*.

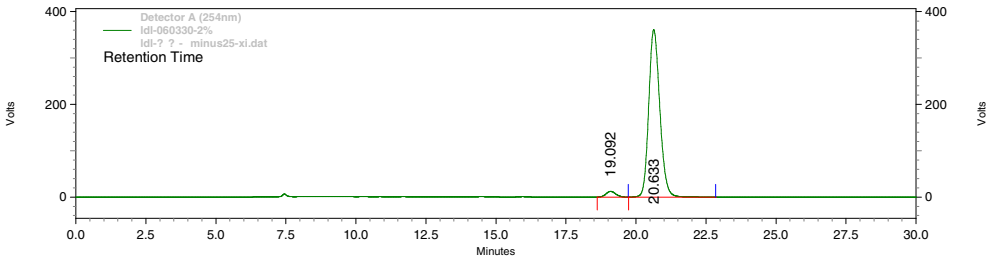


Figure S4. HPLC chromatograms showing the separation **10** using a Daicel Chiralcel OD-H column (hexane: 2-propanol = 98: 2, flow = 0.5 mL/min). Product from asymmetric allylic alkylation using **4a** as ligand at -78°C (Table 1, entry 9), 94.1% *ee*.

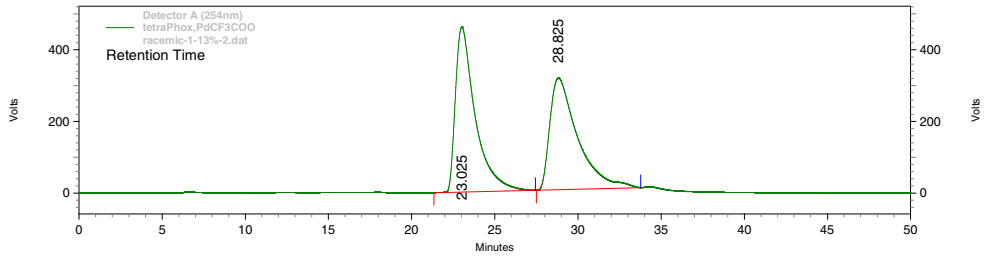


Figure S5. HPLC chromatograms showing the separation **11** using a Daicel Chiralcel OJ-H column (hexane: 2-propanol = 87: 13, flow = 0.5 mL/min). Product from asymmetric allylic amination using PPh_3 at 25°C, racemic isomer.

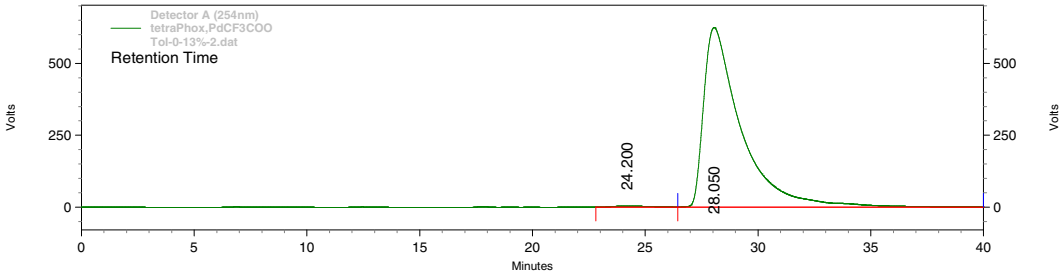


Figure S6. HPLC chromatograms showing the separation **11** using a Daicel Chiralcel OJ-H column (hexane: 2-propanol 9= 87: 13, flow = 0.5 mL/min). Product from asymmetric allylic amination using **1a** at 0°C (Table 2, entry 7), 98.7%ee

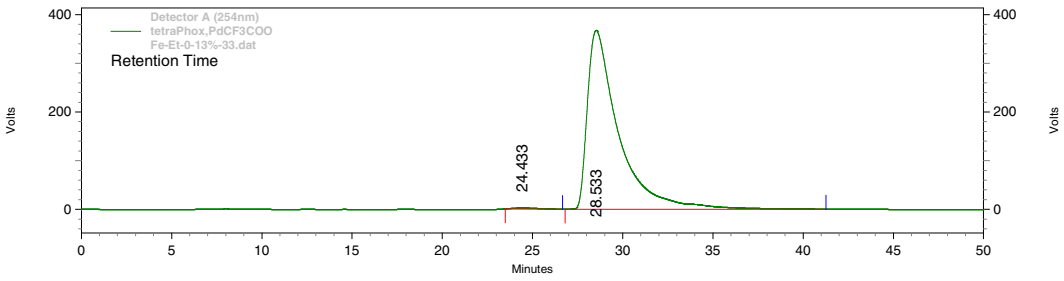


Figure S7. HPLC chromatograms showing the separation **11** using a Daicel Chiralcel OJ-H column (hexane: 2-propanol 9= 87: 13, flow = 0.5 mL/min). Product from asymmetric allylic amination using **1b** at 0°C (Table 2, entry 10), 99.1%ee

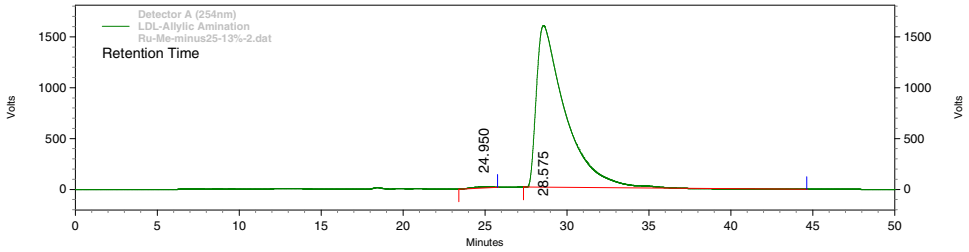


Figure S8. HPLC chromatograms showing the separation **11** using a Daicel Chiralcel OJ-H column (hexane: 2-propanol 9= 87: 13, flow = 0.5 mL/min). Product from asymmetric allylic amination using **4a** at -25°C (Table 3, entry 10), 99.2%ee

