Mild Uncatalyzed Hydroamination of an Electrophilic Alkyne, Ethynylcobalticinium

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Supplementary Material

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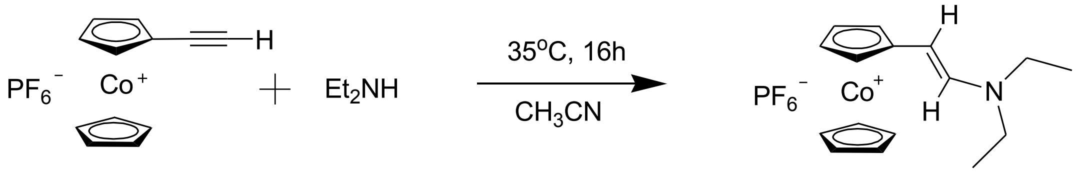
General Information.

Reagent-grade THF, diethyl ether, and pentane were dried over Na foil and distilled from sodium benzophenone anion under nitrogen immediately prior to use. DCM was distilled from calcium hydride and distilled under nitrogen prior to use. CH_3CN was dried over P_2O_5 and distilled under nitrogen prior to use. All other solvents and chemicals were used as received. ^{1}H NMR spectra were recorded at 25°C with a Bruker AC (200, 300, or 600 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 or 150 MHz with a Bruker AC 300 or 600 spectrometer. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si for the ^{1}H and ^{13}C NMR spectra. ^{31}P stands for ^{31}P (^{1}H) in the data, with chemical shifts referenced to H_3PO_4. The mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. The elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France. UV−vis. absorption spectra were measured with Perkin-Elmer Lambda 19 UV− vis. Spectrometer. Electrochemical measurements (CV) were recorded on a PAR 273 potentiostat under nitrogen atmosphere.

Experimental section:

Synthesis of 2

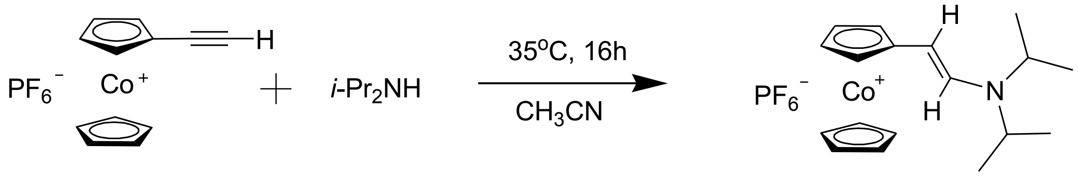


1 **2**

Ethynyl cobalticenium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry CH_3CN, then diethylamine (7.3mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum and the hydroamination product **2** was obtained as a deep red solid without further purification (43.0mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 1.20 (t, 6H, CH_3), 3.31 (m, 4H, CH_2), 4.89 (d, J = 13.44Hz, 1H,), 5.47 (s, 5H,Cp), 5.67 (t , 2H/C_5H_4), 5.68 (t , 2H/C_5H_4), 7.47 (d, J = 13.44Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.89 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}:.12.64 (CH_3), 20.13 (CH_2), 73.06 (2C/C_5H_4), 81.30 (2C/C_5H_4), 82.54 (CH), 84.30 (Cp/unsub.), 117.78 (C/C_5H_4), 146.71 (CH), 29.21, 205.34 $(CD_3)_2CO$). ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.14 (m, PF_6^-). IR (KBr): 1614 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} (ν_{PF6}^-). ESI: calc. *m/z* for M^+ ($C_{16}H_{21}CoN^+$) 286.1, found 286.1. UV-vis.: $\lambda_{max\ 1}$ = 425nm, $\lambda_{max\ 2}$ = 500nm; Anal.Calcd for $C_{16}H_{21}CoNPF_6 \cdot 0.5H_2O$: C, 43.65; H, 5.04; N, 3.18. Found: C, 43.81; H, 4.88; N, 2.81.

Alternatively, the same amount of **1** was dissolved in 10mL of diethylamine, then the color immediately changed from yellow to red and the reaction mixture was further stirred for one hour at 35°C. The remaining (excess) amine was removed under vacuum. The yield was quantitative, and the product was checked by ^{1}H NMR indicating the absence of starting material.

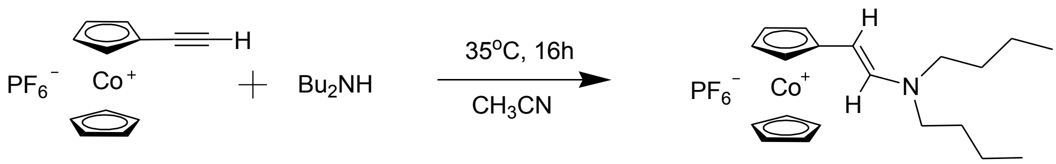
Synthesis of 3



1 **3**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol) was dissolved in 10mL of dry CH_3CN, then diisopropylamine (10.1mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **3** was obtained as a deep red solid without further purification (45.8mg, yield = 99%). Crystals of **3** were obtained using the vaporization method: compound **3** was dissolved in 5mL of CH_3CN in a small container. Place this receptacle inside a larger one that contains 30ml of Et_2O and seal the outer vessel well. The crystals were collected from the inside wall of the inside container after 24h. ^1H NMR (600 MHz, $CDCl_3$), δ_{ppm}: 1.26 (d, 12H, CH_3), 3.74 (m, 1H), 4.83 (d, J = 13.50Hz, 1H), 5.34 (s, 5H,Cp), 5.50 (t , 2H/C_5H_4), 5.60 (t , 2H/C_5H_4), 7.21 (d, J = 13.50Hz, 1H), 7.28 (s, $CDCl_3$), 1.64 (s, H_2O). ^{13}C NMR (150 MHz, $CDCl_3$), δ_{ppm}: 21.36 (CH_3), 48.28 (CH), 72.61 (2C/C_5H_4), 81.06 (2C/C_5H_4), 84.17 (CH), 84.96 (Cp/unsub.), 118.12 (C/C_5H_4), 142.59 (CH), 76.80, 77.02, 77.23 ($CDCl_3$). ^{31}P NMR (121 MHz, $CDCl_3$),δ_{ppm}: -144.11 (m, PF_6^-). IR (KBr): 1608 cm^{-1} ($\nu_{C=C}$), 839 cm^{-1} (ν_{PF6^-}). ESI: calc. *m/z* for M^+ ($C_{18}H_{25}CoN^+$) 314.33, found 314.1. UV-vis.**:** $\lambda_{max\ 1}$ = 420nm, $\lambda_{max\ 2}$ = 505nm; Anal.Calcd for $C_{18}H_{25}CoNPF_6$: C, 47.7; H, 5.49; N, 3.05. Found: C, 47.5; H, 5.82; N, 2.99. Alternatively, the reaction was conveniently conducted without solvent and yielding a quantitative yield of product as indicated in the synthesis of compound **2**.

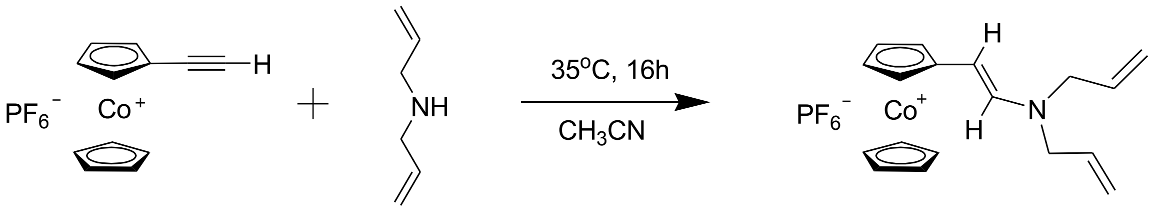
Synthesis of 4



1 **4**

Ethynyl cobaltocenium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry CH_3CN, then dibutylamine (12.9mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **4** was obtained as a deep red solid without further purification (48.5mg, yield = 99%). ^1H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.96 (t, 6H, CH_3), 1.35 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 3.24 (t, 4H, CH_2), 4.89 (d, J = 13.44Hz, 1H), 5.44 (s, 5H, Cp), 5.66 (t , 2H/C_5H_4), 5.79 (t , 2H/C_5H_4), 7.49 (d, J = 13.44Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.92 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.21 (CH_3), 19.73 (CH_2), 73.04 (2C/C_5H_4), 81.32 (2C/C_5H_4), 82.46 (CH), 84.28 (Cp/unsub.), 117.20 (C/C_5H_4), 147.84 (CH), 29.50, 205.42 $(CD_3)_2CO$). ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-). IR (KBr): 1614 cm^{-1} ($\nu_{C=C}$), 835 cm^{-1} (ν_{PF6^-}). ESI: calc. *m/z* for M^+ ($C_{20}H_{29}CoN$) 342.3, found 342.2, UV-vis.: $\lambda_{max\ 1}$ = 415nm, $\lambda_{max\ 2}$ = 496nm, k = 8.45× 10^{-3} s^{-1}; Anal.Calcd for $C_{20}H_{29}CoNPF_6$: C, 49.29; H, 2.87; N, 6.00. Found: C, 48.75; H, 2.85; N, 6.25. Alternatively, the reaction was conveniently conducted without solvent and yielding a quantitative yield of product as indicated in the synthesis of compound **2**.

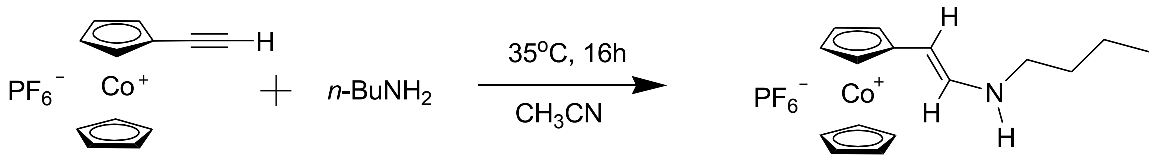
Synthesis of 5



1 **5**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry CH_3CN, diallylamine (9.7mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product was obtained as a deep red solid without further purification (45.0mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 3.88 (t, 4H), 4.93 (d, J = 13.50Hz, 2H), 5.21 (m, 4H), 5.48 (s, 5H, Cp), 5.67 (t , 2H/C_5H_4), 5.81 (t , 2H/C_5H_4), 5.92 (m, 2H), 7.51 (d, J = 13.50Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.90 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 53.34 (CH_2), 73.98 (2C/C_5H_4), 81.66 (2C/C_5H_4), 84.42 (CH), 84.55 (Cp/unsub.), 116.00 (C/C_5H_4), 116.96 (2C), 132.92 (2C), 146.88 (CH), 29.25, 205.42 $(CD_3)_2CO$). ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-). IR (KBr): 1615 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} (ν_{PF6^-}); ESI: calc. *m/z* for M^+ ($C_{18}H_{21}CoN$) 310.1, found 310.1. UV-vis.: $\lambda_{max\ 1}$ = 417nm, $\lambda_{max\ 2}$ = 495nm. Anal.Calcd for $C_{18}H_{21}CoNPF_6$ 0.8 pentane: C, 51.51; H, 6.01; N, 2.73. Found: C, 51.49; H, 5.64; N, 3.03. Alternatively, the reaction was conveniently conducted without solvent and yielding a quantitative yield of product as indicated in the synthesis of compound **2**.

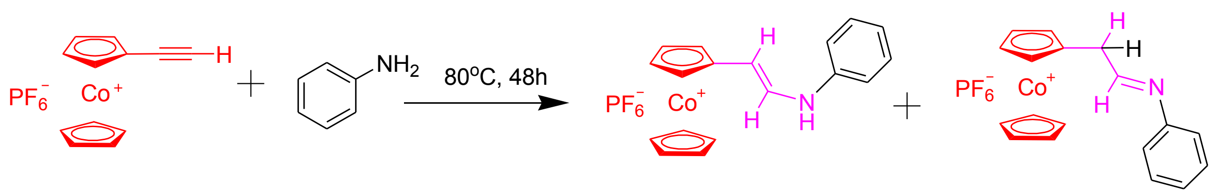
Synthesis of 6



1 **6**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol) was dissolved in 10mL of dry CH_3CN, then butylamine (7.3mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35^{o}C. The colour of the mixture was changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **6** was given as a deep red solid without further purification (42.6mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.94 (t, 3H, CH_3), 1.40 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 3.11 (t, 2H, CH_2), 4.97 (d, J = 13.50Hz, 1H), 5.47 (s, 5H, Cp), 5.66 (t , 2H/C_5H_4), 5.76 (t , 2H/C_5H_4), 7.43 (m, J = 13.56Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.17 (CH_3), 19.84 (CH_2), 30.76 (CH_2), 43.63 (CH_2), 73.59 (2C/C_5H_4), 81.45 (2C/C_5H_4), 83.00 (CH), 84.41 (Cp/unsub.), 116.96 (C/C_5H_4), 145.33 (CH), 29.02, 205.61 $(CD_3)_2CO$). ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-). IR (KBr): 1623 cm^{-1} ($\nu_{C=C}$), 834 cm^{-1} (ν_{PF6^-}), 3434 cm^{-1} (ν_{N-H}). ESI: calc. *m/z* for M^+ ($C_{16}H_{21}CoN$) 286.1, found 286.1. UV-vis.: $\lambda_{max\ 1}$ = 410nm, λ_{max2} = 485nm. Anal. Calcd for $C_{16}H_{21}CoNPF_6$·$0.5CH_2Cl_2$: C, 41.84; H, 4.68; N, 2.96. Found: C, 41.57; H, 4.35; N, 2.67. Alternatively, the reaction was conveniently conducted without solvent and yielding a quantitative yield of product as indicated in the synthesis of compound **2**.

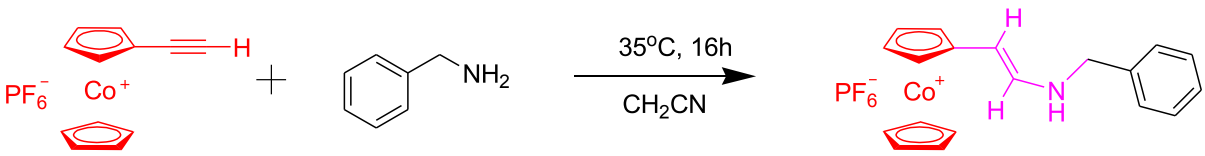
Synthesis of 7 and 7A



1 **7** **7A**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol) was dissolved in 10mL of dry aniline. The solution was stirred for 48h under N_2 at 80°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product was obtained as a red solid that was a mixture of enamine **7** (50%) and the imine **7A** (50%) (45.0mg, yield = 99%) without further purification. ^{1}H NMR of **7** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 5.58 (d, J = 13.35Hz, 1H), 5.64 (s, 5H, Cp), 5.81 (t , 2H/C_5H_4), 6.06 (t , 2H/C_5H_4), 6.98 (t , 2H/Ph), 7.15 (d , 1H/Ph), 7.38 (t , 2H/Ph), 8.06 (m, J = 13.45Hz, 1H), 8.74 (d, 1H/NH), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O). ^{1}H NMR of **7A** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 6.06 (s, 5H, Cp), 6.61 (t , 2H/C_5H_4), 6.52 (t , 2H/C_5H_4), 7.34 (m , 2H/Ph), 7.44 (m, 3H/Ph), 7.78 (d , 2H/CH_2), 9.78 (m, 1H), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 76.06, 82.35, 84.40, 84.78, 84.84, 84.88, 85.53, 86.12 86.46 (Cp/sub.), 91.20 (CH), 114.80 (CH), 120.43 (CH), 121.43, 124.78, 128.83, 129.52, 137.33, 138.20 (Ph), 34.39, 210.85 $(CD_3)_2CO$. ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-). IR (KBr): 1642 cm^{-1} ($\nu_{C=C}$), 1600 cm^{-1} ($\nu_{C=N}$), 837 cm^{-1} (ν_{PF6^-}), 3125 cm^{-1} (ν_{N-H}), 3398 cm^{-1} (ν_{N-H}). ESI: calc. m/z for M^+ ($C_{18}H_{17}CoN$) 306.1, found 306.1; UV-vis.: λ_{max1} = 360nm, $\lambda_{max\,2}$ = 495nm. Anal.Calcd for $C_{18}H_{17}CoNPF_6{\cdot}H_2O$: C, 46.07; H, 4.08; N, 2.98. Found: C, 45.97; H, 4.12; N, 2.99.

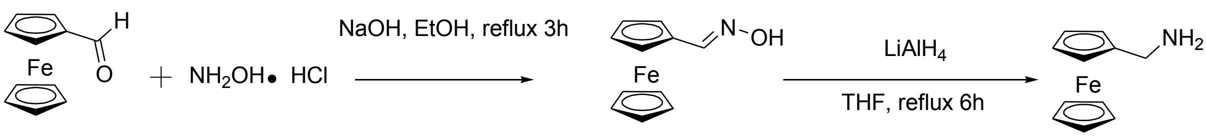
Synthesis of 8



1 **8**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol) was dissolved in 10mL of dry CH_3CN, then benzylamine (10.7mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **8** was given as a deep red solid without further purification (45.8mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 4.37 (d, 2H), 5.00 (d, J = 13.62Hz, 1H), 5.43 (s, 5H, Cp), 5.66 (t , 2H/C_5H_4), 5.77 (t, 2H/C_5H_4), 6.79 (m, 1H/NH), 7.41 (m, 5H/Ph), 7.53 (m, J = 13.67Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.94 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 52.89 (CH_2), 79.60 (2C/C_5H_4), 87.09 (2C/C_5H_4), 89.91 (Cp/unsub.), 92.05 (CH), 120.96 (C/C_5H_4), 144.00 (CH), 132.59, 132.80, 133.91, 150.08 (6C/Ph), 34.39, 210.85 $(CD_3)_2CO$. ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-). IR (KBr): 1622 cm^{-1} ($\nu_{C=C}$), 832 cm^{-1} (ν_{PF6^-}), 3122 cm^{-1} (ν_{N-H}), 3444 cm^{-1} (ν_{N-H}); ESI: calc. m/z for M^+ ($C_{19}H_{19}CoN$) 320.3, found 320.1. UV-vis.: $\lambda_{max\,1}$ = 410nm, $\lambda_{max\,2}$ = 480nm ; Anal.Calcd for $C_{19}H_{29}CoNPF_6{\cdot}0.5H_2O$: C, 48.12; H, 4.25; N, 2.95. Found: C, 48.14; H, 3.94; N, 2.60. Alternatively, the reaction was conveniently conducted without solvent and yielding a quantitative yield of product as indicated in the synthesis of compound **2**.

Synthesis of ferrocenylmethylamine[SI1]

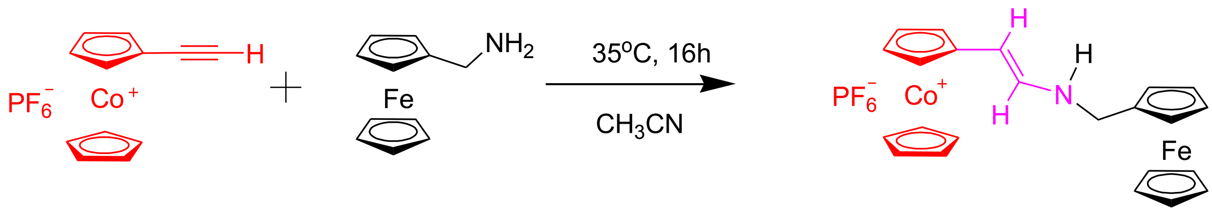


Formylferrocene (1.0g, 4.67mmol), sodium hydride NaOH (1.10g, 27.5mmol) and hydroxylamine chlorhydrate (0.65g, 9.3mmol) were added in EtOH. The mixture was stirred at reflux for 3h. After cooling, the mixture was hydrolysed and extracted by CH_2Cl_2 three times. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed by vacuum to give ferrocenylcarboxaldehyde oxime as an orange solid (0.93g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 7.98 (1H, s, CH=N), 4.53 (2H, m, Cp), 4.37 (2H, m, Cp), 4.22 (5H, m, Cp$'$) 7.26 ($CDCl_3$).

Synthesis of ferrocenylmethylamine

Ferrocenylcarboxaldehyde oxime (1.60g, 7mmol) was dissolved in dry THF 40mL and then added portionwise to a 100ml flask with $LiAlH_4$ (1.40g, 37mmol). The mixture was stirred under reflux for 6h. After cooling, the mixture was hydrolysed and extracted by ether three times. The organic phase was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to give the ferrocenylmethylamine[SI1] as orange oil (1.16g, 73%). The crude product was purified by column chromatography on silica using CH_3OH-NH_4OH (95:5) as eluent. Ferrocenylmethylamine**:** ^{1}H NMR (300 MHz, $CD_3)_2CO$), δ_{ppm}: 1.88 (2H, s, NH_2), 4.07 (2H, t, Cp), 4.13 (5H, s, Cp$'$). 4.17 (2H, s, CH_2), 4.20 (2H, t, Cp).

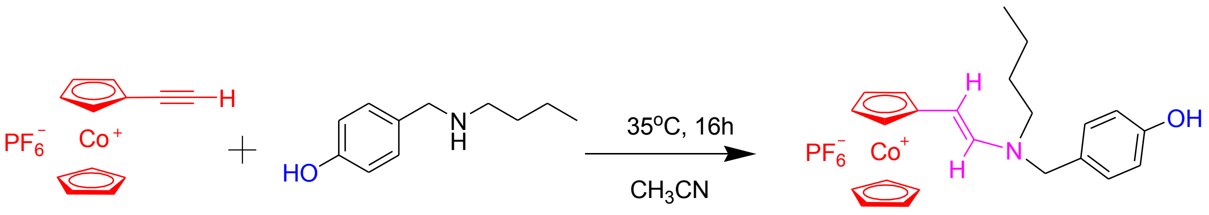
Synthesis of 9



1 **9**

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry CH_3CN, then ferrocenylmethylamine (21.5mg, 0.1mmol, 1equiv.) was added to the solution. The solution was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **9** was obtained as a type of deep red solid without further purification (57.3mg, yield = 95%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 4.08 (d, 2H), 4.16 (t , 2H/C_5H_4), 4.22 (s, 5H, Cp), 4.31 (t , 2H/C_5H_4), 5.08 (d, J = 13.59Hz, 1H), 5.48 (s, 5H, Cp), 5.67 (t , 2H/C_5H_4), 5.79 (t, 2H/C_5H_4), 7.47 (d, J = 13.59Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.94 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.42 (CH_2), 67.90 (2C/C_5H_4/Fc), 68.20 (2C/C_5H_4/Fc), 68.55 (Cp/unsub./Fc), 68.72 (C_5H_4/Fc), 73.88 (2C/C_5H_4), 81.59 (2C/C_5H_4), 83.69 (CH), 84.49(Cp/unsub.), 116.50 (C/C_5H_4), 140.30 (CH), 29.27, 205.48 $(CD_3)_2CO$. ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-). IR (KBr): 1621 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} ($\nu_{PF_6^-}$), 3117 cm^{-1} ($\nu_{N\text{-}H}$), 3429 cm^{-1} ($\nu_{N\text{-}H}$). ESI**:** calc. m/z for M^+ ($C_{23}H_{23}CoFeN$) 428.1, found 428.1. UV-vis.: λ_{max1} = 410nm, $\lambda_{max\ 2}$ = 490nm. Anal.Calcd for $C_{13}H_{23}CoFeNPF_6$·0.8 ether: C, 49.75; H, 4.94; N, 2.21. Found: C, 49.87; H, 4.70; N, 2.39.

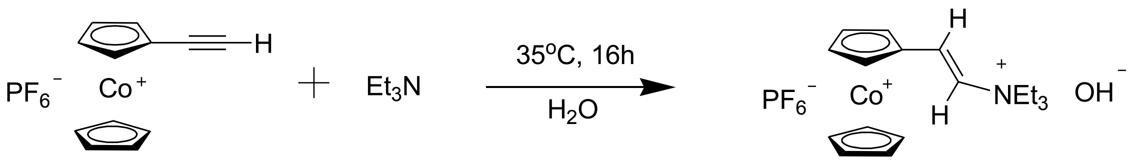
Synthesis of 10



10

Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry CH_3CN, then 4-butylaminomethylphenol (17.9mg, 0.1mmol, 1equiv.) was added to the solution. The mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product **10** was obtained as a deep red solid without further purification (53mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.85 (t, 3H, CH_3), 1.29 (m, 2H/CH_2), 1.53 (m, 2H/CH_2), 3.18 (t, 2H/CH_2), 4.36 (s, 2H/PhCH_2), 4.89 (d, *J* = 13.32Hz, 1H), 5.40 (s, 5H,Cp), 5.64 (t , 2H/C_5H_4), 5.78 (t , 2H/C_5H_4), 6.82 (d, 2H/Ph), 7.14 (d, 2H/Ph), 7.62 (d, *J* = 13.58Hz, 1H), 8.43 (broad, 1H/OH), 2.03 (m, $(CD_3)_2CO$), 2.87 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.18 (CH_3), 19.75(CH_2), 73.48 (2C/C_5H_4/Fc), 81.48 (2C/C_5H_4/Fc), 83.56 (C/C_5H_4/Fc), 84.38 (Cp/unsub.), 115.38 (2C/Ph), 116.96 (CH), 127.83 (CH), 128.84 (2C/Ph), 147.65 (C/Ph), 156.98 (C/Ph), 29.65, 205.37 $(CD_3)_2CO$. δ_{ppm}: -144.12 (m, PF_6^-). IR (KBr): 1614 cm^{-1} ($\nu_{C=C}$), 837 cm^{-1} (ν_{PF6^-}), 3442 cm^{-1} (OH^-). ESI**:** calc. *m/z* for M^+ ($C_{23}H_{27}CoF_6NOP$) 392.4, found 392.1. UV-vis.: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 495nm. Anal.Calcd for $C_{23}H_{27}CoNOPF_6 \cdot 1.5\ H_2O$: C, 48.95; H, 5.36; N, 2.48. Found: C, 48.93; H, 5.55; N, 2.48.

Synthesis of 11

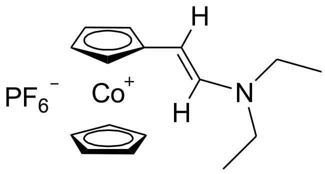


1 **11**

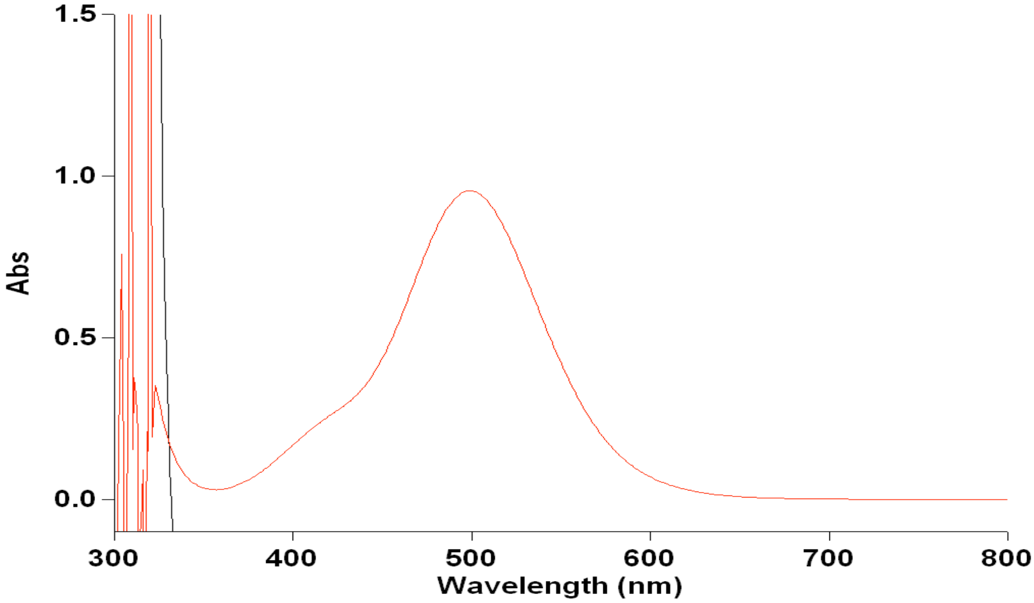
Ethynyl cobalticinium PF_6^- (35.8mg, 0.1mmol), **1**, was dissolved in 10mL of dry Et_3N, then the mixture was stirred for 16h under N_2 at 35°C. The colour of the mixture changed from yellow to deep red during the stirring. Then the solvent was removed under vacuum, and the hydroamination product was obtained as a dark grey solid without further purification (47.0mg, yield = 99%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 1.44 (t, 9H), 3.82 (m, 6H), 5.95 (s, 5H,Cp), 6.06 (t , 2H/C_5H_4), 6.29 (t , 2H/C_5H_4), 7.09 (d, *J* = 14.64Hz, 1H), 7.29 (d, *J* = 14.64Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.93 (s, H_2O). ^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}:7.63 (CH_3), 55.28 (CH_2), 83.20 (2C/C_5H_4), 85.86 (2C/C_5H_4), 86.27 (Cp/unsub.), 96.90 (C/C_5H_4), 123.07 (CH), 136.97 (CH), 29.16, 205.57 $(CD_3)_2CO$). ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-). IR (KBr): 1615 cm^{-1} ($\nu_{C=C}$), 835 cm^{-1} (ν_{PF6^-}), 3651 cm^{-1} (ν_{OH^-}). ESI: calc. *m/z* for M^+ ($C_{18}H_{26}CoNPF_6$) 460.3, found 460.1. UV-vis.: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 505nm; Anal.Calcd for $C_{18}H_{27}CoNOPF_6 \cdot 1.2CHCl_3 \cdot 1.2\ Me_2CO$: C, 39.29; H, 5.08; N, 2.06. Found: C, 39.44; H, 4.21; N, 1.89.

