Radical metallacyclopropene: synthesis, structure and aromaticity

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Supporting Information

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2. HRMS, NMR, and EPR Spectra

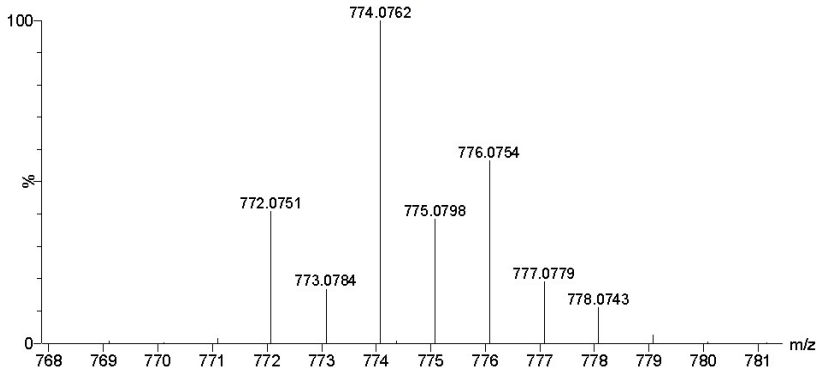


Figure S1. The HRMS result of complex **1**.

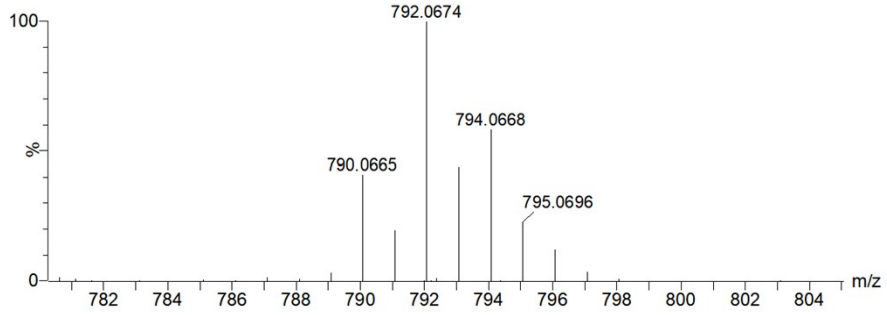


Figure S2. The HRMS result of complex **2**.

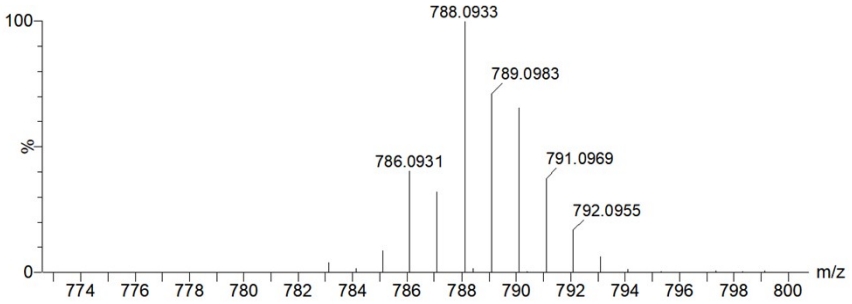


Figure S3. The HRMS result of complex **3**.

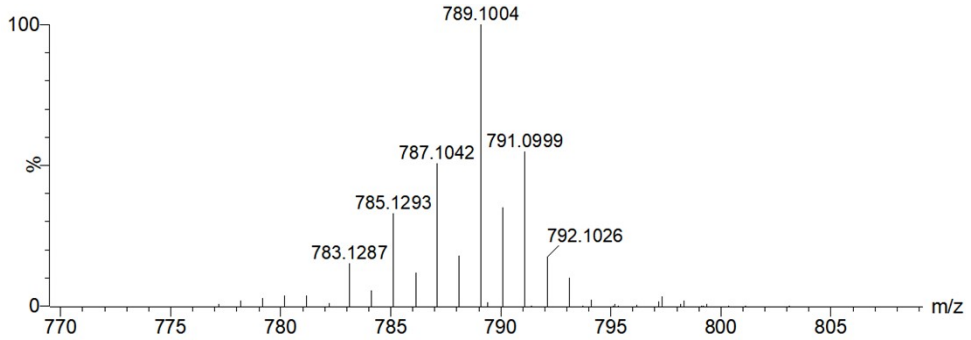


Figure S4. The HRMS result of complex **6**.

