Supporting Information belonging to publication

Preparation of Polynuclear NHC Complexes by Post-Synthetic Modification of Half-Sandwich Rhodium and Iridium Complexes Bearing C-Azolato Ligands

Francisco Aznarez,[a] Wen-Xi Gao,[a] Yue-Jian Lin,[a] F. Ekkehardt Hahn,*[,a,b] and Guo-Xin Jin*[,a]

[a]Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200438, P. R. China.

[b]Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany.

Table of Contents:

1. General Procedures S2

2. X-ray Diffraction Studies (XRD) S2

3. NMR Spectra S8

4. Addition of Br_2 to *trans*-1,4-dibromo-2-butene S23

5. HR-ESI Mass Spectra S24

6. References S31

1. General Procedures

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was oven dried at 100 °C. Solvents were distilled by standard procedures prior to use. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 298 K on Bruker AVANCE I 400 or VANCE-DMX 500 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane or using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz. For assignment of the NMR resonances see the numbering scheme at the molecular plots. Mass spectra were obtained with a Micro TOF II spectrometer. 1,4-Dibromobutane, *trans*-1,4-dibromo-2-butene, 1,4-bis(bromomethyl)benzene, 1,3,5-tris(bromomethyl)benzene and Br_2 were used as received from commercial sources. Complexes **1** and **2** were prepared as described previously in the literature.[1] Satisfactory microanalytical data for complexes **3**Br–**12**Br_3 could not be obtained due to the fluorine content. The record of a satisfactory $^{13}C\{^{1}H\}$ NMR spectrum of **11**Br_2 was not possible due to the low solubility of the complex in all the common solvents used in a laboratory.

2. X-Ray Diffraction Studies (XRD)

X-Ray diffraction data (XRD) for compounds **3**Br·$2CH_2Cl_2$, **4**Br, **5**Br·CH_2Cl_2·H_2O, **7**Br_2·$4CH_2Cl_2$, **8**Br_2·$4CH_2Cl_2$, **9**Br_2·$4CH_2Cl_2$ and **11**Br_2 were recorded on a Bruker APEX-II diffractometer equipped with an area detector and graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data reduction was performed using the APEX software.[2] The structure was refined by full-matrix least-squares methods based on F^2 using SHELXL-2014/7.[3] Hydrogen atoms were positioned geometrically in idealized positions and refined with isotropic displacement parameters as riding atoms. If not noted otherwise all on-hydrogen atoms were refined anisotropically. Geometrical calculations were performed using the SHELXL-2014/7 program.[3]

Table S1. Crystallographic data and structure refinement parameters for complexes **3**Br·$2CH_2Cl_2$, **4**Br, **5**Br·CH_2Cl_2·H_2O.

	3Br·$2CH_2Cl_2$	**4**Br	**5**Br·CH_2Cl_2·H_2O
formula	$C_{30}H_{35}Br_3Cl_8FIrN_4$	$C_{28}H_{29}Br_3Cl_4FIrN_4$	$C_{29}H_{33}Br_3Cl_6FN_4ORh$
Mr	1186.15	985.83	1027.93
crystal system	Triclinic	Monoclinic	Triclinic
space group	*P*-1	$P2_1/n$	*P*-1
a [Å]	10.636(3)	9.6652(12)	11.8662(13)
b [Å]	13.9904(17)	26.138(3)	11.9461(13)
c [Å]	15.5229(19)	13.6356(16)	15.5287(17)
α [º]	114.736(2)	90	72.454(2)
β [º]	100.776(2)	107.956(2)	86.588(2)
γ [º]	92.828(2)	90	60.740(2)
V [Å^3]	2039.7(7)	3276.9(7)	1820.8(3)
T [K]	193(2)	173(2)	173(2)
Z	2	4	2
ρ_{calcd} [g cm^{-3}]	1.931	1.988	1.875
μ [mm^{-1}]	6.768	7.237	4.237
F(000)	1140	1882	1008
independent reflections	0.0284	0.0592	0.0199
data/restraints/parameters	8558/6/429	7366/0/375	7740/0/411
R_1/wR_2 [I>2σ(*I*)][a]	0.0496/0.1570	0.0473/0.1039	0.0763/0.2343
R_1/wR_2 (all data)[a]	0.0645/0.1902	0.0688/0.1131	0.0960/0.2958
goodness-of-fit	1.117	1.106	1.241
largest residuals [e Å^{-3}]	2.749/-2.701	1.616/-1.274	3.013/-3.775

Table S2. Crystallographic data and structure refinement parameters for complexes **7**Br_2·$4CH_2Cl_2$, **8**Br_2·$4CH_2Cl_2$ and **9**Br_2·$4CH_2Cl_2$.

	7Br_2·$4CH_2Cl_2$	**8**Br_2·$4CH_2Cl_2$	**9**Br_2·$4CH_2Cl_2$
formula	$C_{58}H_{64}Br_4Cl_{20}F_2Ir_2N_8$	$C_{58}H_{64}Br_4Cl_{20}F_2N_8Rh_2$	$C_{56}H_{60}Br_4Cl_{16}F_2IrN_8Rh$
Mr	2324.21	2145.63	2065.07
crystal system	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1
a [Å]	11.095(2)	11.105(3)	11.1069(14)
b [Å]	11.944(3)	11.955(3)	11.9474(15)
c [Å]	15.850(3)	15.826(4)	15.827(2)
α [º]	91.503(3)	91.337(5)	91.503(2)
β [º]	100.405(3)	100.502(5)	100.293(2)
γ [º]	100.270(3)	100.203(5)	100.247(2)
V [Å^3]	2029.2(7)	2029.9(10)	2029.8(4)
T [K]	173(2)	203(2)	173(2)
Z	1	1	1
ρ_{calcd} [g cm^{-3}]	1.902	1.755	1.689
μ [mm^{-1}]	5.949	3.079	4.379
F(000)	1120	1056	1004
independent reflections	0.0553	0.0387	0.0335
data/restraints/parameters	8706/30/402	8773/20/402	7857/80/402
R_1/wR_2 [I>2σ(*I*)][a]	0.0748/0.2262	0.0701/0.2087	0.0571/0.1710
R_1/wR_2 (all data)[a]	0.1024/0.2732	0.1035/0.2586	0.0836/0.2118
goodness-of-fit	1.064	1.062	1.060
largest residuals [e Å^{-3}]	3.204/-2.851	2.347/-1.230	1.647/-1.484

Table S3. Crystallographic data and structure refinement parameters for complexes and **11**Br_2.

	11Br_2
formula	$C_{53}H_{60}Br_6Cl_{10}F_2Ir_2N_8O_3$
Mr	2113.45
crystal system	Monoclinic
space group	$P2_1/n$
a [Å]	18.5068(16)
b [Å]	14.4057(13)
c [Å]	27.924(3)
α [º]	90
β [º]	91.462(2)
γ [º]	90
V [Å^3]	7442.3(11)
T [K]	296(2)
Z	4
ρ_{calcd} [g cm^{-3}]	1.886
μ [mm^{-1}]	7.201
F(000)	4040
independent reflections	0.0655
data/restraints/parameters	16423/103/732
R_1/wR_2 [I>2σ(*I*)][a]	0.0450/0.1150
R_1/wR_2 (all data)[a]	0.1013/0.1411
goodness-of-fit	0.984
largest residuals [e Å^{-3}]	1.434/-1.005

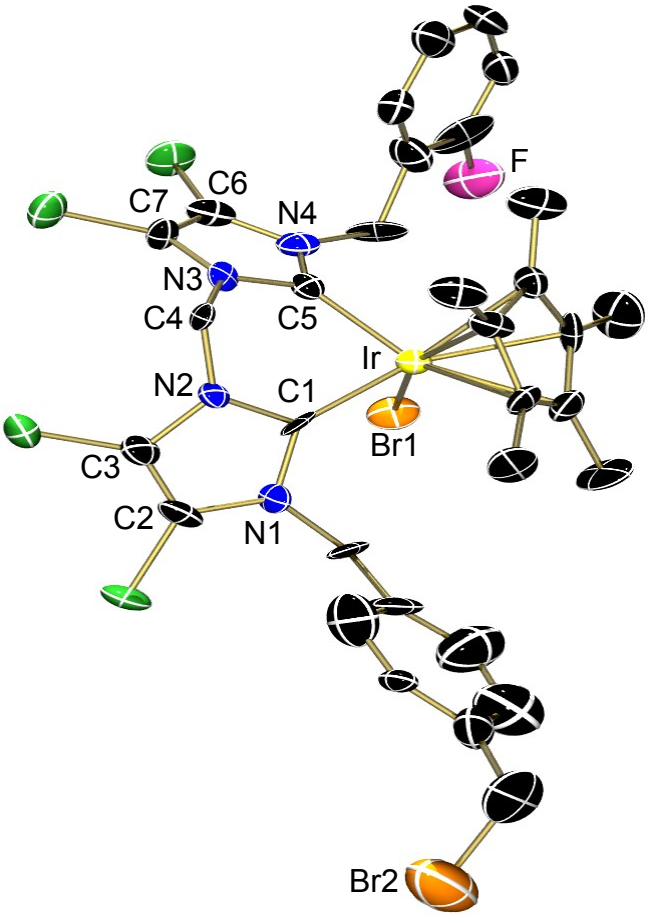


Figure S1. Molecular structure of complex cation $\mathbf{6}^{+}$. While the structure is not publishable due to the low quality of the acquired data, this figure allows the reader to get an idea of the spatial distribution of the atoms.

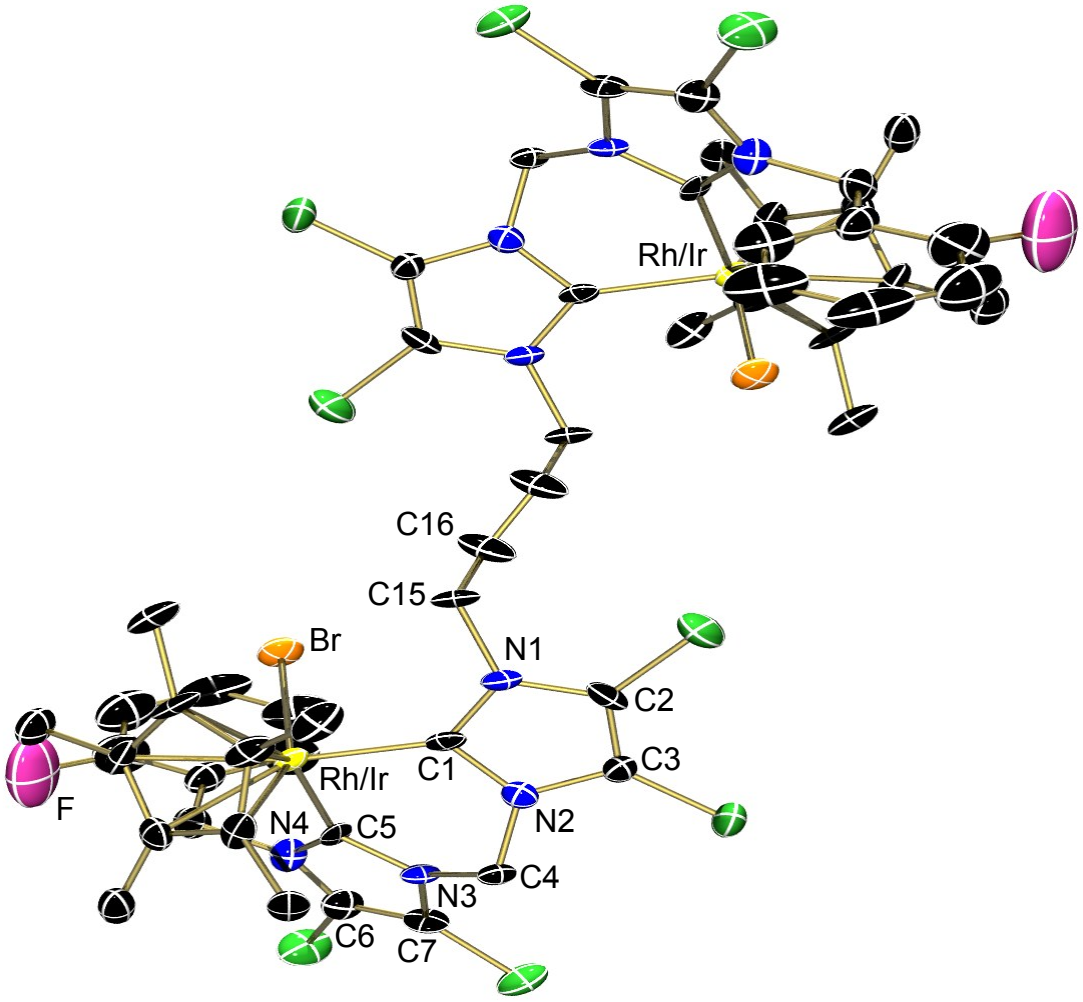


Figure S2. Molecular structure of complex cation $\mathbf{9}^{2+}$ in $\mathbf{9}Br_2 \cdot 4CH_2Cl_2$. Displacement ellipsoids are drawn at the 50% probability level (all hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir/Rh–C1 2.021(9), Ir/Rh–C5 2.056(9), N1–C1 1.330(11), N2–C1 1.349(11), N3–C5 1.312(10), N4–C5 1.343(11); Br–Ir/Rh–C1 91.6(2), Br–Ir/Rh–C5 90.7(2), C1–Ir/Rh–C5 85.3(3), N1–C1–N2 102.5(7), N3–C5–N4 105.7(8).

3. NMR Spectra

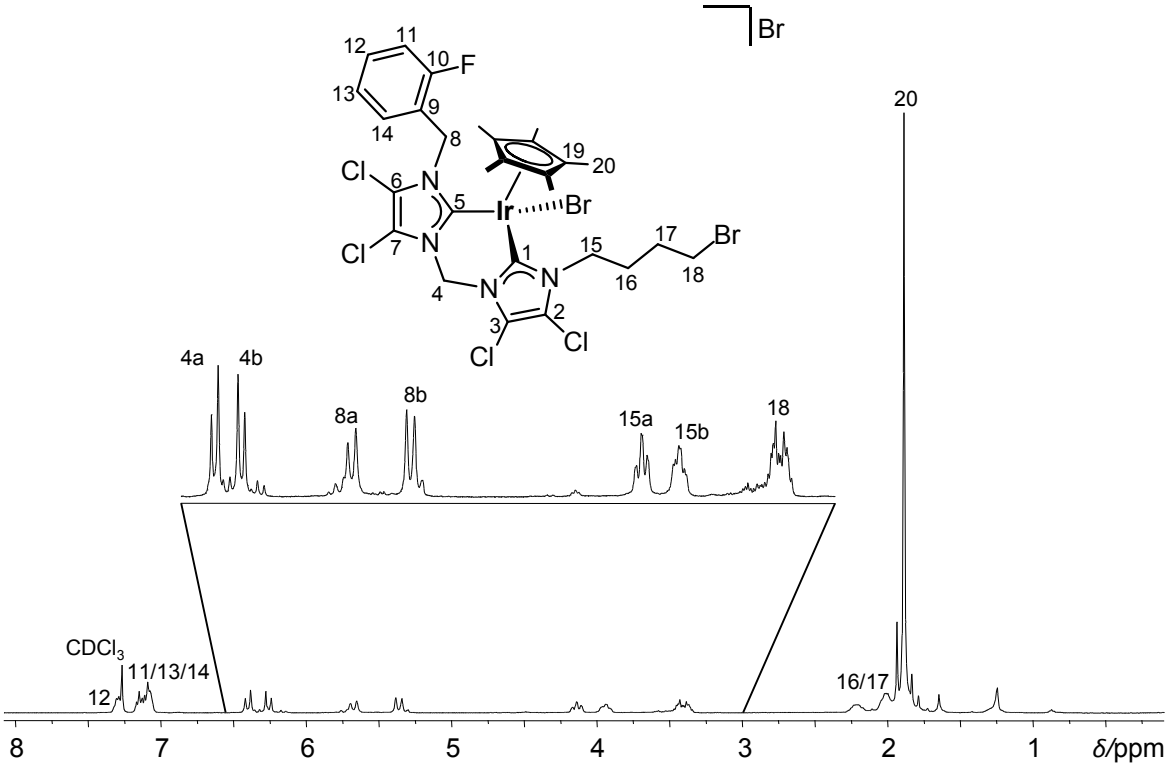


Figure S3. ^{1}H NMR spectrum of complex **3**Br in $CDCl_3$.

