Supplementary Information

For

Novel Cofacial Oxidative Coupling Reaction of Phophinine in the Presence of Cu(I) and ClO_4^-

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Experimental section.

NMR spectra were recorded on JEOL EX-270 and Brucker AVANCE-Series (DPX400) spectrometers. UV-vis spectra were obtained on a Jasco Ubest-55 spectrometer and IR spectra were measured on a Jasco IR model 800 spectrophotometer. FAB-MS spectroscopy was done by using JMS-SX/SX102A tandem mass spectrometer. Elemental analyses were made at the Service Center of Elemental Analysis of Organic Compounds, Kyushu University.

TPP was synthesized according to the procedure reported by Märkl and coworkers.[1]

Synthesis of [Cu(TPP)$_2$]X (X = BF$_4$, PF$_6$). To a solution of [Cu(CH$_3$CN)$_4$]PF$_6$ (45.8 mg, 1.23 X10^{-4} mol) in CH_2Cl_2 (10 mL), was added TPP (74.4 mg, 2.29 X 10^{-4} mol) as solids under N_2. The mixture was stirred for 2h under N_2 at room temperature. The solvent was removed in vacuo and the residue was recrytallized from CH_2Cl_2/hexane to obtain yellow powder of [Cu(TPP)$_2$]PF$_6$ (73.9 mg, 69.4% yield). Anal. Cacld for $CuC_{46}H_{34}P_2$•PF_6•$2H_2O$: C, 61.85; H, 4.29. Found: C, 61.64; H, 4.31. The same procedure was used to prepare [Cu(TPP)$_2$]BF$_4$. Anal. Cacld for $CuC_{46}H_{34}P_2$•BF_4•$2H_2O$: C, 66.16; H, 4.59. Found: C, 65.77; H, 4.55.

X-ray Crystallography of 1. A yellow block crystal of **1** was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. Indexing was performed from 3 oscillations which were exposed for 3 minutes. The camera radius was 127.40 mm. Readout was made in the 0.100 mm pixel mode. The data were collected at –160 ± 1°C to a maximum 2θ value of 54.8°. A total of 114 images, corresponding to 228.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 2.00 minutes per degree. Data were processed by the PROCESS-AUTO program package. A total of 62800 reflections collected, 5244 were unique (R_{int} = 0.088). A symmetry-related absorption correction using the program ABSCOR was applied, which resulted in transmission factor ranging from 0.56 to 0.97. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. All calculations were performed by using the teXsan crystallographic software package of Molecular Structure Corporation.

Table S1. Crystallographic data for **1**.

Experimental Formula	$C_{92}H_{68}O_6P_4$
Formula weight	1393.44
Crystal dimension, mm^3	0.20X0.40X0.35
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	23.4513(5)

b, Å	13.4607
c, Å	24.5485(5)
β, deg	116.1286(4)
V, Å^3	6957.3(2)
Z	4
D(calc), g/cm^3	1.330
μ(Mo Kα), cm^{-1}	1.69
Temperature, °C	-160±1
$2\theta_{max}$, deg	54.8
No. of reflections measured	62800
No of reflections, unique	5244
No of reflections used (all, $2\theta<54.8°$)	15730
No of variables	919
R; Rw	0.159; 0.185
R1 ($I>2\sigma(I)$; 8151 reflections)	0.072
GOF	1.02
Maximum/minimum peaks in final diff. map	1.08/-1.34 e$^-$/Å^3

