Supporting Information

Muon spectroscopy of a 12-phosphatetraphene with extremely efficient radical trapping properties

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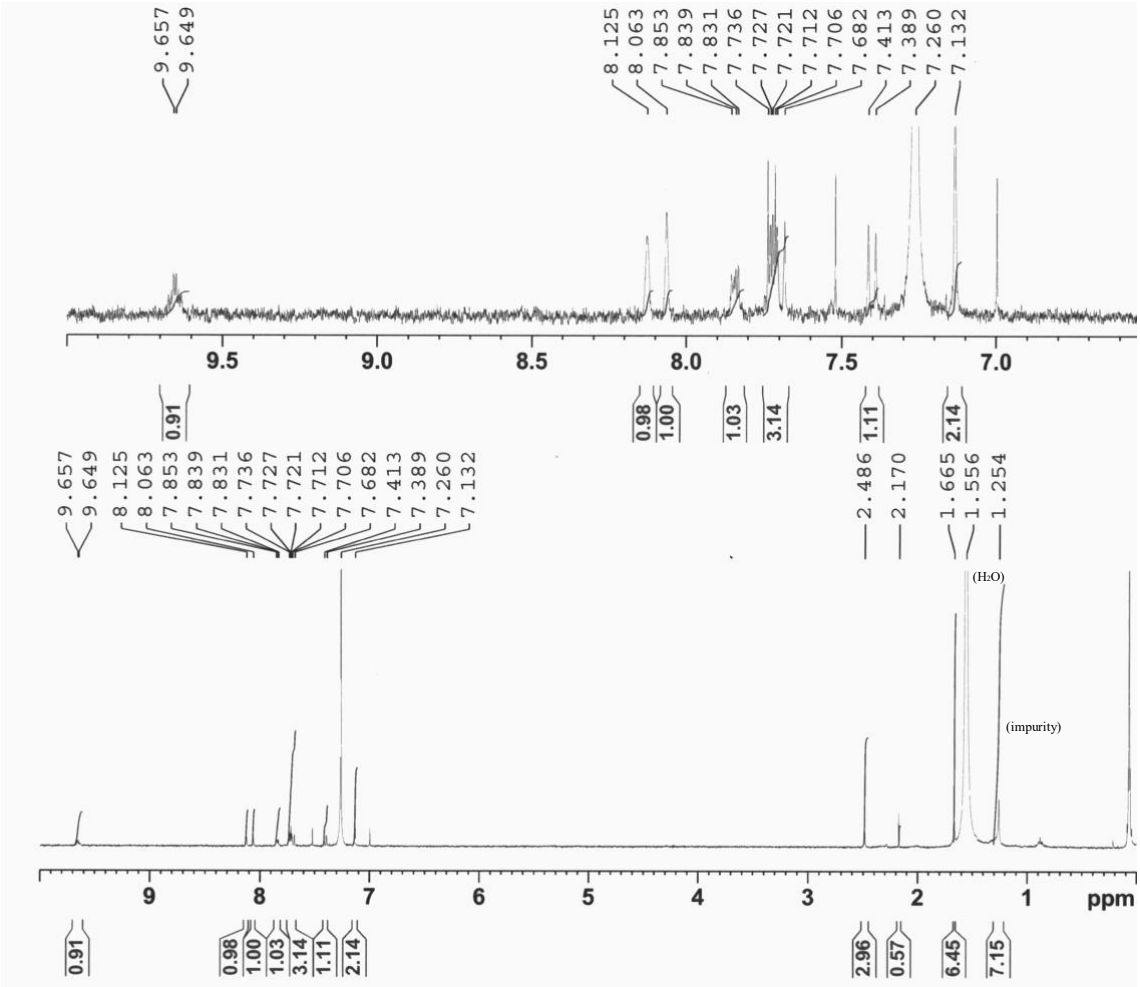
Preparation of 1

A 120 mg of 12-phosphatetraphene **1** was prepared according to the previous paper [16]. The structure was promptly checked by ^{1}H NMR and ^{19}F NMR.

^{19}F NMR (376 MHz, $CDCl_3$) δ –57.7 (d, ^{4}J(P,F) = 67.7 Hz), –63.0 (s).



