

Supplementary Materials

The Synthesis, Crystal Structure, Modification, and Cytotoxic Activity of α -Hydroxy-Alkylphosphonates

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1. Principal X-ray geometry data for hydroxyphosphonate **2a** and hydroxyphosphine oxide **2d** obtained from the X-ray measurements

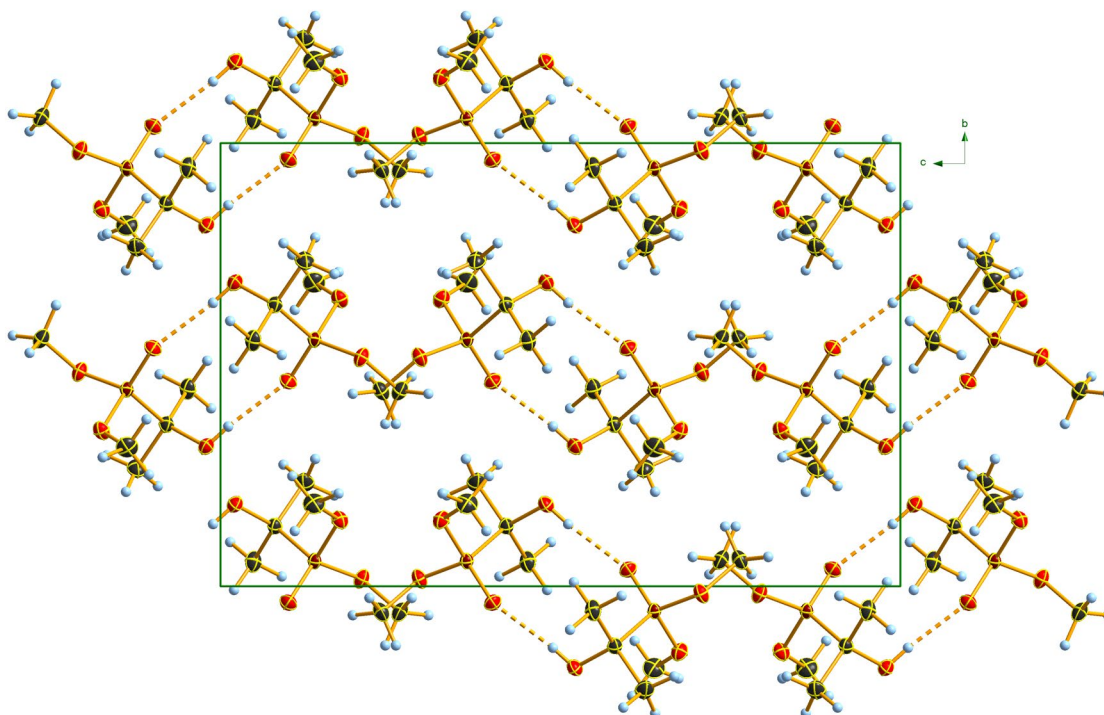


Figure S1. Crystal structure of hydroxyphosphonate **2a**; view of the unit cell along the *a*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

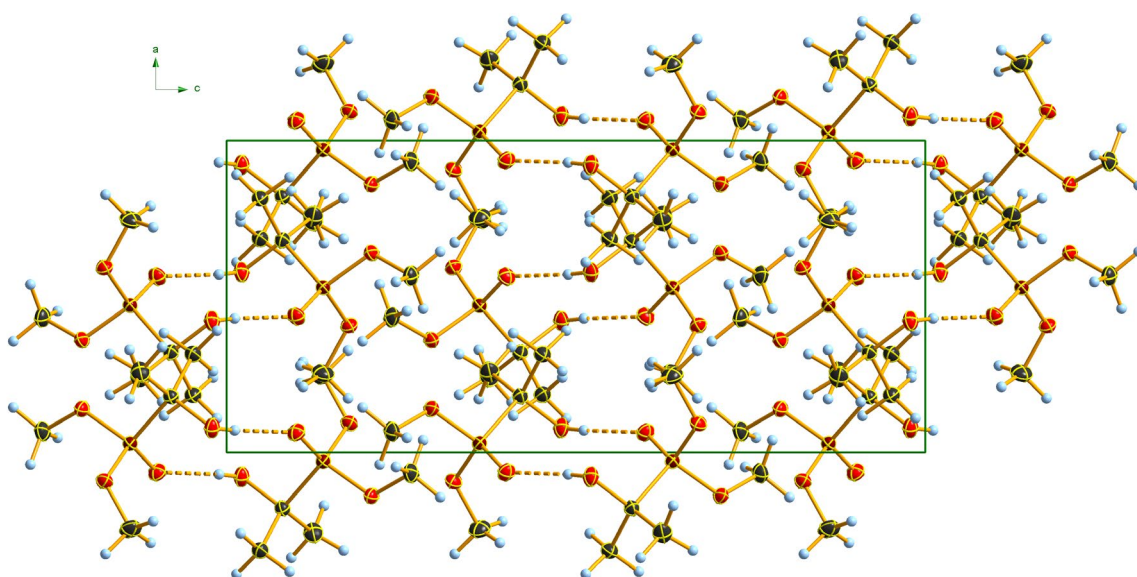


Figure S2. Crystal structure of hydroxyphosphonate **2a**; view of the unit cell along the *b*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

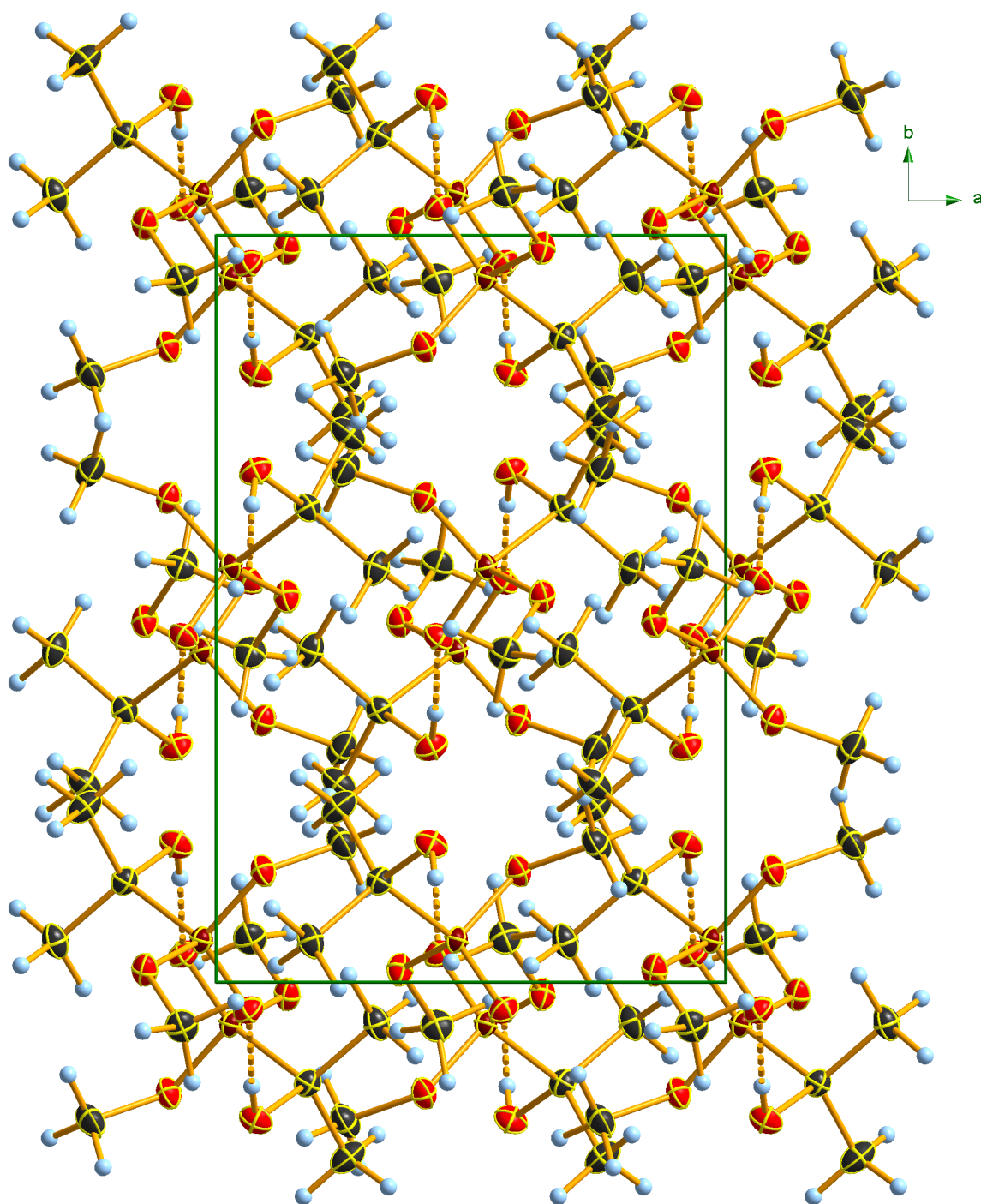


Figure S3. Crystal structure of hydroxyphosphonate **2a**; view of the unit cell along the *c*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

Table S1. Selected bond lengths (Å) of hydroxyphosphonate **2a**.

P1 – O2	1.476(1)	O3 – C4	1.448(1)
P1 – O3	1.576(1)	O4 – C5	1.446(1)
P1 – O4	1.581(1)	C1 – C3	1.520(1)
P1 – C1	1.824(1)	C1 – C2	1.526(1)
O1 – C1	1.432(1)		

Table S2. Selected bond angles (°) of hydroxyphosphonate **2a**.

O2 – P1 – O3	115.0(1)	C5 – O4 – P1	121.0(1)
O2 – P1 – O4	112.9(1)	O1 – C1 – C3	107.5(1)
O3 – P1 – O4	102.2(1)	O1 – C1 – C2	111.4(1)
O2 – P1 – C1	115.3(1)	C3 – C1 – C2	111.3(1)
O3 – P1 – C1	103.0(1)	O1 – C1 – P1	104.4(1)
O4 – P1 – C1	107.1(1)	C3 – C1 – P1	110.7(1)
C4 – O3 – P1	119.6(1)	C2 – C1 – P1	111.3(1)

Table S3. Selected torsion angles (°) of hydroxyphosphonate **2a**.

O2 – P1 – O3 – C4	48.2(1)	O4 – P1 – C1 – O1	65.8(1)
O4 – P1 – O3 – C4	-74.6(1)	O2 – P1 – C1 – C3	-176.2(1)
C1 – P1 – O3 – C4	174.4(1)	O3 – P1 – C1 – C3	57.8(1)
O2 – P1 – O4 – C5	38.9(1)	O4 – P1 – C1 – C3	-49.6(1)
O3 – P1 – O4 – C5	163.1(1)	O2 – P1 – C1 – C2	59.6(1)
C1 – P1 – O4 – C5	-89.0(1)	O3 – P1 – C1 – C2	-66.5(1)
O2 – P1 – C1 – O1	-60.8(1)	O4 – P1 – C1 – C2	-173.9(1)
O3 – P1 – C1 – O1	173.2(1)		

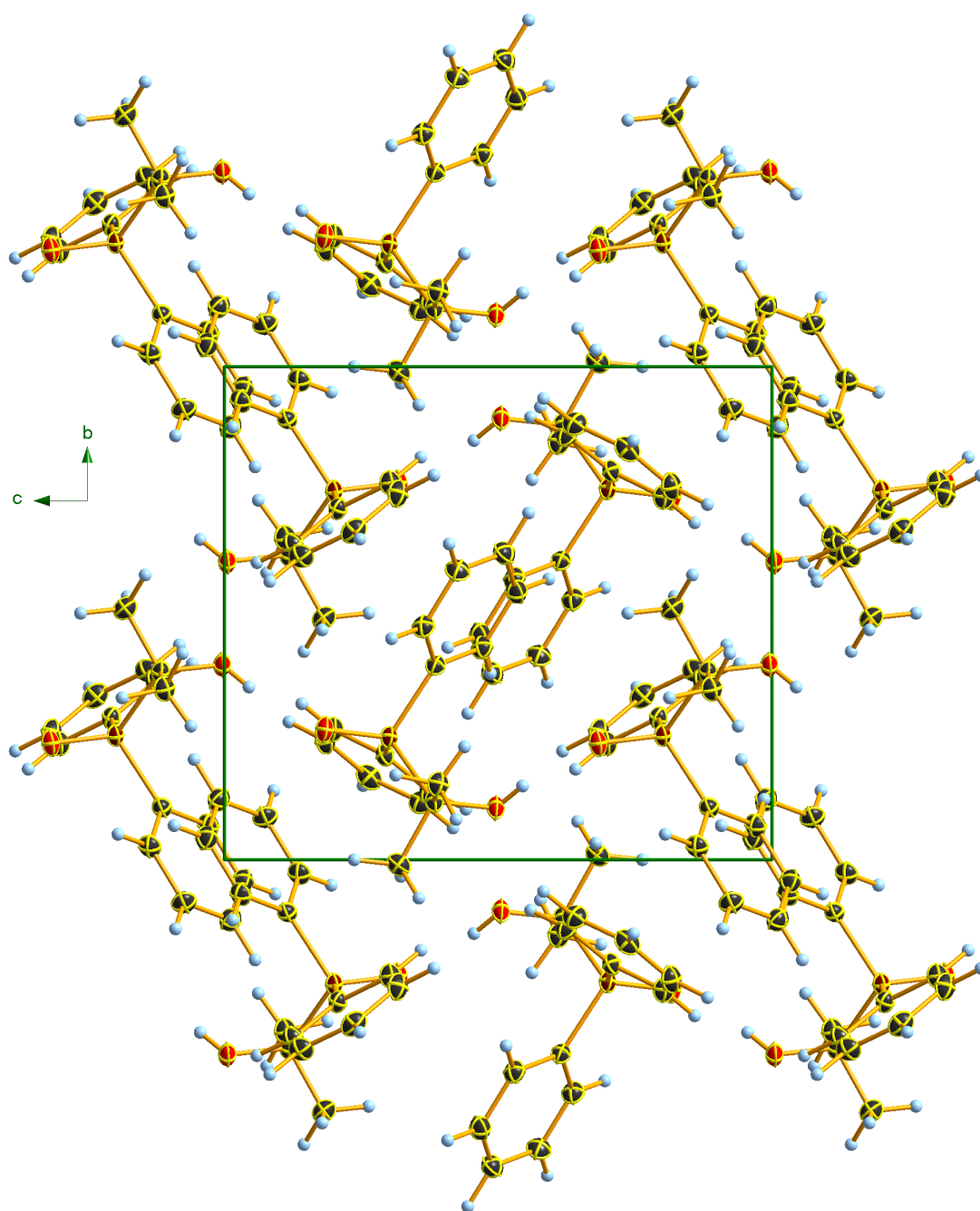


Figure S4. Crystal structure of hydroxyphosphine oxide **2d**; view of the unit cell along the a -axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

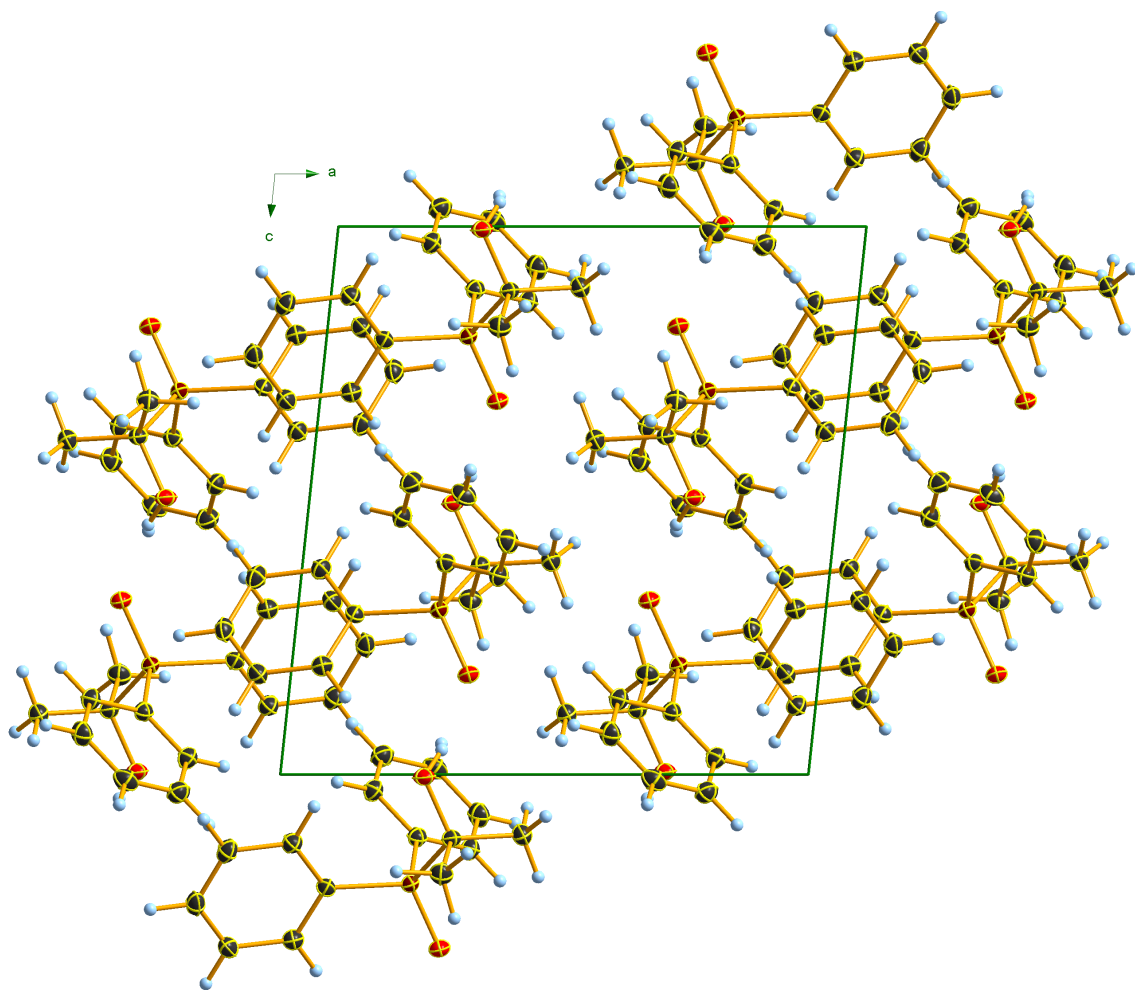


Figure S5. Crystal structure of hydroxyphosphine oxide **2d**; view of the unit cell along the *b*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

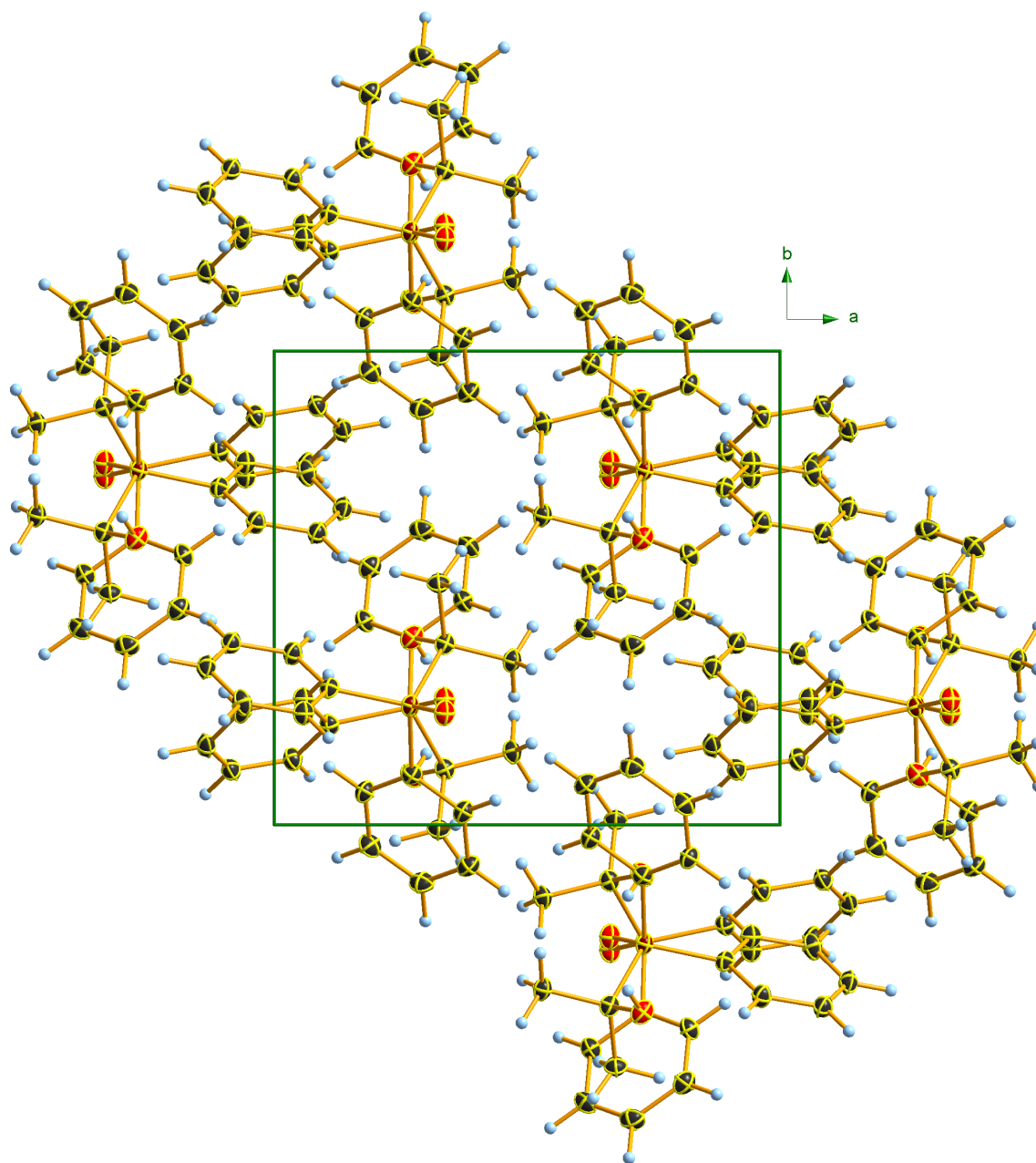


Figure S6. Crystal structure of hydroxyphosphine oxide **2d**; view of the unit cell along the *c*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

