Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Nickel-Catalyzed Diversification of Phosphine Ligands by Formal Substitution at Phosphorus

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1. General information

All air-sensitive manipulations were performed under an inert atmosphere in an argon-filled glovebox (LABmaster Pro SP, MBraun) or by standard Schlenk techniques. The substrates and reagents for catalytic reactions were degassed and stored under an inert atmosphere in the glovebox. Bis(cycloocta-1,5-diene)nickel(0) ($Ni(COD)_2$) was purchased from Strem, and IiPr•HBF_4 (IiPr•HBF_4 = 1,3-di(*iso*-propyl)imidazolium tetrafluoroborate) was purchased from Sigma Aldrich. They were used as received and stored in an argon-filled glovebox. BH_3•SMe_2 and sodium cyanide were purchased from Sigma Aldrich and used as received. Anhydrous potassium phosphate (K_3PO_4) was purchased from Fluorochem and was dried in an oven (120 °C overnight) before it was stored under argon in a glovebox. Phenylboronic acid was purchased from Sigma Aldrich and directly transferred into an argon-filled glovebox for storage. We noticed that older batches of phenylboronic acid performed worse in the reaction, presumably because of the formation of triphenylboroxin (see optimization data). Freshly purchased phenylboronic acid that was stored under inert gas gave reproducible results for more than half a year. Commercial phosphonium salt starting materials were used without further purification or drying. The air-stable Ni(0) pre-catalysts **Ni-1**, **Ni-2**, and **Ni-3** were provided by the groups of Cornella and Engle.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial 400 MHz instruments at the NMR facility of ETH Zürich. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 101 MHz. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were acquired at 376 MHz. Phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectra were acquired at 162 MHz. ^{31}P{^{1}H} NMR spectra that show integration were acquired with inverse-gated decoupling (O1P = 0 ppm, D1 = 20 s). Boron-11 nuclear magnetic resonance (^{11}B NMR) spectra were acquired at 128 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 ppm for $CDCl_3$, 2.08 ppm for tol-d_8) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.16 ppm resonance of $CDCl_3$ or the δ 20.43 ppm resonance of tol-d_8. Coupling constants are reported in Hz. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), pent (quintet), hex (sextet), m (multiplet), and br (broad) or a combination thereof.

GC measurements were conducted on a Shimadzu GC-2025 Series GC system. GC-MS spectra were obtained on an instrument containing a Shimadzu GC-2010 Plus GC system and a Shimadzu GC-MS QP 2020 system.

High-resolution mass spectra were provided by the mass spectrometry service facility in the Laboratories of Organic Chemistry at ETH Zürich. The data was obtained using electron ionisation (EI) on a Thermo scientific Q Exactive GC Orbitrap with direct Probe, electrospray ionisation (ESI) on a Bruker maXis – ESI-Qq-TOF-MS or matrix-assisted laser desorption/ionisation (MALDI) on Bruker solariX – MALDI-FTICR-MS and are reported in m/z.

Analytical thin-layer chromatography was performed on pre-coated, glass-backed silica gel plates (Merck, 0.25 mm silica gel Si 60, F254). Visualization of the developed chromatogram was either performed by UV absorbance at a wavelength of λ = 254 nm or $KMnO_4$ stain. Flash column chromatography was performed on a Biotage Isolera One system with Sfär columns. Silica gel 60 (particle size 40 – 63 μm, Silicycle) was used to fill the cartridge of the Isolera One system.

Preparative HPLC separations were carried out on an Agilent 1260 Infinity II system (C18 5u, 250x21 mm) with reverse phase conditions using gradients of acetonitrile in H_2O (0.1% formic acid).

Safety Note: Sodium cyanide is highly toxic and should only be handled with caution in a fumehood and under basic reaction conditions to avoid the formation of gaseous HCN.

2. Reaction Optimization

Optimization of the reaction of monophosphonium salts

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.1 equiv.), IiPr•HBF_4 (4.8 mg, 0.02 mmol, 0.2 equiv.), benzyltriphenylphosphonium bromide (**1a**) (43.3 mg, 0.1 mmol, 1.0 equiv.), 4-methoxyphenylboronic acid (**S1**) (16.7 mg, 0.11 mmol, 1.1 equiv.), potassium phosphate (42.5 mg, 0.2 mmol, 2.0 equiv.), and dioxane (0.5 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 22 hours. After cooling to room temperature, triphenyl phosphate was added as an internal standard, and the mixture was diluted with 2 mL of dioxane. After shaking the vial for 30 seconds, ca. 0.5 mL of the solution were transferred to an NMR tube. Ca. 0.1 mL of THF-d_8 were also added to the NMR tube. The NMR tube was shaken to allow for mixing, and a $^{31}P\{^1H\}$ NMR spectrum with inverse-gated decoupling was acquired (O1P = 0 ppm, D1 = 20 s).

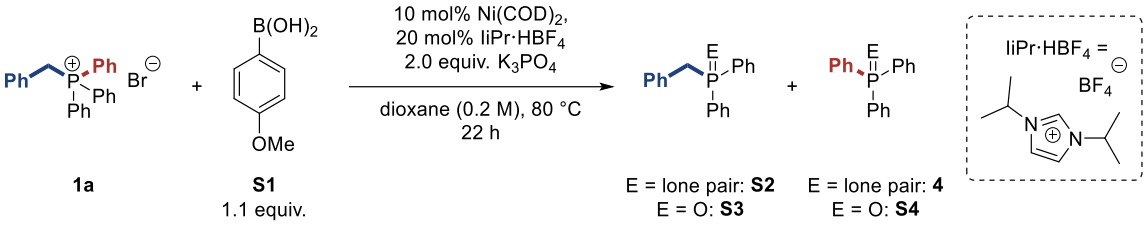


Table S1. Key optimization results for the reaction of monophosphonium salts.

Entry	Deviation from above	Yield **S2** + **S3** (%)[a]	Yield **4** + **S4** (%)[a]	Selectivity[b]
1	None	90	7	12.9
2	Pd_2dba_3 (5 mol%) instead of $Ni(COD)_2$	10	77	0.1
3	$Pd(OAc)_2$ instead of $Ni(COD)_2$	5	79	0.1
4	$NiCl_2$•glyme instead of $Ni(COD)_2$	31	66	0.5
5	SIPr•HCl instead of IiPr•HBF_4	70	9	7.8
6	Phen (10 mol%) instead of IiPr•HBF_4	66	20	3.3
7	dcype (10 mol%) instead of IiPr•HBF_4	54	48	1.1
8	**$PhB(OH)_2$ instead of S1**	**87 (82[c])**	**6**	**14.5**
9	$Ph_3(BO)_3$ instead of **S1**	11	8	1.5
10	B_2pin_2	51	21	2.4
11	PhBpin instead of **S1**	44	17	2.6
12	$PhBF_3K$ instead of **S1**	45	25	1.8
13	4-$MeC_6H_4B(OH)_2$ instead of **S1**	80	9	8.9
14	4-$CF_3C_6H_4B(OH)_2$ instead of **S1**	65	4	16.3
15	60 °C	81	5	16.2
16	10 mol% IiPr•HBF_4	78	5	15.6
17	5 mol% $Ni(COD)_2$, 10 mol% IiPr•HBF_4	74	7	10.6
18	Toluene instead of dioxane	24	46	0.5
19	No $Ni(COD)_2$	6	90	0.1
20	No IiPr•HBF_4	73	5	14.6
21	No **S1**	28	60	0.5
22	No K_3PO_4	0	6	0
23	$PhB(OH)_2$ instead of **S1** $NiCl_2$•glyme instead of $Ni(COD)_2$, 0.2 equiv. Mn	9	85	0.1
24	$PhB(OH)_2$ instead of **S1** $NiCl_2$•glyme instead of $Ni(COD)_2$, 0.2 equiv. Zn	10	88	0.1
25	$PhB(OH)_2$ instead of **S1** $NiBr_2$•glyme instead of $Ni(COD)_2$, 0.2 equiv. Mn	11	81	0.1
26	$PhB(OH)_2$ instead of **S1** $NiBr_2$•glyme instead of $Ni(COD)_2$, 0.2 equiv. Zn	14	86	0.2

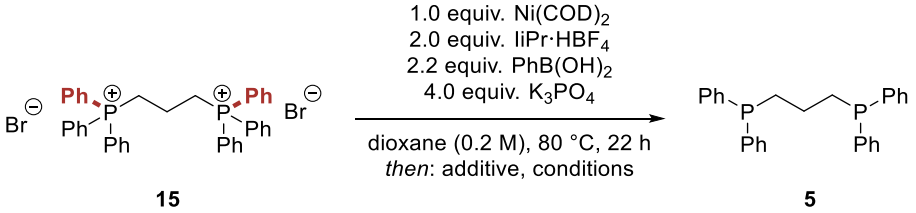
a: Combined $^{31}P\{^1H\}$ qNMR yield of the phosphine product and its corresponding oxide using triphenyl phosphate as internal standard. b: selectivity = (**S2**+**S3**)/(**4**+**S4**). c: isolated yield after derivatization to the borane adduct.

In all reactions, **4** was only observed in trace amounts and the main dealkylation product was triphenylphosphine oxide (**S4**). As **S4** was also formed in 90% in the absence of $Ni(COD)_2$ (Table S1, entry 19), we think that the minor dealkylation side reaction is a non-catalyzed background reaction, potentially as a result of trace moisture in the reaction mixture.
Similarly, we think that the formation of **S4** as the major product in the presence of palladium and nickel(II) catalysts (entries 2-4) might be caused by the same background reaction. The metal(II) precatalysts might be ineffective due to lack of a suitable reductants to access active metal(0) species. Pd_2dba_3 might be inactive at the tested reaction temperature because of inhibition by dba that prevents oxidative addition into the more weakly-binding phosphonium salt starting material.
Isolated phosphine products (typically derivatized to the BH_3 adduct) did not contain measurable amounts of undesired dealkylation products if not indicated.
The fact that the reaction also proceeds in good yield in the absence of the NHC ligand (entry 20) leads us to believe that the phosphine product **S2** can also act as a catalytically active ligand for the Ni-catalyst. The main role of the NHC ligand may therefore simply be to prevent undesired binding of the phosphine product **S2** to nickel, leading to higher yields.

Optimization of the reaction of bisphosphonium salts

Initial decomplexation experiments

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (1.0 equiv.), IiPr•HBF_4 (2.0 equiv.), bisphosphonium salt **15** (1.0 equiv.), phenylboronic acid (2.2 equiv.), potassium phosphate (4.0 equiv.), and dioxane (0.2 M). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 22 hours. The mixture was allowed to cool down and partitioned into multiple vials. Each resulting sample was further diluted with the indicated solvent and was then subjected to different additives and reaction conditions listed below (Table S2). The reaction mixture was analyzed by GC/MS to probe the formation of DPPP (**5**).



15 **5**

Table S2. Initial decomplexation studies.

Entry	Additive	Equiv.	Conditions	Product formation
1	2-2'-Bipy	3.0	dioxane, 100 °C, 22 h	Not detected
2	2-2'-Bipy	5.0	dioxane, 120 °C, 22 h	Not detected
3	4,4'-Dimethoxy-2,2'-bipyridine	5.0	dioxane, 120 °C, 22 h	Not detected
4	4,4'-Dimethoxy-2,2'-bipyridine	10.0	dioxane, 120 °C, 22 h	Not detected
5	4,4'-Dimethoxy-2,2'-bipyridine	10.0	dioxane/DMA, 150 °C, 22 h	Not detected
6	Dcype	3.0	dioxane, 100 °C, 22 h	Not detected
7	TMEDA	5.0	dioxane, 100 °C, 22 h	Not detected
8	TMEDA	5.0	dioxane, 120 °C, 22 h	Not detected
9	TMEDA	10.0	dioxane, 120 °C, 22 h	Not detected
10	TMEDA	10.0	dixoxane/DMA, 150 °C, 22 h	Not detected
11	(L)-Cysteine	6.0	dioxane, 120 °C, 22 h	Not detected
12	Na_2H_2EDTA	5.0	dioxane, 100 °C, 22 h	Not detected
13	Na_2H_2EDTA	5.0	dioxane, 120 °C, 22 h	Not detected
14	Na_2H_2EDTA	10.0	dioxane, 120 °C, 22 h	Not detected
15	Na_2H_2EDTA	10.0	dioxane/DMA, 150 °C, 22 h	Not detected
16	Melamine	6.0	dioxane, 120 °C, 22 h	Not detected
17	NaCN	20.0	dioxane/Toluene/DMA, 150 °C, 22 h	Not detected
18	**NaCN**	**6.0**	**dioxane/Toluene/Water, 80 °C, 22 h**	**Observed**

Optimization of the decomplexation step

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with bis(bis(diphenylphosphino)propane))nickel(0) ($Ni(DPPP)_2$) (22.1 mg, 0.025 mmol, 1.0 equiv.) and dioxane (0.5 mL). The vial was capped with a septum cap and taken out of the glovebox. KCN (9.7 mg, 0.15 mmol, 6.0 equiv.) was added as a solution in water (0.5 mL) through the septum. Then, the co-solvent was added through the septum. The vial was stirred in a pre-heated heating block with 600 rpm at 80 °C for 3 hours. After cooling to room temperature, *n*-dodecane (7.5 µL) was added, the vial was shaken, and a sample was taken for GC analysis.

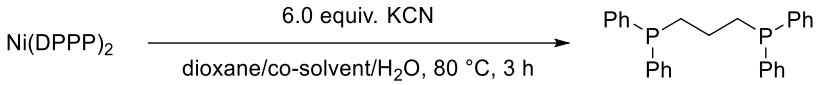


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Table S3. Optimization of the decomplexation step.

Entry	Co-solvent	Other deviation	Yield (%)[a]
1	-	-	< 5%
2	-	100 °C	< 5%
3	tol	-	< 5%
4	C_6H_5Cl	-	< 5%
5	DCM	-	50%
6	DCM	1200 rpm	73%
7	DCM	0.25 mL H_2O	86%
8	DCM	1200 rpm, 0.25 mL H_2O, 50 °C, 20 h	17%
9	**DCE**	**1200 rpm, 0.25 mL H_2O**	**quant.**

a: Yield determined by GC analysis using *n*-dodecane as internal standard.

Optimization of the combined reaction steps

Procedure for optimization reactions:

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (6.9 mg, 0.025 mmol, 0.5 equiv.) bisphosphonium salt **15** (36.3 mg, 0.05 mmol, 1.0 equiv.), phenylboronic acid (13.4 mg, 0.11 mmol, 2.2 equiv.), potassium phosphate (42.5 mg, 0.2 mmol, 4.0 equiv.), and dioxane (0.5 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block with 1200 rpm at 80 °C for 22 hours. After cooling to room temperature, a solution of sodium cyanide (7.4 mg, 0.15 mmol, 3.0 equiv.) in water (0.25 mL) was added through the septum. Then, DCE (0.5 mL) was added through the septum. The vial was stirred in a pre-heated heating block with 1200 rpm at 80 °C for 3 hours. After cooling to room temperature, *n*-dodecane (7.5 µL) was added, the vial was shaken, and a sample was taken for GC analysis.

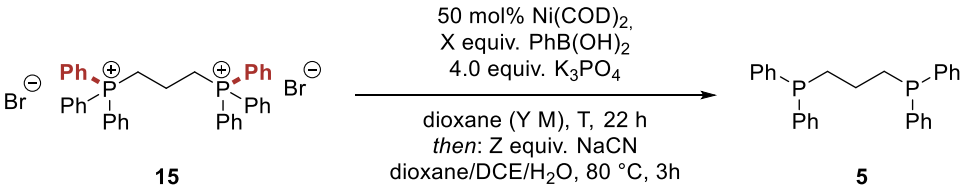


Table S4. Key optimization results for the reaction of bisphosphonium salts.

Entry	X	Y	Z	T (°C)	Other deviation	Yield (%)[a]
1	2.2	0.1	3.0	80	KCN instead of NaCN	23
2	2.2	0.1	3.0	80	-	29
3	2.2	0.1	3.0	80	0.6 equiv $Ni(COD)_2$	28
4	2.2	0.1	3.0	80	1.0 equiv $Ni(COD)_2$	25
5	2.2	0.1	3.0	80	2.2 equiv. K_3PO_4	26
6	3.0	0.1	3.0	80	-	52
7	2.2	0.05	3.0	80	-	31
8	2.2	0.1	4.0	80	-	36
9	2.2	0.1	6.0	80	-	34
10	2.2	0.1	3.0	60	-	40
11	2.2	0.1	3.0	80	1.0 mL DCE	31
12	3.0	0.05	4.0	60	1.0 mL DCE	29
13	**4.0**	**0.05**	**4.0**	**60**	**1.0 mL DCE**	**57**

a: Yield determined by GC analysis using *n*-dodecane as internal standard.

3. Synthesis of starting materials

General procedure for the formation of phosphonium salts (GP1)

Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with phosphine (1.5 mmol, 1.0 equiv.) and toluene (0.5 mL). The vial was capped with a septum cap and taken out of the glovebox. 1-Bromobutane (**3**) (480 µL, 4.5 mmol, 3.0 equiv.) was added through the septum, and the reaction mixture was stirred overnight at 120 °C.
Different protocols were followed to isolate the products:

Workup procedure A:
After cooling to room temperature, volatile materials were evaporated under reduced pressure. The resulting foam was crushed, suspended in Et_2O, and stirred vigorously for 15 minutes. After cooling to 0 °C, the mixture was filtered and washed with cold Et_2O (0 °C) to yield the phosphonium salt.
Workup procedure B:
After cooling to room temperature, volatile materials were evaporated under reduced pressure. The residue was dissolved in a small amount of DCM. Addition of an excess of Et_2O led to the formation of a precipitate. After cooling to 0 °C, the mixture was filtered and washed with cold Et_2O (0 °C) to yield the phosphonium salt.
Workup procedure C:
After cooling to room temperature, an excess of toluene was added to the reaction mixture. After stirring for 5 minutes, the reaction mixture was filtered, and the residue was washed with toluene and diethyl ether to yield the phosphonium salt.

A different workup procedure was followed in some cases.

Commercially available starting materials:

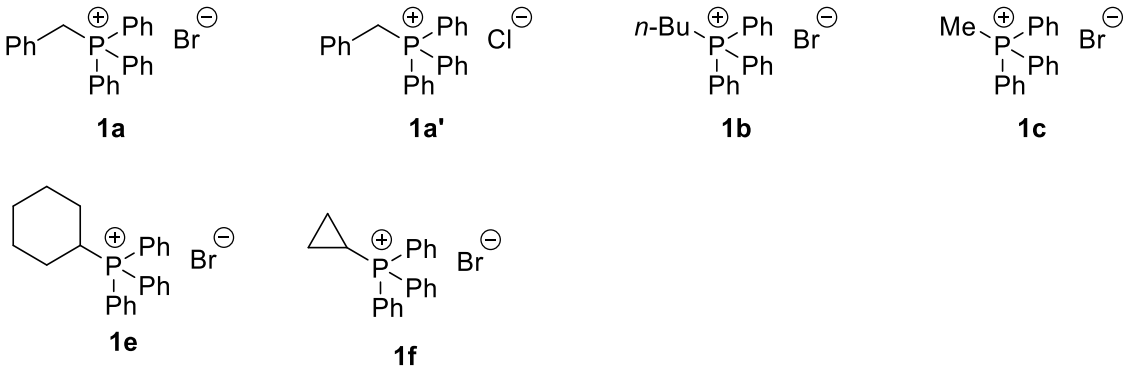
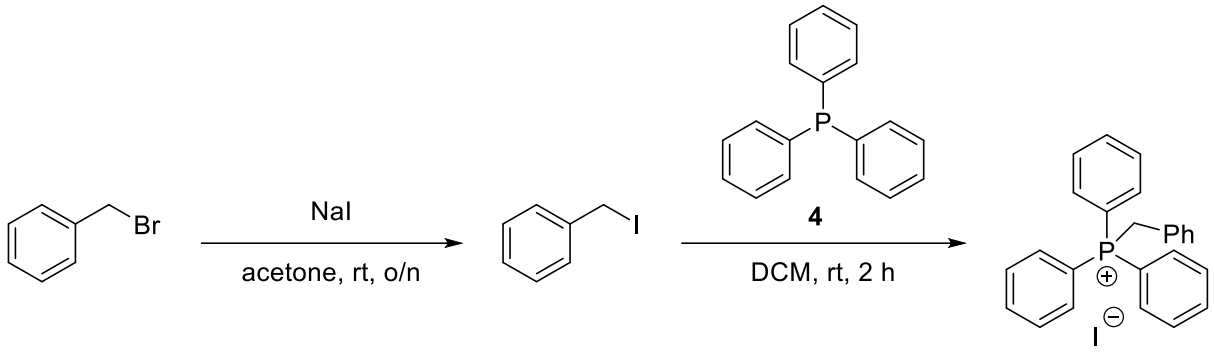


Figure S1. Commercially available starting materials.

The phosphonium salts **1a**, **1a'**, **1b**, **1c**, **1e**, and **1f** are commercially available and were used as received.

Benzyltriphenylphosphonium iodide (1a'')



11 **S5** **1a''**

Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with sodium iodide (540 mg, 3.6 mmol, 2.4 equiv.). The vial was capped with a septum cap and taken out of the glovebox. Benzyl bromide (**11**) (210 µL, 1.8 mmol, 1.2 equiv.) and dry acetone (3.6 mL) were added by syringe through the septum. The reaction mixture was stirred in the dark at room temperature overnight. Afterwards, the reaction mixture was filtered, and the residue was washed with acetone. Volatile materials of the combined filtrate were evaporated under reduced pressure. The residue was dissolved in Et_2O and washed twice with water. The organic layer was dried with magnesium sulfate, and volatile materials were evaporated under reduced pressure to yield a brown oil. DCM (5.7 mL) and subsequently triphenylphosphine (**4**) (390 mg, 1.5 mmol, 1.0 equiv.) were added. The mixture was stirred at room temperature for two hours. Then, an excess of Et_2O was added. After cooling to 0 °C, the mixture was filtered, and the residue washed with cold Et_2O (0 °C) to yield the title compound as a white solid (523 mg, 73%).

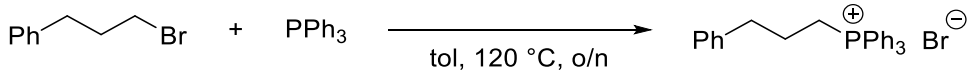
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.74 (m, 3H), 7.75 – 7.68 (m, 6H), 7.67 – 7.60 (m, 6H), 7.25 – 7.21 (m, 1H), 7.16 – 7.11 (m, 2H), 7.10 – 7.07 (m, 2H), 5.26 (d, *J* = 14.2 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 135.3 (d, *J* = 3.1 Hz), 134.6 (d, *J* = 9.8 Hz), 131.6 (d, *J* = 5.5 Hz), 130.4 (d, *J* = 12.5 Hz), 129.1 (d, *J* = 3.4 Hz), 128.7 (d, *J* = 3.8 Hz), 126.9 (d, *J* = 8.6 Hz), 117.8 (d, *J* = 85.8 Hz), 31.4 (d, *J* = 47.2 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 22.9 ppm.

HRMS (ESI+): m/z for $C_{25}H_{22}P$ $[M\text{-}I]^+$ calcd.: 353.1454, found: 353.1452.

Triphenyl(3-phenylpropyl)phosphonium bromide (1d)



S6 **4** **1d**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (2.62 g, 10.0 mmol, 1.0 equiv.), alkyl bromide **S6** (1.52 mL, 12.0 mmol, 1.2 equiv.), and toluene (3.3 mL). The vial was capped, and the reaction mixture was stirred at 120 °C for overnight. After cooling to room temperature, an excess of Et_2O was added to the reaction mixture. After cooling to 0 °C, the reaction mixture was filtered, and the residue washed with cold Et_2O (0 °C) to yield the title compound as a white solid (3.38 g, 73%).

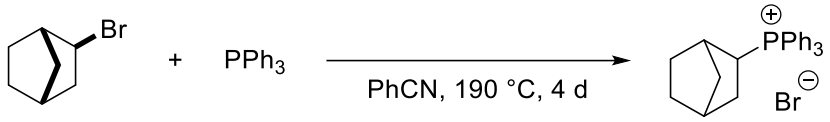
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.67 (m, 9H), 7.67 – 7.58 (m, 6H), 7.24 – 7.18 (m, 2H), 7.18 – 7.11 (m, 3H), 3.89 – 3.71 (m, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 1.92 (hex, *J* = 7.7 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 140.2, 135.1 (d, *J* = 3.0 Hz), 133.7 (d, *J* = 10.0 Hz), 130.5 (d, *J* = 12.6 Hz), 128.8 (d, *J* = 34.7 Hz), 126.4, 118.2 (d, *J* = 86.0 Hz), 35.7 (d, *J* = 16.6 Hz), 24.6 (d, *J* = 4.0 Hz), 21.7 (d, *J* = 50.7 Hz) ppm (1 less signal than expected due to overlapping signals or assignment as doublet instead of singlet).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 24.4 ppm.

The spectroscopic data matched those reported in the literature.[1]

(2-Norbornyl)triphenylphosphonium bromide (1g)



S7 **4** **1g**

A 16-mL screw-cap vial was charged with triphenylphosphine (790 mg, 3.0 mmol, 1.0 equiv.), *exo*-2-bromonorbornane (**S7**) (460 µL, 3.6 mmol, 1.2 equiv.), and benzonitrile (0.6 mL). The vial was capped, and the reaction mixture was stirred at 190 °C for 4 days. After cooling to room temperature, the reaction mixture was triturated with diethyl ether until the solution was colorless (5 times). The residue was dissolved in DCM and filtered through a silica plug, first eluting with DCM and then with 15% MeOH in DCM. The latter fraction was collected and dried to yield the title compound as a 9:1 mixture of diastereomers (766 mg, 58%).

The characterization data for the major isomer are reported here:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.86 (m, 6H), 7.74 – 7.68 (m, 3H), 7.68 – 7.62 (m, 6H), 4.84 (q, *J* = 9.0 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.37 – 2.27 (m, 2H), 2.20 (br, 1H), 1.78 – 1.69 (m, 1H), 1.68 – 1.50 (m, 3H), 0.86 (d, *J* = 10.3 Hz, 1H), -0.02 (d, *J* = 10.4 Hz, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.8 (d, *J* = 3.0 Hz), 134.0 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 12.1 Hz), 118.9 (d, *J* = 84.1 Hz), 39.5, 37.4, 36.4 (d, *J* = 4.0 Hz), 33.1 (d, *J* = 4.8 Hz), 31.4 (d, *J* = 3.8 Hz), 31.3 (d, *J* = 57.0 Hz), 27.8 ppm.

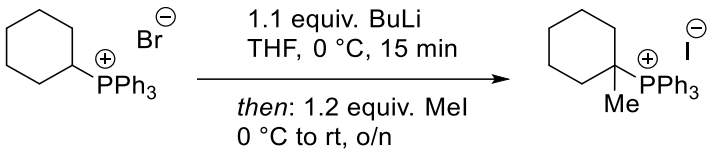
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 27.0 ppm.

HRMS (ESI+): m/z for $C_{25}H_{26}P$ $[M\text{-}Br]^+$ calcd.: 357.1767, found: 357.1766.

The minor isomer has a ^{31}P{^{1}H} NMR shift of 25.3 ppm. Its ^{1}H NMR signals largely overlap with the major isomer. Distinct peaks are visible at 7.85–7.79 ppm (m), 3.01 ppm (br), 1.44–1.19 ppm (m), and 0.61–0.53 ppm (m).

The diastereomeric ratio was determined by ^{31}P{^{1}H} qNMR spectroscopy. Comparison of the spectroscopic data with literature values indicated that the major isomer is the *exo*-isomer.[2]

(1-Methylcyclohexyl)triphenylphosphonium iodide (1h)



1e **1h**

Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with cyclohexyltriphenylphosphonium bromide (**1e**) (640 mg, 1.5 mmol, 1.0 equiv.). The vial was capped with a septum cap and taken out of the glovebox. THF (6 mL) was added through the septum, and the vial was cooled to 0 °C. *n*-Butyllithium (1.6 M in hexanes, 1.05 mL, 1.65 mmol, 1.1 equiv.) was slowly added dropwise. After the addition was complete, the reaction mixture was stirred at 0 °C for 15 min. Then, iodomethane (110 µL, 1.8 mmol, 1.2 equiv.) was slowly added dropwise, and the reaction mixture was allowed to warm to ambient temperature overnight. Next, a saturated aqueous ammonium chloride solution was added, and the mixture was stirred for another 30 minutes. The phases were separated, and the aqueous layer was extracted with DCM three times. The combined organic layers were washed with water twice and subsequently dried with magnesium sulfate. Volatile materials were removed under reduced pressure to yield the title compound as a pale yellow solid (650 mg, 89%).

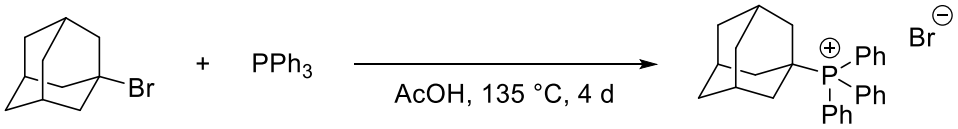
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.80 (m, 3H), 7.79 – 7.71 (m, 6H), 7.69 – 7.62 (m, 6H), 1.99 – 1.81 (m, 4H), 1.74 – 1.54 (m, 8H), 1.28 – 1.11 (m, 1H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 135.3 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 8.5 Hz), 130.9 (d, *J* = 11.7 Hz), 116.9 (d, *J* = 79.2 Hz), 39.7 (d, *J* = 41.5 Hz), 33.1 (d, *J* = 1.4 Hz), 24.5 (d, *J* = 1.6 Hz), 20.6 (d, *J* = 11.5 Hz), 19.9 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 35.2 ppm.

HRMS (ESI+): m/z for $C_{25}H_{28}P$ $[M\text{-}I]^+$ calcd.: 359.1923, found: 359.1921.

Adamant-1-yltriphenylphosphonium bromide (1i)



S8 **4** **1i**

Under an atmosphere of nitrogen, a 50-mL round-bottom flask equipped with a reflux condenser was charged with 1-bromoadamantane (**S8**) (1.5 g, 7.0 mmol, 1.4 equiv.) and triphenylphosphine (**4**) (1.3 g, 5.0 mmol, 1.0 equiv.). Glacial acetic acid (10 mL) was added, and the mixture was heated under reflux (heating block set to 135 °C) for 4 days. After cooling to room temperature, volatile materials were removed under reduced pressure. The residue was dissolved in a minimal amount of ethanol and crashed out with ether. Filtration yielded the product[3] as a white solid (2.3 g, 96%).

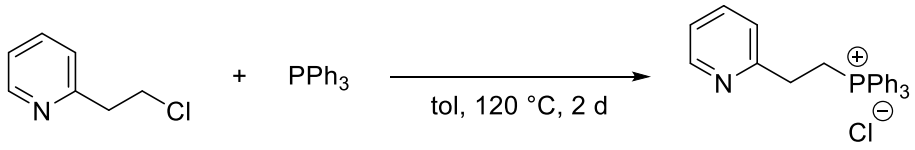
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 – 7.74 (m, 3H), 7.69 (td, *J* = 7.8, 3.5 Hz, 6H), 7.61 – 7.51 (m, 6H), 2.06 (d, *J* = 5.6 Hz, 9H), 1.71 (*pseudo*-q, *J* = 11.9 Hz, 6H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 135.2 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 8.6 Hz), 130.7 (d, *J* = 11.7 Hz), 116.2 (d, *J* = 79.7 Hz), 39.1 (d, *J* = 40.2 Hz), 37.6 (d, *J* = 2.5 Hz), 35.3 (d, *J* = 2.1 Hz), 27.7 (d, *J* = 10.3 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 28.8 ppm.

HRMS (ESI+): m/z for $C_{28}H_{30}P$ $[M\text{-}Br]^+$ calcd.: 397.2080, found: 397.2072.

Triphenyl(2-(pyridin-2-yl)ethyl)phosphonium chloride (1j)



S9 **4** **1j**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (260 mg, 1.0 mmol, 1.0 equiv.), 2-(2-chloroethyl)pyridine (**S9**) (420 mg, 3.0 mmol, 3.0 equiv.), and toluene (0.3 mL). The vial was flushed with nitrogen and capped. The reaction mixture was stirred at 120 °C for two days. After cooling to room temperature, the reaction mixture was loaded on silica and purified by flash column chromatography (3% to 15% methanol in DCM) to yield the title compound as a white solid (315 mg, 78%).

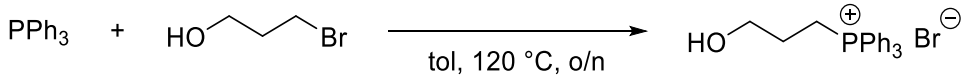
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, J = 4.8 Hz, 1H), 7.84 – 7.74 (m, 6H), 7.74 – 7.67 (m, 3H), 7.65 – 7.58 (m, 6H), 7.54 – 7.47 (m, 2H), 7.03 – 6.95 (m, 1H), 4.20 (dt, *J* = 12.7 Hz, *J* = 7.4 Hz, 2H), 3.27 (*pseudo*-pent, *J* = 7.2 Hz, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 157.0 (d, *J* = 11.9 Hz), 148.6, 137.1, 135.0 (d, *J* = 3.0 Hz), 133.7 (d, *J* = 10.0 Hz), 130.4 (d, *J* = 12.6 Hz), 124.1, 122.1, 118.3 (d, *J* = 86.1 Hz), 30.3 (d, *J* = 3.6 Hz), 21.8 (d, *J* = 51.4 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 24.4 ppm.

HRMS (ESI+): m/z for $C_{25}H_{23}NP$ $[M\text{-}Cl]^+$ calcd.: 368.1563, found: 368.1559.

(3-Hydroxypropyl)triphenylphosphonium bromide (1k)



4 **S10** **1k**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (2.9 g, 11 mmol, 1.1 equiv.), 3-bromopropan-1-ol (**S10**) (900 µL, 10 mmol, 1.0 equiv.), and toluene (4 mL). The vial was capped and the reaction mixture was stirred at 120 °C overnight. After cooling to room temperature, an excess of Et_2O was added. The mixture was filtered, and the residue was washed three times with Et_2O to yield the title compound as a white solid (2.2 g, 55% (containing a small amount of an unidentified impurity)).

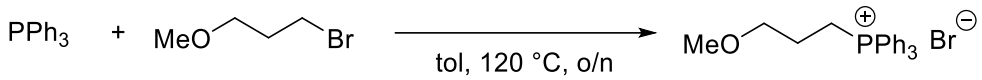
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.61 (m, 15H), 4.89 (br, 1H), 3.83 – 3.72 (m, 2H), 3.72 – 3.62 (m, 2H), 1.88 – 1.75 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 135.1 (d, *J* = 3.0 Hz), 133.5 (d, *J* = 9.9 Hz), 130.6 (d, *J* = 12.6 Hz), 118.3 (d, *J* = 86.2 Hz), 60.3 (d, *J* = 16.6 Hz), 25.9 (d, *J* = 4.4 Hz), 20.2 (d, *J* = 52.6 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 24.3 ppm.

The spectroscopic data matched those reported in the literature.[4]

(3-Methoxypropyl)triphenylphosphonium bromide (1l)



4 **S11** **1l**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (1.03 g, 4.0 mmol, 1.0 equiv.), 1-bromo-3-methoxypropane (**S11**) (680 µL, 6.0 mmol, 1.5 equiv.), and toluene (1.3 mL). The vial was capped and the reaction mixture was stirred at 120 °C overnight. After cooling to room temperature, an excess of Et_2O was added. The mixture was stirred for 5 minutes and cooled to 0 °C. It was then filtered, and the residue was washed three times with cold Et_2O (0 °C) to yield the title compound as a white solid (1.55 g, 93%).

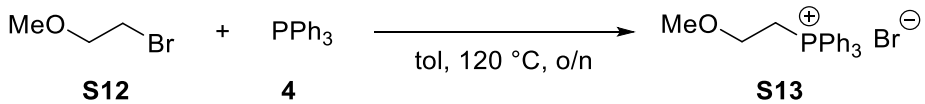
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 – 7.71 (m, 9H), 7.69 – 7.62 (m, 6H), 3.87 – 3.76 (m, 2H), 3.62 (td, *J* = 5.7, 1.3 Hz, 2H), 3.23 (s, 3H), 1.96 – 1.82 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 135.1 (d, *J* = 3.0 Hz), 133.7 (d, *J* = 10.0 Hz), 130.5 (d, *J* = 12.5 Hz), 118.3 (d, *J* = 86.3 Hz), 70.9 (d, *J* = 15.9 Hz), 58.7, 23.3 (d, *J* = 3.9 Hz), 19.9 (d, *J* = 52.6 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 24.8 ppm.

HRMS (ESI+): m/z for $C_{22}H_{24}OP$ $[M\text{-}Br]^+$ calcd.: 355.1559, found: 355.1557.

(2-Methoxyethyl)triphenylphosphonium bromide (S13)



S12 **4** **S13**

A 100-mL round-bottom flask was charged with triphenylphosphine (**4**) (2.62 g, 10.0 mmol, 1.0 equiv.), toluene (10 mL), and 1-bromo-2-methoxyethane (**S12**) (1.2 mL, 13 mmol, 1.3 equiv.). The reaction mixture was stirred at 120 °C overnight. After cooling to room temperature, an excess of Et_2O was added. The mixture was cooled to 0 °C and subsequently filtered. The residue was washed with cold Et_2O (0 °C) to yield the title compound as a white solid (2.65 g, 66%).

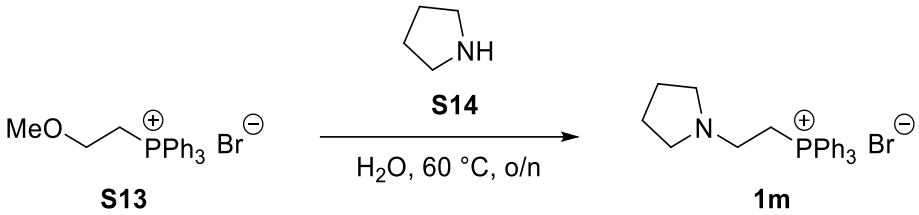
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.67 (m, 9H), 7.62 – 7.56 (m, 6H), 4.04 (dt, *J* = 11.6, 5.7 Hz, 2H), 3.75 (dt, *J* = 22.6, 5.7 Hz, 2H), 2.94 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 134.7 (d, *J* = 3.1 Hz), 133.8 (d, *J* = 10.3 Hz), 130.1 (d, *J* = 12.8 Hz), 118.7 (d, *J* = 86.9 Hz), 65.3 (d, *J* = 7.3 Hz), 58.5, 25.3 (d, *J* = 52.8 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 25.4 ppm.

The spectroscopic data matched those reported in the literature.[5]

Triphenyl(2-(pyrrolidin-1-yl)ethyl)phosphonium bromide (1m)



S13 **1m**

A 16-mL screw-cap vial was charged with phosphonium salt **S13** (800 mg, 2.0 mmol, 1.0 equiv.), water (360 µL), and pyrrolidine (**S14**) (180 µL, 2.2 mmol, 1.1 equiv.). The reaction mixture was stirred at 60 °C overnight. After cooling to room temperature, an excess of acetone was added, and the reaction mixture was stirred vigorously for one hour. The mixture was cooled to 0 °C, subsequently filtered, and washed with cold acetone (0 °C) to yield the title compound as a white solid (530 mg, 60%).

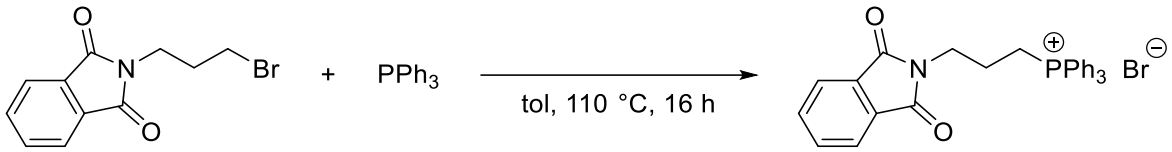
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.74 (m, 6H), 7.75 – 7.68 (m, 3H), 7.66 – 7.58 (m, 6H), 3.90 (dt, *J* = 12.1, 6.3 Hz, 2H), 2.88 (dt, *J* = 21.7, 6.3 Hz, 2H), 2.35 – 2.24 (br, 4H), 1.51 – 1.39 (m, 4H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.7 (d, *J* = 3.1 Hz), 133.9 (d, *J* = 10.2 Hz), 130.1 (d, *J* = 12.6 Hz), 118.8 (d, *J* = 86.4 Hz), 53.6, 48.7 (d, *J* = 5.2 Hz), 24.7 (d, *J* = 51.3 Hz), 23.3 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 25.8 ppm.

The spectroscopic data matched those reported in the literature.[5]

(3-Phthaloylpropyl)triphenylphosphonium bromide (1n)



S15 **4** **1n**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (1.05 g, 4.0 mmol, 1.0 equiv.), alkyl bromide **S15** (1.07 g, 4.0 mmol, 1.0 equiv.), and toluene (0.5 mL). The vial was capped, and the reaction mixture was stirred at 110 °C for 16 hours. After cooling to room temperature, an excess of Et_2O was added to the reaction mixture. After cooling to 0 °C, the reaction mixture was filtered and washed with cold Et_2O (0 °C) to yield the title compound as a white solid (1.45 g, 69%).

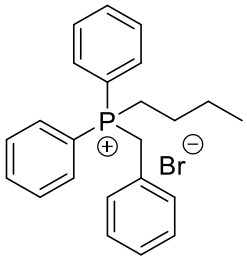
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.76 (m, 6H), 7.76 – 7.58 (m, 13H), 4.07 – 3.96 (m, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 2.16 – 2.01 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.1, 135.2 (d, *J* = 3.1 Hz), 134.3, 133.7 (d, *J* = 10.1 Hz), 131.9, 130.6 (d, *J* = 12.6 Hz), 123.4, 118.0 (d, *J* = 86.3 Hz), 38.1 (d, *J* = 17.0 Hz), 22.0 (d, *J* = 3.7 Hz), 20.8 (d, *J* = 52.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 24.7 ppm.

The spectroscopic data matched those reported in the literature.[6]

Benzylbutyldiphenylphosphonium bromide (1o)



The title compound was prepared following general procedure GP1, using benzyldiphenylphosphine (410 mg, 1.5 mmol, 1.0 equiv.).
Reaction workup following workup procedure A yielded the title compound as a white solid (539 mg, 87%).

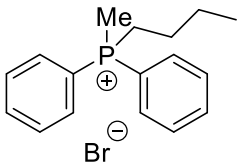
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.76 (m, 4H), 7.76 – 7.67 (m, 2H), 7.64 – 7.55 (m, 4H), 7.16 – 7.11 (m, 1H), 7.10 – 7.00 (m, 4H), 4.91 (d, *J* = 14.8 Hz, 2H), 3.19 – 3.07 (m, 2H), 1.48 – 1.28 (m, 4H), 0.79 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.8 (d, J = 3.0 Hz), 133.8 (d, J = 9.1 Hz), 130.8 (d, J = 5.5 Hz), 130.1 (d, J = 12.1 Hz), 128.8 (d, J = 3.4 Hz), 128.2 (d, J = 4.0 Hz), 127.6 (d, J = 8.6 Hz), 117.2 (d, J = 82.2 Hz), 30.6 (d, J = 45.8 Hz), 24.0 (d, J = 4.6 Hz), 23.7 (d, J = 16.2 Hz), 20.2 (d, J = 49.5 Hz), 13.6 (d, J = 1.0 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 22.8 ppm.

HRMS (ESI+): m/z for $C_{23}H_{26}P$ $[M\text{-}Br]^+$ calcd.: 333.1767, found: 333.1765.

Butylmethyldiphenylphosphonium bromide (1p)



The title compound was prepared following general procedure GP1, using methyldiphenylphosphine (300 mg, 1.5 mmol, 1.0 equiv.).
Reaction workup following workup procedure A yielded the title compound as a tan solid (424 mg, 84%).

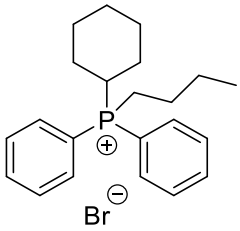
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.82 (m, 4H), 7.77 – 7.70 (m, 2H), 7.65 (td, *J* = 7.5, 3.3, 4H), 3.35 – 3.24 (m, 2H), 2.86 (d, *J* = 13.6 Hz, 3H), 1.60 – 14.5 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.8 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 10.0 Hz), 130.4 (d, *J* = 12.4 Hz), 119.6 (d, *J* = 84.7 Hz), 24.3 (d, *J* = 4.4 Hz), 23.7 (d, *J* = 16.9 Hz), 23.1 (d, *J* = 50.8 Hz), 13.7 (d, *J* = 1.1 Hz), 8.7 (d, *J* = 55.1 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 24.5 ppm.

HRMS (ESI+): m/z for $C_{17}H_{22}P$ $[M\text{-}Br]^+$ calcd.: 257.1454, found: 257.1450.

Butylcyclohexyldiphenylphosphonium bromide (1q)



The title compound was prepared following general procedure GP1, using cyclohexyldiphenylphosphine (400 mg, 1.5 mmol, 1.0 equiv.).
Reaction workup following workup procedure B yielded the title compound as a white solid (380 mg, 62%).

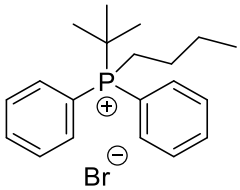
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (m, 4H), 7.75 (m, 2H), 7.67 (m, 4H), 4.11 (qt, *J* = 12.2, 2.9 Hz, 1H), 3.19 – 3.04 (m, 2H), 2.01 (br, 2H), 1.76 – 1.59 (m, 5H), 1.42 (hex, *J* = 7.1 Hz, 2H), 1.32 – 1.17 (m, 2H), 1.03 – 0.87 (m, 3H), 0.77 (t, *J* = 7.3 Hz, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 134.7 (d, *J* = 3.0 Hz), 133.9 (d, *J* = 8.6 Hz), 130.3 (d, *J* = 11.7 Hz), 115.5 (d, *J* = 79.7 Hz), 31.3 (d, *J* = 45.7 Hz), 25.6 (d, *J* = 3.3 Hz), 25.3 (d, *J* = 13.9 Hz), 25.3 (d, *J* = 1.9 Hz), 24.0 (d, *J* = 4.9 Hz), 23.6 (d, *J* = 15.6 Hz), 19.7 (d, *J* = 48.1 Hz), 13.5 (d, *J* = 1.0 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 31.6 ppm.

HRMS (ESI+): m/z for $C_{22}H_{30}P$ $[M\text{-}Br]^+$ calcd.: 325.2080, found: 325.2081.

***tert*-Butyl(butyl)diphenylphosphonium bromide (1r)**



The title compound was prepared following general procedure GP1, using *tert*-butyldiphenylphosphine (360 mg, 1.5 mmol, 1.0 equiv.).
An excess of Et_2O was added to the reaction mixture. After cooling to 0 °C, the reaction mixture was filtered and washed with cold Et_2O (0 °C) to yield the title compound as a white solid (497 mg, 87%).

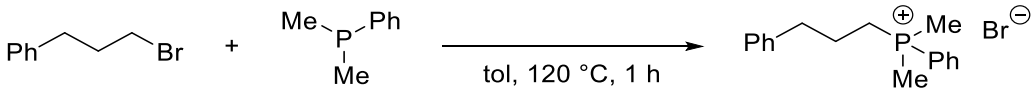
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.84 (m, 4H), 7.80 – 7.73 (m, 2H), 7.72 – 7.66 (m, 4H), 3.36 – 3.25 (m, 2H), 1.56 (hex, *J* = 7.2 Hz, 2H), 1.46 (d, *J* = 16.7 Hz, 9H), 1.28 (hex, *J* = 7.8, 7.4 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 134.7 (d, *J* = 3.0 Hz), 134.2 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 11.4 Hz), 116.2 (d, *J* = 77.3 Hz), 33.5 (d, *J* = 43.0 Hz), 26.5 (d, *J* = 1.0 Hz), 24.9 (d, *J* = 5.6 Hz), 23.7 (d, *J* = 15.1 Hz), 18.7 (d, *J* = 44.8 Hz), 13.8 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 38.3 ppm.

HRMS (ESI+): m/z for $C_{20}H_{28}P$ $[M\text{-}Br]^+$ calcd.: 299.1923, found: 299.1928.

Dimethyl(phenyl)(3-phenylpropyl)phosphonium bromide (1s)



S6 **S16** **1s**

A 8-mL screw-cap vial was charged with 3-phenylpropyl bromide (**S6**) (360 µL, 1.8 mmol, 1.2 equiv.), toluene (0.5 mL), and dimethylphenylphosphine (**S16**) (210 µL, 1.5 mmol, 1.0 equiv.). The vial was immediately flushed with nitrogen and capped. The reaction mixture was stirred at 120 °C for 1 hour. After cooling to room temperature, the reaction mixture was loaded on silica and purified by column chromatography (0% to 10% methanol in DCM) to yield the title compound as a white solid (440 mg, 87%).

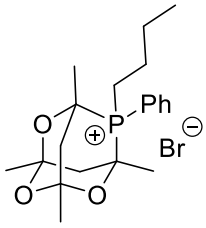
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.78 (m, 2H), 7.70 – 7.63 (m, 1H), 7.62 – 7.54 (m, 2H), 7.25 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 7.11 – 7.05 (m, 2H), 3.09 – 2.94 (m, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.53 (d, *J* = 14.1 Hz, 6H), 1.83 – 1.68 (m, 2H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 140.0 (d, *J* = 1.0 Hz), 134.4 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 9.8 Hz), 130.2 (d, *J* = 12.2 Hz), 128.7, 128.6, 126.5, 120.2 (d, *J* = 83.0 Hz), 36.1 (d, *J* = 16.9 Hz), 23.8 (d, *J* = 4.0 Hz), 23.0 (d, *J* = 51.7 Hz), 8.7 (d, *J* = 54.9 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 25.3 ppm.

HRMS (ESI+): m/z for $C_{17}H_{22}P$ $[M\text{-}Br]^+$ calcd.: 257.1454, found: 257.1461.

Phosphonium bromide 1t



The title compound was prepared following general procedure GP1, using 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (^{me}CgPPh) (290 mg, 1.0 mmol, 1.0 equiv.). Reaction workup following workup procedure A yielded the title compound as a tan solid (270 mg, 63%).

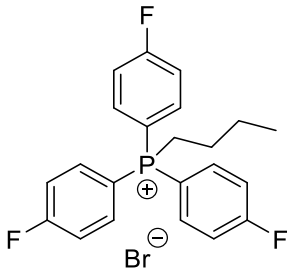
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 – 8.29 (m, 2H), 7.85 – 7.64 (m, 3H), 4.15 (dtd, *J* = 16.1, 11.7, 4.2 Hz, 1H), 2.99 (tdd, *J* = 16.0, 9.9, 5.0 Hz, 1H), 2.81 (dd, *J* = 14.8, 2.8 Hz, 1H), 2.21 (dd, *J* = 25.4, 14.7 Hz, 1H), 2.03 – 1.87 (m, 2H), 1.82 – 1.68 (m, 5H), 1.64 – 1.39 (m, 11H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 135.4 (d, *J* = 3.2 Hz), 134.7 (d, *J* = 8.2 Hz), 131.0 (d, *J* = 11.6 Hz), 112.0 (d, *J* = 66.3 Hz), 97.3 (d, *J* = 1.9 Hz), 97.1 (d, *J* = 2.1 Hz), 73.4 (d, *J* = 41.6 Hz), 72.3 (d, *J* = 45.3 Hz), 41.3 (d, *J* = 4.1 Hz), 39.0 (d, *J* = 3.6 Hz), 27.1 (d, *J* = 37.6 Hz), 25.0, 25.0, 24.2 (d, *J* = 14.9 Hz), 23.1, 14.2 (d, *J* = 35.7 Hz), 14.0 (d, *J* = 1.3 Hz) (1 less signal than expected due to overlapping signals or assignment as doublet instead of singlet) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 7.5 ppm.

HRMS (ESI+): m/z for $C_{20}H_{30}O_3P$ $[M\text{-}Br]^+$ calcd.: 349.1927, found: 349.1927.

Butyltris(4-fluorophenyl)phosphonium bromide (1u)



The title compound was prepared following general procedure GP1, using tris(4-fluorophenyl)phosphine (6.3 g, 20 mmol, 1.0 equiv.).
After cooling to room temperature, the reaction mixture was diluted with 10 mL of toluene and filtered. The residue was washed with toluene and Et_2O to yield the title compound as a white solid (6.2 g, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.83 (m, 6H), 7.38 (td, *J* = 8.5, 2.5 Hz, 6H), 4.24 – 3.50 (m, 2H), 1.64 (hex, *J* = 7.2 Hz, 2H), 1.58 – 1.46 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm.

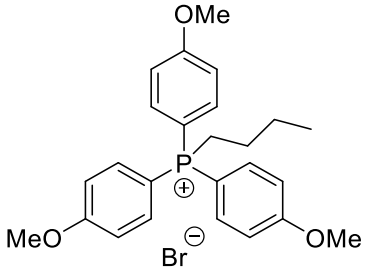
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 166.8 (dd, *J* = 260.7, 3.4 Hz), 136.8 (dd, *J* = 11.8, 9.5 Hz), 118.5 (dd, *J* = 22.1, 14.0 Hz), 114.0 (dd, *J* = 90.5, 3.6 Hz), 24.7 (d, *J* = 4.6 Hz), 23.7 (d, *J* = 16.9 Hz), 23.2 (d, *J* = 50.0 Hz), 13.8 (d, *J* = 1.2 Hz) ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -99.4 (d, *J* = 1.6 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 23.8 ppm.

HRMS (ESI+): m/z for $C_{22}H_{21}F_3P$ $[M\text{-}Br]^+$ calcd.: 373.1327, found: 373.1324.

Butyltris(4-methoxyphenyl)phosphonium bromide (1v)



The title compound was prepared following a slightly modified general procedure GP1 (stirred at 60 °C for 2 days in 0.3 mL toluene), using tris(4-methoxyphenyl)phosphine (300 mg, 0.57 mmol, 1.0 equiv.).
Reaction workup following workup procedure B yielded the title compound as a tan solid (259 mg, 93%).

Note: Higher reaction temperatures lead to partial demethylation. The reaction was therefore conducted at lower temperature and for a longer duration.

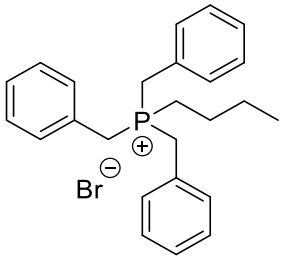
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 11.9, 8.8 Hz, 6H), 7.11 (dd, *J* = 9.0, 2.5 Hz, 6H), 3.84 (s, 9H), 3.35 – 3.23 (m, 2H), 1.61 – 1.42 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 164.5 (d, *J* = 2.9 Hz), 135.3 (d, *J* = 11.5 Hz), 116.2 (d, *J* = 13.6 Hz), 108.9 (d, *J* = 93.9 Hz), 56.0, 24.5 (d, *J* = 4.4 Hz), 23.7 (d, *J* = 16.4 Hz), 23.6 (d, *J* = 53.4 Hz), 13.7 (d, *J* = 1.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 21.5 ppm.

HRMS (ESI+): m/z for $C_{25}H_{30}O_3P$ $[M\text{-}Br]^+$ calcd.: 409.1927, found: 409.1923.

Tribenzylbutylphosphonium bromide (1w)



The title compound was prepared following general procedure GP1 (on 2.0 mmol scale), using tribenzylphosphine (610 mg, 2.0 mmol, 1.0 equiv.).
Reaction workup following workup procedure B yielded the title compound as a white solid (740 mg, 84%).

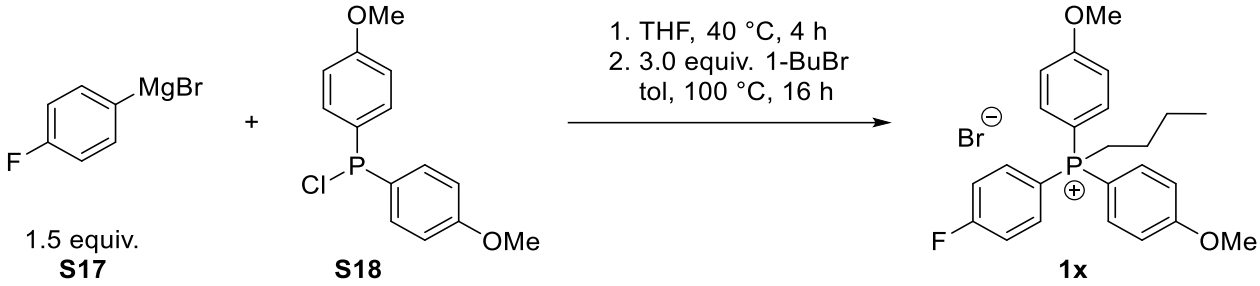
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (s, 15H), 4.16 (d, *J* = 14.9 Hz, 6H), 2.06 – 1.95 (m, 2H), 1.32 – 1.15 (m, 4H), 0.74 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 130.4 (d, *J* = 5.2 Hz), 129.6 (d, *J* = 3.1 Hz), 128.6 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 8.3 Hz), 26.9 (d, *J* = 43.6 Hz), 24.0 (d, *J* = 15.0 Hz), 23.6 (d, *J* = 5.0 Hz), 18.9 (d, *J* = 45.6 Hz), 13.2 (d, *J* = 1.0 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 27.2 ppm.

HRMS (ESI+): m/z for $C_{25}H_{30}P$ $[M\text{-}Br]^+$ calcd.: 361.2080, found: 361.2075.

Butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (1x)



Under an atmosphere of nitrogen, a 50-mL round-bottom flask was charged with *P*-chlorobis(4-methoxyphenyl)phosphine (**S18**) (1.1 g, 4.0 mmol, 1.0 equiv.), and THF (4.0 mL). 4-fluorophenylmagnesium bromide (**S17**) (2.0 M in Et_2O, 3.0 mL, 6.0 mmol, 1.5 equiv.) was added dropwise, and the reaction mixture was stirred at 40 °C for 4 hours. After cooling to room temperature, water (ca. 2 mL) was added to the reaction mixture. The phases were separated, and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with brine and then dried with magnesium sulfate. Volatile materials were removed under reduced pressure. The residue was dissolved in DCM and filtered through a silica plug, eluting with 5% methanol in DCM. The filtrate was transferred into a 25-mL round-bottom flask, and volatile materials were removed under reduced pressure. Toluene (1.3 mL) and 1-bromobutane (1.3 mL, 12.0 mmol, 3.0 equiv.) were added. The flask was flushed with nitrogen and stoppered. The reaction mixture was stirred at 100 °C for 16 hours. Reaction workup following workup procedure C yielded the title compound as a tan solid (1.25 g, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.80 (m, 2H), 7.66 (ddd, *J* = 12.0, 9.0, 0.9 Hz, 4H), 7.33 (td, *J* = 8.6, 2.3 Hz, 2H), 7.15 (dd, *J* = 9.0, 2.6 Hz, 4H), 3.87 (s, 6H), 3.59 – 3.46 (m, 2H), 1.67 – 1.44 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H) ppm.

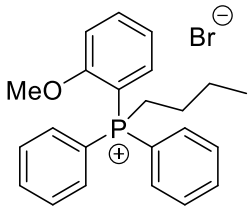
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 166.4 (dd, *J* = 259.5, 3.4 Hz), 164.8 (d, *J* = 2.9 Hz), 136.4 (dd, *J* = 11.7, 9.4 Hz), 135.6 (d, *J* = 11.6 Hz), 118.1 (dd, *J* = 22.0, 13.7 Hz), 116.4 (d, *J* = 13.6 Hz), 115.7 (dd, *J* = 90.4, 3.5 Hz), 108.1 (d, *J* = 94.0 Hz), 56.1, 24.6 (d, *J* = 4.4 Hz), 23.8 (d, *J* = 16.5 Hz), 23.5 (d, *J* = 52.3 Hz)13.8 (d, *J* = 1.2 Hz) ppm.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ = -101.0 (d, *J* = 1.3 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 22.4 (d, *J* = 1.4 Hz) ppm.

HRMS (ESI+): m/z for $C_{24}H_{27}FO_2P$ $[M\text{-}Br]^+$ calcd.: 397.1727, found: 397.1725.

Butyl(2-methoxyphenyl)diphenylphosphonium bromide (1y)



The title compound was prepared following a slightly modified general procedure GP1 (stirred at 60 °C for 2 days), using (2-methoxyphenyl)diphenylphosphine (440 mg, 1.5 mmol, 1.0 equiv.).
Reaction workup following workup procedure C yielded the title compound as a white solid (530 mg, 82%).

Note: Higher reaction temperatures lead to partial demethylation. The reaction was therefore conducted at lower temperature and for a longer duration.

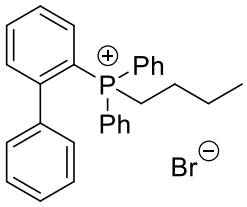
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (ddt, *J* = 8.6, 7.4, 1.4 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.67 – 7.58 (m, 8H), 7.33 (ddd, *J* = 14.1, 7.8, 1.6 Hz, 1H), 7.25 – 7.13 (m, 2H), 3.73 (s, 3H), 3.47 – 3.22 (m, 2H), 1.61 – 1.37 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 161.9 (d, *J* = 2.3 Hz), 138.2 (d, *J* = 2.3 Hz), 135.5 (d, *J* = 8.1 Hz), 134.7 (d, *J* = 3.1 Hz), 133.0 (d, *J* = 10.0 Hz), 130.3 (d, *J* = 12.7 Hz), 122.7 (d, *J* = 12.5 Hz), 118.7 (d, *J* = 87.8 Hz), 113.0 (d, *J* = 6.5 Hz), 105.1 (d, *J* = 88.8 Hz), 56.6, 25.2 (d, *J* = 4.7 Hz), 23.8 (d, *J* = 16.7 Hz), 23.3 (d, *J* = 51.9 Hz), 13.6 (d, *J* = 1.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 23.6 ppm.

HRMS (ESI+): m/z for $C_{23}H_{26}OP$ $[M\text{-}Br]^+$ calcd.: 349.1716, found: 349.1714.

[1,1'-biphenyl]-2-yl(butyl)diphenylphosphonium bromide (1z)



The title compound was prepared following general procedure GP1, using 2-(diphenylphosphino)biphenyl (Ph-JohnPhos) (510 mg, 1.5 mmol, 1.0 equiv.).
Reaction workup following workup procedure C yielded the title compound as an off-white solid (570 mg, 80%).

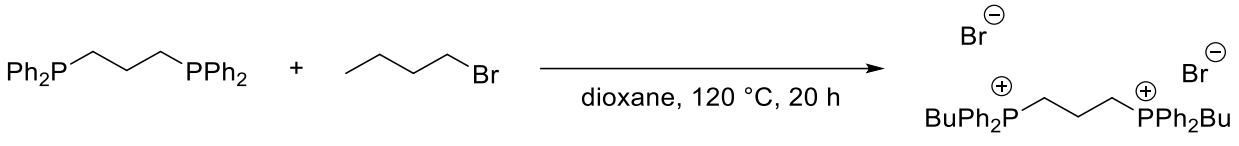
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.81 (m, 1H), 7.80 – 7.74 (m, 2H), 7.73 – 7.63 (m, 6H), 7.61 – 7.54 (m, 4H), 7.49 – 7.44 (m, 1H), 7.34 (tt, *J* = 7.5 ,1.3 Hz, 1H), 7.16 (tt, *J* = 7.7, 1.5 Hz, 2H) 6.81 (dd, *J* = 8.2, 1.3 Hz, 2H), 2.68 – 2.54 (m, 2H), 1.33 – 1.24 (m, 4H), 0.75 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 148.1 (d, *J* = 9.4 Hz), 138.6 (d, *J* = 3.8 Hz), 135.8 (d, *J* = 10.5 Hz), 135.1 (d, *J* = 2.9 Hz), 134.9 (d, *J* = 3.1 Hz), 133.5 (d, *J* = 10.6 Hz), 133.4 (d, *J* = 9.8 Hz), 130.5 (d, *J* = 12.5 Hz), 129.3, 129.2, 129.0 (d, *J* = 12.2 Hz), 128.6, 119.6 (d, *J* = 85.4 Hz), 117.3 (d, *J* = 84.9 Hz), 24.9 (d, *J* = 4.7 Hz), 23.7 (d, *J* = 17.6 Hz), 23.4 (d, *J* = 49.8 Hz), 13.6 (d, *J* = 1.4 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 25.4 ppm.

HRMS (ESI+): m/z for $C_{28}H_{28}P$ $[M\text{-}Br]^+$ calcd.: 395.1923, found: 395.1923.

Bisphosphonium salt 6



5 **3** **6**

Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with DPPP (**5**) (620 mg, 1.5 mmol, 1.0 equiv.) and dioxane (6.0 mL). The vial was capped with a septum cap and taken out of the glovebox. 1-Bromobutane (**3**) (960 µL, 9.0 mmol, 6.0 equiv.) was added through the septum, and the reaction mixture was stirred at 120 °C for 20 hours. After cooling to room temperature, the reaction mixture was diluted with Et_2O, filtered, and the residue was washed with Et_2O and cyclohexane to yield the title compound as a white solid (920 mg, 89%) after drying at 100 °C under vacuum.

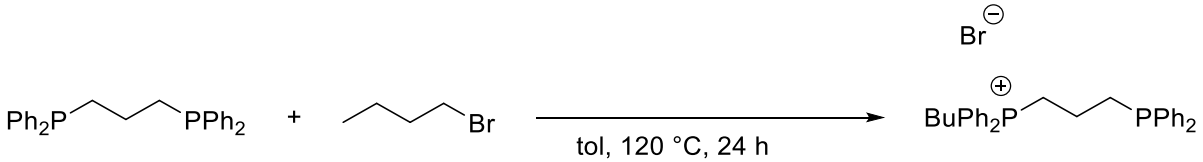
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.87 (m, 8H), 7.68 – 7.62 (m, 4H), 7.61 – 7.54 (m, 8H), 3.80 – 3.69 (m, 4H), 3.32 – 3.19 (m, 4H), 1.98 (dtd, *J* = 16.3, 8.1, 3.0 Hz, 2H), 1.58 – 1.43 (m, 4H), 1.42 – 1.30 (m, 4H), 0.80 (t, *J* = 7.2 Hz, 6H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 134.6 (br), 133.3 (*pseudo*-p, *J* = 4.8 Hz), 130.2 (m), 117.8 (d, *J* = 83.8 Hz), 24.3 (*pseudo*-t, *J* = 2.2 Hz), 23.7 (m), 22.1 (dd, *J* = 52.3 Hz, *J* = 17.0 Hz), 21.3 (d, *J* = 49.6 Hz) 16.9, 13.6 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 27.2 ppm.

HRMS (ESI+): m/z for $C_{35}H_{44}P_2$ (di-cation) **(**$[M\text{-}2Br]^{2+}$)/2 calcd.: 263.1454, found: 263.1447.

Monophosphonium salt 8



5 **3** **8**

In a glovebox filled with argon, a 4-mL screw-cap vial was charged with DPPP (**5**) (870 mg, 2.1 mmol, 1.2 equiv.), 1-bromobutane (**3**) (180 µL, 1.7 mmol, 1.0 equiv.), and toluene (0.7 mL). The vial was capped, and the mixture was stirred at 120 °C for 24 hours. After cooling to room temperature, volatile materials were removed under reduced pressure, and the resulting foam was crushed and suspended in diethyl ether. After cooling to 0 °C, the mixture was filtered, and the residue washed with diethyl ether to yield the title compound as a white powder (740 mg, 65%, contains a small impurity).

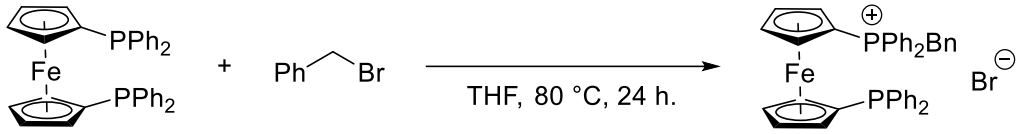
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.76 (m, 4H), 7.75 – 7.69 (m, 2H), 7.65 – 7.58 (m, 4H), 7.34 – 7.24 (m, 10H), 3.63 – 3.54 (m, 2H), 3.27 – 3.18 (m, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.67 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.43 – 1.33 (m, 2H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 137.4 (d, *J* = 11.6 Hz), 134.8 (d, *J* = 3.0 Hz), 133.2 (d, *J* = 9.3 Hz), 132.8 (d, *J* = 18.7 Hz), 130.4 (d, *J* = 12.1 Hz), 129.0, 128.7 (d, *J* = 6.9 Hz), 117.9 (d, *J* = 82.1 Hz), 28.5 (dd, *J* = 15.5, 12.4 Hz), 24.3 (d, *J* = 4.7 Hz), 23.8 (d, *J* = 16.3 Hz), 22.8 (dd, *J* = 48.2, 14.1 Hz), 21.9 (d, *J* = 48.8 Hz), 19.2 (dd, *J* = 18.7, 3.8 Hz), 13.7 (d, *J* = 1.0 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 27.7 (d, *J* = 1.9 Hz), -18.8 (d, *J* = 1.9 Hz) ppm.

HRMS (ESI+): m/z for $C_{31}H_{35}P_2$ $[M\text{-}Br]^+$ calcd.: 469.2209, found: 469.2202.

Monophosphonium salt 12



10 **11** **12**

A 16-mL screw-cap vial was charged with DPPF (**10**) (550 mg, 1.0 mmol, 1.0 equiv.), flushed with nitrogen, and capped with a septum cap. THF (9 mL) and benzyl bromide (**11**) (130 µL, 1.1 mmol, 1.1 equiv.) were added through the septum. After stirring for 24 hours at 80 °C, the reaction mixture was allowed to cool to room temperature, and volatile materials were evaporated under reduced pressure. The resulting crude product was purified by column chromatography (5% MeOH in DCM) yielding the title compound as an orange solid (690 mg, 95%).

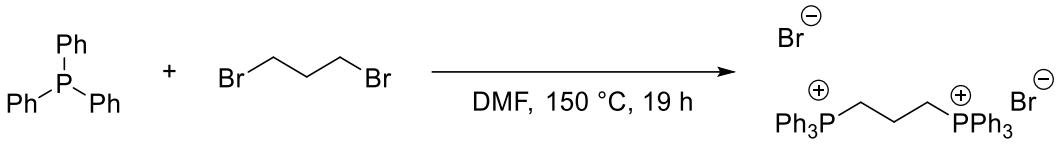
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.69 (m, 6H), 7.66 – 7.54 (m, 4H), 7.35 – 7.16 (m, 11H), 7.10 (d, *J* = 4.5 Hz, 4H), 5.18 (d, *J* = 14.3 Hz, 2H), 4.88 (s, 2H), 4.56 (s, 2H), 4.24 (s, 2H), 4.09 (s, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ = 140.0 (d, *J* = 9.7 Hz), 137.1 (d, *J* = 3.1 Hz), 135.8 (d, *J* = 9.9 Hz), 135.4 (d, *J* = 20.0 Hz), 132.8 (d, *J* = 5.6 Hz), 131.9 (d, *J* = 12.6 Hz), 131.0, 130.9 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 7.1 Hz), 130.0 (d, *J* = 8.2 Hz), 121.6 (d, *J* = 88.7 Hz), 82.7 (d, *J* = 11.6 Hz), 78.0 (dd, *J* = 10.5, 1.7 Hz), 77.2 (d, *J* = 13.9 Hz), 76.2 (d, *J* = 12.0 Hz), 75.5 (d, *J* = 3.4 Hz), 32.1 (d, *J* = 51.3 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_3OD) δ = 26.3, -19.3 ppm.

HRMS (ESI+): m/z for $C_{41}H_{35}FeP_2$ $[M\text{-}Br]^+$ calcd.: 645.1558, found: 645.1552.

Bisphosphonium salt 15



4 **14** **15**

A 16-mL screw-cap vial was charged with triphenylphosphine (**4**) (1.3 g, 5.0 mmol, 2.5 equiv.), alkyl halide **14** (200 µL, 2.0 mmol, 1.0 equiv.), and DMF (6 mL). The vial was flushed with nitrogen and capped. The mixture was stirred at 150 °C for 19 hours. After cooling to room temperature, the reaction mixture was diluted with Et_2O and filtered. The residue was washed with Et_2O and cyclohexane to yield the title compound as a white solid (1.29 g, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.86 (m, 12H), 7.74 – 7.65 (m, 6H), 7.64 – 7.55 (m, 12H), 4.69 – 4.58 (m, 4H), 1.94 – 1.85 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.8 (br), 134.6 – 133.8 (m), 131.9 – 127.5 (m), 118.0 (dd, *J* = 87.5, 1.1 Hz), 23.3 – 21.8 (m), 18.0 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 24.4 ppm.

The spectroscopic data matched those reported in the literature.[7]

4. Product characterization

General procedure for the dearylation of monophosphonium salts (GP2)

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (8.3 mg, 0.03 mmol, 0.1 equiv.), IiPr•HBF_4 (14.4 mg, 0.06 mmol, 0.2 equiv.), phosphonium salt (0.3 mmol, 1.0 equiv.), phenylboronic acid (40.2 mg, 0.33 mmol, 1.1 equiv.), potassium phosphate (127.6 mg, 0.6 mmol, 2.0 equiv.), and dioxane (1.5 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 22 hours. After cooling to room temperature, BH_3•SMe_2 (60 µL, 0.6 mmol, 2.0 equiv.) was added through the septum, and the mixture was stirred for an additional 2 hours at ambient temperature. The reaction mixture was loaded on silica and purified by column chromatography.

Note on purification

Phosphine borane adducts containing an aryl group are typically weakly visible under 254 nm UV light. Still, the phosphine borane adducts are preferably visualized with a $KMnO_4$ stain. For convenience, the products were typically purified on a Biotage Isolera One system. The phosphine borane adducts typically absorb strongly at 220 nm. Thus, 220 nm and 254 nm were used as detection wavelengths. Biphenyl (**S19**) (or the respective substituted biphenyl from the coupling of the cleaved aryl group with phenylboronic acid) elutes first on the column and was flushed out with pure hexane or cyclohexane. The phosphine borane adducts were then eluted with ca. 5% ethyl acetate in hexane or cyclohexane. The separation is typically very good and the compounds can also be readily separated in a manual flash column chromatography purification. A representative TLC plate for the reaction of butyltriphenylphosphonium bromide (**1b**) is shown here (Figure S2).

