Mechanistic Understanding on Rh-Catalyzed *N*-Sulfonylaldimines Insertion to Aryl C-H Bonds

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General Information. If no special indicated, all the reactions were carried out in a Wattecs Parallel Reactor under nitrogen atmosphere. $[Cp^*RhCl_2]_2$ were purchased from Strem. (Cp*2-phenylpyridineRhCl) (**5**)[1] and $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$[2] were prepared according to the literature methods. *t*BuOH was freshly distilled over CaH_2. Acetone used for the catatylst solution in the kinetic research was freshly distilled over $CaSO_4$. Toluene-d_8 used in the kinetic research was freshly distilled over CaH_2. Other reagents and solvents were used as commercially available and without further purification. $AgSbF_6$ was weighted in glove box. NMR Spectra were recorded on a Bruker 500, Bruker 400 or Varian 300 in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm/(CD_3COCD_3 resonance in the ^1H spectrum as 2.05 ppm) and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm/ (CD_3COCD_3 resonance in the ^{13}C spectrum as 30.8 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. FTIR were performed on Fourier transform infrared spectrometer. HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

Reaction of Eq 2.

Eq 2a: The reaction mixture of complex **5** (21.3 mg, 0.05 mmol), imine **2a** (26.0 mg, 0.10 mmol), HOAc (0.05 mmol, 2.9 uL) were stirred in *t*BuOH (0.5 mL) at 90 °C for 4 h. After cooling to rt, the reaction mixture was monitored by TLC and showed no product **3a**.

Eq 2b: The reaction mixture of complex **5** (21.3 mg, 0.05 mmol), imine **2a** (26.0 mg, 0.10 mmol), HOAc (0.05 mmol, 2.9 uL) and $AgSbF_6$ (17.2 mg, 0.05 mmol) were stirred in *t*BuOH (0.5 mL) at 90 °C for 4 h. After cooling to rt, the solvent was removed *in vacuo* and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3a** (3.3 mg, 16% yield) as a white solid.

General Procedure for Synthesis of Complex 6. Method A (Reaction of Eq 3): To the suspension of 427.8 mg of compound (Cp* 2-phenylpyridineRhCl) (**5**) (1.0

mmol) in CH_3CN (5 mL), the solution of $AgSbF_6$ (378.0 mg, 1.1 mmol) of in CH_3CN (15 mL) was added in 2 min and the white solid precipitated immediately. The reaction mixture was stirred for another 30 min at rt. Then the white solid was removed by filtration and the filtrate was evaporated in vacuo. The residue was recrytallized in acetone/Et_2O to afford compound **6** as pale yellow solid (656.9 mg, 98% yield). ^{1}H NMR (300 MHz, CD_3COCD_3): δ 8.97 (d, J = 5.4 Hz, 1H), 8.19-8.07 (m, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.54-7.50 (m, 1H), 7.37-7.31 (m, 1H), 7.24-7.19 (m, 1H), 2.33 (s, 3H), 1.71 (s, 15 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0, 175.6, 167.2, 154.1, 146.5, 141.2 (2C), 138.4, 132.7, 126.2, 126.2 (2C), 125.6, 121.9, 121.8, 100.3, 100.2, 10.2 (5C), 4.1; FTIR (film, cm^{-1}): 2956, 2851, 1459, 1374, 754; HRMS: *m/z*: [Cp*ArRh]$^+$ calculated for $C_{21}H_{23}NRh$: 392.0880, found 392.0885. Crystallographic data of compound **6**: $C_{47}H_{54}Cl_2F_{12}N_4Rh_2Sb_2$, Mr = 1423.16, 173(2) K, yellow, plate, 0.18 x 0.15 x 0.10 mm, Monoclinic, space group *P2(1)/c*, a = 24.200(3), b = 13.4270(16), c = 16.2572(19), β = 95.747(2)°, V = 5256.0(11) Å^3, ρ_{calcd} = 1.799 gcm^{-3}. Z = 4, R_1 = 0.0636 [I>2θ(I)].

Method B (Reaction of Eq 4): To the mixture of $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (50.0 mg, 0.06 mmol) and 2-phenylpyridine (11.2 mg, 0.072 mmol) was added *t*BuOH (5 mL) in a reaction tube. The reaction mixture was stirred at 60 °C for 10 h. After cooling to rt, the solvent was removed *in vacuo* and the residue was detected by ^{1}HNMR (0.06 mmol of CH_2Br_2 was added as an internal standard) and showed ^{1}HNMR yield is 66% based on the signal of 7.37-7.31 and 7.24-7.19 ppm. Most by-product produced in the reaction was identifed as 2-phenylpyridine's $HSbF_6$ based on the comparation of their spectrum.

General Procedure for Synthesis of Complex 8 (Reaction of Eq 5). The suspension of complex **6** (43 mg, 0.064 mmol) and imine **2a** (33.2 mg, 0.128 mmol) in *t*BuOH (4 mL) was stirred at 90 °C for 10 h. After cooling to rt, the solvent was removed *in vacuo*, the residue was washed with Et_2O for several times until TLC showed no existence of compound **2a**. Then the residue was dissolved in DCM (2 mL) and hexane was added to precipitate yellow solid. The solvents were decanted and the solid was dried *in vacuo* to afford complex **8** (53.5 mg, 94% yield). ^{1}H NMR (400

MHz, CD_3COCD_3): δ 9.01-9.00 (m, 1H), 8.42-8.37 (m, 1H), 7.92-7.45 (m, 6H), 7.26-7.13 (m, 8H), 6.88 (d, J = 8.0 Hz, 1H), 5.29 (s, 1H), 2.32 (s, 3H), 1.48 (s, 15H); ^{1}H NMR (75 M, CD_3COCD_3): δ 163.6, 154.1, 145.0, 142.8 (2C), 142.4, 141.9, 141.4, 134.6, 131.9, 131.8, 130.9 (2C), 130.5, 130.1 (2C), 129.9, 129.3, 127.8 (2C), 127.4, 97.7, 97.5, 62.9, 22.4, 22.3, 10.2 (2C), 10.2 (2C); HRMS: *m/z*: $[M\text{-}SbF_6^-]^+$ calculated for $C_{35}H_{36}N_2O_2RhS$: 651.1547, found 651.1555. X-ray quality crystals of **8** was obtained by slow diffusion of a hexane and DCM solution of the above solid at 5 °C. Crystallographic data of complexes **8**: $C_{35}H_{36}F_6N_2O_2RhSSb$, Mr = 887.38, 173(2) K, yellow, plate, 0.50 x 0.40 x 0.20 mm, Monoclinic, space group *P2(1)/c*, a = 18.507(7), b = 10.873(4), c = 17.673(7), β = 103.416(8)˚, V = 3459(2) Å^3, ρ_{calcd} = 1.704 gcm^{-3}. Z = 4, R_1 = 0.1045 [I>2θ(I)].

Reaction of Eq 6.

The reaction of Eq 6 in condition A was carried out in our reported procedure.

The reaction of Eq 6 in condition B. The reaction mixture of complex **6** (7.6 mg, 0.012 mmol), compound **1b** (42.3 mg**,** 0.25 mmol), imine **2a** (130.0 mg, 0.50 mmol), HOAc (0. 012 mmol, 0.7 uL) were stirred in *t*BuOH (1 mL) at 90 °C for 10 h/ 48 h respectively. After cooling to rt, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3c** (73.9 mg, 69% yield, in 10 h; 90.3 mg, 84% yield, in 48 h). Compound **3c** was detected by ^{1}HNMR and GC. Trace compound **3a** only can be oberseved on GC.

Reaction of Eq 7.

The reaction mixture of complex **8** (11.0 mg, 0.012 mmol), compound **1a** (38.8 mg**,** 0.25 mmol), imine **2a** (130.0 mg, 0.50 mmol), HOAc (0. 012 mmol, 0.7 uL) were stirred in *t*-BuOH (1 mL) at 90 °C for 48 h. After cooling to rt, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3a** (70.2 mg, 68% yield).

Reaction of Eq 8

Condition A: The reaction mixture of precatalyst **7** (0.00625 mmol, 5.2 mg), compound **1a** (19.4 mg**,** 0.125 mmol), imine **2a** (64.8 mg, 0.25 mmol), were stirred in

the mixed solvent *t*-BuOH: acetone (0.5 mL : 0.5 mL) at 90 °C for 10 h. Ater cooling to rt, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3a** (31.0 mg, 60% yield).

Condition B: The reaction mixture of complex **6** (0.00625 mmol, 4.2 mg), the solution of HOAc in acetone (10 uL, 0.625 M), compound **1a** (19.4 mg**,** 0.125 mmol), imine **2a** (64.8 mg, 0.25 mmol), were stirred in the mixed solvent *t*-BuOH: acetone (0.5 mL : 0.5 mL) at 90 °C for 10 h. Ater cooling to rt, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3a** (33.7 mg, 65% yield).

Condition C: The reaction mixture of complex **8** (0.00625 mmol, 5.5 mg), the solution of HOAc in acetone (10 uL, 0.625 M), compound **1a** (19.4 mg**,** 0.125 mmol), imine **2a** (64.8 mg, 0.25 mmol), were stirred in the mixed solvent *t*-BuOH: acetone (0.5 mL : 0.5 mL) at 90 °C for 10 h. Ater cooling to rt, the solvent was removed in vacuo and the residue was purified on silica gel chromatography with hexanes/EtOAc/DCM (5:1:1) to afford compound **3a** (33.3 mg, 64% yield).

Reaction of Eq 9.

