

Supplementary Materials

Trivinylphosphine Oxide: Synthesis, Characterization, and Polymerization Reactivity Investigated via Single Crystal Analysis and Density Functional Theory

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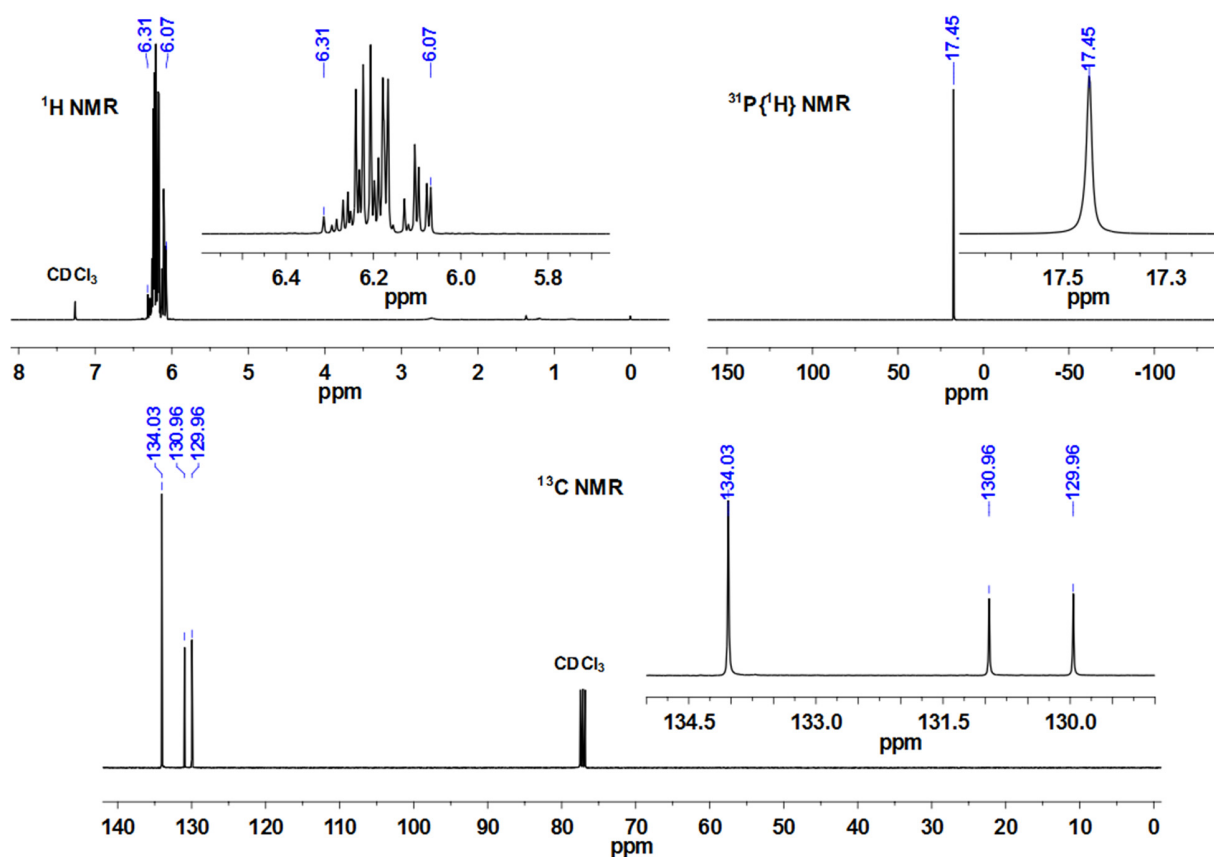


Figure S1: ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (400 MHz, CDCl₃) of trivinylphosphine oxide (TVPO)

Table S1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TVPO. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
C1	3911(2)	6181.5(16)	3041(2)	32.1(4)
C2	4451(3)	7500	-2025(4)	41.1(7)
C3	4785(3)	7500	-220(4)	33.5(6)
C5	3010(2)	5280.9(18)	3340(3)	41.0(5)
O1	2013.5(17)	7500	900(2)	28.6(4)
P1	3486.4(6)	7500	1611.5(9)	24.5(2)

Table S2: Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TVPO. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$

Atom	U11	U22	U33	U23	U13	U12
C1	32.7(9)	32.7(9)	30.9(9)	2.4(7)	-1.7(8)	5.4(8)
C2	46.2(17)	41.4(15)	35.8(15)	0	8.4(13)	0
C3	30.7(14)	33.6(13)	36.2(14)	0	4.8(12)	0
C5	49.2(12)	32.2(10)	41.7(11)	10.4(8)	-4.7(9)	1.0(9)
O1	23.3(9)	27.1(9)	35.4(9)	0	-4.0(8)	0
P1	24.4(4)	22.7(4)	26.3(4)	0	-0.1(2)	0