^{1}H NMR of **1** ($CDCl_3$, 400 MHz, 298 K)

A brief description of TF-μSR

The muon beamline at the TRIUMF cyclotron (M15 beamline) was used, and the Helios spectrometer was equipped. The spin-polarized muons can be monitored by observing the muon's radioactive decay. When a muon decays, a positron e^+ and two neutrinos (ν) are emitted via the reaction of Equation S1. In this process, the positron (e^+) is emitted preferentially along the direction of the muon spin. Therefore, each muon decay gives rise to a positron whose direction contributes to a data point at a particular time t. By acquisition of millions of muon decay events (up to 10^8), it is possible to build up a histogram. The experiment data set is obtained as the collection of measured average spin polarization as a function of time after implantation.

$$\mu^+ \longrightarrow e^+ + \nu_e + \bar{\nu}_\mu \qquad \text{(S1)}$$

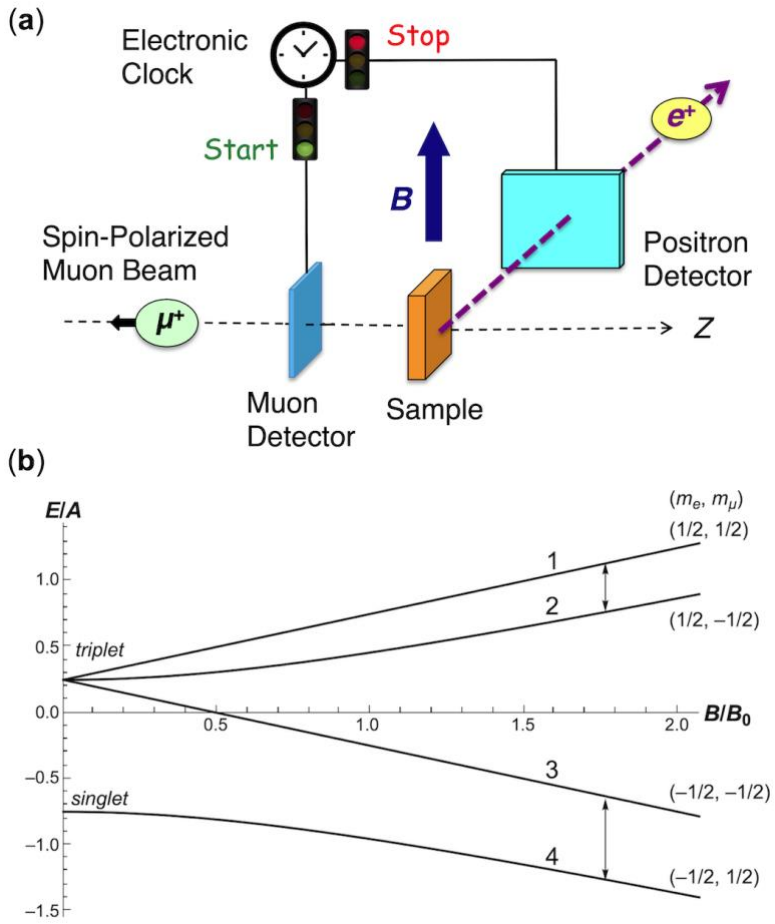
Figure S2a illustrates set-up of a typical TF-μSR experiment. A magnetic field is applied to the sample in a direction perpendicular to the muon beam. Muons are stopped in a sample and the elapsed time between individual muon stops and the detection of their decay positrons is recorded. The probability of detecting a decay positron in a particular direction depends on the orientation of the muon spin at the moment of its decay. Muons in free radicals are subject to the local field of the unpaired electron – the hyperfine interaction. Figure S1b shows a Breit-Rabi diagram for isotropic muonium with a hyperfine constant appropriate for free (vacuum) muonium. At the high fields, only the 1↔2 and 3↔4 transitions can be observed. and the muon precession frequency in a free radical shows two values (Equations 2 and 3), corresponding to the two spin orientations of the unpaired electron,

$$\upsilon_{\mathrm{R1}} = \nu_{\mathrm{D}} - \frac{1}{2}A_\mu \qquad \text{(S2)}$$

$$\upsilon_{\mathrm{R2}} = \nu_{\mathrm{D}} + \frac{1}{2}A_\mu \qquad \text{(S3)}$$

