Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information for

A ruthenium carbolong skeleton with ten carbon atoms

Jiaomei Guo,[a] Zhengyu Lu,[b] Wenhao Zhou,[b] Qingde Zhuo,*[c] Dafa Chen*[b] and Haiping Xia*[ab]

[a]Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

[b]Shenzhen Grubbs Institute and Guangdong Provincial Key Laboratory of Catalysis, Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

[c]Department of Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China

E-mails: zhuoqd@ustc.edu.cn; chendf@sustech.edu.cn; xiahp@sustech.edu.cn

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1. General methods

All syntheses were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques unless otherwise stated. The organic compound **L** was synthesized according to the published literature[1]. The other reagents and solvents were used as purchased from commercial sources without further purification. Column chromatography was performed on silica gel (200–300 mesh) in air. NMR spectra was collected on the Brucker AVIII-400 (400 MHz) or Brucker AVIII-600 spectrometer (600 MHz). ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P{^{1}H} NMR chemical shifts are relative to 85% H_3PO_4. Two-dimensional and one-dimensional NMR spectra are abbreviated as HSQC (heteronuclear single quantum coherence), HMBC (heteronuclear multiple bond coherence). The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). High resolution mass spectra (HRMS) experiments were recorded on a Thermo Scientific Q Exactive instrument. UV-Vis absorption spectra were recorded on a UV3600 spectrometer (Shimadzu, Japan).

2. NMR and HRMS spectra

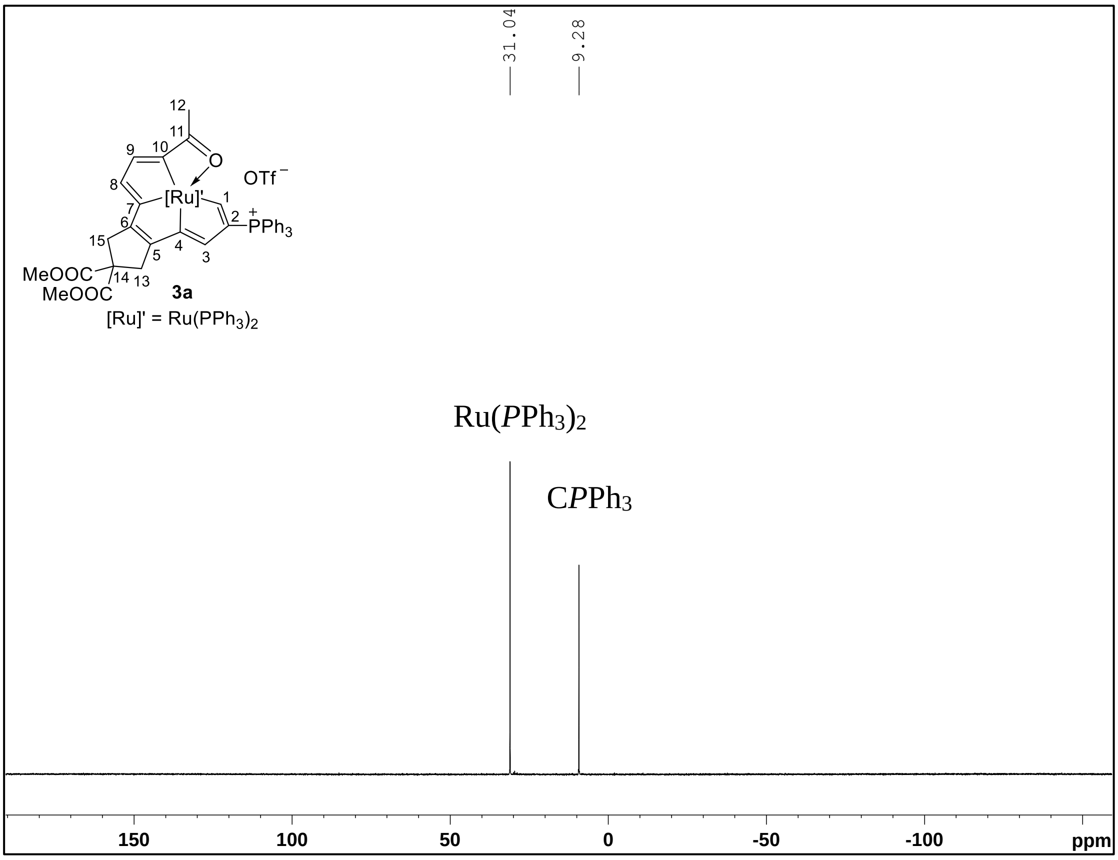


Figure S1 The $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$) spectrum for compound **3a**

