α-Rhenabenzofuran with nonaromatic T_0 and aromatic S_1 states

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Supporting Information

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1. NMR spectra and high-resolution mass spectroscopy data

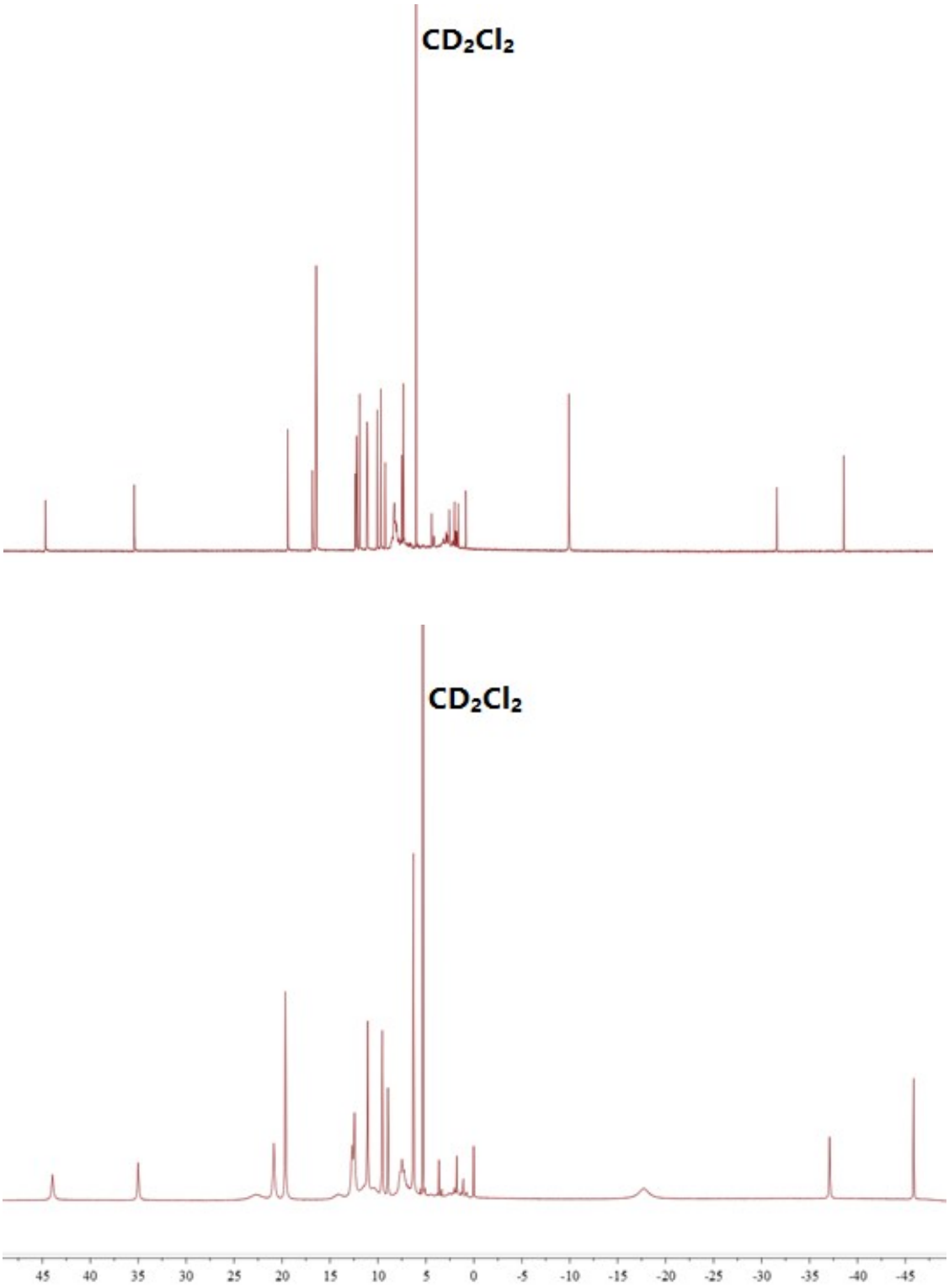


Figure S1. ^{1}H NMR spectra of complex **2** at room temperature (above) and -80 ^{o}C (below) in CD_2Cl_2 at 400.1 MHz.

