Electronic Supplementary Material (ESI) for ChemComm.

Unravelling Lawesson's Reagent – The Structure of Monomeric (4-Methoxyphenyl)phosphine Disulfide

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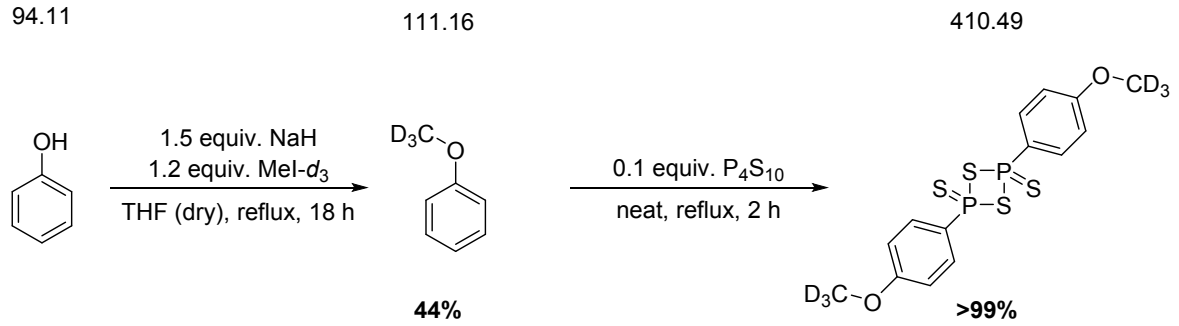
Synthesis of deuterated Lawesson's Reagent



In a flame dried 50 mL Schlenk flask NaH 1.03 g (42.9 mmol, 1.5 equiv.) was suspended in 10 mL dry THF. The mixture was cooled to 0°C and phenol 2.70 g (28.7 mmol, 1.0 equiv.) dissolved in 10 mL dry THF was added slowly *via* syringe. The suspension was allowed to warm to room temperature (r. t) and MeI-d_3 5.00 g (2.15 mL, 34.5 mmol, 1.2 equiv.) was added *via* syringe in one portion. The resulting mixture was refluxed for 18 h, cooled to r.t. and quenched with distilled water (~25 mL). After extraction was *n*-hexane (3 x 50 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the pure anisole-d_3 1.41 g (12.7 mmol, 44%) obtained after distillation (b.p. 154 °C).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.27 (m, 2 H, CH_{Ar}), 6.99 – 6.88 (m, 3 H, CH_{Ar}).

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.7, 129.6, 120.8, 114.0, 54.5 (t, *J* = 22.1 Hz).

P_4S_{10} 0.53 g (1.2 mmol, 1.0 equiv.) was suspended in 1.41 g (12.7 mmol, 10.6 equiv.) anisole-d_3. The mixture was refluxed under evolution of gas (H_2S). After 1 h a clear solution was obtained. Heating was continued until the product started to crystallize from the solution. After cooling to r.t. the product was filtered off under Ar, washed with dry ether and chloroform and dried in vacuum. The deuterated Lawesson's reagent 0.50 g (1.2 mmol, >99%) was obtained as a pale yellow crystalline solid.

Matrix Apparatus Design. For the matrix isolation studies, we used an APD Cryogenics HC-2 cryostat with a closed-cycle refrigerator system, equipped with an inner CsI window for IR measurements. Spectra were recorded with a Bruker IFS 55 FT-IR spectrometer with a spectral range of 4500−400 cm^{-1} and a resolution of 0.7 cm^{-1} and UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer. Matrices were generated by co-deposition of **2** (evaporated at 150 °C from a storage bulb) with a large excess of argon (typically 60−120 mbar from a 2000 mL storage bulb) on the surface of the matrix window at 10 K (20 K). A high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used for irradiation.

Computations. All geometries were optimized and characterized as minima or transition structures by means of analytical harmonic vibrational frequency computations at the B3LYP/6-311++G(3df,3pd) level of theory.[1-3] All computations were performed with the Gaussian16 program.[4]

Supplementary Discussion.