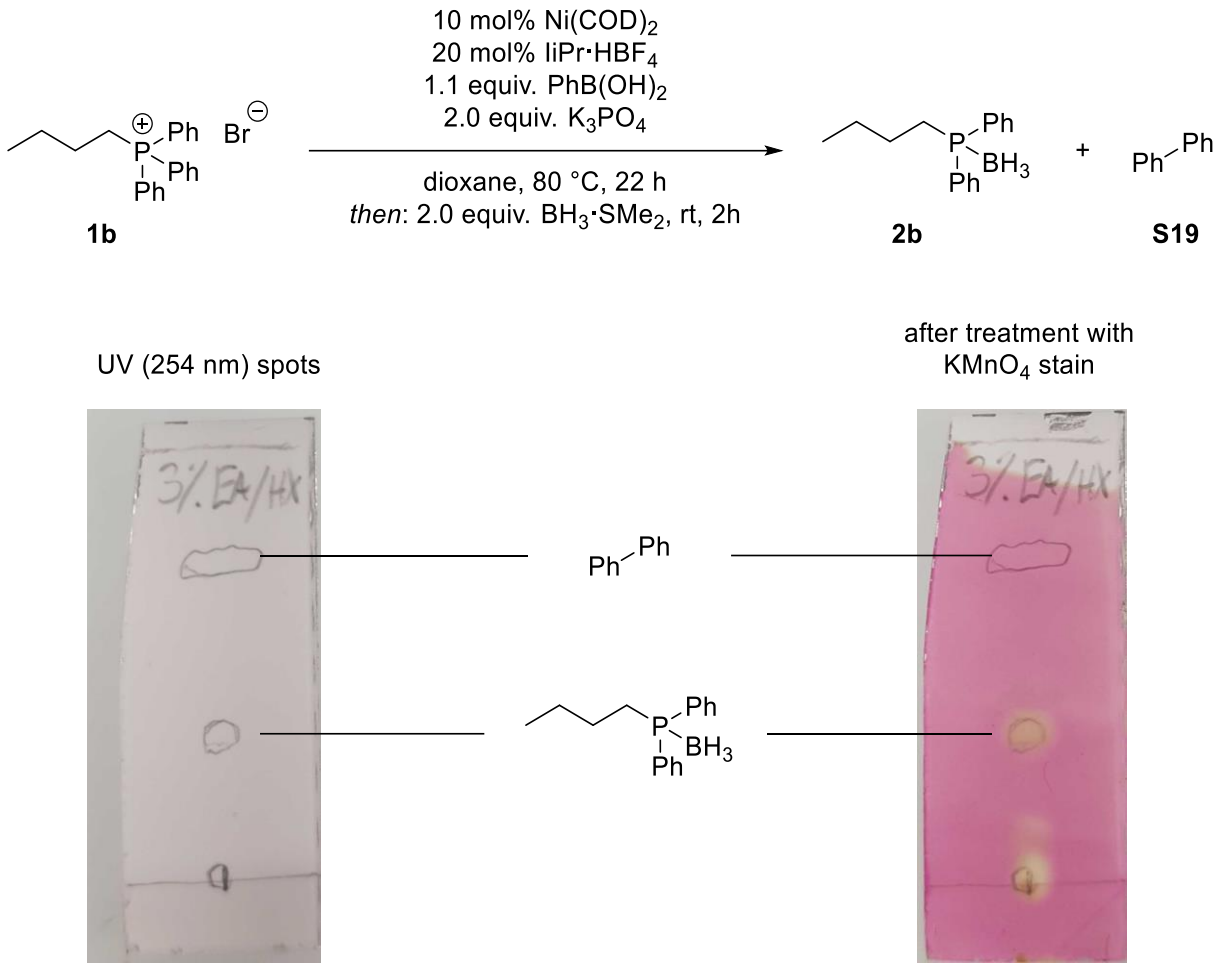


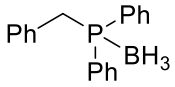
Figure S2. Crude TLC of the reaction of butyltriphenylphosphonium bromide (**1b**) with phenylboronic acid in 3% ethyl acetate in hexane. Visualization after irradiation with UV light (254 nm; peaks marked with a pencil, left) and after treatment of the same TLC plate with $KMnO_4$ stain (right).

Purification of the depicted reaction mixture by manual column chromatography (3% ethyl acetate in cyclohexane) yielded the corresponding phosphine borane adduct **2b** in 86% yield (vs. 92% when purified on the Biotage system).

Note on boronic acid quality

Different boronic acids give good yield in the reaction and can be used instead of phenylboronic acid (see optimization data in table S1). Phenylboronic acid was used because isolation of the products was easier in this case. The quality of the boronic acid is however important as boronic acids that have been stored over a longer time can form boroxines that are nearly inactive in the dearylation reaction (see table S1, entry 9).

Benzyldiphenylphosphine borane adduct (2a)



The title compound was prepared following general procedure GP2, using benzyltriphenylphosphonium bromide (**1a**) (130.0 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in cyclohexane) yielded the title compound as a white solid (71.1 mg, 82%).

Similarly, the title compound was also prepared from benzyltriphenylphosphonium chloride (**1a'**) (116.7 mg, 0.3 mmol, 1.0 equiv.) and benzyltriphenylphosphonium iodide (**1a''**) (144.1 mg, 0.3 mmol, 1.0 equiv.) following general procedure GP2 to yield the product in 63% and 56%, respectively.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.61 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.20 – 7.13 (m, 3H), 6.99 – 6.95 (m, 2H), 3.62 (d, *J* = 12.0 Hz, 2H), 0.99 (br-q, 90 Hz, 3H) ppm.

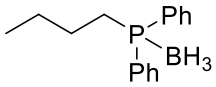
^{11}B NMR (128 MHz, $CDCl_3$) δ = -38.5 (*pseudo*-dt, *J* = 149.1, 92.7 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.8 (d, *J* = 8.8 Hz), 132.0 (d, *J* = 4.4 Hz), 131.4 (d, *J* = 2.5 Hz), 130.4 (d, *J* = 4.6 Hz), 128.8 (d, *J* = 54.0 Hz), 128.8 (d, *J* = 9.8 Hz), 128.1 (d, *J* = 2.7 Hz), 127.0 (d, *J* = 3.2 Hz), 34.2 (d, *J* = 32.2 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 18.0 (br-d, *J* = 75.7 Hz) ppm.

The spectroscopic data matched those reported in the literature.[8]

Butyldiphenylphosphine borane adduct (2b)



The title compound was prepared following general procedure GP2, using butyltriphenylphosphonium bromide (**1b**) (119.8 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 3% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (70.4 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 – 7.63 (m, 4H), 7.51 – 7.40 (m, 6H), 2.30 – 2.12 (m, 2H), 1.58 – 1.44 (m, 2H), 1.41 (hex, *J* = 7.3 Hz, 2H), 1.34 – 0.51 (m (overlapping signals), 6H, including t, *J* = 7.2 Hz at 0.89 ppm) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.3 (*pseudo*-dt, *J* = 157.6, 78.3 Hz) ppm.

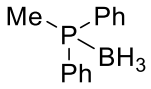
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.2 (d, *J* = 9.0 Hz), 131.2 (d, *J* = 2.5 Hz), 129.8 (d, *J* = 54.8 Hz), 128.9 (d, *J* = 9.8 Hz), 25.5 (d, *J* = 37.2 Hz), 25.1, 24.3 (d, *J* = 14.4 Hz), 13.6 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 15.9 (br-d, *J* = 71.0 Hz) ppm.

The spectroscopic data matched those reported in the literature.[9]

The title compound was also prepared following general procedure GP2, using butyl(2-methoxyphenyl)diphenylphosphonium bromide (**1y**) (85.9 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 4% ethyl acetate in cyclohexane) and subsequently by HPLC (20 min gradient of 50% to 100% MeCN in H_2O (0.1% formic acid)) yielded the title compound as a light yellow oil (31.6 mg, 62%, 8:1 mixture with 2-methoxybiphenyl).

Methyldiphenylphosphine borane adduct (2c)



The title compound was prepared following general procedure GP2, using methyltriphenylphosphonium bromide (**1c**) (107.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (44.7 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 – 7.62 (m, 4H), 7.52 – 7.41 (m, 6H), 1.87 (d, *J* = 10.1 Hz, 3H), 1.04 (br-q, *J* = 93 Hz, 3H) ppm.

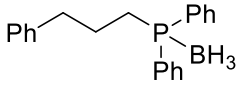
^{11}B NMR (128 MHz, $CDCl_3$) δ = -37.4 (*pseudo*-dt, J = 155.8, 96.3 Hz) ppm

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 131.8 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 2.4 Hz), 130.6 (d, *J* = 56.3 Hz), 128.9 (d, *J* = 10.0 Hz), 12.0 (d, *J* = 40.2 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 10.1 (q, *J* = 55.5 Hz) ppm.

The spectroscopic data matched those reported in the literature.[8]

Diphenyl(3-phenylpropyl)phosphine borane adduct (2d)



The title compound was prepared following general procedure GP2, using triphenyl(3-phenylpropyl)phosphonium bromide (**1d**) (92.2 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in *n*-hexane) yielded the title compound as a colorless oil (46.0 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 – 7.64 (m, 4H), 7.54 – 7.50 (m, 2H), 7.49 – 7.43 (m, 4H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 – 7.15 (m, 2), 2.75 (t, *J* = 7.4 Hz, 2H), 2.29 – 2.22 (m, 2H), 1.96 – 1.91 (m, 2H), 1.34 – 0.76 (br-m, 3H) ppm.

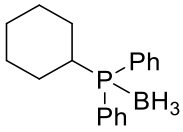
^{11}B NMR (128 MHz, $CDCl_3$) δ = -34.9 – -43.4 (m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 140.9, 132.2 (d, *J* = 9.0 Hz), 131.2 (d, *J* = 2.4 Hz), 129.5 (d, *J* = 54.9 Hz), 128.9 (d, *J* = 9.8 Hz), 128.5 (d, *J* = 4.7 Hz), 126.2, 36.9 (d, *J* = 14.0 Hz), 24.9 (d, *J* = 37.2 Hz), 24.6 (1 less signal than expected due to overlapping signals or assignment as doublet instead of singlet) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 16.0 (br-d, *J* = 67.4 Hz) ppm.

HRMS (ESI+): m/z for $C_{21}H_{24}BNaP$ $[M+Na]^+$ calcd.: 341.1601, found: 341.1595.

Cyclohexyldiphenylphosphine borane adduct (2e)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using cyclohexyltriphenylphosphonium bromide (**1e**) (127.6 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 2% ethyl acetate in cyclohexane) yielded the title compound as a white solid (61.6 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 – 7.70 (m, 4H), 7.50 – 7.40 (m, 6H), 2.49 – 2.34 (m, 1H), 1.87 – 1.75 (m, 2H), 1.75 – 1.61 (m, 3H), 1.56 – 1.38 (m, 2H), 1.38 – 0.52 (m, 6H (overlapping signals)) ppm.

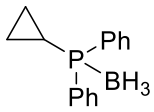
^{11}B NMR (128 MHz, $CDCl_3$) δ = -41.5 (*pseudo*-dt, *J* = 152.2, 90.5 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 132.8 (d, *J* = 8.4 Hz), 131.1 (d, *J* = 2.5 Hz), 128.8 (d, *J* = 9.6 Hz), 128.3, 33.8 (d, *J* = 36.0 Hz), 26.8 (d, *J* = 12.3 Hz), 26.6, 25.9 (d, *J* = 1.5 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 21.1 (br-d, *J* = 76.3 Hz) ppm.

The spectroscopic data matched those reported in the literature.[10]

Cyclopropyldiphenylphosphine borane adduct (2f)



The title compound was prepared following general procedure GP2, using cyclopropyltriphenylphosphonium bromide (**1f**) (115.0 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 3% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (60.5 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 – 7.68 (m, 4H), 7.52 – 7.40 (m, 6H), 1.45 – 1.25 (m, 1H), 1.16 – 0.31 (m, 7H (overlapping signals)) ppm.

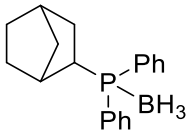
^{11}B NMR (128 MHz, $CDCl_3$) δ = -41.9 (*pseudo*-dt, *J* = 157.2, 96.3 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 132.3 (d, *J* = 9.0 Hz), 131.1 (d, *J* = 2.5 Hz), 130.9 (d, *J* = 58.5 Hz), 128.8 (d, *J* = 9.9 Hz), 4.5 (d, *J* = 61.0 Hz), 4.0 (d, *J* = 1.3 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 24.3 (br-q, *J* = 54.4 Hz) ppm.

HRMS (ESI+): m/z for $C_{15}H_{18}BNaP$ $[M+Na]^+$ calcd.: 263.1131, found: 263.1131.

(2-Norbornyl)diphenylphosphine borane adduct (2g)



The title compound was prepared following general procedure GP2, using (2-norbornyl)triphenylphosphonium bromide (**1g**) (87.5 mg, 0.2 mmol, 1.0 equiv., 9:1 *dr*). Purification by column chromatography (6% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (28.8 mg, 52%, 12:1 mixture of diastereomers).

The characterization data for the major isomer are reported here:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 – 7.64 (m, 4H), 7.53 – 7.37 (m, 6H), 2.53 – 2.44 (m, 1H), 2.44 – 2.39 (m, 1H), 2.34 (br, 1H), 1.82 – 1.72 (m, 2H), 1.66 – 1.60 (m, 2H), 1.53 – 1.44 (m, 1H), 1.39 – 1.32 (m, 1H), 1.32 – 1.27 (m, 1H), 1.17 (br-d, *J* = 9.9, 1H), 1.20 – 0.76 (br-m, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.6 (*pseudo*-dd, *J* = 16.0, 8.4 Hz), 131.0 (*pseudo*-dd, *J* = 3.5, 2.4 Hz), 130.3 (*pseudo*-dd, *J* = 105.5, 53.9 Hz), 128.8 (*pseudo*-dd, *J* = 13.1, 9.5 Hz), 39.0 (d, *J* = 3.1 Hz), 37.2, 36.9, 36.7 (d, *J* = 2.1 Hz), 33.6, 32.6 (d, *J* = 12.0 Hz), 28.7 ppm.

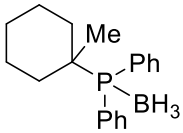
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 21.0 (br-d, *J* = 75.2 Hz) ppm.

HRMS (ESI+): m/z for $C_{19}H_{24}BNaP$ $[M+Na]^+$ calcd.: 317.1601, found: 317.1603.

The ^{1}H and ^{31}P{^{1}H} NMR signals of the minor isomer are identical or largely overlap with the signals of the major isomer. Distinct ^{1}H NMR signals of the minor isomer are visible at 7.64–7.60 ppm (m), 2.86–2.78 ppm (m), and 2.16–2.10 ppm (m).

The diastereomeric ratio was estimated by ^{1}H NMR using the signals at 2.34 ppm (major isomer) and 2.17–2.10 ppm (minor isomer). The slight increase in *dr* from the starting material **1g** to the title compound **2g** indicates a preference for the catalyst to react with the less sterically hindered *exo*-isomer of **1g** compared with the *endo*-isomer of **1g**.

(1-Methylcyclohexyl)diphenylphosphine borane adduct (2h)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using (1-methylcyclohexyl)triphenylphosphonium iodide (**1h**) (97.3 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in cyclohexane) yielded the title compound as a white solid (31.8 mg, 54%; 14:1 mixture with Ph_3P•BH_3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 4H), 7.52 – 7.40 (m, 6H), 1.90 – 1.75 (m, 2H), 1.74 – 1.60 (m, 3H), 1.60 – 1.39 (m, 4H), 1.22 – 0.53 (m (overlapping signals), 8H including d, *J* = 15.3 Hz at 1.31 ppm) ppm (1 proton signal too many; presumably because of overlapping with H_2O signal).

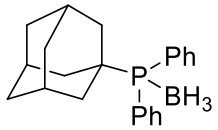
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.8 (*pseudo*-dt, *J* = 159.5, 78.5 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.5 (d, *J* = 7.8 Hz), 131.0 (d, *J* = 2.5 Hz), 128.4 (d, *J* = 9.4 Hz), 127.8 (d, *J* = 50.6 Hz), 34.7 (d, *J* = 31.4 Hz), 32.4 (d, *J* = 1.4 Hz), 25.5 (d, *J* = 1.4 Hz), 21.0 (d, *J* = 10.3 Hz), 18.3 (d, *J* = 1.0 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 35.5 (d, *J* = 69.4 Hz) ppm.

HRMS (ESI+): m/z for $C_{19}H_{26}BNaP$ $[M+Na]^+$ calcd.: 319.1757, found: 319.1760.

Adamant-1-yldiphenylphosphine borane adduct (2i)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using (adamant-1-yltriphenylphosphonium bromide (**1i**) (143.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in cyclohexane) yielded the title compound as a white solid (44.9 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 4H), 7.54 – 7.40 (m, 6H), 2.02 – 1.91 (m, 9H), 1.79 – 1.59 (m, 6H), 0.97 (br-q, *J* = 87.3 Hz, 3H) ppm.

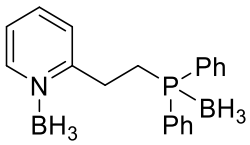
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.46 (*pseudo*-p, *J* = 92.4 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 134.4 (d, *J* = 7.8 Hz), 131.0 (d, *J* = 2.5 Hz), 128.4 (d, *J* = 9.4 Hz), 127.1 (d, *J* = 51.2 Hz), 37.3, 36.4 (d, *J* = 1.6 Hz), 34.4 (d, *J* = 31.1 Hz), 28.2 (d, *J* = 9.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 29.4 (d, *J* = 76.3 Hz) ppm.

HRMS (ESI+): m/z for $C_{22}H_{28}BNaP$ $[M+Na]^+$ calcd.: 357.1914, found: 357.1910.

2-(2-(Diphenylphosphino)ethyl)pyridine di-borane adduct (2j)



The title compound was prepared following a slightly modified general procedure GP2 (4 equiv. of BH_3•SMe_2 added), using triphenyl(2-(pyridin-2-yl)ethyl)phosphonium chloride (**1j**) (80.8 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 20% ethyl acetate in cyclohexane) yielded the title compound as a white solid (43.3 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 5.1 Hz, 1H), 7.78 – 7.70 (m, 5H), 7.48 – 7.38 (m, 7H), 7.25 (ddd, *J* = 7.5, 5.9, 1.5 Hz, 1H), 3.55 – 3.30 (m, 2H), 2.96 – 2.20 (m, 5H), 1.60 – 0.65 (m, 3H) ppm.

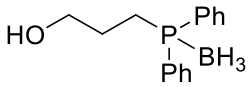
^{11}B NMR (128 MHz, $CDCl_3$) δ = -14.4 (br), -37.1 – -42.6 (br-m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 159.7 (d, *J* = 13.8 Hz), 149.5, 140.1, 132.3 (d, *J* = 9.4 Hz), 131.5 (d, *J* = 2.5 Hz), 129.0 (d, *J* = 10.1 Hz), 128.6 (d, *J* = 55.5 Hz), 127.2, 123.3, 29.4 (d, *J* = 2.1 Hz), 24.2 (d, *J* = 36.8 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.4 (br-d, *J* = 83.6 Hz) ppm.

HRMS (ESI+): m/z for $C_{19}H_{24}B_2NNaP$ $[M+Na]^+$ calcd.: 342.1725, found: 342.1730.

3-(Diphenylphosphino)propan-1-ol borane adduct (2k)



The title compound was prepared following a slightly modified general procedure GP2 (4 equiv. of BH_3•SMe_2 added), using (3-hydroxypropyl)triphenylphosphonium bromide (**1k**) (120.4 mg, 0.3 mmol, 1.0 equiv.). After cooling to room temperature, the reaction solution was stirred with aqueous HCl (1 M) for 5 min. The phases were separated, and the aqueous layer was extracted three times with DCM. The combined organic layer was dried with magnesium sulfate, and volatile materials were removed under reduced pressure. The residue was purified by column chromatography (10% to 50% ethyl acetate in hexane) to yield the title compound as a colorless oil (42.5 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (ddt, *J* = 9.7, 6.7, 1.6 Hz, 4H), 7.51 – 7.40 (m, 6H), 3.66 (t, *J* = 6.1 Hz, 2H), 2.43 – 2.21 (m, 2H), 1.86 – 1.70 (m, 2H), 1.67 (br, 1H), 0.89 (br-q, *J* = 88.3 Hz, 3H) ppm.

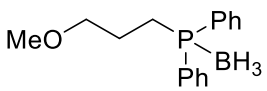
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.4 (*pseudo*-dt, *J* = 162.3, 80.9 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.2 (d, *J* = 9.1 Hz), 131.3 (d, *J* = 2.5 Hz), 129.5 (d, *J* = 55.1 Hz), 129.0 (d, *J* = 9.9 Hz), 62.9 (d, *J* = 14.7 Hz), 26.3, 22.2 (d, *J* = 38.4 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.0 (br-d, *J* = 80.2 Hz) ppm.

HRMS (ESI+): m/z for $C_{15}H_{20}BNaOP$ $[M+Na]^+$ calcd.: 281.1237, found: 281.1235.

(3-Methoxypropyl)diphenylphosphine borane adduct (2l)



The title compound was prepared following general procedure GP2, using (3-methoxypropyl)triphenylphosphonium bromide (**1l**) (124.6 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 7% ethyl acetate in *n*-hexane) yielded the title compound as a colorless oil (64.0 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 – 7.65 (m, 4H), 7.50 – 7.39 (m, 6H), 3.39 (t, *J* = 5.9 Hz, 2H), 3.27 (s, 3H), 2.39 – 2.25 (m, 2H), 1.86 – 1.73 (m, 2H), 1.47 – 0.53 (br-q, *J* = 89.9 Hz, 3H) ppm.

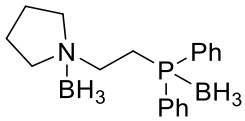
^{11}B NMR (128 MHz, $CDCl_3$) δ = -38.7 (*pseudo*-dt, *J* = 151.9, 91.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.2 (d, *J* = 9.1 Hz), 131.2 (d, *J* = 2.4 Hz), 129.5 (d, *J* = 55.0 Hz), 128.9 (d, *J* = 9.8 Hz), 72.5 (d, *J* = 14.2 Hz), 58.5, 23.4, 22.5 (d, *J* = 38.4 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.1 (br-d, *J* = 69.6 Hz) ppm.

HRMS (ESI+): m/z for $C_{16}H_{22}BNaOP$ $[M+Na]^+$ calcd.: 295.1394, found: 295.1397.

1-(2-(Diphenylphosphino)ethyl)pyrrolidine di-borane adduct (2m)



The title compound was prepared following a slightly modified general procedure GP2 (4 equiv. of BH_3•SMe_2 added), using triphenyl(2-(pyrrolidin-1-yl)ethyl)phosphonium bromide (**1m**) (88.7 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 10% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil solid (15.2 mg, 24%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.69 (m, 4H), 7.54 – 7.43 (m, 6H), 3.28 – 3.15 (m, 2H), 2.98 – 2.90 (m, 2H), 2.90 – 2.77 (m, 2H), 2.74 – 2.63 (m, 2H), 2.25 – 2.11 (m, 2H), 2.01 – 0.53 (m, 8H) ppm.

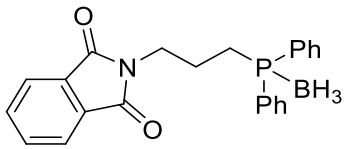
^{11}B NMR (128 MHz, $CDCl_3$) δ = -10.5 – -14.1 (m), -37.6 – -41.3 (m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.2 (d, *J* = 9.5 Hz), 131.8 (d, *J* = 2.5 Hz), 129.2 (d, *J* = 10.1 Hz), 128.3 (d, *J* = 56.1 Hz), 61.8, 58.2 (d, *J* = 7.7 Hz), 22.8, 22.5 (d, *J* = 37.8 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 13.50 (br-d, *J* = 77.7 Hz) ppm.

HRMS (ESI+): m/z for $C_{18}H_{28}B_2NNaP$ $[M+Na]^+$ calcd.: 334.2038, found: 334.2045.

(3-Phthaloylpropyl)diphenylphosphine borane adduct (2n)



The title compound was prepared following general procedure GP2, using (3-Phthaloylpropyl)triphenylphosphonium bromide (**1n**) (160.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (10% to 30% ethyl acetate in hexane) yielded the title compound as a white solid (74.1 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.80 (m, 2H), 7.74 – 7.68 (m, 2H), 7.67 – 7.60 (m, 4H), 7.50 – 7.37 (m, 6H), 3.74 (t, *J* = 6.8 Hz, 2H), 2.33 – 2.19 (m, 2H), 1.96 – 1.85 (m, 2H), 1.40 – 0.49 (br-m, 3H) ppm.

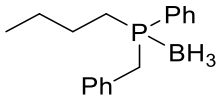
^{11}B NMR (128 MHz, $CDCl_3$) δ = -35.9 – -42.9 (m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.4, 134.2, 132.3 (d, *J* = 9.1 Hz), 132.1, 131.4 (d, *J* = 2.5 Hz), 129.1 (d, *J* = 55.1 Hz), 129.0 (d, *J* = 9.9 Hz), 123.5, 38.8 (d, *J* = 16.4 Hz), 23.4 (d, *J* = 37.7 Hz), 22.8 (d, *J* = 1.2 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.3 (br-d, *J* = 77.9 Hz) ppm.

HRMS (ESI+): m/z for $C_{23}H_{23}BNNaO_2P$ $[M+Na]^+$ calcd.: 410.1452, found: 410.1449.

Butylbenzylphenylphosphine borane adduct (2o)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using butylbenzyldiphenylphosphonium bromide (**1o**) (82.7 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 2% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (36.1 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.51 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.38 (m, 2H), 7.23 – 7.18 (m, 3H), 6.95 – 6.88 (m, 2H), 3.28 – 3.13 (m, 2H), 1.95 – 1.74 (m, 2H), 1.64 – 1.30 (m, 4H), 1.18 – 0.27 (m (overlapping signals), 6H, including: t, *J* = 7.1 Hz at 0.87 ppm) ppm.

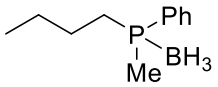
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.8 (*pseudo*-dt, *J* = 154.0, 93.8 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.5, 132.4 (d, *J* = 8.6 Hz), 131.5 (d, *J* = 2.4 Hz), 129.9 (d, *J* = 4.1 Hz), 128.7 (d, *J* = 9.6 Hz), 128.3 (d, *J* = 2.5 Hz), 127.8 (d, *J* = 50.9 Hz), 127.0 (d, *J* = 2.8 Hz), 34.9 (d, *J* = 30.9 Hz), 24.9, 24.4 (d, *J* = 13.8 Hz), 23.2 (d, *J* = 35.8 Hz), 13.7 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.2 (br-d, *J* = 75.8 Hz) ppm.

HRMS (ESI+): m/z for $C_{17}H_{24}BNaP$ $[M+Na]^+$ calcd.: 293.1601, found: 293.1610.

Butylmethylphenylphosphine borane adduct (2p)



The title compound was prepared following general procedure GP2, using butylmethyldiphenylphosphonium bromide (**1p**) (101.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 7% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (35.6 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.66 (m, 2H), 7.59 – 7.40 (m, 3H), 1.90 – 1.75 (m, 2H), 1.54 (d, *J* = 10.2 Hz, 3H), 1.51 – 1.28 (m, 4H), 1.19 – 0.32 (m (overlapping signals), 6H including: t, *J* = 7.1 Hz at 0.86 ppm) ppm.

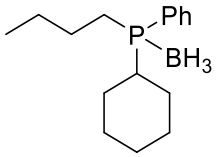
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.0 (qd, *J* = 95.4, 60.1 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 131.5 (d, *J* = 9.0 Hz), 131.3 (d, *J* = 2.5 Hz), 130.0 (d, *J* = 53.4 Hz), 128.9 (d, *J* = 9.7 Hz), 27.3 (d, *J* = 36.5 Hz), 25.1 (d, *J* = 1.5 Hz), 24.2 (d, *J* = 13.6 Hz), 13.6, 10.9 (d, *J* = 38.8 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 8.8 (br-q, *J* = 59.6 Hz) ppm.

HRMS (ESI+): m/z for $C_{11}H_{20}BNaP$ $[M+Na]^+$ calcd.: 217.1288, found: 217.1289.

Butylcyclohexylphenylphosphine borane adduct (2q)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using butylcyclohexyldiphenylphosphonium bromide (**1q**) (121.6 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (60.3 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (ddd, *J* = 9.7, 8.0, 1.6 Hz, 2H), 7.52 – 7.41 (m, 3H), 1.97 – 1.76 (m, 5H), 1.75 – 1.62 (m, 2H), 1.60 – 1.46 (m, 2H), 1.40 – 1.10 (m, 8H), 1.04 -0.20 (m (overlapping signals), 6H including t, *J* = 7.3 Hz at 0.85 ppm) ppm.

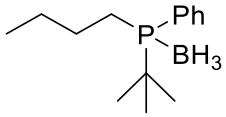
^{11}B NMR (128 MHz, $CDCl_3$) δ = -42.4 (*pseudo*-dt, *J* = 156.4, 92.8 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.7 (d, *J* = 8.1 Hz), 131.1 (d, *J* = 2.4 Hz), 128.7 (d, *J* = 9.3 Hz), 127.5 (d, *J* = 50.2 Hz), 35.2 (d, *J* = 35.2 Hz), 26.8 (d, *J* = 7.9 Hz), 26.7 (d, *J* = 7.4 Hz), 26.6, 26.4 (d, *J* = 1.1 Hz), 25.9 (d, *J* = 1.5 Hz), 24.9 (d, *J* = 1.2 Hz), 24.5 (d, *J* = 13.3 Hz), 22.2 (d, *J* = 35.6 Hz), 13.7 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 21.1 (br-d, *J* = 79.1 Hz) ppm.

HRMS (ESI+): m/z for $C_{16}H_{28}BNaP$ $[M+Na]^+$ calcd.: 285.1914, found: 285.1917.

***tert*-Butylbutylphenylphosphine borane adduct (2r)**



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using *tert*-butyl(butyl)diphenylphosphonium bromide (**1r**) (113.8 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 6% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (36.9 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 – 7.65 (m, 2H), 7.52 – 7.41 (m, 3H), 2.11 (qd, *J* = 14.6, 4.3 Hz, 1H), 1.88 – 1.73 (m, 1H), 1.71 – 1.55 (m, 1H), 1.48 – 1.32 (m, 2H), 1.31 – 0.24 (m (overlapping signals), 16H, including: d, *J* = 13.5 Hz and t, *J* = 7.3 Hz) ppm.

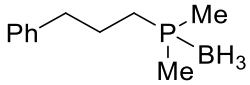
^{11}B NMR (128 MHz, $CDCl_3$) δ = -41.9 (*pseudo*-dt, *J* = 157.2, 79.5 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 133.5 (d, *J* = 7.7 Hz), 131.1 (d, *J* = 2.5 Hz), 128.4 (d, *J* = 9.2 Hz), 126.3 (d, *J* = 48.1 Hz), 29.1 (d, *J* = 32.8 Hz), 25.6 (d, *J* = 2.2 Hz), 25.2 (d, *J* = 0.9 Hz), 24.7 (d, *J* = 13.3 Hz), 18.5 (d, *J* = 34.0 Hz), 13.7 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 31.2 (br-q, *J* = 78.7 Hz) ppm.

HRMS (ESI+): m/z for $C_{14}H_{26}BNaP$ $[M+Na]^+$ calcd.: 259.1757, found: 259.1762.

Dimethyl(3-phenylpropyl)phosphine borane adduct (2s)



The title compound was prepared following general procedure GP2, using Dimethyl(phenyl)(3-phenylpropyl)phosphonium bromide (**1s**) (101.1 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (17.6 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.28 (m, 2H), 7.24 – 7.16 (m, 3H), 2.72 (t, *J* = 7.4 Hz, 2H), 1.94 – 1.76 (m, 2H), 1.70 – 1.57 (m, 2H), 1.27 (d, *J* = 10.3 Hz, 6H), 0.47 (br-dq, *J* = 94.3, 14.8 Hz, 3H) ppm.

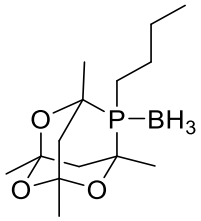
^{11}B NMR (128 MHz, $CDCl_3$) δ = -37.9 (qd, *J* = 94.3, 61.2 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 141.0, 128.7, 128.6, 126.4, 37.1 (d, *J* = 13.1 Hz), 26.4 (d, *J* = 36.4 Hz), 24.7 (d, *J* = 1.6 Hz), 11.1 (d, *J* = 37.4 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 4.0 (br-q, *J* = 61.5 Hz) ppm.

HRMS (ESI+): m/z for $C_{11}H_{16}P$ $[M-BH_4]^+$ calcd.: 179.0984, found: 179.0981.

Phosphine borane adduct 2t



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using phosphonium salt **1t** (85.9 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 9% ethyl acetate in cyclohexane) yielded the title compound as a white solid (47.8 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.36 (dd, *J* = 13.4, 3.8 Hz, 1H), 1.88 – 1.69 (m, 4H), 1.63 – 1.32 (m, 17H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.45 (br-q, *J* = 69 Hz, 3H) ppm.

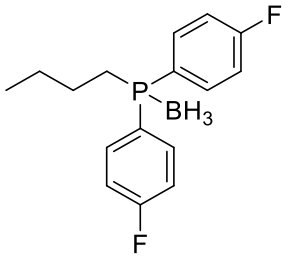
^{11}B NMR (128 MHz, $CDCl_3$) δ = -42.3 – -46.9 (m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 96.7 (d, *J* = 1.3 Hz), 96.2 (d, *J* = 1.6 Hz), 71.0 (d, *J* = 26.8 Hz), 69.8 (d, *J* = 33.7 Hz), 40.4 (d, *J* = 5.5 Hz), 39.3, 27.7 (d, *J* = 29.2 Hz), 26.3, 24.9 (d, *J* = 13.1 Hz), 24.1 (d, *J* = 5.3 Hz), 23.6 (d, *J* = 3.2 Hz), 17.9 (d, *J* = 24.1 Hz), 13.7 ppm (1 less signal than expected due to overlapping signals or assignment as doublet instead of singlet).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 11.4 (d, *J* = 66.0 Hz) ppm.

HRMS (ESI+): m/z for $C_{14}H_{28}BNaO_3P$ $[M+Na]^+$ calcd.: 309.1761, found: 309.1763.

Butylbis(4-fluorophenyl)phosphine borane adduct (2u)



The title compound was prepared following general procedure GP2, using butyltris(4-fluorophenyl)phosphonium bromide (**1u**) (136.0 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in *n*-hexane) yielded the title compound as a colorless oil (76.7 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.55 (m, 4H), 7.21 – 7.05 (m, 4H), 2.27 – 2.05 (m, 2H), 1.59 – 1.33 (m, 4H), 1.30 – 0.52 (m (overlapping signals), 6H including: t, *J* = 7.2 Hz) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.4 (*pseudo*-dt, *J* = 151.1, 93.2 Hz) ppm.

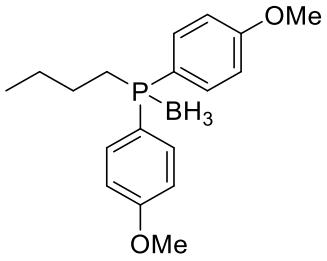
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 164.7 (dd, *J* = 252.9, 2.7 Hz), 134.5 (dd, *J* = 10.3, 8.6 Hz), 125.4 (dd, *J* = 56.6, 3.5 Hz), 116.4 (dd, *J* = 21.3, 10.8 Hz), 25.8 (d, *J* = 37.4 Hz), 25.1, 24.3 (d, *J* = 14.5 Hz), 13.6 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -107.8 (d, *J* = 1.8 Hz) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 15.0 (br-d, *J* = 79.2 Hz) ppm.

HRMS (ESI+): m/z for $C_{16}H_{20}BF_2NaP$ $[M+Na]^+$ calcd.: 315.1261, found: 315.1258.

Butylbis(4-methoxyphenyl)phosphine borane adduct (2v)



The title compound was prepared following a slightly modified general procedure GP2 (SIMes•HCl (13.7 mg, 0.04 mmol, 0.2 equiv.) was used instead of IiPr•HBF_4), using butyltris(4-methoxyphenyl)phosphonium bromide (**1v**) (97.9 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 5% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (44.4 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.53 (m, 4H), 6.99 – 6.90 (m, 4H), 3.82 (s, 6H), 2.18 – 2.07 (m, 2H), 1.47 (hex, *J* = 7.3 Hz, 2H), 1.43 – 1.32 (m, 2H), (m (overlapping signals), 6H including: t, *J* = 7.2 Hz) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -36.0 – -41.5 (m) ppm.

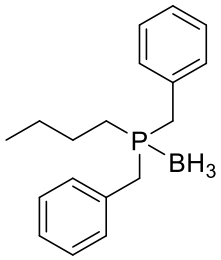
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 161.9 (d, *J* = 2.4 Hz), 133.8 (d, *J* = 10.2 Hz), 120.9 (d, *J* = 59.8 Hz), 114.5 (d, *J* = 10.7 Hz), 55.4, 26.1 (d, *J* = 38.2 Hz), 25.2, 24.4 (d, *J* = 14.4 Hz), 13.7 ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 12.7 (br-d, *J* = 83.1 Hz) ppm.

HRMS (ESI+): m/z for $C_{18}H_{26}BNaO_2P$ $[M+Na]^+$ calcd.: 339.1656, found: 339.1660.

The title compound was also prepared following general procedure GP2, using butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) (143.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (1% to 3% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (36.9 mg, 39%).

Dibenzylbutylphosphine borane adduct (2w)



The title compound was prepared following a slightly modified general procedure GP2 (stirred with BH_3•SMe_2 for 24 h instead of 2 h), using tribenzylbutylphosphonium bromide (**1w**) (88.3 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 5% ethyl acetate in *n*-hexane) yielded the title compound as a white solid (16.3 mg, 19%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.24 (m, 6H), 7.20 – 7.16 (m, 4H), 3.06 – 2.91 (m, 4H), 1.48 – 1.25 (m, 6H), 0.89 – 0.10 (m (overlapping signals), 6H including: t, *J* = 7.3 Hz) ppm.

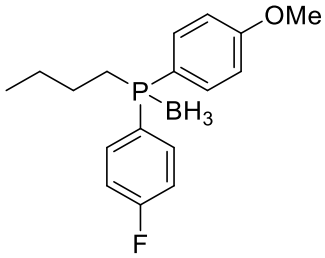
^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.9 (*pseudo*-dt, *J* = 153.6, 93.8, 94.6 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.5 (d, *J* = 6.0 Hz), 130.0 (d, *J* = 4.1 Hz), 128.7 (d, *J* = 2.3 Hz), 127.2 (d, *J* = 2.7 Hz), 31.4 (d, *J* = 29.4 Hz), 24.8 (d, *J* = 1.1 Hz), 24.4 (d, *J* = 13.3 Hz), 21.7 (d, *J* = 32.5 Hz), 13.7 ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 17.9 (br-d, *J* = 78.3 Hz) ppm.

HRMS (ESI+): m/z for $C_{18}H_{26}BNaP$ $[M+Na]^+$ calcd.: 307.1757, found: 307.1758.

Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (2x)



The title compound was prepared following general procedure GP2, using butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) (143.2 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (1% to 3% ethyl acetate in cyclohexane) yielded the title compound as a colorless oil (32.6 mg, 36%).

Butylbis(4-methoxyphenyl)phosphine borane adduct (**2v**) was also isolated as a colorless oil (36.9 mg, 39%). Its analytical data matched the one observed for the reaction of tris(4-methoxyphenyl)phosphonium bromide (**1v**) under the conditions of general procedure GP2 (see above).

Characterization data for the title compound:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 – 7.54 (m, 4H), 7.12 (tq, *J* = 8.7, 1.5 Hz, 2H), 6.99 – 6.95 (m, 2H), 3.83 (s, 3H), 2.24 – 2.06 (m, 2H), 1.56 – 1.34 (m, 4H), 1.32 – 0.46 (m (overlapping signals), 6H, including t, *J* = 7.2 Hz) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -36.9 – -41.4 (m) ppm.

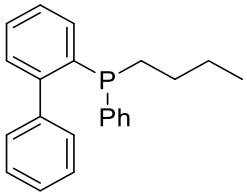
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 164.6 (dd, *J* = 252.2, 2.7 Hz), 162.2 (d, *J* = 2.4 Hz), 134.4 (dd, *J* = 10.3, 8.4 Hz), 134.0 (d, *J* = 10.3 Hz), 126.4 (dd, *J* = 56.5, 3.5 Hz), 119.9 (d, *J* = 59.9 Hz), 116.2 (dd, *J* = 21.3, 10.7 Hz), 114.7 (d, *J* = 10.8 Hz), 55.5, 26.0 (d, *J* = 37.8 Hz), 25.2, 24.4 (d, *J* = 14.4 Hz), 13.7 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -108.6 (d, *J* = 1.7 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 13.9 (br-d, *J* = 81.8 Hz) ppm.

HRMS (ESI+): m/z for $C_{17}H_{23}BFNaOP$ $[M+Na]^+$ calcd.: 327.1456, found: 327.1456.

[1,1'-Biphenyl]-2-yl(butyl)(phenyl)phosphine (2z)



The title compound was prepared following a modified general procedure GP2 (no treatment with BH_3•SMe_2), using [1,1'-biphenyl]-2-yl(butyl)diphenylphosphonium bromide (**1z**) (95.1 mg, 0.2 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in cyclohexane) yielded the title compound as a yellow oil (39.0 mg, 61%).

^{31}P{^{1}H} qNMR spectroscopy of the crude reaction mixture indicated that butyldiphenylphosphine (**S20**) was also formed in ca. 42% NMR yield.

Characterization data for the title compound:

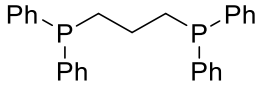
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (dt, *J* = 6.0, 3.1 Hz, 1H), 7.42 (ddd, *J* = 6.7, 4.1, 1.9 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.32 – 7.25 (m, 7H), 1.96 (t, *J* = 7.5 Hz, 2H), 1.43 – 1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 148.4 (d, *J* = 25.2 Hz), 142.1 (d, *J* = 5.3 Hz), 139.9 (d, *J* = 14.2 Hz), 137.3 (d, *J* = 16.3 Hz), 132.9 (d, *J* = 18.7 Hz), 131.6, 130.2 (d, *J* = 4.3 Hz), 129.9 (d, *J* = 3.9 Hz), 128.4, 128.3, 128.2, 128.2, 127.7, 127.4, 127.1, 28.2 (d, *J* = 16.9 Hz), 27.9 (d, *J* = 12.4 Hz), 24.4 (d, *J* = 13.2 Hz), 13.8 (1 more signal than expected, presumably because of assignment as 2 singlets instead of a doublet) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -24.2 ppm.

HRMS (ESI+): m/z for $C_{22}H_{22}P$ $[M-H]^+$ calcd.: 317.1454, found: 317.1450.

DPPP (5)



Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 0.5 equiv.) bisphosphonium salt **15** (145.3 mg, 0.2 mmol, 1.0 equiv.), phenylboronic acid (97.5 mg, 0.8 mmol, 4.0 equiv.), potassium phosphate (169.8 mg, 0.8 mmol, 4.0 equiv.), and dioxane (4.0 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block with 1200 rpm at 60 °C for 22 hours. After cooling to room temperature, a degassed aqueous solution of sodium cyanide (1 mL, 0.8 M, 0.8 mmol, 4.0 equiv.) and degassed DCE (4 mL) were added through the septum. The vial was stirred in a pre-heated heating block with 1200 rpm at 80 °C for 3 hours. The reaction mixture was loaded on silica and purified by column chromatography (2% to 6% ethyl acetate in cyclohexane) to yield the title compound as a white solid (37.8 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.33 (m, 8H), 7.33 – 7.27 (m, 12H), 2.20 (*pseudo*-t, *J* = 7.8 Hz, 4H), 1.68 – 1.54 (m, 2H) ppm.

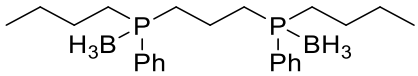
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 138.7 (d, *J* = 12.6 Hz), 132.8 (d, *J* = 18.4 Hz), 128.9 – 128.1 (m), 29.8 (t, *J* = 12.3 Hz), 22.6 (t, *J* = 17.1 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = -17.5 ppm.

HRMS (ESI+): m/z for $C_{27}H_{27}P_2$ $[M+H]^+$ calcd.: 413.1583, found: 413.1588.

The spectroscopic data matched those reported in the literature.[11]

1,3-Bis(butyl(phenyl)phosphino)propane di-borane adduct (7)



Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 0.5 equiv.) bisphosphonium salt **6** (137.3 mg, 0.2 mmol, 1.0 equiv.), phenylboronic acid (97.5 mg, 0.8 mmol, 4.0 equiv.), potassium phosphate (169.8 mg, 0.8 mmol, 4.0 equiv.), and dioxane (4.0 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block with 1200 rpm at 60 °C for 22 hours. After cooling to room temperature, a degassed aqueous solution of sodium cyanide (1 mL, 0.8 M, 0.8 mmol, 4.0 equiv.) and degassed DCE (4 mL) were added through the septum. The vial was stirred in a pre-heated heating block with 1200 rpm at 80 °C for 3 hours. The vial was cooled to 0 °C, and BH_3•SMe_2 (80 µL, 0.8 mmol, 4.0 equiv.) was added through the septum. After stirring at 0 °C for 5 minutes, the vial was allowed to warm to ambient temperature and stirred an additional 2 hours. The reaction mixture was loaded on silica and purified by column chromatography (2% to 6% ethyl acetate in cyclohexane) to yield the title compound as a colorless oil (45.9 mg, 57%, ca. 92% purity by ^{31}P{^{1}H} qNMR). Further purification by reverse-phase HPLC (20 min gradient of 70% to 100% MeCN in H_2O (0.1% formic acid)) yielded the title compound as a colorless oil that solidified to a white solid upon standing (35.2 mg, 44%, *dr* = 2:1, inseparable mixture).

The characterization data for the major isomer are reported here:

Full assignment of the ^{1}H NMR spectrum was not possible because of overlapping signals of the isomers. The spectrum shows the expected overall ratio between the aromatic and alipathatic signals, the characteristic broad BH_3 peak of phosphine borane adducts (1.12 – 0.21 ppm), and the triplet peak of the CH_3 group of the butyl substituents 0.84 (t, J = 7.2 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ = -36.7 – -44.5 (m) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.0 (d, J = 8.7 Hz), 131.4 (d, J = 2.4 Hz), 128.9 (d, J = 9.5 Hz), 128.0 (d, J = 51.5 Hz), 26.8 (dd, J = 35.2, 10.9 Hz), 25.6 (d, J = 36.3 Hz), 24.9 (d, J = 1.2 Hz), 24.3 (d, J = 13.5 Hz), 17.2, 13.6 ppm.

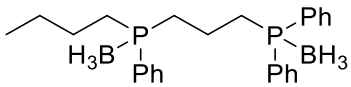
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 14.9 (br-d, J = 72.6 Hz) ppm.

HRMS (ESI+): m/z for $C_{23}H_{44}B_2NP_2$ $[M+NH_4]^+$ calcd.: 418.3130, found: 418.3143.

The ^{1}H, ^{11}B, and $^{31}P\{^{1}H\}$ NMR signals of the minor isomer are identical or largely overlap with the signals of the major isomer. The $^{13}C\{^{1}H\}$ NMR signals of the minor isomer are reported here:

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.1 (d, J = 8.7 Hz), 131.5 (d, J = 2.5 Hz), 129.0 (d, J = 9.5 Hz), 128.2 (d, J = 51.5 Hz), 26.8 (dd, J = 35.2, 10.8 Hz), 25.4 (d, J = 36.3 Hz), 24.9 (d, J = 1.3 Hz), 24.2 (d, J = 13.6 Hz), 17.2, 13.6 ppm.

Bisphosphine di-borane adduct 9



Inside a glovebox filled with argon, a 16-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 0.5 equiv.) monophosphonium salt **8** (109.9 mg, 0.2 mmol, 1.0 equiv.), phenylboronic acid (48.8 mg, 0.4 mmol, 2.0 equiv.), potassium phosphate (85.0 mg, 0.4 mmol, 2.0 equiv.), and dioxane (4.0 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block with 1200 rpm at 60 °C for 22 hours. After cooling to room temperature, a degassed aqueous solution of sodium cyanide (1 mL, 0.8 M, 0.8 mmol, 4.0 equiv.) and degassed DCE (4 mL) were added through the septum. The vial was stirred in a pre-heated heating block with 1200 rpm at 80 °C for 3 hours. The vial was cooled to 0 °C, and BH_3•SMe_2 (80 µL, 0.8 mmol, 4.0 equiv.) was added through the septum. After stirring at 0 °C for 5 minutes, the vial was allowed to warm to ambient temperature and stirred an additional 2 hours. The reaction mixture was loaded on silica and purified by column chromatography (2% to 8% ethyl acetate in cyclohexane) to yield the title compound as a colorless oil (59.2 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.60 (m, 4H), 7.59 – 7.53 (m, 2H), 7.51 – 7.35 (m, 9H), 2.37 – 2.15 (m, 2H), 2.07 – 1.64 (m, 7H), 1.63 – 1.19 (m, 5H), 1.18 – 0.27 (m (overlapping signals), 7H, including t, J = 7.1 Hz) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -36.6 – -42.5 (m) ppm.

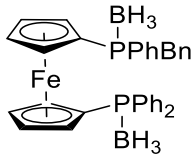
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.2, 132.2, 132.1, 132.1, 132.0, 132.0, 131.4, 131.4, 131.4, 131.4, 131.3, 131.3, 129.4 (d, J = 12.8 Hz), 129.0, 128.9, 128.9, 128.9, 128.8, 128.8, 128.3, 127.8, 27.0, 26.9,

26.9, 26.8, 26.7, 26.6, 26.5, 26.4, 25.4 (d, *J* = 36.3 Hz), 24.9 (d, *J* = 1.2 Hz), 24.2 (d, *J* = 13.6 Hz), 17.3 (d, *J* = 1.1 Hz), 13.6 ppm (Signals for which multiplet assignment is ambiguous are reported as singlets).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 17.0 – 13.6 (m) ppm.

HRMS (ESI+): m/z for $C_{25}H_{40}B_2NP_2$ $[M+NH_4]^+$ calcd.: 438.2817, found: 438.2834.

Bisphosphine di-borane adduct 13



Inside a glovebox filled with argon, a 8-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 0.5 equiv.) bisphosphonium salt **12** (145.1 mg, 0.2 mmol, 1.0 equiv.), phenylboronic acid (26.8 mg, 0.22 mmol, 1.1 equiv.), potassium phosphate (85.0 mg, 0.4 mmol, 2.0 equiv.), and dioxane (1.0 mL). The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block with 1200 rpm at 80 °C for 22 hours. After cooling to room temperature, a degassed aqueous solution of sodium cyanide (1 mL, 0.8 M, 0.8 mmol, 4.0 equiv.) and degassed DCE (4 mL) were added through the septum. The vial was stirred in a pre-heated heating block with 1200 rpm at 80 °C for 3 hours. The vial was cooled to 0 °C, and BH_3•SMe_2 (80 µL, 0.8 mmol, 4.0 equiv.) was added through the septum. After stirring at 0 °C for 5 minutes, the vial was allowed to warm to ambient temperature and stirred an additional 2 hours. The reaction mixture was loaded on silica and purified by column chromatography (0% to 8% ethyl acetate in cyclohexane) to yield the title compound as a yellow solid (90.2 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.54 (m, 2H), 7.54 – 7.47 (m, 4H), 7.47 – 7.32 (m, 9H), 7.20 – 7.11 (m, 3H), 6.84 (dt, *J* = 8.0, 2.0 Hz, 2H), 4.67 – 4.65 (m, 1H), 4.52 – 4.49 (m, 1H), 4.48 – 4.45 (m, 2H), 4.46 – 4.39 (m, 2H), 4.26 – 4.19 (m, 2H), 3.29 – 3.14 (m, 2H), 1.53 – 0.43 (m, 6H) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -38.5 (br) ppm.

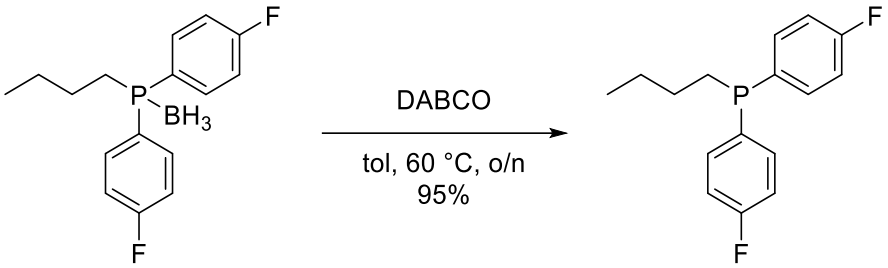
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 132.9, 132.8, 132.6, 132.6, 132.5, 132.5, 132.2 (d, *J* = 4.7 Hz), 131.4, 131.4, 131.4, 131.3, 131.2, 131.2, 130.9 (d, *J* = 20.4 Hz), 130.4 (d, *J* = 4.5 Hz), 129.2 (d, *J* = 54.6 Hz), 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.1, 128.1, 127.0 (d, *J* = 3.2 Hz), 74.7, 74.6, 74.6, 74.6, 74.5, 74.5, 74.3, 74.2, 74.0, 73.9, 73.9, 73.8, 73.7, 73.6, 73.3, 73.2, 71.1 (d, *J* = 47.5 Hz), 70.4 (d, *J* = 52.1 Hz), 35.8 (d, *J* = 33.8 Hz) ppm (Signals for which multiplet assignment is ambiguous are reported as singlets).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) δ = 15.5 (br-d, *J* = 50.8 Hz), 13.4 (br-d, *J* = 53.0 Hz) ppm.

HRMS (ESI+): m/z for $C_{35}H_{40}B_2FeNP_2$ $[M+NH_4]^+$ calcd.: 614.2166, found: 614.2171.

5. Product derivatization

Butylbis(4-fluorophenyl)phosphine (16)



2u **16**

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with phosphine borane adduct **2u** (58.4 mg, 0.2 mmol, 1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (DABCO) (26.9 mg, 0.24 mmol, 1.2 equiv.), and toluene (0.6 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 60 °C overnight (ca. 18 h). After cooling to room temperature, the reaction mixture was filtered through a silica plug under inert atmosphere, eluting with toluene. Volatile materials were evaporated to yield the title compound as a colorless oil (53.0 mg, 95%).

^{1}H NMR (400 MHz, tol-d_8) δ = 7.15 – 7.07 (m, 4H), 6.76 – 6.69 (m, 4H), 1.77 – 1.69 (m, 2H), 1.36 – 1.23 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H) ppm.

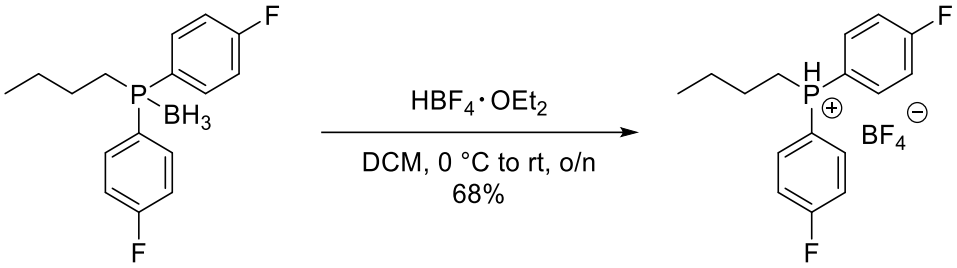
^{13}C{^{1}H} NMR (101 MHz, tol-d_8) δ = 163.6 (d, *J* = 248.2 Hz), 135.1 (dd, *J* = 15.3, 3.6 Hz), 134.8 (dd, *J* = 20.3, 7.8 Hz), 115.8 (dd, *J* = 20.8, 7.1 Hz), 28.6 (d, *J* = 12.4 Hz), 28.4 (d, *J* = 16.5 Hz), 24.6 (d, *J* = 13.3 Hz), 14.0 ppm.

^{19}F{^{1}H} NMR (376 MHz, tol-d_8) δ = -112.6 (d, *J* = 4.3 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, tol-d_8) δ = -18.8 (t, *J* = 4.2 Hz) ppm.

HRMS (ESI+): m/z for $C_{16}H_{18}F_2P$ $[M+H]^+$ calcd.: 279.1109, found: 279.1110.

Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (17)



2u **17**

Under an atmosphere of nitrogen, a 100-mL round-bottom flask was charged with phosphine borane adduct **2u** (292 mg, 1.0 mmol, 1.0 equiv.), and dichloromethane (20 mL). The flask was cooled to 0 °C, and HBF_4•OEt_2 (1.8 mL, 15.0 mmol, 15.0 equiv.) was added dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. It was then warmed to room temperature and stirred for an additional 30 minutes. Aqueous HBF_4 (48%, 24 mL) was added, and the reaction mixture was stirred at room temperature overnight (ca. 16 h). Then, an excess of DCM was added, the phases were separated, and the aqueous phase was extracted twice with DCM. The combined organic phases were dried with magnesium sulfate, and volatile materials were removed under reduced pressure. The crude product was purified by trituration with diethyl ether (4x) to yield the title compound as a light-yellow oil (250 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (br, 0.5H, P-*H* – other half-signal presumably overlapping with signal at 7.31 ppm), 7.98 (ddd, *J* = 13.6, 8.8, 5.0 Hz, 4H), 7.31 (td, *J* = 8.6, 2.3 Hz, 4H), 3.02 – 2.73 (m, 2H), 1.65 – 1.55 (m, 2H), 1.48 (dt, *J* = 14.1, 7.0 Hz, 2H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -0.2 ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 167.0 (dd, *J* = 259.6, 3.4 Hz), 136.3 (dd, *J* = 12.8, 9.7 Hz), 118.4 (dd, *J* = 22.2, 14.6 Hz), 111.9 (d, *J* = 88.6 Hz), 24.9 (d, *J* = 3.8 Hz), 23.4 (d, *J* = 16.7 Hz), 20.0 (d, *J* = 48.3 Hz), 13.3 ppm.

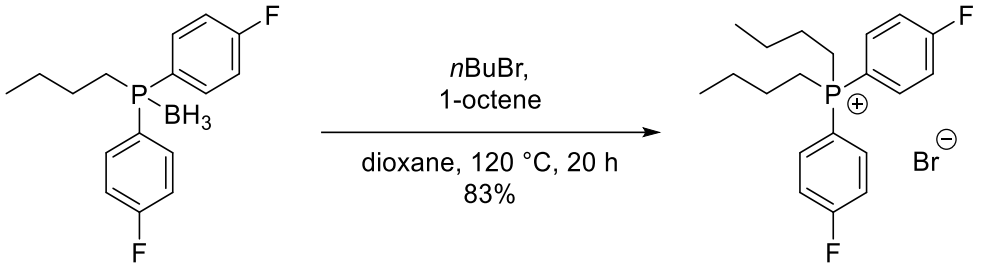
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -100.0, -149.0 ($^{10}BF_4^-$), -149.1 ($^{11}BF_4^-$) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 8.5 ppm.

^{31}P{/} NMR (203 MHz, $CDCl_3$) δ = 8.4 (br-d, *J* = 512.3 Hz) ppm.

HRMS (ESI+): m/z for $C_{16}H_{18}F_2P$ $[M\text{-}BF_4]^+$ calcd.: 279.1109, found: 279.1107.

Dibutylbis(4-fluorophenyl)phosphonium bromide (18)



2u **18**

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with phosphine borane adduct **2u** (58.4 mg, 0.2 mmol, 1.0 equiv.), 1-octene (126 µL, 0.8 mmol, 4.0 equiv.), 1-bromobutane (**3**) (43 µL, 0.4 mmol, 2.0 equiv.), and dioxane (0.6 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 120 °C for 20 h. After cooling to room temperature, the reaction mixture was loaded on silica and purified by column chromatography (2% to 10% MeOH in DCM) to yield the title compound as a white solid (68.7 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (tdd, *J* = 8.8, 5.0, 2.1 Hz, 4H), 7.37 – 7.28 (m, 4H), 3.32 – 3.18 (m, 4H), 1.54 – 1.43 (m, 4H), 1.44 – 1.29 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 6H) ppm.

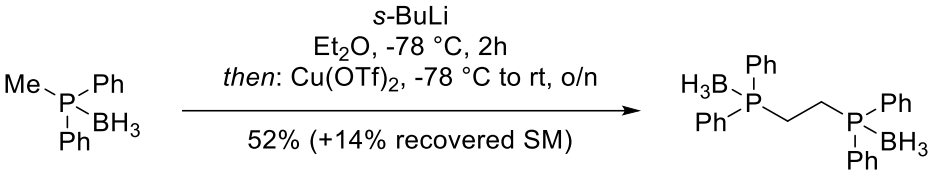
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 166.4 (dd, *J* = 259.4, 3.4 Hz), 136.2 (dd, *J* = 11.2, 9.4 Hz), 118.1 (dd, *J* = 22.0, 13.4 Hz), 113.7 (dd, *J* = 86.3, 3.5 Hz), 24.0 (d, *J* = 4.4 Hz), 23.6 (d, *J* = 16.4 Hz), 21.4 (d, *J* = 49.4 Hz), 13.6 (d, *J* = 1.0 Hz) ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -100.7 (d, *J* = 1.0 Hz) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 27.5 ppm.

HRMS (ESI+): m/z for $C_{20}H_{26}F_2P$ $[M\text{-}Br]^+$ calcd.: 335.1735, found: 335.1728.

1,2-Bis(diphenylphosphino)ethane di-borane adduct (19)



2c **19**

Under an atmosphere of nitrogen, a 10-mL Schlenk flask was charged with phosphine borane adduct **2c** (64.5 mg, 0.3 mmol, 1.0 equiv.) and diethyl ether (1.2 mL). The mixture was cooled to -78 °C and *s*-BuLi (1.3 M in hexanes, 280 µL, 0.36 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred at -78 °C for 2 hours. Then, $Cu(OTf)_2$ (163 mg, 0.45 mmol, 1.5 equiv.) was added in one portion and the reaction mixture was allowed to warm to room temperature overnight. An excess of aqueous ammonia (25%) was added to the reaction mixture. The phases were separated, and the aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with aqueous ammonia (5%), aqueous HCl (2 M), and brine before they were dried with magnesium sulfate. Volatile materials were

removed under reduced pressure, and the residue was purified by column chromatography (4% to 7% ethyl acetate in *n*-hexane) to yield the title compound as a white solid (33.4 mg, 52%).
Starting material **2c** was also recovered as a colorless oil (9.1 mg, 14%).

Characterization data for title compound **19**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.58 (m, 8H), 7.58 – 7.36 (m, 12H), 2.39 (d, *J* = 3.2 Hz, 4H), 1.51 – 0.57 (m, 6H) ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ = -39.8 (br) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 132.9 – 131.9 (m), 131.7 (*pseudo*-t, *J* = 1.3 Hz), 129.5 – 128.8 (m), 128.3 (d, *J* = 55.5 Hz), 19.6 (d, *J* = 37.7 Hz) ppm.

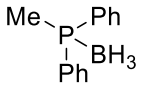
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 18.1 (br-d, *J* = 41.7 Hz) ppm.

HRMS (ESI+): m/z for $C_{26}H_{30}B_2NaP$ $[M+Na]^+$ calcd.: 449.1901, found: 449.1902.

6. Further experiments

Large scale experiments

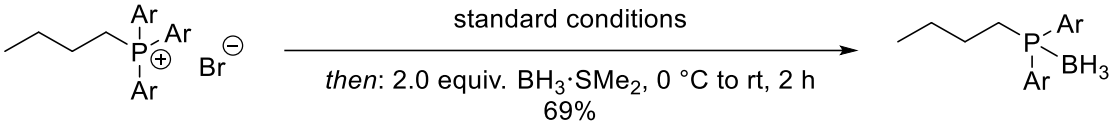
Methyldiphenylphosphine borane adduct (**2c**)



The title compound was prepared following a slightly modified general procedure GP2 (reaction conducted in a 16-mL screw cap vial), using methyltriphenylphosphonium bromide (**1c**) (357.2 mg, 1.0 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in *n*-hexane) yielded the title compound as a colorless oil (148.0 mg, 69%).

The characterization data matched the one reported for the reaction that was set up according to general procedure GP2 (*vide supra*).

Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**)



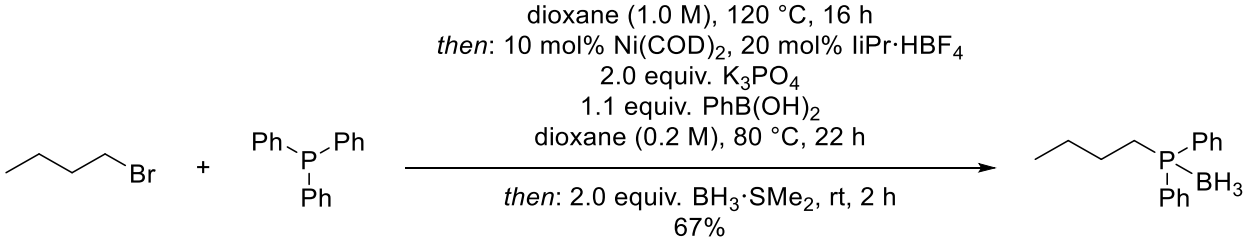
1u **2u**

Ar = 4-FC_6H_4

Inside a glovebox filled with argon, a 250-mL Schlenk flask was charged with $Ni(COD)_2$ (275 mg, 1.0 mmol, 0.1 equiv.), IiPr•HBF_4 (480 mg, 2.0 mmol, 0.2 equiv.), butyltris(4-fluorophenyl)phosphonium bromide (**1u**) (4.53 g, 10.0 mmol, 1.0 equiv.), phenylboronic acid (1.34 g, 11.0 mmol, 1.1 equiv.), potassium phosphate (4.25 g, 20.0 mmol, 2.0 equiv.), and dioxane (50 mL). The flask was taken out of the glovebox and stirred in a pre-heated oil bath at 80 °C for 22 hours. After cooling to 0 °C, BH_3•SMe_2 (1.9 mL, 20.0 mmol, 2.0 equiv.) was added dropwise, and the mixture was stirred for an additional 2 hours at ambient temperature. The reaction mixture was loaded on silica and purified by column chromatography (0% to 8% ethyl acetate in hexane) to yield the title compound as a colorless oil (2.01 g, 69%).

The characterization data matched the one reported for the reaction that was set up according to general procedure GP2 (*vide supra*).

One-pot reaction



3 **4** **2b**

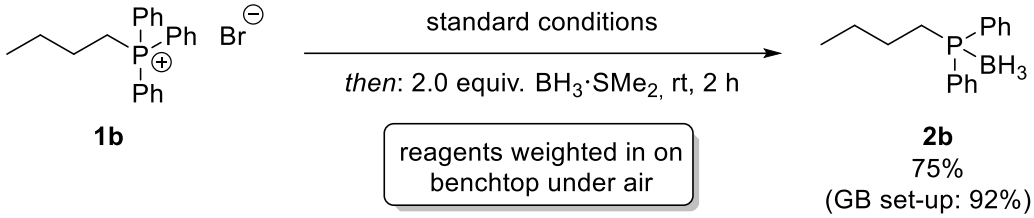
Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with triphenylphosphine (**4**) (78.6 mg, 0.3 mmol, 1.0 equiv.), 1-bromobutane (**3**) (33.8 µL, 0.315 mmol, 1.05 equiv.), and dioxane

(0.3 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 120 °C for 16 hours. After cooling to room temperature, the vial was taken into the glovebox again. $Ni(COD)_2$ (8.3 mg, 0.03 mmol, 0.1 equiv.), IiPr•HBF_4 (14.4 mg, 0.06 mmol, 0.2 equiv.), phenylboronic acid (40.2 mg, 0.33 mmol, 1.1 equiv.), potassium phosphate (127.6 mg, 0.6 mmol, 2.0 equiv.), and dioxane (1.2 mL) were added. The vial was capped with a septum cap, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 22 h. After cooling to room temperature, BH_3•SMe_2 (60 µL, 0.6 mmol, 2.0 equiv.) was added through the septum, and the mixture was stirred for an additional 2 hours at ambient temperature. The reaction mixture was loaded on silica and purified by column chromatography (0% to 8% ethyl acetate in *n*-hexane) to yield a 6.4:1 mixture of the title compound and triphenylphosphine borane adduct as a white solid (67.6 mg, 87%). The mixture was purified by reverse-phase HPLC (20 min gradient of 70% to 100% MeCN in H_2O (0.1% formic acid)) to yield butyldiphenylphosphine borane adduct (**2b**) as a colorless oil (51.4 mg, 67%).

The characterization data matched the one reported for the reaction that was set up according to general procedure GP2 (*vide supra*).

Benchtop setup

Set-up with $NI(COD)_2$ on the benchtop



On a benchtop under air, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (8.3 mg, 0.03 mmol, 0.1 equiv.), IiPr•HBF_4 (14.4 mg, 0.06 mmol, 0.2 equiv.), phosphonium salt **1b** (119.8 mg, 0.3 mmol, 1.0 equiv.), phenylboronic acid (40.2 mg, 0.33 mmol, 1.1 equiv.), and potassium phosphate (127.6 mg, 0.6 mmol, 2.0 equiv.). The vial was capped with a septum cap and connected to a Schlenk line via needle. The vial was evacuated and refilled with nitrogen over three cycles. Then, dioxane (1.5 mL) was added. The vial was placed in a pre-heated heating block at 80 °C and stirred there for 22 hours. After cooling to room temperature, BH_3•SMe_2 (60 µL, 0.6 mmol, 2.0 equiv.) was added through the septum, and the mixture was stirred for an additional 2 hours at ambient temperature. The reaction mixture was loaded on silica and purified by column chromatography (0% to 8% ethyl acetate in cyclohexane) to yield butyldiphenylphosphine borane adduct (**2b**) as a colorless oil (57.6 mg, 75%).

The characterization data matched the one reported for the reaction that was set up according to general procedure GP2 (*vide supra*).

Note: The reagents were stored under argon prior to use and only exposed to air for the setup of the reaction.

Set-up with air-stable Ni(0) pre-catalysts

On a benchtop under air, a 4-mL screw-cap vial was charged with a nickel pre-catalyst (0.01 mmol, 0.1 equiv.), IiPr•HBF_4 (4.8 mg, 0.02 mmol, 0.2 equiv.), phosphonium salt **1b** (39.9 mg, 0.1 mmol, 1.0 equiv.), phenylboronic acid (13.4 mg, 0.11 mmol, 1.1 equiv.), and potassium phosphate (42.5 mg, 0.2 mmol, 2.0 equiv.). The vial was capped with a septum cap and connected to a Schlenk line via needle. The vial was evacuated and refilled with nitrogen over three cycles. Then, dioxane (0.5 mL) was added. The vial was placed in a pre-heated heating block at 80 °C and stirred there for 22 hours. After cooling to room temperature, triphenyl phosphate was added as an internal standard, and the mixture was diluted with 2 mL of dioxane. After shaking the vial for 30 seconds, ca. 0.5 mL of the solution were transferred to an NMR tube. Ca. 0.1 mL of THF-d_8 were also added to the NMR tube. The NMR tube was shaken to allow for mixing, and a $^{31}P\{^1H\}$ NMR spectrum with inverse-gated decoupling was acquired (O1P = 0 ppm, D1 = 20 s).

Note: The reagents were stored under argon prior to use and only exposed to air for the setup of the reactions.

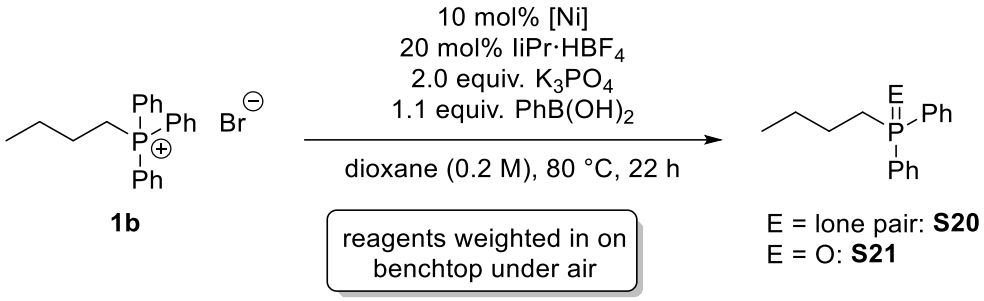
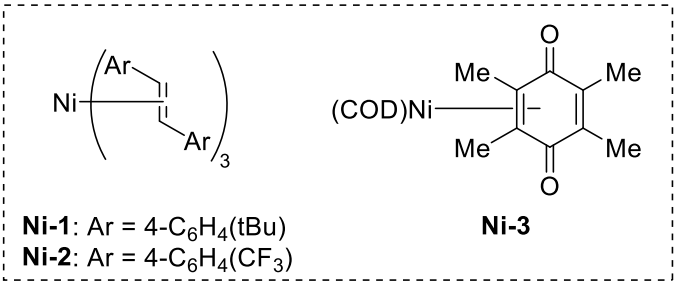


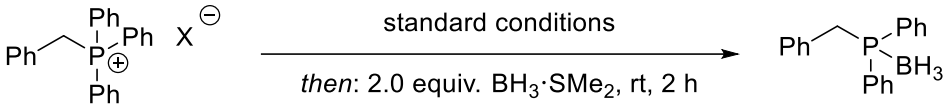
Table S5. Reaction set-up on the benchtop using air-stable Ni(0) pre-catalysts.

Entry	[Ni]	Yield **S19**+**S20** (%)[a]
1	**Ni-1**[12]	quant.
2	**Ni-2**[13]	quant.
3	**Ni-3**[14]	quant.

a: Combined $^{31}P\{^1H\}$ qNMR yield of the phosphine product and its corresponding oxide using triphenyl phosphate as internal standard.



Halide effect on the dearylation reaction

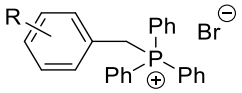


1a: X = Br
1a': X = Cl
1a'': X = I

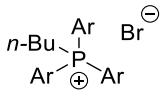
2a
using **1a**: 82%
using **1a'**: 63%
using **1a''**: 56%

Benzyldiphenylphosphine borane adduct (**2a**) was prepared following general procedure GP2, using phosphonium salts **1a** (130.0 mg, 0.3 mmol, 1.0 equiv.), **1a'** (116.7 mg, 0.3 mmol, 1.0 equiv.), or **1a''** (144.1 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography yielded **2a** as a colorless oil in the indicated yields.