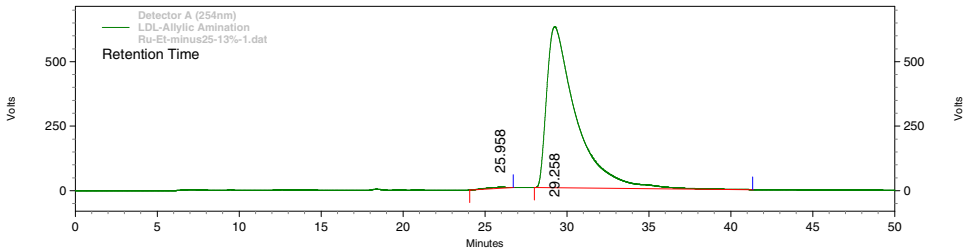
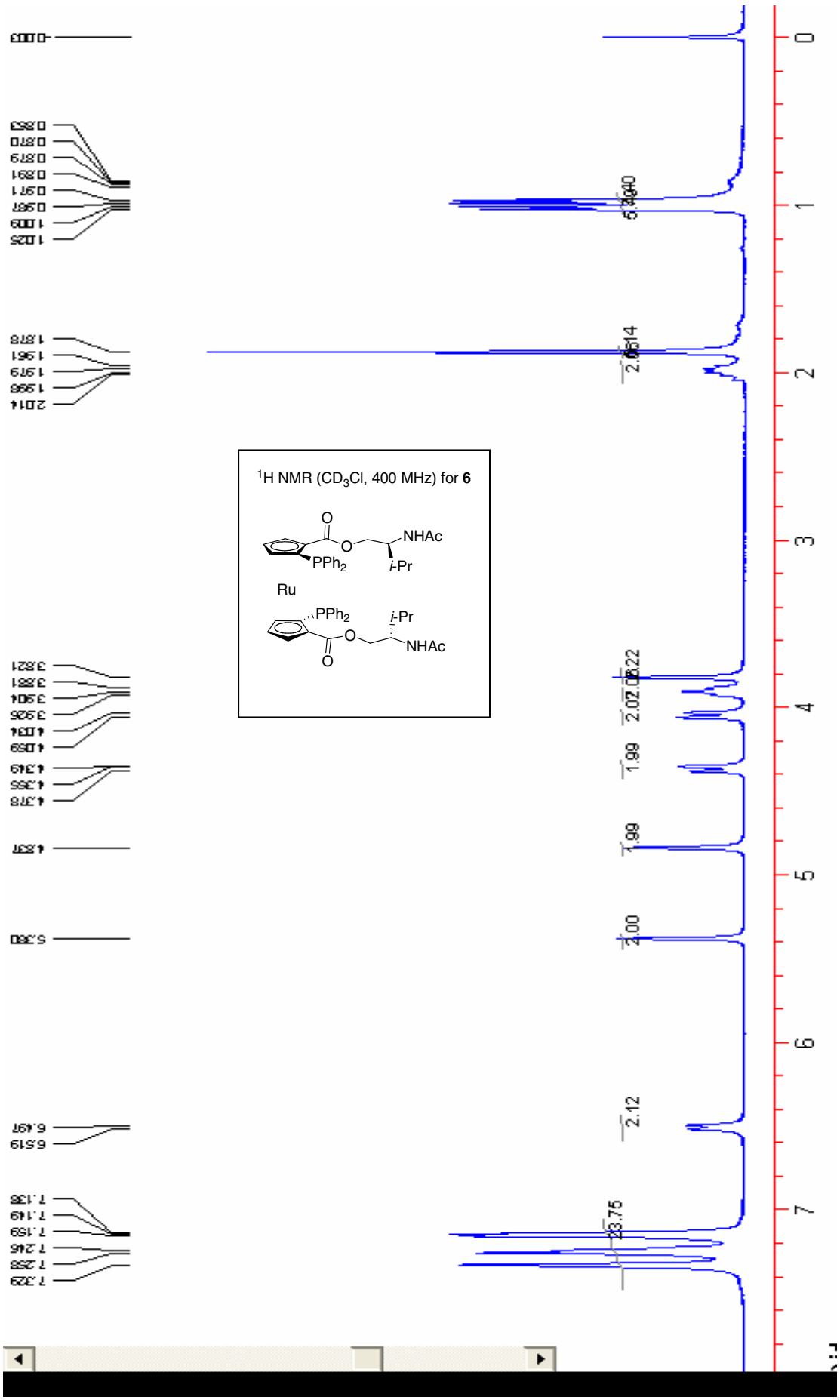


Figure S9. HPLC chromatograms showing the separation **11** using a Daicel Chiralcel OJ-H column (hexane: 2-propanol 9= 87: 13, flow = 0.5 mL/min). Product from asymmetric allylic amination using **4b** at -25°C (Table 3, entry 12), 99.0%ee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PPh2
i-Pr
Ru
PPh2
i-Pr
NHAc
O
O
O
O
0.853
0.870
0.879
0.891
0.971
0.987
1.009
1.025
1.578
1.961
1.979
1.996
2.014
3.821
3.881
3.904
3.926
4.034
4.059
4.349
4.355
4.378
4.837
5.380
6.497
6.519
7.136
7.149
7.159
7.246
7.258
7.329
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1.99
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1.00
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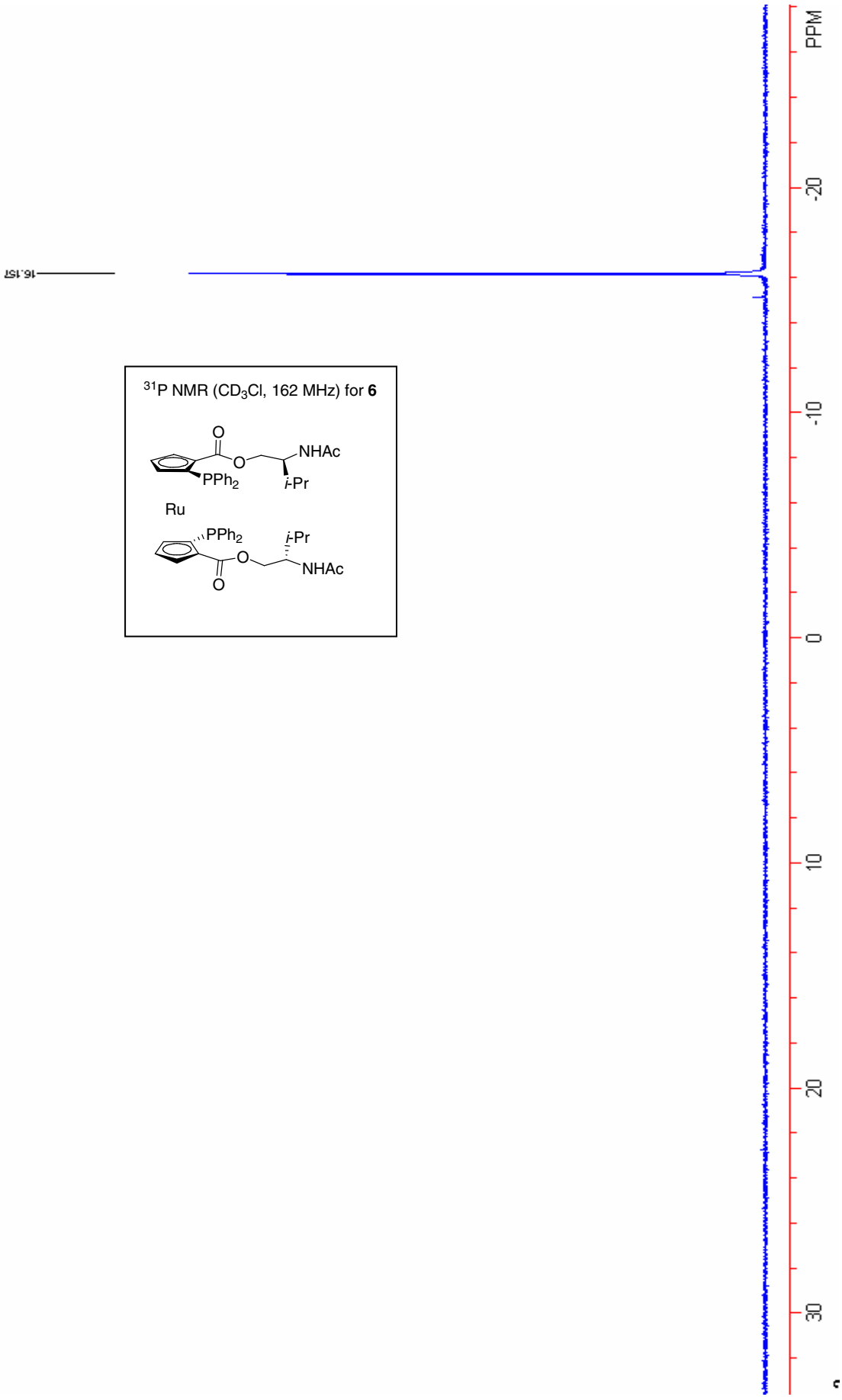
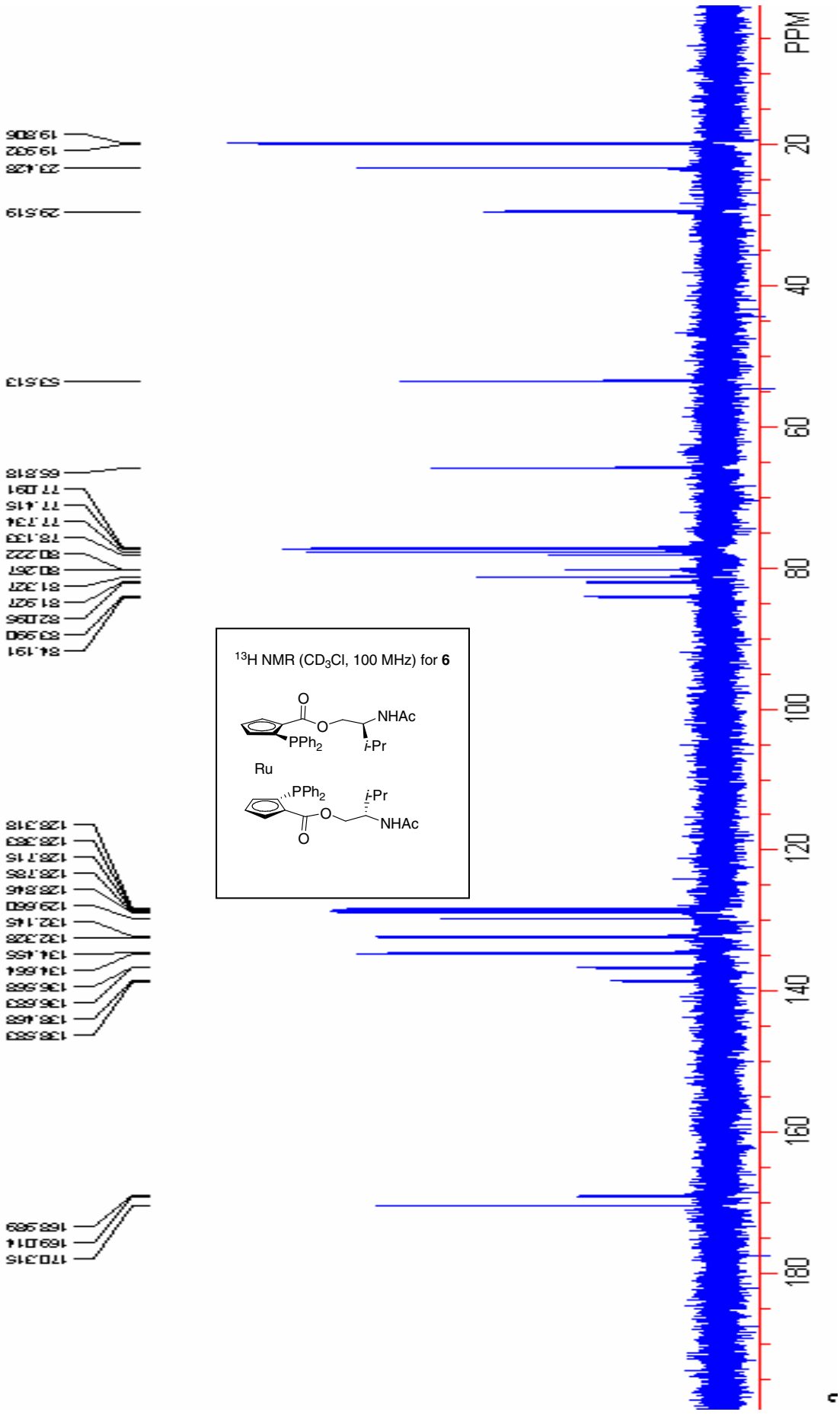
1
2
3
4
5
6
7