Characterization:

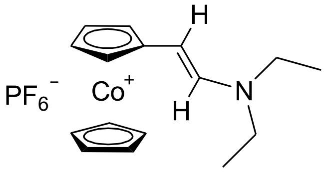
UV-vis. of **2**: $\lambda_{max\ 1} = 425nm$, $\lambda_{max\ 2} = 500nm$



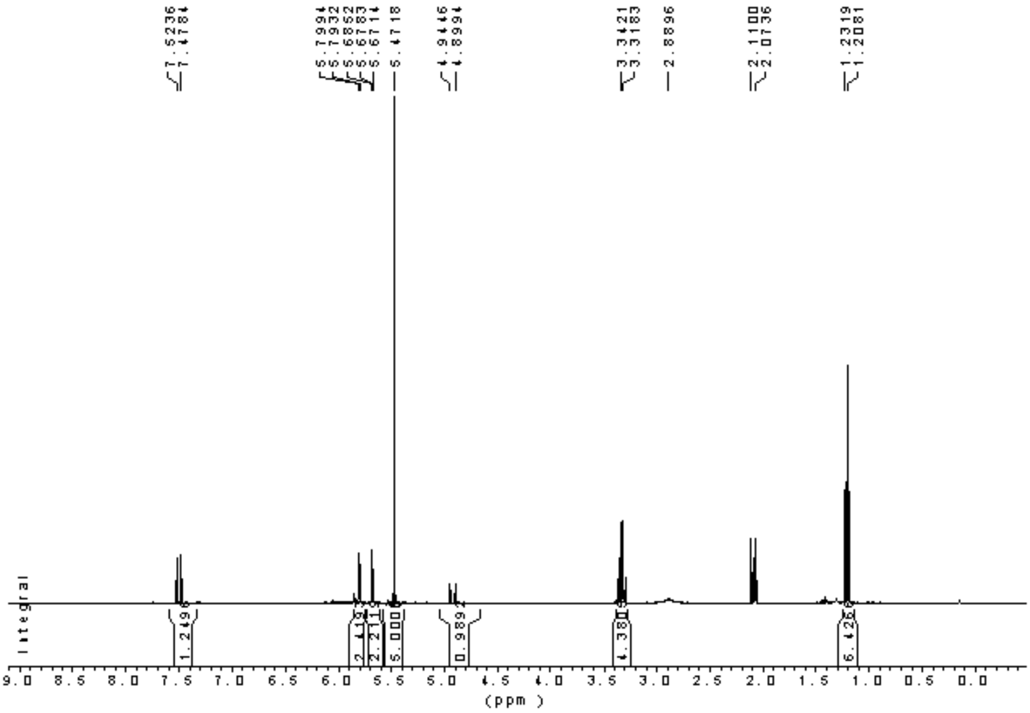
2



^{1}H NMR of **2**

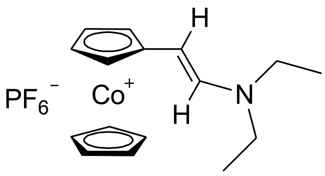


2

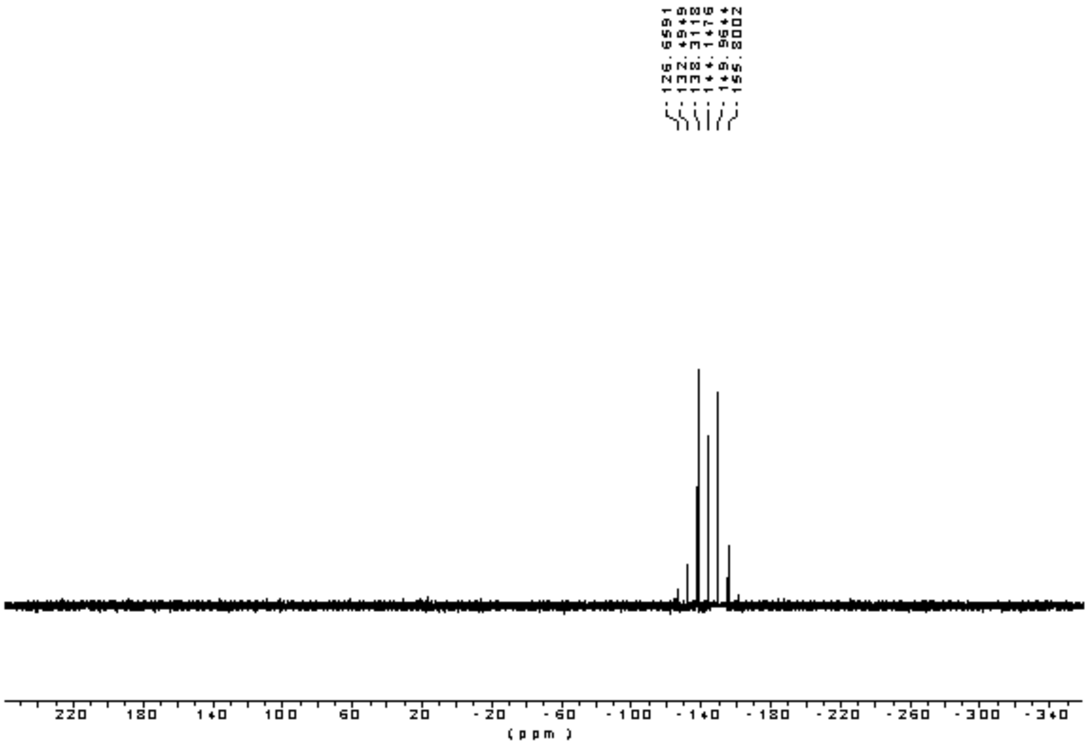


^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 1.20 (t, 6H, CH_3), 3.31 (m, 4H, CH_2), 4.89 (d, J = 13.44Hz, 1H), 5.47 (s, 5H, Cp), 5.67(t , 2H/C_5H_4), 5.68 (t , 2H/C_5H_4), 7.47 (d, J = 13.44Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.89 (s, H_2O).

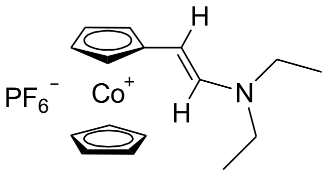
^{31}P NMR of **2** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.14 (m, PF_6^-).



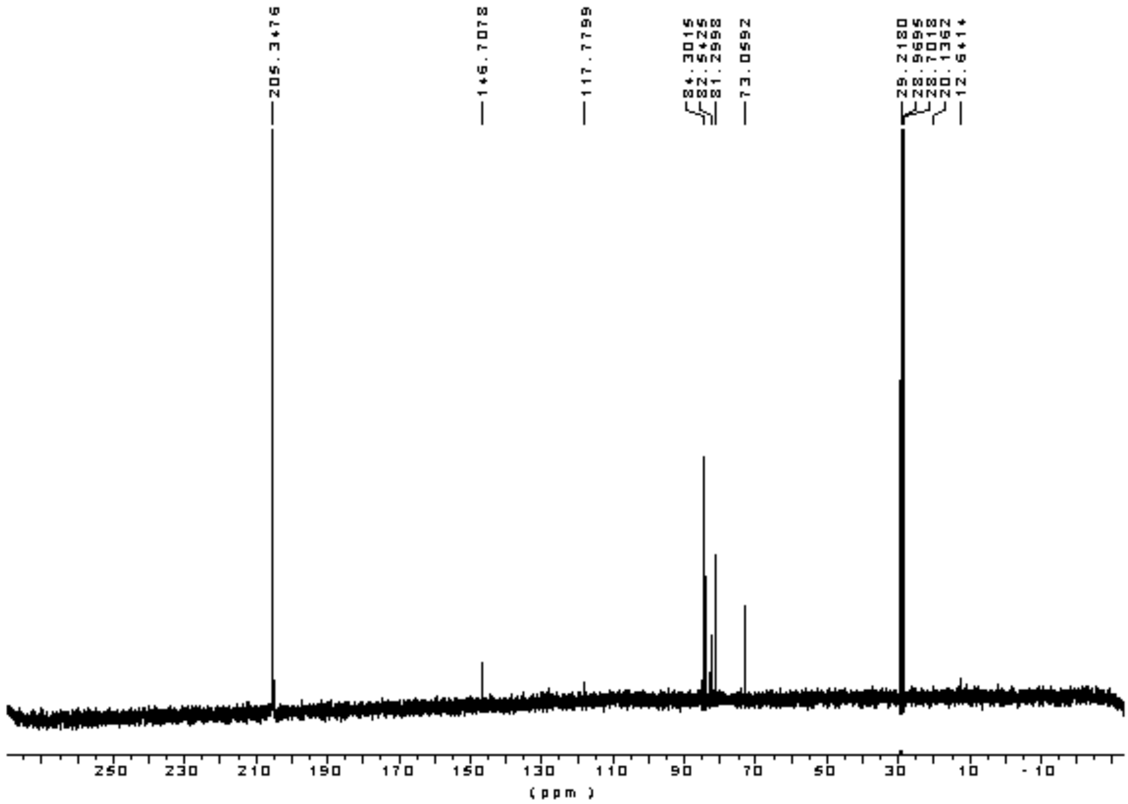
2



^{13}C NMR of **2**

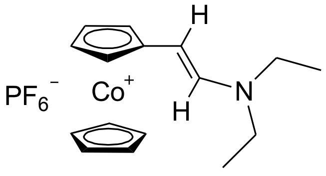


2

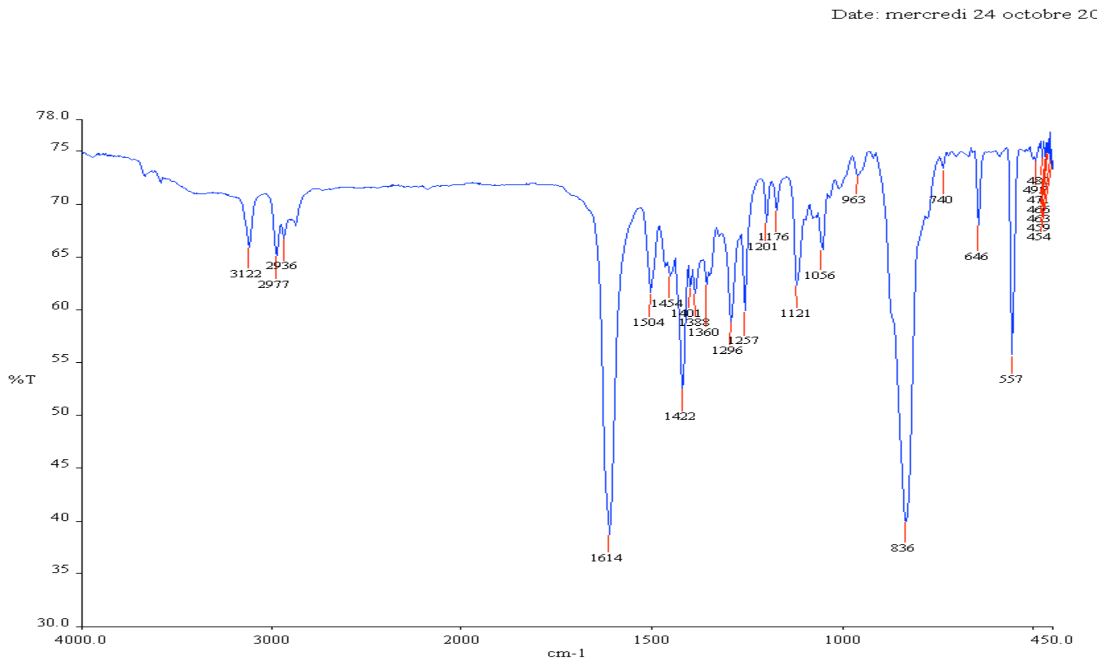


^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 12.64 (CH_3), 20.13 (CH_2), 73.06 (2C/C_5H_4), 81.30 (2C/C_5H_4), 82.54 (CH), 84.30 (Cp/unsub.), 117.78 (C/C_5H_4), 146.71 (CH), 29.21, 205.34 $(CD_3)_2CO$).

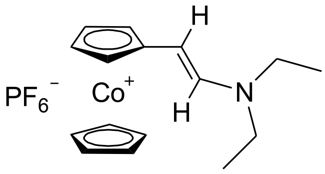
IR (KBr) of **2**: 1614 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} ($\nu_{PF_6^-}$)



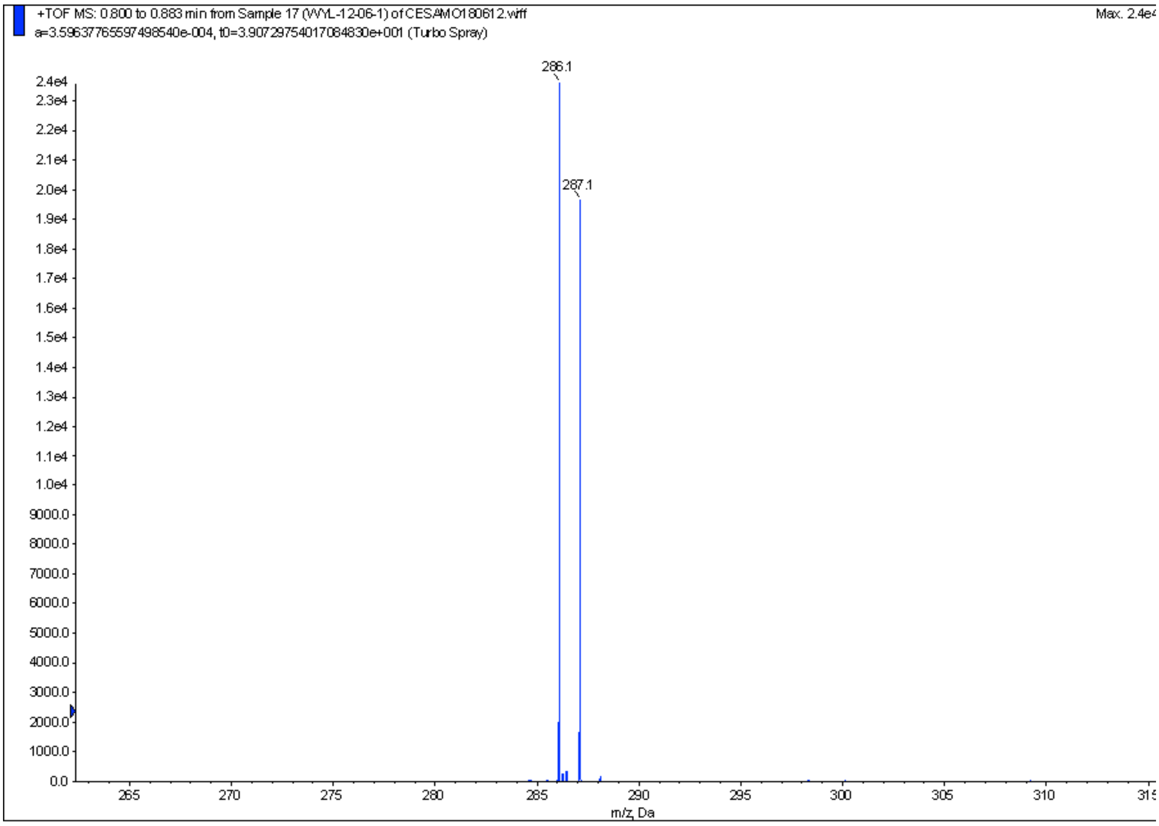
2



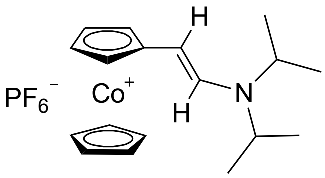
ESI: of **2**:calc. *m/z* for M^+ ($C_{16}H_{21}CoN^+$) 286.1, found 286.1.



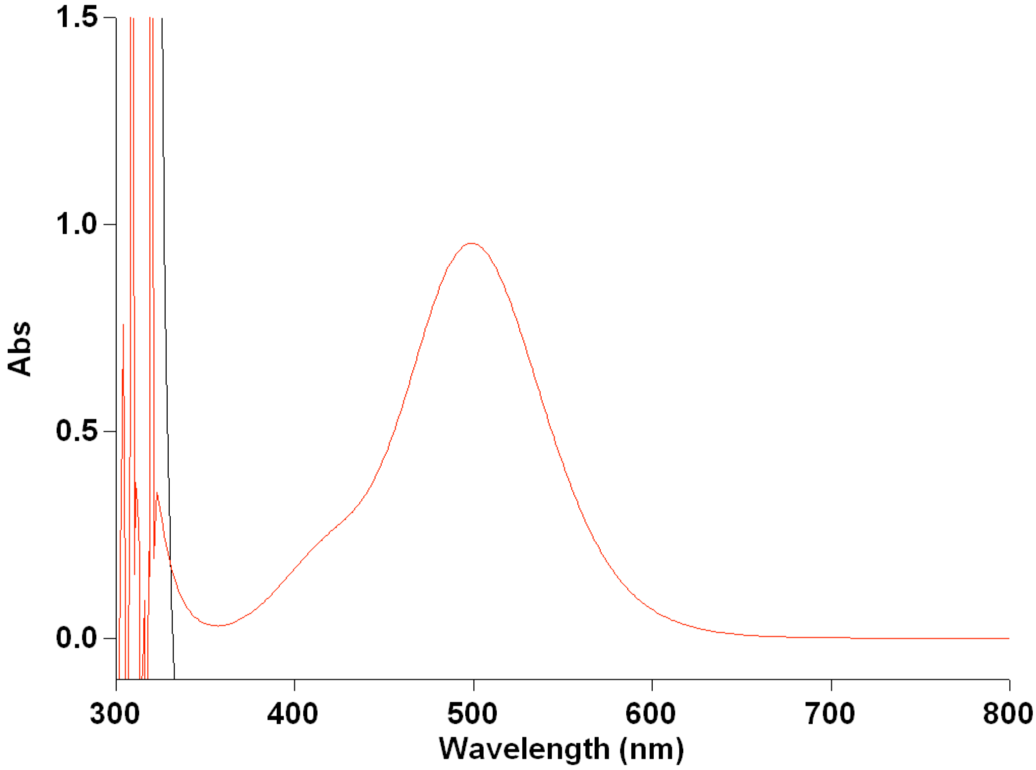
2



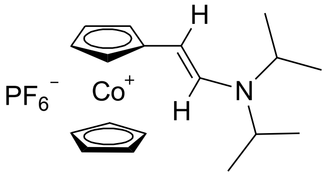
UV-vis. of **3**: $\lambda_{max\ 1}$ = 420nm, $\lambda_{max\ 2}$ = 505nm



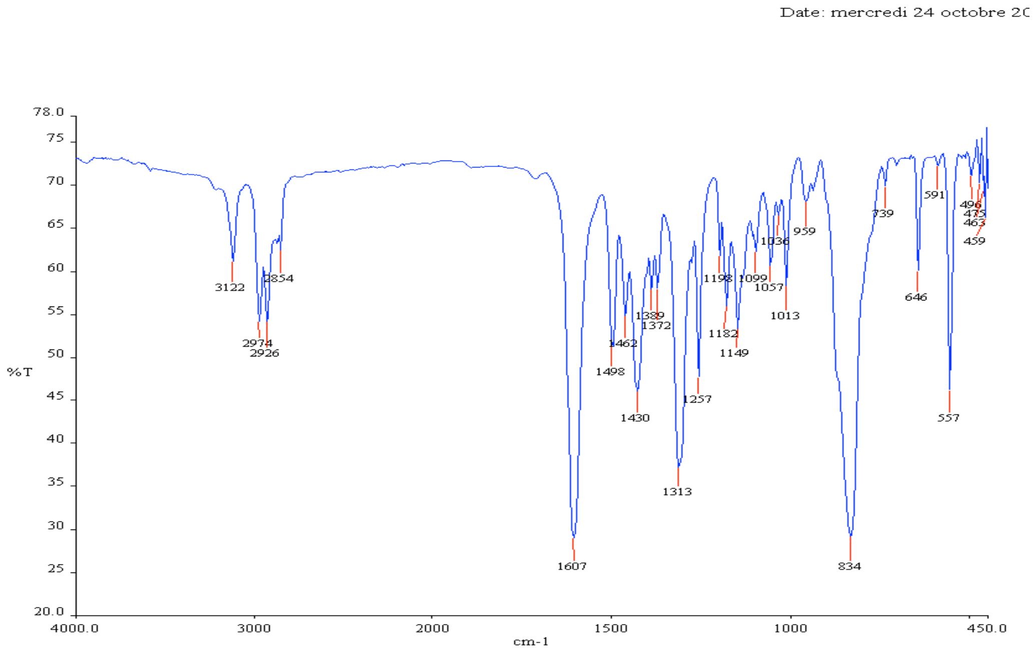
3



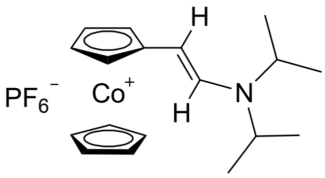
The IR spectrum of **3:** IR (KBr): 1608 cm^{-1} ($\nu_{C=C}$), 839 cm^{-1} (ν_{PF6^-})



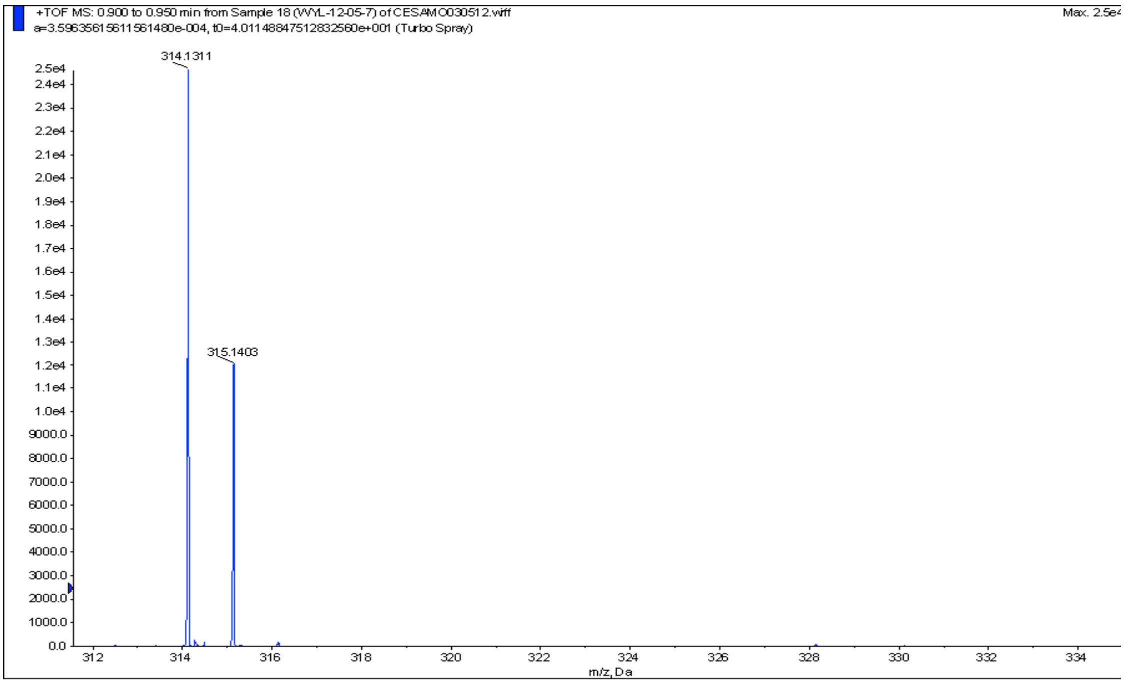
3



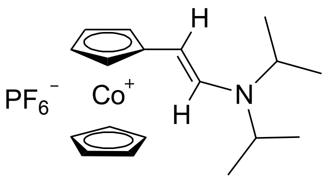
ESI of **3**: calc. *m/z* for M^+ ($C_{18}H_{25}CoN$) 314.3, found 314.1.



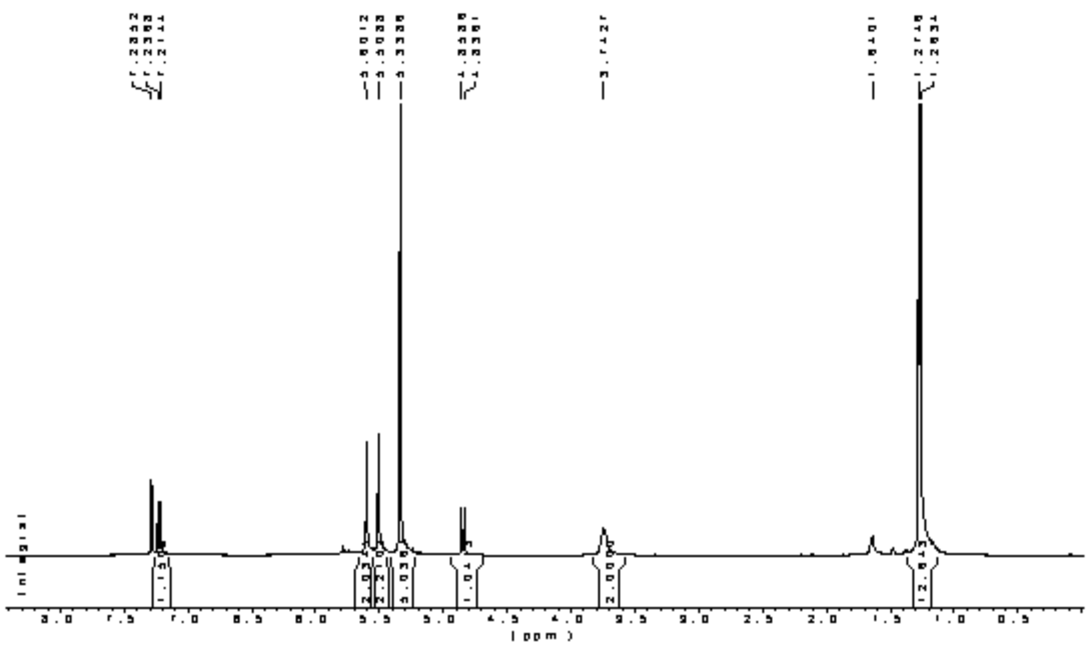
3



^{1}H NMR of **3:**

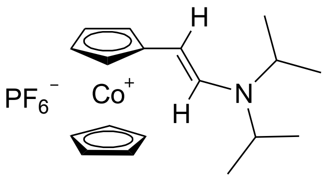


3

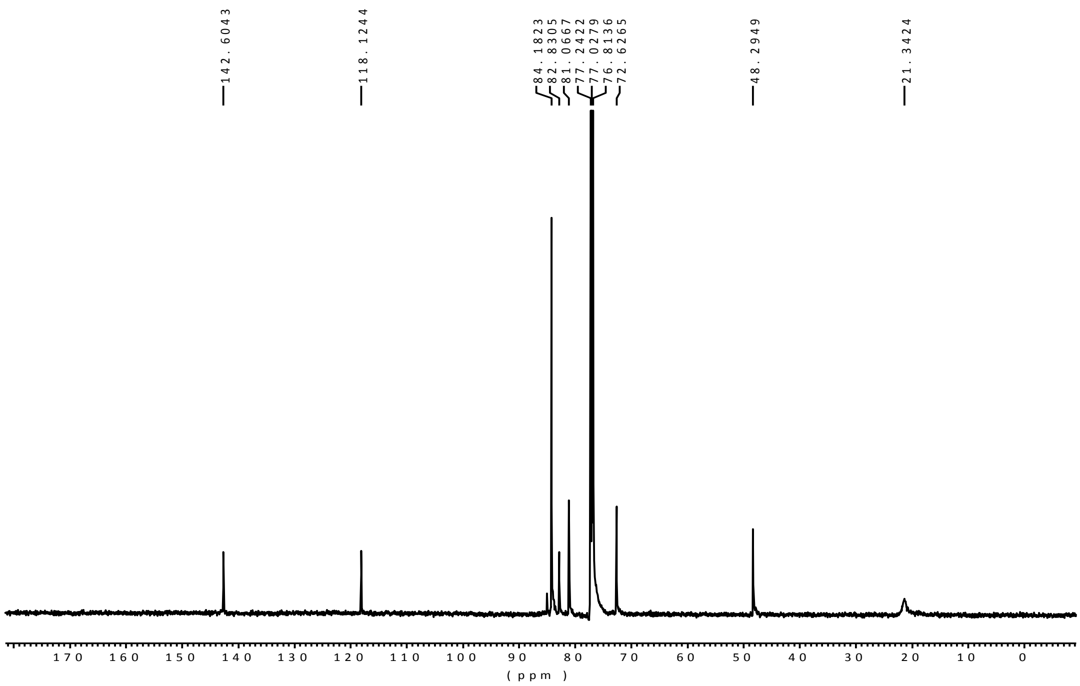


^{1}H NMR (600 MHz, $CDCl_3$), δ_{ppm}: 1.26 (d, 12H, CH_3), 3.74 (m, 1H), 4.83 (d, *J* = 13.50Hz, 1H), 5.34 (s, 5H, Cp), 5.50 (t , 2H/C_5H_4), 5.60 (t , 2H/C_5H_4), 7.21 (d, *J* = 13.50Hz, 1H), 7.28 (s, $CDCl_3$), 1.64 (s, H_2O).