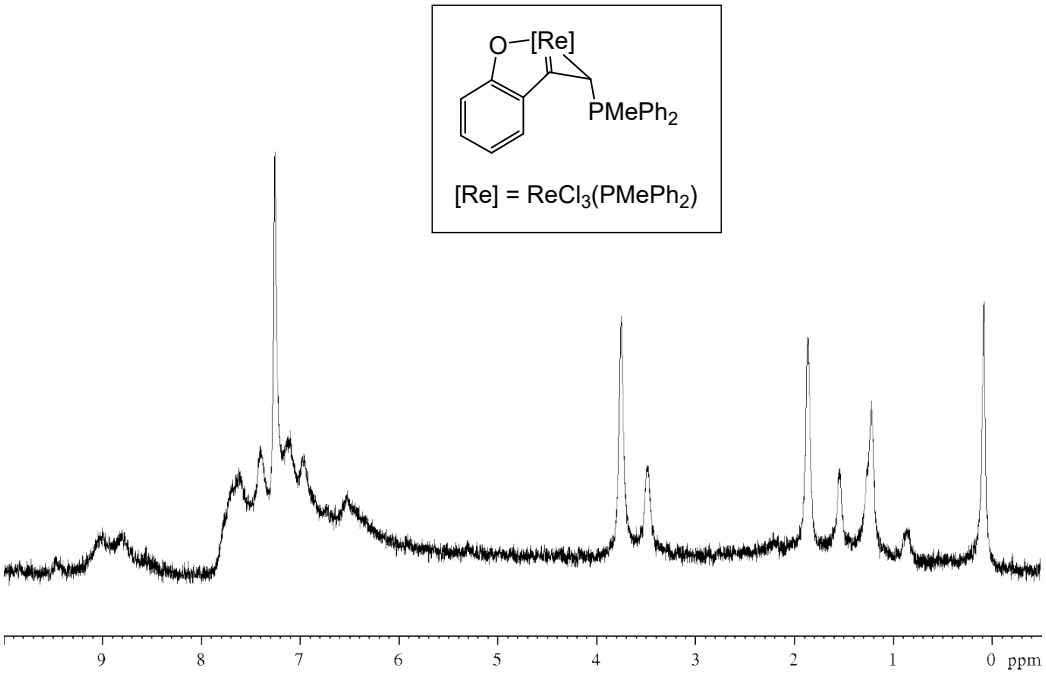


Figure S5. The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at 400.1 MHz.

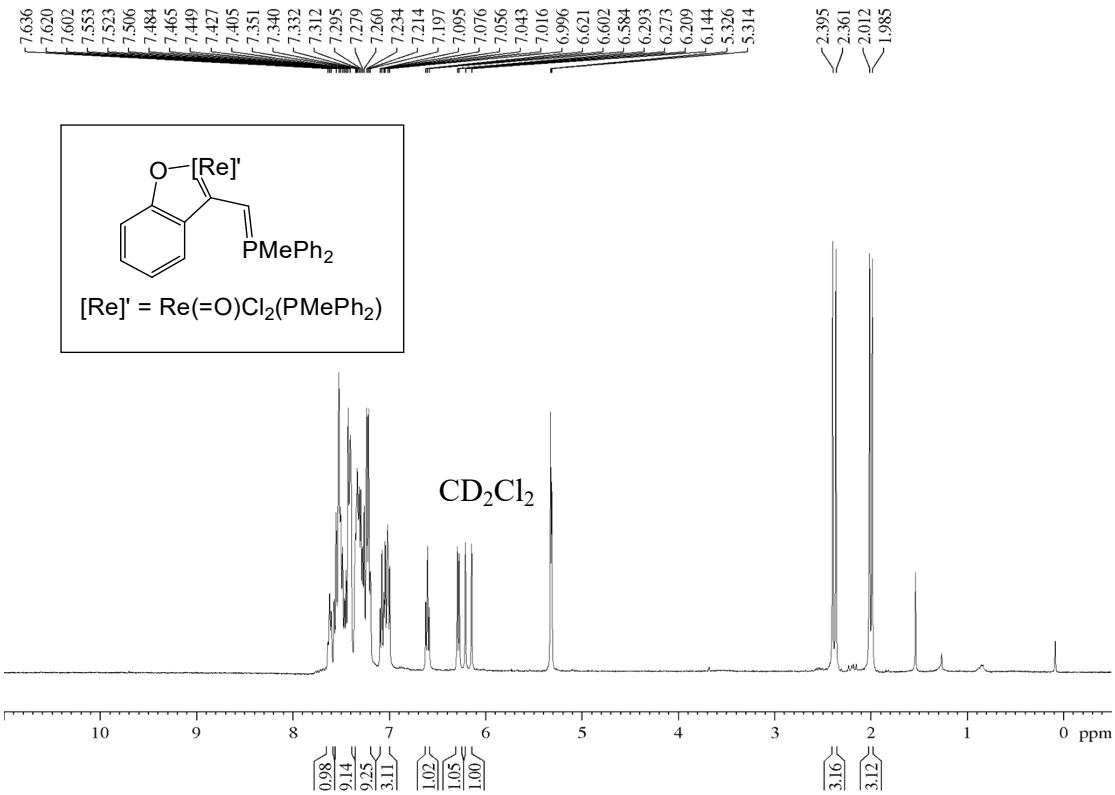


Figure S6. The ^{1}H NMR spectrum of complex **4** in CD_2Cl_2 at 400.1 MHz.