It is well known that the reactivity of LR is not very high.[5] Typically excess of LR and elevated temperatures are required. LR is not stable in solutions above 110 °C at which it decomposes or polymerizes slowly. According to recent computational studies,[6] the dissociation process of LR is endergonic by ~18 kcal mol^{-1} and the dissociation takes place through a barrier of 24-25 kcal mol^{-1}. This value is in the range with the value that we derive from our experiments. As high-vacuum pyrolysis is a non-equilibrium process and we cannot evaluate the contact time of the molecules in the pyrolysis zone, it is difficult to establish a link between the temperature of the pyrolysis zone and the limits of thermally accessible reaction paths. However, we can roughly estimate this limit by experimental means. When we perform the thermolysis experiments at temperatures below 100 °C, we had no spectroscopic evidence for either the LR or monomeric (4-methoxyphenyl)phosphine disulphide. At temperatures above 150 °C, formation 4-methoxyphenyl)phosphine disulphide was observed.

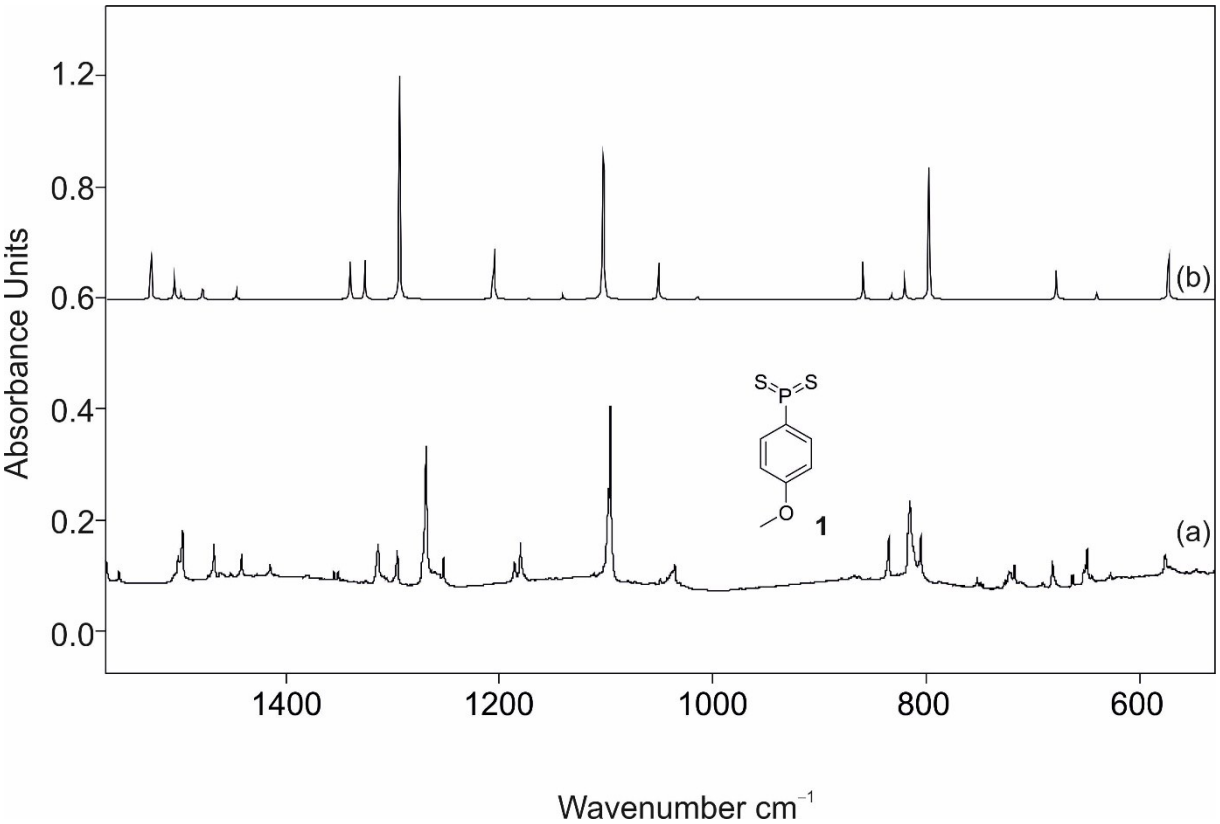


Figure S1. (a) IR spectra showing the products of the pyrolysis of **2** in argon with subsequent trapping in an argon matrix at 10 K: (a) Spectrum obtained after pyrolysis at 150 °C. (b) IR spectrum of **1** computed at B3LYP/6-311++G(3df,3pd) (unscaled).