The mixture of Rh(III) complex **6** (21.0 mg, 0.032 mmol) and imine **2a** (16.6 mg, 0.064 mmol) in *t*-BuOH (1 mL) was stirred at 28 °C for 1 h. Then *t*-BuOH was removed *in vacuo* at rt and the residue was detected by ESI-MS and followed by ^{1}H NMR. In the ESI-MS spectrum, 651.1535 peak was observed as [2-phenylpyridneRhCp*Ts]$^{+}$, in the ^{1}H NMR spectrum, there was no addition complexes **8**'s signal (the single peak at 5.29 ppm in CD_3COCD_3) were observed, then the observed MS peak should be assigned to the coordination complex **9.**

General Procedure for the Protonation of Complex 8 (Reaction of Eq 10).

Condition A: The suspension of complex **8** (22.2 mg, 0.025 mmol), HOAc (2.9 uL, 0.05 mmol) were stirred in *t*-BuOH (1 mL) at 90 °C for 2 h. The reaction was detected by crude ^{1}HNMR and no product signal (6.10 ppm, double peak) was observed. Condition B: The suspension of complex **8** (22.2 mg, 0.025 mmol), compound **1a** (38.8 mg, 0.25 mmol) were stirred in *t*-BuOH (1 mL) at 90 °C for 2 h and detected by

crude ^{1}HNMR, showed that ratio of compound **3a** to **8** is 2 :1 (based on the integration ratio of 6.10 ppm's peak and 5.29 ppm's peak).

Condition C: The suspension of complex **8** (22.1 mg, 0.025 mmol), compound **1a** (38.8 mg, 0.25 mmol) and HOAc (2.9 uL, 0.05mmol) were stirred in *t*-BuOH (1 mL) at 90 °C for 2 h and detected by crude ^{1}HNMR, showed only product **3a** was observed (obvious peak at 6.10 ppm was observed and no peak was observed at 5.29 ppm).

Condition D: The suspension of complex **8** (22.1 mg, 0.025 mmol), pyridine (19.8 mg**,** 0.25 mmol) and HOAc (2.9 uL, 0.05mmol) were stirred in *t*-BuOH (1 mL) at 90 °C for 2 h and detected by crude ^{1}HNMR, showed only product **3a** was observed (obvious peak at 6.10 ppm was observed and no peak was observed at 5.29 ppm).

After completion of hydrolysis, the reaction mixture of condition B was also detected by ESI-MS, showed the obvious peak (392.0880) as the regenerate the possible active catalyst ([2-phenylpyridineRhCp*]$^+$).

Kinetic research:

Comparison of the initial rates of 2-phenylpyridine, 2-[d_1]-phenylpyridine, 2-[d_5]-phenylpyridine.

In a Young Low Pressure/Vacuum NMR tube, precatalyst **7** solution in acetone (1.25 x 10 $^{-3}$ mmol, 250 μL) was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875 x 10 $^{-3}$ mol, 5 μL), used as an internal standard, 2-phenylpyridine (**1a**) or 2-[d_1]-phenylpyridine or 2-[d_5]-phenylpyridine solution in toluene-d_8 (0.025 mmol, 50 μL), tosylimine **2a** solution in toluene-d_8 (0.05 mmol, 200 μL) and toluene-d_8 (150 μL) were added in sequence. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure 1.Then the ratio of k_{HH}/ k_{HD}/ k_{DD} = 1.11 : 1.00 : 1.05.

Kinetic characterization of 2-phenylpyridine.

In a Young Low Pressure/Vacuum NMR tube, precatalyst **7** solution in acetone (1.25 x 10 $^{-3}$ mmol, 250 μL) was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875 x

10^{-3} mol, 5 μL), used as an internal standard, 2-phenylpyridine (**1a**) solution in toluene-d_8 [varied between 24.69 mM (0.4 equiv, 20 μL) and 98.77 mM (1.6 equiv, 80 μL)], tosylimine **2a** solution in toluene-d_8 (0.025 mmol, 100 μL) and toluene-d_8 were added in sequence, keeping the total volume of solution at 405 μL. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure S1a and Plotting ln k_{obs} versus ln[2-phenylpyridine], as presented in Figure S1b.

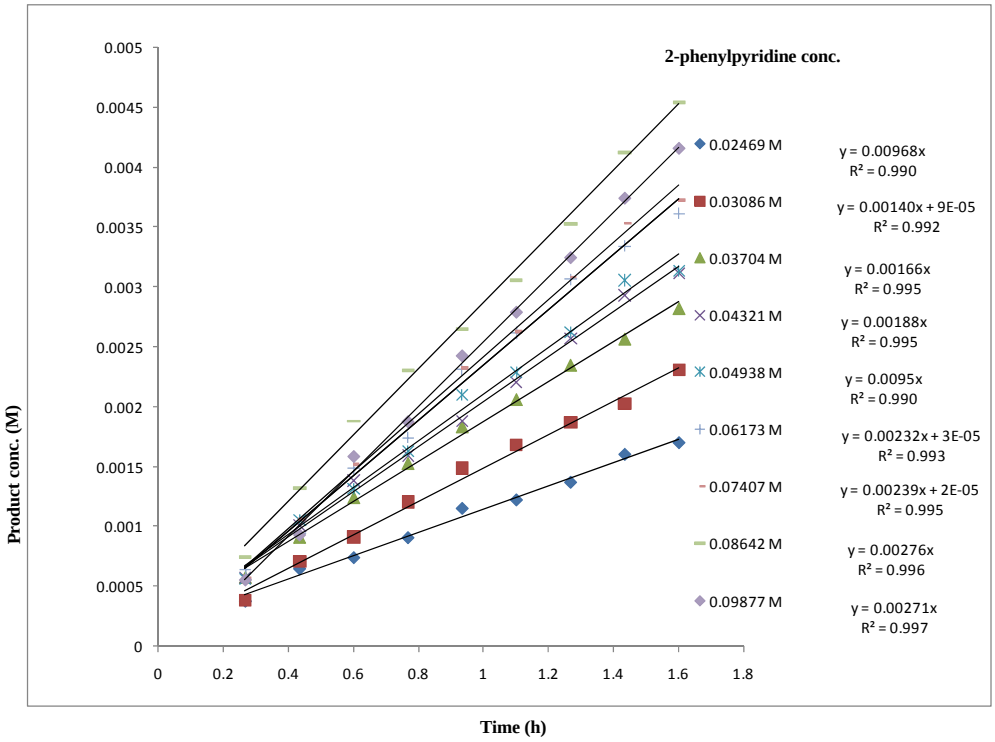

Figure S1a. Product concentration versus time

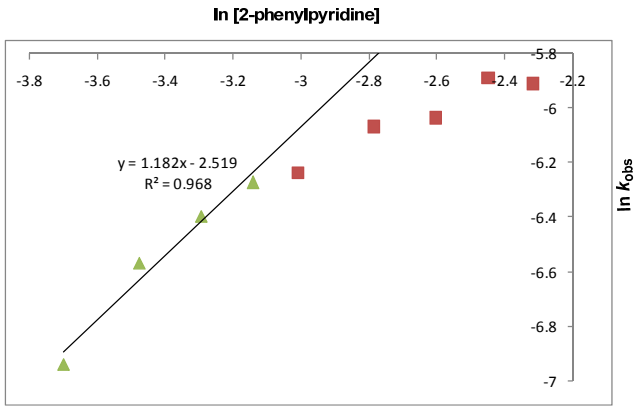

Figure S1b. ln kobs versus ln [2-phenylpyridine]

Kinetic characterization of imine 2a.

In a Young Low Pressure/Vacuum NMR tube, the precatalyst **7** solution in acetone (1.25 x 10^{-3} mmol, 250 µL) was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875 x 10^{-3} mol, 5 µL), used as an internal standard, 2-phenylpyridine (**1a**) solution in toluene-d_8 (0.025 mmol, 50 µL), tosylimine **2a** solution in toluene-d_8 [varied between 43.21 mM (0.7 equiv, 70 µL) and 166.67 mM (2.7 equiv, 270 µL)] and toluene-d_8 were added in sequence, keeping the total volume of solution at 405 µL. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure S2a and Plotting ln k_{obs} versus ln[**2a**], as presented in Figure S2b.

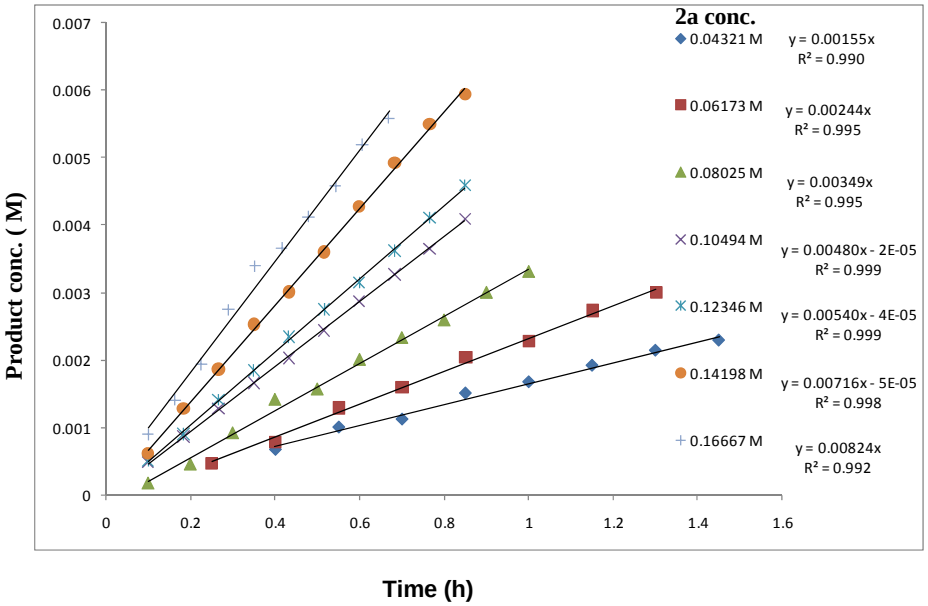

Figure S2a. Product concentration versus time

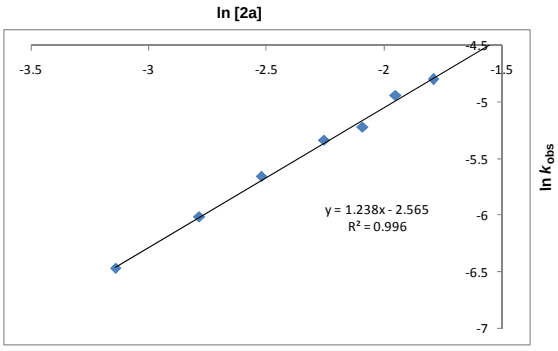

Figure S2b ln kobs versus ln [2a]

Kinetic characterization of precatalyst 7.

