# Supplementary Material

# Highly efficient and extremely simple protocol for the oxidation α-hydroxyphosphonates to α-ketophosphonates using Dess-Martin periodinane

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## Spectral data

*Diethyl (4-chlorobenzoyl) phosphonate*, **2a: $^{1}$H-NMR (300 MHz, $CDCl_3$):** δ 1.34 (t, *J* = 7.2 Hz, 6H, 2 x $OCH_2CH_3$), 4.25 (m, 4H, 2 x $OCH_2CH_3$), 7.44 (d, *J* = 8.4 Hz, 2H, ArHs), 8.18 (d, *J* = 8.4 Hz, 2H, ArHs); **$^{13}$C-NMR (75 MHz, $CDCl_3$):** δ 16.25 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, $OCH_2CH_3$), 64.26 (d, $^{2}J_{C\text{-}P}$ = 7. 5 Hz, $OCH_2CH_3$), 129.24, 131.17, 133.35, 134.21, 141.47, 175.30 (ArCs), 197.63 (d, $^{1}J_{C\text{-}P}$ =177 Hz, ArCO) ppm.

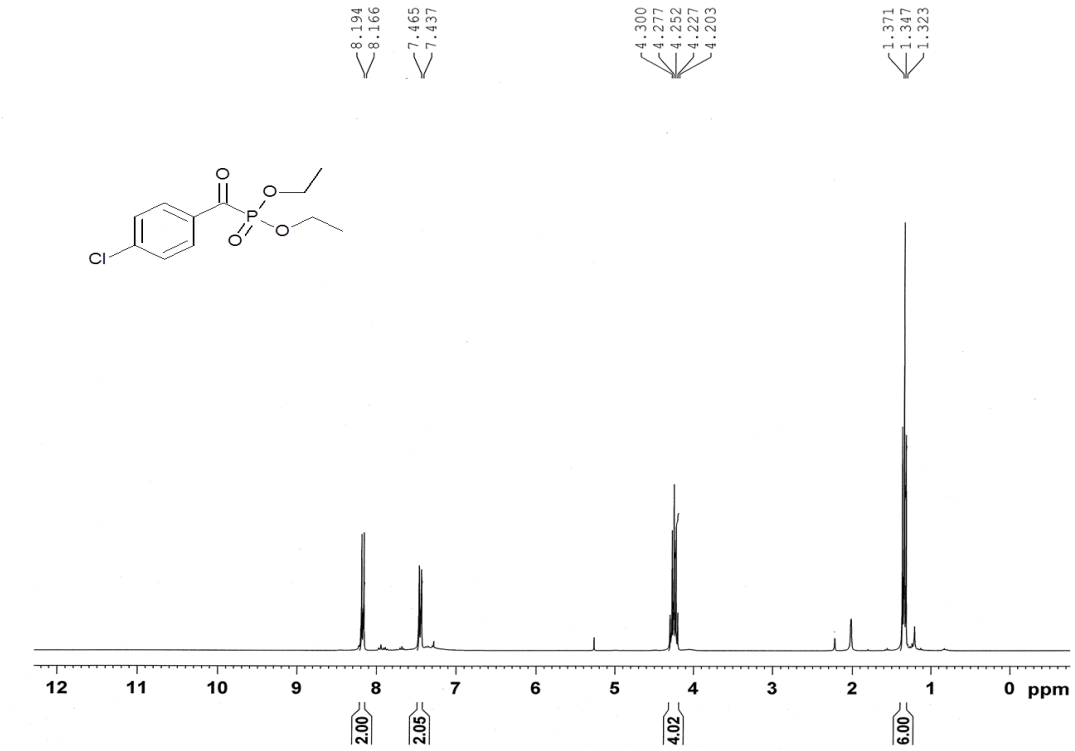



**Figure S 1: $^{1}$H - NMR of compound 2a**

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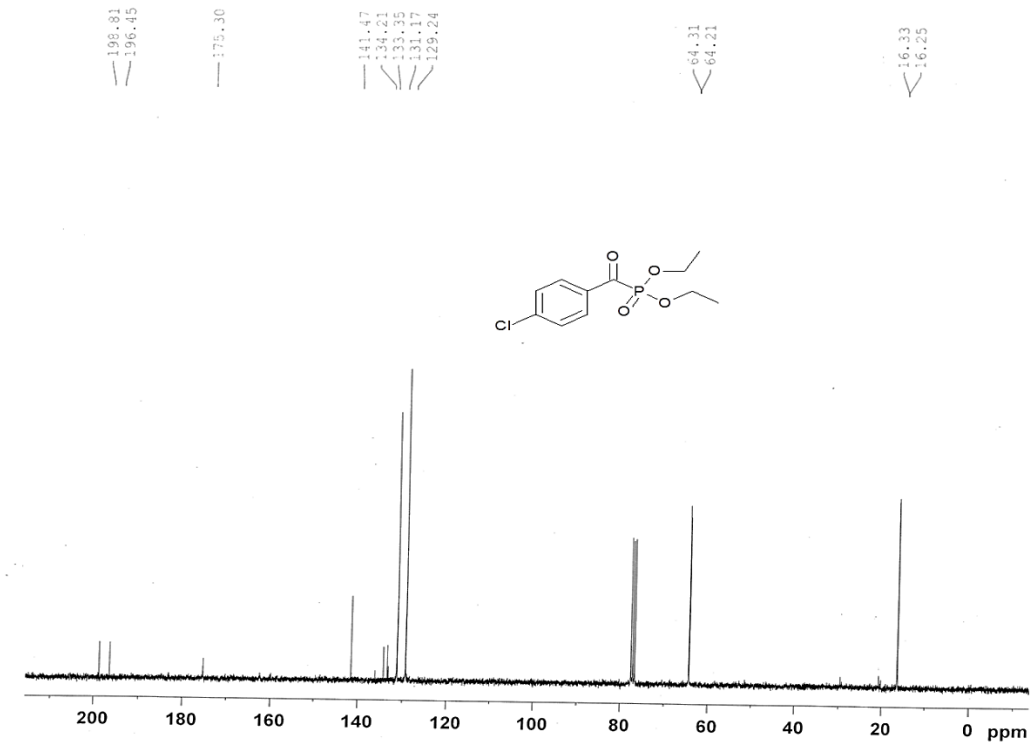



**Figure S 2: $^{13}C$ - NMR of compound 2a**

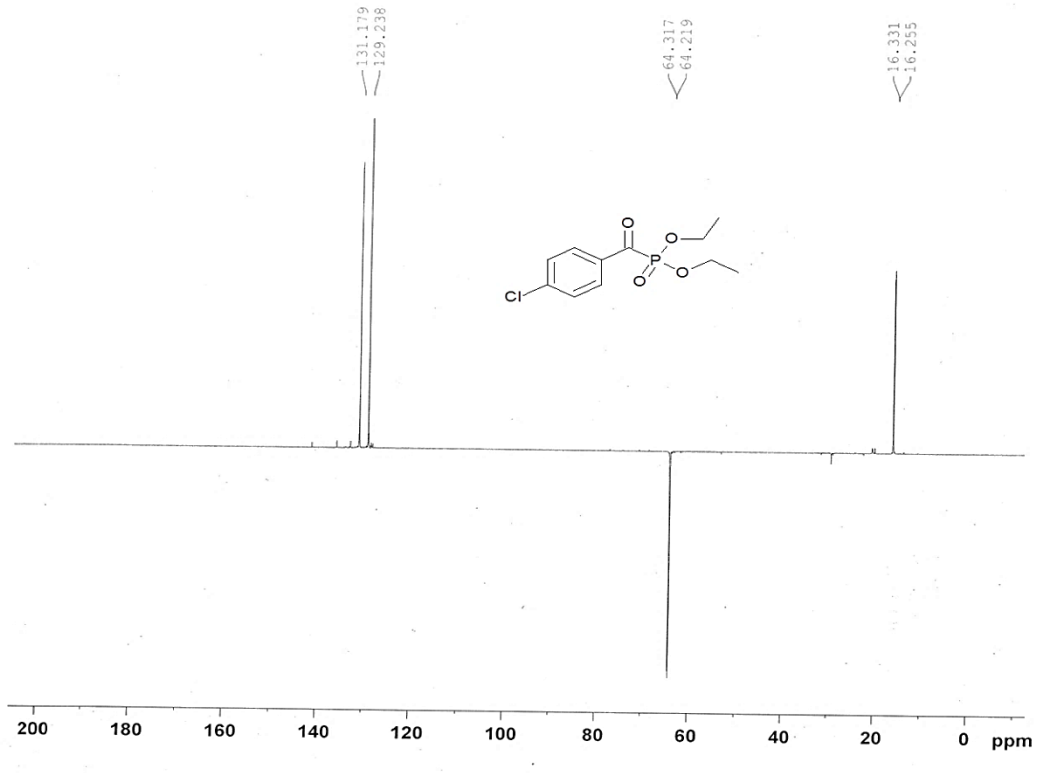



**Figure S 3: DEPT of compound 2a**


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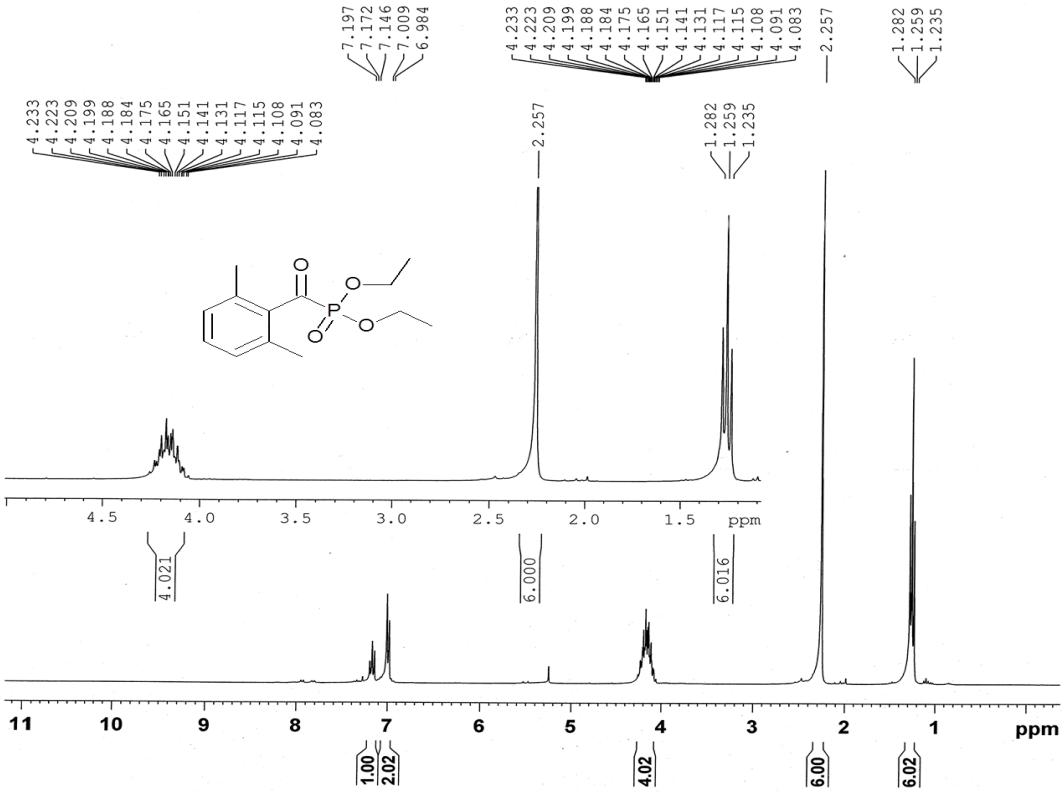