^{31}P NMR (CD_3Cl, 162 MHz) for **6**

Ru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132.328
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136.568
136.683
138.468
138.583
168.589
169.014
170.315
PPM
20
40
60
80
100
120
140
160
180
^{13}H NMR (CD_3Cl, 100 MHz) for **6**
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O
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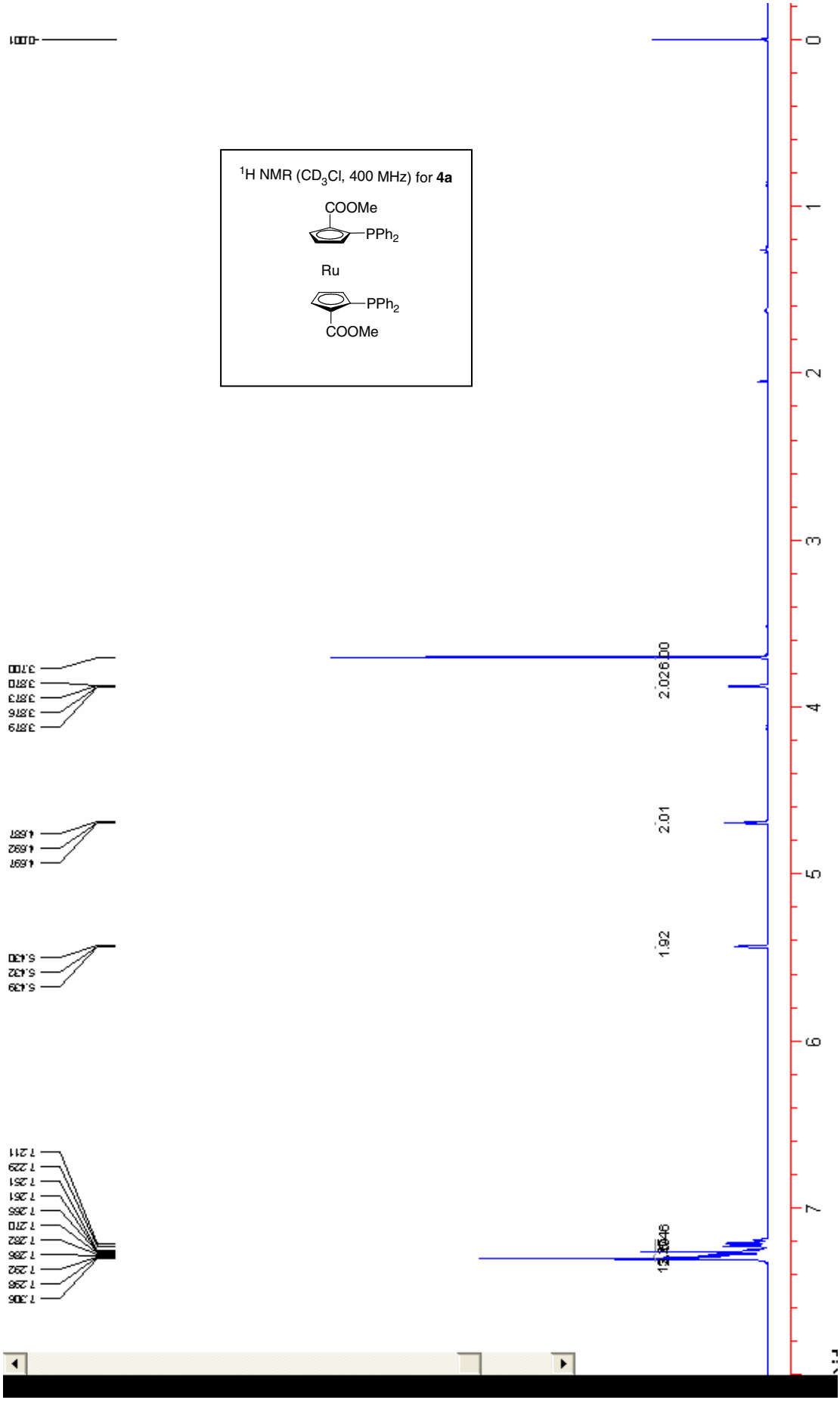
PPh$_2$
i-Pr
Ru
PPh$_2$
i-Pr
O
NHAc
O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COOMe
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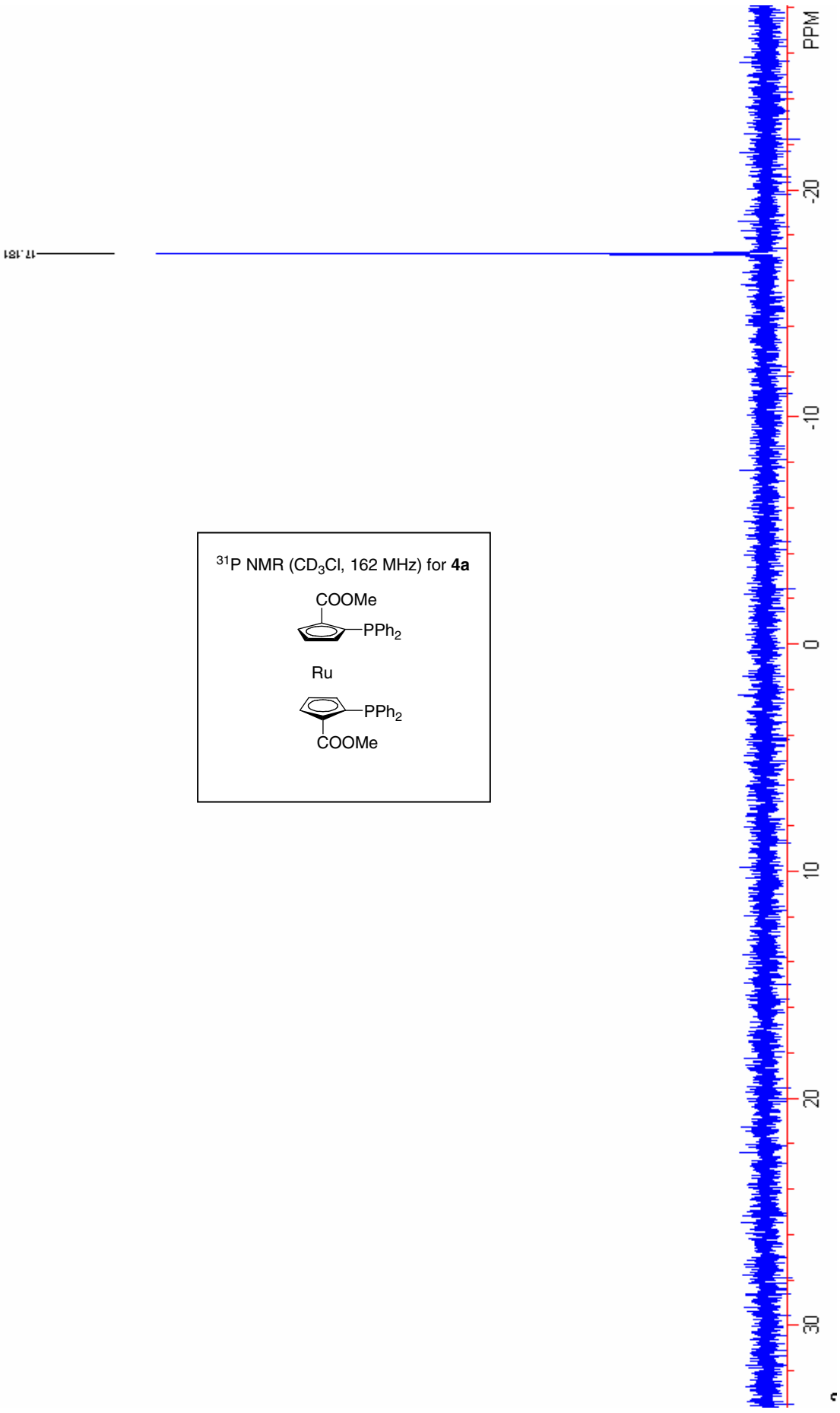
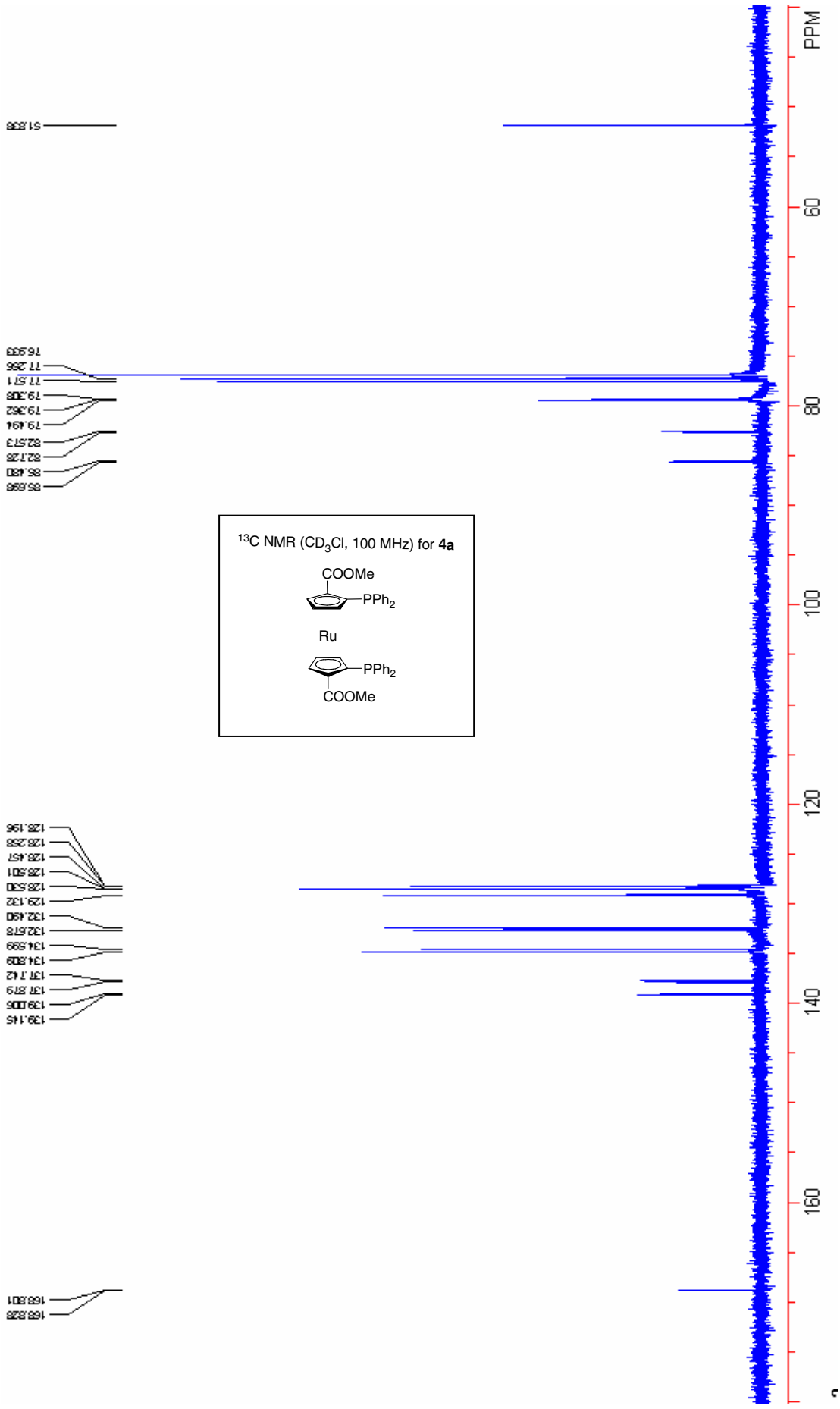
1.92



