Supplementary Material (ESI) for New Journal of Chemistry

Experimental and Theoretical Study of Phosphinine Sulfides

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X-Ray structural data for 3

X-Ray structural data for 4

X-Ray structural data for 2

Listing of coordinates for calculated structures

Table 1. Crystal data for **3**

Molecular formula	$C_{29}H_{21}PS$
Molecular weight	432.49
Crystal habit	pale yellow block
Crystal dimensions(mm)	0.22x0.16x0.16
Crystal system	monoclinic
Space group	$P2_1/n$
a(Å)	10.371(1)
b(Å)	12.926(1)
c(Å)	17.070(1)
α(°)	90.00
β(°)	94.20
γ(°)	90.00
V(Å^3)	2282.2(3)
Z	4
d(g-cm^{-3})	1.259
F000	904
μ(cm^{-1})	0.226
Absorption corrections	multi-scan ; 0.9520 min, 0.9648 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	293.0(10)
Scan mode	phi and omega scans
Maximum θ	25.68
HKL ranges	-12 9 ; -14 15 ; -17 20
Reflections measured	10757
Unique data	4303
Rint	0.0763
Reflections used	2928
Criterion	>2sigma(I)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	280
Reflections / parameter	10
wR2	0.1629
R1	0.0565
Weights a, b	0.0978 ; 0.0000
GoF	1.018
difference peak / hole (e Å^{-3})	0.345(0.063) / -0.422(0.063)

Figure S1 : Ortep view of crystal structure of complex **3**. Ellipsoids are scaled to enclose 50% of the electron density.

