Functionalization of Planar Chiral Fused Arene Ruthenium Complexes: Synthesis, X-ray Structures and Spectroscopic Characterization of Monodentate Triarylposphines

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CONTENTS:

1. Crystallography

The structures of **11b** and **12b** are of low quality due to a strong disorder observed for the counter-ion, the Cp* ring, and the solvent molecules. For both compounds, the Cp* and the PF_6 anion were modeled using two molecules. Distances and angles were restrained to ideal values. Restrains were also applied on anisotropic displacement parameters. Solvent molecules were taken into account using the bypass/squeeze method[1] in the program platon.[2] For **12b**, two voids were located, each containing 43 electrons, which were attributed to two CH_2Cl_2 molecules. For **11b**, four voids were located, each containing 57 electrons, which were attributed to four CH_2Cl_2 molecules. The attribution of CH_2Cl_2 as solvent molecule was straightforward for **11b**, for which the Fourier difference map revealed disordered CH_2Cl_2 molecules that could be identified (but a model using two disordered molecules per void, each with an occupancy of 0.5 was not good enough to model the disorder and hence squeeze was preferred to a disordered model of the solvent). For **12b**, the density in the Fourier difference map was much more diffuse and therefore the solvent molecule could not be attributed to CH_2Cl_2 or hexane (both have a number of electrons compatible with the one found by squeeze). The attribution of the nature of the solvent molecule was based on the elemental analysis. Besides a reasonable fit to the data, reflected in the low R values obtained at the end of the refinement, these disordered models are of lower quality. However, the anisotropic displacement parameters are reasonable in the relevant region of the structure. The phenyl substituents on the phosphine showed elongated anisotropic parameters which are compatible with a pendulum movement with center C13 and axis C13-C16 (Figure S1).

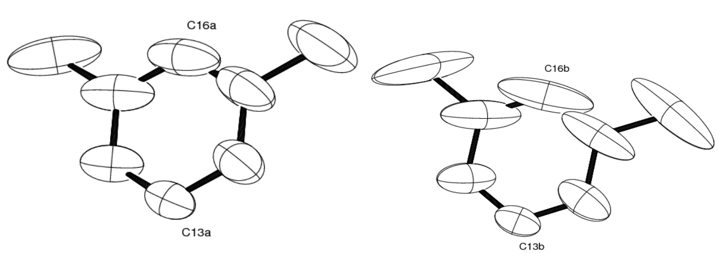
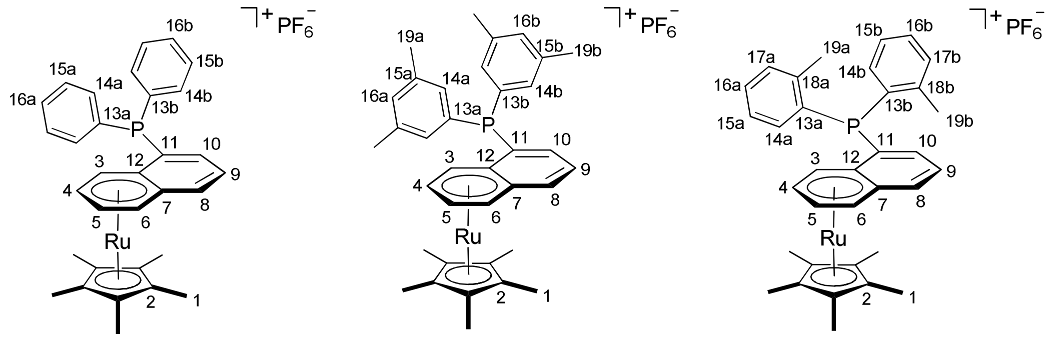


Figure S1. Anisotropic displacement parameters for the phosphine substituents in **11b**.

2. NMR Tables

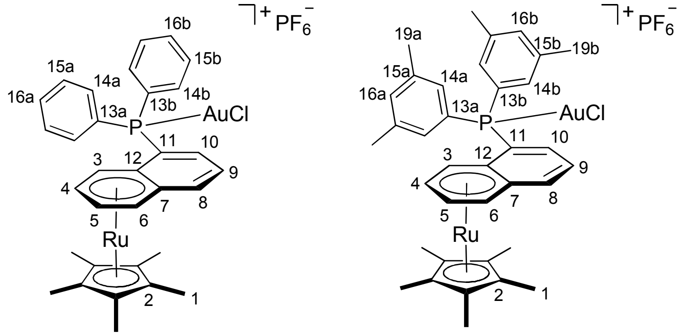
Table S1. ^{13}C NMR Spectroscopic Data for Phosphine Complexes 10b-12b[a]



	10b		11b		12b	
Position	δ_C[b]	multiplicity[c]	δ_C[b]	multiplicity[c]	δ_C[b]	multiplicity[c]
1	10.0	d, J =1.9 Hz	10.0	d, J = 2.0 Hz	10.1	d, J = 1.1 Hz
2	94.9	s	94.7	s	95.0	s
3	83.5	d, J = 26.3Hz	83.6	d, J = 26.0 Hz	83.8	d, J = 23.3 Hz
4	88.0	d, J = 1.6 Hz	87.0	d, J = 1.5 Hz	87.8	d, J = 1.4 Hz
5	88.8	d, J = 1.2 Hz	88.6	d, J = 1.3 Hz	88.7	d, J < 1.0 Hz
6	86.1	d, J = 1.2 Hz	86.0	d, J = 1.4 Hz	85.7	d, J < 1.0 Hz
7	97.2	d, J = 3.2 Hz	97.3	d, J = 3.1 Hz	96.9	d, J = 2.7 Hz
8	128.7	s	128.3	s	128.4	d, J = 1.4 Hz
9	130.6	s	130.7	s	130.8	s
10	136.2	d, J = 1.3 Hz	136.1	d, J = 1.5 Hz	136.3	d, J = 3.5 Hz
11	137.7	d, J = 20.3 Hz	138.4	d, J = 20.7 Hz	136.8	d, J = 21.0 Hz
12	98.8	d, J = 20.8 Hz	98.8	d, J = 20.6 Hz	100.0	d, J = 19.4 Hz
13a	133.8	d, J = 7.0 Hz	133.6	d, J = 6.2 Hz	142.9	d, J = 28.2 Hz
13b	133.3	d, J = 8.5 Hz	133.0	d, J = 7.9 Hz	144.3	d, J = 28.5 Hz
14a	134.5	d, J = 20.6 Hz	132.7	d, J = 21.2 Hz	131.2	d, J = 5.5 Hz
15a	129.5	d, J = 7.9 Hz	139.3	d, J = 8.4 Hz	130.1	s
14b	135.1	d, J = 20.7 Hz	132.1	d, J = 20.9 Hz	130.9	d, J = 5.9 Hz
15b	129.7	d, J = 7.8 Hz	139.1	d, J = 8.4 Hz	130.8	s
16a	130.4	s	132.3	s	126.7	s
16b	130.6	s	132.0	s	127.5	d, J = 1.4 Hz
17a	--	--	--	--	134.0	s
17b	--	--	--	--	135.2	s
18a	--	--	--	--	133.5	d, J = 6.8 Hz
18b	--	--	--	--	130.9	d, J = 8.0 Hz
19a	--	--	21.4	s	21.3	d, J = 22.9 Hz
19b	--	--	21.3	s	22.0	d, J = 22.0 Hz

[a] Spectra recorded in CD_2Cl_2 at 125 MHz. [b] δ_C in ppm. [c] Coupling constants in Hertz (Hz).

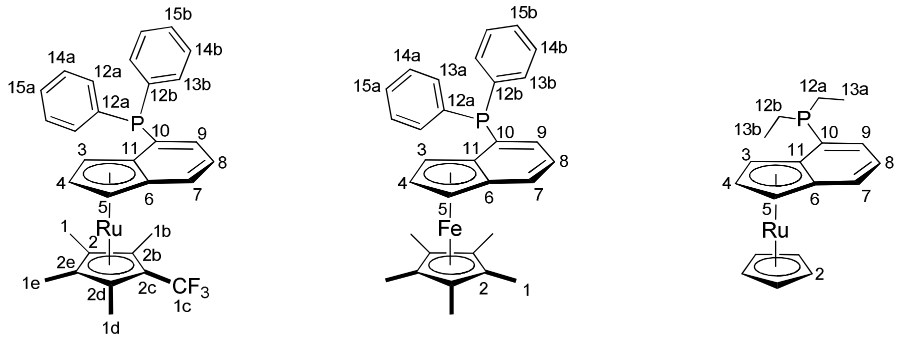
Table S2. ^{13}C NMR Spectroscopic Data for Gold(I) Complexes 13b and 14b[a]



Position	13b δ_C[b]	13b multiplicity[c]	14b δ_C[b]	14b multiplicity[c]
1	10.7	s	10.7	s
2	96.2	s	96.1	s
3	83.2	d, J = 14.4 Hz	83.3	d, J = 14.0 Hz
4	87.6	s	87.5	s
5	89.0	s	88.8	s
6	86.3	d, J < 1.0 Hz	86.2	s
7	95.4	d, J = 6.1 Hz	95.2	d, J = 6.0 Hz
8	134.7	d, J = 2.4 Hz	134.4	d, J = 2.8 Hz
9	129.2	d, J = 10.6 Hz	129.3	d, J = 10.7 Hz
10	140.1	d, J = 5.9 Hz	140.0	d, J = 6.0 Hz
11	126.4	d, J = 19.5 Hz	126.9	d, J = 55.8 Hz
12	99.0	d, J = 11.9 Hz	99.3	d, J = 11.7 Hz
13a	126.1	d, J = 14.3 Hz	125.9	d, J = 19.6 Hz
13b	125.7	d, J = 22.8 Hz	125.4	d, J = 15.9 Hz
14a	135.4	d, J = 14.4 Hz	132.8	d, J = 14.4 Hz
15a	135.3	d, J = 14.5 Hz	132.5	d, J = 14.5 Hz
14b	130.4	d, J = 12.4 Hz	140.5	d, J = 13.0 Hz
15b	130.2	d, J = 12.4 Hz	140.2	d, J = 13.1 Hz
16a	133.6	d, J = 2.7 Hz	135.3	d, J = 2.8 Hz
16b	133.6	d, J = 2.6 Hz	135.3	d, J = 2.5 Hz
19a	--	--	21.5	s
19b	--	--	21.4	s

[a] Spectra recorded in CD_2Cl_2 at 125 MHz. [b] δ_C in ppm. [c] Coupling constants in Hertz (Hz)

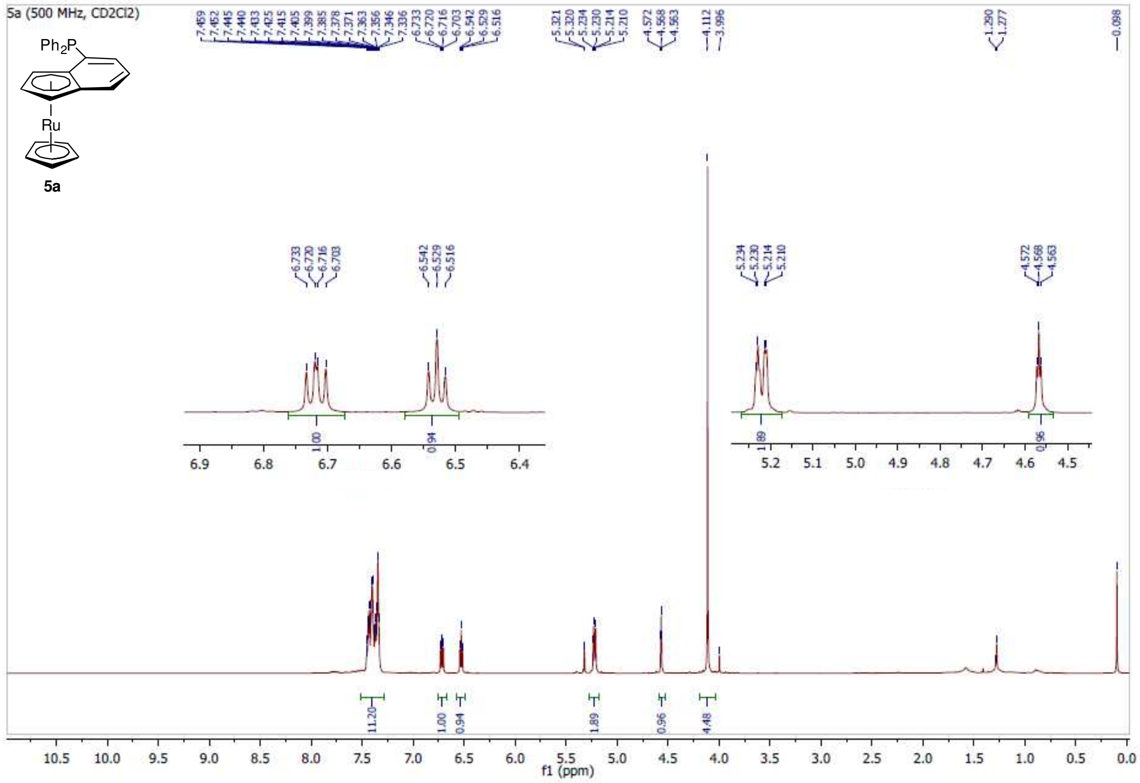
Table S3. ^{13}C NMR Spectroscopic Data for Representative Indenyl Phosphines[a]

