Supplemental Information

Synthesis of Adipic Aldehyde by *n*-Selective Hydroformylation of 4-Pentenal

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S1. Crystallographic Data

S1.1 Ligand L10

Table S1: Crystal data and structure refinement for ligand **L10**.

Identification code	jam2	
Empirical formula	$C_{54}H_{60}O_8P_2$	
Formula weight	898.96	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	a = 10.3454(9) Å	α = 67.6136(16) deg.
	b = 13.9408(12) Å	β = 84.779(2) deg.
	c = 18.1284(15) Å	γ = 81.660(2) deg.
Volume	2390.1(4) $Å^3$	
Density (calculated)	1.25 g/cm^3	
Absorption coefficient	0.14 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.190 x 0.150 x 0.110 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.2 to 25.0 deg.	
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-21 \le l \le 21$	
Reflections collected	19535	
Independent reflections	8403 (R(int) = 0.0426)	
Observed reflections	5407 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	8403 / 1 / 607	
Goodness-of-fit on F^2	1.05	
Final R indices (I>2sigma(I))	R1 = 0.064, wR2 = 0.125	
Largest diff. peak and hole	0.45 and -0.35 $eÅ^{-3}$	

Table S2: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **L10**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
P1	0.1648(1)	0.5028(1)	0.7551(1)	0.0365(3)
P2	0.0066(1)	0.8785(1)	0.6931(1)	0.0366(4)
O2	0.0928(3)	0.7650(2)	0.7229(2)	0.0367(7)
O2C	0.0581(17)	0.9589(13)	0.6398(10)	0.049(7)
P2B	-0.009(2)	0.7760(17)	0.7444(13)	0.049(8)
O2B	0.091(4)	0.831(4)	0.672(2)	0.039(13)
O1	0.0473(2)	0.5756(2)	0.6999(1)	0.0387(6)
O3	0.0785(2)	0.4419(2)	0.8334(1)	0.0365(6)
O4	0.1907(2)	0.4185(2)	0.7102(1)	0.0364(6)
O5	-0.1231(2)	0.8357(2)	0.6784(1)	0.0396(6)
O6	-0.0388(2)	0.8983(2)	0.7749(1)	0.0376(6)
C11	0.0466(3)	0.6300(3)	0.6171(2)	0.0352(8)
C12	-0.0397(4)	0.6017(3)	0.5763(2)	0.0426(10)
C13	-0.0504(4)	0.6588(3)	0.4950(2)	0.0500(11)
H13	-0.1093	0.6410	0.4663	0.060
C14	0.0216(4)	0.7406(3)	0.4545(2)	0.0503(11)
C15	0.1102(4)	0.7639(3)	0.4967(2)	0.0438(10)
H15	0.1625	0.8185	0.4690	0.053
C16	0.1246(4)	0.7093(3)	0.5789(2)	0.0364(9)
C17	-0.1163(4)	0.5098(3)	0.6191(3)	0.0572(12)
H17A	-0.1699	0.5007	0.5809	0.086
H17B	-0.1729	0.5229	0.6614	0.086
H17C	-0.0555	0.4463	0.6425	0.086
C18	0.0081(5)	0.8008(4)	0.3657(2)	0.0741(15)
H18A	0.0951	0.8062	0.3392	0.111
H18B	-0.0369	0.8710	0.3566	0.111
H18C	-0.0427	0.7642	0.3440	0.111
C21	0.2178(4)	0.7557(3)	0.6853(2)	0.0409(9)
C22	0.3244(4)	0.7680(4)	0.7212(3)	0.0542(12)
C23	0.4477(4)	0.7579(3)	0.6859(3)	0.0529(11)
H23	0.5212	0.7669	0.7094	0.064
C24	0.4666(4)	0.7355(3)	0.6183(2)	0.0429(10)
C25	0.3587(4)	0.7216(3)	0.5854(2)	0.0400(9)
H25	0.3712	0.7053	0.5387	0.048
C26	0.2328(4)	0.7306(3)	0.6179(2)	0.0358(9)
C27	0.3054(5)	0.7895(5)	0.7970(3)	0.095(2)
H27A	0.3908	0.7864	0.8177	0.142
H27B	0.2556	0.7369	0.8368	0.142
H27C	0.2572	0.8592	0.7860	0.142
C28	0.6028(4)	0.7253(3)	0.5825(3)	0.0544(11)
H28A	0.6087	0.6761	0.5552	0.082
H28B	0.6659	0.6995	0.6249	0.082
H28C	0.6222	0.7938	0.5441	0.082
C31	-0.0126(3)	0.3742(2)	0.8374(2)	0.0302(8)
C32	-0.1449(4)	0.3957(3)	0.8596(2)	0.0331(8)
C33	-0.2256(3)	0.3213(3)	0.8658(2)	0.0346(8)
H33	-0.3158	0.3334	0.8793	0.042
C34	-0.1797(3)	0.2300(3)	0.8531(2)	0.0315(8)
C35	-0.0486(3)	0.2082(3)	0.8355(2)	0.0303(8)
H35	-0.0169	0.1445	0.8288	0.036
C36	0.0369(3)	0.2807(3)	0.8275(2)	0.0297(8)
C37	-0.2004(4)	0.4911(3)	0.8799(2)	0.0433(10)
O38	-0.2725(2)	0.1650(2)	0.8615(2)	0.0410(6)
C38	-0.2275(4)	0.0689(3)	0.8514(2)	0.0461(10)
H38A	-0.3007	0.0277	0.8610	0.069
H38B	-0.1595	0.0296	0.8896	0.069

H38C	-0.1913	0.0835	0.7969	0.069
C41	0.2541(3)	0.3197(3)	0.7545(2)	0.0312(8)
C42	0.3851(3)	0.2889(3)	0.7367(2)	0.0342(8)
C43	0.4379(3)	0.1902(3)	0.7849(2)	0.0368(9)
H43	0.5267	0.1672	0.7754	0.044
C44	0.3658(4)	0.1229(3)	0.8468(2)	0.0369(9)
C45	0.2358(3)	0.1521(3)	0.8603(2)	0.0326(8)
H45	0.1856	0.1051	0.9008	0.039
C46	0.1784(3)	0.2518(3)	0.8137(2)	0.0291(8)
C47	0.4673(4)	0.3592(3)	0.6675(2)	0.0471(10)
O48	0.4332(2)	0.0284(2)	0.8893(2)	0.0476(7)
C48	0.3692(4)	-0.0386(3)	0.9578(3)	0.0619(13)
H48A	0.4303	-0.1000	0.9858	0.093
H48B	0.2944	-0.0609	0.9417	0.093
H48C	0.3383	-0.0012	0.9934	0.093
C51	-0.2401(4)	0.9032(3)	0.6699(2)	0.0349(8)
C52	-0.2852(4)	0.9597(3)	0.5934(2)	0.0411(9)
C53	-0.4084(4)	1.0156(3)	0.5880(2)	0.0475(10)
H53	-0.4421	1.0540	0.5366	0.057
C54	-0.4847(4)	1.0181(3)	0.6542(2)	0.0465(10)
C55	-0.4320(4)	0.9650(3)	0.7292(2)	0.0388(9)
H55	-0.4811	0.9687	0.7751	0.047
C56	-0.3092(3)	0.9067(3)	0.7382(2)	0.0319(8)
C57	-0.2030(4)	0.9585(4)	0.5209(2)	0.0597(12)
H57A	-0.2511	1.0007	0.4727	0.090
H57B	-0.1828	0.8864	0.5234	0.090
H57C	-0.1215	0.9874	0.5192	0.090
C58	-0.6229(4)	1.0737(4)	0.6474(3)	0.0667(14)
H58A	-0.6473	1.0908	0.6948	0.100
H58B	-0.6832	1.0281	0.6432	0.100
H58C	-0.6275	1.1381	0.5997	0.100
C61	-0.1284(3)	0.8476(3)	0.8356(2)	0.0317(8)
C62	-0.0846(4)	0.8054(3)	0.9139(2)	0.0386(9)
C63	-0.1727(4)	0.7603(3)	0.9749(2)	0.0412(10)
H63	-0.1441	0.7306	1.0281	0.049
C64	-0.3013(4)	0.7565(3)	0.9616(2)	0.0374(9)
C65	-0.3417(4)	0.8033(3)	0.8839(2)	0.0366(9)
H65	-0.4304	0.8035	0.8739	0.044
C66	-0.2574(3)	0.8505(3)	0.8192(2)	0.0310(8)
C67	0.0511(4)	0.8155(4)	0.9318(2)	0.0680(14)
H67A	0.0525	0.8096	0.9874	0.102
H67B	0.0761	0.8837	0.8961	0.102
H67C	0.1130	0.7599	0.9236	0.102
C68	-0.3928(4)	0.7024(3)	1.0302(2)	0.0534(11)
H68A	-0.4782	0.7049	1.0096	0.080
H68B	-0.4032	0.7378	1.0682	0.080
H68C	-0.3563	0.6294	1.0571	0.080
C371	-0.1172(6)	0.5074(6)	0.9354(5)	0.170(4)
H37A	-0.1670	0.5542	0.9595	0.255
H37B	-0.0400	0.5387	0.9060	0.255
H37C	-0.0897	0.4400	0.9774	0.255
C372	-0.2209(7)	0.5863(4)	0.8057(3)	0.119(3)
H37D	-0.2646	0.6447	0.8196	0.179
H37E	-0.2754	0.5727	0.7701	0.179
H37F	-0.1362	0.6038	0.7788	0.179
C373	-0.3337(6)	0.4776(4)	0.9218(4)	0.110(2)
H37G	-0.3646	0.5380	0.9365	0.166
H37H	-0.3276	0.4139	0.9700	0.166
H37I	-0.3953	0.4723	0.8859	0.166
C471	0.5974(4)	0.2988(3)	0.6528(3)	0.0607(13)
H47A	0.6430	0.3435	0.6050	0.091
H47B	0.5800	0.2362	0.6450	0.091
H47C	0.6522	0.2784	0.6990	0.091
C472	0.5001(4)	0.4503(3)	0.6867(3)	0.0678(14)

H47D	0.5537	0.4937	0.6427	0.102
H47E	0.5486	0.4231	0.7360	0.102
H47F	0.4190	0.4924	0.6938	0.102
C473	0.3907(4)	0.3991(4)	0.5898(2)	0.0667(14)
H47G	0.4462	0.4380	0.5446	0.100
H47H	0.3121	0.4451	0.5948	0.100
H47I	0.3654	0.3395	0.5808	0.100

Table S3: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **L10**.

Atom	x	y	z	U_{eq}
H13	-0.1093	0.6410	0.4663	0.060
H15	0.1625	0.8185	0.4690	0.053
H17A	-0.1699	0.5007	0.5809	0.086
H17B	-0.1729	0.5229	0.6614	0.086
H17C	-0.0555	0.4463	0.6425	0.086
H18A	0.0951	0.8062	0.3392	0.111
H18B	-0.0369	0.8710	0.3566	0.111
H18C	-0.0427	0.7642	0.3440	0.111
H23	0.5212	0.7669	0.7094	0.064
H25	0.3712	0.7053	0.5387	0.048
H27A	0.3908	0.7864	0.8177	0.142
H27B	0.2556	0.7369	0.8368	0.142
H27C	0.2572	0.8592	0.7860	0.142
H28A	0.6087	0.6761	0.5552	0.082
H28B	0.6659	0.6995	0.6249	0.082
H28C	0.6222	0.7938	0.5441	0.082
H33	-0.3158	0.3334	0.8793	0.042
H35	-0.0169	0.1445	0.8288	0.036
H38A	-0.3007	0.0277	0.8610	0.069
H38B	-0.1595	0.0296	0.8896	0.069
H38C	-0.1913	0.0835	0.7969	0.069
H43	0.5267	0.1672	0.7754	0.044
H45	0.1856	0.1051	0.9008	0.039
H48A	0.4303	-0.1000	0.9858	0.093
H48B	0.2944	-0.0609	0.9417	0.093
H48C	0.3383	-0.0012	0.9934	0.093
H53	-0.4421	1.0540	0.5366	0.057
H55	-0.4811	0.9687	0.7751	0.047
H57A	-0.2511	1.0007	0.4727	0.090
H57B	-0.1828	0.8864	0.5234	0.090
H57C	-0.1215	0.9874	0.5192	0.090
H58A	-0.6473	1.0908	0.6948	0.100
H58B	-0.6832	1.0281	0.6432	0.100
H58C	-0.6275	1.1381	0.5997	0.100
H63	-0.1441	0.7306	1.0281	0.049
H65	-0.4304	0.8035	0.8739	0.044
H67A	0.0525	0.8096	0.9874	0.102
H67B	0.0761	0.8837	0.8961	0.102
H67C	0.1130	0.7599	0.9236	0.102
H68A	-0.4782	0.7049	1.0096	0.080
H68B	-0.4032	0.7378	1.0682	0.080
H68C	-0.3563	0.6294	1.0571	0.080
H37A	-0.1670	0.5542	0.9595	0.255
H37B	-0.0400	0.5387	0.9060	0.255
H37C	-0.0897	0.4400	0.9774	0.255
H37D	-0.2646	0.6447	0.8196	0.179
H37E	-0.2754	0.5727	0.7701	0.179
H37F	-0.1362	0.6038	0.7788	0.179

H37G	-0.3646	0.5380	0.9365	0.166
H37H	-0.3276	0.4139	0.9700	0.166
H37I	-0.3953	0.4723	0.8859	0.166
H47A	0.6430	0.3435	0.6050	0.091
H47B	0.5800	0.2362	0.6450	0.091
H47C	0.6522	0.2784	0.6990	0.091
H47D	0.5537	0.4937	0.6427	0.102
H47E	0.5486	0.4231	0.7360	0.102
H47F	0.4190	0.4924	0.6938	0.102
H47G	0.4462	0.4380	0.5446	0.100
H47H	0.3121	0.4451	0.5948	0.100
H47I	0.3654	0.3395	0.5808	0.100

Table S4: Anisotropic displacement parameters ($Å^2$) for **L10**. The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	0.0391(6)	0.0307(5)	0.0376(6)	-0.0080(5)	-0.0039(4)	-0.0093(4)
P2	0.0425(7)	0.0352(6)	0.0350(6)	-0.0149(5)	-0.0009(5)	-0.0087(5)
O2	0.0368(18)	0.0355(15)	0.0381(16)	-0.0145(13)	0.0061(13)	-0.0073(12)
O1	0.0357(15)	0.0375(14)	0.0358(15)	-0.0058(12)	-0.0032(11)	-0.0034(11)
O3	0.0445(16)	0.0321(14)	0.0347(14)	-0.0114(12)	0.0008(11)	-0.0145(12)
O4	0.0433(15)	0.0287(13)	0.0323(14)	-0.0061(11)	0.0002(11)	-0.0045(11)
O5	0.0400(15)	0.0479(16)	0.0398(15)	-0.0253(13)	-0.0040(12)	-0.0063(12)
O6	0.0424(15)	0.0440(15)	0.0327(14)	-0.0199(12)	0.0017(11)	-0.0108(12)
C11	0.038(2)	0.032(2)	0.037(2)	-0.0145(17)	-0.0044(17)	-0.0008(16)
C12	0.033(2)	0.050(2)	0.052(3)	-0.028(2)	-0.0039(18)	-0.0009(18)
C13	0.043(2)	0.064(3)	0.050(3)	-0.029(2)	-0.011(2)	-0.001(2)
C14	0.055(3)	0.059(3)	0.032(2)	-0.017(2)	-0.0079(19)	0.011(2)
C15	0.051(3)	0.044(2)	0.033(2)	-0.0132(19)	-0.0002(18)	0.0001(19)
C16	0.041(2)	0.035(2)	0.032(2)	-0.0115(17)	-0.0017(16)	-0.0024(17)
C17	0.046(3)	0.060(3)	0.077(3)	-0.034(3)	-0.008(2)	-0.013(2)
C18	0.090(4)	0.086(4)	0.037(3)	-0.015(3)	-0.014(2)	0.004(3)
C21	0.037(2)	0.043(2)	0.044(2)	-0.0175(19)	0.0048(18)	-0.0096(18)
C22	0.048(3)	0.078(3)	0.055(3)	-0.042(3)	0.010(2)	-0.025(2)
C23	0.039(2)	0.064(3)	0.065(3)	-0.032(2)	0.008(2)	-0.019(2)
C24	0.038(2)	0.037(2)	0.048(2)	-0.0108(19)	0.0081(19)	-0.0063(17)
C25	0.042(2)	0.039(2)	0.034(2)	-0.0082(18)	0.0053(17)	-0.0095(18)
C26	0.040(2)	0.033(2)	0.032(2)	-0.0102(17)	-0.0001(17)	-0.0059(17)
C27	0.059(3)	0.180(6)	0.092(4)	-0.097(4)	0.015(3)	-0.043(4)
C28	0.043(3)	0.049(3)	0.070(3)	-0.022(2)	0.010(2)	-0.009(2)
C31	0.037(2)	0.0243(18)	0.0297(19)	-0.0084(15)	0.0003(15)	-0.0104(15)
C32	0.042(2)	0.030(2)	0.0285(19)	-0.0139(16)	-0.0013(16)	-0.0012(16)
C33	0.033(2)	0.033(2)	0.040(2)	-0.0165(18)	-0.0027(16)	0.0004(16)
C34	0.034(2)	0.0283(19)	0.0315(19)	-0.0098(16)	-0.0035(16)	-0.0058(16)
C35	0.034(2)	0.0264(18)	0.0298(19)	-0.0100(16)	-0.0011(15)	-0.0036(15)
C36	0.032(2)	0.0289(19)	0.0256(18)	-0.0077(15)	-0.0003(15)	-0.0025(15)
C37	0.048(2)	0.031(2)	0.059(3)	-0.027(2)	0.002(2)	-0.0025(18)
O38	0.0344(15)	0.0366(14)	0.0583(17)	-0.0231(13)	0.0021(12)	-0.0110(11)
C38	0.047(2)	0.037(2)	0.064(3)	-0.029(2)	0.008(2)	-0.0125(18)
C41	0.037(2)	0.0265(19)	0.0282(19)	-0.0075(16)	-0.0023(16)	-0.0054(16)
C42	0.033(2)	0.036(2)	0.033(2)	-0.0114(17)	0.0058(16)	-0.0098(16)
C43	0.031(2)	0.039(2)	0.041(2)	-0.0171(19)	-0.0001(17)	-0.0032(17)
C44	0.040(2)	0.032(2)	0.033(2)	-0.0087(17)	-0.0001(17)	0.0004(17)
C45	0.035(2)	0.0309(19)	0.031(2)	-0.0110(16)	0.0049(16)	-0.0060(16)
C46	0.0299(19)	0.0300(19)	0.0282(19)	-0.0117(16)	-0.0022(15)	-0.0030(15)
C47	0.041(2)	0.043(2)	0.049(3)	-0.008(2)	0.0064(19)	-0.0116(19)
O48	0.0441(16)	0.0366(15)	0.0441(16)	-0.0007(13)	0.0046(13)	0.0071(12)
C48	0.056(3)	0.043(3)	0.060(3)	0.005(2)	0.008(2)	0.002(2)

C51	0.040(2)	0.038(2)	0.033(2)	-0.0164(17)	-0.0066(17)	-0.0084(17)
C52	0.053(3)	0.043(2)	0.032(2)	-0.0154(19)	-0.0037(18)	-0.018(2)
C53	0.064(3)	0.045(2)	0.033(2)	-0.0088(19)	-0.017(2)	-0.011(2)
C54	0.055(3)	0.041(2)	0.045(2)	-0.017(2)	-0.020(2)	0.004(2)
C55	0.042(2)	0.040(2)	0.039(2)	-0.0195(19)	-0.0098(18)	-0.0022(18)
C56	0.040(2)	0.0288(19)	0.0304(19)	-0.0135(16)	-0.0068(16)	-0.0063(16)
C57	0.072(3)	0.080(3)	0.031(2)	-0.020(2)	0.004(2)	-0.029(3)
C58	0.068(3)	0.068(3)	0.067(3)	-0.029(3)	-0.039(3)	0.018(2)
C61	0.037(2)	0.0300(19)	0.033(2)	-0.0174(17)	-0.0015(16)	-0.0019(16)
C62	0.041(2)	0.044(2)	0.035(2)	-0.0211(19)	-0.0099(17)	0.0061(18)
C63	0.054(3)	0.043(2)	0.025(2)	-0.0131(18)	-0.0045(18)	0.0039(19)
C64	0.052(3)	0.029(2)	0.031(2)	-0.0118(17)	0.0020(18)	-0.0032(17)
C65	0.044(2)	0.032(2)	0.039(2)	-0.0171(18)	-0.0042(18)	-0.0057(17)
C66	0.043(2)	0.0261(18)	0.0299(19)	-0.0165(16)	-0.0055(16)	-0.0022(16)
C67	0.046(3)	0.117(4)	0.042(3)	-0.032(3)	-0.011(2)	0.001(3)
C68	0.072(3)	0.042(2)	0.043(2)	-0.011(2)	0.005(2)	-0.014(2)
C371	0.103(5)	0.239(9)	0.291(10)	-0.249(9)	-0.085(6)	0.062(5)
C372	0.182(7)	0.039(3)	0.100(5)	-0.013(3)	0.046(4)	0.033(4)
C373	0.112(5)	0.076(4)	0.171(6)	-0.089(4)	0.082(5)	-0.031(3)
C471	0.044(3)	0.060(3)	0.066(3)	-0.015(2)	0.022(2)	-0.009(2)
C472	0.051(3)	0.049(3)	0.101(4)	-0.024(3)	0.015(3)	-0.022(2)
C473	0.063(3)	0.078(3)	0.036(2)	0.003(2)	0.011(2)	-0.016(3)

Table S5: Bond lengths (Å) and angles (deg) for **L10**.

P1-O1	1.612(2)	C22-C27	1.505(5)
P1-O3	1.615(2)	C23-C24	1.368(5)
P1-O4	1.647(2)	C23-H23	0.9500
P2-O2C	1.315(17)	C24-C25	1.382(5)
P2-O2	1.618(3)	C24-C28	1.507(5)
P2-O6	1.626(2)	C25-C26	1.390(5)
P2-O5	1.626(3)	C25-H25	0.9500
O2-C21	1.418(4)	C27-H27A	0.9800
P2B-O2B	1.618(19)	C27-H27B	0.9800
P2B-O5	1.65(2)	C27-H27C	0.9800
P2B-O6	1.96(2)	C28-H28A	0.9800
O2B-C21	1.53(5)	C28-H28B	0.9800
O1-C11	1.401(4)	C28-H28C	0.9800
O3-C31	1.406(4)	C31-C36	1.400(4)
O4-C41	1.402(4)	C31-C32	1.413(5)
O5-C51	1.403(4)	C32-C33	1.390(5)
O6-C61	1.407(4)	C32-C37	1.532(5)
C11-C16	1.388(5)	C33-C34	1.388(4)
C11-C12	1.393(5)	C33-H33	0.9500
C12-C13	1.389(5)	C34-O38	1.375(4)
C12-C17	1.516(5)	C34-C35	1.382(5)
C13-C14	1.379(6)	C35-C36	1.396(4)
C13-H13	0.9500	C35-H35	0.9500
C14-C15	1.391(5)	C36-C46	1.485(5)
C14-C18	1.514(5)	C37-C371	1.480(6)
C15-C16	1.401(5)	C37-C372	1.492(6)
C15-H15	0.9500	C37-C373	1.513(6)
C16-C26	1.499(5)	O38-C38	1.425(4)
C17-H17A	0.9800	C38-H38A	0.9800
C17-H17B	0.9800	C38-H38B	0.9800
C17-H17C	0.9800	C38-H38C	0.9800
C18-H18A	0.9800	C41-C46	1.396(4)
C18-H18B	0.9800	C41-C42	1.408(5)
C18-H18C	0.9800	C42-C43	1.381(5)
C21-C26	1.383(5)	C42-C47	1.538(5)
C21-C22	1.393(5)	C43-C44	1.394(5)
C22-C23	1.387(5)	C43-H43	0.9500

C44-O48	1.369(4)	O3-P1-O4	101.93(12)
C44-C45	1.375(5)	O2C-P2-O2	119.2(8)
C45-C46	1.399(4)	O2C-P2-O6	111.5(8)
C45-H45	0.9500	O2-P2-O6	104.29(14)
C47-C472	1.527(6)	O2C-P2-O5	123.5(8)
C47-C471	1.539(5)	O2-P2-O5	94.72(14)
C47-C473	1.550(6)	O6-P2-O5	100.39(13)
O48-C48	1.414(4)	C21-O2-P2	117.8(2)
C48-H48A	0.9800	O2B-P2B-O5	85(2)
C48-H48B	0.9800	O2B-P2B-O6	92(2)
C48-H48C	0.9800	O5-P2B-O6	87.1(10)
C51-C56	1.386(5)	C21-O2B-P2B	106(3)
C51-C52	1.393(5)	C11-O1-P1	129.6(2)
C52-C53	1.386(5)	C31-O3-P1	125.6(2)
C52-C57	1.504(5)	C41-O4-P1	116.0(2)
C53-C54	1.384(5)	C51-O5-P2	116.3(2)
C53-H53	0.9500	C51-O5-P2B	139.3(8)
C54-C55	1.394(5)	C61-O6-P2	128.7(2)
C54-C58	1.516(5)	C61-O6-P2B	89.5(7)
C55-C56	1.393(5)	C16-C11-C12	122.4(4)
C55-H55	0.9500	C16-C11-O1	121.6(3)
C56-C66	1.484(4)	C12-C11-O1	115.9(3)
C57-H57A	0.9800	C13-C12-C11	117.8(4)
C57-H57B	0.9800	C13-C12-C17	121.2(4)
C57-H57C	0.9800	C11-C12-C17	121.0(4)
C58-H58A	0.9800	C14-C13-C12	122.1(4)
C58-H58B	0.9800	C14-C13-H13	118.9
C58-H58C	0.9800	C12-C13-H13	118.9
C61-C66	1.385(5)	C13-C14-C15	118.3(4)
C61-C62	1.403(5)	C13-C14-C18	120.8(4)
C62-C63	1.380(5)	C15-C14-C18	120.8(4)
C62-C67	1.507(5)	C14-C15-C16	121.9(4)
C63-C64	1.385(5)	C14-C15-H15	119.0
C63-H63	0.9500	C16-C15-H15	119.0
C64-C65	1.384(5)	C11-C16-C15	117.3(3)
C64-C68	1.513(5)	C11-C16-C26	123.7(3)
C65-C66	1.400(5)	C15-C16-C26	118.5(3)
C65-H65	0.9500	C12-C17-H17A	109.5
C67-H67A	0.9800	C12-C17-H17B	109.5
C67-H67B	0.9800	H17A-C17-H17B	109.5
C67-H67C	0.9800	C12-C17-H17C	109.5
C68-H68A	0.9800	H17A-C17-H17C	109.5
C68-H68B	0.9800	H17B-C17-H17C	109.5
C68-H68C	0.9800	C14-C18-H18A	109.5
C371-H37A	0.9800	C14-C18-H18B	109.5
C371-H37B	0.9800	H18A-C18-H18B	109.5
C371-H37C	0.9800	C14-C18-H18C	109.5
C372-H37D	0.9800	H18A-C18-H18C	109.5
C372-H37E	0.9800	H18B-C18-H18C	109.5
C372-H37F	0.9800	C26-C21-C22	121.8(4)
C373-H37G	0.9800	C26-C21-O2	120.9(3)
C373-H37H	0.9800	C22-C21-O2	117.3(3)
C373-H37I	0.9800	C26-C21-O2B	103.3(17)
C471-H47A	0.9800	C22-C21-O2B	122.8(18)
C471-H47B	0.9800	C23-C22-C21	118.1(4)
C471-H47C	0.9800	C23-C22-C27	121.5(4)
C472-H47D	0.9800	C21-C22-C27	120.4(4)
C472-H47E	0.9800	C24-C23-C22	122.0(4)
C472-H47F	0.9800	C24-C23-H23	119.0
C473-H47G	0.9800	C22-C23-H23	119.0
C473-H47H	0.9800	C23-C24-C25	118.2(4)
C473-H47I	0.9800	C23-C24-C28	119.7(4)
O1-P1-O3	98.41(13)	C25-C24-C28	122.0(4)
O1-P1-O4	95.60(13)	C24-C25-C26	122.5(4)

C24-C25-H25	118.7
C26-C25-H25	118.7
C21-C26-C25	117.3(3)
C21-C26-C16	125.1(3)
C25-C26-C16	117.5(3)
C22-C27-H27A	109.5
C22-C27-H27B	109.5
H27A-C27-H27B	109.5
C22-C27-H27C	109.5
H27A-C27-H27C	109.5
H27B-C27-H27C	109.5
C24-C28-H28A	109.5
C24-C28-H28B	109.5
H28A-C28-H28B	109.5
C24-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
C36-C31-O3	116.9(3)
C36-C31-C32	122.5(3)
O3-C31-C32	120.3(3)
C33-C32-C31	115.8(3)
C33-C32-C37	119.7(3)
C31-C32-C37	124.4(3)
C34-C33-C32	122.6(3)
C34-C33-H33	118.7
C32-C33-H33	118.7
O38-C34-C35	124.3(3)
O38-C34-C33	115.2(3)
C35-C34-C33	120.5(3)
C34-C35-C36	119.5(3)
C34-C35-H35	120.3
C36-C35-H35	120.3
C35-C36-C31	119.0(3)
C35-C36-C46	118.0(3)
C31-C36-C46	122.8(3)
C371-C37-C372	111.5(5)
C371-C37-C373	105.7(5)
C372-C37-C373	105.5(4)
C371-C37-C32	111.8(4)
C372-C37-C32	110.7(4)
C373-C37-C32	111.4(3)
C34-O38-C38	116.5(3)
O38-C38-H38A	109.5
O38-C38-H38B	109.5
H38A-C38-H38B	109.5
O38-C38-H38C	109.5
H38A-C38-H38C	109.5
H38B-C38-H38C	109.5
C46-C41-O4	116.5(3)
C46-C41-C42	122.0(3)
O4-C41-C42	121.4(3)
C43-C42-C41	116.4(3)
C43-C42-C47	120.6(3)
C41-C42-C47	123.0(3)
C42-C43-C44	122.4(3)
C42-C43-H43	118.8
C44-C43-H43	118.8
O48-C44-C45	124.6(3)
O48-C44-C43	115.0(3)
C45-C44-C43	120.3(3)
C44-C45-C46	119.3(3)
C44-C45-H45	120.4
C46-C45-H45	120.4
C41-C46-C45	119.4(3)
C41-C46-C36	122.2(3)
C45-C46-C36	118.4(3)
C472-C47-C42	110.3(3)
C472-C47-C471	107.4(3)
C42-C47-C471	111.6(3)
C472-C47-C473	111.0(4)
C42-C47-C473	109.2(3)
C471-C47-C473	107.4(4)
C44-O48-C48	117.4(3)
O48-C48-H48A	109.5
O48-C48-H48B	109.5
H48A-C48-H48B	109.5
O48-C48-H48C	109.5
H48A-C48-H48C	109.5
H48B-C48-H48C	109.5
C56-C51-C52	122.9(3)
C56-C51-O5	118.5(3)
C52-C51-O5	118.5(3)
C53-C52-C51	116.8(3)
C53-C52-C57	122.4(4)
C51-C52-C57	120.9(4)
C54-C53-C52	122.9(4)
C54-C53-H53	118.5
C52-C53-H53	118.5
C53-C54-C55	118.0(4)
C53-C54-C58	122.1(4)
C55-C54-C58	119.9(4)
C56-C55-C54	121.5(4)
C56-C55-H55	119.2
C54-C55-H55	119.2
C51-C56-C55	117.7(3)
C51-C56-C66	122.5(3)
C55-C56-C66	119.8(3)
C52-C57-H57A	109.5
C52-C57-H57B	109.5
H57A-C57-H57B	109.5
C52-C57-H57C	109.5
H57A-C57-H57C	109.5
H57B-C57-H57C	109.5
C54-C58-H58A	109.5
C54-C58-H58B	109.5
H58A-C58-H58B	109.5
C54-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C66-C61-C62	121.9(3)
C66-C61-O6	120.9(3)
C62-C61-O6	116.7(3)
C63-C62-C61	117.8(3)
C63-C62-C67	120.6(3)
C61-C62-C67	121.4(4)
C62-C63-C64	122.6(3)
C62-C63-H63	118.7
C64-C63-H63	118.7
C65-C64-C63	117.6(3)
C65-C64-C68	121.8(4)
C63-C64-C68	120.6(3)
C64-C65-C66	122.7(3)
C64-C65-H65	118.7
C66-C65-H65	118.7
C61-C66-C65	117.2(3)
C61-C66-C56	122.7(3)
C65-C66-C56	120.0(3)
C62-C67-H67A	109.5

C62-C67-H67B	109.5
H67A-C67-H67B	109.5
C62-C67-H67C	109.5
H67A-C67-H67C	109.5
H67B-C67-H67C	109.5
C64-C68-H68A	109.5
C64-C68-H68B	109.5
H68A-C68-H68B	109.5
C64-C68-H68C	109.5
H68A-C68-H68C	109.5
H68B-C68-H68C	109.5
C37-C371-H37A	109.5
C37-C371-H37B	109.5
H37A-C371-H37B	109.5
C37-C371-H37C	109.5
H37A-C371-H37C	109.5
H37B-C371-H37C	109.5
C37-C372-H37D	109.5
C37-C372-H37E	109.5
H37D-C372-H37E	109.5
C37-C372-H37F	109.5
H37D-C372-H37F	109.5
H37E-C372-H37F	109.5
C37-C373-H37G	109.5
C37-C373-H37H	109.5
H37G-C373-H37H	109.5
C37-C373-H37I	109.5
H37G-C373-H37I	109.5
H37H-C373-H37I	109.5
C47-C471-H47A	109.5
C47-C471-H47B	109.5
H47A-C471-H47B	109.5
C47-C471-H47C	109.5
H47A-C471-H47C	109.5
H47B-C471-H47C	109.5
C47-C472-H47D	109.5
C47-C472-H47E	109.5
H47D-C472-H47E	109.5
C47-C472-H47F	109.5
H47D-C472-H47F	109.5
H47E-C472-H47F	109.5
C47-C473-H47G	109.5
C47-C473-H47H	109.5
H47G-C473-H47H	109.5
C47-C473-H47I	109.5
H47G-C473-H47I	109.5
H47H-C473-H47I	109.5

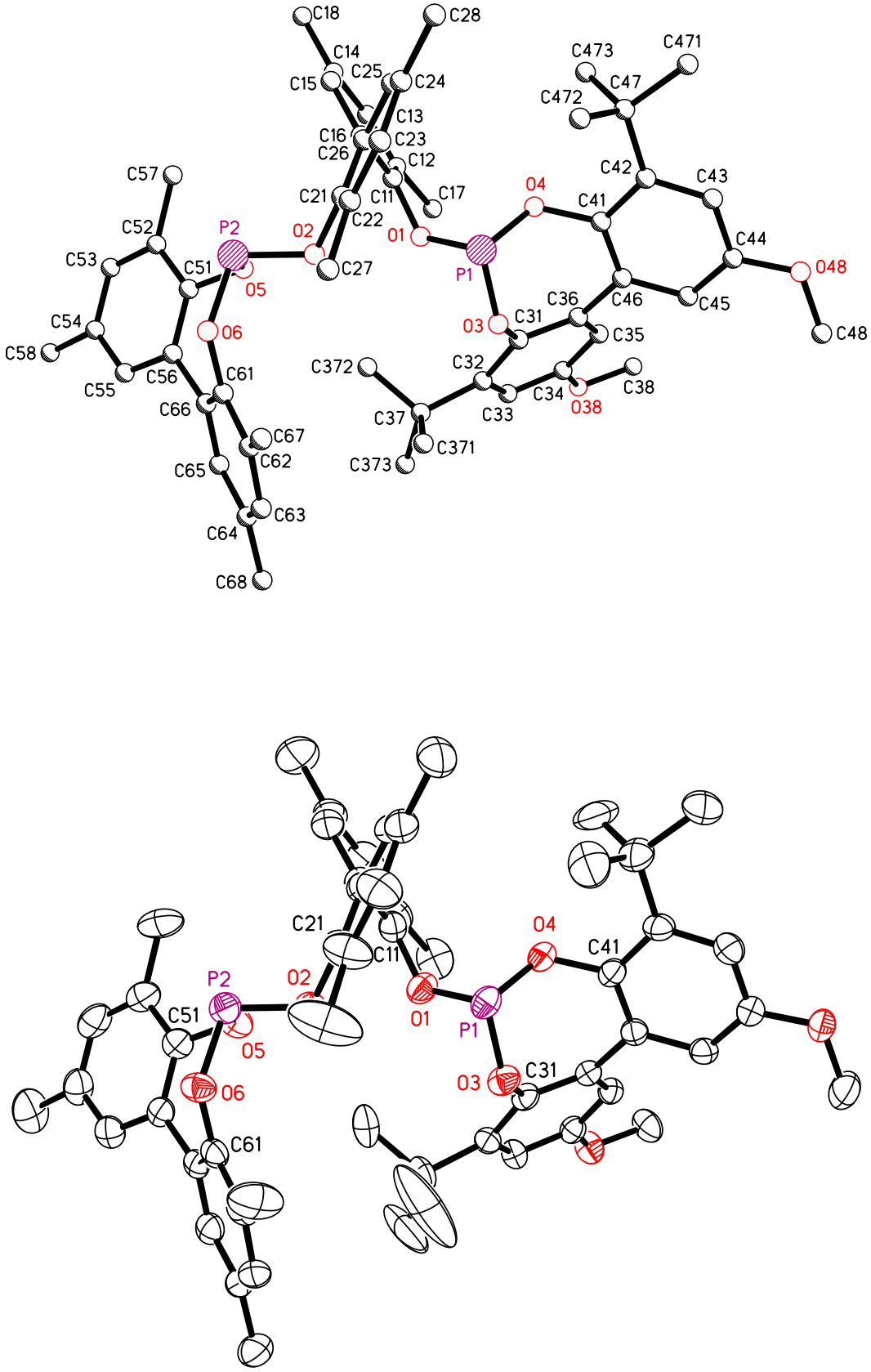


Figure S1: Molecular structure of ligand L10. Hydrogen atoms are omitted for clarity.

S1.2 Catalyst resting state 3

Table S6: Crystal data and structure refinement for **3**.