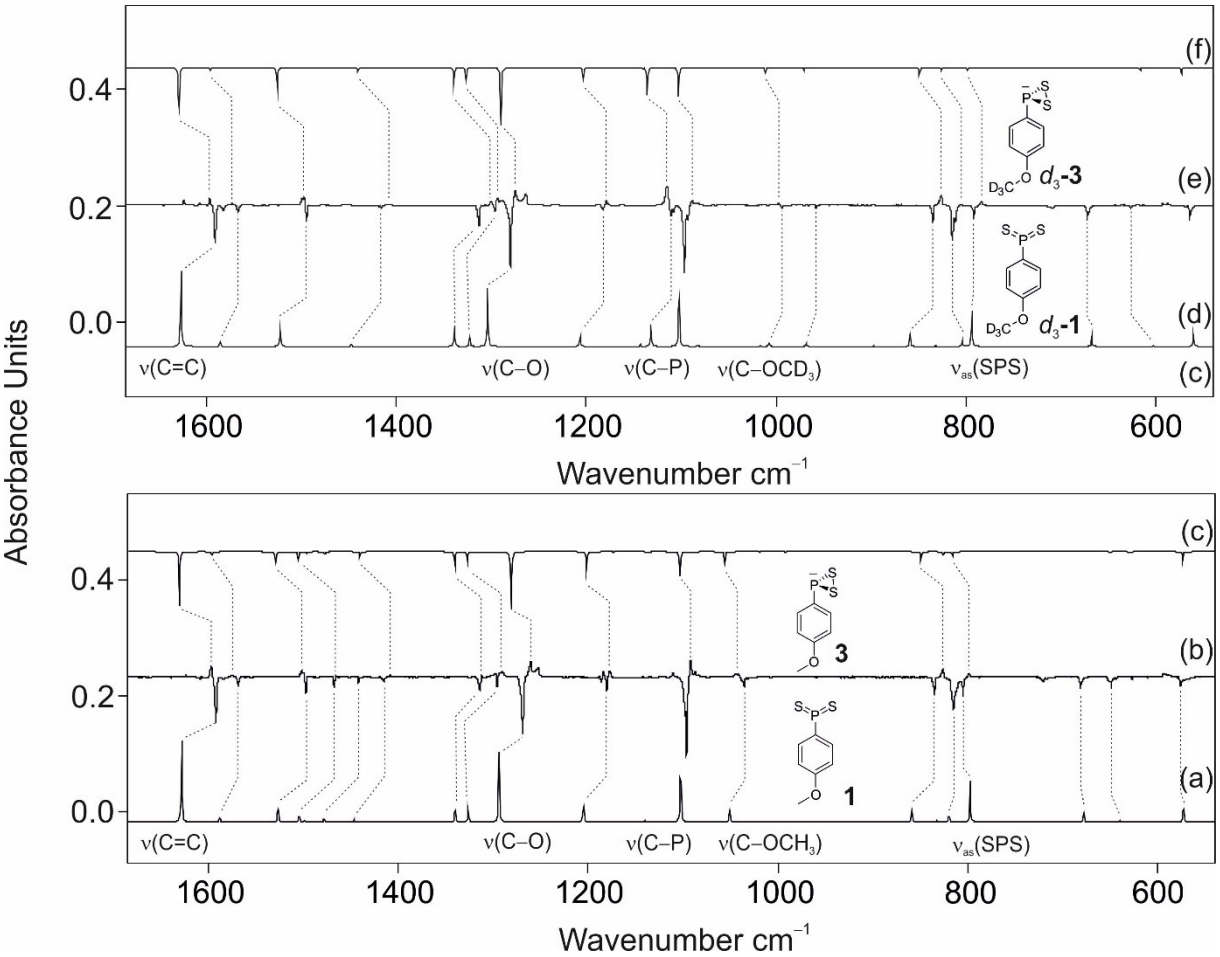


Figure S2. IR spectra showing the product of pyrolysis of **2** in argon matrix with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of **1** computed at B3LYP/6-311++G(3df,3pd) (unscaled). (b) IR difference spectra showing the photochemistry of **1** after irradiation with λ = 334 nm in argon at 10 K. Downward bands assigned to **1** disappear while upward bands assigned to **3** appear after 5 min irradiation time. (c) IR spectrum of **3** computed at B3LYP/6-311++G(3df, 3pd) (unscaled). (d) IR spectrum of