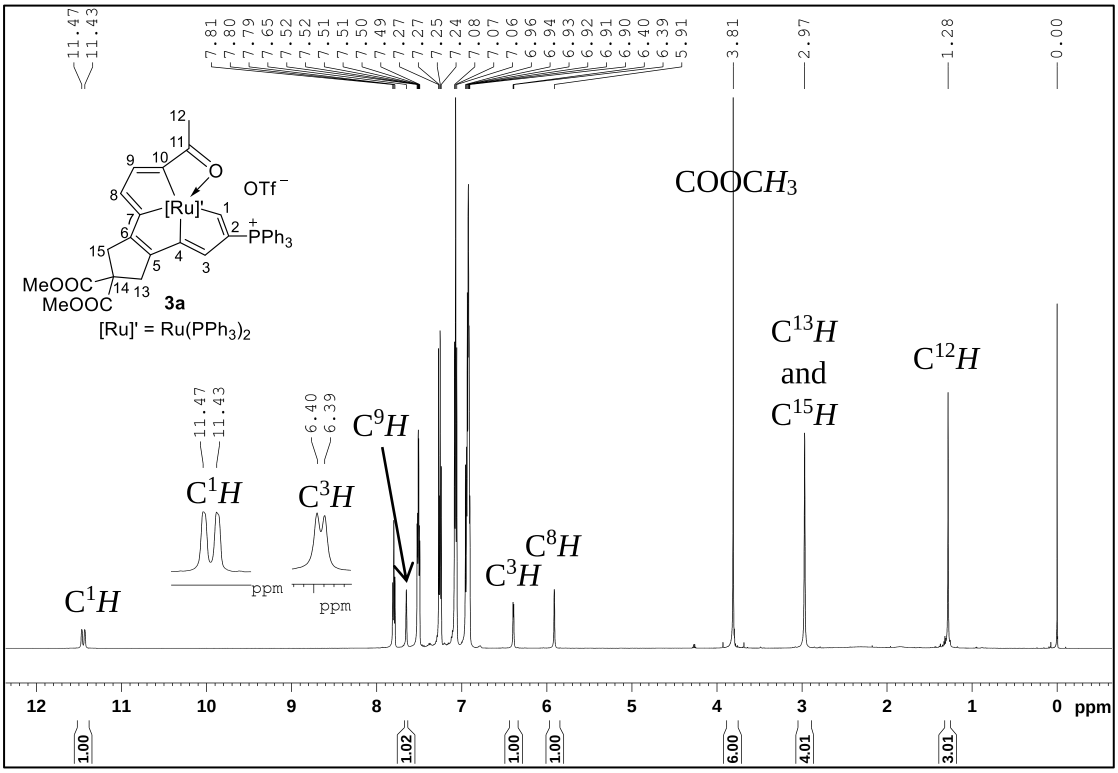


Figure S2 The ^1H NMR (600.1 MHz, $CDCl_3$) spectrum for compound **3a**

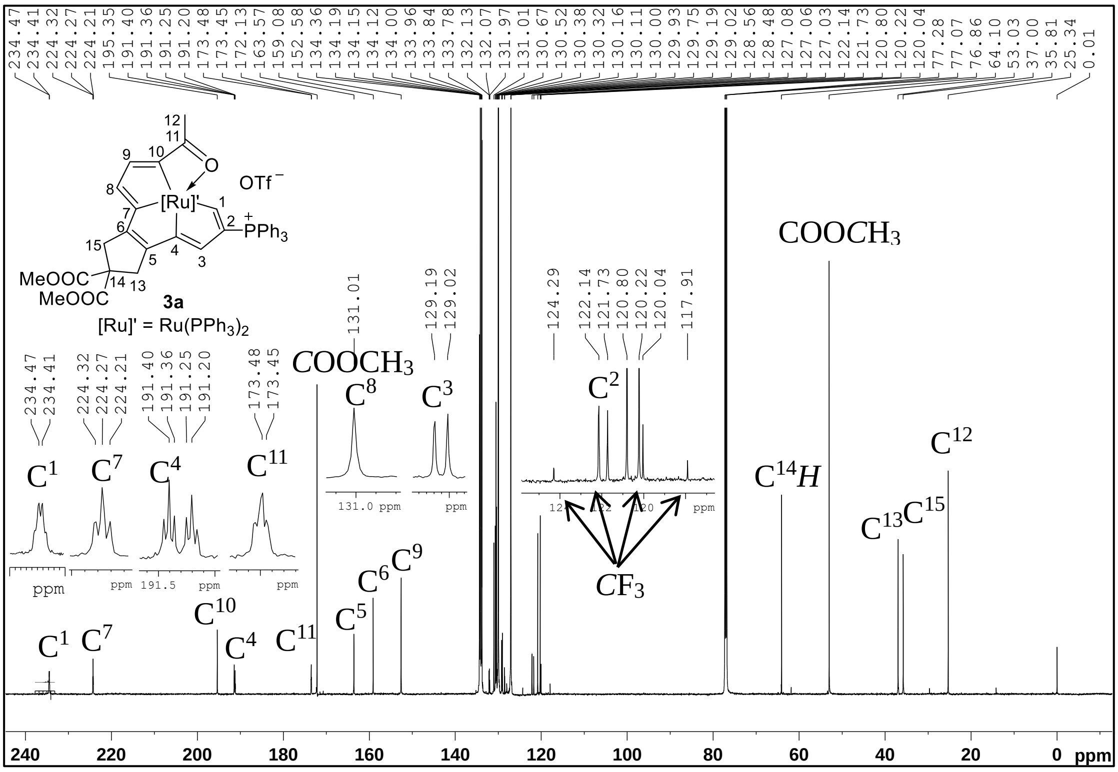


Figure S3 The ^{13}C NMR (150.9 MHz, CDCl$_3$) spectrum for compound **3a**

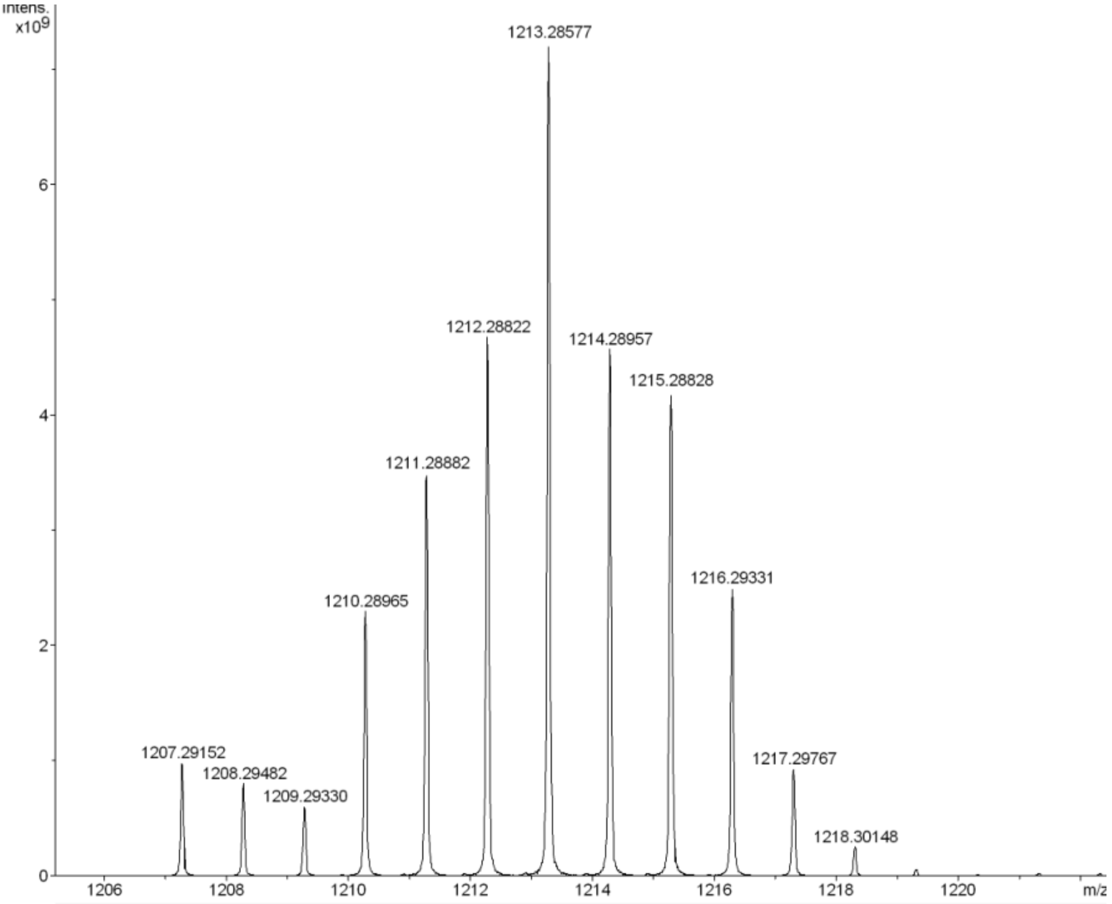


Figure S4 The HRMS spectrum for compound **3a**

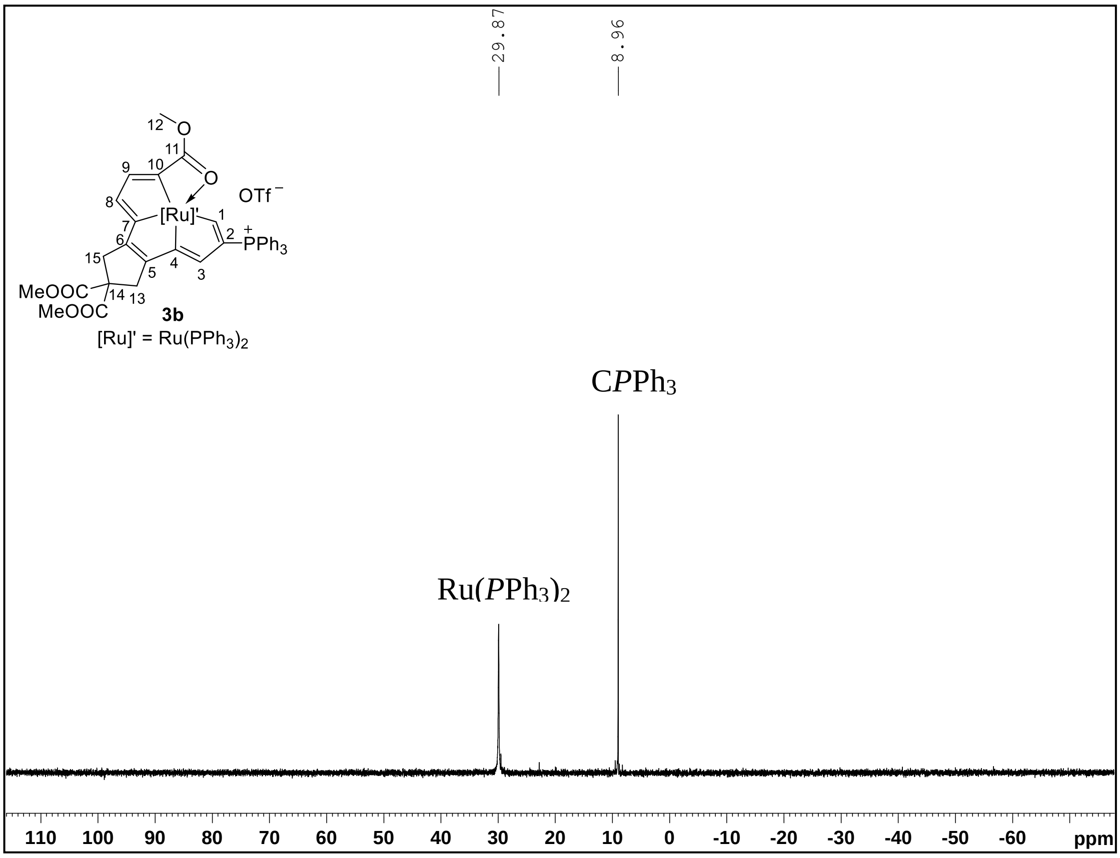