Identification code	jam6	
Empirical formula	$C_{52}H_{49}O_8P_2Rh$	
Formula weight	966.76	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	4	
Unit cell dimensions	a = 11.2578(9) Å	α = 90 deg.
	b = 11.0732(9) Å	β = 94.5295(18) deg.
	c = 37.106(3) Å	γ = 90 deg.
Volume	4611.2(7) $Å^3$	
Density (calculated)	1.39 g/cm^3	
Absorption coefficient	0.49 mm^{-1}	
Crystal shape	polyhedron	
Crystal size	0.170 x 0.160 x 0.150 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.1 to 27.1 deg.	
Index ranges	$-14 \le h \le 14$, $-13 \le k \le 14$, $-47 \le l \le 42$	
Reflections collected	45410	
Independent reflections	10193 (R(int) = 0.0807)	
Observed reflections	7213 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.95 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	10193 / 0 / 580	
Goodness-of-fit on F^2	1.07	
Final R indices (I>2sigma(I))	R1 = 0.052, wR2 = 0.082	
Largest diff. peak and hole	0.53 and -0.68 $eÅ^{-3}$	

Table S7: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Rh1	0.2459(1)	0.8015(1)	0.6228(1)	0.0244(1)
H1	0.314(3)	0.920(4)	0.6168(11)	0.060(13)
P1	0.4043(1)	0.7284(1)	0.5965(1)	0.0244(2)
P2	0.1531(1)	0.6198(1)	0.6299(1)	0.0231(2)
O1	0.4174(2)	0.7405(2)	0.5536(1)	0.0303(6)
O2	0.0830(2)	0.5572(2)	0.5953(1)	0.0268(6)
O3	0.4266(2)	0.5855(2)	0.6002(1)	0.0271(6)
O4	0.5345(2)	0.7824(2)	0.6087(1)	0.0269(6)
O5	0.2394(2)	0.5105(2)	0.6423(1)	0.0256(6)
O6	0.0473(2)	0.6102(2)	0.6565(1)	0.0241(6)
C98	0.1221(4)	0.8854(4)	0.5939(1)	0.0358(10)
O98	0.0572(3)	0.9473(3)	0.5780(1)	0.0576(9)
C99	0.2775(4)	0.8395(4)	0.6728(1)	0.0379(10)
O99	0.3011(3)	0.8700(3)	0.7019(1)	0.0637(10)
C1	0.3403(3)	0.8083(4)	0.5304(1)	0.0275(8)

C2	0.3783(4)	0.9184(4)	0.5184(1)	0.0386(10)
H2	0.4533	0.9498	0.5275	0.046
C3	0.3072(4)	0.9832(4)	0.4931(1)	0.0483(12)
H3	0.3345	1.0581	0.4844	0.058
C4	0.1969(4)	0.9394(4)	0.4807(1)	0.0436(11)
H4	0.1480	0.9842	0.4634	0.052
C5	-0.1363(3)	0.7547(4)	0.5212(1)	0.0367(10)
H5	-0.1867	0.7987	0.5042	0.044
C6	-0.1804(3)	0.7118(4)	0.5528(1)	0.0388(10)
H6	-0.2611	0.7269	0.5572	0.047
C7	-0.1078(3)	0.6472(4)	0.5779(1)	0.0334(9)
H7	-0.1379	0.6178	0.5994	0.040
C8	0.0091(3)	0.6265(3)	0.5709(1)	0.0268(8)
C9	0.1774(3)	0.6428(3)	0.5272(1)	0.0269(8)
H9	0.2294	0.5971	0.5456	0.032
C10	0.0418(3)	0.7676(4)	0.4814(1)	0.0360(10)
H10	-0.0106	0.8186	0.4645	0.043
C11	0.0741(4)	0.6477(4)	0.4640(1)	0.0402(11)
H11A	0.1144	0.6638	0.4417	0.048
H11B	0.0006	0.6011	0.4572	0.048
C12	0.1572(3)	0.5737(4)	0.4907(1)	0.0348(10)
H12A	0.2345	0.5603	0.4804	0.042
H12B	0.1210	0.4939	0.4949	0.042
C17	0.2301(3)	0.7628(3)	0.5181(1)	0.0279(9)
C18	0.1577(3)	0.8305(4)	0.4931(1)	0.0344(10)
C19	0.0550(3)	0.6669(3)	0.5396(1)	0.0259(8)
C20	-0.0192(3)	0.7332(3)	0.5148(1)	0.0311(9)
C31	0.5346(3)	0.5269(3)	0.6094(1)	0.0252(8)
C32	0.5730(3)	0.4444(4)	0.5848(1)	0.0306(9)
C33	0.6754(4)	0.3790(4)	0.5957(1)	0.0383(10)
H33	0.7026	0.3196	0.5798	0.046
C34	0.7393(4)	0.3968(4)	0.6288(1)	0.0387(10)
C35	0.6965(3)	0.4808(4)	0.6520(1)	0.0362(10)
H35	0.7398	0.4948	0.6747	0.043
C36	0.5924(3)	0.5457(3)	0.6434(1)	0.0280(9)
C37	0.5071(4)	0.4264(4)	0.5484(1)	0.0467(12)
H37A	0.5447	0.3611	0.5356	0.070
H37B	0.5095	0.5012	0.5344	0.070
H37C	0.4240	0.4052	0.5515	0.070
C38	0.8513(4)	0.3262(4)	0.6394(1)	0.0600(14)
H38A	0.8587	0.3142	0.6656	0.090
H38B	0.9207	0.3710	0.6322	0.090
H38C	0.8473	0.2475	0.6273	0.090
C39	0.5389(3)	0.6235(3)	0.6715(1)	0.0325(9)
H39A	0.4511	0.6185	0.6672	0.039
H39B	0.5607	0.5873	0.6955	0.039
C41	0.5644(3)	0.8308(4)	0.6432(1)	0.0285(9)
C42	0.5910(3)	0.9529(4)	0.6453(1)	0.0380(10)
C43	0.6256(4)	0.9998(4)	0.6795(1)	0.0459(12)
H43	0.6442	1.0833	0.6816	0.055
C44	0.6338(4)	0.9295(4)	0.7103(1)	0.0453(12)
C45	0.6078(3)	0.8079(4)	0.7065(1)	0.0398(10)
H45	0.6142	0.7582	0.7275	0.048
C46	0.5726(3)	0.7556(4)	0.6734(1)	0.0299(9)
C47	0.5830(4)	1.0304(4)	0.6121(1)	0.0581(14)
H47A	0.6015	1.1142	0.6189	0.087
H47B	0.5022	1.0260	0.6002	0.087
H47C	0.6402	1.0017	0.5954	0.087
C48	0.6705(4)	0.9828(5)	0.7469(1)	0.0615(15)
H48A	0.7145	0.9223	0.7619	0.092
H48B	0.5994	1.0075	0.7587	0.092
H48C	0.7215	1.0533	0.7440	0.092
C51	0.1951(3)	0.4035(3)	0.6571(1)	0.0250(8)
C52	0.1831(3)	0.3004(4)	0.6361(1)	0.0310(9)

C53	0.1368(3)	0.1995(4)	0.6521(1)	0.0383(10)
H53	0.1271	0.1272	0.6384	0.046
C54	0.1041(3)	0.2000(4)	0.6874(1)	0.0370(10)
C55	0.1246(3)	0.3039(4)	0.7076(1)	0.0319(9)
H55	0.1054	0.3049	0.7321	0.038
C56	0.1724(3)	0.4065(3)	0.6932(1)	0.0257(8)
C57	0.2230(4)	0.2966(4)	0.5984(1)	0.0470(11)
H57A	0.2185	0.2134	0.5894	0.070
H57B	0.3053	0.3255	0.5987	0.070
H57C	0.1711	0.3484	0.5826	0.070
C58	0.0465(4)	0.0904(4)	0.7031(1)	0.0564(14)
H58A	0.0640	0.0894	0.7294	0.085
H58B	0.0782	0.0169	0.6927	0.085
H58C	-0.0399	0.0938	0.6974	0.085
C59	0.2085(3)	0.5150(3)	0.7165(1)	0.0272(8)
H59A	0.2335	0.4852	0.7411	0.033
H59B	0.2794	0.5518	0.7068	0.033
C61	0.0470(3)	0.6616(3)	0.6911(1)	0.0232(8)
C62	-0.0337(3)	0.7550(3)	0.6951(1)	0.0277(8)
C63	-0.0409(3)	0.8013(4)	0.7296(1)	0.0339(9)
H63	-0.0943	0.8660	0.7329	0.041
C64	0.0270(3)	0.7567(4)	0.7594(1)	0.0322(9)
C65	0.1053(3)	0.6635(3)	0.7540(1)	0.0300(9)
H65	0.1527	0.6323	0.7742	0.036
C66	0.1172(3)	0.6136(3)	0.7200(1)	0.0241(8)
C67	-0.1093(3)	0.8037(4)	0.6630(1)	0.0406(10)
H67A	-0.1559	0.8726	0.6706	0.061
H67B	-0.1633	0.7403	0.6532	0.061
H67C	-0.0577	0.8298	0.6444	0.061
C68	0.0170(4)	0.8075(4)	0.7968(1)	0.0459(11)
H68A	0.0584	0.7542	0.8147	0.069
H68B	-0.0672	0.8134	0.8015	0.069
H68C	0.0532	0.8880	0.7983	0.069

Table S8: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **3**.

Atom	x	y	z	U_{eq}
H1	0.314(3)	0.920(4)	0.6168(11)	0.060(13)
H2	0.4533	0.9498	0.5275	0.046
H3	0.3345	1.0581	0.4844	0.058
H4	0.1480	0.9842	0.4634	0.052
H5	-0.1867	0.7987	0.5042	0.044
H6	-0.2611	0.7269	0.5572	0.047
H7	-0.1379	0.6178	0.5994	0.040
H9	0.2294	0.5971	0.5456	0.032
H10	-0.0106	0.8186	0.4645	0.043
H11A	0.1144	0.6638	0.4417	0.048
H11B	0.0006	0.6011	0.4572	0.048
H12A	0.2345	0.5603	0.4804	0.042
H12B	0.1210	0.4939	0.4949	0.042
H33	0.7026	0.3196	0.5798	0.046
H35	0.7398	0.4948	0.6747	0.043
H37A	0.5447	0.3611	0.5356	0.070
H37B	0.5095	0.5012	0.5344	0.070
H37C	0.4240	0.4052	0.5515	0.070
H38A	0.8587	0.3142	0.6656	0.090
H38B	0.9207	0.3710	0.6322	0.090

H38C	0.8473	0.2475	0.6273	0.090
H39A	0.4511	0.6185	0.6672	0.039
H39B	0.5607	0.5873	0.6955	0.039
H43	0.6442	1.0833	0.6816	0.055
H45	0.6142	0.7582	0.7275	0.048
H47A	0.6015	1.1142	0.6189	0.087
H47B	0.5022	1.0260	0.6002	0.087
H47C	0.6402	1.0017	0.5954	0.087
H48A	0.7145	0.9223	0.7619	0.092
H48B	0.5994	1.0075	0.7587	0.092
H48C	0.7215	1.0533	0.7440	0.092
H53	0.1271	0.1272	0.6384	0.046
H55	0.1054	0.3049	0.7321	0.038
H57A	0.2185	0.2134	0.5894	0.070
H57B	0.3053	0.3255	0.5987	0.070
H57C	0.1711	0.3484	0.5826	0.070
H58A	0.0640	0.0894	0.7294	0.085
H58B	0.0782	0.0169	0.6927	0.085
H58C	-0.0399	0.0938	0.6974	0.085
H59A	0.2335	0.4852	0.7411	0.033
H59B	0.2794	0.5518	0.7068	0.033
H63	-0.0943	0.8660	0.7329	0.041
H65	0.1527	0.6323	0.7742	0.036
H67A	-0.1559	0.8726	0.6706	0.061
H67B	-0.1633	0.7403	0.6532	0.061
H67C	-0.0577	0.8298	0.6444	0.061
H68A	0.0584	0.7542	0.8147	0.069
H68B	-0.0672	0.8134	0.8015	0.069
H68C	0.0532	0.8880	0.7983	0.069

Table S9: Anisotropic displacement parameters ($Å^2$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.0222(2)	0.0266(2)	0.0238(2)	-0.0001(1)	-0.0011(1)	0.0004(1)
P1	0.0194(5)	0.0312(6)	0.0222(5)	0.0019(4)	-0.0019(4)	-0.0002(4)
P2	0.0216(5)	0.0276(5)	0.0200(5)	0.0000(4)	0.0012(4)	0.0012(4)
O1	0.0227(13)	0.0454(17)	0.0220(13)	0.0059(12)	-0.0030(10)	0.0042(12)
O2	0.0313(14)	0.0300(14)	0.0185(13)	0.0006(11)	-0.0010(11)	-0.0025(12)
O3	0.0195(13)	0.0272(14)	0.0343(15)	0.0010(12)	0.0009(11)	0.0045(11)
O4	0.0219(13)	0.0332(15)	0.0248(13)	0.0010(12)	-0.0041(10)	-0.0038(11)
O5	0.0233(13)	0.0280(14)	0.0259(14)	0.0029(11)	0.0039(11)	0.0041(11)
O6	0.0222(13)	0.0294(14)	0.0205(13)	-0.0012(11)	0.0011(10)	-0.0001(11)
C98	0.036(2)	0.031(2)	0.040(2)	-0.003(2)	-0.0025(19)	-0.0041(19)
O98	0.059(2)	0.046(2)	0.063(2)	0.0043(17)	-0.0246(17)	0.0170(17)
C99	0.036(2)	0.039(3)	0.039(3)	-0.005(2)	0.0017(19)	0.0040(19)
O99	0.071(2)	0.084(3)	0.0355(19)	-0.0239(18)	-0.0037(17)	-0.004(2)
C1	0.0228(19)	0.036(2)	0.0231(19)	0.0045(18)	-0.0014(15)	0.0023(18)
C2	0.027(2)	0.045(3)	0.043(3)	0.007(2)	-0.0027(19)	-0.0068(19)
C3	0.035(3)	0.047(3)	0.062(3)	0.026(2)	0.001(2)	-0.008(2)
C4	0.037(2)	0.050(3)	0.043(3)	0.023(2)	-0.007(2)	-0.001(2)
C5	0.027(2)	0.040(2)	0.042(2)	0.000(2)	-0.0088(18)	0.0010(19)
C6	0.025(2)	0.051(3)	0.040(2)	-0.005(2)	-0.0003(18)	0.000(2)
C7	0.024(2)	0.043(2)	0.033(2)	-0.0030(19)	0.0029(17)	-0.0051(18)
C8	0.025(2)	0.032(2)	0.0226(19)	-0.0008(16)	-0.0062(15)	-0.0051(17)
C9	0.028(2)	0.033(2)	0.0191(18)	-0.0004(16)	-0.0051(15)	0.0009(17)
C10	0.031(2)	0.043(3)	0.033(2)	0.0116(19)	-0.0086(17)	-0.0042(19)
C11	0.036(2)	0.060(3)	0.024(2)	0.000(2)	-0.0010(18)	-0.010(2)
C12	0.035(2)	0.046(3)	0.024(2)	-0.0022(19)	0.0035(17)	-0.006(2)
C17	0.028(2)	0.033(2)	0.0221(19)	0.0047(17)	0.0003(15)	-0.0019(17)
C18	0.028(2)	0.043(3)	0.031(2)	0.0120(19)	-0.0058(17)	-0.0032(19)
C19	0.0222(19)	0.029(2)	0.026(2)	-0.0001(16)	-0.0044(15)	-0.0047(16)
C20	0.026(2)	0.035(2)	0.030(2)	0.0026(18)	-0.0074(16)	-0.0057(17)
C31	0.0187(18)	0.027(2)	0.030(2)	0.0055(17)	0.0034(15)	0.0021(16)
C32	0.027(2)	0.037(2)	0.029(2)	0.0036(18)	0.0078(17)	0.0017(18)
C33	0.033(2)	0.038(2)	0.046(3)	0.005(2)	0.018(2)	0.0053(19)
C34	0.029(2)	0.042(3)	0.045(3)	0.018(2)	0.0057(19)	0.005(2)
C35	0.030(2)	0.045(3)	0.033(2)	0.014(2)	-0.0034(18)	0.0024(19)
C36	0.025(2)	0.031(2)	0.028(2)	0.0106(17)	0.0025(16)	0.0004(17)
C37	0.043(3)	0.058(3)	0.040(3)	-0.010(2)	0.006(2)	0.007(2)
C38	0.043(3)	0.065(3)	0.070(4)	0.021(3)	-0.001(2)	0.022(3)
C39	0.031(2)	0.044(3)	0.022(2)	0.0054(18)	-0.0005(16)	-0.0002(19)
C41	0.0176(18)	0.039(2)	0.028(2)	-0.0025(18)	-0.0057(15)	-0.0009(17)
C42	0.030(2)	0.037(2)	0.045(3)	-0.004(2)	-0.0096(19)	-0.0037(19)
C43	0.033(2)	0.041(3)	0.061(3)	-0.018(2)	-0.011(2)	0.004(2)
C44	0.025(2)	0.062(3)	0.047(3)	-0.023(3)	-0.0075(19)	0.013(2)
C45	0.032(2)	0.057(3)	0.030(2)	-0.004(2)	0.0002(17)	0.007(2)
C46	0.0211(19)	0.044(2)	0.024(2)	0.0004(18)	-0.0020(15)	0.0021(17)
C47	0.067(4)	0.035(3)	0.069(4)	0.007(3)	-0.009(3)	-0.012(2)
C48	0.048(3)	0.078(4)	0.056(3)	-0.036(3)	-0.013(2)	0.016(3)
C51	0.0230(19)	0.025(2)	0.026(2)	0.0017(16)	0.0002(15)	0.0013(16)
C52	0.029(2)	0.031(2)	0.032(2)	-0.0031(19)	-0.0028(16)	0.0077(18)
C53	0.038(2)	0.024(2)	0.050(3)	-0.007(2)	-0.007(2)	0.0059(19)
C54	0.029(2)	0.030(2)	0.050(3)	0.009(2)	-0.0085(19)	0.0000(19)
C55	0.030(2)	0.035(2)	0.031(2)	0.0061(19)	0.0018(16)	0.0033(19)
C56	0.025(2)	0.025(2)	0.026(2)	0.0030(16)	-0.0007(15)	0.0056(16)
C57	0.056(3)	0.048(3)	0.037(2)	-0.012(2)	0.002(2)	0.014(2)
C58	0.047(3)	0.039(3)	0.081(4)	0.015(3)	-0.004(3)	-0.007(2)
C59	0.030(2)	0.031(2)	0.0209(19)	0.0031(16)	-0.0013(15)	0.0033(17)
C61	0.0211(18)	0.026(2)	0.0227(19)	-0.0033(16)	0.0053(15)	-0.0043(15)
C62	0.0216(19)	0.027(2)	0.036(2)	-0.0021(17)	0.0094(16)	0.0012(16)

C63	0.031(2)	0.028(2)	0.045(2)	-0.005(2)	0.0147(18)	-0.0001(18)
C64	0.031(2)	0.034(2)	0.033(2)	-0.0085(18)	0.0119(18)	-0.0080(18)
C65	0.029(2)	0.036(2)	0.026(2)	-0.0028(17)	0.0023(16)	-0.0076(17)
C66	0.0214(19)	0.028(2)	0.0236(19)	0.0007(16)	0.0044(15)	-0.0010(16)
C67	0.030(2)	0.046(3)	0.046(3)	0.003(2)	0.0043(19)	0.010(2)
C68	0.047(3)	0.051(3)	0.040(3)	-0.015(2)	0.012(2)	-0.003(2)

Table S10: Bond lengths (Å) and angles (deg) for **3**.

Rh1-C99	1.911(4)	C32-C33	1.395(5)
Rh1-C98	1.930(4)	C32-C37	1.501(5)
Rh1-P1	2.2489(10)	C33-C34	1.385(6)
Rh1-P2	2.2918(10)	C33-H33	0.9500
Rh1-H1	1.55(4)	C34-C35	1.381(6)
P1-O3	1.607(3)	C34-C38	1.510(5)
P1-O4	1.614(2)	C35-C36	1.390(5)
P1-O1	1.616(2)	C35-H35	0.9500
P2-O5	1.597(2)	C36-C39	1.513(5)
P2-O2	1.609(2)	C37-H37A	0.9800
P2-O6	1.610(2)	C37-H37B	0.9800
O1-C1	1.393(4)	C37-H37C	0.9800
O2-C8	1.409(4)	C38-H38A	0.9800
O3-C31	1.396(4)	C38-H38B	0.9800
O4-C41	1.404(4)	C38-H38C	0.9800
O5-C51	1.415(4)	C39-C46	1.511(5)
O6-C61	1.405(4)	C39-H39A	0.9900
C98-O98	1.131(5)	C39-H39B	0.9900
C99-O99	1.141(5)	C41-C42	1.386(5)
C1-C2	1.377(5)	C41-C46	1.395(5)
C1-C17	1.383(5)	C42-C43	1.398(6)
C2-C3	1.384(5)	C42-C47	1.498(6)
C2-H2	0.9500	C43-C44	1.379(6)
C3-C4	1.380(6)	C43-H43	0.9500
C3-H3	0.9500	C44-C45	1.383(6)
C4-C18	1.377(5)	C44-C48	1.510(6)
C4-H4	0.9500	C45-C46	1.387(5)
C5-C20	1.379(5)	C45-H45	0.9500
C5-C6	1.391(5)	C47-H47A	0.9800
C5-H5	0.9500	C47-H47B	0.9800
C6-C7	1.388(5)	C47-H47C	0.9800
C6-H6	0.9500	C48-H48A	0.9800
C7-C8	1.380(5)	C48-H48B	0.9800
C7-H7	0.9500	C48-H48C	0.9800
C8-C19	1.383(5)	C51-C56	1.382(5)
C9-C17	1.505(5)	C51-C52	1.383(5)
C9-C19	1.510(5)	C52-C53	1.386(5)
C9-C12	1.556(5)	C52-C57	1.503(5)
C9-H9	1.0000	C53-C54	1.388(6)
C10-C20	1.513(5)	C53-H53	0.9500
C10-C18	1.513(5)	C54-C55	1.383(5)
C10-C11	1.533(6)	C54-C58	1.513(5)
C10-H10	1.0000	C55-C56	1.383(5)
C11-C12	1.545(5)	C55-H55	0.9500
C11-H11A	0.9900	C56-C59	1.517(5)
C11-H11B	0.9900	C57-H57A	0.9800
C12-H12A	0.9900	C57-H57B	0.9800
C12-H12B	0.9900	C57-H57C	0.9800
C17-C18	1.401(5)	C58-H58A	0.9800
C19-C20	1.400(5)	C58-H58B	0.9800
C31-C32	1.387(5)	C58-H58C	0.9800
C31-C36	1.389(5)	C59-C66	1.513(5)

C59-H59A	0.9900	C7-C6-H6	119.7
C59-H59B	0.9900	C5-C6-H6	119.7
C61-C66	1.386(5)	C8-C7-C6	118.7(4)
C61-C62	1.392(5)	C8-C7-H7	120.7
C62-C63	1.385(5)	C6-C7-H7	120.7
C62-C67	1.508(5)	C7-C8-C19	122.0(3)
C63-C64	1.386(5)	C7-C8-O2	119.6(3)
C63-H63	0.9500	C19-C8-O2	118.4(3)
C64-C65	1.383(5)	C17-C9-C19	107.3(3)
C64-C68	1.507(5)	C17-C9-C12	105.7(3)
C65-C66	1.393(5)	C19-C9-C12	106.0(3)
C65-H65	0.9500	C17-C9-H9	112.4
C67-H67A	0.9800	C19-C9-H9	112.4
C67-H67B	0.9800	C12-C9-H9	112.4
C67-H67C	0.9800	C20-C10-C18	108.5(3)
C68-H68A	0.9800	C20-C10-C11	105.4(3)
C68-H68B	0.9800	C18-C10-C11	107.0(3)
C68-H68C	0.9800	C20-C10-H10	111.9
C99-Rh1-C98	120.36(17)	C18-C10-H10	111.9
C99-Rh1-P1	114.09(12)	C11-C10-H10	111.9
C98-Rh1-P1	119.65(13)	C10-C11-C12	109.9(3)
C99-Rh1-P2	97.64(13)	C10-C11-H11A	109.7
C98-Rh1-P2	99.83(12)	C12-C11-H11A	109.7
P1-Rh1-P2	96.81(4)	C10-C11-H11B	109.7
C99-Rh1-H1	84.0(15)	C12-C11-H11B	109.7
C98-Rh1-H1	81.7(15)	H11A-C11-H11B	108.2
P1-Rh1-H1	79.9(15)	C11-C12-C9	109.8(3)
P2-Rh1-H1	176.7(15)	C11-C12-H12A	109.7
O3-P1-O4	101.97(13)	C9-C12-H12A	109.7
O3-P1-O1	98.11(13)	C11-C12-H12B	109.7
O4-P1-O1	95.42(13)	C9-C12-H12B	109.7
O3-P1-Rh1	116.14(10)	H12A-C12-H12B	108.2
O4-P1-Rh1	118.57(10)	C1-C17-C18	118.9(3)
O1-P1-Rh1	122.35(10)	C1-C17-C9	127.3(3)
O5-P2-O2	98.72(13)	C18-C17-C9	113.8(3)
O5-P2-O6	103.70(13)	C4-C18-C17	120.4(4)
O2-P2-O6	96.91(13)	C4-C18-C10	126.7(3)
O5-P2-Rh1	115.20(10)	C17-C18-C10	112.8(3)
O2-P2-Rh1	119.08(10)	C8-C19-C20	118.5(3)
O6-P2-Rh1	119.65(10)	C8-C19-C9	127.5(3)
C1-O1-P1	123.5(2)	C20-C19-C9	113.9(3)
C8-O2-P2	120.4(2)	C5-C20-C19	120.5(4)
C31-O3-P1	127.3(2)	C5-C20-C10	126.9(3)
C41-O4-P1	123.0(2)	C19-C20-C10	112.5(3)
C51-O5-P2	121.4(2)	C32-C31-C36	123.4(3)
C61-O6-P2	126.1(2)	C32-C31-O3	117.1(3)
O98-C98-Rh1	171.4(4)	C36-C31-O3	119.3(3)
O99-C99-Rh1	174.6(4)	C31-C32-C33	116.3(4)
C2-C1-C17	120.6(3)	C31-C32-C37	121.6(3)
C2-C1-O1	118.8(3)	C33-C32-C37	122.1(4)
C17-C1-O1	120.5(3)	C34-C33-C32	122.9(4)
C1-C2-C3	120.0(4)	C34-C33-H33	118.6
C1-C2-H2	120.0	C32-C33-H33	118.6
C3-C2-H2	120.0	C35-C34-C33	117.9(4)
C4-C3-C2	120.1(4)	C35-C34-C38	120.7(4)
C4-C3-H3	119.9	C33-C34-C38	121.4(4)
C2-C3-H3	119.9	C34-C35-C36	122.3(4)
C18-C4-C3	119.9(4)	C34-C35-H35	118.9
C18-C4-H4	120.0	C36-C35-H35	118.9
C3-C4-H4	120.0	C31-C36-C35	117.2(4)
C20-C5-C6	119.7(4)	C31-C36-C39	121.8(3)
C20-C5-H5	120.1	C35-C36-C39	120.7(3)
C6-C5-H5	120.1	C32-C37-H37A	109.5
C7-C6-C5	120.6(4)	C32-C37-H37B	109.5

H37A-C37-H37B	109.5
C32-C37-H37C	109.5
H37A-C37-H37C	109.5
H37B-C37-H37C	109.5
C34-C38-H38A	109.5
C34-C38-H38B	109.5
H38A-C38-H38B	109.5
C34-C38-H38C	109.5
H38A-C38-H38C	109.5
H38B-C38-H38C	109.5
C46-C39-C36	118.2(3)
C46-C39-H39A	107.8
C36-C39-H39A	107.8
C46-C39-H39B	107.8
C36-C39-H39B	107.8
H39A-C39-H39B	107.1
C42-C41-C46	122.5(4)
C42-C41-O4	117.4(3)
C46-C41-O4	120.1(3)
C41-C42-C43	117.2(4)
C41-C42-C47	120.9(4)
C43-C42-C47	121.9(4)
C44-C43-C42	122.6(4)
C44-C43-H43	118.7
C42-C43-H43	118.7
C43-C44-C45	117.8(4)
C43-C44-C48	121.4(4)
C45-C44-C48	120.8(5)
C44-C45-C46	122.6(4)
C44-C45-H45	118.7
C46-C45-H45	118.7
C45-C46-C41	117.3(4)
C45-C46-C39	120.0(4)
C41-C46-C39	122.6(3)
C42-C47-H47A	109.5
C42-C47-H47B	109.5
H47A-C47-H47B	109.5
C42-C47-H47C	109.5
H47A-C47-H47C	109.5
H47B-C47-H47C	109.5
C44-C48-H48A	109.5
C44-C48-H48B	109.5
H48A-C48-H48B	109.5
C44-C48-H48C	109.5
H48A-C48-H48C	109.5
H48B-C48-H48C	109.5
C56-C51-C52	123.3(4)
C56-C51-O5	117.1(3)
C52-C51-O5	119.5(3)
C51-C52-C53	116.5(4)
C51-C52-C57	121.7(4)
C53-C52-C57	121.8(4)
C52-C53-C54	122.6(4)
C52-C53-H53	118.7
C54-C53-H53	118.7
C55-C54-C53	118.0(4)
C55-C54-C58	121.1(4)
C53-C54-C58	120.9(4)
C56-C55-C54	121.8(4)
C56-C55-H55	119.1
C54-C55-H55	119.1
C51-C56-C55	117.6(3)
C51-C56-C59	120.6(3)
C55-C56-C59	121.6(3)
C52-C57-H57A	109.5
C52-C57-H57B	109.5
H57A-C57-H57B	109.5
C52-C57-H57C	109.5
H57A-C57-H57C	109.5
H57B-C57-H57C	109.5
C54-C58-H58A	109.5
C54-C58-H58B	109.5
H58A-C58-H58B	109.5
C54-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C66-C59-C56	117.8(3)
C66-C59-H59A	107.8
C56-C59-H59A	107.8
C66-C59-H59B	107.8
C56-C59-H59B	107.8
H59A-C59-H59B	107.2
C66-C61-C62	122.6(3)
C66-C61-O6	120.6(3)
C62-C61-O6	116.6(3)
C63-C62-C61	117.4(4)
C63-C62-C67	121.7(3)
C61-C62-C67	120.9(3)
C62-C63-C64	122.5(4)
C62-C63-H63	118.7
C64-C63-H63	118.7
C65-C64-C63	117.8(4)
C65-C64-C68	120.5(4)
C63-C64-C68	121.7(4)
C64-C65-C66	122.5(4)
C64-C65-H65	118.8
C66-C65-H65	118.8
C61-C66-C65	117.3(3)
C61-C66-C59	124.1(3)
C65-C66-C59	118.6(3)
C62-C67-H67A	109.5
C62-C67-H67B	109.5
H67A-C67-H67B	109.5
C62-C67-H67C	109.5
H67A-C67-H67C	109.5
H67B-C67-H67C	109.5
C64-C68-H68A	109.5
C64-C68-H68B	109.5
H68A-C68-H68B	109.5
C64-C68-H68C	109.5
H68A-C68-H68C	109.5
H68B-C68-H68C	109.5

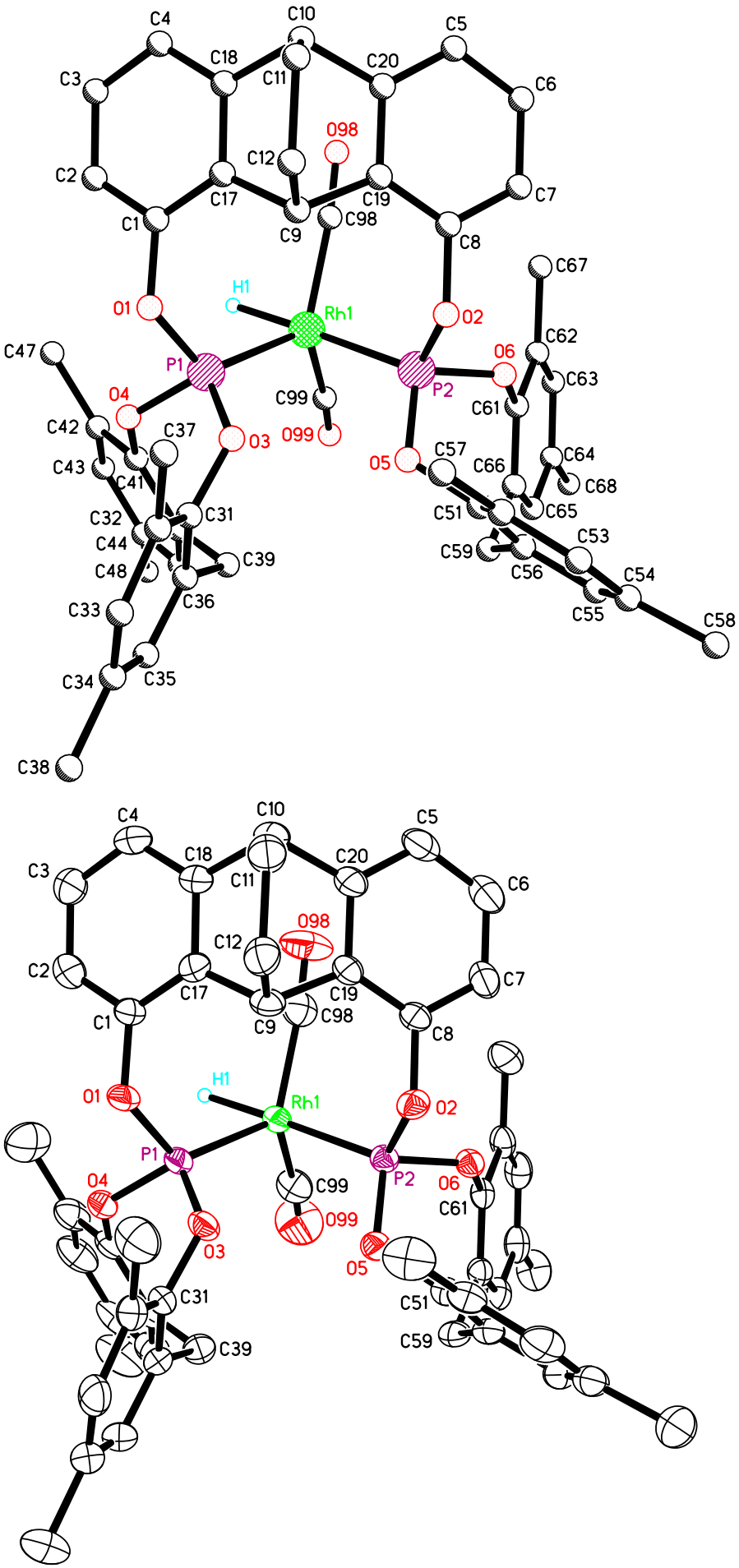


Figure S2: Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity.

S1.3 Catalyst resting state 4

Table S11: Crystal data and structure refinement for **4**.

