Supporting Information for

One-Pot Phosphonylation of Heteroaromatic Lithium Reagents: The Scope and Limitations of Its Use for the Synthesis of Heteroaromatic Phosphonates

Ewa Chmielewska [1,*], Natalia Miodowska [1], Błażej Dziuk [2], Mateusz Psurski [3] and Paweł Kafarski [4]

[1] Department of Bioorganic Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland; natalia.miodowska@pwr.edu.pl
[2] Department of Inorganic and Structural Chemistry, Faculty of Chemistry, University of Opole, ul. Oleska 48, 45-052 Opole, Poland; bdziuk@uni.opole.pl
[3] Laboratory of Experimental Anticancer Therapy, Department Of Experimental Oncology, Ludwik Hirszfeld Institute of Immunology and Experimental Therapy Polish Academy of Sciences, Rudolfa Weigla 12, 53-114 Wrocław, Poland; mateusz.psurski@hirszfeld.pl
[4] Department of Chemistry, Faculty of Agriculture and Forestry, University of Warmia and Mazury, Plac Łódzki 4, 10-721 Olsztyn, Poland; pawel.kafarski@uwm.edu.pl
* Correspondence: ewa.chmielewska@pwr.edu.pl; Tel.: +48-71-320 2977

Copies of ^{31}P NMR, ^{1}H NMR, ^{13}C NMR, MS spectra for representative compounds and relevant crystallographic data for the molecule and the full geometrical information

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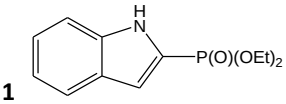

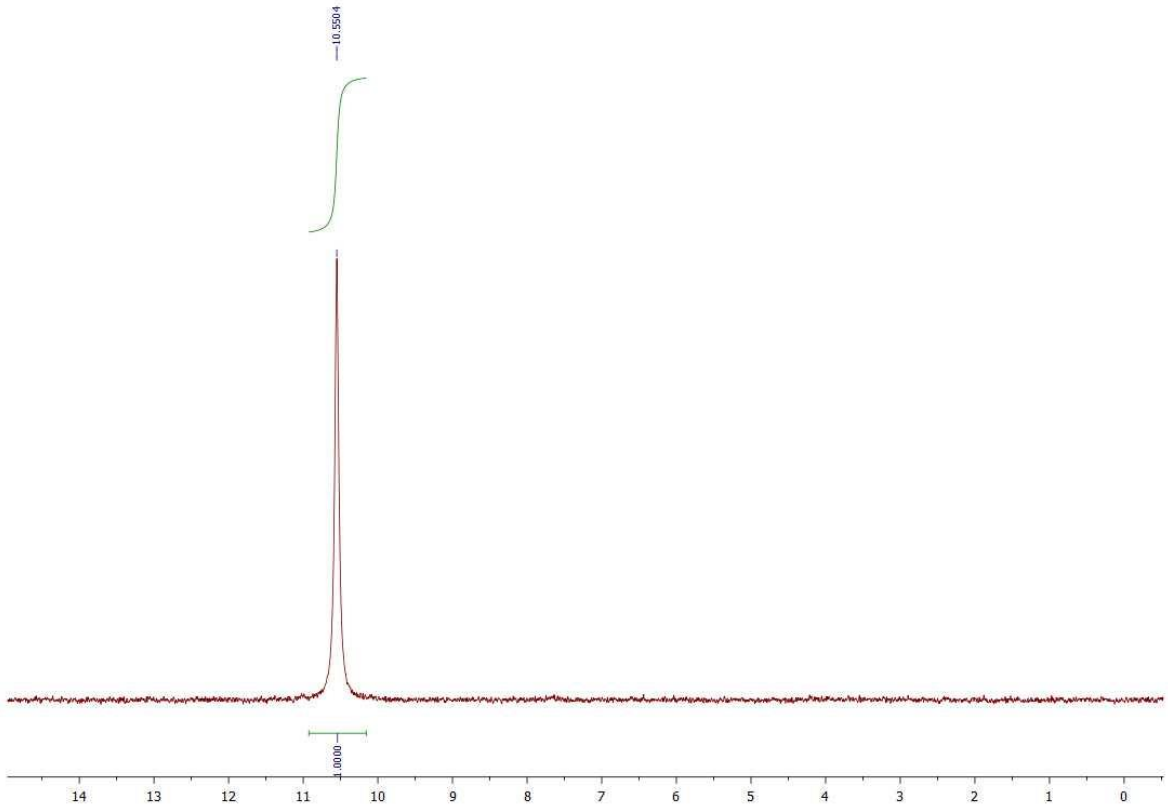

Figure S1: The ^{31}P NMR spectra of the compound **1**

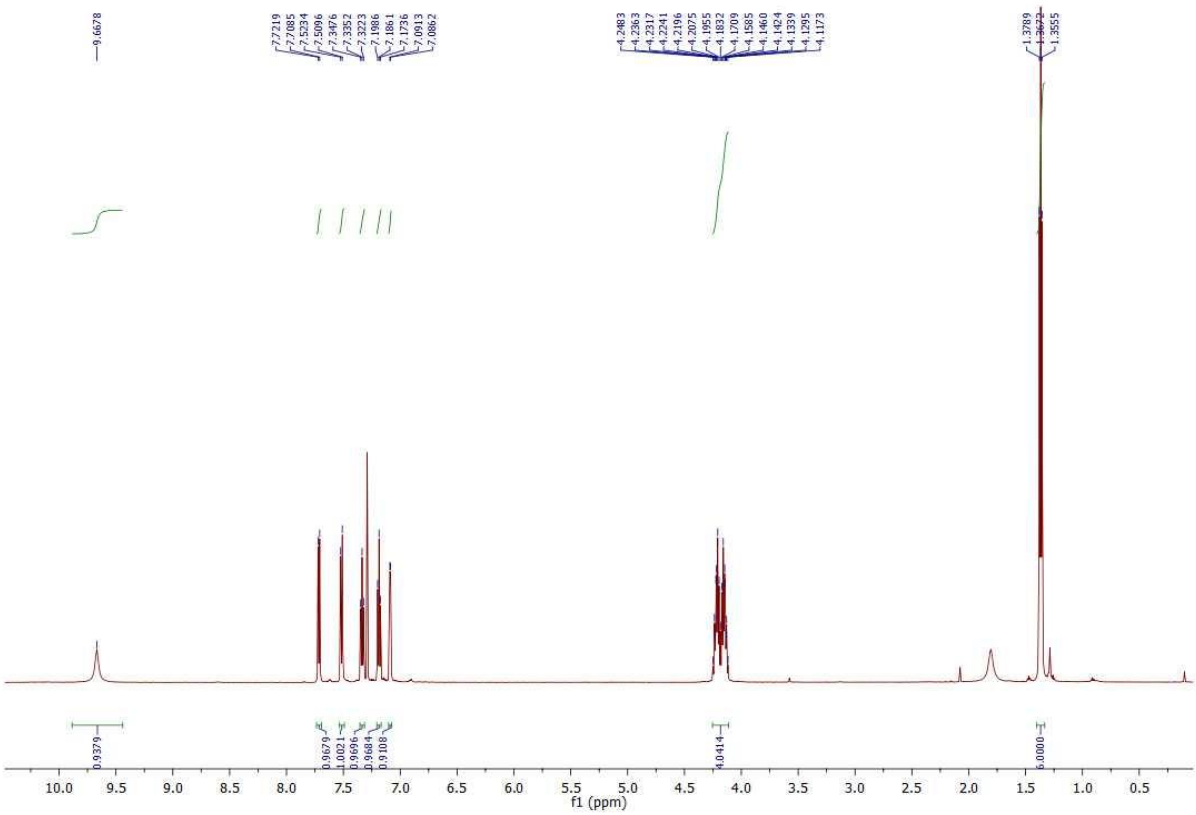

Figure S2: The ^{1}H NMR spectra of the compound **1**

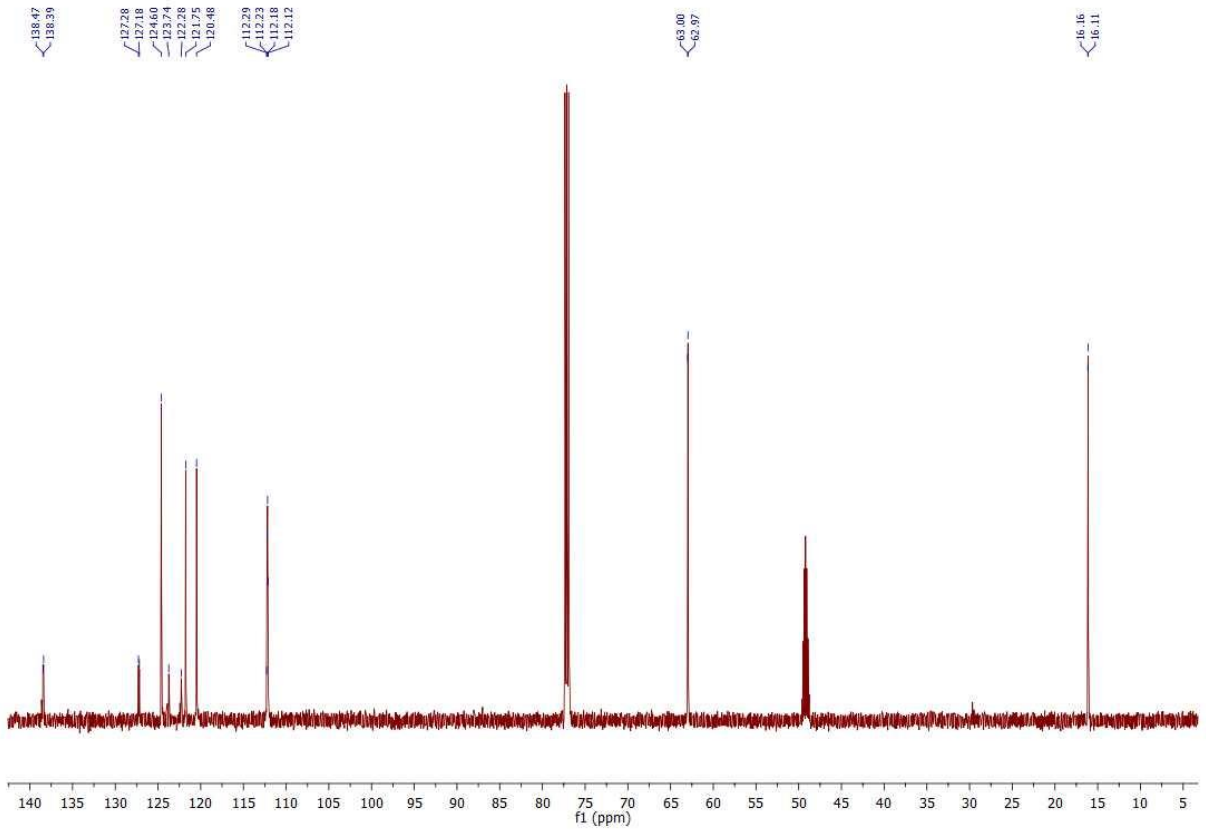

Figure S3: The ^{13}C NMR spectra of the compound **1**

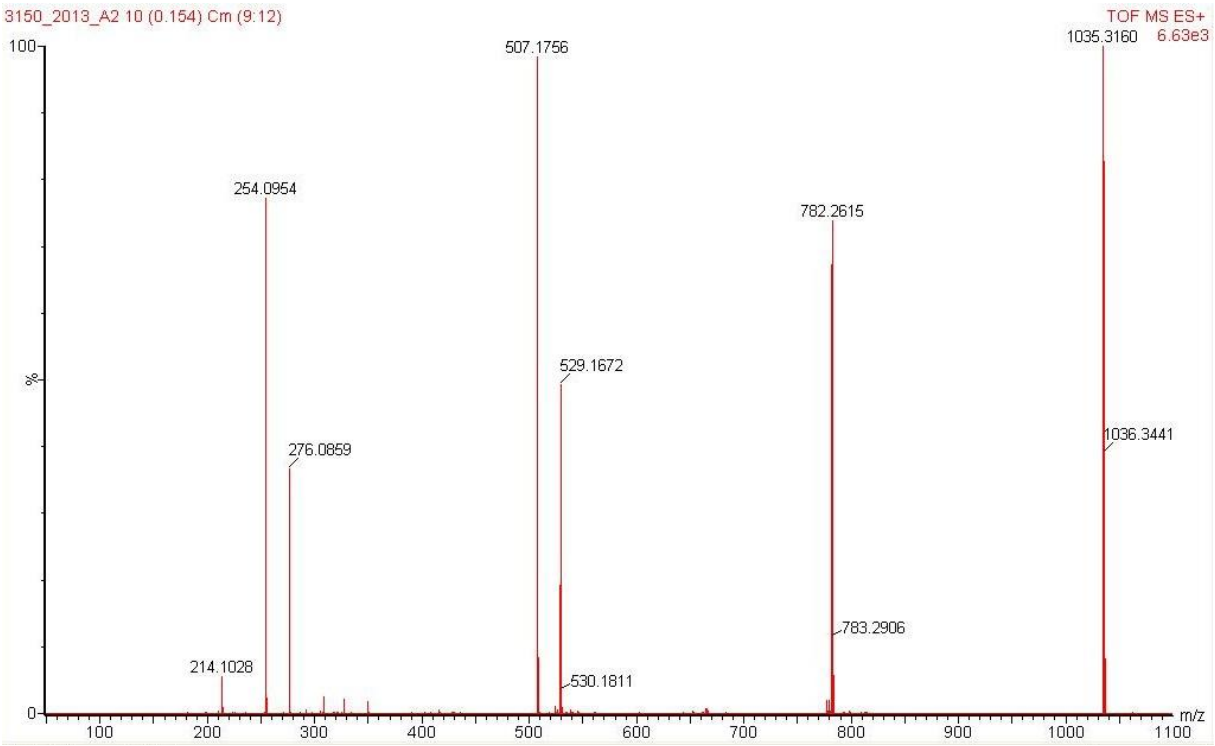

Figure S4: The HRMS spectra of the compound **1**

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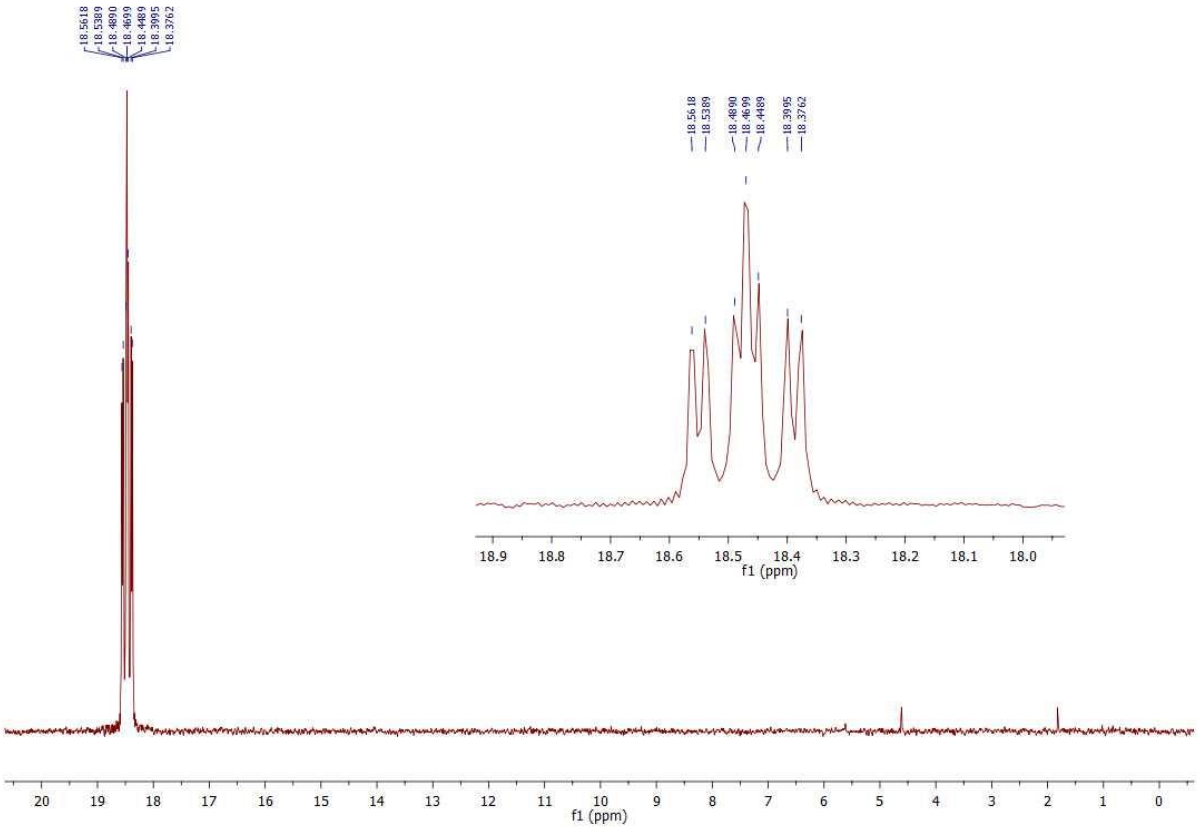


Figure S5: The ^{31}P NMR spectra of the compound **4**

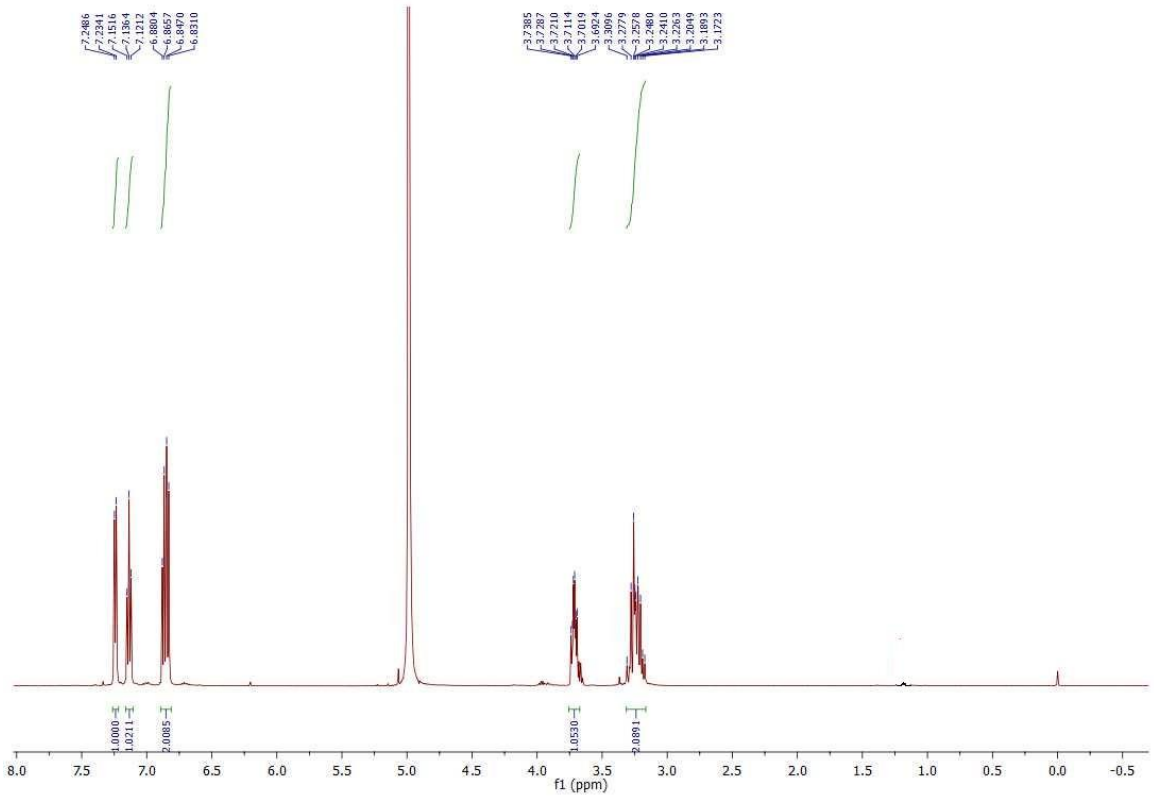


Figure S6: The ^{1}H NMR spectra of the compound **4**

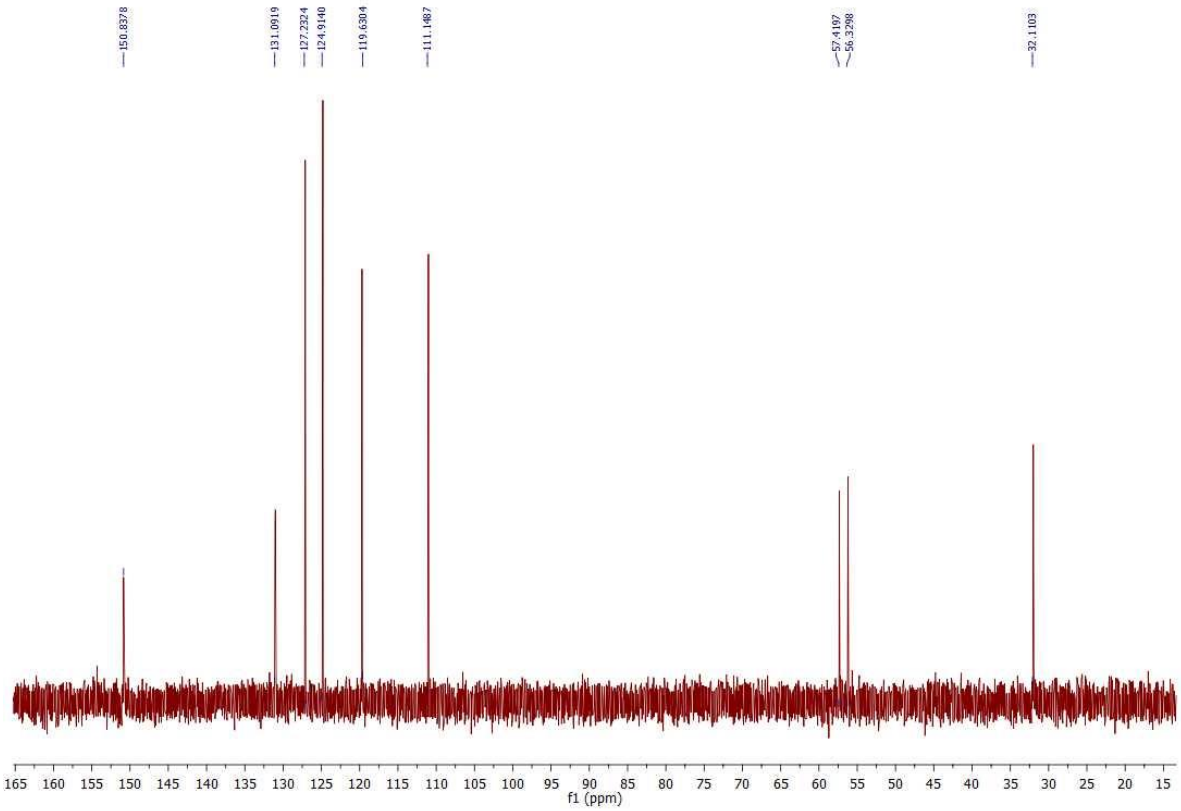


Figure S7: The ^{13}C NMR spectra of the compound **4**

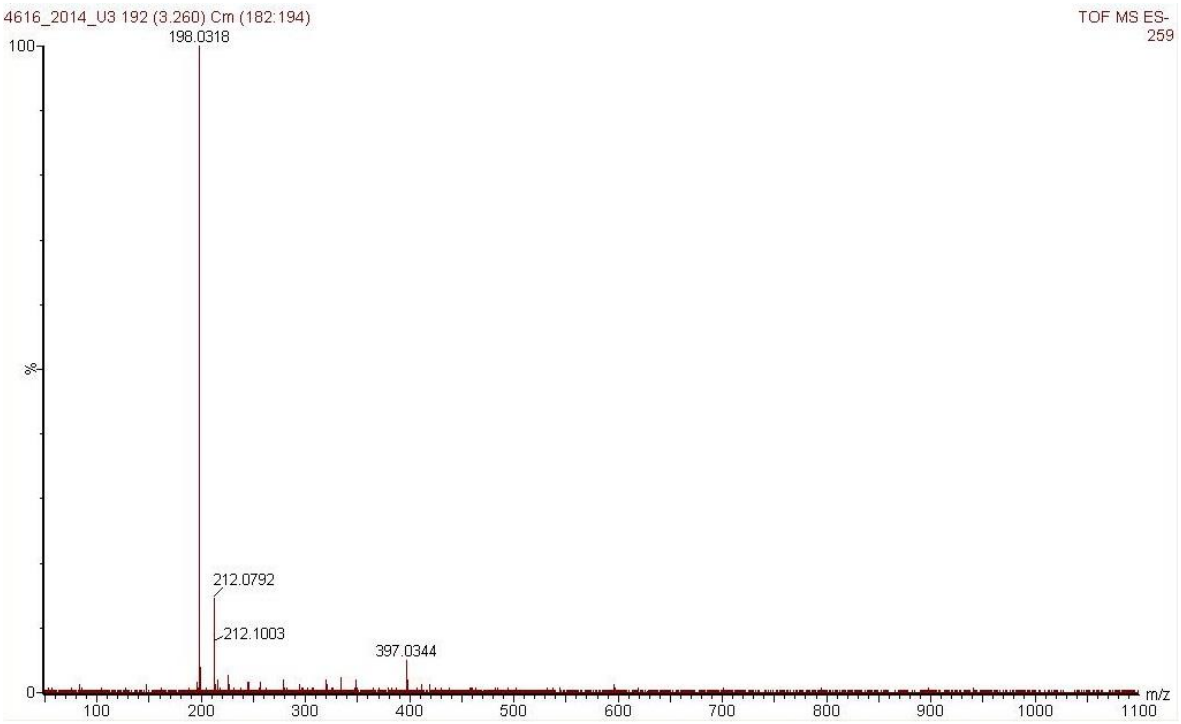
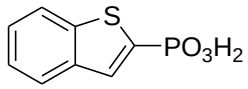


Figure S8: The HRMS spectra of the compound **4**



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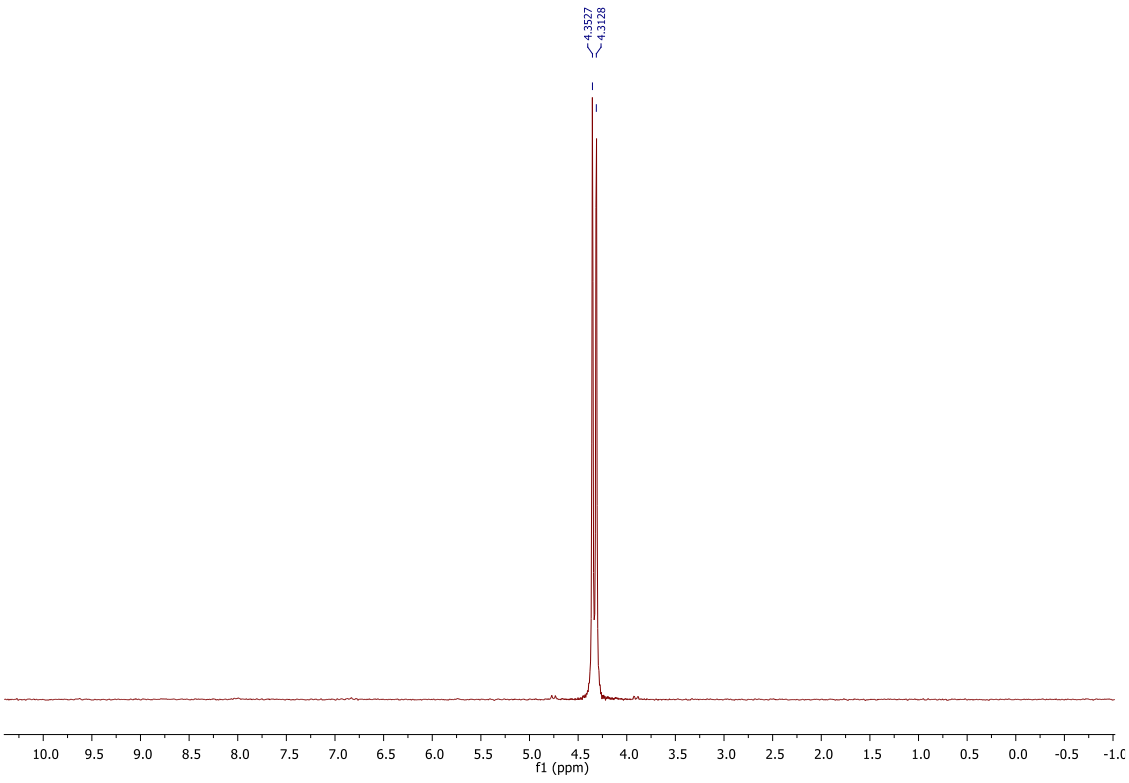


