Cis-Vinylphosphonates and 1,3-Butadienylphosphonates by Zirconation of 1-Alkynylphosphonates

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Supporting Information

Experimental

Preparation of 3.
To 1 mmole (0.292g) Zirconocene dichloride dissolved in 5 ml dry THF, 2 mmoles (1.25 ml of n-BuLi 1.6 M in hexane) were added drop wise at -78^0C , the mixture was stirred 3 hr. and then 0.9 m mole of 1-alkynylphosphonate was added , the mixture was slowly warmed up to r. t. and was stirred overnight. The mixture was worked up by diluted HCl and the vinylphosphonate was extracted in ether and separated on a silica gel (80% PE : 20% ethyl acetate)in a very high yield .

Table 3:- **NMR data and yields of 3**

R	GC Conversion	%Yield[a]	^{31}P ppm	J_{P-H1} (Hz)	J_{P-H2} (Hz)	J_{P-C1} (Hz)	J_{P-C2} (Hz)	J_{P-C3} (Hz)
C_5H_{11}	99%	76%	17.9	20.1	53.1	182.9	5	8
C_4H_9	99%	79%	17.9	19.9	53.1	183.1	4.8	8
ClC_3H_6	99%	63%	17.6	18.9	52.5	183.5	4.3	8.3
Ph	99%	76%	17.1	15.6	51.5	185.1	2	8.8
OSi-*t*BuMe$_2$	85%	78%	17.2	17.2	52.6	182.1	5.1	8.1

[a]Isolated after chromatography and purity determined as >99% by GCMS

3a : Rf = 0.42 (80% PE : 20% ethyl acetate). ^{1}H NMR (300MHz .$CDCl_3$) δ=0.9 (t, 3H , $CH_3CH_2CH_2$), 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 4 H , $CH_2CH_2CH_2$), 2.4 (dt,2H, CH_2CH=C), 3.9, (dq, 4H , CH_3CH_2O), 5.5 (dd, 1H, PCH=CH, $^2J_{P-H}$ = 20, $^3J_{H-H}$=12.9 *cis*), 6.5 (dq, 1H , CH=CP, $^3J_{P-H}$ = 53.05 *trans*). ^{31}P NMR(300MHz.$CDCl_3$): δ= 17.9(s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 154 (d, $^2J_{P-C}$= 4.7 , C=CHP). 117 (d, $^1J_{P-C}$=183, PCH=CH). 61 (d, $^2J_{P-C}$=5.4, OCH_2CH_3) , 31.1 (s, $CH_2CH_2CH_3$). 30 (d, $^3J_{P-C}$= 8 *cis* CH_2CH=C), 22 (s, CH_2CH_3), 16.6 (d, $^3J_{P-C}$=6.6, CH_3CH_2O), 14.1 (s, CH_3CH_2), CH_2CH_3), 16.6 (d, J_{P-C}=6.6, CH_3CH_2O), 14 (s, CH_3CH_2). EIMS *m/z* (%), 220 (M^+, 25.0), 205 (13.0), 191 (100), 163 (52.5), 135 (98.4), 117 (11.9), 81 (19.9), 65 (11.7), 41 (11.2), 29 (11.5).

3b : Rf = 0.44 (80% PE : 20% ethyl acetate). ^{1}H NMR (300MHz .$CDCl_3$) δ=0.9 (t, 3H , $CH_3CH_2CH_2$), 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$), 2.5 (dt, 2H, CH_2CH=C), 4.0 (dq, 4H , CH_3CH_2O), 5.5 (dd, 1H, PCH=CH, $^2J_{P-H}$ = 20, $^3J_{H-H}$=12.9 *cis*) 6.5 (dq, 1H , CH=CP, $^3J_{P-H}$ = 53.1 *trans*). ^{31}P NMR(300MHz.$CDCl_3$): δ= 17.9(s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 154(d, $^2J_{P-C}$= 5, C=CHP). 117 (d, $^1J_{P-C}$=183, PCH=CH). 61 (d, $^2J_{P-C}$=5.4, OCH_2CH_3) , 31 (s, $CH_2CH_2CH_3$). 30 (d, $^3J_{P-C}$= 8 *cis* CH_2CH=C), 28 (d, CH_2CH_2C=C), 22 (s, CH_2CH_3), 16.6 (d, $^3J_{P-C}$=6.6, CH_3CH_2O), 14.1 (s, CH_3CH_2). EIMS *m/z* (%), 234 (M^+, 12.3), 205 (18.2), 191 (100), 163 (36.1), 149 (11.9), 135 (85.9), 117 (11.9), 81 (14.0), 65 (13.9), 41 (14.5), 29 (16.2).