Figure S5 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, $CDCl_3$) spectrum for compound **3b**

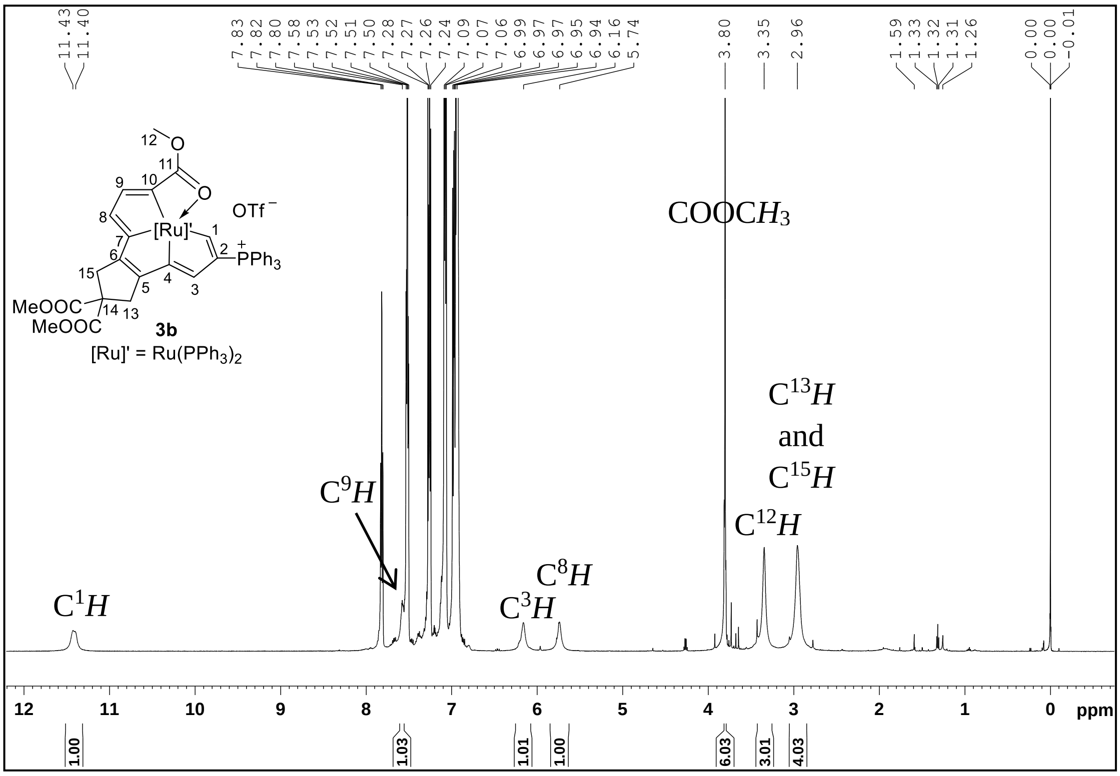


Figure S16 The ^{1}H NMR (600.1 MHz, $CDCl_3$) spectrum for compound **3b**

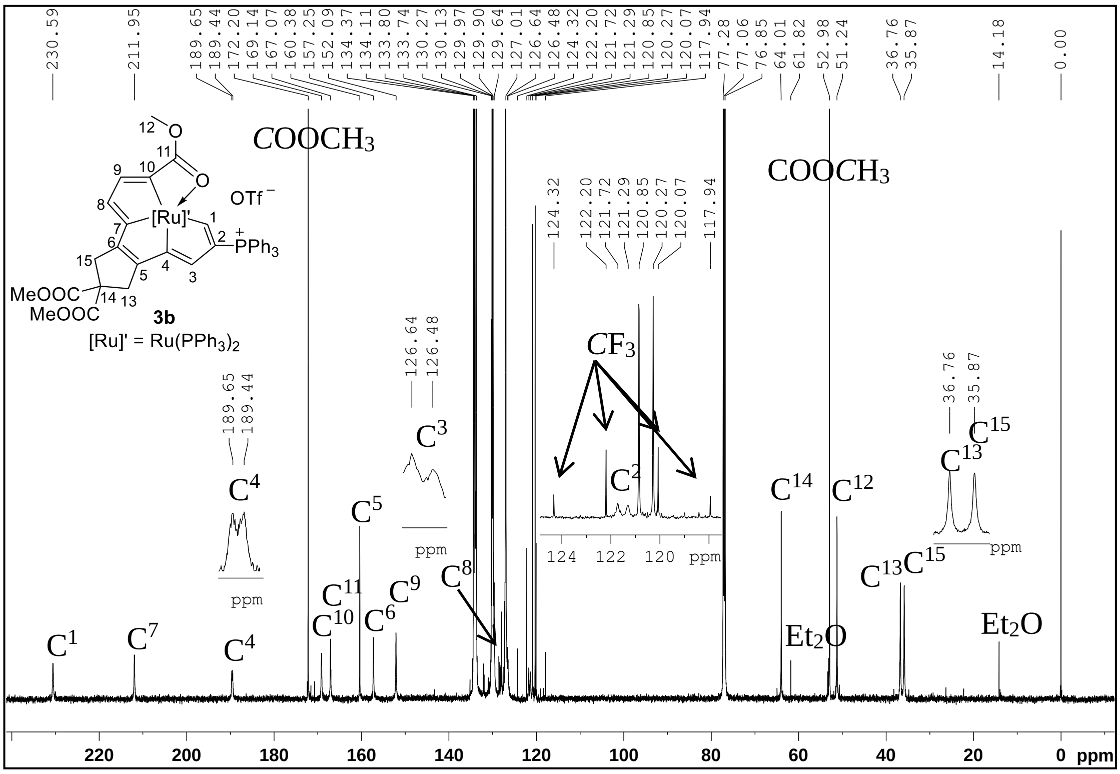


Figure S7 The $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$) spectrum for compound **3b**

