Supporting Information for

Guanidine-Functionalized Rhenium Cyclopentadienyl Carbonyl Complexes: Synthesis and Cooperative Activation of H–H and O–H Bonds

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Table S1. Crystallographic summary for **1–3**.

	1	**2**	**3**
Formula	$C_{13}H_{14}N_3O_3Re$	$C_{13}H_{15}BF_4N_3O_3Re$	$C_{12}H_{15}B_2F_8N_4O_3Re$
fw, g/mol	446.47	534.29	623.10
Temperature/K	100(2)	100(2)	100(2)
cryst. syst.	Monoclinic	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	$Pca2_1$
color	Colorless	Colorless	Yellow
a/Å	9.8852(5)	8.1382(10)	21.1586(9)
b/Å	14.8057(7)	21.483(3)	7.8417(3)
c/Å	9.5666(5)	9.4361(12)	22.8621(10)
α/°	90	90	90
β/°	104.348(2)	90.539(6)	90
γ/°	90	90	90
V/Å^3	1356.47(12)	1649.7(4)	3793.3(3)
ρ (calc.)/(g cm^{-3})	2.186	2.151	2.182
Z	4	4	8
no. refl.	42327	197454	118663
no. unique refl.	7027	13825	12650
R_{int}	0.0379	0.0451	0.0654
R_1[a] (all data)	0.0278	0.0233	0.0445
wR_2[b] (all data)	0.0462	0.0434	0.0888
R_1 [(I > 2σ)]	0.0201	0.0189	0.0386
wR_2 [(I > 2σ)]	0.0437	0.0422	0.0858
GOF[c]	1.019	1.122	1.120

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. [c] $GOF = (\Sigma w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

Table S2. Crystallographic summary for **4** and **7**.

	4	**7**
Formula	$C_{12}H_{14}BF_4N_4O_3Re$	$C_{13}H_{17}N_4O_4Re$
fw, g/mol	535.28	479.51
Temperature/K	100(2)	100(2)
cryst. syst.	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$
color	Orange	Yellow
a/Å	11.1053(4)	8.3732(4)
b/Å	9.9635(3)	7.8158(4)
c/Å	14.9378(5)	23.0017(11)
α/°	90	90
β/°	95.2430(10)	95.791(2)
γ/°	90	90
V/Å^3	1645.92(9)	1497.62(13)
ρ (calc.)/(g cm^{-3})	2.160	2.127
Z	4	4
no. refl.	37996	137916
no. unique refl.	6279	11127
R_{int}	0.0365	0.0642
R_1[a] (all data)	0.0414	0.0470
wR_2[b] (all data)	0.0737	0.0700
R_1 [(I > 2σ)]	0.0341	0.0345
wR_2 [(I > 2σ)]	0.0699	0.0661
GOF[c]	1.148	1.085

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2))^{1/2}$. [c] $GOF = (\Sigma w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where n is the number of data and p is the number of parameters refined.

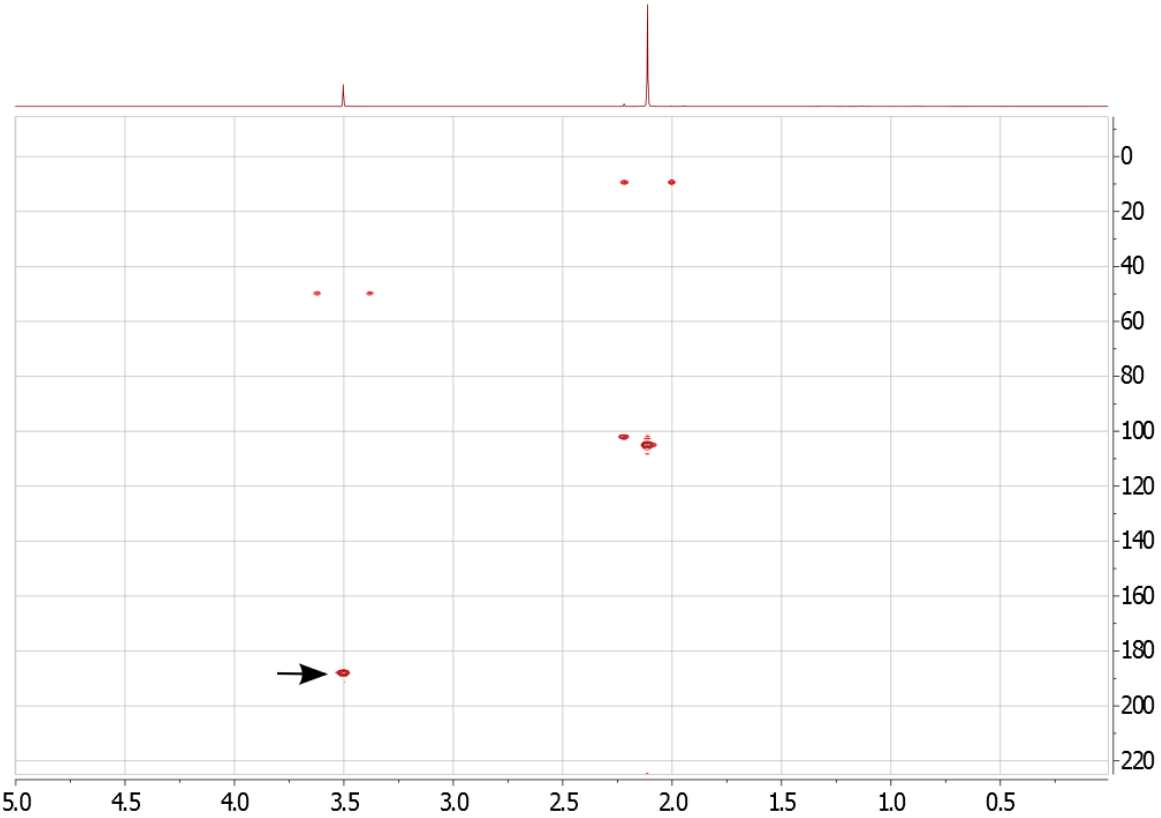


Figure S1. HMBC spectrum for methoxycarbonyl complex **8**, with ^{1}H chemical shift on the horizontal axis and ^{13}C chemical shift on the vertical axis. The correlation between the methoxycarbonyl ^{1}H and ^{13}C resonances is highlighted with an arrow.

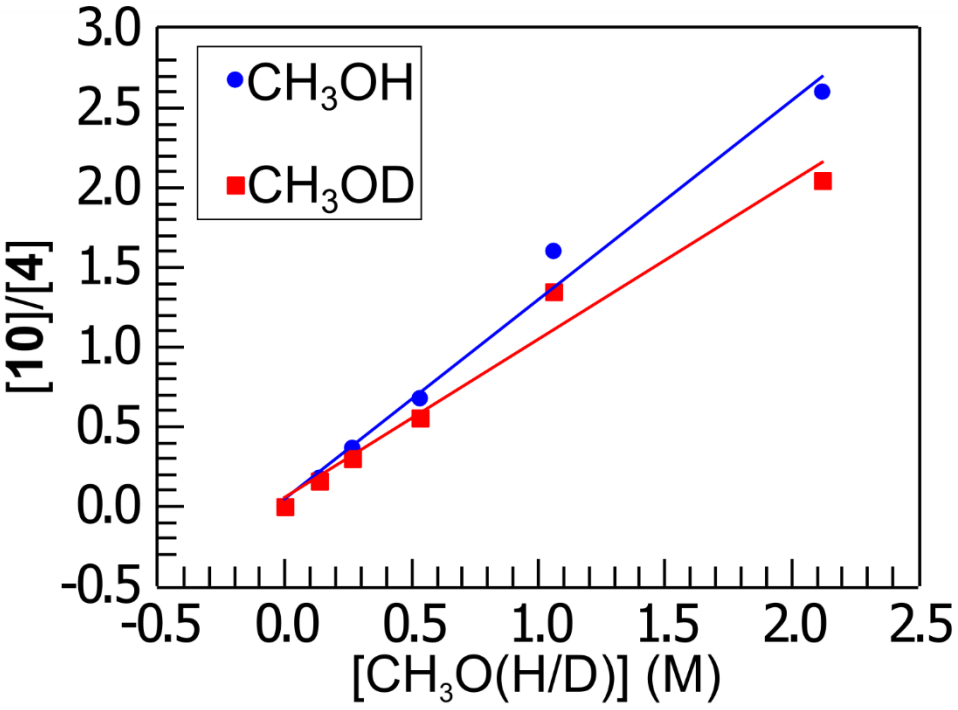


Figure S2. Plot of the ratio [**10**]/[**4**] present at equilibrium when complex **4** (6.0 mM) is treated with varying concentrations of CH_3OH (●, blue) or CH_3OD (■, red). The best-fit lines, which were used to determine K_{eq}, are shown as solid lines of the same color.

