Supporting Information

High Efficient Nitrogen Chelated Ruthenium Carbene Metathesis Catalysts

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Table of contents

General Information

The starting materials were synthesized and purified according to the literature procedures.[1-6] Other chemicals and reagents were obtained from commercial sources. All reactions were monitored by analytical thin layer chromatography on 0.20 mm Yantai Huagong silica gel plates and spots were detected by UV-absorption. Silica gel (200-300 mesh) (from Yantai Huagong Chem. Company, Ltd.) was used for flash chromatography. NMR spectra were obtained on 400 MHz spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$) for ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. For ^{19}F NMR, the (trifluoromethyl)benzene was used as an external standard. Coupling constants (*J*) are quoted in Hz for ^1H. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Conversions were obtained by ^1H NMR analysis of the sample. NMR data of known compounds is in agreement with literature values. Infrared spectra were recorded on FT-IR spectrophotometer. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

References

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NMR-spectra of compounds **13a-f** and **14a-f.**

Figure S1: ^{1}H NMR spectrum of compound **13a** in $CDCl_3$

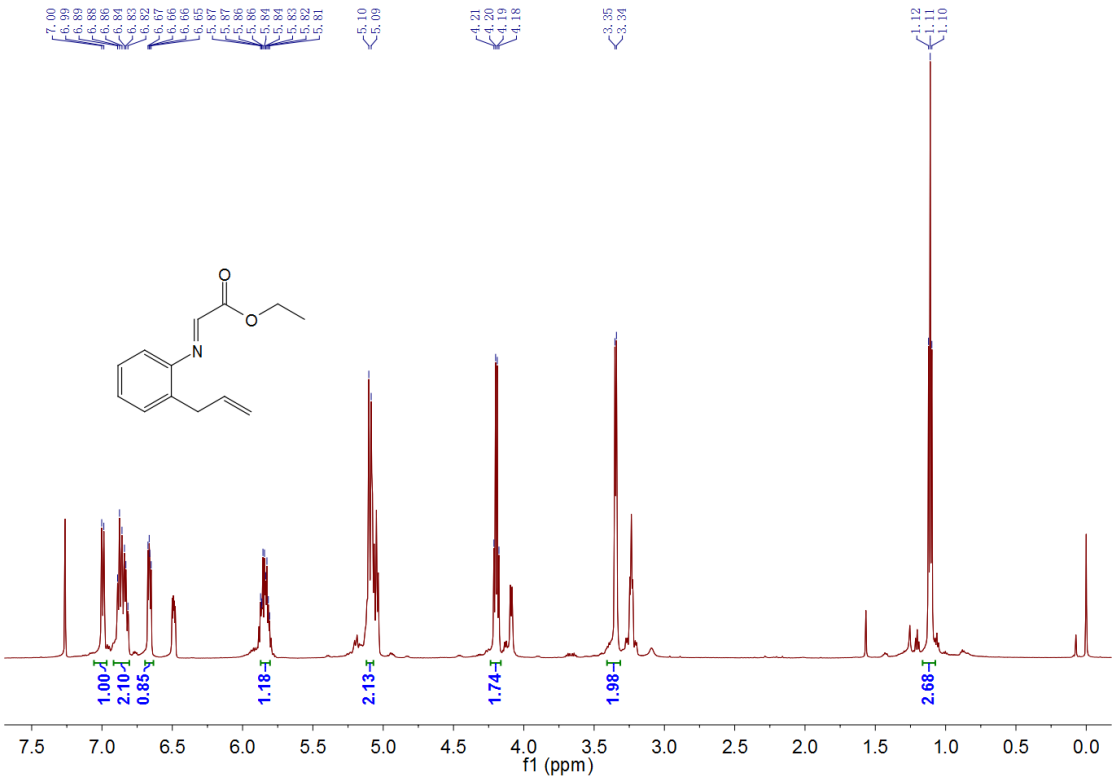


Figure S2: ^{13}C NMR spectrum of compound **13a** in $CDCl_3$

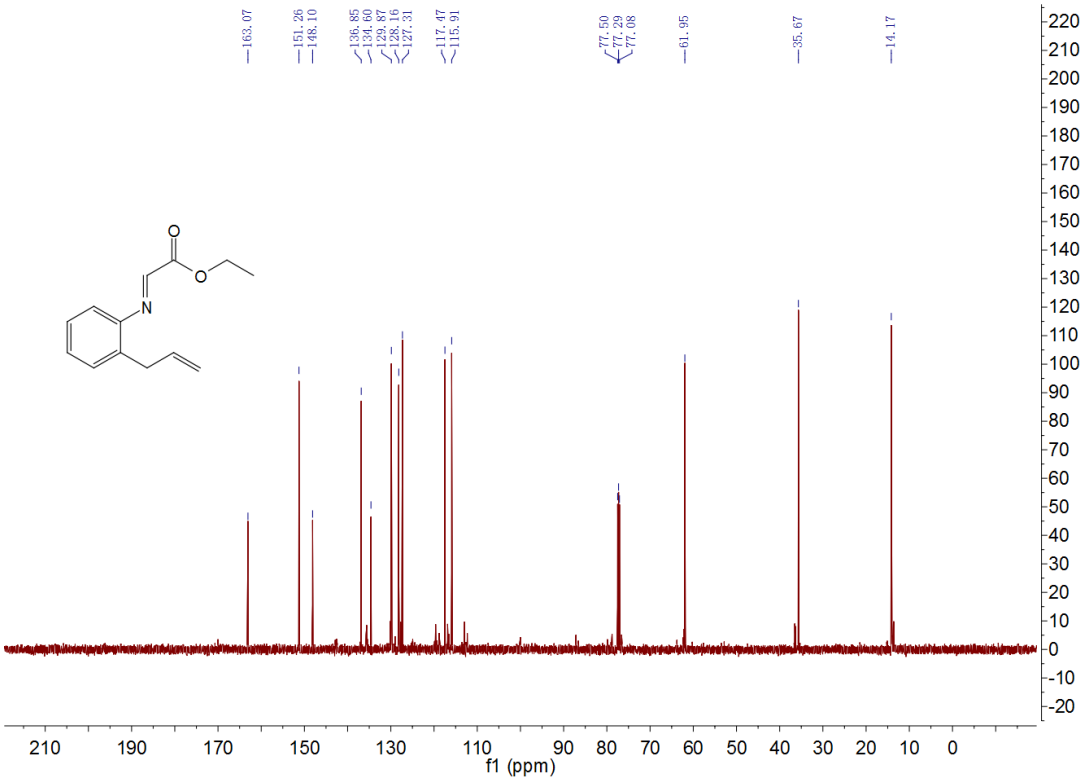


Figure S3: ^{1}H NMR spectrum of compound **13b** in $CDCl_3$

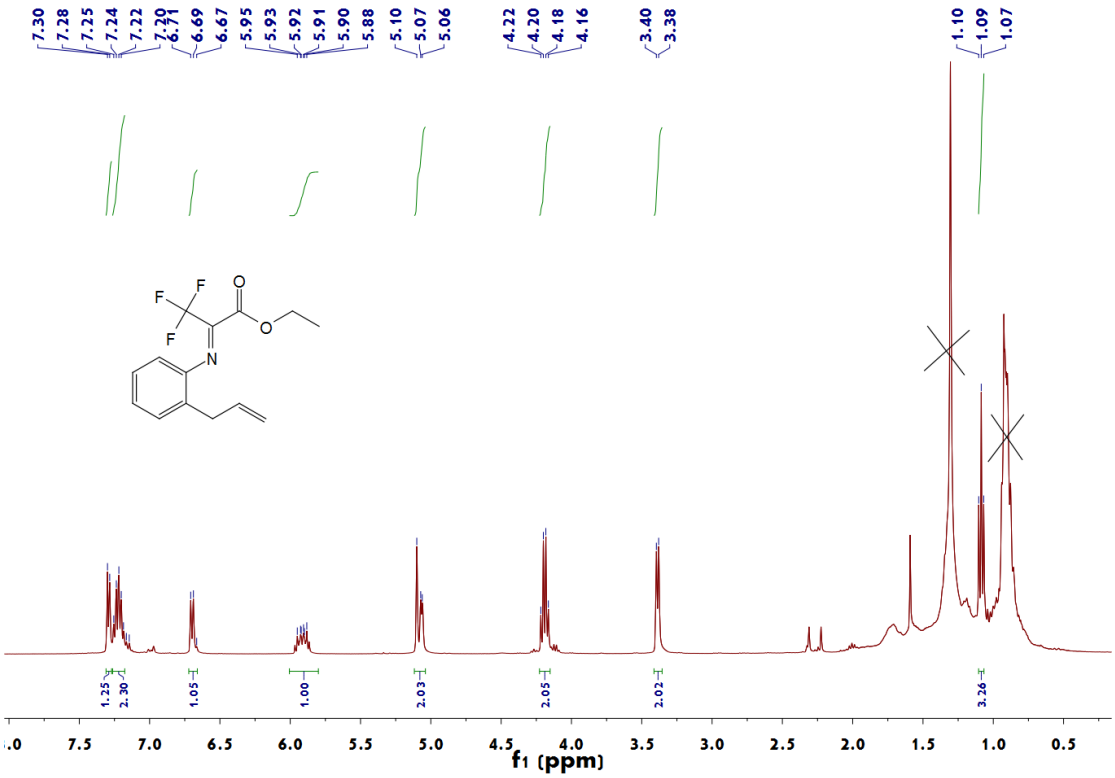


Figure S4: ^{13}C NMR spectrum of compound **13b** in $CDCl_3$

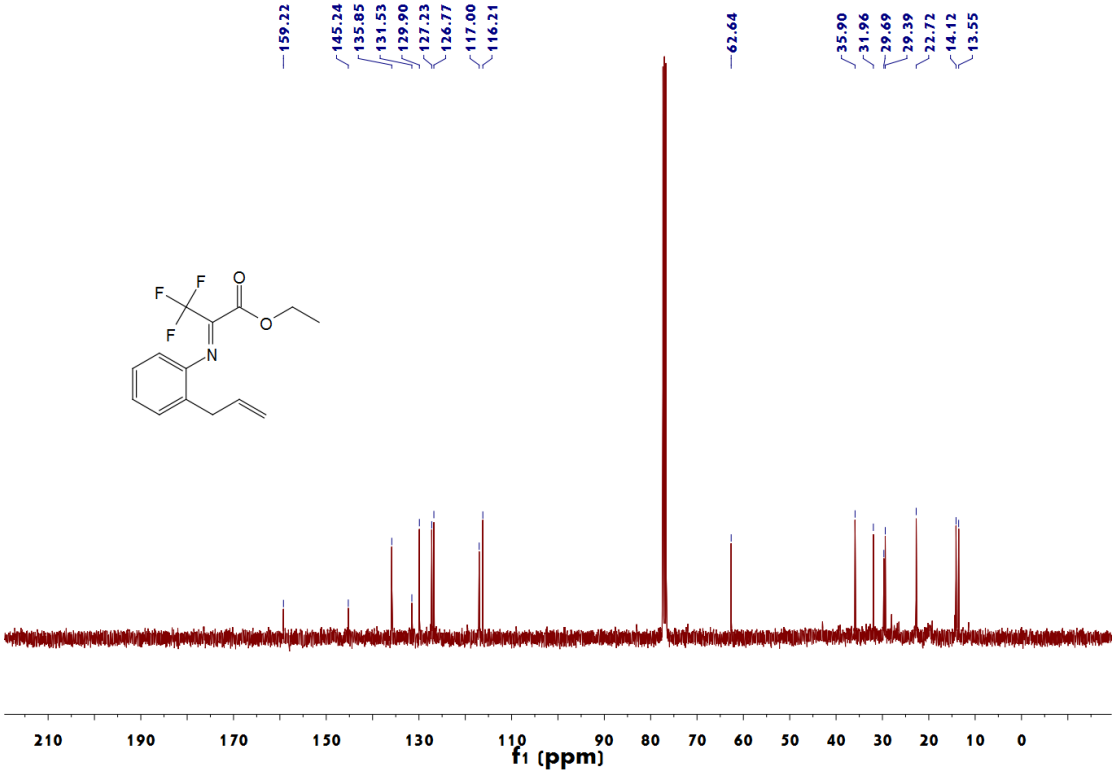


Figure S5: ^{1}H NMR spectrum of compound **13c** in $CDCl_3$

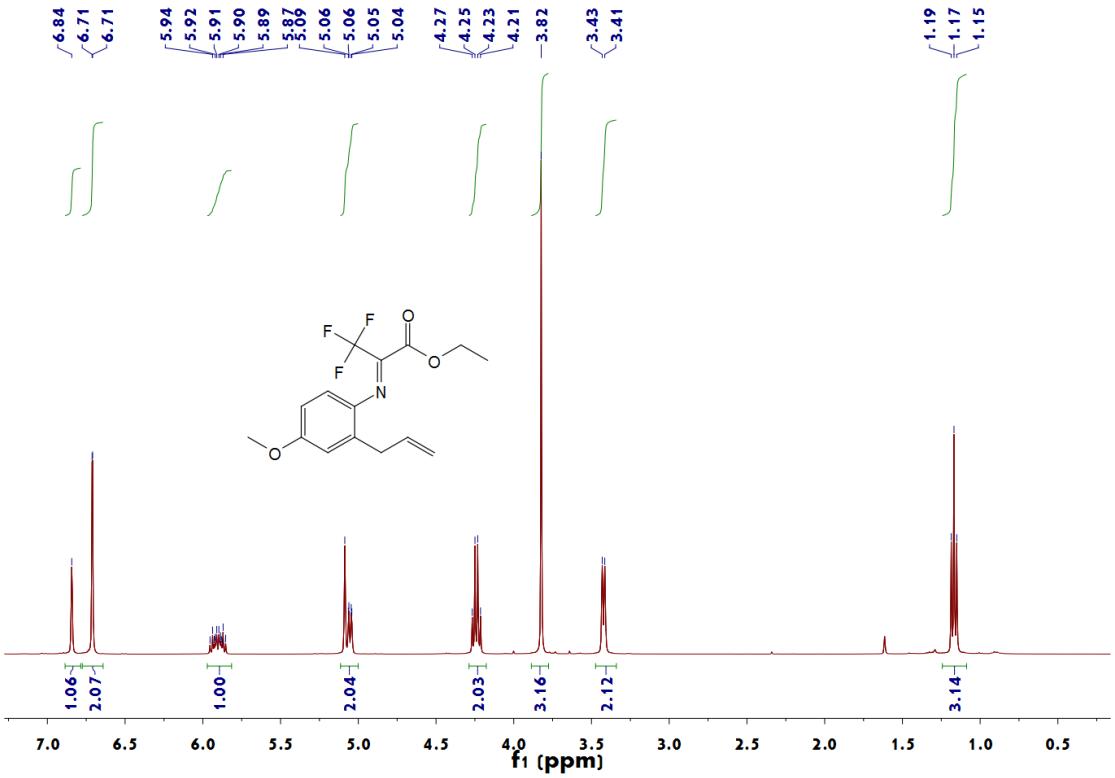


Figure S6: ^{13}C NMR spectrum of compound **13c** in $CDCl_3$

