Supporting Information
for

A Tetraphosphorus Ligand for Highly Regioselective Isomerization-Hydroformylation of Internal Olefins

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Content:

1. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of ligand **1**.

2.Repeated hydroformylation reaction data (to ensure reproducibility, each reaction was run for three times and analyzed by GC for two injections)

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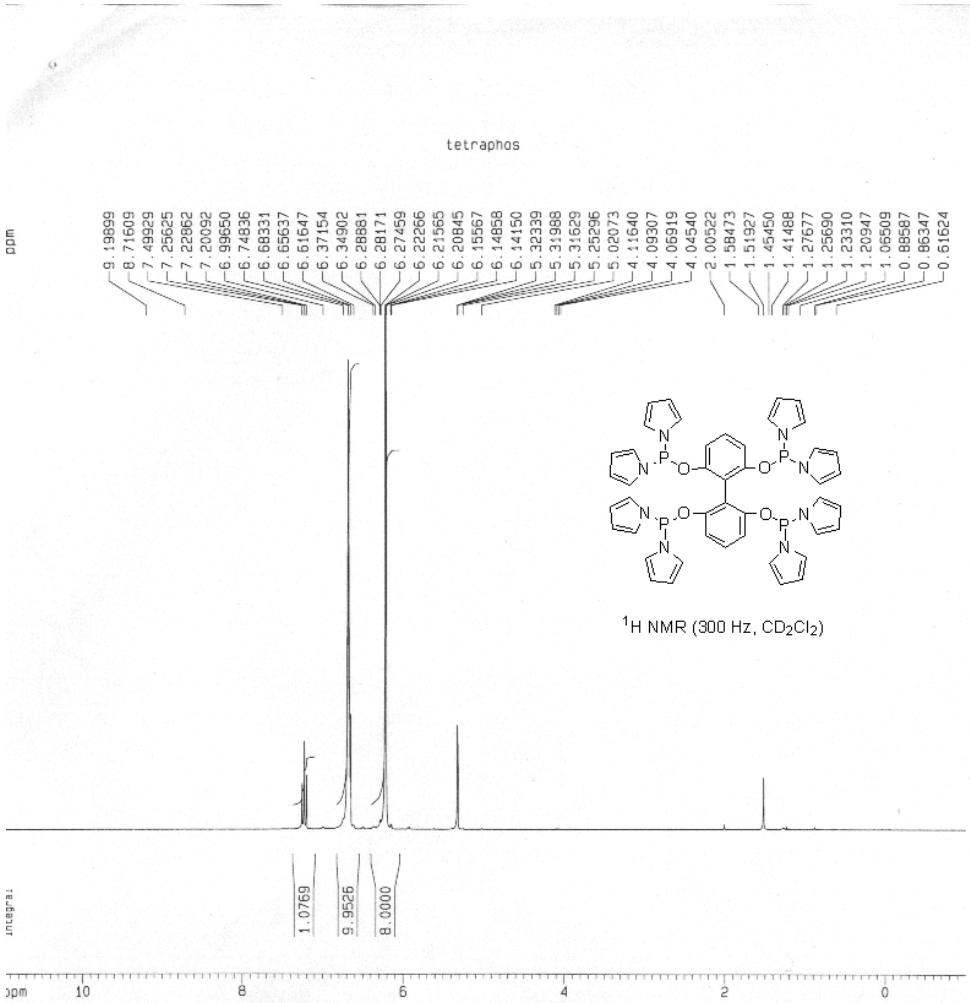
S2



^{1}H NMR (300 Hz, CD_2Cl_2)