3c : Rf = 0.4 (80% PE : 20% ethyl acetate). ^{1}H NMR (300MHz .$CDCl_3$) δ= 1.3 (t , 3H, CH_3CH_2O), 1.9 (dt, 2H, CH_2CH=C), 2.6 (m, CH_2CH_2CH=C) , 3.5 (t, $ClCH_2$), 4.0 (dq, 4H , CH_3CH_2O), 5.6 (dd, 1H, PCH=CH, $^2J_{P-H}$ = 18.9, $^3J_{H-H}$=12.9 *cis*), 6.5 (dq, 1H , CH=CP, $^3J_{P-H}$ = 52.5 *trans*,). ^{31}P

NMR(300MHz.$CDCl_3$): δ= 17.6(s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 152 (d, $^2J_{P-C}$= 4.3 , C=CHP). 116 (d, $^1J_{P-C}$=183.5, PCH=CH). 61 (d, $^2J_{P-C}$=5.4, OCH_2CH_3) , 44.3 (s , CH_2ClCH_2), 32 (s, CH_2CH_2Cl), 28 (d, $^3J_{P-C}$= 8.3 *cis* CH_2CH=C), 16.6 (d, $^3J_{P-C}$=6.6, CH_3CH_2O). EIMS *m/z* (%) 240 (M^+, 6.7), 205 (29.0), 191 (91.7), 163 (37.6), 135 (100), 117 (10.4), 81 (11.7), 67 (20.6), 41 (11.5), 29 (10.9).

3d : Rf = 0.42 (80% PE : 20% ethyl acetate). ^{1}H NMR (300MHz .$CDCl_3$) δ=1.1 (t , 3H, CH_3CH_2O), 4.0 (dq, 4H , CH_3CH_2O), 5.8 (dd, 1H, PCH=CH, $^2J_{P-H}$ = 15.6, $^3J_{H-H}$=15.6 *cis*), 7.2-7.7 (m, 5H , aromaic and 1H , CH=CP, $^3J_{P-H}$ = 51.5 *trans*). ^{31}P NMR(300MHz.$CDCl_3$): δ= 17.1(s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 148 (d, $^2J_{P-C}$= 2 , C=CHP). 128.3-129.7 (C_{orth} , C_{meta}, C_{para} $^3J_{P-C}$= 8.8 *cis*) 117 (d, $^1J_{P-C}$=185.1) , PCH=CH). 61 (d, $^2J_{P-C}$=5.7, OCH_2CH_3), 16.6 (d, $^3J_{P-C}$=6.6, CH_3CH_2O). EIMS *m/z* (%) 220 (M^+, 24.8), 205 (12.3), 191 (100), 163 (52.5), 135 (98.4), 117 (12.4), 81 (20.0), 67 (11.4), 42 (11.4), 29 (11.4).

3e : Rf = 0.46 (80% PE : 20% ethyl acetate). ^{1}H NMR (300MHz .$CDCl_3$) δ= 0.4 (s, 6H , $SiMe_2$) 0.9 (s , 9H , Si-tBu), 1.3 (t , 3H, CH_3CH_2O), 1.9 (dt,2H, CH_2CH=C), 2.6 (m, CH_2CH_2CH=C) , 3.2 (t, OCH_2), 4.1 (dq, 4H , CH_3CH_2O), 5.6 (dd, 1H, PCH=CH, $^2J_{P-H}$ = 17.2, $^3J_{H-H}$=12.9 *cis*), 6.5 (dq, 1H , CH=CP, $^3J_{P-H}$ = 52.6 *transe*). ^{31}P NMR(300MHz.$CDCl_3$): δ= 17.2(s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 151(d, $^2J_{P-C}$= 5.1 , C=CHP). 116 (d, $^1J_{P-C}$=182.1, PCH=CH). 61 (d, $^2J_{P-C}$=5.4, OCH_2CH_3) , 44 (s , OCH_2 CH_2), 32 (s, CH_2CH_2 OSi), 28 (d, $^3J_{P-C}$= 8.1 *cis* CH_2CH=C), 16.6 (d, $^3J_{P-C}$=6.6, CH_3CH_2O), 14 (2s , Si-tBuMe_2O). EIMS *m/z* (%), 205 (M^+, -115), 191 (92.1), 163 (38.1), 149 (11.9), 135 (100), 117 (10.5), 81 (11.8), 67 (19.9), 41 (10.9), 29 (11.3).16.6 (d, J_{P-C}=6.6, CH_3CH_2O), 14 (2s , Si-tBuMe_2O)