Identification code	jam8sq	
Empirical formula	$C_{60}H_{53}O_8P_2Rh$	
Formula weight	1066.87	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	a = 10.857(2) Å	α =112.282(5) deg.
	b = 15.294(3) Å	β =101.524(5) deg.
	c = 18.873(4) Å	γ = 98.096(5) deg.
Volume	2759.1(10) $Å^3$	
Density (calculated)	1.28 g/cm^3	
Absorption coefficient	0.42 mm^{-1}	
Crystal shape	plate	
Crystal size	0.120 x 0.100 x 0.070 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.2 to 20.8 deg.	
Index ranges	$-10\leq h\leq 10$, $-15\leq k\leq 15$, $-18\leq l\leq 18$	
Reflections collected	16635	
Independent reflections	5766 (R(int) = 0.1436)	
Observed reflections	3165 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.97 and 0.81	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	5766 / 0 / 654	
Goodness-of-fit on F^2	0.99	
Final R indices (I>2sigma(I))	R1 = 0.070, wR2 = 0.135	
Largest diff. peak and hole	0.39 and -0.68 $eÅ^{-3}$	

Table S12: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **4**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Rh1	0.7676(1)	0.3777(1)	0.3122(1)	0.0344(3)
H1	0.605(10)	0.343(7)	0.275(6)	0.10(4)
P1	0.6937(3)	0.4588(2)	0.2427(2)	0.0323(8)
P2	0.7279(3)	0.2142(2)	0.2686(2)	0.0321(8)
O1	0.6345(6)	0.4084(5)	0.1464(4)	0.0315(19)
O2	0.7235(6)	0.1459(4)	0.1779(4)	0.0322(19)
O3	0.8019(6)	0.5475(5)	0.2502(4)	0.0334(19)
O4	0.5738(6)	0.5088(5)	0.2623(4)	0.0331(19)
O5	0.8225(6)	0.1659(5)	0.3140(4)	0.0328(19)
O6	0.5895(6)	0.1634(5)	0.2709(4)	0.0329(19)
C11	0.5367(11)	0.3216(8)	0.1107(6)	0.032(3)
C12	0.4075(11)	0.3308(8)	0.0968(7)	0.037(3)
C13	0.3126(10)	0.2442(9)	0.0664(7)	0.040(3)
H13	0.2244	0.2473	0.0576	0.048
C14	0.3403(12)	0.1552(9)	0.0487(7)	0.040(3)
C15	0.4687(11)	0.1492(8)	0.0601(6)	0.032(3)
H15	0.4889	0.0876	0.0472	0.038

C16	0.5674(11)	0.2325(8)	0.0902(6)	0.032(3)
C18	0.2300(11)	0.0645(8)	0.0177(7)	0.055(4)
H18A	0.2610	0.0064	-0.0080	0.083
H18B	0.1583	0.0682	-0.0210	0.083
H18C	0.1999	0.0606	0.0623	0.083
C21	0.7761(10)	0.1848(7)	0.1312(7)	0.033(3)
C22	0.9045(11)	0.1810(8)	0.1282(6)	0.037(3)
C23	0.9550(11)	0.2168(8)	0.0800(7)	0.044(3)
H23	1.0411	0.2152	0.0773	0.053
C24	0.8805(11)	0.2553(8)	0.0355(7)	0.042(3)
C25	0.7576(10)	0.2604(8)	0.0402(7)	0.041(3)
H25	0.7079	0.2867	0.0094	0.049
C26	0.7033(11)	0.2270(7)	0.0906(7)	0.035(3)
C28	0.9390(11)	0.2929(9)	-0.0188(7)	0.061(4)
H28A	0.8860	0.3328	-0.0346	0.092
H28B	0.9406	0.2374	-0.0665	0.092
H28C	1.0274	0.3322	0.0101	0.092
C31	0.7645(10)	0.6182(8)	0.2238(7)	0.038(3)
C32	0.7989(11)	0.6197(8)	0.1548(7)	0.039(3)
C33	0.7688(11)	0.6935(8)	0.1334(8)	0.048(4)
H33	0.7894	0.6972	0.0879	0.057
C34	0.7100(12)	0.7613(9)	0.1767(7)	0.050(4)
C35	0.6803(11)	0.7585(8)	0.2442(7)	0.048(4)
H35	0.6428	0.8068	0.2750	0.058
C36	0.7057(11)	0.6848(8)	0.2664(7)	0.035(3)
C37	0.8636(11)	0.5474(9)	0.1069(7)	0.060(4)
H37A	0.8954	0.5702	0.0703	0.091
H37B	0.8012	0.4843	0.0762	0.091
H37C	0.9365	0.5405	0.1428	0.091
C38	0.6740(12)	0.8416(9)	0.1494(8)	0.075(5)
H38A	0.6817	0.9013	0.1963	0.112
H38B	0.5848	0.8188	0.1152	0.112
H38C	0.7330	0.8549	0.1197	0.112
C41	0.5978(11)	0.5935(8)	0.3341(8)	0.042(3)
C42	0.5404(12)	0.5877(9)	0.3926(8)	0.051(4)
C43	0.5656(12)	0.6744(10)	0.4605(7)	0.054(4)
H43	0.5303	0.6738	0.5026	0.064
C44	0.6403(13)	0.7622(9)	0.4694(7)	0.051(4)
C45	0.6876(11)	0.7643(8)	0.4081(7)	0.041(3)
H45	0.7355	0.8245	0.4134	0.050
C46	0.6681(10)	0.6801(8)	0.3370(6)	0.034(3)
C47	0.4558(11)	0.4947(8)	0.3806(7)	0.060(4)
H47A	0.3933	0.5089	0.4119	0.090
H47B	0.5091	0.4560	0.3980	0.090
H47C	0.4094	0.4580	0.3240	0.090
C48	0.6603(12)	0.8509(9)	0.5459(7)	0.070(4)
H48A	0.6264	0.9012	0.5337	0.105
H48B	0.7530	0.8758	0.5734	0.105
H48C	0.6146	0.8333	0.5802	0.105
C51	0.8392(12)	0.1997(7)	0.3955(6)	0.030(3)
C52	0.9537(12)	0.2614(8)	0.4467(7)	0.034(3)
C53	0.9646(12)	0.3005(8)	0.5294(8)	0.051(4)
H53	1.0441	0.3418	0.5663	0.061
C54	0.8587(13)	0.2788(8)	0.5572(7)	0.051(4)
C55	0.7457(11)	0.2122(8)	0.5016(7)	0.047(4)
H55	0.6747	0.1950	0.5200	0.057
C56	0.7346(11)	0.1706(8)	0.4206(7)	0.041(3)
C57	1.0695(10)	0.2837(8)	0.4189(7)	0.046(3)
H57A	1.1464	0.3156	0.4648	0.069
H57B	1.0554	0.3270	0.3925	0.069
H57C	1.0825	0.2231	0.3813	0.069
C58	0.8675(12)	0.3268(9)	0.6459(7)	0.078(5)
H58A	0.7991	0.3622	0.6535	0.117
H58B	0.9522	0.3724	0.6749	0.117

H58C	0.8567	0.2768	0.6662	0.117
C61	0.5614(10)	0.0851(8)	0.2896(7)	0.031(3)
C62	0.4663(10)	0.0037(8)	0.2335(6)	0.031(3)
C63	0.4241(11)	-0.0687(8)	0.2574(7)	0.044(3)
H63	0.3578	-0.1240	0.2203	0.053
C64	0.4741(11)	-0.0634(8)	0.3318(7)	0.040(3)
C65	0.5749(11)	0.0158(8)	0.3852(7)	0.039(3)
H65	0.6116	0.0200	0.4368	0.047
C66	0.6238(11)	0.0910(8)	0.3634(7)	0.037(3)
C67	0.4110(11)	-0.0053(8)	0.1504(6)	0.052(4)
H67A	0.3324	-0.0581	0.1237	0.078
H67B	0.4749	-0.0195	0.1202	0.078
H67C	0.3898	0.0559	0.1532	0.078
C68	0.4172(10)	-0.1408(8)	0.3578(7)	0.058(4)
H68A	0.4439	-0.1149	0.4160	0.086
H68B	0.4492	-0.1993	0.3352	0.086
H68C	0.3226	-0.1572	0.3387	0.086
C71	0.3706(11)	0.4252(8)	0.1128(7)	0.040(3)
C72	0.2789(13)	0.4502(11)	0.1506(8)	0.067(4)
H72	0.2369	0.4061	0.1676	0.080
C73	0.2442(15)	0.5374(13)	0.1654(9)	0.081(5)
H73	0.1807	0.5534	0.1930	0.097
C74	0.3030(19)	0.6009(12)	0.1396(11)	0.098(7)
H74	0.2793	0.6611	0.1499	0.118
C75	0.3940(16)	0.5795(11)	0.0999(10)	0.076(5)
H75	0.4335	0.6231	0.0816	0.091
C76	0.4274(11)	0.4903(9)	0.0870(7)	0.054(4)
H76	0.4911	0.4740	0.0596	0.065
C81	0.9910(12)	0.1409(9)	0.1737(7)	0.046(3)
C82	0.9457(13)	0.0540(10)	0.1803(7)	0.058(4)
H82	0.8559	0.0236	0.1600	0.070
C83	1.0276(18)	0.0123(11)	0.2150(8)	0.074(5)
H83	0.9954	-0.0474	0.2171	0.088
C84	1.1563(19)	0.0577(14)	0.2467(9)	0.086(6)
H84	1.2123	0.0280	0.2707	0.103
C85	1.2091(14)	0.1452(14)	0.2455(8)	0.081(5)
H85	1.2983	0.1769	0.2689	0.098
C86	1.1199(13)	0.1843(10)	0.2066(8)	0.058(4)
H86	1.1520	0.2434	0.2035	0.070
O98	0.8068(12)	0.4700(7)	0.4932(6)	0.112(4)
C98	0.7974(15)	0.4382(10)	0.4265(8)	0.070(5)
O99	1.0387(8)	0.4182(6)	0.2868(6)	0.082(3)
C99	0.9417(12)	0.4001(8)	0.2969(7)	0.045(4)

Table S13: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **4**.

Atom	x	y	z	U_{eq}
H1	0.605(10)	0.343(7)	0.275(6)	0.10(4)
H13	0.2244	0.2473	0.0576	0.048
H15	0.4889	0.0876	0.0472	0.038
H18A	0.2610	0.0064	-0.0080	0.083
H18B	0.1583	0.0682	-0.0210	0.083
H18C	0.1999	0.0606	0.0623	0.083
H23	1.0411	0.2152	0.0773	0.053
H25	0.7079	0.2867	0.0094	0.049
H28A	0.8860	0.3328	-0.0346	0.092
H28B	0.9406	0.2374	-0.0665	0.092
H28C	1.0274	0.3322	0.0101	0.092
H33	0.7894	0.6972	0.0879	0.057

H35	0.6428	0.8068	0.2750	0.058
H37A	0.8954	0.5702	0.0703	0.091
H37B	0.8012	0.4843	0.0762	0.091
H37C	0.9365	0.5405	0.1428	0.091
H38A	0.6817	0.9013	0.1963	0.112
H38B	0.5848	0.8188	0.1152	0.112
H38C	0.7330	0.8549	0.1197	0.112
H43	0.5303	0.6738	0.5026	0.064
H45	0.7355	0.8245	0.4134	0.050
H47A	0.3933	0.5089	0.4119	0.090
H47B	0.5091	0.4560	0.3980	0.090
H47C	0.4094	0.4580	0.3240	0.090
H48A	0.6264	0.9012	0.5337	0.105
H48B	0.7530	0.8758	0.5734	0.105
H48C	0.6146	0.8333	0.5802	0.105
H53	1.0441	0.3418	0.5663	0.061
H55	0.6747	0.1950	0.5200	0.057
H57A	1.1464	0.3156	0.4648	0.069
H57B	1.0554	0.3270	0.3925	0.069
H57C	1.0825	0.2231	0.3813	0.069
H58A	0.7991	0.3622	0.6535	0.117
H58B	0.9522	0.3724	0.6749	0.117
H58C	0.8567	0.2768	0.6662	0.117
H63	0.3578	-0.1240	0.2203	0.053
H65	0.6116	0.0200	0.4368	0.047
H67A	0.3324	-0.0581	0.1237	0.078
H67B	0.4749	-0.0195	0.1202	0.078
H67C	0.3898	0.0559	0.1532	0.078
H68A	0.4439	-0.1149	0.4160	0.086
H68B	0.4492	-0.1993	0.3352	0.086
H68C	0.3226	-0.1572	0.3387	0.086
H72	0.2369	0.4061	0.1676	0.080
H73	0.1807	0.5534	0.1930	0.097
H74	0.2793	0.6611	0.1499	0.118
H75	0.4335	0.6231	0.0816	0.091
H76	0.4911	0.4740	0.0596	0.065
H82	0.8559	0.0236	0.1600	0.070
H83	0.9954	-0.0474	0.2171	0.088
H84	1.2123	0.0280	0.2707	0.103
H85	1.2983	0.1769	0.2689	0.098
H86	1.1520	0.2434	0.2035	0.070

Table S14: Anisotropic displacement parameters ($Å^2$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.0432(7)	0.0311(6)	0.0316(6)	0.0149(5)	0.0138(5)	0.0075(5)
P1	0.032(2)	0.0321(18)	0.034(2)	0.0139(17)	0.0113(16)	0.0060(16)
P2	0.032(2)	0.0366(18)	0.032(2)	0.0176(17)	0.0157(16)	0.0045(16)
O1	0.028(5)	0.036(4)	0.028(5)	0.014(4)	0.005(4)	0.004(4)
O2	0.045(5)	0.032(4)	0.027(5)	0.016(4)	0.021(4)	0.007(4)
O3	0.036(5)	0.029(4)	0.041(5)	0.017(4)	0.020(4)	0.006(4)
O4	0.030(5)	0.044(5)	0.029(5)	0.015(4)	0.012(4)	0.015(4)
O5	0.035(5)	0.039(4)	0.030(5)	0.019(4)	0.007(4)	0.014(4)
O6	0.035(5)	0.038(4)	0.037(5)	0.025(4)	0.020(4)	0.003(4)
C11	0.035(8)	0.035(8)	0.034(8)	0.018(6)	0.021(6)	0.008(7)
C12	0.037(8)	0.046(8)	0.042(8)	0.026(7)	0.024(7)	0.012(7)
C13	0.014(7)	0.066(9)	0.054(9)	0.035(8)	0.016(6)	0.012(7)
C14	0.045(9)	0.051(9)	0.028(8)	0.018(7)	0.013(7)	0.010(8)
C15	0.037(8)	0.026(7)	0.028(7)	0.010(6)	0.008(6)	0.005(7)

C16	0.042(9)	0.038(8)	0.024(7)	0.012(6)	0.018(6)	0.021(7)
C18	0.048(9)	0.056(8)	0.060(9)	0.026(8)	0.015(7)	0.004(7)
C21	0.027(8)	0.032(7)	0.035(8)	0.007(6)	0.007(6)	0.011(6)
C22	0.032(8)	0.054(8)	0.024(7)	0.011(7)	0.013(6)	0.022(7)
C23	0.024(7)	0.075(9)	0.049(9)	0.034(8)	0.023(7)	0.013(7)
C24	0.037(9)	0.056(8)	0.037(8)	0.020(7)	0.019(7)	0.006(7)
C25	0.016(7)	0.061(8)	0.054(9)	0.031(8)	0.013(6)	0.010(6)
C26	0.029(8)	0.029(7)	0.035(8)	0.004(6)	0.007(6)	0.002(6)
C28	0.057(9)	0.097(11)	0.077(10)	0.068(9)	0.039(8)	0.042(8)
C31	0.036(8)	0.039(8)	0.043(9)	0.024(7)	0.010(7)	0.006(7)
C32	0.045(8)	0.030(7)	0.046(9)	0.016(7)	0.017(7)	0.014(6)
C33	0.049(9)	0.041(8)	0.062(10)	0.033(8)	0.016(8)	0.003(7)
C34	0.065(10)	0.052(9)	0.048(9)	0.034(8)	0.023(8)	0.011(8)
C35	0.070(10)	0.039(8)	0.064(10)	0.038(8)	0.035(8)	0.027(7)
C36	0.043(8)	0.027(7)	0.033(8)	0.009(7)	0.013(7)	0.005(6)
C37	0.060(9)	0.066(9)	0.069(10)	0.034(8)	0.037(8)	0.014(8)
C38	0.094(12)	0.077(10)	0.104(12)	0.068(10)	0.058(10)	0.042(9)
C41	0.037(8)	0.042(8)	0.054(9)	0.027(8)	0.006(7)	0.016(7)
C42	0.068(10)	0.062(9)	0.048(9)	0.036(9)	0.030(8)	0.029(8)
C43	0.069(10)	0.065(9)	0.032(9)	0.023(8)	0.011(8)	0.029(9)
C44	0.070(10)	0.057(9)	0.025(8)	0.008(8)	0.015(8)	0.037(8)
C45	0.056(9)	0.036(7)	0.028(8)	0.006(7)	0.016(7)	0.015(7)
C46	0.037(8)	0.046(8)	0.022(7)	0.011(7)	0.017(6)	0.017(6)
C47	0.070(10)	0.076(10)	0.068(10)	0.053(9)	0.045(8)	0.020(8)
C48	0.079(11)	0.085(11)	0.039(9)	0.017(9)	0.016(8)	0.023(9)
C51	0.049(9)	0.026(6)	0.016(7)	0.016(6)	0.001(7)	-0.002(6)
C52	0.056(9)	0.025(7)	0.032(8)	0.020(6)	0.016(7)	0.012(7)
C53	0.042(9)	0.053(9)	0.054(10)	0.032(8)	-0.002(7)	-0.006(7)
C54	0.076(11)	0.032(7)	0.032(8)	0.004(7)	0.016(8)	-0.002(8)
C55	0.041(9)	0.051(8)	0.042(9)	0.024(8)	0.004(7)	-0.013(7)
C56	0.047(9)	0.037(7)	0.020(8)	0.011(7)	-0.010(7)	-0.019(7)
C57	0.040(8)	0.051(8)	0.050(8)	0.024(7)	0.018(7)	0.008(7)
C58	0.083(11)	0.076(10)	0.034(9)	0.002(8)	0.012(8)	-0.037(9)
C61	0.027(8)	0.037(7)	0.027(8)	0.016(7)	0.005(6)	0.002(6)
C62	0.025(7)	0.051(8)	0.038(8)	0.037(7)	0.015(6)	0.015(7)
C63	0.046(9)	0.033(7)	0.046(9)	0.015(7)	0.011(7)	-0.008(6)
C64	0.042(8)	0.035(7)	0.033(8)	0.003(7)	0.015(7)	0.002(7)
C65	0.046(8)	0.039(7)	0.040(8)	0.020(7)	0.020(7)	0.016(7)
C66	0.045(8)	0.035(7)	0.041(9)	0.020(7)	0.023(7)	0.013(7)
C67	0.050(9)	0.057(8)	0.048(9)	0.029(8)	0.008(7)	-0.003(7)
C68	0.040(8)	0.057(8)	0.090(11)	0.057(8)	0.009(8)	-0.008(7)
C71	0.031(8)	0.036(8)	0.036(8)	0.008(7)	-0.008(7)	0.004(7)
C72	0.065(11)	0.090(12)	0.058(10)	0.025(9)	0.036(9)	0.045(9)
C73	0.073(12)	0.095(13)	0.058(11)	0.003(11)	0.020(9)	0.053(11)
C74	0.111(18)	0.060(11)	0.088(16)	0.014(11)	-0.034(12)	0.047(13)
C75	0.080(13)	0.060(11)	0.072(13)	0.027(10)	-0.018(10)	0.026(10)
C76	0.039(9)	0.054(9)	0.066(10)	0.022(8)	0.007(7)	0.017(8)
C81	0.025(9)	0.068(10)	0.033(8)	0.010(8)	0.009(7)	0.011(8)
C82	0.069(10)	0.072(10)	0.049(9)	0.034(9)	0.022(8)	0.034(9)
C83	0.104(14)	0.100(12)	0.048(10)	0.053(10)	0.021(10)	0.058(12)
C84	0.100(16)	0.134(17)	0.051(11)	0.047(12)	0.032(11)	0.076(14)
C85	0.054(11)	0.147(17)	0.044(10)	0.029(11)	0.012(8)	0.063(12)
C86	0.046(10)	0.084(10)	0.061(10)	0.034(9)	0.032(8)	0.030(9)
O98	0.226(14)	0.073(7)	0.046(7)	0.028(7)	0.037(8)	0.056(8)
C98	0.127(14)	0.066(10)	0.015(8)	0.014(8)	0.017(9)	0.027(9)
O99	0.035(6)	0.070(7)	0.145(10)	0.047(7)	0.037(6)	0.000(5)
C99	0.031(9)	0.044(8)	0.061(9)	0.032(7)	0.000(7)	0.002(7)

Table S15: Bond lengths (Å) and angles (deg) for **4**.

Rh1-C98	1.934(13)	Rh1-C99	1.972(13)

Rh1-P1	2.235(3)	C43-H43	0.9500
Rh1-P2	2.261(3)	C44-C45	1.366(15)
Rh1-H1	1.68(11)	C44-C48	1.509(15)
P1-O3	1.606(7)	C45-C46	1.415(14)
P1-O1	1.626(7)	C45-H45	0.9500
P1-O4	1.635(7)	C47-H47A	0.9800
P2-O6	1.608(7)	C47-H47B	0.9800
P2-O2	1.619(7)	C47-H47C	0.9800
P2-O5	1.635(7)	C48-H48A	0.9800
O1-C11	1.408(11)	C48-H48B	0.9800
O2-C21	1.399(12)	C48-H48C	0.9800
O3-C31	1.426(12)	C51-C52	1.366(13)
O4-C41	1.419(13)	C51-C56	1.395(14)
O5-C51	1.387(11)	C52-C53	1.417(15)
O6-C61	1.384(11)	C52-C57	1.501(14)
C11-C16	1.378(14)	C53-C54	1.405(15)
C11-C12	1.411(14)	C53-H53	0.9500
C12-C13	1.396(13)	C54-C55	1.402(14)
C12-C71	1.489(15)	C54-C58	1.529(15)
C13-C14	1.366(15)	C55-C56	1.387(15)
C13-H13	0.9500	C55-H55	0.9500
C14-C15	1.388(14)	C56-C66	1.472(14)
C14-C18	1.529(13)	C57-H57A	0.9800
C15-C16	1.384(13)	C57-H57B	0.9800
C15-H15	0.9500	C57-H57C	0.9800
C16-C26	1.488(14)	C58-H58A	0.9800
C18-H18A	0.9800	C58-H58B	0.9800
C18-H18B	0.9800	C58-H58C	0.9800
C18-H18C	0.9800	C61-C66	1.384(14)
C21-C26	1.380(14)	C61-C62	1.392(13)
C21-C22	1.415(14)	C62-C63	1.399(13)
C22-C23	1.386(14)	C62-C67	1.509(13)
C22-C81	1.495(15)	C63-C64	1.367(14)
C23-C24	1.394(14)	C63-H63	0.9500
C23-H23	0.9500	C64-C65	1.393(13)
C24-C25	1.366(14)	C64-C68	1.542(13)
C24-C28	1.545(14)	C65-C66	1.431(13)
C25-C26	1.423(14)	C65-H65	0.9500
C25-H25	0.9500	C67-H67A	0.9800
C28-H28A	0.9800	C67-H67B	0.9800
C28-H28B	0.9800	C67-H67C	0.9800
C28-H28C	0.9800	C68-H68A	0.9800
C31-C36	1.364(15)	C68-H68B	0.9800
C31-C32	1.431(15)	C68-H68C	0.9800
C32-C33	1.392(14)	C71-C72	1.353(16)
C32-C37	1.500(15)	C71-C76	1.387(15)
C33-C34	1.380(16)	C72-C73	1.378(18)
C33-H33	0.9500	C72-H72	0.9500
C34-C35	1.389(15)	C73-C74	1.38(2)
C34-C38	1.569(15)	C73-H73	0.9500
C35-C36	1.387(14)	C74-C75	1.36(2)
C35-H35	0.9500	C74-H74	0.9500
C36-C46	1.493(14)	C75-C76	1.406(17)
C37-H37A	0.9800	C75-H75	0.9500
C37-H37B	0.9800	C76-H76	0.9500
C37-H37C	0.9800	C81-C86	1.365(14)
C38-H38A	0.9800	C81-C82	1.410(15)
C38-H38B	0.9800	C82-C83	1.368(16)
C38-H38C	0.9800	C82-H82	0.9500
C41-C42	1.396(16)	C83-C84	1.368(18)
C41-C46	1.408(14)	C83-H83	0.9500
C42-C43	1.395(15)	C84-C85	1.390(19)
C42-C47	1.491(14)	C84-H84	0.9500
C43-C44	1.398(15)	C85-C86	1.430(17)

C85-H85	0.9500
C86-H86	0.9500
O98-C98	1.141(13)
O99-C99	1.121(12)
C98-Rh1-C99	104.1(6)
C98-Rh1-P1	117.8(4)
C99-Rh1-P1	93.3(3)
C98-Rh1-P2	109.9(4)
C99-Rh1-P2	98.1(3)
P1-Rh1-P2	126.24(12)
C98-Rh1-H1	105(4)
C99-Rh1-H1	150(4)
P1-Rh1-H1	68(4)
P2-Rh1-H1	78(4)
O3-P1-O1	98.5(4)
O3-P1-O4	103.2(4)
O1-P1-O4	96.2(4)
O3-P1-Rh1	113.7(3)
O1-P1-Rh1	123.0(3)
O4-P1-Rh1	118.5(3)
O6-P2-O2	99.2(4)
O6-P2-O5	100.2(4)
O2-P2-O5	98.3(4)
O6-P2-Rh1	114.9(3)
O2-P2-Rh1	120.5(3)
O5-P2-Rh1	119.9(3)
C11-O1-P1	119.1(6)
C21-O2-P2	121.1(6)
C31-O3-P1	120.0(6)
C41-O4-P1	118.9(6)
C51-O5-P2	115.6(7)
C61-O6-P2	127.3(7)
C16-C11-O1	120.8(10)
C16-C11-C12	122.3(10)
O1-C11-C12	116.9(10)
C13-C12-C11	115.7(11)
C13-C12-C71	120.5(11)
C11-C12-C71	123.8(10)
C14-C13-C12	123.2(11)
C14-C13-H13	118.4
C12-C13-H13	118.4
C13-C14-C15	119.1(11)
C13-C14-C18	119.5(11)
C15-C14-C18	121.4(11)
C16-C15-C14	120.5(11)
C16-C15-H15	119.8
C14-C15-H15	119.7
C11-C16-C15	119.1(10)
C11-C16-C26	119.0(10)
C15-C16-C26	121.4(10)
C14-C18-H18A	109.5
C14-C18-H18B	109.5
H18A-C18-H18B	109.5
C14-C18-H18C	109.5
H18A-C18-H18C	109.5
H18B-C18-H18C	109.5
C26-C21-O2	119.8(10)
C26-C21-C22	121.7(11)
O2-C21-C22	118.5(10)
C23-C22-C21	118.4(11)
C23-C22-C81	117.0(11)
C21-C22-C81	124.6(11)
C22-C23-C24	120.6(11)
C22-C23-H23	119.7
C24-C23-H23	119.7
C25-C24-C23	120.5(10)
C25-C24-C28	120.3(11)
C23-C24-C28	119.2(11)
C24-C25-C26	120.8(11)
C24-C25-H25	119.6
C26-C25-H25	119.6
C21-C26-C25	117.9(11)
C21-C26-C16	124.7(10)
C25-C26-C16	117.3(10)
C24-C28-H28A	109.5
C24-C28-H28B	109.5
H28A-C28-H28B	109.5
C24-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
C36-C31-O3	120.2(10)
C36-C31-C32	122.4(11)
O3-C31-C32	117.3(11)
C33-C32-C31	116.1(11)
C33-C32-C37	120.5(11)
C31-C32-C37	123.4(11)
C34-C33-C32	121.7(12)
C34-C33-H33	119.1
C32-C33-H33	119.1
C33-C34-C35	120.5(12)
C33-C34-C38	120.3(11)
C35-C34-C38	119.3(13)
C36-C35-C34	119.6(12)
C36-C35-H35	120.2
C34-C35-H35	120.2
C31-C36-C35	119.7(11)
C31-C36-C46	121.3(11)
C35-C36-C46	119.1(12)
C32-C37-H37A	109.5
C32-C37-H37B	109.5
H37A-C37-H37B	109.5
C32-C37-H37C	109.5
H37A-C37-H37C	109.5
H37B-C37-H37C	109.5
C34-C38-H38A	109.5
C34-C38-H38B	109.5
H38A-C38-H38B	109.5
C34-C38-H38C	109.5
H38A-C38-H38C	109.5
H38B-C38-H38C	109.5
C42-C41-C46	124.7(12)
C42-C41-O4	118.7(11)
C46-C41-O4	116.3(11)
C43-C42-C41	115.4(12)
C43-C42-C47	123.6(12)
C41-C42-C47	121.1(12)
C42-C43-C44	123.0(12)
C42-C43-H43	118.5
C44-C43-H43	118.5
C45-C44-C43	118.9(12)
C45-C44-C48	123.3(13)
C43-C44-C48	117.8(12)
C44-C45-C46	122.4(11)
C44-C45-H45	118.8
C46-C45-H45	118.8
C41-C46-C45	115.5(10)
C41-C46-C36	122.0(10)
C45-C46-C36	122.1(10)

C42-C47-H47A	109.5
C42-C47-H47B	109.5
H47A-C47-H47B	109.5
C42-C47-H47C	109.5
H47A-C47-H47C	109.5
H47B-C47-H47C	109.5
C44-C48-H48A	109.5
C44-C48-H48B	109.5
H48A-C48-H48B	109.5
C44-C48-H48C	109.5
H48A-C48-H48C	109.5
H48B-C48-H48C	109.5
C52-C51-O5	119.3(10)
C52-C51-C56	123.4(10)
O5-C51-C56	117.3(10)
C51-C52-C53	118.1(10)
C51-C52-C57	122.5(11)
C53-C52-C57	119.3(11)
C54-C53-C52	120.5(11)
C54-C53-H53	119.8
C52-C53-H53	119.8
C55-C54-C53	118.3(11)
C55-C54-C58	121.2(12)
C53-C54-C58	120.4(11)
C56-C55-C54	121.9(11)
C56-C55-H55	119.0
C54-C55-H55	119.0
C55-C56-C51	117.5(10)
C55-C56-C66	122.0(11)
C51-C56-C66	120.1(11)
C52-C57-H57A	109.5
C52-C57-H57B	109.5
H57A-C57-H57B	109.5
C52-C57-H57C	109.5
H57A-C57-H57C	109.5
H57B-C57-H57C	109.5
C54-C58-H58A	109.5
C54-C58-H58B	109.5
H58A-C58-H58B	109.5
C54-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C66-C61-O6	119.8(9)
C66-C61-C62	122.4(10)
O6-C61-C62	117.7(9)
C61-C62-C63	117.4(10)
C61-C62-C67	121.0(9)
C63-C62-C67	121.6(10)
C64-C63-C62	122.9(11)
C64-C63-H63	118.5
C62-C63-H63	118.5
C63-C64-C65	118.5(11)
C63-C64-C68	121.2(10)
C65-C64-C68	120.3(11)
C64-C65-C66	120.9(11)
C64-C65-H65	119.5
C66-C65-H65	119.5
C61-C66-C65	117.4(10)
C61-C66-C56	123.9(10)
C65-C66-C56	118.7(11)
C62-C67-H67A	109.5
C62-C67-H67B	109.5
H67A-C67-H67B	109.5
C62-C67-H67C	109.5
H67A-C67-H67C	109.5
H67B-C67-H67C	109.5
C64-C68-H68A	109.5
C64-C68-H68B	109.5
H68A-C68-H68B	109.5
C64-C68-H68C	109.5
H68A-C68-H68C	109.5
H68B-C68-H68C	109.5
C72-C71-C76	117.2(12)
C72-C71-C12	122.2(12)
C76-C71-C12	120.6(12)
C71-C72-C73	122.5(14)
C71-C72-H72	118.8
C73-C72-H72	118.8
C74-C73-C72	119.1(16)
C74-C73-H73	120.5
C72-C73-H73	120.5
C75-C74-C73	121.5(17)
C75-C74-H74	119.2
C73-C74-H74	119.2
C74-C75-C76	117.4(16)
C74-C75-H75	121.3
C76-C75-H75	121.3
C71-C76-C75	122.4(14)
C71-C76-H76	118.8
C75-C76-H76	118.8
C86-C81-C82	117.1(13)
C86-C81-C22	120.8(12)
C82-C81-C22	121.9(12)
C83-C82-C81	121.8(14)
C83-C82-H82	119.1
C81-C82-H82	119.1
C82-C83-C84	119.2(15)
C82-C83-H83	120.4
C84-C83-H83	120.4
C83-C84-C85	123.0(17)
C83-C84-H84	118.5
C85-C84-H84	118.5
C84-C85-C86	115.4(15)
C84-C85-H85	122.3
C86-C85-H85	122.3
C81-C86-C85	123.4(14)
C81-C86-H86	118.3
C85-C86-H86	118.3
O98-C98-Rh1	175.2(14)
O99-C99-Rh1	175.0(11)

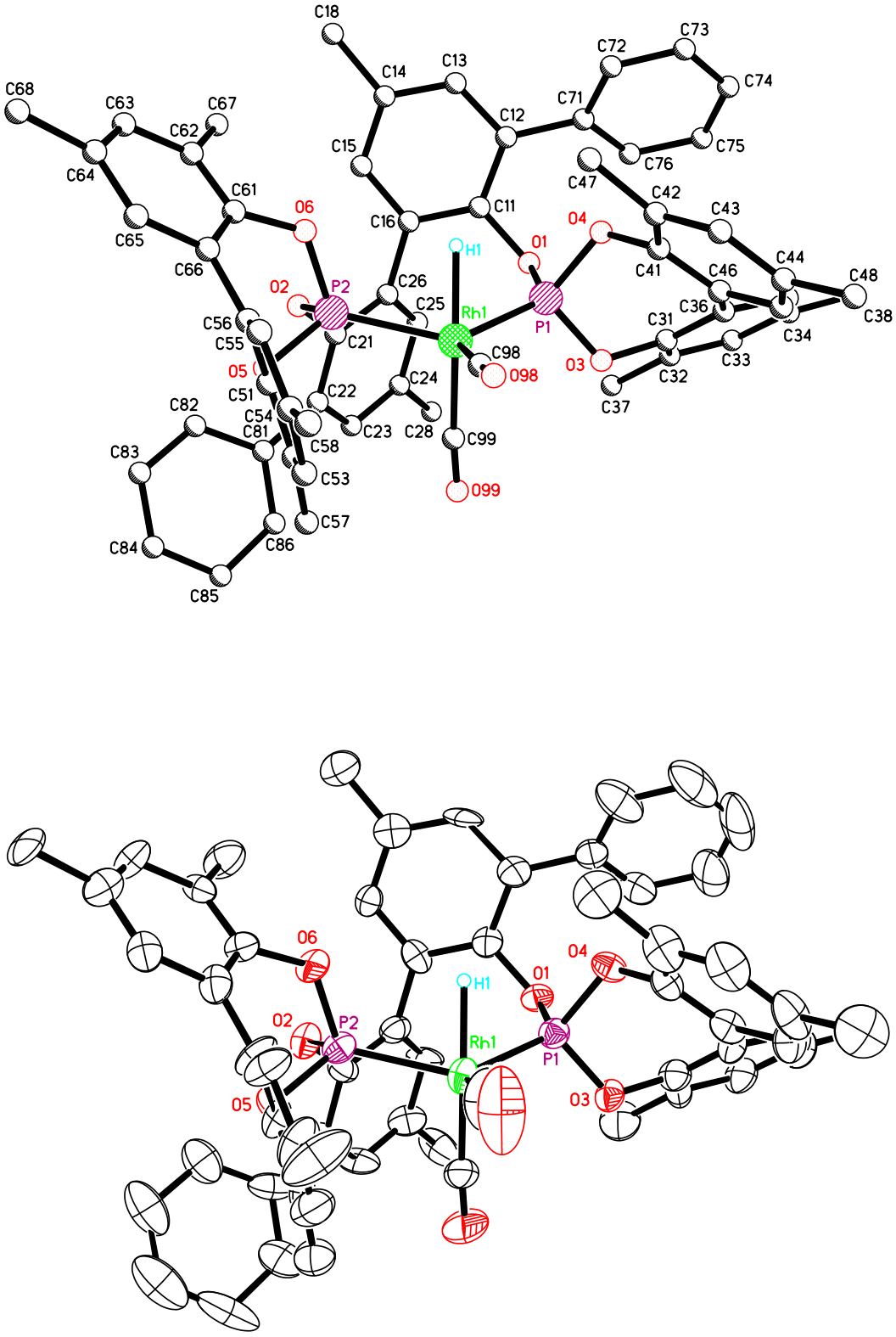


Figure S3: Molecular structure of complex **4**. Hydrogen atoms except H1 are omitted for clarity.

S1.4 Decomposition product 5

Table S16: Crystal data and structure refinement for **5**.

Identification code	jam7sq	
Empirical formula	$C_{67}H_{66}O_{11}P_3Rh$	
Formula weight	1243.01	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Z	8	
Unit cell dimensions	a = 34.2356(16) Å	α = 90 deg.
	b = 13.9198(7) Å	β =119.0980(13) deg.
	c = 31.1781(16) Å	γ = 90 deg.
Volume	12982.8(11) $Å^3$	
Density (calculated)	1.27 g/cm^3	
Absorption coefficient	0.39 mm^{-1}	
Crystal shape	plate	
Crystal size	0.080 x 0.080 x 0.050 mm^3	
Crystal colour	colourless	
Theta range for data collection	1.4 to 23.3 deg.	
Index ranges	$-38\leq h\leq 37$, $-15\leq k\leq 15$, $-34\leq l\leq 34$	
Reflections collected	48982	
Independent reflections	9323 (R(int) = 0.1134)	
Observed reflections	6154 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.98 and 0.87	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	9323 / 732 / 755	
Goodness-of-fit on F^2	1.03	
Final R indices (I>2sigma(I))	R1 = 0.051, wR2 = 0.102	
Largest diff. peak and hole	0.36 and -0.45 $eÅ^{-3}$	

Table S17: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **5**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Rh1	0.5978(1)	0.1463(1)	0.6785(1)	0.0208(1)
P1	0.6105(1)	0.2768(1)	0.7301(1)	0.0210(3)
P2	0.5309(1)	0.2054(1)	0.6190(1)	0.0188(3)
P3	0.6599(1)	0.0530(1)	0.7279(1)	0.0258(4)
O1	0.5780(1)	0.3640(2)	0.6997(1)	0.0228(8)
O2	0.5229(1)	0.3119(2)	0.5971(1)	0.0191(8)
O3	0.6605(1)	0.3167(2)	0.7560(1)	0.0250(8)
O4	0.5983(1)	0.2788(2)	0.7746(1)	0.0217(8)
O5	0.5099(1)	0.1442(2)	0.5691(1)	0.0205(8)
O6	0.4939(1)	0.1992(2)	0.6360(1)	0.0182(8)
O7	0.7075(1)	0.0970(2)	0.7390(1)	0.0275(9)
O8	0.6652(1)	0.0504(2)	0.7824(1)	0.0258(9)
O9	0.6571(1)	-0.0435(2)	0.7073(1)	0.0349(9)
C11	0.5849(2)	0.4602(4)	0.6913(2)	0.0219(12)
C12	0.5773(2)	0.5305(4)	0.7180(2)	0.0332(14)
C13	0.5798(2)	0.6245(4)	0.7057(2)	0.0389(15)

H13	0.5743	0.6739	0.7231	0.047
C14	0.5899(2)	0.6512(4)	0.6693(2)	0.0302(13)
C15	0.5981(2)	0.5771(4)	0.6450(2)	0.0273(13)
H15	0.6058	0.5927	0.6204	0.033
C16	0.5954(2)	0.4808(3)	0.6551(2)	0.0214(12)
C17	0.5667(2)	0.5054(4)	0.7583(2)	0.0461(16)
H17A	0.5576	0.5635	0.7688	0.069
H17B	0.5934	0.4781	0.7862	0.069
H17C	0.5424	0.4582	0.7460	0.069
C18	0.5921(2)	0.7547(4)	0.6576(2)	0.0522(18)
H18A	0.5917	0.7596	0.6261	0.078
H18B	0.6196	0.7833	0.6835	0.078
H18C	0.5662	0.7889	0.6556	0.078
C19	0.6064(2)	0.4044(4)	0.6277(2)	0.0240(12)
H19A	0.6354	0.4204	0.6298	0.029
H19B	0.6099	0.3419	0.6444	0.029
C21	0.5314(2)	0.3486(3)	0.5599(2)	0.0219(11)
C22	0.4975(2)	0.3452(3)	0.5113(2)	0.0224(12)
C23	0.5071(2)	0.3851(3)	0.4764(2)	0.0292(13)
H23	0.4849	0.3823	0.4428	0.035
C24	0.5470(2)	0.4282(4)	0.4884(2)	0.0302(13)
C25	0.5790(2)	0.4337(3)	0.5379(2)	0.0253(12)
H25	0.6065	0.4655	0.5470	0.030
C26	0.5718(2)	0.3937(3)	0.5745(2)	0.0228(12)
C27	0.4524(2)	0.3044(4)	0.4958(2)	0.0317(14)
H27A	0.4309	0.3311	0.4638	0.048
H27B	0.4432	0.3207	0.5201	0.048
H27C	0.4534	0.2343	0.4931	0.048
C28	0.5560(2)	0.4699(4)	0.4491(2)	0.0479(17)
H28A	0.5848	0.5035	0.4647	0.072
H28B	0.5322	0.5152	0.4289	0.072
H28C	0.5569	0.4179	0.4284	0.072
C31	0.6814(2)	0.3745(4)	0.7984(2)	0.0261(12)
C32	0.7017(2)	0.4588(4)	0.7952(2)	0.0339(14)
C33	0.7252(2)	0.5121(4)	0.8380(2)	0.0557(19)
H33	0.7379	0.5715	0.8360	0.067
C34	0.7310(2)	0.4838(4)	0.8826(2)	0.060(2)
C35	0.7104(2)	0.3982(4)	0.8842(2)	0.0432(16)
H35	0.7130	0.3782	0.9146	0.052
C36	0.6863(2)	0.3413(4)	0.8429(2)	0.0264(12)
C37	0.6999(2)	0.4916(4)	0.7486(2)	0.0459(17)
H37A	0.7301	0.5079	0.7549	0.069
H37B	0.6806	0.5484	0.7362	0.069
H37C	0.6877	0.4401	0.7241	0.069
C38	0.7571(3)	0.5444(5)	0.9286(2)	0.109(3)
H38A	0.7488	0.5256	0.9534	0.163
H38B	0.7501	0.6124	0.9204	0.163
H38C	0.7892	0.5341	0.9415	0.163
C41	0.6239(2)	0.2209(3)	0.8159(2)	0.0190(11)
C42	0.6038(2)	0.1411(4)	0.8238(2)	0.0217(11)
C43	0.6300(2)	0.0865(4)	0.8648(2)	0.0264(13)
H43	0.6170	0.0317	0.8711	0.032
C44	0.6741(2)	0.1071(4)	0.8972(2)	0.0283(13)
C45	0.6919(2)	0.1888(4)	0.8885(2)	0.0280(13)
H45	0.7221	0.2049	0.9108	0.034
C46	0.6676(2)	0.2489(4)	0.8482(2)	0.0212(12)
C47	0.5553(2)	0.1181(4)	0.7898(2)	0.0356(15)
H47A	0.5507	0.0486	0.7894	0.053
H47B	0.5470	0.1400	0.7565	0.053
H47C	0.5367	0.1509	0.8012	0.053
C48	0.7019(2)	0.0436(4)	0.9406(2)	0.0414(16)
H48A	0.7236	0.0829	0.9679	0.062
H48B	0.7179	-0.0036	0.9315	0.062
H48C	0.6825	0.0101	0.9506	0.062

C51	0.4867(2)	0.0573(3)	0.5639(2)	0.0208(12)
C52	0.5058(2)	-0.0273(4)	0.5592(2)	0.0274(13)
C53	0.4794(2)	-0.1091(4)	0.5472(2)	0.0372(14)
H53	0.4911	-0.1678	0.5427	0.045
C54	0.4368(2)	-0.1082(4)	0.5413(2)	0.0397(15)
C55	0.4197(2)	-0.0224(4)	0.5475(2)	0.0370(15)
H55	0.3904	-0.0213	0.5435	0.044
C56	0.4446(2)	0.0627(3)	0.5595(2)	0.0225(12)
C57	0.5519(2)	-0.0311(4)	0.5650(2)	0.0347(14)
H57A	0.5553	-0.0906	0.5504	0.052
H57B	0.5740	-0.0294	0.5999	0.052
H57C	0.5563	0.0242	0.5483	0.052
C58	0.4076(2)	-0.1982(4)	0.5253(3)	0.071(2)
H58A	0.3812	-0.1877	0.5292	0.106
H58B	0.4248	-0.2527	0.5456	0.106
H58C	0.3982	-0.2118	0.4908	0.106
C61	0.4486(2)	0.2187(4)	0.6019(2)	0.0204(11)
C62	0.4305(2)	0.3017(4)	0.6102(2)	0.0245(12)
C63	0.3856(2)	0.3190(4)	0.5771(2)	0.0290(13)
H63	0.3720	0.3750	0.5815	0.035
C64	0.3599(2)	0.2585(4)	0.5383(2)	0.0312(13)
C65	0.3798(2)	0.1758(4)	0.5330(2)	0.0290(13)
H65	0.3625	0.1331	0.5067	0.035
C66	0.4244(2)	0.1538(4)	0.5648(2)	0.0220(12)
C67	0.4577(2)	0.3678(4)	0.6530(2)	0.0326(14)
H67A	0.4414	0.4281	0.6486	0.049
H67B	0.4864	0.3812	0.6546	0.049
H67C	0.4628	0.3369	0.6835	0.049
C68	0.3116(2)	0.2808(4)	0.5025(2)	0.0452(17)
H68A	0.3012	0.2384	0.4739	0.068
H68B	0.3090	0.3479	0.4919	0.068
H68C	0.2933	0.2705	0.5185	0.068
C71	0.7363(2)	0.1552(4)	0.7783(2)	0.0260(12)
C72	0.7505(2)	0.2403(4)	0.7657(2)	0.0324(13)
C73	0.7816(2)	0.2960(4)	0.8037(2)	0.0371(14)
H73	0.7916	0.3538	0.7960	0.045
C74	0.7988(2)	0.2710(4)	0.8528(2)	0.0374(14)
C75	0.7852(2)	0.1860(4)	0.8633(2)	0.0329(14)
H75	0.7975	0.1674	0.8967	0.039
C76	0.7539(2)	0.1251(4)	0.8267(2)	0.0261(12)
C77	0.7330(2)	0.2664(4)	0.7127(2)	0.0436(16)
H77A	0.7472	0.3260	0.7105	0.065
H77B	0.7006	0.2756	0.6968	0.065
H77C	0.7398	0.2146	0.6961	0.065
C78	0.8307(2)	0.3374(5)	0.8923(2)	0.0590(19)
H78A	0.8521	0.2996	0.9205	0.088
H78B	0.8139	0.3800	0.9025	0.088
H78C	0.8468	0.3759	0.8796	0.088
C81	0.7003(2)	-0.0058(4)	0.8178(2)	0.0257(12)
C82	0.6894(2)	-0.0949(4)	0.8292(2)	0.0311(13)
C83	0.7236(2)	-0.1461(4)	0.8668(2)	0.0404(15)
H83	0.7170	-0.2068	0.8757	0.048
C84	0.7675(2)	-0.1122(4)	0.8922(2)	0.0394(15)
C85	0.7764(2)	-0.0242(4)	0.8777(2)	0.0356(14)
H85	0.8062	-0.0008	0.8939	0.043
C86	0.7434(2)	0.0314(4)	0.8405(2)	0.0257(12)
C87	0.6428(2)	-0.1341(4)	0.8027(2)	0.0467(17)
H87A	0.6417	-0.1963	0.8168	0.070
H87B	0.6337	-0.1424	0.7678	0.070
H87C	0.6223	-0.0892	0.8059	0.070
C88	0.8037(2)	-0.1713(4)	0.9325(2)	0.064(2)
H88A	0.8266	-0.1285	0.9565	0.095
H88B	0.8173	-0.2138	0.9183	0.095
H88C	0.7908	-0.2099	0.9487	0.095

C98	0.5658(2)	0.0383(4)	0.6865(2)	0.0299(14)
O98	0.5476(1)	-0.0251(3)	0.6911(2)	0.0515(12)
C99	0.6233(2)	0.1517(4)	0.6356(2)	0.0307(13)
O99	0.6383(1)	0.1526(3)	0.6105(2)	0.0535(12)

Table S18: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **5**.