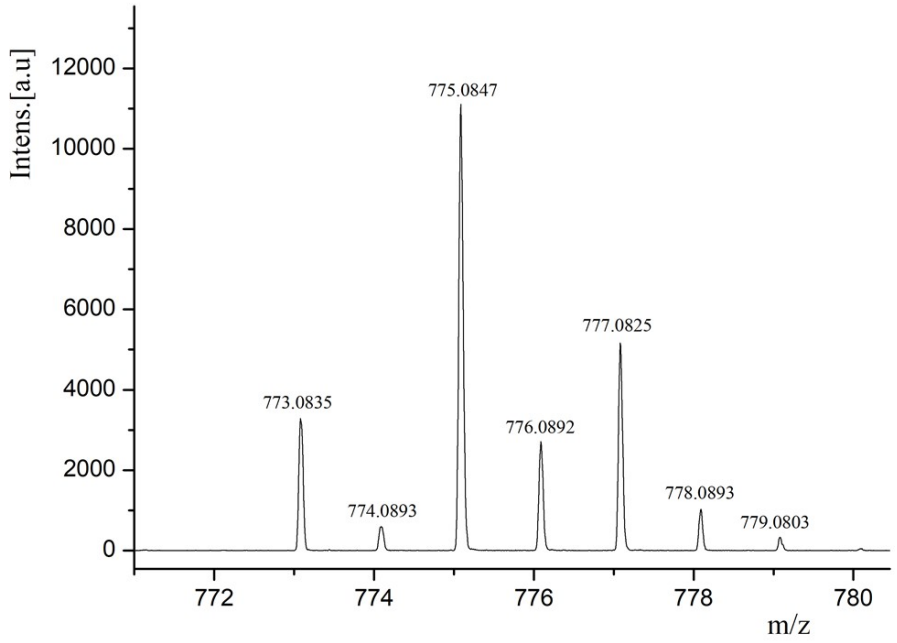


Figure S2. HRMS (ALDI-TOF) result of complex **2** $[M\text{-}Cl]^+$.

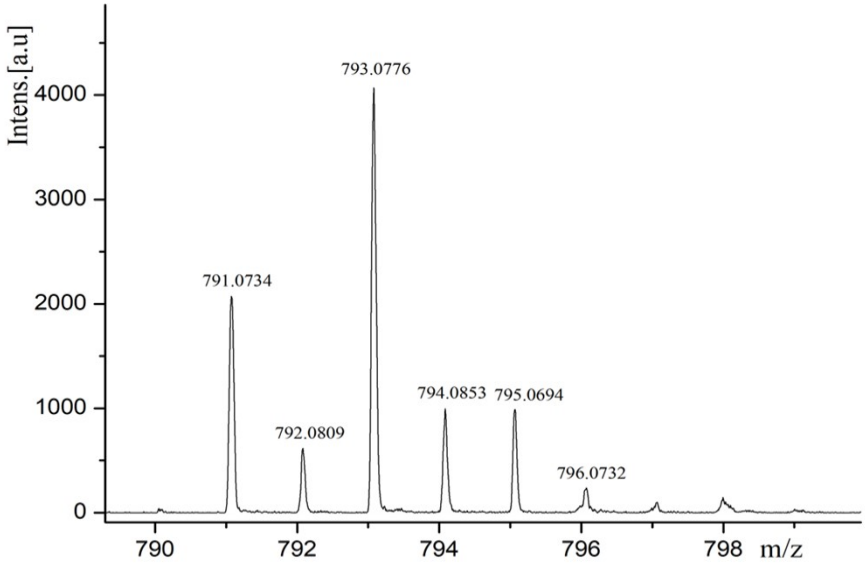


Figure S3. HRMS (ALDI-TOF) result of complex **3** $[M\text{-}Cl]^+$.

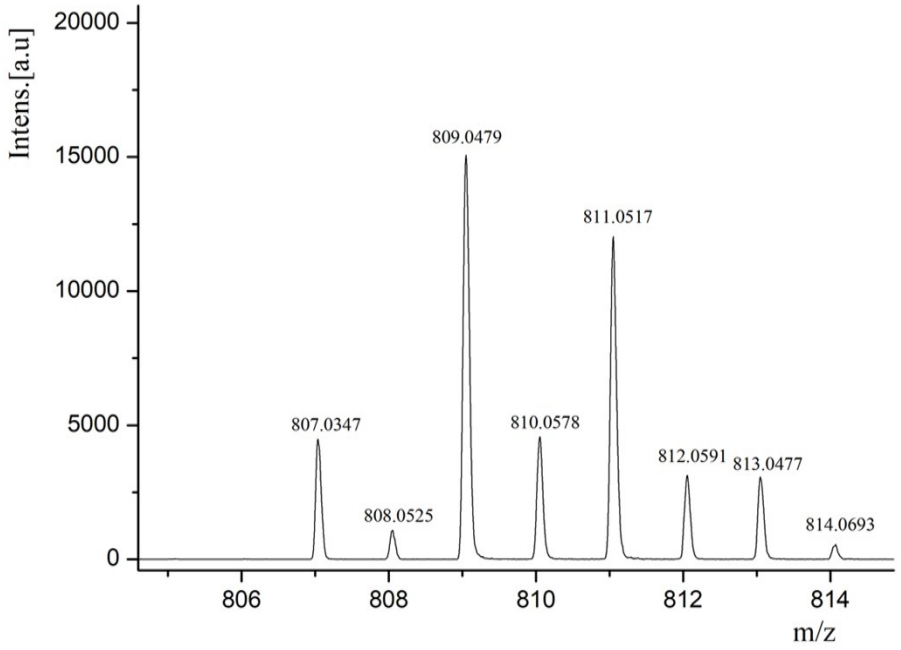


Figure S4. HRMS (ALDI-TOF) result of complex **4** $[M\text{-}Cl]^+$.

