# Supporting Information

## 2,4,6-triphenylphosphinine and 2,4,6-triphenylposphabarrelene revisited: synthesis, reactivity and coordination chemistry

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**General remarks:**
Unless otherwise stated, all the experiments were performed under an inert argon atmosphere using modified Schlenk techniques or in a MBraun dry box. All common chemicals were commercially available and were used as received. Li granules were obtained from Sigma Aldrich.
The pyrylium salts,[S1] the phosphabarrelene,[S2] $LiP(TMS)_2$, $NaP(TMS)_2$ and $KP(TMS)_2$ were prepared according to literature.[S3]
Dry and deoxygenated solvents were prepared using standard techniques or used from a MBraun solvent purification system.
The $^{1}H$, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a JEOL ECX400 (400 MHz) spectrometer and chemical shifts are reported relative to the residual resonance in the deuterated solvents.
IR spectra were measured on a Nicolet iS10 FTIR-ATR spectrometer by Thermo Scientific in the solid state.
For reactions under UV radiation a Philips HPK 125W high-pressure mercury vapor lamp was used.

**X-ray crystal structure determination of 10:**
Crystals suitable for X-ray diffraction were obtained from a saturated solution of **10** in toluene.
*Crystallographic data*: $C_{29}H_{21}PSe$; *F*w=479.39; 0.38×0.29×0.17 $mm^3$; colourless block, triclinic; P -1; *a*= 9.8524(2), *b*= 12.4381(2), *c*=18.8967(3) Å; α=87.80(7)°, β=89.78(8), γ=75.57(6)°; *V*=2240.98(7) $Å^3$; *Z*=4; *D*x=1.421 $gcm^{-3}$; μ=1.761$mm^{-1}$. 76227 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation; $\lambda$ = 0.71073 Å)[S7,S8] up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.62 $Å^{-1}$ at a temperature of 100.0 K. 7511 reflections were unique ($R_{int}$ =0.073). The structures were solved with SHELXS-2013[S9] by using direct methods and refined with SHELXL-2013[S9] on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 559 parameter were refined with one restraint. $R_1$=0.036 for 7511 reflections with $I>2\sigma(I)$ and $wR_2$=0.083 for 9231 reflections, *S*=1.066, residual electron density was between -0.53 and 0.75 $eÅ^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[S10]
CCDC- 1424313 (**10**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**X-ray crystal structure determination of 11:**
Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **11** in pentane. *Crystallographic data*: $C_{28}H_{17}O_5PW$; *F*w= 648.23; 0.16×0.15×0.02 $mm^3$; yellow plate,

monoclinic; *-P2yn, a*= 11.1311(4), *b*= 19.9977(7), *c*= 11.6468(4) Å; α=90°, β= 109.4260(11), γ=90°; *V*= 2444.95(15) Å$^3$; *Z*=4; *D*x= 1.761 gcm$^{-3}$; μ= 4.827 mm$^{-1}$. 34007 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation; $\lambda$ = 0.71073 Å)[S7,S8] up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.67 Å$^{-1}$ at a temperature of 100.00 K. 5320 reflections were unique ($R_{int}$ =0.021). The structures were solved with SHELXS-2013[S9] by using direct methods and refined with SHELXL-2013[S9] on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 316 parameter were refined with one restraint. $R_1$=0.021 for 5320 reflections with *I*>2σ(*I*) and $wR_2$=0.044 for 6093 reflections, *S*=1.055, residual electron density was between -0.85 and 1.80 eÅ$^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[S10]
CCDC-1424312 (**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**X-ray crystal structure determination of 12:**
Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **12** in pentane. *Crystallographic data*: $C_{34}H_{21}O_5PW$; *F*w=724.33; 0.23×0.14×0.11 mm$^3$; colourless chunk, monoclinic; *-P2yn*; *a*= 11.5473(2), *b*=12.8913(2), *c*=19.8913(3) Å; α=90°, β=102.46, γ=90°; *V*=2891.29(8) Å$^3$; *Z*=4; *D*x=1.156 gcm$^{-3}$; μ=1.837 mm$^{-1}$. 12965 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation; $\lambda$ = 0.71073 Å)[S7,S8] up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.98 Å$^{-1}$ at a temperature of 100.00 K. 18773 reflections were unique ($R_{int}$ =0.029). The structures were solved with SHELXS-2013[S9] by using direct methods and refined with SHELXL-2013[S9] on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 370 parameter were refined with one restraint. $R_1$=0.029 for 18773 reflections with *I*>2σ(*I*) and $wR_2$=0.070 for 22892 reflections, *S*=1.057, residual electron density was between -2.51 and 4.54 eÅ$^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[S10]
CCDC-1424314 (**12**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**X-ray crystal structure determination of 13:**
Crystals suitable for X-ray diffraction were obtained by cooling slowly down a hot saturated solution of **13** in acetonitrile. *Crystallographic data*: $C_{54}H_{40}N_2O_4P_2W$; *F*w= 1026.67; 0.28×0.2×0.03 mm$^3$; yellow plate, monoclinic; *C-2yc*; *a*= 29.1358(14), *b*= 11.5350(6), *c*= 15.4712(7) Å; α=90°, β= 119.7420(10), γ=90°; *V*= 4514.6(4) Å$^3$; *Z*=4; *D*x=1.510 gcm$^{-3}$; μ=2.679 mm$^{-1}$. 32070 reflections were measured by using a D8 Venture, Bruker Photon CMOS Detector (MoKα radiation; $\lambda$ = 0.71073 Å) [S7,S8] up to a resolution of $(\sin\theta/\lambda)_{max}$= 0.66 Å$^{-1}$ at a temperature of 100.00 K. 9315 reflections were unique ($R_{int}$ = 0.029). The structures were solved with SHELXS-2013[S9] by using direct methods and refined with SHELXL-2013[S9] on *F*2 for all reflections. Non-hydrogen atoms were refined by using anisotropic displacement parameters. The positions of the hydrogen atoms were calculated for idealized positions. 571 parameter were refined with one restraint. $R_1$=0.029 for 9315 reflections with *I*>2σ(*I*) and $wR_2$=0.068 for 9939 reflections, *S*=1.017, residual electron density was between -0.77 and 3.97 eÅ$^{-3}$. Geometry calculations and checks for higher symmetry were performed with the PLATON program.[S10]
CCDC- 1424399 (**13**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Optimization of the synthesis of 2,4,6-triphenylphosphinine (1):**
The optimization of the reaction conditions was performed with 2,4,6-triphenylpyrylium tetrafluoroborate.

**Table 1.** Reaction conditions: 6h refluxing in THF

| | $Li[P(TMS)_2]$ | $Na\ [P(TMS)_2]$ | $K[P(TMS)_2]$ |
|---|---|---|---|
| 1 eq. | 56 % | 45 % | 46 % |
| 2 eq. | 76 % | 47 % | 51 % |

**Table 2.** Choice of the ratio. Reaction conditions: $Li[P(TMS)_2]$, refluxing for 6h in THF:

| Ratio | 1:1 | 1:1.4 | 1:1.6 | 1:2 |
|---|---|---|---|---|
| Isolated yield | 56 % | 52 % | 54 % | 76 % |

**Table 3.** Choice of the reaction time. Reaction conditions: 1 eq. $Li[P(TMS)_2]$, refluxing in THF:

| Time | 1h | 6h | 16h |
|---|---|---|---|
| Isolated yield | 33 % | 56 % | 55 % |

An overnight reaction does not change significantly the outcome of the reaction.

**Table 4.** Choice of the reaction temperature. Reaction conditions: 1 eq. $Li[P(TMS)_2]$ in THF:

| Temperature | rt for 16h | Reflux for 6h | 100°C for 3h |
|---|---|---|---|
| Isolated yield | 28 % | 56 % | 31% |

Different temperatures were screened: an overnight reaction at room temperature and a microwave reaction at T = 100°C were performed, resulting in lower yields.