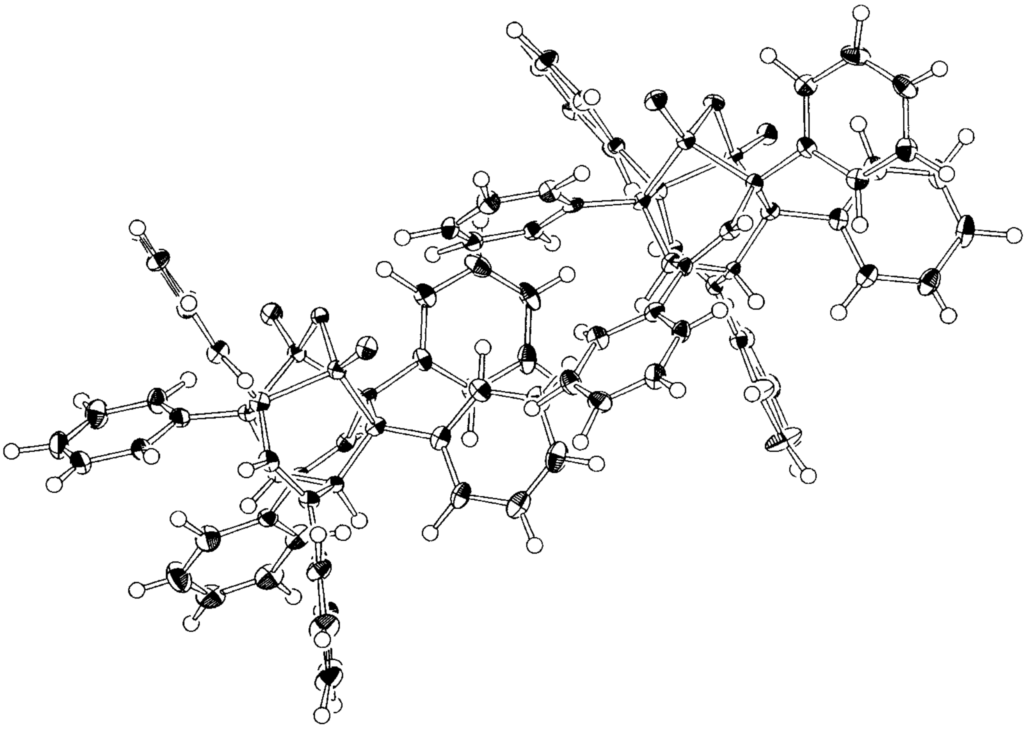


Figure S1. Crystal structures of *R*- and *S*-**1** in the asymmetric unit.

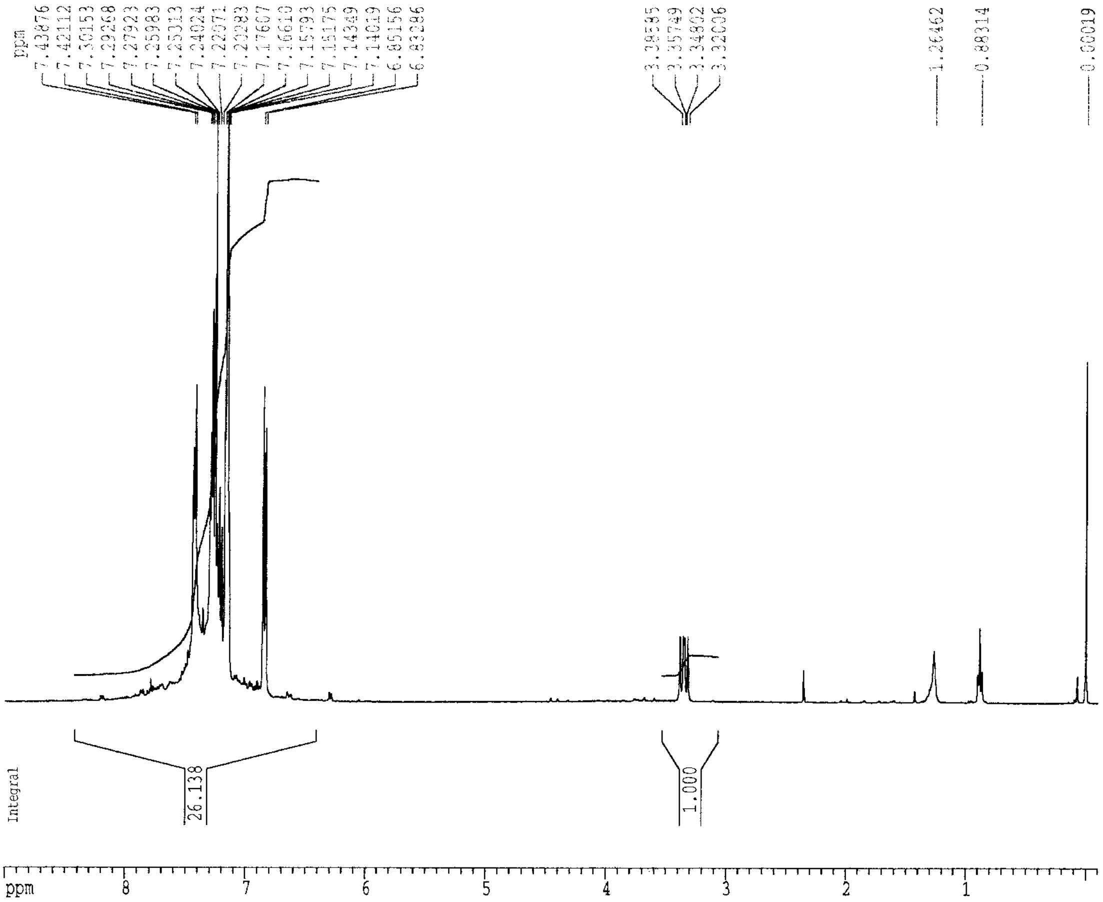


Figure S2. ^{1}H NMR spectrum of **1** (in $CDCl_3$).

