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.

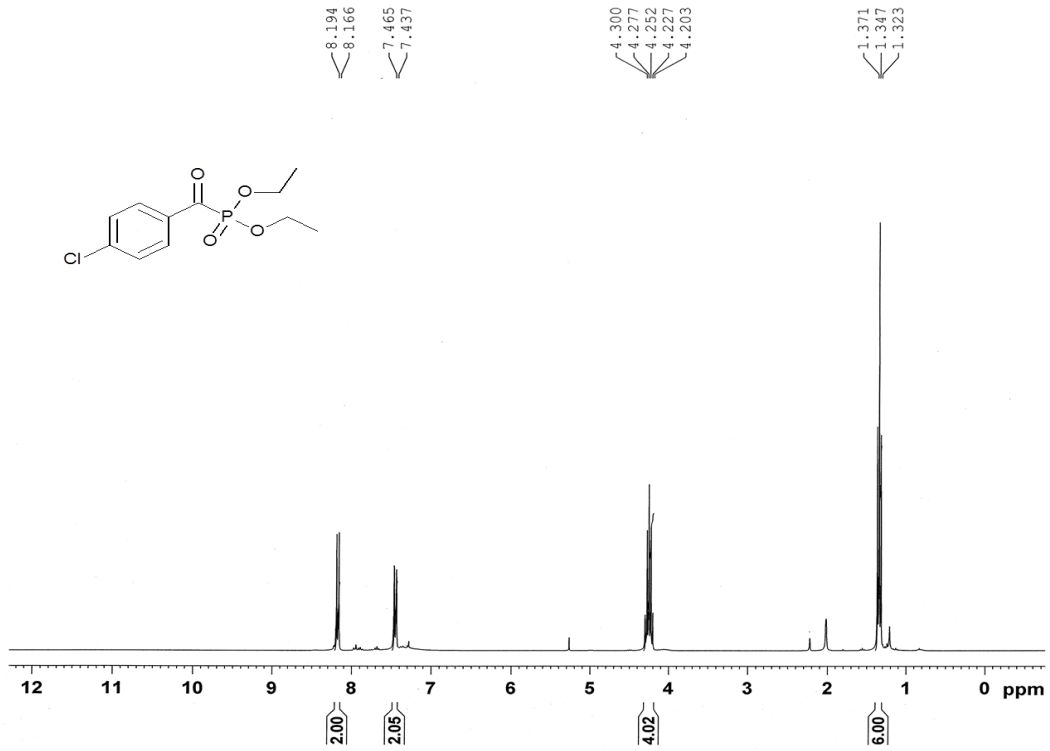

Figure S 1: ^{1}H - NMR of compound 2a

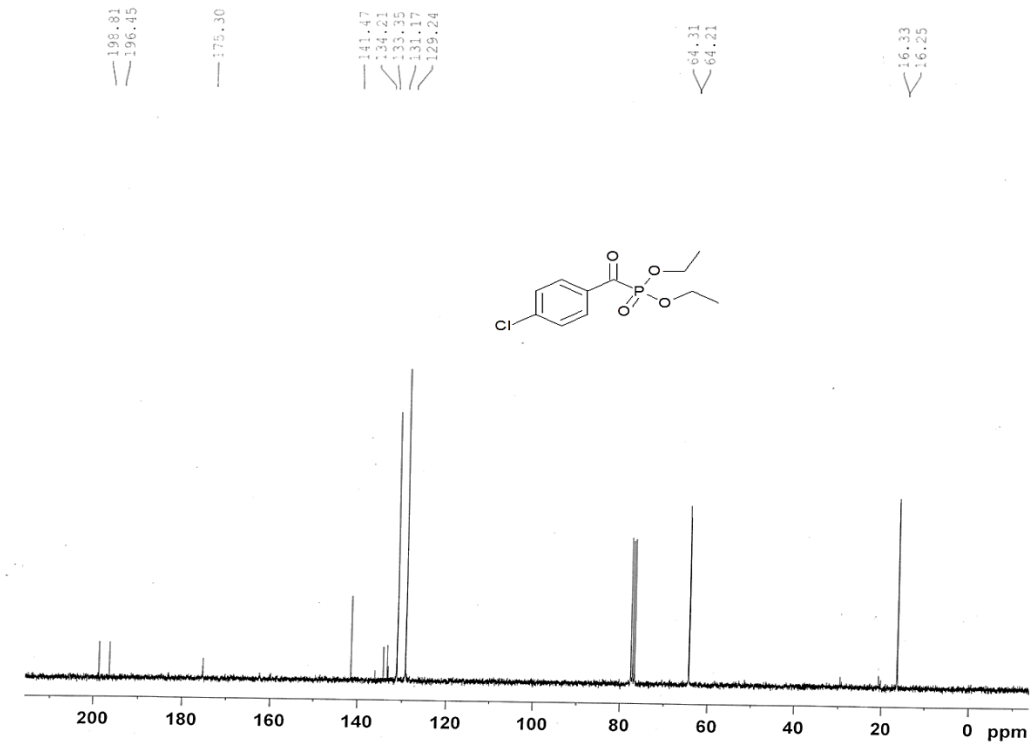

Figure S 2: ^{13}C - NMR of compound 2a

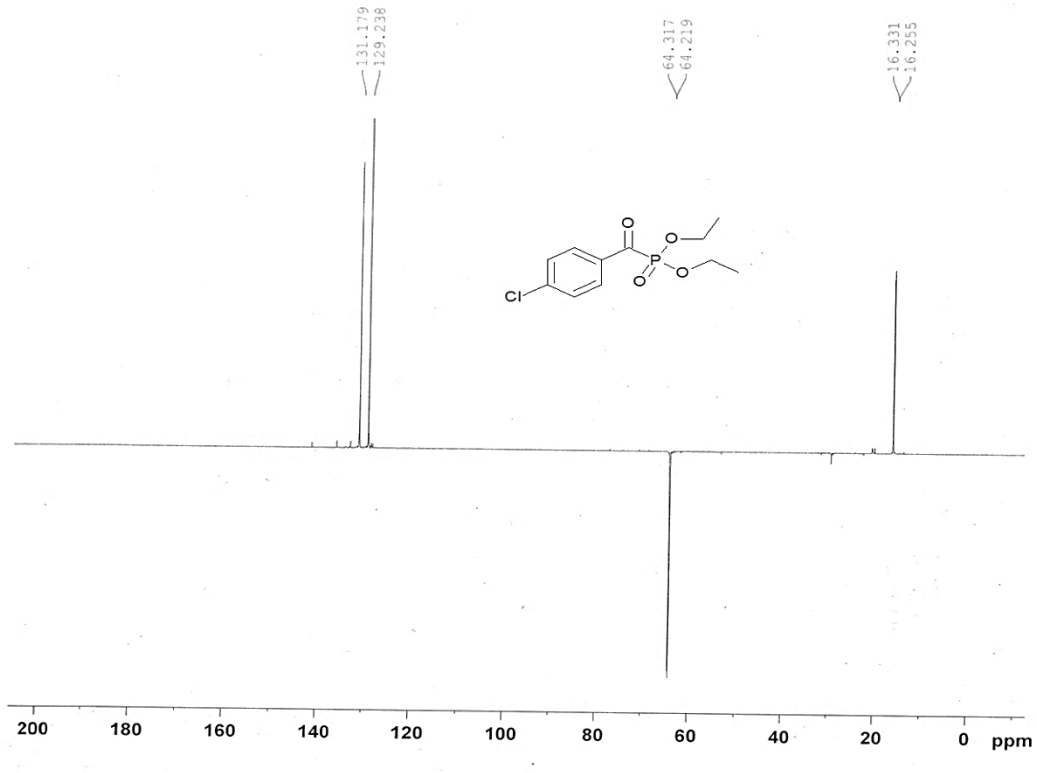

Figure S 3: DEPT of compound 2a

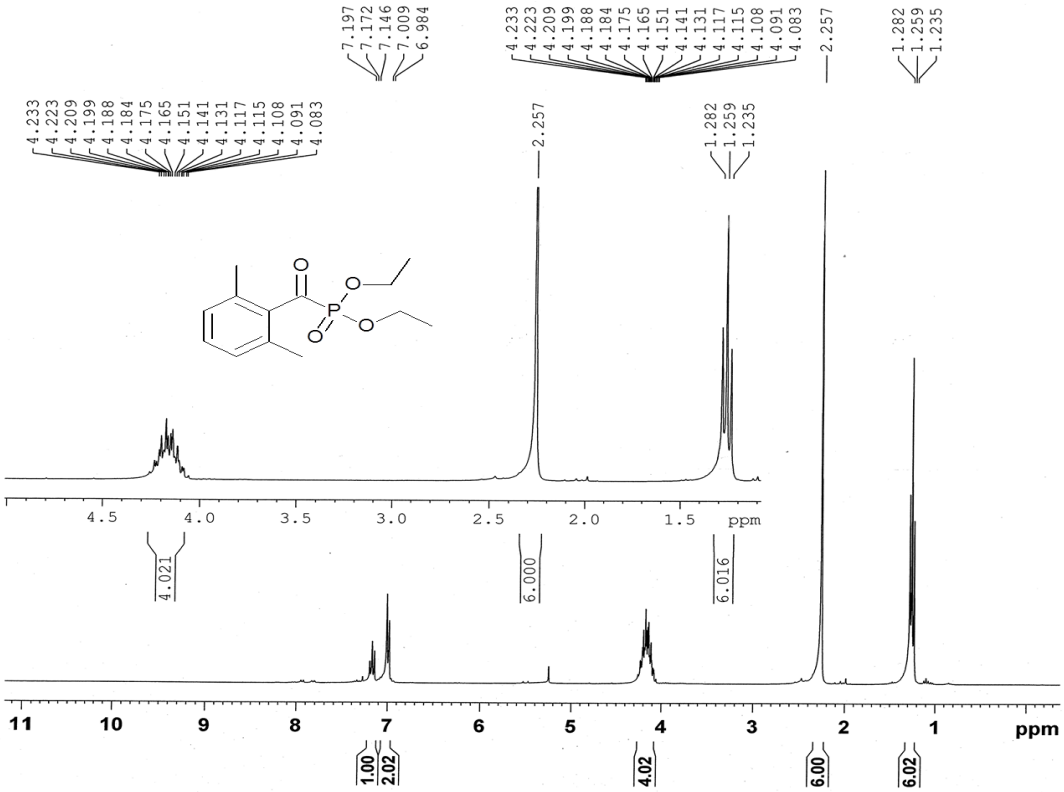