In a Young Low Pressure/Vacuum NMR tube, precatalyst **7** solution in acetone [varied between 1.23 mM (2 mol%, 100 μL) and 4.23 mM (7 mol%, 350 μL)] was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875×10^{-3} mol, 5 μL), used as an internal standard, 2-phenylpyridine (**1a**) solution in toluene-d_8 (0.025 mmol, 50 μL), tosylimine **2a** solution in toluene-d_8 (0.050 mmol, 200 μL) and toluene-d_8 were added in sequence, keeping the total volume of solution at 405 μL. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure S3a. Plotting ln k_{obs} versus ln $[Cp^*Rh(CH_3CN)_3][SbF_6]_2]$, as presented in Figure 3b.

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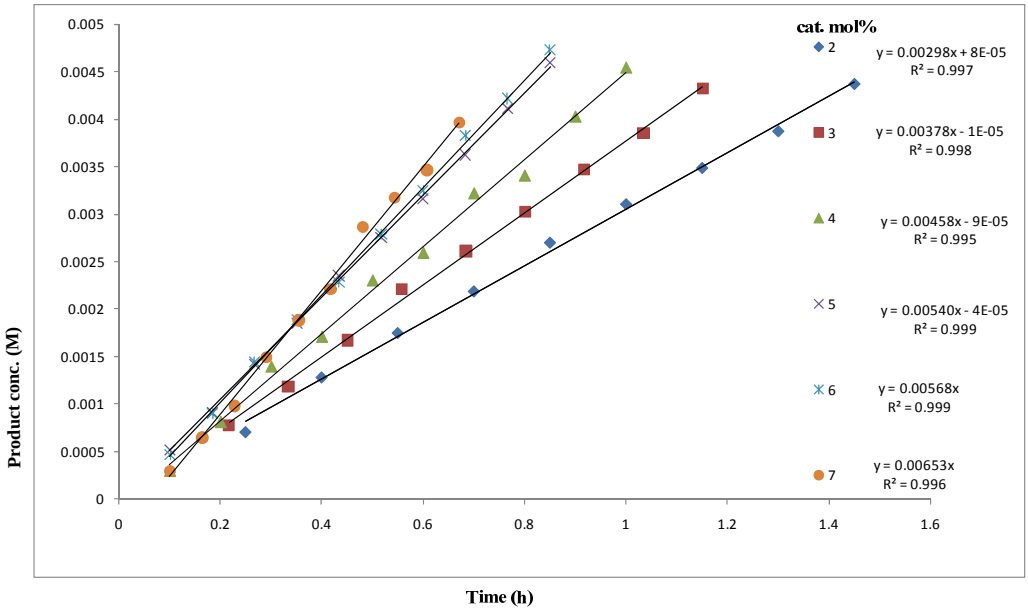

Figure S3a. Product concentration versus time

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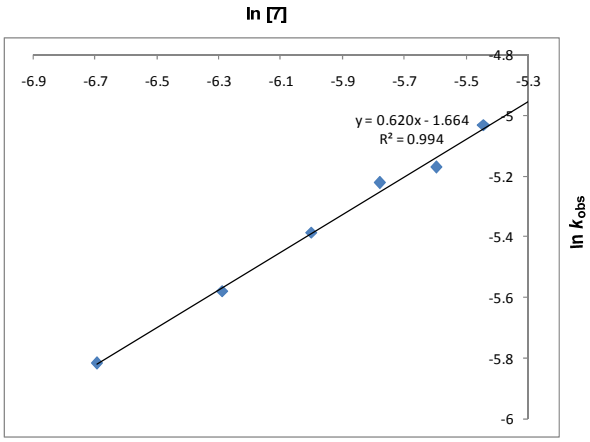

Figure 3b. ln k_{obs} versus ln [**7**]

Kinetic characterization of complex 6.

In a Young Low Pressure/Vacuum NMR tube, complex **6** solution in acetone [varied between 1.23 mM (2 mol%, 100 μL) and 4.23 mM (7 mol%, 350 μL)] was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875 x 10^{-3} mol, 5 μL), used as an internal standard, 2-phenylpyridine (**1a**) solution in toluene-d_8 (0.025 mmol, 50 μL), tosylimine **2a** solution in toluene-d_8 (0.050 mmol, 200 μL), HOAc solution in toluene-d_8 [varied between 1.23 mM (2 mol%, 4 μL) and 4.23 mM (7 mol%, 14 μL)] and toluene-d_8 were added in sequence, keeping the total volume of solution at 405 μL. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure S4. Plotting ln k_{obs} versus ln[6], as presented in Figure 2a.

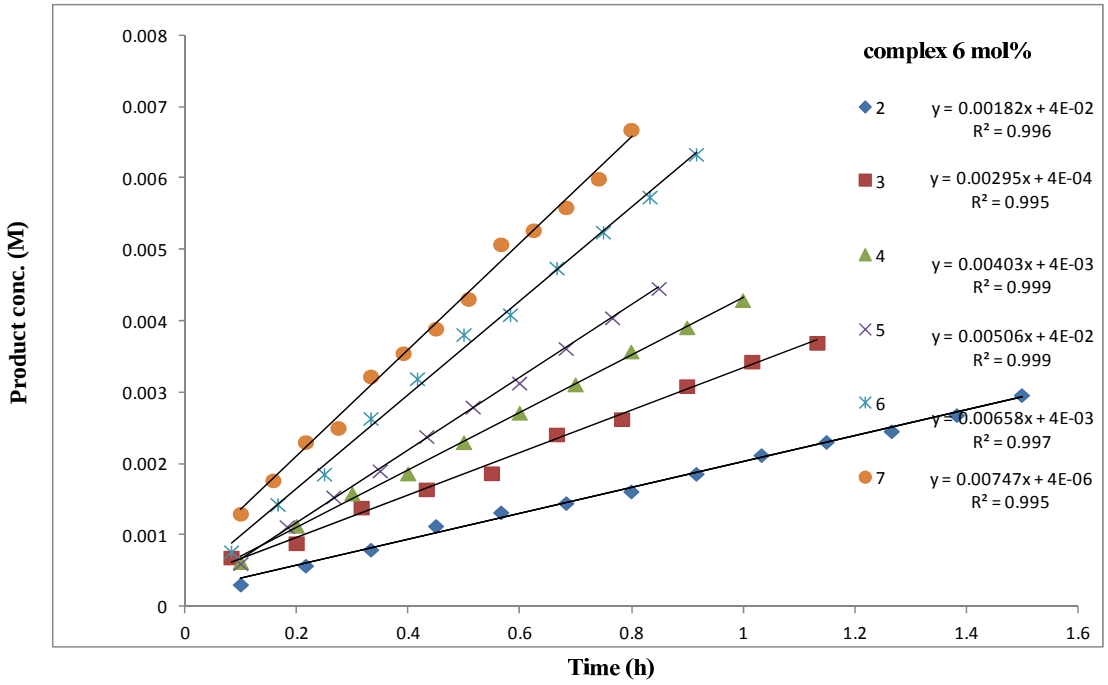

Figure S4. Product concentration versus time

Kinetic characterization of complex 8.

In a Young Low Pressure/Vacuum NMR tube, complex **8** solution in acetone [varied between 1.23 mM (2 mol%, 100 μL) and 4.23 mM (7 mol%, 350 μL)] was added. Then acetone was removed in *vacuo* and the NMR tube was charged with N_2. Then benzyl methyl ether in mesitylene solution (1.875 x 10^{-3} mol, 5 μL), used as an internal standard, 2-phenylpyridine (**1a**) solution in toluene-d_8 (0.025 mmol, 50 μL), tosylimine **2a** solution in toluene-d_8 (0.050 mmol, 200 μL), HOAc solution in toluene-d_8 [varied between 1.23 mM (2 mol%, 4 μL) and 4.23 mM (7 mol%, 14 μL)] and toluene-d_8 were added in sequence, keeping the total volume of solution at 405 μL. After the addition, the NMR tube was sealed in N_2 atmosphere and detected by Bruker 500 M Hz NMR instrument that had been equilibrated at 90°C. The product concentration (M) versus time (h) as showed in Figure S5. Plotting ln k_{obs} versus ln[**8**], as presented in Figure 2b.