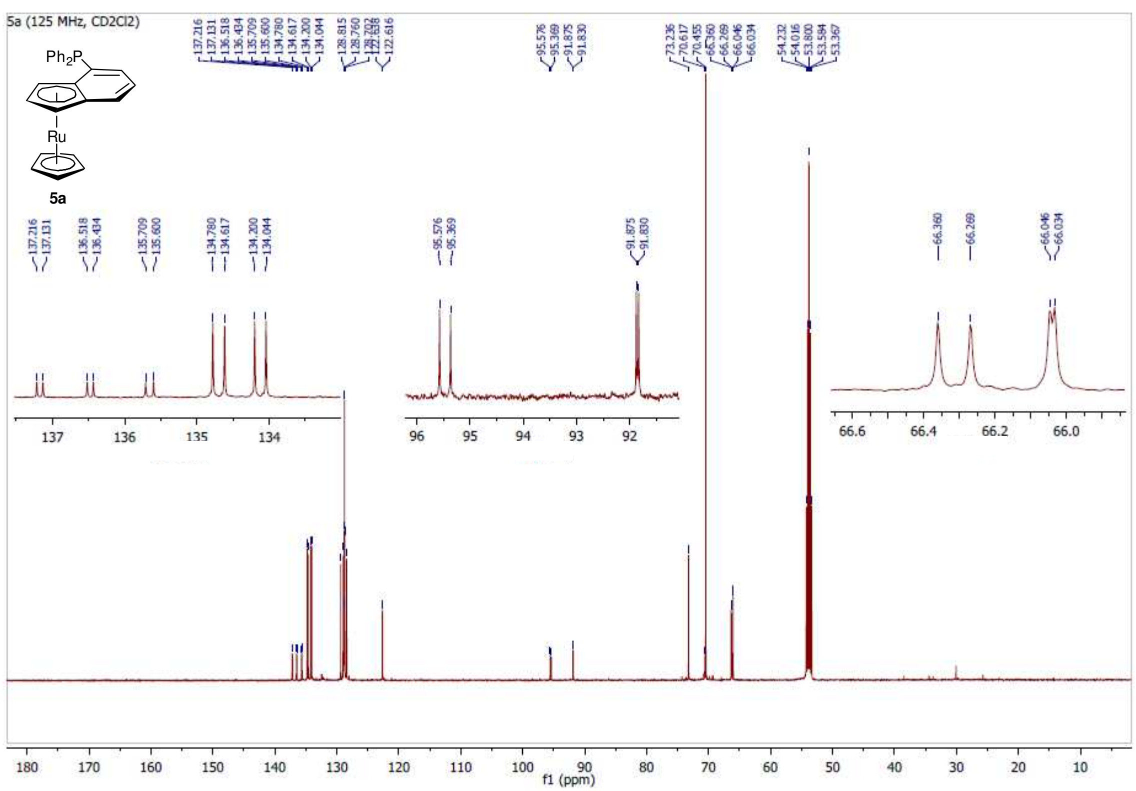


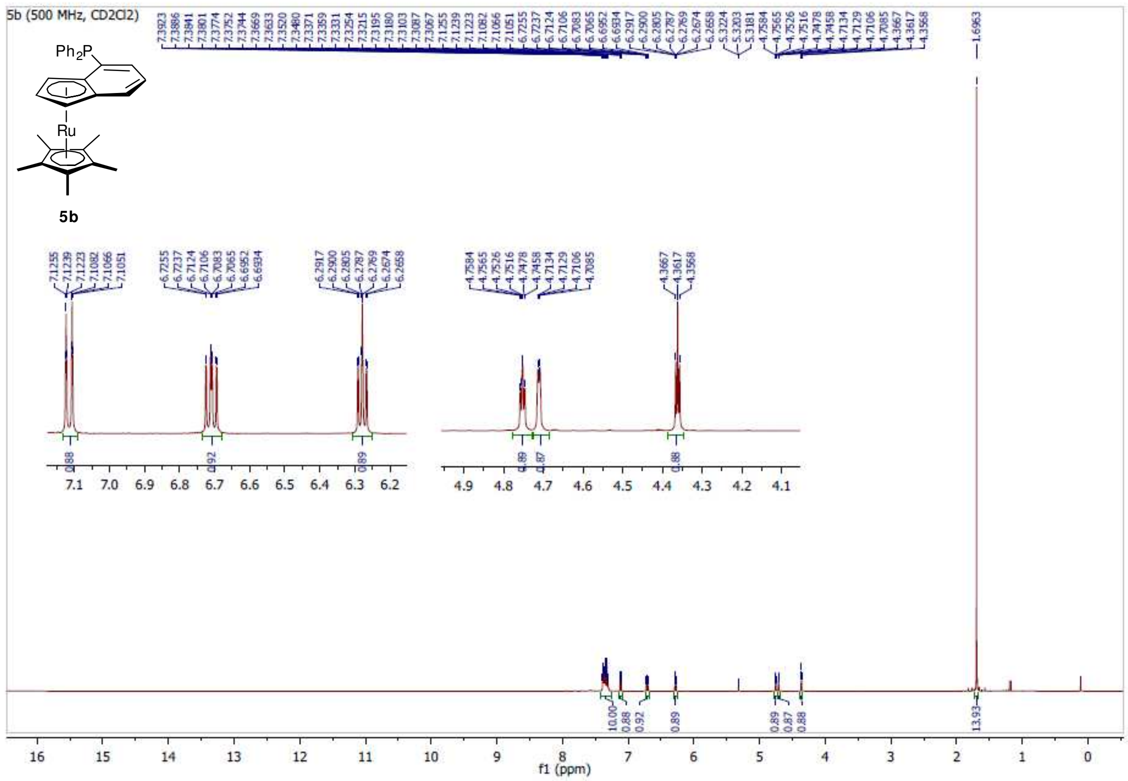
	5c		8b[d]		7a	
Position	δ_C[b]	multiplicity[c]	δ_C[b]	multiplicity[c]	δ_C[b]	multiplicity[c]
1	9.7	d, J =3.0Hz	10.4	d, J =2.5Hz	--	--
2	85.7	s	78.0	s	70.4	s
2b	81.8	q, $J_{(C,F)}$ = 1.4 Hz	--	--	--	--
1b	10.5	q, $J_{(C,F)}$ = 1.8 Hz	--	--	--	--
2c	76.2	q, $J_{(C,F)}$ = 35.8 Hz	--	--	--	--
1c	128.6	q, $J_{(C,F)}$ = 270 Hz	--	--	--	--
2d	82.1	q, $J_{(C,F)}$ = 1.4 Hz	--	--	--	--
1d	11.7	pent, $J \approx 2.0$ Hz	--	--	--	--
2e	86.0	s	--	--	--	--
1e	10.4	d, J = 2.7 Hz	--	--	--	--
3	69.8	d, J = 11.0 Hz	66.7	d, J = 10.4 Hz	66.1	d, J = 9.6 Hz
4	77.7	s	76.8	s	73.2	s
5	69.2	d, J = 1.9 Hz	66.3	d, J = 1.9 Hz	66.0	d, overlap
6	92.8	d, J = 6.0 Hz	88.2	d, J = 6.0 Hz	92.0	d, J = 4.6 Hz
7	126.2	s	128.8	s	127.6	s
8	122.2	s	122.2	s	122.7	s
9	127.1	s	127.4	s	126.0	s
10	134.8	d, J = 14.0 Hz	137.2	d, J = 13.7 Hz	136.4	d, J = 19.2 Hz