Figure S 4: ^{1}H - NMR of compound 2d

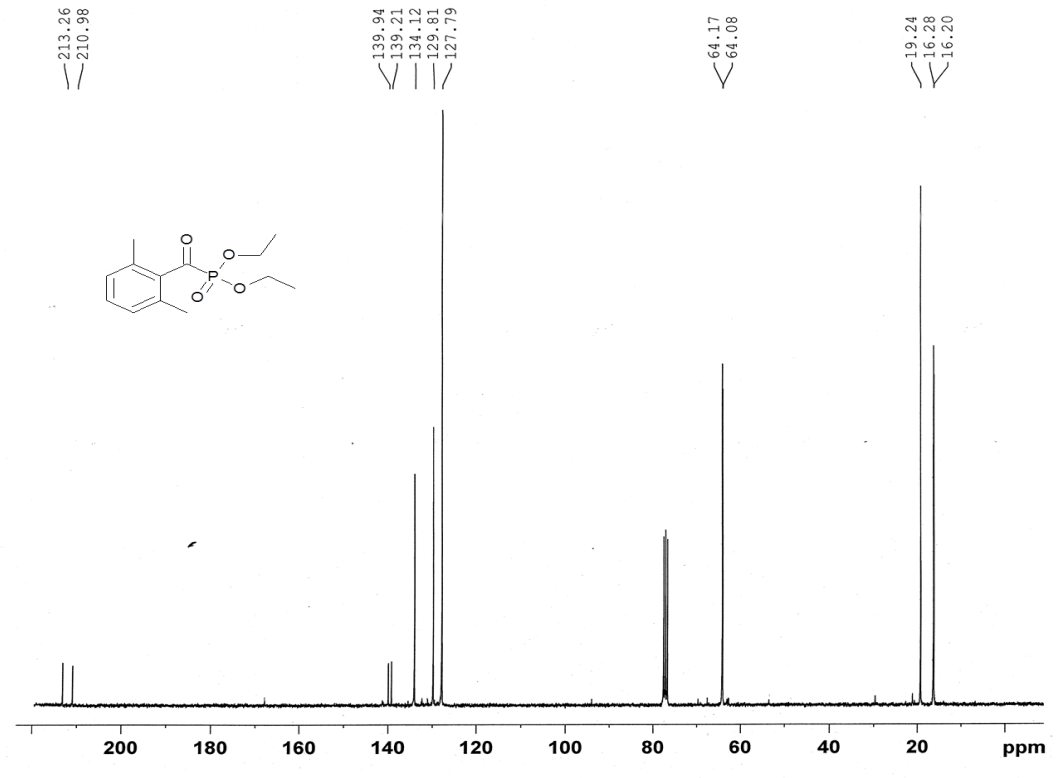

Figure S 5: ^{13}C - NMR of compound 2d

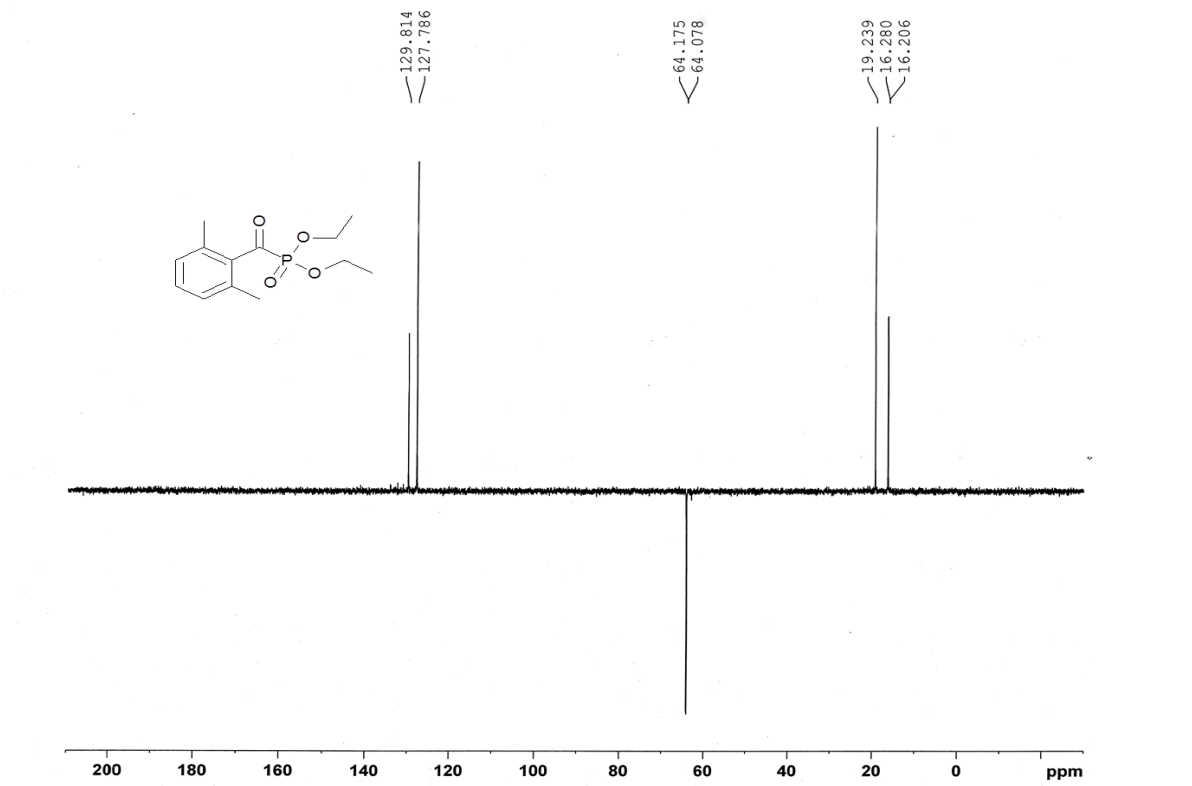

Figure S 6: DEPT of compound 2d

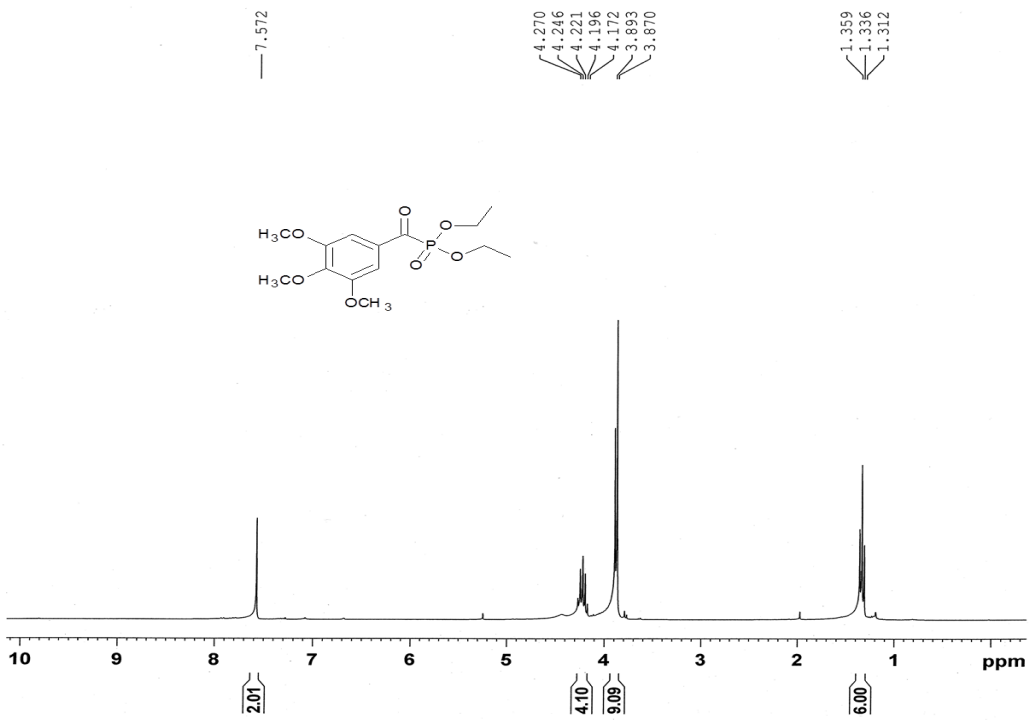

Figure S 7: ^{1}H - NMR of compound 2f

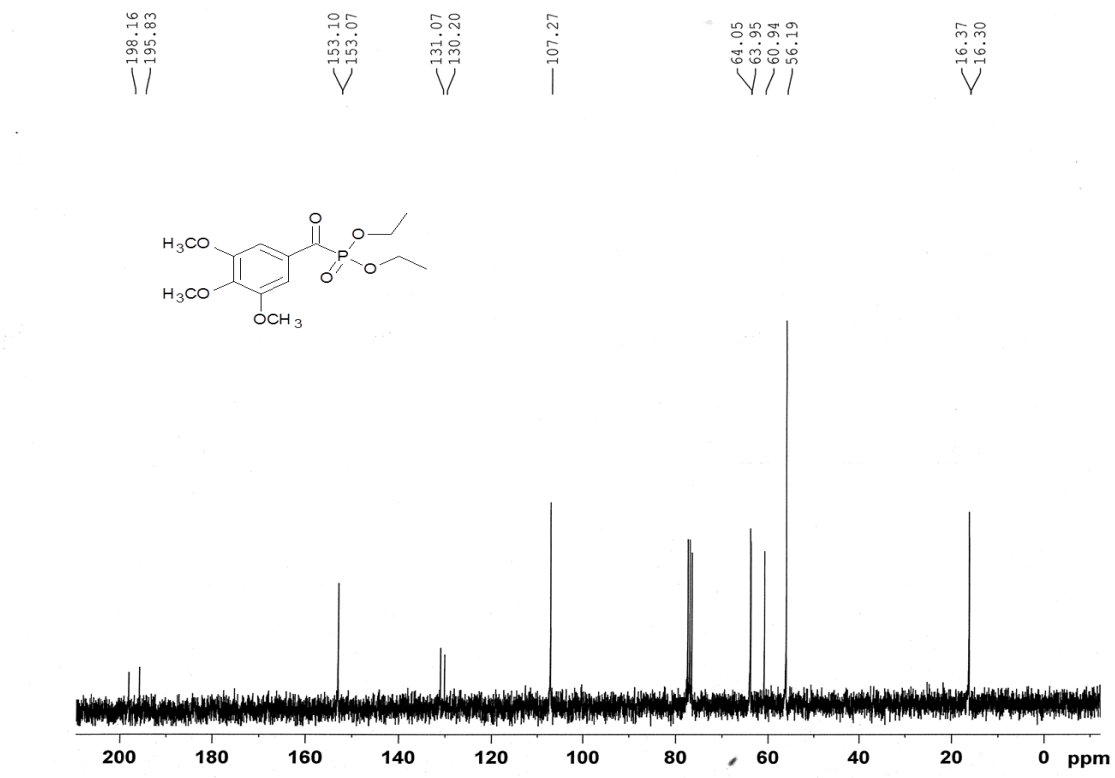

