Supplementary Information

Umpolung Catalyzed by Organophosphines: Efficient β,β-Dimerization of Vinylphosphonates Affording Linear Dimers

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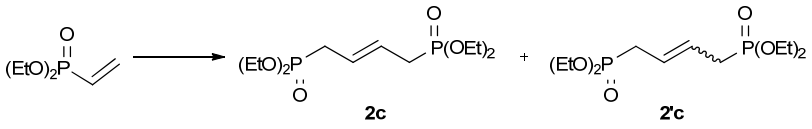
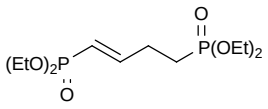
Contents

General Procedure for β,β-Addition of Vinylphosphonates (1)

General procedure for β,β-addition of vinylphosphonates (**1**): In a glove box, a glass tube was charged with vinylphosphonate (0.4 mmol) and 0.46 mL solvent, then sealed with a Teflon screw cap with a hole and rubber liner. After the tube was removed from the glove box, PMe_3/THF (1.0 mol/L, 0.04mL) was injected into it with a syringe. The reaction was monitored by NMR. Removal of the solvent and PMe_3 under a reduced pressure gave the crude product. β,β-adducts **2**/**2'** were obtained by passing the crude product through a short silica gel column using hexane then $CHCl_3$ as eluent.

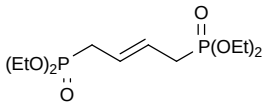
Structure determination of the isomers (a representative example): The structure of the products were determined on the basis of NMR spectra. Isomers **2c** and **2'c** could be distinguished by 1H NMR based on the chemical shifts and coupling constants of vinyl protons. The *E*/*Z* isomers of **2'c** was estimated based on the chemical shifts of their ally CH_2 group (the E isomer is more downfield than the Z isomer: *Carbon-13 NMR Spectroscopy*, H.-O. Kalinowski, S. Berger, S. Braun, John Wiley & Sons, Chichester, 1988). Thus, the ratio of **2c**/**2'c** was based on the vinyl protons of ^{1}H NMR (**2c**: 6.84–6.74 ppm (m, 1H), 5.76–5.69 ppm (m, 1H); **2'c**: 5.69–5.62 ppm (m, 2H)). The *E*/*Z* ratio of **2'c** was based on the ^{31}P NMR (*Z*-**2'**: 27.0 ppm; *E*-**2'**: 26.8 ppm) and the allyl CH_2 carbons of ^{13}C NMR (*Z*-**2'**: 27.5 ppm (dd, $J_{C,P}$ = 23.8 Hz); *E*-**2'**: 31.5 ppm (dd, $J_{C,P}$ = 142.6 Hz)) (J. M. Kauffman, G. Moyna, *J. Org. Chem.* **2003**, *68*, 839-853).





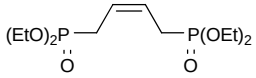
(**2c**)

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84–6.74 (m, 1H), 5.76–5.69 (m, 1H), 4.14–4.06 (m, 8H), 2.72–2.51 (m, 2H), 1.92–1.85 (m, 2H), 1.38–1.32 (m, 12H). ^{31}P NMR (200 MHz, $CDCl_3$): 30.1, 17.9. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8 (dd, $J_{C,P}$ = 17.6 Hz), 118.9 (d, $J_{C,P}$ = 188.1 Hz), 62.42 ($J_{C,P}$ = 3.0 Hz), 62.2 ($J_{C,P}$ = 8.3 Hz), 25.6 (dd, $J_{C,P}$ = 4.1 Hz), 24.9 ($J_{C,P}$ = 142.7 Hz), 16.74, 16.68.



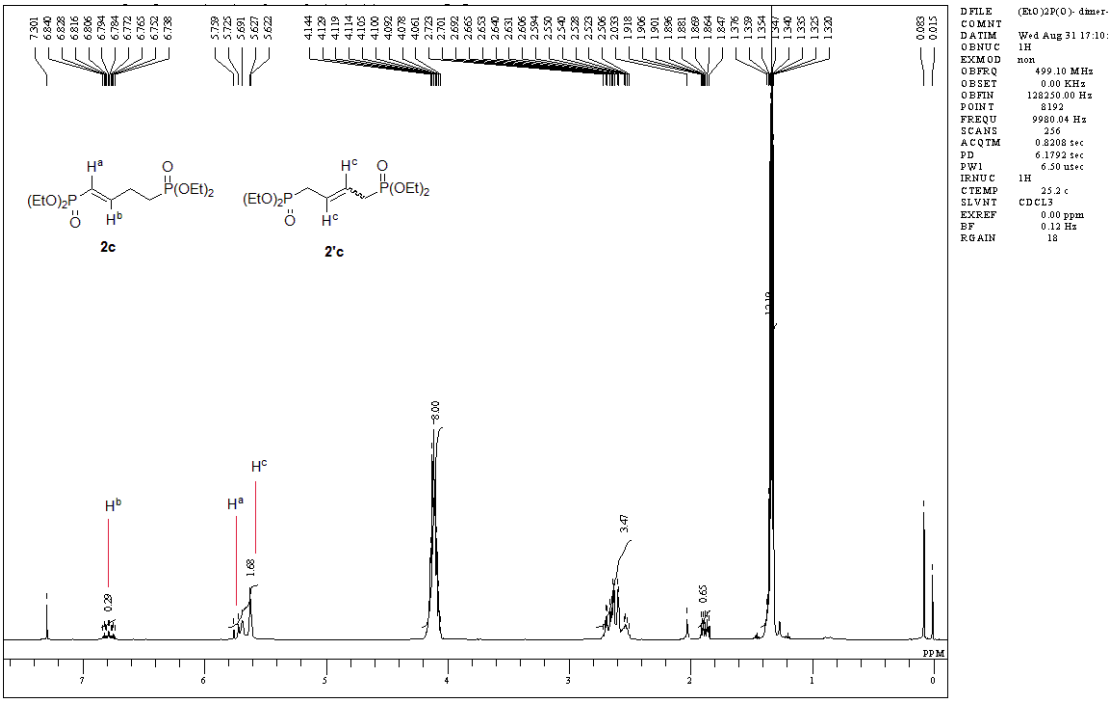
(*E*-**2'c**)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69–5.62 (m, 2H), 4.14–4.06 (m, 8H), 2.72–2.51 (m, 4H), 1.38–1.32 (m, 12H). ^{31}P NMR (200 MHz, $CDCl_3$): 26.8. ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.9 ($J_{C,P}$ = 43.4 Hz), 62.37 ($J_{C,P}$ = 3.1 Hz), 31.5 (dd, $J_{C,P}$ = 142.6 Hz), 16.8.



(*Z*-**2'c**)

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69–5.62 (m, 2H), 4.14–4.06 (m, 8H), 2.72–2.51 (m, 4H), 1.38–1.32 (m, 12H). ^{31}P NMR (200 MHz, $CDCl_3$): 27.0. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.3 ($J_{C,P}$ = 39.3 Hz), 62.39 ($J_{C,P}$ = 6.1 Hz), 27.5 (dd, $J_{C,P}$ = 23.8 Hz), 16.8.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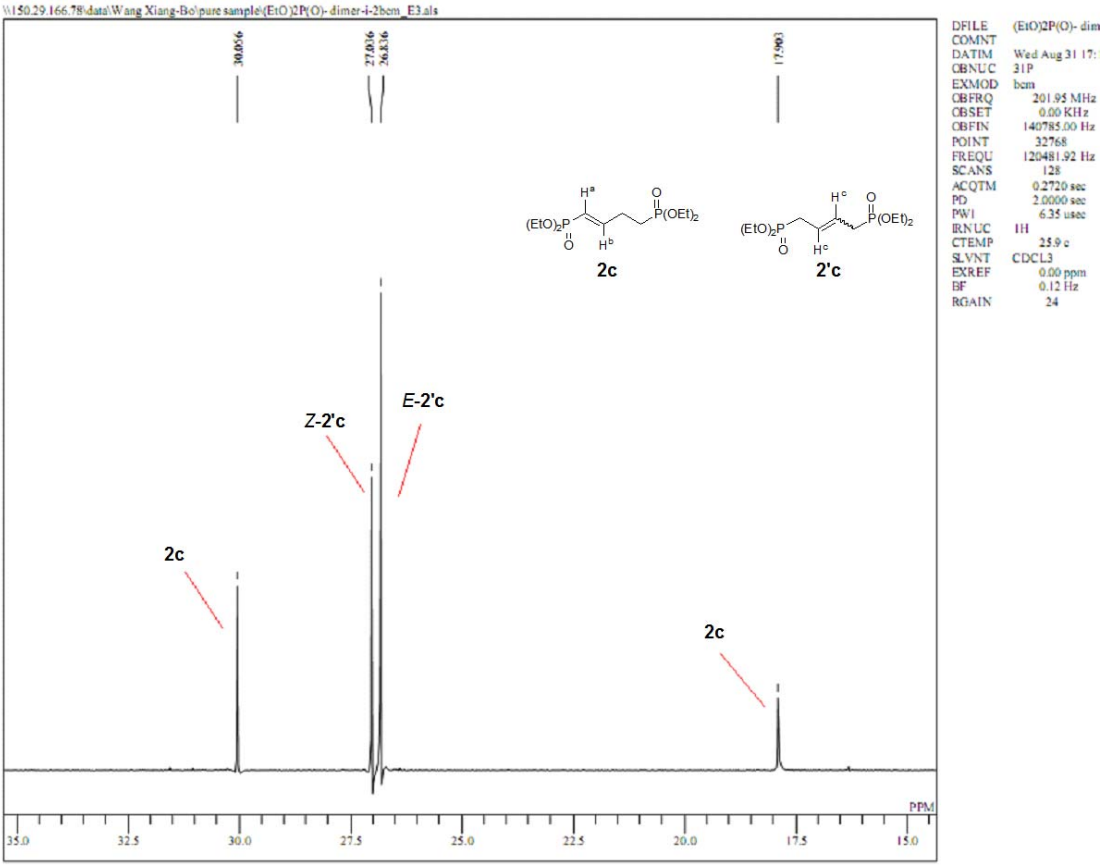
Ha
Hb
Hc
PPM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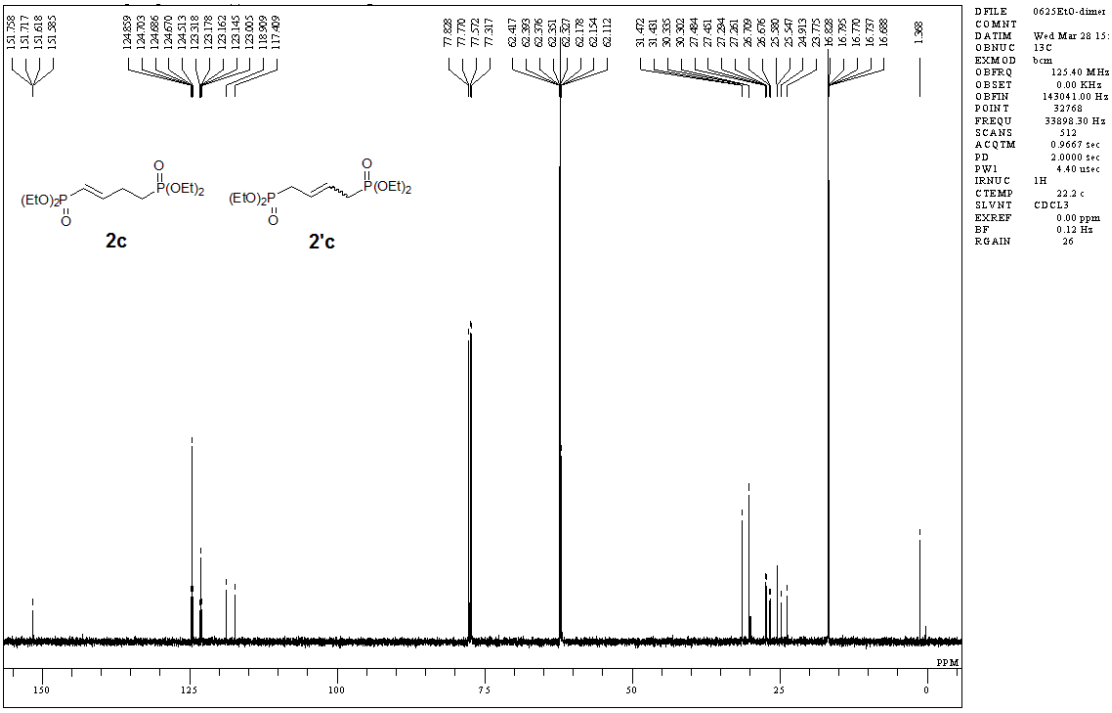
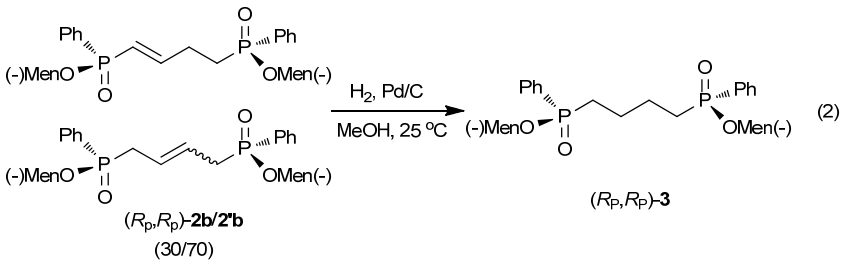
2'c
Z-2'c
E-2'c
2c
2c
PPM



Hydrogenation of 2b and 2b' to Produce (R_p, R_p)-3

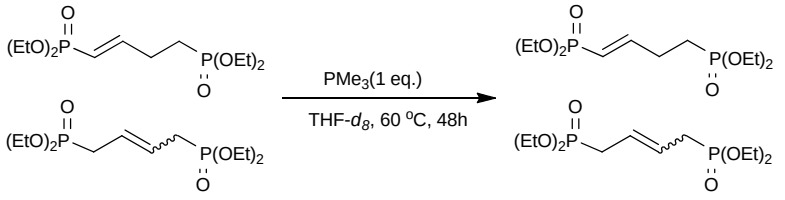


A solution of **2b**/**2b'** (0.25 g, 0.41 mmol) in 15 mL methanol was hydrogenated with 13 mg of 10% Pd/C under 5 atm of H_2 pressure at RT overnight. The reaction mixture was filtered and evaporated to remove the solvent and passed through a short silica gel column using $CHCl_3$ as eluent to give 0.242 g (97 % yield) of the product.

White solid, m.p. 159-160 ^{O}C. $[\alpha]_D^{23}$ -24.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.68 (m, 4H), 7.54–7.42 (m, 6H), 5.39–5.37 (m, 2H), 4.38–4.20 (m, 2H), 2.78–2.44 (m, 4H), 2.23–2.19 (m, 2H), 1.77–1.61 (m, 4H), 1.77–1.61 (m, 4H), 1.40–1.29 (m, 4H), 1.03–0.75 (m, 24H). ^{31}P NMR (200 MHz, $CDCl_3$): 42.1. ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4 ($J_{C,P}$ = 123.0 Hz), 131.8, 131.3 ($J_{C,P}$ = 9.5 Hz), 128.4 ($J_{C,P}$ = 12.4 Hz), 48.8 ($J_{C,P}$ = 5.7 Hz), 43.1, 34.0, 31.4, 30.6 ($J_{C,P}$ = 100.1 Hz), 25.7, (dd, $J_{C,P}$ = 2.8 Hz, $J_{C,P}$ = 18.1 Hz), 22.8, 21.9, 21.1,15.7.