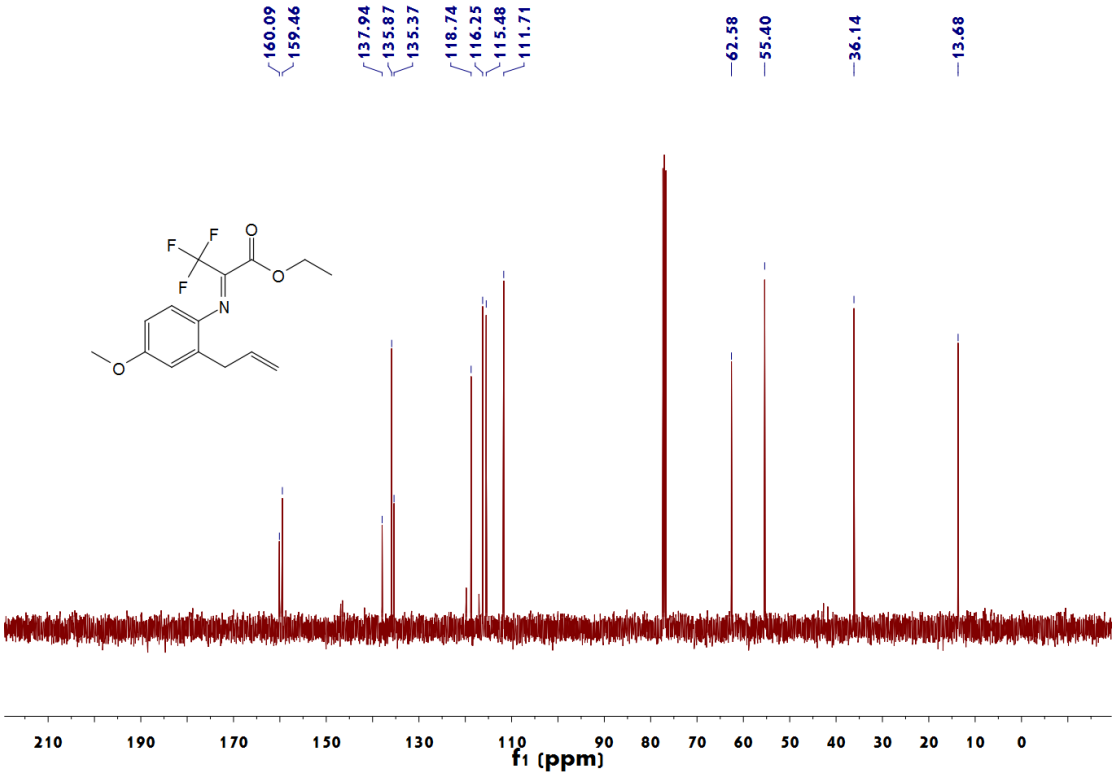


Figure S7: ^{1}H NMR spectrum of compound **13d** in $CDCl_3$

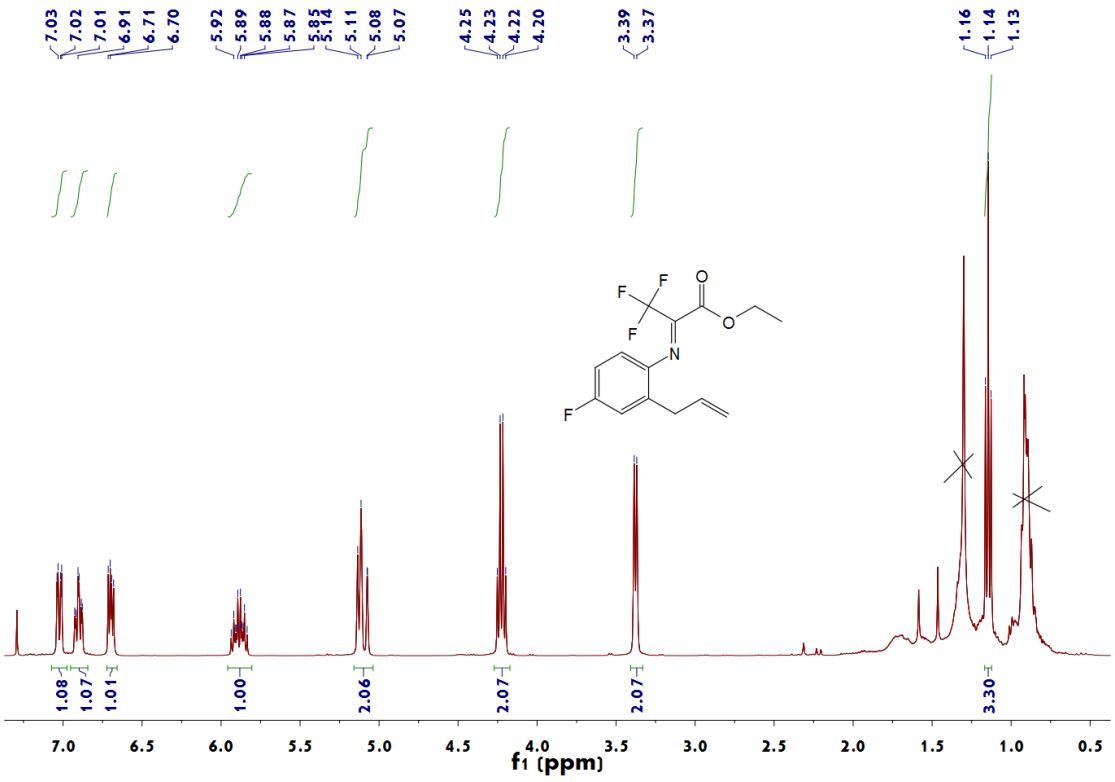


Figure S8: ^{13}C NMR spectrum of compound **13d** in $CDCl_3$

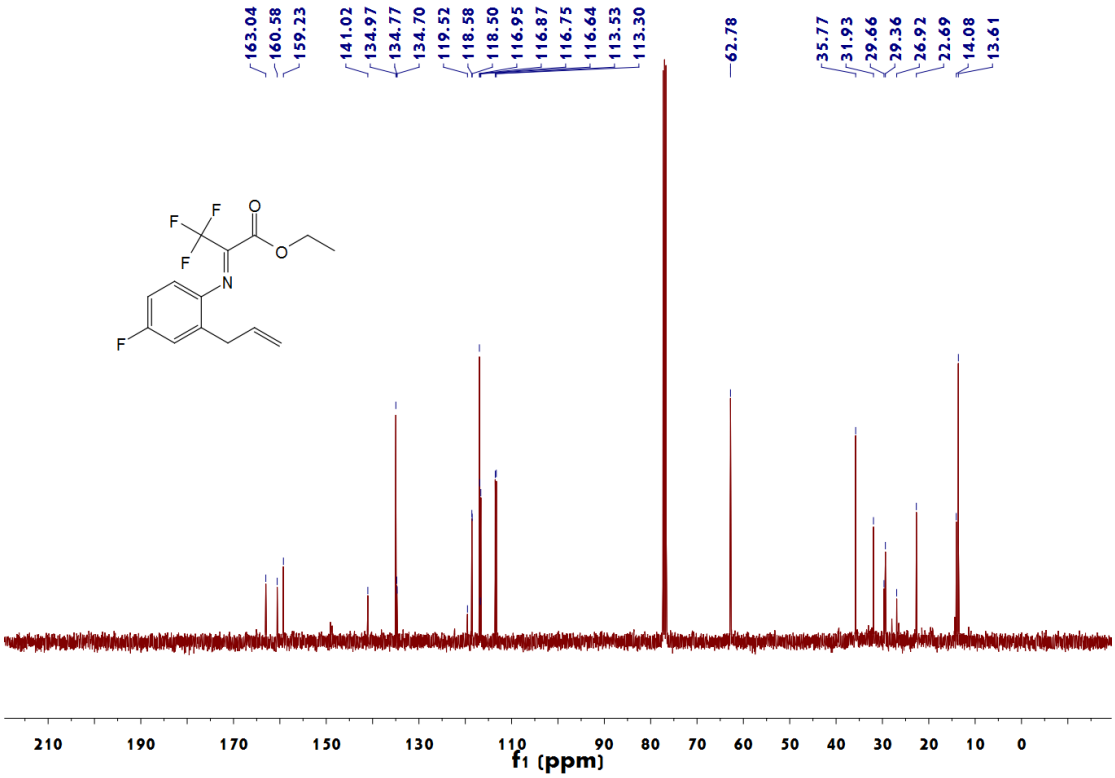


Figure S9: ^{1}H NMR spectrum of compound **13e** in $CDCl_3$

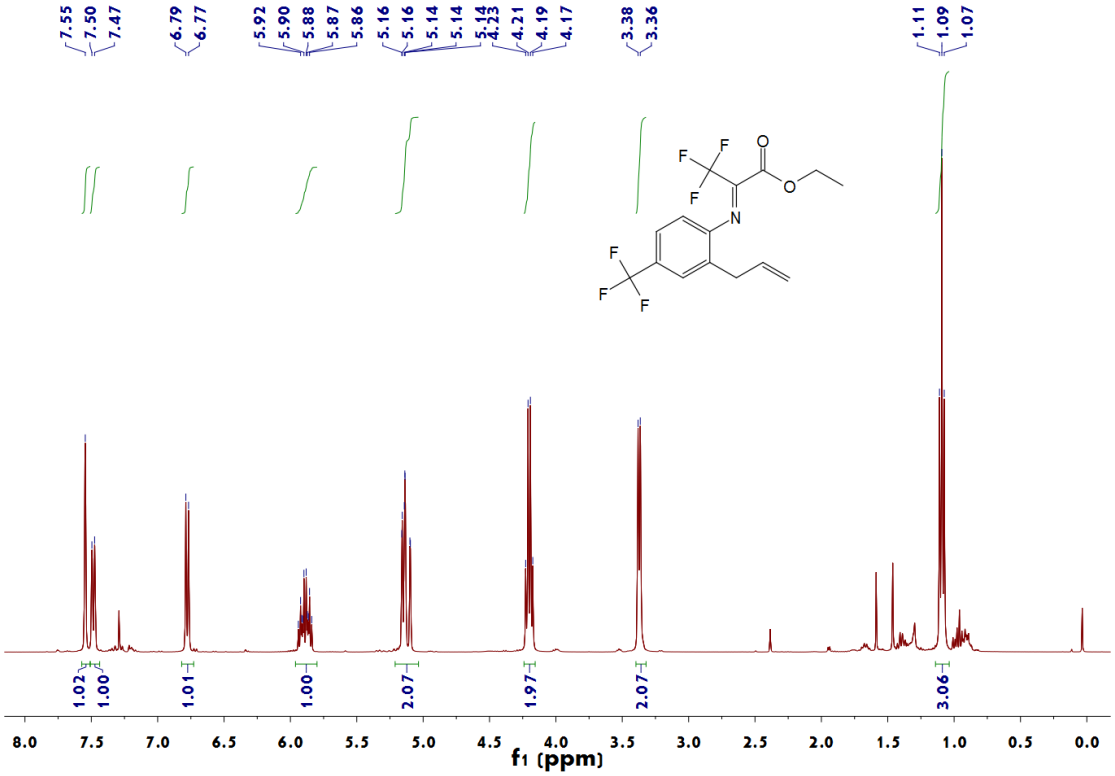


Figure S10: ^{13}C NMR spectrum of compound **13e** in $CDCl_3$

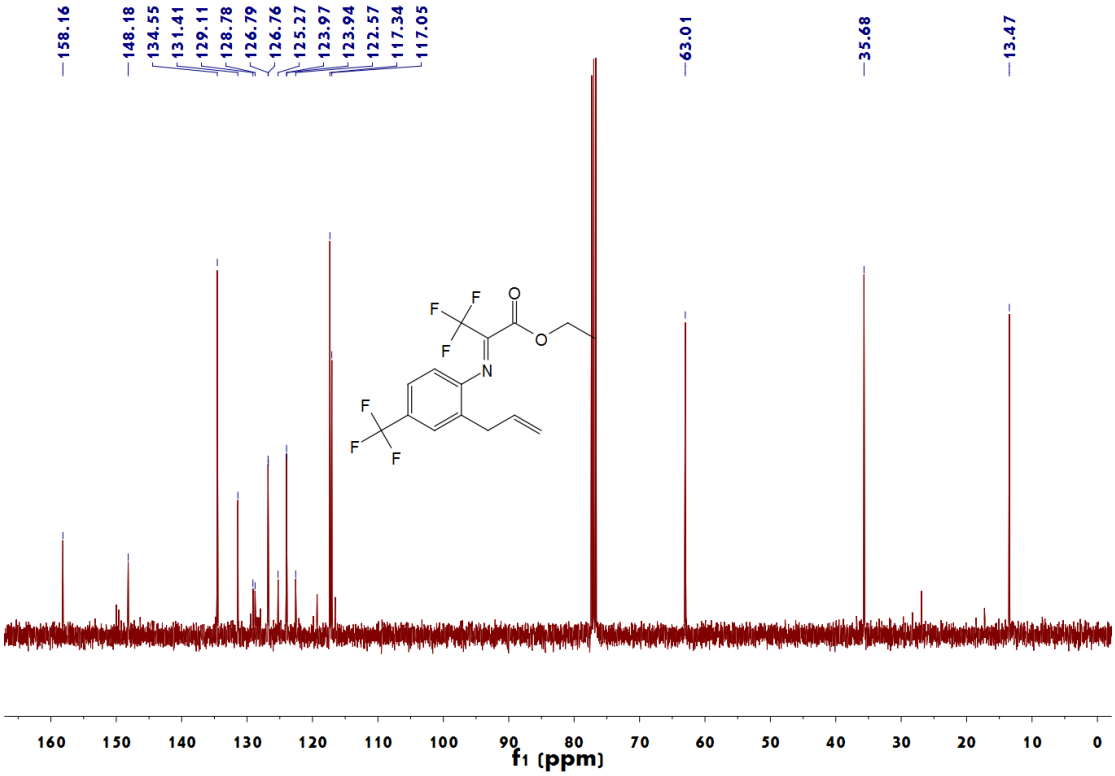


Figure S11: ^{1}H NMR spectrum of compound **13f** in $CDCl_3$

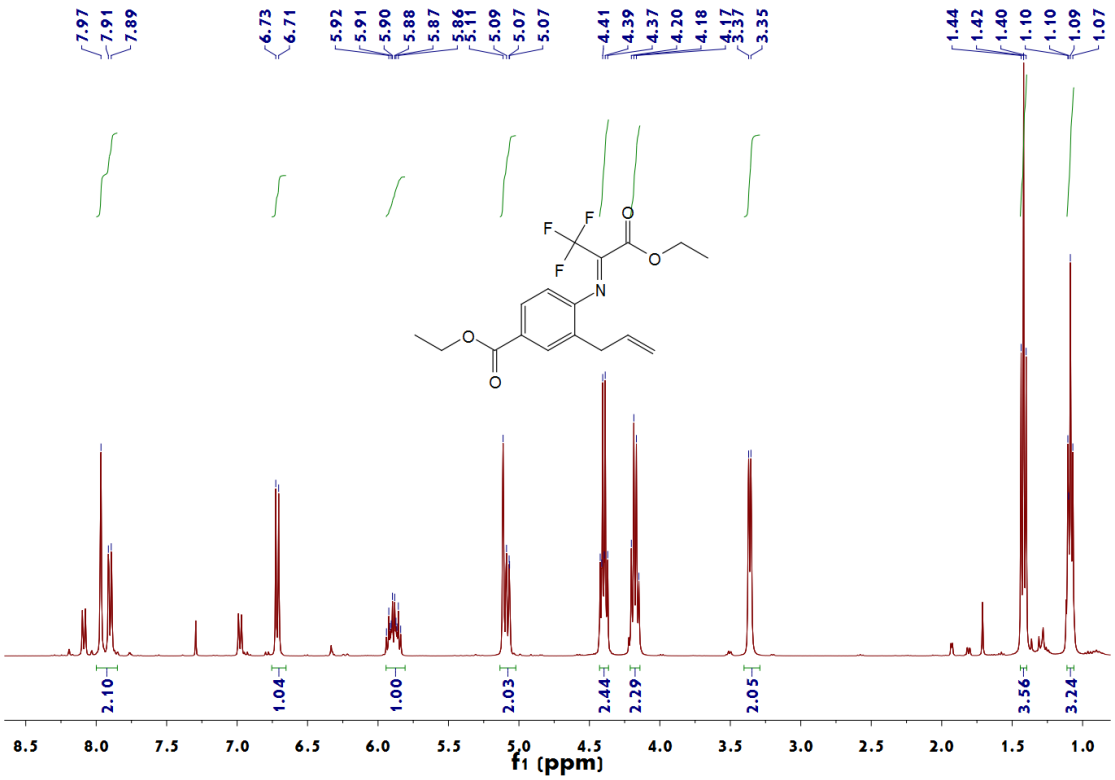


Figure S12: ^{13}C NMR spectrum of compound **13f** in $CDCl_3$

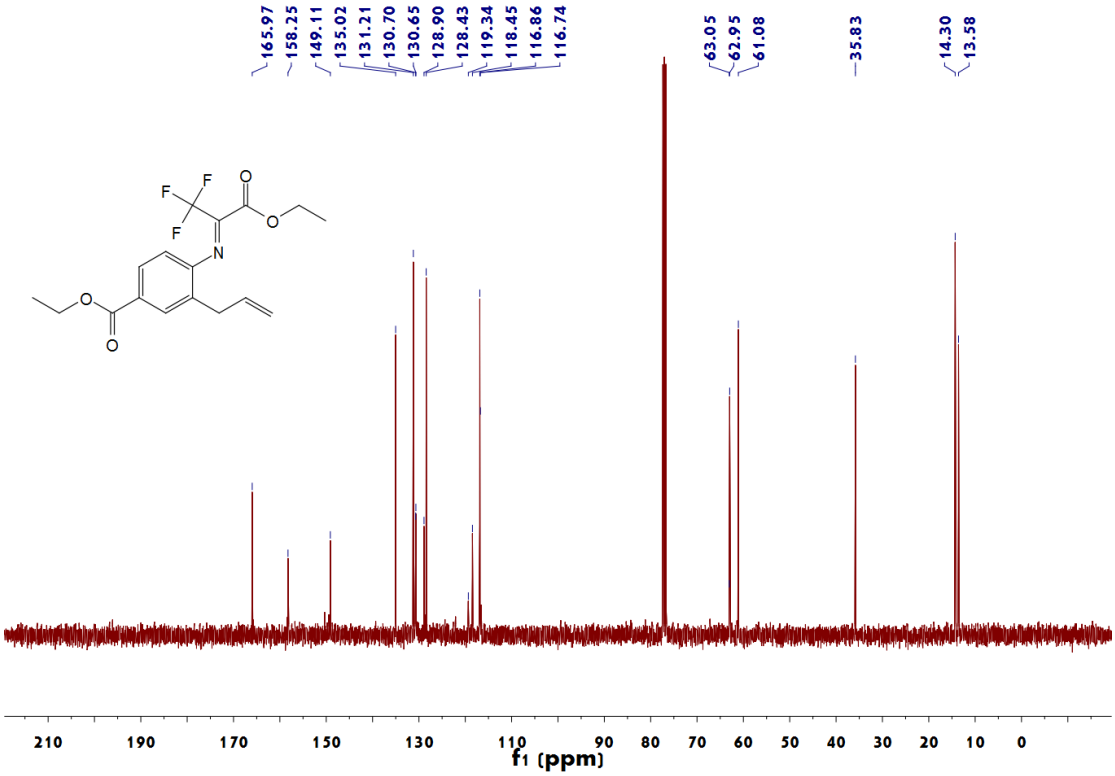


Figure S13: ^{1}H NMR spectrum of compound **14a** in $CDCl_3$

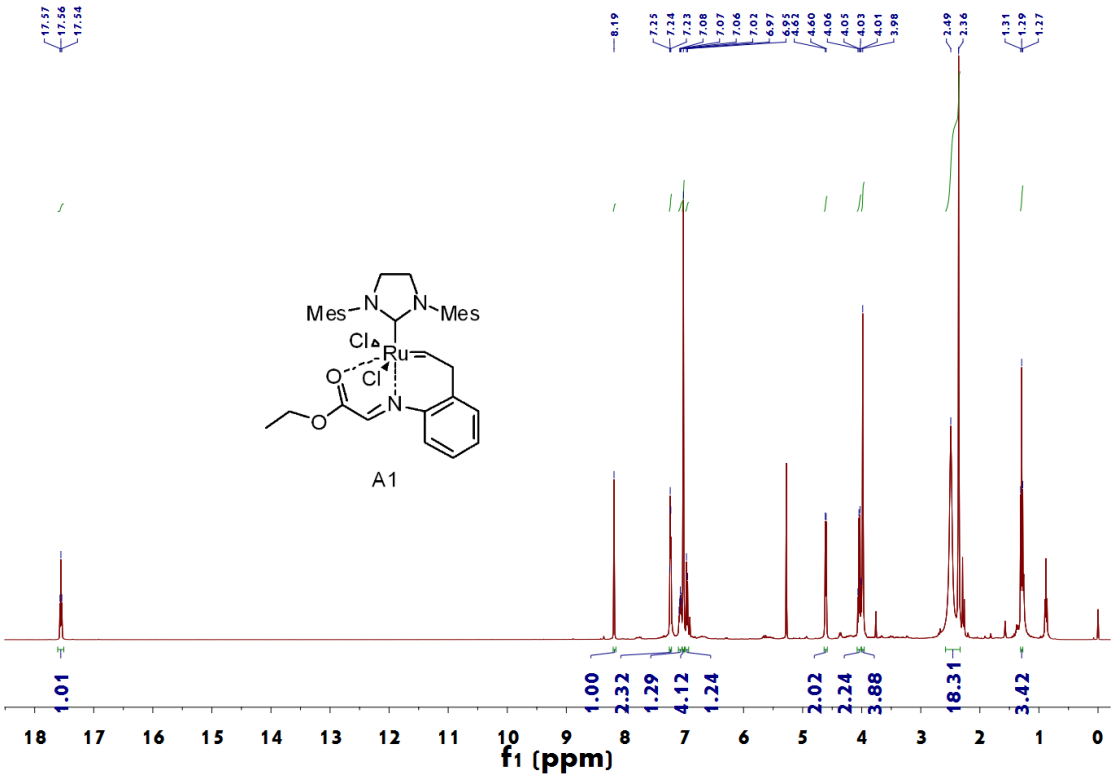


Figure S14: ^{13}C NMR spectrum of compound **14a** in $CDCl_3$

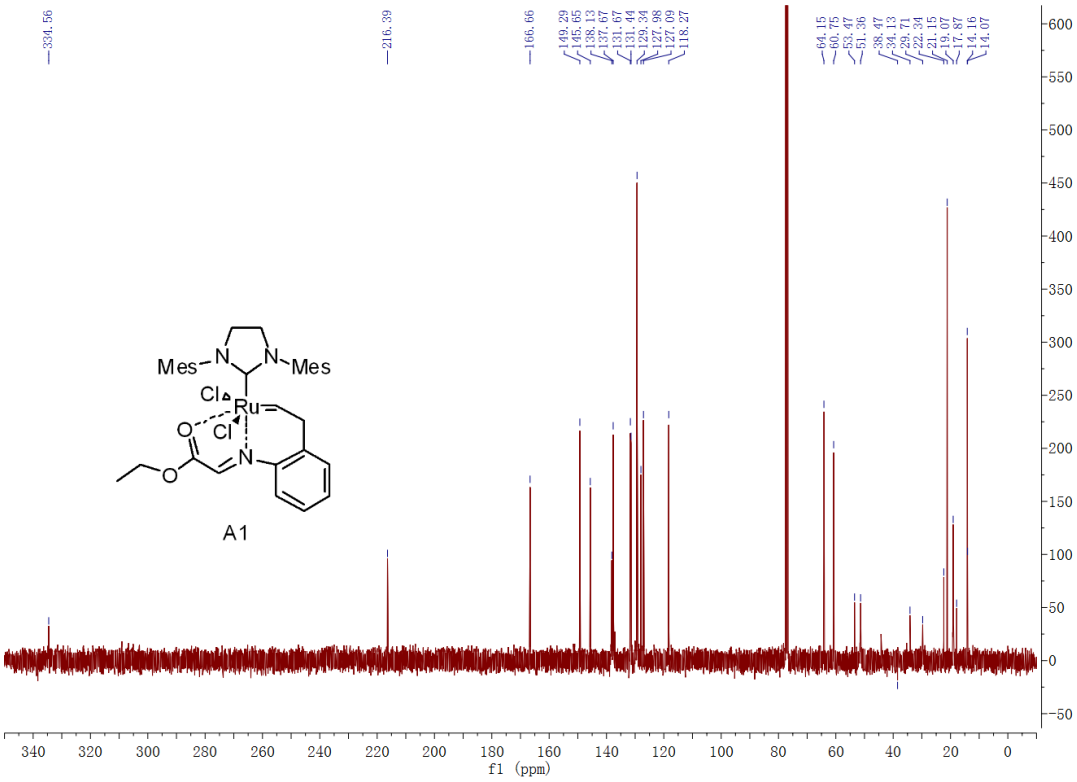


Figure S15: ^{1}H NMR spectrum of compound **14b** in $CDCl_3$

