Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Chiral Sensor for Recognition of Varied Amines Based on ^{19}F NMR Signals of new designed Rhodium Complexes

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Abstract: Chiral sensor is one of the most common methods for chiral recognition and various nuclear magnetic resonance (NMR) chiral sensor have been developed for chiral analysis. However, the chiral recognition of an analyte with a NMR chiral sensor is typically based on the 1H NMR signals. Complex hydrogen spectrum signals are very easy to overlap, which limits the application scope of the method. Here, we describe a chirality sensing system based on ^{19}F NMR signals of chiral metal complexes to detect multi-types of analytes. A novel chiral octahedral rhodium complex containing fluorine has been developed to be an excellent chiral sensor for a variety of amines including diamines, monoamines, amino alcohols and amino acids, giving well distinguishable ^{19}F NMR signals and accurate measurement of enantiomeric determination.

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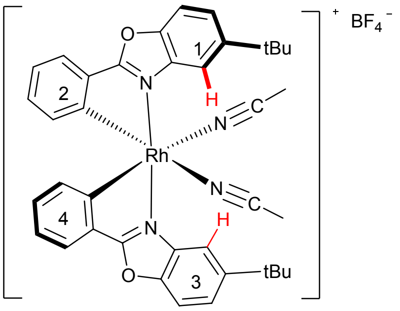
Experimental Procedures

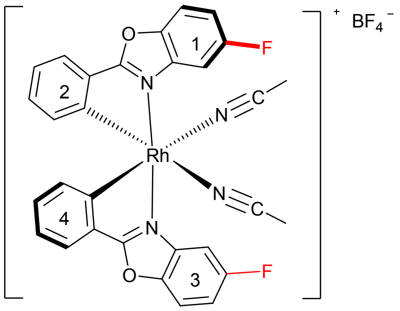
1. General Methods

All commercial reagents were used as received without further purification unless otherwise stated. All reactions were run under N_2 unless otherwise indicated. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker Advance III (400 MHz) spectrometers at ambient temperature. Chemical shifts were reported in parts per million (ppm) and referenced with $CDCl_3$ (δ_H = 7.26, δ_C = 77.16), CD_2Cl_2 (δ_H = 5.32, δ_C = 53.8), CD_3OD (δ_H = 3.31), DMSO-D_6 (δ_H = 2.50), CD_3CN (δ_H = 1.94), and $CFCl_3$ (δ_F = 0 ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources using TOF MS technique.

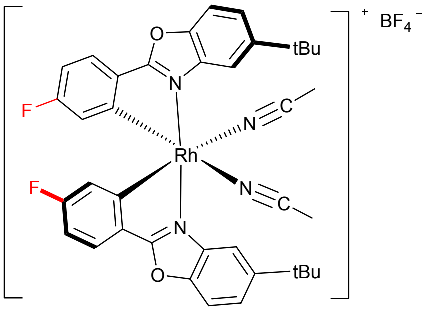
2. Synthesis of Chiral Rhodium Agents



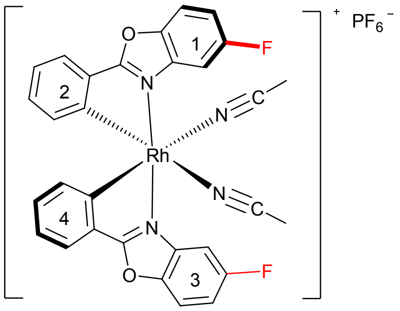
Rh 1



Rh 3



Rh 4



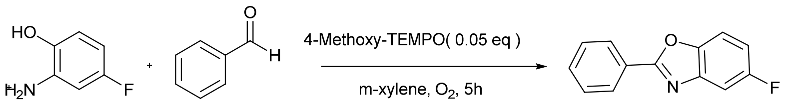
Rh 3'

2.1 Synthesis of Chiral Rhodium Agent Rh 1

The compound was synthesized full according to Eric Meggers's procedure,[1] and the characterization of the product was consistent with that reported in the literature.

2.2 Synthesis of Chiral Rhodium Agent Rh 3

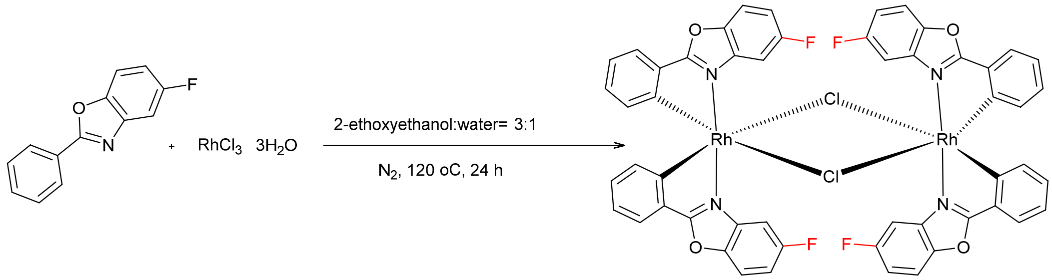
2.2.1 Procedure of 5-fluor-2-phenylbenzo[d]oxazole (I)



I

The compound was synthesized following a published procedure with slight modifications. A solution of 2-Amino-4-fluorophenol (0.508 g, 4.0 mmol) and benzaldehyde (0.425 g, 4.0 mmol) in *m*-xylene (15.0 mL) was stirred at 120 °C for 0.5 h. 4-Methoxy-TEMPO (37.3 mg, 0.2 mmol) was added to the mixture which was stirred at 120 °C for additional 5 h under an oxygen atmosphere. The reaction mixture was cooled and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EtOAc = 100/1) to afford the desired product **I** (577 mg, 68 %) as a white solid. M.P.: 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28-8.26 (m, 2H), 7.59-7.52 (m, 4H), 7.49-7.46 (dd, J = 8.4 Hz, J = 2.5 Hz, 1H), 7.14-7.09 (td, J = 9.2 Hz, J = 2.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 160.3 (d, J = 240.0 Hz), 147.2, 143.1, 142.9, 131.9, 129.1, 127.8, 126.9, 112.8 (d, J = 26.5 Hz), 110.97 (d, J = 10.2 Hz), 106.5(d, J = 25.6 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -117.72.

2.2.2 Procedure of Precursor rac-Rhodium Complex (II)

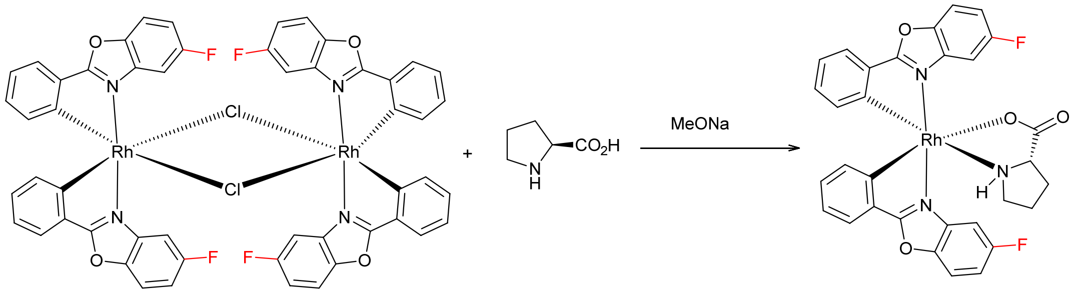


I

II

Compound **(II)** was synthesized according to a route reported by Eric Meggers for rhodium(III) *μ*-chloro-bridged dimers with related cyclometalated ligands. Under an atmosphere of nitrogen, 5-fluor-2-phenylbenzo[d]oxazole (1.889 g, 8.86 mmol) was added to RhCl3•3H2O (1.138 g, 4.32 mmol) in a mixture of 2-ethoxyethanol and water (3:1, 106 mL). The reaction mixture was heated at 120 °C for 24 h. The resulting precipitate was collected by centrifugation, removed solvent, washed with methanol until the supernatant was colorless and dried to obtain the product **II** (1.514g, yield: 62 %) as a yellow-green solid. M.P.: >300 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.96-7.93 (dd, J = 8.9, J = 2.6 Hz, 4H), 7.76-7.74 (dd, J = 7.6 Hz, J = 1.2 Hz, 4H), 7.41-7.38 (dd, J = 9.0, 4.1 Hz, 4H), 7.02 (t, J = 7.3 Hz, 4H), 6.90-6.81 (m, 8H), 6.21(d, J = 7.8 Hz, 4H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 172.6 (d, J = 4.0 Hz), 164.1 (d, J = 33.9 Hz), 159.9 (d, J = 242.6 Hz), 146.6, 140.5 (d, J = 14.2 Hz), 133.4, 132.0, 130.1, 126.1, 123.6, 113.3 (d, J = 26.8 Hz), 111.8 (d, J = 10.2 Hz), 105.6 (d, J = 29.0 Hz). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -115.75.

2.2.3 Procedure of chiral Rhodium Auxiliary Complexes (III)

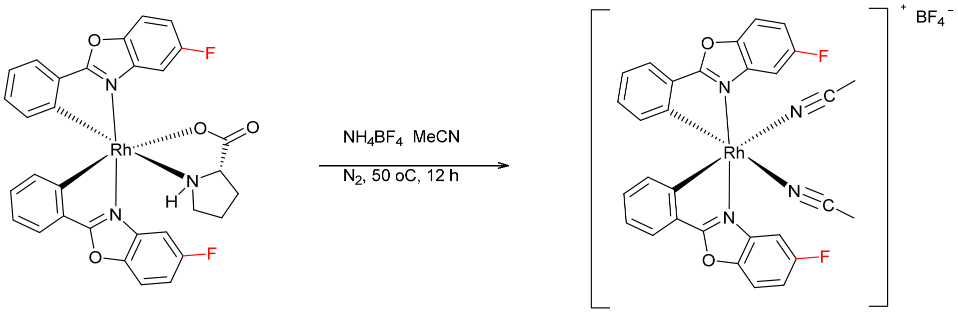


II

III

The rhodium auxiliary complexes **III** were synthesized according to a reported method. To a solution of NaOMe (151 mg, 2.8 mmol) in methanol (150 mL), L-proline (322 mg, 2.8 mmol) was added in one portion. The mixture was stirred for 10 min, to which a suspension of rhodium dimer **II** (1.576 g, 1.4 mmol) was added. The mixture was stirred and heated at 50 °C for 12 h. After the mixture cooled to room temperature, DCM (150 mL) was added. The reaction mixture was stirred for a further 12 h to give a clear, yellow solution. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (elution with methanol/DCM = 1:100~1:20) to afford the desired product III (629 mg, 70%) as a yellow solid. M.P.: >300 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79-7.68 (m, 5H), 7.29-7.22 (m, 3H), 7.06-7.01 (m, 2H), 6.94-6.89 (m, 2H), 6.68 (d, J = 7.7 Hz, 1H), 6.33 (d, J = 7.7 Hz, 1H), 4.28-4.22 (m, 1H), 4.14-4.05 (m, 2H), 2.71-2.64 (m, 1H), 2.26-2.16 (m, 1H), 2.12-2.04 (m, 1H), 1.97-1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.2, 174.3 (d, J =3.8 Hz), 174.3 (d, J =3.8 Hz), 172.8 (d, J =3.8 Hz), 166.6 (d, J =30.2 Hz), 165.6 (d, J =31.8 Hz), 161.2 (d, J = 245.8 Hz), 161.0 (d, J = 244.0 Hz), 146.7, 146.6, 139.4 (d, J = 12.6 Hz), 138.8 (d, J = 13.4 Hz),135.0, 133.9, 132.0, 131.7, 130.1, 129.8, 126.5, 126.2, 123.4, 123.1, 114.0 (d, J = 26.4 Hz), 113.2 (d, J = 26.0 Hz), 113.1 (d, J =10.2 Hz),112.2 (d, J = 9.9 Hz), 105.6 (d, J = 27.8 Hz), 101.9 (d, J = 27.5 Hz), 63.9, 49.7, 30.5, 26.9. ^{19}F NMR (376 MHz, CD_2Cl_2) δ -113.7, -115.0. HRMS (ESI): calc for $C_{31}H_{22}F_2N_3O_4Rh$ $[M+Na]^+$ 664.0531, found 664.0526.

2.2.4 Procedure of Chiral Rhodium Complexes Rh 3

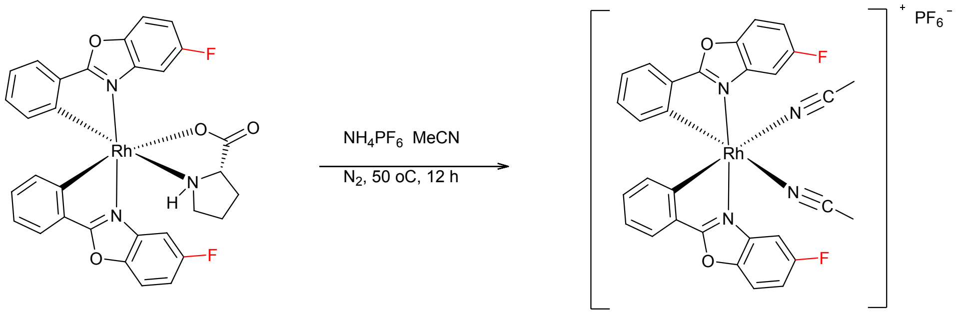


III

Rh 3

The chiral rhodium complexe Rh **3** was synthesized according to a published procedure. Using Schlenk operation, a solution of compound **III** (500 mg, 0.78 mmol) and NH_4BF_4 (817 mg, 7.8 mmol) were added in one portion in acetonitrile (140.0 mL). The mixture was stirred for 12 h at 50 °C under nitrogen in the dark. After the mixture cooled to room temperature, The solvent was removed in vacuo and purified by flash chromatography on silica gel (elution with acetonitrile/DCM = 1:100-1:25) to afford the desired product Rh **3** (244 mg, 45%) as a yellow solid. M.P.: >300 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4H), 7.62-7.60 (m, 2H), 7.36-7.31(m, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.7 Hz, 2H), 6.35 (d, J = 7.9 Hz, 2H), 2.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (d, *J* = 4.2 Hz), 161.1 (d, *J* = 246.7 Hz), 160.1 (d, *J* = 31.2 Hz), 146.5, 138.6 (d, *J* = 13.0 Hz), 132.8, 132.5, 129.5, 126.3, 124.4, 122.4, 114.4 (d, *J* = 26.5 Hz), 112.9 (d, *J* = 10.2 Hz), 104.4 (d, *J* = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2, -152.6. HRMS (ESI): calc for $C_{30}H_{20}BF_6N_4O_2Rh$ $[M-CH_3CN-BF_4]^+$ 568.0344, found 568.0341.