Figure S 8: ^{13}C - NMR of compound 2f

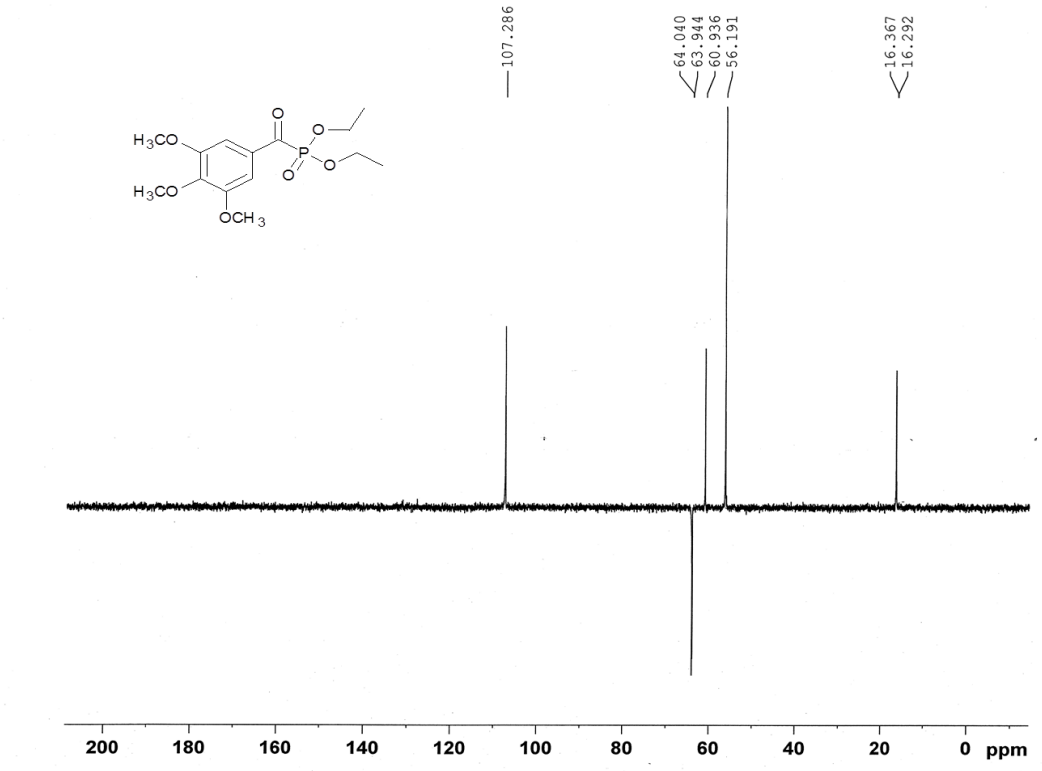

Figure S 9: DEPT of compound 2f

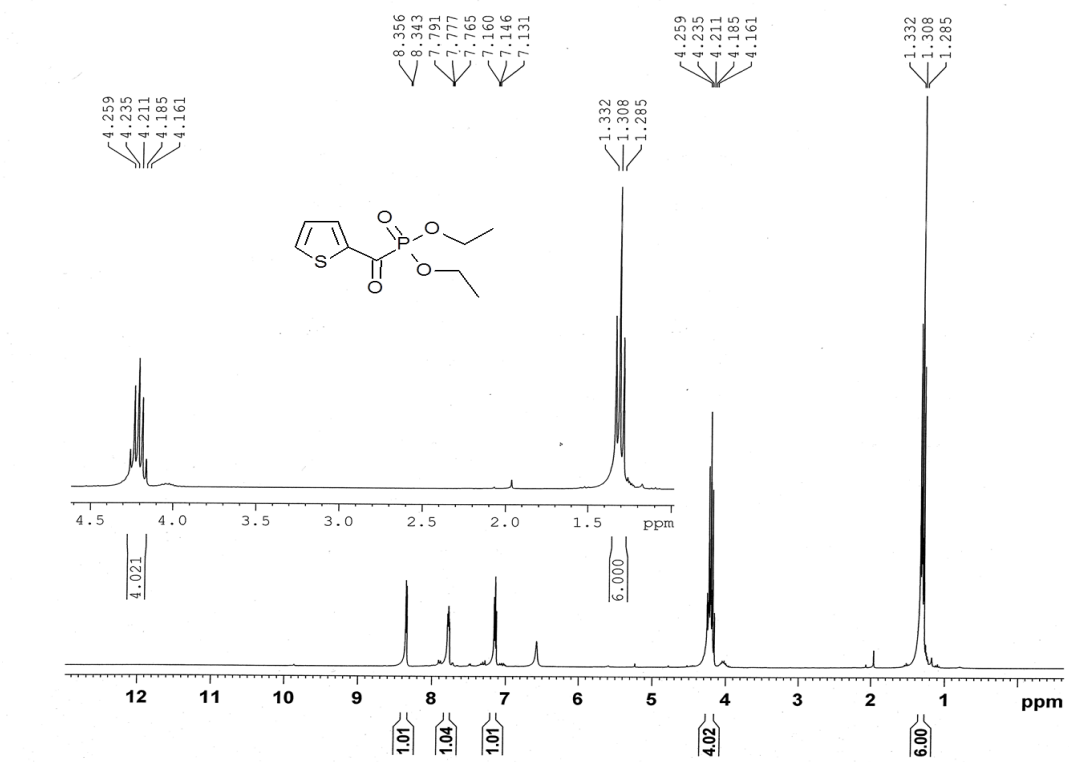

Figure S 10: ^{1}H - NMR of compound 2k

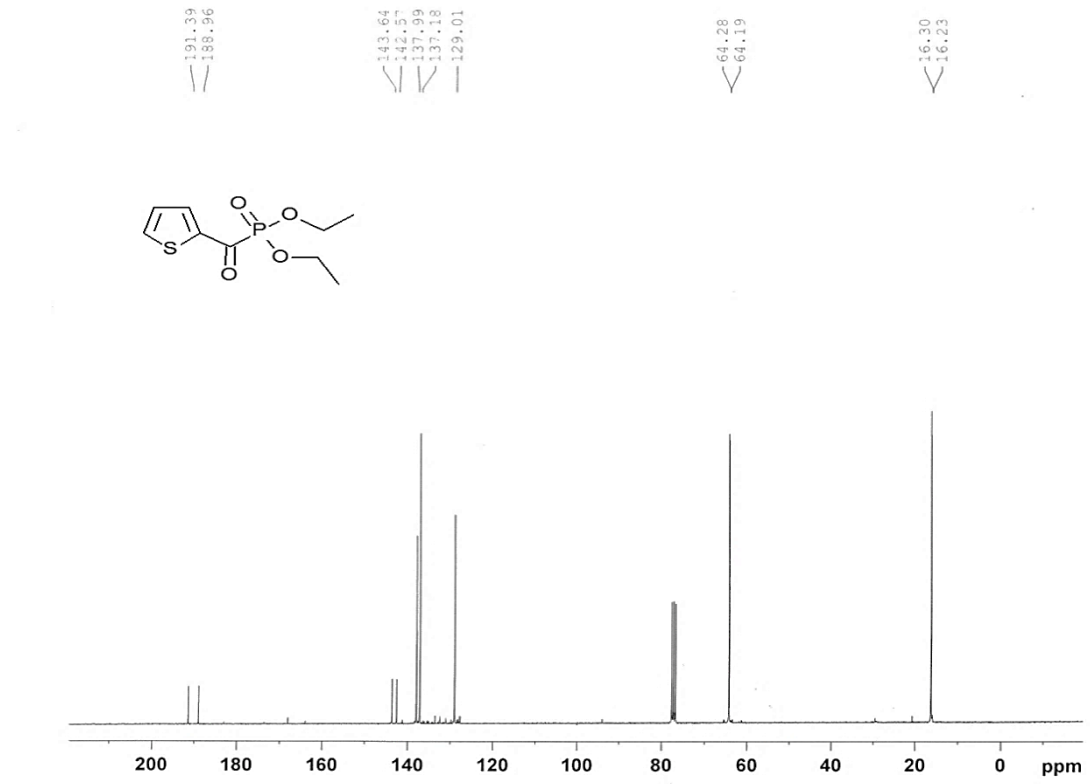

Figure S 11: ^{13}C - NMR of compound 2k

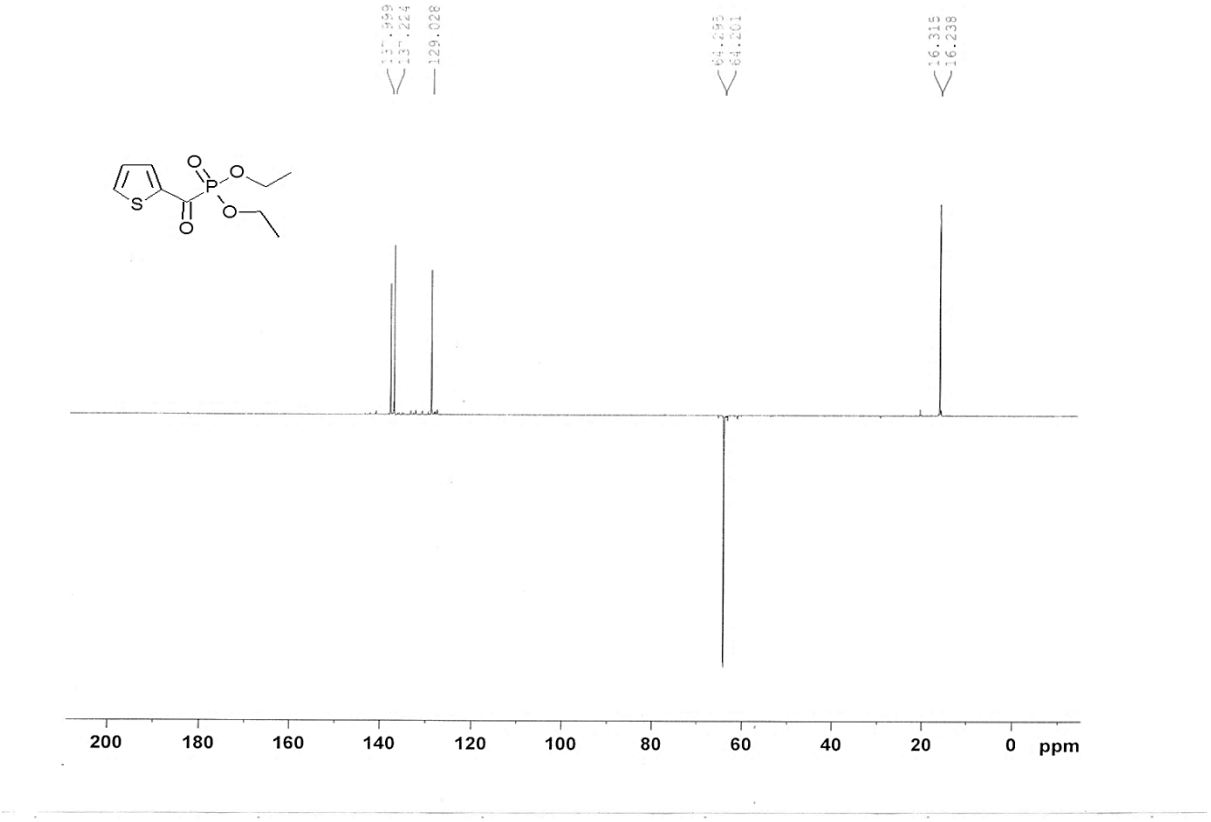

