Phosphorus-Containing Bis-allenes: Synthesis and Heterocyclization Reactions Mediated by Iodine or Copper Dibromide

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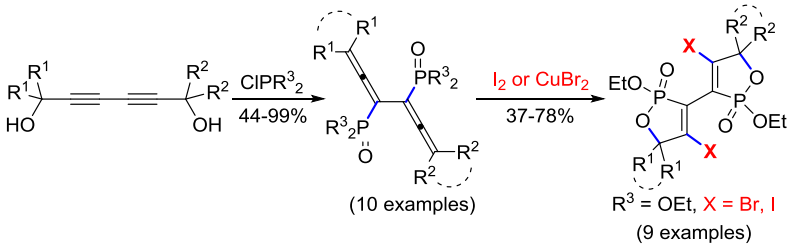
Abstract: Bisphosphorylallenes are easily obtained in multigram scale from the Wittig-type rearrangement of bispropargyl alcohols. Unlike other conjugated bis-allenes, these reagents give a double cyclization mediated by iodine or copper dibromide leading to the formation of bis-1,2-oxaphospholenes.



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1. General informations

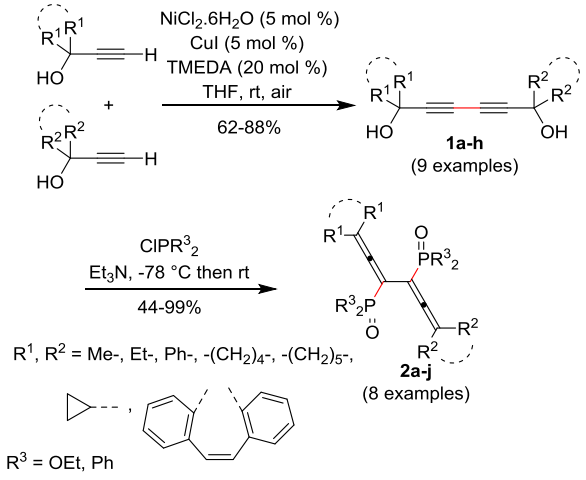
All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques otherwise stated. Solvents were carefully dried by conventional or were purified with an MBRAUN Solvent Purification System. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a bruker Avance 400 spectrometer. The resonances were calibrated relative to the residual deuterated solvent peaks and are reported with positive values downfield from TMS. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. HRMS were obtained from dichloromethane solutions with a Xevo G2 Q TOF spectrometer by the electrospray method or with a LC-TOF spectrometer (Micromass).

2. Bis alkynyl diols 1a-1h

2.1. Typical procedure procedure

In a round bottom flask were introduced successively CuI (5 mol%), $NiCl_2.6H_2O$ (5 mol%) and 2-Methyl-3-butyn-2-ol (1 eq) in THF (0.66 $mol.l^{-1}$) then TMEDA was added (20 mol%). The reaction mixture was stirred at room temperature under air atmosphere for 12 hours. After completion of the reaction, as indicated by TLC, THF was removed under reduced pressure. The reaction was diluted with ethyl acetate and washed with HCl 5%. The organic layer was filtered and washed with water, brine, and dried over magnesium sulfate. After concentration under vacuum, the product was purified by crystallization in the appropriate solvent or by a chromatography on silica gel.

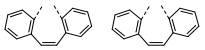
Reactions were carried out using 5.00 to 10.00 g scale of alkyne. Larger quantities led to lower yields. If more diyne diols **1a-h** are needed, we recommend to use several flasks in parallel.



Scheme 1. Synthesis of bisphosphonylallenes **2a-j** from diyne-diols **1a-h**.

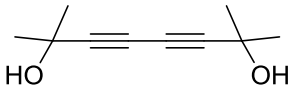
Table 1. Yields of diynes **1a-h** and bis-allenes **2a-i**.

diyne diol	R^1	R^2	yield (%)[a]	bis-allene	R^3	yield (%)[a]
1a	Me-	Me-	82	**2a**	OEt	82
1b	Et-	Et-	76	**2b**	OEt	92
1c			70	**2c**	OEt	-
1d	-$(CH_2)_4$-	-$(CH_2)_4$-	80	**2d**	OEt	44
1e	-$(CH_2)_5$-	-$(CH_2)_5$-	88	**2e**	OEt	99
1f	Ph-	Ph-	76	**2f**	OEt	83
1g	Ph-	Me-	62	**2g**	OEt	62

1h			85	**2h**	OEt	61		-$(CH_2)_5$-	-$(CH_2)_5$-	**2j**	Ph	71
	Me-	Me-		**2i**	Ph	82						

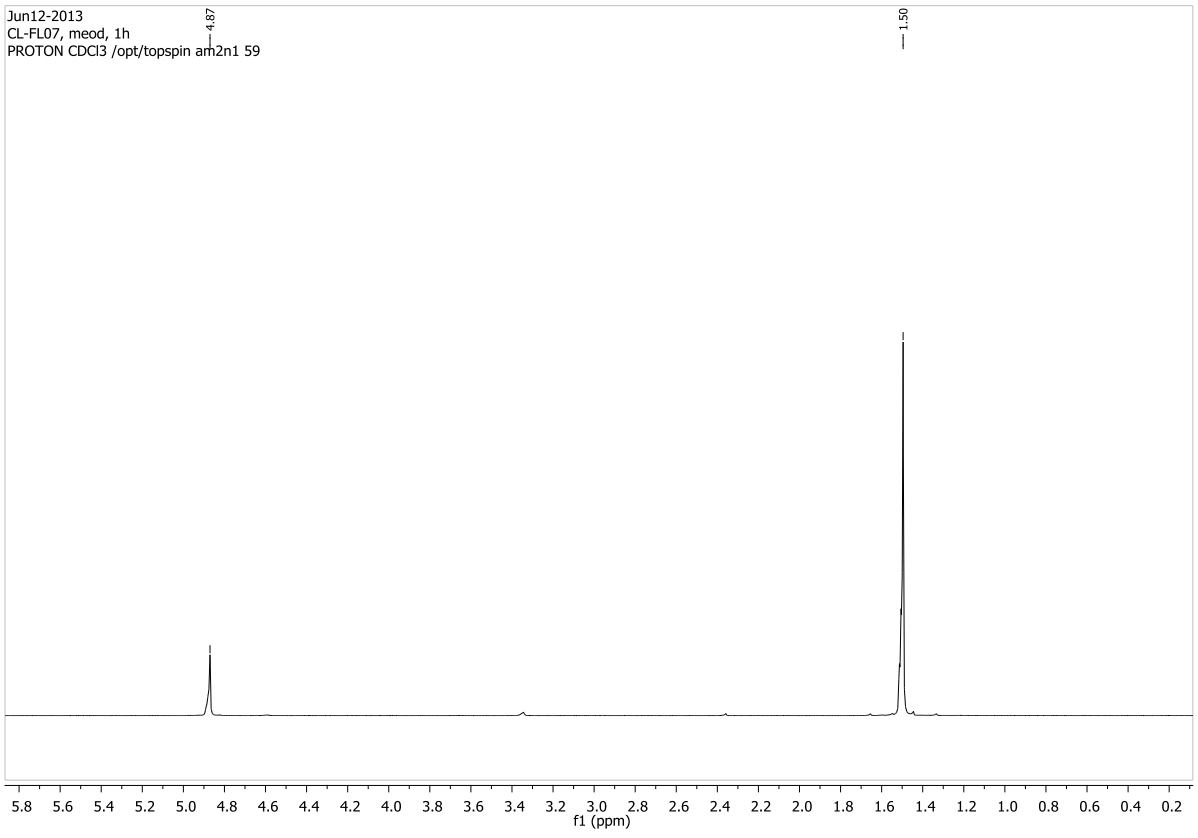
2.2. 2,7-Dimethylocta-3,5-diyne-2,7-diol (1a)

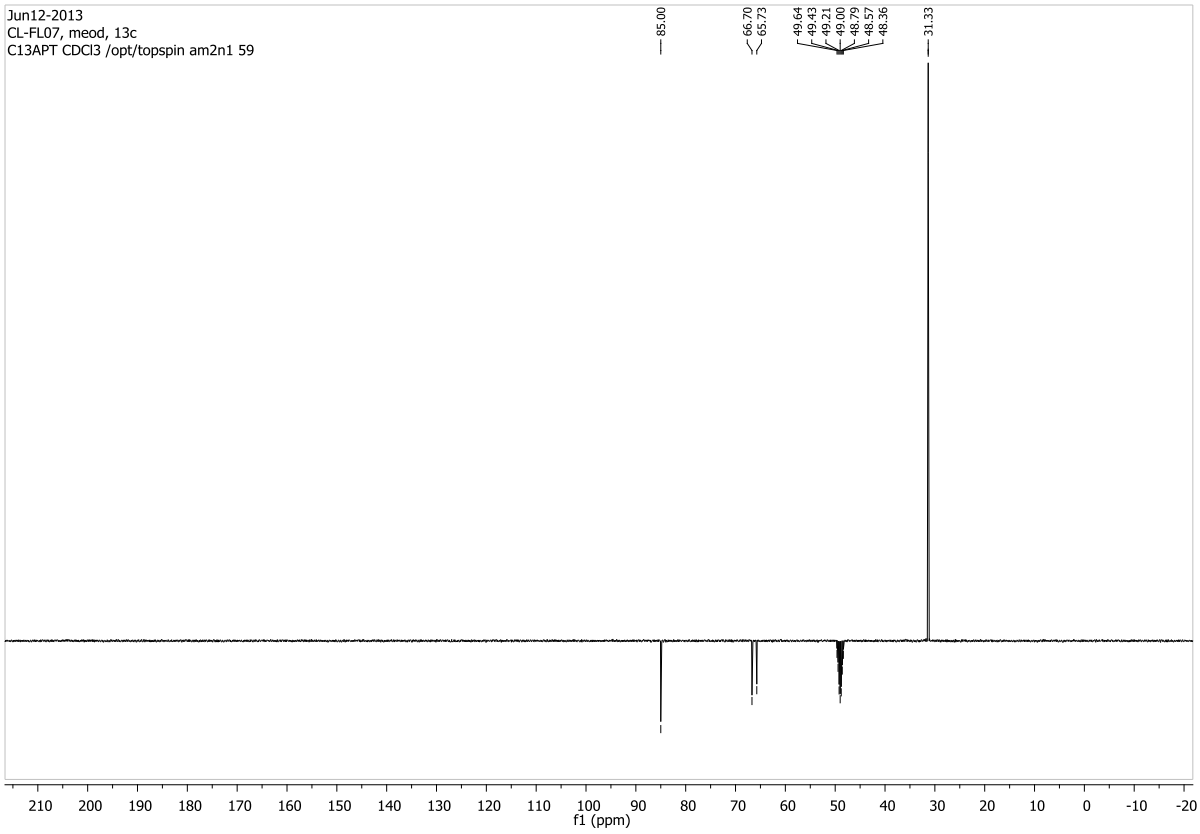
This product is also described in Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969. Doi: 10.1021/jo011098i



Reaction was carried out using 2-methyl-3-butyn-2-ol (4.00 g, 47.6 mmol). The crude product was purified by recrystallization in toluene. The resulting solid is filtered off and dried under vacuum. White solid, 3.24 g, yield = 82%.

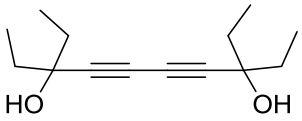
^{1}H NMR (CD_3OD, 400,13 MHZ) δ (ppm) = 1.50 (s, 12H, CH_3); ^{13}C NMR (CD_3OD, 100,61 MHZ) δ (ppm) = 31.3 (s, CH_3), 65.7 (s, CC), 66.7 (s, CO), 85.0 (s, CC).




Jun12-2013
CL-FL07, meod, 13c
C13APT CDCl3 /opt/topspin am2n1 59
85.00
66.70
65.73
49.64
49.43
49.21
49.00
48.79
48.57
48.36
31.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

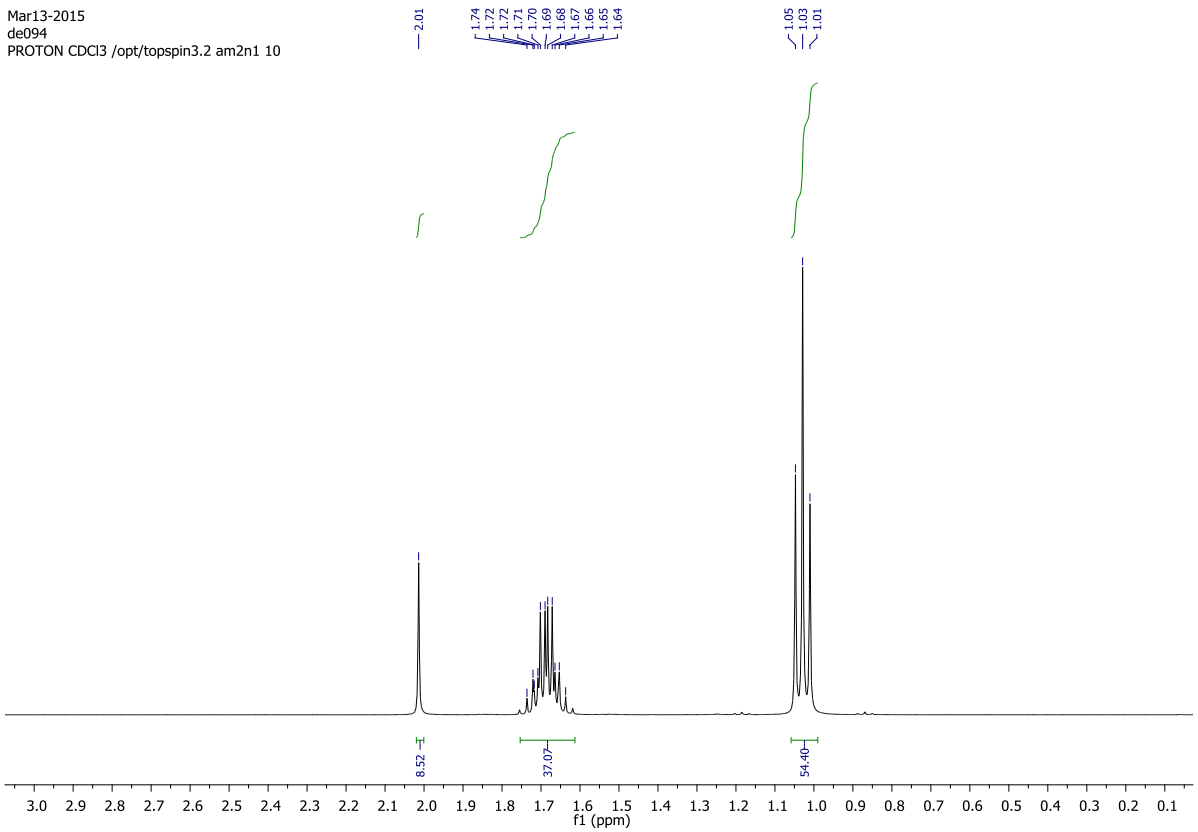
2.3. 3,8-Diethyldeca-4,6-diyne-3,8-diol (1b)

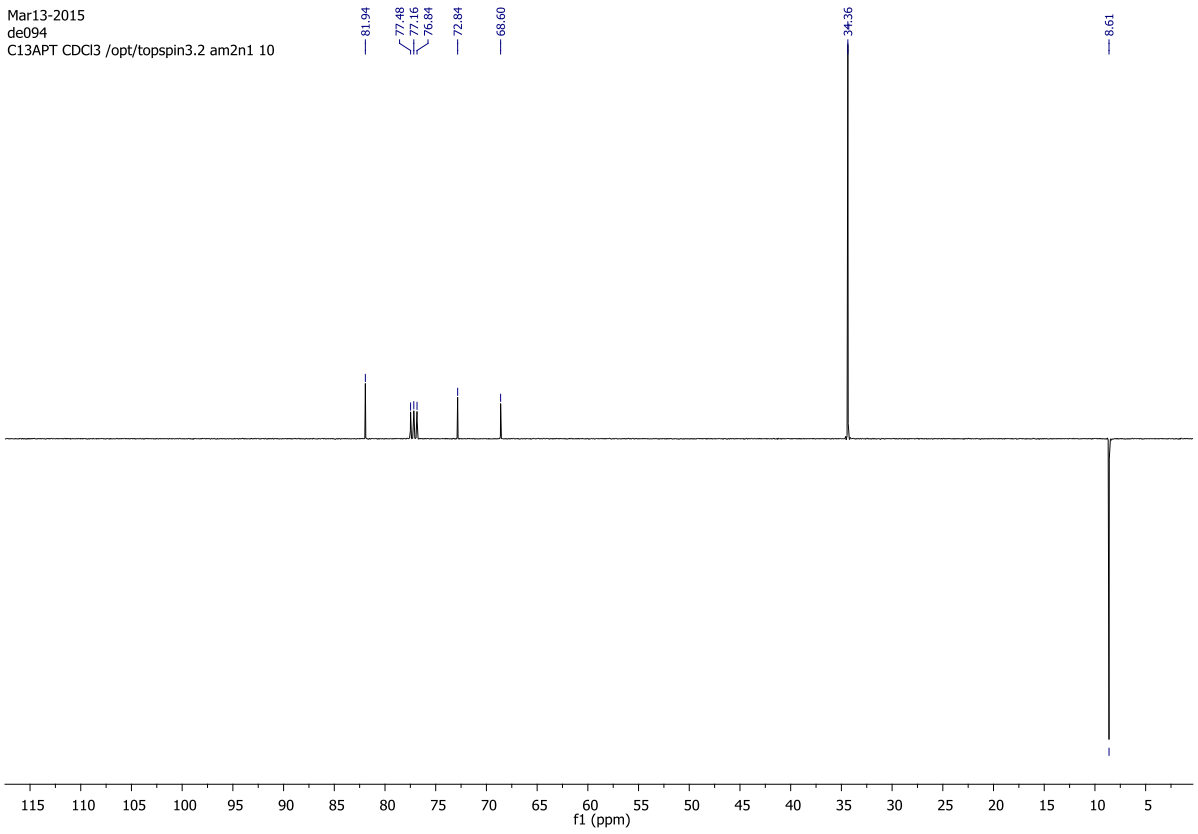
This product is also described in Wu, W.; Gao, Y.; Jiang, H.; Huang, Y. *J. Org. Chem.* **2013**, *78*, 4580. Doi: 10.1021/jo400276e



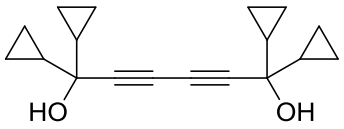
Reaction was carried out using 3-ethyl-3-pent-1-yn-3-ol (5.34 g, 47.6 mmol). The crude product was purified by recrystallization in toluene. The resulting solid is filtered off and dried under vacuum. White solid, 4.02 g, yield = 76%.

^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.03 (t, *J* = 7.5 Hz, 12H, 4 CH_3), 1.81–1.56 (m, 8H, 4 CH_2), 2.01 (s, 2 H, OH); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 8.6 (s, CH_3), 34.4 (s, *C*H_2), 68.6 (s, C), 72.8 (s, CO), 81.9 (s, C).



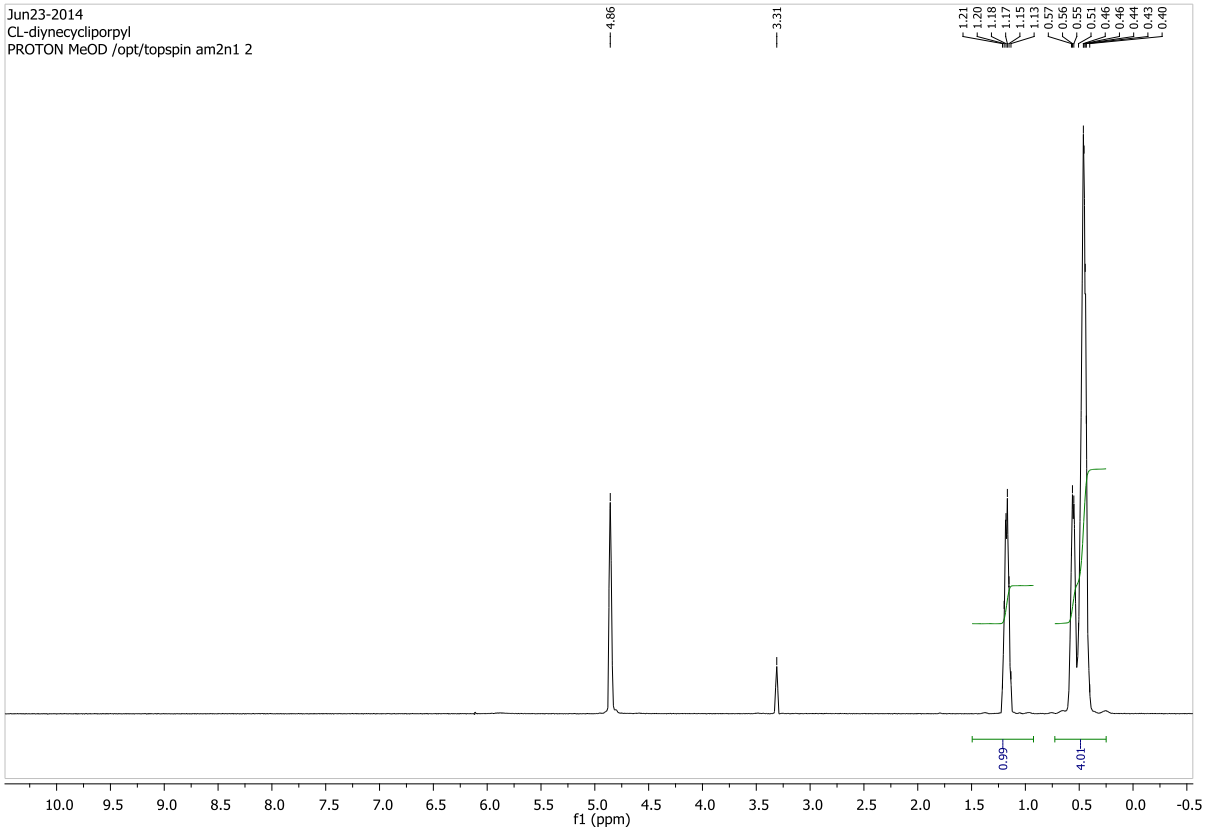

Mar13-2015
de094
C13APT CDCl3 /opt/topspin3.2 am2n1 10
81.94
77.48
77.16
76.84
72.84
68.60
34.36
8.61
115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

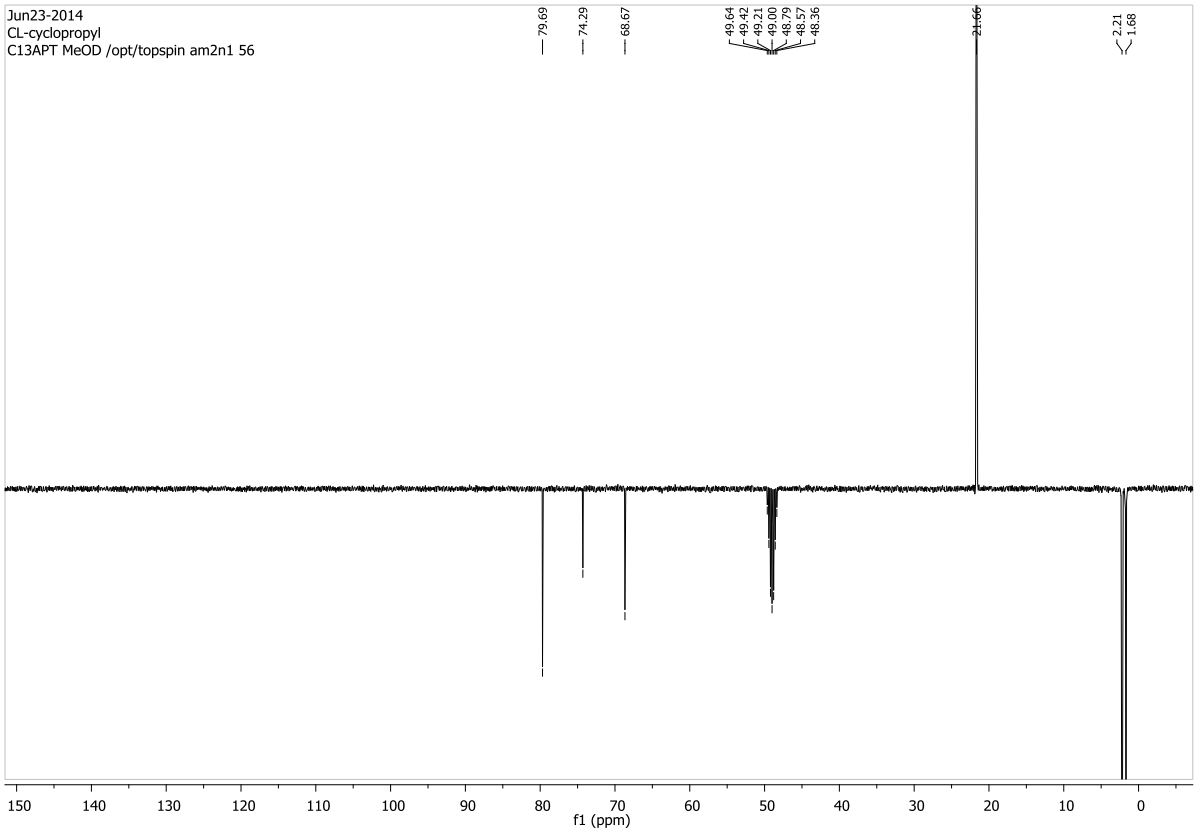
2.4. 1,1'-(Buta-1,3-diyne-1,4-diyl)bis(cyclopropan-1-ol) (1c)



Reaction was carried out using 1,1-dicylopropyl-prop-2-yn-2-ol (7.00 g, 51.4 mmol). The crude product was purified by recrystallization in heptane. The resulting precipitate is filtered off and dried under vacuum. White solid, 4.86 g, yield = 70%.

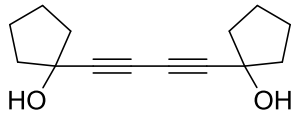
^{1}H NMR (CD_3OD, 400,13 MHz) δ(ppm) = 0.40-0.57 (m, 16H, 4 CH_2), 1.13-1.21 (m, 4H, 4 CH); ^{13}C NMR (CD_3OD, 100,61 MHz) δ(ppm) = 1.7 (s, CH_2), 2.2 (s, CH_2), 21.7 (s, CH), 68. 7 (s, C), 74.3 (s, C), 79.7 (s, C).




Jun23-2014
CL-cyclopropyl
C13APT MeOD /opt/topspin am2n1 56
79.69
74.29
68.67
49.64
49.42
49.21
49.00
48.79
48.57
48.36
21.66
2.21
1.68
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

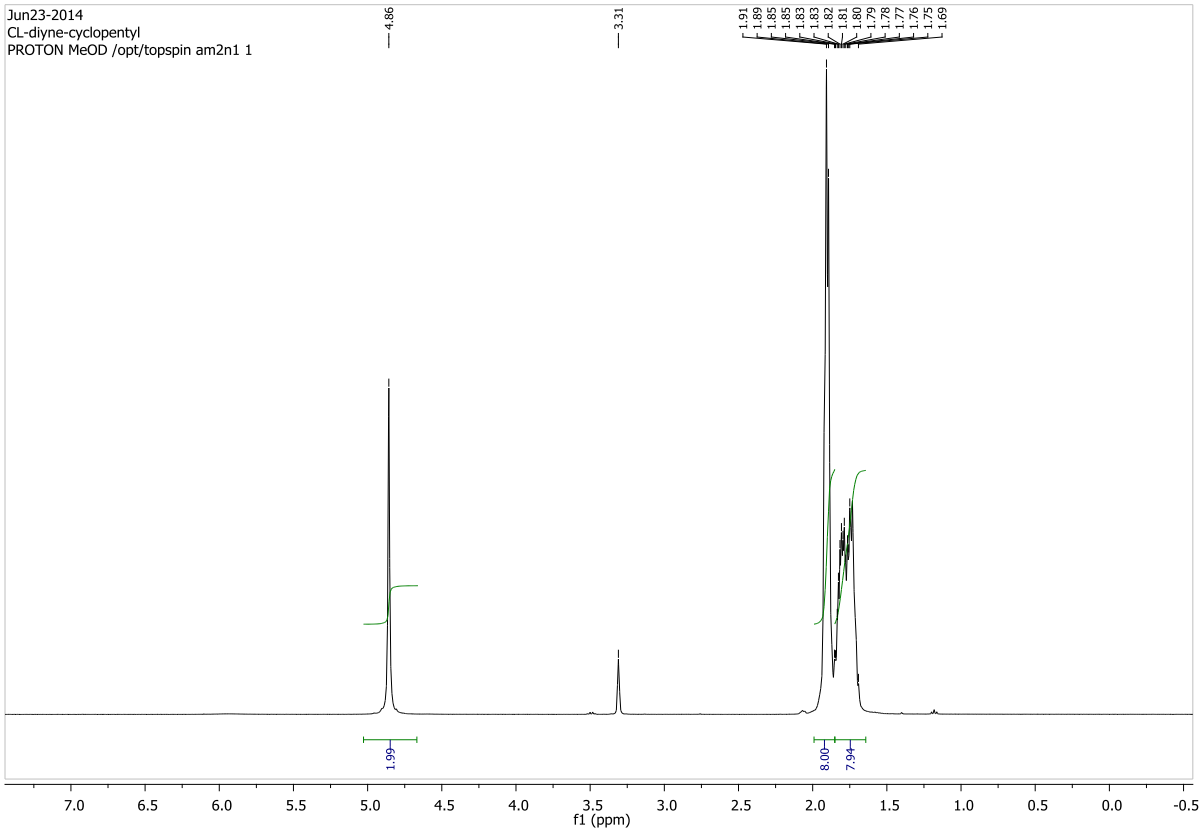
2.5. 1,1'-(Buta-1,3-diyne-1,4-diyl)bis(cyclopentan-1-ol) (1d)

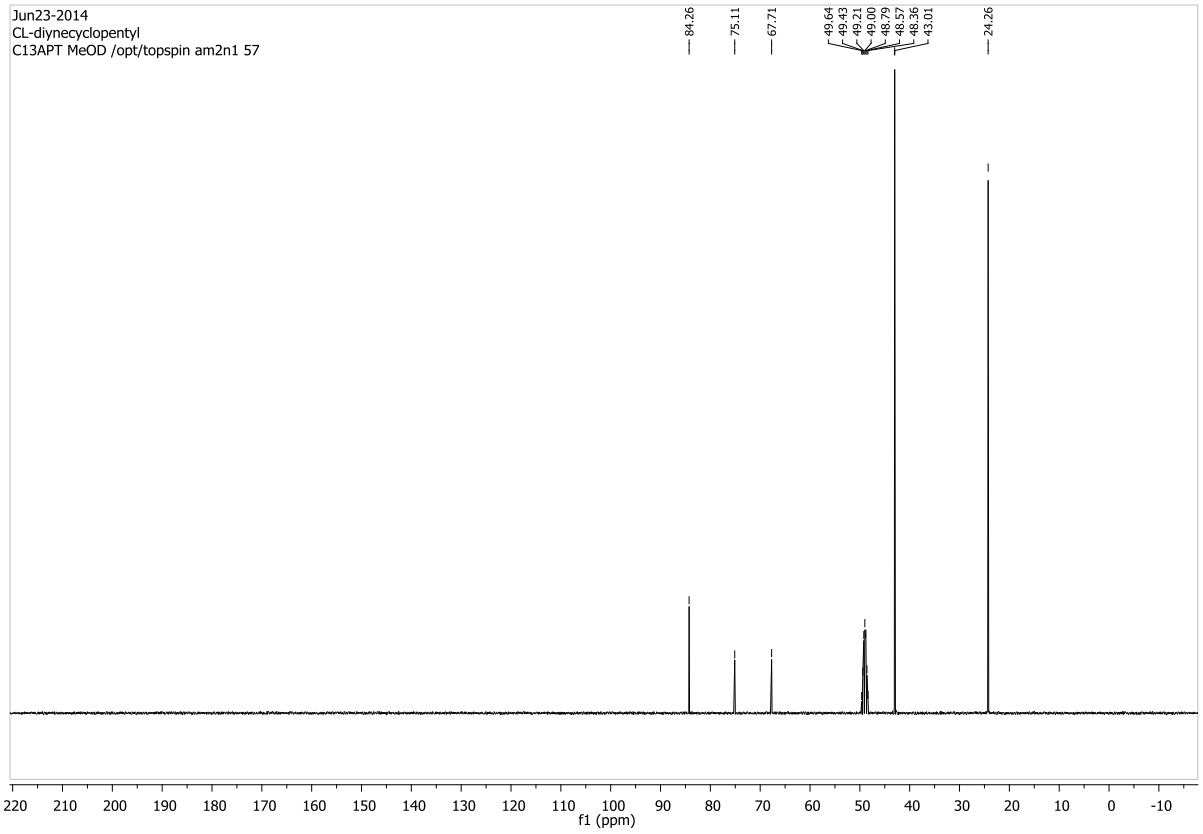
This product is also described in Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969. Doi: 10.1021/jo011098i



Reaction was carried out using 1-ethynylcyclopentanol (5.00 g, 45.4 mmol). The crude product was purified by recrystallization in toluene. The resulting solid is filtered off and dried under vacuum. White solid, 3.95 g, yield = 80%.

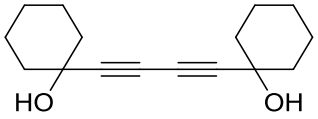
^{1}H NMR (CD_3OD, 400,13 MHZ) δ (ppm) = 1.69–1.83 (m, 8H, CH_2), 1.89–1.92 (m, 8H, CH_2); ^{13}C NMR (CD_3OD, 100,61 MHZ) δ (ppm) = 24.3 (s, *C*H_2), 43.0 (s, *C*H_2), 67.7 (s, C), 75.1 (s, CO), 84.3 (s, C).




Jun23-2014
CL-diynecyclopentyl
C13APT MeOD /opt/topspin am2n1 57
84.26
75.11
67.71
49.64
49.43
49.21
49.00
48.79
48.57
48.36
43.01
24.26
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

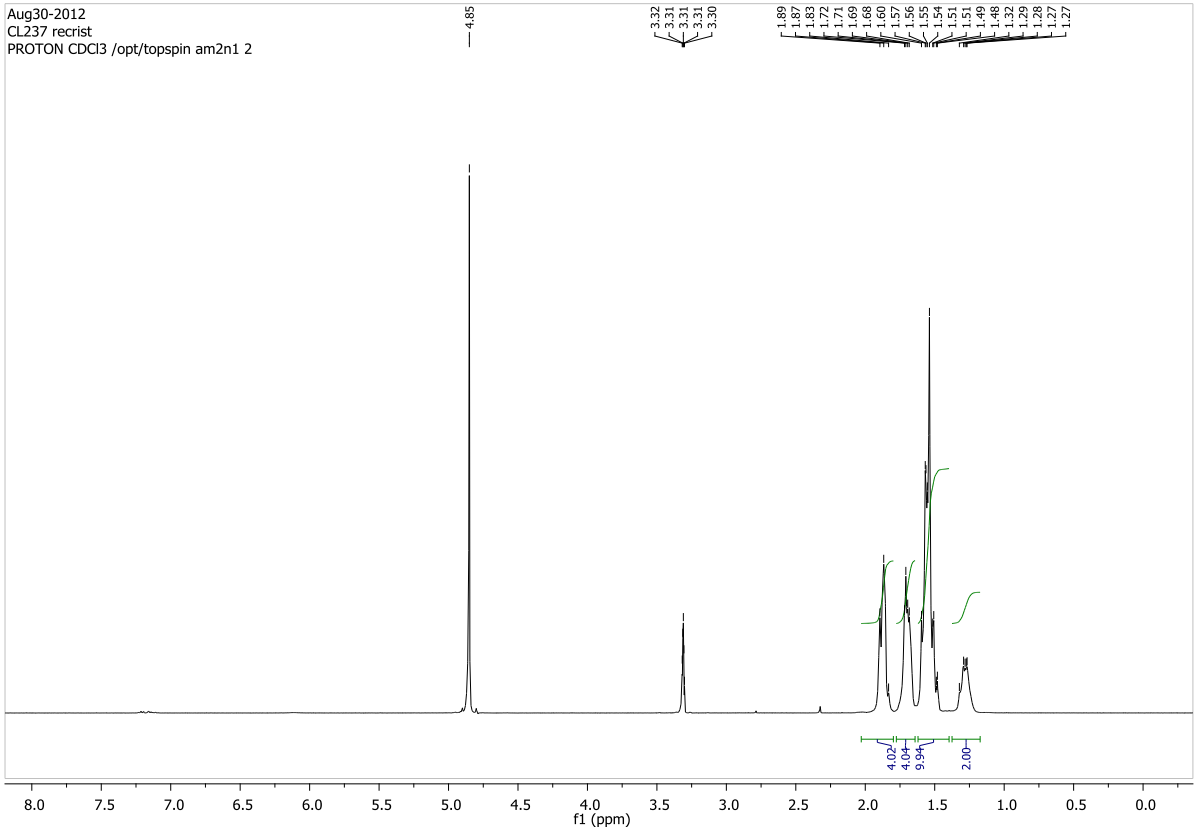
2.6. 1,1'-(Buta-1,3-diyne-1,4-diyl)bis(cyclohexan-1-ol) (1e)

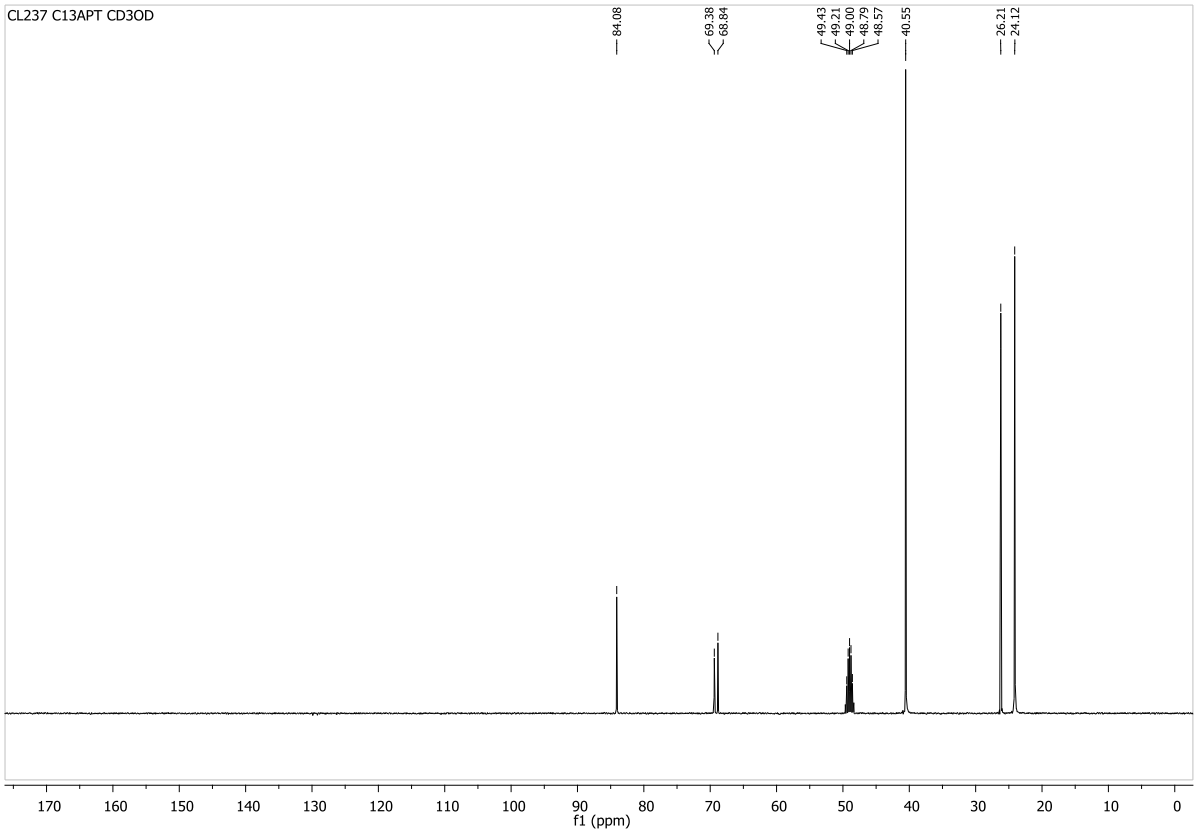
This product is also described in Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969. Doi: 10.1021/jo011098i



The Reaction was carried out using 1-ethynylcyclohexan-1-ol (10.08 g, 81.24 mmol). **1e** was obtained by recrystallization in toluene. The resulting solid is filtered off and dried under vacuum. White solid, 8.81 g, yield = 88%.

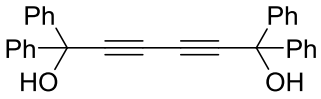
^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.27-1.32 (m, 2H, CH_2), 1.48–1.60 (m, 10H, CH_2), 1.68–1.72 (m, 4H, CH_2), 1.83–1.89 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 24.1 (s, CH_2), 26.2 (s, *C*H_2), 40.6 (s, *C*H_2), 68.8 (s, C), 69.4, (S, C), 84.1 (s, C).




CL237 C13APT CD3OD
84.08
69.38
68.84
49.43
49.21
49.00
48.79
48.57
40.55
26.21
24.12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

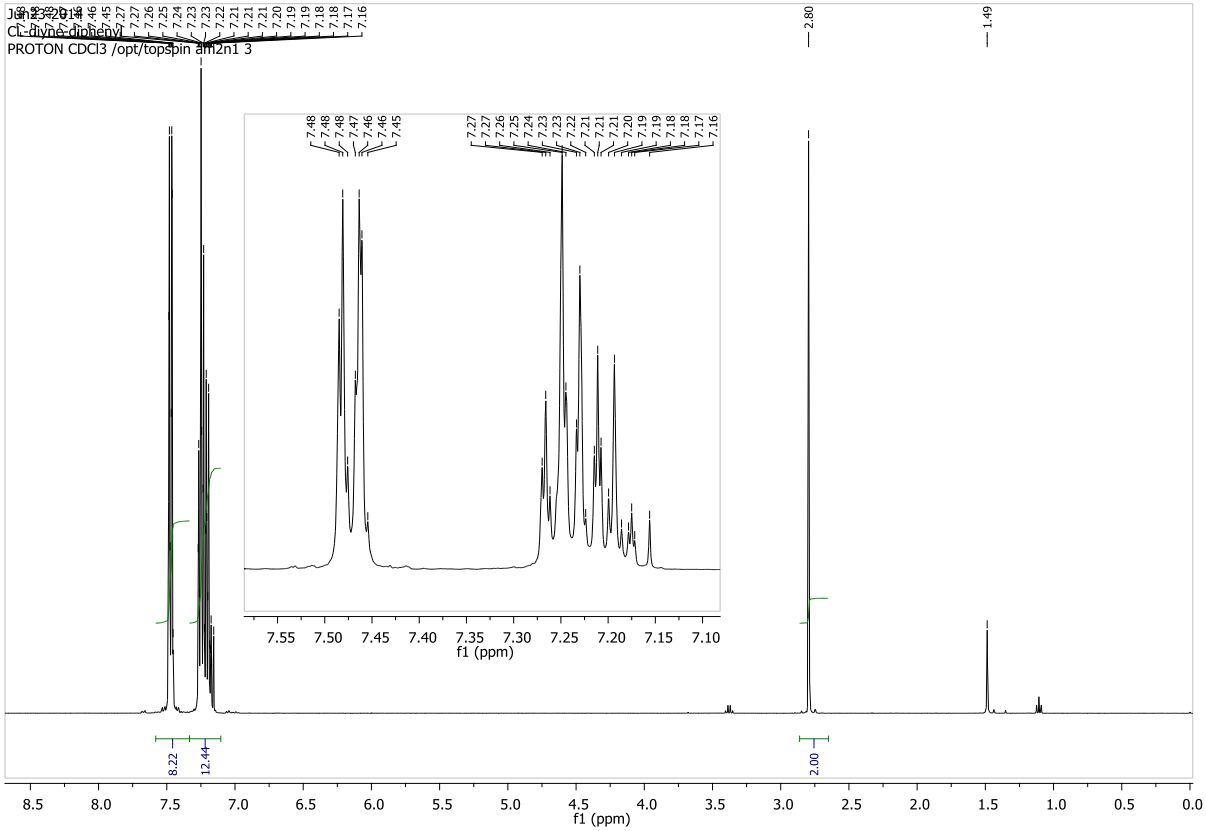
2.7. 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (1f)

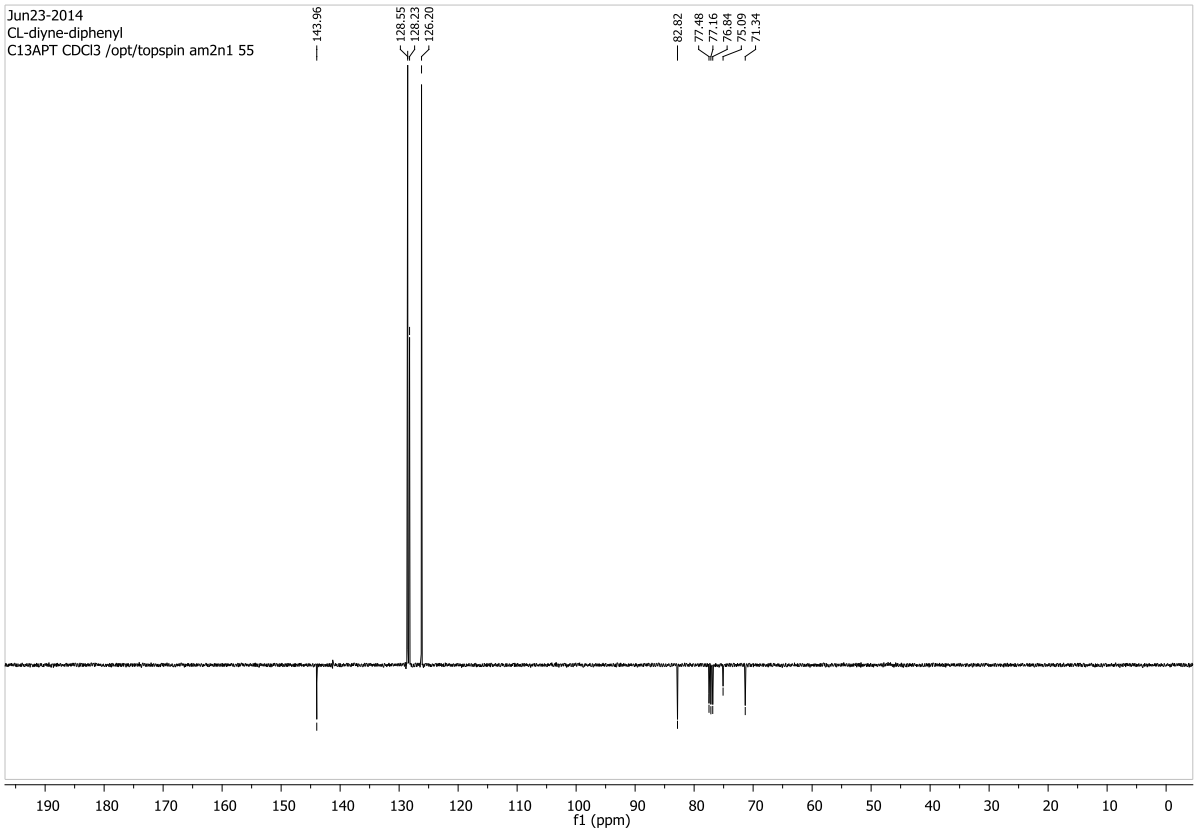
This product is also described in Kuwatani, Y.; Yamamoto, G.; Oda, M.; Iyoda, M. *Bull. Chem. Soc. Jpn.* **2005**, 78, 2188. Doi: 10.1246/bcsj.78.2188



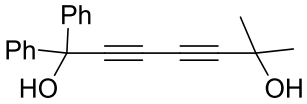
The Reaction was carried out using 1,1-diphenylprop-2-yn-1-ol (3.52 g, 16.9 mmol). **1f** was obtained by precipitation in heptane and recrystallization in toluene. The resulting solid is filtered off and dried under vacuum. White solid, 2.65 g, yield = 76%.

^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 2.8 (s, 2H, OH), 7.16-7.27 (m, 12H, Ph), 7.45-7.48 (m, 8H, Ph); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 71.3 (s, C), 75.1 (s, C), 82.8 (s, C), 126.2 (s, CH_{Ph}), 128.2 (s, CH_{Ph}), 128.5 (s, CH_{Ph}), 144.0 (s, C_{Ph}).