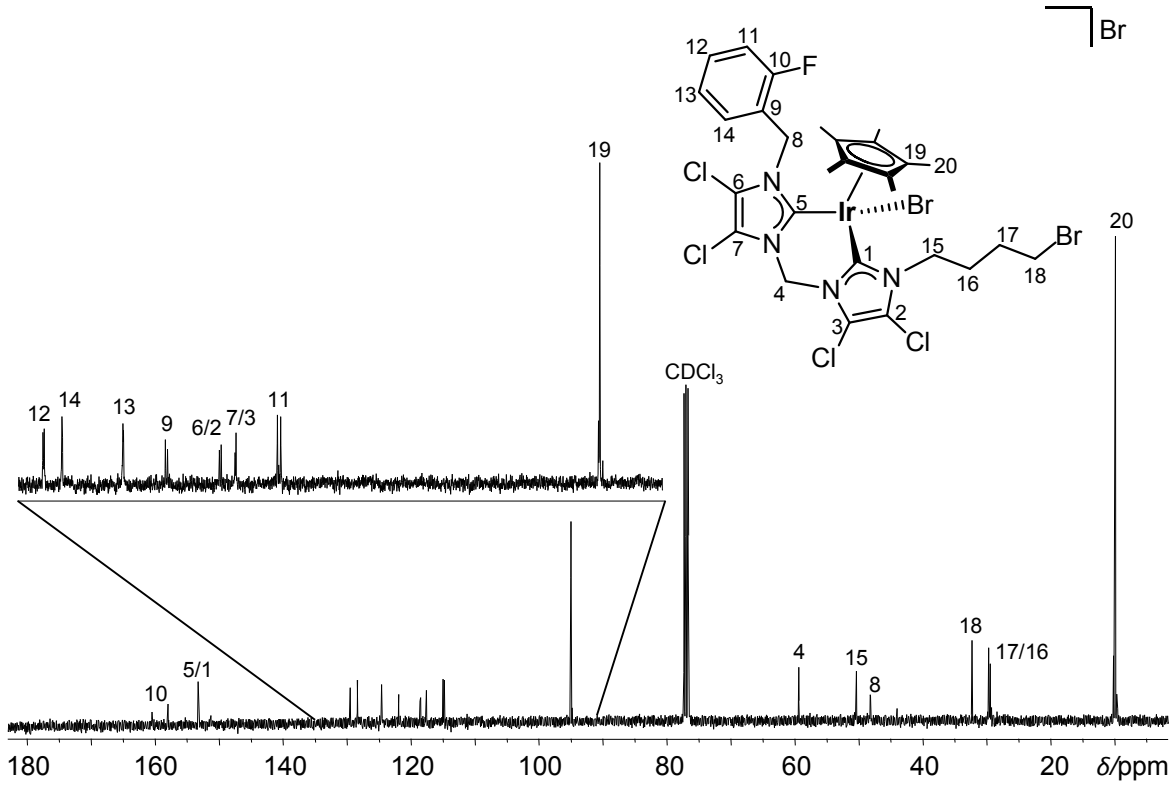


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3**Br in $CDCl_3$.

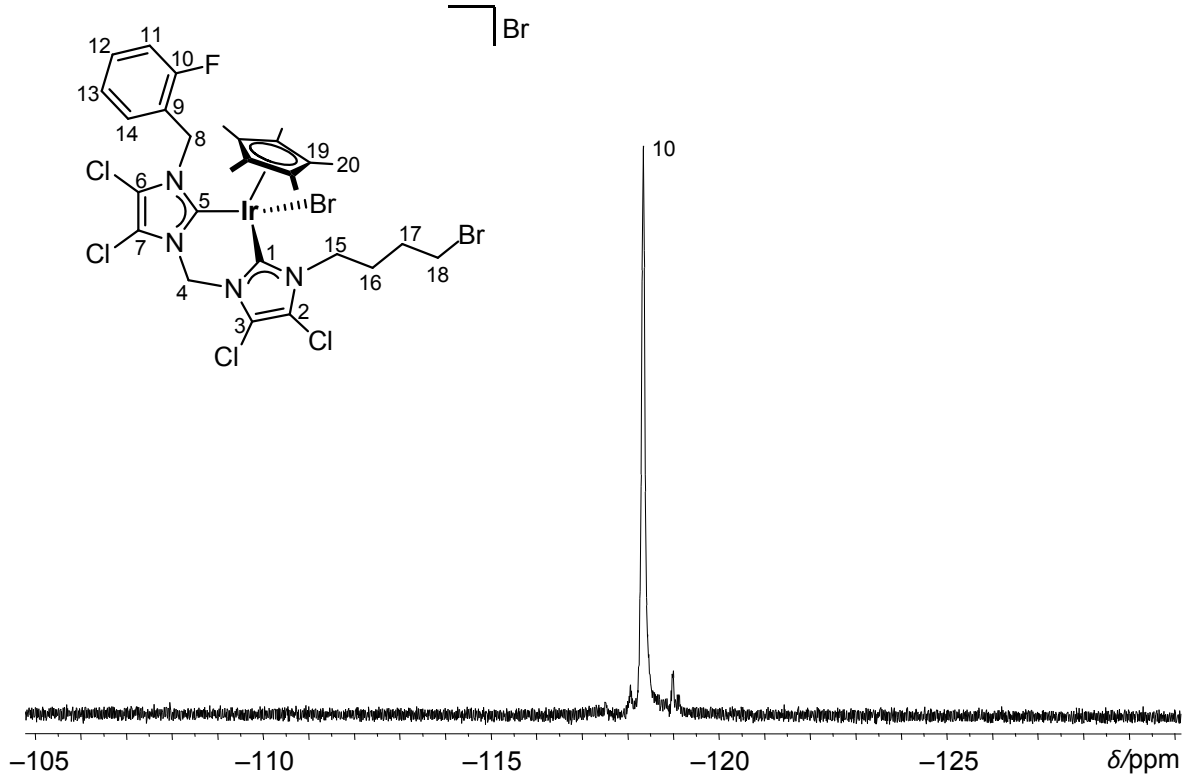


Figure S5. $^{19}F\{^{1}H\}$ NMR spectrum of complex **3**Br in $CDCl_3$.

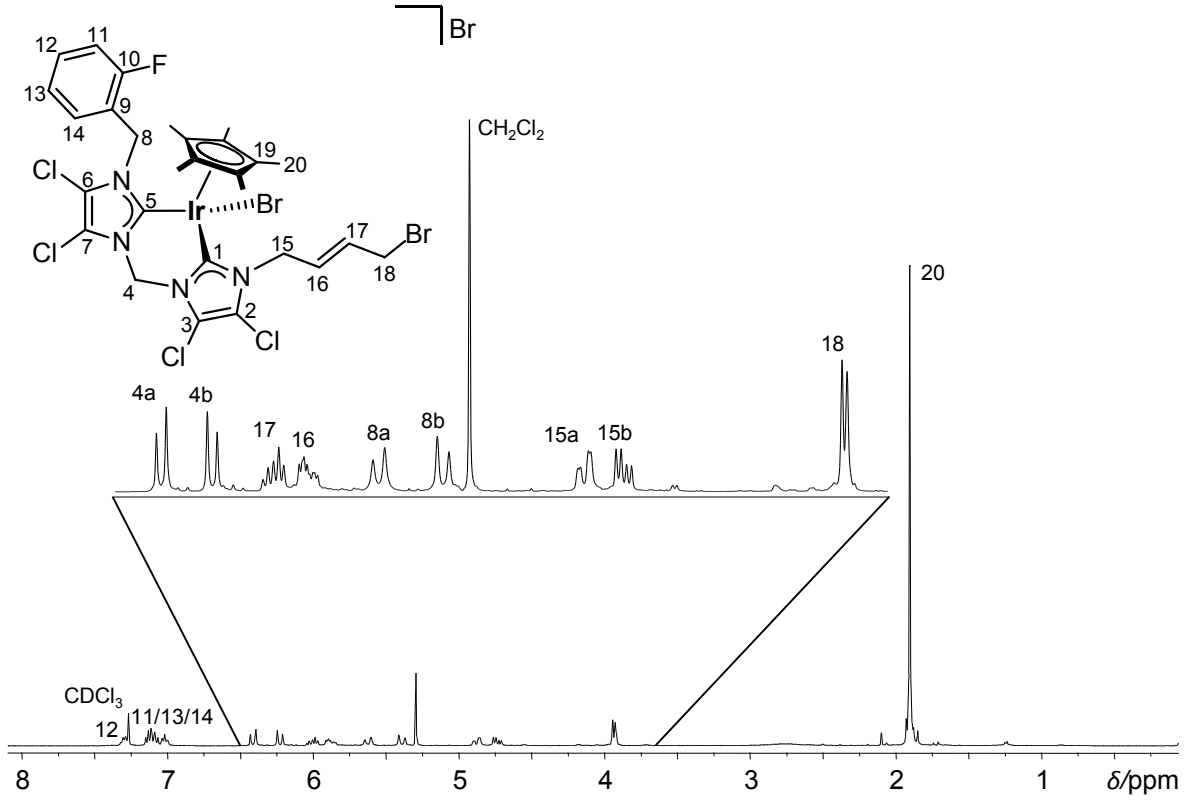


Figure S6. ^{1}H NMR spectrum of complex **4**Br in $CDCl_3$.

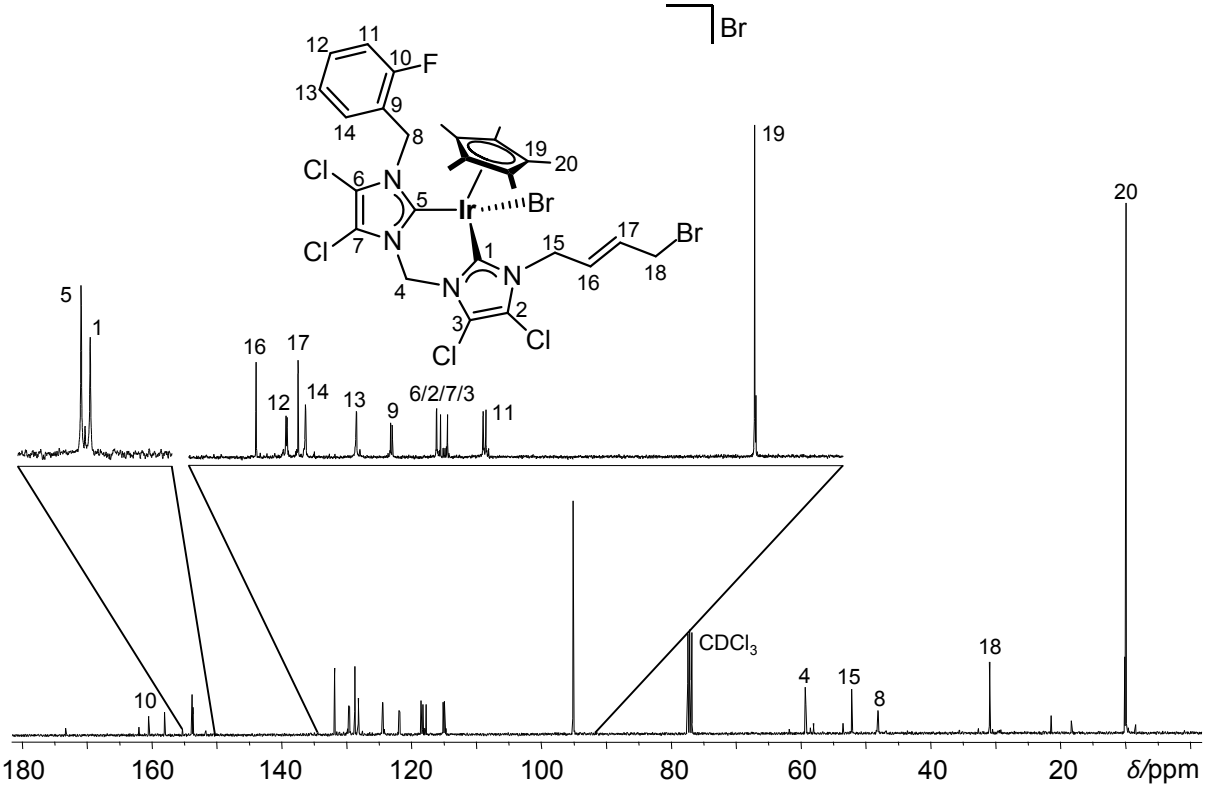


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of complex **4**Br in $CDCl_3$.

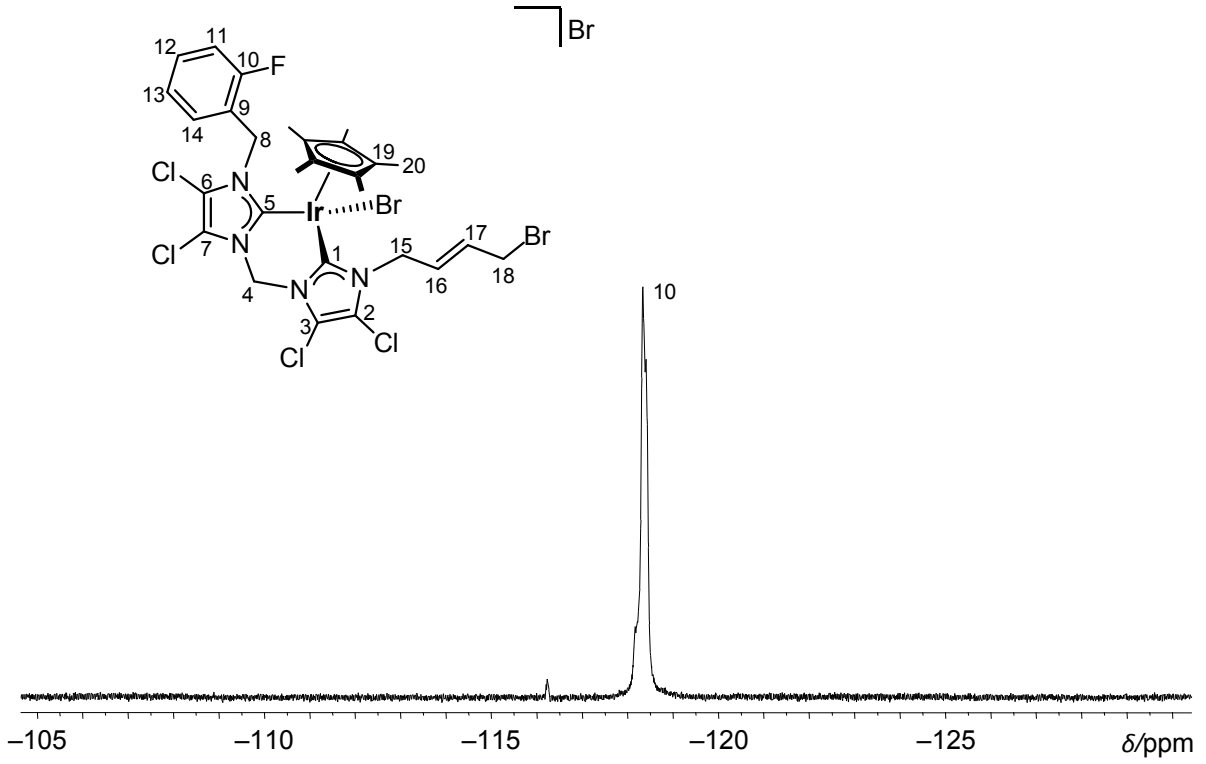


Figure S8. $^{19}F\{^{1}H\}$ NMR spectrum of complex **4**Br in $CDCl_3$.

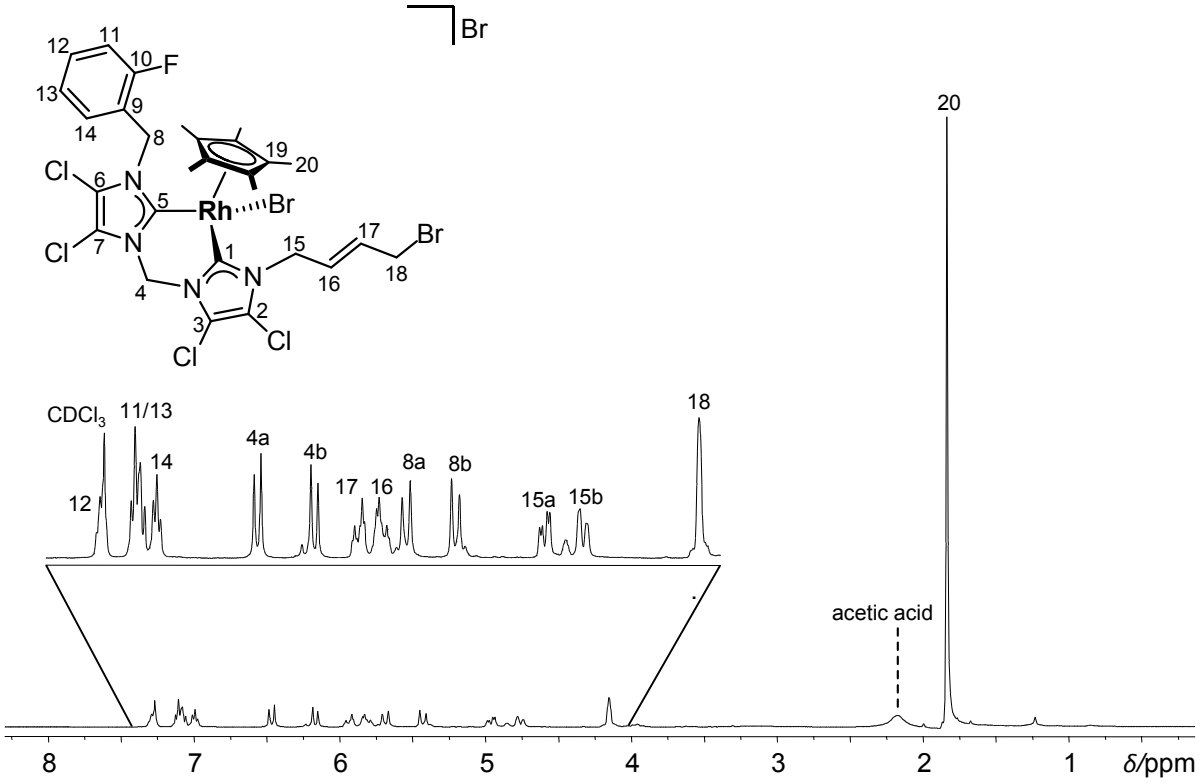


Figure S9. ^{1}H NMR spectrum of complex **5**Br in $CDCl_3$.