Figure S9: The ^{31}P NMR spectra of the compound **8**

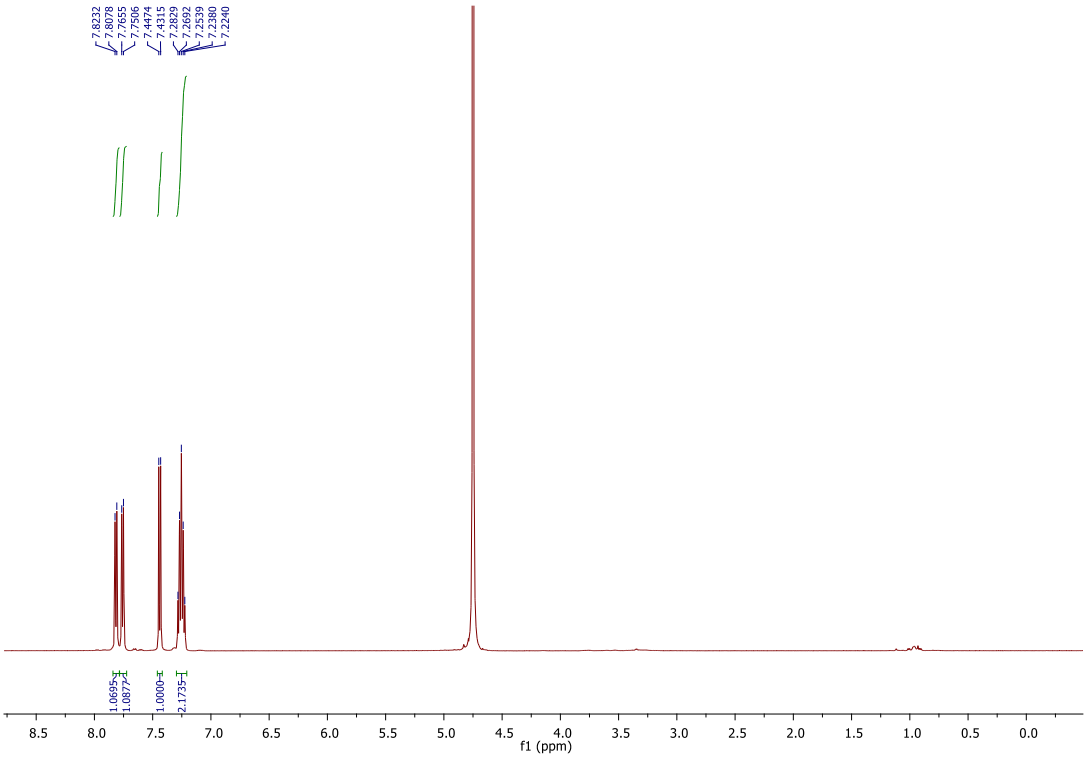


Figure S10: The ^{1}H NMR spectra of the compound **8**

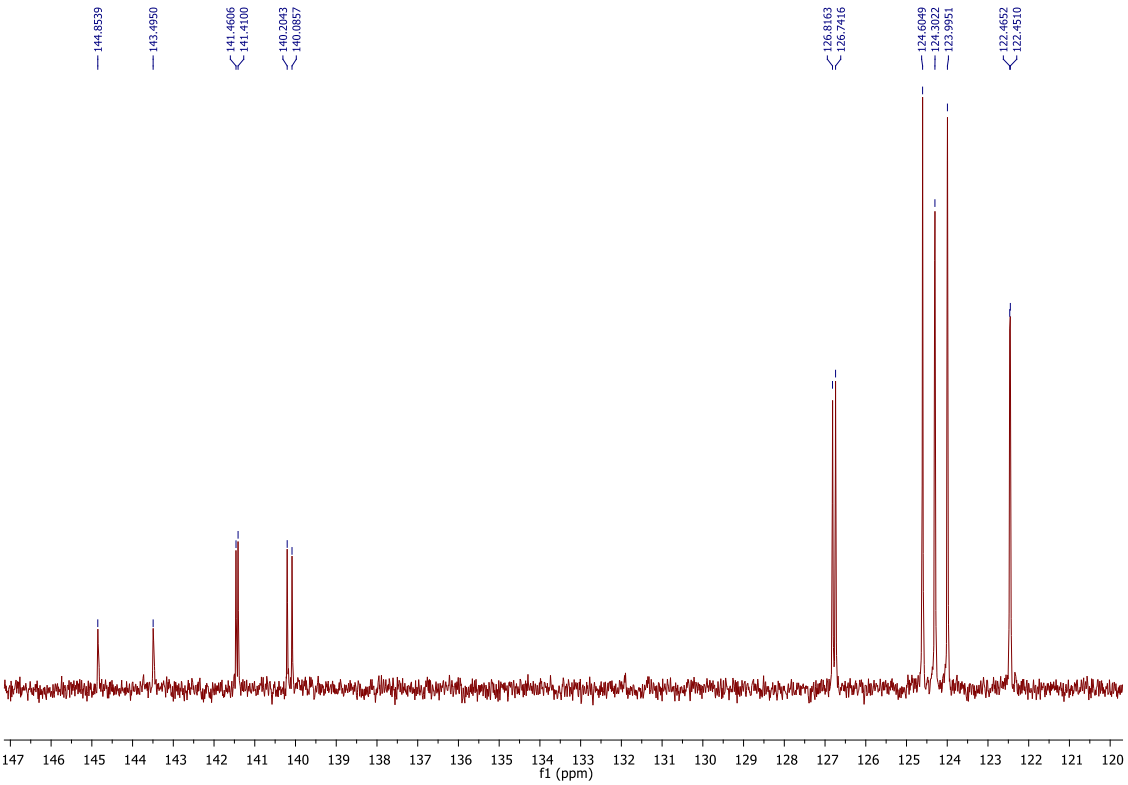


Figure S11: The ^{13}C NMR spectra of the compound **8**

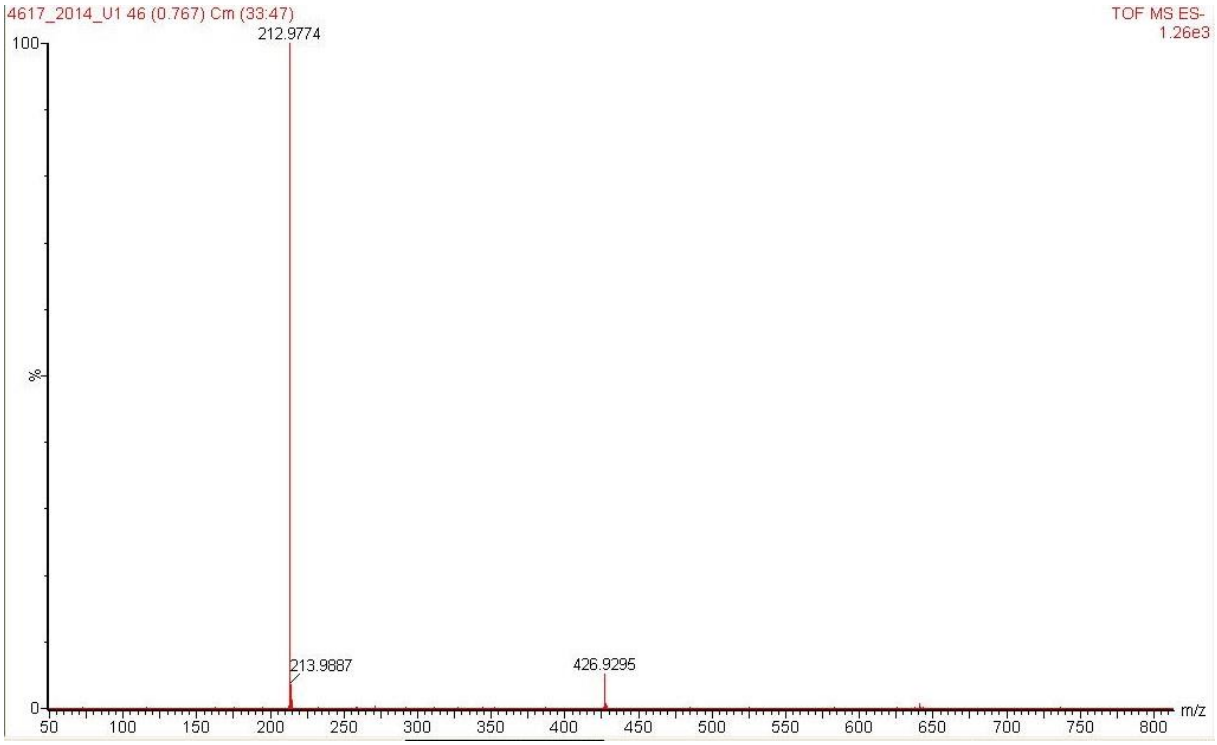
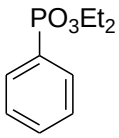


Figure S12: The HRMS spectra of the compound **8**



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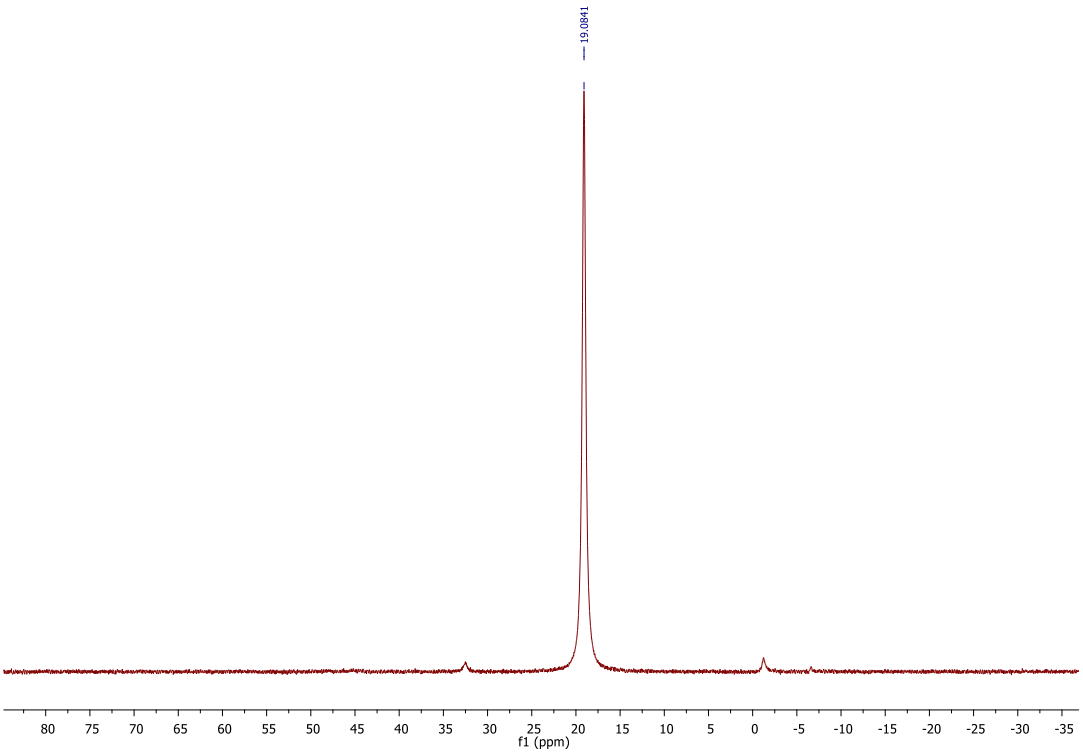


Figure S13: The ^{31}P NMR spectra of the compound **21**

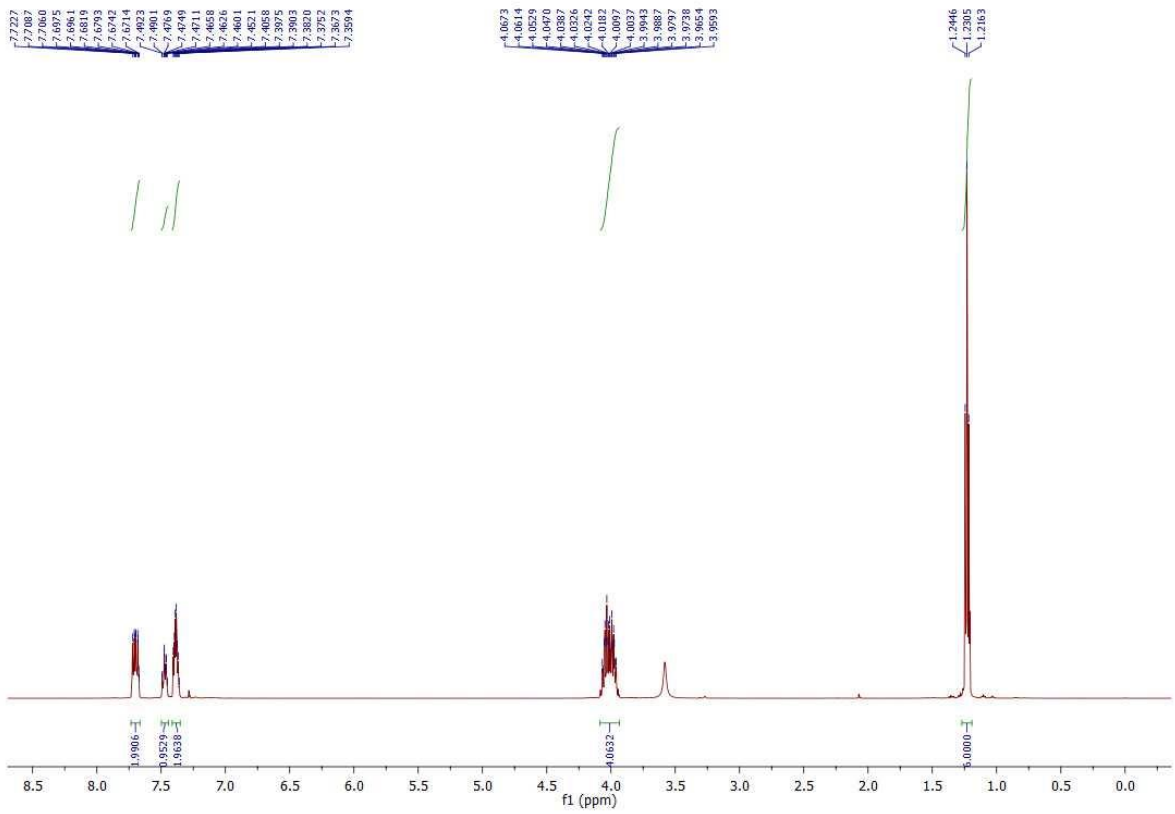


Figure S14: The ^{1}H NMR spectra of the compound **21**

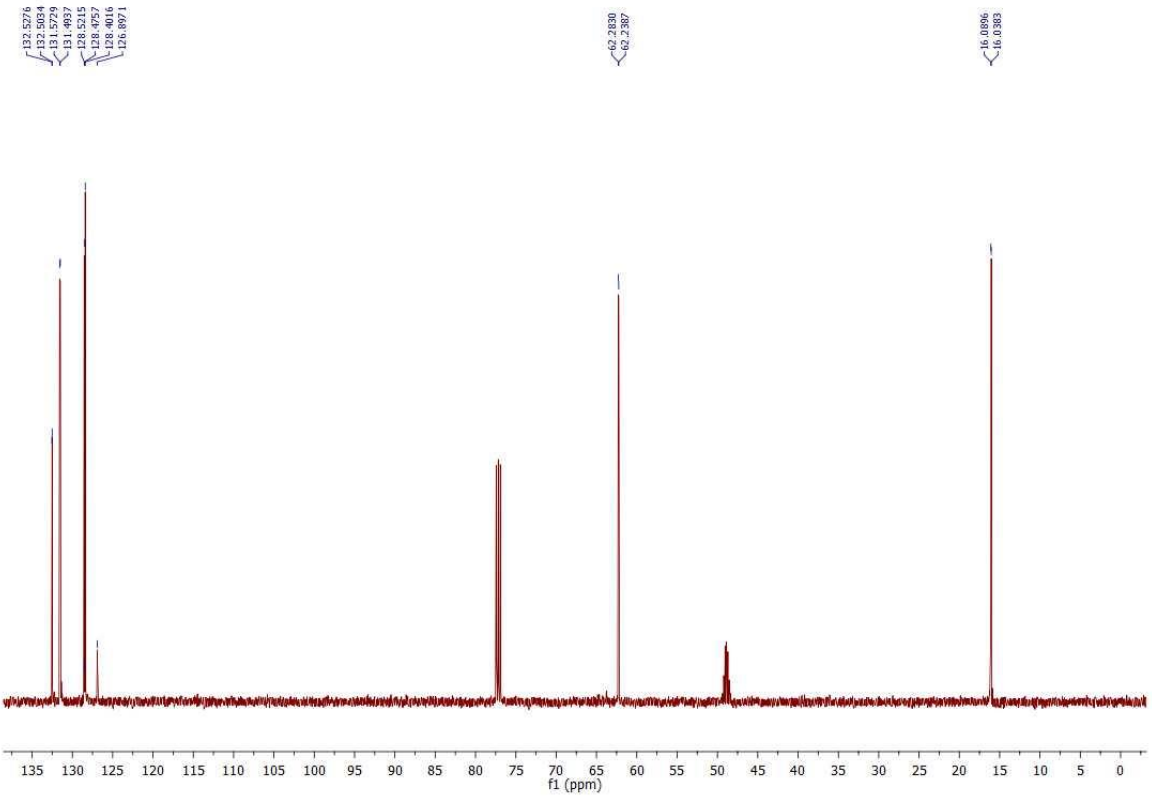
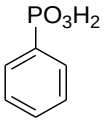


Figure S15: The ^{13}C NMR spectra of the compound **21**

Figure S16: The HRMS spectra of the compound **21**



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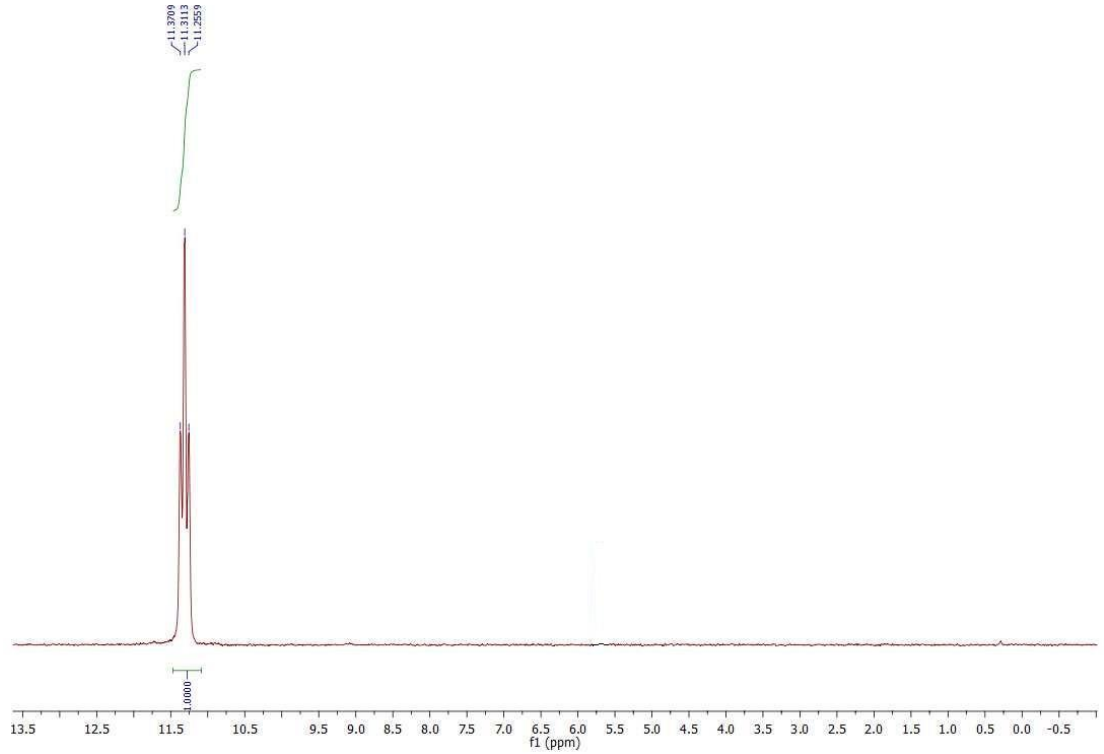

Figure S17: The ^{31} P NMR spectra of the compound **24**

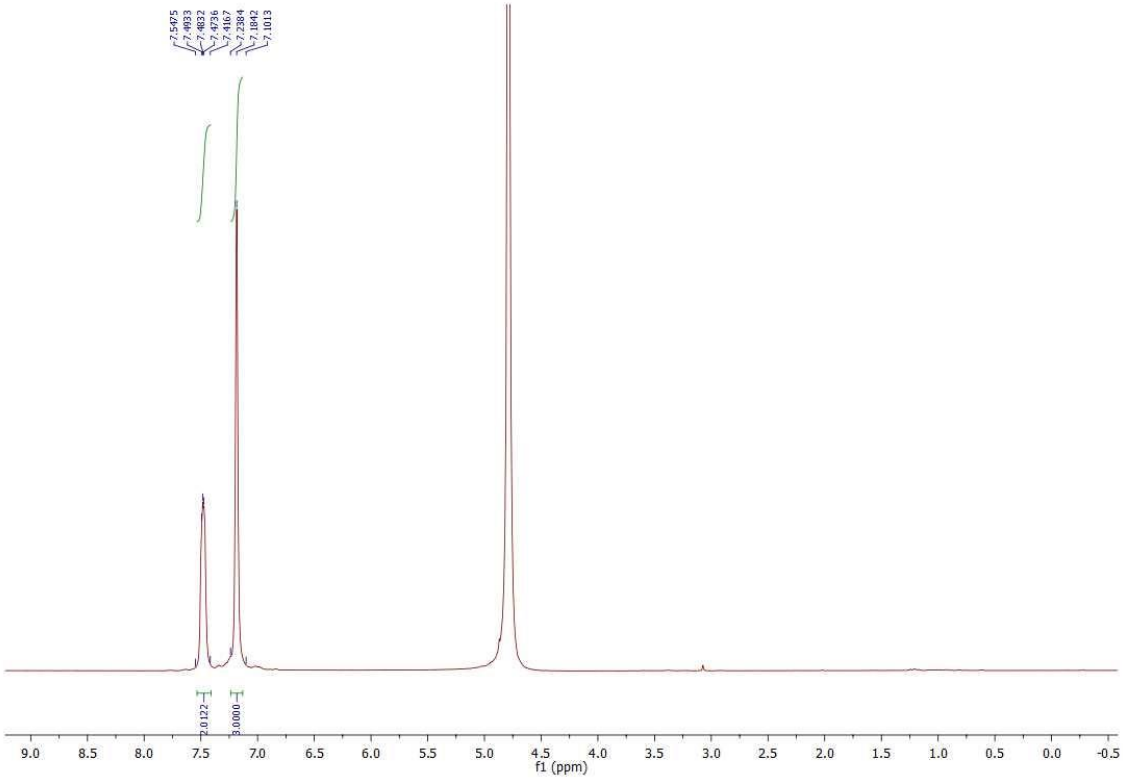

Figure S18: The ^{1}H NMR spectra of the compound **24**

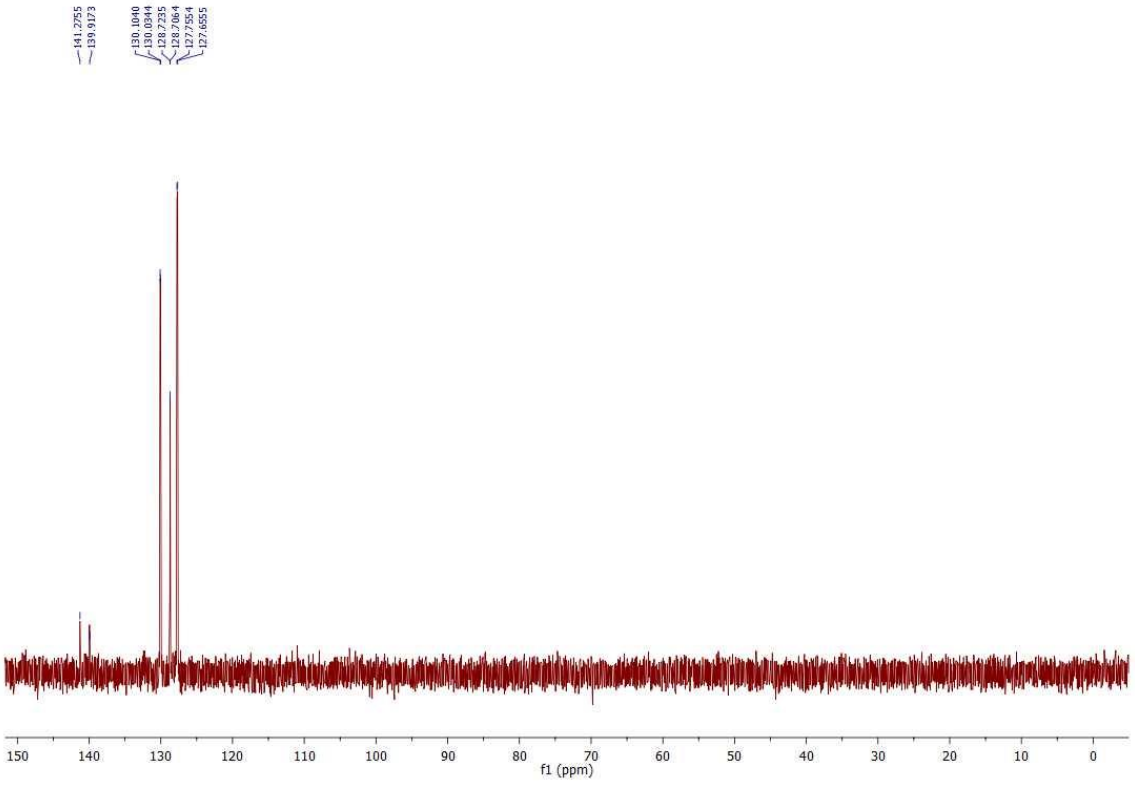

Figure S19: The ^{13}C NMR spectra of the compound **24**

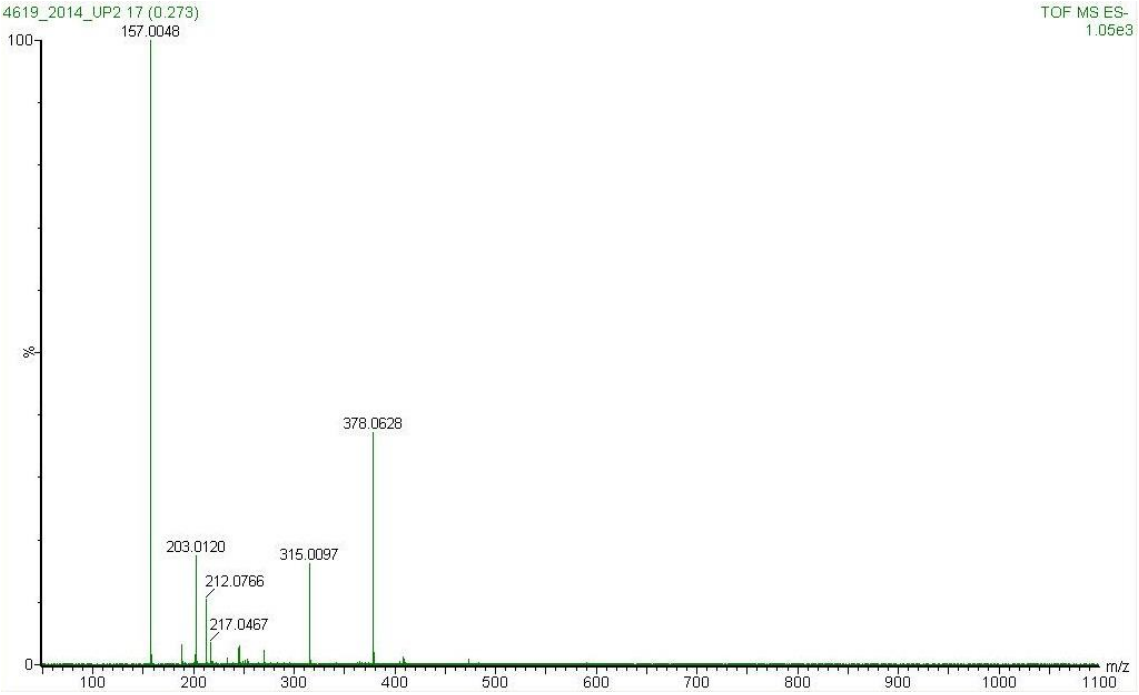

Figure S20: The HRMS spectra of the compound **24**

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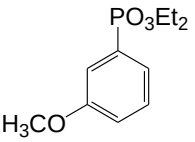