^{31}P NMR (CD_3Cl, 162 MHz) for **4a**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79.362
79.494
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128.501
128.530
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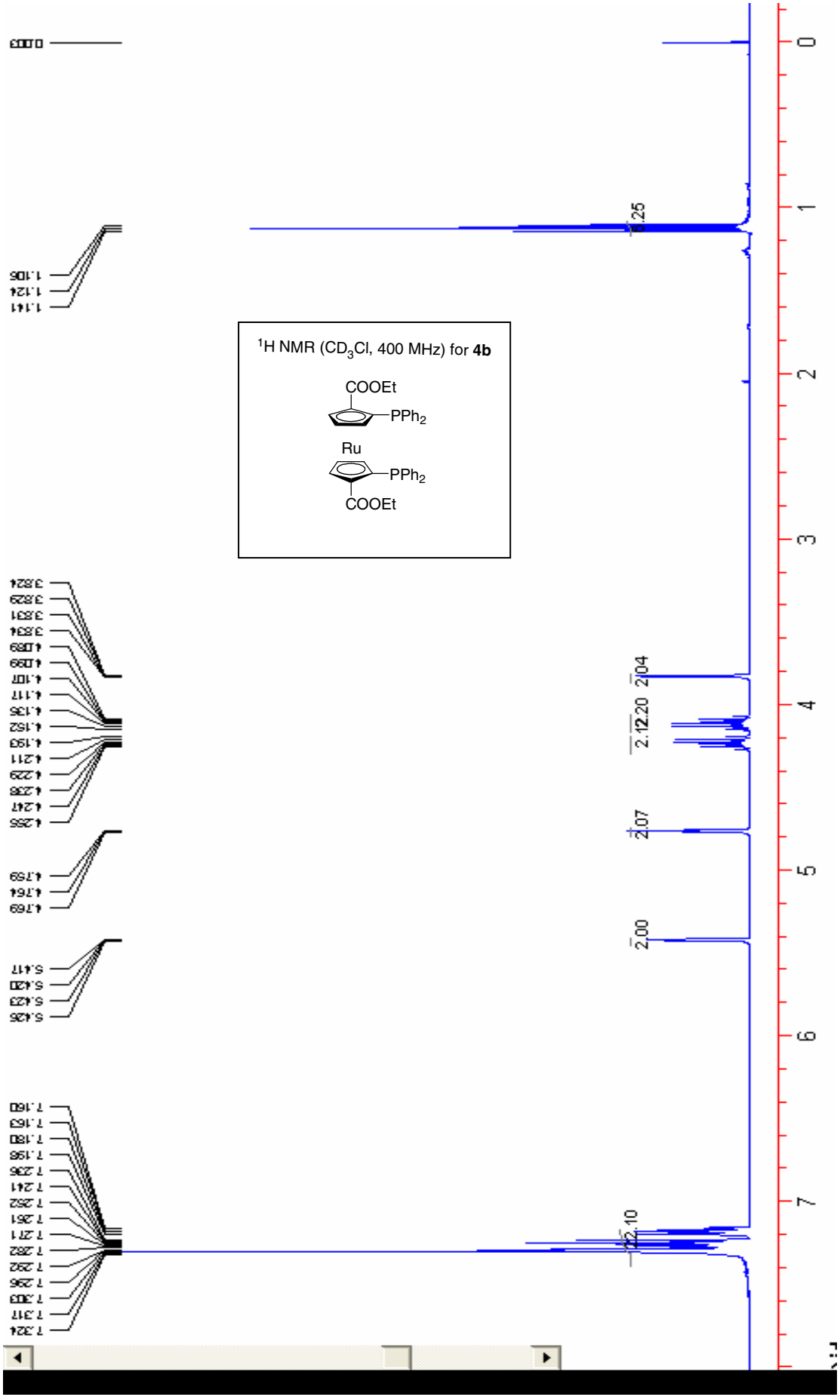
134.599
134.809
137.142
137.879
139.006
139.145
168.328
168.801
PPM
60
80
100
120
140
160
^{13}C NMR (CD_3Cl, 100 MHz) for **4a**
COOMe
PPh_2
Ru
PPh_2
COOMe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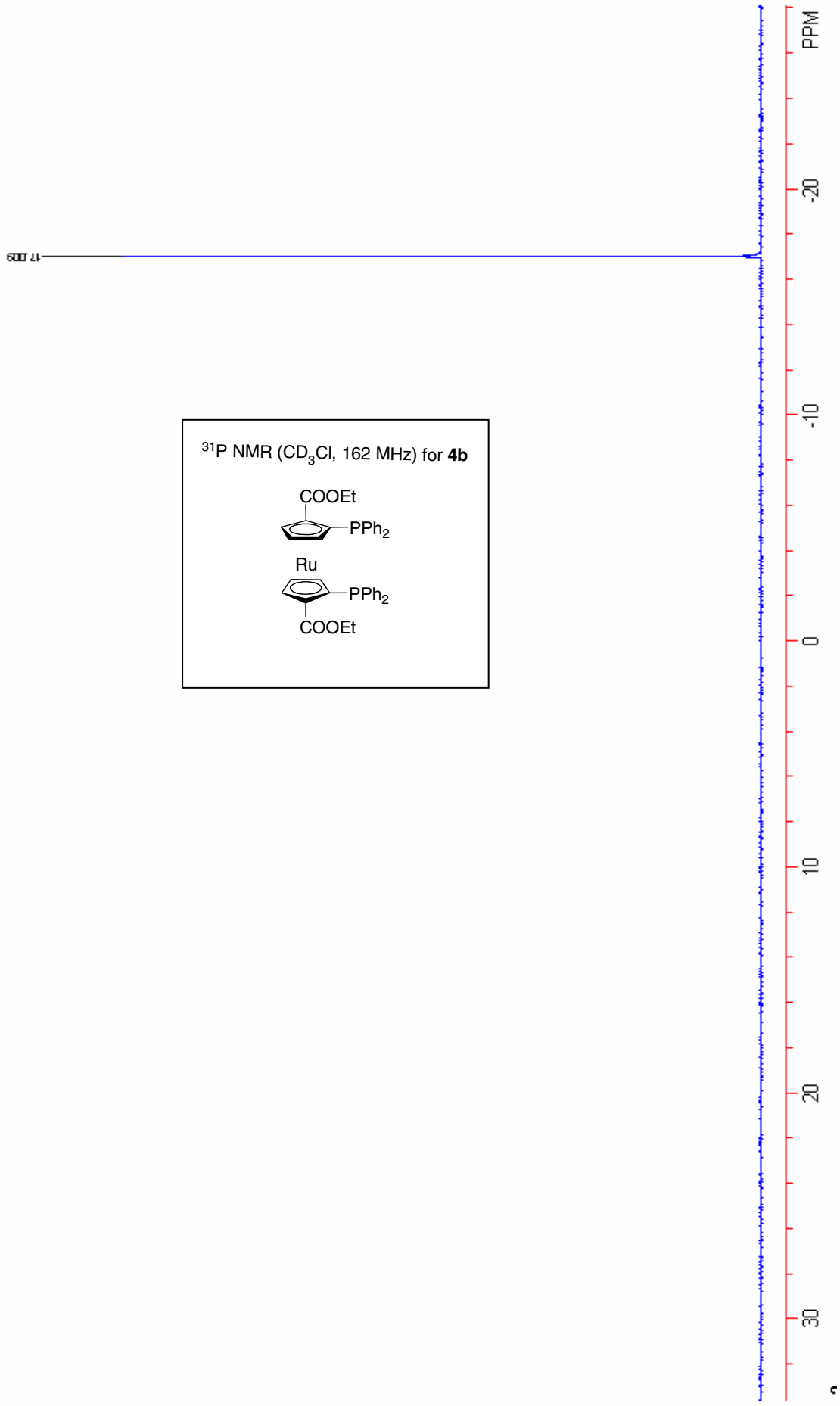
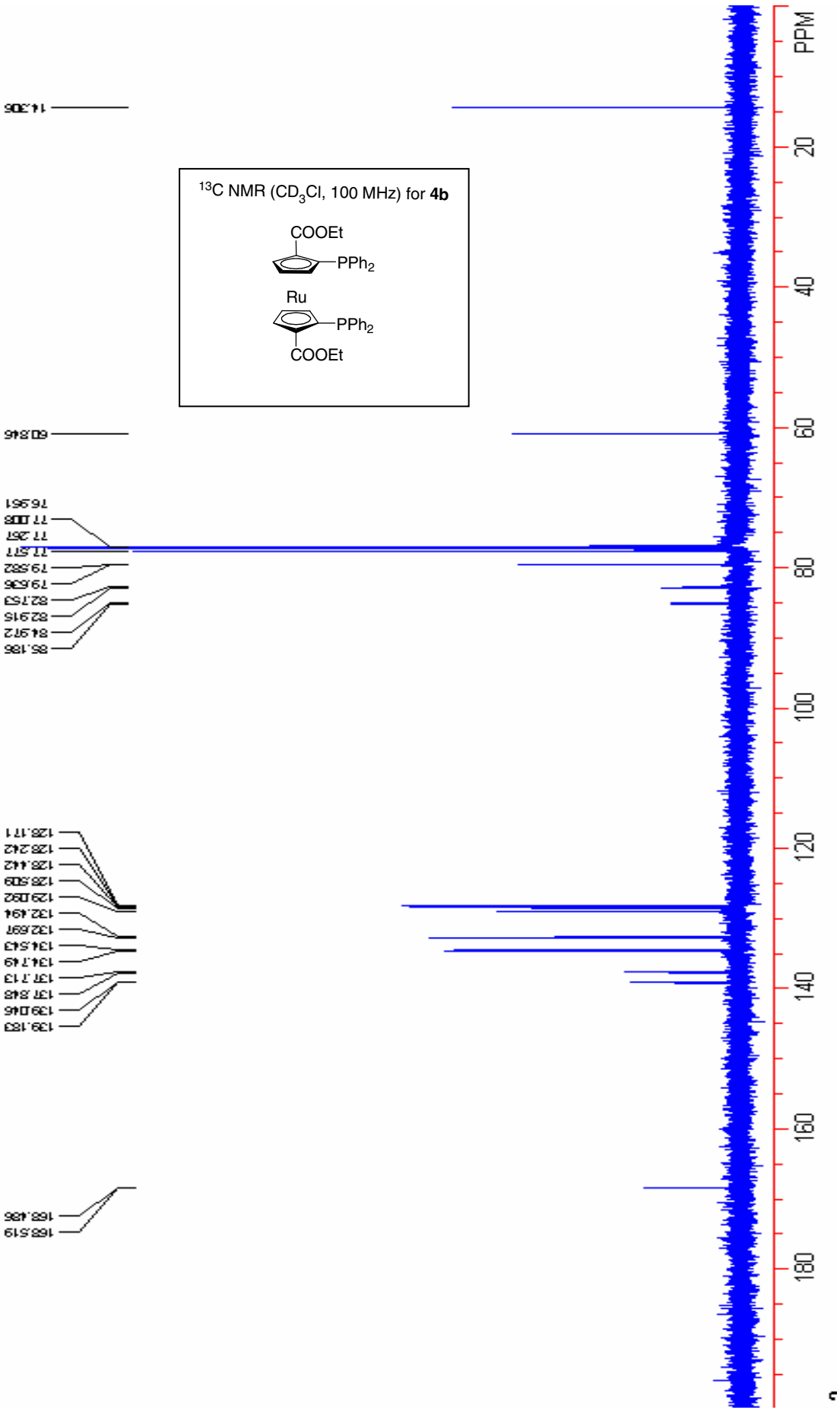
PPh_2
Ru
PPh_2
COOEt