Figure S 12: DEPT of compound 2k

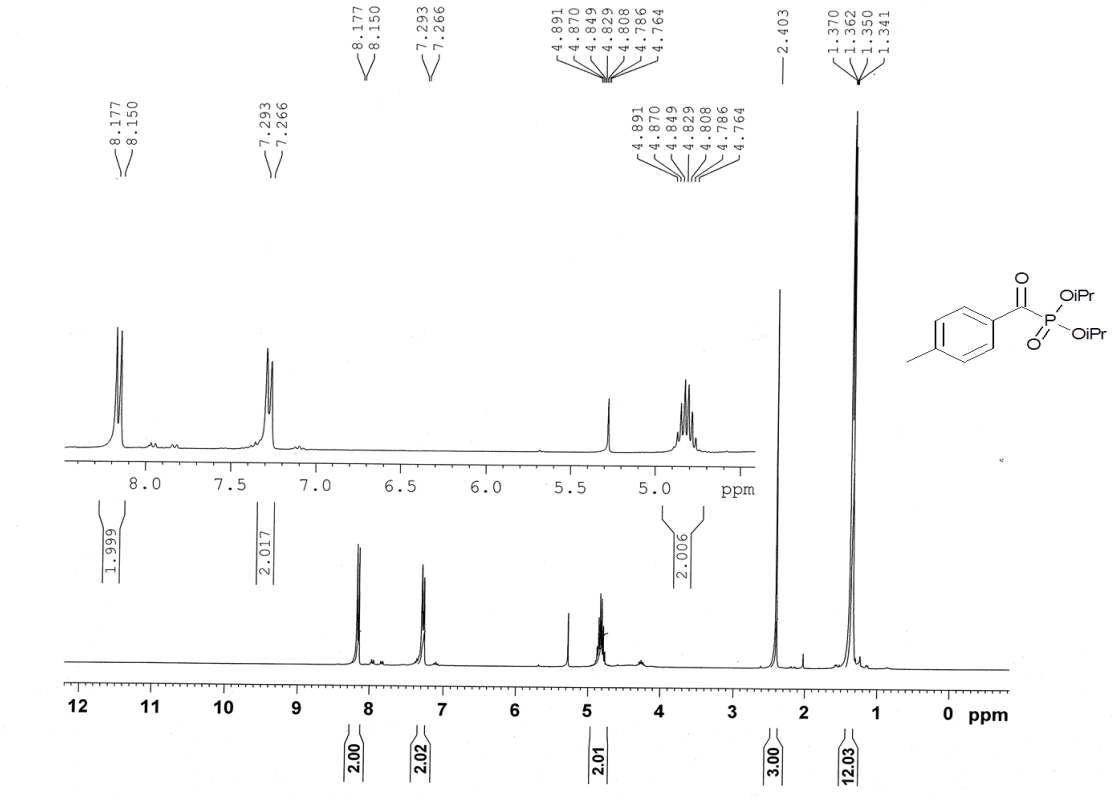

Figure S 13: ^{1}H - NMR of compound 2l

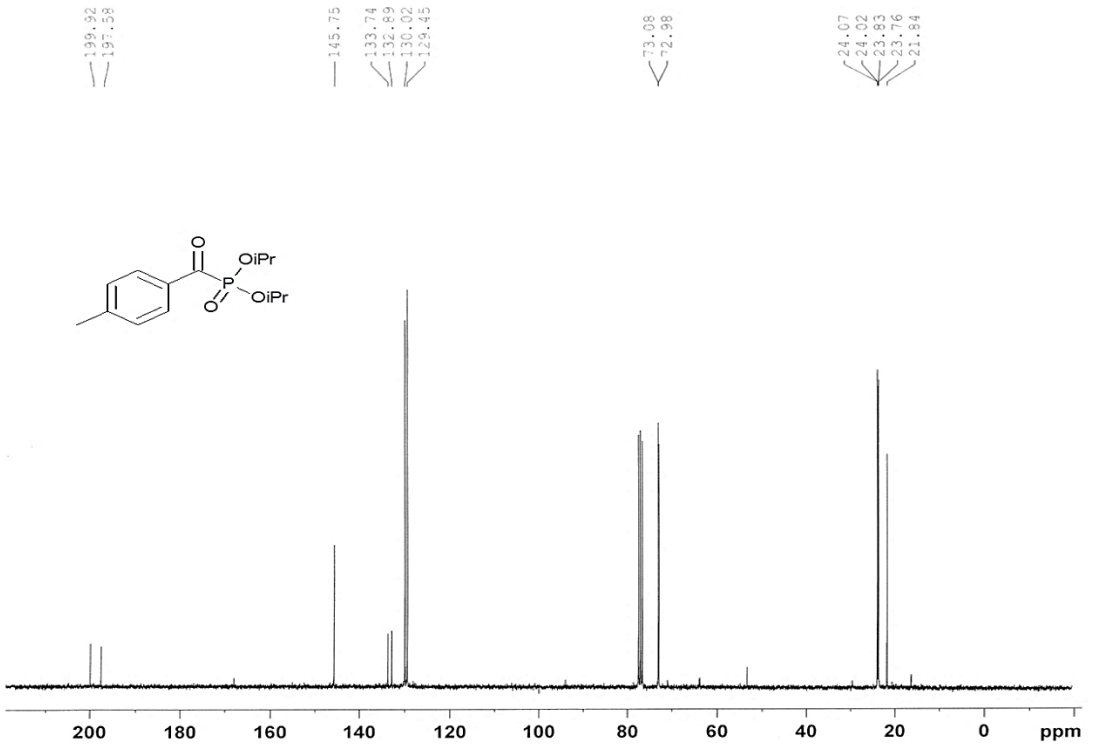

Figure S 14: ^{13}C - NMR of compound 2l

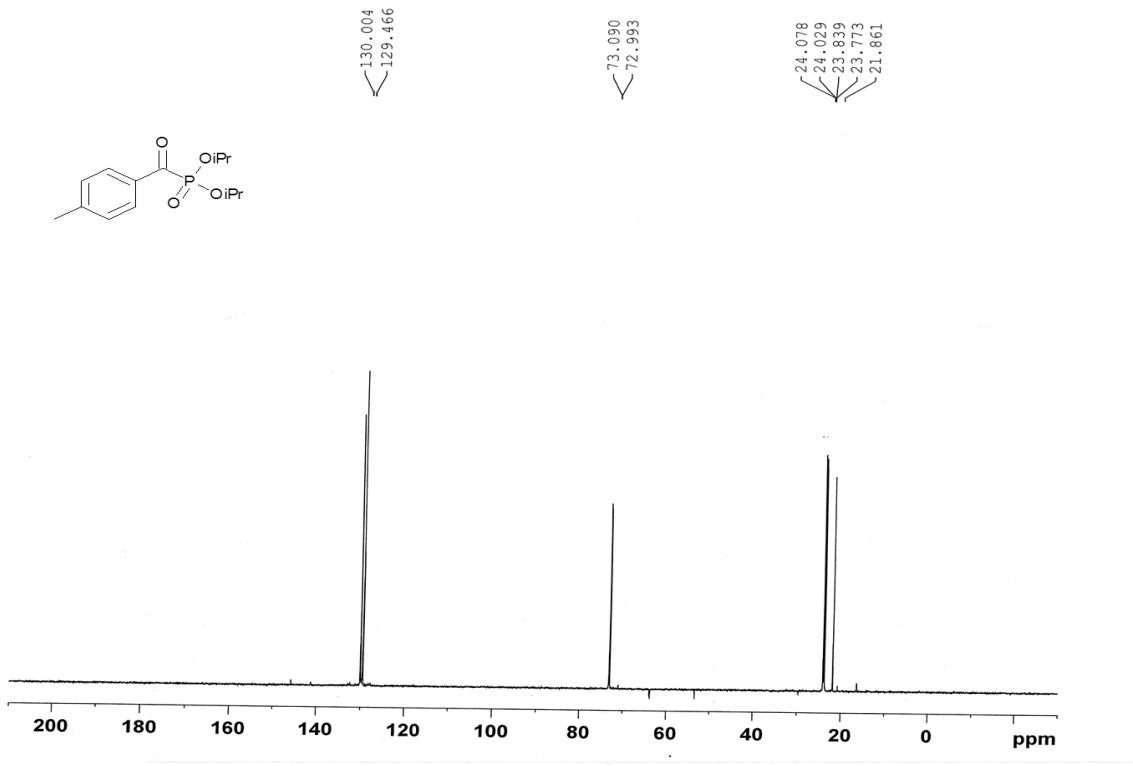

Figure S 15: DEPT of compound 2l

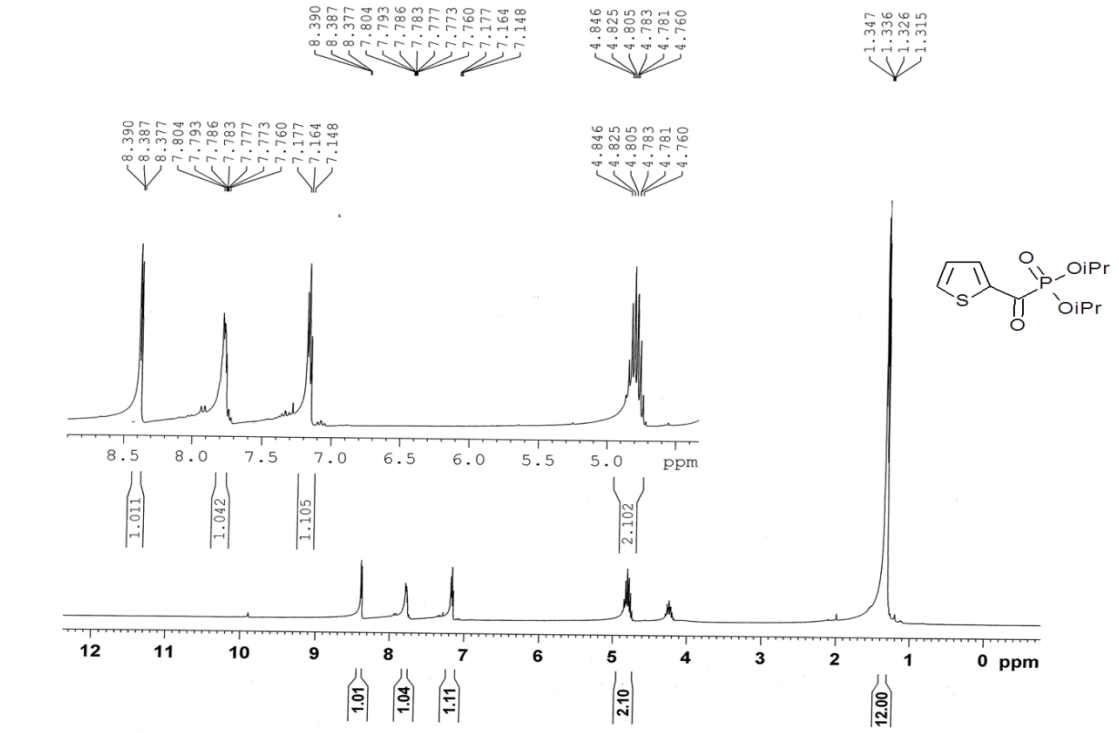