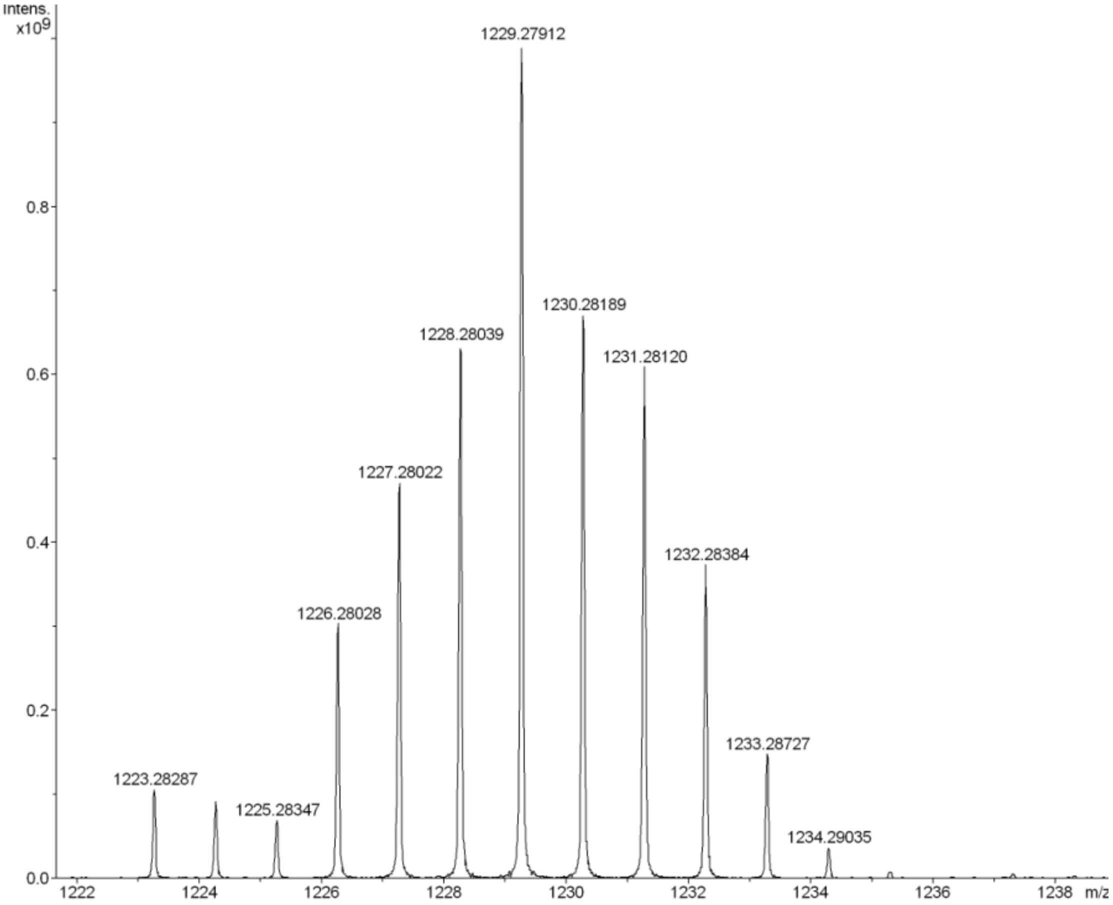


Figure S8 The HRMS spectrum for compound **3b**

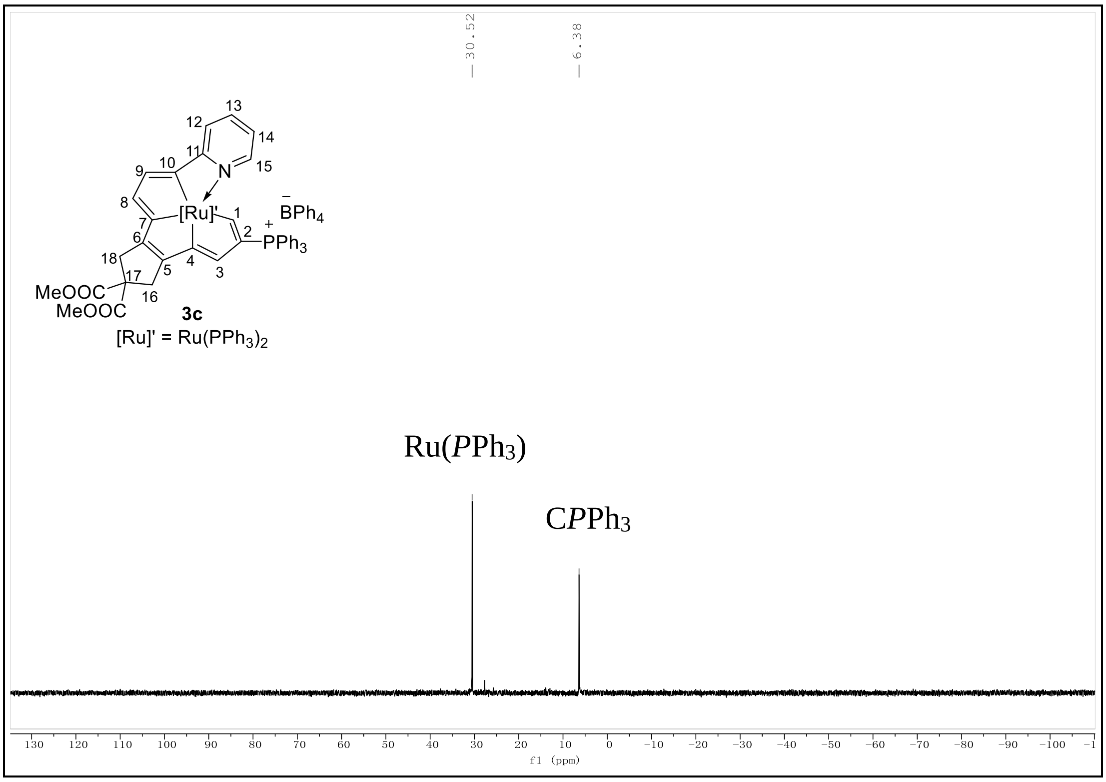


Figure S9 The $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2) spectrum for compound **3c**