^{31}P NMR (CD_3Cl, 162 MHz) for **4b**


^{13}C NMR (CD_3Cl, 100 MHz) for **4b**
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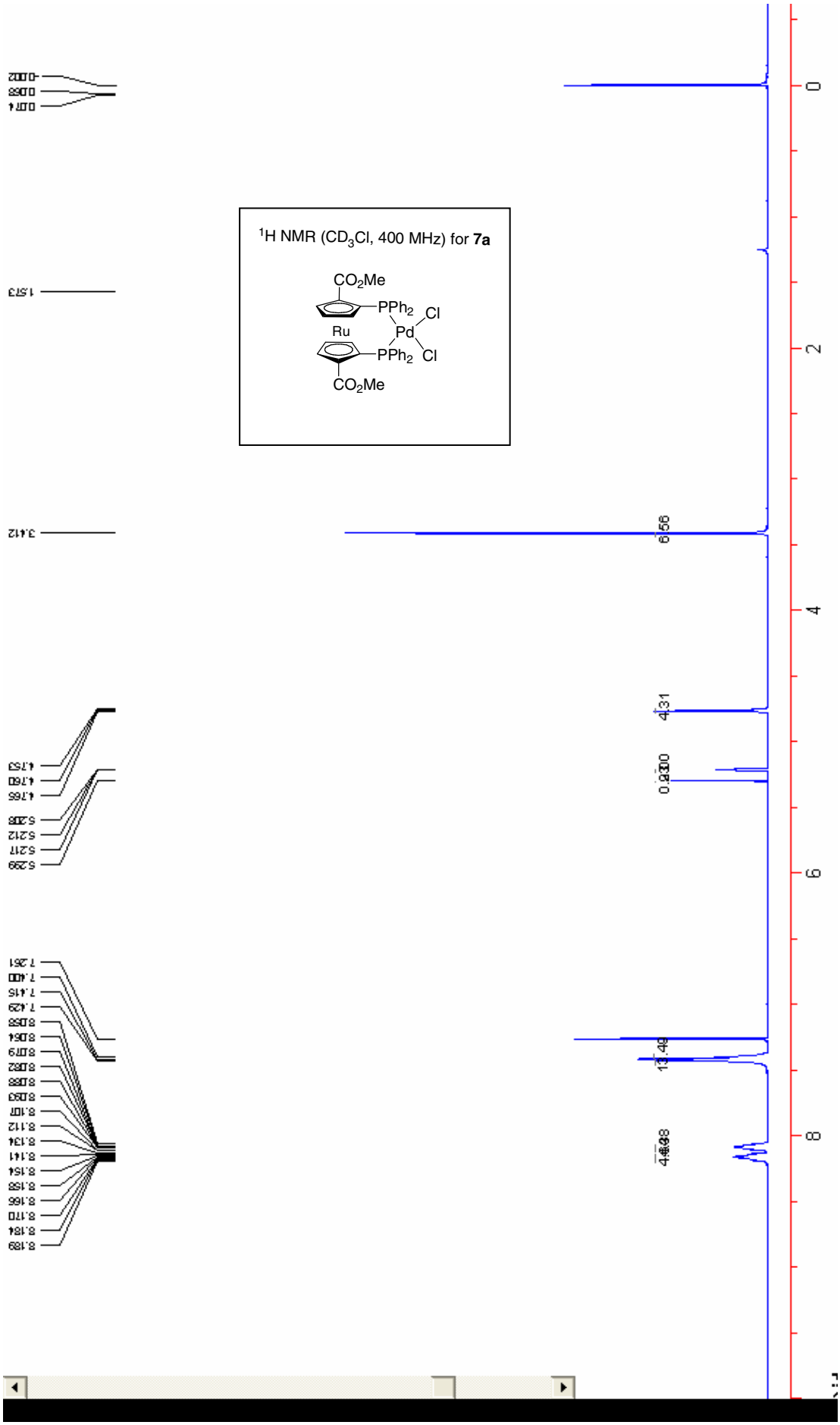
PPh2
Ru
PPh2
COOEt
PPM