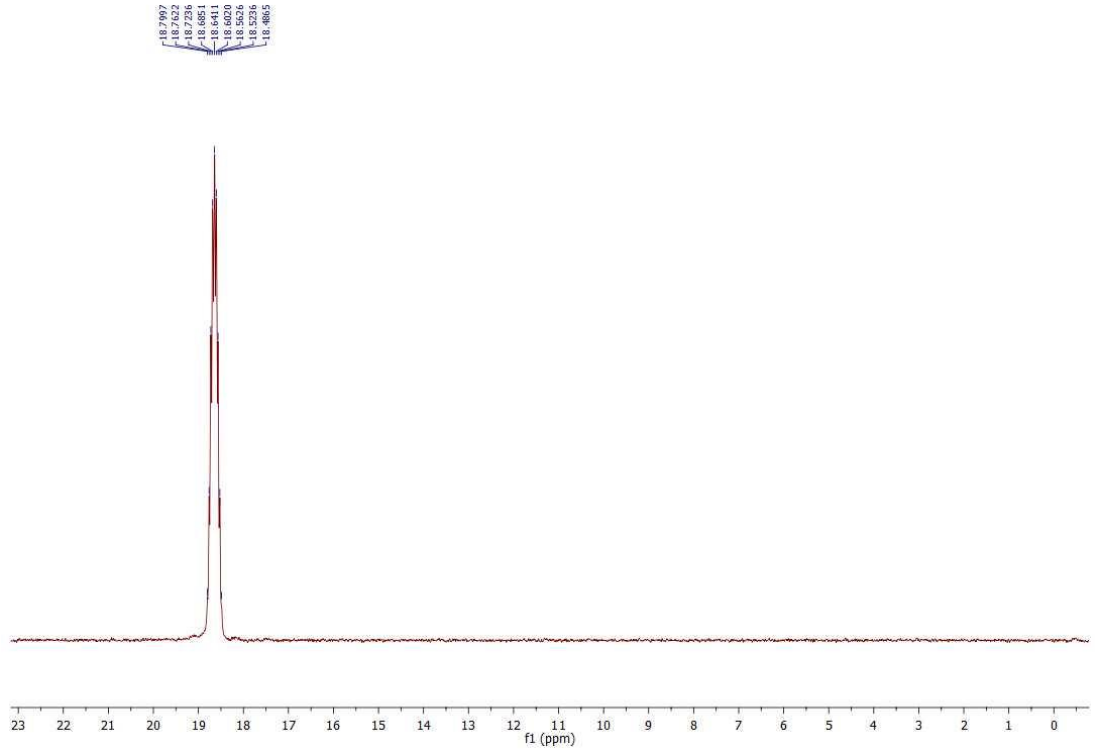

Figure S21: The ^{31} P NMR spectra of the compound **22**

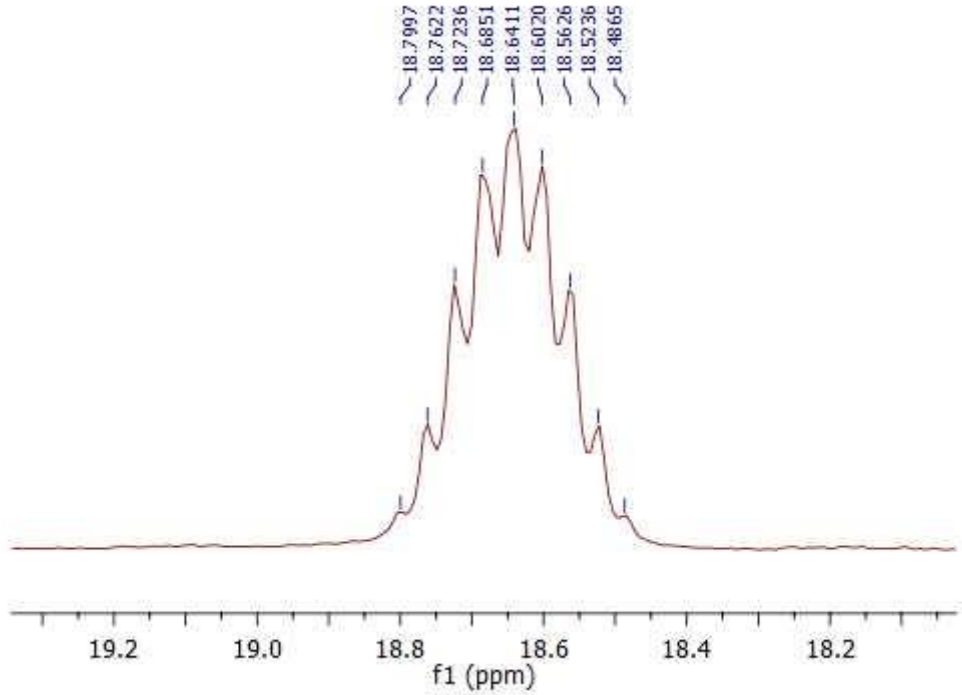

Figure S22: The ^{31} P NMR spectra of the compound **22**

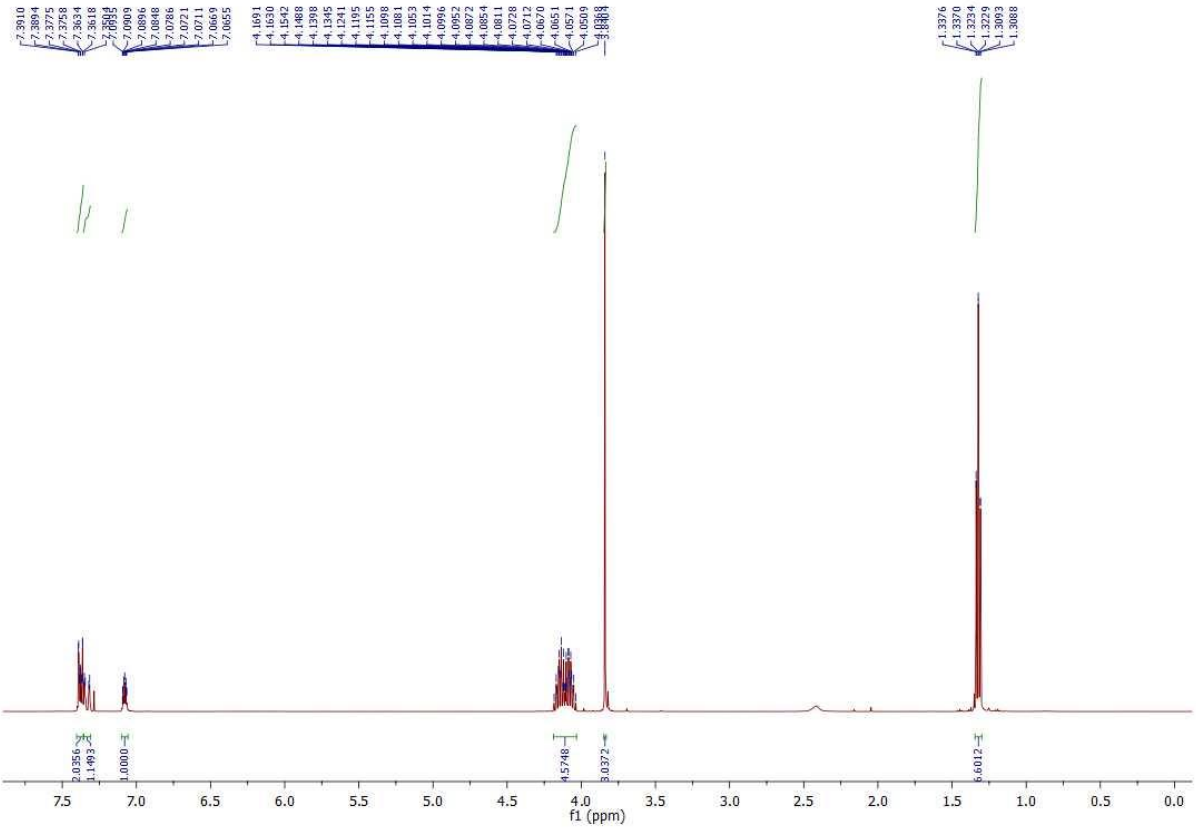

Figure S23: The ^{1} H NMR spectra of the compound **22**

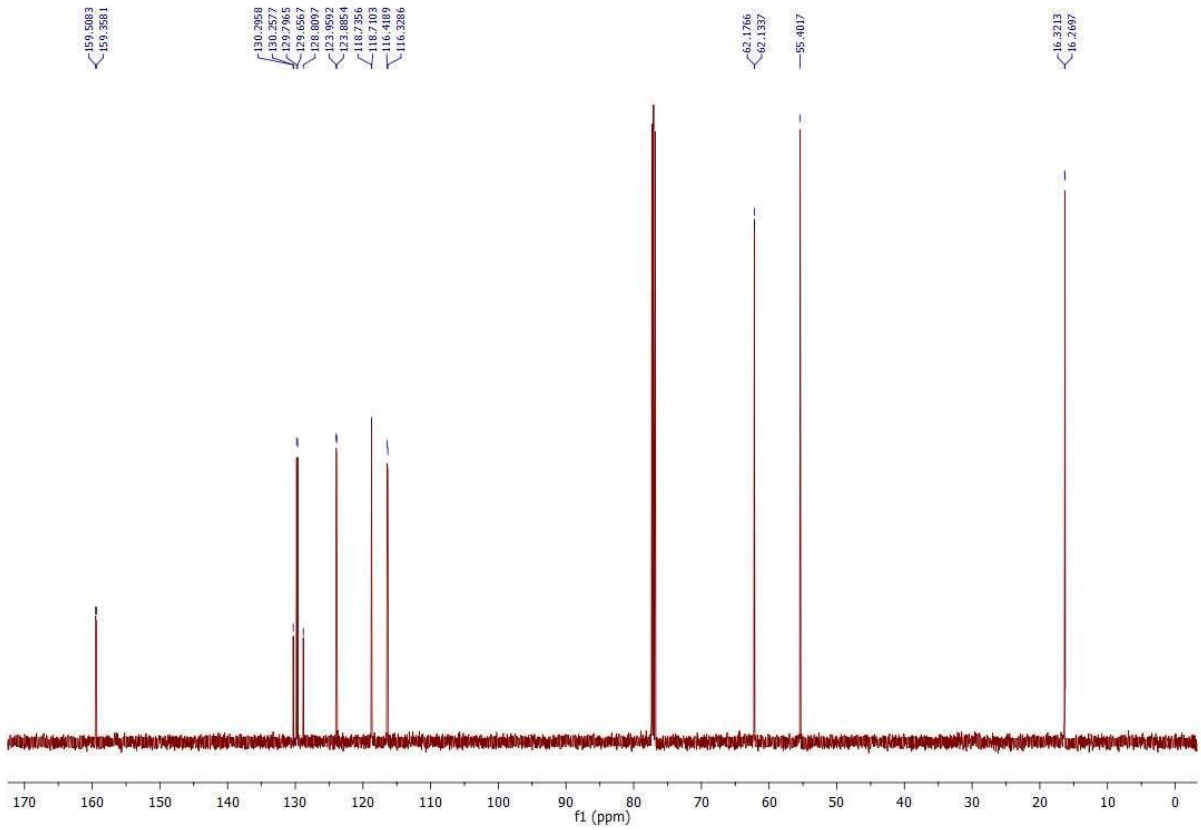

Figure S24: The ^{13} C NMR spectra of the compound **22**

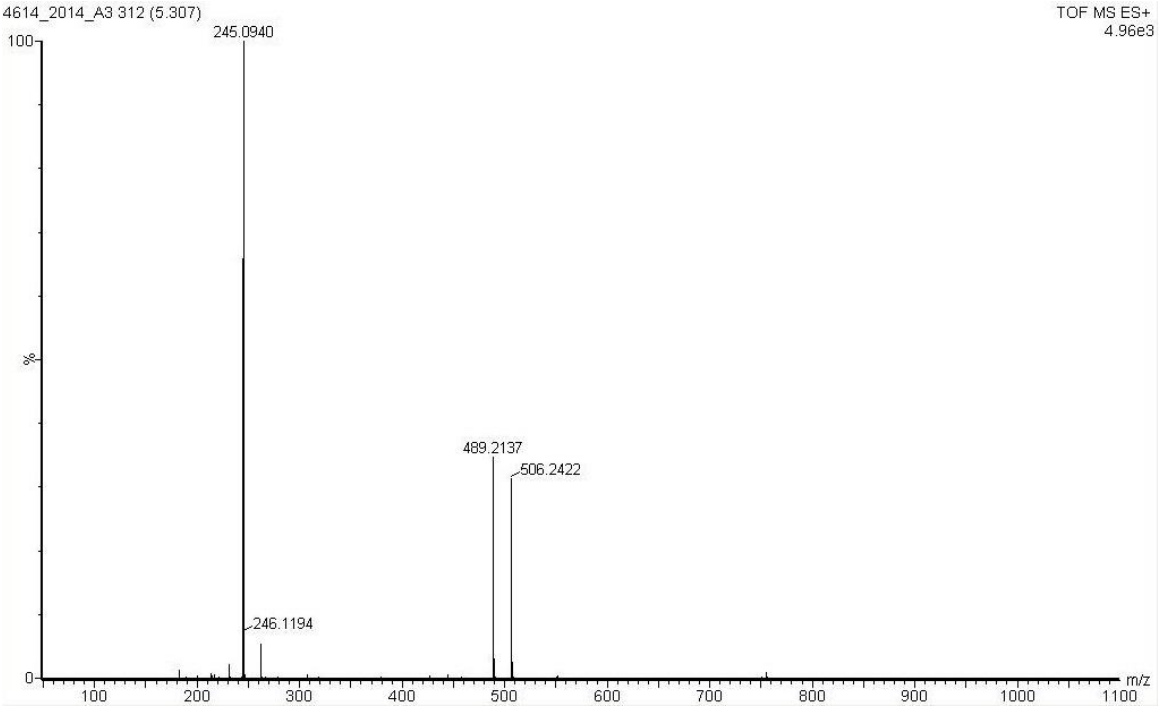

Figure S25: The HRMS spectra of the compound **22**

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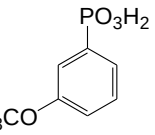

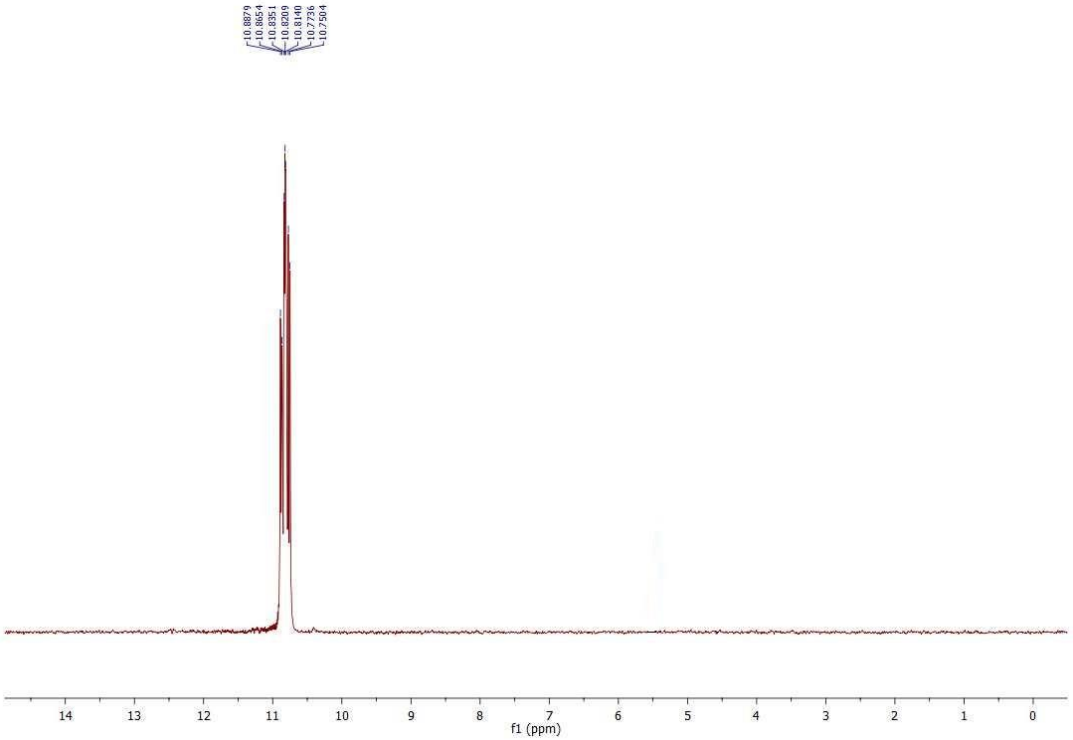

Figure S26: The ^{31} P NMR spectra of the compound **25**

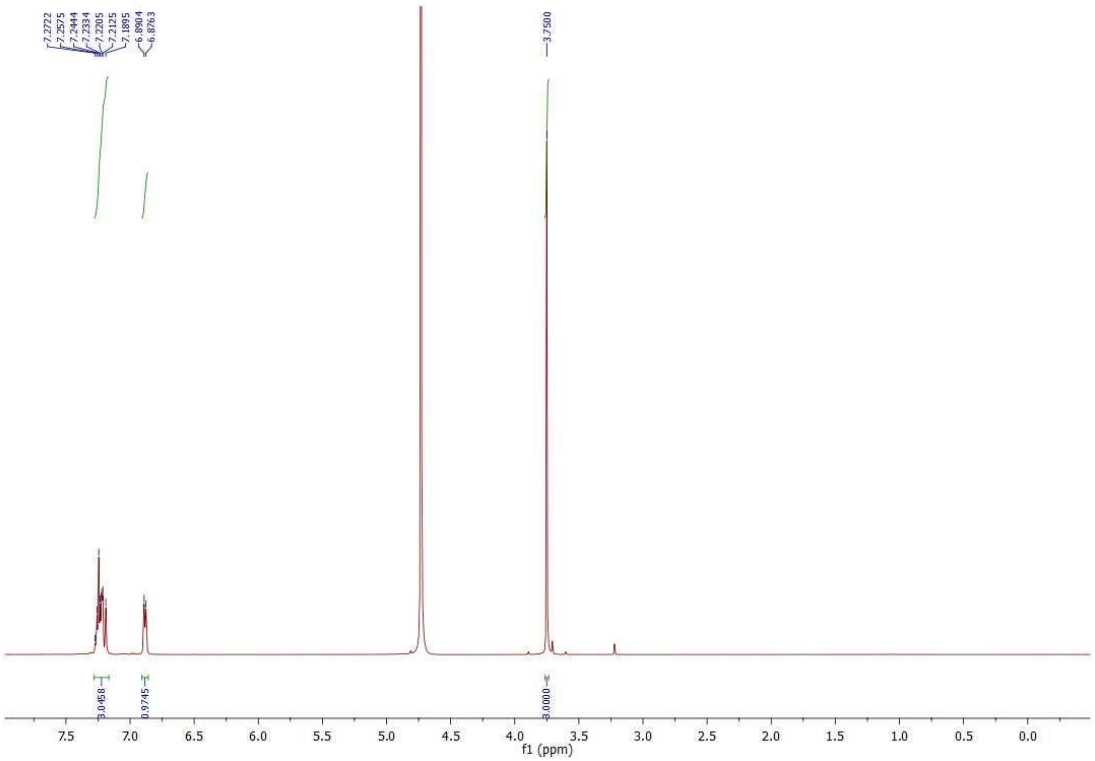

Figure S27: The ^{1} H NMR spectra of the compound **25**

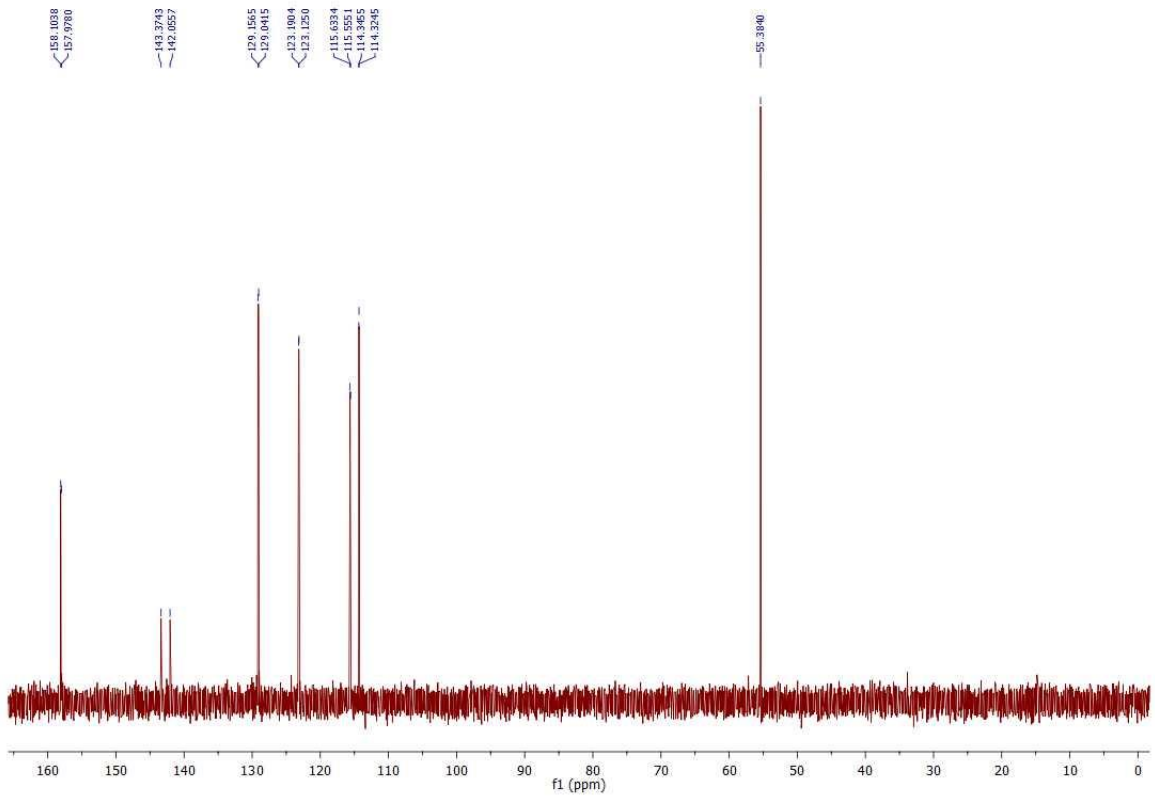

Figure S28: The ^{13} C NMR spectra of the compound **25**

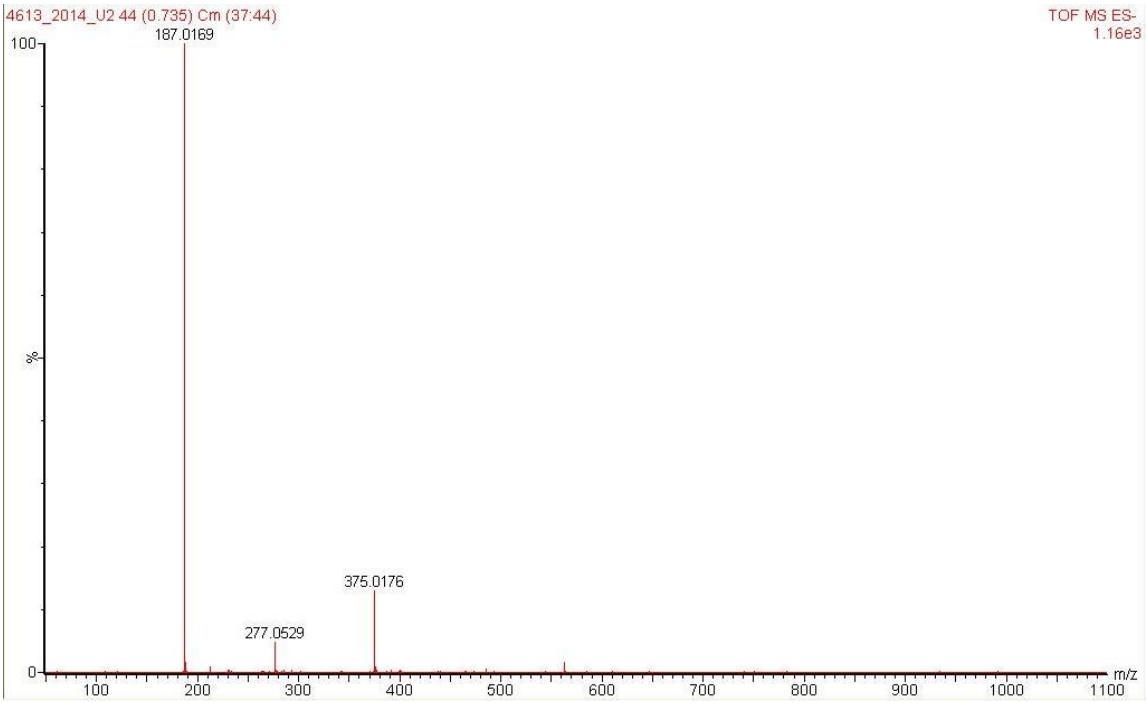

Figure S29: The HRMS spectra of the compound **25**

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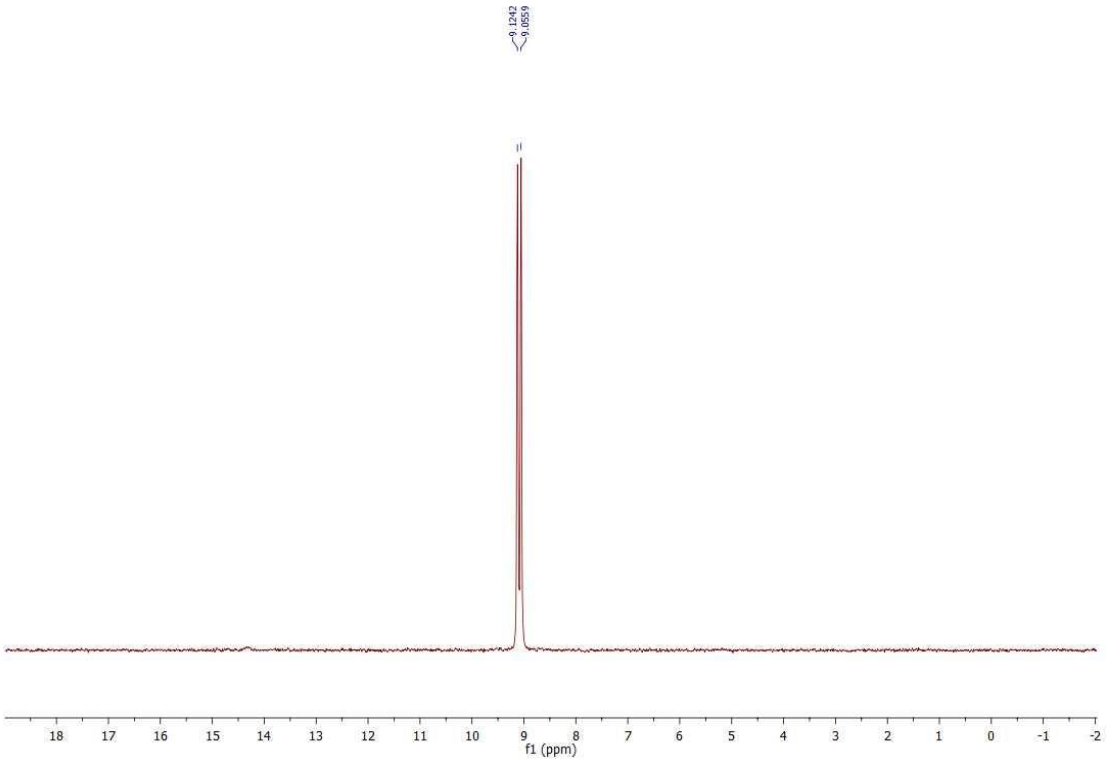