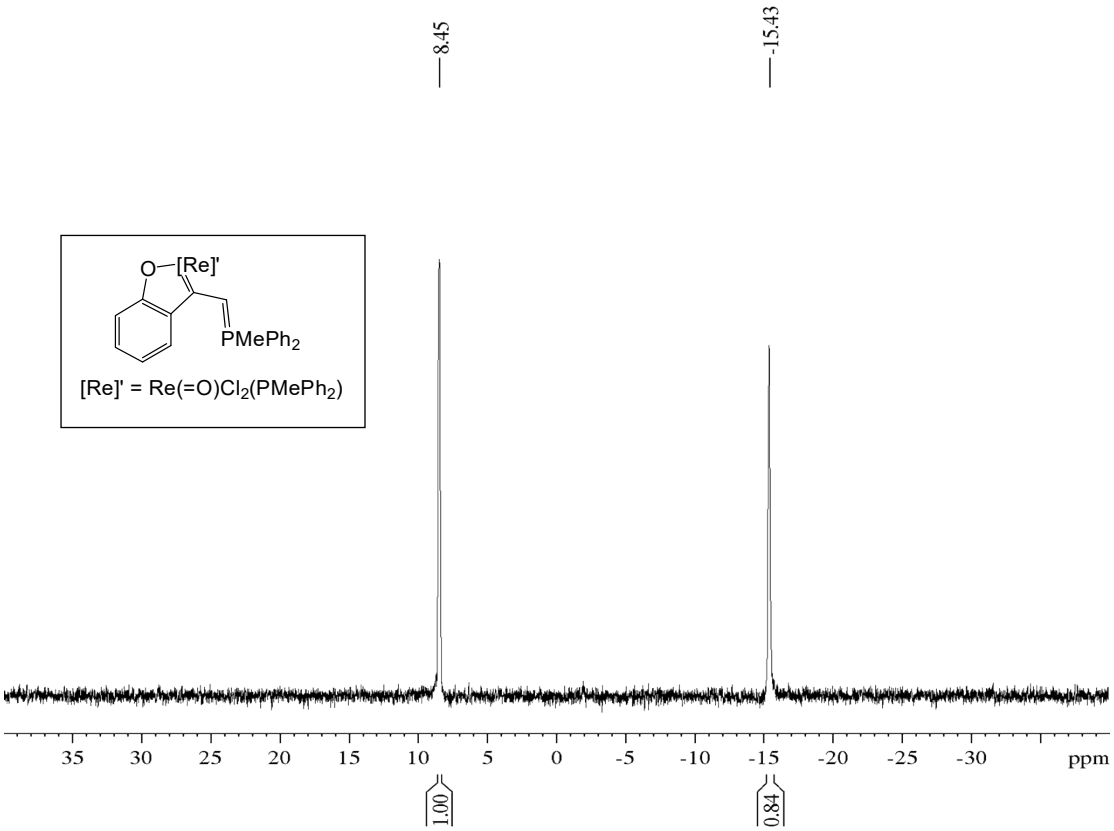


Figure S7. The ^{31}P $\{^{1}H\}$ NMR spectrum of complex **4** in CD_2Cl_2 at 162.0MHz.

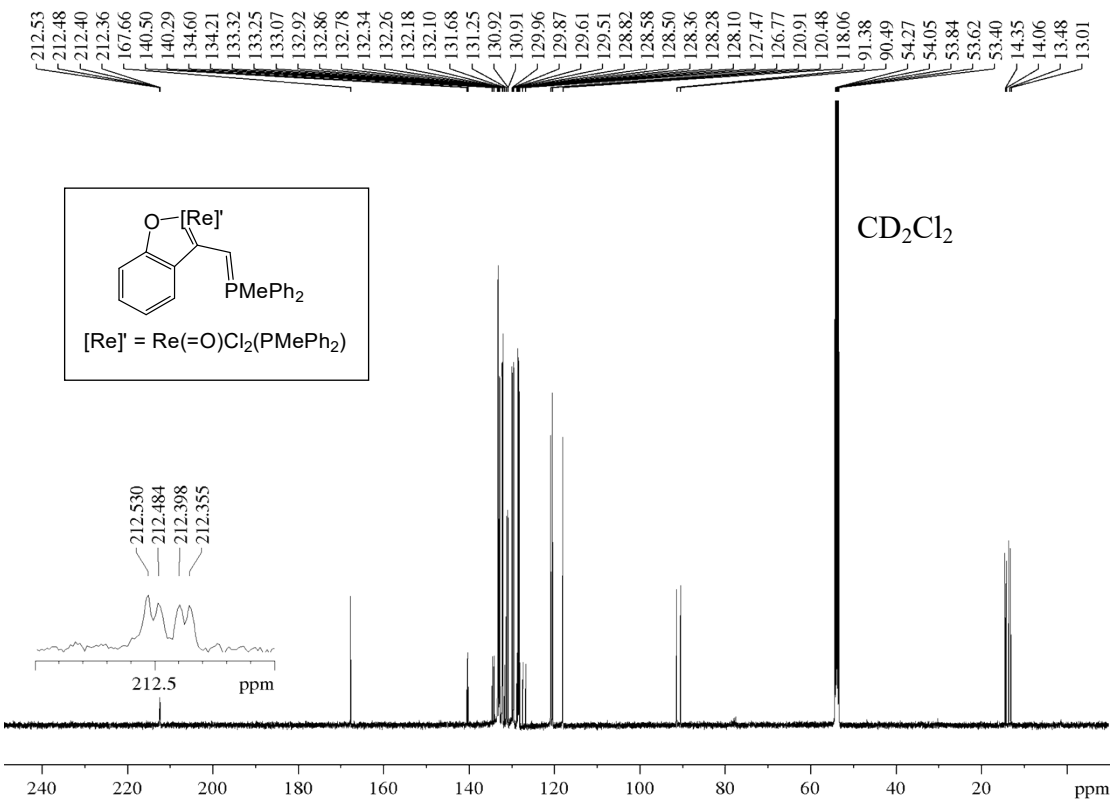


Figure S8. The ^{13}C $\{^{1}H\}$ NMR spectrum of complex **4** in CD_2Cl_2 at 125.0 MHz.