2.3 Synthesis of Chiral Rhodium Agent Rh 3'



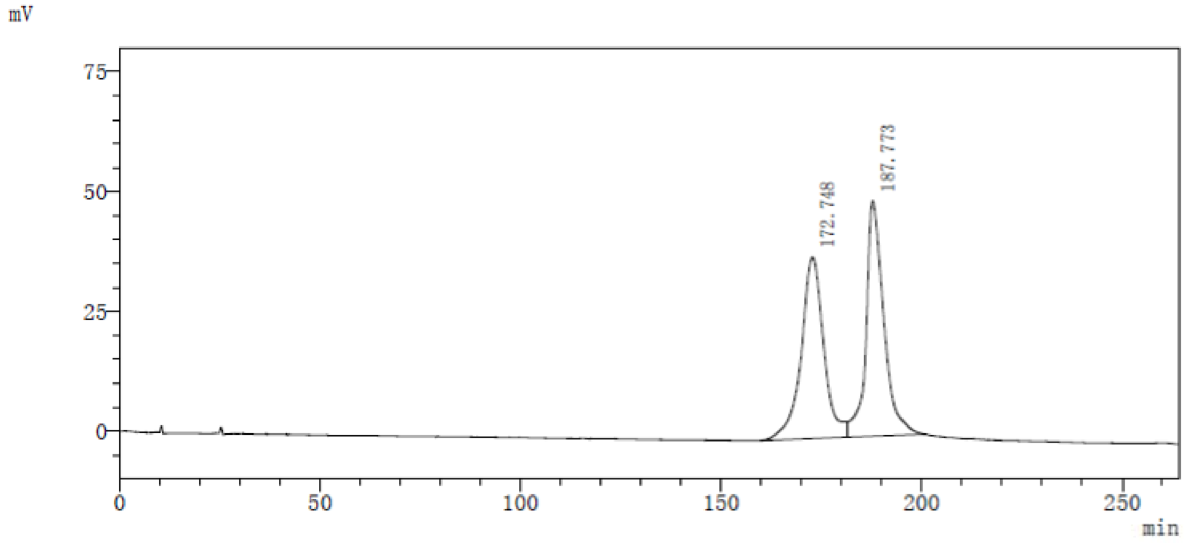
III

Rh 3'

The chiral rhodium complexes **3'** (Λ–Rh **3'**) was synthesized according to the procedure of Rh **3**, only replacing NH_4BF_4 with NH_4PF_6. Yield 89.6%, a yellow solid. The enantiomeric purity was verified by HPLC analysis with a chiral stationary phase.[1b] M.P.: >300 °C. $[\alpha]_D^{28.2}$ +304.03 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 4H), 7.59-7.57 (m, 2H), 7.36-7.31(m, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.36 (d, J = 7.9 Hz, 2H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (d, *J* = 3.4 Hz), 161.1 (d, *J* = 245.4 Hz), 160.0 (d, *J* = 31.2 Hz), 146.5, 138.5 (d, *J* = 13.2 Hz), 132.8, 132.6, 129.5, 126.3, 124.4, 122.1, 114.3 (d, *J* = 26.5 Hz), 113.0 (d, *J* = 9.6 Hz), 104.2 (d, *J* = 27.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.0, -73.9, -112.2. HRMS (ESI): calc for $C_{30}H_{20}F_8N_4O_2PRh$ $[M-PF_6]^+$ 609.0609, found 609.0604.

2.3.1 Enantiomeric Purities of the Chiral Rhodium Agent Rh 3’

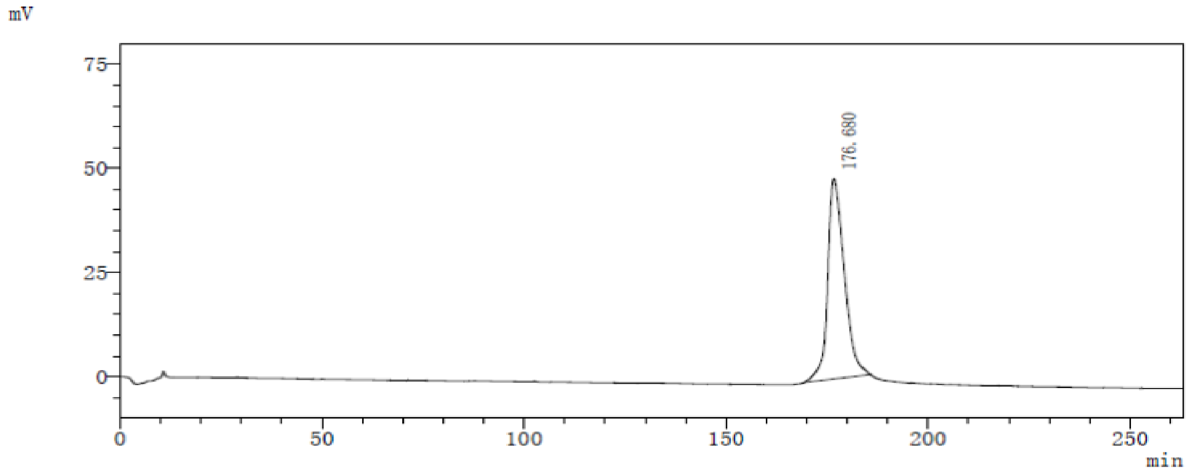
The analysis was performed with two series connect Daicel Chiralpak IB (250 × 4.6 mm) HPLC columns on an HPLC System. The column temperature was 25 °C and UV-absorption was measured at 254 nm. Solvent A = H_2O (0.1%TFA), Solvent B = MeCN.



检测器A Ch1 254nm

Peak	Ret. Time	Area	Area%	Height	Height%	solution (US	Conc. %
1	172.748	14894655	49.560	37901	43.560	--	49.560
2	187.773	15158977	50.440	49107	56.440	1.796	50.440

Figure S1. HPLC trace for the racemic reference complexes Rh **3’**. (Daicel Chiralpak IB × 2, with 35% MeCN/65% H_2O, flow rate = 0.6 mL/min).



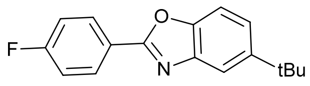
检测器A Ch1 254nm

Peak	Ret. Time	Area	Area%	Height	Height%	solution (US	Conc. %
1	176.680	13724213	100.000	48092	100.000	--	100.000

Figure S2. HPLC trace for the chiral complex Rh **3’** (Λ–Rh **3’**). Integration of peak areas > 100:1 e.r. (Daicel Chiralpak IB × 2, with 35% MeCN/65% H_2O, flow rate = 0.6 mL/min).

2.4 Synthesis of Chiral Rhodium Agent Rh 4

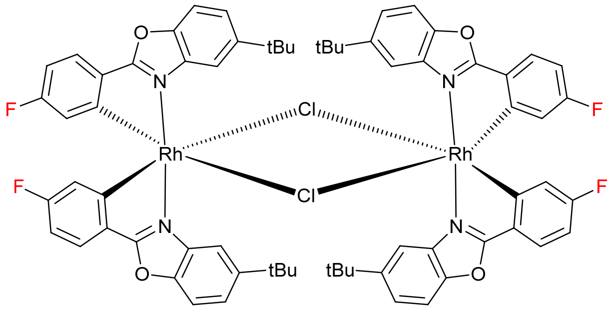
2.4.1 Procedure of 5-(tert-butyl)-2-(4-fluorophenyl)benzo[d]oxazole (IV)



IV

IV was synthesized according to the procedure of **I**, white solid, yield 54%, M.P.: 127-128 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28-8.24 (m, 2H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.51-7.42 (m, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), 1.42 (s, 9H).^{13}C NMR (101 MHz, CDCl$_3$) δ 164.8 (d, *J* = 252.4 Hz), 162.4, 148.9, 148.4, 142.1, 129.8 (d, *J* = 9.0 Hz), 123.8, 123.0, 116.5 (d, *J* = 23.0 Hz), 116.2, 109.8, 35.1, 31.9. ^{19}F NMR (376 MHz, CDCl$_3$) δ -107.7.

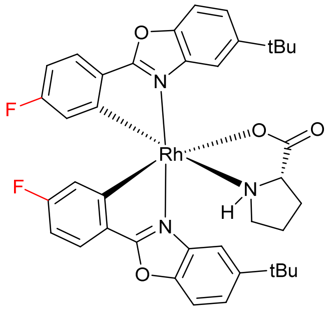
2.4.2 Procedure of Precursor rac-Rhodium Complex (V)



V

V was synthesized according to the procedure of **II**, pale yellow solid. Yield 20%, M.P.: >300 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, J = 1.6 Hz, 4H), 7.66-7.62 (m, 4H), 7.22-7.16 (m, 8H), 6.69-6.64 (m, 4H), 5.85-5.81 (m, 4H), 1.26 (s, 36H).^{13}C NMR (101 MHz, CDCl$_3$) δ 169.5 (d, *J* = 3.6 Hz), 167.5 (d, *J* = 6.3 Hz), 167.1 (d, *J* = 6.3 Hz), 162.4 (d, *J* = 256.6 Hz), 148.8, 147.5, 138.8, 126.8, 126.5 (d, *J* = 9.7 Hz), 123.5, 120.2 (d, *J* = 19.2 Hz), 115.2, 110.7(d, *J* = 24.0 Hz), 110.1, 35.1, 31.7. ^{19}F NMR (376 MHz, CDCl$_3$) δ -106.1.

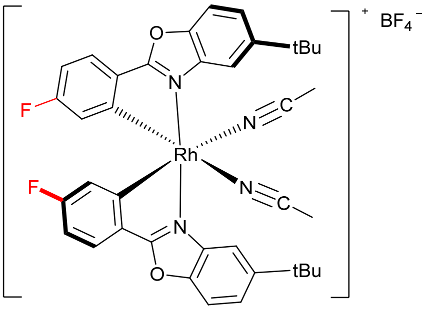
2.4.3 Procedure of Chiral Rhodium Auxiliary Complexes VI



VI

VI was synthesized according to the procedure of **III**, yellow solid. Yield, 40% M.P.: >300 °C. $[\alpha]_D^{19.8}$ +276.1 (c 1.0, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, J = 1.7 Hz, 1H), 7.82-7.73 (m, 2H), 7.69-7.64 (m, 2H), 7.60-7.57 (m, 2H), 7.23 (d, J = 1.5 Hz, 1H), 6.79-6.70 (m, 2H), 6.41-6.38 (m, 1H), 6.10-6.07 (m, 1H), 4.30-4.09 (m, 3H), 2.82-2.75 (m, 1H), 2.28-2.18 (m, 1H), 2.04-1.99 (m, 1H),1.58-1.52 (m, 1H), 1.44(s, 9H), 1.41(s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 180.8, 171.7 (d, *J* = 3.0 Hz), 170.2 (d, *J* = 3.8 Hz), 169.4 (d, *J* = 5.9 Hz), 169.1 (d, *J* = 5.9 Hz), 168.7 (d, *J* = 5.9 Hz), 168.4 (d, *J* = 5.9 Hz), 163.9 (d, *J* = 259.8 Hz), 163.6 (d, *J* = 259.8 Hz), 151.3, 150.2, 148.4, 148.3, 138.1, 137.4, 127.6 (d, *J* = 9.5 Hz), 127.3 (d, *J* = 9.7 Hz), 126.8, 126.6, 123.9, 123.8, 121.6 (d, *J* = 18.3 Hz), 120.7 (d, *J* = 18.8 Hz), 115.1, 120.0, 111.1 (d, *J* = 24.0 Hz), 110.8 (d, *J* = 24.0 Hz), 110.7, 110.5, 63.9, 49.4, 35.4, 35.2, 31.8, 31.7, 30.0, 27.0. ^{19}F NMR (376 MHz, CDCl$_3$) δ -105.5, -105.6.

2.4.4 Procedure of Chiral Rhodium Agent Rh 4



Rh 4

Rh **4** was synthesized according to the procedure of Rh **3**, yellow solid. Yield 71%, M.P.: >300 °C. $[\alpha]_D^{20.8}$ +168.2 (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 1.5 Hz, 2H), 7.76-7.64 (m, 6H), 6.80-6.75 (m, 2H), 6.02-5.99 (m, 2H), 2.42 (s, 6H), 1.47 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1 (d, *J* = 3.7 Hz), 163.8 (d, *J* = 256.8 Hz), 162.8 (d, *J* = 31.6 Hz), 151.1, 148.1, 137.3, 127.4 (d, *J* = 10.2 Hz), 126.3, 125.0, 122.5, 120.1 (d, *J* = 19.9 Hz), 113.2, 112.0 (d, *J* = 23.9 Hz), 111.5, 35.4, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.8, -152.1. HRMS (ESI): calc for $C_{38}H_{36}BF_6N_4O_2Rh$ $[M-CH_3CN-BF_4]^+$ 721.1861, found 721.1857.

3. Optimization of the Discriminating Conditions for DPEN by Chiral Rhodium Agent.[a]

Entry	Rhodium Agent	Solvent	$\Delta\Delta\delta_F$ (ppm)
1	Rh **3**	$CDCl_3$	0.16
2	Rh **4**	$CDCl_3$	0.03
3	Rh **3’**	$CDCl_3$	0.16
4	Rh **3’**	CD_3CN	0.19
5	Rh **3’**	CD_2Cl_2	0.03
6	Rh **3’**	CD_3COCD_3	0.12
7	Rh **3’**	**DMSO-D6**	**0.21**
8	Rh **3’**	C_6D_6	0
9	Rh **3’**	Toluene-D8	0.02

[a] at ambient temperature, ^{19}F NMR spectra (64 scans each) of mixtures of Rh complex (0.01 mmol) and different rac-DPEN (1.0 equiv) in different solvents (0.5 mL).

4. Chiral Discrimination of amines with Rh 3’ Sensor

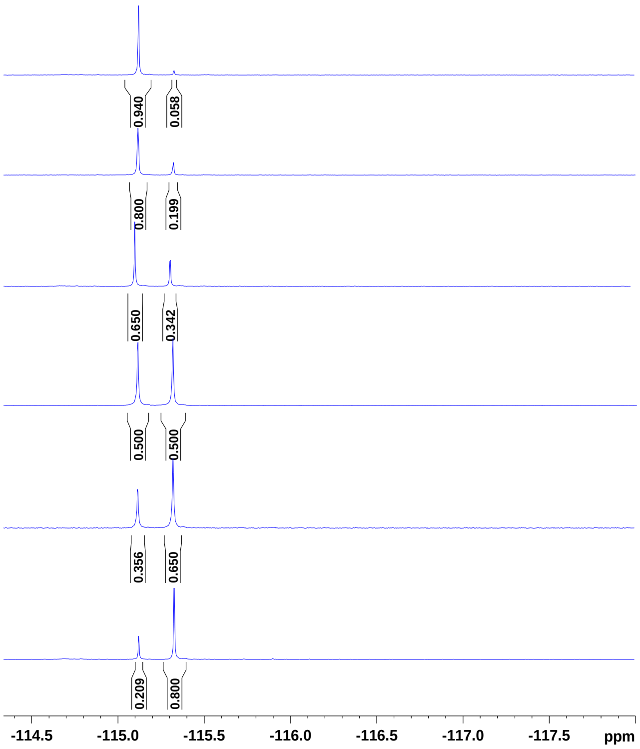
Chiral Discrimination of Racemic Diamines with Rh **3’** Sensor: Rh **3’** (7.6 mg, 0.01 mmol), diamine (0.01 mmol) were added to 0.5 ml DMSO-D_6. The solution was stirred at RT for 5 minutes. The solution was transferred to a NMR tube for ^{19}F NMR spectra (64 scans each).