Preparation of 6 and 7.

1.25 ml of 1.6 M n-BuLi (2 mmol) were added dropwise to 0.292 g (1mmol) zirconocene dichloride dissolved in 5ml dry THF at –78^{0}C and the mixture was stirred for 3 hours. Then 0.238 g (0.9 mmol) of 1-heptynylphosphonate was added and the mixture was warmed gradually to room temperature and stirred overnight. The mixture was again cooled to –78^{0}C and 1 mmol of alkyne was added. The mixture was gradually warmed to room temperature and was stirred for additional 24 hours. The reaction mixture was worked up with diluted HCl and the product was extracted with ether .

Two 1,3-butadienyl phophonate isomers were obtained , The first isomer (compound **6**) showed that the alkyne coupled to the 1-alkynylphosphonate on C_1 position to phosphorous, while the second isomer (compound **7**) showed that the alkyne coupled at C_2 to phosphor **(Scheme 1)**.

These two isomers were separated on a silica gel column (90% Petroleum Ether : 10% Ethyl Acetate)

Table 1 : NMR data and yields of 6

R	**E**	**GC Conversion**	**Isolated Yield %**[a]	**^{31}P** ppm	**J_{H-H}** (Hz)	**J_{P-Ha}** (Hz)	**J_{P-C1}** (**Hz**)	**J_{P-C2}** (Hz)	**J_{P-C3}** (Hz)	**J_{P-C4}** **(Hz)**
C_4H_9	H	80%	68	18.8	15.4	48.8	172	11.7	5.4	12.3
C_5H_{11}	H	70%	60	19.9	15.7	48.9	171	11.6	5.6	12.6
Ph	H	85%	73	18.2	16.2	48.9	162	11.2	6.5	6.60
C_3H_6Cl	H	70%	57	18.6	15.9	54.0	173	11.46	6.6	12.8
C_2H_5	C_2H_5	3%	Not isolated							

[a]Isolated after chromatography and purity determined as >99% by GCMS

Table 2: NMR data and yields of 7

R	E	GC Conversion	Isolated Yield %[a]	^{31}P ppm	J_{H-H} (Hz)	J_{P-H} (Hz)	J_{P-C1} (Hz)	J_{P-C2} (Hz)	J_{P-C3} (Hz)	J_{P-C4} (Hz)
C_4H_9	H	20%	15	19.9	15.9	17.7	192	8.60	5.6	28.0
C_5H_{11}	H	30%	19	19.9	15.8	17.6	192	8.57	5.6	27.8
Ph	H	15%	11	19.2	17.2	16.8	179	10.9	5.7	26.7
C_3H_6Cl	H	30%	20	18.7	15.9	16.9	175	11.2	6.4	26.6
C_2H_5	C_2H_5	97%	83	19.5	-	18.3	188	7.95	6.5	23.0

[a]Isolated after chromatography and purity determined as >99% by GCMS.