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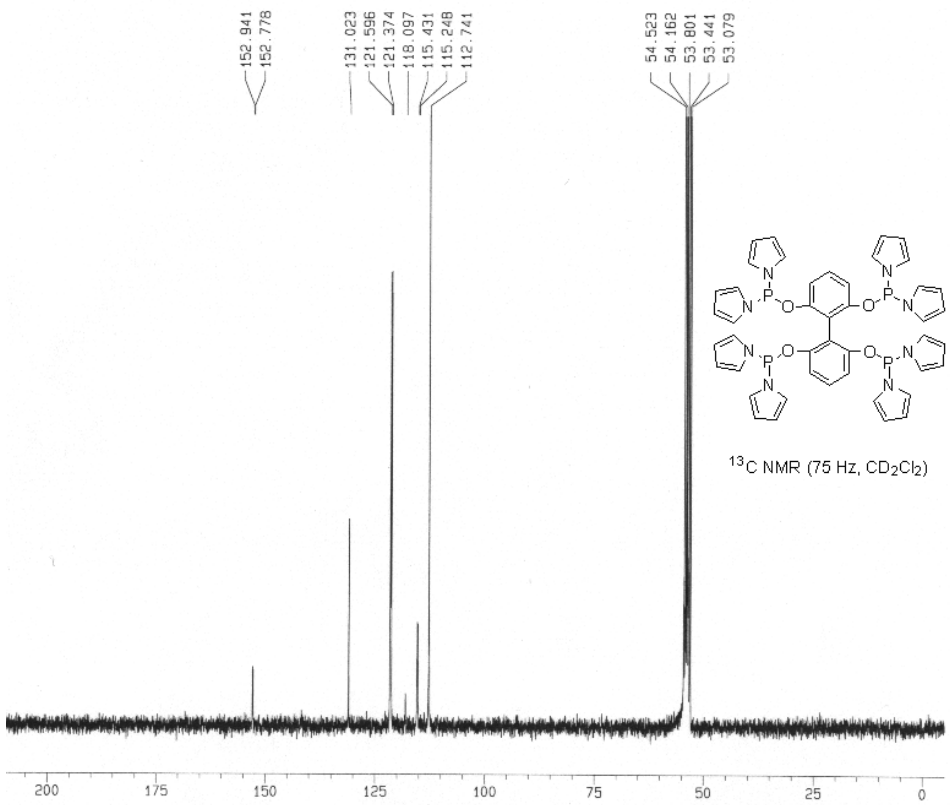
tetraphos



^{13}C NMR (75 Hz, CD_2Cl_2)

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^{31}P NMR (146Hz, CD_2Cl_2)

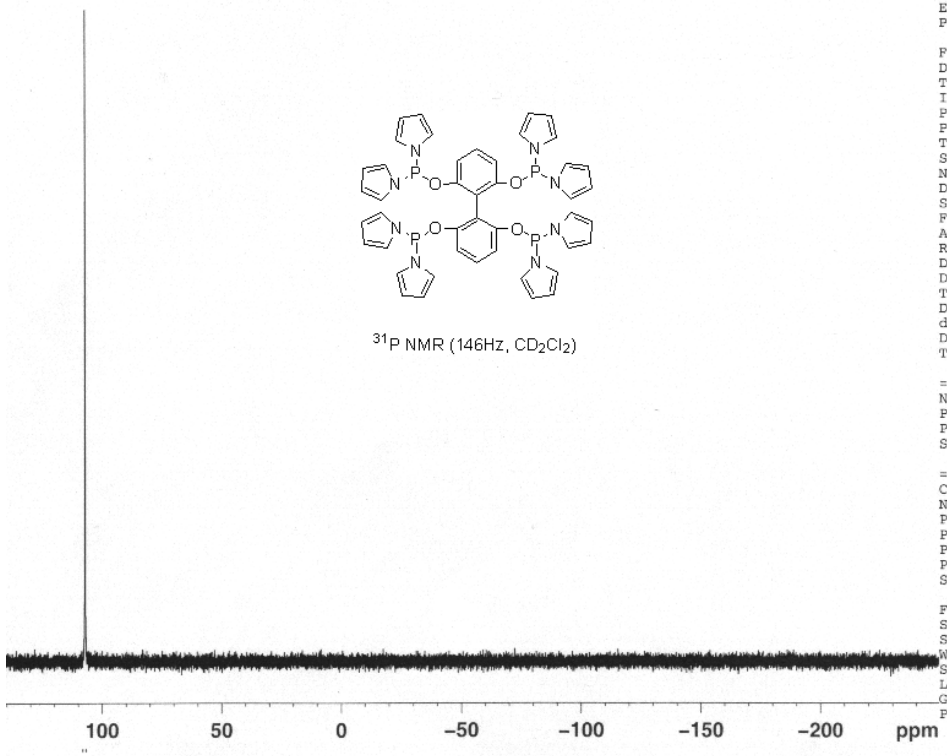


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Table **1**. Isomerization-hydroformylation of 2-octene with ligand **1** under different reaction conditions[a]