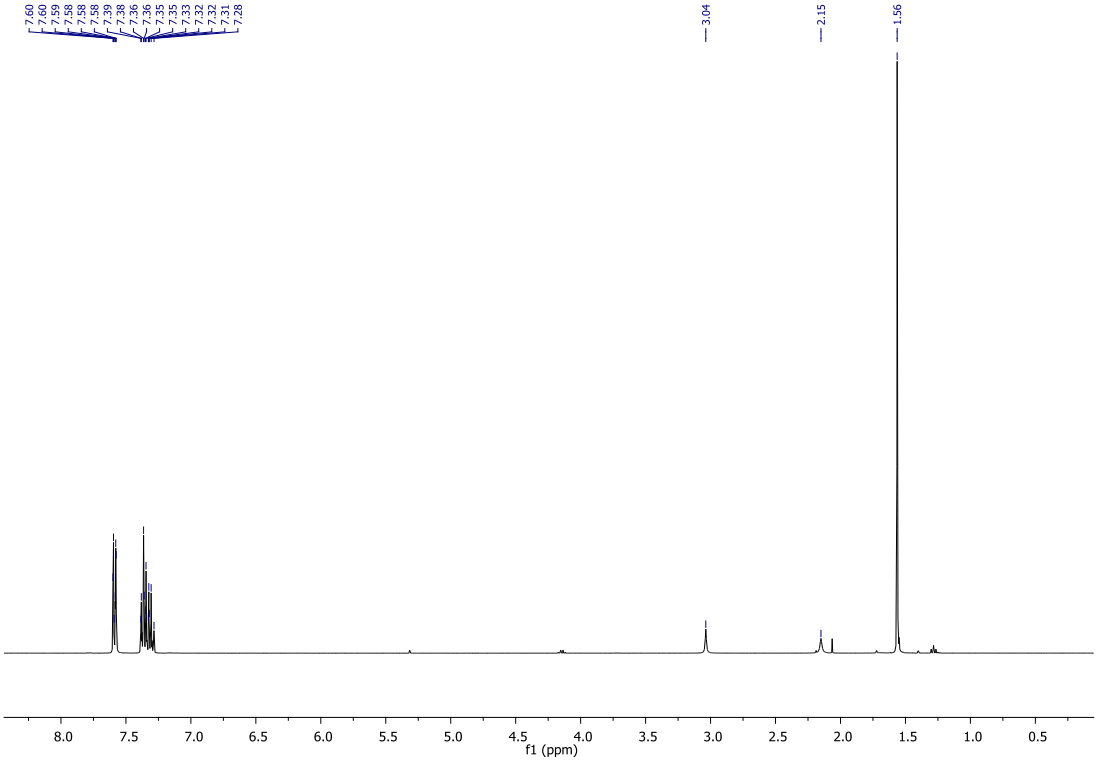

Jun23-2014
CL-diyne-diphenyl
C13APT CDCl3 /opt/topspin am2n1 55
143.96
128.55
128.23
126.20
82.82
77.48
77.16
76.84
75.09
71.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

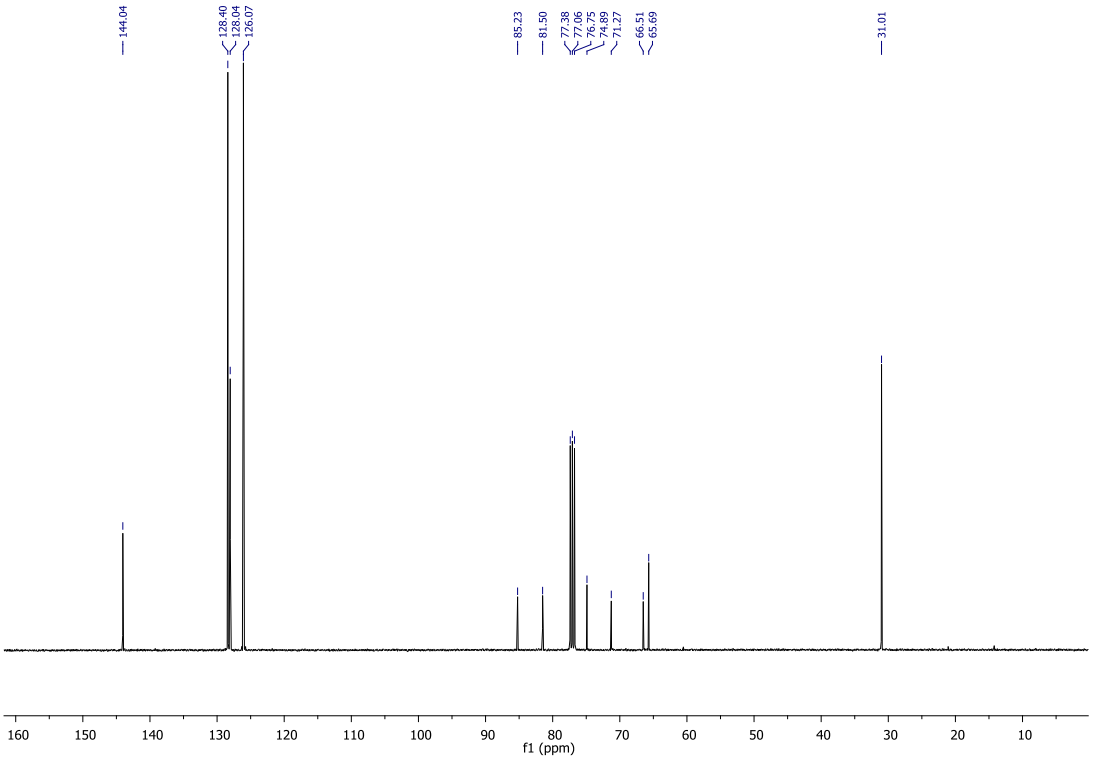
2.8. 6-Methyl-1,1-diphenylhepta-2,4-diyne-1,6-diol (1g)



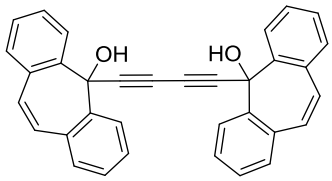
The Reaction was carried out using 1,1-diphenylprop-2-yn-1-ol (2.08 g, 10.0 mmol) and 1-methylbut-2-yn-1ol (0.841 g, 10.0 mmol). **1g** was obtained by chromatography (silica gel, hexane/AcOEt (8:2). White solid, 1.80 g, yield = 62%.

^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 1.56 (s, 2 CH_3), 2.15 (s, 1H, OH), 3.04 (s, 1H, OH), 7.28-7.60 (m, 10H, 2 Ph); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 31.0 (s, CH_3), 65.7 (s, C), 66.5 (s, $C(CH_3)_2$), 71.3 (s, C), 74.9 (s, $C(Ph)_2$), 81.5 (s, C), 85.2 (s, C), 126.1, 128.0, 128.4 (s, CH_{Ph}), 144.0 (s, C_{Ph}).



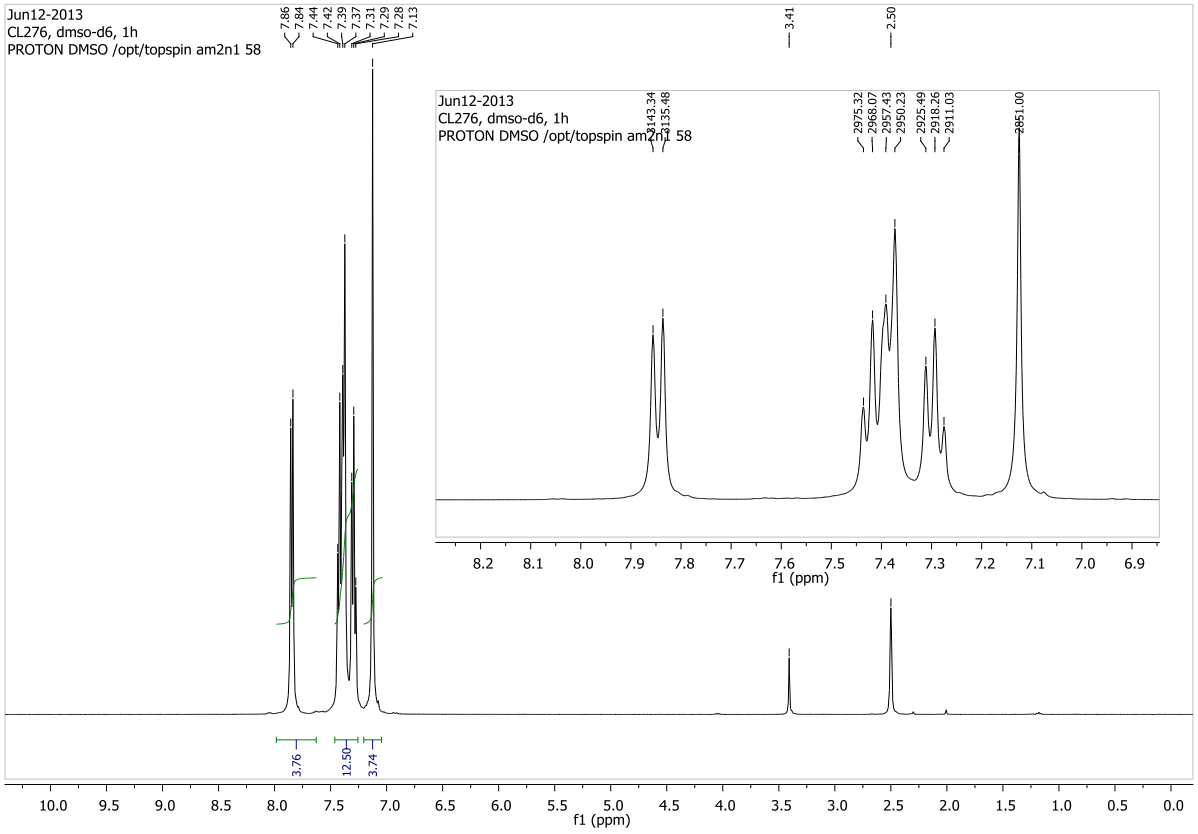

144.04
128.40
128.04
126.07
85.23
81.50
77.38
77.06
76.75
74.89
71.27
66.51
65.69
31.01
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

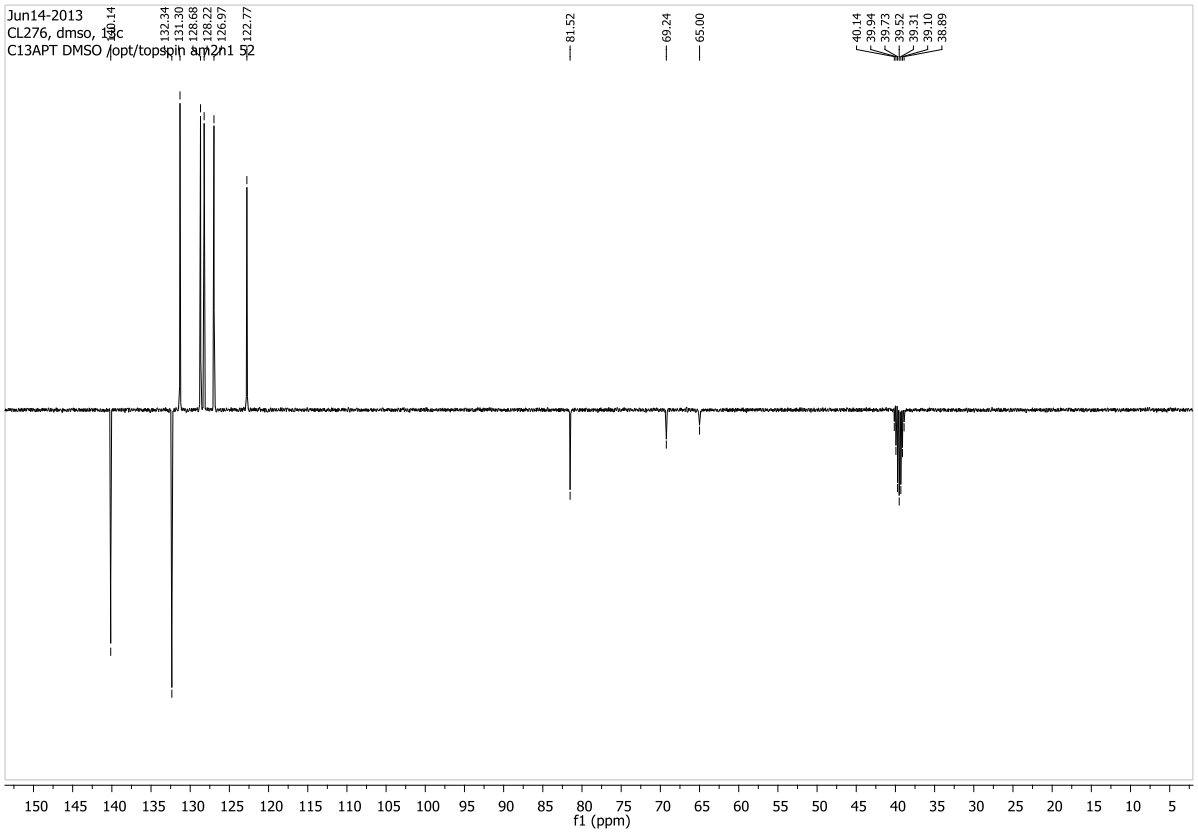
2.9. 5,5'-(Buta-1,3-diyne-1,4-diyl)bis(5H-dibenzo[a,d][7]annulen-5-ol) (1h)



The Reaction was carried out using alkyne alcohol (3.5 g, 15.1 mmol). **1h** was obtained by precipitation in $CHCl_3$. Pink solid, 2.98g, yield = 85%.

^{1}H NMR (DMSO-d_6, 400.13 MHz): δ (ppm) = 7.13 (s, 4 H, 4 CH=), 7.28-7.44 (m, 12H, CH_{Ph}), 7.85 (d, *J* = 7.9 Hz, 4H, CH_{Ph}); ^{13}C NMR (DMSO-d_6, 400.13 MHz): δ (ppm) = 65.0 (s, C), 69.2 (s, C), 81.5 (s, C), 122.8 (s, CH), 127.0 (s, CH), 128.2 (s, CH), 128. 7 (s, CH), 131.3 (s, CH), 132.3 (s, C), 140.1 (s, C).

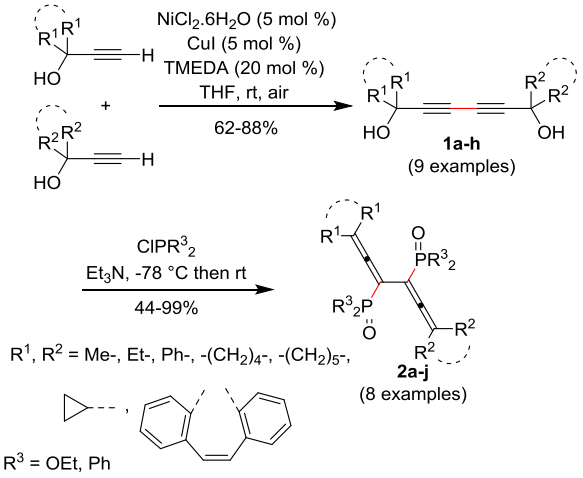



Jun14-2013
CL276, dmso, 13c
C13APT DMSO /opt/topspin a m2 n1 52
140.14
132.34
131.30
128.68
128.22
126.97
122.77
81.52
69.24
65.00
40.14
39.94
39.73
39.52
39.31
39.10
38.89
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

3. Bis-(allenyl)phosphorus derivatives 2a-j

3.1. General procedure

In a round bottom flask under nitrogen containing a solution of diyne-diol derivative **1** (24 mmol, 1 eq) and dry trietylamine (6.6 mL, 48 mmol, 2 eq) in anhydrous CH_2Cl_2 (50 mL) at -76 °C was added dropwise diethyl chlorophosphite (48 mmol, 2eq). After complete addition, the reaction mixture was gradually warmed and stirred at room temperature for 12 hours. After completion of the reaction (monitored by ^{31}P NMR), the reaction was washed with 5% aqueous HCl (50 mL) and water. The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residues were purified by chromatography (silica gel) or otherwise precised.



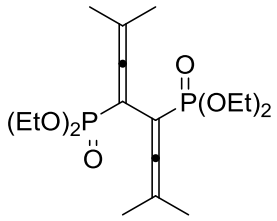
Scheme 1. Synthesis of bisphosphonylallenes **2a-j** from diyne-diols **1a-h**.

Table 1. Yields of diynes **1a-h** and bis-allenes **2a-i**.

diyne diol	R^1	R^2	yield (%)[a]	bis-allene	R^3	yield (%)[a]
1a	Me-	Me-	82	**2a**	OEt	82
1b	Et-	Et-	76	**2b**	OEt	92
1c			70	**2c**	OEt	-
1d	-$(CH_2)_4$-	-$(CH_2)_4$-	80	**2d**	OEt	44
1e	-$(CH_2)_5$-	-$(CH_2)_5$-	88	**2e**	OEt	99
1f	Ph-	Ph-	76	**2f**	OEt	83
1g	Ph-	Me-	62	**2g**	OEt	62
1h			85	**2h**	OEt	61
	Me-	Me-		**2i**	Ph	82
	-$(CH_2)_5$-	-$(CH_2)_5$-		**2j**	Ph	71

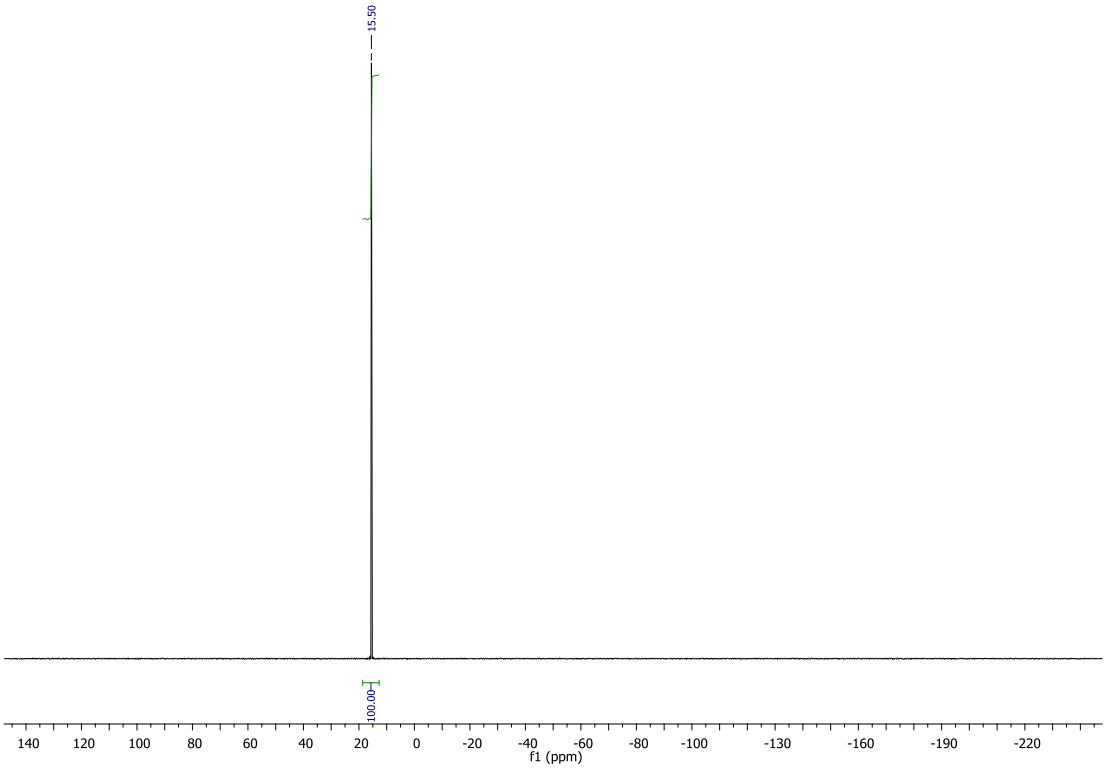
[a] Isolated yields.

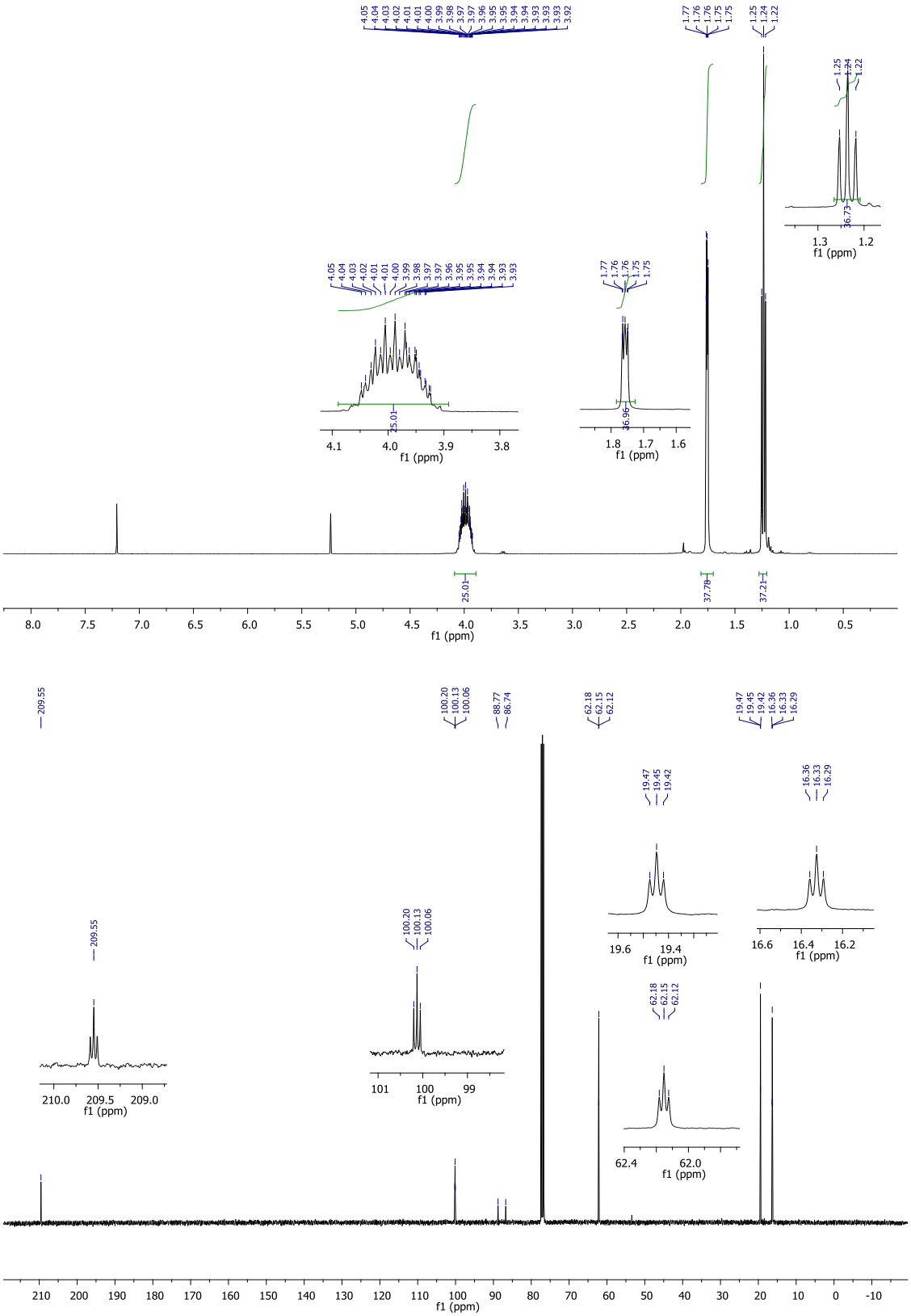
3.2. Tetraethyl (2,7-dimethylocta-2,3,5,6-tetraene-4,5-diyl)bis(phosphonate) (2a)

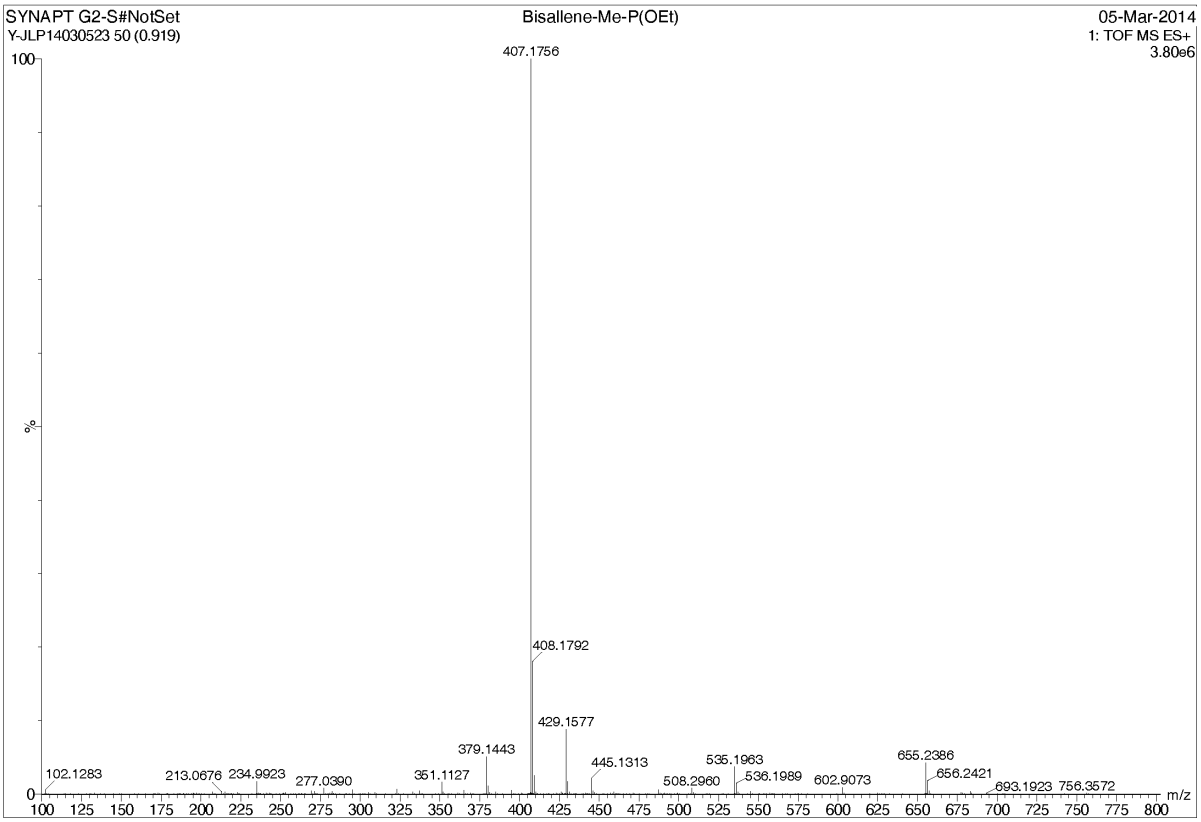


The reaction was carried out using diyne diol **1a** (4.00 g, 24.0 mmol) and $ClP(OEt)_2$ (7.51 g, 48 mmol). The crude material is purified by chromatography (silica gel, EtOH/AcOEt/CH_2Cl_2 0.4/50/49.6). Yellow oil, 8.00 g, yield =82%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 15.5 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.24 (t, *J* = 7.1 Hz, 12H, 4 CH_3), 1.75 (d, *J* = 4.4 Hz, 6 H, 2 CH_3), 1.76 (d, *J* = 4.4, 6 H, 2 CH_3), 3.93–4.05 (m, 8H, 4 CH_2O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 16.3 (t, J_{CP} = 3.5 Hz, *C*H_3), 19.4 (t, J_{CP} = 5.4 Hz, CH_3), 62.1 (t, J_{CP} = 3.0 Hz, CH_2O), 87.7 (d, J_{CP} = 204.3 Hz, CP), 100.1 (t, J_{CP} = 7.4 Hz, C=C), 209.5 (t, J_{CP} = 3.9 Hz, Csp). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{18}H_{33}O_6P_2$ 407.1752 found 407.1756.



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Bisallene-Me-P(OEt)
05-Mar-2014
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407.1756
408.1792
429.1577
379.1443
445.1313
535.1963
655.2386
102.1283
213.0676
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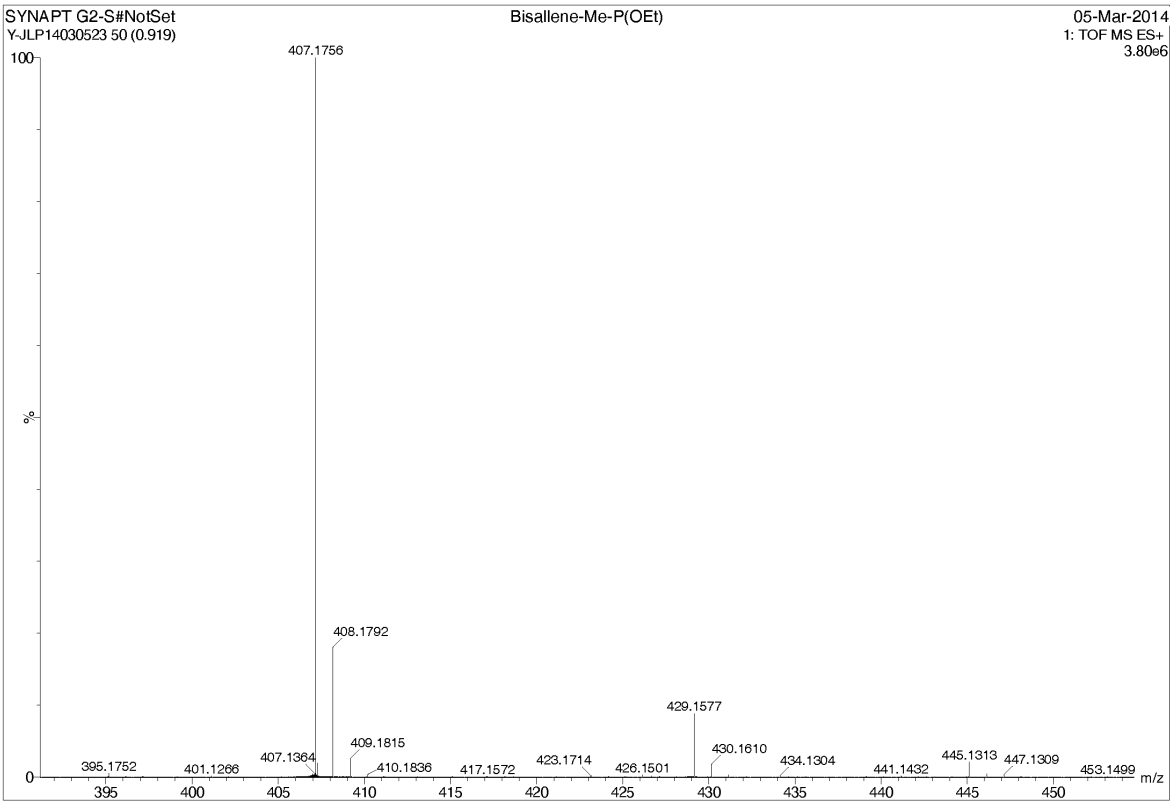
508.2960
536.1989
602.9073
656.2421
693.1923
756.3572
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030523 50 (0.919)
Bisallene-Me-P(OEt)
05-Mar-2014
1: TOF MS ES+
3.80e6
407.1756
408.1792
429.1577
409.1815
430.1610
395.1752
401.1266
407.1364
410.1836
417.1572
423.1714
426.1501
434.1304
441.1432
445.1313
447.1309
453.1499
%
m/z

Elemental Composition Report **Page 1**

Single Mass Analysis

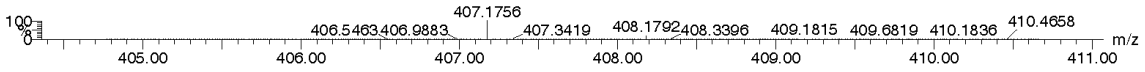
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
212 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030523 50 (0.919)

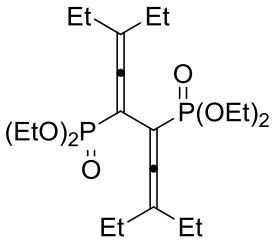
Bisallene-Me-P(OEt)

05-Mar-2014
1: TOF MS ES+
3.80e+006



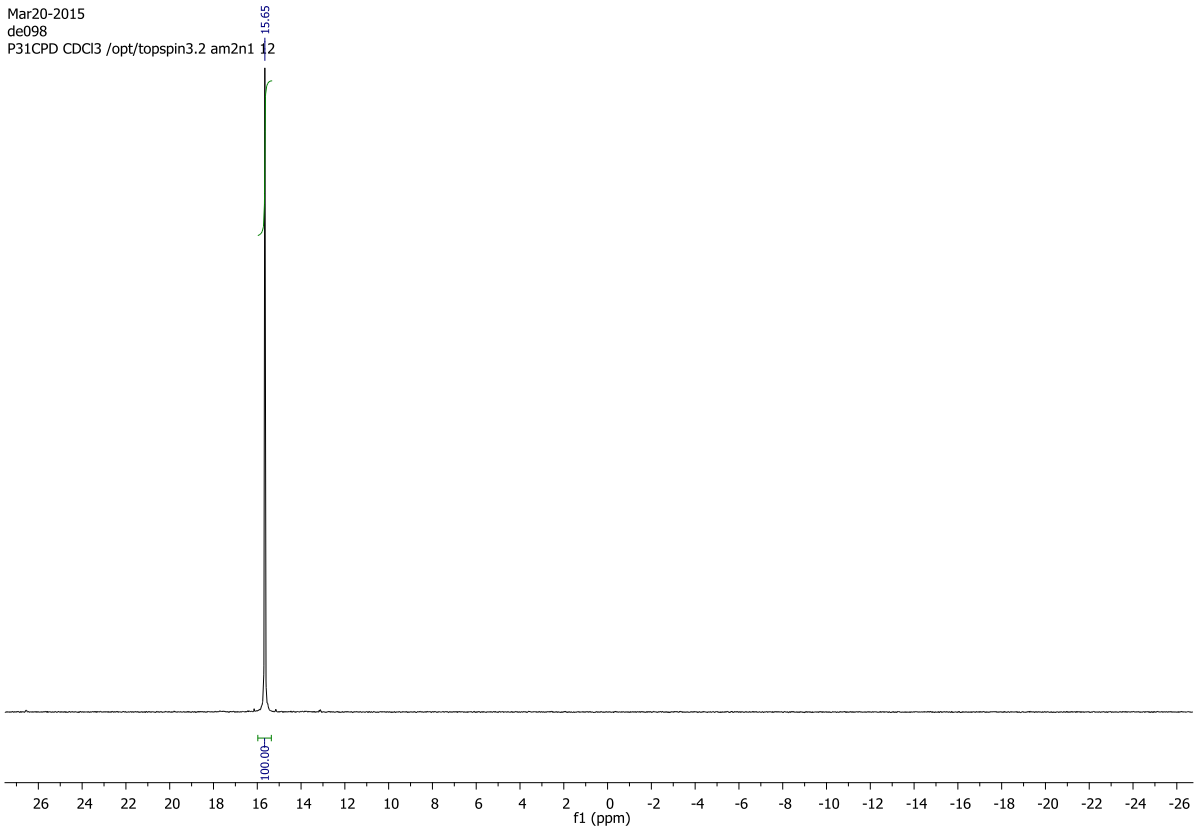
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
407.1756	407.1752	0.4	1.0	3.5	1830.5	n/a	n/a	C18 H33 O6 P2

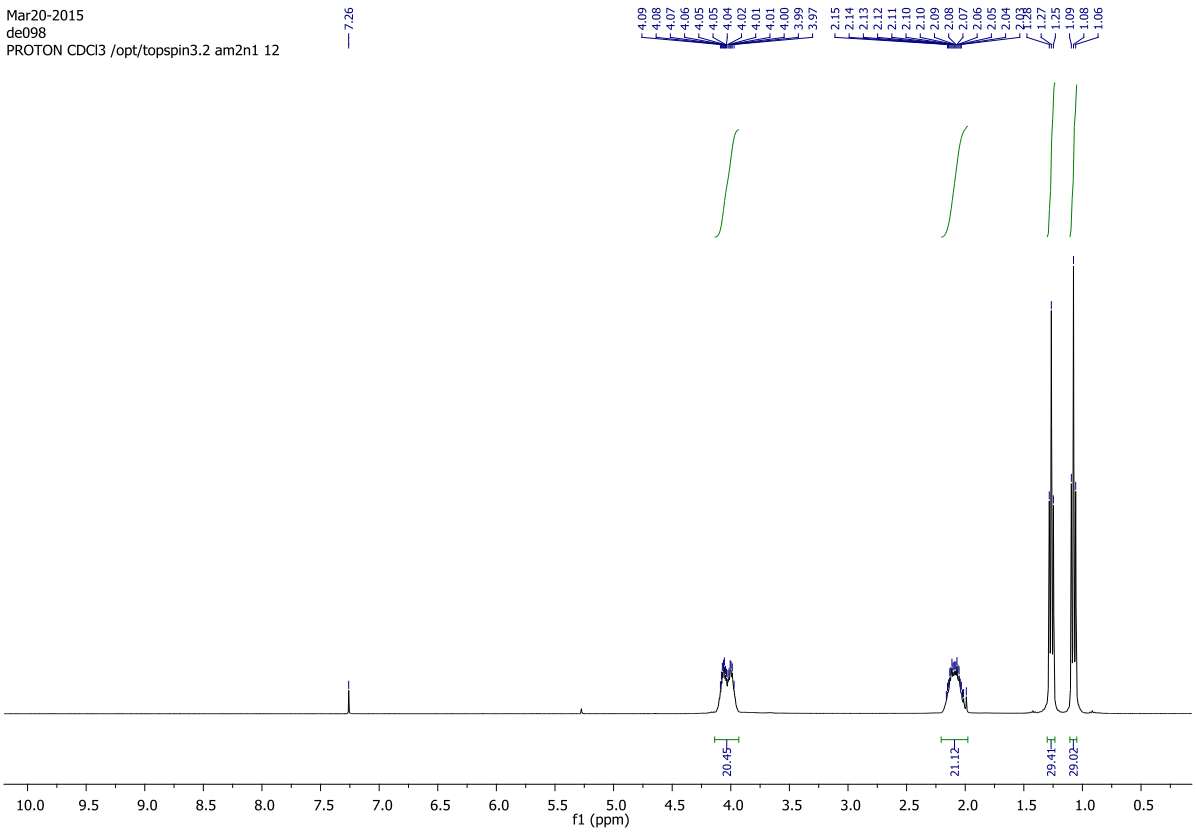
3.3. Tetraethyl (3,8-diethyldeca-3,4,6,7-tetraene-5,6-diyl)bis(phosphonate) (2b)



The reaction was carried out using diyne diol **1b** (5.34 g, 24.0 mmol) and $ClP(OEt)_2$ (7.51 g, 48 mmol). The crude material is purified by chromatography (silica gel, EtOH/AcOEt/CH_2Cl_2 0.4/50/49.6). Yellow oil, 10.21 g, yield =92%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 15.7 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.08 (t, *J* = 7.4 Hz, 6 H, 2 CH_3), 1.27 (t, *J* = 7.0 Hz, 6 H, 2 CH_3), 2.03-2.15 (m, 8H, 4 CH_2), 3.97-4.09 (m, 8H, 4 CH_2O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 11.8 (s, *C*H_3), 16.4 (t, J_{PC} = 3.2 Hz, *C*H_3), 25.4 (t, J_{PC} = 2.3 Hz, CH_2), 62.0 (bt, CH_2O), 91.4 (d, J_{PC} = 205.3 Hz, CP), 112.3 (t, J_{PC} = 7.2 Hz, C=C), 208.70 (t, J_{PC} = 4.0 Hz, C); HRMS (EI): m/z calcd. For $C_{22}H_{41}O_6P_2$, $[M+H]^+$: 463.2378 Found: 463.2375.




Mar20-2015
de098
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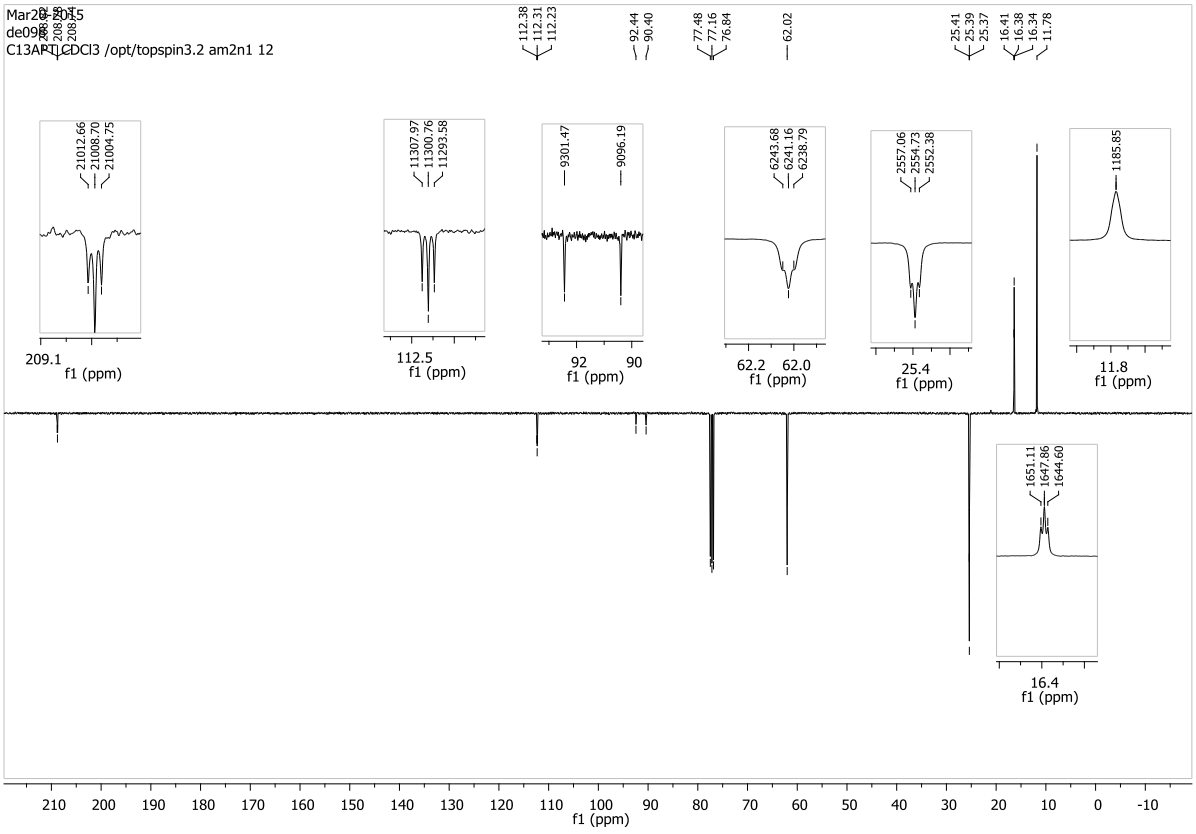
4.08
4.07
4.06
4.05
4.05
4.04
4.02
4.01
4.01
4.00
3.99
3.97
2.15
2.14
2.13
2.12
2.11
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.04
1.28
1.27
1.25
1.09
1.08
1.06
20.45
21.12
29.41
29.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Mar20-2015
de098
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112.31
112.23
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77.48
77.16
76.84
62.02
25.41
25.39
25.37
16.41
16.38
16.34
11.78
21012.66
21008.70
21004.75
209.1
f1 (ppm)
11307.97
11300.76
11293.58
112.5
f1 (ppm)
9301.47
9096.19
92
90
f1 (ppm)
6243.68
6241.16
6238.79
62.2
62.0
f1 (ppm)
2557.06
2554.73
2552.38
25.4
f1 (ppm)
1185.85
11.8
f1 (ppm)
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16.4
f1 (ppm)
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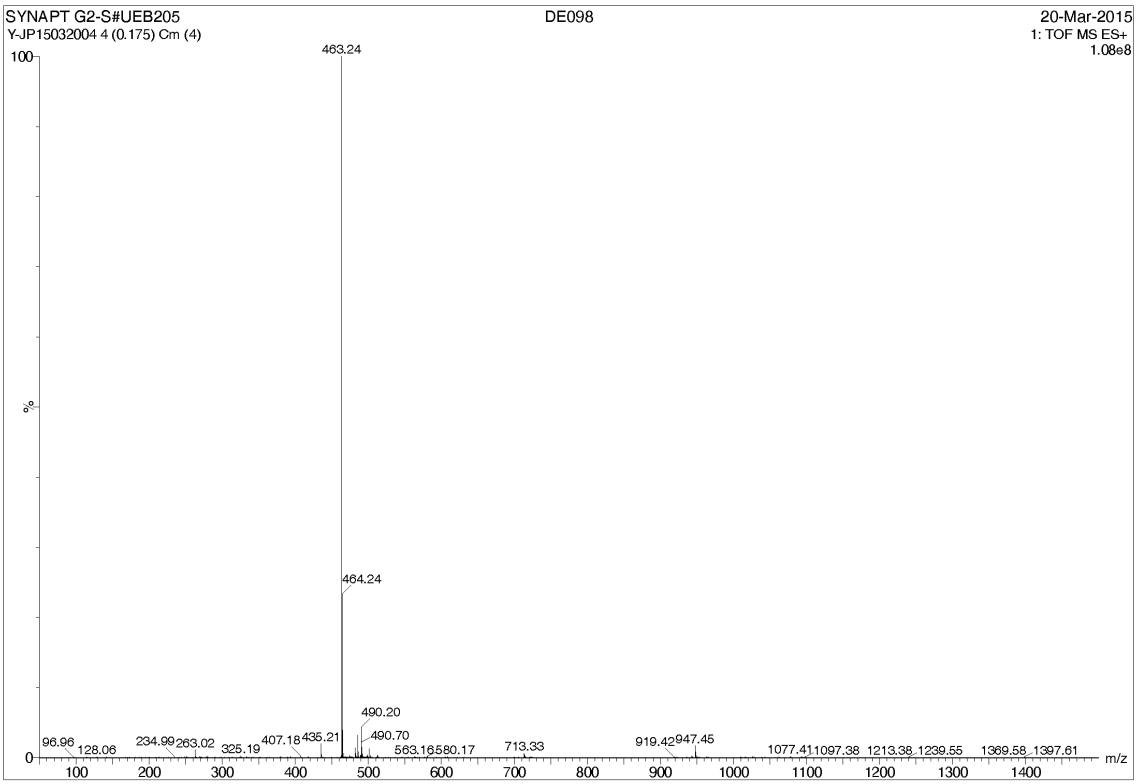
f1 (ppm)


SYNAPT G2-S#UEB205
DE098
20-Mar-2015
Y-JP15032004 4 (0.175) Cm (4)
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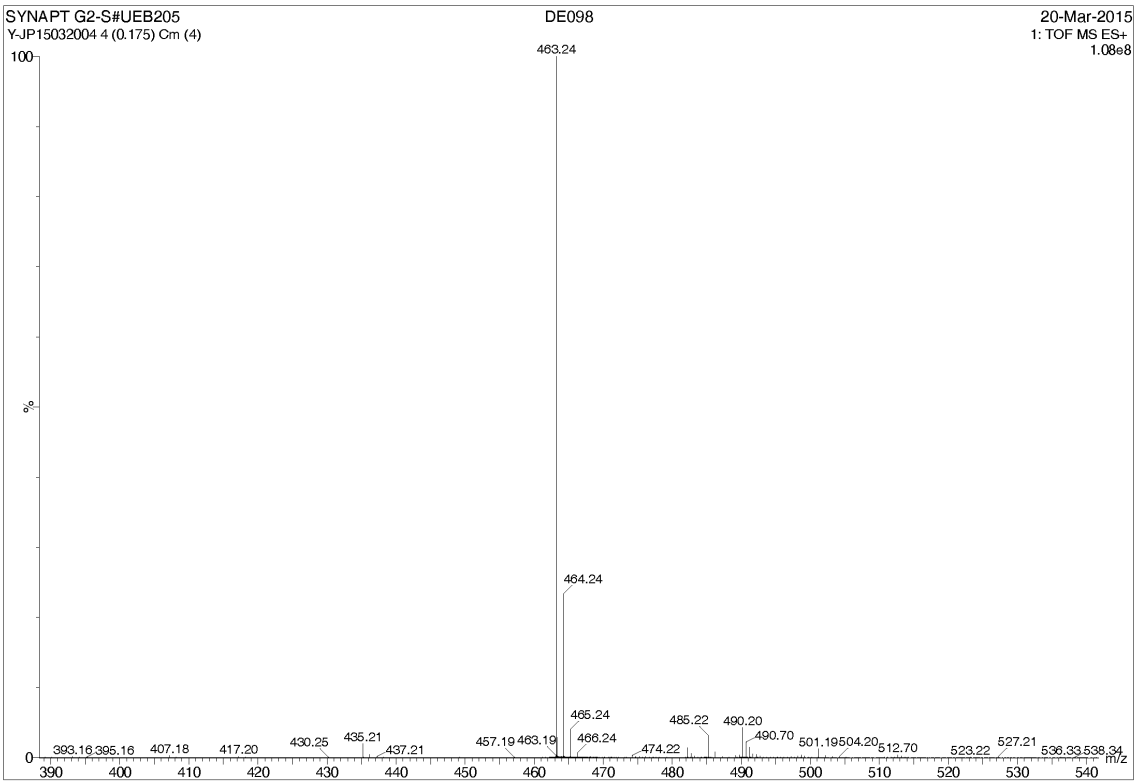
1.08e8
463.24
464.24
490.20
490.70
%
m/z


SYNAPT G2-S#UEB205
DE098
20-Mar-2015
Y-JP15032004 4 (0.175) Cm (4)
1: TOF MS ES+
1.08e8
463.24
464.24
465.24
485.22
490.20
490.70
%
m/z

Elemental Composition Report

Single Mass Analysis

Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
307 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-50 P: 0-2

SYNAPT G2-S#UEB205
Y-JP15032004 4 (0.175) Cm (4)

DE098

20-Mar-2015
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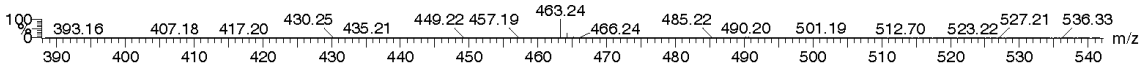
1.08e+008



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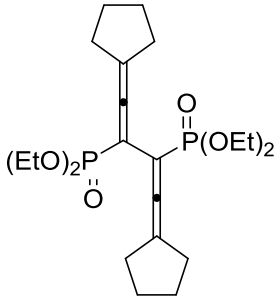
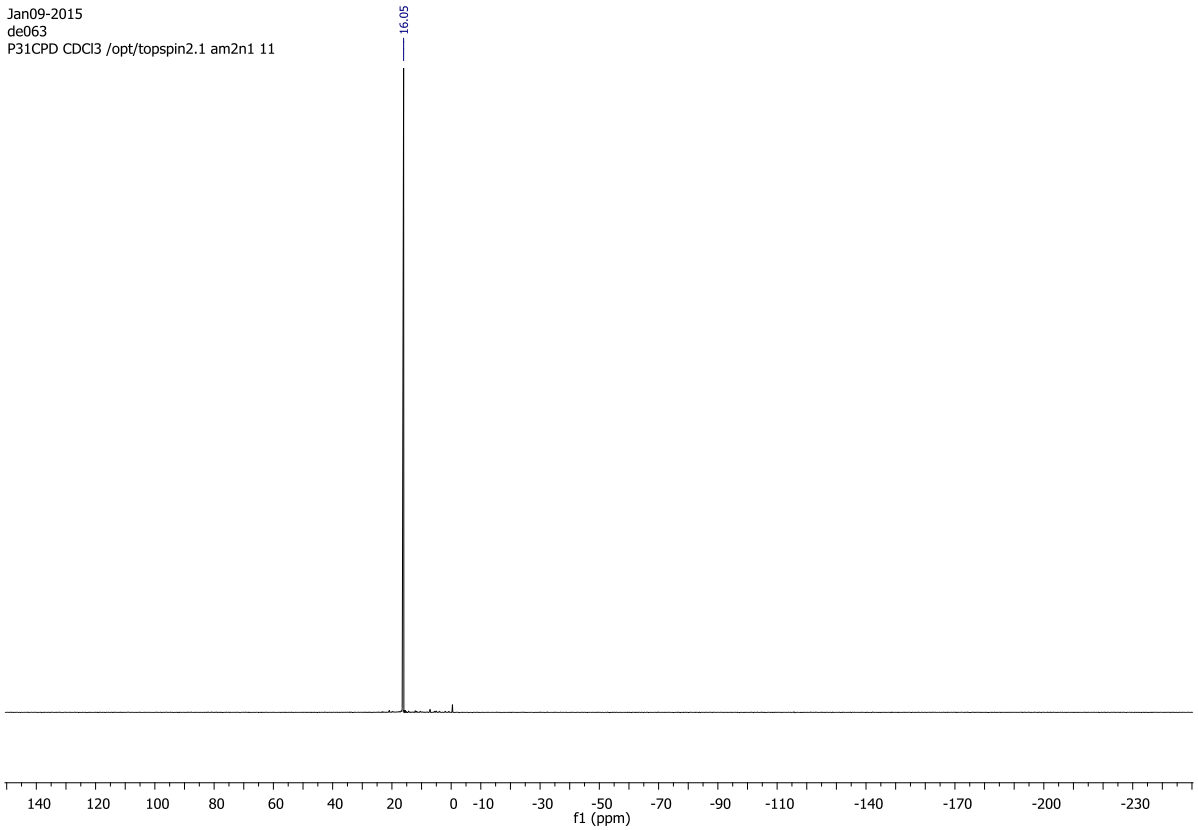
Maximum:		30.0	2.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
463.2375	463.2378	-0.3	-0.6	3.5	1588.7	n/a	n/a	C22 H41 O6 P2

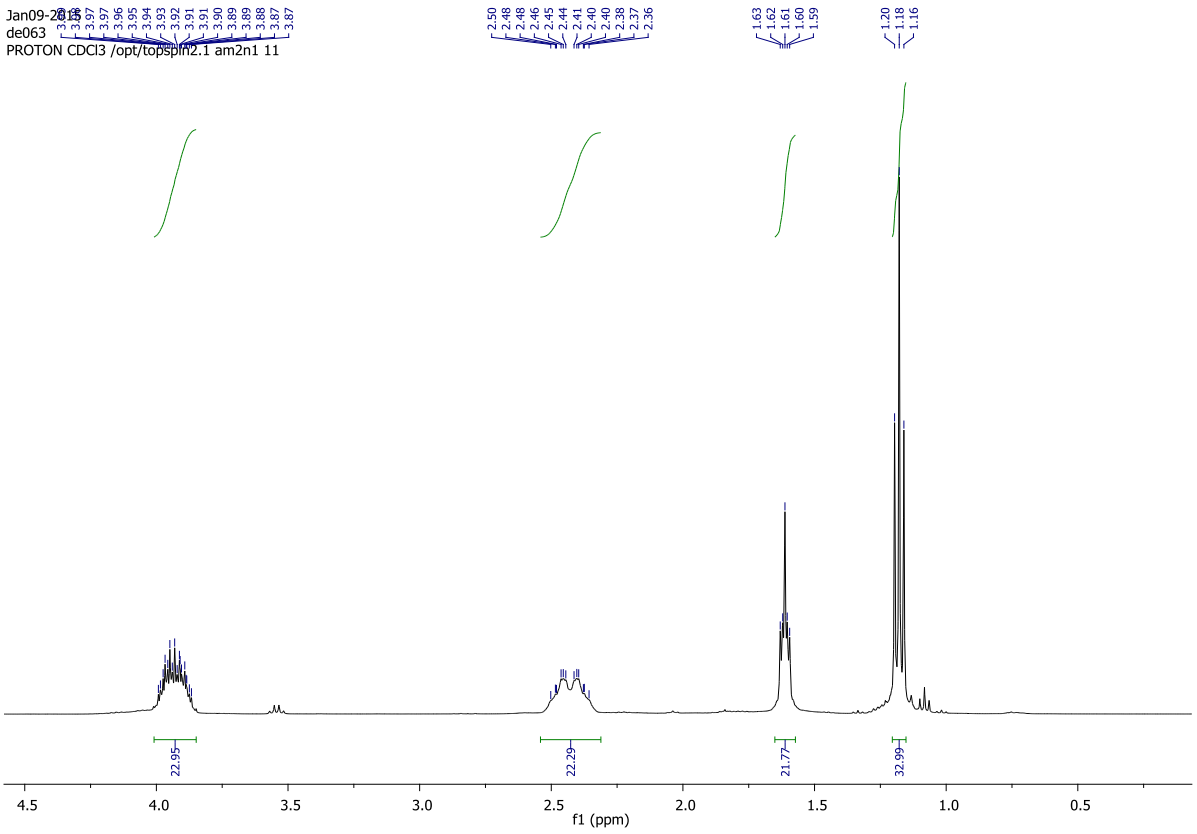
3.4. Tetraethyl (1,4-dicyclopentylidenebuta-1,3-diene-2,3-diyl)bis(phosphonate) (2d)



The reaction was carried out using diyne diol **1d** (5.24 g, 24.0 mmol) and $ClP(OEt)_2$ (7.51 g, 48 mmol). The crude material is purified by chromatography (silica gel, EtOH/AcOEt/CH_2Cl_2 0.4/50/49.6). Brown solid, 4.84 g, yield = 44%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 16.0 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.18 (t, *J* = 7.1 Hz, 12H, 4 *C*H_3), 1.59–1.63 (m, 8H, 4 *C*H_2), 2.36-2.50 (m, 8H, 4 *C*H_2), 3.87-3.99 (m, 8H, 4 *C*H_2O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 16.2 (t, J_{PC} = 3.3 Hz, *C*H_3), 27.2 (s, *C*H_2), 31.0 (t, J_{PC} = 2.4 Hz, *C*H_2), 62.1 (t, J_{PC} = 2.9 Hz, *C*H_2), 89.7 (t, J_{PC} = 205.6 Hz, CP), 108.3 (t, J_{PC} = 7.6 Hz, C=C), 205.05 (t apparent, J_{CP} = 3.9 Hz, C). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{22}H_{37}O_6P_2$ 459.2065 found 459.2067.




