

Synthesis of diphenyl-(2-thienyl)phosphine, its chalcogenide derivatives and a series of novel complexes of lanthanide nitrates and triflates

Supplementary Information

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Table of Contents

X-Ray data

A. Ph ₂ thienylP=O (4).....	2
B. Ph ₂ thienylP=S (5).....	5
C. Ph ₂ thienylP=Se (6).....	7
D. La(4) ₃ (NO ₃) ₃	9
E. Sm(4) ₃ (NO ₃) ₃	12
F. Pr(4) ₃ (NO ₃) ₃	15
G. Tb(4) ₃ (NO ₃) ₃ (C ₆ H ₆).....	19
H. Er(4) ₃ (NO ₃) ₃ (C ₆ H ₆).....	22
I. Tb(4) ₄ (OTf) ₂ •OTf.....	25

NMR data

A. Ph ₂ thienylP (3).....	30
B. Ph ₂ thienylP=O (4).....	33
C. Ph ₂ thienylP=S (5).....	37
D. Ph ₂ thienylP=Se (6).....	41
E. La(4) ₃ (NO ₃) ₃	44
F. La(4) ₃ (OTf) ₃	46
G. Sm(4) ₃ (OTf) ₃	48

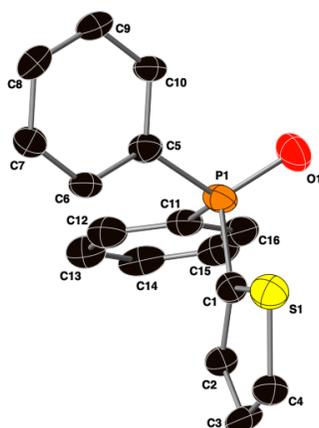
I. X-Ray Crystallography

For all figures in this section thermal ellipsoids are shown at the 50% probability level. Standard CPK colors are used throughout, and all non-polar hydrogen atoms have been omitted for clarity.

- For the free ligands **4-6**, the numbering scheme for all atoms is shown on the thermal ellipsoid plot.
- For the Ln-ligand complexes, the numbering scheme for all atoms but the pendant phenyl rings are shown with a ball and stick model.

A. Ph₂thienylP=O (**4**)

In this structure, the electron density corresponding to the thienyl ring was disordered. This disorder was modelled over two positions on the trigonal pyramid of the phosphorus atom with a 0.80:0.20 occupancy ratio. Only one part is shown below for clarity. All hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors. SADI commands were used to give bond lengths and angles that are consistent with literature values, and EADP commands were used to give reasonable thermal values.



Experimental

Single crystals of C₁₆H₁₃OPS (**4**) were grown by slow evaporation from a solution in CDCl₃. A suitable crystal was selected and mounted on a nylon loop using a very small amount of paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 99.98(13) K during data collection. Using Olex2 [1], the structure was solved with the the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of **4**

Crystal Data for C₁₆H₁₃OPS ($M=284.29$ g/mol): monoclinic, space group P2₁/n (no. 14), $a = 9.6867(2)$ Å, $b = 9.9115(2)$ Å, $c = 14.6285(3)$ Å, $\beta = 96.773(2)^\circ$, $V = 1394.67(5)$ Å³, $Z = 4$, $T = 99.98(13)$ K, $\mu(\text{CuK}\alpha) = 3.040$ mm⁻¹, $D_{\text{calc}} = 1.354$ g/cm³, 10173 reflections measured ($10.414^\circ \leq 2\theta \leq 153.192^\circ$), 2697 unique ($R_{\text{int}} = 0.0393$, $R_{\text{sigma}} = 0.0359$) which were used in all calculations. The final R_1 was 0.0713 ($I > 2\sigma(I)$) and wR_2 was 0.2002 (all data).

Refinement model description

Number of restraints - 2, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Restrained distances

$C5-S1A \approx C5-C6$

with sigma of 0.02

$C7-S1A \approx C7-C6$

with sigma of 0.02

3. Uiso/Uanis restraints and constraints

$U_{\text{anis}}(C3A) = U_{\text{anis}}(C8)$

$U_{\text{anis}}(C6) = U_{\text{anis}}(C10)$

$U_{\text{anis}}(S1A) = U_{\text{anis}}(S1)$

$U_{\text{anis}}(C2A) = U_{\text{anis}}(C9)$

$U_{\text{anis}}(C10A) = U_{\text{anis}}(C7A)$

$U_{\text{anis}}(C2) = U_{\text{anis}}(C6A)$

$U_{\text{anis}}(C4A) = U_{\text{anis}}(C7)$

$U_{\text{anis}}(C10A) = U_{\text{anis}}(C4)$

$U_{\text{anis}}(C9A) = U_{\text{anis}}(C2)$

$U_{\text{anis}}(C8A) = U_{\text{anis}}(C6A)$

$U_{\text{anis}}(C6A) = U_{\text{anis}}(C2)$

4. Others

Fixed Sof: S1(0.8) C6A(0.2) H6A(0.2) C7A(0.2) H7A(0.2) C8A(0.2) H8A(0.2)

C9A(0.2) H9A(0.2) C10A(0.2) H10A(0.2) C2(0.8) H2(0.8) C3(0.8) H3(0.8) C4(0.8)

H4(0.8) C6(0.8) H6(0.8) C7(0.8) H7(0.8) C8(0.8) H8(0.8) C9(0.8) H9(0.8)

C10(0.8) H10(0.8) S1A(0.2) C2A(0.2) H2A(0.2) C3A(0.2) H3A(0.2) C4A(0.2)

H4A(0.2)

5.a Aromatic/amide H refined with riding coordinates:

C6A(H6A), C7A(H7A), C8A(H8A), C9A(H9A), C10A(H10A), C2(H2), C3(H3), C4(H4),

C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13), C14(H14),

C15(H15), C16(H16), C2A(H2A), C3A(H3A), C4A(H4A)

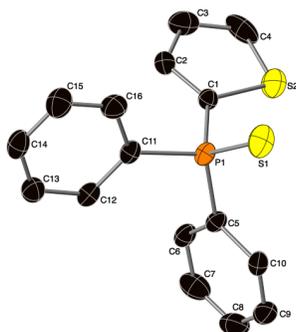
5.b Fitted hexagon refined as free rotating group:

C1(C6A,C7A,C8A,C9A,C10A), C5(C6,C7,C8,C9,C10)

Table 1 Crystal data and structure refinement for 4.

CCDC Number	2096359
Empirical formula	C ₁₆ H ₁₃ OPS
Formula weight	284.29
Temperature/K	99.98(13)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.6867(2)
b/Å	9.9115(2)
c/Å	14.6285(3)
α/°	90
β/°	96.773(2)
γ/°	90
Volume/Å ³	1394.67(5)
Z	4
ρ _{calc} /cm ³	1.354
μ/mm ⁻¹	3.040
F(000)	592.0
Crystal size/mm ³	0.262 × 0.136 × 0.049
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	10.414 to 153.192
Index ranges	-11 ≤ h ≤ 12, -8 ≤ k ≤ 12, -18 ≤ l ≤ 16
Reflections collected	10173
Independent reflections	2697 [R _{int} = 0.0393, R _{sigma} = 0.0359]
Data/restraints/parameters	2697/2/169
Goodness-of-fit on F ²	1.088
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0713, wR ₂ = 0.1953
Final R indexes [all data]	R ₁ = 0.0761, wR ₂ = 0.2002
Largest diff. peak/hole / e Å ⁻³	1.50/-0.77

B. Ph₂thienylP=S (5)



Experimental

Single crystals of C₁₆H₁₃PS₂ were grown by slow evaporation of a CDCl₃ solution. A suitable crystal was selected and mounted using a small amount of paratone oil on a nylon loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 296(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization.

4. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
5. Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
6. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of [5]

Crystal Data for C₁₆H₁₃PS₂ (*M* = 300.35 g/mol): monoclinic, space group P2₁/n (no. 14), *a* = 10.18080(10) Å, *b* = 9.50350(10) Å, *c* = 14.9030(2) Å, β = 94.0376(5)°, *V* = 1438.33(3) Å³, *Z* = 4, *T* = 296(2) K, μ (CuK α) = 4.246 mm⁻¹, *D*_{calc} = 1.387 g/cm³, 17457 reflections measured (10.196° ≤ 2 Θ ≤ 144.3°), 2831 unique (*R*_{int} = 0.0344, *R*_{sigma} = 0.0237) which were used in all calculations. The final *R*₁ was 0.0548 (*I* > 2 σ (*I*)) and *wR*₂ was 0.1564 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2.a Aromatic/amide H refined with riding coordinates:

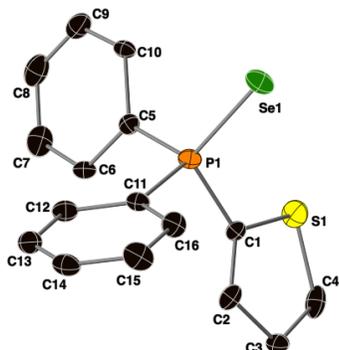
C2(H2), C3(H3), C4(H4), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16)

Table 1 Crystal data and structure refinement for **5**

Identification code	5
CCDC Number	1844568
Empirical formula	C ₁₆ H ₁₃ PS ₂
Formula weight	300.35
Temperature/K	296(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.18080(10)
b/Å	9.50350(10)
c/Å	14.9030(2)
α/°	90
β/°	94.0376(5)
γ/°	90
Volume/Å ³	1438.33(3)
Z	4
ρ _{calc} /cm ³	1.387
μ/mm ⁻¹	4.246
F(000)	624.0
Crystal size/mm ³	0.388 × 0.221 × 0.053
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	10.196 to 144.3
Index ranges	-11 ≤ h ≤ 12, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	17457
Independent reflections	2831 [R _{int} = 0.0344, R _{sigma} = 0.0237]
Data/restraints/parameters	2831/0/172
Goodness-of-fit on F ²	1.058
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0548, wR ₂ = 0.1545
Final R indexes [all data]	R ₁ = 0.0569, wR ₂ = 0.1564
Largest diff. peak/hole / e Å ⁻³	0.90/-0.88

C. Ph₂thienylP=Se (6)

In this structure the electron density corresponding to the thienyl ring was disordered. This disorder was modeled as two rotational isomers (rotated 180 ° around the P1-C1 bond) with a 0.893:0.107 ratio.



Experimental

Single crystals of C₁₆H₁₃PSSe were grown by slow evaporation of a CDCl₃ solution. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of [6]

Crystal Data for C₁₆H₁₃PSSe (*M* = 347.25 g/mol): monoclinic, space group P2₁/n (no. 14), *a* = 10.398(3) Å, *b* = 9.531(3) Å, *c* = 14.811(5) Å, *β* = 93.489(4)°, *V* = 1465.2(8) Å³, *Z* = 4, *T* = 173(2) K, *μ*(MoKα) = 2.797 mm⁻¹, *D*_{calc} = 1.574 g/cm³, 11733 reflections measured (4.656° ≤ 2θ ≤ 50.702°), 2683 unique (*R*_{int} = 0.0445, *R*_{sigma} = 0.0386) which were used in all calculations. The final *R*₁ was 0.0465 (*I* > 2σ(*I*)) and *wR*₂ was 0.1324 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2.a Aromatic/amide H refined with riding coordinates:

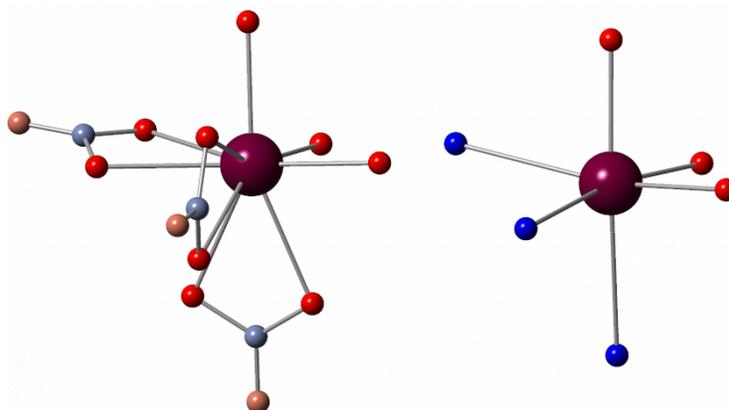
C2(H2), C3(H3), C4(H4), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16)

Table 1 Crystal data and structure refinement for **6**.

Identification code	6
CCDC Number	1844765
Empirical formula	C ₁₆ H ₁₃ PSSe
Formula weight	347.25
Temperature/K	173(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.398(3)
b/Å	9.531(3)
c/Å	14.811(5)
α/°	90
β/°	93.489(4)
γ/°	90
Volume/Å ³	1465.2(8)
Z	4
ρ _{calc} /cm ³	1.574
μ/mm ⁻¹	2.797
F(000)	696.0
Crystal size/mm ³	0.368 × 0.219 × 0.034
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.656 to 50.702
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	11733
Independent reflections	2683 [R _{int} = 0.0445, R _{sigma} = 0.0386]
Data/restraints/parameters	2683/0/172
Goodness-of-fit on F ²	1.065
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0465, wR ₂ = 0.1233
Final R indexes [all data]	R ₁ = 0.0607, wR ₂ = 0.1324
Largest diff. peak/hole / e Å ⁻³	0.73/-0.70

Details regarding modeling of the complete molecular disorder present in structures $\text{Ln}(\mathbf{4})_3(\text{NO}_3)_3$ (Ln = La, Pr, Sm)

The electron density of each of these structures was disordered for each atom except for the Ln metal. The asymmetric unit of these structures contain the Ln metal, one phosphine ligand, and one bidentate nitrate anion. Due to the high symmetry of the space group the data was solved in (R-3), when the asymmetric unit is grown the full structure depicts six ligands and six bidentate nitrates occupying the same positions around the metal center. Since the La metal carries a 3+ charge, and there are no outer sphere nitrate anions present, there must be three bidentate nitrates bound directly to the metal center. This means that there is complete molecular disorder in this structure. For ease of discussion, if the bidentate nitrate groups are considered to be monodentate ligands, then the La^{3+} center would be six-coordinate with pseudo-octahedral geometry (see figure below).

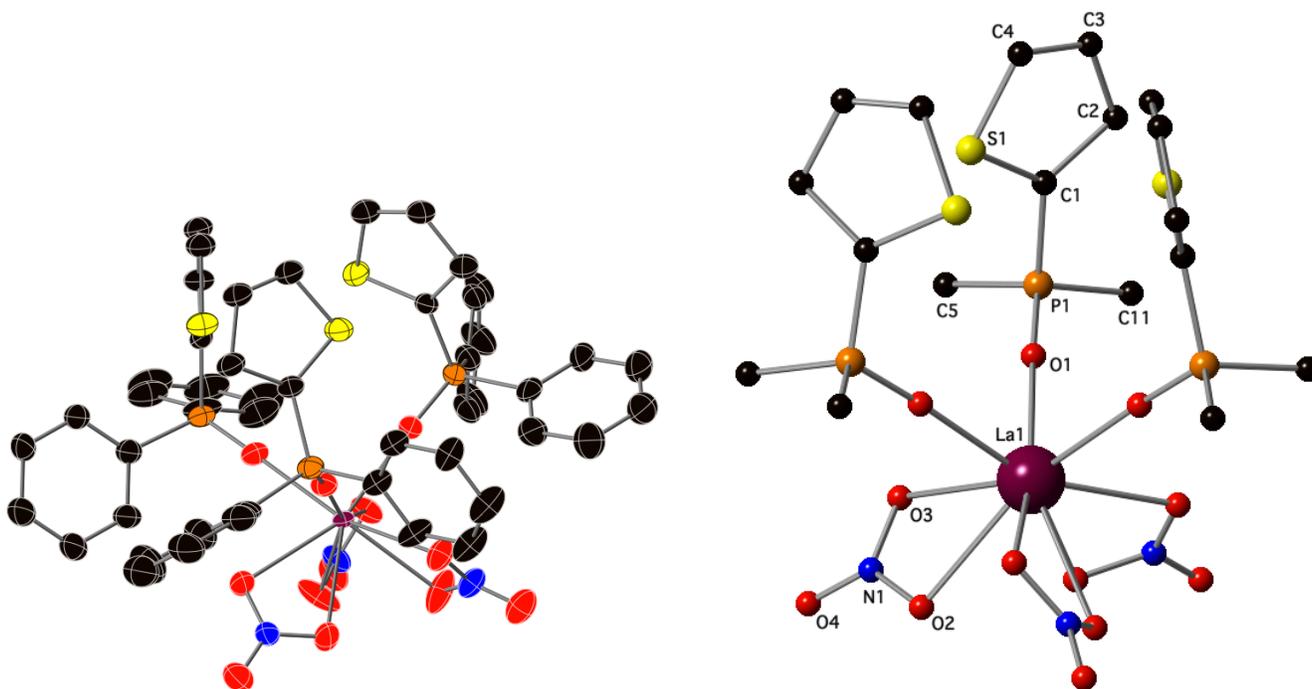


The metal coordination sphere of the $[\text{Ln}(\mathbf{4})_3(\text{NO}_3)_3]$ crystal structures. Left: all nine oxygen atoms (red) that coordinate to the metal (nitrogen and non-coordinating oxygen atom of the nitrate groups are depicted with lighter blue and red colors) with a tricapped trigonal prism polyhedral schematic (magenta) generated using CrystalMaker; Right: depiction of the bidentate nitrates as monodentate ligands through the nitrogen atom to give a six-coordinate metal (octahedral geometry).