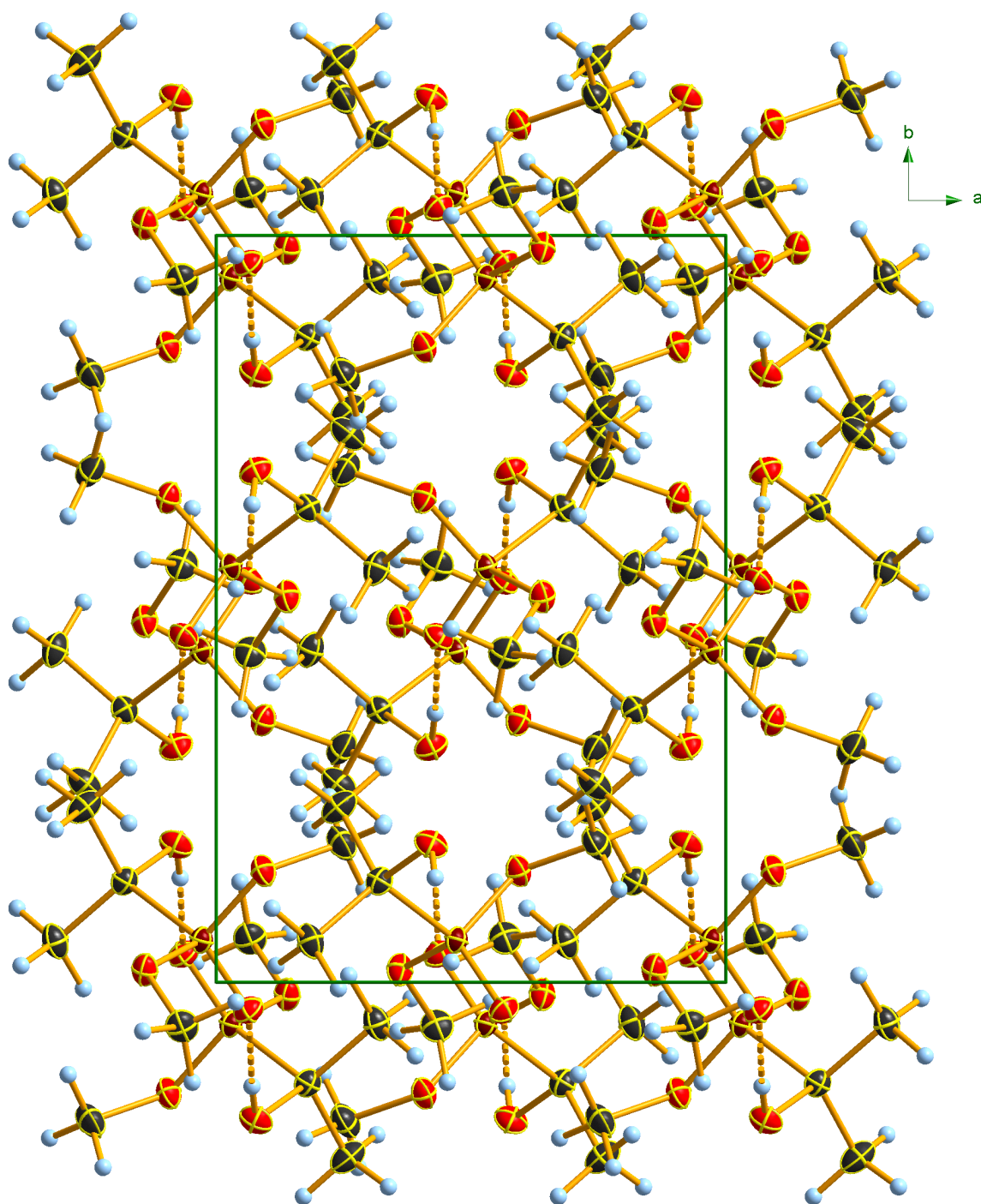


Figure S7. Crystal structure of hydroxyphosphine oxide **2d**; view of the unit cell along the *c*-axis. DIAMOND [50] representation; thermal ellipsoids are drawn at 50% probability level.

Table S4. Selected bond lengths (Å) of hydroxyphosphine oxide **2d**.

P1 – O1	1.499(1)	C14 – C15	1.389(2)
P1 – C10	1.803(1)	C14 – C13	1.389(2)
P1 – C4	1.808(1)	C11 – C12	1.391(2)
P1 – C1	1.858(1)	C9 – C8	1.389(2)
O2 – C1	1.425(1)	C12 – C13	1.392(2)
C1 – C2	1.526(2)	C8 – C7	1.387(2)
C1 – C3	1.528(2)	C6 – C5	1.393(2)
C4 – C9	1.398(2)	C10 – C11	1.395(2)
C4 – C5	1.400(2)	C10 – C15	1.398(2)
C6 – C7	1.389(2)		

Table S5. Selected bond angles (°) of hydroxyphosphine oxide **2d**.

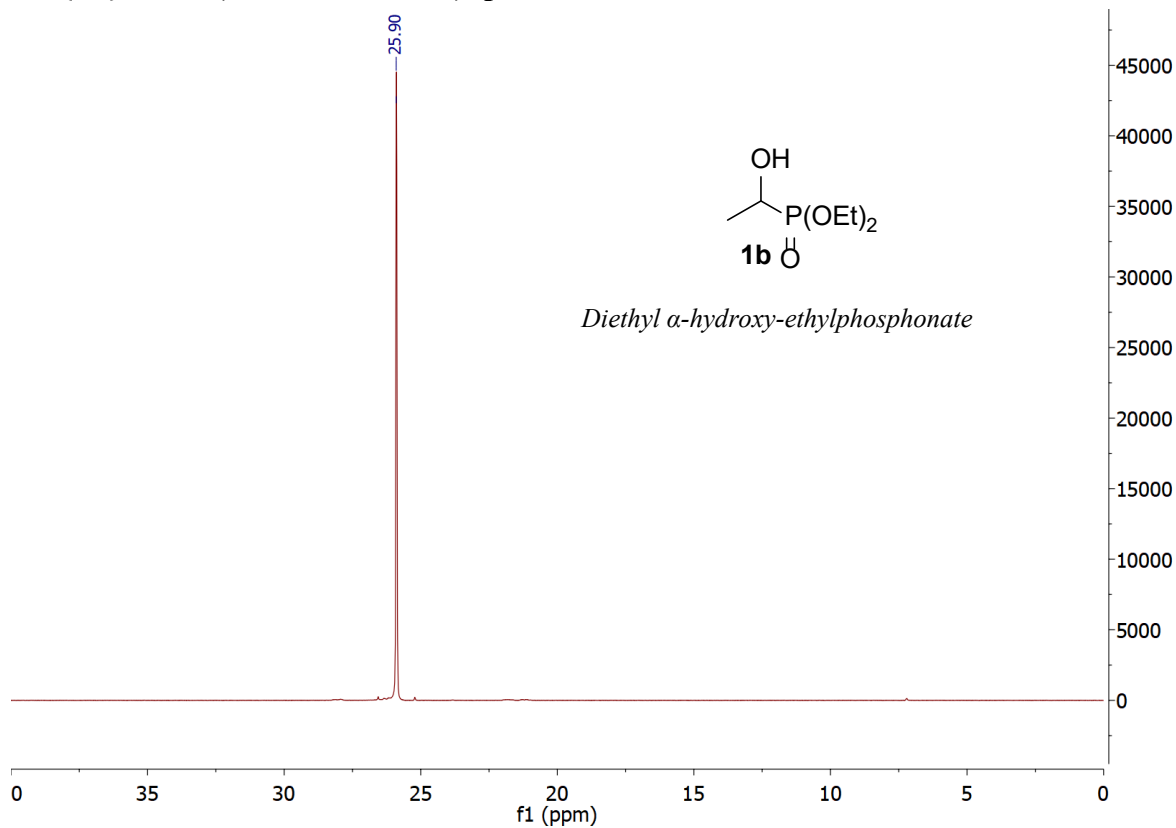
O1 – P1 – C10	111.6(1)	C14 – C15 – C10	120.4(1)
O1 – P1 – C4	112.5(1)	C12 – C11 – C10	120.1(1)
C10 – P1 – C4	106.0(1)	C8 – C9 – C4	120.6(1)
O1 – P1 – C1	110.4(1)	C11 – C12 – C13	120.0(1)
C10 – P1 – C1	106.8(1)	C14 – C13 – C12	120.3(1)
C4 – P1 – C1	109.4(1)	C7 – C8 – C9	120.1(1)
O2 – C1 – C2	111.6(1)	C8 – C7 – C6	120.0(1)
O2 – C1 – C3	107.4(1)	C6 – C5 – C4	120.2(1)
C2 – C1 – C3	111.6(1)	C5 – C4 – P1	125.1(1)
O2 – C1 – P1	110.0(1)	C7 – C6 – C5	120.1(1)
C2 – C1 – P1	107.9(1)	C11 – C10 – C15	119.4(1)
C3 – C1 – P1	108.3(1)	C11 – C10 – P1	123.6(1)
C9 – C4 – C5	119.0(1)	C15 – C10 – P1	117.0(1)
C9 – C4 – P1	115.9(1)	C15 – C14 – C13	119.8(1)

Table S6. Selected torsion angles (°) of hydroxyphosphine oxide **2d**.

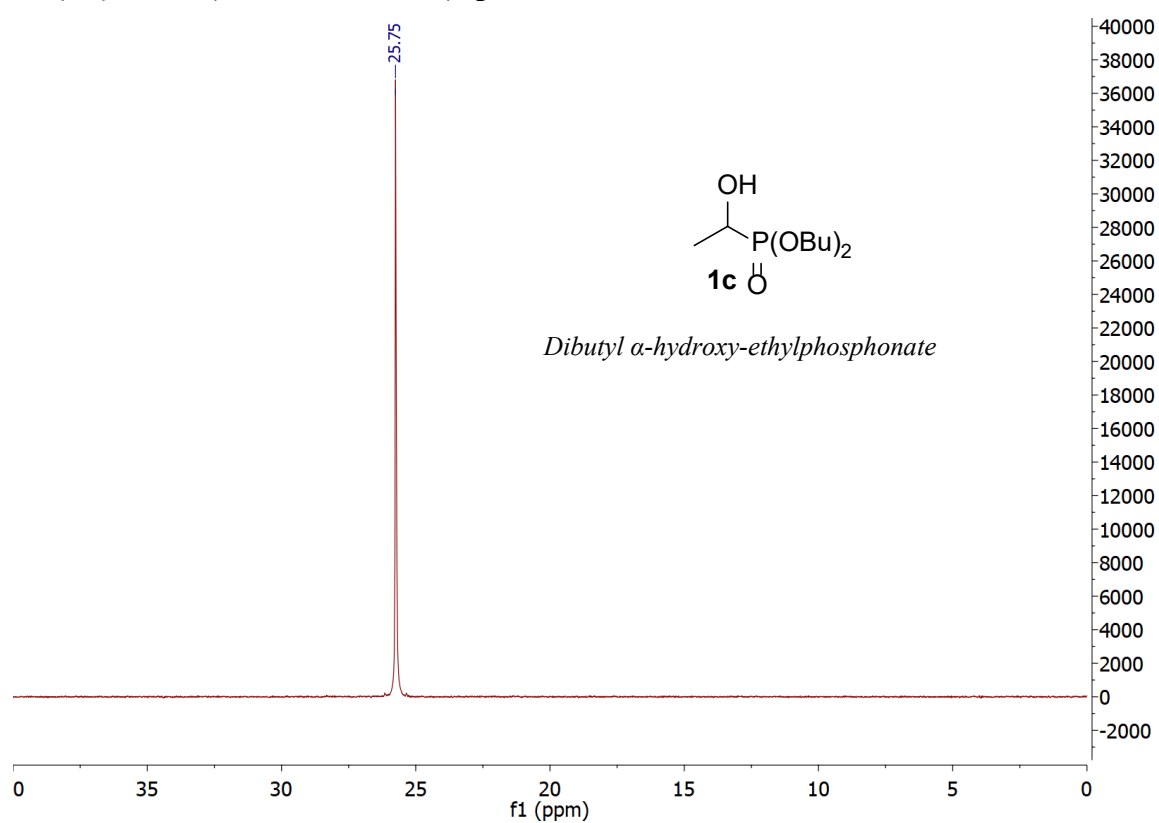
O1 – P1 – C1 – O2	179.2(1)	C4 – P1 – C10 – C15	-152.5(1)
C10 – P1 – C1 – O2	57.8(1)	C1 – P1 – C10 – C15	91.0(1)
C4 – P1 – C1 – O2	-56.5(1)	C13 – C14 – C15 – C10	-0.1(2)
O1 – P1 – C1 – C2	57.3(1)	C11 – C10 – C15 – C14	0.4(2)
C10 – P1 – C1 – C2	-64.1(1)	P1 – C10 – C15 – C14	-179.8(1)
C4 – P1 – C1 – C2	-178.4(1)	C15 – C10 – C11 – C12	-0.5(2)
O1 – P1 – C1 – C3	-63.7(1)	P1 – C10 – C11 – C12	179.7(1)
C10 – P1 – C1 – C3	174.9(1)	C5 – C4 – C9 – C8	-0.6(2)
C4 – P1 – C1 – C3	60.6(1)	P1 – C4 – C9 – C8	179.8(1)
O1 – P1 – C4 – C9	-30.7(1)	C10 – C11 – C12 – C13	0.3(2)
C10 – P1 – C4 – C9	91.5(1)	C15 – C14 – C13 – C12	-0.2(2)
C1 – P1 – C4 – C9	-153.7(1)	C11 – C12 – C13 – C14	0.0(2)
O1 – P1 – C4 – C5	149.7(1)	C4 – C9 – C8 – C7	-0.4(2)
C10 – P1 – C4 – C5	-88.1(1)	C9 – C8 – C7 – C6	1.3(2)
C1 – P1 – C4 – C5	26.7(1)	C5 – C6 – C7 – C8	-1.1(2)
O1 – P1 – C10 – C11	150.1(1)	C7 – C6 – C5 – C4	0.1(2)
C4 – P1 – C10 – C11	27.3(1)	C9 – C4 – C5 – C6	0.8(2)
C1 – P1 – C10 – C11	-89.3(1)	P1 – C4 – C5 – C6	-179.7(1)
O1 – P1 – C10 – C15	-29.7(1)		

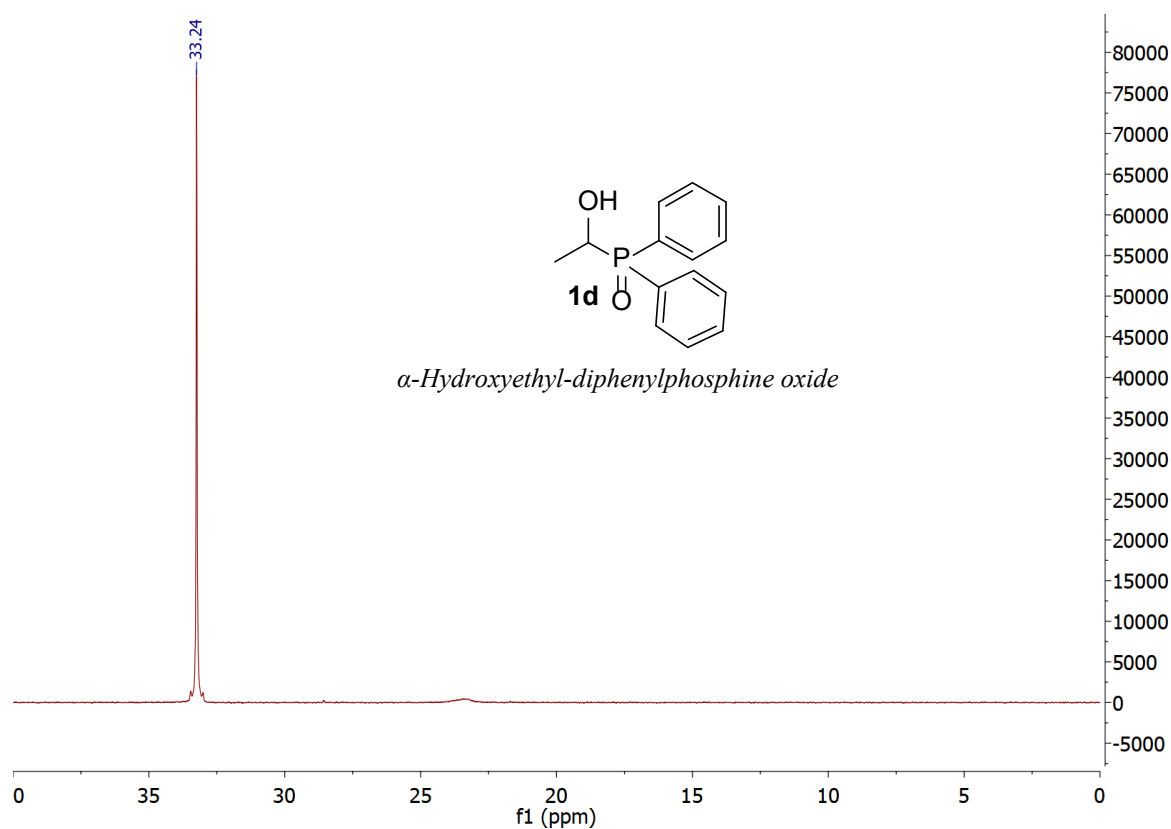
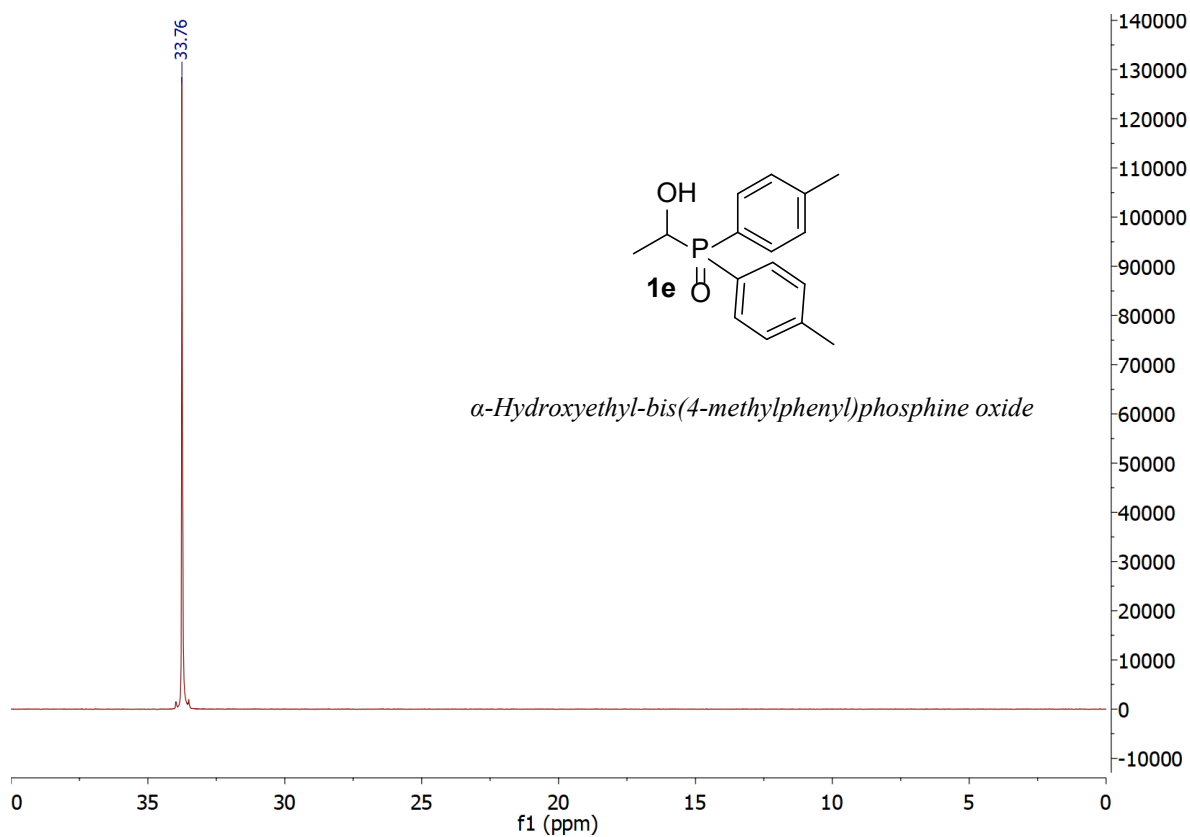
2. Spectra for the compounds 1b-f, 2a-f, 3Ab-Db, 3Ac, 3Ad, 4Ab-Cb, 4Ac, 5, 6a and 6b synthesized