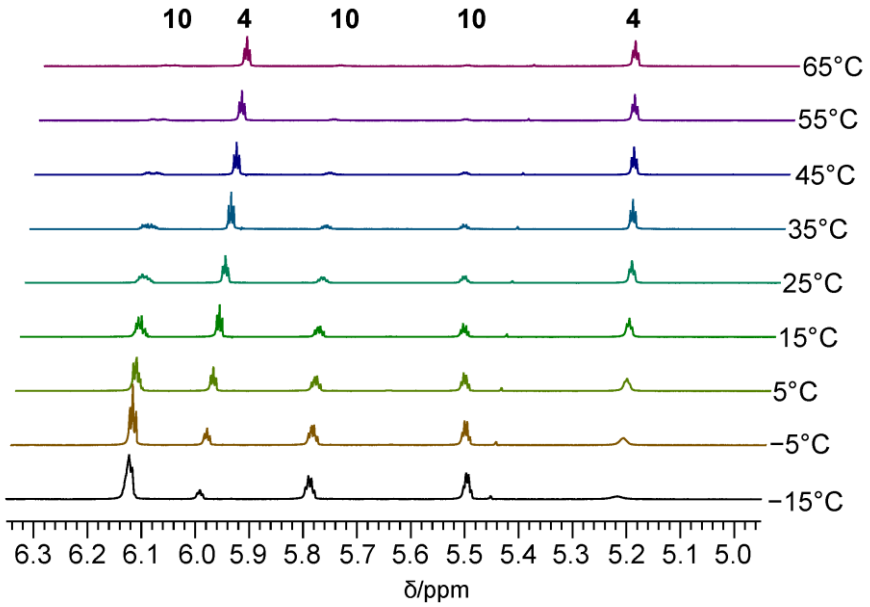


Figure S3. Partial variable-temperature ^1H NMR spectra for complex **4** in the presence of 0.60 M CH_3OH in CD_3CN. The cyclopentadienyl region is shown, with peaks attributed to **4** and **10** labeled.

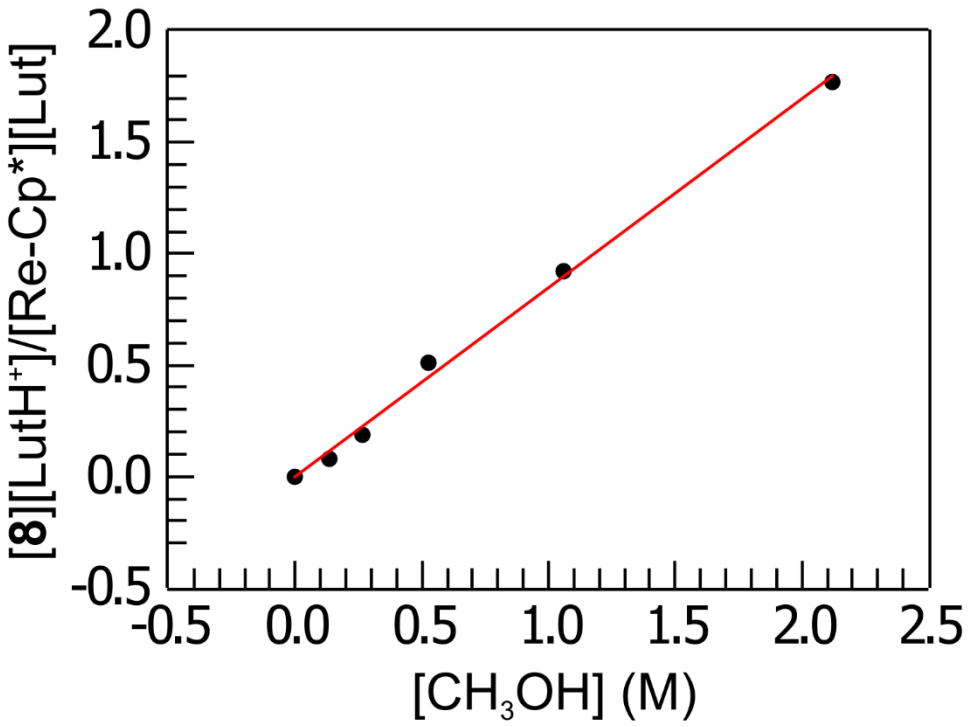


Figure S4. Plot of the ratio [**8**][LutH$^+$]/[Re-Cp*][Lut] (LutH$^+$ = 2,6-lutidinium, Lut = 2,6-lutidine, Re-Cp* = [Re(η^5-Cp*)(CO)$_2$(NO)]$^+$) present at equilibrium when [Re(η^5-Cp*)(CO)$_2$(NO)](BF$_4$) (6.5 mM) is treated with varying concentrations of CH$_3$OH in the presence of 2,6-lutidine (ca. 6.5 mM) in CD$_3$CN. The slope of the best-fit line gives K_{eq}.

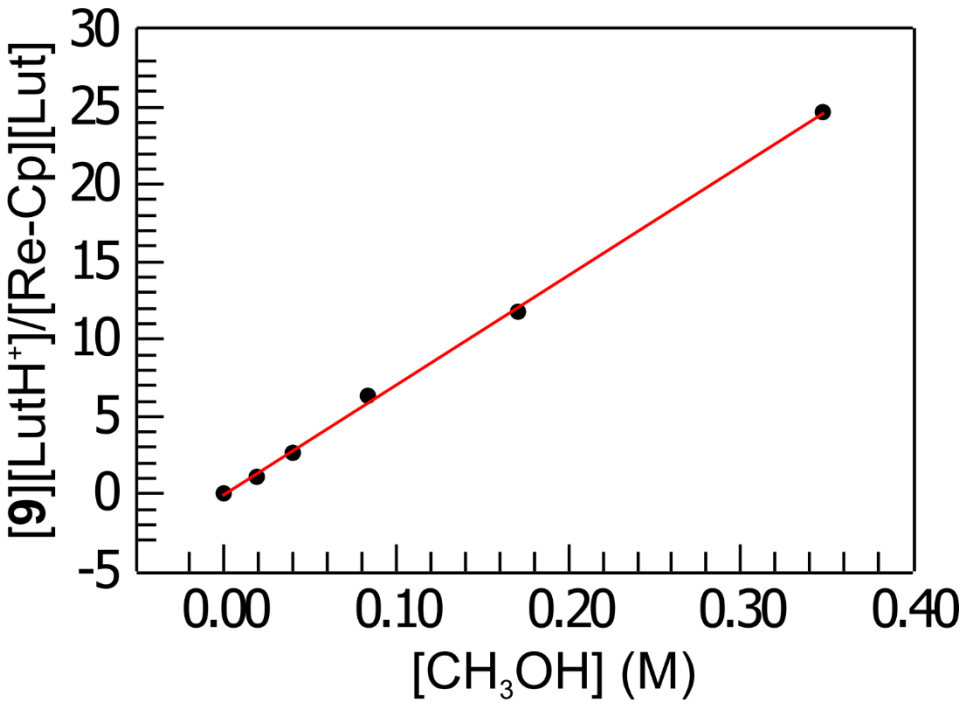


Figure S5. Plot of the ratio [**9**][LutH$^+$]/[Re-Cp][Lut] (LutH$^+$ = 2,6-lutidinium, Lut = 2,6-lutidine, Re-Cp = [Re(η^5-Cp)(CO)$_2$(NO)]$^+$) present at equilibrium when [Re(η^5-Cp)(CO)$_2$(NO)](BF$_4$) (5.9 mM) is treated with varying concentrations of CH$_3$OH in the presence of 2,6-lutidine (ca. 5.5 mM) in CD$_3$CN. The slope of the best-fit line gives K_{eq}.

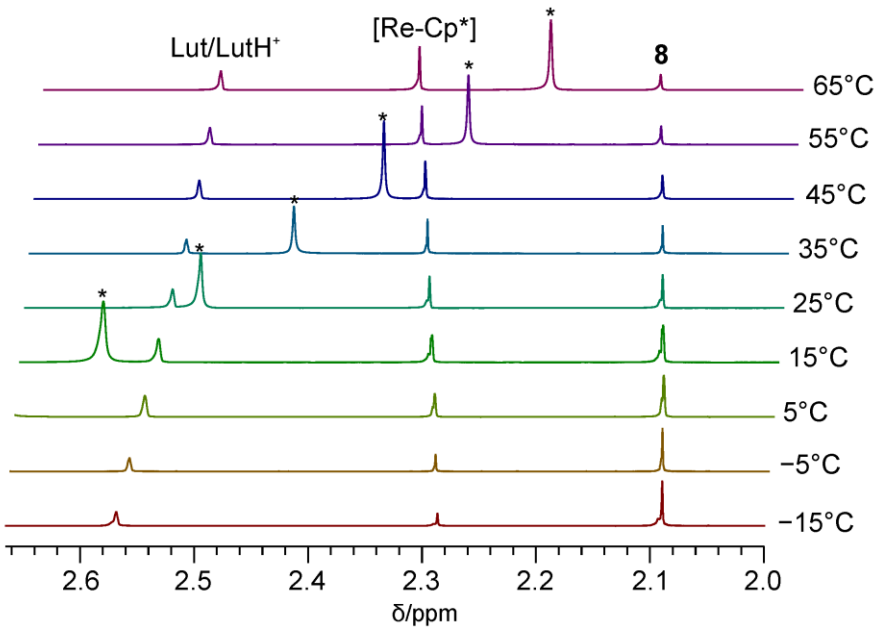


Figure S6. Partial variable-temperature ^{1}H NMR spectra for complex [Re(η^5-Cp*)$(CO)_2(NO)$](BF_4) (abbreviated [Re-Cp*]) in the presence of 1 equivalent of 2,6-lutidine with 0.79 M CH_3OH in CD_3CN. The upfield region is shown, with peaks attributed to **8**, [Re-Cp*], and the averaged peak for 2,6-lutidine/2,6-lutidinium (Lut/$LutH^+$) labeled. Peaks for the O*H* group of the added methanol are labeled with an asterisk (*).