Atom	x	y	z	U_{eq}
H13	0.5743	0.6739	0.7231	0.047
H15	0.6058	0.5927	0.6204	0.033
H17A	0.5576	0.5635	0.7688	0.069
H17B	0.5934	0.4781	0.7862	0.069
H17C	0.5424	0.4582	0.7460	0.069
H18A	0.5917	0.7596	0.6261	0.078
H18B	0.6196	0.7833	0.6835	0.078
H18C	0.5662	0.7889	0.6556	0.078
H19A	0.6354	0.4204	0.6298	0.029
H19B	0.6099	0.3419	0.6444	0.029
H23	0.4849	0.3823	0.4428	0.035
H25	0.6065	0.4655	0.5470	0.030
H27A	0.4309	0.3311	0.4638	0.048
H27B	0.4432	0.3207	0.5201	0.048
H27C	0.4534	0.2343	0.4931	0.048
H28A	0.5848	0.5035	0.4647	0.072
H28B	0.5322	0.5152	0.4289	0.072
H28C	0.5569	0.4179	0.4284	0.072
H33	0.7379	0.5715	0.8360	0.067
H35	0.7130	0.3782	0.9146	0.052
H37A	0.7301	0.5079	0.7549	0.069
H37B	0.6806	0.5484	0.7362	0.069
H37C	0.6877	0.4401	0.7241	0.069
H38A	0.7488	0.5256	0.9534	0.163
H38B	0.7501	0.6124	0.9204	0.163
H38C	0.7892	0.5341	0.9415	0.163
H43	0.6170	0.0317	0.8711	0.032
H45	0.7221	0.2049	0.9108	0.034
H47A	0.5507	0.0486	0.7894	0.053
H47B	0.5470	0.1400	0.7565	0.053
H47C	0.5367	0.1509	0.8012	0.053
H48A	0.7236	0.0829	0.9679	0.062
H48B	0.7179	-0.0036	0.9315	0.062
H48C	0.6825	0.0101	0.9506	0.062
H53	0.4911	-0.1678	0.5427	0.045
H55	0.3904	-0.0213	0.5435	0.044
H57A	0.5553	-0.0906	0.5504	0.052
H57B	0.5740	-0.0294	0.5999	0.052
H57C	0.5563	0.0242	0.5483	0.052
H58A	0.3812	-0.1877	0.5292	0.106
H58B	0.4248	-0.2527	0.5456	0.106
H58C	0.3982	-0.2118	0.4908	0.106
H63	0.3720	0.3750	0.5815	0.035
H65	0.3625	0.1331	0.5067	0.035
H67A	0.4414	0.4281	0.6486	0.049
H67B	0.4864	0.3812	0.6546	0.049
H67C	0.4628	0.3369	0.6835	0.049
H68A	0.3012	0.2384	0.4739	0.068
H68B	0.3090	0.3479	0.4919	0.068
H68C	0.2933	0.2705	0.5185	0.068
H73	0.7916	0.3538	0.7960	0.045

H75	0.7975	0.1674	0.8967	0.039
H77A	0.7472	0.3260	0.7105	0.065
H77B	0.7006	0.2756	0.6968	0.065
H77C	0.7398	0.2146	0.6961	0.065
H78A	0.8521	0.2996	0.9205	0.088
H78B	0.8139	0.3800	0.9025	0.088
H78C	0.8468	0.3759	0.8796	0.088
H83	0.7170	-0.2068	0.8757	0.048
H85	0.8062	-0.0008	0.8939	0.043
H87A	0.6417	-0.1963	0.8168	0.070
H87B	0.6337	-0.1424	0.7678	0.070
H87C	0.6223	-0.0892	0.8059	0.070
H88A	0.8266	-0.1285	0.9565	0.095
H88B	0.8173	-0.2138	0.9183	0.095
H88C	0.7908	-0.2099	0.9487	0.095

Table S19: Anisotropic displacement parameters ($Å^2$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh1	0.0188(2)	0.0200(2)	0.0193(2)	0.0010(2)	0.0059(2)	0.0024(2)
P1	0.0183(7)	0.0228(8)	0.0184(8)	0.0014(7)	0.0061(6)	0.0002(6)
P2	0.0188(7)	0.0177(8)	0.0169(8)	0.0003(6)	0.0063(6)	-0.0002(6)
P3	0.0224(8)	0.0251(8)	0.0268(9)	0.0011(7)	0.0097(7)	0.0049(6)
O1	0.0231(18)	0.0198(18)	0.0195(19)	0.0018(16)	0.0057(15)	0.0019(15)
O2	0.0227(18)	0.0188(18)	0.0144(18)	0.0021(15)	0.0079(15)	-0.0008(14)
O3	0.0200(18)	0.033(2)	0.0191(19)	-0.0016(16)	0.0071(15)	-0.0088(15)
O4	0.0199(18)	0.027(2)	0.0169(18)	0.0024(16)	0.0075(15)	0.0017(15)
O5	0.0229(18)	0.0223(18)	0.0153(18)	-0.0012(16)	0.0086(15)	-0.0018(15)
O6	0.0153(16)	0.0219(19)	0.0137(18)	0.0003(15)	0.0043(14)	0.0004(14)
O7	0.0176(18)	0.040(2)	0.024(2)	0.0013(17)	0.0095(16)	0.0047(16)
O8	0.0217(18)	0.027(2)	0.024(2)	0.0052(16)	0.0074(16)	0.0062(15)
O9	0.036(2)	0.024(2)	0.039(2)	-0.0052(18)	0.0139(19)	0.0074(17)
C11	0.020(3)	0.018(3)	0.020(3)	0.002(2)	0.004(2)	0.004(2)
C12	0.045(3)	0.022(3)	0.031(3)	-0.004(2)	0.018(3)	-0.002(3)
C13	0.058(4)	0.023(3)	0.037(3)	-0.002(3)	0.025(3)	0.004(3)
C14	0.036(3)	0.021(3)	0.024(3)	-0.002(2)	0.006(3)	-0.004(2)
C15	0.031(3)	0.025(3)	0.017(3)	0.003(2)	0.005(3)	-0.002(2)
C16	0.022(3)	0.018(3)	0.017(3)	0.001(2)	0.003(2)	0.002(2)
C17	0.069(4)	0.036(4)	0.049(4)	0.001(3)	0.041(4)	0.008(3)
C18	0.081(5)	0.025(3)	0.050(4)	0.003(3)	0.032(4)	-0.007(3)
C19	0.022(3)	0.025(3)	0.026(3)	0.003(2)	0.013(2)	-0.002(2)
C21	0.029(3)	0.017(3)	0.019(3)	0.003(2)	0.011(2)	0.007(2)
C22	0.031(3)	0.012(3)	0.021(3)	-0.001(2)	0.010(2)	0.003(2)
C23	0.039(3)	0.022(3)	0.021(3)	0.002(2)	0.011(3)	0.007(2)
C24	0.043(3)	0.023(3)	0.026(3)	0.005(2)	0.018(2)	0.009(2)
C25	0.029(3)	0.018(3)	0.031(3)	0.004(2)	0.017(2)	0.006(2)
C26	0.028(3)	0.018(3)	0.022(3)	0.001(2)	0.012(2)	0.005(2)
C27	0.033(3)	0.022(3)	0.028(3)	-0.001(3)	0.005(3)	0.000(2)
C28	0.072(4)	0.042(4)	0.040(4)	0.012(3)	0.034(3)	0.009(3)
C31	0.019(3)	0.030(3)	0.020(3)	-0.002(2)	0.003(2)	-0.004(2)
C32	0.025(3)	0.035(3)	0.026(3)	0.006(2)	0.000(2)	-0.012(2)
C33	0.070(4)	0.035(4)	0.037(3)	0.006(3)	0.006(3)	-0.032(3)
C34	0.080(5)	0.039(4)	0.032(3)	0.000(3)	0.004(3)	-0.029(3)
C35	0.057(4)	0.039(3)	0.021(3)	-0.001(3)	0.009(3)	-0.014(3)
C36	0.025(3)	0.028(3)	0.018(3)	0.001(2)	0.005(2)	-0.003(2)
C37	0.036(3)	0.053(4)	0.036(3)	0.013(3)	0.007(3)	-0.019(3)
C38	0.167(8)	0.075(6)	0.043(4)	-0.017(4)	0.018(5)	-0.074(6)
C41	0.019(2)	0.024(3)	0.014(3)	0.001(2)	0.007(2)	0.004(2)
C42	0.023(2)	0.023(3)	0.022(3)	-0.002(2)	0.013(2)	0.002(2)
C43	0.029(3)	0.023(3)	0.030(3)	0.003(2)	0.016(2)	0.001(2)

C44	0.029(3)	0.032(3)	0.024(3)	0.004(2)	0.013(2)	0.003(2)
C45	0.023(3)	0.035(3)	0.020(3)	0.003(2)	0.006(2)	0.004(2)
C46	0.023(2)	0.028(3)	0.013(3)	-0.001(2)	0.009(2)	0.000(2)
C47	0.025(3)	0.045(4)	0.032(3)	0.000(3)	0.010(3)	-0.008(2)
C48	0.037(3)	0.046(4)	0.033(3)	0.013(3)	0.011(3)	0.009(3)
C51	0.023(2)	0.017(3)	0.017(3)	-0.002(2)	0.006(2)	-0.003(2)
C52	0.030(3)	0.023(3)	0.021(3)	-0.003(2)	0.007(2)	0.003(2)
C53	0.048(3)	0.023(3)	0.034(4)	-0.003(3)	0.014(3)	0.000(2)
C54	0.049(3)	0.024(3)	0.041(4)	-0.008(3)	0.019(3)	-0.009(2)
C55	0.032(3)	0.034(3)	0.039(4)	-0.007(3)	0.012(3)	-0.005(2)
C56	0.022(3)	0.021(3)	0.015(3)	0.002(2)	0.002(2)	0.001(2)
C57	0.039(3)	0.029(3)	0.035(4)	-0.003(3)	0.016(3)	0.009(3)
C58	0.061(4)	0.038(4)	0.103(6)	-0.017(4)	0.032(4)	-0.019(3)
C61	0.015(2)	0.025(3)	0.018(3)	0.009(2)	0.006(2)	0.003(2)
C62	0.026(3)	0.026(3)	0.026(3)	0.005(2)	0.016(2)	0.002(2)
C63	0.027(3)	0.035(3)	0.031(3)	0.012(2)	0.019(2)	0.011(2)
C64	0.022(3)	0.044(3)	0.025(3)	0.010(3)	0.009(2)	0.007(2)
C65	0.019(3)	0.039(3)	0.020(3)	0.002(2)	0.002(2)	-0.001(2)
C66	0.017(2)	0.024(3)	0.024(3)	0.004(2)	0.008(2)	0.000(2)
C67	0.036(3)	0.032(3)	0.030(3)	-0.003(3)	0.016(3)	0.004(3)
C68	0.026(3)	0.061(4)	0.040(4)	0.012(3)	0.009(3)	0.012(3)
C71	0.017(3)	0.036(3)	0.027(3)	0.000(2)	0.012(2)	0.007(2)
C72	0.028(3)	0.038(3)	0.034(3)	0.004(2)	0.017(3)	0.002(2)
C73	0.034(3)	0.039(4)	0.042(3)	0.000(3)	0.021(3)	-0.009(3)
C74	0.028(3)	0.046(4)	0.036(3)	-0.003(3)	0.014(3)	-0.007(3)
C75	0.021(3)	0.045(3)	0.029(3)	0.004(3)	0.010(2)	0.005(2)
C76	0.019(3)	0.035(3)	0.025(3)	0.002(2)	0.011(2)	0.004(2)
C77	0.048(4)	0.047(4)	0.038(3)	0.009(3)	0.023(3)	-0.001(3)
C78	0.049(4)	0.072(5)	0.048(4)	-0.011(4)	0.017(3)	-0.024(3)
C81	0.022(3)	0.027(3)	0.023(3)	0.007(2)	0.007(2)	0.009(2)
C82	0.032(3)	0.029(3)	0.033(3)	0.008(3)	0.017(3)	0.006(2)
C83	0.041(3)	0.036(3)	0.042(3)	0.014(3)	0.018(3)	0.009(3)
C84	0.038(3)	0.042(3)	0.033(3)	0.009(3)	0.014(3)	0.013(3)
C85	0.025(3)	0.048(3)	0.028(3)	0.004(3)	0.008(2)	0.007(2)
C86	0.023(3)	0.036(3)	0.019(3)	-0.002(2)	0.011(2)	0.002(2)
C87	0.041(3)	0.043(4)	0.046(4)	0.012(3)	0.013(3)	-0.004(3)
C88	0.053(4)	0.062(5)	0.059(4)	0.030(4)	0.014(3)	0.021(3)
C98	0.025(3)	0.025(3)	0.032(3)	0.002(3)	0.008(3)	0.000(2)
O98	0.049(3)	0.036(3)	0.063(3)	0.009(2)	0.022(2)	-0.016(2)
C99	0.023(3)	0.038(3)	0.025(3)	0.003(3)	0.008(2)	0.005(3)
O99	0.056(3)	0.069(3)	0.051(3)	-0.002(2)	0.038(2)	-0.002(2)

Table S20: Bond lengths (Å) and angles (deg) for **5**.

Rh1-C99	1.921(6)	O5-C51	1.413(5)
Rh1-C98	1.946(6)	O6-C61	1.416(5)
Rh1-P2	2.2874(13)	O7-C71	1.397(6)
Rh1-P3	2.3225(14)	O8-C81	1.407(5)
Rh1-P1	2.3235(14)	C11-C16	1.373(7)
P1-O3	1.595(3)	C11-C12	1.389(7)
P1-O1	1.607(3)	C12-C13	1.377(7)
P1-O4	1.631(3)	C12-C17	1.506(7)
P2-O6	1.593(3)	C13-C14	1.389(7)
P2-O2	1.600(3)	C13-H13	0.9500
P2-O5	1.606(3)	C14-C15	1.387(7)
P3-O9	1.472(3)	C14-C18	1.497(7)
P3-O7	1.615(3)	C15-C16	1.389(6)
P3-O8	1.618(3)	C15-H15	0.9500
O1-C11	1.406(5)	C16-C19	1.521(7)
O2-C21	1.419(5)	C17-H17A	0.9800
O3-C31	1.408(6)	C17-H17B	0.9800
O4-C41	1.408(5)	C17-H17C	0.9800

C18-H18A	0.9800	C55-H55	0.9500
C18-H18B	0.9800	C56-C66	1.493(6)
C18-H18C	0.9800	C57-H57A	0.9800
C19-C26	1.507(6)	C57-H57B	0.9800
C19-H19A	0.9900	C57-H57C	0.9800
C19-H19B	0.9900	C58-H58A	0.9800
C21-C26	1.380(6)	C58-H58B	0.9800
C21-C22	1.391(6)	C58-H58C	0.9800
C22-C23	1.393(7)	C61-C66	1.382(6)
C22-C27	1.488(6)	C61-C62	1.394(6)
C23-C24	1.368(7)	C62-C63	1.394(6)
C23-H23	0.9500	C62-C67	1.511(7)
C24-C25	1.393(7)	C63-C64	1.382(7)
C24-C28	1.518(7)	C63-H63	0.9500
C25-C26	1.394(7)	C64-C65	1.390(7)
C25-H25	0.9500	C64-C68	1.509(6)
C27-H27A	0.9800	C65-C66	1.390(6)
C27-H27B	0.9800	C65-H65	0.9500
C27-H27C	0.9800	C67-H67A	0.9800
C28-H28A	0.9800	C67-H67B	0.9800
C28-H28B	0.9800	C67-H67C	0.9800
C28-H28C	0.9800	C68-H68A	0.9800
C31-C32	1.392(7)	C68-H68B	0.9800
C31-C36	1.393(7)	C68-H68C	0.9800
C32-C33	1.390(7)	C71-C76	1.391(7)
C32-C37	1.495(7)	C71-C72	1.406(7)
C33-C34	1.365(8)	C72-C73	1.384(7)
C33-H33	0.9500	C72-C77	1.504(7)
C34-C35	1.398(7)	C73-C74	1.389(7)
C34-C38	1.523(8)	C73-H73	0.9500
C35-C36	1.391(7)	C74-C75	1.368(7)
C35-H35	0.9500	C74-C78	1.501(7)
C36-C46	1.481(7)	C75-C76	1.408(7)
C37-H37A	0.9800	C75-H75	0.9500
C37-H37B	0.9800	C76-C86	1.470(7)
C37-H37C	0.9800	C77-H77A	0.9800
C38-H38A	0.9800	C77-H77B	0.9800
C38-H38B	0.9800	C77-H77C	0.9800
C38-H38C	0.9800	C78-H78A	0.9800
C41-C42	1.390(6)	C78-H78B	0.9800
C41-C46	1.392(6)	C78-H78C	0.9800
C42-C43	1.381(6)	C81-C86	1.390(6)
C42-C47	1.506(6)	C81-C82	1.392(7)
C43-C44	1.377(6)	C82-C83	1.386(7)
C43-H43	0.9500	C82-C87	1.498(7)
C44-C45	1.379(7)	C83-C84	1.396(7)
C44-C48	1.504(7)	C83-H83	0.9500
C45-C46	1.398(6)	C84-C85	1.390(7)
C45-H45	0.9500	C84-C88	1.509(7)
C47-H47A	0.9800	C85-C86	1.394(7)
C47-H47B	0.9800	C85-H85	0.9500
C47-H47C	0.9800	C87-H87A	0.9800
C48-H48A	0.9800	C87-H87B	0.9800
C48-H48B	0.9800	C87-H87C	0.9800
C48-H48C	0.9800	C88-H88A	0.9800
C51-C56	1.381(6)	C88-H88B	0.9800
C51-C52	1.388(6)	C88-H88C	0.9800
C52-C53	1.385(7)	C98-O98	1.128(6)
C52-C57	1.501(7)	C99-O99	1.128(6)
C53-C54	1.380(7)	C99-Rh1-C98	126.4(2)
C53-H53	0.9500	C99-Rh1-P2	92.06(15)
C54-C55	1.385(7)	C98-Rh1-P2	88.69(15)
C54-C58	1.526(7)	C99-Rh1-P3	84.53(15)
C55-C56	1.400(7)	C98-Rh1-P3	82.76(15)

P2-Rh1-P3	166.31(5)
C99-Rh1-P1	117.13(17)
C98-Rh1-P1	116.28(17)
P2-Rh1-P1	93.26(5)
P3-Rh1-P1	100.11(5)
O3-P1-O1	107.45(18)
O3-P1-O4	102.66(17)
O1-P1-O4	95.71(17)
O3-P1-Rh1	114.59(13)
O1-P1-Rh1	109.80(13)
O4-P1-Rh1	124.24(13)
O6-P2-O2	101.25(16)
O6-P2-O5	103.98(16)
O2-P2-O5	100.00(17)
O6-P2-Rh1	110.78(12)
O2-P2-Rh1	125.10(12)
O5-P2-Rh1	113.23(12)
O9-P3-O7	106.53(19)
O9-P3-O8	112.9(2)
O7-P3-O8	101.35(18)
O9-P3-Rh1	112.08(15)
O7-P3-Rh1	115.66(14)
O8-P3-Rh1	107.99(13)
C11-O1-P1	134.3(3)
C21-O2-P2	128.6(3)
C31-O3-P1	127.3(3)
C41-O4-P1	117.7(3)
C51-O5-P2	121.7(3)
C61-O6-P2	119.8(3)
C71-O7-P3	128.1(3)
C81-O8-P3	116.9(3)
C16-C11-C12	123.2(5)
C16-C11-O1	119.1(4)
C12-C11-O1	117.6(5)
C13-C12-C11	116.5(5)
C13-C12-C17	121.7(5)
C11-C12-C17	121.8(5)
C12-C13-C14	123.8(5)
C12-C13-H13	118.1
C14-C13-H13	118.1
C15-C14-C13	116.4(5)
C15-C14-C18	122.4(5)
C13-C14-C18	121.2(5)
C14-C15-C16	122.7(5)
C14-C15-H15	118.6
C16-C15-H15	118.6
C11-C16-C15	117.4(5)
C11-C16-C19	123.5(5)
C15-C16-C19	119.1(5)
C12-C17-H17A	109.5
C12-C17-H17B	109.5
H17A-C17-H17B	109.5
C12-C17-H17C	109.5
H17A-C17-H17C	109.5
H17B-C17-H17C	109.5
C14-C18-H18A	109.5
C14-C18-H18B	109.5
H18A-C18-H18B	109.5
C14-C18-H18C	109.5
H18A-C18-H18C	109.5
H18B-C18-H18C	109.5
C26-C19-C16	114.2(4)
C26-C19-H19A	108.7
C16-C19-H19A	108.7
C26-C19-H19B	108.7
C16-C19-H19B	108.7
H19A-C19-H19B	107.6
C26-C21-C22	123.0(5)
C26-C21-O2	117.7(4)
C22-C21-O2	119.1(4)
C21-C22-C23	116.7(5)
C21-C22-C27	123.4(5)
C23-C22-C27	119.9(5)
C24-C23-C22	123.0(5)
C24-C23-H23	118.5
C22-C23-H23	118.5
C23-C24-C25	118.0(5)
C23-C24-C28	121.1(5)
C25-C24-C28	121.0(5)
C24-C25-C26	121.8(5)
C24-C25-H25	119.1
C26-C25-H25	119.1
C21-C26-C25	117.4(5)
C21-C26-C19	122.2(5)
C25-C26-C19	120.3(4)
C22-C27-H27A	109.5
C22-C27-H27B	109.5
H27A-C27-H27B	109.5
C22-C27-H27C	109.5
H27A-C27-H27C	109.5
H27B-C27-H27C	109.5
C24-C28-H28A	109.5
C24-C28-H28B	109.5
H28A-C28-H28B	109.5
C24-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
C32-C31-C36	121.9(5)
C32-C31-O3	117.3(5)
C36-C31-O3	120.3(4)
C33-C32-C31	117.2(5)
C33-C32-C37	120.1(5)
C31-C32-C37	122.7(5)
C34-C33-C32	123.7(5)
C34-C33-H33	118.2
C32-C33-H33	118.2
C33-C34-C35	117.2(6)
C33-C34-C38	121.9(6)
C35-C34-C38	120.9(6)
C36-C35-C34	122.2(6)
C36-C35-H35	118.9
C34-C35-H35	118.9
C35-C36-C31	117.7(5)
C35-C36-C46	119.0(5)
C31-C36-C46	123.3(5)
C32-C37-H37A	109.5
C32-C37-H37B	109.5
H37A-C37-H37B	109.5
C32-C37-H37C	109.5
H37A-C37-H37C	109.5
H37B-C37-H37C	109.5
C34-C38-H38A	109.5
C34-C38-H38B	109.5
H38A-C38-H38B	109.5
C34-C38-H38C	109.5
H38A-C38-H38C	109.5
H38B-C38-H38C	109.5
C42-C41-C46	123.3(5)

C42-C41-O4	118.4(4)
C46-C41-O4	118.2(4)
C43-C42-C41	116.6(4)
C43-C42-C47	122.3(5)
C41-C42-C47	121.1(4)
C44-C43-C42	123.6(5)
C44-C43-H43	118.2
C42-C43-H43	118.2
C43-C44-C45	117.3(5)
C43-C44-C48	121.8(5)
C45-C44-C48	120.9(5)
C44-C45-C46	123.0(5)
C44-C45-H45	118.5
C46-C45-H45	118.5
C41-C46-C45	116.2(5)
C41-C46-C36	122.3(4)
C45-C46-C36	121.3(4)
C42-C47-H47A	109.5
C42-C47-H47B	109.5
H47A-C47-H47B	109.5
C42-C47-H47C	109.5
H47A-C47-H47C	109.5
H47B-C47-H47C	109.5
C44-C48-H48A	109.5
C44-C48-H48B	109.5
H48A-C48-H48B	109.5
C44-C48-H48C	109.5
H48A-C48-H48C	109.5
H48B-C48-H48C	109.5
C56-C51-C52	123.8(5)
C56-C51-O5	117.9(4)
C52-C51-O5	118.1(4)
C53-C52-C51	116.7(5)
C53-C52-C57	120.7(5)
C51-C52-C57	122.6(5)
C54-C53-C52	122.3(5)
C54-C53-H53	118.8
C52-C53-H53	118.8
C53-C54-C55	118.8(5)
C53-C54-C58	121.2(5)
C55-C54-C58	120.0(5)
C54-C55-C56	121.5(5)
C54-C55-H55	119.2
C56-C55-H55	119.2
C51-C56-C55	116.8(5)
C51-C56-C66	123.6(4)
C55-C56-C66	119.5(5)
C52-C57-H57A	109.5
C52-C57-H57B	109.5
H57A-C57-H57B	109.5
C52-C57-H57C	109.5
H57A-C57-H57C	109.5
H57B-C57-H57C	109.5
C54-C58-H58A	109.5
C54-C58-H58B	109.5
H58A-C58-H58B	109.5
C54-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5
C66-C61-C62	123.8(4)
C66-C61-O6	119.7(4)
C62-C61-O6	116.4(4)
C61-C62-C63	115.9(5)
C61-C62-C67	121.9(4)
C63-C62-C67	122.1(5)
C64-C63-C62	123.1(5)
C64-C63-H63	118.5
C62-C63-H63	118.5
C63-C64-C65	117.9(5)
C63-C64-C68	121.6(5)
C65-C64-C68	120.4(5)
C64-C65-C66	122.0(5)
C64-C65-H65	119.0
C66-C65-H65	119.0
C61-C66-C65	117.2(5)
C61-C66-C56	121.8(4)
C65-C66-C56	121.0(5)
C62-C67-H67A	109.5
C62-C67-H67B	109.5
H67A-C67-H67B	109.5
C62-C67-H67C	109.5
H67A-C67-H67C	109.5
H67B-C67-H67C	109.5
C64-C68-H68A	109.5
C64-C68-H68B	109.5
H68A-C68-H68B	109.5
C64-C68-H68C	109.5
H68A-C68-H68C	109.5
H68B-C68-H68C	109.5
C76-C71-O7	121.6(5)
C76-C71-C72	122.1(5)
O7-C71-C72	115.9(5)
C73-C72-C71	117.4(5)
C73-C72-C77	122.4(5)
C71-C72-C77	120.2(5)
C72-C73-C74	122.7(5)
C72-C73-H73	118.7
C74-C73-H73	118.7
C75-C74-C73	118.0(5)
C75-C74-C78	122.1(5)
C73-C74-C78	119.9(5)
C74-C75-C76	122.8(5)
C74-C75-H75	118.6
C76-C75-H75	118.6
C71-C76-C75	117.0(5)
C71-C76-C86	123.2(5)
C75-C76-C86	119.7(5)
C72-C77-H77A	109.5
C72-C77-H77B	109.5
H77A-C77-H77B	109.5
C72-C77-H77C	109.5
H77A-C77-H77C	109.5
H77B-C77-H77C	109.5
C74-C78-H78A	109.5
C74-C78-H78B	109.5
H78A-C78-H78B	109.5
C74-C78-H78C	109.5
H78A-C78-H78C	109.5
H78B-C78-H78C	109.5
C86-C81-C82	123.5(5)
C86-C81-O8	118.9(4)
C82-C81-O8	117.6(4)
C83-C82-C81	117.0(5)
C83-C82-C87	121.1(5)
C81-C82-C87	121.9(5)
C82-C83-C84	122.7(5)
C82-C83-H83	118.7
C84-C83-H83	118.7

C85-C84-C83	117.3(5)
C85-C84-C88	122.0(5)
C83-C84-C88	120.6(5)
C84-C85-C86	122.9(5)
C84-C85-H85	118.5
C86-C85-H85	118.5
C81-C86-C85	116.5(5)
C81-C86-C76	122.0(5)
C85-C86-C76	121.5(5)
C82-C87-H87A	109.5
C82-C87-H87B	109.5
H87A-C87-H87B	109.5
C82-C87-H87C	109.5
H87A-C87-H87C	109.5
H87B-C87-H87C	109.5
C84-C88-H88A	109.5
C84-C88-H88B	109.5
H88A-C88-H88B	109.5
C84-C88-H88C	109.5
H88A-C88-H88C	109.5
H88B-C88-H88C	109.5
O98-C98-Rh1	179.1(5)
O99-C99-Rh1	178.3(5)

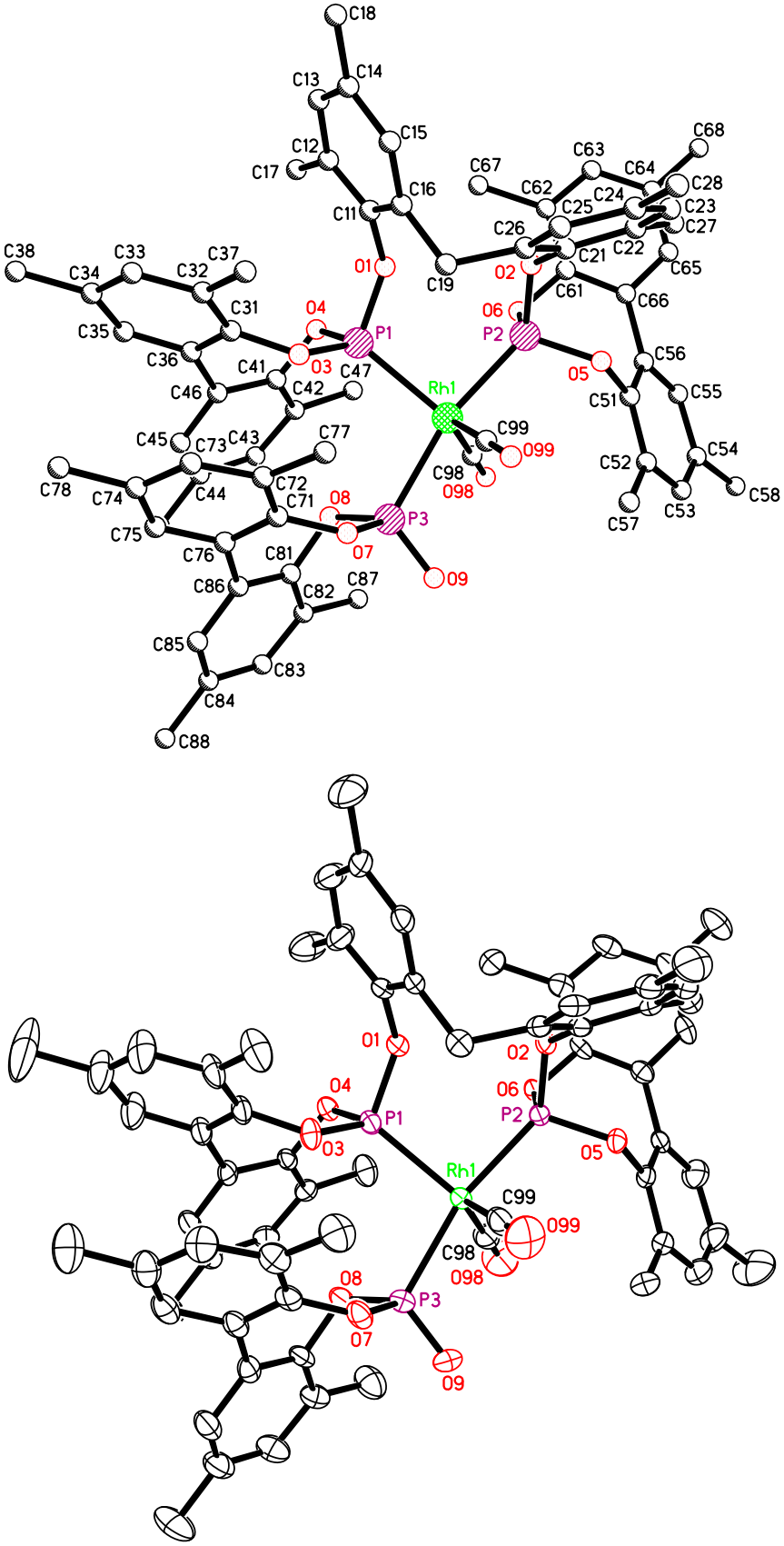
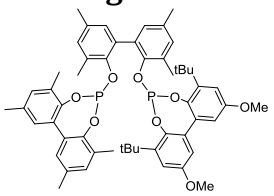


Figure S4: Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity.