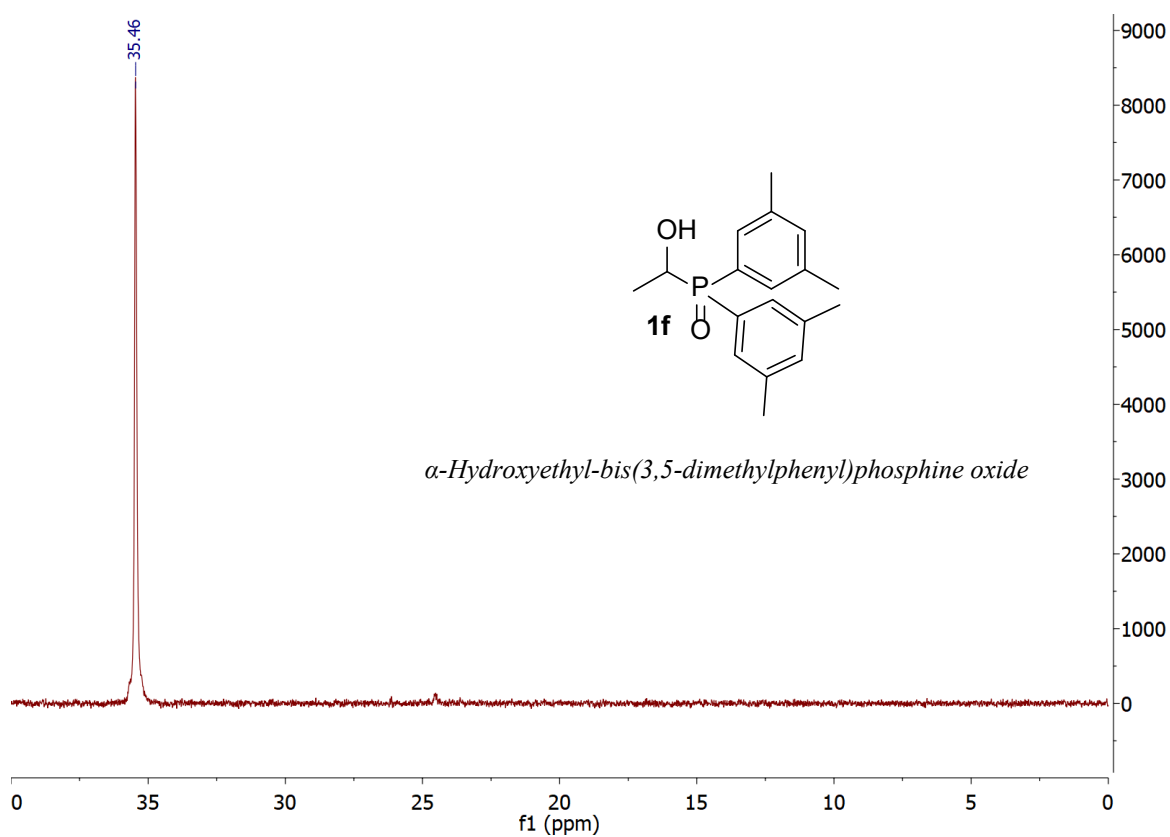
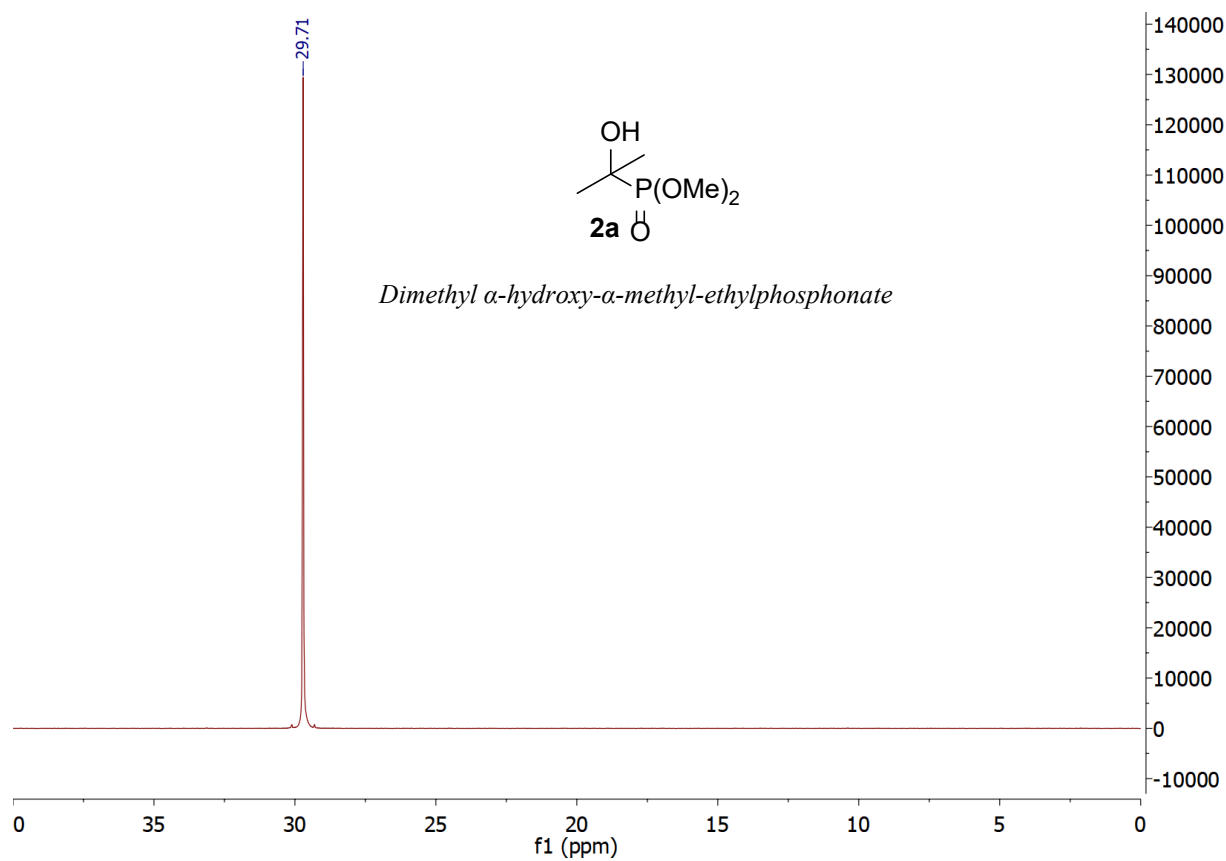
^{31}P $\{^1\text{H}\}$ NMR (122 MHz, CDCl_3) spectra for 1b

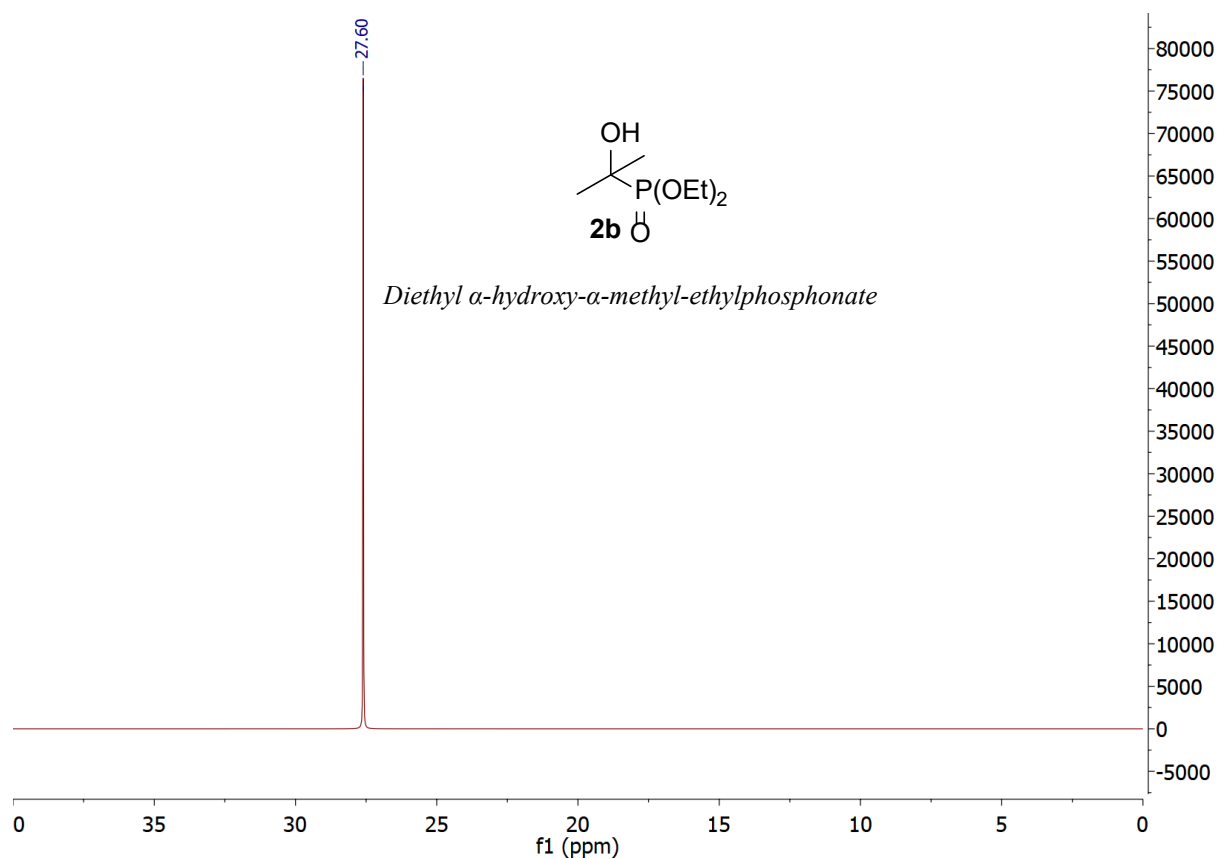
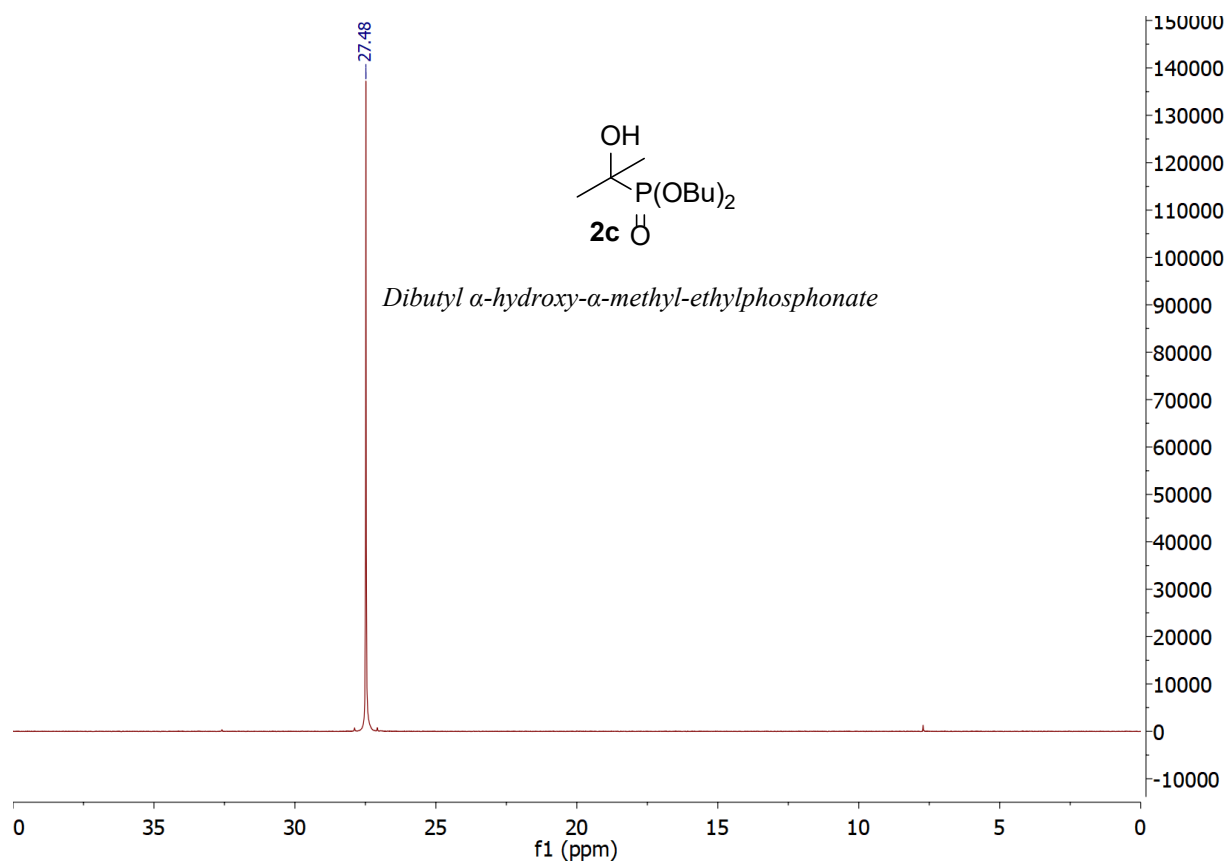


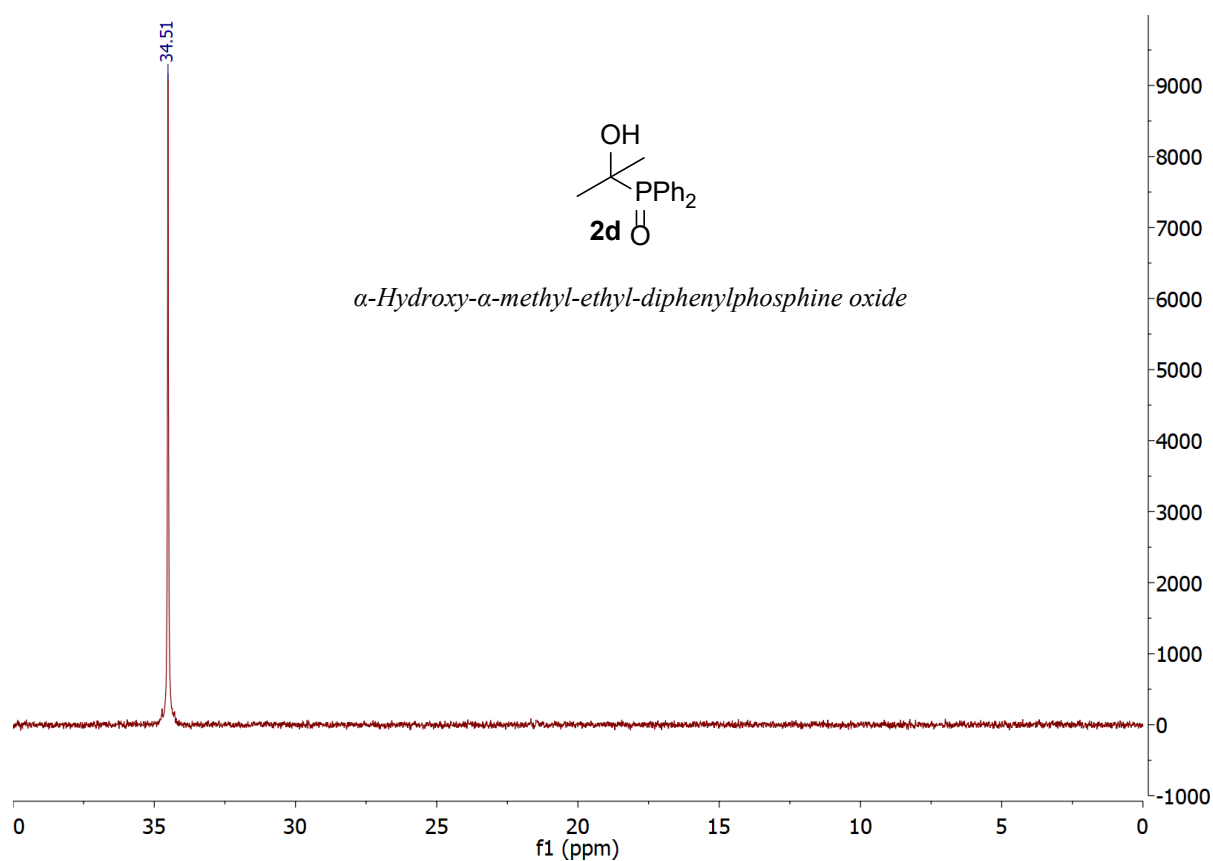
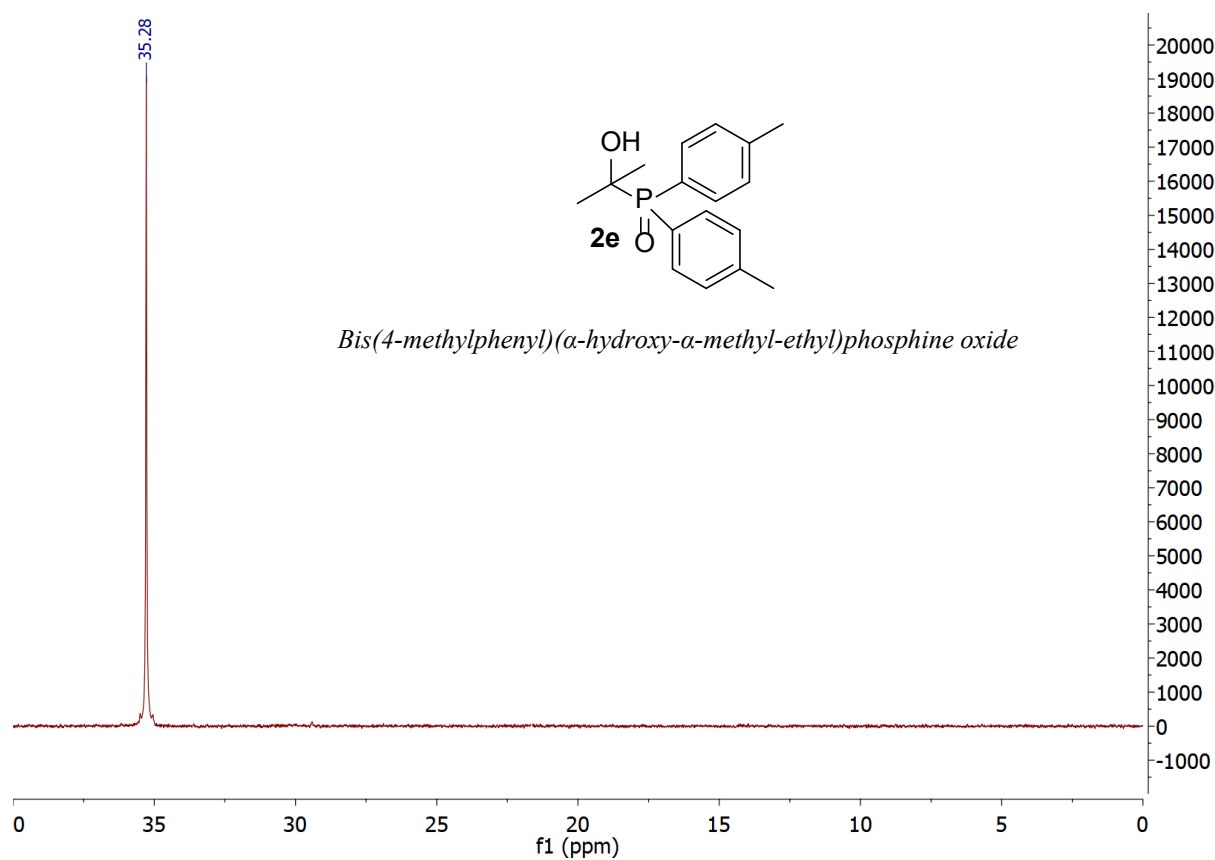
^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 1c