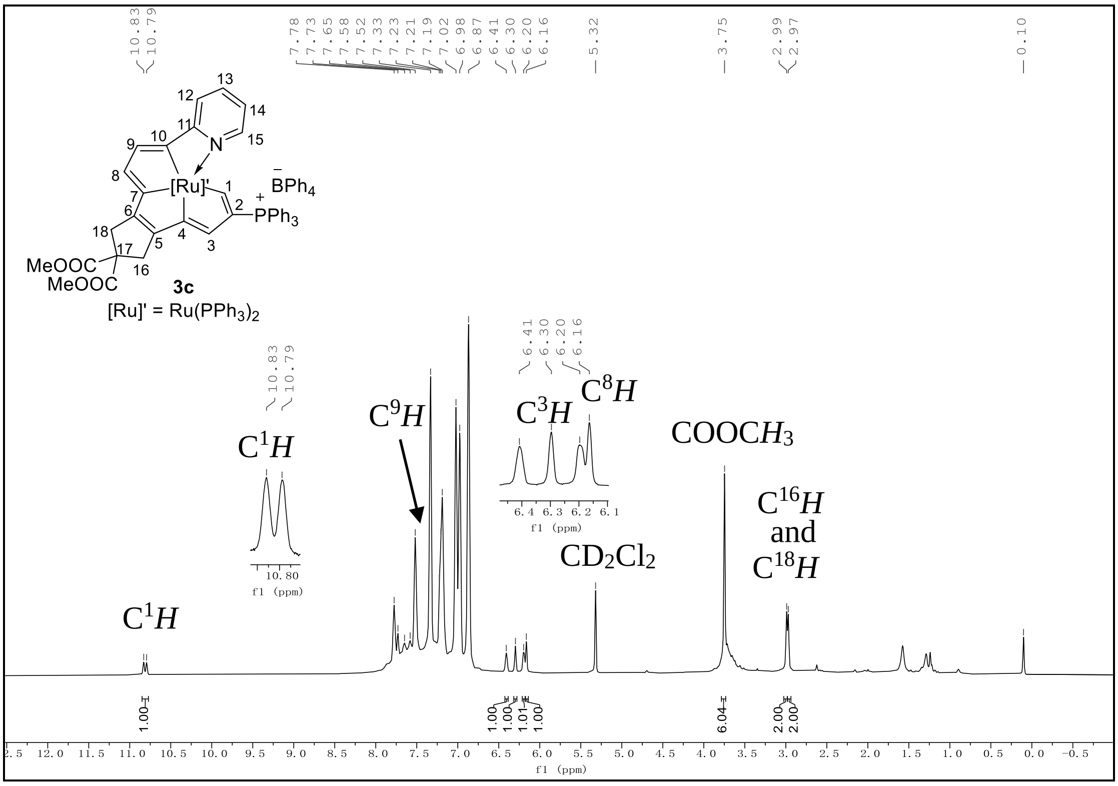


Figure S10 The ^1H NMR (600.1 MHz, CD_2Cl_2) spectrum for compound **3c**

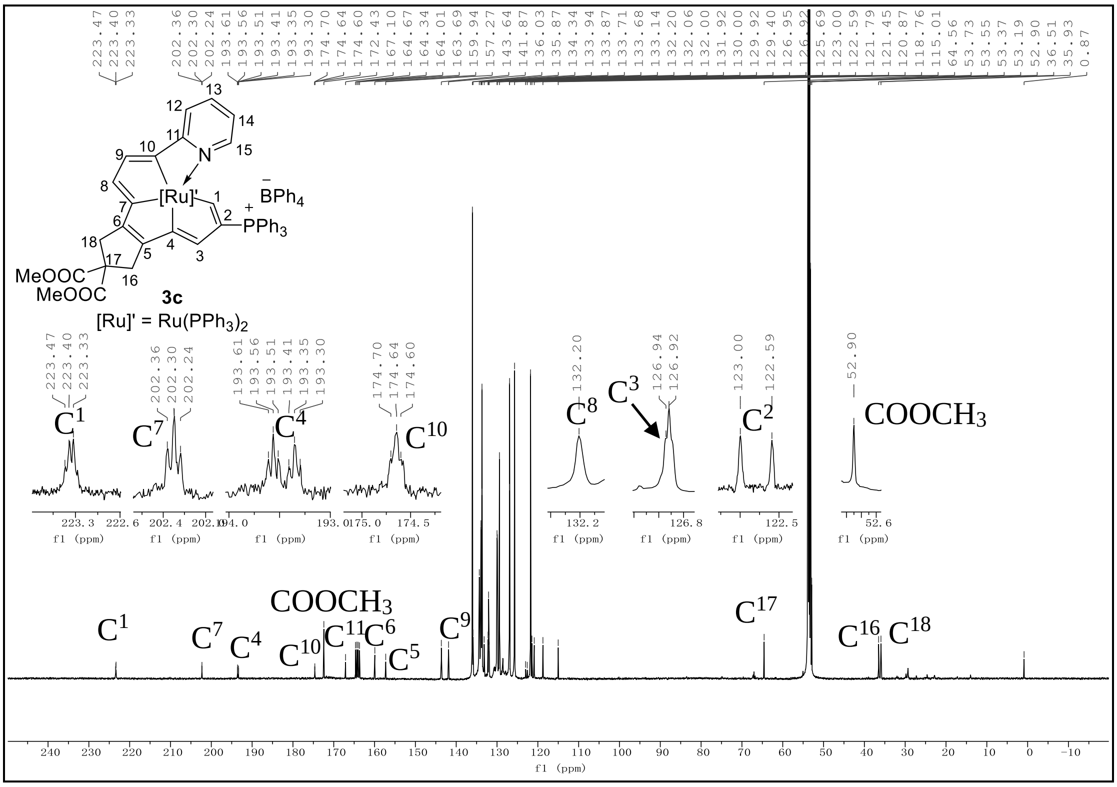


Figure S11 The $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2) spectrum for compound **3c**