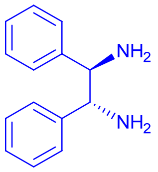
Chiral Discrimination of Racemic amino acids with Rh **3’** Sensor: Rh **3’** (19 mg, 0.025 mmol), amino acid (0.01 mmol), NaOMe (0.6 mg, 0.01 mmol) were added to a CD_3OD (0.5 ml). The solution was stirred at RT for 2 h. Then the solution was transferred to a NMR tube for ^{19}F NMR spectra (64 scans each).

Chiral Discrimination of Racemic Primary Amines/Amino Alcohols with Rh **3’** Sensor: Rh **3’** (7.6 mg, 0.01 mmol), amine or amine alcohol (0.01 mmol), 5-Nitrosalicylaldehyde (1.7 mg, 0.01 mmol), Na_2CO_3 (1.1 mg, 0.01 mmol) were added to 0.5 ml CD_3OD sequentially. The solution was stirred at 50 °C for 2 h, cooled to RT and transferred to a NMR tube for ^{19}F NMR spectra (64 scans each).

5. Examples of NMR Experiment to Determine the ee Value

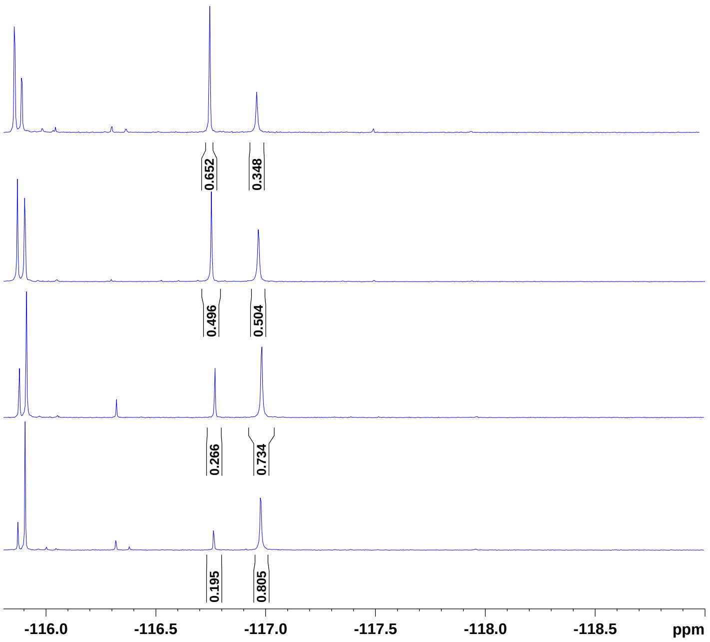
5.1 Quantitative Determination of ee of 1,2-Diphenylethylenediamine

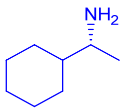




actual ee (%)	calcd ee (%)(*R*)	absolute error(%)
90	88.4	1.6
60	60.2	0.2
30	31.0	1
0	0	0
-30	-29.2	0.8
-60	-58.6	1.4

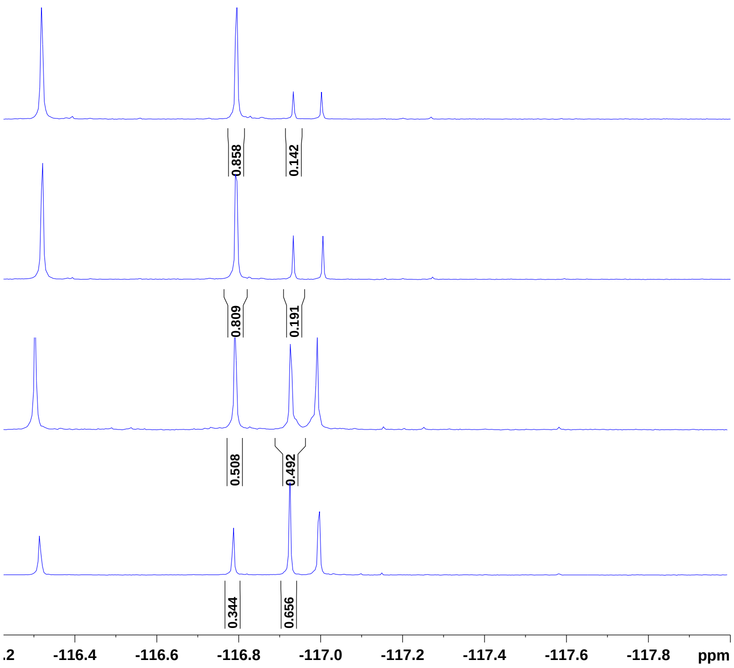
5.2 Quantitative Determination of ee of 1-Cyclohexylethanamine

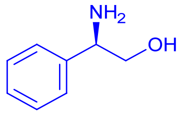




actual ee (%)	calcd ee (%)(*R*)	absolute error(%)
30	30.4	0.4
0	0.8	0.8
-47	-46.8	0.2
-60	-61.0	1.0

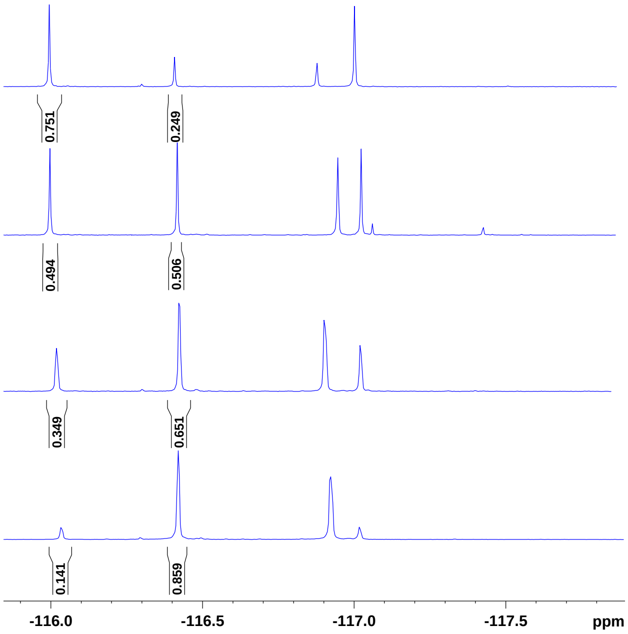
5.3 Quantitative Determination of ee of 2-Amino-2-phenylethanol

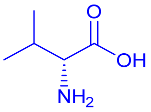




actual ee (%)	calcd ee (%)(*R*)	absolute error(%)
70	71.6	1.6
60	61.8	1.8
0	1.6	1.6
-30	-31.2	1.2

5.4 Quantitative Determination of ee of Valine

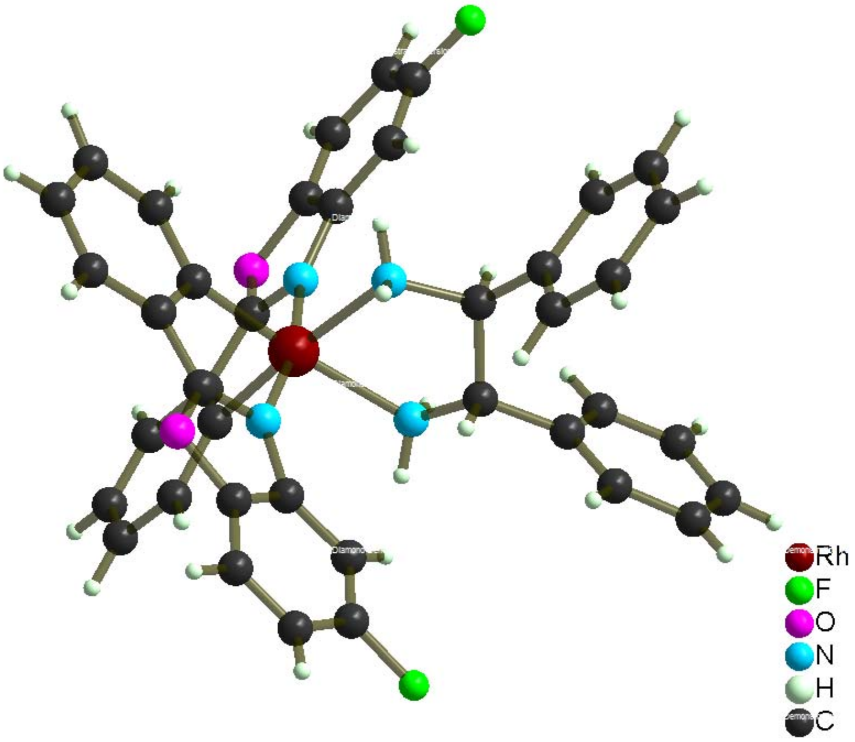




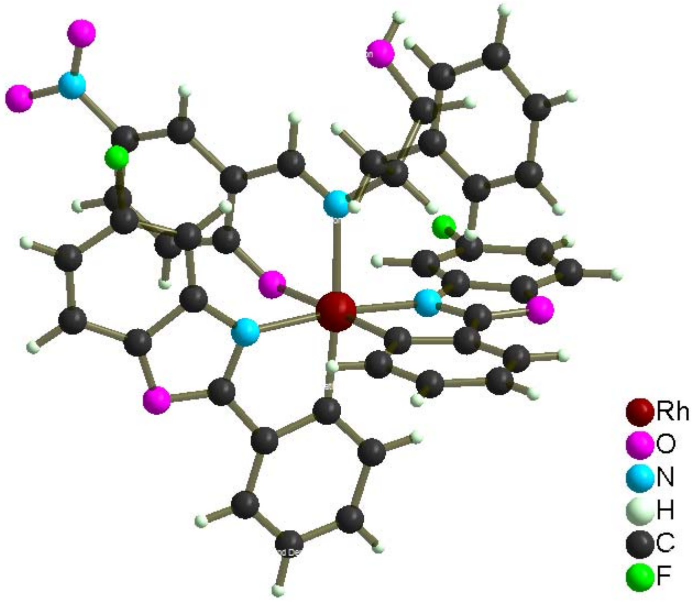
actual ee (%)	calcd ee (%)(*R*)	absolute error(%)
50	50.2	0.2
0	1.2	1.2
-30	30.2	0.2
-70	71.8	1.8

6. X-ray structures of Rh complexes

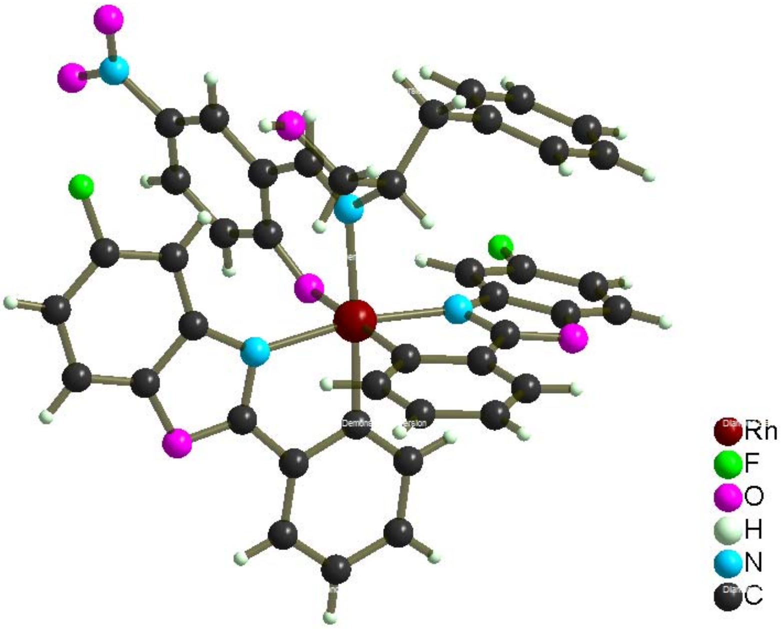
6.1 X-ray structure of Rh 3/ (*S*, *S*)-DPEN (CCDC1887397)