6a : Rf = 0.41 (90% PE : 10% ethyl acetate). ^{1}H NMR (300MHz.$CDCl_3$) δ=0.8 (2t, 6H , $2CH_3CH_2CH_2$). 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 10 H , $CH_2CH_2CH_2$ + CH_2CH_2), 2.0 (dt,2H , $CHCH_2$), 2.6 (dt, 2H , CCH_2), 4.1 (dq, 4H , CH_3CH_2O),), 5.9 (m, 2H , CH=CH , $^{3}J_{H-H}$ = 15.4 , *trans*), 6.4 (dt, 1H, CH=CP, $^{3}J_{P-H}$ = 48.8, *trans*),. ^{31}P NMR(300MHz. $CDCl_3$): δ= 18.9 (s). ^{13}C NMR (300MHz. CDCl3): δ= 149 (d, $^{2}J_{P-C}$=11.6 , C=CHP). 132 (d, $^{4}J_{P-C}$ = 7.2 ,CH=CHC). 129 (d, $^{2}J_{P-C}$=12.3, CH=$CHCH_2$).127 (d, $^{1}J_{P-C}$=172, CPCH=CH). 61 (d, $^{3}J_{P-C}$=5.3, OCH_2CH_3) , 33 (s, CH_2CH=CH), 31.6 (s, $2CH_2CH_2CH_3$). 30.2 (d, $^{3}J_{P-C}$=5.4 *cis* CH_2CH=C), 29.3 (d, CH_2CH_2C=), 22.5 (s, 2 CH_2CH_3), 16.5 (d, $^{3}J_{P-C}$=6.6, CH_3CH_2O), 14 (s, $2CH_3CH_2$). EIMS *m/z* (%), 316 (M^+, 60.1), 287 (12.6), 273 (62.8), 245 (33.6), 217 (28.8), 203 (12.8), 147 (25.9), 135 (52.9), 107 (34.6), 91 (55.7), 79 (100), 55 (38.0), 41 (56.6), 29 (42.8), 18 (48.0).

7a : Rf = 0.47 (90% PE : 10% ethyl acetate). ^{1}H NMR (300MHz . $CDCl_3$): δ = 0.9 (2t, 6H, $2CH_3CH_2CH_2$. 1.3 (t , 3H, CH3CH_2O), 1.2-1.5 (overlap , 10 H , $2CH_2CH_2CH_2$) , 2.1 (dt, 2H CH_2CH) , 2.6 (t, 2H , CCH_2CH_2), 4.0 (dq, 4H , CH_3CH_2O), 5.3 (d, 1H , $^{2}J_{P-C}$ =17.7 , CHP), 5.9 (m, 2H , $^{3}J_{H-H}$=15.9 *trans* , CH=CH). ^{31}P NMR($CDCl_3$): ^{31}P NMR(300MHz. $CDCl_3$): δ=19.9 (s). ^{13}C NMR (300MHz. $CDCl_3$): δ= 160.6 (d, $^{2}J_{P-C}$= 8.6 , C=CHP). 136 (d, $^{4}J_{P-C}$= 1.6 ,CH=CHC). 132 (d, $^{3}J_{P-C}$ = 28, *trans*, CH=$CHCH_2$).112 (d, $^{1}J_{P-C}$ = 192 , CPCH=CH). 61 (d, $^{2}J_{P-C}$=5.5, OCH_2CH_3) , 32 (s, CH_2CH=CH), 31 (2 s, $2CH_2CH_2CH_3$). 29 (s, CH_2CH_2C=), 30 (d, $^{3}J_{P-C}$=5.6 *cis* CH_2C=C), 22 (2 s, 2 CH_2CH_3), 16.5 (d, $^{3}J_{P-C}$=6.6, CH_3CH_2O), 14.1 (2s , $2CH_3CH_2$). EIMS *m/z* (%), 316 (M^+, 19.5), 287 (12.8), 273 (53.0), 245 (19.7), 217 (26.4), 204 (13.3), 178 (16.6), 152 (37.7), 121 (65.0), 107 (51.3), 93 (56.0), 79 (42.9), 55 (29.7), 41 (41.4), 29 (36.3), 18 (100).