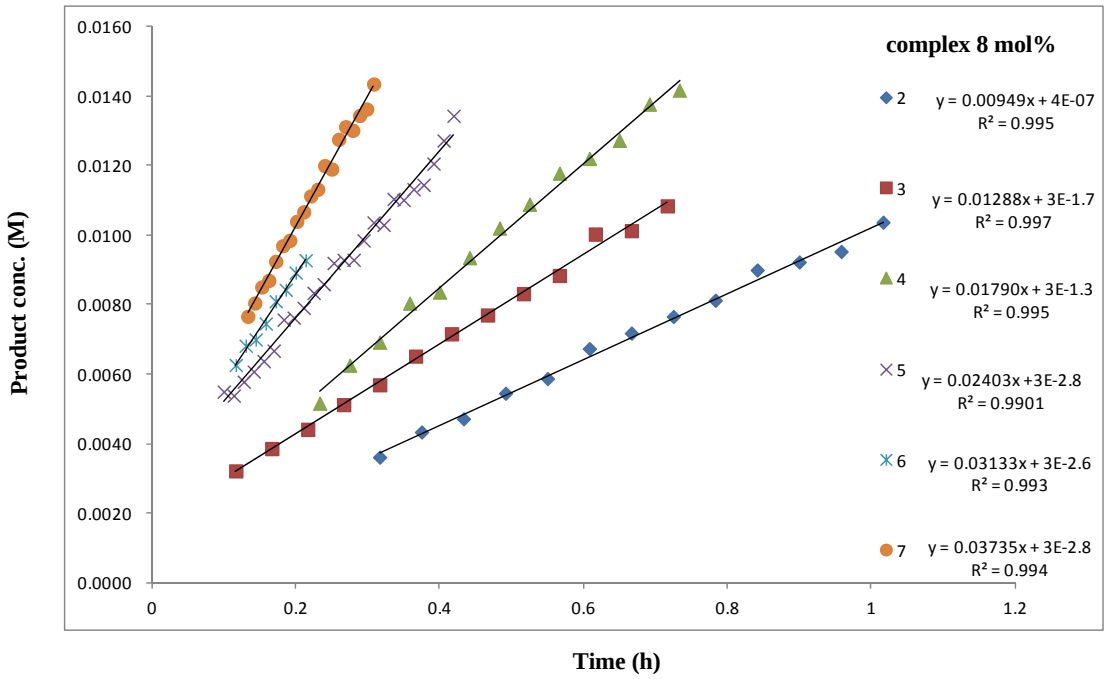

Figure S5. Product concentration versus time

Detection of reaction constant of the insertion step.

Complex **6** (0.00625 mmol, 4.2 mg), Tosimine **2a** (0.0625 mmol, 16.2 mg) and *t*BuOH (0.50 mL) were added to a reaction tube in sequence. Such 6 reaction tubes were stirred in a Wattecs Parallel Reactor in the same time at 90°C at the same time. The reactions were quenched by ice-water bath at 2 min, 4 min, 6 min, 8 min, 10 min, 12 min, respectively. The residue was transformed to a flask by acetone, the solvent was removed in vacuo below 30°C. Then benzyl methyl ether in mesitylene solution was added as an internal standard. The reaction mixture was detected by Bruker 400 M Hz NMR instrument. Plotting ln[**6**] versus time, as presented in Figure 6.

The tries to detect the reaction constant of protonolysis step.

Complex 8 (0.00625 mmol, 5.5 mg), 2-phenylpyridine **1a** (0.0625 mmol, 8.9 uL) and *t*BuOH (0.50 mL) were added to a reaction tube in sequence, the reaction tube was put into the parallel reactor which had been equilibrated at 90°C. After that, HOAc (0.0625 mmol, 3.6 uL) was added immediately. The reaction was quenched by ice-water bath at 1 min. The residue was transformed to a flask by acetone, the solvent was removed in vacuo below 30°C. Then benzyl methyl ether in mesitylene solution was added as an internal standard. The reaction mixture was detected by

Bruker 400 M Hz NMR instrument. ^{1}HNMR spectrum showed the full conversion with 107% ^{1}HNMR yield. The same reaction was also conducted at 30°C, ^{1}HNMR spectrum also showed the full conversion with 110% ^{1}HNMR yield.

References:

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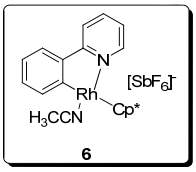
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Rh
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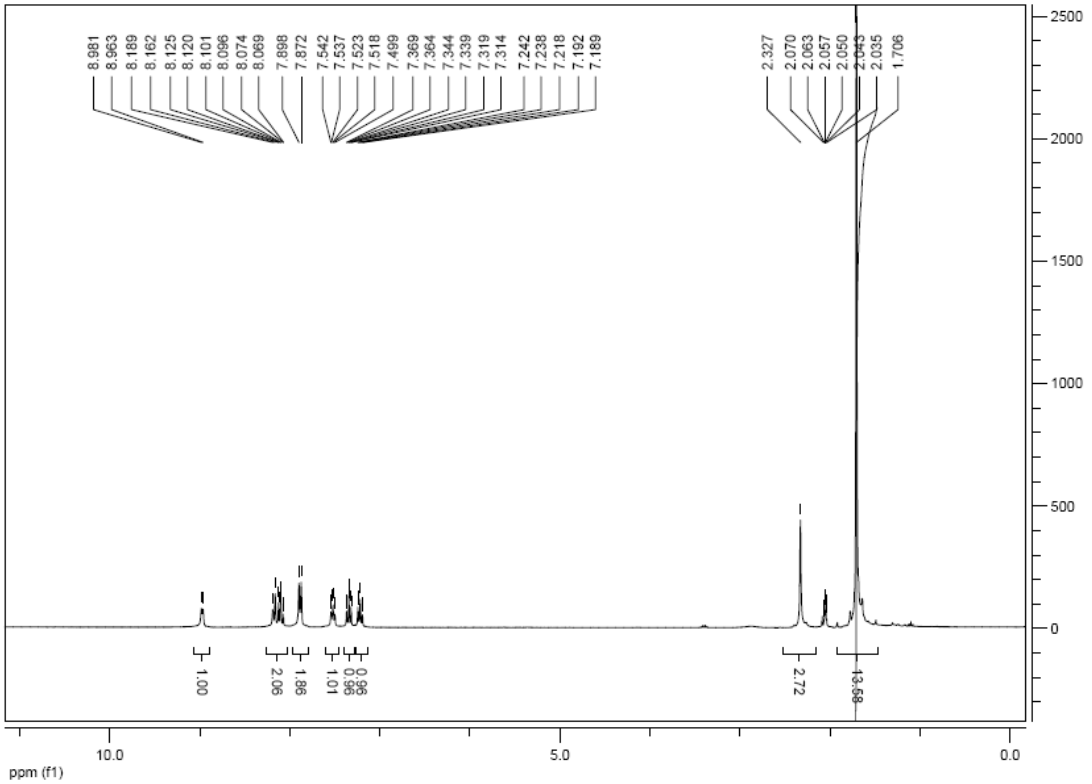
H3CCN
Cp*