If the complex's geometry is thought of as an octahedron, it cannot be determined directly from the electron density data whether the *facial* or *meridional* isomer of this octahedron exists. However, when we built the model of the *meridional* isomer by hand, steric clashing existed between aromatic rings of neighboring phosphine oxide ligands. When we built the model of the *facial* isomer by hand, there was no steric clashing between ligands. Based on this analysis we concluded that the *facial* isomer is present in the solid state. The figures here, and in the body of the manuscript, were prepared by building this model by hand (by manually deleting the atoms not present in the *fac*-isomer).

D. $\text{La(4)}_3(\text{NO}_3)_3$

In this structure, the electron density corresponding to the thienyl rings were disordered. This disorder was modelled over two orientations with a 0.84:0.16 occupancy ratio. Only one part is shown below for clarity. All hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (La = magenta). AFIX 66 and RIGU commands were used to give bond lengths and angles that are consistent with literature values. The figure on the left depicts the thermal ellipsoids of all atoms; the figure on the right shows the atom numbering scheme for all unique atoms, with the pendant phenyl rings omitted for clarity.



Experimental

Single crystals of $\text{C}_{48}\text{H}_{39}\text{LaN}_3\text{O}_{12}\text{P}_3\text{S}_3$ were grown by slow evaporation from a solution of $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ and used as received. A suitable crystal was selected and mounted on a nylon loop using small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of $(\text{La}(\text{4})_3(\text{NO}_3)_3)$

Crystal Data for $\text{C}_{48}\text{H}_{39}\text{LaN}_3\text{O}_{12}\text{P}_3\text{S}_3$ ($M = 1177.80$ g/mol): trigonal, space group R-3 (no. 148), $a = 19.720(5)$ Å, $c = 11.549(3)$ Å, $V = 3890(2)$ Å³, $Z = 3.00006$, $T = 173(2)$ K, $\mu(\text{MoK}\alpha) = 1.099$ mm⁻¹, $D_{\text{calc}} = 1.508$ g/cm³, 9924 reflections measured ($4.13^\circ \leq 2\theta \leq 50.688^\circ$), 1595 unique ($R_{\text{int}} = 0.0607$, $R_{\text{sigma}} = 0.0381$) which were used in all calculations. The final R_1 was 0.0906 ($I > 2\sigma(I)$) and wR_2 was 0.2962 (all data).

Refinement model description

Number of restraints - 168, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Shared sites

{S2, C2}

{S1, C17}

3. Uiso/Uanis restraints and constraints

Uanis(S2) = Uanis(C2)

Uanis(S1) = Uanis(C17)

4. Rigid body (RIGU) restrains

O2, O3, O4, N1

with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

P1, O1, C1, C5, C11, S1, C2, C6, C10, C12, C16, C4, H1, H2, C3, H6, C7, C9,

H10, H12, C13, C15, H16, H4, H3, H7, C8, H9, H13, C14, H15, H8, H14

with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004

5. Others

Fixed Sof: O2(0.5) O3(0.5) O4(0.5) N1(0.5) S1(0.42) P1(0.5) O1(0.5) C1(0.5)

C2(0.42) H2(0.42) C3(0.5) H3(0.5) C4(0.5) H4(0.5) C5(0.5) C6(0.5) H6(0.5)

C7(0.5) H7(0.5) C8(0.5) H8(0.5) C9(0.5) H9(0.5) C10(0.5) H10(0.5) C11(0.5)

C12(0.5) H12(0.5) C13(0.5) H13(0.5) C14(0.5) H14(0.5) C15(0.5) H15(0.5)

C16(0.5) H16(0.5) C17(0.08) H1(0.42) S2(0.08)

6.a Riding coordinates:

C17(H1)

6.b Aromatic/amide H refined with riding coordinates:

C2(H2), C3(H3), C4(H4), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12),

C13(H13), C14(H14), C15(H15), C16(H16)

6.c Fitted hexagon refined as free rotating group:

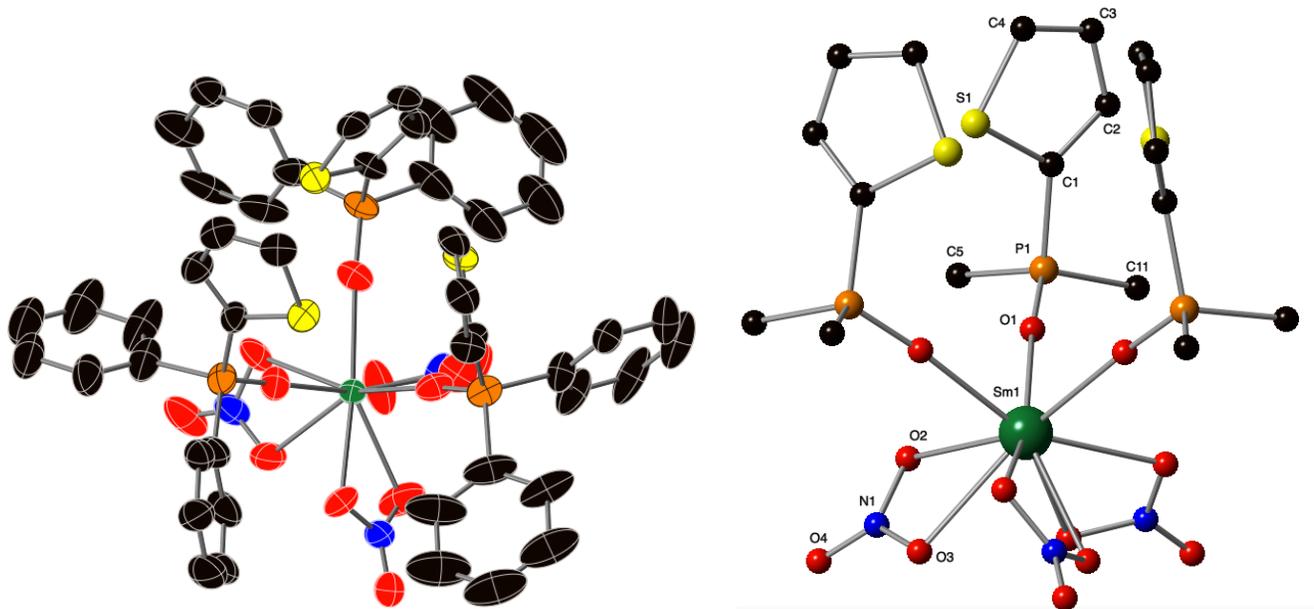
C5(C6,C7,C8,C9,C10), C11(C12,C13,C14,C15,C16)

Table 1 Crystal data and structure refinement for La(4)₃(NO₃)₃

CCDC Number	1846830
Empirical formula	C ₄₈ H ₃₉ LaN ₃ O ₁₂ P ₃ S ₃
Formula weight	1177.80
Temperature/K	173(2)
Crystal system	trigonal
Space group	R-3
a/Å	19.720(5)
b/Å	19.720(5)
c/Å	11.549(3)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	3890(2)
Z	3.00006
ρ _{calc} /cm ³	1.508
μ/mm ⁻¹	1.099
F(000)	1782.0
Crystal size/mm ³	0.256 × 0.247 × 0.157
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.13 to 50.688
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -13 ≤ l ≤ 13
Reflections collected	9924
Independent reflections	1595 [R _{int} = 0.0607, R _{sigma} = 0.0381]
Data/restraints/parameters	1595/168/186
Goodness-of-fit on F ²	1.202
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0906, wR ₂ = 0.2957
Final R indexes [all data]	R ₁ = 0.0910, wR ₂ = 0.2962
Largest diff. peak/hole / e Å ⁻³	1.26/-1.11

E. $\text{Sm}(\text{4})_3(\text{NO}_3)_3$

In this structure, the electron density corresponding to the thienyl rings were disordered. This disorder was modelled over two orientations with a 0.70:0.30 occupancy ratio. Only one part is shown below for clarity. All hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (Sm = green). AFIX 66, DFIX and DANG commands were used to give bond lengths and angles that are consistent with literature values. SIMU and DELU commands were used to ensure ellipsoids with reasonable thermal values. The figure on the left depicts the thermal ellipsoids of all atoms; the figure on the right shows the atom numbering scheme for all unique atoms, with the pendant phenyl rings omitted for clarity.



Experimental

Single crystals of $\text{C}_{48}\text{H}_{39}\text{N}_3\text{O}_{12}\text{P}_3\text{S}_3\text{Sm}$ [$\text{Sm}(\text{4})_3(\text{NO}_3)_3$] were grown from slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ solution used as received. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of [$\text{Sm}(\text{4})_3(\text{NO}_3)_3$]

Crystal Data for $\text{C}_{48}\text{H}_{39}\text{N}_3\text{O}_{12}\text{P}_3\text{S}_3\text{Sm}$ ($M=1189.24$ g/mol): trigonal, space group R-3 (no. 148), $a = 19.608(9)$ Å, $c = 11.469(5)$ Å, $V = 3819(4)$ Å³, $Z = 3.00006$, $T = 173$ K, $\mu(\text{MoK}\alpha) = 1.434$ mm⁻¹, $D_{\text{calc}} = 1.551$ g/cm³, 10213 reflections measured ($4.154^\circ \leq 2\theta \leq 50.91^\circ$), 1577 unique ($R_{\text{int}} = 0.0912$, $R_{\text{sigma}} = 0.0598$) which were used in all calculations. The final R_1 was 0.0769 ($I > 2\sigma(I)$) and wR_2 was 0.2379 (all data).

Refinement model description

Number of restraints - 191, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Restrained distances

S1-C4 = S1-C1

1.7 with sigma of 0.01

C3-C4 = C1-C2

1.34 with sigma of 0.01

C2-C3

1.3 with sigma of 0.01

3. Rigid bond restraints

C1, C2, C3, C4, S1

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C1A, C2A, C3A, C4A, S1A

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C11, C12, C13, C14, C15, C16

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C5, C10, C9, C8, C7, C6

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

4. Uiso/Uanis restraints and constraints

C1 ≈ C2 ≈ C3 ≈ C4 ≈ S1: within 2A with sigma of 0.02 and sigma for terminal atoms of 0.04

C1A ≈ C2A ≈ C3A ≈ C4A ≈ S1A: within 2A with sigma of 0.02 and sigma for terminal atoms of 0.04

C11 ≈ C12 ≈ C13 ≈ C14 ≈ C15 ≈ C16: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08

C5 ≈ C10 ≈ C9 ≈ C8 ≈ C7 ≈ C6: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08

Uanis(C1) = Uanis(C1A)

5. Same fragment restrains

{C1, C2, C3, C4, S1} sigma for 1-2: 0.01, 1-3: 0.02

as

{C1A, C2A, C3A, C4A, S1A}

6. Others

Fixed Sof: O2(0.5) O3(0.5) O4(0.5) N1(0.5) P1(0.5) O1(0.5) C1(0.35) C2(0.35)

H2(0.35) C3(0.35) H3(0.35) C4(0.35) H4(0.35) S1(0.35) C5(0.5) C6(0.5) H6(0.5)

C7(0.5) H7(0.5) C8(0.5) H8(0.5) C9(0.5) H9(0.5) C10(0.5) H10(0.5) C11(0.5)

C12(0.5) H12(0.5) C13(0.5) H13(0.5) C14(0.5) H14(0.5) C15(0.5) H15(0.5)

C16(0.5) H16(0.5) C1A(0.15) C2A(0.15) H2A(0.15) C3A(0.15) H3A(0.15) C4A(0.15)

H4A(0.15) S1A(0.15)

7.a Aromatic/amide H refined with riding coordinates:

C2(H2), C3(H3), C4(H4), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13), C14(H14), C15(H15), C16(H16), C2A(H2A), C3A(H3A), C4A(H4A)

7.b Fitted hexagon refined as free rotating group:

C5(C6,C7,C8,C9,C10), C11(C12,C13,C14,C15,C16)

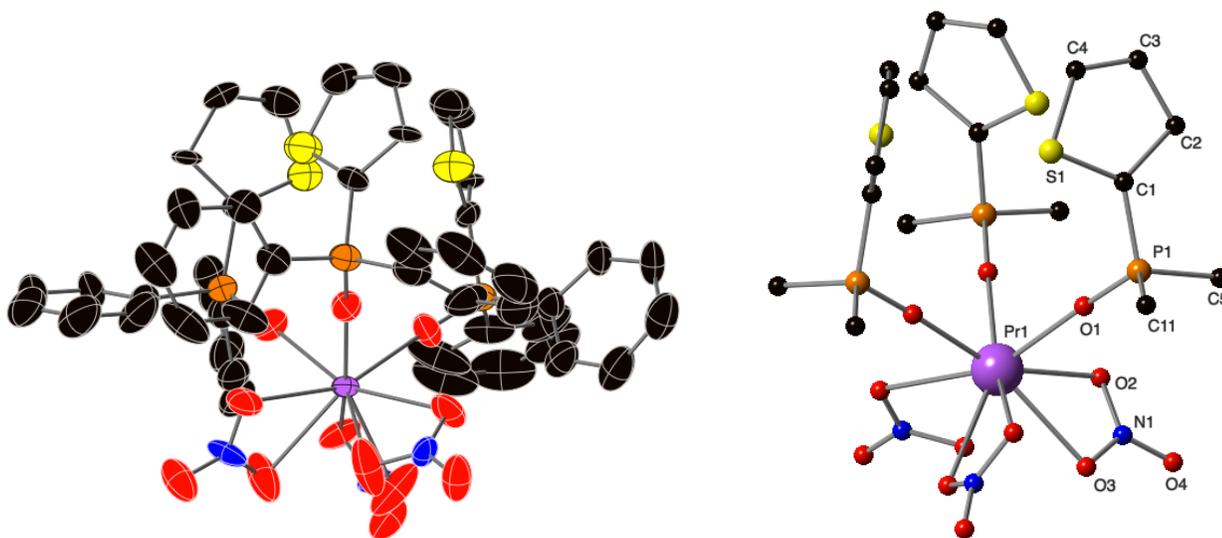
Table 1 Crystal data and structure refinement for Sm(4)₃(NO₃)₃.

CCDC Number	1922734
Empirical formula	C ₄₈ H ₃₉ N ₃ O ₁₂ P ₃ S ₃ Sm
Formula weight	1189.24
Temperature/K	173(2)
Crystal system	trigonal
Space group	R-3
a/Å	19.608(9)
b/Å	19.608
c/Å	11.469(5)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	3819(4)
Z	3.00006
ρ _{calc} /cm ³	1.551
μ/mm ⁻¹	1.434
F(000)	1797.0
Crystal size/mm ³	0.114 × 0.098 × 0.081
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.154 to 50.91
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -13 ≤ l ≤ 13
Reflections collected	10213
Independent reflections	1577 [R _{int} = 0.0912, R _{sigma} = 0.0598]
Data/restraints/parameters	1577/191/225
Goodness-of-fit on F ²	1.124
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0769, wR ₂ = 0.2368
Final R indexes [all data]	R ₁ = 0.0782, wR ₂ = 0.2379
Largest diff. peak/hole / e Å ⁻³	1.21/-0.95

F. Pr(4)₃(NO₃)₃

In this structure, we suspect there is some rotational disorder with the thiophene ring (as was seen with the La and Sm structures). However, this disorder seemed to be a very minor component in this case, so we did not model it. Furthermore, the data set already had a poor data/parameter ratio and we did not want to exacerbate this by adding another component. When we attempted to build a model that accounted for this disorder it resulted in a structure with statistically worse refinement values.

All hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (Pr = purple). The figure on the left depicts the thermal ellipsoids of all atoms; the figure on the right shows the atom numbering scheme for all unique atoms, with the pendant phenyl rings omitted for clarity.



Experimental

Single crystals of C₄₈H₃₉N₃O₁₂P₃PrS₃ [Pr(4)₃(NO₃)₃] were grown from slow evaporation of a CH₂Cl₂/CHCl₃ solution and used as received. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [Pr(4)₃(NO₃)₃]

Crystal Data for C₄₈H₃₉N₃O₁₂P₃PrS₃ (*M* = 1179.80 g/mol): trigonal, space group R-3 (no. 148), *a* = 19.836(11) Å, *c* = 11.610(6) Å, *V* = 3956(5) Å³, *Z* = 3.00006, *T* = 173.15 K, μ(MoKα) = 1.194 mm⁻¹, *D*_{calc} = 1.486 g/cm³, 7002 reflections measured (4.106° ≤ 2Θ ≤ 52.858°), 1778 unique (*R*_{int} = 0.0790, *R*_{sigma} = 0.0660) which were used in all calculations. The final *R*₁ was 0.0947 (*I* > 2σ(*I*)) and *wR*₂ was 0.2915 (all data).

