Synthesis of the first metal-free phosphanylphosphonate and its use in the "phospha-Wittig-Horner" Reaction

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Supporting Information

Experimental Details

Synthesis of phosphaalkene 4 via the phospha-Wittig-Horner reaction – pWH reagent (0.25 mmol, 104 mg) was exposed to the reaction conditions as specified in the main manuscript and the reaction mixture purified by column chromatography (silica gel, heptane/ethyl acetate, 4:1) to give a mixture of isomers (yellow solid). Yield: 69 mg, 71%. The chemical shifts of *E*-**4** match the NMR data reported in the literature.[1] ^{1}H NMR and ^{31}P NMR data for *Z*-**4** were however detectable from the spectrum of the pure isomeric mixture (Appendices, Figure S4): ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 7.79 (d, $^2J_{H\text{-}P}$ = 36.9 Hz, 1H, P=C*H*), 7.63 (s, 2H), 7.19 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 2H, Ar*H*), 6.20 (d, $^4J_{H\text{-}P}$ = 8.5, 2.2 Hz, 2H, Ar*H*), 1.43 (s, 18H), 1.40 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 265.3 (s).

Both column chromatography and oxalyl chloride treatment were tested as the purification processes. The former afforded pure phosphaalkene **4** as a mixture of isomers but the proportion of the *Z* isomer increased after the purification. The latter gave the phosphaalkene products with high *E*-selectivity without changing the *E/Z* ratio through the purification process (Figure S1), although some traces of unknown impurities was detectable. It is noteworthy that 4-cyanobenzaldehyde does not dissolve in pentane and was filtered off before the addition of oxalyl chloride.

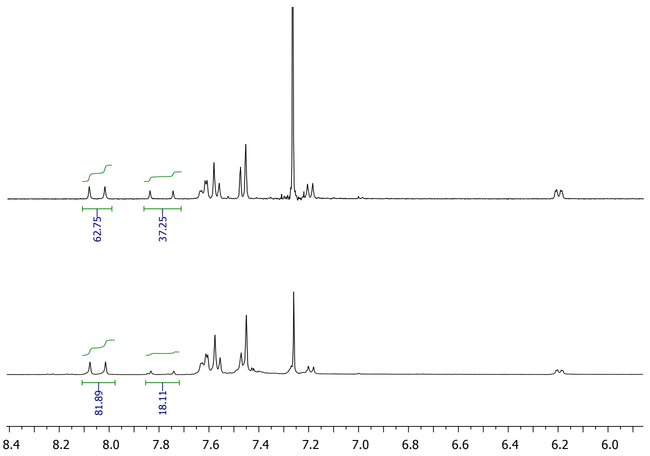


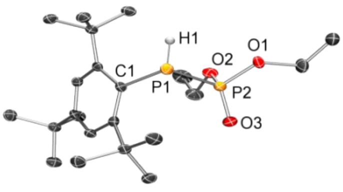
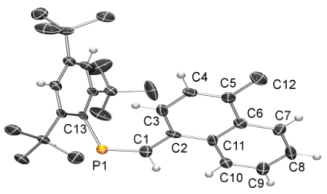
Figure S1 – ^{1}H NMR spectra of **4** in two different reactions, purified with column chromatography (top) or oxalyl chloride treatment (bottom). The doublets at 8.04 and 7.79 ppm correspond to the P=C*H* of *E*-**4** and *Z*-**4**, respectively. According to the integration of these protons, it is clearly shown that oxalyl chloride addition keeps the *E*-stereoselectivity high even after the purification.

Synthesis of phosphaalkene 6[2] **via the phospha-Wittig-Horner reaction –** pWH reagent (0.25 mmol, 104 mg) was applied to the reaction conditions to give a crude mixture which was chromatographed on silica gel using pentane/ethyl acetate, 95:5, as the eluent. Final product was isolated as yellow solid with small impurity of *Z*-**6**. Yield: 53 mg, 65%. ^{1}H NMR ($CDCl_3$, 399.8 MHz): δ 8.12 (d, $^2J_{H\text{-}P}$ = 24.0 Hz, 1H, P=C*H*), 7.44 (s, 2H, Ar*H*), 7.17 (d, $^3J_{H\text{-}H}$ = 5.4 Hz, 1H), 6.92-6.99 (m, 2H), 1.53 (s, 18H, *ortho*-C(C*H*$_3$)), 1.35 (s, 9H, *para*- C(C*H*$_3$)). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz): δ 246.8 (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz): δ 166.2 (d, $^1J_{C\text{-}P}$ = 30.8 Hz, P=*C*), 154.3 (d, $^3J_{C\text{-}P}$ = 1.2 Hz, *ortho*-Ar*C*), 150.0 (s, *para*-Ar*C*), 145.3 (d, $^2J_{C\text{-}P}$ = 17.3 Hz, Thienyl-*C*), 138.5 (d, $^1J_{C\text{-}P}$ = 53.1 Hz, *ipso*-Ar*C*), 127.8 (d, *J* = 4.2 Hz), 125.6 (d, *J* = 22.7 Hz), 125.0 (d, $J_{C\text{-}P}$ = 14.2 Hz, Thienyl-*C*), 121.9 (d, $^3J_{C\text{-}P}$ = 1.4 Hz, *meta*-Ar*C*), 38.4 (s, *ortho*-*C*(CH_3)$_3$), 35.1 (s, *para*-*C*(CH_3)$_3$), 34.0 (d, $^4J_{C\text{-}P}$ = 6.9 Hz, *ortho*-*C*(*C*H$_3$)$_3$), 31.5 (s, *para*-*C*(*C*H$_3$)$_3$).