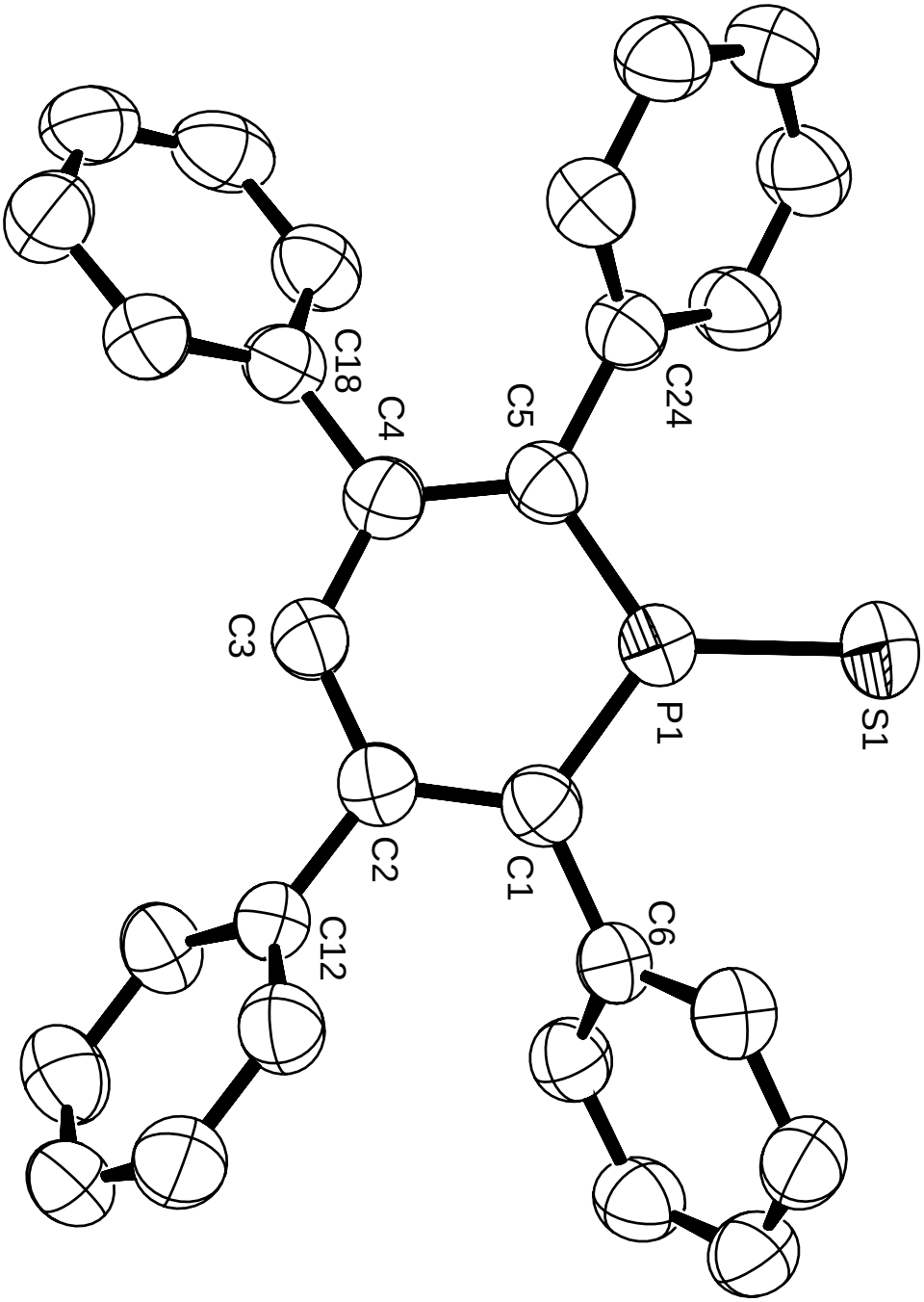

Table 2. Crystal data for **4**

Compound	**4**
Molecular formula	$C_{23}H_{29}PSSi_2$
Molecular weight	424.68
Crystal habit	pale yellow needle
Crystal dimensions(mm)	0.20x0.12x0.10
Crystal system	orthorhombic
Space group	Pbcn
a(Å)	17.932(1)
b(Å)	12.292(1)
c(Å)	20.981(1)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	4624.6(5)
Z	8
d(g-cm^{-3})	1.220
F(000)	1808
μ(cm^{-1})	0.319
Absorption corrections	multi-scan ; 0.9389 min, 0.9688 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.45
HKL ranges	-23 21 ; -15 15 ; -27 27
Reflections measured	19073
Unique data	5271
Rint	0.0267
Reflections used	4326
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	279
Reflections / parameter	15
wR2	0.0998
R1	0.0332
Weights a, b	0.0598 ; 0.9132
GoF	1.045
difference peak / hole (e Å^{-3})	0.274(0.048) / -0.340(0.048)

Figure S2 : Ortep view of crystal structure of complex **4.** Ellipsoids are scaled to enclose 50% of the electron density.