Refinement model description

Number of restraints - 96, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Rigid bond restraints

C5, C10, C9, C8, C7, C6

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C11, C12, C13, C14, C15, C16

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

3. Uiso/Uaniso restraints and constraints

C5 ≈ C10 ≈ C9 ≈ C8 ≈ C7 ≈ C6: within 2Å with sigma of 0.04

and sigma for terminal atoms of 0.08

C11 ≈ C12 ≈ C13 ≈ C14 ≈ C15 ≈ C16: within 2Å with sigma of

0.04 and sigma for terminal atoms of 0.08

4. Others

Fixed Sof: S1(0.5) P1(0.5) O1(0.5) O2(0.5) O3(0.5) O4(0.5) N1(0.5) C1(0.5)

C2(0.5) H2(0.5) C3(0.5) H3(0.5) C4(0.5) H4(0.5) C5(0.5) C10(0.5) H10(0.5)

C9(0.5) H9(0.5) C8(0.5) H8(0.5) C7(0.5) H7(0.5) C6(0.5) H6(0.5) C11(0.5)

C12(0.5) H12(0.5) C13(0.5) H13(0.5) C14(0.5) H14(0.5) C15(0.5) H15(0.5)

C16(0.5) H16(0.5)

5.a Aromatic/amide H refined with riding coordinates:

C2(H2), C3(H3), C4(H4), C10(H10), C9(H9), C8(H8), C7(H7), C6(H6), C12(H12),

C13(H13), C14(H14), C15(H15), C16(H16)

5.b Fitted hexagon refined as free rotating group:

C5(C10,C9,C8,C7,C6)

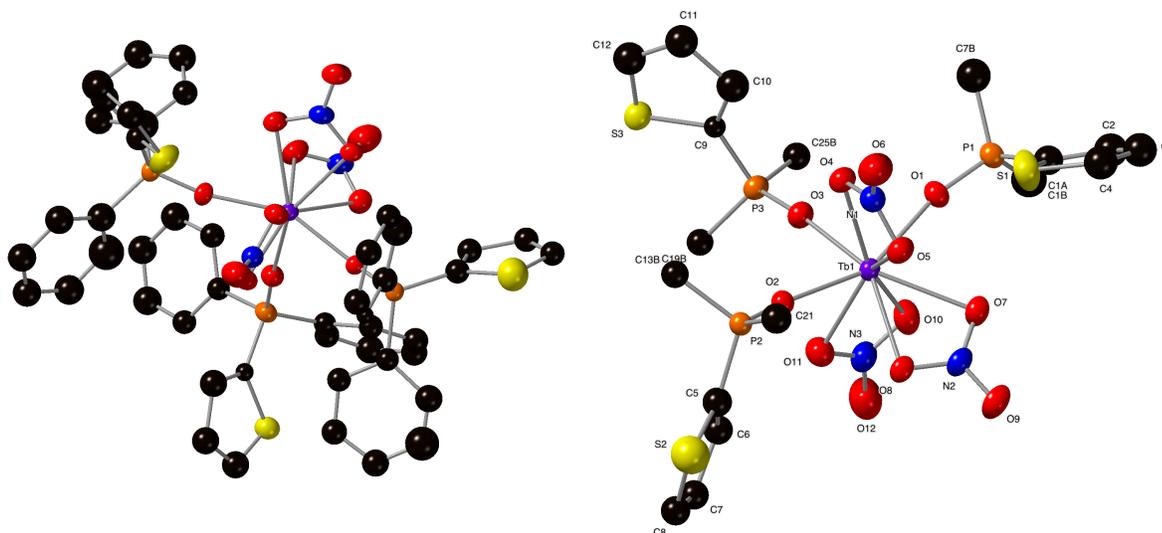
Table 1 Crystal data and structure refinement for Pr(4)₃(NO₃)₃

CCDC code	1922657
Empirical formula	C ₄₈ H ₃₉ N ₃ O ₁₂ P ₃ PrS ₃
Formula weight	1179.80
Temperature/K	173
Crystal system	trigonal
Space group	R-3
a/Å	19.836(11)
b/Å	19.836(11)
c/Å	11.610(6)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	3956(5)
Z	3.00006
ρ _{calc} /cm ³	1.486
μ/mm ⁻¹	1.194
F(000)	1788.0
Crystal size/mm ³	0.23 × 0.213 × 0.166
Radiation	MoKα (λ = 0.71073)

2 Θ range for data collection/ $^{\circ}$ 4.106 to 52.858
Index ranges -22 \leq h \leq 22, -24 \leq k \leq 24, -12 \leq l \leq 14
Reflections collected 7002
Independent reflections 1778 [$R_{\text{int}} = 0.0790$, $R_{\text{sigma}} = 0.0660$]
Data/restraints/parameters 1778/96/198
Goodness-of-fit on F^2 1.157
Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0947$, $wR_2 = 0.2897$
Final R indexes [all data] $R_1 = 0.0964$, $wR_2 = 0.2915$
Largest diff. peak/hole / e \AA^{-3} 1.09/-1.15

G. $\text{Tb(4)}_3(\text{NO}_3)_3(\text{C}_6\text{H}_6)$

The electron density for this structure was very disordered and was modeled as both rotational and positional isomers of the thienyl ring. The carbon atoms were left as isotropic in the final structure. In the figure below all hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (Tb = purple). The figure on the left depicts the thermal ellipsoids the Tb, O, N, P, and S atoms (50% probability); the figure on the right shows the atom numbering scheme for all atoms, with the pendant phenyl rings and solvent benzene molecule omitted for clarity.



Experimental.

Single colourless irregular crystals of $[\text{Tb(4)}_3(\text{NO}_3)_3(\text{C}_6\text{H}_6)]$ were grown by vapor diffusion of benzene into a solution of acetonitrile and used as received. A suitable crystal with dimensions $0.24 \times 0.10 \times 0.08 \text{ mm}^3$ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady $T = 100.00(10) \text{ K}$ during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 1.3-alpha (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

A colourless irregular-shaped crystal with dimensions $0.24 \times 0.10 \times 0.08 \text{ mm}^3$ was mounted on a nylon loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at $T = 100.00(10) \text{ K}$.

Data were measured using ω scans of 0.5° per frame for 2.0/7.9 s using $\text{Cu K}\alpha$ radiation (micro-focus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.84a, 2020). The actually achieved resolution was $\theta = 77.659$.

Cell parameters were retrieved using the CrysAlisPro (Rigaku, V1.171.40.84a, 2020) software and refined using CrysAlisPro (Rigaku, V1.171.40.84a, 2020) on 51200 reflections, 58 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Rigaku, V1.171.40.84a, 2020) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 77.659 in θ CrysAlisPro 1.171.40.84a (Rigaku Oxford

Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The structure was solved in the space group *Pbca* (# 61) by using dual methods using the ShelXT (Sheldrick, 2015) structure solution program. The structure was refined by Least Squares using version 2018/2 of XL (Sheldrick, 2008) incorporated in Olex2 (Dolomanov et al., 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the hydrogen atom on the non-carbon atom(s) which were found by difference Fourier methods and refined isotropically when data permits.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Citations

CrysAlisPro (Rigaku, V1.171.40.84a, 2020)

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

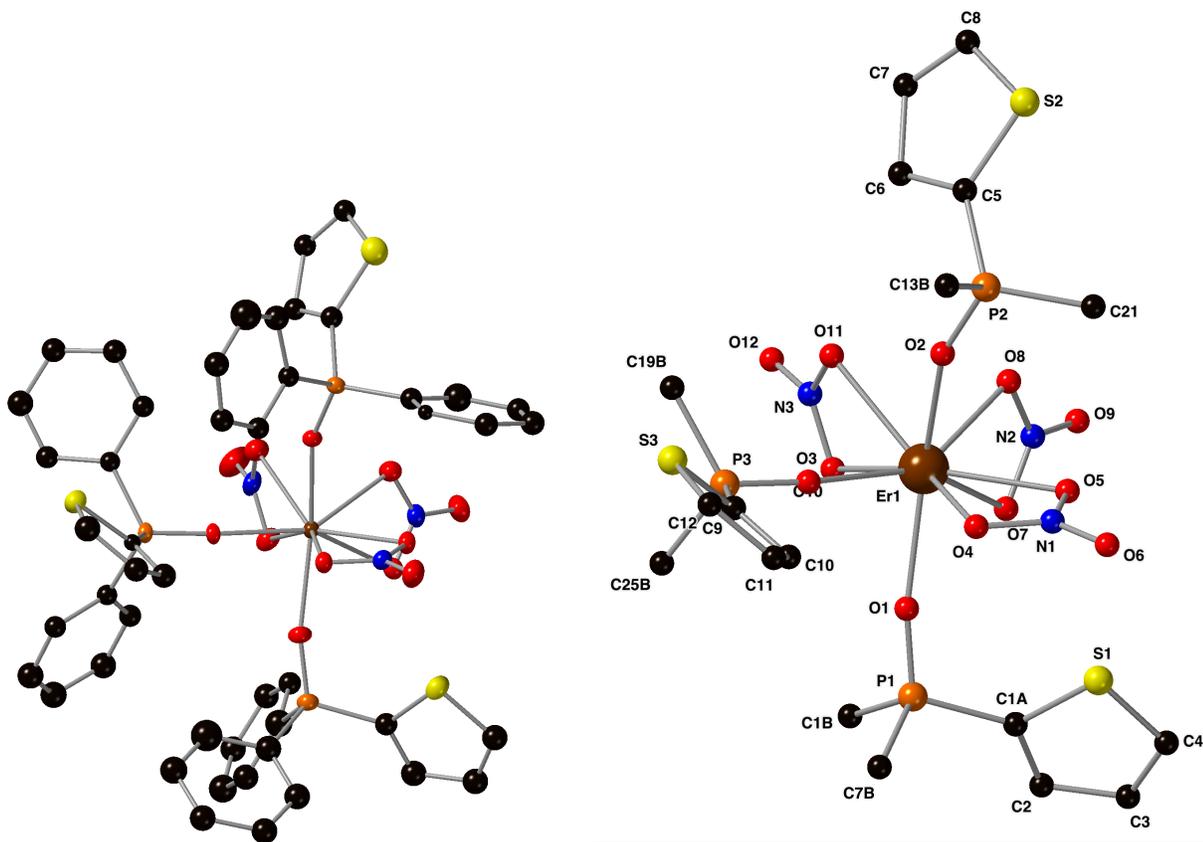
Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

Crystal Data. C₅₄H₄₅N₃O₁₂P₃S₃Tb, $M_r = 1275.94$, orthorhombic, *Pbca* (No. 61), $a = 20.75550(10) \text{ \AA}$, $b = 17.56580(10) \text{ \AA}$, $c = 30.25370(10) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 11030.10(9) \text{ \AA}^3$, $T = 100.00(10) \text{ K}$, $Z = 8$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 8.725$, 88674 reflections measured, 11654 unique ($R_{\text{int}} = 0.0353$) which were used in all calculations. The final wR_2 was 0.1640 (all data) and R_1 was 0.0608 ($I \geq 2 \sigma(I)$).

Compound	Tb(4)₃(NO₃)₃(C₆H₆)
CCDC number	2173564
Formula	C ₅₄ H ₄₅ N ₃ O ₁₂ P ₃ S ₃ Tb
<i>D</i> _{calc.} / g cm ⁻³	1.537
μ /mm ⁻¹	8.725
Formula Weight	1275.94
Colour	colourless
Shape	irregular
Size/mm ³	0.24×0.10×0.08
<i>T</i> /K	100.00(10)
Crystal System	orthorhombic
Space Group	<i>Pbca</i>
<i>a</i> /Å	20.75550(10)
<i>b</i> /Å	17.56580(10)
<i>c</i> /Å	30.25370(10)
α [°]	90
β [°]	90
γ [°]	90
<i>V</i> /Å ³	11030.10(9)
<i>Z</i>	8
<i>Z</i> '	1
Wavelength/Å	1.54184
Radiation type	Cu K α
θ _{min} [°]	3.606
θ _{max} [°]	77.659
Measured Refl's.	88674
Indep't Refl's	11654
Refl's I \geq 2 \square (I)	10855
<i>R</i> _{int}	0.0353
Parameters	452
Restraints	65
Largest Peak	1.730
Deepest Hole	-2.214
Goof	1.076
<i>wR</i> ₂ (all data)	0.1640
<i>wR</i> ₂	0.1612
<i>R</i> ₁ (all data)	0.0636
<i>R</i> ₁	0.0608

H. Er(4)₃(NO₃)₃(C₆H₆)

The electron density for this structure was very disordered and was modeled as both rotational and positional isomers of the thienyl ring. The carbon atoms were left as isotropic in the final structure. In the figure below all hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (Er = mocha). The figure on the left depicts the thermal ellipsoids of the Er, O, N, P and S atoms (50% probability); the figure on the right shows the atom numbering scheme using a ball and stick model, with the pendant phenyl rings and solvent benzene molecule omitted for clarity.



Experimental.

Single colourless irregular crystals of [Er(4)₃(NO₃)₃(C₆H₆)] were grown by vapor diffusion of benzene into acetonitrile and used as received. A suitable crystal with dimensions 0.19 × 0.12 × 0.07 mm³ was selected and mounted on a nylon loop with paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at a steady $T = 100.00(10)$ K during data collection. The structure was solved with the **ShelXT** (Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8) solution program using dual methods and by using **O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Olex2: a complete structure solution, refinement and analysis program.** *J. Appl. Cryst.* (2009). 42, 339-341. as the graphical interface. The model was refined with **ShelXL** (Sheldrick, *Acta Cryst.* A64 2008, 112-122) using full matrix least squares minimisation on F^2 .

Crystal Data. C₅₄H₄₅ErN₃O₁₂P₃S₃, $M_r = 1284.28$, orthorhombic, *Pbca* (No. 61), $a = 20.75560(10)$ Å, $b = 17.56230(10)$ Å, $c = 30.2522(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 11027.41(11)$ Å³, $T = 100.00(10)$ K, $Z = 8$, $Z' = 1$, $\mu(\text{Cu K}\alpha) = 5.245$, 89327 reflections measured, 11680 unique ($R_{\text{int}} = 0.0386$) which were used in all calculations. The final wR_2 was 0.1738 (all data) and R_1 was 0.0686 ($I \geq 2 \sigma(I)$).

Citations.

CrysAlisPro (Rigaku, V1.171.41.90a, 2020)

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

A colourless irregular-shaped crystal with dimensions $0.19 \times 0.12 \times 0.07$ mm³ was mounted on a nylon loop with paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at $T = 100.00(10)$ K.

Data were measured using ω scans of 0.5° per frame for 1.0/4.1 s using Cu K α radiation (micro-focus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.90a, 2020). The actually achieved resolution was $\theta = 77.665$.

Cell parameters were retrieved using the CrysAlisPro (Rigaku, V1.171.41.90a, 2020) software and refined using CrysAlisPro (Rigaku, V1.171.41.90a, 2020) on 43288 reflections, 48 % of the observed reflections. Data reduction was performed using the CrysAlisPro (Rigaku, V1.171.41.90a, 2020) software which corrects for Lorentz polarization. The final completeness is 100.00 out to 77.665 in θ CrysAlisPro 1.171.41.90a (Rigaku Oxford Diffraction, 2020) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The structure was solved in the space group *Pbca* (# 61) by using dual methods using the ShelXT (Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8) structure solution program. The structure was refined by Least Squares using version 2018/2 of XL (Sheldrick, 2008) incorporated in Olex2 (Dolomanov et al., 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the hydrogen atom on the non-carbon atom(s) which were found by difference Fourier methods and refined isotropically when data permits.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

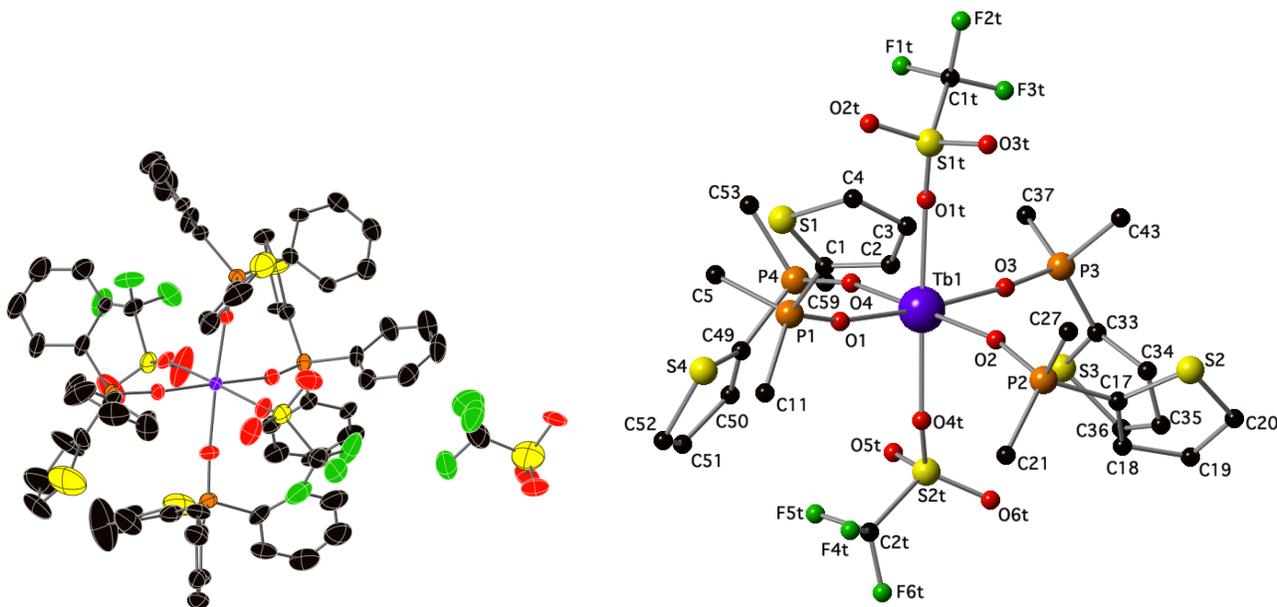
Compound	Er(4)₃(NO₃)₃(C₆H₆)
CCDC number	2173657
Formula	C ₅₄ H ₄₅ ErN ₃ O ₁₂ P ₃ S ₃
<i>D</i> _{calc.} / g cm ⁻³	1.547
μ /mm ⁻¹	5.245
Formula Weight	1284.28
Colour	colourless
Shape	irregular
Size/mm ³	0.19×0.12×0.07
<i>T</i> /K	100.00(10)
Crystal System	orthorhombic
Space Group	<i>Pbca</i>
<i>a</i> /Å	20.75560(10)
<i>b</i> /Å	17.56230(10)
<i>c</i> /Å	30.2522(2)
α [°]	90
β [°]	90
γ [°]	90
<i>V</i> /Å ³	11027.41(11)
<i>Z</i>	8
<i>Z</i> '	1
Wavelength/Å	1.54184
Radiation type	Cu K α
θ _{min} [°]	2.921
θ _{max} [°]	77.665
Measured Refl's.	89327
Indep't Refl's	11680
Refl's I \geq 2 σ (I)	10842
<i>R</i> _{int}	0.0386
Parameters	452
Restraints	65
Largest Peak	1.860
Deepest Hole	-2.279
Goof	1.038
<i>wR</i> ₂ (all data)	0.1738
<i>wR</i> ₂	0.1712
<i>R</i> ₁ (all data)	0.0722
<i>R</i> ₁	0.0686

I. $\text{Tb}(\mathbf{4})(\text{OTf})_3$

In this structure, the electron density corresponding to two of the thienyl rings, one coordinated triflate and the outer sphere triflate anion were disordered. This disorder was modelled over two orientations with a 50:50 and 33:67 occupancy ratio. DFIX, DANG and SAME commands were used to ensure bond lengths consistent with accepted values, and SIMU, DELU and EADP commands were used to ensure reasonable thermal values. In the figures below, only one part is shown below for clarity. All hydrogen atoms have been omitted for clarity, and atoms are depicted using standard CPK colors (Tb = purple). The figure on the left shows all atoms as thermal ellipsoids at the 30% probability level; the figure on the right omits the pendant phenyl groups and uncoordinated triflate anion, and shows the atom numbering scheme using a ball and stick model.