11	95.6	d, J = 24.3 Hz	91.2	d, J = 23.6 Hz	95.9	d, J = 21.8 Hz
12a	136.9	d, J = 11.0 Hz	137.0	d, J = 10.9 Hz	18.6	d, J = 11.7 Hz
12b	136.2	d, J = 11.7 Hz	137.0	d, J = 12.0 Hz	18.1	d, J = 11.2 Hz
13a	134.9	d, J = 20.2 Hz	135.2	d, J = 20.2 Hz	10.4	d, J = 15.0 Hz
13b	134.5	d, J = 20.3 Hz	134.4	d, J = 20.1 Hz	10.1	d, J = 12.2 Hz
14a	128.9	d, J = 7.3 Hz	128.8	d, J = 7.3 Hz	--	--
14b	128.9	d, J = 7.3 Hz	128.7	d, J = 7.1 Hz	--	--
15a	129.4	s	129.2	s	--	--
15b	129.2	s	128.8	s	--	--

[a] Spectra recorded in CD_2Cl_2 at 125 MHz. [b] δ_C in ppm. [c] Coupling constants in Hertz (Hz).
[d] Spectrum recorded in C_6D_6 at at 125 MHz.

3. NMR Spectra



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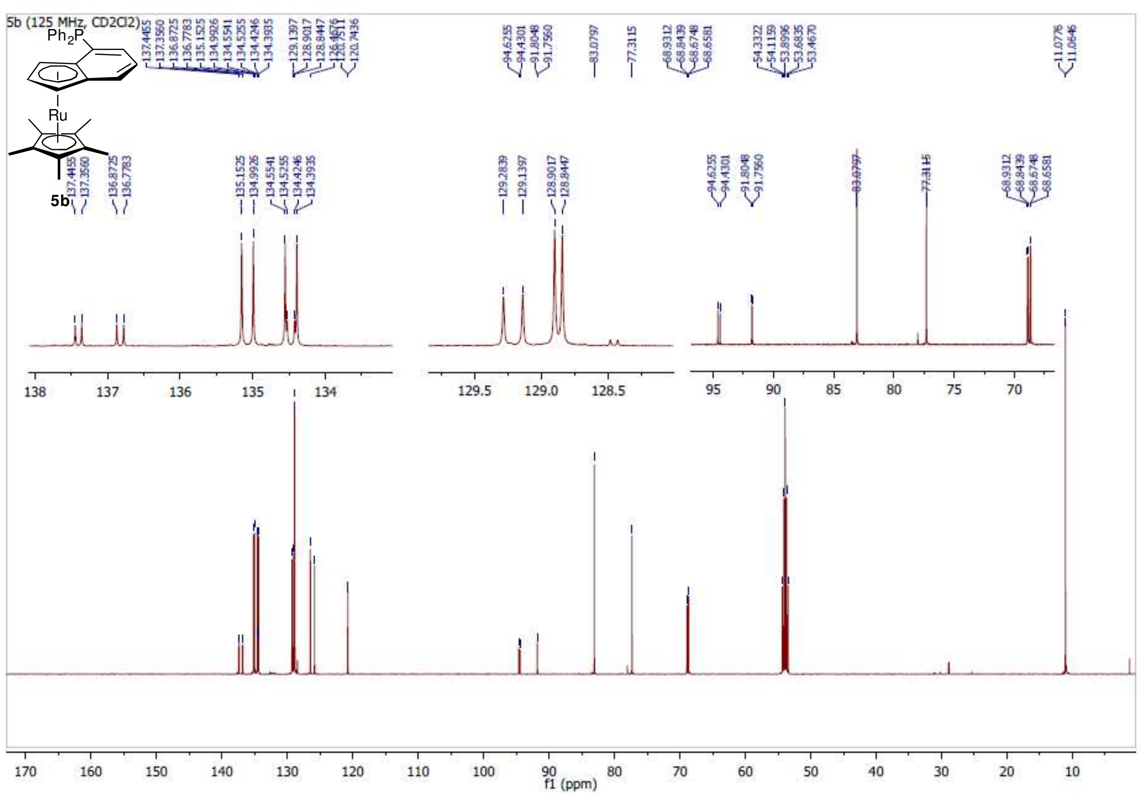
Ru
5b
f1 (ppm)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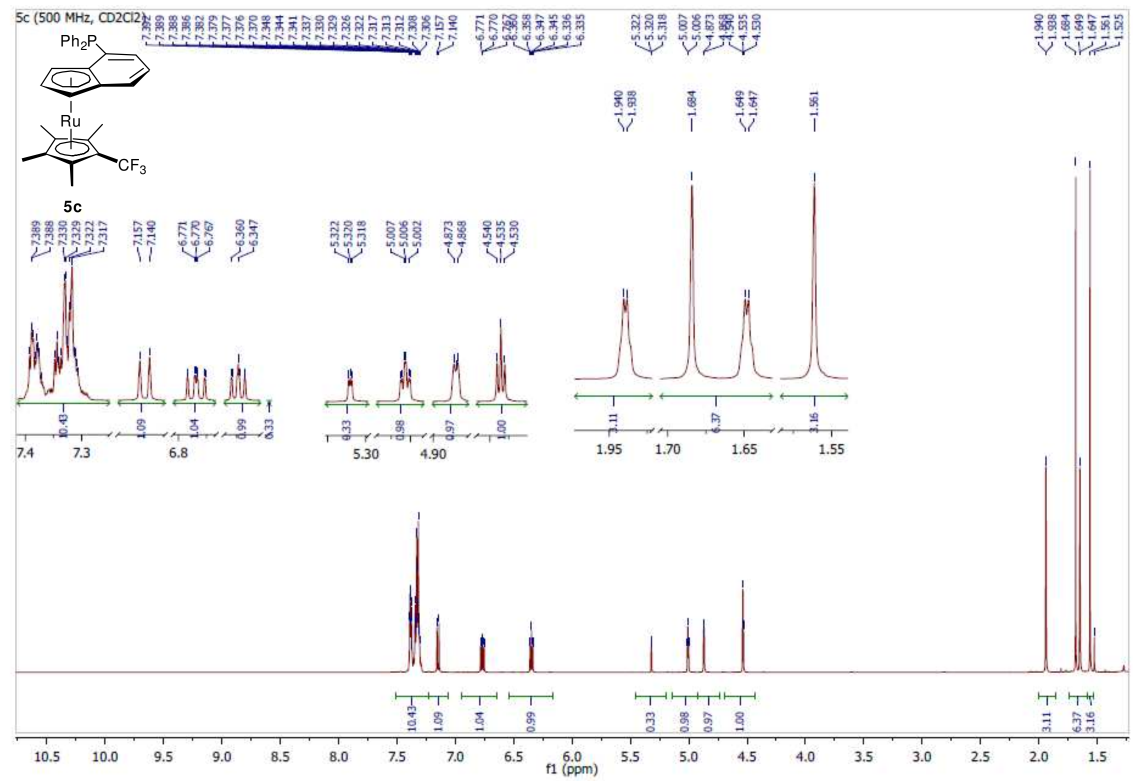
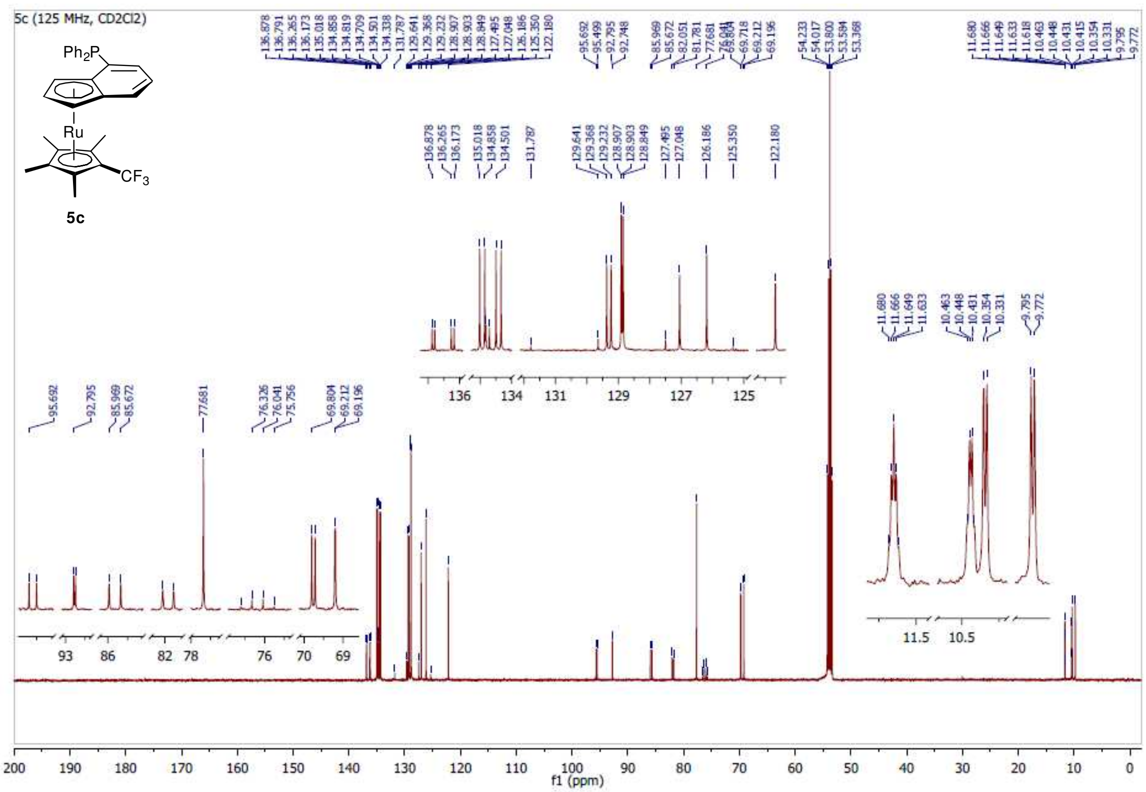
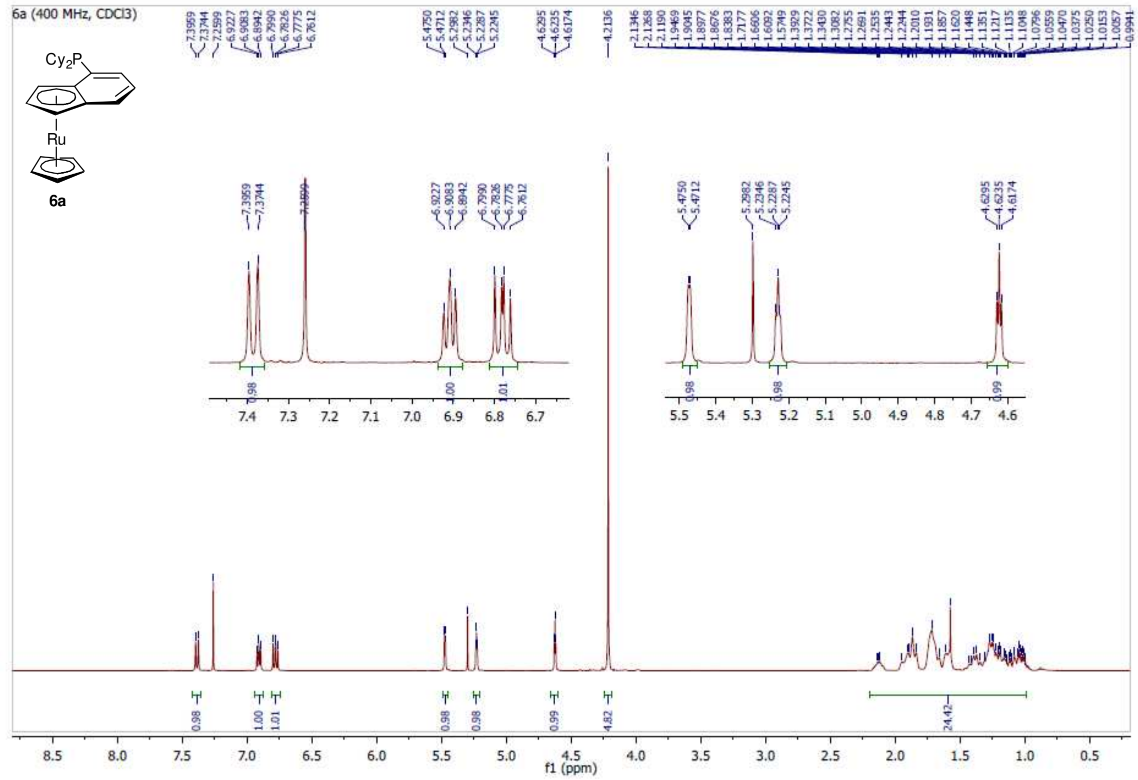
f1 (ppm)