^{13}C NMR of **3:**

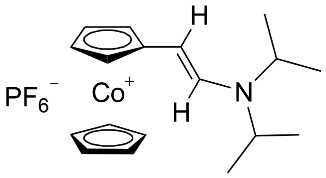


3



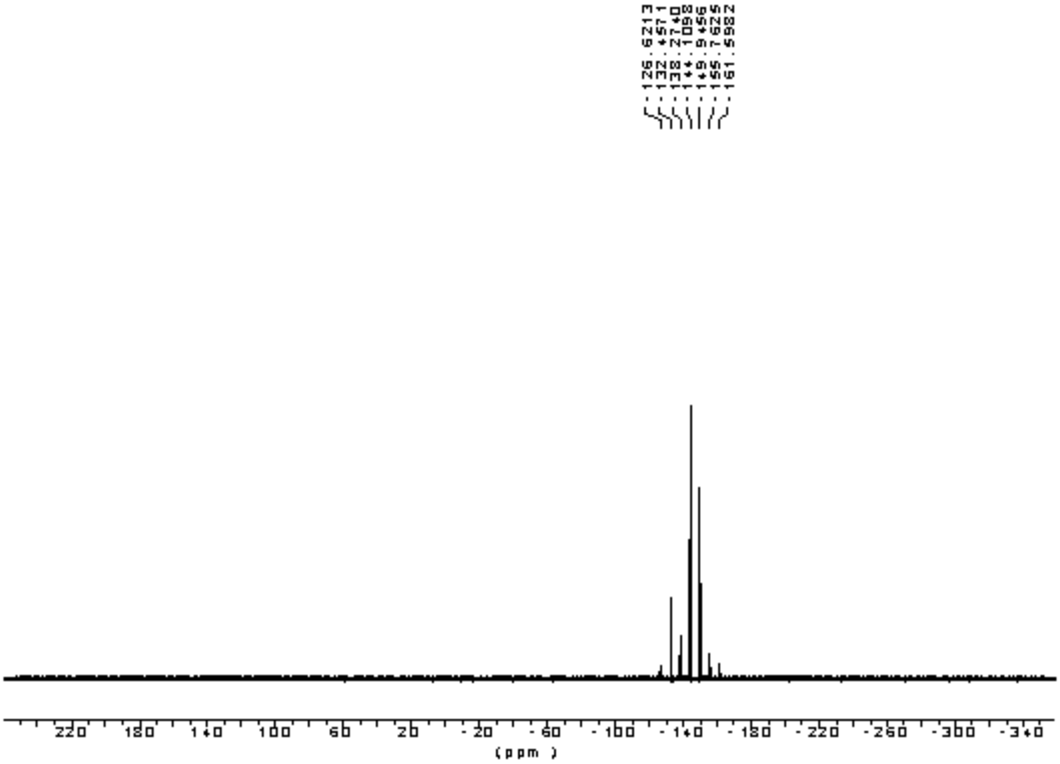
^{13}C NMR (150 MHz, $CDCl_3$), δ_{ppm}: 21.36 (CH_3), 48.28 (CH), 72.61 (2C/C_5H_4), 81.06 (2C/C_5H_4), 84.17 (CH), 84.96 (Cp/unsub.), 118.12 (C/C_5H_4), 142.59 (CH), 76.80, 77.02, 77.23 ($CDCl_3$).

^{31}P NMR of **3:**

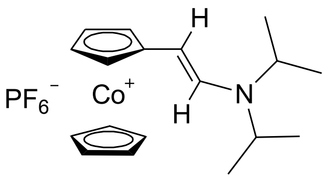


3

^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-).



The X-Ray of **3**:



3

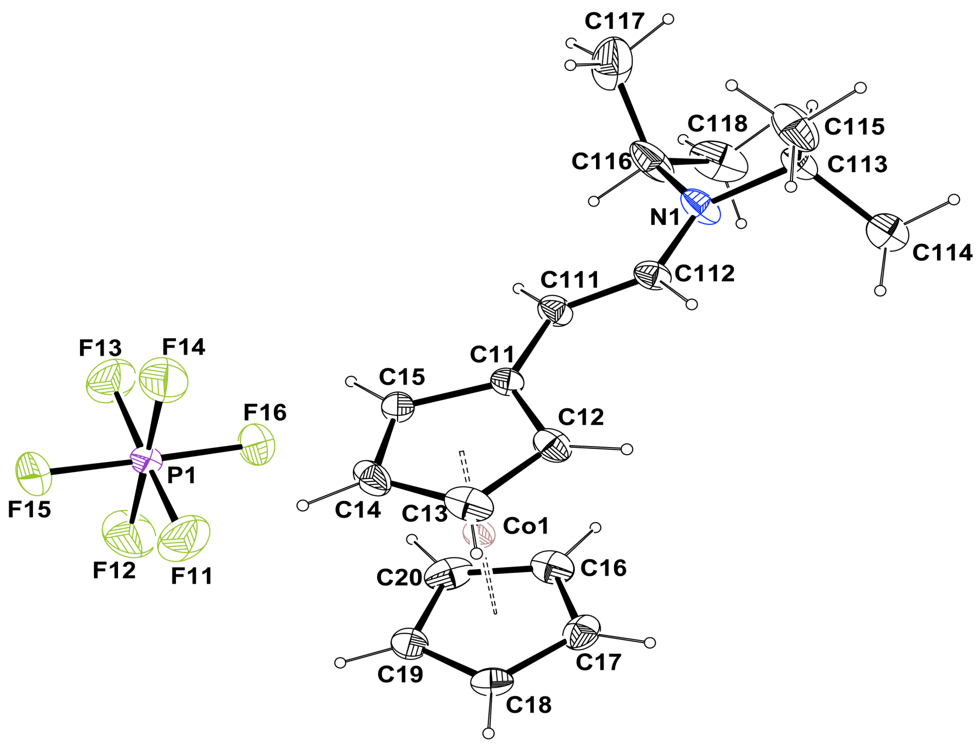


Table 1. Crystal data and structure refinement for **3**.

Identification code	**DA16**	
Empirical formula	$(C_{18}H_{25}CoN)$, (PF_6)	
Formula weight	459.29	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 27.2309(4) Å	a= 90°.
	b = 11.3692(2) Å	b= 90°.
	c = 13.2763(2) Å	g = 90°.

Volume	4110.26(11) Å^3
Z	8
Density (calculated)	1.484 Mg/m^3
Absorption coefficient	0.968 mm^{-1}
F(000)	1888
Crystal size	0.38 x 0.24 x 0.10 mm^3
Theta range for data collection	2.99 to 27.48°.
Index ranges	-35<=h<=35, -14<=k<=14, -17<=l<=17
Reflections collected	85626
Independent reflections	9384 [R(int) = 0.0364]
Completeness to theta = 27.48°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.62834
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9384 / 1 / 495
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0681
R indices (all data)	R1 = 0.0376, wR2 = 0.0712
Absolute structure parameter	-0.014(9)
Largest diff. peak and hole	0.325 and -0.273 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **3**.

Molecule I		***Molecule II***	
Co(1)-Ct(1)	1.6434(11)	Co(2)-Ct(3)	1.6421(10)
Co(1)-Ct(2)	1.6456(12)	Co(2)-Ct(4)	1.6461(17)
C(11)-C(111)	1.429(3)	C(21)-C(211)	1.435(3)
C(11)-C(12)	1.436(3)	C(21)-C(25)	1.434(3)
C(11)-C(15)	1.444(3)	C(21)-C(22)	1.443(3)
C(12)-C(13)	1.421(4)	C(22)-C(23)	1.417(3)
C(13)-C(14)	1.423(4)	C(23)-C(24)	1.425(3)
C(14)-C(15)	1.411(4)	C(24)-C(25)	1.421(3)
C(16)-C(20)	1.406(4)	C(26)-C(27)	1.390(6)
C(16)-C(17)	1.410(4)	C(26)-C(30)	1.395(6)
C(17)-C(18)	1.417(4)	C(27)-C(28)	1.373(6)
C(18)-C(19)	1.409(4)	C(28)-C(29)	1.343(5)
C(19)-C(20)	1.423(4)	C(29)-C(30)	1.358(5)
C(111)-C(112)	1.367(3)	C(211)-C(212)	1.360(3)
C(112)-N(1)	1.338(3)	C(212)-N(2)	1.344(3)
N(1)-C(116)	1.478(4)	N(2)-C(216)	1.477(4)
N(1)-C(113)	1.484(3)	N(2)-C(213)	1.480(3)
C(113)-C(114)	1.506(4)	C(213)-C(214)	1.508(4)
C(113)-C(115)	1.521(4)	C(213)-C(215)	1.511(4)
C(116)-C(118)	1.512(5)	C(216)-C(218)	1.495(5)
C(116)-C(117)	1.520(5)	C(216)-C(217)	1.521(5)
P(1)-F(12)	1.564(2)	P(2)-F(23)	1.5781(18)
P(1)-F(11)	1.575(2)	P(2)-F(25)	1.5936(16)
P(1)-F(13)	1.581(2)	P(2)-F(22)	1.5949(18)
P(1)-F(15)	1.5937(18)	P(2)-F(21)	1.5958(18)
P(1)-F(16)	1.5955(17)	P(2)-F(24)	1.5992(18)
P(1)-F(14)	1.602(2)	P(2)-F(26)	1.6031(16)

Ct(1)-Co(1)-Ct(2)	178.73(7)	Ct(3)-Co(2)-Ct(4)	179.81(7)
C(111)-C(11)-C(12)	130.0(2)	C(211)-C(21)-C(22)	129.1(2)
C(111)-C(11)-C(15)	124.5(2)	C(25)-C(21)-C(211)	125.2(2)
C(12)-C(11)-C(15)	105.6(2)	C(25)-C(21)-C(22)	105.7(2)

C(13)-C(12)-C(11)	109.2(3)	C(23)-C(22)-C(21)	108.9(2)
C(12)-C(13)-C(14)	107.7(2)	C(22)-C(23)-C(24)	108.3(2)
C(15)-C(14)-C(13)	108.1(2)	C(25)-C(24)-C(23)	107.3(2)
C(14)-C(15)-C(11)	109.2(2)	C(24)-C(25)-C(21)	109.6(2)
C(20)-C(16)-C(17)	108.1(3)	C(27)-C(26)-C(30)	106.5(3)
C(16)-C(17)-C(18)	108.3(3)	C(28)-C(27)-C(26)	107.4(3)
C(19)-C(18)-C(17)	107.7(2)	C(29)-C(28)-C(27)	109.1(3)
C(18)-C(19)-C(20)	108.0(2)	C(28)-C(29)-C(30)	108.9(4)
C(16)-C(20)-C(19)	107.9(2)	C(29)-C(30)-C(26)	108.1(3)
C(112)-C(111)-C(11)	122.6(2)	C(212)-C(211)-C(21)	122.8(2)
N(1)-C(112)-C(111)	128.5(2)	N(2)-C(212)-C(211)	128.8(2)
C(112)-N(1)-C(116)	121.6(2)	C(212)-N(2)-C(216)	121.2(2)
C(112)-N(1)-C(113)	120.0(2)	C(212)-N(2)-C(213)	120.5(2)
C(116)-N(1)-C(113)	117.6(2)	C(216)-N(2)-C(213)	117.9(2)
N(1)-C(113)-C(114)	111.3(2)	N(2)-C(213)-C(214)	112.3(2)
N(1)-C(113)-C(115)	112.0(2)	N(2)-C(213)-C(215)	111.3(2)
C(114)-C(113)-C(115)	111.5(2)	C(214)-C(213)-C(215)	111.6(3)
N(1)-C(116)-C(118)	111.4(3)	N(2)-C(216)-C(218)	110.3(3)
N(1)-C(116)-C(117)	111.4(3)	N(2)-C(216)-C(217)	112.5(3)
C(118)-C(116)-C(117)	112.8(3)	C(218)-C(216)-C(217)	113.2(3)
F(12)-P(1)-F(11)	91.25(16)	F(23)-P(2)-F(25)	89.87(11)
F(12)-P(1)-F(13)	91.51(15)	F(25)-P(2)-F(22)	90.17(10)
F(11)-P(1)-F(13)	177.23(15)	F(23)-P(2)-F(21)	179.54(13)
F(12)-P(1)-F(15)	90.68(12)	F(23)-P(2)-F(22)	90.58(12)
F(11)-P(1)-F(15)	89.68(12)	F(25)-P(2)-F(21)	89.97(11)
F(13)-P(1)-F(15)	90.31(12)	F(22)-P(2)-F(21)	89.85(11)
F(12)-P(1)-F(16)	91.18(12)	F(23)-P(2)-F(24)	90.67(12)
F(11)-P(1)-F(16)	90.05(12)	F(25)-P(2)-F(24)	90.17(10)
F(13)-P(1)-F(16)	89.87(12)	F(21)-P(2)-F(24)	88.90(11)
F(15)-P(1)-F(16)	178.12(12)	F(22)-P(2)-F(24)	178.71(12)
F(12)-P(1)-F(14)	179.29(16)	F(25)-P(2)-F(26)	179.28(11)
F(11)-P(1)-F(14)	89.41(15)	F(23)-P(2)-F(26)	90.84(10)
F(13)-P(1)-F(14)	87.83(14)	F(22)-P(2)-F(26)	89.94(9)
F(15)-P(1)-F(14)	89.07(12)	F(21)-P(2)-F(26)	89.32(10)
F(16)-P(1)-F(14)	89.07(13)	F(24)-P(2)-F(26)	89.71(9)

Computational details of 3:

The geometry of complex **3** was optimized using Gaussian09 package,[SI1] employing the B3PW91 functional,[SI2] and using the general double-ζ LANL2DZ[SI3] basis set augmented by polarization functions on all atoms. The optimized geometry has been fully characterized as a true minimum via analytical frequency calculations. The composition of the molecular orbitals were calculated using the AOmix program.[SI4]

.

Table 3. Energy and Cartesian coordinates of the optimized geometry of complex **3**

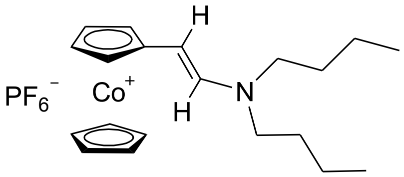
E= -900.477205502 u.a.

	X	Y	Z
Co	1.804839	10.356606	5.685584
C	2.171456	13.595971	6.368592
C	3.278457	14.096787	7.031403
C	1.623247	12.317650	6.672701
C	2.156077	11.253388	7.499593
H	3.115222	11.257401	8.004557
C	1.193690	10.202584	7.602936
H	1.296855	9.300810	8.195806
C	0.096537	10.532140	6.745650
H	-0.786379	9.927849	6.571328
C	0.394039	11.785318	6.128798
H	-0.232893	12.292496	5.403247
C	3.604688	9.645031	4.987954
H	4.547324	9.737533	5.515666
C	3.062541	10.591193	4.065065
H	3.513298	11.533921	3.777201
C	1.785603	10.103866	3.645017
H	1.101282	10.608870	2.972437
C	1.551484	8.844891	4.287056
H	0.660464	8.235505	4.186617
C	2.674788	8.562301	5.120235
H	2.791456	7.698266	5.764561
H	1.636059	14.190243	5.633694

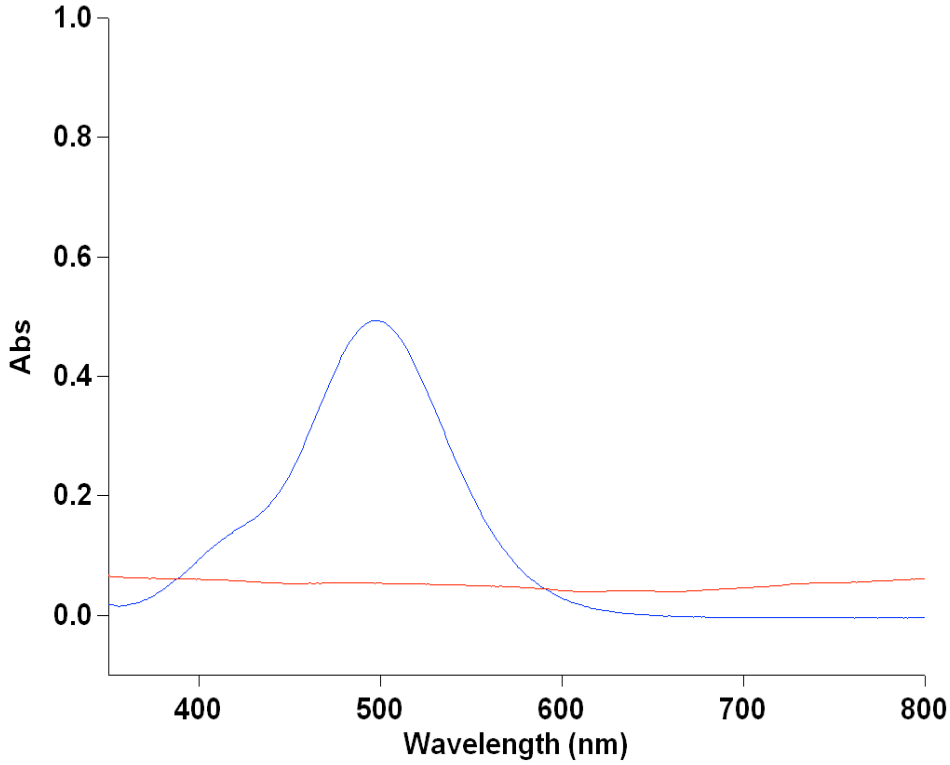
N	3.895723	15.274609	6.897092
H	3.724180	13.462661	7.797056
C	3.464027	16.286295	5.914158
H	2.665687	15.819410	5.331796
C	5.015207	15.609108	7.810984
H	5.329944	16.615323	7.519305
C	4.562685	15.670461	9.272766
H	4.265343	14.684822	9.650542
H	5.386551	16.025534	9.901039
H	3.717250	16.354076	9.399124
C	6.211173	14.673697	7.612690
H	5.981484	13.646921	7.923000
H	6.532826	14.654266	6.566396
H	7.053996	15.014840	8.223128
C	2.877271	17.523651	6.601184
H	3.631034	18.064954	7.184264
H	2.492179	18.215700	5.844699
H	2.051554	17.253040	7.267573
C	4.589834	16.639010	4.937011
H	4.983416	15.743845	4.443643
H	4.201751	17.310371	4.163688
H	5.420040	17.158109	5.428508

See the references [SI2] to [SI5] at the end of the S.I.

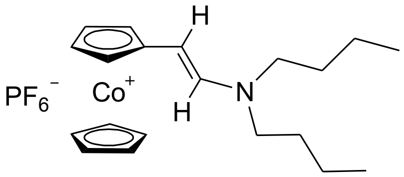
UV-vis. of **4** in acetone: $\lambda_{max\ 1}$ = 415nm, $\lambda_{max\ 2}$ = 496nm, $\varepsilon = 1.25\times 10^4$ L/mol.cm



4



UV-vis. of **4** in acetone/CH_2Cl_2/DMSO: $\lambda_{max\ 1}$ = 415nm



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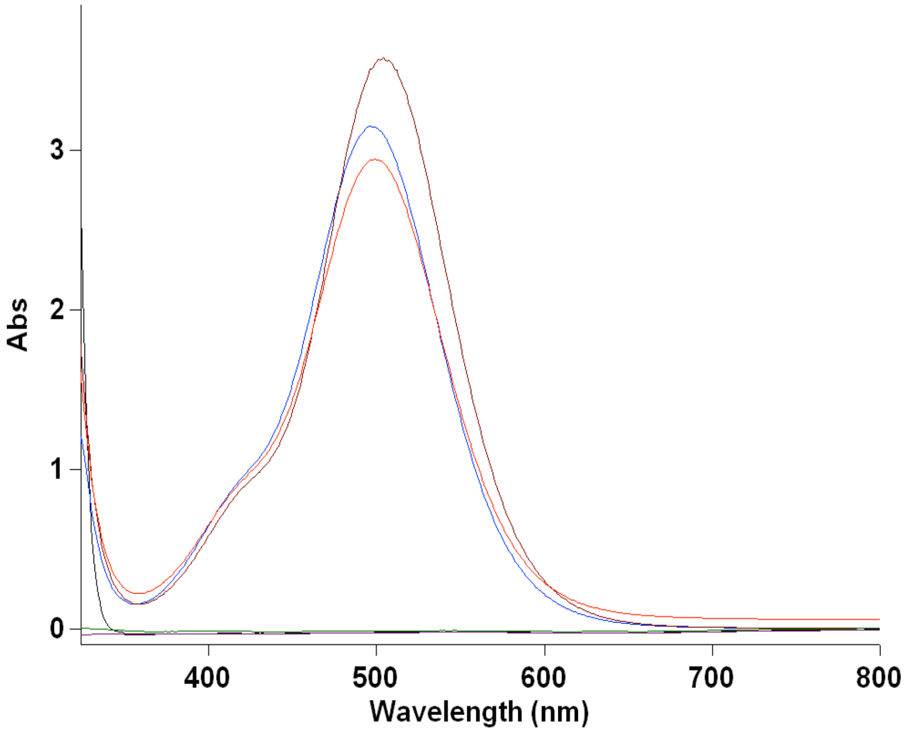
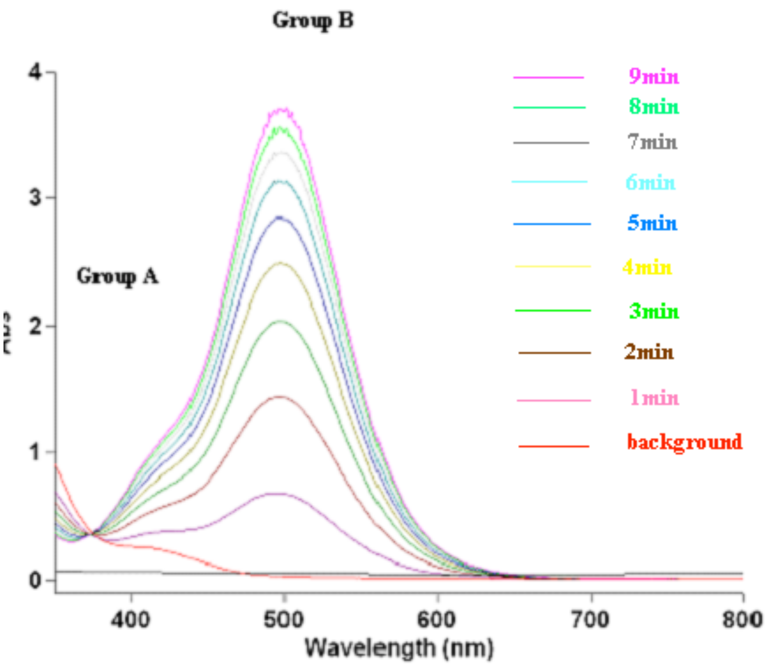
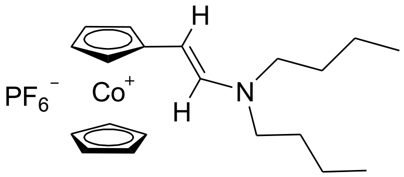


Blue line (Acetone): $\lambda_{max\ 2}$ = 496nm
Violet line (CH_2Cl_2): $\lambda_{max\ 2}$ = 504 nm
Red line (DMSO): $\lambda_{max\ 2}$ = 499nm

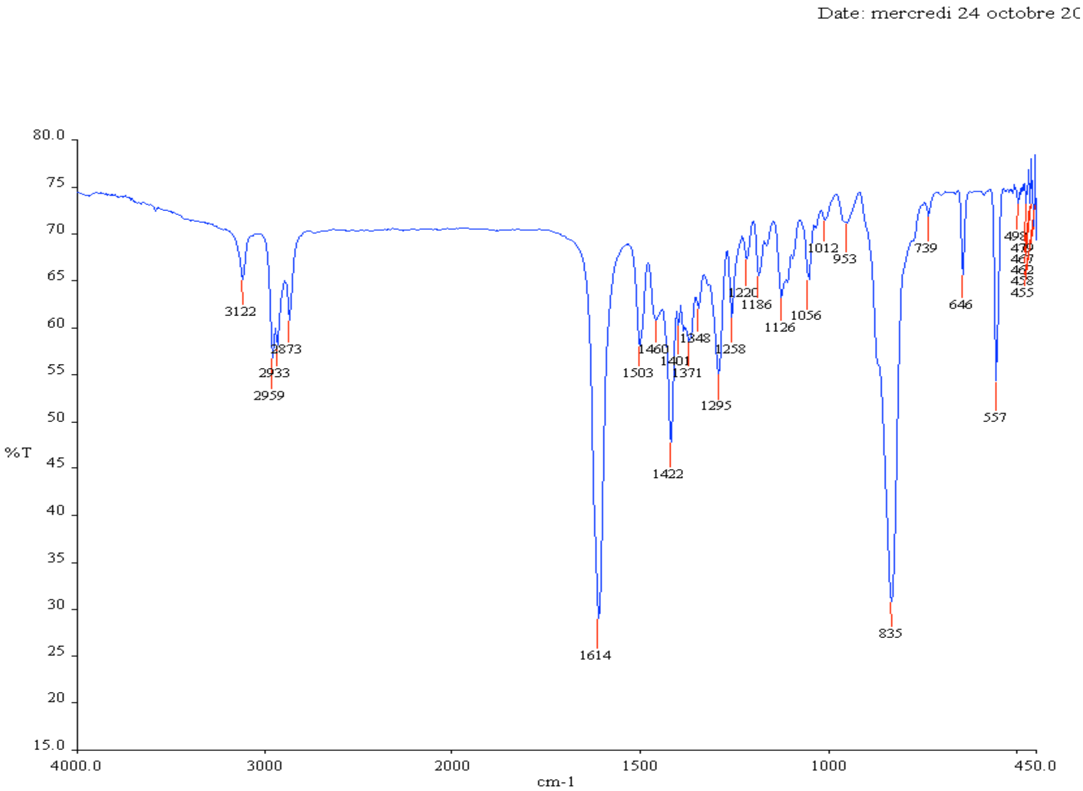
Kinetic process of the formation of **4** in acetone: $\lambda_{max\ 1}$ = 415nm, $\lambda_{max\ 2}$ = 496nm, k = $8.45\times 10^{-3}s^{-1}$



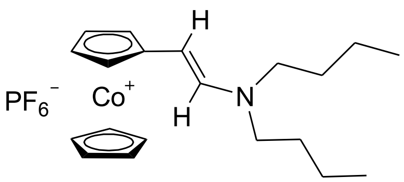
The IR spectrum of **4:** IR (KBr): 1614 cm^{-1} ($\nu_{C=C}$), 835 cm^{-1} ($\nu_{PF_6^-}$)



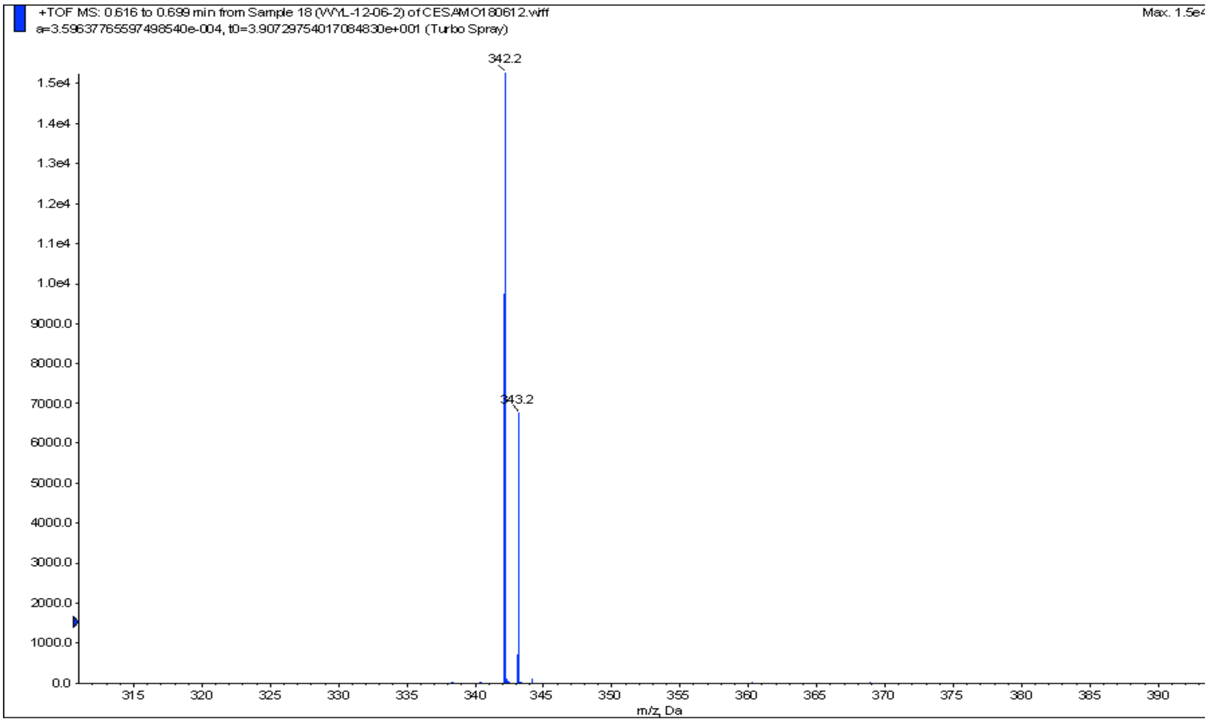
4



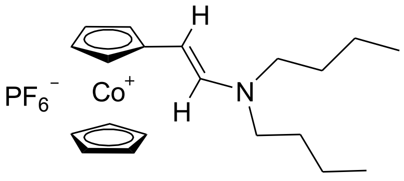
ESI of **4**: calc. *m/z* for M^+ ($C_{20}H_{29}CoN$) 342.3, found 342.2.