6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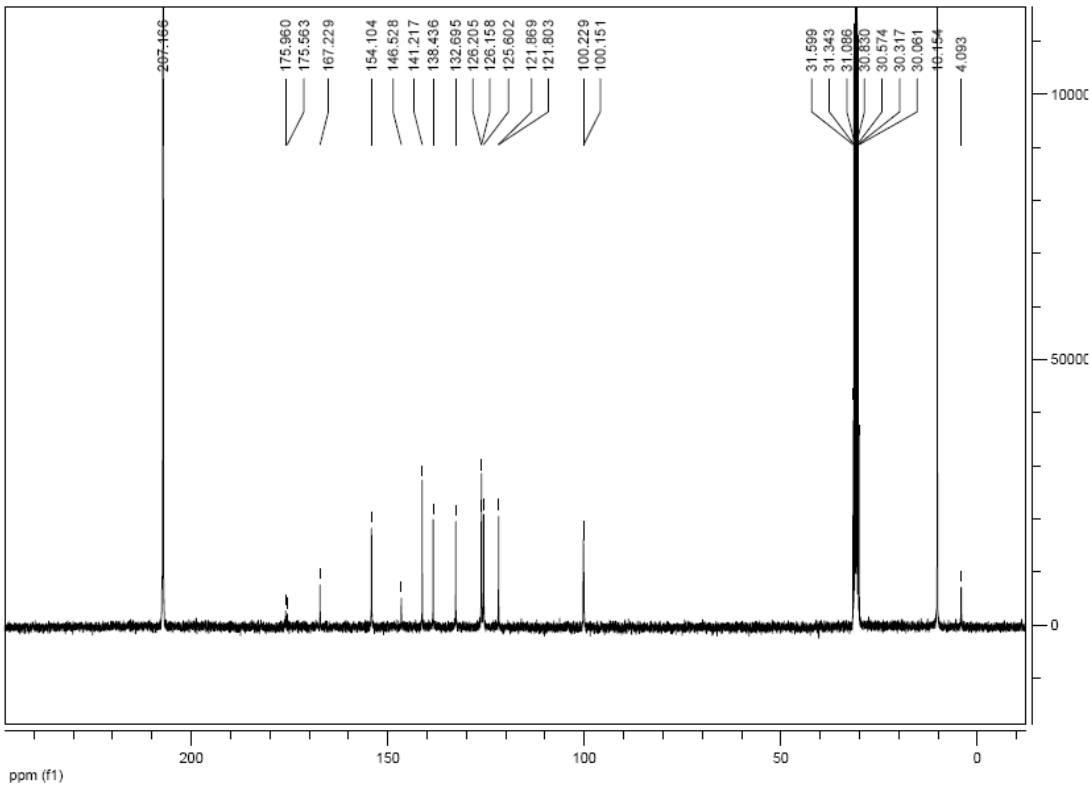
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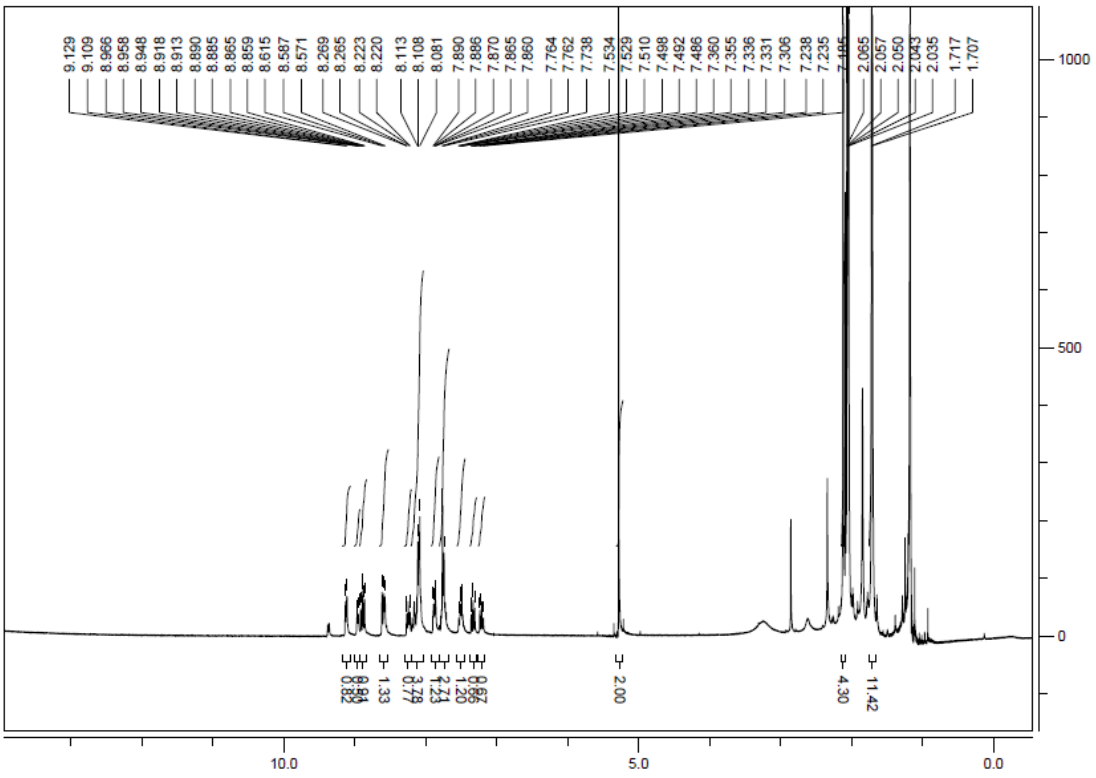
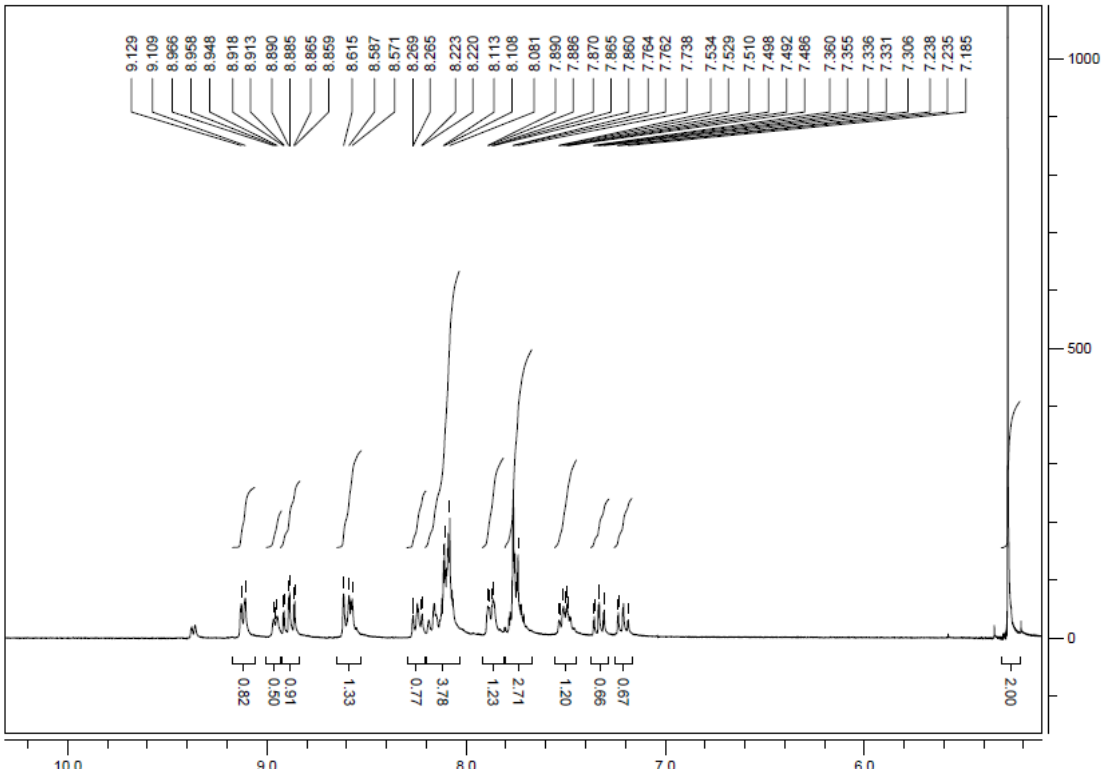
125.602
121.869
121.803
100.229
100.151
31.599
31.343
31.086
30.830
30.574
30.317
30.061
16.154
4.093
10000
5000
0
200
150
100
50
0
ppm (f1)

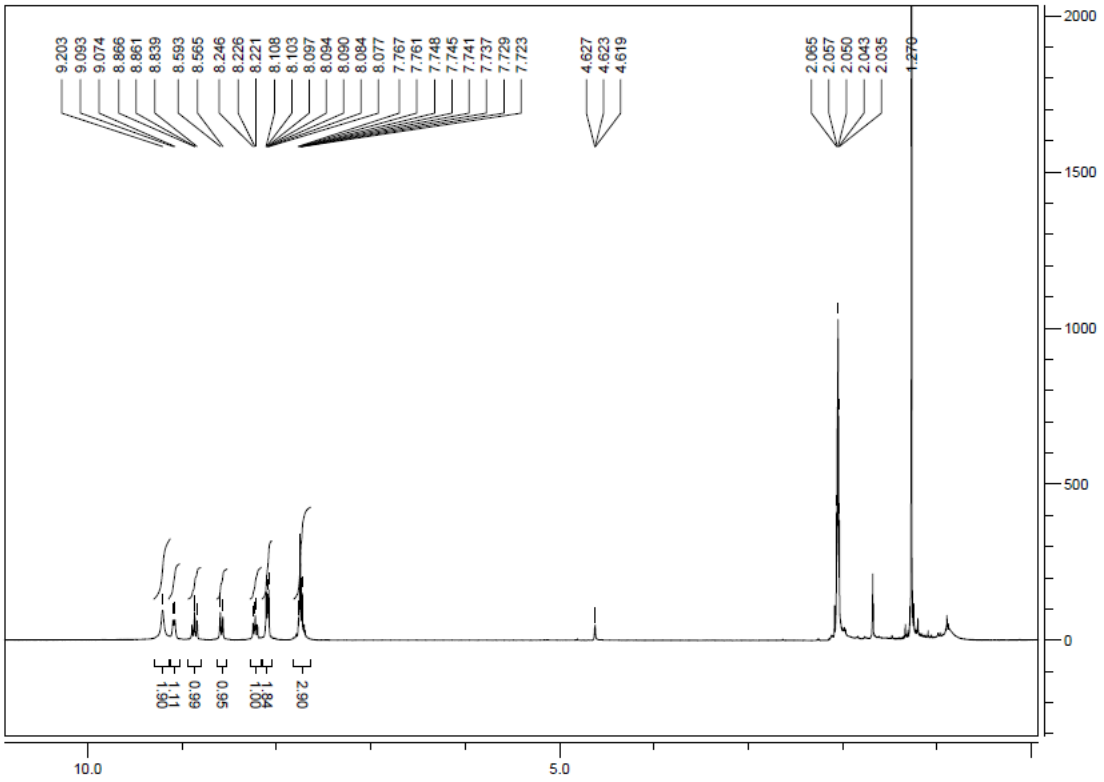
The crude ^{1}H NMR for the synthesis of complex **6** using *t*-BuOH (0.06 mmol of CH_2Br_2 was added as inner standard) as slovent. The most by-product was 2-phenylpyridine.$HSbF_6$ salt based on the salt's NMR as below.