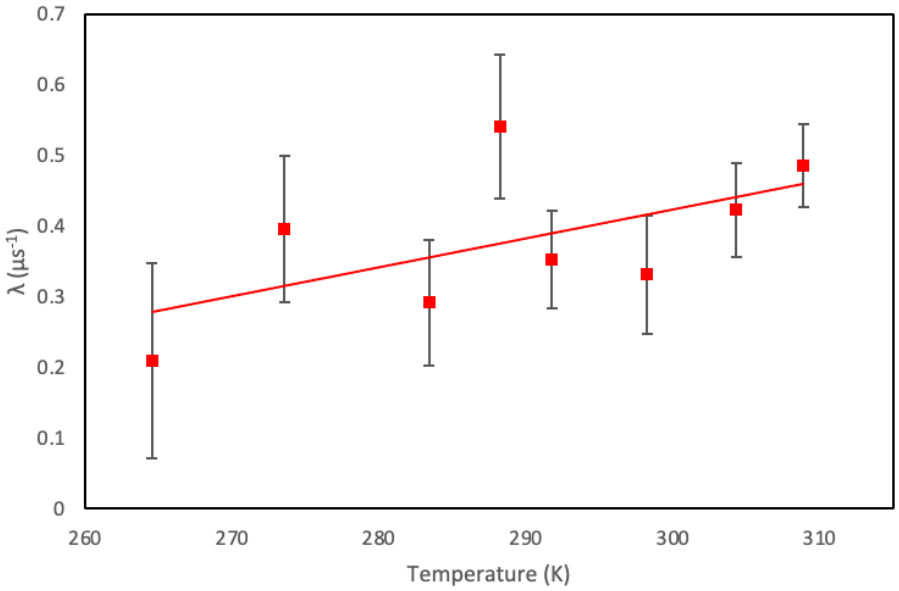
where n_{D} is the precession frequency of muons in diamagnetic environments (closed shell: 135.53 MHz/T), and A_μ is readily found from the difference of the two precession frequencies of the paramagnetic muoniums.

Figure S2



(**a**) A schematic representation of the TF-μSR experiment. The external transverse magnetic field is denoted as *B*. (**b**) Sublevel energies of the Mu (= [μ^+e^-]) hyperfine interaction as a function of external magnetic field. Transitions 1↔2 and 3↔4 at the high field correlate with the radical signals ν_{R1} and ν_{R2} in Equations 2 and 3.

Figure S3



A plot of relaxation ratio (λ) *versus* temperature determined by the TF-μSR spectra.

A brief description of μLCR (ALC-μSR)

In muon *avoided* level-crossing resonance (μLCR) measurements, the magnetic field is oriented parallel to the muon beam polarization, and the positron rate is measured in the forward and backward directions (Figure S2a). The difference in the rates is the muon asymmetry $A(t)$, which is proportional to the longitudinal muon spin polarization (Equation S4). N_F is the total number of positrons detected in the forward counters and N_B is the total number of positrons detected in the backward counters.