Figure S30: The ^{31}P NMR spectra of the compound **26**

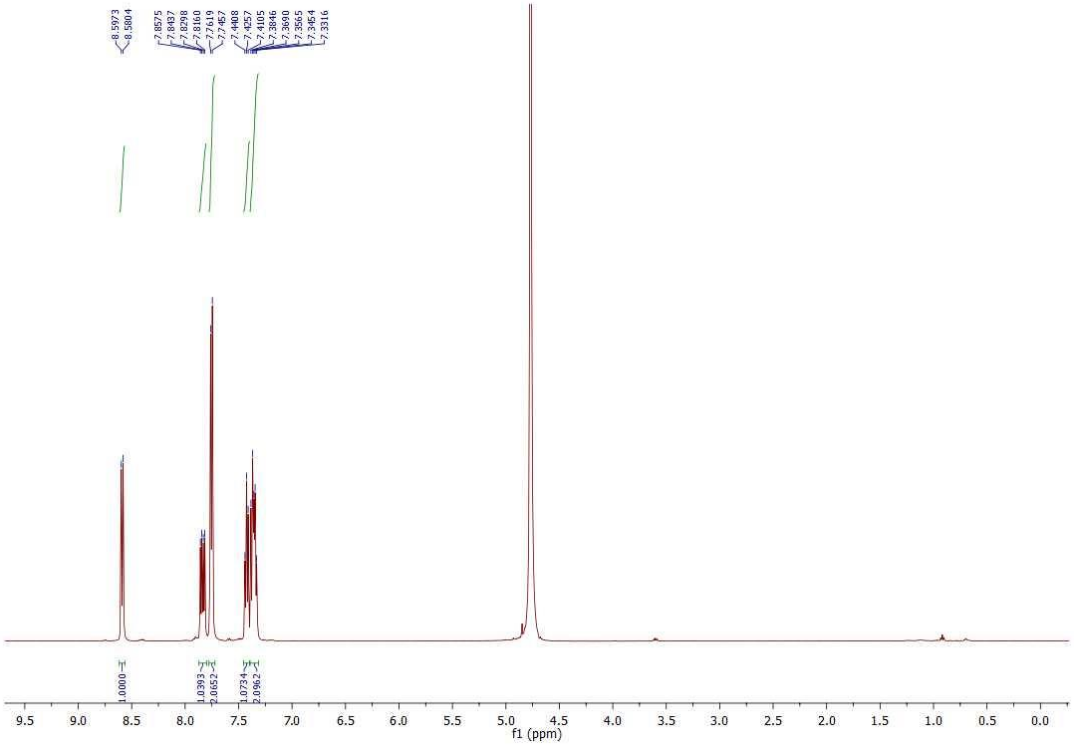

Figure S31: The ^{1}H NMR spectra of the compound **26**

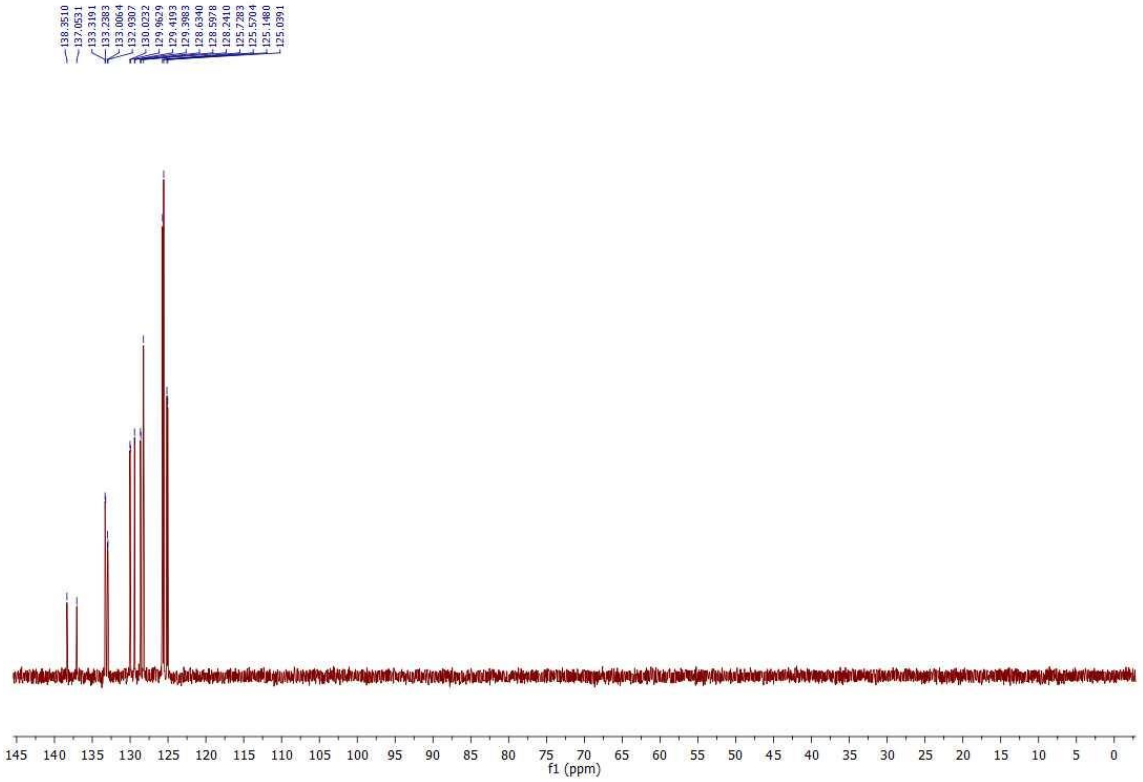

Figure S32: The ^{13} C NMR spectra of the compound **26**

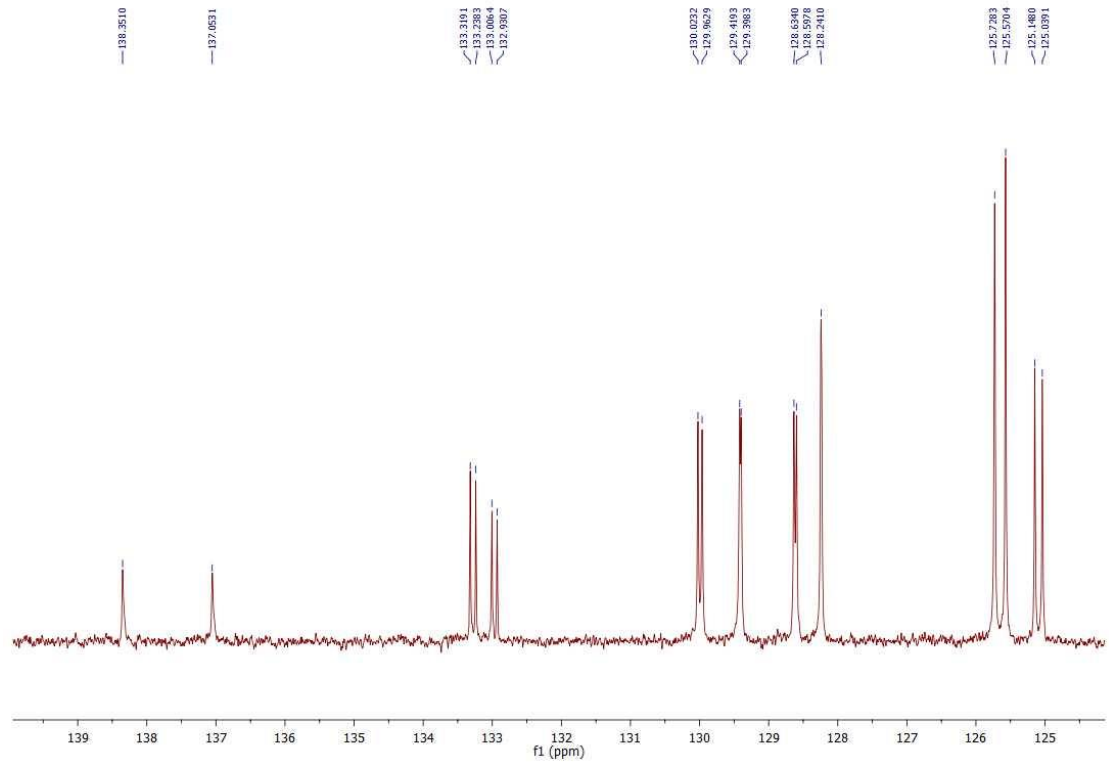

Figure S33: The ^{13} C NMR spectra of the compound **26**

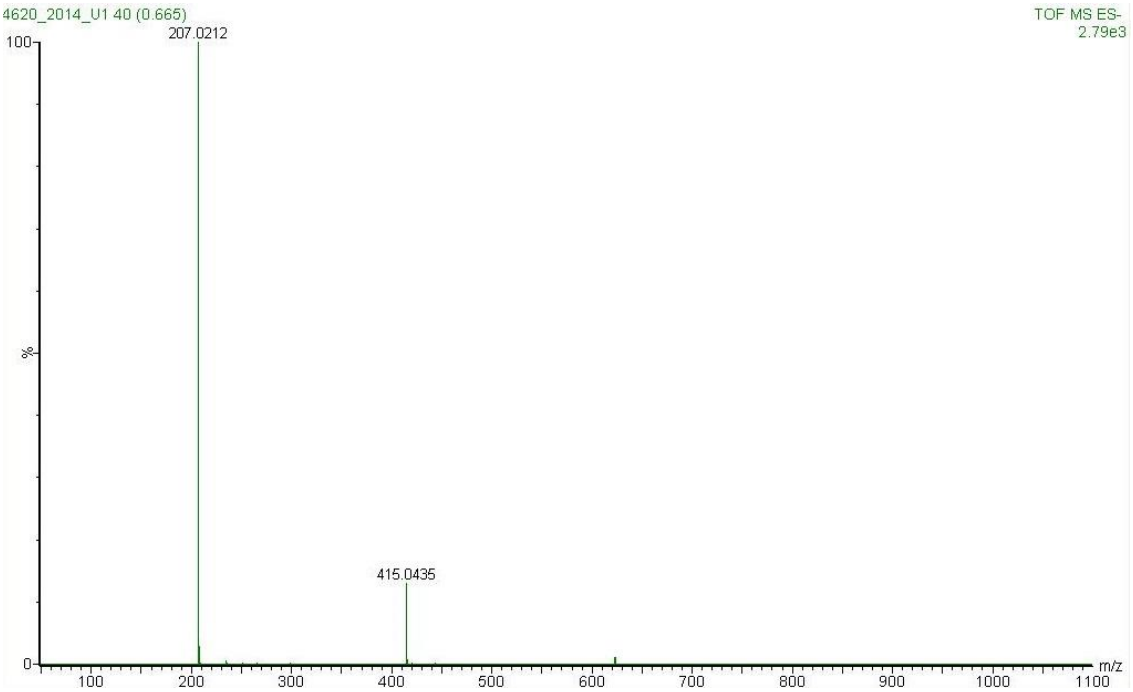

Figure S34: The HRMS spectra of the compound **26**

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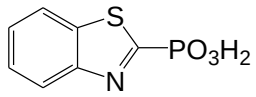


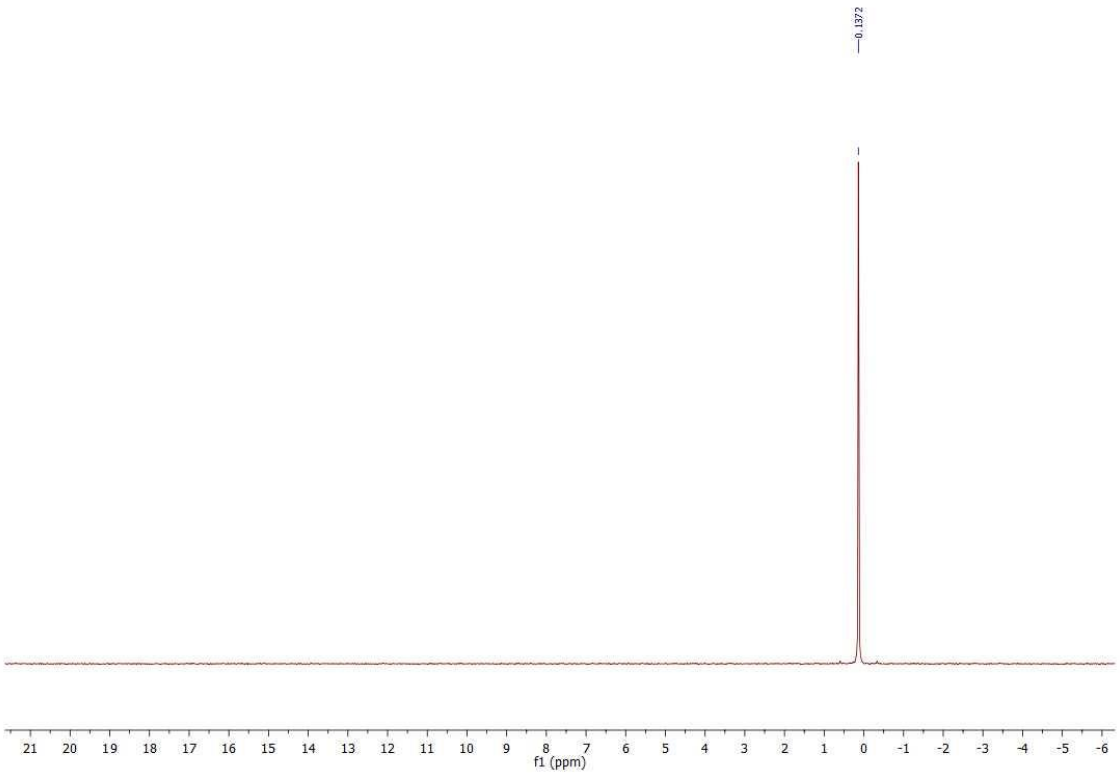


Figure S35: The ^{31}P NMR spectra of the compound **7**

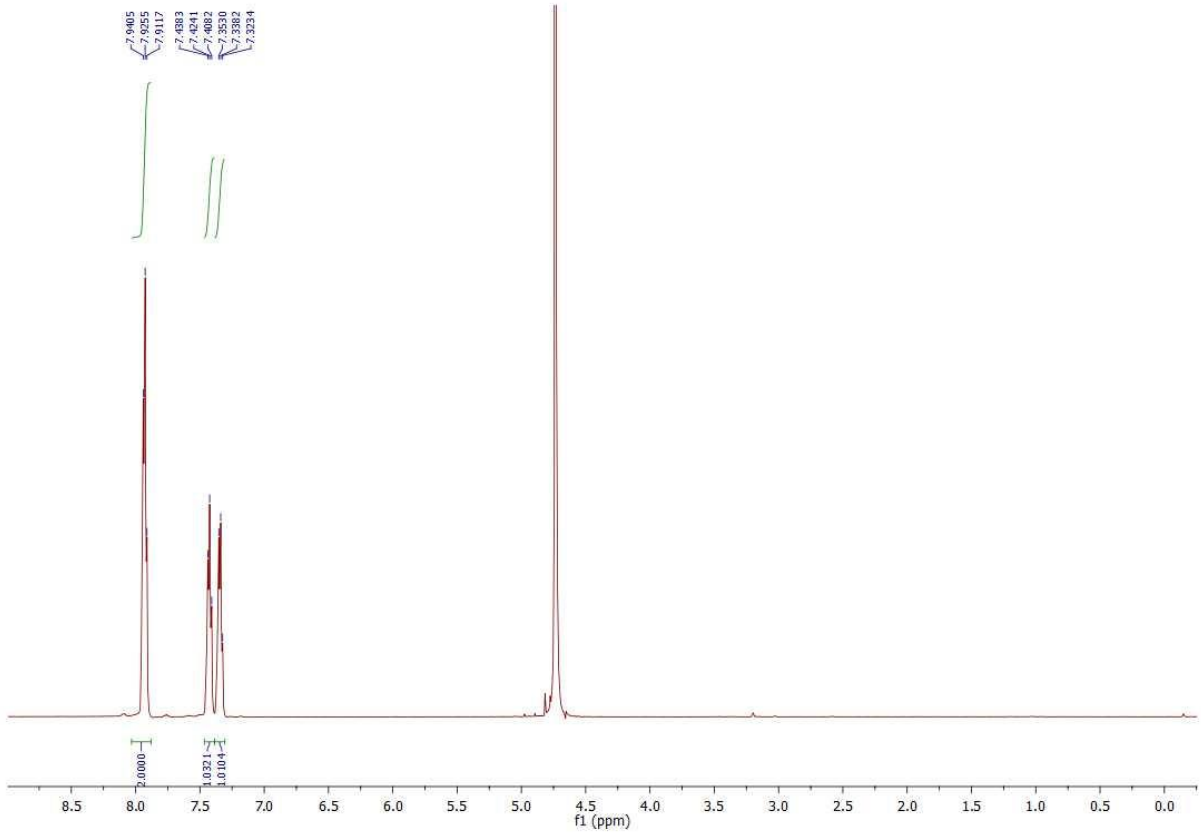


Figure S36: The ^{1} H NMR spectra of the compound **7**

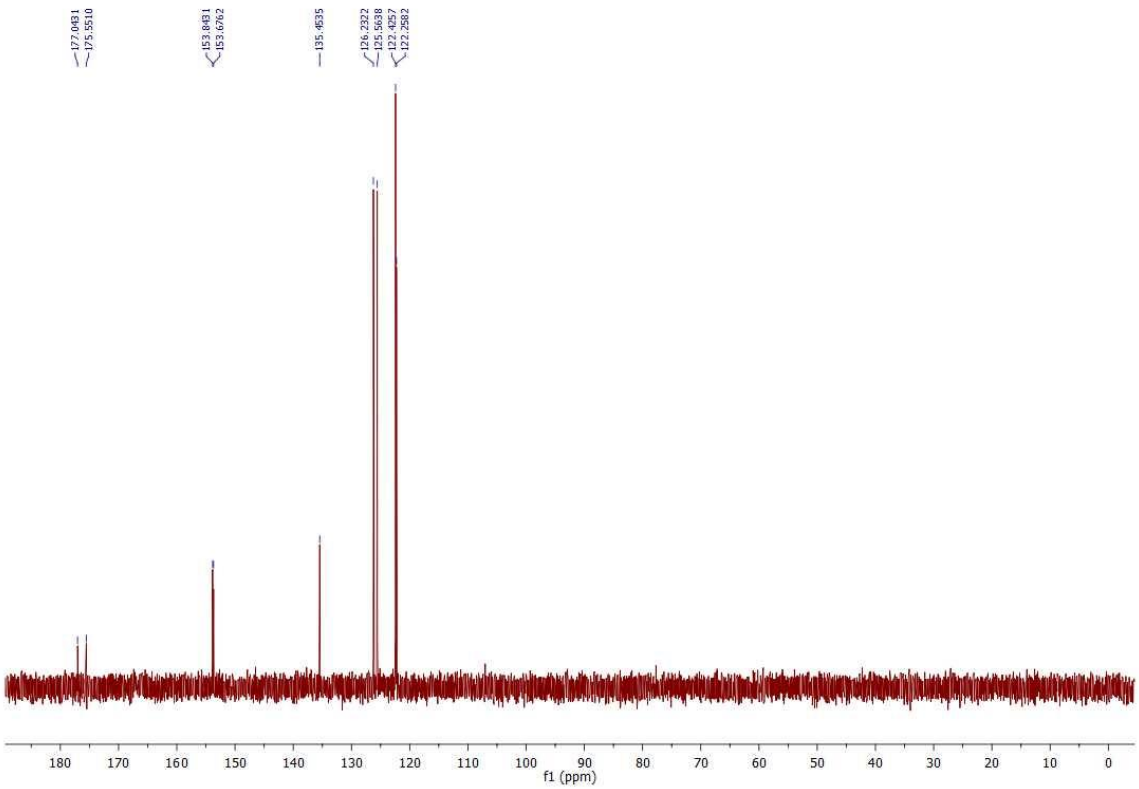


Figure S37: The ^{13} C NMR spectra of the compound **7**

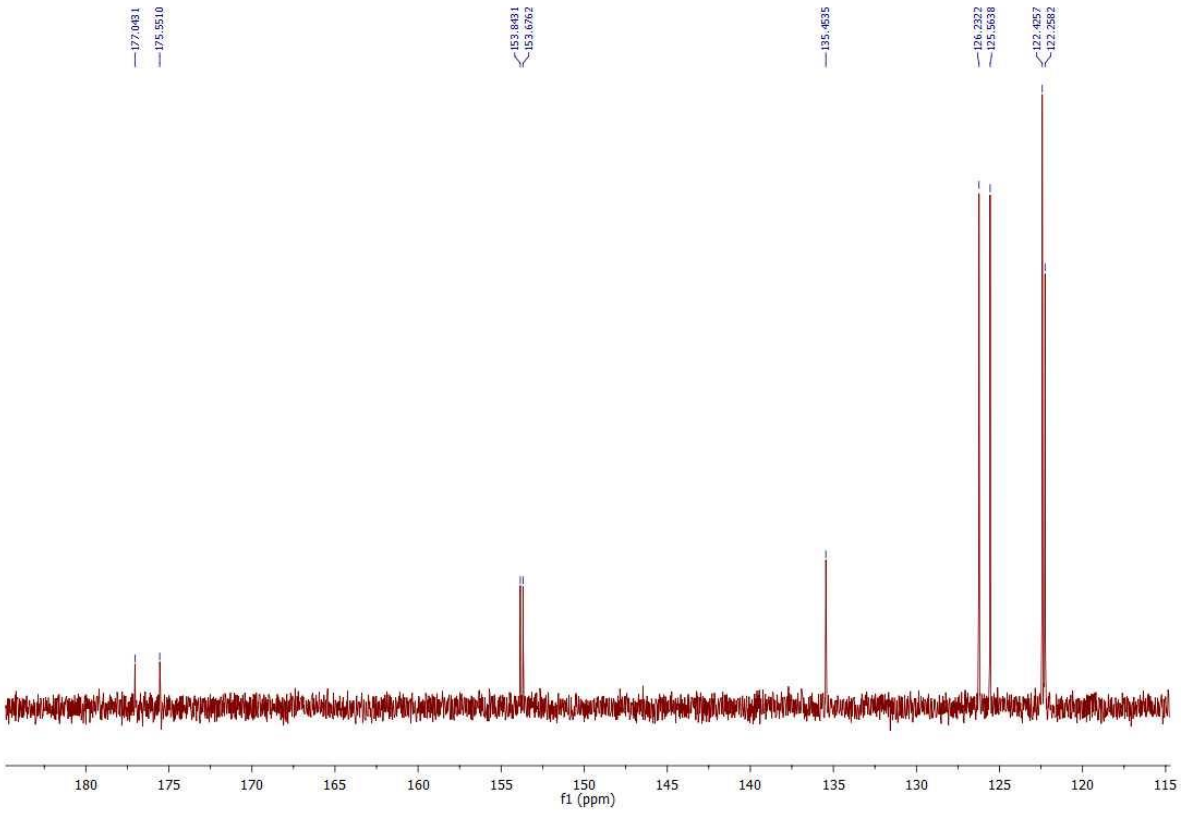


Figure S38: The ^{13} C NMR spectra of the compound **7**

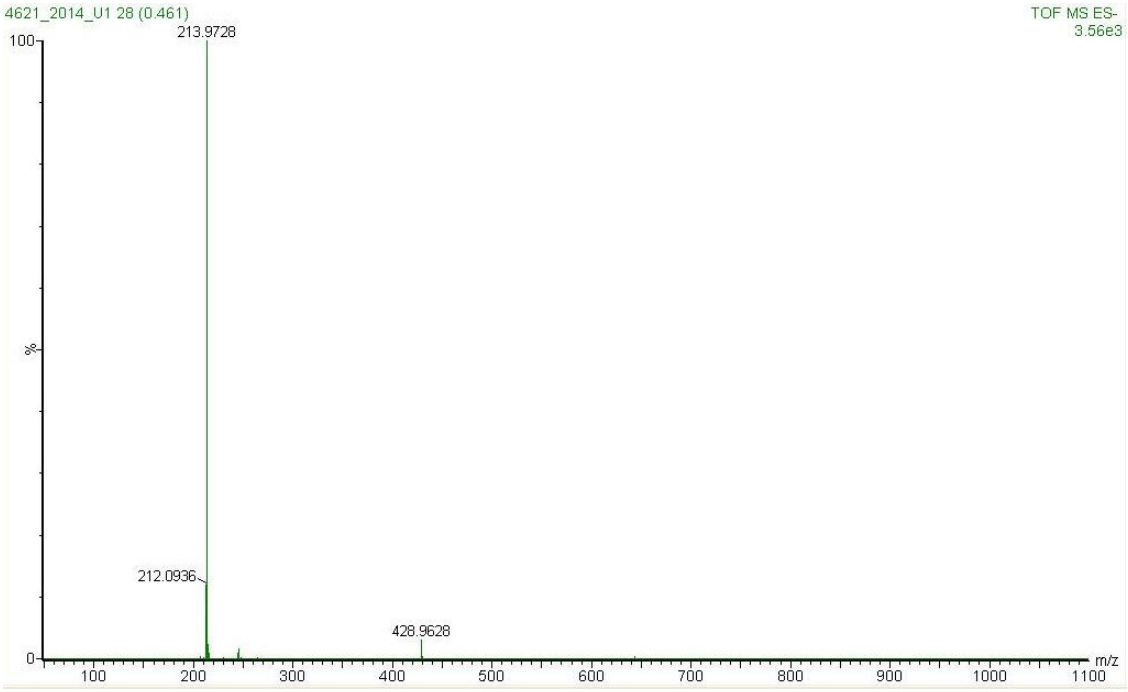


Figure S39: The HRMS spectra of the compound **7**

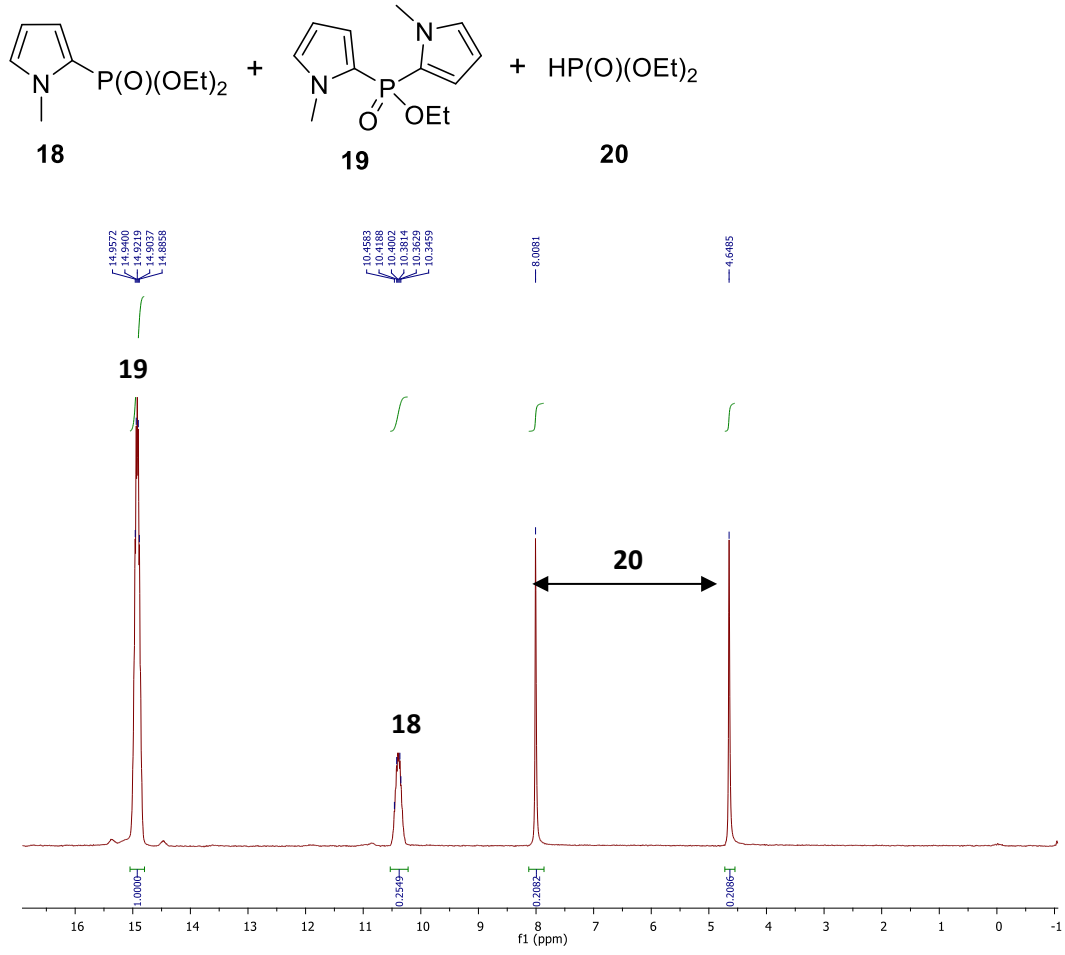


Figure S40: The ^{31}P NMR spectra of the compounds **18**, **19** and **20**

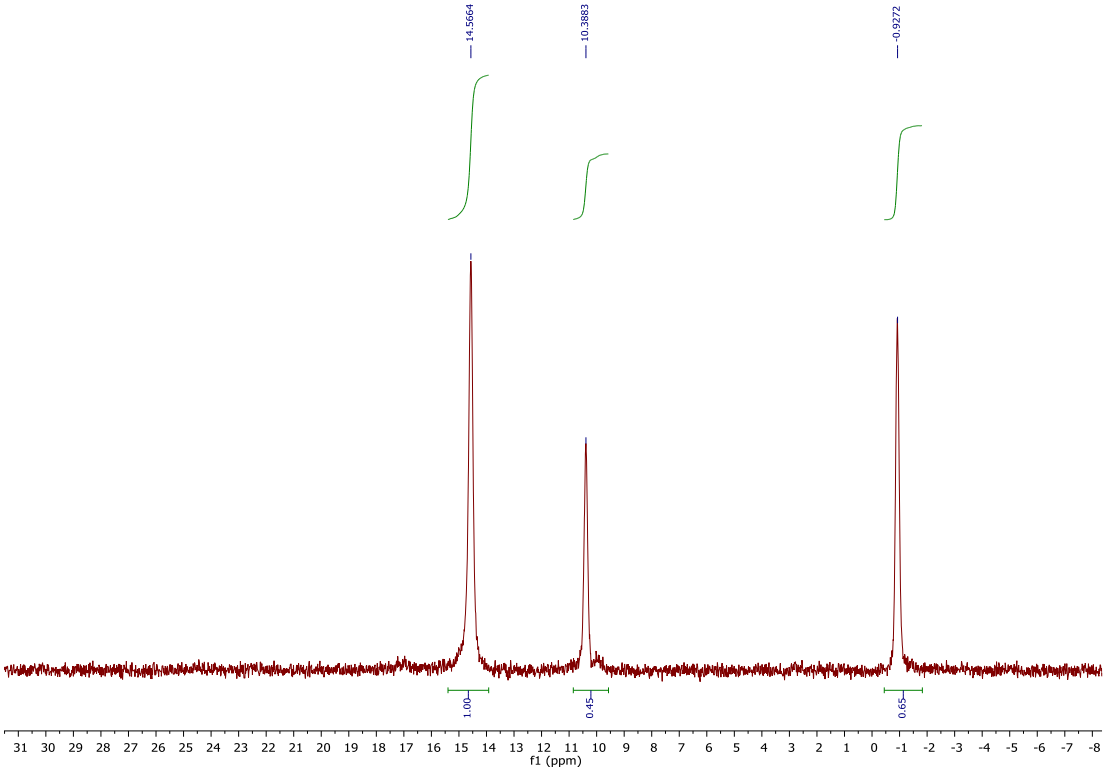


Figure S41: The $^{31}P\{^{1}H\}$ NMR spectra of the compounds **18**, **19** and **20**