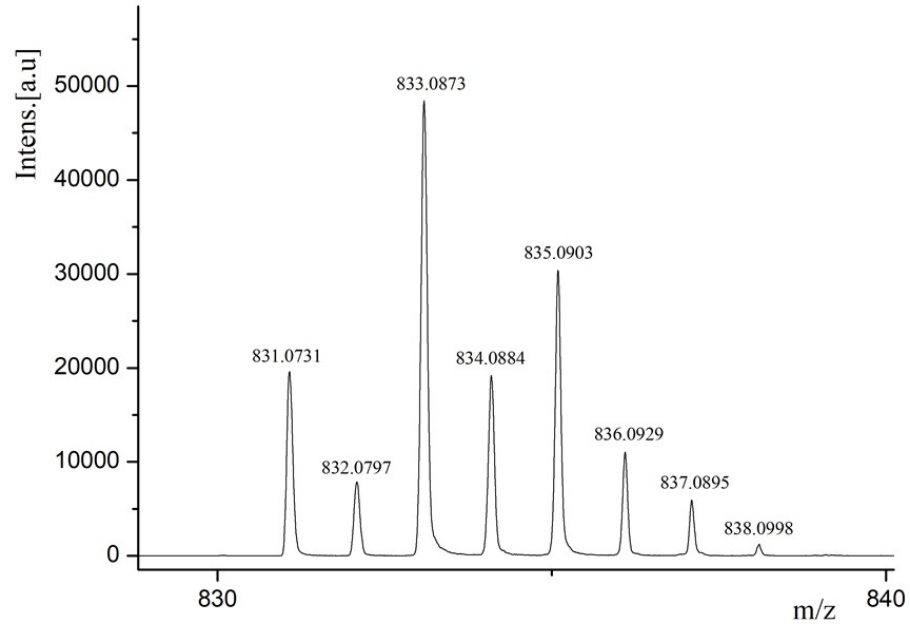
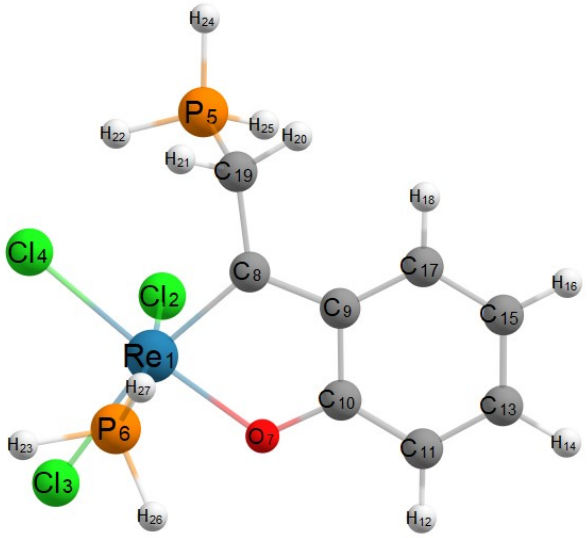


Figure S5. HRMS (ALDI-TOF) result of complex **5** $[M\text{-}Cl]^+$.

2.Computational details

All the optimizations were performed with the Gaussian 16 software package.[4] All of these structures evaluated were optimized at the B3LYP level of density functional theory (DFT).[5] DFT/GENECP level had been done by implementing def2-TZVP basis set for Re atom.[6] On the other hand, 6-311G(2d,p) basis set had been used for the rest of atoms.[7] Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level.[8] 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 Rev A.03 program with the geometries previously obtained for **M**.[9] GIMIC analysis was finished by GIMIC code [10] based on the formatted check point file of Gaussian and rendered by ParaView visualization program.[11] Current densities were obtained from the wavefunction for GIAO NMR computations for a magnetic field applied perpendicular to the ring plane of the molecules within the context of the Quantum Theory of Atoms in Molecules using AIMAll.[12] Using RunEDDB script,[13] electron density of delocalized bond (EDDB)[14] based on natural atomic orbitals (NAOs) is analyzed. The molecular orbital composition and MO pictures were analyzed using Multiwfn, a multifunctional wavefunction analyzer.[15] The calculations of HOMA, MCI and ELFπ were also carried out by Multiwfn package. The MO pictures were drawn using the software of VMD.[16] VMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign (http://www.ks.uiuc.edu/Research/vmd/).