Isomerization Experiments of 2c/2c'

The dimers **2c**/**2c'** (55/45) (105 mg, 0.32 mmol) was dissolved in 0.4 mL THF-d_8 in a sealed NMR tube, Then PMe_3 (33 μL, 0.32 mmol) was injected with a syringe. After heating at 60 ^{O}C for 12h, 24h and 48h, the dimer-isomer ratio was checked by ^{1}H NMR spectra. (Figure 1).



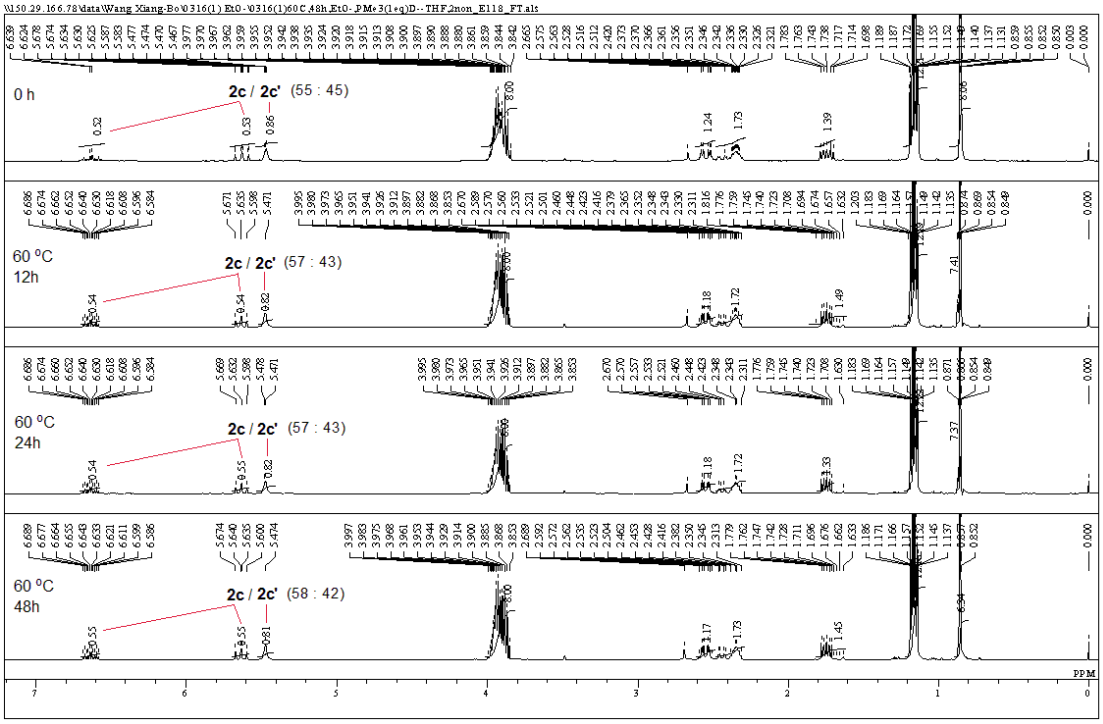


Figure 1.

Synthesis of 9 and 9a

Under nigrogen, a 20 mL tube containing a magnetic stir bar was charged with vinylphosphonate **1c** (0.272 mL, 1.6 mmol), 2.4 mL THF and 0.8 mL H_2O. After stirring at RT for 5 min., PMe_3/THF(1.0 mol/L, 0.4 mL) was added with a syringe then stirred at RT for 12h. After removal of the solvent and PMe_3 under a reduced pressure, the crude product was obtained as a white solid, then pure **9** was obtained by washing with $CHCl_3$ and hexane in 92 % yield (0.312 g). The structure of **9** was determined by X-ray analysis.

White solid, m.p.69-72 ^{O}C. ^{1}H NMR (500 MHz, D_2O): δ 3.89–3.83 (m, 2H), 2.32–2.24 (m, 12H), 1.82–1.81 (d, J = 6.1Hz, 9H), 1.80–1.69 (m, 2H), 1.20–1.17 (m, 2H). ^{31}P NMR (200 MHz, D_2O) 28.7 (d, J = 63.9 Hz), 22.9 (d, J = 61.9 Hz). ^{13}C NMR (125 MHz, D_2O): δ 61.1 (d, 5.8 Hz), 18.8 (dddd, J = 5.8 Hz, 3.8 Hz, 3.8 Hz, 4.8 Hz), 16.1 (d, 5.8 Hz), 7.2, 6.7.

***d*-9** was synthesized following the same procedure using D_2O (Figure 2).

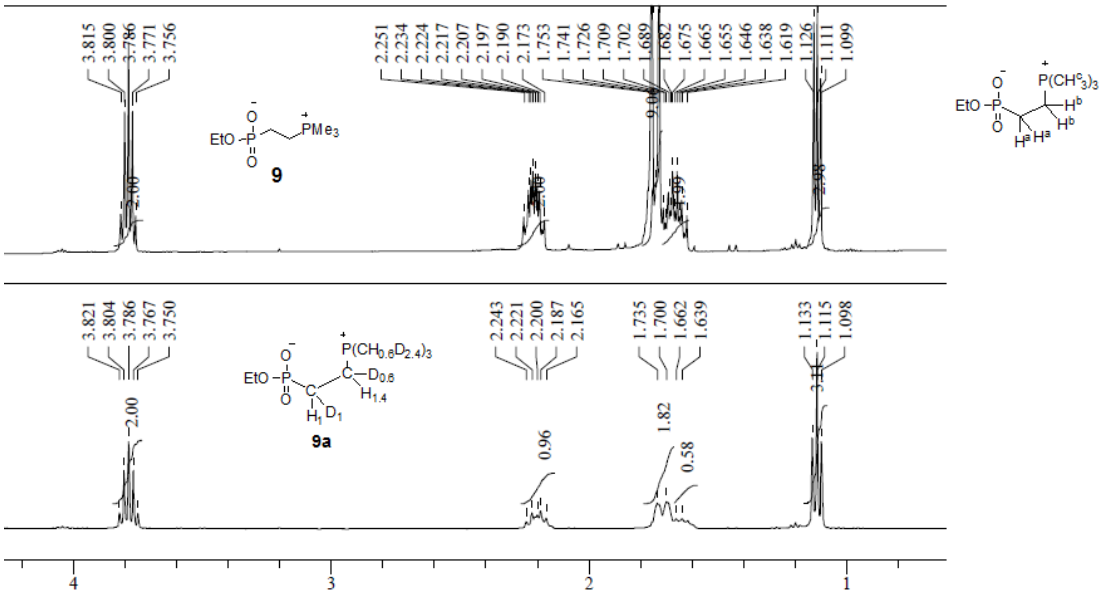
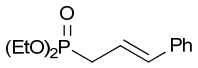


Figure 2. ^{1}H NMR spectra of **9** and **d-9**: H^{a}, H^{b} and H^{c} were deuterated.

Reaction of Diethyl Vinylphosphonate (1c) with Aldehydes

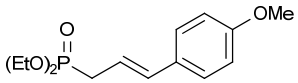
General procedure: into a nigrogen-charged tube was placed diethyl vinylphosphonate **1c** (0.4 mmol), aldehyde (0.4 mmol) and 0.6 mL DMF with 0.1eq H_2O in it. Then PMe_3/THF (1.0 mol/L, 0.4 mL) was added with a syringe and stirred at RT. The reaction was monitored by GC until the reactant disappeared. After removal of the solvent and PMe_3 under a reduced pressure, the crude product was passed through a silica gel column using hexane then EtOAc/hexane (1/5) as eluent to give corresponding olefin. (E)-diethyl 4-methoxycinnamylphosphonate, 45 % yield. (E)-diethyl cinnamylphosphonate, 65 % yield. (S. Ghosh, S. U. Kumar, J. Shashidhar. *J. Org. Chem.* **2008**, *73*, 1582-1585; N. N. Demik, M. M. Kabachnik, Z. S. Novikova, I. P. Beletskaya, *Russ. J. Org. Chem*. **1994**,*30*, 935-940)

(*E*)-diethyl cinnamylphosphonate



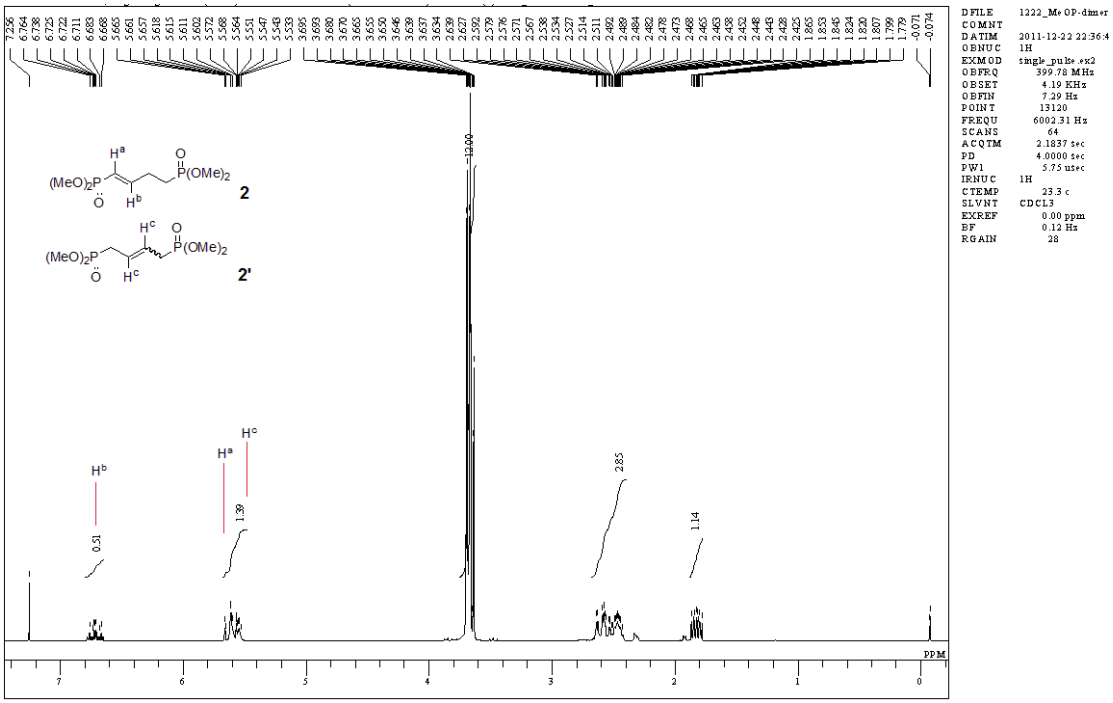
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.17 (m, 5H), 6.52–6.46 (dd, J= 4.8, 5.2 Hz, 1H), 6.18–6.09 (m, 1H), 4.15–4.02 (m, 4H), 2.77–2.69 (m, 2H), 1.31–1.24 (m, 6H). ^{31}P NMR (200 MHz, $CDCl_3$): 27.6. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 ($J_{C,P}$ = 2.8 Hz), 134.7 ($J_{C,P}$ = 15.3 Hz), 128.6, 127.6, 126.2, 118.9 ($J_{C,P}$ = 11.6 Hz), 62.1 ($J_{C,P}$ = 6.7 Hz), 31.9 ($J_{C,P}$ = 139.8 Hz), 16.6 ($J_{C,P}$ = 5.7 Hz).

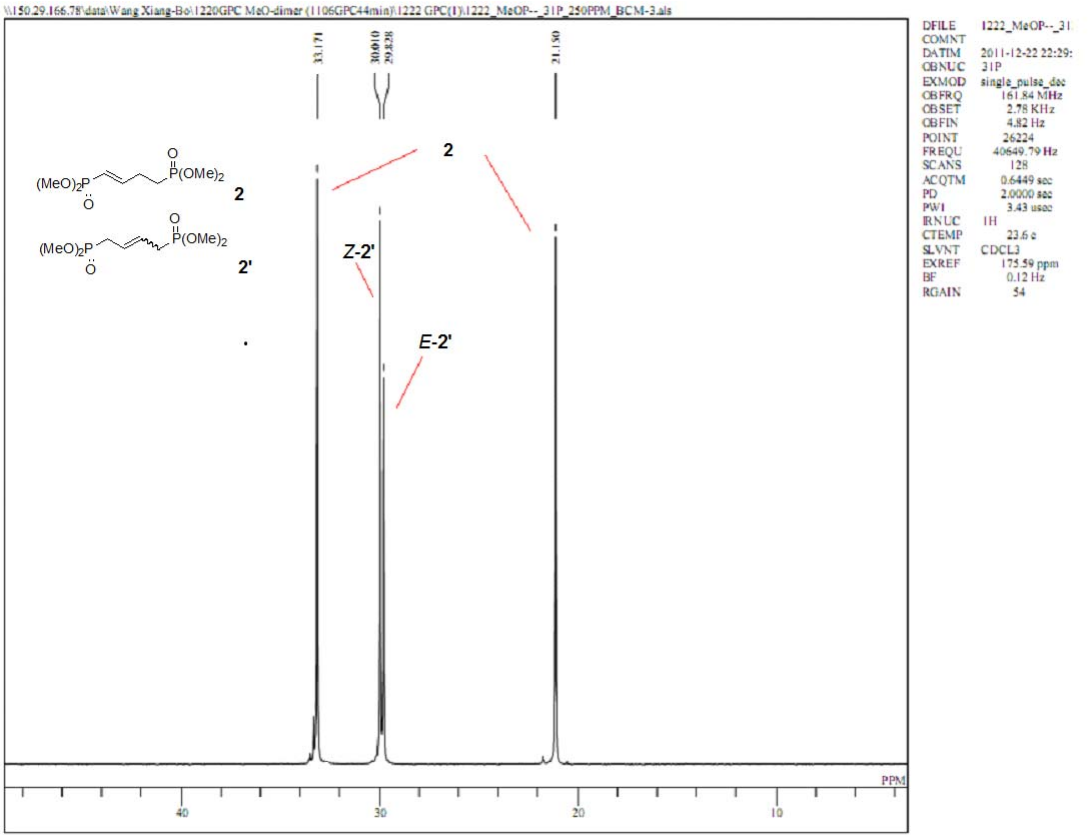
(*E*)-diethyl 4-methoxycinnamylphosphonate

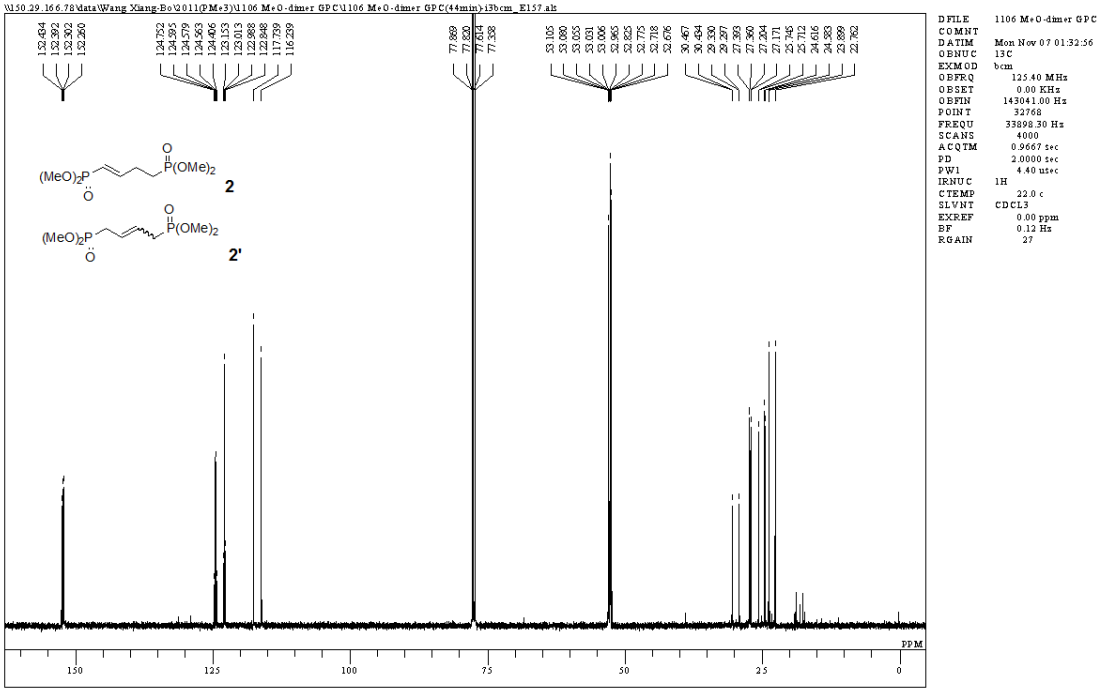


^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.33 (d, J=8.5 Hz, 2H), 7.89–7.88 (d, J=9.0 Hz, 2H), 6.53–6.49 (dd, J=5.0, 5.0 Hz, 1H), 1.37–1.37 (t, 6H). ^{31}P NMR (200 MHz, $CDCl_3$): 27.2. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 134.6 ($J_{C,P}$ = 14.4 Hz), 130.2 ($J_{C,P}$ = 3.1 Hz), 127.8 ($J_{C,P}$ = 2.0 Hz), 116.9 ($J_{C,P}$ = 12.4 Hz), 114.4, 62.5 ($J_{C,P}$ = 6.1 Hz), 55.7, 32.0 ($J_{C,P}$ = 139.6 Hz), 17.0 ($J_{C,P}$ = 6.3 Hz).