6.2 X-ray structure of Rh 3'/ (*R*)-phenylalaninol (CCDC1887396)

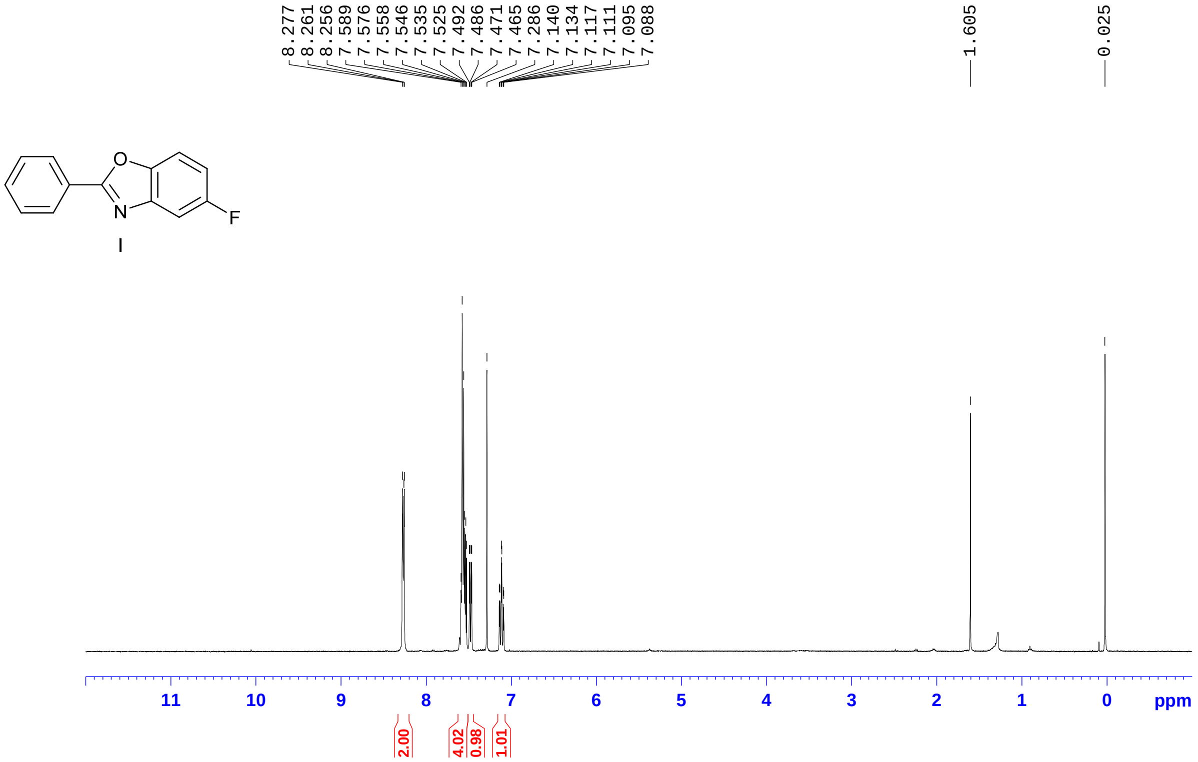


6.3 X-ray structure of Rh 3'/ (*S*)-phenylalaninol (CCDC1887618)

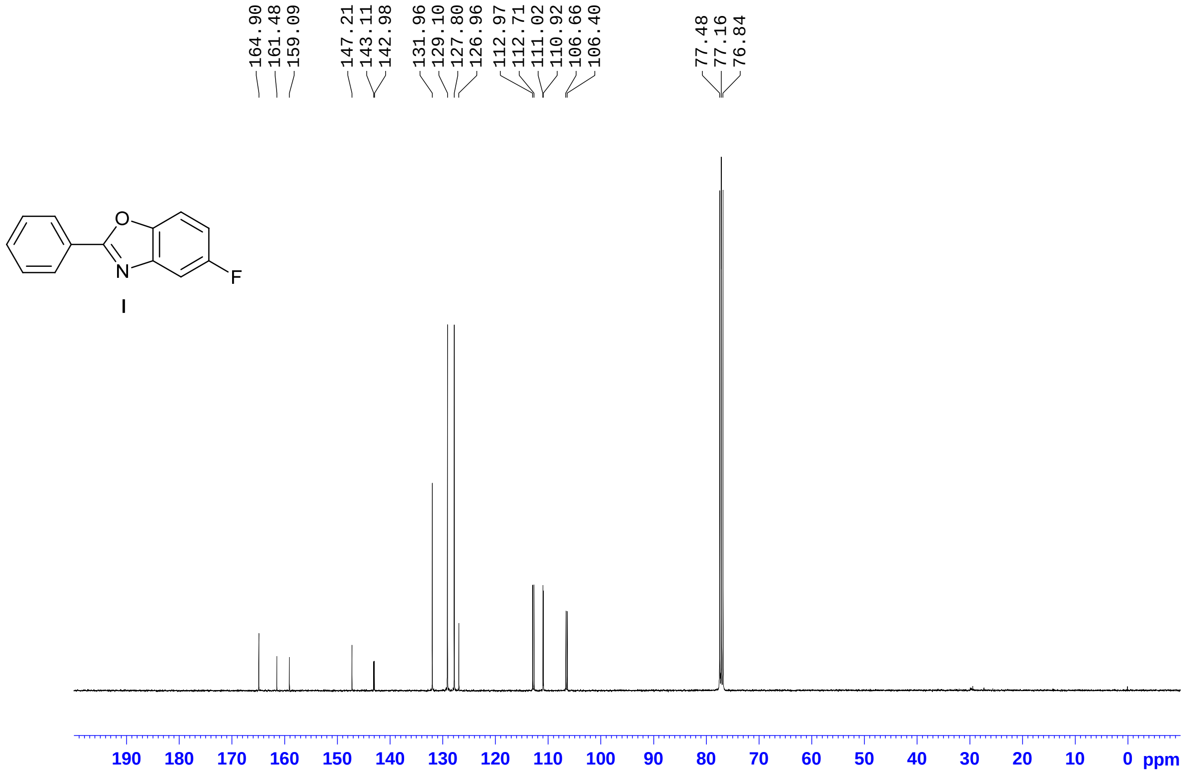


7. ^{1}H, ^{13}C and ^{19}F NMR Spectrum of Intermediates and Rh Complexes

^{1}H NMR Spectrum of 5-fluor-2-phenylbenzo[*d*]oxazole (Ⅰ)

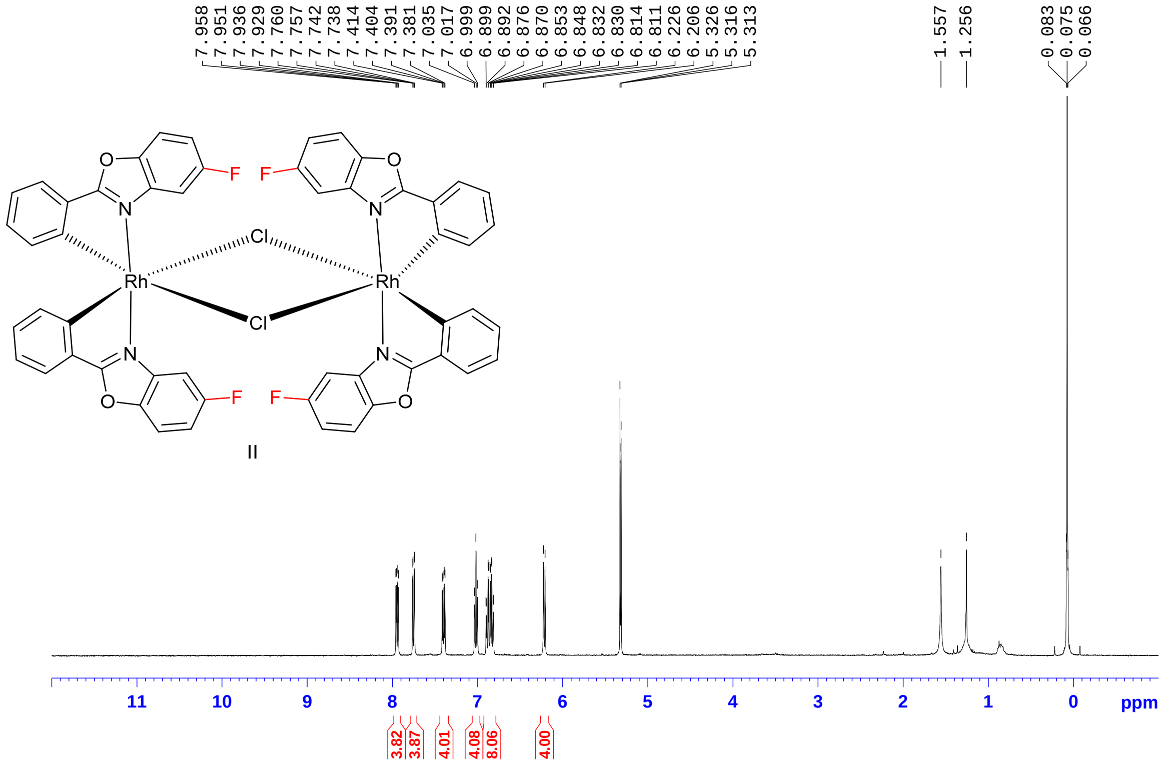


^{13}C NMR Spectrum of 5-fluor-2-phenylbenzo[*d*]oxazole

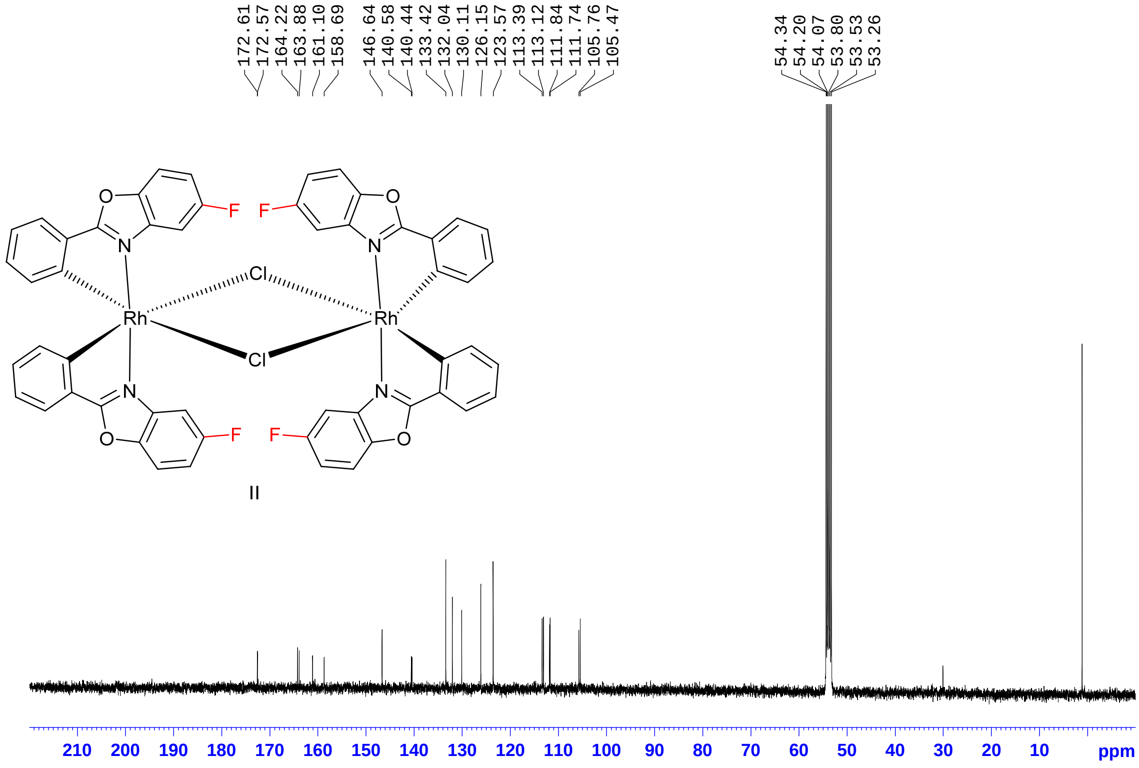


^{19}F NMR Spectrum of 5-fluor-2-phenylbenzo[*d*]oxazole

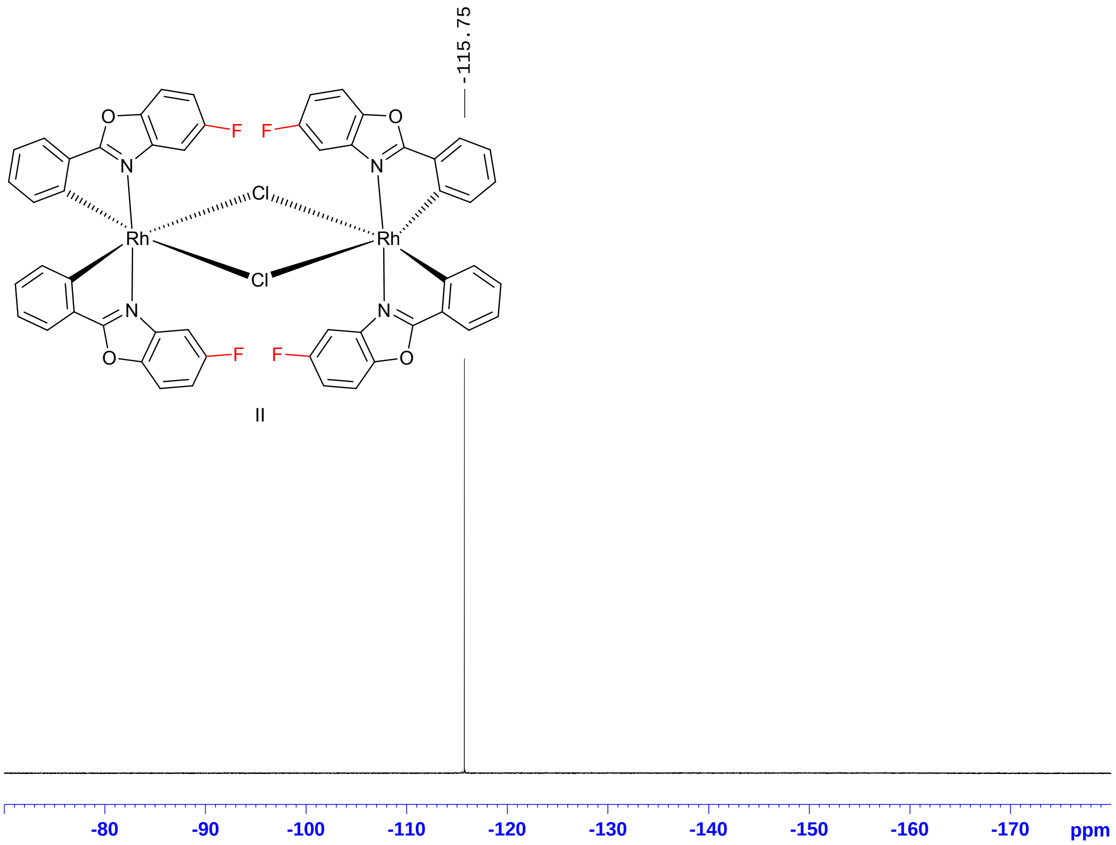
^{1}H NMR Spectrum of *rac*-Rhodium Complex (II)



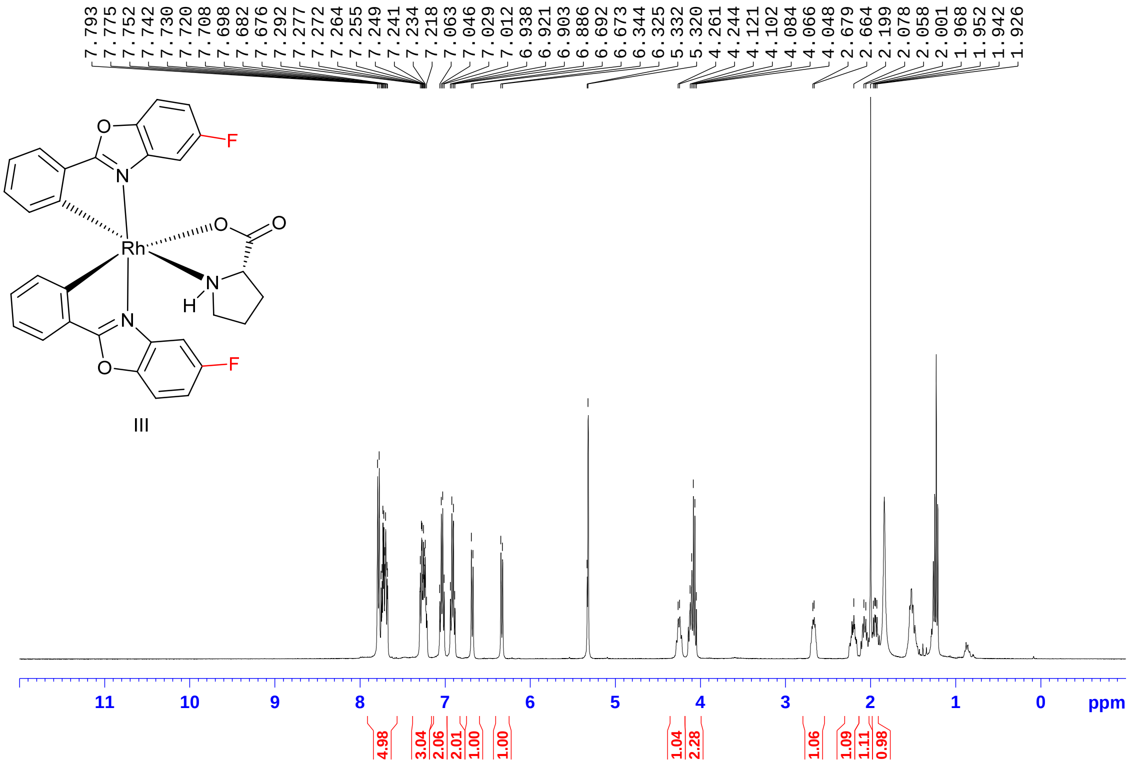
^{13}C NMR Spectrum of *rac*-Rhodium Complex (II)