^{1}H NMR (CD_3Cl, 400 MHz) for **7a**
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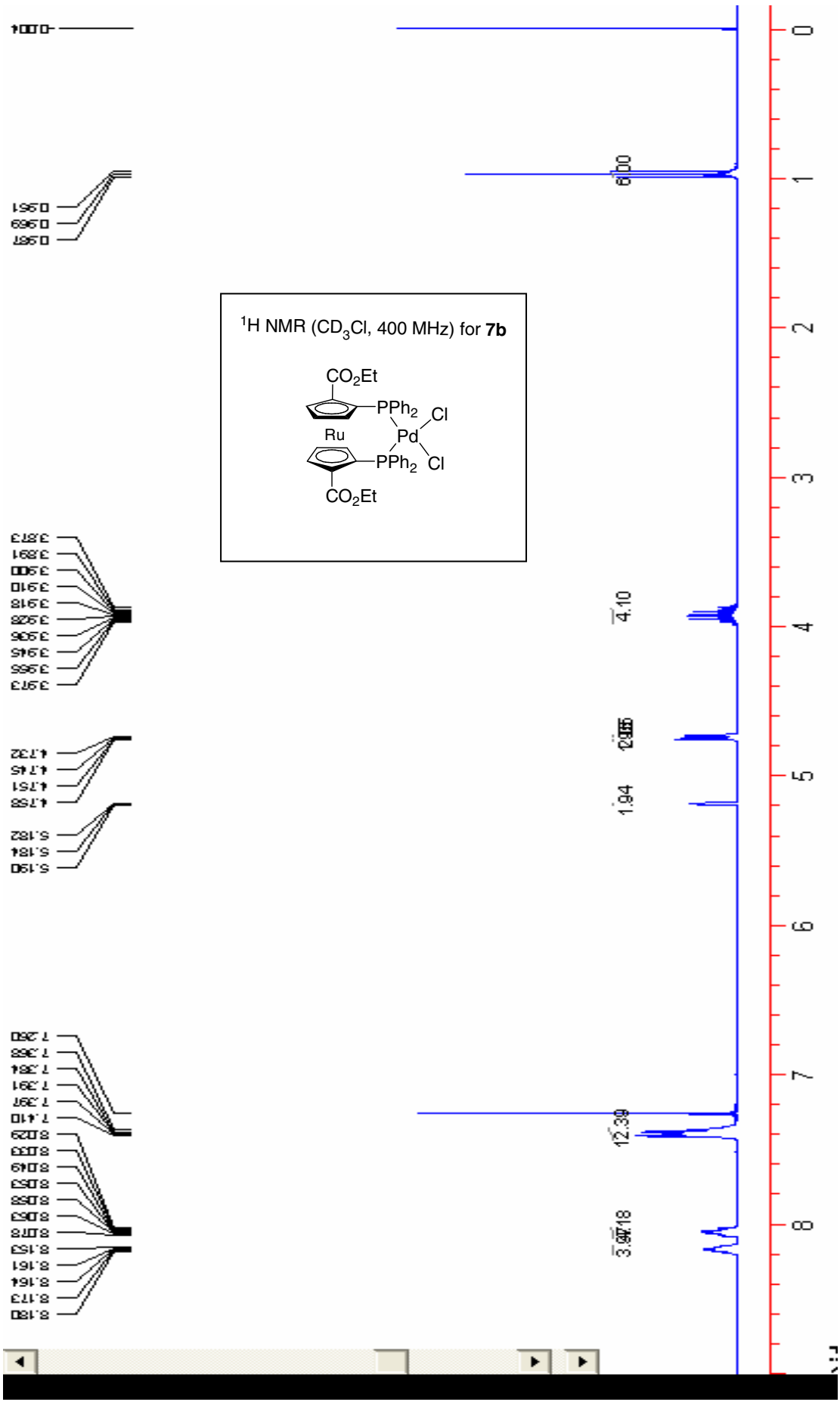
Cl
Ru
Pd
PPh_2
Cl
CO_2Me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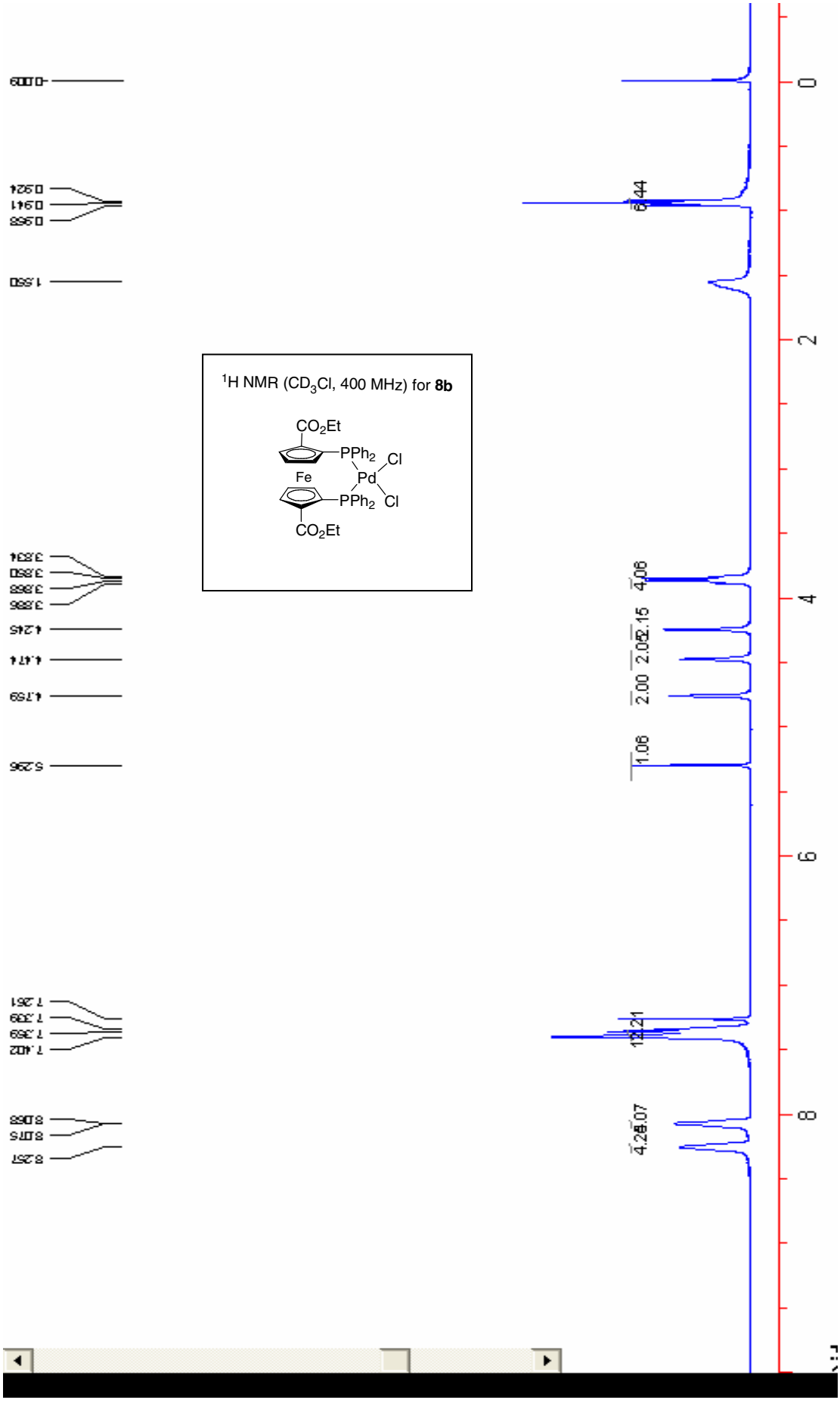