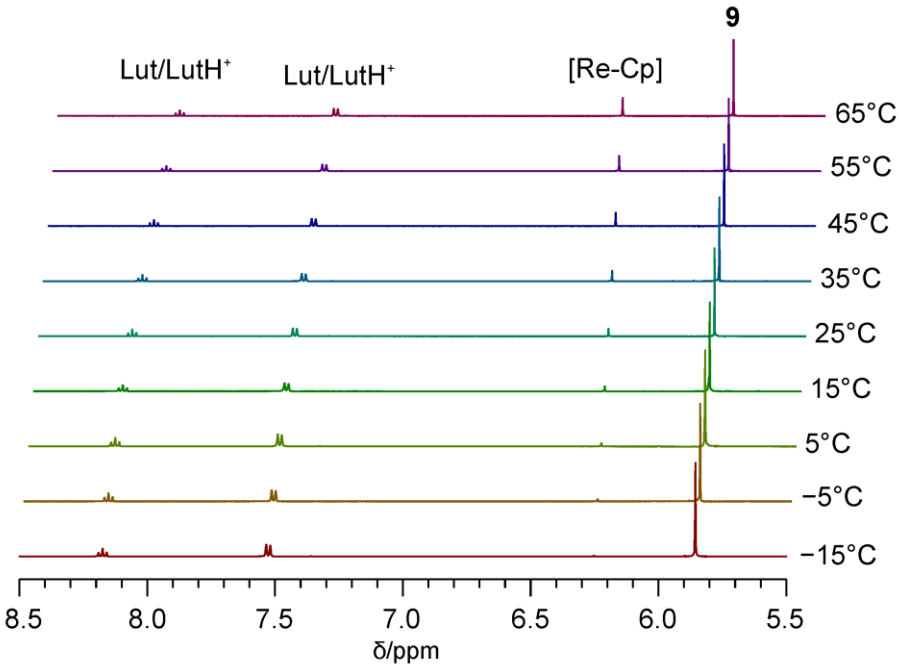
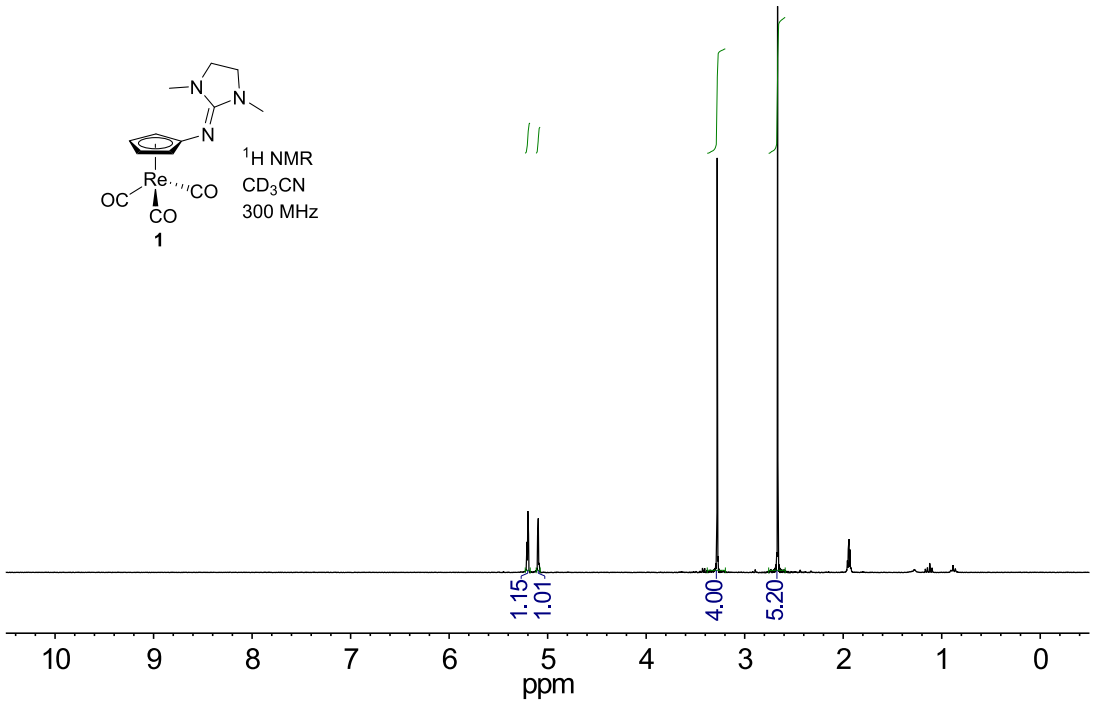
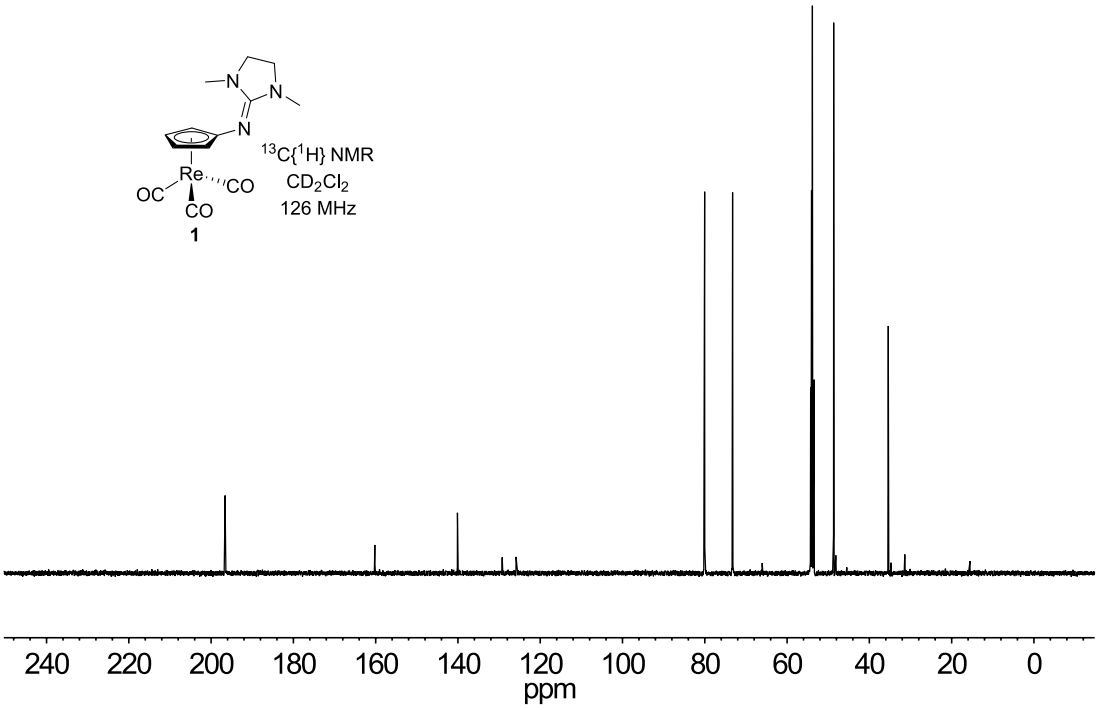
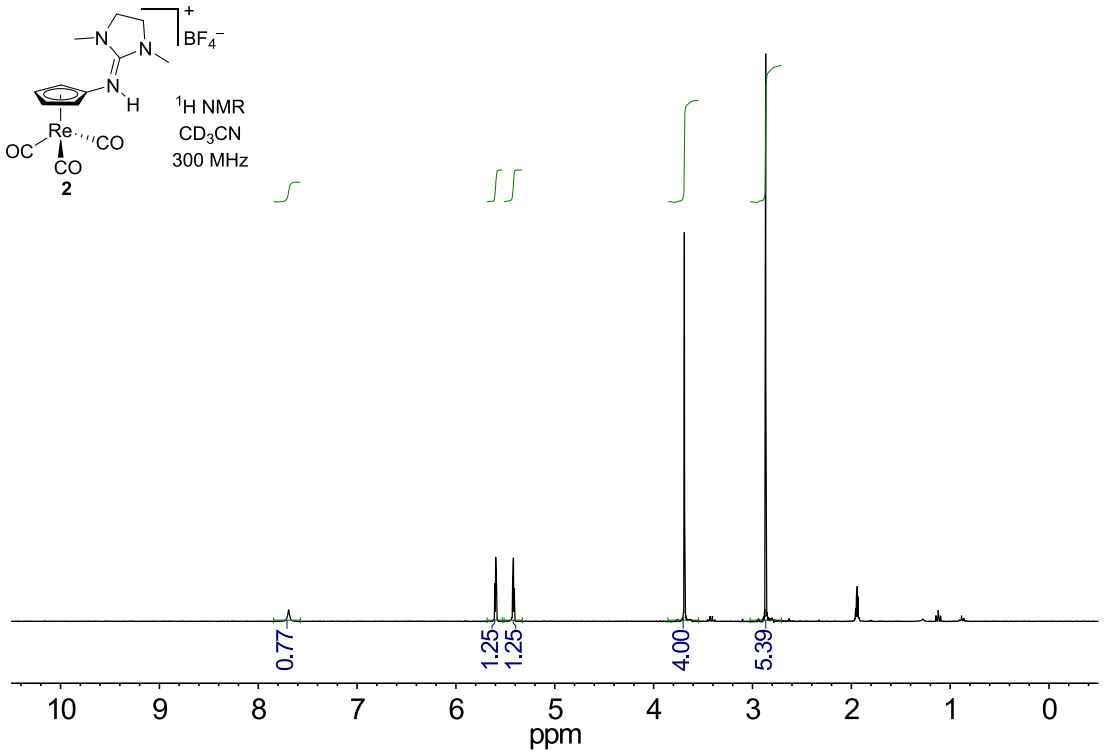
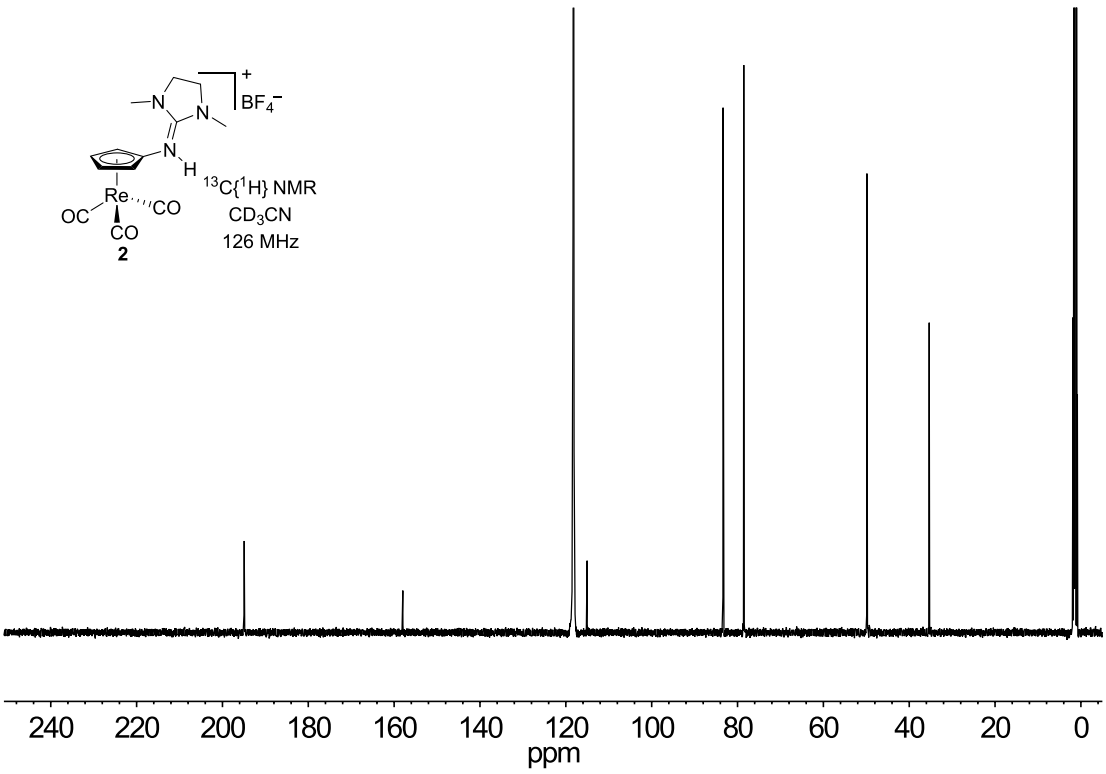