**Table 5.** Choice of the solvent. Reaction conditions: 1 eq. $Li[P(TMS)_2]$, refluxing for 6h:

| Solvent | THF | MeCN | DME | toluene | Solid state |
|---|---|---|---|---|---|
| Isolated yield | 56 % | - | 44 % | - | 48 % |

THF and DME turned out to best solvents. Acetonitrile could not be used (reaction with $Li[P(TMS)_2]$ was observed) and the solubility of the pyrylium salt was too low in toluene. A solid state reaction, performed stirring the solids together in a Schlenk flask, resulted in good yields.

The optimal conditions are: 2 eq. $Li[P(TMS)_2]$, refluxing for 6h in THF.

**2-(2-Pyridyl)-4,6-diphenyl-phosphinine (8):**
2-(2-pyridyl)-4,6-diphenylpyrylium tetrafluoroborate (876 mg, 2.0 mmol) and $Li[P(TMS)_2] \cdot 0.5$ THF (870 mg, 2 eq.) were put together in a 50 mL Schlenk flask under an argon atmosphere. 25 mL of THF were added. Upon addition a dark reaction mixture was obtained which was heated to reflux for 6 h. Subsequently, all volatiles were removed in vacuo to obtain a red-brown solid. The crude product was purified by means of column chromatography over silica with hexane at first and hexane/ethyl acetate 9:1 to afford the product as a yellow solid (271 mg, 37%).

**2,4-Diphenyl-5-methyl-6-(2,3-dimethylphenyl)-phosphinine (9):**
2,4-Diphenyl-5-methyl-6-(2,3-dimethylphenyl)pyrylium tetrafluoroborate (790 mg, 2.0 mmol) and $Li[P(TMS)_2] \cdot 0.5$ THF (870 mg, 2 eq.) were put together in a 50 mL Schlenk flask under an argon atmosphere. 25 mL of THF were added. Upon addition a dark reaction mixture was obtained which was heated to reflux for 6 h. Subsequently, all volatiles were removed in vacuo to obtain a yellow-brown solid. The crude product was purified by means of column chromatography over silica with hexane at first and hexane/ethyl acetate 9:1 to afford the product as a yellow solid (240 mg, 37%).

**$[W(CO)_5 \cdot THF]$:**
$[W(CO)_5 \cdot THF]$ was synthesized following a modified literature procedure.[S4]
A suspension of $W(CO)_6$ (50 mg, 0.14 mmol) in 2 ml THF was stirred for 2 hours under UV light. The CO overpressure was released from time to time and the solution, which becomes yellow from colourless, was degassed after 1 hour of exposition, to allow the CO to leave the reaction. Performing the reaction in a big vessel (100 mL flask) is also a good way to remove the CO from the reaction, but degassing is recommended.

**[2,4,6-triphenylphosphinine]-pentacarbonyltungsten(0), $[(1)W(CO)_5]$ (11):**
The compound was synthesized following a modified literature procedure.[S5] A solution of **1** (50 mg, 0.154 mmol) in 2 mL of dry THF was added dropwise to a solution of $[W(CO)_5 \cdot THF]$ (1 eq.) in dry THF. The mixture was then heated up to 60°C for 1h. Afterwards the solvent was removed in vacuo and the residue was washed with cold pentane, yielding the product as an orange powder (86%). Crystals suitable for X-ray analysis were obtained by slow evaporation from a pentane solution.
$^1H$ NMR (400 MHz, $CD_2Cl_2$): δ = 7.38-7.44 (m, 1H, Ar-H), 7.45-7.54 (m, 12H, Ar-H), 7.66 (m, 2H, Ar-H), 8.12 ppm (d, $^3J_{H-P}$ = 17.3 Hz, 2H, Ar-H)
$^{13}C\{^1H\}$ NMR (101 MHz, $CD_2Cl_2$): δ = 128.00 (d, *J* = 3.0 Hz), 128.81 (d, *J* = 0.9 Hz), 128.89 (d, *J* = 2.1 Hz), 129.20 (d, *J* = 1.0 Hz), 129.68 (d, *J* = 0.9 Hz), 130.47 (d, *J* = 8.5 Hz), 136.55 (d, *J* = 11.6 Hz), 140.92 (d, *J* = 22.7 Hz), 141.40 (d, *J* = 5.3 Hz), 142.49 (d, *J* = 14.5 Hz), 168.89 (d, *J* = 12.0 Hz), 195.10 (d, $^2J_{C-P}$ = 9.0 Hz, with $^{183}W$ satellites, $^1J_{C-W}$ = 126.1 Hz, CO *cis*), 198.75 ppm (d, $^2J_{C-P}$ = 32.0 Hz, CO *trans*).
$^{31}P\{^1H\}$ NMR (162 MHz, $CD_2Cl_2$): δ = 159.1 ppm (s, with $^{183}W$ satellites, $^1J_{P-W}$ = 273 Hz).
IR: 2073 (w, CO), 1992 (w, CO), 1932 (shoulder), 1909 (s, CO) $cm^{-1}$.