Jan09-2015
de063
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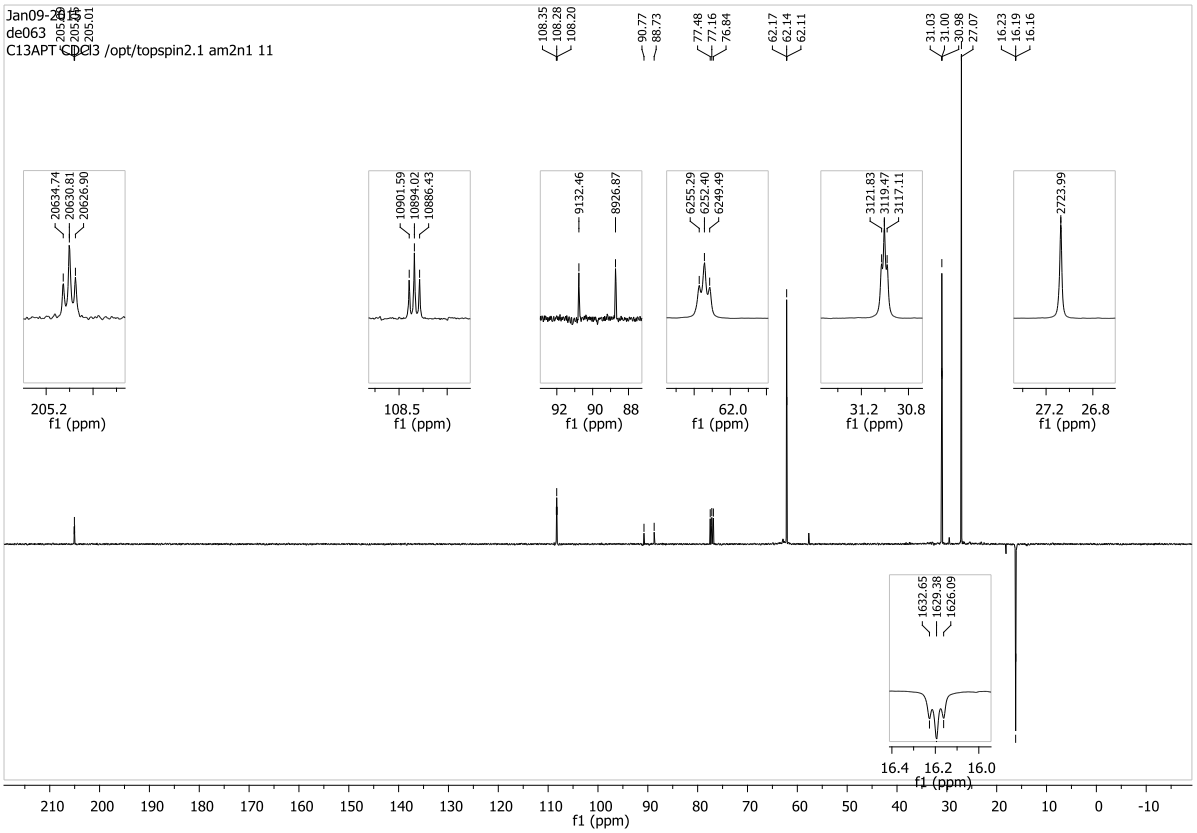
f1 (ppm)


Jan09-2015
de063
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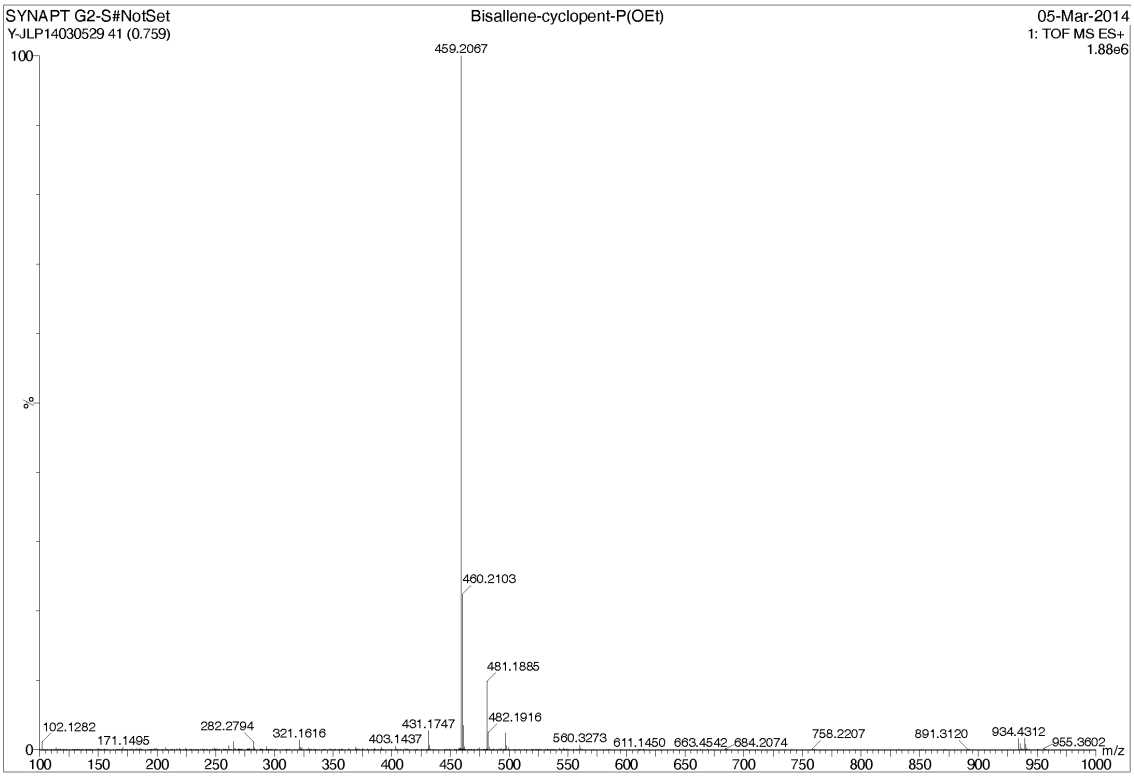
f1 (ppm)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Bisallene-cyclopent-P(OEt)
05-Mar-2014
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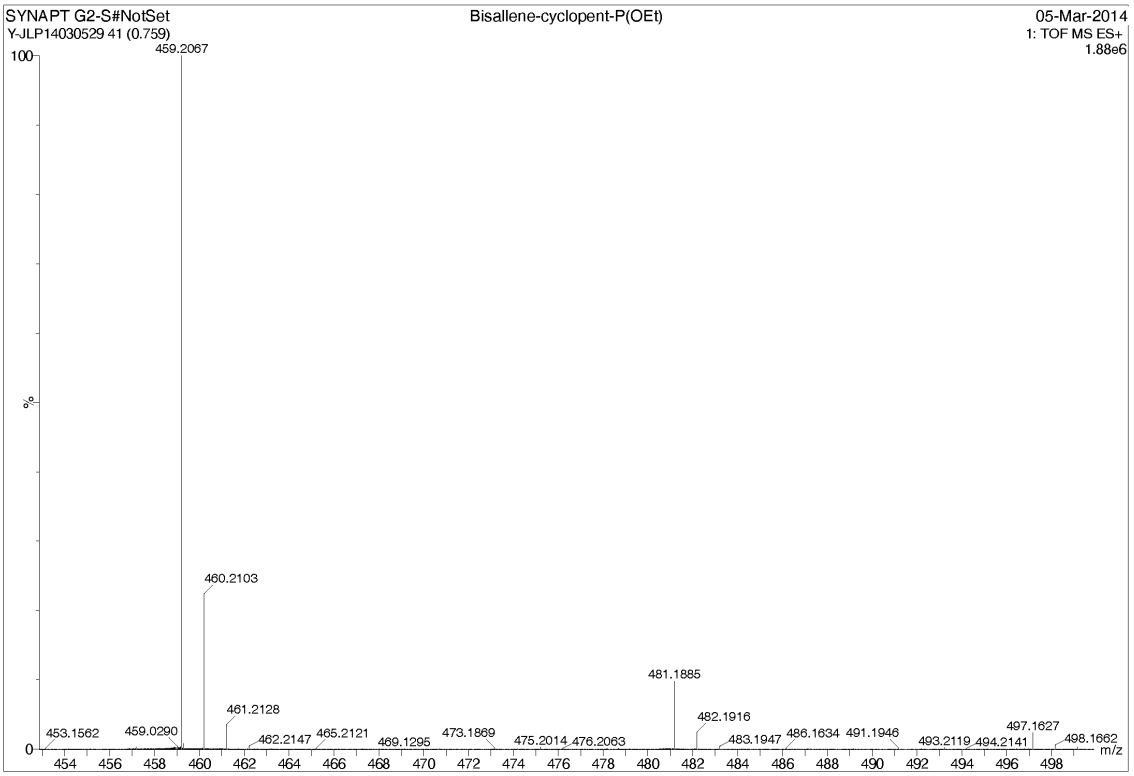
481.1885
482.1916
102.1282
171.1495
282.2794
321.1616
403.1437
431.1747
560.3273
611.1450
663.4542
684.2074
758.2207
891.3120
934.4312
955.3602
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030529 41 (0.759)
Bisallene-cyclopent-P(OEt)
05-Mar-2014
1: TOF MS ES+
1.88e6
459.2067
460.2103
481.1885
461.2128
482.1916
453.1562
459.0290
462.2147
465.2121
469.1295
473.1869
475.2014
476.2063
483.1947
486.1634
491.1946
493.2119
494.2141
497.1627
498.1662
%
m/z

Single Mass Analysis

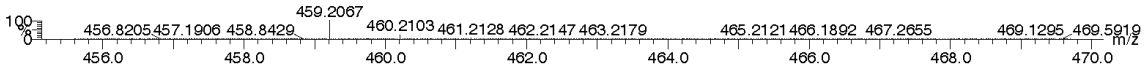
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3817 formula(e) evaluated with 4 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 N: 0-30 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030529 41 (0.759)

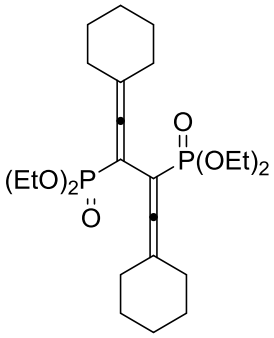
Bisallene-cyclopent-P(OEt)

05-Mar-2014
1: TOF MS ES+
1.88e+006



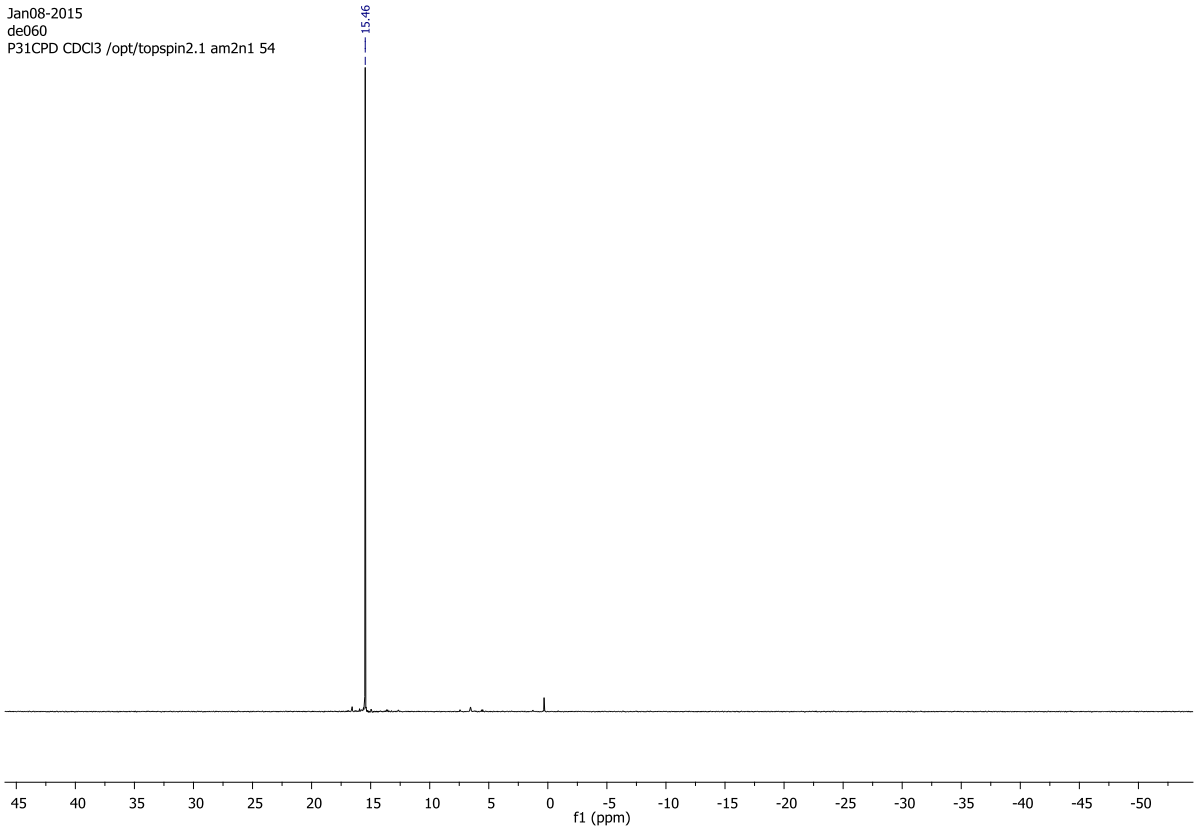
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
459.2067	459.2065	0.2	0.4	5.5	1449.2	0.049	95.26	C22 H37 O6 P2
	459.2068	-0.1	-0.2	6.5	1452.2	3.051	4.73	C17 H34 N8 O P3
	459.2067	0.0	0.0	8.5	1459.9	10.829	0.00	C10 H24 N18 O2 P
	459.2070	-0.3	-0.7	-1.5	1460.8	11.641	0.00	C7 H33 N12 O7 P2

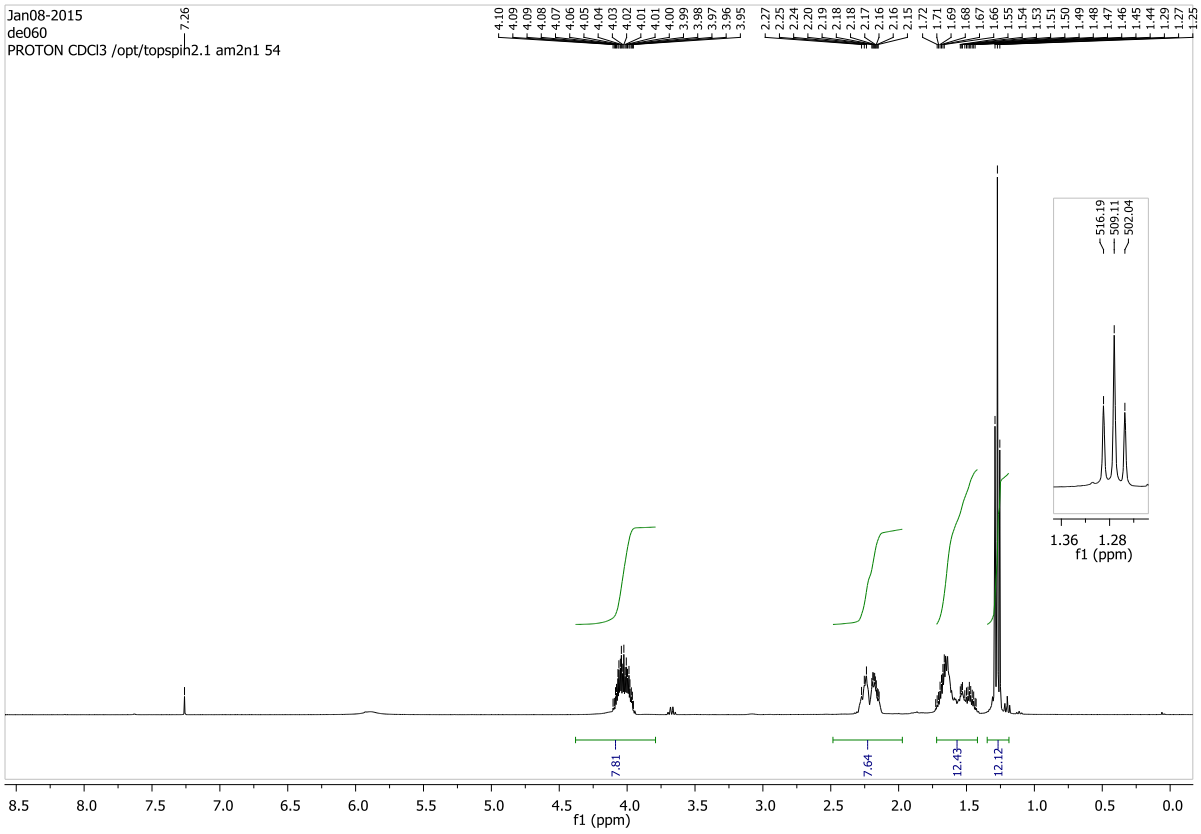
3.5. Tetraethyl (1,4-dicyclohexylidenebuta-1,3-diene-2,3-diyl)bis(phosphonate) (2e)

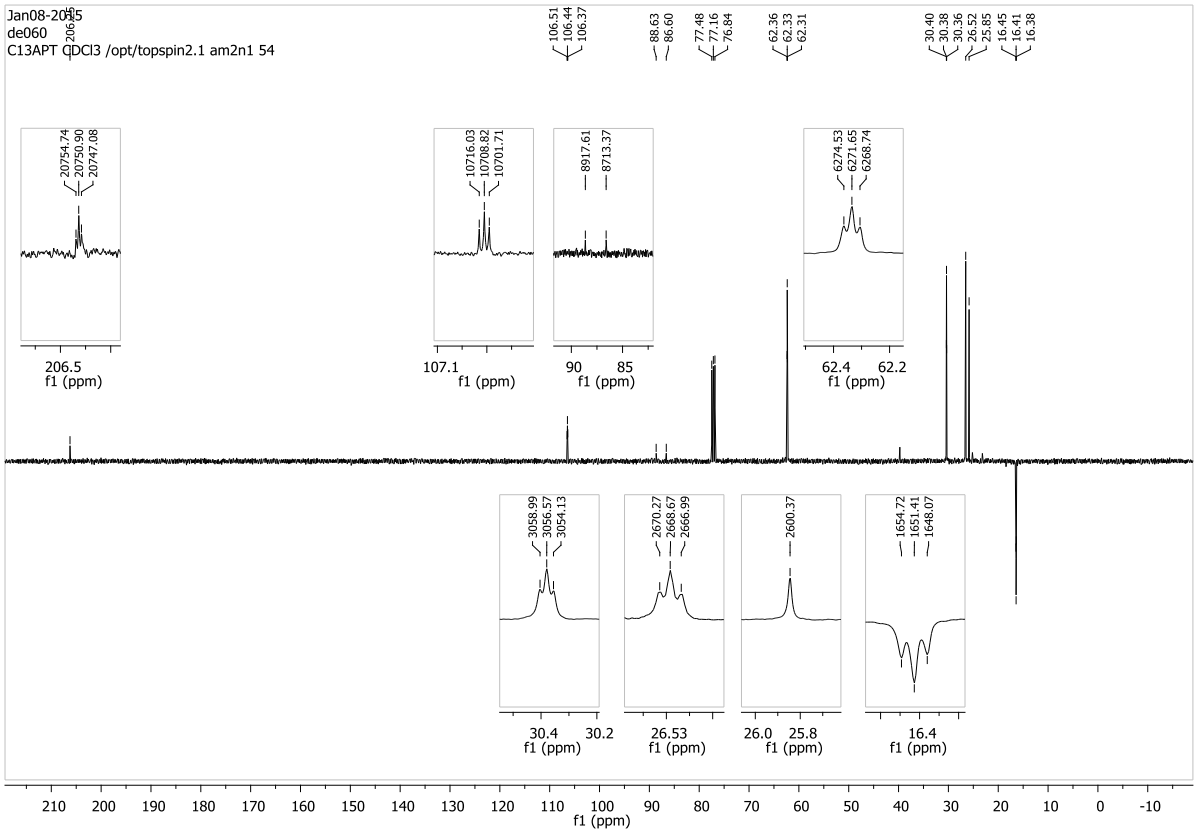


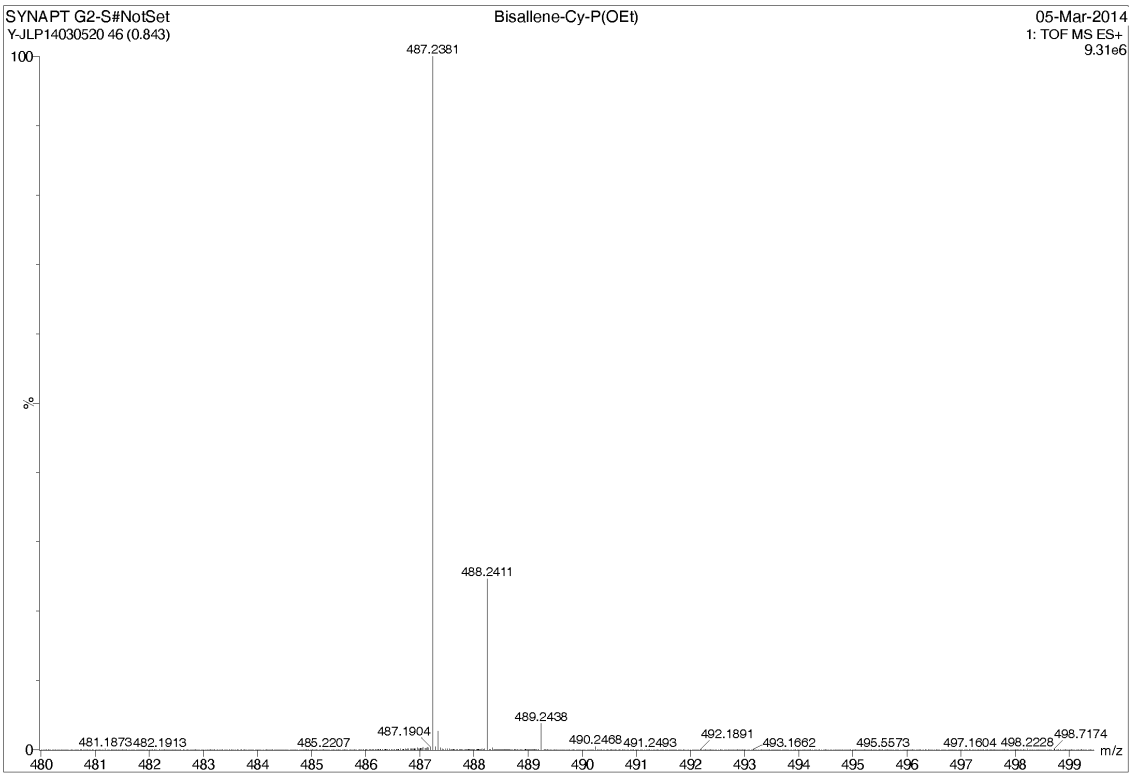
The reaction was carried out using diyne diol **1e** (4.00 g, 16.2 mmol) and $ClP(OEt)_2$ (5.08 g, 32.5 mmol). The crude material was used without purification. Yellow solid, 7.82 g, yield = 99%.

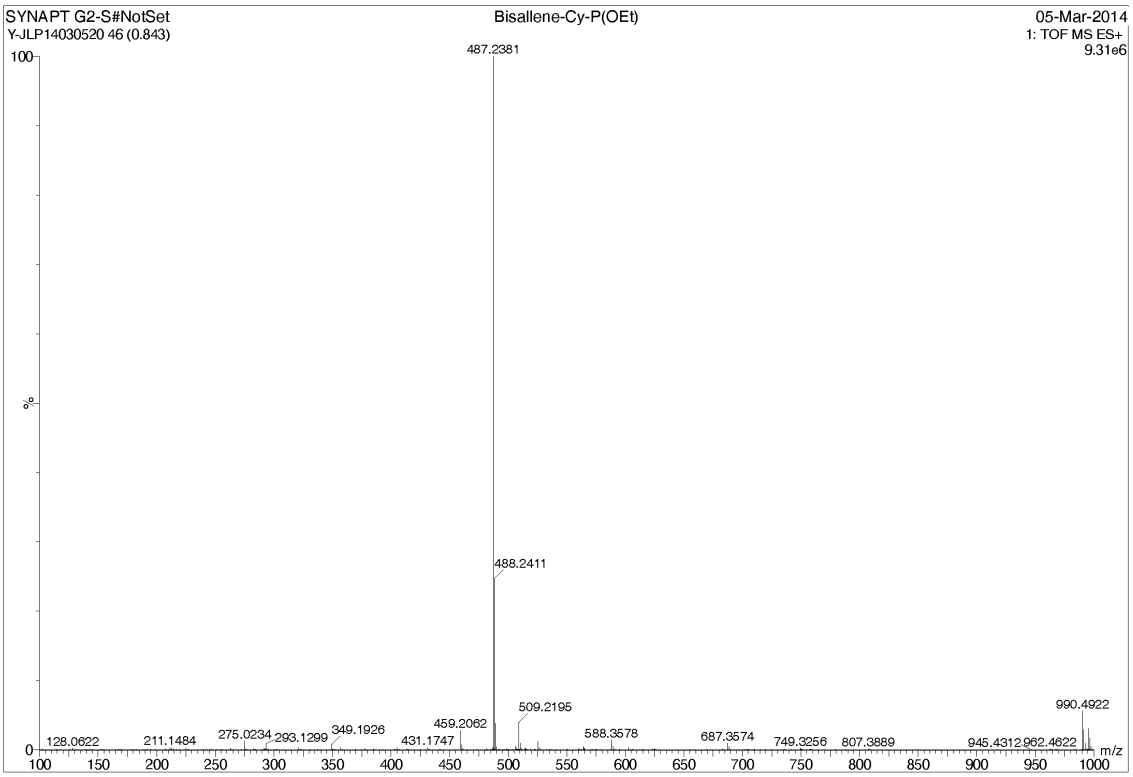
^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 15.5 (s). ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) =1.27 (t, *J* = 7.1 Hz, 12 H, 4 *C*H_3), 1.44-1.72 (m, 12H, 6 *C*H_2), 2.15-2.27 (m, 8H, 6 *C*H_2), 3.95-4.10 (m, 8H, 4 *C*H_2O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 16.4 (t, J_{CP} = 3.3 Hz, CH_3), 25.8 (s, *C*H_2), 26.5 (t, J_{CP} = 1.6 Hz, CH_2), 30.4 (t, J_{CP} = 2.4 Hz, CH_2), 62.3 (t, J_{CP} = 2.9 Hz, CH_2O), 87.6 (d, J_{CP} = 204.2 Hz, CP), 106.4 (t, J_{CP} = 7.2 Hz, C=C), 206.2 (t, J_{CP} = 3.9 Hz, Csp). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{24}H_{41}O_6P_2$ 487.2378 found 487.2381.




Jan08-2015
de060
PROTON CDCl3 /opt/topspin2.1 am2n1 54
7.26
7.81
7.64
12.43
12.12
516.19
509.11
502.04
1.36
1.28
f1 (ppm)


Jan08-2015
de060
C13APT CDCl3 /opt/topspin2.1 am2n1 54
206.5
106.51
106.44
106.37
88.63
86.60
77.48
77.16
76.84
62.36
62.33
62.31
30.40
30.38
30.36
26.52
25.85
16.45
16.41
16.38
20754.74
20750.90
20747.08
10716.03
10708.82
10701.71
8917.61
8713.37
6274.53
6271.65
6268.74
3058.99
3056.57
3054.13
2670.27
2668.67
2666.99
2600.37
1654.72
1651.41
1648.07
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030520 46 (0.843)
Bisallene-Cy-P(OEt)
05-Mar-2014
1: TOF MS ES+
9.31e6
100
%
0
487.2381
488.2411
489.2438
481.1873
482.1913
485.2207
487.1904
490.2468
491.2493
492.1891
493.1662
495.5573
497.1604
498.2228
498.7174
m/z
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499


SYNAPT G2-S#NotSet
Y-JLP14030520 46 (0.843)
Bisallene-Cy-P(OEt)
05-Mar-2014
1: TOF MS ES+
9.31e6
100
%
0
487.2381
488.2411
509.2195
990.4922
128.0622
211.1484
275.0234
293.1299
349.1926
431.1747
459.2062
588.3578
687.3574
749.3256
807.3889
945.4312
962.4622
m/z
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

Single Mass Analysis

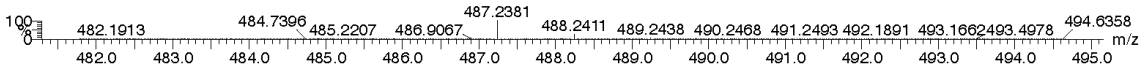
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
298 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030520 46 (0.843)

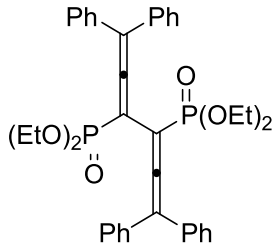
Bisallene-Cy-P(OEt)

05-Mar-2014
1: TOF MS ES+
9.31e+006



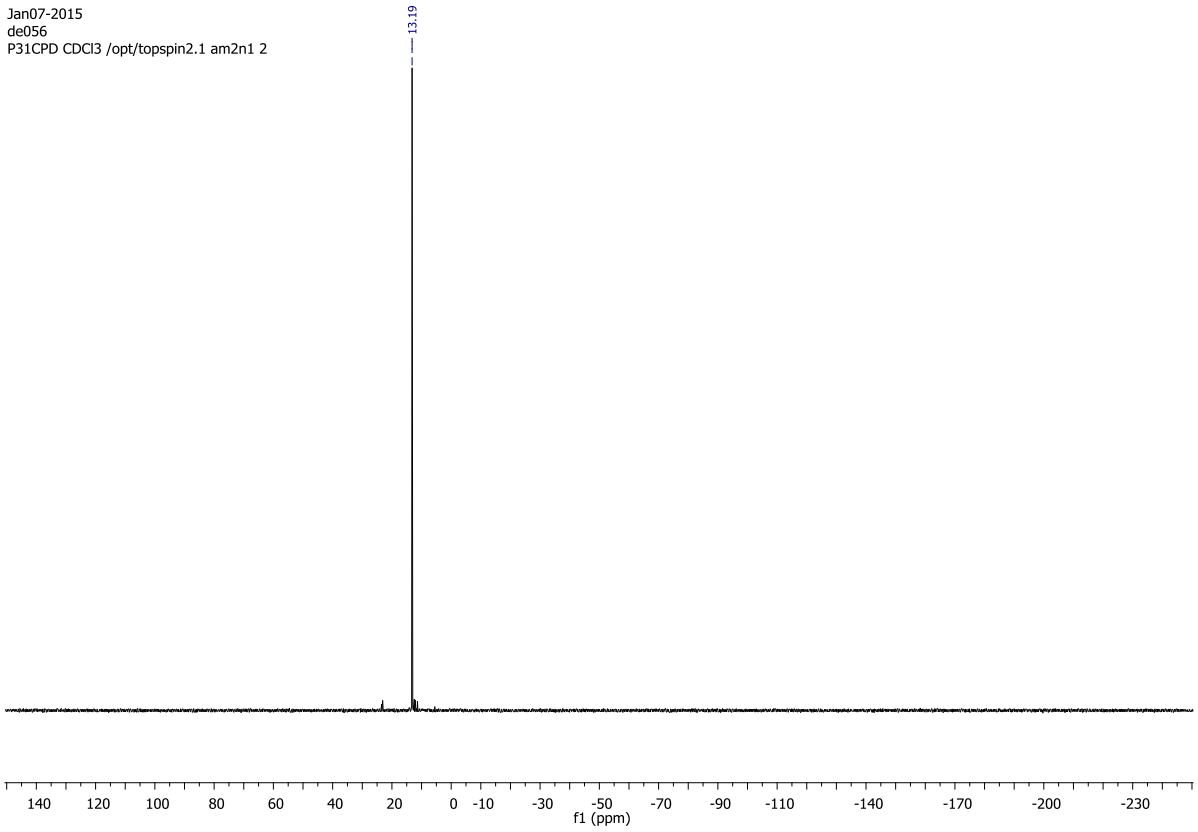
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
487.2381	487.2378	0.3	0.6	5.5	1767.5	n/a	n/a	C24 H41 O6 P2

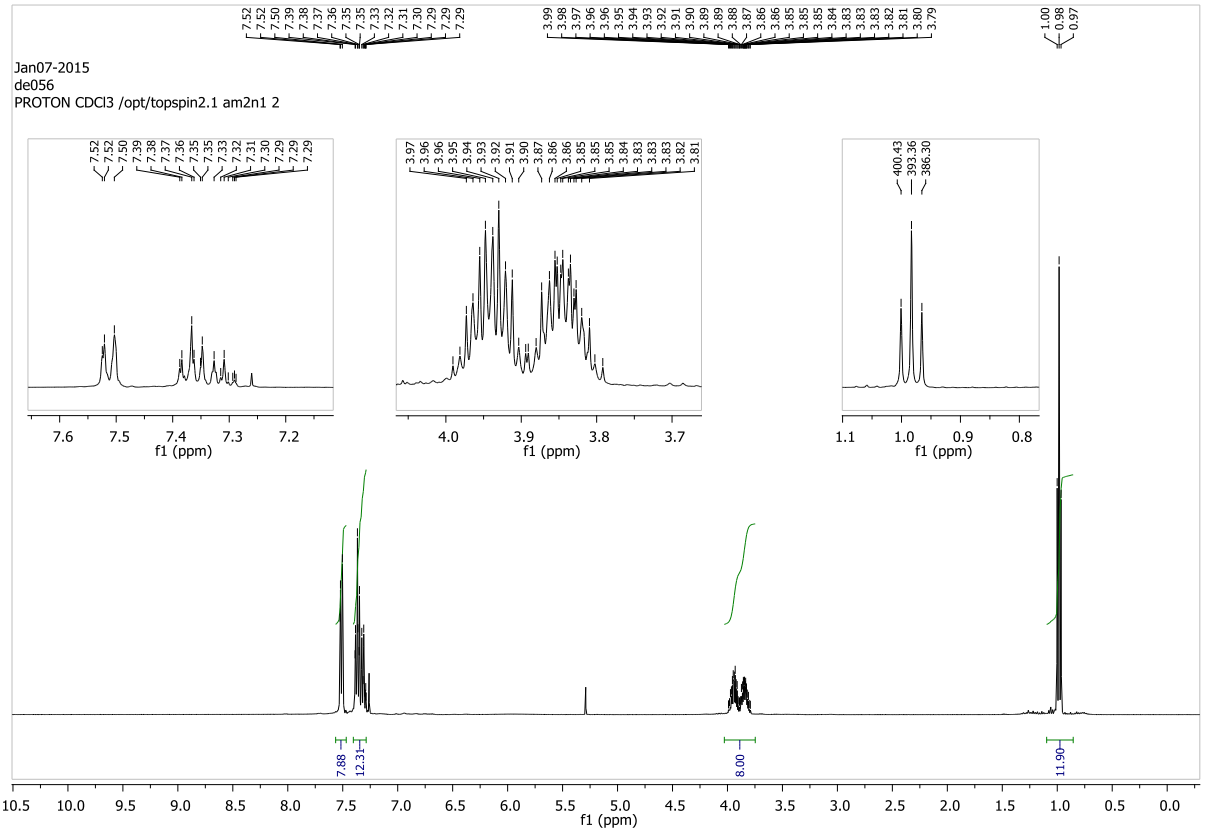
3.6. Tetraethyl (1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene-3,4-diyl)bis(phosphonate) (2f)

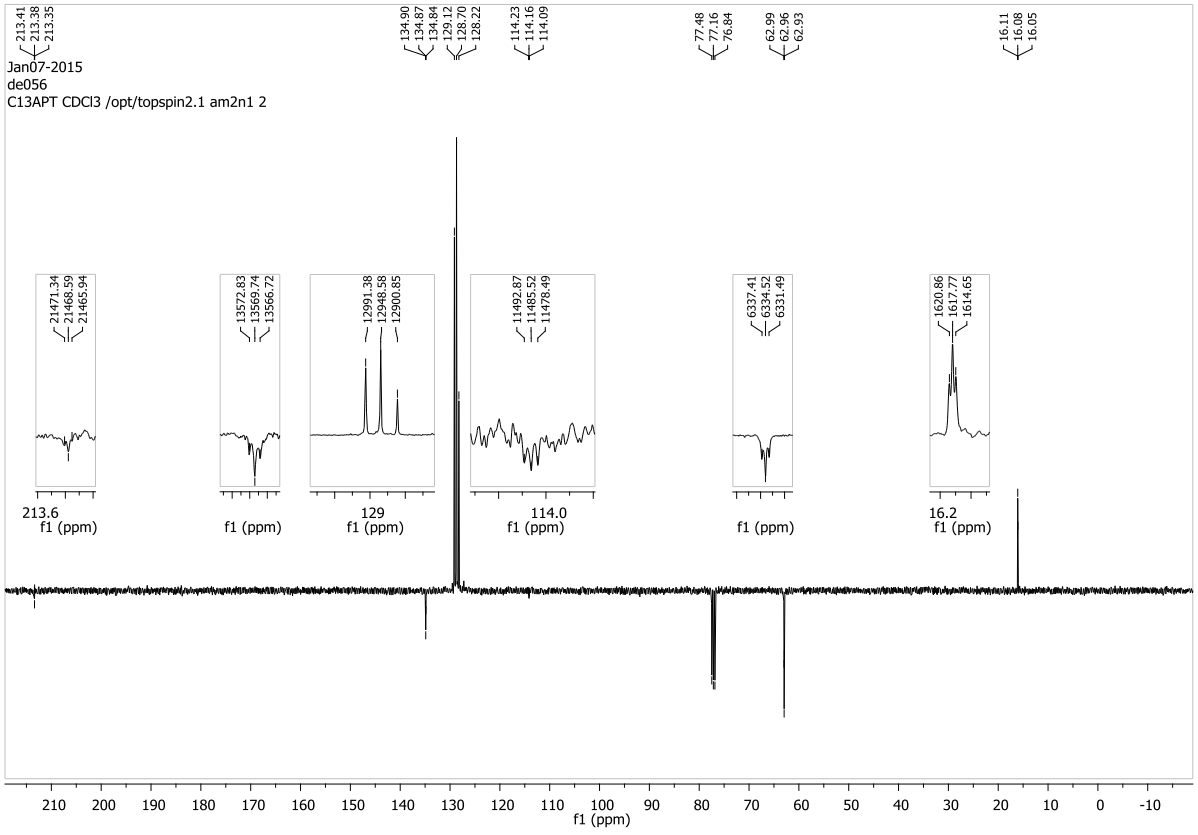


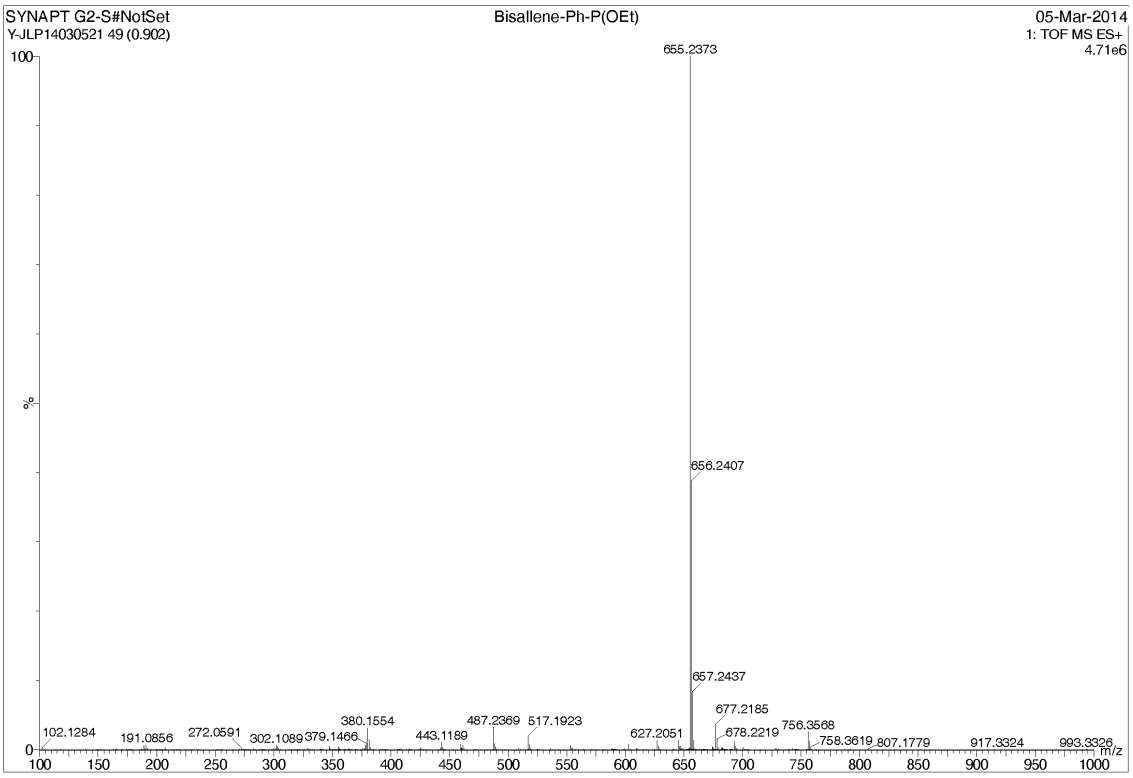
The reaction was carried out using diyne diol **1f** (9.95 g, 24.0 mmol) and $ClP(OEt)_2$ (7.51 g, 48 mmol). The crude material is purified by chromatography (silica gel, EtOH/AcOEt/CH_2Cl_2 0.4/50/49.6). Red solid, 13.04 g, yield = 83%.

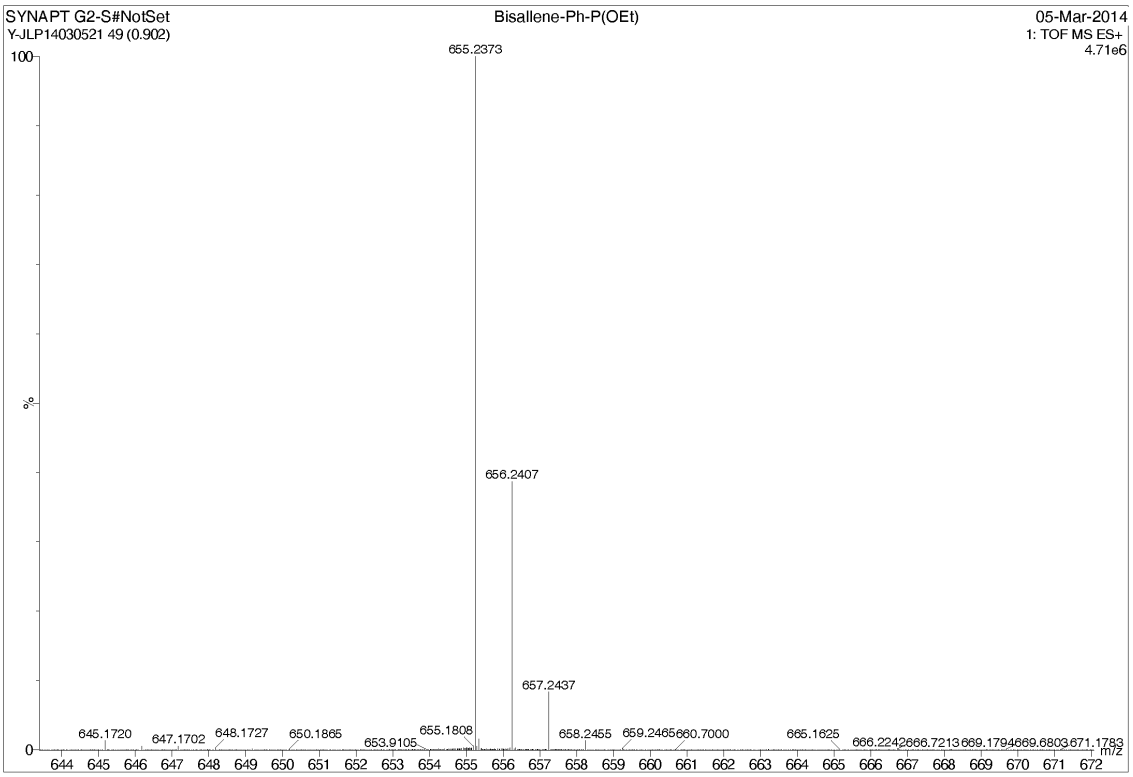
^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 13.2 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 0.98 (t, *J* = 7.1 Hz, 12H, 4 CH_3), 3.81-3.97 (m, 8H, 4 OCH_2), 7.29-7.39 (m, 12H, CH_{Ph}), 7.50-7.52 (m, 8H, CH_{Ph}); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 16.1 (t, J_{PC} = 3.1 Hz, CH_3), 63.0 (t, J_{PC} = 3.0 Hz, CH_2O), 114.03 (t, J_{PC} = 7.2 Hz, C), 128.2, 128.7, 129.1 (s, CH_{Ph}), 134.9 (t, J_{PC} = 3.1 Hz, C_{Ph}), 213.4 (t, J_{PC} = 2.7 Hz, C). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{38}H_{41}O_6P_2$ 655.2378 found 655.2373.