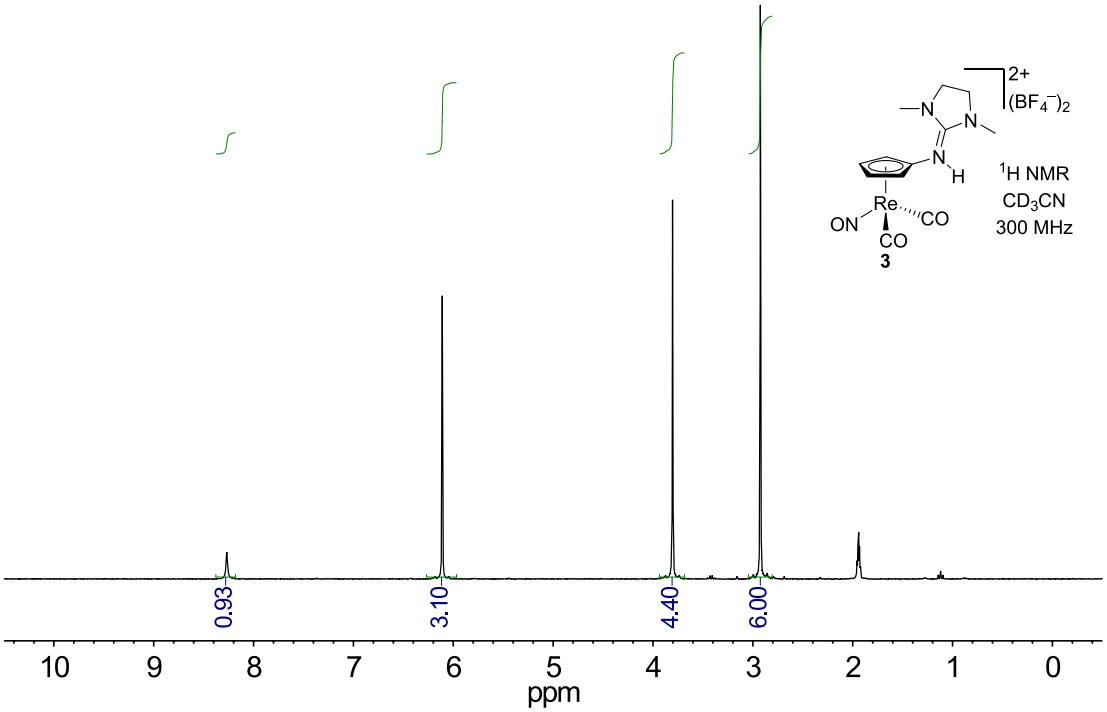
Figure S7. Partial variable-temperature ^{1}H NMR spectra for complex [Re(η^5-Cp)$(CO)_2(NO)$][BF_4] (abbreviated [Re-Cp]) in the presence of 1 equivalent of 2,6-lutidine with 0.79 M CH_3OH in CD_3CN. The downfield region is shown, with peaks attributed to **9**, [Re-Cp], and the averaged peaks for 2,6-lutidine/2,6-lutidinium (Lut/LutH^+) labeled.