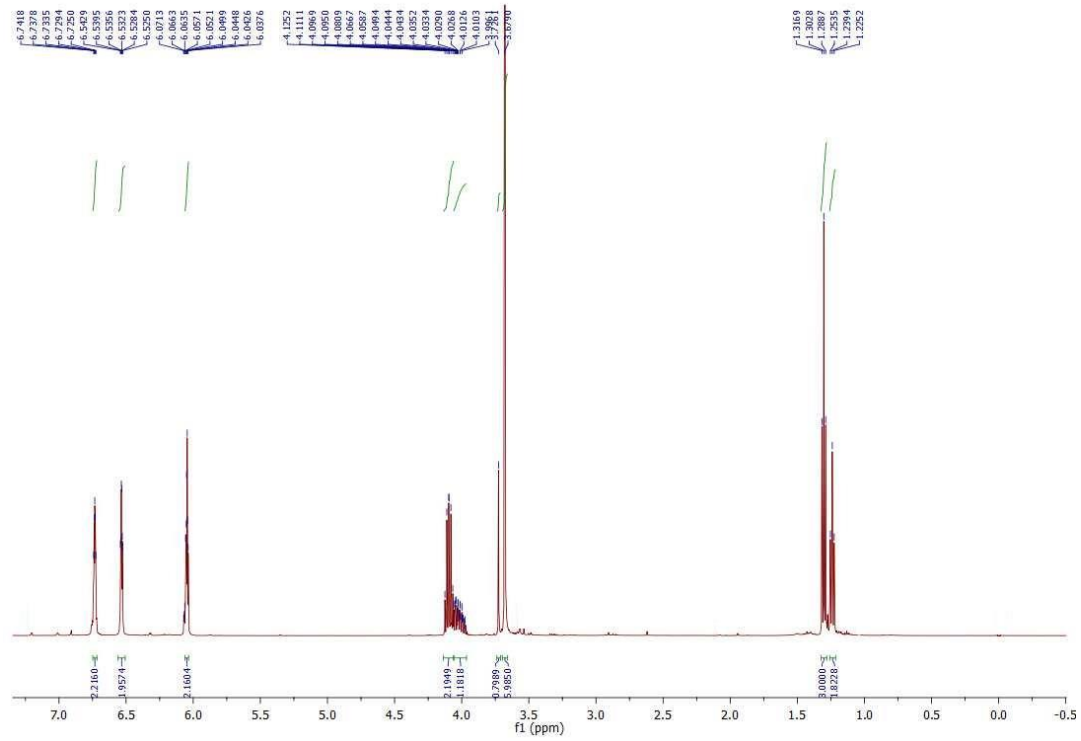


Figure S42: The ^{1}H NMR spectra of the compounds **18**, **19** and **20**

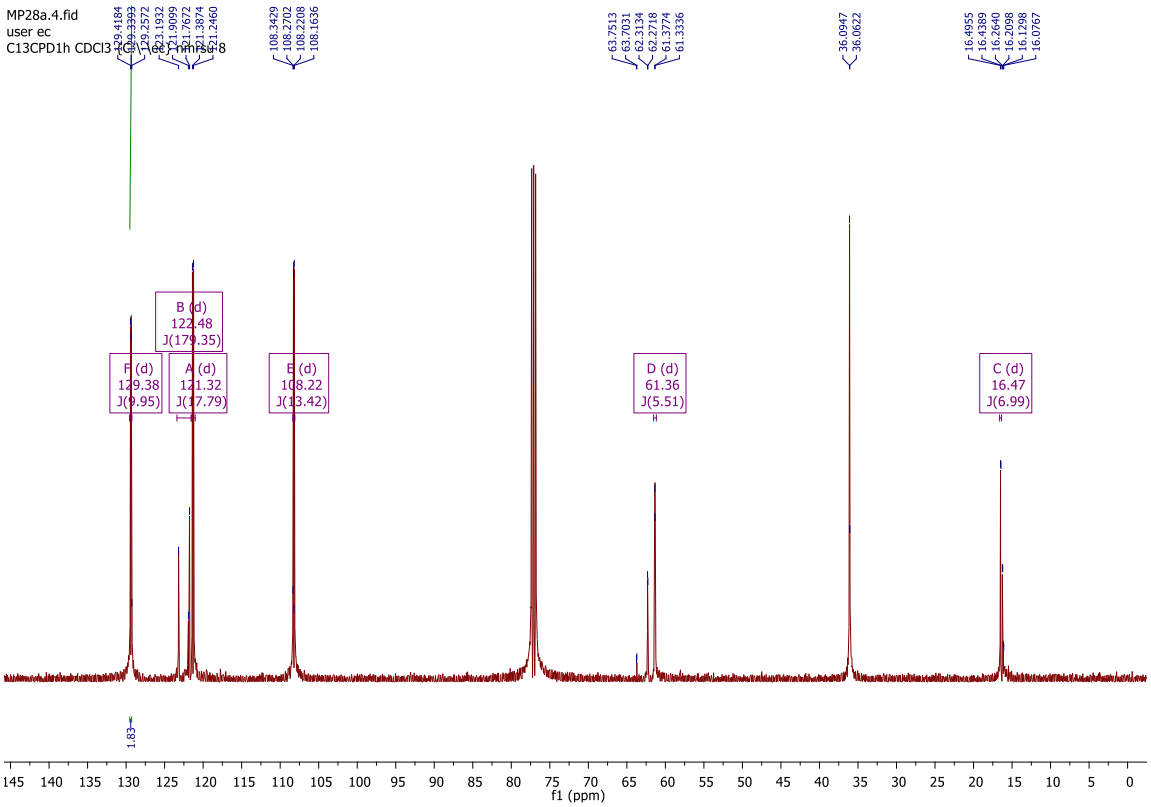


Figure S43: The ^{1}H NMR spectra of the compounds **18**, **19** and **20**

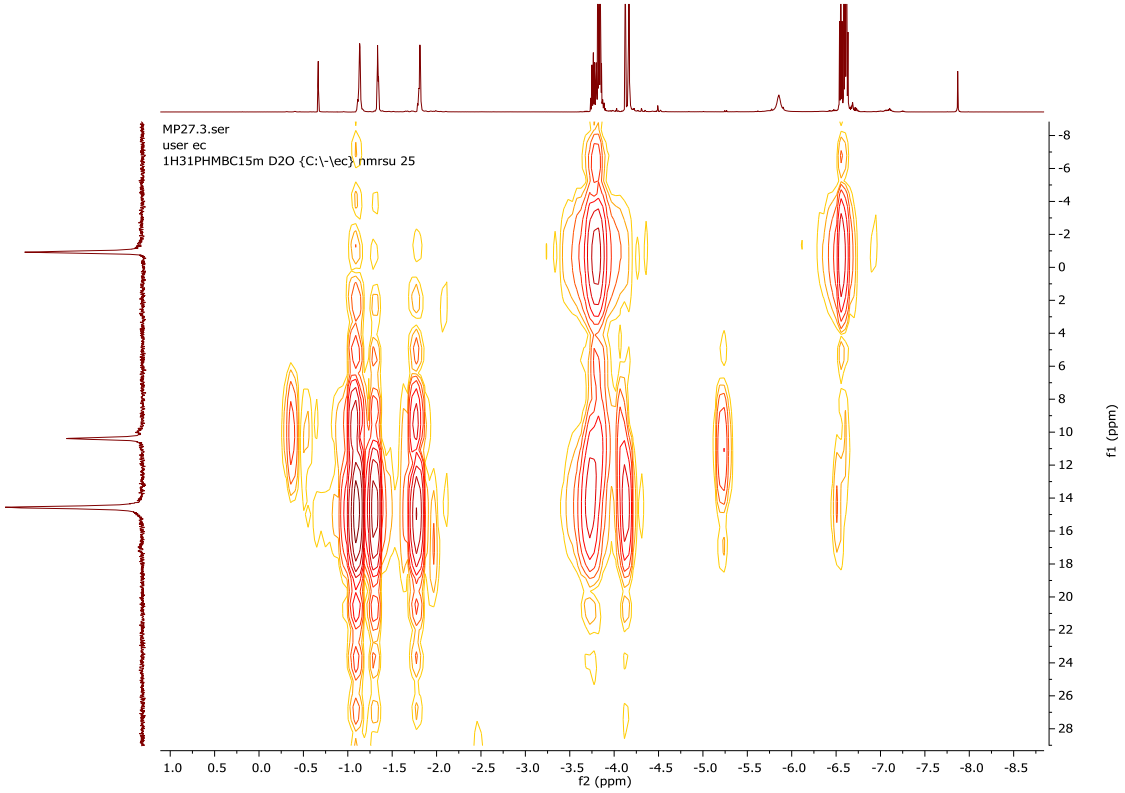
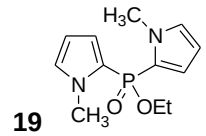


Figure S44: The ^{1}H -^{31}P NMR spectra of the compounds **18**, **19** and **20**



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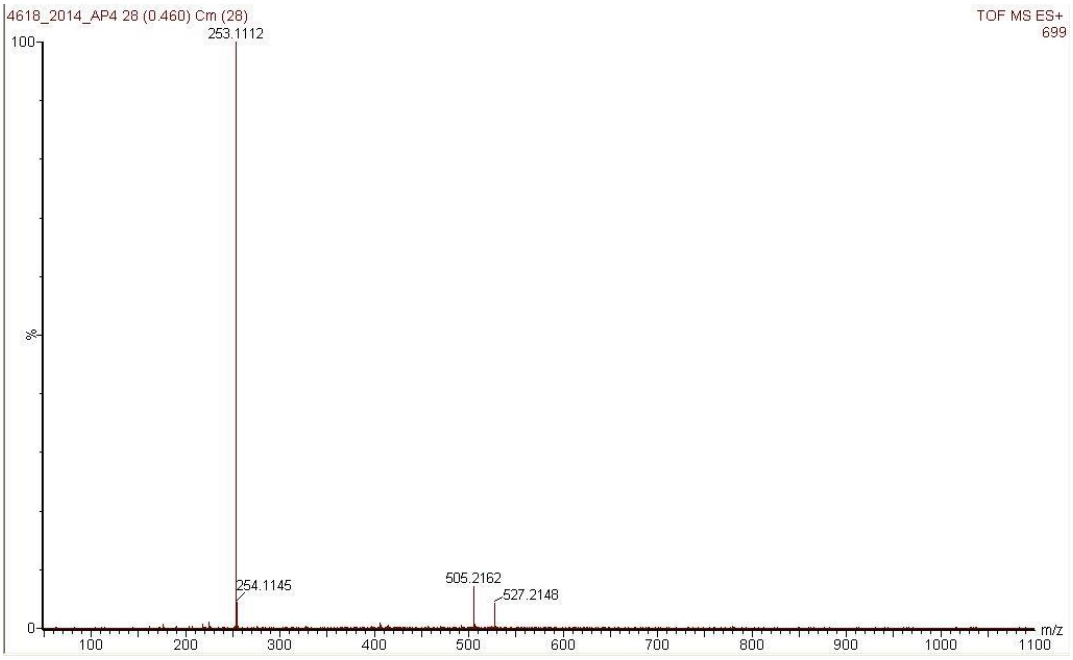
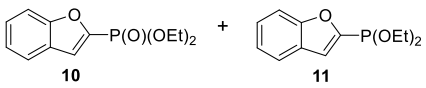


Figure S45: The HRMS spectra of the compound **19**



10 **11**

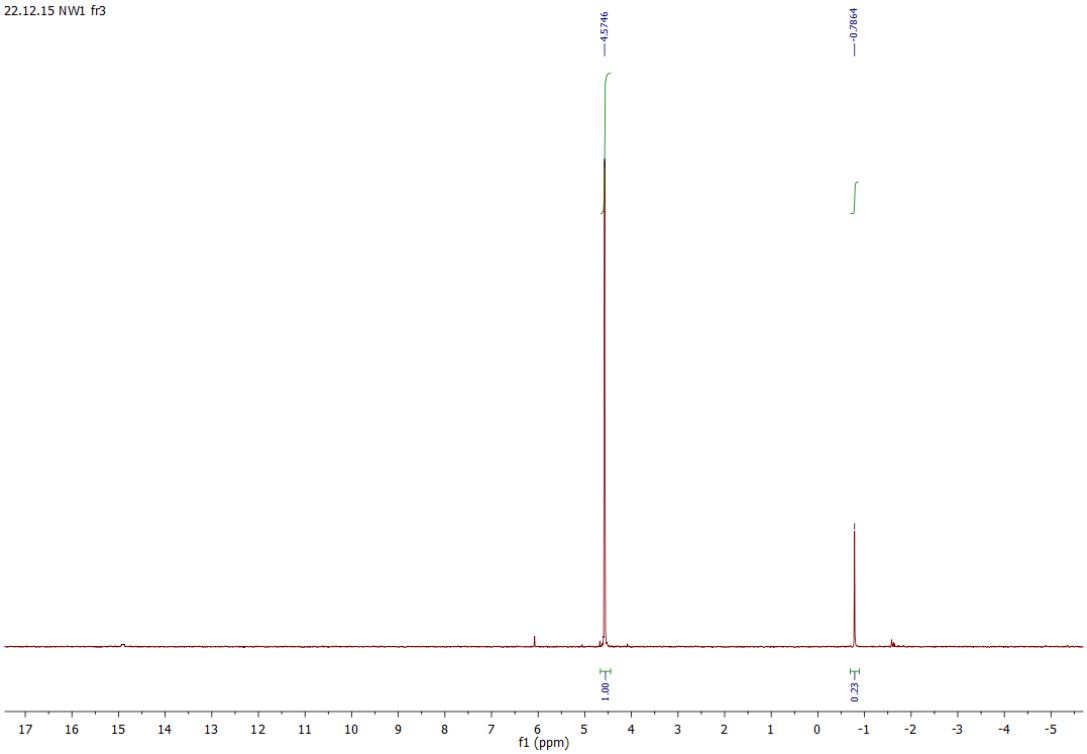


Figure S46: The ^{31} P NMR spectra of the compounds **10** and **11**

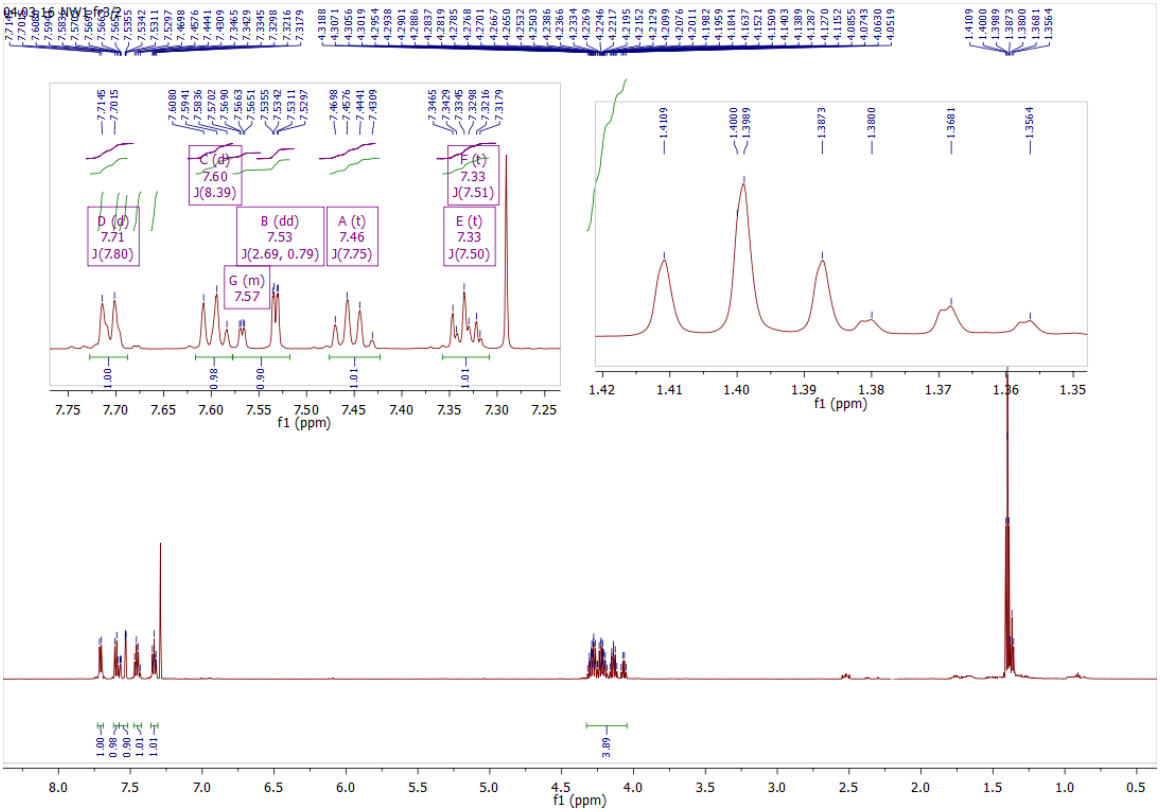


Figure S47: The [1] H NMR spectra of the compounds **10** and **11**

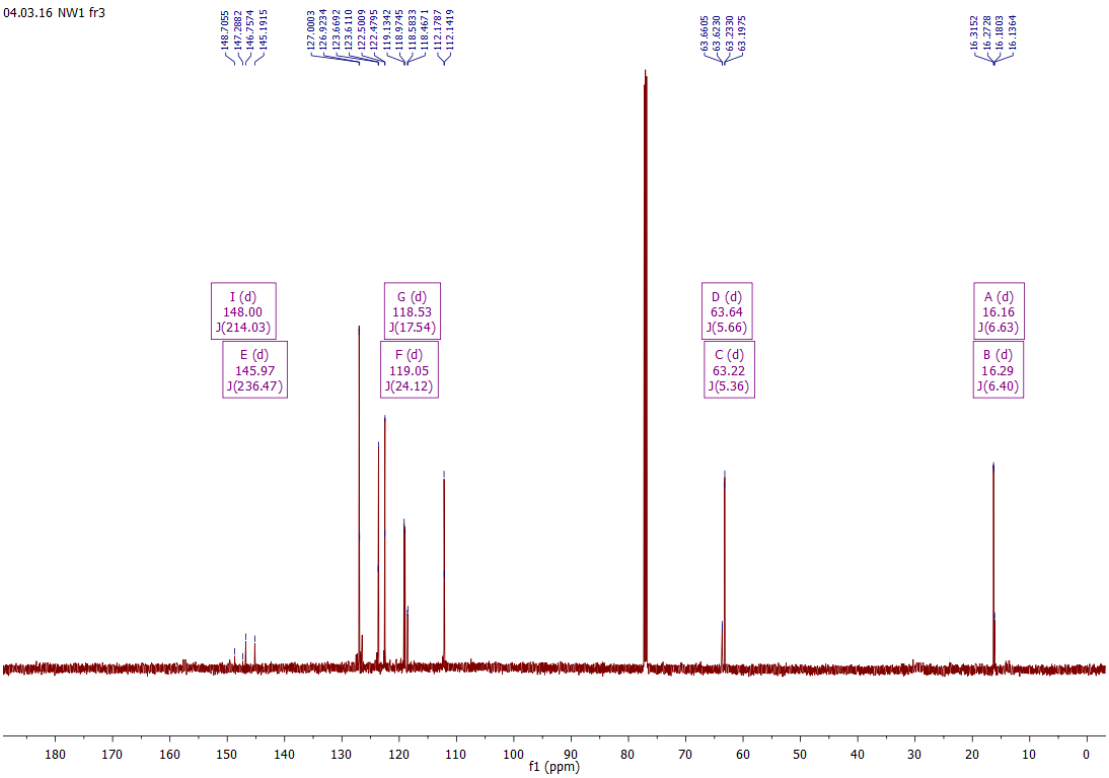


Figure S48: The [13] C NMR spectra of the compounds **10** and **11**

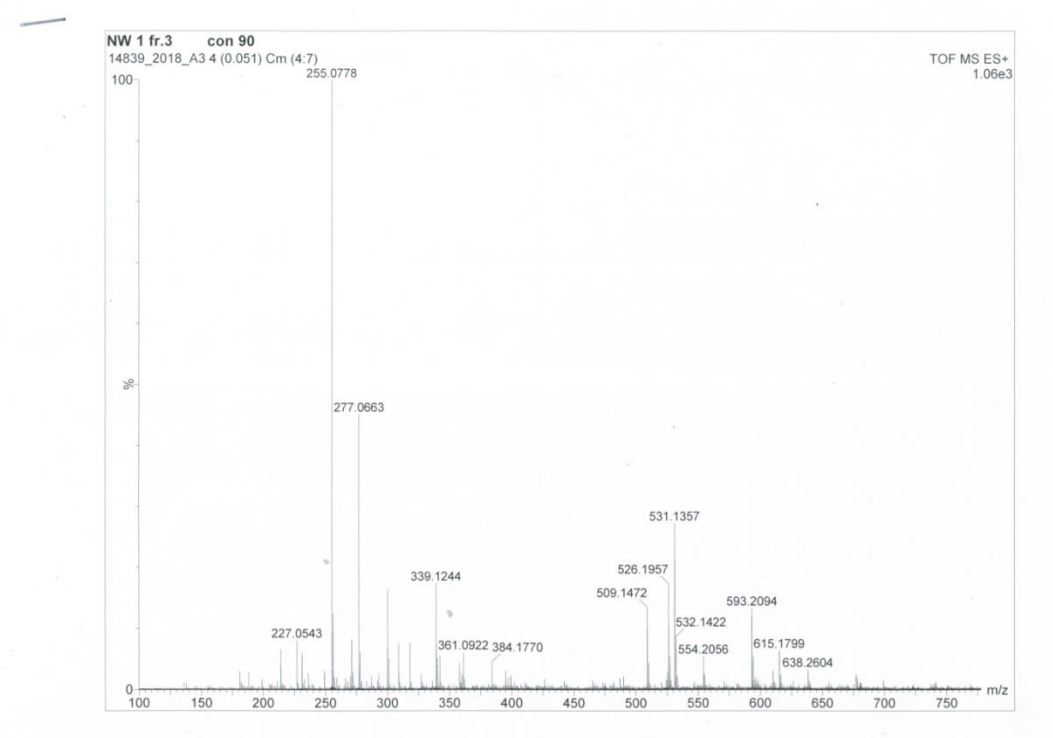
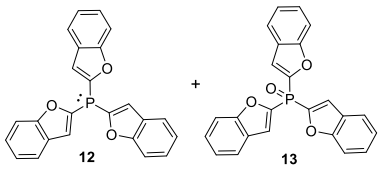