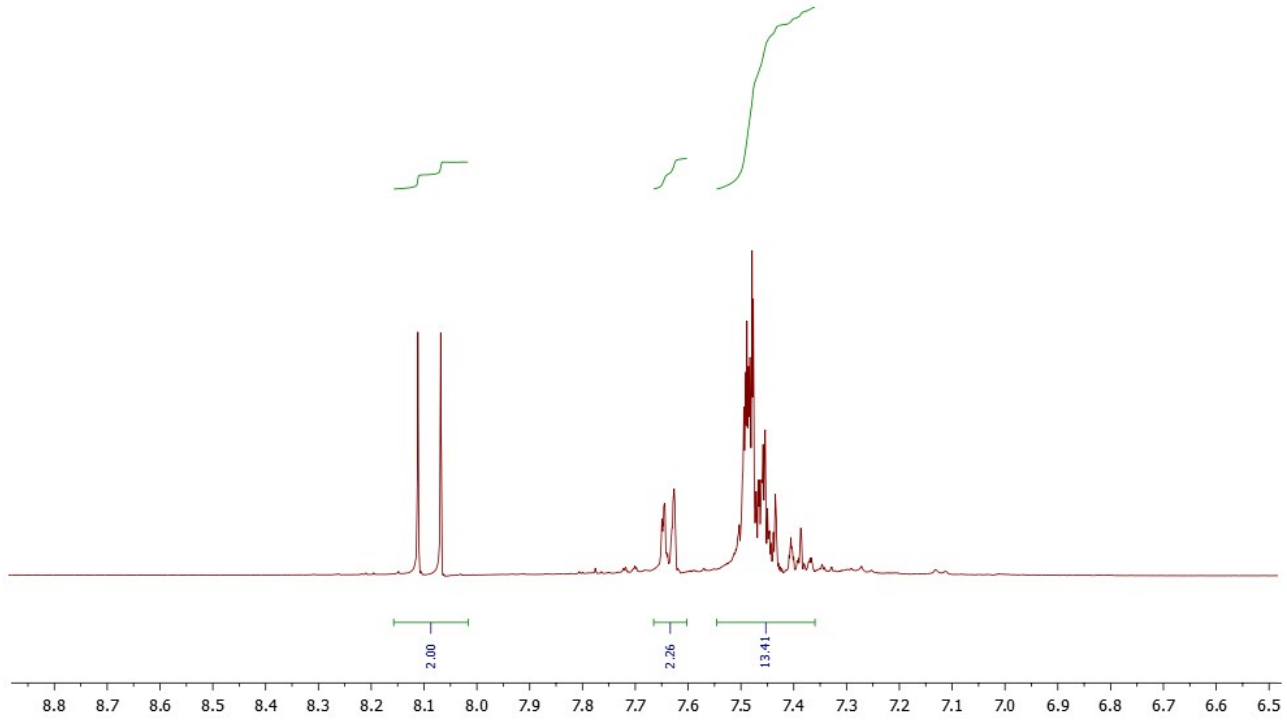


**Figure 1.** $^{1}H$ NMR spectrum of compound **11**.

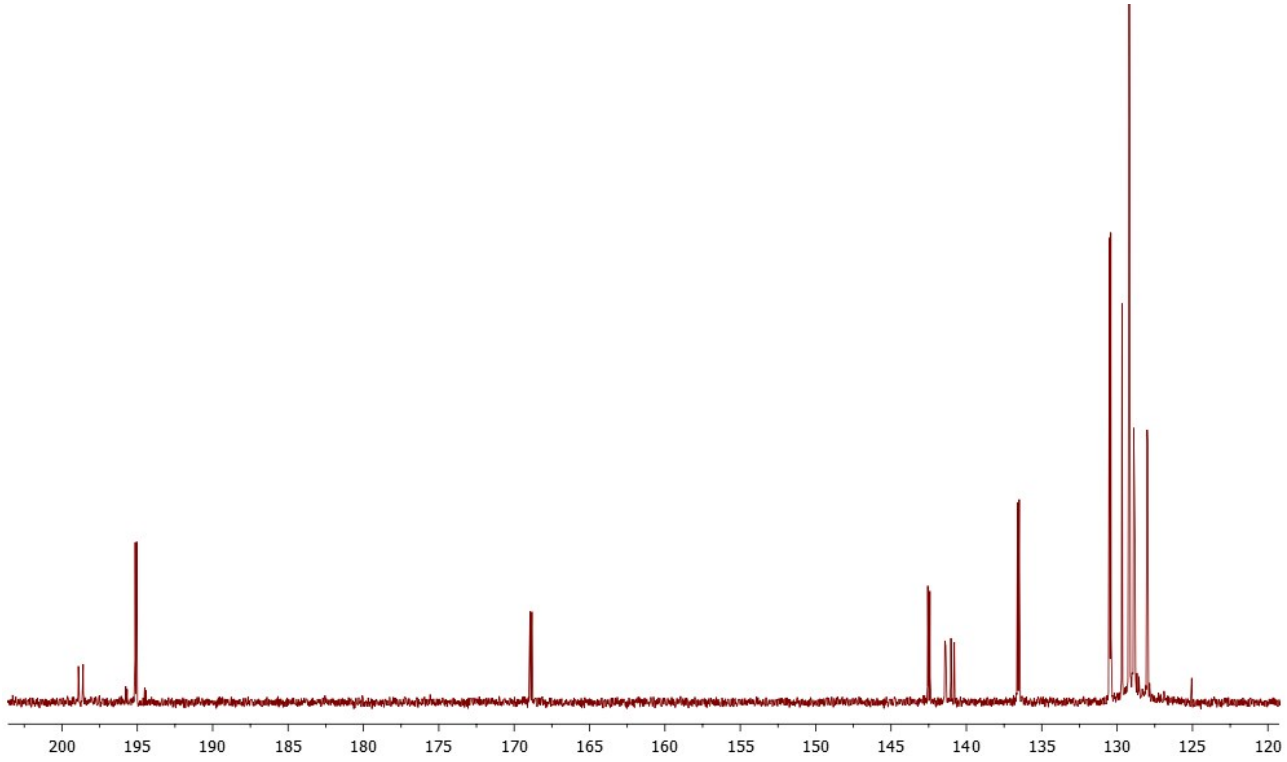


**Figure 2.** $^{13}C\{^{1}H\}$ NMR spectrum of compound **11**.

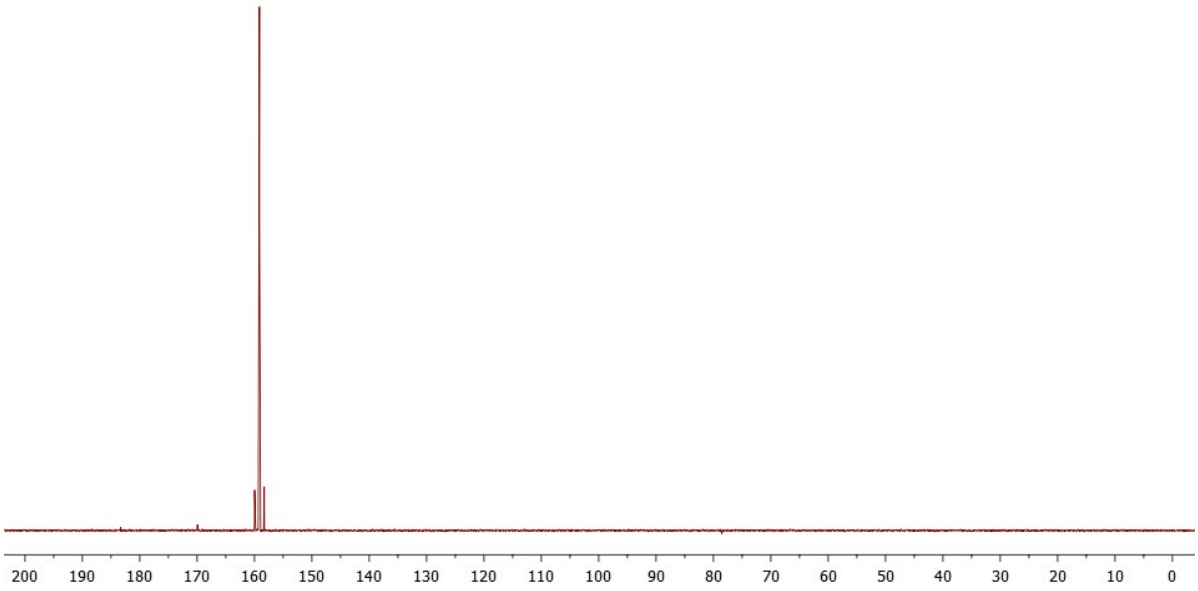


**Figure 3.** $^{31}P\{^{1}H\}$ NMR spectrum of compound **11**.

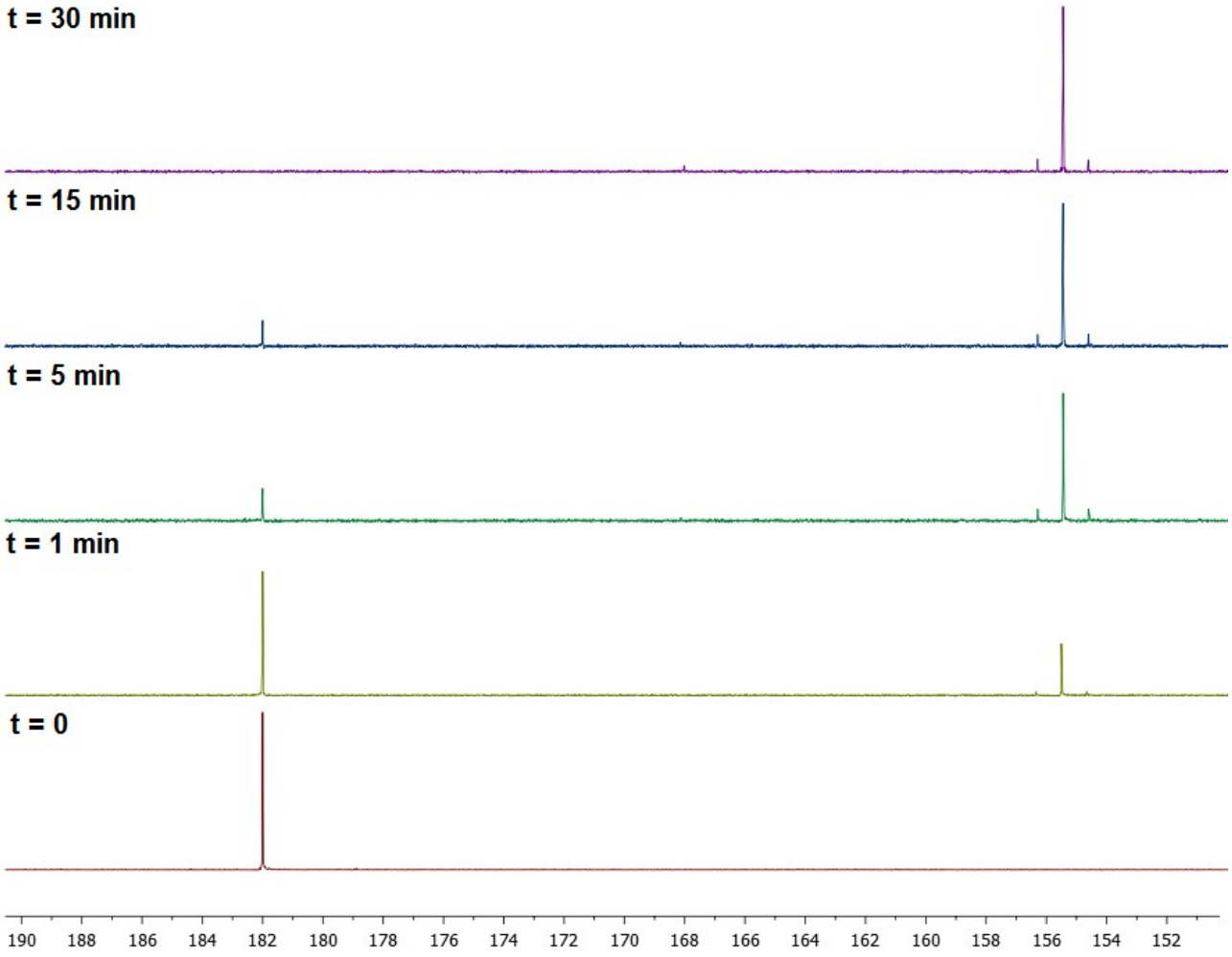


**Figure 4.** Time dependent $^{31}P\{^{1}H\}$ NMR spectra of compound **11**.

***cis*-Bis-[2,4,6-triphenylphosphinine]-tetracarbonyltungsten(0), [(1)$_2$W(CO)$_4$] (13):**

The compound was synthesized following a modified literature procedure.[S5] A solution of **1** (37.8 mg, 0.116 mmol) in THF was added dropwise to a solution of $W(CO)_4(CH_3CN)_2$[S6] (0.5 eq.) in THF and the mixture was heated up to 60°C for 1h. Afterwards the solvent was removed in vacuo and the crude product was washed