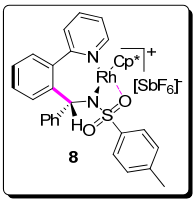


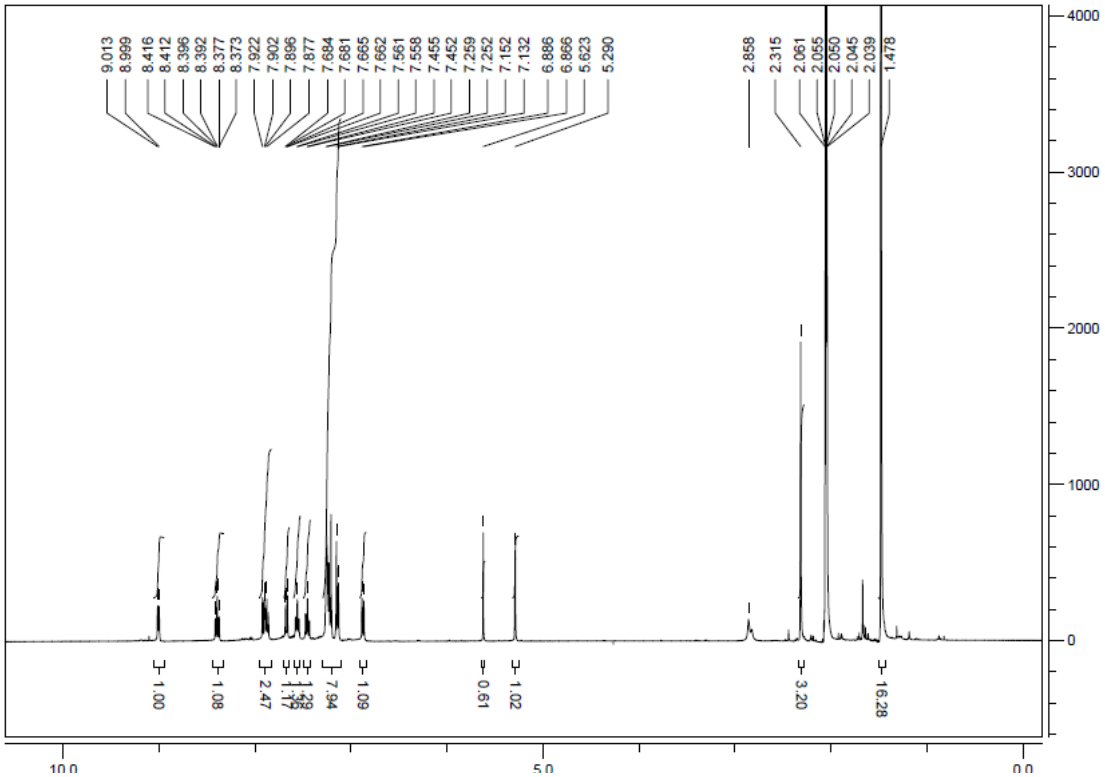
Expanded spectrum of **6**

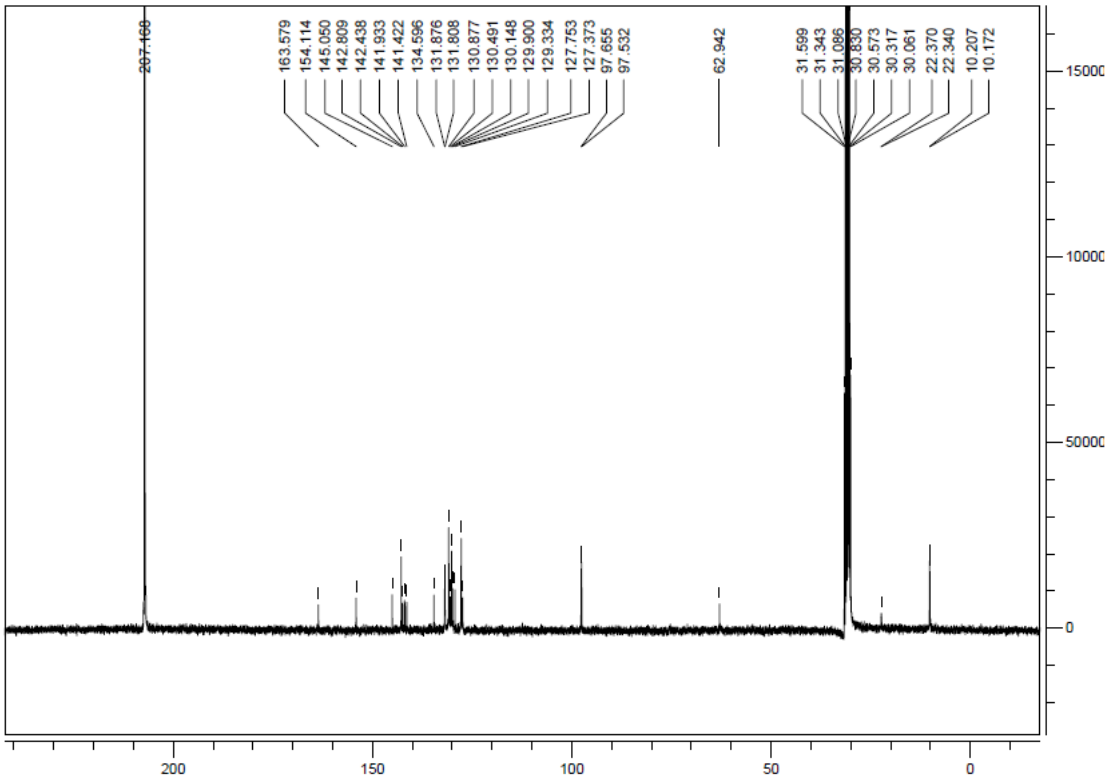


2-Phenylpyridine.$HSbF_6$ salt's ^{1}HNMR included some *t*-BuOH.