**Figure S 4: $^{1}$H - NMR of compound 2d**

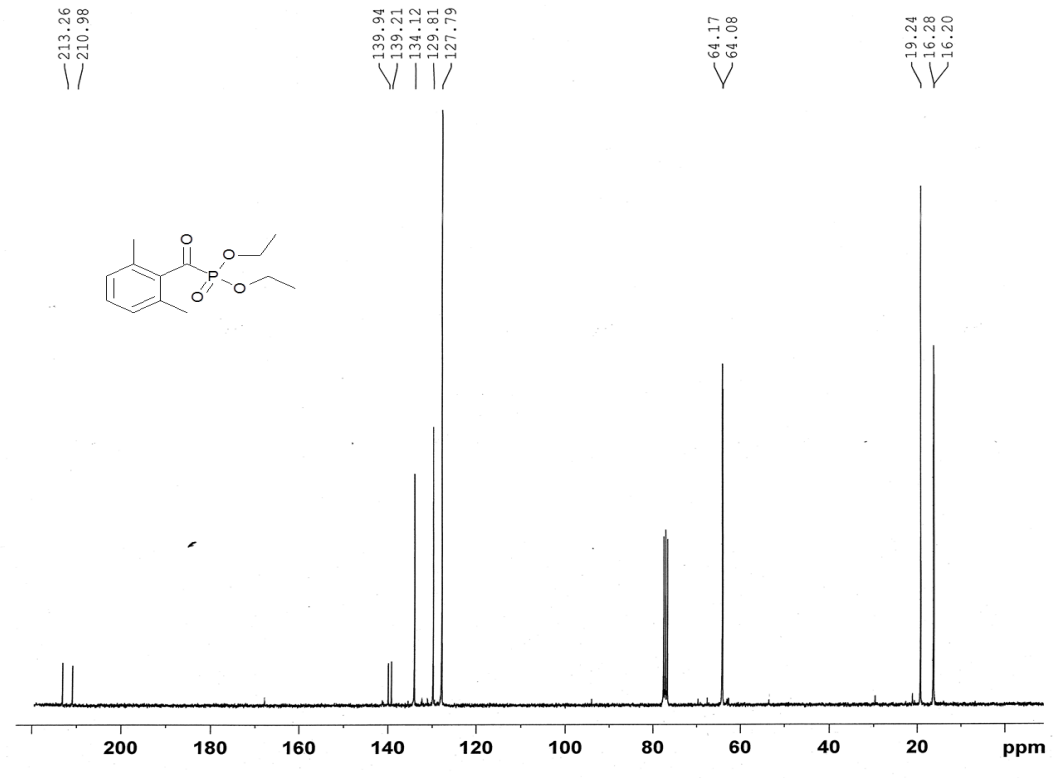



**Figure S 5: $^{13}$C - NMR of compound 2d**


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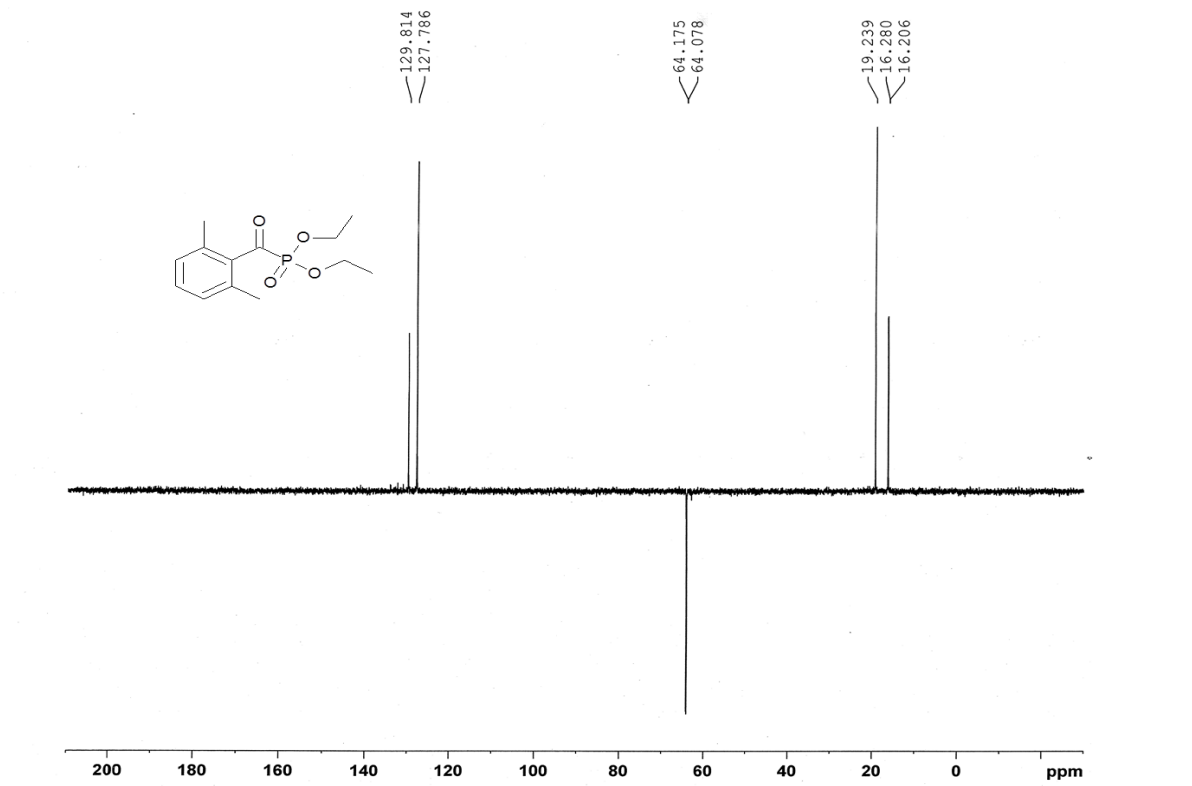



**Figure S 6: DEPT of compound 2d**

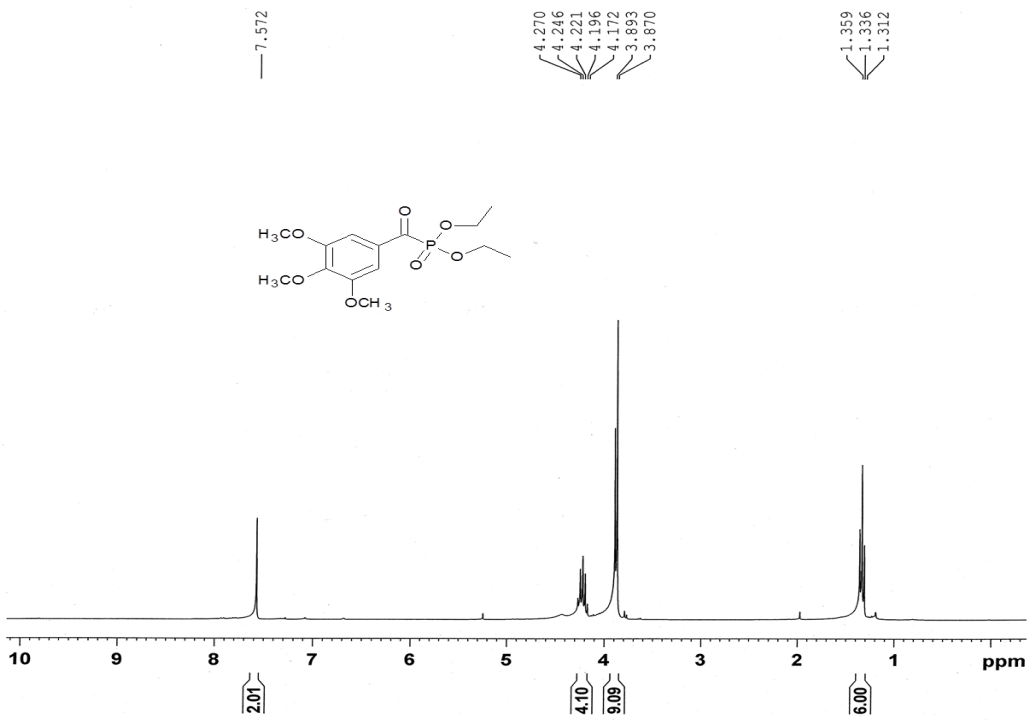



**Figure S 7: $^{1}$H - NMR of compound 2f**


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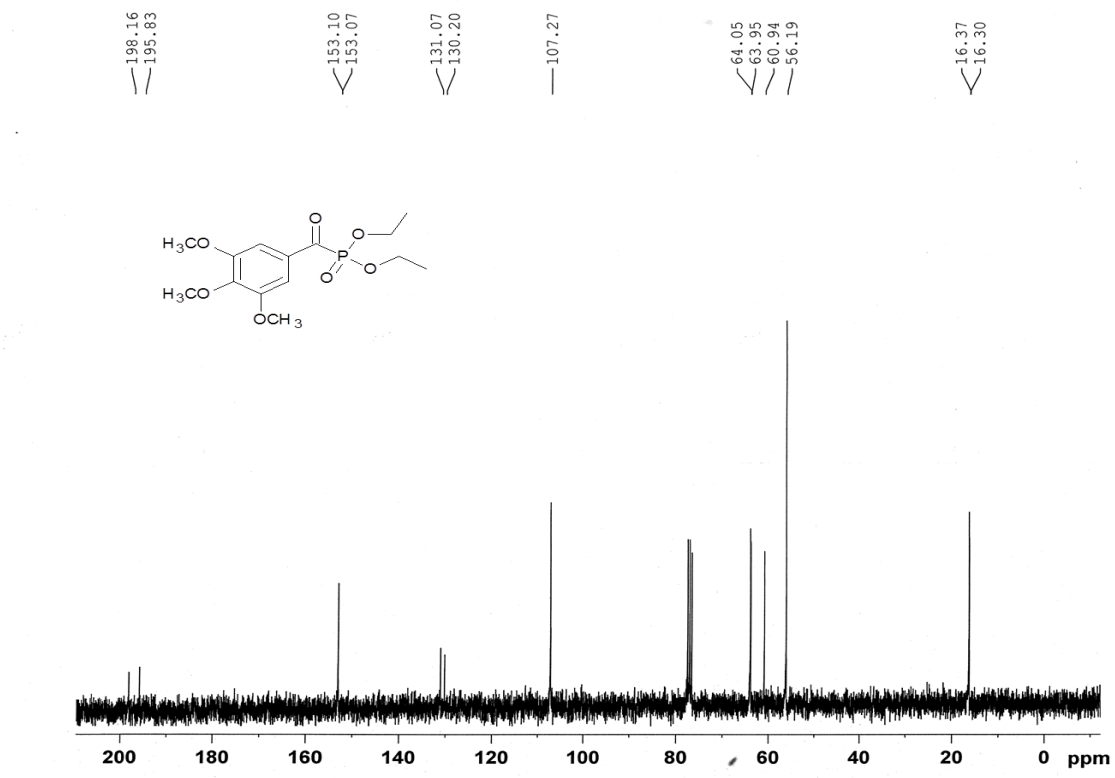