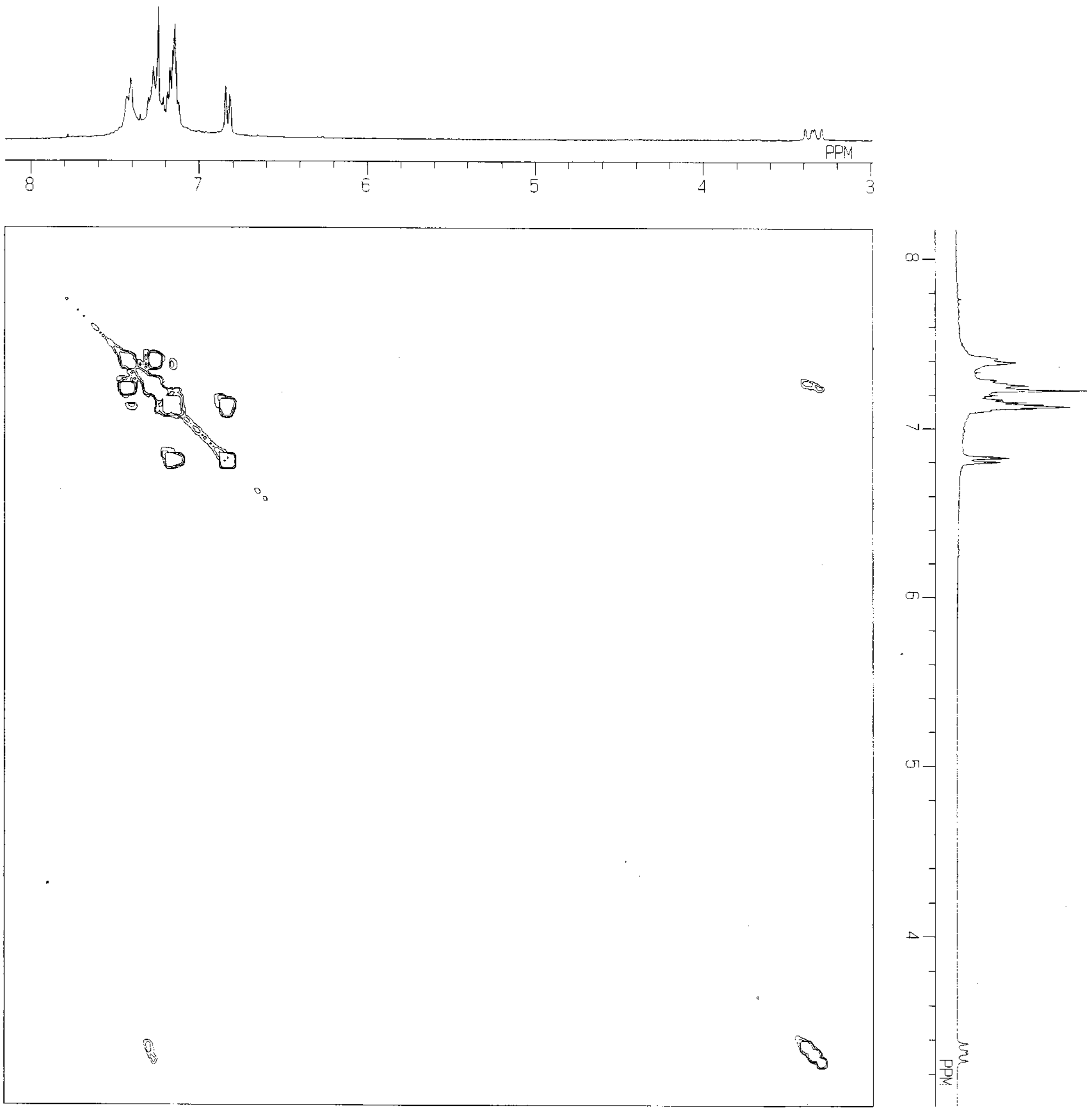


Figure S3. ^{1}H-^{1}H COSY spectrum of (in CDCl$_3$).