4



^{1}H NMR of **4**



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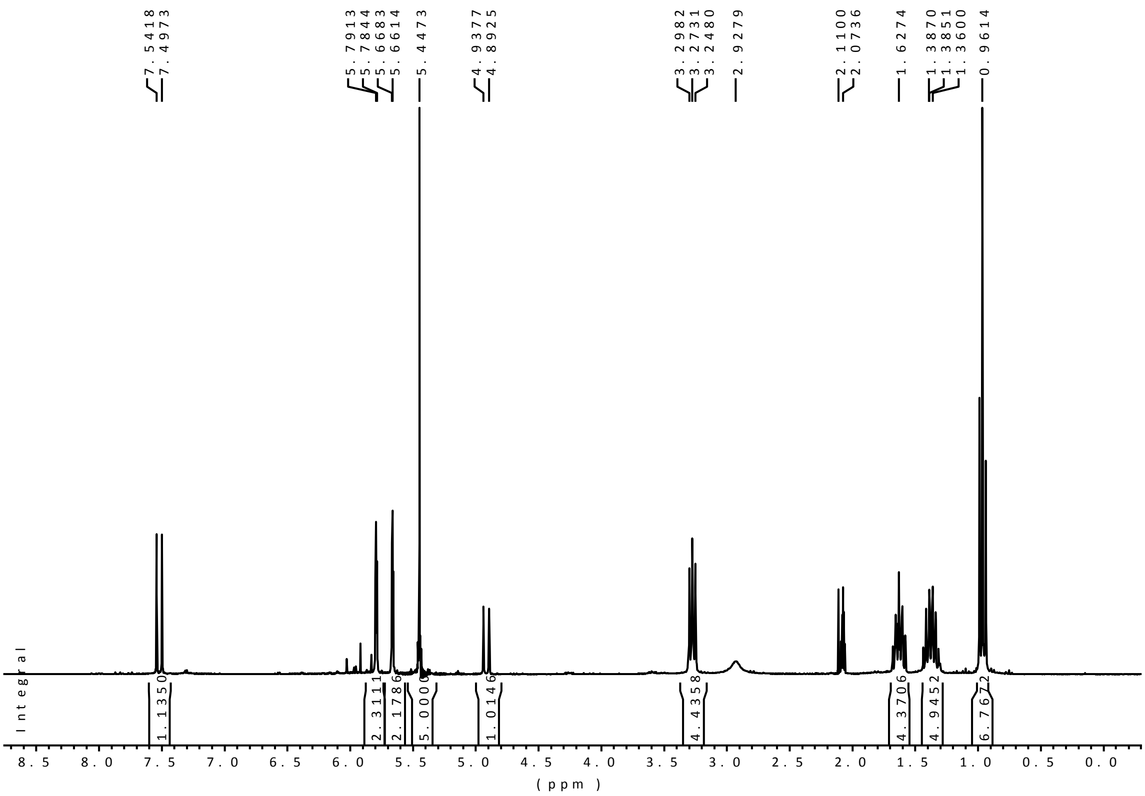
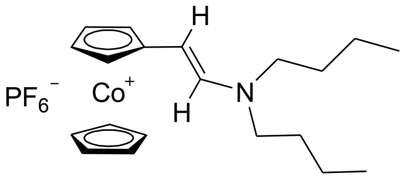


^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.96 (t, 6H, CH_3), 1.35 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 3.24 (t, 4H, CH_2), 4.89 (d, J = 13.44Hz, 1H), 5.44 (s, 5H, Cp), 5.66 (t , 2H/C_5H_4), 5.79 (t , 2H/C_5H_4), 7.49 (d, J = 13.44Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.92 (s, H_2O).

^{31}P NMR of **4** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-).



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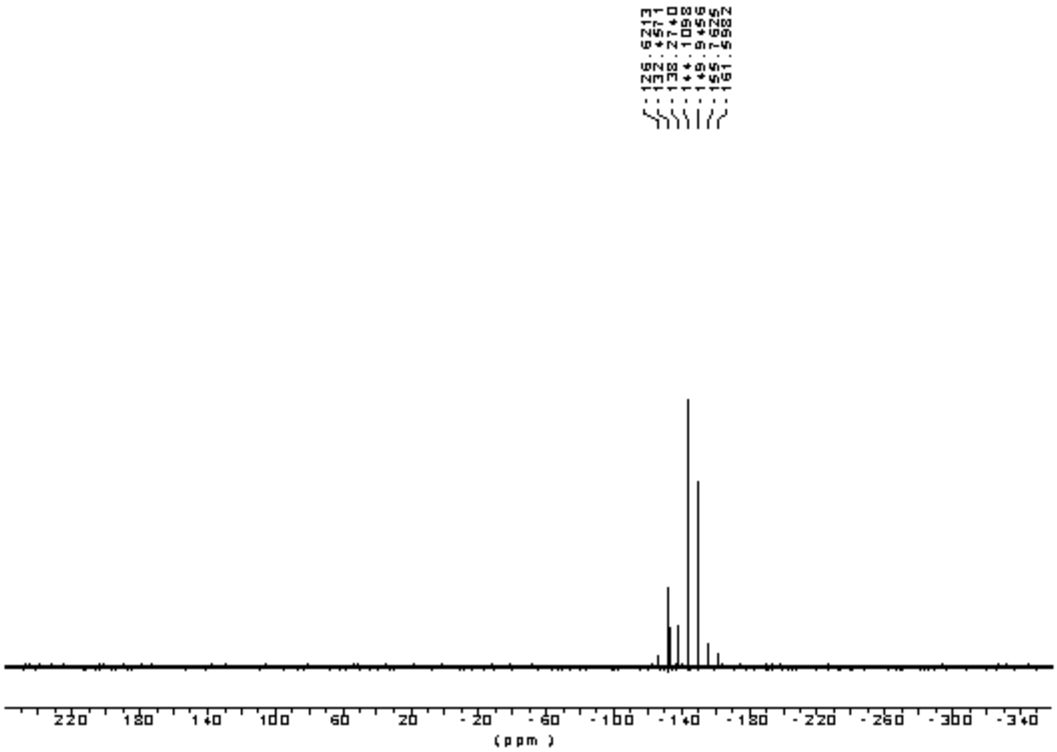
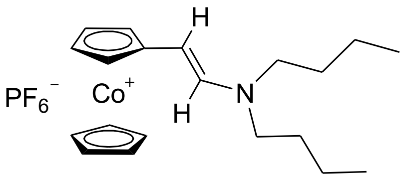


^{13}C NMR of **4**



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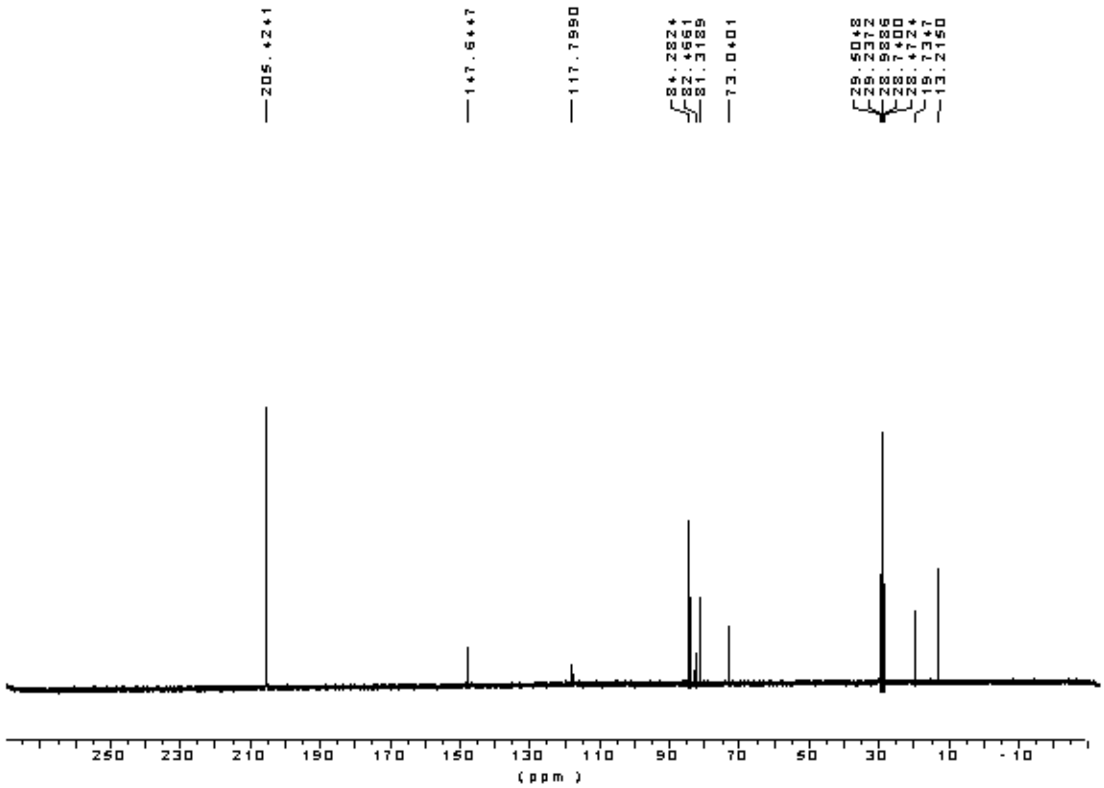
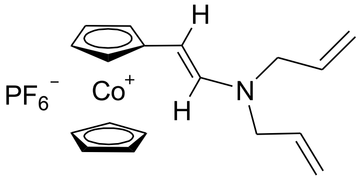
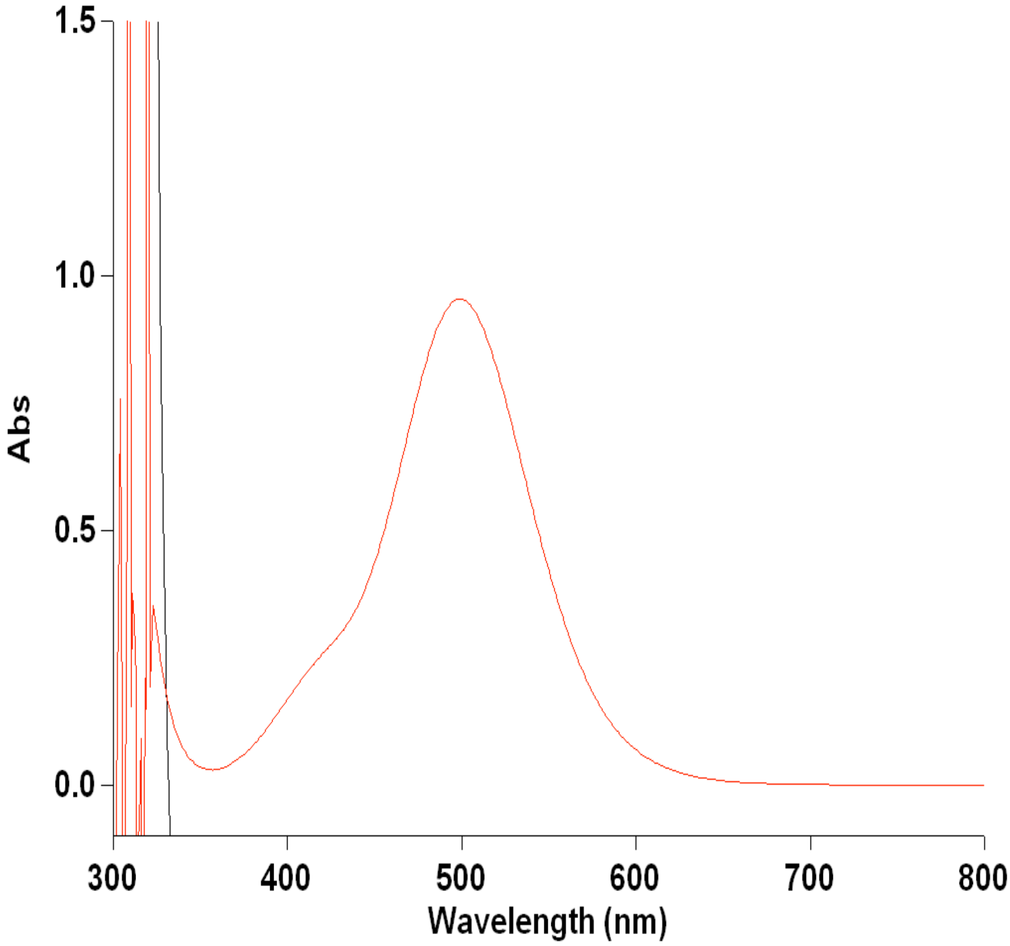


^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.21 (CH_3), 19.73 (CH_2), 73.04 ($2C/C_5H_4$), 81.32 ($2C/C_5H_4$), 82.46 (CH), 84.28 (Cp/unsub.), 117.20 (C/C_5H_4), 147.84 (CH), 29.50, 205.42 $(CD_3)_2CO$).

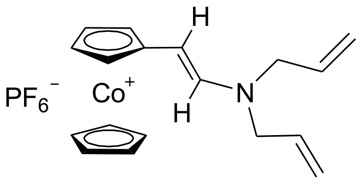
UV-vis. for **5**: $\lambda_{max\ 1}$ = 417nm, $\lambda_{max\ 2}$ = 495nm



5



The IR spectrum of **5**: IR (KBr): 1615 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} (ν_{PF6^-})



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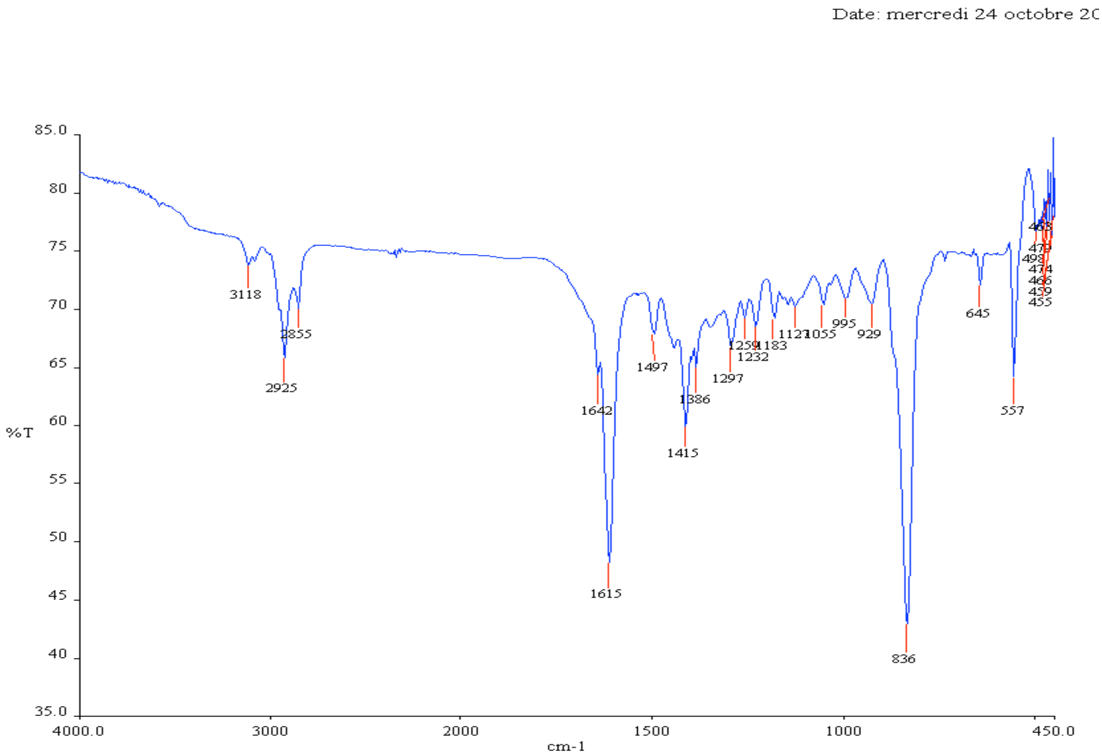
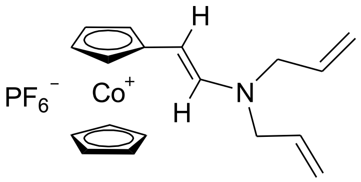


ESI of **5**: calc. *m/z* for M^+ ($C_{18}H_{21}CoN$) 310.1, found 310.1.



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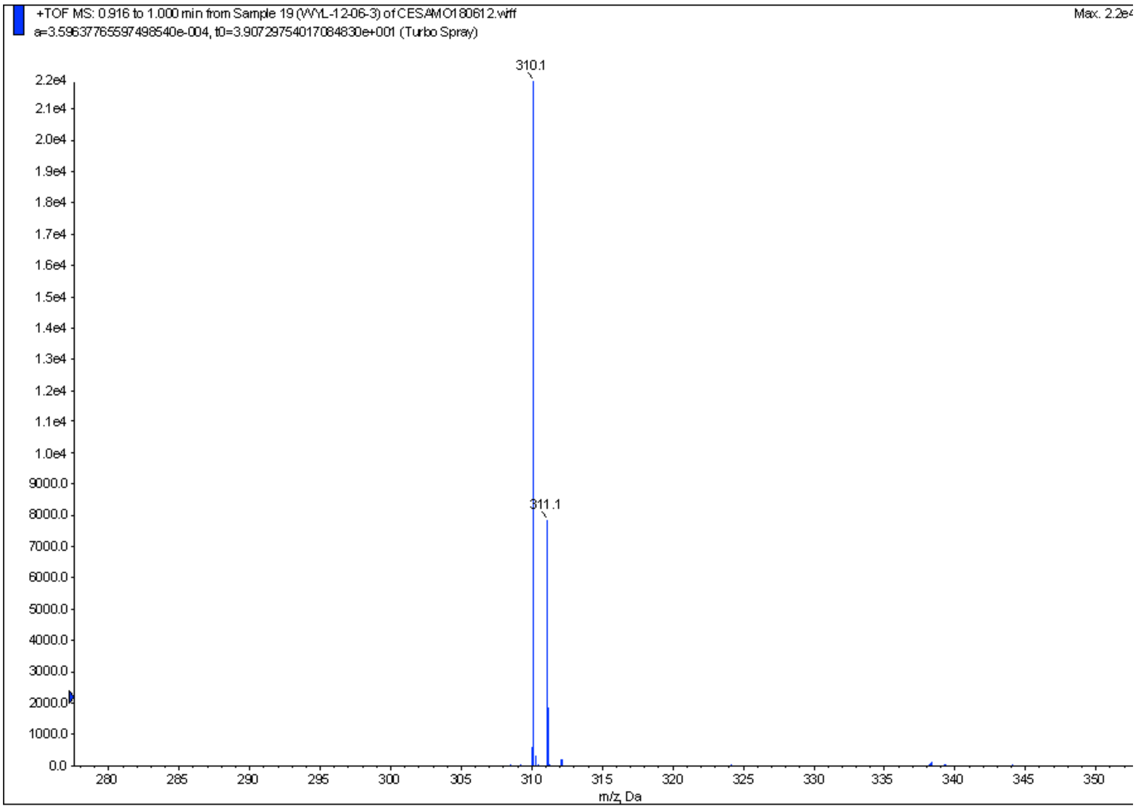
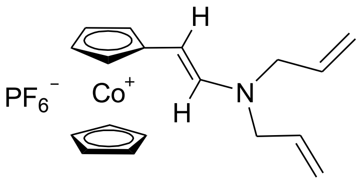


^{1}H NMR of **5**



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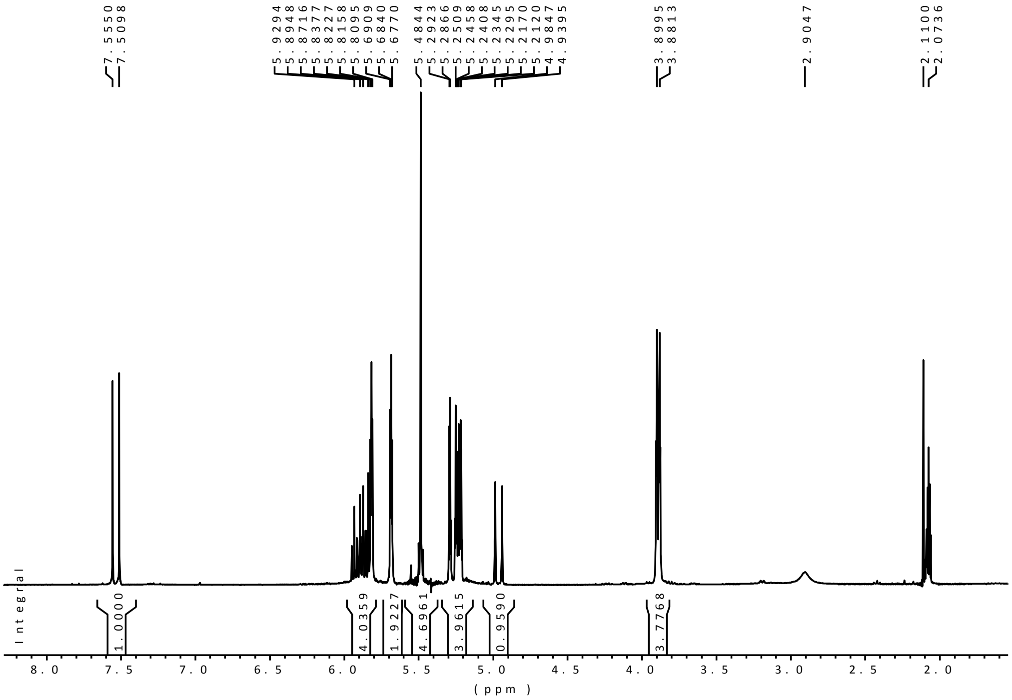
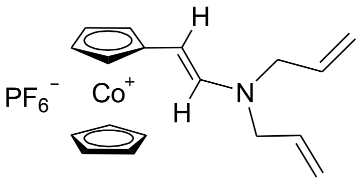


^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 3.88 (t, 4H), 4.93 (d, J = 13.50Hz, 2H), 5.21 (m, 4H), 5.48 (s, 5H, Cp), 5.67 (t , 2H/C_5H_4), 5.81 (t , 2H/C_5H_4), 5.92 (m, 2H), 7.51 (d, J = 13.50Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.90 (s, H_2O).

^{31}P NMR of **5** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-).



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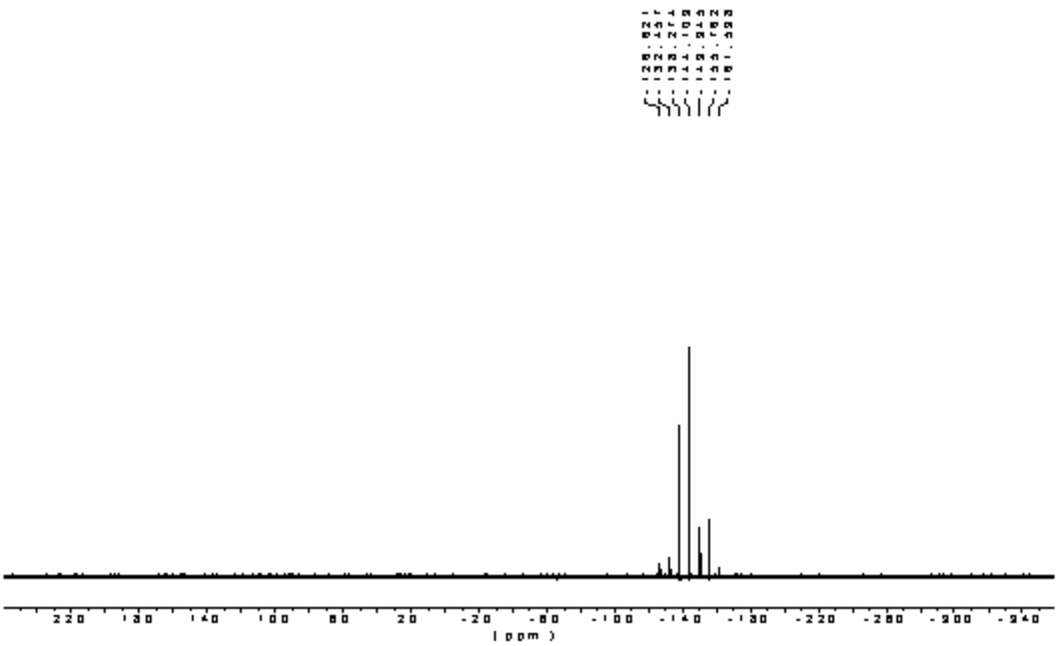
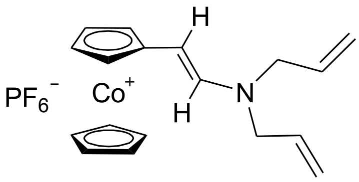


^{13}C NMR of **5**



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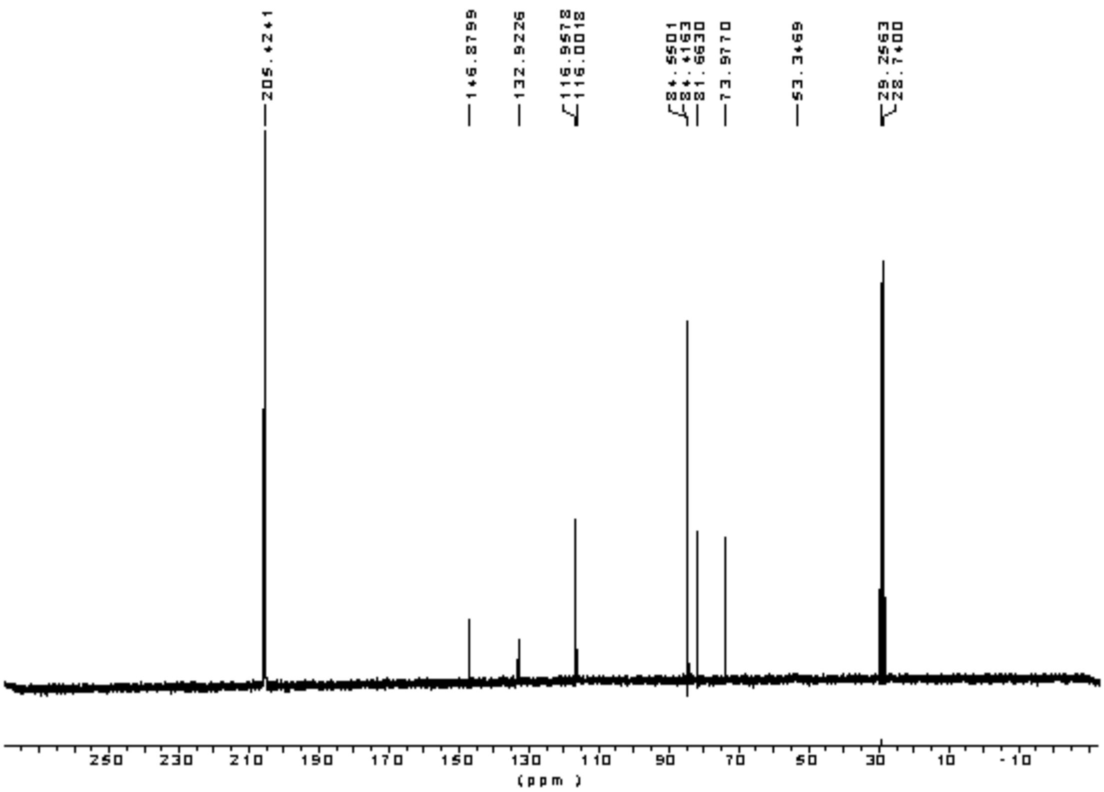
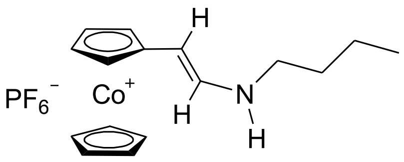
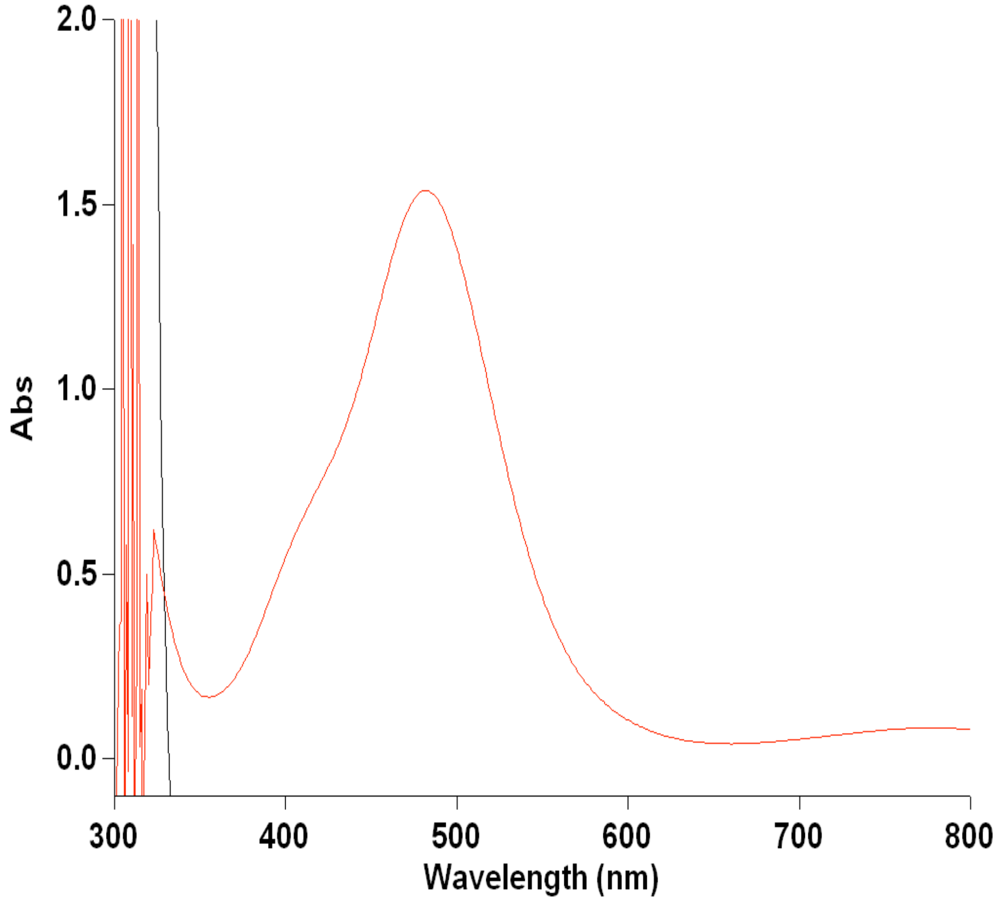


^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 53.34 (CH_2), 73.98 (2C/C_5H_4), 81.66 (2C/C_5H_4), 84.42 (C/C_5H_4), 84.55 (Cp/unsub.), 116.00 (CH), 116.96 (2C), 132.92 (2C), 146.88 (CH), 29.25, 205.42 $(CD_3)_2CO$).