**Figure S 8: $^{13}C$ - NMR of compound 2f**

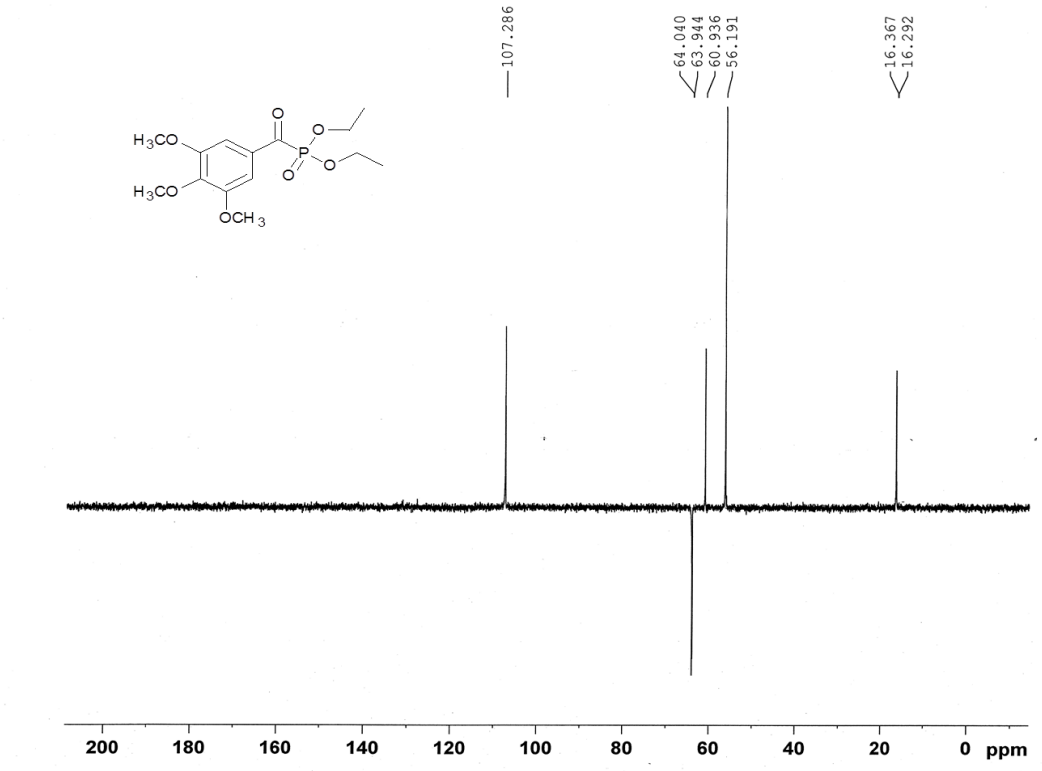



**Figure S 9: DEPT of compound 2f**


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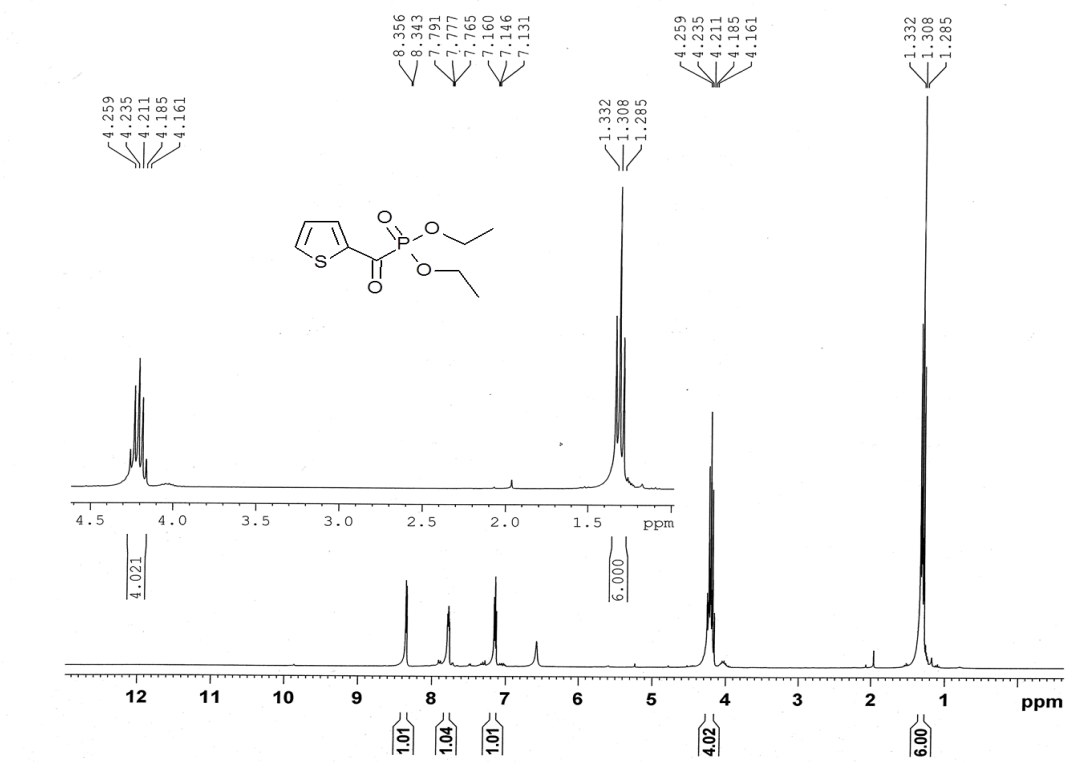



**Figure S 10: $^{1}$H - NMR of compound 2k**

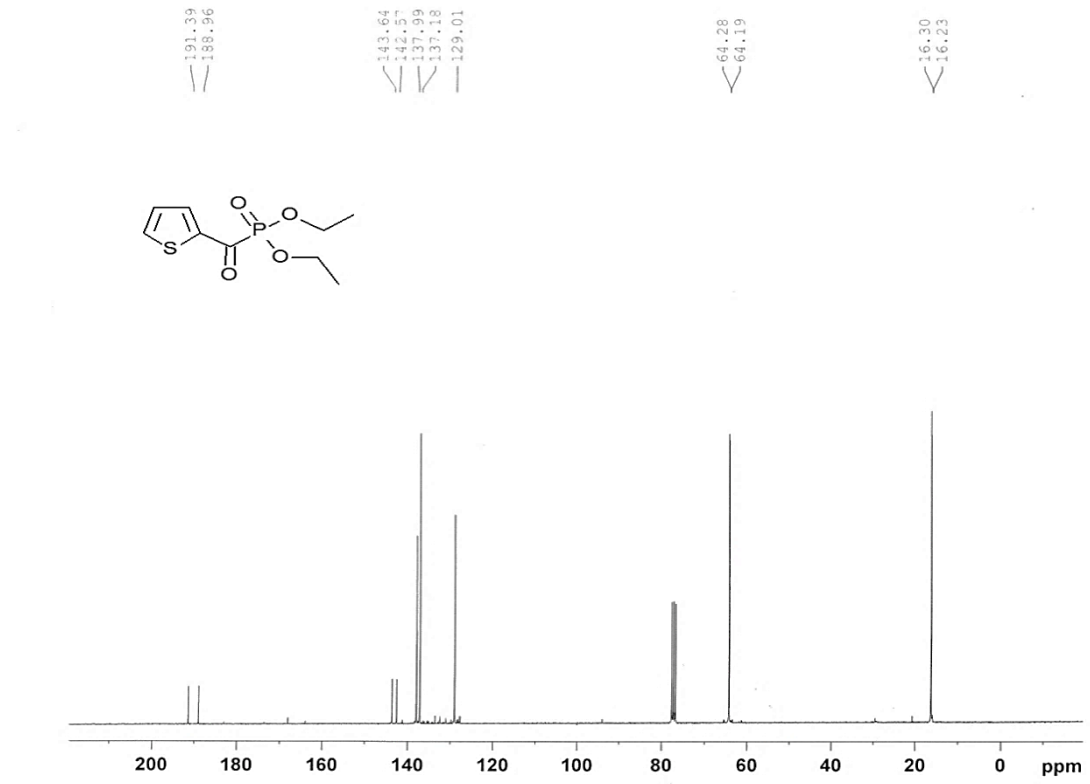



**Figure S 11: $^{13}$C - NMR of compound 2k**


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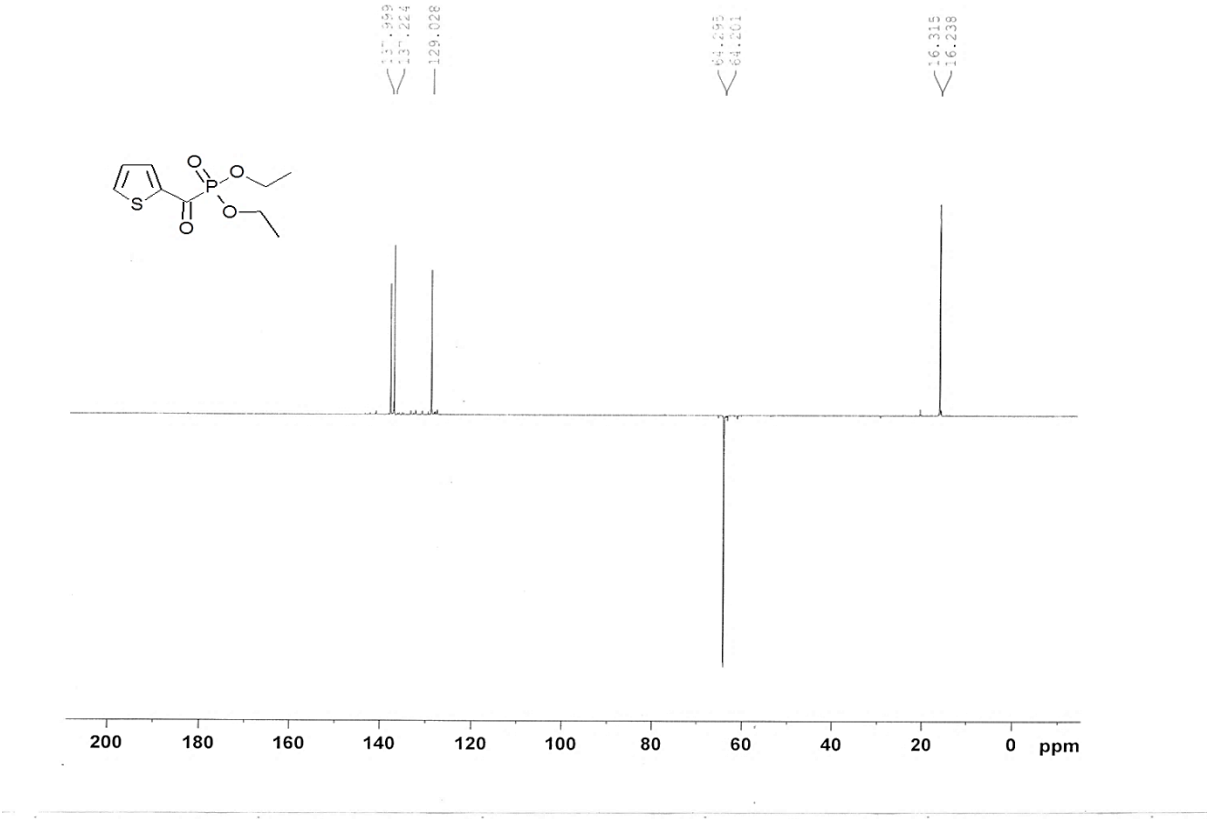