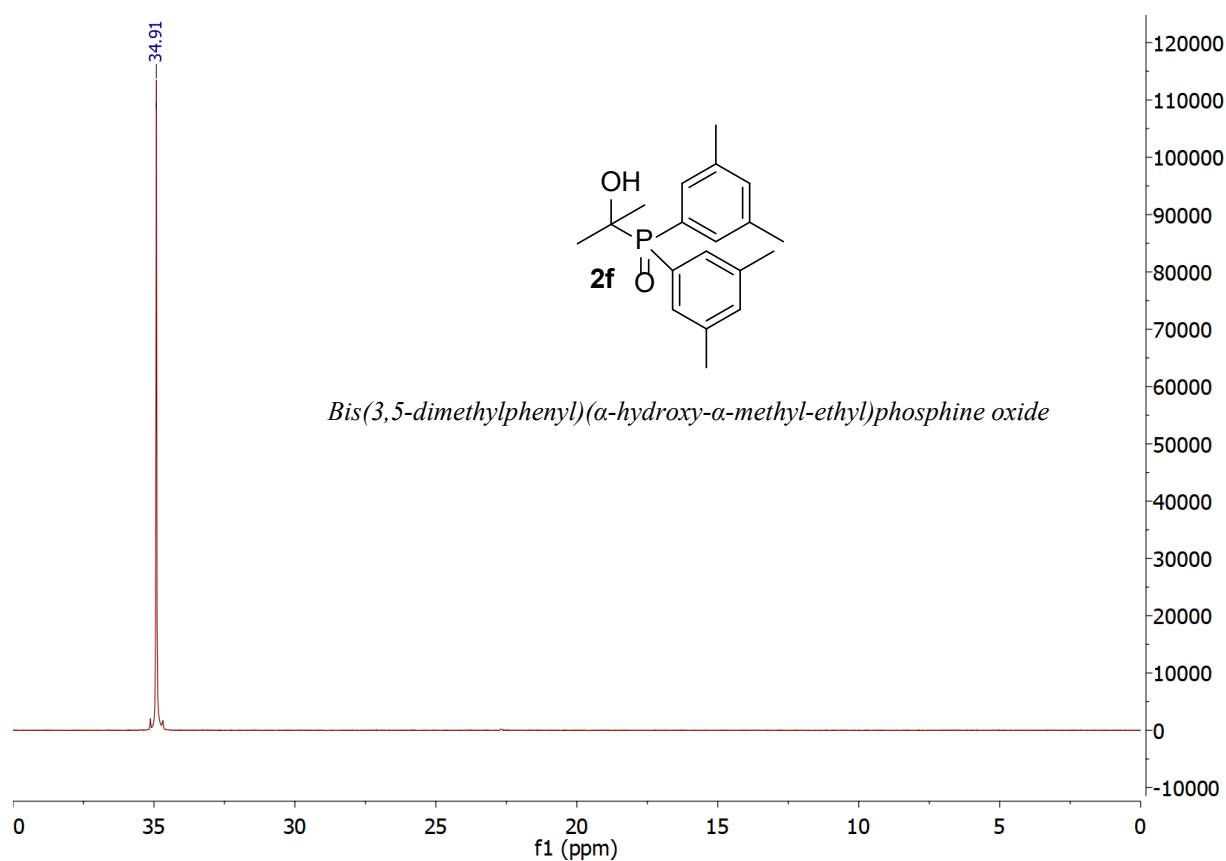
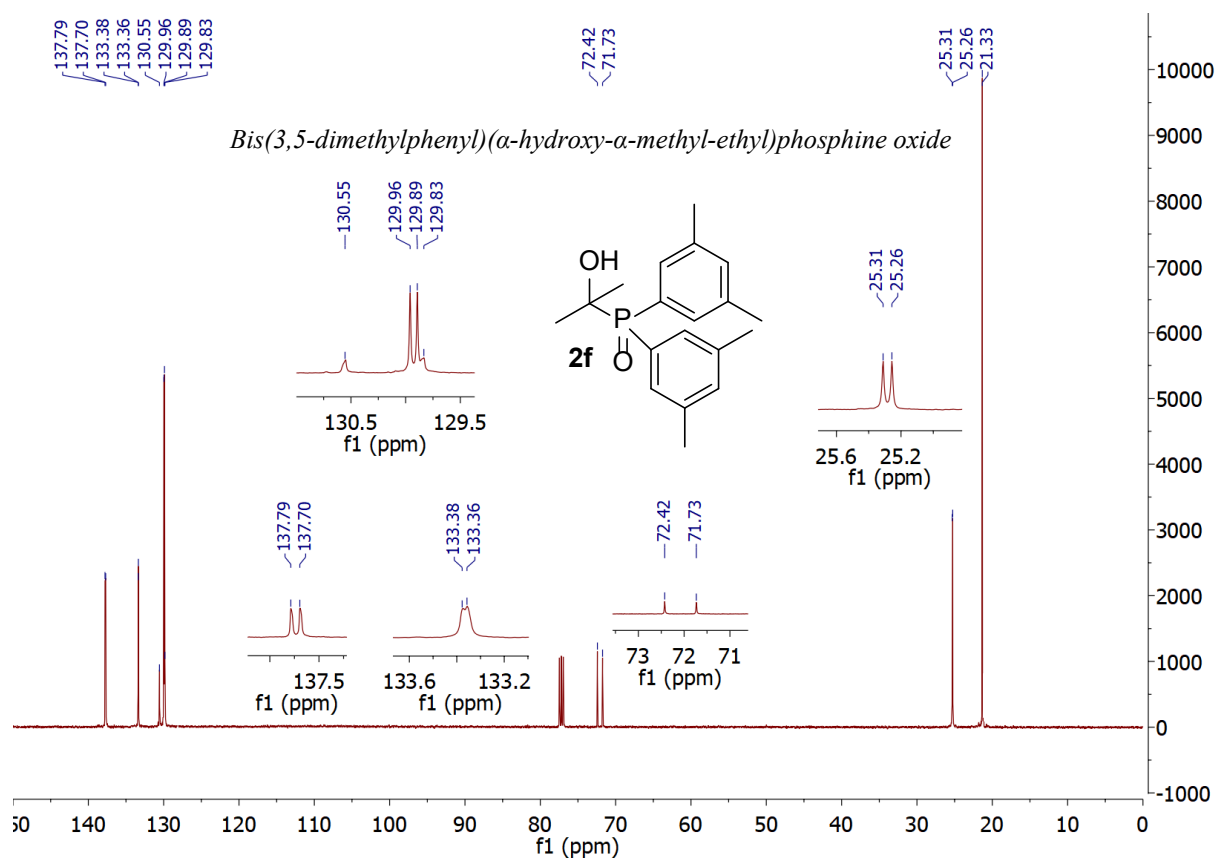


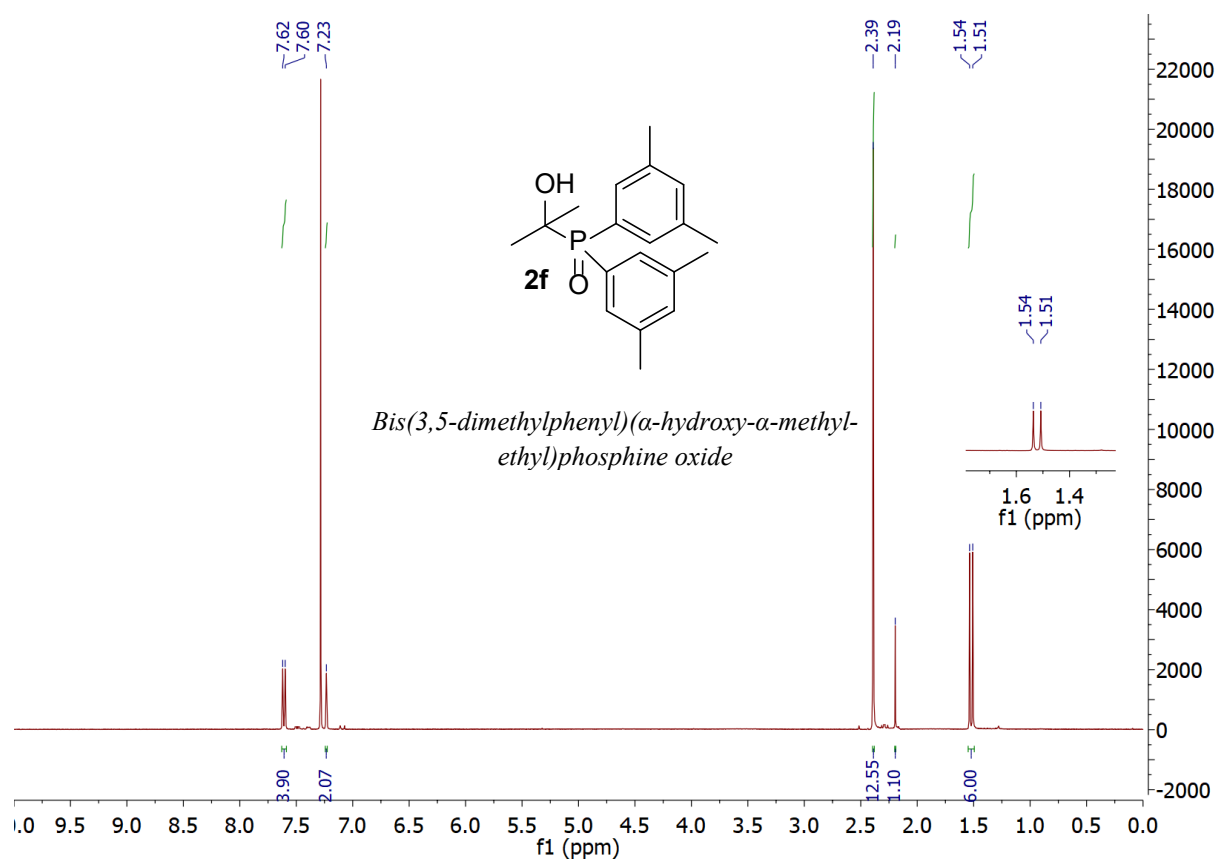
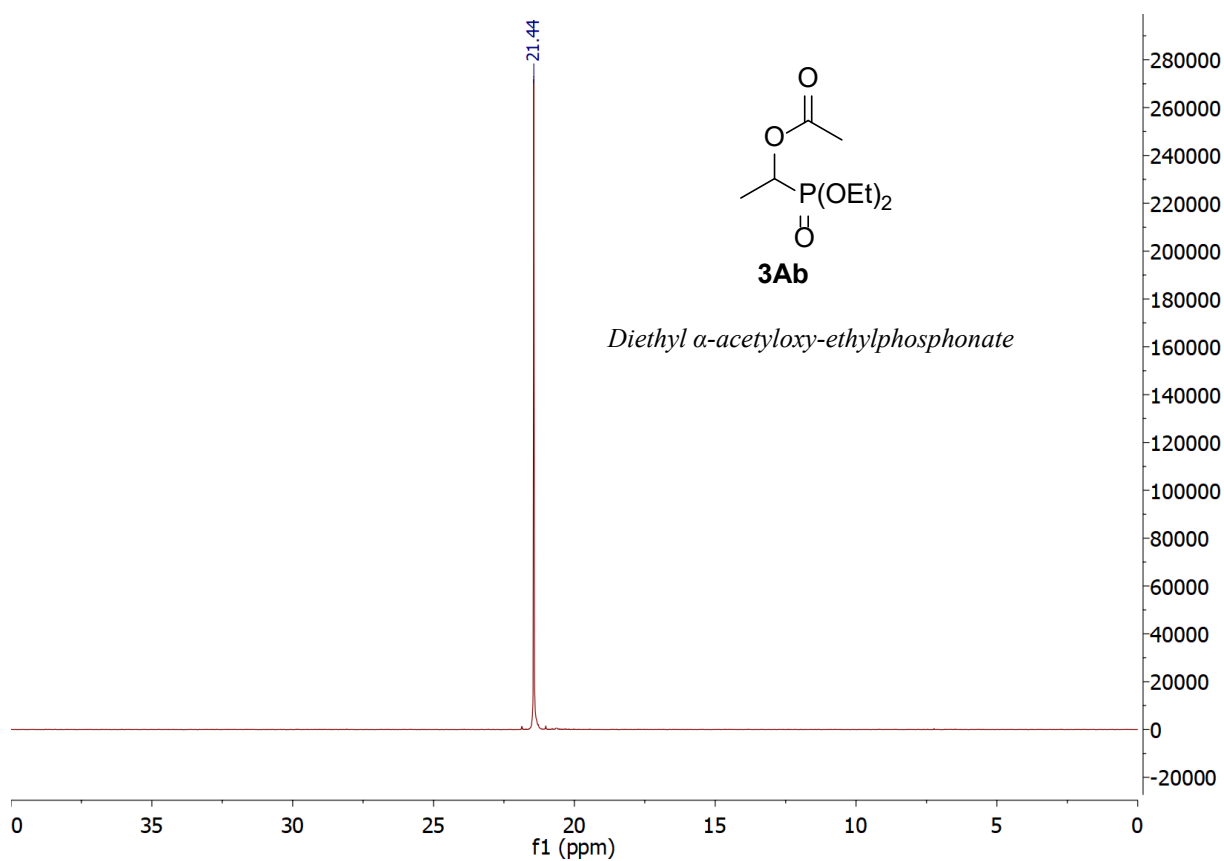
^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 1d **^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 1e**

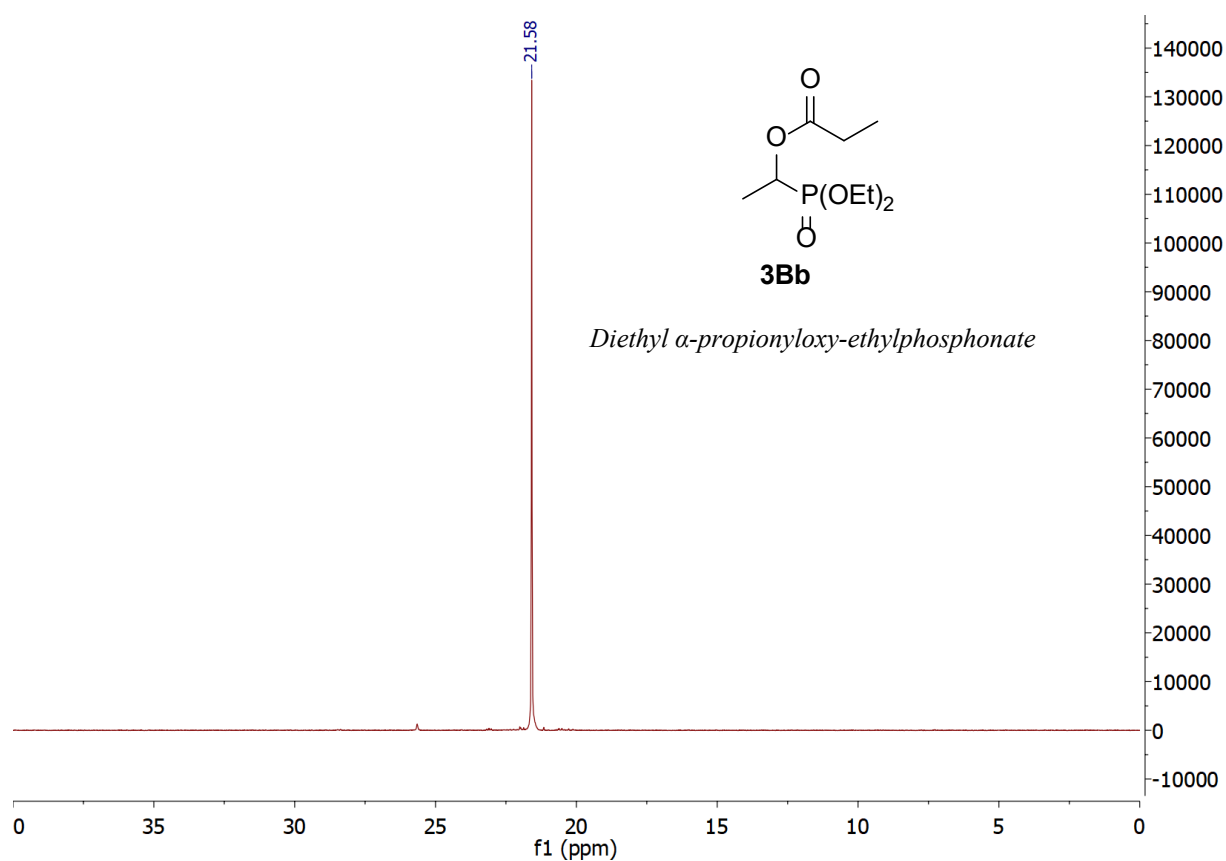
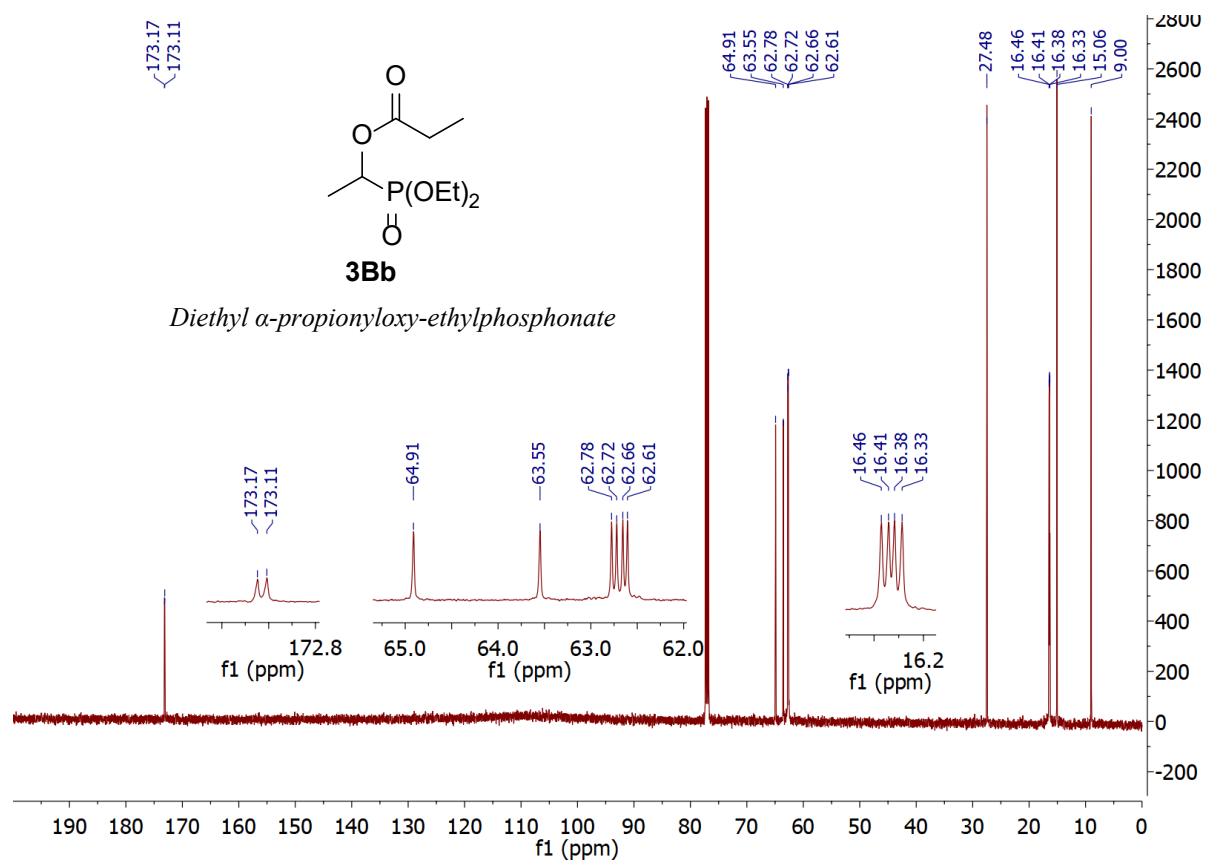
^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 1f **^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 2a**

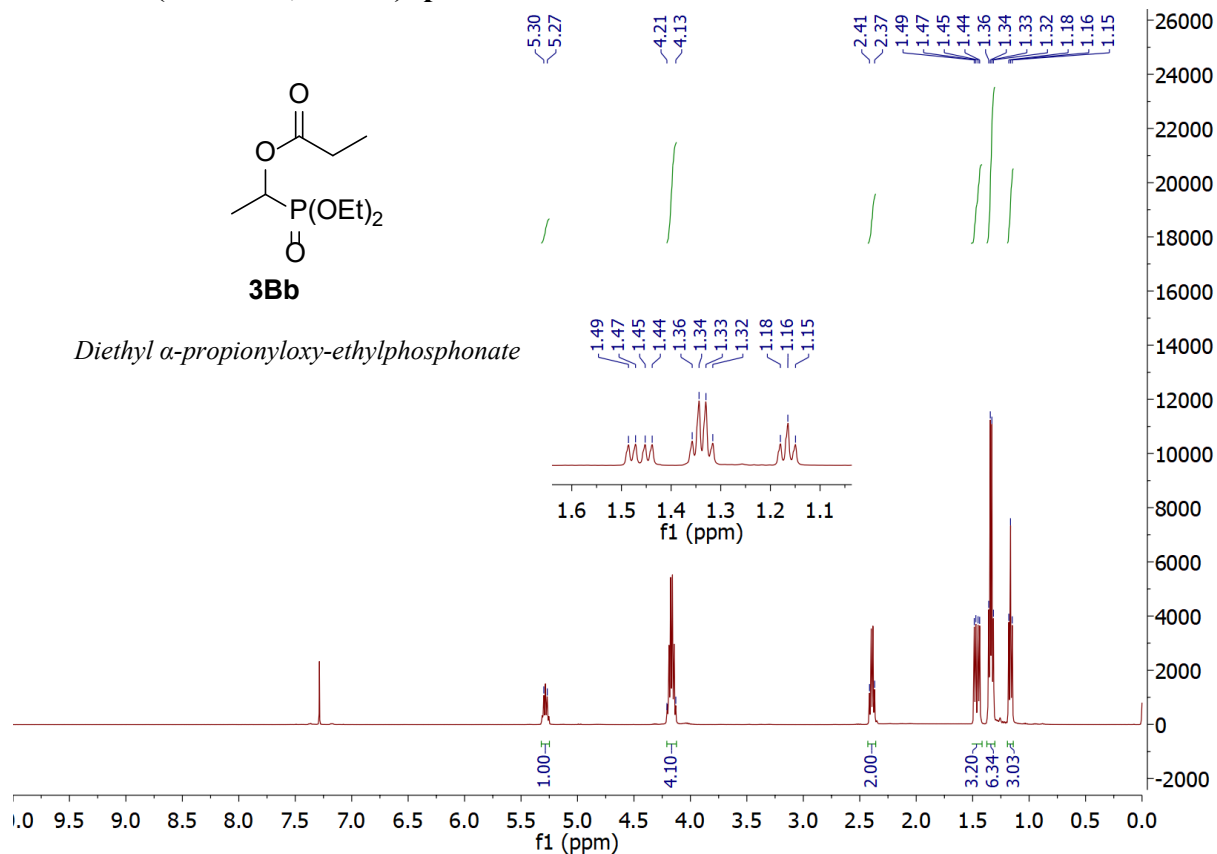
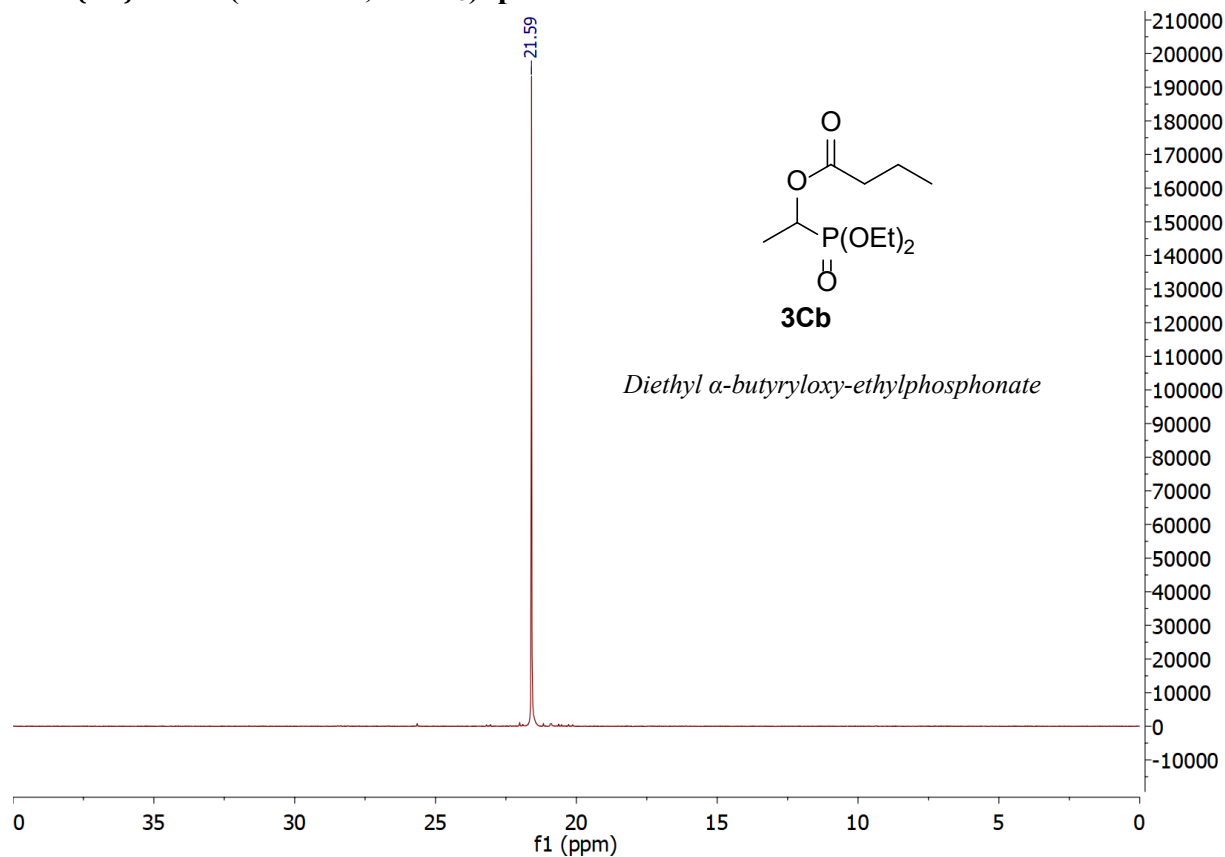
^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 2b **^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 2c**