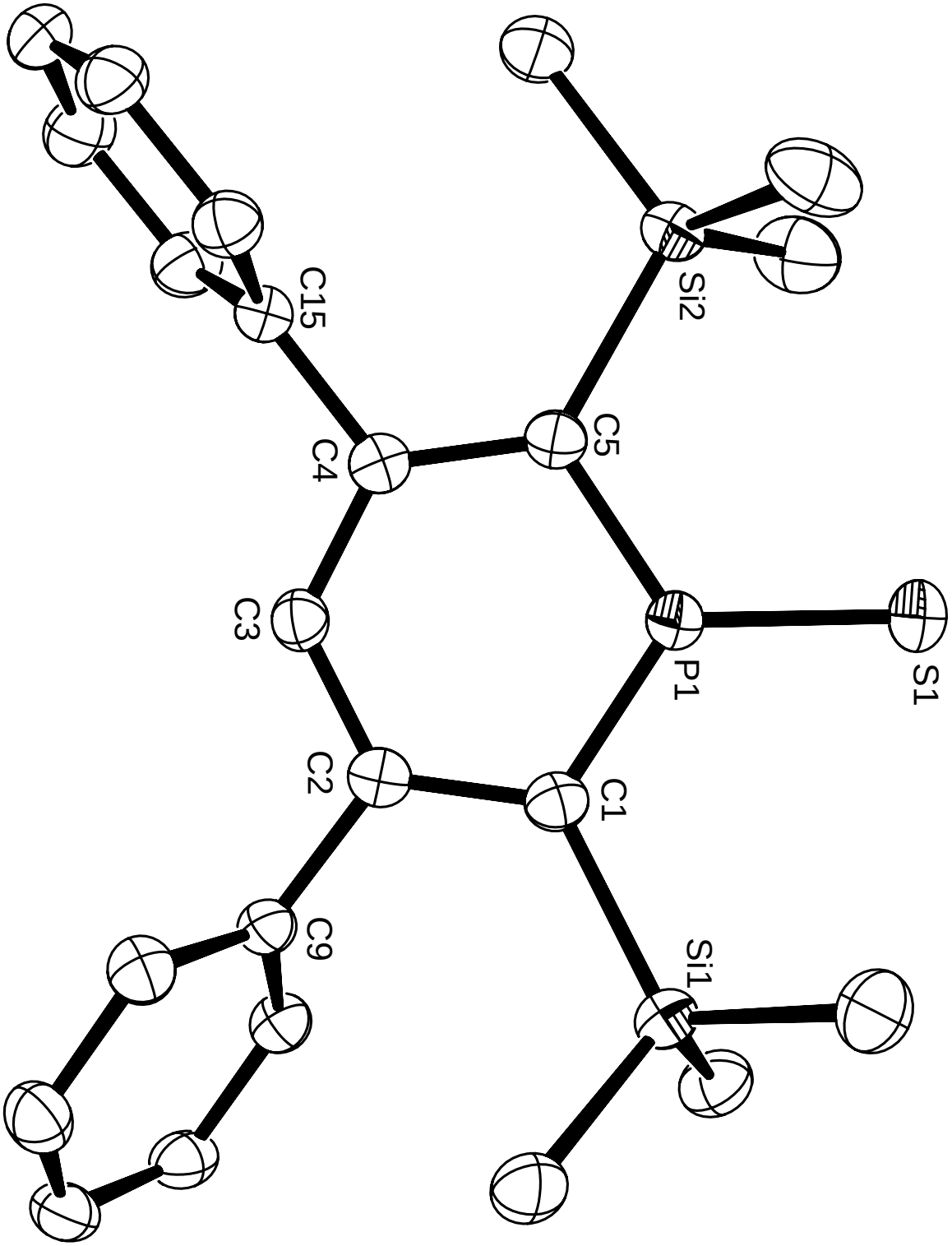

Table 3. Crystal data for **2**

Compound	psi2ph2
Molecular formula	$C_{23}H_{29}PSi_2$
Molecular weight	392.61
Crystal habit	colorless block
Crystal dimensions(mm)	0.20x0.20x0.16
Crystal system	monoclinic
Space group	$P2_1/n$
a(Å)	12.081(1)
b(Å)	17.513(1)
c(Å)	12.328(1)
α(°)	90.00
β(°)	118.0220(10)
γ(°)	90.00
V(Å^3)	2302.5(3)
Z	4
d(g-cm^{-3})	1.133
F000	840
μ(cm^{-1})	0.228
Absorption corrections	multi-scan ; 0.9558 min, 0.9644 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.01
HKL ranges	-16 16 ; -20 24 ; -17 17
Reflections measured	11250
Unique data	6684
Rint	0.0209
Reflections used	5111
Criterion	>2sigma(I)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	241
Reflections / parameter	21
wR2	0.1197
R1	0.0410
Weights a, b	0.0620 ; 0.1790
GoF	1.076
difference peak / hole (e Å^{-3})	0.389(0.051) / -0.333(0.051)

Figure S3 : Ortep view of crystal structure of complex **2**. Ellipsoids are scaled to enclose 50% of the electron density.