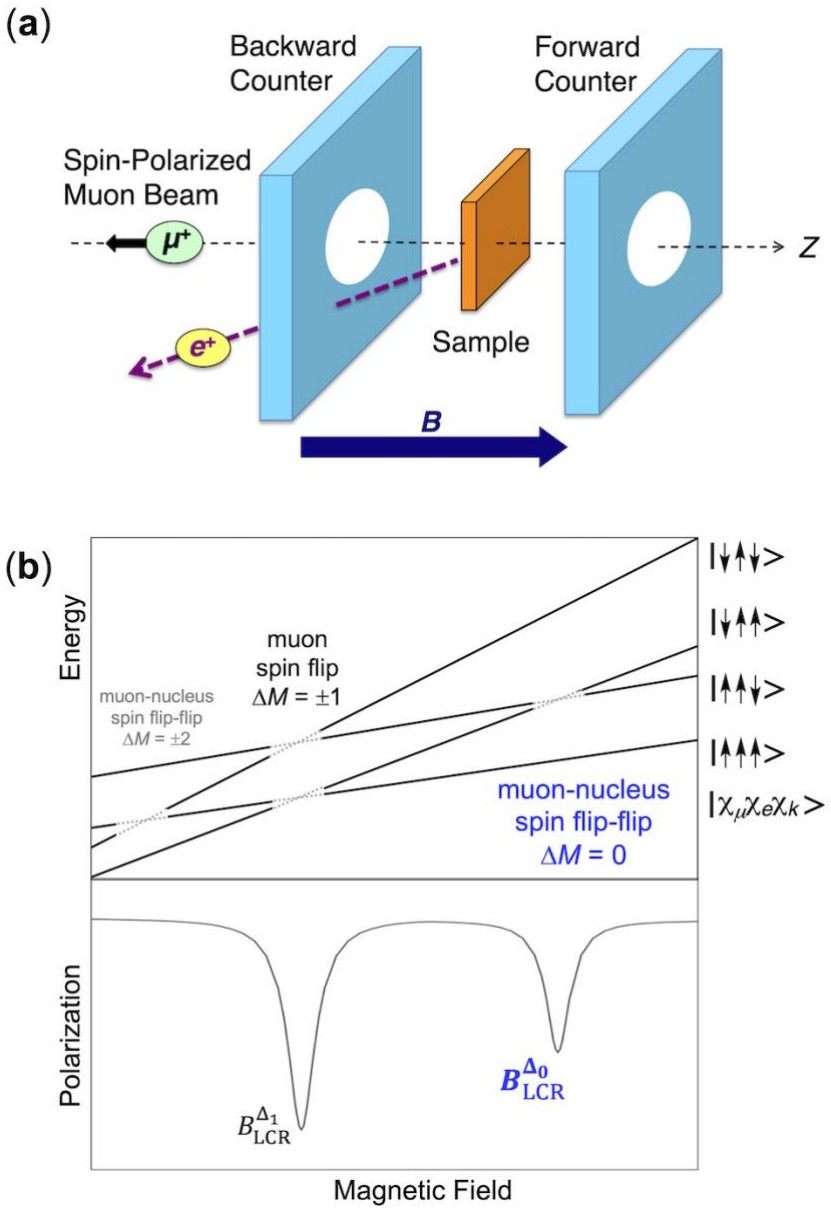
$$A(t) = \frac{N_B - N_F}{N_B + N_F} \qquad (S4)$$

For the coupled spin system of a muoniated free radical, there are some fields where the mixing of a pair of spin states results in an avoided crossing. If the mixed states involve different muon spin orientations, there is a partial loss of spin polarization at the resonance field. In Figure S2b, M is the sum of the spin quantum numbers of the muon (μ), electron (e), and I=1/2 nucleus (k). For Δ_0 (ΔM=0) transitions, the resonant state involves an exchange between the muon spin and a nuclear spin. The level-crossing is avoided by indirect coupling of both Zeeman states to a third one. This avoided resonance occurs at a magnetic field according to Equation S5:

$$B_{LCR}^{\Delta_0} = \frac{1}{2}\left[\frac{A_\mu - A_k}{\gamma_\mu - \gamma_k} - \frac{A_\mu + A_k}{\gamma_e}\right] \qquad (S5)$$

where γ_μ, γ_k, and γ_e refer to the gyromagnetic ratios of the muon, nucleus of I=1/2 spin, and electron, respectively. A_k is the hyperfine coupling constant of I=1/2 nuclei. The Δ_0 transitions are normally promoted by the isotropic motion of the muoniated radicals.

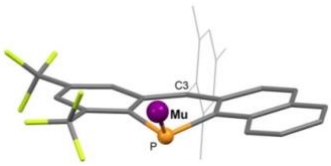
Figure S4



(**a**) A schematic of μLCR geometry. The longitudinal external field is denoted as B. (**b**) Top panel: Energy diagram for a three-spin system [muon (μ), electron (e), $I = 1/2$ nucleus (k)]. Bottom panel: LCR resonances occur when states with opposite muon spin become near-degenerate in energy. A transition with $\Delta M = \pm 2$, a muon-nucleus spin flip-flip transition, is usually very weak negligible.