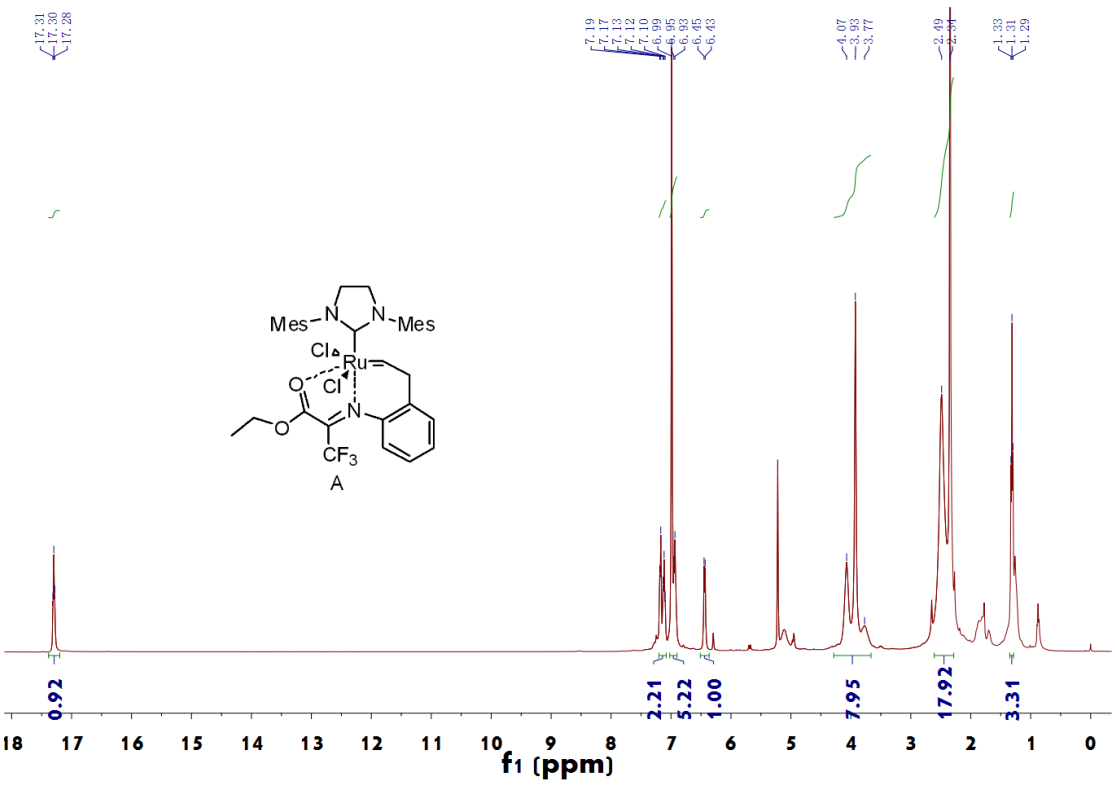


Figure S16: ^{13}C NMR spectrum of compound**14b** in $CDCl_3$

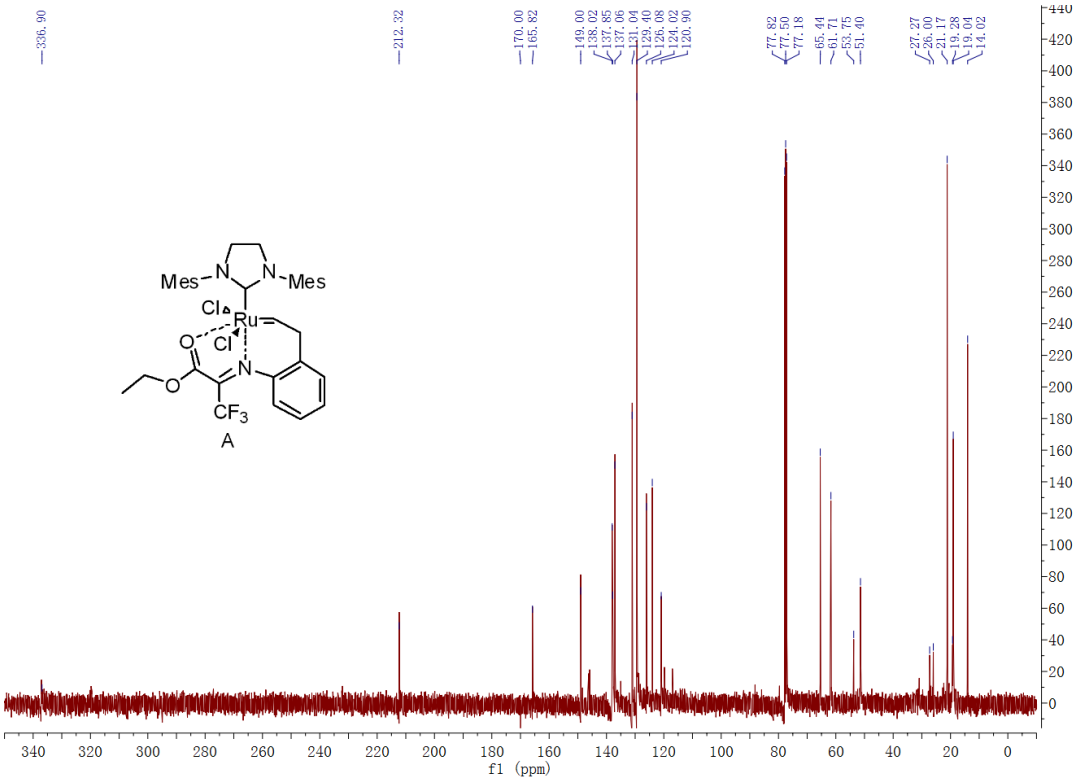


Figure S17: ^{19}F NMR spectrum of compound **14b** in $CDCl_3$

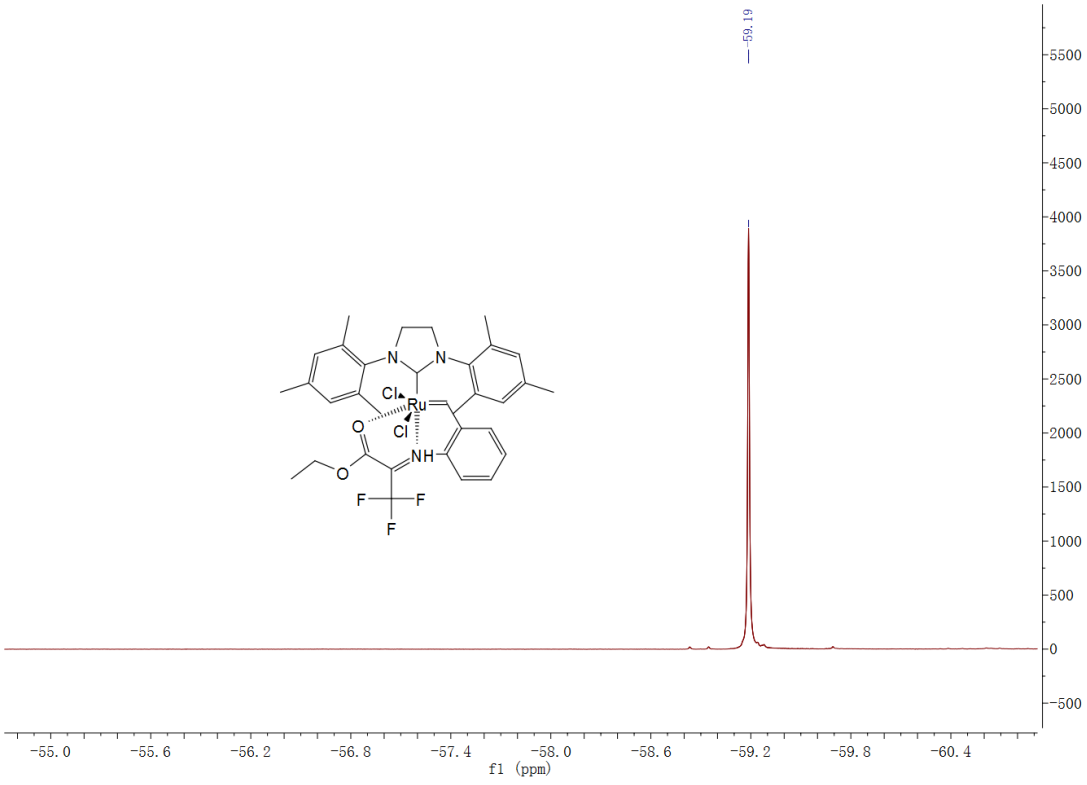


Figure S18: ^{1}H NMR spectrum of compound **14c** in $CDCl_3$

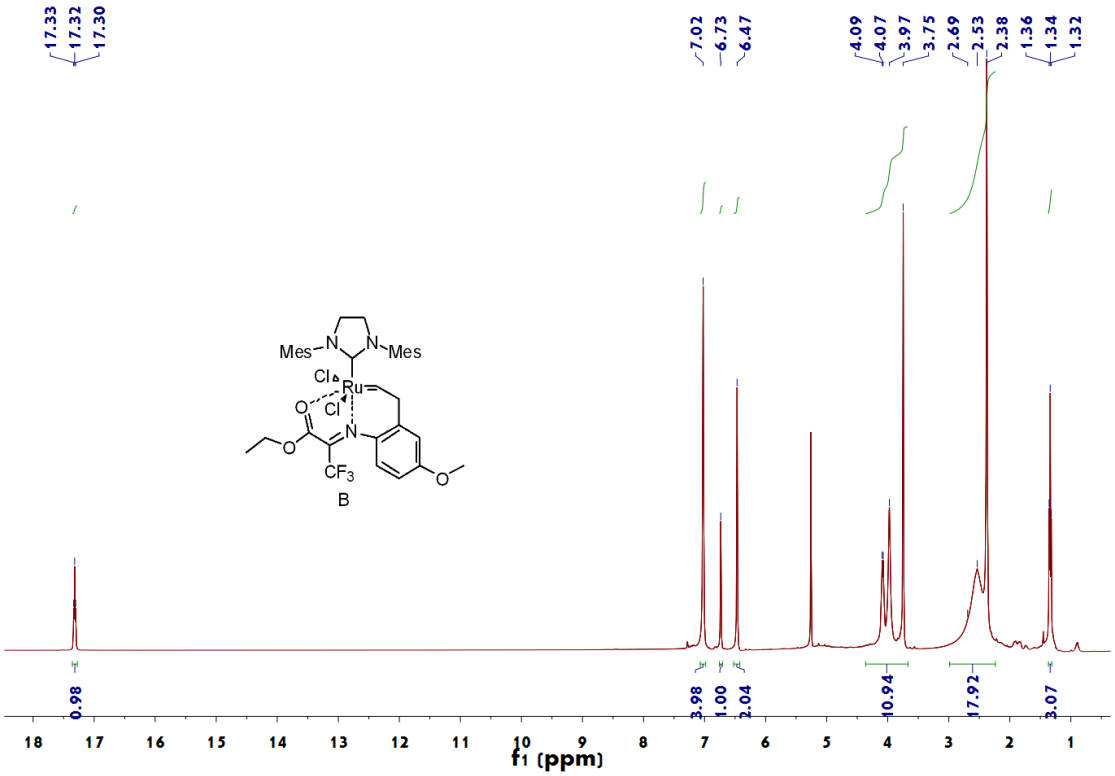


Figure S19: ^{13}C NMR spectrum of compound **14c** in $CDCl_3$

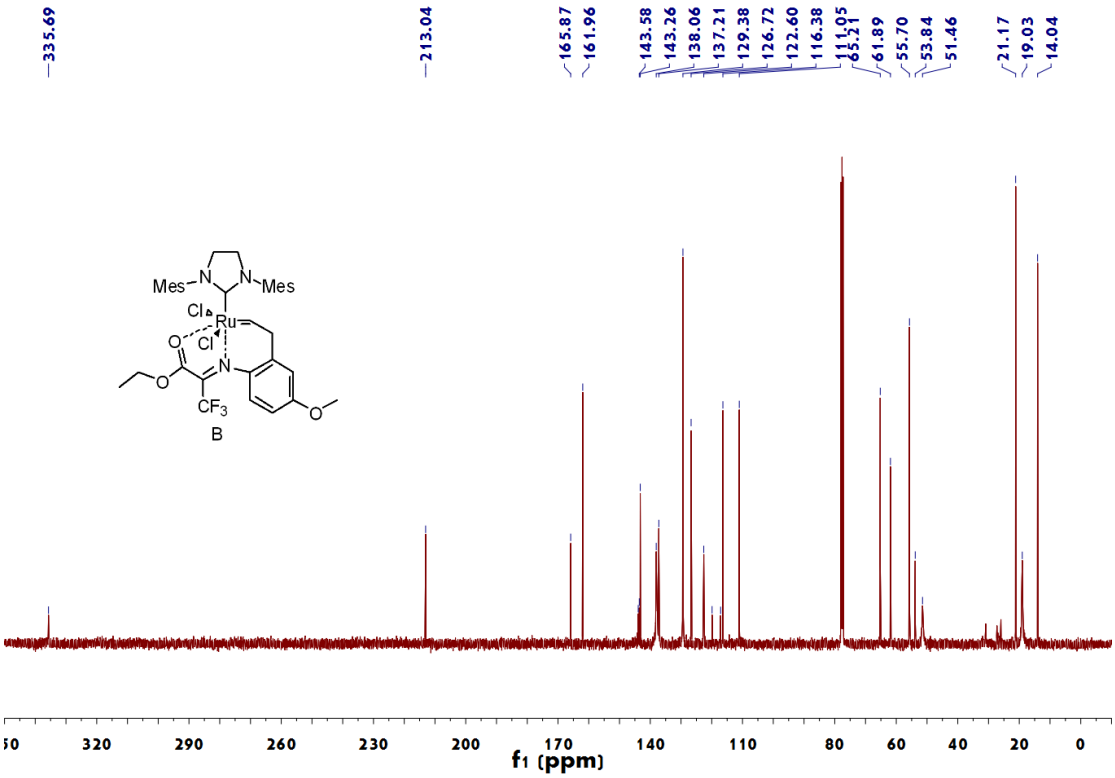


Figure S20: ^{19}F NMR spectrum of compound **14c** in $CDCl_3$

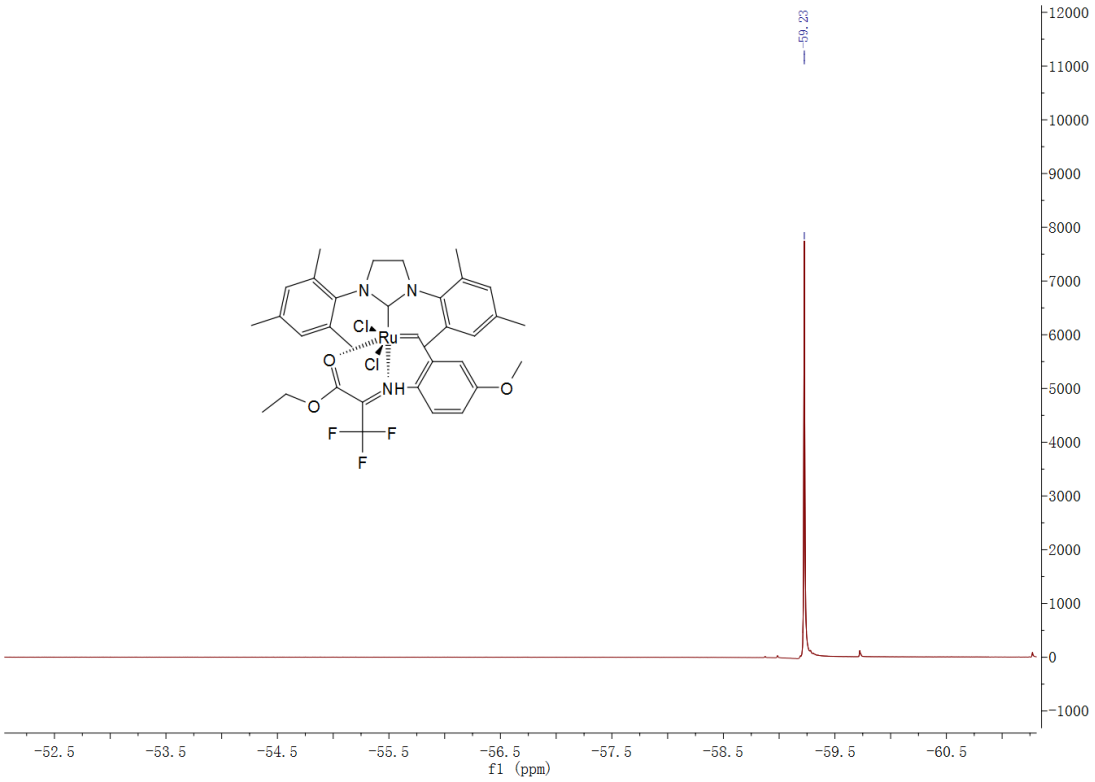


Figure S21: ^{1}H NMR spectrum of compound **14d** in $CDCl_3$

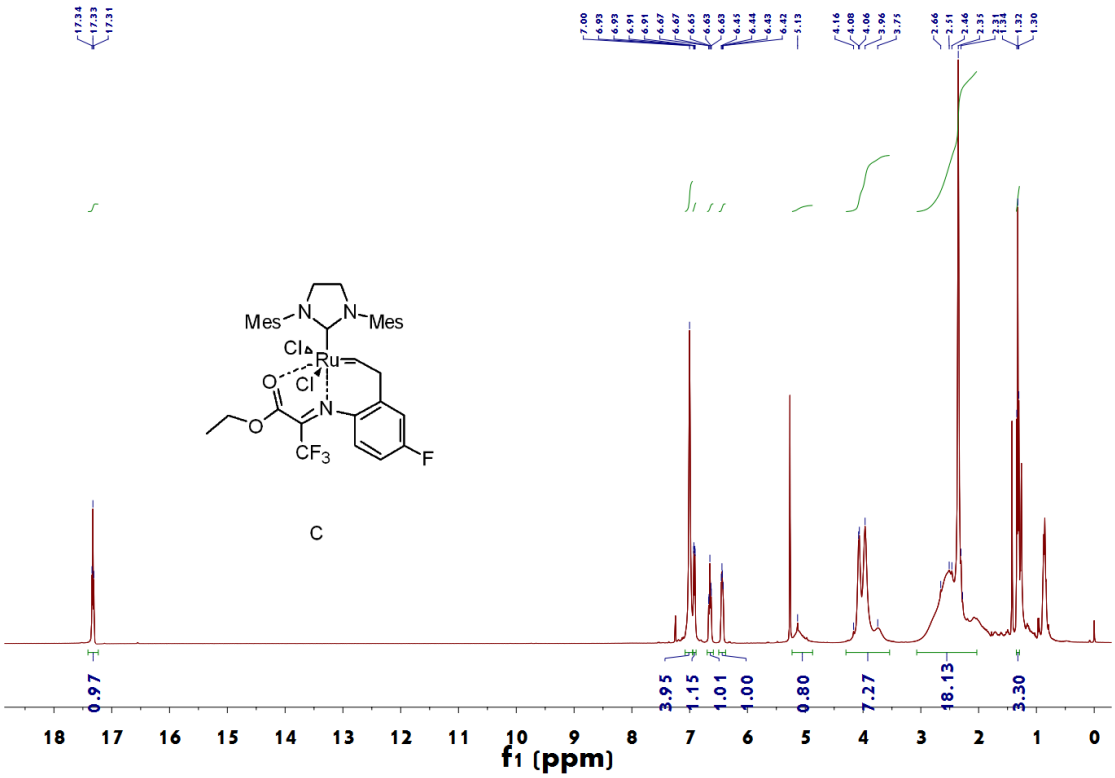


Figure S22: ^{13}C NMR spectrum of compound **14d** in $CDCl_3$

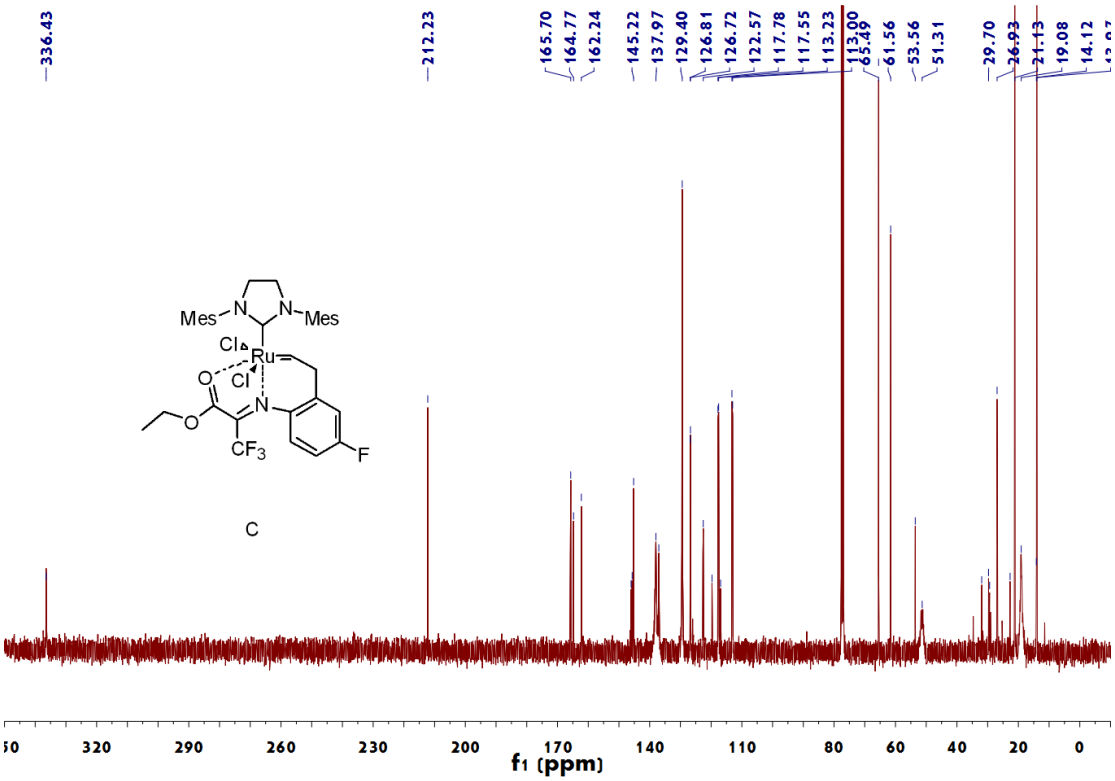


Figure S23: ^{19}F NMR spectrum of compound **14d** in $CDCl_3$

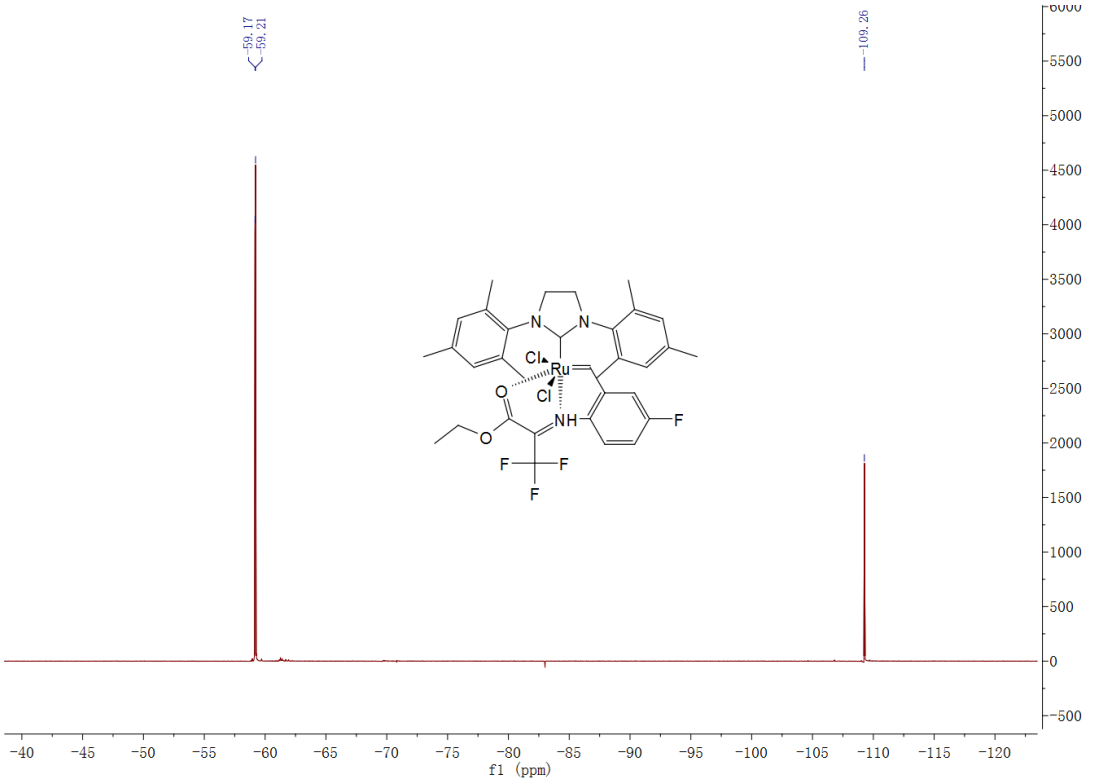