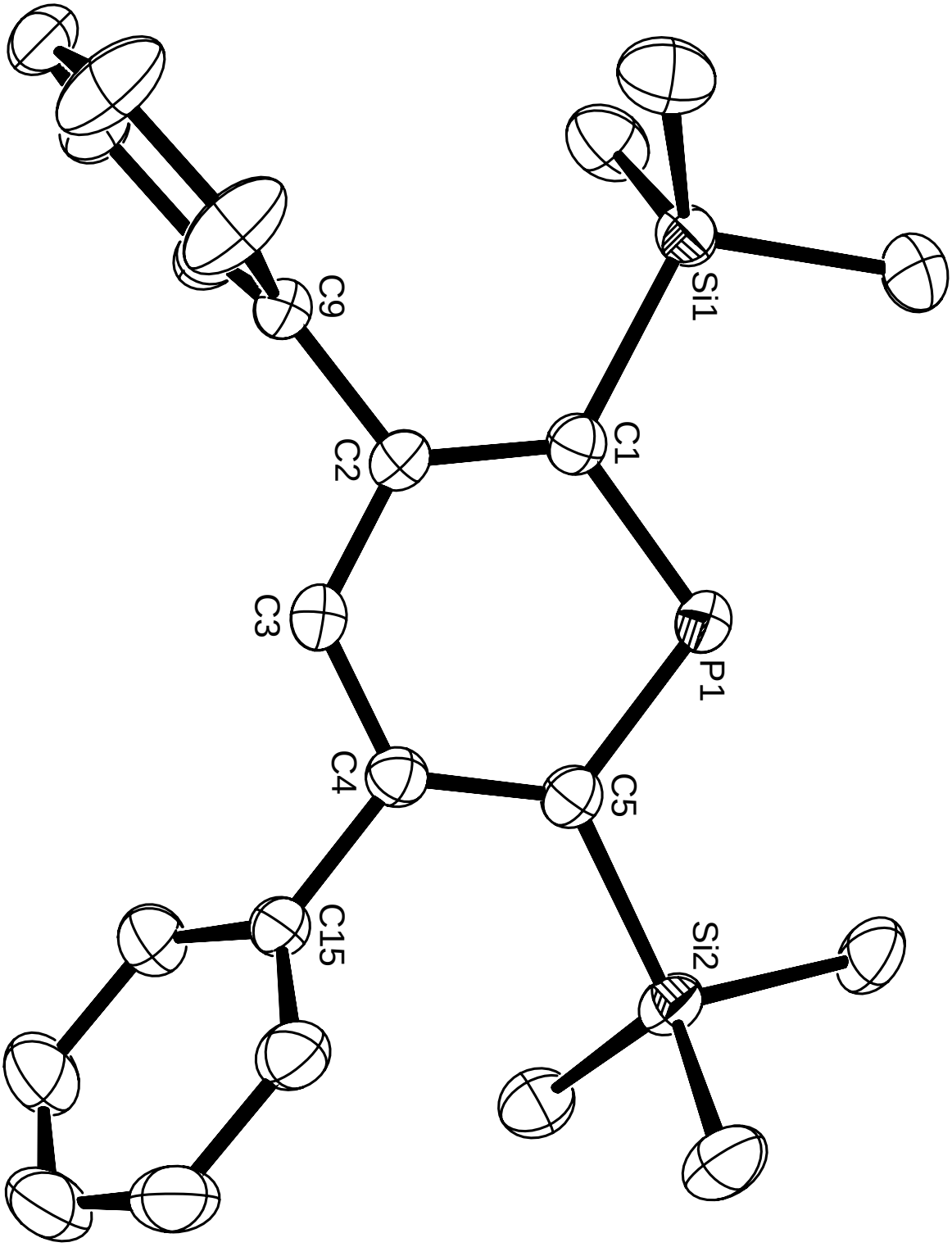

Table 4 : Optimized geometry for **III**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.370908	0.000000	-0.129018
2	6	0	-1.349460	0.000000	1.265300
3	6	0	-0.192235	0.000000	2.045732
4	6	0	1.090121	0.000000	1.494544
5	6	0	1.370945	0.000000	0.128630
6	1	0	-2.307304	0.000000	-0.672456
7	1	0	-2.309222	0.000000	1.773756
8	1	0	-0.293562	0.000000	3.124038
9	1	0	1.938360	0.000000	2.172896
10	1	0	2.392186	0.000000	-0.230851
11	15	0	0.094536	0.000000	-1.006037
12	8	0	0.233841	0.000000	-2.488495

Three lowest frequencies :

	1	2	3
	B1	B1	B2
Frequencies --	185.9116	291.6674	295.6435
Red. masses --	6.0429	7.1725	8.7766
Frc consts --	0.1231	0.3595	0.4520
IR Inten --	3.6711	5.6226	13.3026