Figure S49: The HRMS spectra of the compounds **10** and **11**



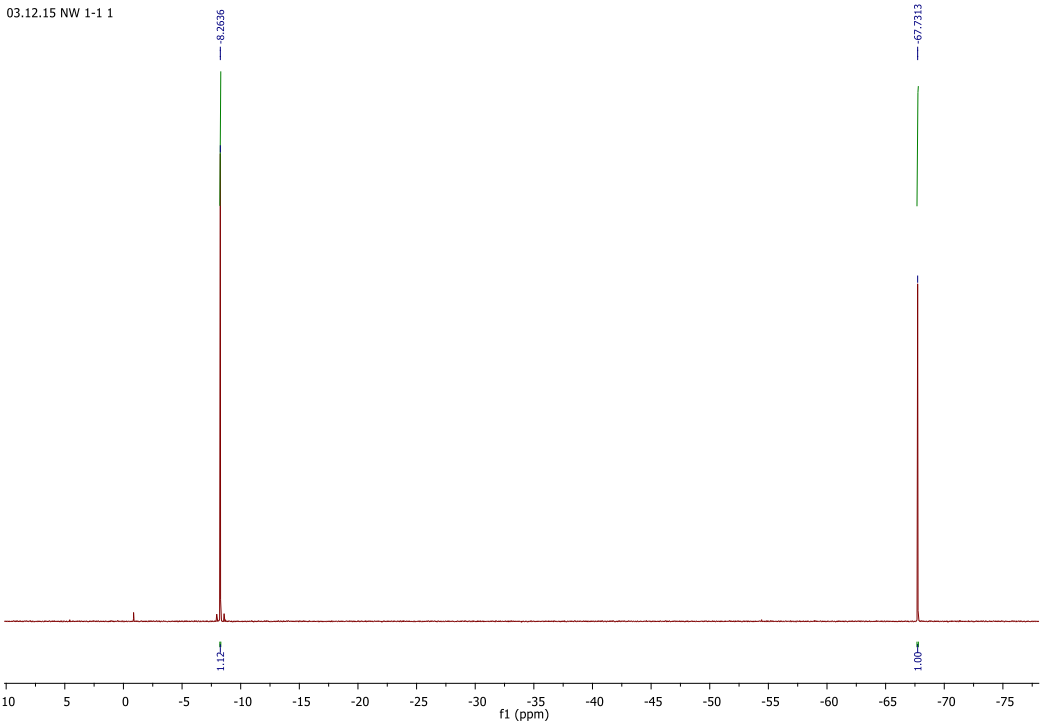


Figure S50: The ^{31} P NMR spectra of the compounds **12** and **13**

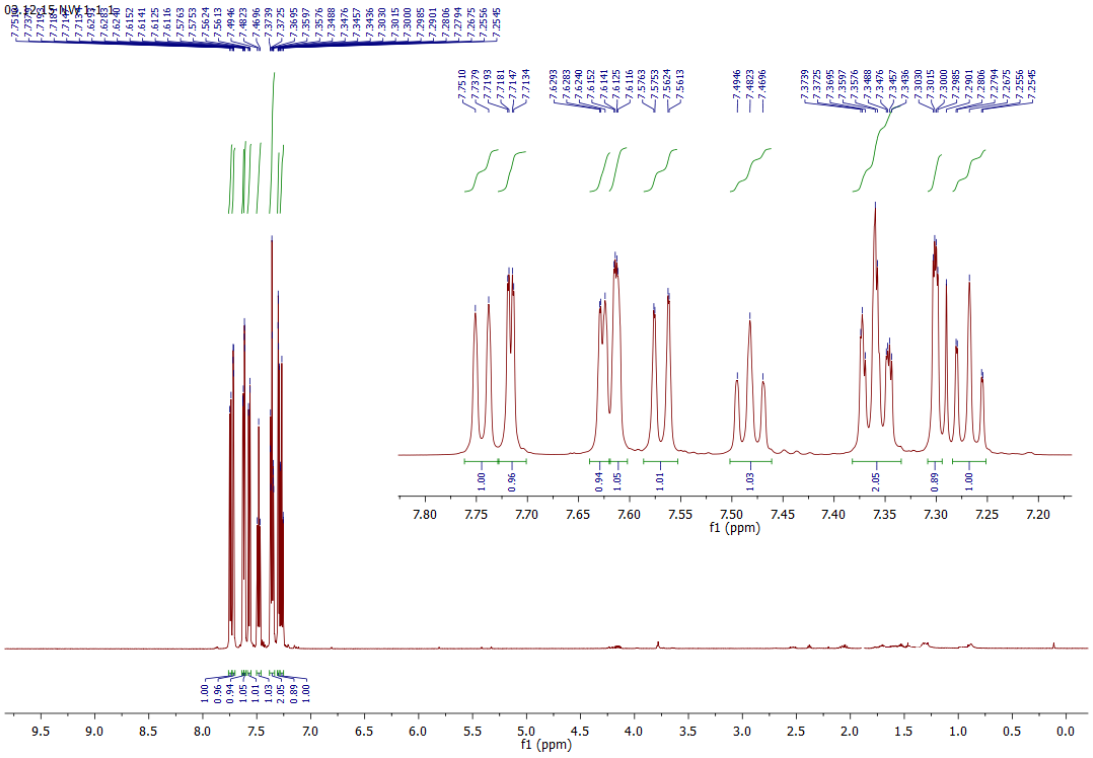


Figure S51: The ^{31}P NMR spectra of the compounds **12** and **13**

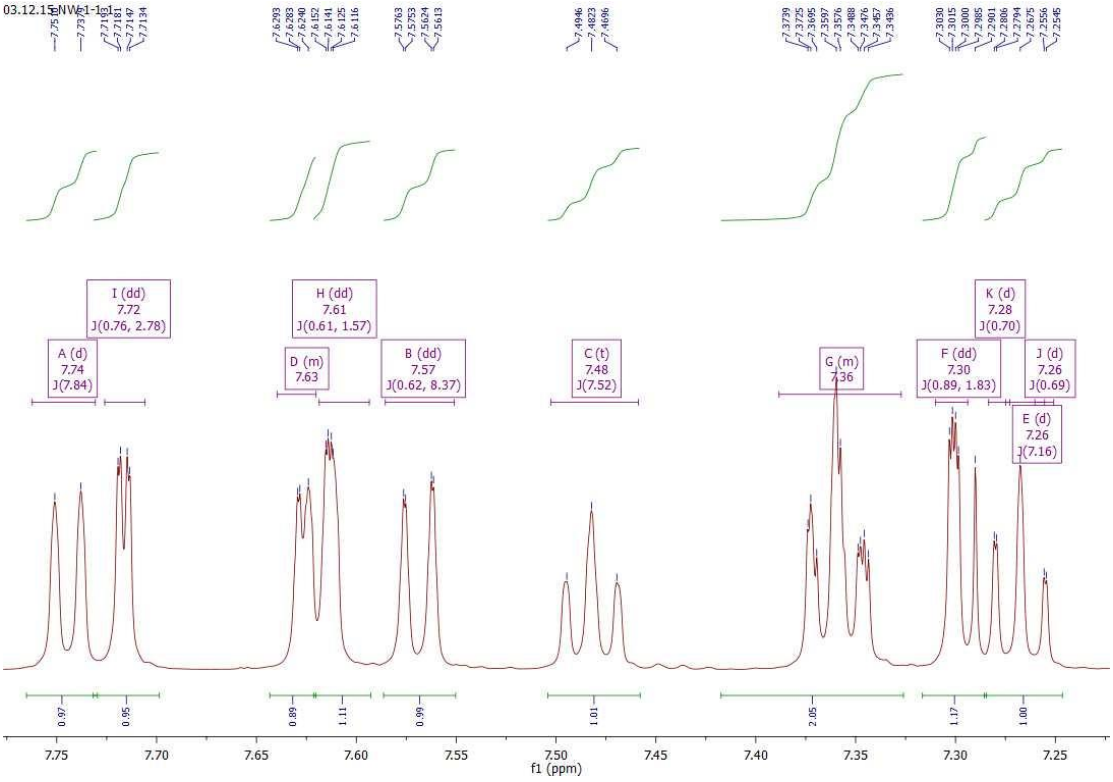


Figure S52: The ^{1}H NMR spectra of the compounds **12** and **13**

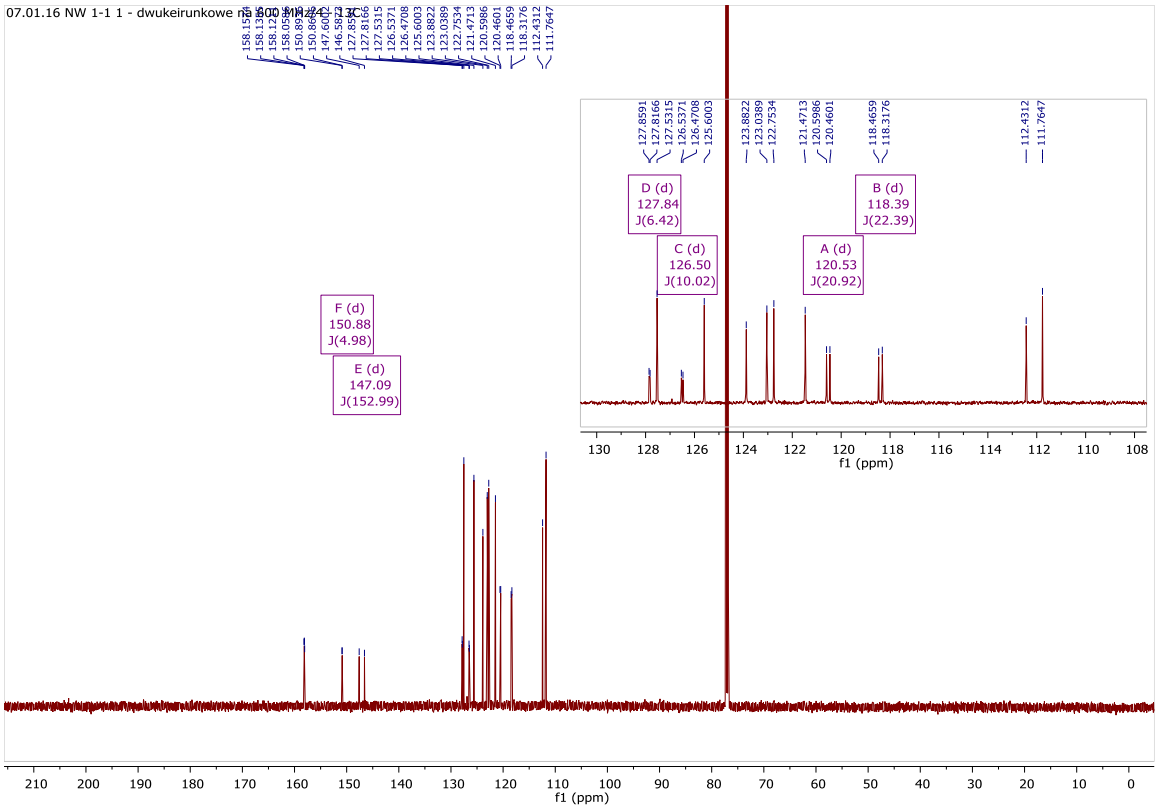


Figure S53: The ^{13} C NMR spectra of the compounds **12** and **13**

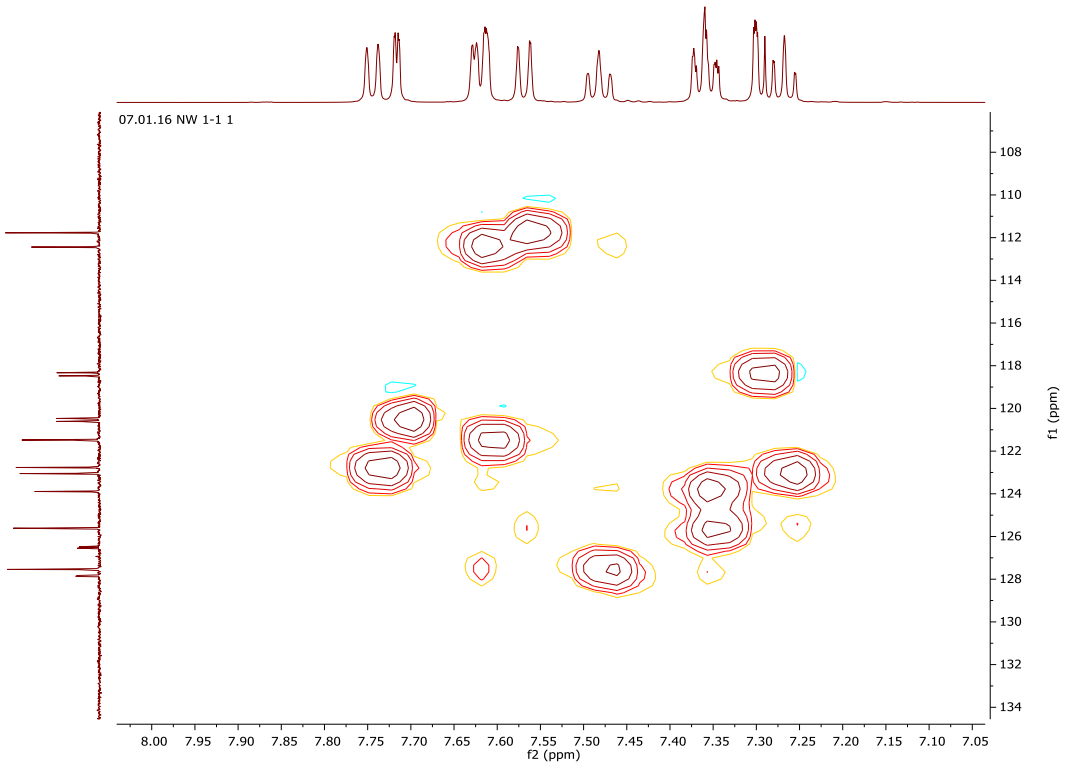


Figure S54: The ^{1} H - ^{13}C NMR spectra of the compounds **12** and **13**

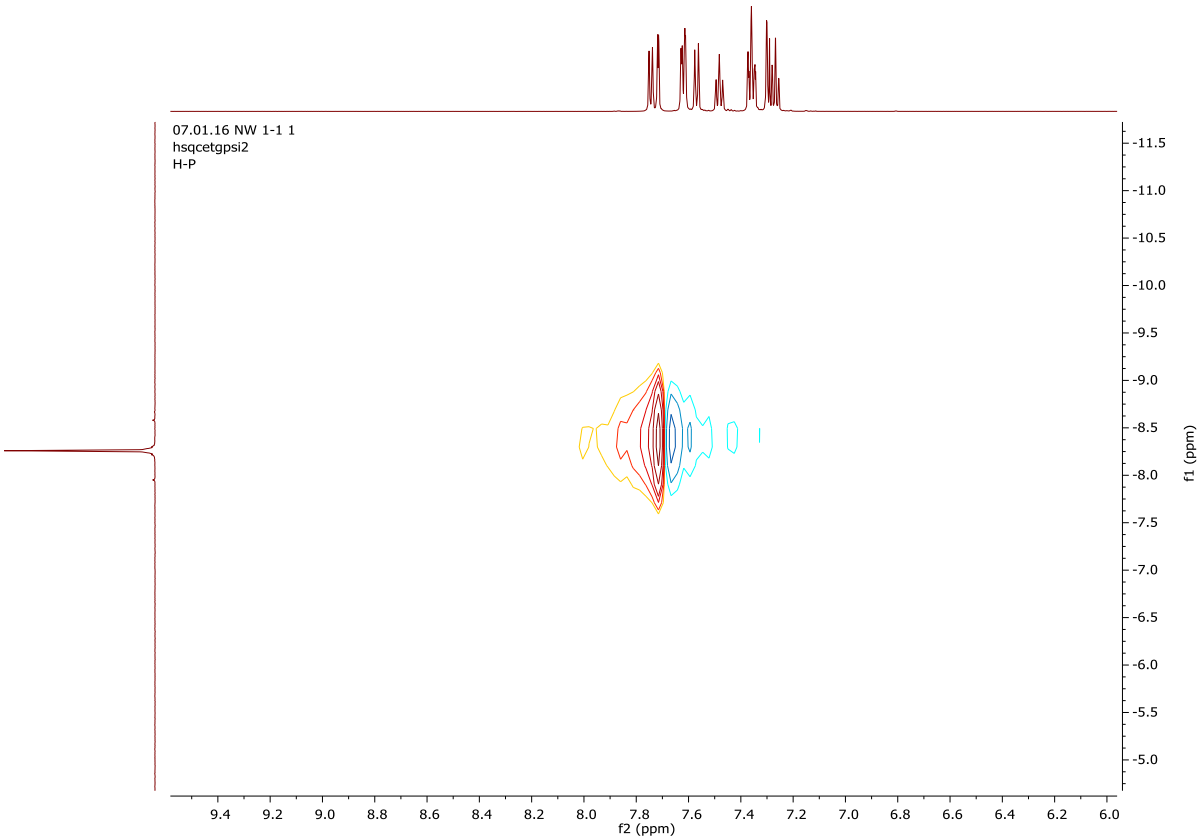


Figure S55: The ^{1}H - ^{31}P NMR spectra of the compounds **12** and **13**

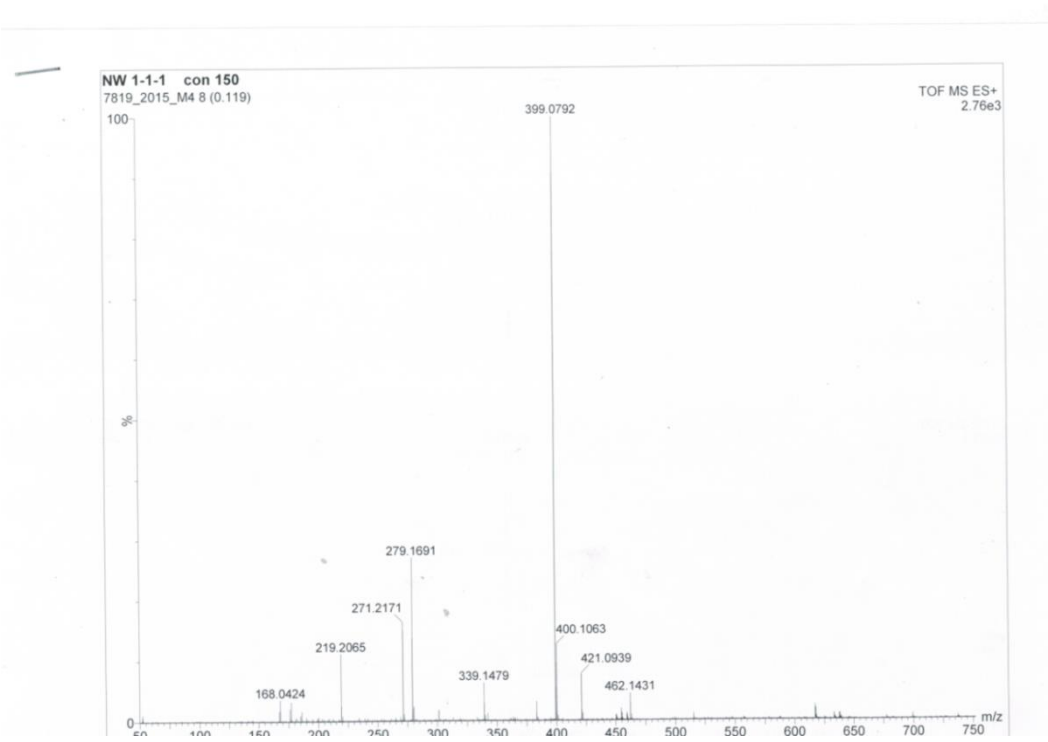
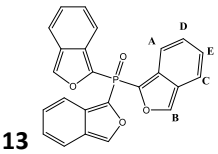


Figure S56: The HRMS NMR spectra of the compounds **12** and **13**



13

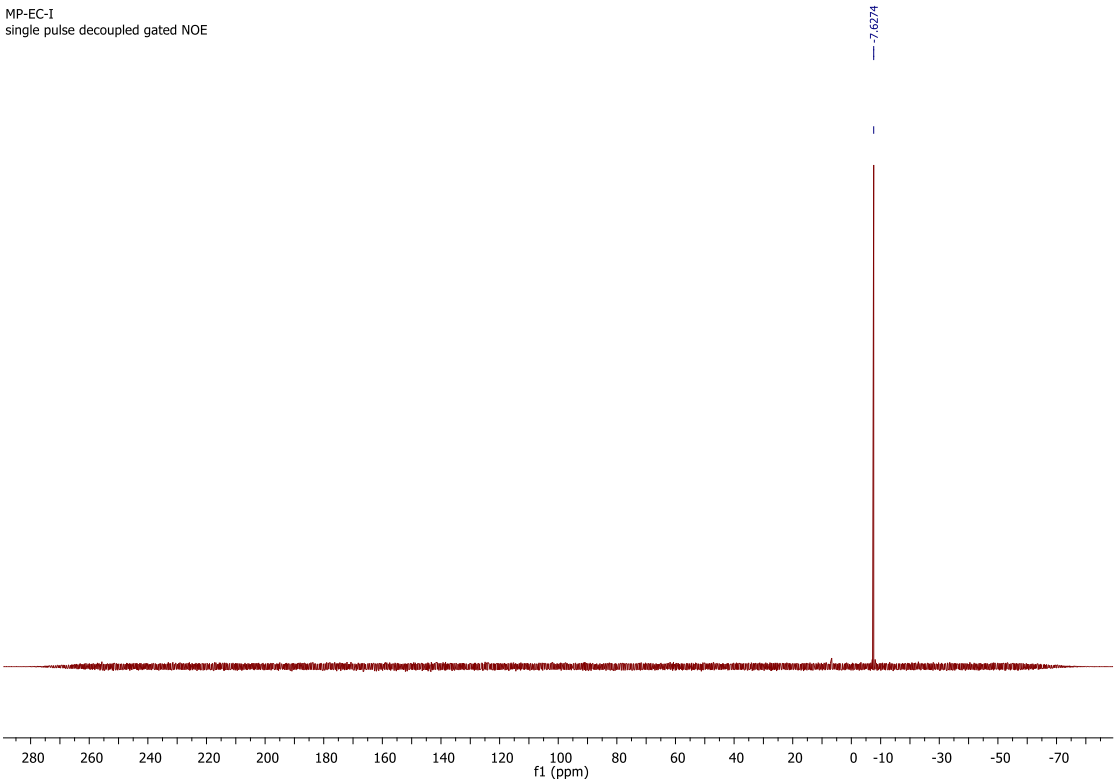


Figure S57: The ^{31}P NMR spectra of the compound **13**

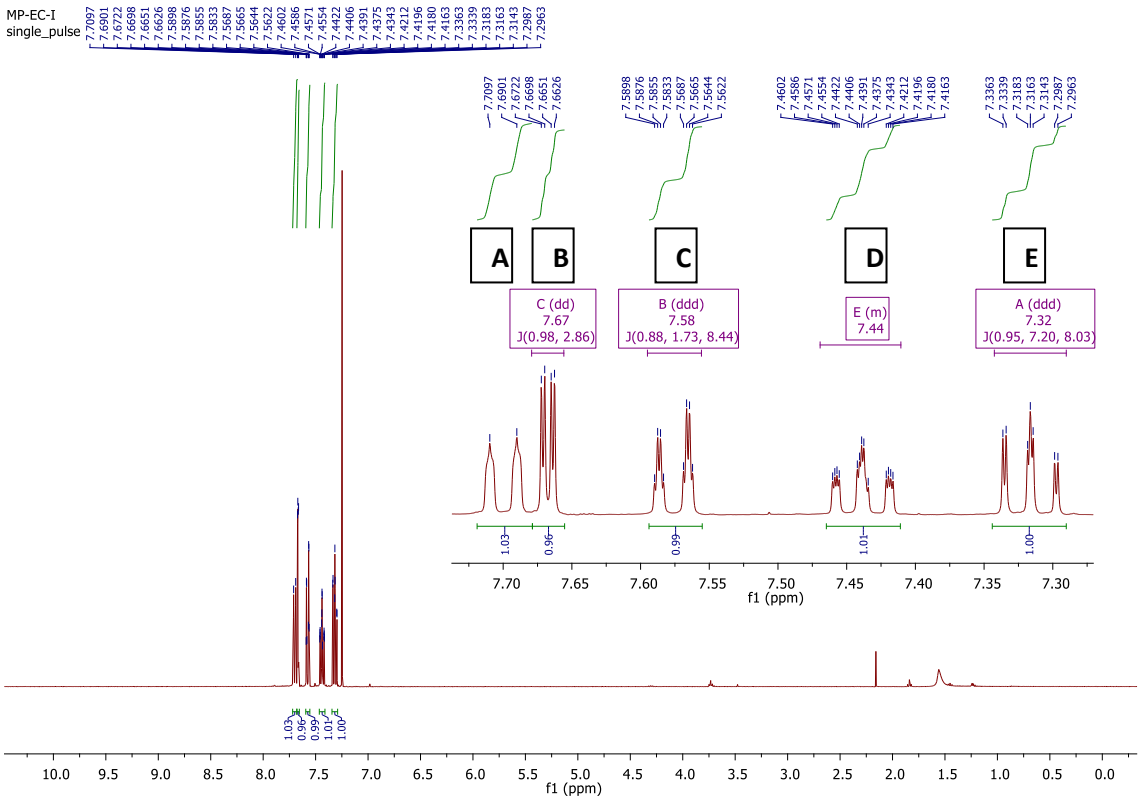


Figure S58: The [1] H NMR spectra of the compound **13**

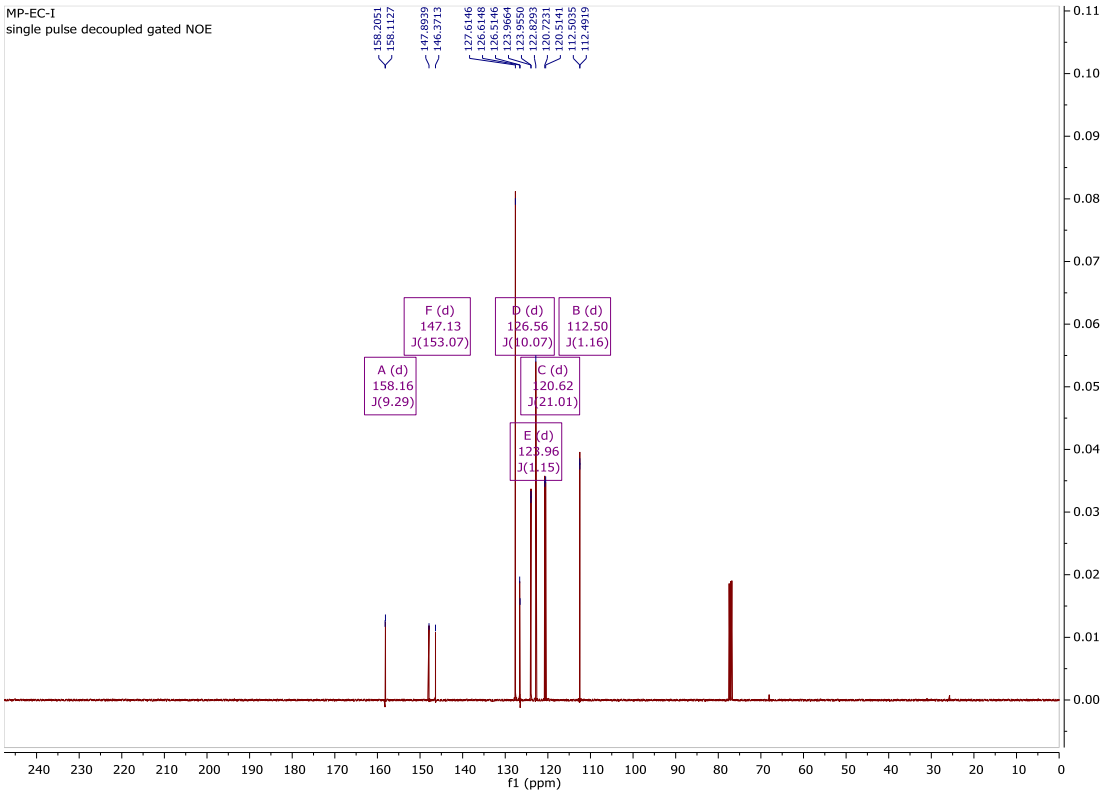


Figure S59: The [13] C NMR spectra of the compound **13**

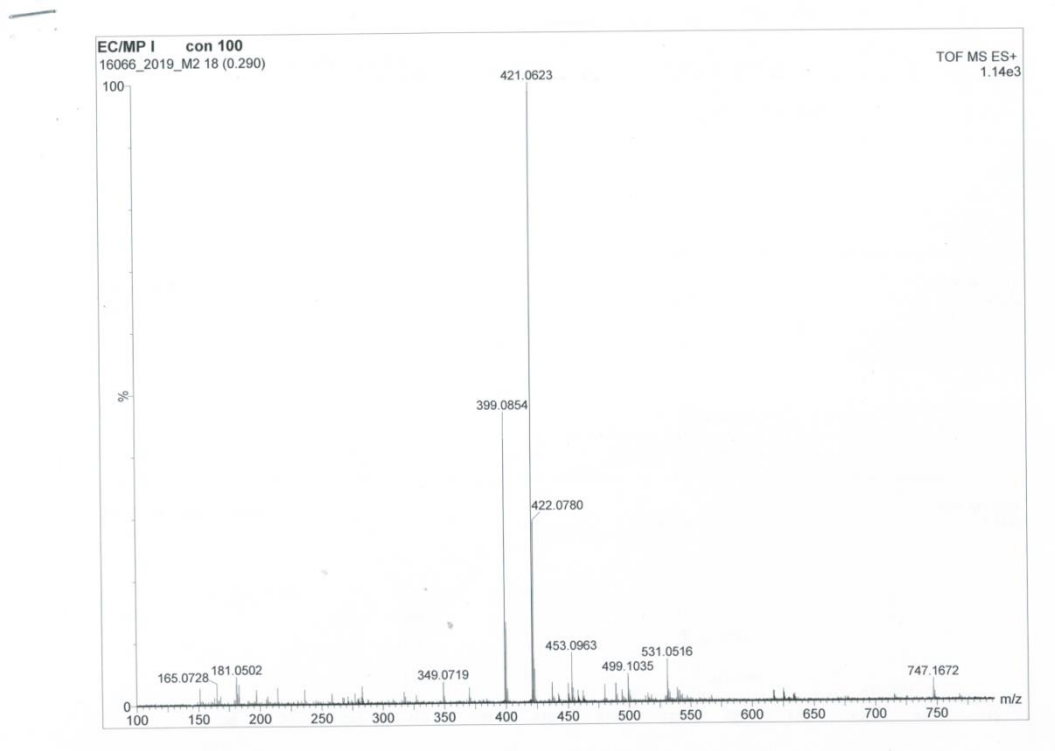
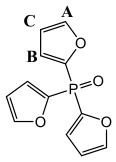