Figure S 16: ^{1}H - NMR of compound 2n

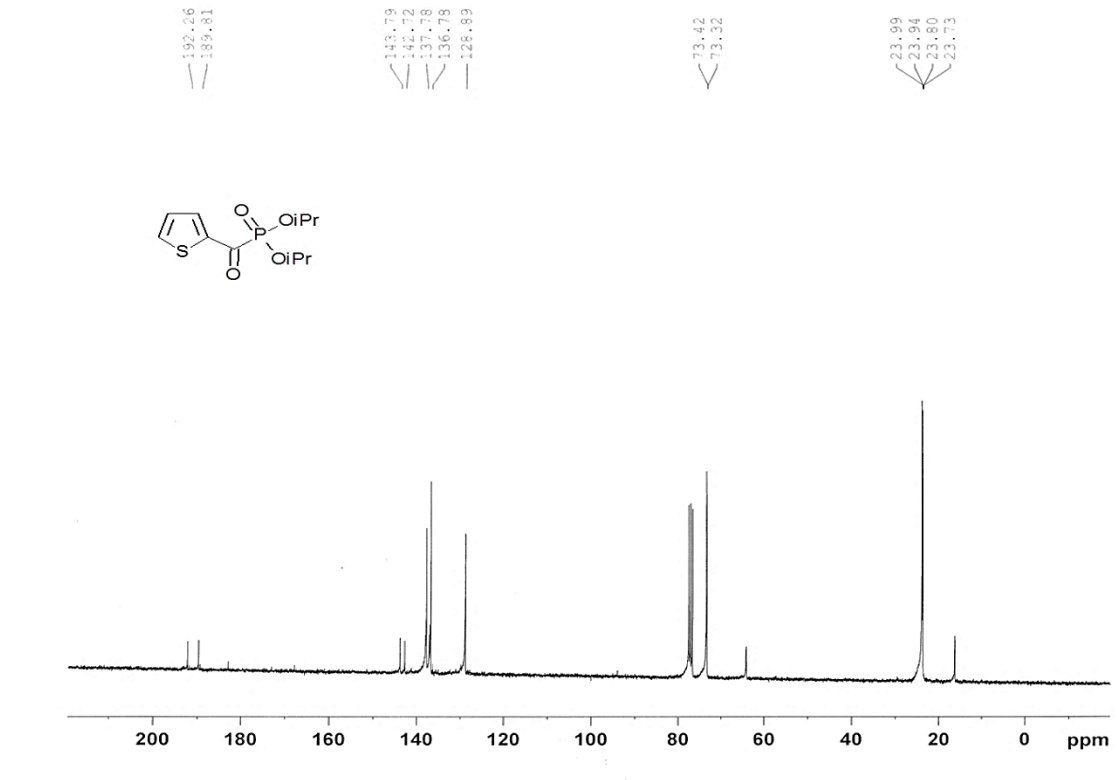

Figure S 17: ^{13}C - NMR of compound 2n

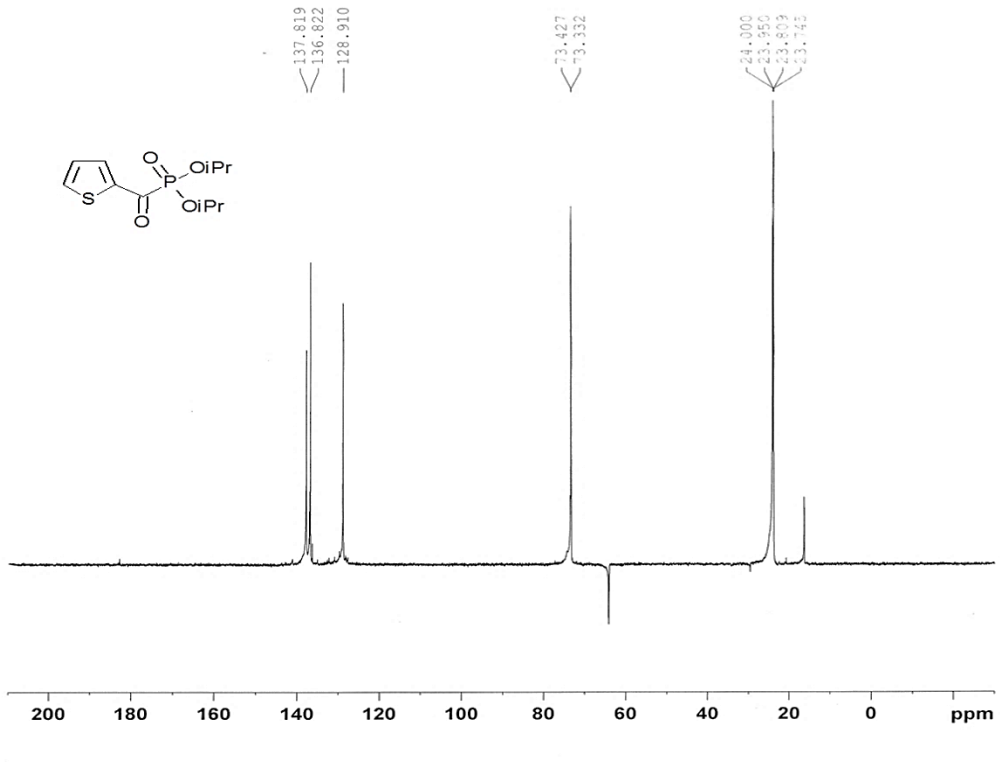

Figure S 18: DEPT of compound 2n

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

^{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.