S2. NMR spectra

S2.1 Ligand L10



L10

S2.1.1 $^{31}P\{^{1}H\}$ NMR

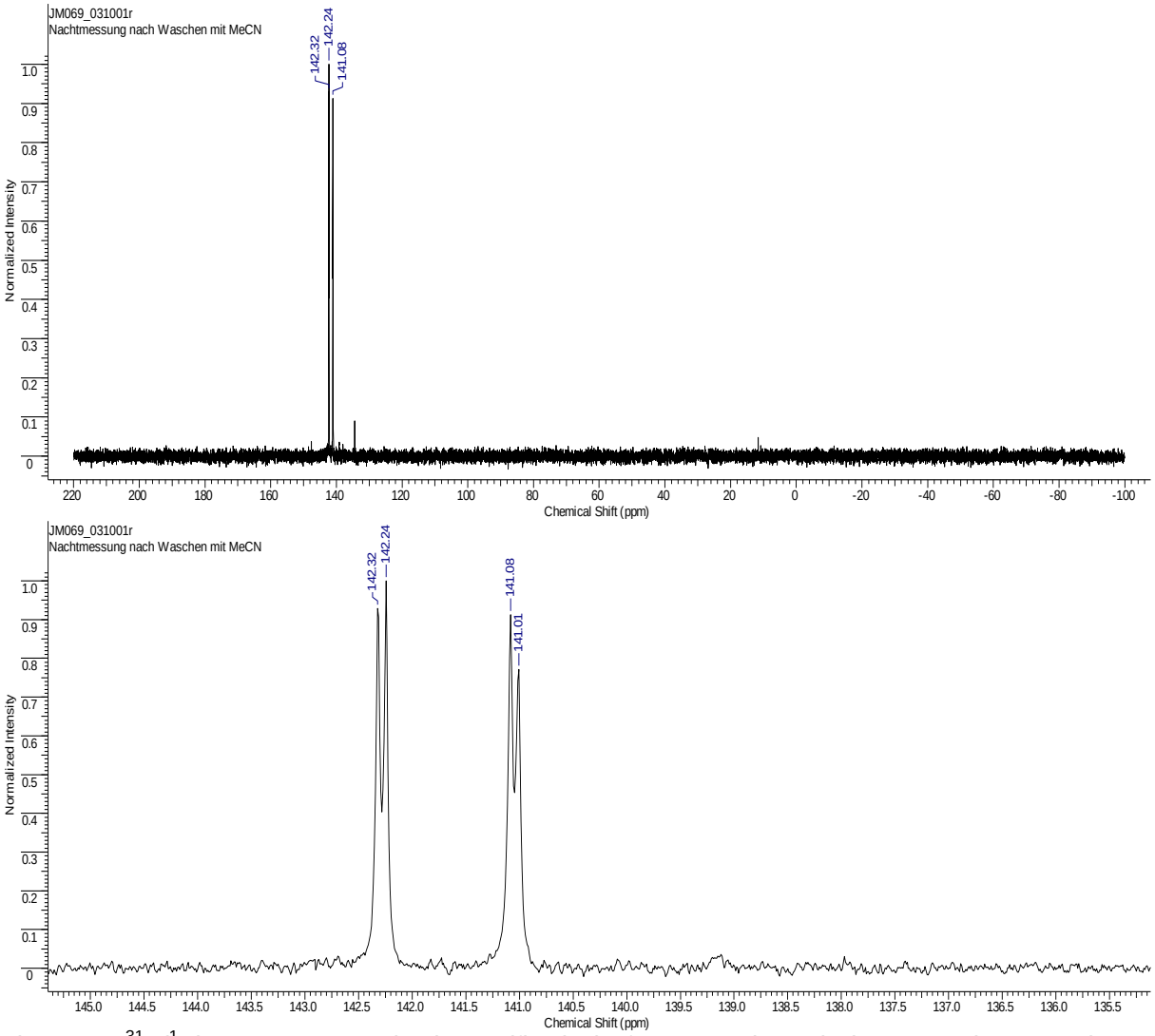


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum (and magnification) of compound **L10** (solvent: $CDCl_3$, 81 MHz).

S2.1.2 ^{1}H NMR

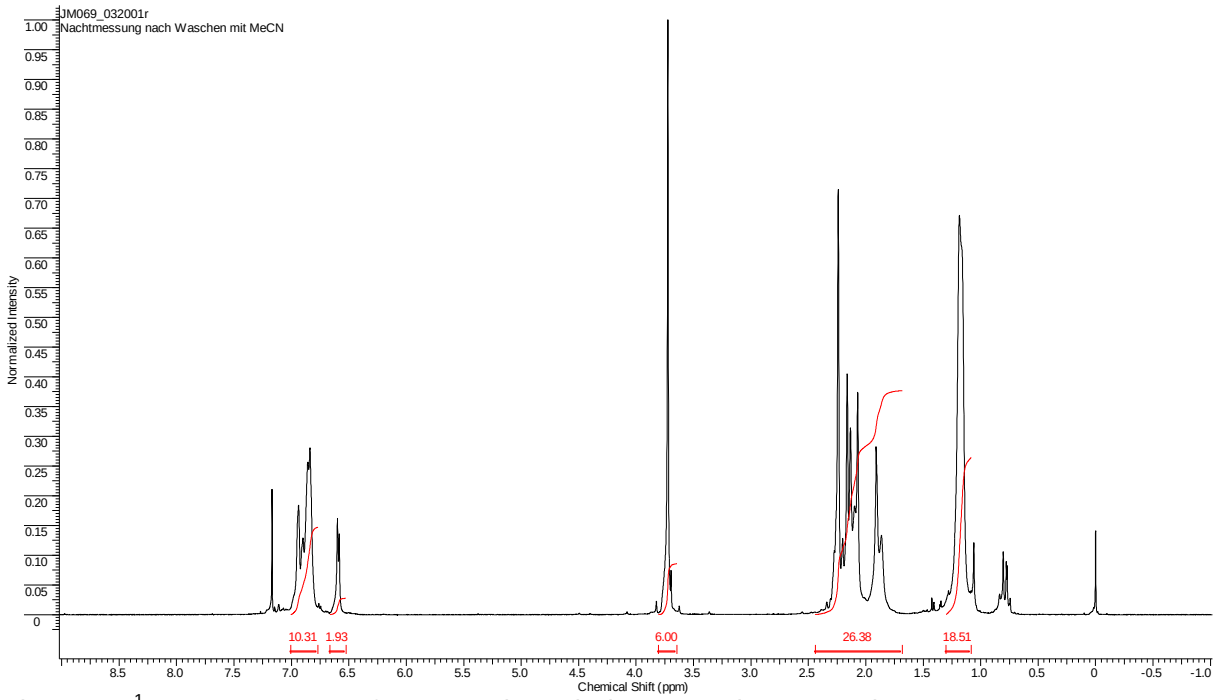


Figure S6: ^{1}H NMR spectrum of compound **L10** (solvent: $CDCl_3$, 200 MHz).

S2.1.3 ^{13}C{^{1}H} NMR

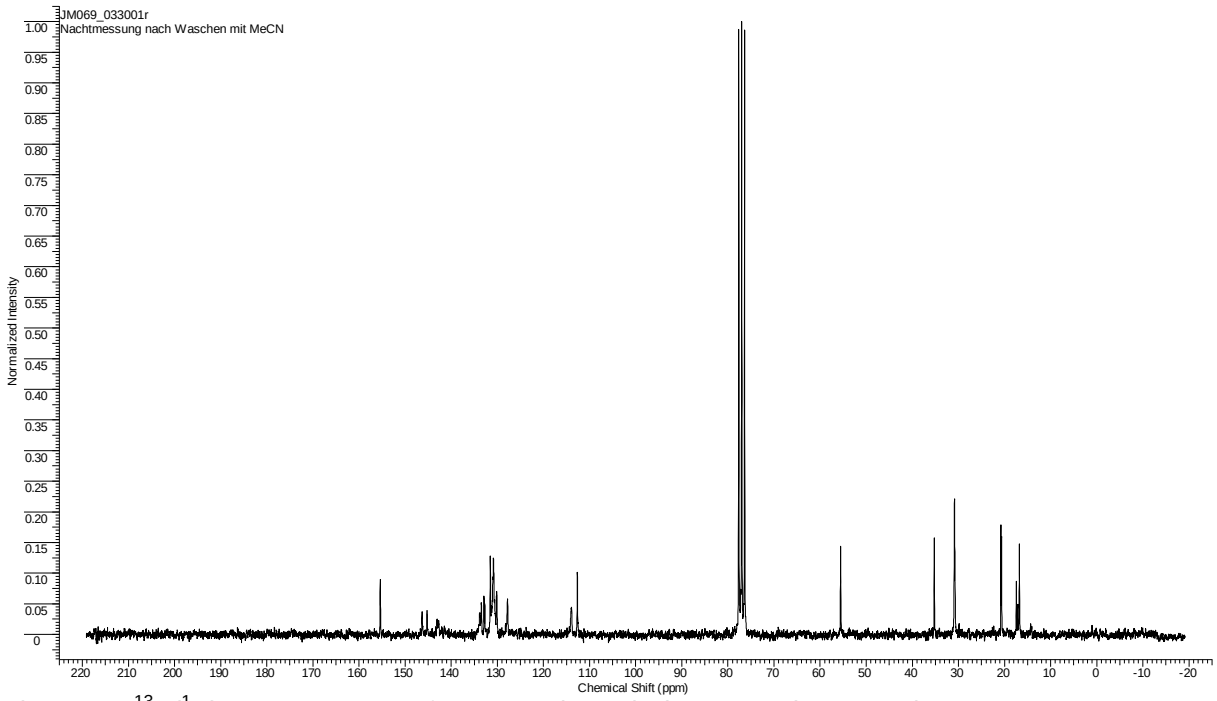
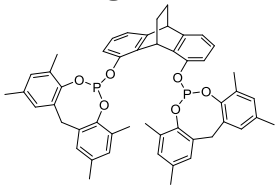


Figure S7: ^{13}C{^{1}H} NMR spectrum of compound **L10** (solvent: $CDCl_3$, 50 MHz).

S2.2 Ligand L8



L8

S2.2.1 $^{31}P\{^{1}H\}$ NMR

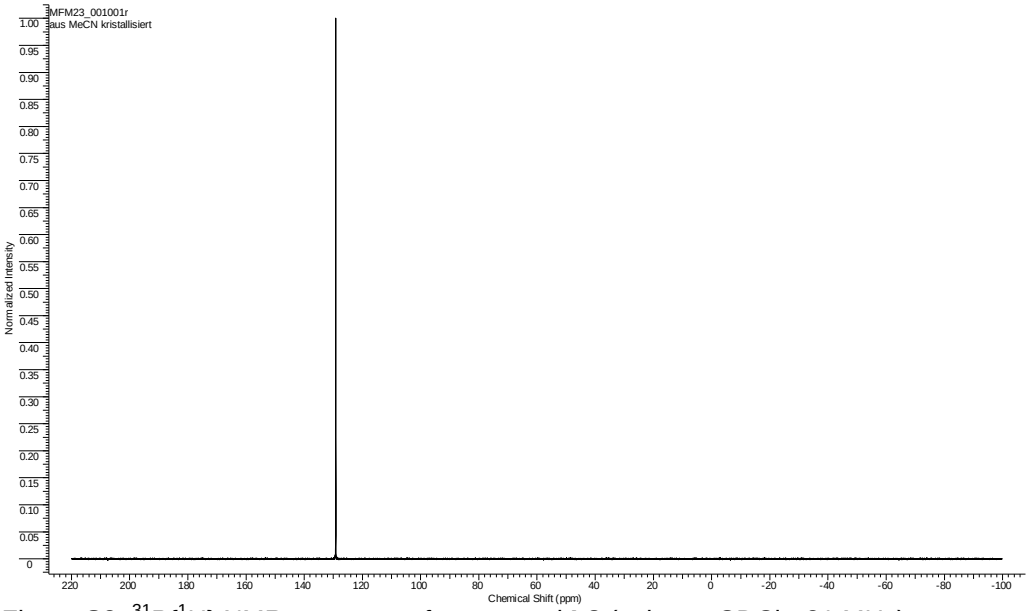


Figure S8: $^{31}P\{^{1}H\}$ NMR spectrum of compound **L8** (solvent: $CDCl_3$, 81 MHz).

S2.2.2 ^{1}H NMR

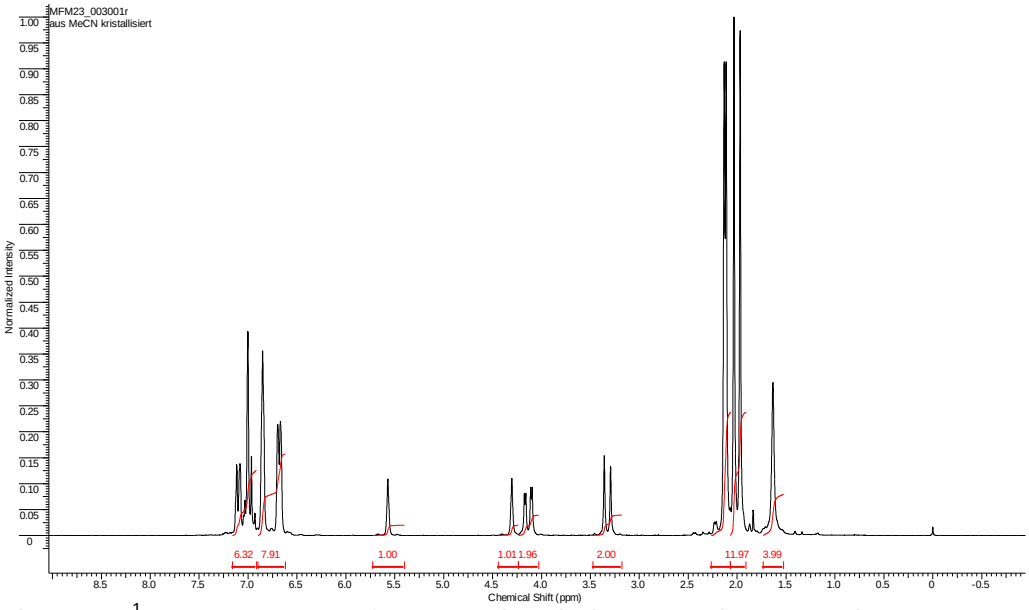
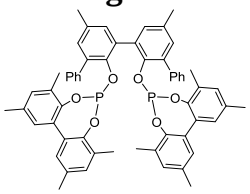


Figure S9: ^{1}H NMR spectrum of compound **L8** (solvent: $CDCl_3$, 200 MHz).

S2.3 Ligand L9



L9

S2.3.1 $^{31}P\{^{1}H\}$ NMR

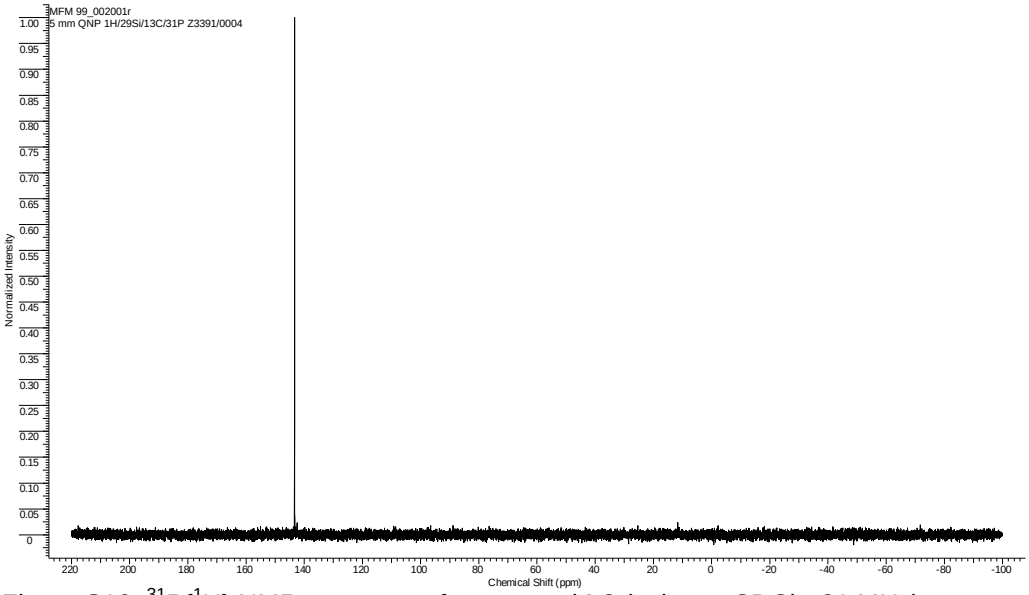


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of compound **L9** (solvent: $CDCl_3$, 81 MHz).

S2.3.2 ^{1}H NMR

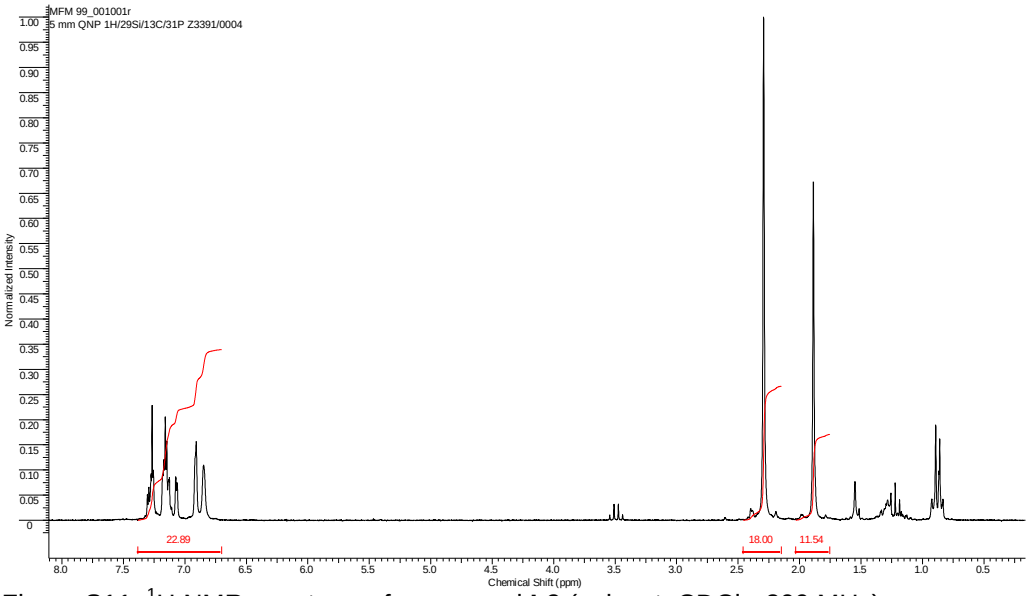
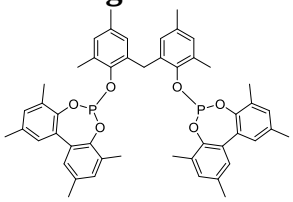


Figure S11: ^{1}H NMR spectrum of compound **L9** (solvent: $CDCl_3$, 200 MHz).

S2.4 Ligand L12



L12

S2.4.1 $^{31}P\{^{1}H\}$ NMR

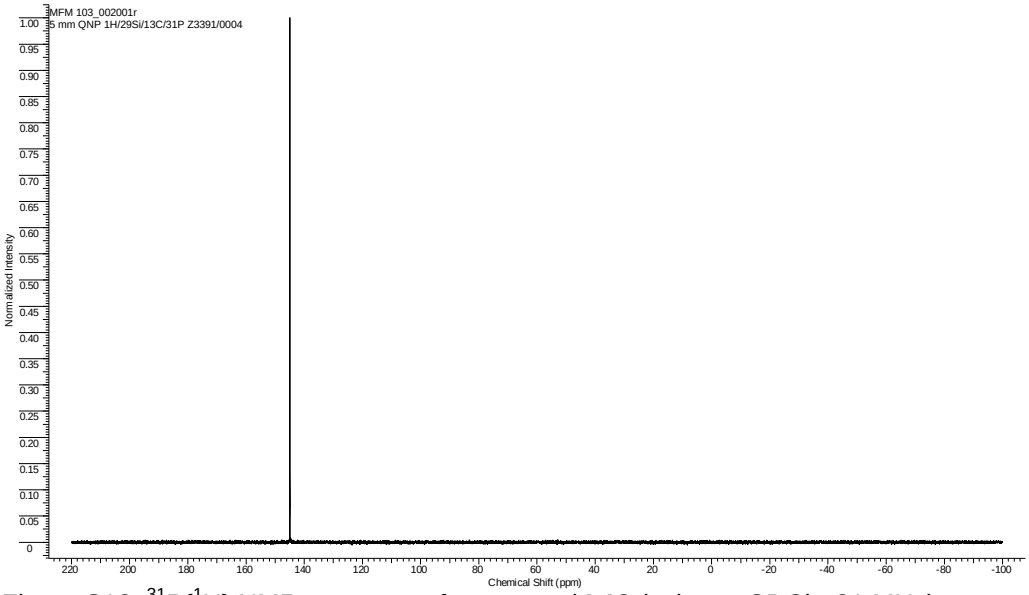


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of compound **L12** (solvent: $CDCl_3$, 81 MHz).

S2.4.2 ^{1}H NMR

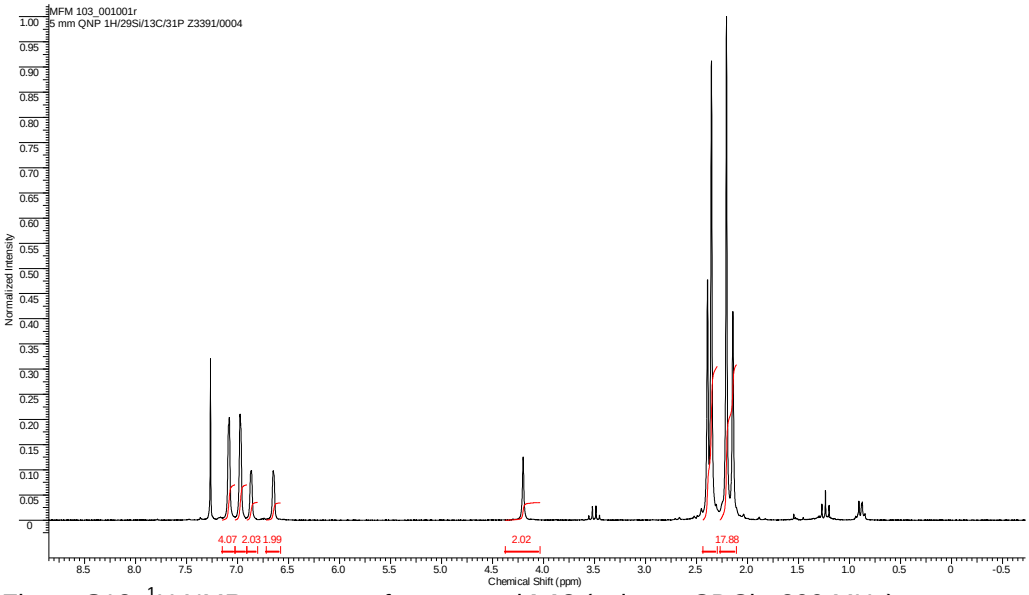
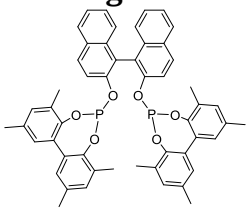


Figure S13: ^{1}H NMR spectrum of compound **L12** (solvent: $CDCl_3$, 200 MHz).

S2.5 Ligand L13



L13

S2.5.1 $^{31}P\{^{1}H\}$ NMR

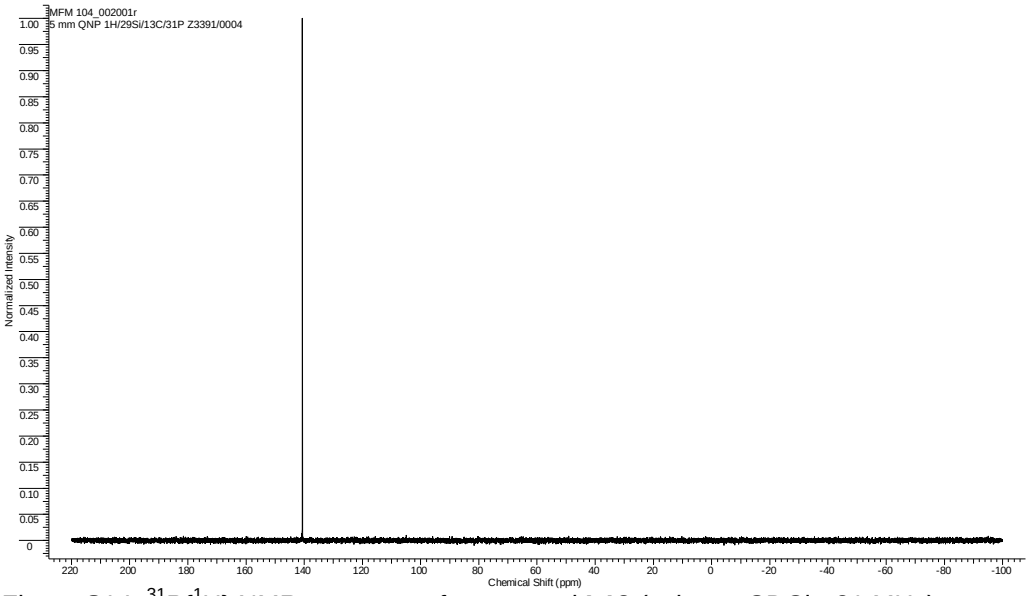


Figure S14: $^{31}P\{^{1}H\}$ NMR spectrum of compound **L13** (solvent: $CDCl_3$, 81 MHz).

S2.5.2 ^{1}H NMR

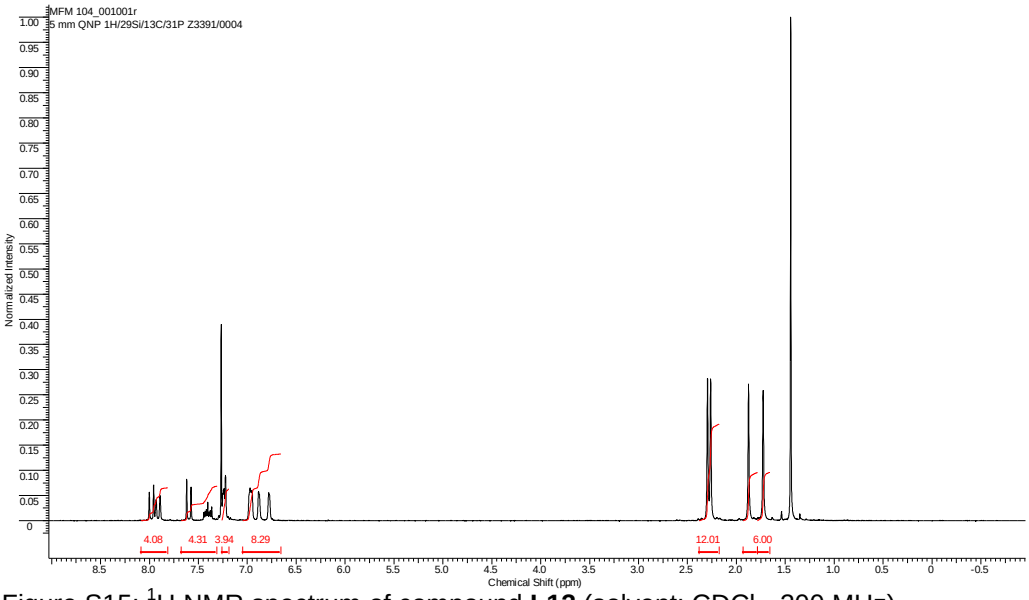


Figure S15: ^{1}H NMR spectrum of compound **L13** (solvent: $CDCl_3$, 200 MHz).

S3. GC data

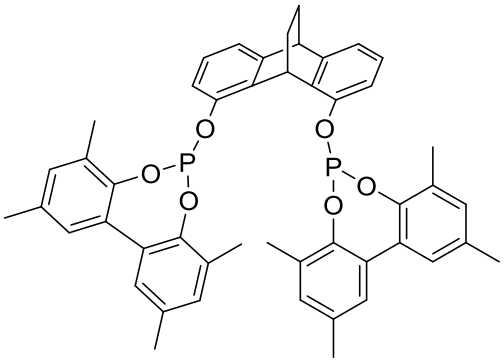
Each ligand was tested three times for reproducibility. Retention times are approx. (min):

Table S21: Retention times (GC) of typical products after the catalysis.

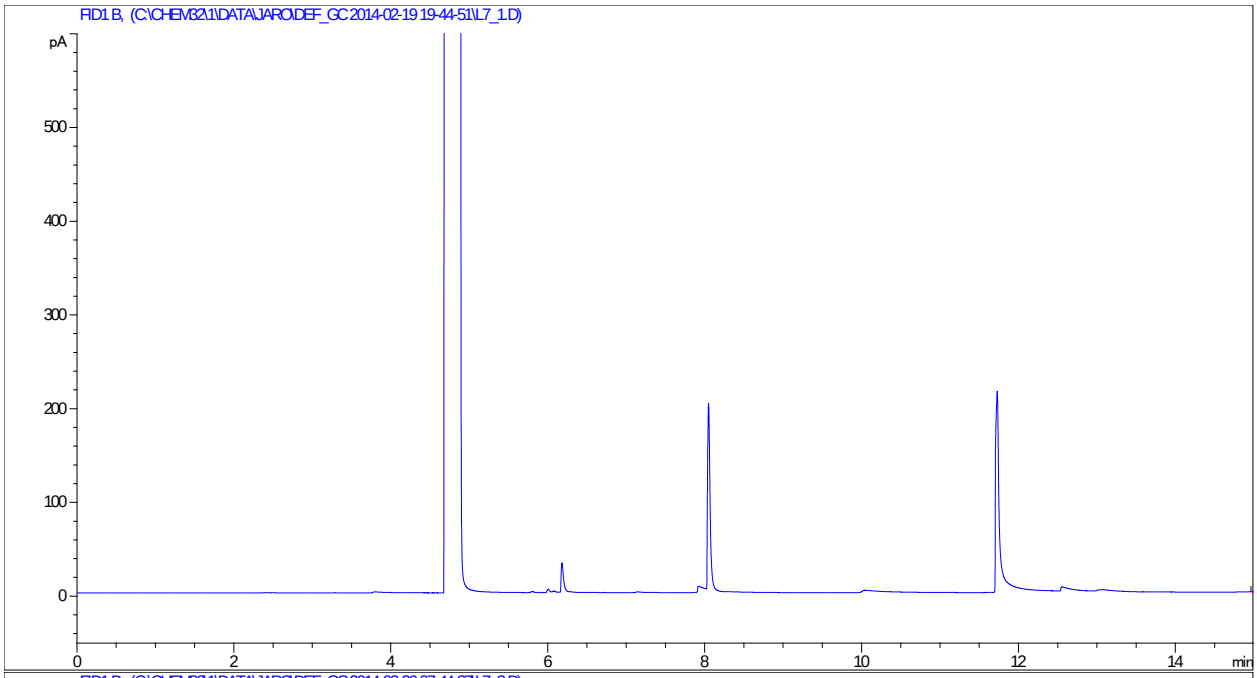
4-Pentenal	3,5
Pentanal	3,6
E-3-pentenal	3,7
Z-3-pentenal	3,8
2-pentenal	4,5
cyclopent-1-enecarbaldehyde	7,8
nonane	8,1
2-ethylbutanedial	9,2
2-methylpentanedial	9,7
adipic aldehyde	11,7

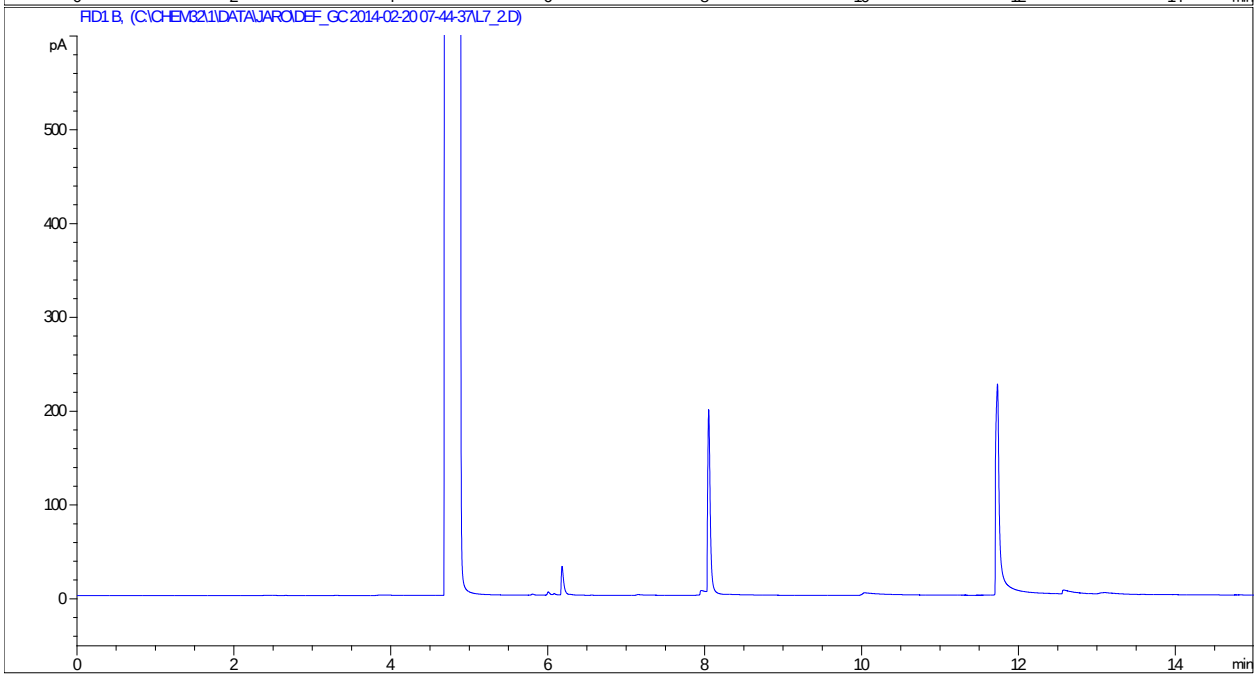
The peak at about 6.2 min comes from the used toluene (see blank run **3.15**). Adipic aldehyde smears quite much and sometimes gives shoulders at 12.5 and 13 mins.

S3.1 Ligand L1



L1





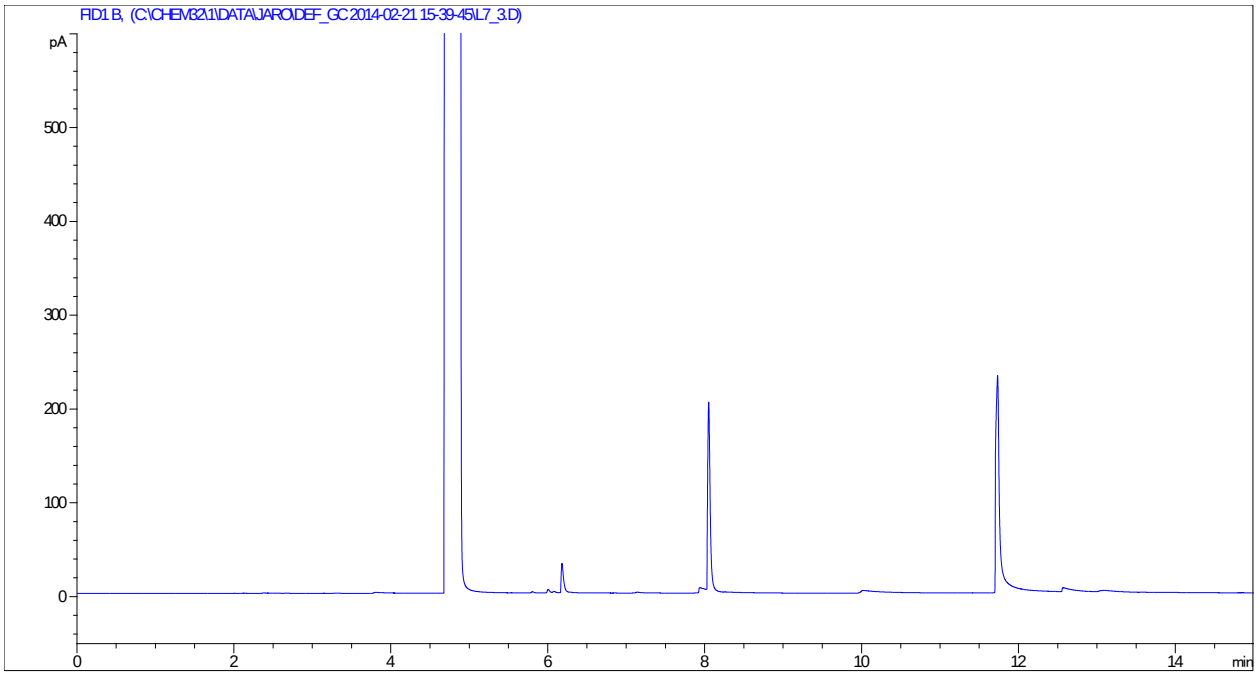
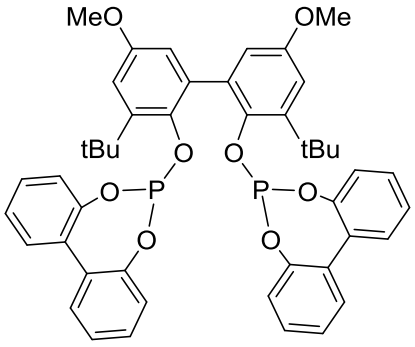
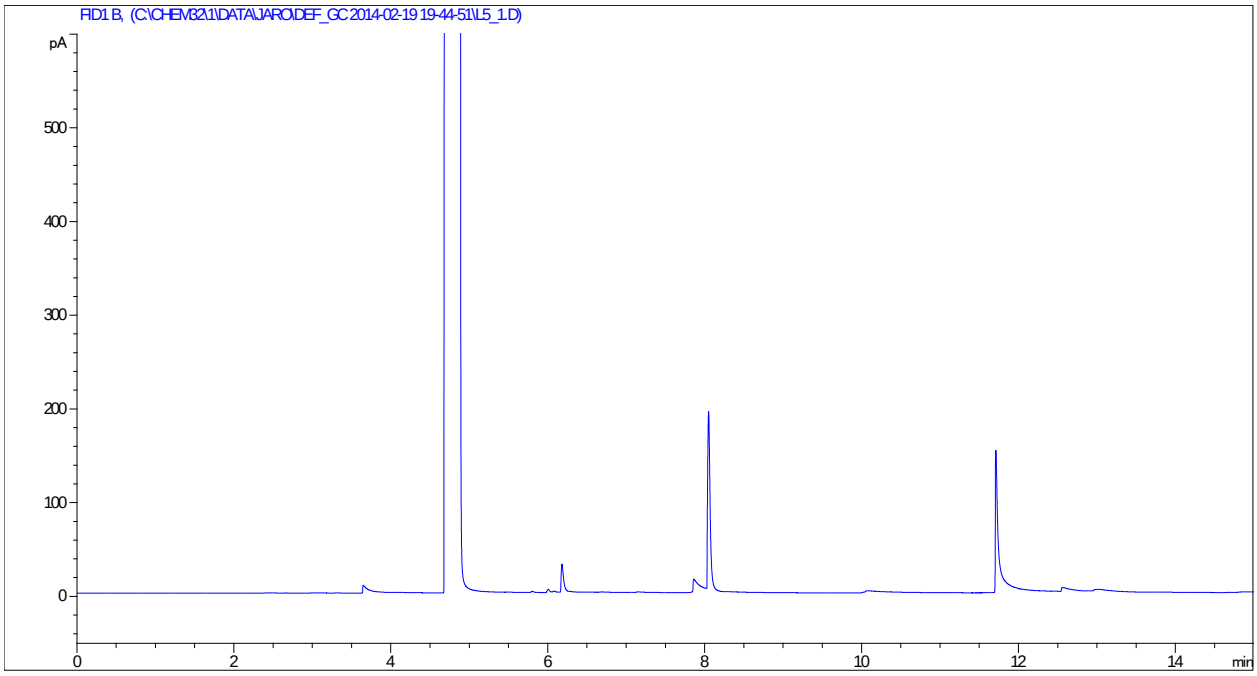