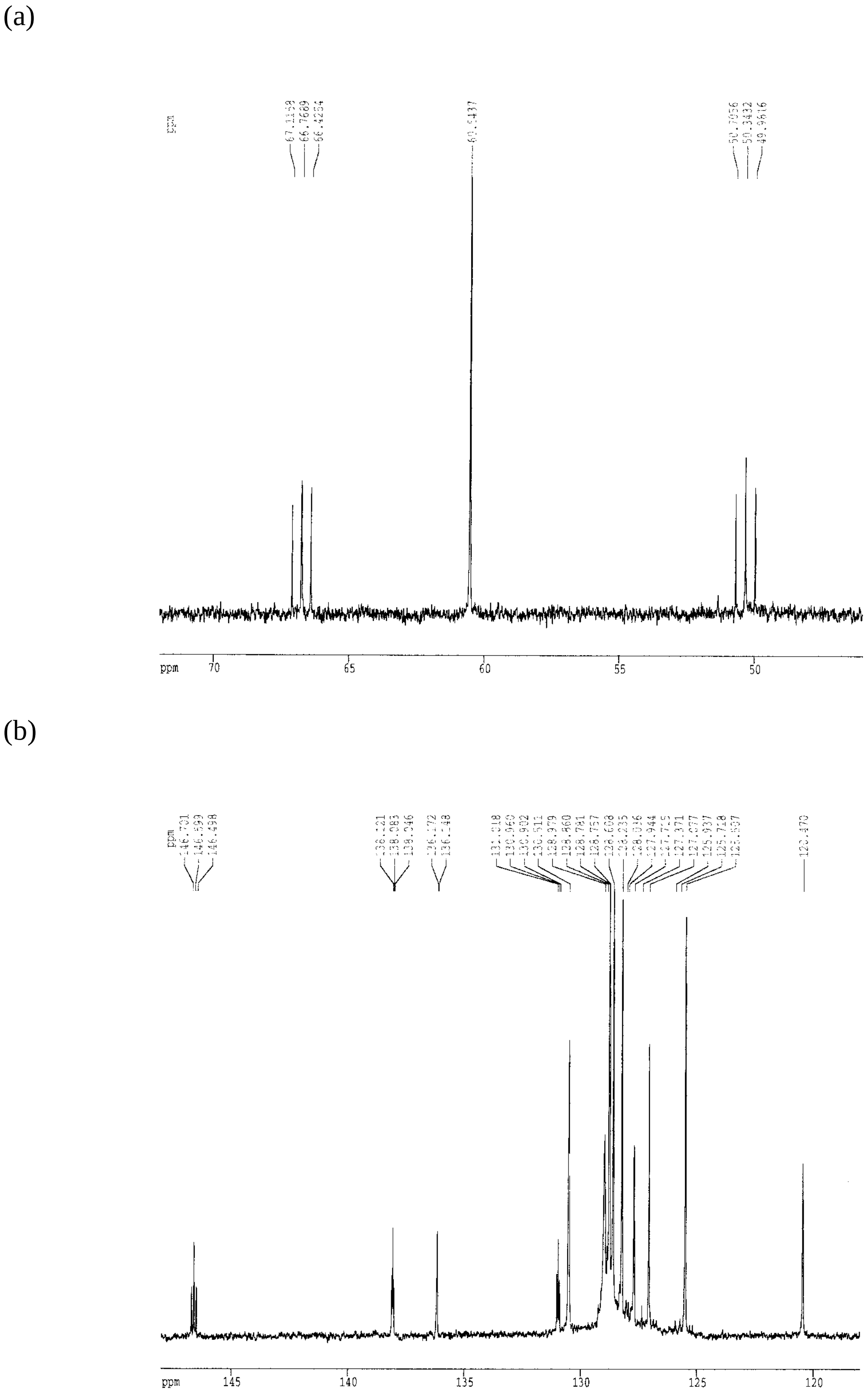


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **1** (in $CDCl_3$): (a) aliphatic region, (b) aromatic region.