**Figure S 12: DEPT of compound 2k**

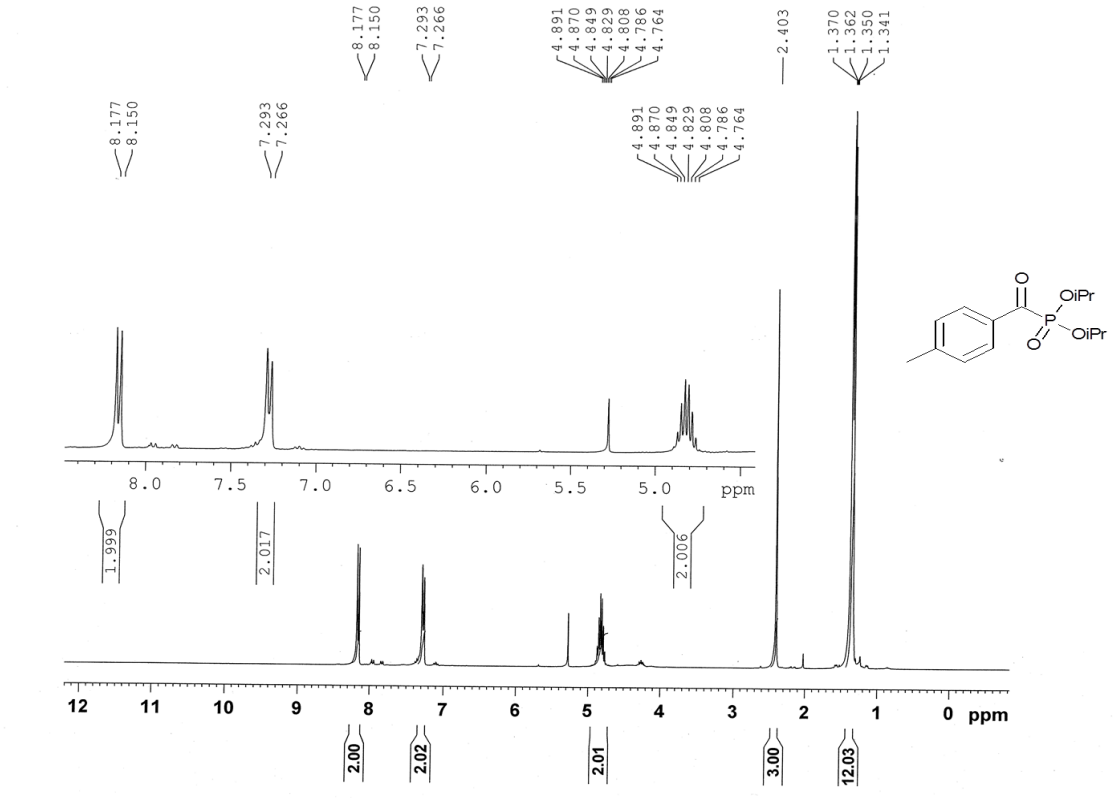



**Figure S 13: $^{1}$H - NMR of compound 2l**


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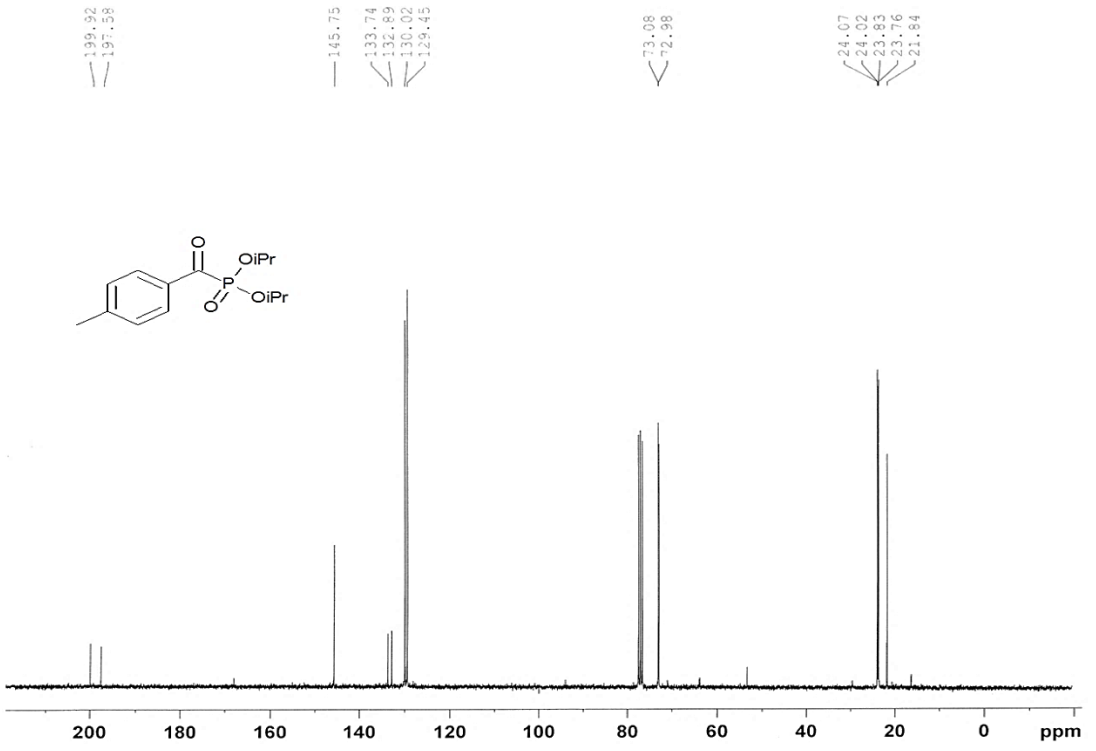



**Figure S 14: $^{13}$C - NMR of compound 2l**

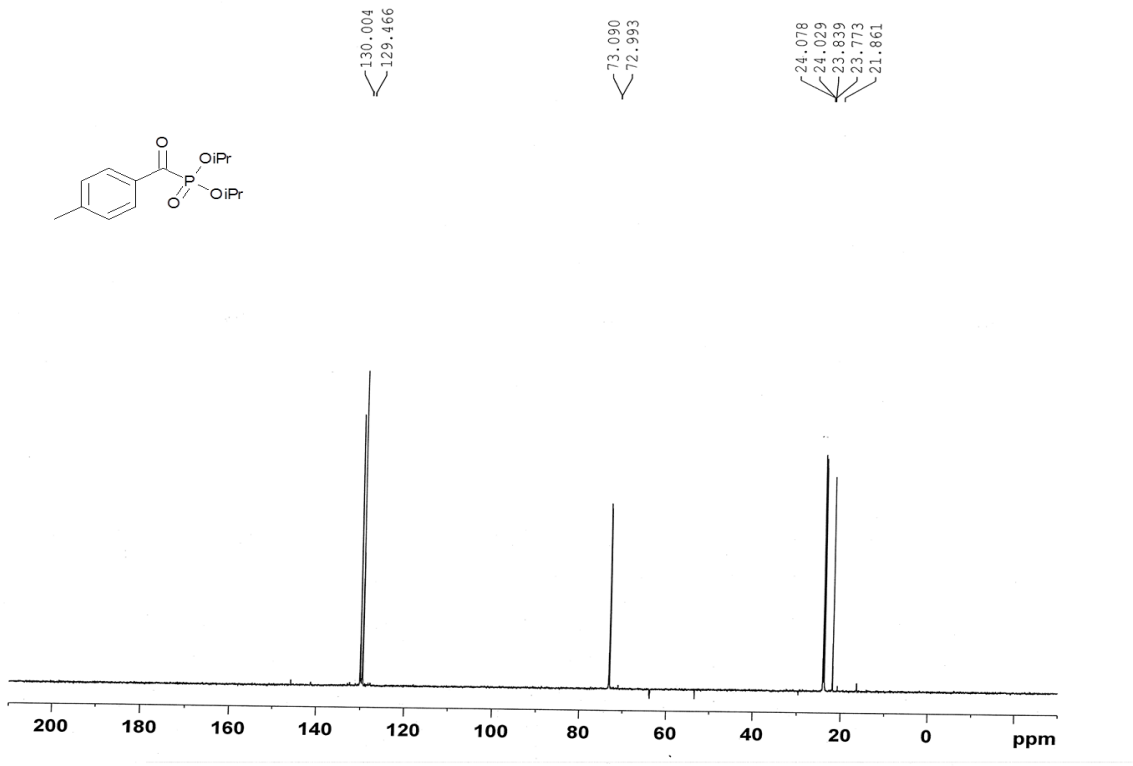



**Figure S 15: DEPT of compound 2l**


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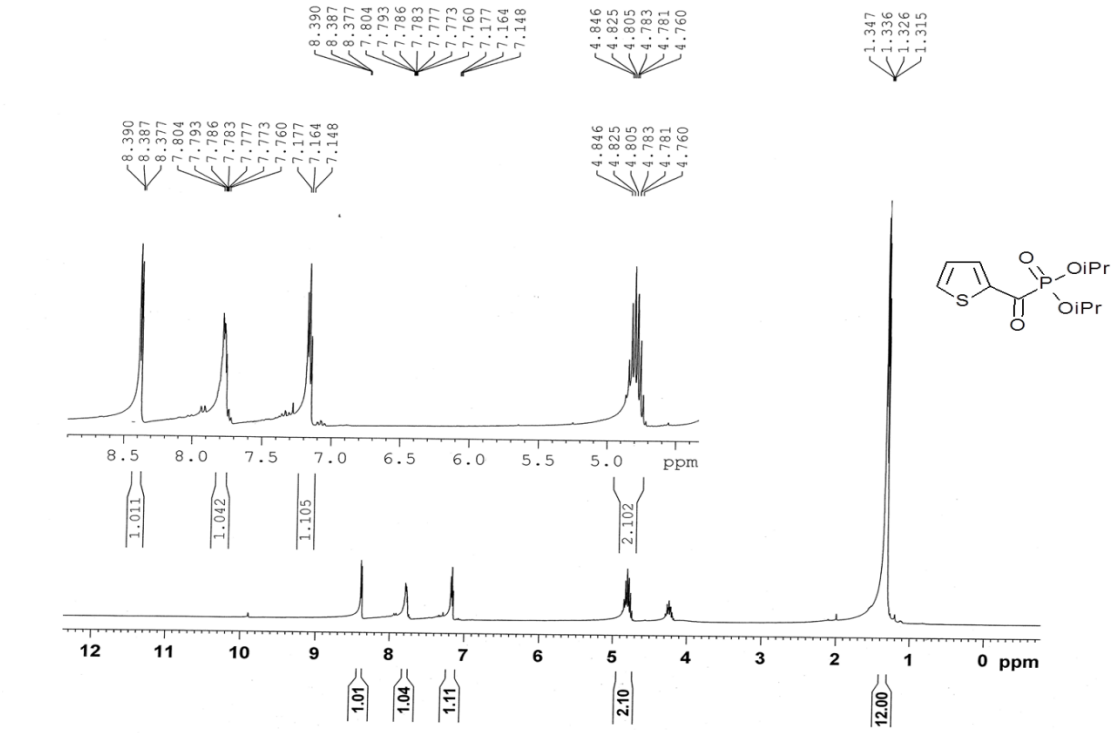