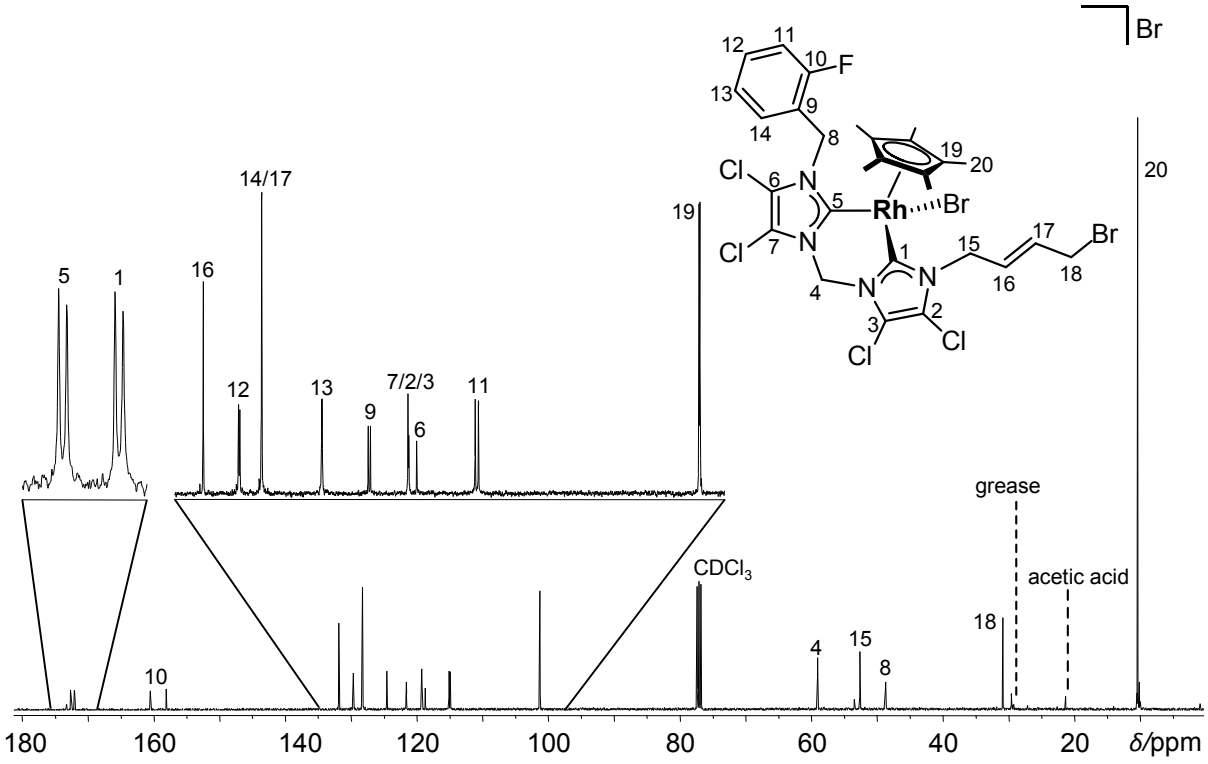


Figure S10. ^{13}C{^{1}H} NMR spectrum of complex **5**Br in $CDCl_3$.

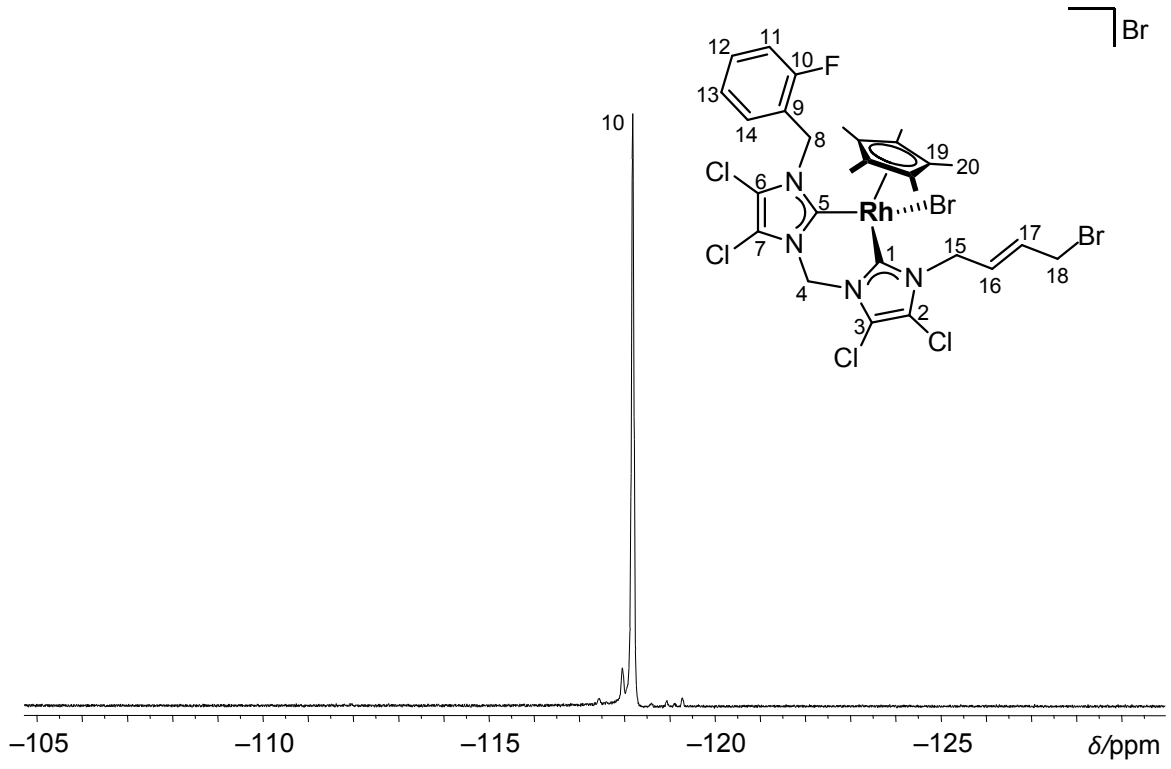


Figure S11. $^{19}F\{^{1}H\}$ NMR spectrum of complex **5**Br in $CDCl_3$.

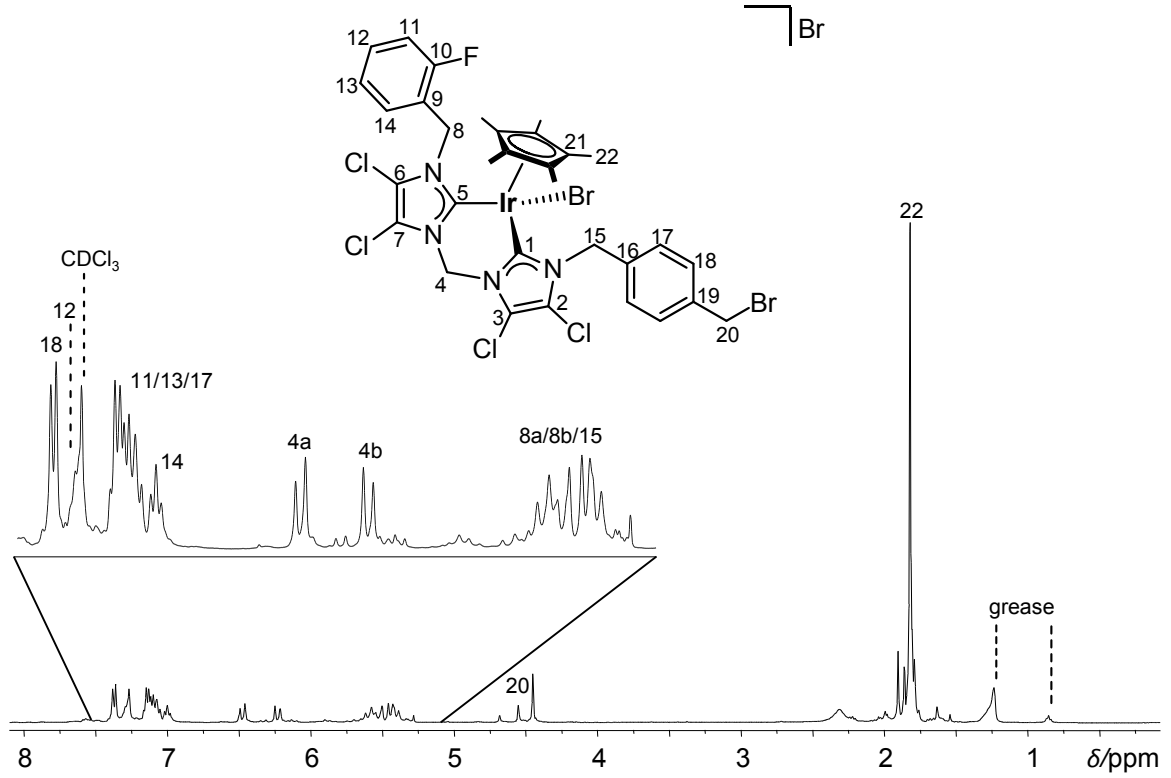


Figure S12. ^{1}H NMR spectrum of complex **6**Br in $CDCl_3$.

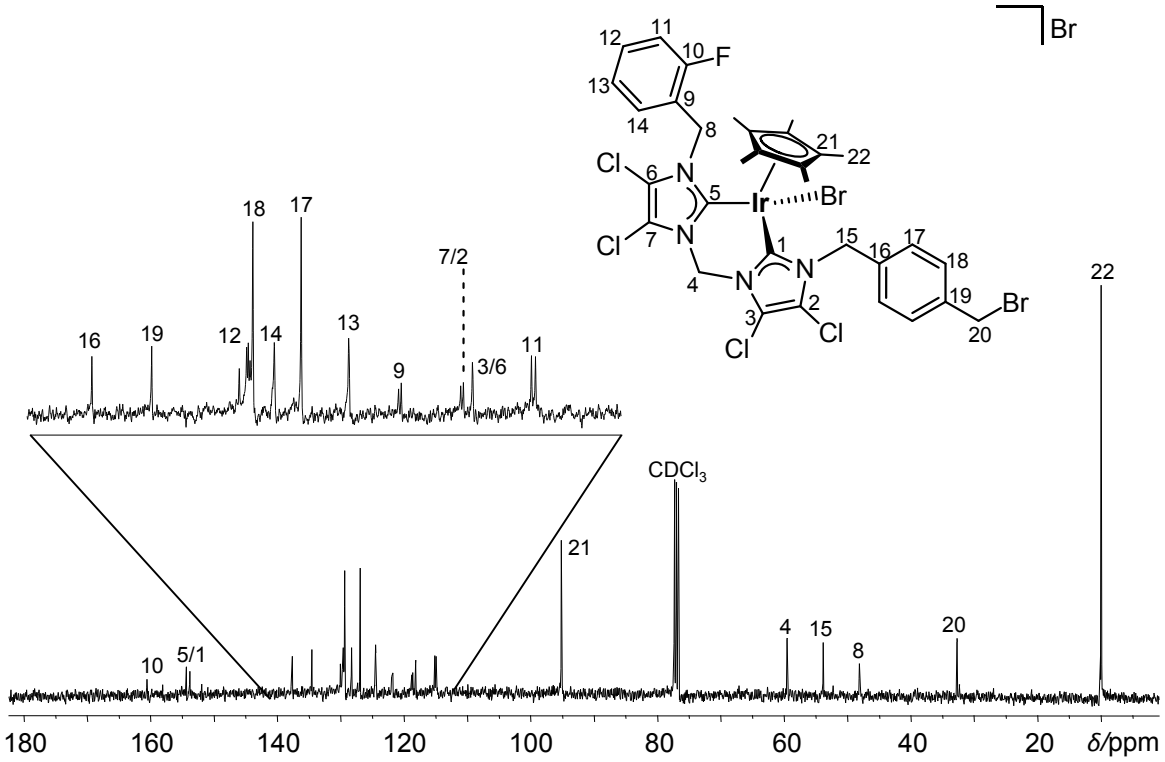


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of complex **6**Br in $CDCl_3$.

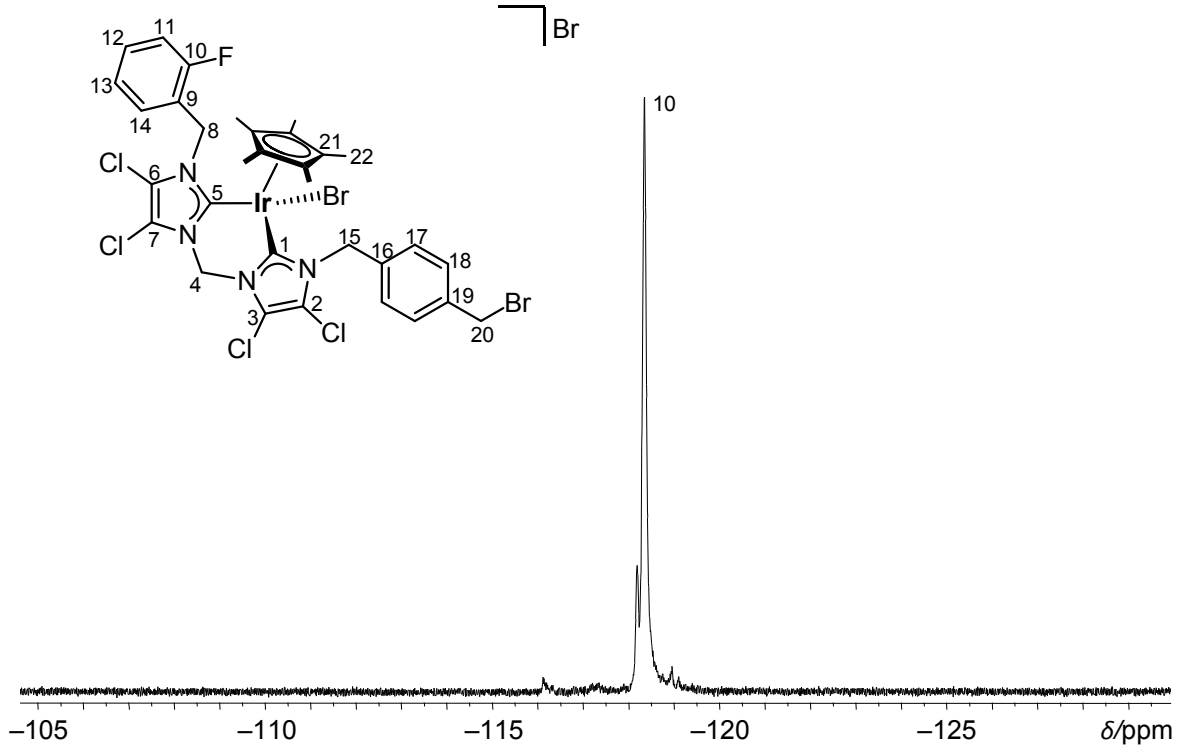


Figure S14. $^{19}F\{^{1}H\}$ NMR spectrum of complex **6**Br in $CDCl_3$.

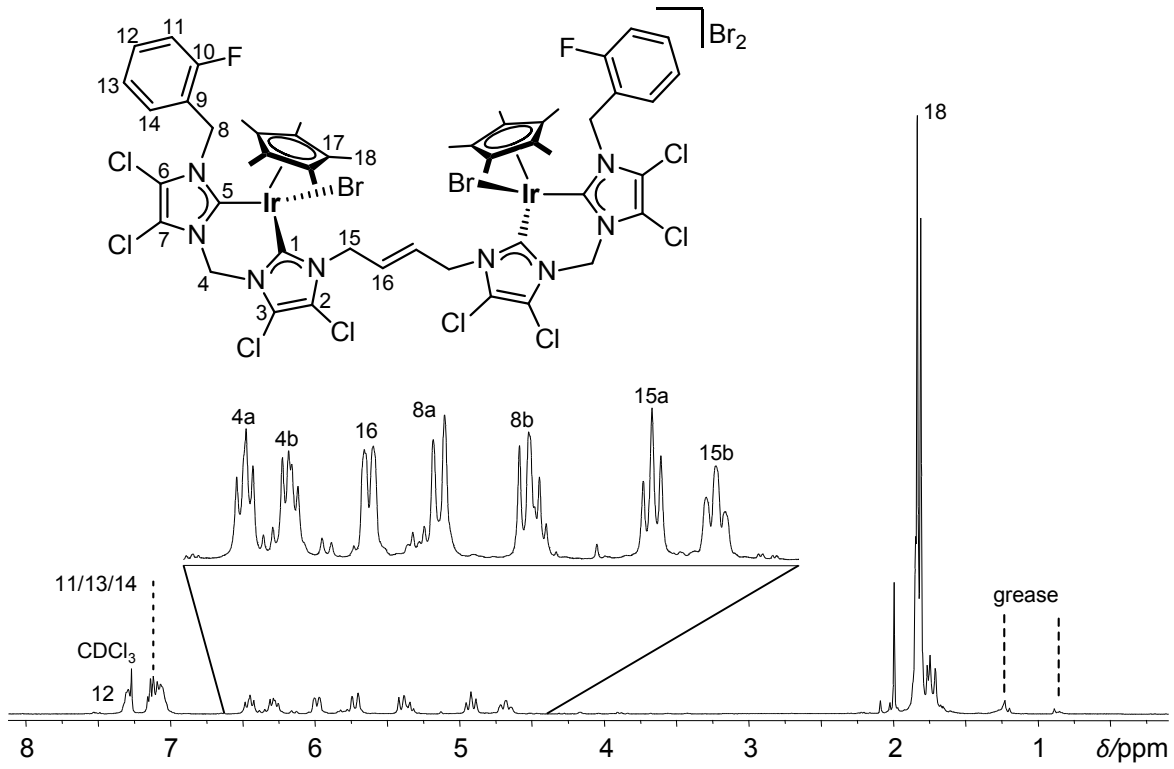


Figure S15. ^{1}H NMR spectrum of complex **7**Br_2 in $CDCl_3$.