Figure S60: The HRMS spectra of the compound **13**



15

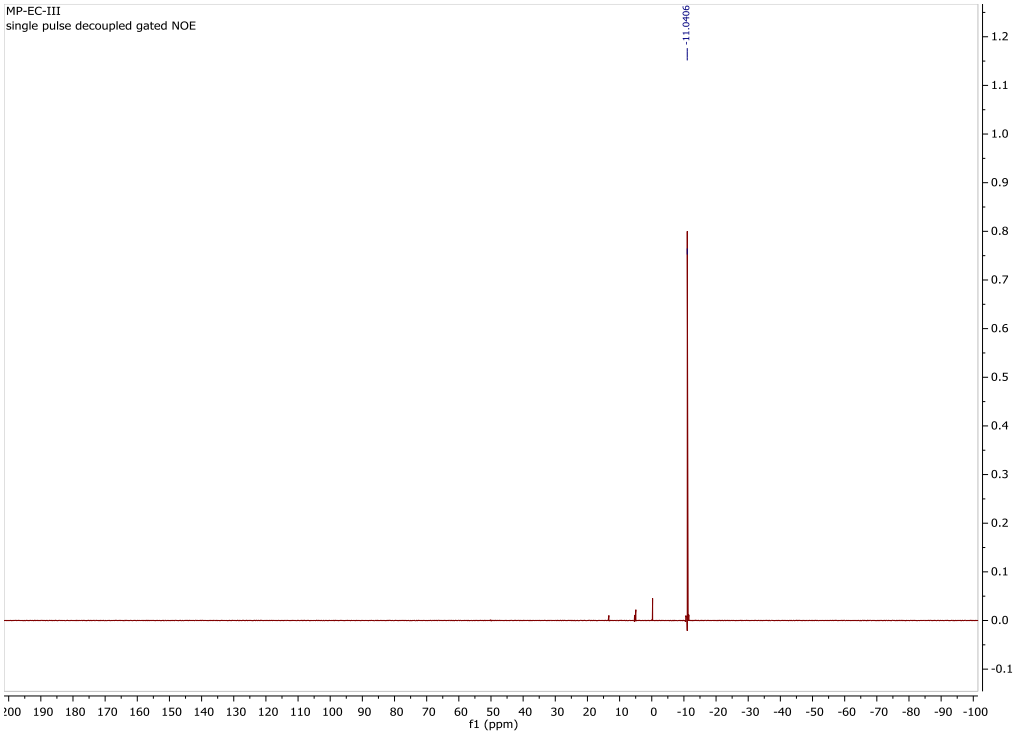


Figure S61: The ^{31} P NMR spectra of the compound **13**

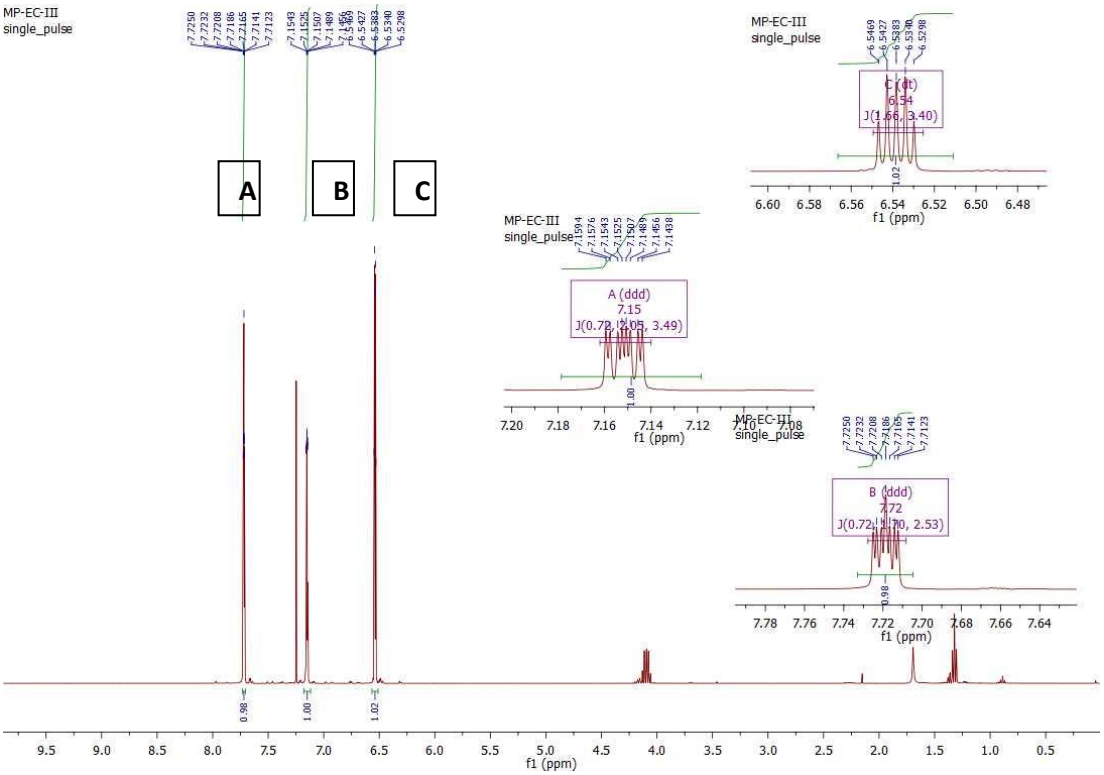


Figure S62: The [1] H NMR spectra of the compound **13**

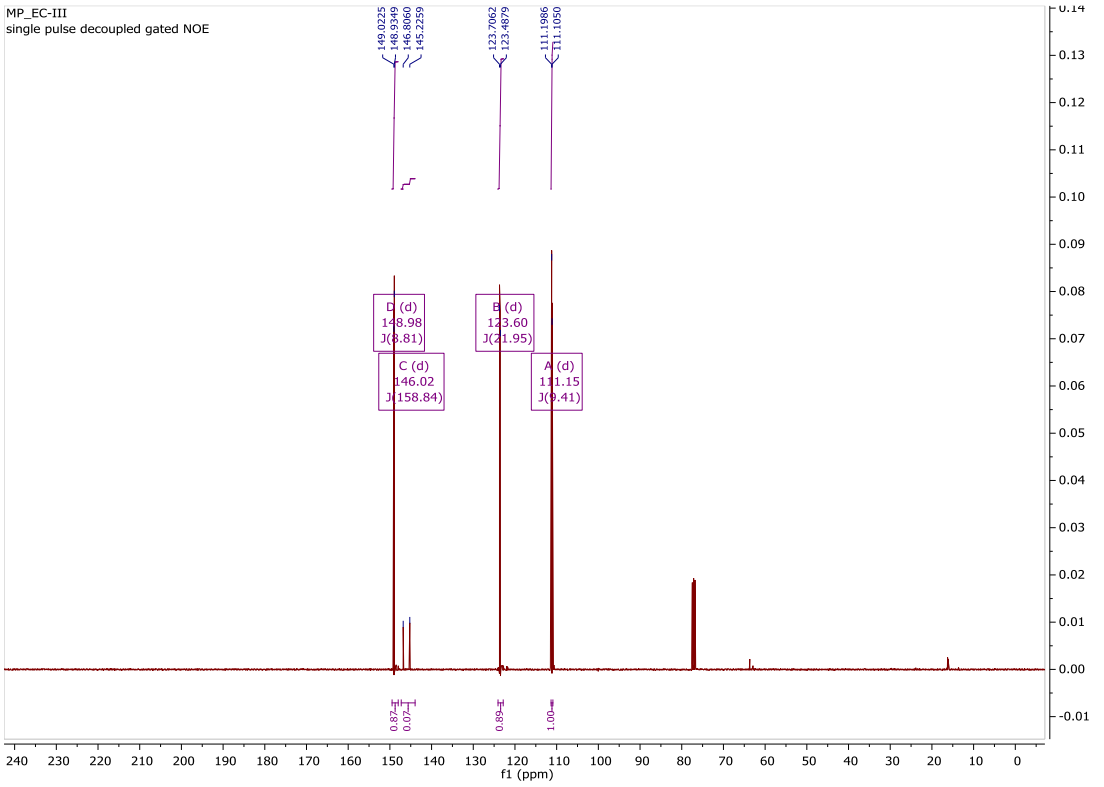


Figure S63: The [13] C NMR spectra of the compound **13**

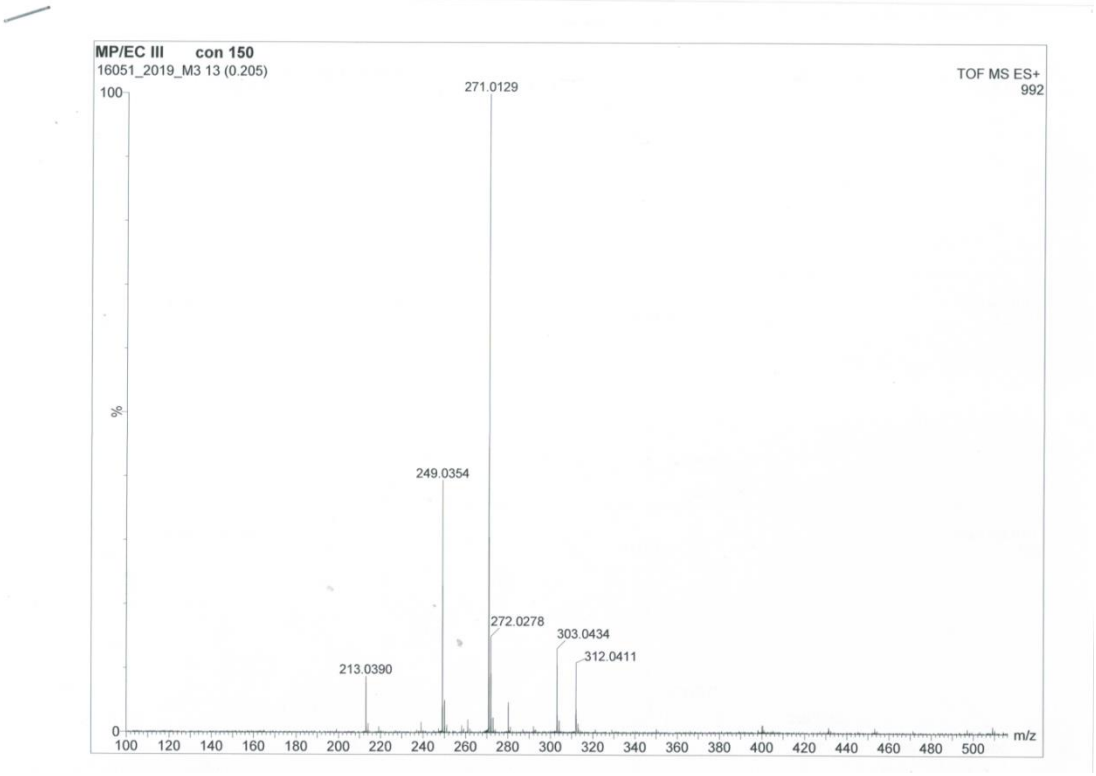
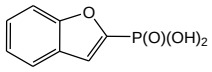


Figure S64: The HRMS spectra of the compound **13**

14



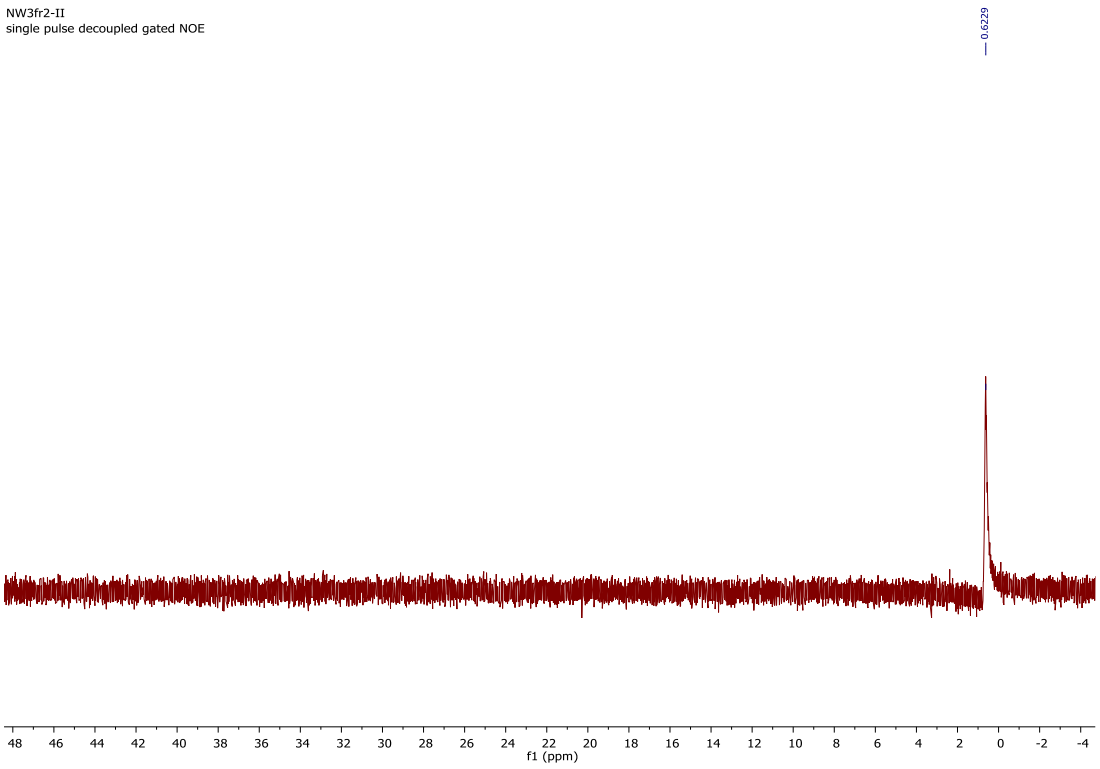


Figure S65: The ^{31}P NMR spectra of the compound **14**

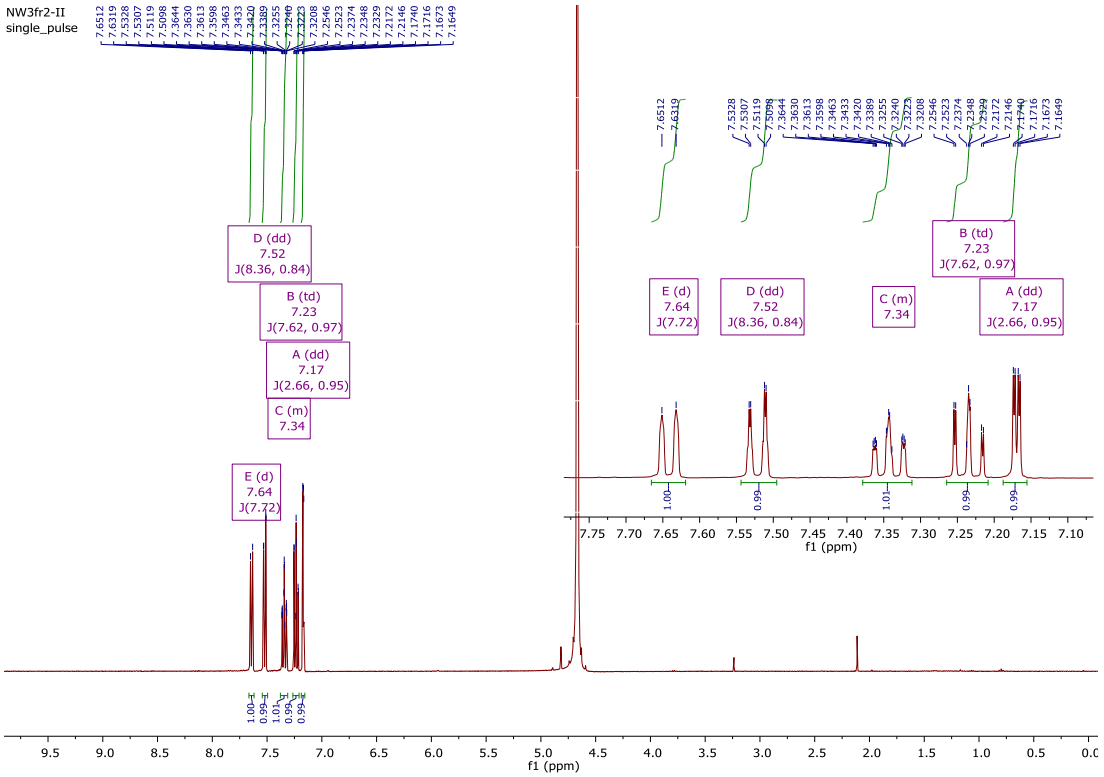


Figure S66: The [1] H NMR spectra of the compound **14**

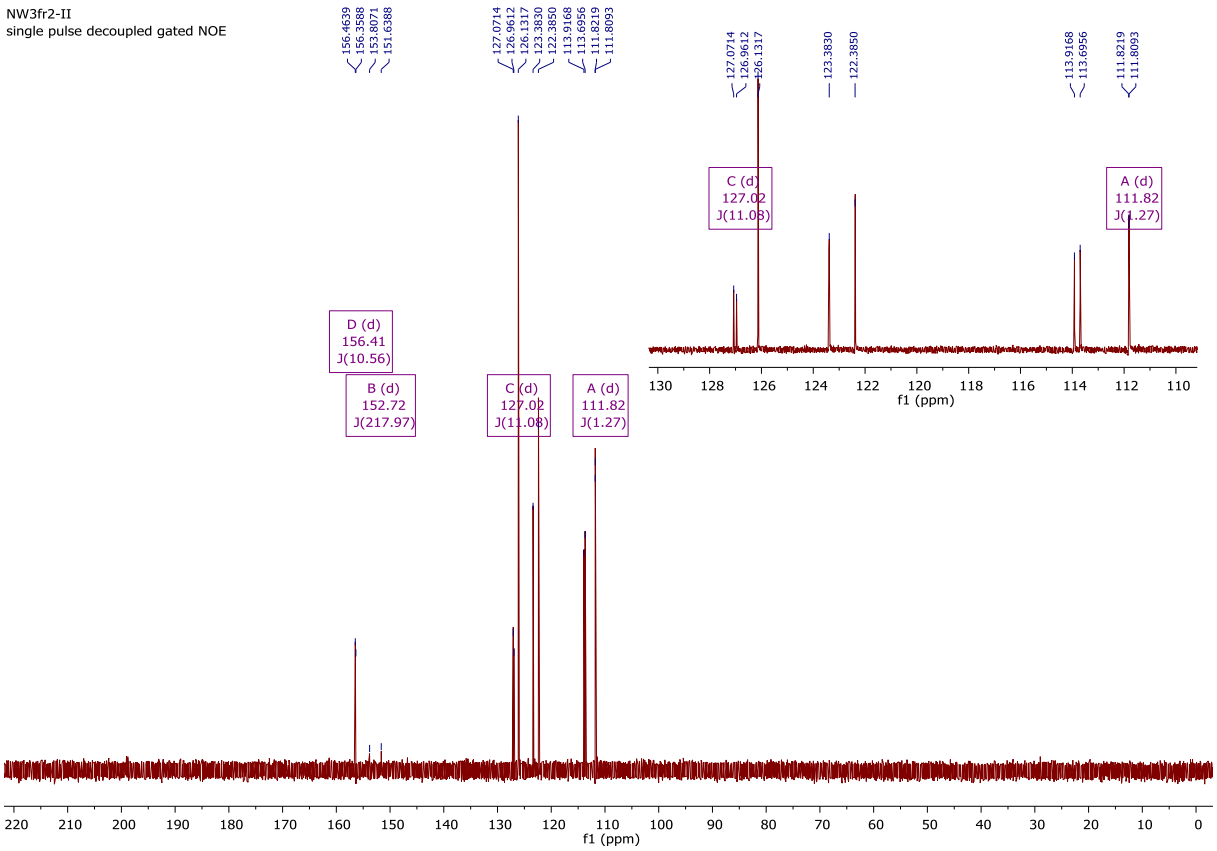


Figure S67: The [13] C NMR spectra of the compound **14**

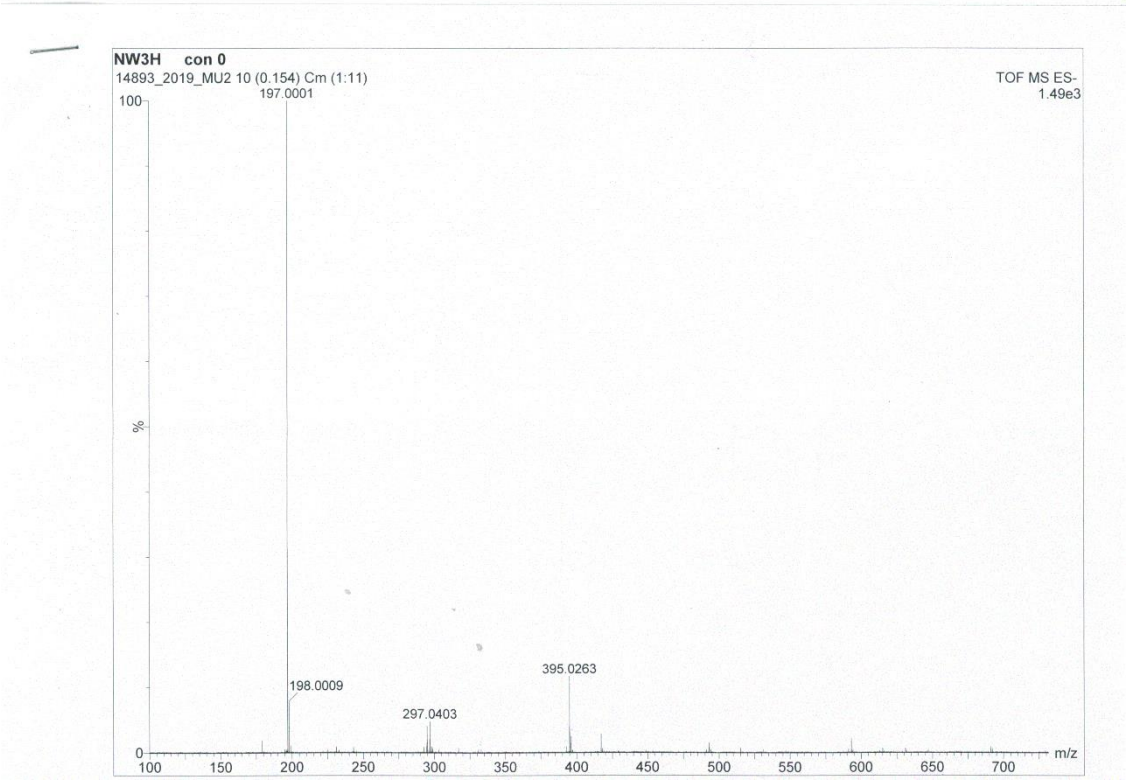
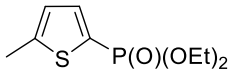


Figure S68: The HRMS spectra of the compound **14**

16



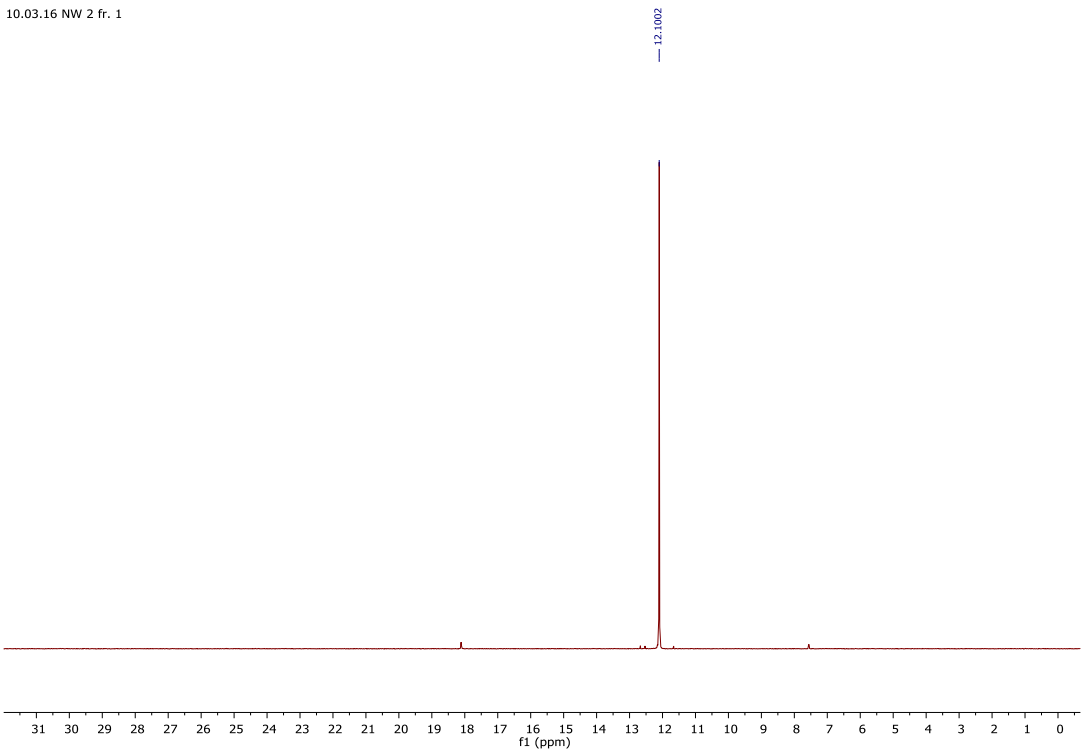


Figure S69: The ^{31}P NMR spectra of the compound **16**

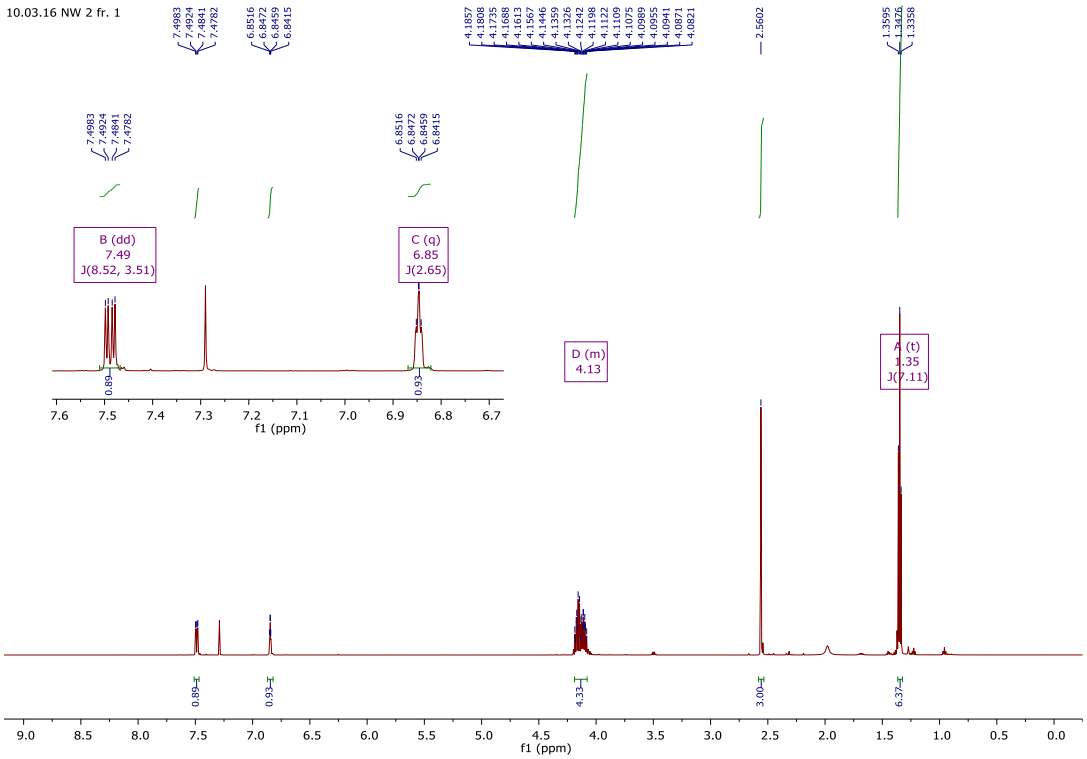


Figure S70: The [1] H NMR spectra of the compound **16**

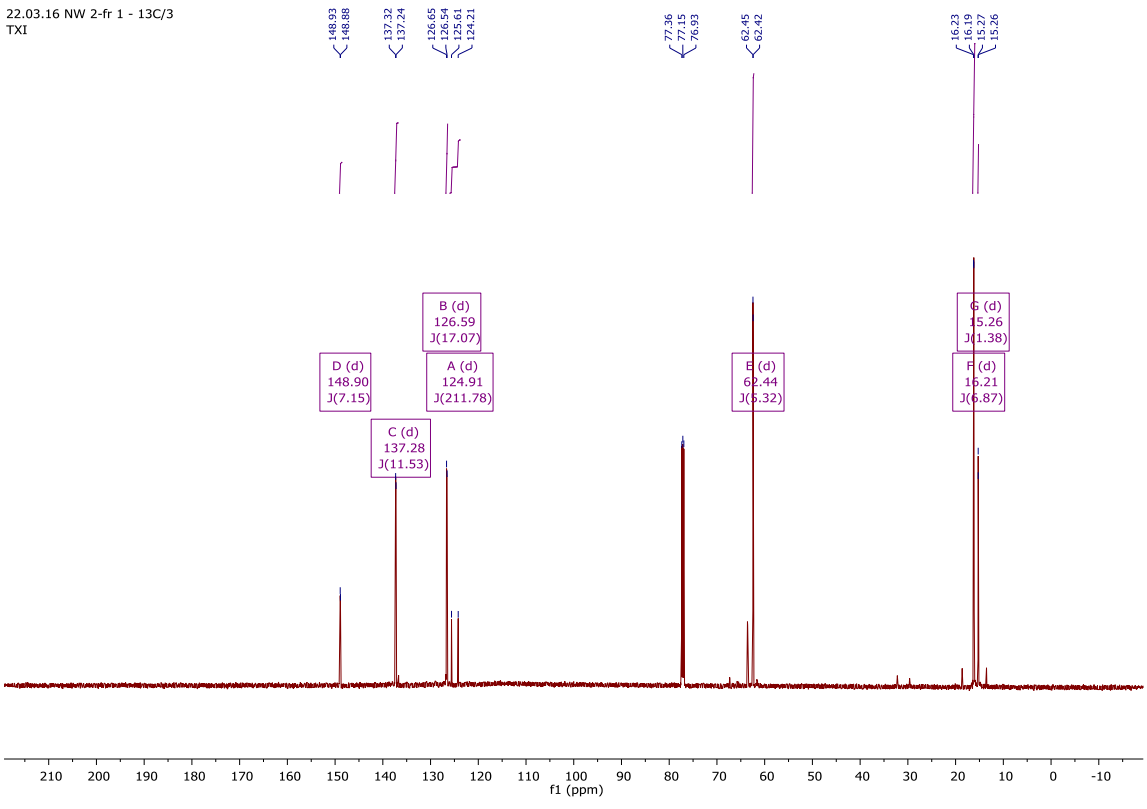


Figure S71: The [13] C NMR spectra of the compound **16**

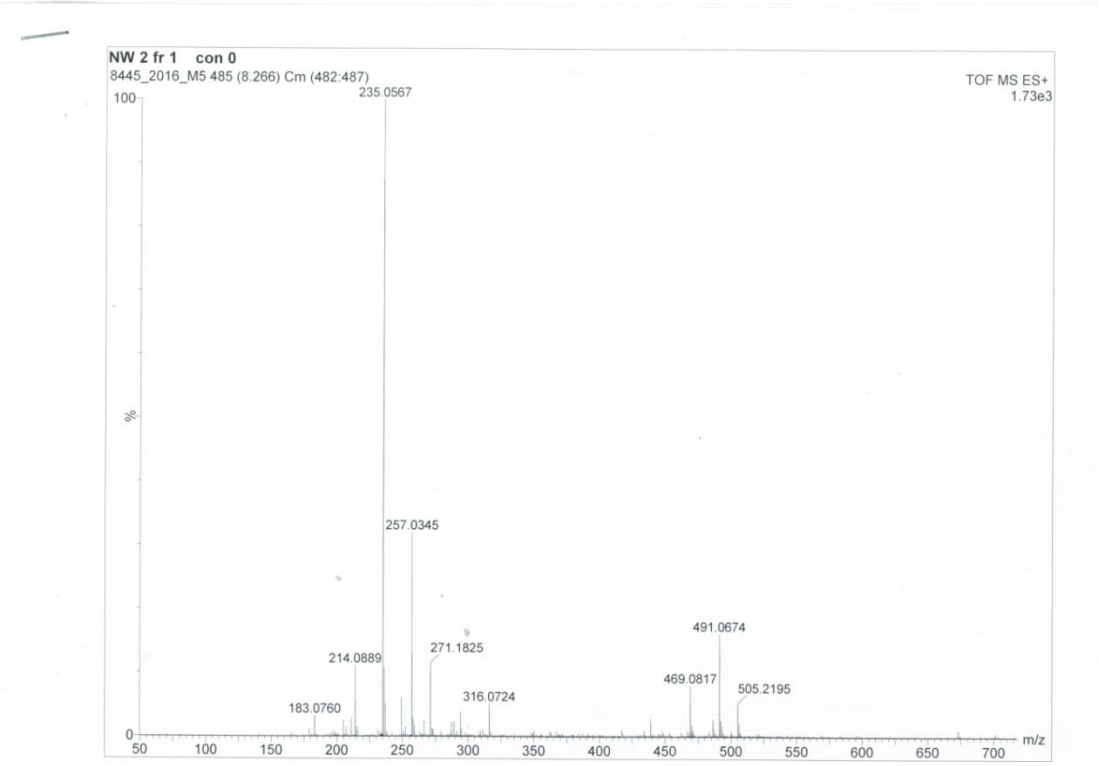
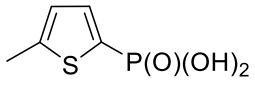