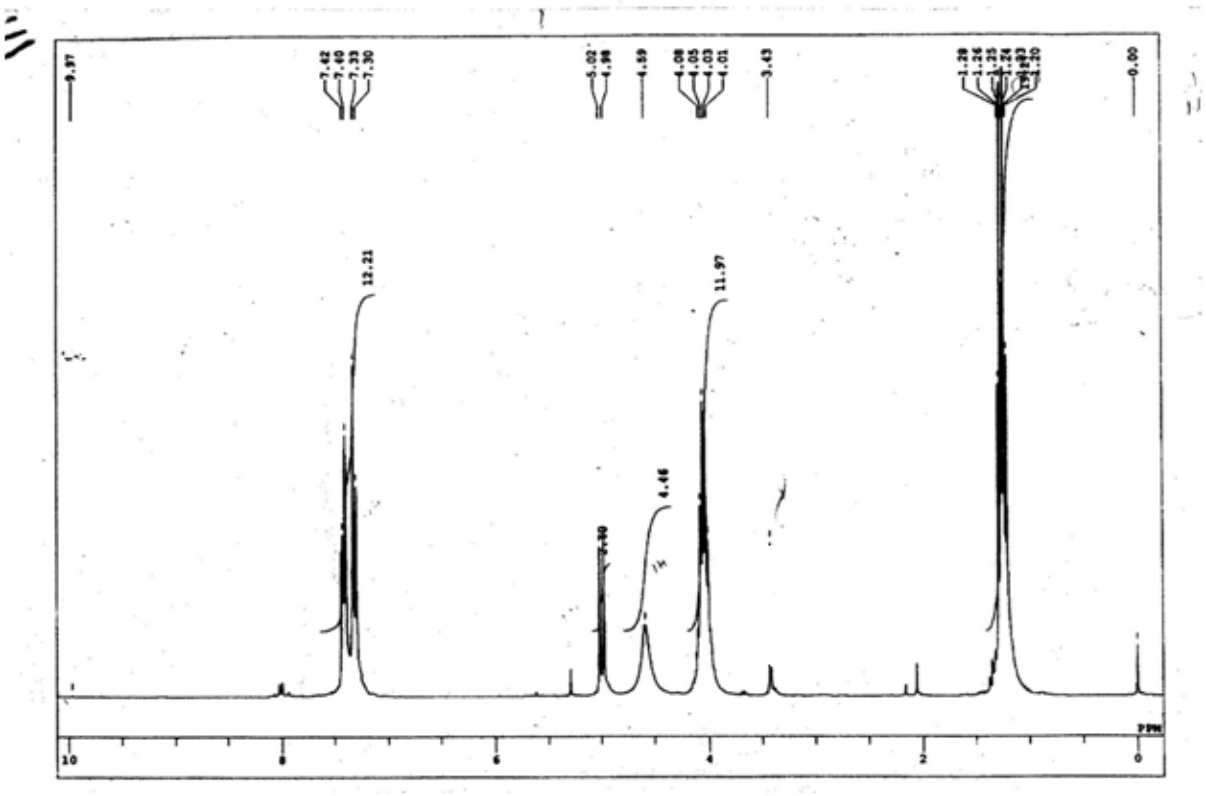

Figure AHP-1:PMR Spectrum α-hydroxyphosphonate-1

21 May 2007

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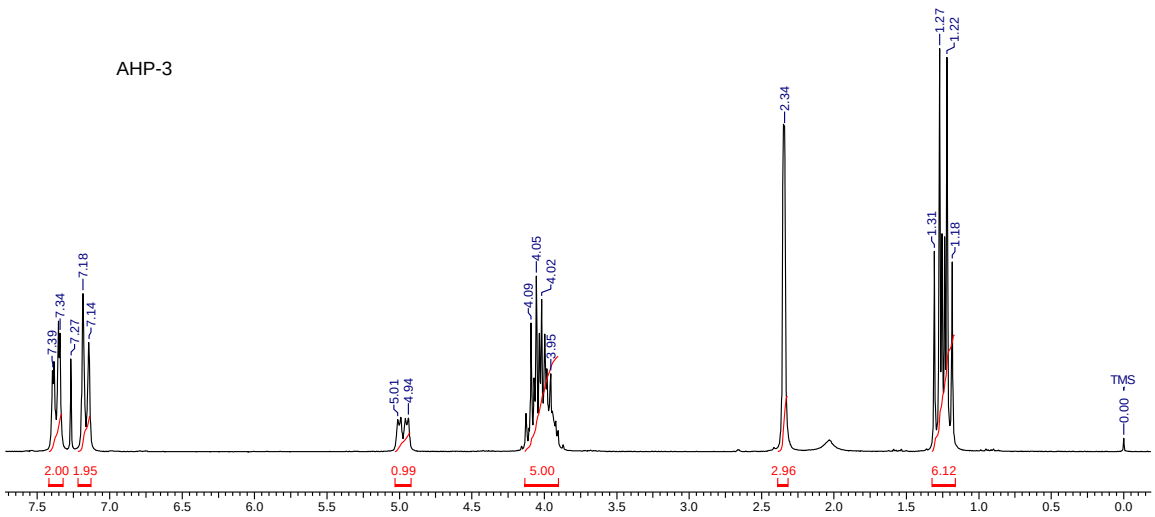


No.	(ppm)	Height
1	0.00	0.033
2	1.18	0.471
3	1.22	0.979
4	1.27	1.000
5	1.31	0.498
6	2.34	0.807
7	3.95	0.193
8	4.02	0.378
9	4.05	0.436

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

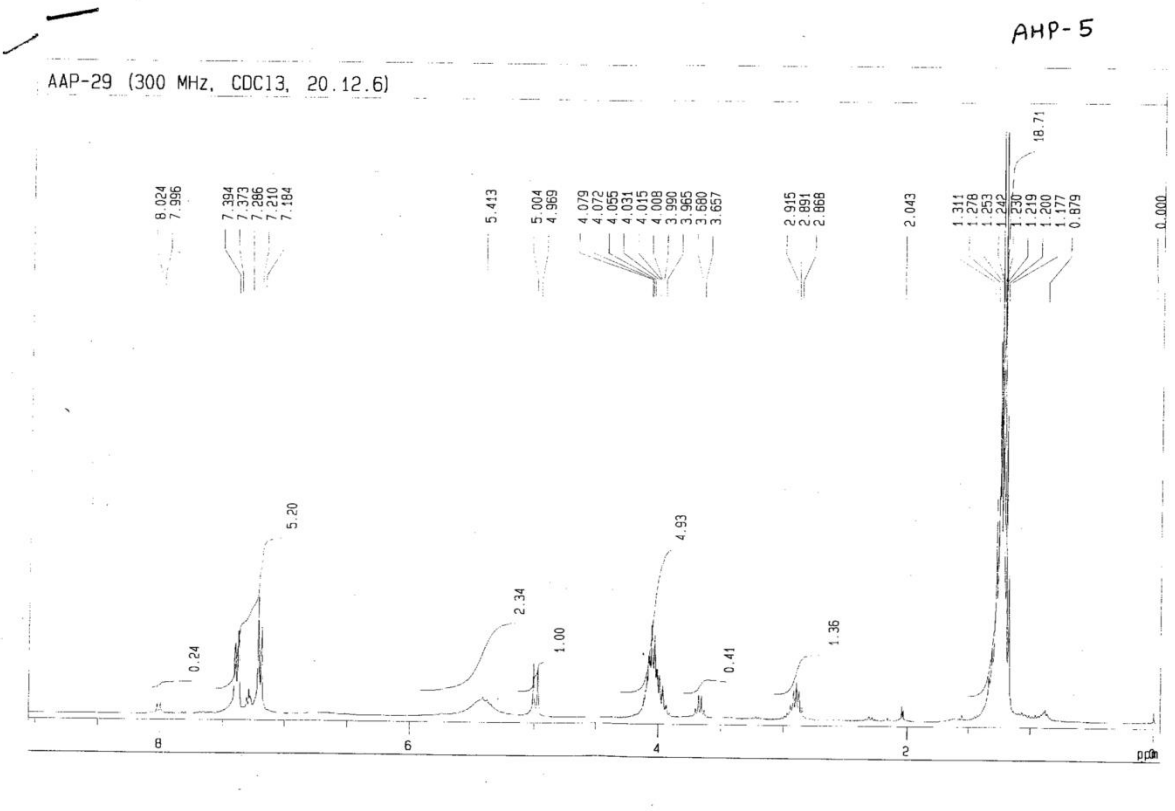
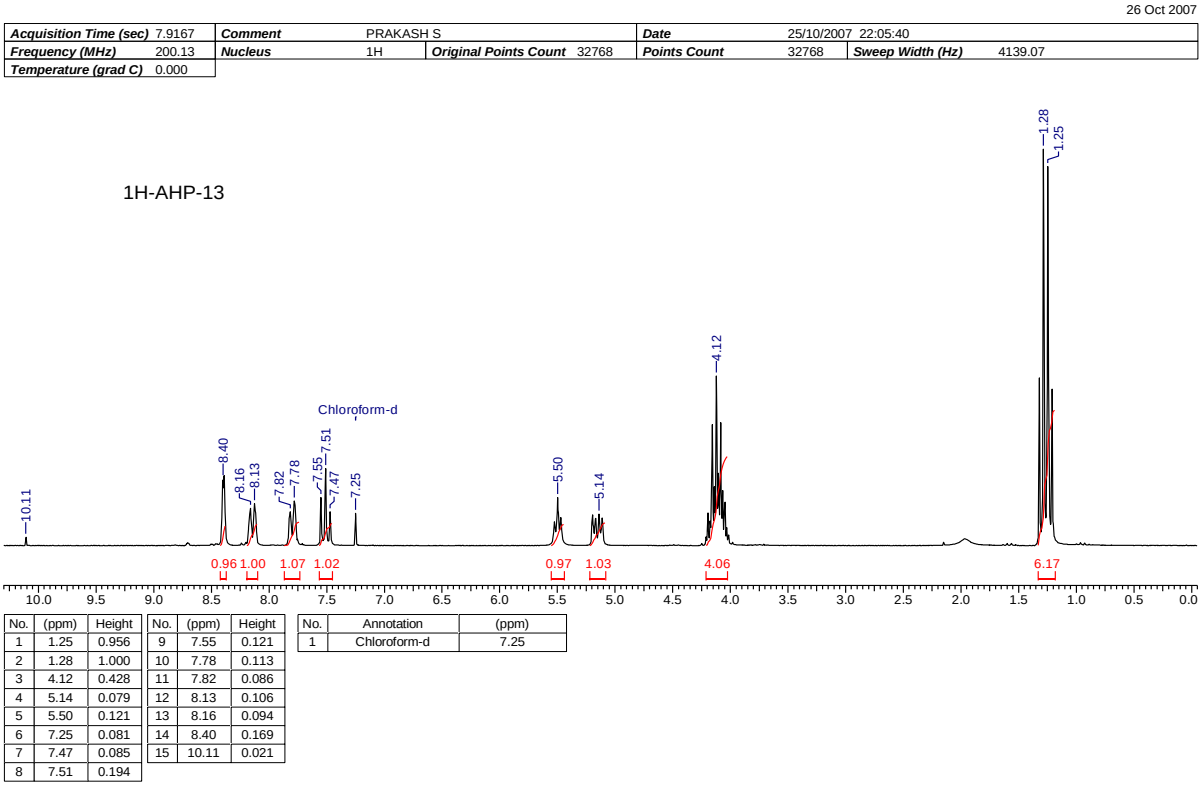