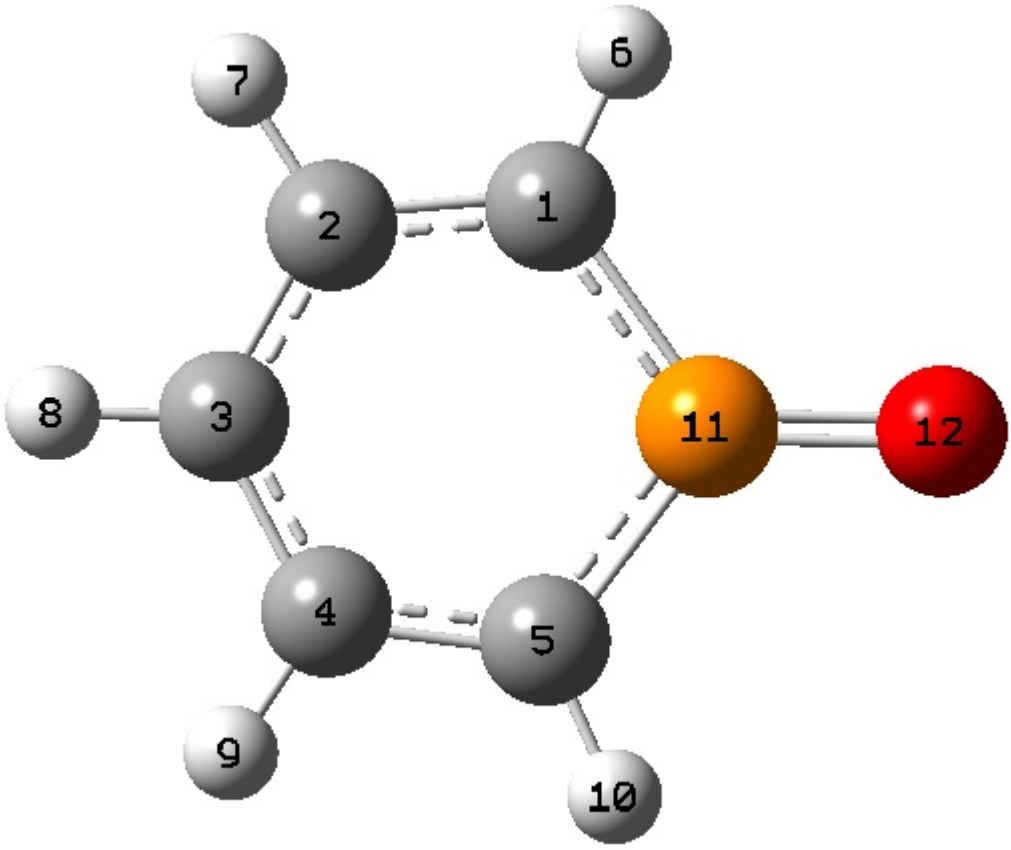

Table 5 : Optimized geometry for **IV**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	1.374200	-0.424654
2	6	0	0.000000	1.226308	-1.807905
3	6	0	0.000000	0.000000	-2.476372
4	6	0	0.000000	-1.226308	-1.807905
5	6	0	0.000000	-1.374200	-0.424654
6	1	0	0.000000	2.356586	0.030485
7	1	0	0.000000	2.134119	-2.404213
8	1	0	0.000000	0.000000	-3.559470
9	1	0	0.000000	-2.134119	-2.404213
10	1	0	0.000000	-2.356586	0.030485
11	15	0	0.000000	0.000000	0.608353
12	16	0	0.000000	0.000000	2.551911

Three lowest frequencies :

	1	2	3
	B1	B2	B1
Frequencies --	127.8485	198.1675	273.2197
Red. masses --	8.0781	8.3551	5.1352
Frc consts --	0.0778	0.1933	0.2259
IR Inten --	0.1915	1.1137	0.0076