Jan07-2015
de056
PROTON CDCl3 /opt/topspin2.1 am2n1 2
f1 (ppm)
7.88
12.31
8.00
11.90


Jan07-2015
de056
C13APT CDCl3 /opt/topspin2.1 am2n1 2
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030521 49 (0.902)
Bisallene-Ph-P(OEt)
05-Mar-2014
1: TOF MS ES+
4.71e6
655.2373
656.2407
657.2437
677.2185
678.2219
756.3568
758.3619
807.1779
917.3324
993.3326
487.2369
517.1923
627.2051
380.1554
379.1466
443.1189
302.1089
272.0591
191.0856
102.1284
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030521 49 (0.902)
Bisallene-Ph-P(OEt)
05-Mar-2014
1: TOF MS ES+
4.71e6
655.2373
656.2407
657.2437
645.1720
647.1702
648.1727
650.1865
653.9105
655.1808
658.2455
659.2465
660.7000
665.1625
666.2242
666.7213
669.1794
669.6803
671.1783
%
m/z

Single Mass Analysis

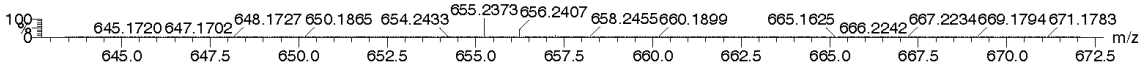
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
491 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030521 49 (0.902)

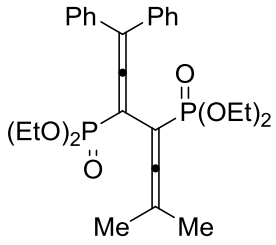
Bisallene-Ph-P(OEt)

05-Mar-2014
1: TOF MS ES+
4.71e+006



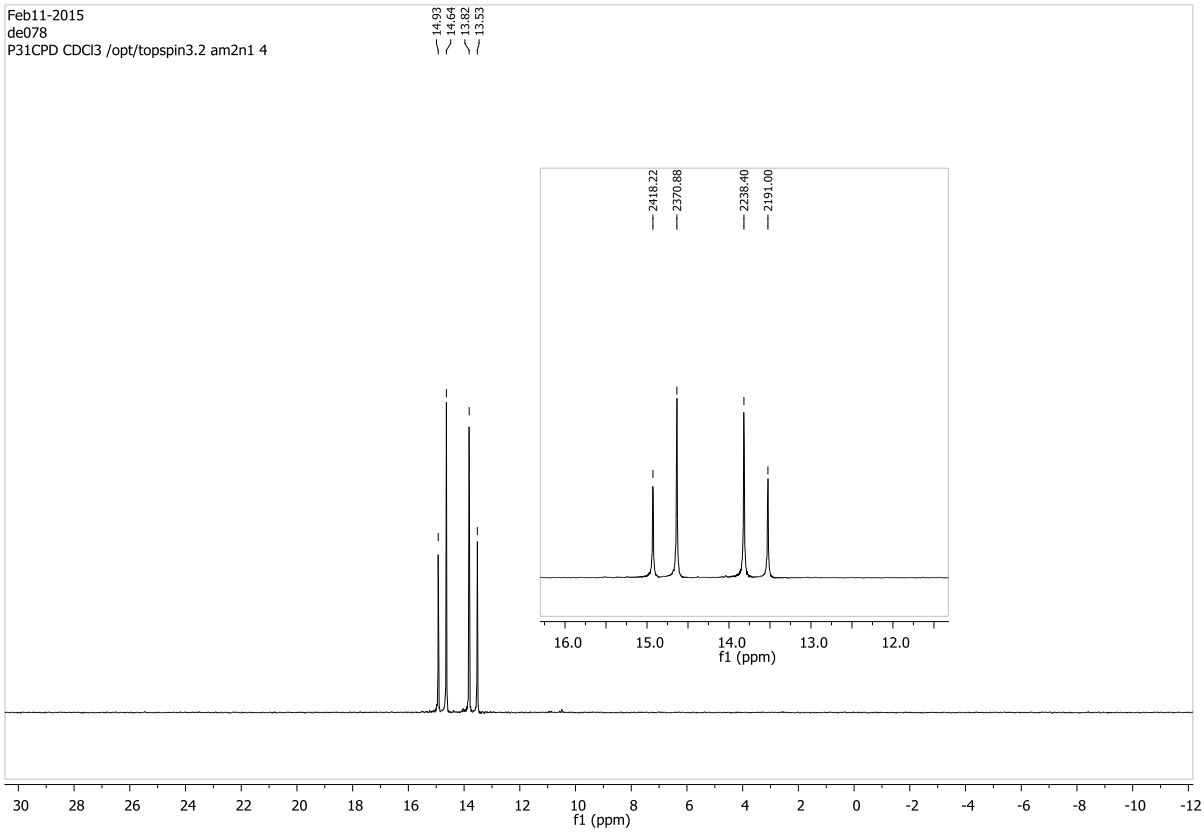
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
655.2373	655.2378	-0.5	-0.8	19.5	1383.9	0.020	98.06	C38 H41 O6 P2
	655.2367	0.6	0.9	6.5	1387.8	3.945	1.94	C27 H44 O16 P

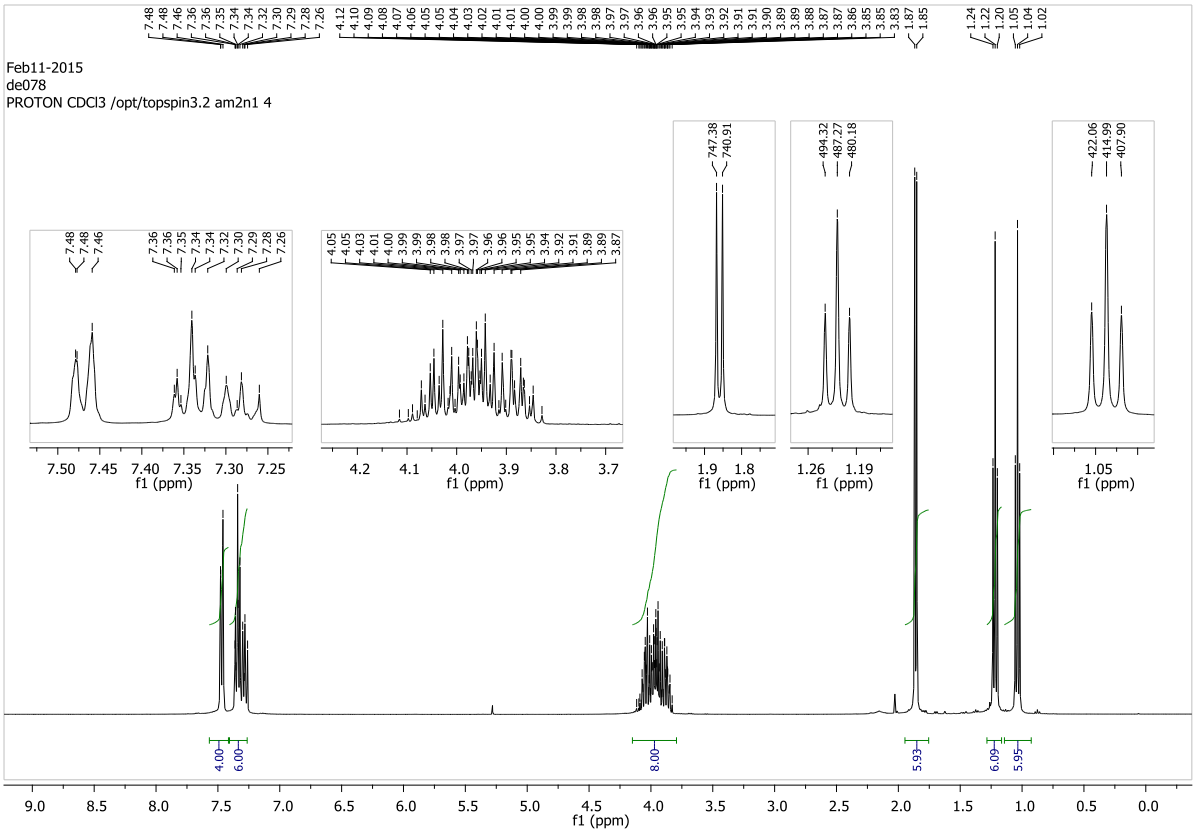
3.7. Tetraethyl (6-methyl-1,1-diphenylhepta-1,2,4,5-tetraene-3,4-diyl)bis(phosphonate) (2g)

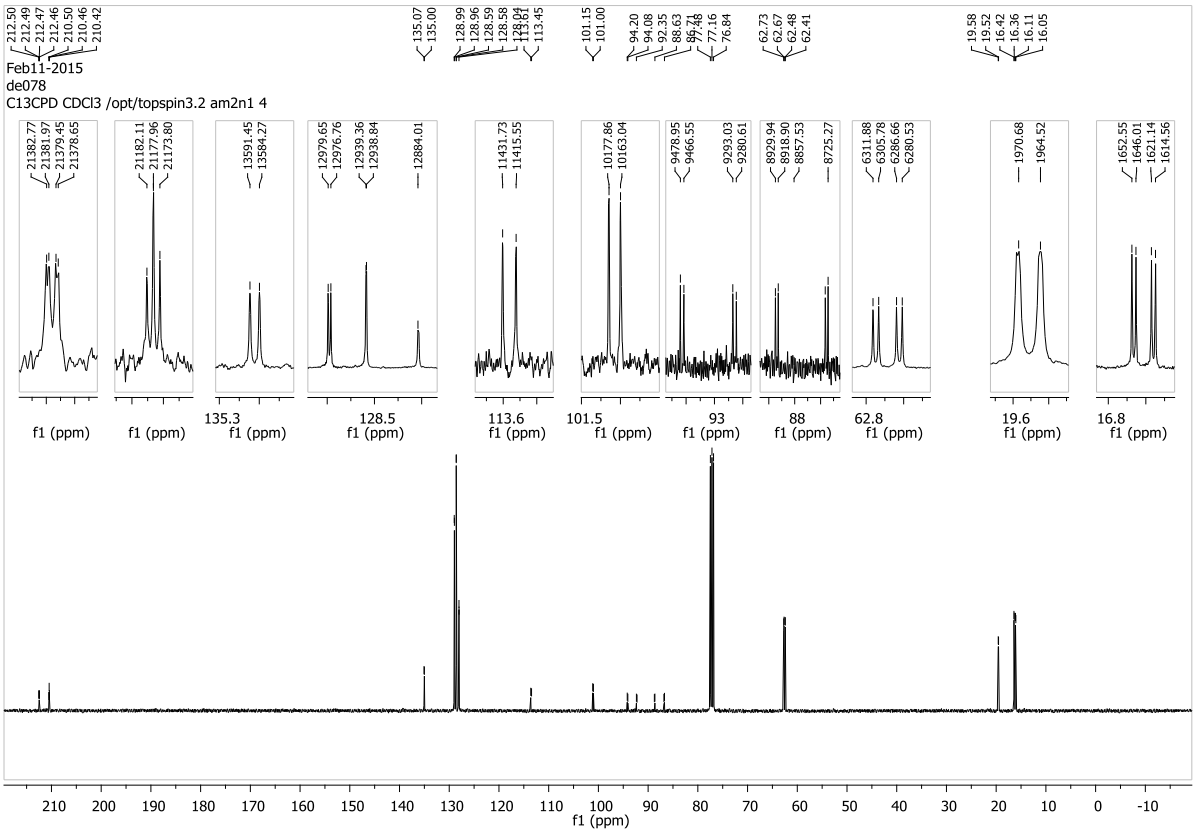


The reaction was carried out using diyne diol **1g** (6.97 g, 24.0 mmol) and $ClP(OEt)_2$ (7.51 g, 48 mmol). The crude material is purified by chromatography (silica gel, EtOH/AcOEt/CH_2Cl_2 0.4/50/49.6). Yellow solid, 7.89 g, yield = 62%.

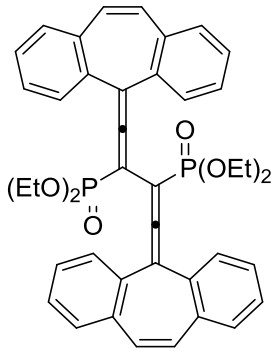
^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 13.7 (d, *J* = 47.4 Hz), 14.8 (d, *J* = 47.3 Hz); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.04 (t, *J* = 7.1 Hz, 6H, 2 C*H*$_3$), 1.22 (t, *J* = 7.1 Hz, 6H, 2 C*H*$_3$), 1.85 (s, CH_3), 1.86 (s, CH_3), 3.83-4.12 (m, 8H, 4 C*H*$_2$O), 7.28-7.36 (m, 6H, CH_{Ph}), 7.46-7.48 (m, 4H, CH_{Ph}). ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 16.1 (d, J_{PC} = 6.6 Hz, CH_3), 16.4 (d, *J* = 6.5 Hz, CH_3), 19.5 (s, CH_3), 19.6 (s, CH_3), 62.4 (d, *J* = 6.1 Hz, *C*H_2O), 62.7 (d, *J* = 6.1 Hz, *C*H_2O), 87.7 (dd, *J* = 193.6, 11.1 Hz, CP), 93.2 (dd, *J* = 185.9, 12.4 Hz, CP), 101.1 (d, *J* = 14.8 Hz, C=C), 113.52 (d, *J* = 16.2 Hz, C=C), 128.0, 128.1, 128.6, 128.6, 128.9, 129.0 (s, CH_{Ph}), 135.0 (d, *J* = 7.2 Hz, C=C), 210.5 (t, J_{CP} = 4.2 Hz, C_{sp}), 212.5 (dd, J_{CP} = 3.3, 0.8 Hz, Csp). HRMS (ESI): m/z calcd. For $C_{28}H_{37}O_6P_2$, $[M+H]^+$: 531.2065 Found: 531.2065.




Feb11-2015
de078
PROTON CDCl3 /opt/topspin3.2 am2n1 4
f1 (ppm)

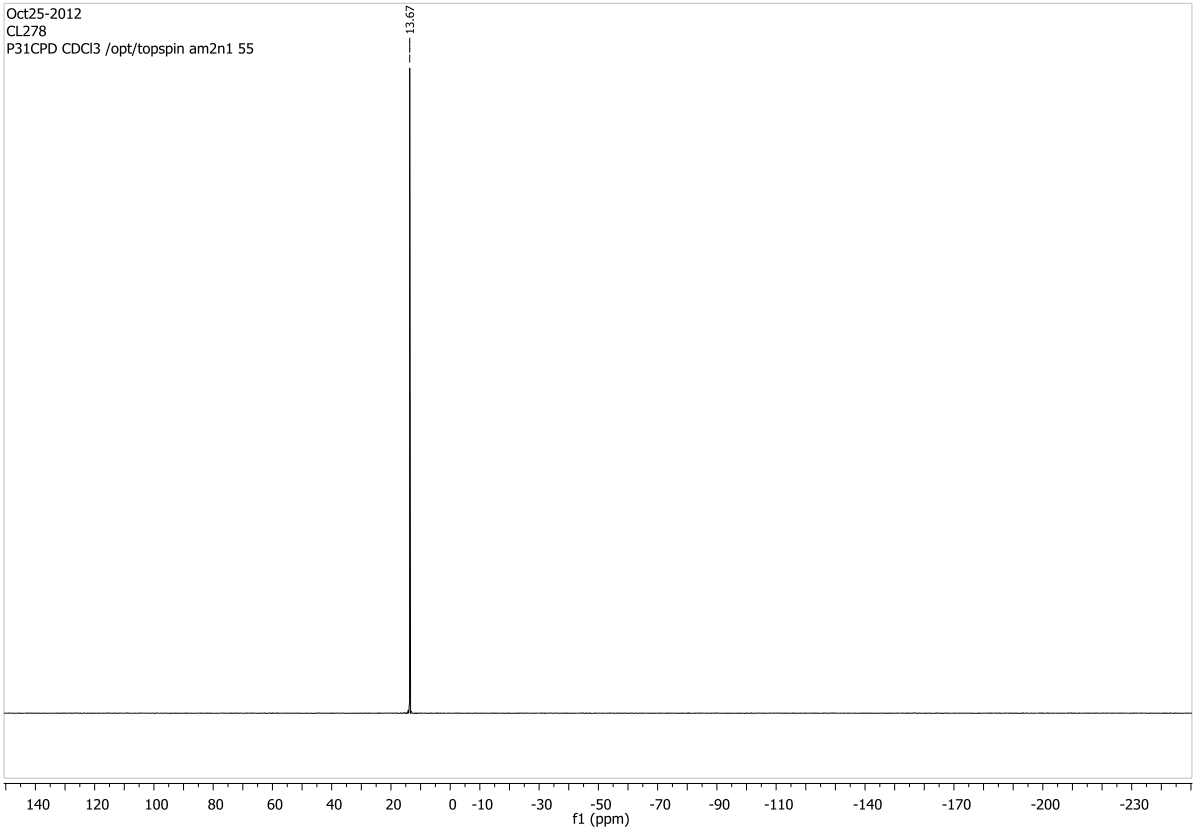

Feb11-2015
de078
C13CPD CDCl3 /opt/topspin3.2 am2n1 4
f1 (ppm)

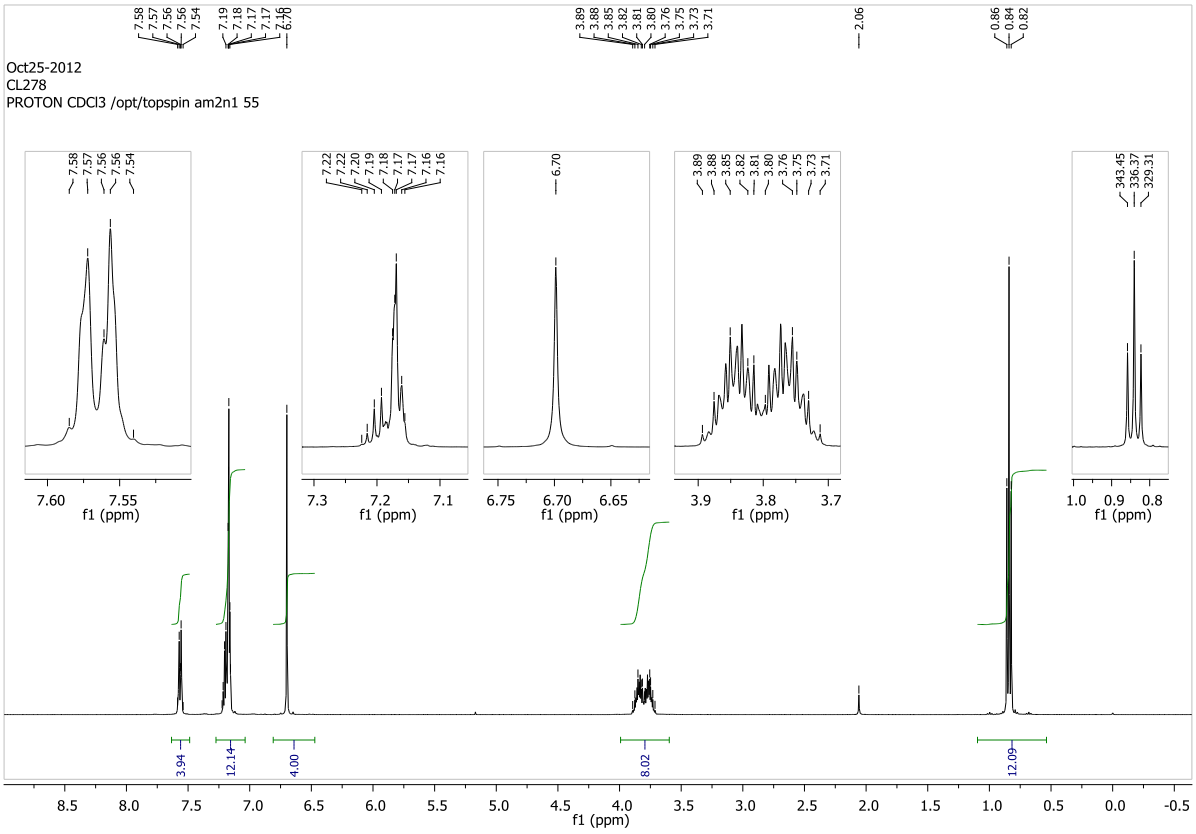
3.8. Tetraethyl (1,4-bis(5H-dibenzo[a,d][7]annulen-5-ylidene)-1l5,4l5-buta-1,3-diene-2,3-diyl)bis(phosphonate) (2h)

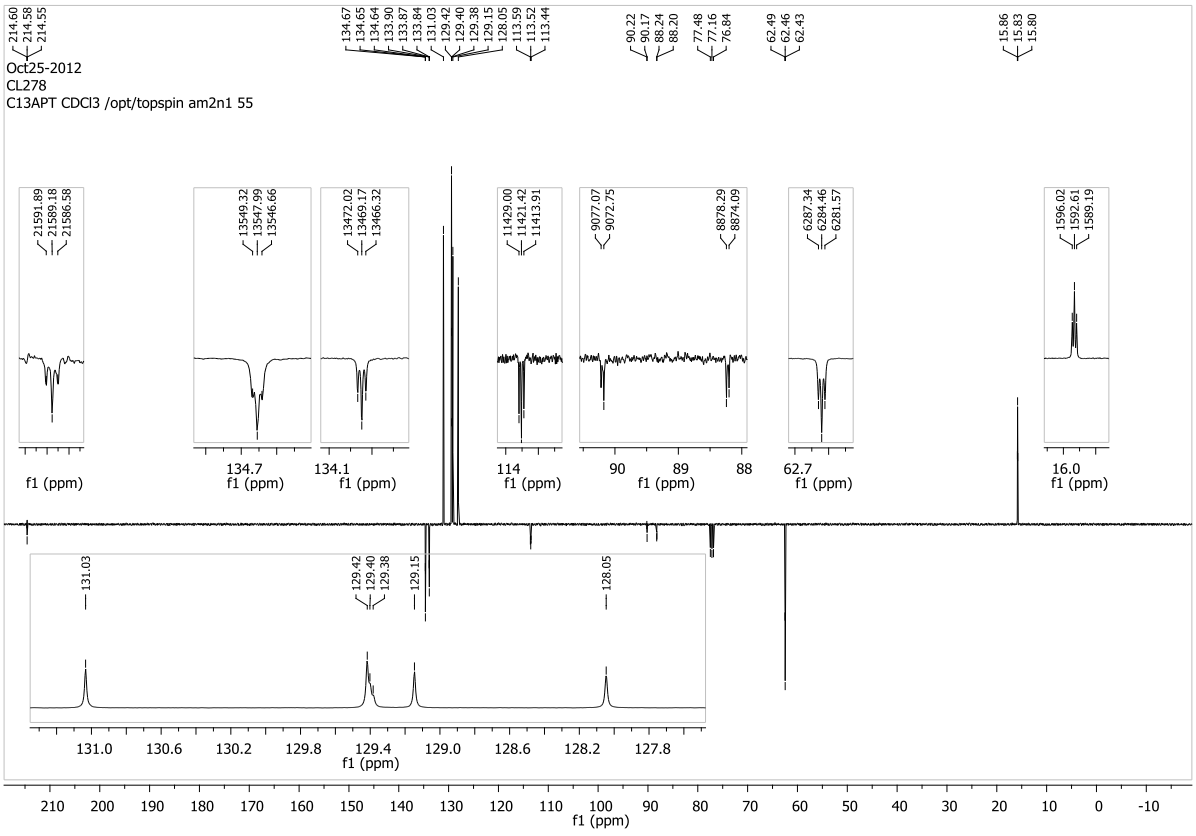


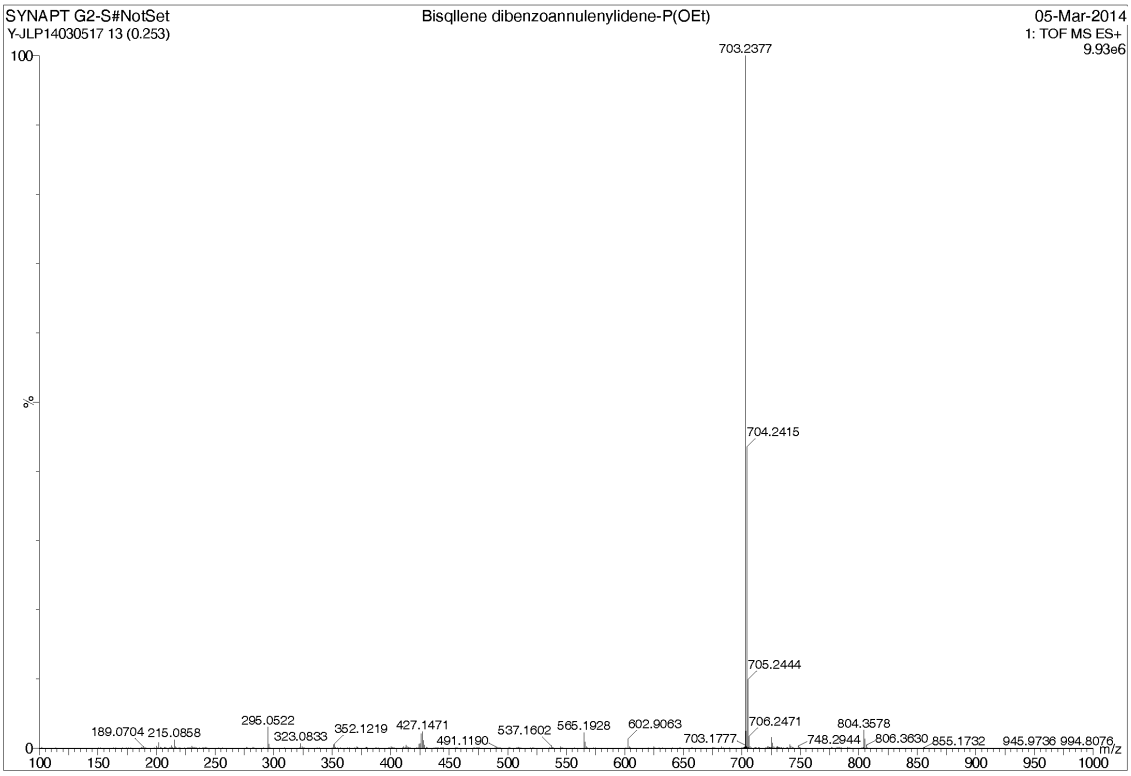
The reaction was carried out using diyne diol **1h** (2.00 g, 4.31 mmol) and $ClP(OEt)_2$ (1.35 g, 8.62 mmol). The crude material is purified by chromatography (silica gel, gradient from CH_2Cl_2 100 % to CH_2Cl_2/EtOH 98/2). White solid solid, 1.83 g, yield = 61%.

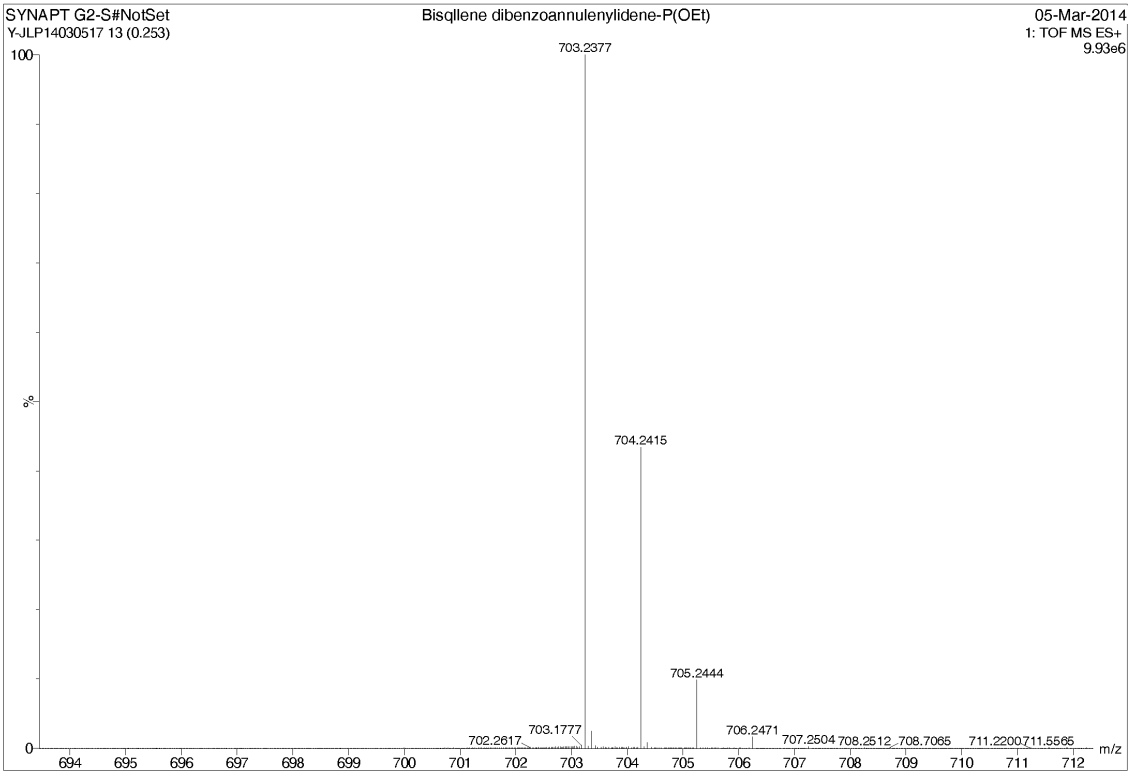
^{31}P ($CDCl_3$, 161.97 MHz) δ(ppm) : 13.7 (s); ^{1}H ($CDCl_3$, 400,13 MHz) δ(ppm) : 0.84 (t, *J* = 7.1 Hz, 12H, 4 CH_3), 3.71-3.89 (m, 8H, 4 CH_2), 6.70 (s, CH=), 7.16-7.22 (m, 12H, CH_{Ar}), 7.54-7.58 (m, 4H, CH); ^{13}C ($CDCl_3$, 100,61 MHz) δ(ppm) : 15.83 (t, *J* = 3.4 Hz, CH_3), 62.5 (t, *J* = 2.9 Hz, CH_2), 89.2 (dd, *J* = 198.8, 4.3 Hz, CP), 113.5 (t, *J* = 7.5 Hz, C), 128.0 (s, CH), 129.1 (s, CH), 129.4 (s, CH), 129.4 (s, CH), 129.4 (s, CH), 131.0 (s, CH), 133.9 (t , *J* = 2.8 Hz, C), 134.6 (t, *J* = 1.3 Hz, C), 214.6 (t, *J* = 2.7 Hz, C); HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{42}H_{41}O_6P_2$ 703.2378 found 703.2377.




Oct25-2012
CL278
PROTON CDCl3 /opt/topspin am2n1 55
f1 (ppm)


Oct25-2012
CL278
C13APT CDCl3 /opt/topspin am2n1 55
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030517 13 (0.253)
Bisqllene dibenzoannulenylidene-P(OEt)
05-Mar-2014
1: TOF MS ES+
9.93e6
703.2377
704.2415
705.2444
706.2471
189.0704
215.0858
295.0522
323.0833
352.1219
427.1471
491.1190
537.1602
565.1928
602.9063
703.1777
748.2944
804.3578
806.3630
855.1732
945.9736
994.8076
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030517 13 (0.253)
Bisqllene dibenzoannulenylidene-P(OEt)
05-Mar-2014
1: TOF MS ES+
9.93e6
703.2377
704.2415
705.2444
706.2471
702.2617
703.1777
707.2504
708.2512
708.7065
711.2200
711.5565
%
m/z

Elemental Composition Report **Page 1**

Single Mass Analysis

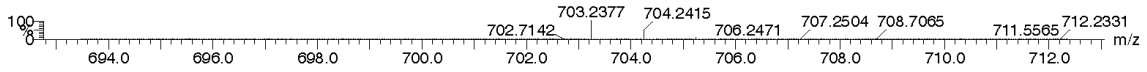
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
545 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030517 13 (0.253)

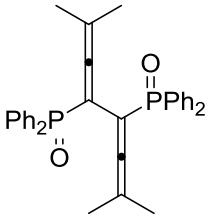
Bisqllene dibenzoannulenylidene-P(OEt)

05-Mar-2014
1: TOF MS ES+
9.93e+006



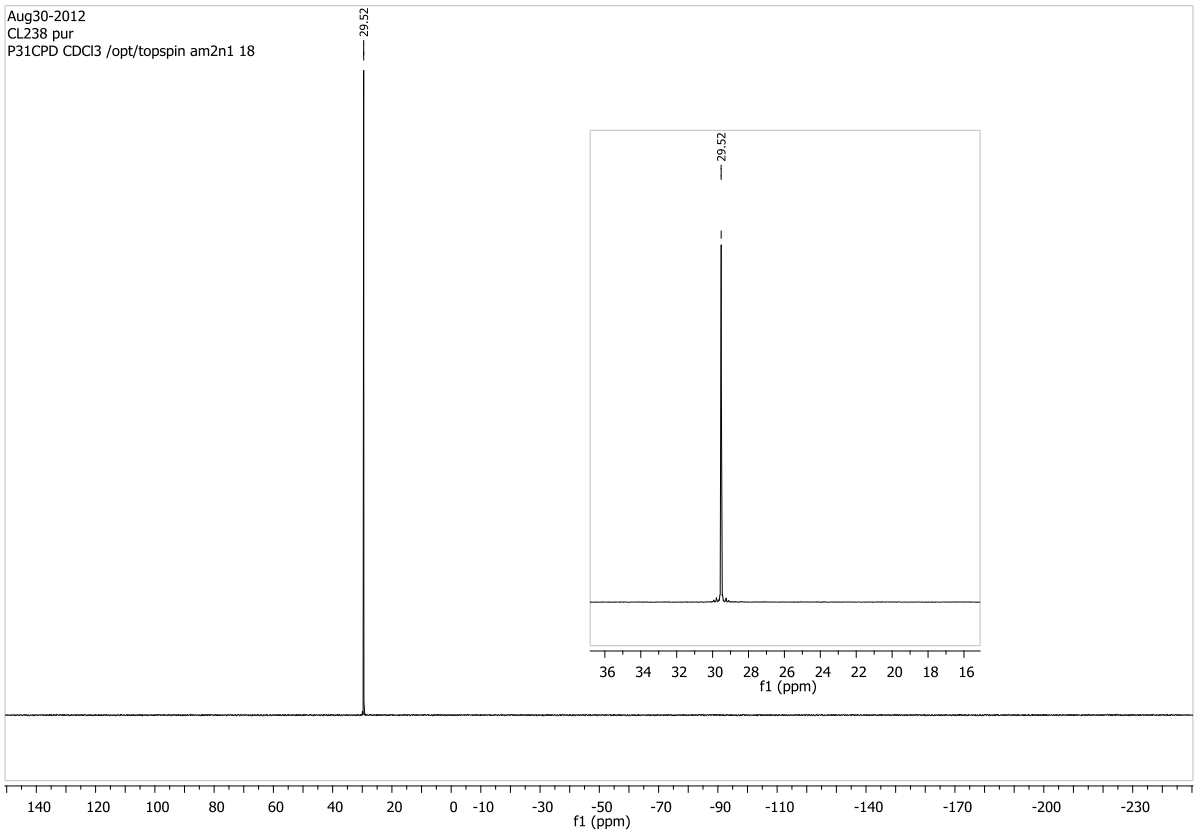
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
703.2377	703.2378	-0.1	-0.1	23.5	1250.9	n/a	n/a	C42 H41 O6 P2

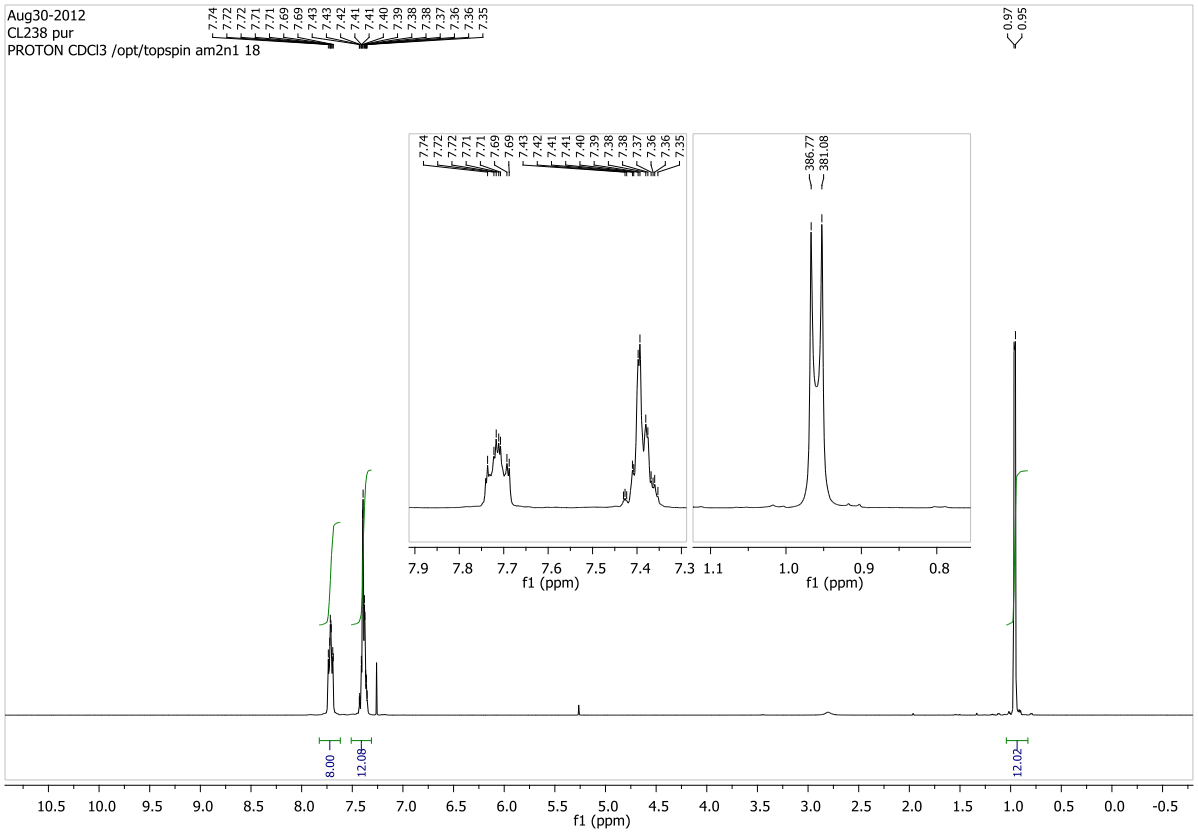
3.8. (2,7-Dimethyl-3λ5,6λ5-octa-2,3,5,6-tetraene-4,5-diyl)bis(diphenylphosphine oxide) (2i)

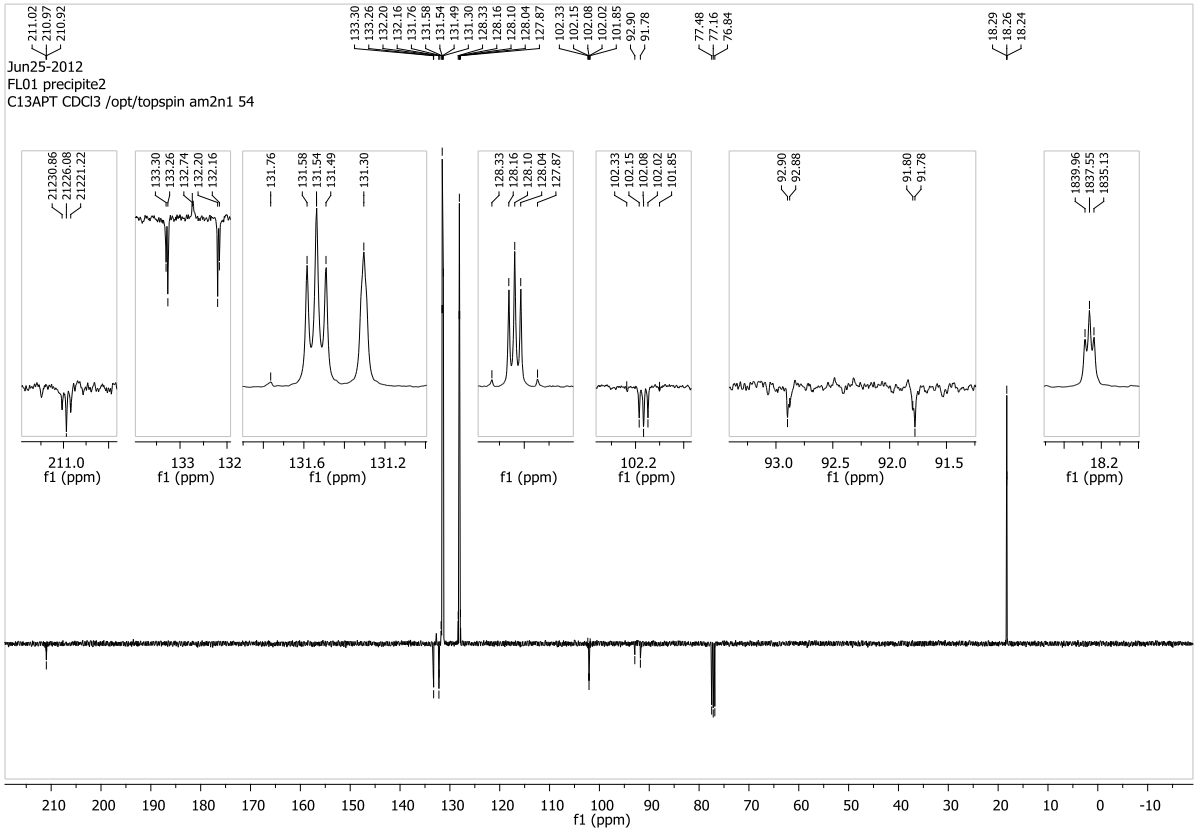


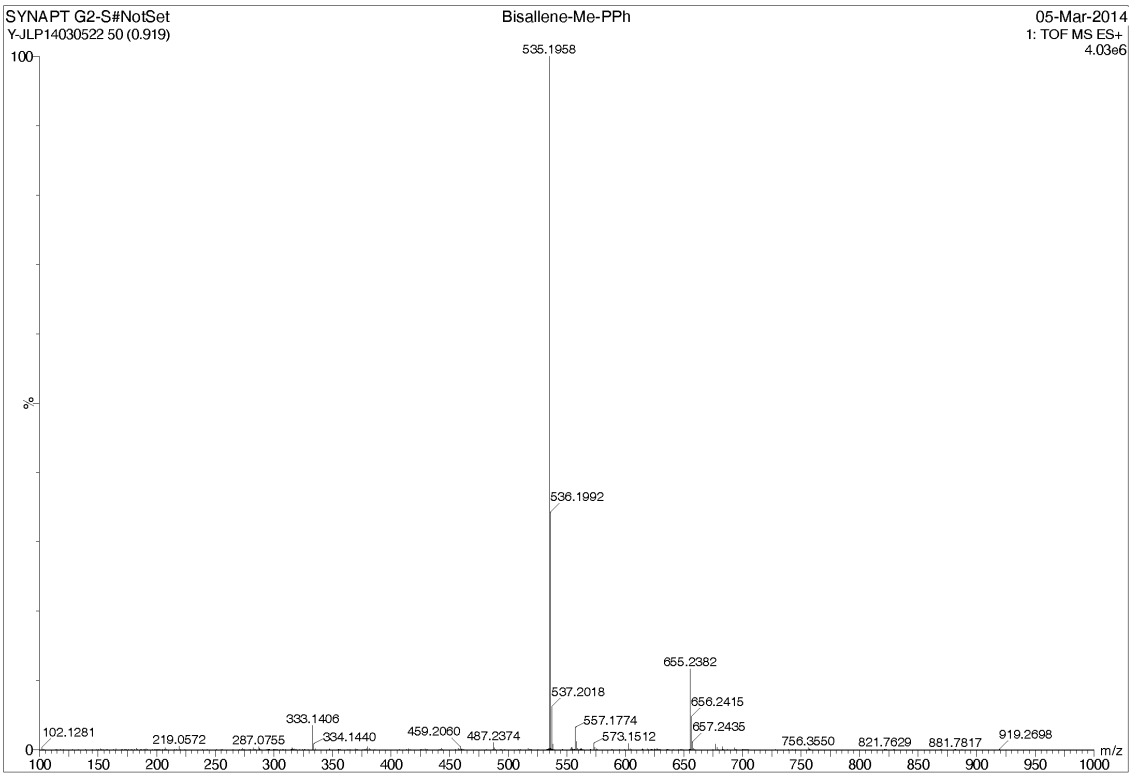
Reaction was carried out using Ph_2PCl (10.60 g, 48.0 mmol) and diynes diol **1a** (4.00 g, 24 mmol). The crude product was dissolved in the minimum quantity of dichloromethane and then added dropwise to a large volume of diethyl ether. The resulting precipitate is filtered off and dried under vacuum. White solid, 10.46 g, yield = 82%.

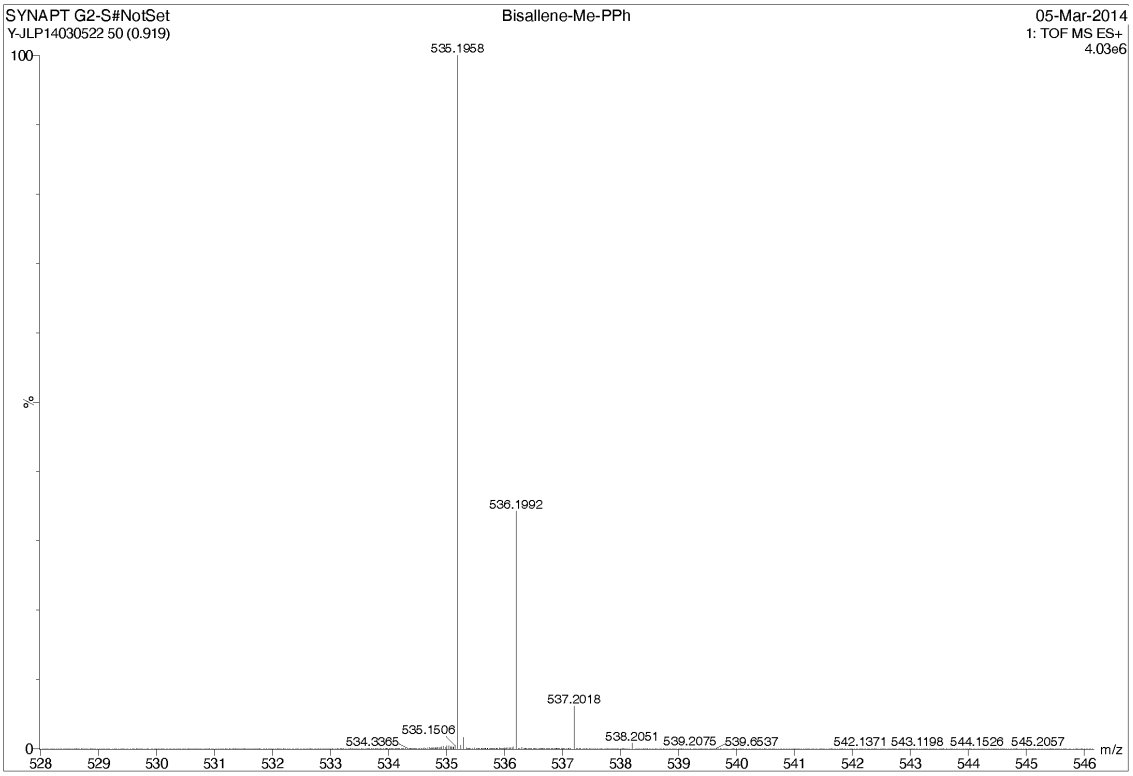
^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 29.5 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) = 0.96 (d, *J* = 5.7 Hz, 12H, 4 CH_3), 7.35-7.43 and 7.69-7.74 (2 m, 20 H, 20 CH_{Ph}); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 18.3 (t, J_{CP} = 2.4 Hz, CH_3), 91.8-92.9 (m, PC), 101.8-102.3 (m, C), 127.9-128.3 (m, CH_{Ph}), 131.3 (bs, CH_{Ph}), 131.3-131.8 (m, CH_{Ph}), 132.2-133.3 (m, C), 210.9 (t, J_{CP} = 4.8 Hz, C). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{34}H_{33}O_2P_2$ 535.1956 found 535.1958.




Aug30-2012
CL238 pur
PROTON CDCl3 /opt/topspin am2n1 18
f1 (ppm)


Jun25-2012
FL01 precipite2
C13APT CDCl3 /opt/topspin am2n1 54
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030522 50 (0.919)
Bisallene-Me-PPh
05-Mar-2014
1: TOF MS ES+
4.03e6
535.1958
536.1992
655.2382
537.2018
656.2415
557.1774
657.2435
333.1406
102.1281
219.0572
287.0755
334.1440
459.2060
487.2374
573.1512
756.3550
821.7629
881.7817
919.2698
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030522 50 (0.919)
Bisallene-Me-PPh
05-Mar-2014
1: TOF MS ES+
4.03e6
535.1958
536.1992
537.2018
535.1506
534.3365
538.2051
539.2075
539.6537
542.1371
543.1198
544.1526
545.2057
%
m/z

Single Mass Analysis

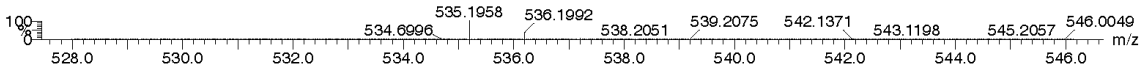
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
356 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030522 50 (0.919)

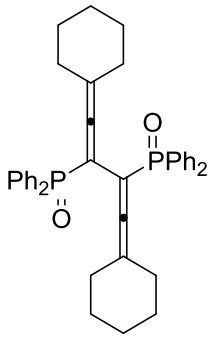
Bisallene-Me-PPh

05-Mar-2014
1: TOF MS ES+
4.03e+006



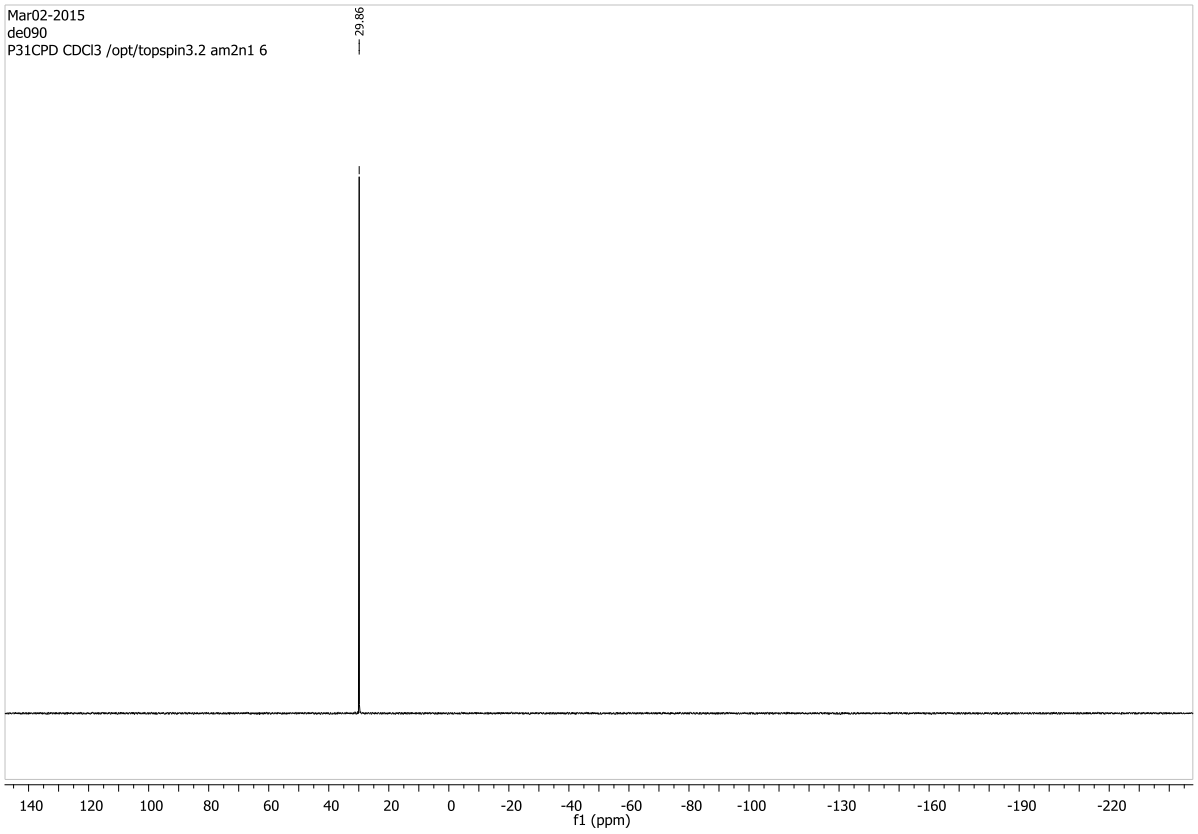
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
535.1958	535.1956	0.2	0.4	19.5	1591.9	n/a	n/a	C34 H33 O2 P2

3.9. (1,4-Dicyclohexylidene-1λ5,4λ5-buta-1,3-diene-2,3-diyl)bis(diphenylphosphine oxide) (2j)



Reaction was carried out using Ph_2PCl (10.60 g, 48.0 mmol) and diynes diol **1e** (5.91 g, 24 mmol). The crude product was dissolved in the minimum quantity of dichloromethane and then added dropwise to a large volume of diethyl ether. The resulting precipitate is filtered off and dried under vacuum. White solid, 10.51 g, yield = 71%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 29.9 (s); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) δ (ppm) **=** 0.69-0.80 (m, 4H, 2 CH2), 1.02-1.17 (m, 8H, 4 CH2), 1.32-1.49 (m, 8H, 4 CH2), 7.26-7.44 (m, 12H, 12 CH_{Ph}), 7.68-7.78 (m, 8H, 8 CH_{Ph}); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 25.2 (s, CH2), 25.6 (t, *J* = 1.2 Hz, CH2), 29.1 (t, *J* = 2.2 Hz, CH2), 92.0 (dd, *J* = 111.4, 2.4 Hz, CP), 128.0-128.4 (m, CH_{Ph}), 131.3 (t, *J* = 1.3 Hz, CH_{Ph}), 131.5-132.0 (m, CH_{Ph}), 133.0 (dd, *J* = 110.2, 3.6 Hz, C_{Ph}), 207.6 (t, *J* = 5.2 Hz, C). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{40}H_{41}O_2P_2$ 615.2582 found 615.2586.