with small amounts of cold acetonitrile and pentane, yielding the product as a red powder (56%). Crystals suitable for X-ray analysis were obtained recrystallizing from hot acetonitrile.

$^1$H NMR (400 MHz, $CD_2Cl_2$): δ = 7.15 (d, 4H, *J* = 7.6 Hz), 7.29 (m, 4H), 7.40 (m, 3H), 7.50 (m, 2H), 7.47-7.52 (m, 6H, Ar-H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.81(m, 2H) ppm.

$^{13}$C{$^1$H} NMR (101 MHz, $CD_2Cl_2$): 127.83 (s), 128.09 (s), 128.53 (s), 128.69 (s), 129.68 (s), 130.52 (t, *J* = 4.4 Hz), 136.30 (t, *J* = 6.6 Hz), 139.68 (m), 141.79 (m), 142.77 (t, *J* = 7.0 Hz), 168.37 (t, *J* = 6.4 Hz), 197.53 (t, *J* = 8.6 Hz, $CO_{cis}$), 203.87 (m, $CO_{trans}$) ppm.

$^{31}$P{$^1$H} NMR (162 MHz, $CD_2Cl_2$): δ = 169.9 ppm (s, with $^{183}$W satellites, $^1J_{P\text{-}W}$ = 263 Hz).

IR: 2024 (s, CO), 1915 (s, CO), 1884 (s, CO) cm$^{-1}$.