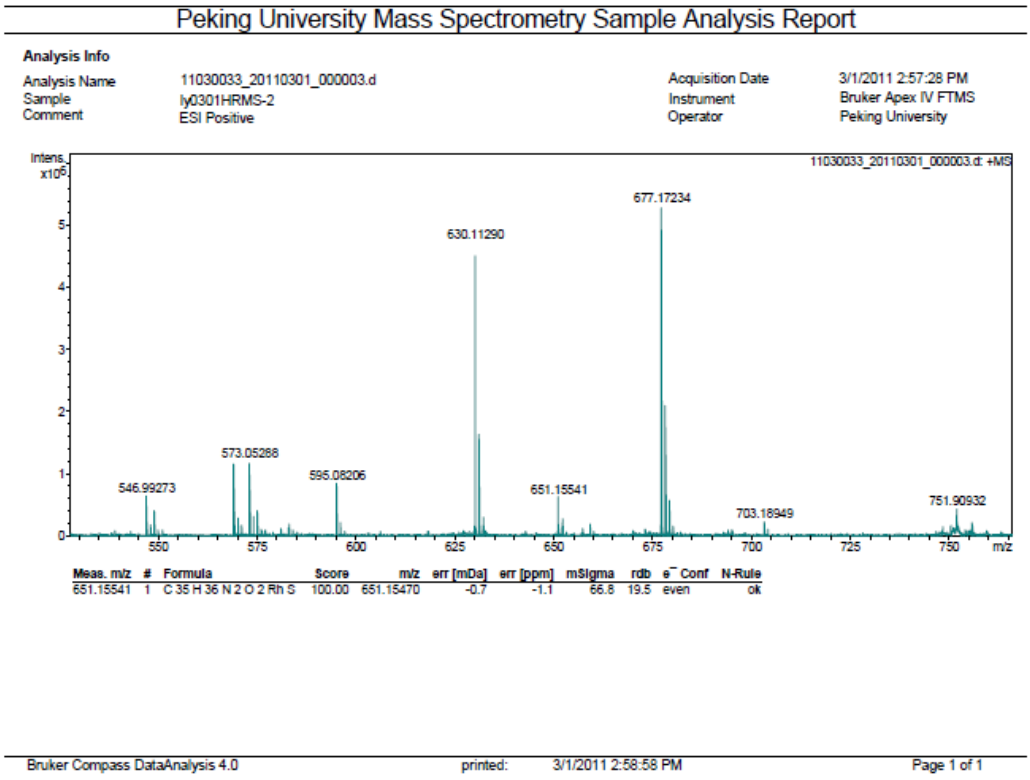



N
Cp*
+
Rh
[SbF6]-
N
O
Ph
H
O
S
8

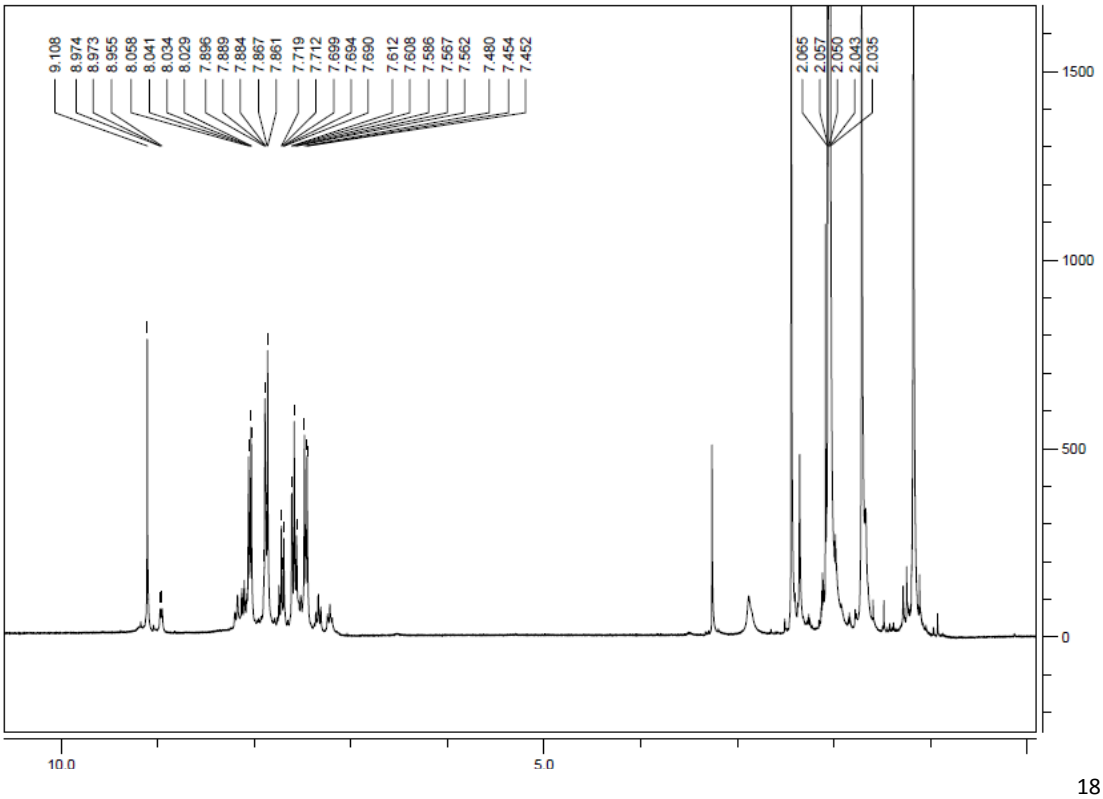

9.013
8.999
8.416
8.412
8.396
8.392
8.377
8.373
7.922
7.902
7.896
7.877
7.684
7.681
7.665
7.662
7.561
7.558
7.455
7.452
7.259
7.252
7.152
7.132
6.886
6.866
5.623
5.290
2.858
2.315
2.061
2.055
2.050
2.045
2.039
1.478
1.00
1.08
2.47
7.94
1.09
0.61
1.02
3.20
16.28
4000
3000
2000
1000
0
10.0
5.0
0.0


207.168
163.579
154.114
145.050
142.809
142.438
141.933
141.422
134.596
131.876
131.808
130.877
130.491
130.148
129.900
129.334
127.753
127.373
97.655
97.532
62.942
31.599
31.343
31.086
30.830
30.573
30.317
30.061
22.370
22.340
10.207
10.172
150000
100000
50000
0
200
150
100
50
0

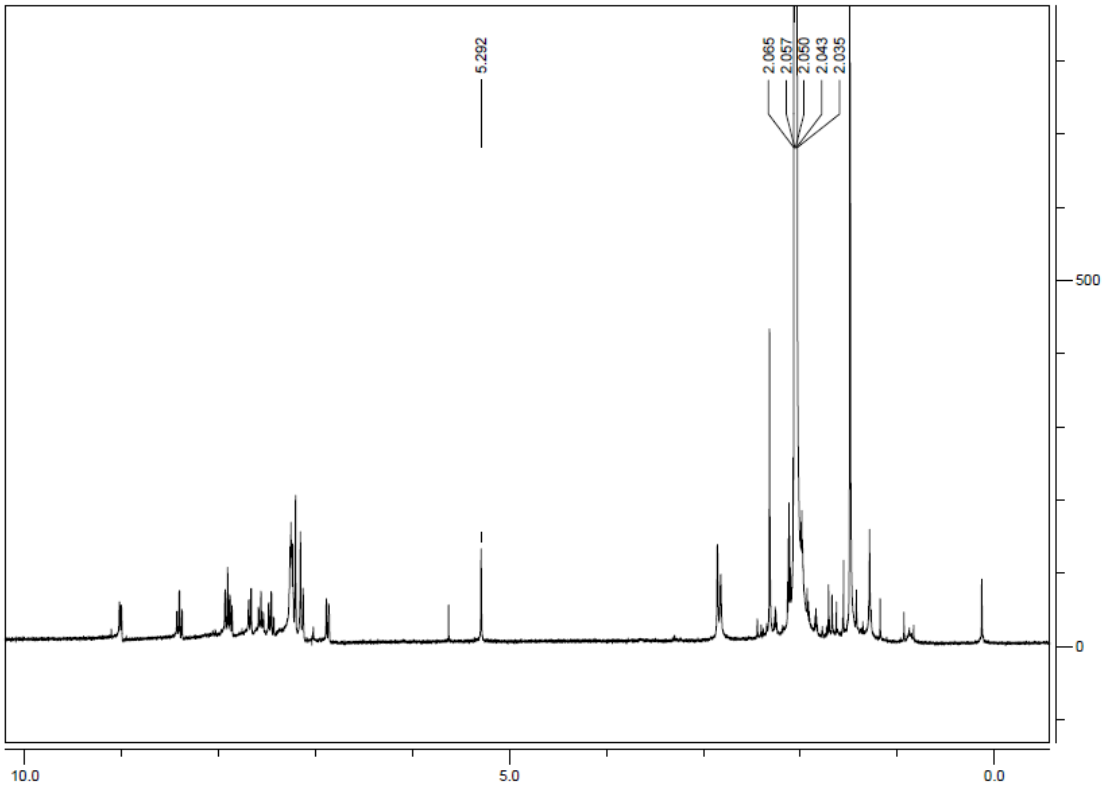
Detection of coordination of sulfonylimine to key intermediate **6** by *in-situ* ESI-MS



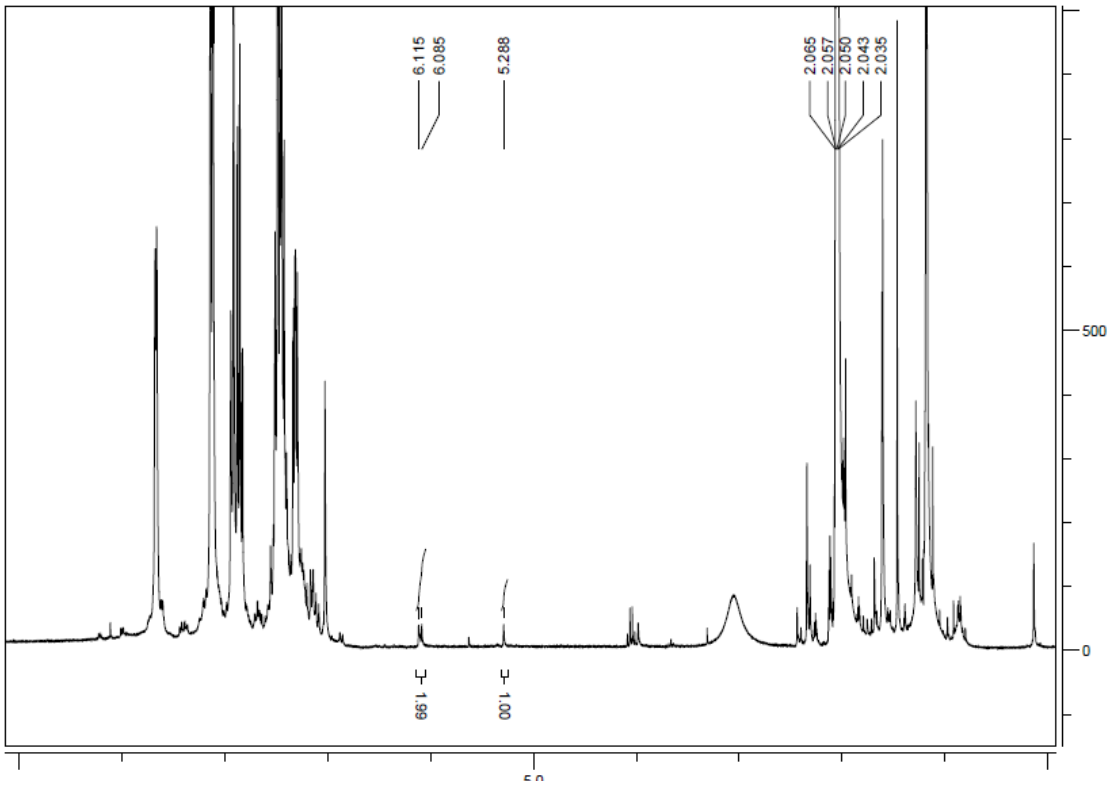
The ^{1}H NMR spectrum after ESI-MS detection (No the characteristic peak of complex **8** (5.29 ppm) was observed, the spectrum only showed the simple combination of complex **6** and the Tosimine **2a** with some *t*-BuOH)