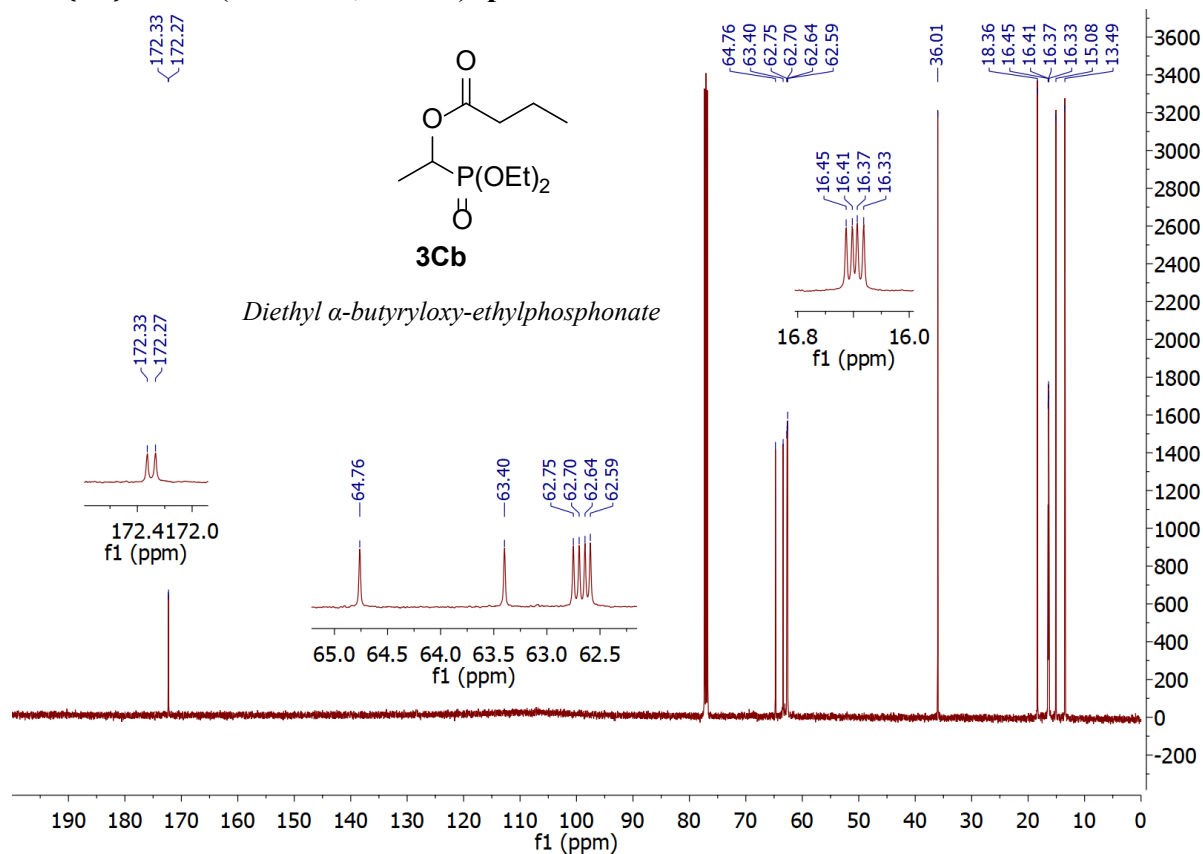
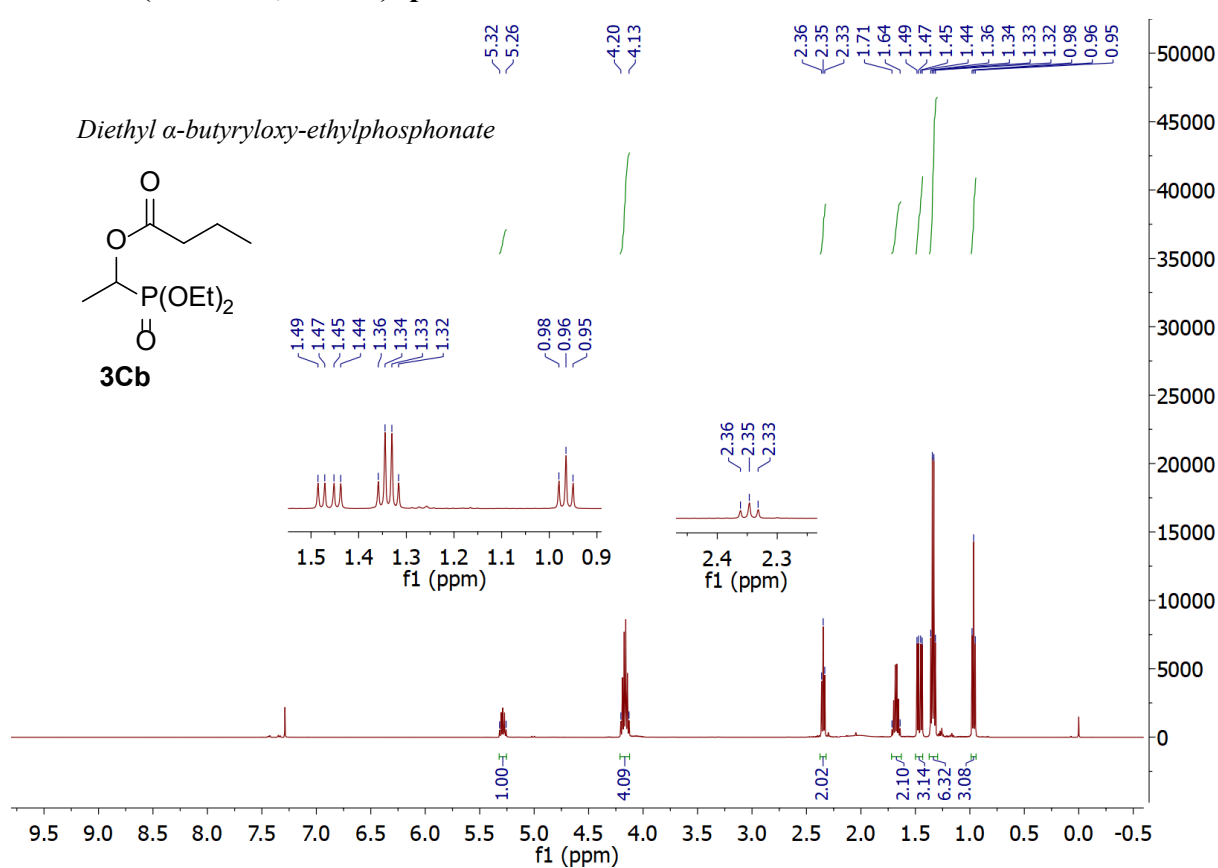
^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 2d **^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 2e**

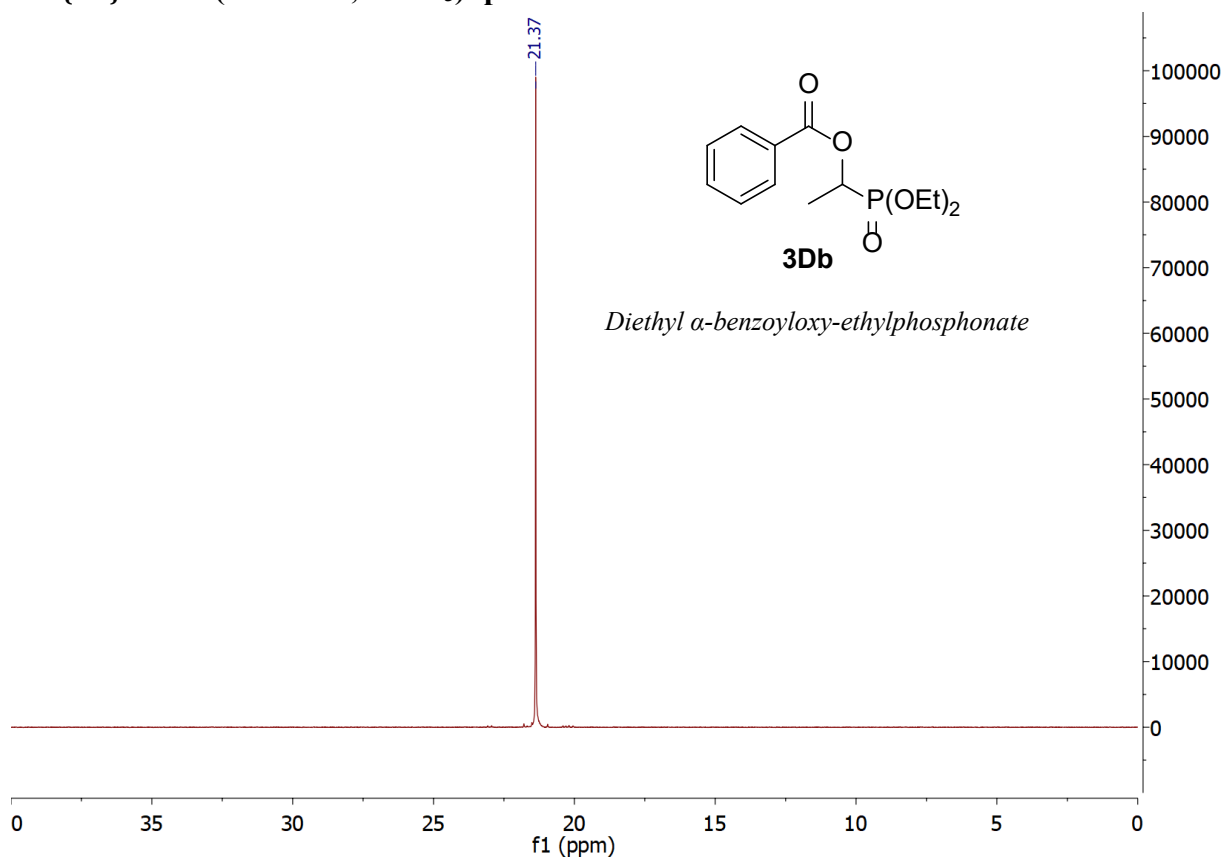
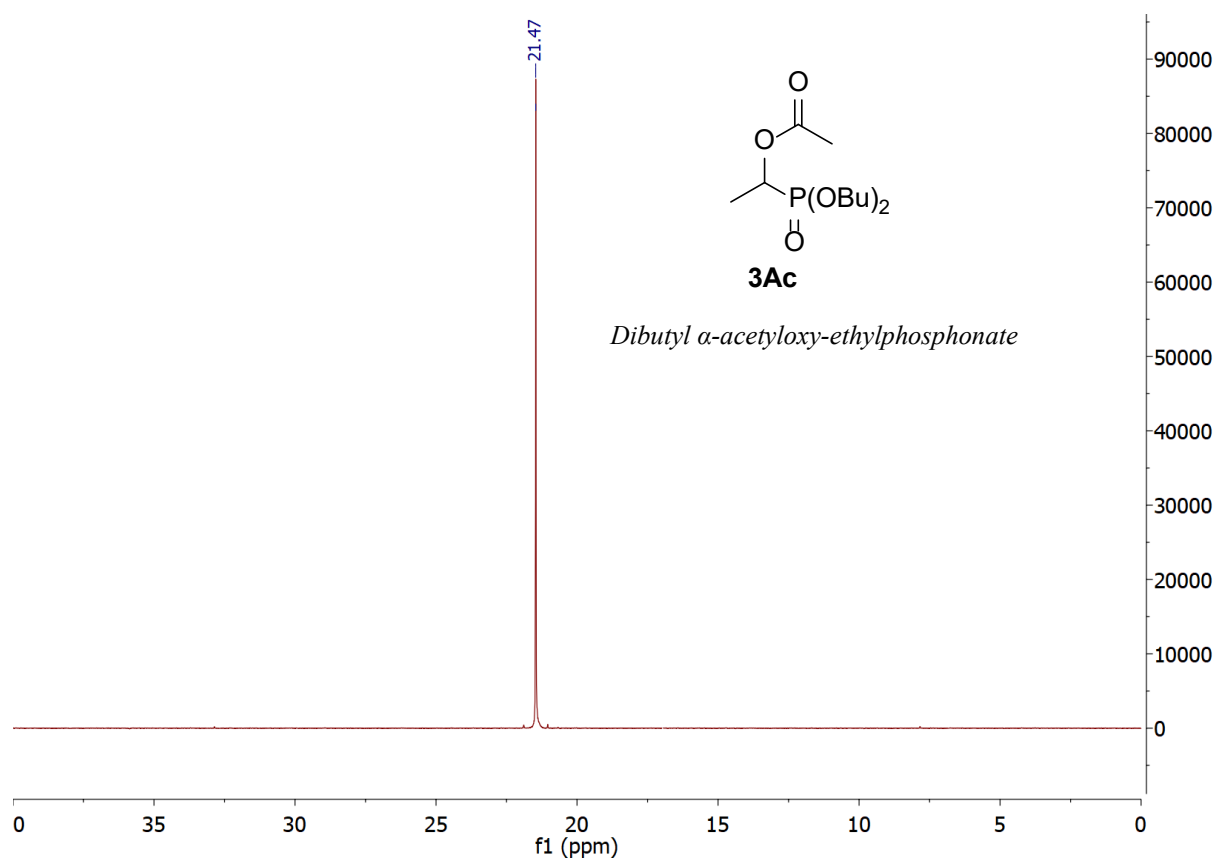
^{31}P { ^1H } NMR (202 MHz, CDCl_3) spectra for 2f **^{13}C { ^1H } NMR (126 MHz, CDCl_3) spectra for 2f**

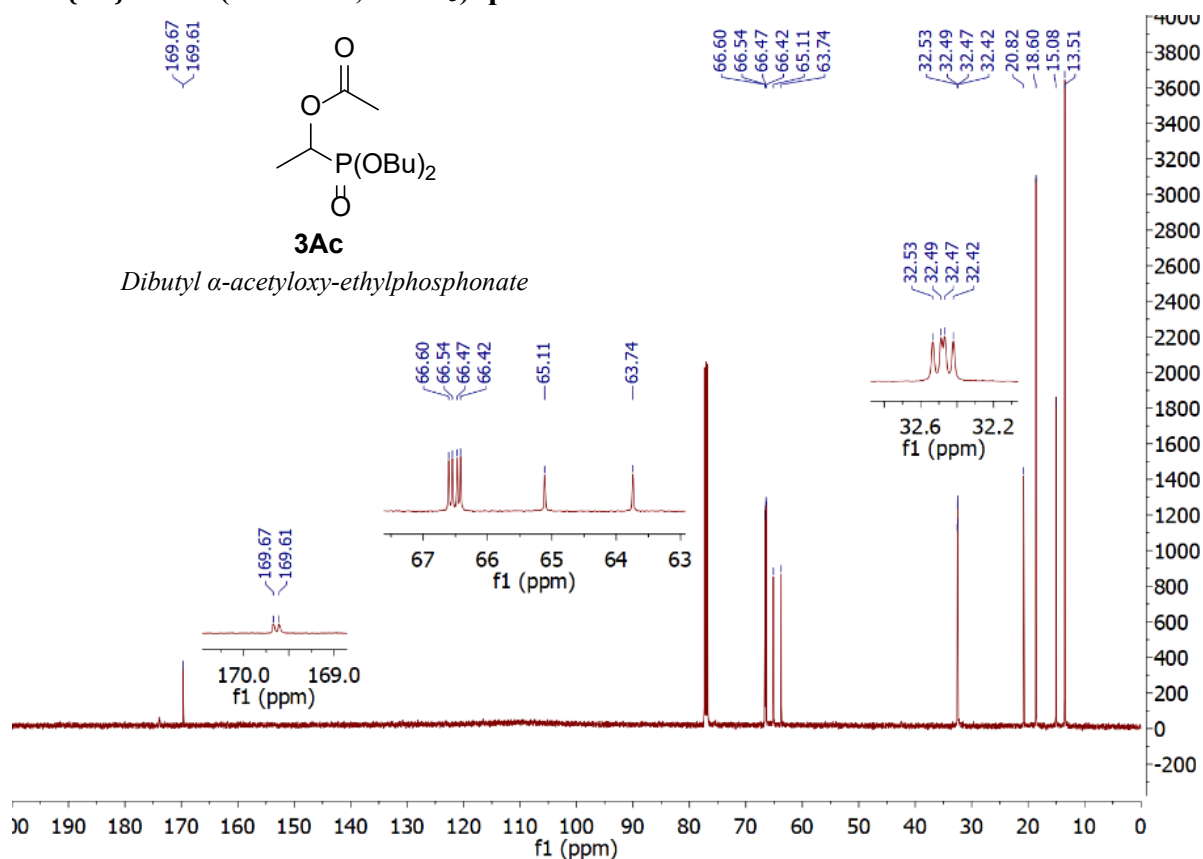
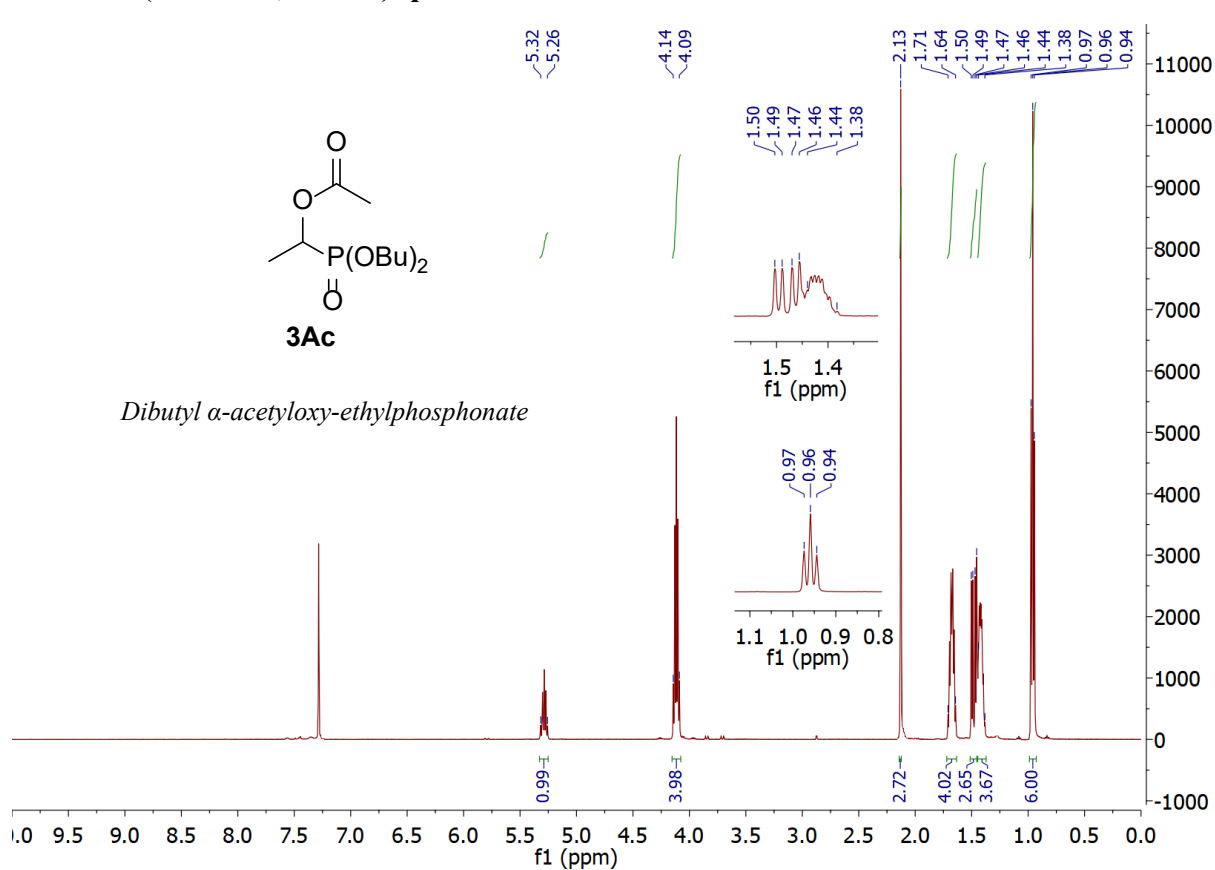
¹H NMR (500 MHz, CDCl₃) spectra for 2f**³¹P {¹H} NMR (202 MHz, CDCl₃) spectra for 3Ab**