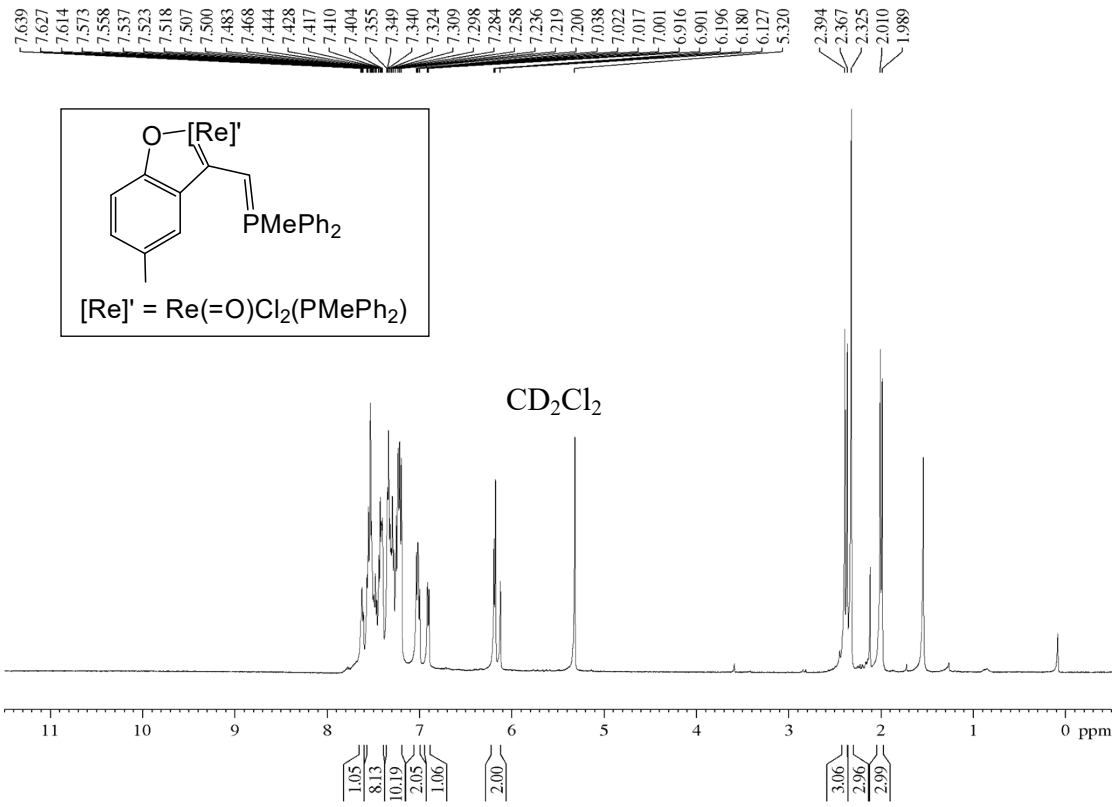


Figure S9. The ^{1}H NMR spectrum of complex **5** in CD_2Cl_2 at 400.1 MHz.

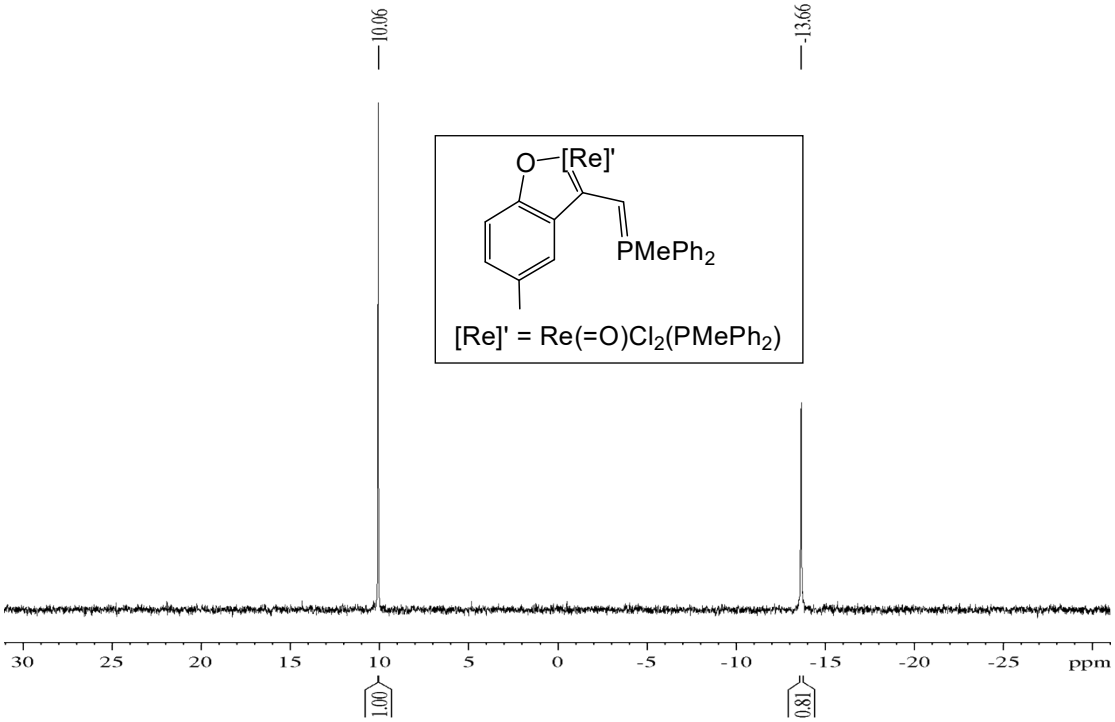


Figure S10. The ^{31}P $\{^{1}H\}$ NMR spectrum of complex **5** in CD_2Cl_2 at 162.0MHz.