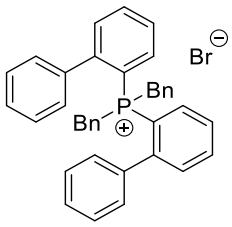
Reactions of further substrates



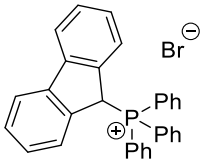
R = 4-vinyl: benzylic cleavage
R = 2-Cl: benzylic cleavage or C-Cl Suzuki coupling
R = 4-Br: predominant C-Br Suzuki coupling



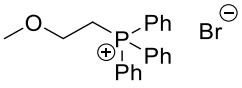
Ar = *o*-tol: <10%
Ar = 2-C_6H_4OMe: 18%
Ar = 2-thienyl: ca. 30%
Ar = 2-furyl: low yield
Ar = 4-tol: ca. 50% (80% purity)
Ar = 3,5-$(CF_3)_2C_6H_3$: ca. 15%



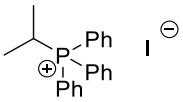
<10%



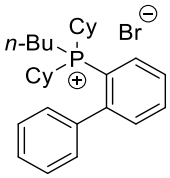
messy reaction



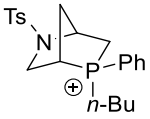
25%
de-Ph:de-Alk = 1:7.5



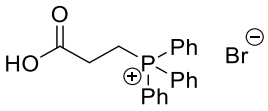
42%
(the reaction might work
better using the bromide salt)



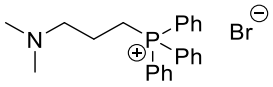
<10%



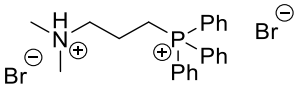
traces



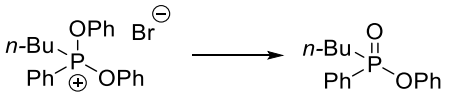
traces
(PPh_3 as major product)



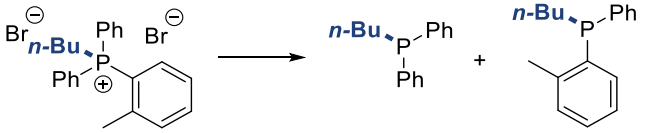
traces
(poor conversion)



traces
(poor conversion)

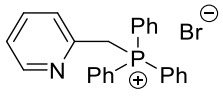


exclusive
product

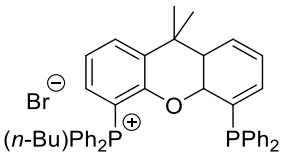


50%

ca. 28%
(slightly impure)



benzylic cleavage



backbone cleaved

Figure S3. Further substrates tested under the conditions of GP2.

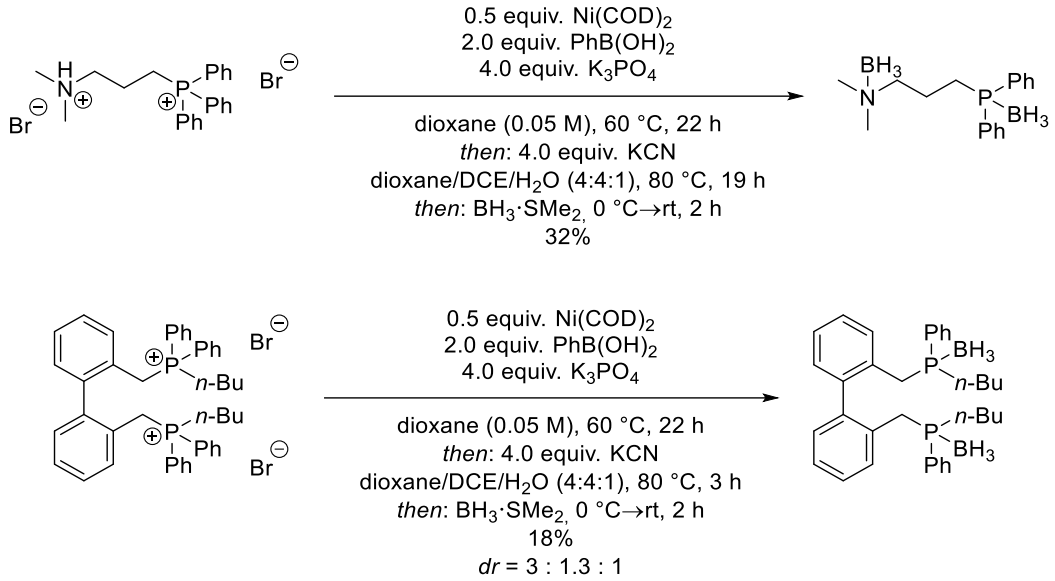
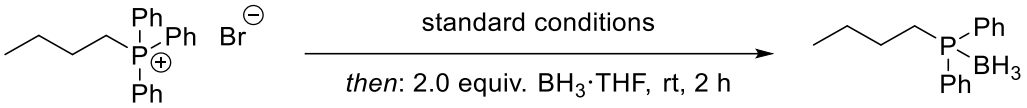


Figure S4. Further modifications of bidentate phosphines.

Borane protection with BH_3•THF



1b **2b**

88%

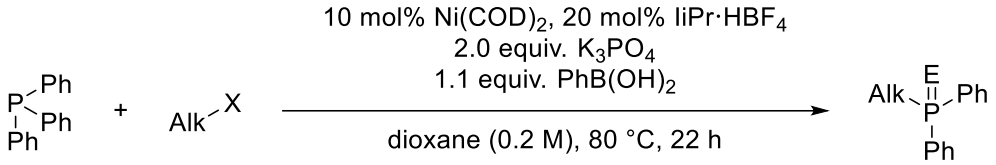
(quench with $BH_3·SMe_2$: 92%)

Butyldiphenylphosphine borane adduct (**2b**) was prepared following a slightly modified general procedure GP2 (BH_3•THF (1 M in THF, 0.6 mL, 0.6 mmol, 2.0 equiv.) used instead of BH_3•SMe_2), using butyltriphenylphosphonium bromide (**1b**) (119.8 mg, 0.3 mmol, 1.0 equiv.). Purification by column chromatography (0% to 8% ethyl acetate in cyclohexane) yielded the desired product as a colorless oil (67.3 mg, 88%).

The characterization data matched the one reported for the reaction that was set up according to general procedure GP2 (*vide supra*).

Attempted direct alkylative dearylation

Inside an argon-filled glovebox, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.1 equiv.), IiPr•HBF_4 (4.8 mg, 0.02 mmol, 0.2 equiv.), triphenylphosphine (**4**) (26.2 mg, 0.1 mmol, 1.0 equiv.), *n*-butyl halide (0.1 mmol, 1.0 equiv. or 0.2 mmol, 2.0 equiv.), phenylboronic acid (13.4 mg, 0.11 mmol, 1.1 equiv.), potassium phosphate (42.6 mg, 0.2 mmol, 2.0 equiv.), and dioxane (0.5 mL). The vial was capped, placed in a pre-heated heating block at 80 °C, and stirred there for 22 hours. After cooling to room temperature, triphenyl phosphate was added as an internal standard, and the mixture was diluted with 2 mL of dioxane. After shaking the vial for 30 seconds, ca. 0.5 mL of the solution were transferred to an NMR tube. Ca. 0.1 mL of THF-d_8 were also added to the NMR tube. The NMR tube was shaken to allow for mixing of the solutions, and a $^{31}P\{^1H\}$ NMR spectrum with inverse-gated decoupling was acquired (O1P = 0 ppm, D1 = 20 s).



4

Alk = *n*-Bu, X = Cl: **S22**
Alk = *n*-Bu,X = Br: **3**
Alk = *n*-Bu,X = I: **S23**
Alk = Cy, X = Br: **S24**
Alk = *t*-Bu, X = Br: **S25**

Alk = *n*-Bu, E = lone pair: **S20**
Alk = *n*-Bu, E = O: **S21**
Alk = Cy, E = lone pair: **S26**
Alk = Cy, E = O: **S27**
Alk = *t*-Bu, E = lone pair: **S28**
Alk = *t*-Bu, E = O: **S29**

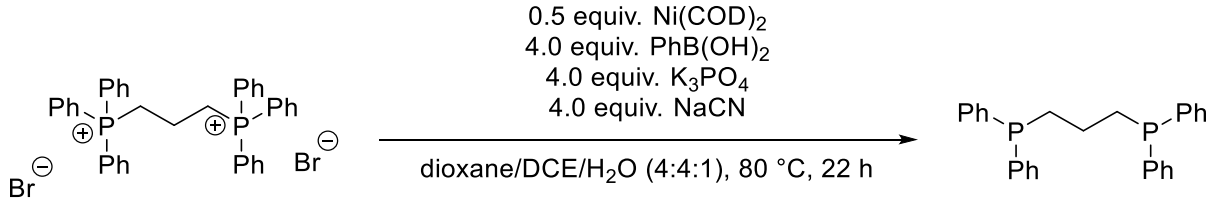
Table S6. Attempted direct reaction between an alkyl halide and triphenylphosphine (**4**).

Entry	AlkX (equiv.)	Desired products	Yield of desired products (%)[a]
1	**3** (1.0)	**S20** + **S21**	< 5%
2	**3** (1.5)	**S20** + **S21**	5%
3	**3** (2.0)	**S20** + **S21**	11%
4	**S22** (2.0)	**S20** + **S21**	< 5%
5	**S23** (2.0)	**S20** + **S21**	< 5%
6	**S24** (2.0)	**S26** + **S27**	not observed
7	**S25** (2.0)	**S28** + **S29**	not observed

a: Combined $^{31}P\{^{1}H\}$ qNMR yield of the phosphine product and its corresponding oxide using triphenyl phosphate as internal standard.

Attempted single step dearylation and decomplexation

Inside an argon-filled glovebox, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (6.9 mg, 0.025 mmol, 0.5 equiv.), bisphosphonium salt **15** (36.3 mg, 0.05 mmol, 1.0 equiv.), phenylboronic acid (24.4 mg, 0.2 mmol, 4.0 equiv.), potassium phosphate (42.6 mg, 0.2 mmol, 4.0 equiv.), and dioxane (1.0 mL). The vial was capped with a septum cap and taken out of the glovebox. A solution of sodium cyanide (9.8 mg, 0.2 mmol, 4.0 equiv.) in water (0.25 mL) was added by syringe. Then, DCE (1.0 mL) was added by syringe. The vial was placed in a pre-heated heating block at 80 °C and stirred there for 22 hours. After cooling to room temperature, *n*-dodecane (7.5 µl) was added as an internal standard, and the mixture was diluted with 2 mL of acetone. After shaking the vial for 30 seconds, a sample was taken for GC analysis.

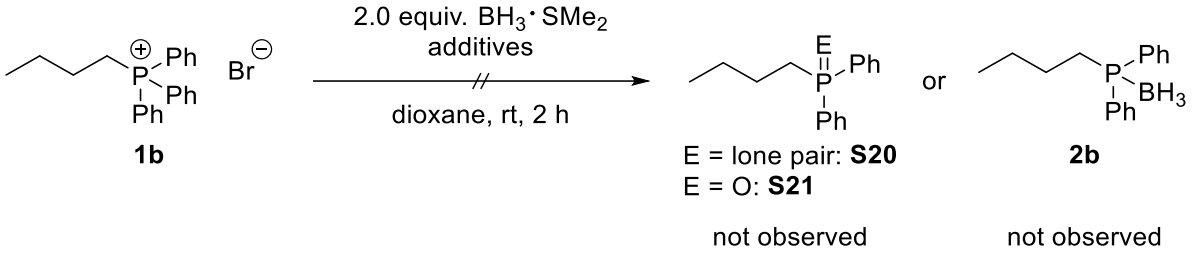


15

5
traces

Control reactions for a direct reaction of phosphonium salt and borane

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with butyltriphenylphosphonium bromide (**1b**) (39.9 mg, 0.1 mmol, 1.0 equiv.), additives (see Table S6), and dioxane (0.5 mL). The vial was capped with a septum cap and taken out of the glovebox. BH_3•SMe_2 (20 µL, 0.2 mmol, 2.0 equiv.) was added through the septum, and the reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was analyzed by $^{31}P\{^{1}H\}$ NMR spectroscopy and GC/MS to probe the formation of butyldiphenylphosphine (**S20**) and its corresponding oxide (**S21**) and borane adduct (**2b**).



1b

E = lone pair: **S20**
E = O: **S21**

not observed

2b

not observed

Table S7. Control reactions to probe for a direct reaction between phosphonium salts and BH_3•SMe_2.

Entry	Additive
1	None
2	IiPr•HBF_4 (0.2 equiv.)
3	K_3PO_4 (2.0 equiv.)
4	$PhB(OH)_2$ (1.1 equiv.)
5	IiPr•HBF_4 (0.2 equiv.) K_3PO_4 (2.0 equiv.) $PhB(OH)_2$ (1.1 equiv.)

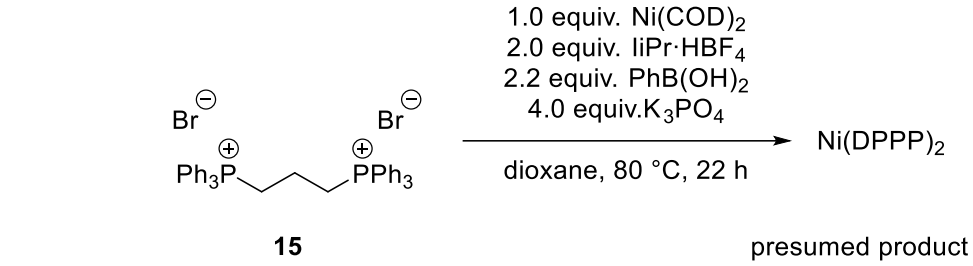
These experiments show that BH_3•SMe_2 is not able to reduce the phosphonium salt to the corresponding phosphine under the reaction conditions of general procedure GP2.

Analysis of nickel complexes formed during the reaction of bisphosphonium salts

A - Reaction NMR spectrum of the stoichiometric dearylation reaction

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 1.0 equiv.), bisphosphonium salt **15** (72.6 mg, 0.1 mmol, 1.0 equiv.), phenylboronic acid (26.8 mg, 0.22 mmol, 2.2 equiv.), potassium phosphate (84.8 mg, 0.4 mmol, 4.0 equiv.), and dioxane (0.5 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 22 hours. The mixture was allowed to cool to room temperature and taken into the glovebox. A few drops of THF-d_8 were added. The sample was transferred into an NMR tube for analysis.

$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) δ = 11.8 ppm.



15 presumed product

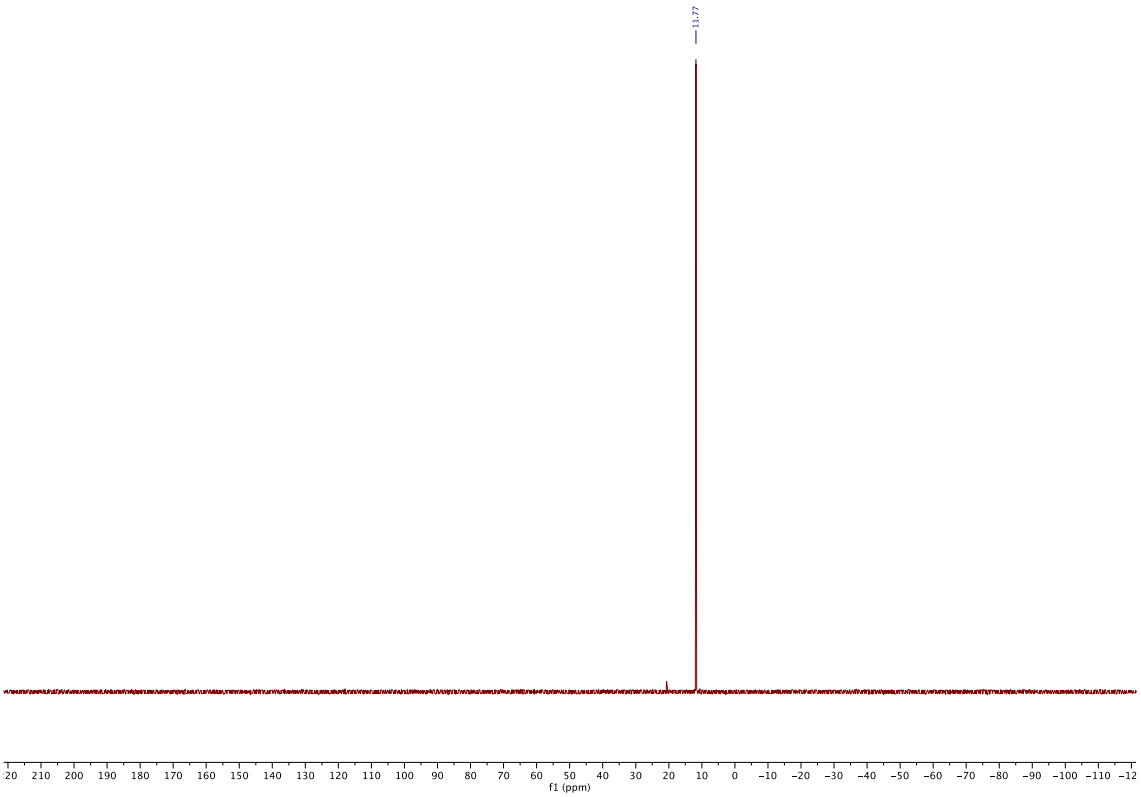


Figure S5. $^{31}P\{^{1}H\}$ reaction NMR spectrum (dioxane spiked with THF-d_8) of the stoichiometric dearylation reaction of salt **15**.

B - Independent synthesis of $Ni(DPPP)_2$ according to literature[15]

Inside a glovebox filled with argon, a 4-mL screw-cap vial was charged with $Ni(COD)_2$ (27.5 mg, 0.1 mmol, 1.0 equiv.), DPPP (**5**) (82.5 mg, 0.2 mmol, 2.0 equiv.), and dioxane (0.5 mL). The vial was capped, taken out of the glovebox, and stirred in a pre-heated heating block at 80 °C for 18 hours. The mixture was allowed to cool to room temperature and taken into the glovebox. A few drops of THF-d_8 were added. The sample was transferred into an NMR tube for analysis.

$^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8) δ = 11.8 ppm.

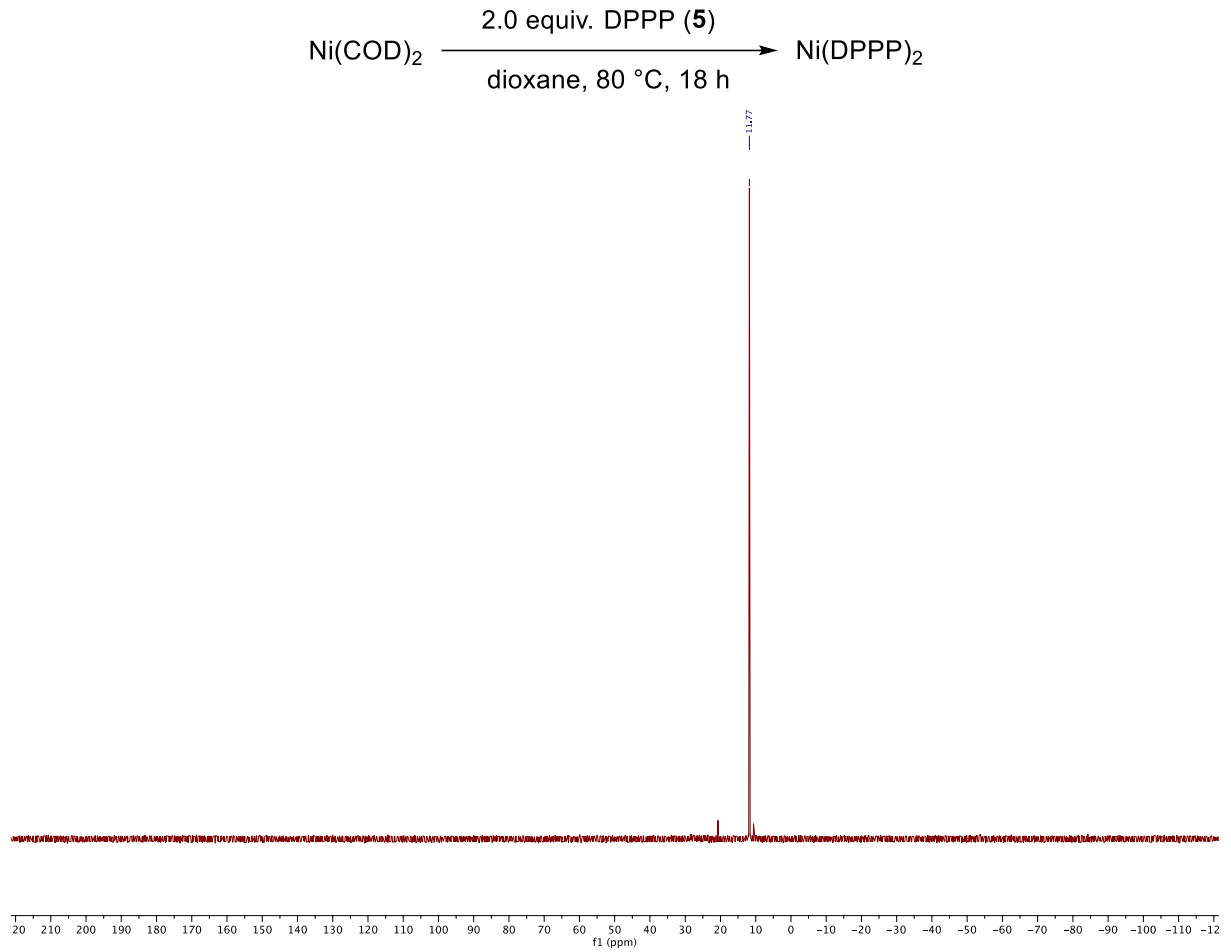


Figure S6. $^{31}P\{^1H\}$ NMR spectrum (dioxane spiked with THF-d_8) of the formation of $Ni(DPPP)_2$.

C - Mixture of A and B

Inside a glovebox filled with argon, a 1:1 mixture of the solutions generated in A and B was prepared. For that purpose, 0.2 mL of each sample was mixed with THF-d_8 (0.2 mL).

$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) δ = 11.8 ppm.

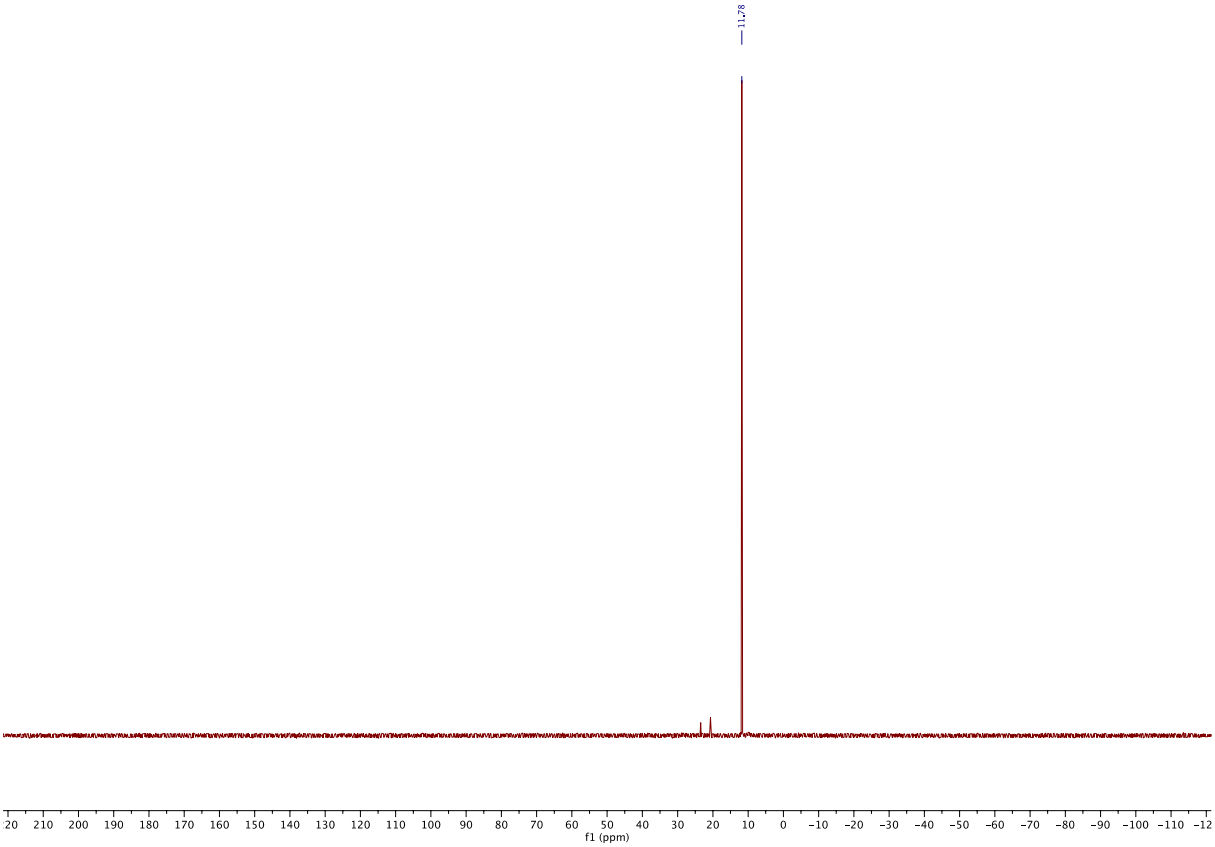
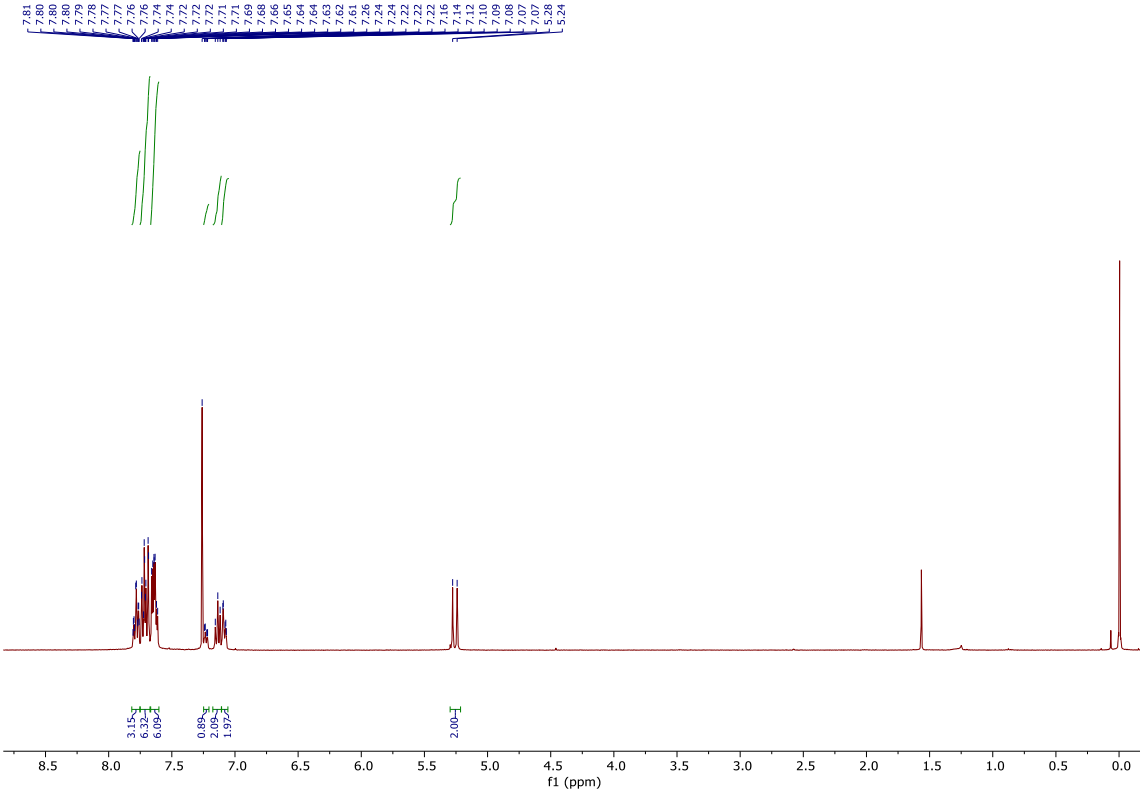


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (dioxane spiked with THF-d_8) of the combined solutions generated in part A and B.

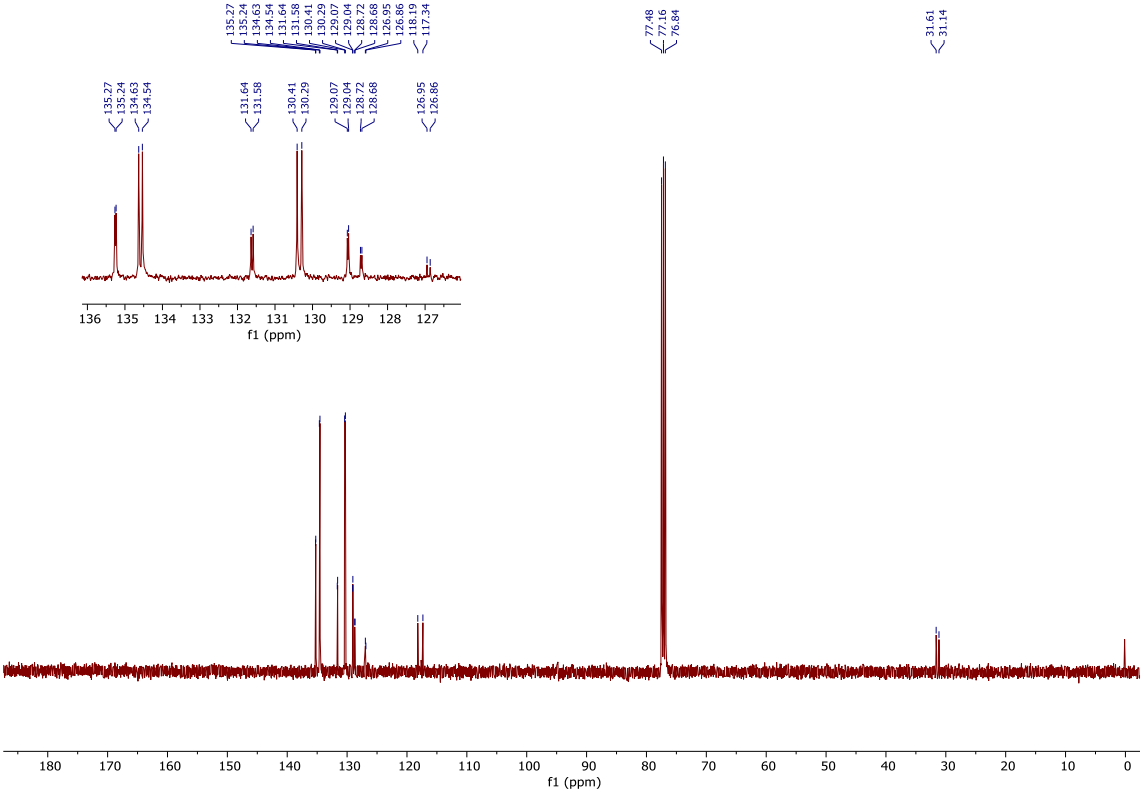
The singlet NMR peaks of the reaction NMR spectrum (A) (Figure S5) and the independent formation of $Ni(DPPP)_2$ (B) (Figure S6) have the same chemical shift. Furthermore, a mixture of both samples shows the same peak (Figure S7). The experiments strongly suggest that $Ni(DPPP)_2$ is generated in the dearylation reaction of bisphosphonium salt **15**, indicating that the desired dearylation of **15** had occurred and that the dearylation product is bound to the nickel center.

7. NMR spectra

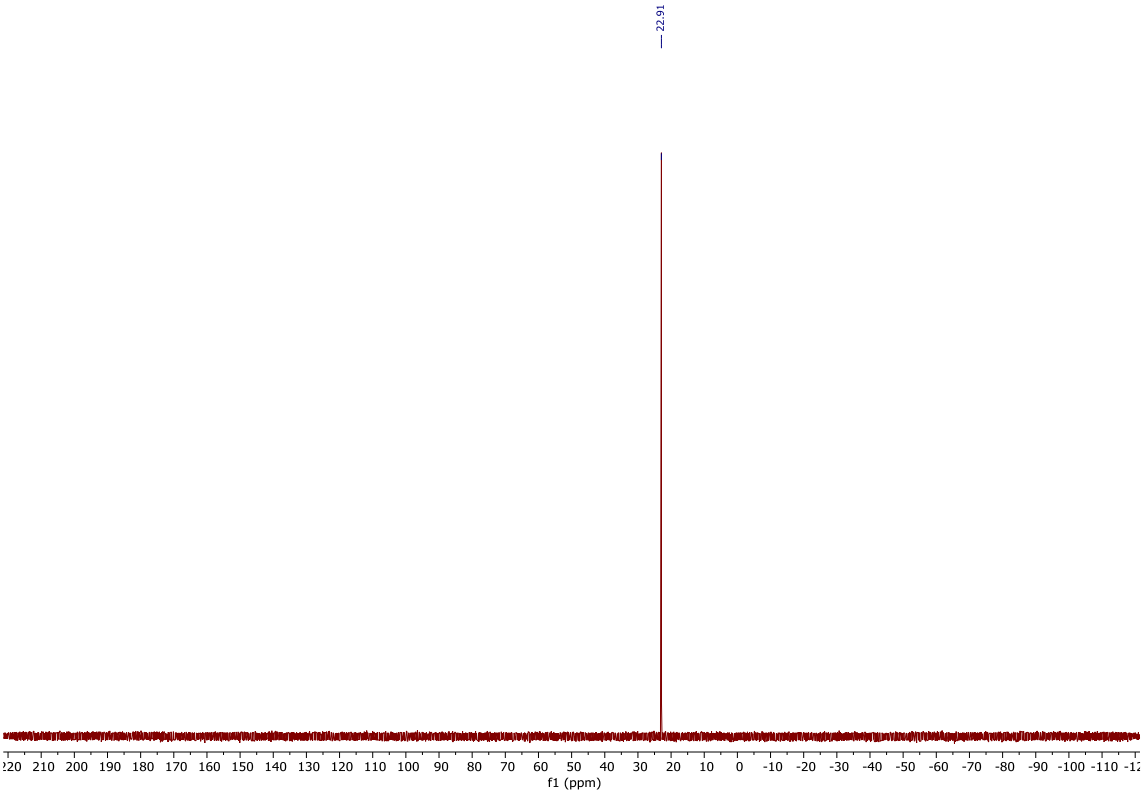
Benzyltriphenylphosphonium iodide (**1a''**) – ^{1}H NMR spectrum ($CDCl_3$)



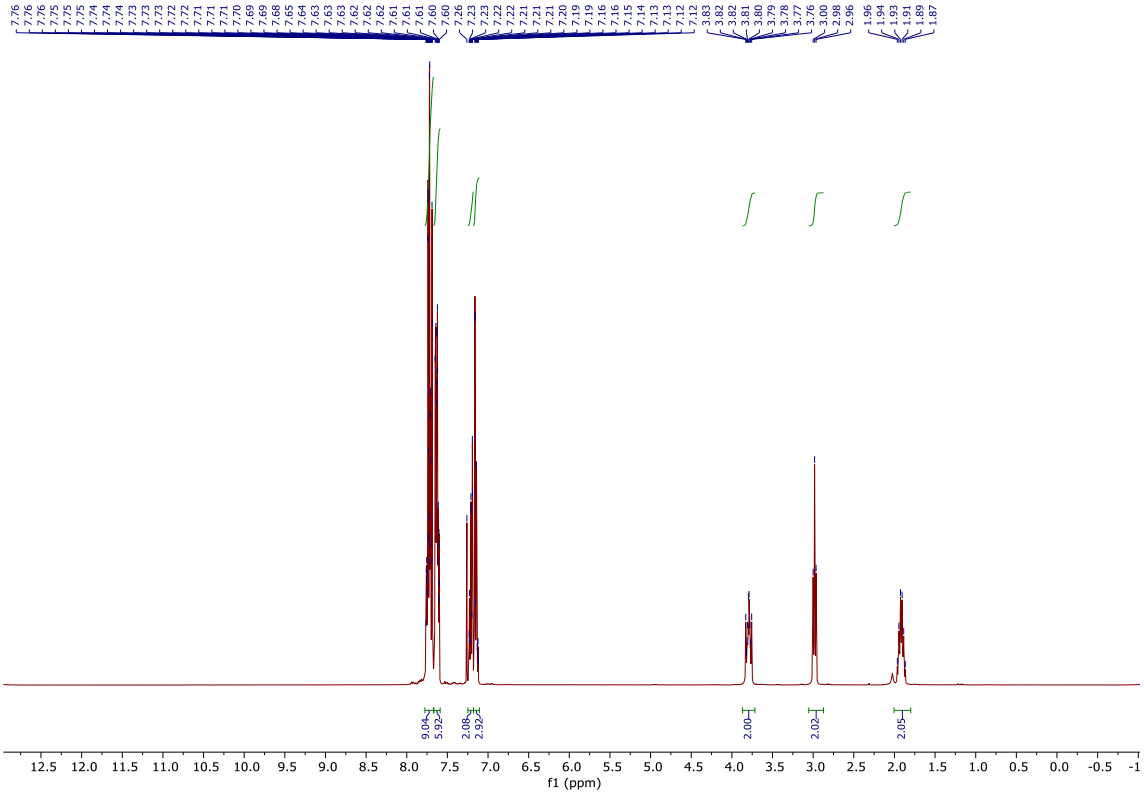
Benzyltriphenylphosphonium iodide (**1a''**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



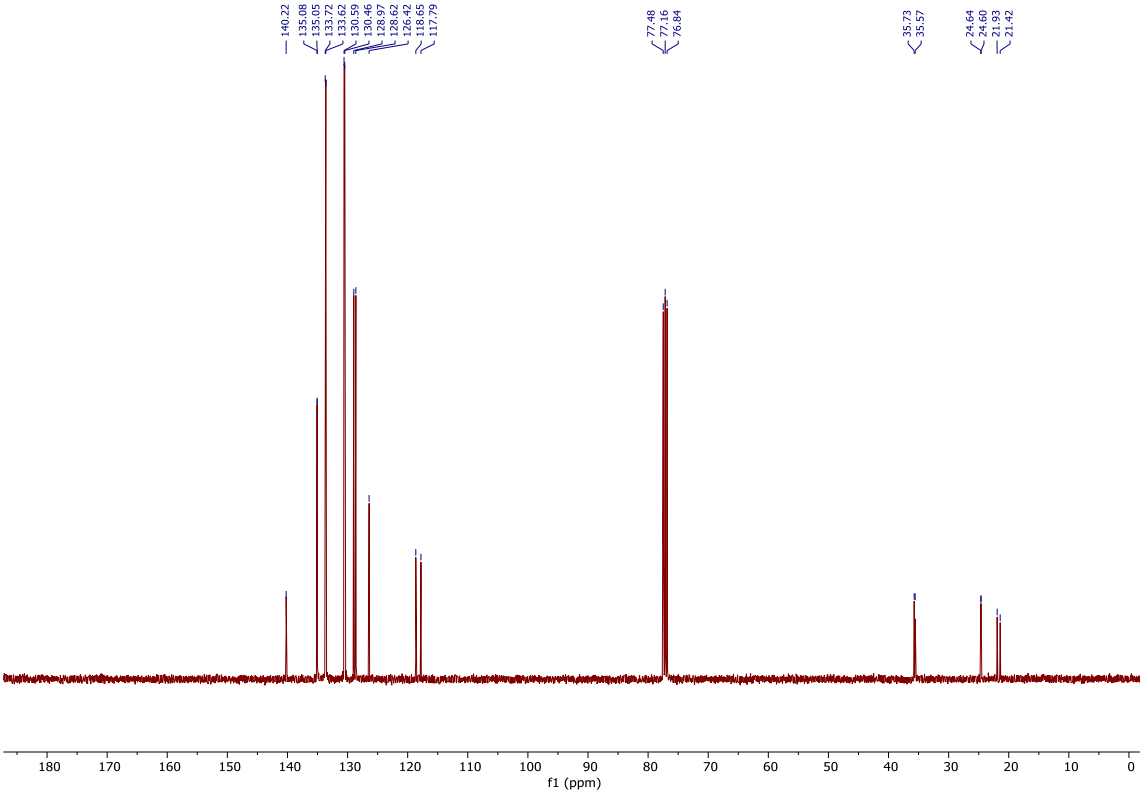
Benzyltriphenylphosphonium iodide (**1a''**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



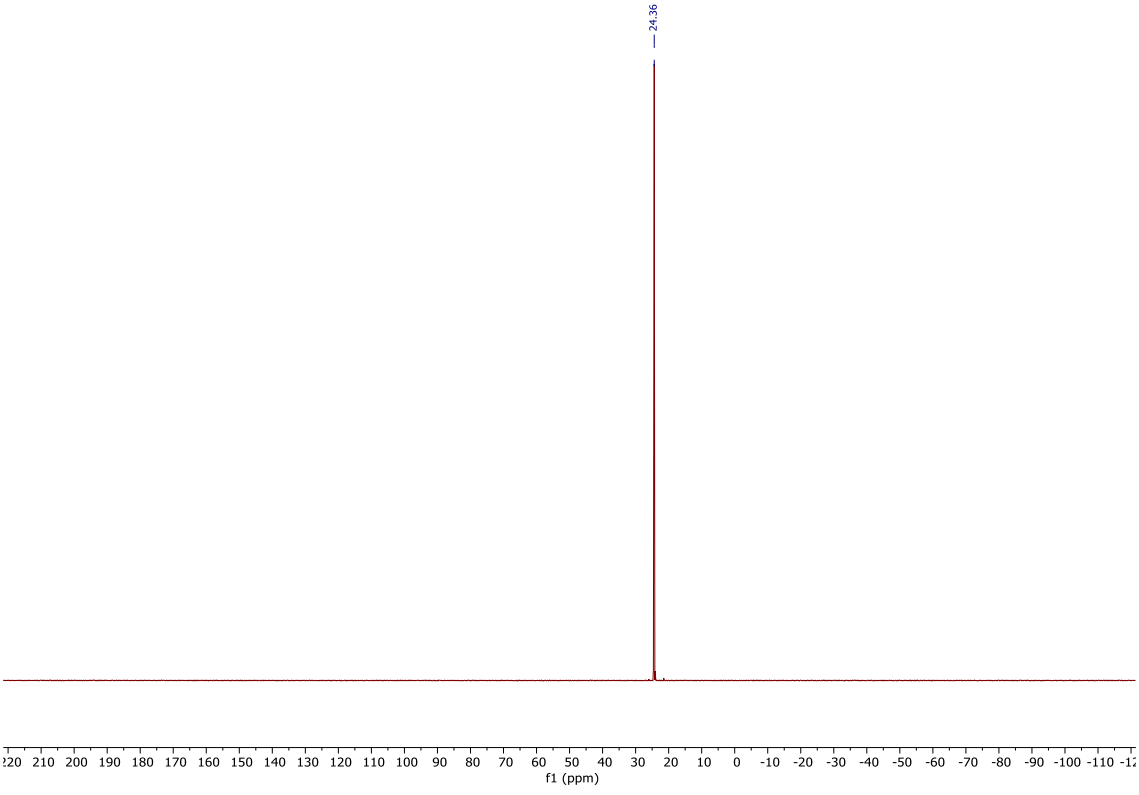
Triphenyl(3-phenylpropyl)phosphonium bromide (**1d**) – ^{1}H NMR spectrum ($CDCl_3$)



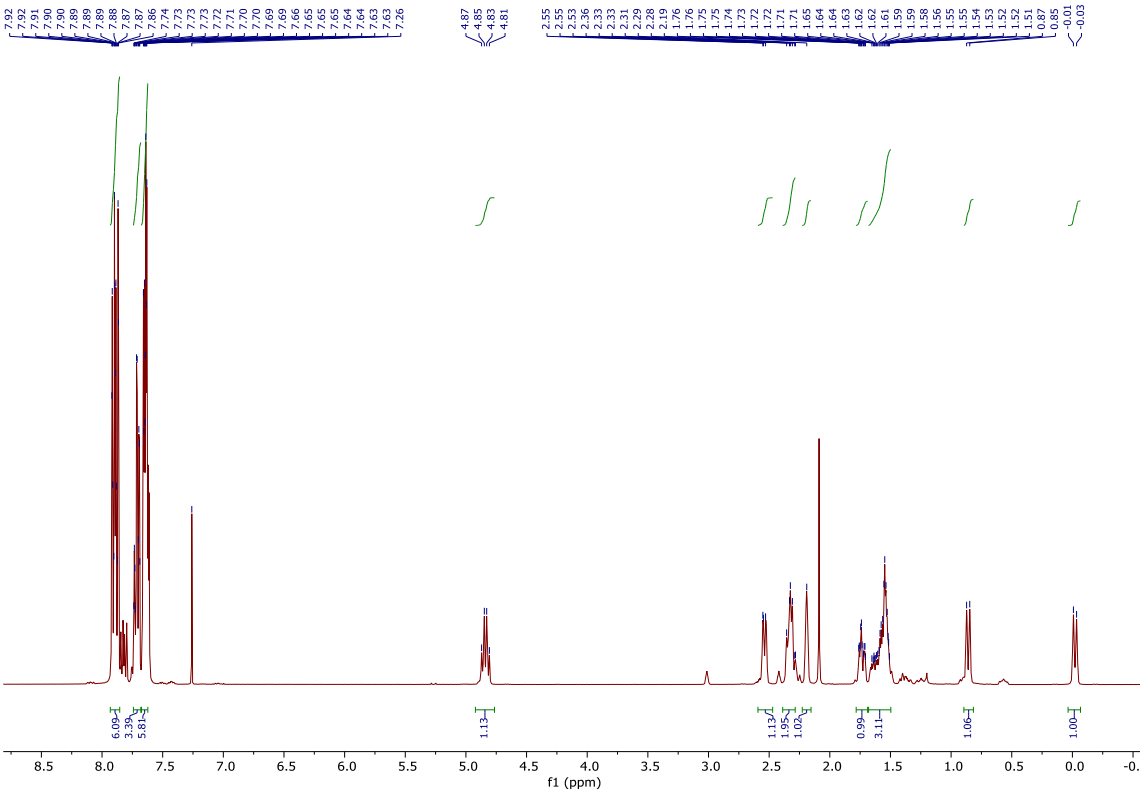
Triphenyl(3-phenylpropyl)phosphonium bromide (**1d**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



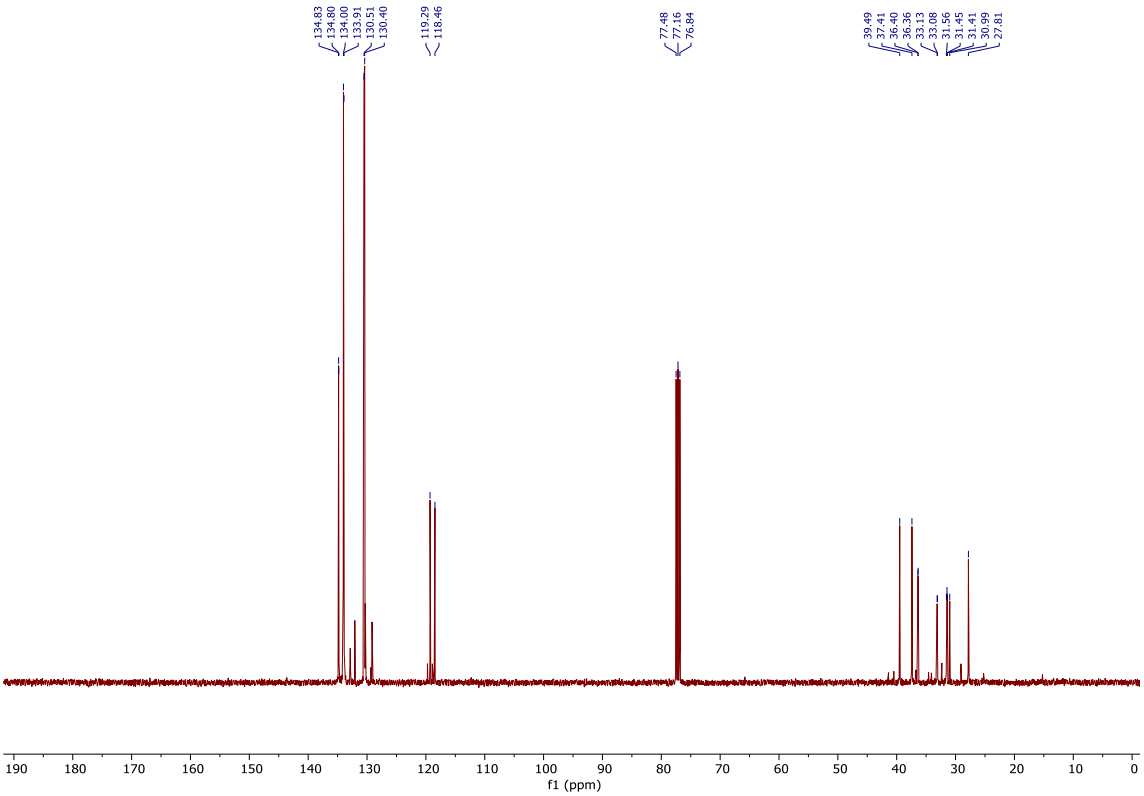
Triphenyl(3-phenylpropyl)phosphonium bromide (**1d**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



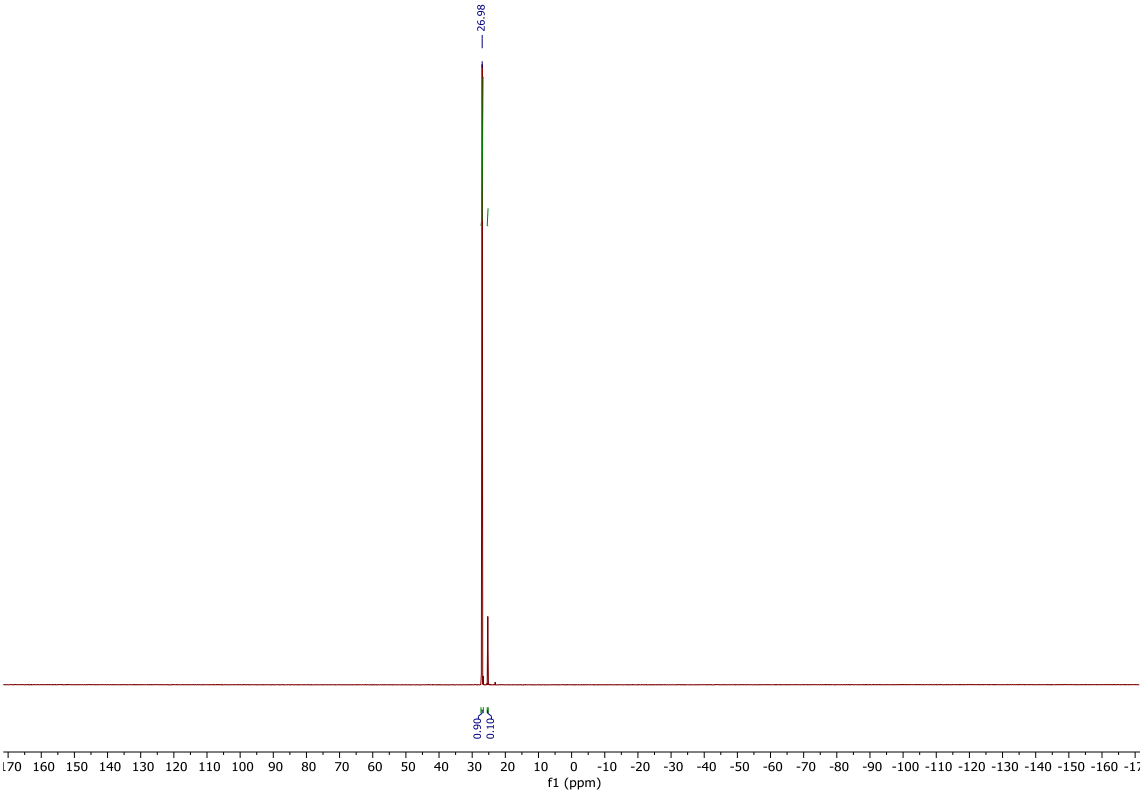
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – ^{1}H NMR spectrum ($CDCl_3$)



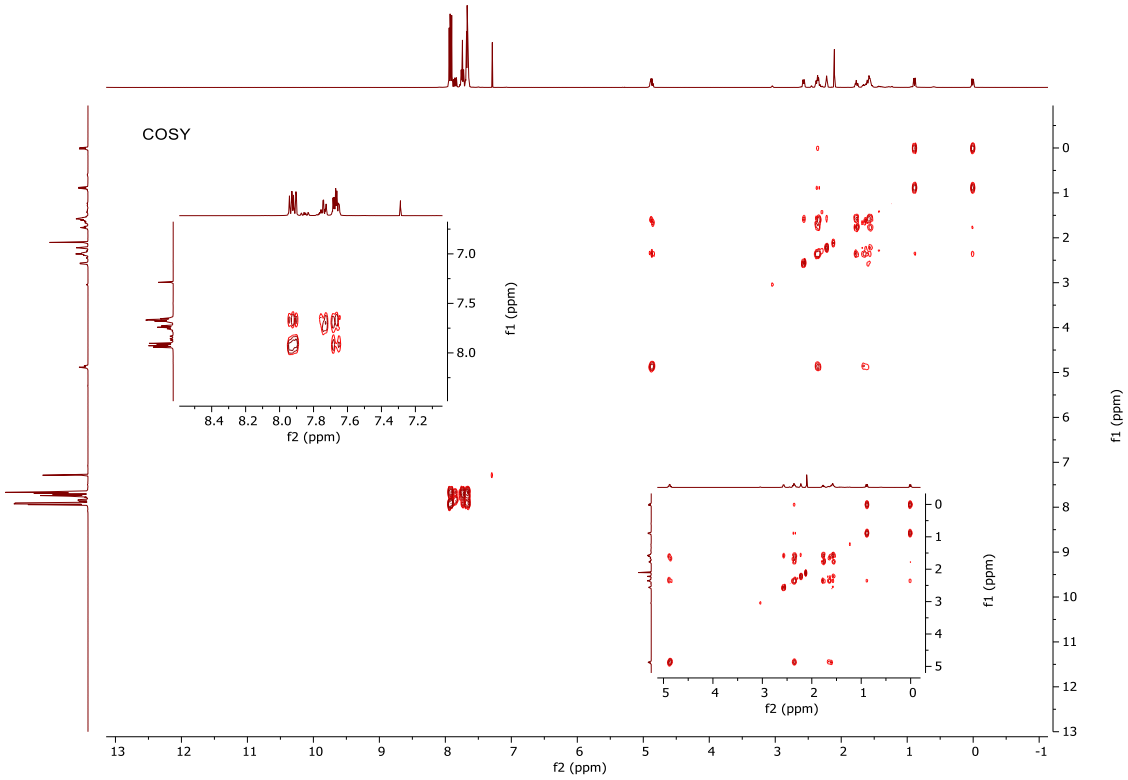
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



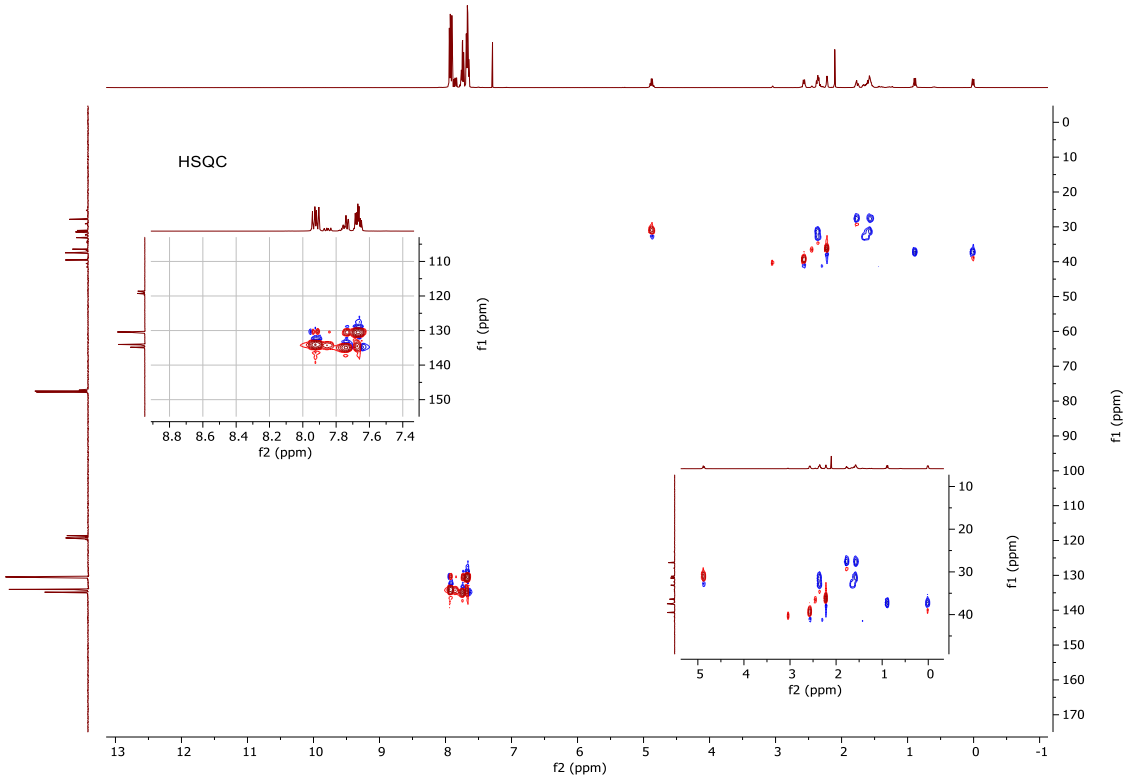
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



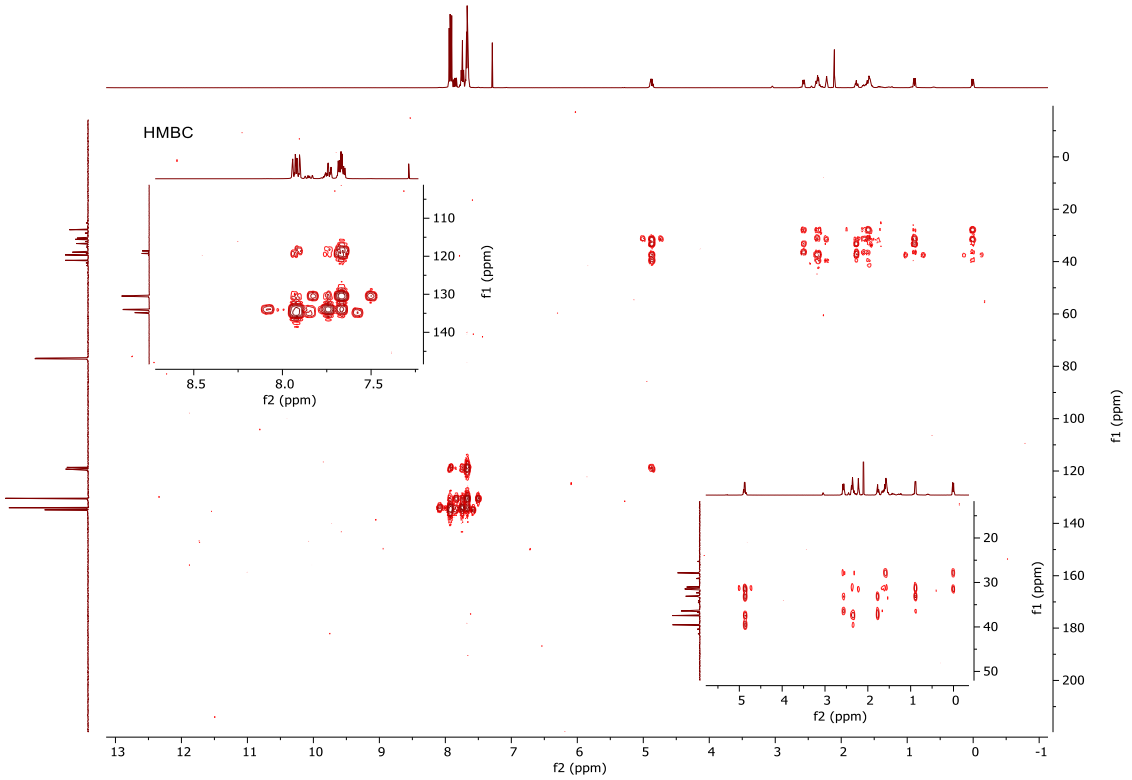
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – COSY NMR spectrum ($CDCl_3$)



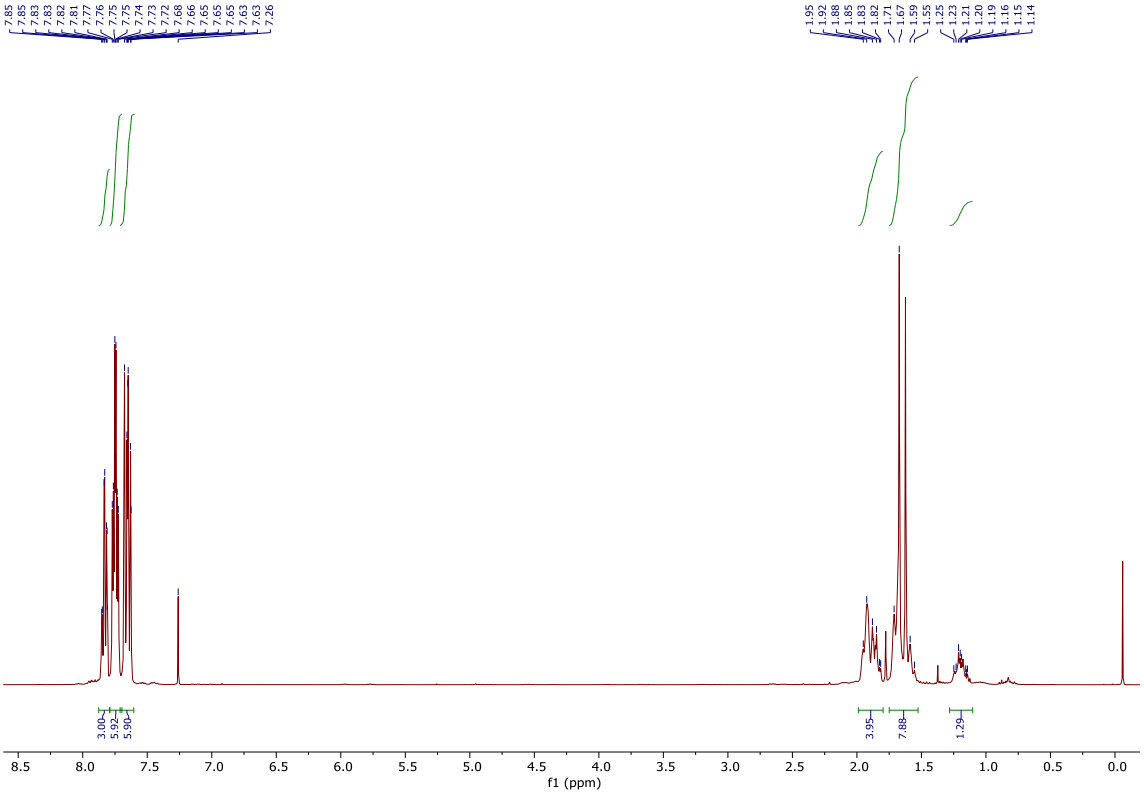
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – HSQC NMR spectrum ($CDCl_3$)



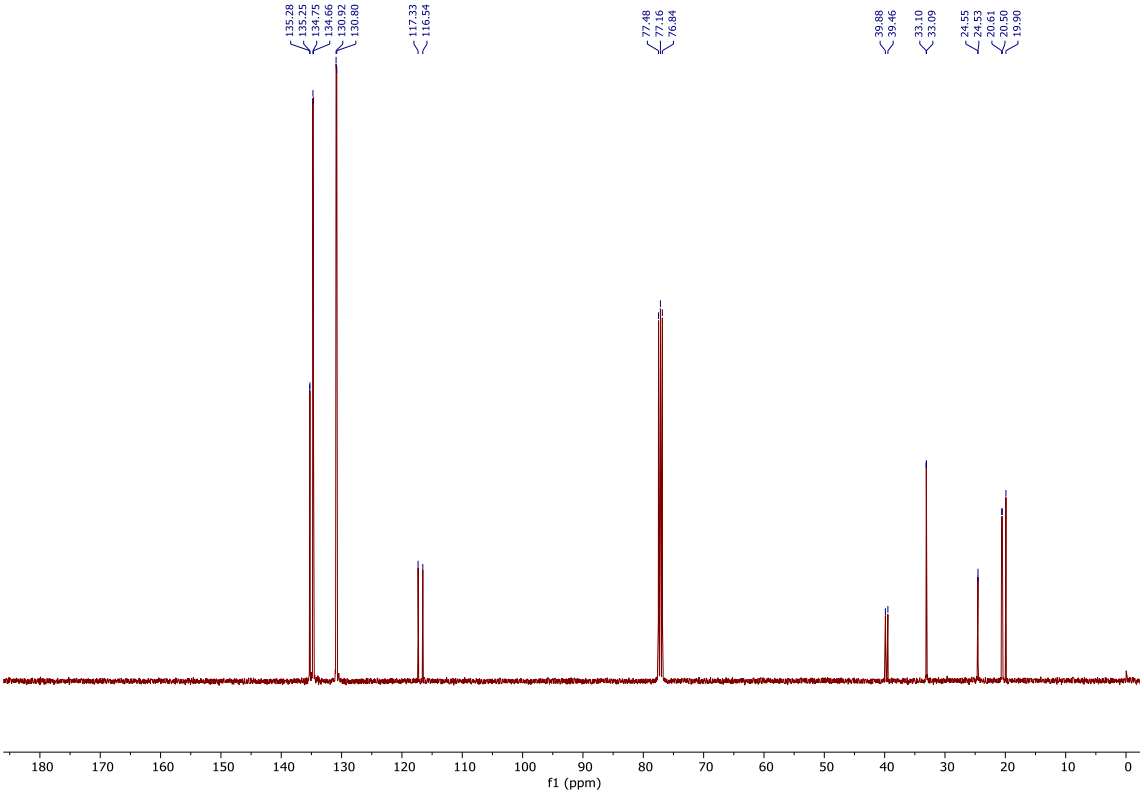
(2-Norbornyl)triphenylphosphonium bromide (**1g**) – HMBC NMR spectrum ($CDCl_3$)



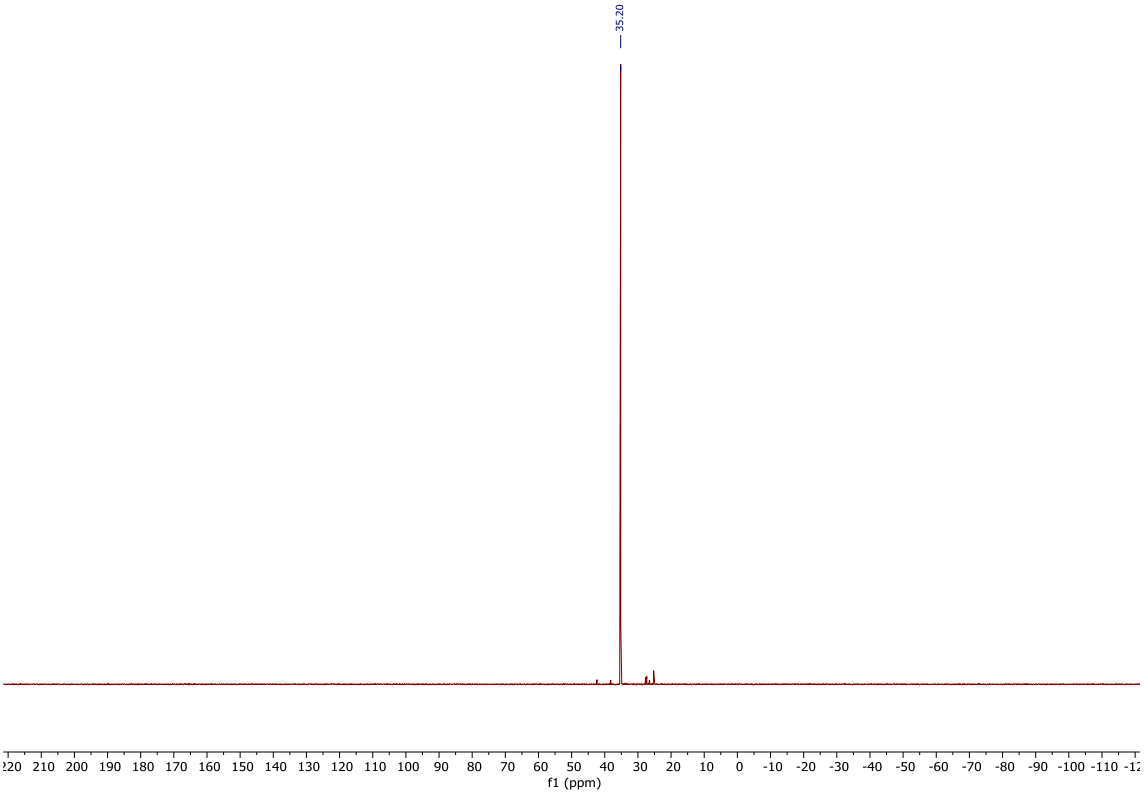
(1-Methylcyclohexyl)triphenylphosphonium iodide (**1h**) – ^{1}H NMR spectrum ($CDCl_3$)



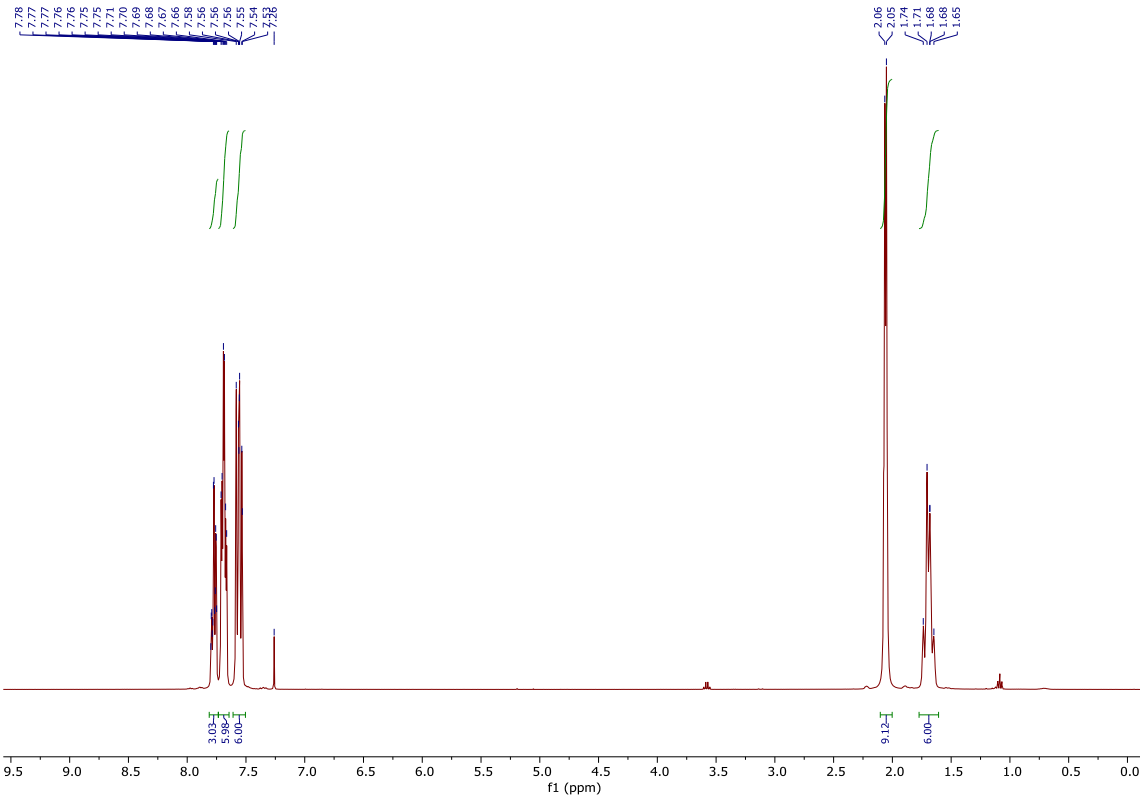
(1-Methylcyclohexyl)triphenylphosphonium iodide (**1h**) – ^{13}C{^{1}H} NMR spectrum ($CDCl_3$)



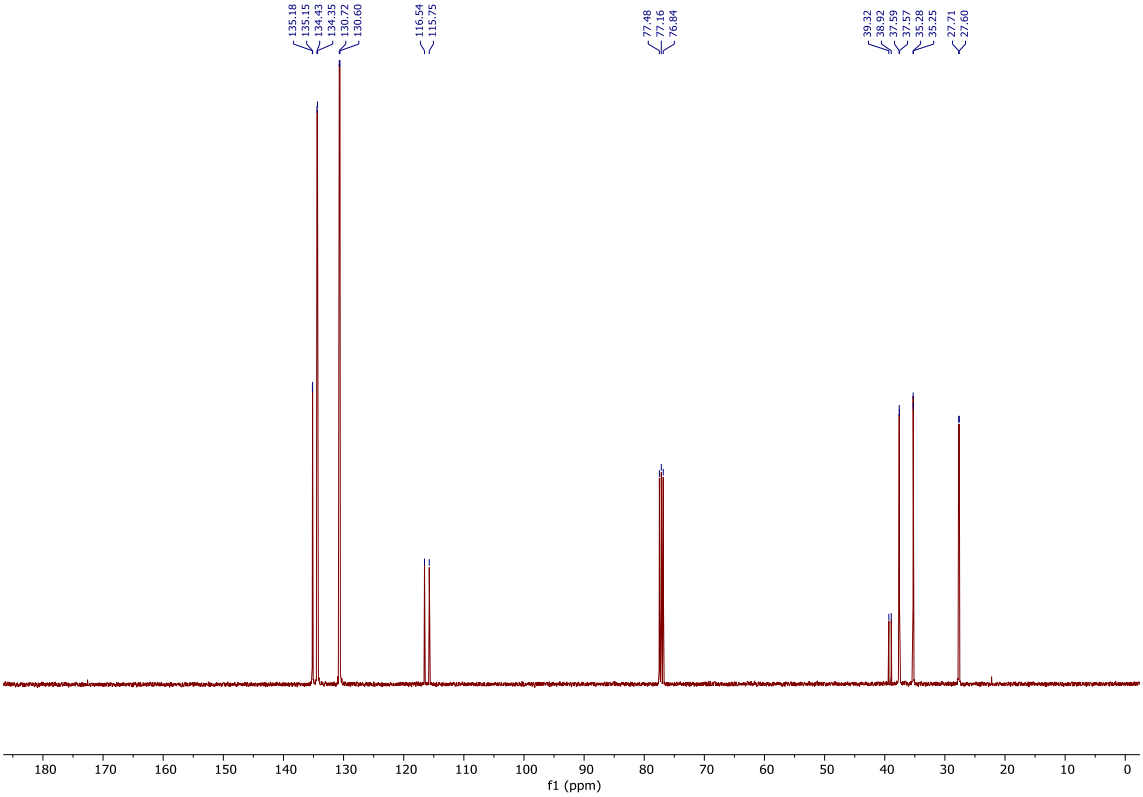
(1-Methylcyclohexyl)triphenylphosphonium iodide (**1h**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