X-ray diffraction data

All measurements were performed using graphite-monochromatized Mo K_α radiation at 100K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/7).[1] The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C-H distances of 0.99Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with tetrahedral angles, enabling rotation around the X-C bond, and C-H distances of 0.98Å.

Table 1. Crystal data and structure refinement for compounds **2-H** and *Z*-**5.**

Crystal data	**Compound 2-H** 	**Compound *Z*-5** 
CCDC-No.	1423585	1423584
Empirical formula	$C_{22}H_{40}O_3P_2$	$C_{30}H_{39}P_1$
Formula weight	414.48	430.58
Crystal description	colorless block	colorless needle
Crystal size	0.3x0.26x0.22	0.30x0.12x0.12
Crystal system, space group	triclinic, P-1	triclinic, P-1
Unit cell dimensions: a	9.5128(3)	10.3513(12)
b	10.5246(4)	10.3810(13)
c	12.6133(5)	24.524(3)
α, β, γ	74.848(2), 74.761(2), 88.062(2)	94.404(3), 98.422(4), 94.918(4)
Volume	1175.24(8)	2586.6(6)
Z	2	4
Calculated density	1.171	1.106
F(000)	452	936
Linear absorption coefficient μ	0.203	0.121
Absorption correction	multi-scan, SADABS 2008	multi-scan, SADABS 2008
Max. and min. transmission	0.5095, 0.7456	0.6037 and 0.7454

Unit cell determination	$1.7 < \theta < 25.2°$	$2.4 < \theta < 25.2°$
	3964 reflections used at 100K	4389 reflections used at 100K
Data collection		
Temperature	100(2)K	100(2)K
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube	fine-focus sealed tube
Radiation and wavelength	MoK_{α}, 0.71073Å	MoK_{α}, 0.71073Å
Monochromator	Graphite	Graphite
Scan type	ω scans	ω scans
Θ range for data collection	1.73 to 27.96°	2.41 to 26.45°
Index ranges	$-12 \leq h \leq 11$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-30 \leq l \leq 30$
Reflections collected / unique	18027 / 5613	21308/ 10361
Significant unique reflections	3964 with $I > 2\sigma(I)$	4389 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0492, 0.0758	0.1187, 0.2347
Completeness to Θ_{max}	99.2%	97.5%
Refinement		
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / parameters / restraints	5613/ 259/ 0	10361/ 559/ 0
Goodness-of-fit on F^2	1.067	0.956
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0480, wR2 = 0.1106	R1 = 0.0828, wR2 = 0.1658
R indices (all data)	R1 = 0.0810, wR2 = 0.1237	R1 = 0.2216, wR2 = 0.2228
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(aP)^2]$, where $P=(F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b	0.0564, 0.0511	0.0936
Largest Δ/σ in last cycle	0.000	0.001
Largest difference peak and hole	0.470 and -0.590 e/Å^3	0.383 and -0.322 e/Å^3
Structure Solution Program	SHELXS-2014 (Sheldrick, 2008)	SHELXS-2014 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014 (Sheldrick, 2008)	SHELXL-2014 (Sheldrick, 2008)

References

1 A. Termaten, M. van der Sluis and F. Bickelhaupt, *Eur. J. Org. Chem.*, 2003, **2003**, 2049–2055.

2 M. van der Sluis, A. Klootwijk, J. B. M. Wit, F. Bickelhaupt, N. Veldman, A. L. Spek and P. W. Jolly, *J. Organomet. Chem.*, 1997, **529**, 107–119.