Copies of NMR Charts of the Products



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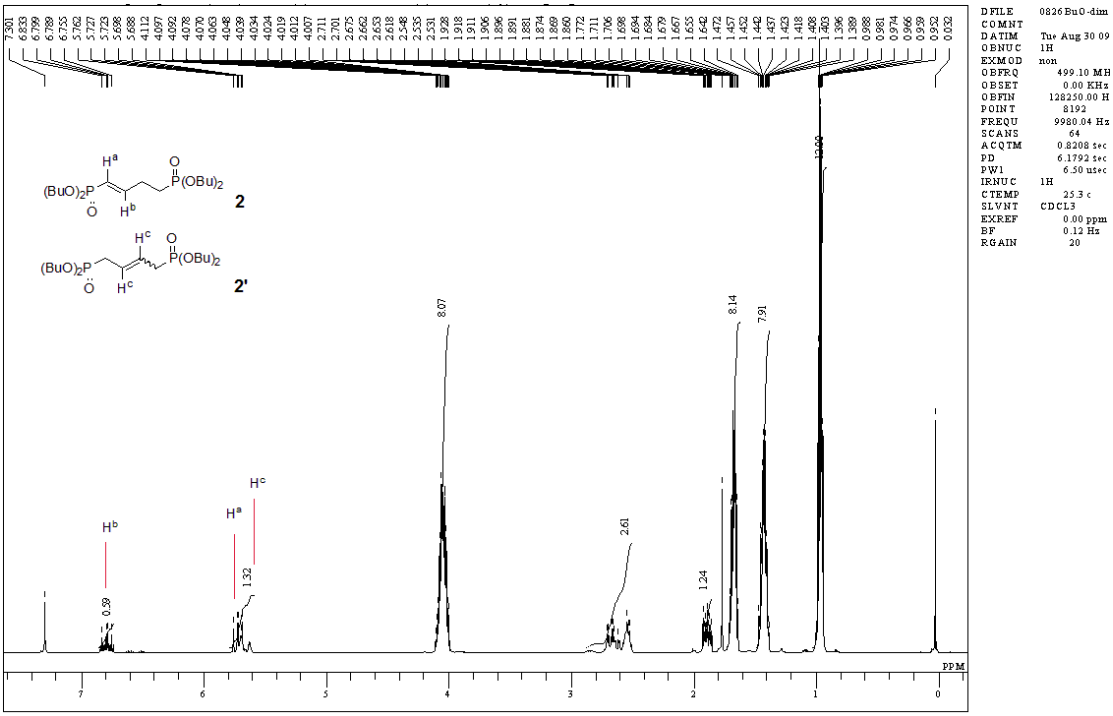
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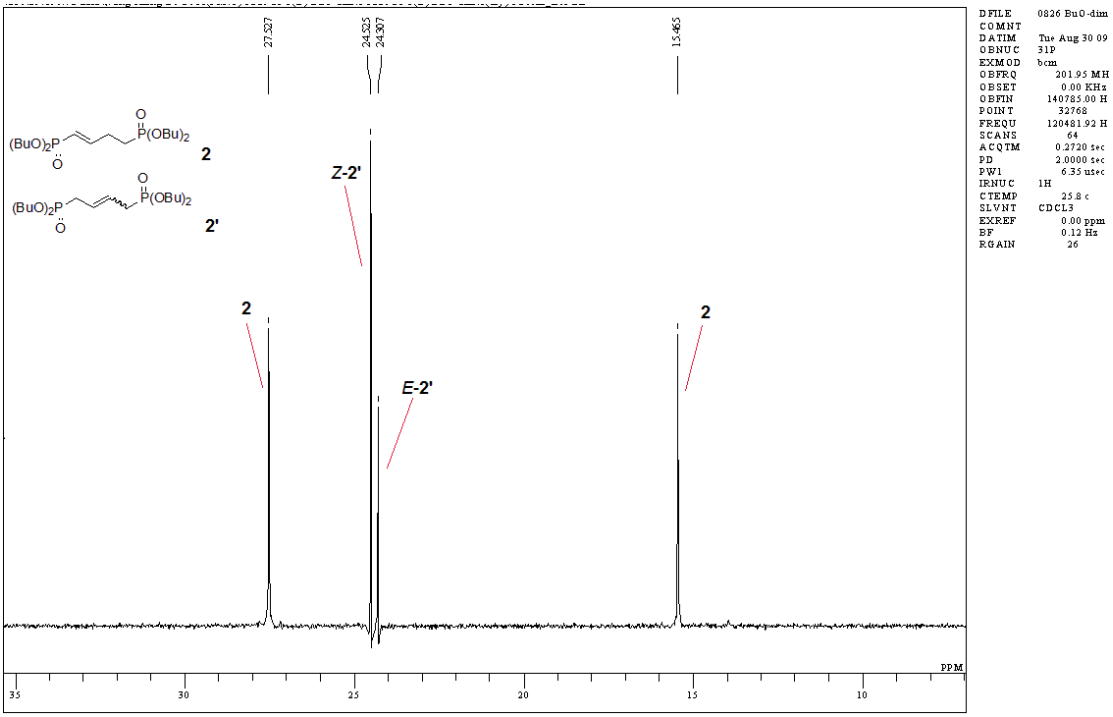
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Z-2'
2'
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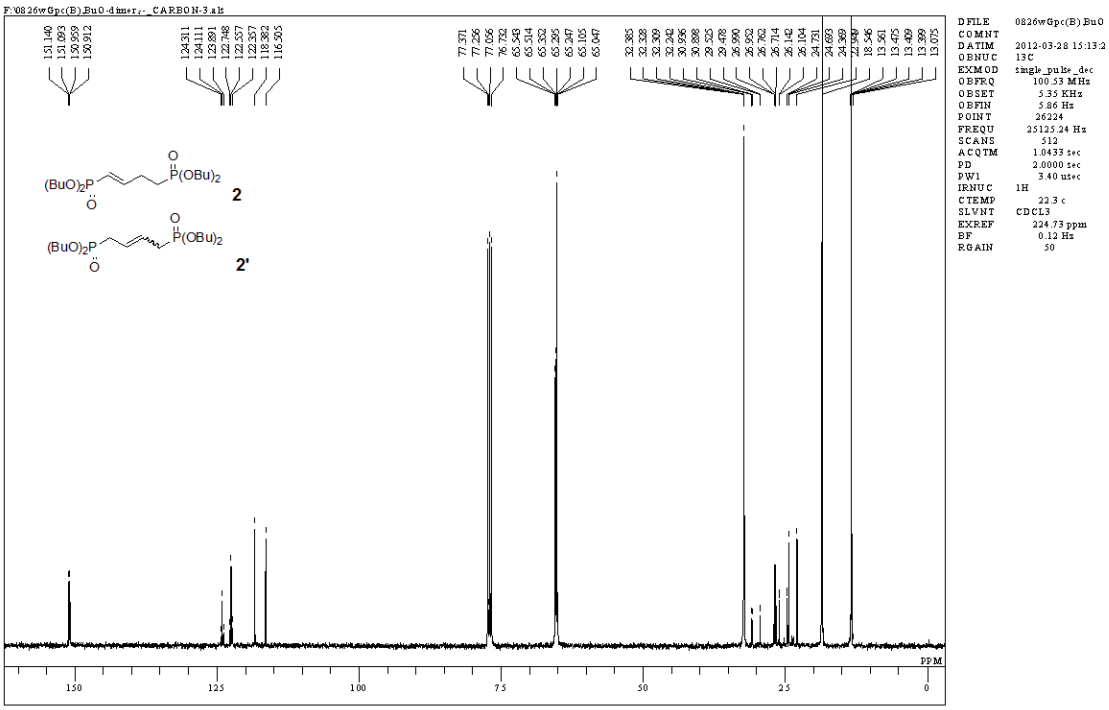
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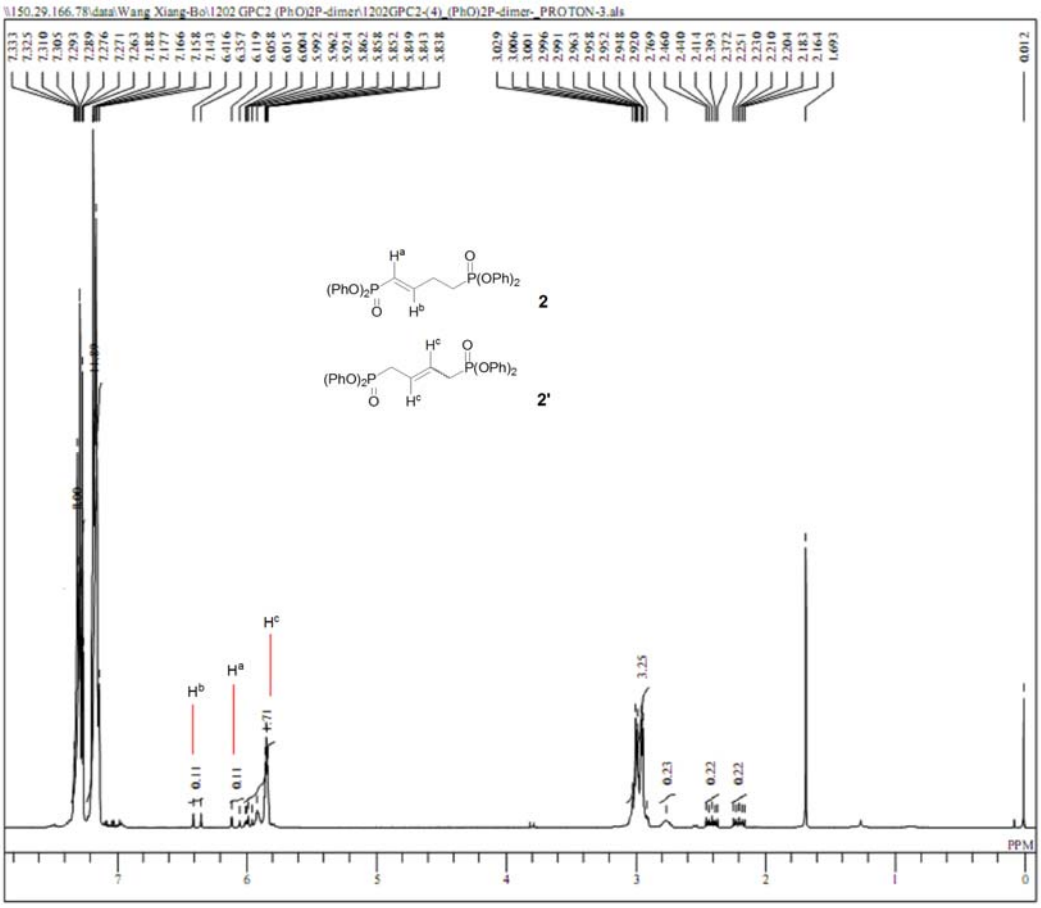
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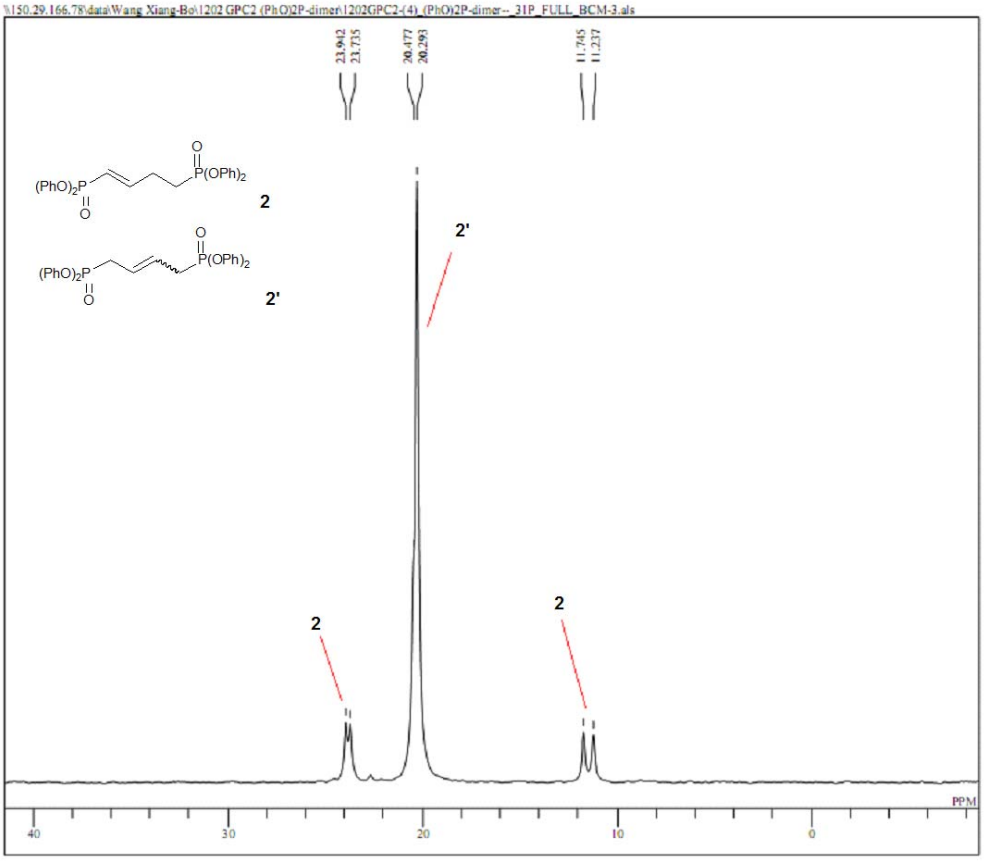
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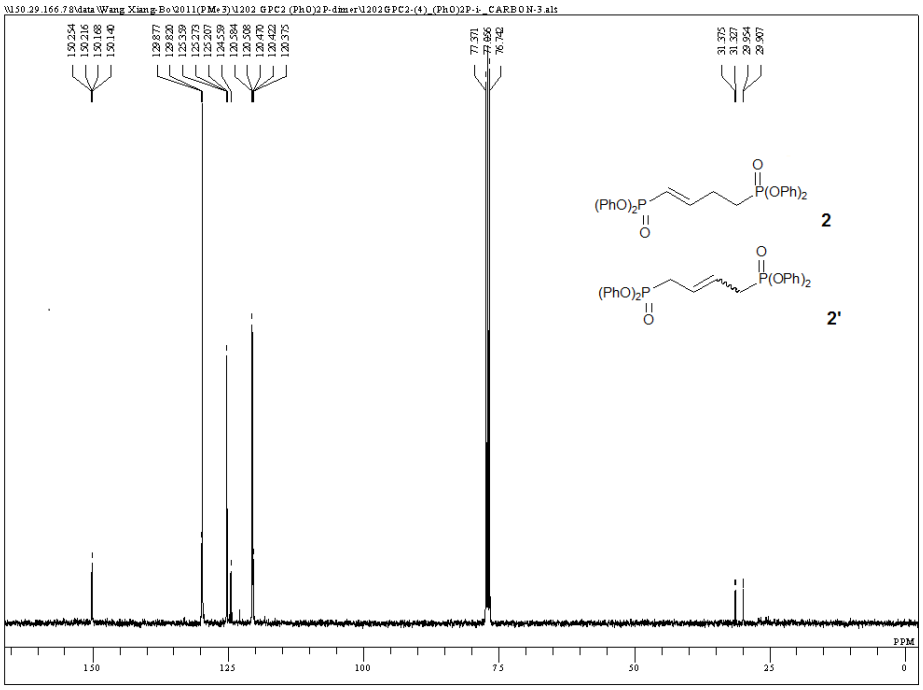