Mar02-2015
de090
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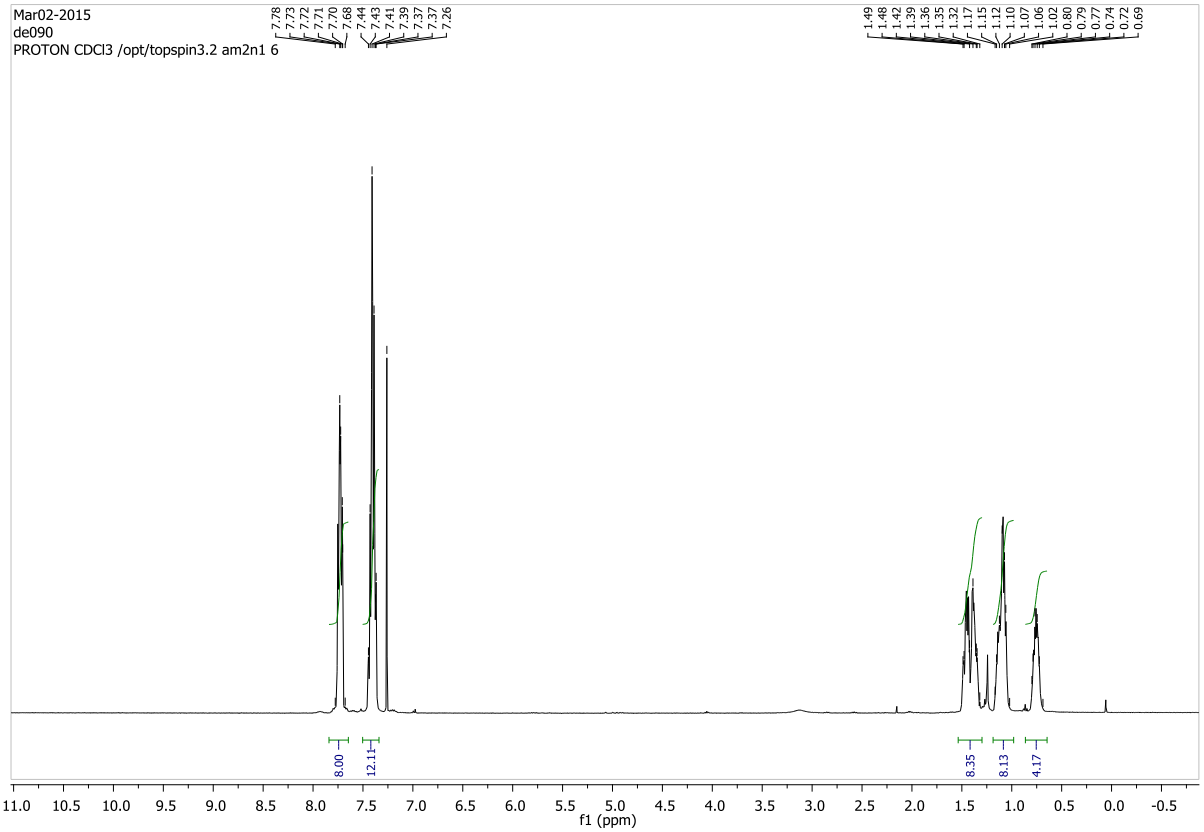
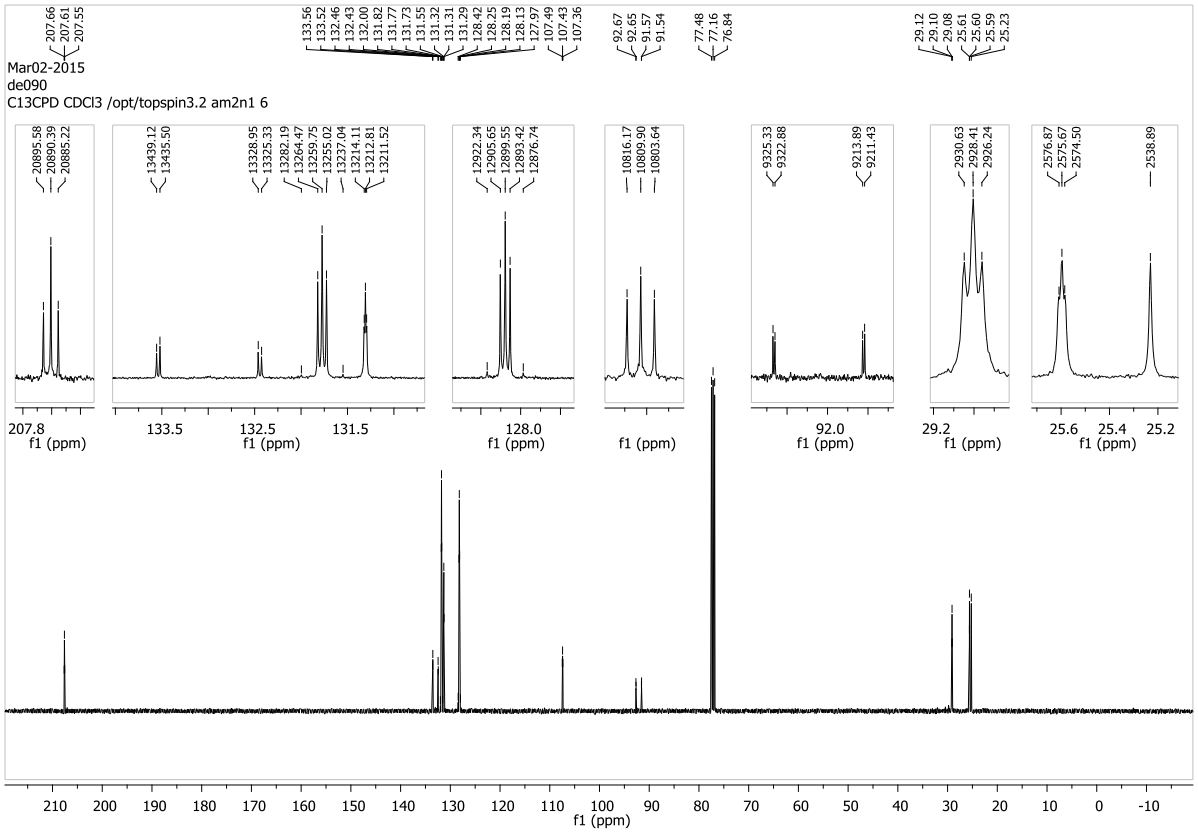
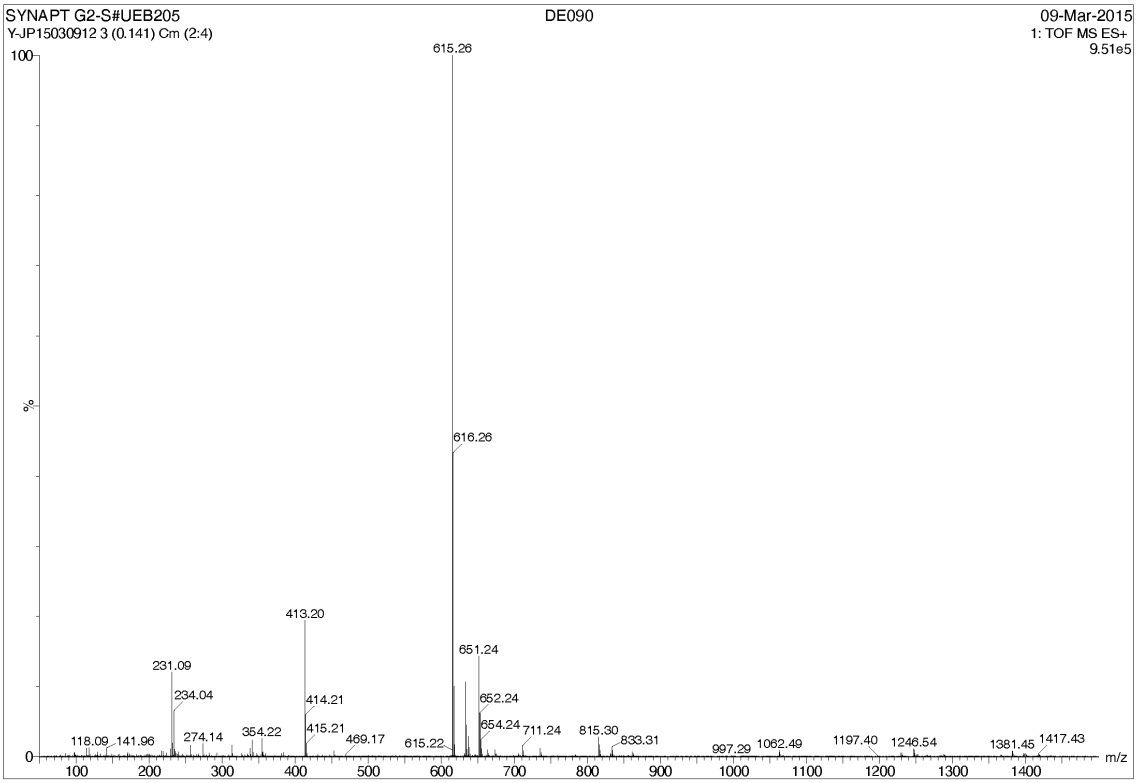
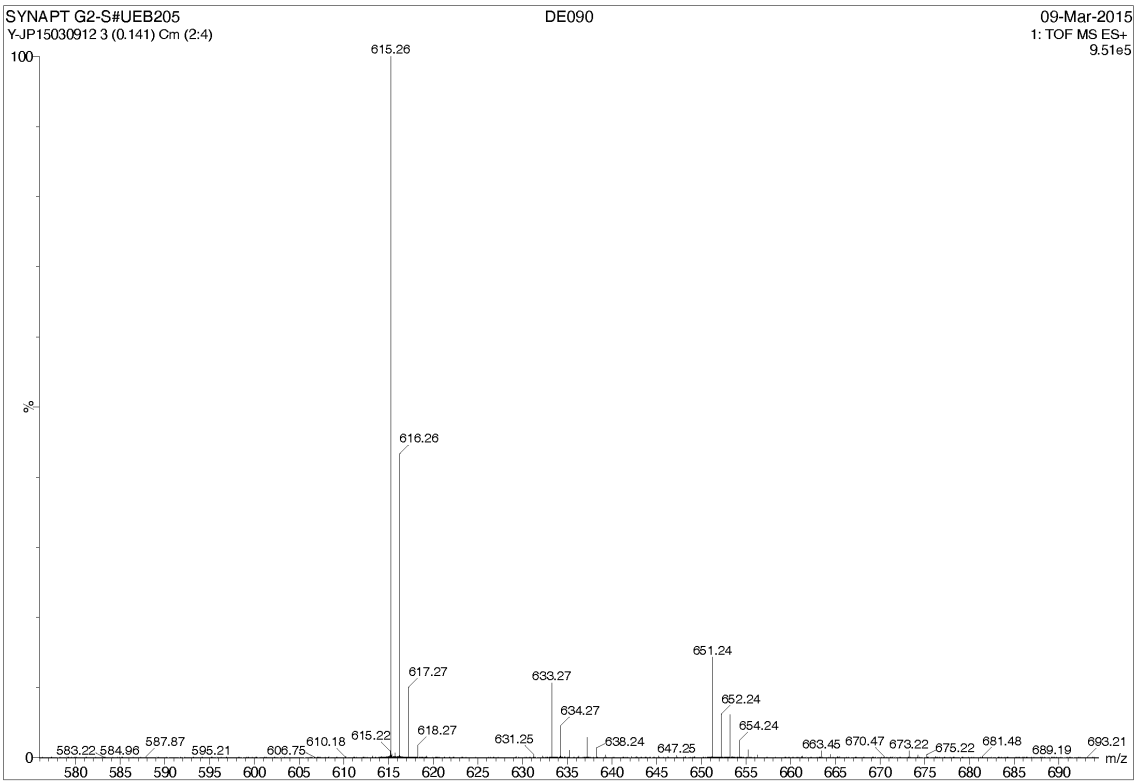
29.86
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220
f1 (ppm)


Mar02-2015
de090
PROTON CDCl3 /opt/topspin3.2 am2n1 6
7.78 7.73 7.72 7.71 7.70 7.68 7.44 7.43 7.41 7.39 7.37 7.37 7.26
1.49 1.48 1.42 1.39 1.36 1.35 1.32 1.17 1.15 1.12 1.10 1.07 1.06 1.02 0.80 0.79 0.77 0.74 0.72 0.69
8.00 12.11 8.35 8.13 4.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Mar02-2015
de090
C13CPD CDCl3 /opt/topspin3.2 am2n1 6
f1 (ppm)


SYNAPT G2-S#UEB205
Y-JP15030912 3 (0.141) Cm (2:4)
DE090
09-Mar-2015
1: TOF MS ES+
9.51e5
615.26
616.26
413.20
651.24
231.09
234.04
414.21
652.24
654.24
415.21
711.24
815.30
833.31
997.29
1062.49
1197.40
1246.54
1381.45
1417.43
m/z

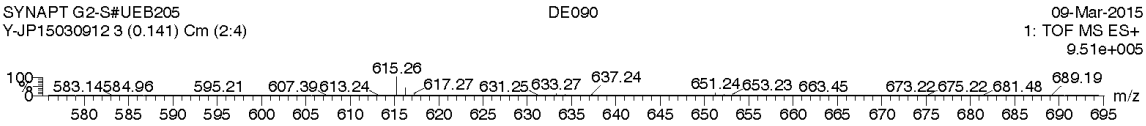


Elemental Composition Report

Single Mass Analysis

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
6115 formula(e) evaluated with 6 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 N: 0-50 O: 0-50 P: 1-2

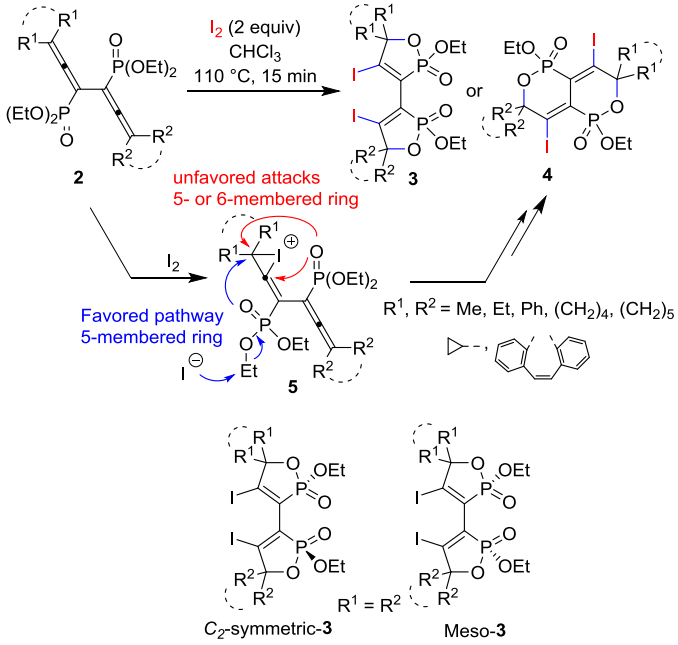


Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
615.2586	615.2582	0.4	0.7	21.5	1407.3	0.000	100.00	C40 H41 O2 P2
	615.2584	0.2	0.3	13.5	1418.7	11.395	0.00	C30 H40 N4 O8 P
	615.2587	-0.1	-0.2	14.5	1422.1	14.763	0.00	C25 H37 N12 O3 P2
	615.2589	-0.3	-0.5	6.5	1425.9	18.598	0.00	C15 H36 N16 O9 P
	615.2592	-0.6	-1.0	7.5	1428.4	21.084	0.00	C10 H33 N24 O4 P2
	615.2578	0.8	1.3	2.5	1428.7	21.378	0.00	C9 H37 N20 O8 P2

4. Bis-iodooxaphospholenes 3a, 3d, 3e spectra

4.1. General procedure

To a solution of bisallenyl compounds **2a**, **2d** or **2e** in chloroform (0.1 mol.l^{-1}) was added iodine (2 eq). Then, the reaction mixture was warmed and stirred at 120°C for 15 minutes. After completion of the reaction, as indicated by ^{31}P NMR, the reaction was washed with aqueous $Na_2S_2O_3$ solution (10% w/w), water, brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. The title compounds were purified by precipitation in diethyl ether.



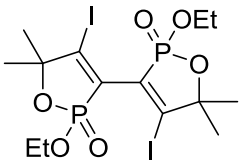
Scheme 2. Cyclization of bis-allenylphosphonates **2** promoted by iodine, and C_2-symmetric and meso representation of bisoxaphospholenes **3** ($R^1 = R^2$).

Table 2. Diiodo- and dibromobisoxaphospholenes **3**.

Compound	R^1	R^2	X	Diastereomeric ratio[a]	Yield (%)[b]
3a	Me	Me	I	62/38	68
3d	$(CH_2)_4$	$(CH_2)_4$	I	53/47	37
3e	$(CH_2)_5$	$(CH_2)_5$	I	53/47	60

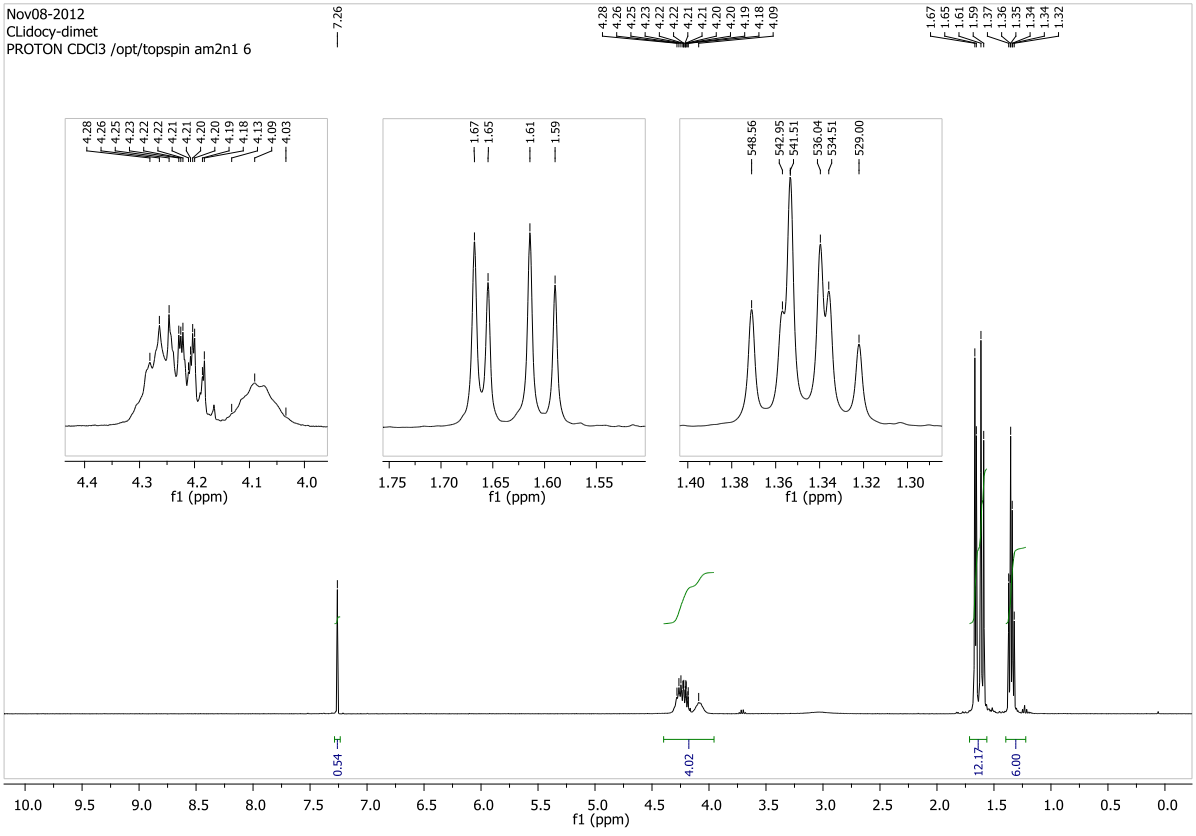
[a] Determined by ^{31}P-NMR experiments, [b] Isolated yields.

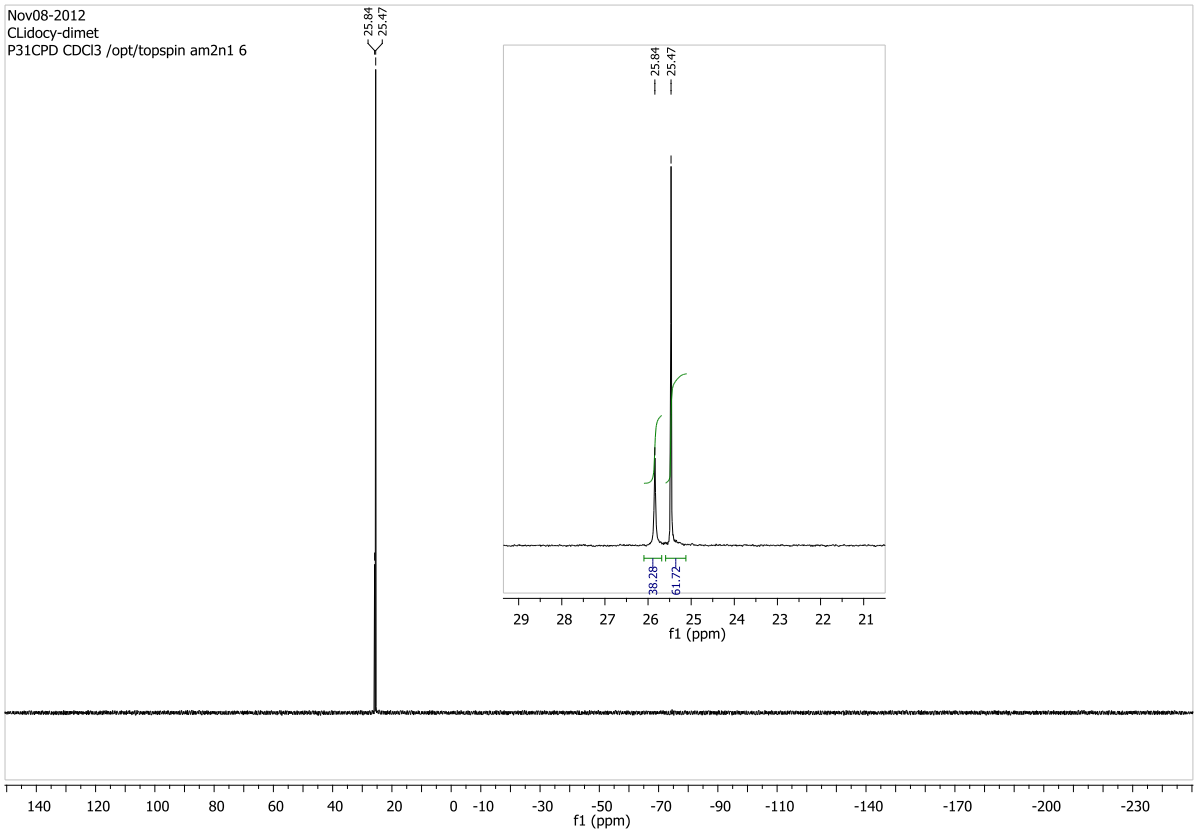
4.2. 4,4'-Diiodo-2,2'-diethoxy-5,5,5',5'-tetramethyl-5H,5'H-[3,3'-bi(1,2-oxaphosphole)] 2,2'-dioxide (3a)



Reaction was carried out using allene **2a** (500.0 mg, 1.23 mmol). The resulting crude is purified by precipitation in diethyl ether. Light yellow oil, 492 mg, 68% yield.

^{31}P ($CDCl_3$, 161.97 MHz) δ(ppm): 25.5 (s, 62%, diastereomer 1), 25.8 (s, 38%, diastereomer 2); ^{1}H ($CDCl_3$, 400,13 MHz) δ(ppm) = 1.34 and 1.35 (2t, *J* = 7.0 Hz and *J* = 7.0 Hz, 6H, 2 CH_3), 1.59, 1.61, 1.65 and 1.67 (4 s, 12H, 4 CH_3), 4.03-4.28 (m, 4H, 2 CH_2). ^{13}C ($CDCl_3$, 100,61 MHz) only the major diastereomer (2) is described. δ(ppm) : 16.3-16.4 (m, CH_3), 16.5 (d, *J* = 5.7 Hz, CH_3), 27.3, 27.6, 28.2, 28.6 (4 s, 4 CH_3), 64.0-64.1 (m, CH_2), 64.6-64.8 (m, CH_2), 88.3 (s, CO), 88.7 (s, CO), 129.9 (dd, *J* = 34.1, 7.7 Hz, C); HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{14}H_{23}I_2O_6P_2$ 602.9059 found 602.9063.

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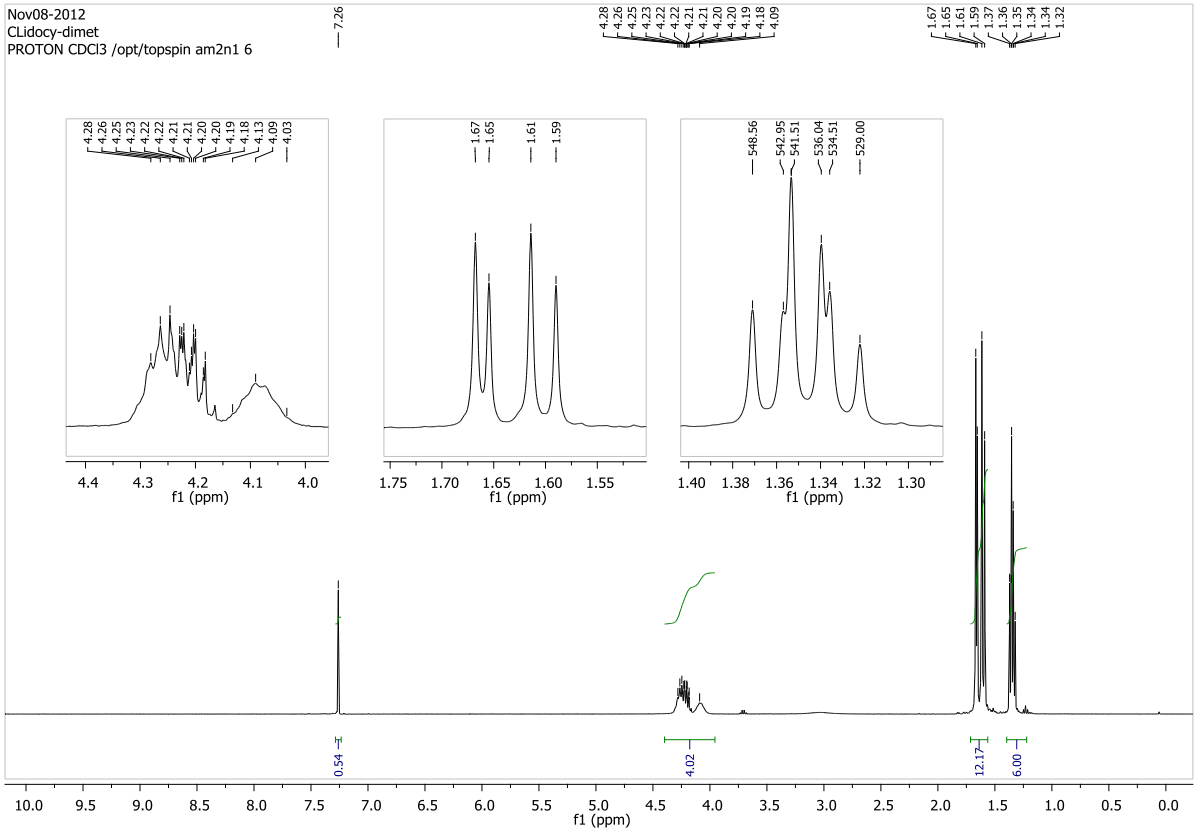
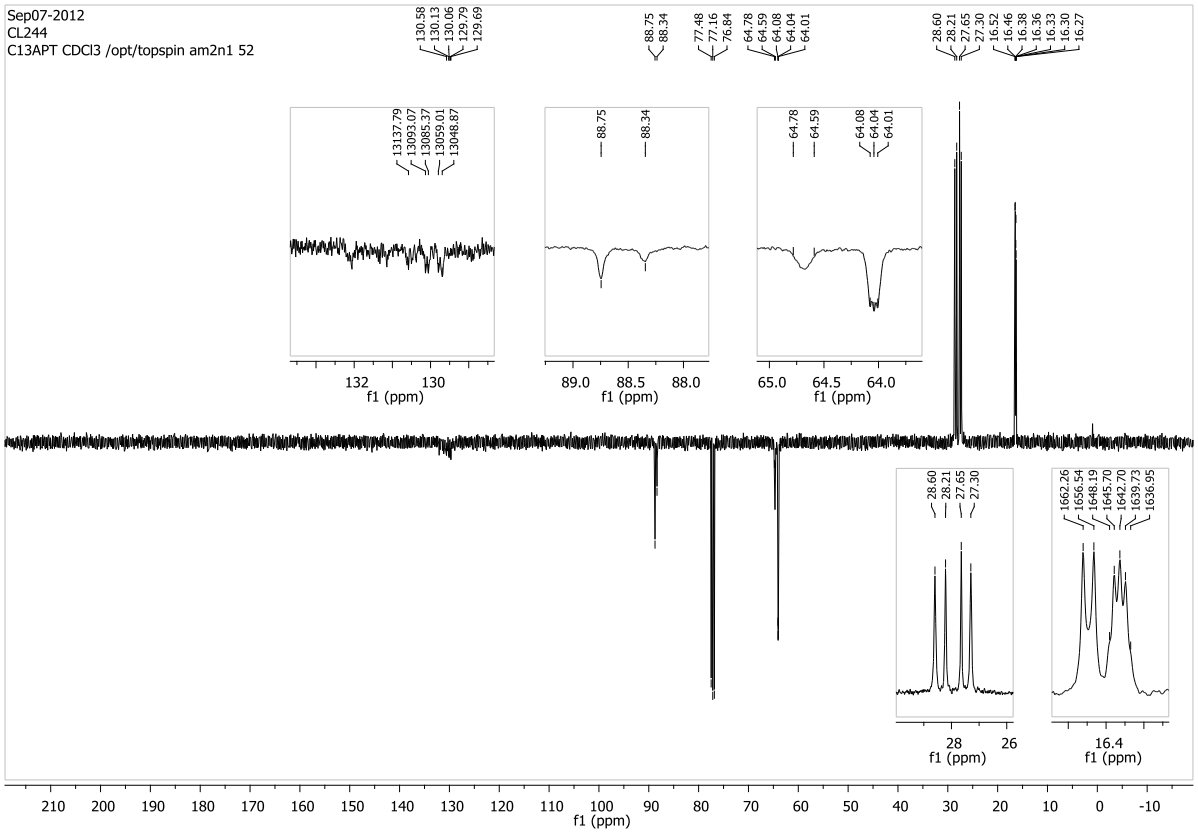
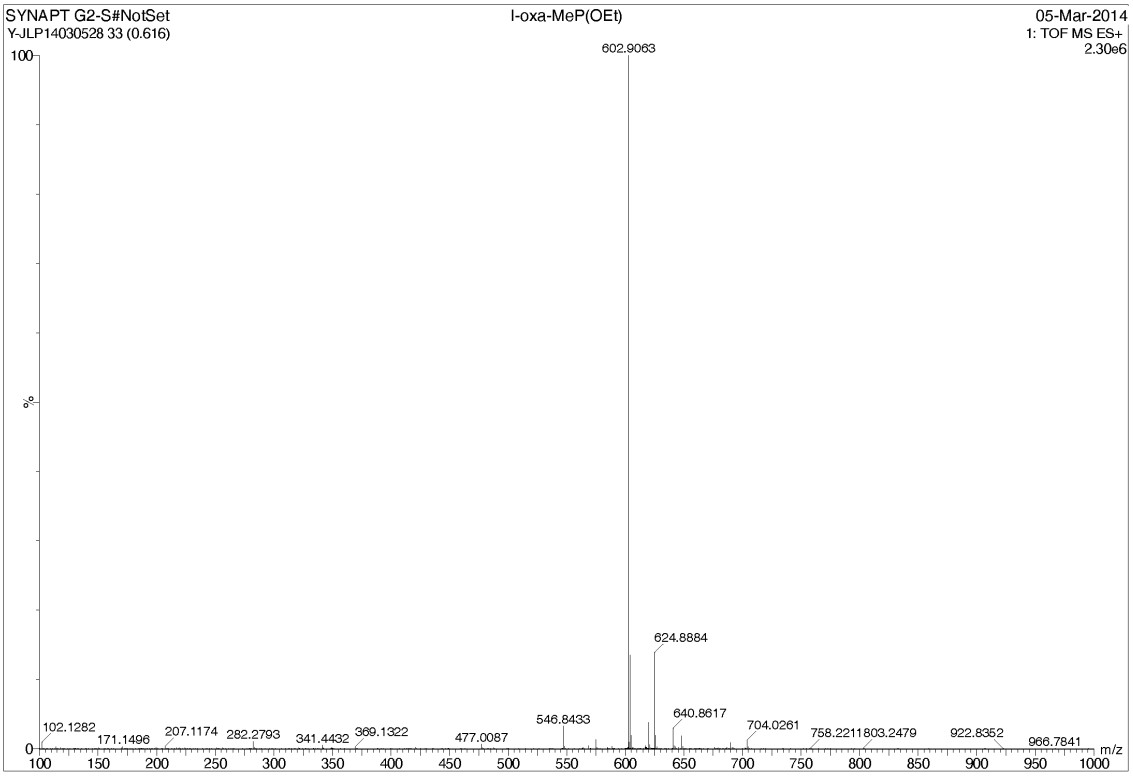
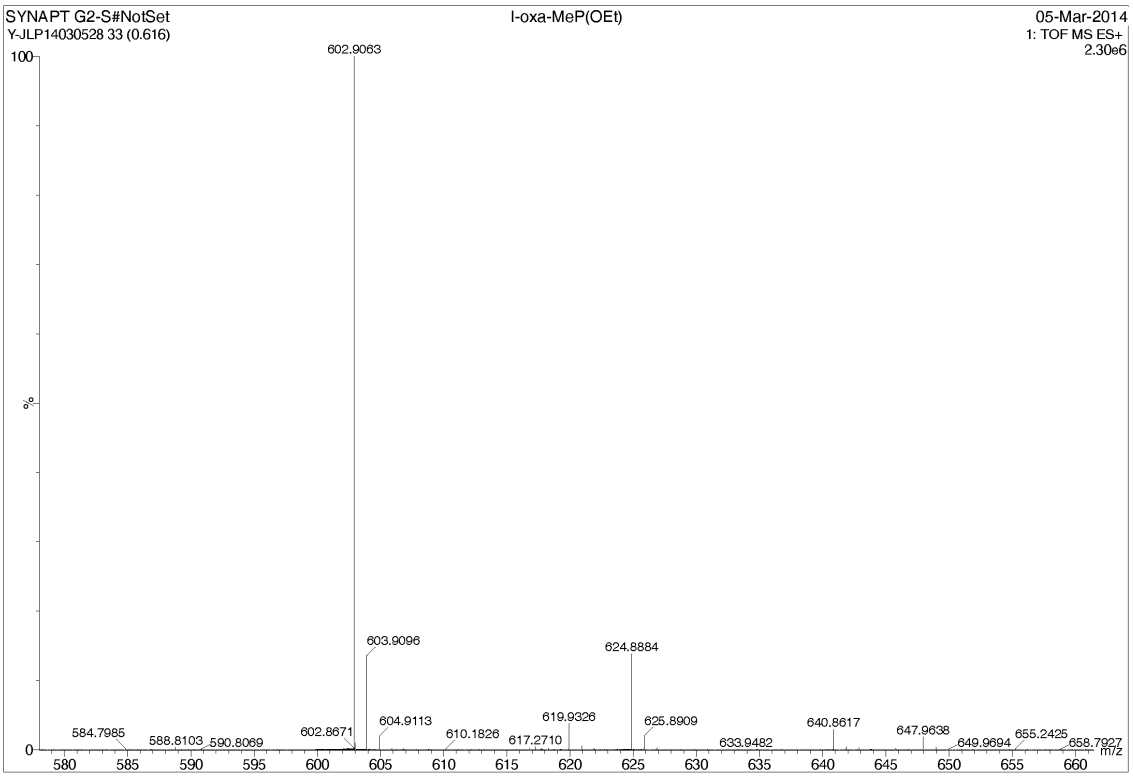
CLidocy-dimet
P31CPD CDCl3 /opt/topspin am2n1 6
25.84
25.47
38.28
61.72
f1 (ppm)


Nov08-2012
CLidocy-dimet
PROTON CDCl3 /opt/topspin am2n1 6
7.26
0.54
4.02
12.17
6.00
f1 (ppm)


Sep07-2012
CL244
C13APT CDCl3 /opt/topspin am2n1 52
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030528 33 (0.616)
I-oxa-MeP(OEt)
05-Mar-2014
1: TOF MS ES+
2.30e6
602.9063
624.8884
m/z

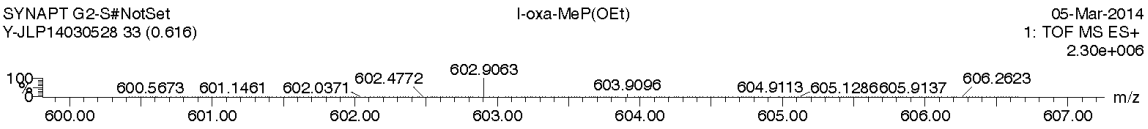


Elemental Composition Report

Single Mass Analysis

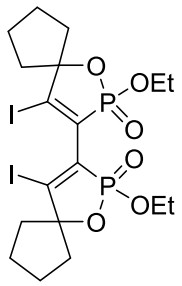
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
494 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3 I: 1-3



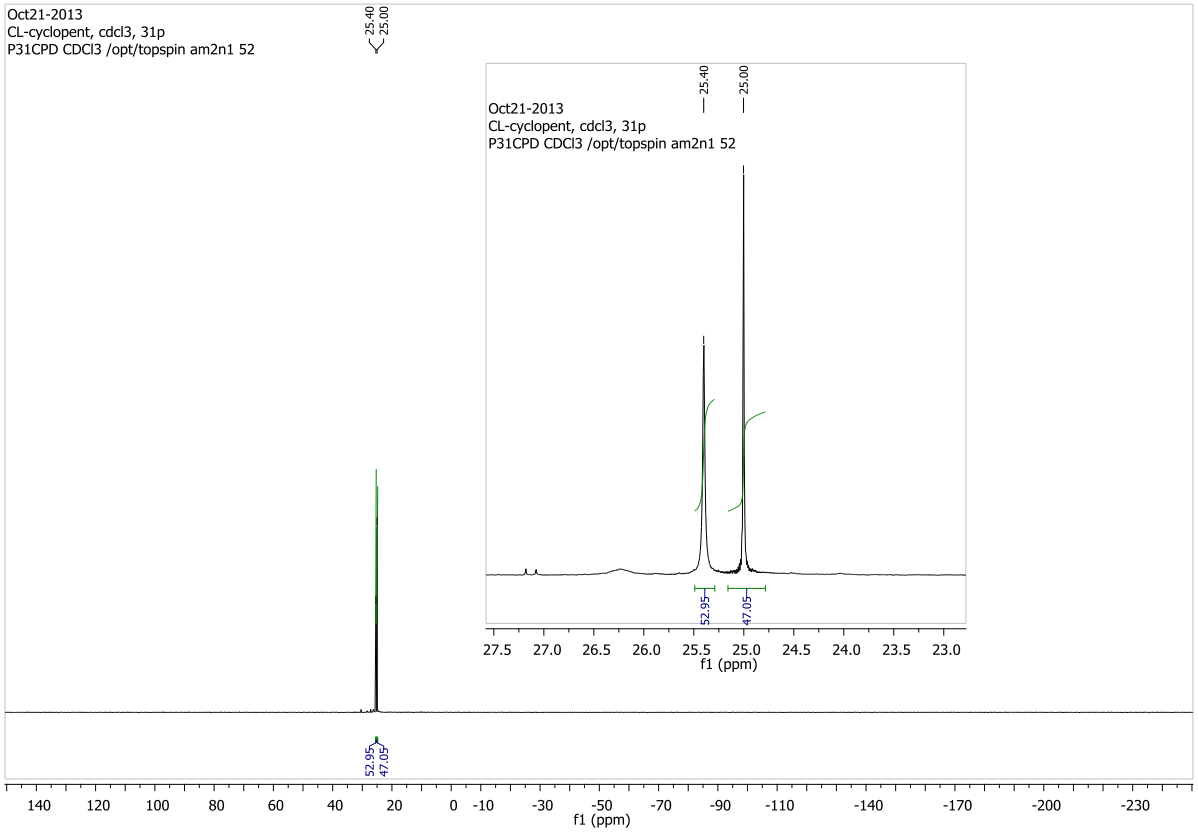
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
602.9063	602.9059	0.4	0.7	3.5	1152.3	n/a	n/a	C14 H23 O6 P2 I2

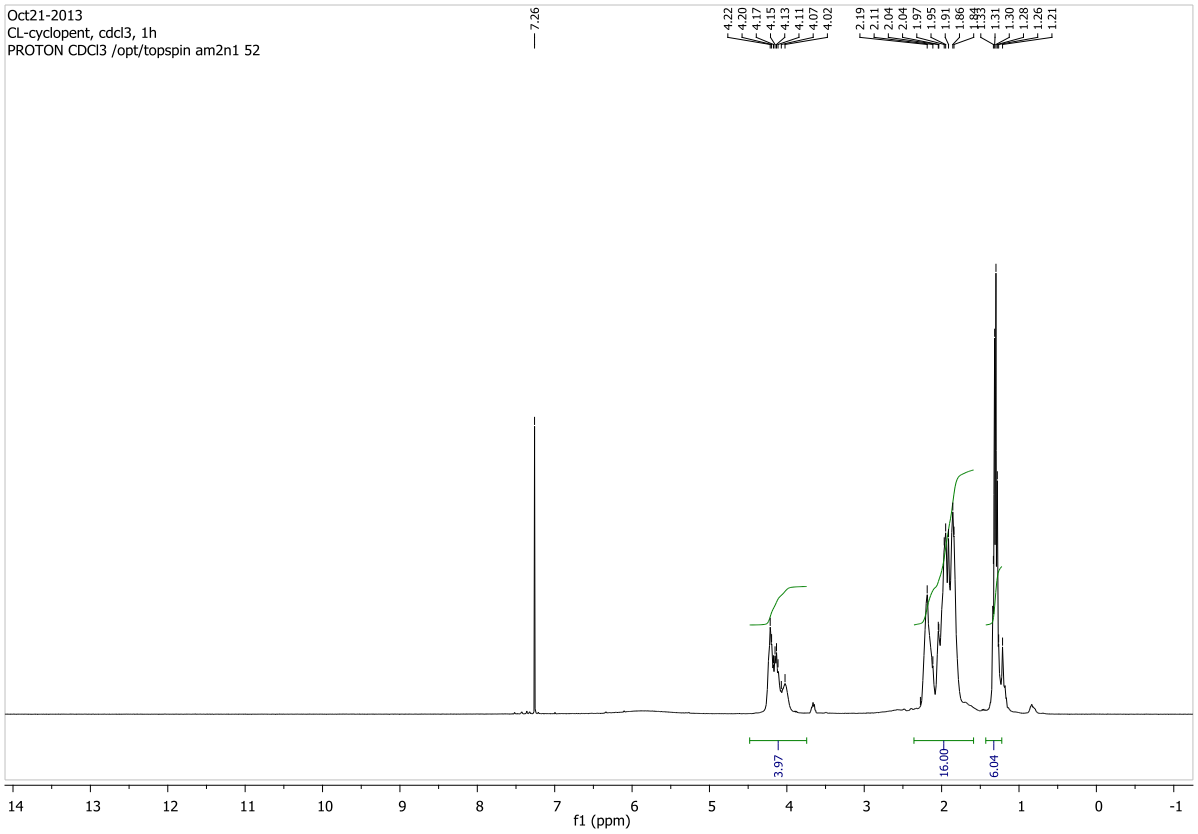
4.3. 4,4'-Diiodo-2,2'-diethoxy-1,1'-dioxa-2,2'-diphospha-[3,3'-bispiro[4.4]nonane-3,3'-diene] 2,2'-dioxide (3d)



Reaction was carried out using allene **2d** (500.0 mg, 1.09 mmol). The resulting crude is purified by precipitation in diethyl ether. Light yellow solid, 264 mg, 37% yield.

^{31}P ($CDCl_3$, 161.97 MHz) δ(ppm) : 25.0 (s, 47%, diastereomer 1), 25.4 (s, 53%, diastereomer 2); ^{1}H ($CDCl_3$, 400,13 MHz) δ(ppm) = 1.21-1.33 (m, 6H, 2 CH_3), 1.84-2.19 (m, 16H, 8 CH_2), 4.02-4.22 (m, 4H, 2 CH_2). ^{13}C ($CDCl_3$, 100,61 MHz) δ(ppm) : 16.3-16.4 (m, CH_3), 16.5-16.5 (m, CH_3), 24.6, 24.6, 24.7, 24.8 (4 s, 4 CH_3), 64.1-64.1 (m, CH_2), 64.8-64.9 (m, CH_2), 98.2 (s, CO), 98.7 (s, CO); HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{18}H_{27}I_2O_6P_2$ 654.9372 found 654.9377.