Sum of electronic and zero-point Energies= -933.092690

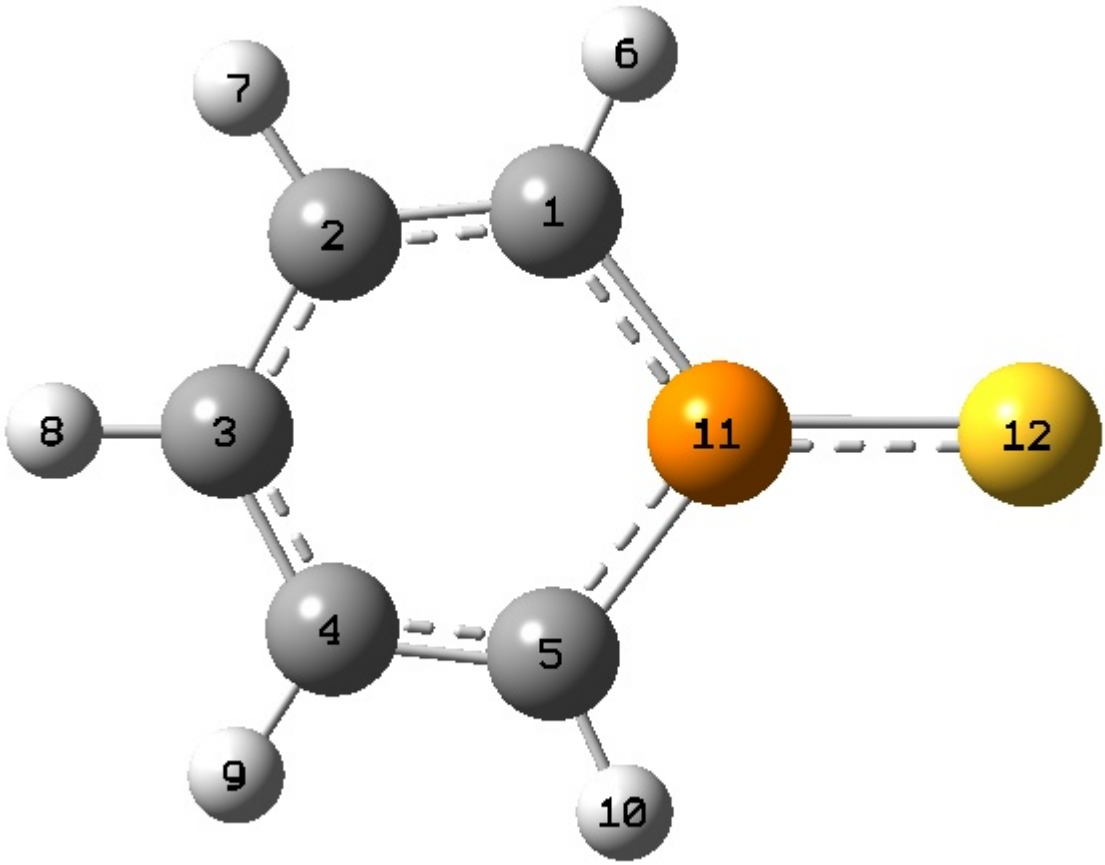

Table 6 : Optimized geometry for **V**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-.616002	-.445755	-.333315
2	6	0	-.611127	-.456462	1.509098
3	6	0	.575863	-.490670	2.249153
4	6	0	-1.839586	-.422913	2.179790
5	6	0	.533438	-.480095	3.643199
6	1	0	1.533631	-.534138	1.745087
7	6	0	-1.876959	-.406712	3.571217
8	1	0	-2.760335	-.428032	1.607738
9	6	0	-.691081	-.434216	4.305364
10	1	0	1.457967	-.513371	4.208684
11	1	0	-2.832844	-.381290	4.082198
12	1	0	-.722749	-.428151	5.389168
13	6	0	1.062858	-1.028580	-.819492
14	6	0	1.282557	-2.406170	-.937980
15	6	0	2.115829	-.140497	-1.065172
16	6	0	2.543159	-2.886779	-1.280947
17	1	0	.459690	-3.093559	-.778500
18	6	0	3.375767	-.626338	-1.414158
19	1	0	1.957393	.928698	-.994379
20	6	0	3.592056	-1.998315	-1.518605
21	1	0	2.704006	-3.955182	-1.370990
22	1	0	4.184286	.069315	-1.609096
23	1	0	4.571487	-2.374644	-1.792032
24	6	0	-.657968	1.335802	-.801200
25	6	0	-1.038660	1.674400	-2.105228
26	6	0	-.317011	2.349549	.100944
27	6	0	-1.060773	3.007968	-2.503770
28	1	0	-1.333099	.892117	-2.795435
29	6	0	-.346136	3.684764	-.301086
30	1	0	-.036911	2.104927	1.118291
31	6	0	-.713733	4.015277	-1.603255
32	1	0	-1.357444	3.260960	-3.515425
33	1	0	-.086639	4.464244	.406521
34	1	0	-.737986	5.053817	-1.913927
35	16	0	-2.083211	-1.507466	-1.127213

Three lowest frequencies :

	1	2	3
	A	A	A
Frequencies --	23.9079	23.9580	43.0691
Red. masses --	3.8273	3.8265	3.7040
Frc consts --	.0013	.0013	.0040
IR Inten --	.1597	.1620	.0485