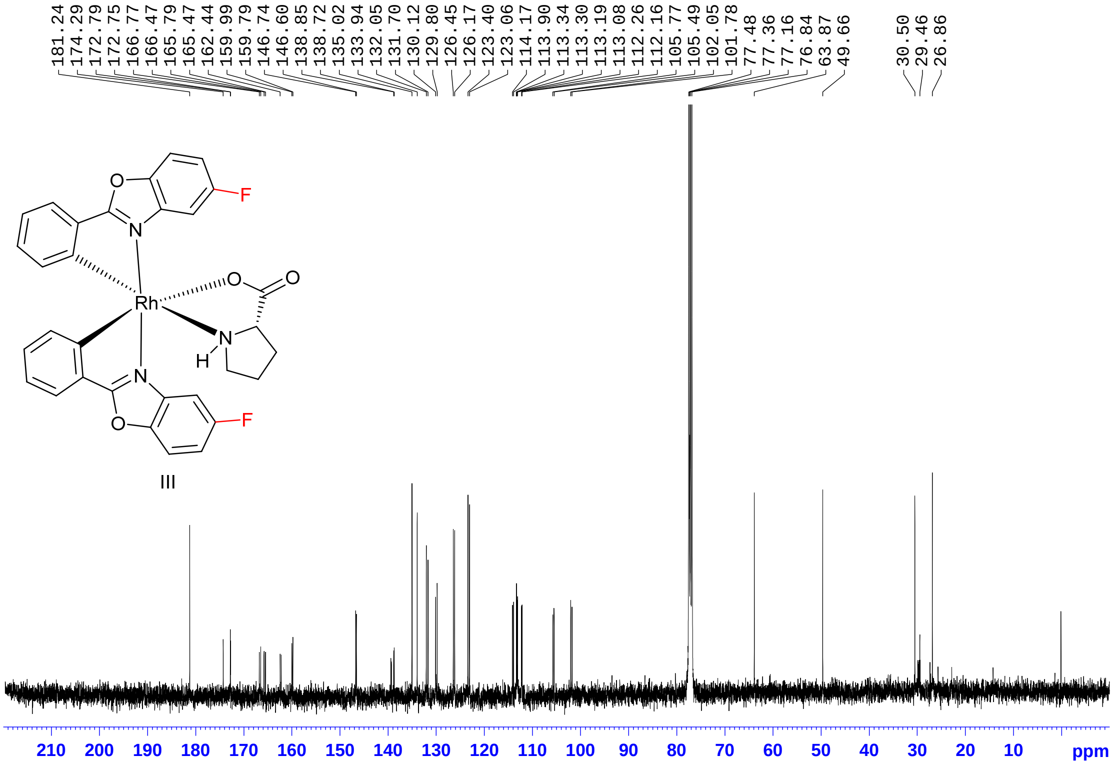
^{19}F NMR Spectrum of *rac*-Rhodium Complex (II)



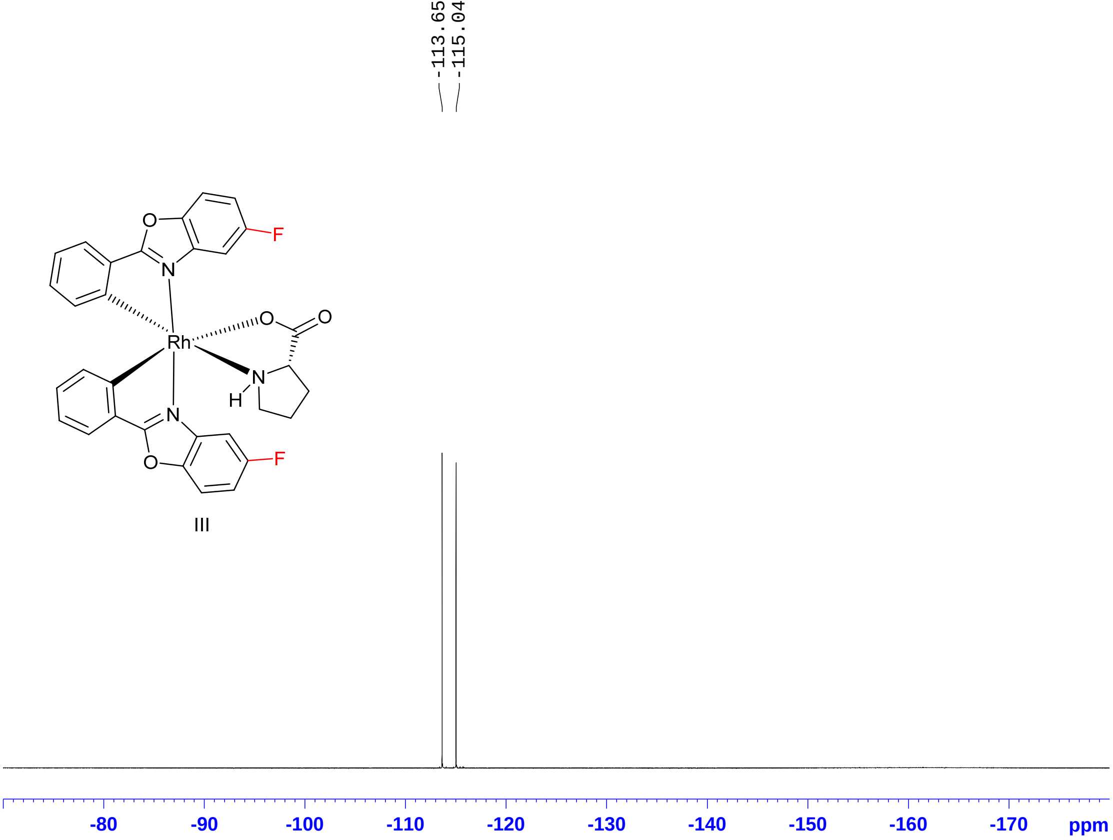
^{1}H NMR Spectrum of chiral Rhodium Auxiliary Complexes (III)



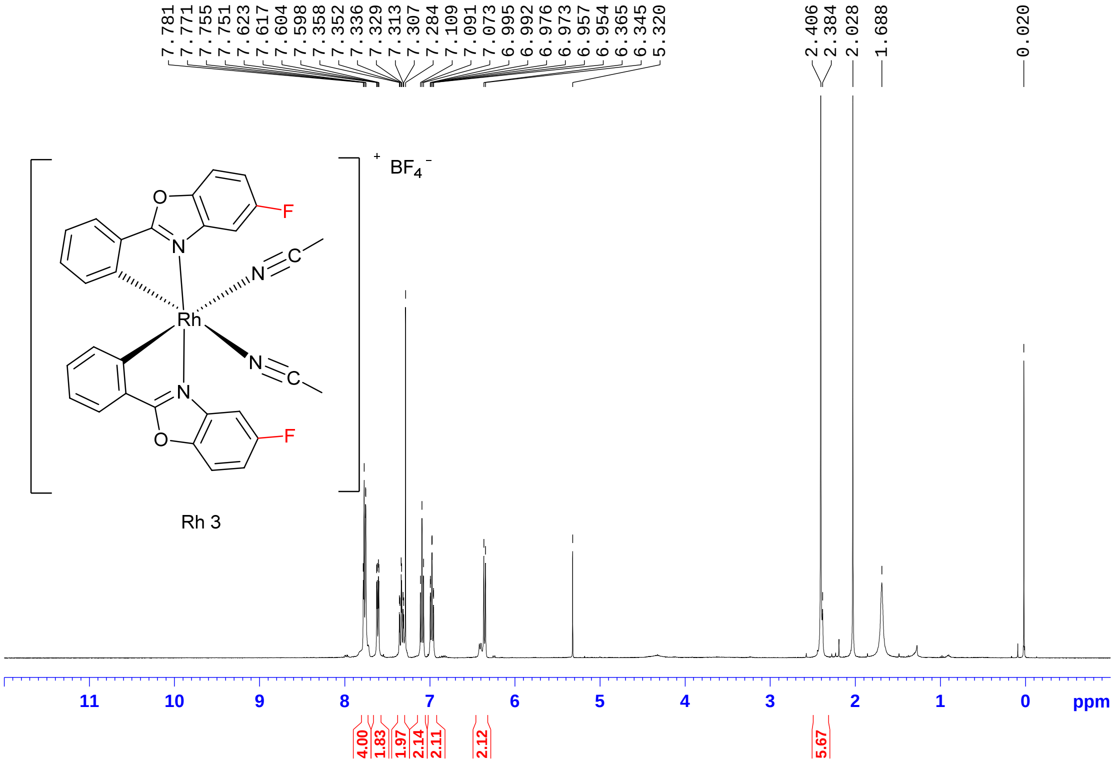
^{13}C NMR Spectrum of chiral Rhodium Auxiliary Complexes (III)



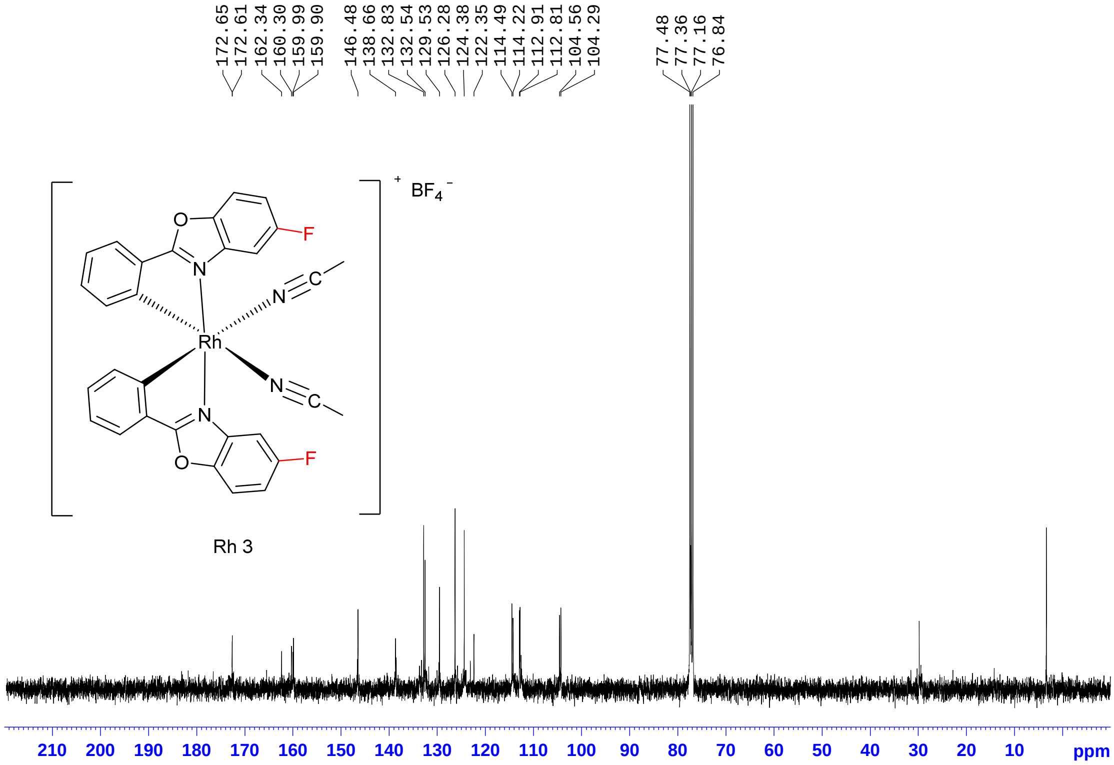
^{19}F NMR Spectrum of chiral Rhodium Auxiliary Complexes (III)



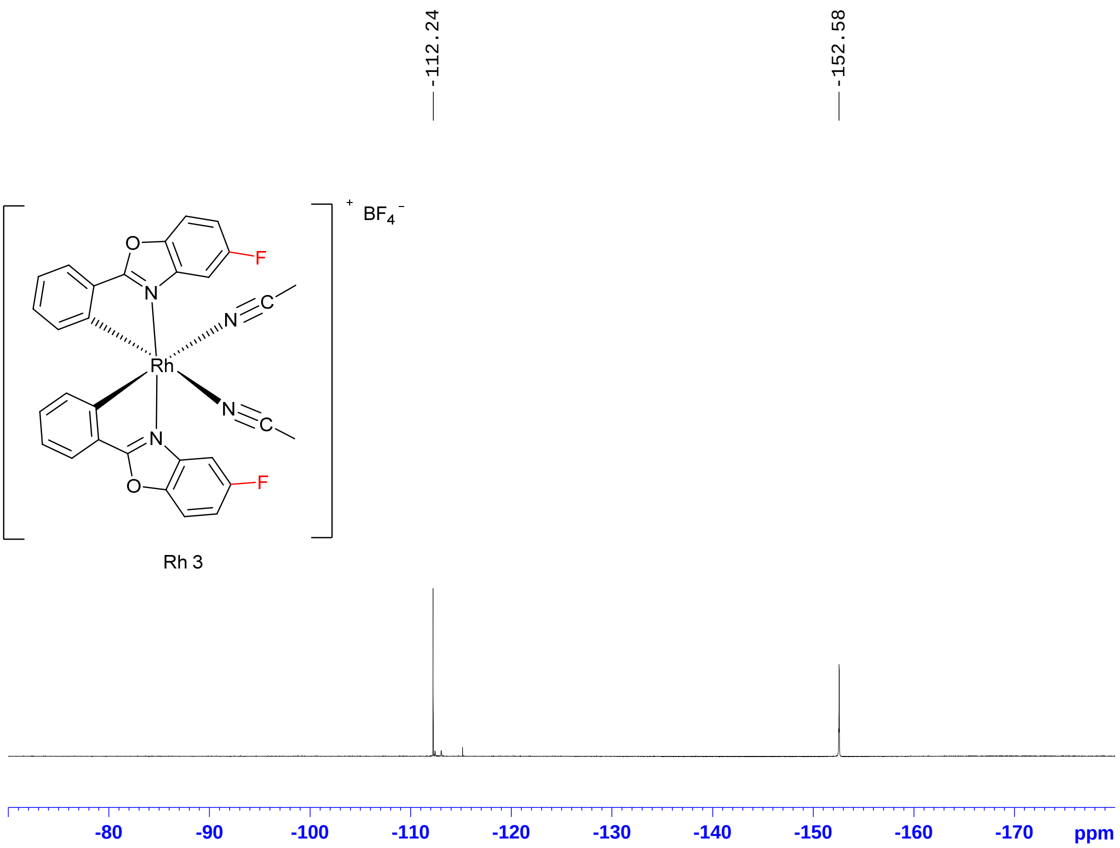
^{1}H NMR Spectrum of Chiral Rhodium Complexes Rh 3