d_3-**1** computed at B3LYP/6-311++G(3df,3pd) (unscaled). (e) IR difference spectra showing the photochemistry of d_3-**1** after irradiation with λ = 334 nm in argon at 10 K. Bands pointing downwards assigned to d_3-**1** disappear and bands pointing upwards assigned d_3-**3** appear after 5 min irradiation time. (e) IR spectrum of d_3-**3** computed at B3LYP/6-311++G(3df,3pd) (unscaled).

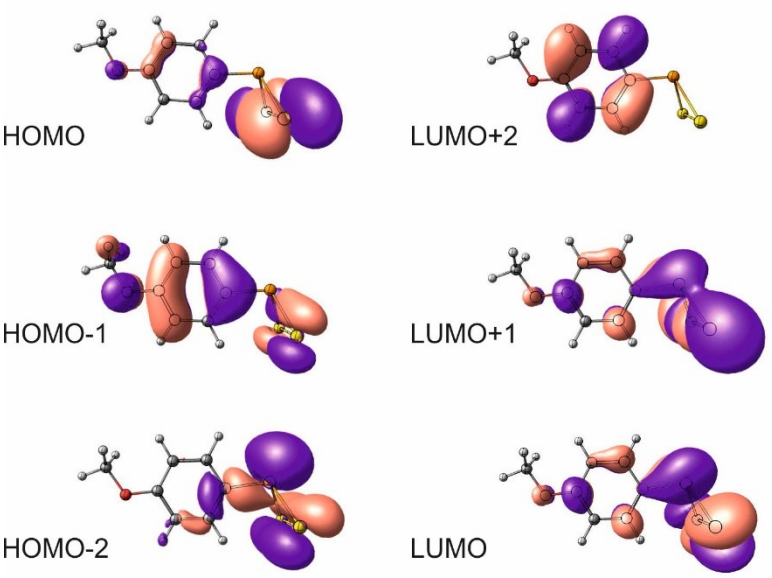


Figure S3. Molecular orbitals of **3** in its singlet ground state as computed at the B3LYP/6-311++G(3df,3pd) level of theory.