Entry	L/Rh	T (°C)	CO/H_2 (atm)	Run #	*n*:*i*[b]	Linear[c] (%)	TON[d]
1	1:1	100	10/10	1	17.2	94.5	1.7×10^3
				1[e]	17.5	94.6	1.8×10^3
				2	16.5	94.3	1.8×10^3
				2[e]	16.9	94.4	1.8×10^3
				3	17.6	94.6	1.7×10^3
				3[e]	17.3	94.6	1.7×10^3
2	2:1	100	10/10	1	41.3	97.6	1.6×10^3
				1[e]	42.2	97.7	1.5×10^3
				2	43.2	97.7	1.6×10^3
				2[e]	41.4	97.6	1.6×10^3
				3	41.4	97.7	1.5×10^3
				3[e]	43.1	97.7	1.5×10^3
3	4:1	100	10/10	1	45.5	97.8	1.6×10^3
				1[e]	44.8	97.8	1.6×10^3
				2	44.7	97.8	1.9×10^3
				2[e]	45.2	97.8	1.8×10^3
				3	46.0	97.9	1.8×10^3
				3[e]	46.0	97.9	1.7×10^3
4	3:1	120	10/10	1	30.2	96.8	3.1×10^3
				1[e]	31.0	96.9	3.1×10^3
				2	30.5	96.8	2.7×10^3
				2[e]	30.5	96.8	2.6×10^3
				3	30.5	96.8	2.9×10^3
				3[e]	30.4	96.8	3.0×10^3
5	3:1	100	10/10	1	48.0	98.0	1.6×10^3
				1[e]	47.8	97.9	1.6×10^3
				2	46.9	97.9	1.3×10^3
				2[e]	45.2	97.8	1.3×10^3
				3	46.6	97.9	1.6×10^3
				3[e]	45.6	97.9	1.6×10^3
6	3:1	80	10/10	1	47.0	97.9	8.9×10^2
				1[e]	47.7	97.9	7.7×10^2
				2	47.9	98.0	7.7×10^2
				2[e]	47.6	97.9	7.7×10^2
				3	47.8	97.9	8.1×10^2
				3[e]	47.9	98.0	8.1×10^2

7	3:1	60	10/10	1	54.4	98.2	1.5 x10^2
				1 [e]	53.5	98.2	1.5 x10^2
				2	53.2	98.2	1.5 x10^2
				2 [e]	54.1	98.2	1.5 x10^2
				3	54.1	98.2	1.4 x10^2
				3 [e]	53.3	98.2	1.5 x10^2
8	3:1	100	30/30	1	22.3	95.7	3.9 x10^2
				1 [e]	24.5	96.1	3.9 x10^2
				2	24.0	96.0	3.9 x10^2
				2 [e]	24.4	96.1	3.9 x10^2
				3	23.1	95.9	3.9 x10^2
				3 [e]	23.7	95.9	3.8 x10^2
9	3:1	100	20/20	1	29.0	96.7	5.7 x10^2
				1 [e]	29.6	96.7	6.3 x10^2
				2	29.7	96.7	5.5 x10^2
				2 [e]	31.0	96.9	5.6 x10^2
				3	30.8	96.9	5.1 x10^2
				3 [e]	30.0	96.8	5.1 x10^2
10	3:1	100	5/5	1	53.1	98.2	1.5 x10^2
				1 [e]	52.0	98.1	1.5 x10^2
				2	53.1	98.2	1.5 x10^2
				2 [e]	49.7	98.0	1.5 x10^2
				3	50.5	98.1	1.5 x10^2
				3 [e]	52.1	98.1	1.5 x10^2

[a]S/C = 10000, [Rh] = 0.57 mM, t = 1 h, toluene as solvent, decane as internal standard. [b]Linear/branched ratio, determined based on GC. [c]Percentage of linear aldehyde in all aldehydes. [d]Turn over number, determined based on GC. [e]Data obtained after second GC injection.