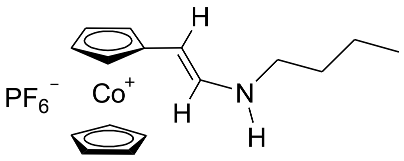
UV-vis. of **6**: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 485nm



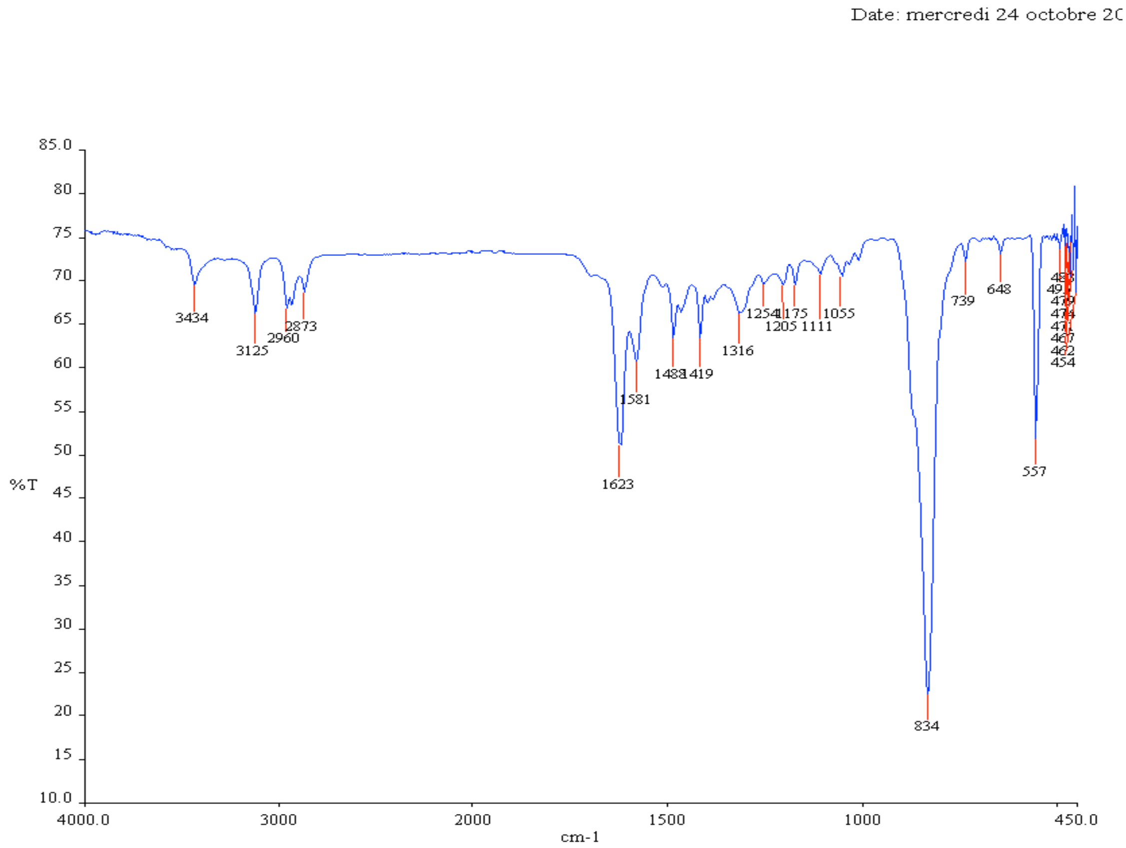
6



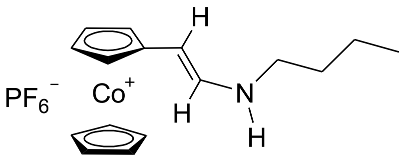
The IR spectrum of **6:** IR (KBr): 1623 cm^{-1} ($\nu_{C=C}$), 834 cm^{-1} (ν_{PF6^-}), 3434 cm^{-1} (ν_{N-H}).



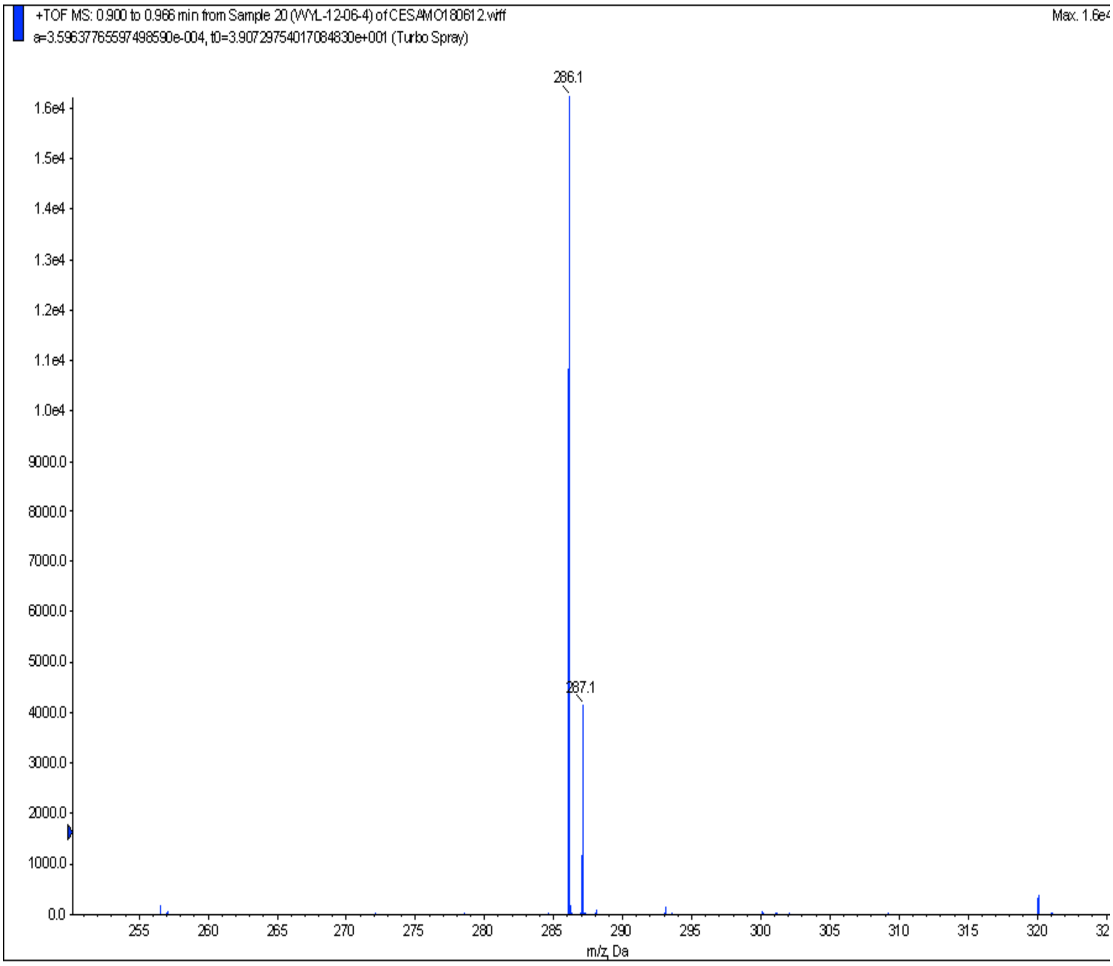
6



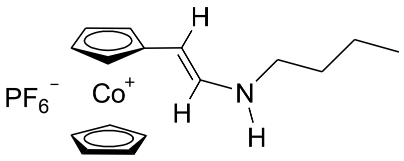
ESI of **6**: calc. *m/z* for M^+ ($C_{16}H_{21}CoN$) 286.1, found 286.1.



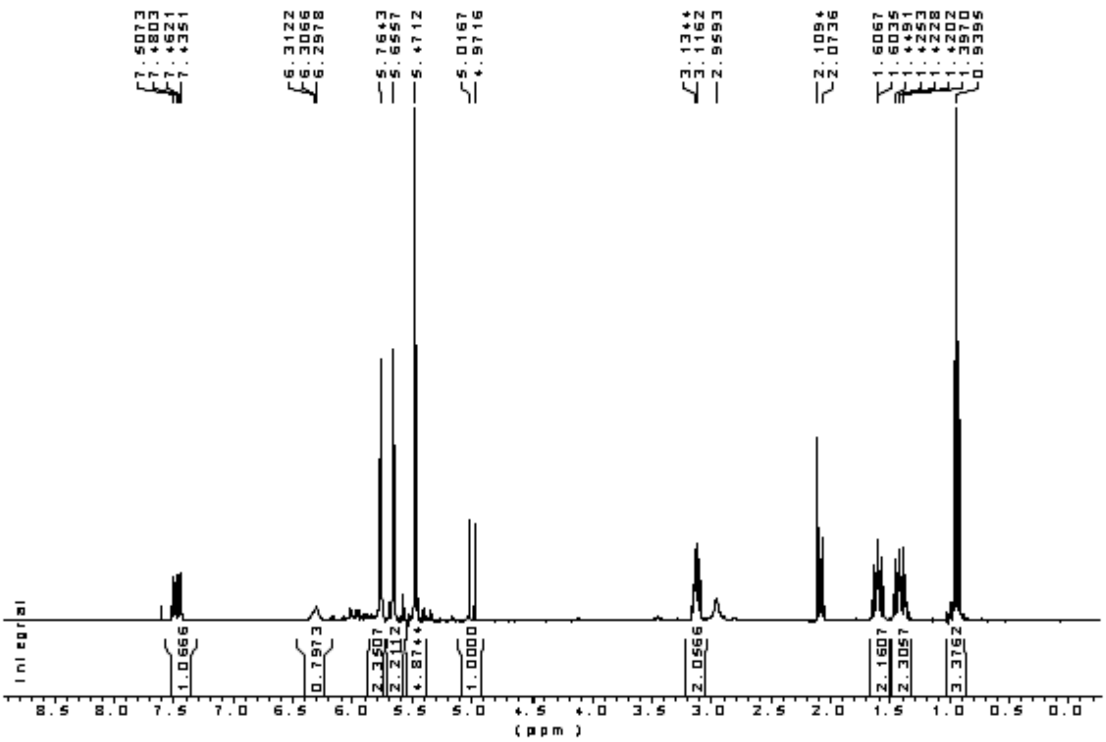
6



^{1}H NMR of **6**

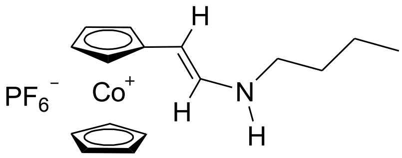


6

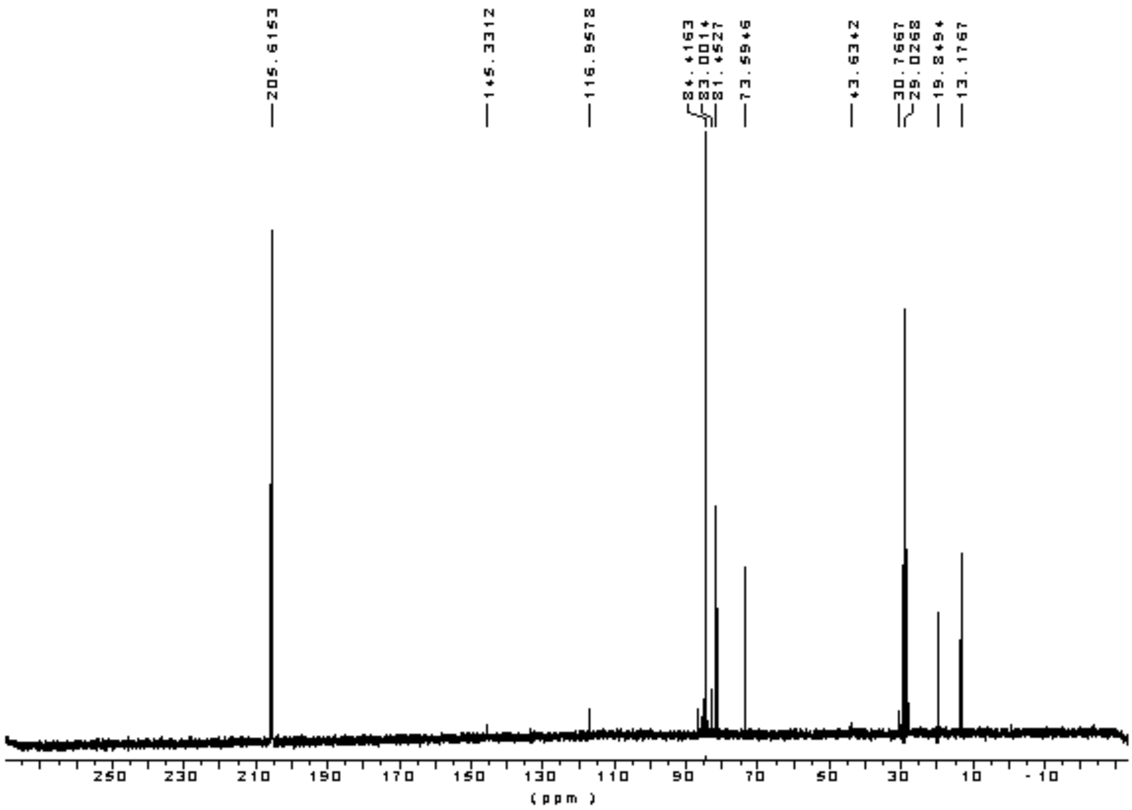


^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.94 (t, 3H, CH_3), 1.40 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 3.11 (t, 2H, CH_2), 4.97 (d, J = 13.50Hz, 1H), 5.47 (s, 5H, Cp), 5.66 (t , 2H/C_5H_4), 5.76 (t , 2H/C_5H_4), 7.43 (m, J = 13.56Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O).

^{13}C NMR of **6**

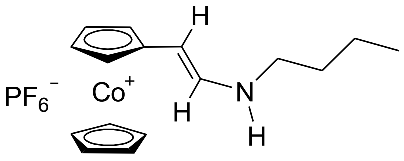


6



^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.17 (CH_3), 19.84 (CH_2), 30.76 (CH_2), 43.63 (CH_2), 73.59 (2C/C_5H_4), 81.45 (2C/C_5H_4), 83.00 (C/C_5H_4), 84.41 (Cp/unsub.), 116.96 (CH), 145.33 (CH), 29.02, 205.61 $(CD_3)_2CO$).

^{31}P NMR of **6** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-).



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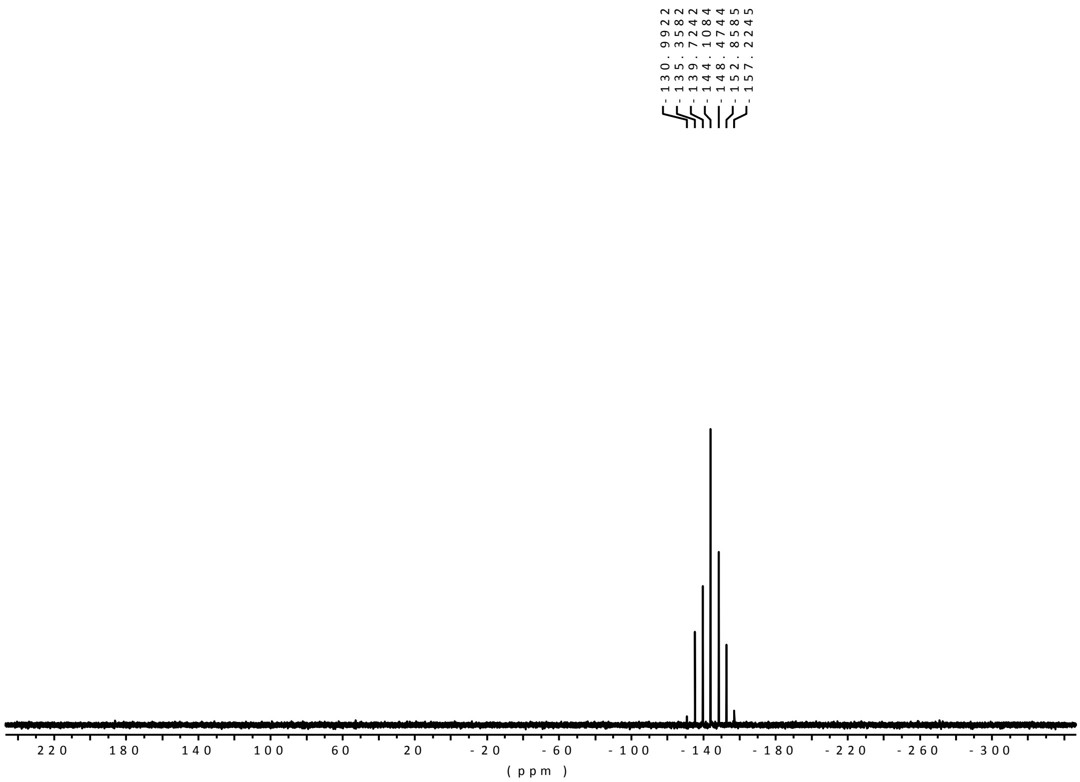
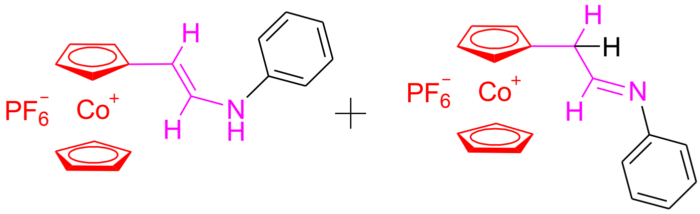
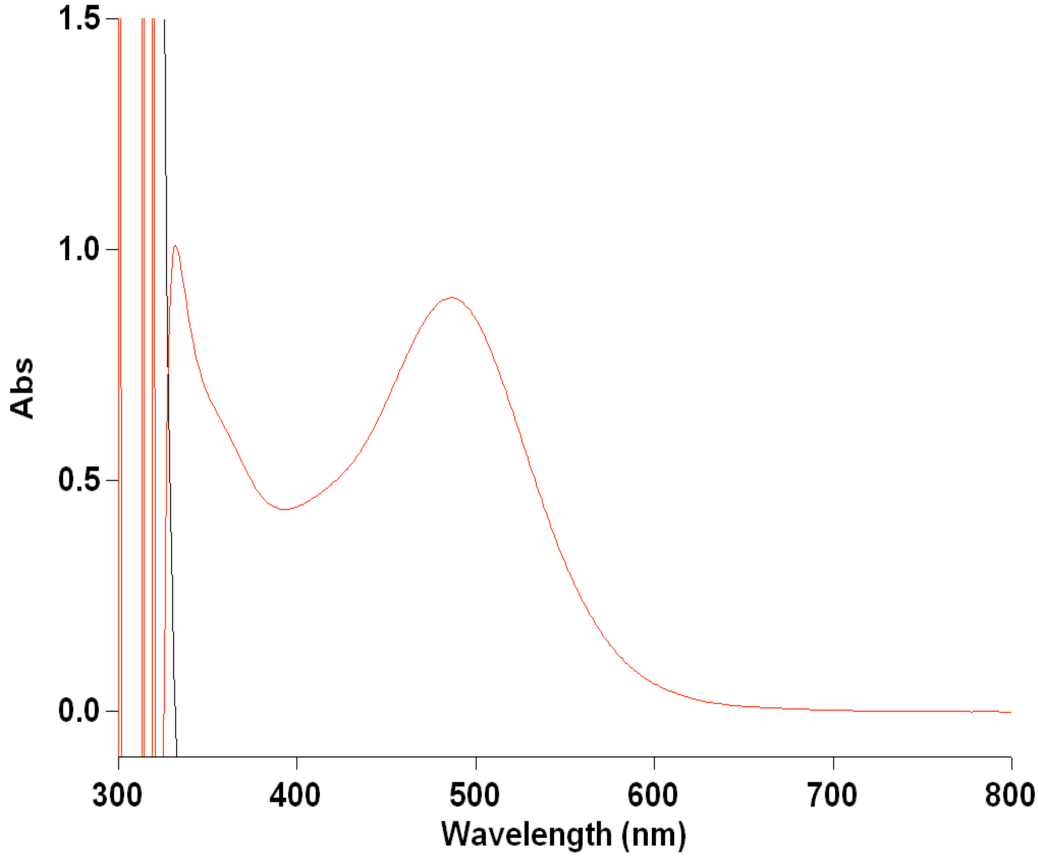


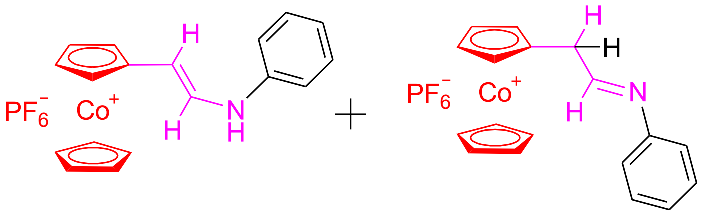
UV-vis. for **7** and **7A**: $\lambda_{max\ 1}$ = 360nm, $\lambda_{max\ 2}$ = 495nm



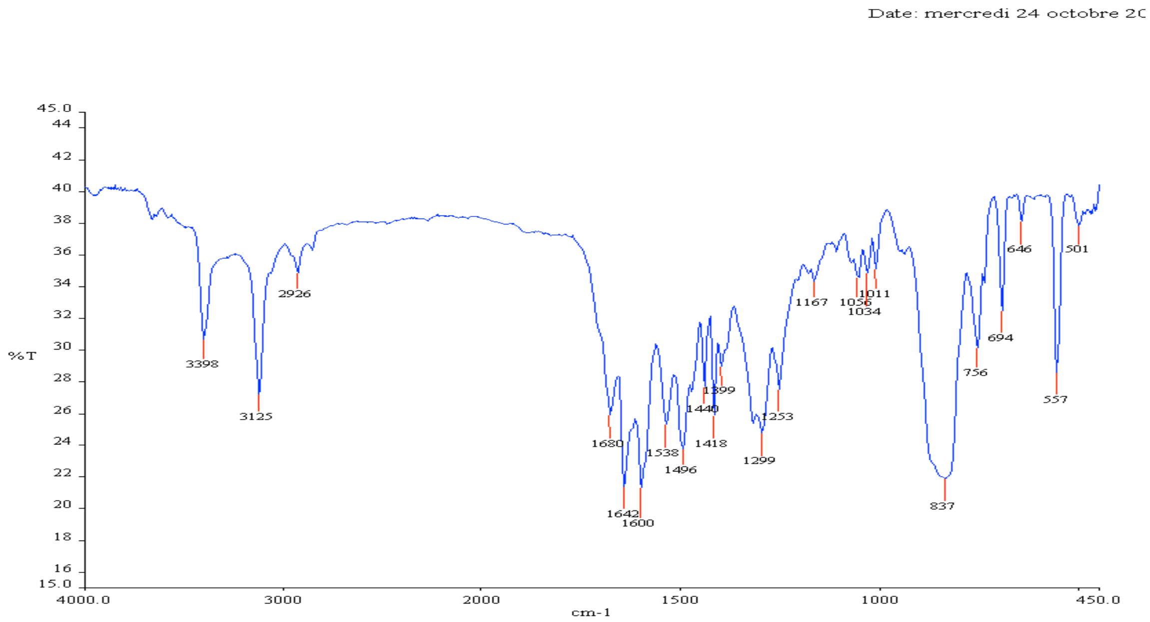
7 **7A**



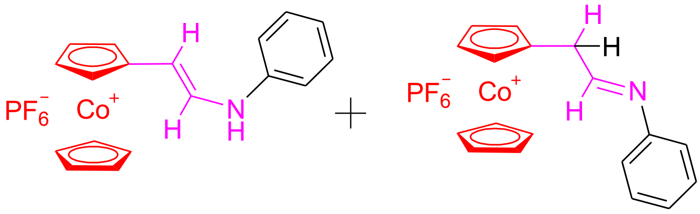
The IR spectrum of **7** and **7A:** IR (KBr): 1642 cm^{-1} ($\nu_{C=C}$), 1600 cm^{-1} ($\nu_{C=N}$), 837 cm^{-1} ($\nu_{PF_6^-}$), 3398 cm^{-1} (ν_{N-H}).