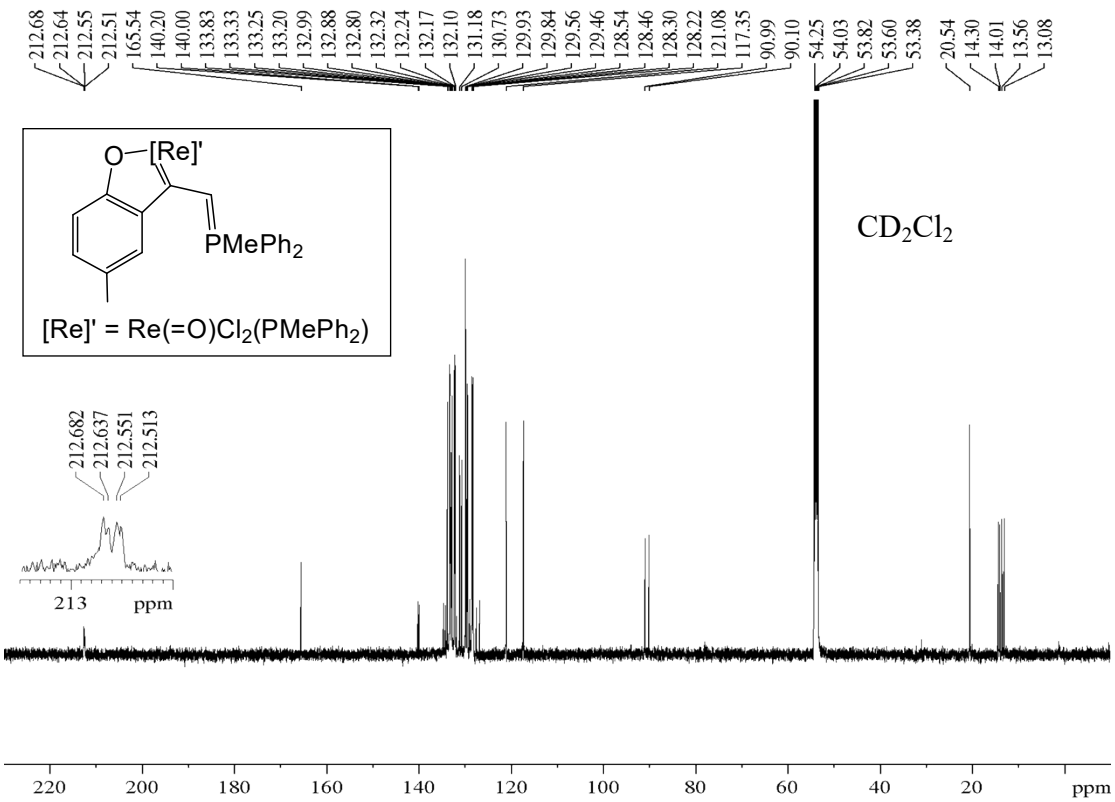


Figure S11. The ^{13}C {^{1}H} NMR spectrum of complex **5** in CD_2Cl_2 at 125.0 MHz.

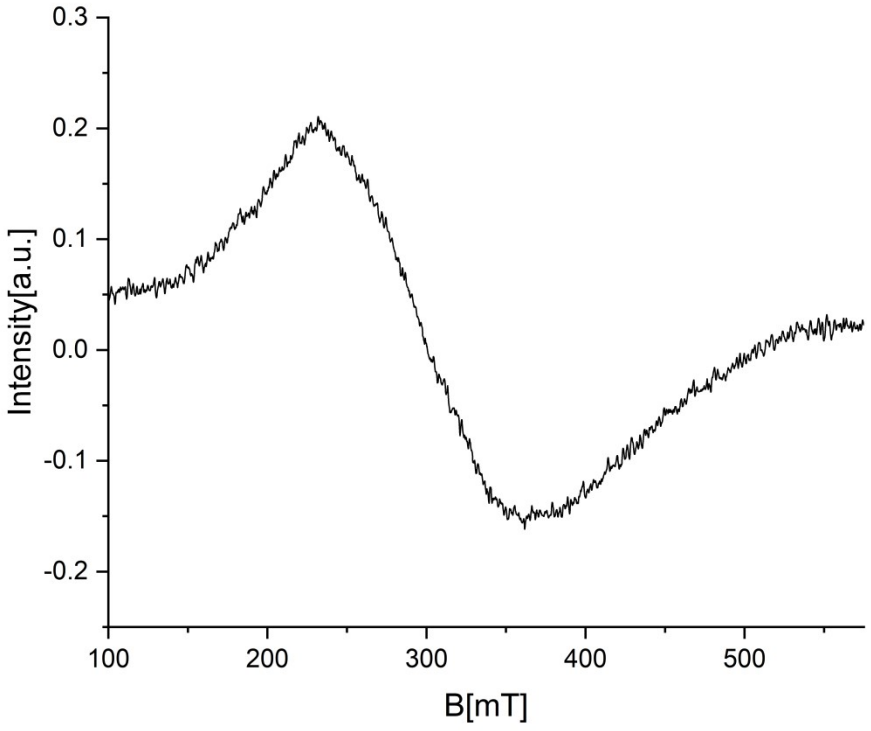


Figure S12. The EPR spectrum of complex **2** (powder) at room temperature.