Table **2**. Isomerization-hydroformylation of internal olefins with ligand **1** and **2**[a]

Entry	Substrate	L	t (h)	Run #	*n:i*[b]	Linear [c] (%)	TON[d]
1	2-octene	**1**	1	1	53.1	98.2	1.5 x10^3
				1 [e]	52.0	98.1	1.5 x10^3
				2	53.1	98.2	1.5 x10^3
				2 [e]	49.7	98.0	1.5 x10^3
				3	50.5	98.1	1.5 x10^3
				3 [e]	52.1	98.1	1.5 x10^3
2	2-octene	**1**	12	1	36.1	97.3	7.9 x10^3

				1 [e]	36.5	97.3	8.0 x10^3
				2	38.8	97.5	7.8 x10^3
				2 [e]	39.1	97.5	7.8 x10^3
				3	36.6	97.3	7.7 x10^3
				3 [e]	37.6	97.4	7.8 x10^3
3	2-octene	**2**	1	1	10.8	91.5	2.6 x10^3
				1 [e]	10.9	91.6	2.5 x10^3
				2	11.2	91.8	2.4 x10^3
				2 [e]	11.2	91.8	2.4 x10^3
				3	11.2	91.8	2.6 x10^3
				3 [e]	11.3	91.9	2.2 x10^3
4	2-octene	**2**	12	1	5.94	85.6	8.6 x10^3
				1 [e]	6.40	86.5	8.6 x10^3
				2	6.15	86.0	8.7 x10^3
				2 [e]	6.37	86.4	8.4 x10^3
				3	5.72	85.1	8.3 x10^3
				3 [e]	6.44	86.5	8.3 x10^3
5	2-hexene	**1**	1	1	80.8	98.8	1.8 x10^3
				1 [e]	80.0	98.8	1.8 x10^3
				2	75.9	98.7	1.8 x10^3
				2 [e]	75.5	98.7	1.8 x10^3
				3	76.3	98.7	1.8 x10^3
				3 [e]	76.6	98.7	1.8 x10^3
6	2-hexene	**1**	12	1	52.9	98.1	6.2 x10^3
				1 [e]	51.7	98.1	6.0 x10^3
				2	52.9	98.1	6.2 x10^3
				2 [e]	53.1	98.2	6.1 x10^3
				3	52.1	98.1	6.0 x10^3
				3 [e]	53.9	98.1	6.0 x10^3
7	2-hexene	**2**	1	1	15.1	93.8	2.3 x10^3
				1 [e]	15.4	93.9	2.3 x10^3
				2	15.0	93.8	2.3 x10^3
				2 [e]	15.0	93.7	2.3 x10^3
				3	15.0	93.7	2.2 x10^3
				3 [e]	15.1	93.8	2.2 x10^3
8	2-hexene	**2**	12	1	13.5	93.1	6.7 x10^3
				1 [e]	13.6	93.1	6.8 x10^3
				2	13.7	93.2	6.8 x10^3
				2 [e]	14.0	93.2	6.7 x10^3
				3	14.0	93.3	6.7 x10^3
				3 [e]	13.8	93.2	6.8 x10^3

[a]S/C = 10000, [Rh] = 0.69 mM (for 2-hexene) or 0.57 mM (for 2-octene), Ligand/Rh ratio = 3:1, temperature = 100°C, CO/H_2 = 5/5 atm, toluene as solvent, decane as internal standard. [b,c,d,e] See Table 1

Table **3**: Hydroformylation of 1-octene with ligand 1 under different reaction conditions[a]