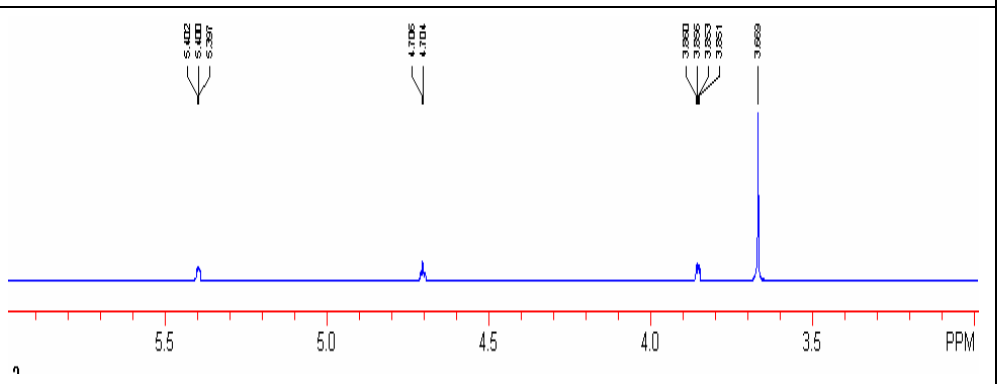
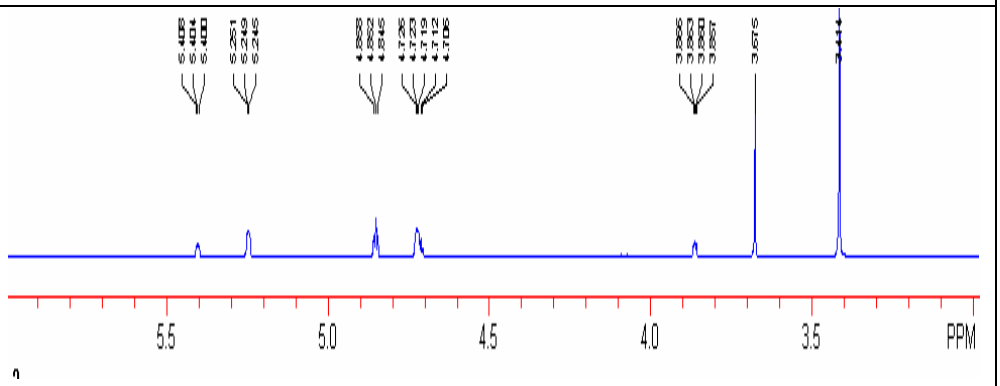
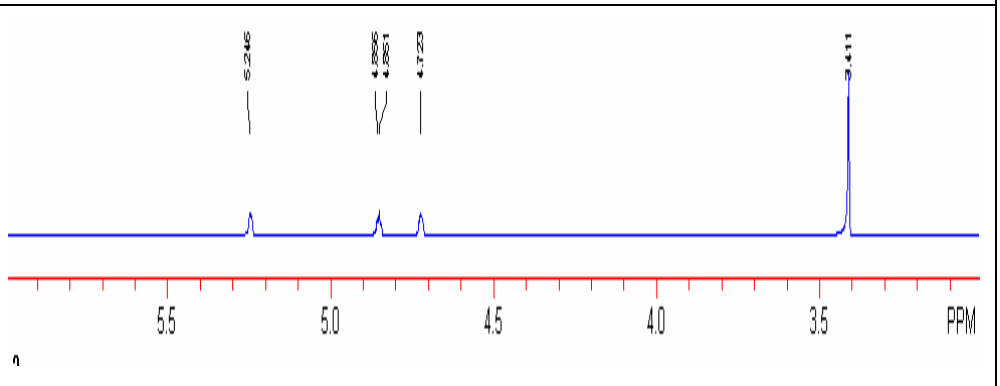
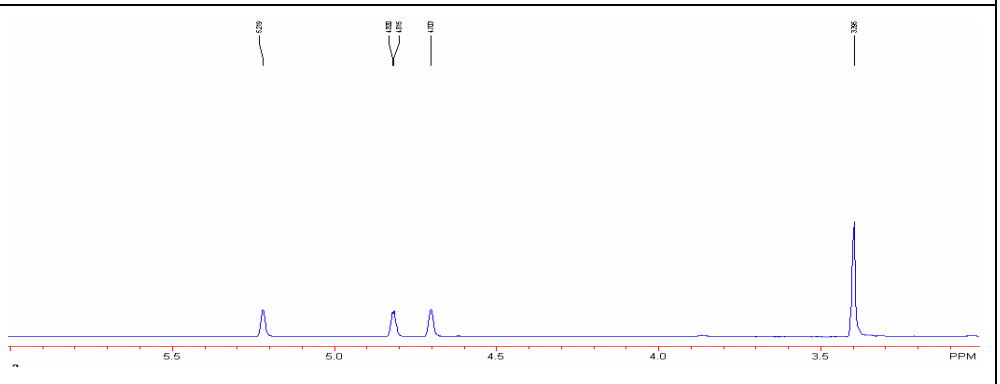
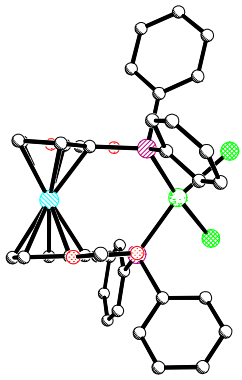
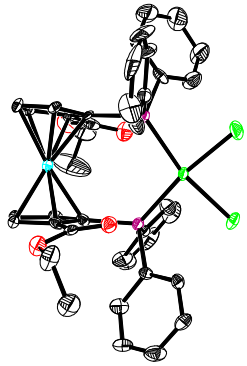
PPh_2
Cl
Ru
Pd
Cl
PPh_2
CO_2Et