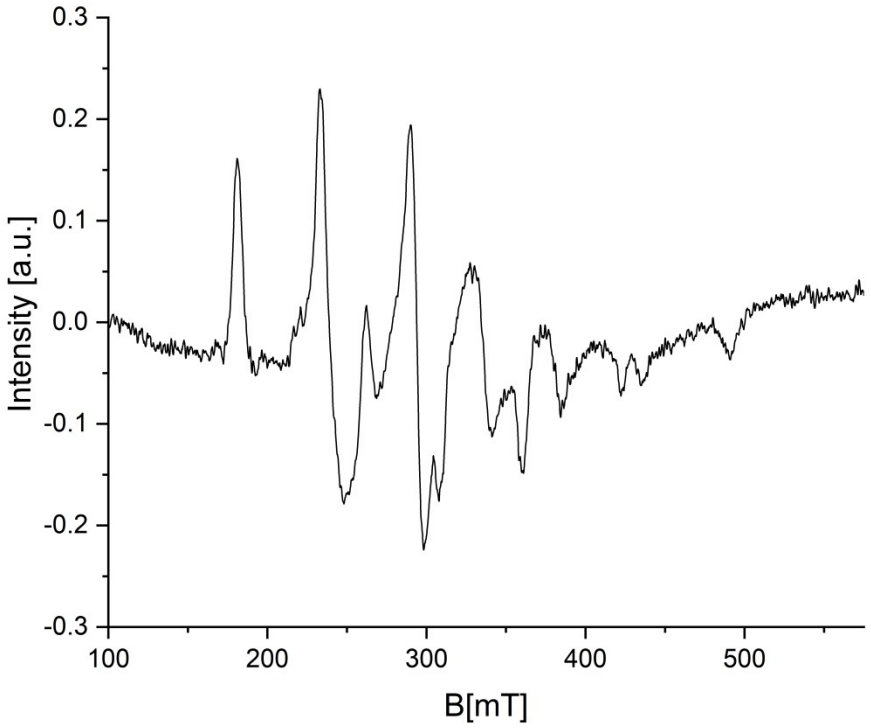


Figure S13. The EPR spectrum of complex **6** (powder) at room temperature.

2. Computational Details

All the optimizations were performed with the Gaussian 16 software package.[1] The structures evaluated were optimized at the B3LYP level of density functional theory (DFT).[2] DFT/GENECP level had been done by implementing def2-TZVP basis set for Re atom,[3] while 6-311G(2d,p) basis set had been used for the rest of atoms.[4] Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level.[5] The anisotropy of the current density was calculated with the AICD 2.0 program computing the NMR properties using the CSGT method with the Gaussian16 with the geometries previously obtained.[6] GIMIC analysis was finished by GIMIC code [7] based on the formatted check point file of Gaussian. Using RunEDDB script,[8] electron density of delocalized bond (EDDB) [9] based on natural atomic orbitals (NAOs) is analyzed.

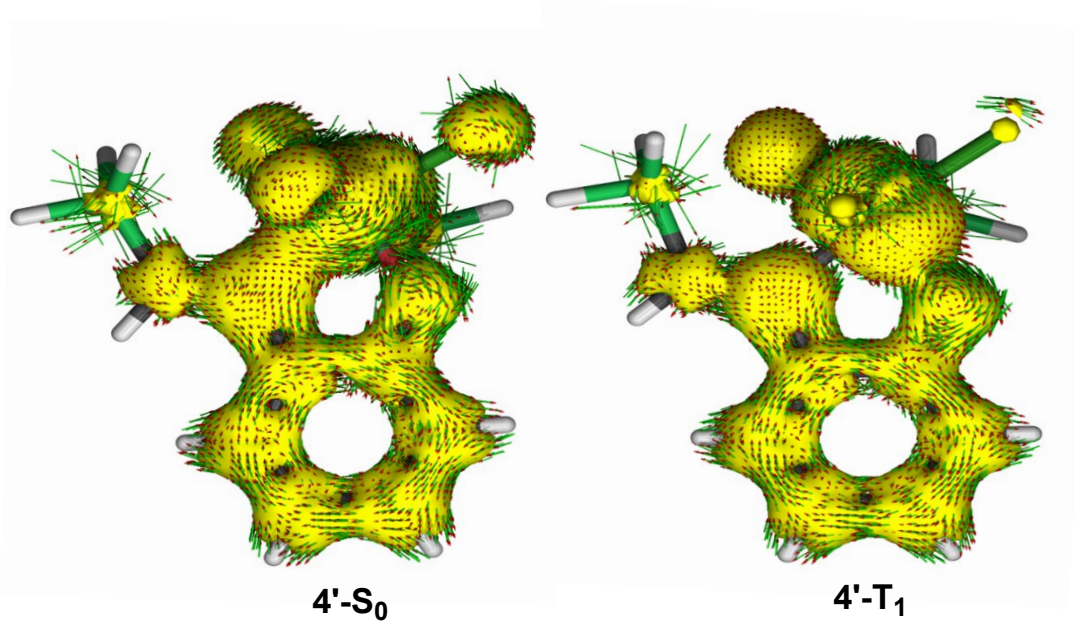


Figure S14. The AICD plots of **4'**. The isovalue for the surface is 0.050 a.u.