DFT calculation data (UB3LYP/def2-SVP)

1Mu: normal



E_{total} = –2018.14271907 au, ν_{min} = 15.92 cm^{-1}

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1	15	0	-1.737047	-1.745939	0.638257
2	6	0	-1.562933	0.996769	0.012178
3	6	0	0.630448	-0.307093	0.096422
4	6	0	-3.834387	-0.003917	-0.013650
5	6	0	0.028289	-1.603834	0.165171
6	6	0	-2.409125	-0.134235	0.111905
7	6	0	2.048199	-0.241463	-0.020162
8	1	0	2.528331	0.735198	-0.052841
9	6	0	0.847041	-2.751516	0.041071
10	6	0	-4.408324	1.286878	-0.266837
11	6	0	-2.186908	2.280153	-0.205803
12	1	0	-1.550176	3.162236	-0.268895
13	6	0	-0.124121	0.930110	0.091161
14	6	0	0.648117	2.218415	0.089518
15	6	0	-3.538641	2.415264	-0.348001
16	1	0	-3.974030	3.402733	-0.523496
17	6	0	2.828685	-1.380129	-0.116355
18	6	0	2.229295	-2.646405	-0.111494
19	1	0	2.836563	-3.543640	-0.221210
20	6	0	-4.726603	-1.110314	0.103665
21	1	0	-4.335147	-2.106774	0.316129
22	6	0	-6.092220	-0.953327	-0.038416
23	1	0	-6.749188	-1.821266	0.057885
24	6	0	-5.811322	1.417631	-0.413643
25	1	0	-6.226285	2.409630	-0.612190
26	6	0	0.958463	2.847629	1.317044
27	6	0	1.058692	2.810867	-1.127938
28	6	0	1.770737	4.017367	-1.092562
29	1	0	2.081933	4.471854	-2.038159
30	6	0	-6.644435	0.319778	-0.305181
31	1	0	-7.725170	0.433449	-0.419308
32	6	0	1.672761	4.053543	1.304326
33	1	0	1.906304	4.536276	2.258242
34	6	0	2.092147	4.655921	0.111981
35	6	0	0.525452	2.239374	2.630525
36	1	0	0.948064	1.230787	2.769511
37	1	0	0.847409	2.858828	3.480157
38	1	0	-0.570020	2.131522	2.685241
39	6	0	0.733273	2.165182	-2.454571
40	1	0	1.121562	2.762823	-3.291928
41	1	0	1.167352	1.155060	-2.532780
42	1	0	-0.353986	2.051581	-2.594715
43	6	0	2.890901	5.936674	0.124224
44	1	0	2.693096	6.545948	-0.771071

45	1	0	2.664205	6.547308	1.011506
46	1	0	3.974939	5.726846	0.141281
47	1	0	-2.192385	-2.583385	-0.420602
48	6	0	0.252282	-4.147087	0.016268
49	6	0	4.332570	-1.276417	-0.192221
50	9	0	-0.493424	-4.348269	-1.089605
51	9	0	-0.551612	-4.374366	1.073537
52	9	0	1.195092	-5.100106	0.029342
53	9	0	4.846038	-2.177786	-1.048928
54	9	0	4.736910	-0.059903	-0.592223
55	9	0	4.901701	-1.509884	1.005837

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.404858 (Hartree/Particle)

Thermal correction to Energy= 0.435535

Thermal correction to Enthalpy= 0.436479

Thermal correction to Gibbs Free Energy= 0.339615

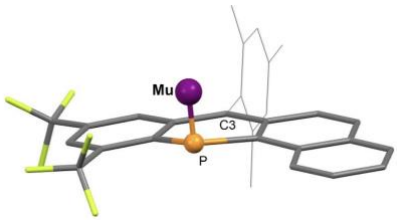
Sum of electronic and zero-point Energies= -2017.737861