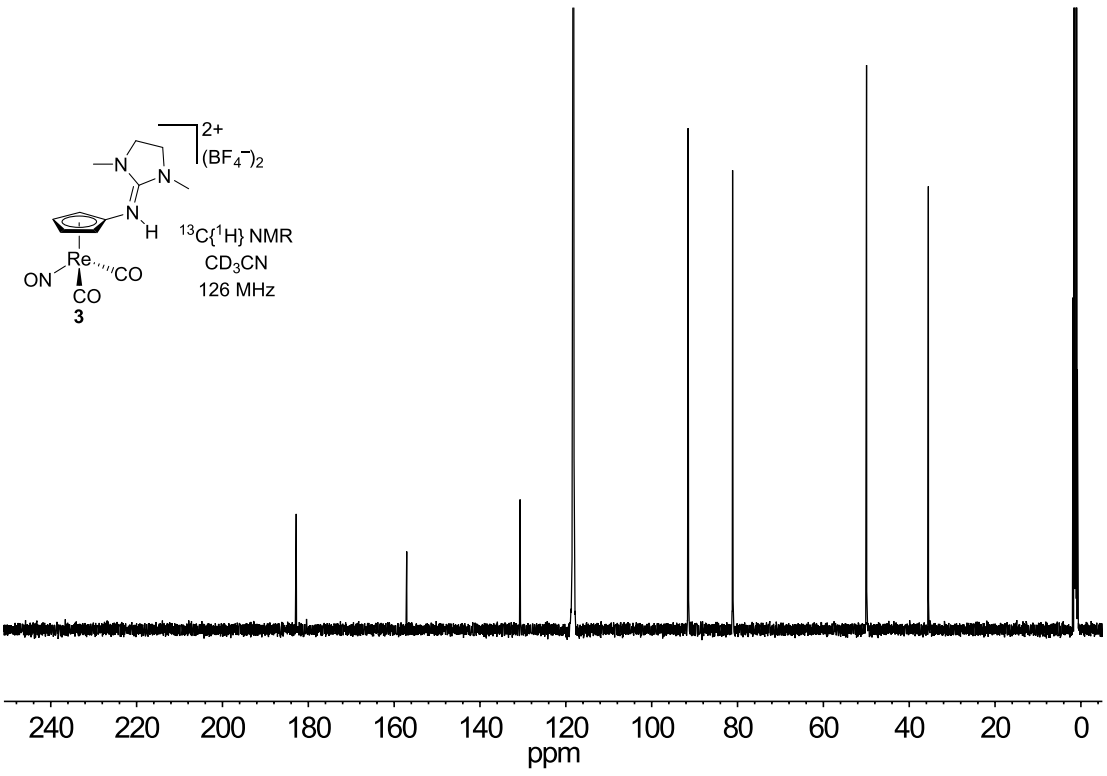

^{1}H NMR
CD_3CN
300 MHz
1
1.15
1.01
4.00
5.20
10 9 8 7 6 5 4 3 2 1 0
ppm

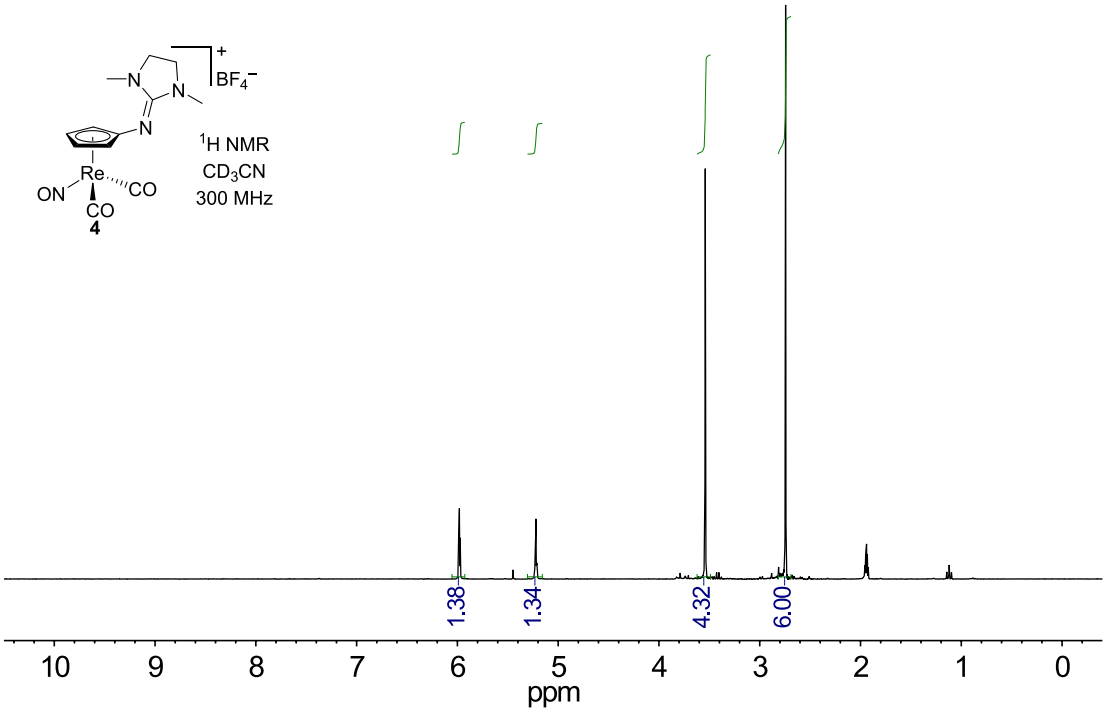

$^{13}C\{^1H\}$ NMR
CD_2Cl_2
126 MHz
1
240 220 200 180 160 140 120 100 80 60 40 20 0
ppm

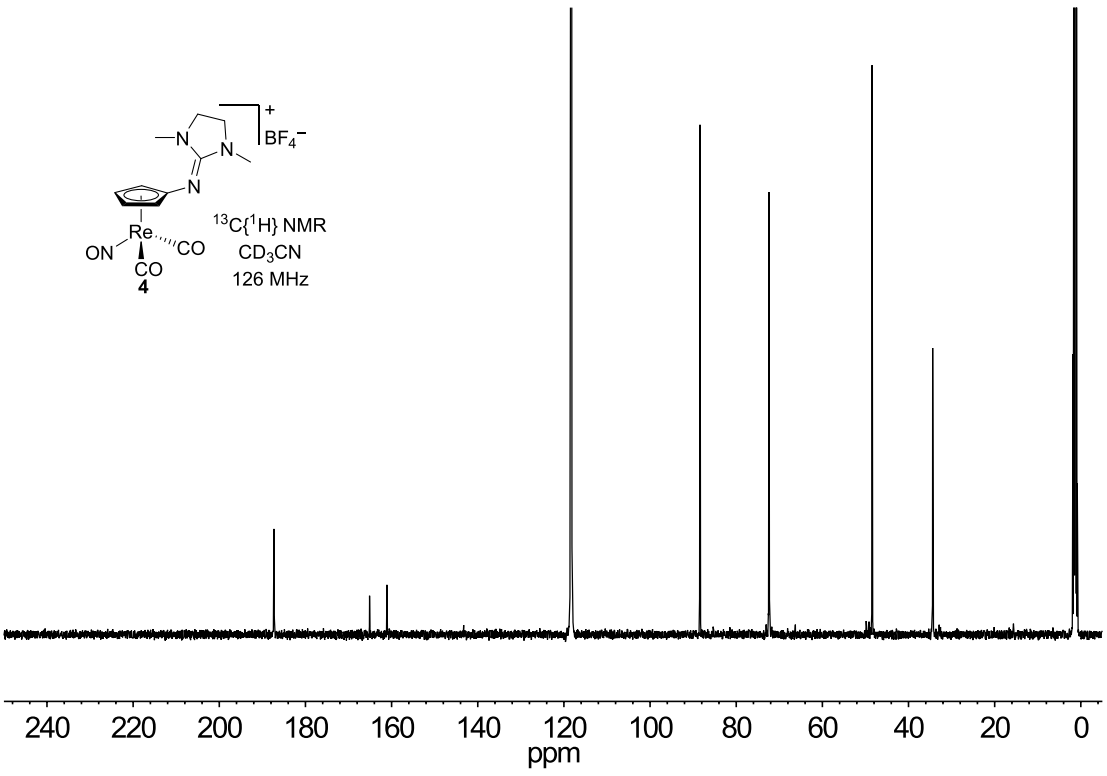

BF4−
1H NMR
CD3CN
300 MHz
2
0.77
1.25
1.25
4.00
5.39
10 9 8 7 6 5 4 3 2 1 0
ppm

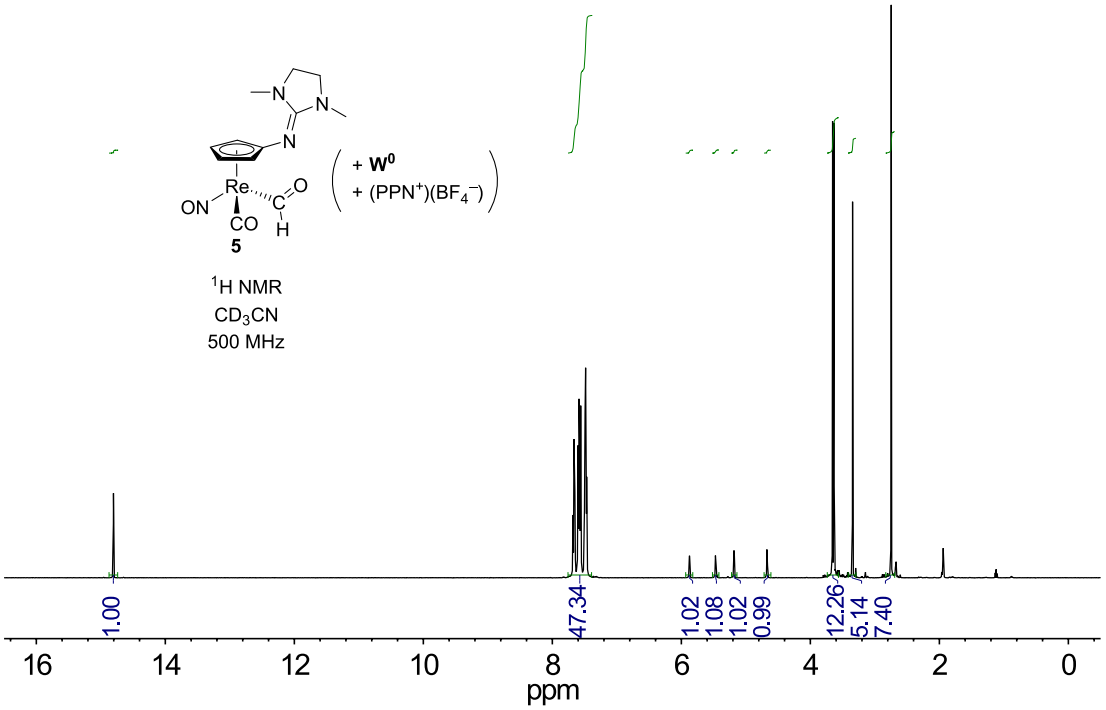

BF4−
13C{1H} NMR
CD3CN
126 MHz
2
240 220 200 180 160 140 120 100 80 60 40 20 0
ppm