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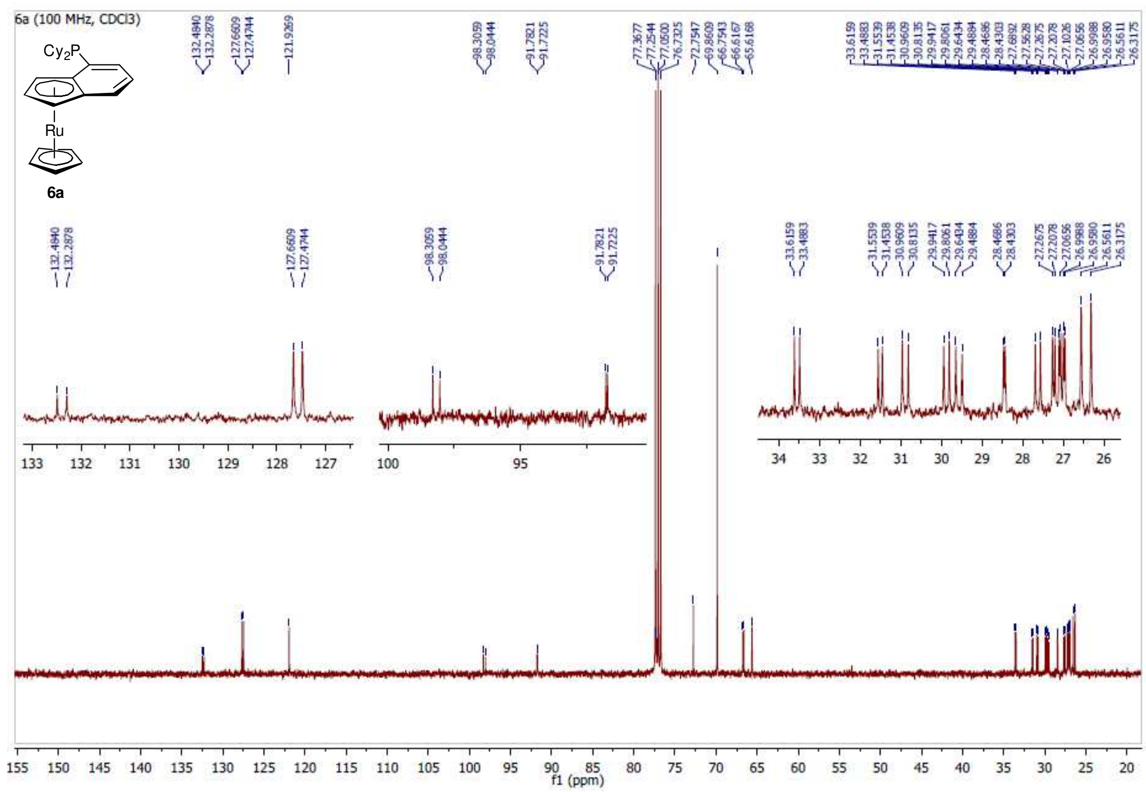
Ru
6a
f1 (ppm)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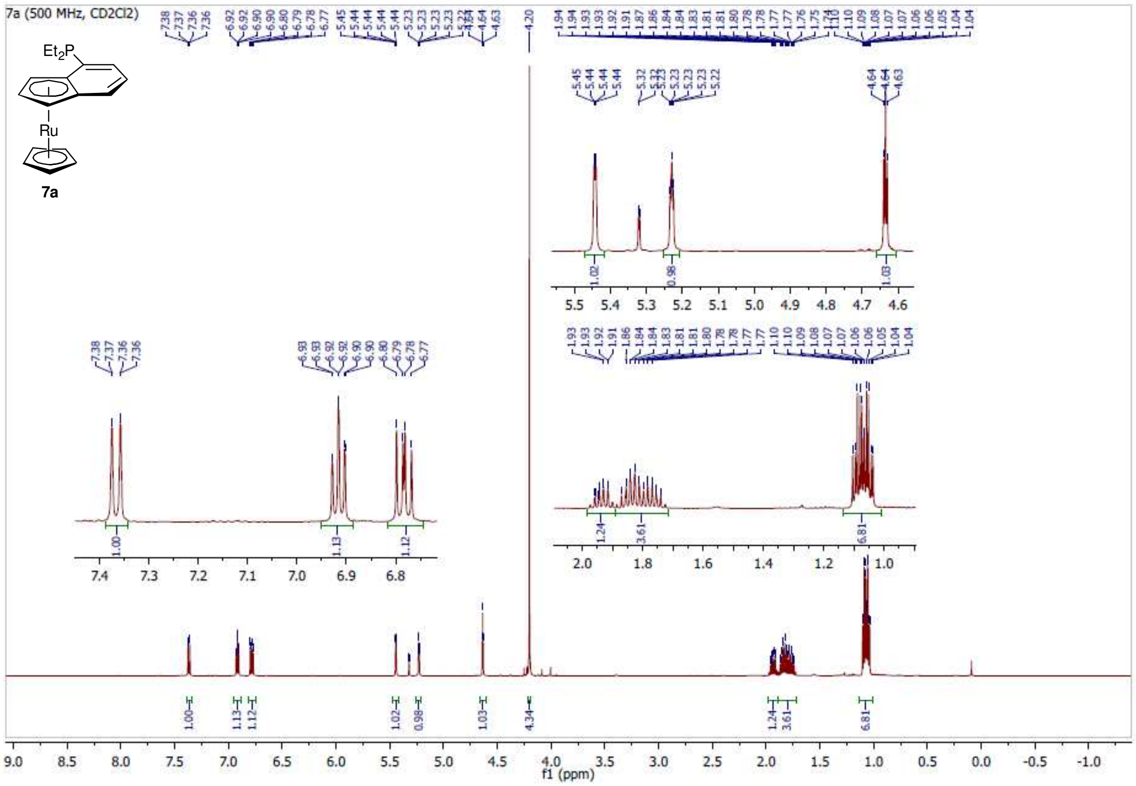
Ru
6a
f1 (ppm)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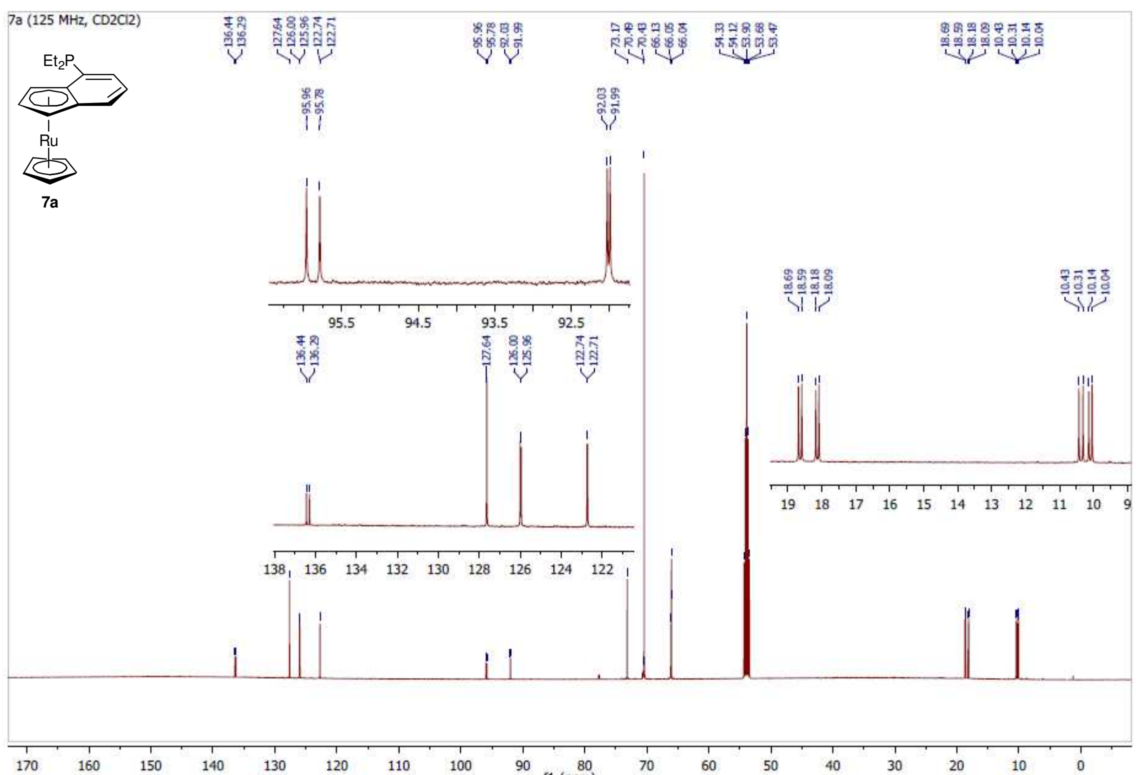
Et2P
Ru
7a
f1 (ppm)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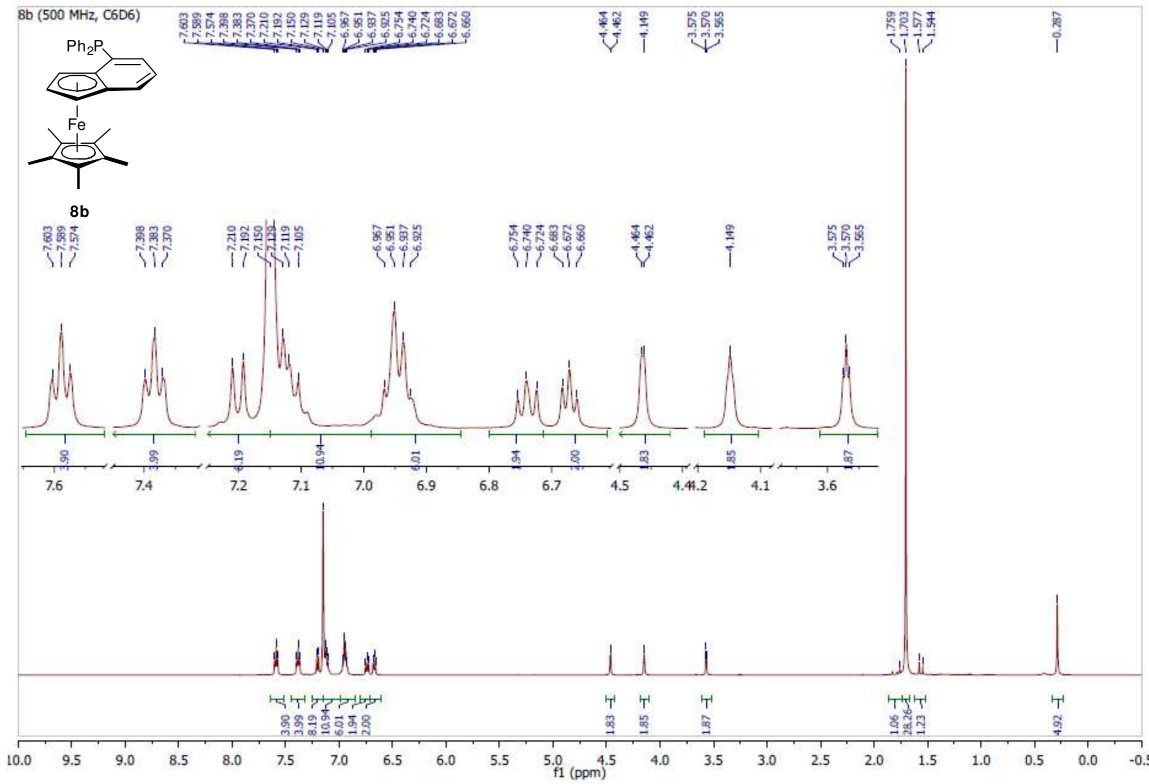
Et2P
Ru
7a
f1 (ppm)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Ph2P
Fe
8b
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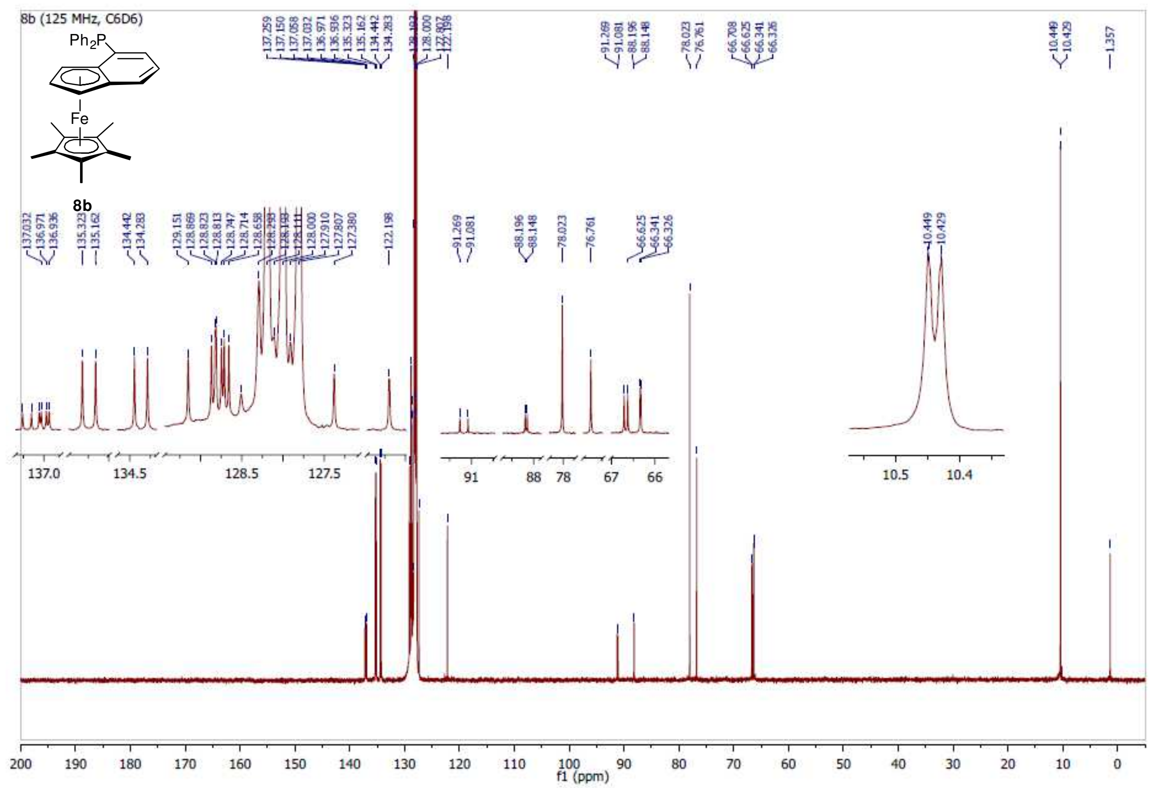
4.464 4.462
4.149
3.575 3.570 3.565
1.759 1.703 1.577 1.544
0.287
3.90 3.99 8.19 10.94 6.01 1.94 2.00 1.83 1.85 1.87
1.06 28.26 1.23 4.92
f1 (ppm)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Ph2P
Fe
8b
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128.000 127.807 122.198
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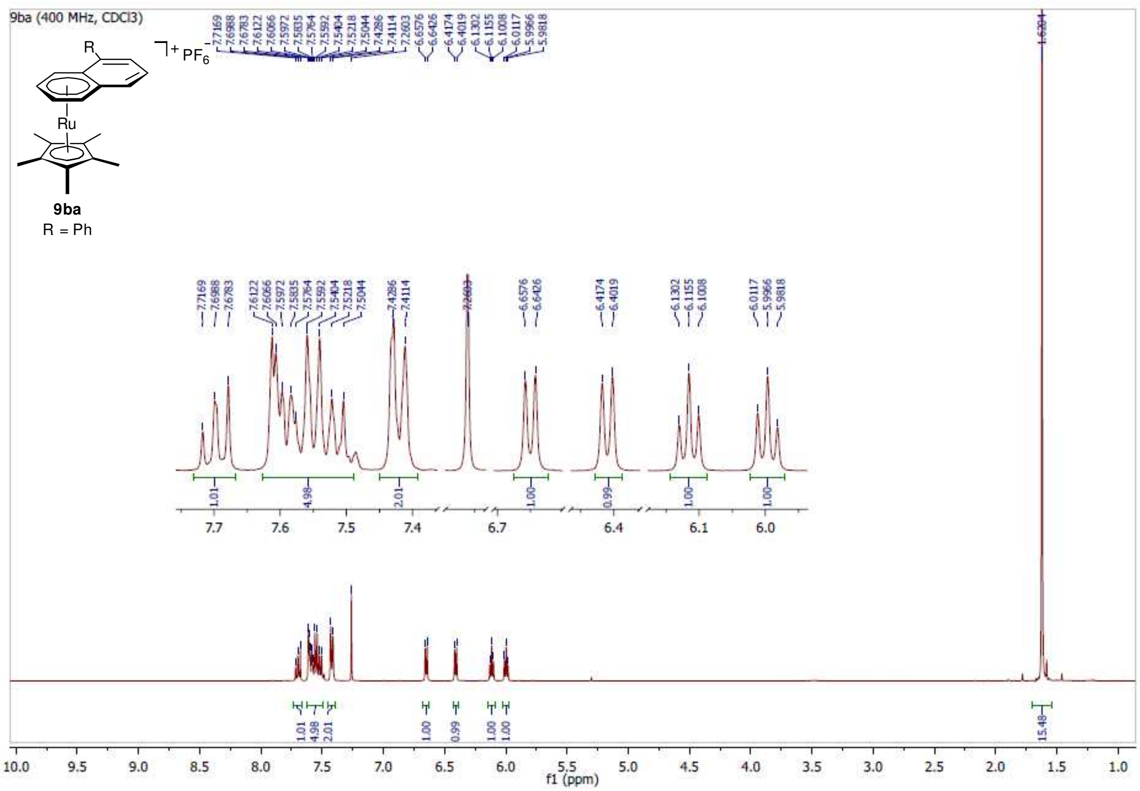
10.449 10.429
1.357
f1 (ppm)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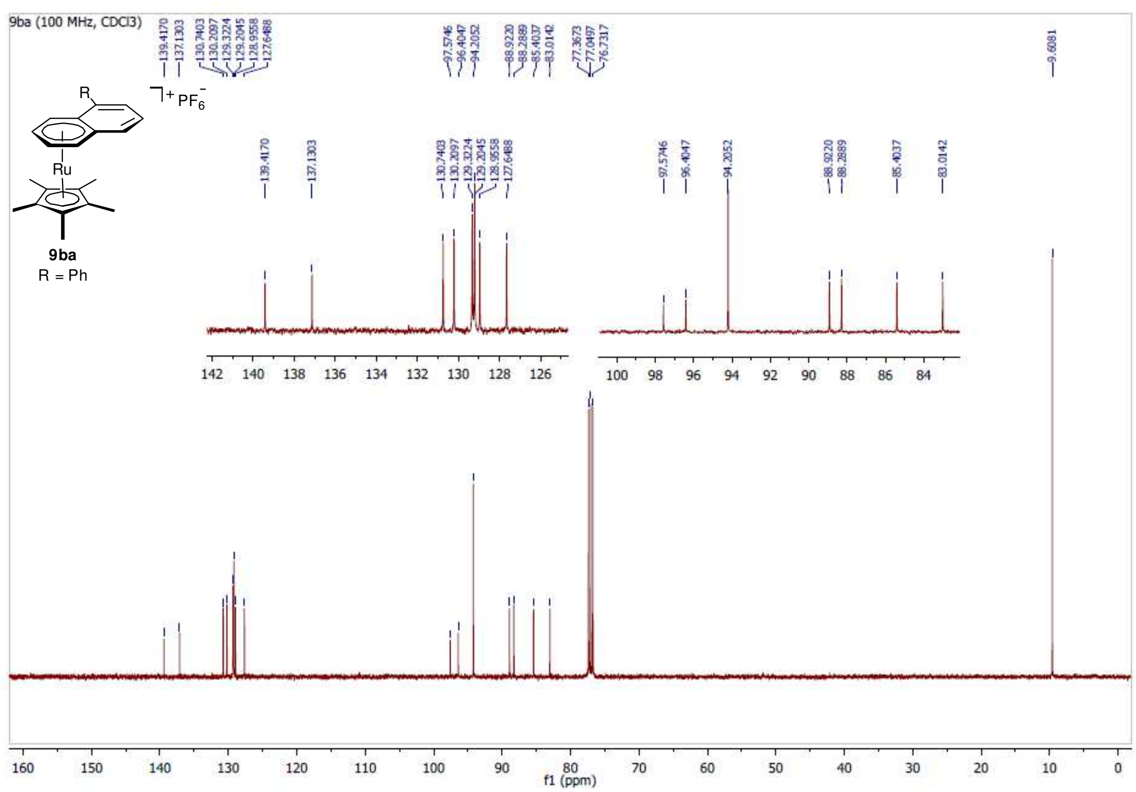
f1 (ppm)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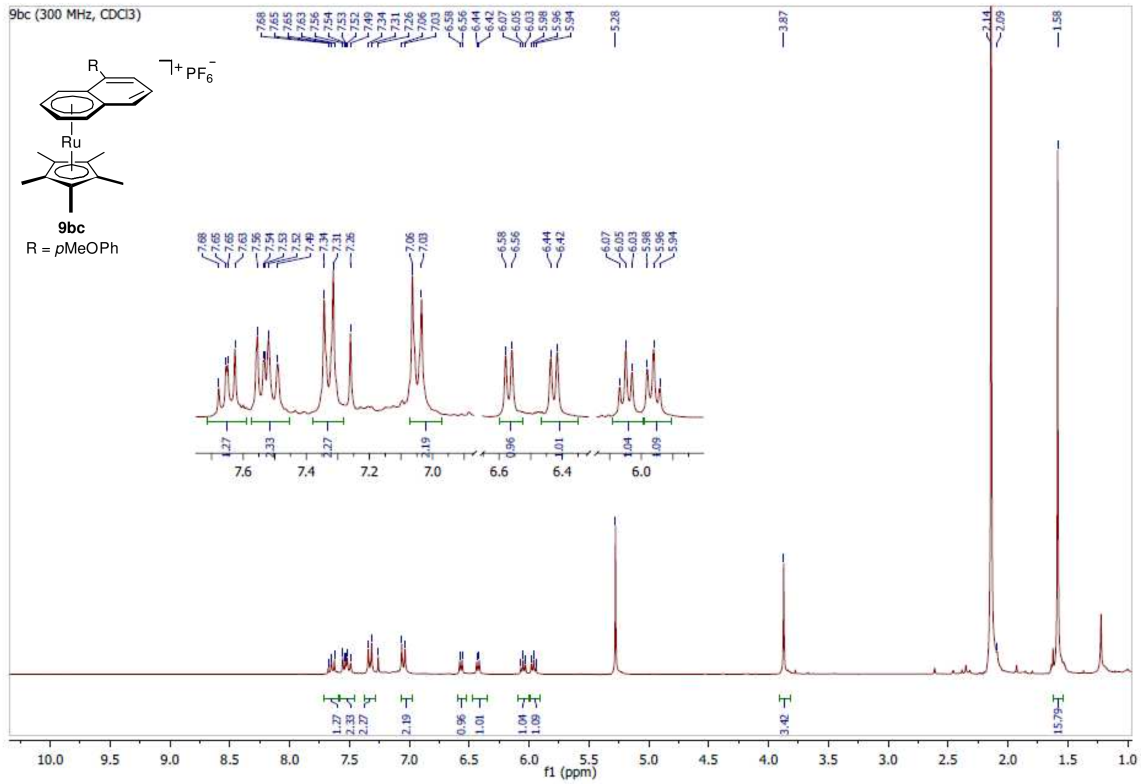
R = Ph
f1 (ppm)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9bc
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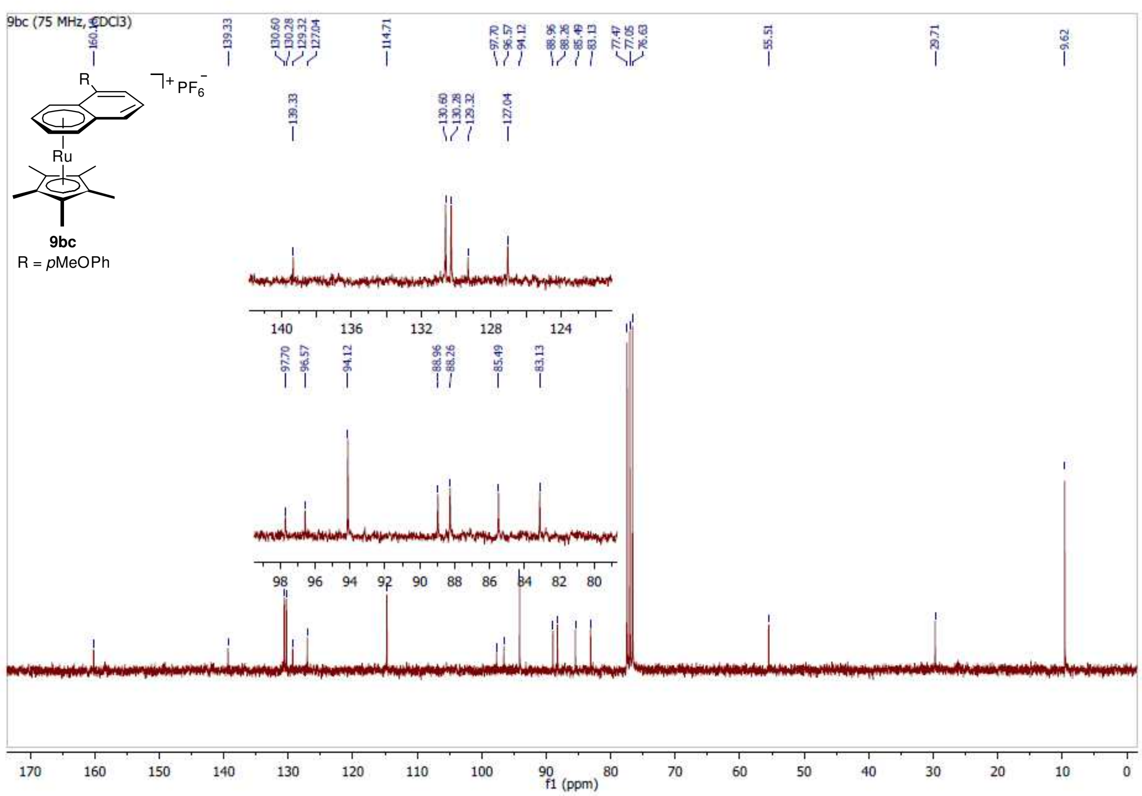
f1 (ppm)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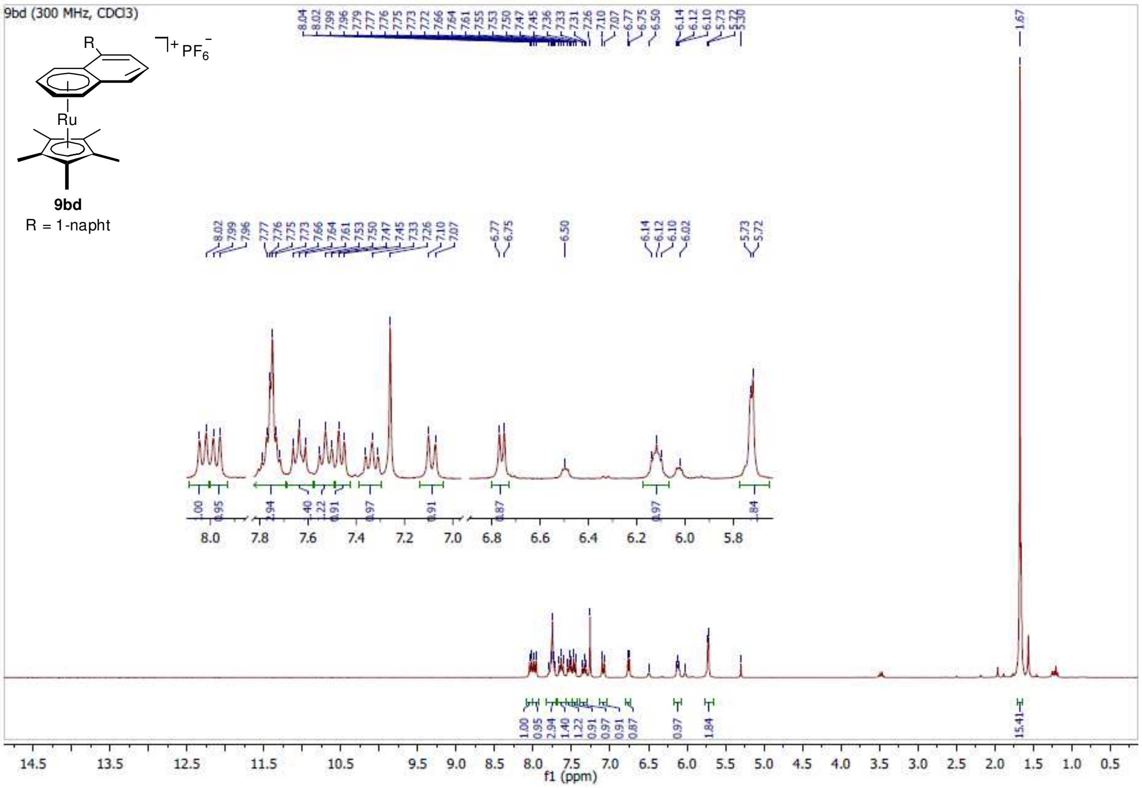