6b : Rf = 0.42 (90% PE : 10% ethyl acetate) 1H NMR (400MHz .$CDCl_3$) δ=0.9 (2t, 6H , $2CH_3CH_2CH_2$), 1.4 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 12 H , $2CH_2CH_2CH_2$), 2.1 (dt,2H CH_2CH) 2.6 (dt, 2H , CCH_2), 4.1 (dq, 4H , CH_3CH_2O), 6.4 (dt, 1H, CH=CP, , $^{3}J_{P-H}$ = 48.9 *trans*), 6 (m, 2H , $^{3}J_{H-H}$=15.8, *trans*). ^{31}P NMR (400MHz .$CDCl_3$): δ=19.9 (s). ^{13}C NMR (400MHz. $CDCl_3$): δ= 149 (d, $^{2}J_{P-C}$=11.6 , C=CHP). 132 (d, $^{2}J_{P-C}$=11.7 ,CH=CHC). 129 (d, $^{3}J_{P-C}$=12.6, CH=$CHCH_2$).127 (d, $^{1}J_{P-C}$=171, CPCH=CH). 61 (d, $^{2}J_{P-C}$=5.3, OCH_2CH_3) , 33 (s, CH_2CH=CH), 31 (s, $2CH_2CH_2CH_3$). 30 (d, $^{3}J_{P-C}$=5.6 *cis* CH_2CH=C), 29 (d, 2 CH_2CH_2C=), 22 (s, 2 CH_2CH_3), 16.5 (d, $^{3}J_{P-C}$=6.6, CH_3CH_2O). EIMS *m/z* (%), 330 (M^+, 61.1), 301 (10.9), 287 (13.0), 273 (62.5), 245 (31.6), 217 (29.0), 203 (11.8), 147 (26.1), 135 (52.3), 107 (35.1), 91 (54.9), 79 (100), 55 (31.8), 41 (60.1), 29 (57.0), 18 (40.1).

7b : Rf = 0.48 (90% PE : 10% ethyl acetate). ^{1}H NMR (300MHz. $CDCl_3$): δ = 0.9 (2t, 6H, $2CH_3CH_2CH_2$. 1.4 (t , 3H, CH3CH_2O), 1.2-1.5 (overlap , 12 H , $2CH_2CH_2CH_2$), 2.2 (dt,2H $CHCH_2$), 2.6 (t, 2H , CCH_2CH_2), 4.1 (dq, 4H , CH_3CH_2O), 5.4 (d, 1H , $^{2}J_{P-C}$ =17.6 , CHP) , 6 (m, 2H , $^{3}J_{H-H}$=15.8 *trans* , CHCH). ^{31}P NMR($CDCl_3$): δ= 19 (s). ^{13}C NMR (300MHz. $CDCl_3$): δ= 160 (d, $^{2}J_{P-C}$= 8.5 , C=CHP). 136 (d, $^{4}J_{P-C}$= 1.6 ,CH=CHC). 132 (d, $^{3}J_{P-C}$=27.8, *trans*, CH=$CHCH_2$).112 (d, $^{1}J_{P-C}$=192, CPCH=CH). 61 (d, $^{2}J_{P-C}$=5.5, OCH_2CH_3) , 33 (s, CH_2CH=CH), 31 (2s, $2CH_2CH_2CH_3$). 29 (2s, 2 CH_2CH_2C=), 30(d, $^{3}J_{P-C}$=5.6 *cis* CH_2C=C), 22 (2s, 2 CH_2CH_3), 16.5 (d, $^{3}J_{P-C}$=6.6, CH_3CH_2O), 14 (2 s, $2CH_3CH_2$). EIMS *m/z* (%), 330 (M^+, 20.1), 301 (13.1), 287 (12.7), 245 (18.9), 217 (27.3), 209 (14.1), 190 (40.3), 152 (36.9), 121 (66.5), 108 (53.4), 93 (56.8), 79 (42.8), 55 (30.1), 41 (42.1), 29 (35.5), 18 (100).

6c : Rf = 0.41 (90% PE : 10% ethyl acetate). 1H NMR (300MHz .$CDCl_3$) δ=0.8 (t, 3H ,$CH_3CH_2CH_2$). 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$), 2.7 (dt,2H , $CHCH_2$), 4.1 (4H, OCH_2CH_3), 6.6 (dt, 1H, CH=CP , $^3J_{P-H}$ = 48.9 trans) 7.1-7.4 (m, 7H , overlap CH=CH and the aromatic) $^3J_{H-H}$=16.2, trans). ^{31}P NMR(300MHz. $CDCl_3$): δ= 18.2 (s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 151 (d, $^2J_{P-C}$=11.2 , C=CHP). 137 (d, $^3J_{P-C}$ = 1.2, CH=CHC). 130 (d, $^2J_{P-C}$=6.6 , CH=CHPh), 128-126 (C *orth* , C *meta* , C *para* and CP). 61.7 (d, $^2J_{P-C}$=5.1, OCH_2CH_3) , 31 (d, CH_2CH=CH, $^3J_{P-C}$=5.4), 30.5 (s, $CH_2CH_2CH_3$). 29.3 (s, CH_2CH=C), 22.5 (s, CH_2CH_3), 16.5 (d, $^3J_{P-C}$=6.5, CH_3CH_2O), 14 (s, CH_3CH_2). EIMS *m/z* (%), 336 (M^+, 100), 293 (14.5), 279 (25.2), 245 (13.6), 223 (23.5), 197 (52.2), 169 (12.4), 154 (74.5), 141 (88.5), 128 (48.0), 107 (35.1), 91 (71.5), 77 (10.0), 29 (20.5).