Table S1. The positive and negative values of total induced currents contributed by the diatropic and paratropic currents in the singlet and triplet states.



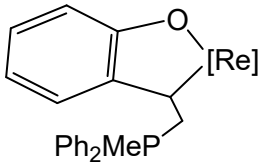
Bond	diatropic contribution(S_1/T_0)	paratropic contribution(S_1/T_0)	Total induced current (S_1/T_0)
1-7	10.220204/6.639485	-5.770334/-7.066479	4.449870/-0.426994
7-10	11.677843/8.198671	-6.848873/-8.365040	4.828970/-0.166369
10-11	12.967212/11.992386	-4.209623/-4.523966	8.757588/7.468421
11-13	14.573696/13.622006	-5.690694/-6.003618	8.883001/7.618389
13-15	14.326973/13.366617	-5.354122/-5.703843	8.972850/7.662775
15-17	14.718166/13.817001	-5.807493/-6.186534	8.910673/7.630467
17-9	13.550121/12.879307	-6.058419/-6.476036	7.491702/6.403271
9-8	11.061803/8.498420	-6.715433/-8.545832	4.346370/-0.047411
8-1	9.421343/6.956005	-5.271217/-6.921324	4.150125/0.034681

3. X-ray crystallographic study of complex 2

Table S2. Crystallographic data and refinement details for **2**

	2
CCDC Number	2128119
Empirical formula	$C_{34}H_{31}OP_2Cl_3Re$
Color & habit	brown, block
Crystal size (mm^3)	0.10 x 0.10 x 0.10
Temperature (K)	120K
Crystal system	triclinic
Space group	*P-1*
a(Å)	9.653(3)
b(Å)	9.994(3)
c(Å)	17.068(5)
α(°)	96.175(11)
β(°)	99.797(11)
γ(°)	95.144(11)
V($Å^3$), Z	1603.3(9), 2
D_{cal} (Mg/m^3)	1.678
Abs. coeff.(mm^{-1})	4.166
2θ range for data collection (°)	2.44 to 50.854
Reflections collected	20984
Indep. Reflection, R(int)	5785, 0.0552
Completeness of data	97.6 %
Data/ restraints / parameters	5785/0/372
Goodness-of-fit on F^2	1.088
R1 [I>2sigma(I)], wR2	0.0331, 0.0898
R1 (all data), wR2	0.0380, 0.0934
Largest diff. peak and hole (e • $Å^{-3}$)	0.70, -1.29

4. The Calculated Cartesian Coordinates with Electronic Energies



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Cl	-0.22756000	0.81464600	-2.84961200
P	2.95390500	0.04384400	-0.46590100
P	-2.45649600	1.13746800	-0.42327900
O	-1.45547900	-2.12279800	0.23258400
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C	0.10660000	-0.97884300	1.47596800
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H	-0.59222000	-3.31026800	4.49577000
C	0.54170100	-1.62820500	3.76360300
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C	0.79800000	-0.79877700	2.69252300
H	1.52862500	-0.00498100	2.80102500
C	1.33418700	0.72999500	0.09780200
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H	1.10589200	1.50411500	-0.63539700
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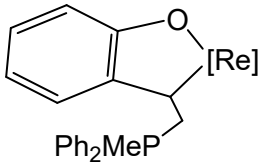

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P	-2.56596800	1.14001000	-0.42186600
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C	-1.25776900	-2.70451100	2.56612000
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H	1.74889500	-0.23795200	2.74701500
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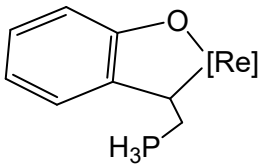

M (S_1)

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Cl	-1.760608850	-3.309841613	-0.161623458
P	0.854611650	-3.362031951	1.584301881
P	-1.959499087	-0.701993197	-2.259970869
O	-0.788112152	0.948002463	-0.054402791
C	0.507956045	-1.171561737	-0.039664418
C	1.307717113	0.000000000	0.015952409
C	0.489524319	1.164996081	0.037335542
C	1.057357189	2.449949340	0.112476267
H	0.410137594	3.317027781	0.134242824
C	2.428267658	2.558030818	0.168574613
H	2.882084225	3.540176984	0.234395948
C	3.261299619	1.417423743	0.144266971
H	4.336204158	1.541595799	0.184511261
C	2.714348301	0.158943083	0.069240954
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C	1.226177945	-2.509463385	-0.000582138
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H	0.850324682	-3.170075132	-0.781149412
H	-0.209892226	-2.650989539	2.290646266
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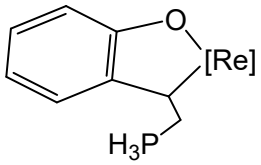

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