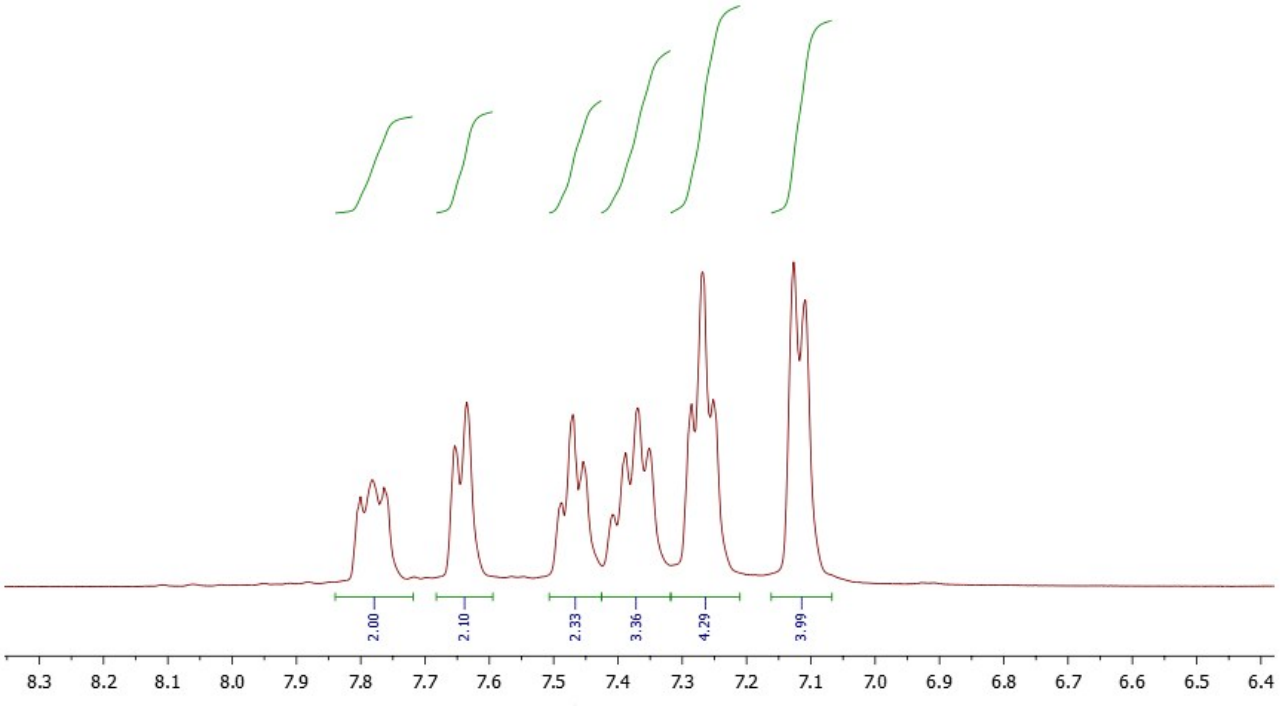


**Figure 5.** $^1$H NMR spectrum of compound **13.**

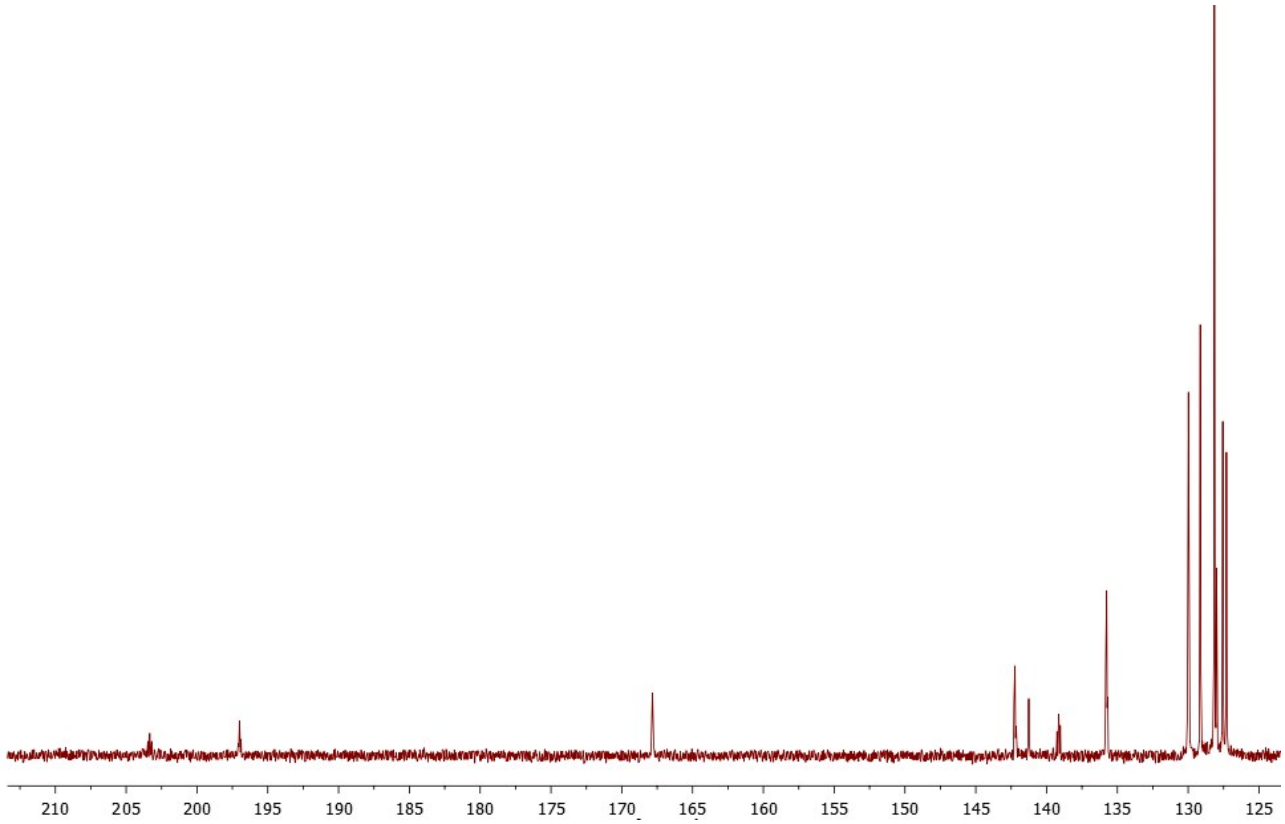


**Figure 6.** $^{13}C\{^{1}H\}$ NMR spectrum of compound **13.**

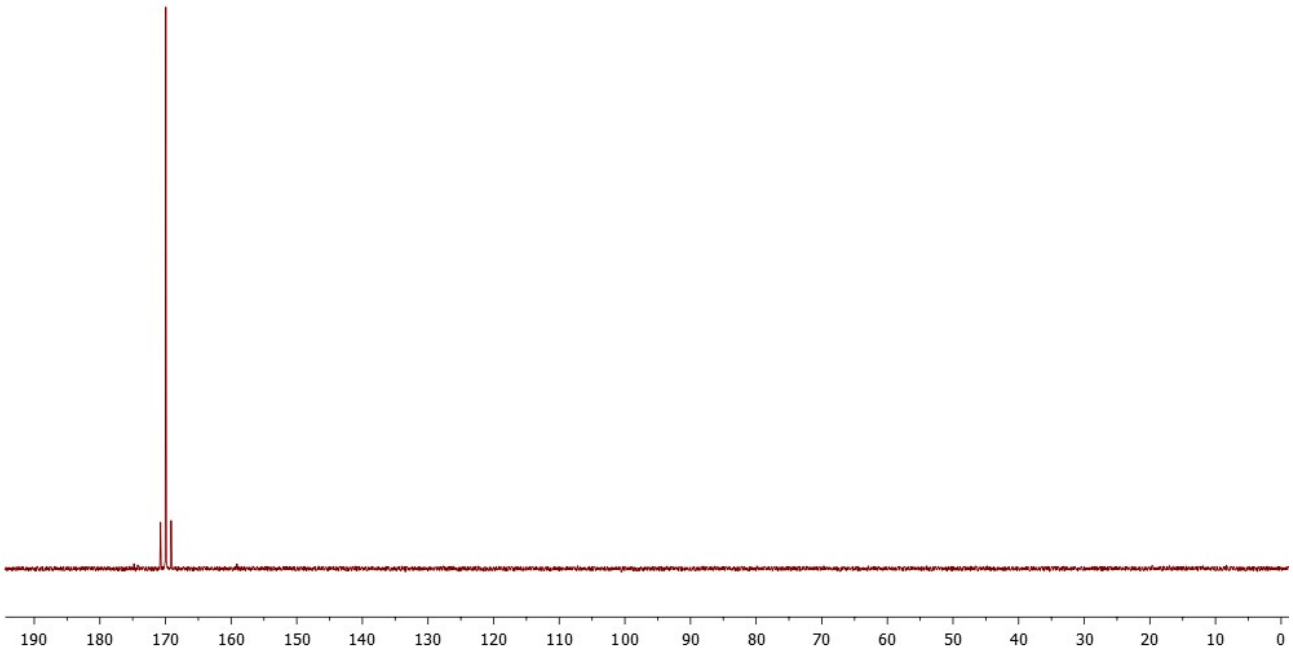


**Figure 7.** $^{31}P\{^{1}H\}$ NMR spectrum of compound **13.**

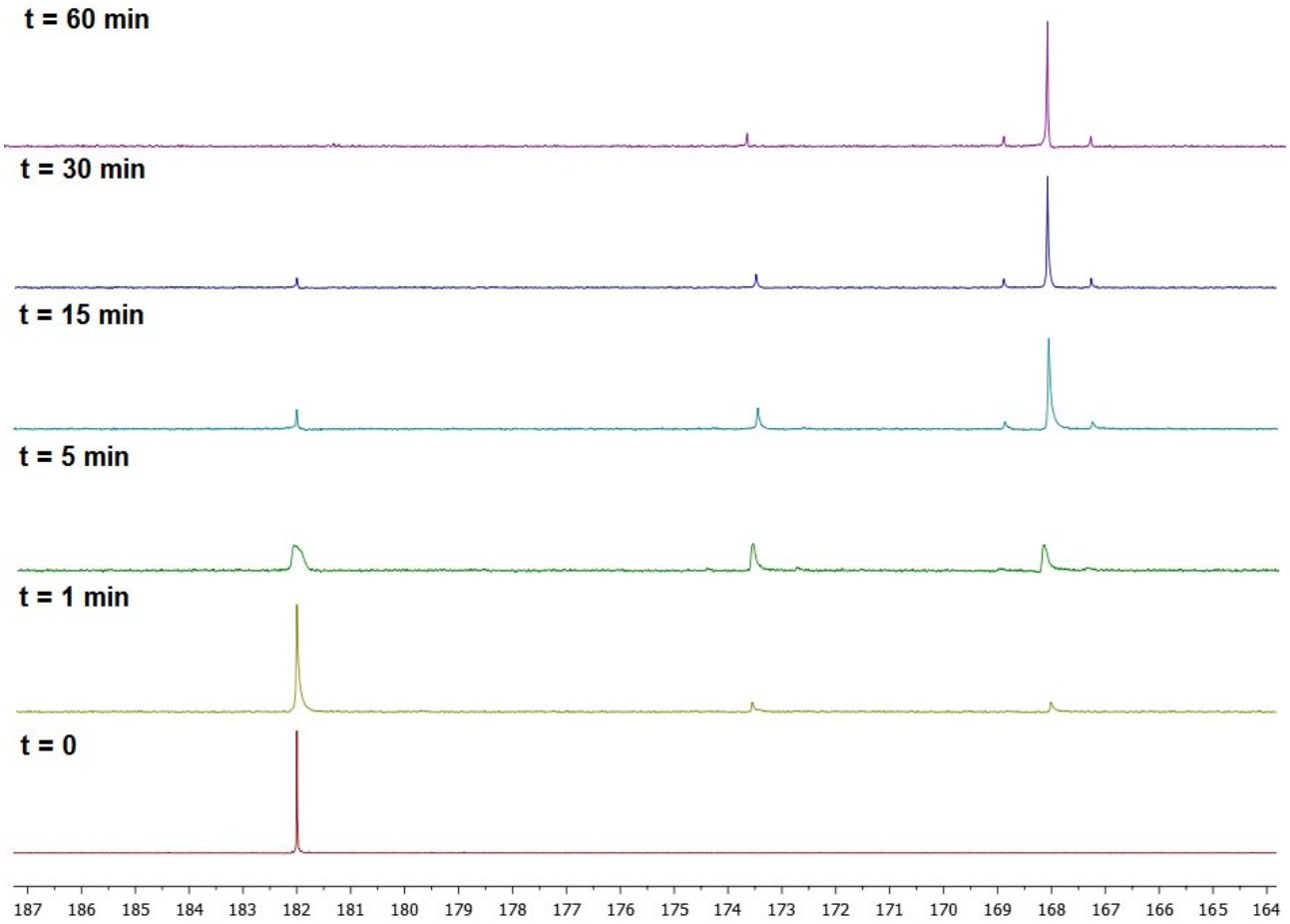


**Figure 8.** Time dependent $^{31}P\{^{1}H\}$ NMR spectrum of compound **13**.

**2,4,10-triphenyl-4H-1,4-ethenophosphinoline]-pentacarbonyltungsten(0), [(2)W(CO)$_5$] (12):**
A solution of **2** (30 mg, 0.075 mmol) in THF was added dropwise to a solution of [W(CO)$_5$·THF] (1 eq.) in THF and heated at 80°C for 3 hours. Afterwards the solvent was removed in vacuo and the residue washed with cold pentane, yielding the product as a white powder (85%). Crystals suitable for X-ray analysis were obtained by slow evaporation from a pentane solution.