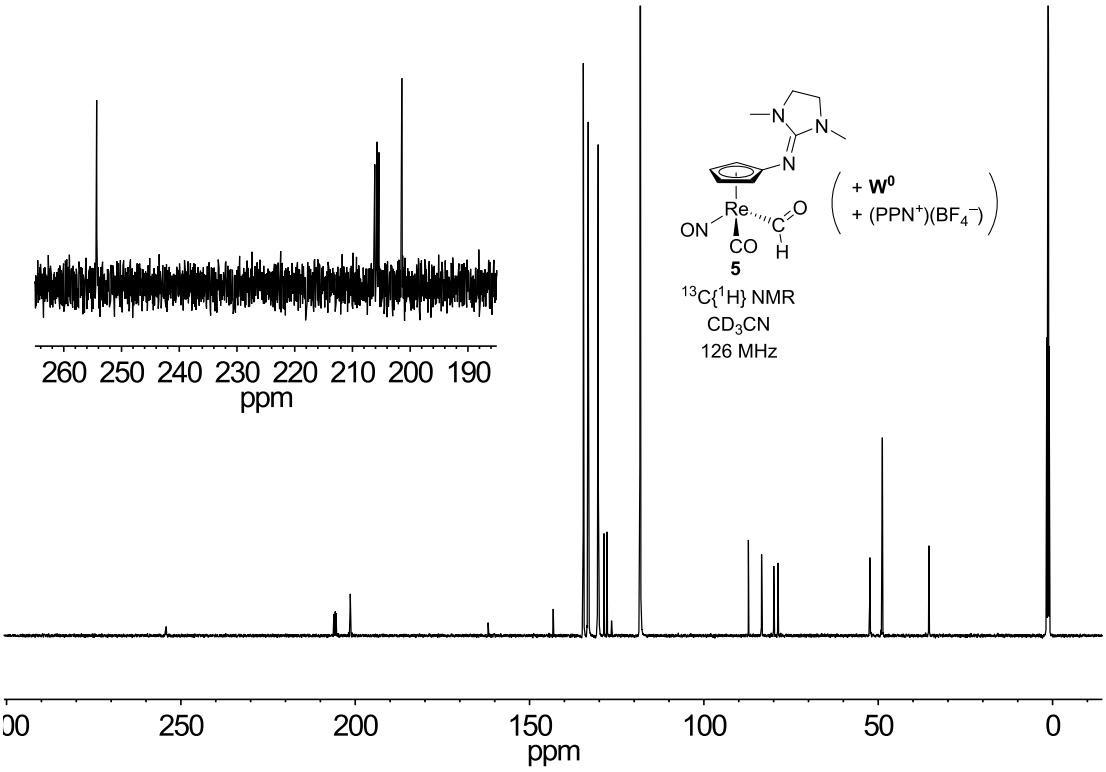

2+
(BF4−)2
1H NMR
CD3CN
300 MHz
3
0.93
3.10
4.40
6.00
10
9
8
7
6
5
4
3
2
1
0
ppm

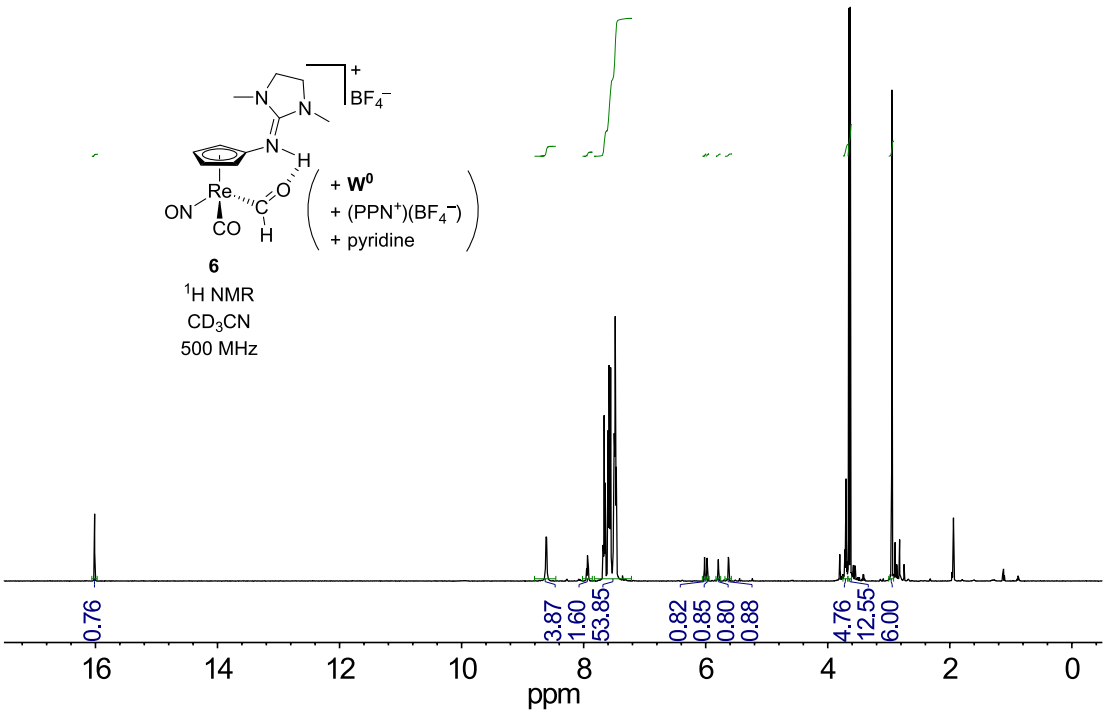

2+
(BF4−)2
13C{1H} NMR
CD3CN
126 MHz
3
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

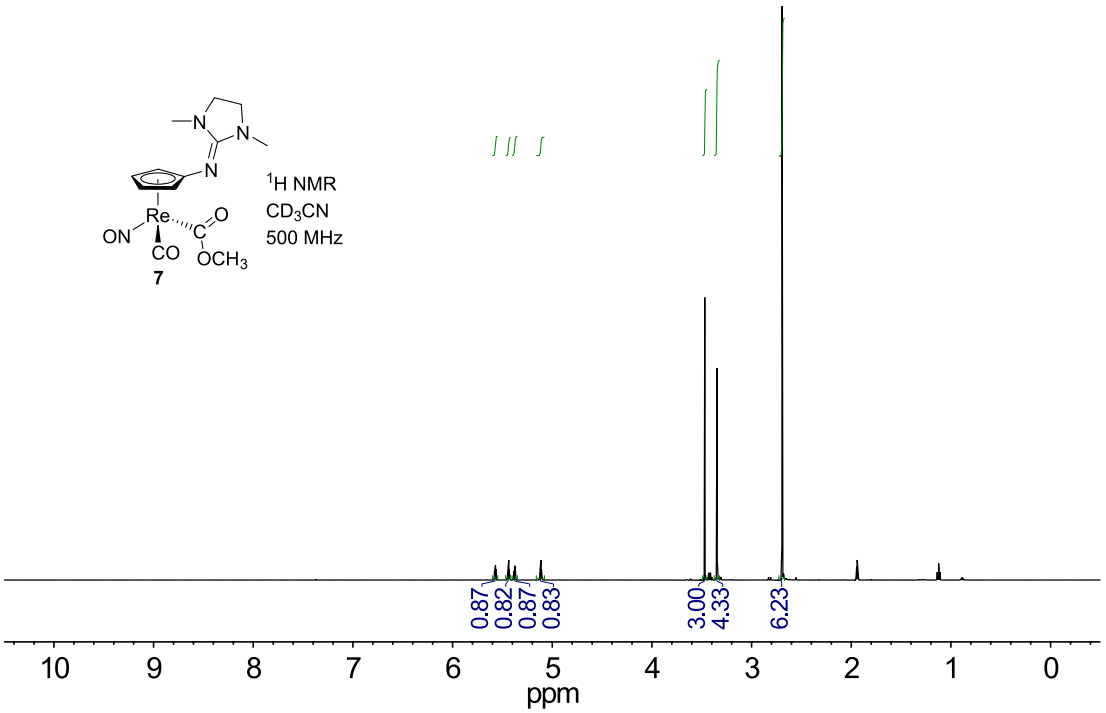

BF4−
1H NMR
CD3CN
300 MHz
4
1.38
1.34
4.32
6.00
10 9 8 7 6 5 4 3 2 1 0
ppm

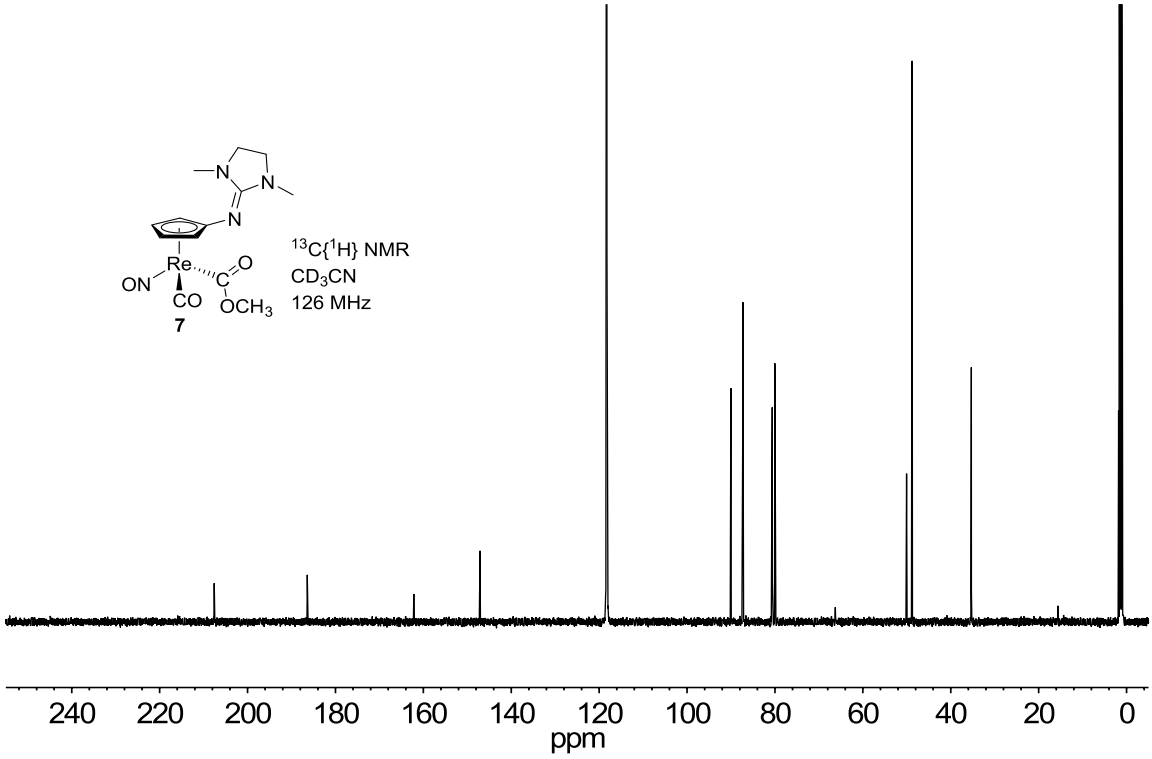

BF4−
13C{1H} NMR
CD3CN
126 MHz
4
240 220 200 180 160 140 120 100 80 60 40 20 0
ppm