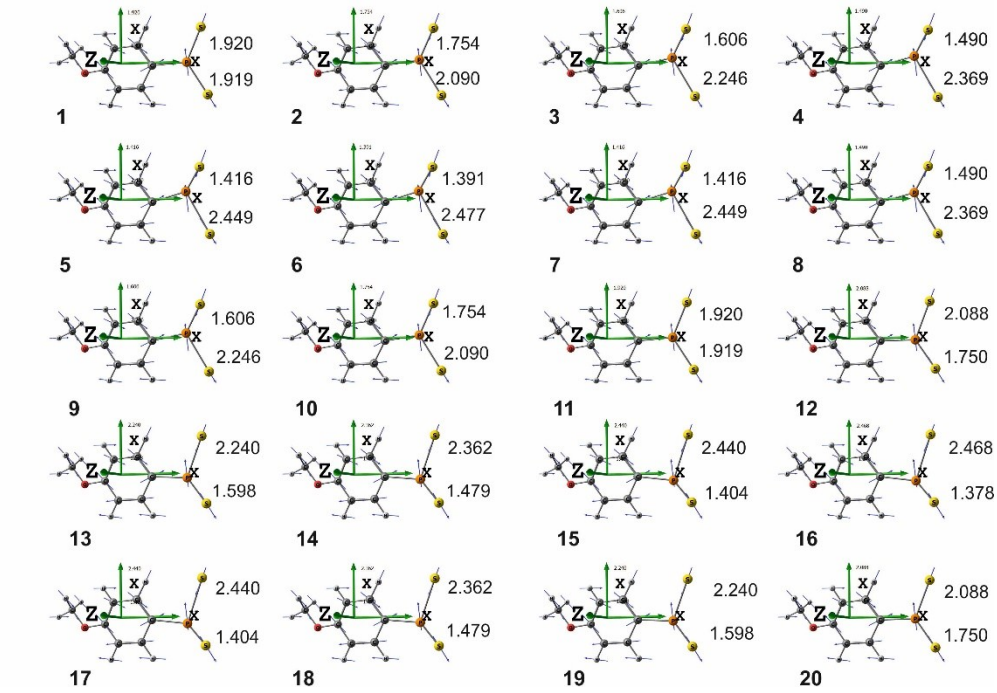


Figure S4. Vector displacements of SPS asymmetric vibration in **1**, which displays arrows pointing the in direction each atom is moving.

Table S1. Experimental (Ar matrix, 10 K) and computed IR frequencies of **1** and d_3-**1** , band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**1** Computed[a]	**1** Ar, 10 K[b]	d_3-**1** Computed[a]	d_3-**1** Ar, 10 K[b]	Assignment
15	573 (74.4)	576 (m)	561 (57.5)	565 (m)	ring distortion
16	640 (8.2)	648(m)	603 (5.8)	627 (w)	ring distortion
17	678 (41.8)	681 (m)	668 (54.3)	672 (m)	ring distortion
18	716 (0.2)	-	716 (0.2)	-	ring breathing
19	798 (162.6)	805 (m)	794 (157.8)	792 (m)	SPS asym. str.
20	820 (32.7)	815 (s)	804 (27)	811 (s)	ring breathing
21	833 (5.8)		832 (6)	-	CH o.o.p. def.
22	859 (46.7)	835 (m)	859 (46.3)	835 (m)	CH o.o.p. def.
23	988 (0.2)	-	988 (0.1)	-	CH o.o.p. def.
24	1008 (0.02)	-	1008 (0.0)	-	CH o.o.p. def.
25	1015 (3.9)	-	1016 (1.2)	-	ring distortion
26	1051 (50.2)	1035 (m)	1008 (20.5)	994 (w)	C–OCH_3 str.
27	1103 (276.9)	1096 (s)	1102 (270)	1096 (s)	C–P str.
28	1141 (5.6)	-	1143 (8.2)	-	CH def.
29	1172 (0.9)	-	898 (2.1)	-	CH_3 rocking
30	1205 (68.8)	1180 (m)	1207 (54.5)	1182 (m)	CH def.
31	1206 (20.9)	1186 (m)	969 (12.5)	958 (w)	CH_3 rocking
32	1294 (293.2)	1267 (s)	1304 (246.1)	1279 (s)	C–O str.
33	1326 (50.4)	1295 (m)	1323 (40.6)	1296 (m)	CH def.
34	1340 (65.6)	1313 (m)	1339 (89.8)	1312 (m)	CH def.
35	1447 (10.7)	1415 (m)	1447 (8.5)	1415 (w)	C=C str./ CH def.
36	1478 (17.6)	1441 (m)	1082 (3.3)	-	CH_3 sym. def.
37	1498 (9.5)	1462 (m)	1083 (1.7)	1063 (w)	CH_3 asym. def.
38	1504 (36)	1467 (m)	1132 (102.9)	1110 (m)	CH_3 asym. def.
39	1527 (68.7)	1497 (m)	1522 (90.9)	1494 (m)	CH def.
40	1587 (22.4)	1568 (m)	1585 (20.7)	1567 (m)	C=C str.
41	1628 (332.5)	1591 (s)	1626 (339.8)	1590 (s)	C=C str.

[a]B3LYP/6-311++G(3df,3pd), harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: medium, s: strong).