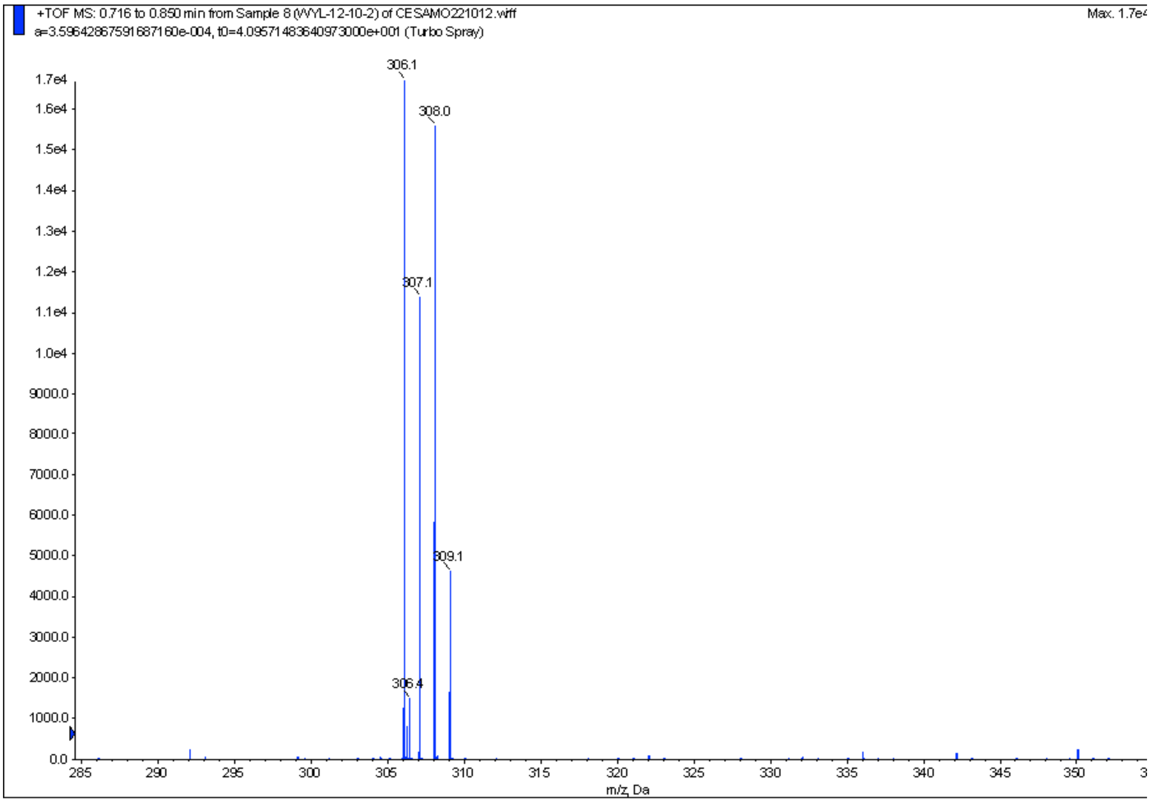
7 **7A**



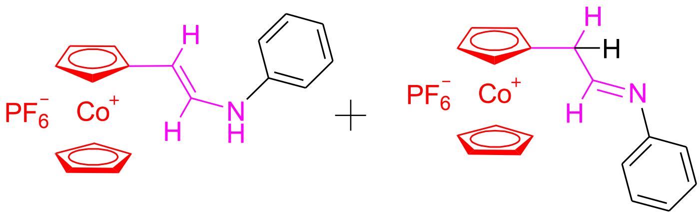
ESI of **7** and **7A**: calc. *m/z* for M^+ ($C_{18}H_{17}CoN$) 306.1, found 306.1



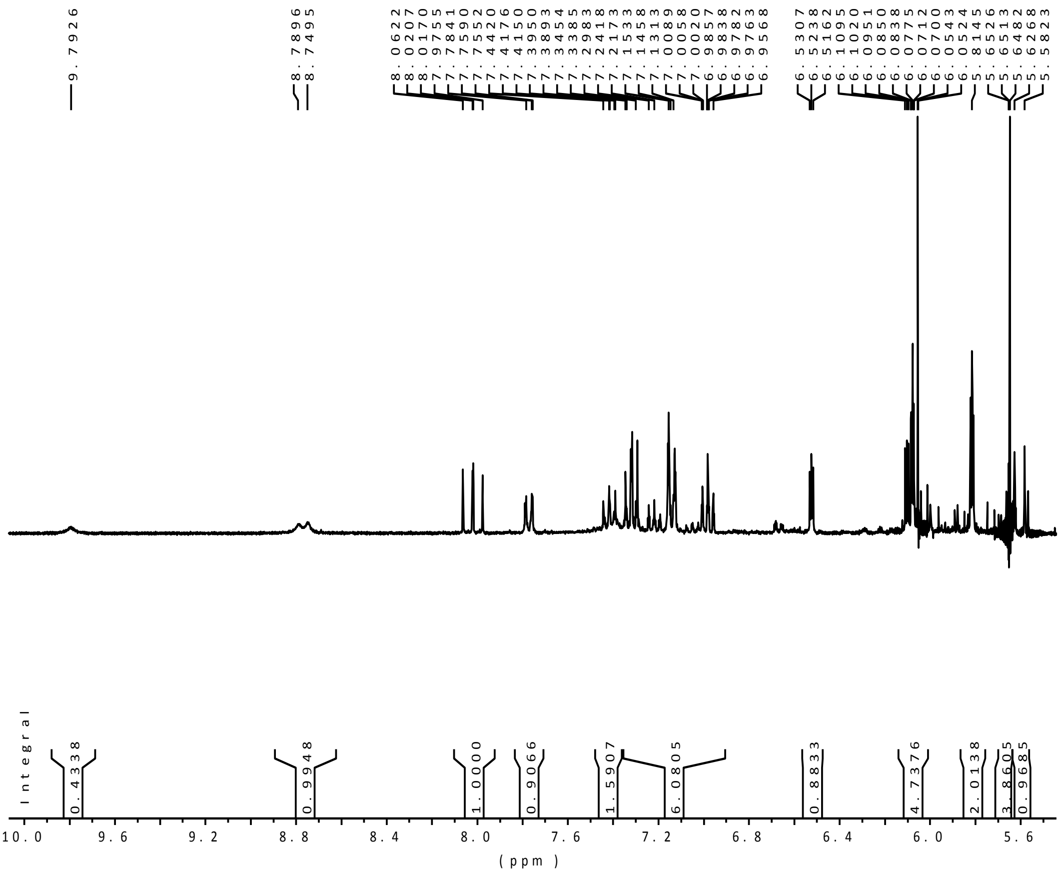
7 **7A**



^{1}H NMR of **7** and **7A**



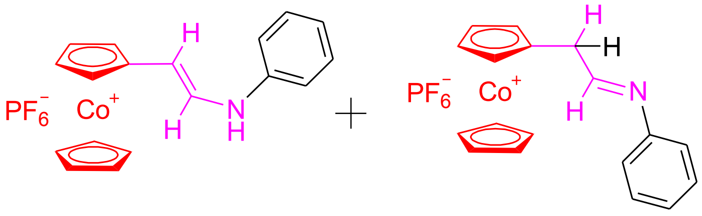
7 **7A**



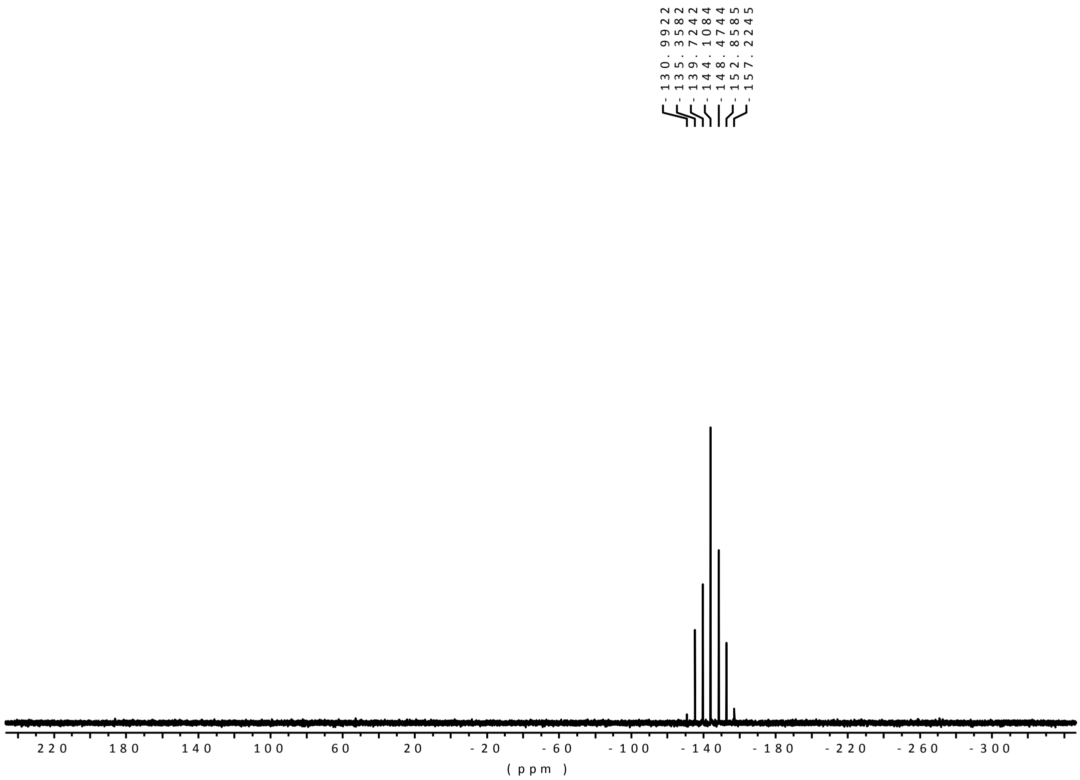
^{1}H NMR of **7** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 5.58 (d, *J* = 13.35Hz, 1H), 5.64 (s, 5H, Cp), 5.81 (t , 2H/C_5H_4), 6.06 (t , 2H/C_5H_4), 6.98 (t , 2H/Ph), 7.15 (d , 1H/Ph), 7.38 (t , 2H/Ph), 8.06 (m, *J* = 13.45Hz, 1H), 8.74 (d, 1H/NH), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O).

^{1}H NMR **7A** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 6.06 (s, 5H, Cp), 6.61 (t , 2H/C_5H_4), 6.52 (t , 2H/C_5H_4), 7.34 (m , 2H/Ph), 7.44 (m, 3H/Ph), 7.78 (d , 2H/CH_2), 9.78 (m, 1H), 2.07 (m, $(CD_3)_2CO$), 2.96 (s, H_2O).

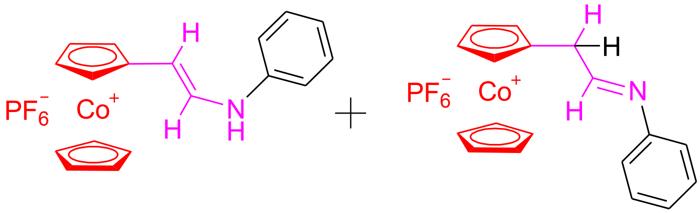
^{31}P NMR of **7** and **7A** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-).



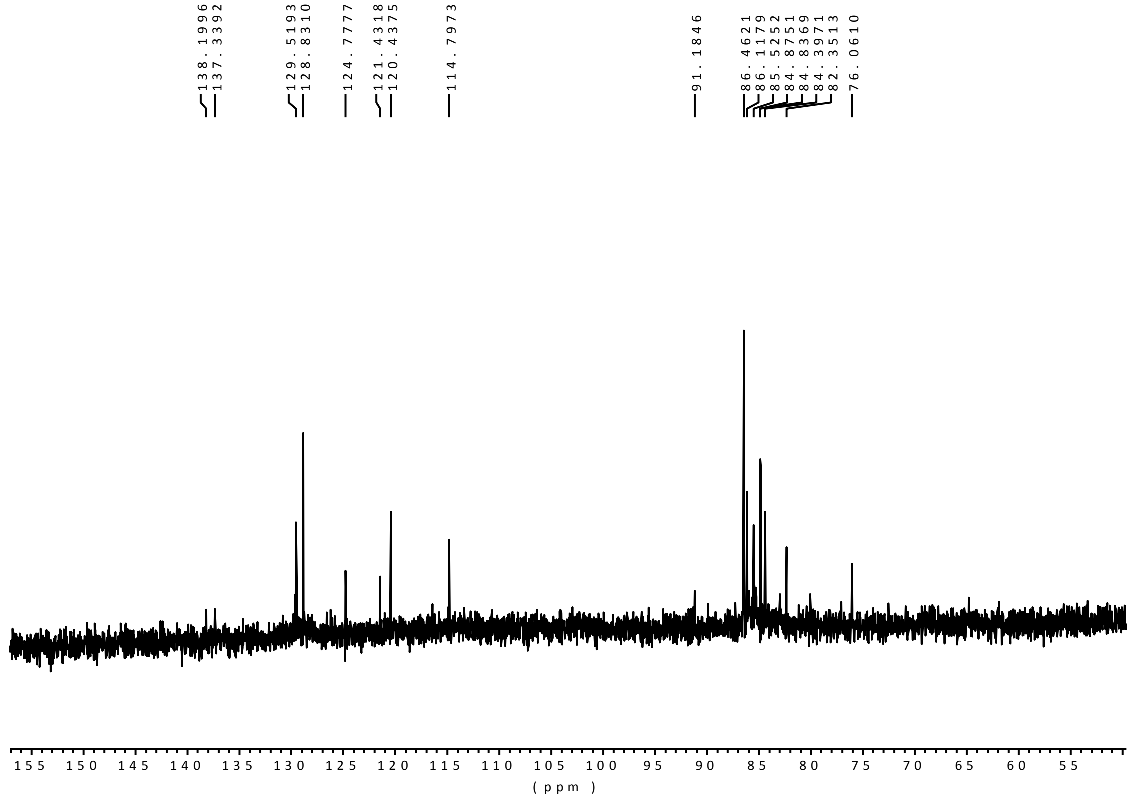
7 **7A**



^{13}C NMR of **7** and **7A**

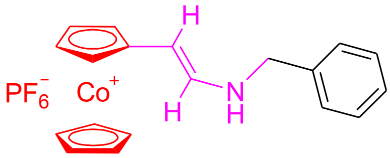


7 **7A**



^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 76.06, 82.35, 84.40, 84.78, 84.84, 84.88, 85.53, 86.12 86.46 (Cp/sub.), 91.20 (CH), 114.80 (CH), 120.43 (CH), 121.43, 124.78, 128.83, 129.52, 137.33, 138.20 (Ph), 34.39, 210.85 $(CD_3)_2CO$.

UV-vis **8**: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 480nm



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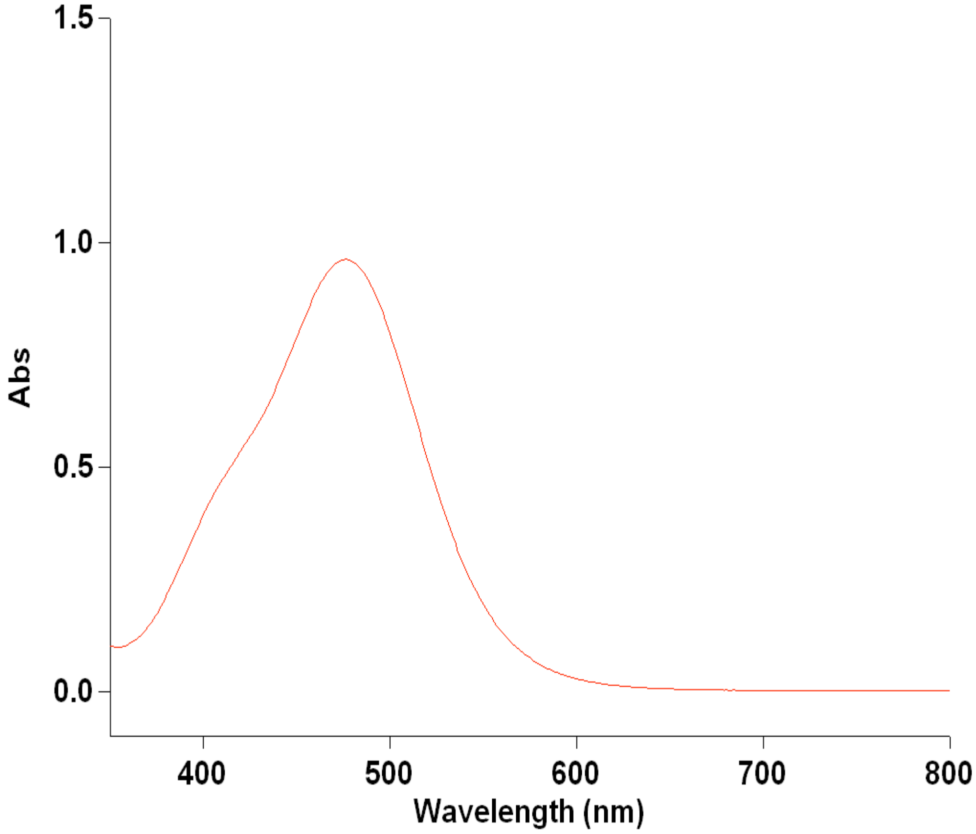
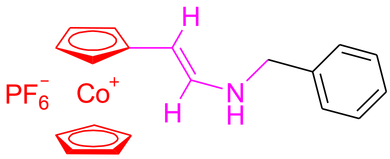


The IR spectrum of **8**: IR (KBr): 1622 cm^{-1} ($\nu_{C=C}$), 832 cm^{-1} (ν_{PF6^-}), 3444 cm^{-1} (ν_{N-H}).



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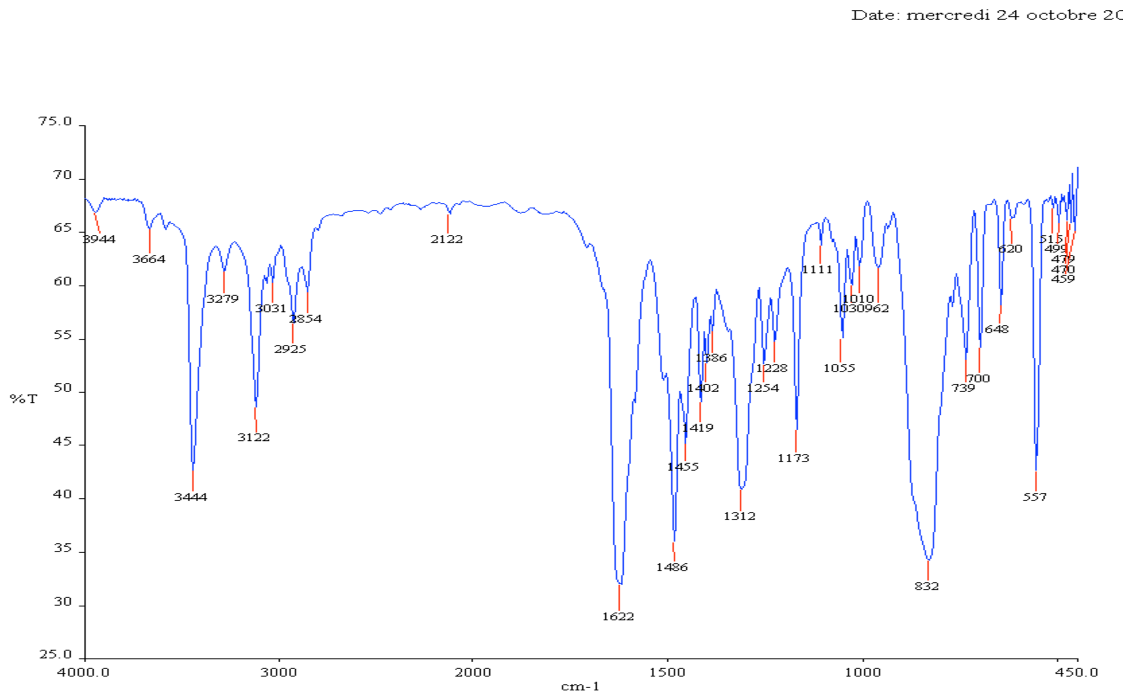
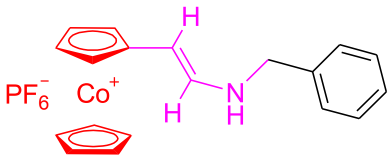


ESI of **8**: calc. *m/z* for M$^+$ ($C_{19}H_{19}CoN$) 320.3 found 320.1



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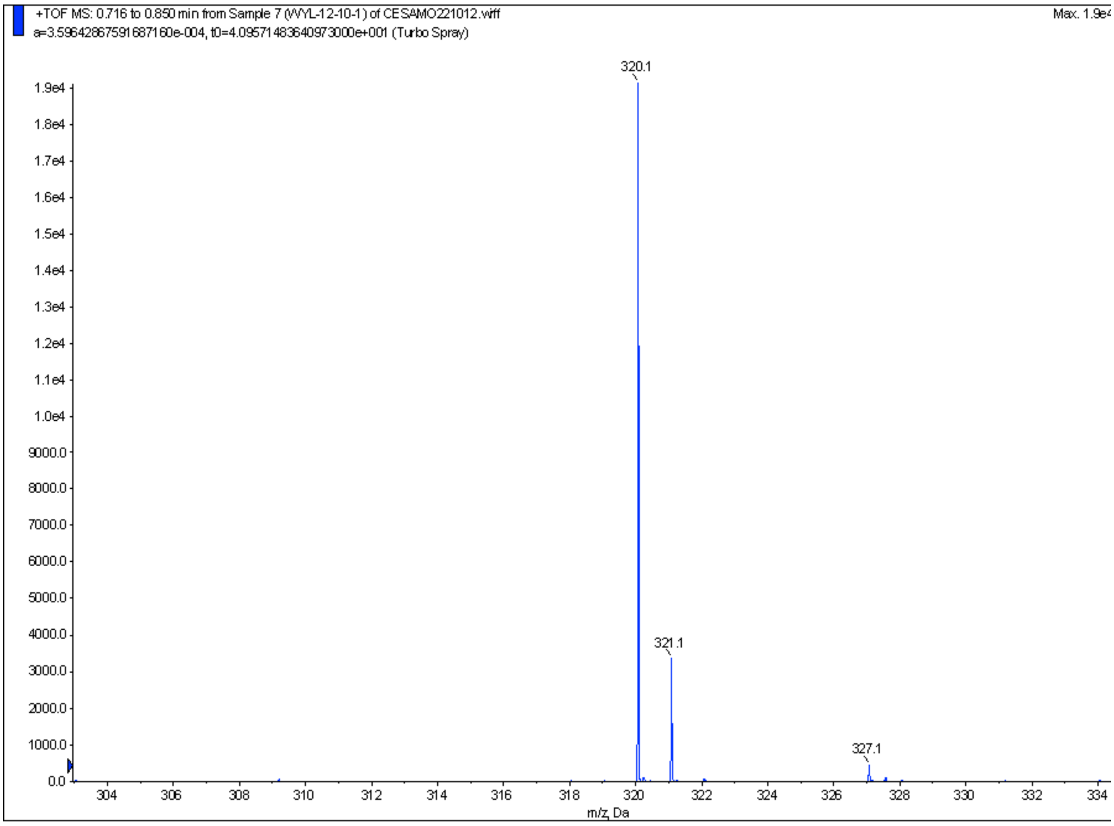
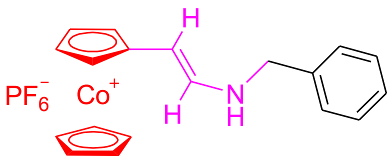


^{1}H NMR of **8**



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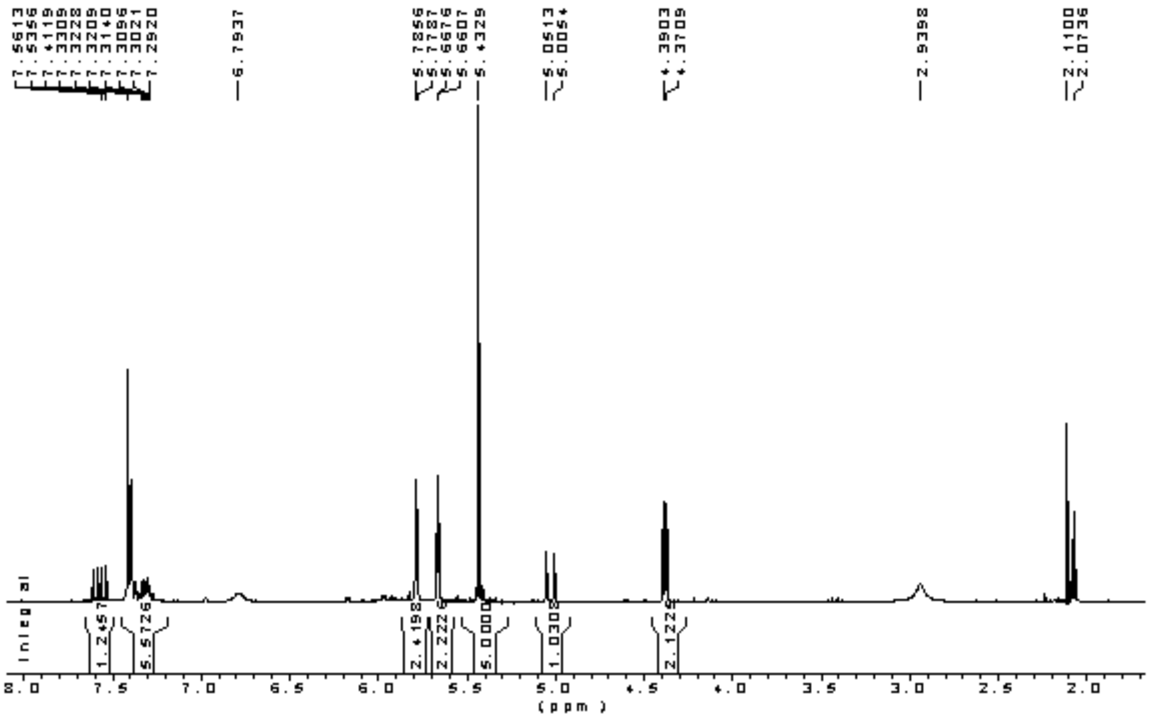
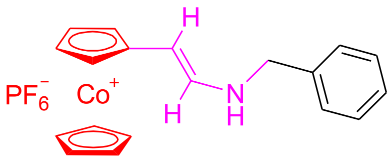
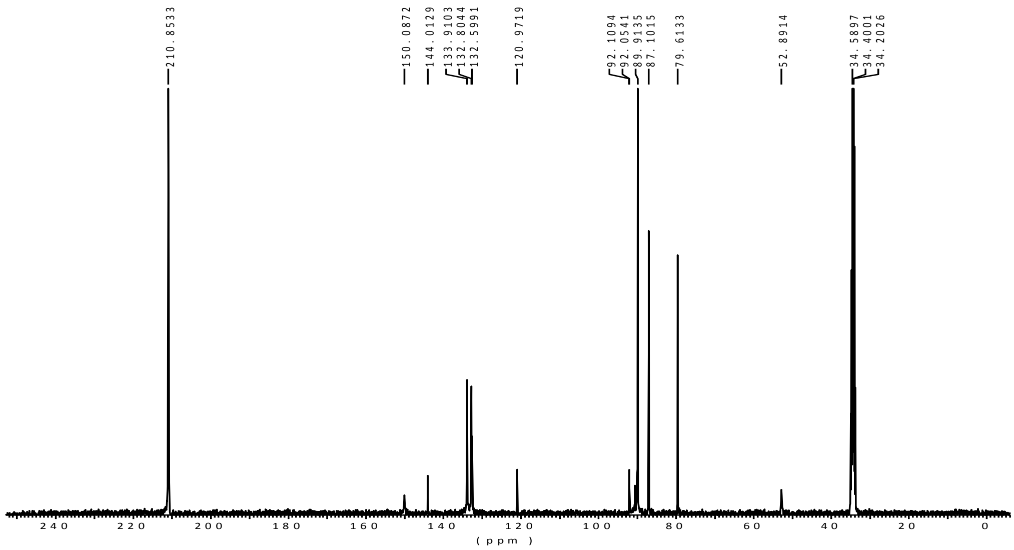


^{1}H NMR of **8** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 4.37 (d, 2H), 5.00 (d, *J* = 13.62Hz, 1H), 5.43 (s, 5H, Cp), 5.66 (t, 2H/C_5H_4), 5.77 (t, 2H/C_5H_4), 6.79 (m, 1H/NH), 7.41 (m, 5H/Ph), 7.53 (m, *J* = 13.67Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.94 (s, H_2O).

^{13}C NMR of **8**



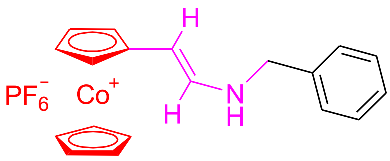
8



^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 52.89 (CH_2), 79.60 ($2C/C_5H_4$), 87.09 ($2C/C_5H_4$), 89.91 (Cp/unsub.), 92.05 (CH), 120.96 (C/C_5H_4), 144.00 (CH), 132.59, 132.80, 133.91, 150.08 (6C/Ph), 34.39, 210.85 $(CD_3)_2CO$.

Electronic Supplementary Material (ESI) for Chemical Communications

^{31}P NMR of **8** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-).