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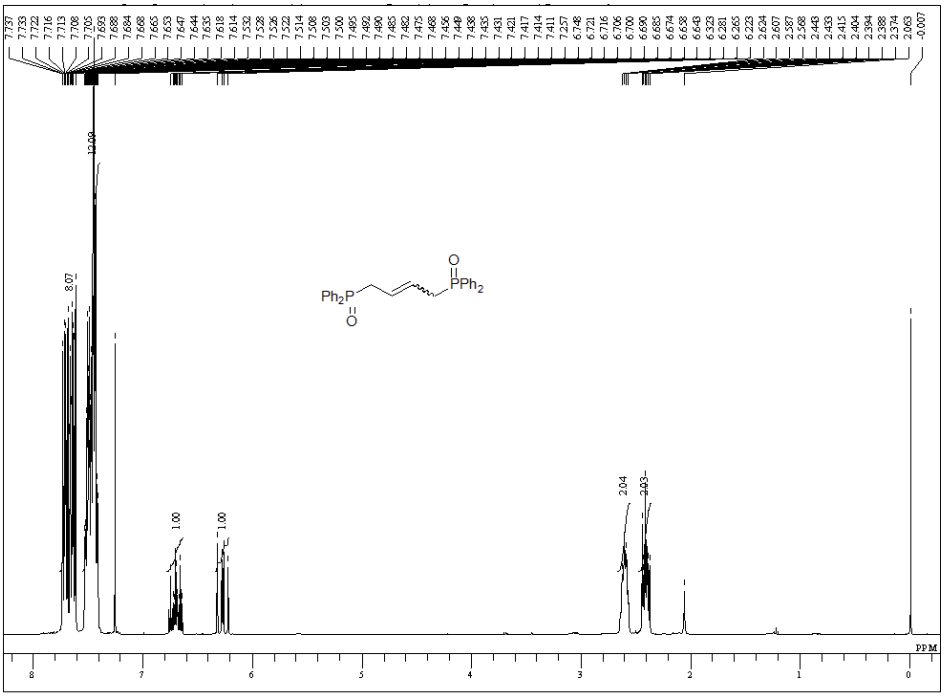

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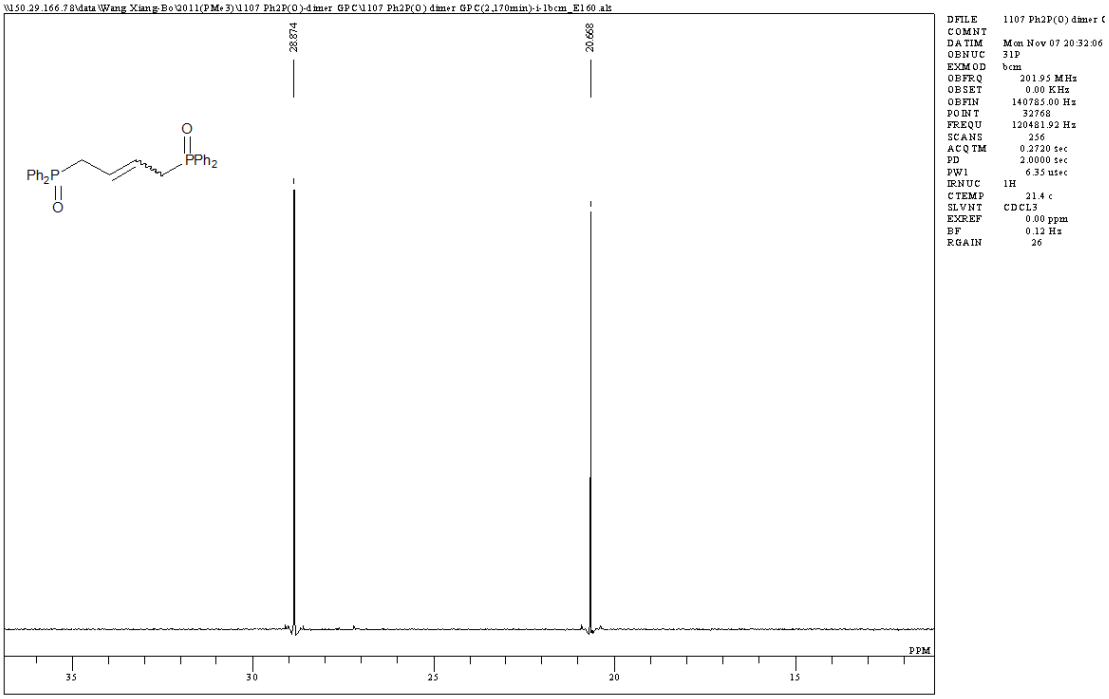
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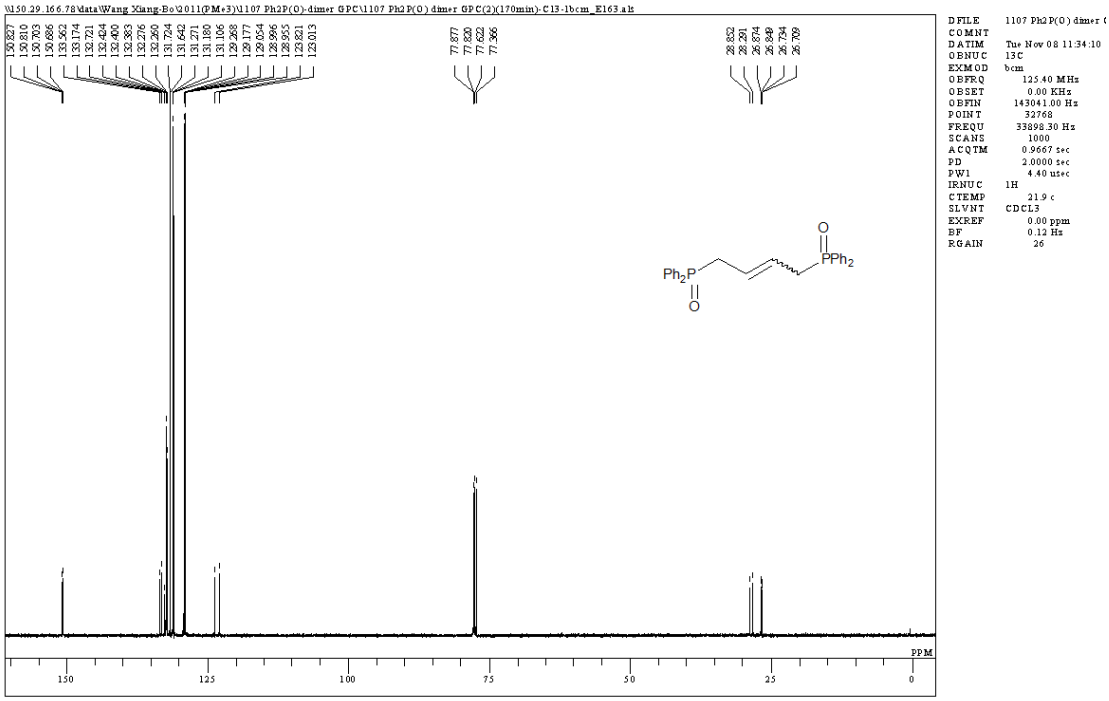
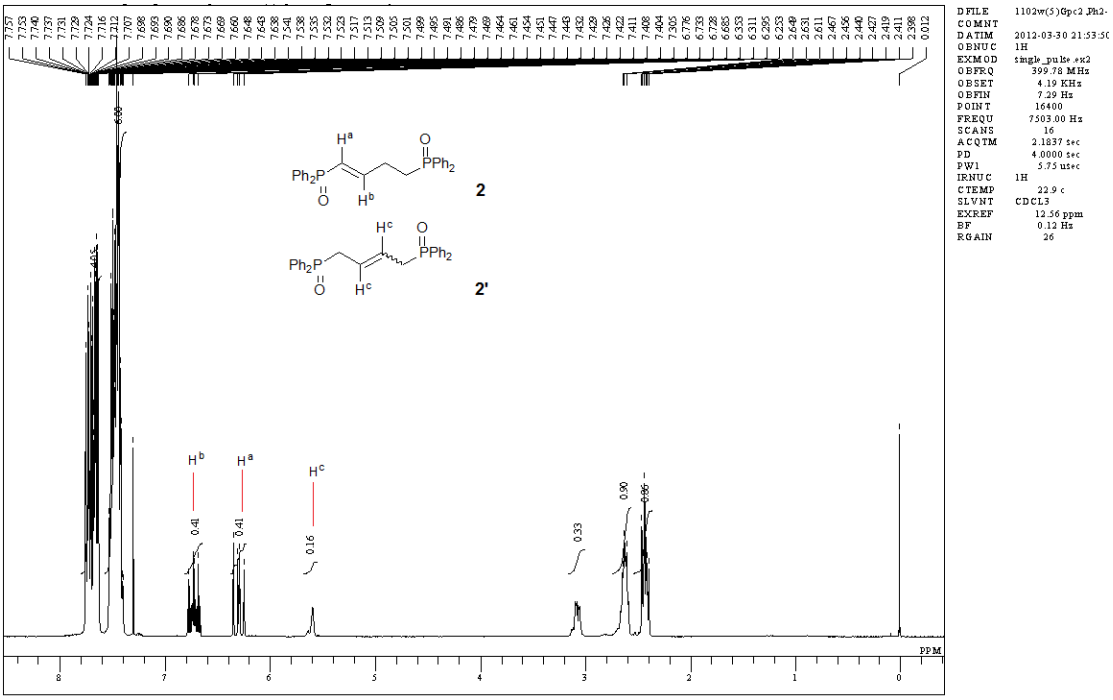
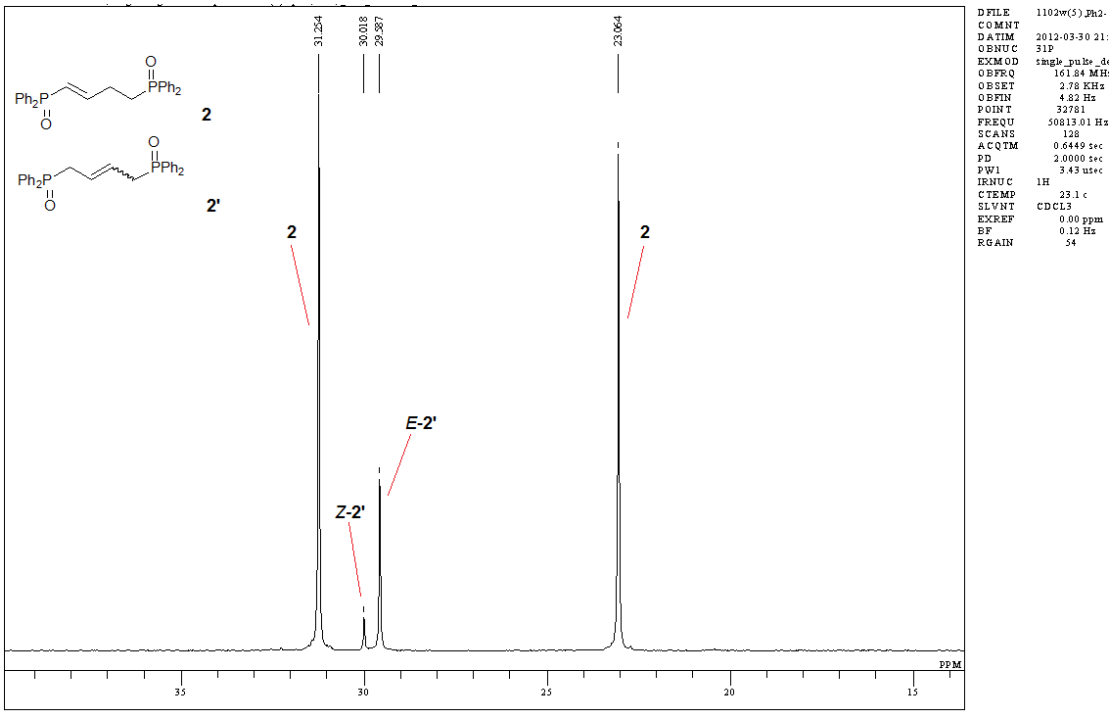
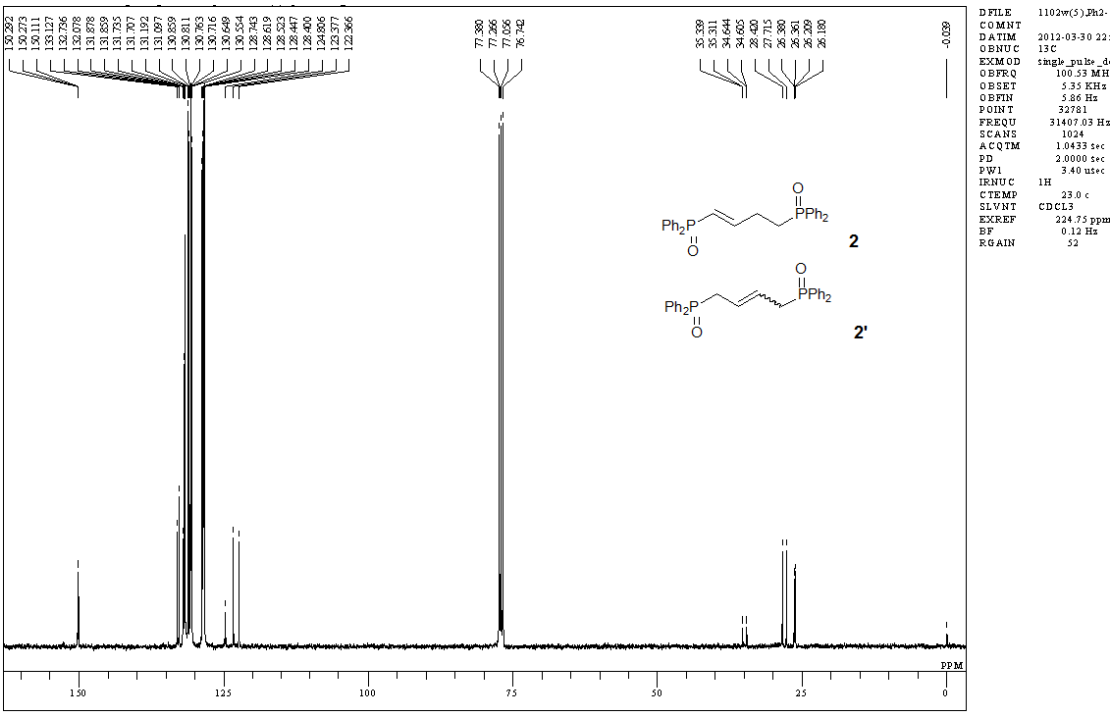
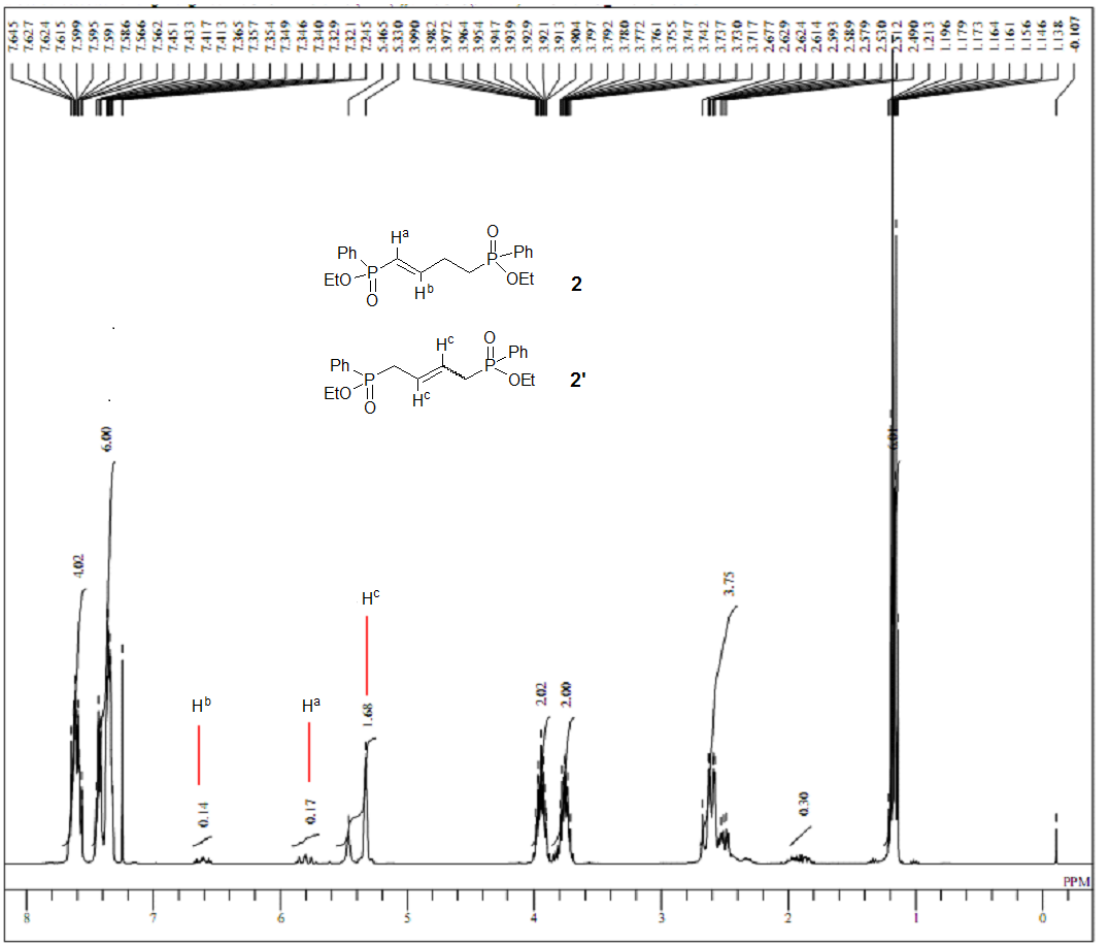
O
PPM
35
30
25
20
15
DFILE 1107 Ph2P(O) dimer (
COMNT
DATIM Mon Nov 07 20:32:06
OBNUC 31P
EXMOD bcm
OBFRQ 201.95 MHz
OBSET 0.00 KHz
OBFIN 140785.00 Hz
POINT 32768
FREQU 120481.92 Hz
SCANS 256
ACQTM 0.2720 sec
PD 2.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26