$^{1}H$ NMR (400 MHz, $CDCl_3$): δ = 6.64 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H, Ar-H), 7.08-7.15 (m, 5H, Ar-H), 7.28 (m, 1H, Ar-H), 7.32-7.38 (m, 6H, Ar-H), 7.50 (t, $^{3}J_{H-H}$ = 7.2 Hz, 1H, Ar-H), 7.58 (t, $^{3}J_{H-H}$ = 7.8 Hz, 2H, Ar-H), 7.68 (d, 7.8 Hz, 2H, Ar-H), 7.88 (d, $^{3}J_{H-P}$ = 16.9 Hz, 2H, C-H), 8.09 ppm (dd, $^{3}J_{H-H}$ = 7.3 Hz, $^{3}J_{H-P}$ = 12.3 Hz, 1H, Ar-H)
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 61.78 (d, *J* = 9.7 Hz), 124.92 (d, *J* = 12.7 Hz), 125.23 (m), 128.00 (s), 128.21 (s), 128.44 (s), 128.8 (s), 129.42 (s), 131.83 (d, *J* = 5.3 Hz), 131.95 (d, *J* = 5.3 Hz), 138.91 (d, *J* = 15.4 Hz), 138.92 (d, *J* = 32.8 Hz), 139.79 (bs), 150.98 (bs), 152.17 (d, *J* = 21.3 Hz), 152.42 (d, *J* = 3.6 Hz), 195.33 (d, $^{2}J_{C-P}$ = 7.6 Hz, with $^{183}W$ satellites, $^{1}J_{C-W}$ = 125.5 Hz, CO *cis*), 197.31 (d, $^{2}J_{C-P}$ = 26.7 Hz, CO *trans*).
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = -8.5 ppm (s, with $^{183}W$ satellites, $^{1}J_{P-W}$ = 266 Hz).
IR: 2071 (w, CO), 1989 (w, CO), 1930 (shoulder), 1907 (s, CO) $cm^{-1}$.