We suspect that there is additional positional disorder of the thienyl rings present in this structure (meaning: some thienyl rings may be disordered with a phenyl ring of the parent phosphine ligand). This is supported by thermal values for carbon atoms on adjacent benzene rings that are smaller than their neighbors. The residual electron density present from this disorder is minimal. We have chosen not to model the positional disorder of the thienyl rings because it is minimal and because we'd rather maintain a higher data to parameter ratio.

The intensity contribution of additional disordered electron density was removed using the `BYPASS`¹ command as implemented in `OLEX2`.² We suspect that this electron density corresponds to one molecule of toluene that is rotationally disordered on a symmetry site. The space is located at average x,y,z coordinates of [0.500, 0.000, 0.000], has a calculated volume of 176.2 Å³ and contains approximately 44.5 electrons.



Experimental

Single crystals of $\text{C}_7\text{H}_{52}\text{F}_9\text{O}_{13}\text{P}_4\text{S}_7\text{Tb}$ [$\text{Tb}(\mathbf{4})(\text{OTf})_3$] were grown by vapor diffusion of toluene/hexane into a solution of the complex. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection.

Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [4] refinement package using Least Squares minimization.

1. van der Sluis, P.; Spek, A. L., "BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions". *Acta Cryst.* **1990**, *A46*, 194-201.
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* **42**, 339-341.
3. Sheldrick, G.M. (2015). *Acta Cryst.* **A71**, 3-8.
4. Sheldrick, G.M. (2015). *Acta Cryst.* **C71**, 3-8.

Crystal structure determination of [Tb(4)₄(OTf)₃]

Crystal Data for C₆₇H₅₂F₉O₁₃P₄S₇Tb (*M*=1743.30 g/mol): triclinic, space group P-1 (no. 2), *a* = 13.7126(11) Å, *b* = 14.5867(12) Å, *c* = 19.8641(17) Å, *α* = 86.1680(10)°, *β* = 71.5830(10)°, *γ* = 89.4960(10)°, *V* = 3761.0(5) Å³, *Z* = 2, *T* = 173.15 K, *μ*(MoKα) = 1.300 mm⁻¹, *D*_{calc} = 1.539 g/cm³, 61327 reflections measured (3.13° ≤ 2θ ≤ 50.806°), 13819 unique (*R*_{int} = 0.0467, *R*_{sigma} = 0.0410) which were used in all calculations. The final *R*₁ was 0.0537 (*I* > 2σ(*I*)) and *wR*₂ was 0.1563 (all data).

Refinement model description

Number of restraints - 349, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. Restrained distances

S1-C1 = S1-C4

1.7 with sigma of 0.01

C4-C3 = C2-C1

1.34 with sigma of 0.01

C3-C2

1.3 with sigma of 0.01

P3-C33A

1.78 with sigma of 0.01

P3-S3A

3 with sigma of 0.01

3. Restrained planarity

C17, S2, C20, C19, C18

with sigma of 0.1

C49, S4, C52, C51, C50

with sigma of 0.1

C49A, C50A, C51A, C52A, S4A

with sigma of 0.1

C33A, C34A, C36A, C35A, S3A, P3

with sigma of 0.1

S3, C33, C34, C35, C36

with sigma of 0.1

4. Rigid bond restraints

C33, S3, C36, C35, C34

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C33A, C34A, C35A, C36A, S3A

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

C49A, C50A, C51A, C52A, S4A

with sigma for 1-2 distances of 0.02 and sigma for 1-3 distances of 0.04
C49, S4, C52, C51, C50

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C17, C18, C19, C20, S2

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.02
C33A, S3A, C36A, C35A, C34A

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C3T, F7T, F8T, F9T

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C2R, F4R, F5R, F6R

with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01

5. Uiso/Uanis restraints and constraints

C49A \approx C50A \approx C51A \approx C52A \approx S4A: within 2A with sigma of 0.01
and sigma for terminal atoms of 0.02

C17 \approx C18 \approx C19 \approx C20 \approx S2: within 2A with sigma of 0.02 and
sigma for terminal atoms of 0.04

C2R \approx F4R \approx F5R \approx F6R: within 2A with sigma of 0.04 and sigma for
terminal atoms of 0.08

Uanis(C34A) = Uanis(C34)

Uanis(C50) = Uanis(C50A)

Uanis(C33A) = Uanis(C33)

Uanis(C49) = Uanis(C49A)

6. Same fragment restrains

{S1, C1, C2, C3, C4} sigma for 1-2: 0.02, 1-3: 0.04

as

{S2, C17, C18, C19, C20}

{S1, C1, C2, C3, C4} sigma for 1-2: 0.01, 1-3: 0.02

as

{S3, C33, C34, C35, C36}

{S1, C1, C2, C3, C4} sigma for 1-2: 0.02, 1-3: 0.04

as

{S3A, C33A, C34A, C35A, C36A}

{S1, C1, C2, C3, C4} sigma for 1-2: 0.02, 1-3: 0.04

as

{S4, C49, C50, C51, C52}

{S1, C1, C2, C3, C4} sigma for 1-2: 0.02, 1-3: 0.04

as

{S4A, C49A, C50A, C51A, C52A}

{S1T, O1T, O2T, O3T, C1T, F1T, F2T, F3T} sigma for 1-2: 0.01, 1-3: 0.02

as

{S2T, O4T, O5T, O6T, C2T, F4T, F5T, F6T}

{S1T, O1T, O2T, O3T, C1T, F1T, F2T, F3T} sigma for 1-2: 0.02, 1-3: 0.04

as

{S2R, O4R, O5R, O6R, C2R, F4R, F5R, F6R}

{C1T, F1T, F2T, F3T} sigma for 1-2: 0.02, 1-3: 0.04

as

{C3T, F7T, F8T, F9T}

{S3T, O7T, O8T, O9T, C3T, F7T, F8T, F9T} sigma for 1-2: 0.02, 1-3: 0.04

as

{S3R, O7R, O8R, O9R, C3R, F7R, F8R, F9R}

7. Others

Fixed Sof: S3(0.66667) C33(0.66667) C34(0.66667) H34(0.66667) C35(0.66667)
H35(0.66667) C36(0.66667) H36(0.66667) S3A(0.33333) C33A(0.33333)
C34A(0.33333) H34A(0.33333) C35A(0.33333) H35A(0.33333) C36A(0.33333)
H36A(0.33333) S4(0.5) C49(0.5) C50(0.5) H50(0.5) C51(0.5) H51(0.5) C52(0.5)
H52(0.5) S4A(0.5) C49A(0.5) C50A(0.5) H50A(0.5) C51A(0.5) H51A(0.5) C52A(0.5)
H52A(0.5) S2T(0.5) O4T(0.5) O5T(0.5) O6T(0.5) C2T(0.5) F4T(0.5) F5T(0.5)
F6T(0.5) S2R(0.5) O4R(0.5) O5R(0.5) O6R(0.5) C2R(0.5) F4R(0.5) F5R(0.5)
F6R(0.5) S3T(0.5) O7T(0.5) O8T(0.5) O9T(0.5) C3T(0.5) F7T(0.5) F8T(0.5)
F9T(0.5) S3R(0.5) O7R(0.5) O8R(0.5) O9R(0.5) C3R(0.5) F7R(0.5) F8R(0.5)
F9R(0.5)

8.Aromatic/amide H refined with riding coordinates:

C2(H2), C3(H3), C4(H4), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12),
C13(H13), C14(H14), C15(H15), C16(H16), C18(H18), C19(H19), C20(H20), C22(H22),
C23(H23), C24(H24), C25(H25), C26(H26), C28(H28), C29(H29), C30(H30),
C31(H31), C32(H32), C34(H34), C35(H35), C36(H36), C34A(H34A), C35A(H35A),
C36A(H36A), C38(H38), C39(H39), C40(H40), C41(H41), C42(H42), C44(H44),
C45(H45), C46(H46), C47(H47), C48(H48), C50(H50), C51(H51), C52(H52),
C50A(H50A), C51A(H51A), C52A(H52A), C54(H54), C55(H55), C56(H56), C57(H57),
C58(H58), C60(H60), C61(H61), C62(H62), C63(H63), C64(H64)

Table 1 Crystal data and structure refinement for Tb(4)₄(OTf)₃.

CCDC Number	1850479
Empirical formula	C ₆₇ H ₅₂ F ₉ O ₁₃ P ₄ S ₇ Tb
Formula weight	1743.30
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.7126(11)
b/Å	14.5867(12)
c/Å	19.8641(17)
α/°	86.1680(10)
β/°	71.5830(10)
γ/°	89.4960(10)
Volume/Å ³	3761.0(5)
Z	2
ρ _{calc} /cm ³	1.539
μ/mm ⁻¹	1.300
F(000)	1752.0
Crystal size/mm ³	0.324 × 0.193 × 0.126
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.13 to 50.806
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -23 ≤ l ≤ 23
Reflections collected	61327
Independent reflections	13819 [R _{int} = 0.0467, R _{sigma} = 0.0410]
Data/restraints/parameters	13819/349/1120

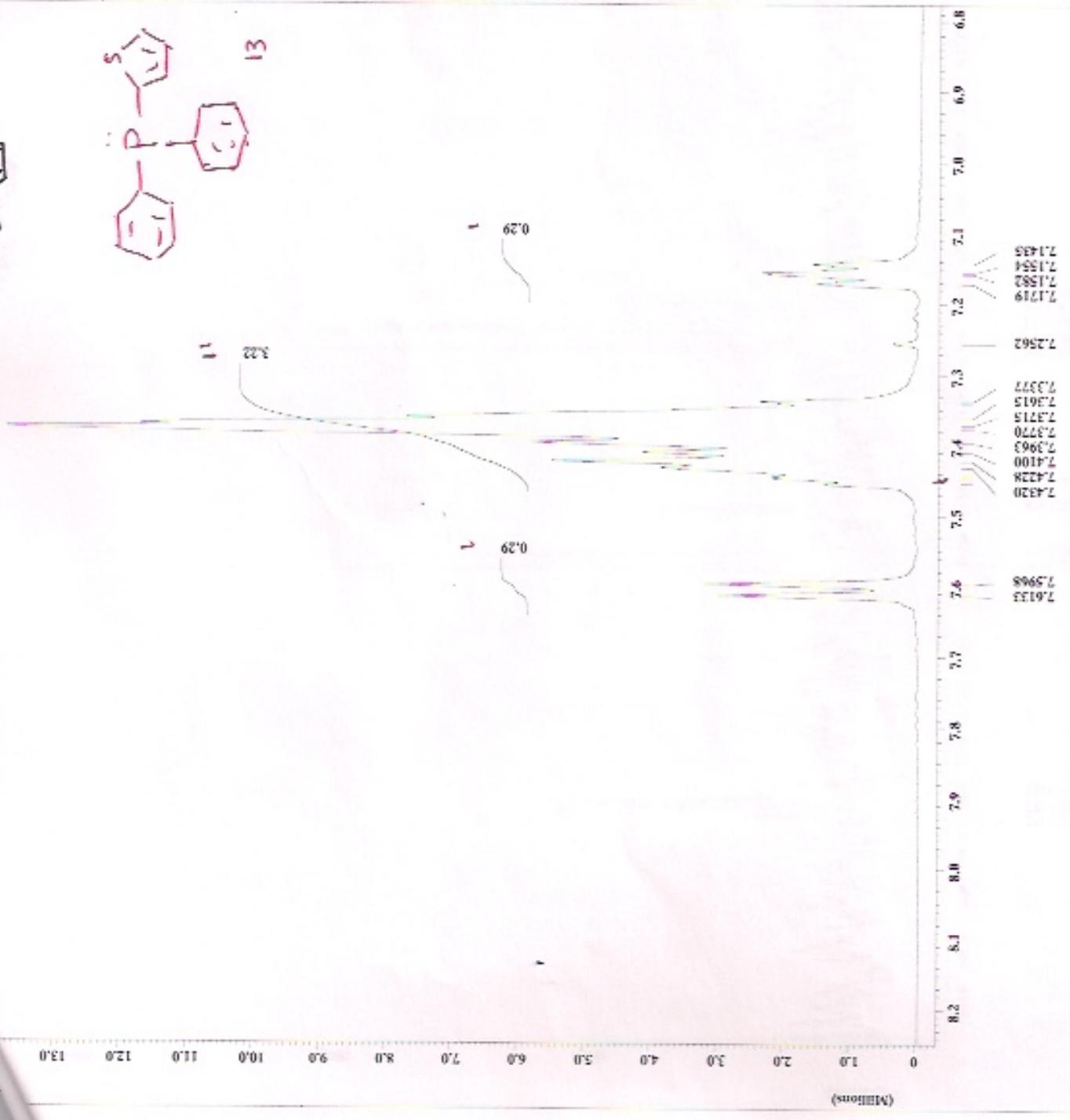
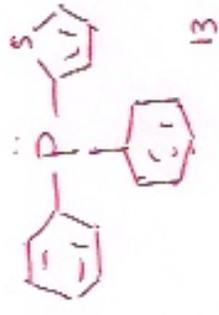
Goodness-of-fit on F^2 1.060
Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0537$, $wR_2 = 0.1459$
Final R indexes [all data] $R_1 = 0.0636$, $wR_2 = 0.1563$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 1.68/-1.36

Solvent masks information for $Tb(4)_4(OTf)_3$.

Number	X	Y	Z	Volume	Electron count	Content
1	0.500	0.000	0.000	176.2	44.5	toluene (?)