Table S3: Bond Angles for TVPO

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	C1	P1	122.14(15)	C3	P1	C1	104.65(8)
C2	C3	P1	122.4(2)	O1	P1	C1 ¹	113.74(7)
C1	P1	C11	105.19(12)	O1	P1	C1	113.74(7)
C3	P1	C11	104.65(8)	O1	P1	C3	113.89(11)

¹+X,3/2-Y,+Z

Table S4: Torsion Angles for TVPO

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C3	P1	C1	124.81(7)	C5	C1	P1	C1 ¹	128.18(15)
C2	C3	P1	C1 ¹	-124.81(7)	C5	C1	P1	C3	-121.83(18)
C2	C3	P1	O1	0.000(0)	C5	C1	P1	O1	3.1(2)

¹+X,3/2-Y,+Z
Table S5: Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for TVPO

Atom	x	y	z	U(eq)
H1	4818.4	6132.44	3602.21	39
H2A	3489.29	7500	-2396.93	49
H2B	5171.16	7500	-2959.75	49
H3	5752.26	7500	124.25	40
H5A	2097.83	5315.47	2788.91	49
H5B	3269.33	4593.46	4106.6	49

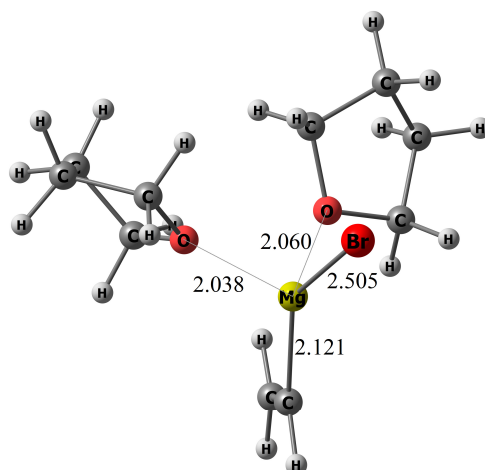


Figure S2: 3-D view of the structure of model compound TVPO.2THF.

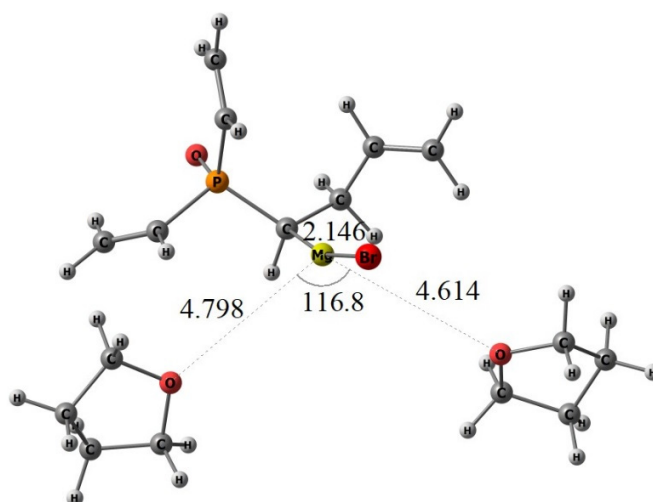


Figure S3: 3-D view of the structure of I1 in the presence of two explicit THF molecules. The distance between the Mg metal ion and the closest THF is about 4.6 Å. The effect of THF on the geometry of I1 is insignificant.