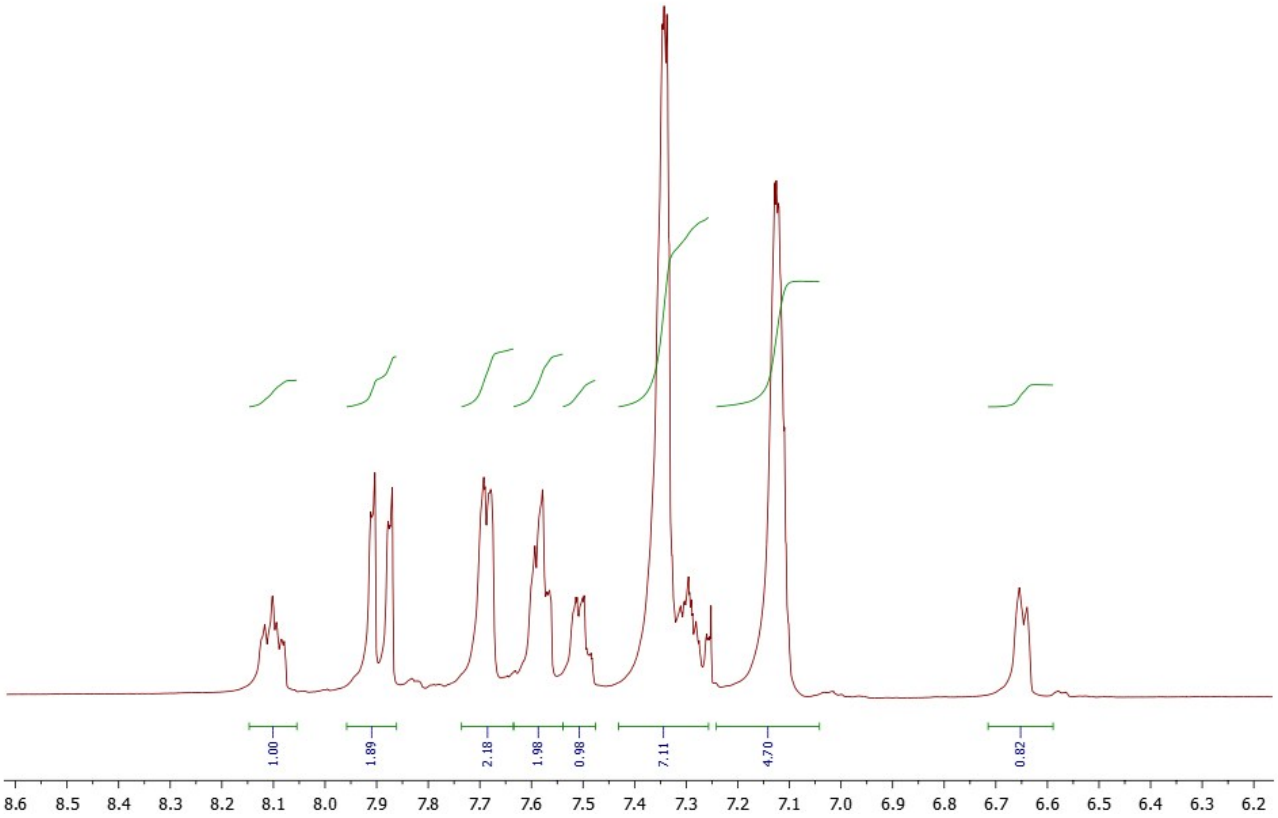


**Figure 9.** $^{1}H$ NMR spectrum of compound **12.**

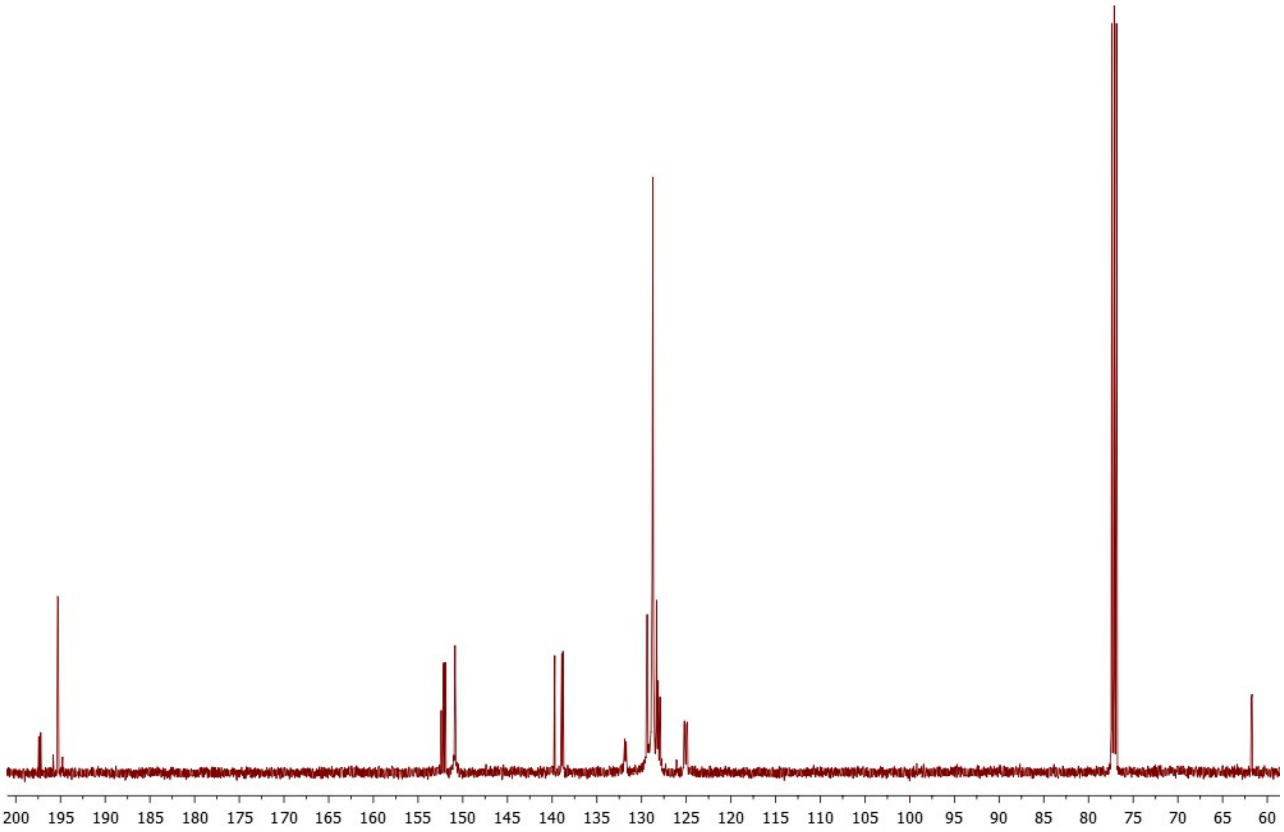


**Figure 10.** $^{13}C\{^{1}H\}$ NMR spectrum of compound **12.**

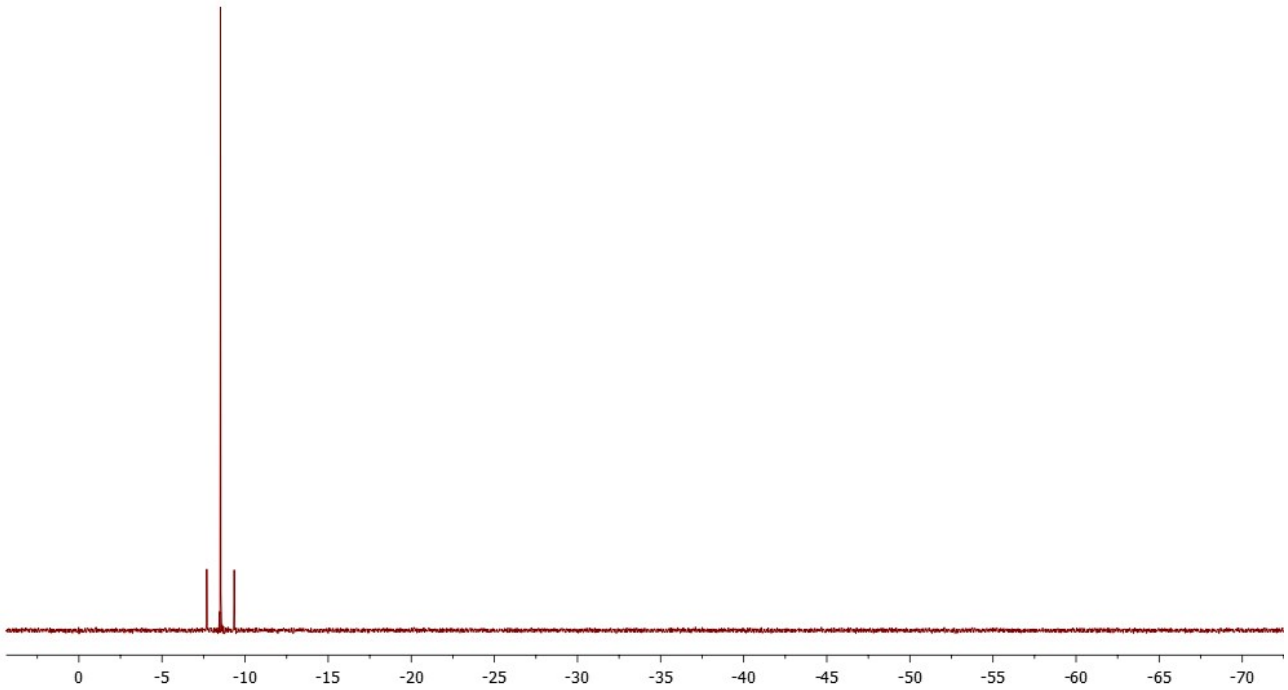

**Figure 11.** $^{31}P\{^{1}H\}$ NMR spectrum of compound **12.**

**[2,4,10-triphenyl-4H-1,4-ethenophosphinoline]-selenide (10):**

To a solution of **2** (30 mg, 0.075 mmol) in toluene, an excess of grey selenium was added and the solution was heated up to reflux overnight. Afterwards the solution was filtered over celite and the solvent was removed in vacuo, yielding the product as a white solid (34 mg, 95%).

$^{1}H$ NMR (THF-$d_8$, 400 MHz): δ = 6.56 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (m, 7H), 7.58 (m, 7H), 7.88 (d, *J* = 7.2 Hz 2H), 8.07 (d, *J* = 28.8 Hz, 2H), 8.14 (m, 1H) ppm.

$^{13}C\{^{1}H\}$ NMR (THF-$d_8$, 101 MHz): δ = 59.78 (d, *J* = 22.2 Hz), 124.88 (d, *J* = 6.4 Hz), 125.85 (d, *J* = 13.4 Hz), 128.73 (s), 128.96 (s), 128.97 (s), 129.32 (d, *J* = 3.4 Hz), 129.66 (d, *J* = 5.6 Hz), 129.76 (s), 130.19 (s), 130.20 (d, *J* = 11.2 Hz), 135.64 (d, *J* = 9.6 Hz), 135.84 (d, *J* = 67.6 Hz), 140.59 (d, *J* = 1.5 Hz), 146.23 (d, *J* = 52.1 Hz), 150.86 (s), 152.56 (s) ppm.

$^{31}P\{^{1}H\}$ NMR (THF-$d_8$, 162 MHz): δ = 6.6 (s, with $^{77}Se$ satellites, $^{1}J_{P\text{-}Se}$ = 833.9 Hz) ppm.