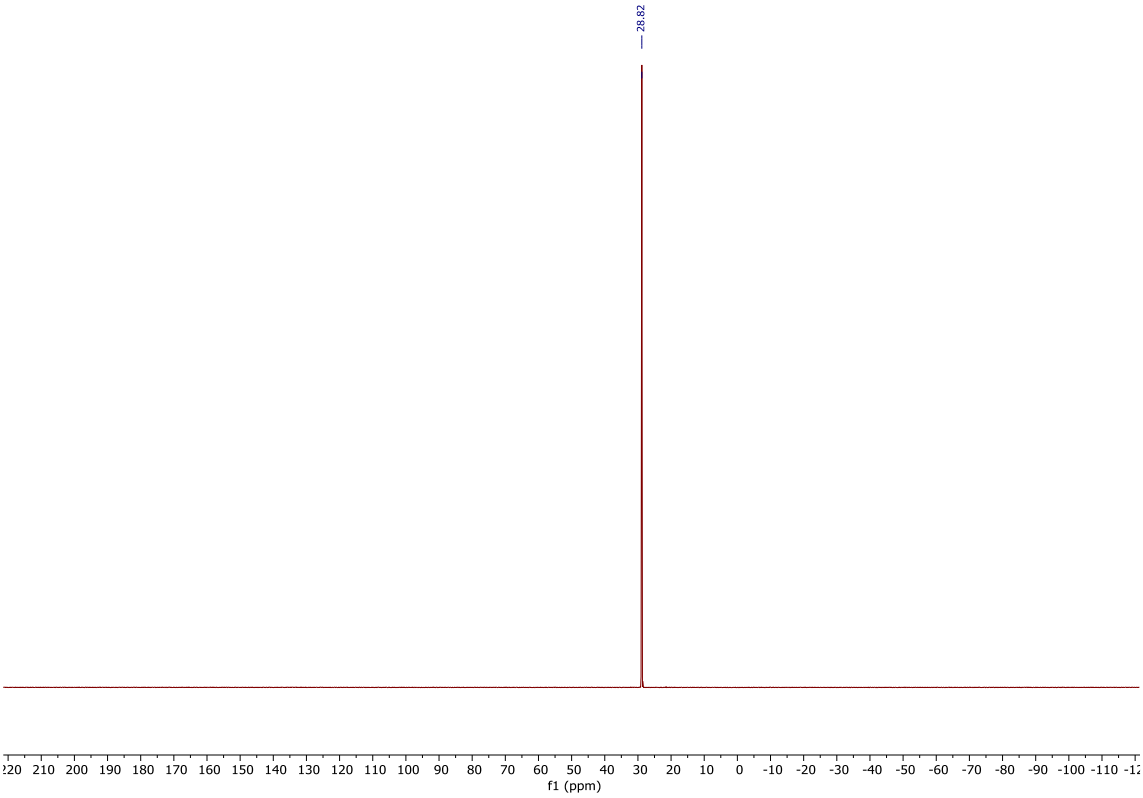
Adamant-1-yltriphenylphosphonium bromide (**1i**) – ^{1}H NMR spectrum ($CDCl_3$)



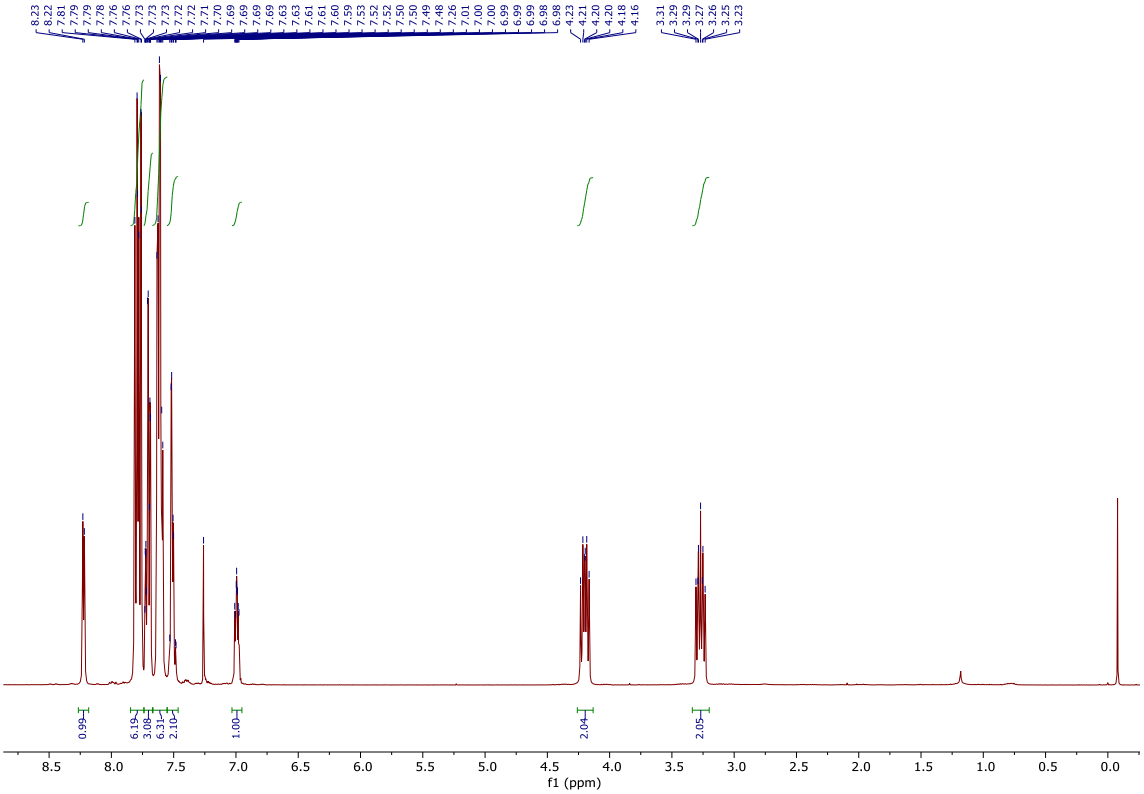
Adamant-1-yltriphenylphosphonium bromide (**1i**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



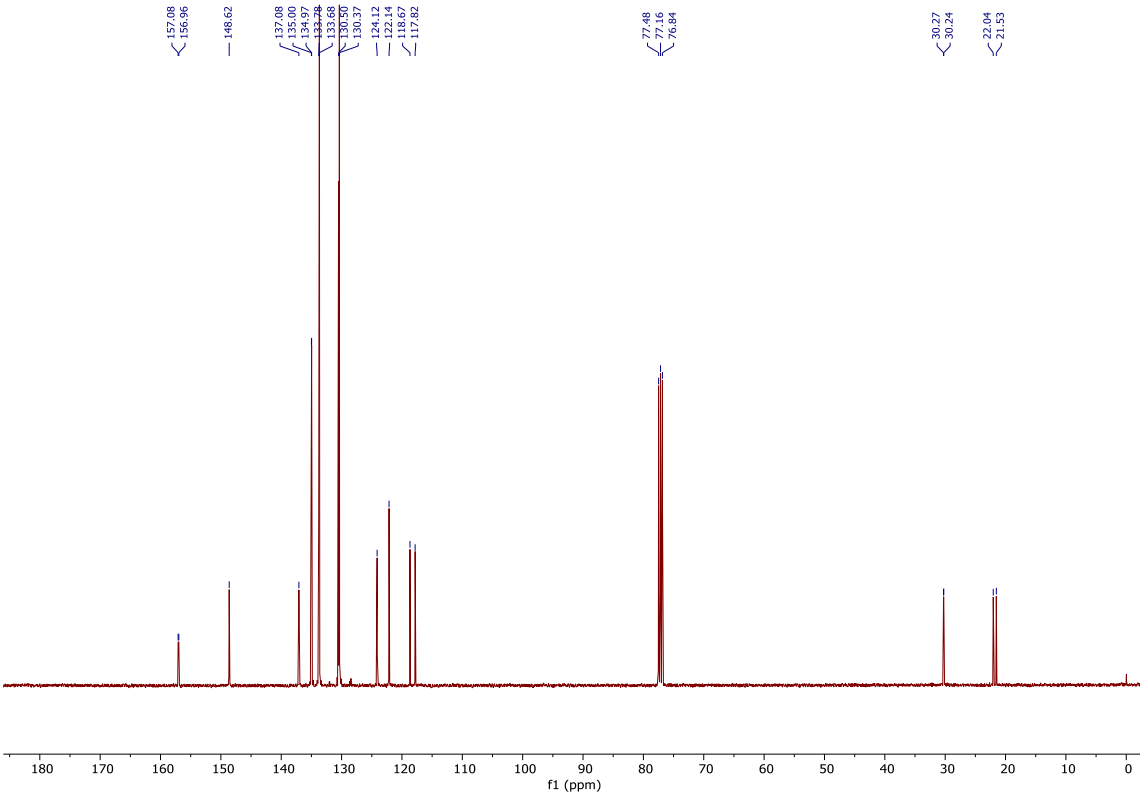
Adamant-1-yltriphenylphosphonium bromide (**1i**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



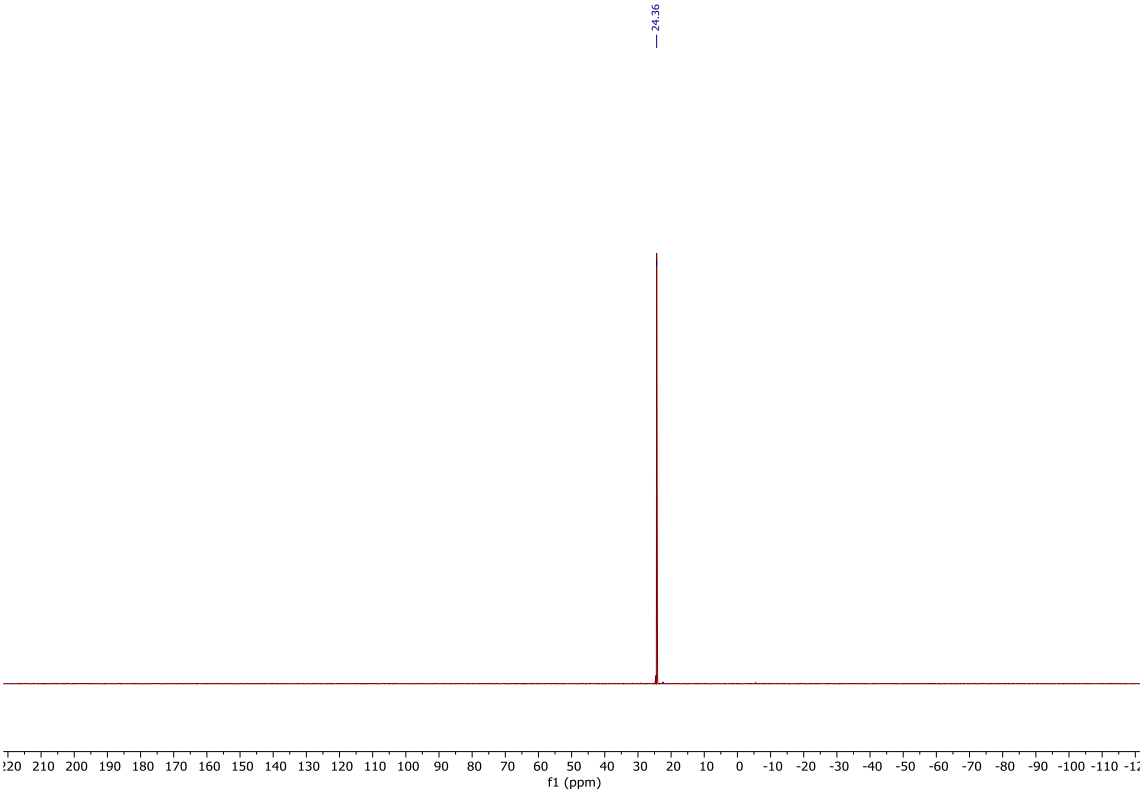
Triphenyl(2-(pyridin-2-yl)ethyl)phosphonium chloride (**1j**) – ^{1}H NMR spectrum ($CDCl_3$)



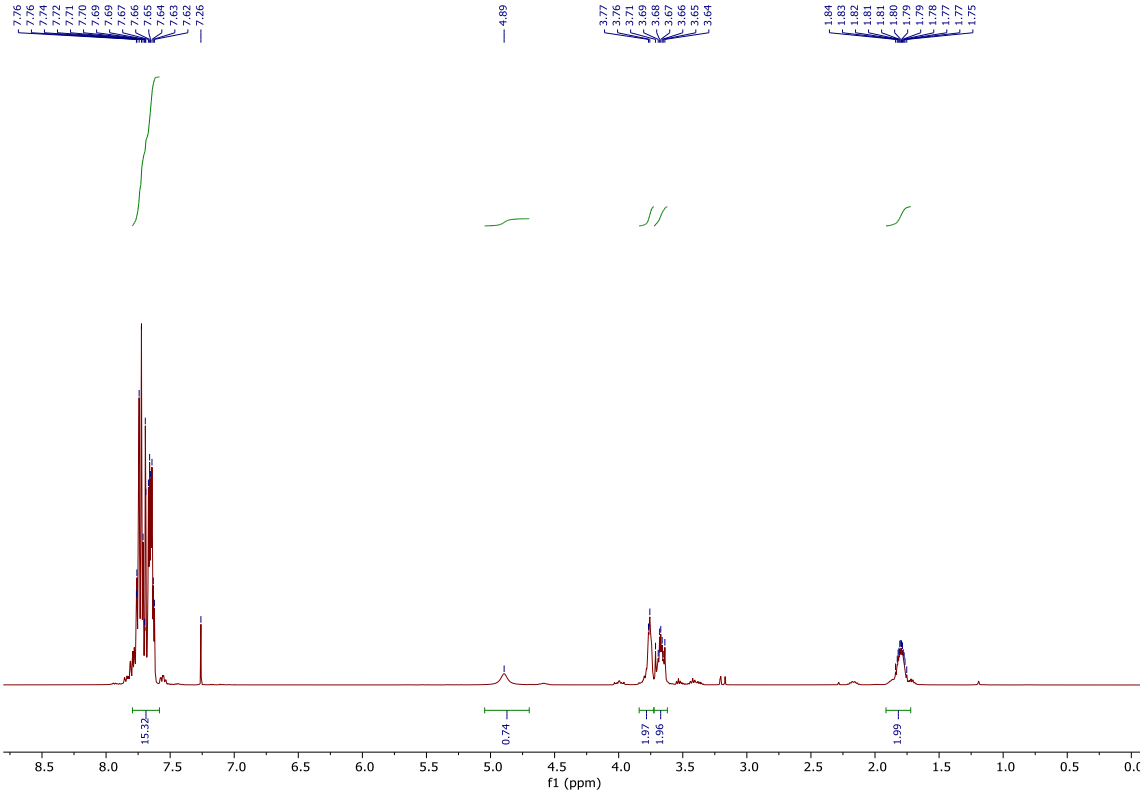
Triphenyl(2-(pyridin-2-yl)ethyl)phosphonium chloride (**1j**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



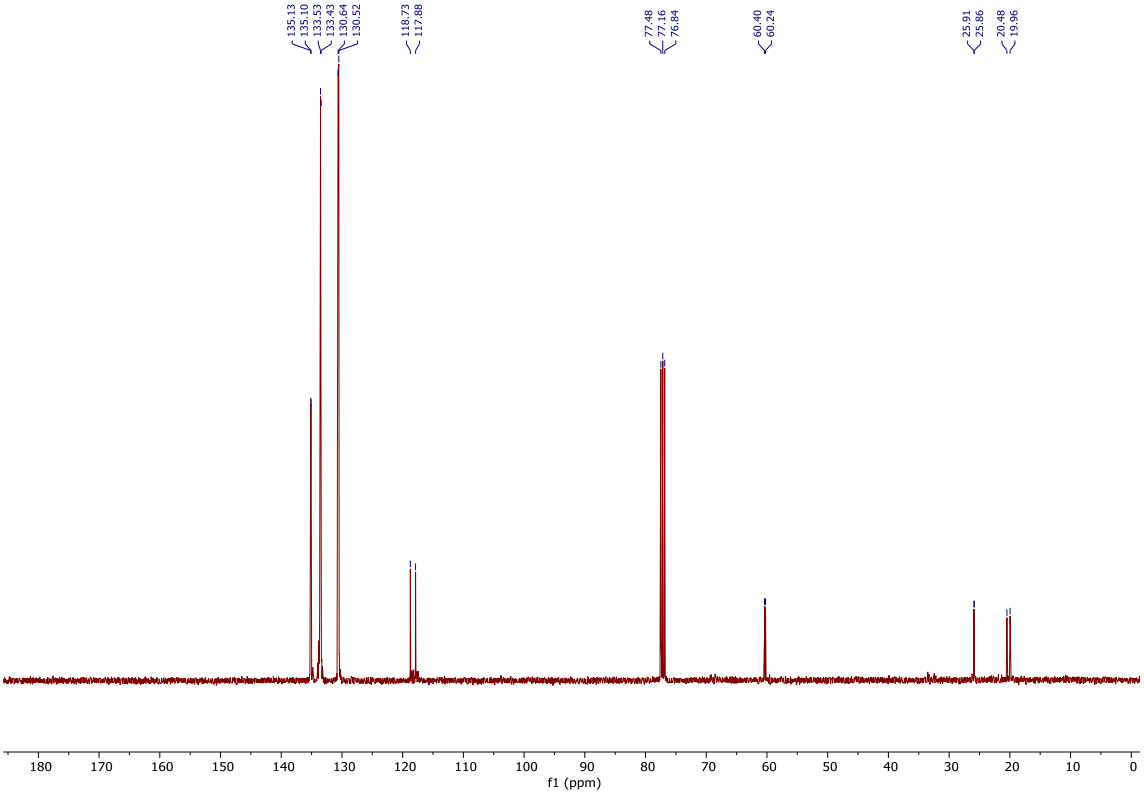
Triphenyl(2-(pyridin-2-yl)ethyl)phosphonium chloride (**1j**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



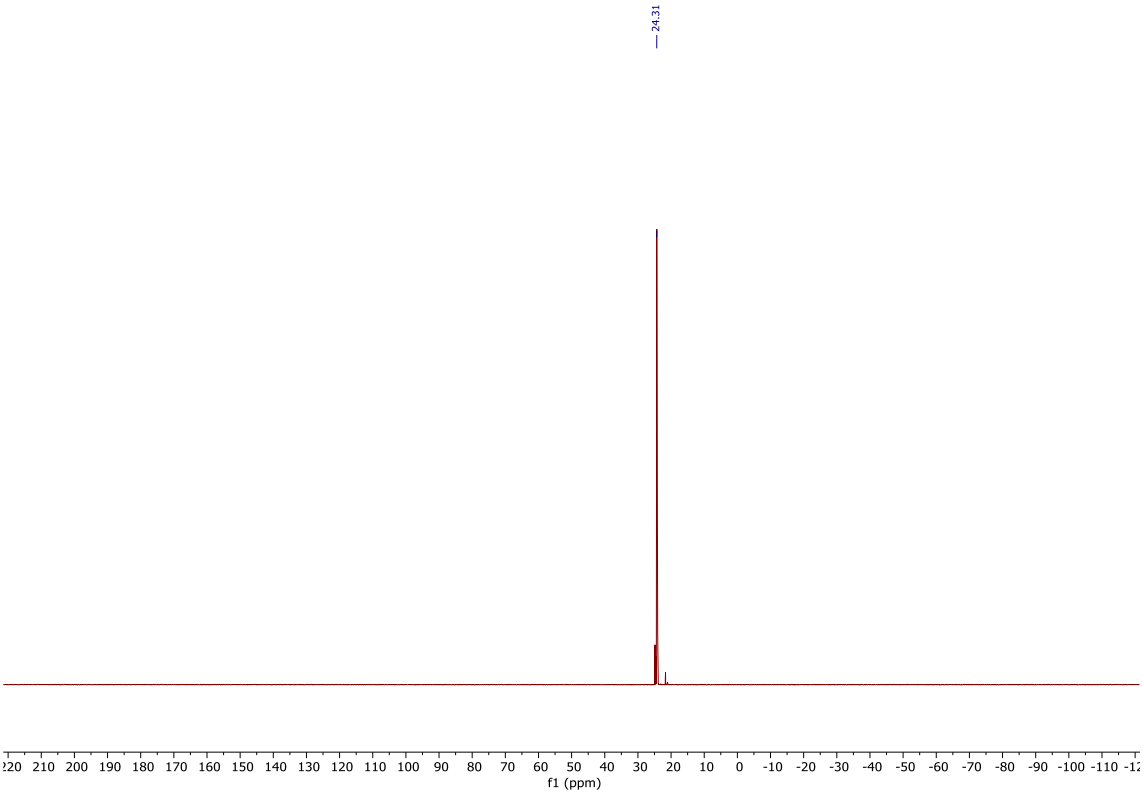
(3-Hydroxypropyl)triphenylphosphonium bromide (**1k**) – ^{1}H NMR spectrum ($CDCl_3$)



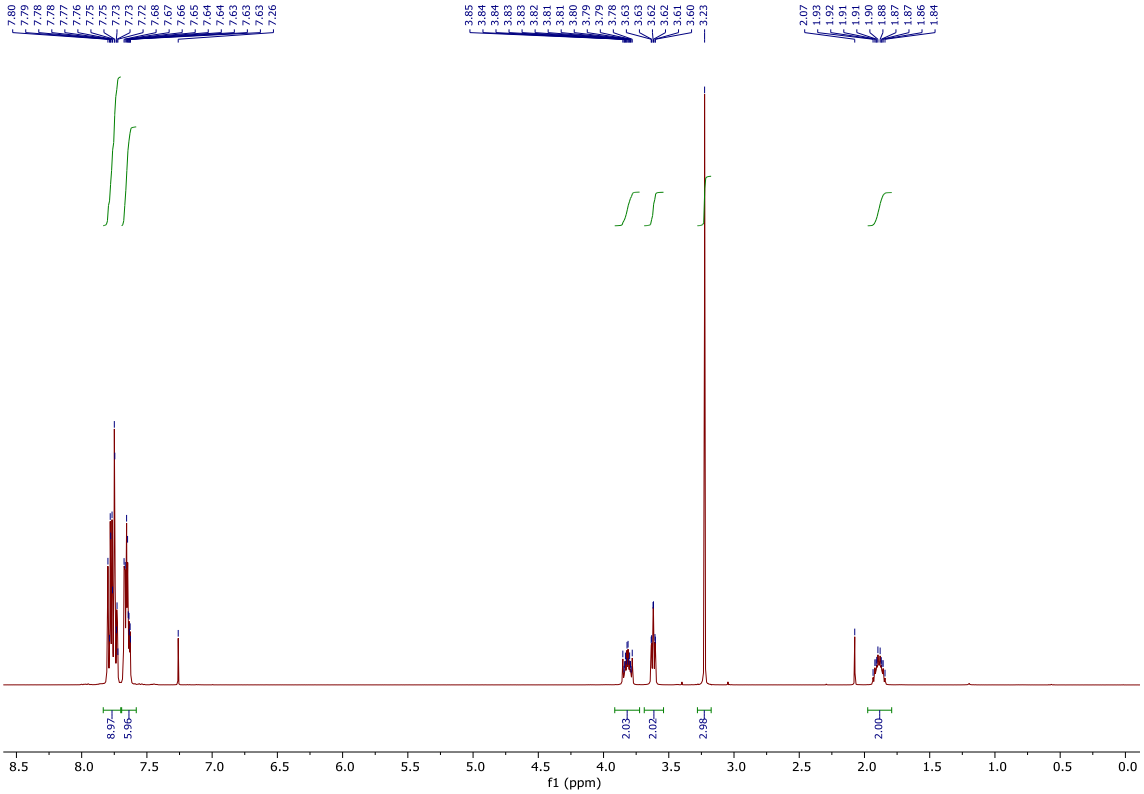
(3-Hydroxypropyl)triphenylphosphonium bromide (**1k**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



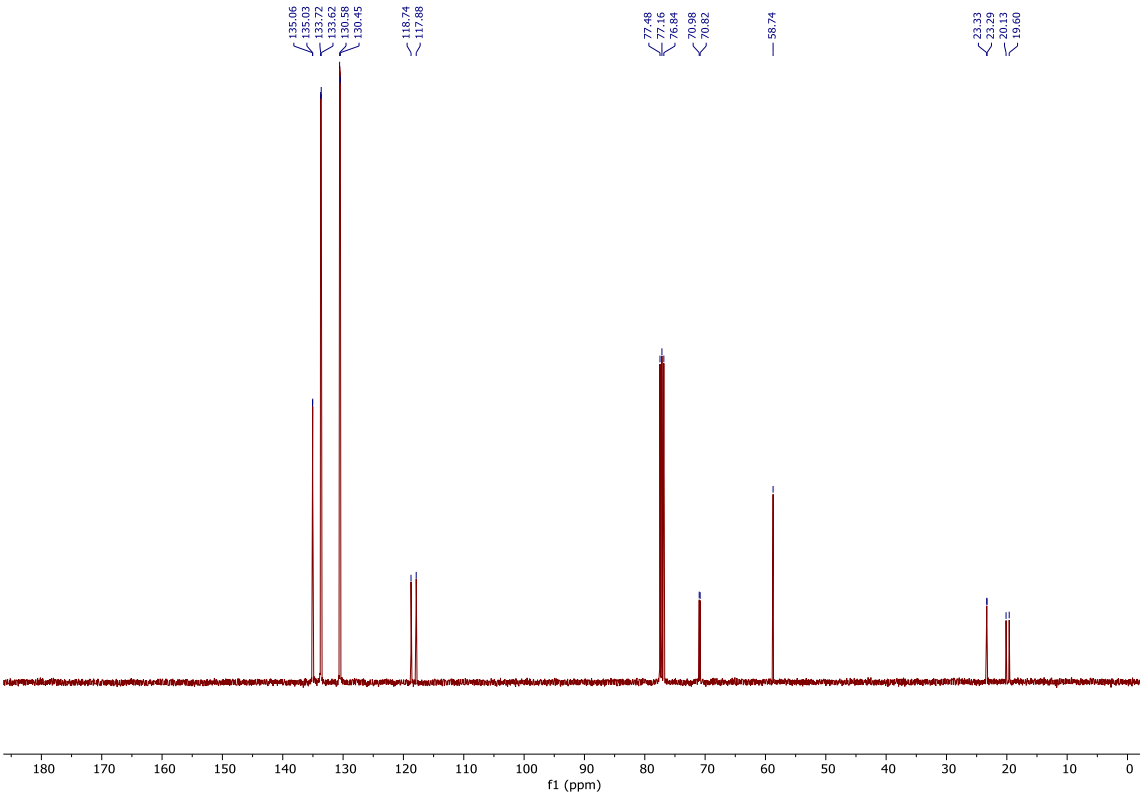
(3-Hydroxypropyl)triphenylphosphonium bromide (**1k**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



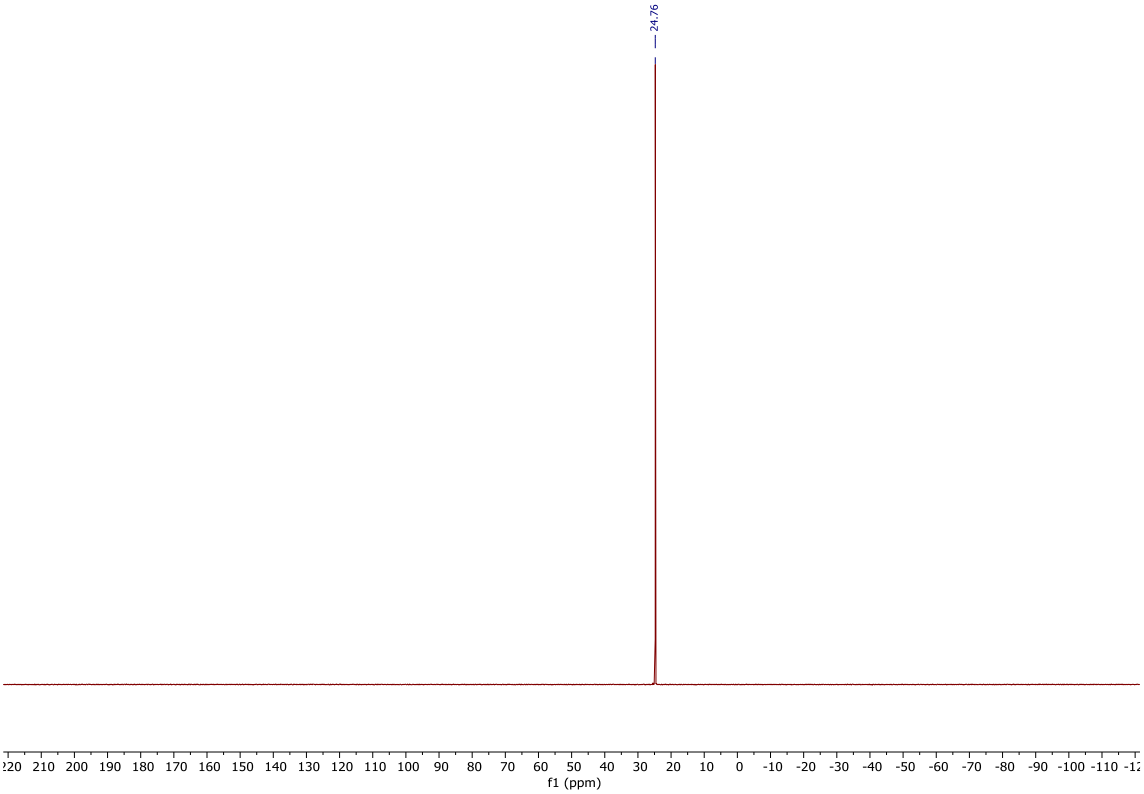
(3-Methoxypropyl)triphenylphosphonium bromide (**1l**) – ^{1}H NMR spectrum ($CDCl_3$)



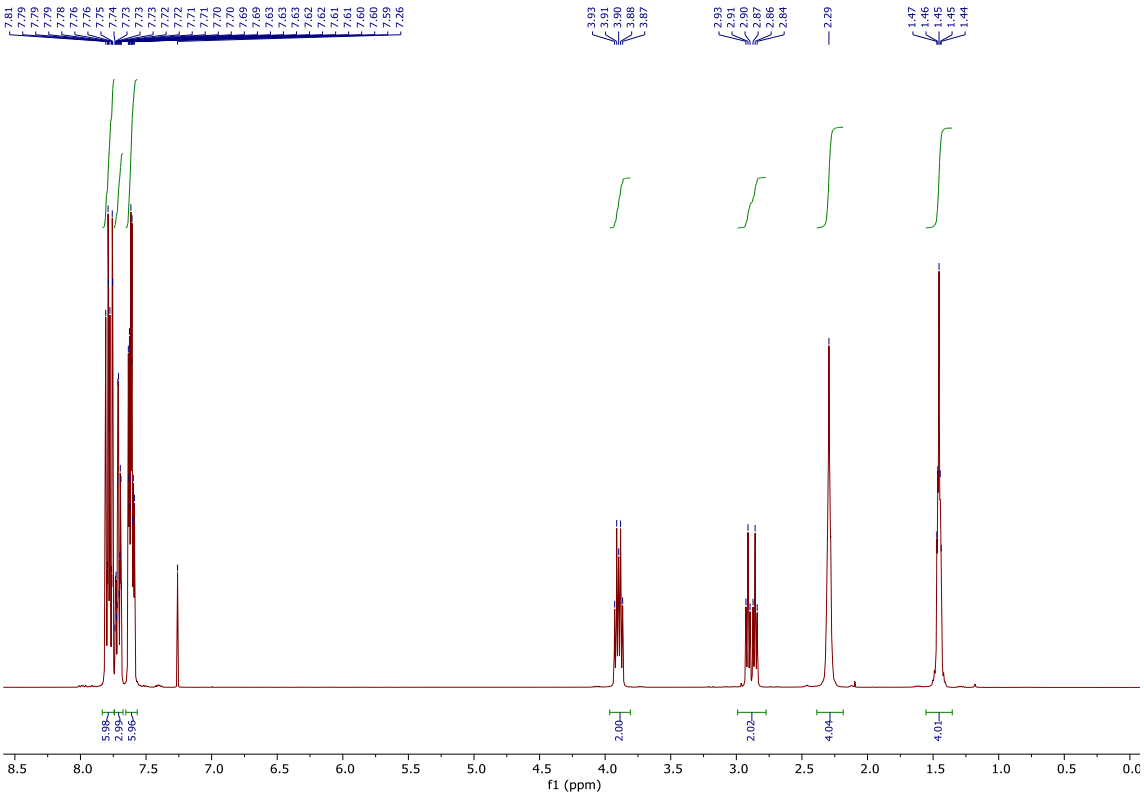
(3-Methoxypropyl)triphenylphosphonium bromide (**1l**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



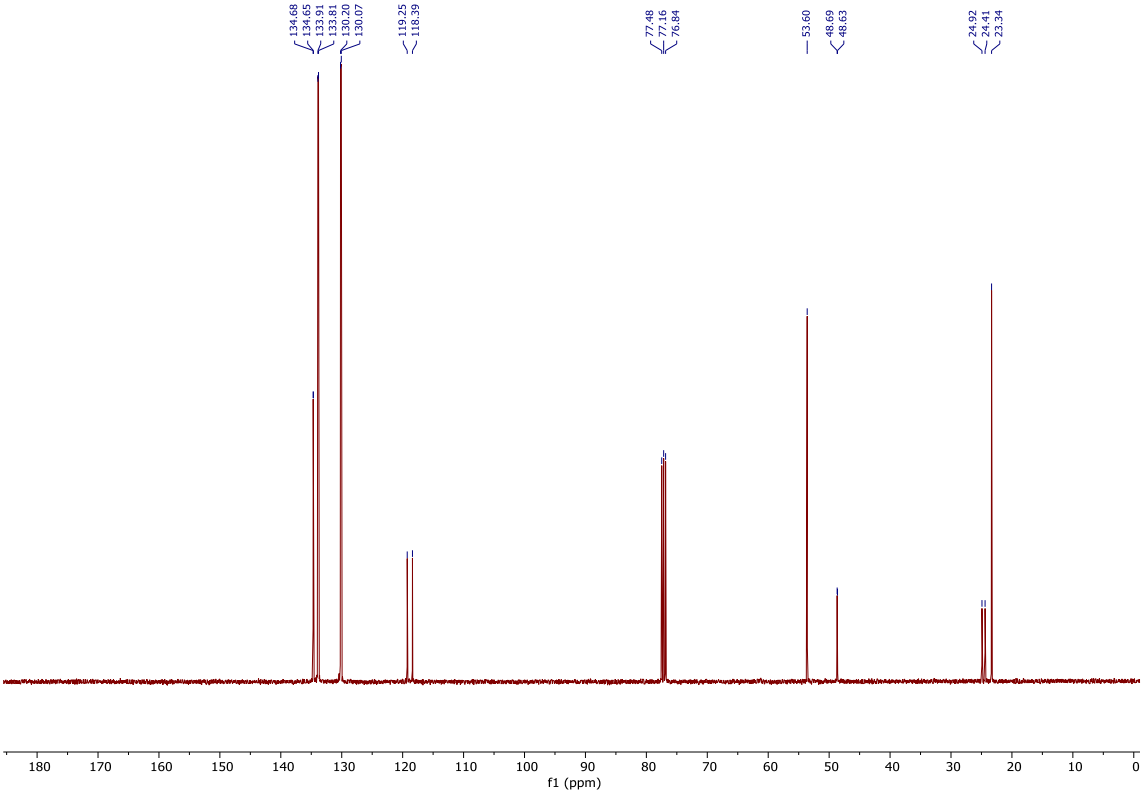
(3-Methoxypropyl)triphenylphosphonium bromide (**1l**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



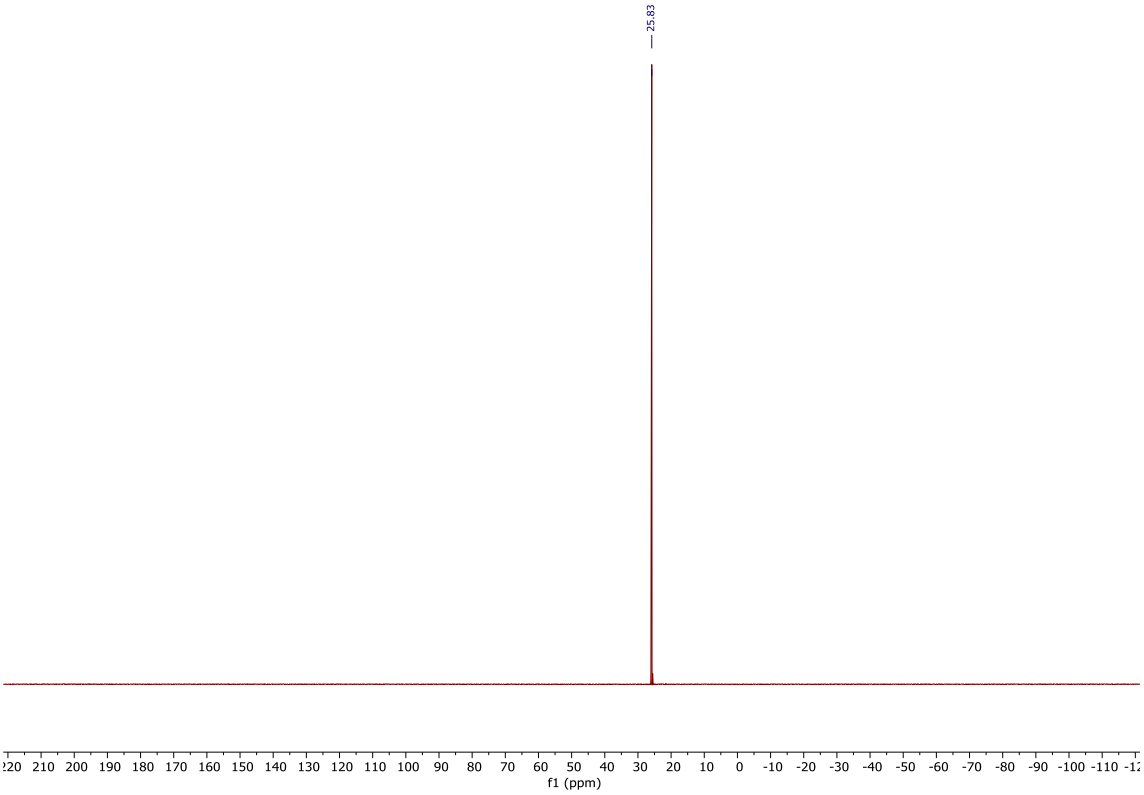
Triphenyl(2-(pyrrolidin-1-yl)ethyl)phosphonium bromide (**1m**) – ^{1}H NMR spectrum ($CDCl_3$)



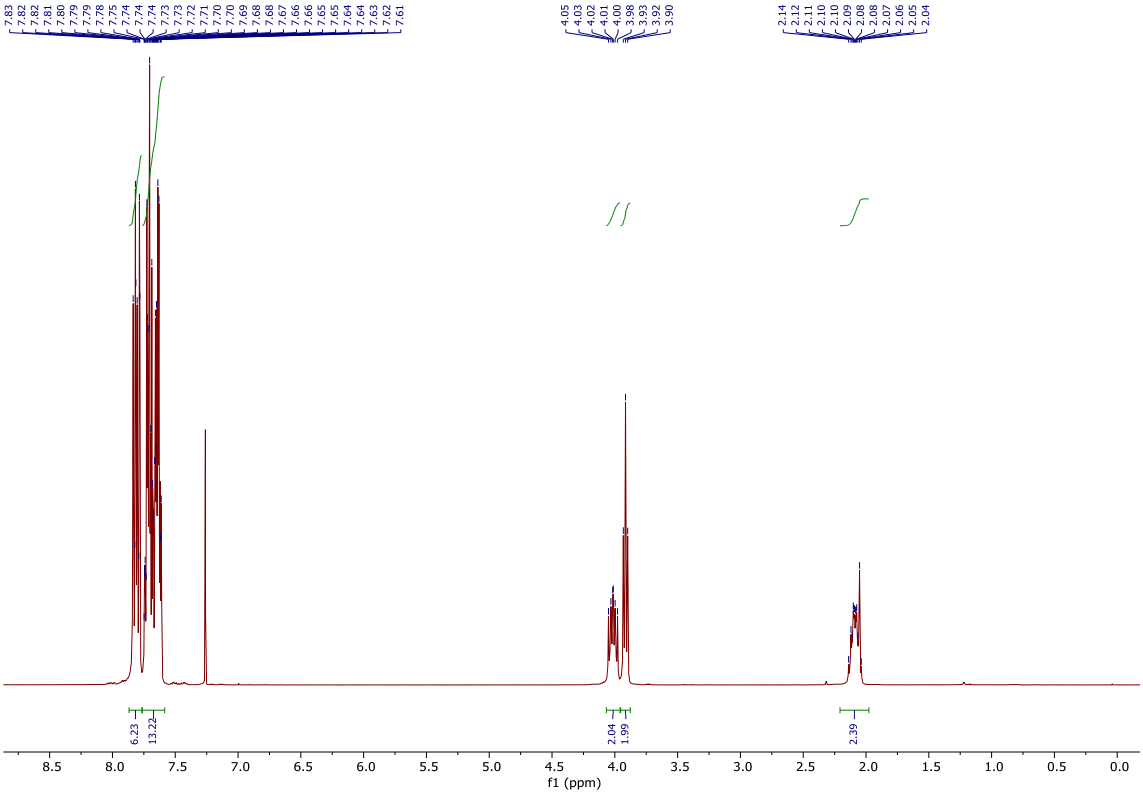
Triphenyl(2-(pyrrolidin-1-yl)ethyl)phosphonium bromide (**1m**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



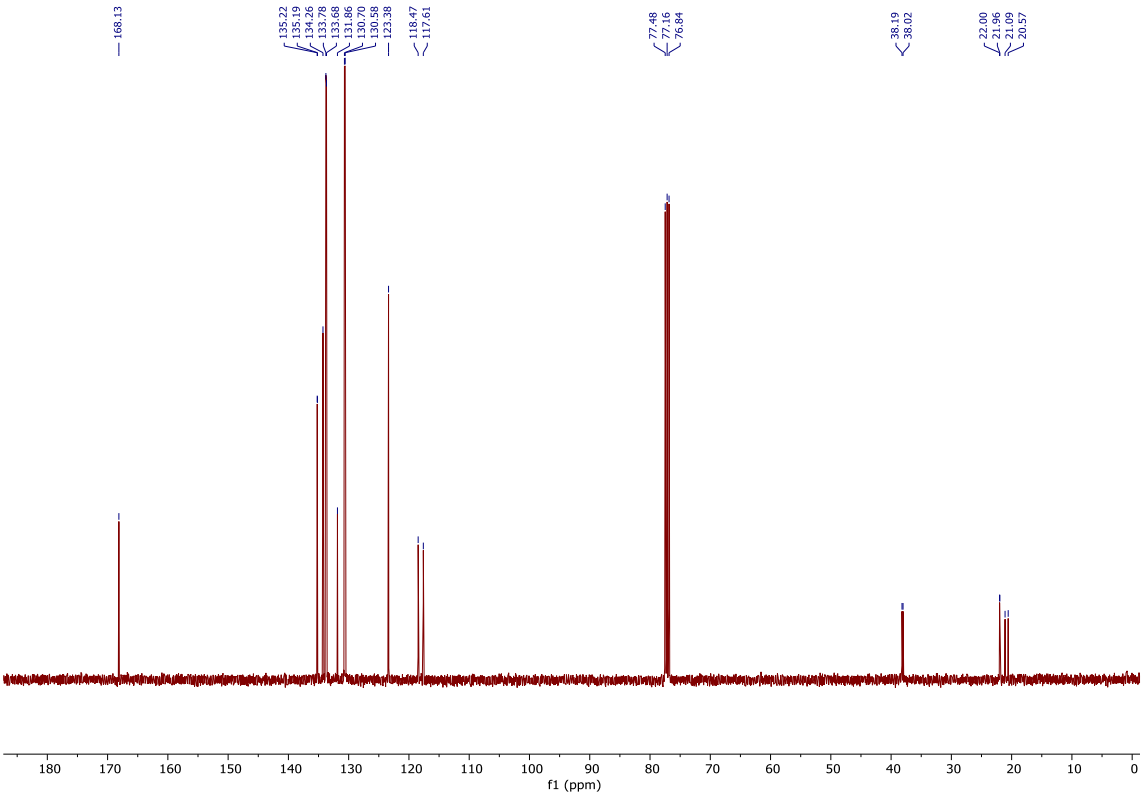
Triphenyl(2-(pyrrolidin-1-yl)ethyl)phosphonium bromide (**1m**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



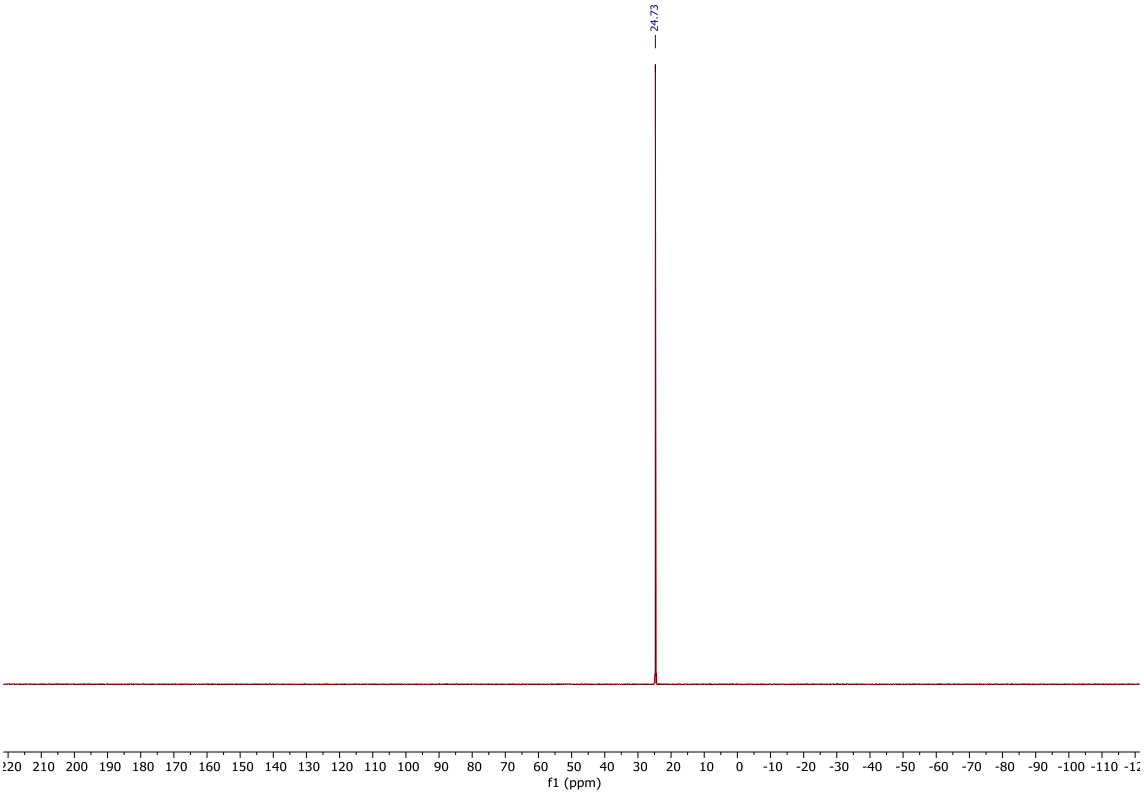
(3-Phthaloylpropyl)triphenylphosphonium bromide (**1n**) – ^{1}H NMR spectrum ($CDCl_3$)



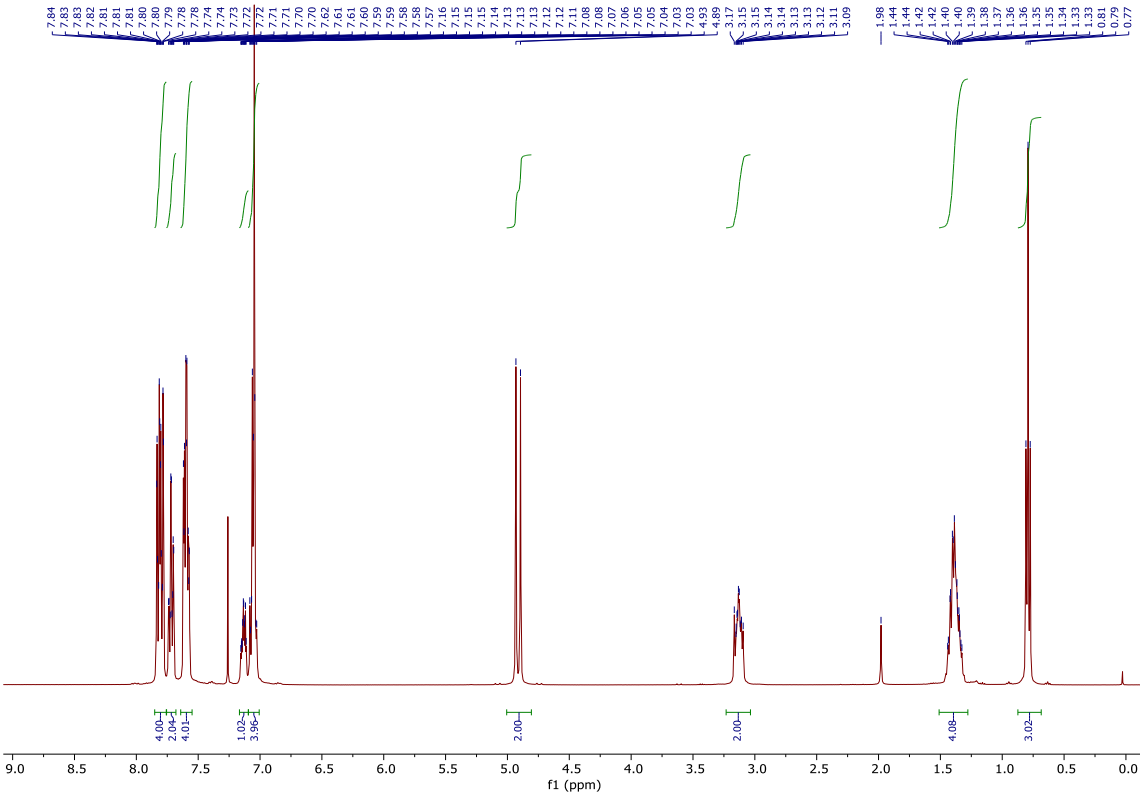
(3-Phthaloylpropyl)triphenylphosphonium bromide (**1n**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



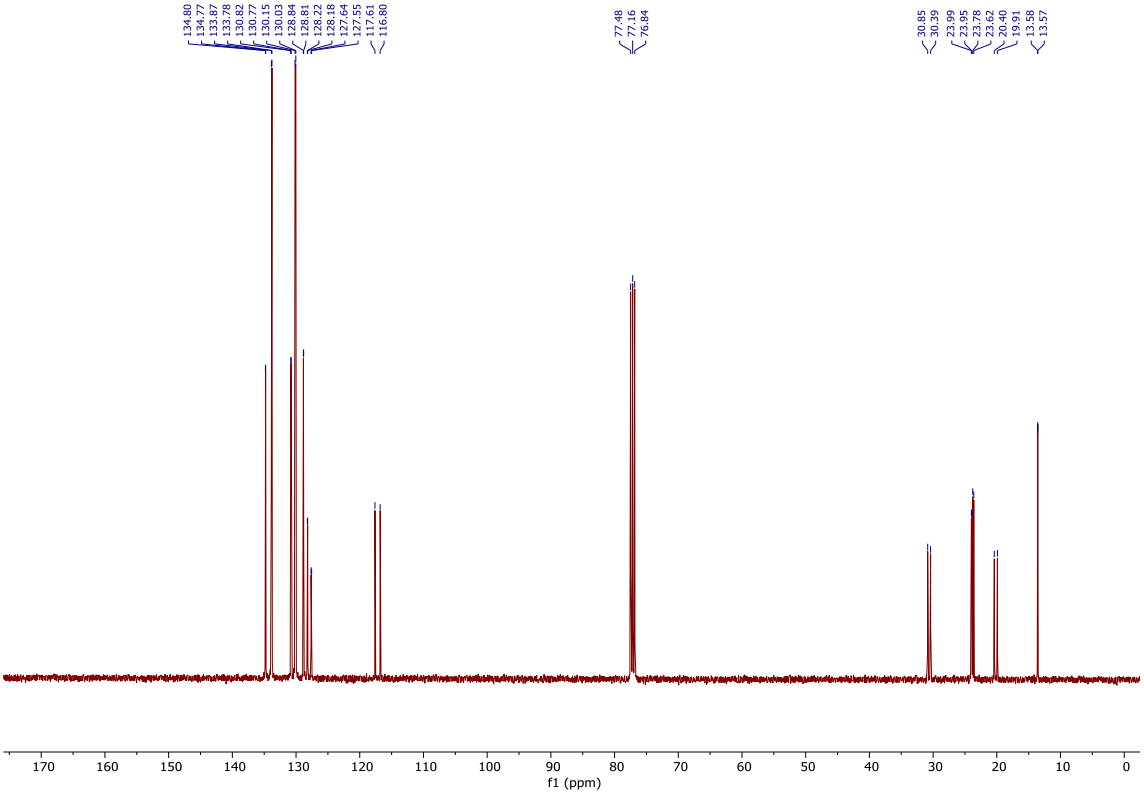
(3-Phthaloylpropyl)triphenylphosphonium bromide (**1n**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



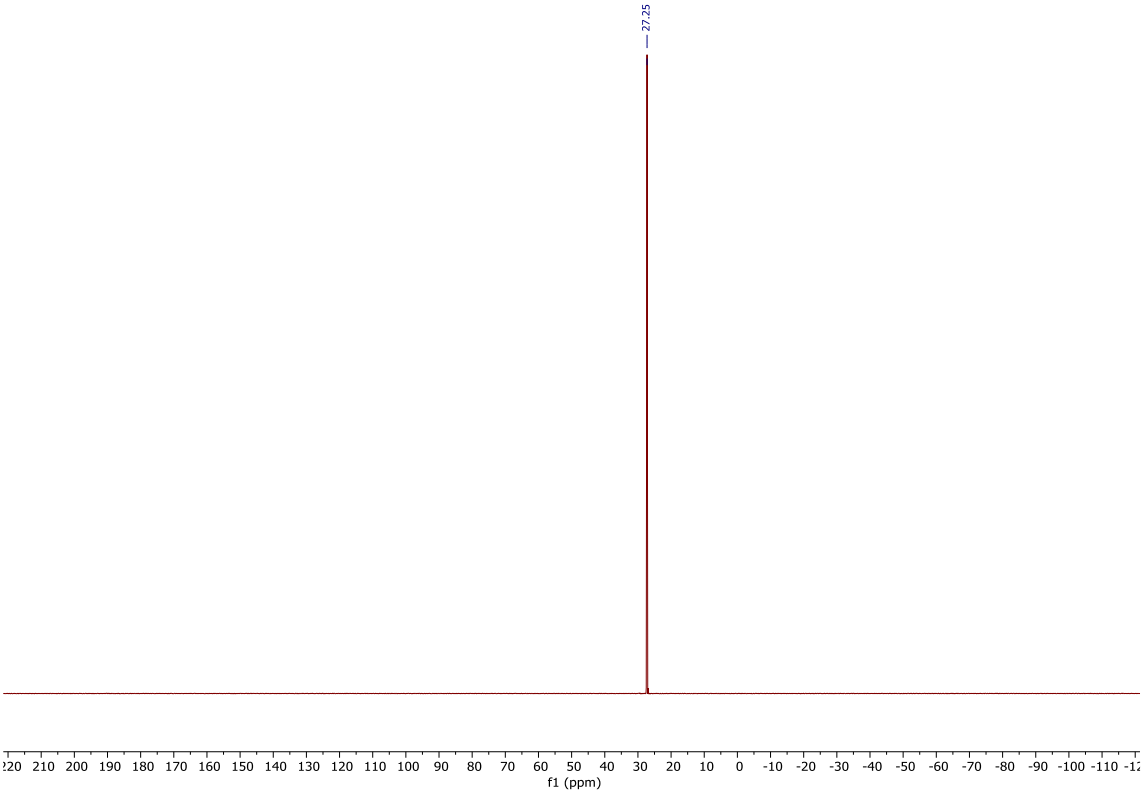
Benzylbutyldiphenylphosphonium bromide (**1o**) – ^{1}H NMR spectrum ($CDCl_3$)



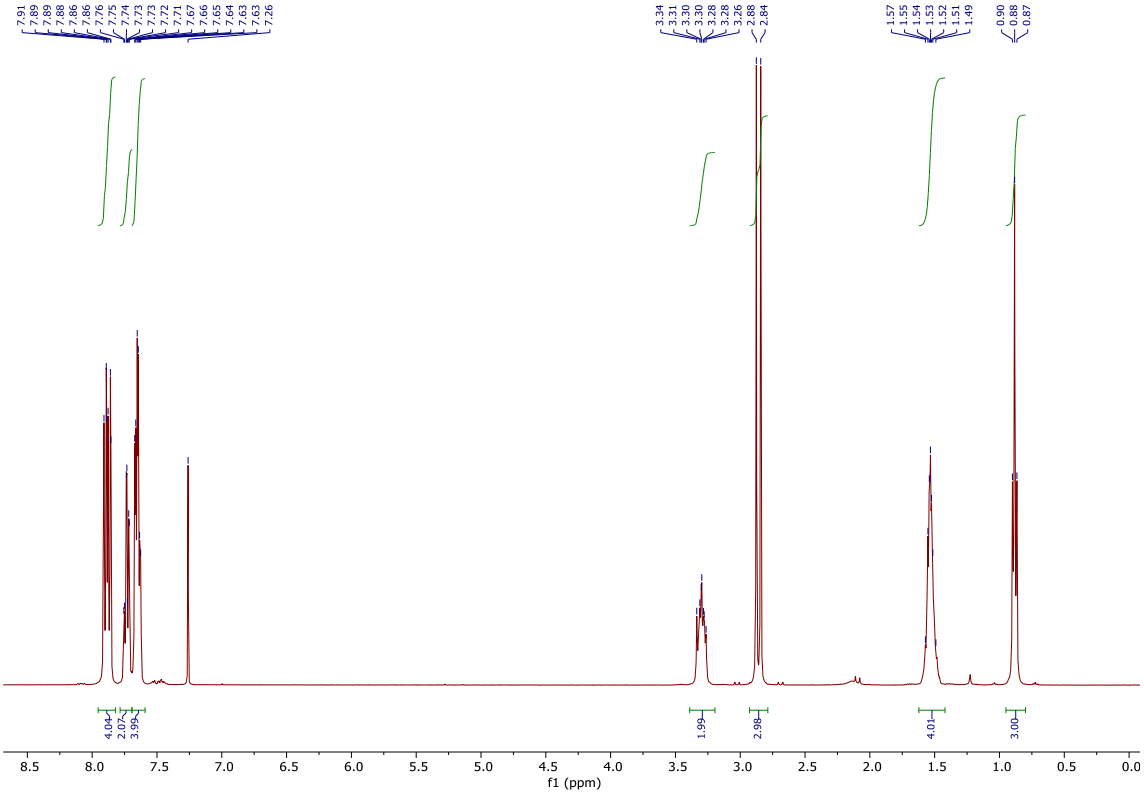
Benzylbutyldiphenylphosphonium bromide (**1o**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



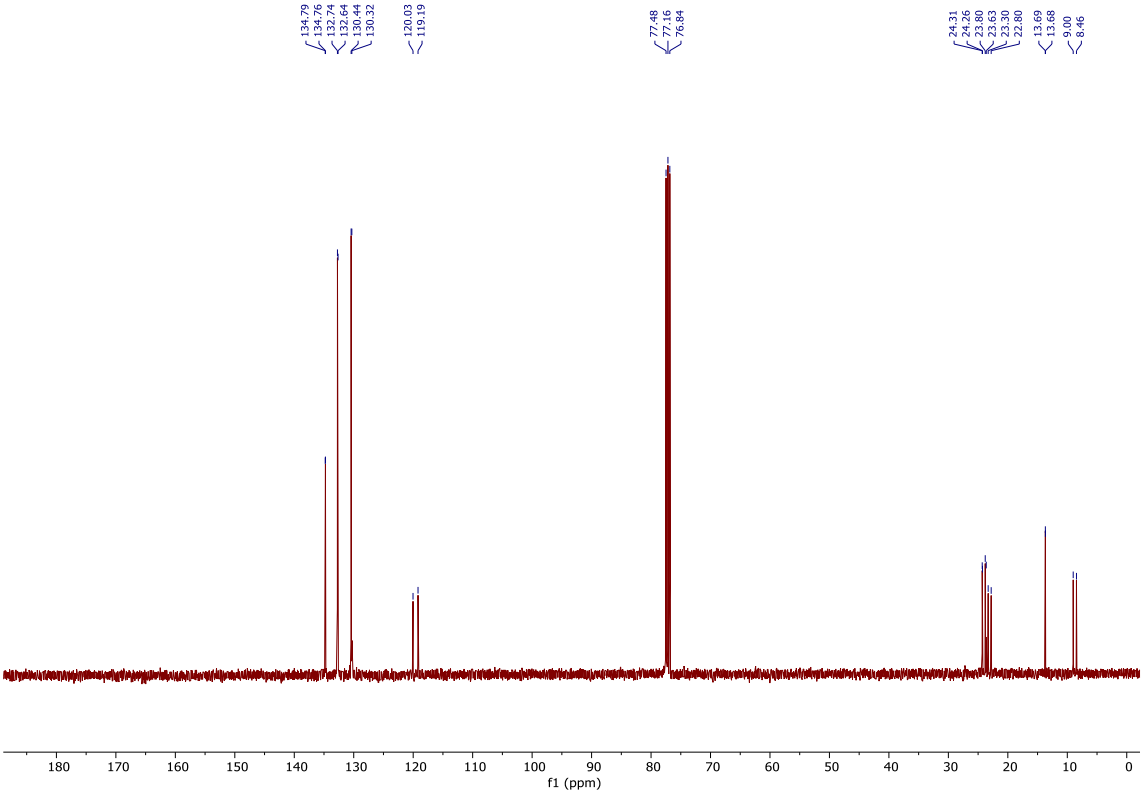
Benzylbutyldiphenylphosphonium bromide (**1o**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



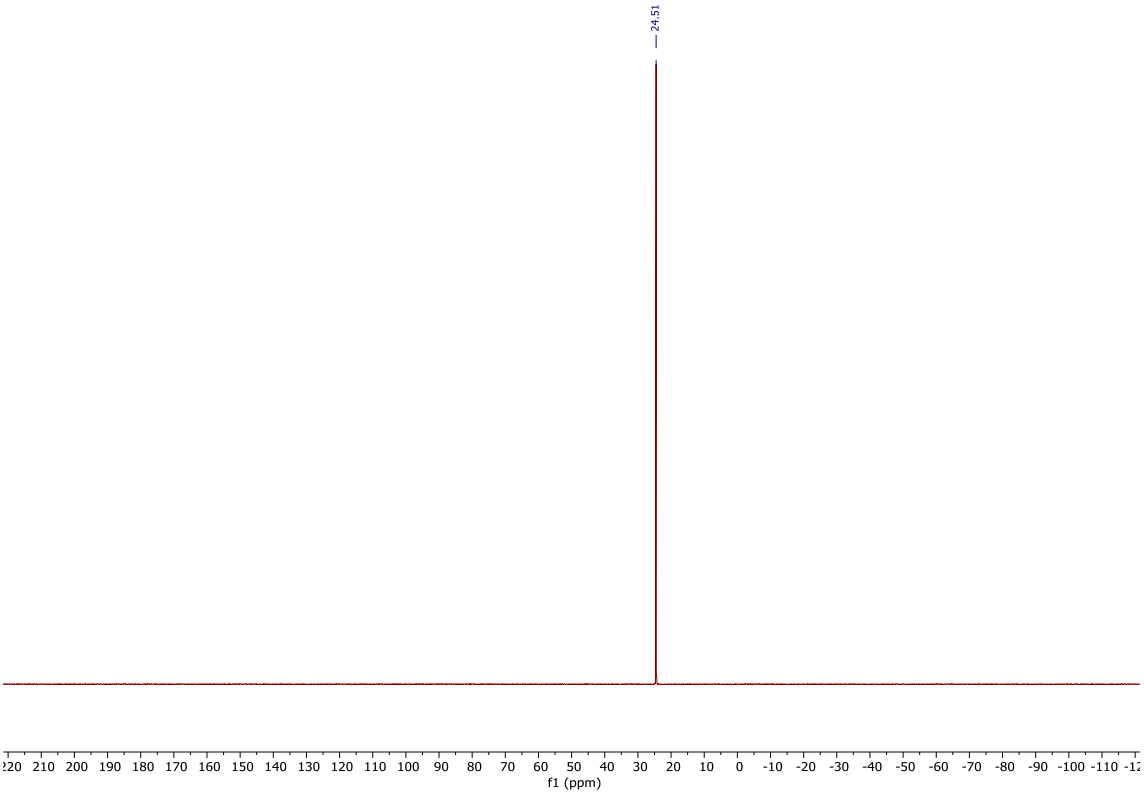
Butylmethyldiphenylphosphonium bromide (**1p**) – ^{1}H NMR spectrum ($CDCl_3$)



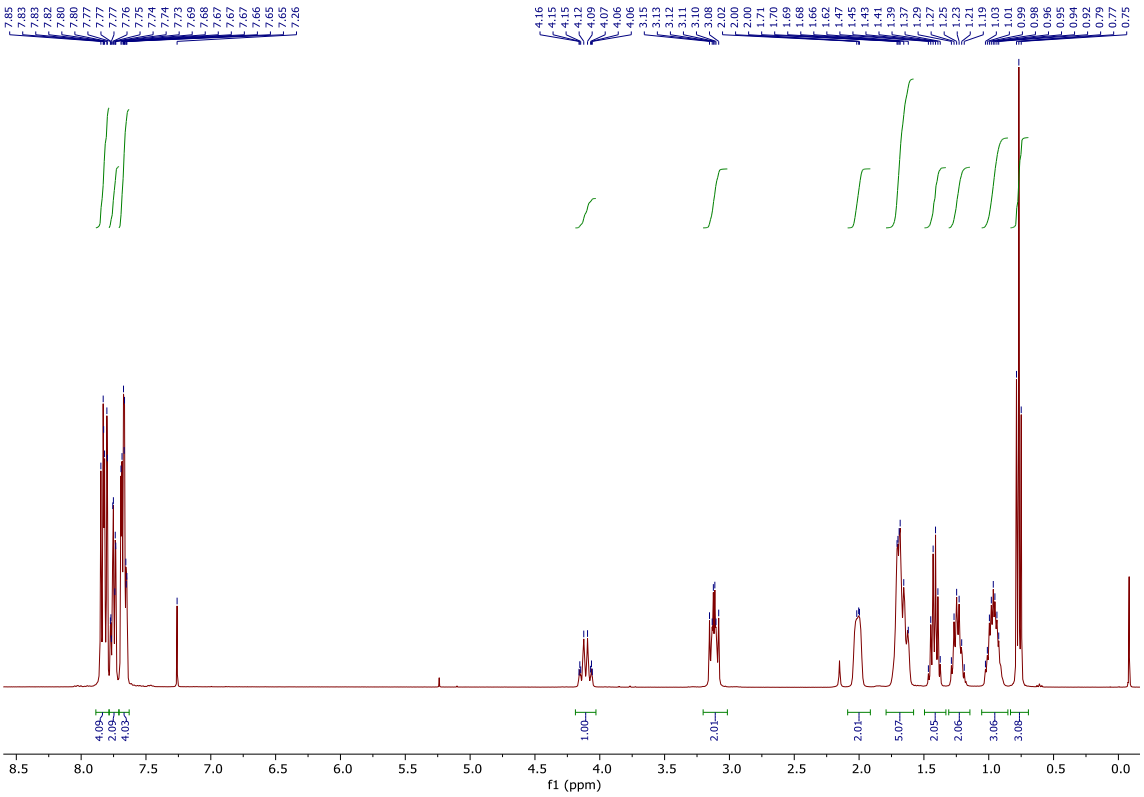
Butylmethyldiphenylphosphonium bromide (**1p**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



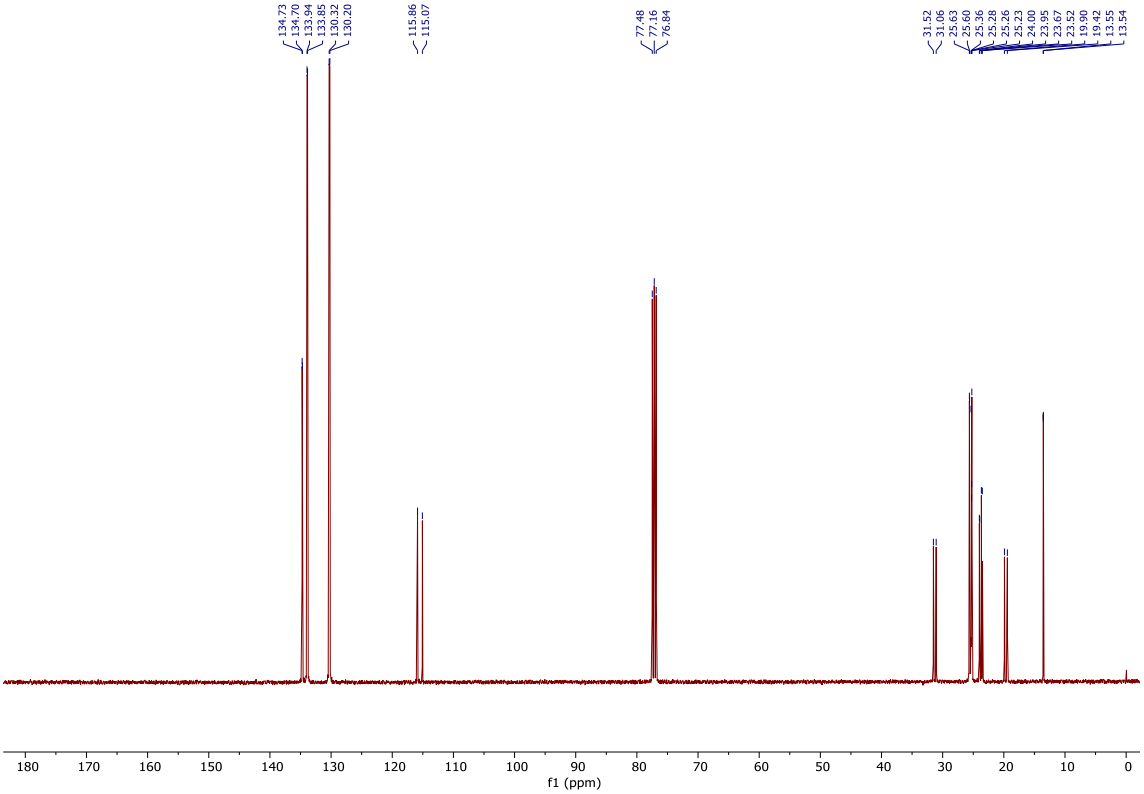
Butylmethyldiphenylphosphonium bromide (**1p**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



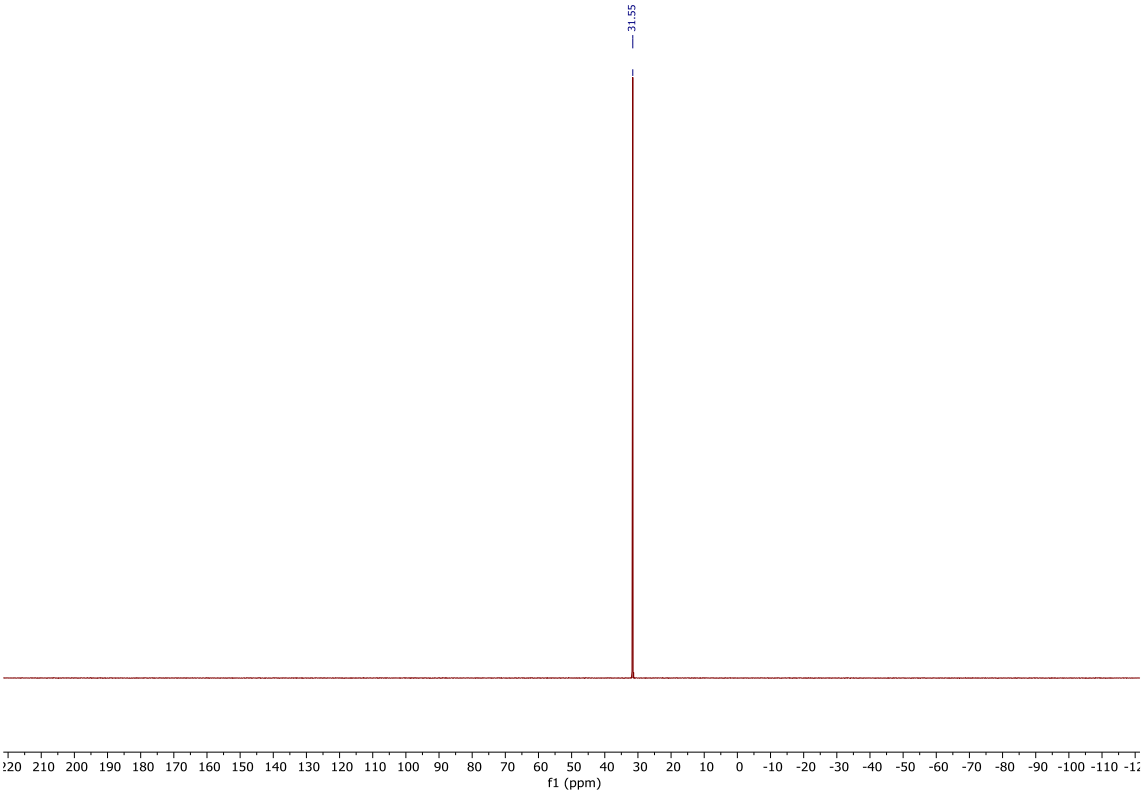
Butylcyclohexyldiphenylphosphonium bromide (**1q**) – ^{1}H NMR spectrum ($CDCl_3$)