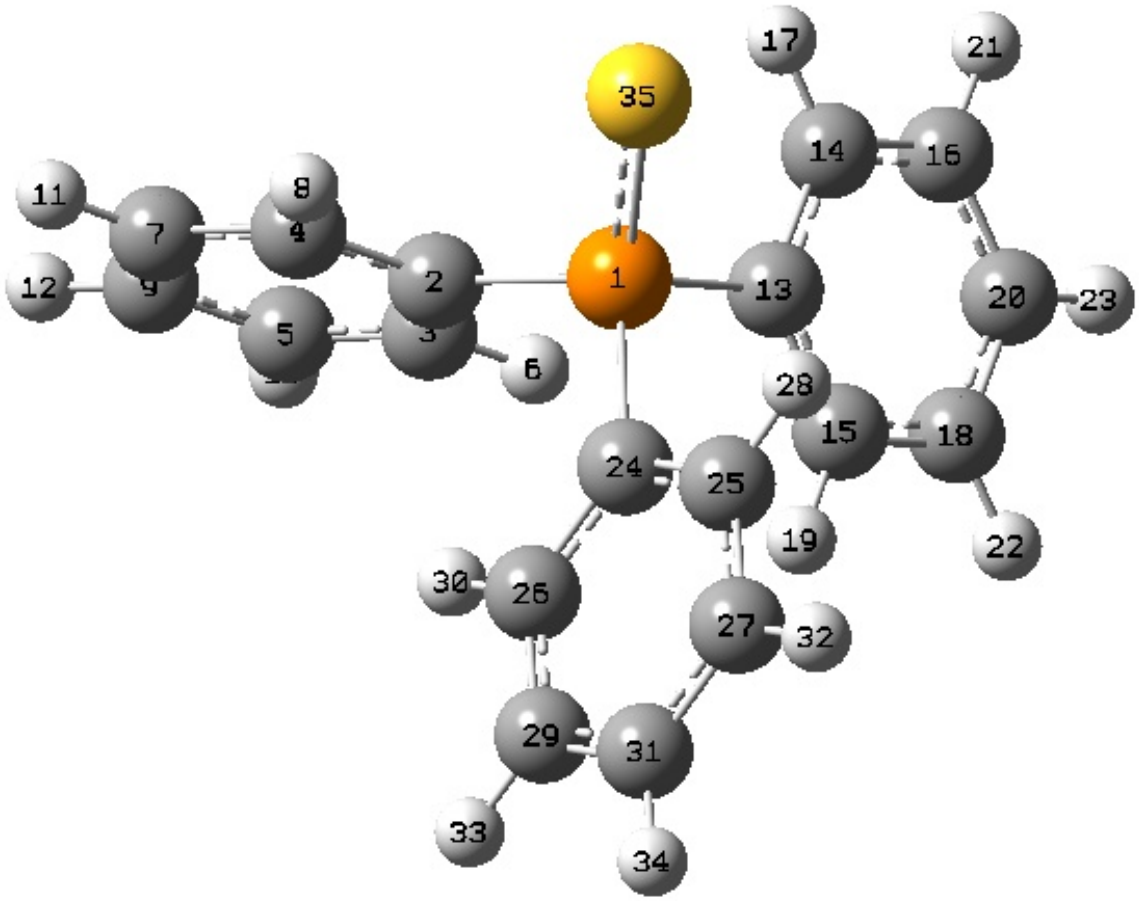

Table 7 : Optimized geometry for **barrelene sulfide**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.625792	0.000086	-0.321730
2	6	0	-0.534020	-0.001155	1.518821
3	6	0	0.711507	-0.000507	1.981519
4	6	0	1.858346	0.000247	0.955080
5	6	0	1.696609	1.244955	0.064572
6	6	0	0.559404	1.381606	-0.608566
7	1	0	0.960483	-0.000768	3.037419
8	1	0	2.826257	0.000338	1.452465
9	1	0	2.511406	1.959771	0.019580
10	1	0	0.299974	2.196838	-1.271240
11	1	0	-1.438838	-0.001690	2.112371
12	6	0	0.559832	-1.381278	-0.609040
13	6	0	1.697190	-1.244309	0.064006
14	1	0	0.300604	-2.196795	-1.271384
15	1	0	2.511925	-1.959237	0.019442
16	16	0	-2.367384	0.000181	-1.216940

Three lowest frequencies :

	1	2	3
	A	A	A
Frequencies --	177.2999	177.4269	352.3556
Red. masses --	7.1989	7.2059	2.7519
Frc consts --	0.1333	0.1337	0.2013
IR Inten --	1.7088	1.7008	0.3664