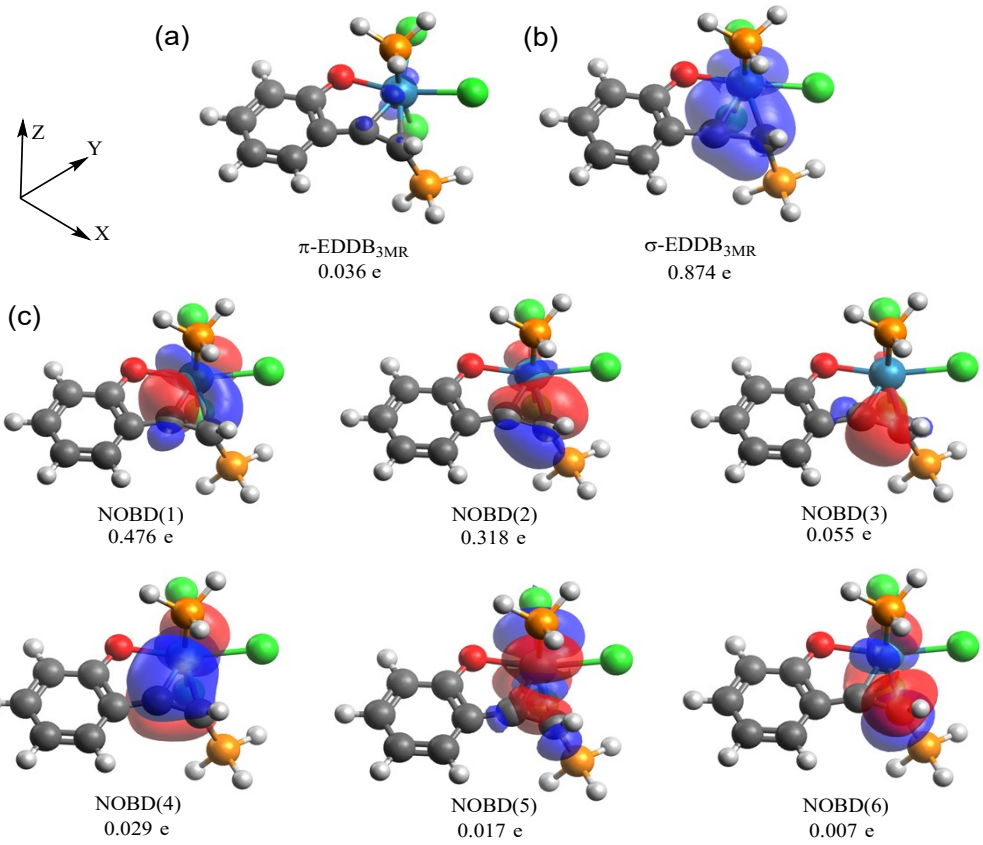


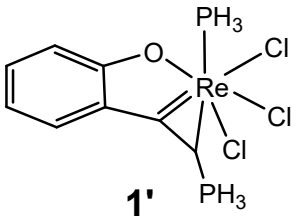
Figure S15. EDDB_F(r) results for the **3MR** in **1'** and key NOBDs of the ring. Isovalues is 0.001 for π-EDDB and σ-EDDB, Isovalue for NOBD contours is 0.040.

3. X-ray crystallographic study of complexes 1 and 4

Table S1. Crystallographic data and refinement details for **1** and **4**

	1	**4**
Empirical formula	$C_{34}H_{31}Cl_3OP_2Re \cdot C_4H_8O$	$C_{34}H_{31}Cl_2O_2P_2Re$
Color & habit	dark brown, block	orange, block
Crystal size (mm^3)	0.10 x 0.08 x 0.06	0.10 x 0.06 x 0.02
Temperature (K)	150K	150K
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	*P-1*
a(Å)	11.0621(2)	10.5704(4)
b(Å)	18.0532(4)	11.4035(5)
c(Å)	18.0532(4)	13.9505(6)
α/°	90	107.3720(10)
β/°	90	92.398(2)
γ/°	90	106.532(2)
V($Å^3$), Z	3605.34(13), 4	1523.69(11), 2
D_{cal} (Mg/m^3)	1.492	1.723
Abs. coeff.(mm^{-1})	3.705	4.299
2θ range for data collection (°)	4.318 to 52.732	3.088 to 52.828
Reflections collected	40698	17755
Indep. Reflection, R(int)	7399, 0.0419	6197, 0.0408
Data/ restraints / parameters	7399/6/373	6197/6/366
Goodness-of-fit on F^2	1.045	1.086
R1 [I>2sigma(I)], wR2	0.0296, 0.0727	0.0398, 0.1033
R1 (all data), wR2	0.0346, 0.0747	0.0441, 0.1063
Largest diff. peak and hole (e • $Å^{-3}$)	0.51, -0.45	4.82, -2.01