7c : Rf = 0.46 (90% PE : 10% ethyl acetate). ^{1}H NMR (300MHz . $CDCl_3$): δ = 0.9 (t, 3H, $CH_3CH_2CH_2$. 1.3 (t , 3H, CH3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$) , 2.7 (t, 2H , CCH_2CH_2) , 4.1 (dq, 4H , CH_3CH_2O), 5.6 (d, 1H , $^2J_{P-C}$ =16.8 , CHP), 6.8 (dd, 2H , $^3J_{H-H}$=17.2 *trans* , CH=CH). ^{31}P NMR(300MHz.$CDCl_3$): δ= 19.2 (s). ^{13}C NMR (300MHz. $CDCl_3$): δ= 161, (d, $^2J_{P-C}$= 10.9 , C=CHP). 132 (d, $^3J_{P-C}$ = 26.7, *trans*, CH=CHPh). 128-126 (C *orth* , C *meta* , C *para* and CP). 61. (d, $^2J_{P-C}$=5.1, OCH_2CH_3) , 31 (s, CH_2CH=CH), 30.5 (s, $CH_2CH_2CH_3$). 29.3 (s, CH_2CH=C), 61 (d, $^2J_{P-C}$=5.5, OCH_2CH_3) , 31.5 (d, CH_2CH=CH, $^3J_{P-C}$=5.7), 30.5 (s, $CH_2CH_2CH_3$). 29.3 (s, CH_2CH=C), 22.5 (s, CH_2CH_3), 16.5 (d, $^3J_{P-C}$=6.4, CH_3CH_2O), 14 (s, CH_3CH_2). EIMS *m/z* (%), 336 (M^+, 15.5), 293 (11.0), 198 (82.0), 155 (100), 141 (99.5), 115 (34.0), 91 (35.5), 77 (25.6), 29 (37.2), 18 (65.1).

6d : Rf = 0.39 (90% PE : 10% ethyl acetate). 1H NMR (300MHz .$CDCl_3$) δ=0.8 (t, 3H , CH_3CH_2). 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$), 1.9 (dt,2H , $CHCH_2$), 2.2 (q ,2H, CH_2C_2Cl), 2.6 (d t, 2H , $CHCH_2$), 3.5 (t, 2H, CH_2Cl), 4.0 (dq, 4H , CH_3CH_2O), 5.9 (m, 2H , $^3J_{H-H}$ = 15.9, CH=CH, *trans*), 6.3 (dt, 1H, $CCHCH_2$, $^3J_{P-H}$ = 56 , *trans*). ^{31}P NMR(300MHz. $CDCl_3$): δ= 18.6 (s). ^{13}C NMR (300MHz. $CDCl_3$): δ= 150 (d, $^2J_{P-C}$=11.5 , C=CHP). 130.8 (d, $3JP_{-C}$ = 6.5,CH=CHC). 130.4 (d, $^3J_{P-C}$=12.8 , CH=$CHCH_2$).127 (d, $^1J_{P-C}$=173.1, CPCH=CH). 61 (d, $^2J_{P-C}$=5.4, OCH_2CH_3) , 44 (s, CH_2CH=CH), 32 (s , $CH_2CH_2CH_2Cl$) 31.6 (s, $CH_2CH_2CH_3$). 30.3 (d, $^3J_{P-C}$ = 7.7 *cis* CH_2CH=C), 29.3 (d, CH_2CH_2C), 22.5 (s, CH_2CH_3), 22 (s , CH_2CH_2Cl), 16.5 (d, $^3J_{P-C}$=6.6, CH_3CH_2O), 14.2 (s, CH_3CH_2). EIMS *m/z* (%), 336 (M^+, 64.1), 301 (26.0), 293 (29.8), 273 (33.9), 245 (22.7), 217 (22.2), 155 (35.5), 137 (33.8), 105 (73.5), 91 (94.7), 79 (100), 55 (31.2), 42 (59.0), 29 (65.0), 18 (8.7).