**Figure S 16: $^{1}$H - NMR of compound 2n**

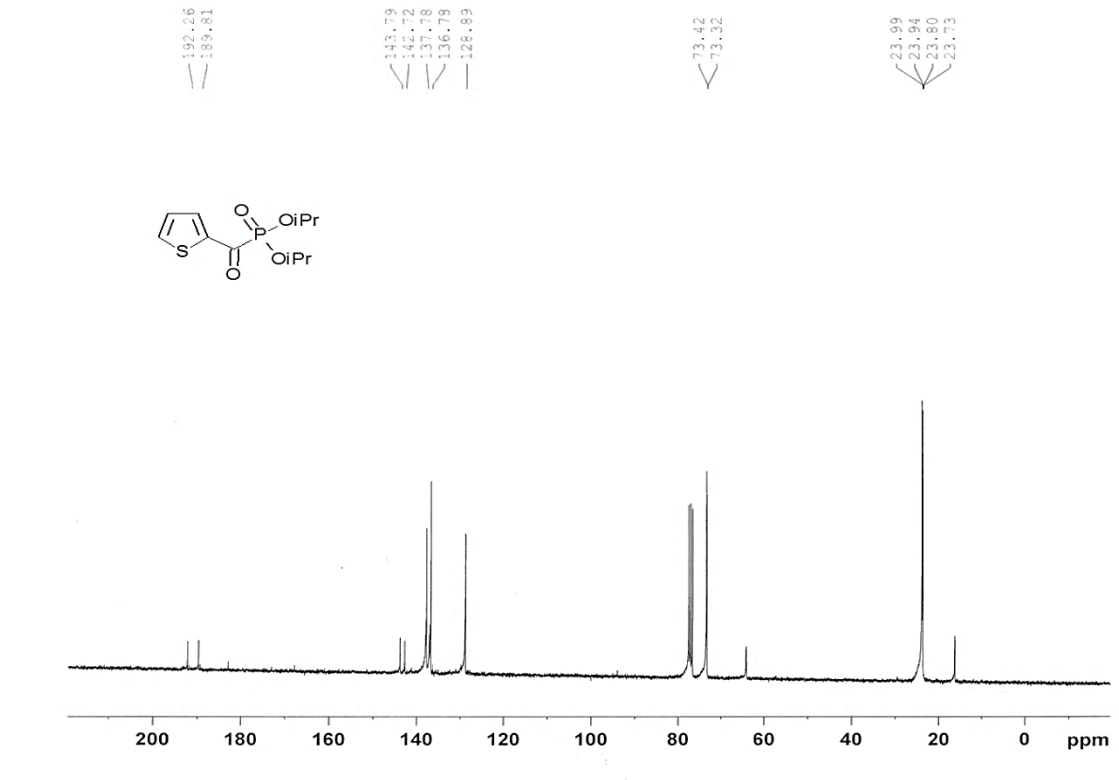



**Figure S 17: $^{13}$C - NMR of compound 2n**

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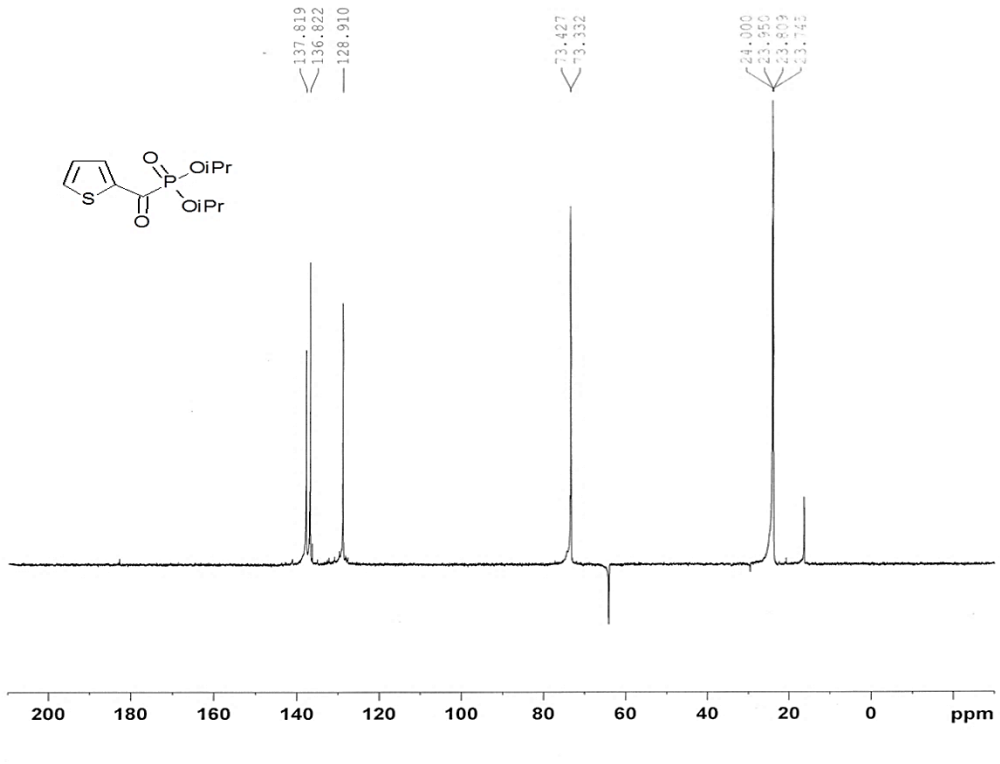



**Figure S 18: DEPT of compound 2n**


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**Spectroscopic data of α-hydroxyphosphonates**

**AHP-1 Dethyl-1-hydroxy-1-(4-chlorophenyl) methyl phosphonate**

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.23(t, *J* = 8Hz, 3H) 1.26 (t, *J* = 8Hz, 3H), 4.01- 4.08 (m, 4H ), 4.59(bs, 1H), 5.00(d, $^1J_{PH}$ 12Hz, 1H), 7.31 (d *J* = 6Hz 2H), 7.41(d, *J* = 6Hz, 2H).

**AHP-2 Dethyl-1-hydroxy-1-(4-methylphenyl) methyl phosphonate**

$^1$H NMR (200 MHz, $CDCl_3$): δ 1.22(t, *J* = 8Hz, 3H) 1.27(t, *J* = 8Hz, 3H), 2.34 (s, 3H), 2.05(bs, 1H), 3.90-4.20 (m, 4H), 4.98(d, $^1J_{PH}$ 11Hz, 1H), 7.16 (d *J* = 8Hz 2H), 7.36(dd, *J*=8Hz, 2Hz, 2H);

$^{13}$CNMR (75MHz, $CDCl_3$):δ 16.18, 21.04, 63.11, 70.37(d, $^1J_{PC}$ = 169.5Hz), 127.02, 128.72, 133.70, 137.52

**AHP-3 Dethyl-1-hydroxy-1-(4-isopropylphenyl) methyl phosphonate**

$^1$H NMR (300 MHz, $CDCl_3$): δ 1.17-1.31(m, 6H), 2.89 (septet, *J*=6.9Hz, 1H ), 3.96-4.08(m, 4H), 4.98(d, $^1J_{PH}$ 10.5Hz, 1H), 5.41(bs, 1H), 7.19(d, *J* = 7.8Hz, 2H);7.38(d, *J* = 7.8Hz,2H);

$^{13}$CNMR (75MHz, $CDCl_3$): δ 16.20, 23.59, 23.82, 33.69, 63.13(d, $^2J_{PC}$ = 7.0Hz), 63.45(d, $^2J_{PC}$ = 7.0Hz), 126.20, 127.06, 133.78, 148.62

**AHP-4 Diethyl [(2,6-dimethylphenyl)(hydroxy)methyl]phosphonate:** 1H -NMR (300 MHz, CDCl3): δ 1.22 (t, J = 7.2 Hz, 3H, OCH2CH3), 1.30 (t, J = 7.2 Hz, 3H, OCH2CH3), 2.50 (s, 6H, 2 x Ar-CH3), 3.68 (s, CHOH), 3.92 – 4.15 (m, 4H, 2 x OCH2CH3), 5.51 (d, J = 15.9 Hz, CH-P), 6.98 – 7.10 (m, 3H, ArHs); 13C-NMR (75 MHz, CDCl3): δ 16.18 (d, 3JC-P = 6 Hz, OCH2CH3), 16.40 (d, 3JC-P = 6 Hz, OCH2CH3), 21.12 (2 x CH3), 62.64 (d, 2JC-P = 7.5 Hz, OCH2CH3), 63.05 (d, 2JC-P = 7.5 Hz, OCH2CH3), 68.78 (d, 1JC-P = 158.25 Hz, ArCH), 127.81, 127.86, 129.39, 132.43, 137.77 (ArCs) ppm.AHP-5 5.

**AHP-7 Dethyl-1-hydroxy-1-(3-nitrophenyl) methyl phosphonate**

$^1$H NMR (200 MHz, $CDCl_3$): δ 1.25 (t, *J* = 8Hz, 3H) 1.28 (t, *J* = 8Hz, 3H), 4.00-4.25 (m, 4H ), 5.16 (dd, $^1J_{PH}$ =12Hz, $^1J_{H\text{-}OH}$ = 6Hz, 1H), 5.50 (t, *J* = 6Hz, 1H), 7.49 (t, *J* = 8Hz, 1H), 7.80 (d, *J* = 8Hz, 1H), 8.14 (d, *J* = 8Hz, 1H), 8.40(bs, 1H);

**AHP-8 Dethyl-1-hydroxy-1-(cinnamyl) methyl phosphonate**


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$^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.20-1.40(2 X t, 6H), 4.0-4.25(m 1H), 4.5(bs, 1H), 4.68-4.78 6.26-6.40(m, 1H), 6.75-6.87(m, 1H), 7.28-7.38(m, 5H);$^{13}$CNMR (75MHz, CDCl3): δ 53.47, 53.61, 53.80, 67.29, 70.52, 123.67, 126.47, 128.37, 132.10, 132.37, 136.15;

**AHP-9 Diethyl-1-hydroxy-1-(4-benzloxyphenyl) methyl phosphonate**

$^{1}$H NMR (200 MHz, $CDCl_3$): δ 1.21(t, *J* = 8Hz, 3H) 1.26 (t, *J* = 8Hz, 3H), 3.9- 4.2 (m, 4H ), 4.95 (d, $^{1}J_{PH}$ 10Hz, 1H), 5.06(s, 2H), 6.96 (d, *J* = 8Hz, 2H), 7.31(m, 5H), 7.39 (d, *J* = 8Hz, 1H),

$^{13}$CNMR (50 MHz, $CDCl_3$): 16.20, 63.02, 69.80, 70.08 (d, $^{1}J_{PH}$ = 160.5Hz), 114.44, 127.31, 128.40, 127.87, 129.10, 136.74, 158.47;