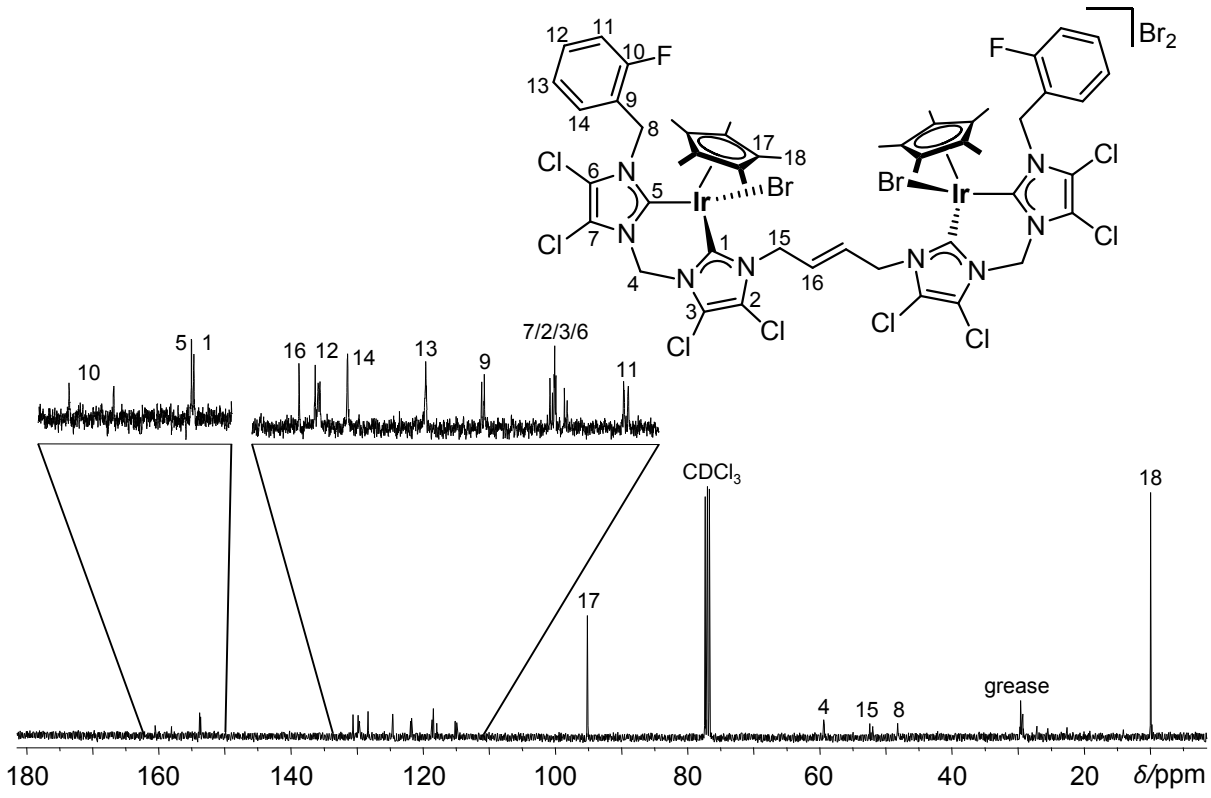


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of complex **7**Br_2 in $CDCl_3$.

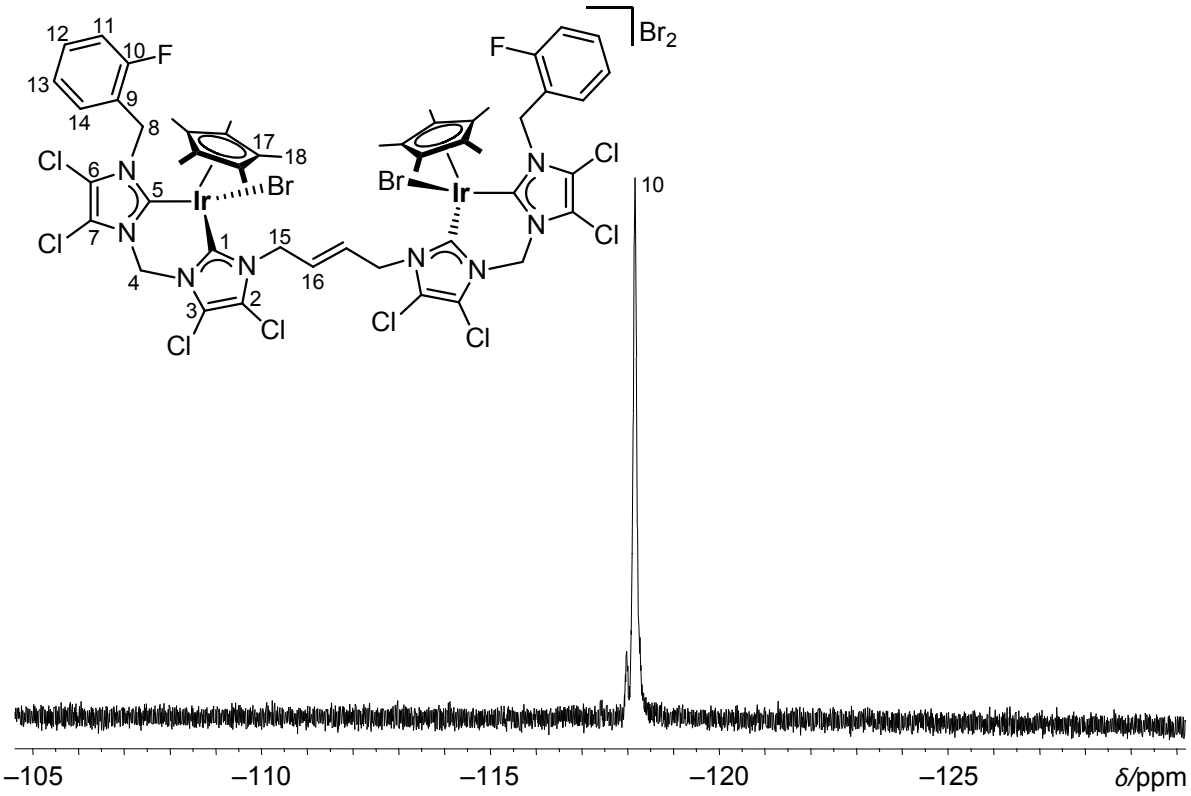


Figure S17. $^{19}F\{^{1}H\}$ NMR spectrum of complex **7**Br_2 in $CDCl_3$.

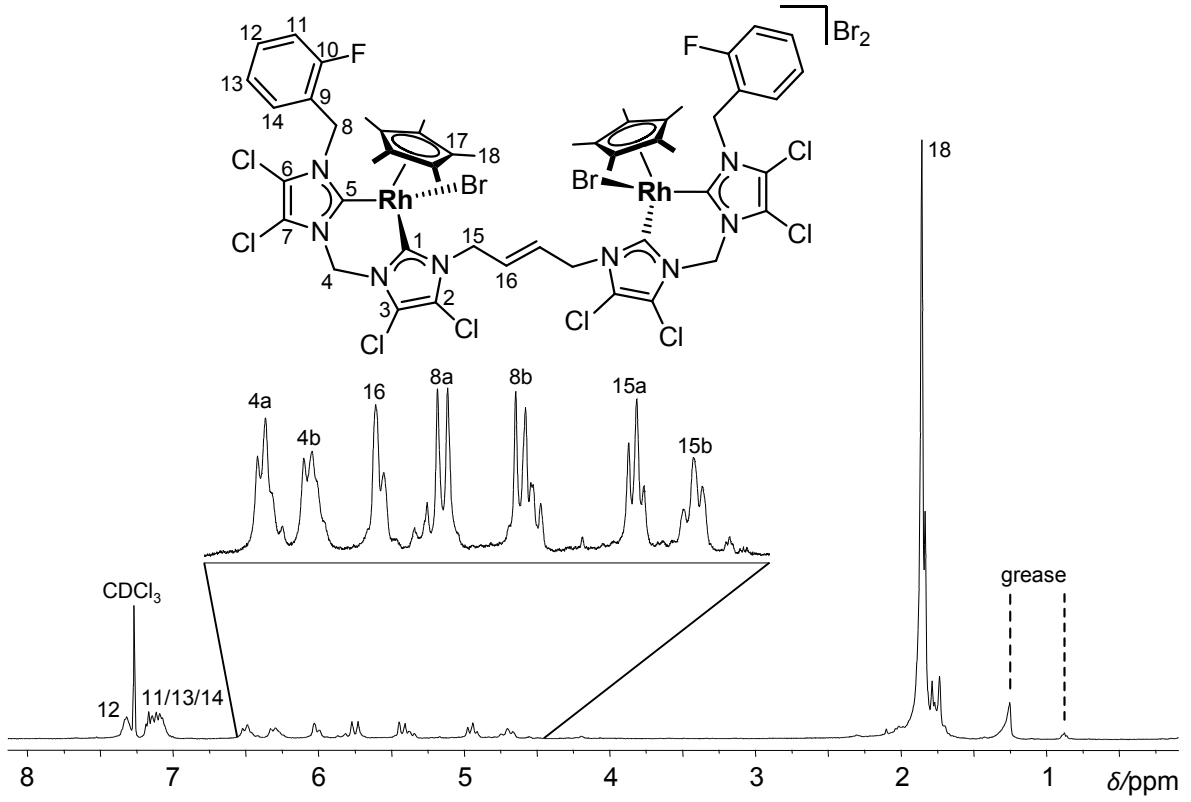


Figure S18. ^{1}H NMR spectrum of complex **8**Br_2 in $CDCl_3$.

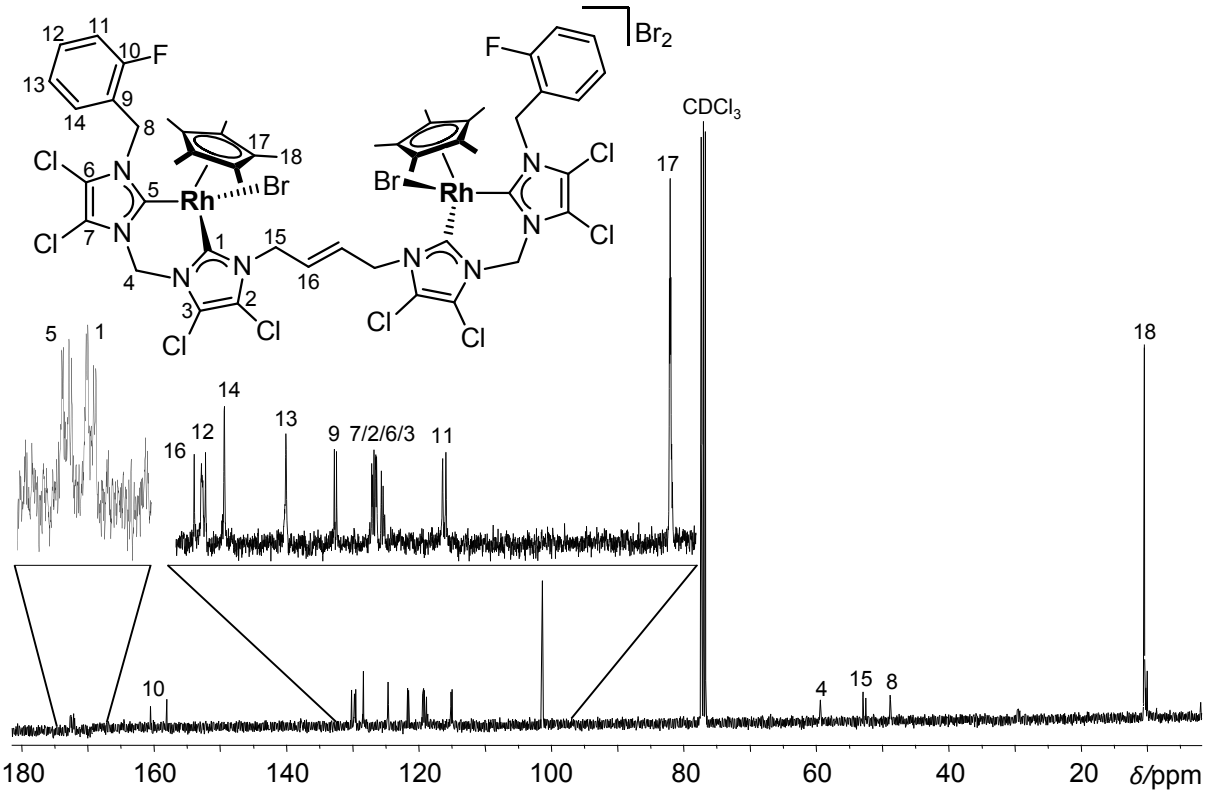


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of complex **8**Br_2 in $CDCl_3$.

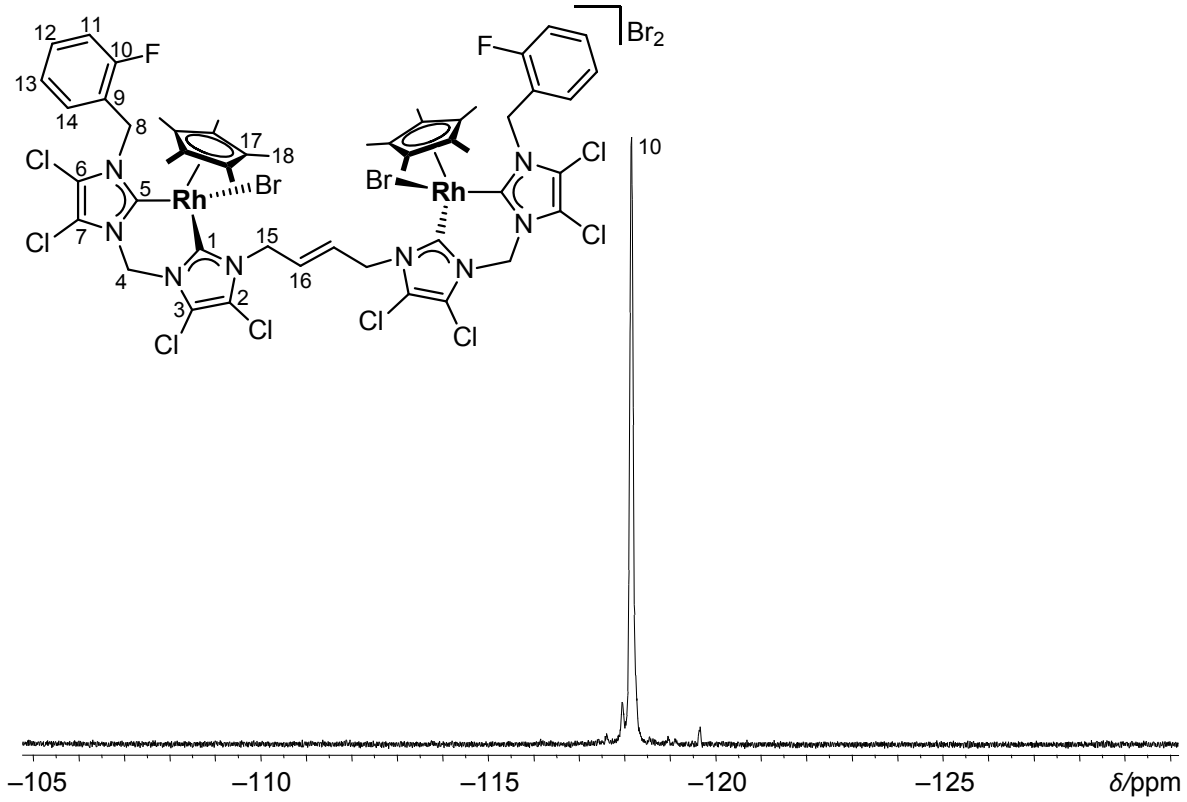


Figure. S20. $^{19}F\{^{1}H\}$ NMR spectrum of complex **8**Br_2 in $CDCl_3$.

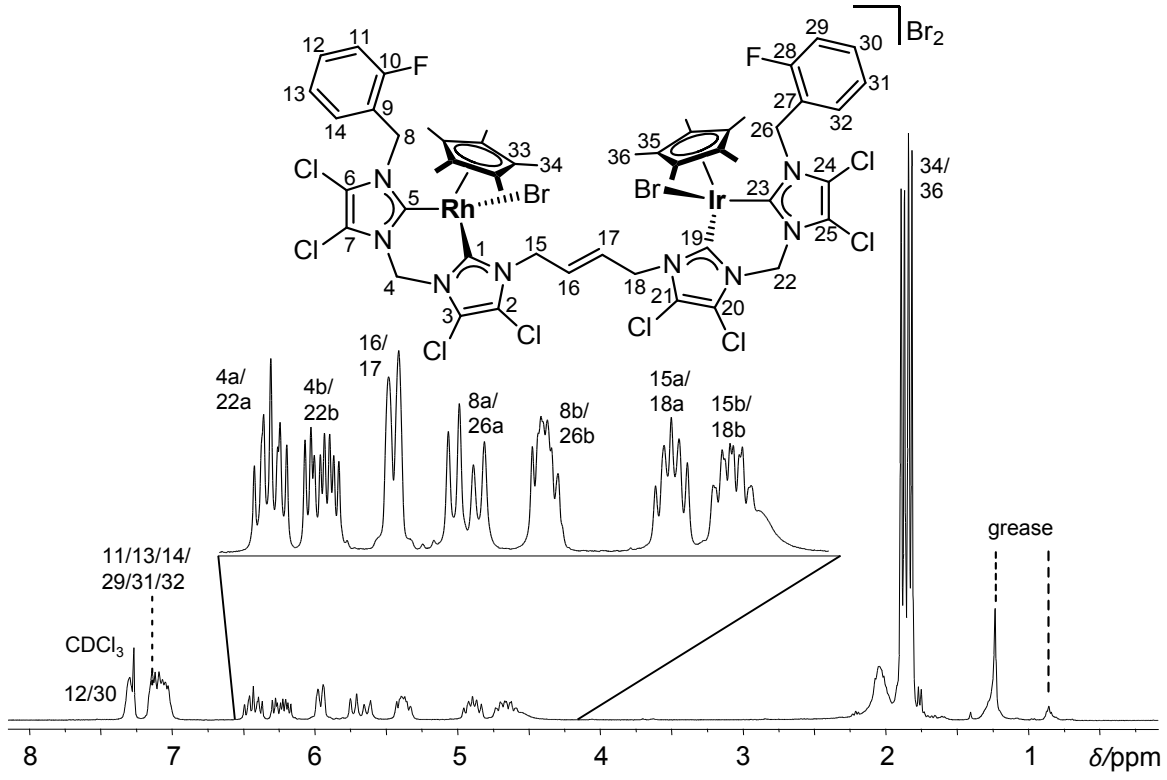


Figure S21. ^{1}H NMR spectrum of complex **9**Br_2 in $CDCl_3$.