7d : Rf = 0.45 (90% PE : 10% ethyl acetate). 1H NMR (300MHz .$CDCl_3$) δ=0.8 (t, 3H , CH_3CH_2). 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$), 1.9 (dt,2H , $CHCH_2$), 2.6 (q ,2H, CH_2C_2Cl), 2.5 (d t, 2H , $CHCH_2$), 3.5 (t, 2H, CH_2Cl) 4.0 (dq, 4H , CH_3CH_2O), 5.7 (d, 1H , $^2J_{P-H}$ = 17.5, CHCP), 6.2 (m, 2H, CH=CH , $^3J_{H-H}$ = 15.9 , *trans*). ^{31}P NMR(300MHz.$CDCl_3$): δ= 18.6 (s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 161 (d, $^2J_{P-C}$=11.2 , C=CHP)., 132 (d, $^4J_{P-C}$= 1.6 ,CH=CHC). 130 (d, $^3J_{P-C}$ = 26.6, *trans*, CH=$CHCH_2$).120 (d, $^1J_{P-C}$ = 190 , CPCH=CH). 61 (d, $^2J_{P-C}$=5.5, OCH_2CH_3) , 32 (s, CH_2CH=CH), 31 (s, $CH_2CH_2CH_3$).30 (s, CH2CH2Cl) 29 (s, CH_2CH_2C=), 30 (d, $^3J_{P-C}$=6.4 *cis* CH_2C=C), 22 (s, CH_2CH_3), 21.5 (s , CH_2CH_2Cl), 16.5 (d, $^3J_{P-C}$=6.6, CH_3CH_2O), 14.1 (2s , $2CH_3CH_2$). EIMS *m/z* (%), 336 (M^+, 20.1), 301 (13.3), 293 (23.0), 273 (39.9), 245 (17.5), 217 (25.8), 135 (48.8), 91 (57.0), 79 (44.1), 55 (28.2), 42 (39.0), 29 (35.0), 18 (100).

7e : Rf = 0.40 (90% PE : 10% ethyl acetate). ^{1}H NMR (300MHz . $CDCl_3$): δ = 0.8 (3t,6H, $CH_3CH_2CH_2$, CH_3CH_2C, CH_3CH_2CH), 1.3 (t , 3H, CH_3CH_2O), 1.2-1.5 (overlap , 6 H , $CH_2CH_2CH_2$) , 2.15 (2q, 4H , CCH_2CH_3 , CH_2CH_3), 2.6 (t, 2H , CCH_2CH_2) , 4.1 (dq, 4H , OCH_2CH_3) , 5.4 (d, 1H ,

^{31}P NMR(300MHz. $CDCl_3$): δ= 19.5 (s). ^{13}C NMR (300MHz.$CDCl_3$): δ= 165 (d, $^2J_{P-C}$= 7.9 , C=CHP). 141 (d, $^3J_{P-C}$= 23 , *trans* ,C=$CHCH_2$). 132 (s , $CHCH_2CH_3$).112-109 (d, $^1J_{P-C}$=188, CP), 61 (d, $^2J_{P-C}$=5.7 , OCH_2CH_3) , 32 (s, CH_2CC), 31 (d , $^3J_{P-C}$=5.6 *cis* CH_2C=C). 29 (2s, CH_2CH_2C=, CH2C), 22.6 (s, CH_2CH_3), 21.7 (s , $CH_2CH_2CH_3$), 21.19 (s , CH_2CH_2) , 16.5 (d, $^3J_{P-C}$=6.5, CH_3CH_2O), 14 (2 s, $2CH_3CH_2$). 13.6 (s , CH_3CH_2). EIMS *m/z* (%), 316 (M^+, 21.4), 287 (22.5), 273 (13.8), 231 (10.3), 178 (38.3), 149 (45.8), 135 (38.1), 121 (100), 107 (55.8), 93 (46.6), 54 (25.7), 41 (34.0), 29 (31.0), 18 (93.2).