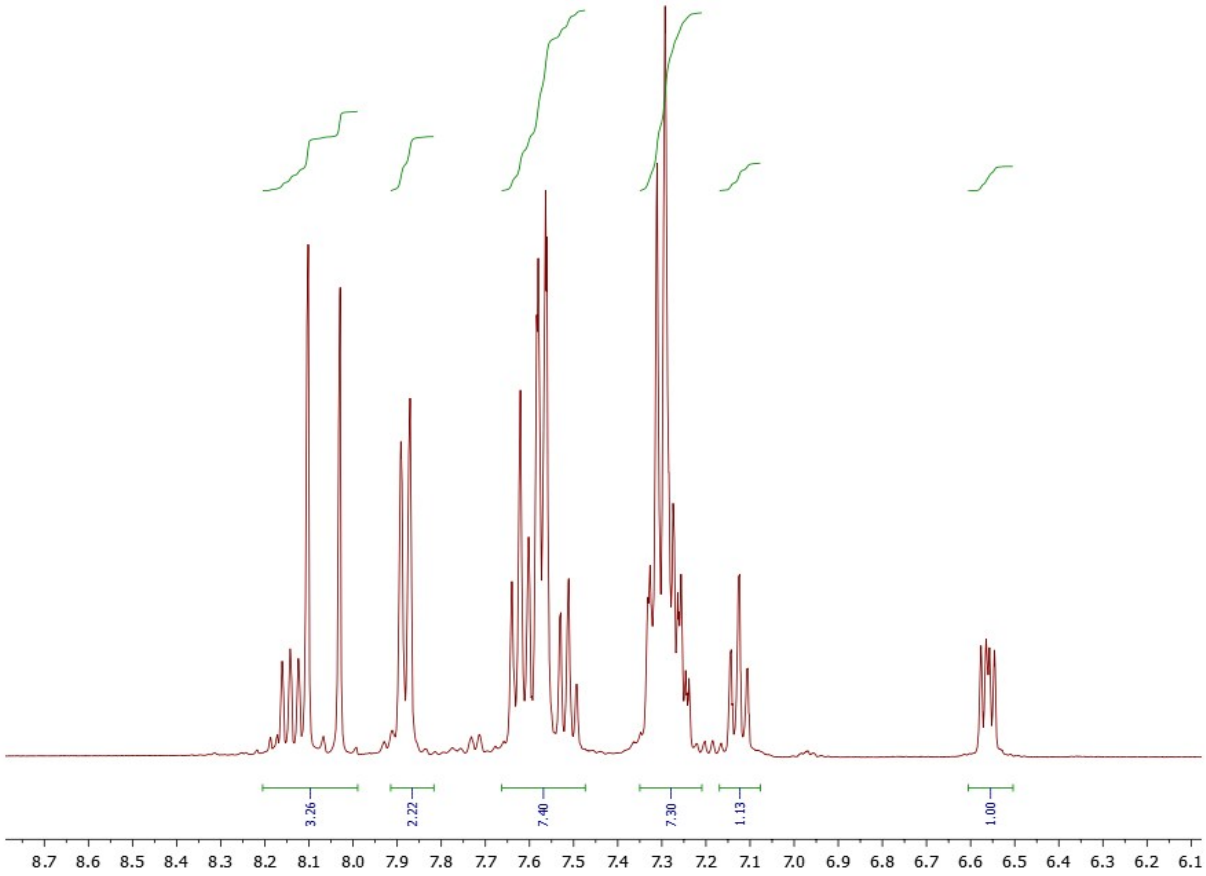


**Figure 12.** $^{1}H$ NMR spectrum of compound **10.**

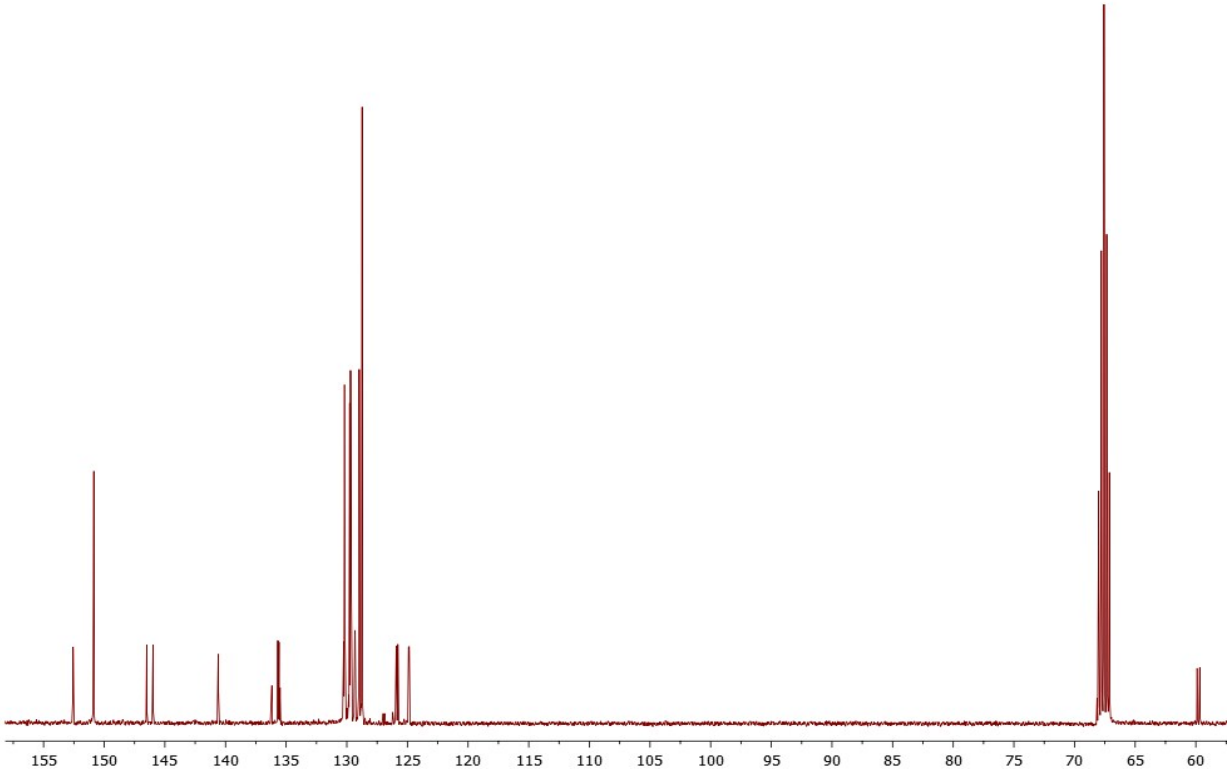


**Figure 13.** $^{13}C\{^{1}H\}$ NMR spectrum of compound **10.**

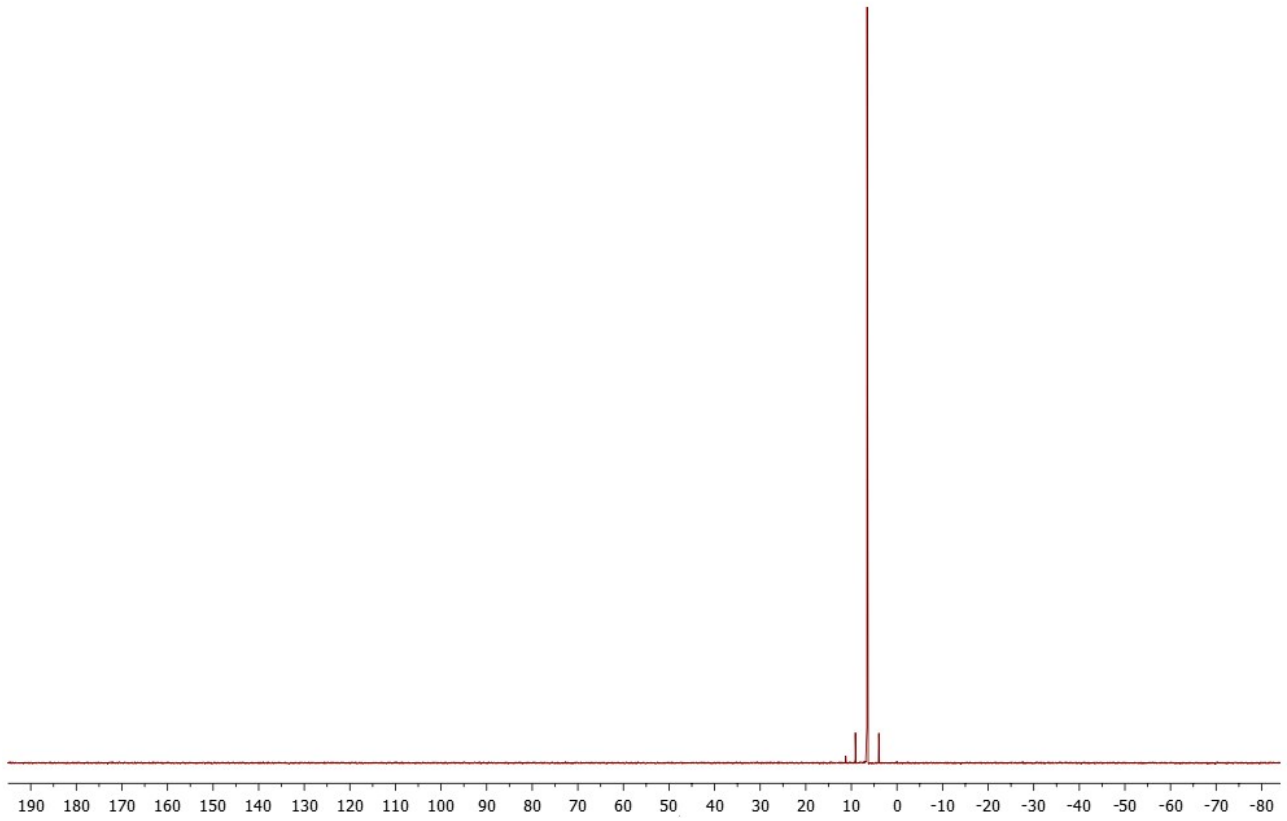


**Figure 14.** $^{31}P\{^{1}H\}$ NMR spectrum of compound **10.**

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