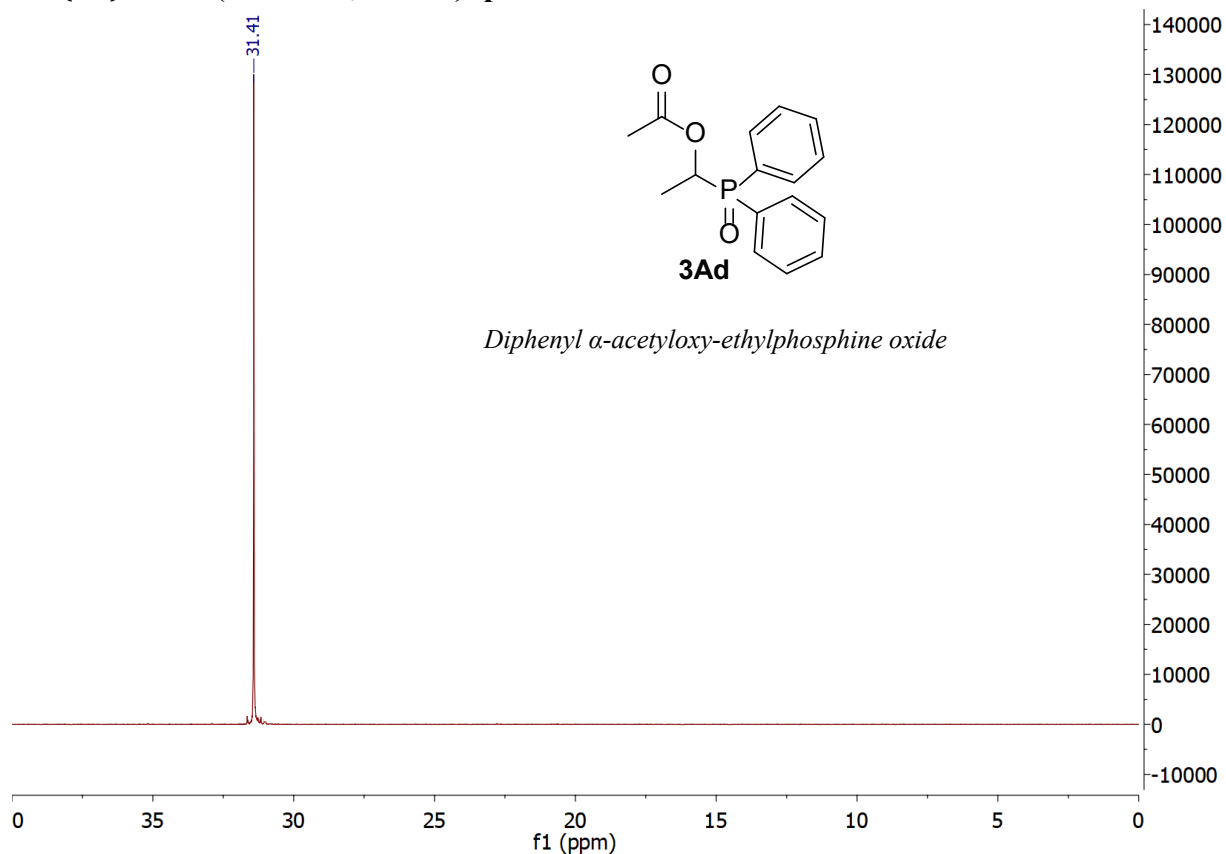
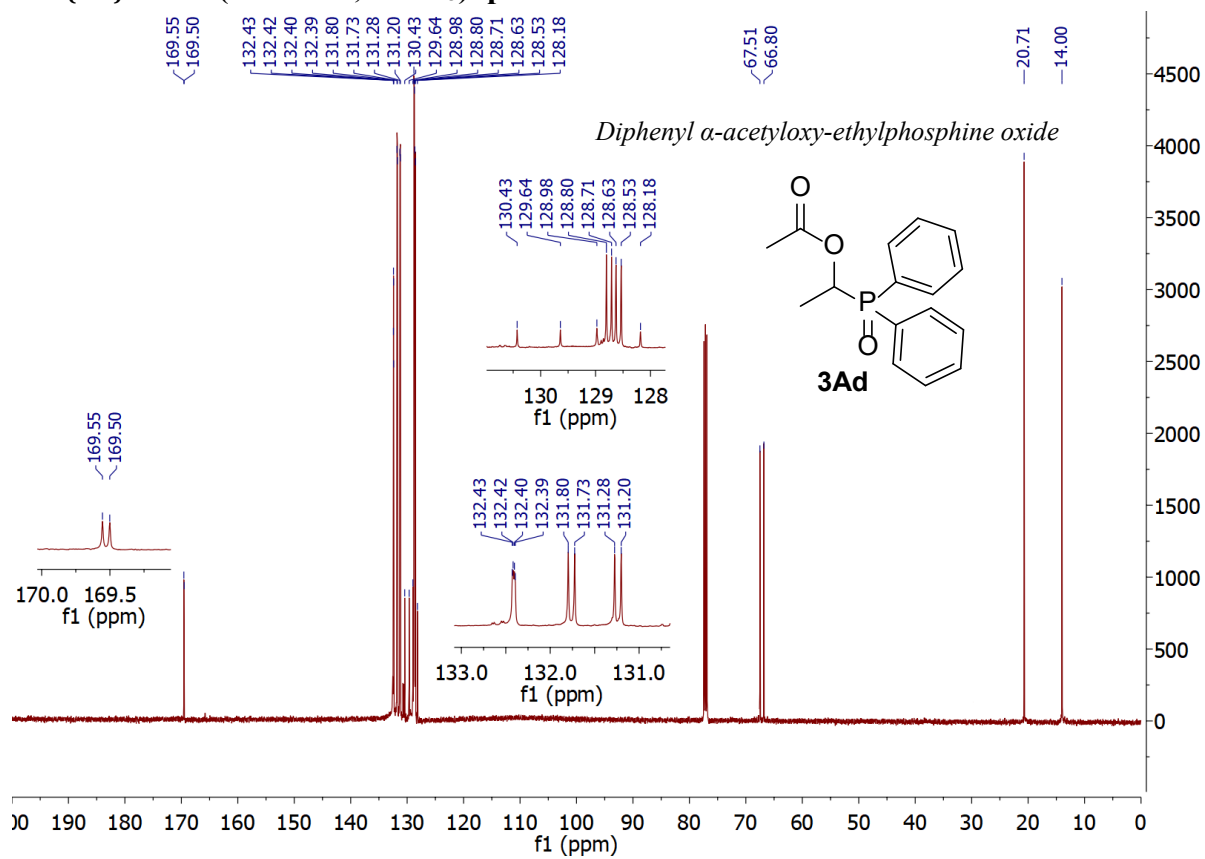
^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 3Bb **^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectra for 3Bb**

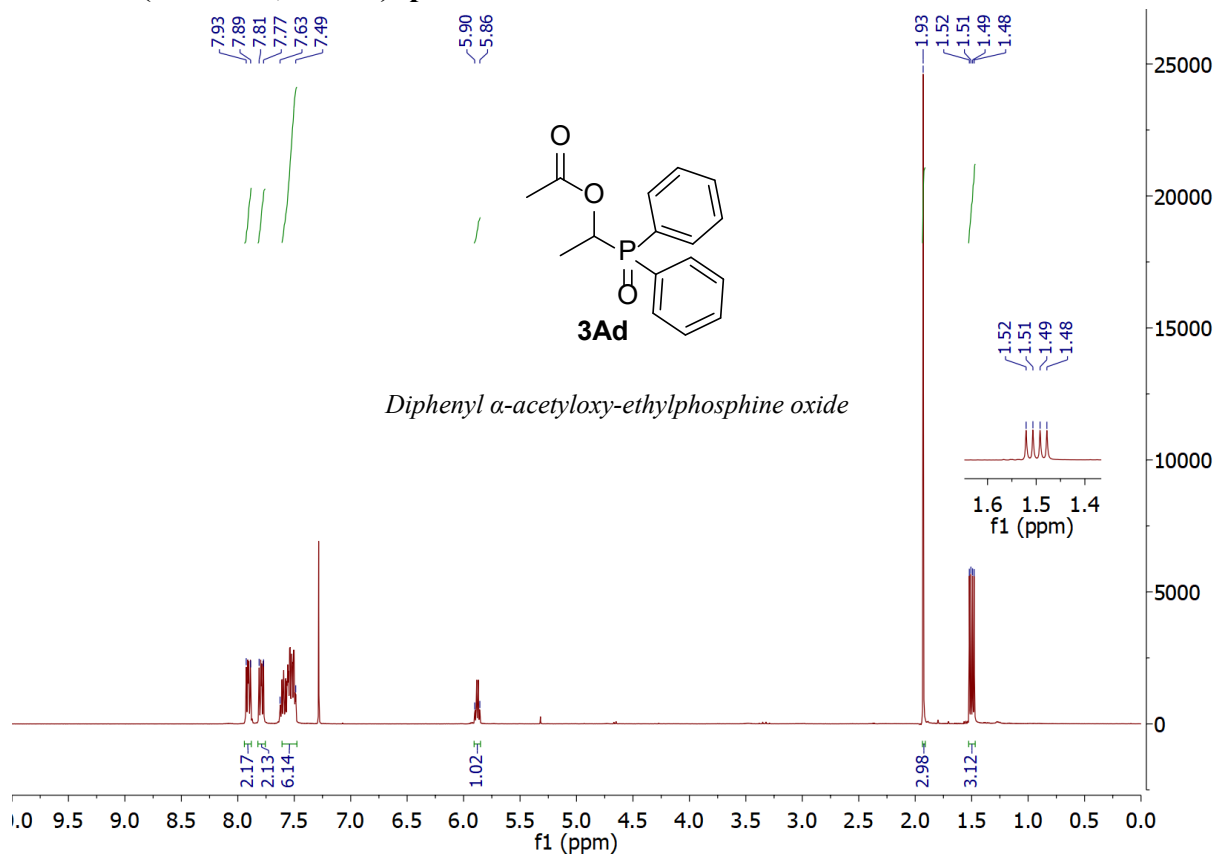
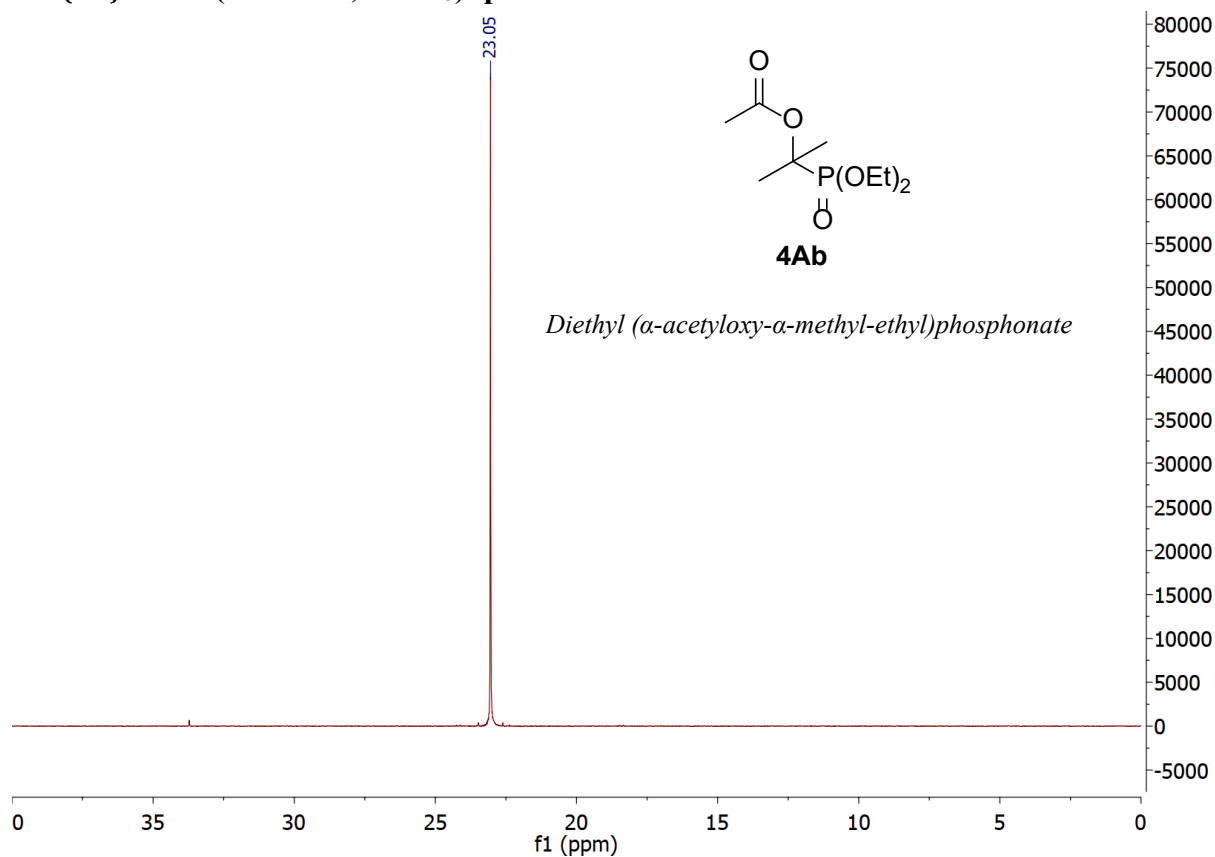
¹H NMR (500 MHz, CDCl₃) spectra for 3Bb**³¹P {¹H} NMR (202 MHz, CDCl₃) spectra for 3Cb**

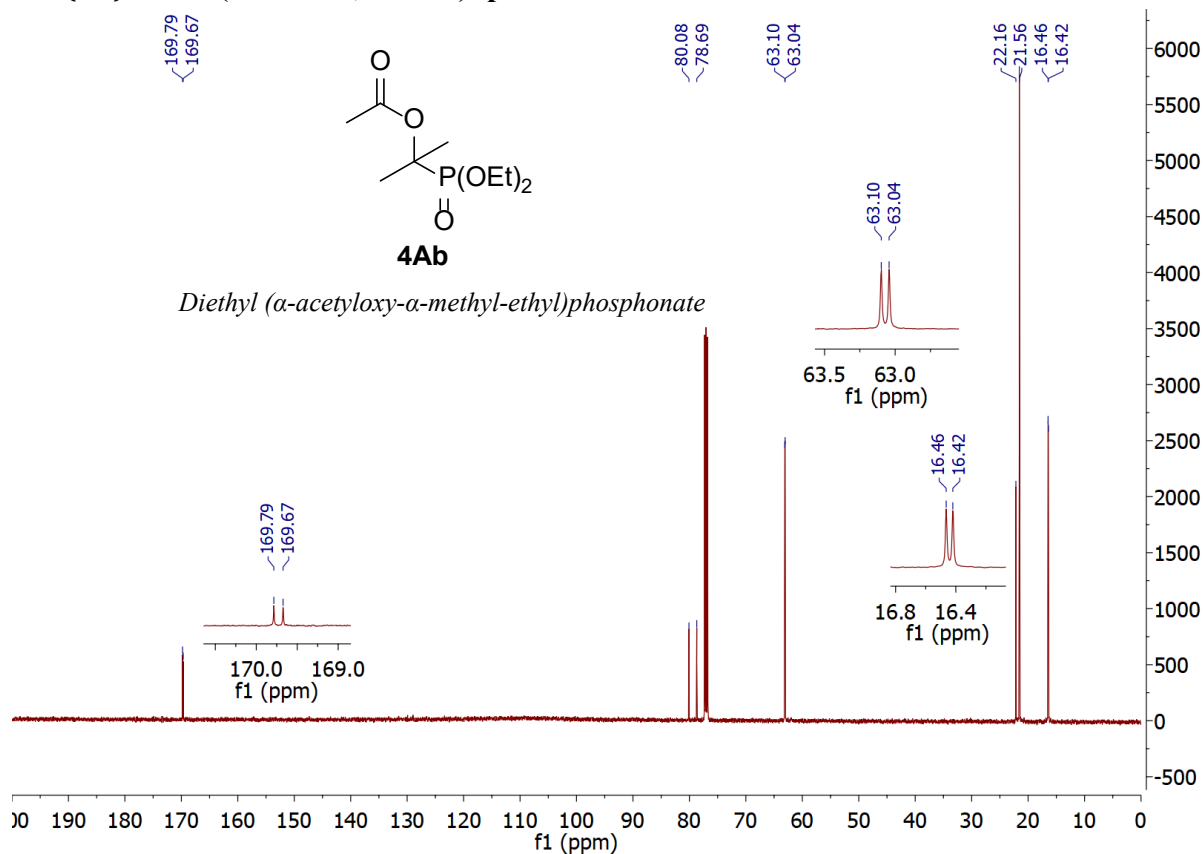
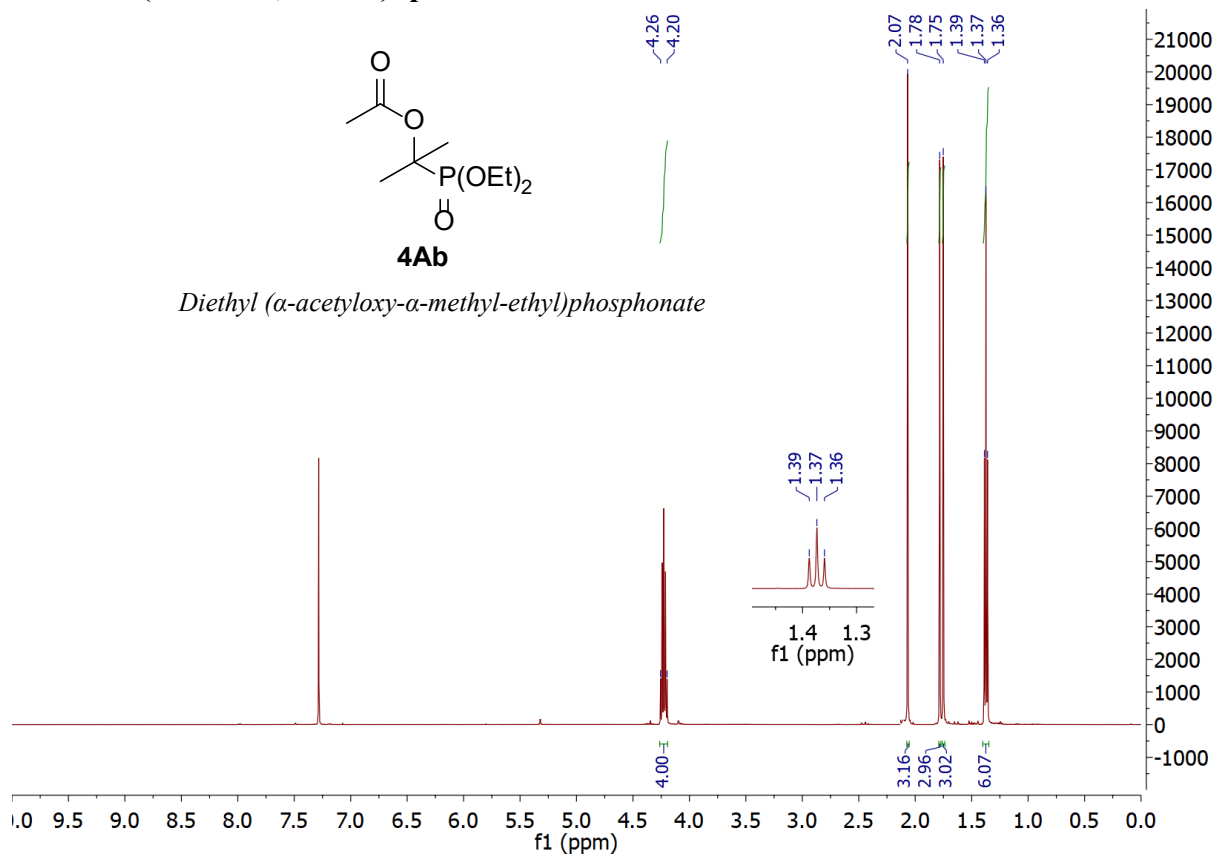
^{13}C { ^1H } NMR (126 MHz, CDCl_3) spectra for 3Cb **^1H NMR (500 MHz, CDCl_3) spectra for 3Cb**