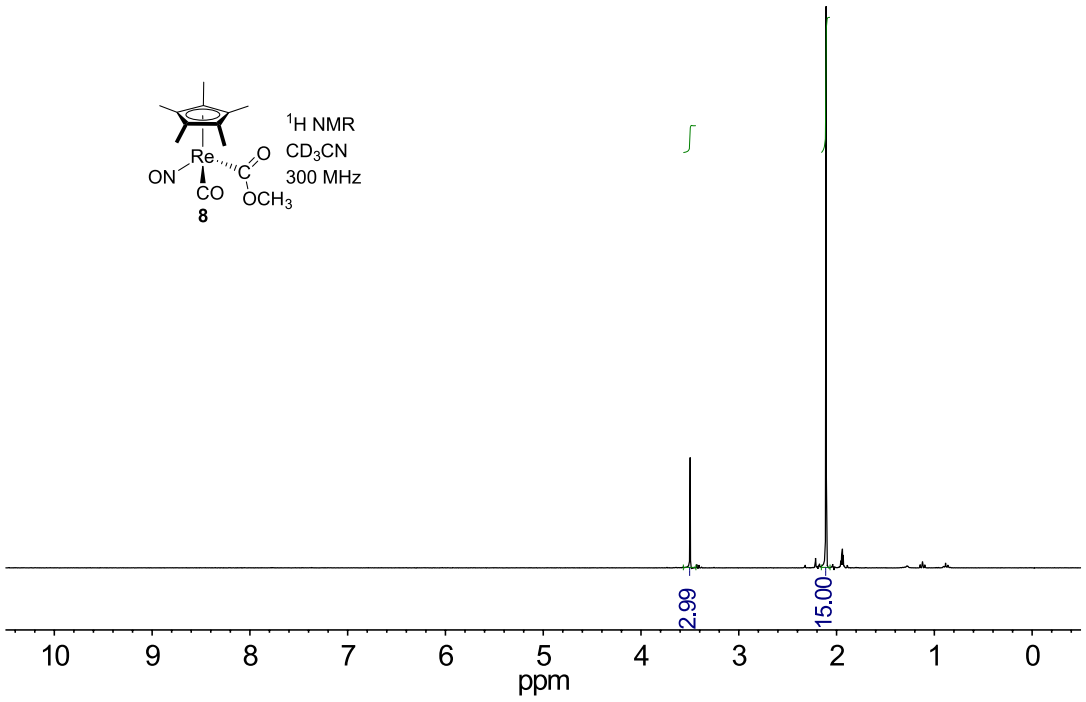

+ W0
+ (PPN+)(BF4−)
5
1H NMR
CD3CN
500 MHz
1.00
47.34
1.02
1.08
1.02
0.99
12.26
5.14
7.40
16
14
12
10
8
6
4
2
0
ppm

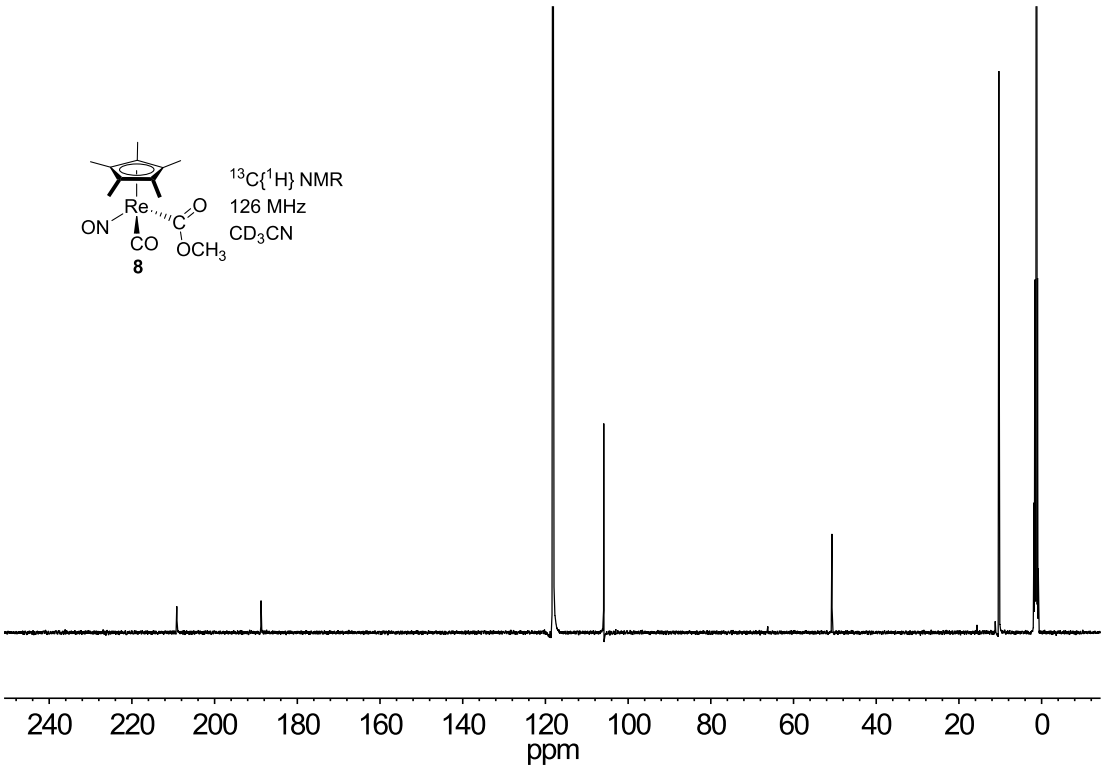

260 250 240 230 220 210 200 190
ppm
+ W0
+ (PPN+)(BF4−)
5
13C{1H} NMR
CD3CN
126 MHz
250
200
150
100
50
0
ppm

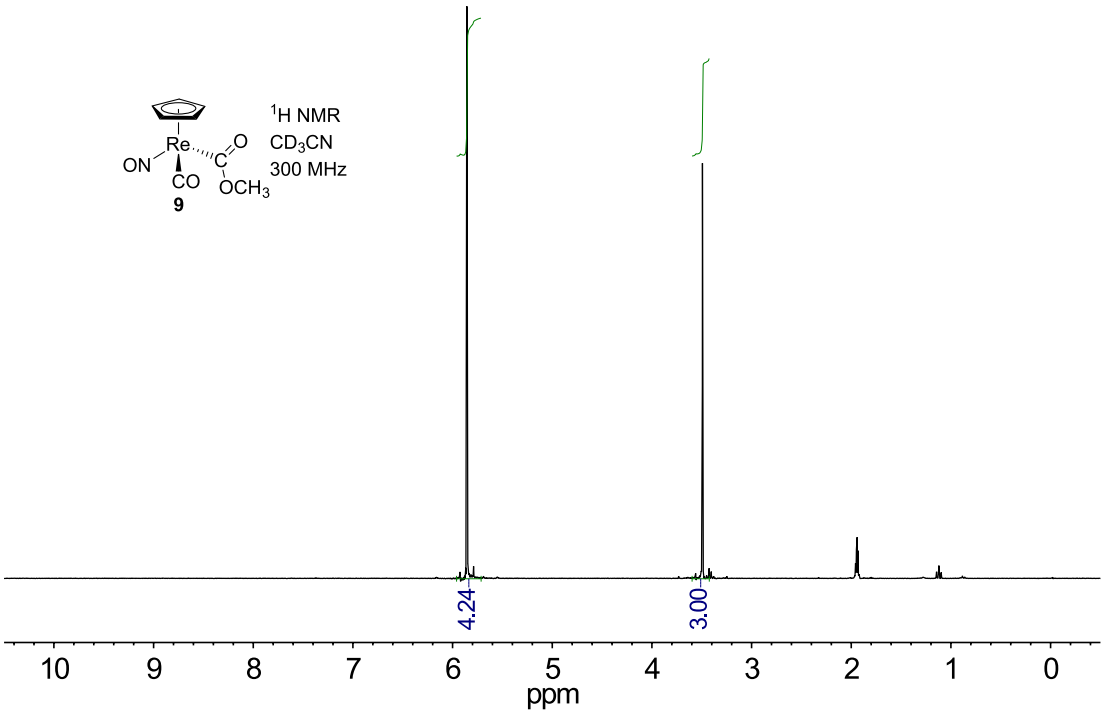

+ W⁰
+ (PPN⁺)(BF₄⁻)
+ pyridine
6
¹H NMR
CD₃CN
500 MHz
0.76
3.87
1.60
53.85
0.82
0.85
0.80
0.88
4.76
12.55
6.00
16
14
12
10
8
6
4
2
0
ppm