Oct21-2013
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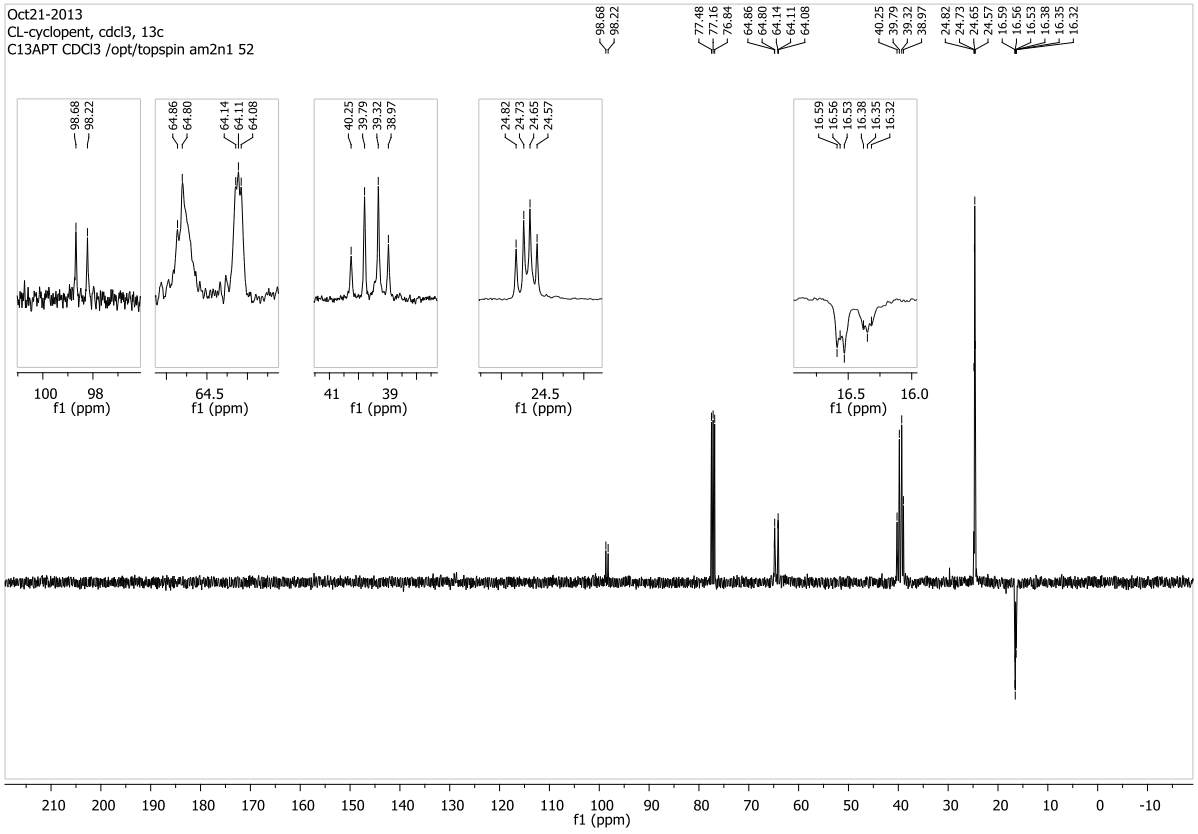
PROTON CDCl3 /opt/topspin am2n1 52
7.26
4.22
4.20
4.17
4.15
4.13
4.11
4.07
4.02
2.19
2.11
2.04
2.04
1.97
1.95
1.91
1.86
1.84
1.33
1.31
1.30
1.28
1.26
1.21
3.97
16.00
6.04
f1 (ppm)


Oct21-2013
CL-cyclopent, cdcl3, 13c
C13APT CDCl3 /opt/topspin am2n1 52
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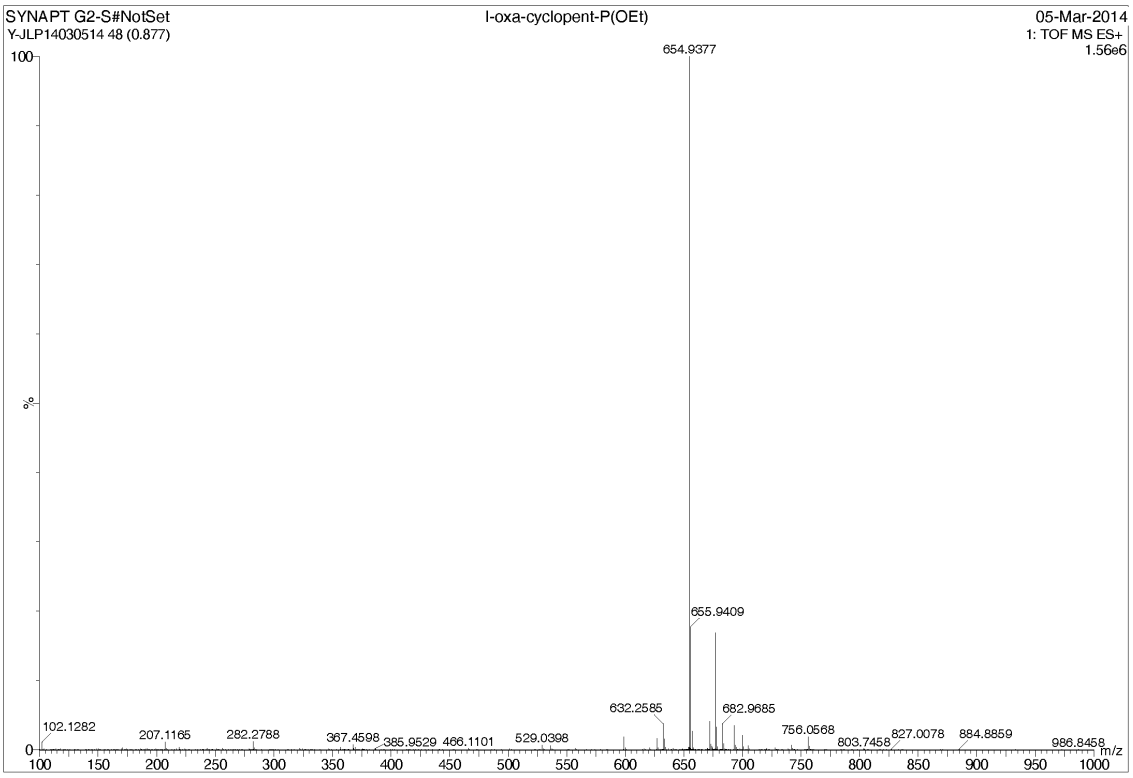
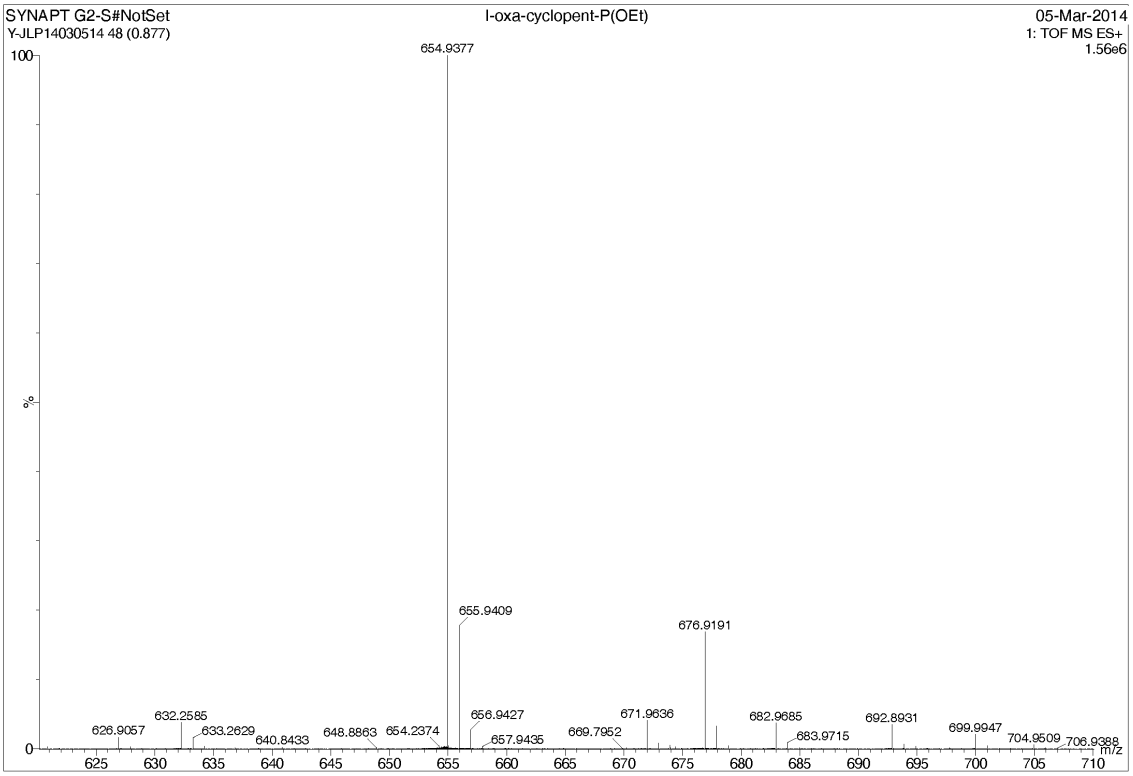
98.22
77.48
77.16
76.84
64.86
64.80
64.14
64.11
64.08
40.25
39.79
39.32
38.97
24.82
24.73
24.65
24.57
16.59
16.56
16.53
16.38
16.35
16.32
f1 (ppm)


SYNAPT G2-S#NotSet
I-oxa-cyclopent-P(OEt)
05-Mar-2014
Y-JLP14030514 48 (0.877)
1: TOF MS ES+
1.56e6
654.9377
655.9409
632.2585
682.9685
102.1282
207.1165
282.2788
367.4598
385.9529
466.1101
529.0398
756.0568
803.7458
827.0078
884.8859
986.8458
m/z


SYNAPT G2-S#NotSet
I-oxa-cyclopent-P(OEt)
05-Mar-2014
Y-JLP14030514 48 (0.877)
1: TOF MS ES+
1.56e6
654.9377
655.9409
676.9191
632.2585
626.9057
633.2629
640.8433
648.8863
654.2374
656.9427
657.9435
669.7952
671.9636
682.9685
683.9715
692.8931
699.9947
704.9509
706.9388
m/z

Elemental Composition Report **Page 1**

Single Mass Analysis

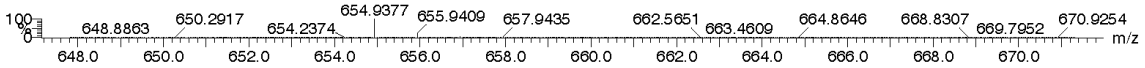
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
638 formula(e) evaluated with 1 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 1-3 I: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030514 48 (0.877)

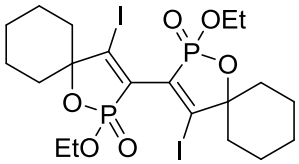
I-oxa-cyclopent-P(OEt)

05-Mar-2014
1: TOF MS ES+
1.56e+006



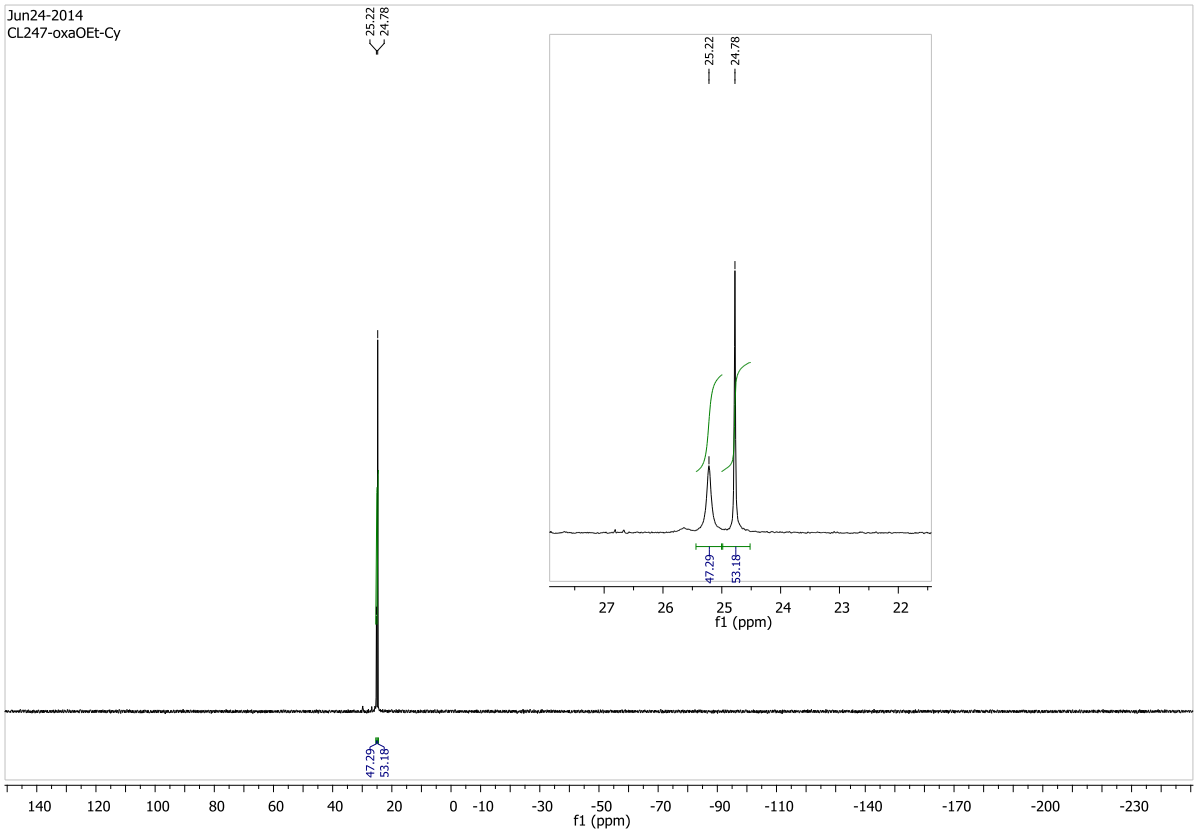
Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
654.9377	654.9372	0.5	0.8	5.5	1110.6	n/a	n/a	C18 H27 O6 P2 I2

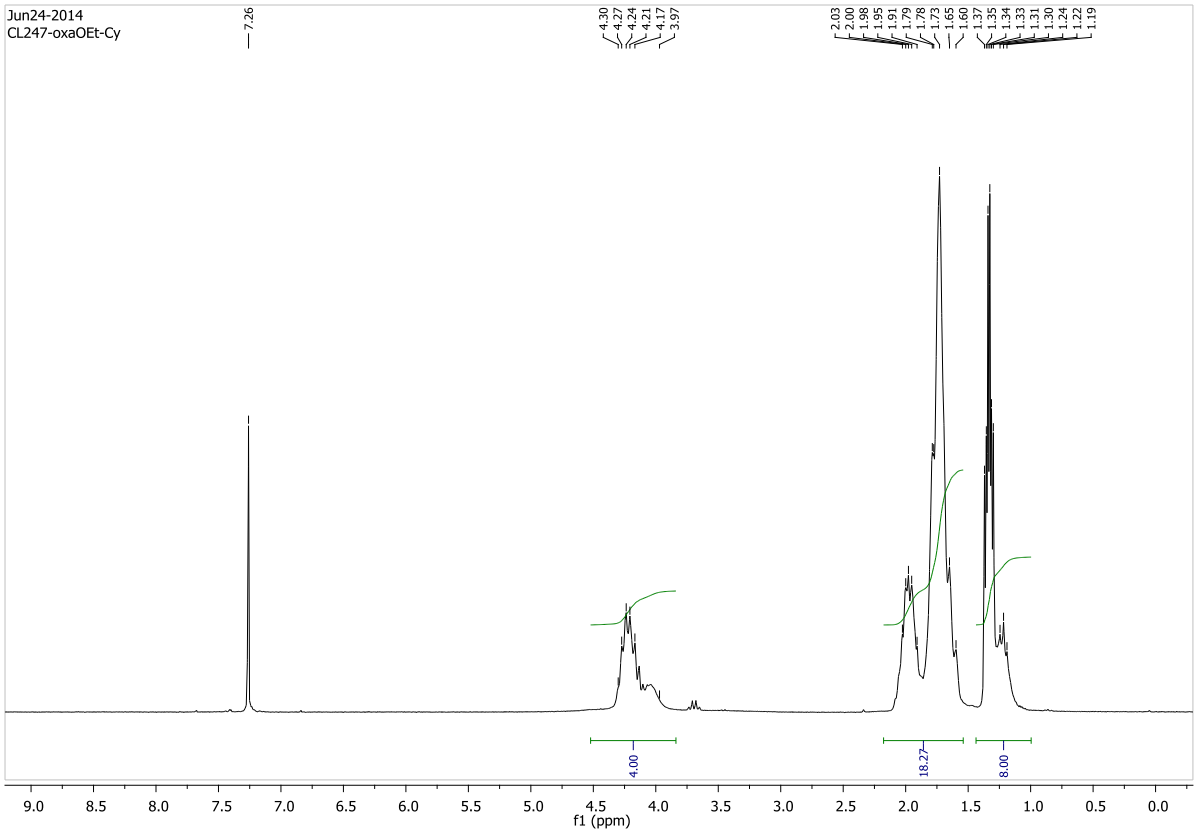
4.4. 4,4'-Diiodo-2,2'-diethoxy-1,1'-dioxa-2,2'-diphospha-[3,3'-bispiro[4.5]decane-3,3'-diene] 2,2'-dioxide (3e)



Reaction was carried out using allene **2e** (500.0 mg, 1.03 mmol). The resulting crude is purified by precipitation in diethyl ether. Light yellow oil, 422 mg, 60% yield.

^{31}P ($CDCl_3$, 161.97 MHz) δ(ppm) = 24.8 (s, 53%, dia 1), 25.2 (s, 47%, dia 2); ^{1}H ($CDCl_3$, 400,13 MHz) δ(ppm) = 1.19-1.37 (m, 8H, 2 CH_3 and 1 CH_2), 1.60-2.03 (m, 18H, 9 CH_2), 3.97-4.30 (m, 4H, 4 CH_2). ^{13}C ($CDCl_3$, 100,61 MHz) δ(ppm) = 16.4 (bs, CH_3), 16.5-16.6 (m, CH_3), 21.4, 21.4, 21.4, 21.5 (4 s, $^{2}CH_2$), 24.4 (s, CH_2), 35.1-36.3 (m, CH_2), 64.0 (bs, OCH_2). HRMS (ESI) m/z calcd for $[M+H]^+$, $C_{20}H_{31}I_2O_6P_2$ 682.9685 found 682.9686.




Jun24-2014
CL247-oxaOEt-Cy
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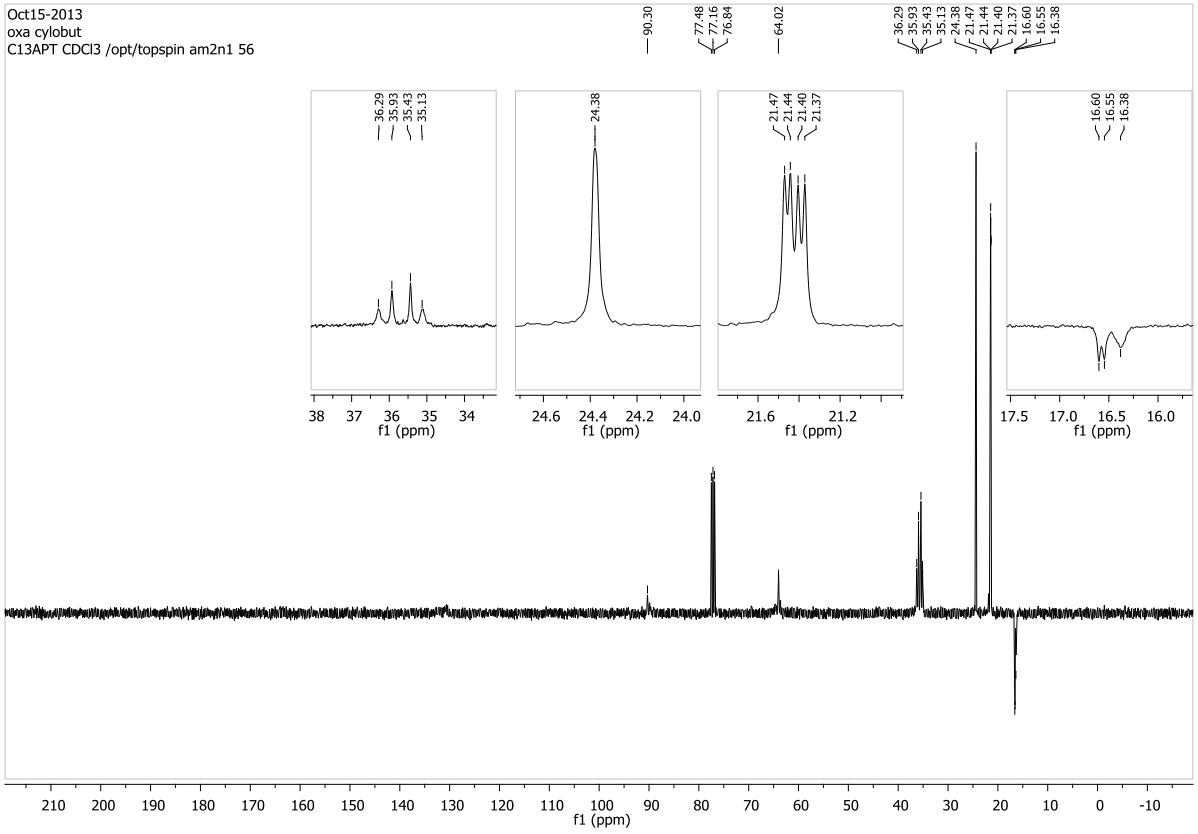
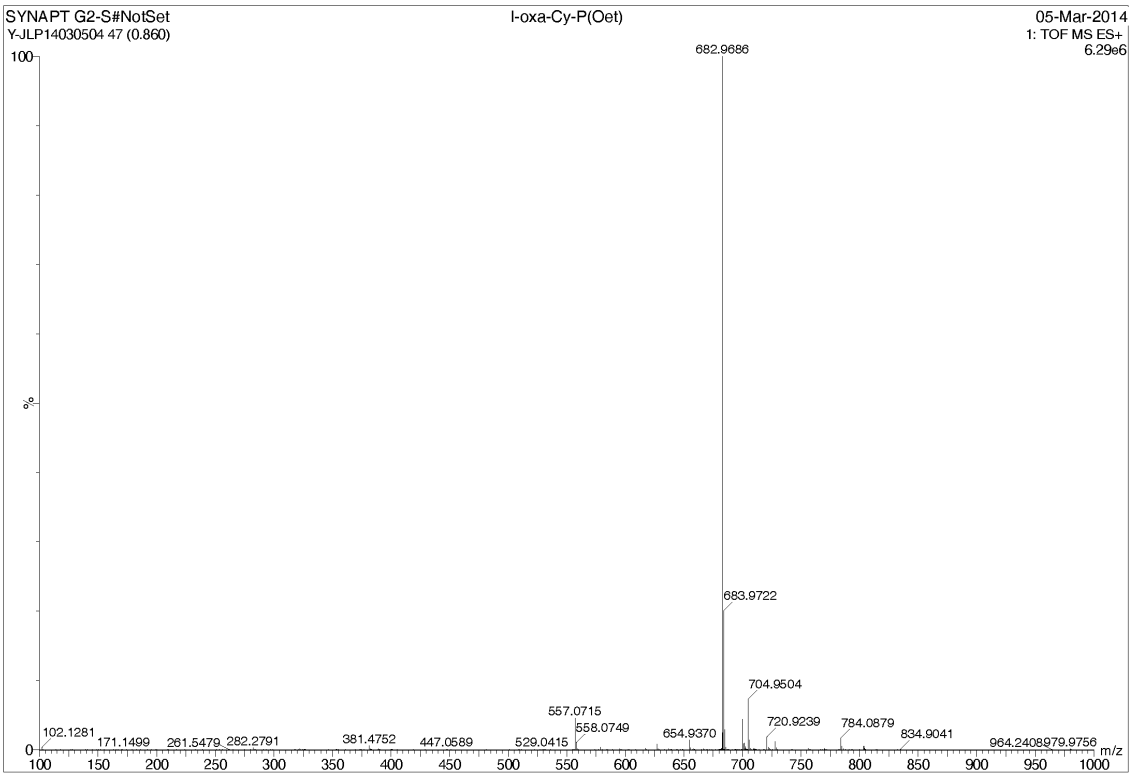
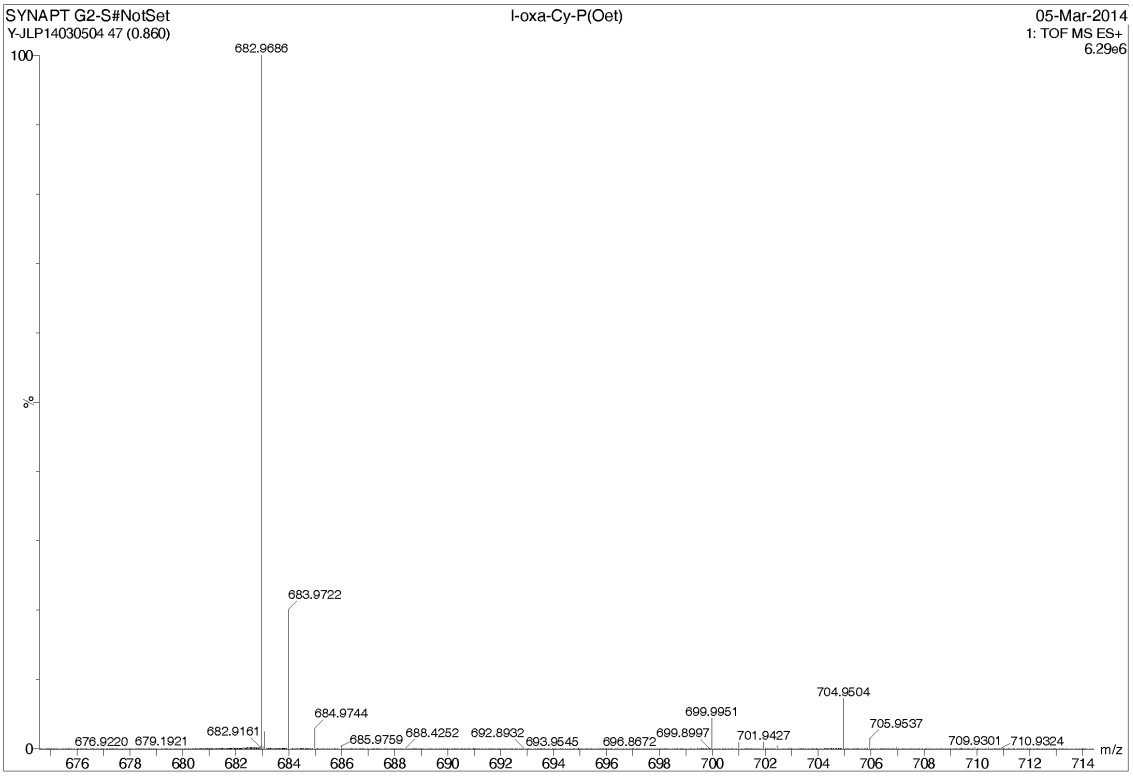
4.30
4.27
4.24
4.21
4.17
3.97
2.03
2.00
1.98
1.95
1.91
1.79
1.78
1.73
1.65
1.60
1.37
1.35
1.34
1.33
1.31
1.30
1.24
1.22
1.19
4.00
18.27
8.00
f1 (ppm)


Oct15-2013
oxa cylobut
C13APT CDCl3 /opt/topspin am2n1 56
90.30
77.48
77.16
76.84
64.02
36.29
35.93
35.43
35.13
24.38
21.47
21.44
21.40
21.37
16.60
16.55
16.38
f1 (ppm)


SYNAPT G2-S#NotSet
Y-JLP14030504 47 (0.860)
I-oxa-Cy-P(Oet)
05-Mar-2014
1: TOF MS ES+
6.29e6
682.9686
683.9722
704.9504
557.0715
558.0749
720.9239
784.0879
834.9041
654.9370
102.1281
171.1499
261.5479
282.2791
381.4752
447.0589
529.0415
964.2408979.9756
%
m/z


SYNAPT G2-S#NotSet
Y-JLP14030504 47 (0.860)
I-oxa-Cy-P(Oet)
05-Mar-2014
1: TOF MS ES+
6.29e6
682.9686
683.9722
704.9504
684.9744
699.9951
705.9537
682.9161
685.9759
688.4252
692.8932
693.9545
696.8672
699.8997
701.9427
709.9301
710.9324
676.9220
679.1921
%
m/z

Single Mass Analysis

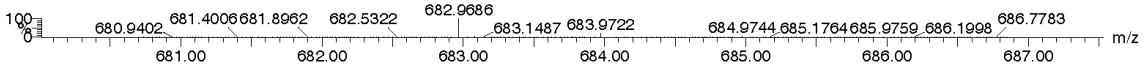
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1003 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-150 O: 0-30 P: 0-3 I: 1-3

SYNAPT G2-S#NotSet
Y-JLP14030504 47 (0.860)

I-oxa-Cy-P(Oet)

05-Mar-2014
1: TOF MS ES+
6.29e+006

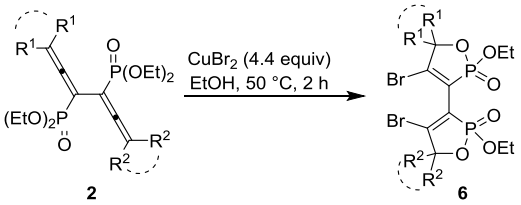


Minimum:				-1.5				
Maximum:		1000.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
682.9686	682.9685	0.1	0.1	5.5	1162.2	0.002	99.85	C20 H31 O6 P2 I2
	682.9686	0.0	0.0	21.5	1168.7	6.475	0.15	C29 H16 O12 I

5. Bis-bromooxaphospholenes 6a-b and 6d-g

5.1. General procedure

In a round bottom flask, bis-allenylphosphonate **2** (1.0 mmol), $CuBr_2$ (4.4 mmol) were dissolved in ethanol (4 mL) and heated to 50 °C for 2 h. The reaction was monitored by TLC (silica gel). After completion of the reaction, ammonia solution (15 mL, 12%) was added, and the mixture was extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4).



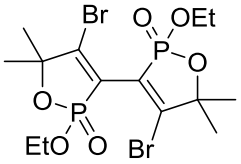
Scheme 3. Cyclization of bis-allenylphosphonates **2** promoted by $CuBr_2$.

Table 2. Diiodo- and dibromobisoxaphospholenes **6**.

Compound	R^1	R^2	X	Diastereomeric ratio[a]	Yield (%)[b]
6a	Me	Me	Br	64/36	78
6b	Et	Et	Br	92/8	63
6d	$(CH_2)_4$	$(CH_2)_4$	Br	64/36	53
6e	$(CH_2)_5$	$(CH_2)_5$	Br	69/31	58
6f	Ph	Ph	Br	100/0	49
6g	Ph	Me	Br	93/7	42

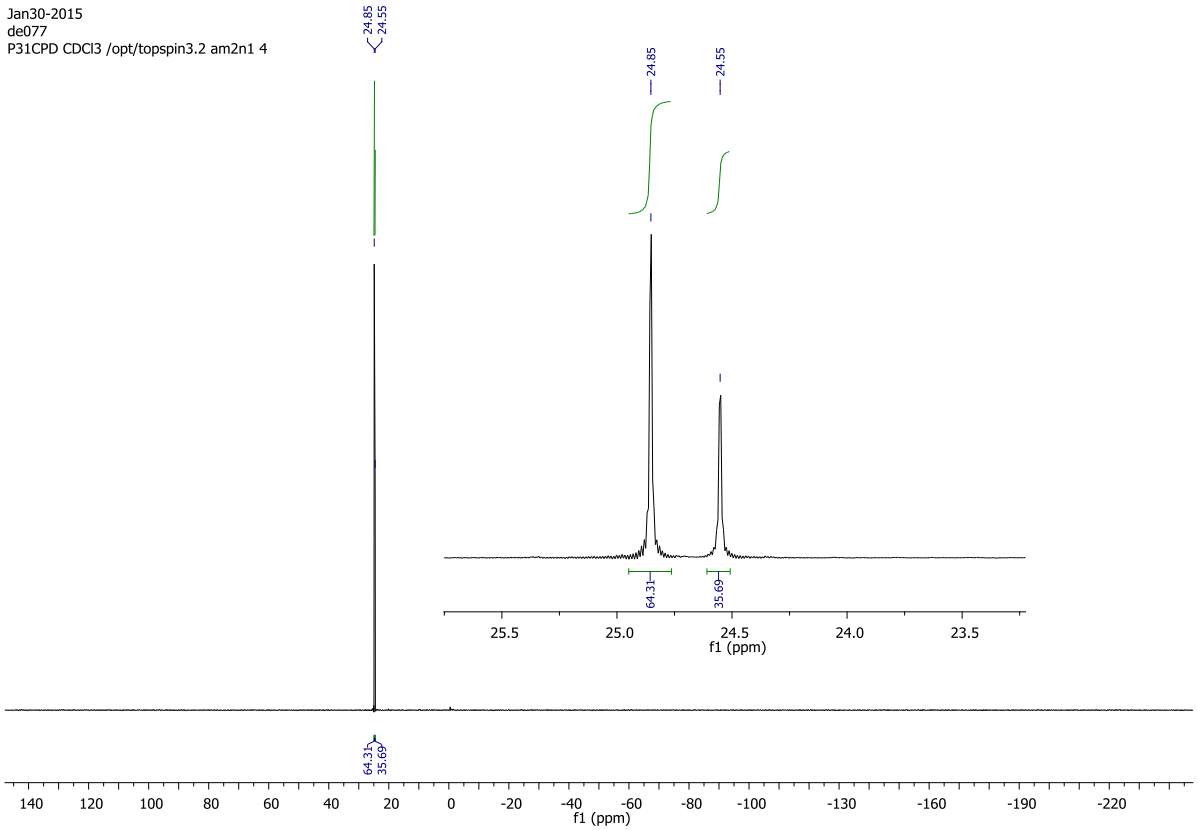
[a] Determined by ^{31}P-NMR experiments, [b] Isolated yields.

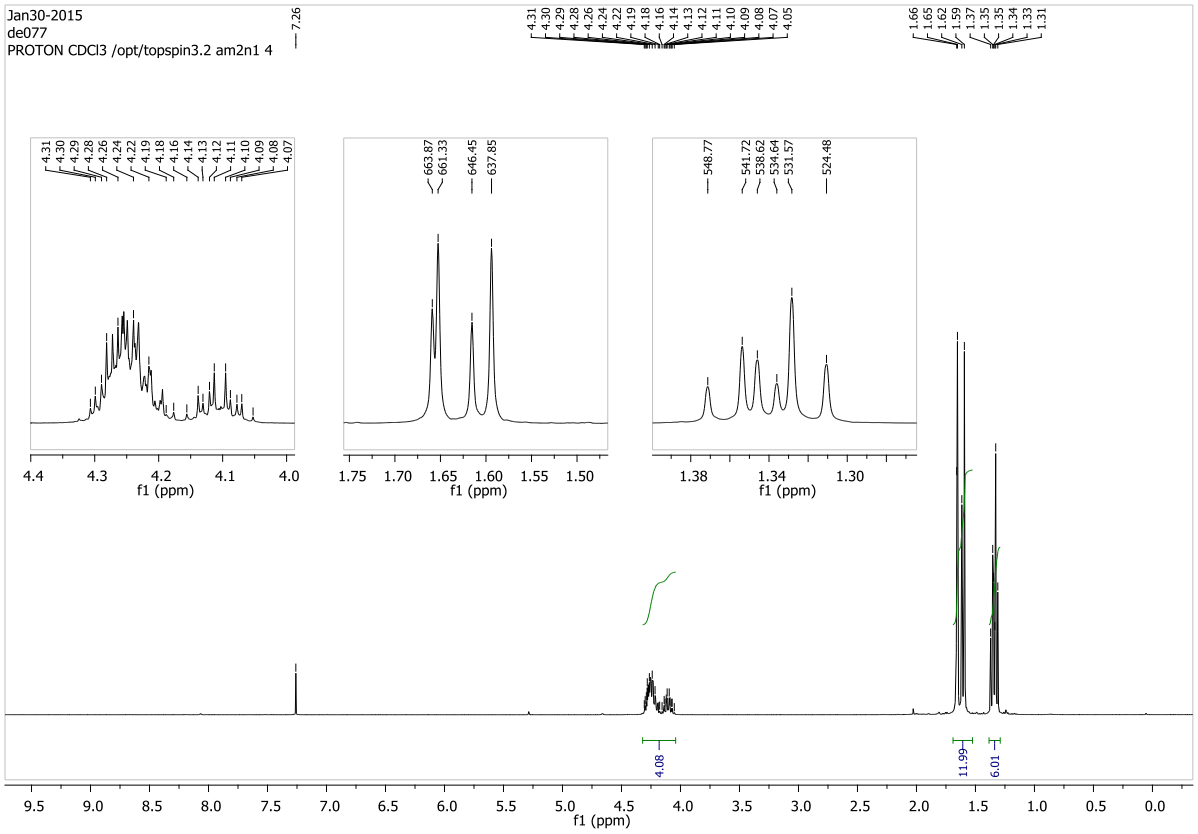
5.2. 4,4'-Dibromo-2,2'-diethoxy-5,5,5',5'-tetramethyl-5H,5'H-[3,3'-bi(1,2-oxaphosphole)] 2,2'-dioxide (6a)



Bis-allenylphosphonate **2a** (406 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). Yellow solid, 396 mg, yield = 78%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 24.5 (s, 36%, diastereomer 1), 24.8 (s, 64%, diastereomer 2); ^{1}H ($CDCl_3$, 400,13 MHZ) δ (ppm) = 1.33 and 1.35 (2 t, diastereomer 2: *J* = 7.1 Hz, diastereomer 1: *J* = 7.1 Hz, 6H, 2 C*H*$_3$), 1.59 (diastereomer 2), 1.62 (diastereomer 1), 1.65 (diastereomer 2)and 1.66 (diastereomer 1) (4 s, 12H, 4 CH_3), 4.07-4.31 (m, 4H, 4 C*H*$_2$O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) : diastereomer 1 δ (ppm) = 16.4-16.51 (m, *C*H_3), 26.7 (t, *J* = 2.0 Hz, CH_3), 28.0 (t, *J* = 1.8 Hz, CH_3), 64.3-64.4 (m, CH_2O), 87.8 (s, OC), 121.3 (dd, *J* = 163.7, 10.7 Hz, CP), 149.9 (dd, *J* = 42.8, 8.1 Hz, CBr), diastereomer 2 δ (ppm) = 16.5–16.6 (m, *C*H_3), 27.0 (t, *J* = 1.6 Hz, CH_3), 27.5 (t, *J* = 2.2 Hz, CH_3), 64.8-64.9 (m, CH_2O), 87.4 (s, OC), 122.3 (dd, *J* = 164.3, 10.5 Hz, CP), 148.7 (dd, *J* = 42.9, 8.3 Hz, CBr); HRMS (ESI^+) m/z calcd for $[M+H]^+$, $C_{14}H_{23}O_6Br_2P_2$ 506.9337 found 506.9337.




Jan30-2015
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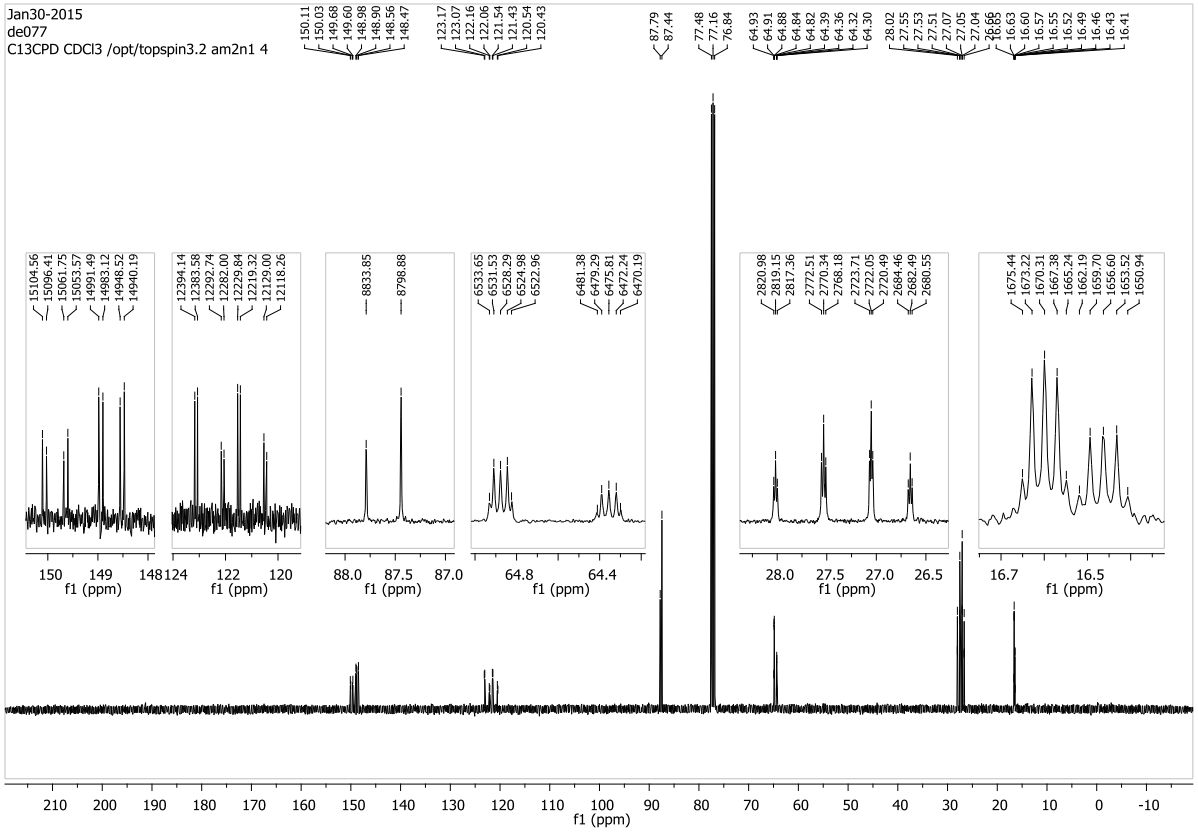
f1 (ppm)


Jan30-2015
de077
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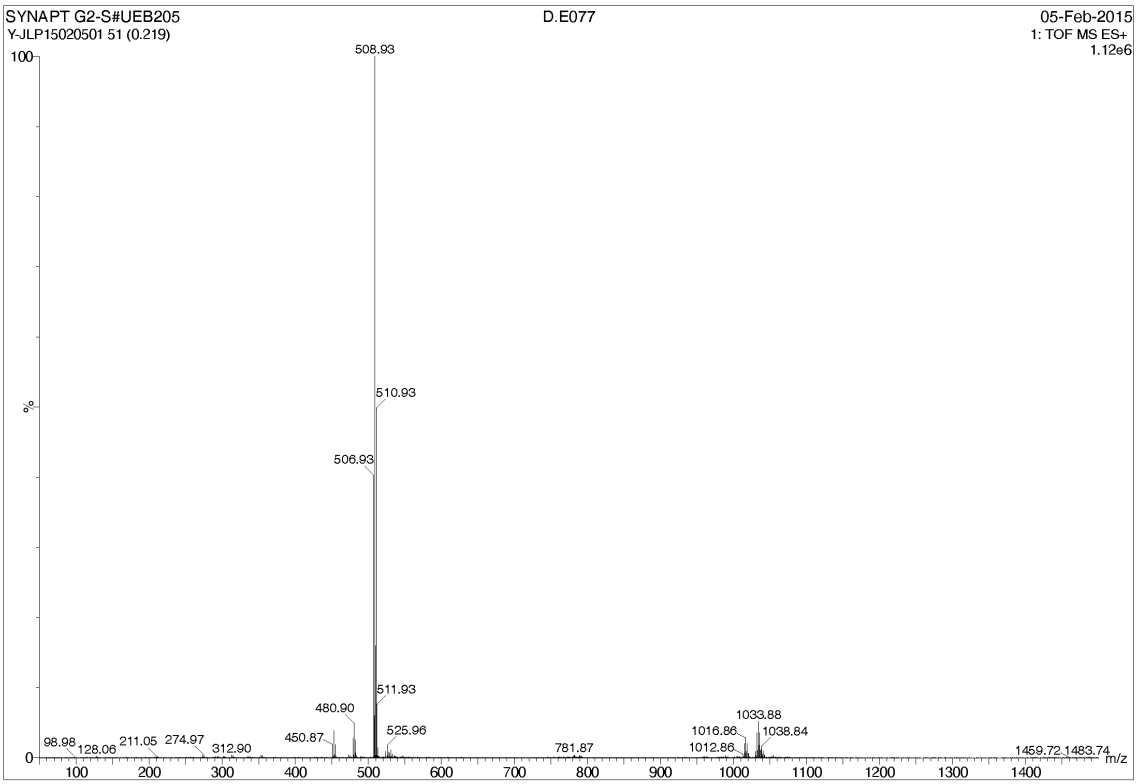
f1 (ppm)


SYNAPT G2-S#UEB205
D.E077
05-Feb-2015
Y-JLP15020501 51 (0.219)
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100
%
0
508.93
510.93
506.93
511.93
480.90
525.96
450.87
1033.88
1038.84
1016.86
1012.86
781.87
98.98
128.06
211.05
274.97
312.90
1459.72
1483.74
m/z
100
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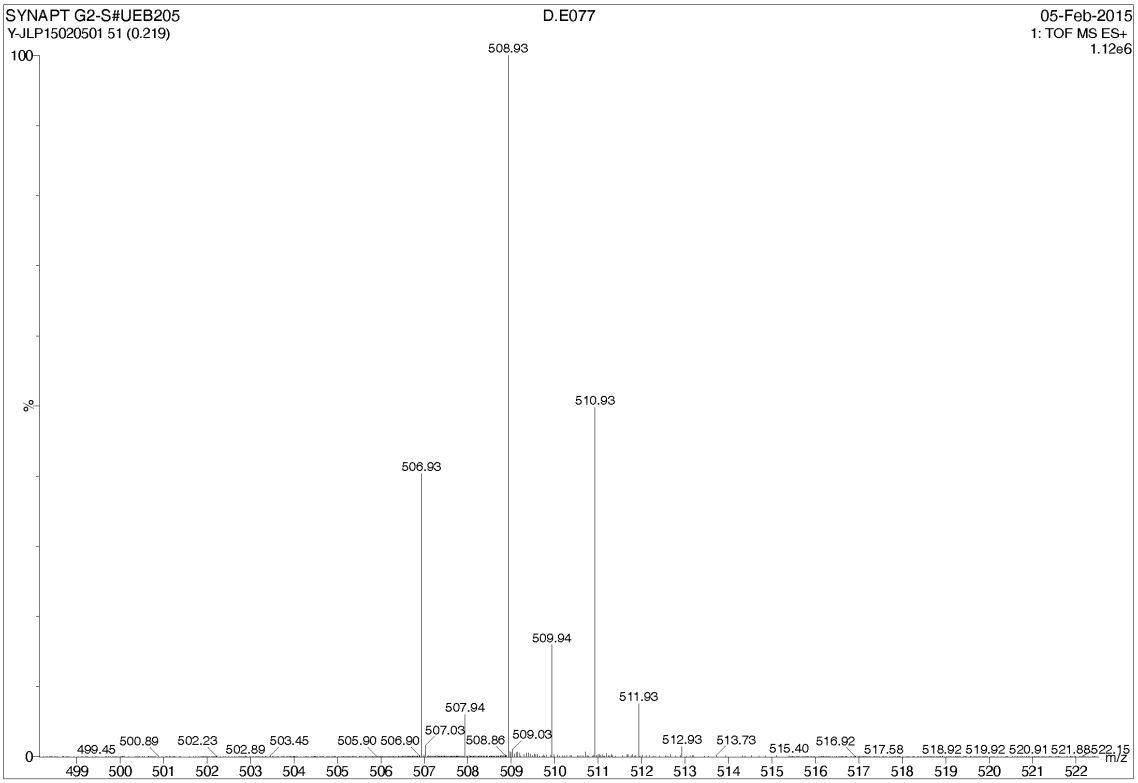
600
700
800
900
1000
1100
1200
1300
1400


SYNAPT G2-S#UEB205
D.E077
05-Feb-2015
Y-JLP15020501 51 (0.219)
1: TOF MS ES+
1.12e6
100
%
0
508.93
510.93
506.93
509.94
511.93
507.94
507.03
509.03
499.45
500.89
502.23
502.89
503.45
505.90
506.90
508.86
512.93
513.73
515.40
516.92
517.58
518.92
519.92
520.91
521.88
522.15
m/z
499
500
501
502
503
504
505
506
507
508
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510
511
512
513
514
515
516
517
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519
520
521
522

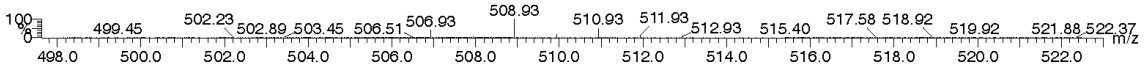
Elemental Composition Report **Page 1**

Single Mass Analysis

Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
379 formula(e) evaluated with 2 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-30 Br: 1-2 P: 1-3

SYNAPT G2-S#UEB205 D.E077 05-Feb-2015
Y-JLP15020501 51 (0.219) 1: TOF MS ES+
1.12e+006



Minimum:				-1.5				
Maximum:		5.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
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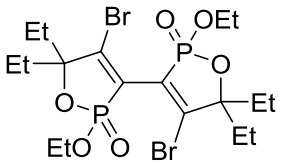
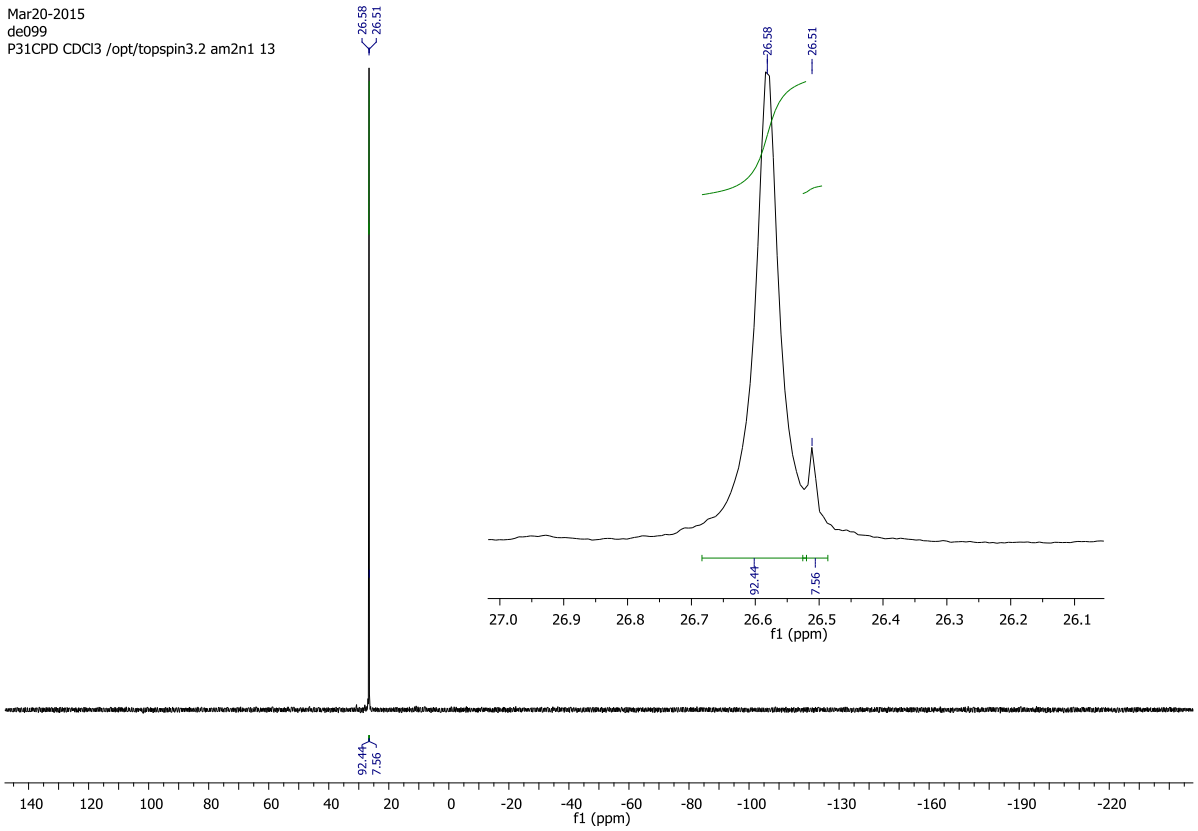
	506.9339	-0.2	-0.4	23.5	1321.7	6.335	0.18	C27 H10 O2 Br P2

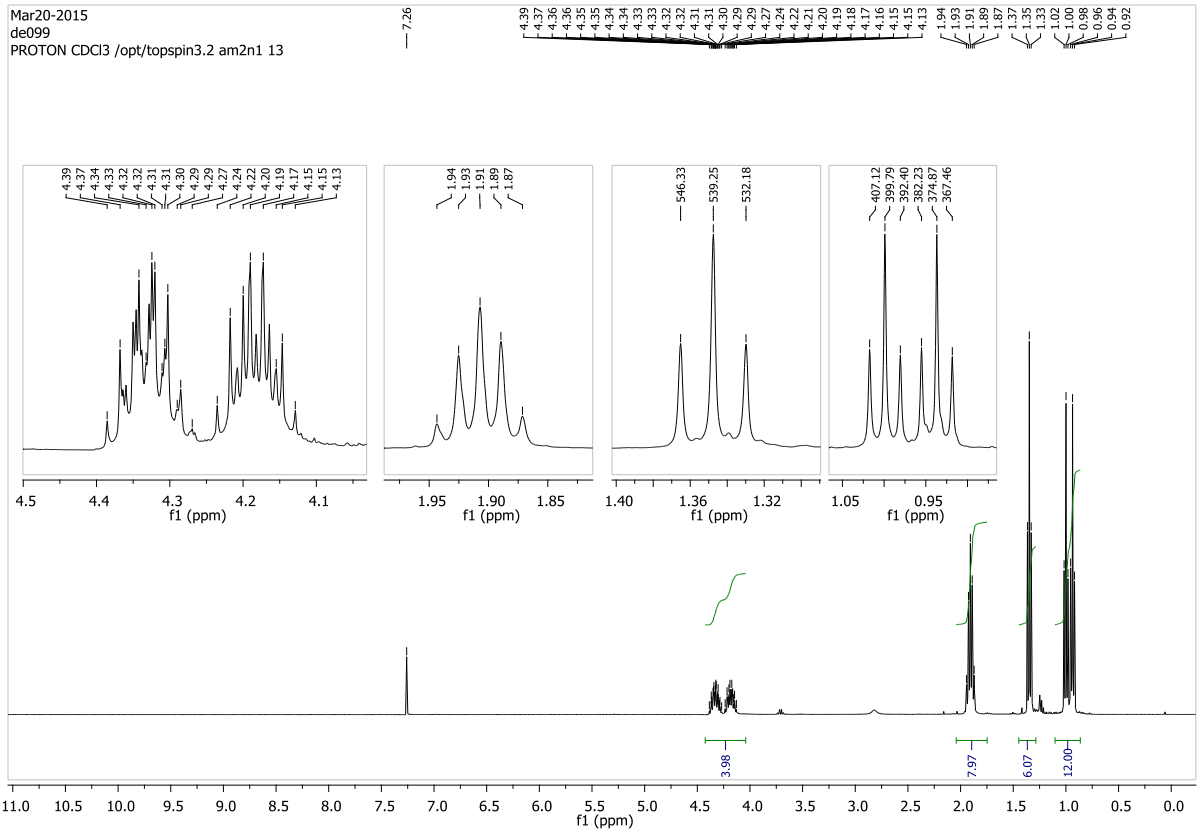
5.3. 4,4'-dibromo-2,2'-diethoxy-5,5,5',5'-tetraethyl-5H,5'H-[3,3'-bi(1,2-oxaphosphole)] 2,2'-dioxide (6b)



Bis-allenylphosphonate **2b** (462 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). With solid solid, 355 mg, yield = 63%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = 26.5 (s, 8%, diastereomer 1), 26.6 (s, 92%, diastereomer 2); ^{1}H NMR ($CDCl_3$, 400,13 MHZ) only the major diastereoisomer (2) was described δ (ppm) = 0.94 and 1.00 (2 t, *J* = 7.4 Hz and *J* = 7.4 Hz, 12H, 4 C*H*$_3$), 1.35 (t, *J* = 7.1 Hz, 6H, 2 C*H*$_3$-CH$_2$-O), 1.91 (q, *J* = 7.3 Hz, 8H, 4 CH_2), 4.13-4.24 and 4.27-4.39 (2 m, 4H, 2 CH_2O); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) δ (ppm) = 7.4 (s, CH_3), 7.5 (s, CH_3), 16.8-16.8 (m, *C*H_3), 31.1 (t, *J* = 1.8 Hz, *C*H_2), 31.4 (t, *J* = 1.6 Hz, *C*H_2), 64.4-64.5 (m, OCH_2), 93.5 (s, OC), 124.8 (dd, *J* = 166.4, 10.3 Hz, CP), 146.06 (dd, *J* = 44.4, 7.7 Hz, CBr); HRMS (ESI^+) m/z calcd for $[M+H]^+$, $C_{18}H_{31}Br_2O_6P_2$ 562.9969 found 562.9963.