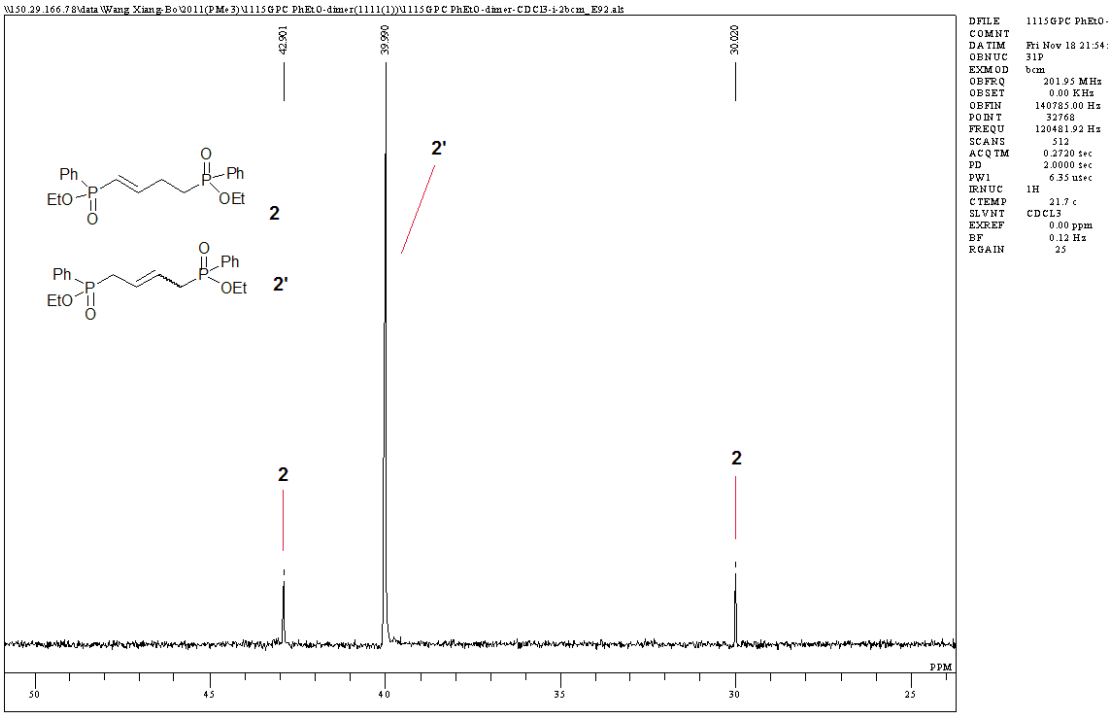

\\150.29.166.78\data\Wang Xiang-Bo\2011(PMe3)\1107 Ph2P(O)-dimer GPC\1107 Ph2P(O) dimer GPC(2)(170min)-C13-1bcm_E163.alt
150.807
150.810
150.703
150.686
133.562
133.174
132.721
132.424
132.400
132.383
132.276
132.260
131.724
131.642
131.271
131.186
131.106
129.268
129.177
129.054
128.996
128.955
123.821
123.013
77.877
77.820
77.622
77.366
28.852
28.291
25.874
25.849
25.734
25.709
O
PPh2
Ph2P
O
PPM
150
125
100
75
50
25
0
DFILE 1107 Ph2P(O) dimer (
COMNT
DATIM Tue Nov 08 11:34:10
OBNUC 13C
EXMOD bcm
OBFRQ 125.40 MHz
OBSET 0.00 KHz
OBFIN 143041.00 Hz
POINT 32768
FREQU 33898.30 Hz
SCANS 1000
ACQTM 0.9667 sec
PD 2.0000 sec
PW1 4.40 usec
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 26