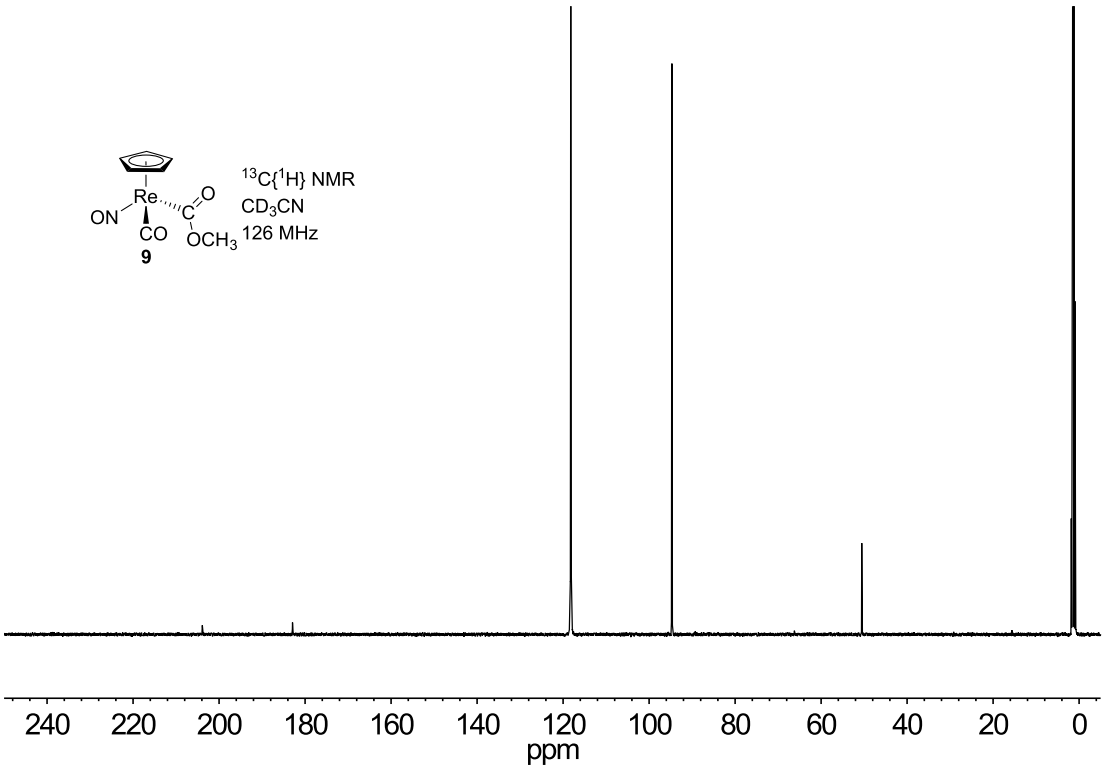

¹H NMR
CD₃CN
500 MHz
7
0.87
0.82
0.87
0.83
3.00
4.33
6.23
10
9
8
7
6
5
4
3
2
1
0
ppm

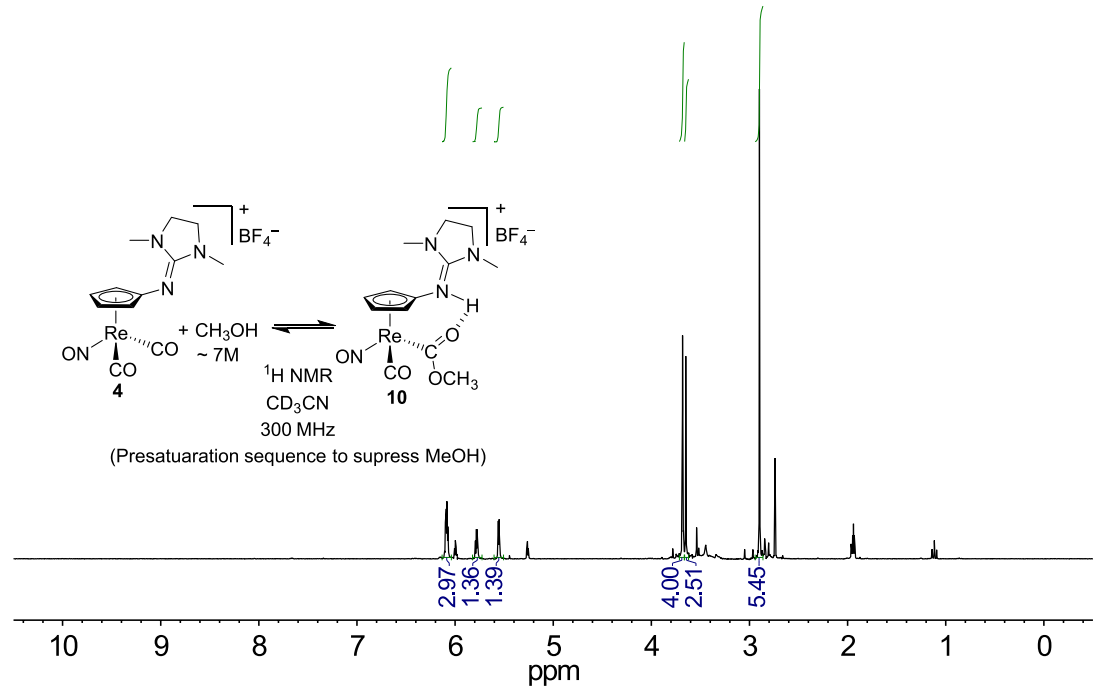

$^{13}C\{^{1}H\}$ NMR
CD_3CN
126 MHz
7
240 220 200 180 160 140 120 100 80 60 40 20 0
ppm

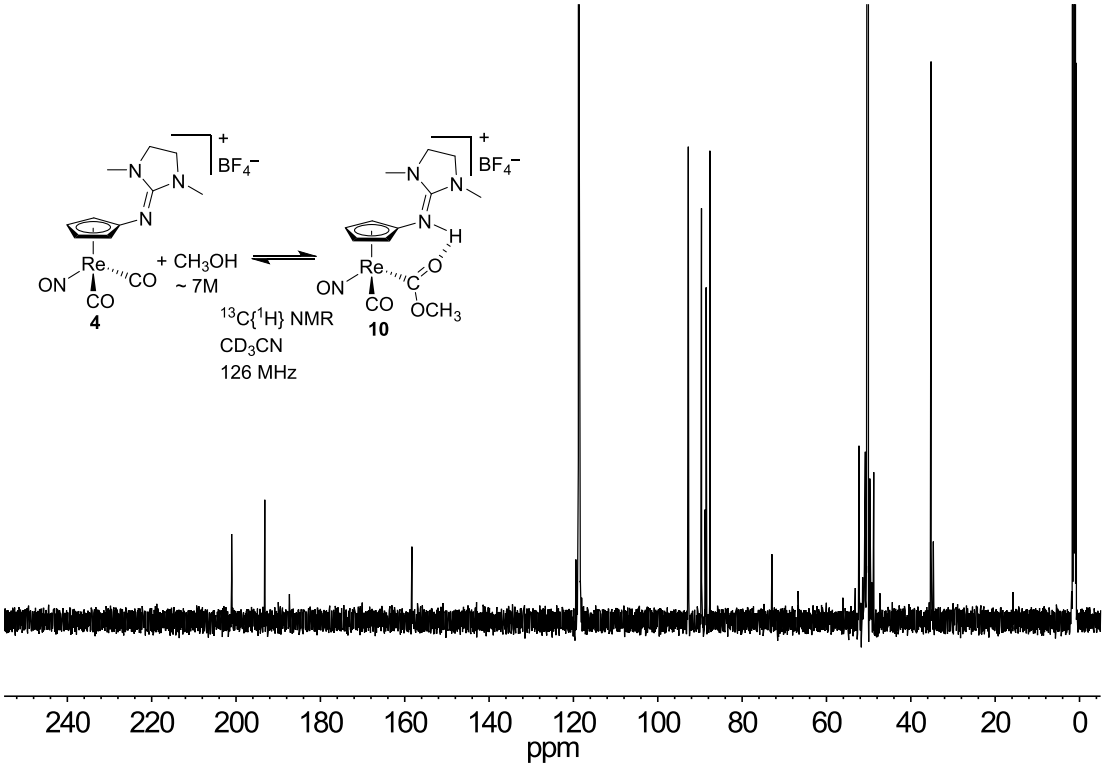

^{1}H NMR
CD_3CN
300 MHz
8
2.99
15.00
10 9 8 7 6 5 4 3 2 1 0
ppm


Re
ON
CO
C
O
OCH3
8
13C{1H} NMR
126 MHz
CD3CN
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Re
ON
CO
C
O
OCH3
9
1H NMR
CD3CN
300 MHz
4.24
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm


$^{13}C\{^1H\}$ NMR
CD_3CN
126 MHz
9
240 220 200 180 160 140 120 100 80 60 40 20 0
ppm


+ CH_3OH
~ 7M
4
10
^1H NMR
CD_3CN
300 MHz
(Presatuaration sequence to supress MeOH)
2.97
1.36
1.39
4.00
2.51
5.45
10 9 8 7 6 5 4 3 2 1 0
ppm


+ CH3OH
~ 7M
13C{1H} NMR
CD3CN
126 MHz
4
10
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm