Supporting Information for the Article:

Dehydrogenative Coupling of 4-Substituted Pyridines Catalyzed by a Trinuclear Complex of Ruthenium and Cobalt

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1. Results of the dehydrogenative coupling of 4-picoline catalyzed by 4 and 5

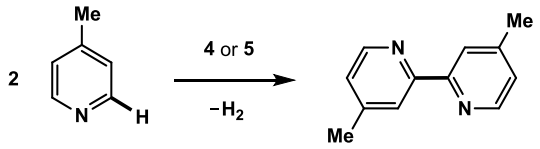


Table S-1. Results of the Dehydrogenative Coupling of 4-Picoline Catalyzed by **4** and **5**.[a]

entry	catalyst	S/C	solvent	time [h]	temp. [°C]	yield[b] [%]
1	$(Cp^*Ru)_2(\mu\text{-}H)_4$ (**4**)	20	heptane	24	180	50
2		100	mesitylene	19	160	53
3	$(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**5**)	500	decane	120	180	32
4		20	heptane	96	180	48
5		100	mesitylene	100	180	43
6		500	mesitylene	72	180	20
7		500	DME	72	180	2

[a] The reactions were carried out using of 4-picoline (45 μL, 0.46 mmol) and the catalyst in 4 mL solvent in a sealed reaction tube in appropriate reaction conditions. [b] Yield was determined by GC analysis.

2. Time course of the dehydrogenative coupling of 4-picoline catalyzed by 1, 4, and 5

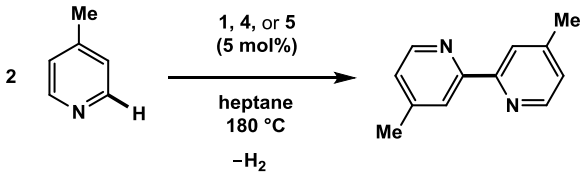


Table S-2. Time course of the Dehydrogenative Coupling of 4-Picoline Catalyzed by **1**, **4**, and **5**[a]

entry	cat.	time [h]	yield [%][b]	TON	TOF [h^{-1}]
1	$(Cp^*Ru)_2(Cp^*Co)(\mu\text{-}H)_3(\mu_3\text{-}H)$ (**1**)	1	10	1.0	1
2		3	15	1.5	0.5
3		12	33	3.3	0.3
4		24	53	5.3	0.2
5		48	73	7.3	0.2
6		102	86	8.6	0.08
7		168	87	8.7	0.05
8	$(Cp^*Ru)_2(\mu\text{-}H)_4$ (**4**)	0.5	31	3.1	6.2
9		1	47	4.7	4.7
10		3	48	4.8	0.5
11		24	50	5.0	0.2
12		48	55	5.5	0.1
13		96	53	5.3	0.07
14		168	52	5.2	0.04
15	$(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**5**)	1	*trace*	—	—
16		3	9	0.9	0.3
17		12	13	1.3	0.1
18		24	20	2.0	0.08
19		48	34	3.4	0.07
20		96	48	4.8	0.05
21		168	56	5.6	0.03

[a] The reactions were carried out at 180 °C in a sealed reaction tube using of 3 mL of the stock solution, which was prepared by the 5 mM heptane solution of the catalyst and 4-picoline (20 equiv.). [b] Yield was determined by GC analysis.

3. NMR spectra of 9, 10, 11, 12, 13, 15, 16, and the reaction mixture at the end of the catalytic reaction

Figure S-1. ^{1}H NMR spectrum of **9** (400 MHz, rt, benzene-d_6).

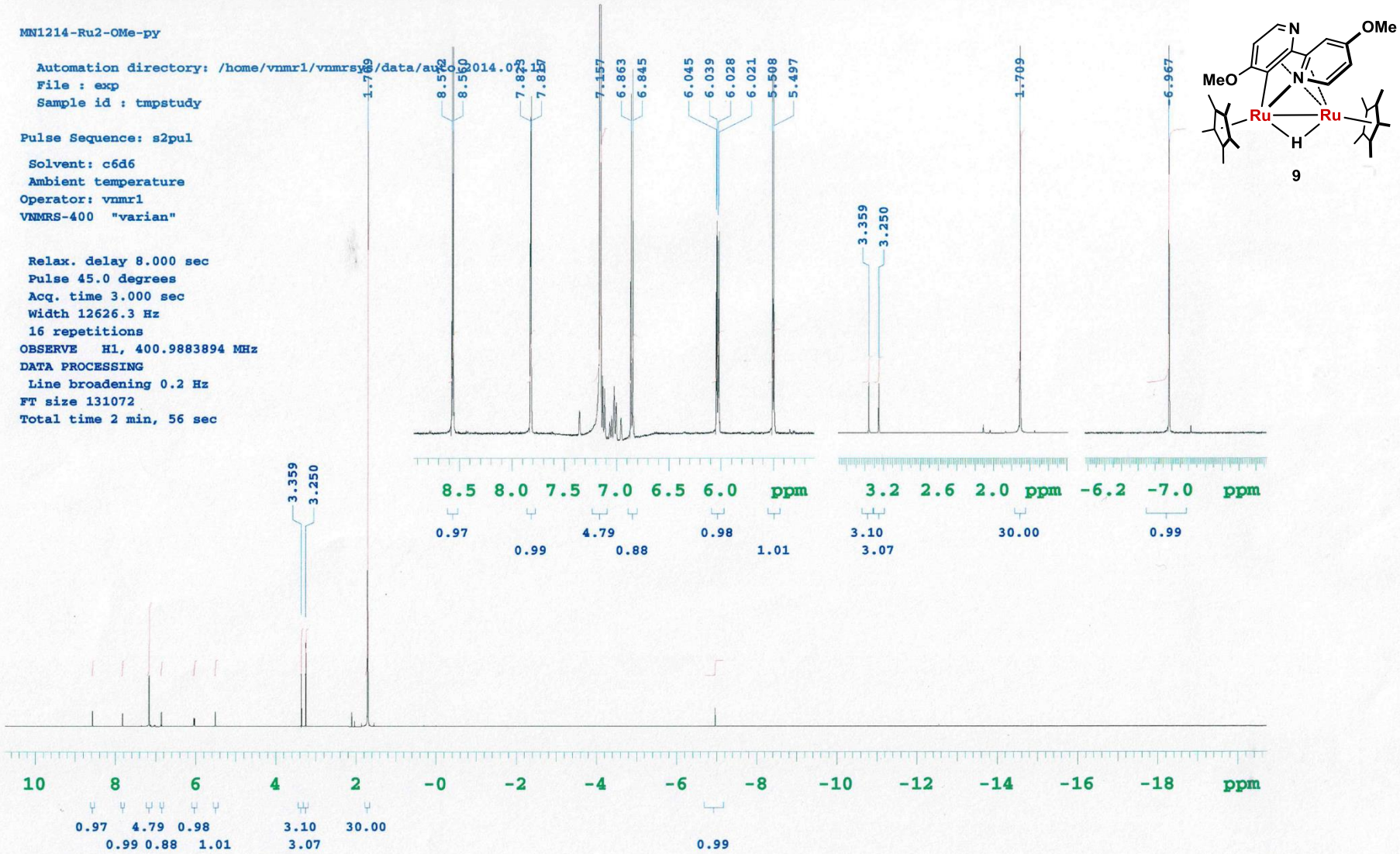
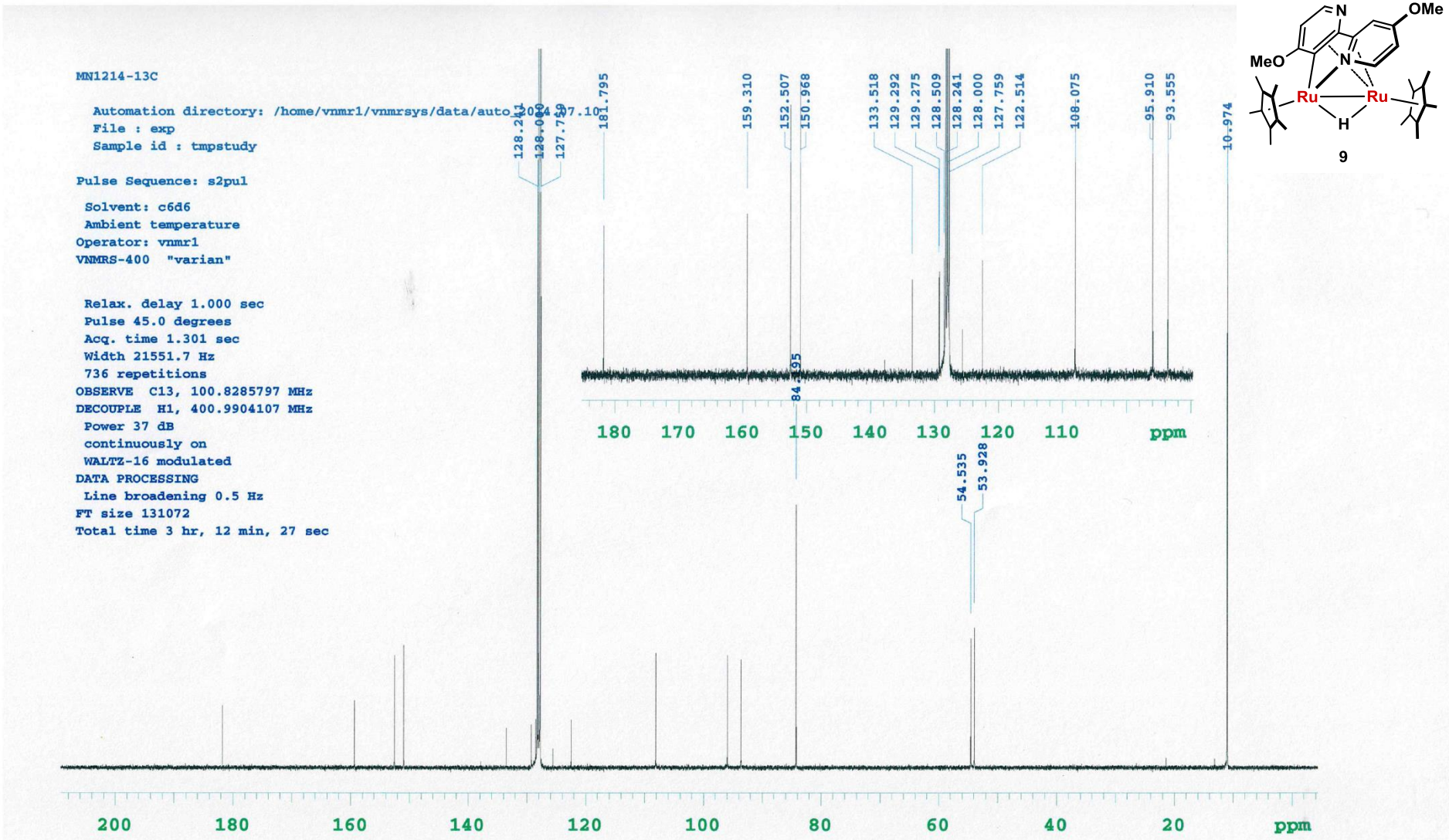


Figure S-2. $^{13}C\{^{1}H\}$ NMR spectrum of **9** (100 MHz, rt, benzene-d_6).



9

Figure S-3. ^{1}H NMR spectrum of **12** (400 MHz, rt, benzene-d_6).

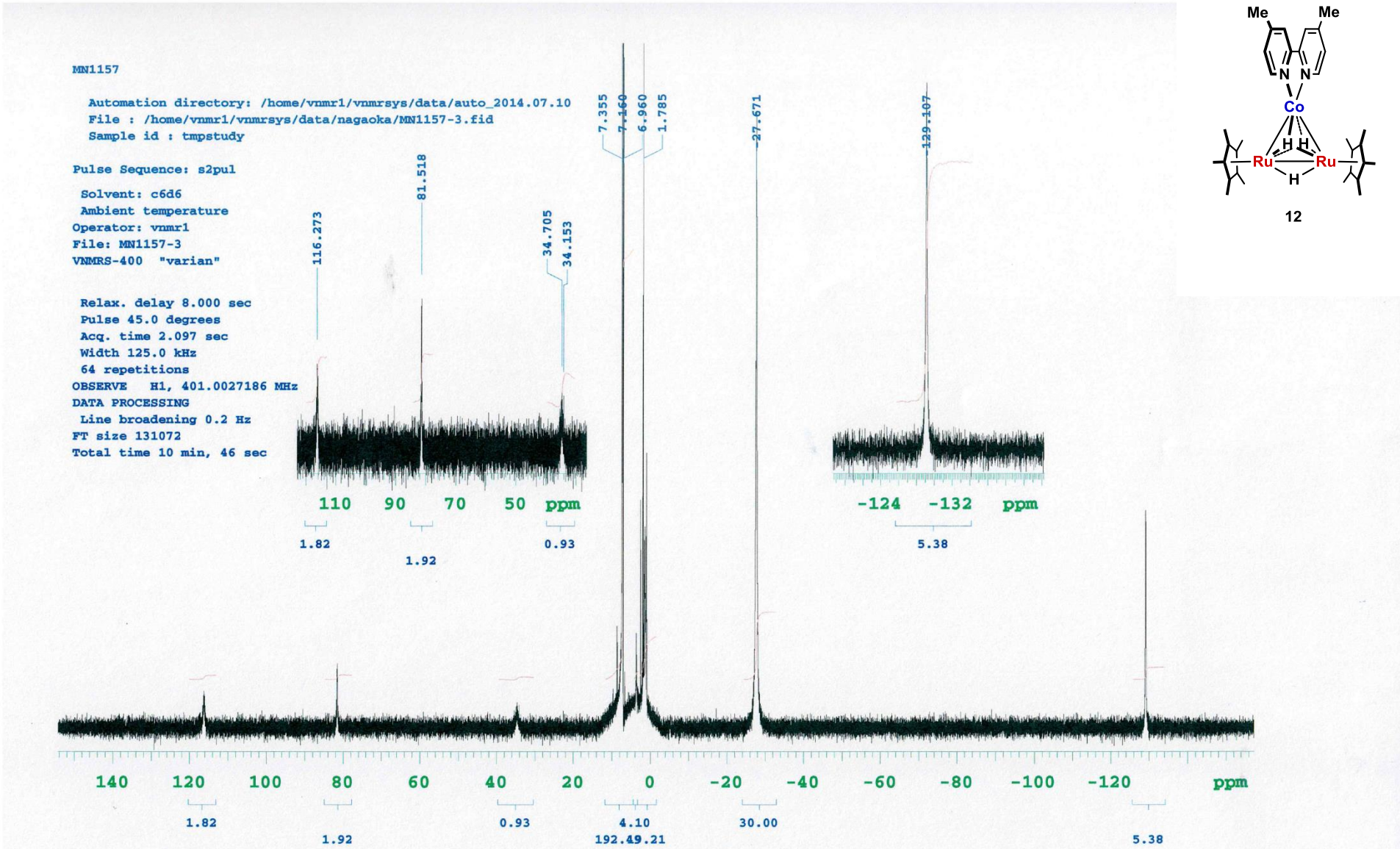


Figure S-4. ^{1}H NMR spectrum of **13** (400 MHz, –40 °C, toluene-d_8).

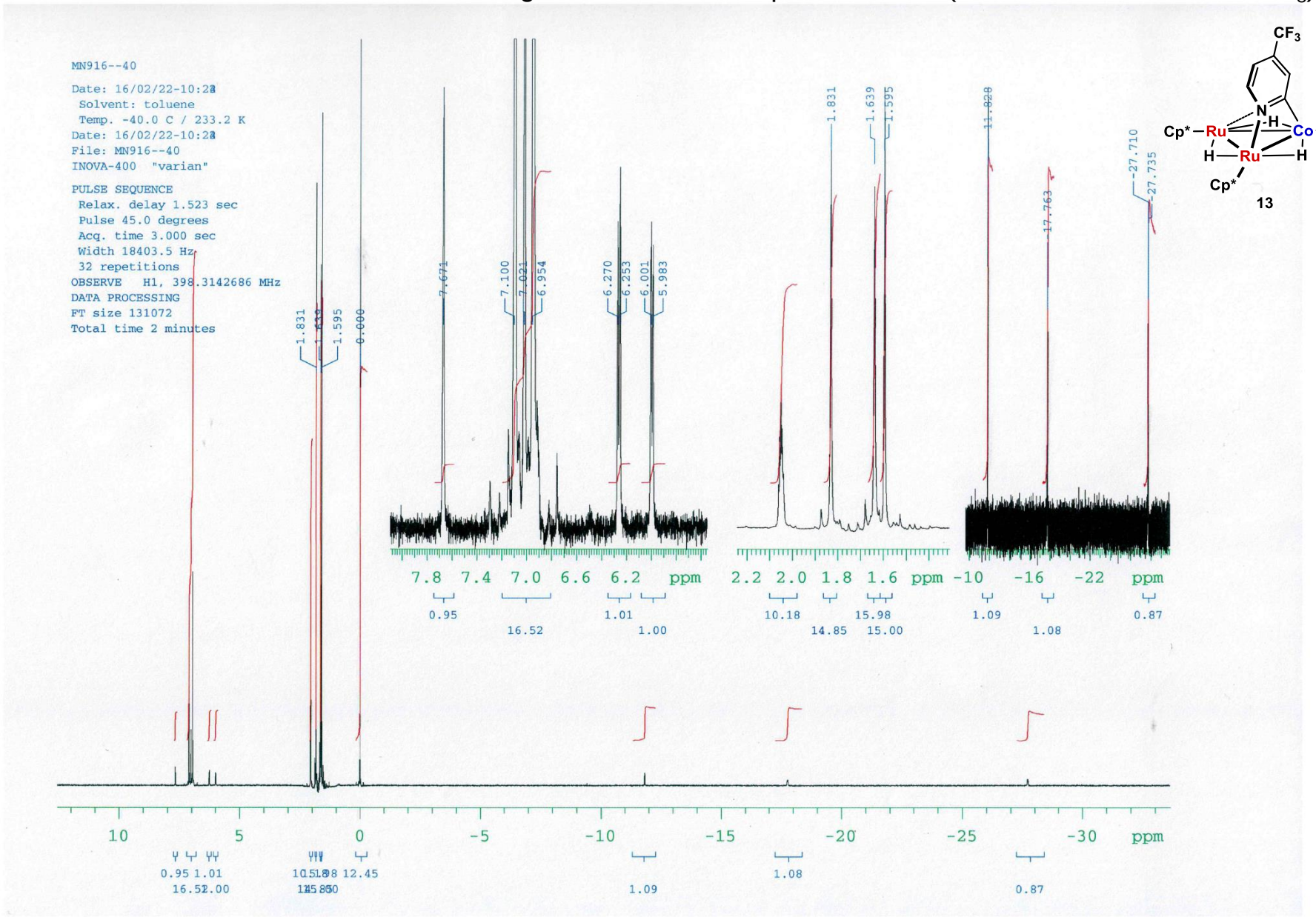


Figure S-5. $^{13}C\{^{1}H\}$ NMR spectrum of **13** (100 MHz, –40 °C, THF-d_8).

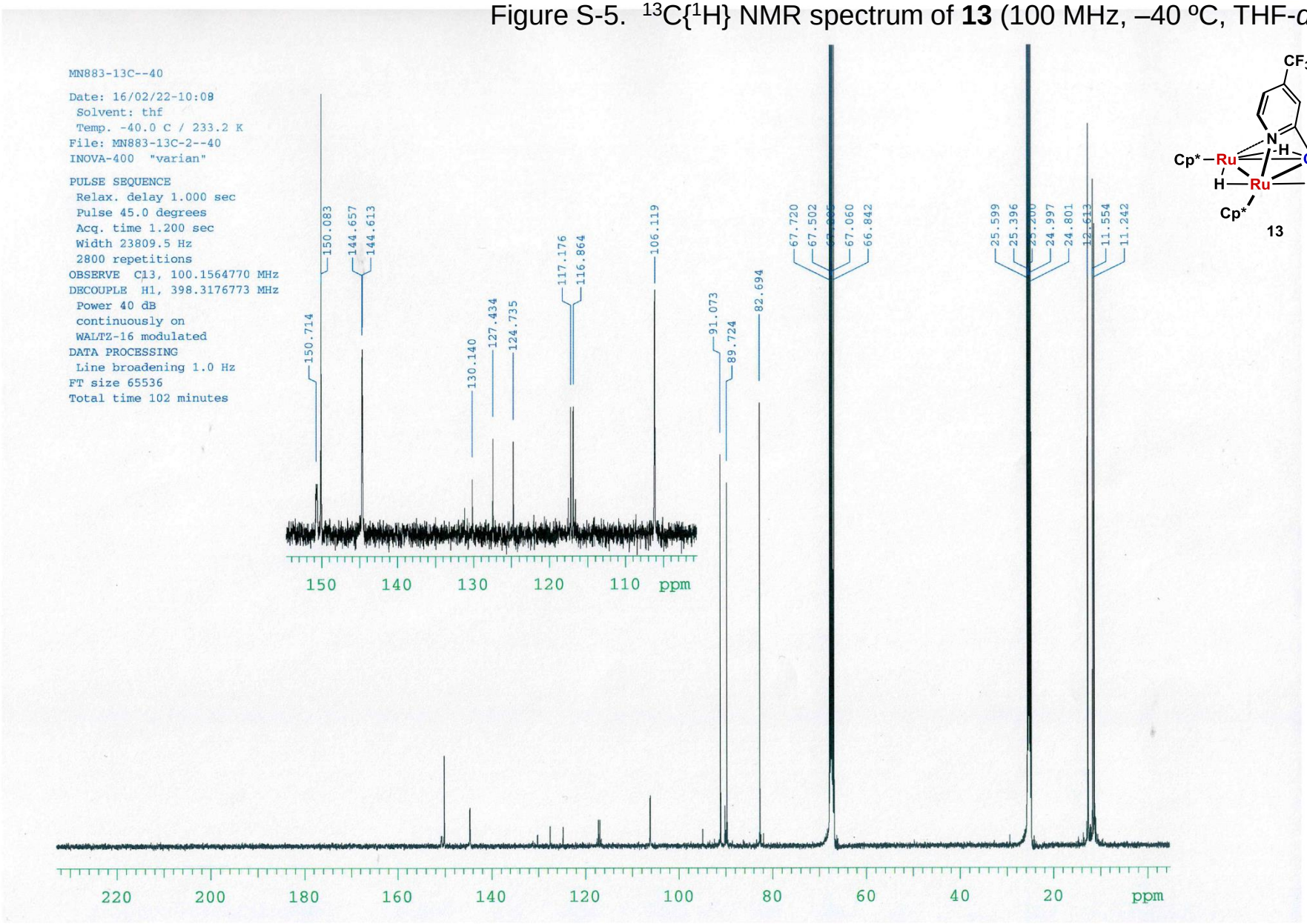


Figure S-6. ^{1}H NMR spectrum of **15** (400 MHz, –80 ºC, THF-d_8).

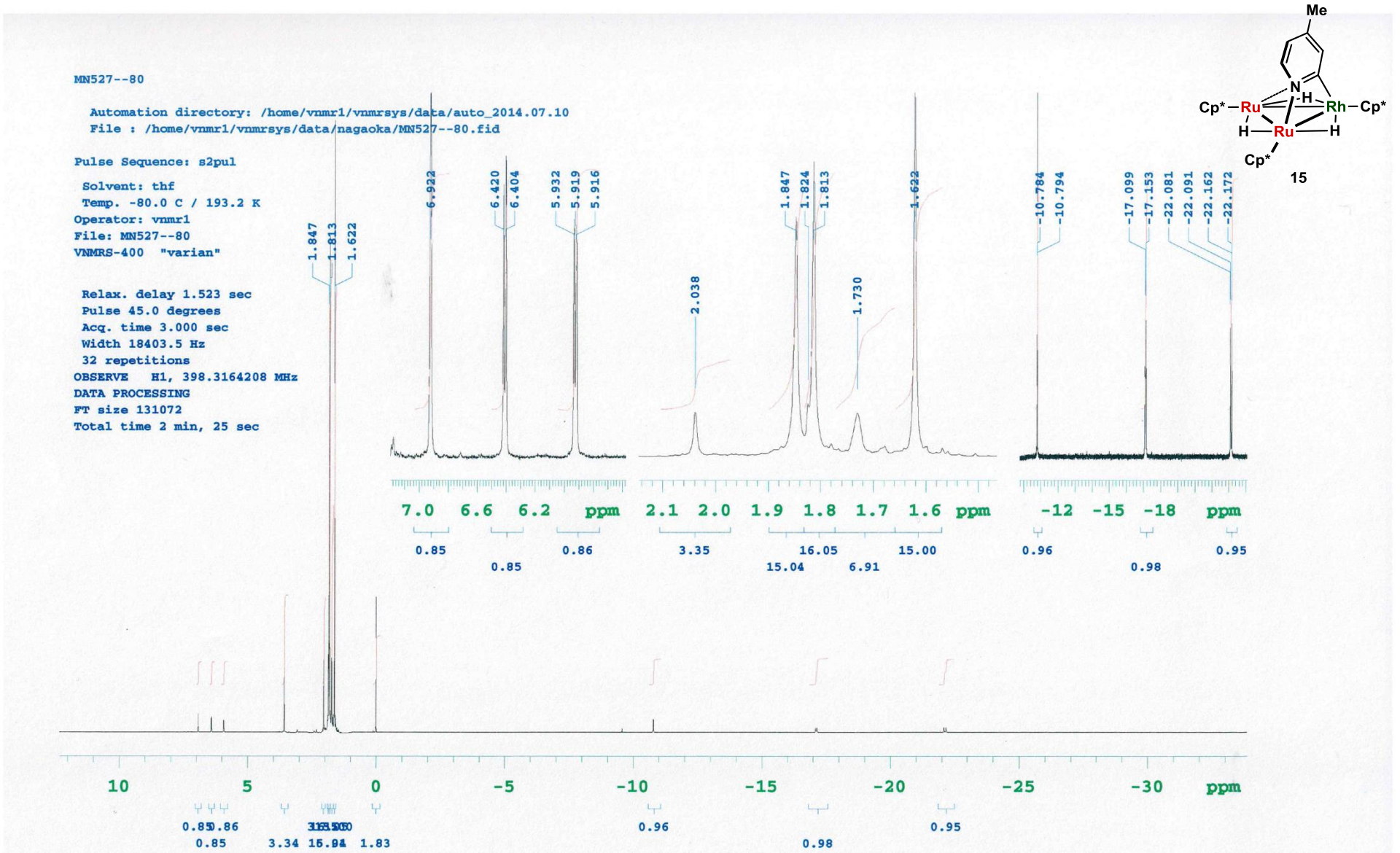


Figure S-7. $^{13}C\{^{1}H\}$ NMR spectrum of **15** (100 MHz, –80 ºC, THF-d_8).

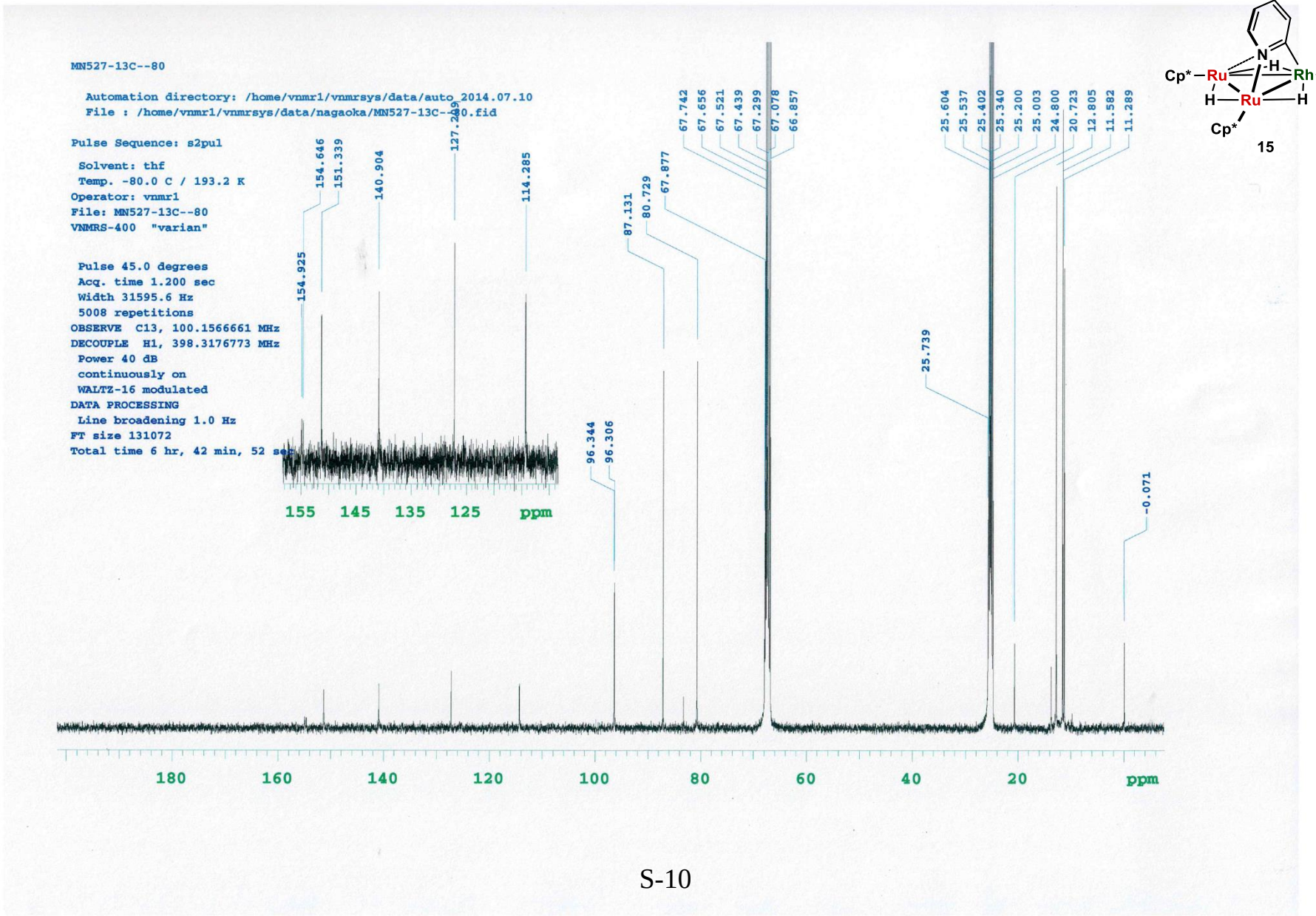


Figure S-8. ^{1}H NMR spectrum of **16** (400 MHz, –70 ºC, THF-d_8).

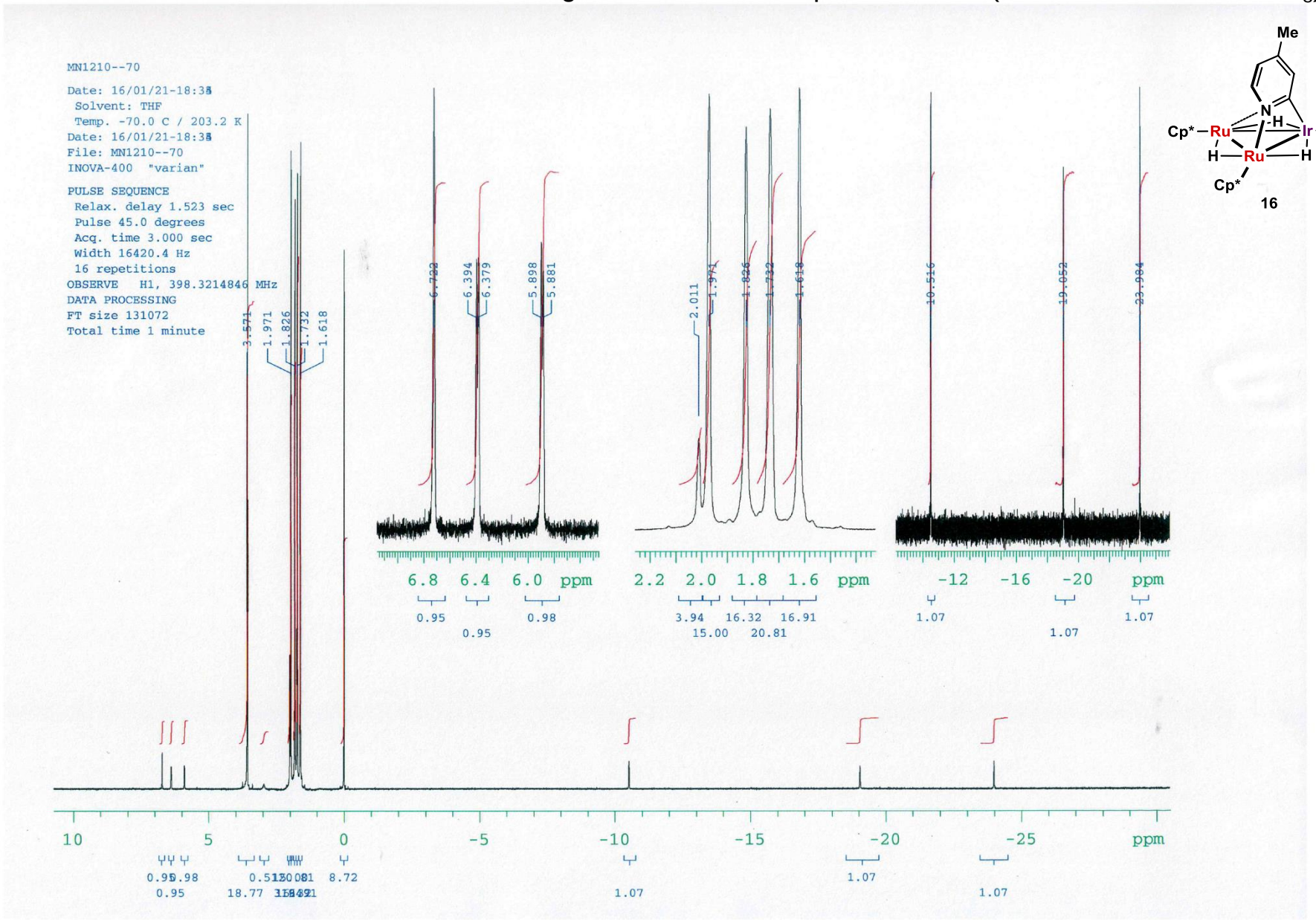
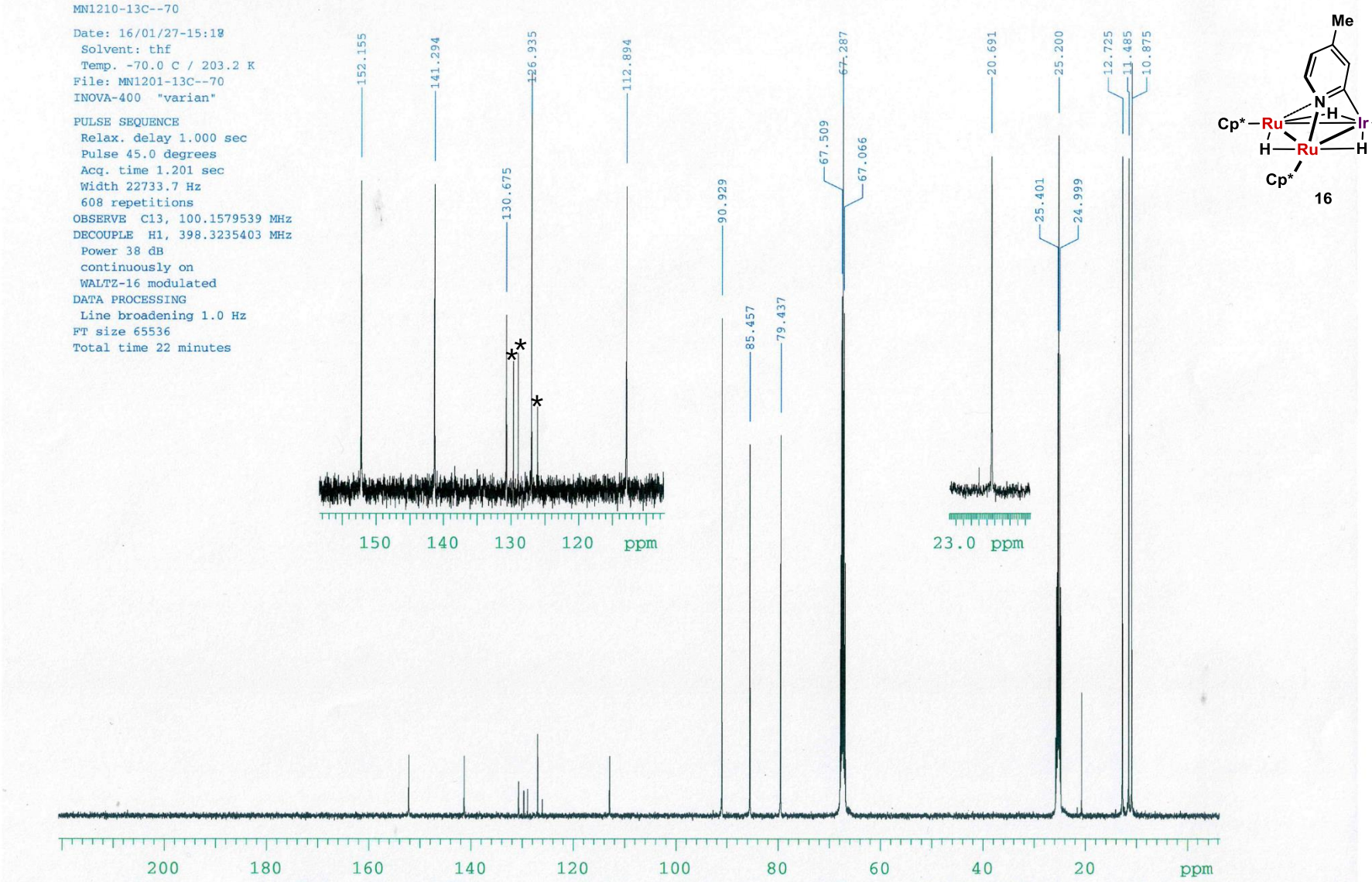
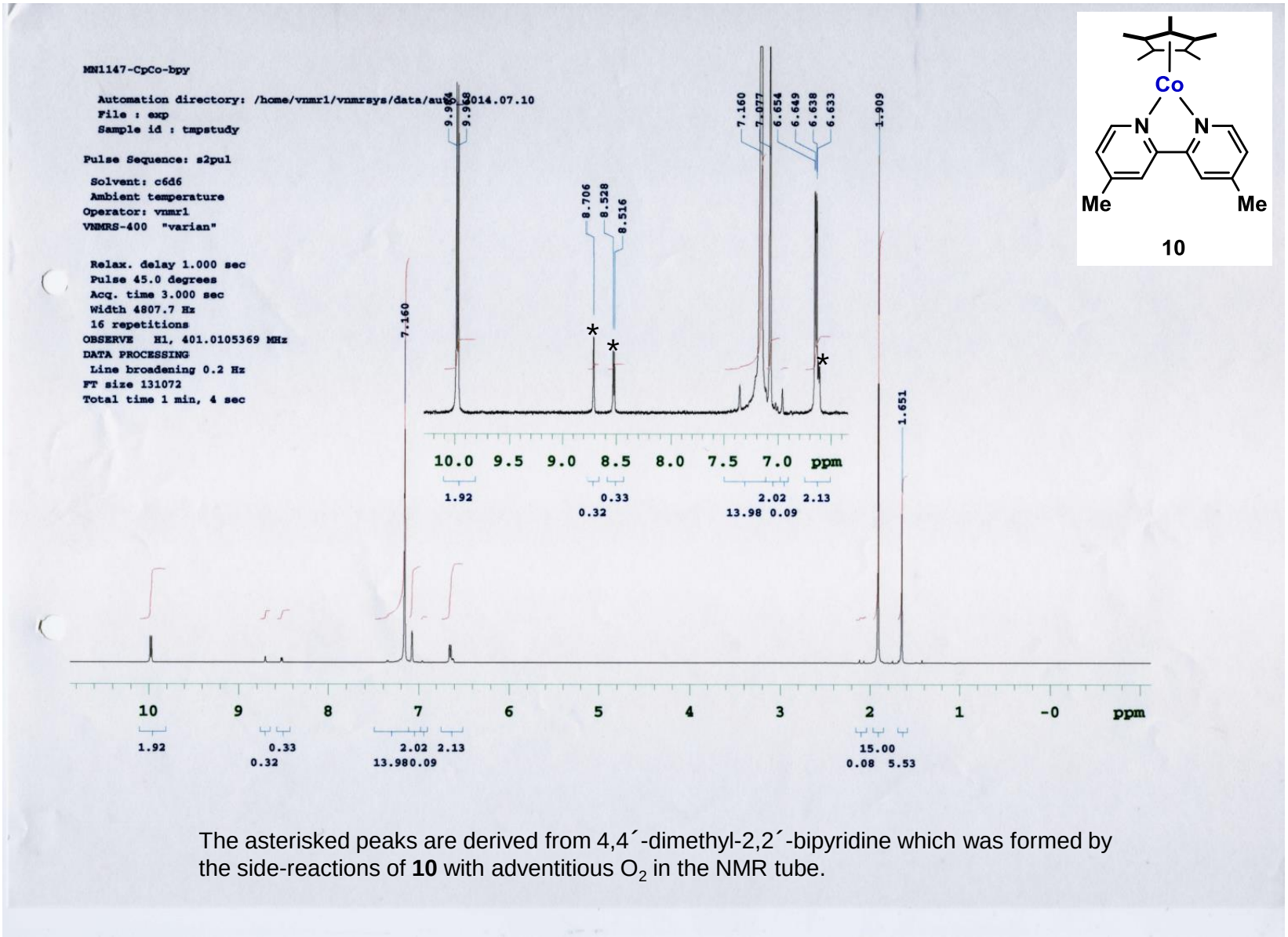


Figure S-9. $^{13}C\{^{1}H\}$ NMR spectrum of **16** (100 MHz, –70 ºC, THF-d_8).



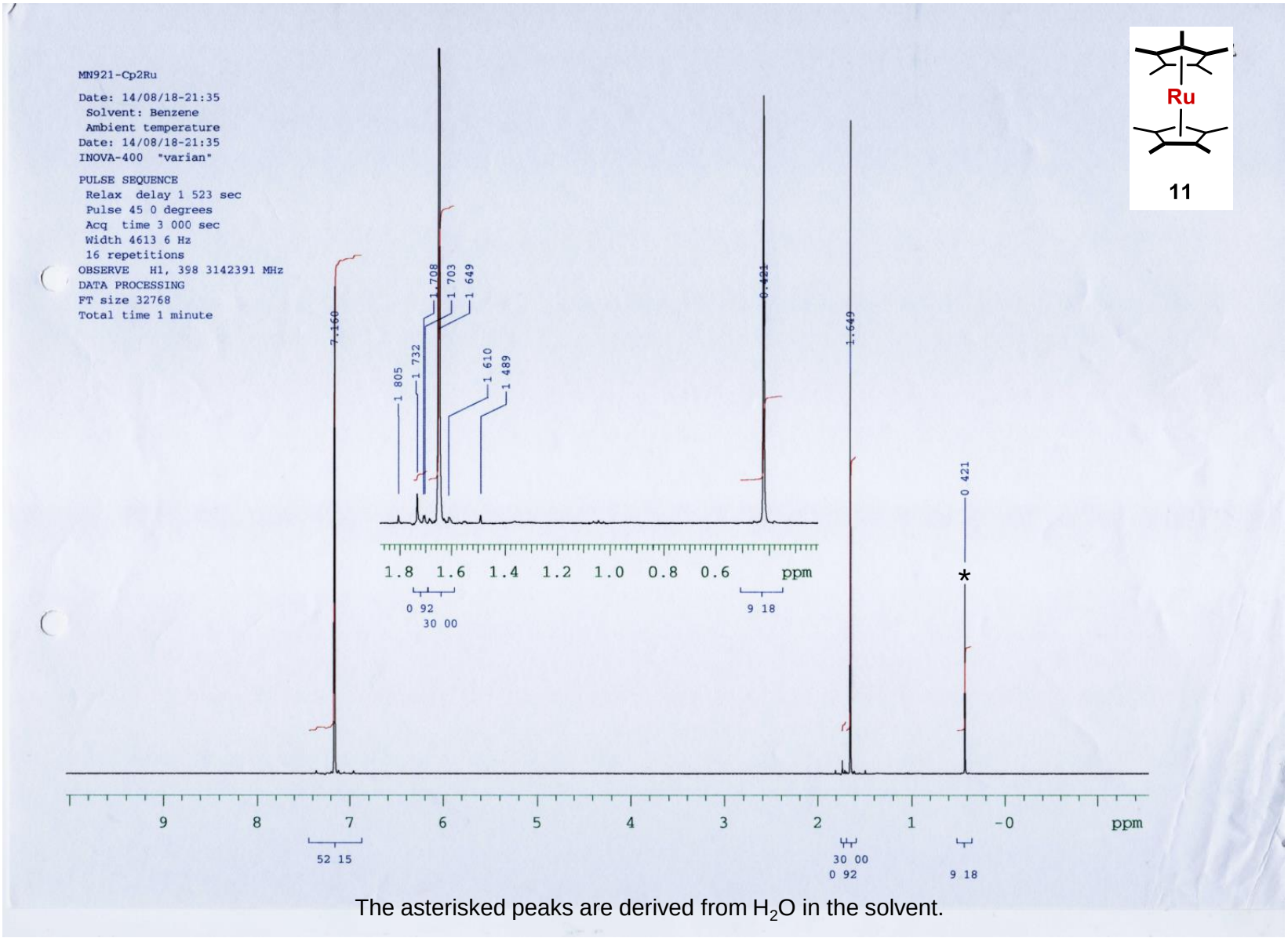
The asterisked peaks are derived from impurities which were formed by the side-reactions of **16** with adventitious O_2 in the NMR tube.

Figure S-10. ^{1}H NMR spectrum of **10** (400 MHz, rt, Benzene-d_6).



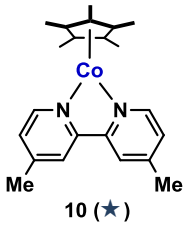
The asterisked peaks are derived from 4,4´-dimethyl-2,2´-bipyridine which was formed by the side-reactions of **10** with adventitious O_2 in the NMR tube.

Figure S-11. ^{1}H NMR spectrum of **11** (400 MHz, rt, Benzene-d_6).

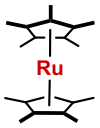


The asterisked peaks are derived from H_2O in the solvent.

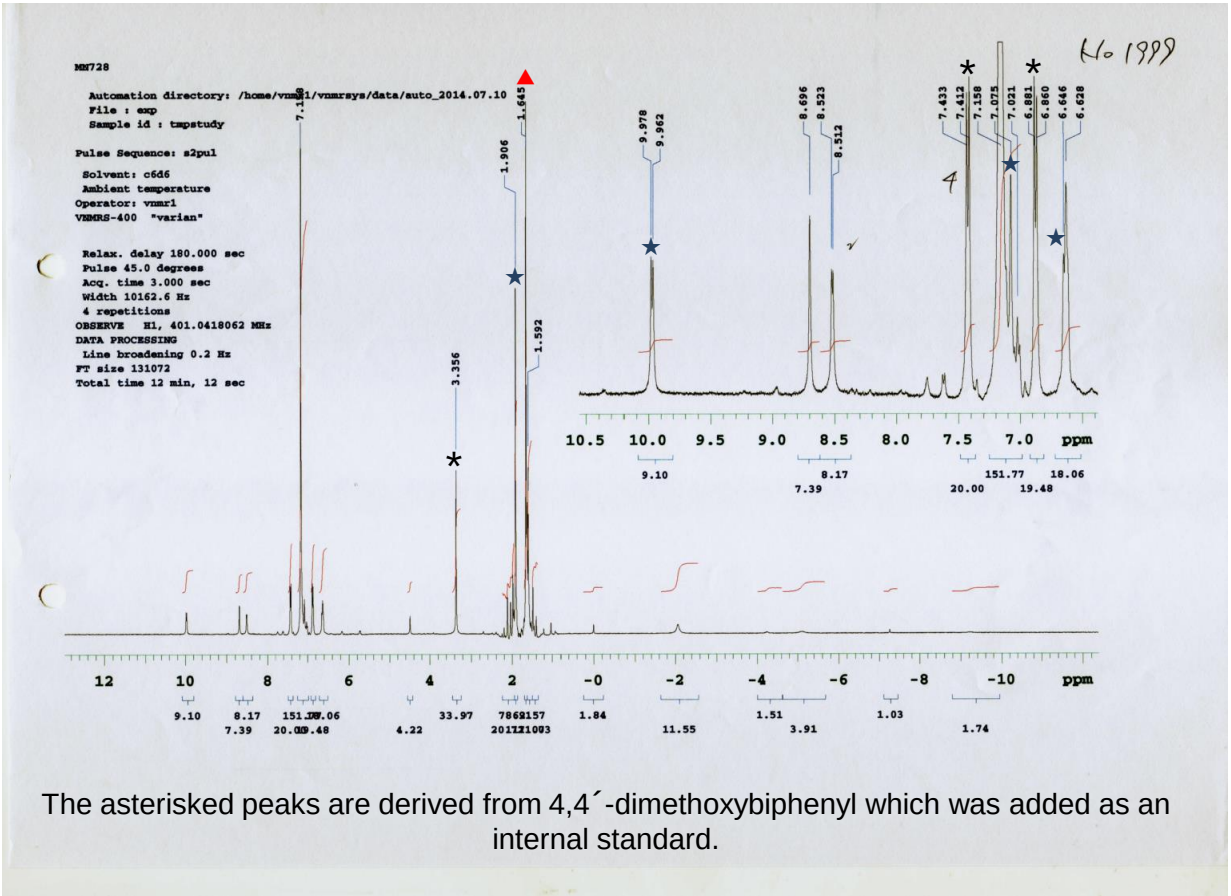
Figure S-12. ^{1}H NMR spectrum of the reaction mixture at the end of the catalytic reaction. (400 MHz, rt, Benzene-d_6).



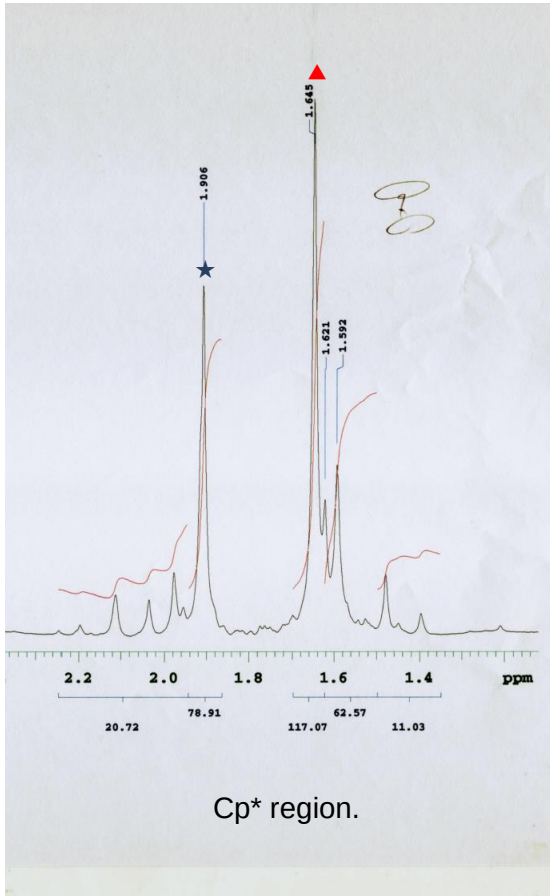
10 (★)



11 (▲)



The asterisked peaks are derived from 4,4´-dimethoxybiphenyl which was added as an internal standard.



Cp* region.

4. VT-NMR spectra of 15

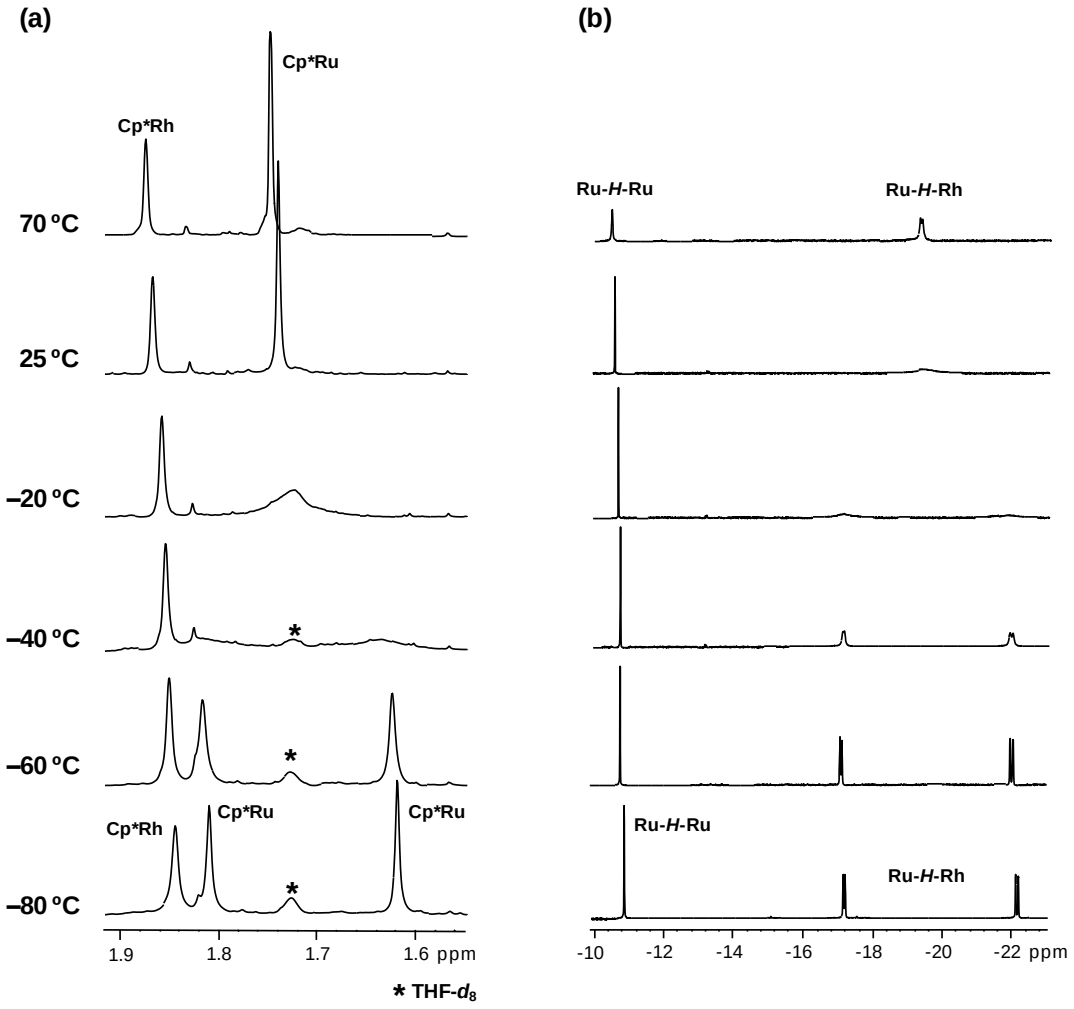
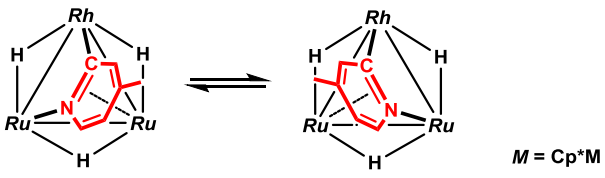


Figure S-13. VT-NMR spectra of **15** showing Cp* regions (a) and hydrido regions (b) (400 MHz, THF-d_8).



Scheme S-1. Dynamic Behavior of the μ_3-pyridyl ligand of **15**.

5. Results of the DFT calculations on 12, 13, and 13´

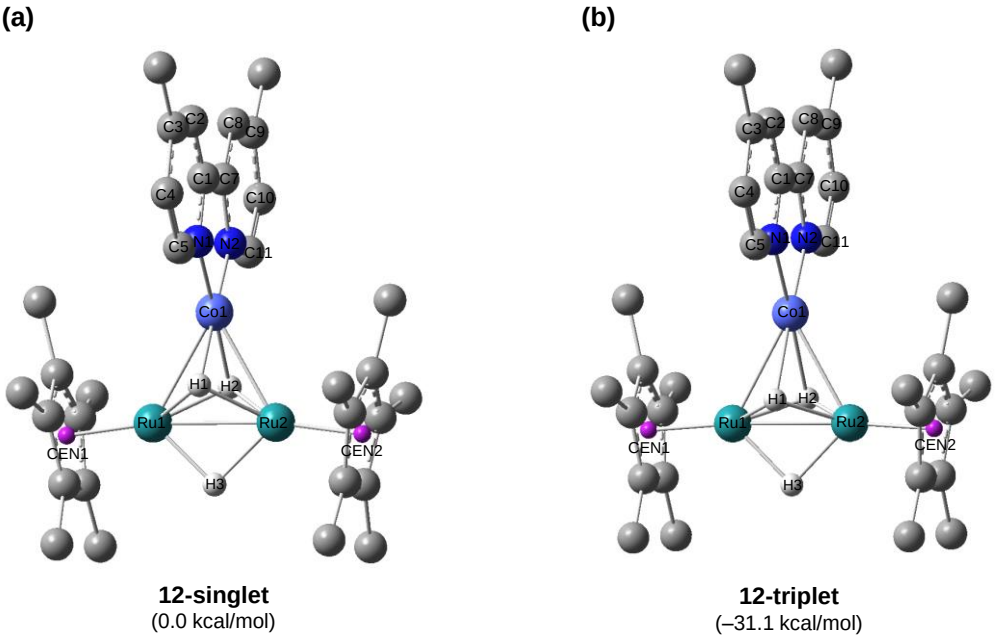
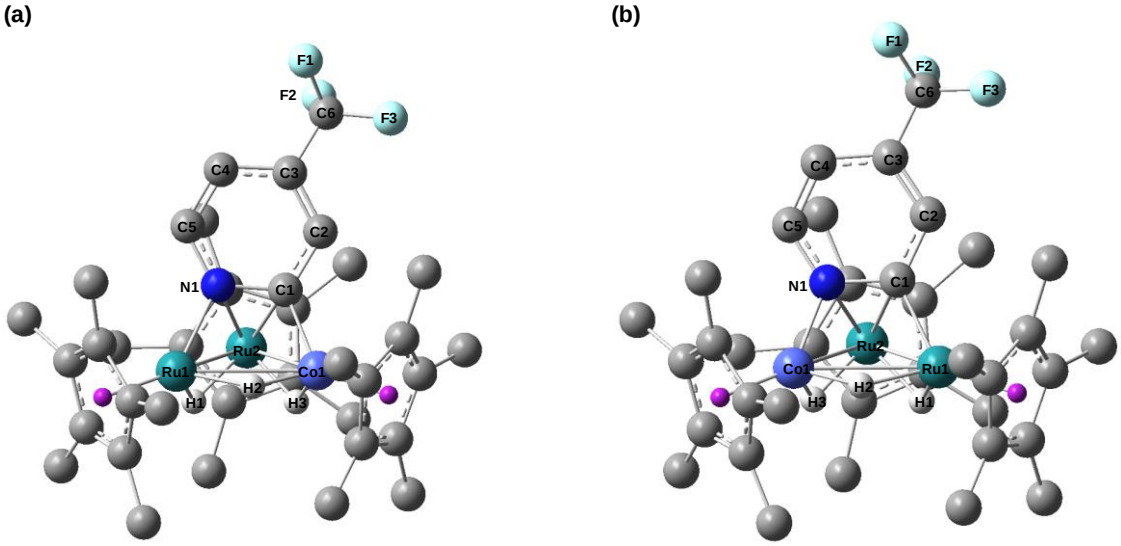


Figure S-14. Calculated structures and relative energies for **12-singlet** (a) and **12-triplet** (b). Hydrogen atoms bonded to the carbon atoms were omitted for clarity.

Table S-3. Selected geometric parameters for the calculated structures for **12-singlet** and **12-triplet**.

	12-singlet	**12-triplet**	cf. **12** (X-ray)
(a) Bond Lengths (Å)			
Ru1–Co1	2.5506	2.5876	2.5618(3)
Ru2–Co1	2.5434	2.5869	2.5558(3)
Ru1–Ru2	2.5428	2.5035	2.5087(2)
Co1–N1	1.8567	2.0147	1.9710(18)
Co1–N2	1.8569	2.0147	1.9718(17)
N1–C1	1.3682	1.3721	1.367(3)
N2–C7	1.3682	1.3720	1.370(3)
C1–C7	1.4487	1.4468	1.458(3)
Co1–H1	1.8682	2.1509	–
Co1–H2	1.8700	2.1453	–
Ru1–CEN1	1.8015	1.8089	1.7977
Ru2–CEN2	1.8035	1.8089	1.7975
(b) Bond Angles (º)			
Ru1–Co1–Ru2	59.891	57.869	58.709(8)
Co1–Ru1–Ru2	59.914	61.051	60.526(8)
Ru1–Ru2–Co1	60.195	61.080	60.765(8)
Ru2–Ru1–CEN1	172.531	176.082	178.70
Ru1–Ru2–CEN2	172.378	176.058	178.52



13
(0.0 kcal mol^{-1})

13´
(+1.1 kcal mol^{-1})

Figure S-15. Calculated structures and relative energies for **13** (a) and **13´** (b). Hydrogen atoms bonded to the carbon atoms were omitted for clarity.

Table S-4. Selected geometric parameters for the calculated structures for **13** and **13´**.

	13	**13´**	cf. **13** (X-ray)
(a) Bond Lengths (Å)			
Ru1–Co1	2.9073	2.8754	2.8822(4)
Ru2–Co1	2.7090	2.6998	2.6987(4)
Ru1–Ru2	2.8251	2.8137	2.8063(3)
Ru1–N1	2.0714	2.8639	2.066(2)
Ru1–C1	2.9015	1.9902	–
Co1–C1	1.8844	2.7295	1.903(3)
Co1–N1	2.7404	1.9075	–
Ru2–N1	2.2382	2.1869	2.218(2)
Ru2–C1	2.1721	2.2808	2.152(3)
N1–C1	1.3951	1.4031	1.406(3)
C1–C2	1.4304	1.4387	1.435(4)
C2–C3	1.3699	1.3672	1.363(4)
C3–C4	1.4263	1.4276	1.427(4)
C4–C5	1.3621	1.3616	1.355(4)
C5–N1	1.3780	1.3764	1.383(3)
(b) Bond Angles (°)			
Ru1 –Co1–Ru2	60.278	60.522	60.271(10)
Co1–Ru1–Ru2	56.381	56.649	56.624(9)
Co1–Ru2–Ru1	63.341	62.829	63.106(10)

6. Molecular structure of 10

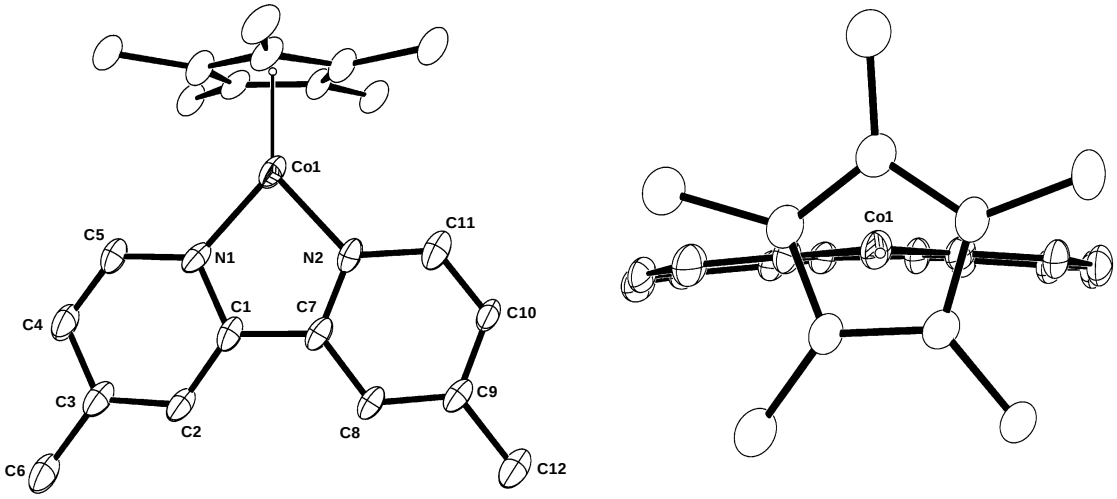


Figure S-16. Molecular structure and labeling of **10** with ellipsoids set at 30% probability.

Table S-5. Selected bond distances (Å) and angles (º) for **10**

Co1-N1	1.872(7)	Co1-N2	1.861(6)	N1-C1	1.376(10)
C1-C2	1.420(10)	C2-C3	1.368(11)	C3-C4	1.399(12)
C4-C5	1.382(11)	C5-N1	1.368(9)	C1-C2	1.420(10)
C2-C3	1.368(11)	C3-C4	1.399(12)	C5-N1	1.368(9)
N2-C7	1.377(9)	C7-C8	1.406(10)	C8-C9	1.377(10)
C9-C10	1.407(11)	C10-C11	1.342(11)	C11-N2	1.378(10)
C1-C7	1.425(10)				
N1-Co1-N2	83.0(3)	Co1-N1-C1	115.3(5)	N1-C1-C7	113.4(7)
C1-C7-N2	111.4(7)	C7-N2-Co1	116.9(5)		

7. Crystallographic data for 9, 10, 12, 13, 15 and 16

Table S-6. Crystallographic data for **9**, **10**, **12**, **13**, **15** and **16**.

	9	**10**	**12**	**13**	**15**
(a) Crystal Data					
Empirical Formula	$C_{32}H_{42}N_2O_2Ru_2$	$C_{22}H_{27}CoN_2$	$C_{32}H_{45}CoN_2Ru_2 \cdot C_{12}H_{15}$	$C_{36}H_{51}CoF_3NRu_2$	$C_{36}H_{54}NRhRu_2$
Formula Weight	688.82	378.39	878.01	815.85	805.84
Crystal Description	Platelet	Platelet	Platelet	Block	Platelet
Crystal Color	Black	Purple	Green	Green	Purple
Crystal size (mm)	0.38 × 0.18 × 0.06	0.18 × 0.11 × 0.04	0.17 × 0.09 × 0.03	0.10×0.09×0.03	0.11 × 0.05 × 0.02
Crystallizing Solution	Diethyl ether (–30 ºC)	Diethyl ether (–20 ºC)	*m*-Xylene (–30 °C)	Heptane (–30 ºC)	Acetone/Toluene = 2/1 (–30 °C)
Crystal System	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$ (#14)	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)	$P2_1/n$ (#14)
Lattice Parameters	12.0336(4)	9.3575(12)	11.7127(6)	9.0941(4)	13.8717(5)
a (Å)	8.7530(3)	10.5822(12)	13.9723(6)	10.9854(5)	17.7171(5)
b (Å)	28.6544(8)	10.6591(12)	14.2409(8)	17.6963(8)	14.1363(6)
c (Å)	–	113.522(3)	73.4000(16)	84.2500(12)	–
α (°)	102.1110(11)	106.077(4)	74.3520(18)	88.1210(16)	104.1440(14)
β (°)	–	93.945(4)	70.2350(14)	80.3400(16)	–
V (Å^3)	2950.99(16)	910.47(18)	2062.78(18)	1733.84(13)	3368.9(2)
Z value	4	2	2	2	4
D_{calc} (g/cm^3)	1.550	1.380	1.414	1.563	1.589
Measuremant Temp (ºC)	–150	–150	–145	–150	–150
μ(MoKα) (mm^{-1})	1.054	0.949	1.151	1.374	3.902
(b) Intensity Measurements					
Diffractometer	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID	RAXIS-RAPID
radiation	MoKα	MoKα	MoKα	MoKα	MoKα
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite
2θ max (º)	55	55	55	55	55
Reflections Collected	26198	6899	20662	17219	26559
Independent reflections	6743 (R_{int} = 0.0250)	3281 (R_{int} = 0.0765)	9394 (R_{int} = 0.0215)	7873 (R_{int} = 0.0294)	6383 (R_{int} = 0.0347)
Reflections Observed (> 2σ)	6084	1952	8443	6689	5196
Abs. Correction type	Empirical	Empirical	Numerical	Empirical	Empirical
Abs. Transmission	0.7662 (min.)	0.5807 (min.)	0.8981 (min.)	0.6455 (min.)	0.6381 (min.)
	1.0000 (max.)	1.0000 (max.)	0.9779 (max.)	1.0000 (max.)	1.0000 (max.)
(c) Refinement (Shelxl-97-2)					
R_1 (I<2σ(I))	0.0235	0.0783	0.0281	0.0323	0.0237
wR_2 (I<2σ(I))	0.0568	0.1833	0.0726	0.0743	0.0513
R_1 (all data)	0.0276	0.1446	0.0319	0.0412	0.0326
wR_2 (all data)	0.0587	0.2455	0.0747	0.0791	0.0555
Data/Restraints/Parameters	6743 / 0 / 383	3281 / 0 / 254	9394 / 0 / 461	7873 / 0 / 446	6383 / 0 / 431
GOF	1.050	1.136	1.074	1.043	1.040
Lagest diff. peak and hole (e. Å^{-3})	0.698 and –0.659	0.862 and –1.037	0.898 and –0.405	0.973 and –0.621	0.575 and –0.431

Table S-6. Crystallographic data for **9**, **10**, **12**, **13**, **15** and **16**. (Continued)

	16
(a) Crystal Data	
Empirical Formula	$C_{36}H_{54}IrNRu_2$
Formula Weight	895.14
Crystal Description	Platelet
Crystal Color	Red
Crystal size (mm)	0.23 × 0.07 × 0.02
Crystallizing Solution	Acetone/Toluene = 2/1 (–30 °C)
Crystal System	Triclinic
Space Group	*P*-1 (#2)
Lattice Parameters	10.8621(11)
a (Å)	11.0651(9)
b (Å)	15.7699(13)
c (Å)	99.090(3)
α (°)	91.631(3)
β (°)	113.366(3)
V (Å^3)	1709.4(3)
Z value	2
D_{calc} (g/cm^3)	1.739
Measuremant Temp (ºC)	–150
μ(MoKα) (mm^{-1})	4.779
(b) Intensity Measurements	
Diffractometer	RAXIS-RAPID
radiation	MoKα
Monochromator	Graphite
2θ max (º)	55
Reflections Collected	17012
Independent reflections	7776 (R_{int} = 0.0414)
Reflections Observed (> 2σ)	6806
Abs. Correction type	Empirical
Abs. Transmission	0.5355 (min.)
	1.0000 (max.)
(c) Refinement (Shelxl-97-2)	
R_1 (I<2σ(I))	0.0504
wR_2 (I<2σ(I))	0.1279
R_1 (all data)	0.0577
wR_2 (all data)	0.1331
Data/Restraints/Parameters	7776 / 0 / 272
GOF	1.030
Lagest diff. peak and hole (e. Å^{-3})	4.626 and –2.273