**AHP-10 Dethyl-1-hydroxy-1-(4-allyloxyphenyl) methyl phosphonate**

$^{1}$H NMR (200 MHz, $CDCl_3$): δ 1.20(t, *J* = 8Hz, 3H) 1.26 (t, *J* = 8Hz, 3H), 2.2(bs, 1H), 3.9- 4.2 (m, 4H ), 4.52 (d, *J* = 6Hz, 2H), 4.93 (d, $^{1}J_{PH}$ = 10Hz, 1H), 5.30 (d, *J* = 9Hz, 1H), 5.37(dd, *J* = 16Hz, 2Hz, 2H), 5.9-6.3(m, 1H), 7.00 (d, *J* = 8Hz, 2H), 7.39 (d, *J* = 8Hz, 2H), $^{13}$CNMR (50 MHz, $CDCl_3$): 16.20, 62.80, 68.64, 70.18(d, $^{1}J_{PH}$ = 154Hz), 114.32, 117.54, 128.32, 128.78, 130.04, 158.33

**AHP-12 Diethyl [hydroxy(thiophen-2-yl)methyl]phosphonate** $^{1}$H -NMR (300 MHz, $CDCl_3$): δ 1.17 – 1.24 (m, 6H, 2 x $OCH_2CH_3$ ), 3.99 - 4.09 (m, 4H, 2 x $OCH_2CH_3$), 5.20 (d, J = 11.4 Hz, CH - P), 5.62 (s, OH), 6.92 (t, J = 4.8 Hz, 1H, ArH), 7.01 (t, J = 3.0 Hz, 1H, ArH), 7.22 (d, J = 5.1 Hz, 1H, ArH); $^{13}$C -NMR (75 MHz, $CDCl_3$): δ 16.30 (d, 3JC-P = 5. 2 Hz, 2 x $OCH_2CH_3$), 63.40 (d, 2JC-P = 7.5 Hz, $OCH_2CH_3$), 63.74 (d, 2JC-P = 6.75 Hz, $OCH_2CH_3$), 66.70 (d, 1JC-P = 168.00 Hz, ArCH), 125.46, 125.88, 126.67, 139.93 (ArCs) ppm.

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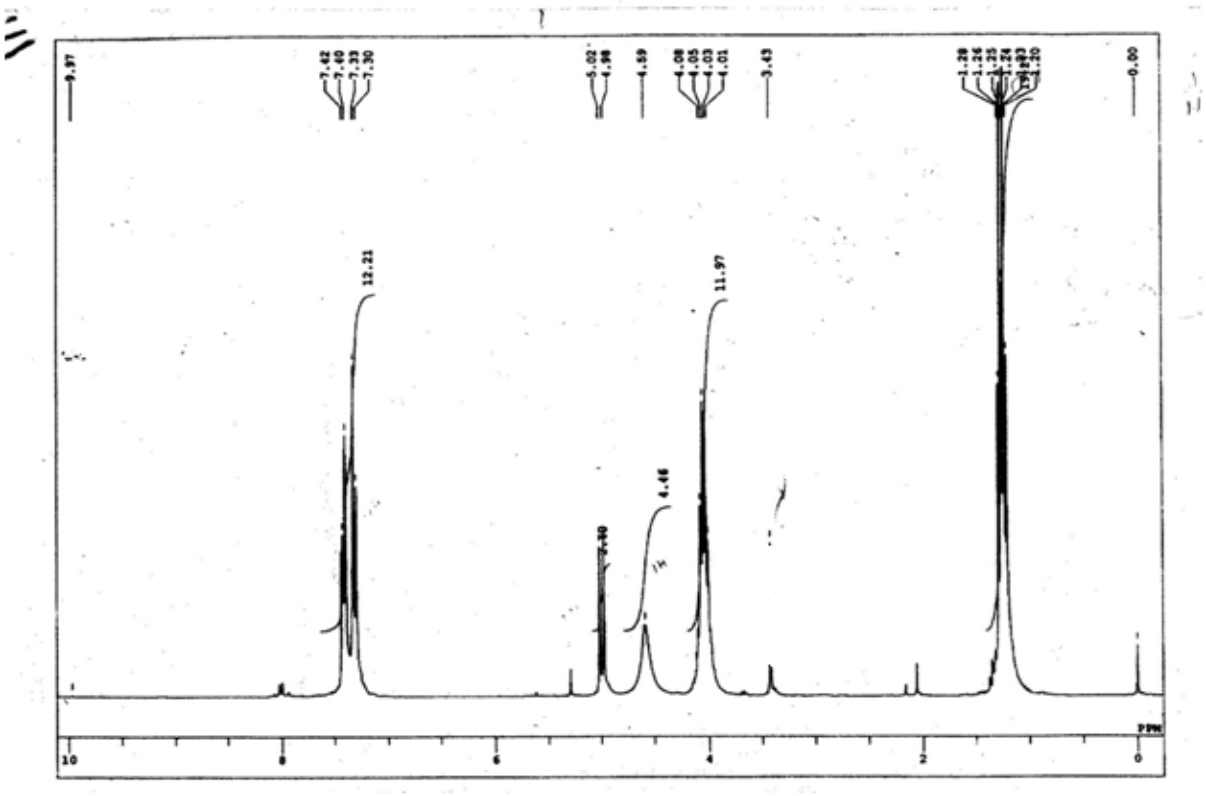
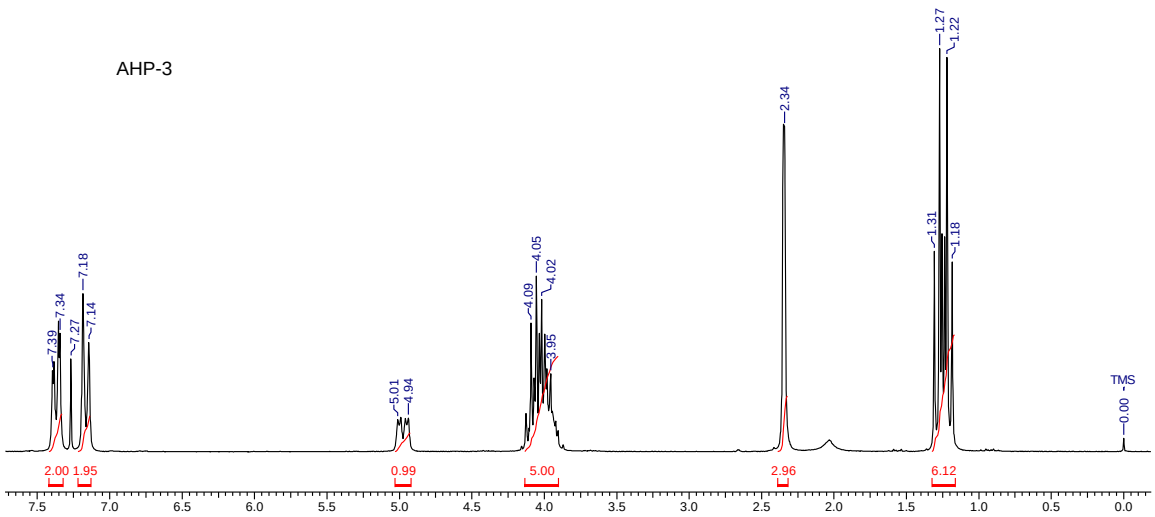



**Figure AHP-1:PMR Spectrum α-hydroxyphosphonate-1**

21 May 2007

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** 7.9167 | ***Comment*** P SANE | ***Date*** 15/05/2007 18:40:10 | | | ***Frequency (MHz)*** 200.13 |
| ***Nucleus*** 1H | ***Original Points Count*** 32768 | ***Points Count*** 32768 | ***Sweep Width (Hz)*** 4139.07 | | ***Temperature (grad C)*** 0.000 |



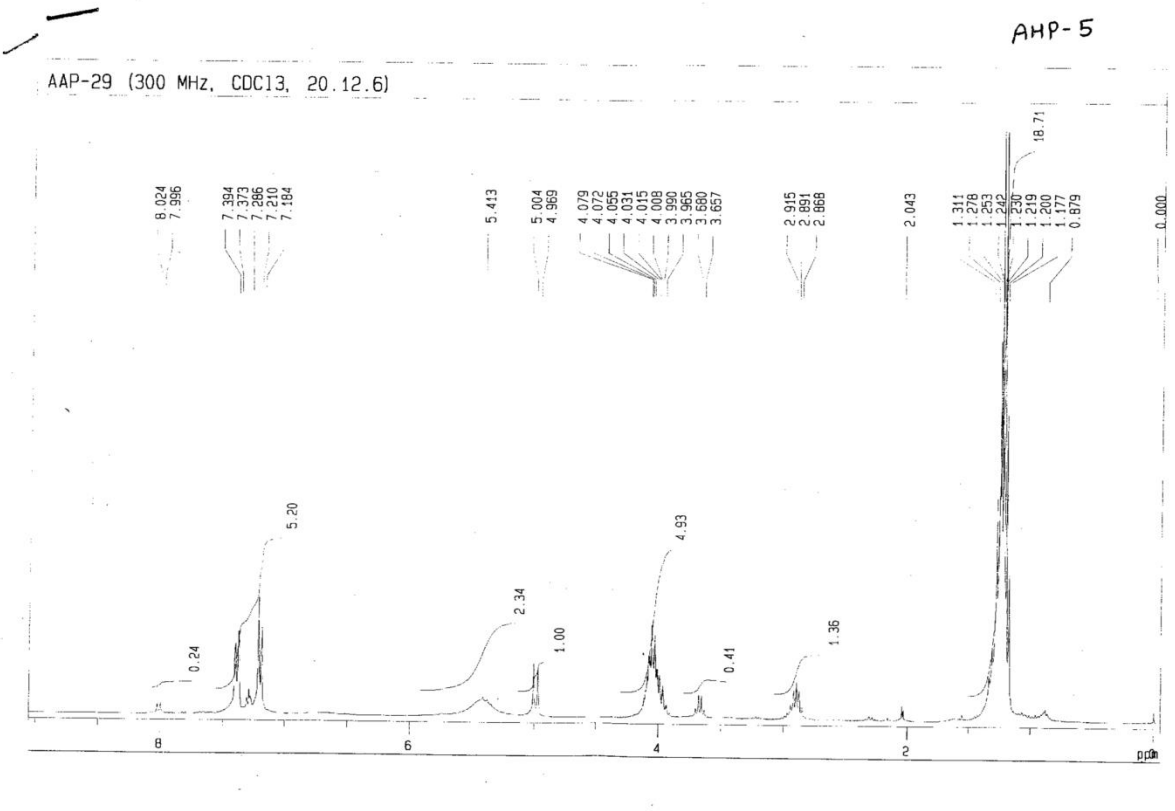

| No. | (ppm) | Height |
|---|---|---|
| 1 | 0.00 | 0.033 |
| 2 | 1.18 | 0.471 |
| 3 | 1.22 | 0.979 |
| 4 | 1.27 | 1.000 |
| 5 | 1.31 | 0.498 |
| 6 | 2.34 | 0.807 |
| 7 | 3.95 | 0.193 |
| 8 | 4.02 | 0.378 |
| 9 | 4.05 | 0.436 |

| No. | (ppm) | Height |
|---|---|---|
| 10 | 4.09 | 0.319 |
| 11 | 4.94 | 0.083 |
| 12 | 5.01 | 0.079 |
| 13 | 7.14 | 0.271 |
| 14 | 7.18 | 0.392 |
| 15 | 7.27 | 0.230 |
| 16 | 7.34 | 0.294 |
| 17 | 7.39 | 0.200 |