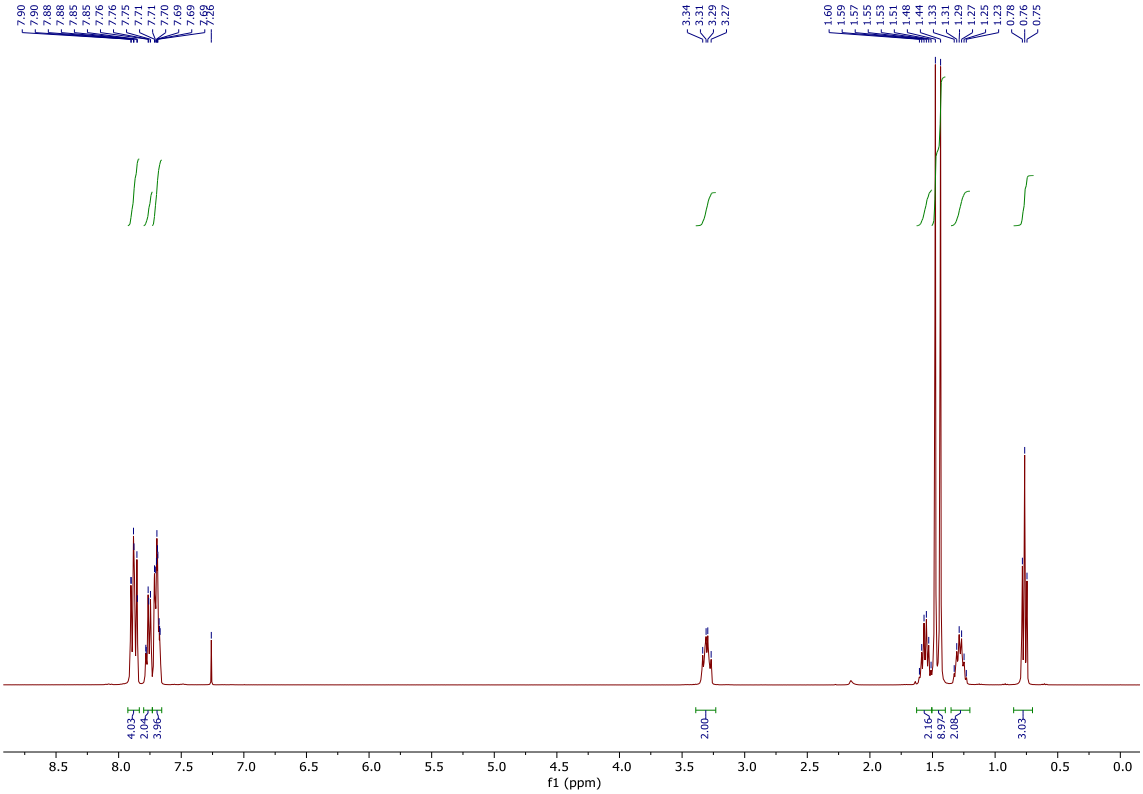
Butylcyclohexyldiphenylphosphonium bromide (**1q**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



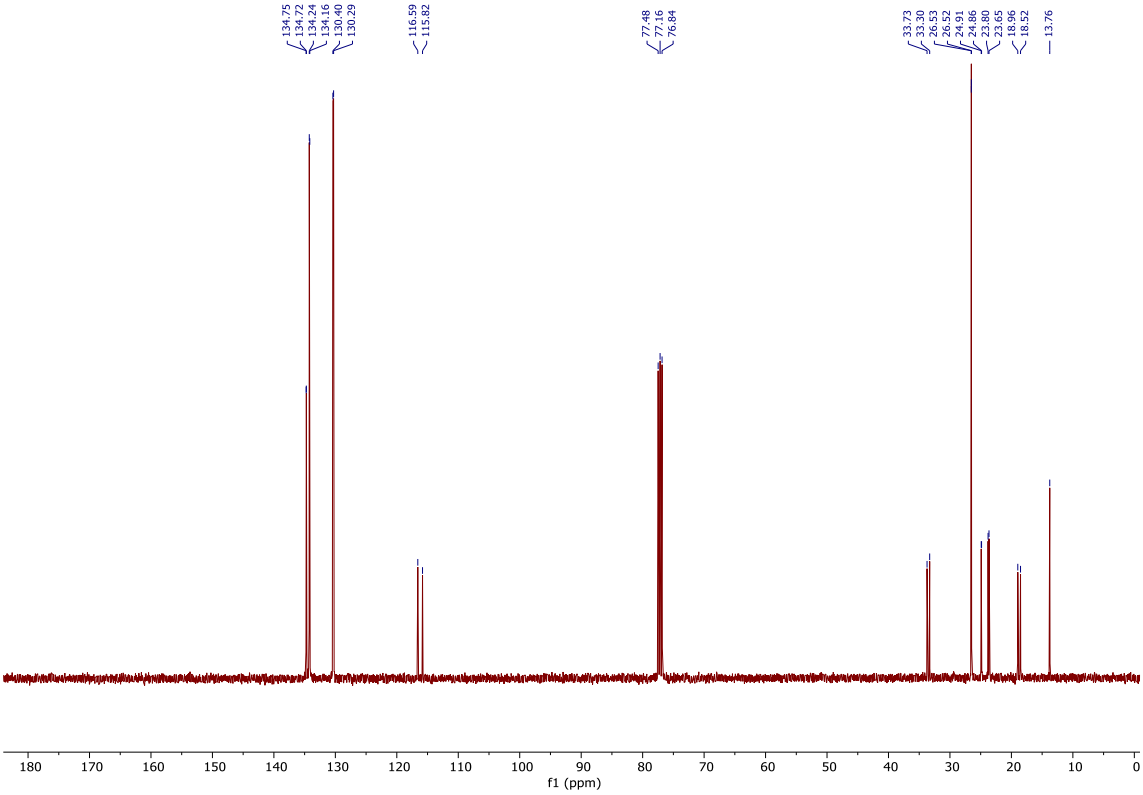
Butylcyclohexyldiphenylphosphonium bromide (**1q**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



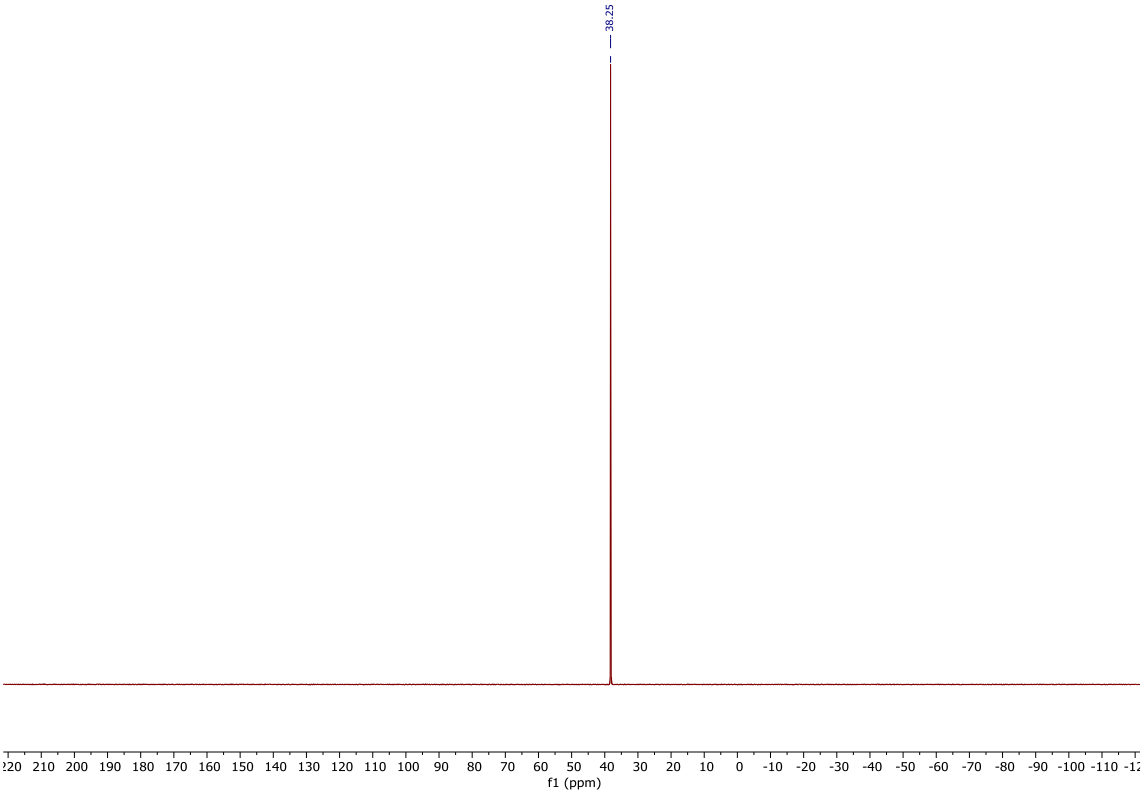
tert-Butyl(butyl)diphenylphosphonium bromide (**1r**) – ^{1}H NMR spectrum ($CDCl_3$)



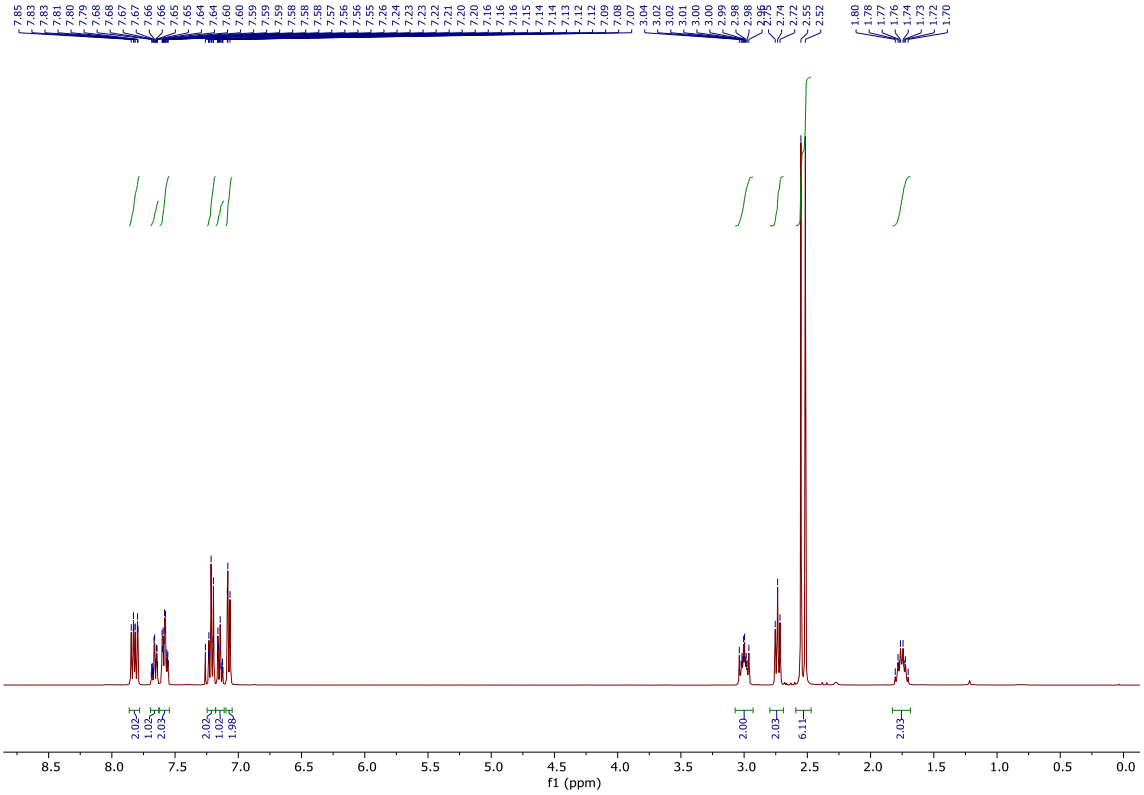
tert-Butyl(butyl)diphenylphosphonium bromide (**1r**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



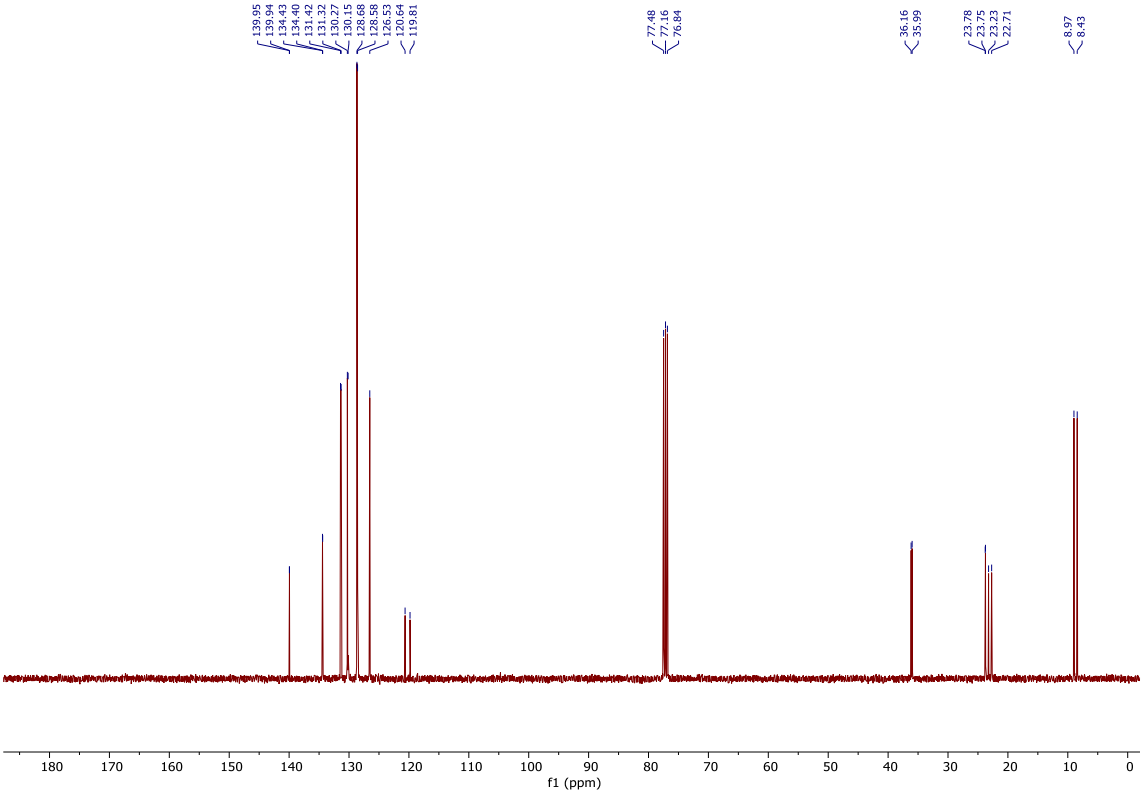
tert-Butyl(butyl)diphenylphosphonium bromide (**1r**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



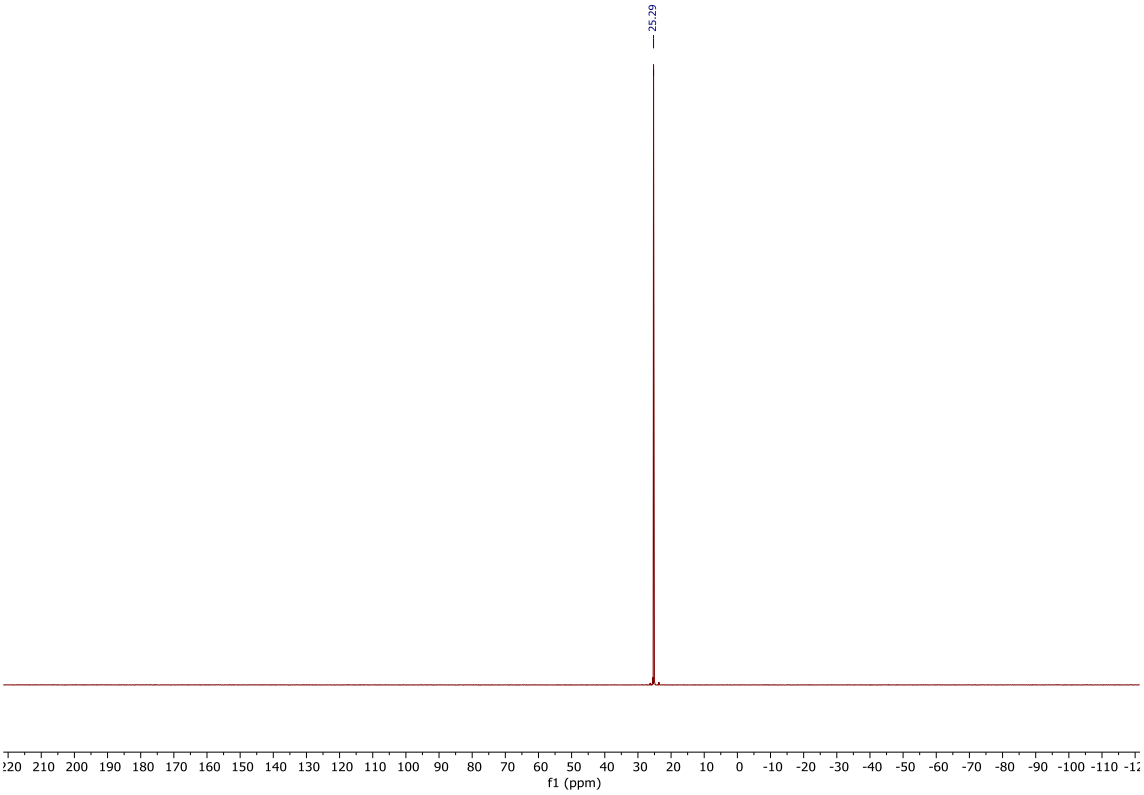
Dimethyl(phenyl)(3-phenylpropyl)phosphonium bromide (**1s**) – ^{1}H NMR spectrum ($CDCl_3$)



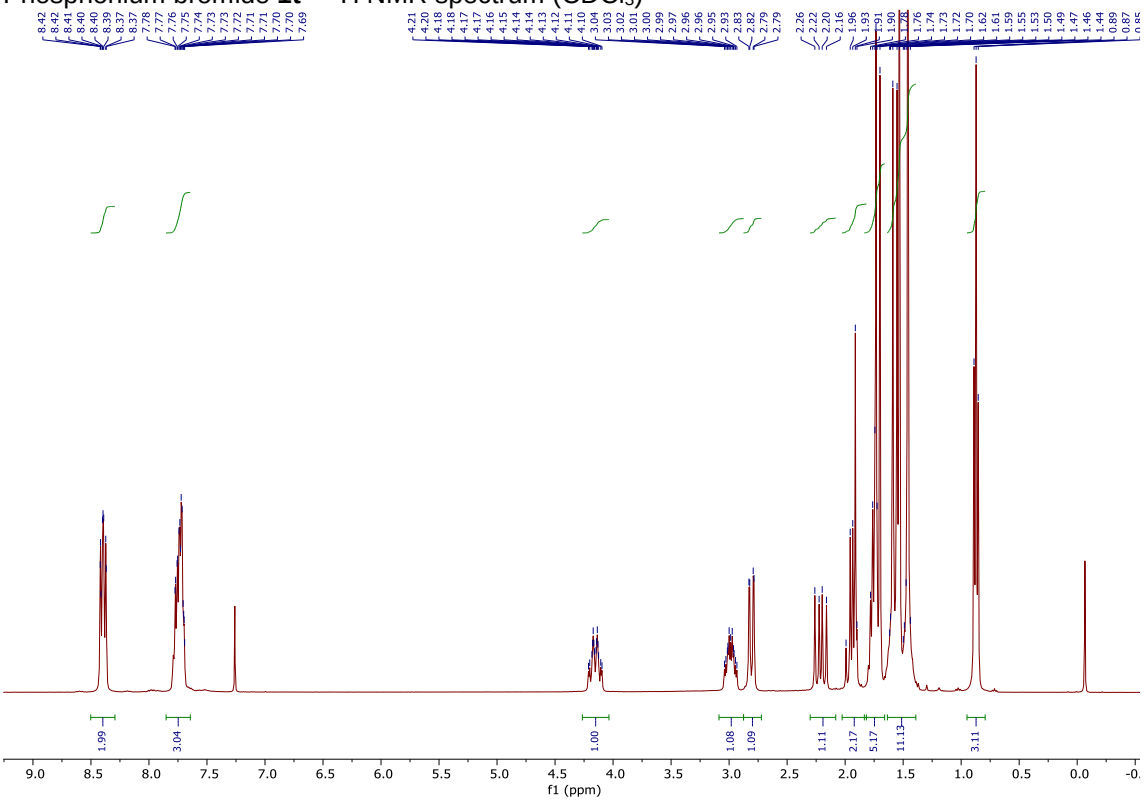
Dimethyl(phenyl)(3-phenylpropyl)phosphonium bromide (**1s**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



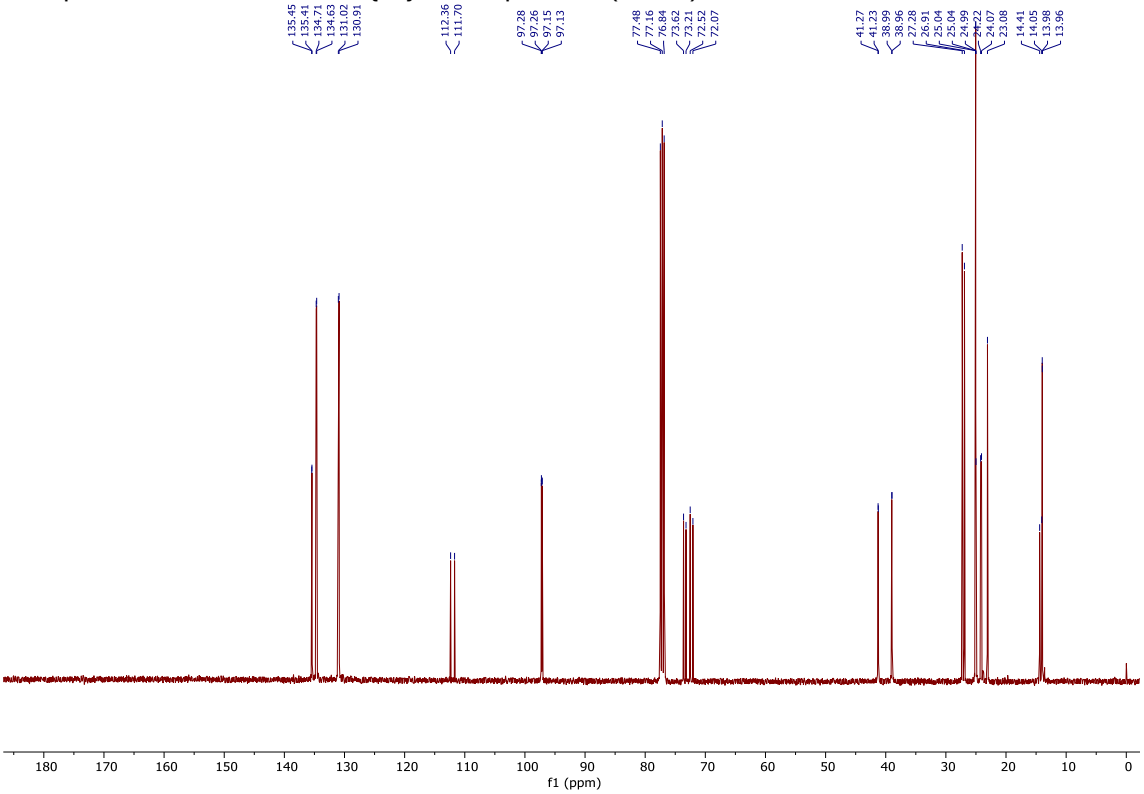
Dimethyl(phenyl)(3-phenylpropyl)phosphonium bromide (**1s**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



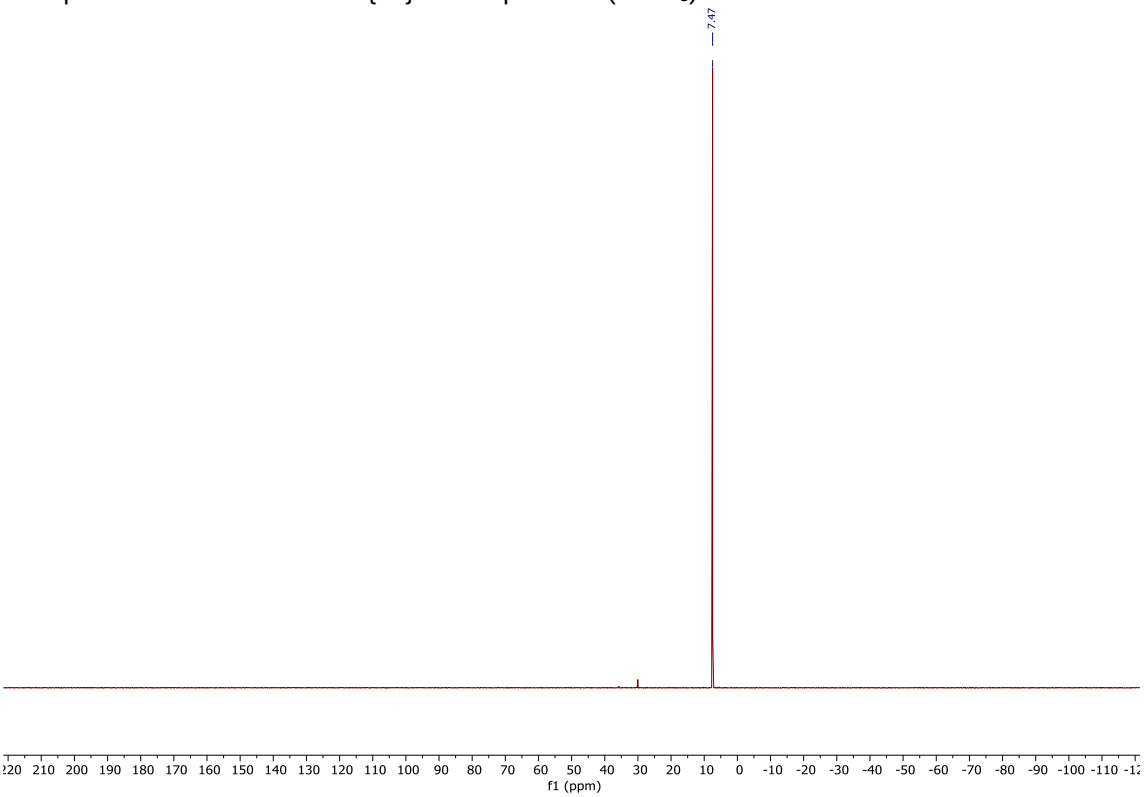
Phosphonium bromide **1t** – ^{1}H NMR spectrum ($CDCl_3$)



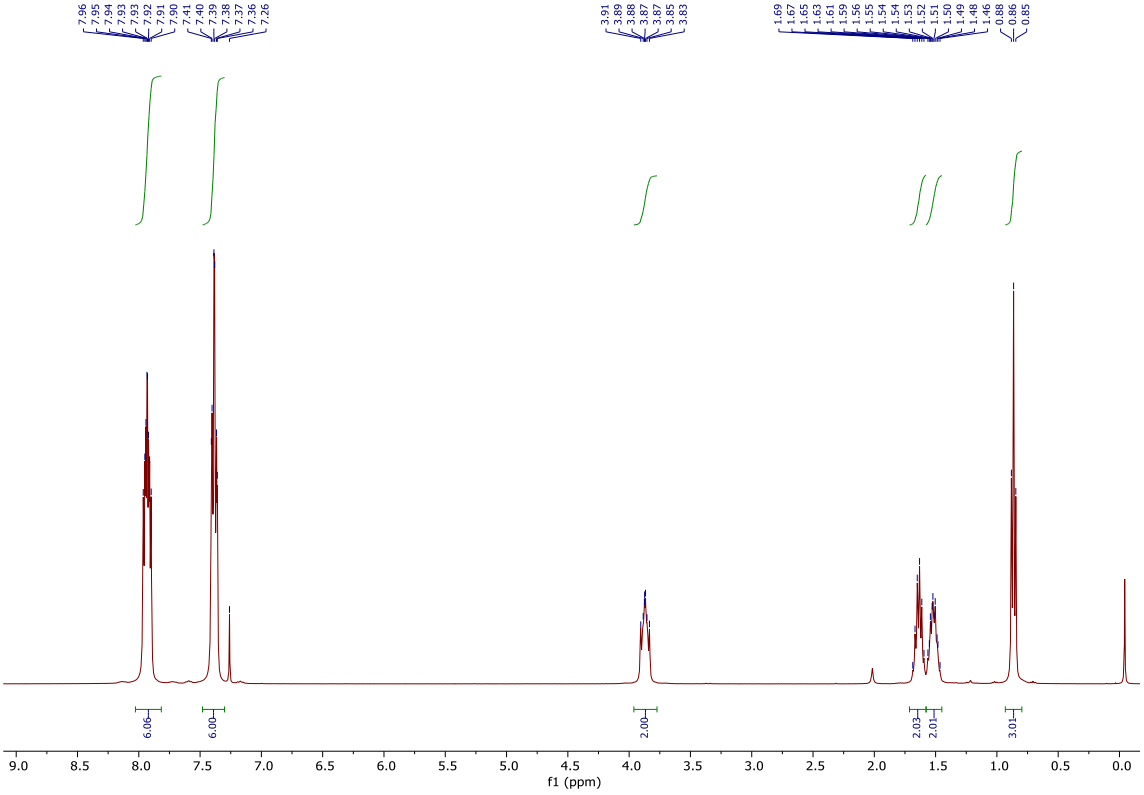
Phosphonium bromide **1t** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



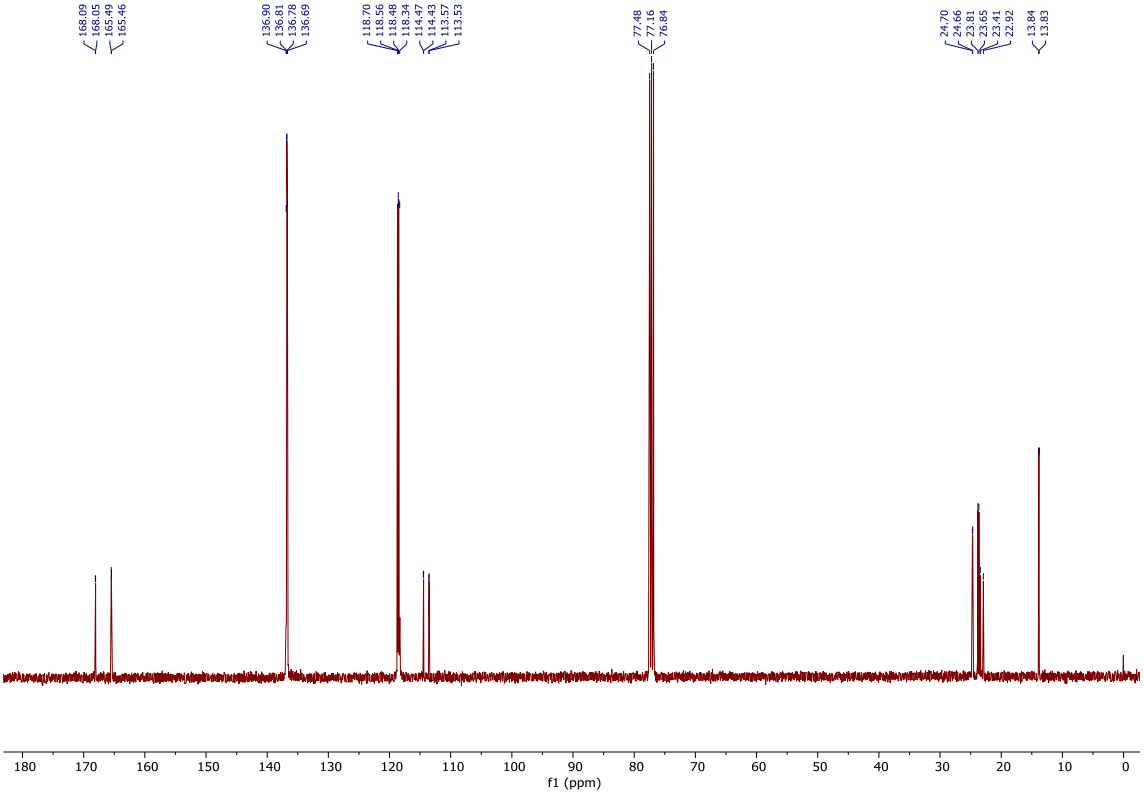
Phosphonium bromide **1t** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



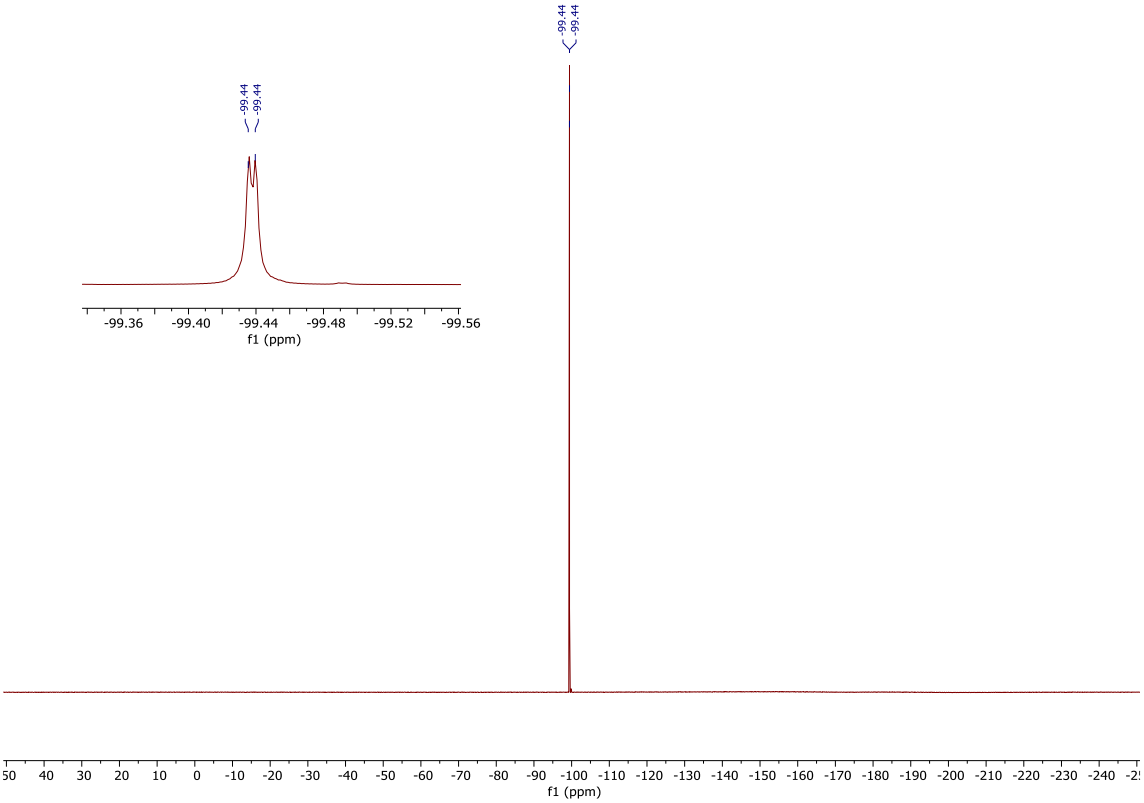
Butyltris(4-fluorophenyl)phosphonium bromide (**1u**) – ^{1}H NMR spectrum ($CDCl_3$)



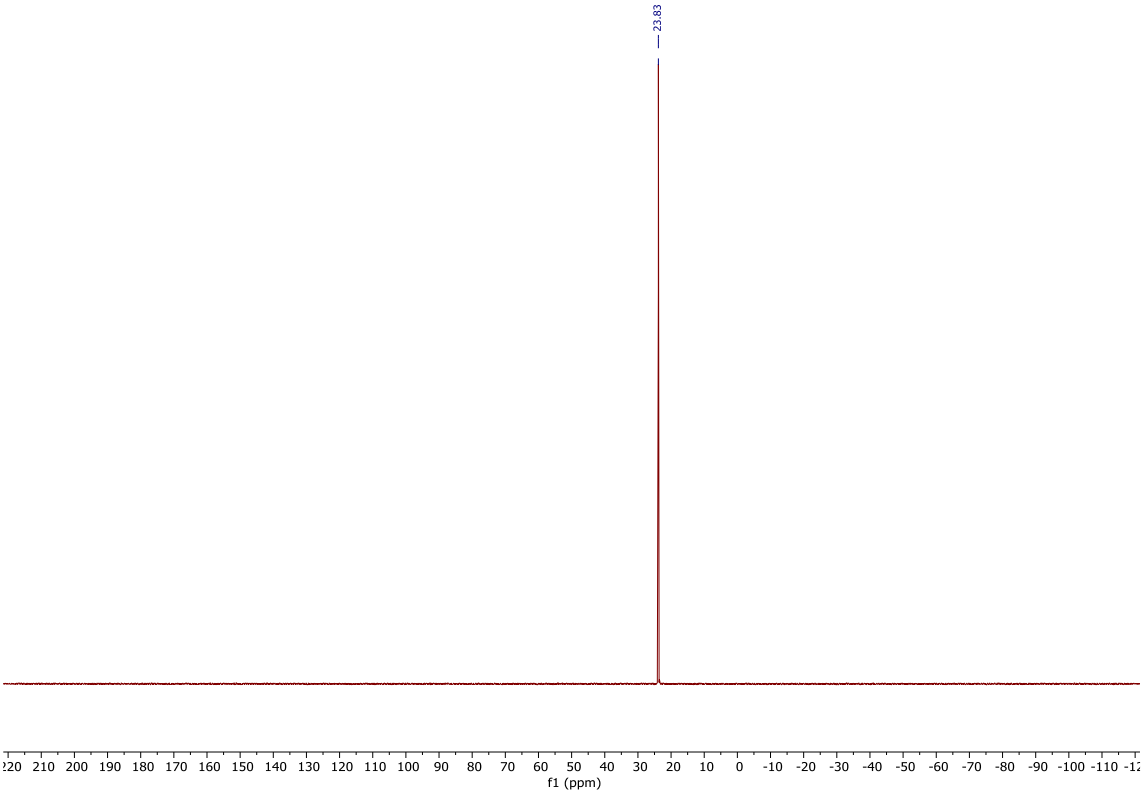
Butyltris(4-fluorophenyl)phosphonium bromide (**1u**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



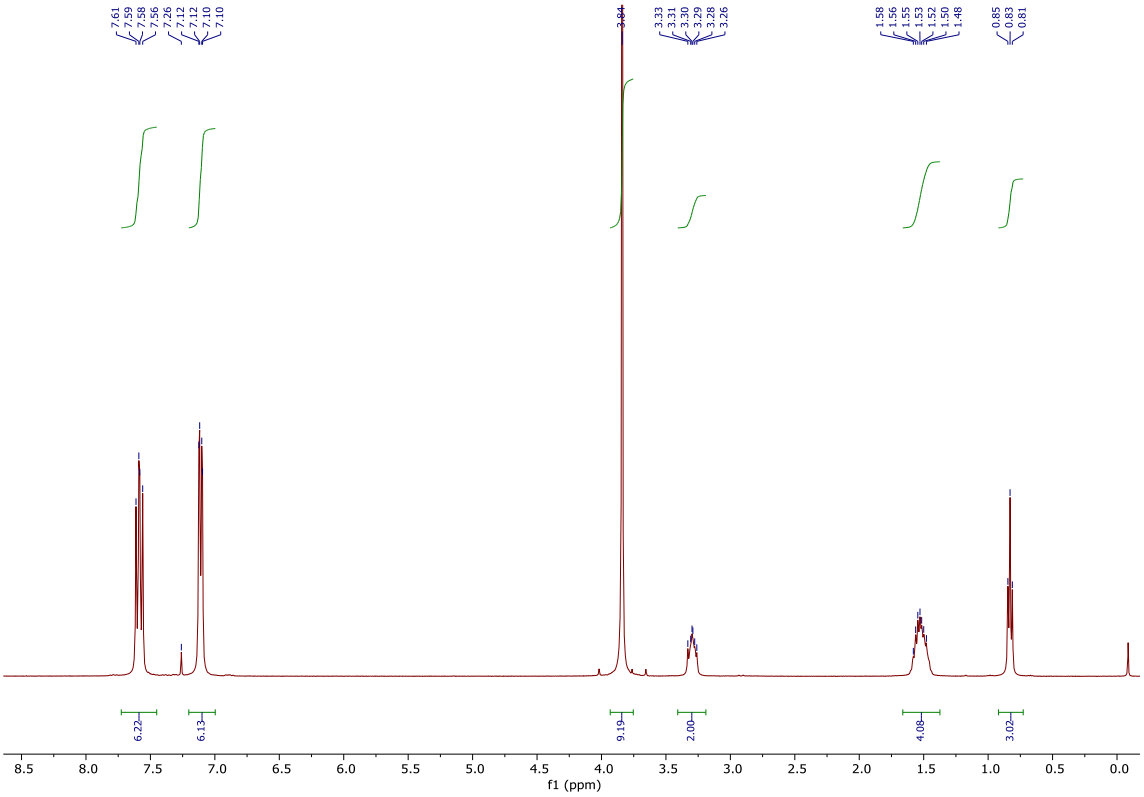
Butyltris(4-fluorophenyl)phosphonium bromide (**1u**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



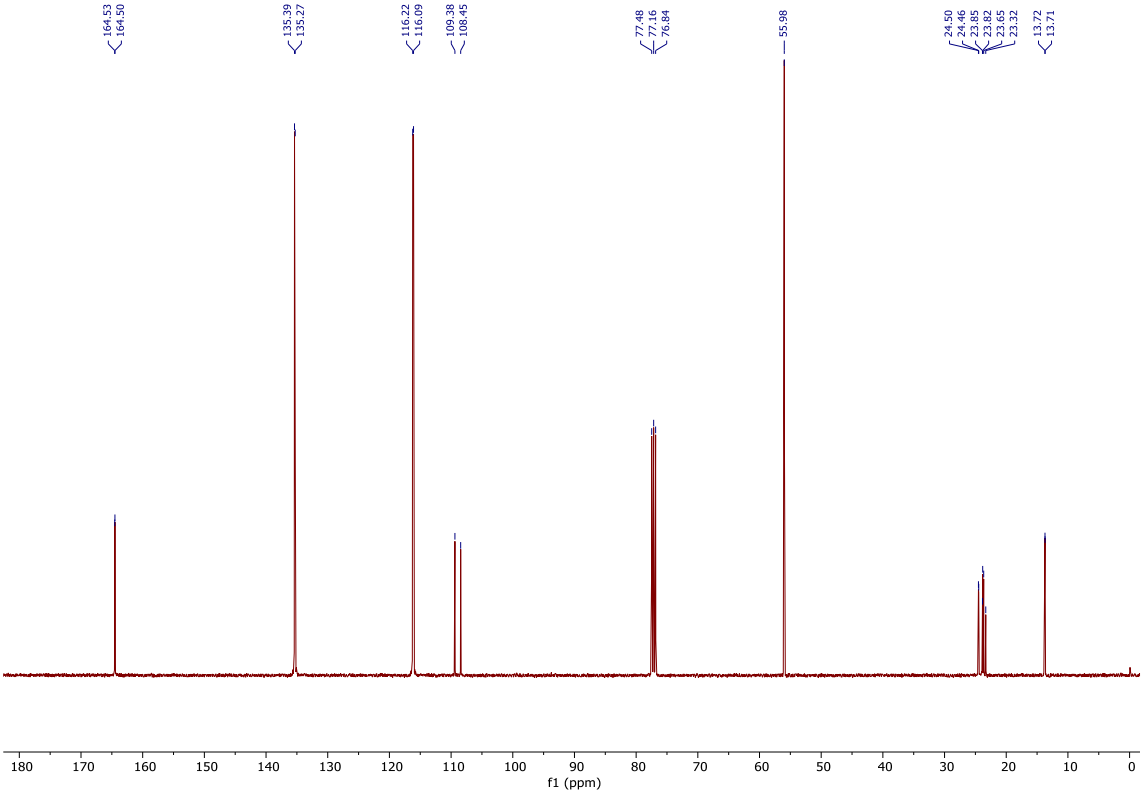
Butyltris(4-fluorophenyl)phosphonium bromide (**1u**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



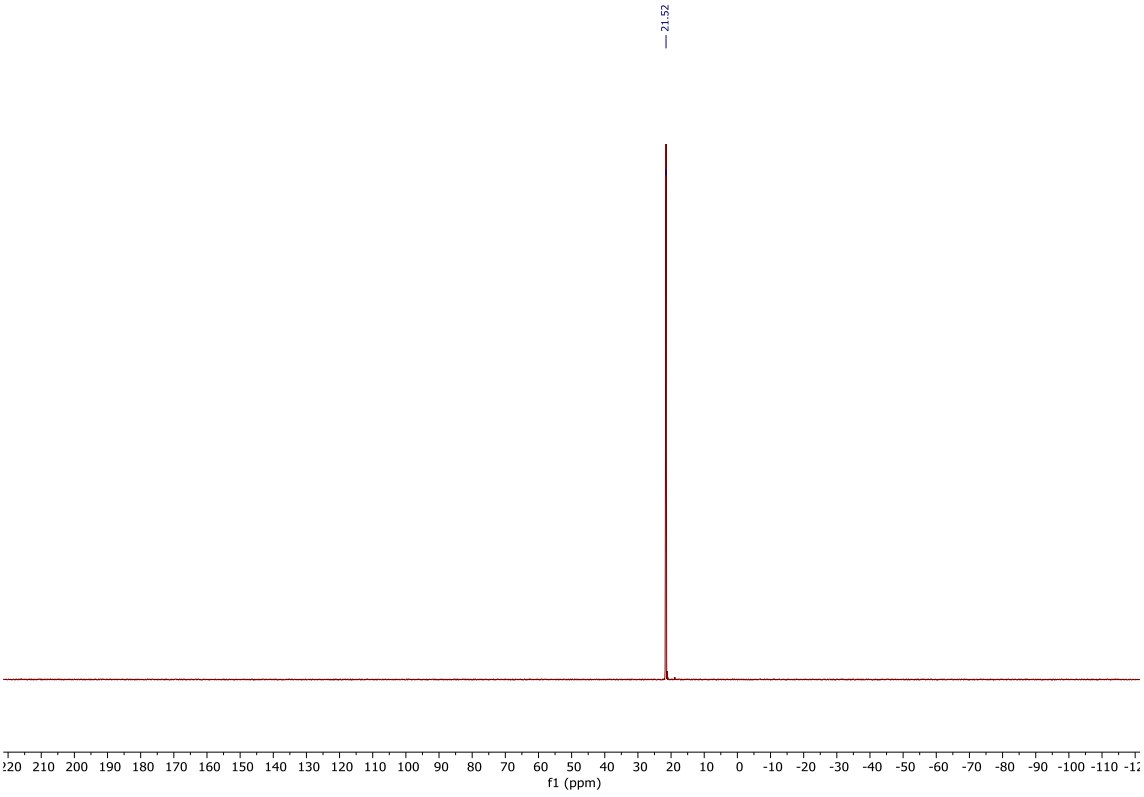
Butyltris(4-methoxyphenyl)phosphonium bromide (**1v**) – ^{1}H NMR spectrum ($CDCl_3$)



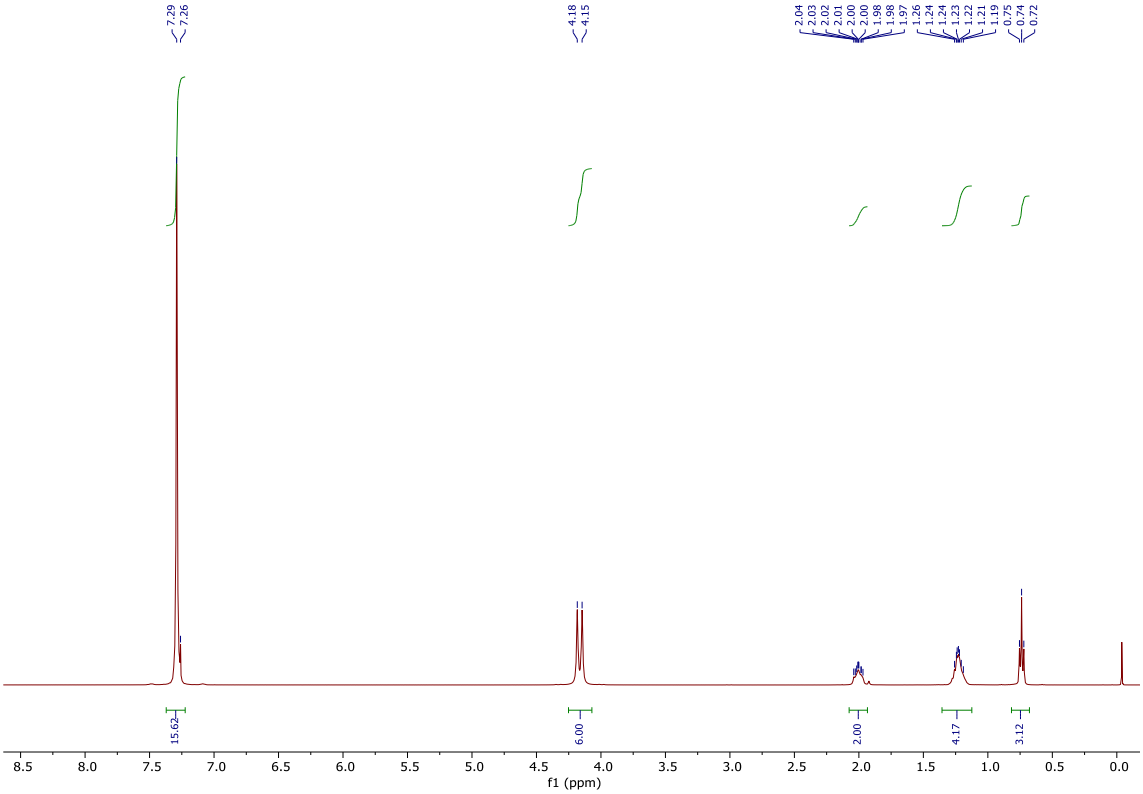
Butyltris(4-methoxyphenyl)phosphonium bromide (**1v**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



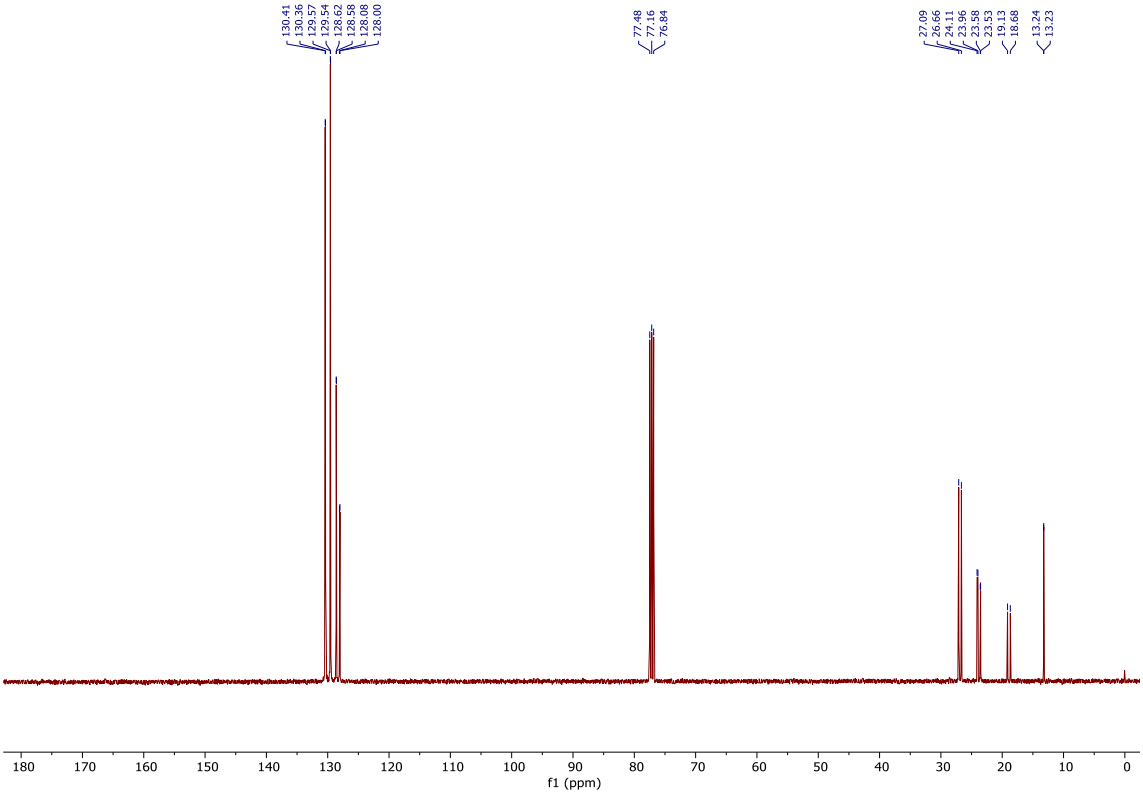
Butyltris(4-methoxyphenyl)phosphonium bromide (**1v**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



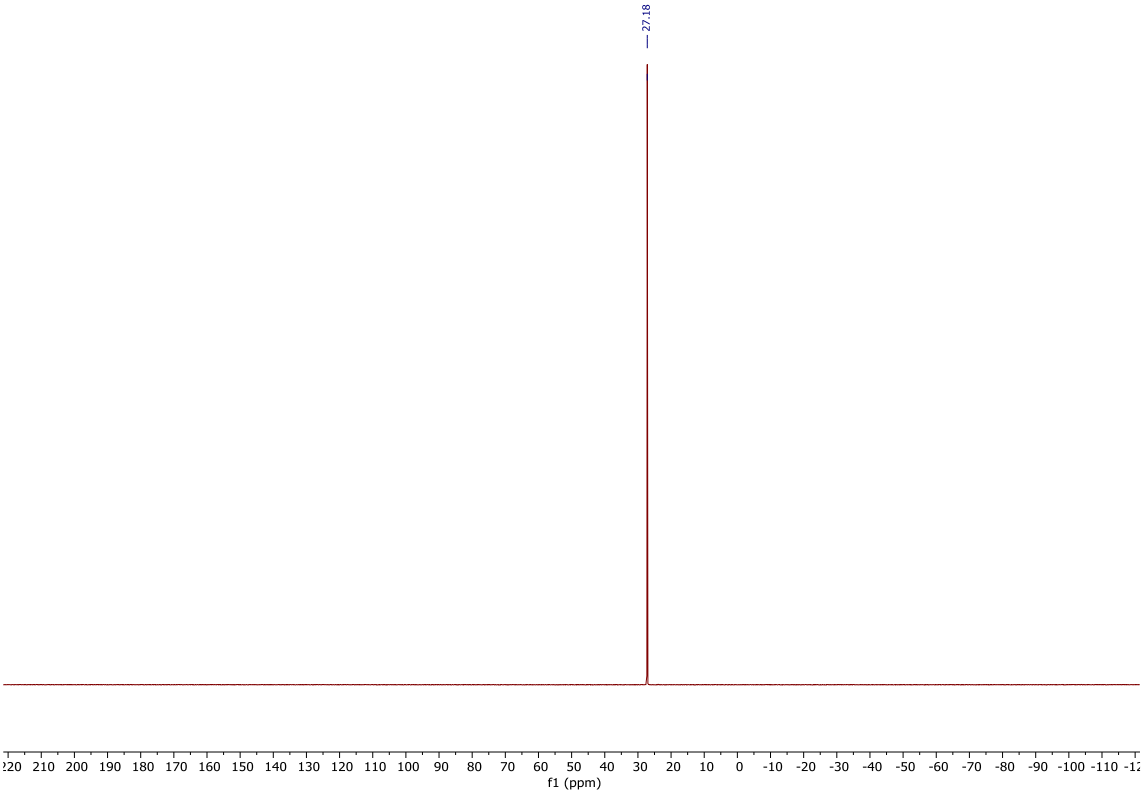
Tribenzylbutylphosphonium bromide (**1w**) – ^{1}H NMR spectrum ($CDCl_3$)



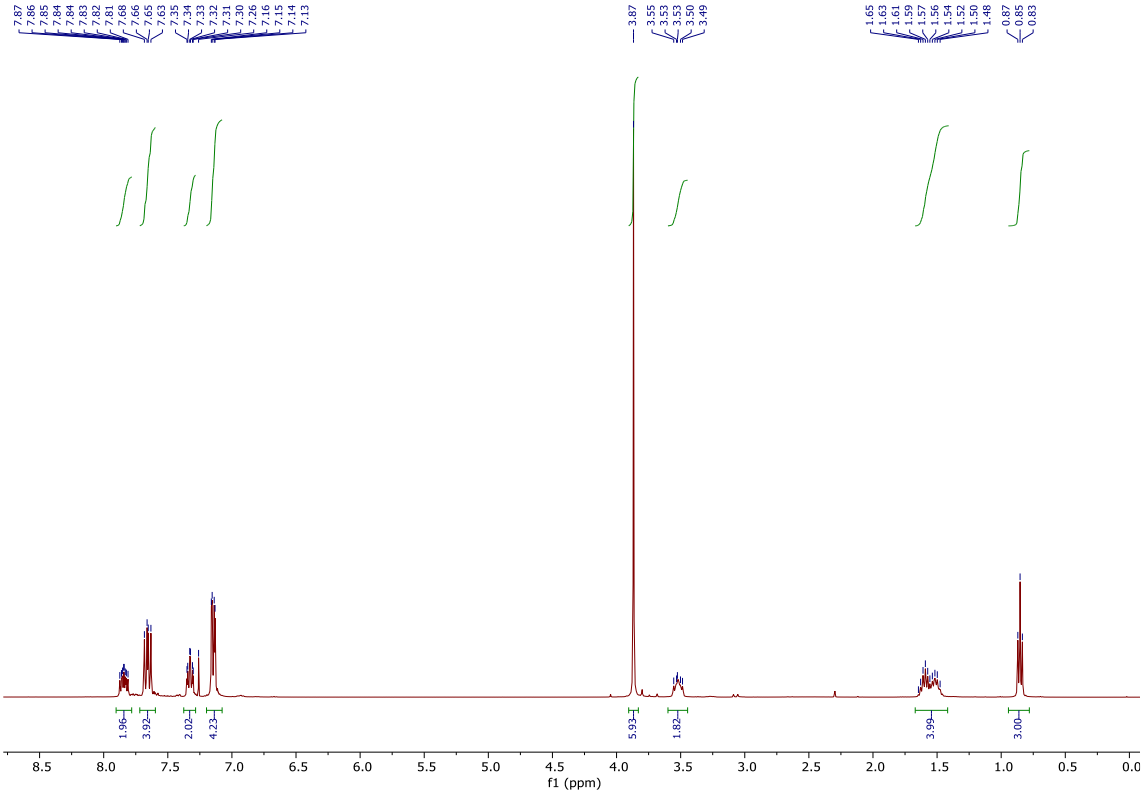
Tribenzylbutylphosphonium bromide (**1w**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



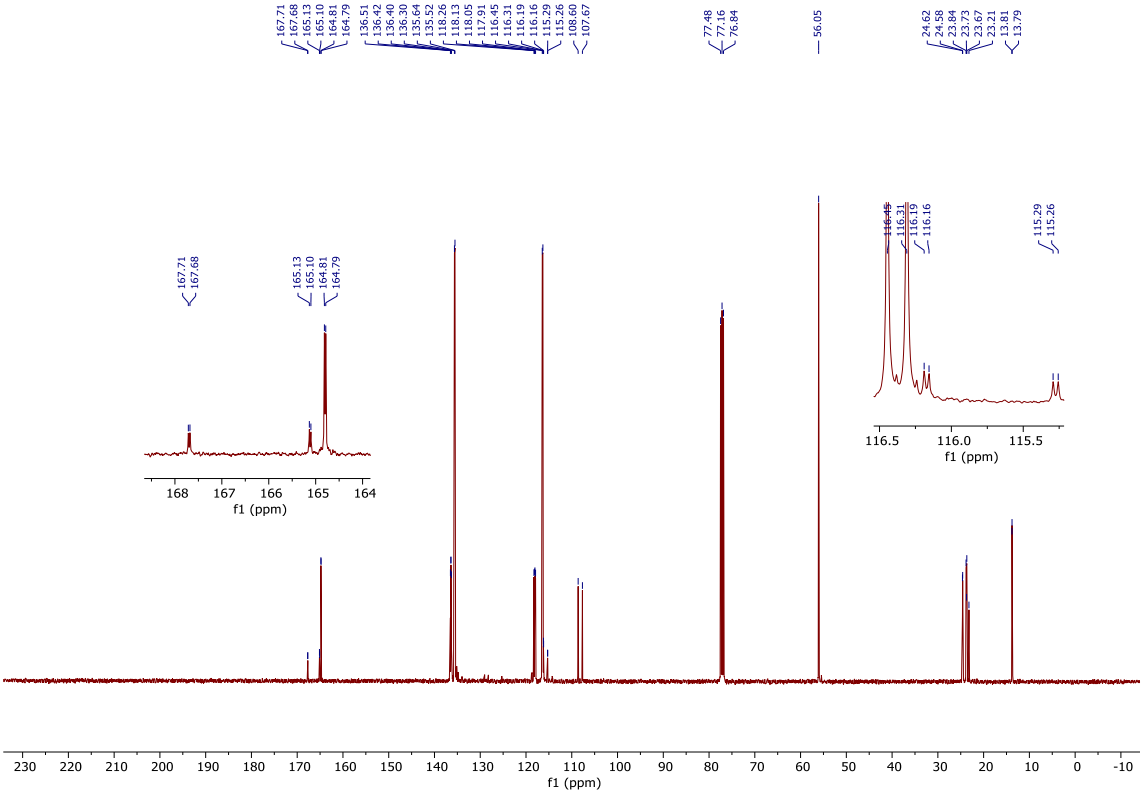
Tribenzylbutylphosphonium bromide (**1w**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



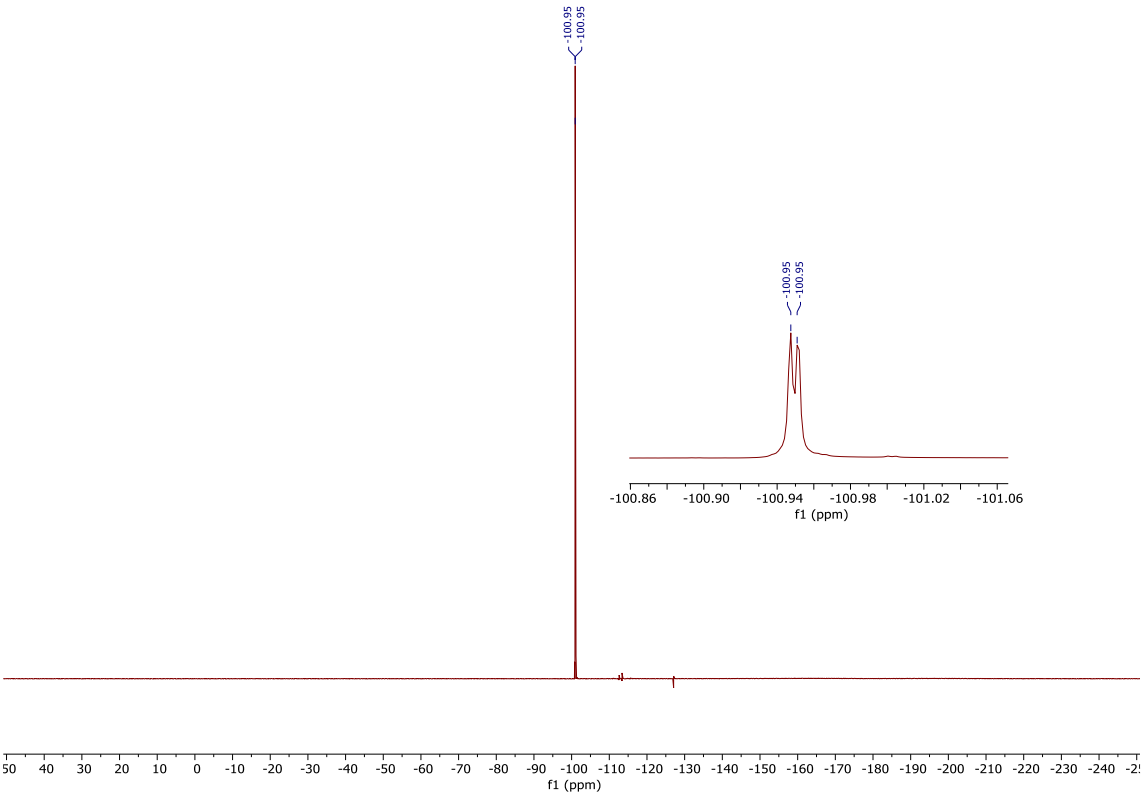
Butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) – ^{1}H NMR spectrum ($CDCl_3$)



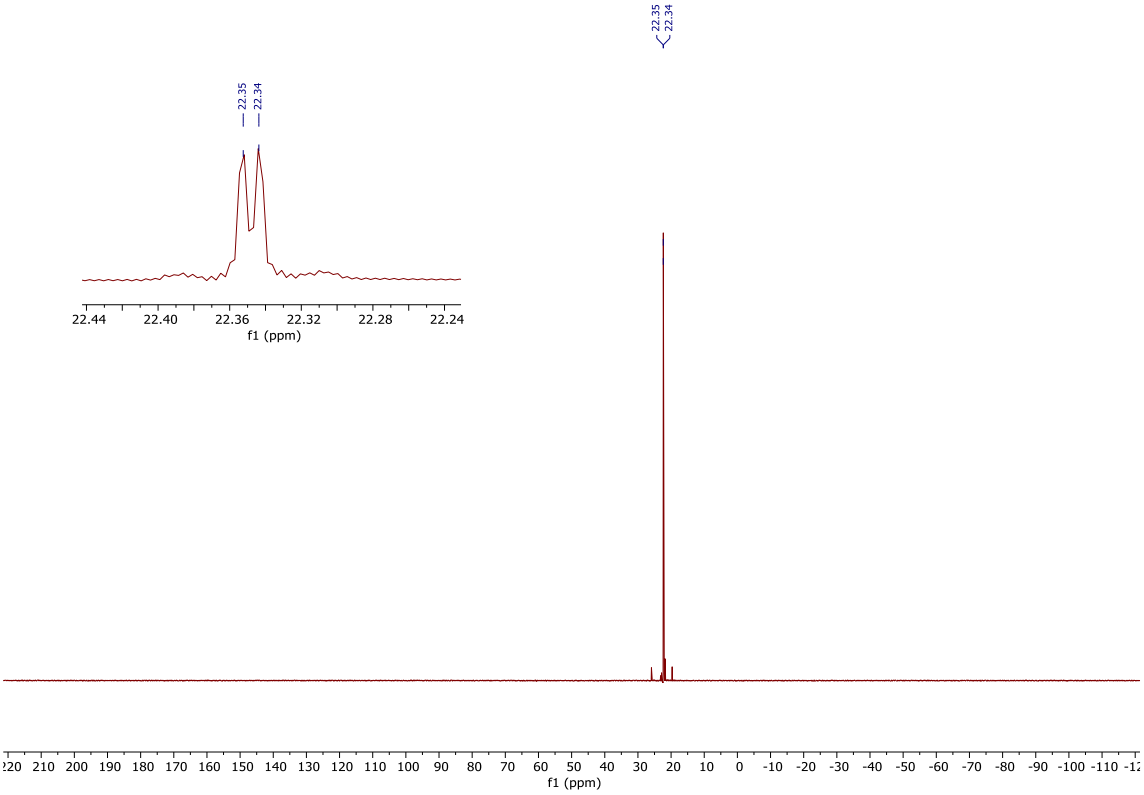
Butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



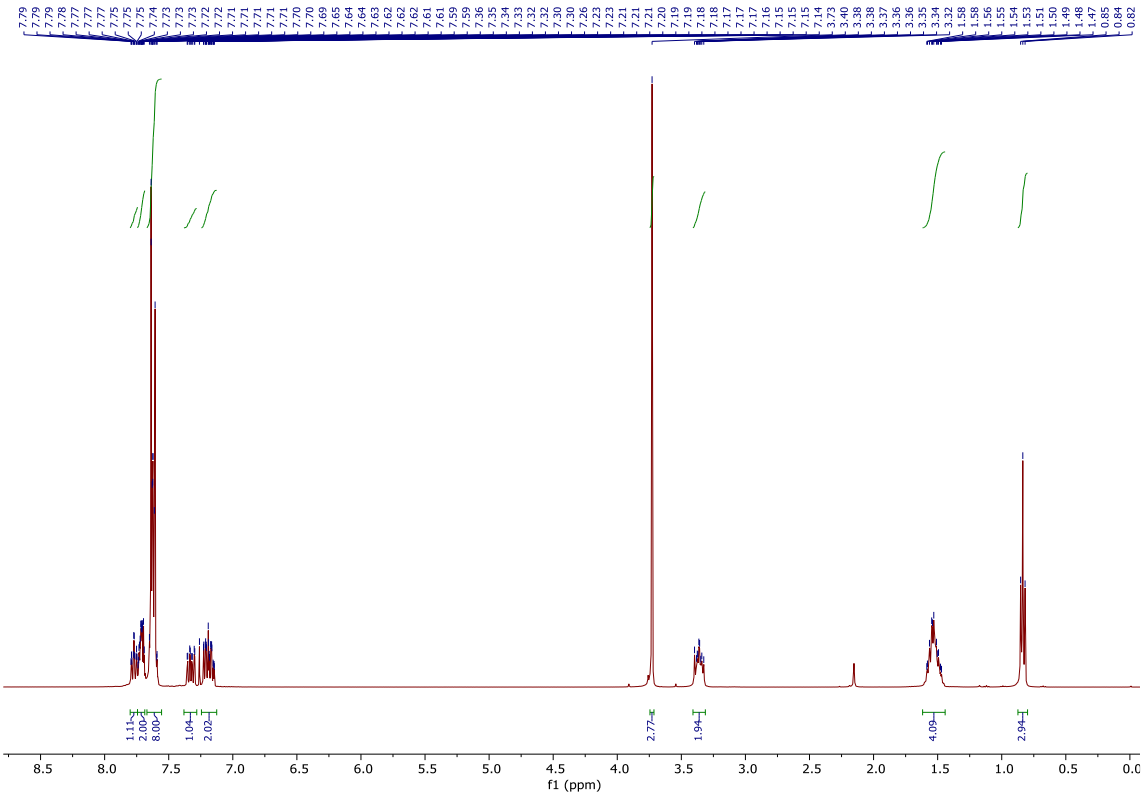
Butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



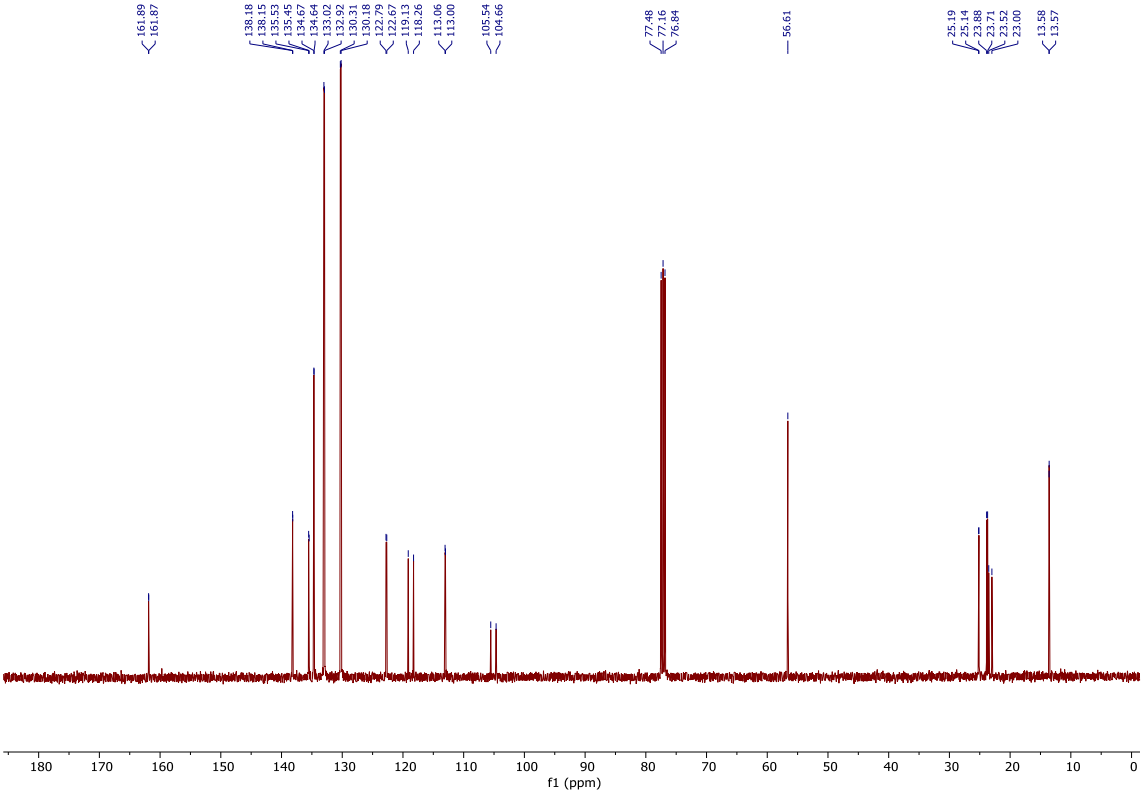
Butyl(4-fluorophenyl)bis(4-methoxyphenyl)phosphonium bromide (**1x**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