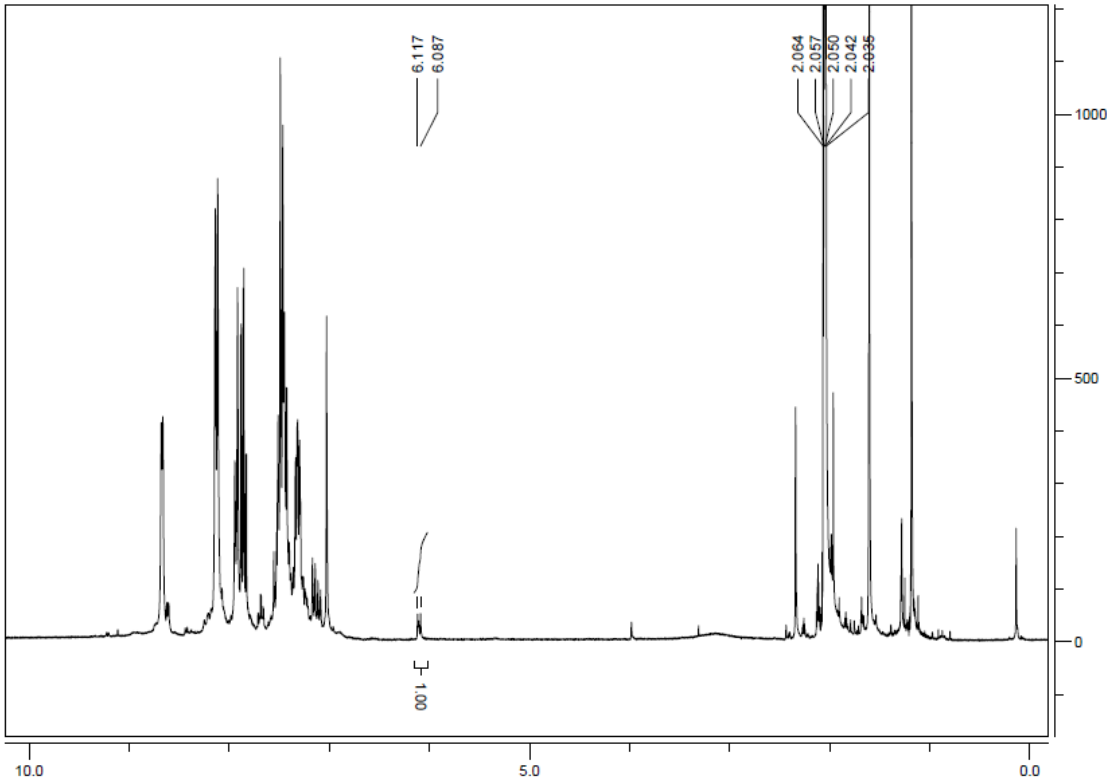
Crude ^{1}HNMR of protonation in condition A, no product peak (6.10 ppm) was observed.



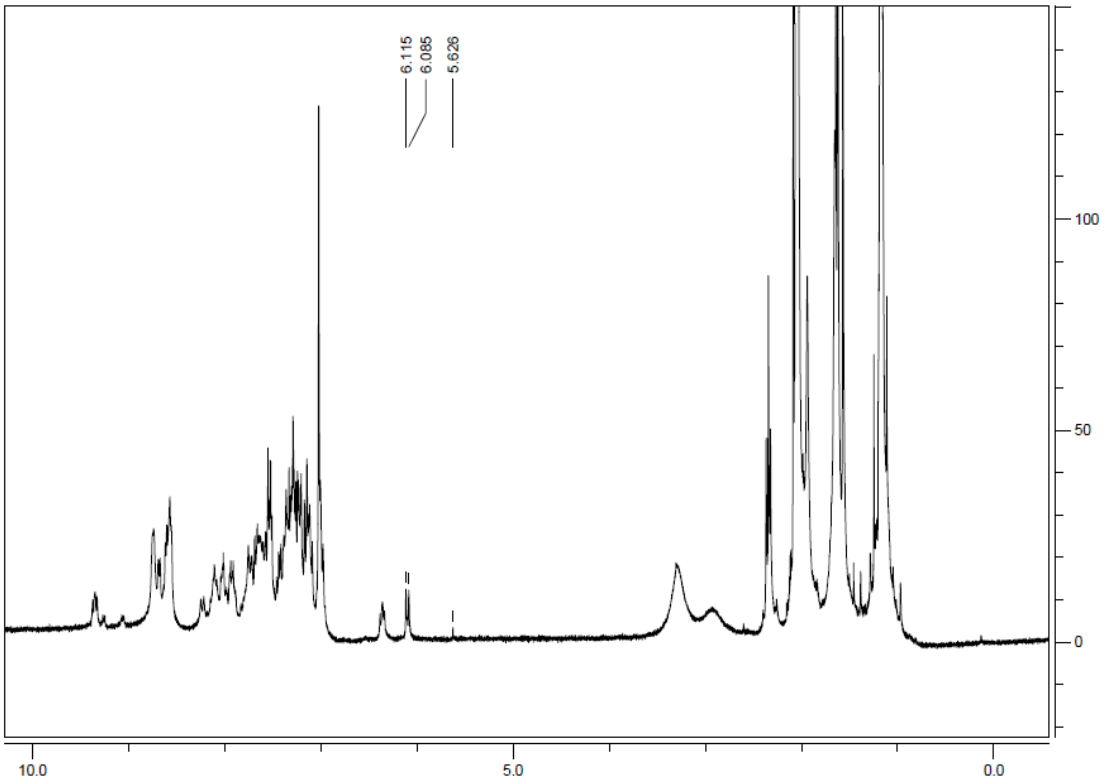
Crude ^{1}HNMR of protonation in condition B, the ratio of **3a** (6.10 ppm) to **8** (5.29 ppm) is 2.0 :1**.**



Crude ^{1}HNMR of protonation with in condition C, no complex **8** was observed and only compound **3a** was observed.



Crude ^{1}HNMR of protonation in condition D, no complex **8** was observed and only compound **3a** was observed.

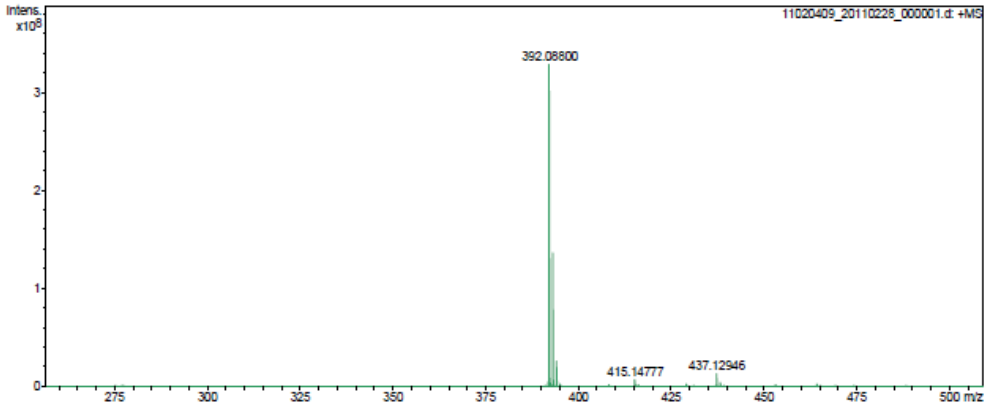


Detection of hydrolysis in condition B by ESI-MS.

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

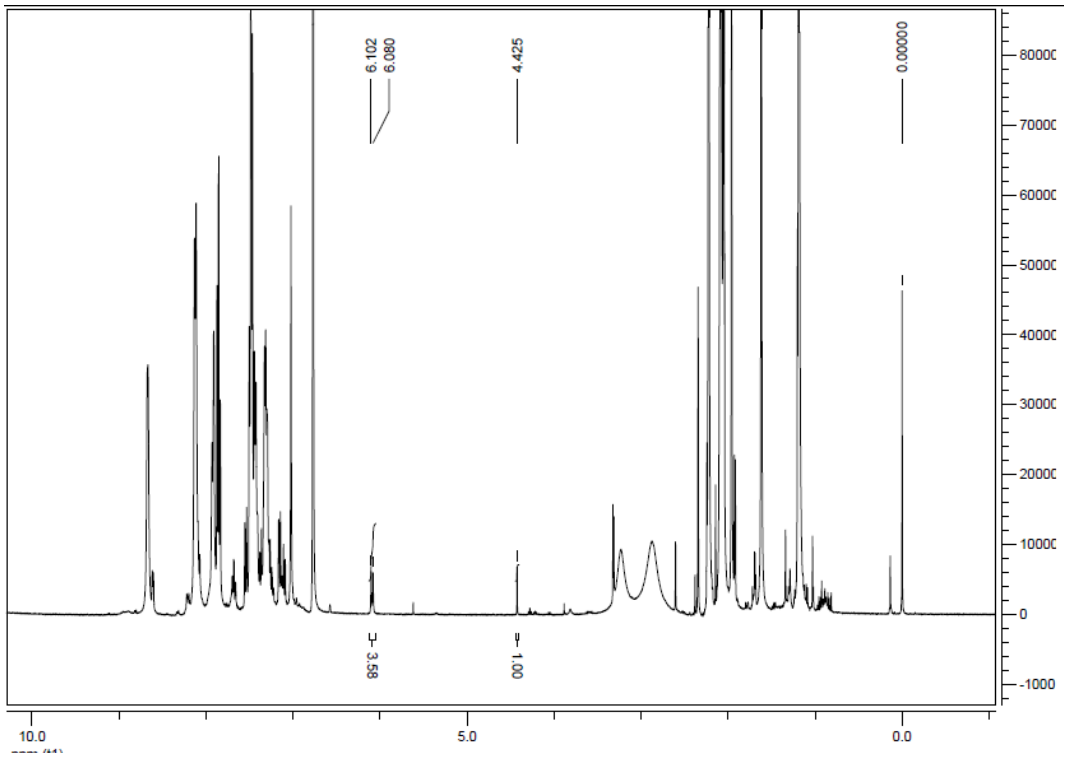
Analysis Name	11020409_20110228_000001.d	Acquisition Date	2/28/2011 4:23:54 PM
Sample	ly0228	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
392.08800	1	C 21 H 23 N Rh	100.00	392.08801	0.0	0.0	117.8	11.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 2/28/2011 4:29:23 PM Page 1 of 1

The protonolysis of complex **8** in the presence of **1a** (10 eq.) and HOAc (10 eq.) in *t*BuOH at 90°C in 1 min. [1] HNMR yield = 30% x 3.58= 107%. No complex **8** peak (5.29 ppm) was observed.



The protonolysis of complex **8** in the presence of **1a** (10 eq.) and HOAc (10 eq.) in *t*BuOH at 30°C in 1 min. [1] HNMR yield = 30% x 3.67= 110%. No complex **8** peak (5.29 ppm) was observed.