Appendices

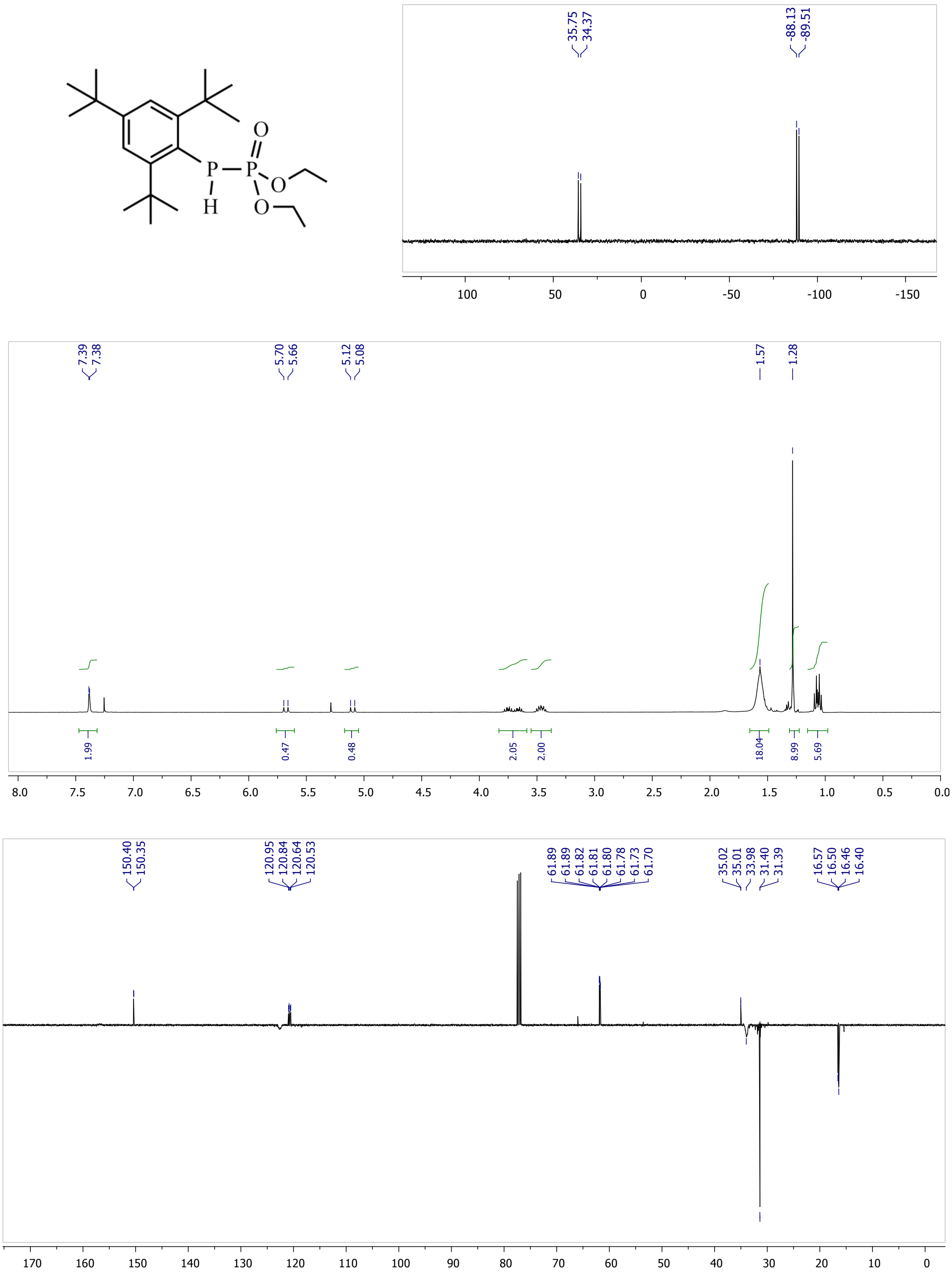
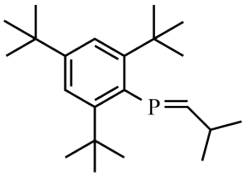
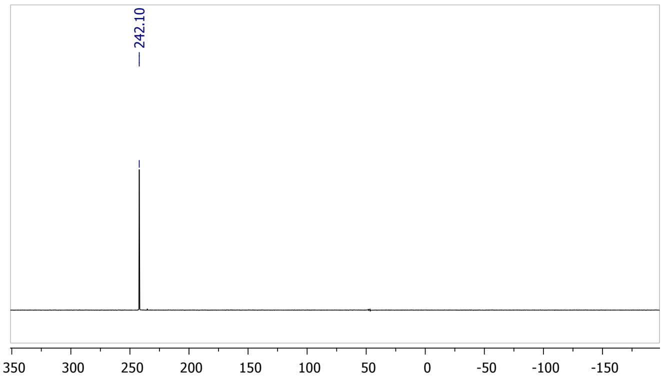
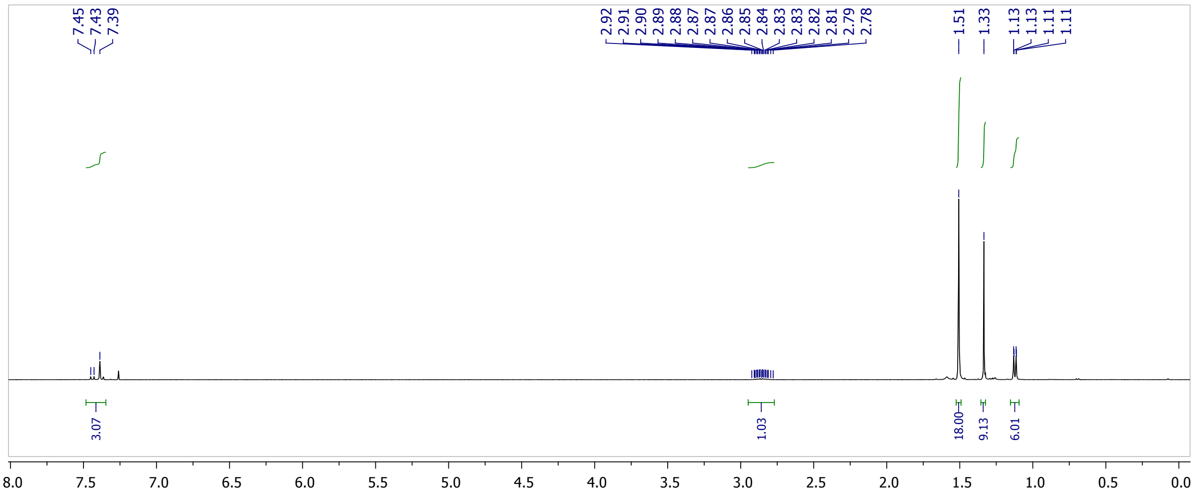