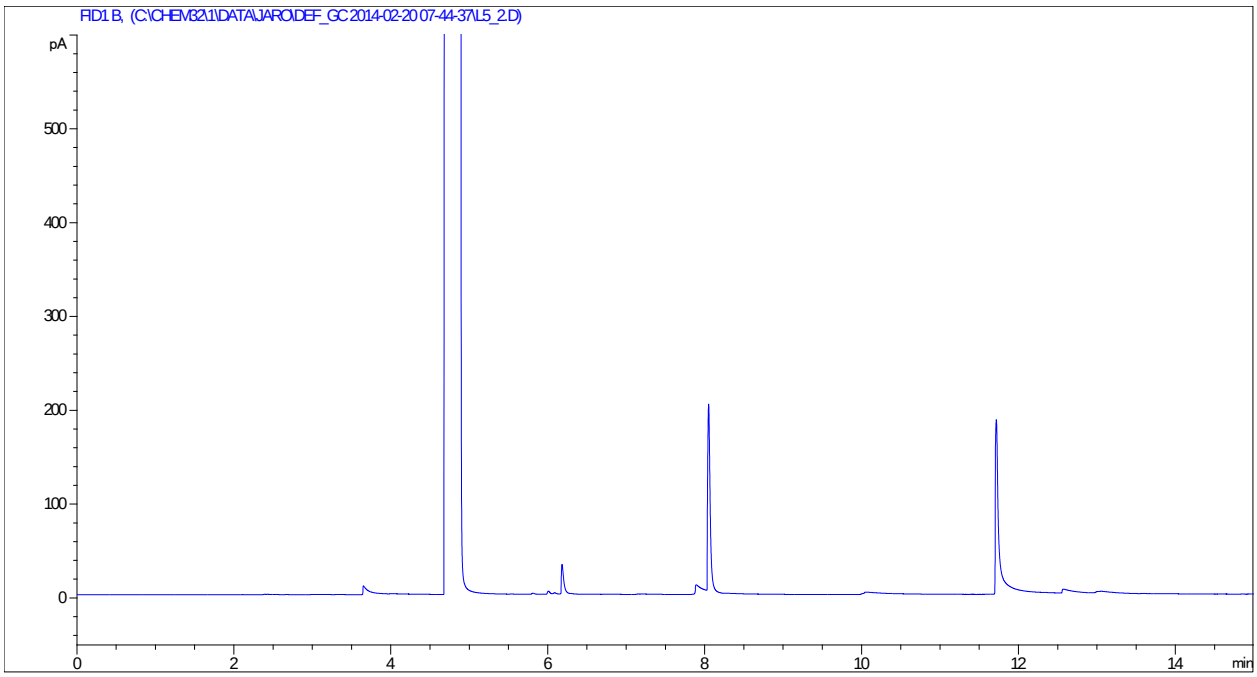
Figure S16: GC spectra after using ligand **L1**. (Reaction was done three times for reproducibility)

S3.2 Ligand L2



L2





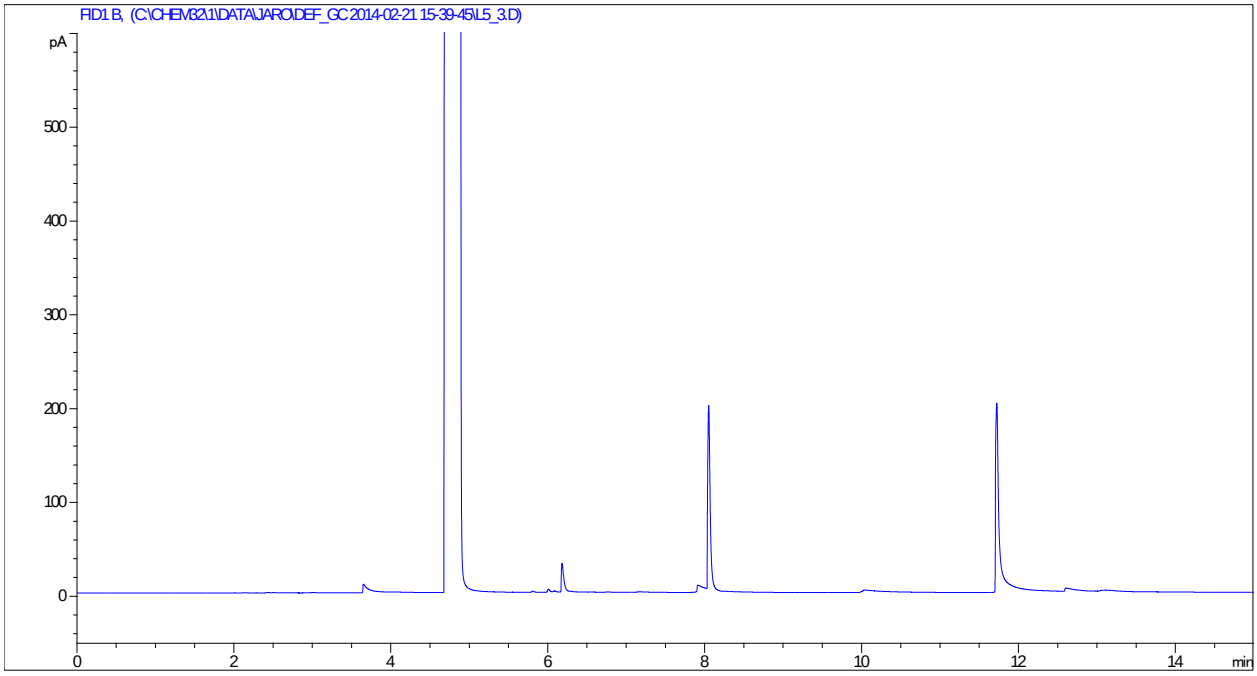
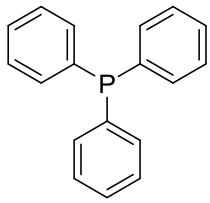
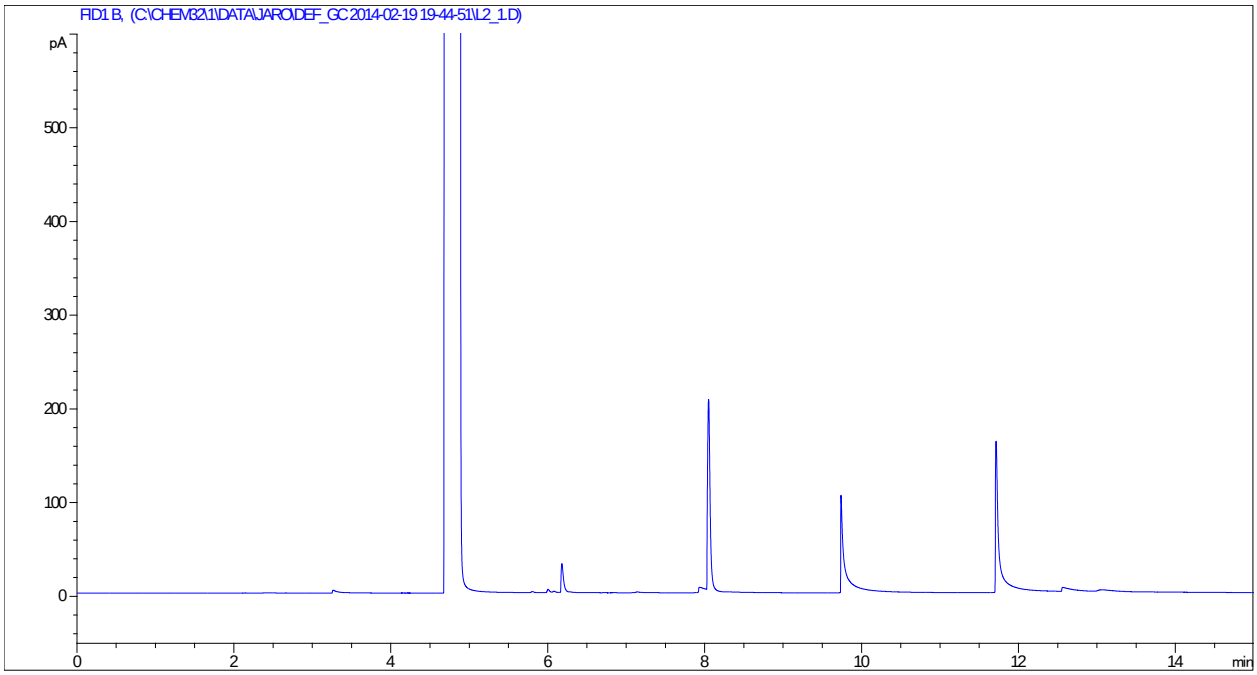


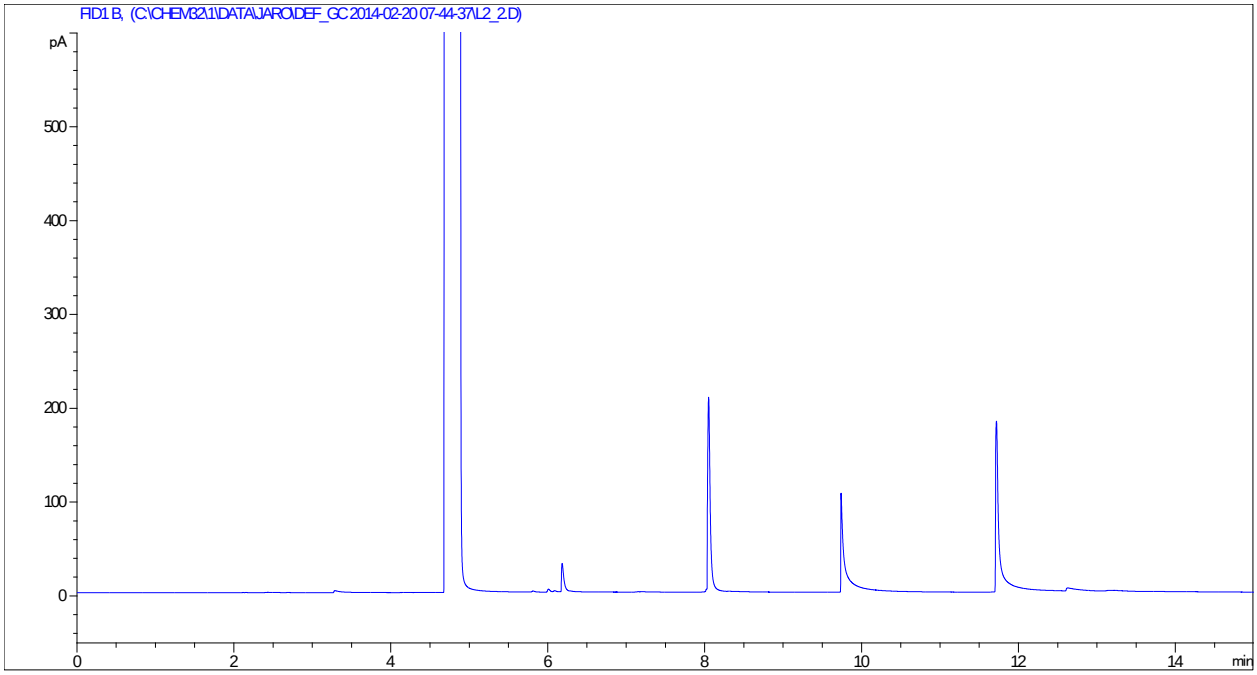
Figure S17: GC spectra after using ligand **L2**. (Reaction was done three times for reproducibility)

S3.3 Ligand L3



L3





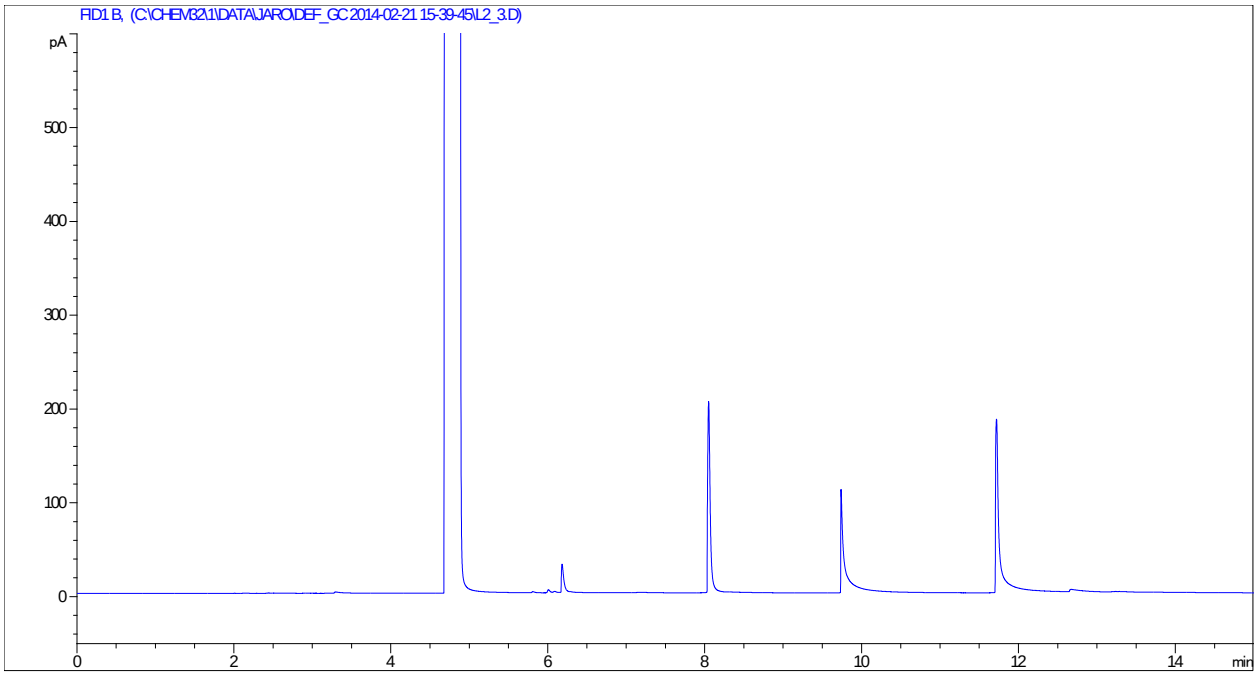
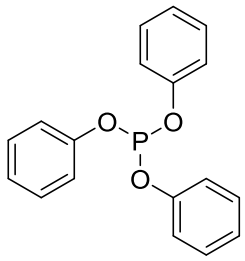
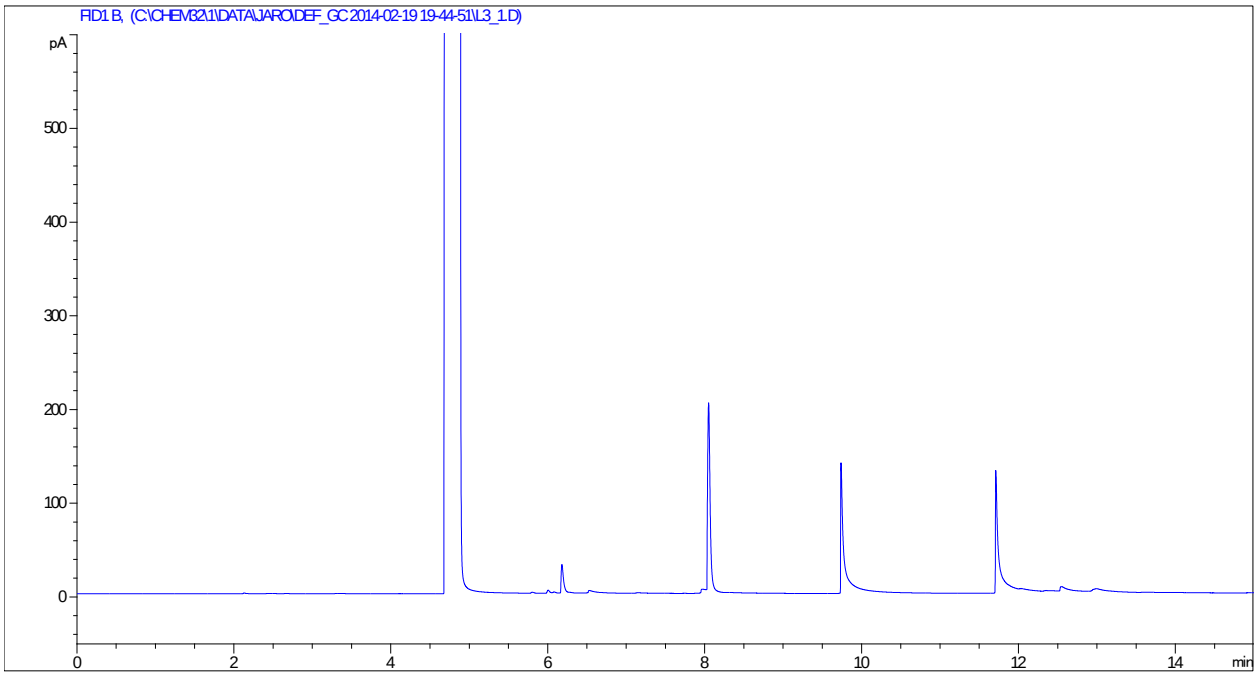


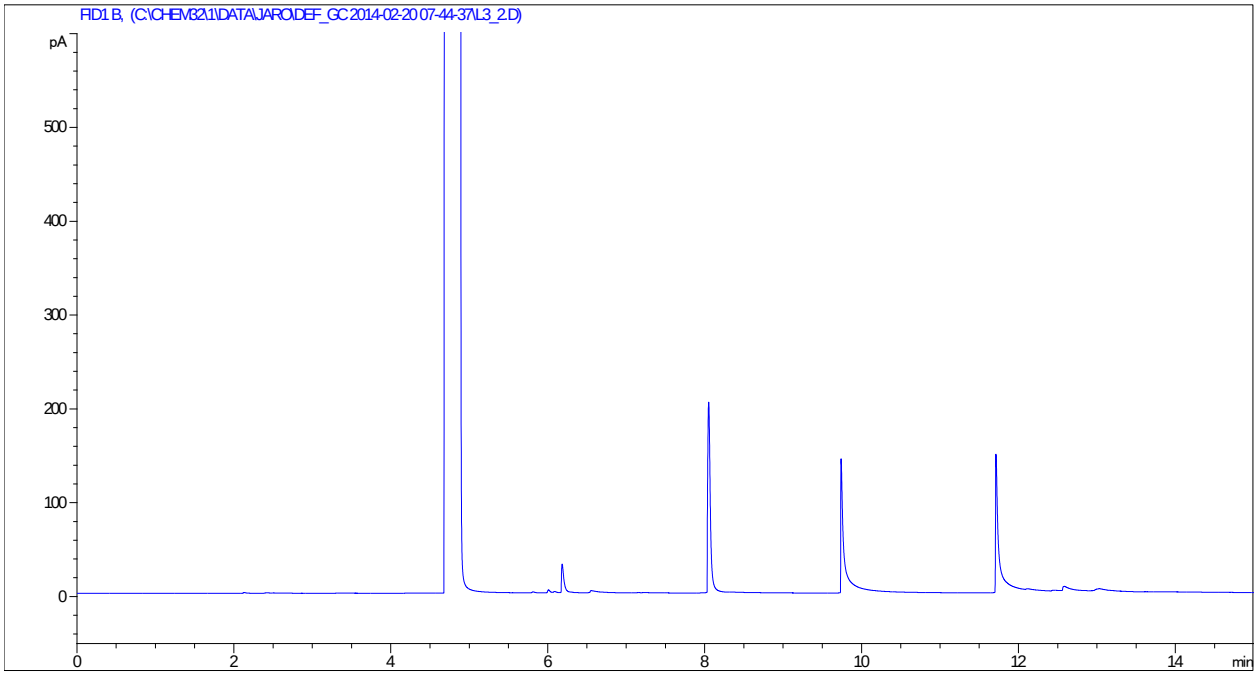
Figure S18: GC spectra after using ligand **L3**. (Reaction was done three times for reproducibility)

S3.4 Ligand L4



L4





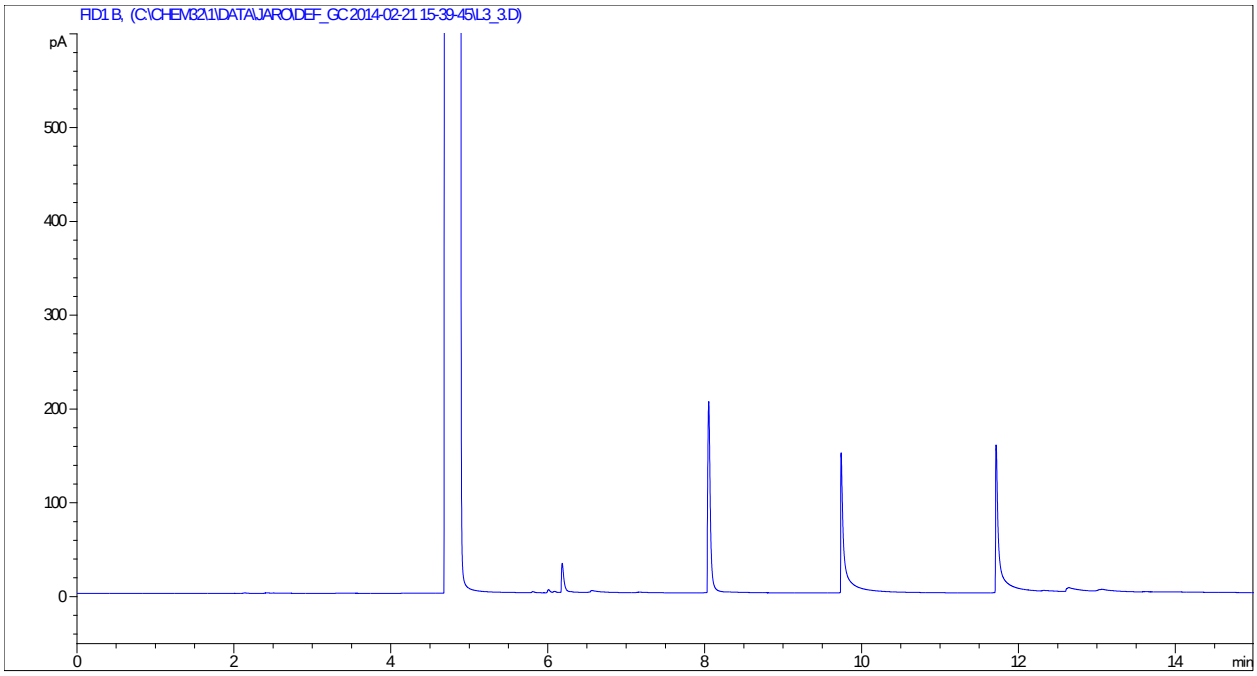
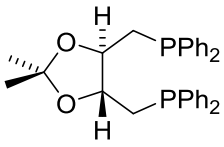
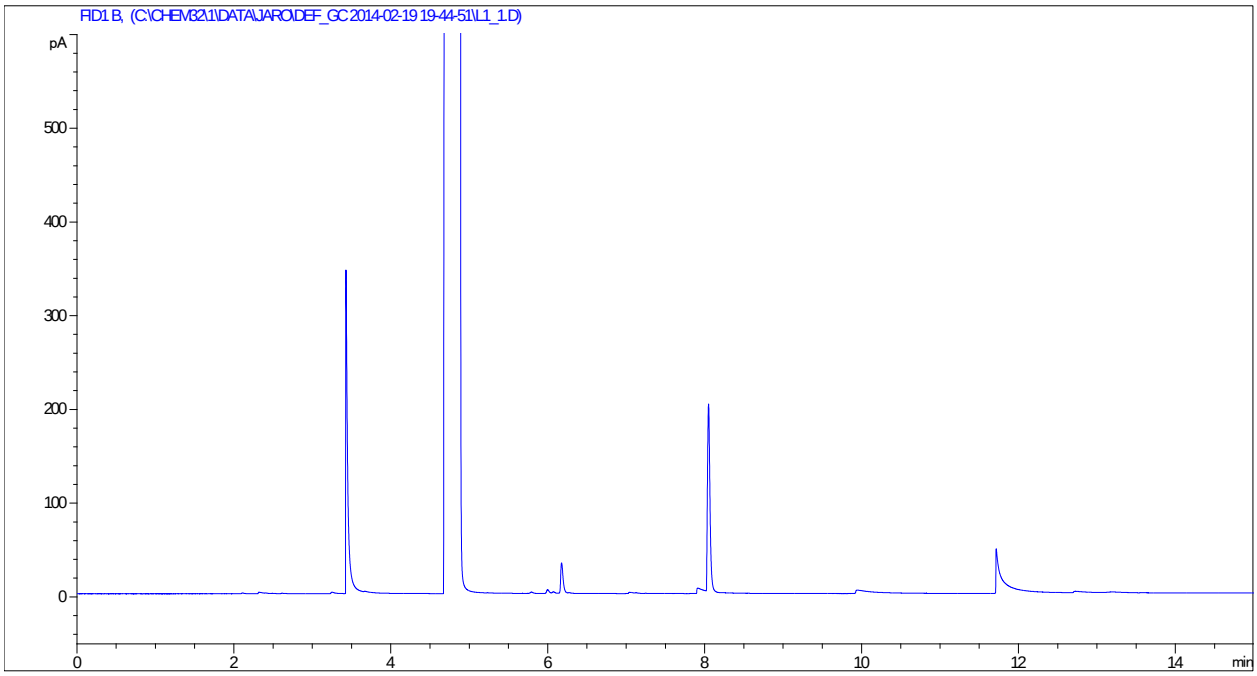


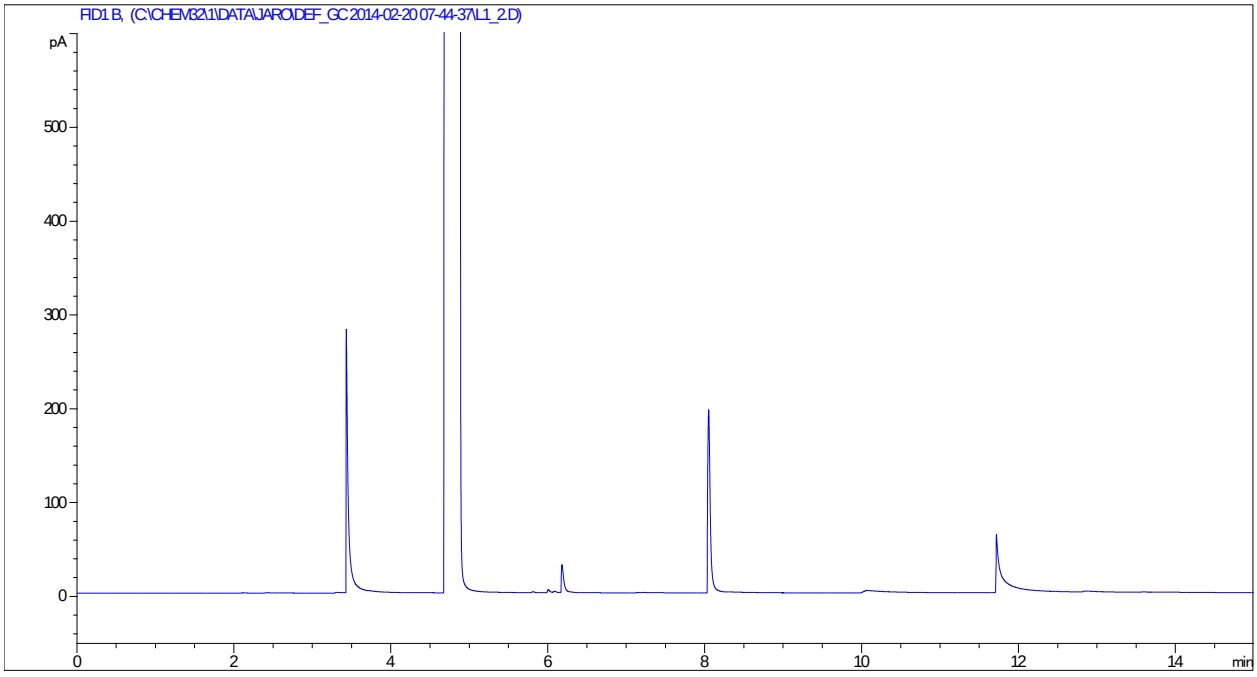
Figure S19: GC spectra after using ligand **L4**. (Reaction was done three times for reproducibility)

S3.5 Ligand L5



L5





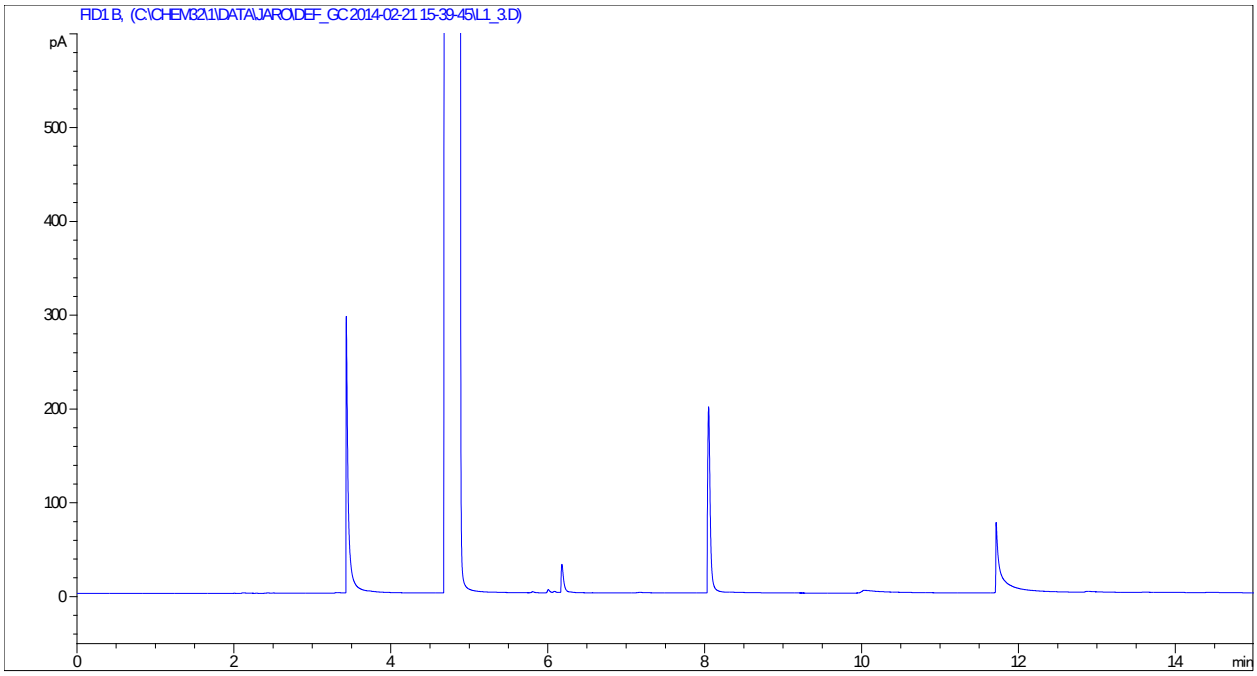
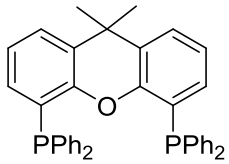
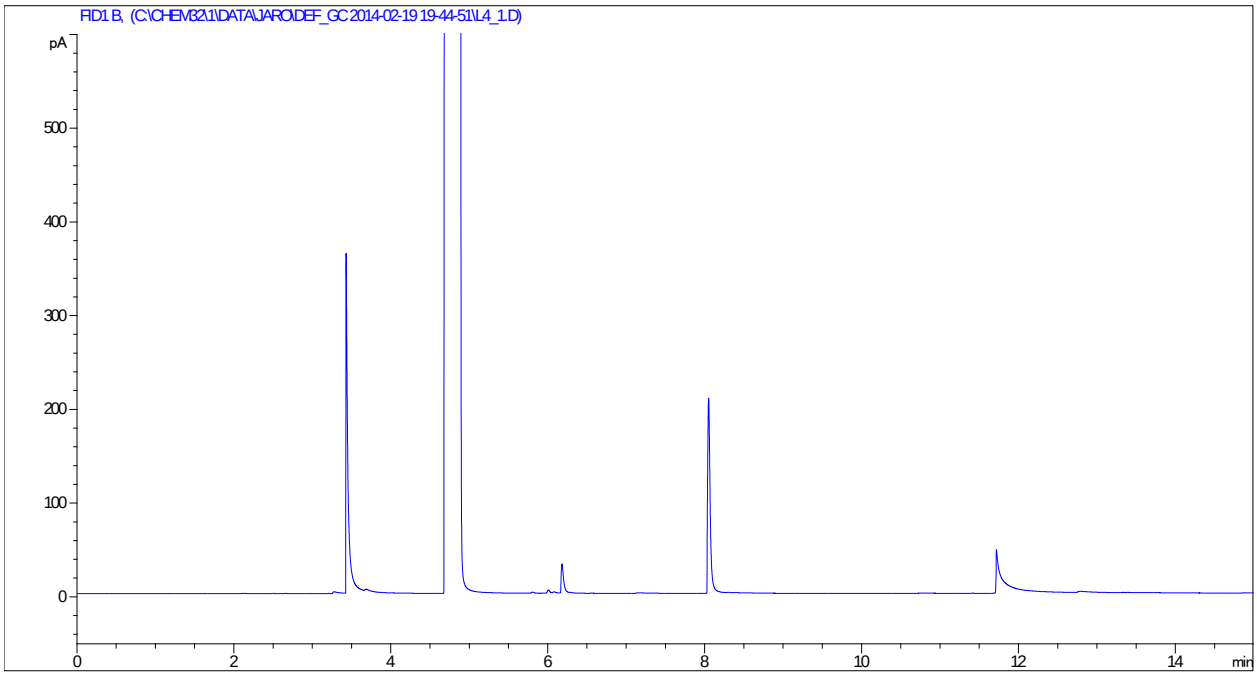


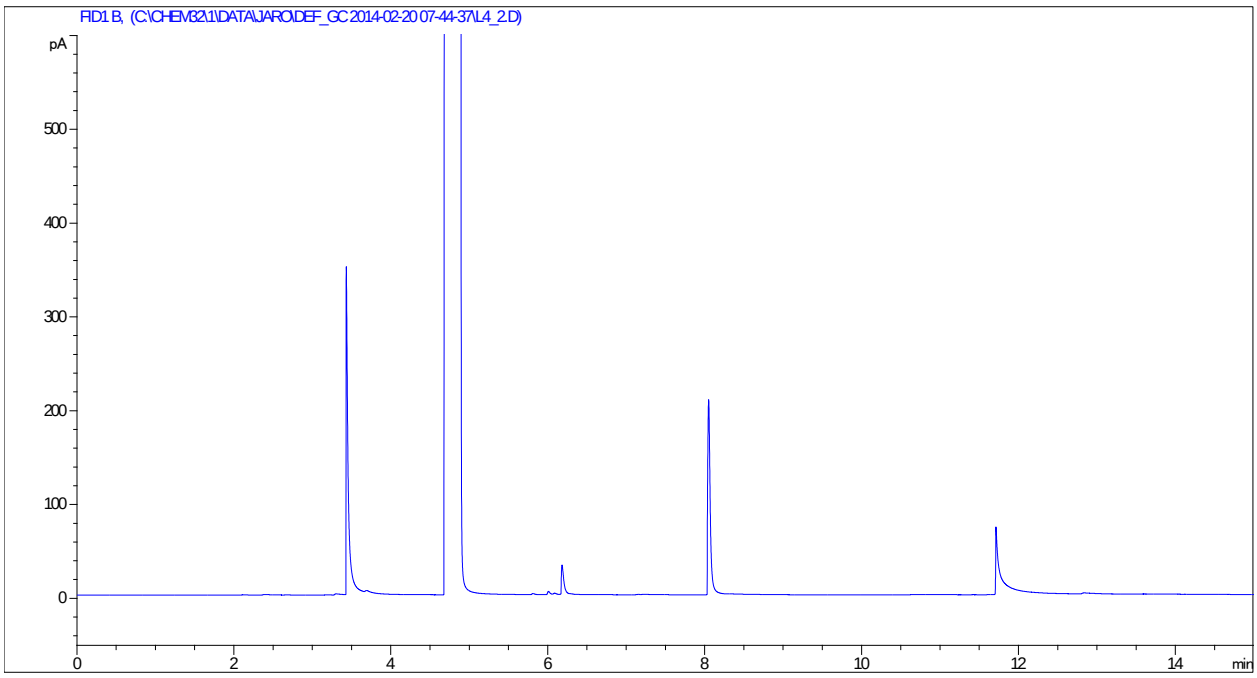
Figure S20: GC spectra after using ligand **L5**. (Reaction was done three times for reproducibility)