Sum of electronic and thermal Energies= -2017.707184

Sum of electronic and thermal Enthalpies= -2017.706240

Sum of electronic and thermal Free Energies= -2017.803104

1Mu: flat



E_{total} = –2018.14019169 au, ν_{min} = 10.81 cm^{-1}

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2	6	0	1.593661	0.959323	0.064421
3	6	0	-0.630026	-0.300935	0.090348
4	6	0	3.843591	-0.078744	-0.053083
5	6	0	-0.062359	-1.613132	0.115991
6	6	0	2.415388	-0.194821	0.063193
7	6	0	-2.048291	-0.193323	0.013450
8	1	0	-2.502097	0.796150	0.002875
9	6	0	-0.918770	-2.735967	0.042095
10	6	0	4.448606	1.222601	-0.127576
11	6	0	2.243815	2.245789	-0.015933
12	1	0	1.624536	3.142345	-0.007886
13	6	0	0.153492	0.918168	0.076874
14	6	0	-0.592964	2.222050	0.066930
15	6	0	3.601738	2.369238	-0.097342
16	1	0	4.058298	3.361587	-0.146225
17	6	0	-2.864414	-1.309018	-0.044010
18	6	0	-2.304533	-2.592604	-0.036725
19	1	0	-2.943890	-3.472944	-0.080568
20	6	0	4.714087	-1.210053	-0.091455
21	1	0	4.285685	-2.213913	-0.064967
22	6	0	6.084113	-1.063028	-0.184972
23	1	0	6.721524	-1.950106	-0.218730
24	6	0	5.857143	1.342959	-0.222909
25	1	0	6.293884	2.343949	-0.277009
26	6	0	-0.945550	2.829945	-1.160478
27	6	0	-0.937734	2.848326	1.286765
28	6	0	-1.628476	4.067486	1.255801
29	1	0	-1.889119	4.548116	2.203722
30	6	0	6.667116	0.223450	-0.247778
31	1	0	7.752243	0.328836	-0.321838
32	6	0	-1.636434	4.049062	-1.143319
33	1	0	-1.903542	4.515101	-2.096722
34	6	0	-1.991407	4.685520	0.052753
35	6	0	-0.580906	2.186018	-2.477663
36	1	0	-1.017529	1.178399	-2.572278
37	1	0	-0.938011	2.787939	-3.325764
38	1	0	0.509875	2.067070	-2.582086
39	6	0	-0.564907	2.224020	2.611051
40	1	0	-0.910195	2.842014	3.452489
41	1	0	-1.007133	1.220848	2.725627
42	1	0	0.526043	2.099409	2.706890
43	6	0	-2.767120	5.980327	0.044873
44	1	0	-2.553366	6.586297	0.938564
45	1	0	-2.534757	6.586521	-0.844144

46	1	0	-3.854789	5.789818	0.033086
47	1	0	1.761965	-1.876017	1.768690
48	6	0	-0.370015	-4.154001	0.035071
49	6	0	-4.362037	-1.161832	-0.168252
50	9	0	0.438173	-4.382020	1.090697
51	9	0	0.338456	-4.411560	-1.074939
52	9	0	-1.351264	-5.069811	0.095056
53	9	0	-5.009471	-2.053002	0.603743
54	9	0	-4.781867	0.063210	0.185863
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Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.404421 (Hartree/Particle)

Thermal correction to Energy= 0.435195

Thermal correction to Enthalpy= 0.436139

Thermal correction to Gibbs Free Energy= 0.338388

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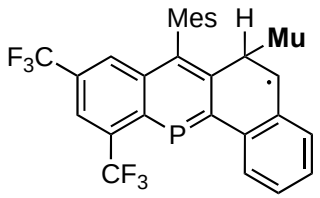
Sum of electronic and thermal Enthalpies= -2017.704053

Sum of electronic and thermal Free Energies= -2017.801804



C6-Mu

E_{total} = –2018.12591503 au, ν_{min} = 14.57 cm^{-1}

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1	15	0	1.695045	-1.886172	-0.000072
2	9	0	0.333929	-4.418233	1.083252
3	9	0	0.333907	-4.418206	-1.083546
4	9	0	-1.418303	-5.063959	-0.000138
5	9	0	-4.923155	-1.731014	1.079646
6	9	0	-4.922796	-1.731327	-1.080747
7	9	0	-4.777331	0.142488	-0.000799
8	6	0	-0.636301	-0.291829	0.000301
9	6	0	1.558334	0.920758	0.000933
10	6	0	3.837760	-0.168538	-0.000171
11	6	0	2.360592	-0.267963	0.000228
12	6	0	-0.058071	-1.604381	0.000094
13	6	0	-0.949198	-2.737332	-0.000104
14	6	0	4.478944	1.124796	0.000616
15	6	0	-2.058931	-0.170280	0.000017
16	1	0	-2.503658	0.823384	0.000106
17	6	0	2.230574	2.287295	0.001948
18	1	0	1.861094	2.873063	0.866242
19	6	0	0.160149	0.907101	0.000840
20	6	0	-2.877451	-1.274838	-0.000281
21	6	0	-0.420359	-4.162896	-0.000134
22	6	0	3.713669	2.291173	0.001705
23	1	0	4.218237	3.261436	0.002380
24	6	0	-0.566629	2.226041	0.001345
25	6	0	-2.317676	-2.572937	-0.000277
26	1	0	-2.970208	-3.445401	-0.000429
27	6	0	6.056730	-1.214077	-0.001718
28	1	0	6.659459	-2.125148	-0.002667
29	6	0	4.668207	-1.307960	-0.001365
30	1	0	4.217243	-2.301819	-0.002070
31	6	0	5.909634	1.192671	0.000249
32	1	0	6.378678	2.180218	0.000878
33	6	0	-4.379153	-1.139009	-0.000542
34	6	0	-0.904107	2.848890	-1.222798
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36	1	0	-1.822404	4.561303	2.150859
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44	1	0	0.498536	1.982872	-2.648009