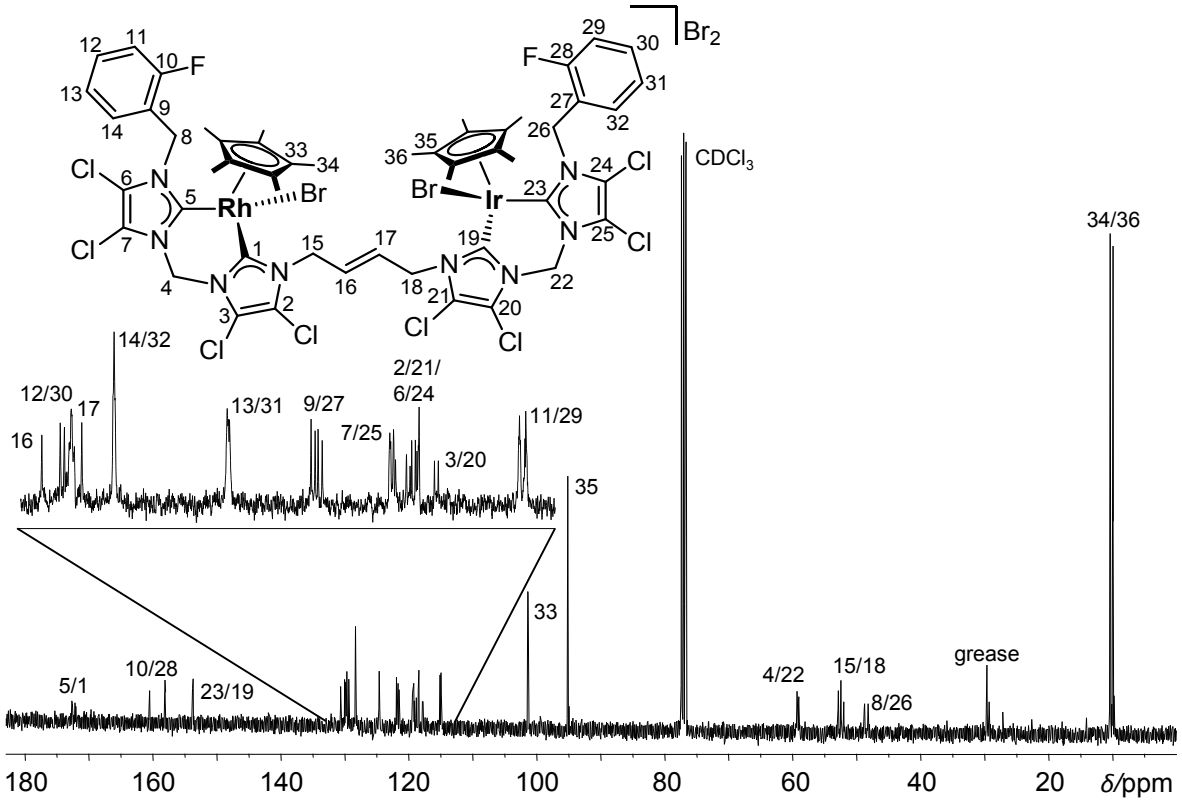


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of complex **9**Br_2 in $CDCl_3$.

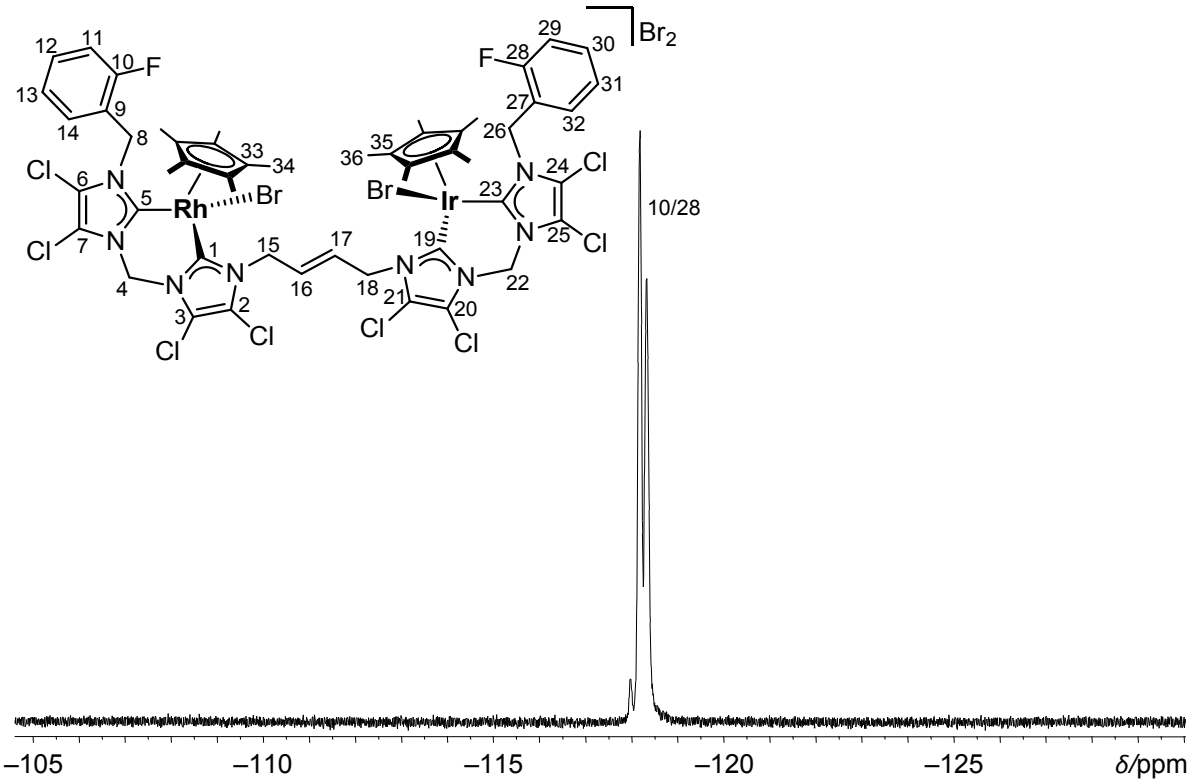


Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of complex **9**Br_2 in $CDCl_3$.

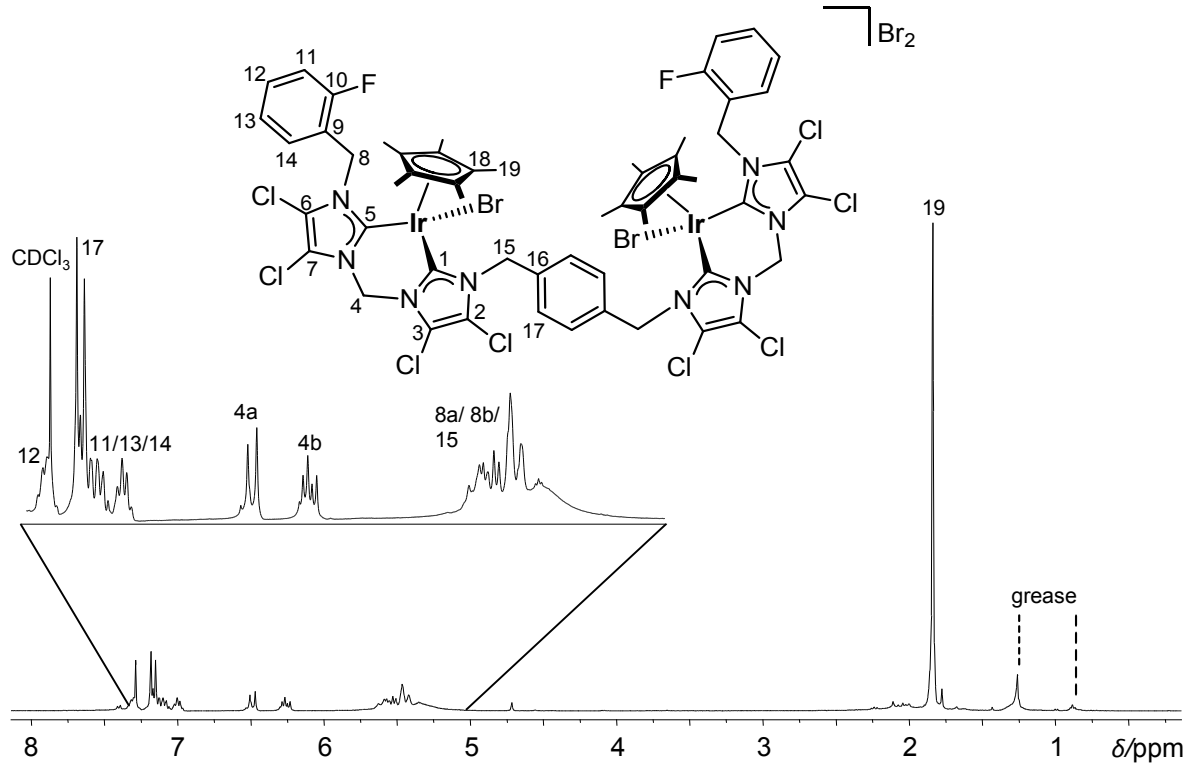


Figure S24. ^{1}H NMR spectrum of complex **10**Br_2 in $CDCl_3$.

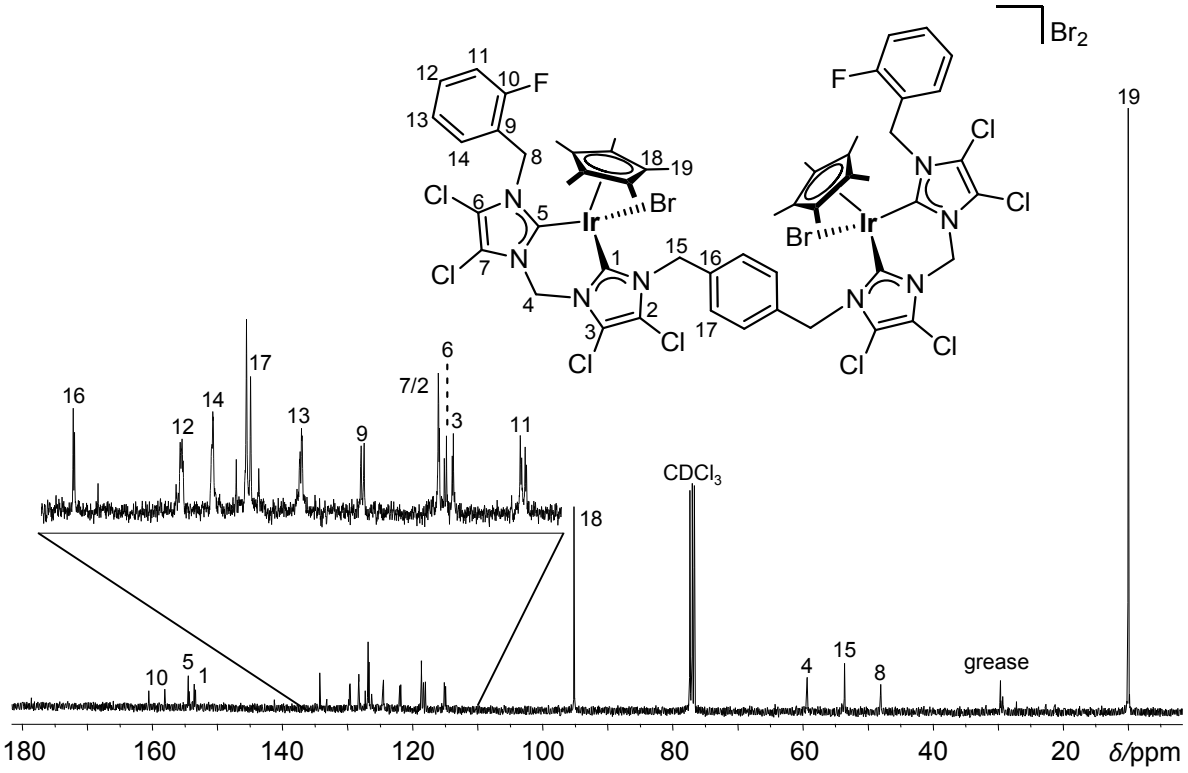


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of complex **10**Br_2 in $CDCl_3$.

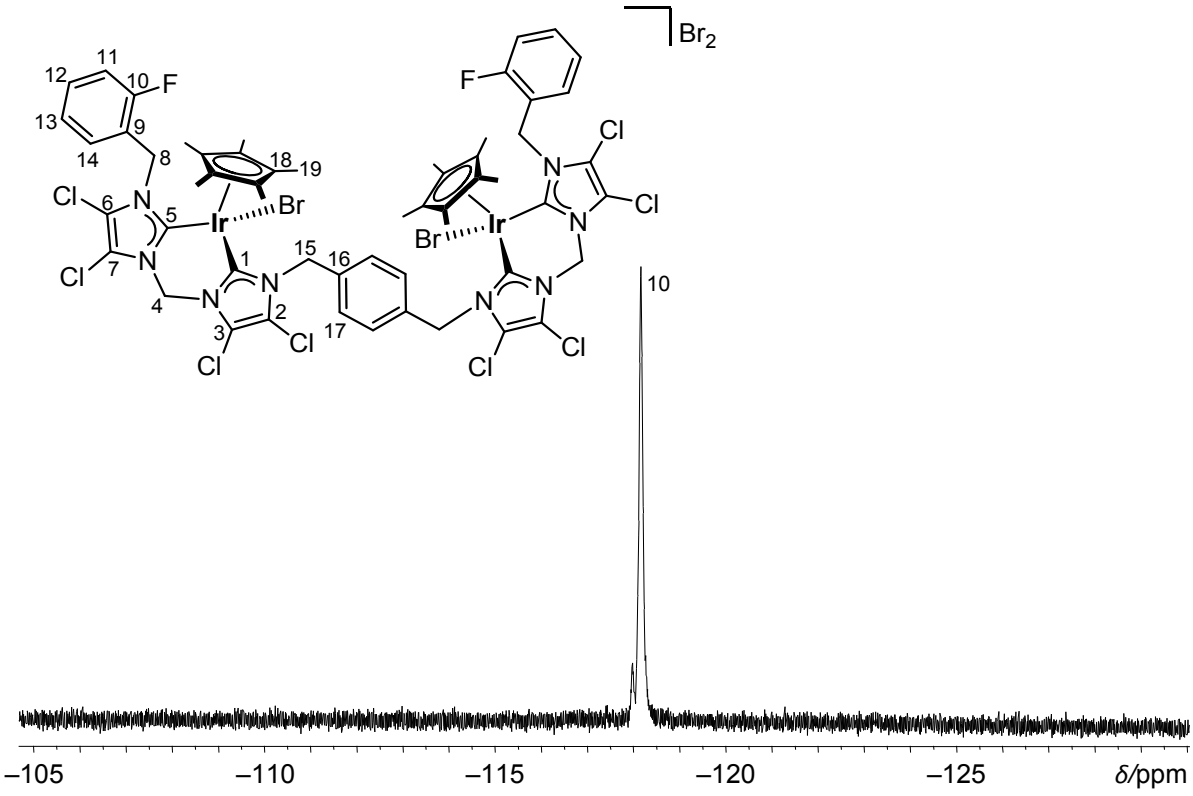


Figure S26. $^{19}F\{^{1}H\}$ NMR spectrum of complex **10**Br_2 in $CDCl_3$.

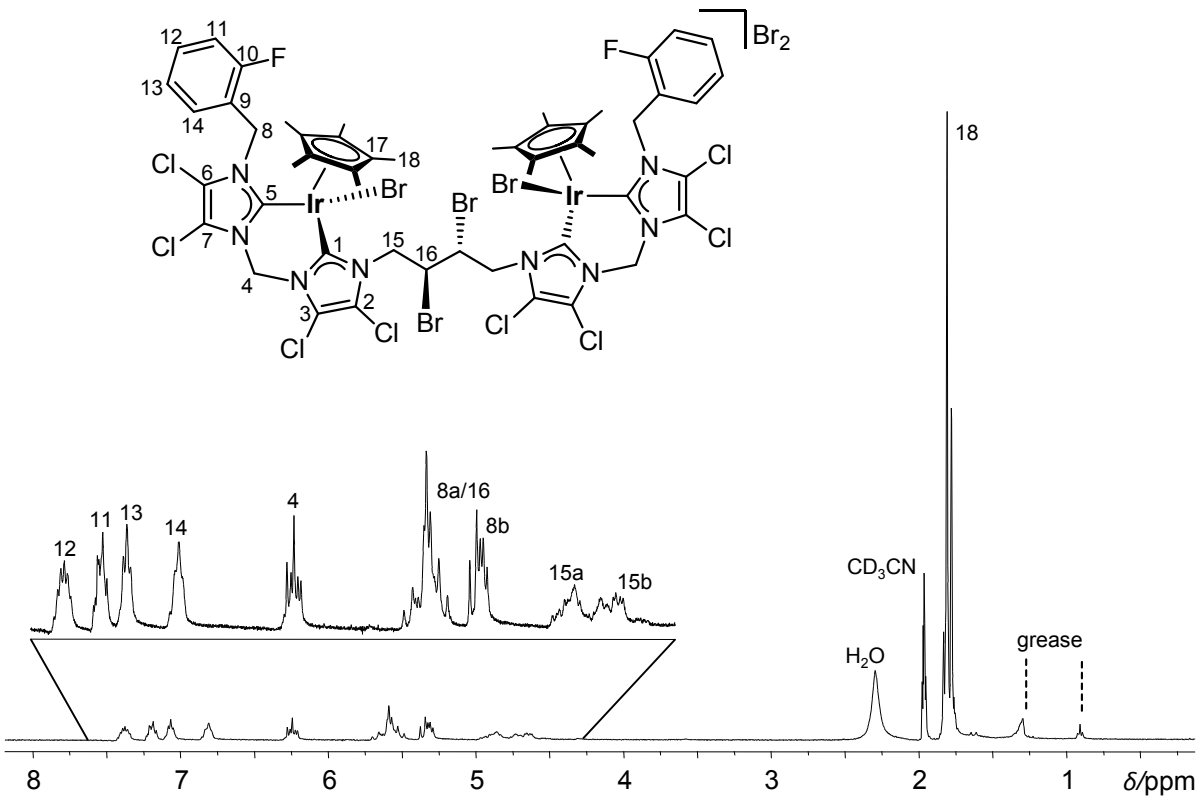


Figure S27. ^{1}H NMR spectrum of complex **11**Br_2 in CD_3CN.