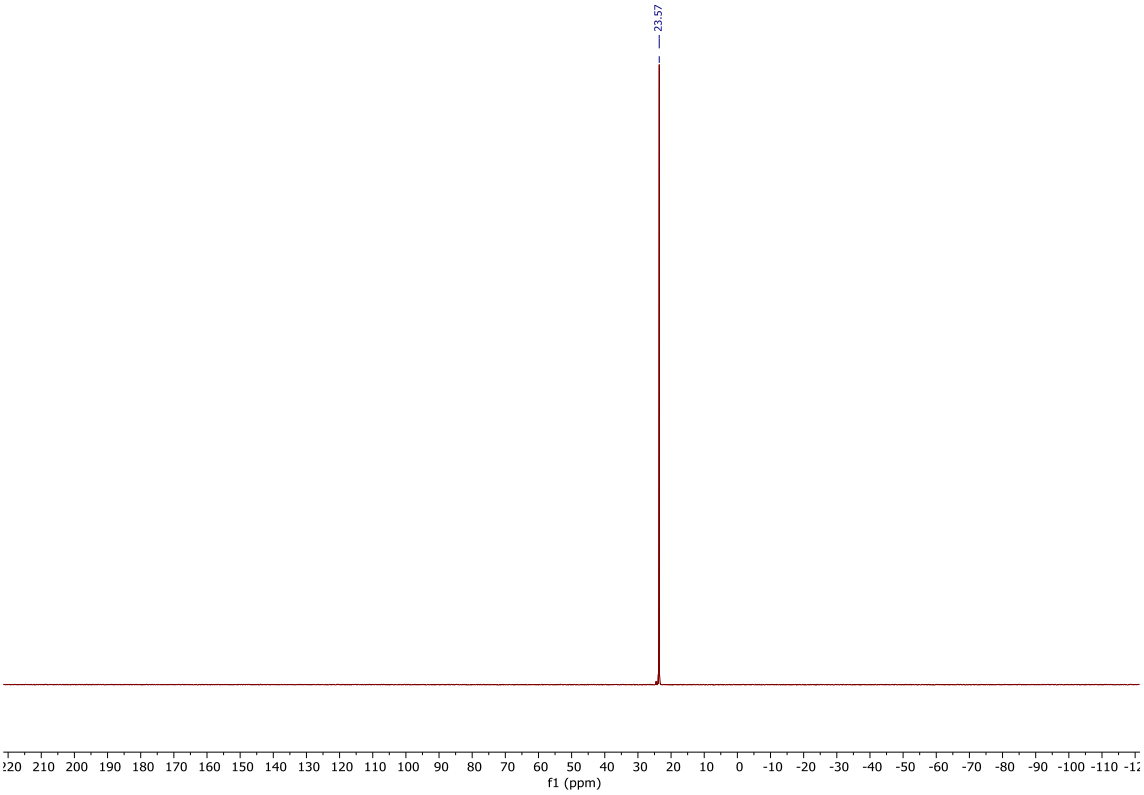
Butyl(2-methoxyphenyl)diphenylphosphonium bromide (**1y**) – ^{1}H NMR spectrum ($CDCl_3$)



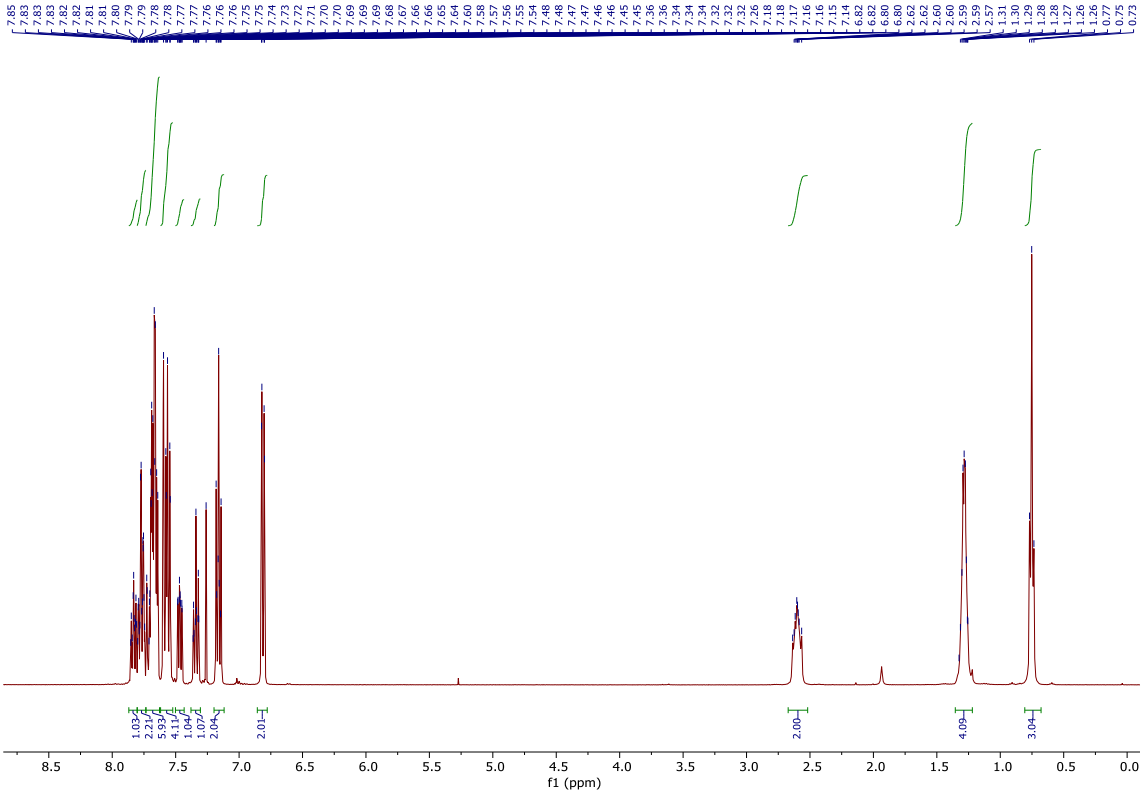
Butyl(2-methoxyphenyl)diphenylphosphonium bromide (**1y**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



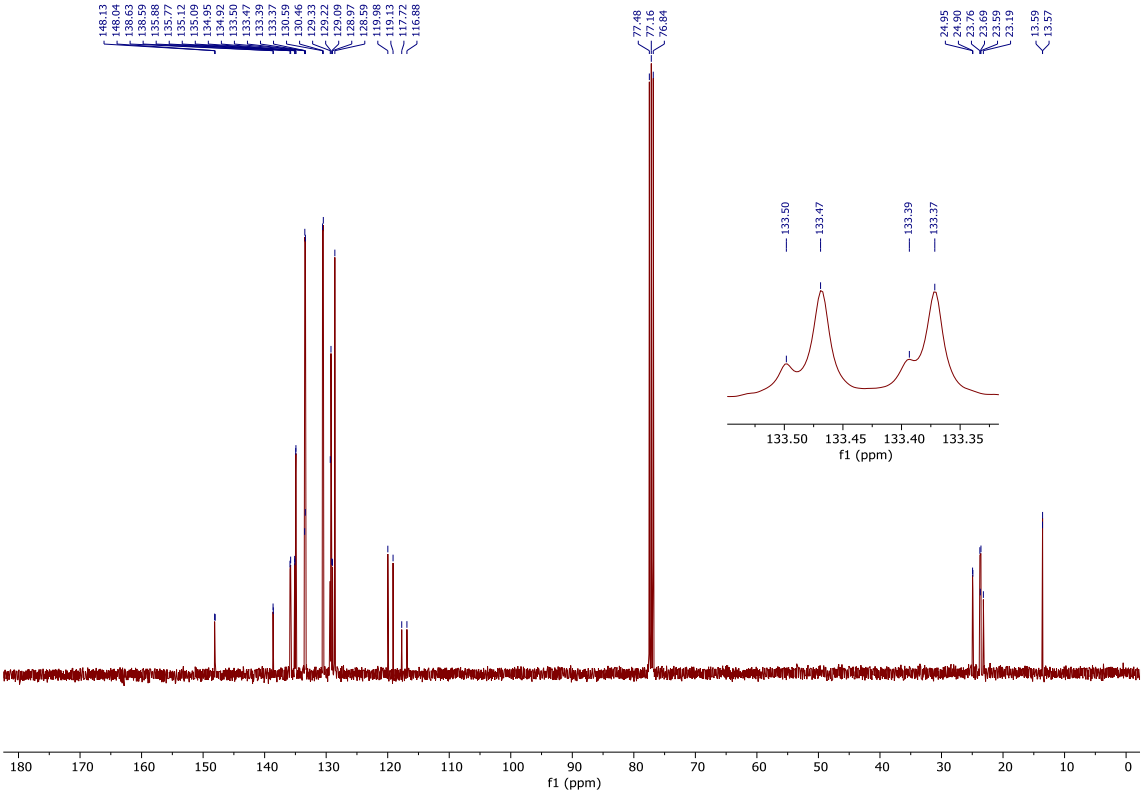
Butyl(2-methoxyphenyl)diphenylphosphonium bromide (**1y**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



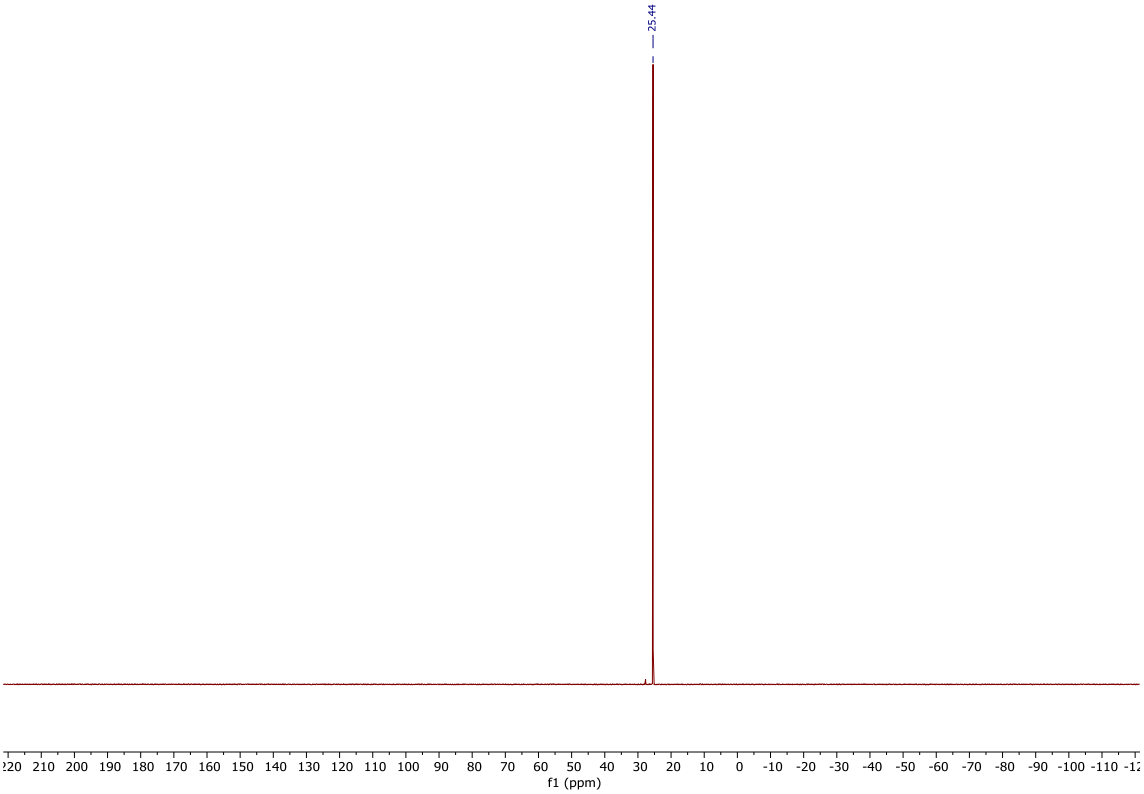
[1,1'-biphenyl]-2-yl(butyl)diphenylphosphonium bromide (**1z**) – ^{1}H NMR spectrum ($CDCl_3$)



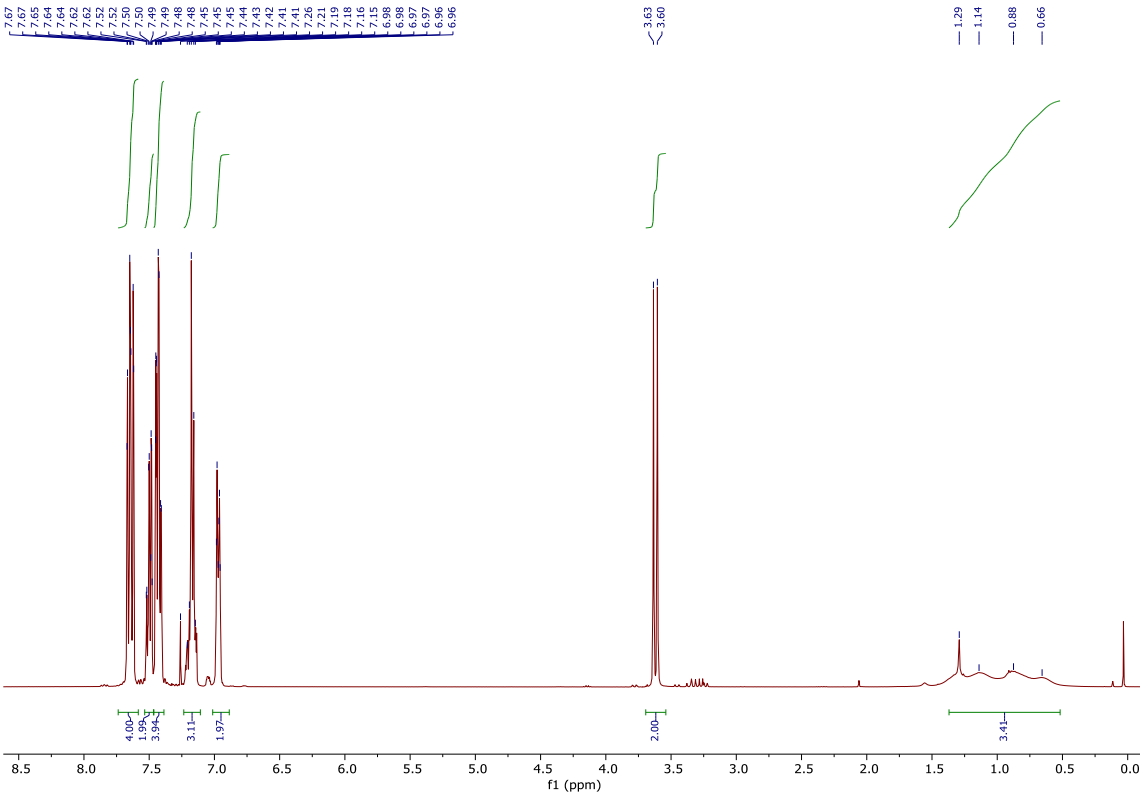
[1,1'-biphenyl]-2-yl(butyl)diphenylphosphonium bromide (**1z**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



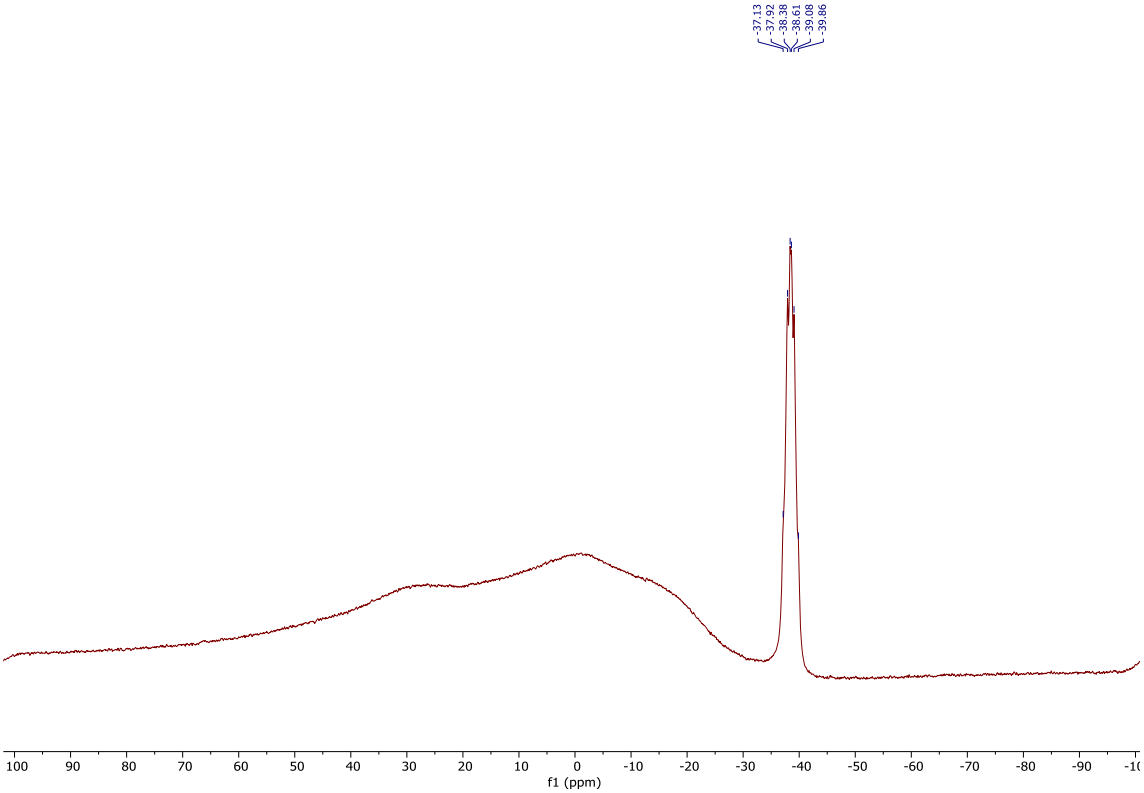
[1,1'-biphenyl]-2-yl(butyl)diphenylphosphonium bromide (**1z**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



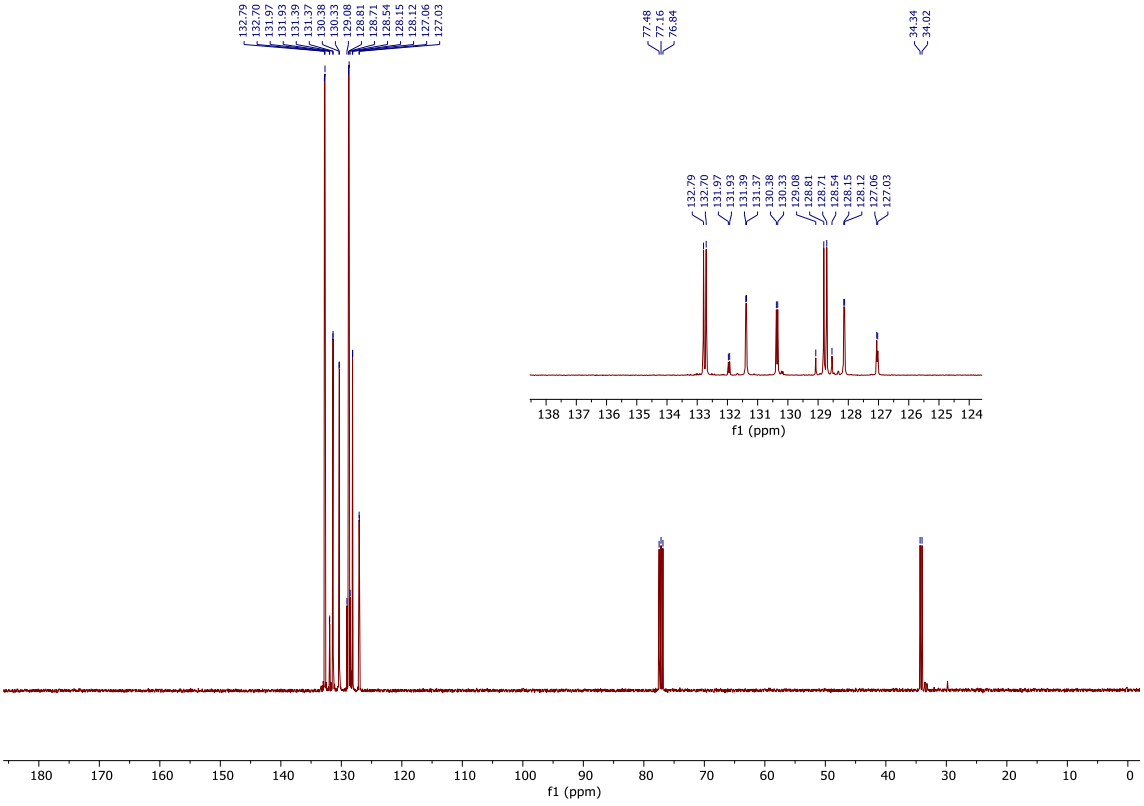
Benzyldiphenylphosphine borane adduct (**2a**) – ^{1}H NMR spectrum ($CDCl_3$)



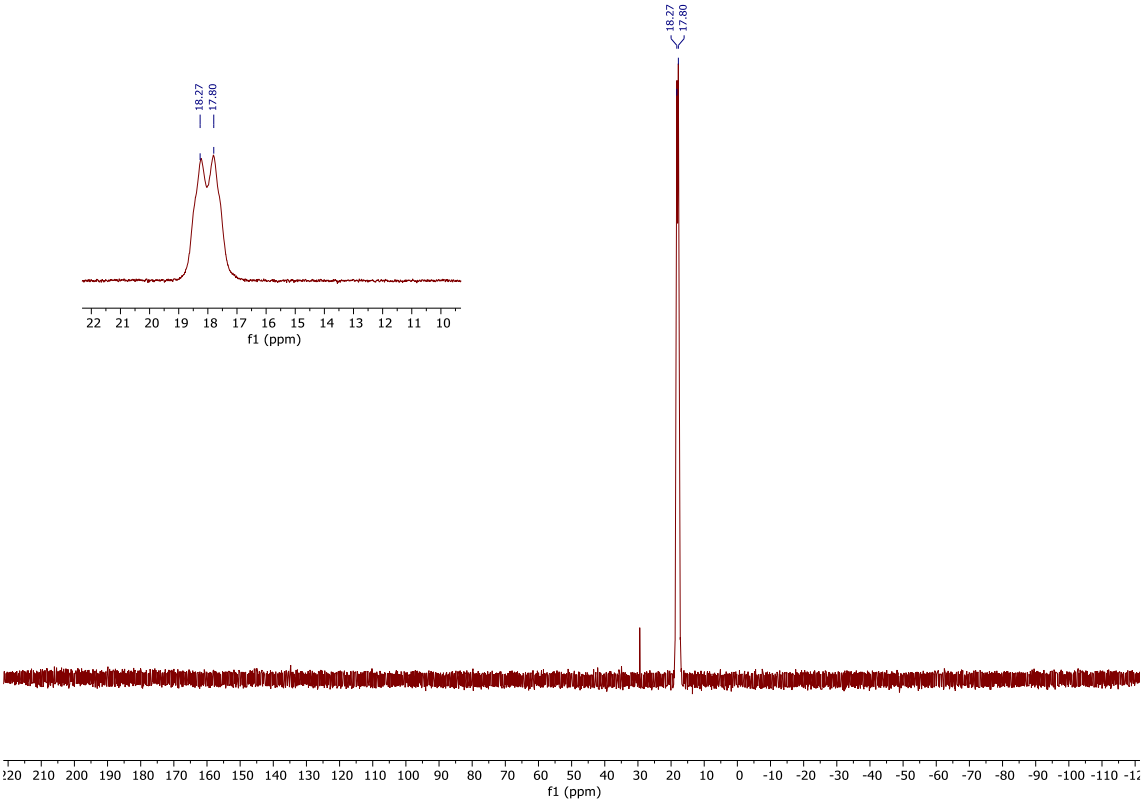
Benzyldiphenylphosphine borane adduct (**2a**) – ^{11}B NMR spectrum ($CDCl_3$)



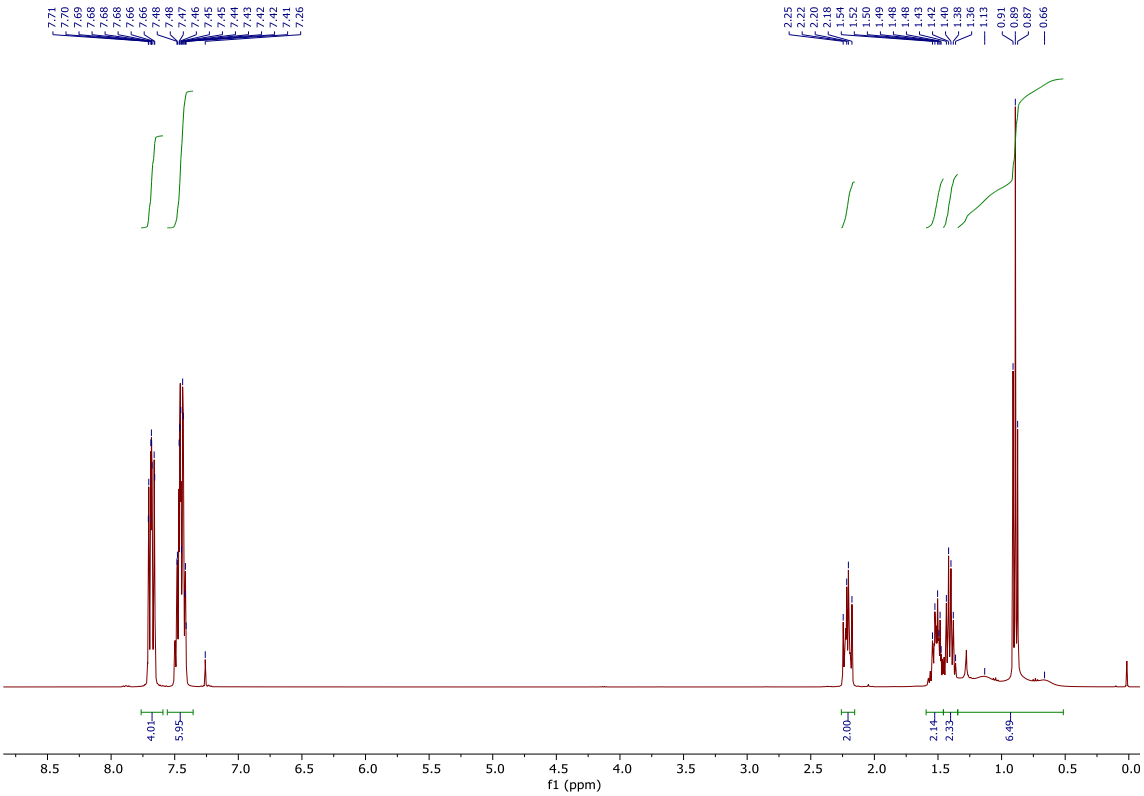
Benzyldiphenylphosphine borane adduct (**2a**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



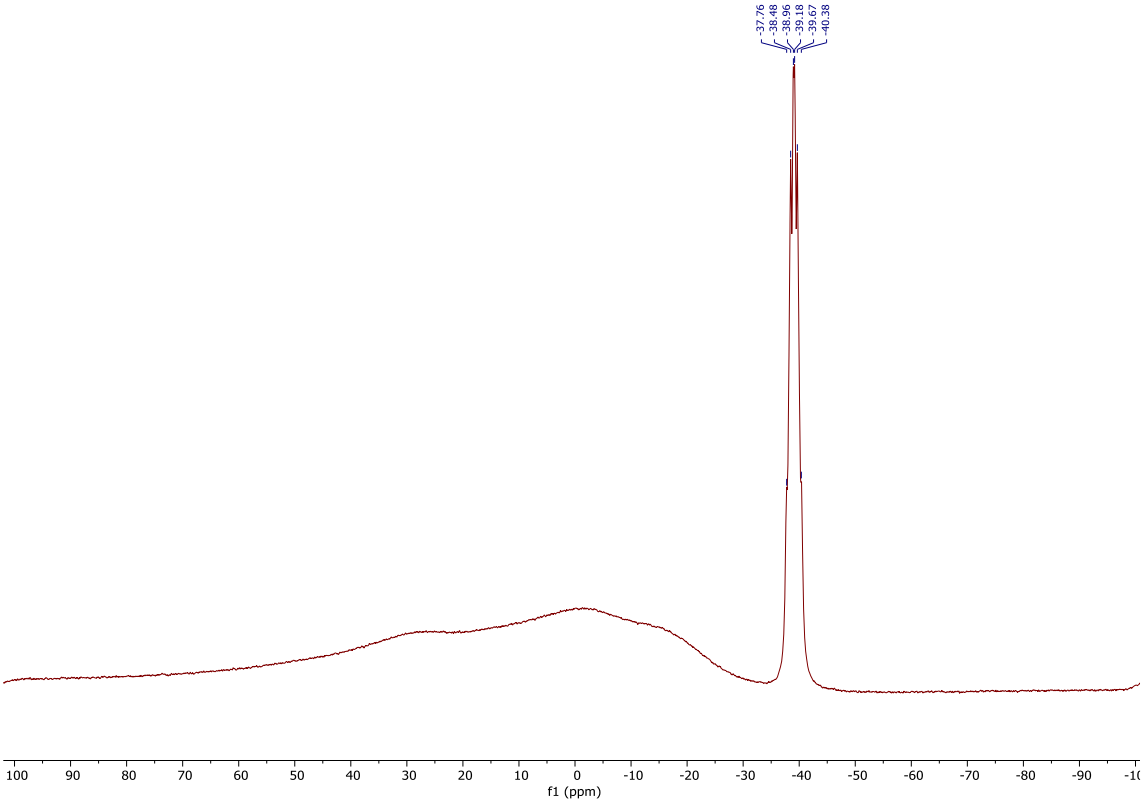
Benzyldiphenylphosphine borane adduct (**2a**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



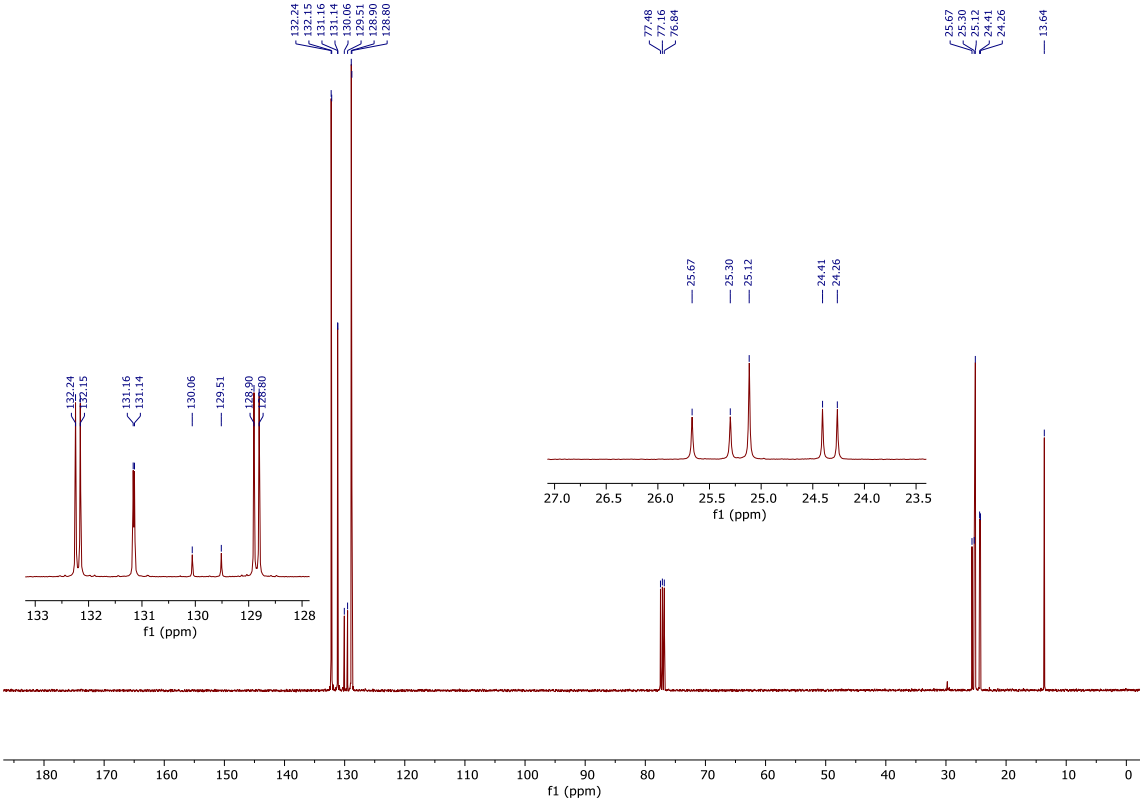
Butyldiphenylphosphine borane adduct (**2b**) – ^{1}H NMR spectrum ($CDCl_3$)



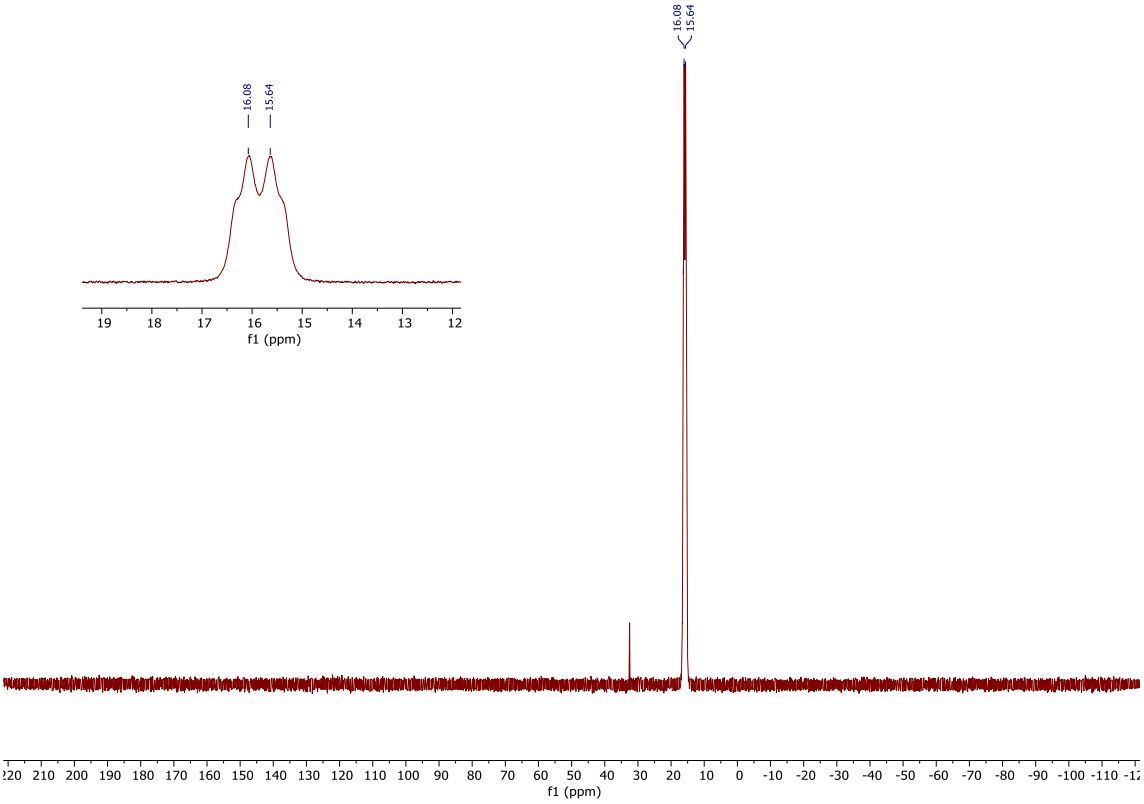
Butyldiphenylphosphine borane adduct (**2b**) – ^{11}B NMR spectrum ($CDCl_3$)



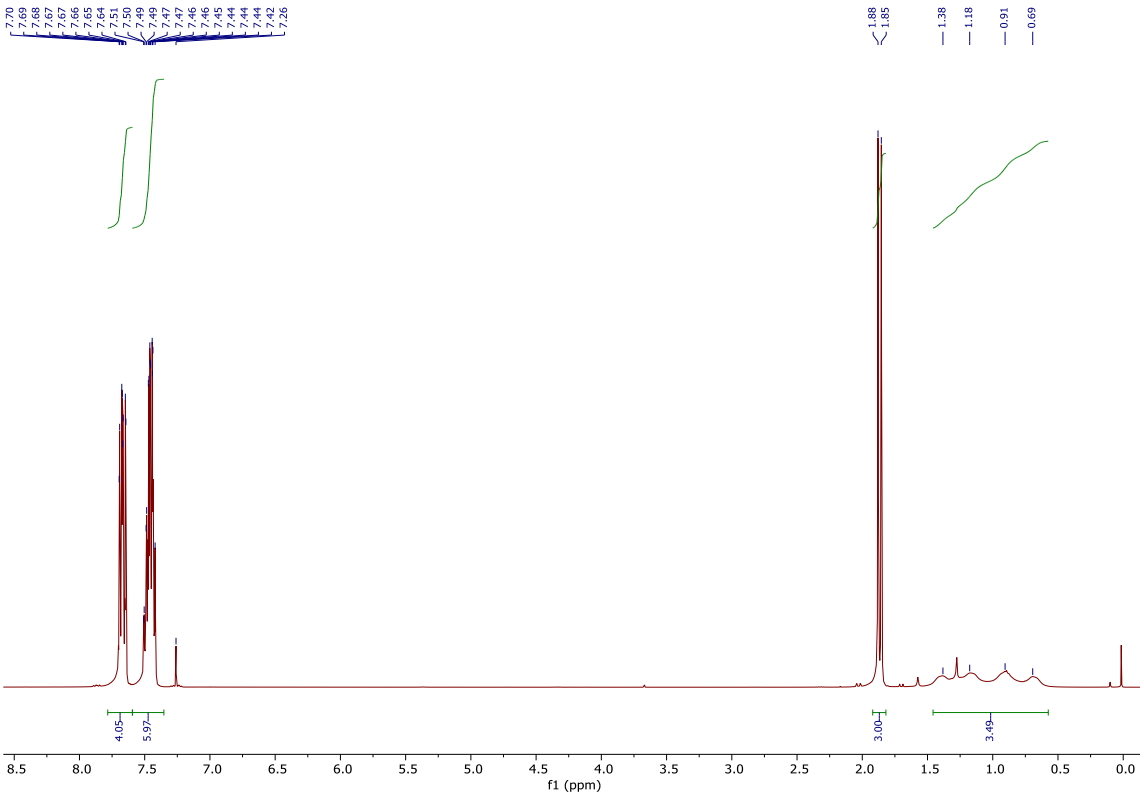
Butyldiphenylphosphine borane adduct (**2b**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



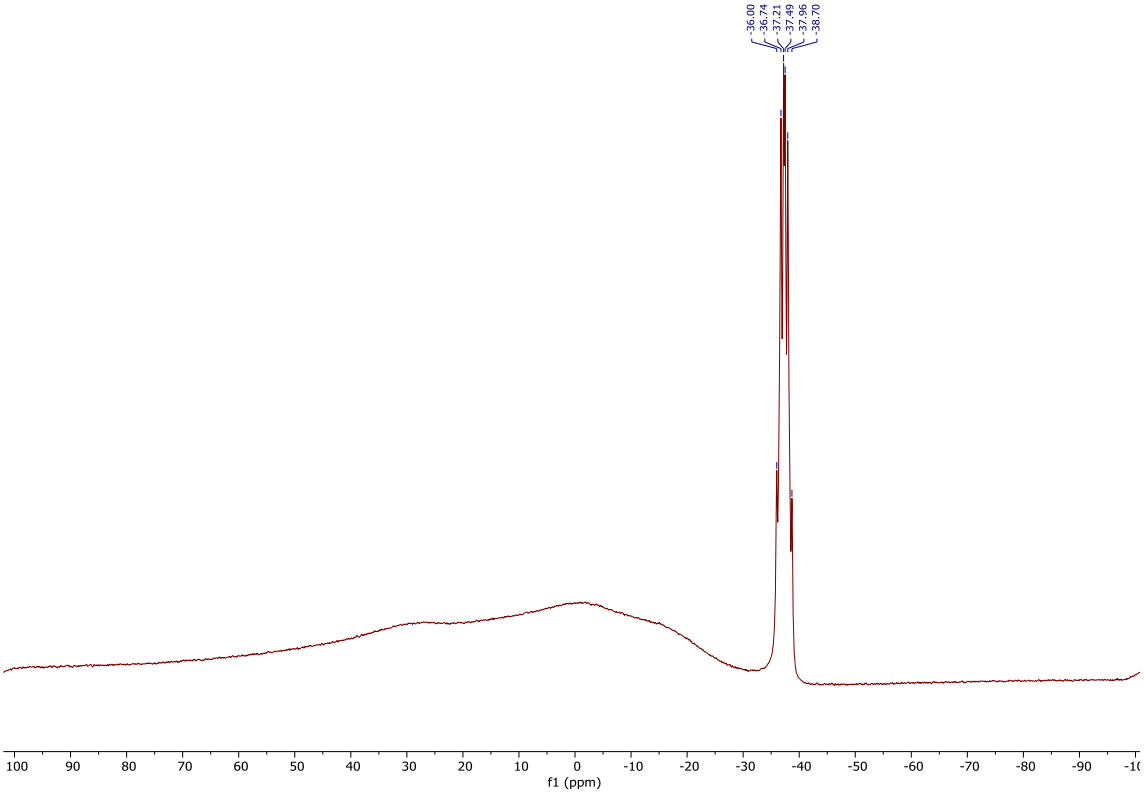
Butyldiphenylphosphine borane adduct (**2b**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



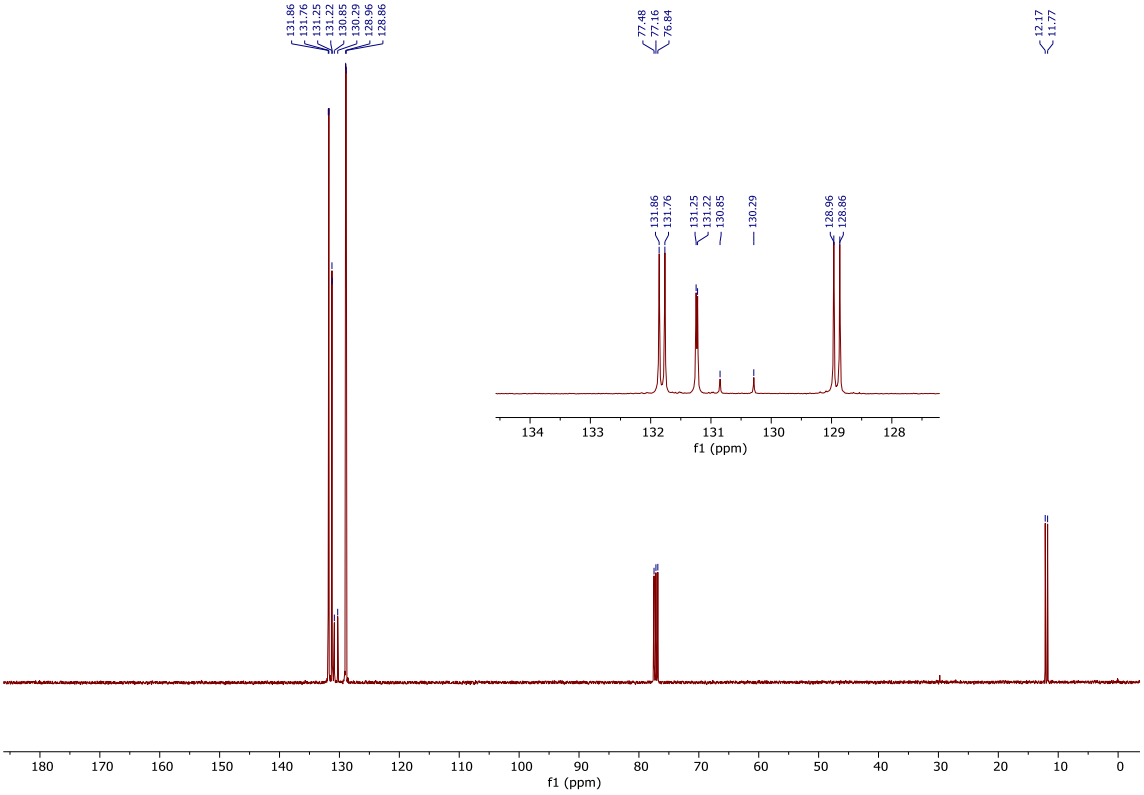
Methyldiphenylphosphine borane adduct (**2c**) – ^{1}H NMR spectrum ($CDCl_3$)



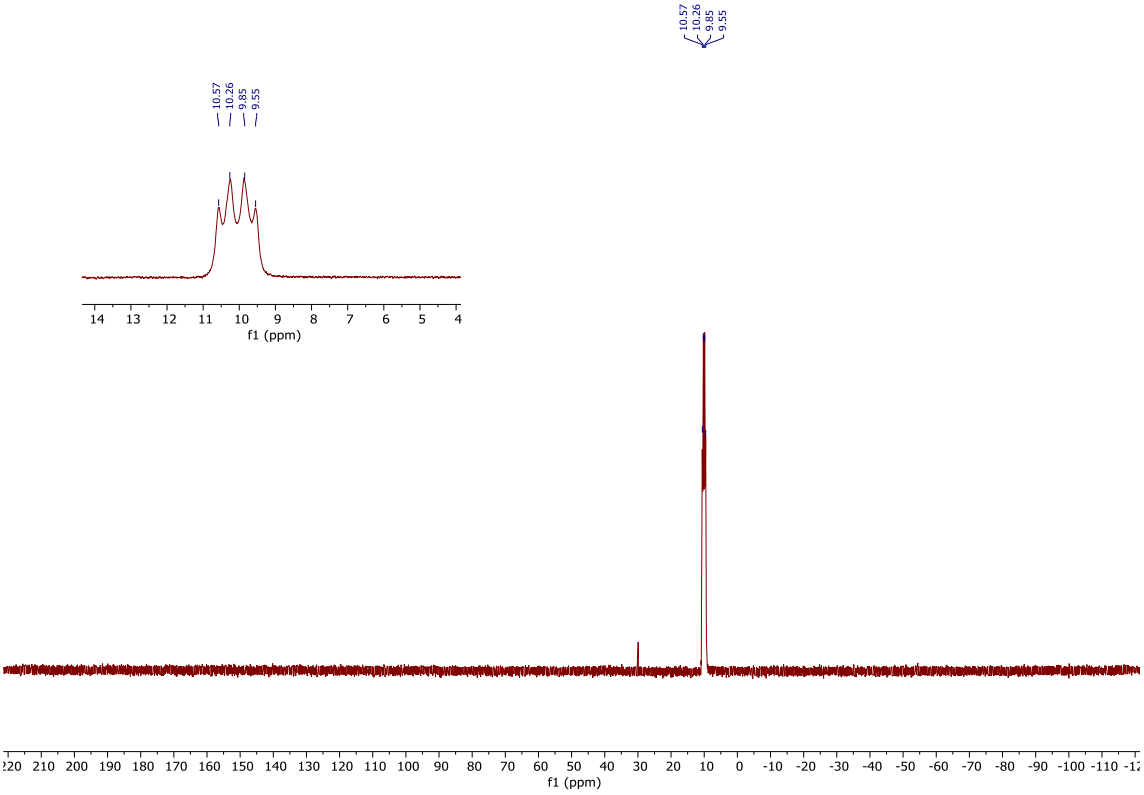
Methyldiphenylphosphine borane adduct (**2c**) – ^{11}B NMR spectrum ($CDCl_3$)



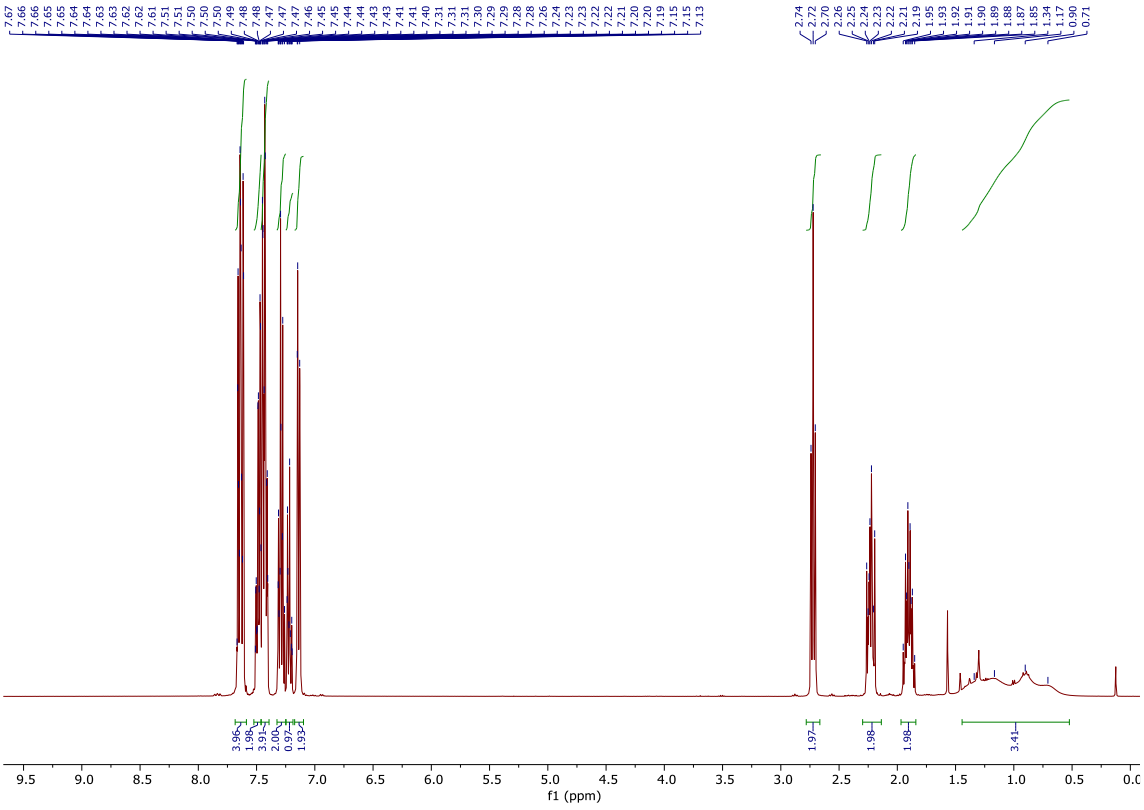
Methyldiphenylphosphine borane adduct (**2c**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



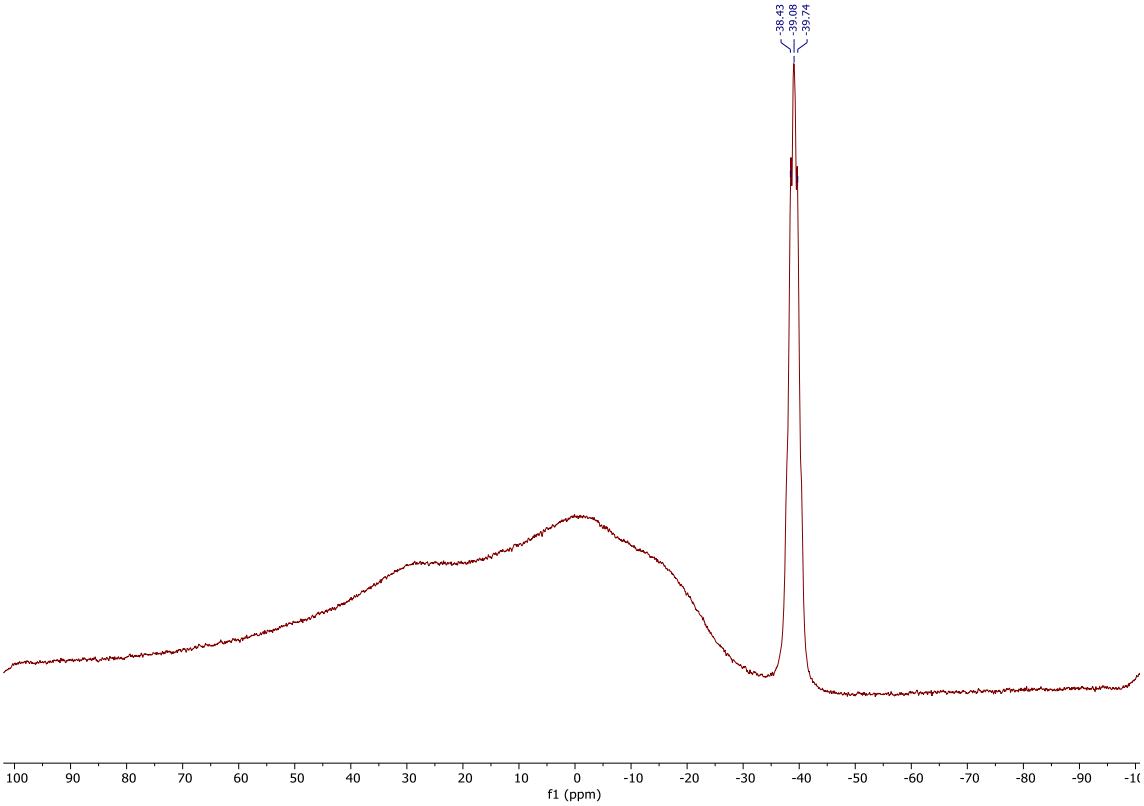
Methyldiphenylphosphine borane adduct (**2c**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



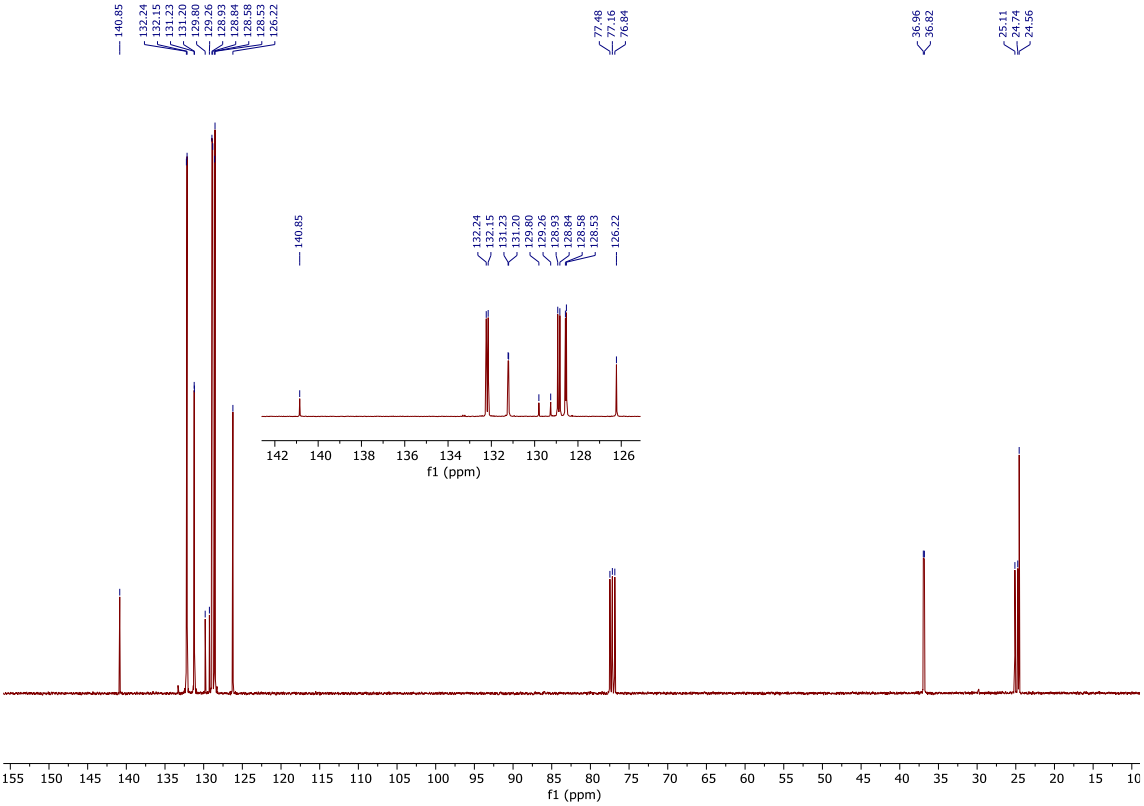
Diphenyl(3-phenylpropyl)phosphine borane adduct (**2d**) – ^{1}H NMR spectrum ($CDCl_3$)



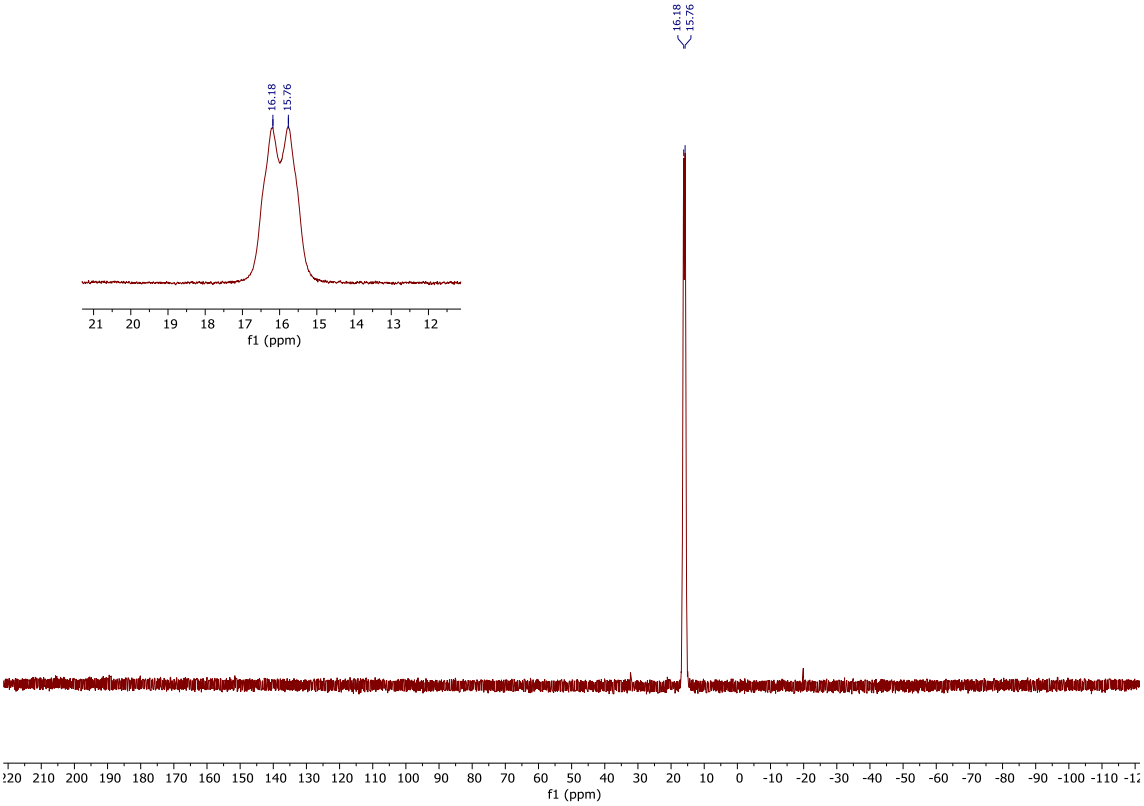
Diphenyl(3-phenylpropyl)phosphine borane adduct (**2d**) – ^{11}B NMR spectrum ($CDCl_3$)



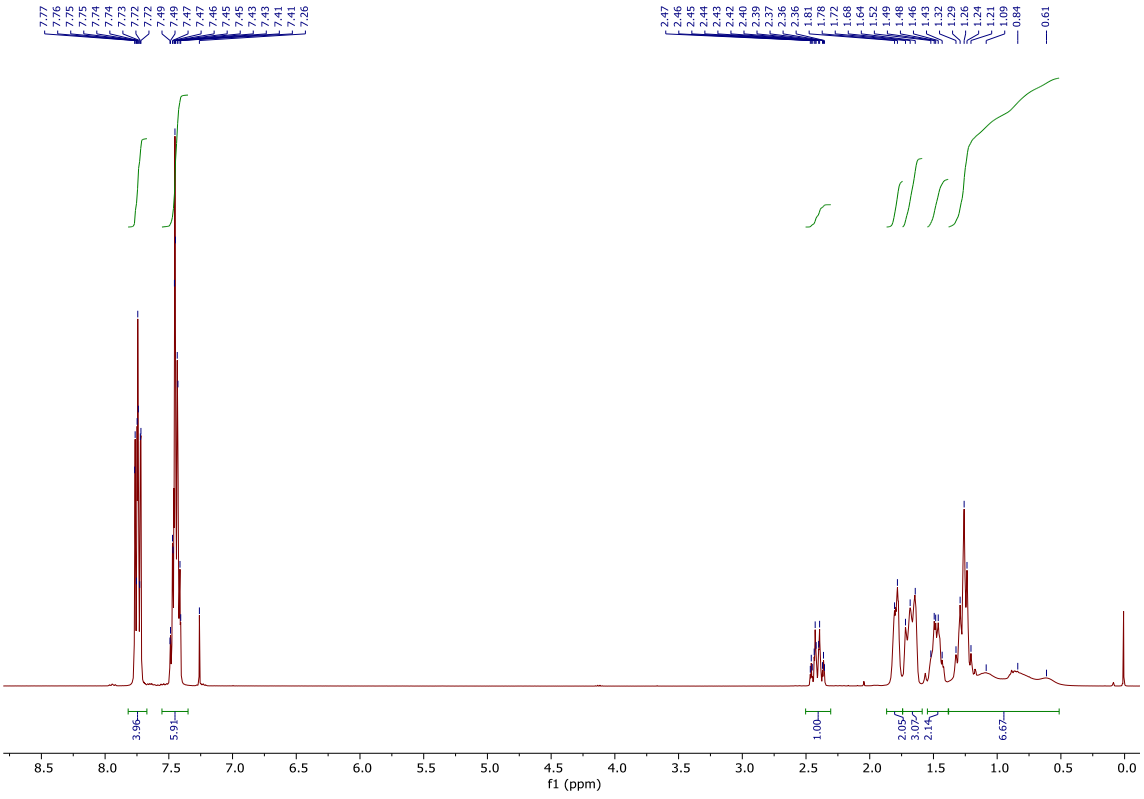
Diphenyl(3-phenylpropyl)phosphine borane adduct (**2d**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



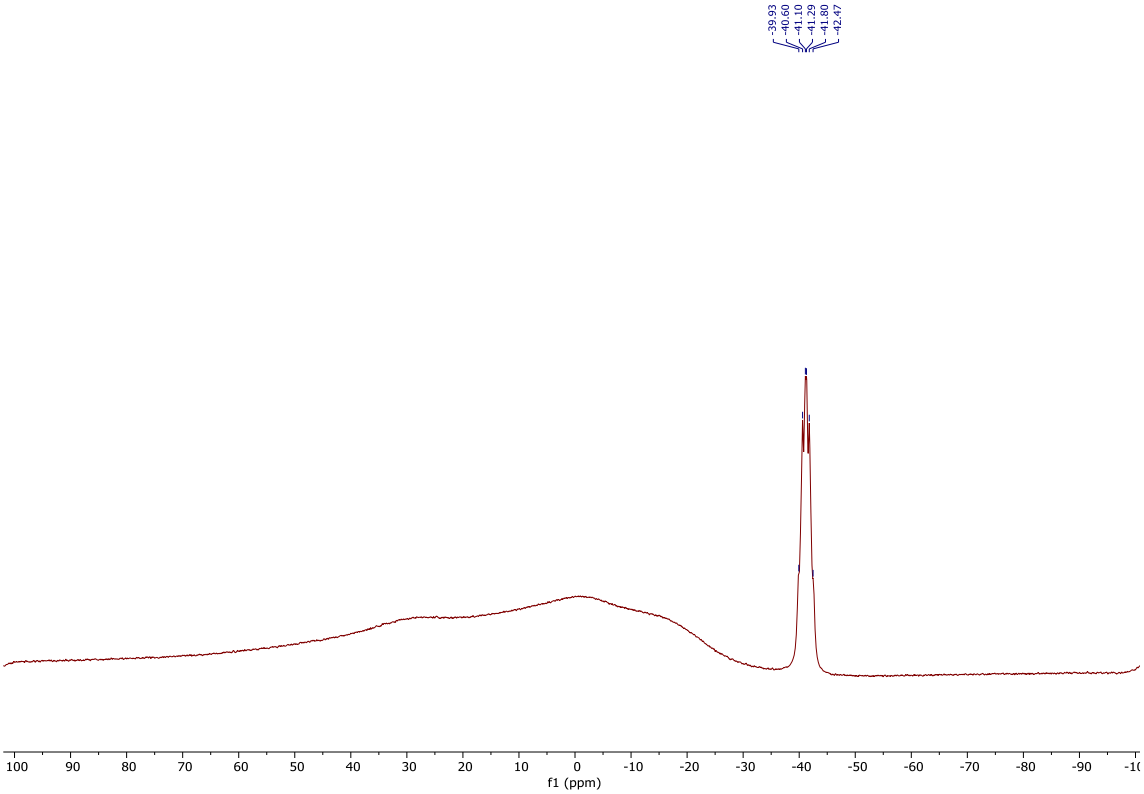
Diphenyl(3-phenylpropyl)phosphine borane adduct (**2d**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



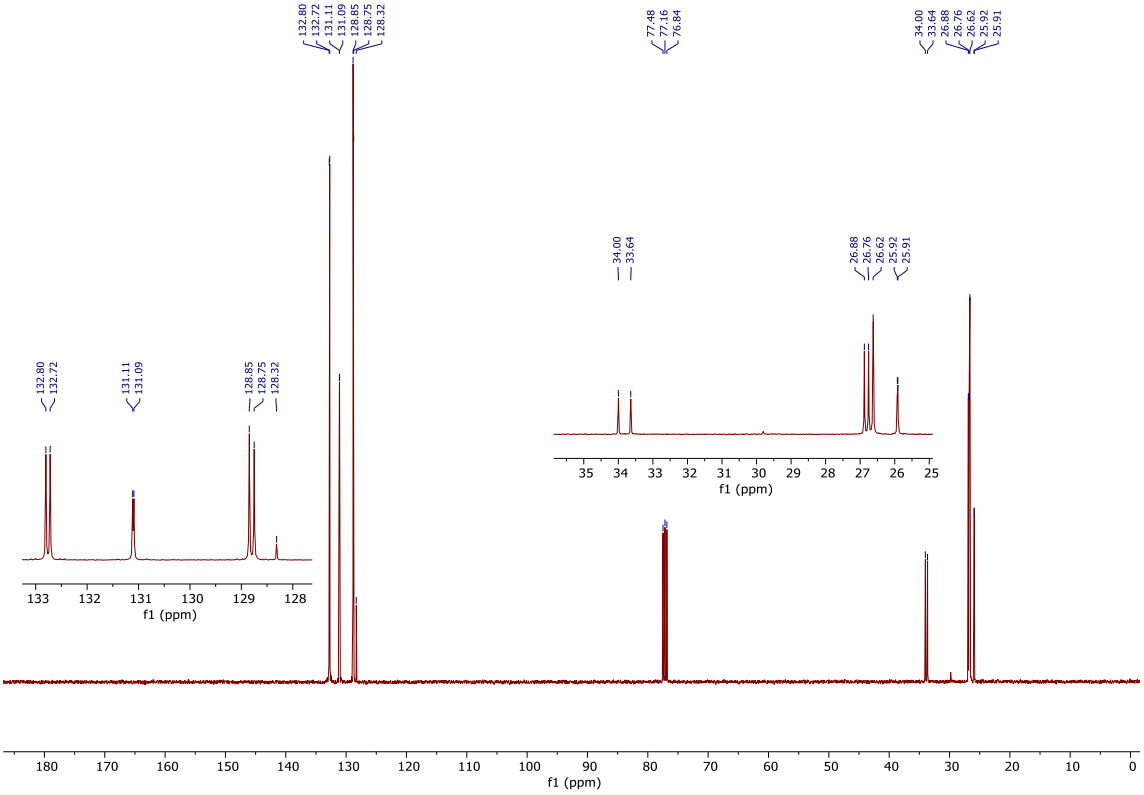
Cyclohexyldiphenylphosphine borane adduct (**2e**) – ^{1}H NMR spectrum ($CDCl_3$)



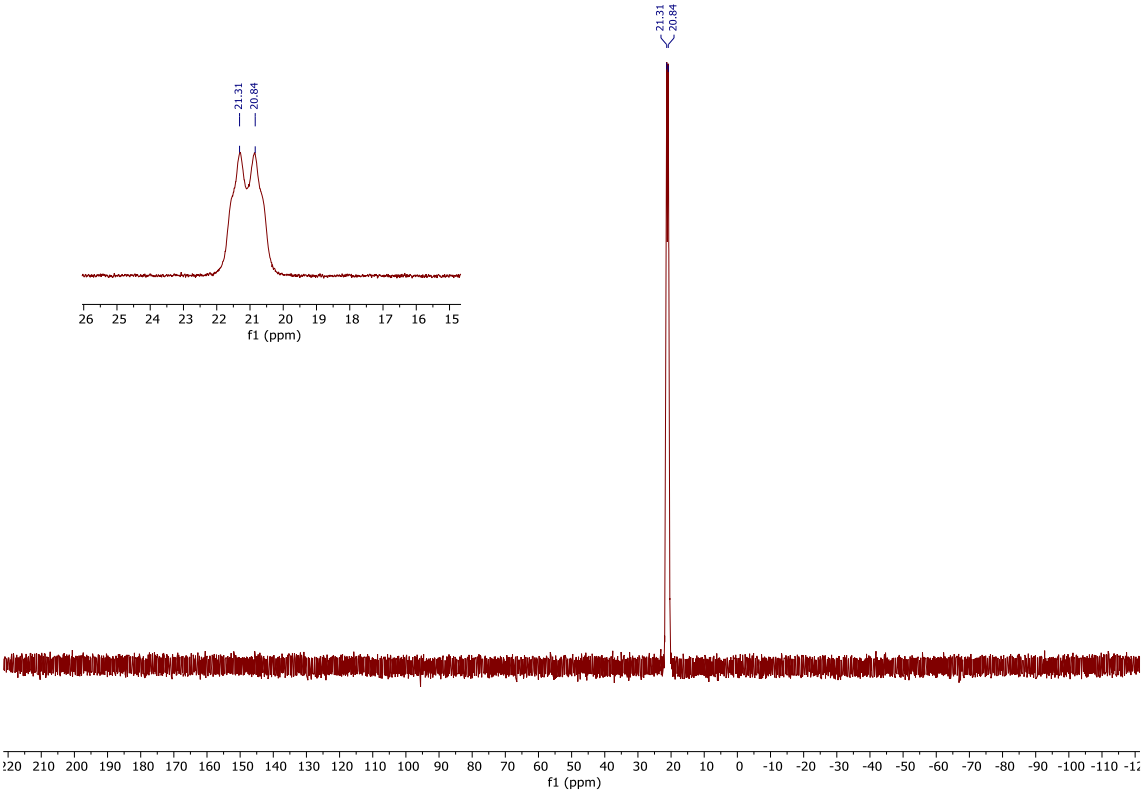
Cyclohexyldiphenylphosphine borane adduct (**2e**) – ^{11}B NMR spectrum ($CDCl_3$)



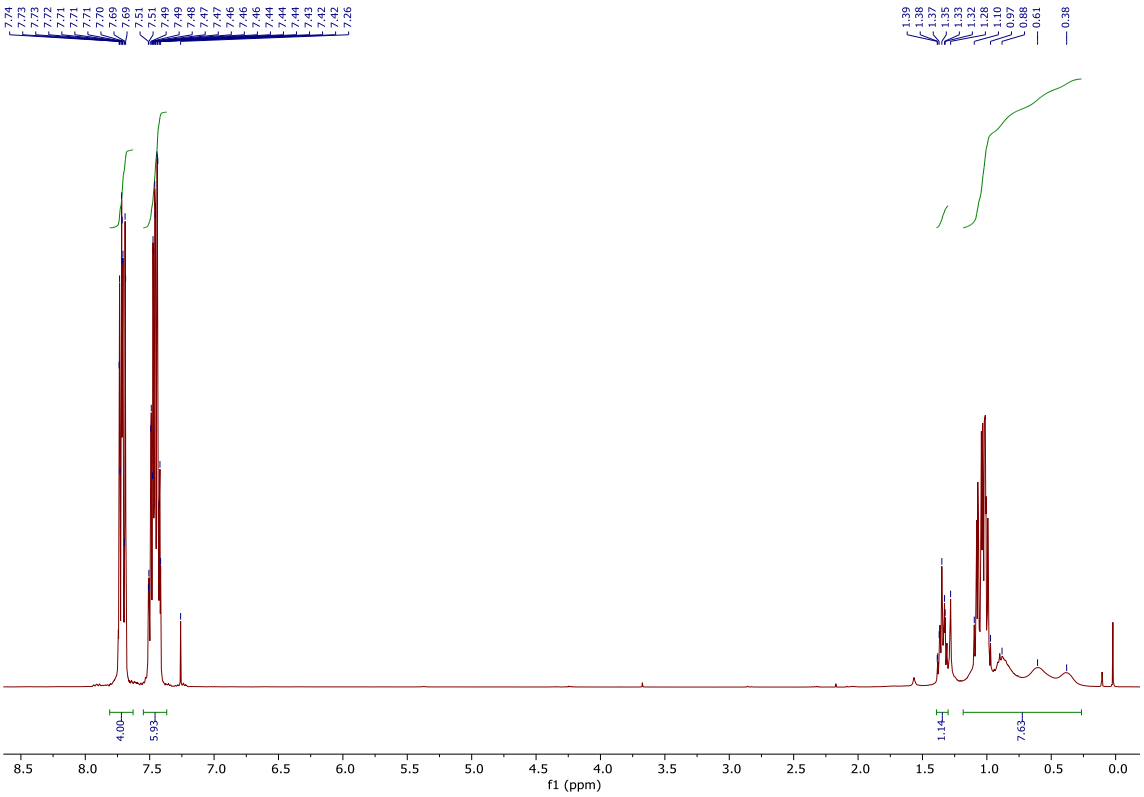
Cyclohexyldiphenylphosphine borane adduct (**2e**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



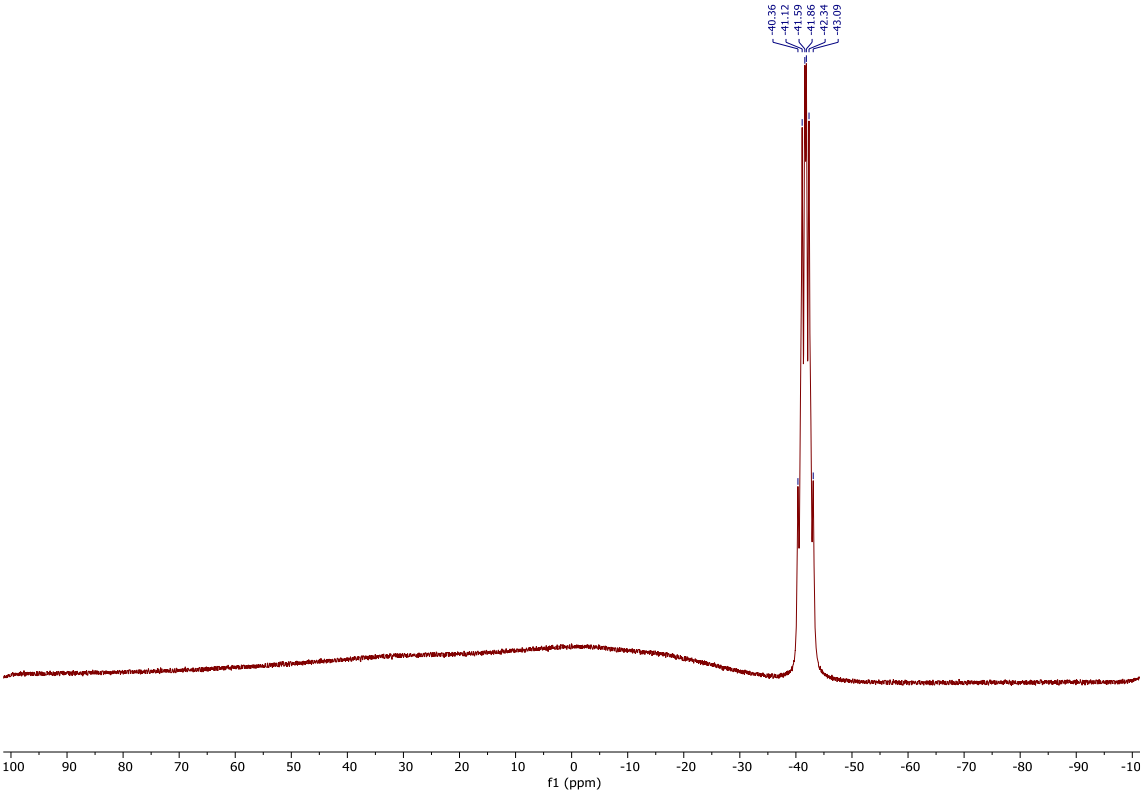
Cyclohexyldiphenylphosphine borane adduct (**2e**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