Figure S24: ^{1}H NMR spectrum of compound **14e** in $CDCl_3$

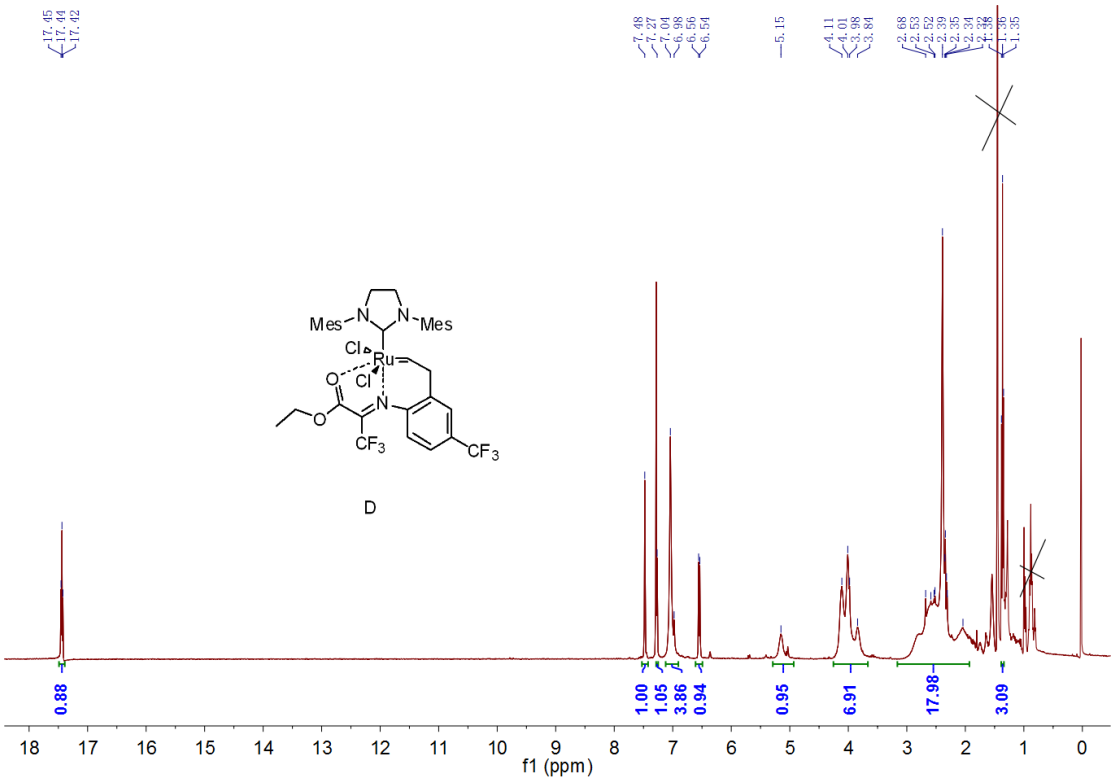


Figure S25: ^{13}C NMR spectrum of compound **14e** in $CDCl_3$

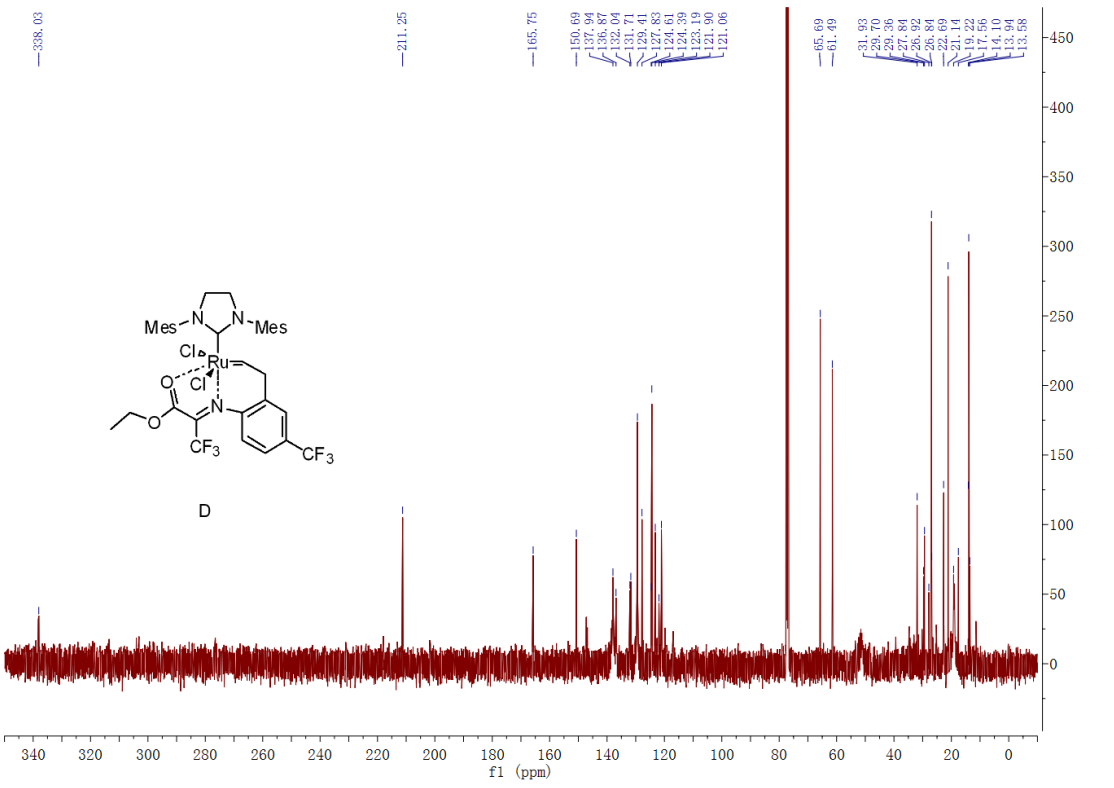


Figure S26: ^{19}F NMR spectrum of compound **14e** in $CDCl_3$

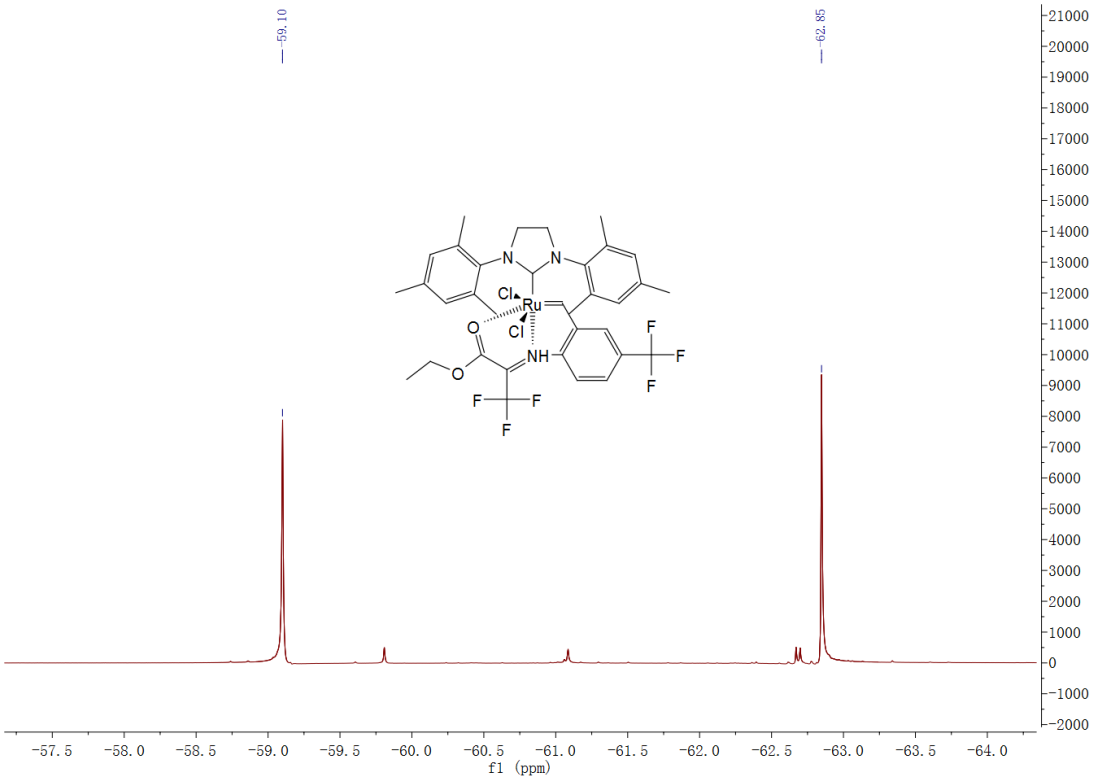


Figure S27: ^{1}H NMR spectrum of compound **14f** in $CDCl_3$

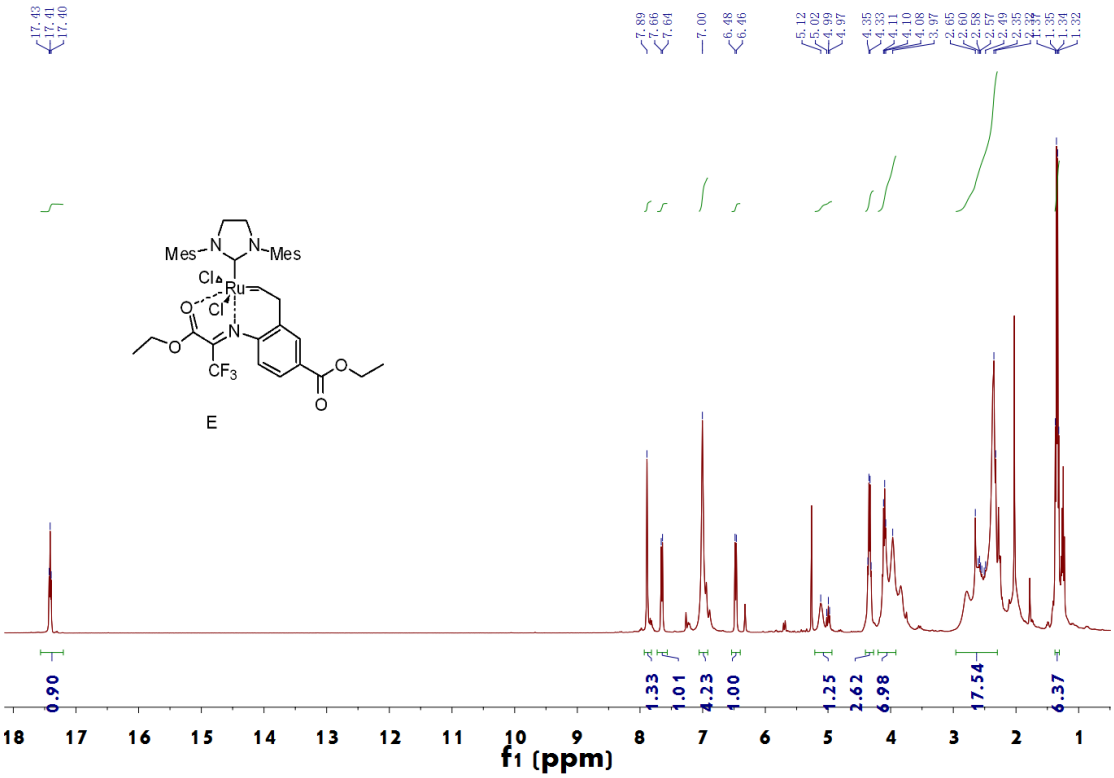


Figure S28: ^{13}C NMR spectrum of compound **14f** in $CDCl_3$

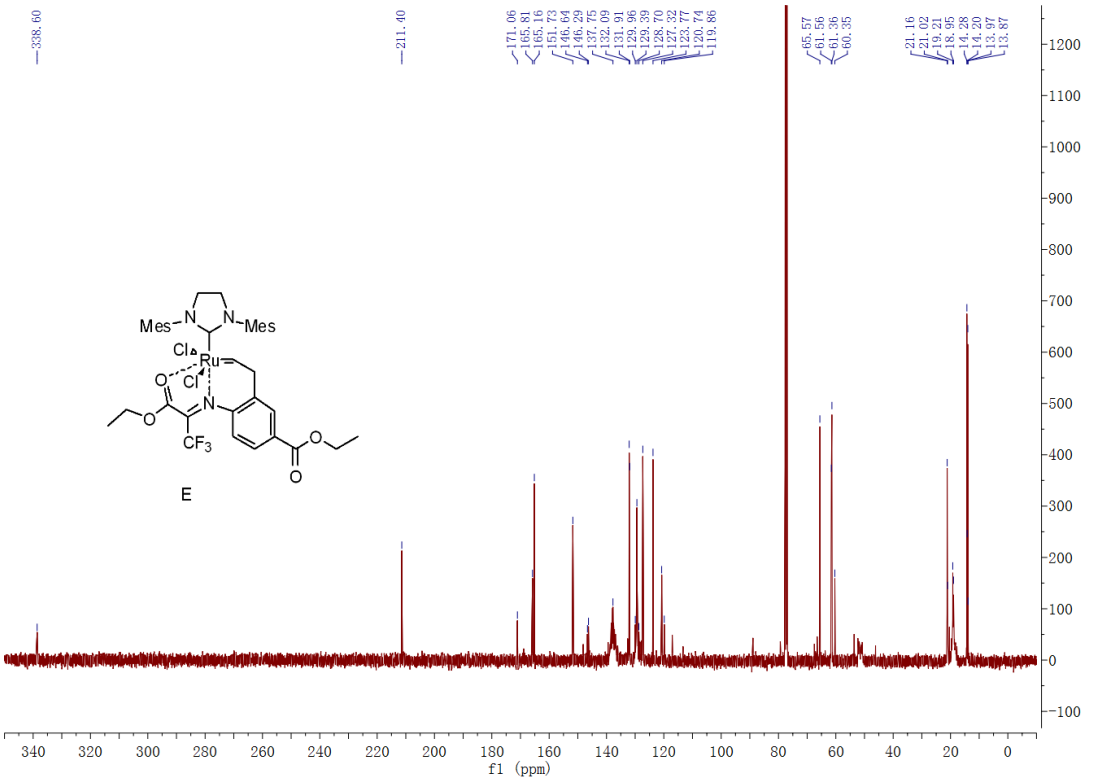
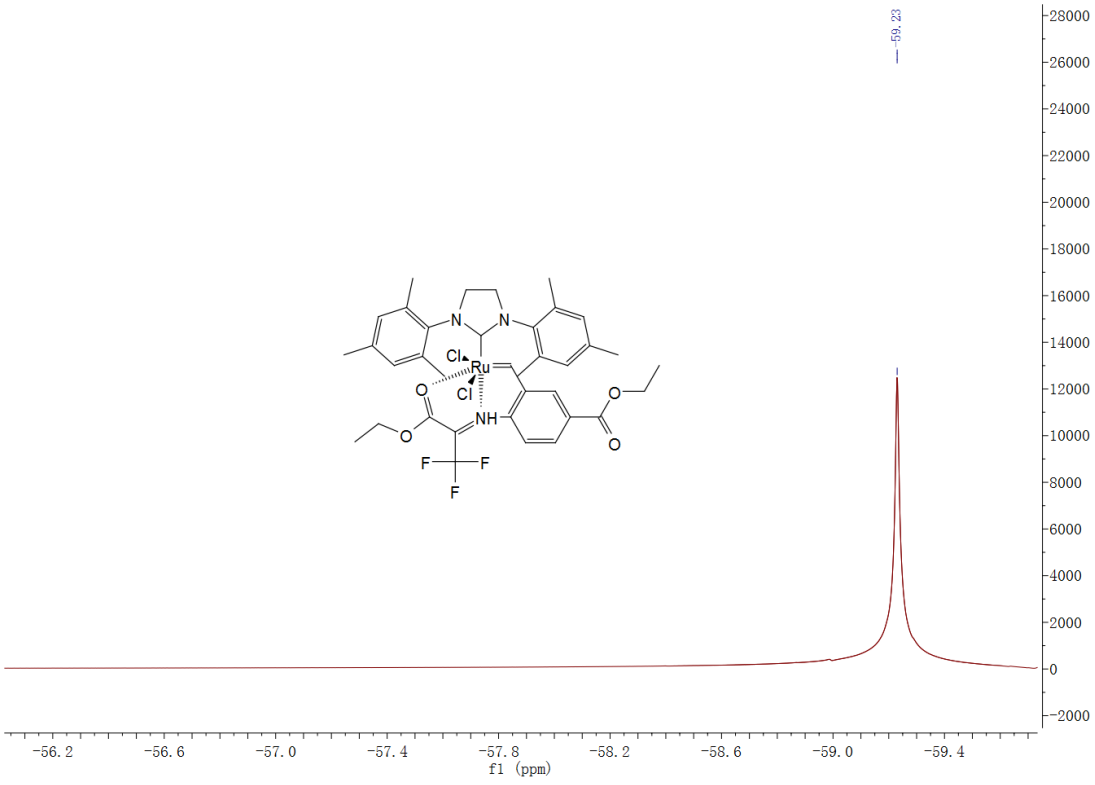


Figure S29: ^{19}F NMR spectrum of compound **14f** in $CDCl_3$



Crystallographic details for **14d**

Table S1. Crystal data and structure refinement for **14d** (A160311C, CCDC: 1504010).

Identification code	**A160311C**
Empirical formula	$C_{70}H_{81}Cl_8F_7N_6O_4Ru_2$
Formula weight	1689.14
Temperature/K	100.1(4)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.0736(9)
b/Å	15.5696(6)