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Ru
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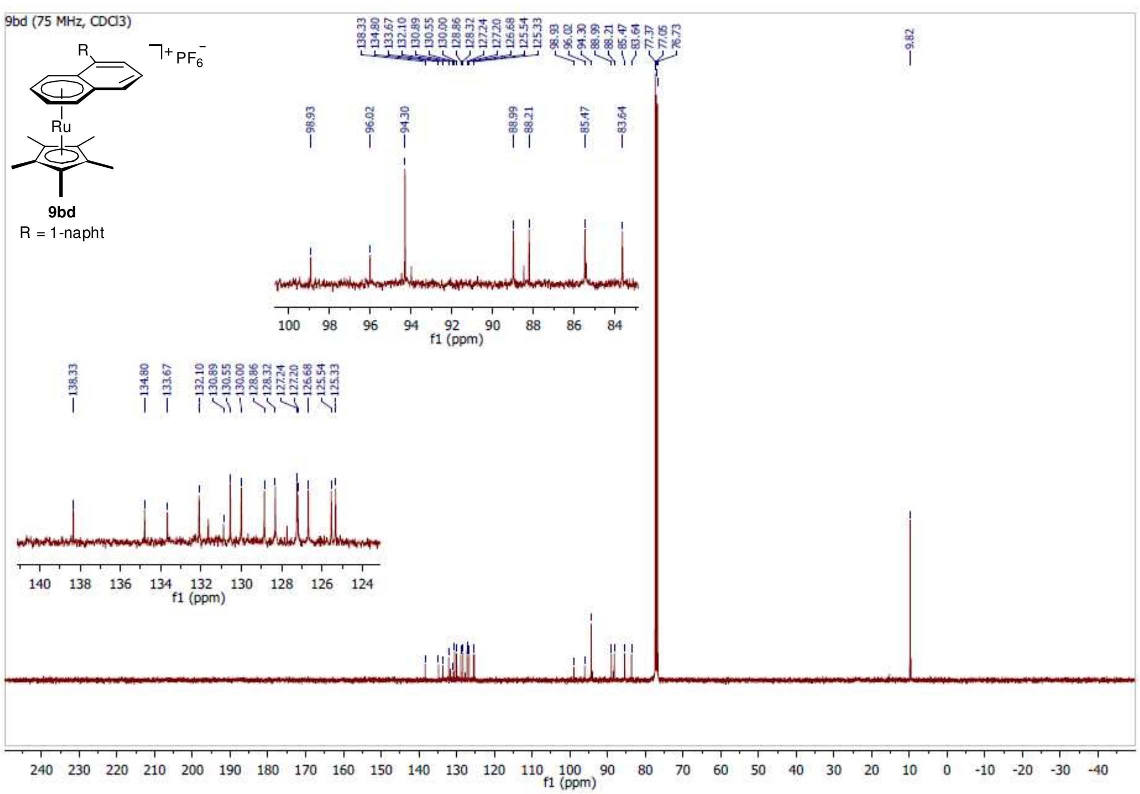
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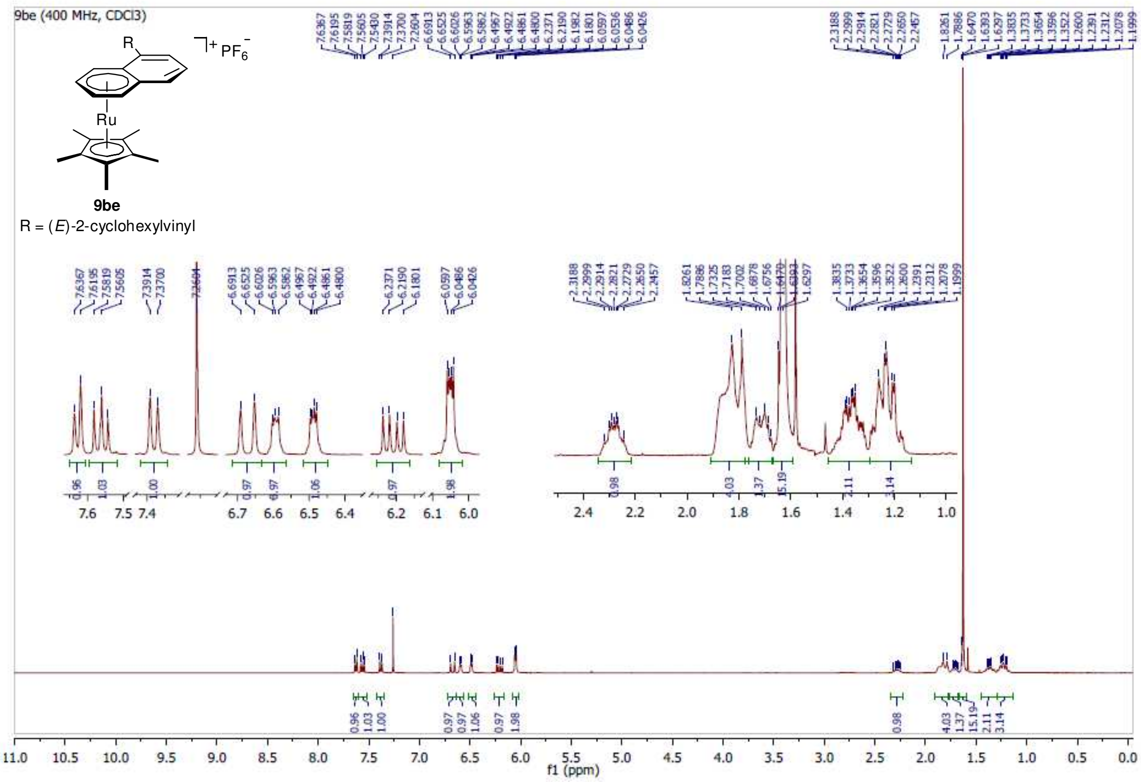
f1 (ppm)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Ru
PF6
9be
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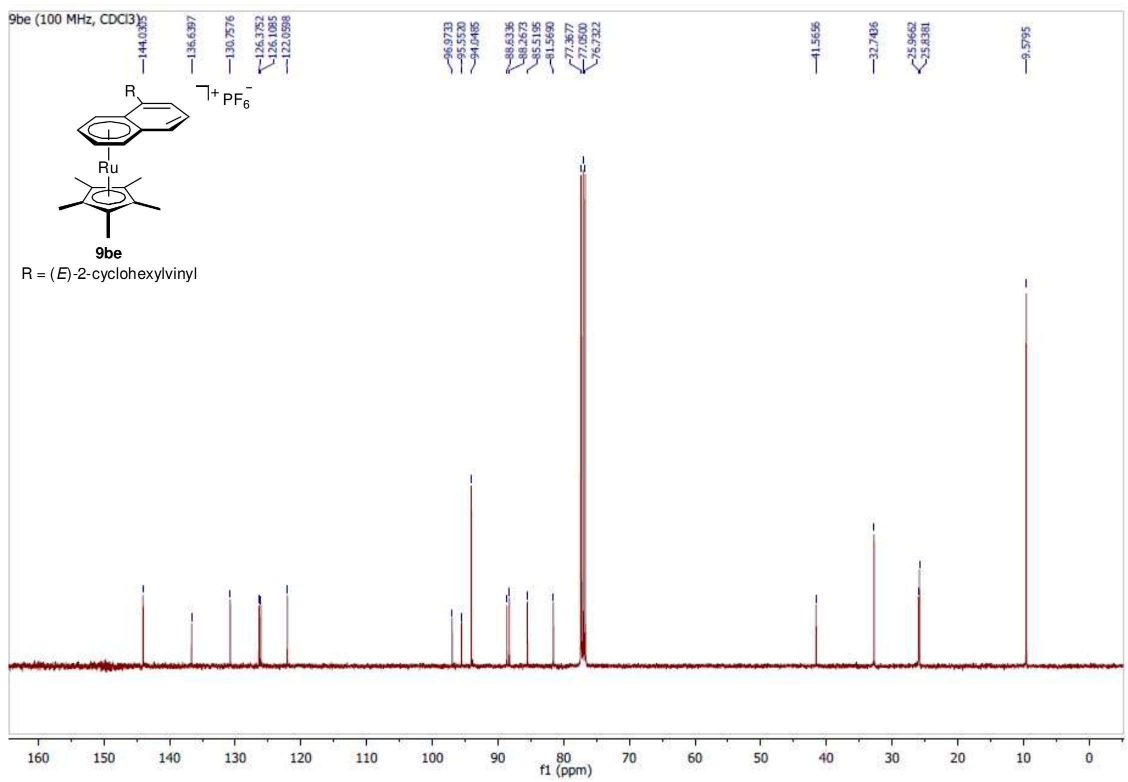
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Ru
PF6
9be
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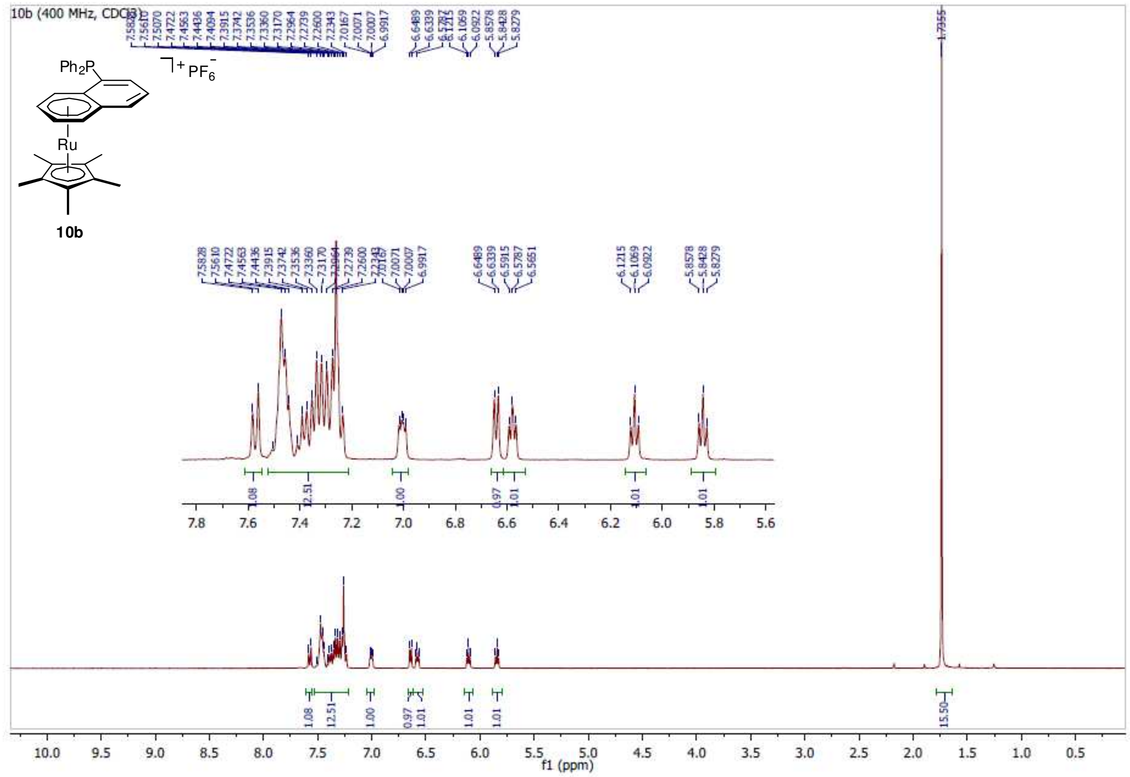
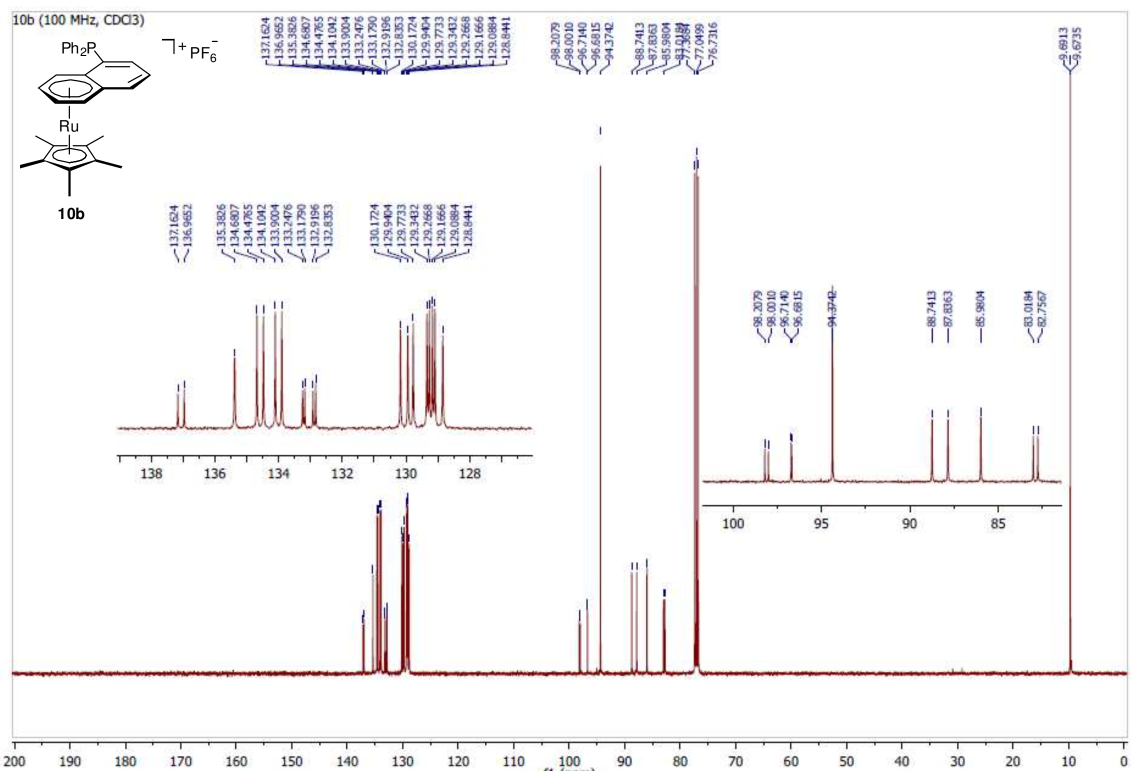
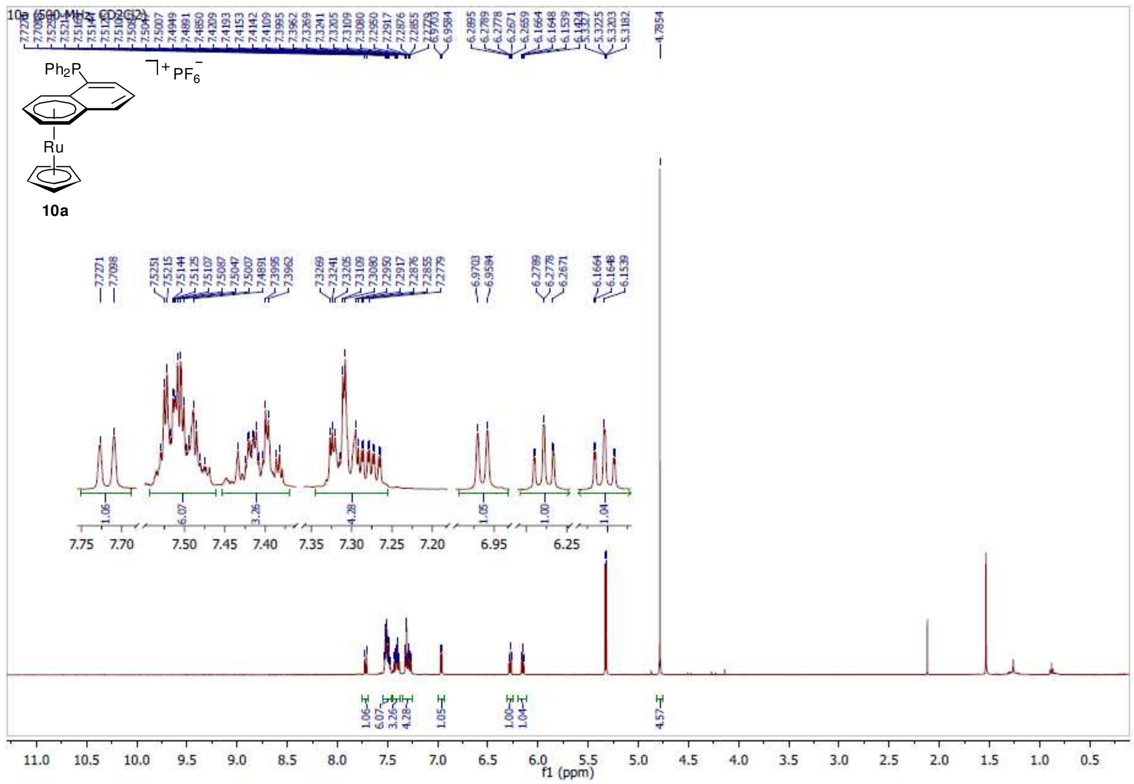
f1 (ppm)