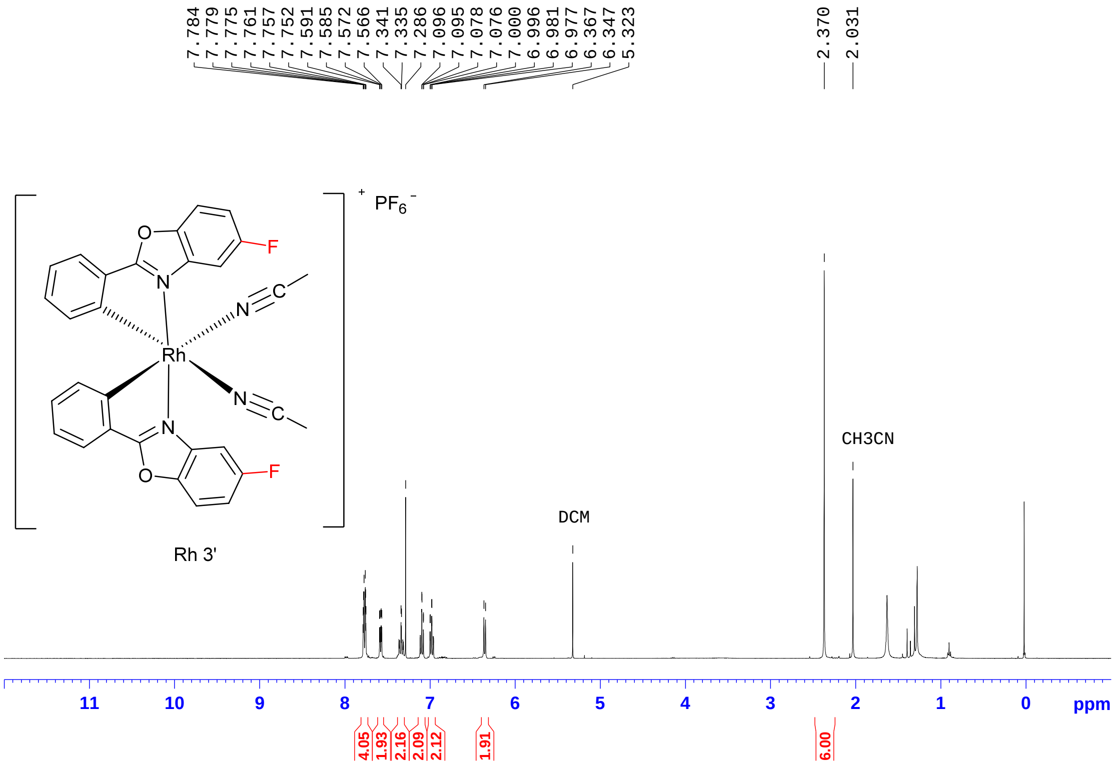
^{13}C NMR Spectrum of Chiral Rhodium Complexes Rh 3



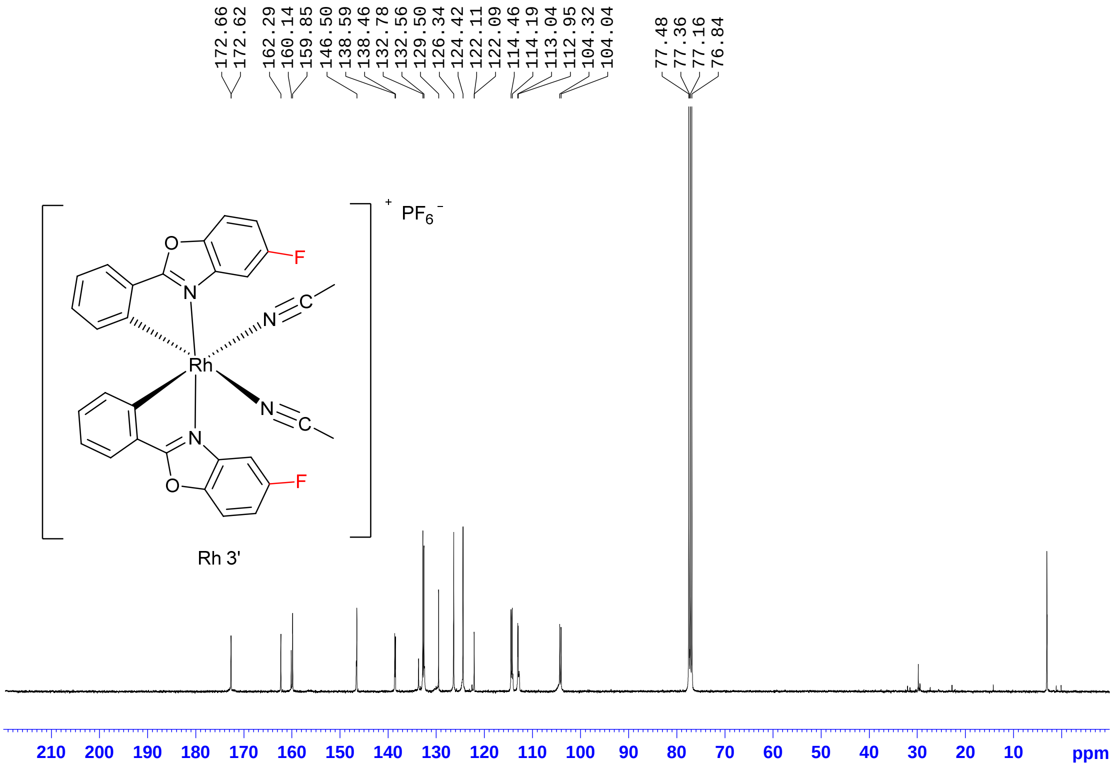
^{19}F NMR Spectrum of Chiral Rhodium Complexes Rh 3



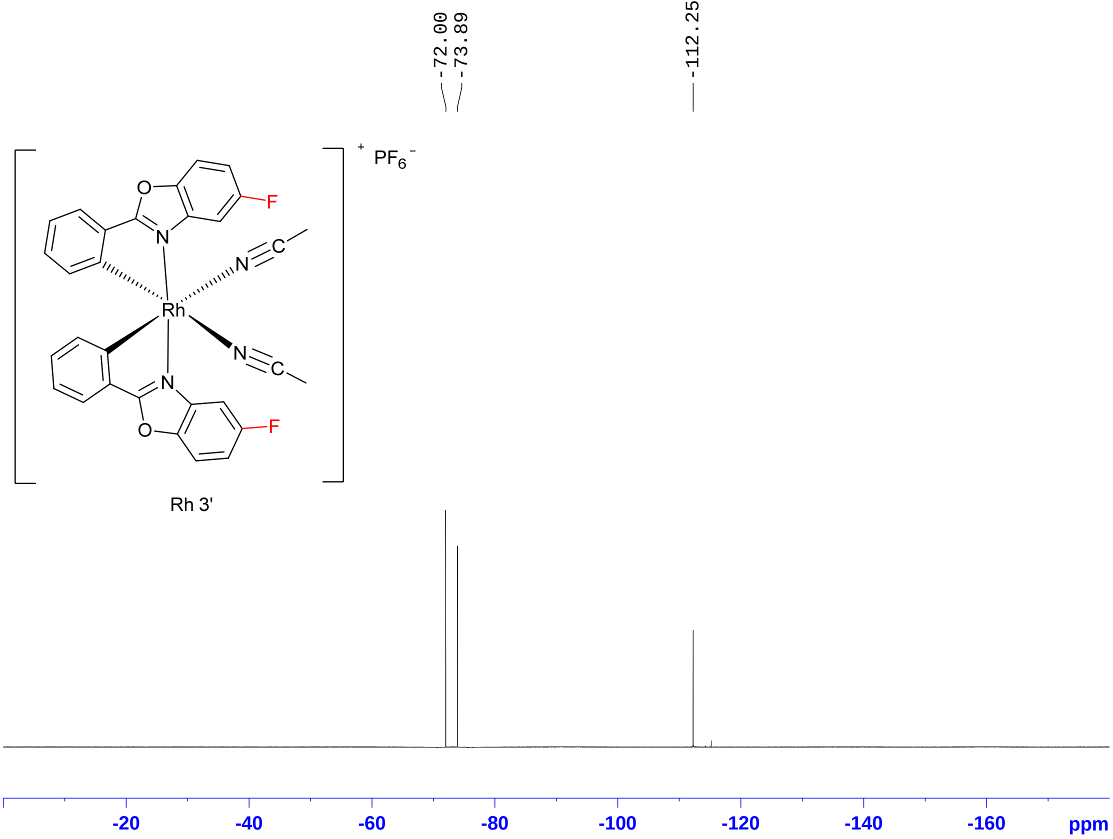
^1H NMR Spectrum of Chiral Rhodium Complexes Rh 3’



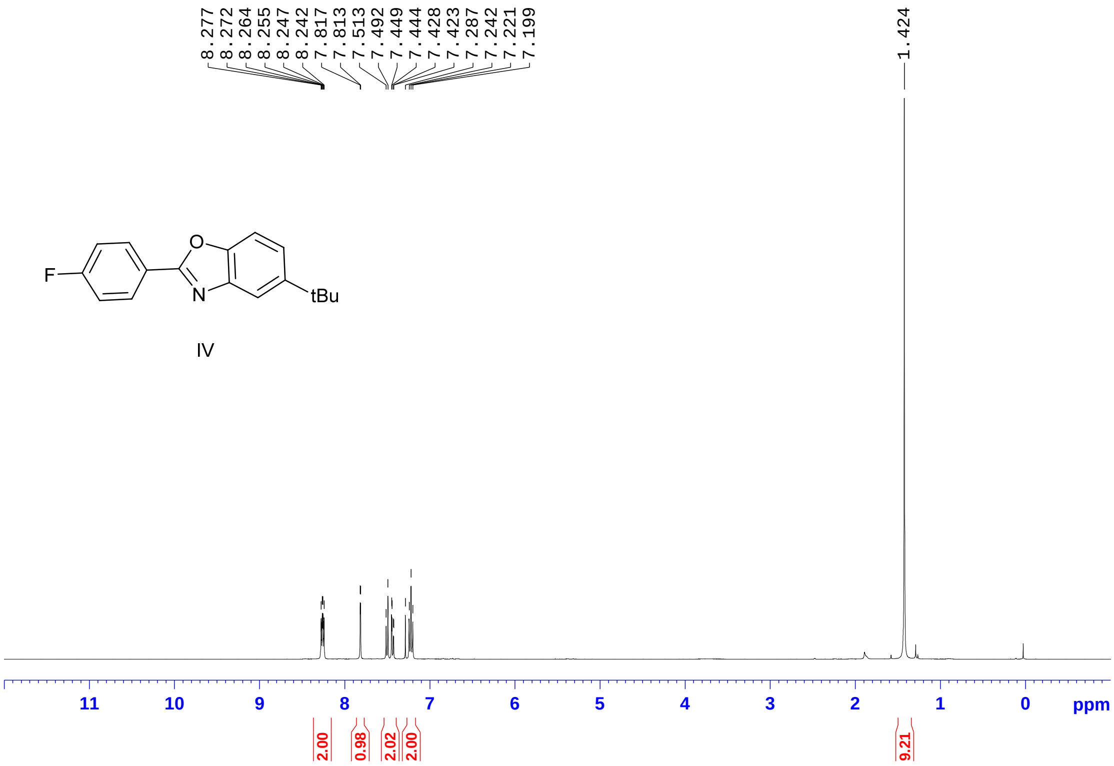
^{13}C NMR Spectrum of Chiral Rhodium Complexes Rh 3’



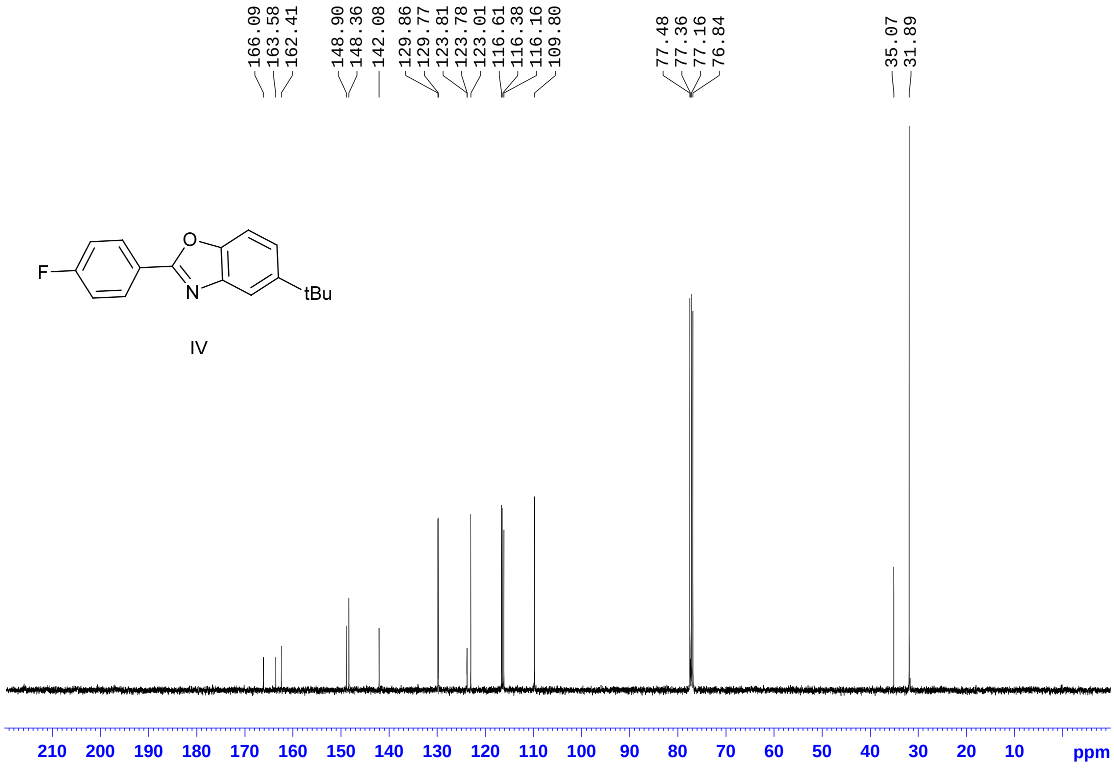
^{19}F NMR Spectrum of Chiral Rhodium Complexes Rh 3’