Table S2. Experimental (Ar matrix, 10 K) and computed IR frequencies of **3** and d_3-**3**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**1** Computed[a]	**1** Ar, 10 K[b]	d_3-**1** Computed[a]	d_3-**1** Ar, 10 K[b]	Assignment
15	531 (14.4)	517 (w)	531 (14.8)	517 (w)	ring distortion
16	574 (37.2)	592 (w)	574 (33.4)	592 (w)	ring distortion
17	629 (6)	-	617 (11.3)	-	ring distortion
18	650 (2.7)	-	648 (2)	-	ring breathing
19	723 (0.0)	-	723 (0.0)	-	SPS asym. str.
20	816 (20.7)	798 (m)	799 (15.3)	784	ring breathing
21	826 (12.1)		826 (12.3)	-	CH o.o.p. def.
22	850 (34.8)	826 (s)	849 (34.4)	826 (s)	CH o.o.p. def.
23	962 (0.0)	-	962 (0.0)	-	CH o.o.p. def.
24	992 (0.4)	-	992 (0.4)	-	CH o.o.p. def.
25	1019 (0.6)	-	1021 (0.2)	-	ring distortion
26	1056 (44.4)	1043 (m)	1012 (19.3)	997 (w)	C–OCH_3 str.
27	1103 (137.8)	1092 (s)	1103 (112.8)	1089 (s)	C–P str.
28	1138 (6.4)	-	1140 (4.3)	-	CH def.
29	1173 (0.9)	-	907 (2.1)	-	CH_3 rocking
30	1202 (74.9)	1176 (m)	1203 (46.8)	1178 (m)	CH def.
31	1206 (5.1)	1184 (w)	971 (8.4)	959 (w)	CH_3 sym. def.
32	1281 (268)	1260 (s)	1290 (232.5)	1274 (s)	C–O str.
33	1327 (39.9)	1306 (m)	1326 (47.9)	1306 (m)	CH def.
34	1340 (60.4)	1311 (w)	1339 (65.3)	1310 (w)	CH def.
35	1440 (22.3)	1408 (w)	1441 (17.4)	1408 (w)	C=C str./ CH def.
36	1477 (10.7)	-	1082 (2.9)	-	CH_3 sym. def.
37	1497 (8.8)	-	1084 (1.3)	-	CH_3 asym. def.
38	1505 (33.8)	1465 (w)	1136 (117.8)	1115 (s)	CH_3 asym. def.
39	1529 (69)	1501 (m)	1525 (89)	1497(m)	CH def.
40	1596 (17.4)	1576 (w)	1596 (17)	1475 (w)	C=C str.
41	1630 (211.5)	1596 (s)	1629 (216)	1596 (m)	C=C str.

[a] B3LYP/6-311++G(3df,3pd), harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: moderate, s: strong).

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Geometric Structures and Electronic energies

2: LR – (C_{2h} point group)

0 1

15	1.050921000	-1.063197000	0.000001000
16	0.000002000	0.000018000	1.546420000
16	0.871081000	-2.987731000	0.000002000
6	2.747935000	-0.446555000	0.000001000
6	3.022799000	0.929134000	0.000000000
6	3.809580000	-1.347300000	0.000001000
6	4.323799000	1.381275000	-0.000001000
1	2.215828000	1.648862000	-0.000001000
6	5.125318000	-0.900577000	0.000001000
1	3.604955000	-2.408222000	0.000002000
6	5.388212000	0.469319000	0.000000000
1	4.545834000	2.438812000	-0.000001000
1	5.926546000	-1.622824000	0.000002000
16	0.000003000	0.000016000	-1.546420000
15	-1.050927000	1.063220000	-0.000001000
16	-0.871109000	2.987757000	-0.000002000
6	-2.747934000	0.446559000	-0.000001000
6	-3.809590000	1.347291000	-0.000001000
6	-3.022782000	-0.929134000	0.000000000
6	-5.125323000	0.900553000	-0.000001000
1	-3.604978000	2.408216000	-0.000002000
6	-4.323776000	-1.381289000	0.000001000
1	-2.215802000	-1.648852000	0.000001000
6	-5.388200000	-0.469347000	0.000000000
1	-5.926559000	1.622790000	-0.000002000
1	-4.545799000	-2.438830000	0.000001000
8	6.626488000	1.010898000	0.000000000
8	-6.626469000	-1.010940000	0.000000000
6	-7.756417000	-0.149064000	-0.000001000
1	-7.773712000	0.480211000	-0.892147000
1	-8.625864000	-0.799350000	0.000000000
1	-7.773712000	0.480212000	0.892145000
6	7.756425000	0.149009000	0.000000000
1	8.625879000	0.799285000	0.000000000
1	7.773713000	-0.480266000	0.892146000
1	7.773713000	-0.480268000	-0.892145000