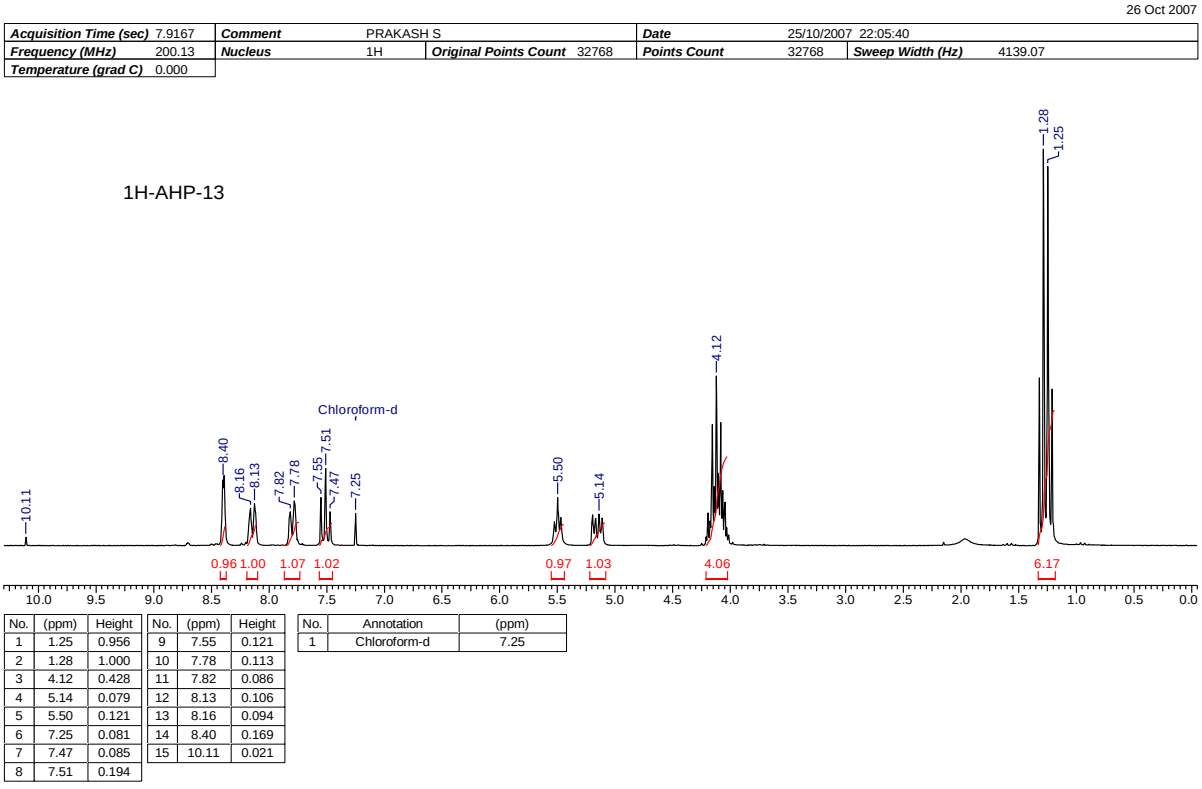
| No. | Annotation | (ppm) |
|---|---|---|
| 1 | TMS | 0.00 |

**Figure AHP-2: PMR Spectrum α-hydroxyphosphonate-2**


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## Figure AHP-3: PMR Spectrum α-hydroxyphosphonate-3



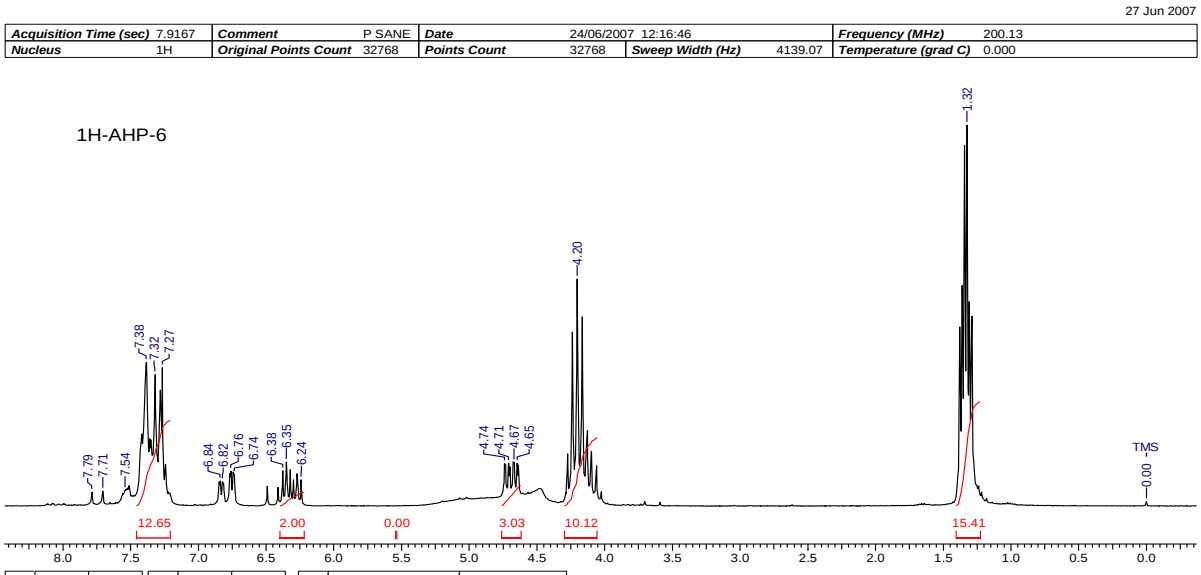

| No. | (ppm) | Height |
|---|---|---|
| 1 | 1.25 | 0.956 |
| 2 | 1.28 | 1.000 |
| 3 | 4.12 | 0.428 |
| 4 | 5.14 | 0.079 |
| 5 | 5.50 | 0.121 |
| 6 | 7.25 | 0.081 |
| 7 | 7.47 | 0.085 |
| 8 | 7.51 | 0.194 |

| No. | (ppm) | Height |
|---|---|---|
| 9 | 7.55 | 0.121 |
| 10 | 7.78 | 0.113 |
| 11 | 7.82 | 0.086 |
| 12 | 8.13 | 0.106 |
| 13 | 8.16 | 0.094 |
| 14 | 8.40 | 0.169 |
| 15 | 10.11 | 0.021 |

| No. | Annotation | (ppm) |
|---|---|---|
| 1 | Chloroform-d | 7.25 |

## Figure AHP-7: PMR Spectrum α-hydroxyphosphonate-7


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| No. | (ppm) | Height |
|---|---|---|
| 1 | 0.00 | 0.012 |
| 2 | 1.32 | 1.000 |
| 3 | 4.20 | 0.596 |
| 4 | 4.65 | 0.112 |
| 5 | 4.67 | 0.114 |
| 6 | 4.71 | 0.112 |
| 7 | 4.74 | 0.111 |
| 8 | 6.24 | 0.068 |
| 9 | 6.35 | 0.115 |
| 10 | 6.38 | 0.092 |

| No. | (ppm) | Height |
|---|---|---|
| 11 | 6.74 | 0.083 |
| 12 | 6.76 | 0.091 |
| 13 | 6.82 | 0.064 |
| 14 | 6.84 | 0.066 |
| 15 | 7.27 | 0.363 |
| 16 | 7.32 | 0.345 |
| 17 | 7.38 | 0.377 |
| 18 | 7.54 | 0.041 |
| 19 | 7.71 | 0.039 |
| 20 | 7.79 | 0.036 |