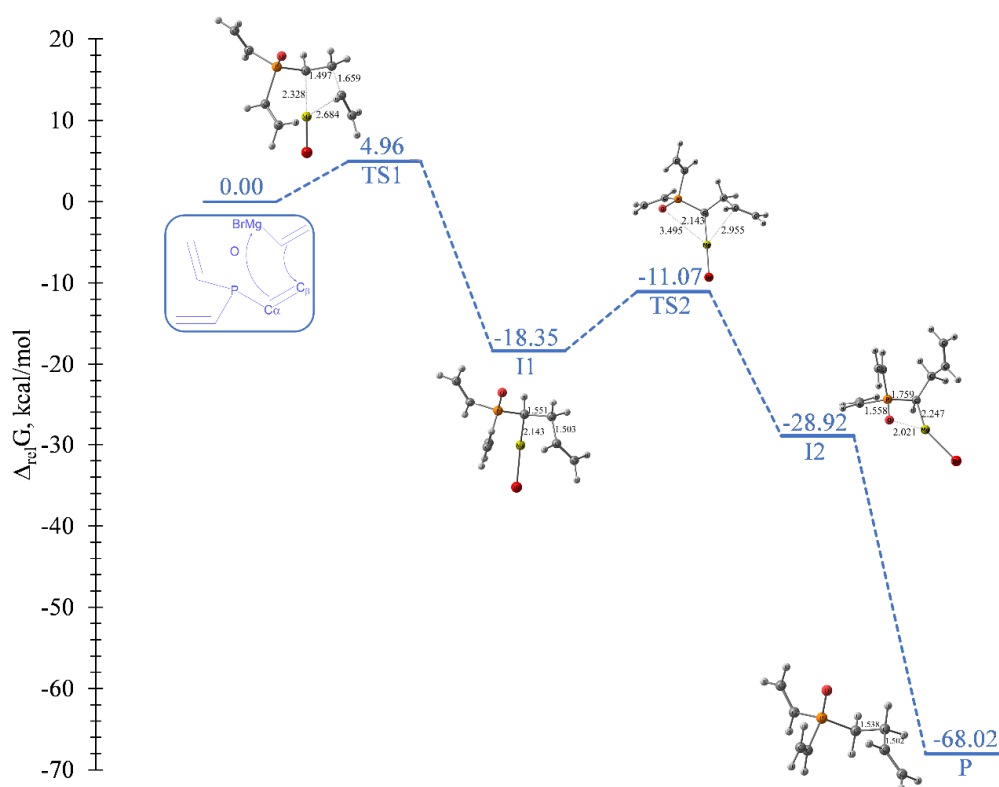


Figure S4: The Potential Energy Diagram for the Reaction of TVPO with VMB. The energies calculated at M062x/6-311++G(d,p) level of theory.

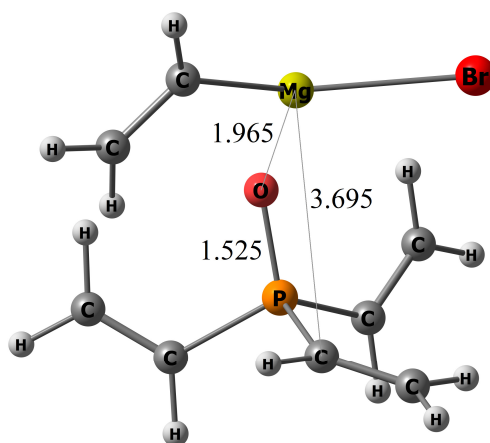


Figure S5: 3-D view of the structure of model compound TVPO-Mg(Br)(CHCH₂). Less stable by 6.5 kcal/mol than the structure I1 shown in **Figure 3** (blue pathway).

Table S6: Cartesian coordinates for the reaction of TVPO with Piperazine (Pip) or Vinylmagnesium bromide (VMB)

S6a) Cartesian coordinates for TVPO			
Atoms (Atomic number)	x	y	z
6	-1.63975	-0.15682	-0.65514
1	-1.7184	-0.16457	-1.73922
6	1.110538	2.470534	0.125639
1	1.114974	2.485606	1.189904
1	1.525196	3.384219	-0.28577
6	0.67104	1.499762	-0.6539
1	0.704304	1.571083	-1.73803
6	-2.6947	-0.26135	0.121226
1	-2.6763	-0.25983	1.189793
1	-3.69358	-0.36002	-0.28929
8	0.014867	0.014296	1.566887
15	-0.0063	0.005182	0.063814
6	0.951565	-1.32835	-0.65413
1	0.996662	-1.39298	-1.73826
6	1.574787	-2.19237	0.125614
1	1.58442	-2.20382	1.189396
1	2.160753	-3.00711	-0.28539

S6b) Cartesian coordinates for TS1 of the reaction of TVPO and Pip (1:1 molar ratio)			
Atoms (Atomic number)	x	y	z
6	-3.68942	-0.45027	-0.53582
1	-3.70163	0.032025	-1.51044
6	-1.41193	1.785305	1.614663
1	-1.49994	1.21842	2.536656
1	-1.1505	2.835086	1.69199
6	-1.61125	1.202854	0.437784
1	-1.53213	1.757045	-0.49469
6	-4.79043	-0.96118	0.005093
1	-4.75918	-1.43678	0.980603
1	-5.74684	-0.91934	-0.50446
8	-2.21865	-1.20308	1.686388
15	-2.10894	-0.53273	0.342566
6	-1.01174	-1.38923	-0.83897
1	0.400702	-0.45951	-1.19846
6	0.278074	-1.83741	-0.22536
1	0.12587	-1.9629	0.849501
1	0.54214	-2.82768	-0.6363