1H NMR (CD3Cl, 400 MHz) for 8b
CO2Et
PPh2
Cl
Fe
Pd
PPh2
Cl
CO2Et

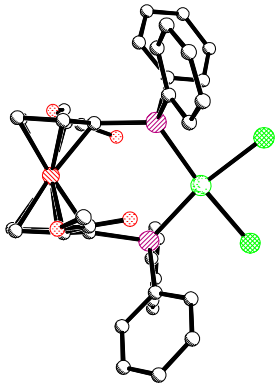
Ligand/ Pd(II)	Complexation Behavior of **4a** with Dichlorobis(acetonitrile)palladium
1 : 0	
1 : 0.5	
1 : 1	
1 : 2	



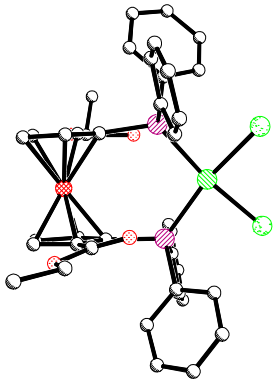
ORTEP view for twist angle of **7a** (twist angle: 23.63°)



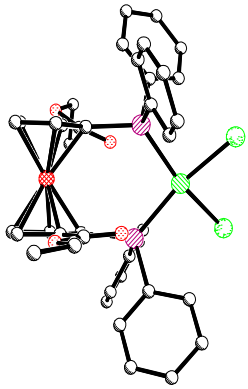
ORTEP view for twist angle of **7b** (twist angle:16.05°)



ORTEP view for twist angle of **8a** (twist angle: 8.15°)



ORTEP view for twist angle of **8b-A** (twist angle: 10.28°)



ORTEP view for twist angle of **8b-B** (twist angle: 16.20°)