Figure AHP-3: PMR Spectrum α-hydroxyphosphonate-3

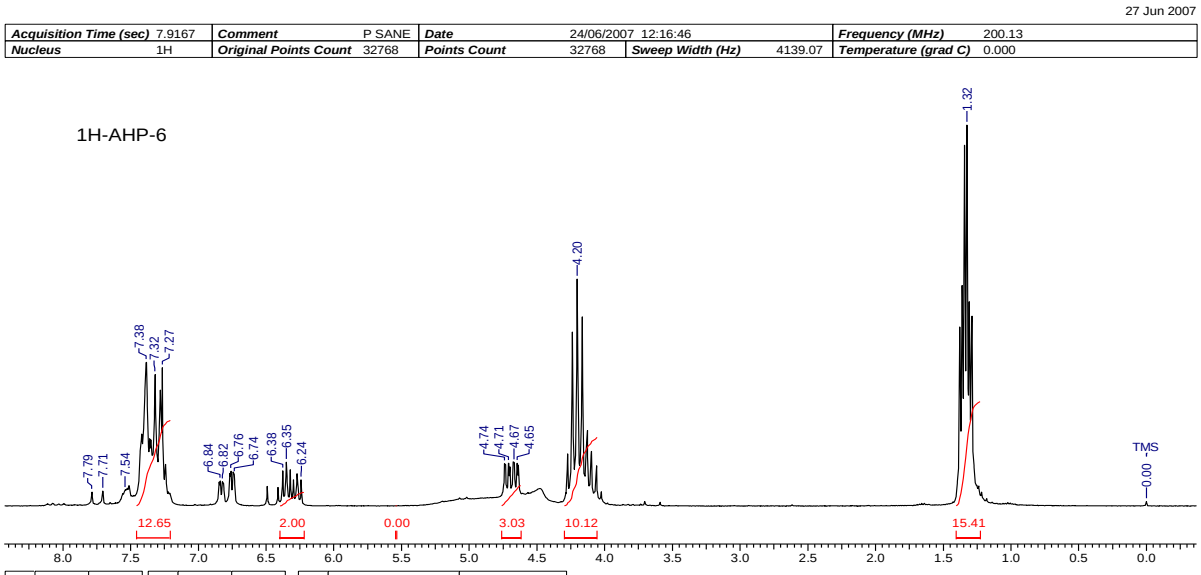


No.	(ppm)	Height
1	1.25	0.956
2	1.28	1.000
3	4.12	0.428
4	5.14	0.079
5	5.50	0.121
6	7.25	0.081
7	7.47	0.085
8	7.51	0.194