Figure S2 – ^{31}P NMR (top), ^{1}H NMR (middle) and APT (bottom) spectra of phosphanylphosphonate **2-H**.



(E)-**3**





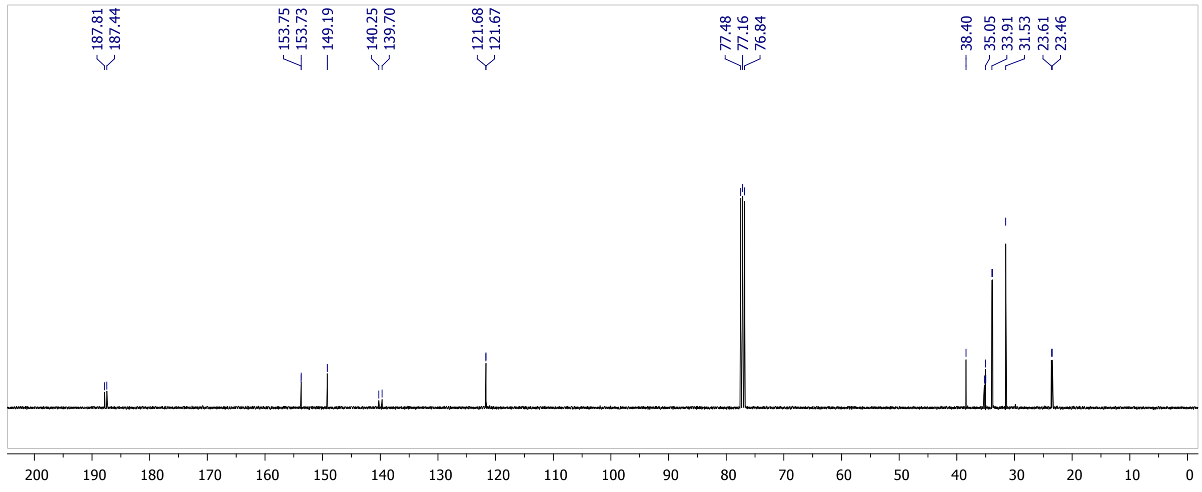
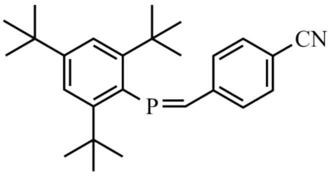


Figure S3 – ^{31}P NMR (top), ^{1}H NMR (middle) and ^{13}C{^{1}H} NMR (bottom) spectra of phosphaalkene *E*-**3**.