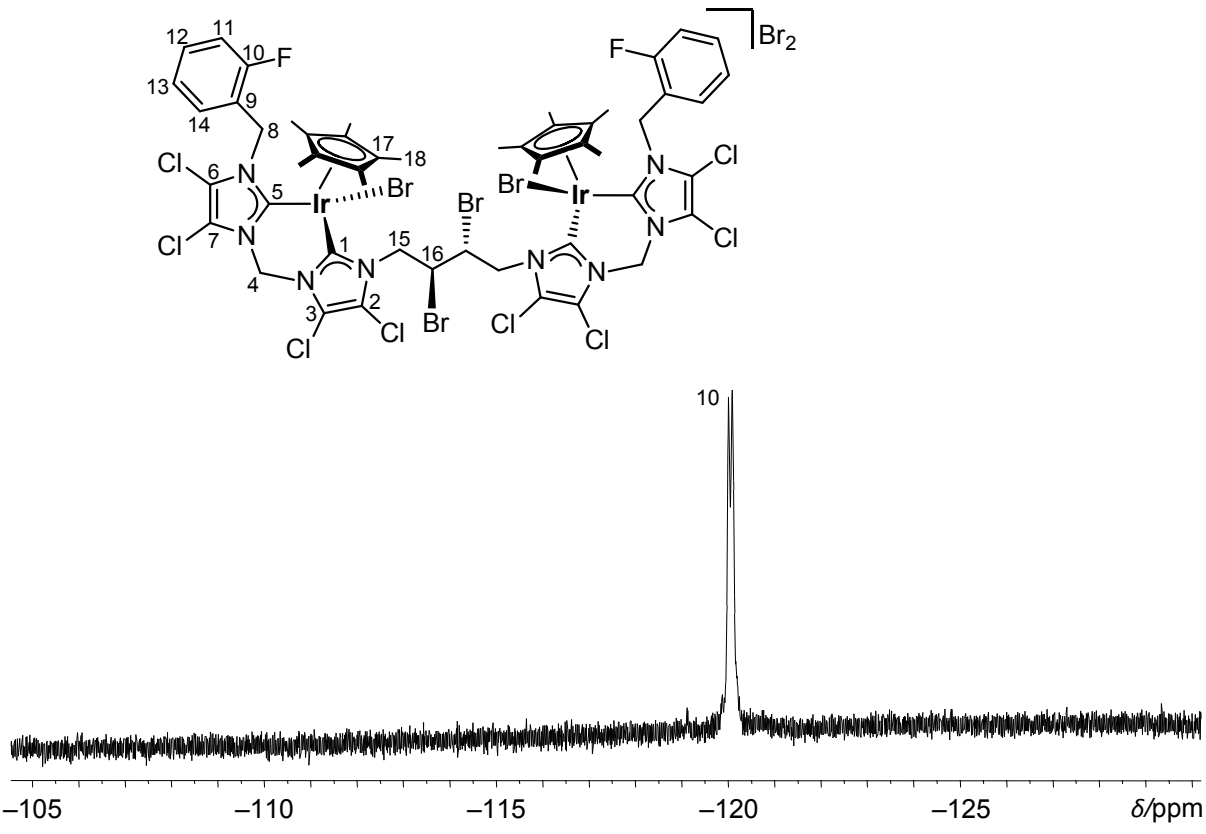


Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of complex **11**Br_2 in CD_3CN.

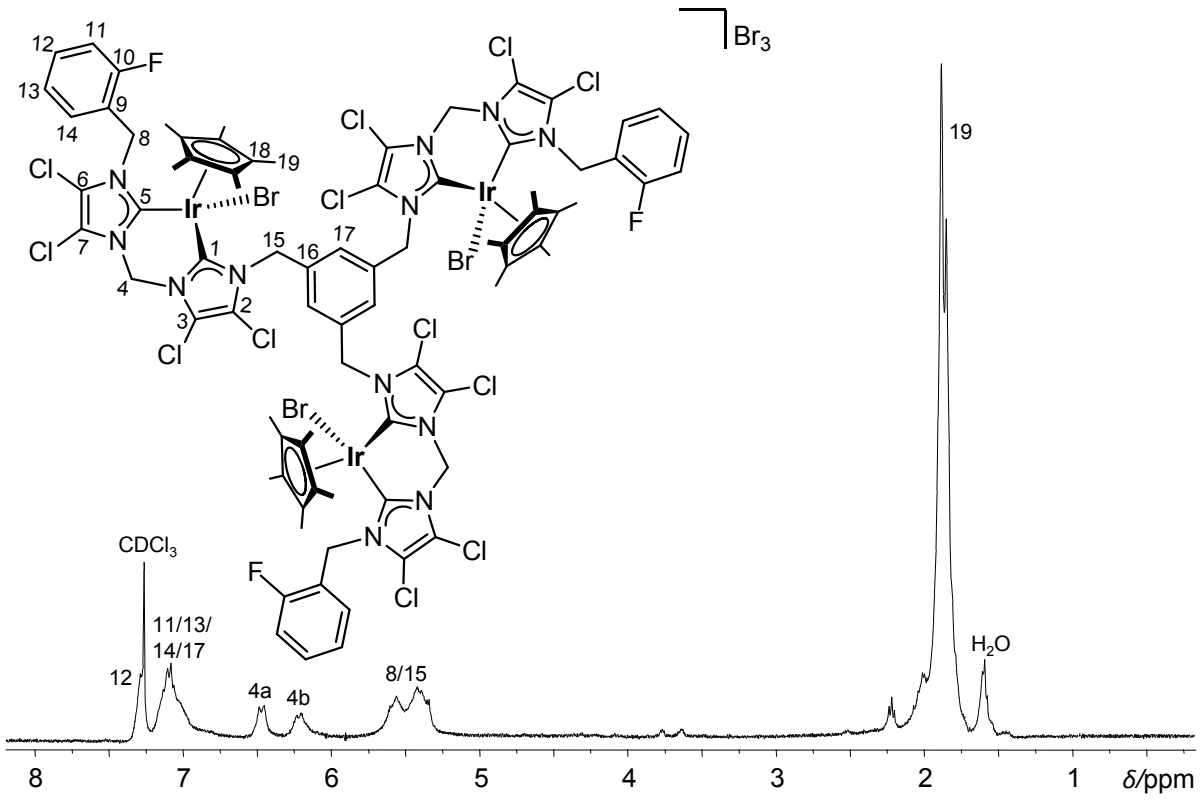


Figure S29. ^{1}H NMR spectrum of complex **12**Br_3 in $CDCl_3$.

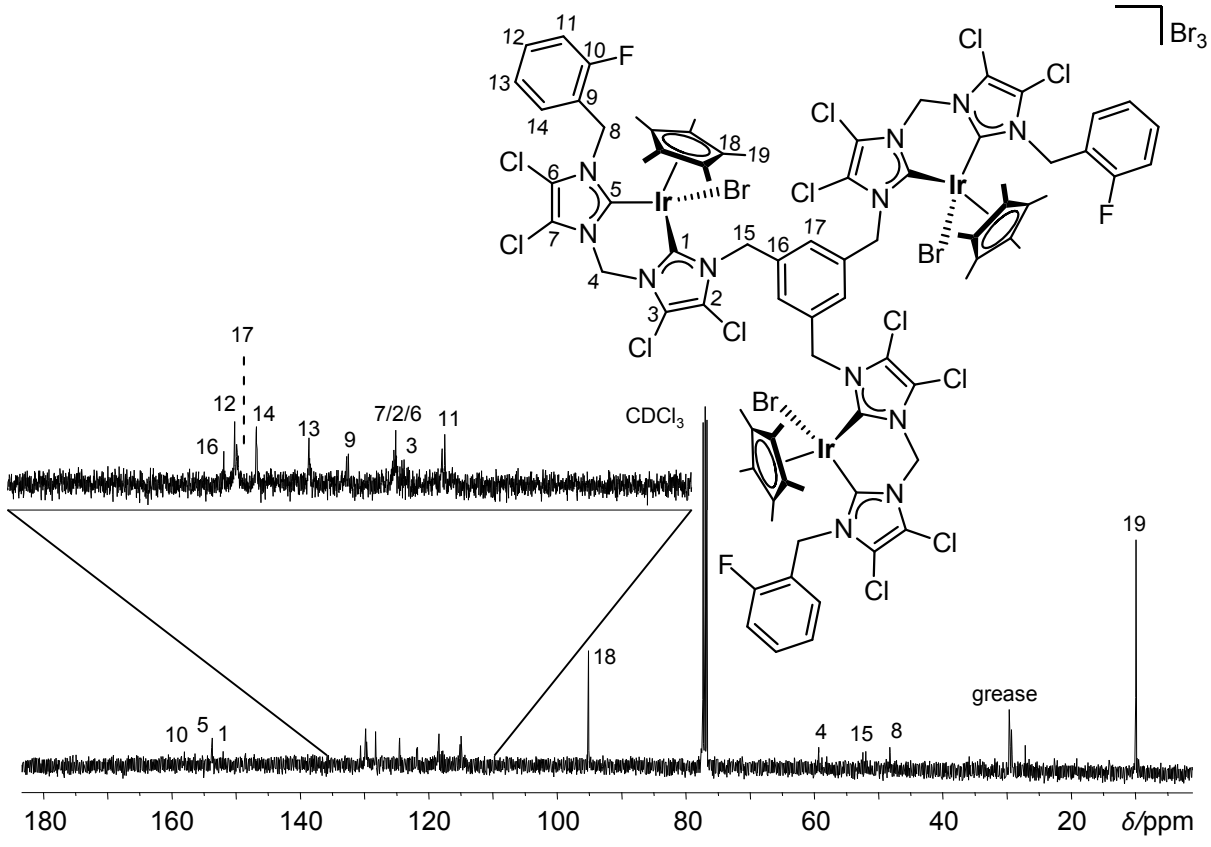


Figure S30. ^{13}C{^{1}H} NMR spectrum of complex **12**Br_3 in $CDCl_3$.

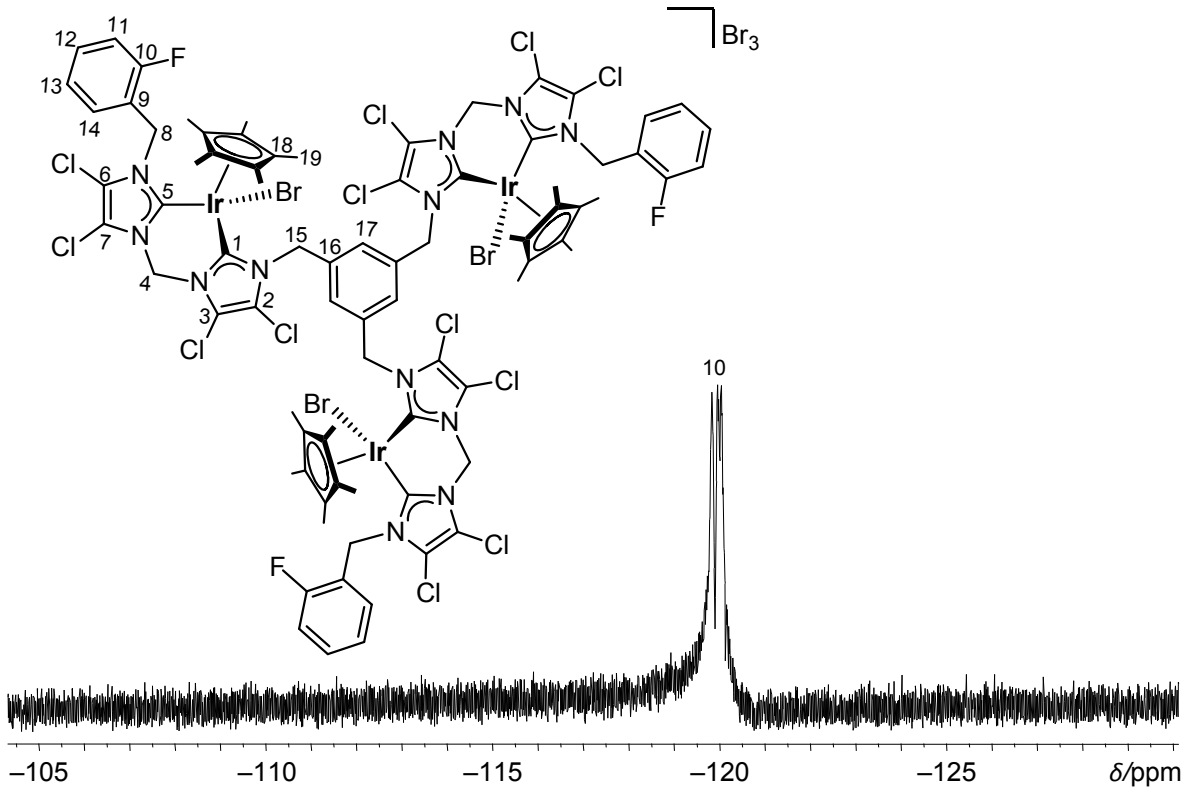


Figure S31. $^{19}F\{^{1}H\}$ NMR spectrum of complex **12**Br_3 in CD_3CN.

4. Addition of Br_2 to *trans*-1,4-dibromo-2-butene

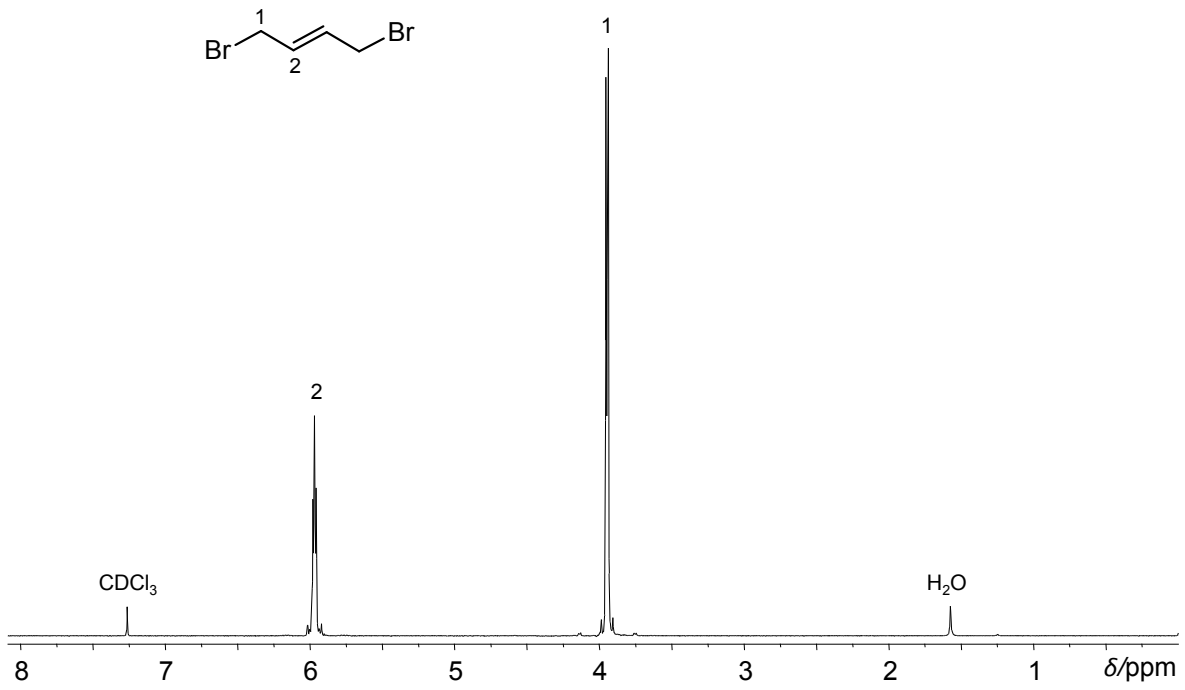


Figure S32. ^{1}H NMR spectrum of *trans*-1,4-dibromo-2-butene in $CDCl_3$.