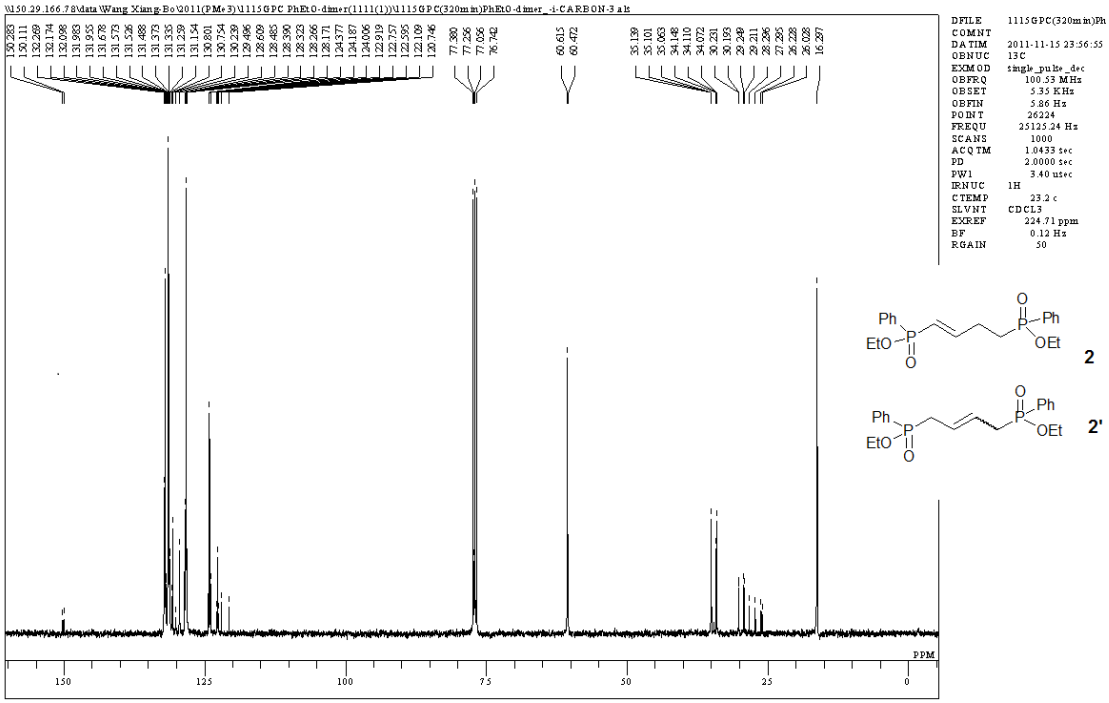

2
2'
H^a
H^b
H^c
0.44
0.41
0.16
0.33
0.90
0.86
PPM

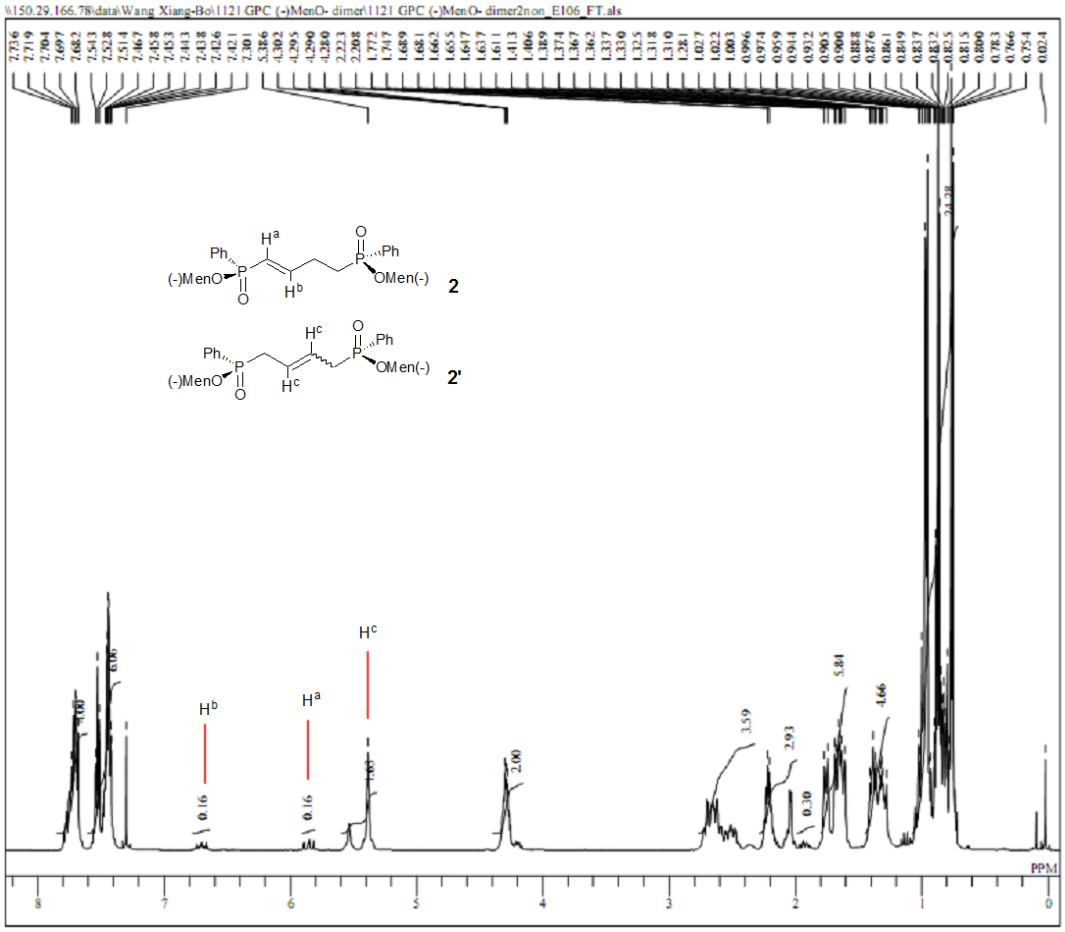

2
2'
31.254
30.018
29.587
23.064
E-2'
Z-2'
PPM

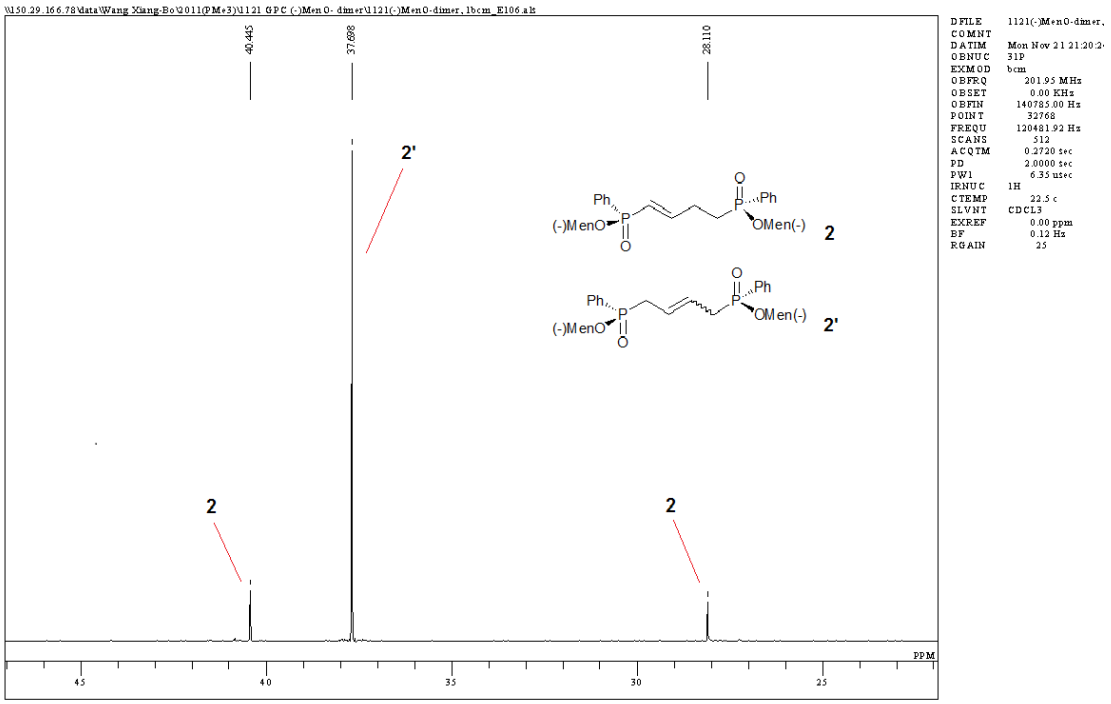

2
2'
PPM

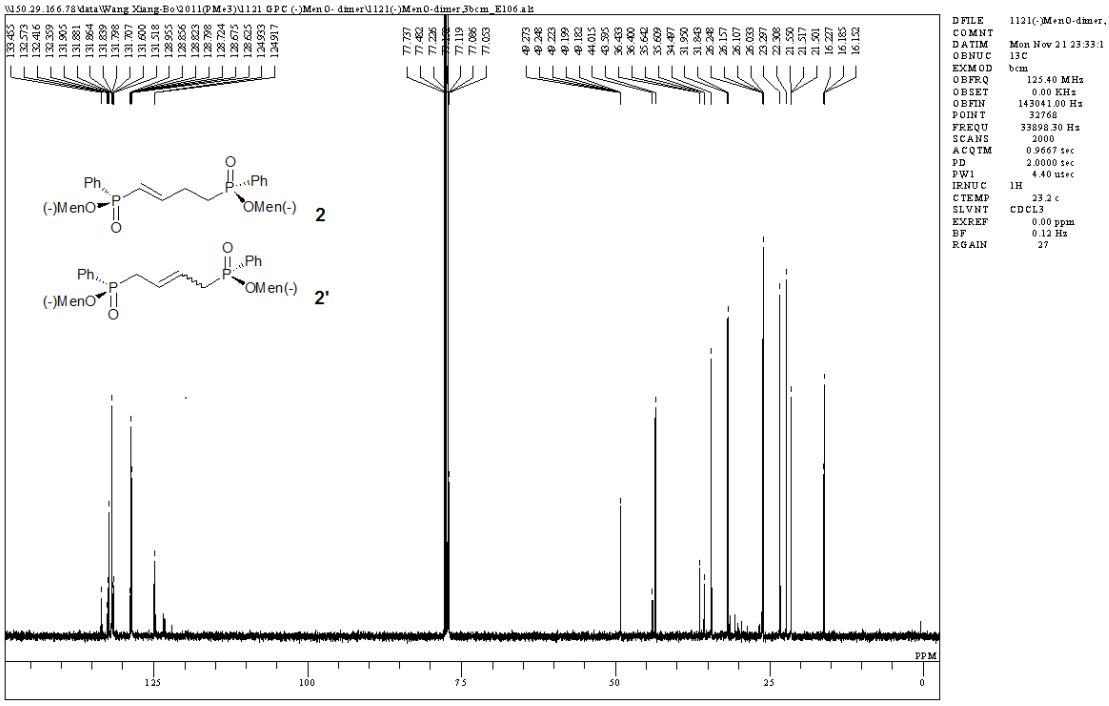

2
2'
Hᵃ
Hᵇ
Hᶜ
PPM

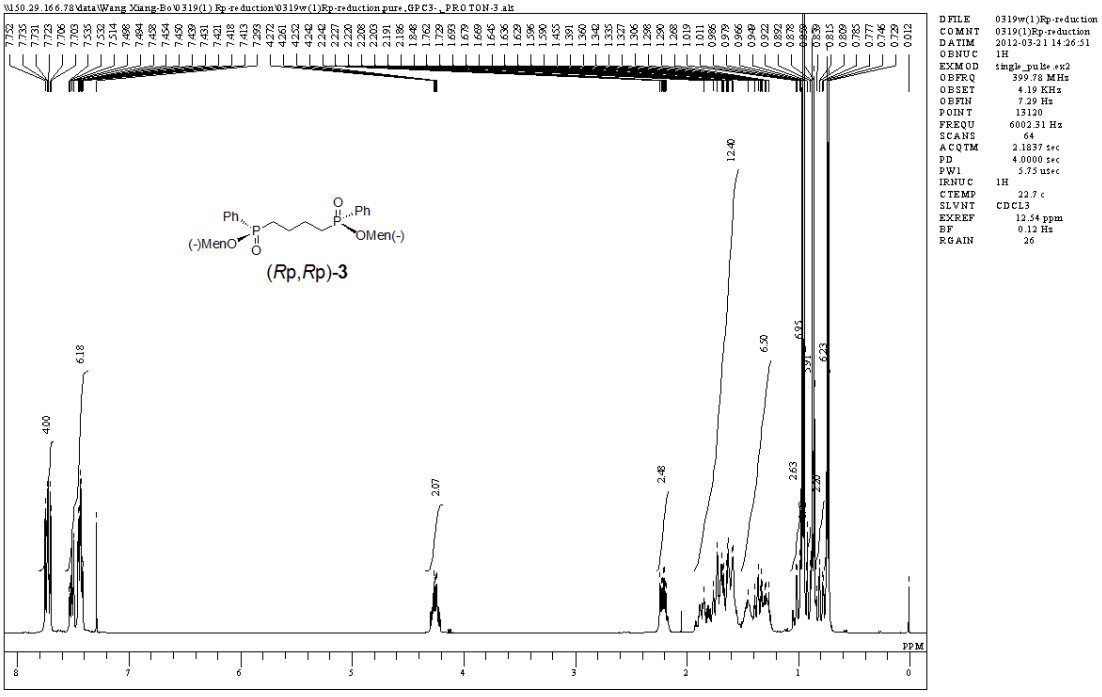

\\150.29.166.78\data\Wang Xiang-Bo\2011(PMe3)\1115GPC PhEtO-dimer(1111(1))\1115GPC PhEtO-dimer-CDCl3-i-2bcm_E92.alt
42.901
39.990
30.020
2'
2
2
2'
2
PPM
50
45
40
35
30
25
DFILE 1115GPC PhEtO-
COMNT
DATIM Fri Nov 18 21:54:
OBNUC 31P
EXMOD bcm
OBFRQ 201.95 MHz
OBSET 0.00 KHz
OBFIN 140785.00 Hz
POINT 32768
FREQU 120481.92 Hz
SCANS 512
ACQTM 0.2720 sec
PD 2.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25

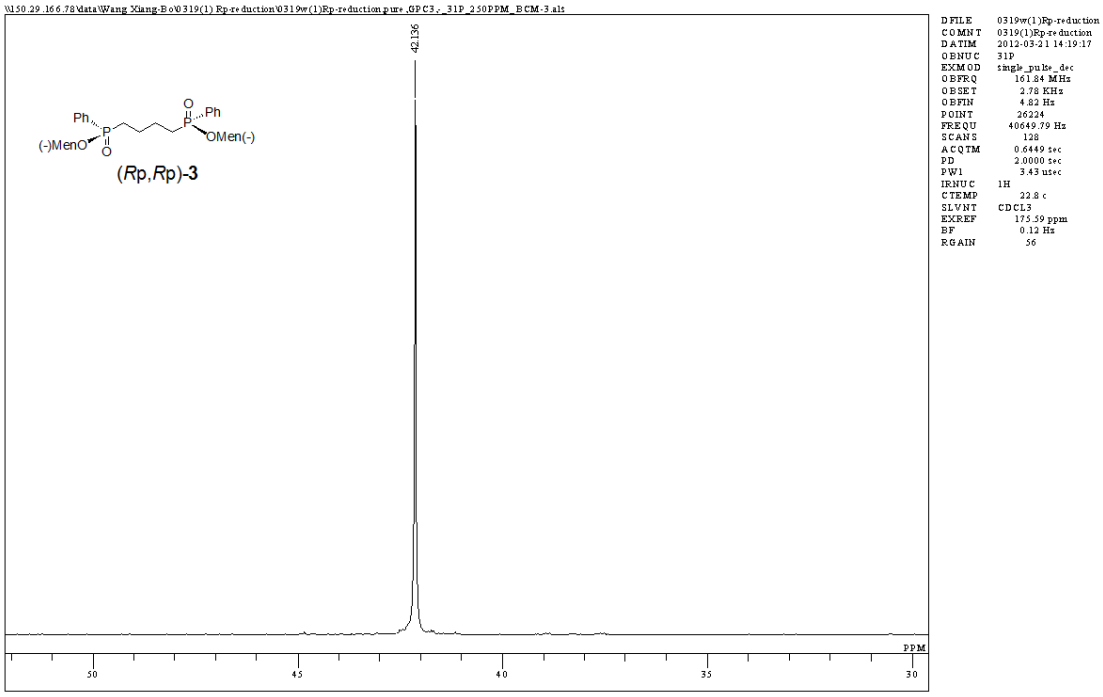

\\150.29.166.78\data\Wang Xiang-Bo\2011(PMe3)\1115GPC PhEtO-dimer(1111(1))\1115GPC(320min)PhEtO-dimer_-i-CARBON-3.alt
77.380
77.256
77.056
76.742
60.615
60.472
35.139
35.101
35.063
34.148
34.110
34.072
30.221
30.193
29.249
29.211
27.256
27.228
26.028
16.297
2
2'
PPM
150
125
100
75
50
25
0
DFILE 1115GPC(320min)Ph
COMNT
DATIM 2011-11-15 23:56:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.24 Hz
SCANS 1000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 224.71 ppm
BF 0.12 Hz
RGAIN 50

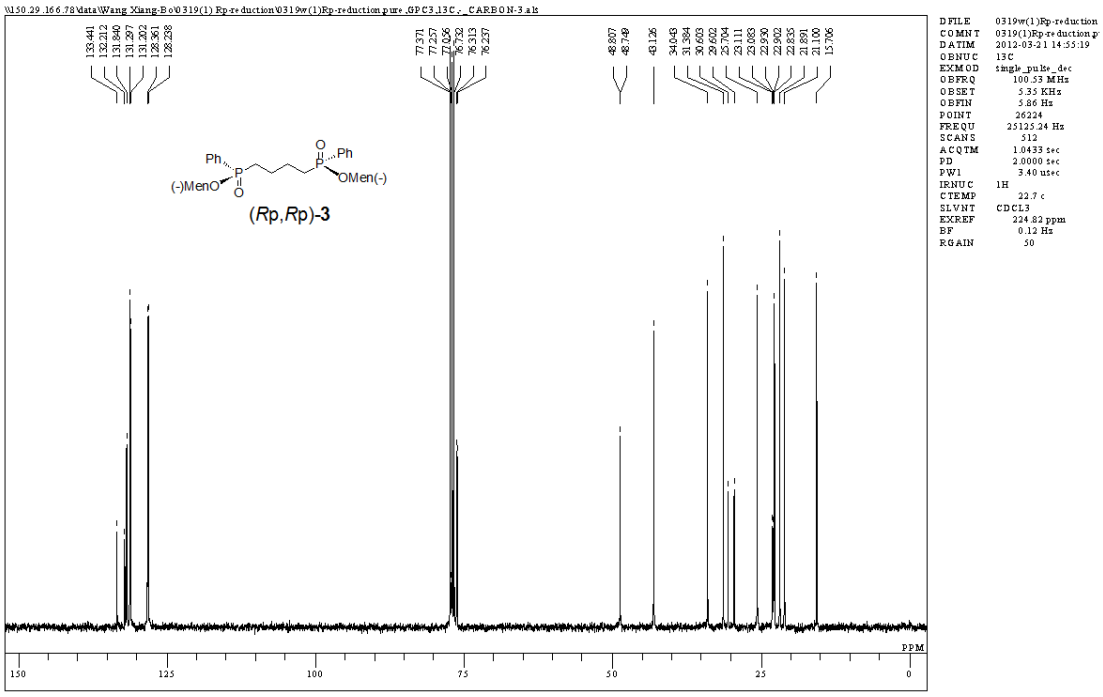

\\150.29.166.78\data\Wang Xiang-Bo\1121 GPC (-)MenO- dimer\1121 GPC (-)MenO- dimer2non_E106_FT.als
Ph
(-)MenO
P
O
Ha
Hb
OMen(-)
2
Hc
2'
Hb
Ha
Hc
PPM