(Z)-**4**

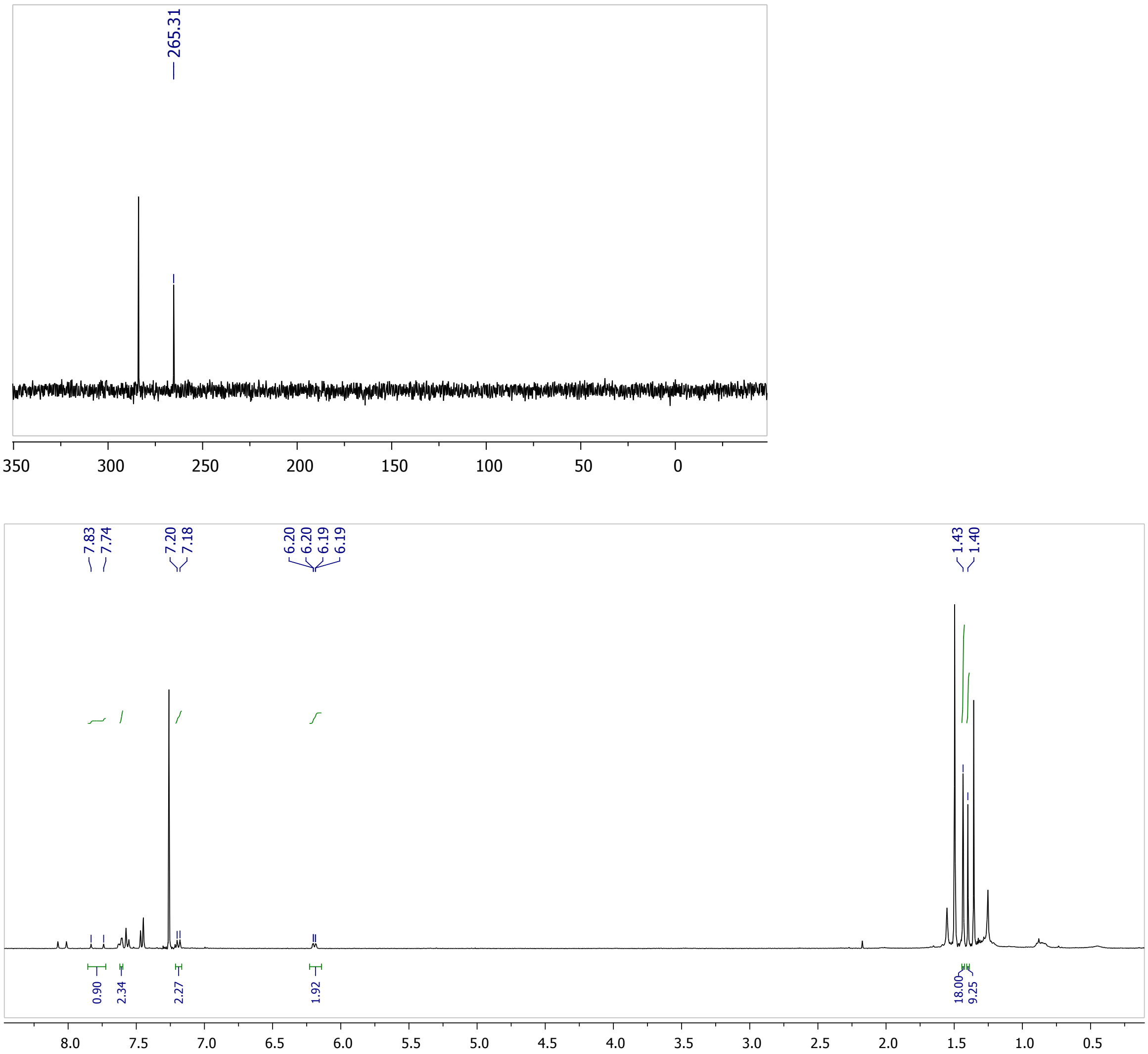


Figure S4 – ^{31}P NMR (top), ^{1}H NMR (bottom) spectra of phosphaalkene **4**, as mixture of the two isomers. The assigned signals belong to *Z*-**4**.