Ph₂P(S)

Proton Pure Mg¹⁸, 2016



```

=====
File Name = TL phos A CDCL3-d.1d
Author = benderj_lab
Experiment = single_pulse.exp
Sample_ID = NO-1-5
Solvent = CHLOROFORM-D
Creation Time = 22-MAY-2006 01:53:21
Revision Time = 19-MAY-2016 11:23:43
Current List = 19-MAY-2016 11:23:54

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Comment = Single Pulse Experiment
Data Format = 1D COMPLEX
Bin Size = 16384
Bin Title =
Bin Units = (ppm)
Dimensions = X
Site = Eclipse-300
Spectrometer = ECLIPSE-RMR

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Field Strength = 7.0556013(7) 1300 (MHz)
Acq Duration = 3.5219712(s)
RG = 18
X Freq = 300.52965492 (MHz)
X Offset = 5(ppm)
X Points = 16384
X Prescans = 0
X Resolution = 0.37518105 (Hz)
X Sfreq = 4.5085628 (kHz)
Clipped = FALSE
Cod Return = 1
Scans = 16
Total Scans = 16

=====
X Sd Width = 15.32(us)
X Acq Time = 3.6139712(s)
X Angle = 45(deg)
X Pulse = 7.66(us)
Initial Wait = 1(s)
Phase Preset = 3(us)
Sacr Gain = 18
Relaxation Delay = 4(s)
Verg Get = 2.3(dc)
Vb Blank Time = 2(us)
=====

```

X : parts per Million : 1H

Ph₂P-65

Carbon Pure May 18 2016



```

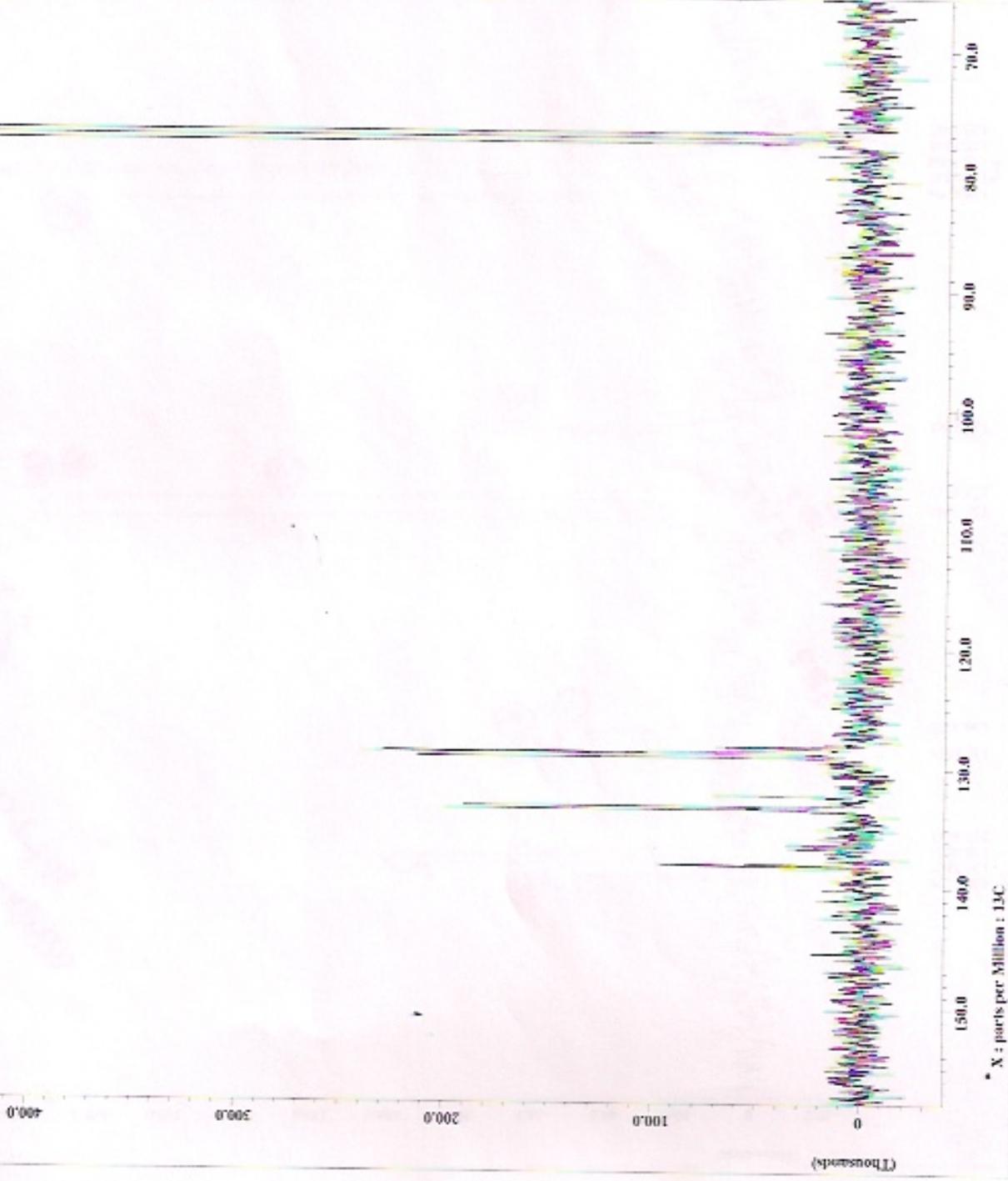
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Author = bender1_lab
Experiment = single_pulse_dec
Sample_id = 8447384
Solvent = CHLOROFORM-D
Creation_time = 22-MAY-2015 04:23:43
Revision_time = 19-MAY-2015 12:54:16
Current_time = 19-MAY-2015 12:54:25

Comment = Single Pulse with Bco
Data_format = 1D COMPLEX
Dir_size = 32768
Dir_title = 13C
Dir_units = (ppm)
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_RMR

Field_strength = 7.0486013171 (300 MHz)
X_acc_duration = 1.7334272(s)
X_domain = 13C
X_freq = 75.56823426 (MHz)
X_offset = 100 (ppm)
X_points = 32768
X_prescans = 4
X_resolution = 0.57683184 (Hz)
X_sweep = 18.50339168 (kHz)
Irr_domain = 1R
Irr_freq = 300.52955392 (MHz)
Irr_offset = 5 (ppm)
Clipped = FALSE
Mod_return = 1
Scans = 603
Total_scans = 603

X_90_width = 10.86 (us)
X_acq_line = 1.7334272 (s)
X_angle = 30 (deg)
X_pulse = 3.62 (us)
Initial_wait = 1 (s)
Phase_preset = 3 (us)
Recvr_gain = 30
Relaxation_delay = 1 (s)
Torgg_out = 22.1 (CC)
Doblock_time = 2 (us)

```



Yellow oil/Solid
 Test tube 4-7
 Troy L.

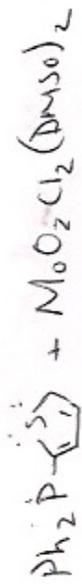
Ph₂P(=O) (pure)

Std proton
 Std proton
 File: Pncphorus
 PPM2 schwaiber 42.pu1 - 1437

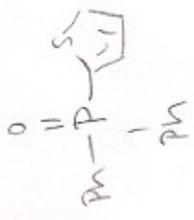
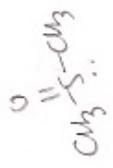
date	time	temp	loop	not used
May 15 2016	14:37	300	1	
solvent	cdcl3	gain	32	
file	exp	spin	22	
acq	exp	nsf	1.205	
sc	21036.0	nsf	21.002	
at	1.600	offa	13.002	
cp	67316			
fb	12000	13		
bs	13			
el	1.000	sp		
et	256	ns		
ct	256	ns		
tr	TRANSMITTER	256	1b	1.02
tr	161.835	fn		not used
trf	5211.1	sp		DISPLAY
tpwr	55	wp		-6553.7
sw	12.300	rfi		21335.7
de	DECOUPLER	rfp		6554.3
dn	0	rp		
drf	0	lp		-152.2
dx	592	vc		-151.5
dtn	44	sc		253
gpr	9200	sc		3
gtf		sc		5705
		ch		4
		st		cdc ph

18.922





May June 2nd, 2016
 Troy Luster
 (purple crystals)

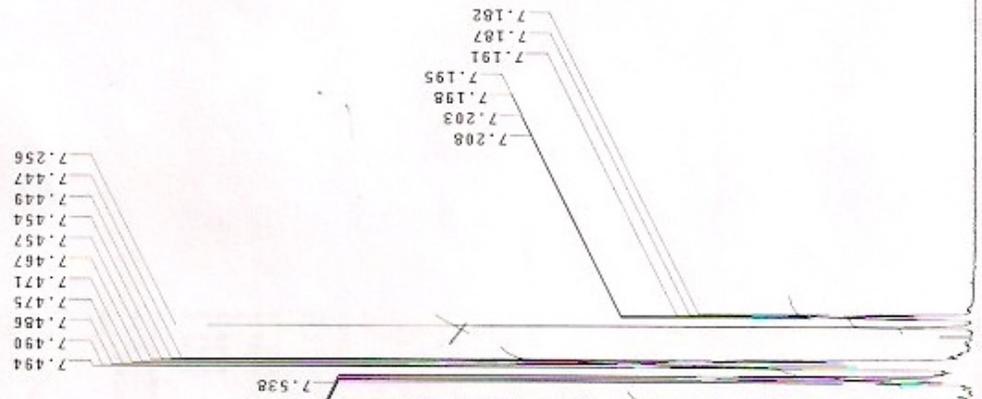


Std proton

File: Proton

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
 Operator: chm241
 INOVA-400 "woodward.gvsu.edu"

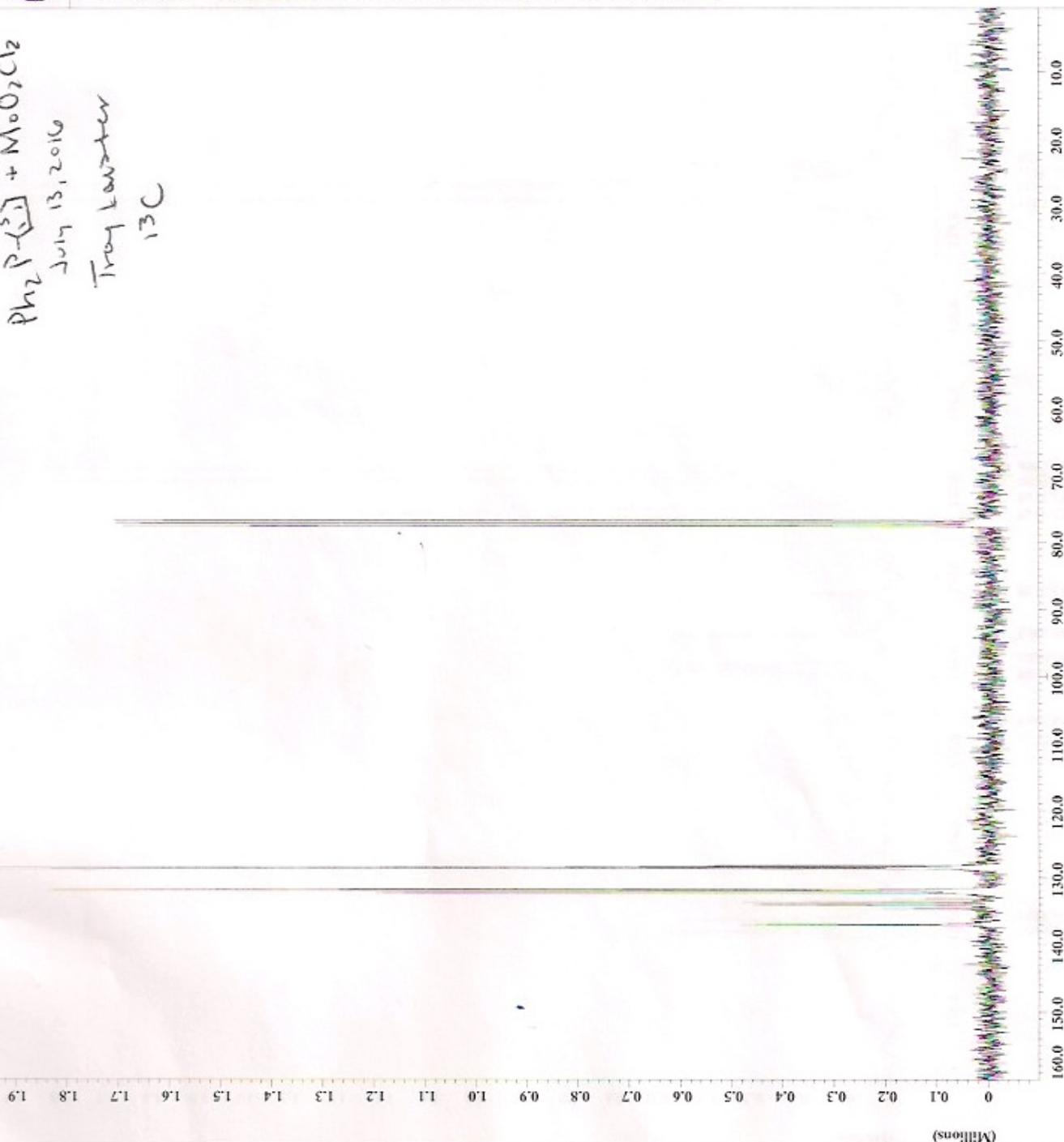
Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6386.4 Hz
 15 repetitions
 OBSERVE H1 399.7695340 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 20 min, 55 sec





Ph₂P-(⁶³) + MoO₃Cl₂
July 13, 2016
Troy Lawster
13C

Filename = TL (Ar)3P=O 13C CD
Author = benderj_lab
Experiment = single_pulse_dec
Sample_id = S#545611
Solvent = CHLOROFORM-D
Creation_time = 16-JUL-2000 06:48:19
Revision_time = 13-JUL-2016 15:22:18
Current_time = 13-JUL-2016 15:22:28
Comment = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_NMR
Field_strength = 7.0586013[T] (300)[MHz]
X_acq_duration = 1.7334272[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.57689184[Hz]
X_sweep = 10.90359168[KHz]
Irr_domain = H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 259
Total_scans = 259
X_90_width = 10.86[us]
X_acq_time = 1.7334272[s]
X_angle = 30[deg]
X_pulse = 3.62[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 1[s]
Temp_get = 23.2[dc]
Unblank_time = 2[us]



X : parts per Million : 13C



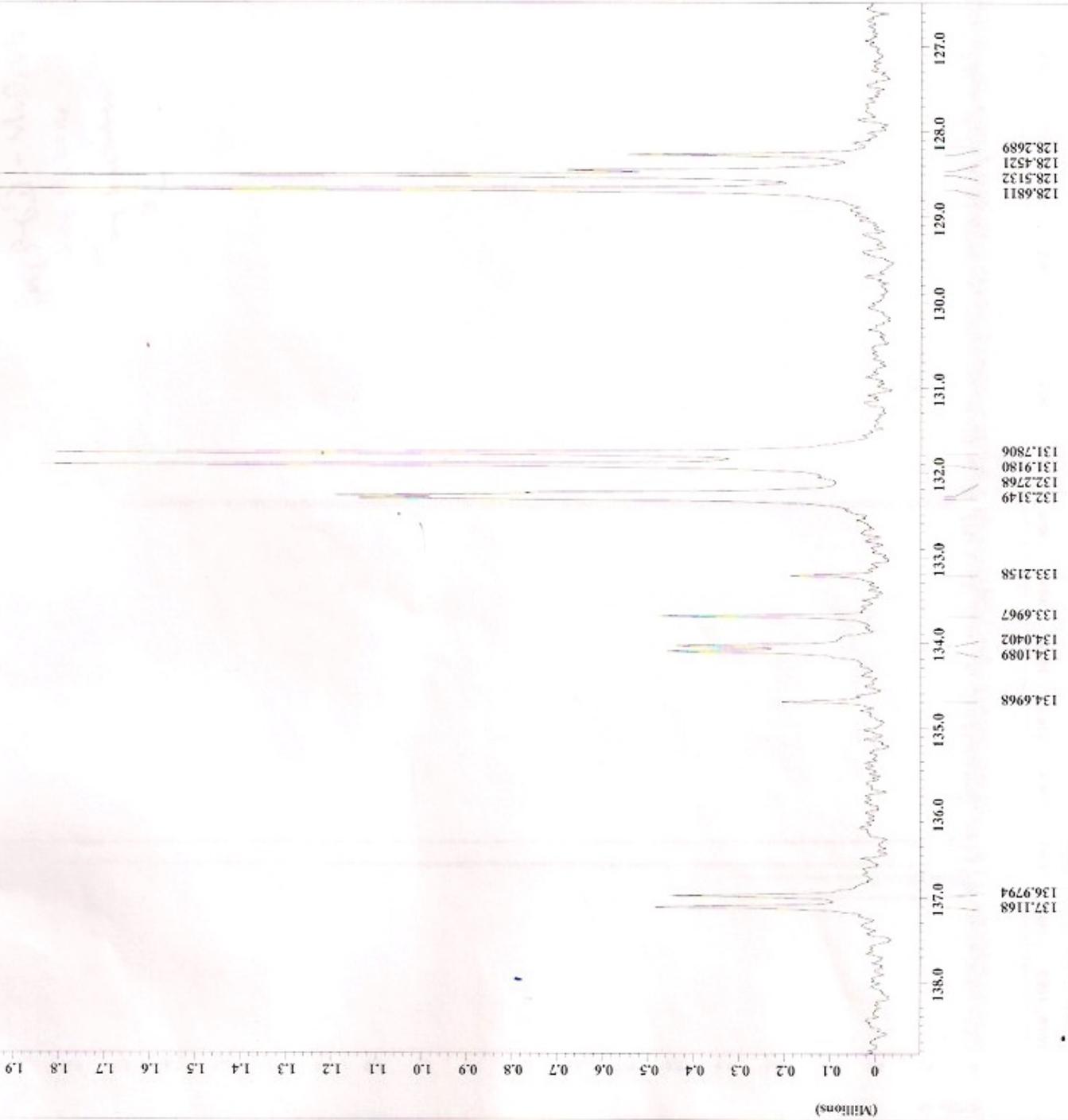
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Filename = TL (Ar)3p=O 13C CD
Author = benderj_lab
Experiment = single_pulse_dec
Sample_id = S#545611
Solvent = CHLOROFORM-D
Creation_time = 16-JUL-2000 06:48:19
Revision_time = 13-JUL-2016 15:23:25
Current_time = 13-JUL-2016 15:23:31

Comment = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_NMR

Field_strength = 7.0586013[T] (300[MHz]
X_acq_duration = 1.7334272[s]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 0.57689184[Hz]
X_sweep = 16.90359168[kHz]
Irr_domain = 1H
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 259
Total_scans = 259