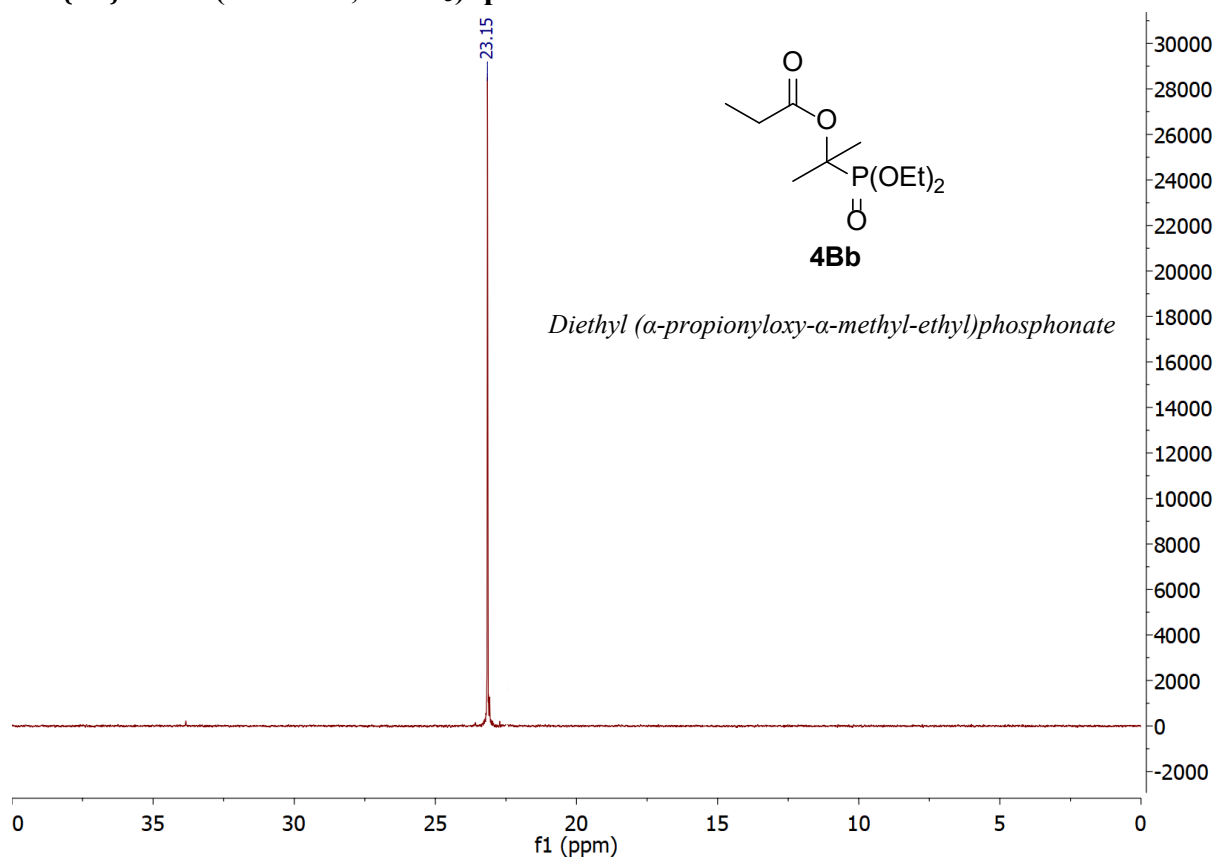
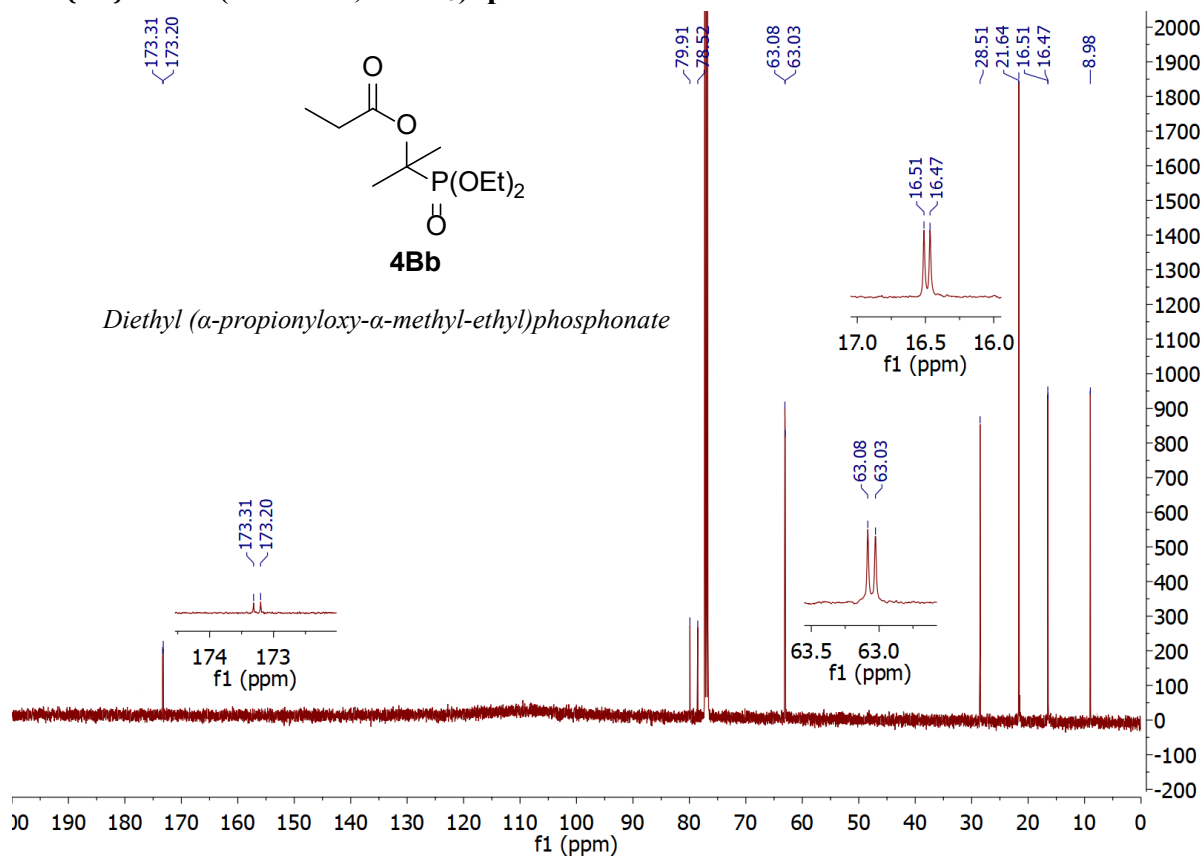
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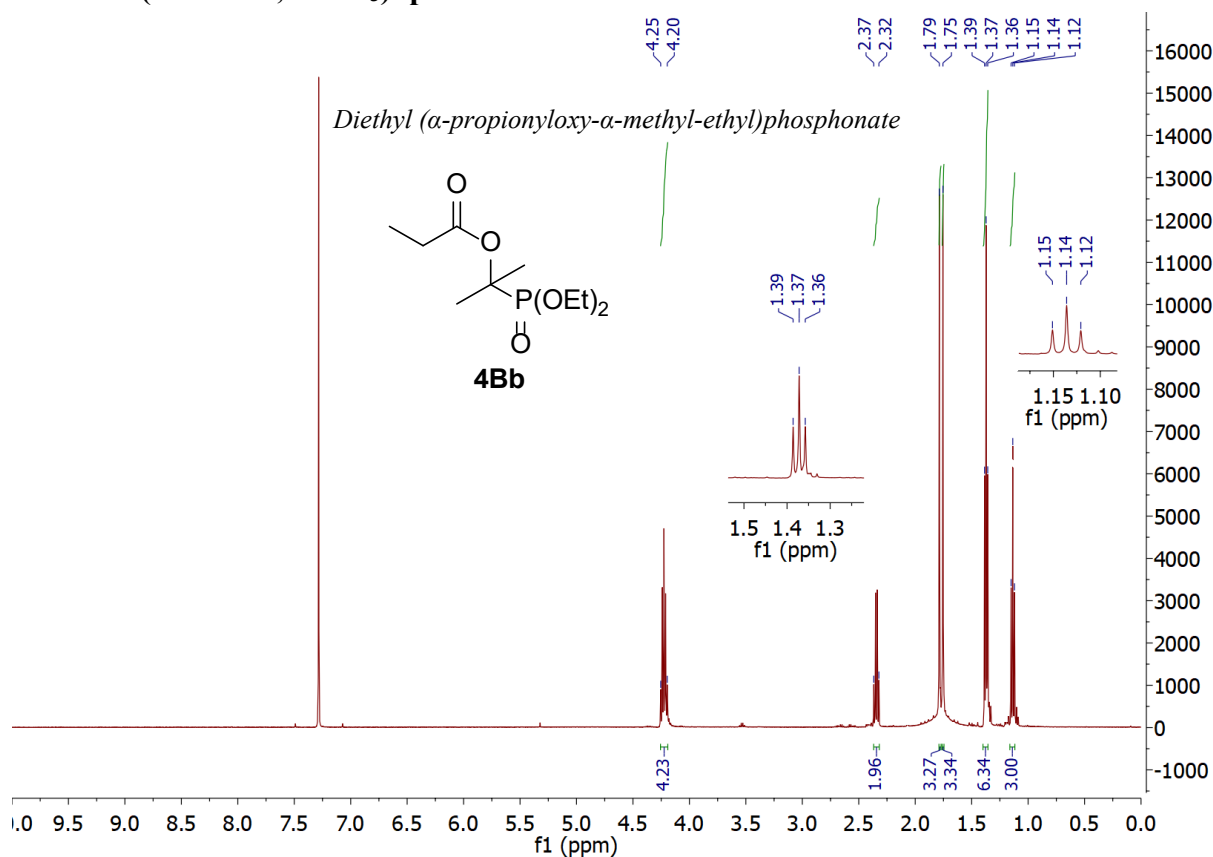
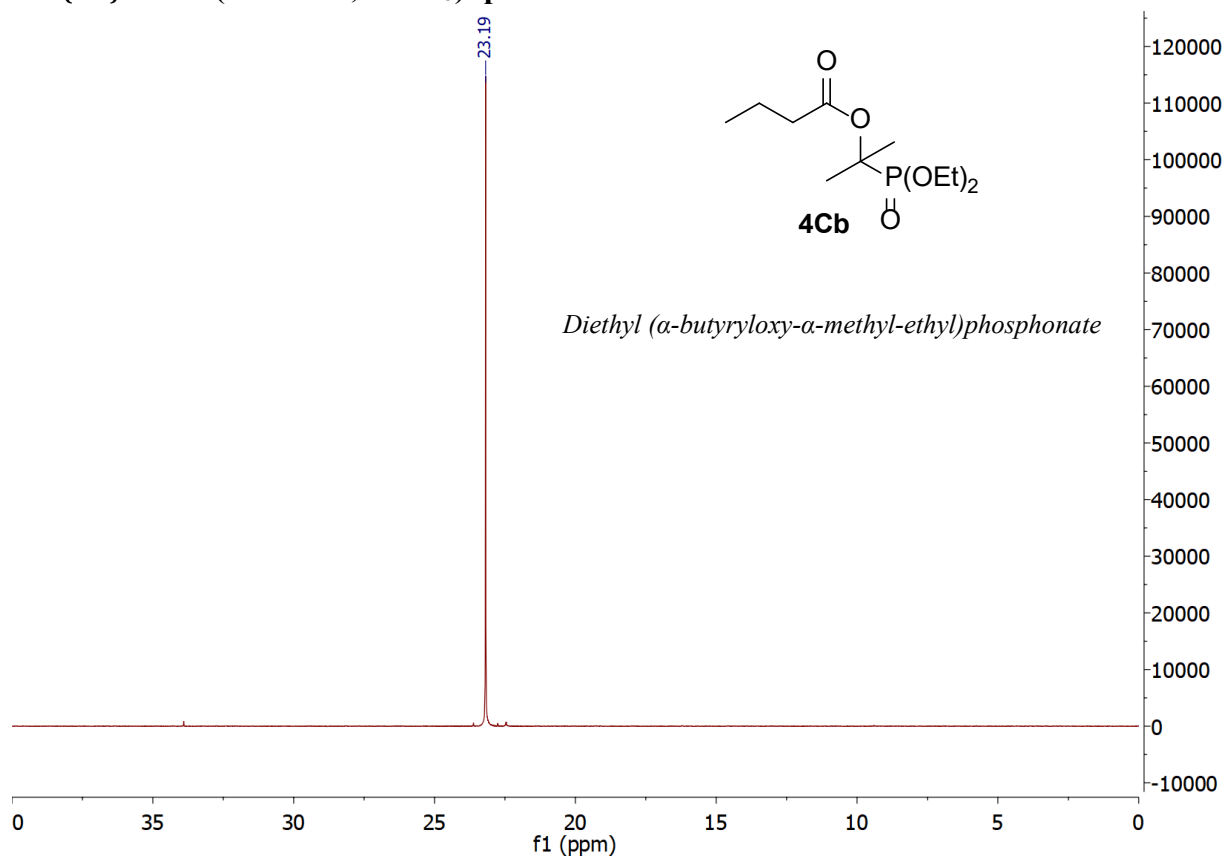
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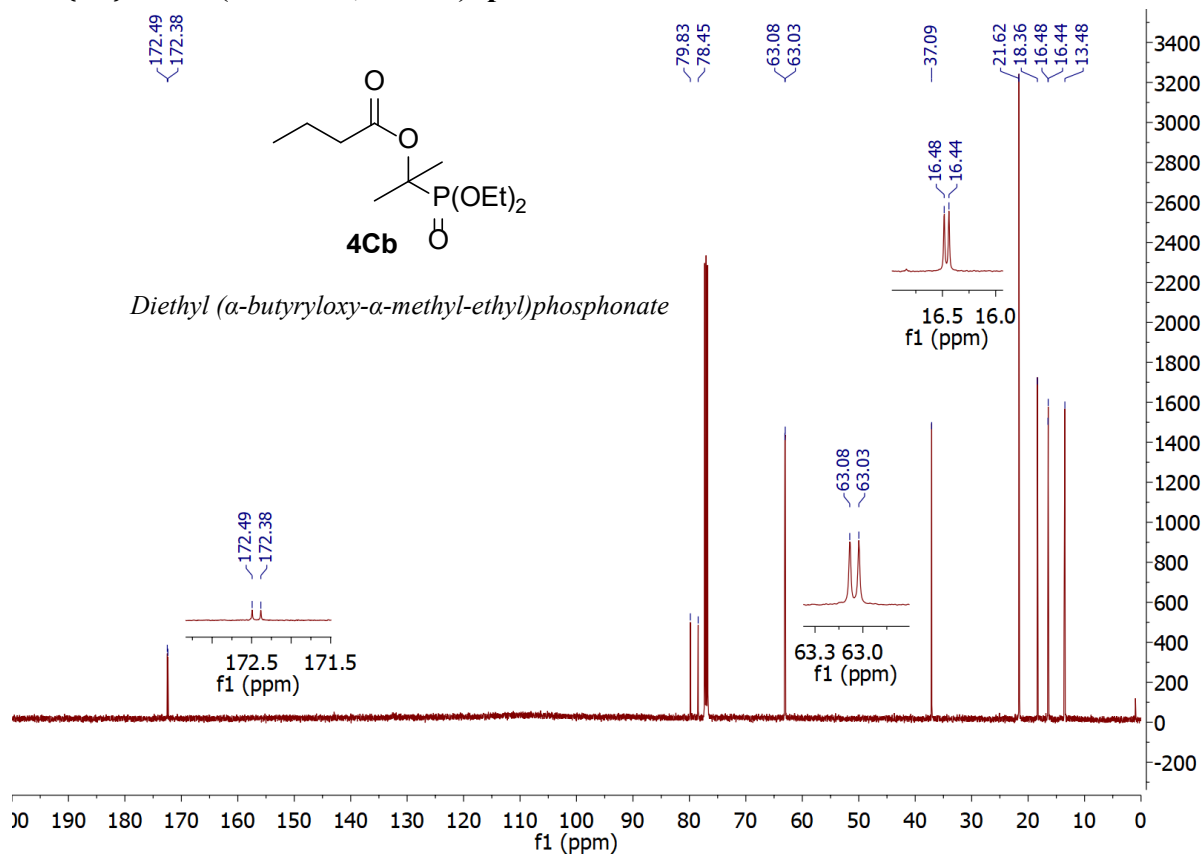
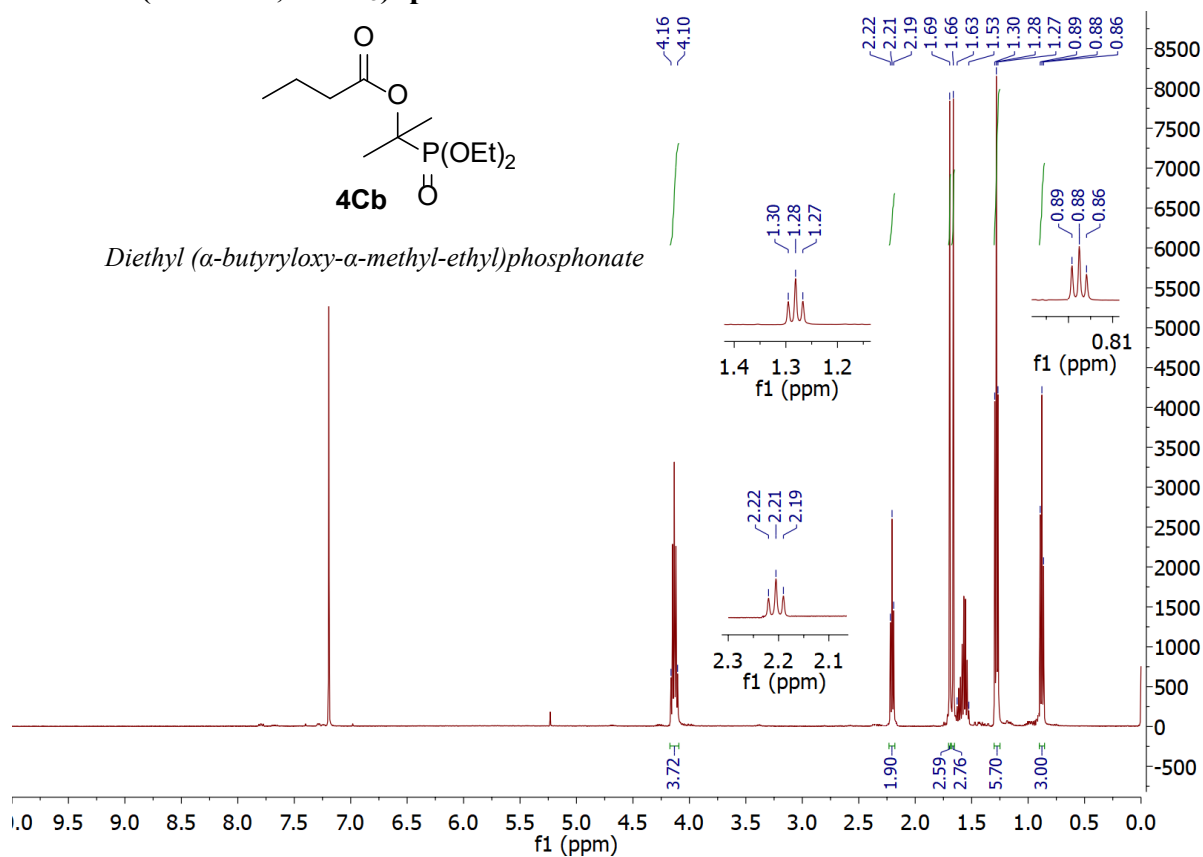
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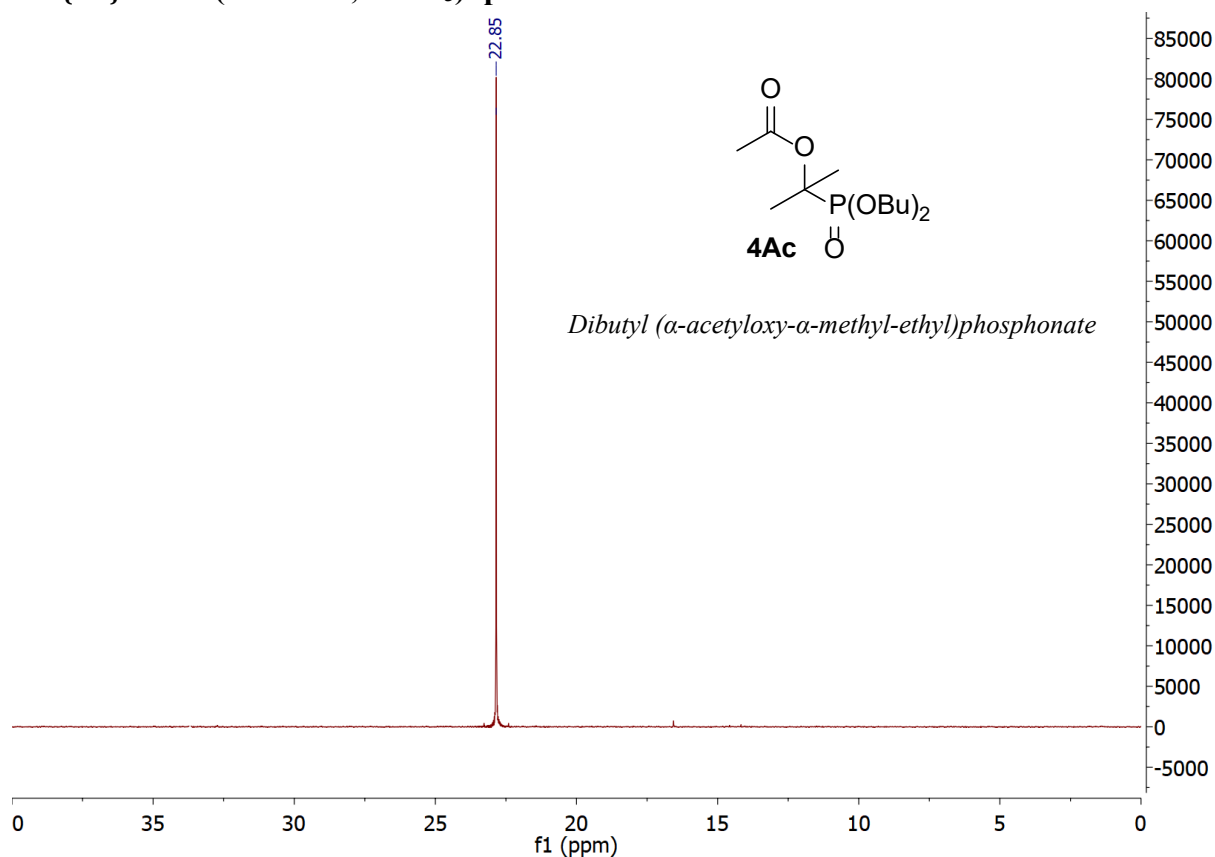
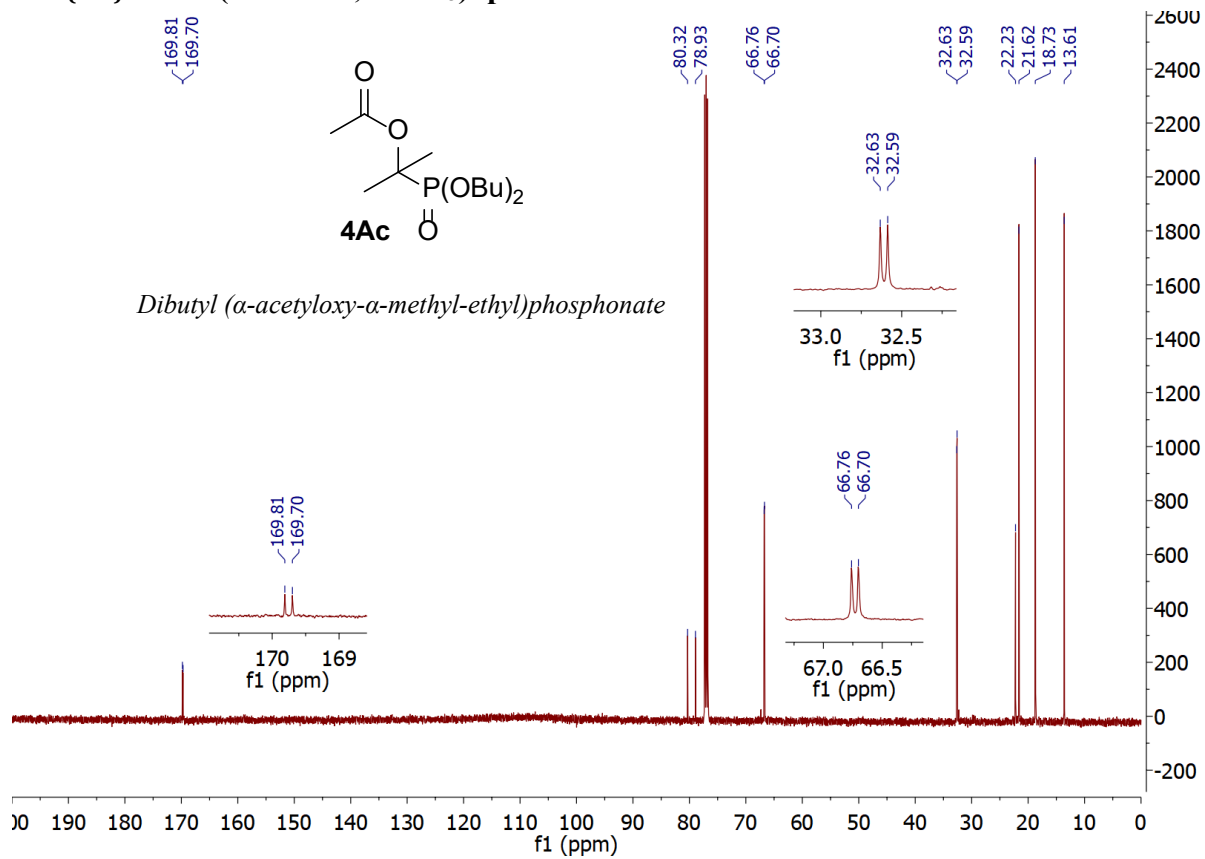
^1H NMR (500 MHz, CDCl_3) spectra for 3Ad **^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 4Ab**