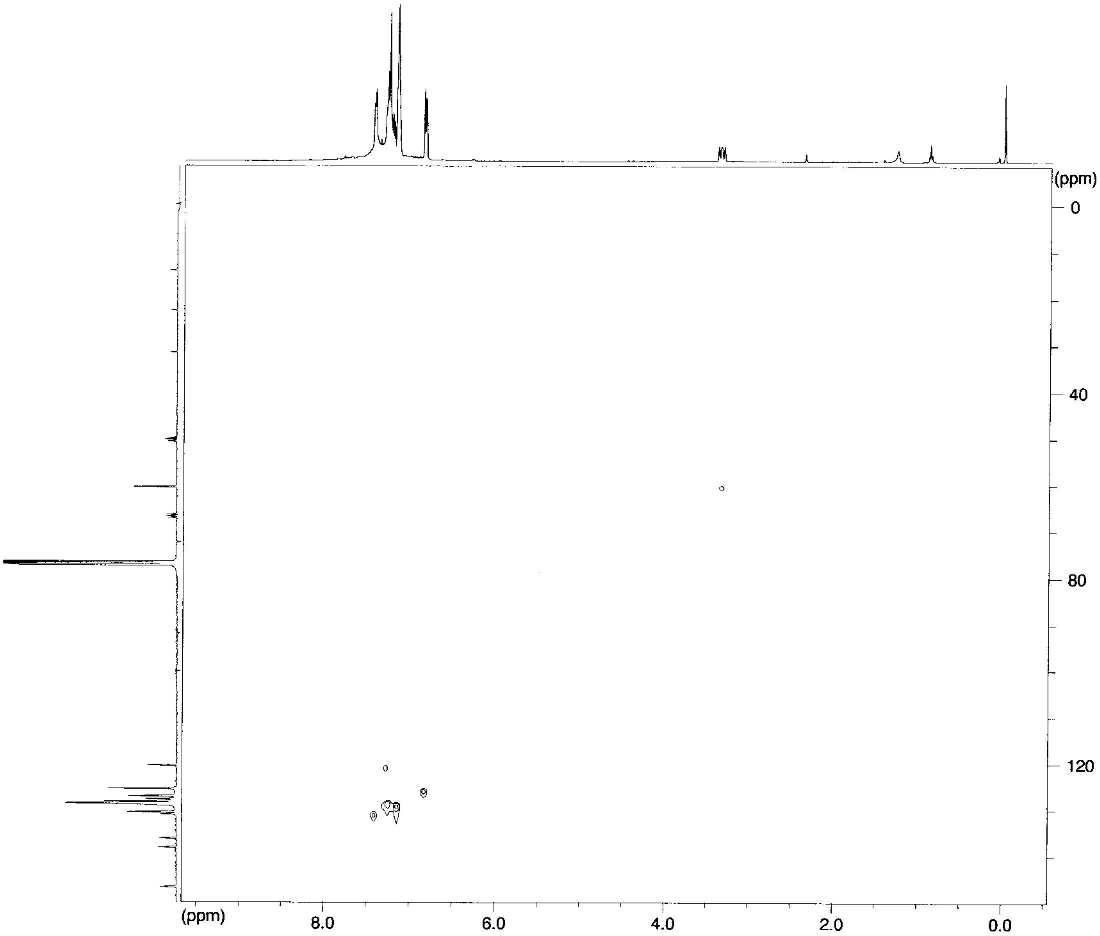
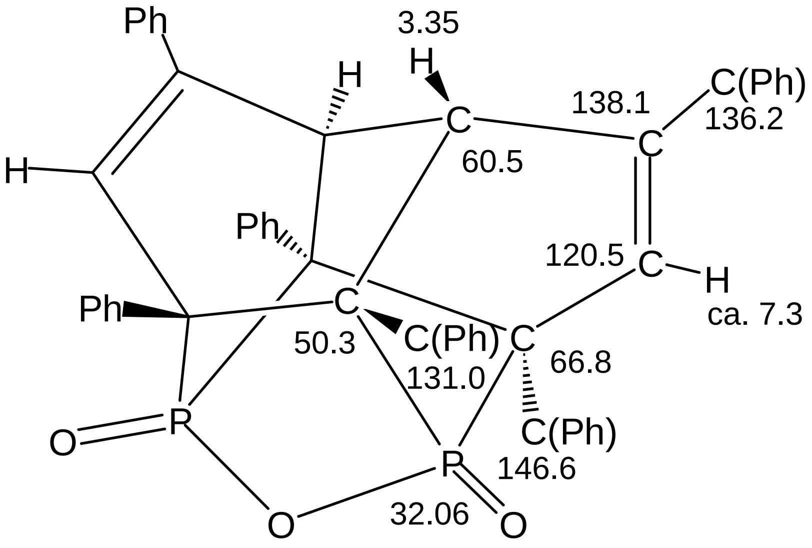


Figure S5. HMQC spectrum of **1** (in $CDCl_3$).



Chemical Shifts of each nucleus (ppm) in $CDCl_3$.

Figure S6. Peak assignments for the core moiety of **1**.