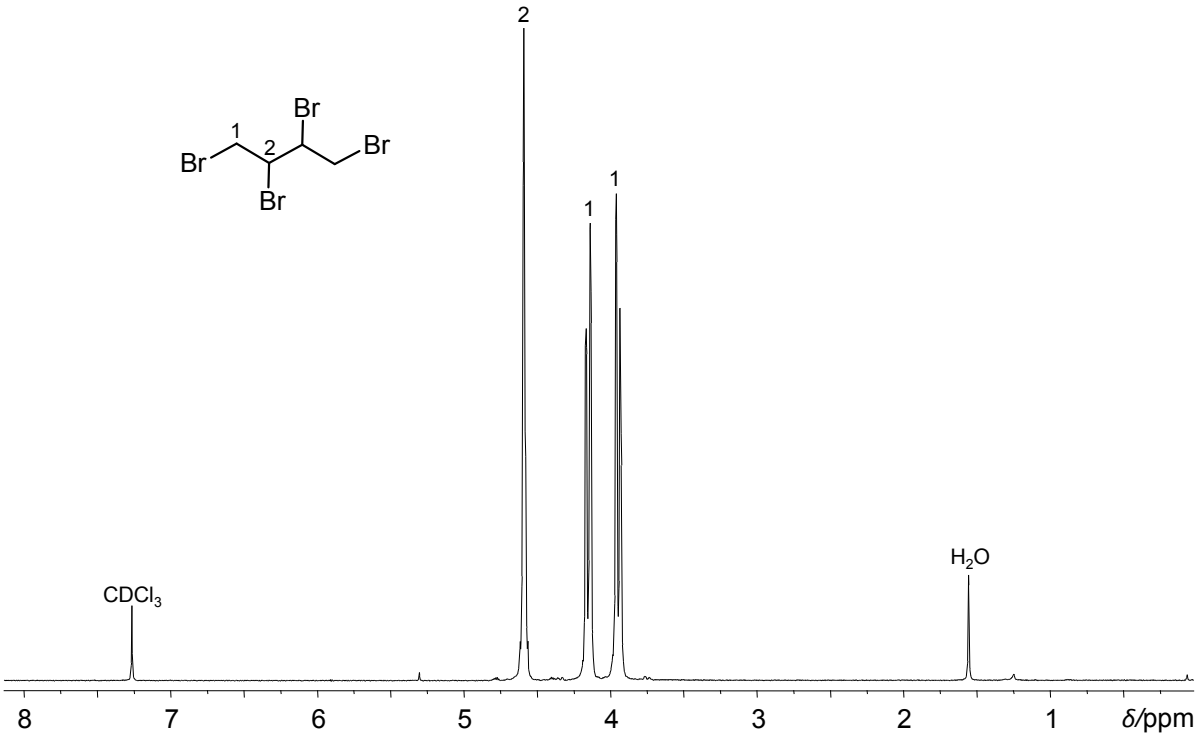


Figure S33. ^{1}H NMR spectrum of 1,2,3,4-tetrabromobutane in $CDCl_3$.

5. HR-ESI Mass Spectra

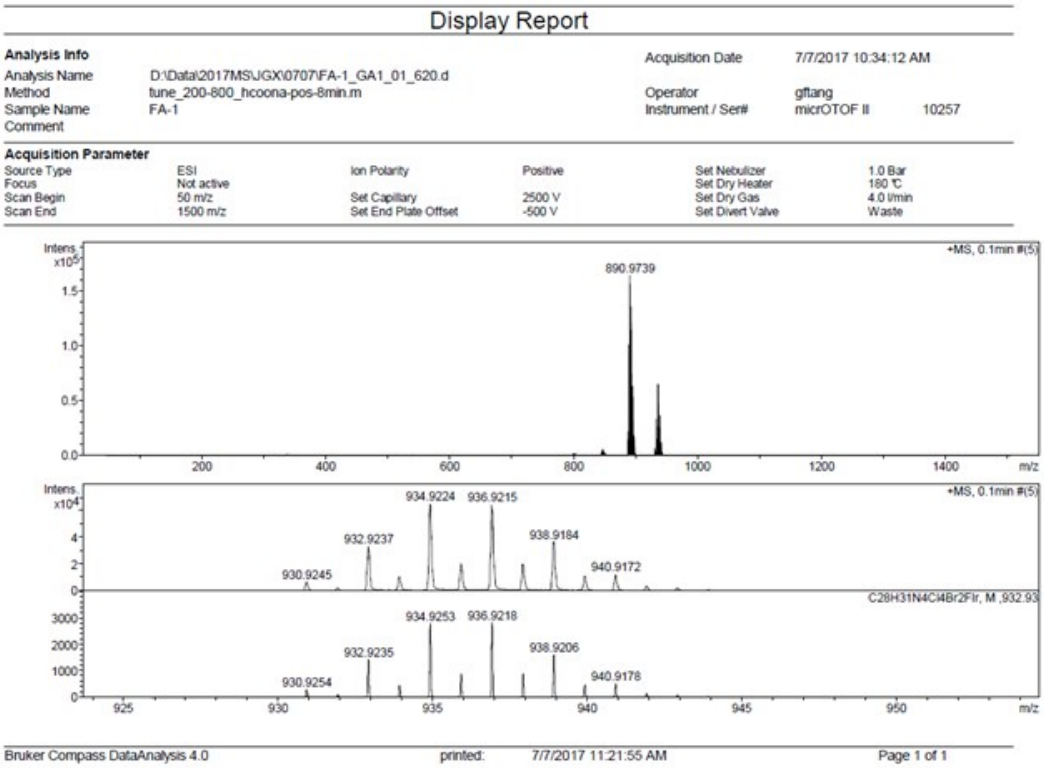


Figure S34. HR-ESI mass spectrum of complex **3**Br in CH_3OH.

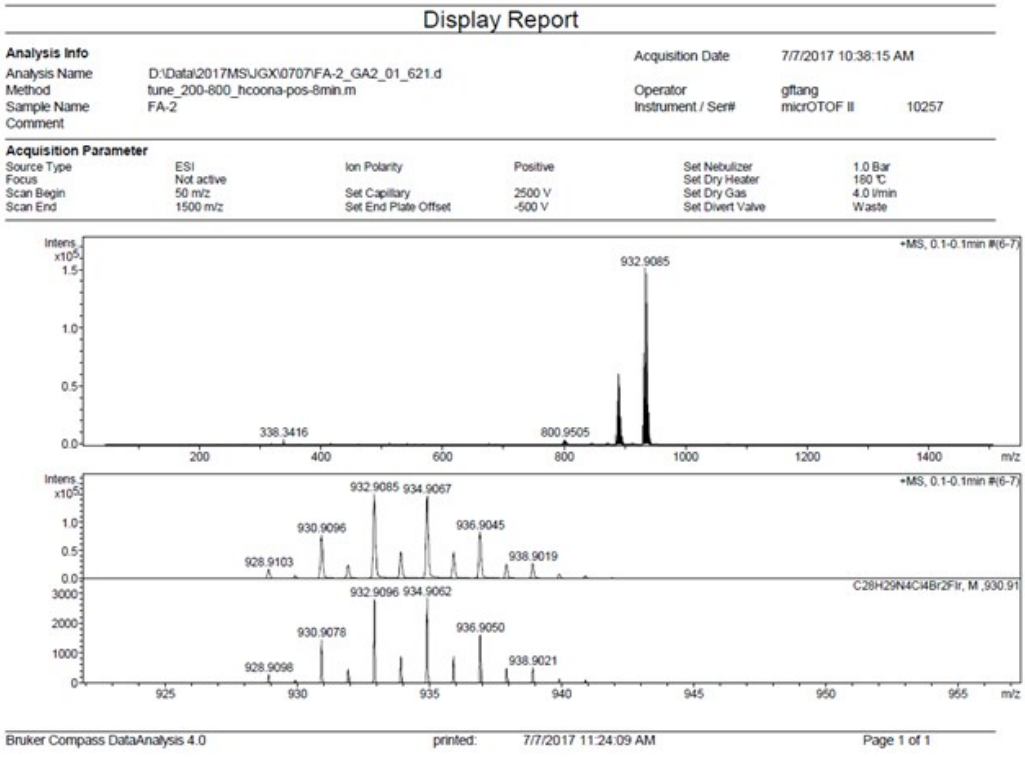


Figure S35. HR-ESI mass spectrum of complex **4**Br in CH_3OH.

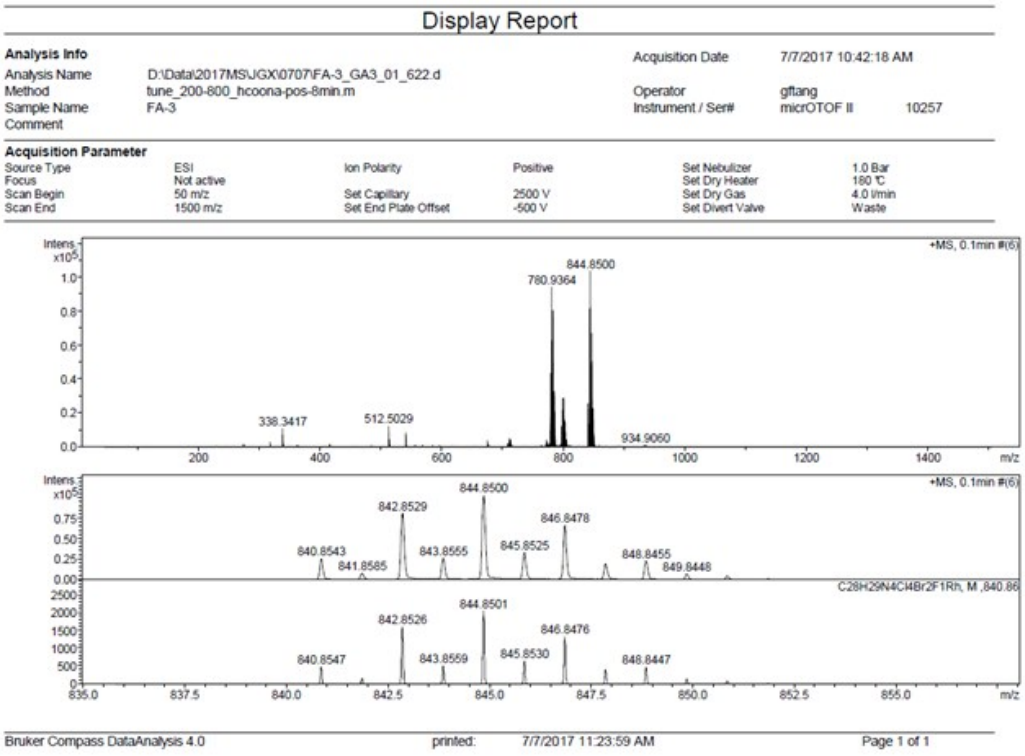


Figure S36. HR-ESI mass spectrum of complex **5**Br in CH_3OH.

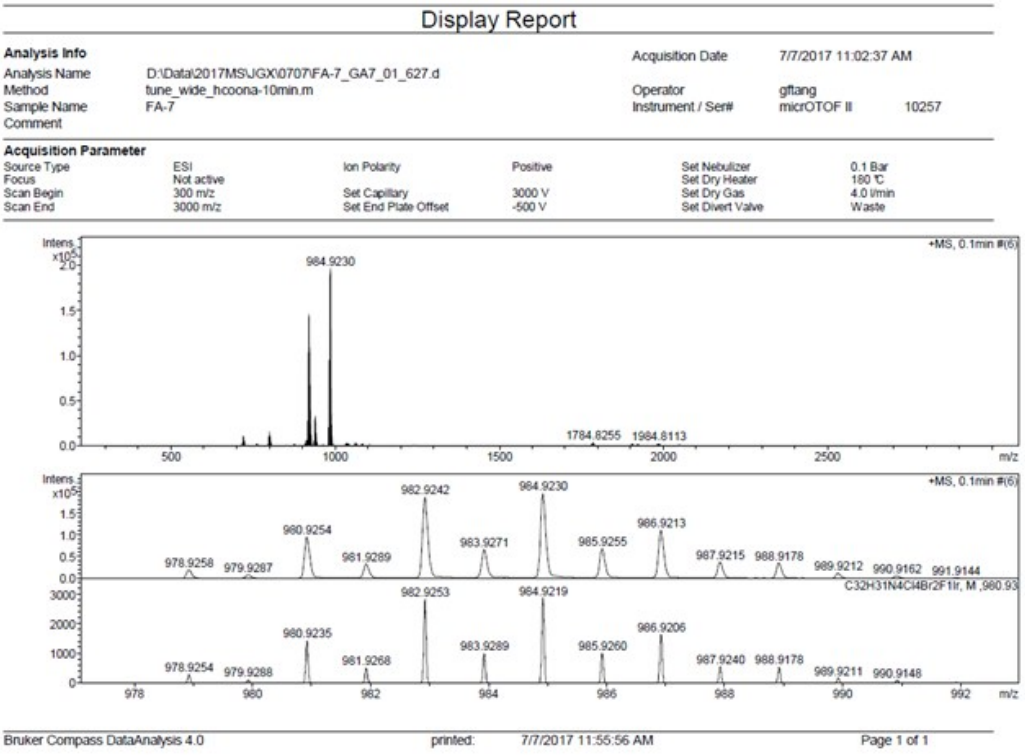


Figure S37. HR-ESI mass spectrum of complex **6**Br in CH_3OH.

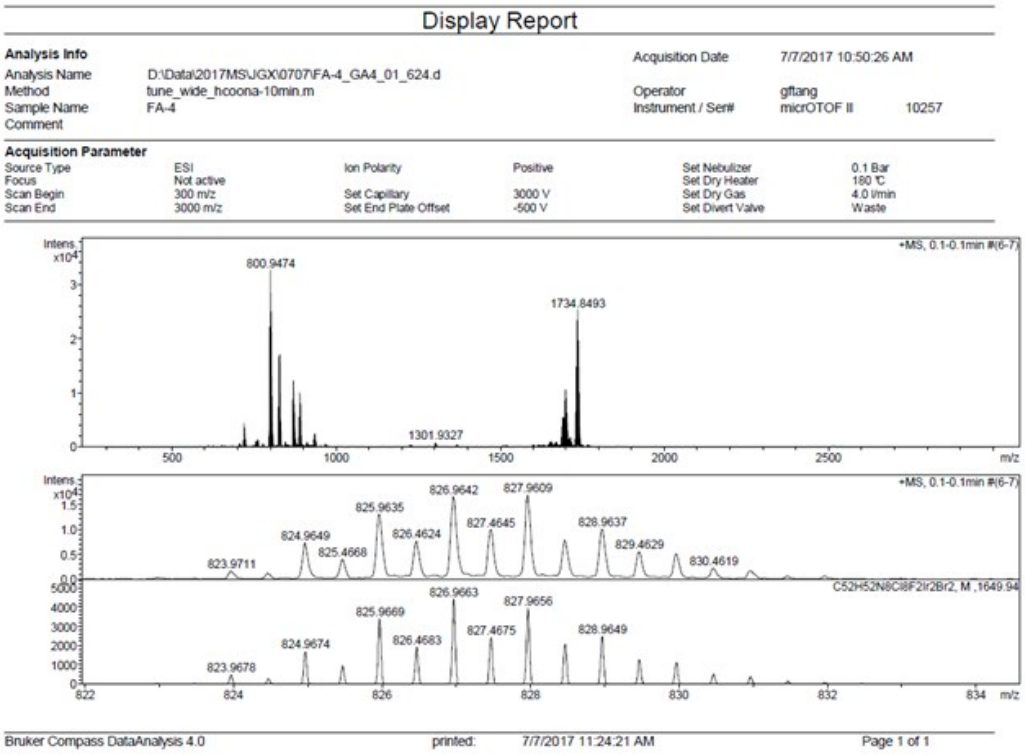
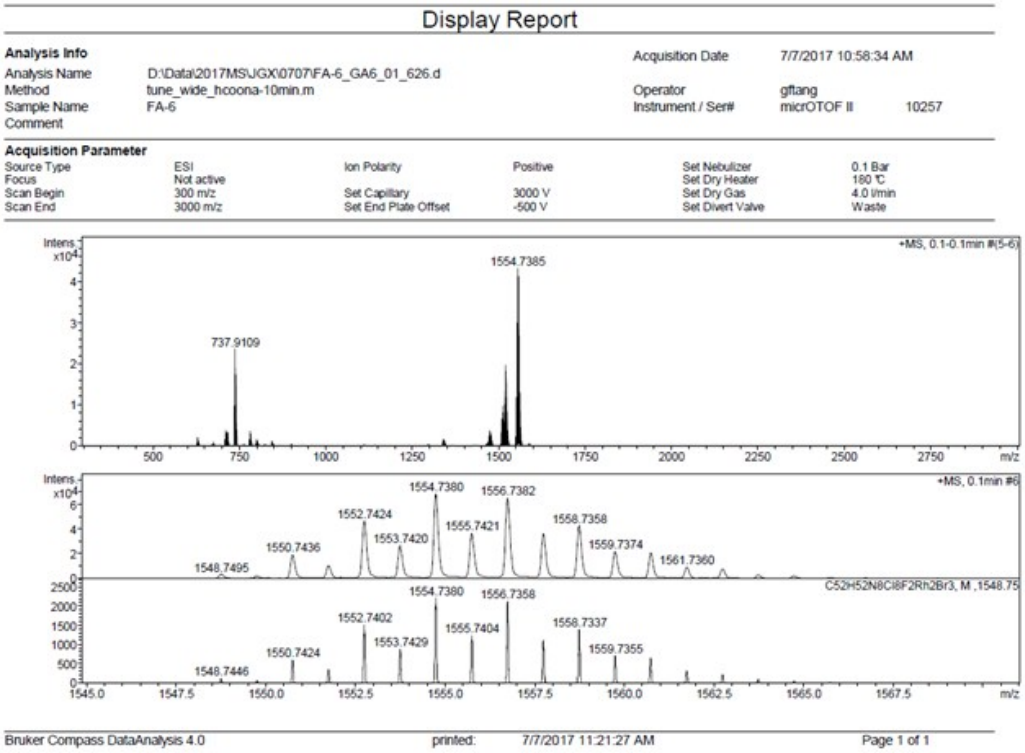


Figure S38. HR-ESI mass spectrum of complex **7**Br_2 in CH_3OH.