6	2.60396	-1.14403	0.409322
6	1.864344	-0.68713	-1.82163
6	3.698877	-0.09153	0.267152
1	3.008325	-2.13412	0.125393
1	2.276153	-1.20331	1.450878
6	2.959206	0.363567	-1.97157
1	2.230179	-1.66253	-2.19528
1	1.00737	-0.39837	-2.43438
1	4.566211	-0.37223	0.868018
1	3.321823	0.864317	0.646765
1	3.284374	0.414389	-3.01264
1	2.545372	1.339945	-1.69822
7	1.454194	-0.79811	-0.42365
7	4.122609	0.112532	-1.1194
1	4.59004	-0.73042	-1.44472
1	-1.56546	-2.2642	-1.19017

S6c) Cartesian coordinates for I of the reaction of TVPO and Pip (1:1 molar ratio)			
Atoms (Atomic number)	x	y	z
6	-3.45973	0.048589	-0.63188
1	-3.53219	0.226319	-1.7023
6	-0.67299	2.424513	0.550673
1	-0.71625	2.167332	1.60479
1	-0.27522	3.398158	0.285797
6	-1.08738	1.566987	-0.37504
1	-1.05575	1.810544	-1.43456
6	-4.5404	-0.1074	0.125514
1	-4.44825	-0.2815	1.193216
1	-5.53976	-0.06528	-0.29355
8	-1.83077	-0.25356	1.586966
15	-1.80543	-0.02315	0.099169
6	-0.97818	-1.34295	-0.85333
1	-0.86061	-1.00181	-1.88549
6	0.338636	-1.80051	-0.22688
1	0.121175	-2.26278	0.739179
1	0.786156	-2.57936	-0.86902
6	2.387924	-1.14217	0.84239
6	1.769561	-0.12861	-1.23685
6	3.313434	0.031954	1.145151
1	2.963236	-1.94174	0.338287
1	1.989977	-1.5537	1.774109
6	2.695927	1.046157	-0.94199
1	2.311929	-0.89198	-1.82672

1	0.930619	0.222594	-1.8419
1	4.162283	-0.30675	1.74251
1	2.762583	0.773654	1.733677
1	3.092554	1.449208	-1.87601
1	2.114287	1.834778	-0.45305
7	1.269697	-0.70692	0.008373
7	3.811244	0.696479	-0.06079
1	4.429081	0.056343	-0.55414
1	-1.67578	-2.18454	-0.87769

S6d) Cartesian coordinates for TS2 of the reaction of TVPO and Pip (2:1 molar ratio)			
Atoms (Atomic number)	x	y	z
6	-2.07989	-0.49799	-1.91229
1	-1.27344	-1.11582	-1.52545
6	-1.20755	3.114303	-0.68503
1	-2.06396	3.620637	-1.12025
1	-0.33258	3.711716	-0.45351
6	-1.24294	1.807599	-0.44825
1	-0.39676	1.280595	-0.0133
6	-2.60041	-0.70459	-3.11749
1	-3.40473	-0.07614	-3.48711
1	-2.24276	-1.49847	-3.76394
8	-3.79338	1.624587	-1.54965
15	-2.70894	0.837134	-0.86404
6	-3.19052	-0.00912	0.680465
1	-3.90431	-1.28155	1.663008
6	-2.27991	-1.14588	1.073174
1	-1.94091	-1.65795	0.155546
1	-1.38973	-0.73275	1.556579
6	-2.31752	-3.47509	1.995494
6	-2.82652	-1.63435	3.432484
6	-2.97454	-4.41713	2.988754
1	-1.23324	-3.41979	2.203907
1	-2.45967	-3.8771	0.991105
6	-3.47907	-2.57984	4.425652
1	-1.7693	-1.48872	3.717222
1	-3.32451	-0.66209	3.474609
1	-2.48159	-5.39176	2.944156
1	-4.03365	-4.55651	2.707264
1	-3.34311	-2.17721	5.430981
1	-4.56304	-2.6419	4.218408
7	-2.92586	-2.15031	2.0707
7	-2.86404	-3.90062	4.34862