c/Å	16.6456(8)
α/°	90
β/°	116.710(7)
γ/°	90
Volume/Å^3	3721.2(4)
Z	2
ρ_{calc}g/cm^3	1.508
μ/mm^{-1}	6.504
F(000)	1724.0
Crystal size/mm^3	0.2 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.222 to 134.156
Index ranges	$-18 \leq h \leq 19$, $-18 \leq k \leq 18$, $-19 \leq l \leq 12$
Reflections collected	16049
Independent reflections	6616 [R_{int} = 0.0755, R_{sigma} = 0.0952]
Data/restraints/parameters	6616/0/449
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R_1 = 0.0500, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1276
Largest diff. peak/hole / e Å^{-3}	0.96/-1.03

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **14d**.

Atom	***x***	***y***	***z***	**U(eq)**
Ru1	5438.1(2)	7127.6(2)	3300.0(2)	21.37(12)
Cl1	3835.8(7)	6859.5(7)	2865.2(7)	28.6(2)
Cl2	6991.3(7)	7410.1(8)	3548.5(7)	29.7(2)
F1	5013(3)	4028(2)	1958(2)	45.1(8)
F2	3687(2)	4626(2)	1596.5(19)	42.8(7)
F0AA	4526(2)	4243.3(19)	2956.4(19)	37.7(7)