(E)-**5**

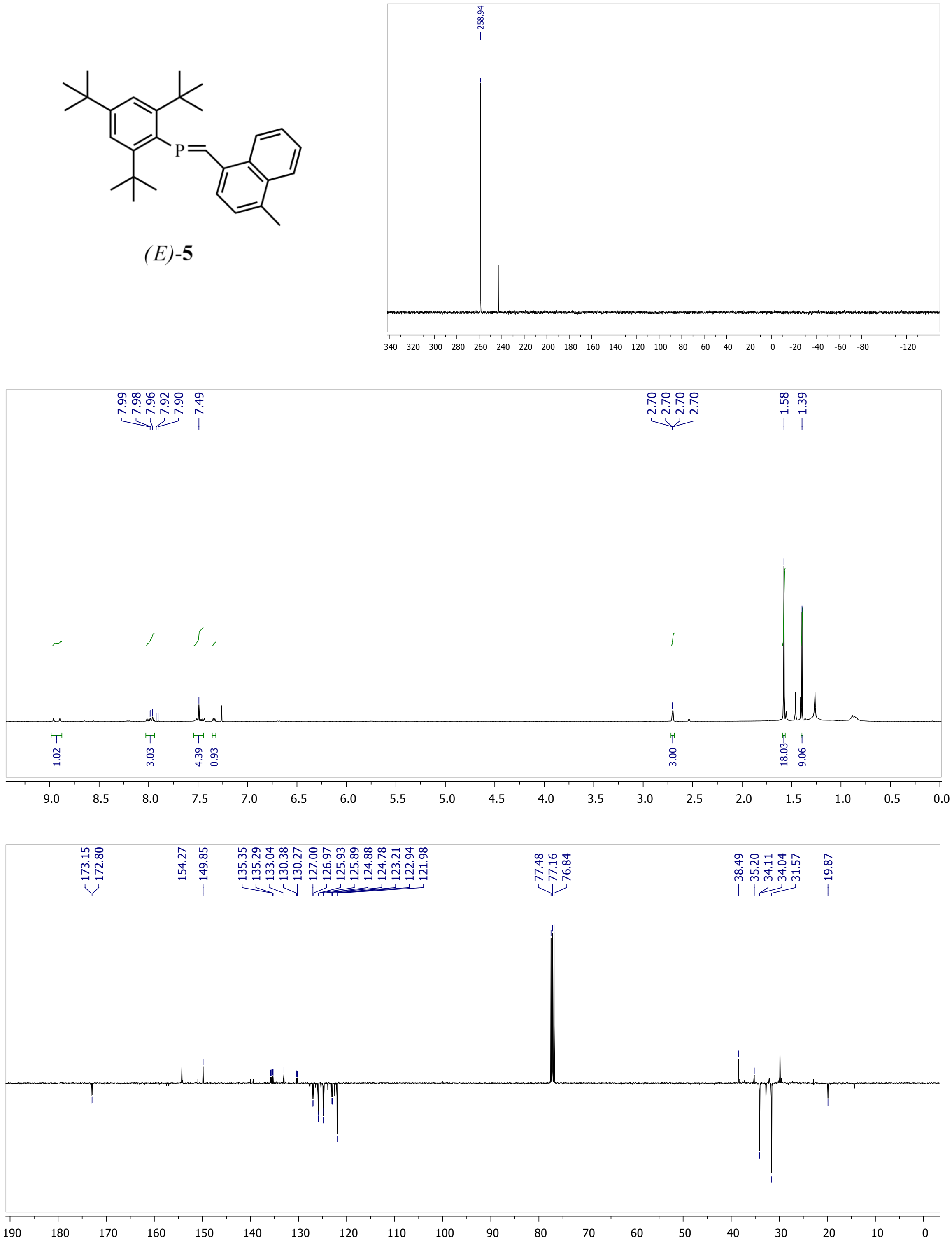


Figure S5 – 31P NMR (top), 1H NMR (middle) and APT NMR (bottom) spectra of phosphaalkene *E*-**5**. The small peaks observable in these spectra belong to the other isomer, *Z*-**5**.

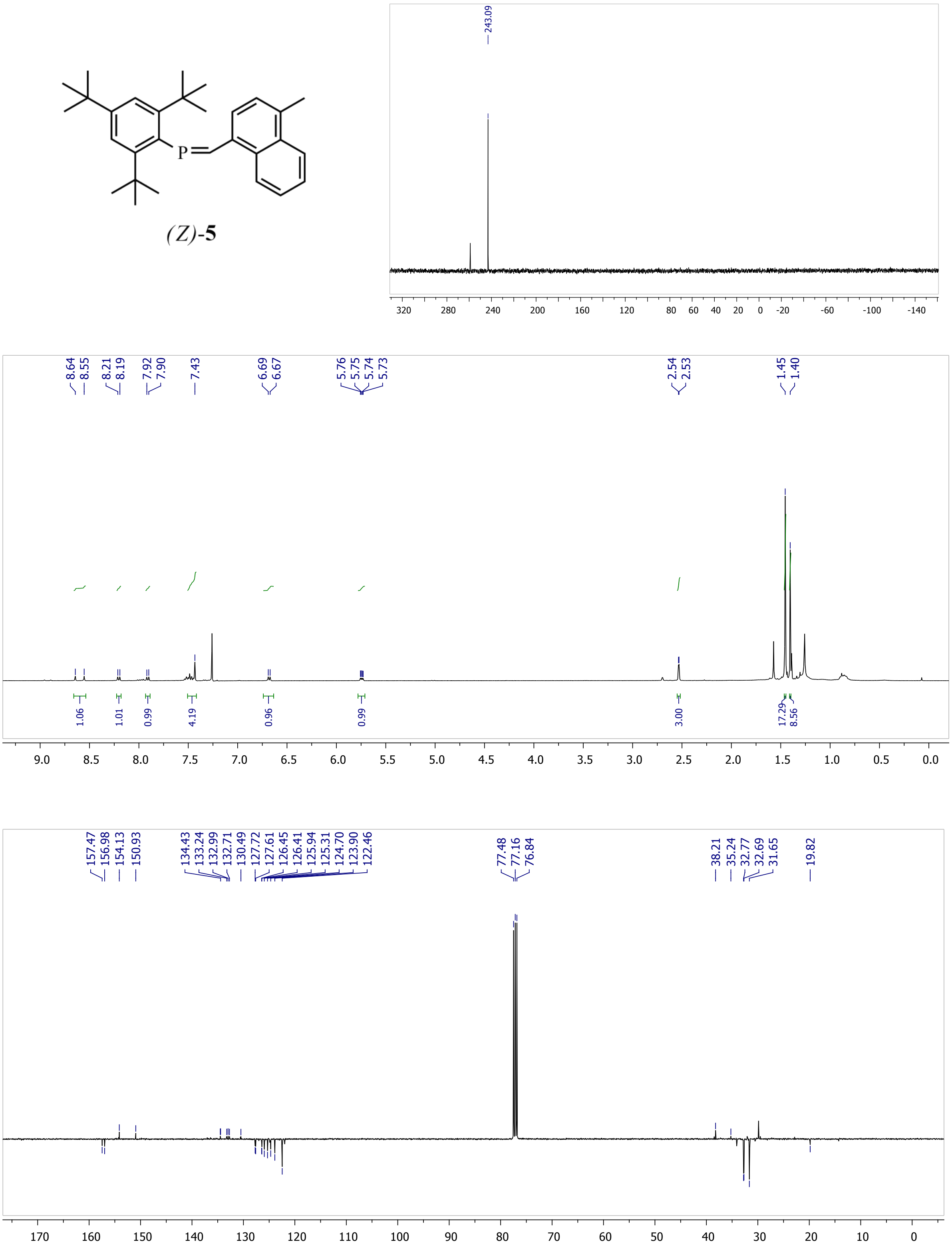


Figure S6 – ^{31}P NMR (top), ^{1}H NMR (middle) and APT NMR (bottom) spectra of phosphaalkene *Z*-**5**. The small peaks observable in these spectra belong to the other isomer, *E*-**5**.