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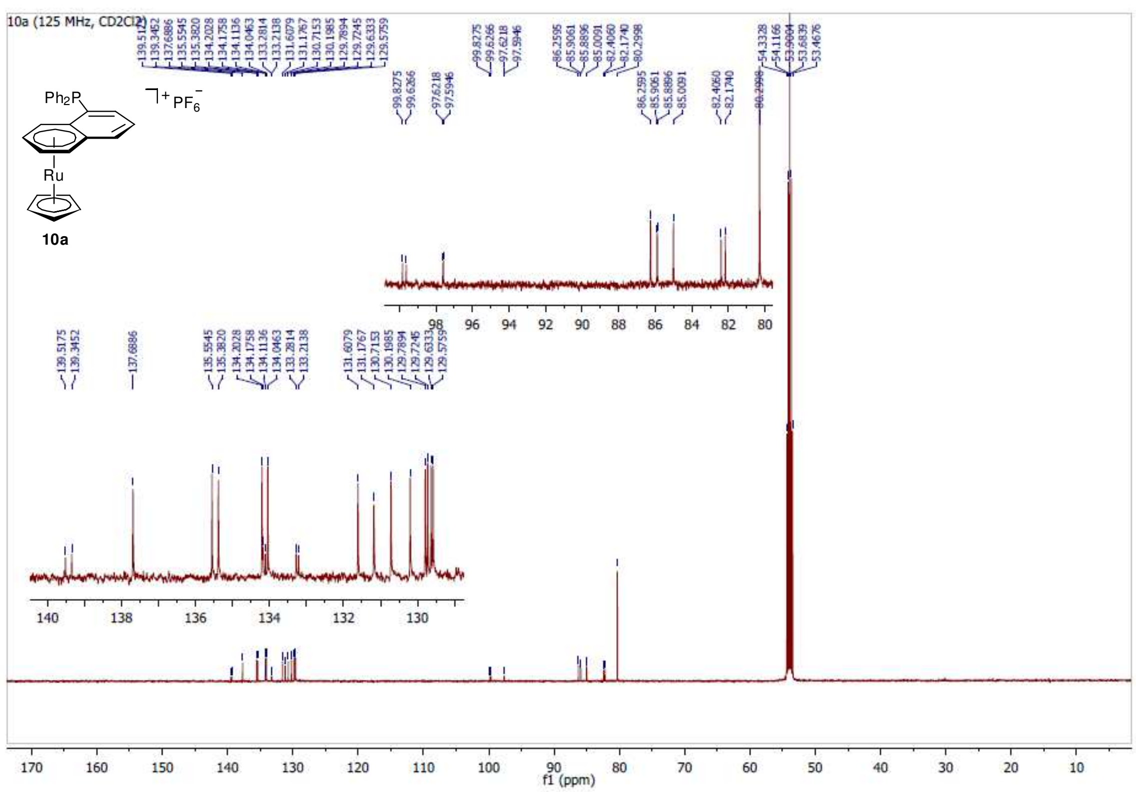
+ PF6−
Ru
10a
f1 (ppm)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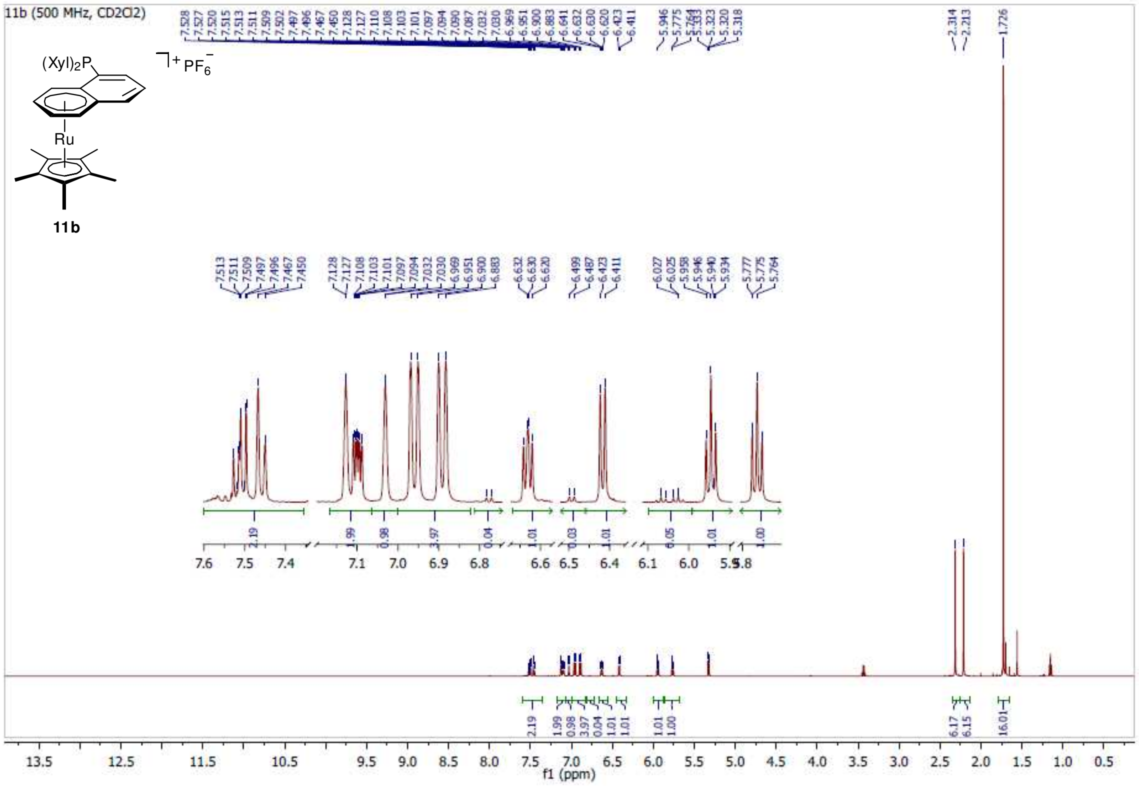
Ph2P
+ PF6−
Ru
10a
f1 (ppm)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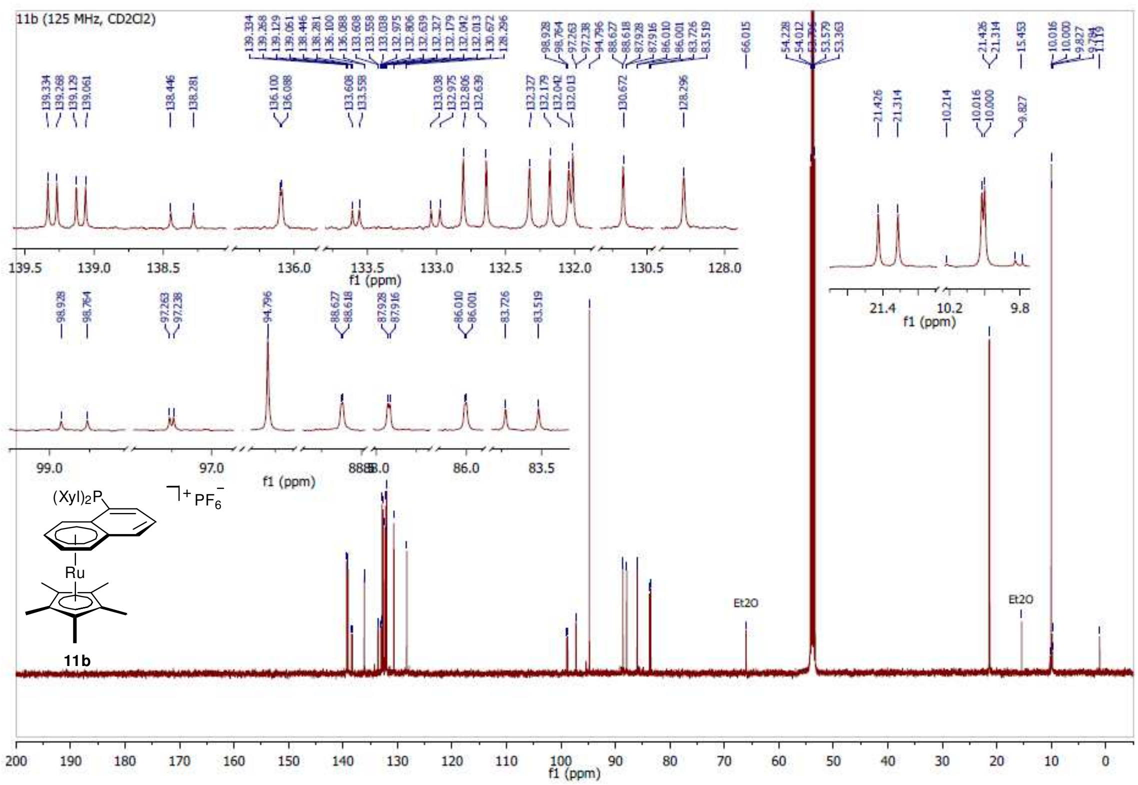
(Xyl)2P
+ PF6−
Ru
11b
f1 (ppm)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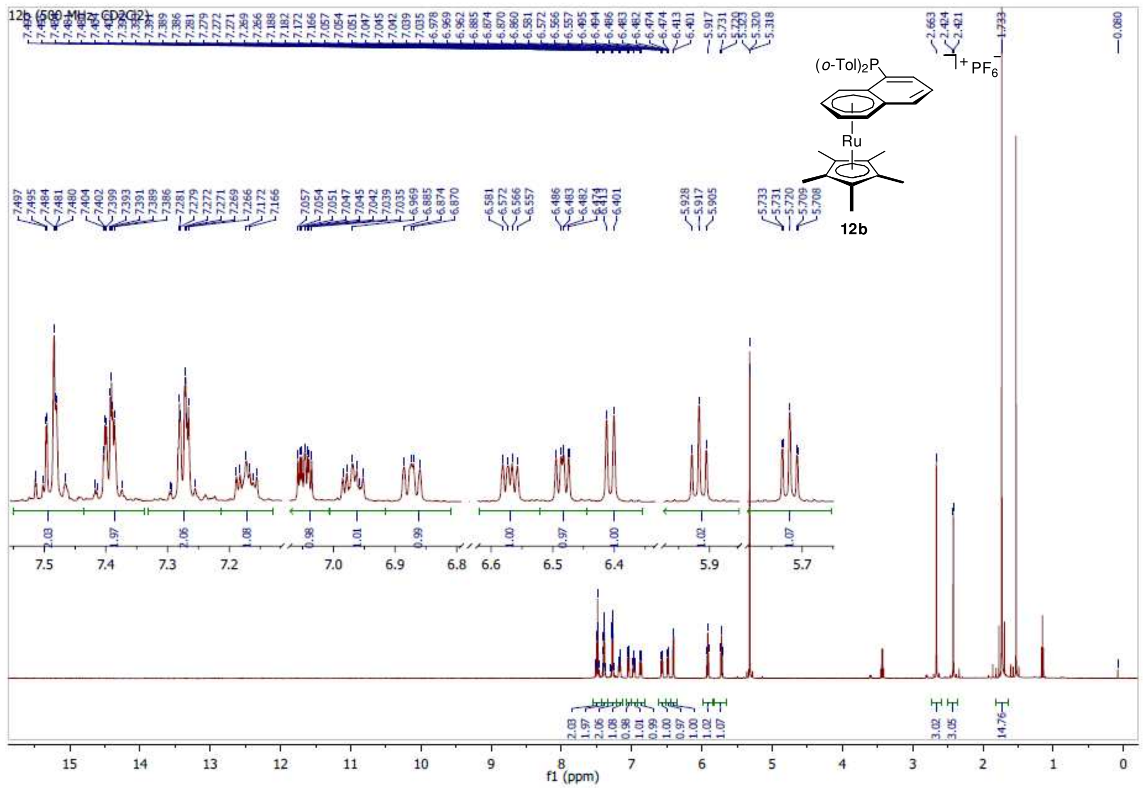
Ru
11b
Et2O
Et2O
f1 (ppm)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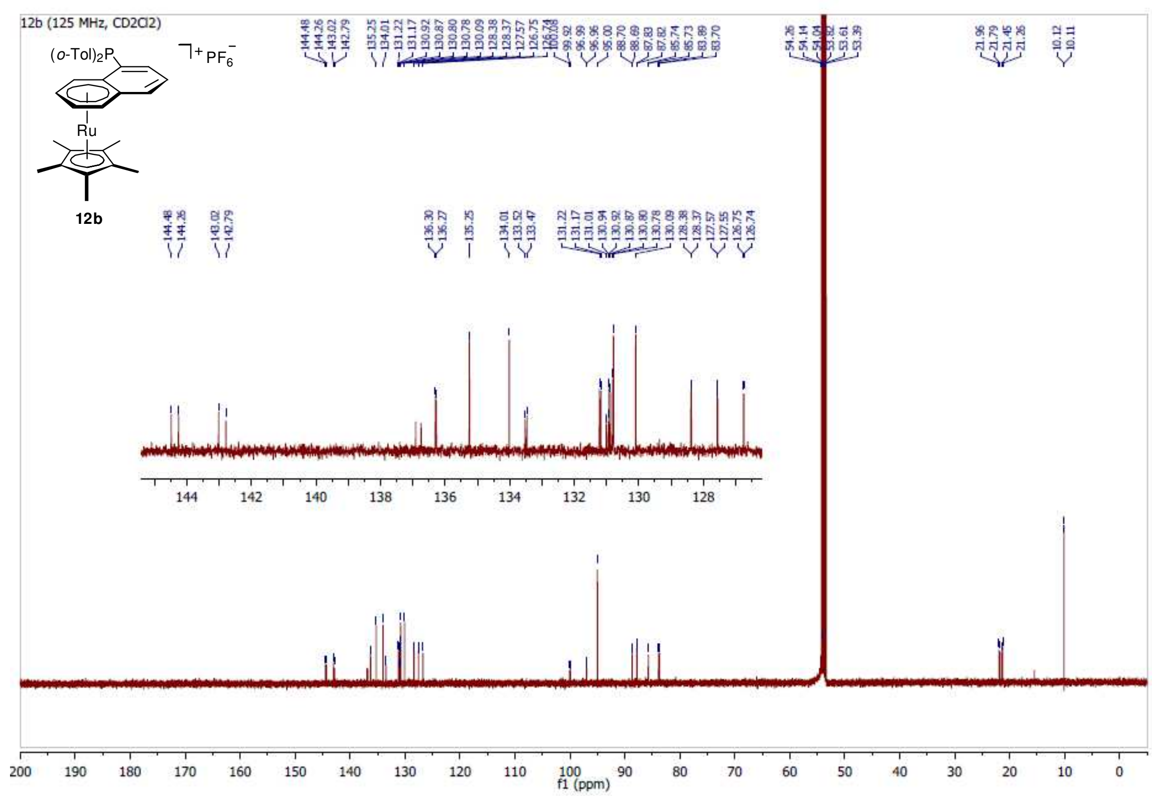
+ PF6−
Ru
12b
f1 (ppm)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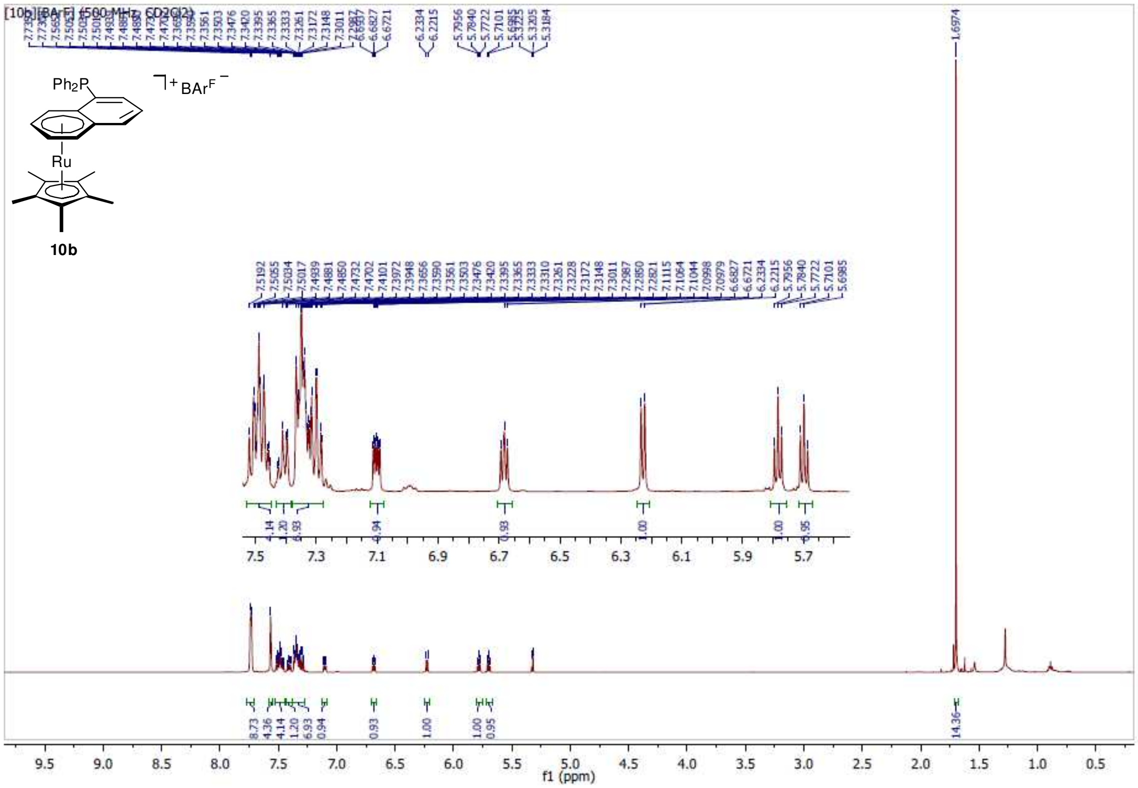
+ PF6−
Ru
12b