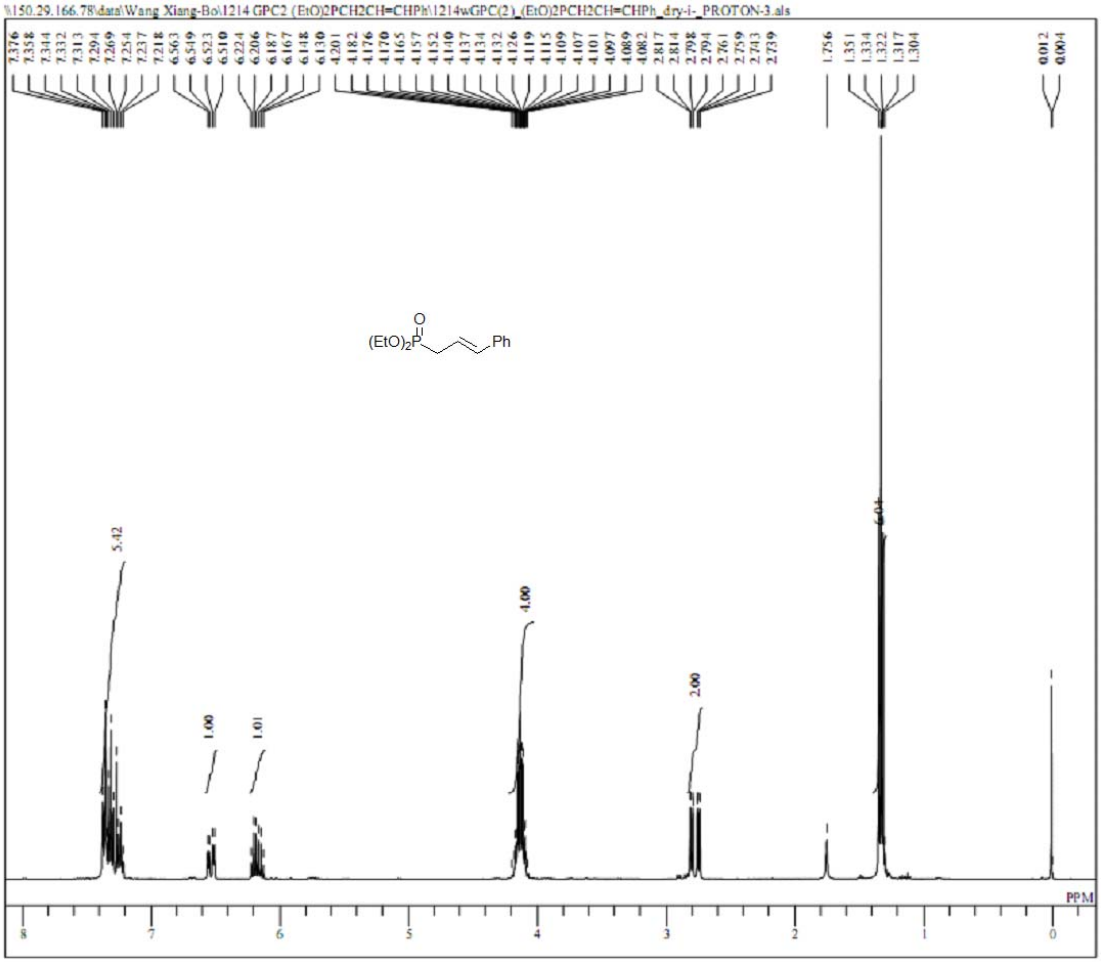

\\150.29.166.78\data\Wang Xiang-Bo\2011(PM+3)\1121 GPC (-)MenO- dimer\1121(-)MenO-dimer, 1bcm_E106.als
40.445
37.698
28.110
2'
2
2
2
2'
PPM
DFILE 1121(-)MenO-dimer,
COMNT
DATIM Mon Nov 21 21:20:2
OBNUC 31P
EXMOD bcm
OBFRQ 201.95 MHz
OBSET 0.00 KHz
OBFIN 140785.00 Hz
POINT 32768
FREQU 120481.92 Hz
SCANS 512
ACQTM 0.2720 sec
PD 2.0000 sec
PW1 6.35 usec
IRNUC 1H
CTEMP 22.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 25

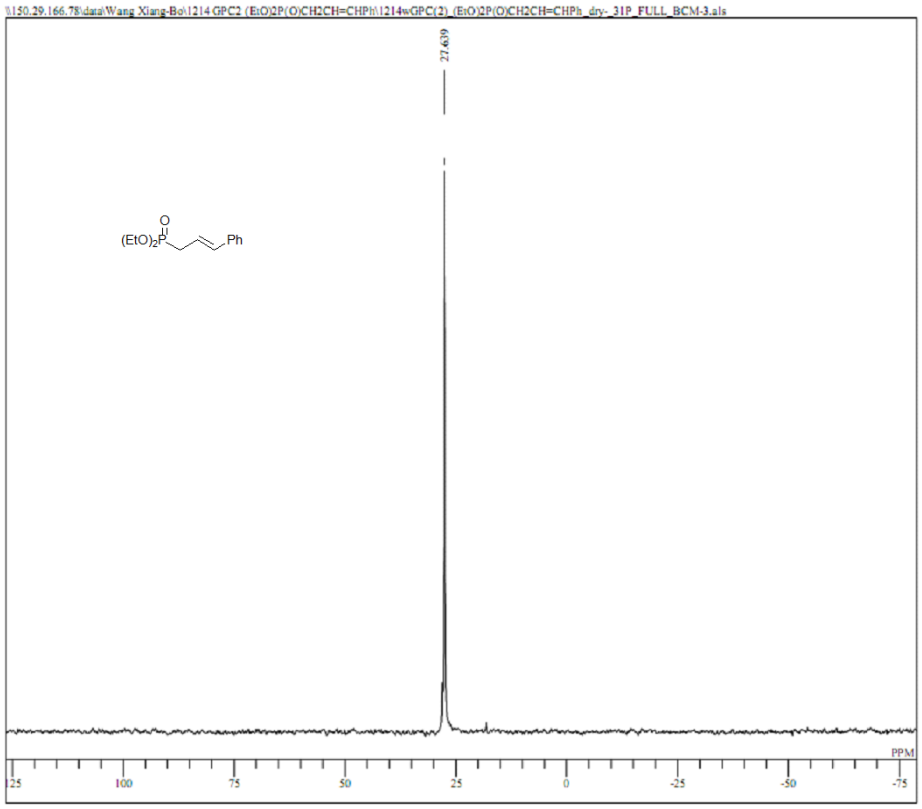

\\150.29.166.78\data\Wang Xiang-Bo\2011(PMe3)\1121 GPC (-)MenO- dimer\1121(-)MenO-dimer_3bcm_E106.als
Ph
(-)MenO
P
O
O
Ph
OMen(-)
2
2'
PPM
125
100
75
50
25
0

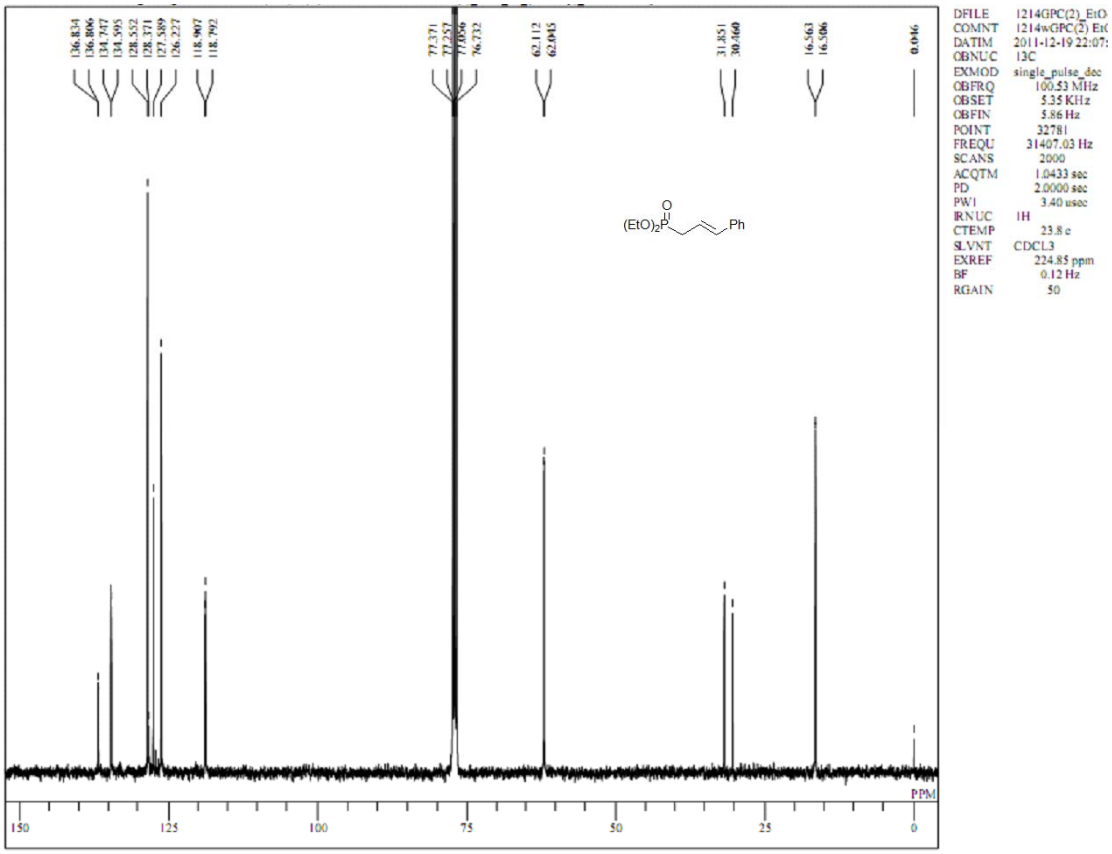

\\150.29.166.78\data\Wang Xiang-Bo\0319(1) Rp-reduction\0319w(1)Rp-reduction.pure,GPC3-,_PROTON-3.als
Ph
(-)MenO
P
O
O
Ph
OMen(-)
(Rp,Rp)-3
4.00
6.18
2.07
2.48
12.40
6.30
6.45
3.91
6.23
2.63
2.20
PPM
8
7
6
5
4
3
2
1
0

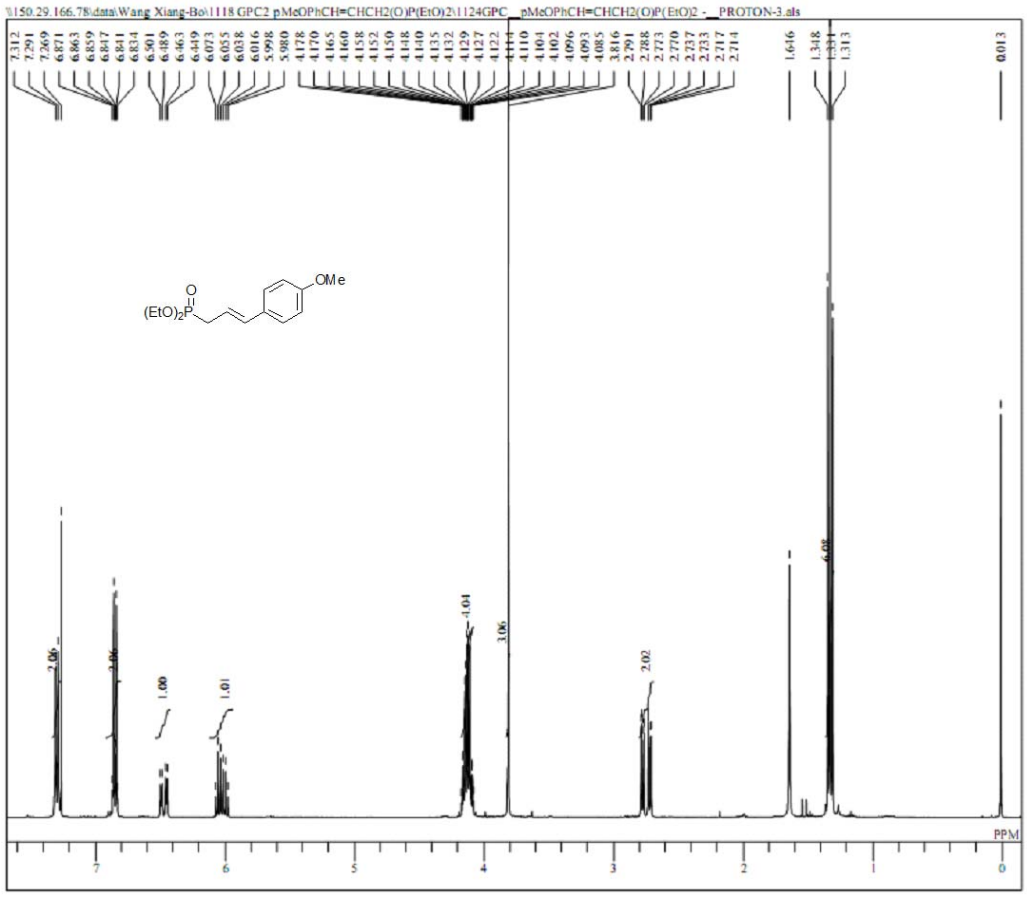

\\150.29.166.78\data\Wang Xiang-Bo\0319(1) Rp-reduction\0319w(1)Rp-reduction.pure,GPC3,_31P_250PPM_BCM-3.als
42.136
Ph
(-)MenO
OMen(-)
(Rp,Rp)-3
PPM
50
45
40
35
30
DFILE 0319w(1)Rp-reduction
COMNT 0319(1)Rp-reduction
DATIM 2012-03-21 14:19:17
OBNUC 31P
EXMOD single_pulse_dec
OBFRQ 161.84 MHz
OBSET 2.78 KHz
OBFIN 4.82 Hz
POINT 26224
FREQU 40649.79 Hz
SCANS 128
ACQTM 0.6449 sec
PD 2.0000 sec
PW1 3.43 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 175.59 ppm
BF 0.12 Hz
RGAIN 56

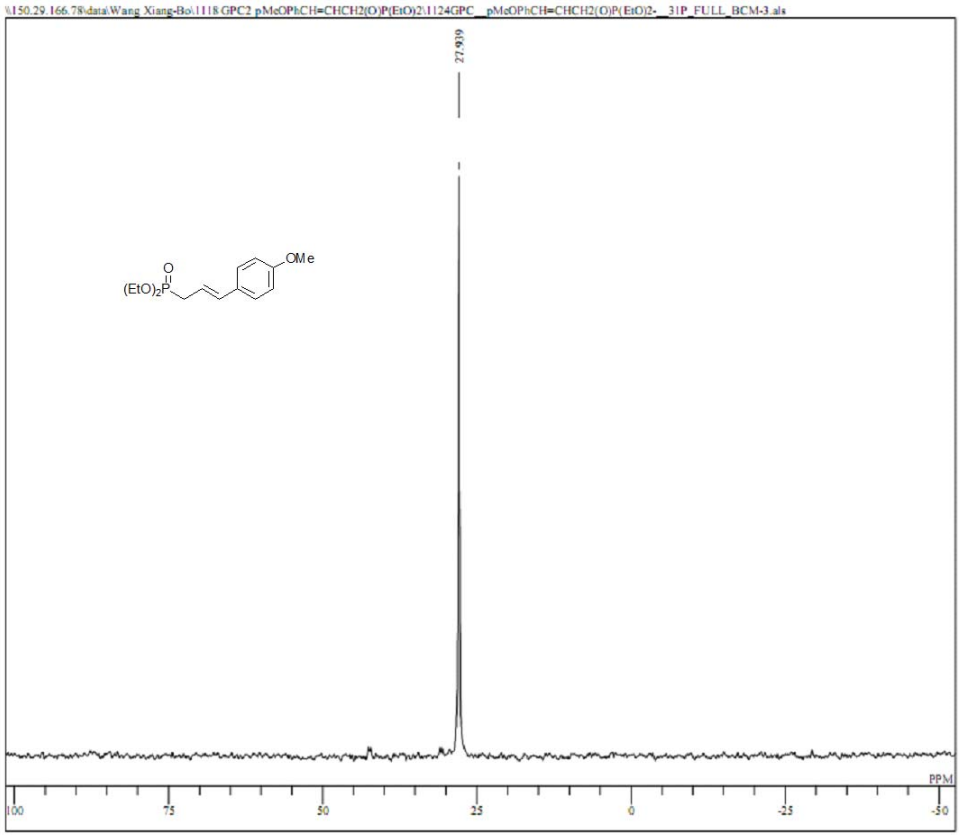

\\150.29.166.78\data\Wang Xiang-Bo\0319(1) Rp-reduction\0319w(1)Rp-reduction.pure,GPC3,13C,_CARBON-3.als
133.441
132.212
131.840
131.297
131.202
128.361
128.238
77.371
77.257
77.026
76.732
76.313
76.237
48.807
48.749
43.126
34.043
31.384
30.603
29.602
25.704
25.111
23.085
22.930
22.902
22.835
21.891
21.100
15.706
Ph
(-)MenO
OMen(-)
(Rp,Rp)-3
PPM
150
125
100
75
50
25
0
DFILE 0319w(1)Rp-reduction
COMNT 0319(1)Rp-reduction.p
DATIM 2012-03-21 14:55:19
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26224
FREQU 25125.24 Hz
SCANS 512
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 224.82 ppm
BF 0.12 Hz
RGAIN 50