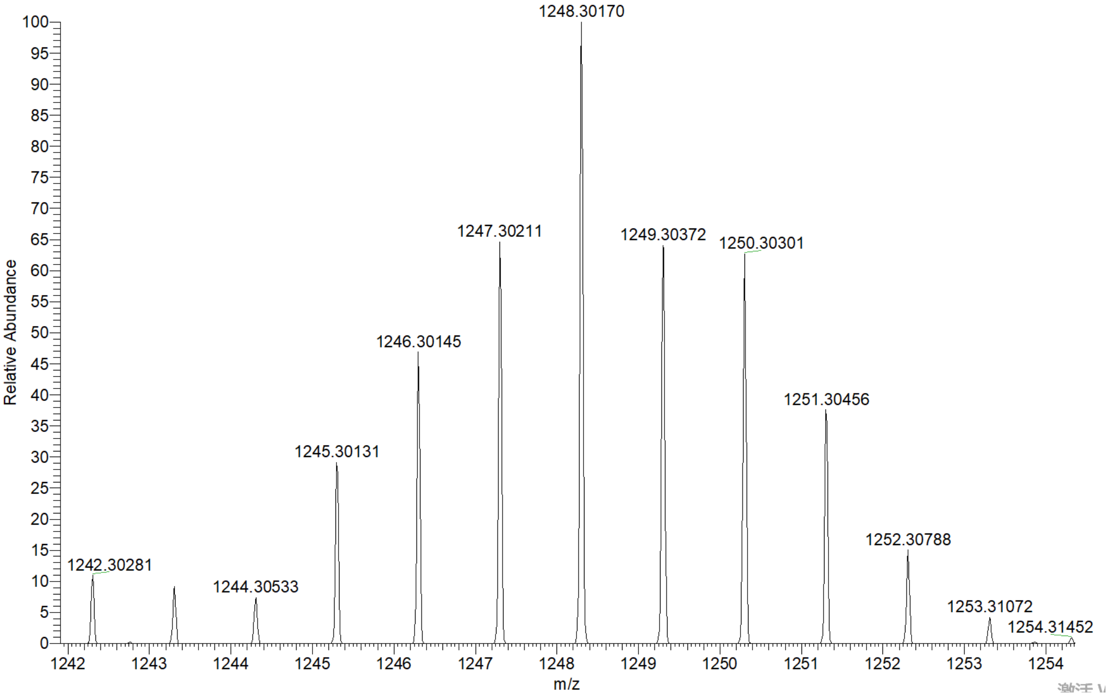


Figure S12 The HRMS spectrum for compound **3c**

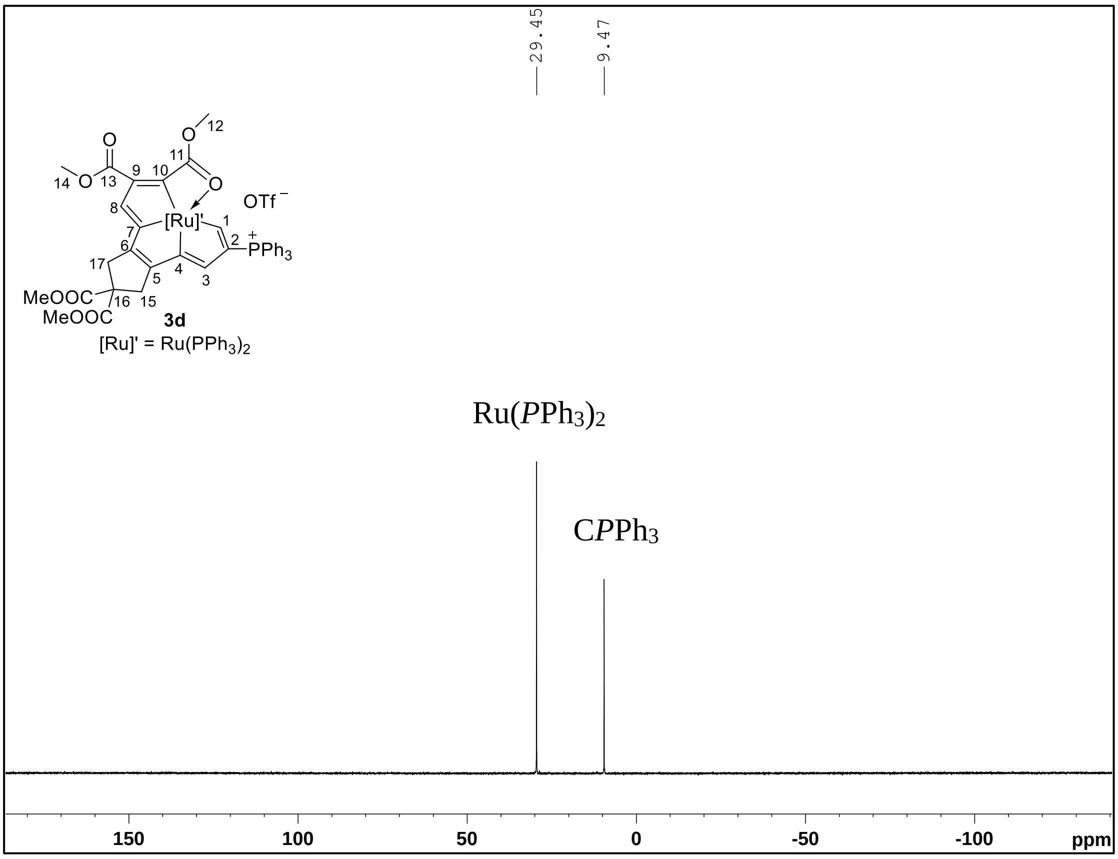


Figure S13 The $^{31}P\{^{1}H\}$ NMR (242.9 MHz, $CDCl_3$) spectrum for compound **3d**