S3.6 Ligand L6



L6





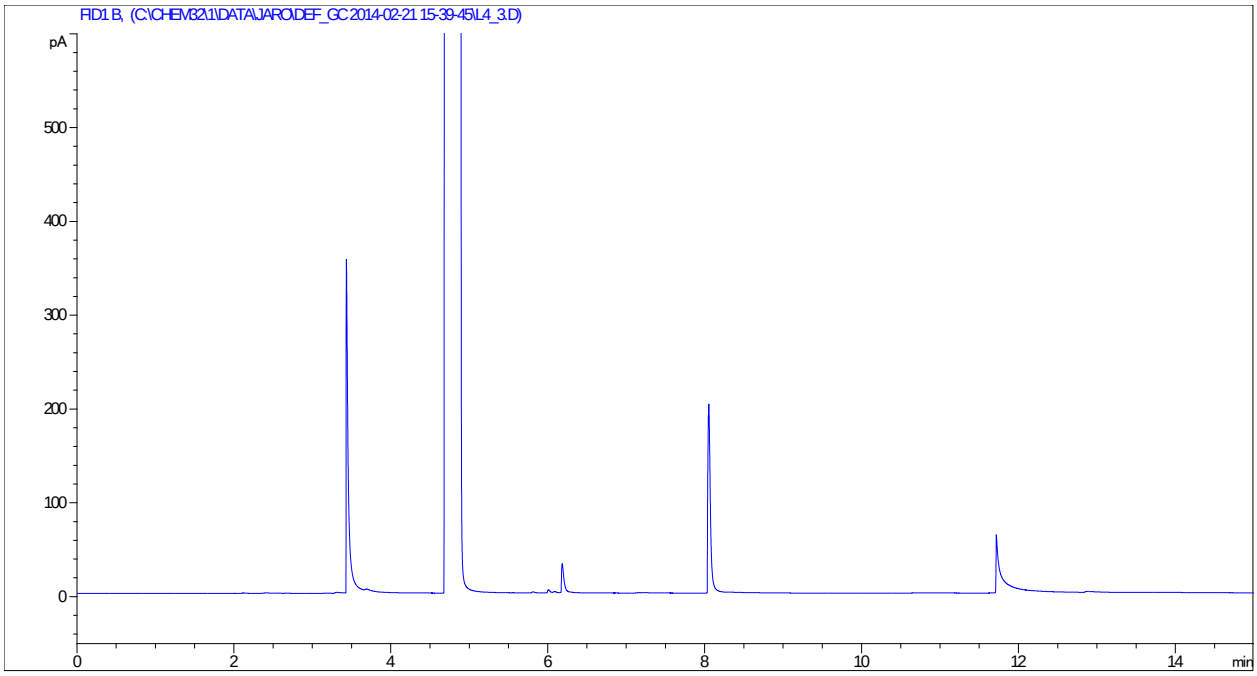
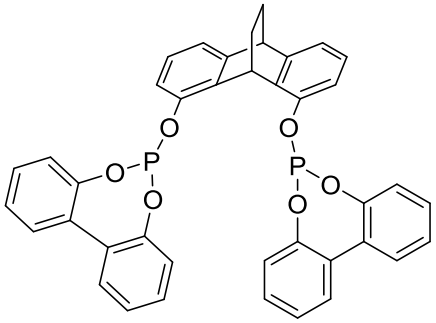
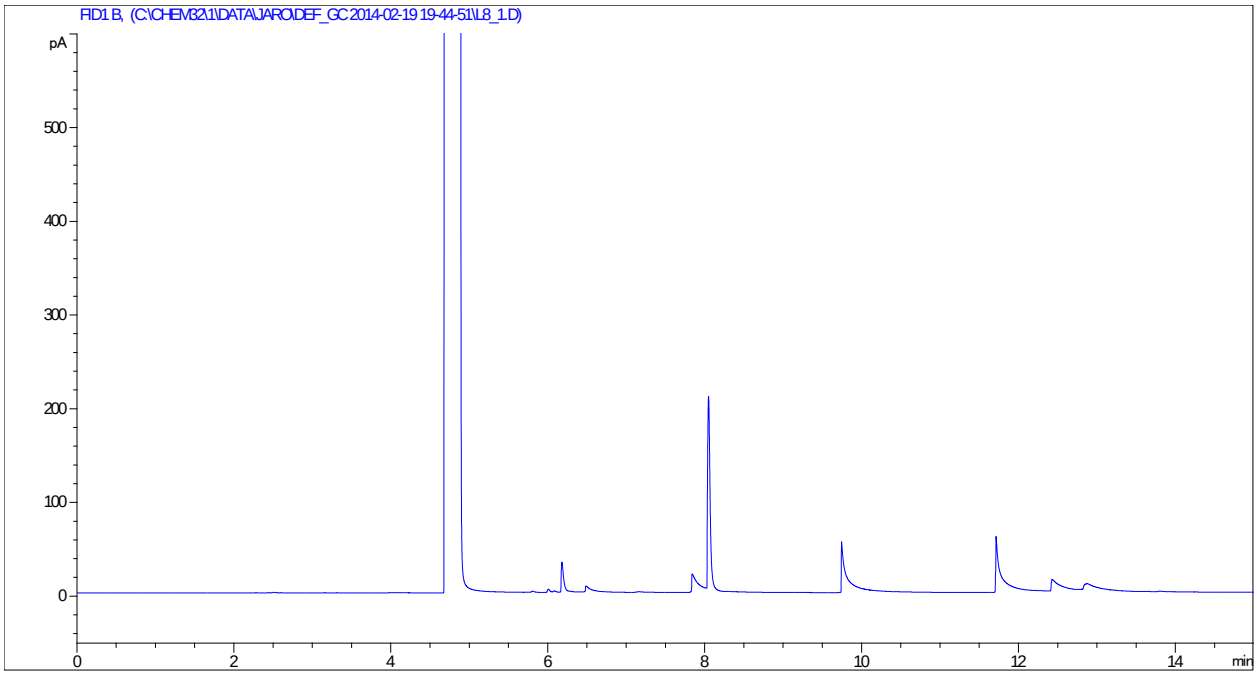


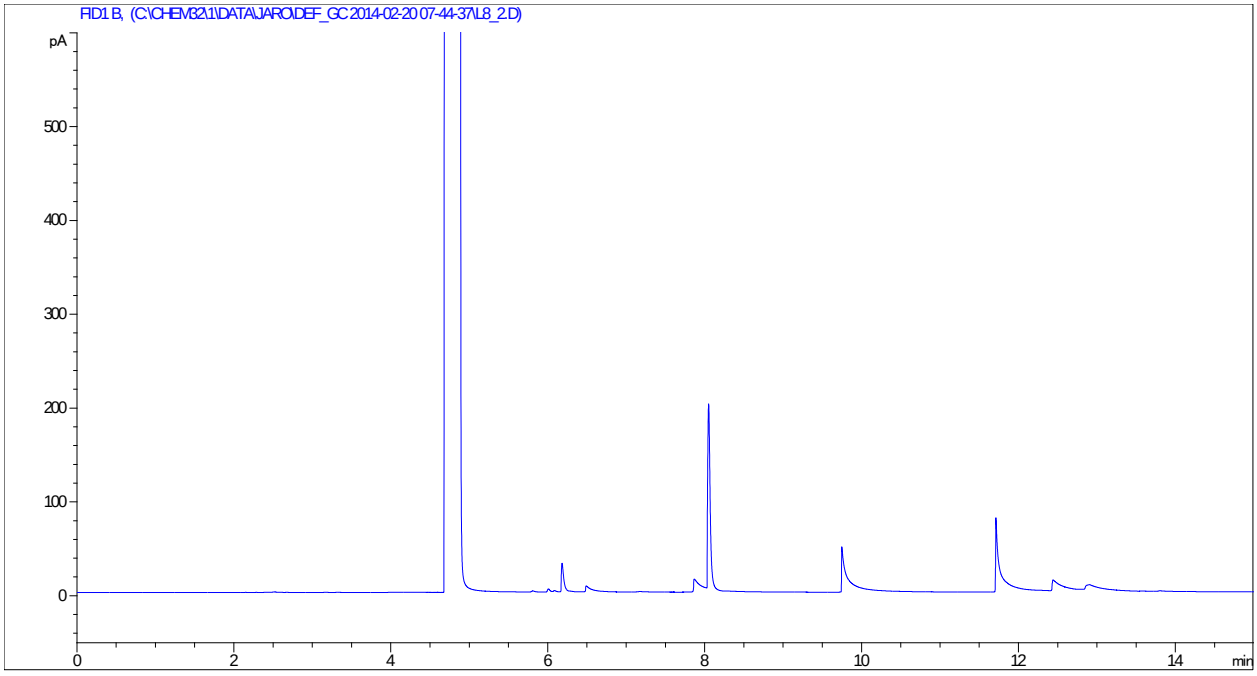
Figure S21: GC spectra after using ligand **L6**. (Reaction was done three times for reproducibility)

S3.7 Ligand L7



L7





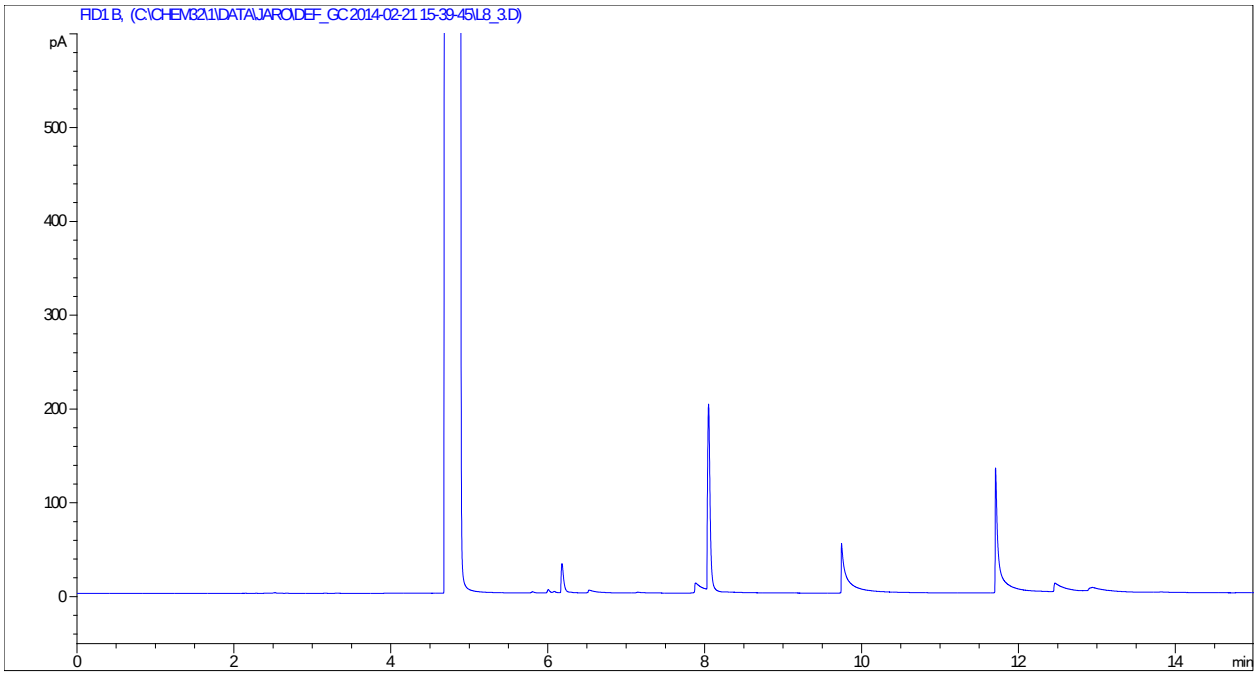
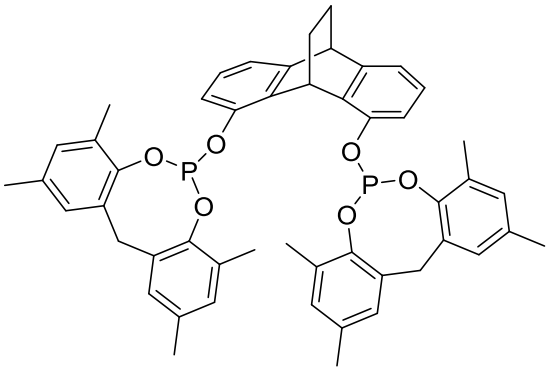
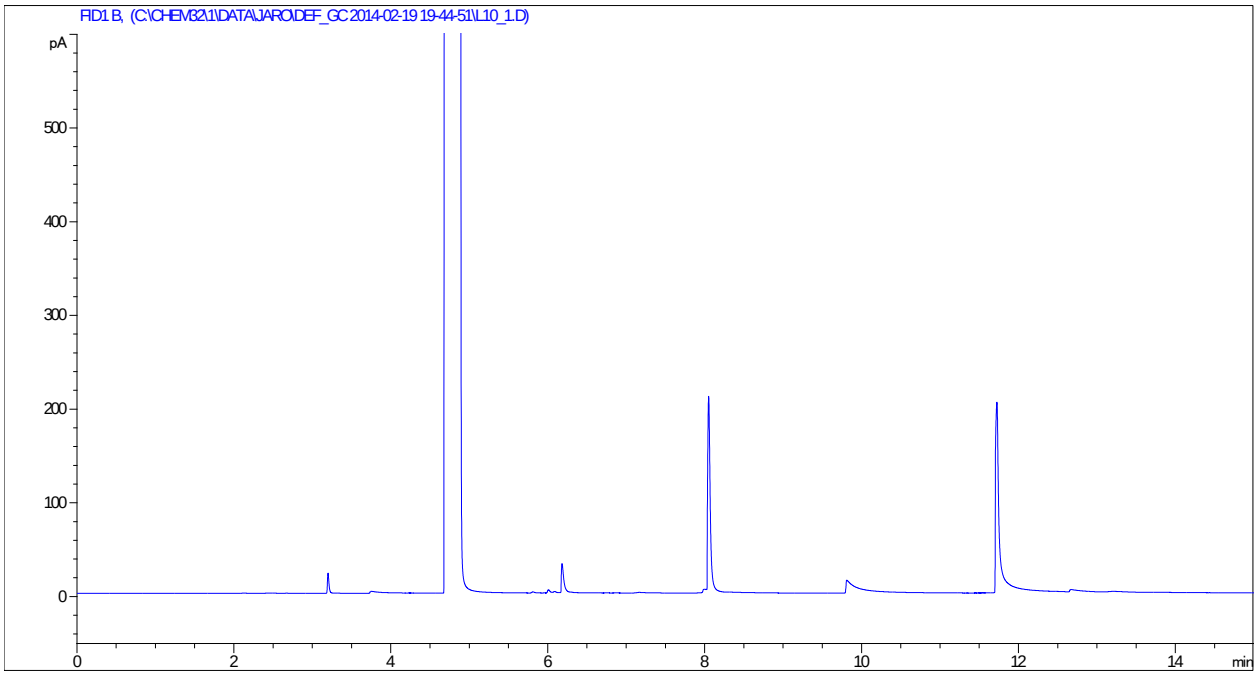


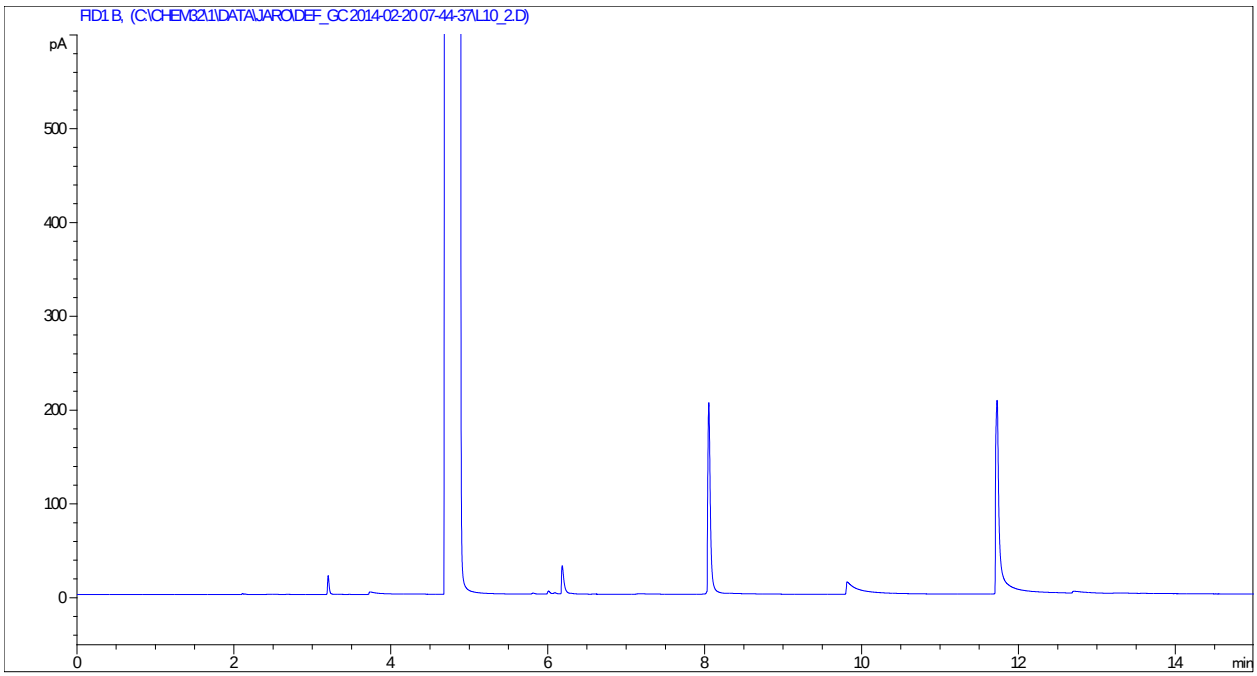
Figure S22: GC spectra after using ligand **L7**. (Reaction was done three times for reproducibility)

S3.8 Ligand L8



L8





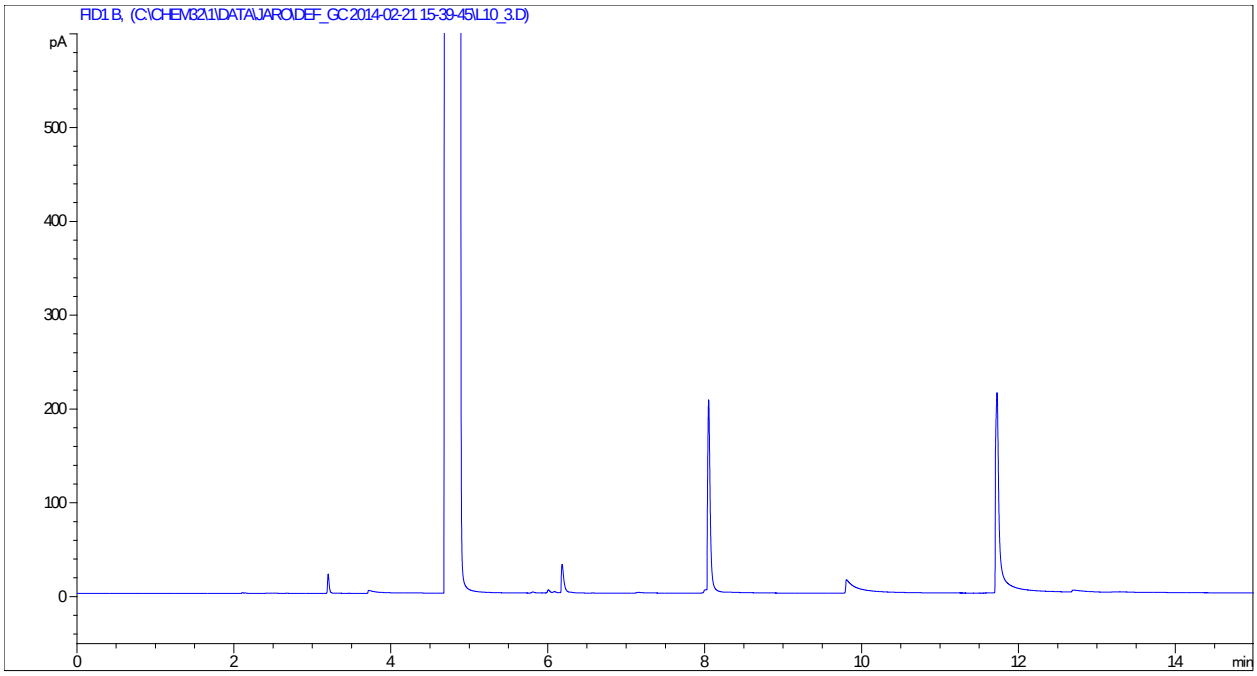
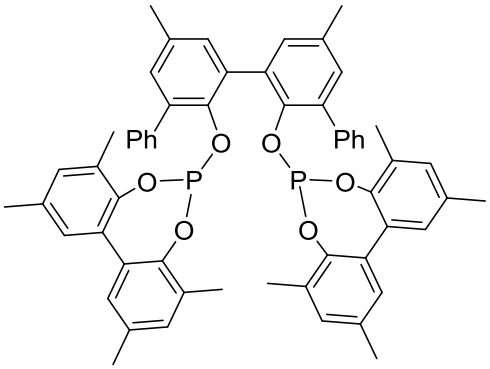
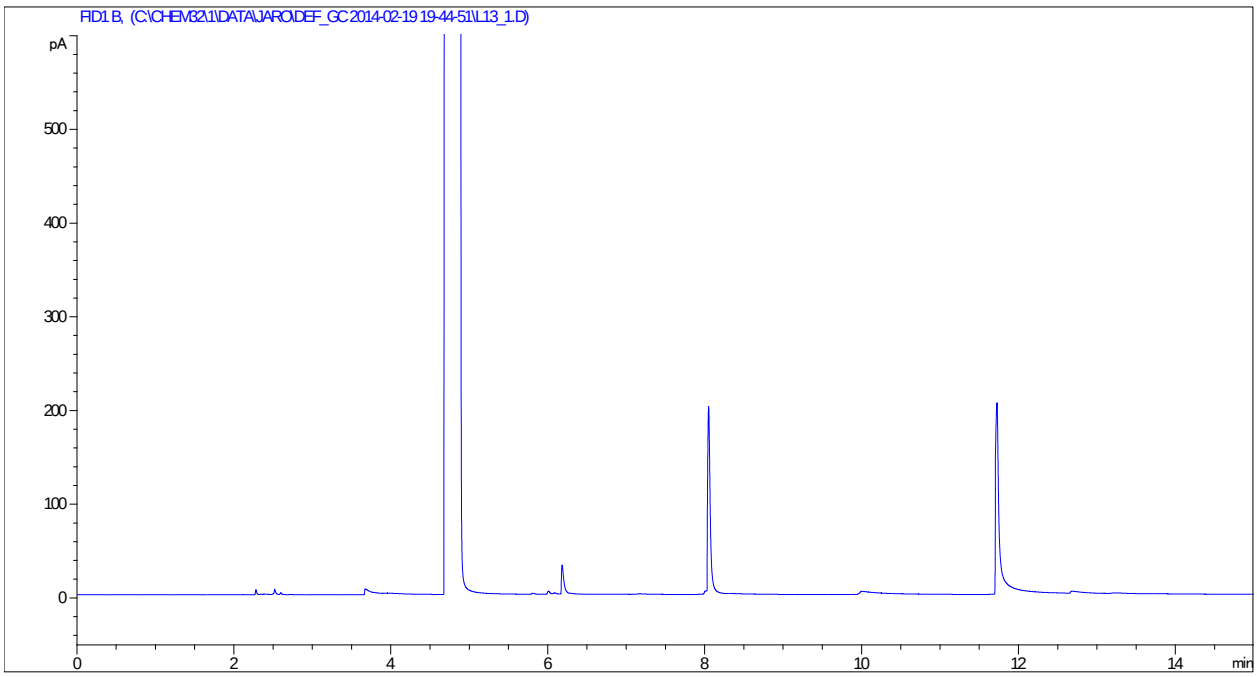


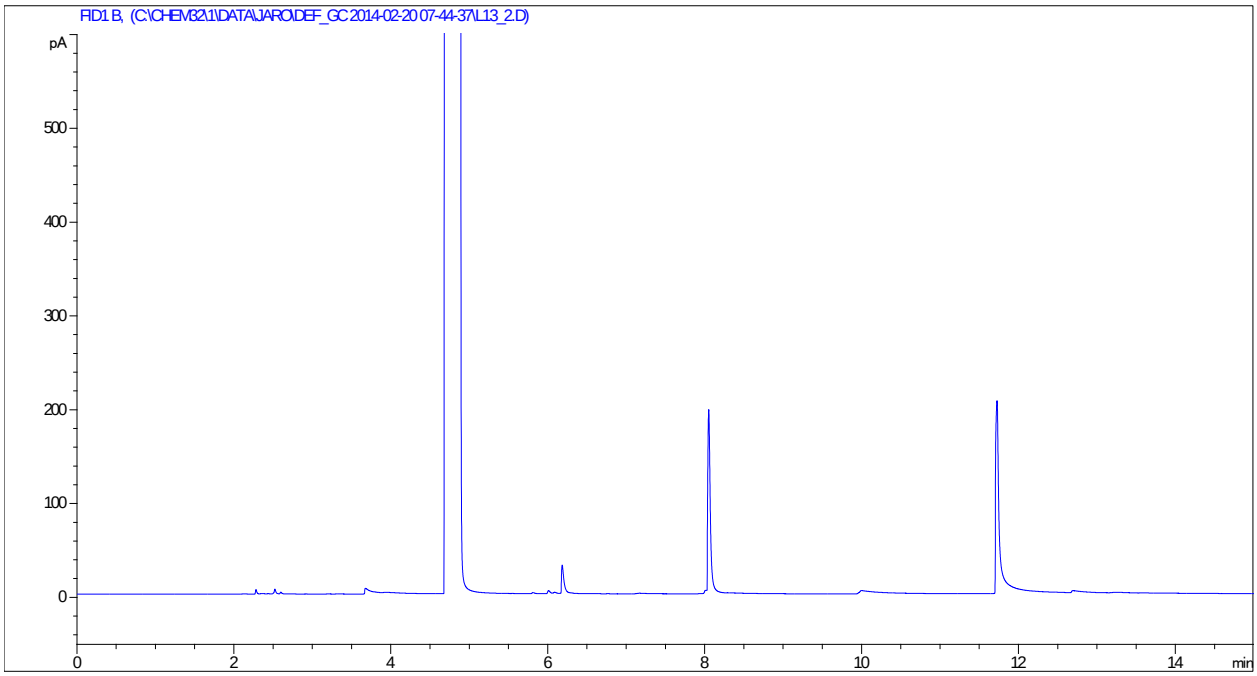
Figure S23: GC spectra after using ligand **L8**. (Reaction was done three times for reproducibility)

S3.9 Ligand L9



L9





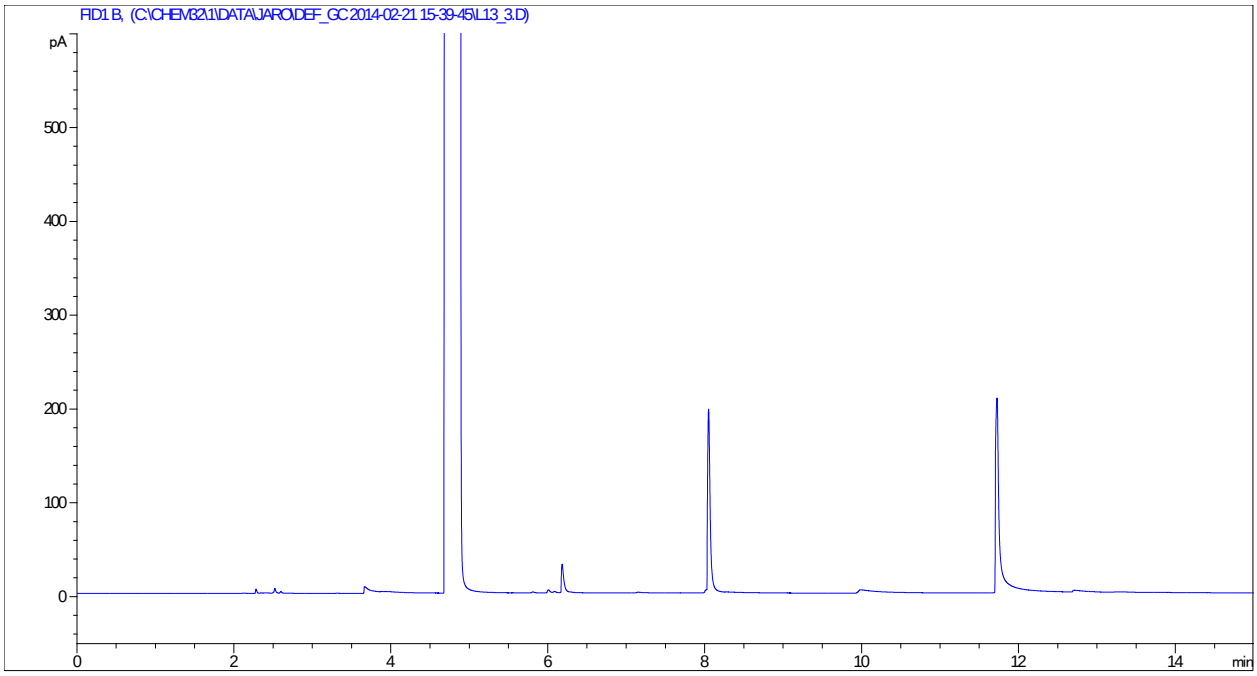
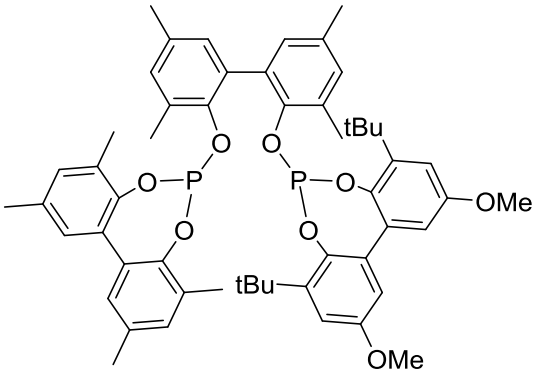
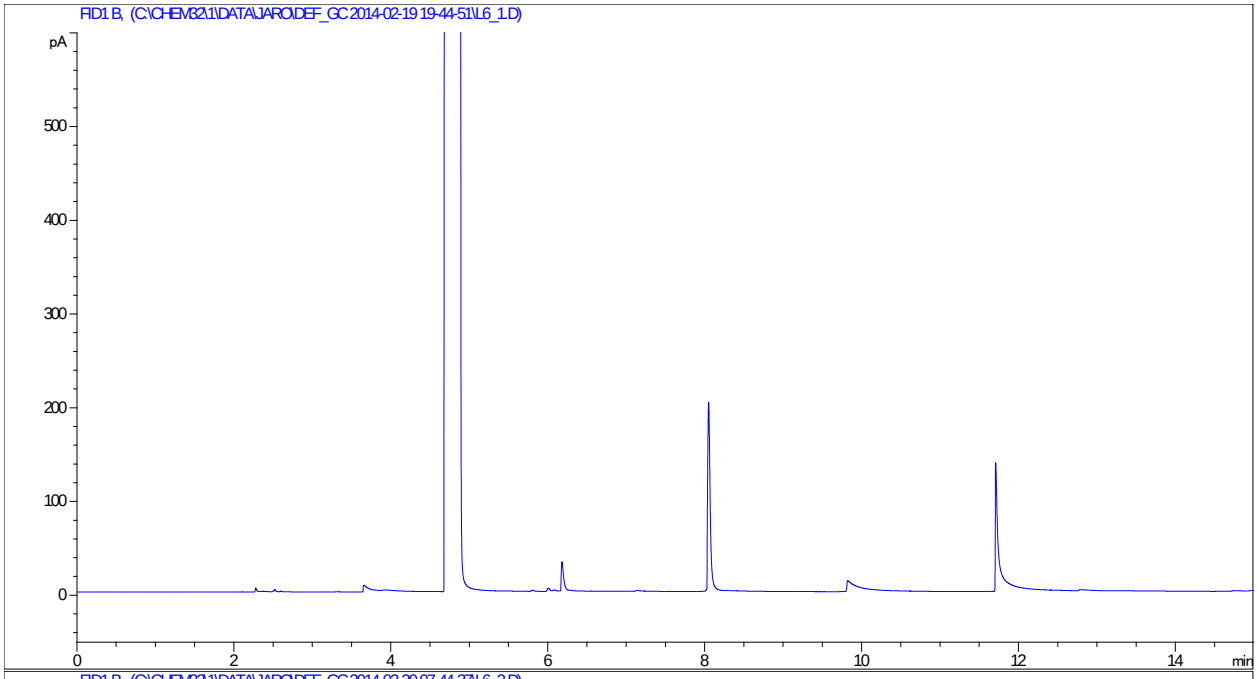


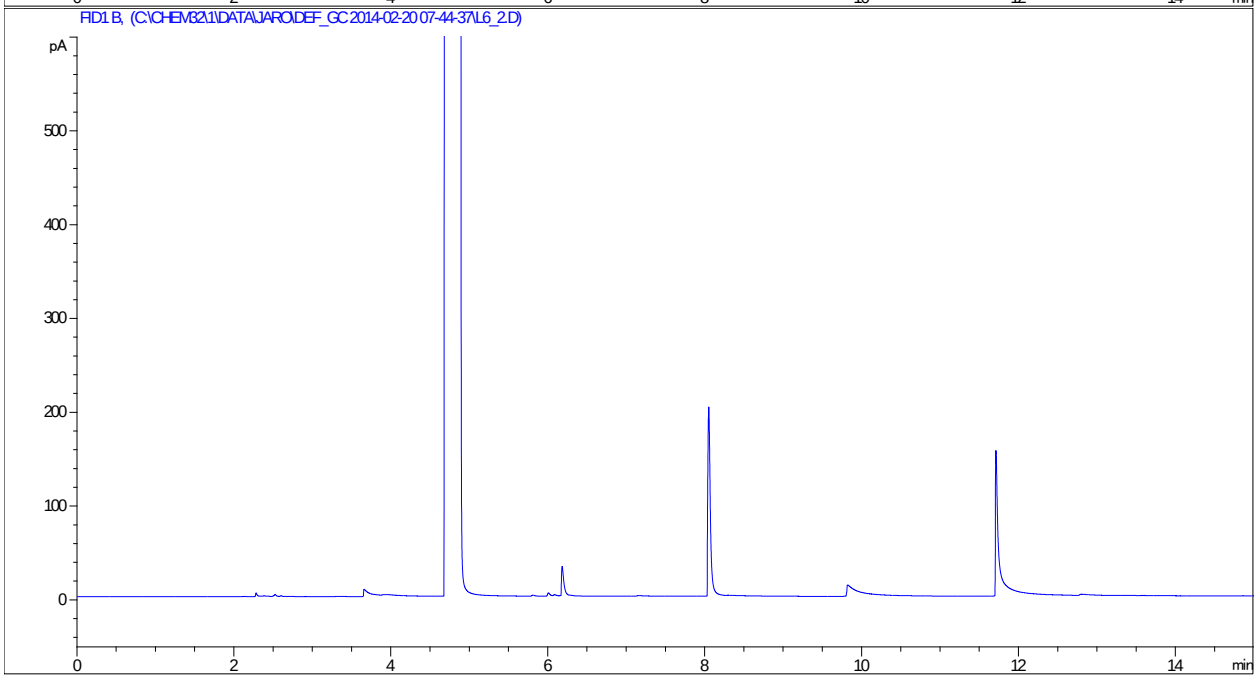
Figure S24: GC spectra after using ligand **L9**. (Reaction was done three times for reproducibility)

S3.10 Ligand L10



L10





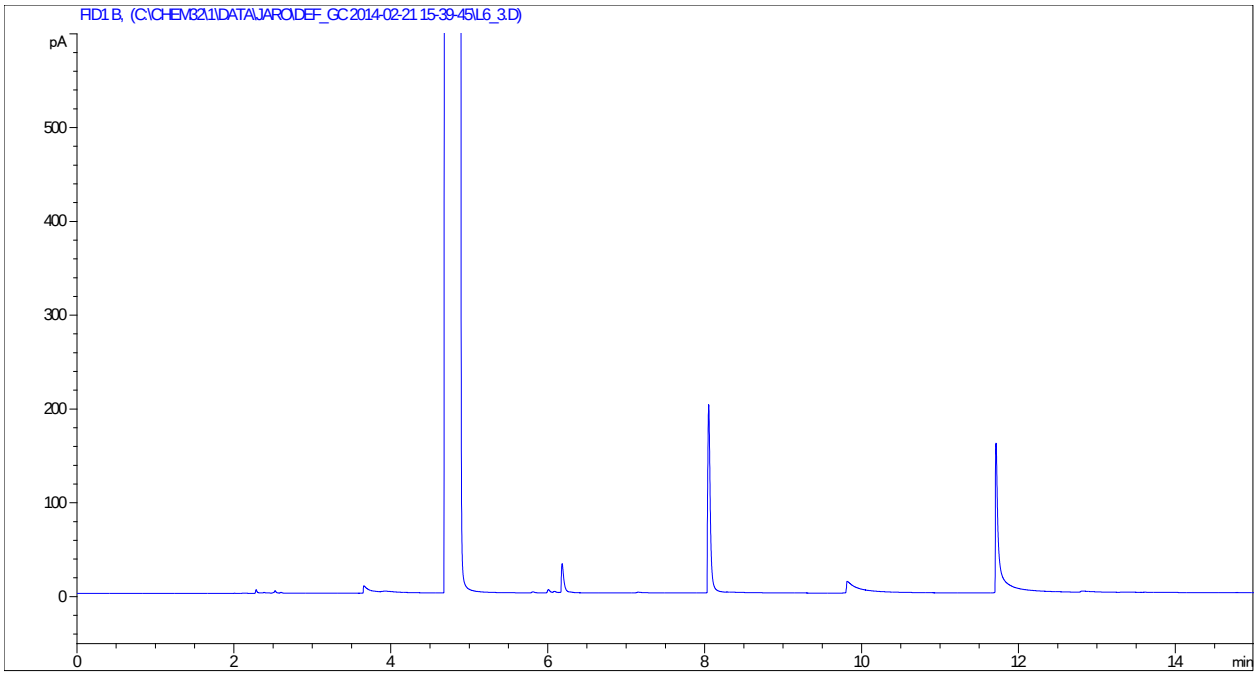
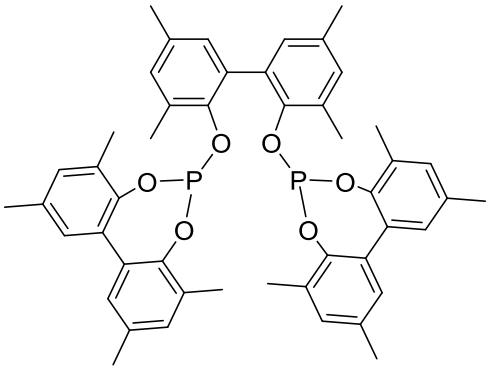
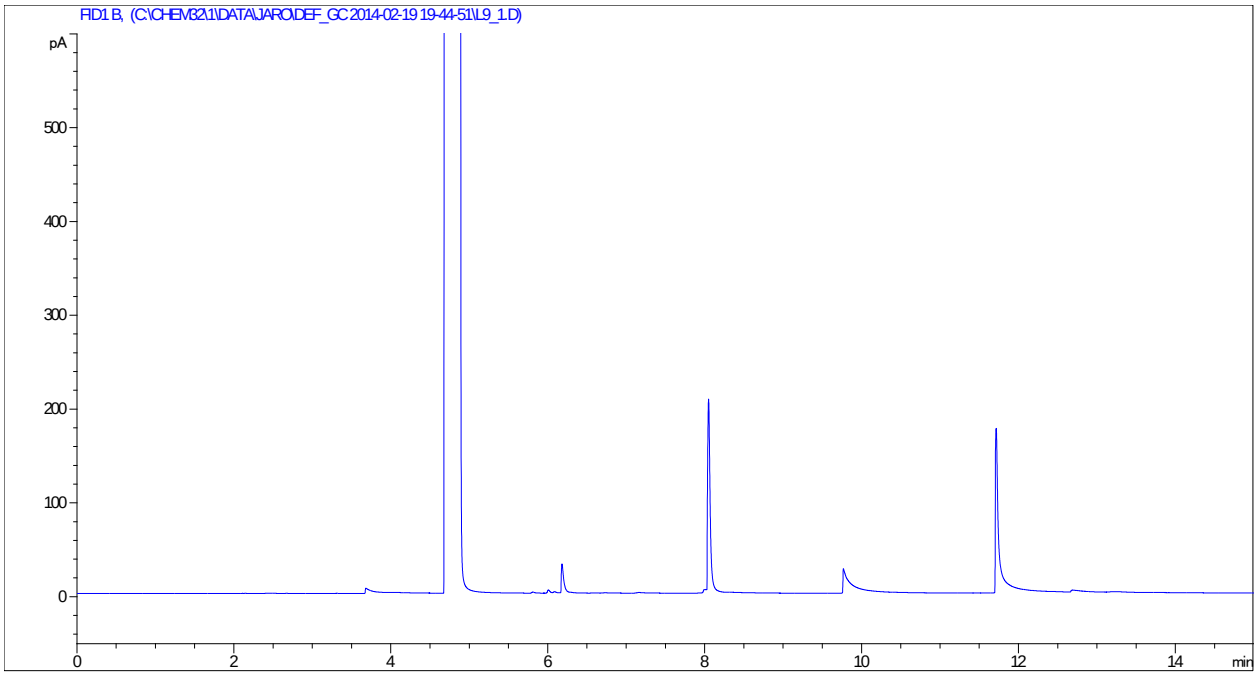