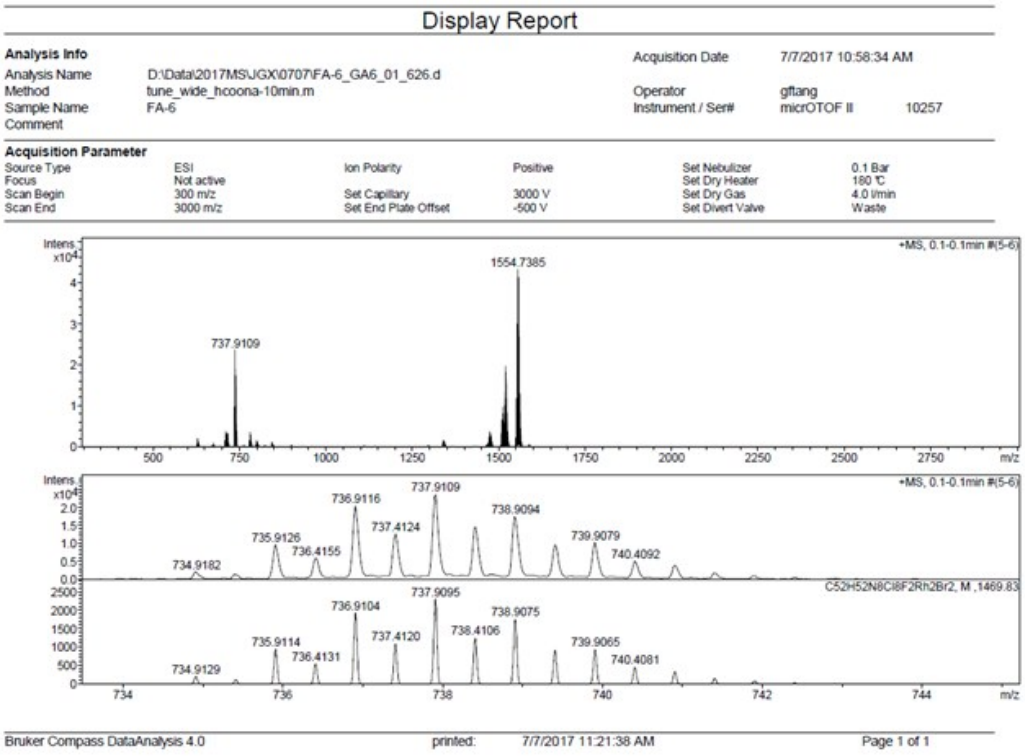
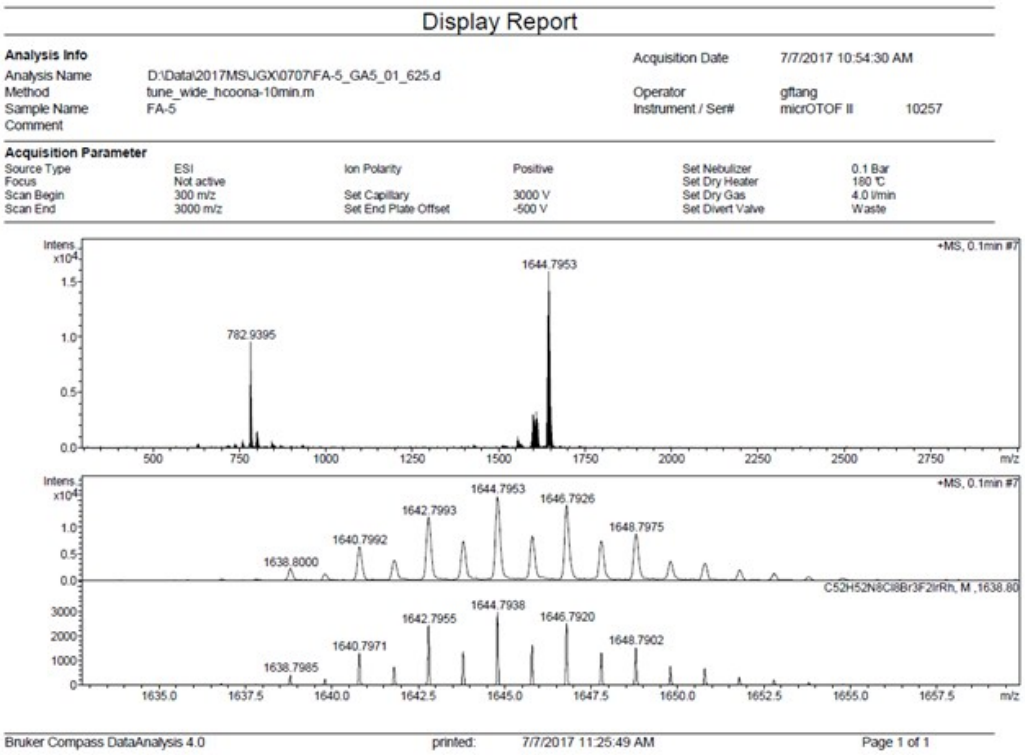


Figure S39. HR-ESI mass spectra of complex **8**Br_2 in CH_3OH.



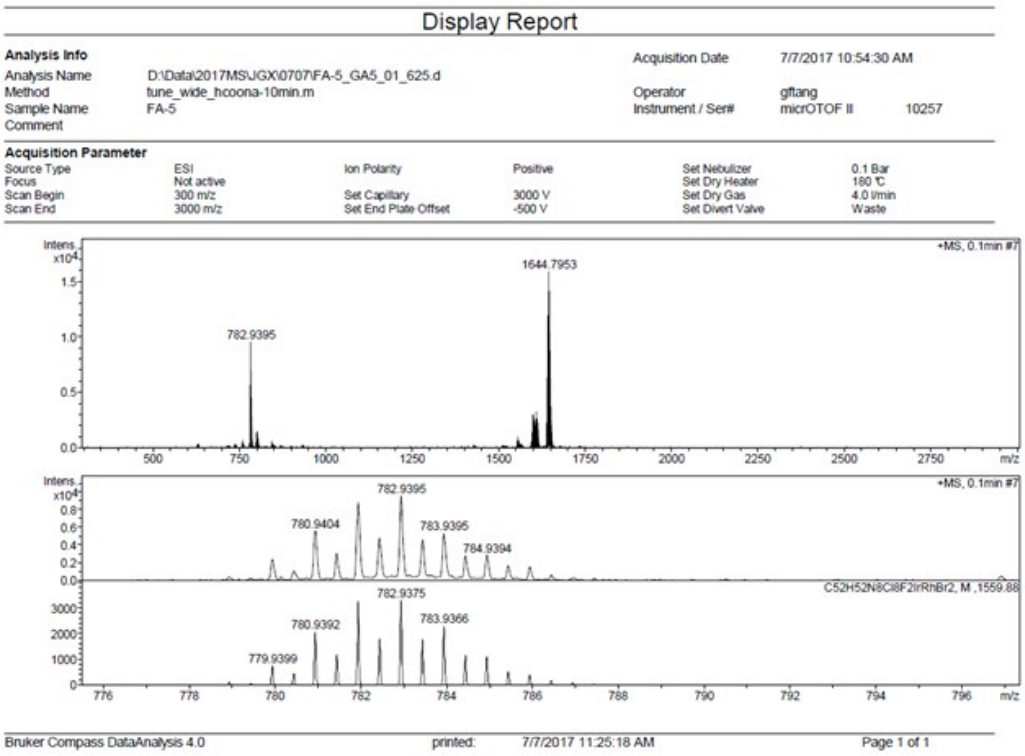
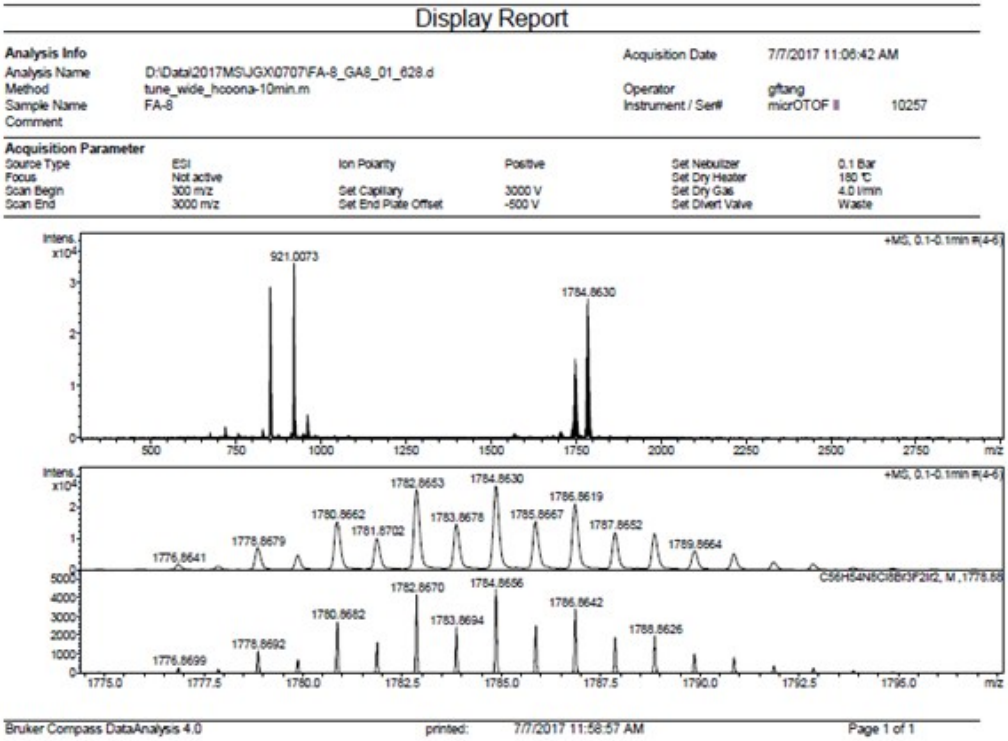


Figure S40. HR-ESI mass spectra of complex **9**Br_2 in CH_3OH.



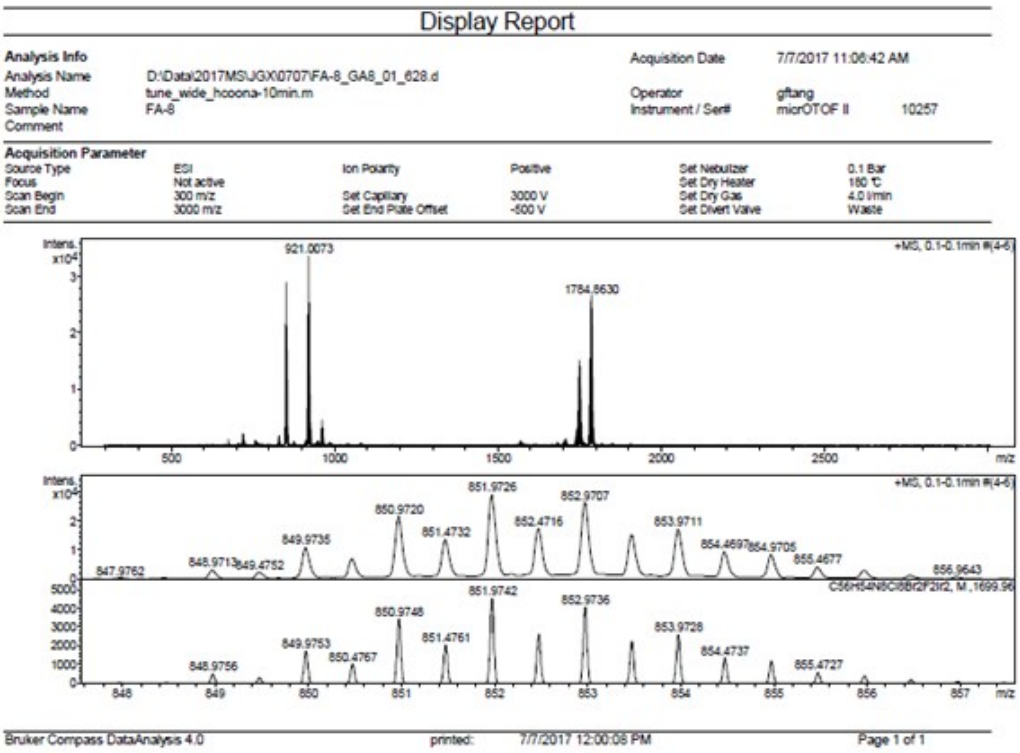


Figure S41. HR-ESI mass spectra of complex **10**Br_2 in CH_3OH.

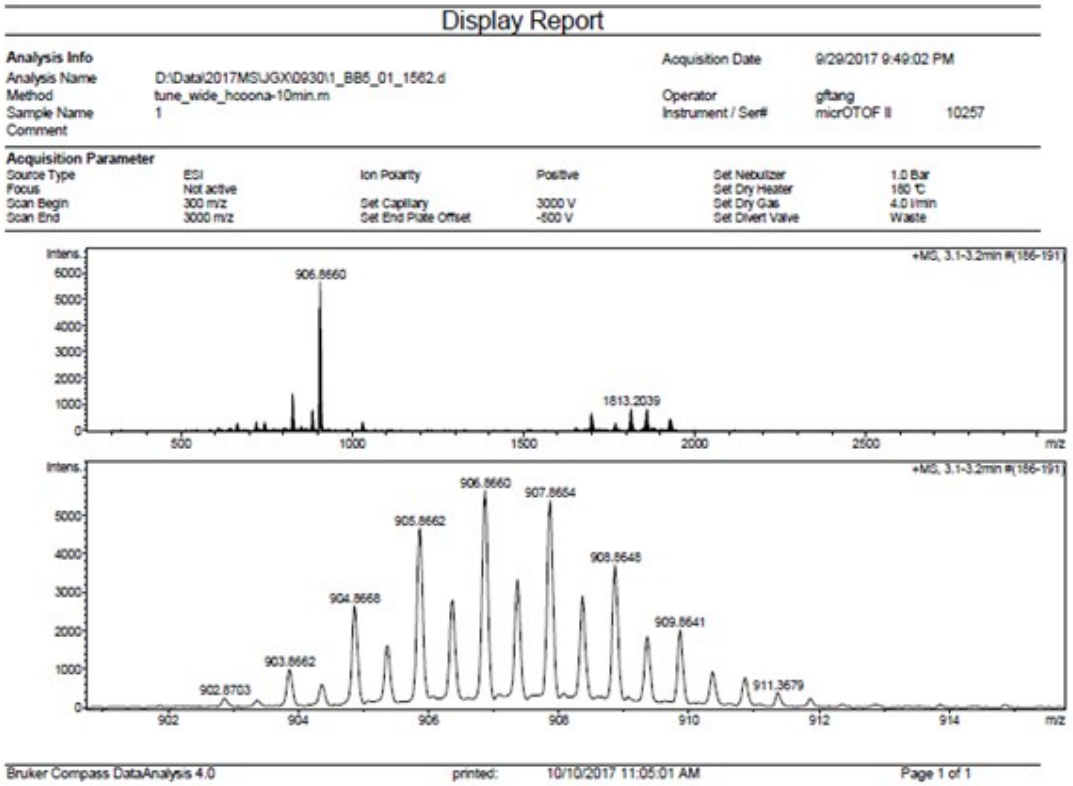


Figure S42. HR-ESI mass spectrum of complex **11**Br_2 in CH_3OH.

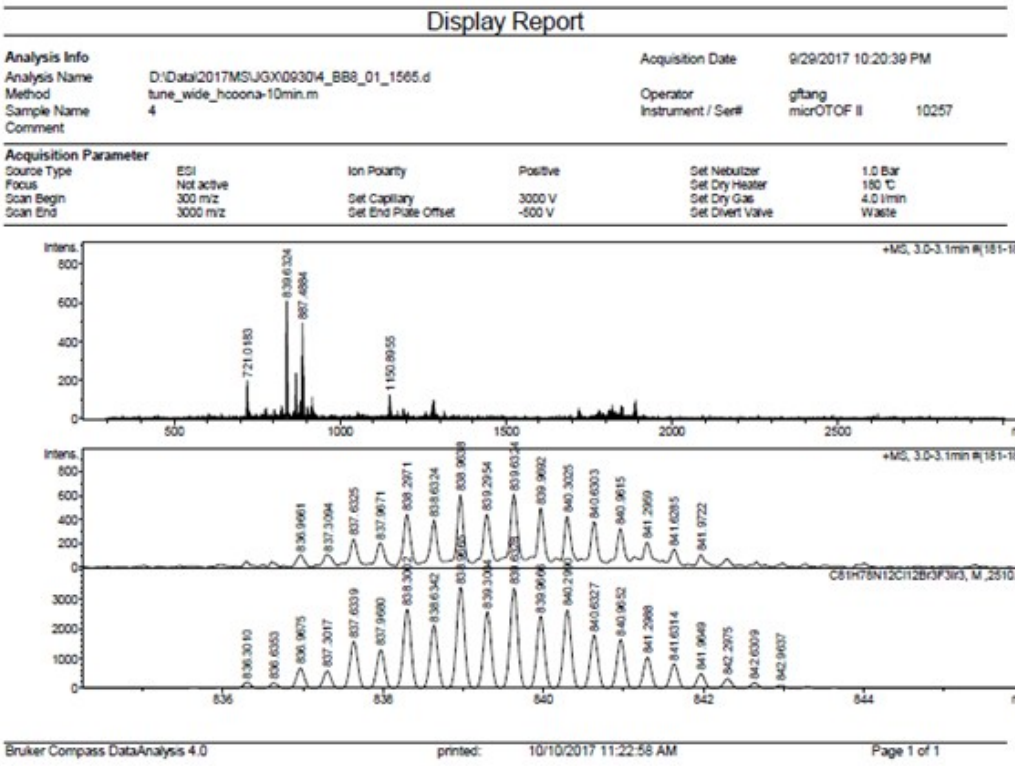


Figure S43. HR-ESI mass spectrum of complex **12**Br_2 in CH_3OH.

6. References

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