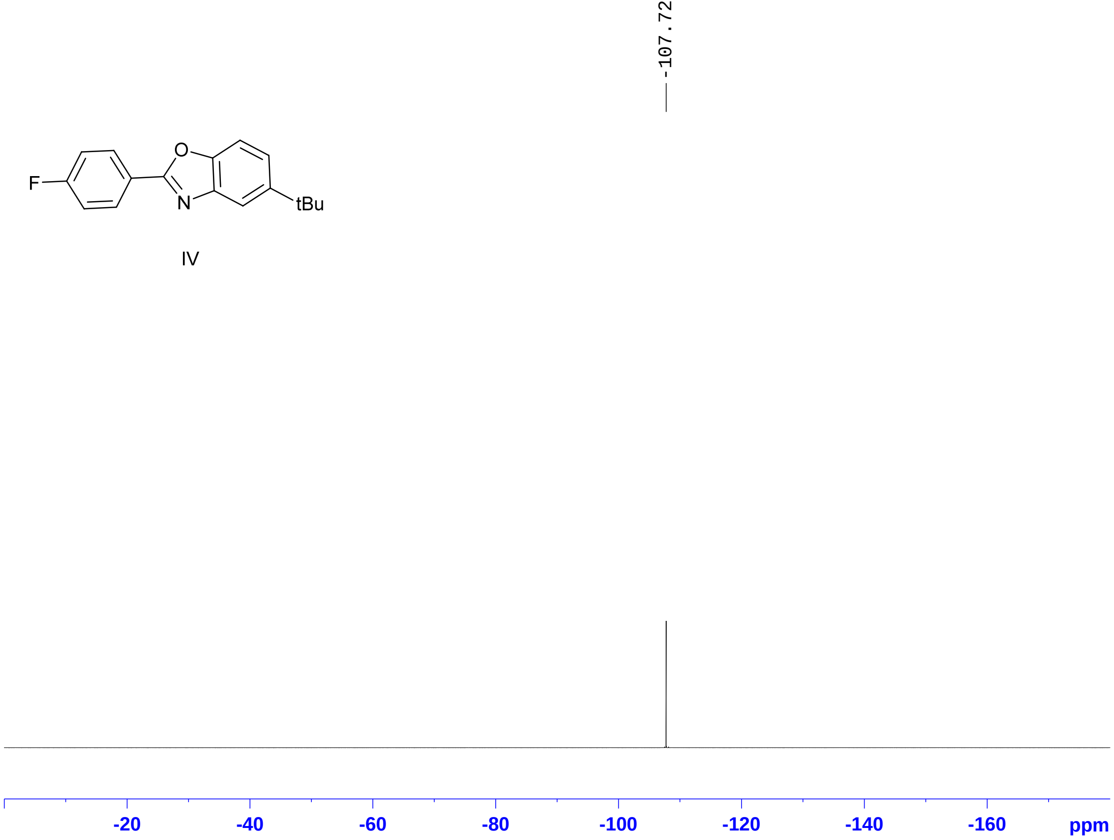
^{1}H NMR Spectrum of 5-(tert-butyl)-2-(4-fluorophenyl)benzo[d]oxazole (IV)



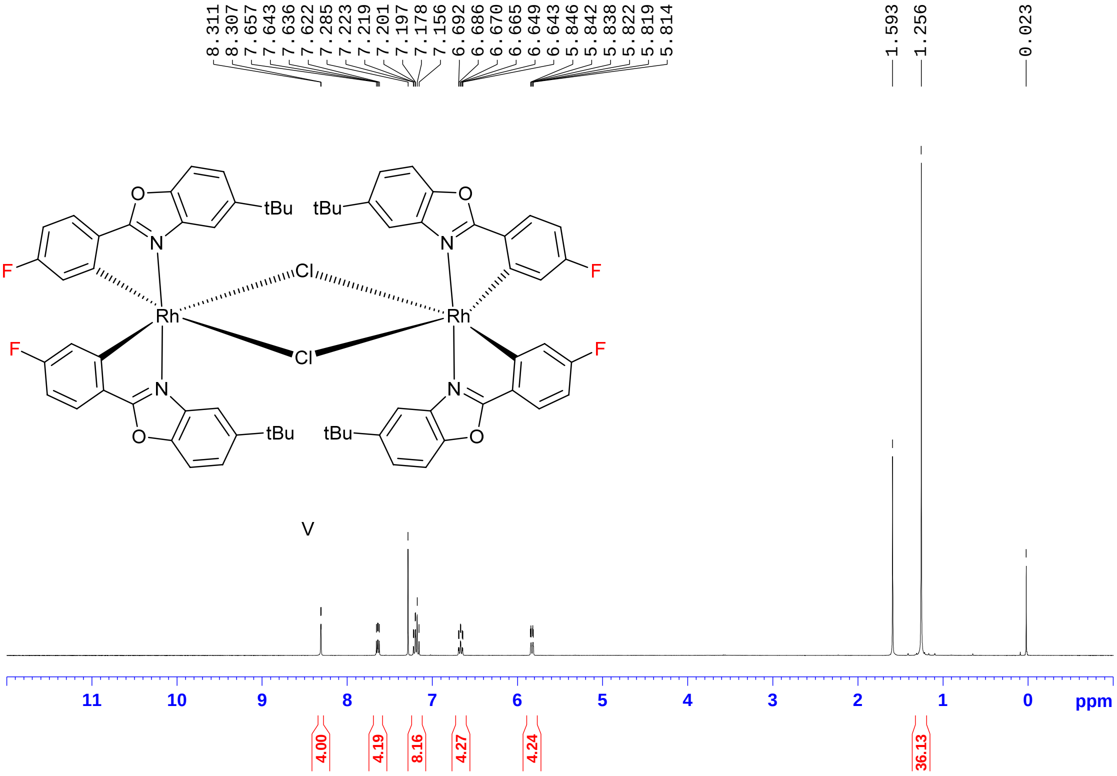
^{13}C NMR Spectrum of 5-(tert-butyl)-2-(4-fluorophenyl)benzo[d]oxazole (IV)



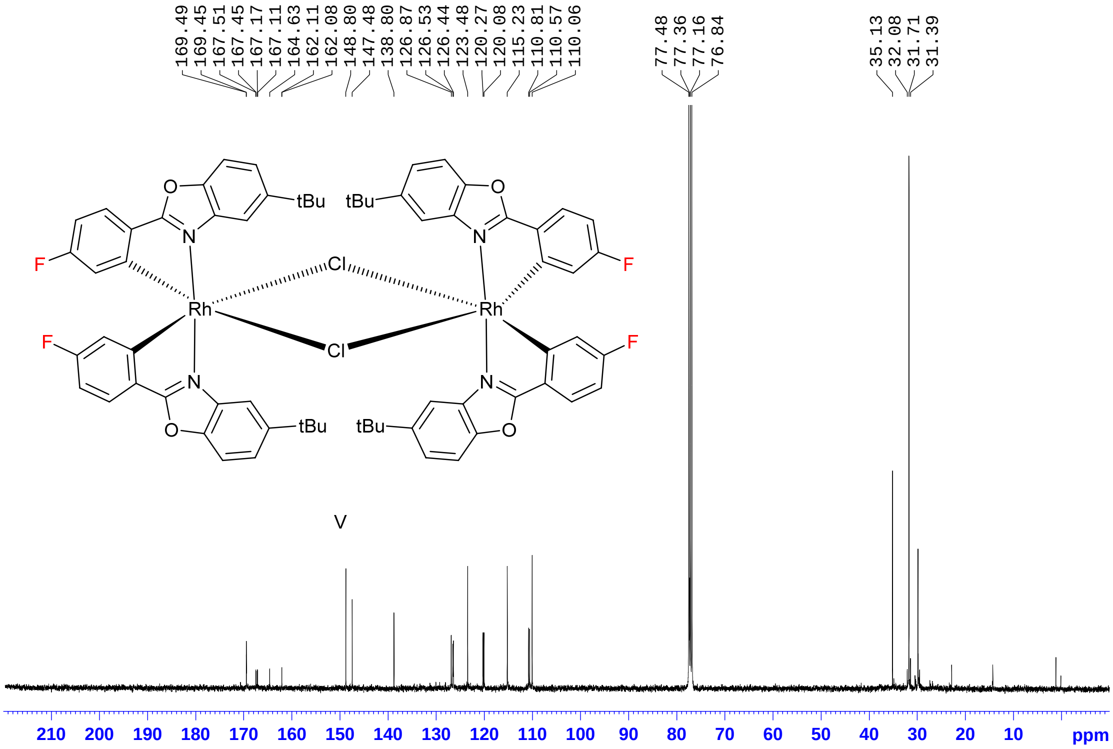
^{19}F NMR Spectrum of 5-(tert-butyl)-2-(4-fluorophenyl)benzo[d]oxazole (IV)



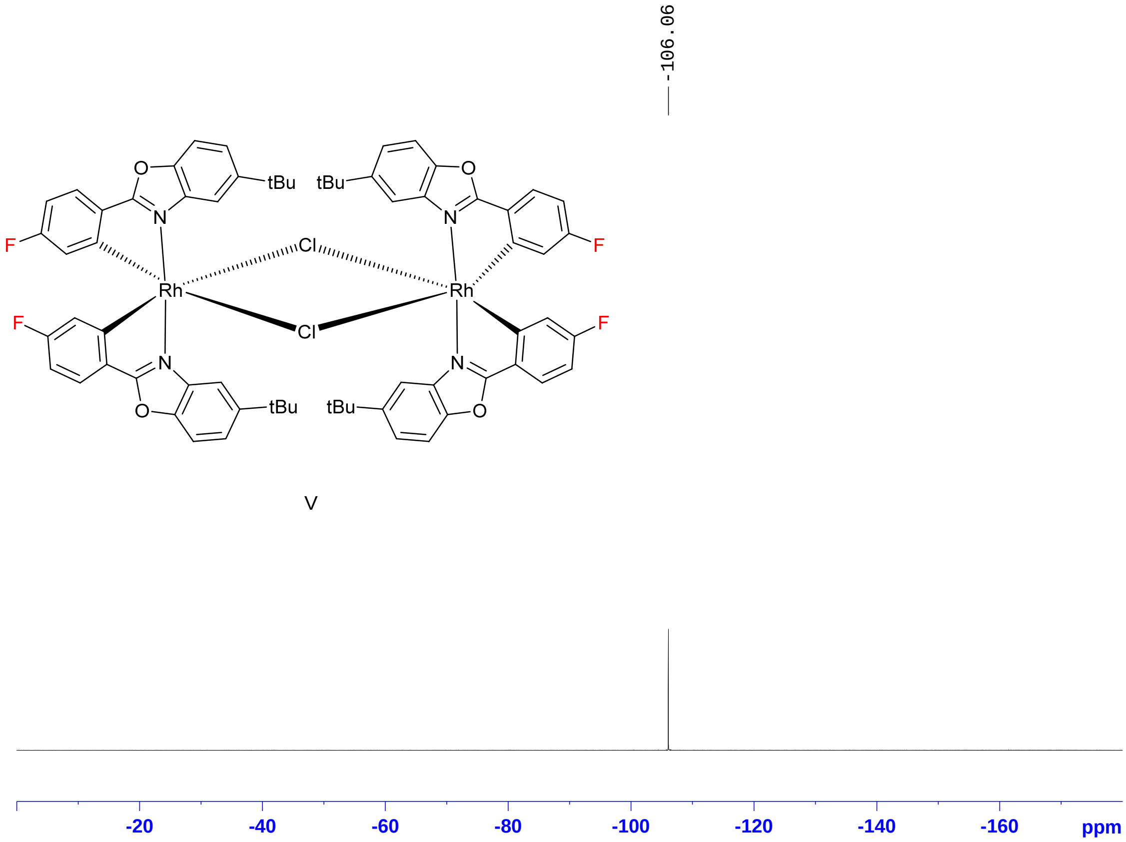
^{1}H NMR Spectrum of *rac*-Rhodium Complex (V)



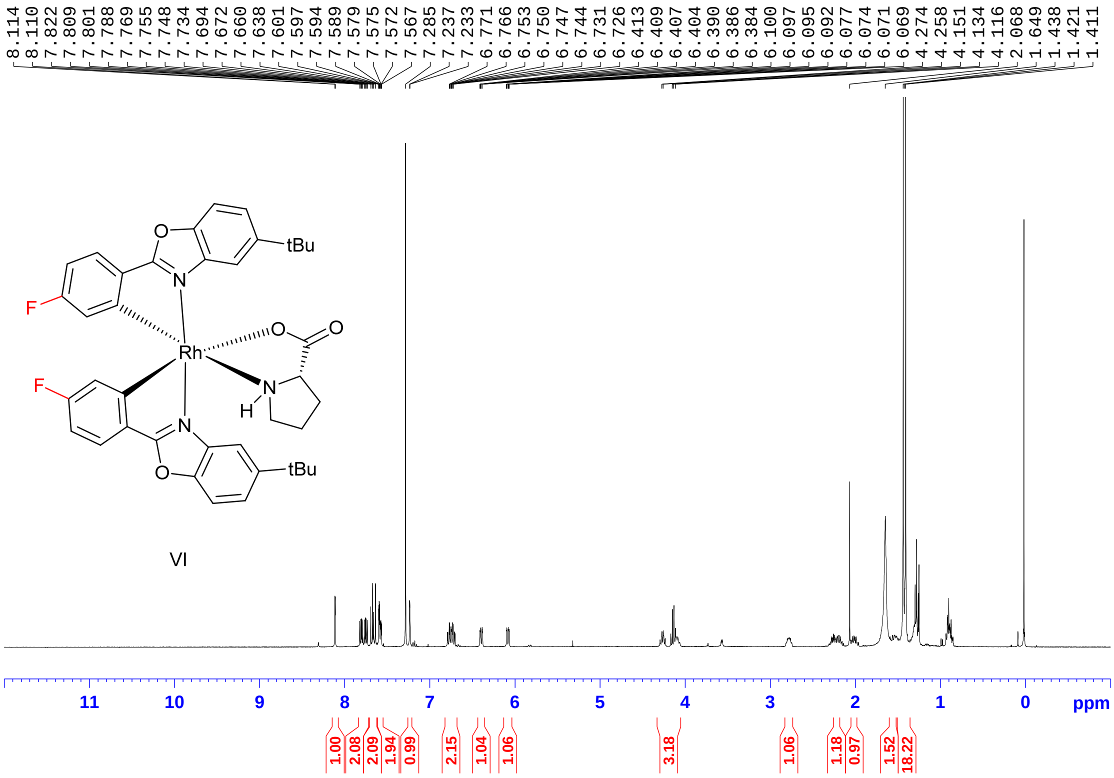
^{13}C NMR Spectrum of *rac*-Rhodium Complex (V)