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



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

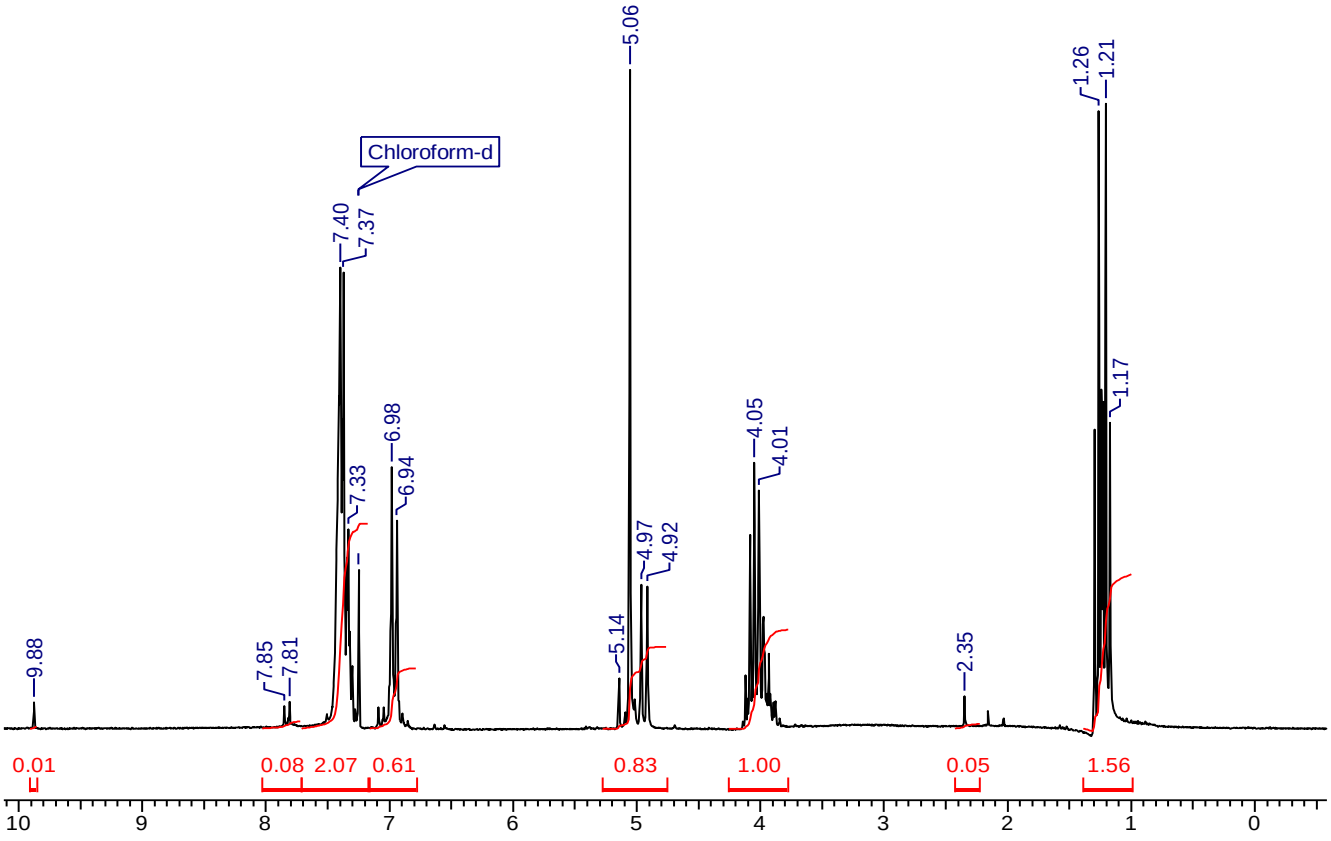


Figure AHP-9: PMR Spectrum α-hydroxyphosphonate-9

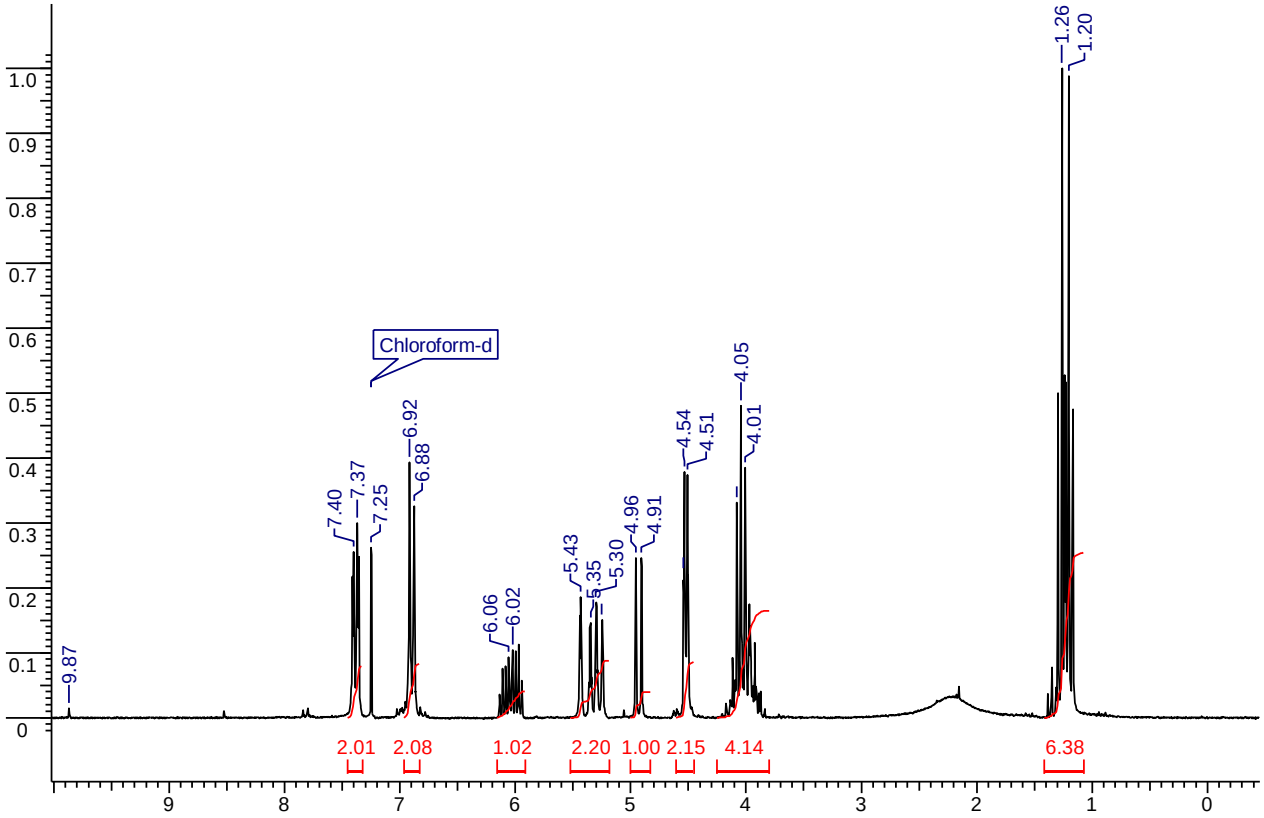


Figure AHP-10: PMR Spectrum α-hydroxyphosphonate-10

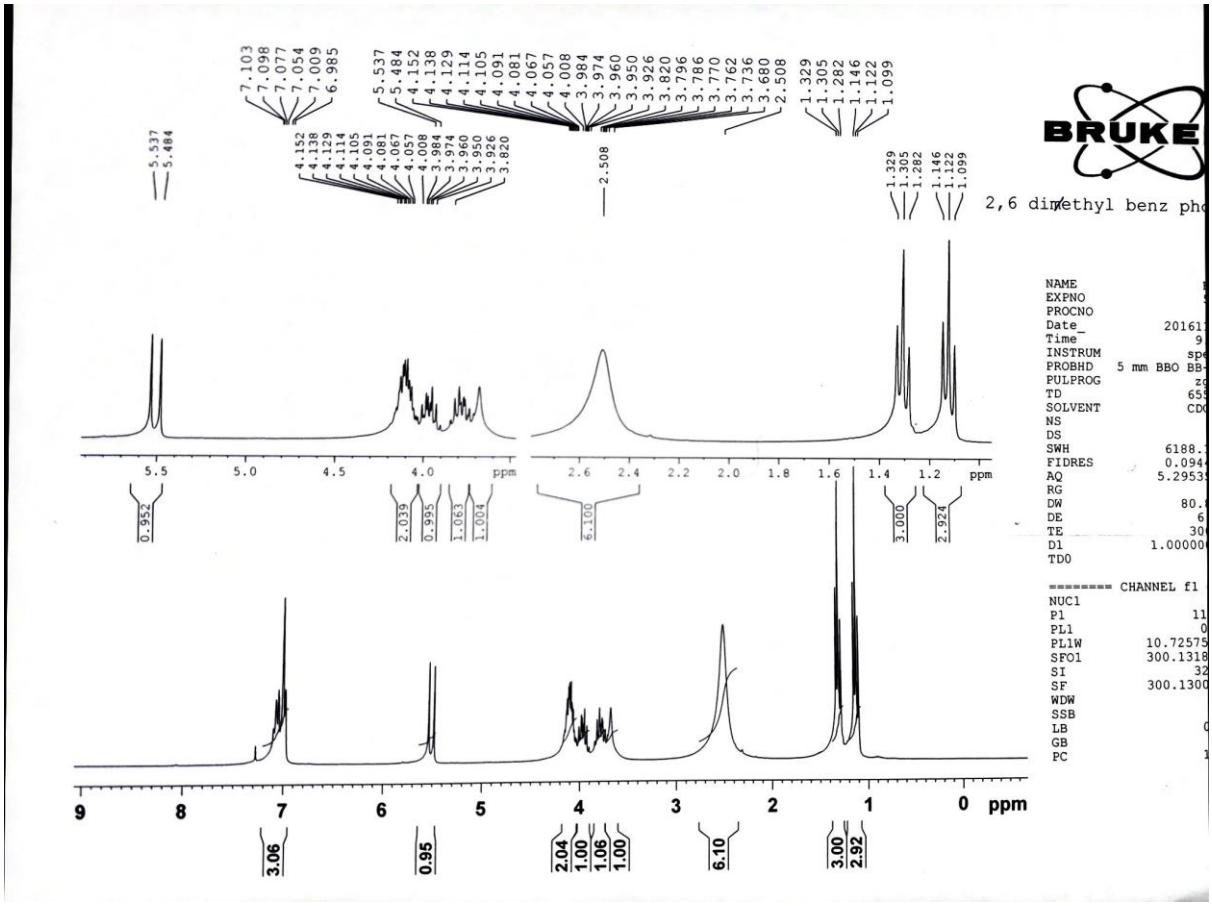


Figure AHP-13: PMR Spectrum α-hydroxyphosphonate-13

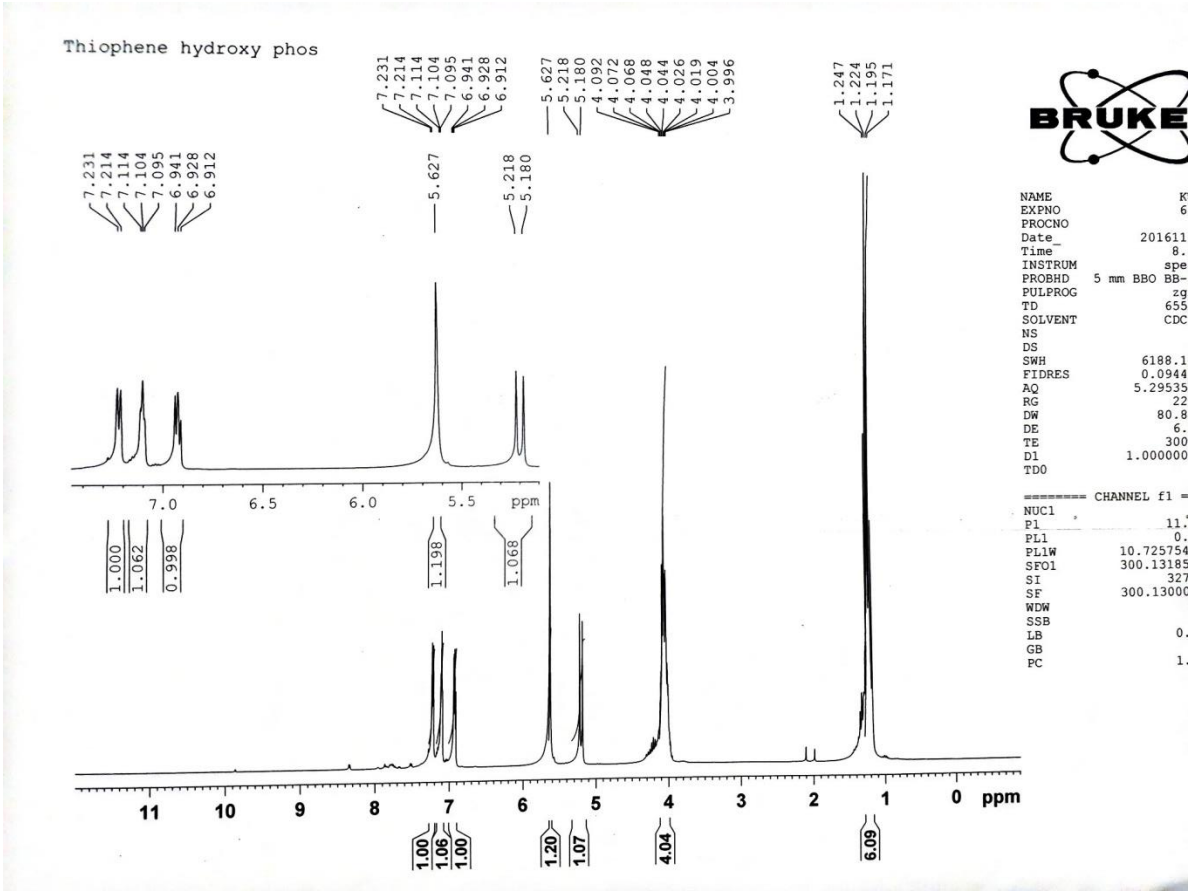


Figure AHP-14: PMR Spectrum α-hydroxyphosphonate-14