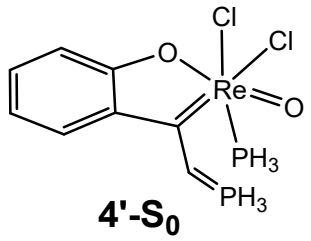
4. The Calculated Cartesian Coordinates with Electronic Energies



1'

0 2 **E = -2528.678738 a.u.**

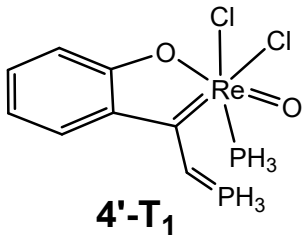
Re	-0.59266201	-0.22386859	-0.04024686
Cl	-2.87196421	0.46292042	0.57617106
Cl	-0.68420812	1.11522143	-2.05829002
Cl	-1.57043176	-2.14332297	-1.12793139
O	1.10172410	-1.25526133	-0.66039401
C	0.91735183	0.74713859	0.65772730
C	2.27490759	-0.76528196	-0.34053365
C	-0.09794420	1.64188433	1.05933993
H	-0.45358660	1.70739020	2.08469406
C	2.26045925	0.42955936	0.43296805
C	3.46260810	1.05063591	0.82276396
H	3.44185318	1.95826118	1.41511341
C	4.65562754	0.47717647	0.44238881
H	5.59506165	0.93419690	0.72683557
C	3.50086895	-1.34179667	-0.71120085
H	3.51021975	-2.24937670	-1.30068230
C	4.66504418	-0.71138327	-0.31876490
H	5.61868475	-1.13964624	-0.60557110
P	-0.50307991	3.12524001	0.16495980
H	-1.79317845	3.14760045	-0.36926284
H	-0.48846130	4.20938421	1.06241322
H	0.39687319	3.51056507	-0.82612754
P	-0.84028127	-1.69451446	1.90225727
H	0.06335633	-2.76725416	2.00117805
H	-0.71268743	-1.14905761	3.19626920
H	-2.07312914	-2.35022937	2.01127520



4'-S_0

0 1 **E = -2143.705834 a.u.**

Re	0.80962315	-0.23776949	0.00090975
Cl	2.10083754	-2.21255190	-0.49475676
Cl	1.08657453	0.49287964	-2.25574673
O	-0.79361276	-1.37897880	-0.41157389
O	1.79730943	0.93732252	0.75657056
C	-0.80740041	1.11925024	0.19111493
C	-2.02090853	-0.87065502	-0.31014117
C	-2.11184296	0.49530705	0.01850880
C	-3.38010083	1.08229680	0.12222560
H	-3.47743973	2.13349280	0.36707575
C	-4.40627321	-1.03448115	-0.40948660
H	-5.30313361	-1.61947491	-0.57724989
C	-3.16644005	-1.64171008	-0.52129092
H	-3.06250294	-2.68800472	-0.77826614
C	-4.51843602	0.32300228	-0.08619477
H	-5.49743363	0.77845494	-0.00371193
C	-0.69194355	2.46772183	0.40758207
H	-1.54793367	3.12969470	0.48770585
P	0.37594081	-1.27462019	2.21238451
H	0.79566196	-2.60569218	2.38137010
H	0.95145885	-0.67514636	3.34792047
H	-0.96226804	-1.37467741	2.63629571
P	0.82168787	3.32734312	0.36229046
H	0.49436451	4.67595901	0.15736741
H	1.63564335	3.39419959	1.50340149
H	1.69191192	3.01634919	-0.68558616



4'-T_1

0 3 **E = -2143.681963 a.u.**

Re	0.73883476	-0.24568425	-0.12194192
Cl	2.29688029	-2.07697851	-0.31314675
Cl	0.77929051	0.24865728	-2.39423397
O	-0.86895521	-1.42893848	-0.15336952
O	1.67480193	1.15866628	0.53586875
C	-0.87202995	1.13312302	0.17594997
C	-2.09270770	-0.88912982	-0.10797326
C	-2.17649113	0.50443805	0.08414377
C	-3.44094903	1.10360379	0.16913590
H	-3.52343094	2.17406397	0.31789232
C	-4.48029676	-1.04904692	-0.13862989
H	-5.38118106	-1.64467638	-0.23045712
C	-3.24507151	-1.67083436	-0.21642686
H	-3.15193722	-2.73853688	-0.36779317
C	-4.58477316	0.33364851	0.05673477
H	-5.56125373	0.79779934	0.11639091
C	-0.63229022	2.45058482	0.34846939
H	-1.40917668	3.20725490	0.40086785
P	0.79296202	-1.03243178	2.29565541
H	0.45487071	-2.37423169	2.52563512
H	2.04544938	-0.94968808	2.92393383
H	-0.00990838	-0.39765382	3.26534357
P	1.02251628	3.11869830	0.36375830
H	0.66411607	4.49600141	0.27584270
H	1.78848504	3.22853216	1.52972607
H	1.84516461	3.07877224	-0.76588756

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