X_90_width = 10.86[us]
X_acq_time = 1.7334272[s]
X_angle = 30[deg]
X_pulse = 3.02[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 1[s]
Temp_Set = 23.2[degC]
Unblank_time = 2[us]
  
```

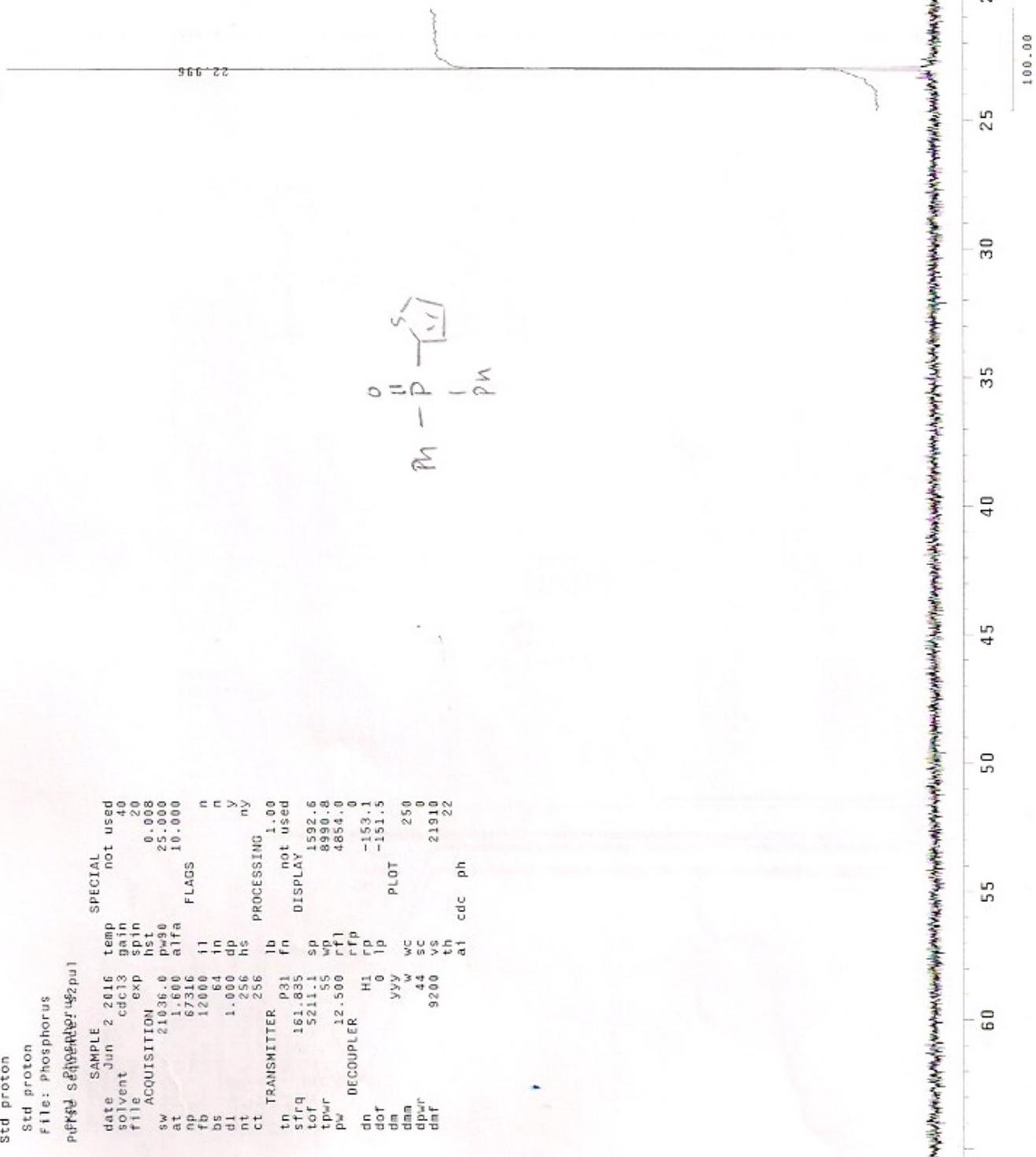
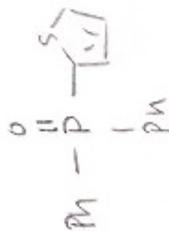


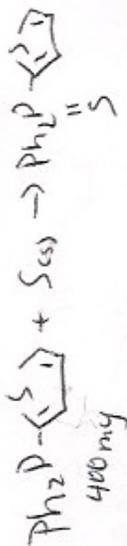
X : parts per Million : 13C

$\text{Ph}_2\text{P}(\text{Li})_2 + \text{Na}_2\text{O}_2\text{Cl}_2 (\text{DMSO})_2$
 June 2, 2016
 Troy Luster
 (Purple crystals)

Std proton
 Std proton
 file: Phosphorus
 PFTSD_S8106101_452.pu1

SAMPLE	temp	SPECIAL
date Jun 2 2016	not used	
solvent cdcl3	40	
file	gain 20	
ACQUISITION exp	nsf 0.008	
sw 21036.0	pw90 25.000	
at 1.600	rlfa 10.000	FLAGS
np 67316	ll	n
fb 12000	ln	n
bs 64	ln	n
dl 1.000	dp	y
nt 256	hs	ny
ct 256	PROCESSING	
TRANSMITTER p31	lb 1.00	
fn	not used	
sfrcq 161.835	fn	DISPLAY
tof 5211.1	sp	1592.6
tpwr 8990.8	wp	8990.8
pw 12.500	rfl	4854.0
DECOUPLER H1	rfp	0
dn 0	fp	-153.1
dof 0	lp	-151.5
da yyy	wc	250
daw	w	0
dpwr 44	sc	0
daf 9200	vs	21910
	th	22
	at	cdc
		ph





May 31, 2016

(yellow solid)

Std proton

File: Proton

Pulse Sequence: s2pu1

Solvent: cdcl3

Ambient temperature

Operator: Chm241

INOVA-400 "woodward.gvsu.edu"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.03000000 sec

Width 6396.4 Hz

16 repetitions

ORSEVE HI 399.1695340 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 0 min, 55 sec

7.787
7.784
7.780
7.767
7.763
7.752
7.749
7.745

7.249
7.177
7.175
7.173
7.170
7.166
7.163
7.158
7.156
7.154
7.151
7.149

1.566

15.47

29.29
43.02
5.62

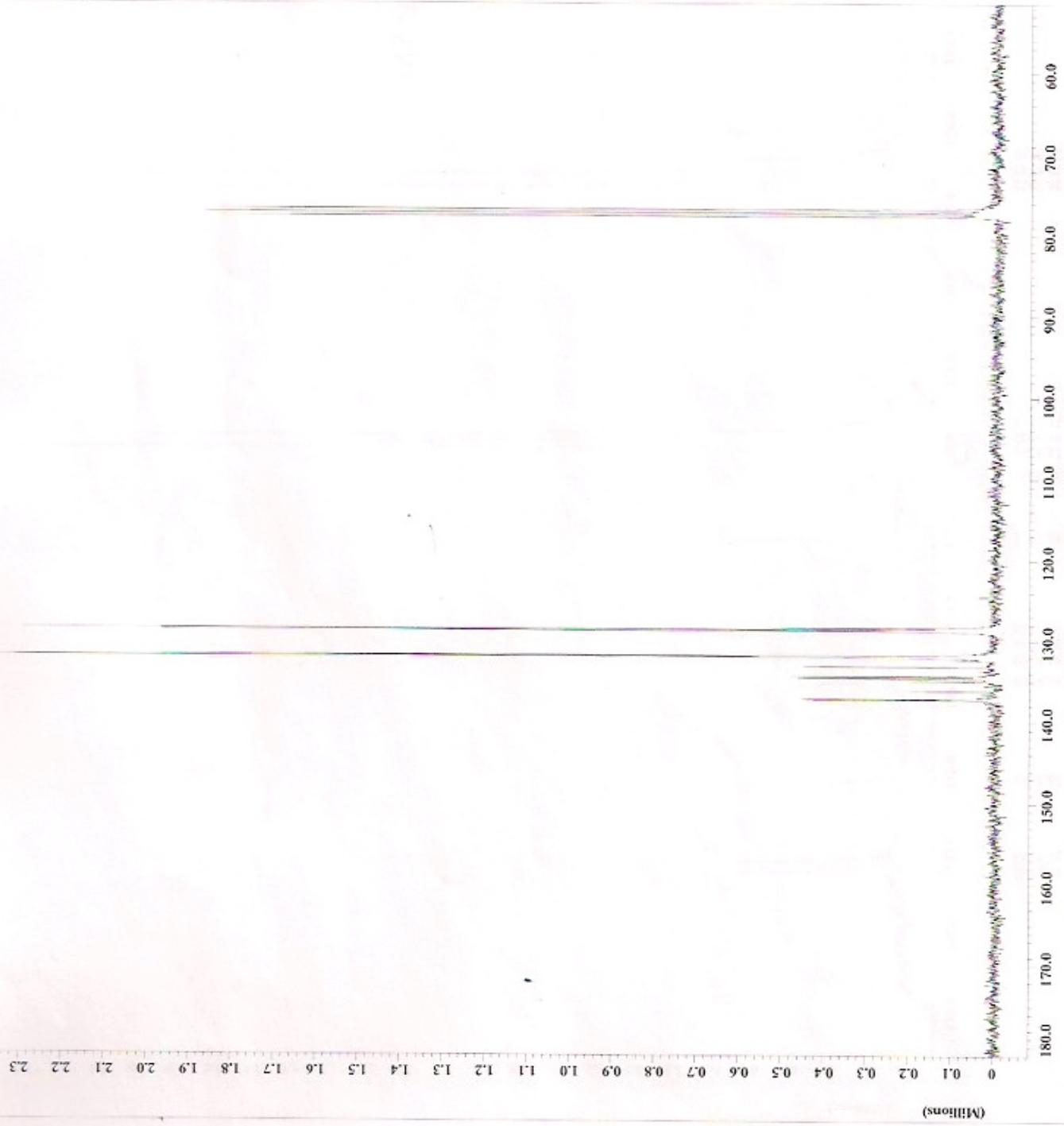
6.60



5
Ph₂P(O)₂
6-13-16
CDCl₃



Filename = TL_13C_Ar3P=S_CDCl
Author = bender_lab
Experiment = single_pulse_dec
Sample_id = S#370134
Solvent = CHLOROFORM-D
Creation_time = 16-JUN-2000 02:20:51
Revision_time = 13-JUN-2016 10:51:10
Current_time = 13-JUN-2016 10:51:22
Comment = Single Pulse with Bro
Data_format = ID COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = (ppm)
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_NMR
Field_strength = 7.0586013(T) (300)(MHz)
X_acq_duration = 1.7334272(is)
X_domain = 13C
X_freq = 75.56823426(MHz)
X_offset = 100(ppm)
X_points = 32768
X_prescans = 4
X_resolution = 0.57689184(Hz)
X_sweep = 18.90359168(kHz)
Irr_domain = 1H
Irr_freq = 300.52965592(MHz)
Irr_offset = 5(ppm)
Clipped = FALSE
Mod_return = 1
Scans = 727
Total_scans = 727
X_90_width = 10.86(us)
X_acq_time = 1.7334272(is)
X_angle = 30(deg)
X_pulse = 3.62(us)
Initial_wait = 1(is)
Phase_preset = 3(us)
Recvr_gain = 30
Relaxation_delay = 1(is)
Temp_get = 22.8(dc)
Unblank_time = 2(us)



X : parts per Million : 13C

6-17-16

Ph₂P(S)
AD3



```

Filename = TL 13C Ar3P=S CDC1
Author = benderj_lab
Experiment = single_pulse_dec
Sample_id = S#370134
Solvent = CHLOROFORM-D
Creation_time = 16-JUN-2000 02:20:51
Revision_time = 13-JUN-2016 10:52:00
Current_time = 13-JUN-2016 10:52:16

Comment = Single Pulse with Bro
Data_format = 1D COMPLEX
Dim_size = 32768
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = Eclipse+ 300
Spectrometer = DELTA_NMR

Field_strength = 7.0586013(T) (300)[MHz]
X_acq_duration = 1.7334272[ls]
X_domain = 13C
X_freq = 75.56823426[MHz]
X_offset = 32768
X_points = 4
X_prescans = 0.57689184[Hz]
X_resolution = 18.90359168[KHz]
X_sweep = 18.90359168[KHz]
Irr_domain = 13C
Irr_freq = 300.52965592[MHz]
Irr_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 727
Total_scans = 727