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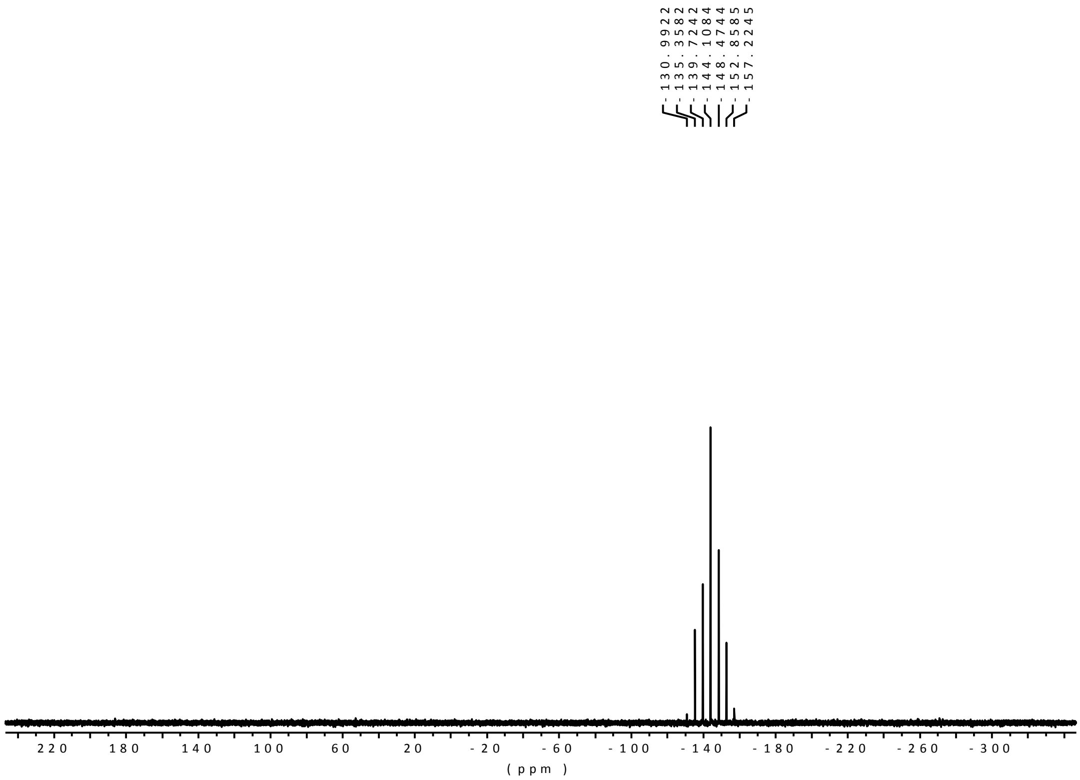
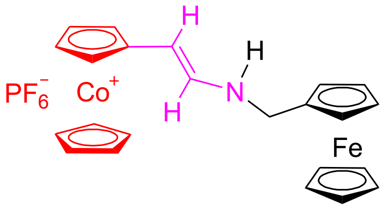
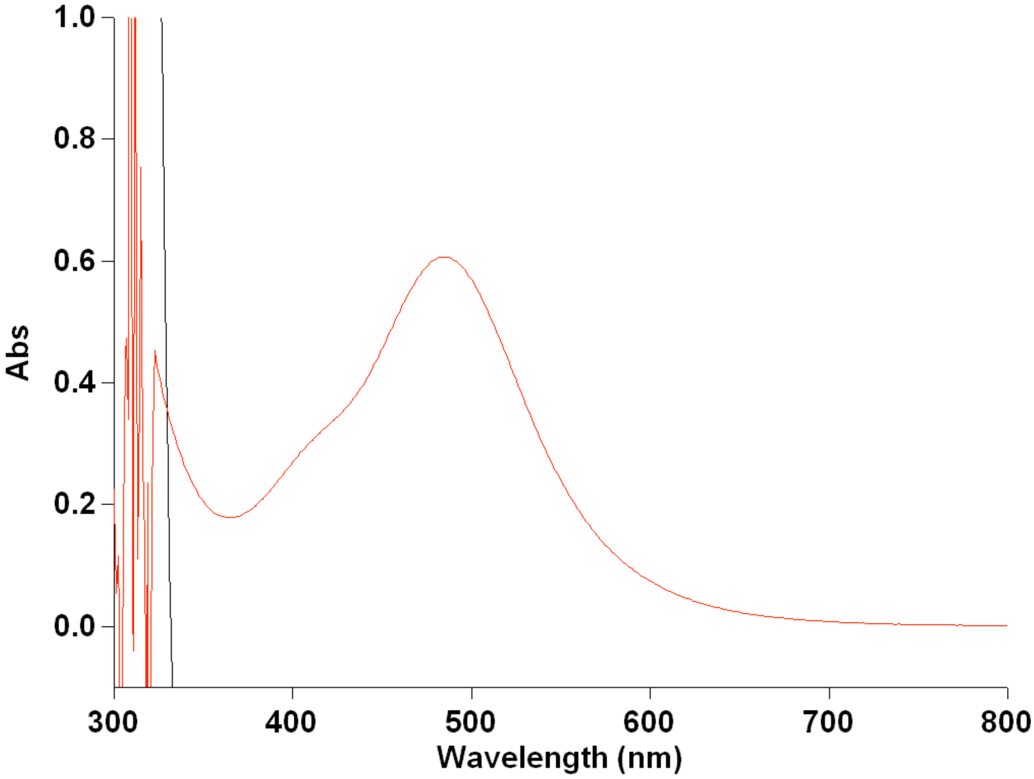


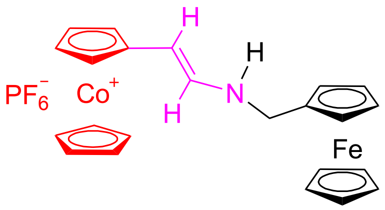
UV-vis. of **9**: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 490nm



9



The IR spectrum of **9:** IR (KBr): 1621 cm^{-1} ($\nu_{C=C}$), 836 cm^{-1} (ν_{PF6^-}), 3429 cm^{-1} (ν_{N-H}).



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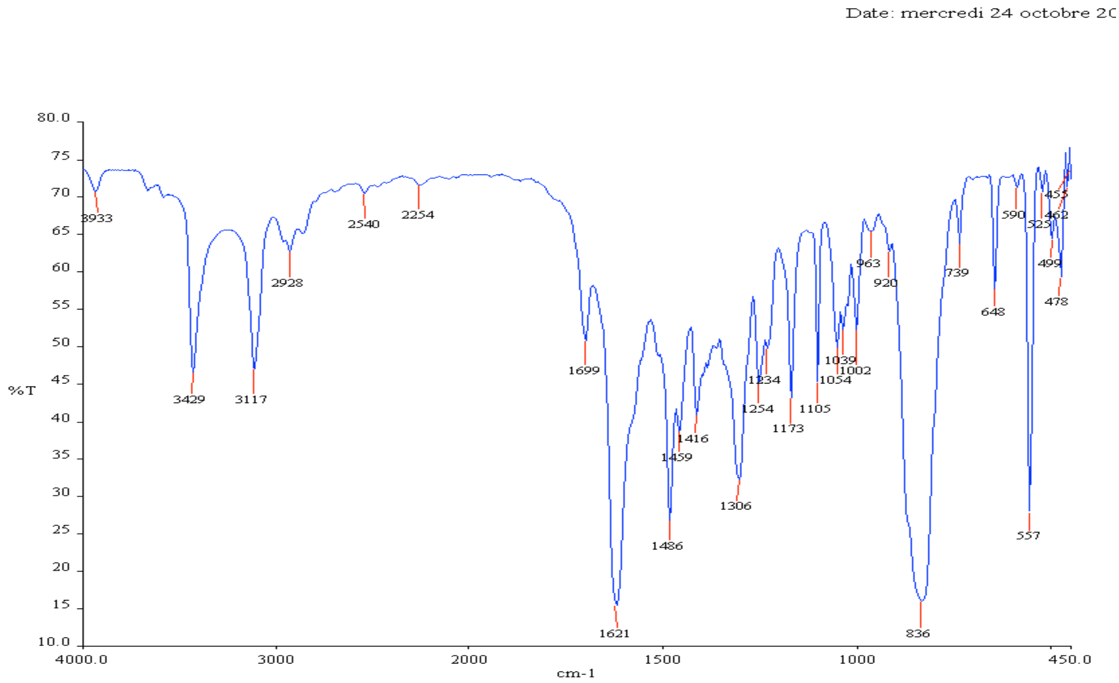
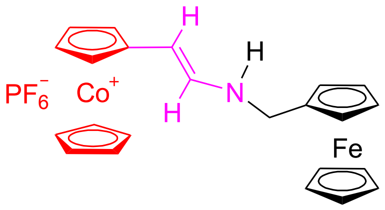


^{1}H NMR of **9:**



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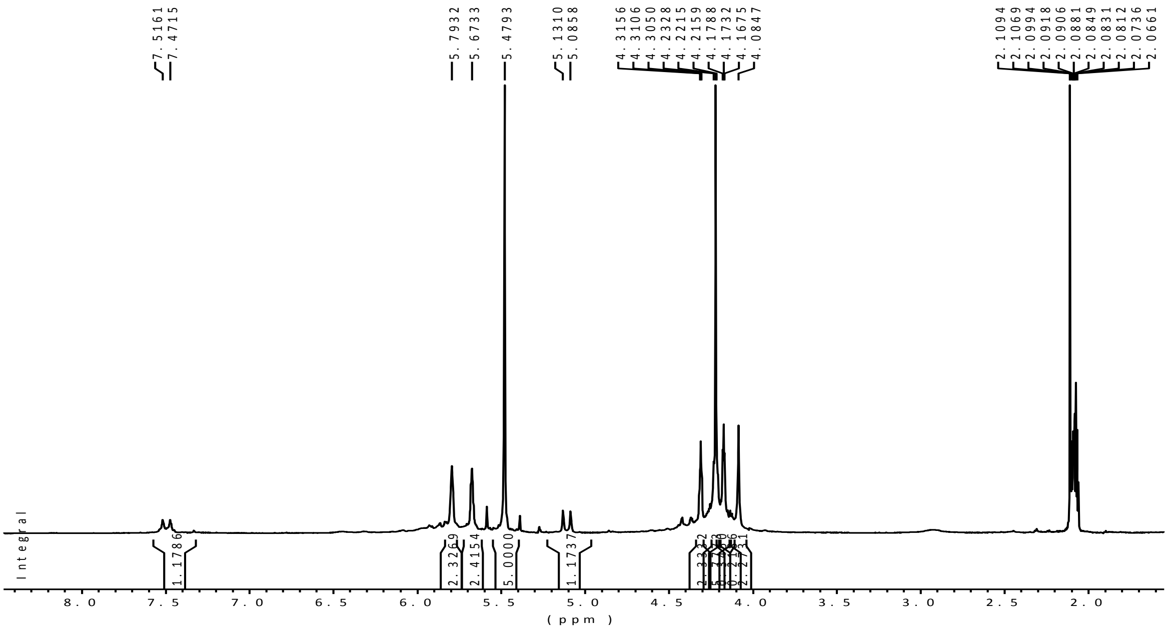
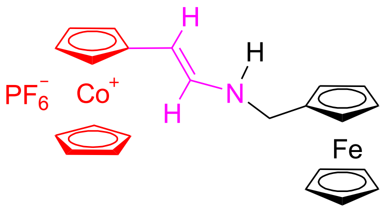


^{1}H NMR of **9** (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 4.08 (d, 2H), 4.16 (t , 2H/C_5H_4), 4.22 (s, 5H, Cp), 4.31 (t , 2H/C_5H_4), 5.08 (d, J = 13.59Hz, 1H), 5.48 (s, 5H, Cp), 5.67 (t , 2H/C_5H_4), 5.79 (t, 2H/C_5H_4), 7.47 (d, J = 13.59Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.94 (s, H_2O).

^{31}P NMR of **9** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.12 (m, PF_6^-)



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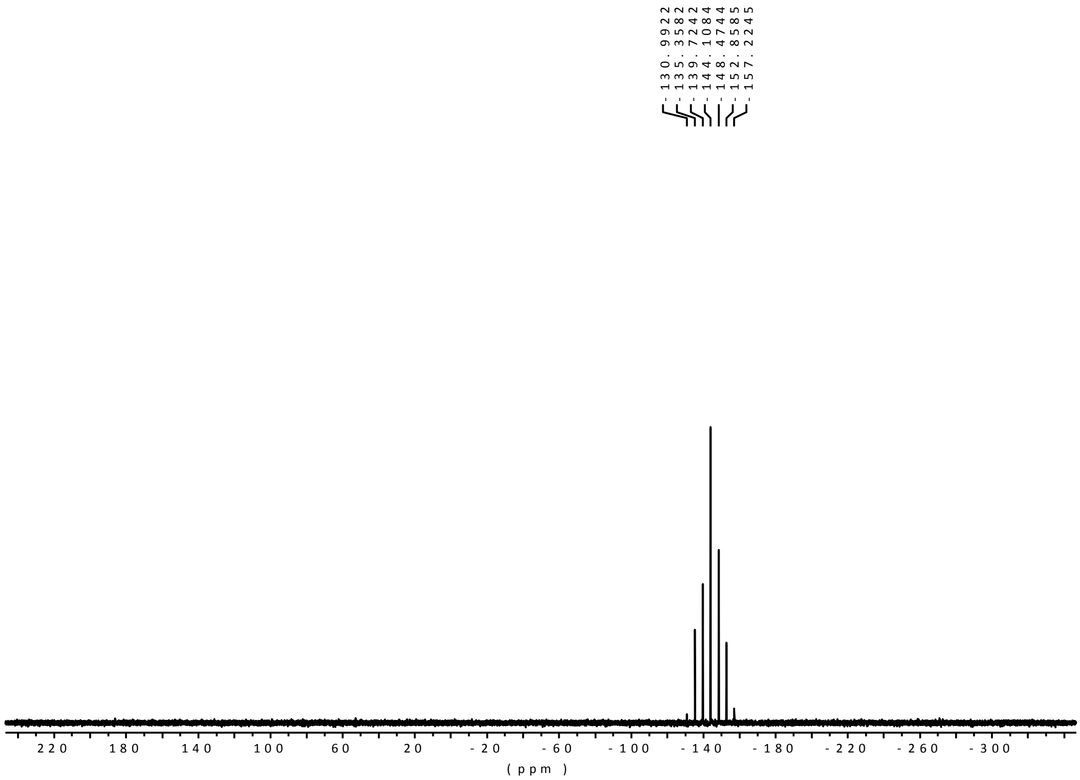
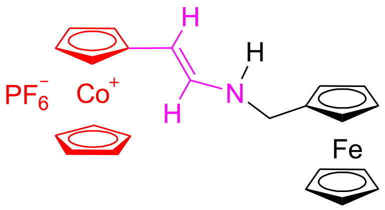


^{13}C NMR of **9**



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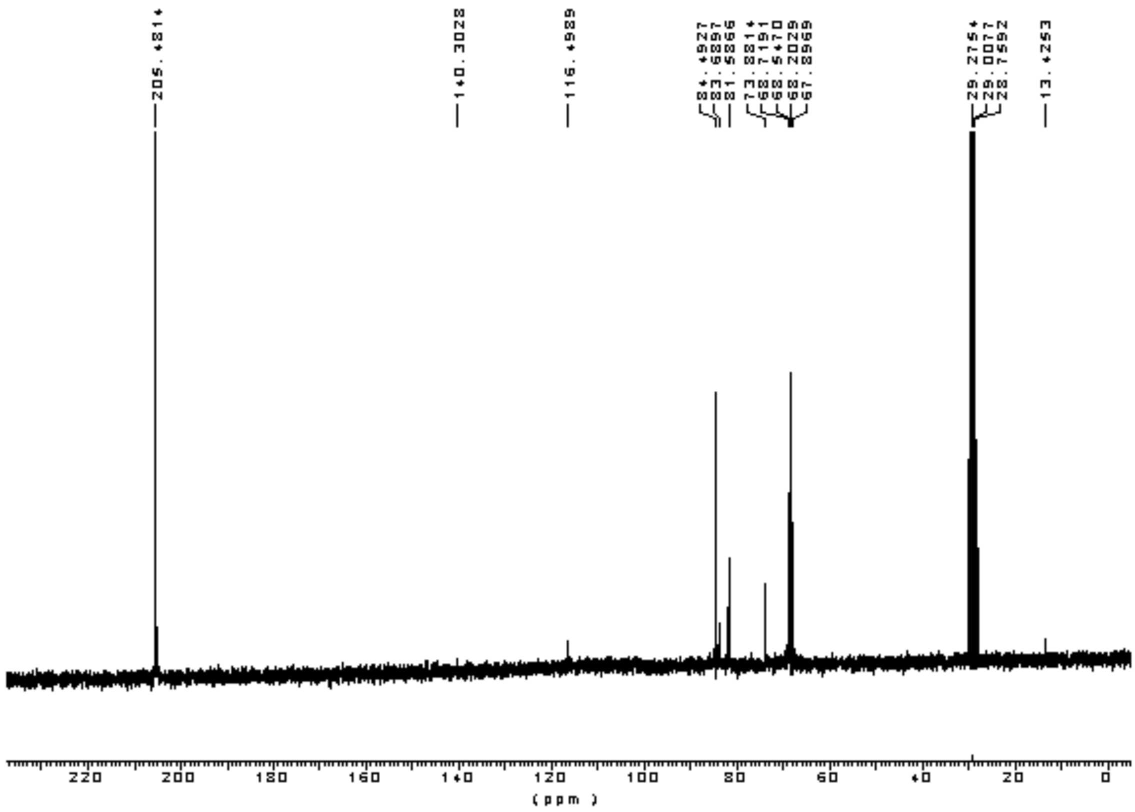
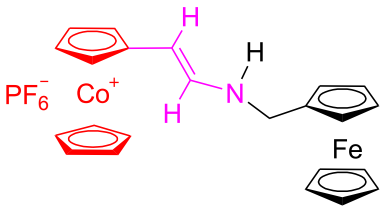
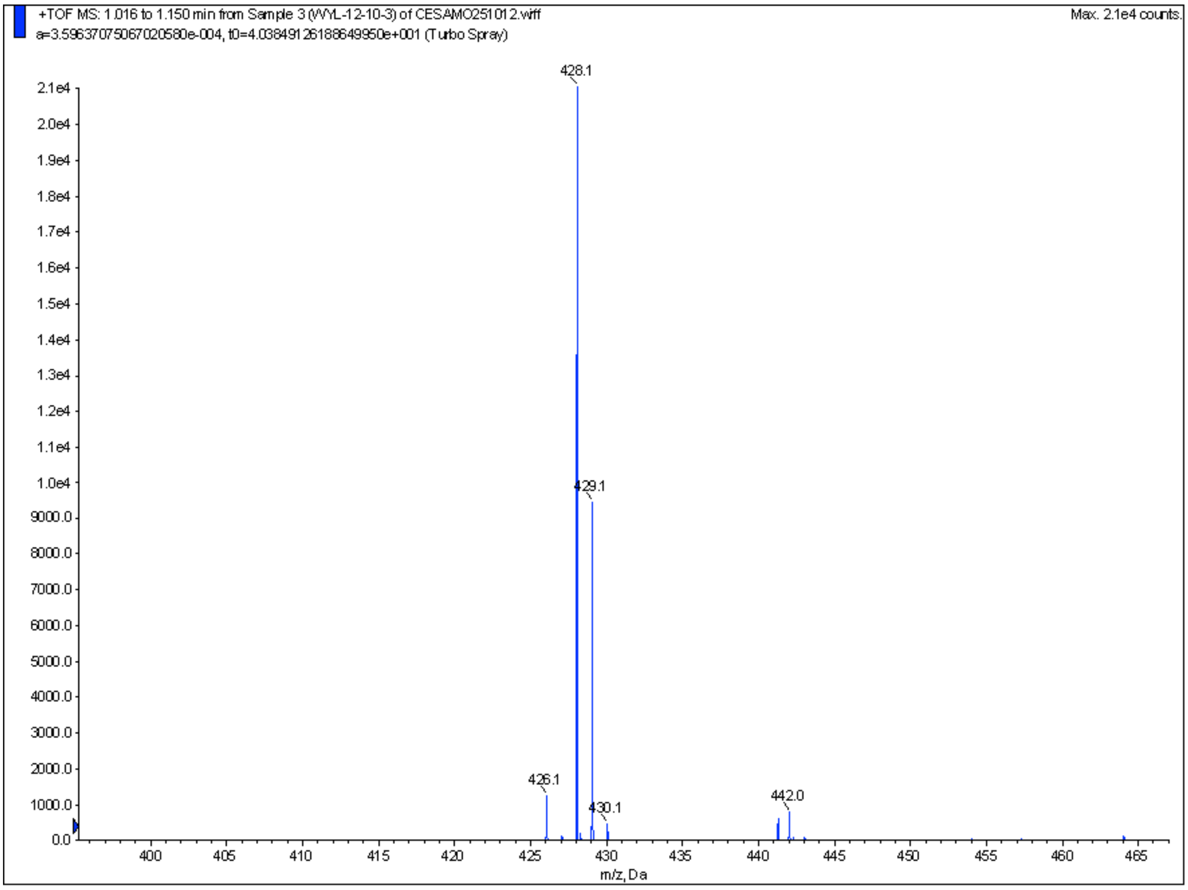


^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.42 (CH_2), 67.90 (2C/C_5H_4/Fc), 68.20 (2C/C_5H_4/Fc), 68.55 (Cp/unsub./Fc), 68.72 (C_5H_4/Fc), 73.88 (2C/C_5H_4), 81.59 (2C/C_5H_4), 83.69 (CH), 84.49 (Cp/unsub.), 116.50 (C/C_5H_4), 140.30 (CH), 29.27, 205.48 $(CD_3)_2CO$.

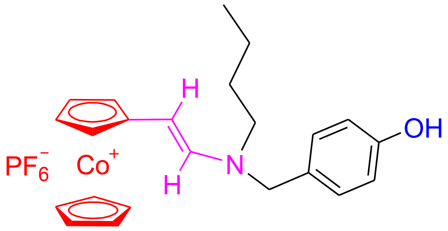
ESI of **9:** calc. *m/z* for M^+ ($C_{23}H_{23}CoFeN$) 428.1, found 428.1.



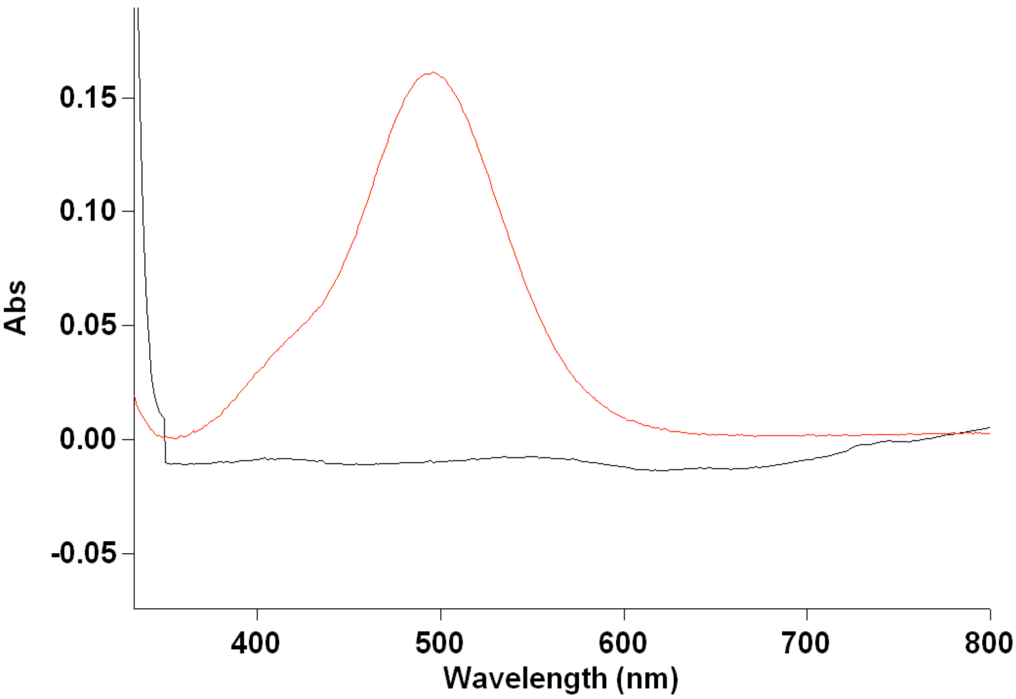
9



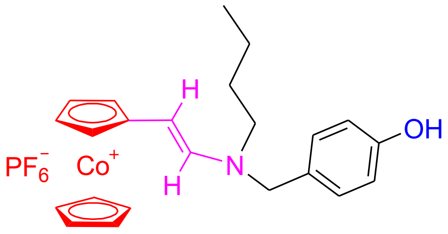
UV-vis. of **10**: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 495nm



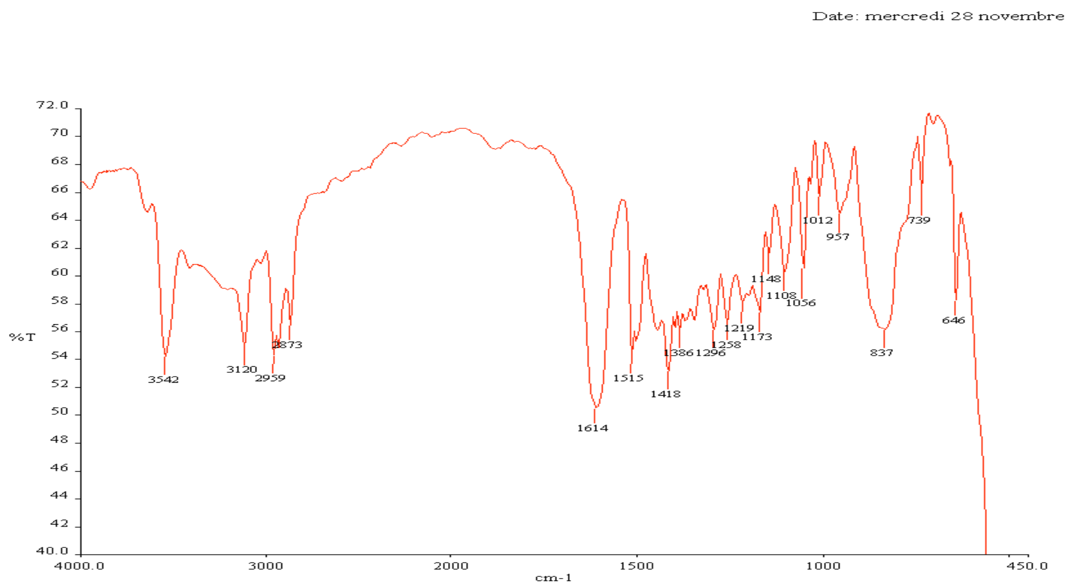
10



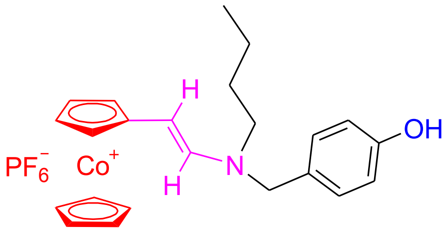
IR (KBr) of **10**: 1614 cm^{-1} ($\nu_{C=C}$), 837 cm^{-1} (ν_{PF6-}), 3442 cm^{-1} (ν_{OH}).



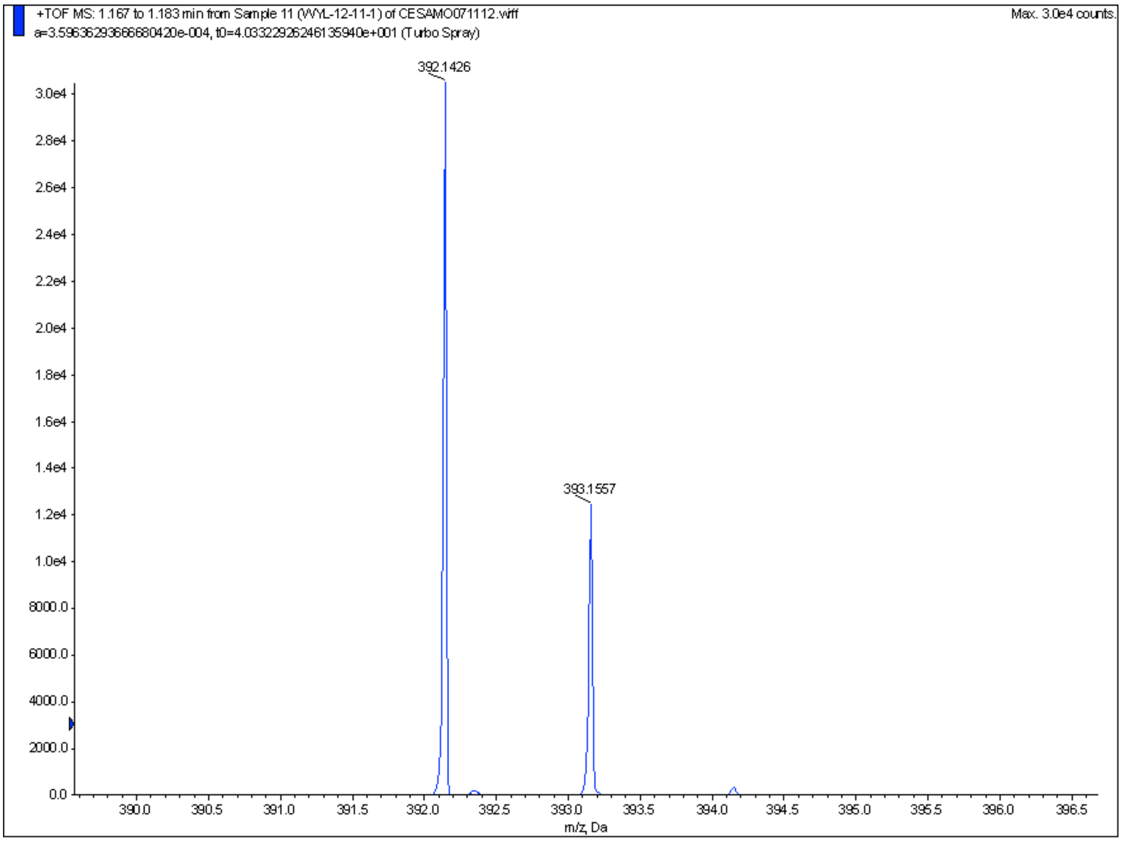
10



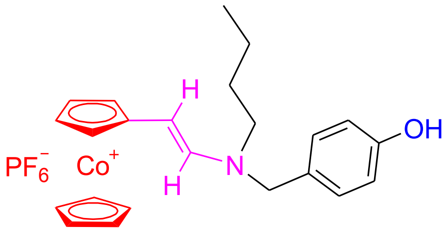
ESI of **10:** calc. *m/z* for M^+ ($C_{23}H_{27}CoFeF_6NOP$) 392.4, found 392.1.