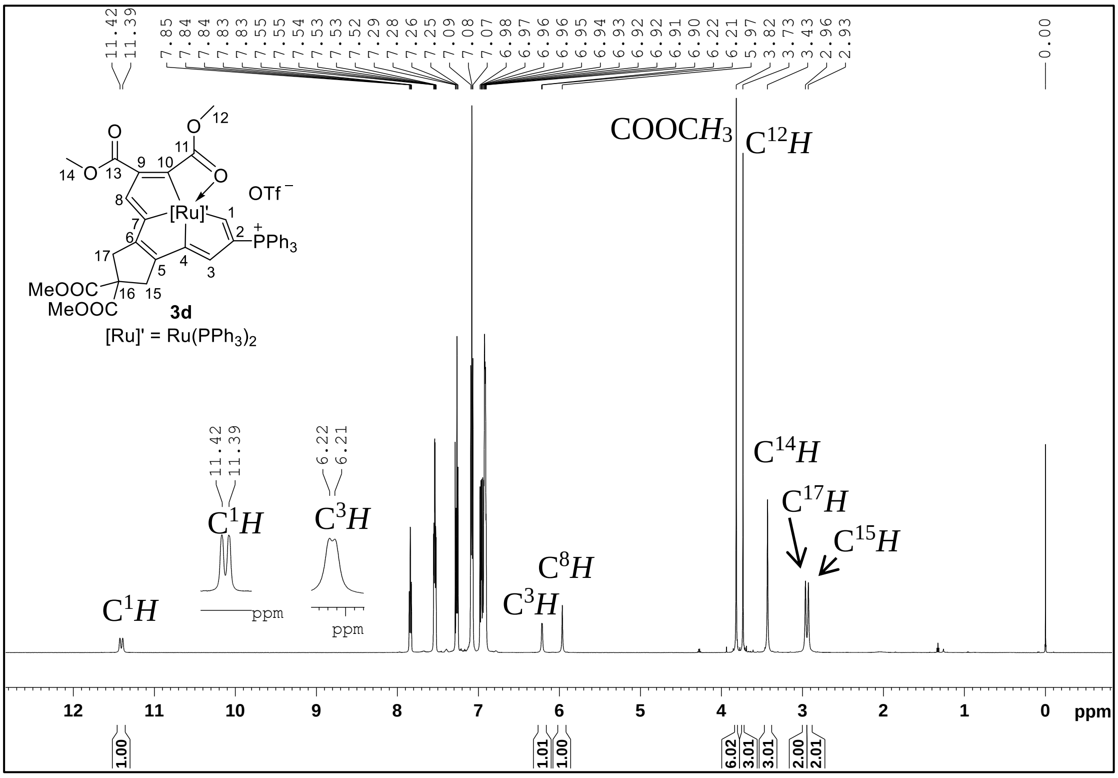


Figure S14 The ^{1}H NMR (600.1 MHz, $CDCl_3$) spectrum for compound **3d**

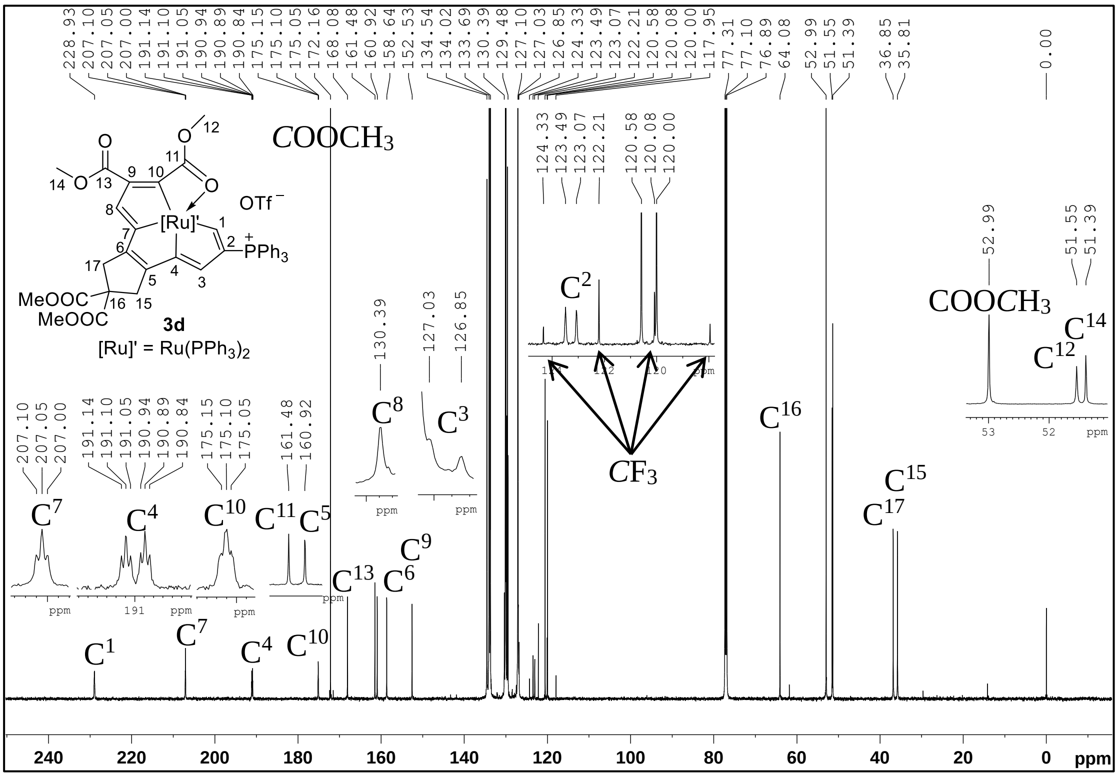


Figure S15 The $^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$) spectrum for compound **3d**

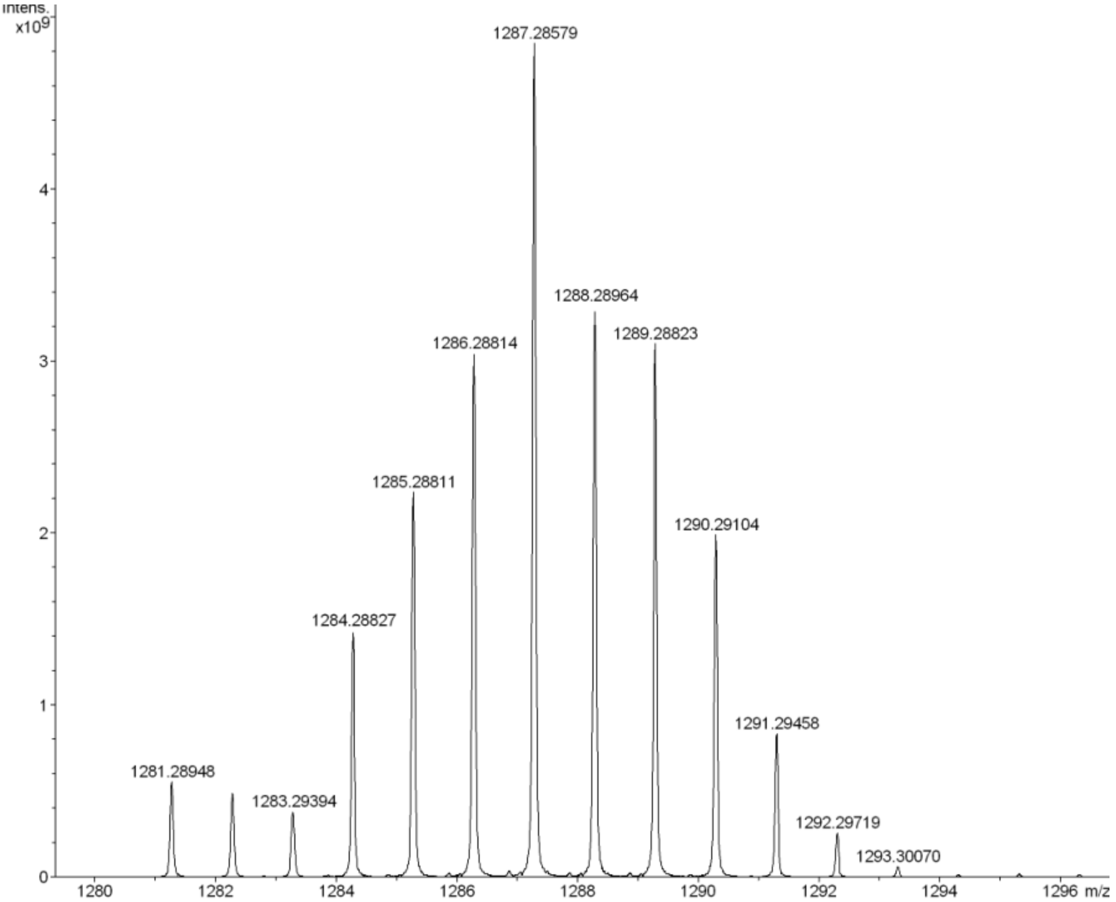


Figure S16 The HRMS spectrum for compound **3d**

3. Crystallographic details

The single-crystals suitable for X-ray diffraction were grown from dichloromethane solution layered with hexane. Single-Crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector for **3a** with a Cu Kα radiation (λ = 1.54178 Å). Multi-scan absorption corrections were applied for **3a**. Using Olex2[2], the structures were solved with ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. CCDC-2447172 (**3a**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http:// www.ccdc.cam.ac.uk/structures/.

Table S1 Selected Bond Lengths and Bond Angles for Complex **3a**.

Bond Distances (Å)					
Ru(1)-C(1)	2.069(3)	C(4)-C(5)	1.428(4)	C(11)-C(12)	1.494(5)
Ru(1)-C(4)	2.134(3)	C(5)-C(6)	1.348(4)	C(5)-C(13)	1.503(4)
Ru(1)-C(7)	2.145(3)	C(6)-C(7)	1.421(4)	C(13)-C(14)	1.558(4)
Ru(1)-C(10)	2.079(3)	C(7)-C(8)	1.386(4)	C(14)-C(15)	1.567(4)
Ru(1)-O(1)	2.249(2)	C(8)-C(9)	1.398(5)	C(6)-C(15)	1.504(4)
C(1)-C(2)	1.367(4)	C(9)-C(10)	1.366(5)	Ru(1)-P(1)	2.3842(8)
C(2)-C(3)	1.433(4)	C(10)-C(11)	1.387(5)	Ru(1)-P(2)	2.3827(8)
C(3)-C(4)	1.358(4)	C(11)-O(1)	1.285(4)	C(2)-P(3)	1.789(3)

Bond Angles (°)			
C(1)-Ru(1)-C(4)	73.41(12)	C(5)-C(6)-C(7)	116.7(3)
C(4)-Ru(1)-C(7)	74.91(11)	C(6)-C(7)-Ru(1)	116.0(2)
C(7)-Ru(1)-C(10)	69.94(12)	C(8)-C(7)-Ru(1)	120.9(2)
C(10)-Ru(1)-O(1)	60.61(10)	C(7)-C(8)-C(9)	112.8(3)
C(2)-C(1)-Ru(1)	121.0(2)	C(8)-C(9)-C(10)	110.9(3)
C(1)-C(2)-C(3)	113.3(3)	C(9)-C(10)-Ru(1)	125.4(2)
C(2)-C(3)-C(4)	113.4(3)	C(11)-C(10)-Ru(1)	96.9(2)
C(3)-C(4)-Ru(1)	118.9(2)	O(1)-C(11)-C(10)	110.0(3)
C(5)-C(4)-Ru(1)	116.8(2)	C(11)-O(1)-Ru(1)	92.36(18)
C(4)-C(5)-C(6)	115.5(3)		