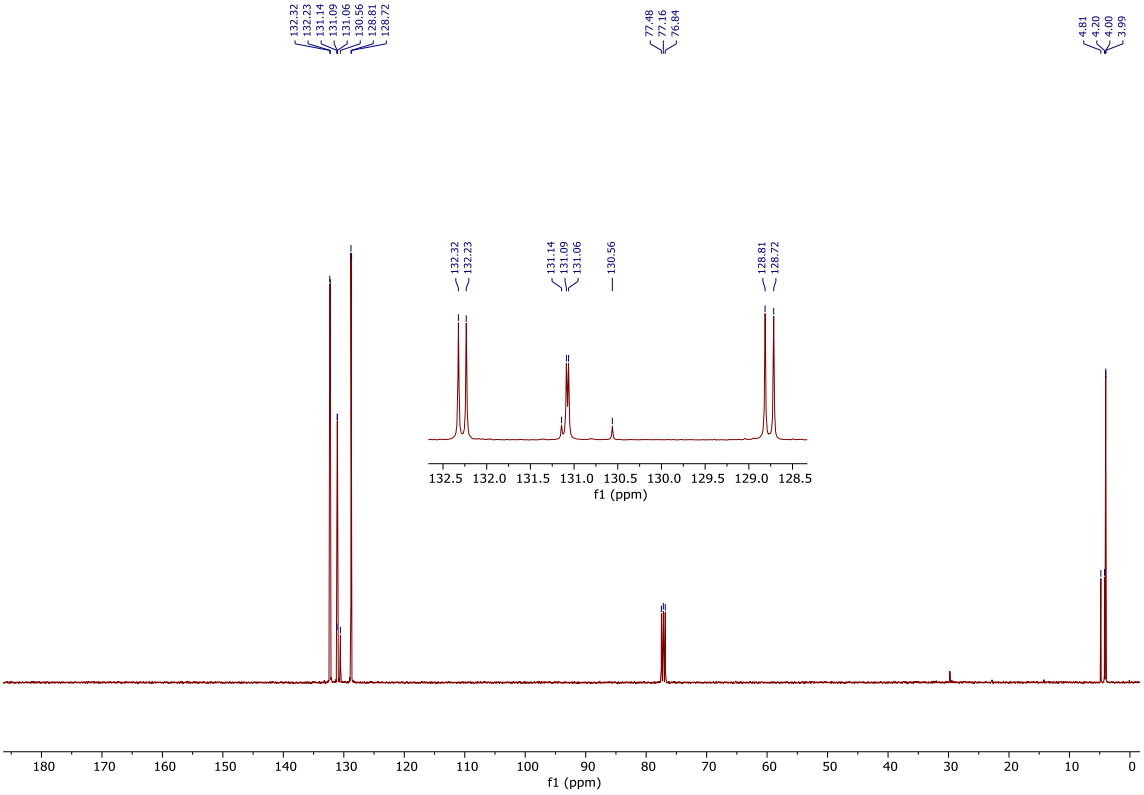
Cyclopropyldiphenylphosphine borane adduct (**2f**) – ^{1}H NMR spectrum ($CDCl_3$)



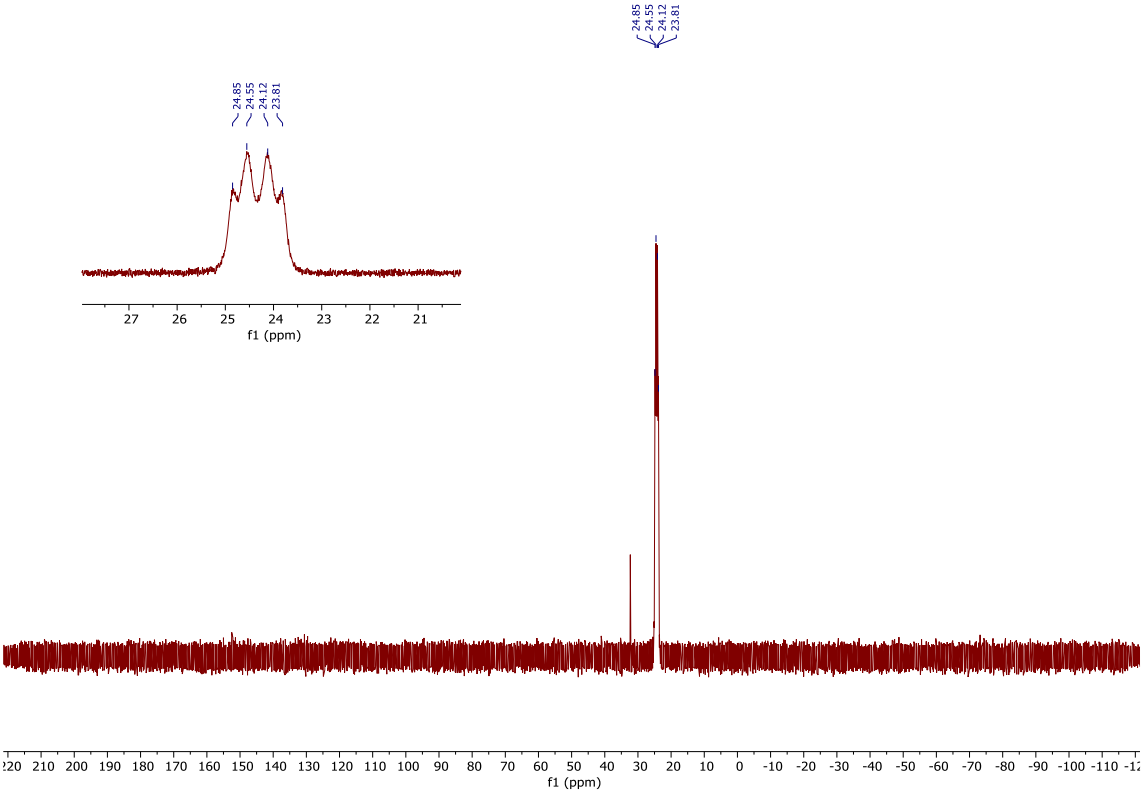
Cyclopropyldiphenylphosphine borane adduct (**2f**) – ^{11}B NMR spectrum ($CDCl_3$)



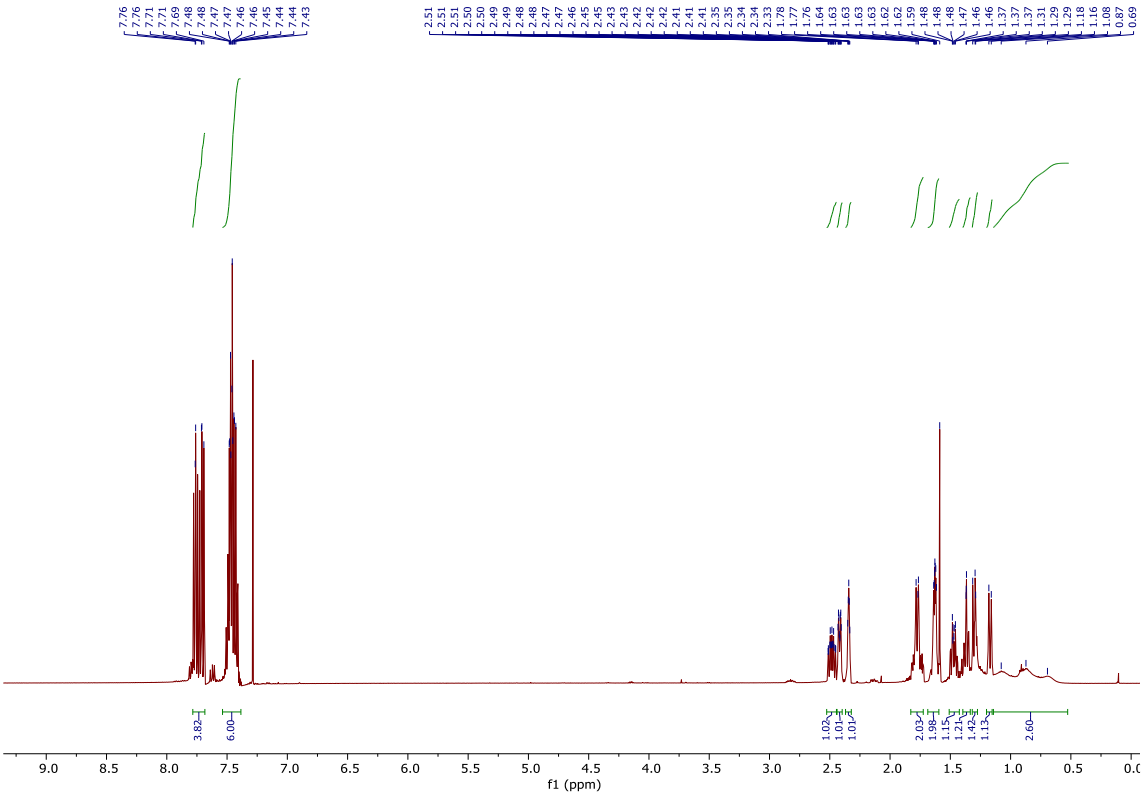
Cyclopropyldiphenylphosphine borane adduct (**2f**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



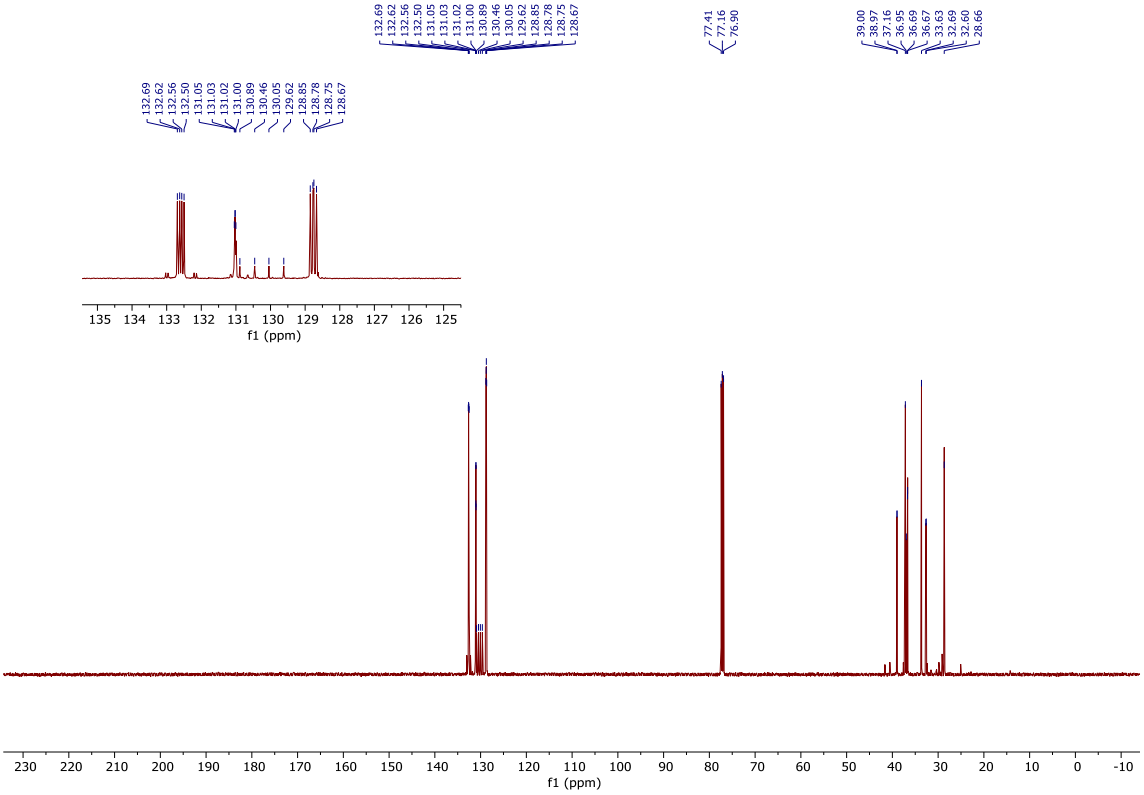
Cyclopropyldiphenylphosphine borane adduct (**2f**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



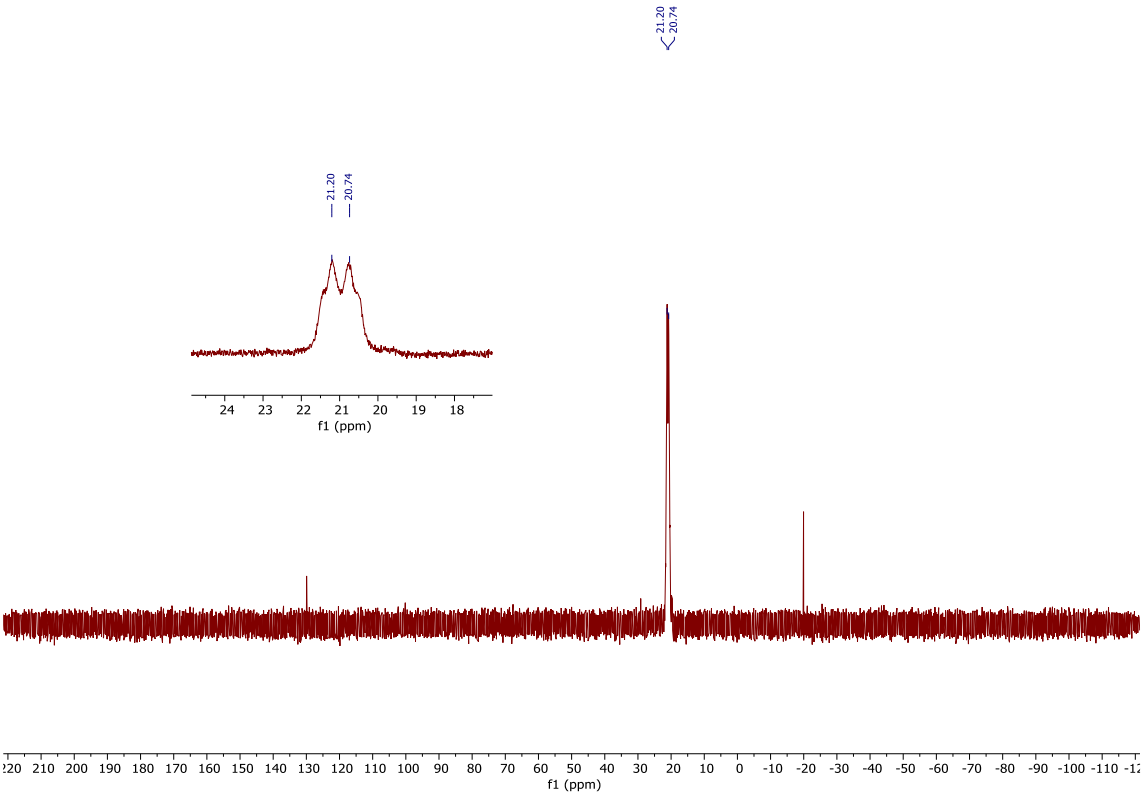
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – ^{1}H NMR spectrum ($CDCl_3$)



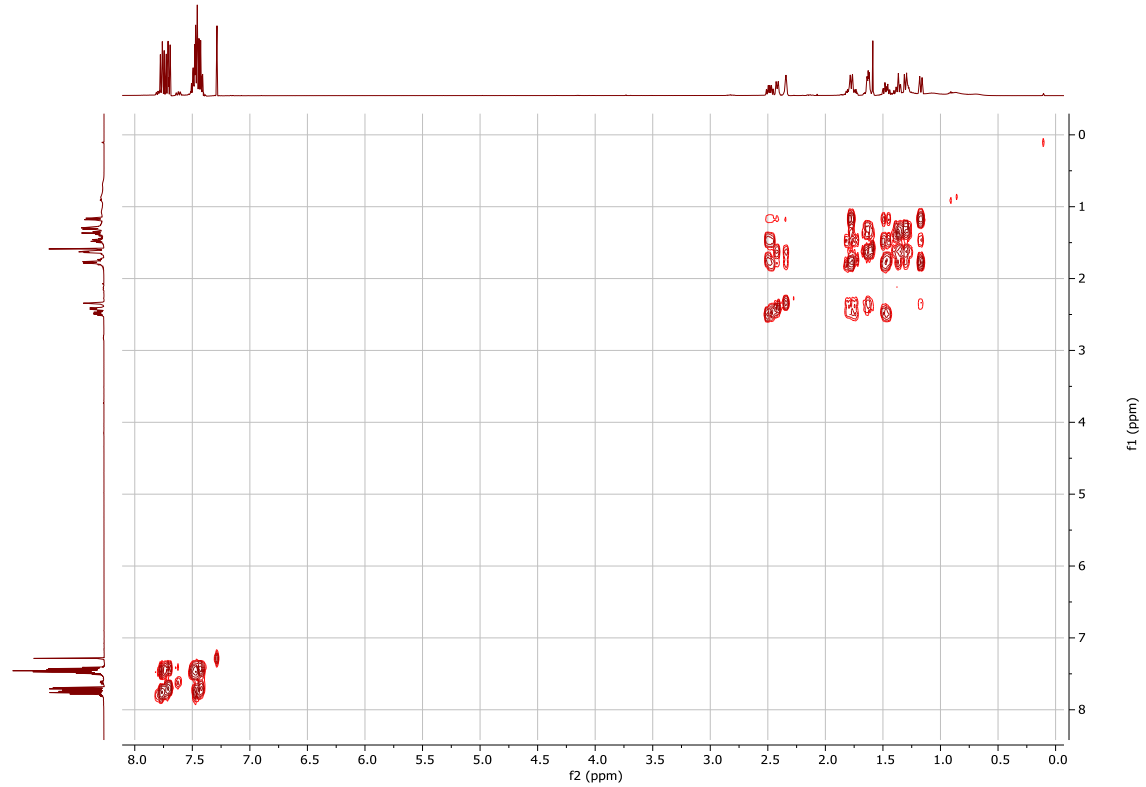
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



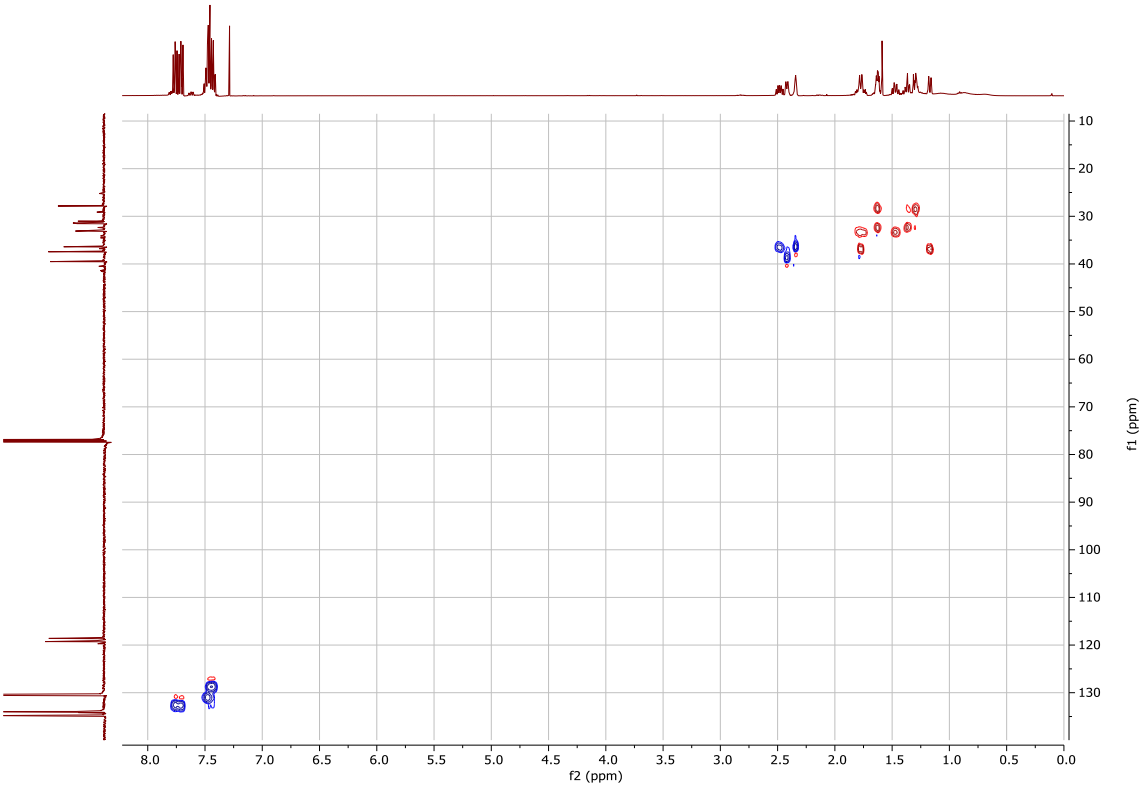
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



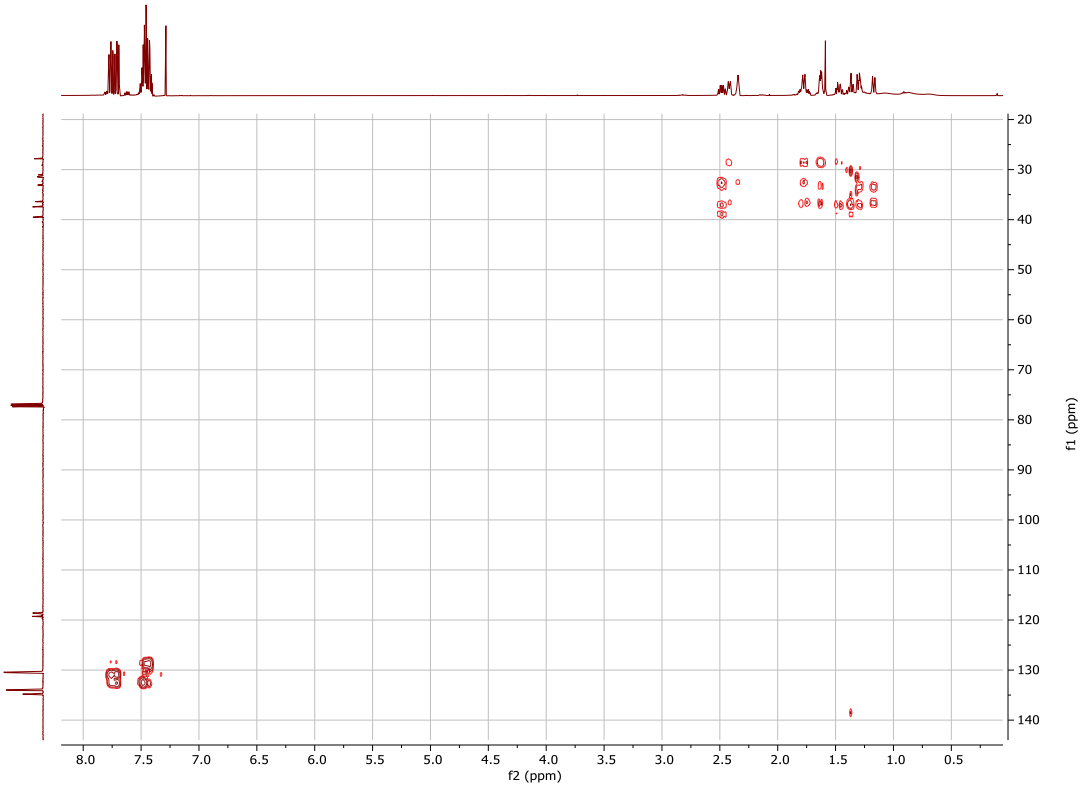
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – COSY NMR spectrum ($CDCl_3$)



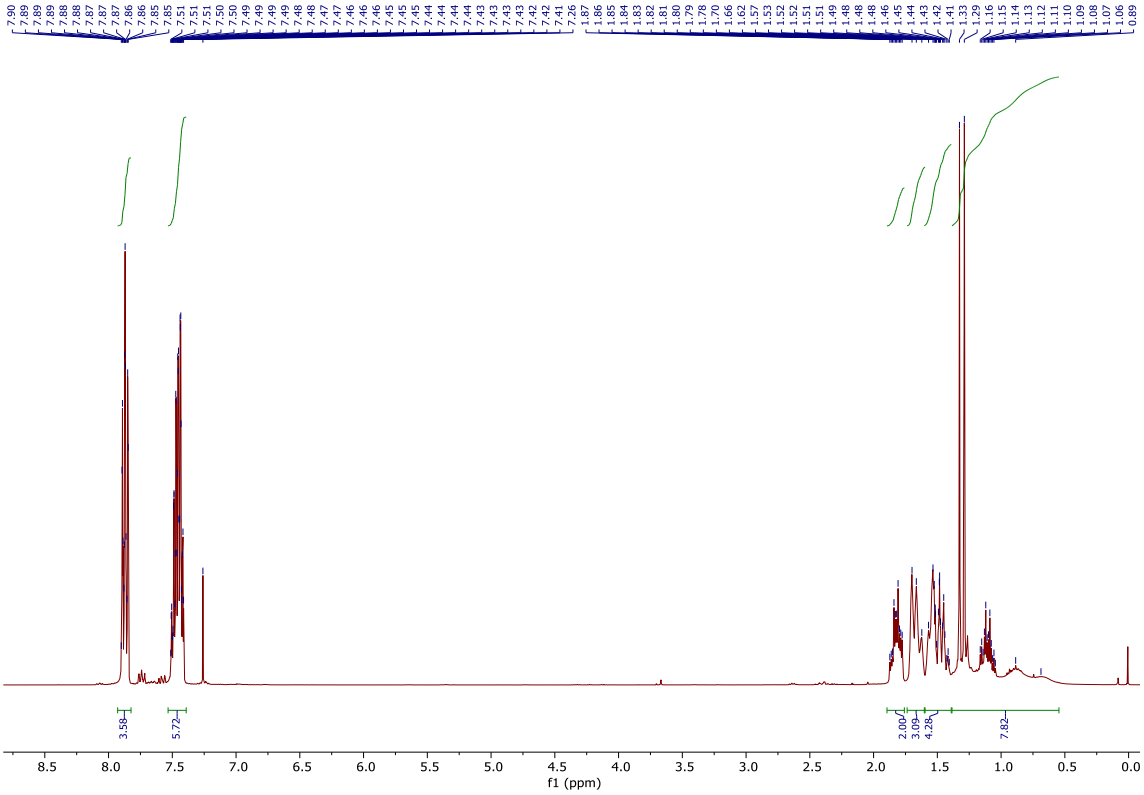
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – HSQC NMR spectrum ($CDCl_3$)



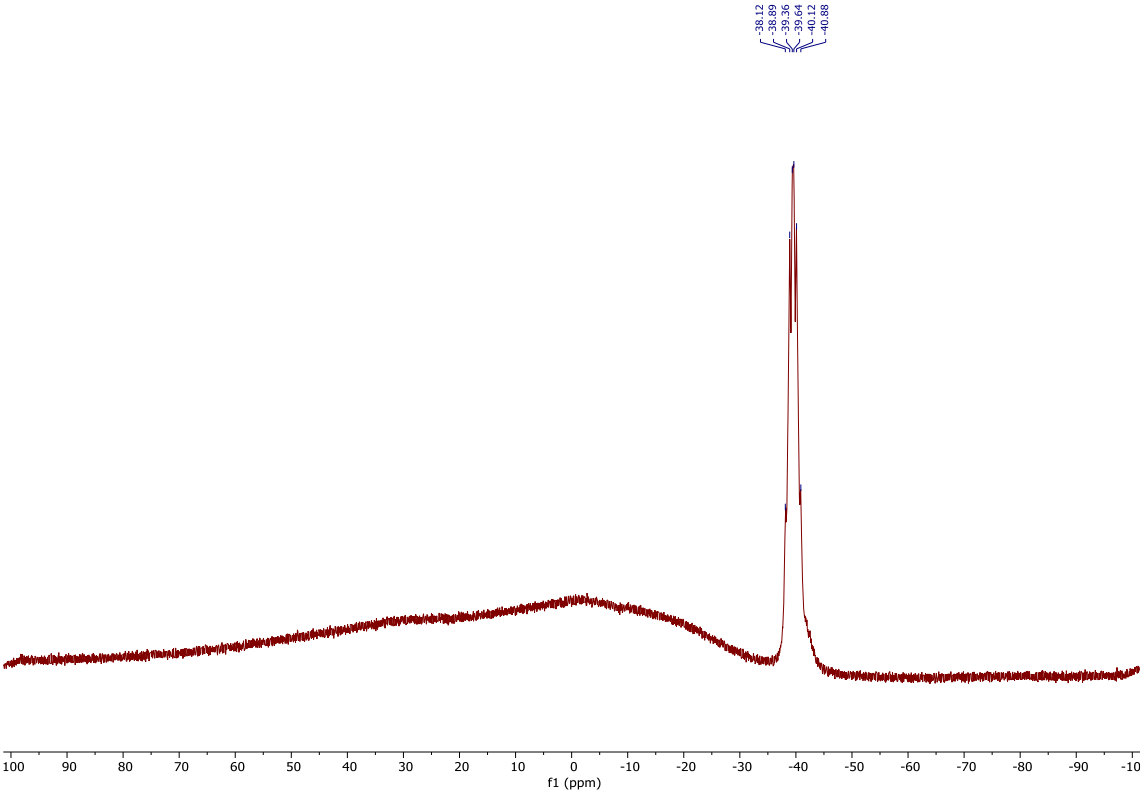
(2-Norbornyl)diphenylphosphine borane adduct (**2g**) – HMBC NMR spectrum ($CDCl_3$)



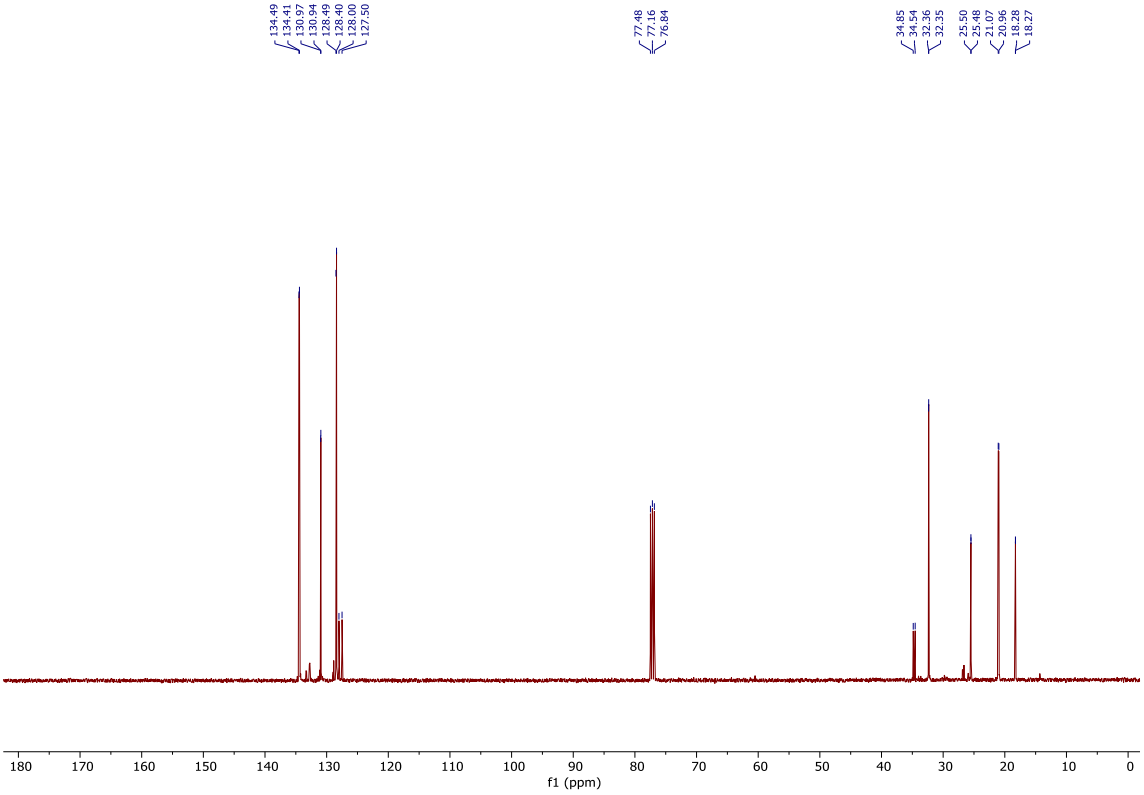
(1-Methylcyclohexyl)diphenylphosphine borane adduct (**2h**) – ^1H NMR spectrum ($CDCl_3$)



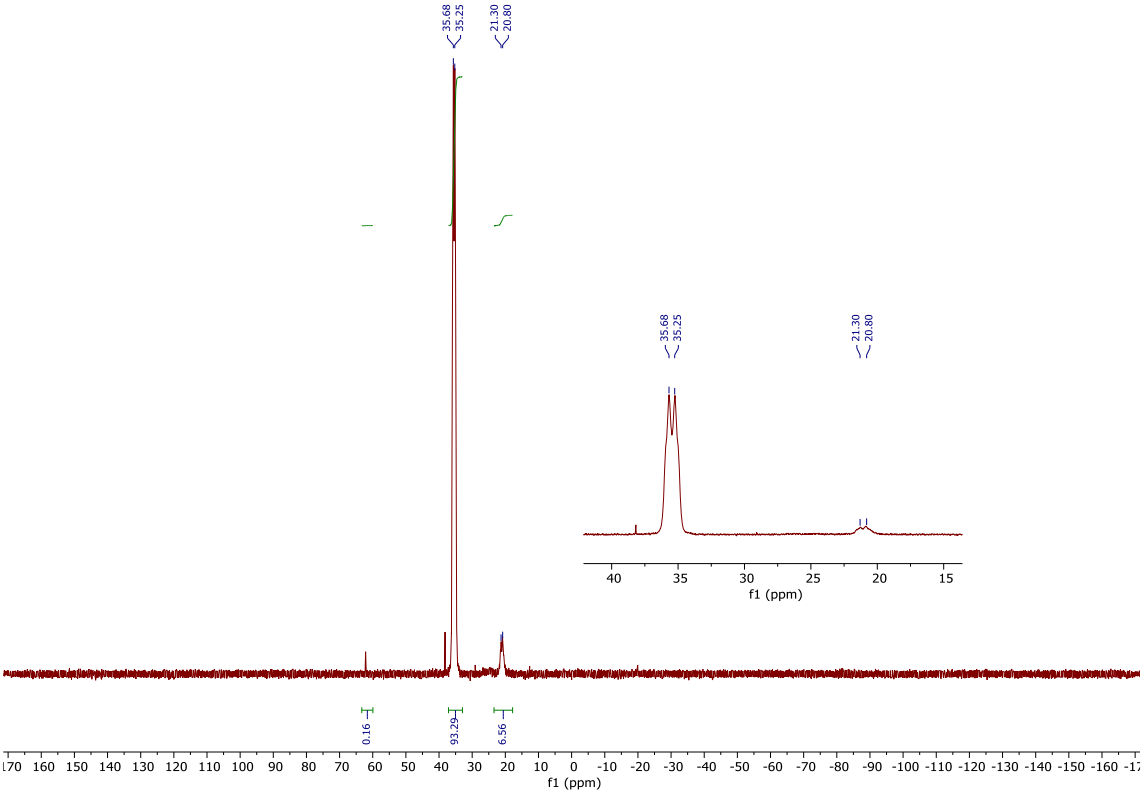
(1-Methylcyclohexyl)diphenylphosphine borane adduct (**2h**) – ^{11}B NMR spectrum ($CDCl_3$)



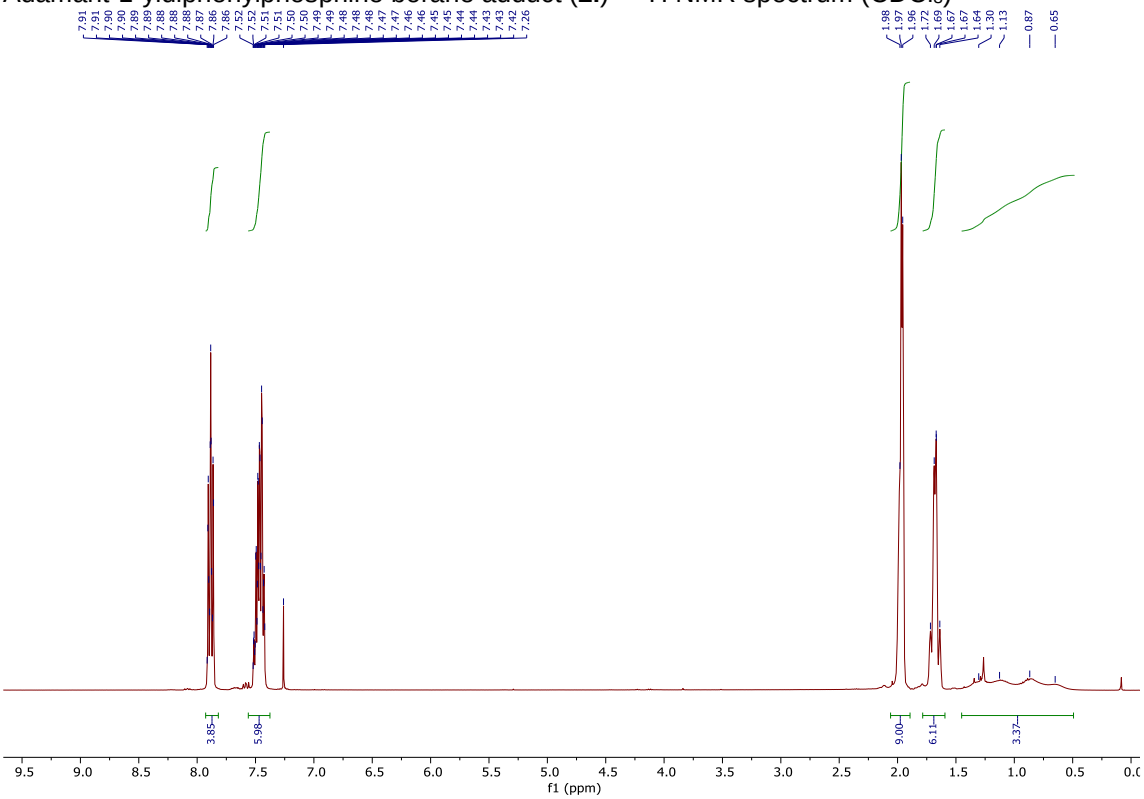
(1-Methylcyclohexyl)diphenylphosphine borane adduct (**2h**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



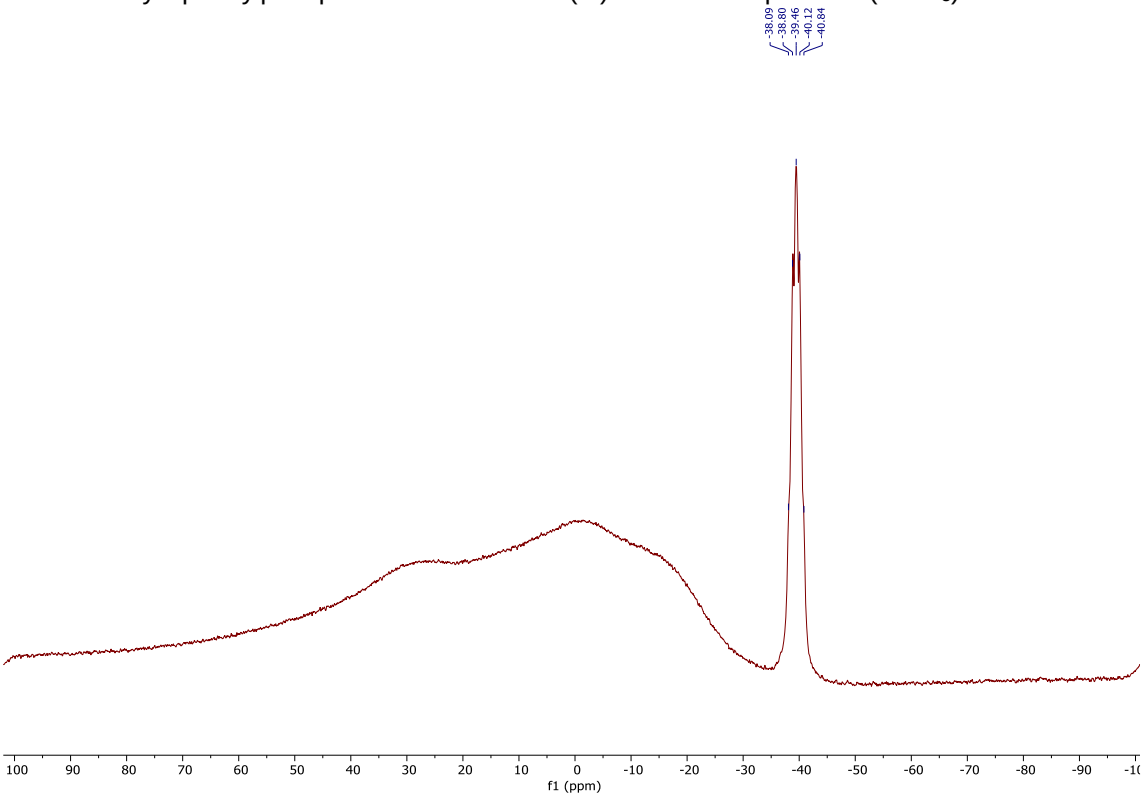
(1-Methylcyclohexyl)diphenylphosphine borane adduct (**2h**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



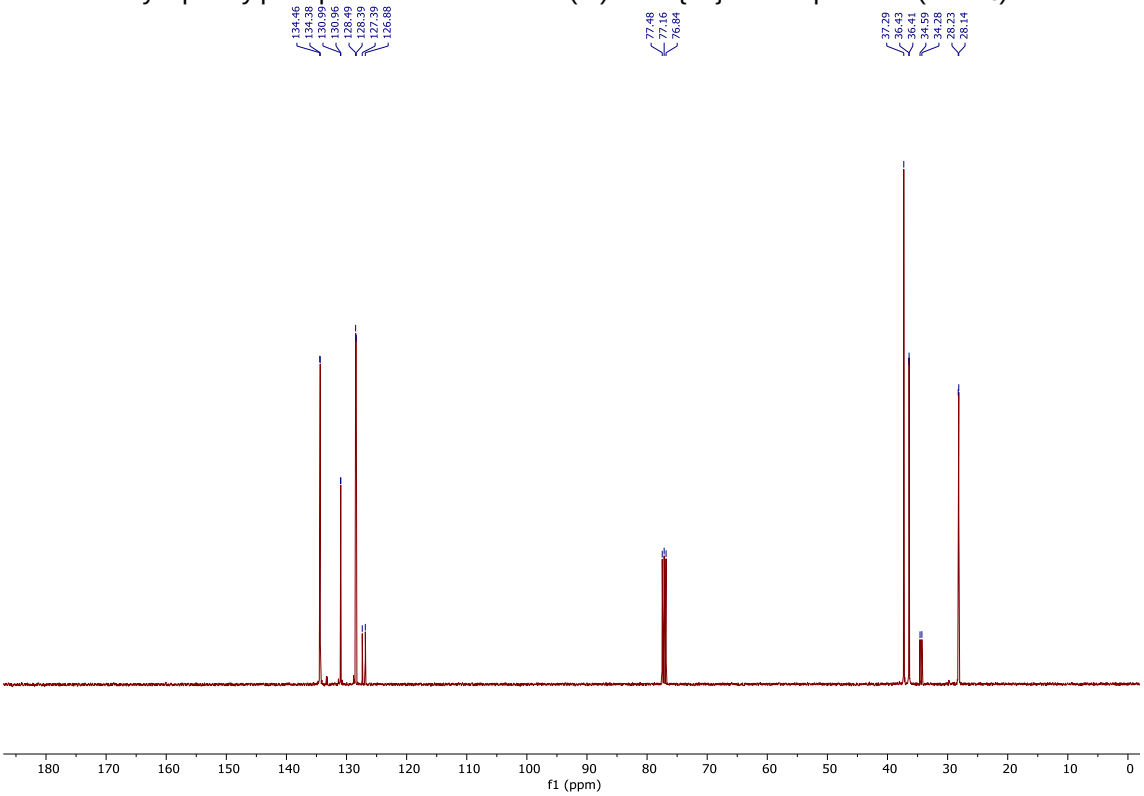
Adamant-1-yldiphenylphosphine borane adduct (**2i**) – ^{1}H NMR spectrum ($CDCl_3$)



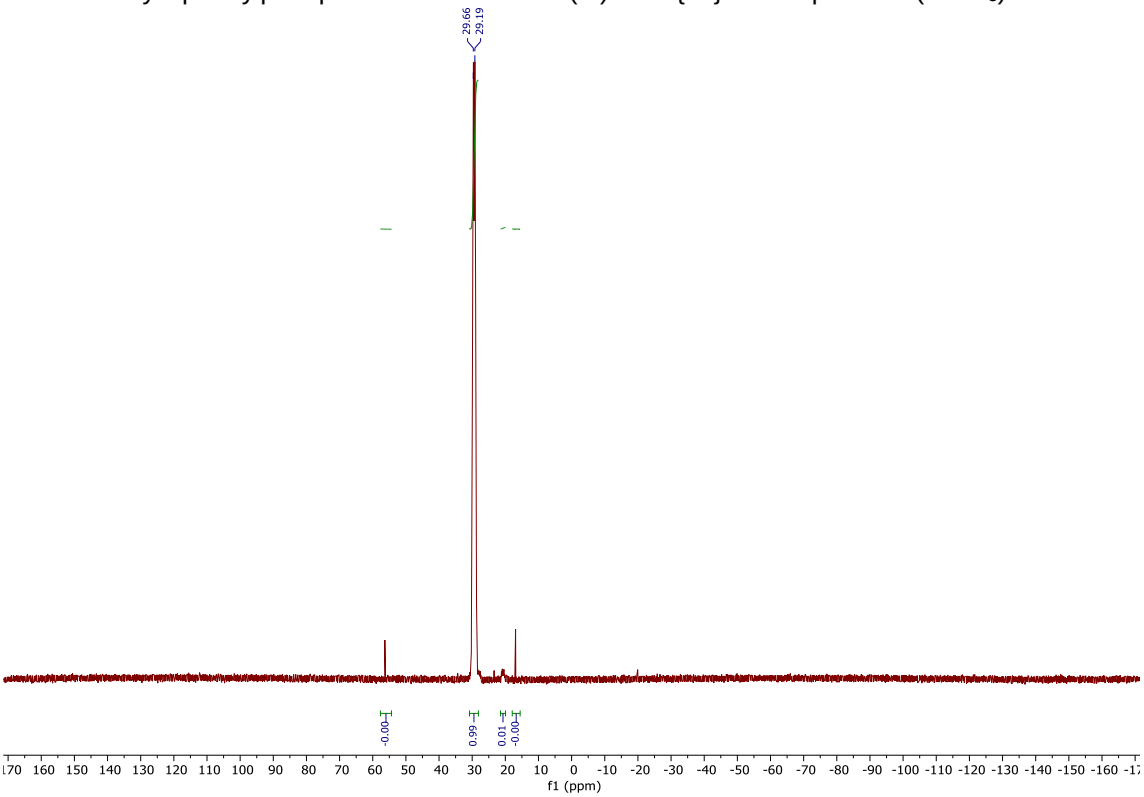
Adamant-1-yldiphenylphosphine borane adduct (**2i**) – ^{11}B NMR spectrum ($CDCl_3$)



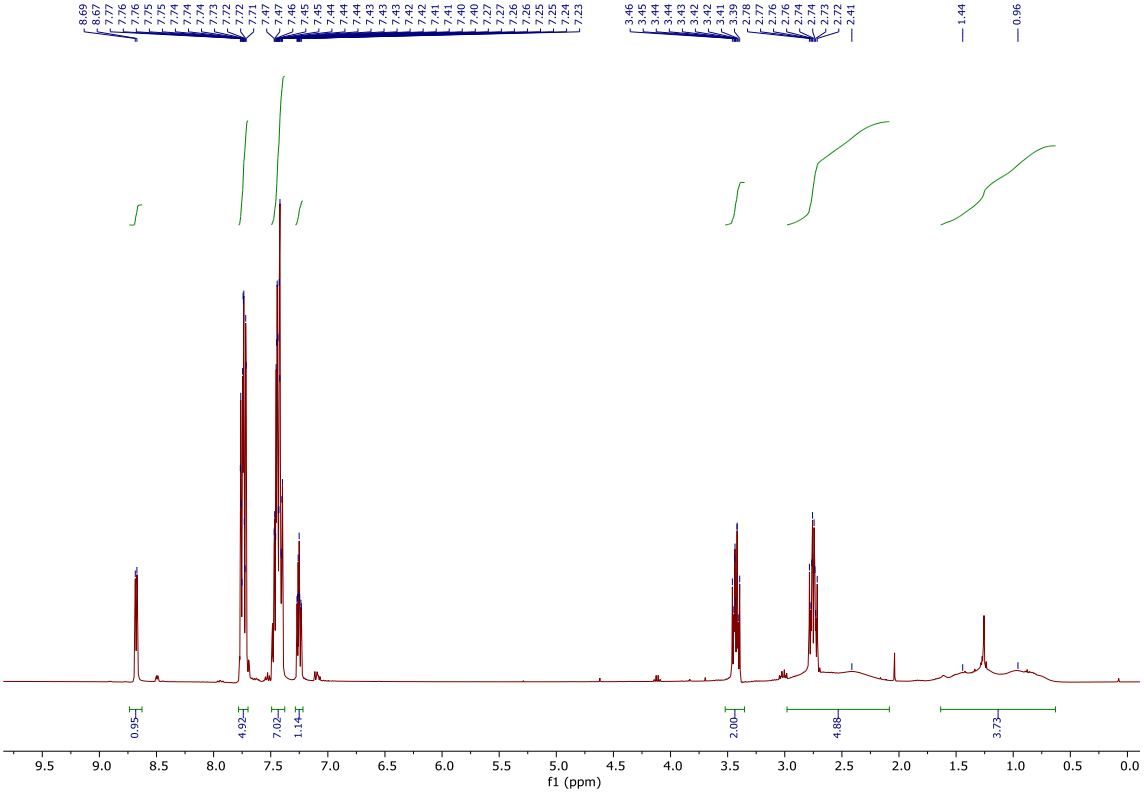
Adamant-1-yldiphenylphosphine borane adduct (**2i**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



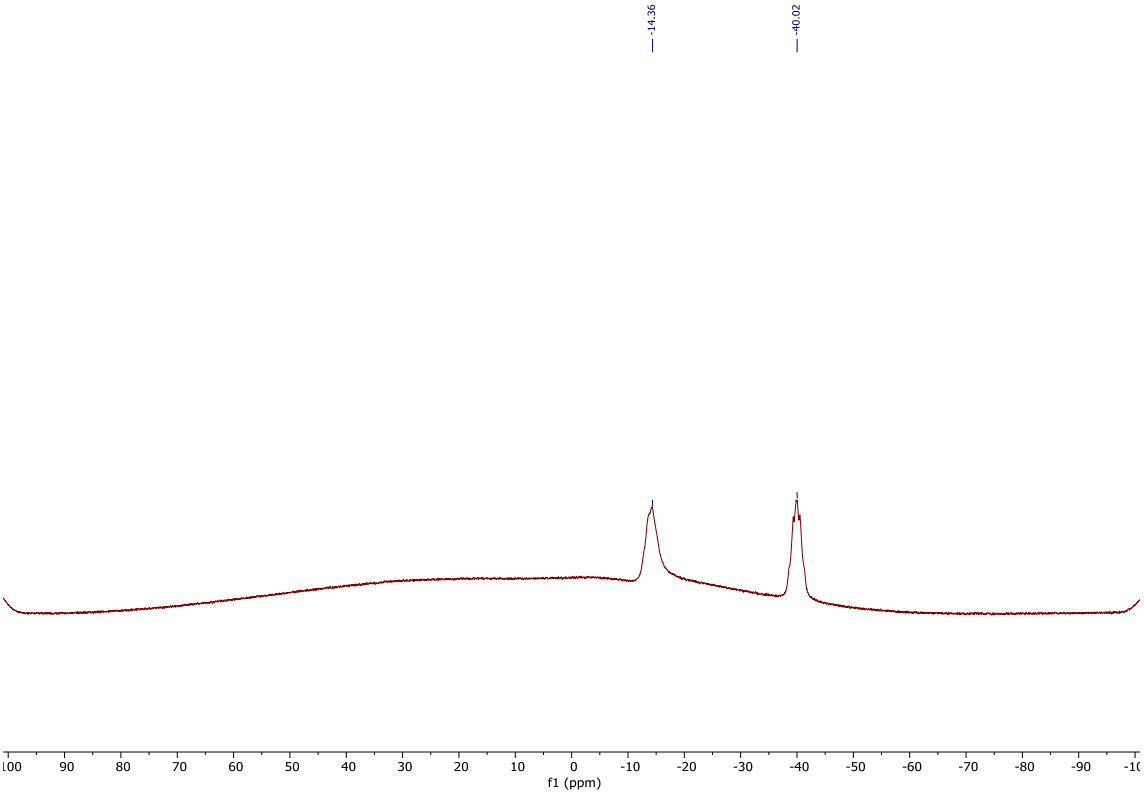
Adamant-1-yldiphenylphosphine borane adduct (**2i**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



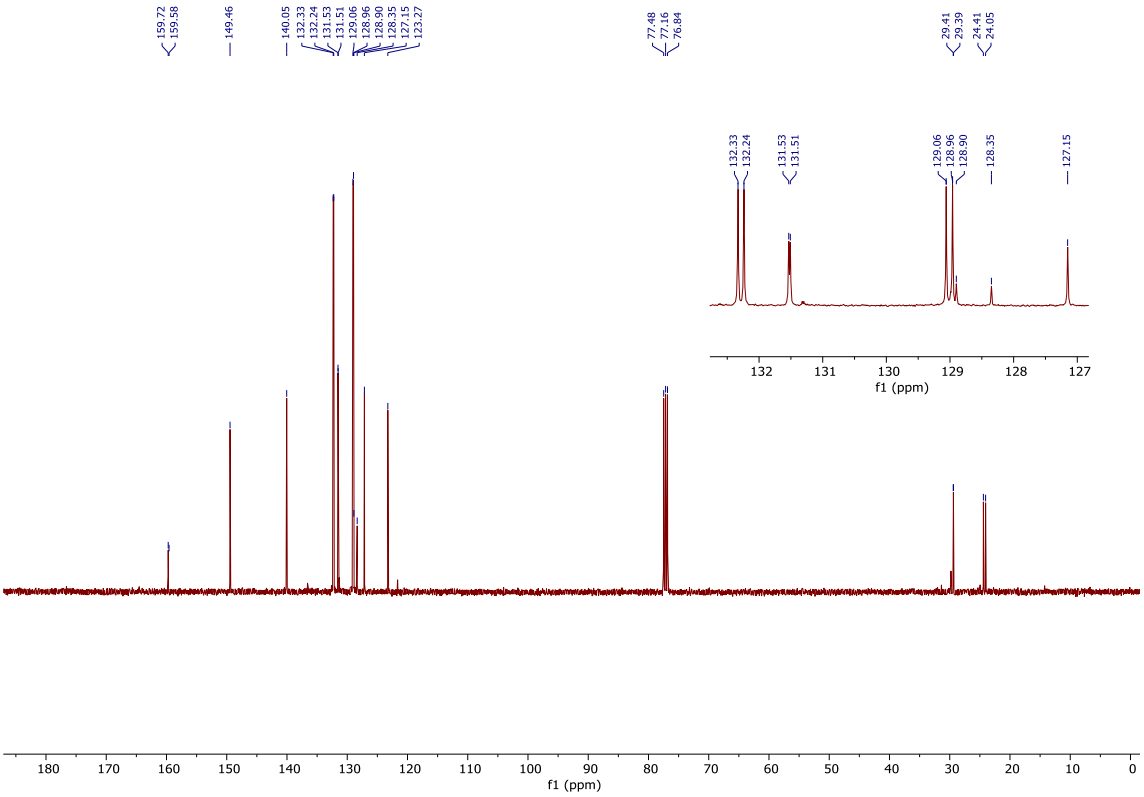
2-(2-(Diphenylphosphino)ethyl)pyridine di-borane adduct (**2j**) – ^{1}H NMR spectrum ($CDCl_3$)



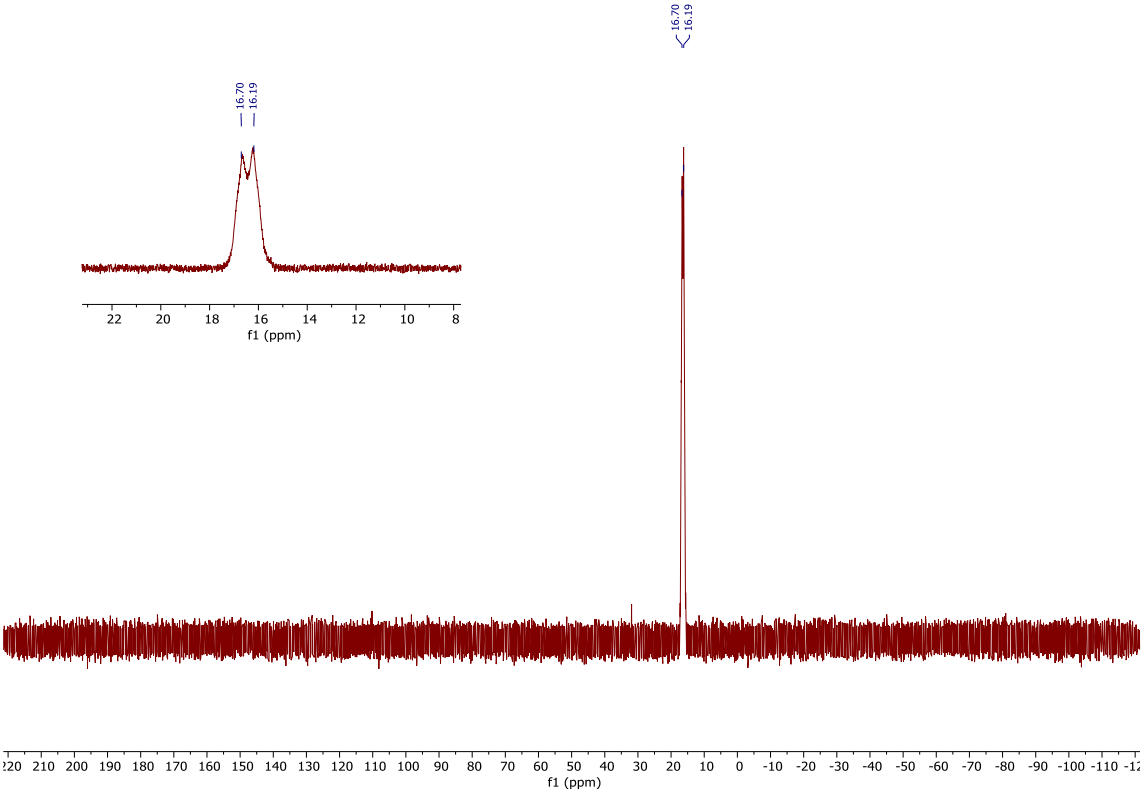
2-(2-(Diphenylphosphino)ethyl)pyridine di-borane adduct (**2j**) – ^{11}B NMR spectrum ($CDCl_3$)



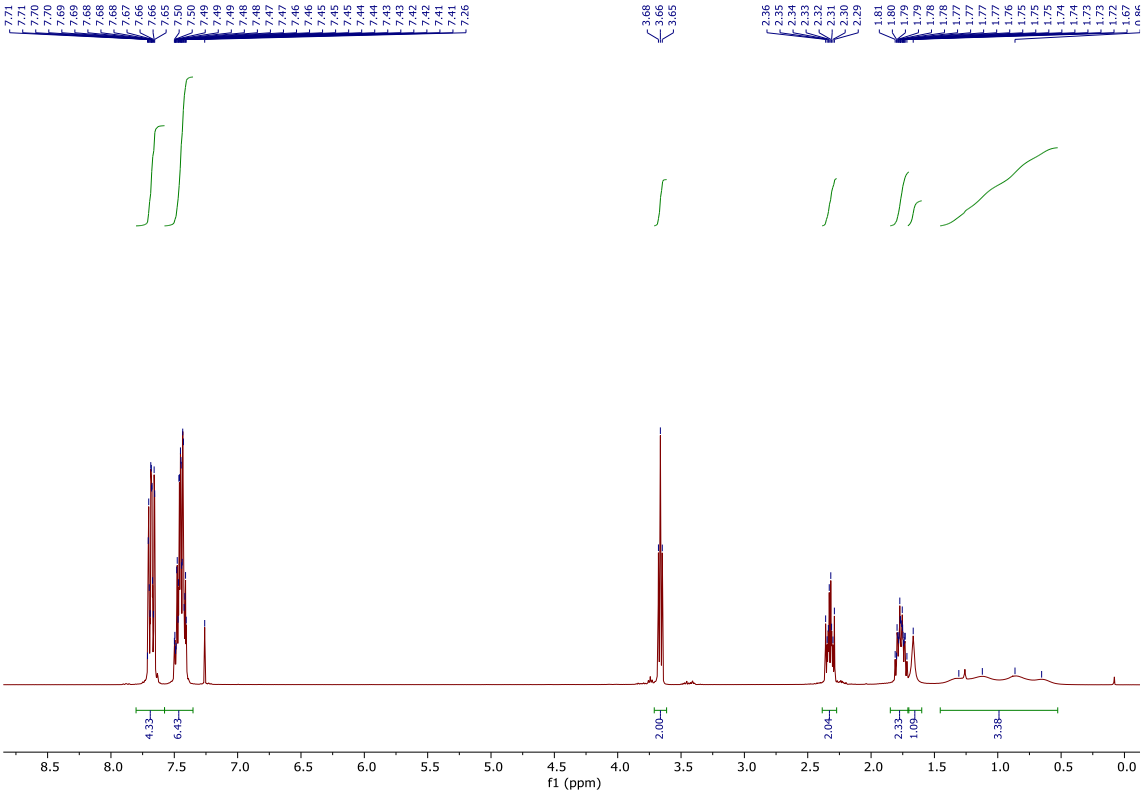
2-(2-(Diphenylphosphino)ethyl)pyridine di-borane adduct (**2j**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



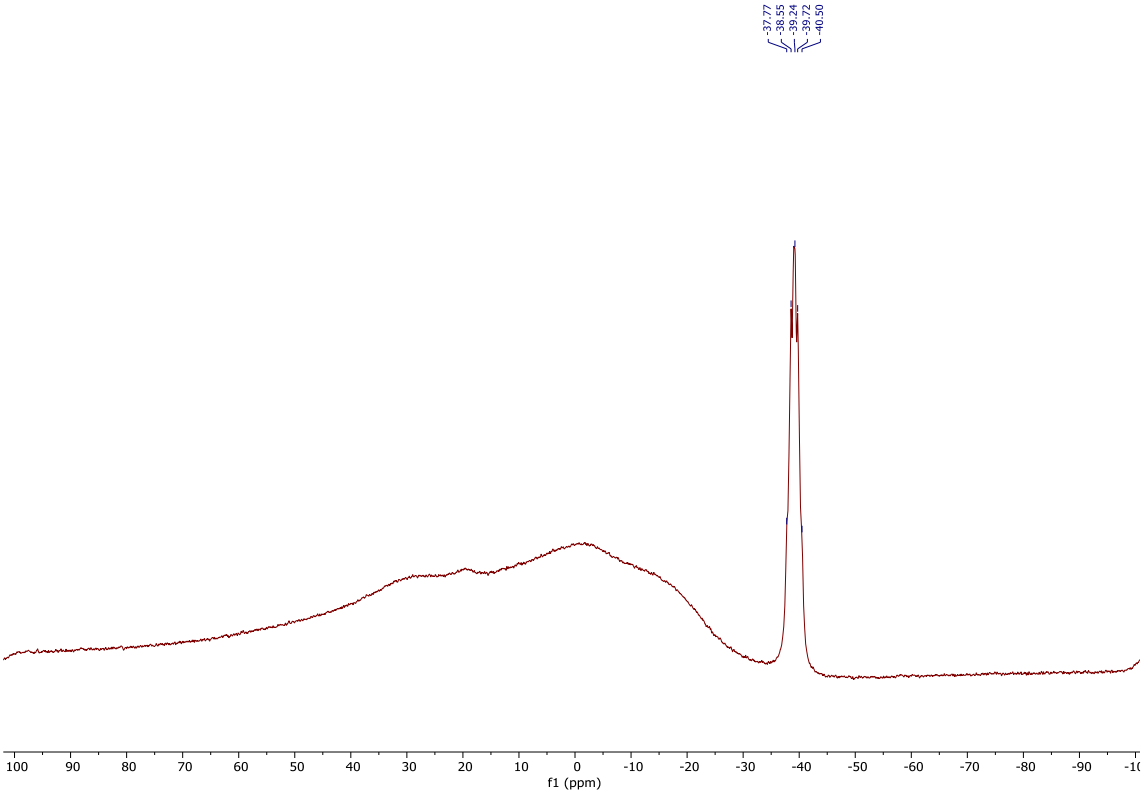
2-(2-(Diphenylphosphino)ethyl)pyridine di-borane adduct (**2j**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



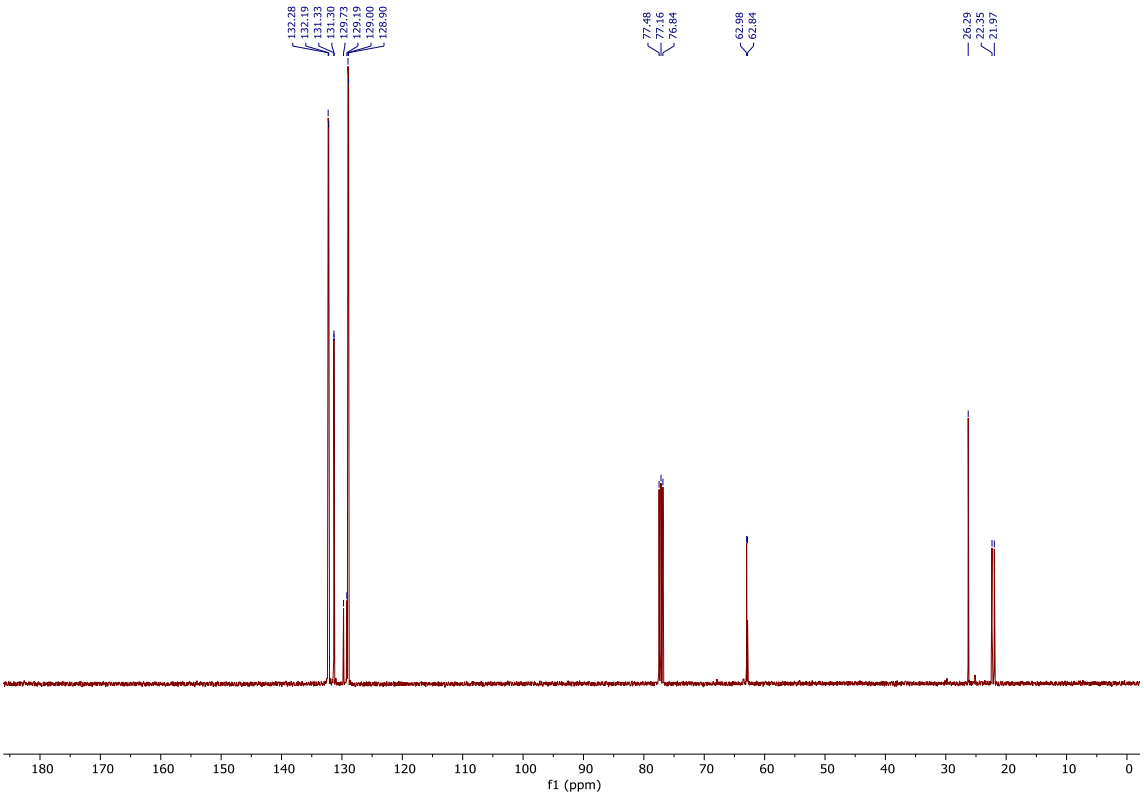
3-(Diphenylphosphino)propan-1-ol borane adduct (**2k**) – ^{1}H NMR spectrum ($CDCl_3$)



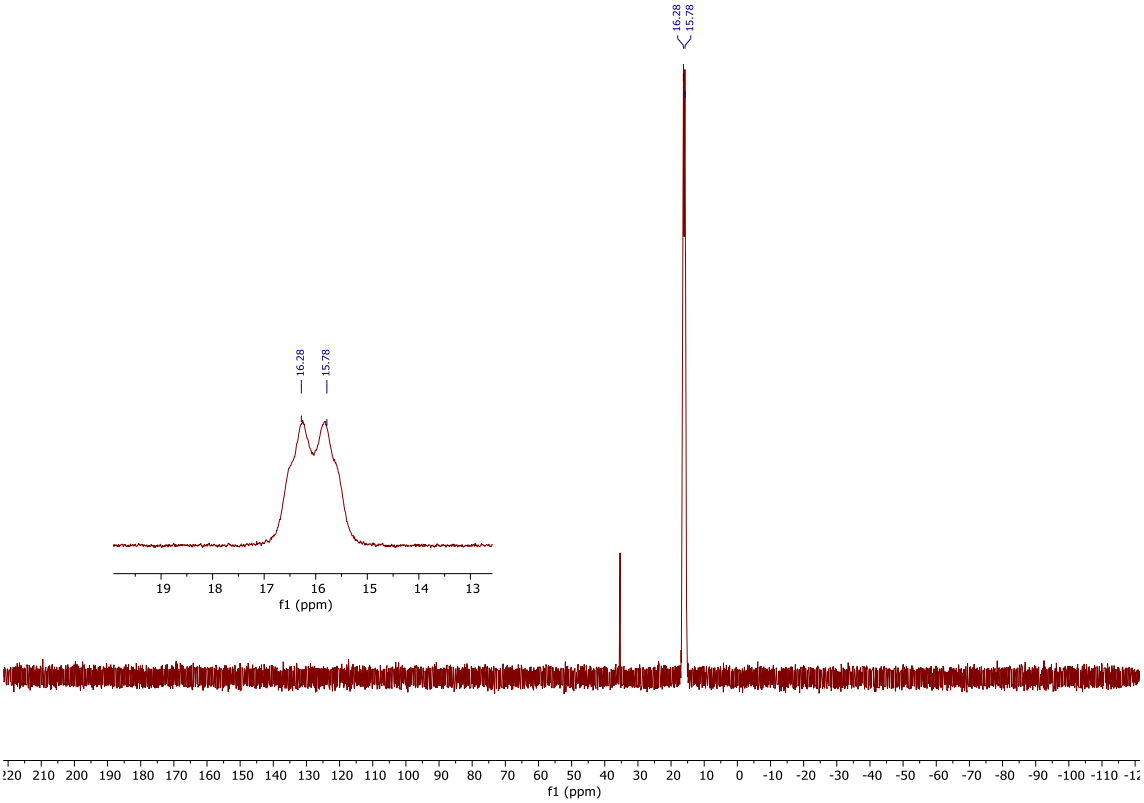
3-(Diphenylphosphino)propan-1-ol borane adduct (**2k**) – ^{11}B NMR spectrum ($CDCl_3$)



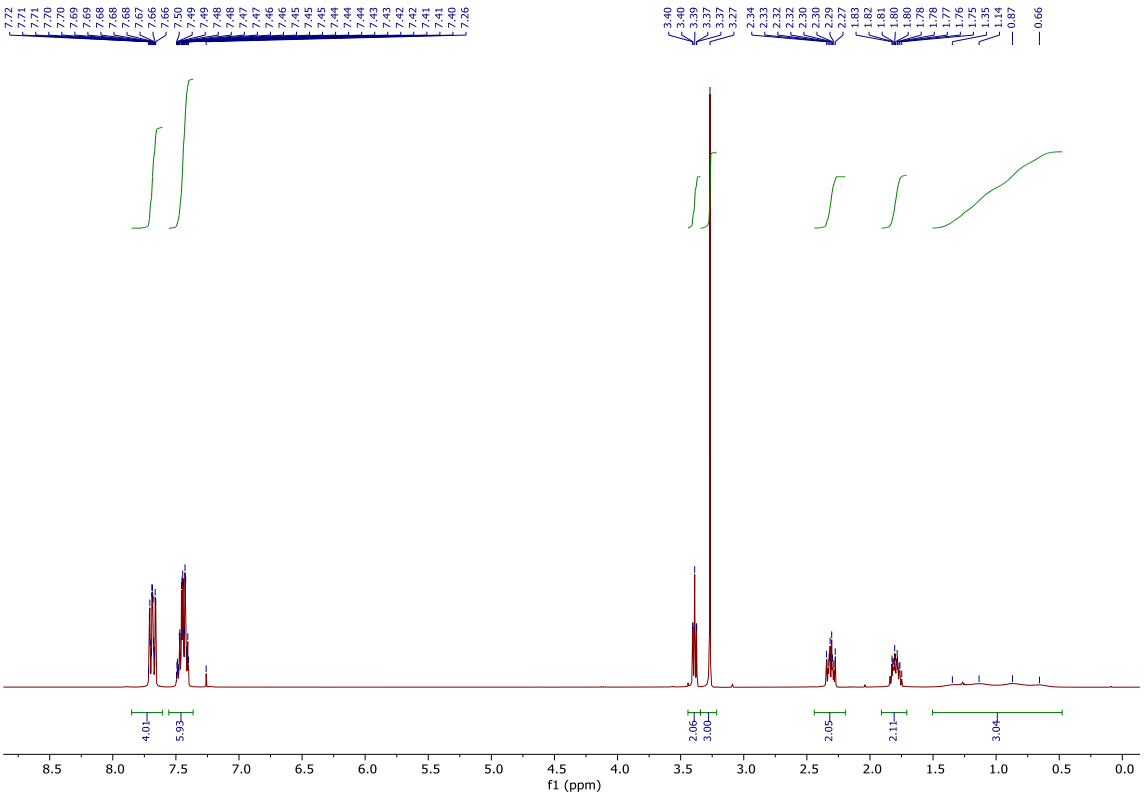
3-(Diphenylphosphino)propan-1-ol borane adduct (**2k**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