Figure S25: GC spectra after using ligand **L10**. (Reaction was done three times for reproducibility)

S3.11 Ligand L11



L11



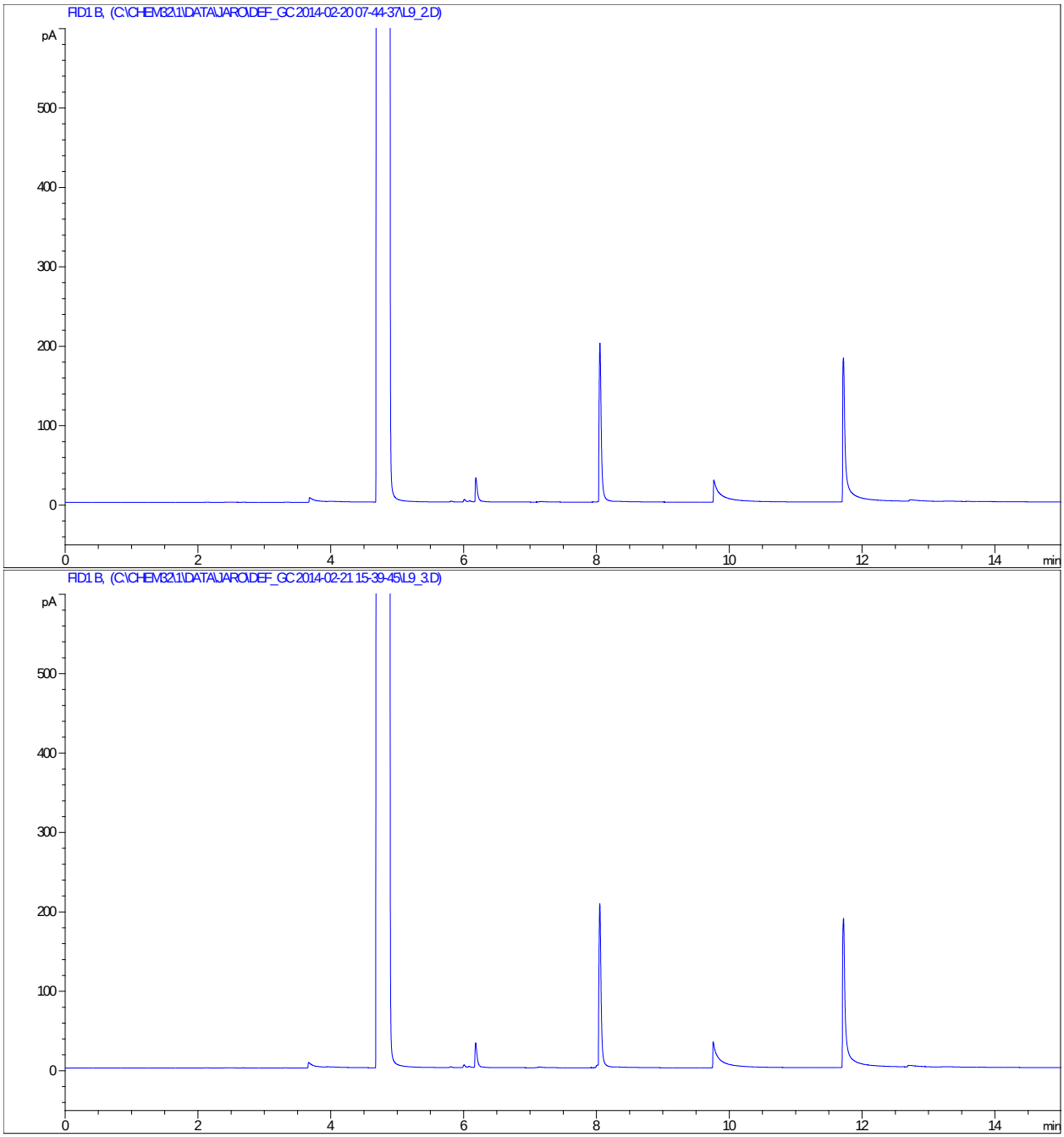
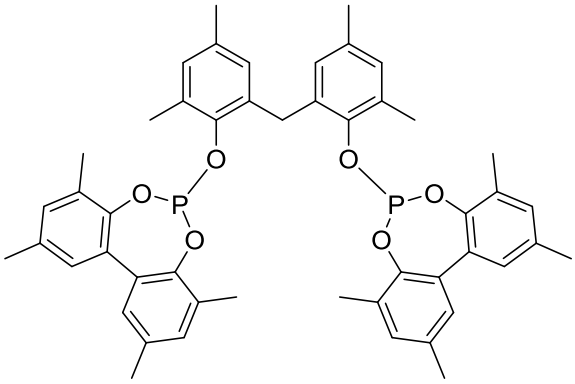
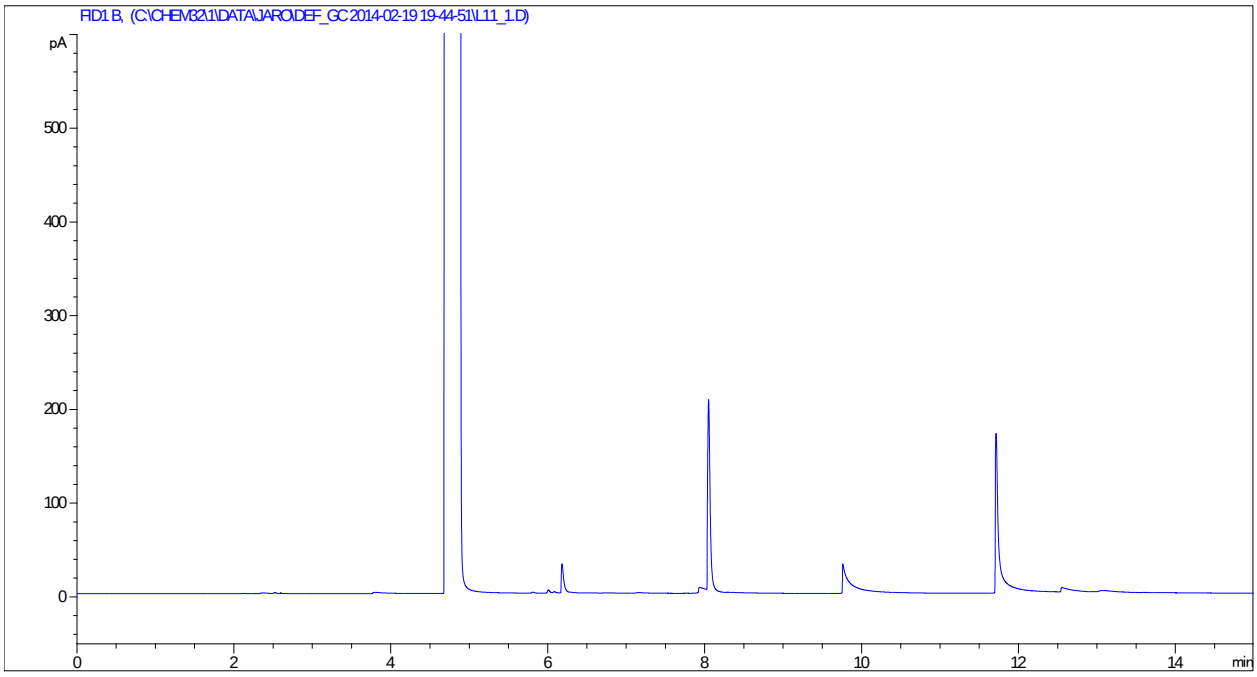


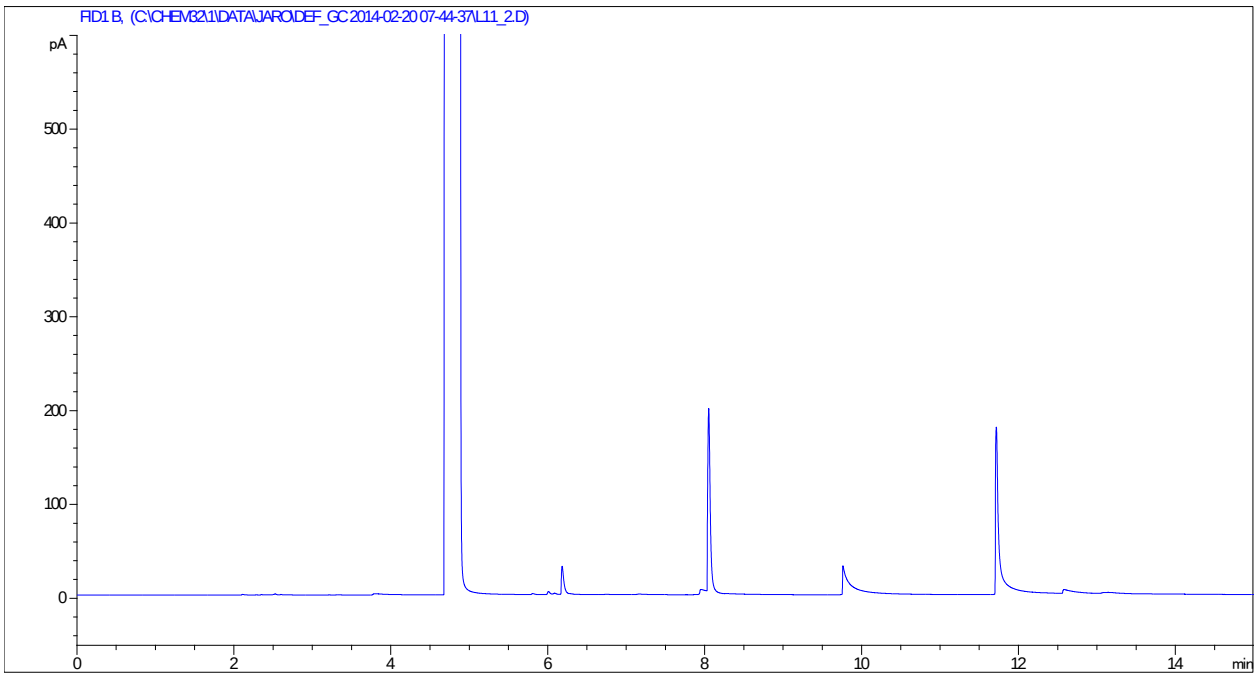
Figure S26: GC spectra after using ligand **L11**. (Reaction was done three times for reproducibility)

S3.12 Ligand L12



L12





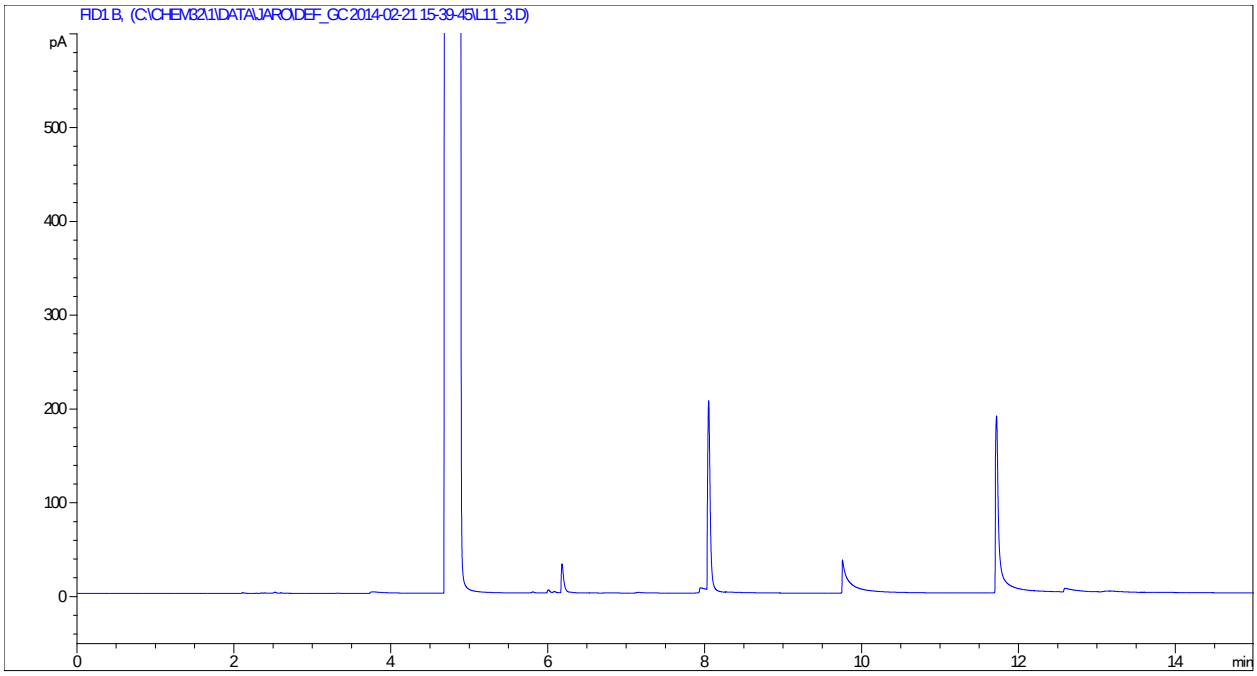
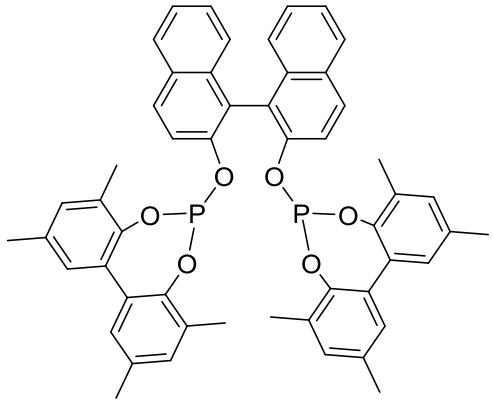
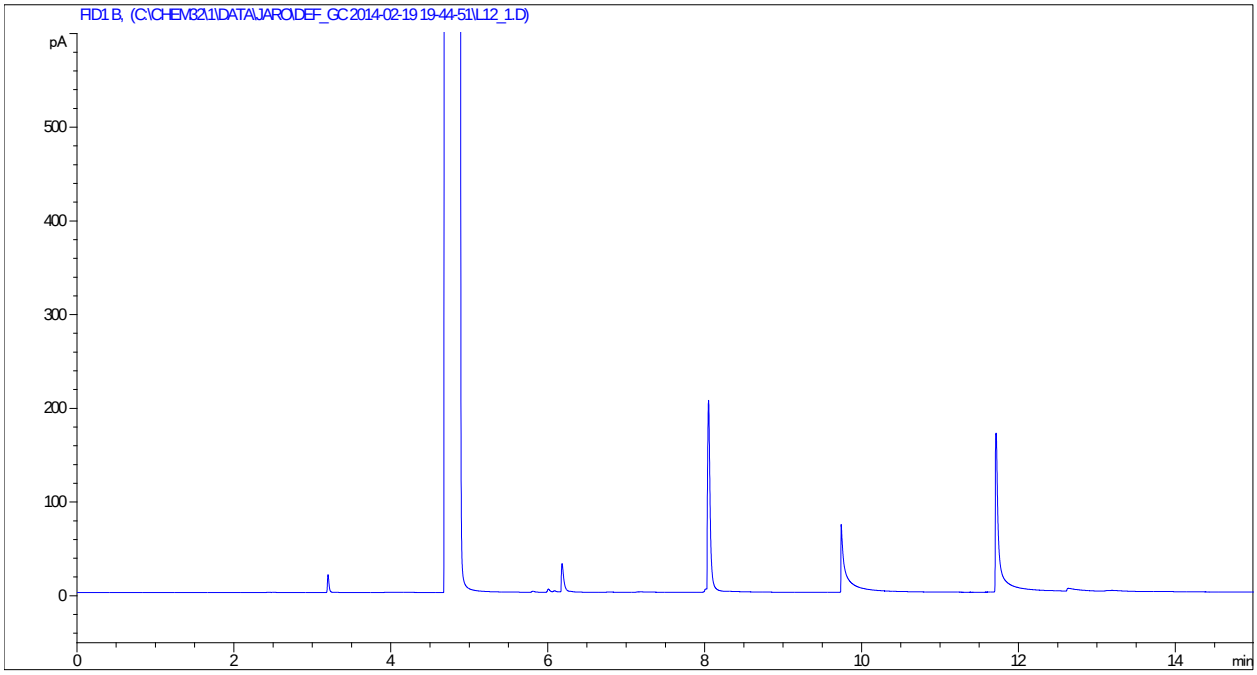


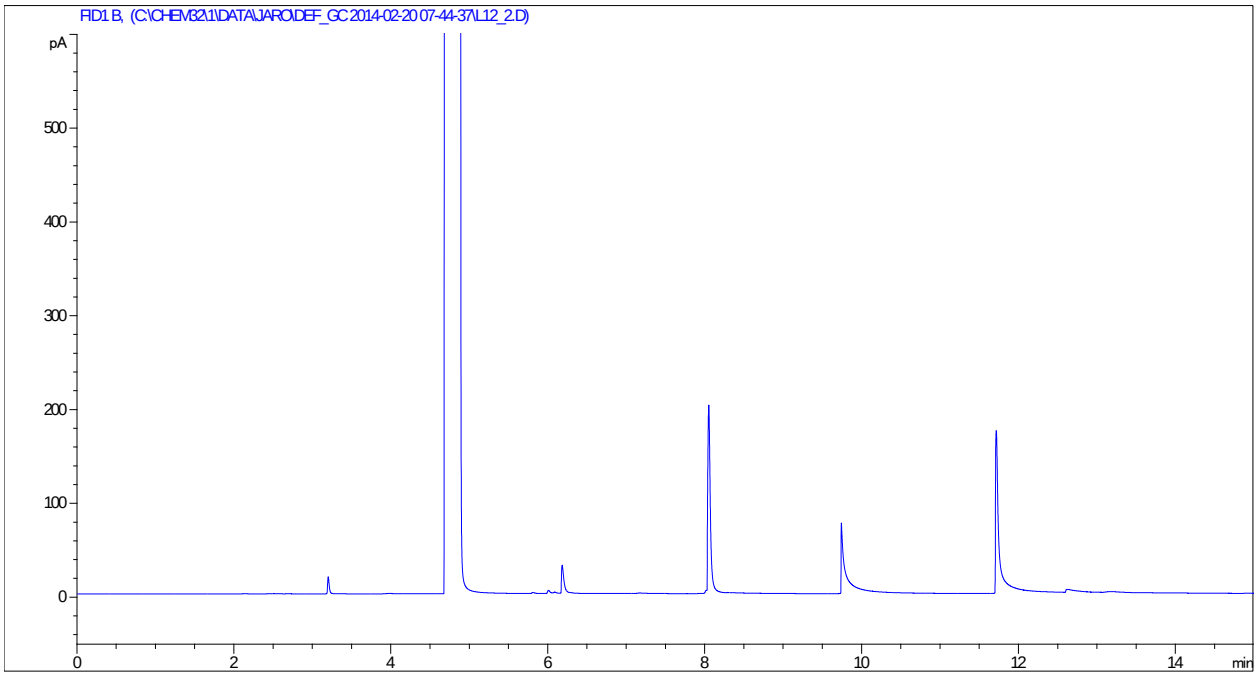
Figure S27: GC spectra after using ligand **L12**. (Reaction was done three times for reproducibility)

S3.13 Ligand L13



L13





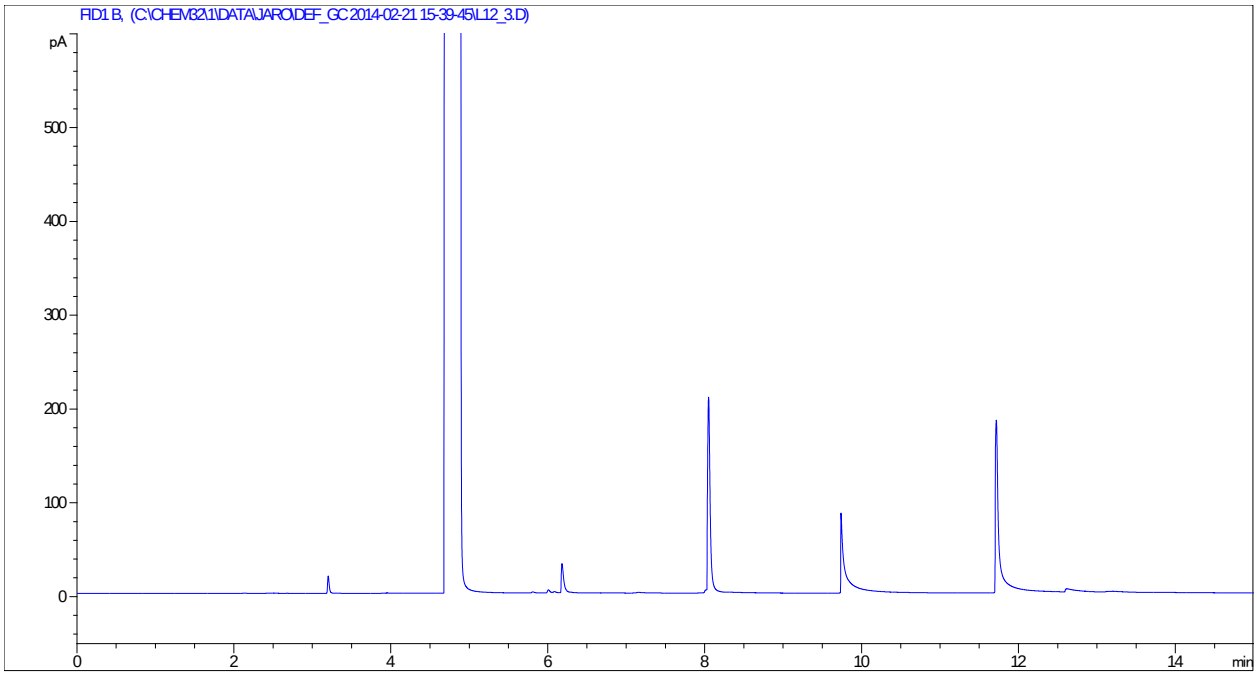
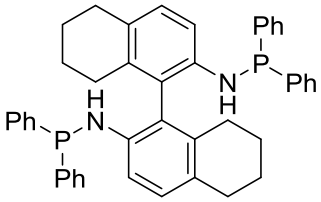
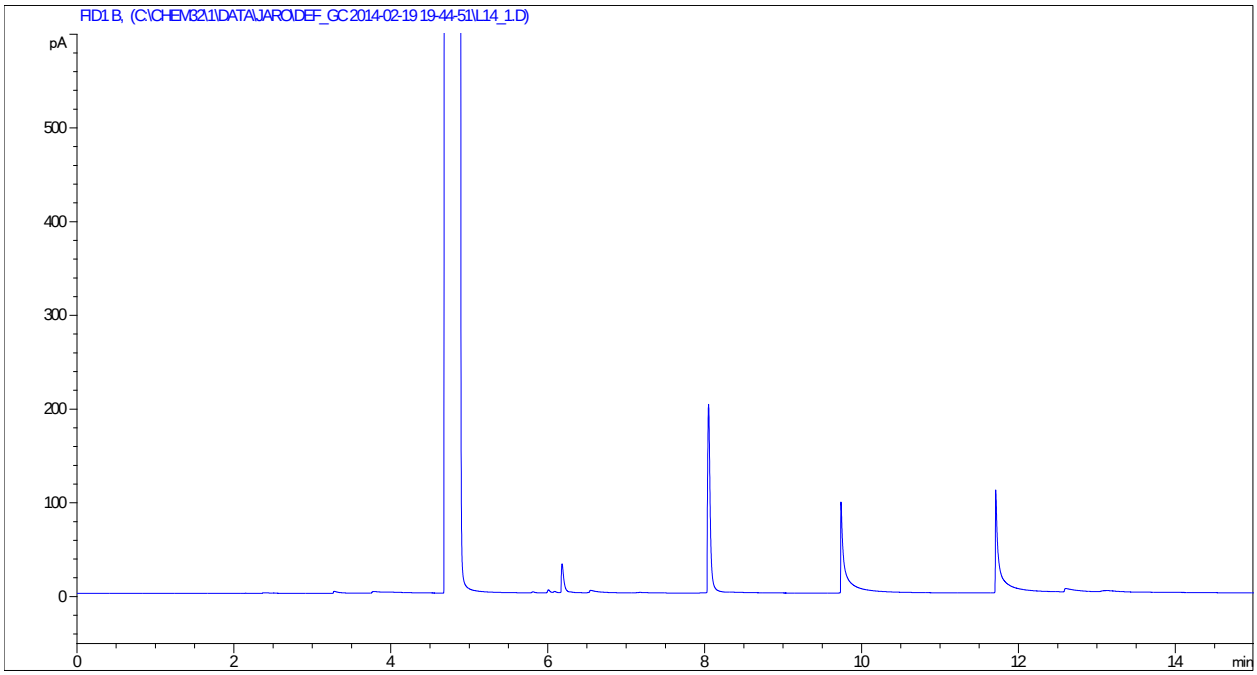


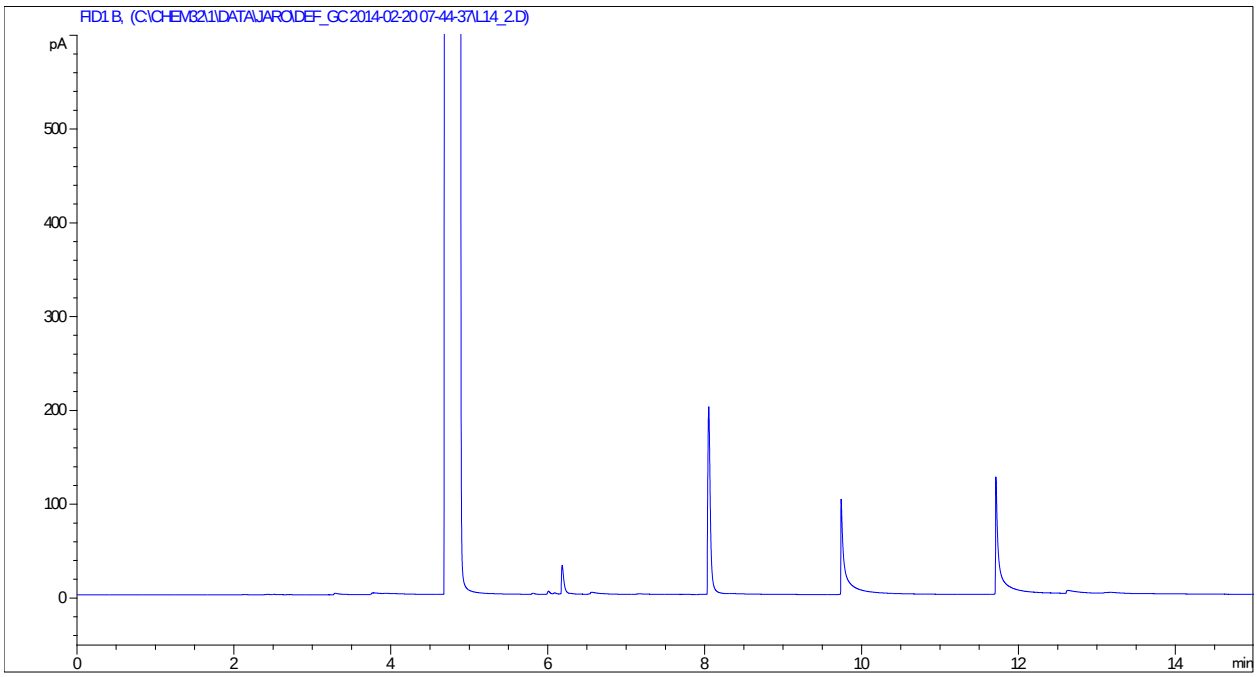
Figure S28: GC spectra after using ligand **L13**. (Reaction was done three times for reproducibility)

S3.14 Ligand L14



L14





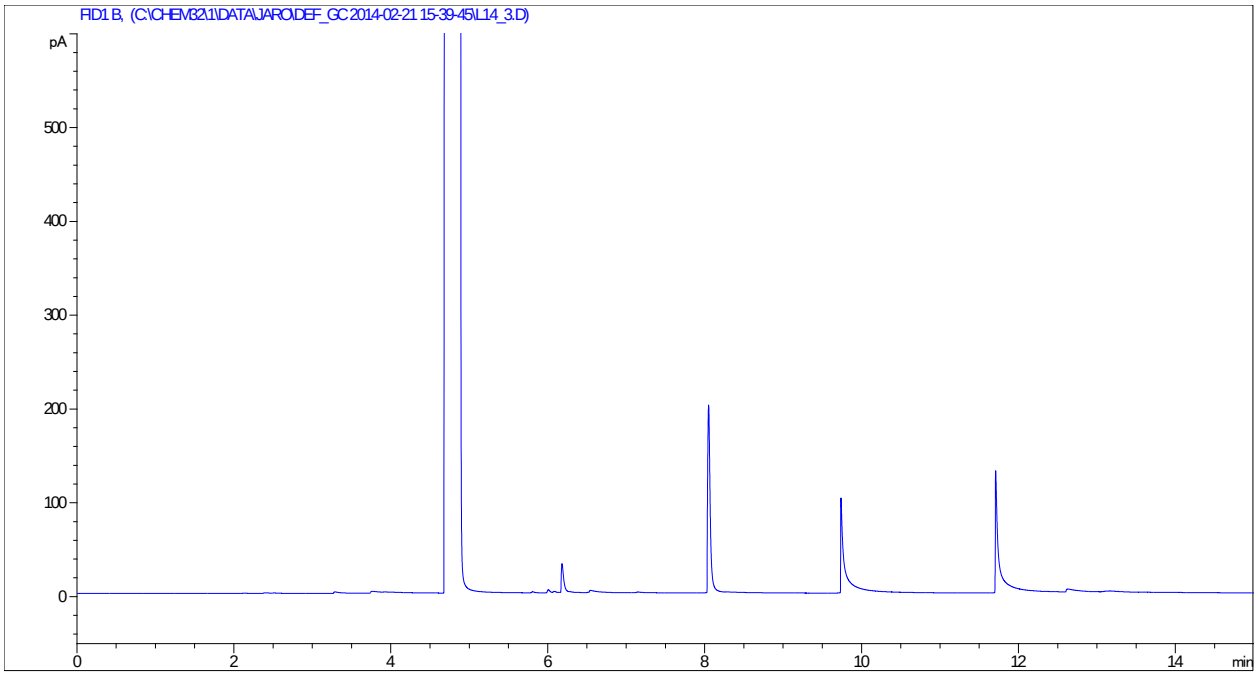
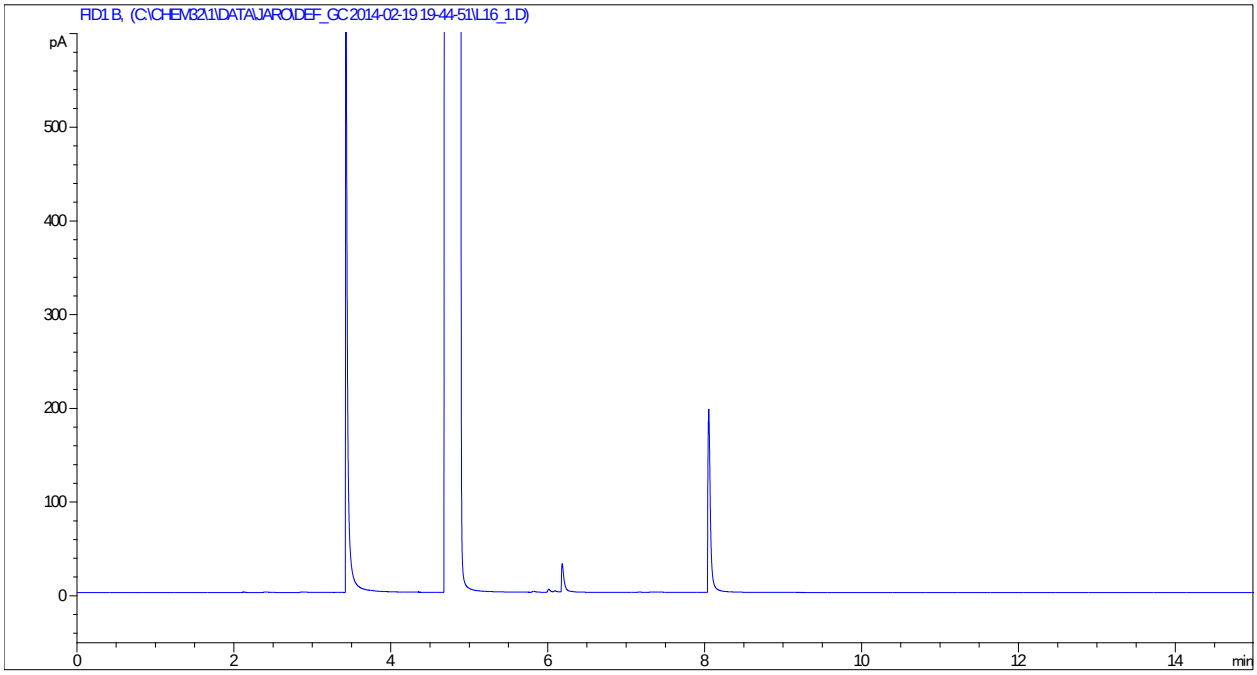
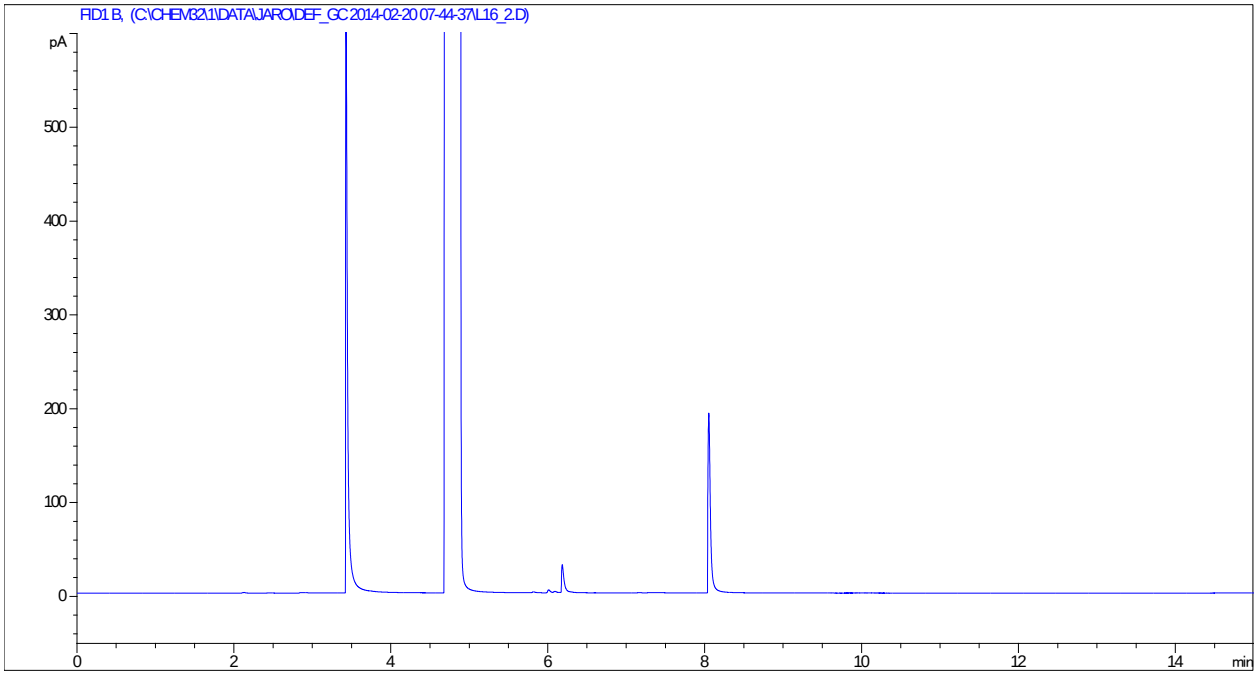


Figure S29: GC spectra after using ligand **L14**. (Reaction was done three times for reproducibility)

S3.15 No ligand





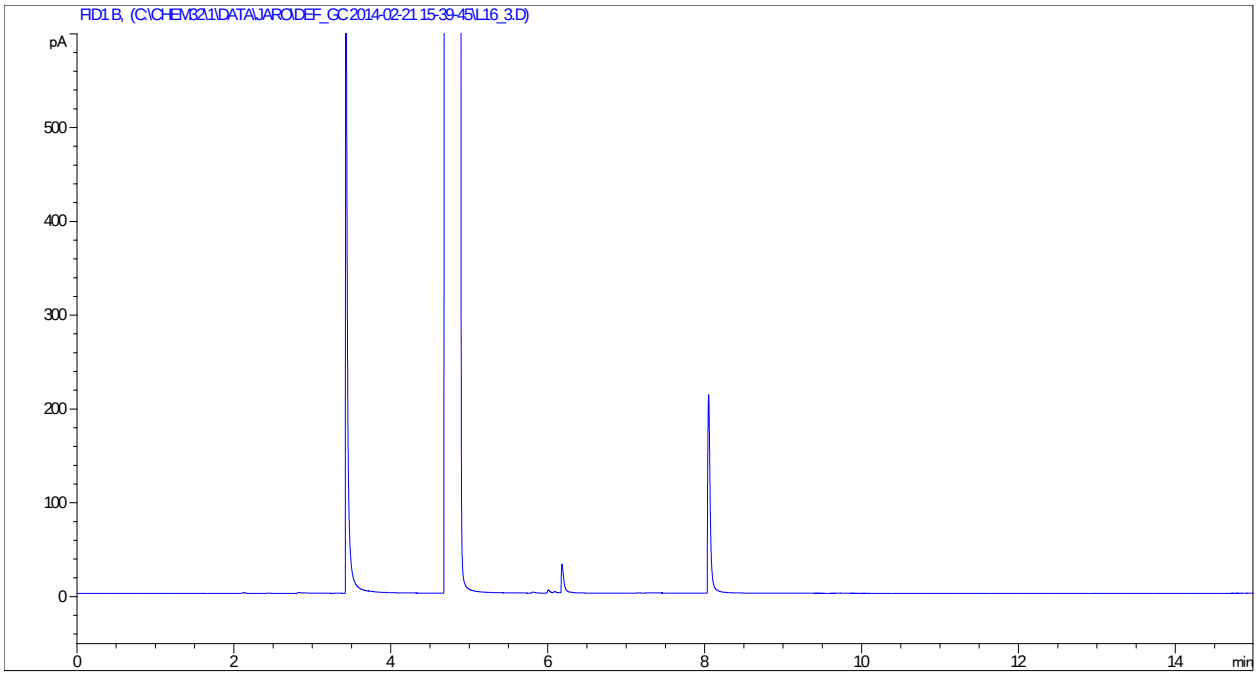


Figure S30: GC spectra after doing the reaction with no additional ligand. (Reaction was done three times for reproducibility)