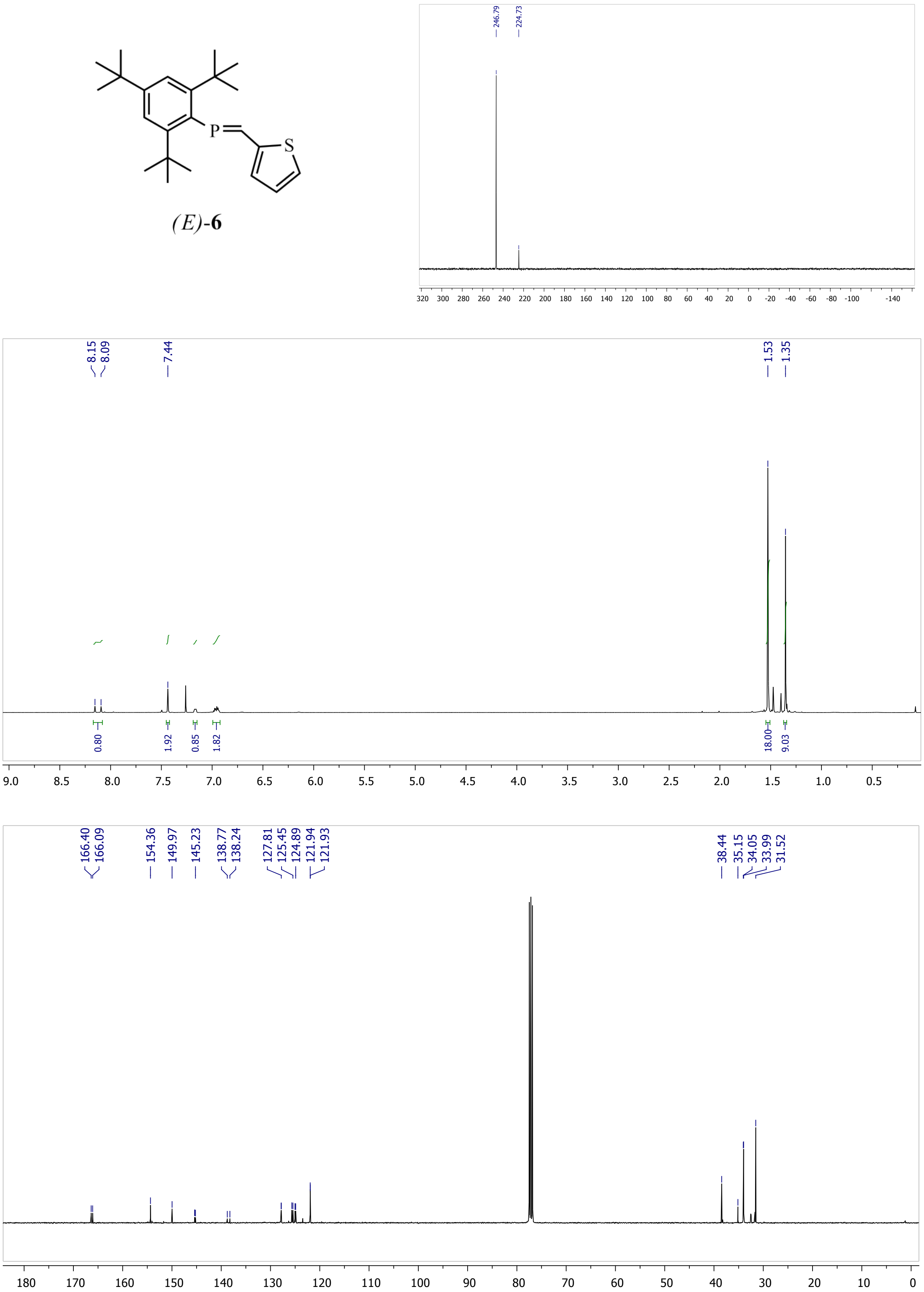
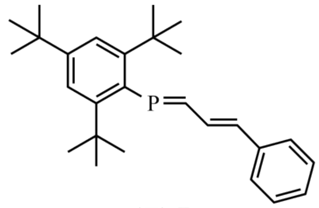
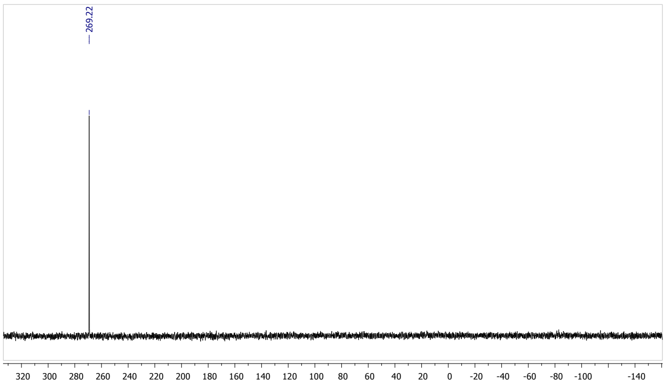
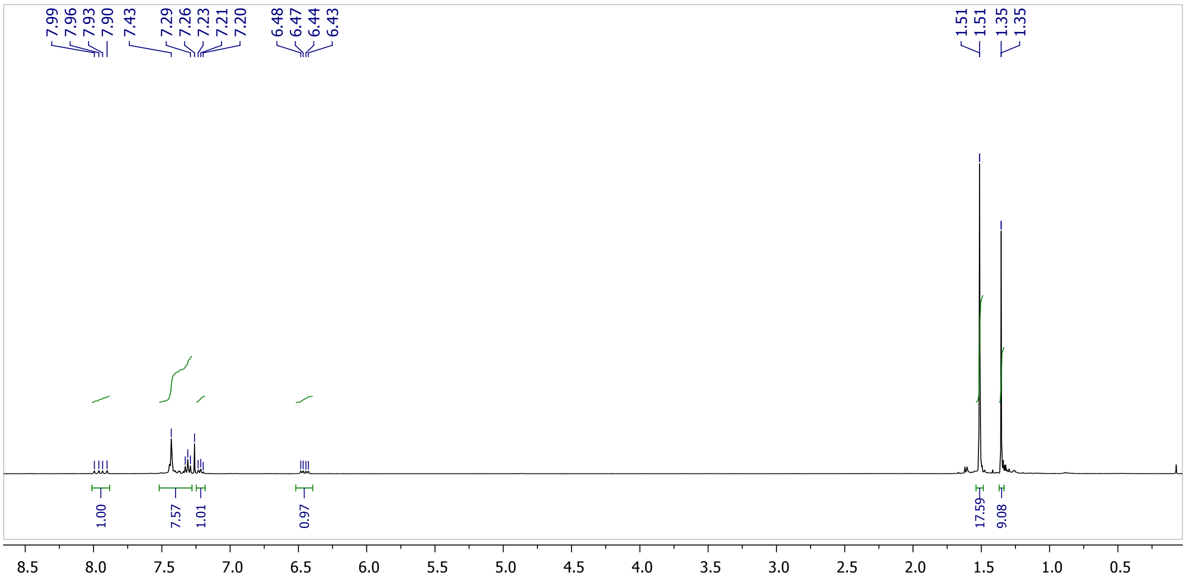