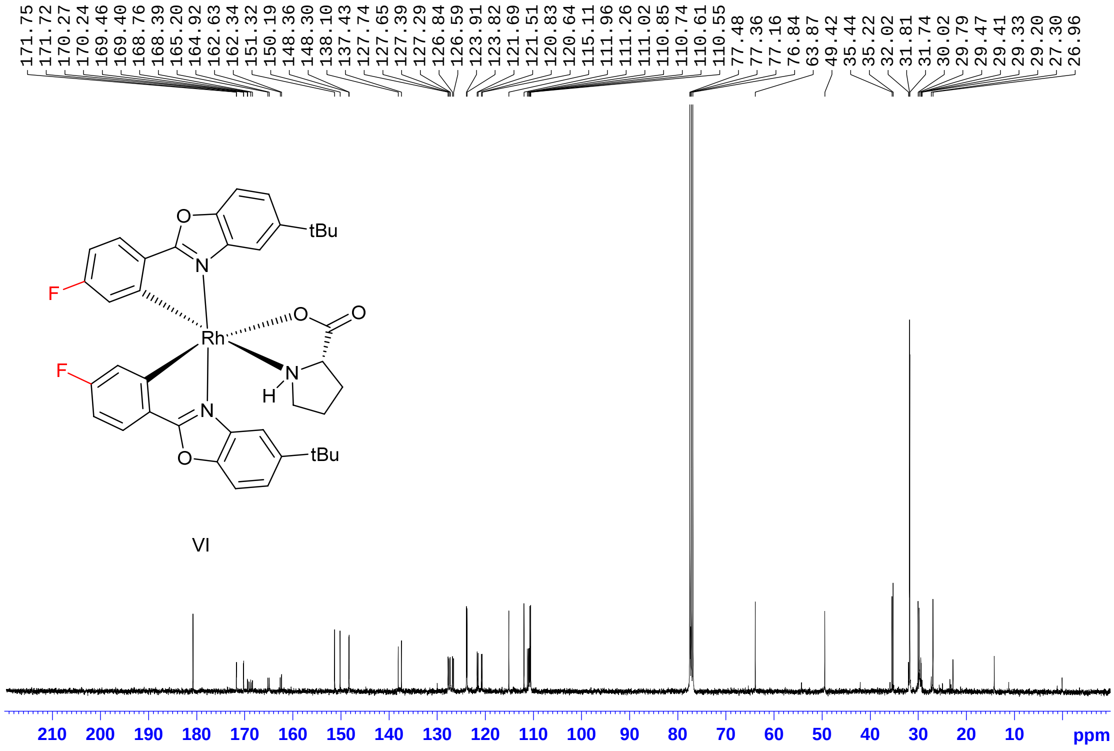
^{19}F NMR Spectrum of *rac*-Rhodium Complex (V)



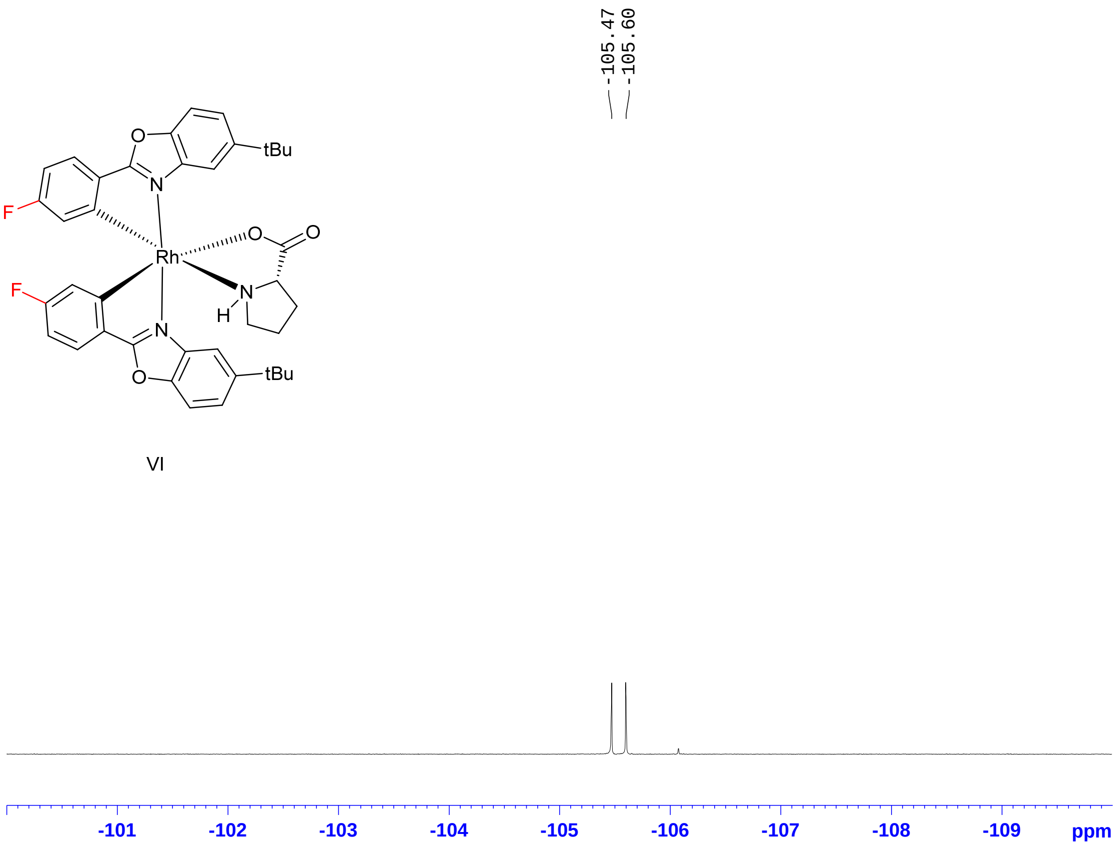
^{1}H NMR Spectrum chiral Rhodium Auxiliary Complexe (VI)



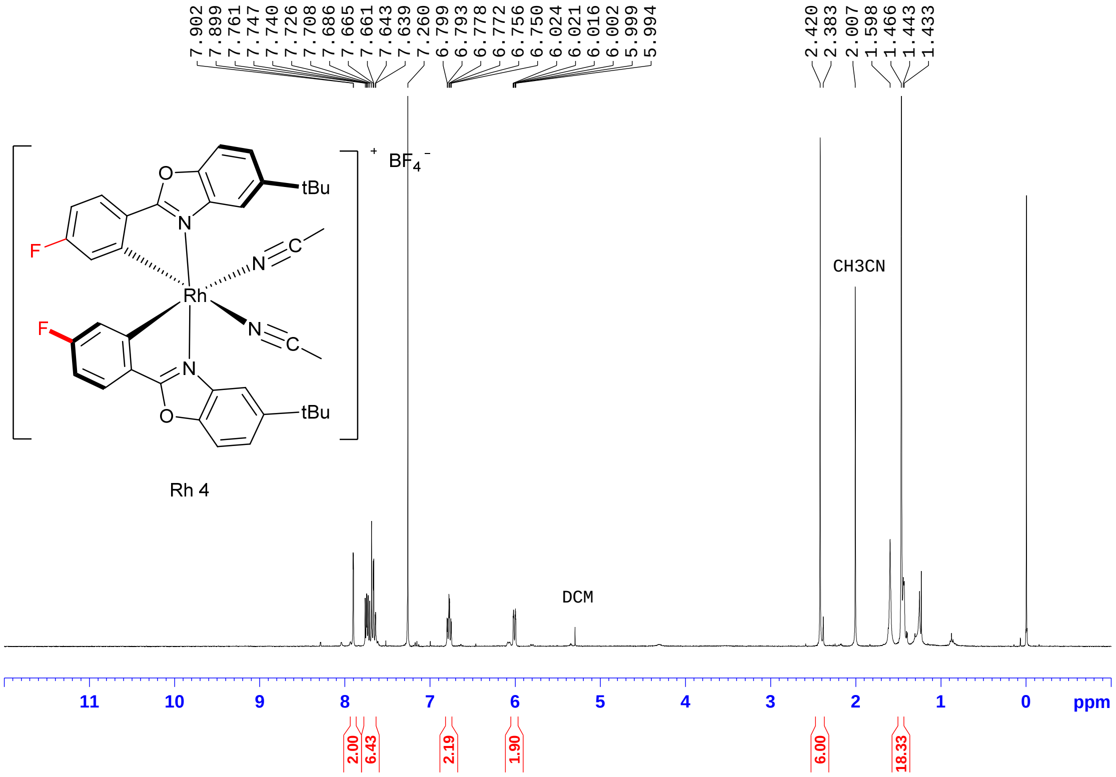
^{13}C NMR Spectrum chiral Rhodium Auxiliary Complexe (VI)



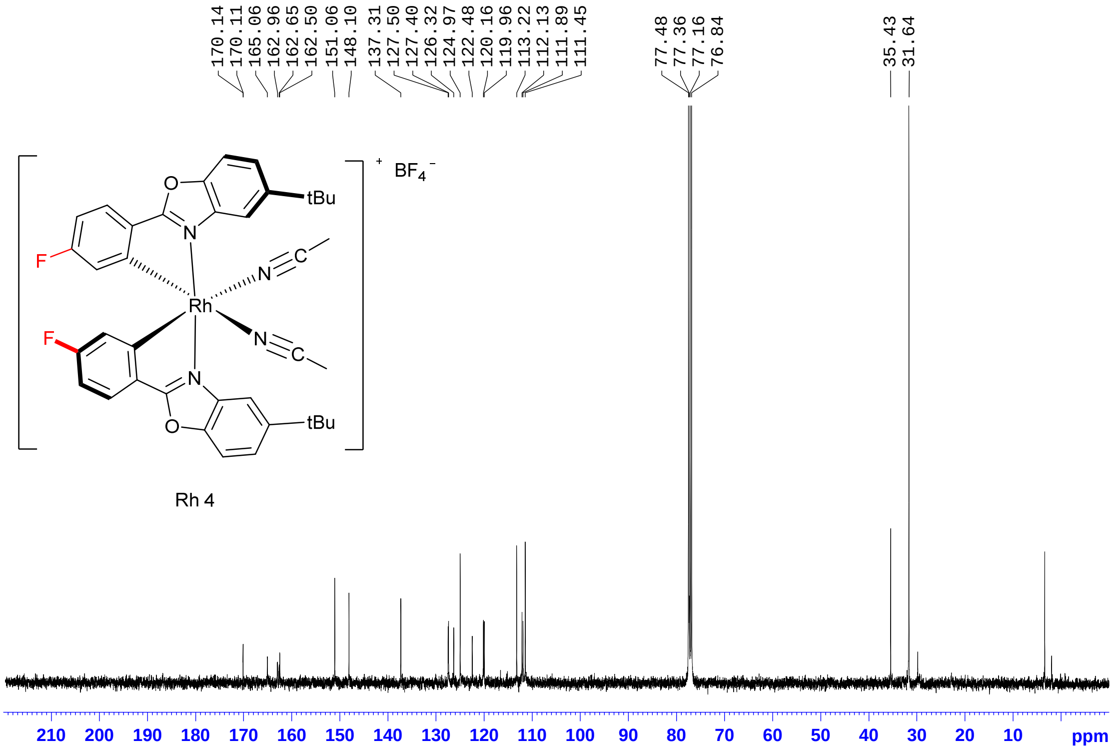
^{19}F NMR Spectrum chiral Rhodium Auxiliary Complexe (VI)


VI

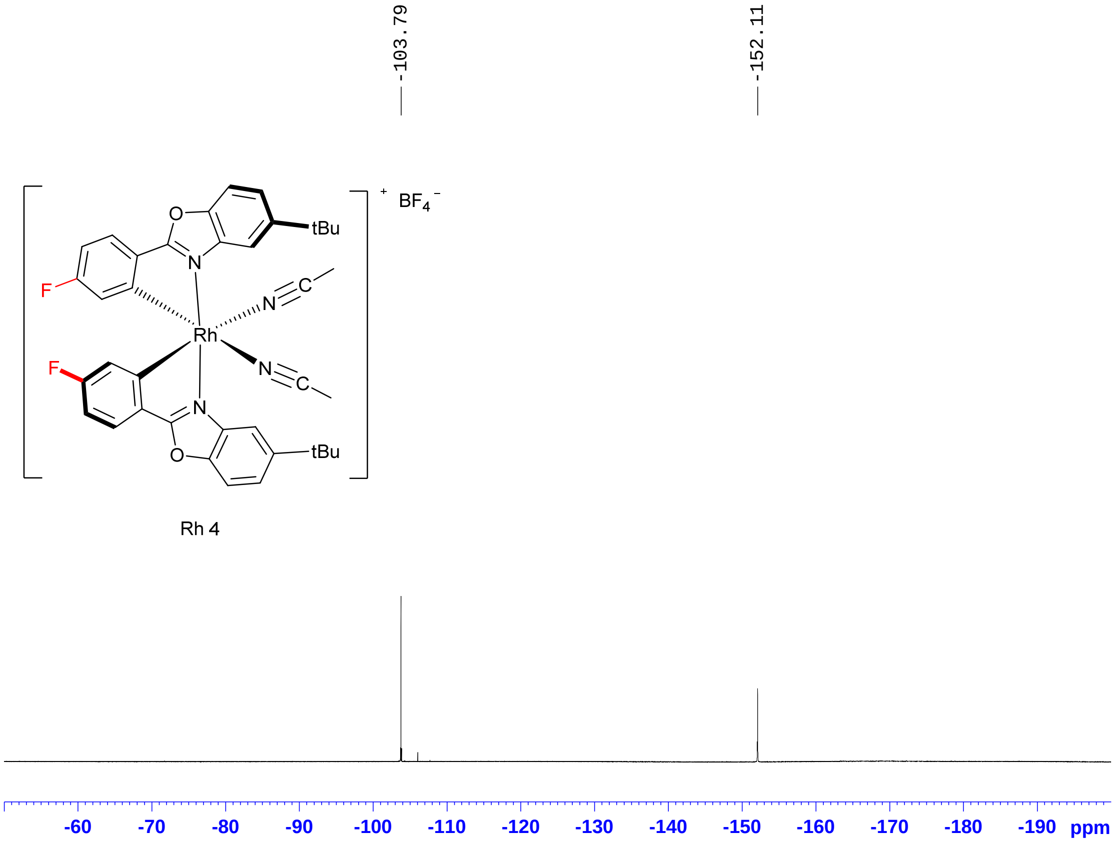
^{1}H NMR Spectrum chiral Rhodium Complexe Rh 4


Rh 4

^{13}C NMR Spectrum chiral Rhodium Auxiliary Complexe Rh 4



^{19}F NMR Spectrum chiral Rhodium Auxiliary Complexe Rh 4



8. Reference

[1] a) H. H. Huo, X. D. Shen, C. Y. Wang, L. L. Zhang, P. Rose, L. A. Chen, K. Harms, M. Marsch, G. Hilt, E. Meggers, *Nature* **2014**, *515*, 100-103; b) C. Y. Wang, L. A. Chen, H. H. Huo, X. D. Shen, K. Harms, L. Gong, E. Meggers, *Chem. Sci.* **2015**, *6*, 1094-1100.