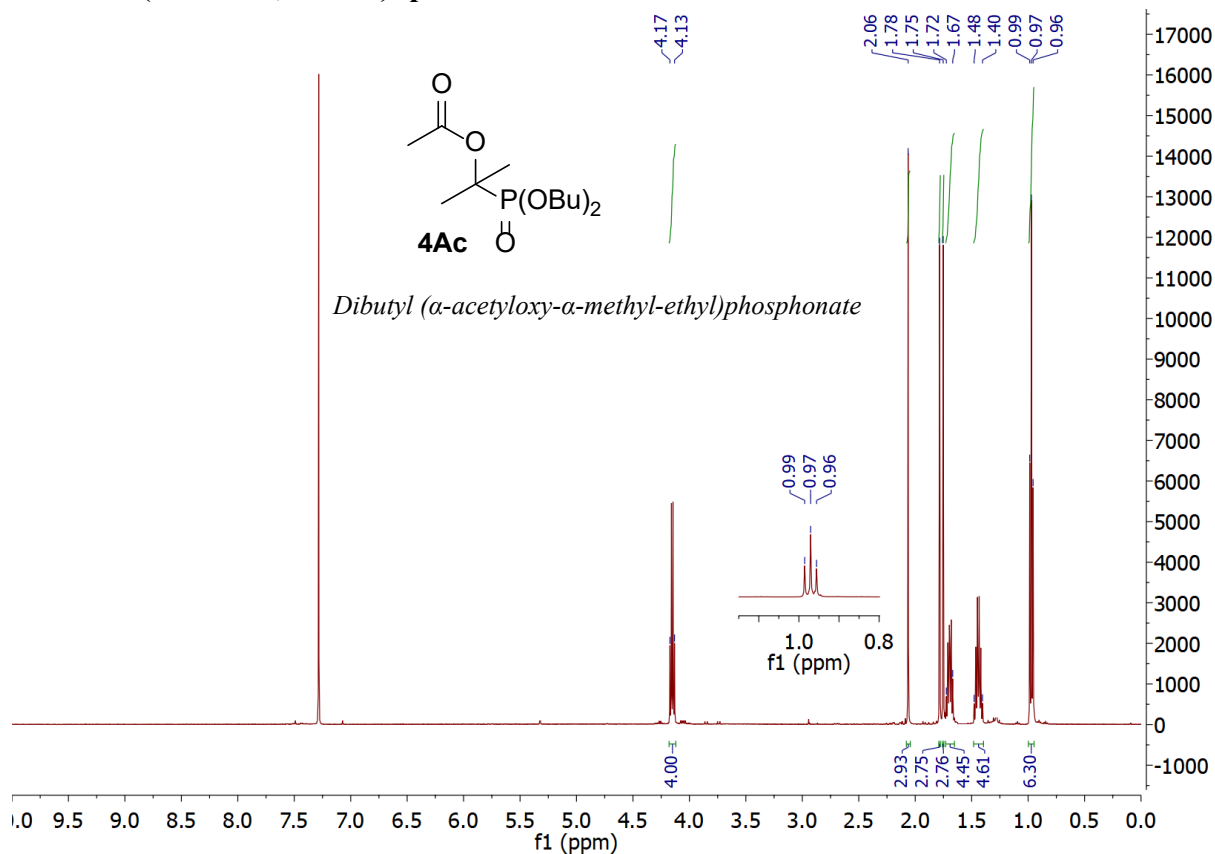
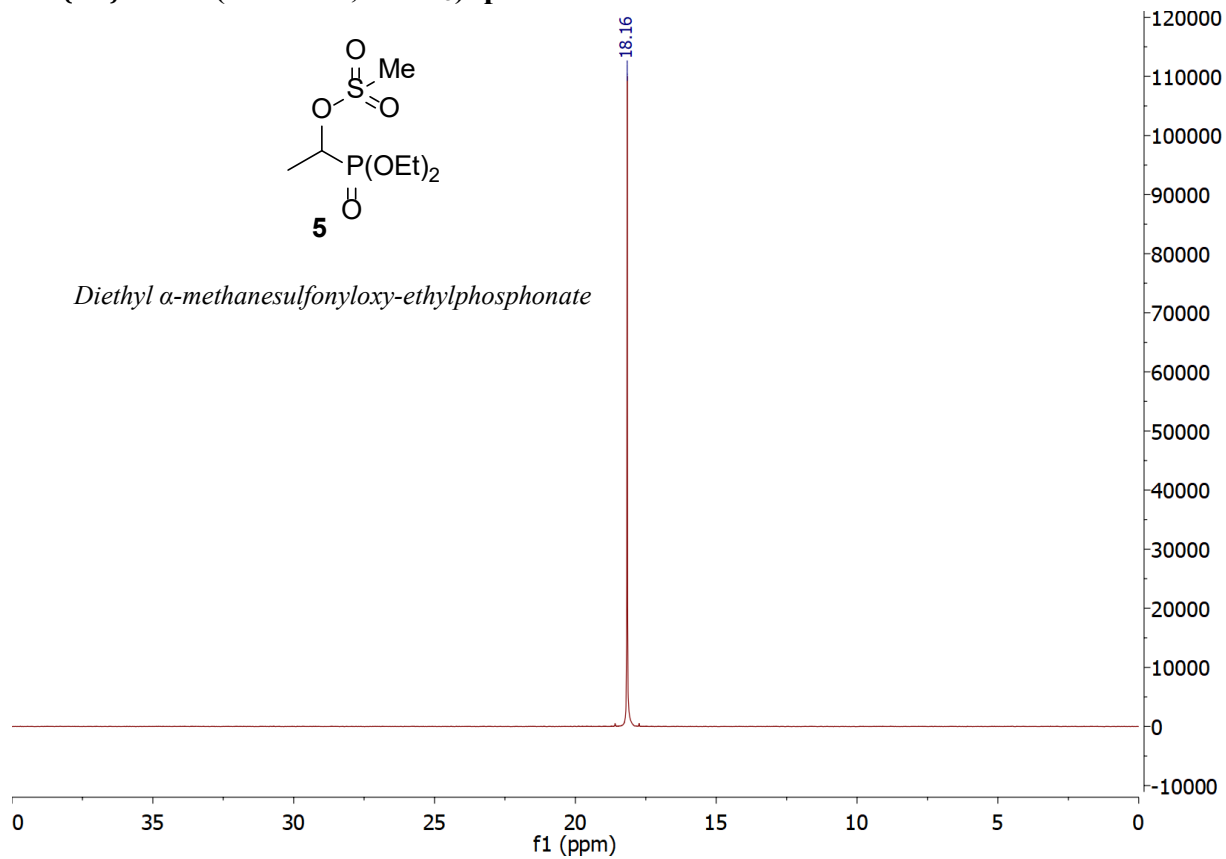
^{13}C { ^1H } NMR (126 MHz, CDCl_3) spectra for 4Ab **^1H NMR (500 MHz, CDCl_3) spectra for 4Ab**

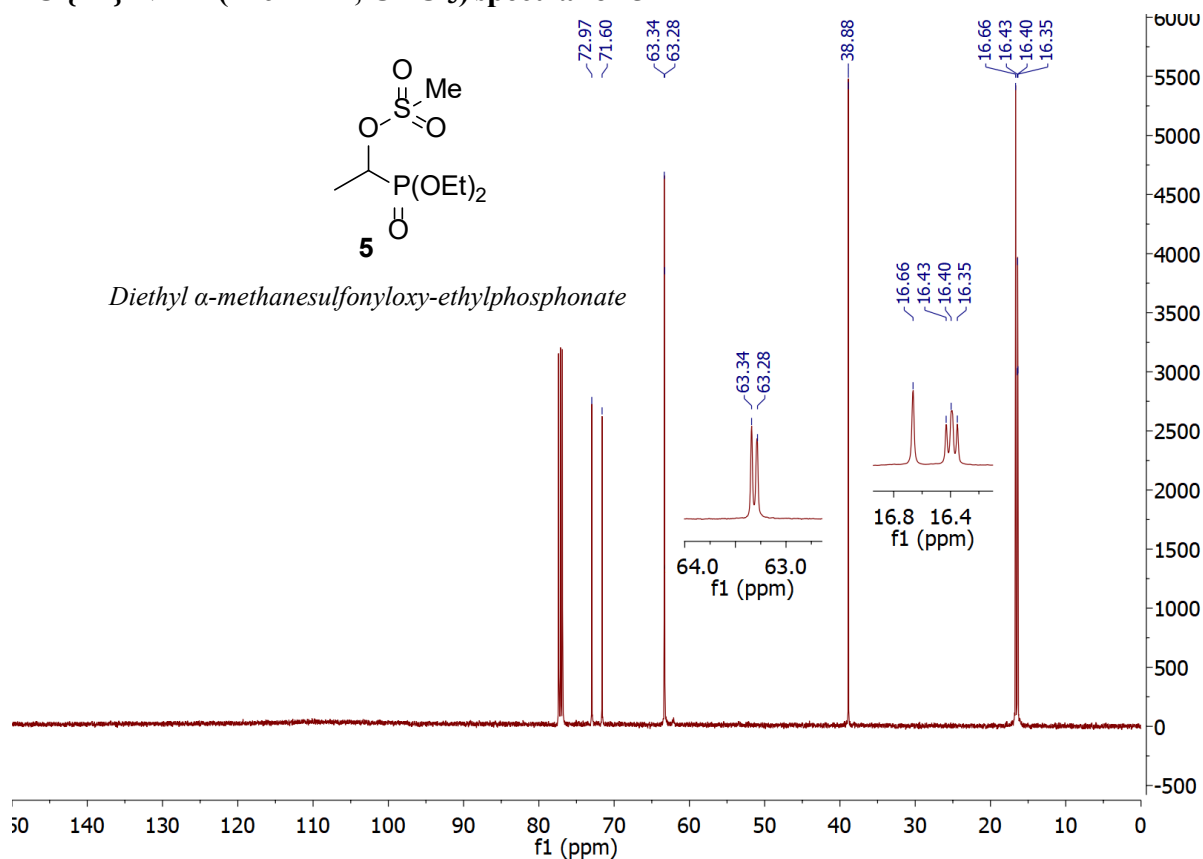
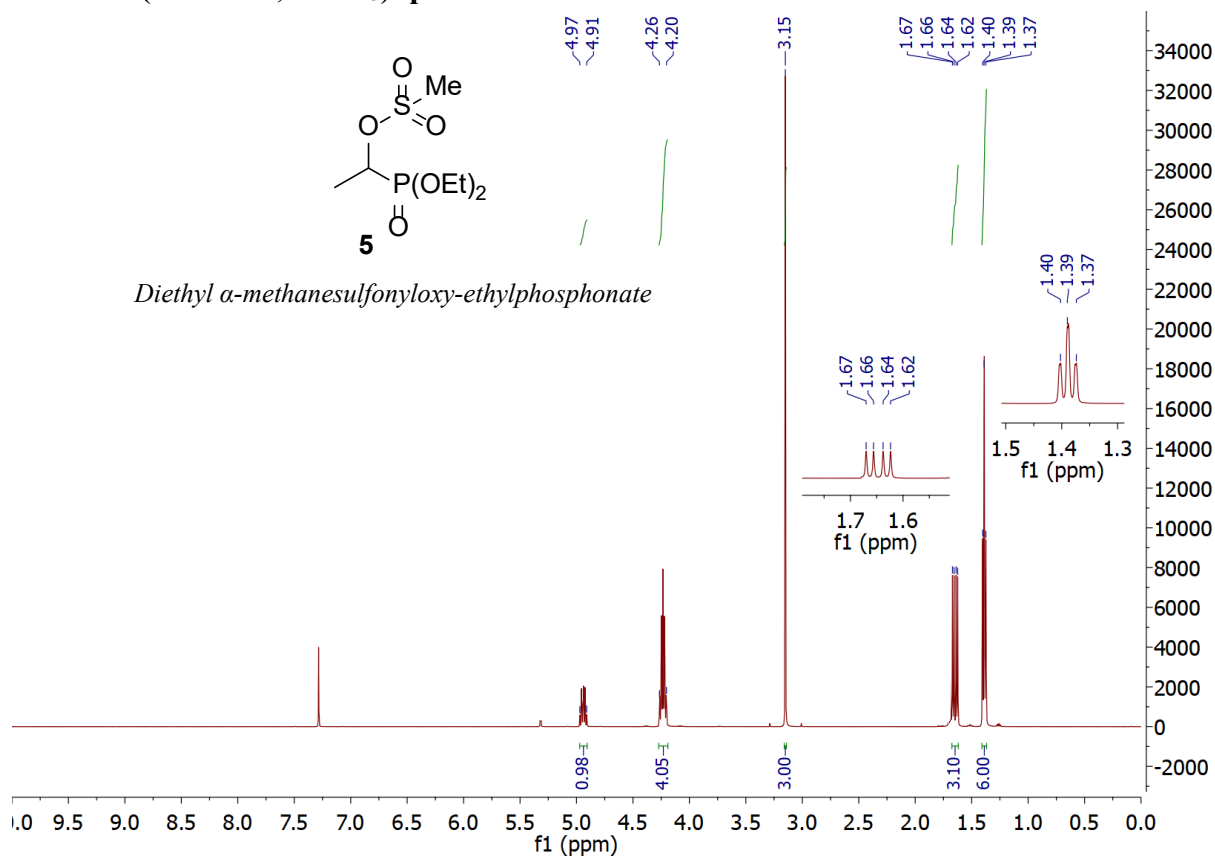
^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 4Bb ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectra for 4Bb

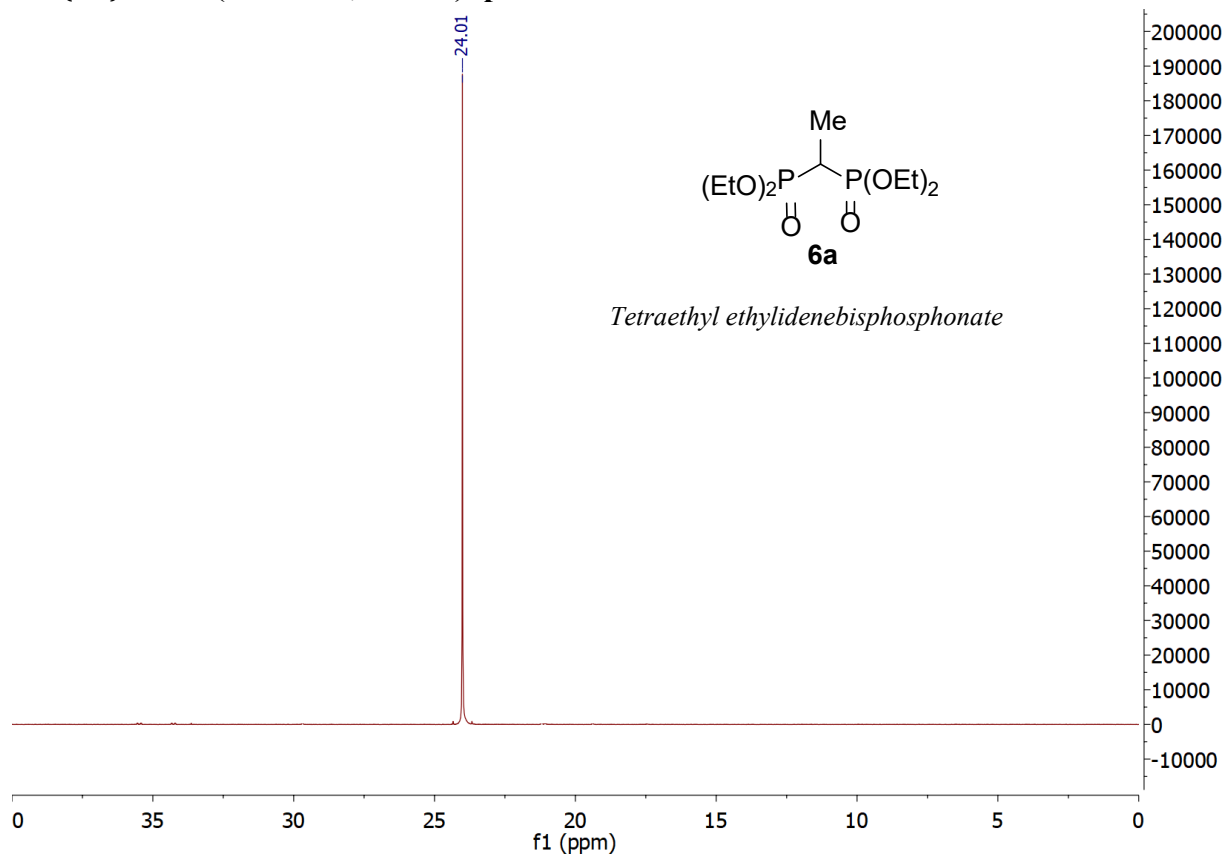
¹H NMR (500 MHz, CDCl₃) spectra for 4bB**³¹P {¹H} NMR (202 MHz, CDCl₃) spectra for 4Cb**

^{13}C { ^1H } NMR (126 MHz, CDCl_3) spectra for 4Cb **^1H NMR (500 MHz, CDCl_3) spectra for 4Cb**

^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 4Ac ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) spectra for 4Ac

¹H NMR (500 MHz, CDCl₃) spectra for 4Ac**³¹P {¹H} NMR (202 MHz, CDCl₃) spectra for 5**

^{13}C { ^1H } NMR (126 MHz, CDCl_3) spectra for 5 **^1H NMR (500 MHz, CDCl_3) spectra for 5**

^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 6a ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) spectra for 6b