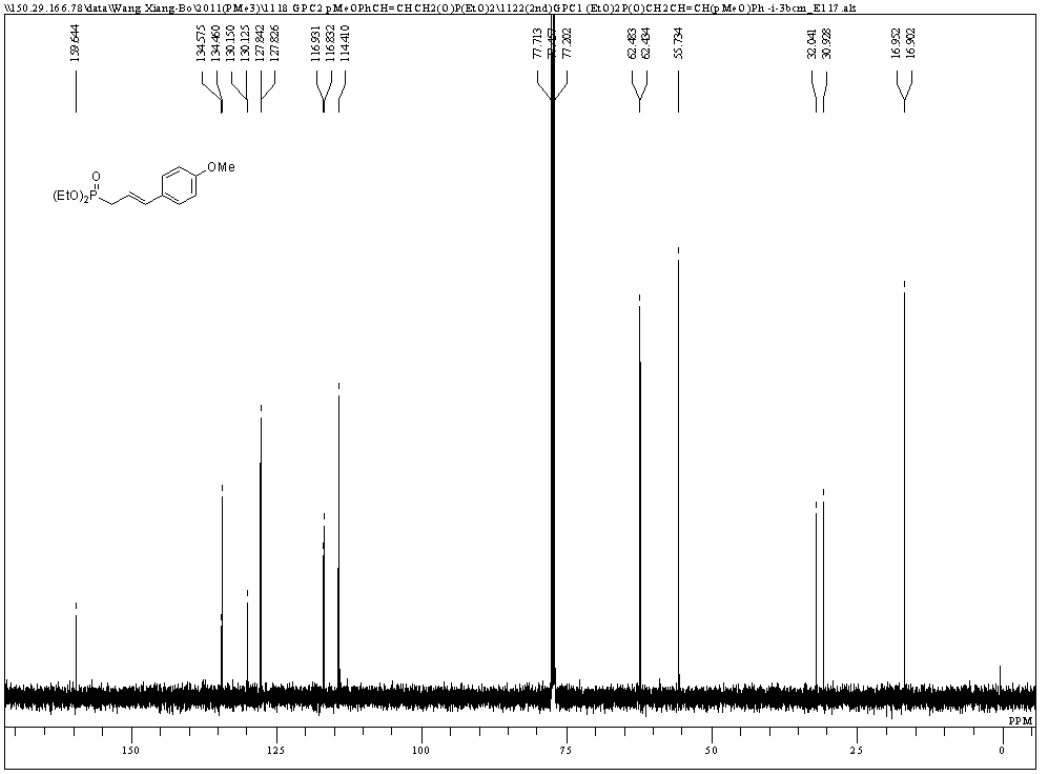

\\150.29.166.78\data\Wang Xiang-Bo\1214 GPC2 (EtO)2PCH2CH=CHPh\1214wGPC(2)_(EtO)2PCH2CH=CHPh_dry-i-_PROTON-3.als
7.376
7.358
7.344
7.332
7.313
7.294
7.269
7.254
7.237
7.218
6.563
6.549
6.523
6.510
6.224
6.206
6.187
6.167
6.148
6.130
4.201
4.182
4.176
4.170
4.165
4.157
4.152
4.140
4.137
4.134
4.132
4.126
4.119
4.115
4.109
4.107
4.101
4.097
4.089
4.082
2.817
2.814
2.798
2.794
2.761
2.759
2.743
2.739
1.756
1.351
1.334
1.322
1.317
1.304
0.012
0.004
O
(EtO)2P
Ph
5.42
1.00
1.01
4.00
2.00
6.04
PPM
8
7
6
5
4
3
2
1
0

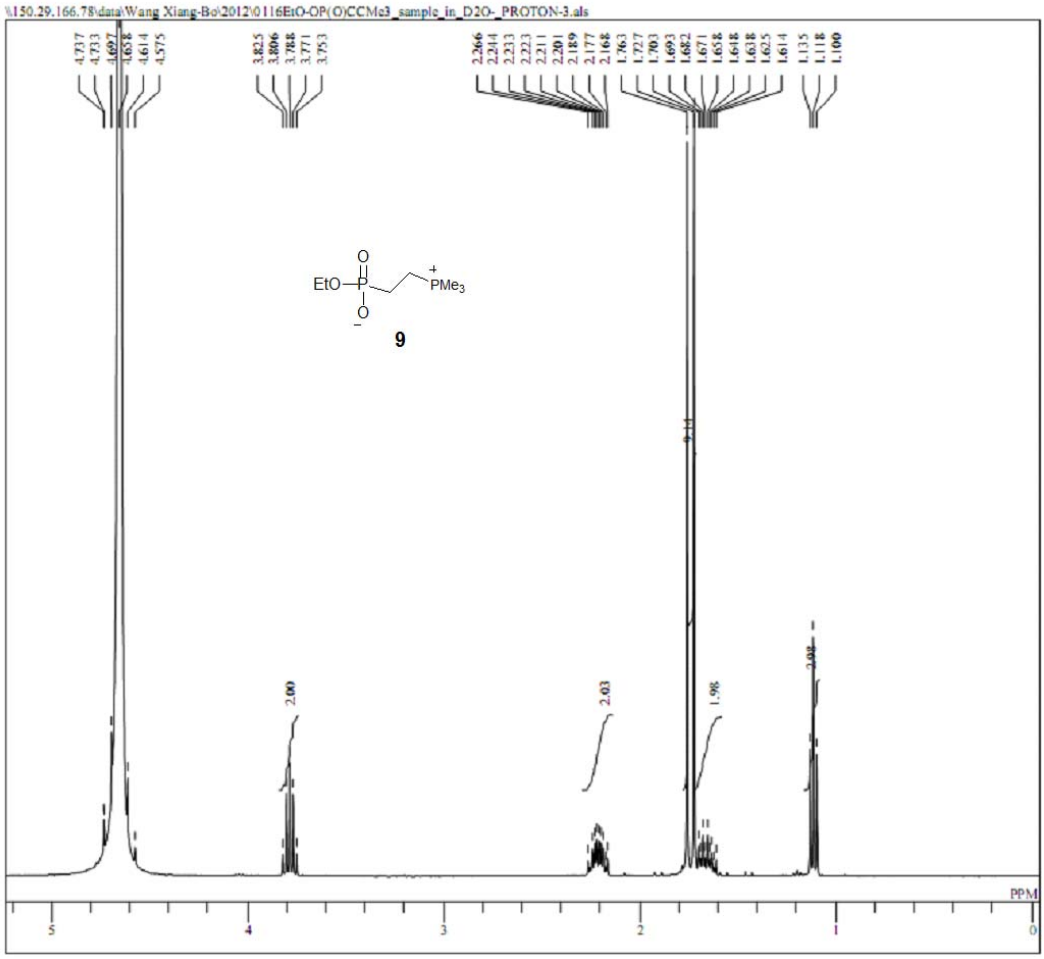

\\150.29.166.78\data\Wang Xiang-Bo\1214 GPC2 (EtO)2P(O)CH2CH=CHPh\1214wGPC(2)_(EtO)2P(O)CH2CH=CHPh_dry-_31P_FULL_BCM-3.als
27.639
O
(EtO)2P
Ph
PPM
125
100
75
50
25
0
-25
-50
-75

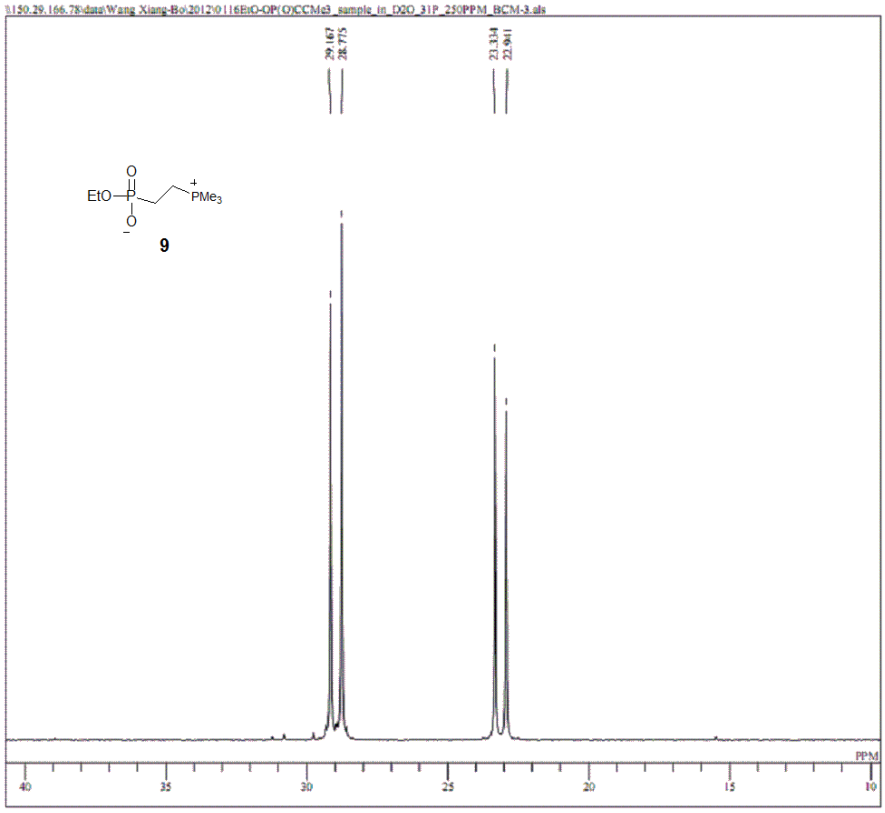

136.834
136.806
134.747
134.595
128.532
128.371
127.589
126.227
118.907
118.792
77.371
77.057
76.744
76.732
62.112
62.045
31.851
30.560
16.563
16.506
0.046
O
(EtO)2P
Ph
PPM
150
125
100
75
50
25
0
DFILE 1214GPC(2)_EtO
COMNT 1214wGPC(2) Et(
DATIM 2011-12-19 22:07:
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32781
FREQU 31407.03 Hz
SCANS 2000
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 224.85 ppm
BF 0.12 Hz
RGAIN 50

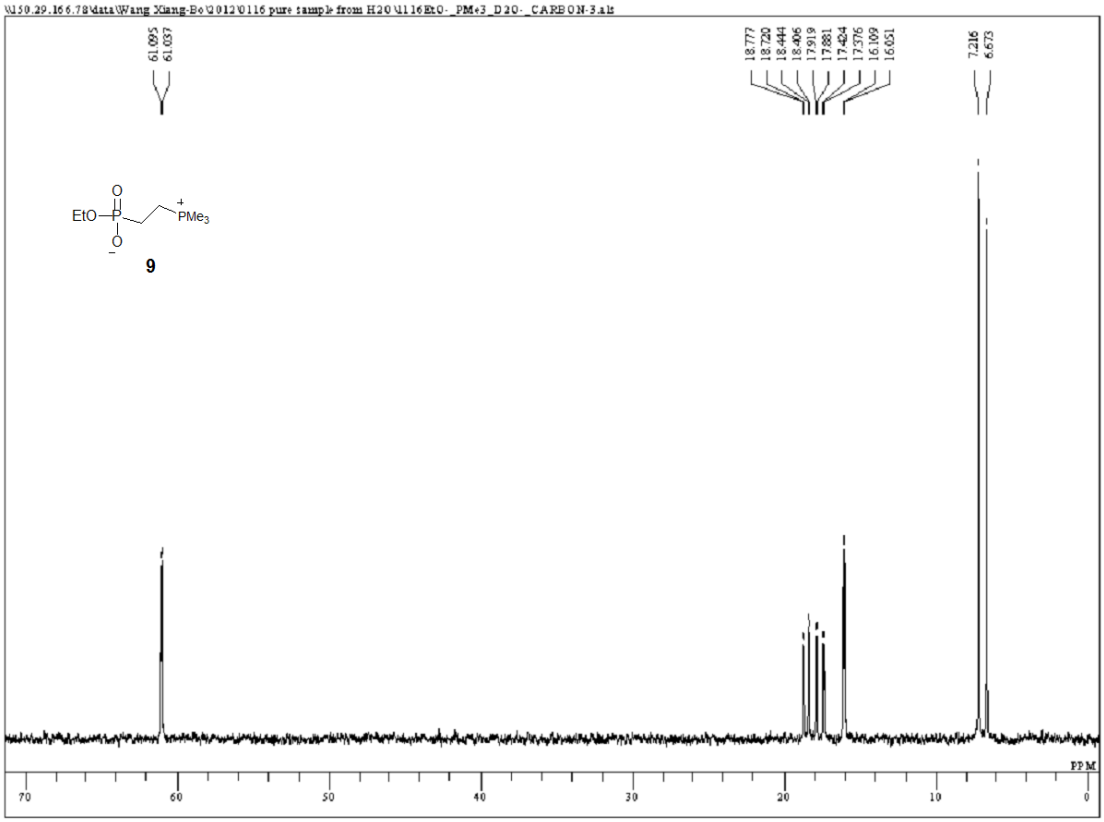

\\150.29.166.78\data\Wang Xiang-Bo\1118 GPC2 pMeOPhCH=CHCH2(O)P(EtO)2\1124GPC__pMeOPhCH=CHCH2(O)P(EtO)2 -__PROTON-3.als
7.312
7.291
7.269
6.871
6.863
6.859
6.847
6.841
6.834
6.501
6.489
6.463
6.449
6.073
6.055
6.038
6.016
5.998
5.980
4.178
4.170
4.165
4.160
4.158
4.152
4.150
4.148
4.140
4.135
4.132
4.129
4.127
4.122
4.114
4.110
4.104
4.102
4.096
4.093
4.085
3.816
2.991
2.988
2.773
2.770
2.737
2.733
2.717
2.714
1.616
1.348
1.334
1.313
0.013
OMe
O
(EtO)2P
2.06
2.06
1.00
1.01
4.04
3.06
2.02
6.08
PPM
7
6
5
4
3
2
1
0


\\150.29.166.78\data\Wang Xiang-Bo\1118.GPC2.pMeOPhCH=CHCH2(O)P(EtO)2\1124GPC__pMeOPhCH=CHCH2(O)P(EtO)2-__31P_FULL_BCM-3.als
27.939
OMe
(EtO)2P
O
PPM
100
75
50
25
0
-25
-50


\\150.29.166.78\data\Wang Xiang-Bo\2011(PMe3)\1118 GPC2 pMeOPhCH=CHCH2(O)P(EtO)2\1122(2nd)GPC1 (EtO)2P(O)CH2CH=CH(pMeO)Ph -i-3bcm_E117.als
139.644
134.575
134.460
130.150
130.125
127.842
127.826
116.931
116.832
114.410
77.713
77.202
62.483
62.434
55.734
32.041
30.928
16.952
16.902
OMe
(EtO)2P
O
PPM
150
125
100
75
50
25
0






\\150.29.166.78\data\Wang Xiang-Bo\2012\0116 pure sample from H20\1116EtO-_PMe3_D20-_CARBON-3.als
61.095
61.037
18.777
18.720
18.444
18.406
17.919
17.881
17.404
17.376
16.109
16.051
7.216
6.673
EtO
P
PMe3
9
PPM
70
60
50
40
30
20
10
0