f1 (ppm)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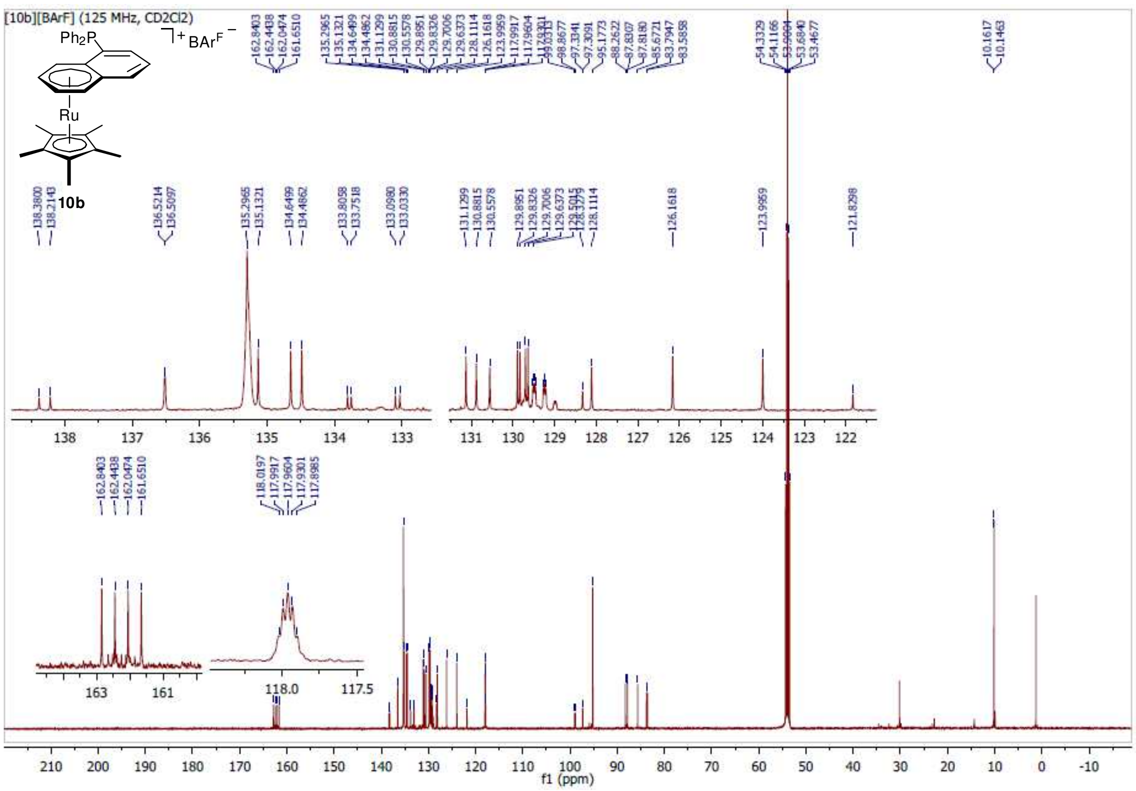
10b
f1 (ppm)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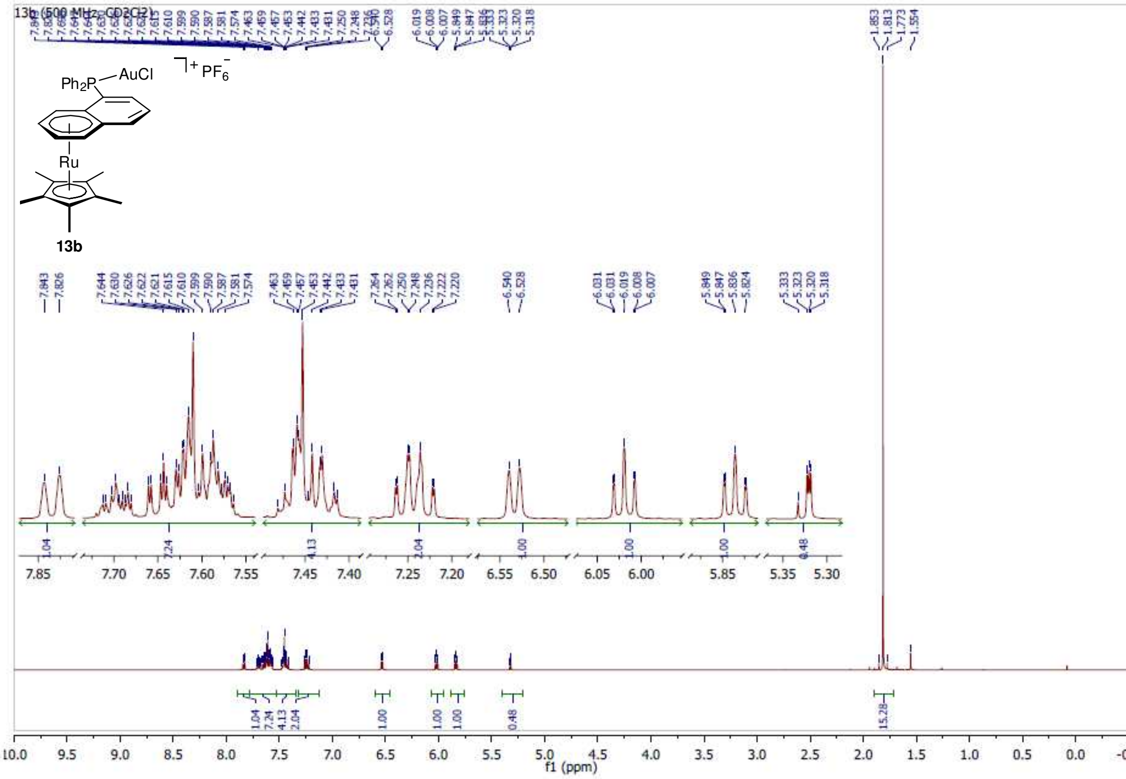
10b
f1 (ppm)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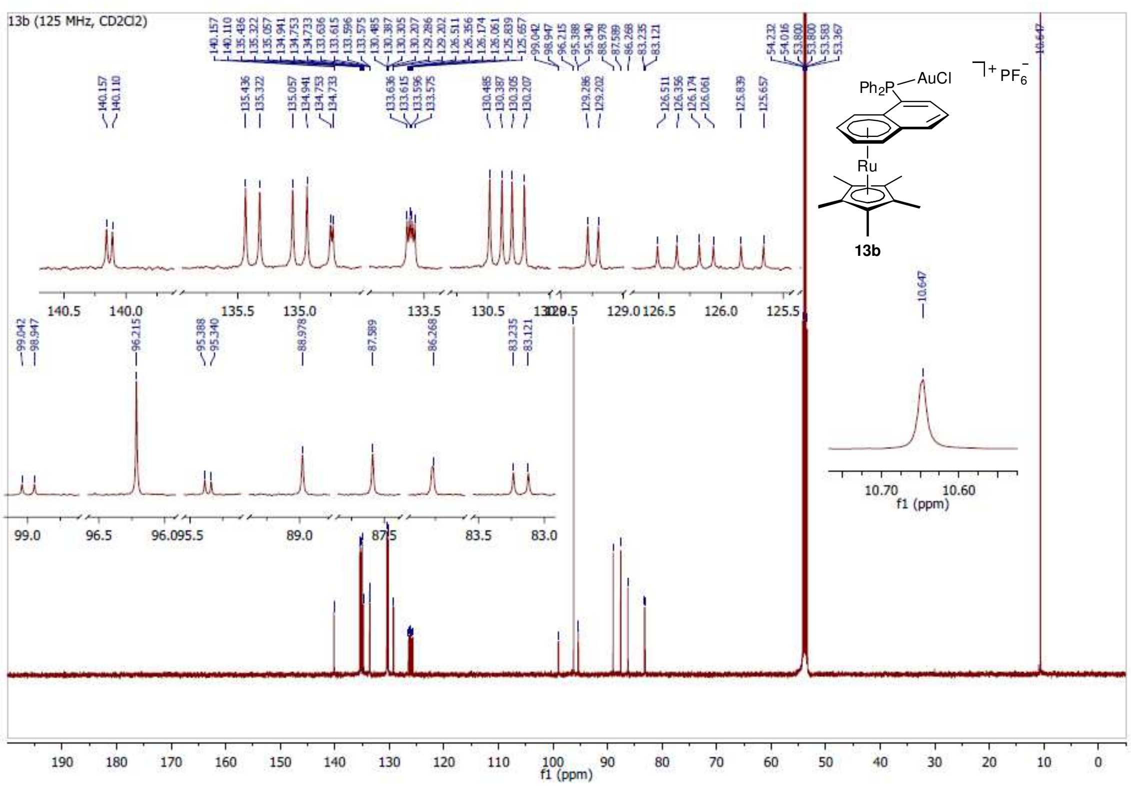
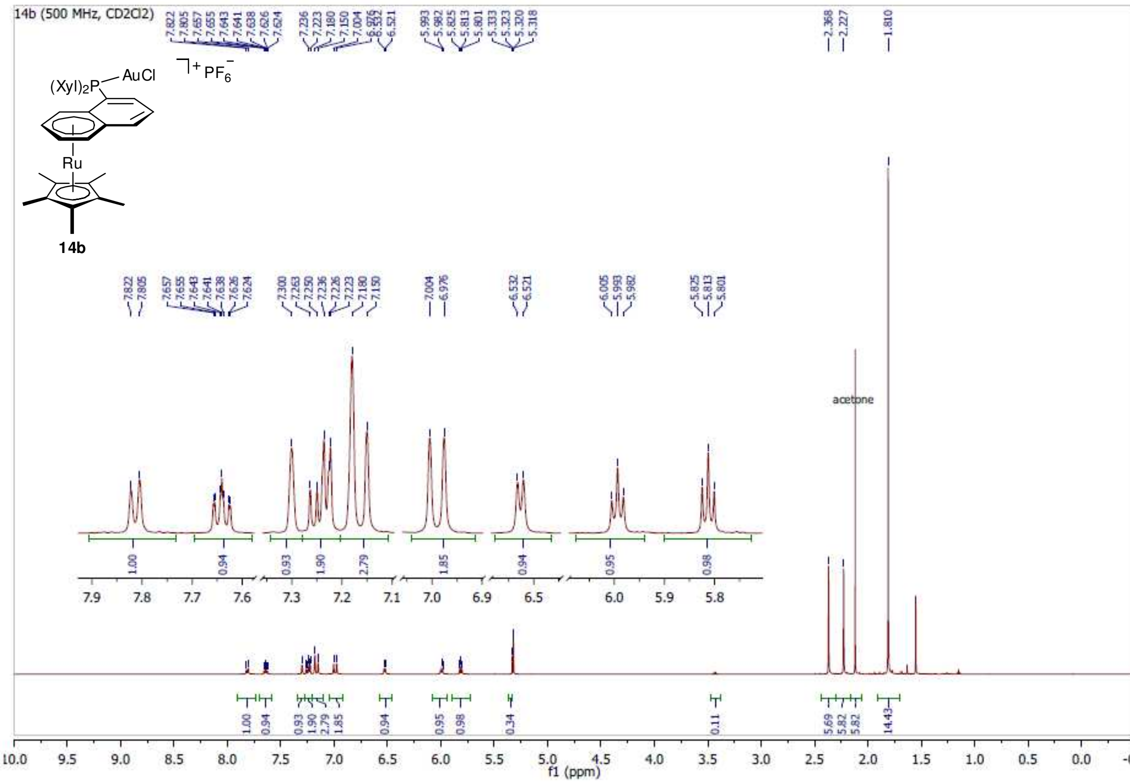
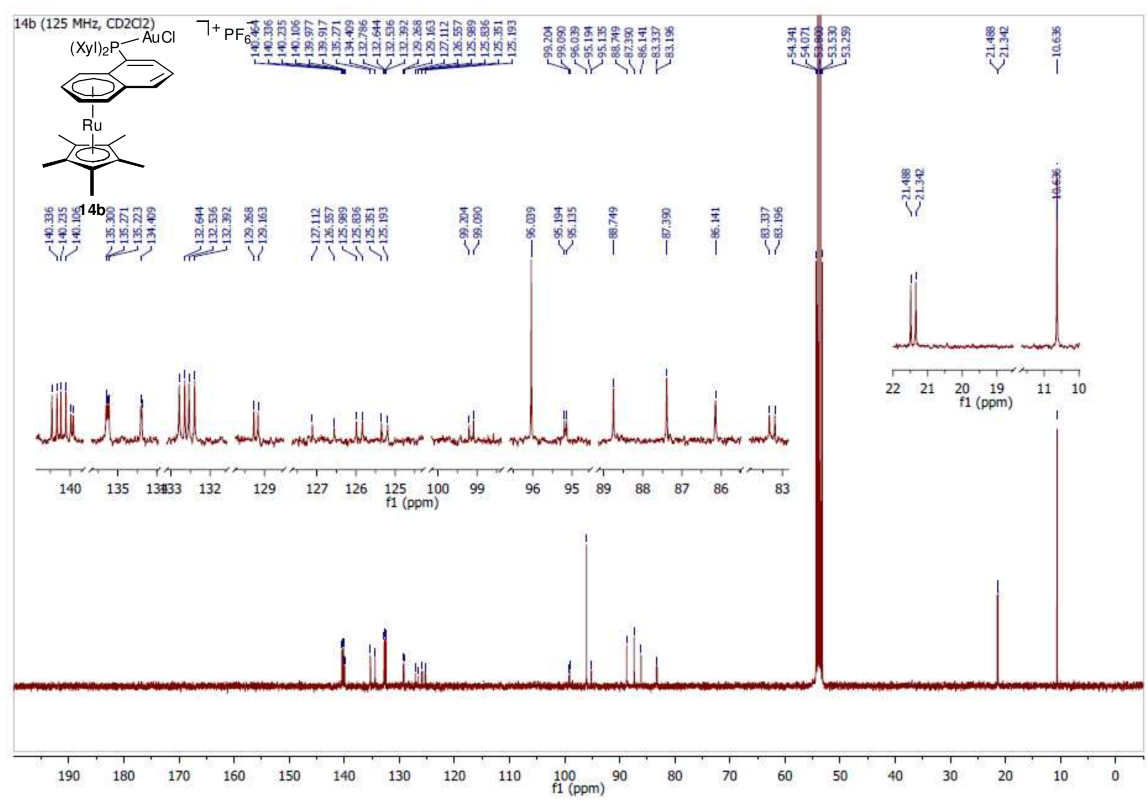
Ph2P AuCl
+ PF6−
Ru
13b
f1 (ppm)


13b (125 MHz, CD2Cl2)
Ph2P AuCl
+ PF6−
Ru
13b
f1 (ppm)


14b (500 MHz, CD2Cl2)
(Xyl)2P
AuCl
PF6
Ru
14b
acetone
f1 (ppm)


14b (125 MHz, CD2Cl2)
(Xyl)2P
AuCl
PF6
Ru
14b
f1 (ppm)

4. References

[1] Van der Sluis, P.; Spek, A. L. *Acta Cryst. A* **1990**, *46*, 194−201.

[2] Spek, A. L. *Acta Cryst. A* **1990**, *46*, C34.