Figure S72: The HRMS spectra of the compound **16**

17



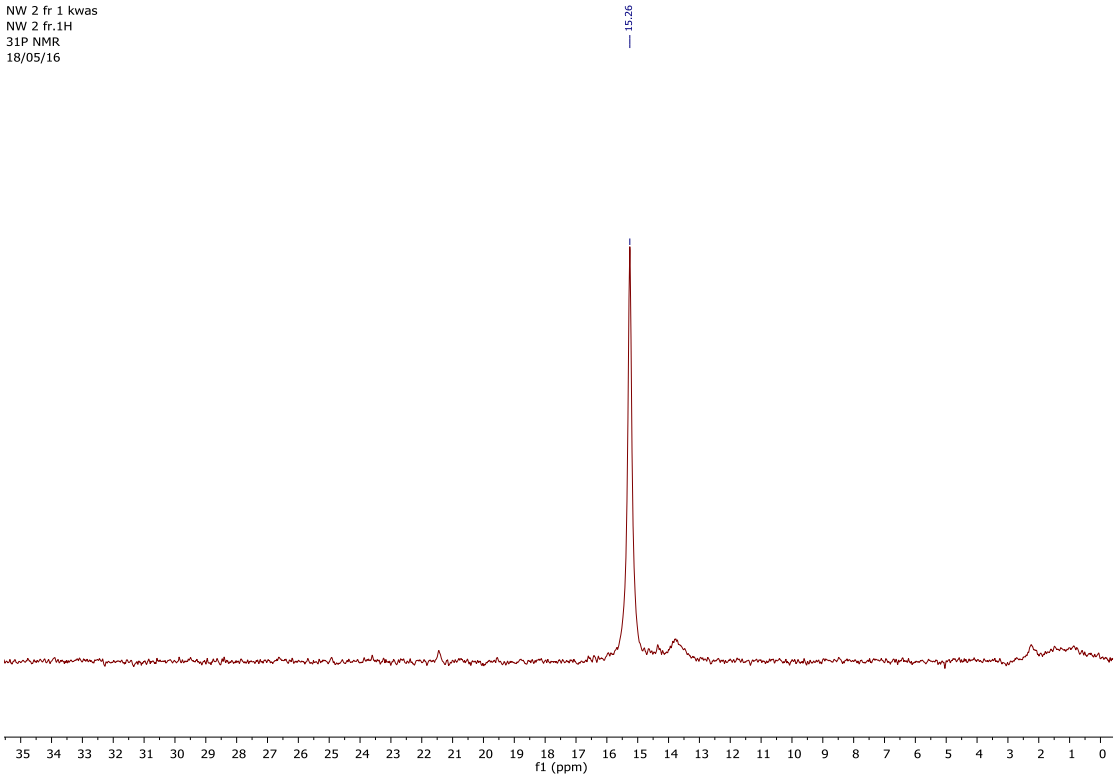


Figure S73: The ^{31} P NMR spectra of the compound **17**

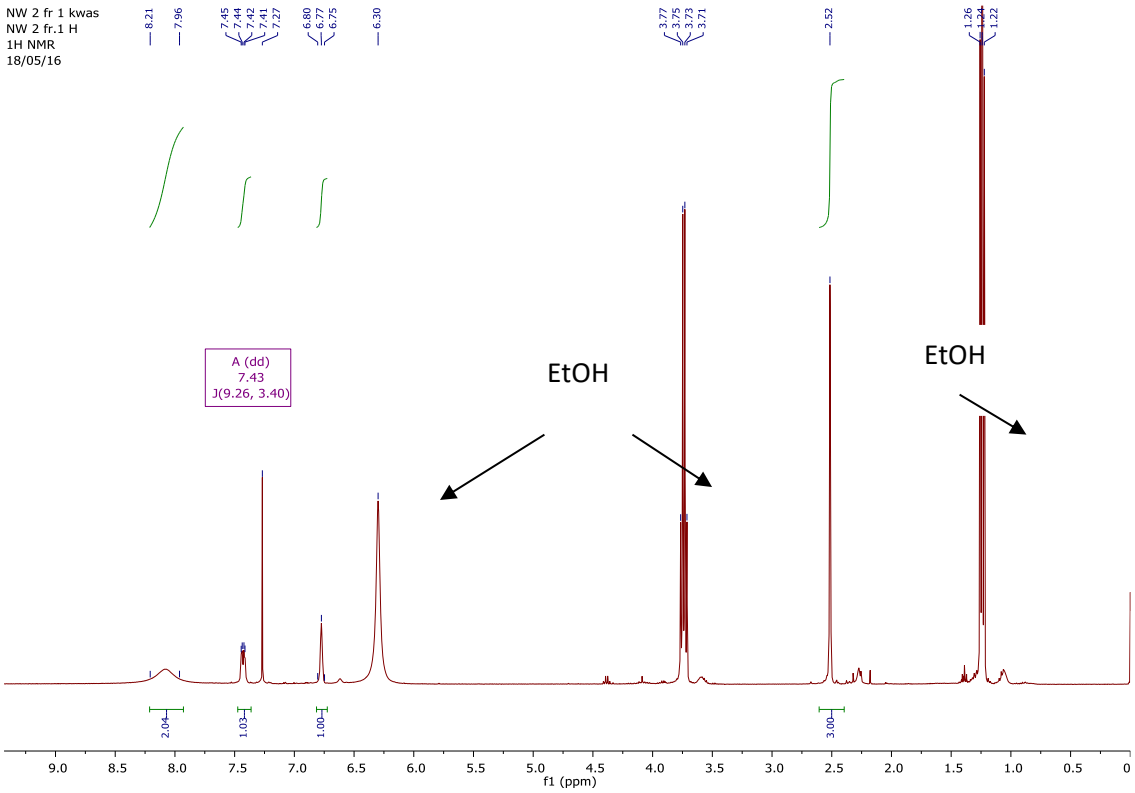


Figure S74: The ^{1}H NMR spectra of the compound **17**

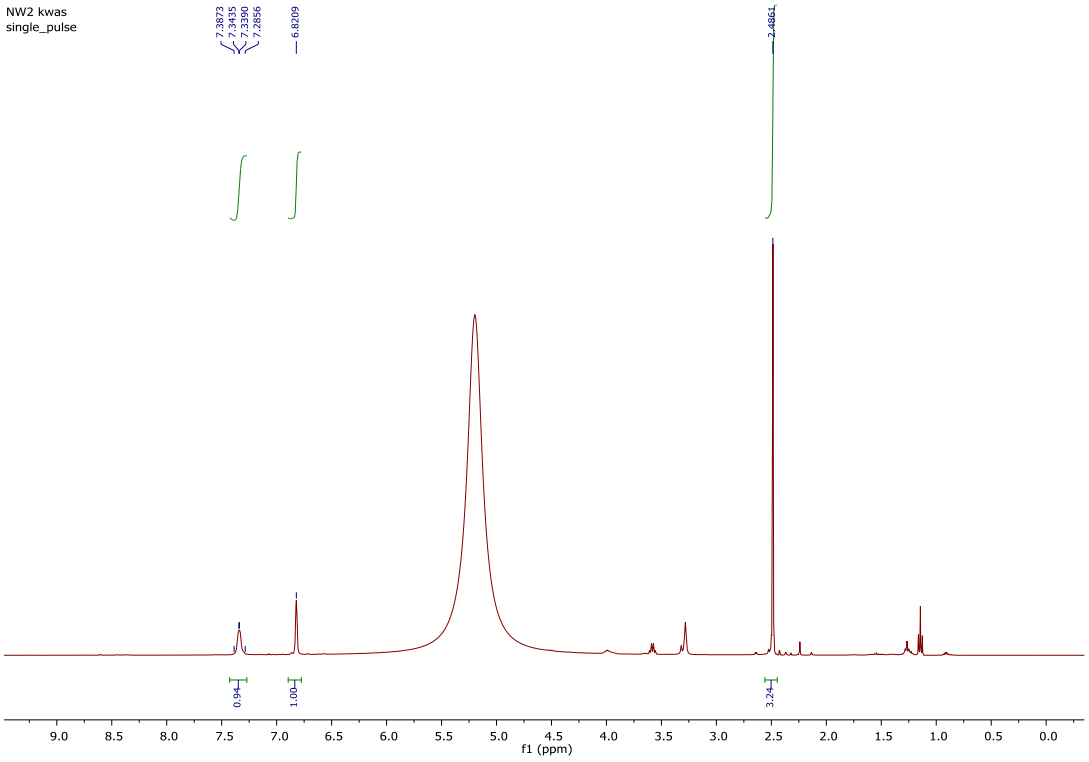


Figure S75: The ^{1}H NMR spectra of the compound **17**

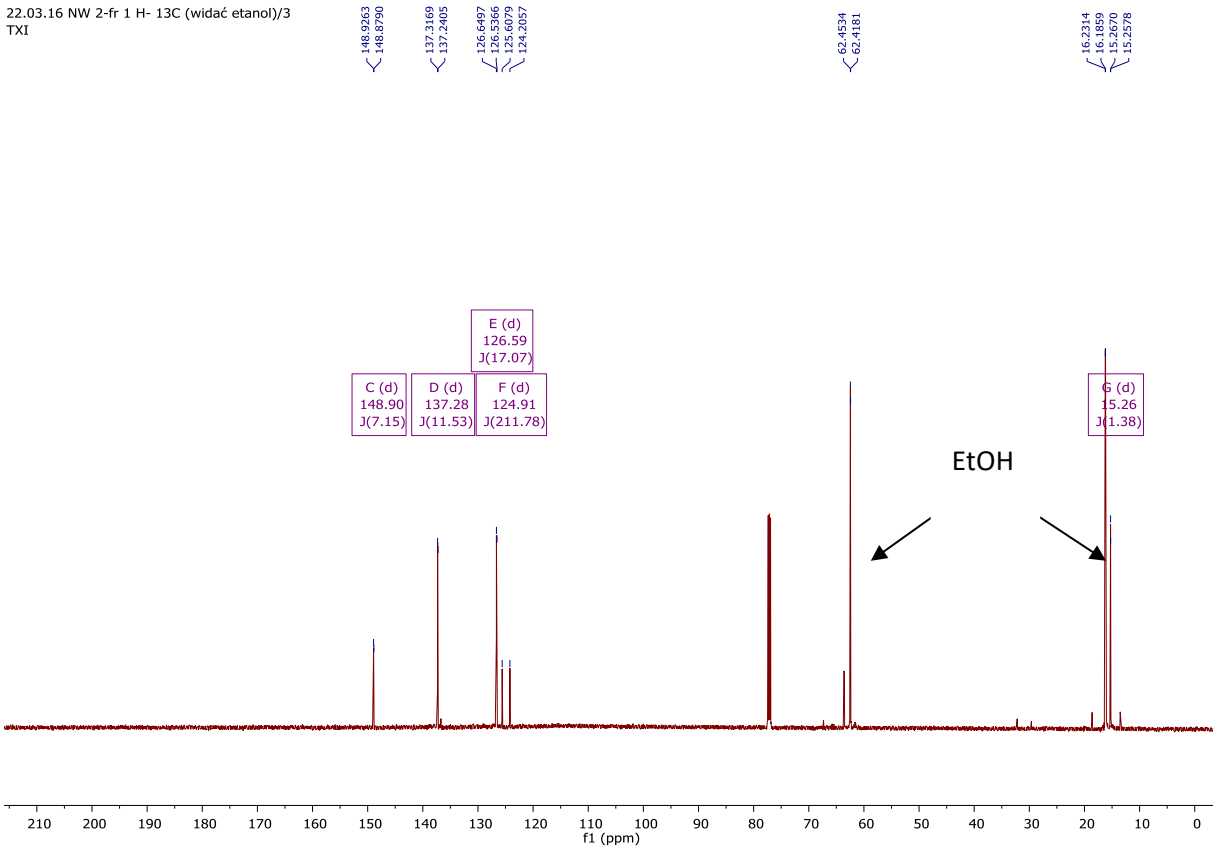


Figure S76: The ^{13} C NMR spectra of the compound **17**

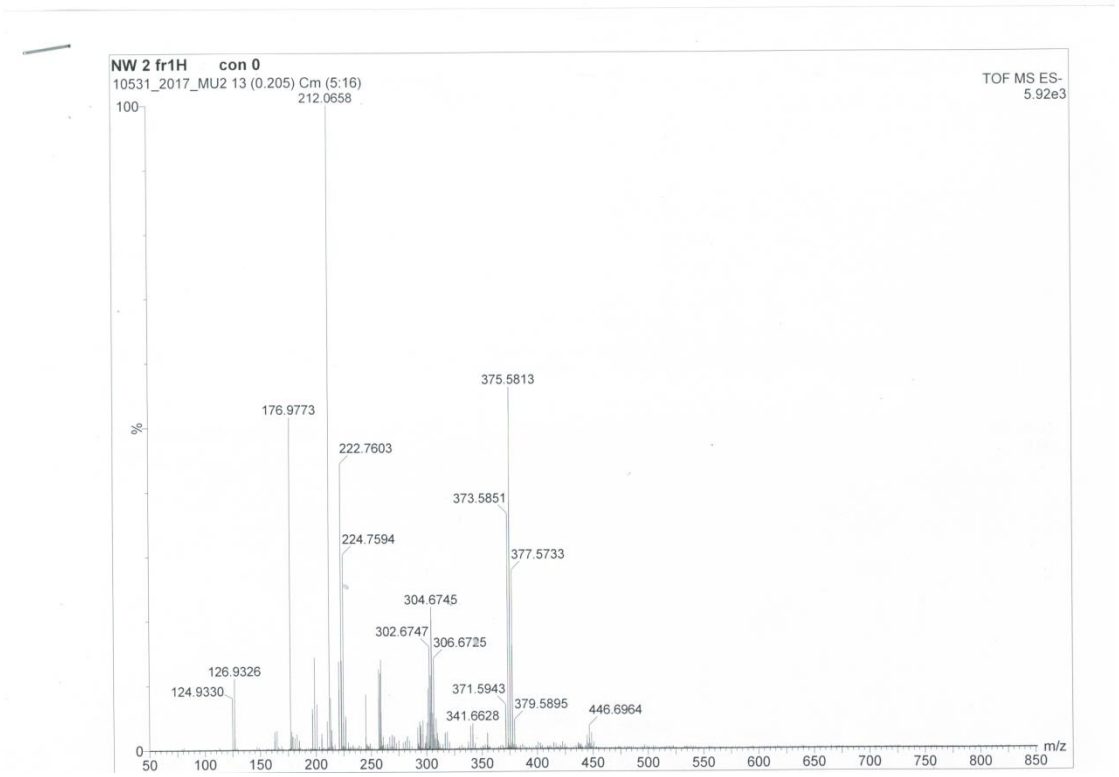


Figure S77: The CHRMS spectra of the compound **17**

Table S1: Relevant crystallographic data for the molecule and the full geometrical information (Å, º)

13			
P1—O1	1.447 (3)	C10—C11	1.437 (2)
P1—C1	1.7930 (19)	C10—H10	0.9300
P1—C17	1.7936 (19)	C11—C16	1.383 (2)
P1—C9	1.7947 (19)	C11—C12	1.400 (2)
O2—C8	1.382 (2)	C12—C13	1.375 (3)
O2—C1	1.404 (2)	C12—H12	0.9300
O3—C16	1.381 (2)	C13—C14	1.386 (3)
O3—C9	1.394 (2)	C13—H13	0.9300
O4—C24	1.380 (2)	C14—C15	1.370 (2)
O4—C17	1.384 (2)	C14—H14	0.9300
O5—H5A	1.08 (9)	C15—C16	1.382 (2)
O5—H5B	1.09 (7)	C15—H15	0.9300
C1—C2	1.338 (2)	C17—C18	1.336 (2)
C4—C5	1.374 (3)	C18—C19	1.430 (2)
C4—C3	1.406 (3)	C18—H18	0.9300
C4—H4	0.9300	C19—C24	1.377 (2)
C3—C8	1.382 (3)	C19—C20	1.403 (3)
C3—C2	1.437 (3)	C20—C21	1.388 (3)
C2—H2	0.9300	C20—H20	0.9300
C5—C6	1.388 (3)	C21—C22	1.393 (3)
C5—H5	0.9300	C21—H21	0.9300
C6—C7	1.382 (3)	C22—C23	1.362 (3)
C6—H6	0.9300	C22—H22	0.9300
C7—C8	1.382 (3)	C23—C24	1.381 (3)
C7—H7	0.9300	C23—H23	0.9300
C9—C10	1.342 (2)		
O1—P1—C1	115.48 (13)	C16—C11—C10	105.64 (16)
O1—P1—C17	119.54 (13)	C12—C11—C10	136.13 (19)
C1—P1—C17	101.55 (9)	C13—C12—C11	118.49 (19)
O1—P1—C9	113.30 (13)	C13—C12—H12	120.8
C1—P1—C9	103.49 (9)	C11—C12—H12	120.8
C17—P1—C9	101.24 (9)	C12—C13—C14	121.31 (19)
C8—O2—C1	105.36 (15)	C12—C13—H13	119.3
C16—O3—C9	105.62 (14)	C14—C13—H13	119.3
C24—O4—C17	105.37 (14)	C15—C14—C13	121.65 (19)
H5A—O5—H5B	113 (5)	C15—C14—H14	119.2
C2—C1—O2	110.94 (17)	C13—C14—H14	119.2
C2—C1—P1	129.31 (17)	C14—C15—C16	116.28 (19)
O2—C1—P1	119.73 (14)	C14—C15—H15	121.9
C5—C4—C3	118.3 (2)	C16—C15—H15	121.9
C5—C4—H4	120.9	O3—C16—C15	125.58 (18)
C3—C4—H4	120.9	O3—C16—C11	110.41 (16)

C8—C3—C4	118.5 (2)	C15—C16—C11	124.01 (18)
C8—C3—C2	105.92 (18)	C18—C17—O4	111.12 (17)
C4—C3—C2	135.5 (2)	C18—C17—P1	134.34 (16)
C1—C2—C3	107.37 (19)	O4—C17—P1	114.53 (13)
C1—C2—H2	126.3	C17—C18—C19	107.51 (17)
C3—C2—H2	126.3	C17—C18—H18	126.2
C4—C5—C6	121.5 (2)	C19—C18—H18	126.2
C4—C5—H5	119.2	C24—C19—C20	118.01 (19)
C6—C5—H5	119.2	C24—C19—C18	105.40 (17)
C7—C6—C5	121.6 (2)	C20—C19—C18	136.6 (2)
C7—C6—H6	119.2	C21—C20—C19	118.1 (2)
C5—C6—H6	119.2	C21—C20—H20	120.9
C6—C7—C8	116.1 (2)	C19—C20—H20	120.9
C6—C7—H7	122.0	C20—C21—C22	120.7 (2)
C8—C7—H7	122.0	C20—C21—H21	119.6
C3—C8—O2	110.40 (18)	C22—C21—H21	119.6
C3—C8—C7	124.1 (2)	C23—C22—C21	122.5 (2)
O2—C8—C7	125.5 (2)	C23—C22—H22	118.8
C10—C9—O3	110.96 (16)	C21—C22—H22	118.8
C10—C9—P1	130.01 (15)	C22—C23—C24	115.4 (2)
O3—C9—P1	118.88 (13)	C22—C23—H23	122.3
C9—C10—C11	107.33 (17)	C24—C23—H23	122.3
C9—C10—H10	126.3	C19—C24—O4	110.58 (17)
C11—C10—H10	126.3	C19—C24—C23	125.2 (2)
C16—C11—C12	118.22 (18)	O4—C24—C23	124.1 (2)
C8—O2—C1—C2	0.8 (2)	C10—C11—C12—C13	−179.1 (2)
C8—O2—C1—P1	179.29 (13)	C11—C12—C13—C14	−0.6 (3)
O1—P1—C1—C2	9.8 (2)	C12—C13—C14—C15	−1.3 (3)
C17—P1—C1—C2	−121.06 (19)	C13—C14—C15—C16	1.3 (3)
C9—P1—C1—C2	134.24 (19)	C9—O3—C16—C15	−179.29 (17)
O1—P1—C1—O2	−168.28 (17)	C9—O3—C16—C11	1.09 (19)
C17—P1—C1—O2	60.81 (16)	C14—C15—C16—O3	−178.86 (17)
C9—P1—C1—O2	−43.89 (16)	C14—C15—C16—C11	0.7 (3)
C5—C4—C3—C8	0.4 (3)	C12—C11—C16—O3	177.03 (16)
C5—C4—C3—C2	177.2 (2)	C10—C11—C16—O3	−1.8 (2)
O2—C1—C2—C3	−0.7 (2)	C12—C11—C16—C15	−2.6 (3)
P1—C1—C2—C3	−178.93 (14)	C10—C11—C16—C15	178.52 (17)
C8—C3—C2—C1	0.2 (2)	C24—O4—C17—C18	0.4 (2)
C4—C3—C2—C1	−176.9 (2)	C24—O4—C17—P1	179.45 (12)
C3—C4—C5—C6	−0.4 (3)	O1—P1—C17—C18	−122.2 (2)
C4—C5—C6—C7	0.6 (4)	C1—P1—C17—C18	6.2 (2)
C5—C6—C7—C8	−0.6 (3)	C9—P1—C17—C18	112.7 (2)
C4—C3—C8—O2	177.98 (16)	O1—P1—C17—O4	59.10 (19)
C2—C3—C8—O2	0.3 (2)	C1—P1—C17—O4	−172.55 (13)
C4—C3—C8—C7	−0.5 (3)	C9—P1—C17—O4	−66.08 (14)
C2—C3—C8—C7	−178.15 (18)	O4—C17—C18—C19	0.2 (2)
C1—O2—C8—C3	−0.7 (2)	P1—C17—C18—C19	−178.62 (15)
C1—O2—C8—C7	177.74 (19)	C17—C18—C19—C24	−0.7 (2)

C6—C7—C8—C3	0.6 (3)	C17—C18—C19—C20	178.7 (2)
C6—C7—C8—O2	−177.61 (18)	C24—C19—C20—C21	0.0 (3)
C16—O3—C9—C10	0.2 (2)	C18—C19—C20—C21	−179.3 (2)
C16—O3—C9—P1	−175.86 (12)	C19—C20—C21—C22	0.9 (3)
O1—P1—C9—C10	17.1 (2)	C20—C21—C22—C23	−1.0 (3)
C1—P1—C9—C10	−108.72 (19)	C21—C22—C23—C24	0.2 (3)
C17—P1—C9—C10	146.35 (18)	C20—C19—C24—O4	−178.54 (16)
O1—P1—C9—O3	−167.76 (16)	C18—C19—C24—O4	0.9 (2)
C1—P1—C9—O3	66.44 (15)	C20—C19—C24—C23	−0.9 (3)
C17—P1—C9—O3	−38.49 (15)	C18—C19—C24—C23	178.6 (2)
O3—C9—C10—C11	−1.3 (2)	C17—O4—C24—C19	−0.9 (2)
P1—C9—C10—C11	174.16 (14)	C17—O4—C24—C23	−178.54 (19)
C9—C10—C11—C16	1.9 (2)	C22—C23—C24—C19	0.8 (3)
C9—C10—C11—C12	−176.7 (2)	C22—C23—C24—O4	178.13 (19)
C16—C11—C12—C13	2.5 (3)		
15			
P1—O1	1.4843 (16)	C3—H3	0.9300
P1—C5	1.774 (2)	C4—H4	0.9300
P1—C9	1.777 (2)	C5—C6	1.355 (3)
P1—C1	1.788 (2)	C6—C7	1.423 (4)
O2—C4	1.372 (3)	C6—H6	0.9300
O2—C1	1.380 (2)	C7—C8	1.341 (4)
O3—C8	1.357 (3)	C7—H7	0.9300
O3—C5	1.377 (3)	C8—H8	0.9300
O4—C12	1.366 (3)	C9—C10	1.345 (4)
O4—C9	1.374 (3)	C10—C11	1.420 (4)
C1—C2	1.340 (3)	C10—H10	0.9300
C2—C3	1.425 (3)	C11—C12	1.332 (4)
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.339 (3)	C12—H12	0.9300
O1—P1—C5	115.84 (11)	O3—C5—P1	115.52 (15)
O1—P1—C9	111.50 (11)	C5—C6—C7	106.4 (2)
C5—P1—C9	104.79 (11)	C5—C6—H6	126.8
O1—P1—C1	110.82 (10)	C7—C6—H6	126.8
C5—P1—C1	105.84 (11)	C8—C7—C6	106.5 (2)
C9—P1—C1	107.50 (11)	C8—C7—H7	126.7
C4—O2—C1	105.79 (16)	C6—C7—H7	126.7
C8—O3—C5	106.22 (17)	C7—C8—O3	111.0 (2)
C12—O4—C9	106.0 (2)	C7—C8—H8	124.5
C2—C1—O2	110.05 (18)	O3—C8—H8	124.5
C2—C1—P1	132.50 (17)	C10—C9—O4	109.8 (2)
O2—C1—P1	117.42 (15)	C10—C9—P1	129.7 (2)
C1—C2—C3	107.03 (19)	O4—C9—P1	120.43 (18)
C1—C2—H2	126.5	C9—C10—C11	106.7 (2)
C3—C2—H2	126.5	C9—C10—H10	126.6
C4—C3—C2	106.3 (2)	C11—C10—H10	126.6
C4—C3—H3	126.8	C12—C11—C10	106.6 (2)

C2—C3—H3	126.8	C12—C11—H11	126.7
C3—C4—O2	110.8 (2)	C10—C11—H11	126.7
C3—C4—H4	124.6	C11—C12—O4	110.8 (2)
O2—C4—H4	124.6	C11—C12—H12	124.6
C6—C5—O3	109.8 (2)	O4—C12—H12	124.6
C6—C5—P1	134.64 (19)		
C4—O2—C1—C2	0.3 (2)	C1—P1—C5—O3	−62.84 (18)
C4—O2—C1—P1	−178.03 (17)	O3—C5—C6—C7	0.3 (3)
O1—P1—C1—C2	−7.3 (3)	P1—C5—C6—C7	−179.7 (2)
C5—P1—C1—C2	119.0 (3)	C5—C6—C7—C8	−0.3 (3)
C9—P1—C1—C2	−129.4 (3)	C6—C7—C8—O3	0.1 (3)
O1—P1—C1—O2	170.58 (15)	C5—O3—C8—C7	0.1 (3)
C5—P1—C1—O2	−63.07 (18)	C12—O4—C9—C10	1.0 (3)
C9—P1—C1—O2	48.5 (2)	C12—O4—C9—P1	178.51 (18)
O2—C1—C2—C3	−0.4 (3)	O1—P1—C9—C10	−9.1 (3)
P1—C1—C2—C3	177.62 (19)	C5—P1—C9—C10	−135.2 (2)
C1—C2—C3—C4	0.3 (3)	C1—P1—C9—C10	112.5 (3)
C2—C3—C4—O2	−0.1 (3)	O1—P1—C9—O4	173.96 (18)
C1—O2—C4—C3	−0.1 (3)	C5—P1—C9—O4	47.9 (2)
C8—O3—C5—C6	−0.3 (2)	C1—P1—C9—O4	−64.4 (2)
C8—O3—C5—P1	179.76 (16)	O4—C9—C10—C11	−1.0 (3)
O1—P1—C5—C6	−119.5 (2)	P1—C9—C10—C11	−178.2 (2)
C9—P1—C5—C6	3.8 (3)	C9—C10—C11—C12	0.6 (3)
C1—P1—C5—C6	117.2 (3)	C10—C11—C12—O4	0.0 (3)
O1—P1—C5—O3	60.38 (19)	C9—O4—C12—C11	−0.6 (3)
C9—P1—C5—O3	−176.31 (16)		

Table S2: Selected hydrogen-bond parameters

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
13				
O5—H5A···O1^{i}	1.08 (9)	1.91 (9)	2.862 (3)	145 (7)
C2—H2···O5	0.93	2.45	3.190 (3)	136.5
15				
C2—H2···O2^{ii}	0.93	2.44	3.348 (3)	165.6
C4—H4···O1^{iii}	0.93	2.49	3.286 (3)	143.5
C7—H7···O3^{iv}	0.93	2.65	3.342 (3)	132.1
C6—H6···O1^{v}	0.93	2.47	3.373 (3)	164.7
C8—H8···O1^{vi}	0.93	2.39	3.264 (3)	155.7

Symmetry code(s): (i) *y*+1/3, −*x*+*y*+2/3, −*z*+2/3; (ii) −*x*+1, *y*+1/2, −*z*+1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2; (iv) *x*+1/2, −*y*+1/2, −*z*+1; (v) −*x*+2, *y*−1/2, −*z*+1/2; (vi) −*x*+3/2, −*y*+1, *z*+1/2.