O1	5055(2)	6836(2)	1843(2)	29.0(7)
O2	4418(3)	5741(2)	882(2)	34.1(8)
N1	4982(3)	8838(3)	3915(3)	30.1(9)
N2	4994(3)	8995(2)	2626(3)	28.4(8)
N3	5507(3)	5806(2)	3229(2)	23.1(7)
C1	5183(3)	8550(3)	4802(3)	25.9(9)
C2	4459(4)	8288(3)	4988(3)	30.1(10)
C3	4673(4)	8046(3)	5865(3)	30.8(10)
C4	5580(4)	8075(3)	6547(3)	31.8(10)
C5	6292(3)	8365(3)	6348(3)	28.8(9)
C6	6099(3)	8621(3)	5487(3)	28.6(9)
C7	3455(4)	8280(4)	4277(3)	41.5(12)
C8	5804(5)	7807(4)	7496(3)	44.0(13)
C9	6875(4)	8959(4)	5300(4)	39.2(12)
C10	5153(3)	8423(3)	3289(3)	23.5(9)
C11	4684(6)	9730(4)	3687(4)	50.8(17)
C12	4694(5)	9848(3)	2784(3)	39.8(13)
C13	5073(3)	8886(3)	1802(3)	23.7(9)
C14	4302(3)	8627(3)	1031(3)	27.9(9)
C15	4369(4)	8611(3)	219(3)	30(1)
C16	5185(4)	8841(3)	181(3)	34.2(11)
C17	5931(4)	9118(3)	962(3)	33.3(11)
C18	5894(3)	9159(3)	1784(3)	29.5(10)
C19	3397(4)	8390(4)	1034(3)	36.3(11)
C20	6699(4)	9516(4)	2598(3)	43.0(12)
C21	5260(4)	8801(4)	-689(3)	41.8(13)
C22	5866(3)	7015(3)	4516(3)	27.2(9)