1	-2.80979	0.690511	1.28833
6	-3.14214	-4.48433	6.756198
1	-3.67852	-3.59364	7.09347
6	0.466734	-5.24868	5.374095
1	0.716615	-4.2204	5.130187
1	1.018605	-6.03513	4.871039
6	-0.48745	-5.52025	6.257696
1	-0.75521	-6.54244	6.515436
6	-3.443	-4.83714	5.299835
1	-4.53665	-4.91611	5.171251
1	-3.02364	-5.82406	5.084092
8	-0.85632	-2.80938	6.769487
15	-1.37203	-4.18566	7.096034
6	-1.19585	-4.57109	8.855758
1	-1.49448	-5.55977	9.194992
6	-0.71755	-3.66003	9.696788
1	-0.42423	-2.67793	9.339008
1	-0.60503	-3.8661	10.75555
1	-3.46481	-5.30987	7.397168

S6e) Cartesian coordinates of VMB			
Atoms (Atomic number)	x	y	z
6	1.55608	3.428501	0
1	2.486441	2.862015	0
1	1.686234	4.512488	0
6	0.353224	2.834925	0
1	-0.48196	3.544073	0
12	0	0.761701	0
35	-0.43276	-1.64684	0

S6f) Cartesian coordinates for TS of the reaction of TVPO and VMB			
Atoms (Atomic number)	x	y	z
6	-1.01002	-0.97038	1.104701
1	-0.94824	-2.0634	0.958646
6	-4.41958	-1.59268	-0.82185
1	-5.0628	-0.90098	-0.25687
1	-4.93181	-2.41383	-1.34148
6	-3.09778	-1.42285	-0.85714
1	-2.4478	-2.10473	-1.42418
6	-0.14698	-0.39687	1.969739
1	-0.20239	0.673758	2.217856
1	0.588492	-0.97282	2.549796

8	-3.26132	0.978143	0.806389
15	-2.28601	0.022177	0.024404
6	-0.97742	0.708112	-1.16373
1	-1.28771	0.440348	-2.18637
6	-0.93475	2.199689	-1.04708
1	-1.91709	2.662149	-0.8289
1	-0.55886	2.627809	-1.99329
6	0.129205	2.565475	0.171649
1	-0.30864	2.773061	1.162853
6	1.471659	2.483112	0.047994
1	1.951696	2.35125	-0.93159
1	2.147769	2.673013	0.889844
12	1.023603	0.057404	-0.1677
35	3.038984	-0.91178	-0.18221

S6g) Cartesian coordinates for I of the reaction of TVPO and VMB			
Atoms (Atomic number)	x	y	z
6	-1.51537	-0.09924	1.64809
1	-0.55959	-0.54863	1.911208
6	-3.25307	-2.60408	-0.71485
1	-4.16811	-2.02816	-0.81697
1	-3.30543	-3.67172	-0.89922
6	-2.11606	-2.00691	-0.37266
1	-1.19287	-2.57059	-0.25915
6	-2.26813	0.496536	2.56735
1	-3.22286	0.935865	2.294502
1	-1.95618	0.564504	3.604138
8	-3.44591	0.408505	-0.22508
15	-2.07649	-0.21581	-0.07841
6	-0.78953	0.394951	-1.15722
1	-1.05898	-0.02184	-2.13691
6	-0.78483	1.942618	-1.26397
1	-1.80719	2.323066	-1.38396
1	-0.23026	2.229363	-2.16218
6	-0.14981	2.607056	-0.07416
1	-0.6775	2.515021	0.873331
6	1.011875	3.25731	-0.10693
1	1.565411	3.371817	-1.03531
1	1.443488	3.69863	0.784086
12	1.194705	-0.30144	-0.74364
35	3.392507	-0.77544	0.2278

S6h) Cartesian coordinates for P of the reaction of TVPO and VMB			
Atoms (Atomic number)	x	y	z
6	0.298544	1.530273	-0.68674
1	0.142726	1.552809	-1.76239
6	3.387068	-0.74911	-0.04381
1	3.365693	-0.683	1.039678
1	4.325159	-1.02244	-0.51423
6	2.295224	-0.50063	-0.75929
1	2.294082	-0.55954	-1.84485
6	0.193587	2.623704	0.060759
1	0.351627	2.577766	1.134174
1	-0.05654	3.586431	-0.3712
8	0.874965	0.023871	1.564483
15	0.752421	-0.05028	0.067284
6	-0.45191	-1.29112	-0.51928
1	0.062691	-2.25498	-0.47444
6	-1.739	-1.35009	0.320106
1	-1.46381	-1.5693	1.356117
1	-2.34717	-2.18268	-0.04214
6	-2.54458	-0.08271	0.274044
1	-2.11314	0.785034	0.76843
6	-3.72506	0.030472	-0.32636
1	-4.1863	-0.81709	-0.82515
1	-4.26961	0.967513	-0.3355
1	-0.6747	-1.08202	-1.57027