Figure S7 – ^{31}P NMR (top), ^{1}H NMR (middle) and ^{13}C{^{1}H}NMR (bottom) spectra of phosphaalkene *E*-**6**. The small peaks observable in these spectra belong to the other isomer, *E*-**6**.



(E)-**7**





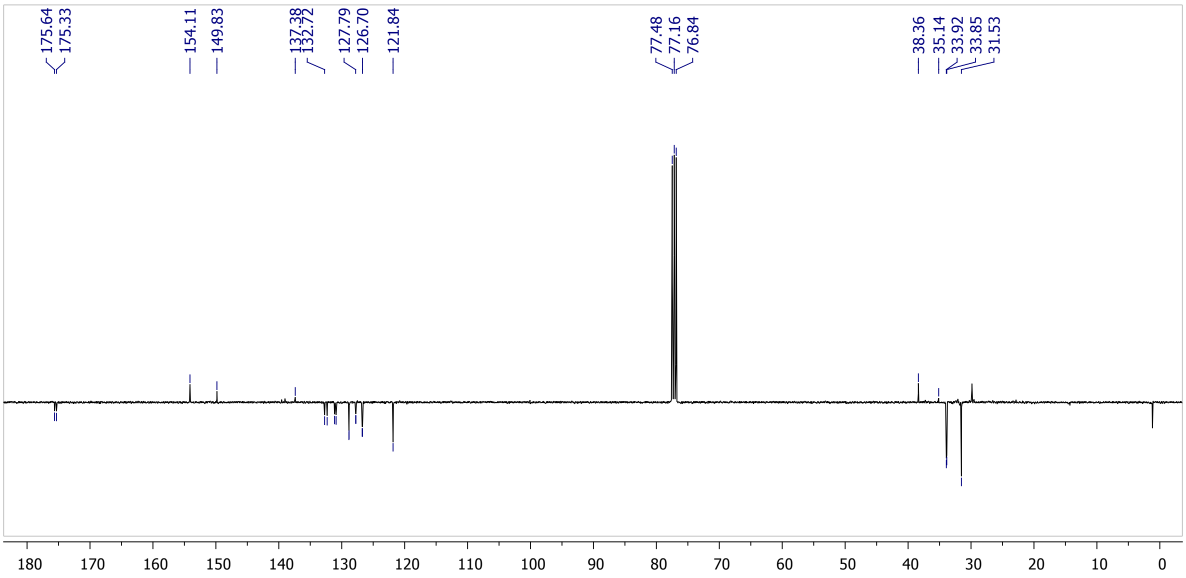


Figure S8 – ^{31}P NMR (top), ^{1}H NMR (middle) and APT NMR (bottom) spectra of phosphaalkene *E*-**7**.