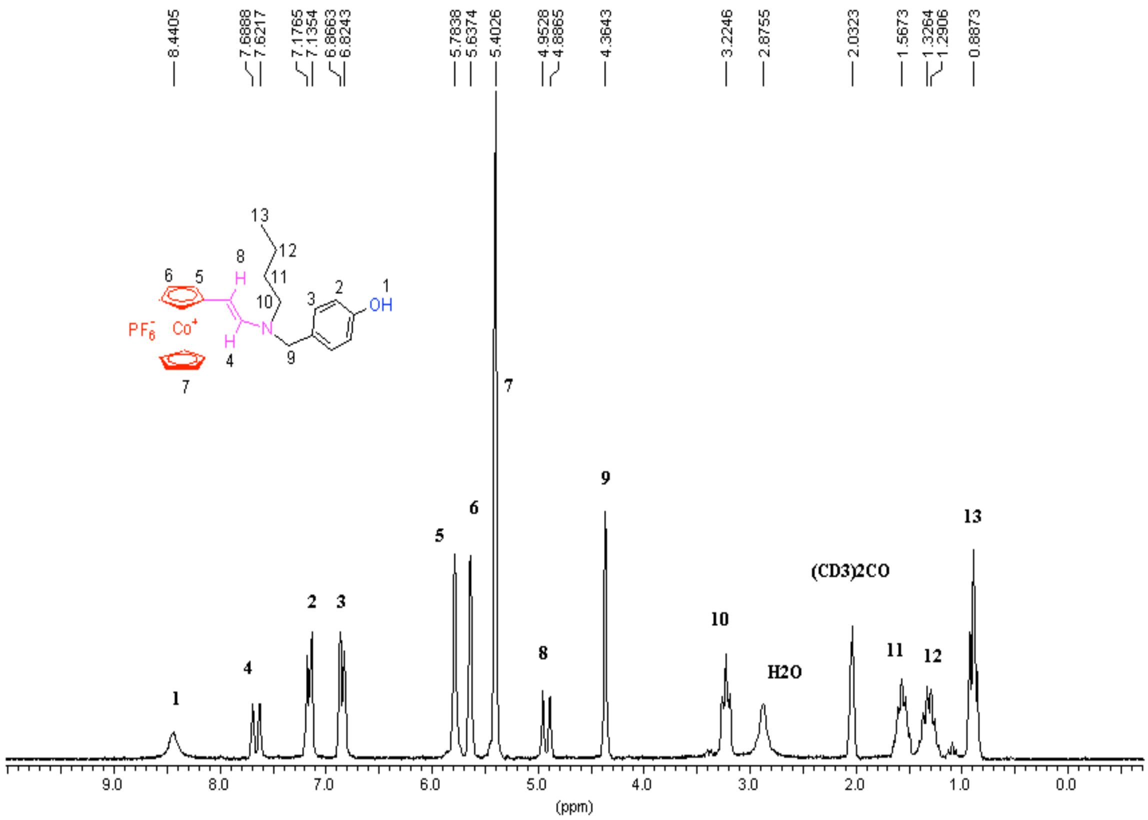
10



^{1}H NMR of **10**



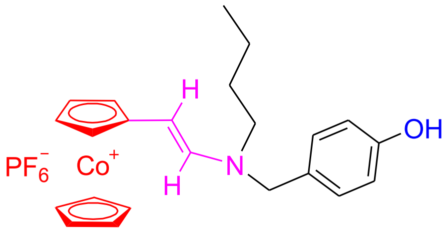
10



^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.85 (t, 3H, CH_3), 1.29 (m, 2H/CH_2), 1.53 (m, 2H/CH_2), 3.18 (t, 2H/CH_2), 4.36 (s, 2H/PhCH_2), 4.89 (d, J = 13.32Hz, 1H), 5.40 (s, 5H, Cp), 5.64 (t , 2H/C_5H_4), 5.78 (t , 2H/C_5H_4), 6.82 (d, 2H/Ph), 7.14 (d, 2H/Ph), 7.62 (d, J = 13.58Hz, 1H), 8.43 (broad, 1H/OH), 2.03 (m, $(CD_3)_2CO$), 2.87 (s, H_2O).

n

^{13}C NMR of **10**: (75 MHz, $(CD_3)_2CO$)



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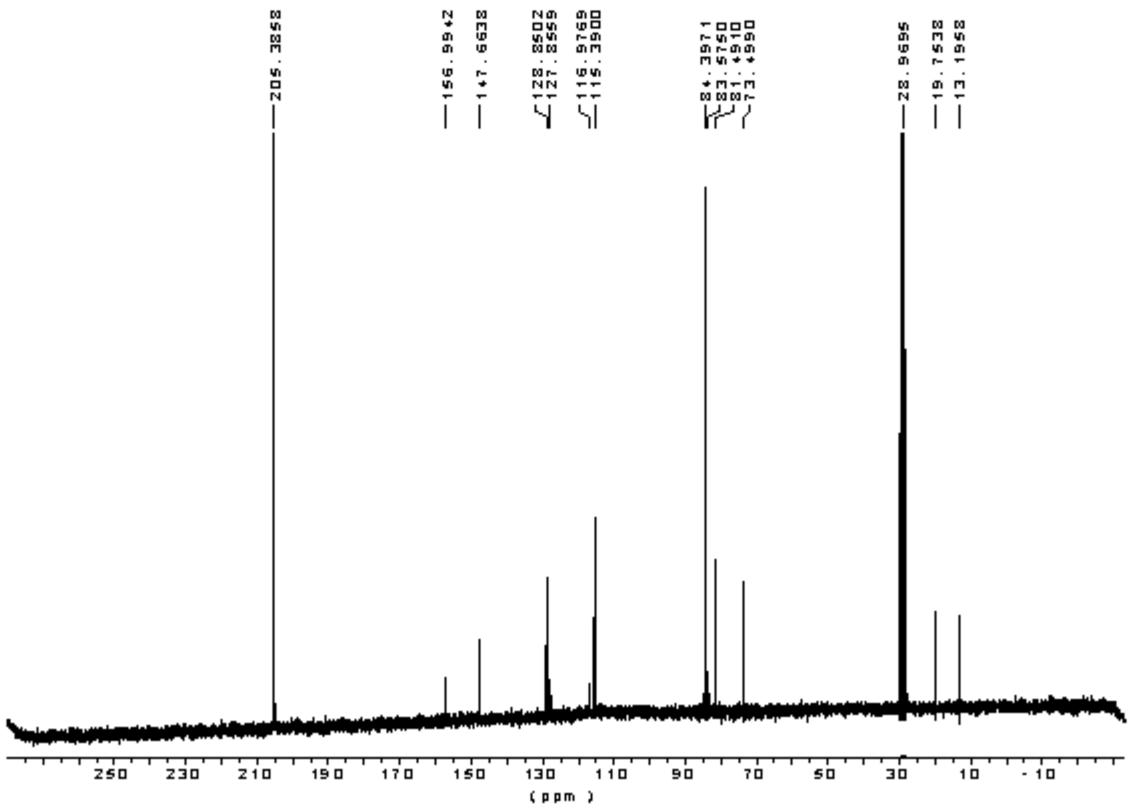
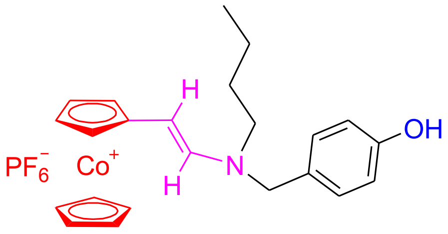
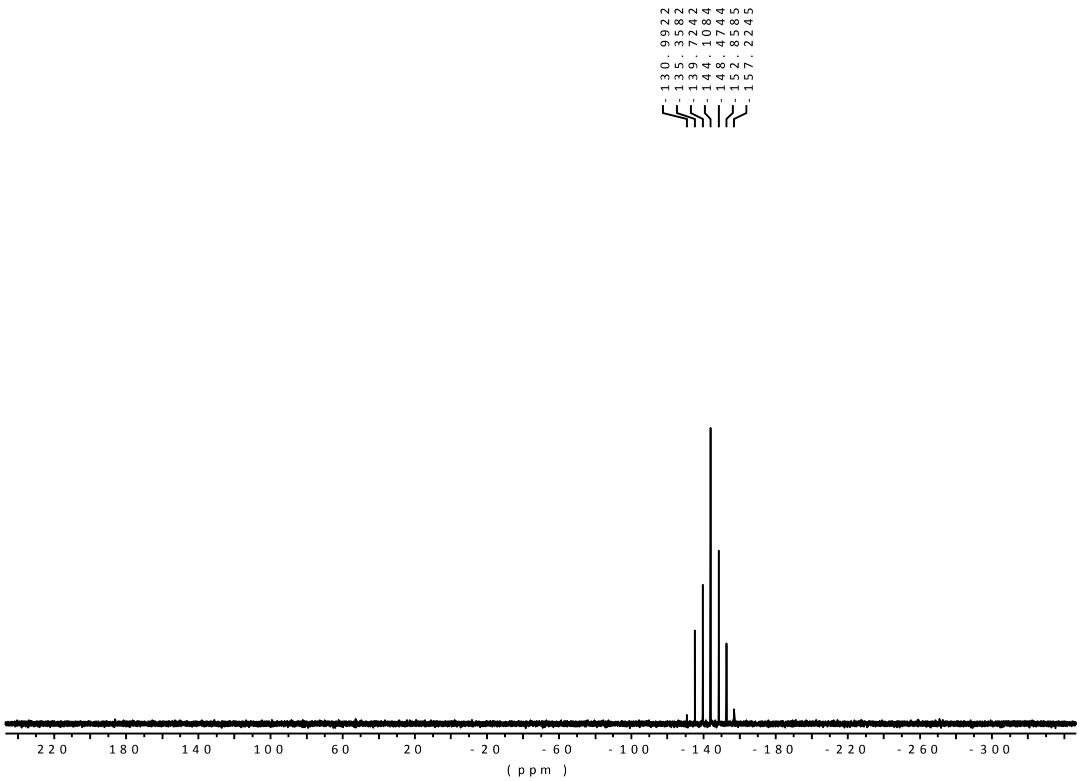


^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 13.18 (CH_3), 19.75 (CH_2), 73.48 (2C/C_5H_4/Fc), 81.48 (2C/C_5H_4/Fc), 83.56 (C/C_5H_4/Fc), 84.38 (Cp/unsub.), 115.38 (2C/Ph), 116.96 (CH), 127.83 (CH), 128.84 (2C/Ph), 147.65 (C/Ph), 156.98 (C/Ph), 29.65, 205.37 $(CD_3)_2CO$.

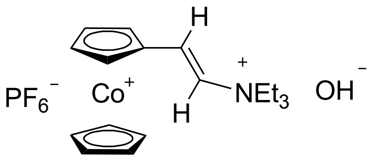
^{31}P NMR (121 MHz, CD_3COCD_3) of **10**, δ_{ppm}: -144.12 (m, PF_6^-)



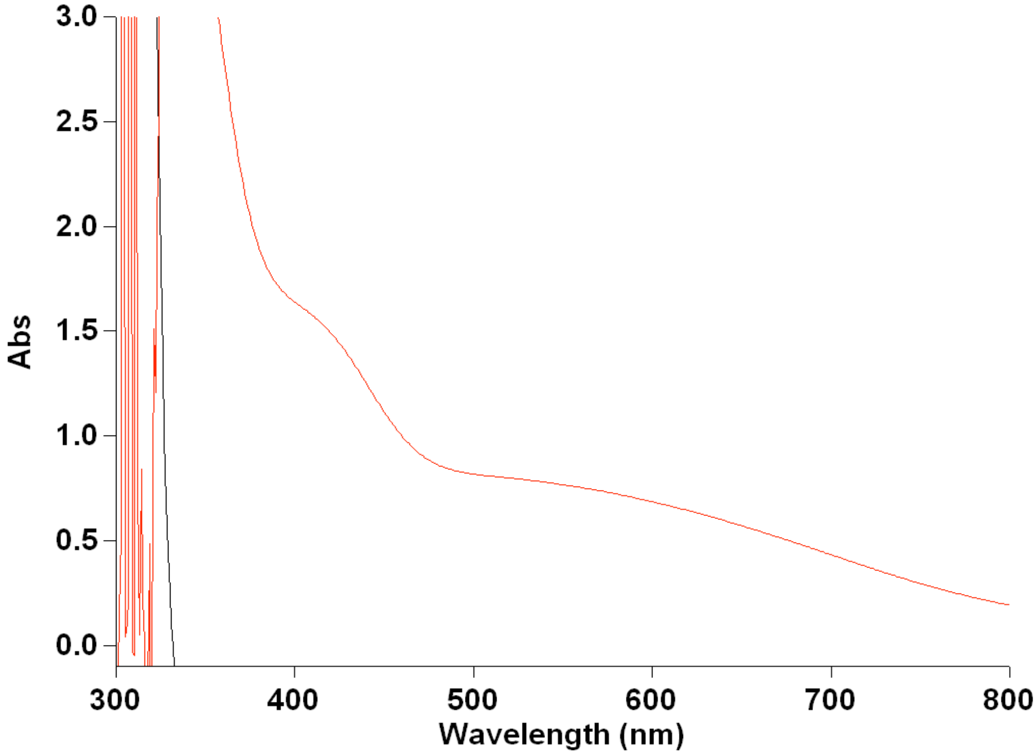
10



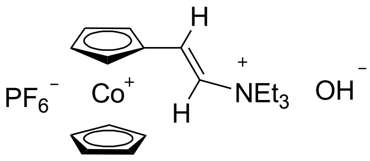
UV-vis. of **11**: $\lambda_{max\ 1}$ = 410nm, $\lambda_{max\ 2}$ = 505nm



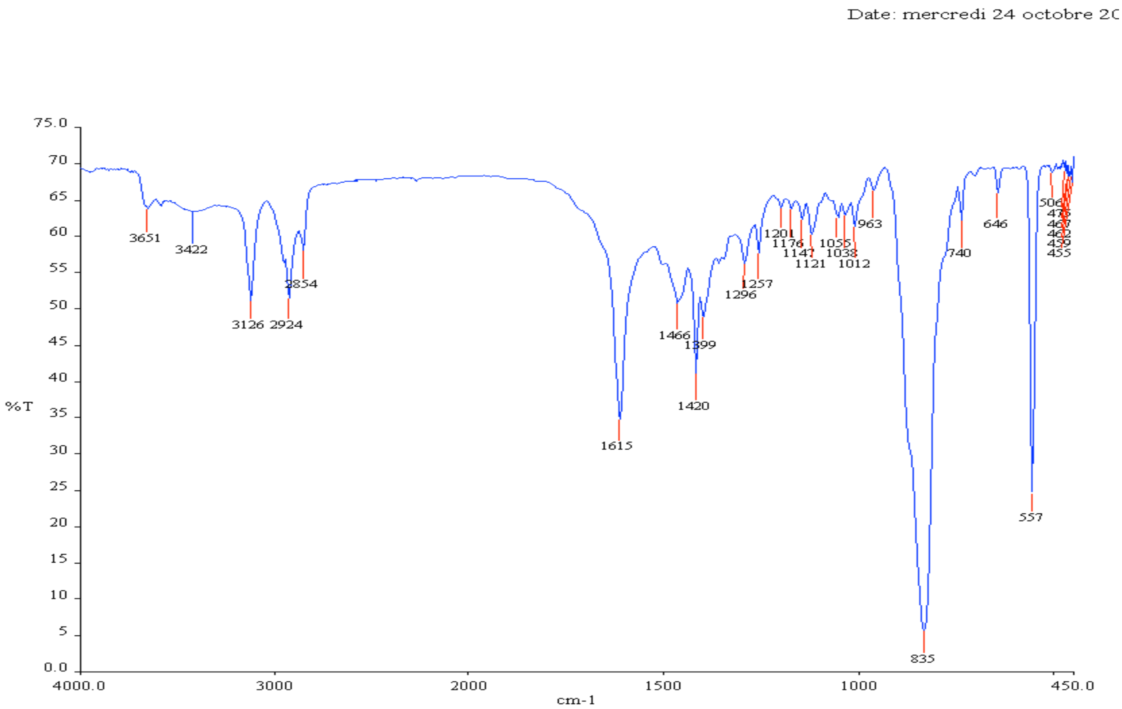
11



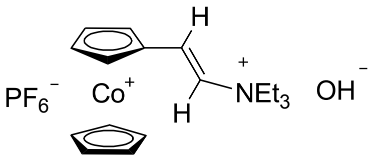
The IR (KBr) spectrum of **11**: 1615 cm^{-1} ($\nu_{C=C}$), 835 cm^{-1} (ν_{PF6^-}), 3651 cm^{-1} (ν_{OH^-})



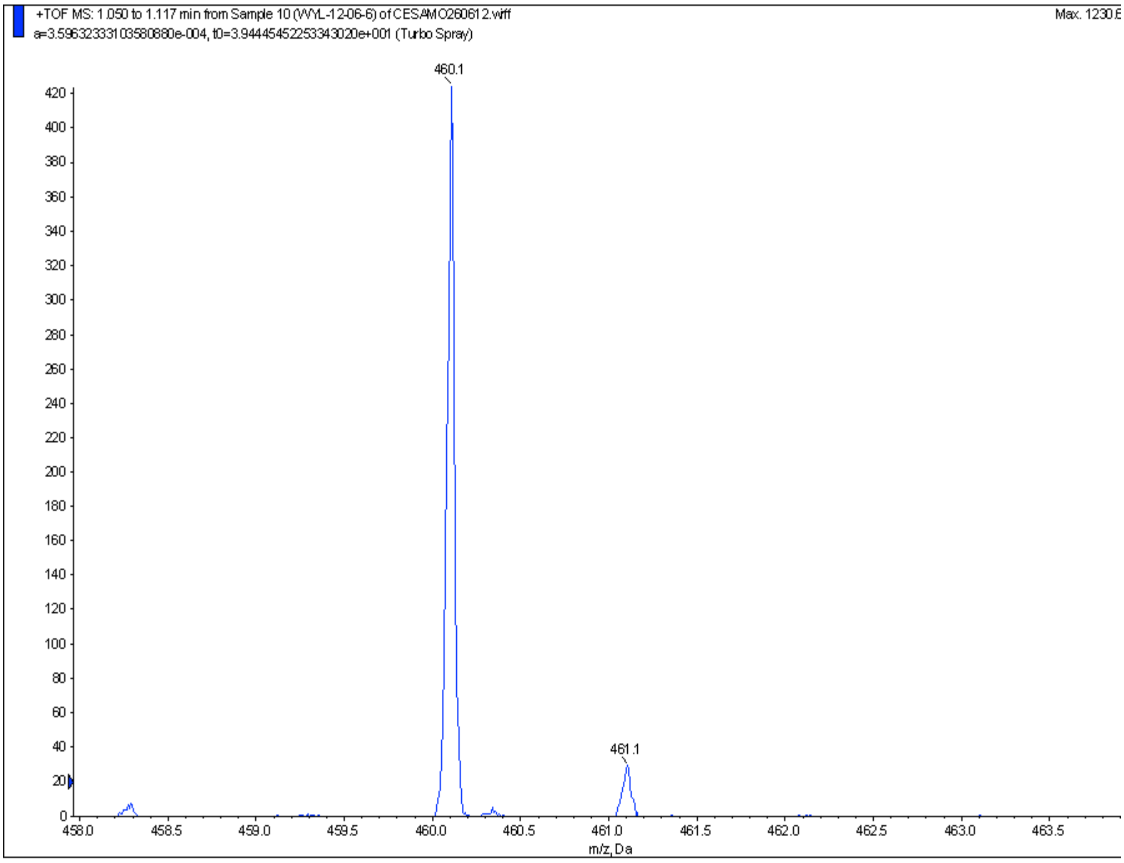
11



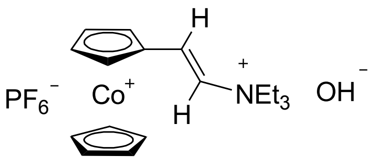
ESI of **11**: calc. *m/z* for M$^+$ ($C_{18}H_{26}CoNPF_6$) 460.3, found 460.1.



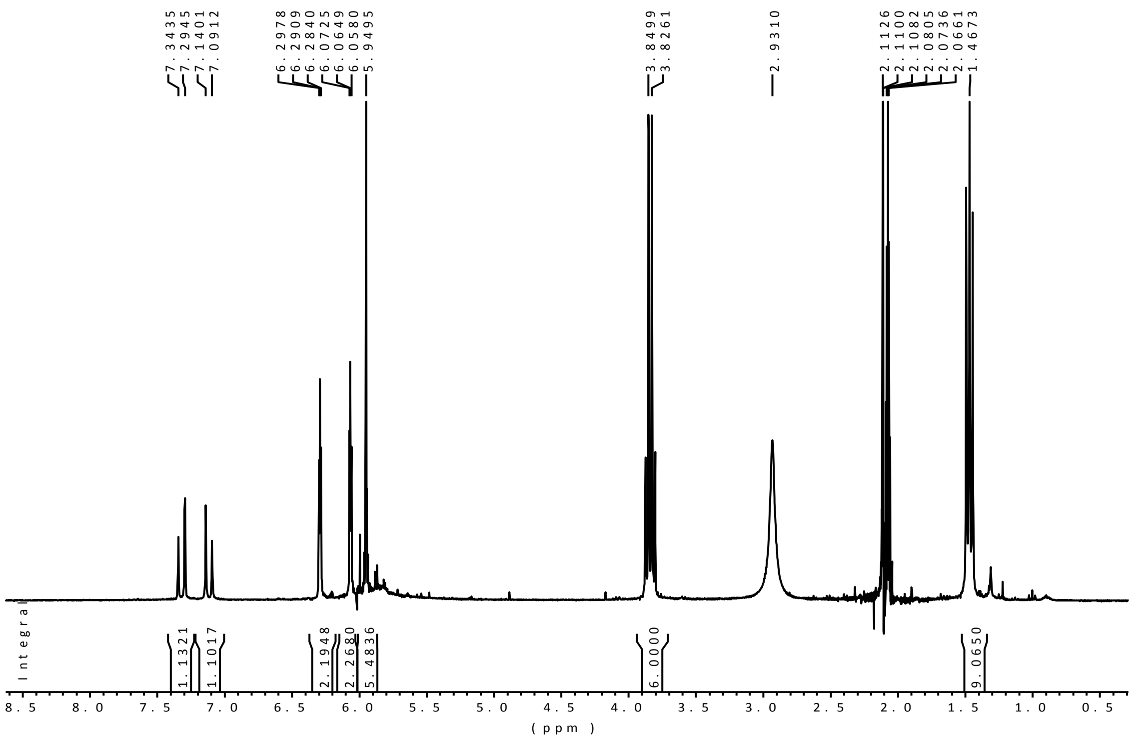
11



^{1}H NMR of **11**

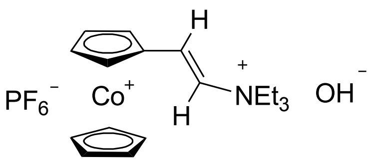


11

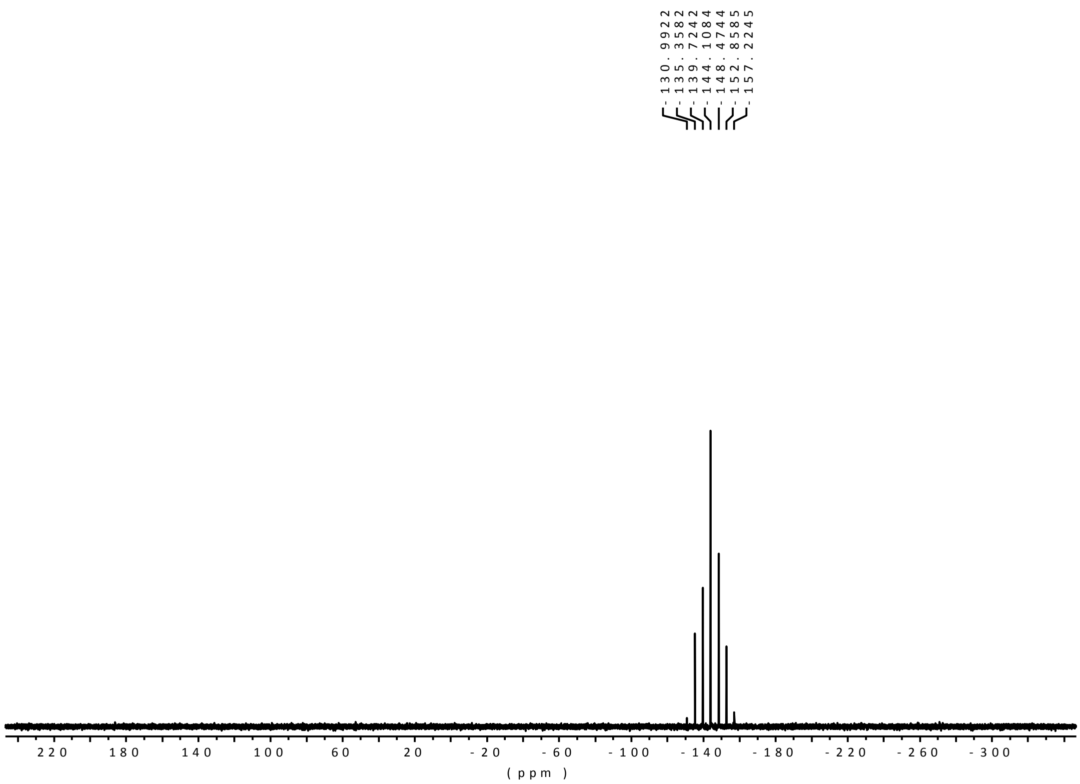


^{1}H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 1.44 (t, 9H), 3.82 (m, 6H), 5.95 (s, 5H, Cp), 6.06 (t , 2H/C_5H_4), 6.29 (t, 2H/C_5H_4), 7.09 (d, J = 14.64Hz, 1H), 7.29 (d, J = 14.64Hz, 1H), 2.07 (m, $(CD_3)_2CO$), 2.93 (s, H_2O).

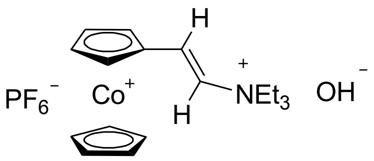
^{31}P NMR of **11** (121 MHz, CD_3COCD_3), δ_{ppm}: -144.11 (m, PF_6^-).



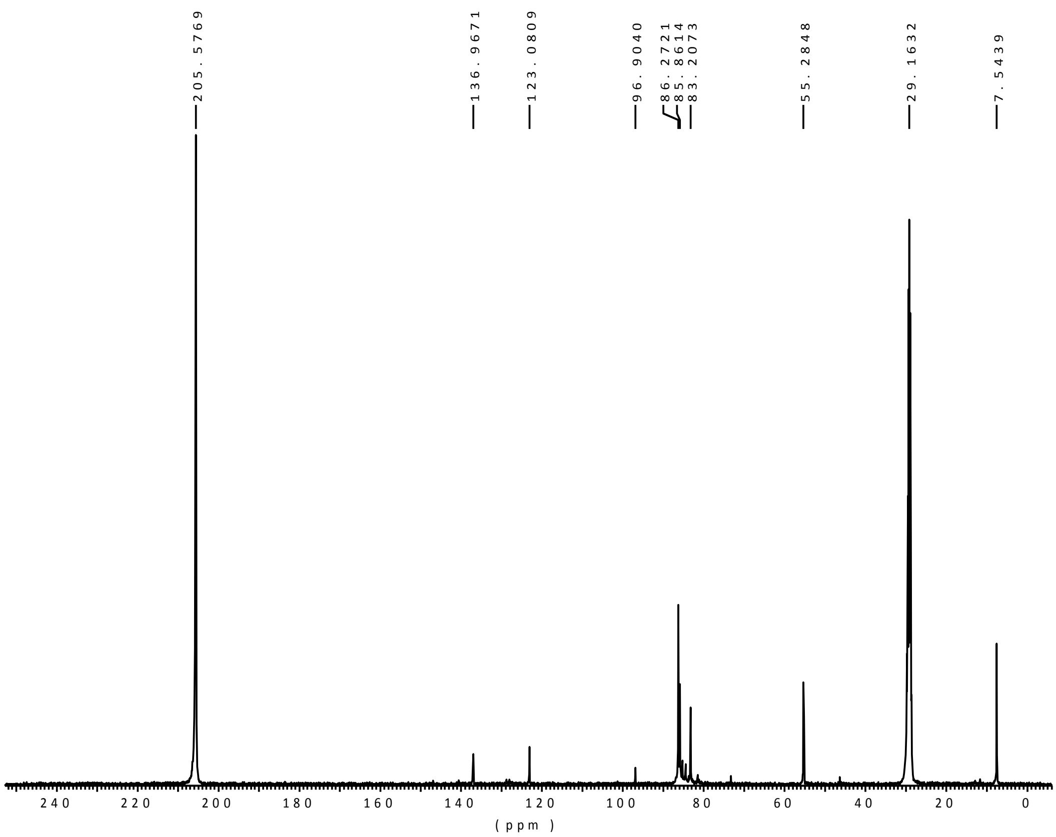
11



^{13}C NMR of **11**



11



^{13}C NMR (75 MHz, $(CD_3)_2CO$), δ_{ppm}: 7.63 (CH_3), 55.28 (CH_2), 83.20 ($2C/C_5H_4$), 85.86 ($2C/C_5H_4$), 86.27 (Cp/unsub.), 96.90 (C/C_5H_4), 123.07 (CH), 136.97 (CH), 29.16, 205.57 $(CD_3)_2CO$).

References of the S.I.

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