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46	1	0	-1.095124	1.226268	-2.654343
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48	1	0	-1.099445	1.224641	2.655947
49	1	0	-0.883344	2.830385	3.390113
50	1	0	0.494863	1.980014	2.651332
51	6	0	-2.636236	6.042236	-0.003695
52	1	0	-3.715398	5.893587	-0.183527
53	1	0	-2.266138	6.707867	-0.799277
54	1	0	-2.533318	6.567865	0.957431
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Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.405906 (Hartree/Particle)

Thermal correction to Energy= 0.436798

Thermal correction to Enthalpy= 0.437743

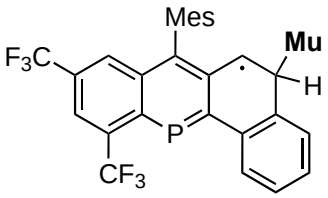
Thermal correction to Gibbs Free Energy= 0.339921

Sum of electronic and zero-point Energies= -2017.720009

Sum of electronic and thermal Energies= -2017.689117

Sum of electronic and thermal Enthalpies= -2017.688172

Sum of electronic and thermal Free Energies= -2017.785994



C7-Mu

E_{total} = –2018.12666199 au, ν_{min} = 3.20 cm^{-1}

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2	9	0	0.333929	-4.418233	1.083252
3	9	0	0.333907	-4.418206	-1.083546
4	9	0	-1.418303	-5.063959	-0.000138
5	9	0	-4.923155	-1.731014	1.079646
6	9	0	-4.922796	-1.731327	-1.080747
7	9	0	-4.777331	0.142488	-0.000799
8	6	0	-0.636301	-0.291829	0.000301
9	6	0	1.558334	0.920758	0.000933
10	6	0	3.837760	-0.168538	-0.000171
11	6	0	2.360592	-0.267963	0.000228
12	6	0	-0.058071	-1.604381	0.000094
13	6	0	-0.949198	-2.737332	-0.000104
14	6	0	4.478944	1.124796	0.000616
15	6	0	-2.058931	-0.170280	0.000017
16	1	0	-2.503658	0.823384	0.000106
17	6	0	2.230574	2.287295	0.001948
18	1	0	1.861094	2.873063	0.866242
19	6	0	0.160149	0.907101	0.000840
20	6	0	-2.877451	-1.274838	-0.000281
21	6	0	-0.420359	-4.162896	-0.000134
22	6	0	3.713669	2.291173	0.001705
23	1	0	4.218237	3.261436	0.002380
24	6	0	-0.566629	2.226041	0.001345
25	6	0	-2.317676	-2.572937	-0.000277
26	1	0	-2.970208	-3.445401	-0.000429
27	6	0	6.056730	-1.214077	-0.001718
28	1	0	6.659459	-2.125148	-0.002667
29	6	0	4.668207	-1.307960	-0.001365
30	1	0	4.217243	-2.301819	-0.002070
31	6	0	5.909634	1.192671	0.000249
32	1	0	6.378678	2.180218	0.000878
33	6	0	-4.379153	-1.139009	-0.000542
34	6	0	-0.904107	2.848890	-1.222798
35	6	0	-1.564069	4.084878	1.200348
36	1	0	-1.822404	4.561303	2.150859
37	6	0	-0.905454	2.846979	1.224363
38	6	0	6.682817	0.050961	-0.000885
39	1	0	7.773334	0.123514	-0.001166
40	6	0	-1.561912	4.085512	-1.198486
41	1	0	-1.818886	4.563009	-2.149075
42	6	0	-1.901305	4.723811	0.001646
43	6	0	-0.578324	2.193922	-2.545354
44	1	0	0.498536	1.982872	-2.648009