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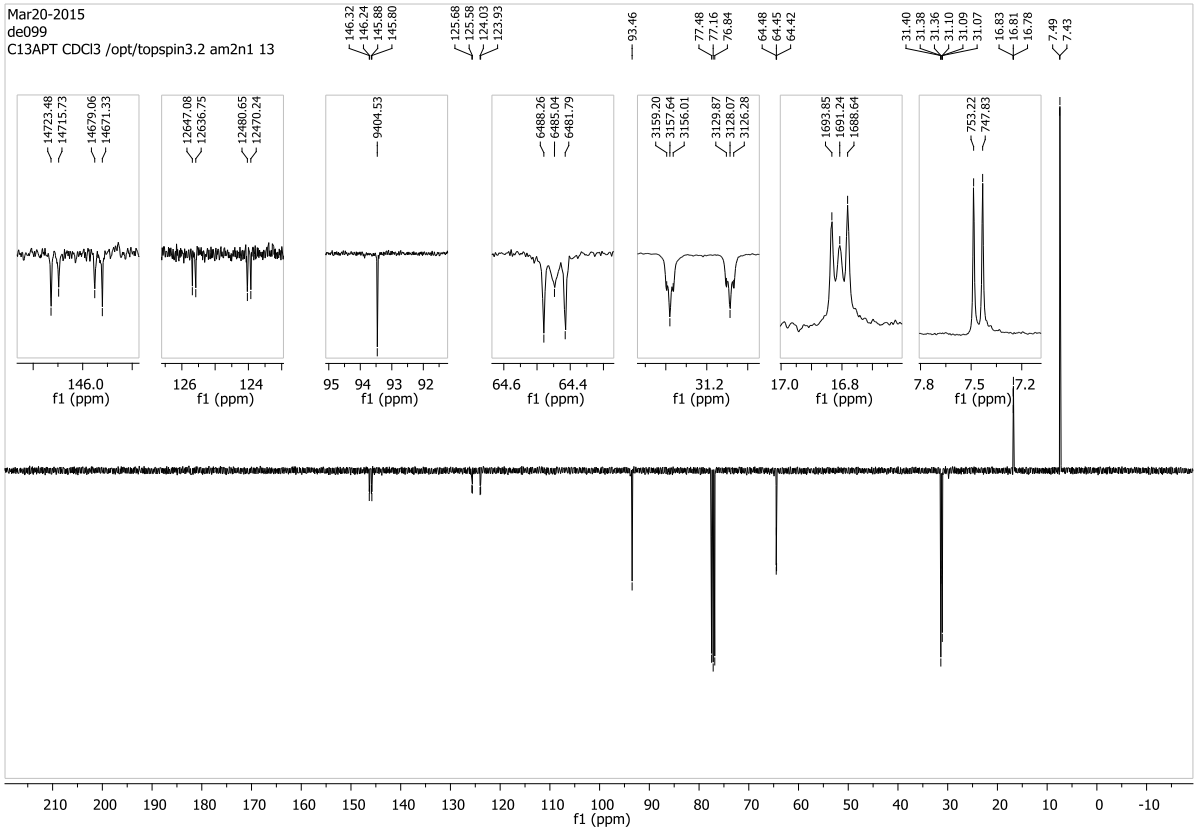
f1 (ppm)


Mar20-2015
de099
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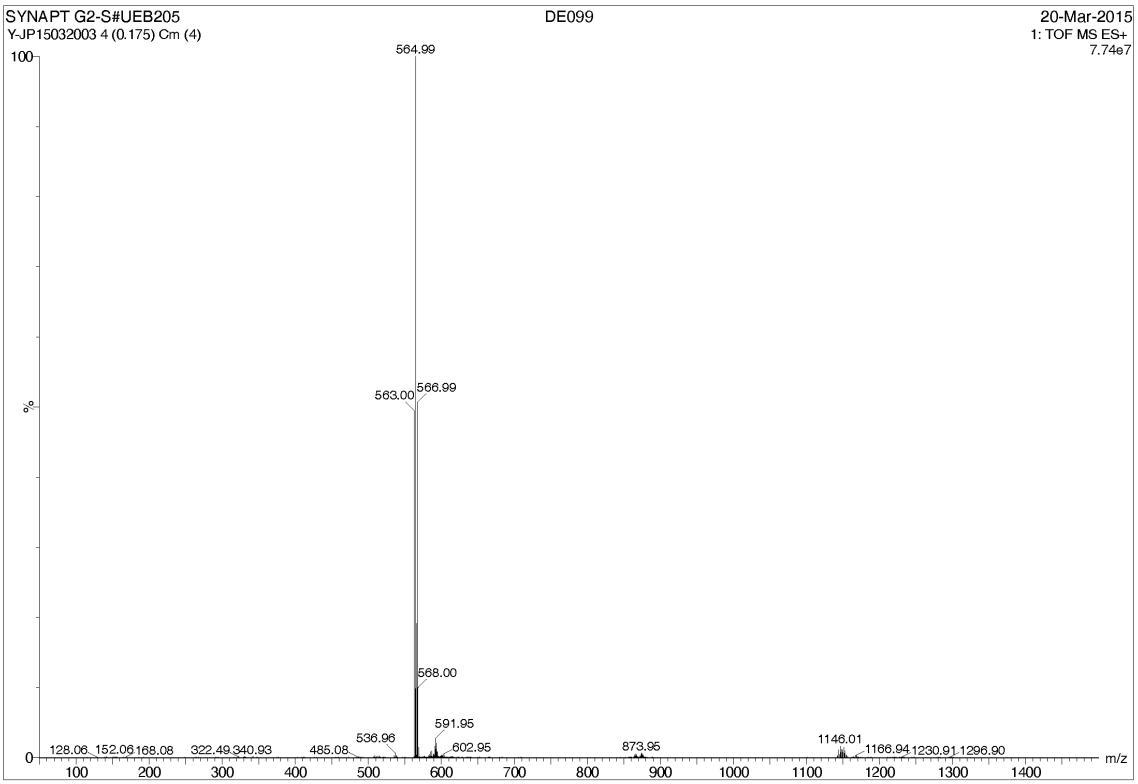
f1 (ppm)


SYNAPT G2-S#UEB205
DE099
20-Mar-2015
Y-JP15032003 4 (0.175) Cm (4)
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100
%
0
564.99
563.00
566.99
568.00
591.95
536.96
602.95
128.06
152.06
168.08
322.49
340.93
485.08
873.95
1146.01
1166.94
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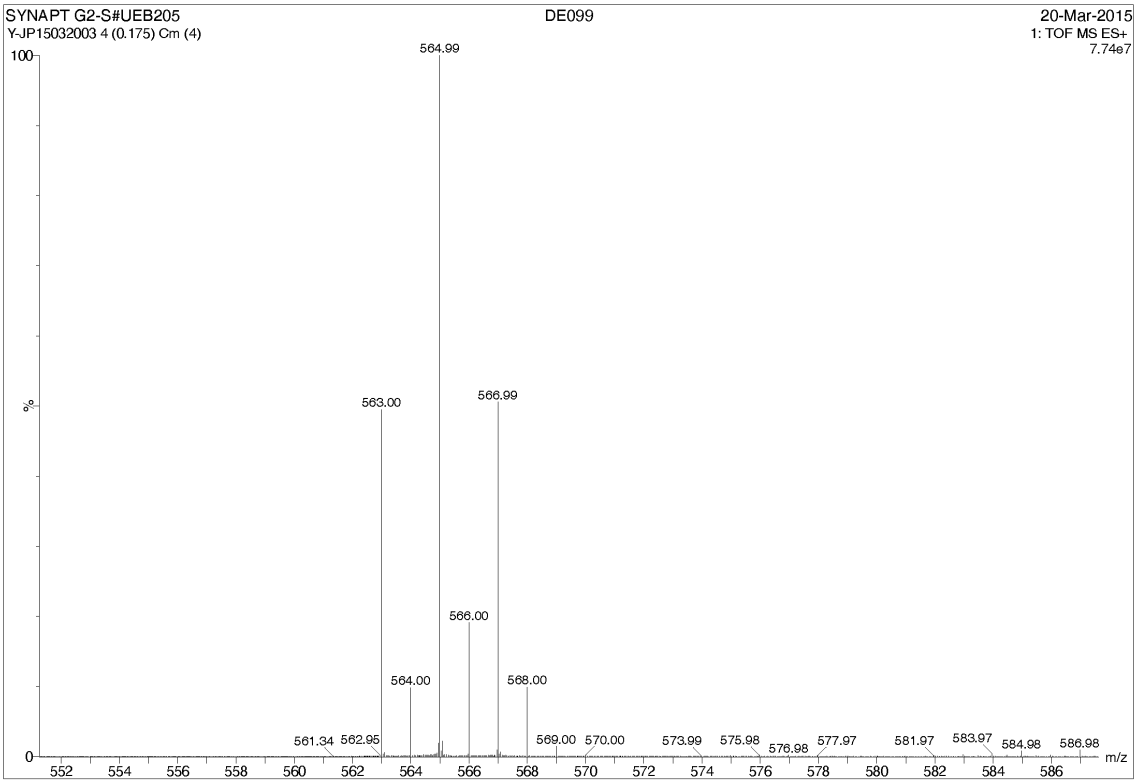
600
700
800
900
1000
1100
1200
1300
1400

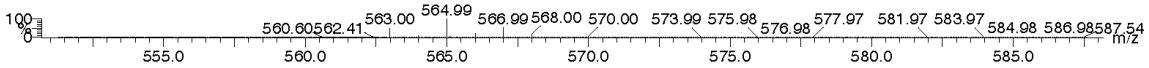

SYNAPT G2-S#UEB205
DE099
20-Mar-2015
Y-JP15032003 4 (0.175) Cm (4)
1: TOF MS ES+
7.74e7
100
%
0
564.99
563.00
566.99
566.00
564.00
568.00
561.34
562.95
569.00
570.00
573.99
575.98
576.98
577.97
581.97
583.97
584.98
586.98
m/z
552
554
556
558
560
562
564
566
568
570
572
574
576
578
580
582
584
586

Single Mass Analysis

Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

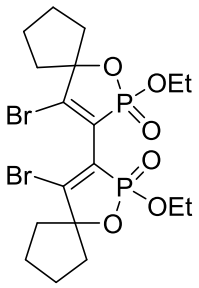
Monoisotopic Mass, Even Electron Ions
548 formula(e) evaluated with 4 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-50 Br: 1-2 P: 0-2

SYNAPT G2-S#UEB205 DE099 20-Mar-2015
Y-JP15032003 4 (0.175) Cm (4) 1: TOF MS ES+
7.74e+007



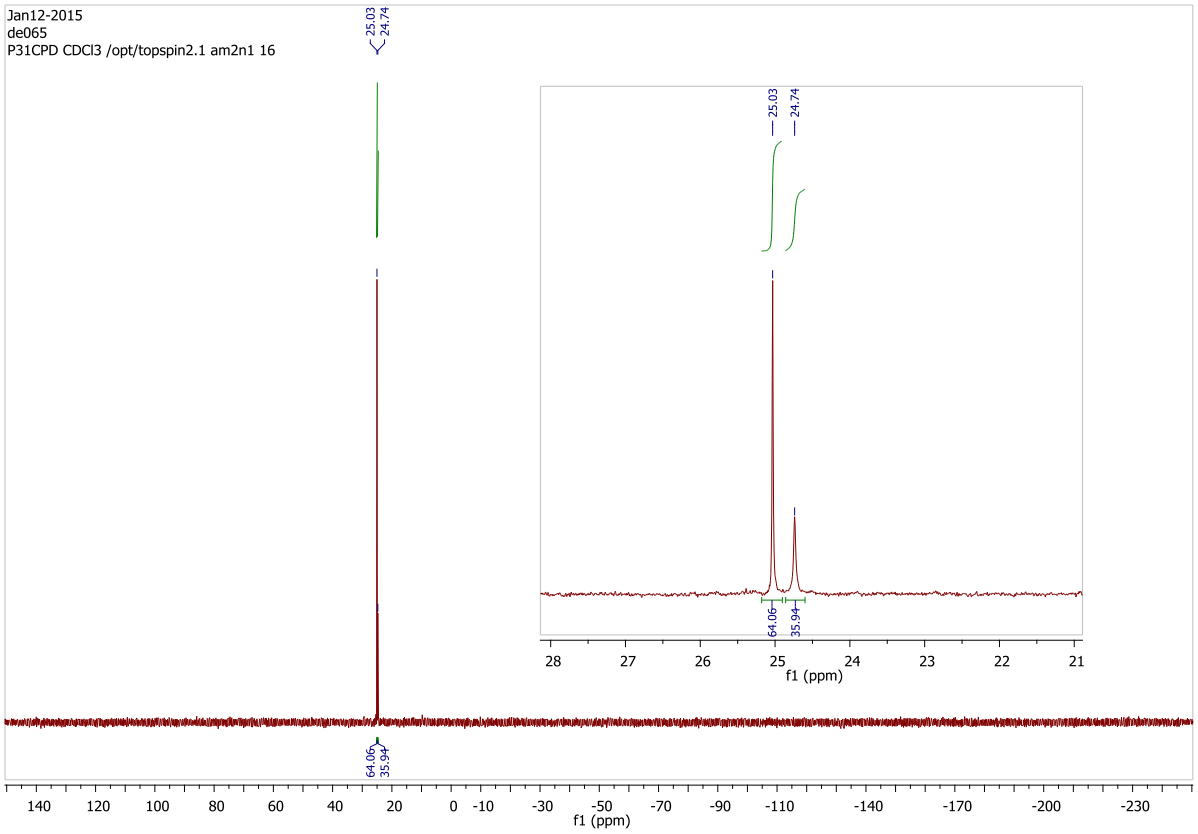
Minimum:				-1.5				
Maximum:		30.0	2.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
562.9969	562.9963	0.6	1.1	3.5	1361.2	0.003	99.74	C18 H31 O6 Br2 P2
	562.9975	-0.6	-1.1	-0.5	1367.2	5.961	0.26	C14 H29 O13 Br2
	562.9965	0.4	0.7	23.5	1375.5	14.249	0.00	C31 H18 O2 Br P2
	562.9978	-0.9	-1.6	19.5	1376.9	15.658	0.00	C27 H16 O9 Br

5.4. 4,4'-dibromo-2,2'-diethoxy-1,1'-dioxa-2,2'-diphospha-[3,3'-bispiro[4.4]nonane-3,3'-diene] 2,2'-dioxide (6d)



Bis-allenylphosphonate **2d** (459 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). Yellow solid, 297 mg, yield = 53%.

^{31}P NMR ($CDCl_3$, 161.99 MHz): δ (ppm) = 24.7 (s, 36%, diastereomer 1), 25.0 (s, 64%, diastereomer 2); ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 1.32 and 1.35 (2 t, diastereomer 2: *J* = 7.1 Hz, diastereomer 1: *J* = 6.9 Hz, 6H, 2 CH_3), 1.85-2.04 and 2.14-2.26 (2 m, 16H, 8 CH_2), 4.03-4.31 (m, 4H, 2 CH_2O); ^{13}C NMR ($CDCl_3$, 100.61 MHz): diastereomer 1 δ (ppm) = 16.4 (d, *J* = 6.3 Hz, CH_3), 24.8 (s, CH_2), 24.9 (s, CH_2), 38.3 (t, *J* = 6.3 Hz, CH_2), 39.5 (t, *J* = 1.6 Hz, CH_2), 64.3 (d, *J* = 7.0 Hz, OCH_2), 97.6 (s, OC), 122.4 (dd, *J* = 163.4, 11.2 Hz, CP), 147.9 (dd, *J* = 42.5, 8.3 Hz, CBr), diastereomer 2 δ (ppm) = 16.5-16.6 (m, CH_3), 24.8 (s, CH_2), 24.9 (s, CH_2), 38.6 (t, *J* = 1.4 Hz, CH_2), 39.0 (t, *J* = 4.1 Hz, CH_2), 64.7-64.8 (m, OCH_2), 97.1 (s, OC), 123.5 (dd, *J* = 164.1, 10.5 Hz, CP), 146.7 (dd, *J* = 42.6, 8.2 Hz, CBr); HRMS (ESI^+): m/z calcd for $[M+H]^+$, $C_{18}H_{27}Br_2O_6P_2$ 558.9650 Found: 558.9655.


Jan12-2015
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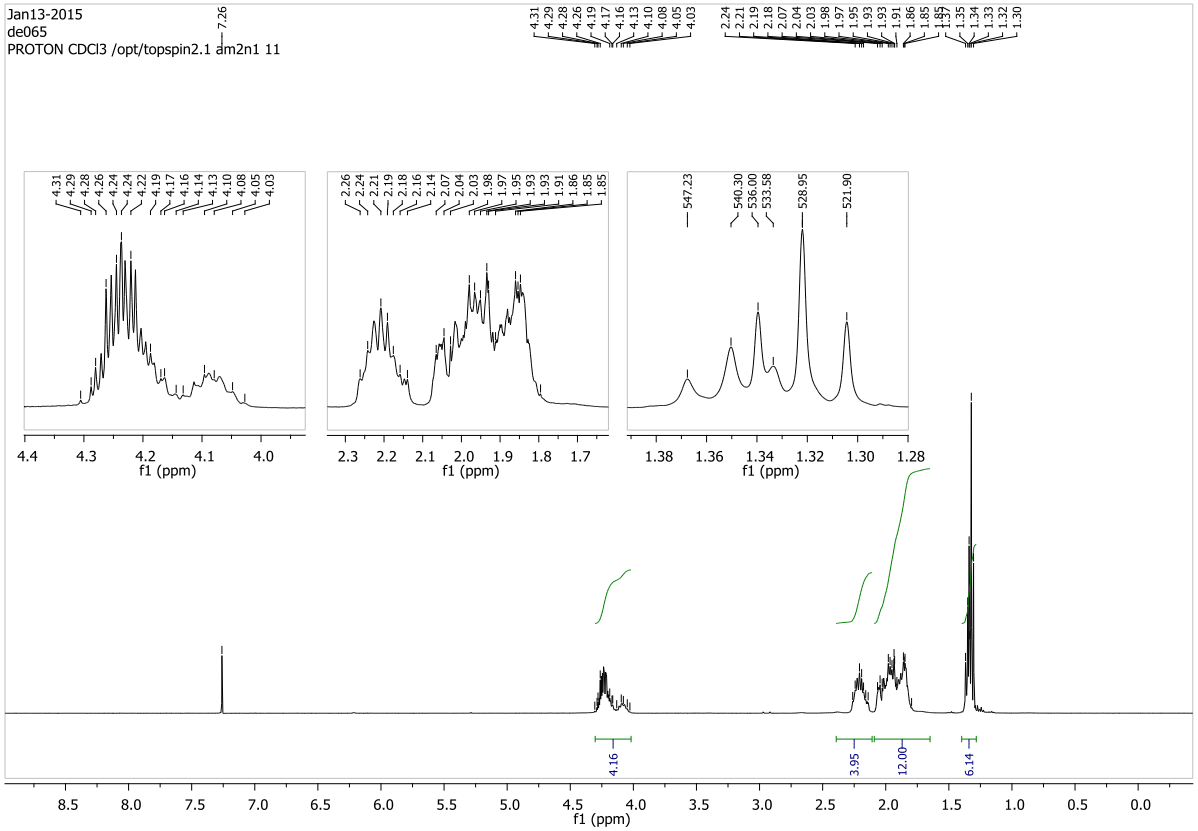
24.74
64.06
35.94
f1 (ppm)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de065
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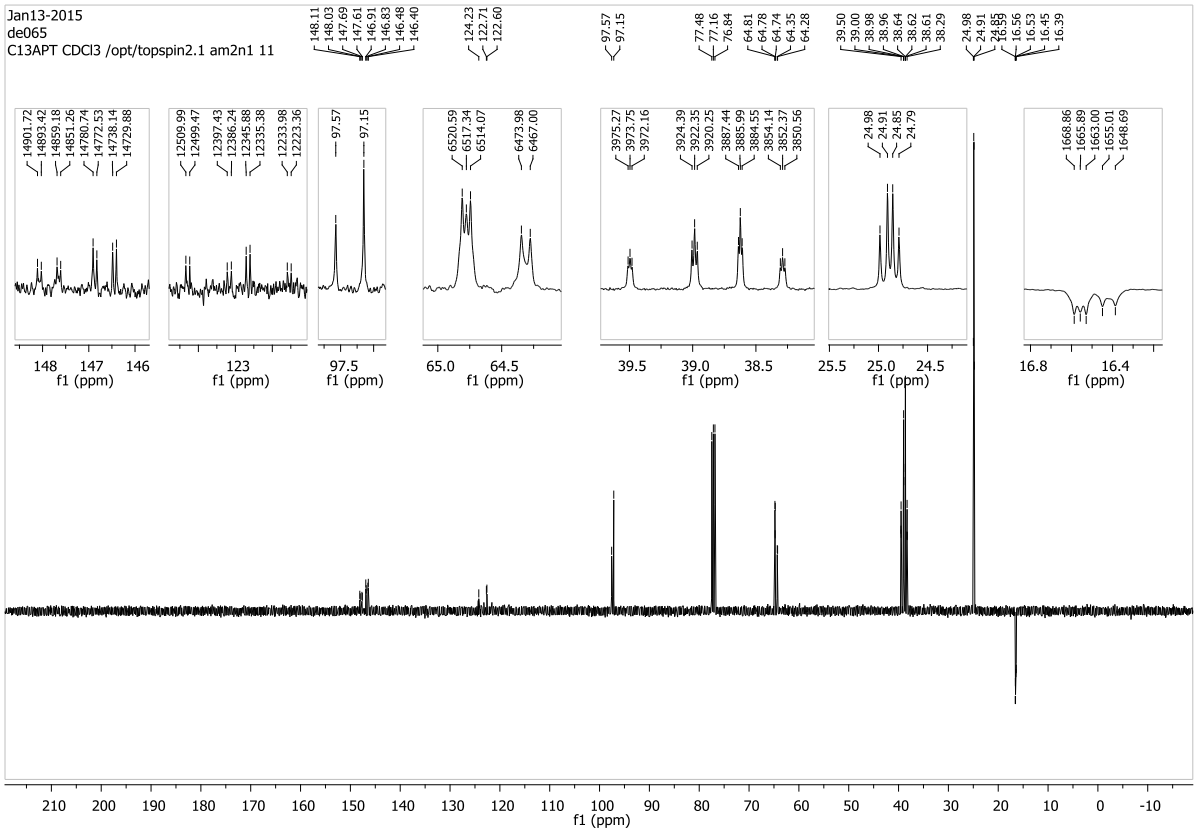
6.14
f1 (ppm)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de065
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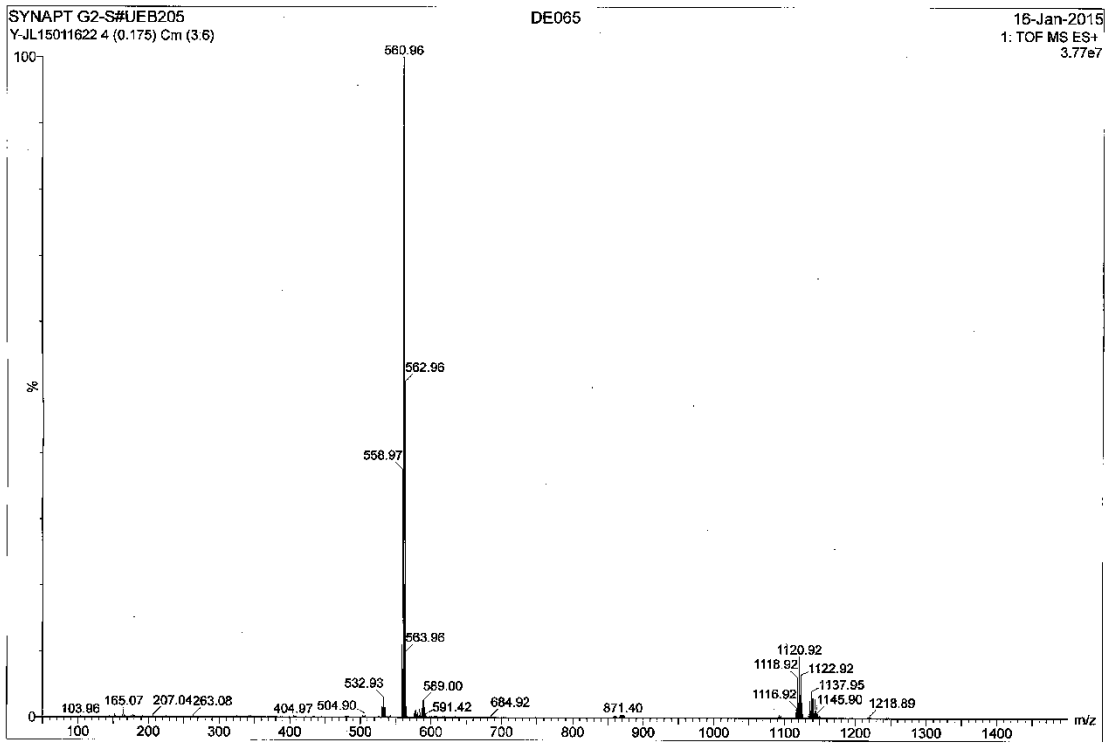
f1 (ppm)


SYNAPT G2-S#UEB205
Y-JL15011622 4 (0.175) Cm (3.6)
DE065
16-Jan-2015
1: TOF MS ES+
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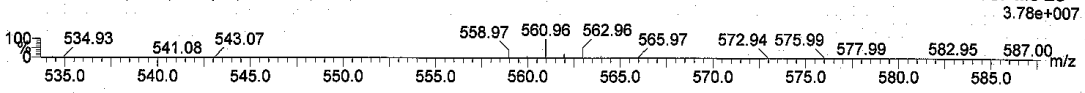
560.96
562.96
558.97
563.96
532.93
569.00
591.42
684.92
871.40
1120.92
1118.92
1122.92
1137.95
1116.92
1145.90
1218.89
103.96
165.07
207.04
263.08
404.97
504.90
%
m/z

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

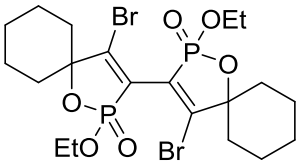
Monoisotopic Mass, Even Electron Ions
999 formula(e) evaluated with 5 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-10 O: 0-10 Br: 1-2 P: 2-2

SYNAPT G2-S#UEB205 DE065 16-Jan-2015
Y-JL15011622 4 (0.175) Cm (3:6) 1: TOF MS ES+
3.78e+007



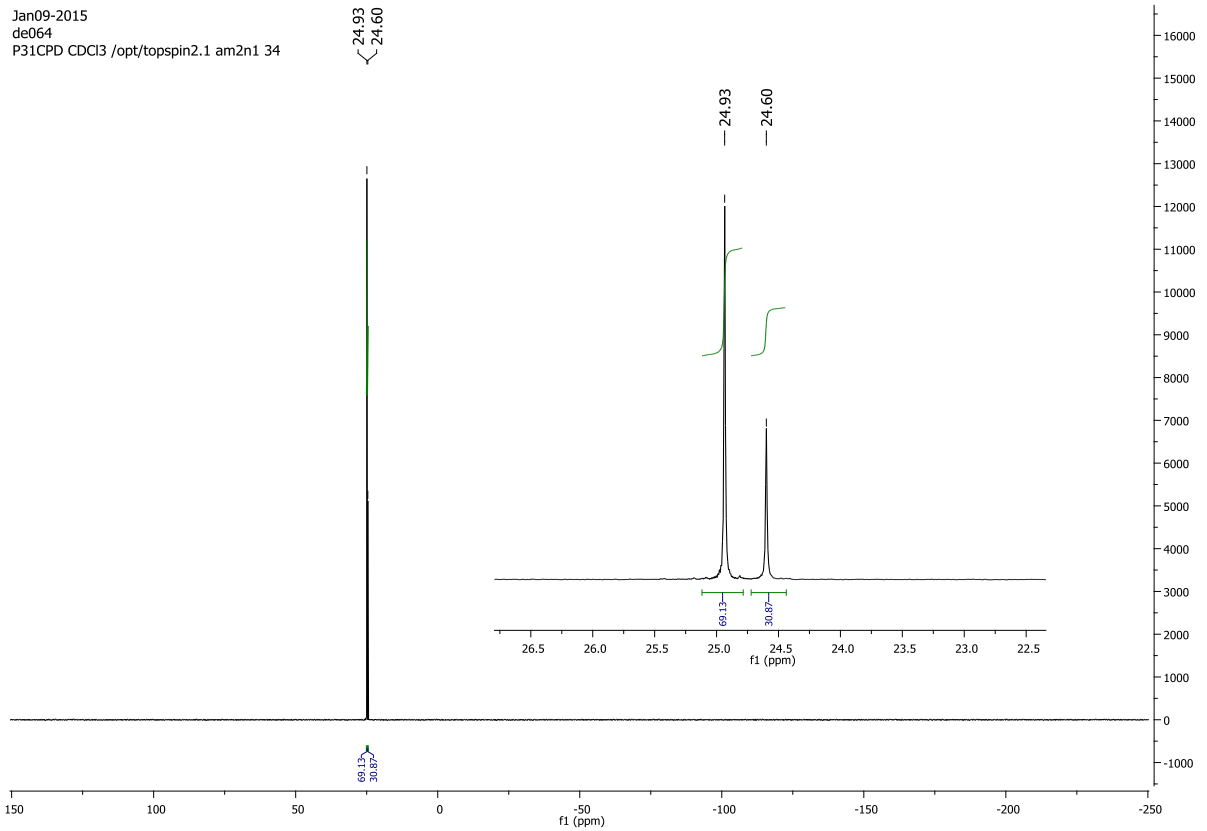
Minimum:				-1.5				
Maximum:		1.0	3.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
558.9655	558.9650	0.5	0.9	5.5	1183.1	0.291	74.73	C18 H27 O6 Br2 P2
	558.9663	-0.8	-1.4	10.5	1184.3	1.394	24.80	C19 H23 N4 O2 Br2 P2
	558.9652	0.3	0.5	25.5	1188.4	5.591	0.37	C31 H14 O2 Br P2
	558.9644	1.1	2.0	13.5	1190.5	7.612	0.05	C15 H14 N8 O7 Br P2
	558.9671	-1.6	-2.9	12.5	1190.6	7.758	0.04	C19 H18 N2 O9 Br P2

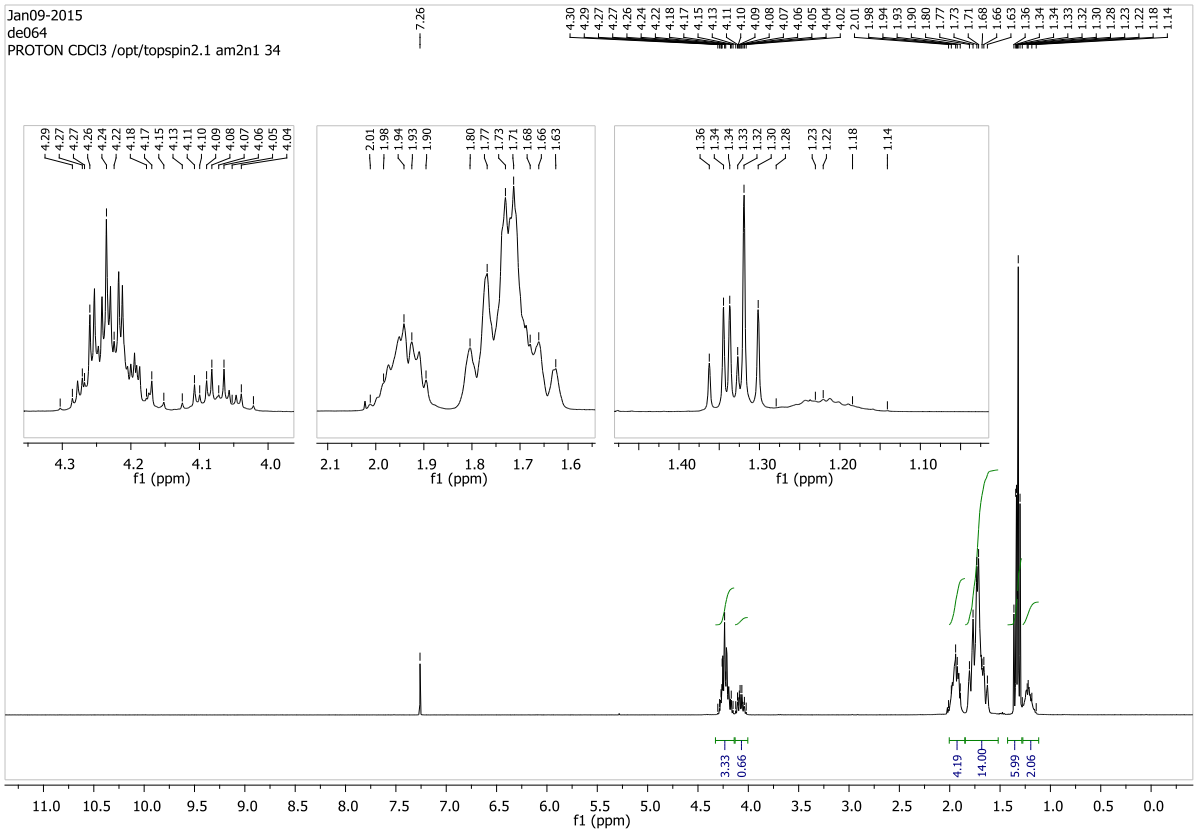
5.5. 4,4'-Dibromo-2,2'-diethoxy-1,1'-dioxa-2,2'-diphospha-[3,3'-bispiro[4.5]decane-3,3'-diene] 2,2'-dioxide (6e)



Bis-allenylphosphonate **2e** (487 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). Yellow solid, 341 mg, yield = 58%.

^{31}P NMR ($CDCl_3$, 161.99 MHz): δ (ppm) = 24.6 (s, 31%, diastereomer 1), 24.9 (s, 69%, diastereomer 2); ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 1.14-1.28 (m, 2H, CH_2), 1.32 and 1.34 (2 t, diastereomer 2: *J* = 7.1 Hz, diastereomer 1: *J* = 7.1 Hz, 6H, 2 CH_3), 1.63-1.80 and 1.90-2.01 (2 m, 18H, 9 CH_2), 4.04-4.13 and 4.15-4.29 (2 m, 4H, 2 CH_2O); ^{13}C NMR ($CDCl_3$, 100.61 MHz): diastereomer 1 δ (ppm) = 16.4-16.5 (m, CH_3), 21.4 (s, CH_2), 21.5 (s, CH_2), 24.4 (s, CH_2), 34.4 (t, *J* = 1.5 Hz, CH_2), 35.6 (t, *J* = 1.4 Hz, CH_2), 64.1-64.2 (m, OCH_2), 89.6 (s, OC), 121.01 (dd, *J* = 163.6, 11.0 Hz, CP), 150.1 (m, *J* = 43.5, 7.9 Hz, CBr), diastereomer 2 δ (ppm) = 16.5-16.6 (m, CH_3), 21.4 (s, CH_2), 21.6 (s, CH_2), 24.4 (s, CH_2), 34.8 (t, *J* = 1.2 Hz, CH_2), 35.2 (t, *J* = 1.8 Hz, CH_2), 64.7-64.8 (m, OCH_2), 89.2 (s, OC), 122.3 (dd, *J* = 164.4, 10.4 Hz, CP), 148.67-149.18 (dd, *J* = 43.7, 8.2 Hz, CBr); HRMS (ESI^+): m/z calcd for $[M+H]^+$, $C_{20}H_{31}Br_2O_6P_2$, 586.9963 Found: 586.9967.




Jan09-2015
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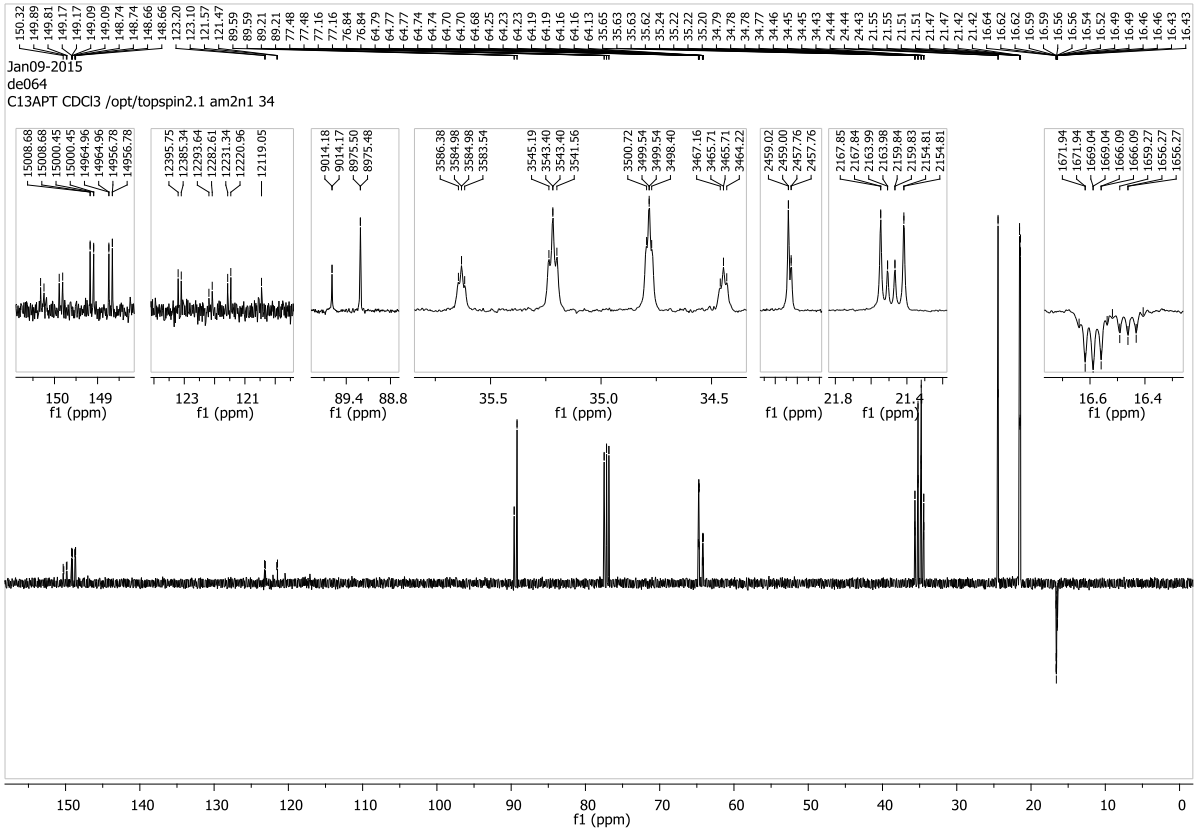
f1 (ppm)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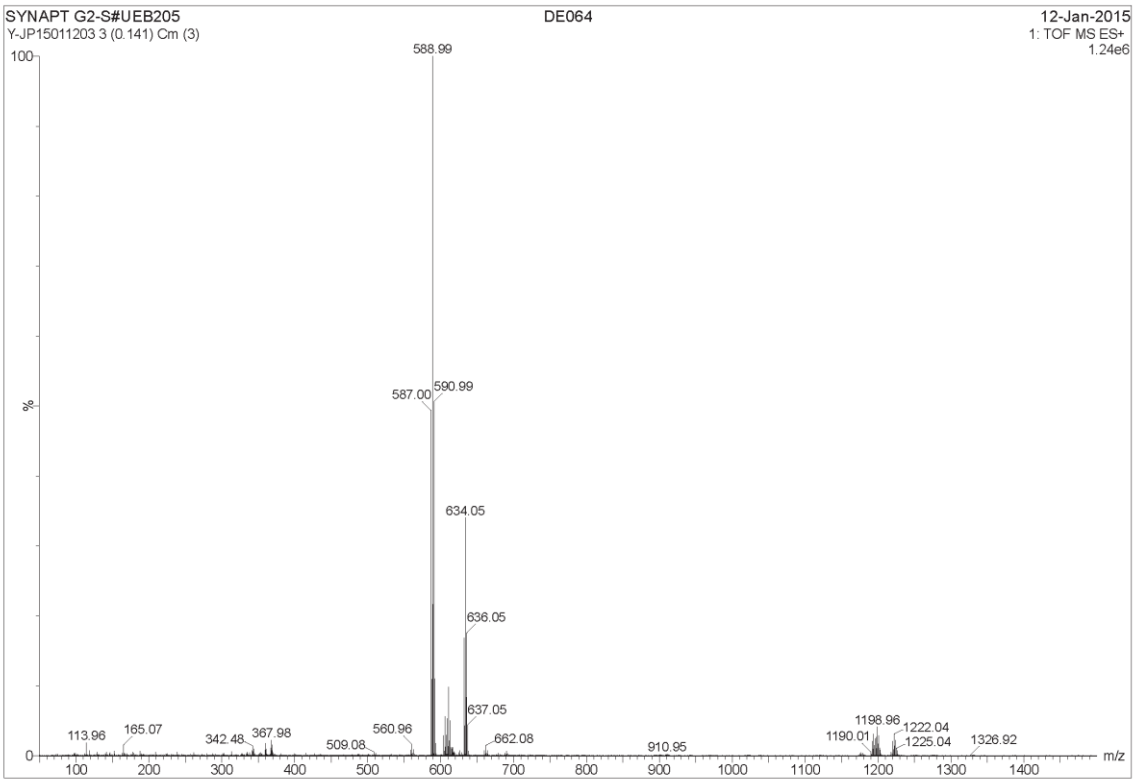
f1 (ppm)

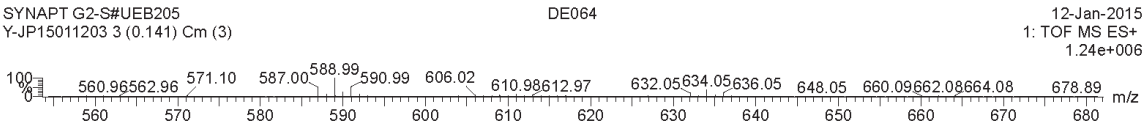


Elemental Composition Report

Single Mass Analysis

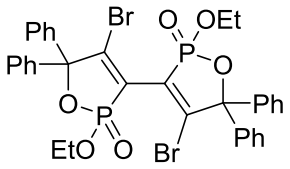
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
9577 formula(e) evaluated with 23 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-110 N: 0-30 O: 0-30 Br: 1-2 P: 0-2



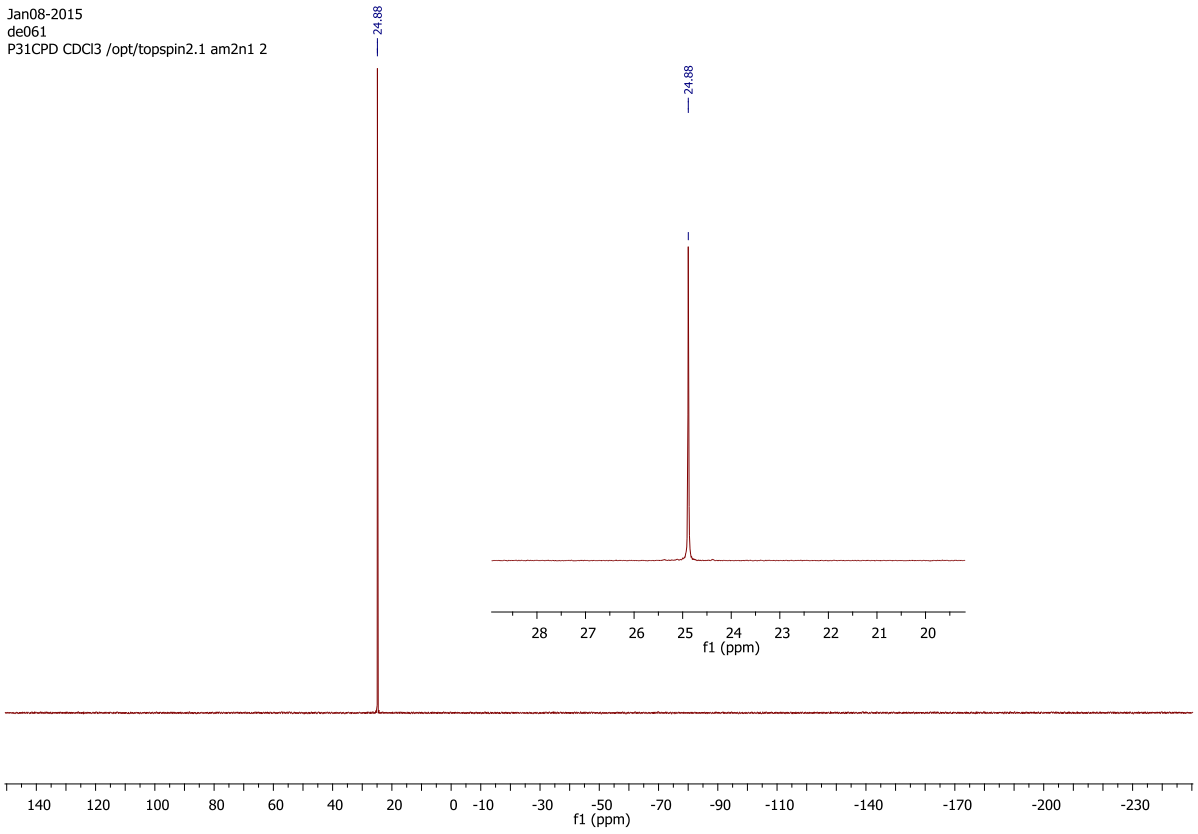
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		1.0	5.0	50.0				
586.9967	586.9963	0.4	0.7	5.5	875.1	0.033	96.79	C20 H31 O6 Br2 P2
	586.9975	-0.8	-1.4	12.5	879.0	3.904	2.02	C14 H17 N14 O3 Br2
	586.9976	-0.9	-1.5	10.5	879.9	4.871	0.77	C21 H27 N4 O2 Br2 P2
	586.9975	-0.8	-1.4	1.5	880.8	5.709	0.33	C16 H29 O13 Br2
	586.9961	0.6	1.0	7.5	882.7	7.608	0.05	C13 H21 N10 O7 Br2
	586.9959	0.8	1.4	15.5	883.2	8.160	0.03	C23 H22 N6 O Br2 P
	586.9970	-0.3	-0.5	19.5	883.9	8.859	0.01	C29 H21 N2 O2 Br2
	586.9964	0.3	0.5	8.5	887.1	12.080	0.00	C8 H18 N18 O2 Br2 P
	586.9973	-0.6	-1.0	-0.5	888.4	13.341	0.00	C10 H25 N2 O19 Br P
	586.9967	0.0	0.0	17.5	888.6	13.507	0.00	C23 H17 N4 O8 Br P
	586.9965	0.2	0.3	25.5	889.0	13.939	0.00	C33 H18 O2 Br P2
	586.9968	-0.1	-0.2	-1.5	889.3	14.240	0.00	C5 H27 N12 O7 Br2 P2
	586.9969	-0.2	-0.3	9.5	889.3	14.271	0.00	C13 H16 N8 O14 Br
	586.9964	0.3	0.5	27.5	889.9	14.814	0.00	C26 H8 N10 O3 Br
	586.9970	-0.3	-0.5	18.5	890.0	14.920	0.00	C18 H14 N12 O3 Br P2
	586.9957	1.0	1.7	13.5	891.0	15.976	0.00	C17 H18 N8 O7 Br P2
	586.9976	-0.9	-1.5	0.5	892.3	17.224	0.00	C5 H22 N10 O14 Br P2
	586.9972	-0.5	-0.9	10.5	892.5	17.477	0.00	C8 H13 N16 O9 Br P
	586.9969	-0.2	-0.3	20.5	892.9	17.814	0.00	C11 H4 N22 O4 Br
	586.9959	0.8	1.4	5.5	893.0	17.918	0.00	C7 H17 N12 O13 Br P

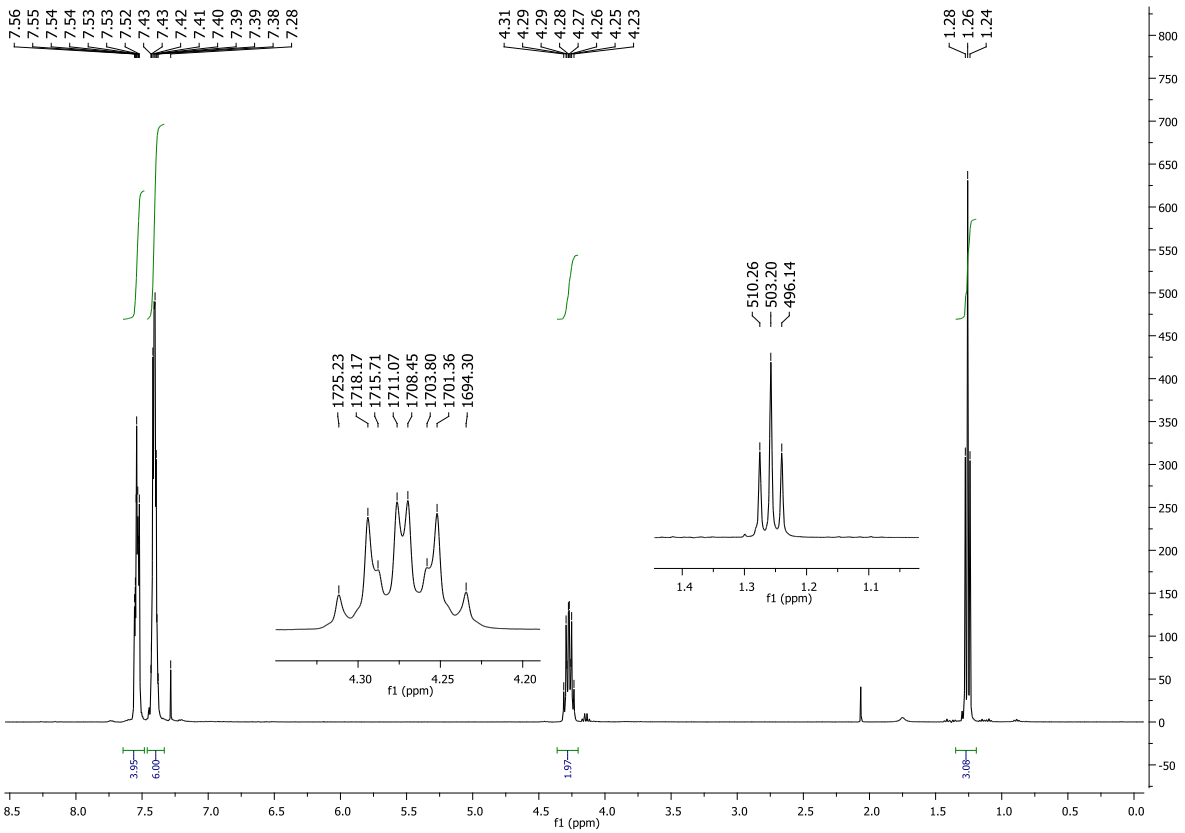
5.6. 4,4'-Dibromo-2,2'-diethoxy-5,5,5',5'-tetraphenyl-5H,5'H-[3,3'-bi(1,2-oxaphosphole)] 2,2'-dioxide (6f)



Bis-allenylphosphonate **2f** (654 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). Yellow solid, 371 mg, yield = 49%.

^{31}P NMR ($CDCl_3$, 161.99 MHz): δ (ppm) = 24.9 (s); ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ (ppm) = 1.26 (t, *J* = 7.1 Hz, 6H, 2 CH_3), 4.23-4.31 (m, 4H, 2 CH_2O), 7.38-7.43 (m, 12H, 12 CH_{Ph}), 7.52-7.56 (m, 8H, 8 CH_{Ph}); ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ (ppm) = 16.4-16.5 (m, CH_3), 65.2-65.3 (m, CH_2O), 93.25 (s, C), 124.9 (dd, *J* = 162.9, 10.1 Hz, CP), 128.3 (s, CH),128.4 (s, CH), 128.8 (s, CH), 129.2 (s, CH), 129.3 (s, CH_{Ph}), 138.6 (t, *J* = 2.2 Hz, C), 138.8 (t, *J* = 1.8 Hz, C), 146.2 (dd, *J* = 40.7, 8.2 Hz, CBr); HRMS (ESI^+): m/z calcd for $[M+H]^+$, $C_{34}H_{31}Br_2O_6P_2$, 754.9963 Found: 754.9965.

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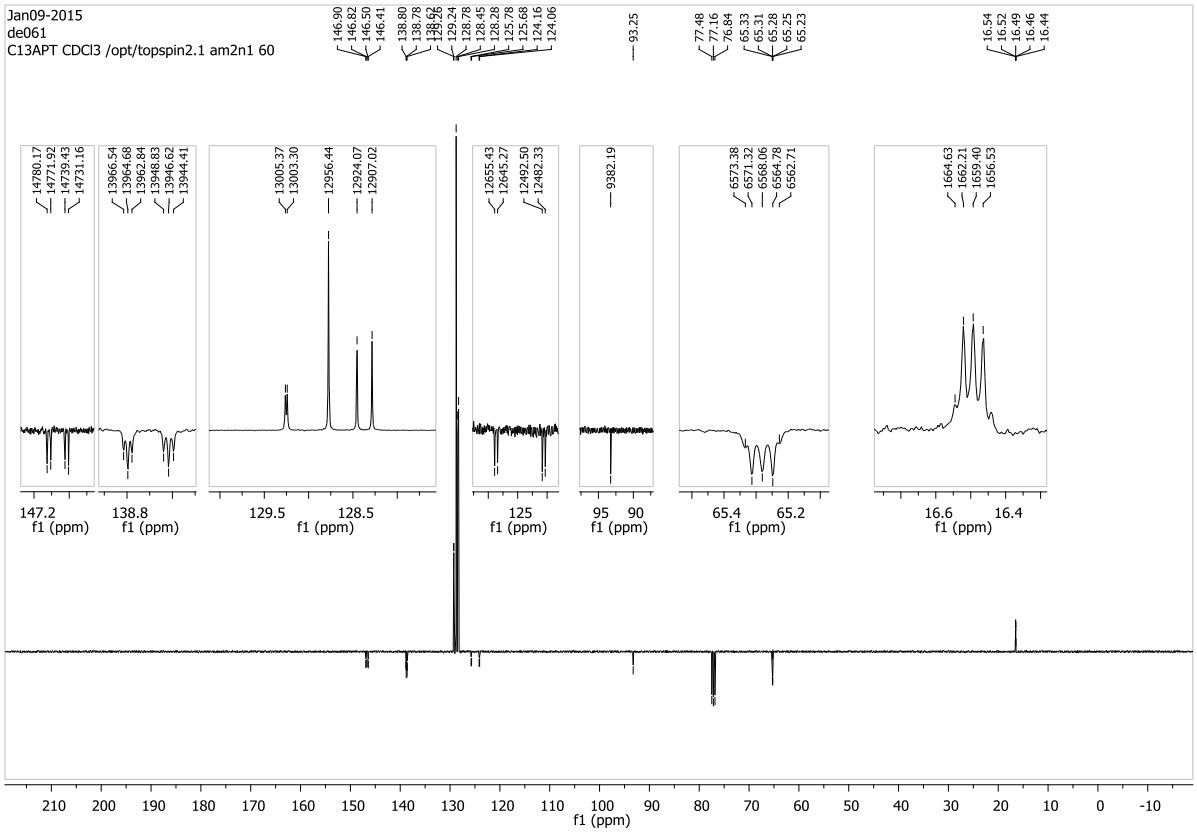
4.31 4.29 4.29 4.28 4.27 4.26 4.25 4.23
1.28 1.26 1.24
1725.23 1718.17 1715.71 1711.07 1708.45 1703.80 1701.36 1694.30
510.26 503.20 496.14
f1 (ppm)


Jan09-2015
de061
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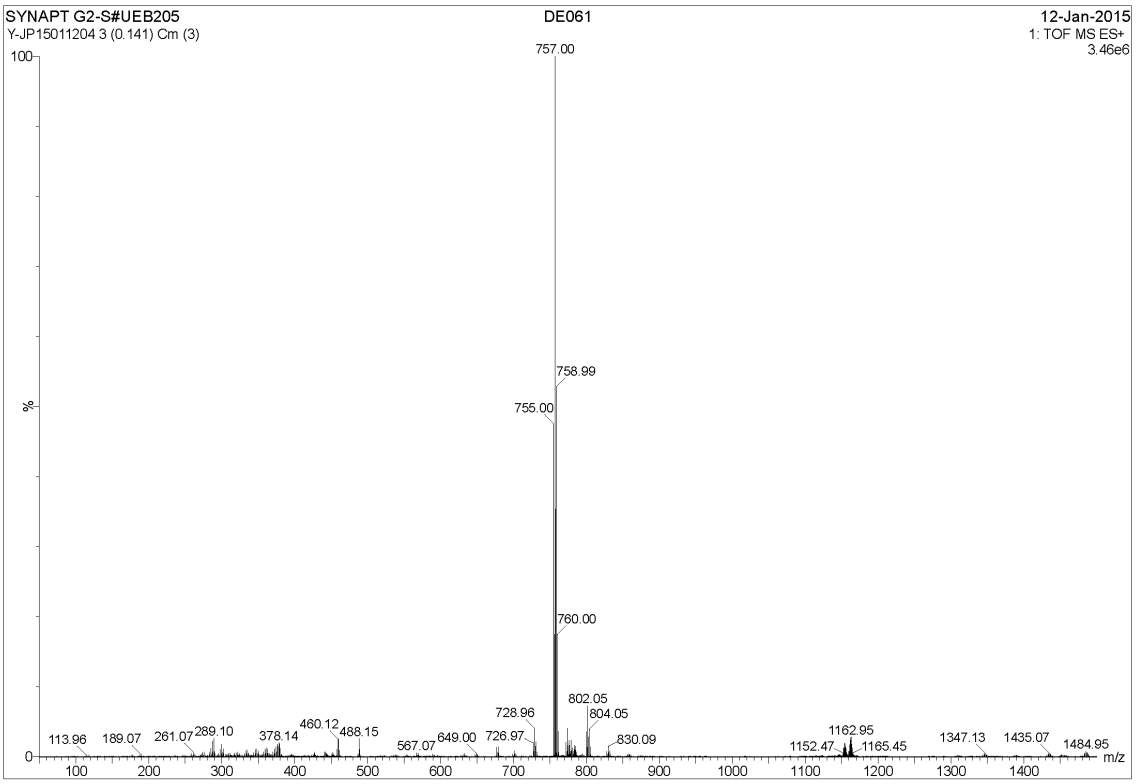
f1 (ppm)

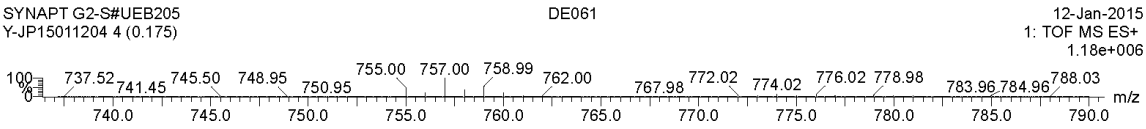


Elemental Composition Report

Single Mass Analysis

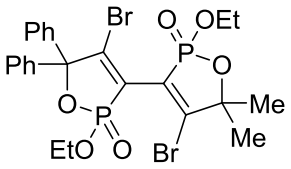
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
20541 formula(e) evaluated with 30 results within limits (up to 20 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-110 N: 0-30 O: 0-30 P: 0-2 Br: 1-2



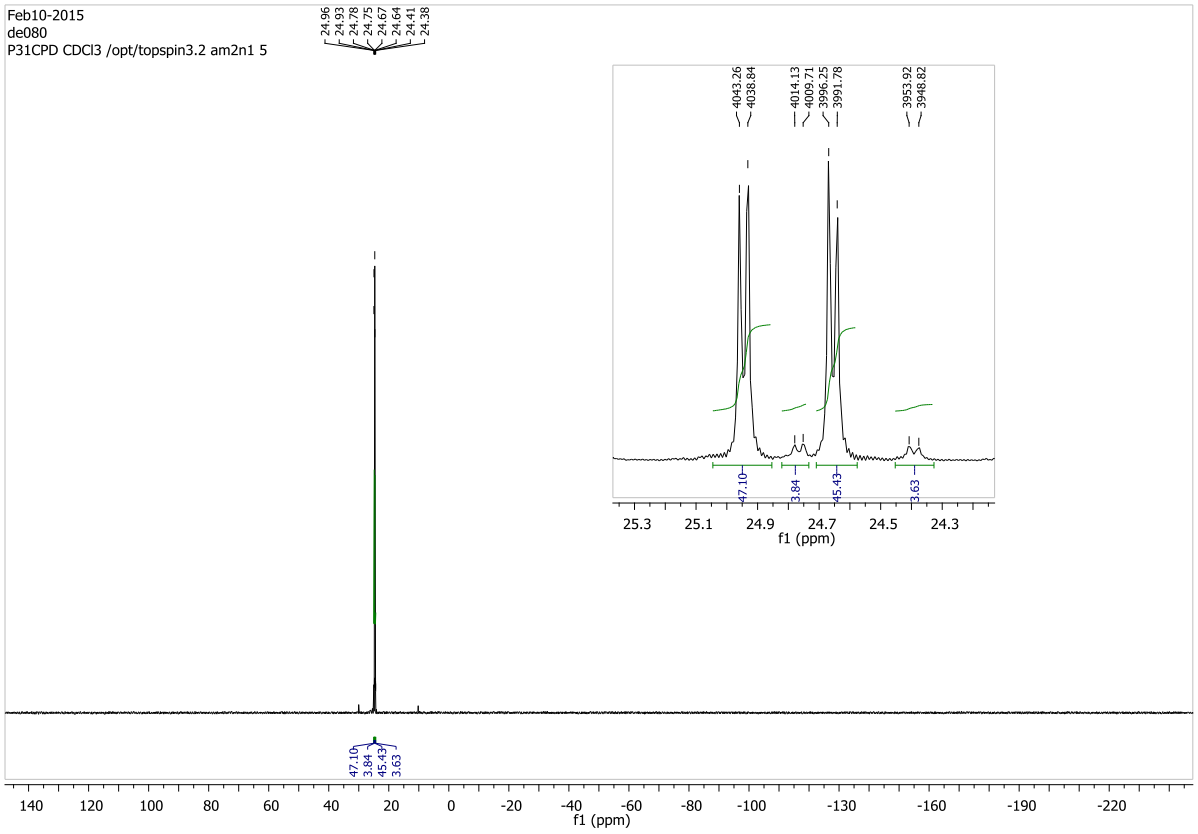
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
754.9965	754.9963	0.2	0.3	19.5	1192.5	0.006	99.43	C34 H31 O6 P2 Br2
	754.9959	0.6	0.8	29.5	1198.4	5.897	0.27	C37 H22 N6 O P Br2
	754.9961	0.4	0.5	21.5	1198.6	6.114	0.22	C27 H21 N10 O7 Br2
	754.9970	-0.5	-0.7	33.5	1200.4	7.964	0.03	C43 H21 N2 O2 Br2
	754.9965	0.0	0.0	11.5	1200.9	8.458	0.02	C24 H30 N4 O12 P Br2
	754.9964	0.1	0.1	22.5	1201.2	8.726	0.02	C22 H18 N18 O2 P Br2
	754.9968	-0.3	-0.4	12.5	1202.6	10.127	0.00	C19 H27 N12 O7 P2 Br2
	754.9967	-0.2	-0.3	3.5	1204.2	11.677	0.00	C14 H29 N8 O18 Br2
	754.9966	-0.1	-0.1	14.5	1206.3	13.796	0.00	C12 H17 N22 O8 Br2
	754.9969	-0.4	-0.5	23.5	1206.4	13.942	0.00	C27 H16 N8 O14 Br
	754.9973	-0.8	-1.1	13.5	1206.5	13.973	0.00	C24 H25 N2 O19 P Br
	754.9967	-0.2	-0.3	31.5	1206.5	13.993	0.00	C37 H17 N4 O8 P Br
	754.9965	0.0	0.0	39.5	1206.8	14.365	0.00	C47 H18 O2 P2 Br
	754.9961	0.4	0.5	0.5	1206.9	14.380	0.00	C13 H28 N2 O29 Br
	754.9970	-0.5	-0.7	32.5	1206.9	14.389	0.00	C32 H14 N12 O3 P2 Br
	754.9962	0.3	0.4	9.5	1206.9	14.392	0.00	C18 H26 N6 O18 P2 Br
	754.9970	-0.5	-0.7	4.5	1206.9	14.464	0.00	C9 H26 N16 O13 P Br2
	754.9964	0.1	0.1	41.5	1207.0	14.534	0.00	C40 H8 N10 O3 Br
	754.9972	-0.7	-0.9	24.5	1207.4	14.904	0.00	C22 H13 N16 O9 P Br
	754.9959	0.6	0.8	19.5	1207.9	15.401	0.00	C21 H17 N12 O13 P Br

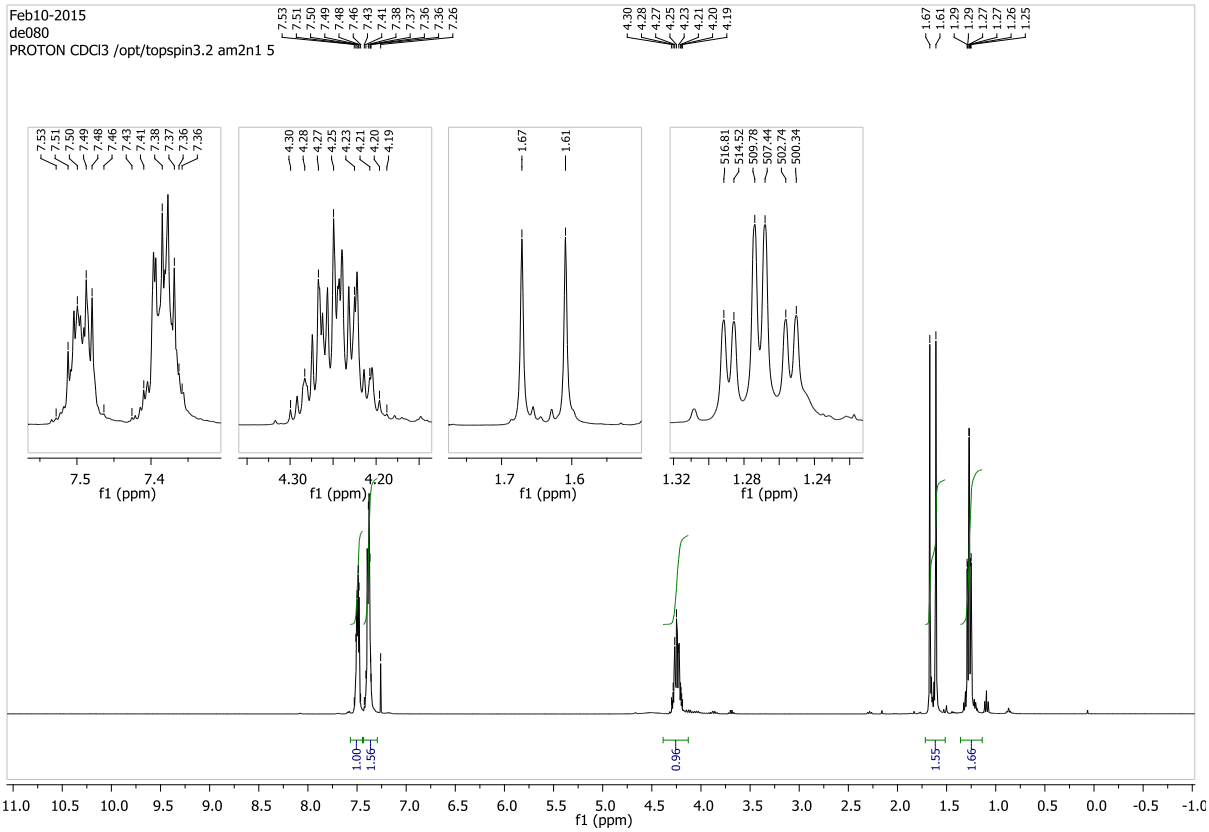
5.7. 4,4'-Dibromo-2,2'-diethoxy-5,5-dimethyl-5',5'-diphenyl-5H,5'H-[3,3'-bi(1,2-oxaphosphole)] 2,2'-dioxide (6g)

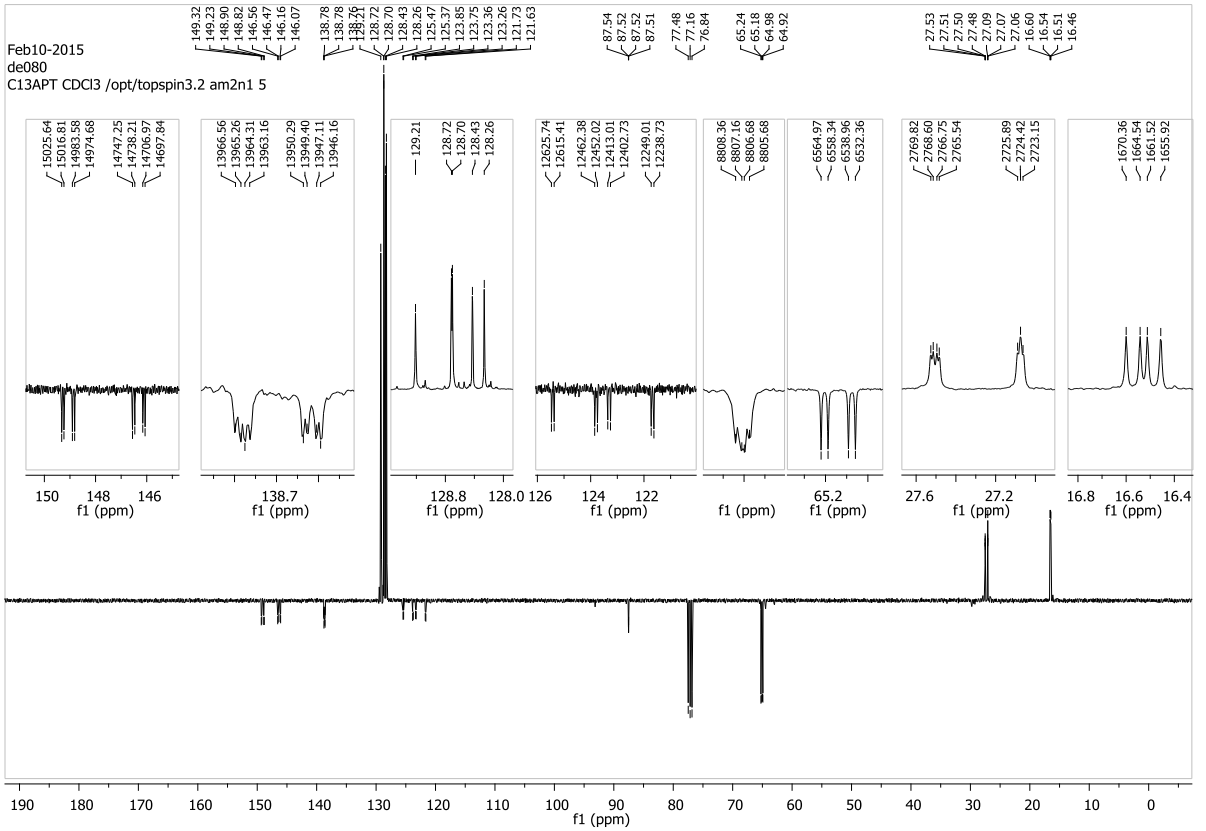


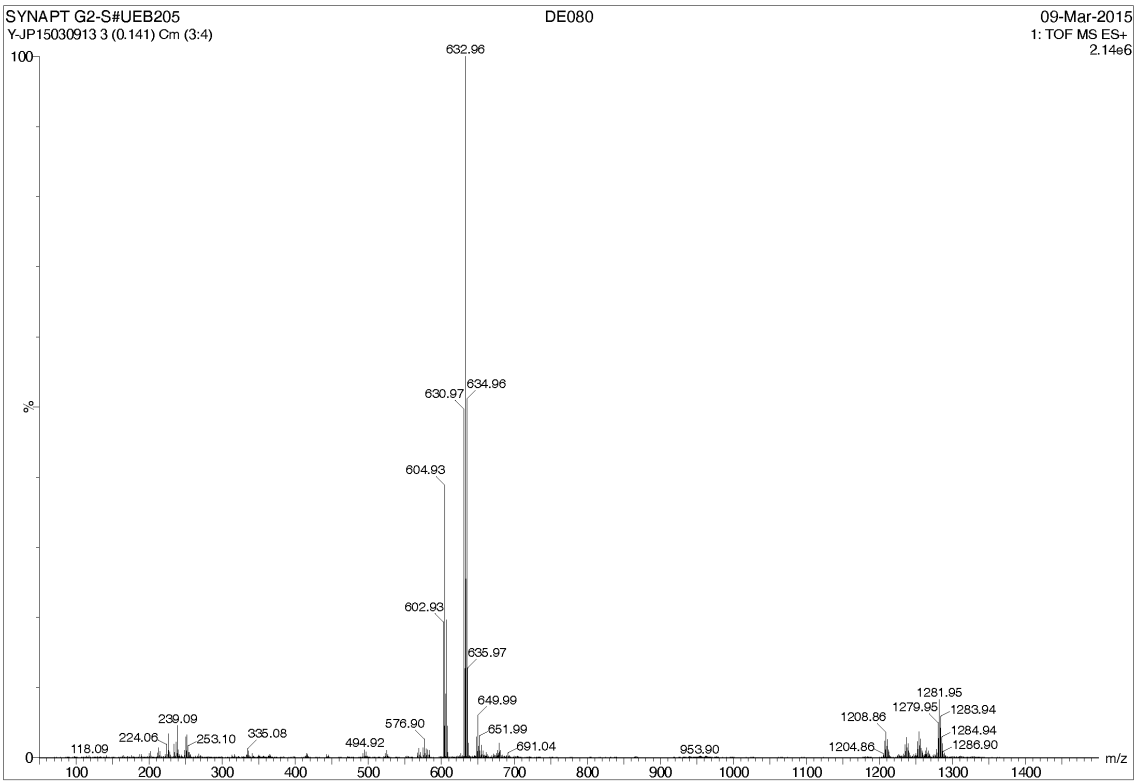
Bis-allenylphosphonate **2g** (531 mg, 1.0 mmol). The residue was purified by chromatography (silica gel, CH_2Cl_2/AcOEt 6:4). Yellow solid, 266 mg, yield = 42%.

^{31}P ($CDCl_3$, 161.97 MHZ) δ (ppm) = (diastereomer 1 – 7%), 24.4 (d, *J* = 5.1 Hz), 24.8 (d, *J* = 4.5 Hz), (diastereomer 2 – 93%), δ (ppm) = 24.7 (d, *J* = 4.4 Hz), 24.9 (d, *J* = 4.4 Hz); Only the major diastereomer (2) will be described. ^{1}H NMR ($CDCl_3$, 400,13 MHZ): δ (ppm) = 1.27 (t, *J* = 7.1 Hz, 3H, CH_3), 1.27 (t, *J* = 6.9 Hz, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 4.19-4.30 (m, 4H, 2 CH_2O), 7.36-7.43 (m, 6H, CH_{Ph}), 7.46-7.53 (m, 4H, CH_{Ph}); ^{13}C NMR ($CDCl_3$, 100,61 MHZ) : δ (ppm) = 16.5 (d, *J* = 5.6 Hz, CH_3), 16.6 (d, *J* = 5.8 Hz, CH_3), 27.1 (t, *J* = 1.4 Hz, CH_3), 27.5 (dd, *J* = 3.1, 1.2 Hz, CH_3), 64.9 (d, *J* = 6.6 Hz, OCH_2), 65.2 (d, *J* = 6.6 Hz, OCH_2), 87.5-87.5 (m, CO), 122.5 (dd, *J* = 164.0, 10.3 Hz, CP), 124.6 (dd, *J* = 163.4, 10.3 Hz, CP), 128.3, 128.4, 128.7, 128.7, 129.2 (s, CH_{Ph}), 138.6 (dd, *J* = 3.2, 0.9 Hz, C), 138.8 (dd, *J* = 2.2, 1.2 Hz, C), 146.3 (dd, *J* = 40.3, 9.0 Hz, CBr), 146.3 (dd, *J* = 40.3, 9.0 Hz, CBr), 149.07 (dd, *J* = 42.0, 8.8 Hz, CBr); HRMS (ESI^+): m/z calcd for $[M+H]^+$, $C_{24}H_{27}Br_2O_6P_2$, 630.9650 Found: 630.9658.




Feb10-2015
de080
PROTON CDCl3 /opt/topspin3.2 am2n1 5
f1 (ppm)


Feb10-2015
de080
C13APT CDCl3 /opt/topspin3.2 am2n1 5
f1 (ppm)


SYNAPT G2-S#UEB205
DE080
09-Mar-2015
Y-JP15030913 3 (0.141) Cm (3:4)
1: TOF MS ES+
2.14e6
100
%
0
632.96
630.97
634.96
604.93
602.93
635.97
649.99
651.99
691.04
576.90
494.92
239.09
224.06
253.10
335.08
118.09
953.90
1281.95
1279.95
1283.94
1208.86
1284.94
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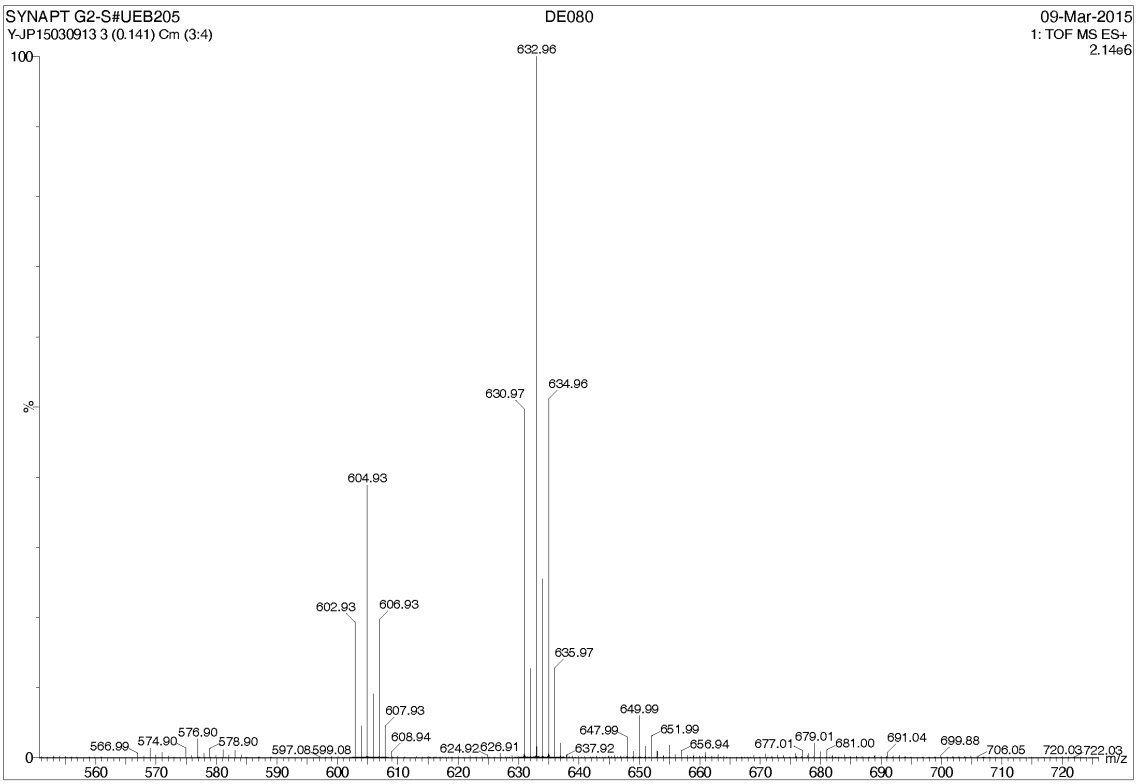
600
700
800
900
1000
1100
1200
1300
1400

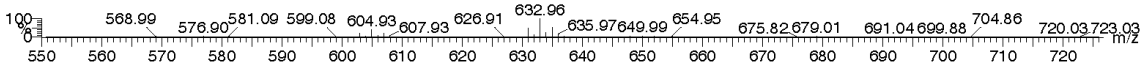

SYNAPT G2-S#UEB205
DE080
09-Mar-2015
Y-JP15030913 3 (0.141) Cm (3:4)
1: TOF MS ES+
2.14e6
100
%
0
632.96
630.97
634.96
604.93
602.93
606.93
635.97
649.99
607.93
608.94
651.99
647.99
566.99
574.90
576.90
578.90
597.08
599.08
624.92
626.91
637.92
656.94
677.01
679.01
681.00
691.04
699.88
706.05
720.03
722.03
m/z
560
570
580
590
600
610
620
630
640
650
660
670
680
690
700
710
720

Single Mass Analysis

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

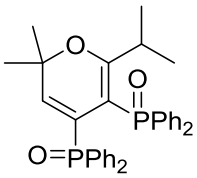
Monoisotopic Mass, Even Electron Ions
84 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)
Elements Used:
C: 1-150 H: 1-200 O: 0-50 P: 2-2 Br: 2-2

SYNAPT G2-S#UEB205 DE080 09-Mar-2015
Y-JP15030913 3 (0.141) Cm (3:4) 1: TOF MS ES+
2.14e+006



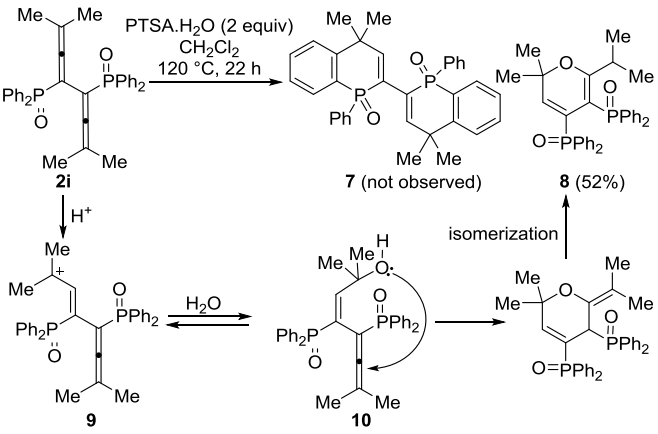
Minimum:				-1.5				
Maximum:		1.0	1.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
630.9658	630.9650	0.8	1.3	11.5	1626.2	n/a	n/a	C24 H27 O6 P2 Br2

7. (6-Isopropyl-2,2-dimethyl-2H-pyran-4,5-diyl)bis(diphenylphosphine oxide) 8

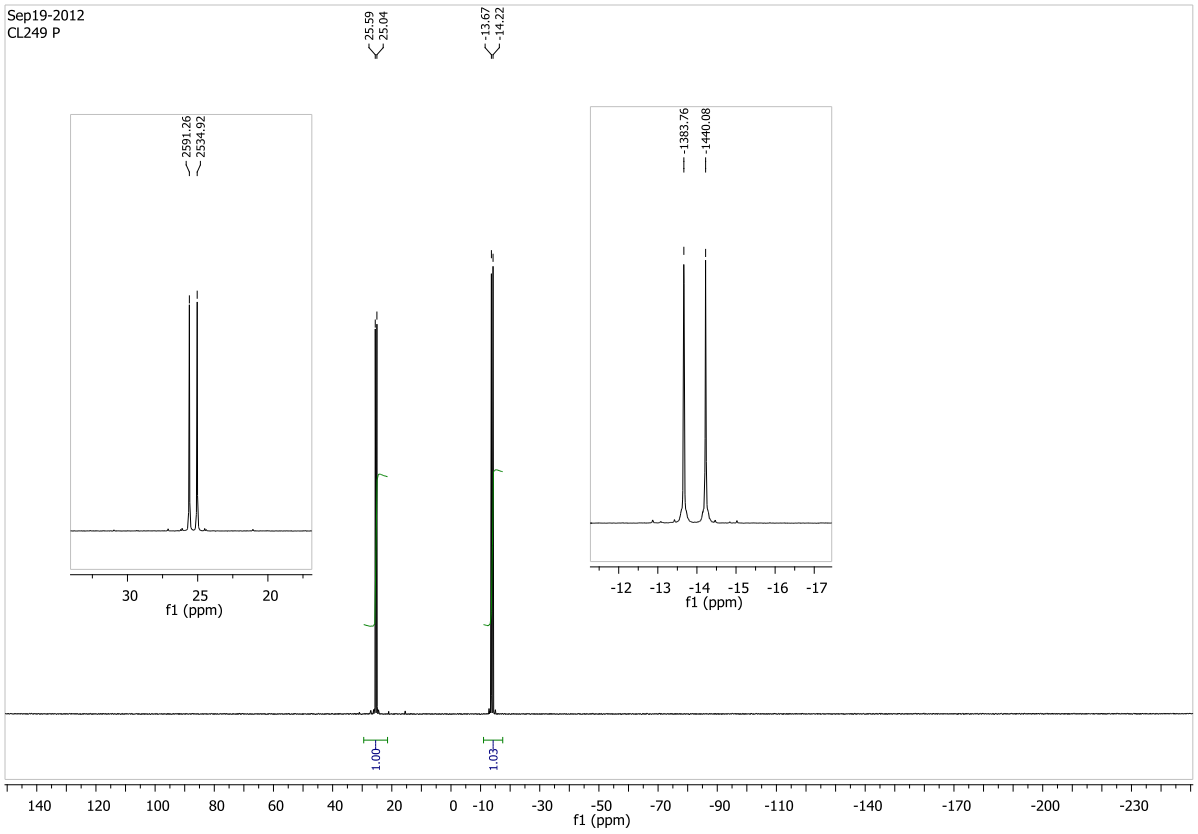


To a solution of bisallenylphosphine oxide **2i** (535 mg, 1 mmol) in CH_2Cl_2 (20 mL) and water (10 mL) was added para-toluenesulfonic acid monohydrate (380 mg, 2 mmol). The reaction mixture was stirred at 120°C for 22h. After extraction with CH_2Cl_2, the combined organic phases were washed with water with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, dichloromethane / isopropanol) giving **8** as a white solid, 287 mg, yield = 52 %.

Scheme 4. Proposed mechanism for the reaction of bisallene 2i with PTSA.



^{31}P ($CDCl_3$, 161.97 MHz) δ(ppm) = -13.9 (d, *J* = 56.3 Hz, 1P), 25.3 (d, *J* = 56.3 Hz, 1P); ^{1}H ($CDCl_3$, 400,13 MHz) δ(ppm) = 0.73 (d, J_{HH} = 6.7 Hz, 6H, CH_3), 0.89 (s, 6H, CH_3), 2.93 (hep, J_{HH} = 6.5 Hz, 1H, CH), 5.63 (d, *J* = 60.7 Hz, 1H, CH=), 7.19-7.36 (m, 12H, 12 CH_{Ph}), 7.56-7.69 (m, 8H, 8 CH_{Ph}); ^{13}C ($CDCl_3$, 100,61 MHz) δ(ppm) = 19.5 (s, CH_3), 28.7 (s, CH_3), 30.1 (s, $CHMe_2$), 79.2 (d, *J* = 6.1 Hz, C), 90.7 (dd, *J* = 127.1, 20.7 Hz, C), 125.4 (dd, *J* = 122.5, 12.1 Hz, C), 127.6 (d, *J* = 15.5 Hz, CH_{Ph}), 128.2 (d, *J* = 12.1 Hz, CH_{Ph}), 130.0 (d, *J* = 3.2 Hz, CH_{Ph}), 131.3 (d, *J* = 2.3 Hz, CH_{Ph}), 131.5 (d, *J* = 10.0 Hz, CH_{Ph}), 131.7 (d, *J* = 11.6 Hz, CH_{Ph}), 134.4 (d, *J* = 106.9 Hz, PC), 137.9 (d, *J* = 161.9 Hz, PC), 142.6 (d, *J* = 23.4 Hz, CH), 181.6 (dd, *J* = 17.1, 2,9 Hz, C-O).


Sep19-2012
CL249 P
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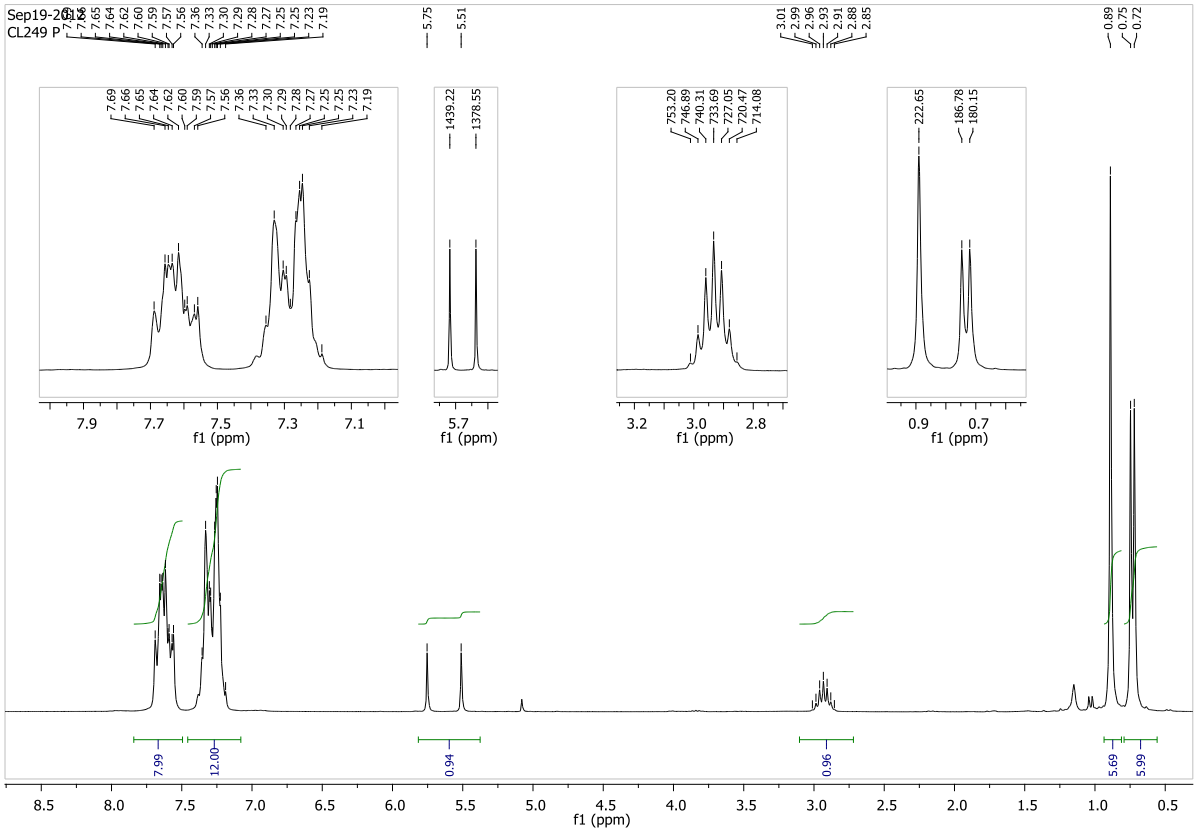
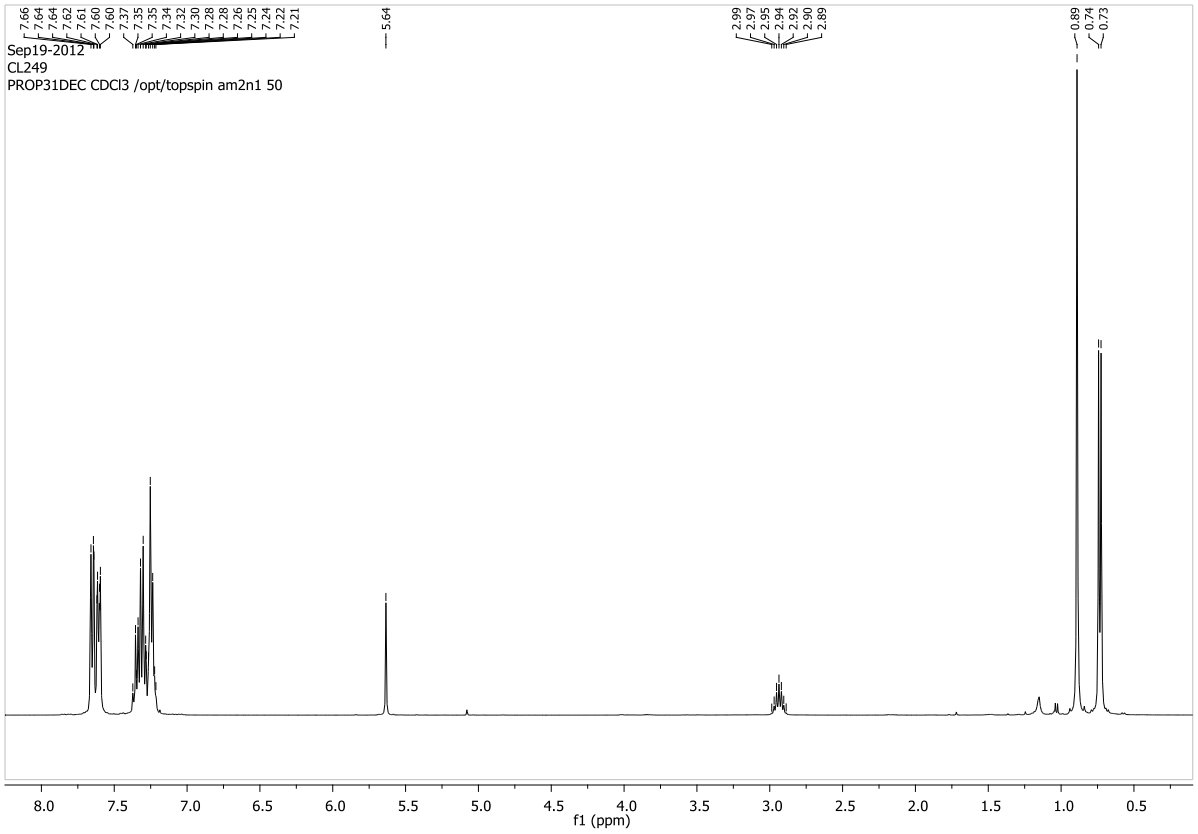
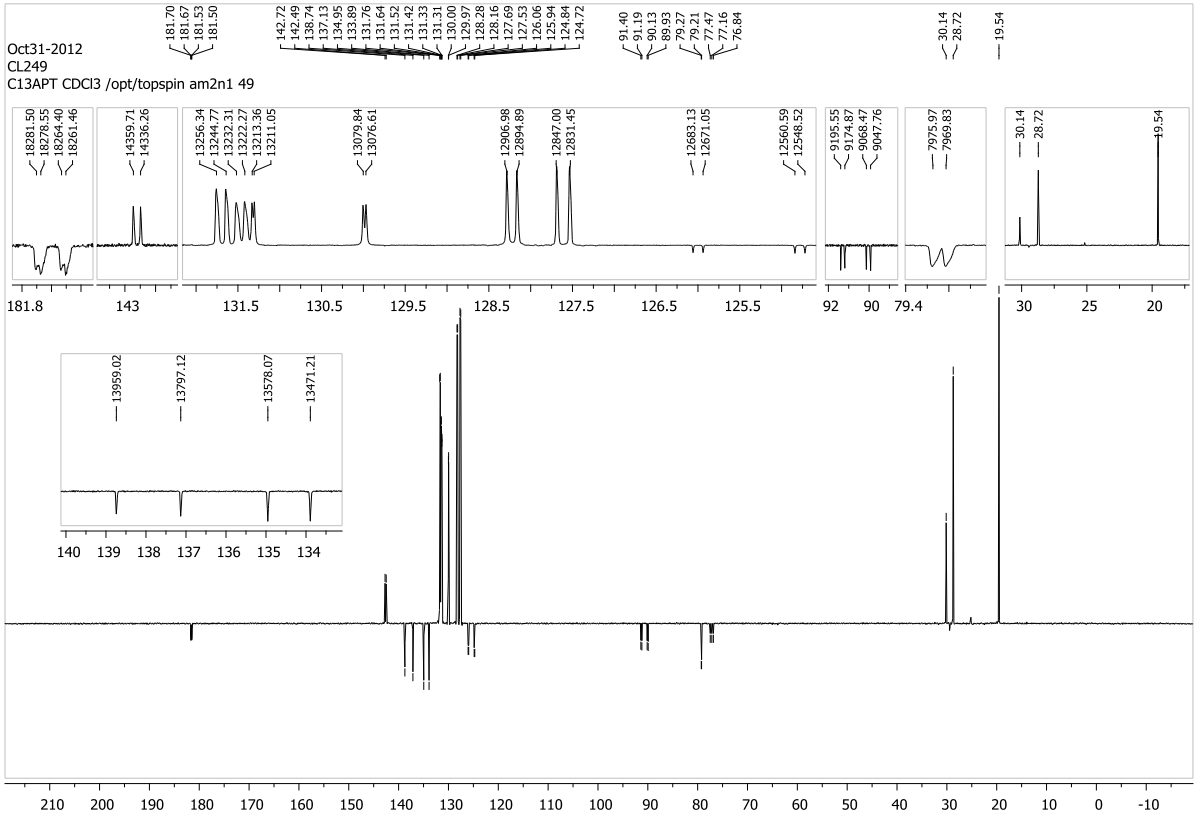
25.04
-13.67
-14.22
2591.26
2534.92
-1383.76
-1440.08
f1 (ppm)
1.00
1.03


Sep19-2012
CL249 P
f1 (ppm)
7.99
12.00
0.94
0.96
5.69
5.99


Sep19-2012
CL249
PROP31DEC CDCl3 /opt/topspin am2n1 50
f1 (ppm)


Oct31-2012
CL249
C13APT CDCl3 /opt/topspin am2n1 49

8. Crystallographic information of dibromobisoxaphospholenes [6f-OH]

Crystal data for [**6f-OH**]: $C_{30}H_{22}Br_2O_6P_2$, *M* = 700.23, orthorhombic, space group Pcca (no. 54), *a* = 27.0189(6) Å, *b* = 14.0226(4) Å, *c* = 7.2637(2) Å, *V* = 2752.04(13) Å^3, *T* = 100 K, *Z* = 4, d_C = 1.690 g cm^{-3}, μ(Cu Kα, λ = 1.54184 Å) = 5.217 mm^{-1}, 51749 reflections collected, 2514 unique [R_{int} = 0.1683], which were used in all calculations. Refinement on F^2, final R(F) = 0.0572, R_w(F2) = 0.1519. CCDC number 1530156.

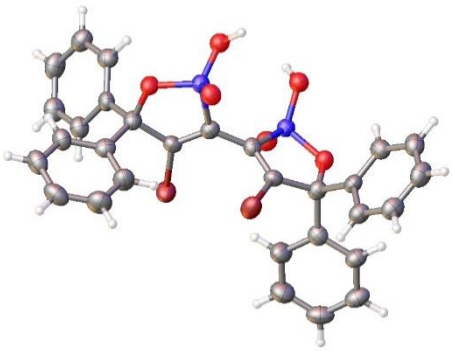


Figure 3. X-ray representation of dibromo-bisoxaphospholene **6f-OH**.

Crystal data and structure refinement for [6e].

Molecular formula	$C_{30}H_{22}Br_2O_6P_2$
Formula weight	700.23
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pcca
a/Å	27.0189(6)
b/Å	14.0226(4)
c/Å	7.2637(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2752.04(13)
Z	4
ρ_{calc}g/cm^3	1.690
μ/mm^{-1}	5.217
F(000)	1400.0
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.304 to 136.116
Index ranges	-32 ≤ h ≤ 32, -15 ≤ k ≤ 16, -8 ≤ l ≤ 8
Reflections collected	51749
Independent reflections	2514 [R_{int} = 0.1683, R_{sigma} = 0.0505]
Data/restraints/parameters	2514/0/181

Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1519
Final R indexes [all data]	R_1 = 0.0753, wR_2 = 0.1731
Largest diff. peak/hole / e $Å^{-3}$	1.91/-0.68