X_90_width = 10.86[us]
X_acq_time = 1.7334272[s]
X_angle = 30[deg]
X_pulse = 3.62[us]
Initial_wait = 1[s]
Phase_preset = 3[us]
Recvr_gain = 30
Relaxation_delay = 1[s]
Temp_get = 22.8[dc]
Unblank_time = 2[us]

```



X : parts per Million : 13C



400my

May 31, 2014

31P (400MHz CDCl3)

Std proton

F1f1: Phosphorus

Pulse Sequence: zgpg30

Solvent: cdcl3

Ambient Temperature

Operator: chm241

INOVA-400 "woodward_@su.edu"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. Time 1.000 sec

Width 21036.0 Hz

256 repetitions

OBSERVE F31, 161.8294930 MHz

DECOUPLE H1, 399.7715331 MHz

Power 44 dB

continuously on

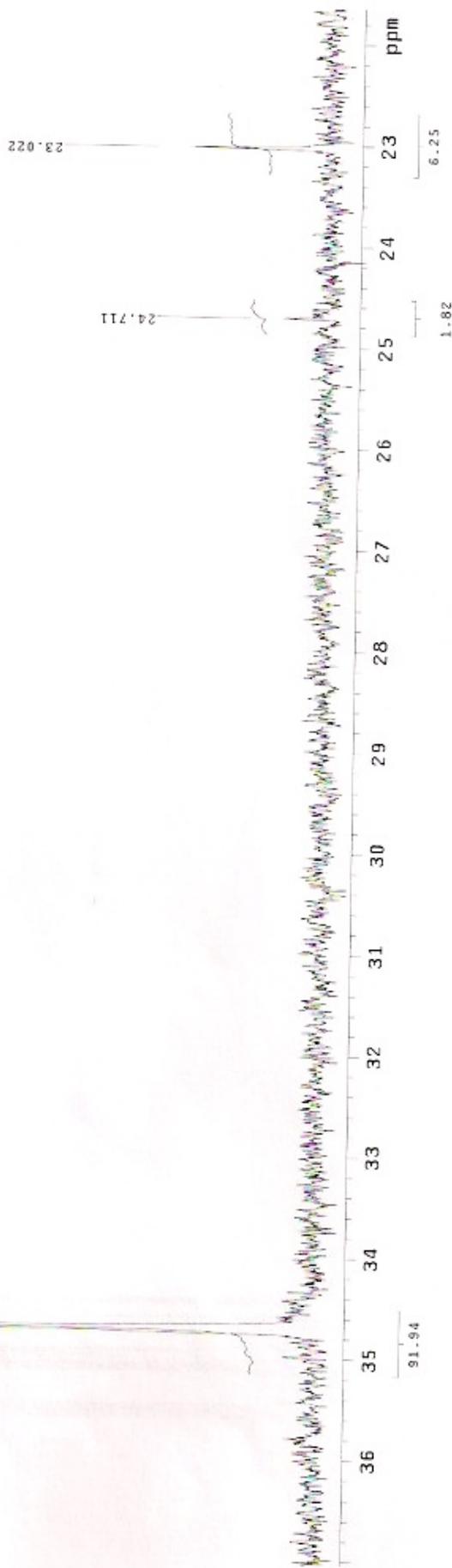
WALTZ-16 modulated

DATA PROCESSING

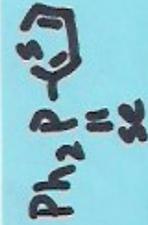
Line broadening 1.0 Hz

FT size 131072

Total time 11 min, 7 sec



Ph₂(thienyl)PSe 1H NMR in CDCl₃, 400 MHz



Ph₂P-(S) + Se
June 9, 2016
Troy Luster
(Acetone d₆)

std proton

File: Proton

Pulse Sequence: s2pul

Solvent: cd3cn

Ambient temperature

Operator: chm241

INOVA-400 "woodward.gvsu.edu"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.0490 sec

Width 5335.4 Hz

16 repetitions

OBSERVE H1 399.771587 MHz

LINE PROCESSING

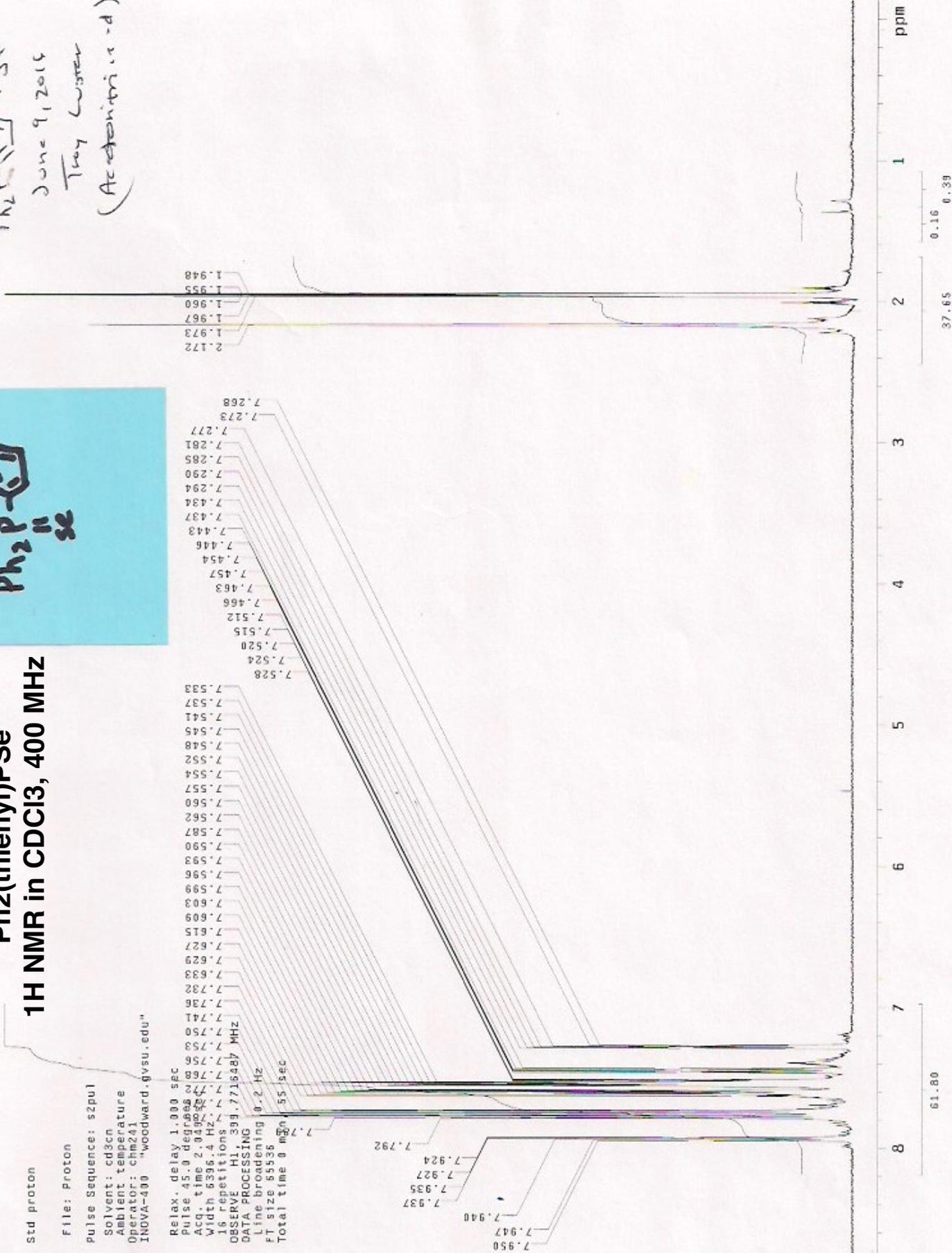
Line broadening 0.2 Hz

FT SIZE 65536

Total time 8 min 55 sec

7.950
7.947
7.940
7.937
7.935
7.927
7.924
7.792
7.792
7.528
7.524
7.512
7.515
7.466
7.463
7.457
7.454
7.448
7.437
7.434
7.294
7.290
7.285
7.281
7.277
7.273
7.268

2.172
1.973
1.967
1.960
1.955
1.948



61.80

37.65

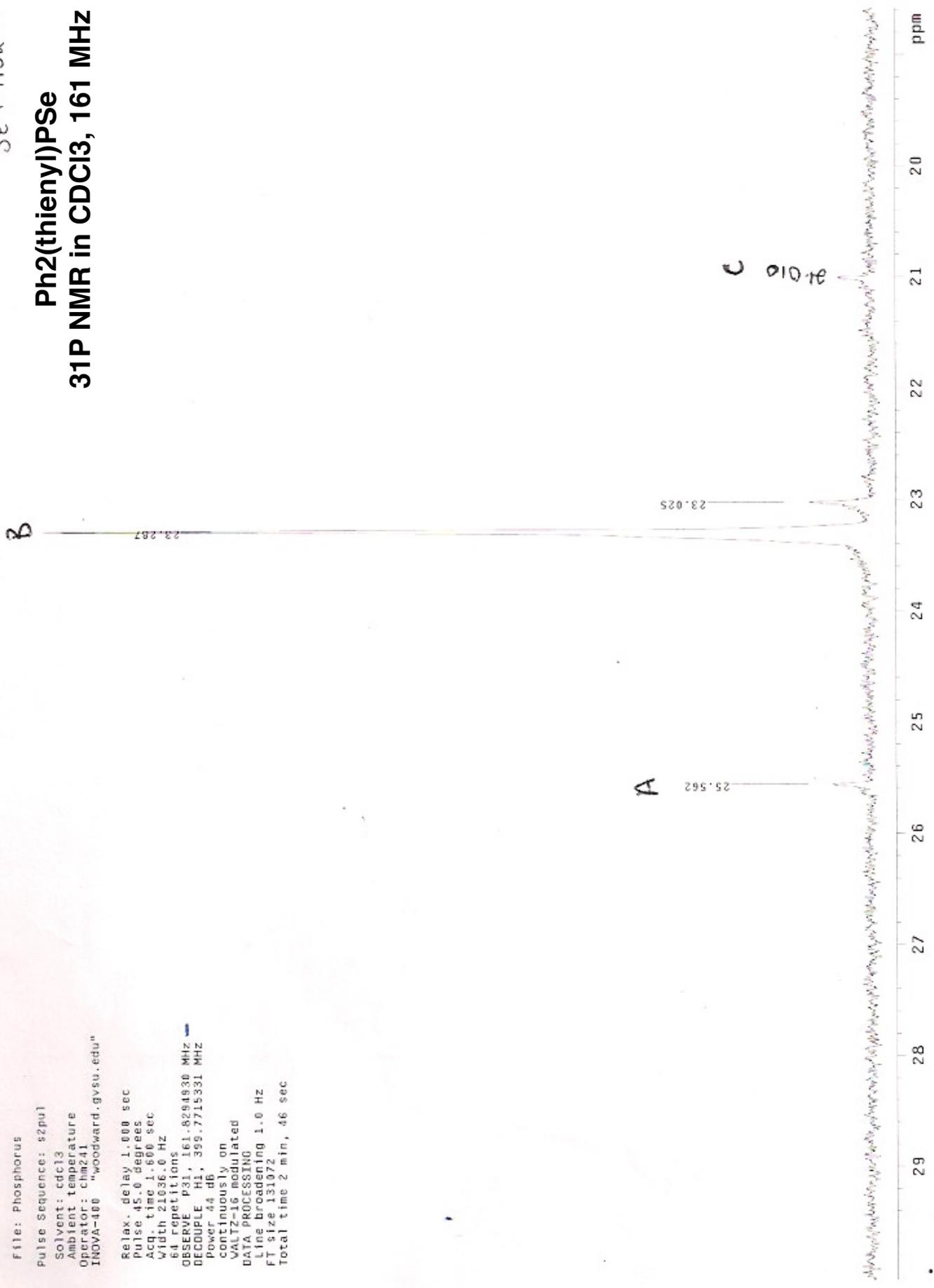
0.16
0.39

Spec. 1

Troy L.
Se + Product

Ph₂(thienyl)PSe 31P NMR in CDCl₃, 161 MHz

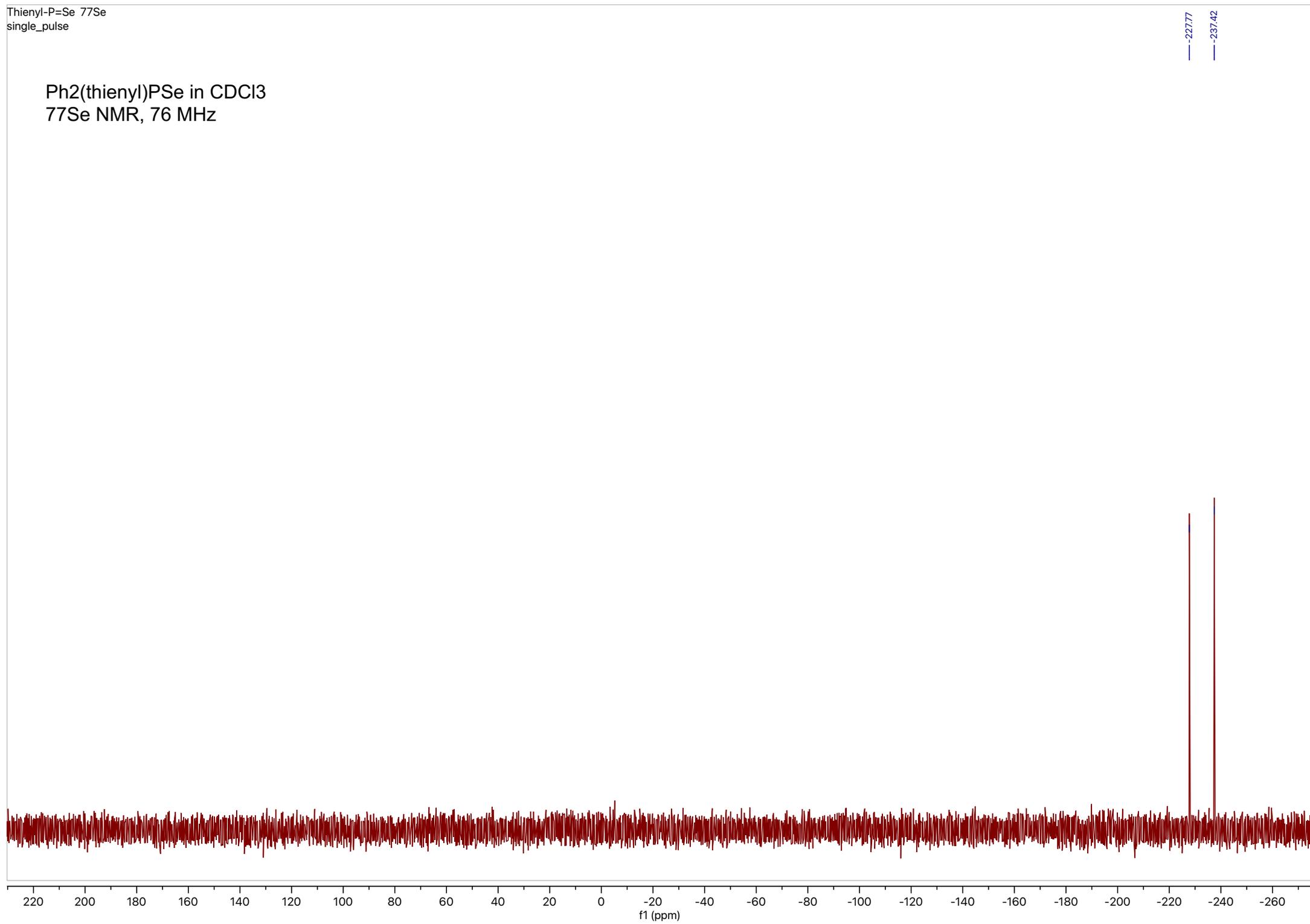
Std proton
File: Phosphorus
Pulse Sequence: s2pu1
Solvent: cdcl3
Ambient temperature
Operator: chm241
INOVA-400 "woodward.gvsu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.600 sec
Width 21036.0 Hz
64 repetitions
OBSERVE P31, 161.8294930 MHz
DECOUPLE H1, 399.7715331 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 2 min, 46 sec



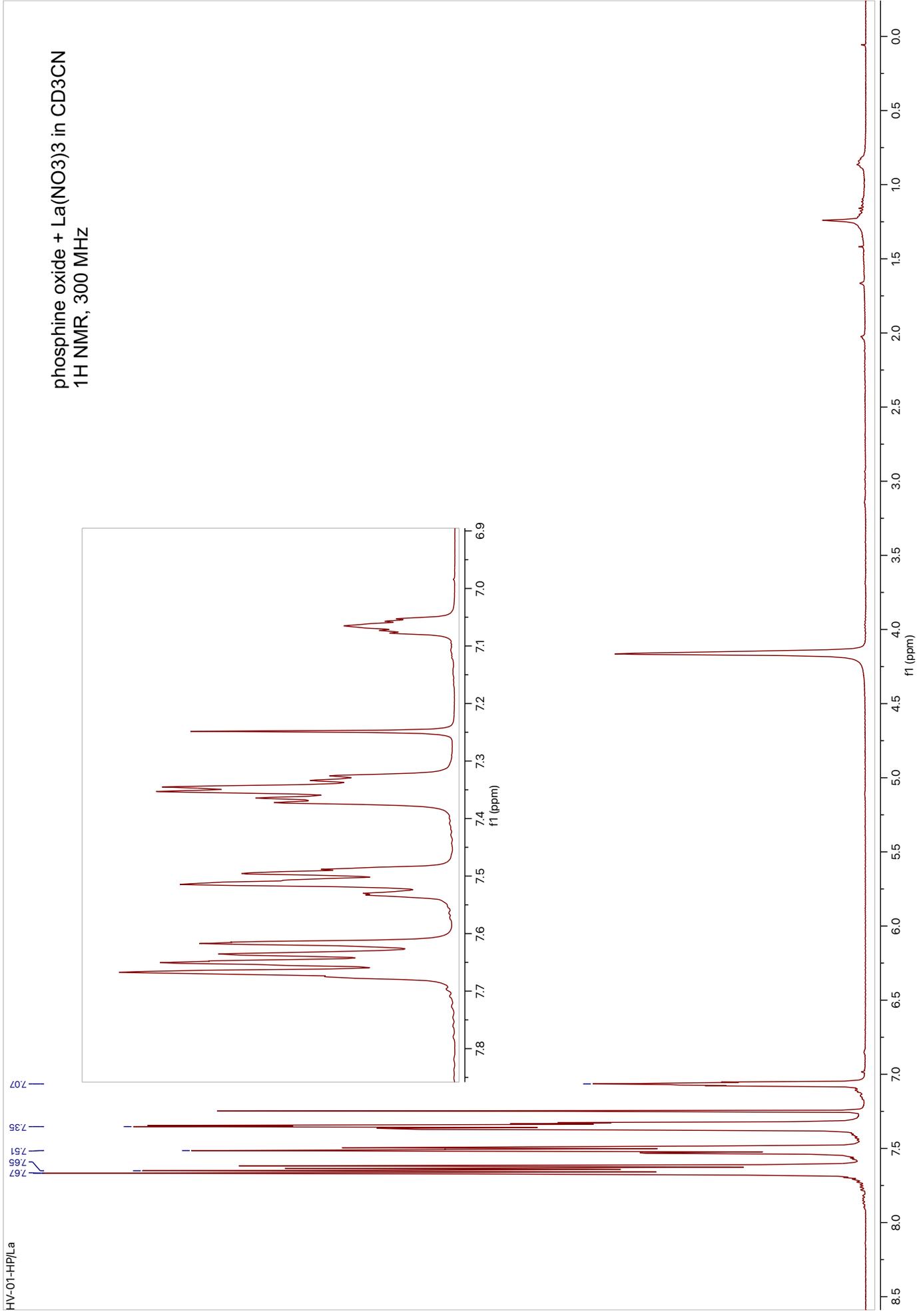
Thienyl-P=Se 77Se
single_pulse

Ph2(thienyl)PSe in CDCl3
77Se NMR, 76 MHz

-227.77
-237.42



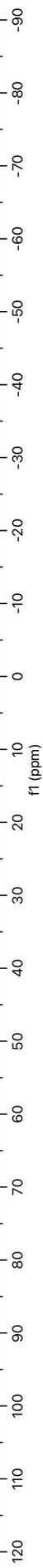
phosphine oxide + La(NO₃)₃ in CD₃CN
1H NMR, 300 MHz



phosphine oxide + La(NO₃)₃ in CD₃CN
31P NMR, 121 MHz

26.96

26.96





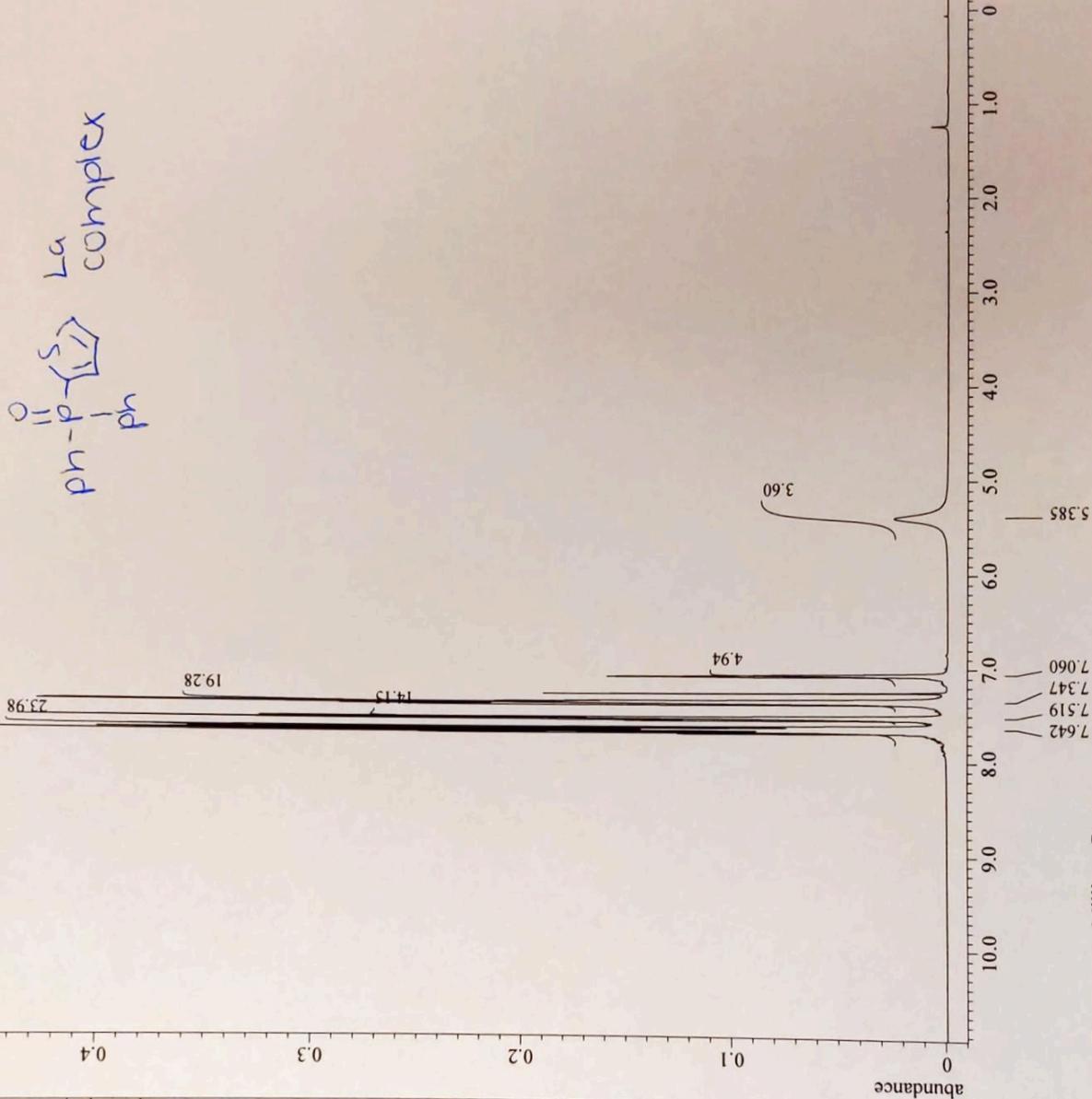
Filename = GS (OTF) 3La (O=PAR3)3
Author = biros
Experiment = proton.jxp
Sample Id = GS (OTF) 3La (O=PAR3)3
Solvent = CHLOROFORM-D
Actual_Start_Time = 29-JUN-2021 13:54:11
Revision_Time = 29-JUN-2021 13:54:13

Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = GVSU-NMR
Spectrometer = JNM-ECZ400S/L1

Field_Strength = 9.389766[T] (400 [MHZ])
X_Acq_Duration = 3.27155712[s]
X_Domain = Proton
X_Freq = 399.78219838 [MHZ]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 0
X_Resolution = 0.30566485 [Hz]
X_Sweep = 10.01602564 [kHz]
X_Sweep_Clippped = 8.01282051 [kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838 [MHZ]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838 [MHZ]
Tri_Offset = 5[ppm]
Blanking = 2[us]
Clipped = FALSE
Scans = 16
Total_Scans = 16

Relaxation_Delay = 4[s]
Recvr_Gain = 52
Temp_Get = 19.1 [dC]
X_90_Width = 6.344 [us]
X_Acq_Time = 3.27155712 [s]
X_Angle = 45 [deg]
X_Atn = 3.3 [dB]
X_Pulse = 3.172 [us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Loop = 400
Dante_Presat = FALSE
Decimation_Rate = 0
Experiment_Path = c:\Program Files\JEOL
Initial_Wait = 1[s]
Phase = (0, 90, 270, 180, 1
Preset_Time = 4[s]
Preset_Time_Flag = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 4[s]
Repetition_Time = 7.27155712 [s]

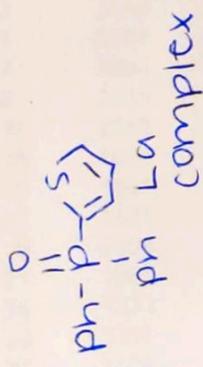
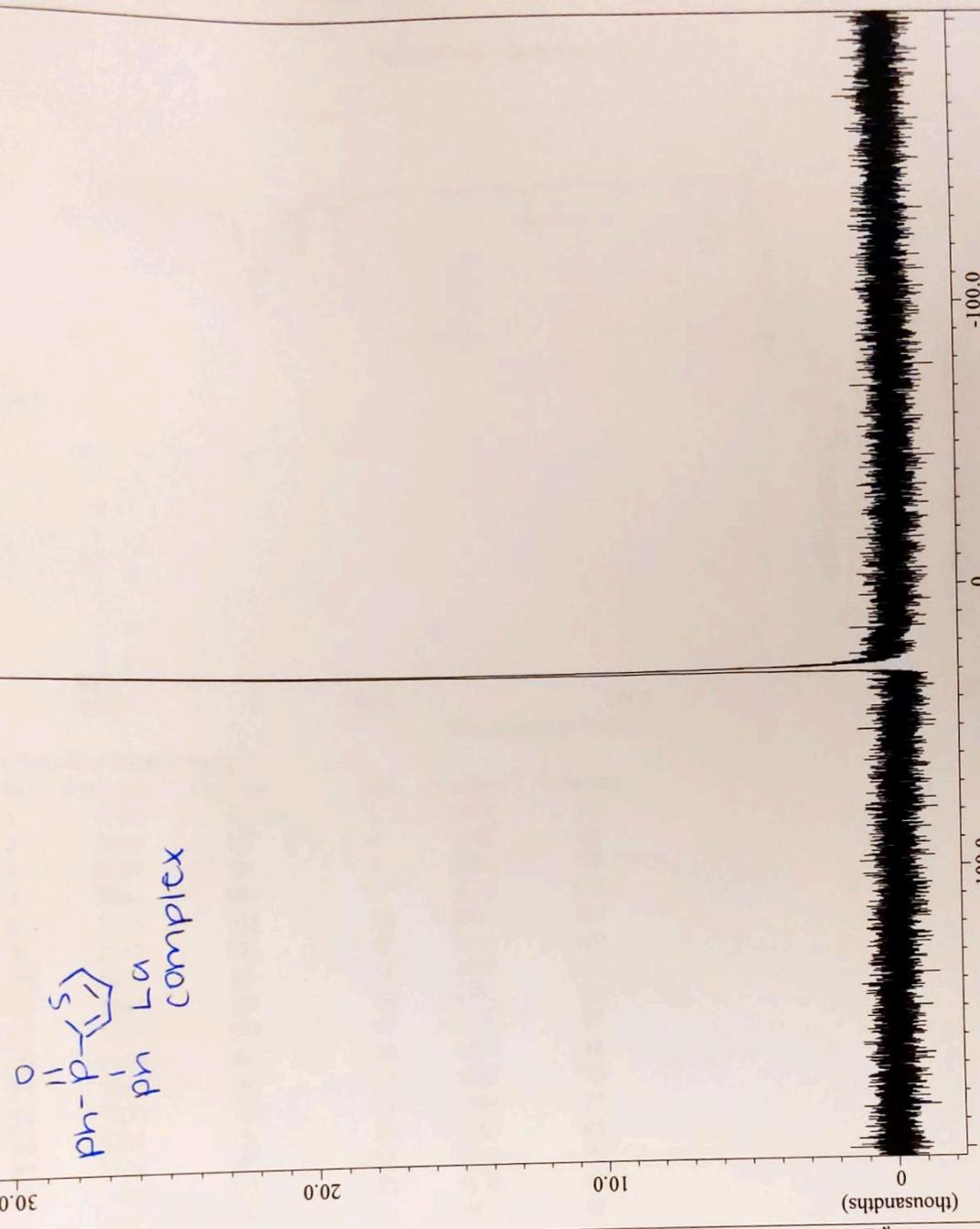
GS(OTF)3La(O=PAR3)3_90_PROTON-1-2.jdf



X : parts per Million : Proton



GS(OTF)3La(O=PAR)3_54_PHOSPHORUS_1H_DECOUPLED-1-2.jdf