45	1	0	-0.879467	2.832141	-3.388522
46	1	0	-1.095124	1.226268	-2.654343
47	6	0	-0.581719	2.191857	2.547356
48	1	0	-1.099445	1.224641	2.655947
49	1	0	-0.883344	2.830385	3.390113
50	1	0	0.494863	1.980014	2.651332
51	6	0	-2.636236	6.042236	-0.003695
52	1	0	-3.715398	5.893587	-0.183527
53	1	0	-2.266138	6.707867	-0.799277
54	1	0	-2.533318	6.567865	0.957431
55	1	0	1.860898	2.874595	-0.861222

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.405992 (Hartree/Particle)

Thermal correction to Energy= 0.436941

Thermal correction to Enthalpy= 0.437886

Thermal correction to Gibbs Free Energy= 0.338164

Sum of electronic and zero-point Energies= -2017.720670

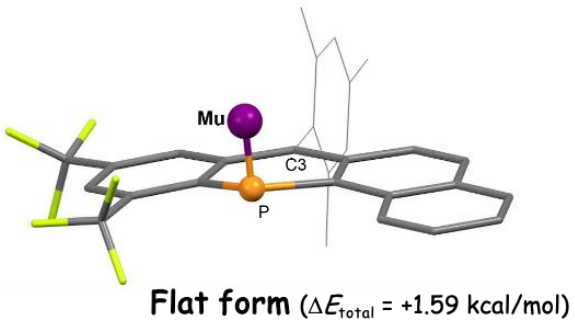
Sum of electronic and thermal Energies= -2017.689721

Sum of electronic and thermal Enthalpies= -2017.688776

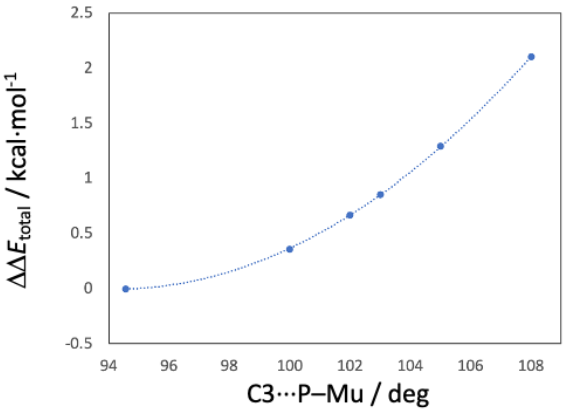
Sum of electronic and thermal Free Energies= -2017.788498

Figure S5

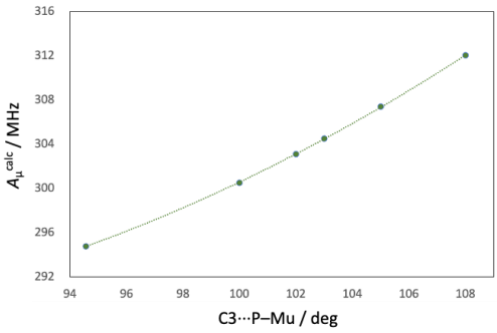
(**a**)



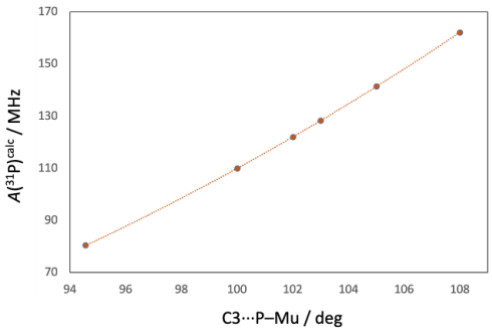
(**b**)



(**c**)



(**d**)



(a) A DFT-optimized structure of **1Mu** (flat form) under the UB3LYP/def2-SVP level. The angle of C3···P–Mu is 94.6°. (b) Relative total energy *versus* the C3···P–Mu angle. (c) DFT-calculated A_μ *versus* the C3···P–Mu angle. (d) DFT-calculated $A(^{31}P)$ *versus* the C3···P–Mu angle.