C23	5522(3)	6324(3)	4908(3)	30.3(10)
C24	5998(3)	5516(3)	4833(3)	28.5(9)
C25	5978(3)	5272(3)	4013(3)	26.1(9)
C26	6483(4)	4560(3)	3968(3)	32.4(10)
C27	6983(4)	4075(3)	4726(4)	37.6(11)
C28	6978(4)	4292(4)	5525(4)	38.5(12)
C29	6491(4)	5000(3)	5583(3)	32.7(10)
C30	5008(4)	5466(3)	2436(3)	28.9(10)
C31	4569(4)	4595(3)	2241(3)	34.0(11)
C32	4808(3)	6080(3)	1687(3)	27.7(9)
C33	4190(4)	6338(4)	128(3)	39.9(12)
C34	3965(5)	5814(4)	-681(4)	53.0(16)
F3	7551(5)	3888(5)	6257(4)	50.1(16)
Cl3	8163.4(11)	7565.8(12)	2115.7(10)	57.3(4)
Cl4	6803.5(15)	6633.4(14)	559.0(12)	71.3(5)
C35	7080(4)	7030(4)	1641(4)	44.0(13)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **14d**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	27.64(17)	17.19(18)	23.82(17)	0.56(12)	15.60(12)	1.71(13)
Cl1	28.0(5)	26.5(6)	33.7(5)	-0.4(4)	16.1(4)	-1.1(4)
Cl2	29.5(5)	35.1(6)	31.2(5)	1.9(4)	19.7(4)	1.0(5)
F1	74(2)	25.0(16)	49.7(17)	-4.7(13)	39.8(17)	1.7(16)
F2	48.9(18)	33.3(17)	38.3(14)	-2.0(12)	12.6(14)	-8.0(15)
F0AA	57.0(19)	26.3(15)	37.6(14)	-1.5(11)	28.2(14)	-7.7(14)
O1	40.8(18)	19.0(17)	33.2(15)	3.9(12)	22.0(14)	2.8(14)
O2	53(2)	24.4(18)	26.3(15)	-0.8(13)	19.4(15)	4.4(16)
N1	50(2)	20(2)	27.8(18)	3.0(15)	24.1(18)	8.4(18)
N2	49(2)	13.9(18)	29.0(18)	3.9(14)	23.5(17)	8.0(17)
N3	28.2(18)	15.6(18)	28.1(17)	-2.2(14)	15.0(15)	0.6(15)
C1	37(2)	21(2)	22.5(19)	2.7(16)	15.5(18)	5.4(19)
C2	39(3)	29(3)	28(2)	-6.6(18)	20(2)	2(2)
C3	45(3)	21(2)	38(2)	-5.4(18)	29(2)	-5(2)
C4	58(3)	18(2)	28(2)	-1.8(17)	27(2)	2(2)
C5	32(2)	24(2)	27(2)	-3.6(17)	10.7(18)	4(2)
C6	36(2)	22(2)	32(2)	-4.8(17)	19(2)	0(2)
C7	45(3)	46(3)	35(2)	-7(2)	20(2)	4(3)
C8	73(4)	29(3)	31(2)	0(2)	25(2)	6(3)
C9	44(3)	35(3)	45(3)	-13(2)	27(2)	-14(2)
C10	33(2)	16(2)	24.4(19)	-3.5(16)	15.2(17)	-1.7(18)
C11	102(5)	25(3)	41(3)	8(2)	45(3)	21(3)
C12	70(4)	25(3)	31(2)	6.1(19)	29(2)	16(3)
C13	34(2)	18(2)	21.9(19)	0.7(15)	15.0(17)	1.5(18)
C14	35(2)	22(2)	27(2)	3.1(17)	13.9(19)	3(2)
C15	40(3)	24(2)	25(2)	1.7(17)	14.1(19)	1(2)
C16	52(3)	29(3)	26(2)	0.9(18)	20(2)	1(2)
C17	39(3)	34(3)	34(2)	5(2)	22(2)	-1(2)
C18	37(3)	25(2)	28(2)	3.0(17)	15.5(19)	-2(2)
C19	35(3)	39(3)	33(2)	4(2)	13(2)	1(2)
C20	46(3)	39(3)	39(3)	-1(2)	15(2)	-11(3)
C21	62(4)	41(3)	33(2)	6(2)	31(3)	9(3)
C22	35(2)	20(2)	37(2)	-5.3(18)	25.7(19)	-1.1(19)
C23	36(2)	35(3)	25(2)	5.4(18)	17.2(18)	4(2)

C24	31(2)	26(2)	31(2)	-1.7(18)	16.4(19)	-4(2)
C25	35(2)	15(2)	35(2)	6.3(17)	21.5(19)	3.9(19)
C26	45(3)	21(2)	41(2)	0.1(19)	28(2)	1(2)
C27	41(3)	25(3)	51(3)	5(2)	25(2)	5(2)
C28	40(3)	33(3)	41(3)	16(2)	17(2)	10(2)
C29	39(3)	31(3)	35(2)	4.5(19)	22(2)	-1(2)
C30	39(2)	26(2)	27(2)	0.4(18)	19.8(19)	7(2)
C31	53(3)	19(2)	37(2)	-3.3(19)	26(2)	-2(2)
C32	40(2)	23(2)	28(2)	-0.9(18)	22(2)	6(2)
C33	59(3)	35(3)	30(2)	4(2)	24(2)	8(3)
C34	76(4)	48(4)	31(2)	2(2)	21(3)	14(3)
F3	54(4)	45(4)	48(3)	24(3)	19(3)	14(3)
Cl3	57.0(8)	74.1(11)	56.5(8)	-8.0(7)	39.4(7)	-15.4(8)
Cl4	91.1(13)	78.5(13)	56.1(9)	-22.6(8)	43.6(9)	-16.3(11)
C35	58(3)	38(3)	46(3)	0(2)	34(3)	-6(3)

Table S4 . Bond Lengths for **14d.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	Cl1	2.3782(11)	C5	C6	1.383(7)
Ru1	Cl2	2.3809(11)	C6	C9	1.510(7)
Ru1	O1	2.264(3)	C11	C12	1.523(6)
Ru1	N3	2.068(4)	C13	C14	1.383(7)
Ru1	C10	2.067(4)	C13	C18	1.399(7)
Ru1	C22	1.830(4)	C14	C15	1.403(6)
F1	C31	1.348(6)	C14	C19	1.505(7)
F2	C31	1.340(7)	C15	C16	1.388(7)
F0AA	C31	1.340(5)	C16	C17	1.382(8)
O1	C32	1.231(6)	C16	C21	1.507(6)
O2	C32	1.308(6)	C17	C18	1.398(6)
O2	C33	1.471(6)	C18	C20	1.499(7)
N1	C1	1.434(5)	C22	C23	1.488(6)
N1	C10	1.355(5)	C23	C24	1.507(7)
N1	C11	1.462(6)	C24	C25	1.405(6)
N2	C10	1.349(6)	C24	C29	1.393(7)
N2	C12	1.477(6)	C25	C26	1.394(7)
N2	C13	1.444(5)	C26	C27	1.377(8)
N3	C25	1.442(6)	C27	C28	1.376(8)
N3	C30	1.309(6)	C28	C29	1.379(8)
C1	C2	1.393(7)	C28	F3	1.311(8)
C1	C6	1.403(7)	C30	C31	1.495(7)
C2	C3	1.392(7)	C30	C32	1.489(6)
C2	C7	1.513(7)	C33	C34	1.473(7)
C3	C4	1.389(8)	Cl3	C35	1.765(6)
C4	C5	1.402(7)	Cl4	C35	1.762(5)
C4	C8	1.513(6)			

Table S5. Bond Angles for **14d**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Ru1	Cl2	173.15(4)	N2	C12	C11	102.4(4)
O1	Ru1	Cl1	84.41(9)	C14	C13	N2	119.4(4)
O1	Ru1	Cl2	89.00(9)	C14	C13	C18	121.9(4)
N3	Ru1	Cl1	83.45(11)	C18	C13	N2	118.1(4)
N3	Ru1	Cl2	96.62(11)	C13	C14	C15	118.3(4)
N3	Ru1	O1	74.63(13)	C13	C14	C19	122.2(4)
C10	Ru1	Cl1	87.89(13)	C15	C14	C19	119.5(4)
C10	Ru1	Cl2	91.85(13)	C16	C15	C14	121.5(5)
C10	Ru1	O1	103.52(14)	C15	C16	C21	121.2(5)
C10	Ru1	N3	171.28(16)	C17	C16	C15	118.4(4)
C22	Ru1	Cl1	97.88(14)	C17	C16	C21	120.4(5)
C22	Ru1	Cl2	88.97(14)	C16	C17	C18	122.2(5)
C22	Ru1	O1	162.10(17)	C13	C18	C20	122.2(4)
C22	Ru1	N3	87.95(17)	C17	C18	C13	117.6(4)
C22	Ru1	C10	94.32(18)	C17	C18	C20	120.2(4)
C32	O1	Ru1	108.9(3)	C23	C22	Ru1	121.7(3)
C32	O2	C33	116.1(4)	C22	C23	C24	105.3(4)
C1	N1	C11	117.4(4)	C25	C24	C23	121.1(4)
C10	N1	C1	127.8(4)	C29	C24	C23	120.9(4)
C10	N1	C11	114.1(4)	C29	C24	C25	118.0(4)
C10	N2	C12	113.9(3)	C24	C25	N3	119.8(4)
C10	N2	C13	129.4(4)	C26	C25	N3	119.5(4)
C13	N2	C12	116.7(3)	C26	C25	C24	120.5(4)
C25	N3	Ru1	122.8(3)	C27	C26	C25	120.1(4)
C30	N3	Ru1	115.9(3)	C28	C27	C26	119.7(5)
C30	N3	C25	120.9(4)	C27	C28	C29	120.9(5)
C2	C1	N1	119.8(4)	F3	C28	C27	118.2(6)
C2	C1	C6	121.2(4)	F3	C28	C29	120.2(6)
C6	C1	N1	118.7(4)	C28	C29	C24	120.7(4)
C1	C2	C7	122.2(4)	N3	C30	C31	127.0(4)
C3	C2	C1	118.4(5)	N3	C30	C32	112.9(4)
C3	C2	C7	119.5(4)	C32	C30	C31	119.9(4)
C4	C3	C2	121.5(4)	F1	C31	C30	113.4(4)
C3	C4	C5	119.1(4)	F2	C31	F1	106.2(4)
C3	C4	C8	121.0(5)	F2	C31	C30	111.6(4)

C5	C4	C8	119.9(5)	F0AA	C31	F1	106.9(4)
C6	C5	C4	120.7(5)	F0AA	C31	F2	105.6(4)
C1	C6	C9	121.5(4)	F0AA	C31	C30	112.7(4)
C5	C6	C1	119.0(4)	O1	C32	O2	124.3(4)
C5	C6	C9	119.5(5)	O1	C32	C30	120.7(4)
N1	C10	Ru1	125.4(3)	O2	C32	C30	114.9(4)
N2	C10	Ru1	127.6(3)	O2	C33	C34	107.1(4)
N2	C10	N1	106.6(4)	Cl4	C35	Cl3	111.6(3)
N1	C11	C12	102.9(4)				

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **14d**

Atom	***x***	***y***	***z***	**U(eq)**
H3	4198	7860	5996	37
H5	6902	8386	6801	35
H7A	3182	8833	4251	62
H7B	3116	7852	4425	62
H7C	3430	8148	3703	62
H8A	5938	8307	7871	66
H8B	6336	7433	7725	66
H8C	5280	7510	7495	66
H9A	6912	8623	4834	59
H9B	7455	8922	5837	59
H9C	6753	9548	5112	59
H11A	5113	10122	4134	61
H11B	4064	9818	3635	61
H12A	4080	9994	2316	48
H12B	5132	10291	2815	48
H15	3856	8442	-305	36
H17	6476	9283	939	40
H19A	3488	7894	1407	54
H19B	2940	8263	432	54
H19C	3184	8861	1266	54
H20A	6511	10037	2781	64
H20B	7204	9637	2458	64
H20C	6897	9105	3078	64
H21A	5630	8314	-679	63
H21B	5548	9317	-759	63
H21C	4649	8747	-1182	63
H22A	6537	6951	4774	33
H22B	5749	7557	4734	33
H23A	4850	6268	4576	36
H23B	5683	6448	5532	36
H26	6481	4413	3426	39
H27	7323	3602	4698	45
H28	7307	3957	6034	46
H29	6493	5135	6128	39

H33A	4717	6710	244	48
H33B	3662	6693	45	48
H34A	3786	6183	-1194	80
H34B	3461	5432	-774	80
H34C	4502	5485	-601	80
H35A	7100	6557	2029	53
H35B	6597	7424	1605	53