```

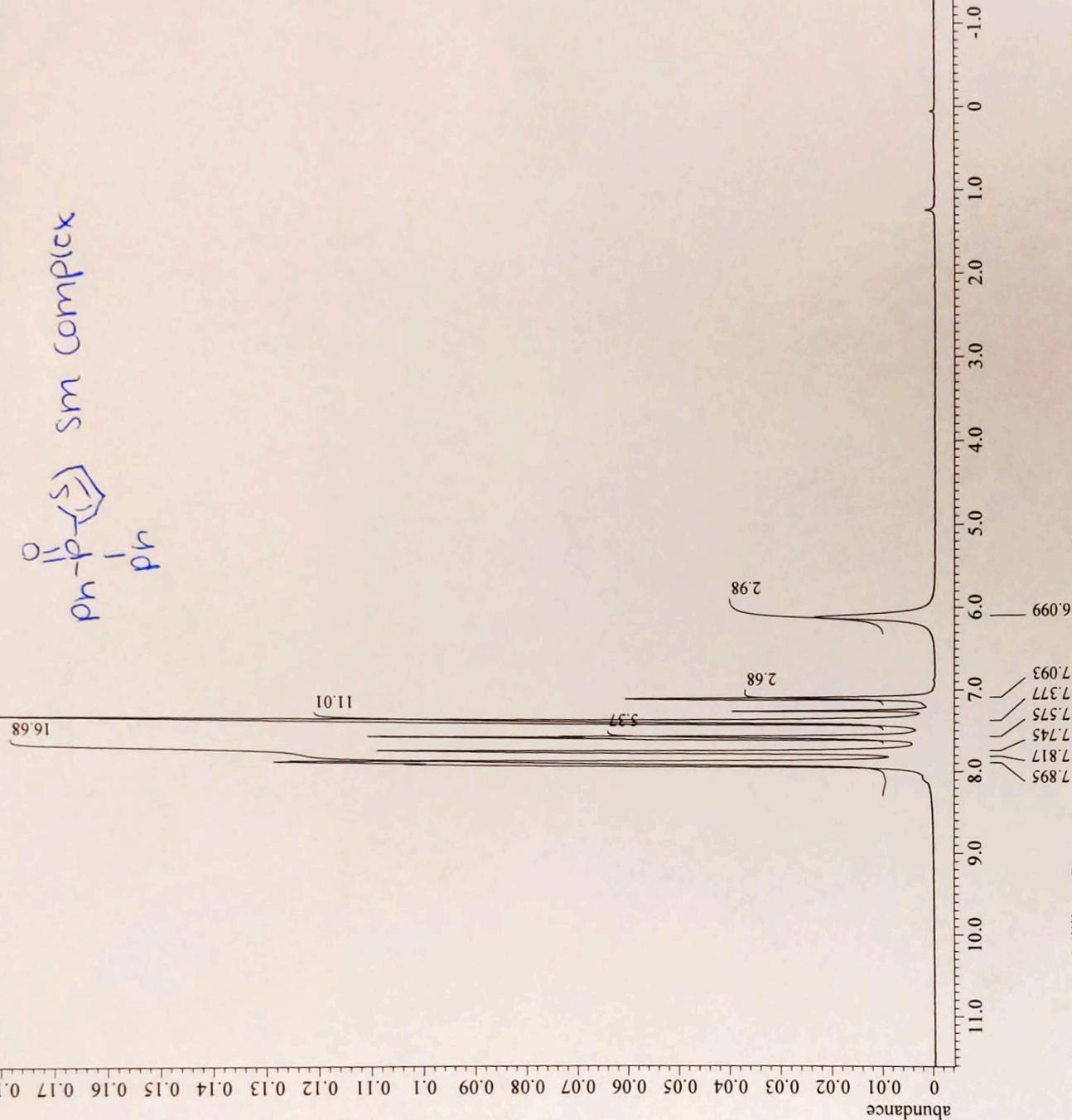
Filename = GS (OTF) 3La (O=PAR
Author = biros
Experiment = single pulse dec
Sample_Id = GS (OTF) 3La (O=PAR
Solvent = CHLOROFORM-D
Actual_Start_Time = 9-JUN-2021 13:4
Revision_Time = 9-JUN-2021 13:3
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Phosphorus31
Dim_Title = Phosphorus31
Dim_Units = [ppm]
Dimensions = X
Site = GVSU-NMR
Spectrometer = JNM-ECZ400S/L1
Field_Strength = 9.389766[T] (400
X_Acq_Duration = 0.39845888[s]
X_Domain = Phosphorus31
X_Freq = 161.83469309[MHz]
X_Offset = 0[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 2.50966925[Hz]
X_Sweep = 82.23684211[kHz]
X_Sweep_Clippped = 65.78947368[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Blanking = 5[us]
Clipped = FALSE
Total_Scans = 64
Relaxation_Delay = 2[s]
Recvr_Gain = 52
Temp_Get = 18.4[dc]
X_90_Width = 15.324[us]
X_Acq_Time = 0.39845886[s]
X_Angle = 30[deg]
X_Atn = 6.8[db]
X_Pulse = 5.108[us]
Irr_Atn_Dec = 29.239[db]
Irr_Atn_Dec_Calc = 29.239[db]
Irr_Atn_Dec_Default_Calc = 29.239[db]
Irr_Atn_No = 29.239[db]
Irr_Dec_Bandwidth_Hz = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm = 11.96303566[ppm]
Irr_Dec_Freq = 399.78219838[MHz]
Irr_Dec_Merit_Factor = 2.2
Irr_Decoupling = TRUE
Irr_No = TRUE
Irr_Noise = WALTZ
Irr_Offset_Default = 5[ppm]
Irr_Pwidth_Default = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Temp1 = 0.115[ms]
Irr_Wurst = FALSE
Decimation_Rate = 0
Experiment_Path = c:\Program Files
Initial_Wait = 1[s]
Noe_Time = 2[s]
  
```

X : parts per Million : Phosphorus31

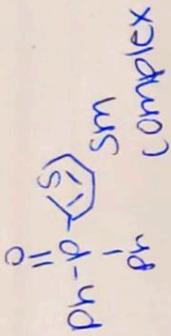


Filename = GS(OTF)3Sm(O=Ar3)3
Author = biros
Experiment = proton_jxp
Sample_Id = GS(OTF)3Sm(O=Ar3)3
Solvent = CHLOROFORM-D
Actual_Start_Time = 29-JUN-2021 13:59:2
Revision_Time = 29-JUN-2021 13:57:5
Data_Format = 1D_COMPLEX
Dim_Size = 26214
X_Domain = Proton
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = GVSU-NMR
Spectrometer = JNM-ECZ400S/L1
Field_Strength = 9.389766[T] (400[MH
X_Acq_Duration = 3.27155712[s]
X_Domain = Proton
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 32768
X_Prescans = 0
X_Resolution = 0.30566485[Hz]
X_Sweep = 10.01602564[kHz]
X_Sweep_Clippped = 8.01282051[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Blanking = 2[us]
Clipped = FALSE
Scans = 16
Total_Scans = 16
Relaxation_Delay = 4[s]
Recvr_Gain = 52
Temp_Get = 19.1[dC]
X_90_Width = 6.344[us]
X_Acq_Time = 3.27155712[s]
X_Angle = 45[deg]
X_Atn = 3.3[dB]
X_Pulse = 3.172[us]
Irr_Mode = Off
Tri_Mode = Off
Dante_Loop = 400
Dante_Presat = FALSE
Decimation_Rate = 0
Experiment_Path = c:\Program Files\JE
Initial_Wait = 1[s]
Phase = (0, 90, 270, 180, 1
Preset_Time = 4[s]
Preset_Time_Flag = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 4[s]
Repetition_Time = 7.27155712[s]

GS(OTF)3Sm(O=Ar3)3_90_PROTON-1+2.jdf



X : parts per Million : Proton

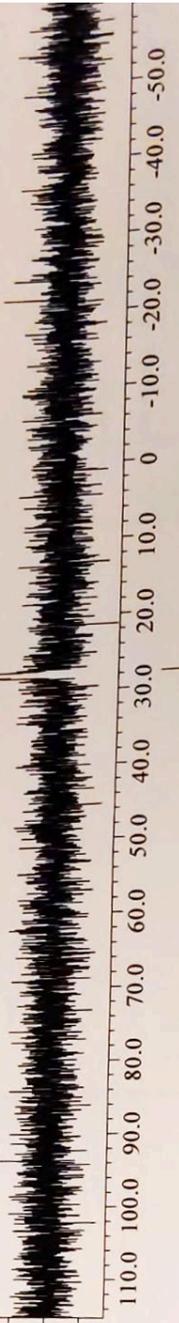


30.0

```

Filename = GS(OTF)3Sm(O=PAR
Author = birsa
Experiment = single_pulse_dec
Sample_Id = GS(OTF)3Sm(O=PAR
Solvent = CHLOROFORM-D
Actual_Start_Time = 10-JUN-2021 13:2
Revision_Time = 10-JUN-2021 13:2
Data_Format = 1D COMPLEX
Dim_Size = 26214
X_Domain = Phosphorus31
Dim_Title = Phosphorus31
Dim_Units = [ppm]
Dimensions = X
Site =
Spectrometer = GVSU-NMR
= JNM-ECZ400S/LI
Field_Strength = 9.389766[T] (400
X_Acq_Duration = 0.39845888[s]
X_Domain = Phosphorus31
X_Freq = 161.83469309[MHz]
X_Offset = 0[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 2.50966925[Hz]
X_Sweep = 82.23684211[kHz]
X_Sweep_Clippped = 65.78947368[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Blanking = 5[us]
Clipped = FALSE
Scans = 64
Total_Scans = 64
Relaxation_Delay = 2[s]
Recvr_Gain = 52
Temp_Get = 18.2[dc]
X_90_Width = 15.324[us]
X_Acq_Time = 0.39845888[s]
X_Angle = 30[deg]
X_Atn = 6.8[db]
X_Pulse = 5.108[us]
Irr_Atn_Dec = 29.239[db]
Irr_Atn_Dec_Calc = 29.239[db]
Irr_Atn_Dec_Default_Calc = 29.239[db]
Irr_Atn_Noise = 29.239[db]
Irr_Dec_Bandwidth_Hz = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm = 11.96303566[ppm]
Irr_Dec_Freq = 399.78219838[MHz]
Irr_Dec_Merit_Factor = 2.2
Irr_Decoupling = TRUE
Irr_Noise = WALTZ
Irr_Offset_Default = 5[ppm]
Irr_Pwidth = 0.115[ms]
Irr_Pwidth_Default = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Templ = 0.115[ms]
Irr_Wurst = FALSE
Decimation_Rate = 0
Experiment_Path = c:\Program Files
Initial_Wait = 1[s]
Noe_Time = 2[s]
    
```

(thousands)



27.867

X : parts per Million : Phosphorus31