| No. | Annotation | (ppm) |
|---|---|---|
| 1 | TMS | 0.00 |

**Figure AHP-8: PMR Spectrum α-hydroxyphosphonate-8**

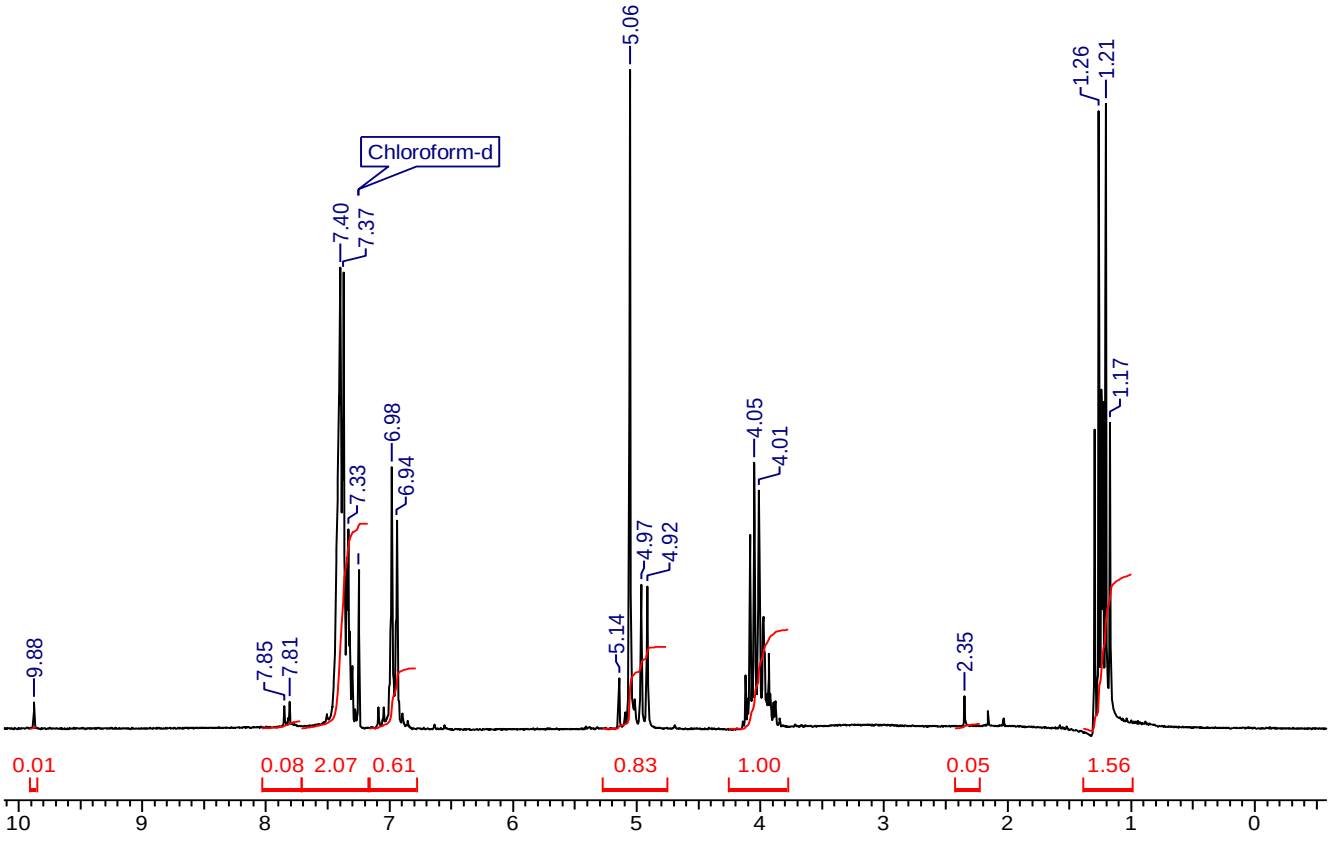



**Figure AHP-9: PMR Spectrum α-hydroxyphosphonate-9**


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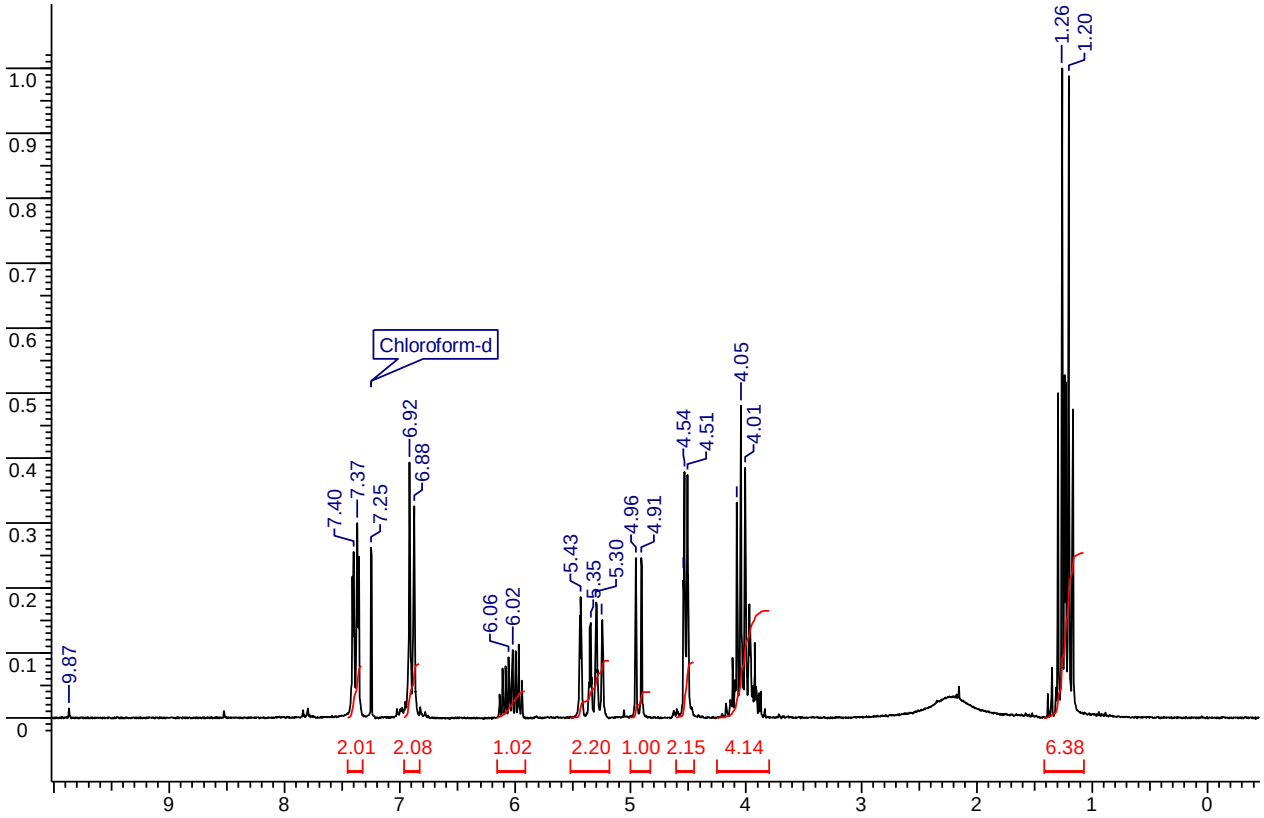



**Figure AHP-10: PMR Spectrum α-hydroxyphosphonate-10**

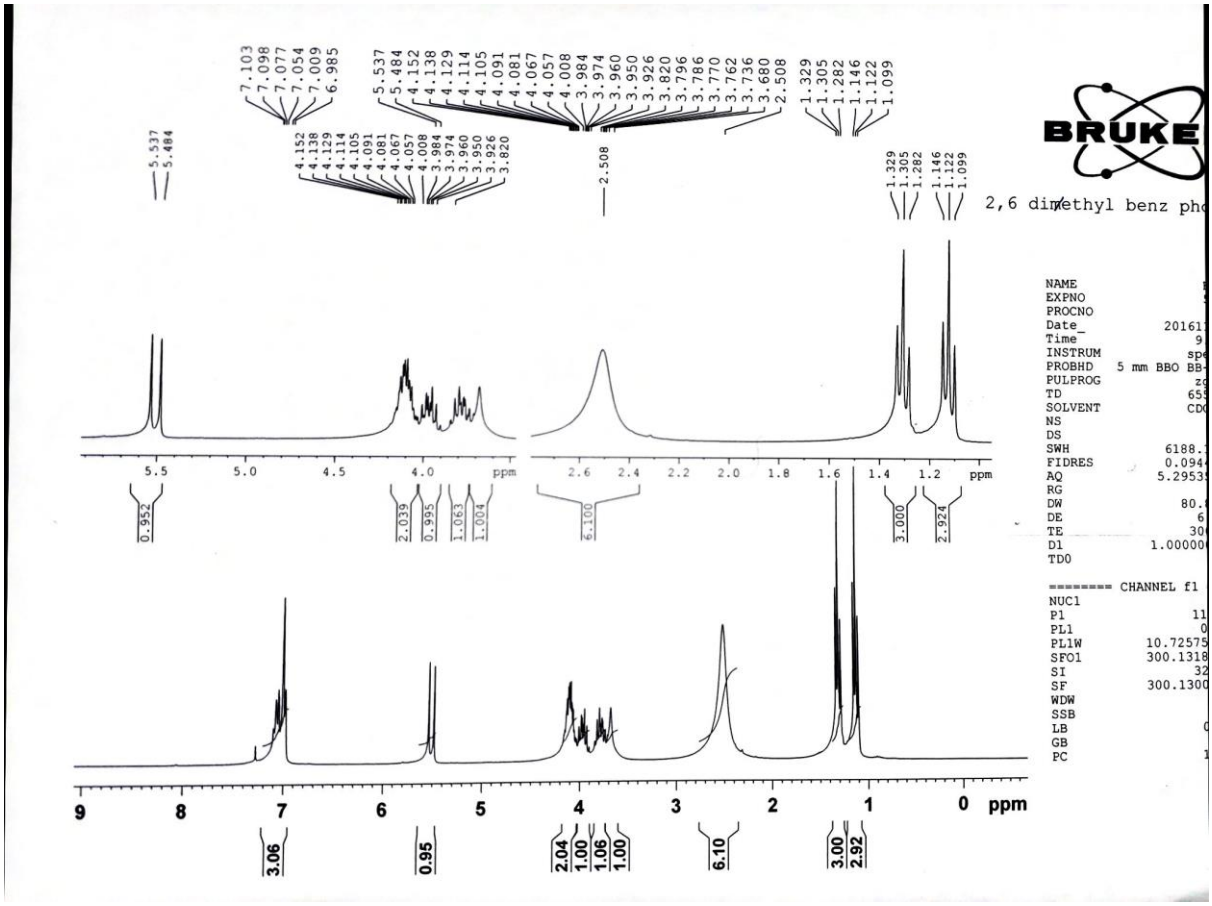



**Figure AHP-13: PMR Spectrum α-hydroxyphosphonate-13**


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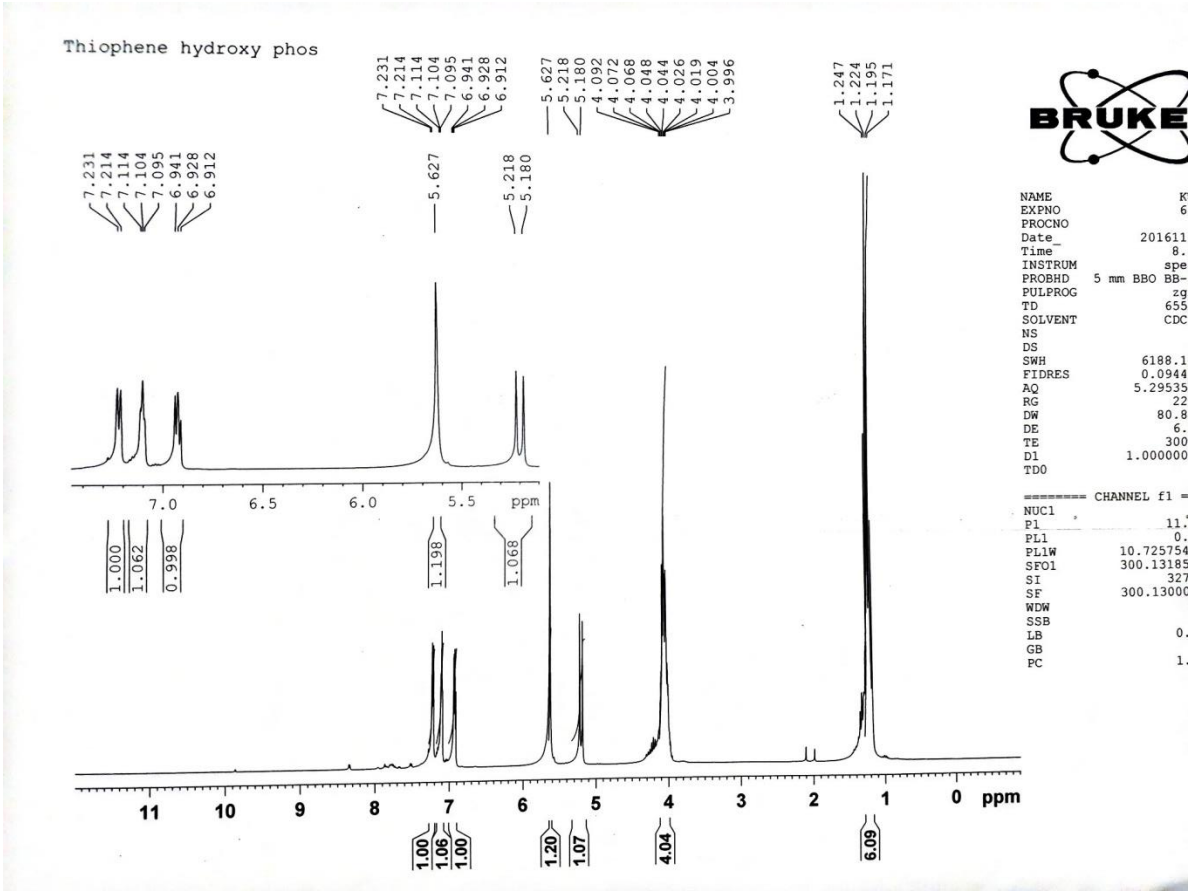



**Figure AHP-14: PMR Spectrum α-hydroxyphosphonate-14**


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