E[B3LYP] = -2968.353346
ZPVE[B3LYP] = 0.257419

1: 4-methoxy-phenylphosphine disulfide – (C_1 point group)

0 1

15	2.016710000	0.066526000	0.000161000
6	0.232277000	-0.078363000	0.000109000
6	-0.572094000	1.064841000	0.000095000
6	-0.384567000	-1.340780000	0.000079000
6	-1.953655000	0.965101000	0.000060000
6	-1.756910000	-1.449471000	0.000045000
6	-2.555464000	-0.297302000	0.000035000
1	-0.105799000	2.039419000	0.000115000
1	0.228927000	-2.229847000	0.000087000
1	-2.548391000	1.864978000	0.000053000
1	-2.241284000	-2.415418000	0.000025000
16	2.984569000	-1.590968000	-0.000171000
16	2.707539000	1.857926000	-0.000149000
8	-3.886840000	-0.505343000	0.000001000
6	-4.766619000	0.613281000	-0.000012000
1	-5.770237000	0.199736000	-0.000040000
1	-4.625363000	1.225399000	0.892538000
1	-4.625319000	1.225414000	-0.892544000

E[B3LYP] = -1484.1662556
ZPVE[B3LYP] = 0.128074

^{3}1: triplet -4-methoxy-phenylphosphine disulfide – (C_1 point group)

0 3

15	1.964160000	0.025118000	-0.527690000
6	0.182880000	-0.092772000	-0.243478000
6	-0.602312000	1.055948000	-0.164552000
6	-0.443237000	-1.346644000	-0.213948000
6	-1.981981000	0.969072000	-0.032959000
6	-1.812579000	-1.442812000	-0.082851000
6	-2.595195000	-0.284907000	0.007962000
1	-0.134909000	2.031141000	-0.185120000
1	0.150067000	-2.249111000	-0.274636000
1	-2.562594000	1.875229000	0.042098000
1	-2.303610000	-2.404770000	-0.043499000
16	3.054845000	-1.403418000	0.375921000
16	2.826314000	1.680577000	0.218187000
8	-3.927215000	-0.481767000	0.134391000
6	-4.785417000	0.646482000	0.232743000
1	-5.791060000	0.247645000	0.324363000
1	-4.551326000	1.245930000	1.114907000
1	-4.722747000	1.270567000	-0.661117000

E[B3LYP] = -1484.10592283
ZPVE[B3LYP] = 0.126523

3: 3-(4-methoxyphenyl)-1,2,3-dithiaphosphirane (C_1 point group)

0 1

6	1.560361000	-1.311730000	0.000002000
6	2.559651000	-0.326038000	0.000001000
6	2.203231000	1.020476000	-0.000001000
6	0.854267000	1.366470000	-0.000002000
6	-0.146767000	0.396741000	-0.000001000
6	0.231193000	-0.953302000	0.000001000
1	1.860948000	-2.350135000	0.000004000
1	2.951438000	1.797564000	-0.000001000
1	0.586229000	2.416419000	-0.000003000
1	-0.531539000	-1.720016000	0.000002000
15	-1.848748000	1.043089000	-0.000003000
16	-3.010599000	-0.398698000	-1.060942000
16	-3.010600000	-0.398694000	1.060942000
8	3.834001000	-0.782582000	0.000003000
6	4.899907000	0.155632000	0.000002000
1	5.813518000	-0.431208000	0.000003000
1	4.873374000	0.785248000	-0.891989000
1	4.873373000	0.785251000	0.891991000