Table S2 Crystal Data and Structure Refinement for **3a**

Identification code	**3a** 1.5CH_2Cl_2
Empirical formula	$C_{75.5}H_{67}Cl_3F_3O_9RuP_3S$
Formula weight	1507.68
Temperature/K	173.00(14)
λ [Å] (CuKα radiation)	1.54178
crystal system	Triclinic
space group	P-1
a [Å]	12.7589(4)
b [Å]	16.0325(4)
c [Å]	17.4998(6)
α [°]	91.986(2)
β [°]	94.645(3)
γ [°]	103.761(2)
Volume/[$Å^3$]	3460.16
Z	2
ρ_{calc} [gcm^{-3}]	1.447
μ [mm^{-1}]	4.387
F(000)	1550
crystal size [mm^3]	0.2×0.2×0.2
2θ range [°]	7.164 to 124.278
reflns collected	29700
independent reflns	10882
data/restraints/params	10882/2/868
GOF on F^2	1.044
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0439/0.1137
R_1/wR_2 (all data)	0.0470/0.1168
largest peak/hole [e $Å^{-3}$]	1.28 /-1.05

4. Theoretical calculations

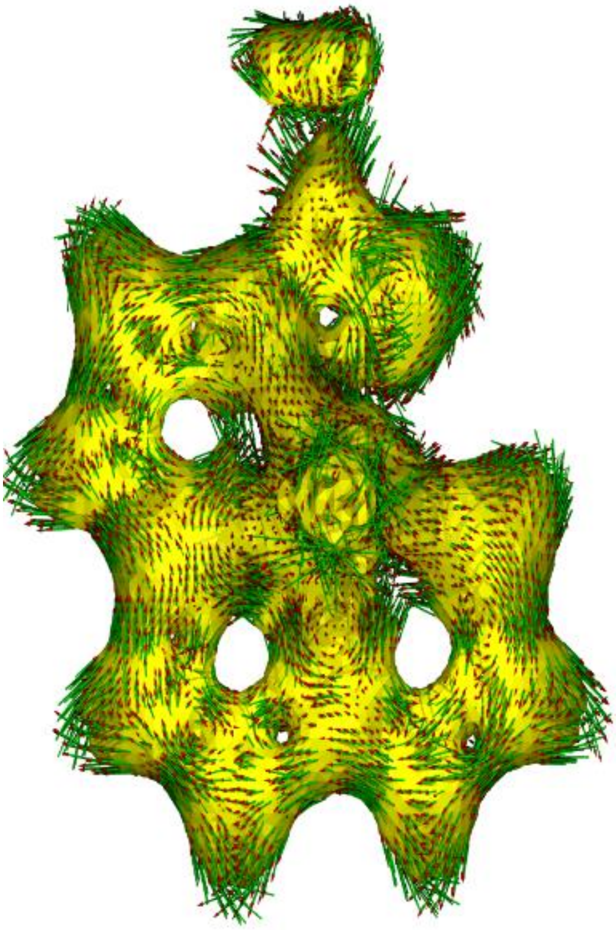
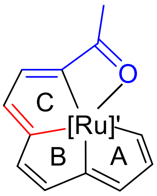


Figure S17 ACID plot of **3a'**

Computational Details All structures were optimized at the B3LYP level of density functional theory[4-6]. Frequency calculations were performed to identify all the stationary points as minima. All these structures evaluated were optimized by B3LYP-D3BJ/Def2-TZVP[7]. NICS values were calculated at the B3LYP-GIAO/Def2-TZVP level and the ACID calculations were carried out at the same level with NICS with the ACID program[8,9]. All calculations were done in Gaussian 16 program package, Revision A.03[10].

5. Optimized Cartesian coordinates for all stationary points



[Ru]' = Ru(PH_3)$_2$

3a'

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O	0.965912702	2.018697679	0.069515108
C	1.995308620	-0.573462914	0.000000000
H	2.745251351	0.214433838	-0.002221470
C	2.338309086	-1.886738590	0.004677567
C	1.217659104	-2.763808369	0.003808301
H	1.308698190	-3.847751070	-0.002280938
C	0.000000000	-2.136043843	0.000000000
C	-1.246794806	-2.794997873	-0.016663508
C	-2.337696259	-1.974546592	-0.052405303
C	-2.049997696	-0.590457472	-0.057058795
C	-3.049367609	0.387591218	-0.091895012
H	-4.105315114	0.136337200	-0.129224965
C	-2.565552671	1.693185409	-0.068011985
H	-3.202227835	2.574062874	-0.089134613
C	-1.191344584	1.729551869	-0.014028691
C	-0.159797625	2.646623528	0.047178358
C	-0.195980001	4.139560768	0.096151657
H	0.280317150	4.493903544	1.013530168
H	-1.219300306	4.511514852	0.058979030
H	0.367093123	4.553849411	-0.743551765
H	0.099823732	1.026340810	3.065517778
H	-1.206179666	-0.660574937	2.913189956
H	0.917389333	-0.948883870	2.941993245
H	0.707733322	-1.102548879	-2.940057663
H	-1.148278533	-0.035023701	-3.025909019
H	0.699749735	1.039729789	-2.959495542
H	-3.359329310	-2.342080525	-0.074344227
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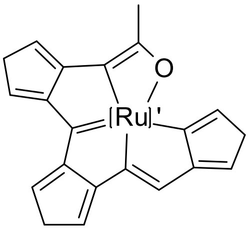

[Ru]' = Ru(PH_3)$_2$

***iso*-3a'-1**

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O	-0.87574800	-2.35935100	-0.60217800
C	-2.45733500	-0.31458500	0.15344900
C	-3.13644300	0.96978200	0.41188700
C	-2.24398700	2.08925600	0.39988100
H	-2.58508000	3.10891700	0.55924300
C	-0.94926600	1.78974300	0.16391500
C	0.10968900	2.76374900	0.02482800
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C	1.44332800	0.72662900	0.04864600
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C	2.52717900	-1.46515800	0.11594100
C	1.17979200	-1.79037200	-0.17600500
C	0.37004500	-2.80368500	-0.53458900
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H	-3.20715200	-2.34518700	0.00705100
C	2.37597800	3.12319900	-0.22728300
H	3.43790200	2.99385100	-0.36437300
C	3.94746300	0.30445400	0.58992500
H	4.35891100	1.27712800	0.80829600
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H	-5.45117100	-0.90720300	-0.37427800
H	-5.19854800	-1.11714500	1.34573000
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H	1.87889500	4.95608200	-1.25389500
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H	5.57550200	-0.94226700	-0.04144300
H	5.19104300	-1.08979200	1.65407200
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H	-5.21887400	1.52342300	0.77416200
C	3.73278200	-2.04996200	0.34968400
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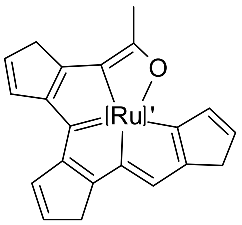

[Ru]' = Ru(PH_3)$_2$

3a'-1

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O	0.70448000	-2.58356000	0.11749400
C	2.45265900	-0.44249100	-0.02940800
C	3.17875100	0.73584400	-0.04491600
C	2.41175700	1.90879700	-0.03015000
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C	1.04878100	1.68940400	-0.00206700
C	0.06075000	2.67064400	0.00741500
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C	-1.43380400	0.83571000	-0.02157600
C	-2.66467400	0.16401300	-0.05210600
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C	-0.55925500	-2.85994000	0.10389100
C	-1.02149200	-4.27804500	0.18813300
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H	-2.10882400	-4.34004900	0.15950800
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H	1.26889400	0.43991800	-2.96932600
H	1.57949800	0.13304200	2.97202900
H	-0.44347100	0.82808600	2.87660400
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H	-4.16343700	-2.44746300	0.82106000
H	-4.11074600	-2.47392600	-0.93122600

6. References

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