entry	T (°C)	CO/H_2 (atm)	Run #	*n*:*i*[b]	linear(%)[c]	isomerization (%)[d]	TON[e]
1	100	10/10	1	208	99.5	19.6	6.9 x10^3
			1[f]	238	99.6	19.7	7.0 x10^3
			2	211	99.5	22.3	6.8 x10^3
			2[f]	207	99.5	22.5	6.9 x10^3
			3	205	99.5	22.2	6.8 x10^3
			3[f]	228	99.6	21.7	6.9 x10^3
2	80	10/10	1	362	99.7	18.3	7.3 x10^3
			1[f]	375	99.7	18.1	7.4 x10^3
			2	362	99.7	19.5	7.3 x10^3
			2[f]	364	99.7	18.5	7.1 x10^3
			3	375	99.7	18.8	7.3 x10^3
			3[f]	364	99.7	18.7	7.0 x10^3
3	60	10/10	1	432	99.8	5.9	3.9 x10^3
			1[f]	436	99.8	5.9	3.9 x10^3
			2	447	99.8	5.7	3.5 x10^3
			2[f]	430	99.8	5.6	3.6 x10^3
			3	426	99.8	5.8	3.8 x10^3
			3[f]	435	99.8	5.9	3.7 x10^3
4	40	10/10	1	451	99.8	3.5	0.59 x10^3
			1[f]	458	99.8	3.4	0.60 x10^3
			2	441	99.8	3.5	0.60 x10^3
			2[f]	460	99.8	3.6	0.63 x10^3
			3	456	99.8	3.2	0.64 x10^3
			3[f]	451	99.8	3.6	0.61 x10^3
5	80	30/30	1	239	99.6	7.4	7.6 x10^3
			1[f]	265	99.6	7.5	7.6 x10^3
			2	270	99.6	7.3	7.1 x10^3
			2[f]	268	99.6	6.9	7.1 x10^3
			3	254	99.6	6.2	7.7 x10^3
			3[f]	244	99.6	6.3	7.7 x10^3

6	80	5/5	1	373	99.7	26.4	5.8 x10^3
			1[f]	399	99.8	26.8	6.1 x10^3
			2	406	99.8	27.5	5.7 x10^3
			2[f]	407	99.8	27.8	5.7 x10^3
			3	405	99.8	30.7	6.6 x10^3
			3[f]	386	99.7	26.9	5.6 x10^3

[a]S/C = 10000, [Rh] = 0.2 mM, ligand/Rh ratio = 3:1, reaction time = 1 h, toluene as solvent, decane as internal standard. [b,c,e] See Table 1. [d]Isomerization to 2-olefin. [f]Data obtained after second GC injection.

Table 4: Hydroformylation of terminal olefins with ligand **1** and **2** [a]

entry	substrate	L	Run #	*n:i*[b]	linear (%)[c]	isomerization (%)[d]	TON[e]
1	1-octene	**1**	1	362	99.7	18.3	7.3 x10^3
			1[f]	375	99.7	18.1	7.4 x10^3
			2	362	99.7	19.5	7.3 x10^3
			2[f]	364	99.7	18.5	7.1 x10^3
			3	375	99.7	18.8	7.3 x10^3
			3[f]	364	99.7	18.7	7.0 x10^3
2	1-octene	**2**	1	69.5	98.6	10.6	8.0 x10^3
			1[f]	70.3	98.6	9.74	8.1 x10^3
			2	73.5	98.7	9.75	8.2 x10^3
			2[f]	73.1	98.6	10.1	8.0 x10^3
			3	76.7	98.7	11.1	8.1 x10^3
			3[f]	76.6	98.7	10.8	8.0 x10^3
3	1-hexene	**1**	1	380	99.7	14.6	7.5x10^3
			1[f]	382	99.7	17.1	7.1 x10^3
			2	360	99.7	17.1	8.2 x10^3
			2[f]	364	99.7	15.4	7.4 x10^3
			3	377	99.7	15.9	7.3 x10^3
			3[f]	372	99.7	18.6	6.9 x10^3
4	1-hexene	**2**	1	79.6	98.8	12.3	8.0 x10^3
			1[f]	80.3	98.8	12.3	8.0 x10^3
			2	80.0	98.8	12.3	8.0 x10^3
			2[f]	79.8	98.8	12.3	8.0 x10^3
			3	78.6	98.7	12.3	8.0 x10^3
			3[f]	80.7	98.8	12.3	8.0 x10^3

[a]S/C = 10000, [Rh] = 0.2 mM, ligand/Rh ratio = 3:1, temperature = 80 ^{o}C, CO/H_2 = 10/10 atm, reaction time = 1h, toluene as solvent, decane as internal standard. [b,c,e] See Table 1. [d,,f] See Table 3.