E[B3LYP] = -1484.1384692
ZPVE[B3LYP] = 0.127079

TS1: (C_1 point group)

0 1

6	-1.791066000	1.433298000	0.009286000
6	-2.572723000	0.275094000	-0.043788000
6	-1.977174000	-0.967535000	0.172707000
6	-0.613662000	-1.039026000	0.437595000
6	0.177809000	0.106069000	0.483916000
6	-0.437602000	1.346150000	0.272221000
1	-2.265936000	2.388489000	-0.165248000
1	-2.555846000	-1.877315000	0.133052000
1	-0.169043000	-2.013122000	0.596360000
1	0.149294000	2.254956000	0.300005000
15	1.931228000	0.005144000	1.001331000
16	2.851978000	-1.195486000	-0.506810000
16	3.000140000	0.912405000	-0.608917000
8	-3.889234000	0.459740000	-0.311251000
6	-4.739471000	-0.674275000	-0.384950000
1	-5.730488000	-0.290061000	-0.607572000
1	-4.427511000	-1.353599000	-1.181384000
1	-4.765567000	-1.213777000	0.564527000

E[B3LYP] = -1484.1327018
ZPVE[B3LYP] = 0.126741

4: Phenyldioxophosphorane – (C_{2v} point group)

0 1
15 0.000001000 1.702331000 0.000000000
6 0.000000000 -0.076035000 0.000000000
6 0.000000000 -0.769645000 1.214971000
6 0.000000000 -0.769645000 -1.214971000
6 0.000000000 -2.156398000 1.208801000
6 0.000000000 -2.156398000 -1.208801000
6 0.000000000 -2.846563000 0.000000000
1 0.000000000 -0.217101000 2.143221000
1 0.000000000 -0.217101000 -2.143221000
1 0.000000000 -2.698784000 2.143969000
1 0.000000000 -2.698784000 -2.143969000
1 0.000000000 -3.928316000 0.000000000
8 -0.000001000 2.304577000 1.330123000
8 -0.000001000 2.304577000 -1.330123000

E[B3LYP] = -723.6699971
ZPVE[B3LYP] = 0.099442

5: phenylphosphirane – (C_s point group)

0 1
6 2.414412000 -0.983717000 0.000011000
6 2.828901000 0.342025000 0.000007000
6 1.891375000 1.375396000 0.000001000
6 0.537384000 1.084245000 -0.000002000
6 0.110109000 -0.248750000 0.000002000
6 1.055291000 -1.277774000 0.000008000
1 3.143353000 -1.782422000 0.000016000
1 2.223539000 2.404781000 -0.000002000
1 -0.198240000 1.876624000 -0.000007000
1 0.726881000 -2.310650000 0.000011000
8 -2.392079000 0.532174000 0.759653000
8 -2.392074000 0.532166000 -0.759673000
1 3.885292000 0.575537000 0.000009000
15 -1.635495000 -0.735143000 -0.000001000

E[B3LYP] = -723.5231891
ZPVE[B3LYP] = 0.097287

TS-2:
0 1
6 -0.885859000 2.718863000 0.000000000
6 -0.610151000 2.080978000 1.204475000
6 -0.057205000 0.806245000 1.205444000

6	0.211849000	0.155551000	0.000000000
6	-0.057205000	0.806245000	-1.205444000
6	-0.610151000	2.080978000	-1.204475000
1	-1.316548000	3.711002000	0.000000000
1	-0.828127000	2.573870000	2.142236000
1	0.147688000	0.315403000	2.148910000
1	0.147688000	0.315403000	-2.148910000
1	-0.828127000	2.573870000	-2.142236000
8	-0.057205000	-2.455156000	0.758755000
8	-0.057205000	-2.455156000	-0.758755000
15	1.043001000	-1.473347000	0.000000000

E[B3LYP] = -723.513991
ZPVE[B3LYP] = 0.096874