Sum of electronic and zero-point Energies= -1010.441280

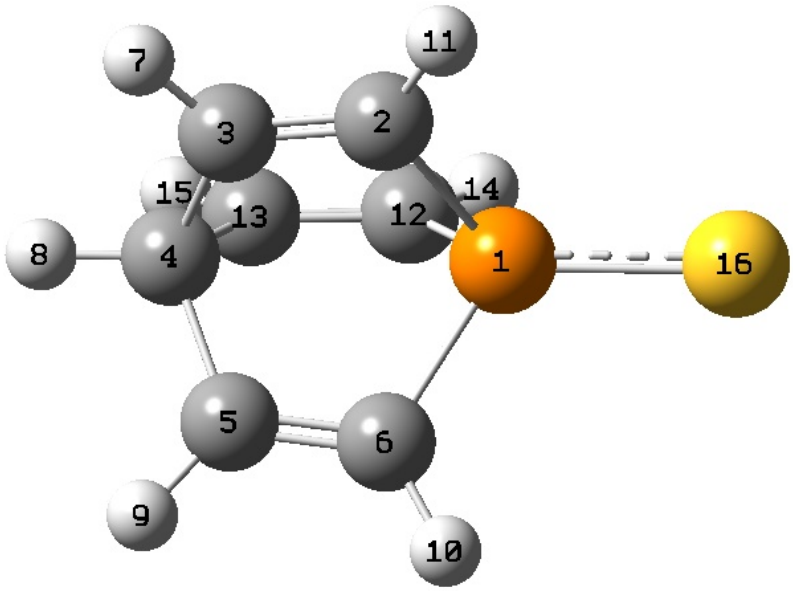

Table 8 : Optimized geometry for **Diels Alder TS**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.738332	-0.186754	0.000429
2	6	0	0.186054	-0.741336	1.384389
3	6	0	1.542225	-0.728147	1.247563
4	6	0	2.183024	-0.452686	0.000984
5	6	0	1.545405	1.831361	-0.003693
6	6	0	0.306986	1.869474	-0.003815
7	1	0	2.171553	-0.881772	2.119389
8	1	0	3.266667	-0.414600	0.000912
9	1	0	2.558005	2.164051	-0.004342
10	1	0	-0.568132	2.492699	-0.005167
11	1	0	-0.312249	-0.885721	2.334203
12	6	0	0.186064	-0.747027	-1.381231
13	6	0	1.542234	-0.733264	-1.244453
14	1	0	-0.312222	-0.895344	-2.330448
15	1	0	2.171568	-0.890481	-2.115635
16	16	0	-2.678373	0.019440	-0.000003

Three lowest frequencies :

	1	2	3
	A	A	A
Frequencies --	-430.1769	137.8314	179.1669
Red. masses --	6.5064	7.6903	5.2968
Frc consts --	0.7094	0.0861	0.1002
IR Inten --	15.6731	0.1065	0.7821
Raman Activ --	0.0000	0.0000	0.0000
Depolar --	0.0000	0.0000	0.0000

Sum of electronic and zero-point Energies= -1010.382049

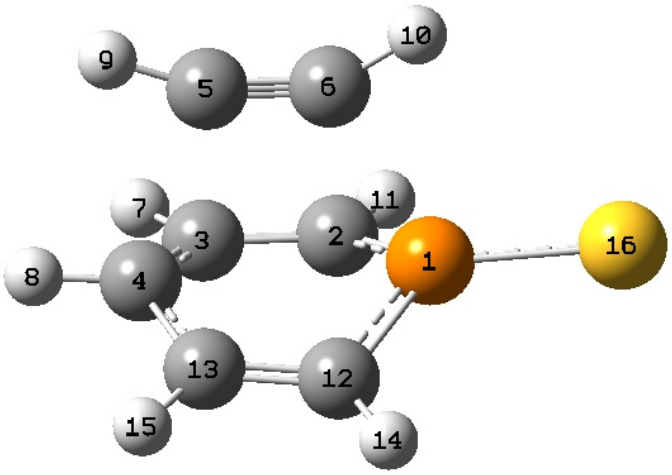

Table 9 : Optimized geometry for **acetylene**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.599682	0.000000	0.000000
2	1	0	-1.662278	0.000000	0.000000
3	6	0	0.599682	0.000000	0.000000
4	1	0	1.662278	0.000000	0.000000

Three lowest frequencies :

	1	2	3
	PIG	PIG	PIU
Frequencies --	653.6818	653.6818	769.9351
Red. masses --	1.5729	1.5729	1.0848
Frc consts --	0.3960	0.3960	0.3789
IR Inten --	0.0000	0.0000	110.9693

Sum of electronic and zero-point Energies= -77.329621