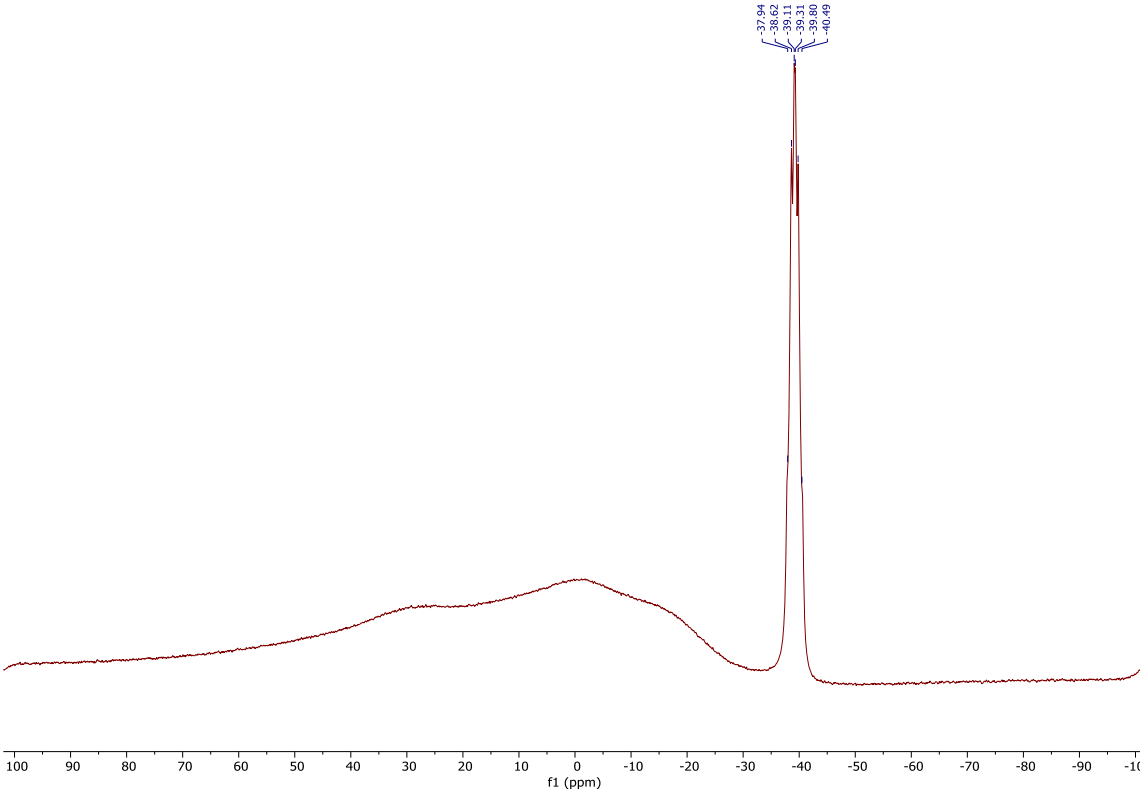
3-(Diphenylphosphino)propan-1-ol borane adduct (**2k**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



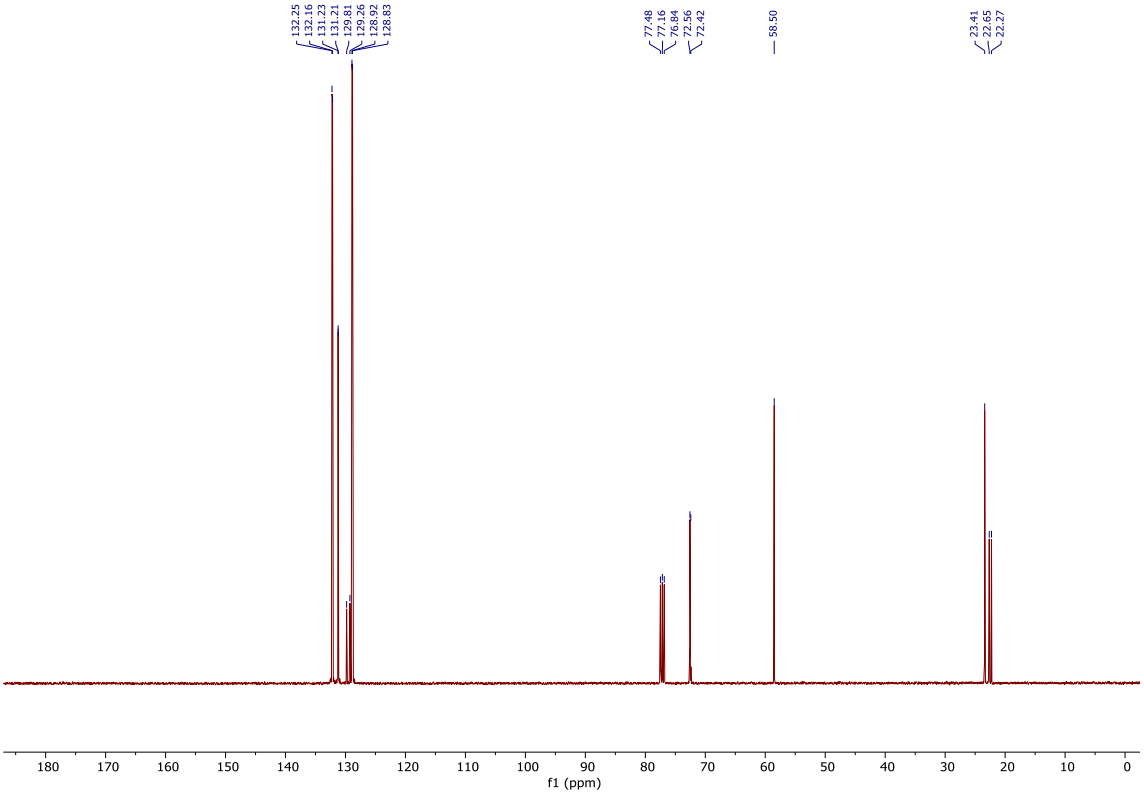
(3-Methoxypropyl)diphenylphosphine borane adduct (**2l**) – ^{1}H NMR spectrum ($CDCl_3$)



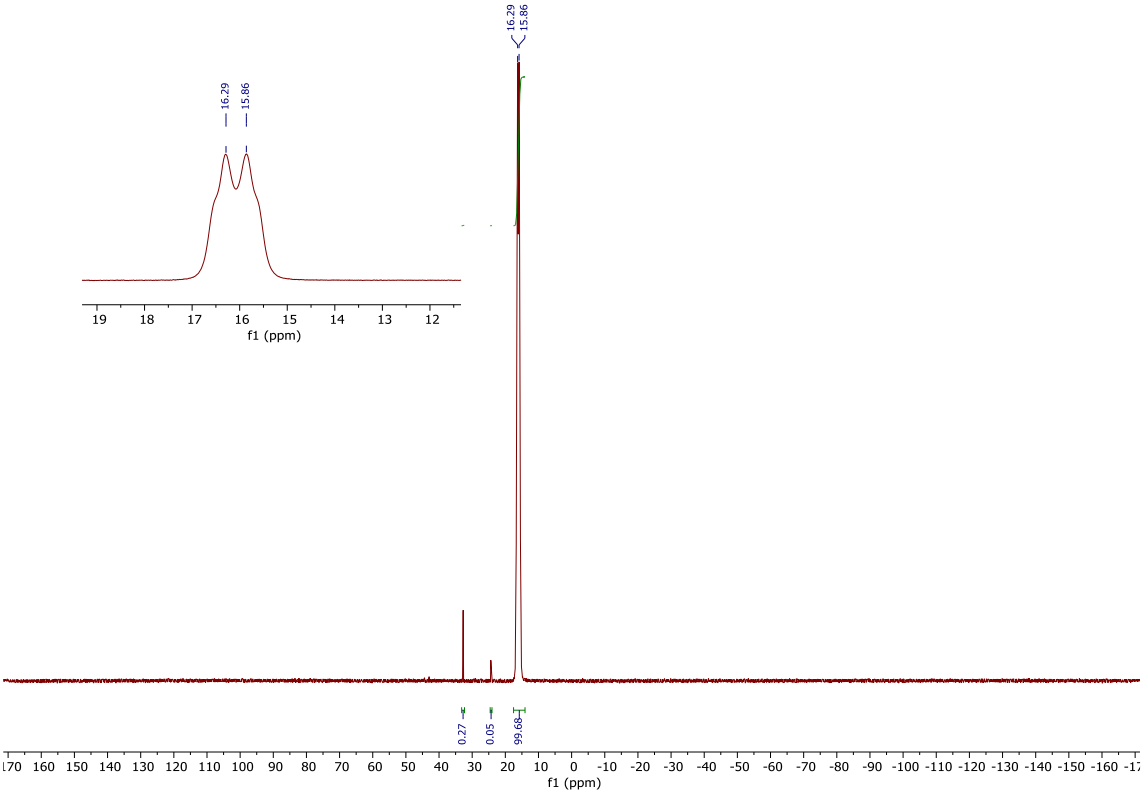
(3-Methoxypropyl)diphenylphosphine borane adduct (**2l**) – ^{11}B NMR spectrum ($CDCl_3$)



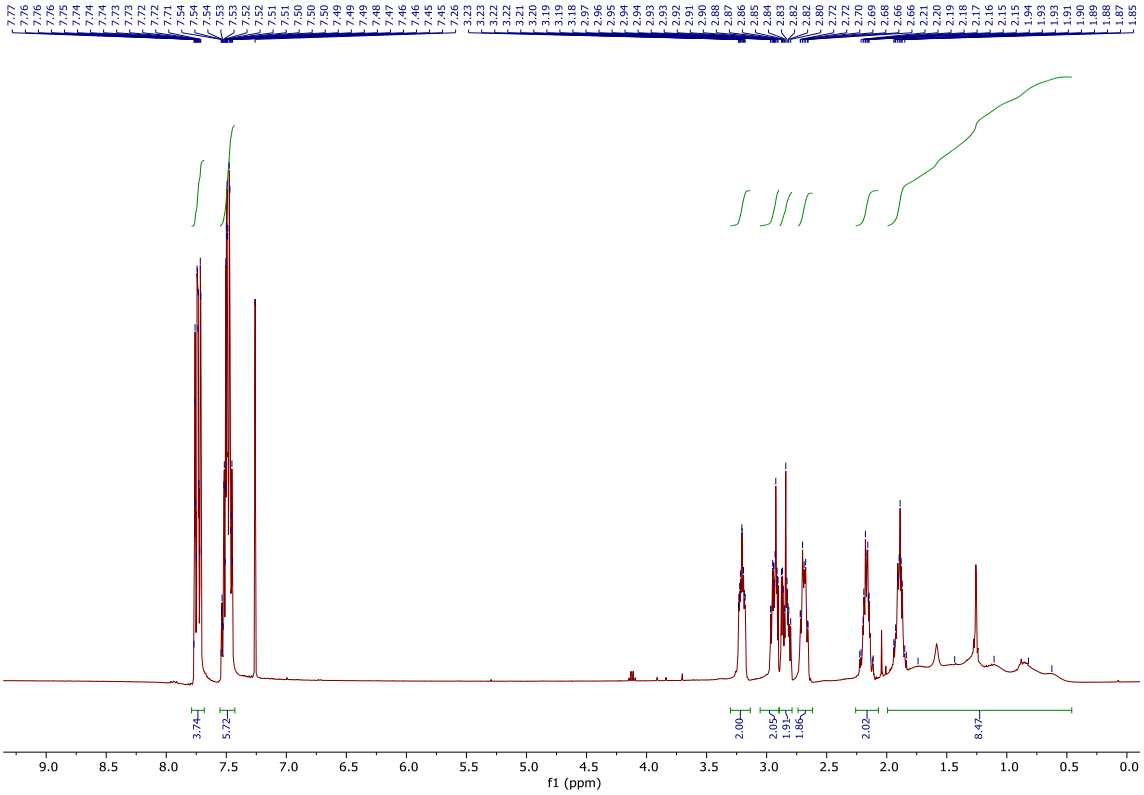
(3-Methoxypropyl)diphenylphosphine borane adduct (**2l**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



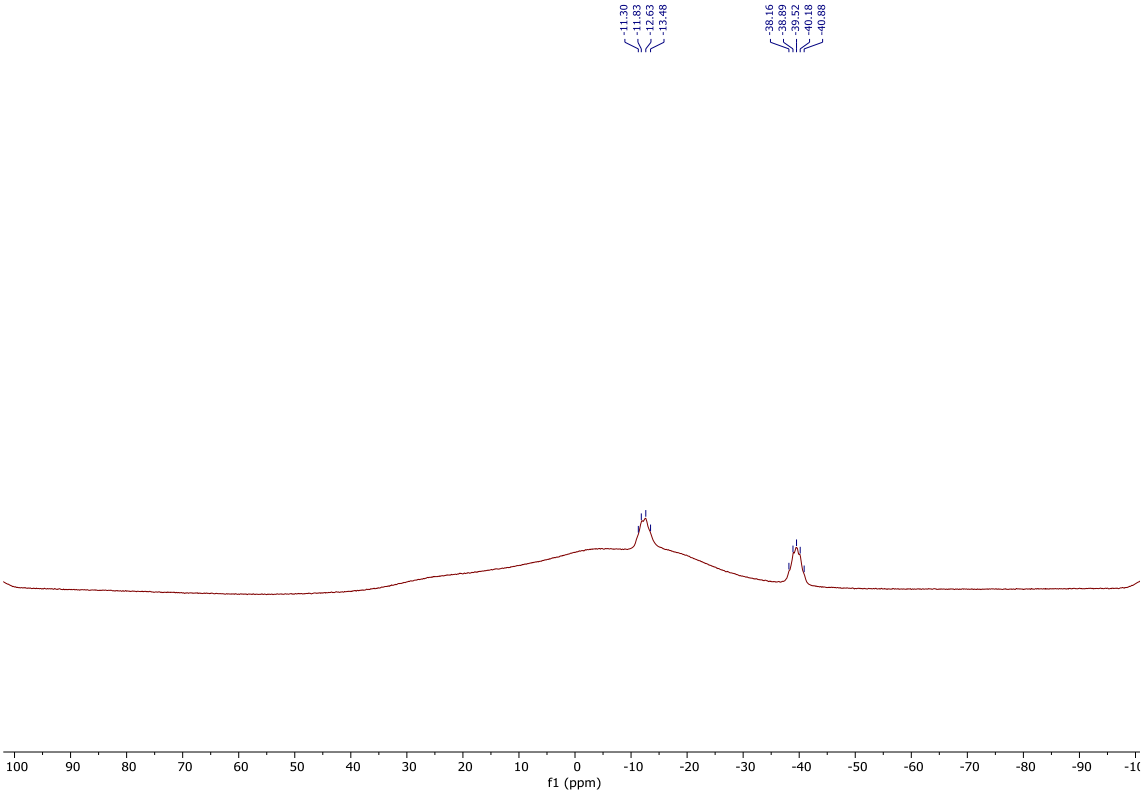
(3-Methoxypropyl)diphenylphosphine borane adduct (**2l**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



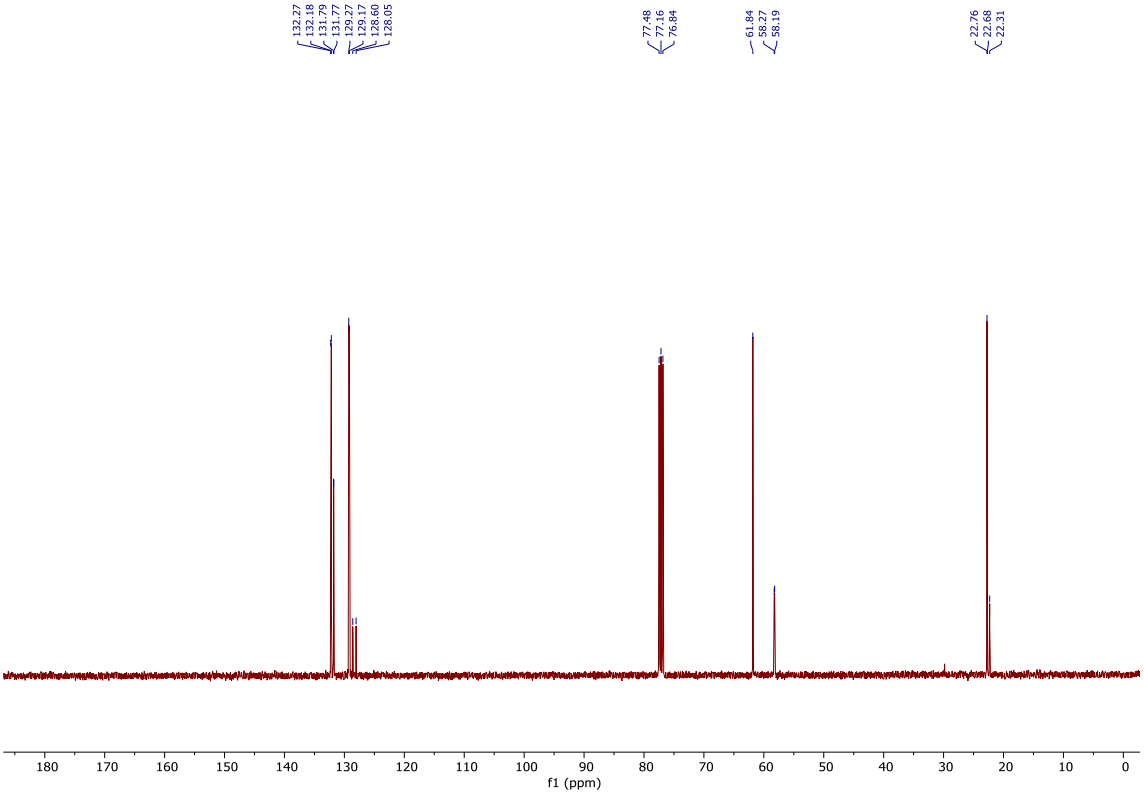
1-(2-(Diphenylphosphino)ethyl)pyrrolidine di-borane adduct (**2m**) – ^{1}H NMR spectrum ($CDCl_3$)



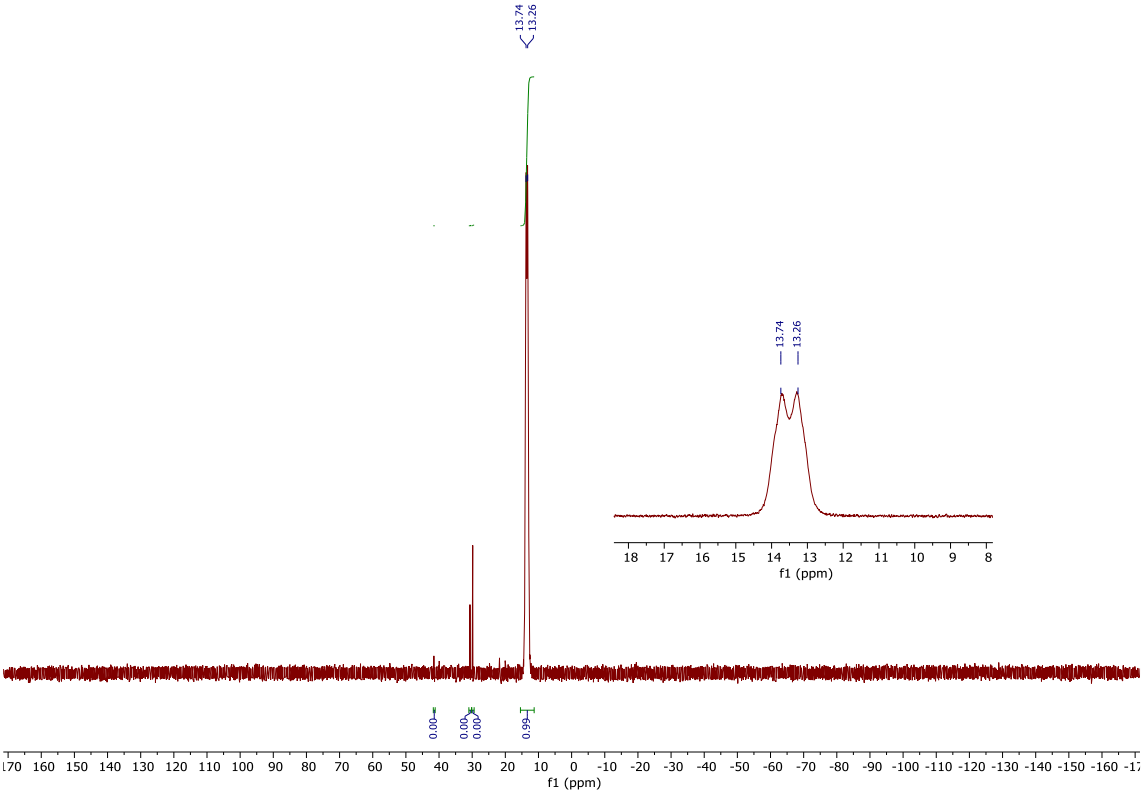
1-(2-(Diphenylphosphino)ethyl)pyrrolidine di-borane adduct (**2m**) – ^{11}B NMR spectrum ($CDCl_3$)



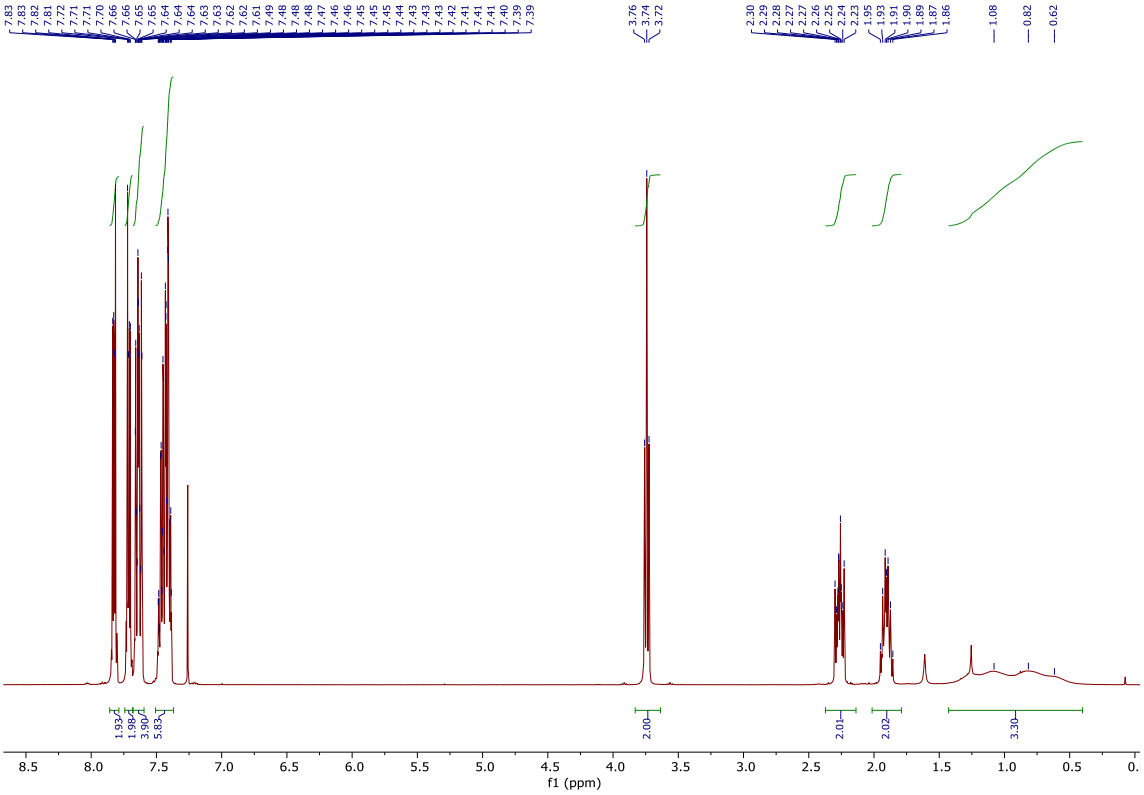
1-(2-(Diphenylphosphino)ethyl)pyrrolidine di-borane adduct (**2m**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



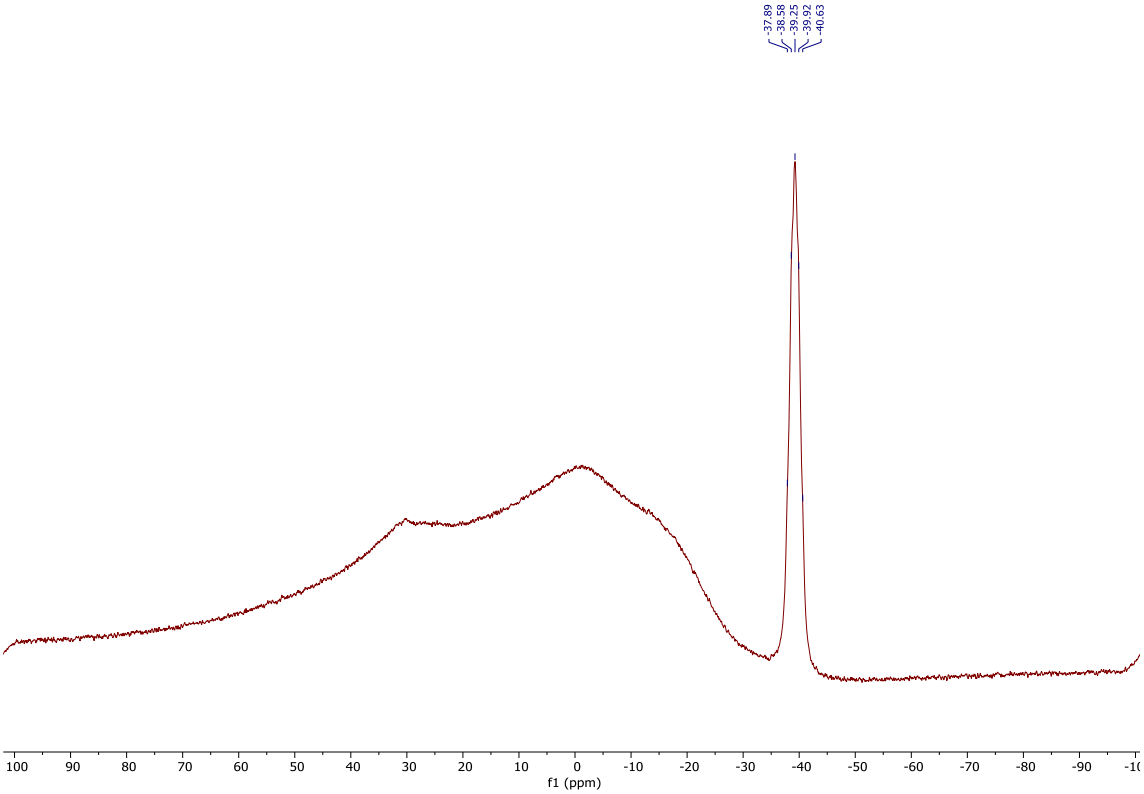
1-(2-(Diphenylphosphino)ethyl)pyrrolidine di-borane adduct (**2m**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



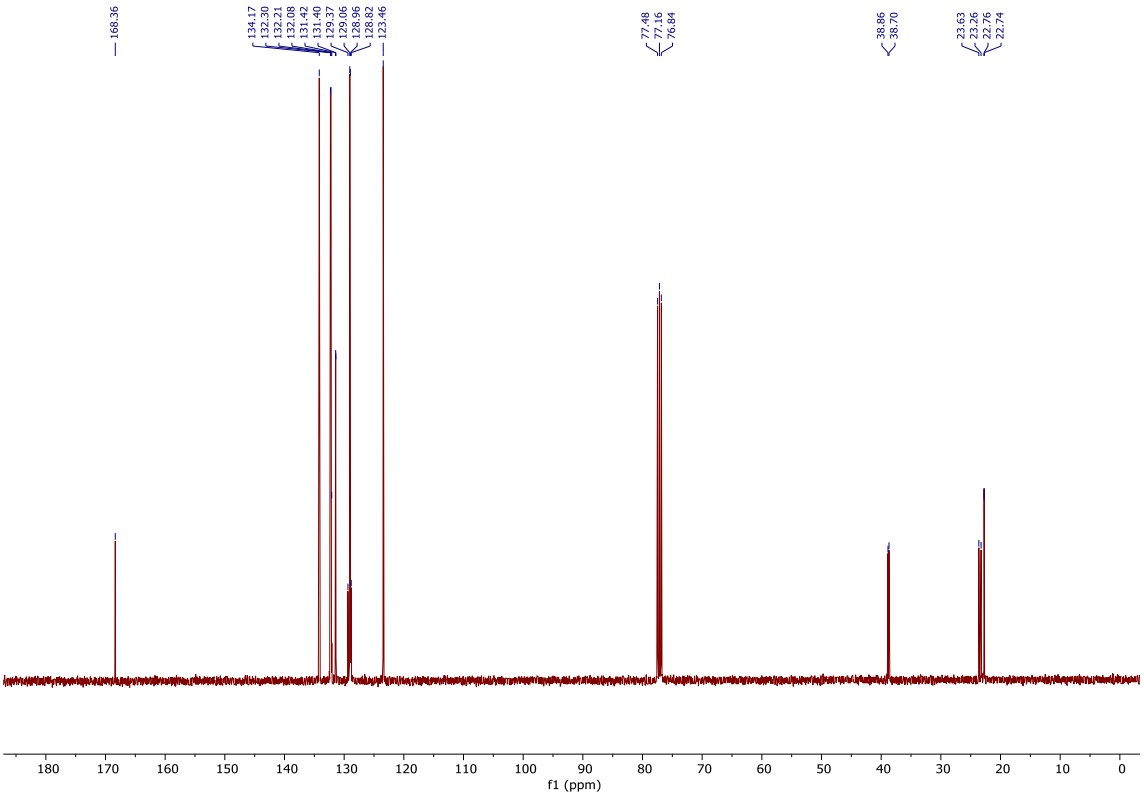
(3-Phthaloylpropyl)diphenylphosphine borane adduct (**2n**) – ^{1}H NMR spectrum ($CDCl_3$)



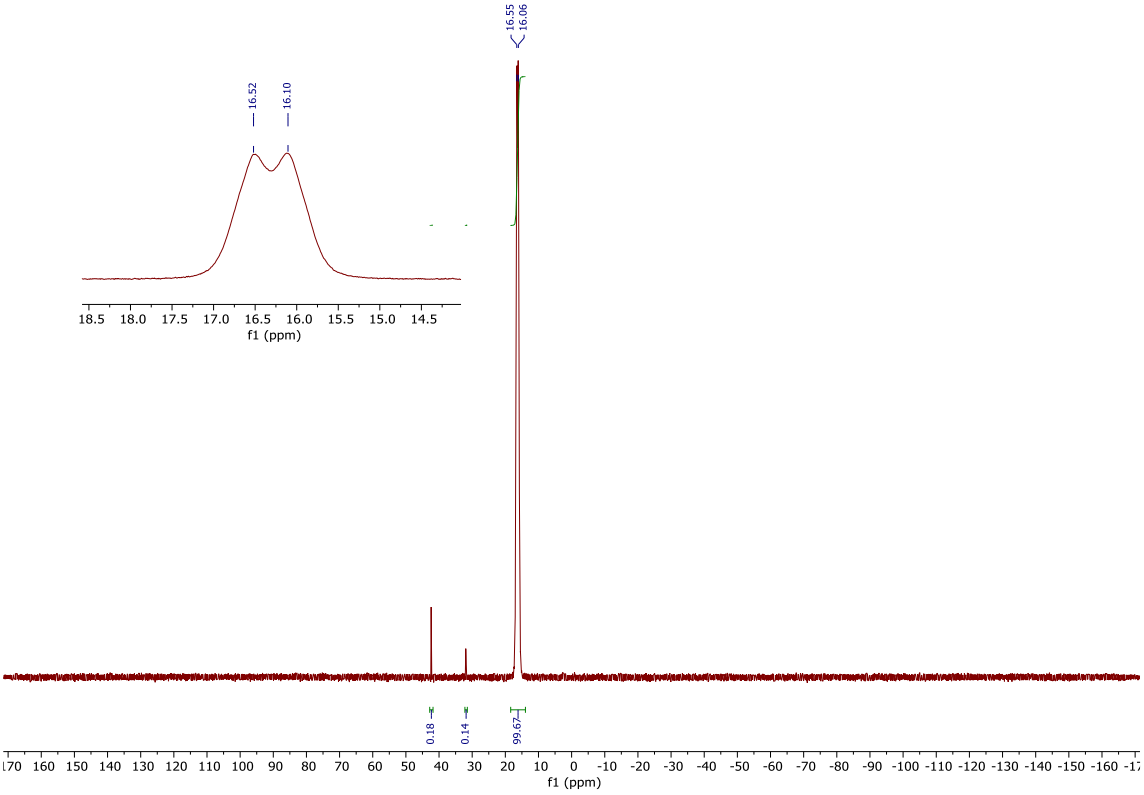
(3-Phthaloylpropyl)diphenylphosphine borane adduct (**2n**) – ^{11}B NMR spectrum ($CDCl_3$)



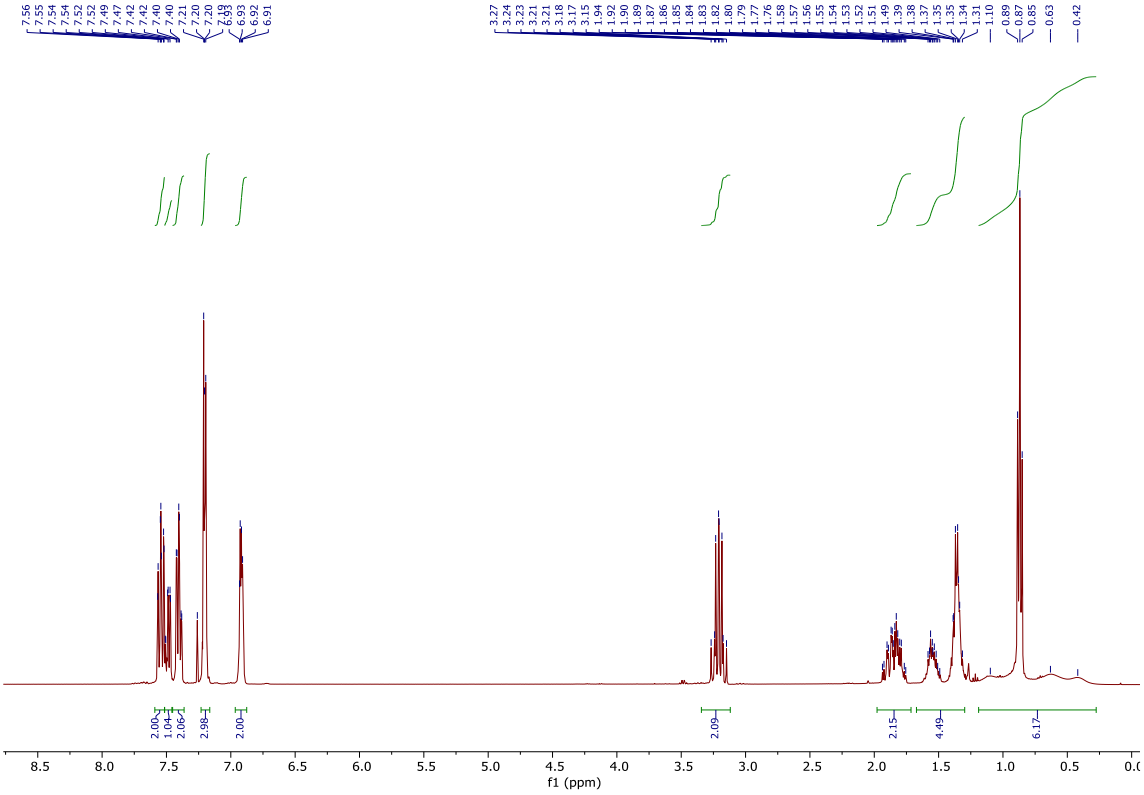
(3-Phthaloylpropyl)diphenylphosphine borane adduct (**2n**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



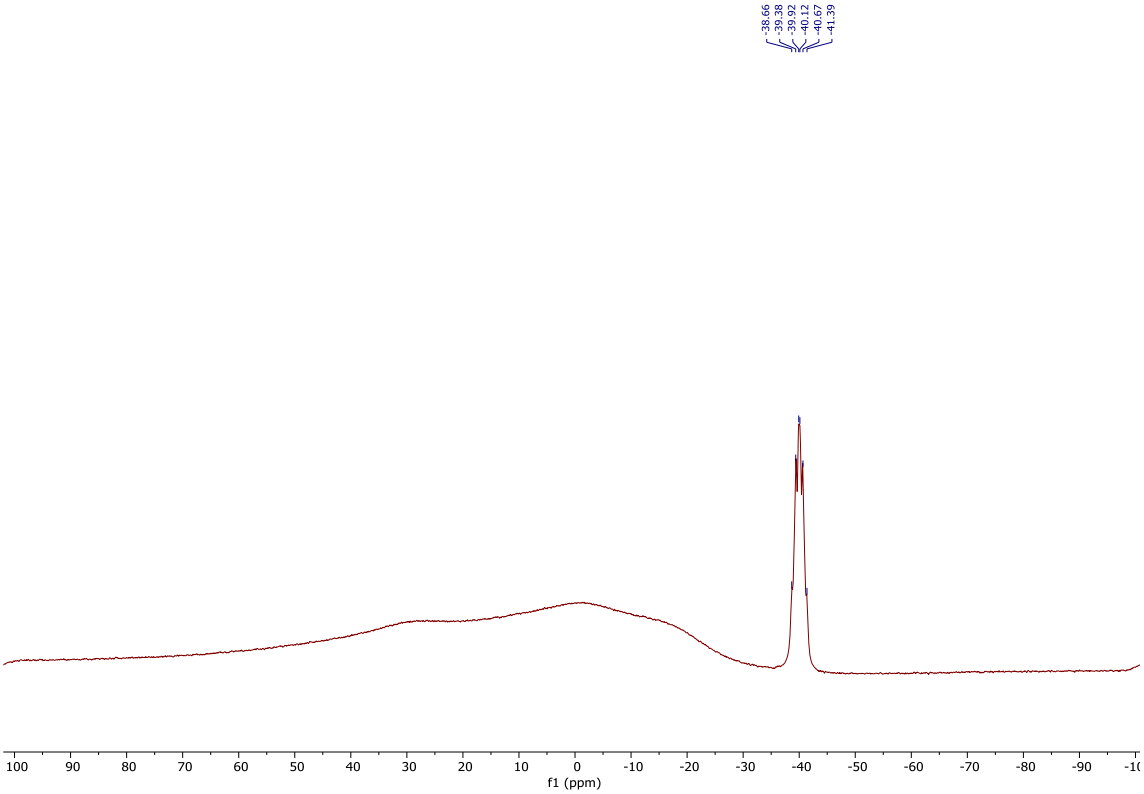
(3-Phthaloylpropyl)diphenylphosphine borane adduct (**2n**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



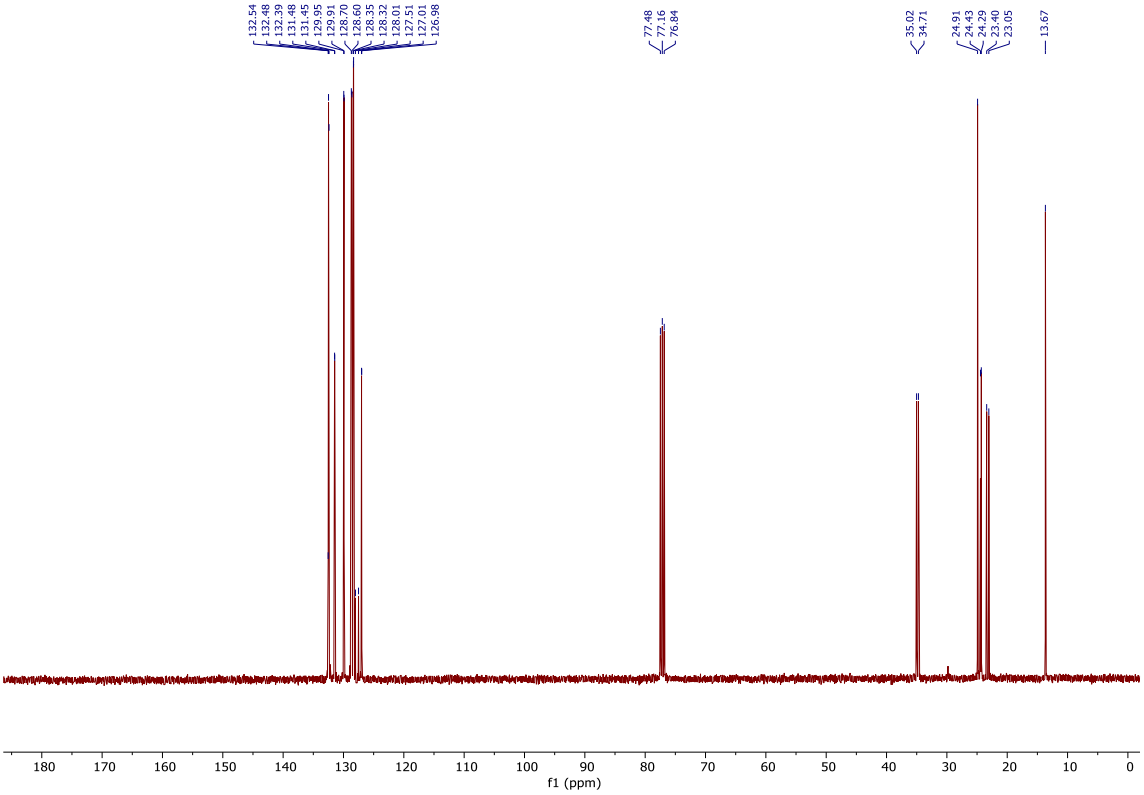
Butylbenzylphenylphosphine borane adduct (**2o**) – ^{1}H NMR spectrum ($CDCl_3$)



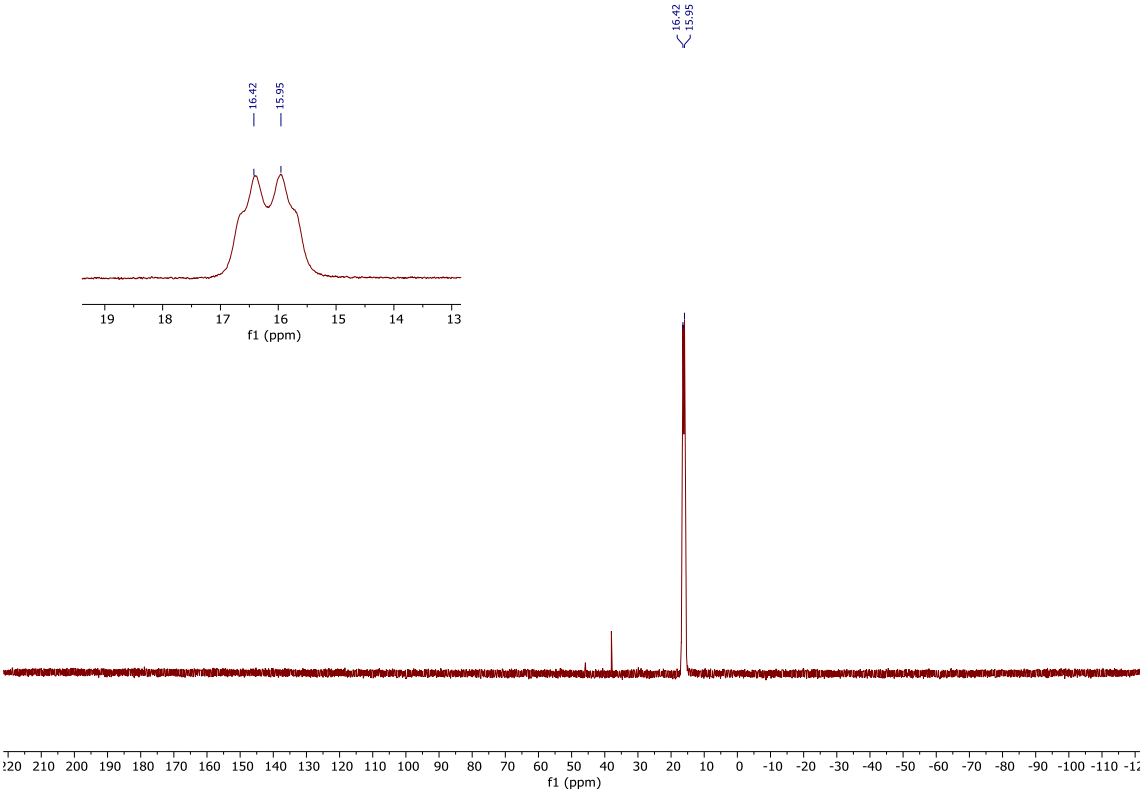
Butylbenzylphenylphosphine borane adduct (**2o**) – ^{11}B NMR spectrum ($CDCl_3$)



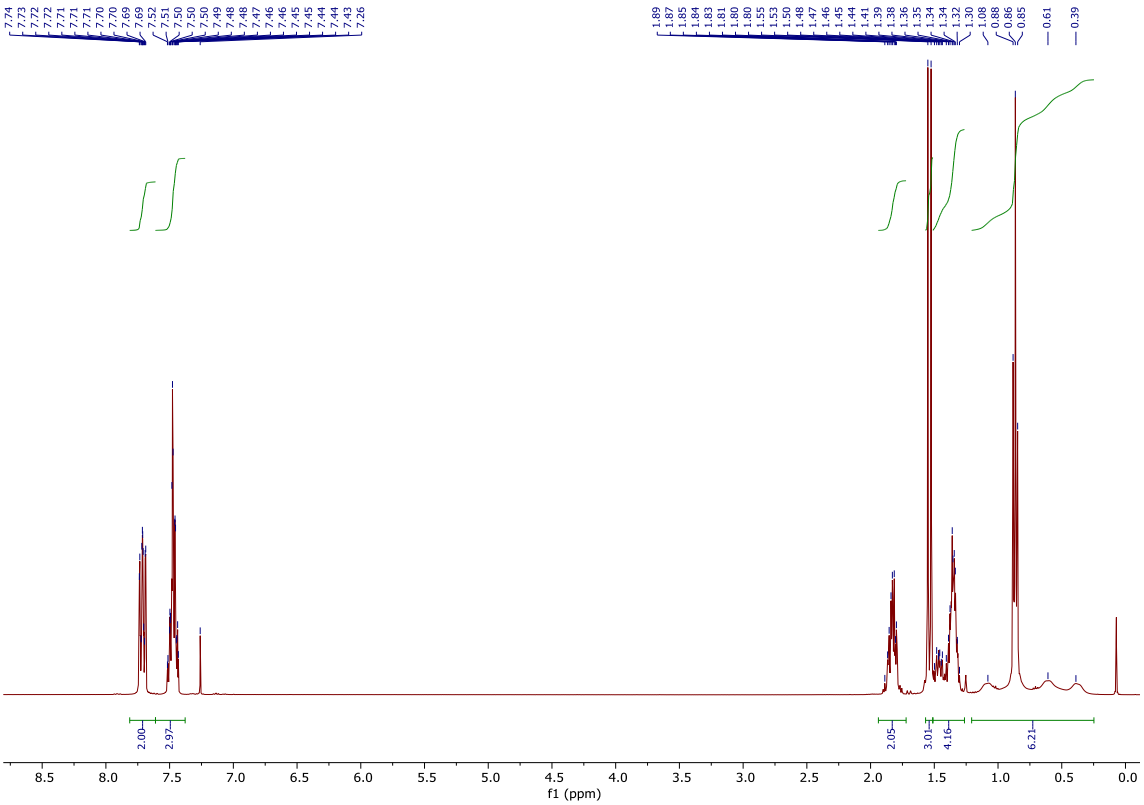
Butylbenzylphenylphosphine borane adduct (**2o**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



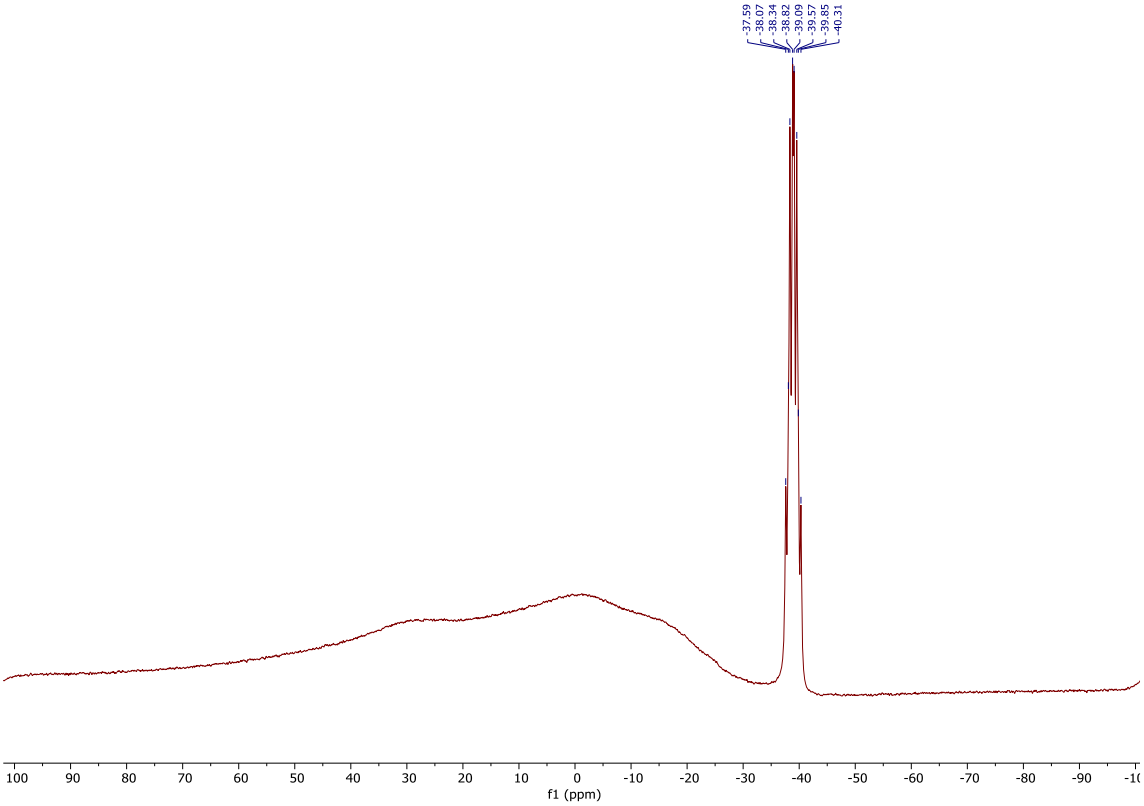
Butylbenzylphenylphosphine borane adduct (**2o**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



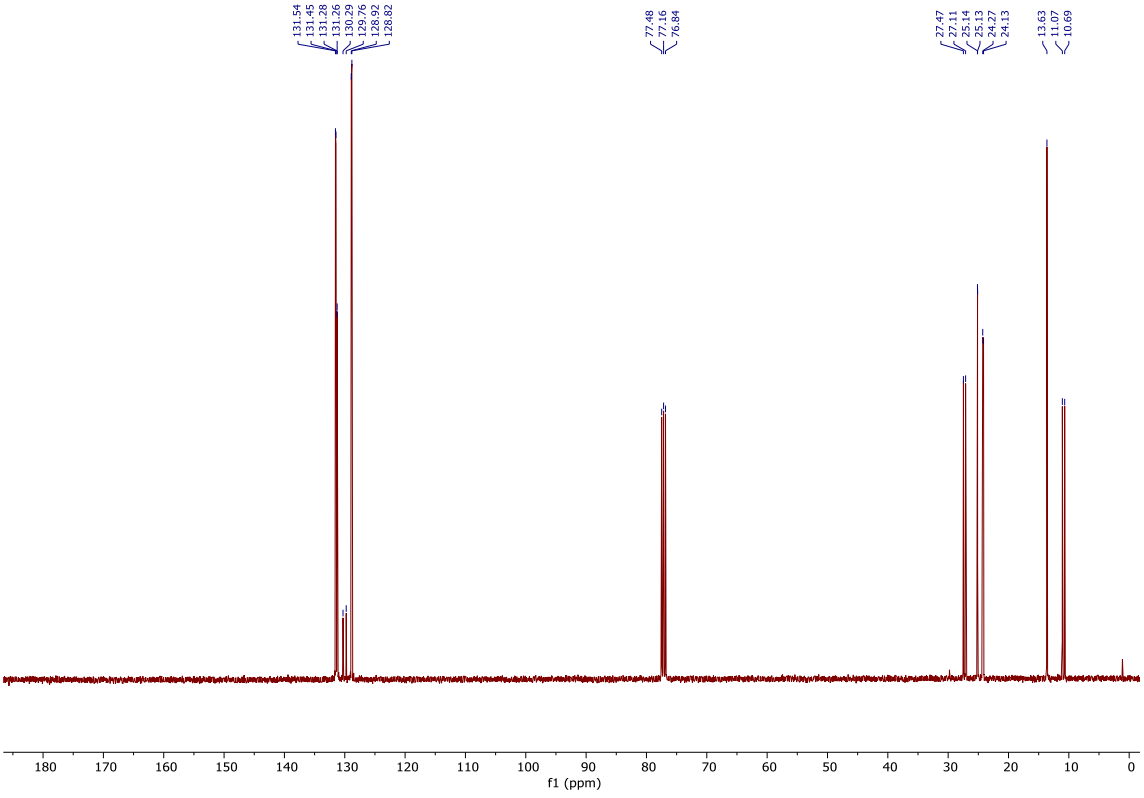
Butylmethylphenylphosphine borane adduct (**2p**) – ^{1}H NMR spectrum ($CDCl_3$)



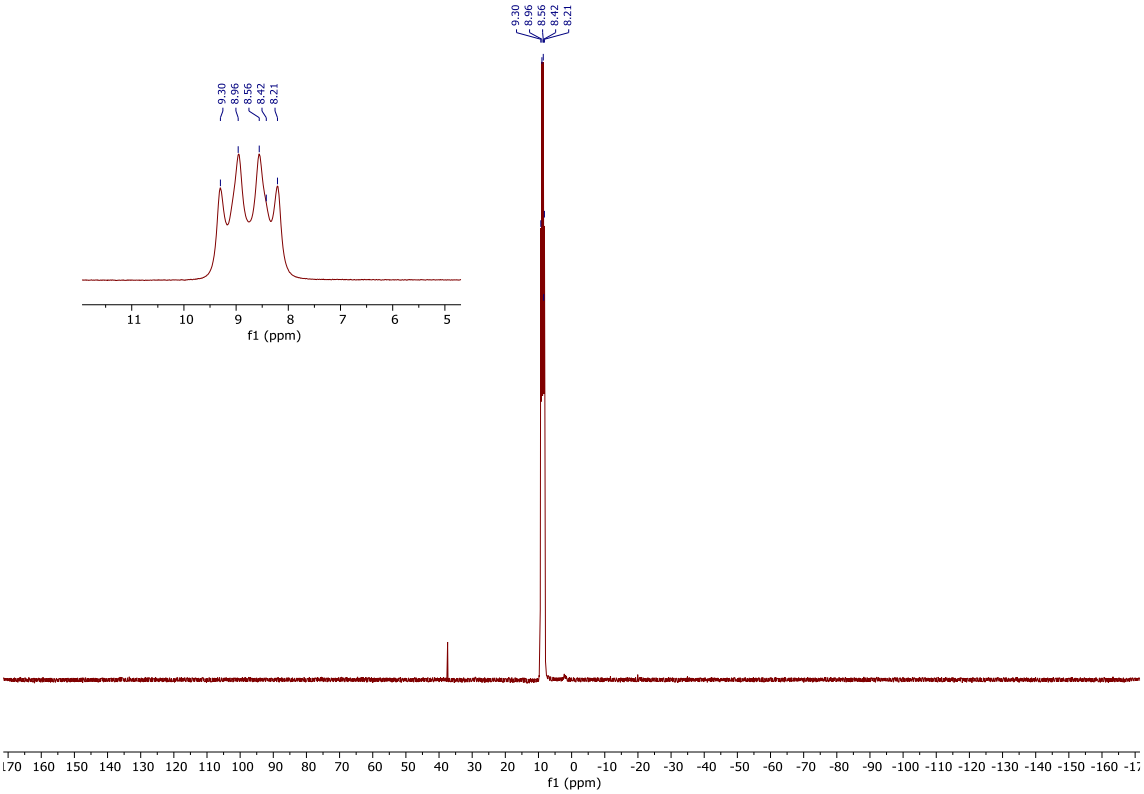
Butylmethylphenylphosphine borane adduct (**2p**) – ^{11}B NMR spectrum ($CDCl_3$)



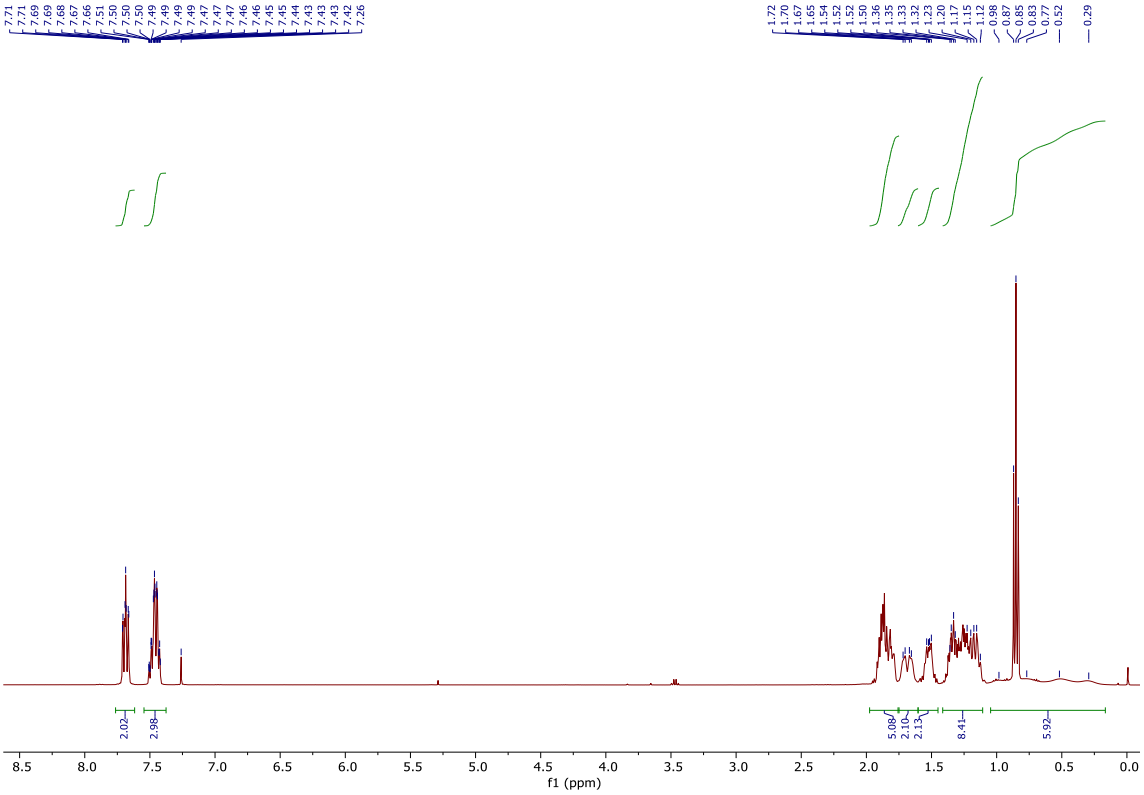
Butylmethylphenylphosphine borane adduct (**2p**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



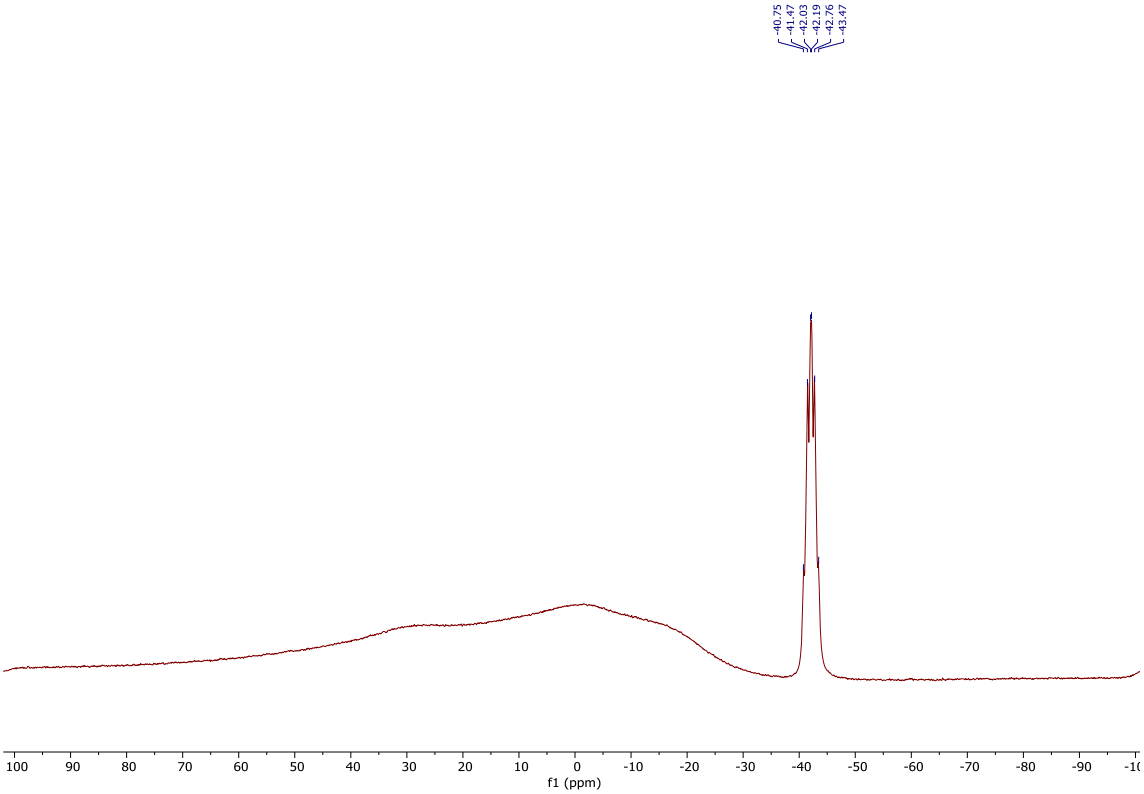
Butylmethylphenylphosphine borane adduct (**2p**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



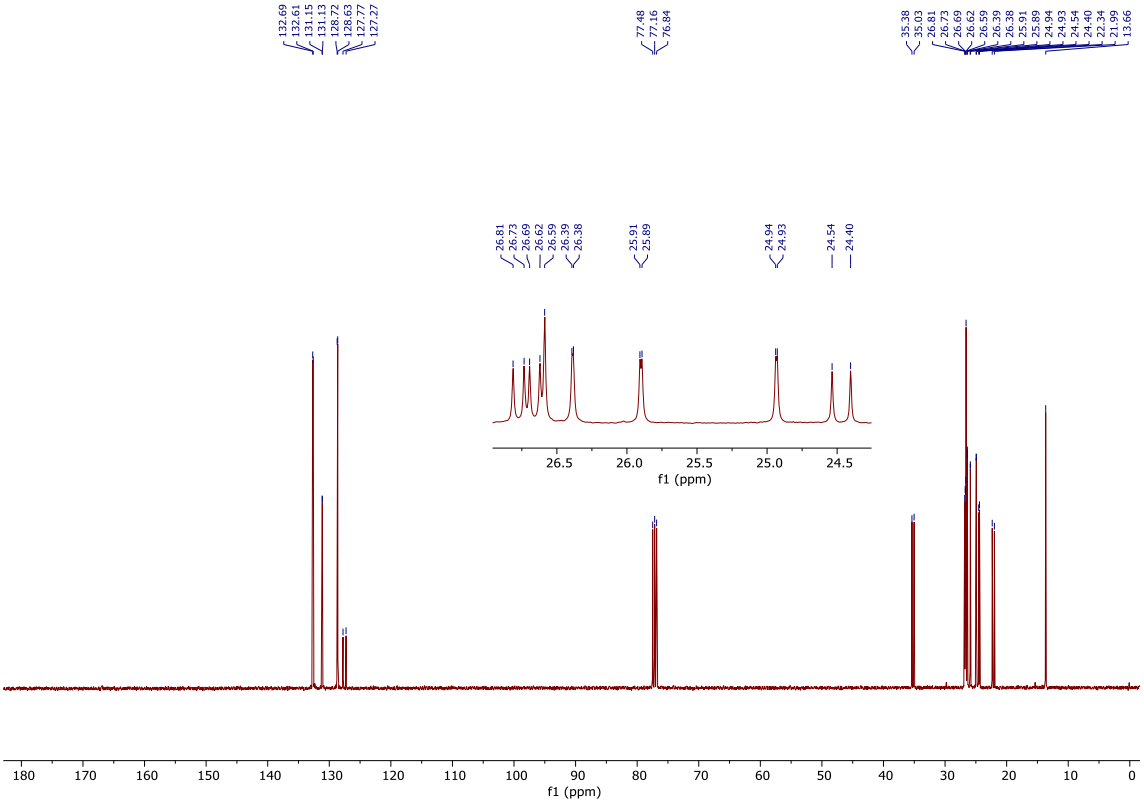
Butylcyclohexylphenylphosphine borane adduct (**2q**) – ^{1}H NMR spectrum ($CDCl_3$)



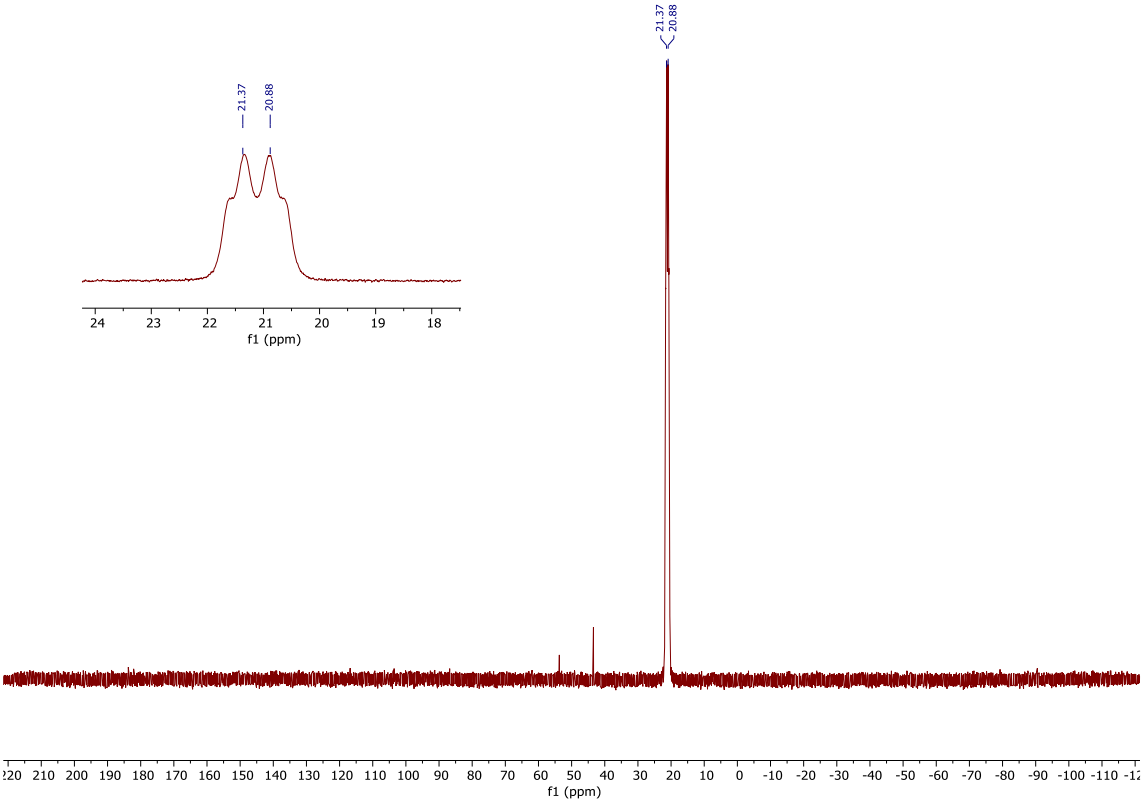
Butylcyclohexylphenylphosphine borane adduct (**2q**) – ^{11}B NMR spectrum ($CDCl_3$)



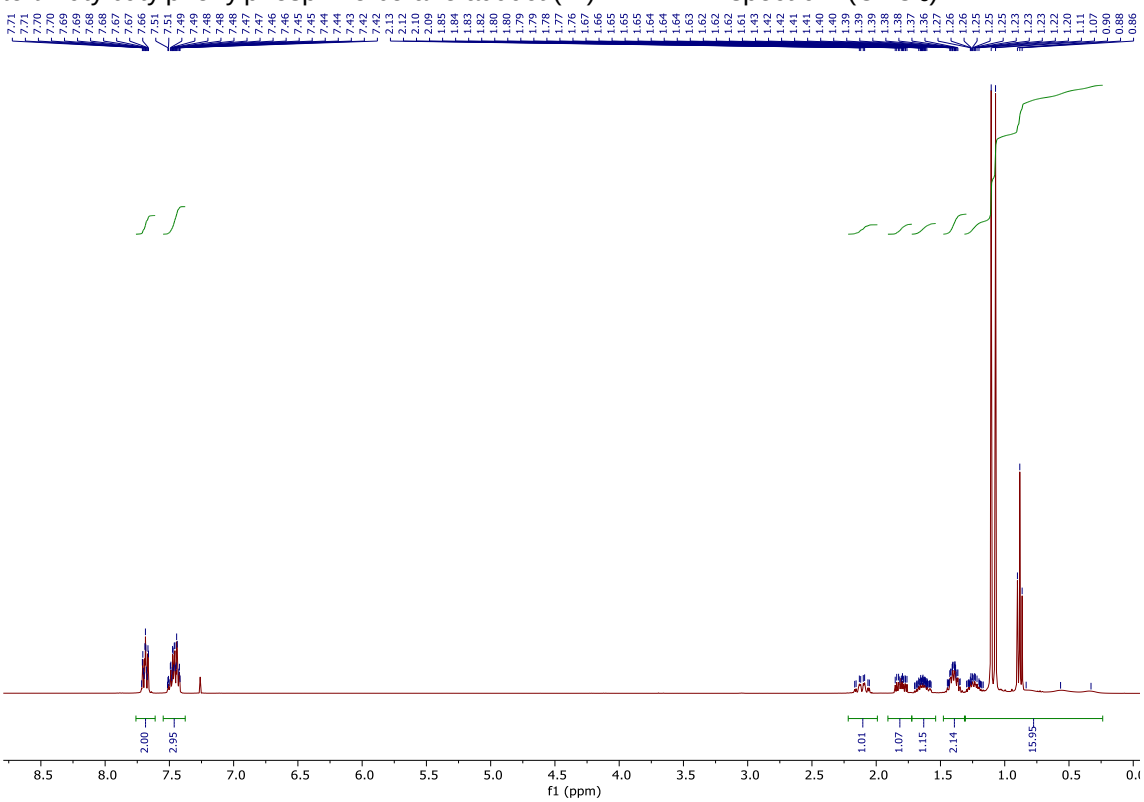
Butylcyclohexylphenylphosphine borane adduct (**2q**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



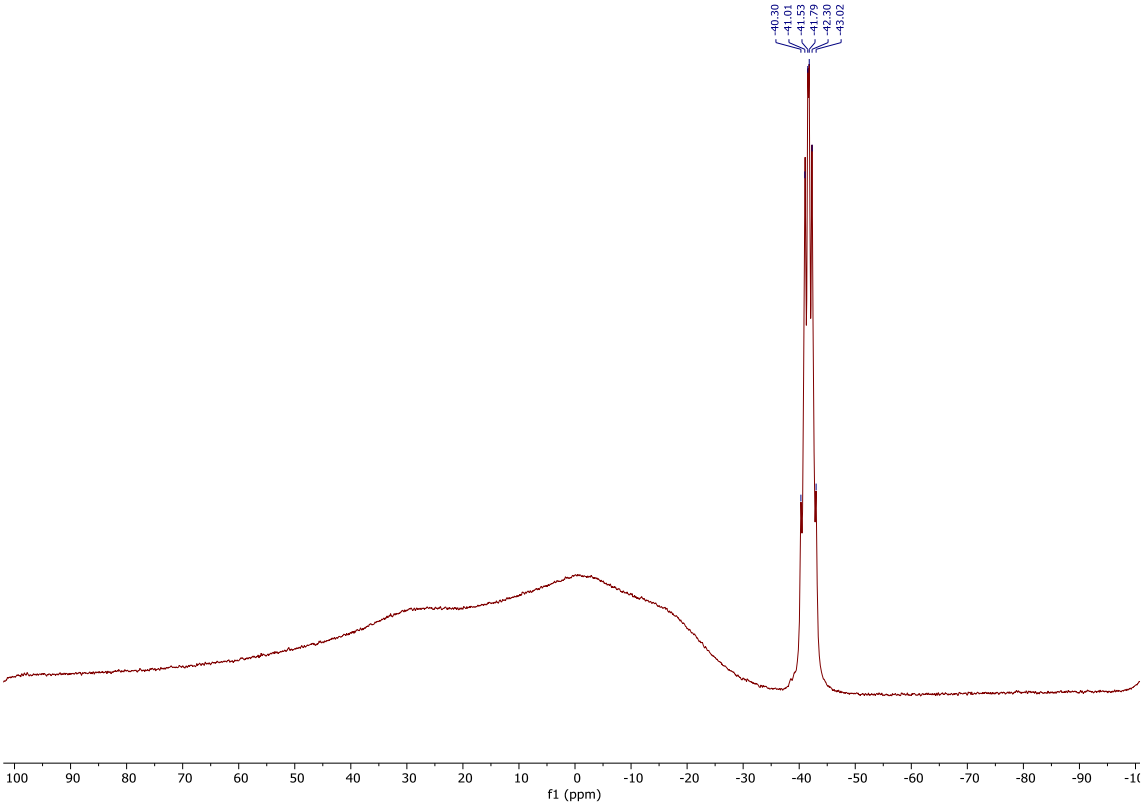
Butylcyclohexylphenylphosphine borane adduct (**2q**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



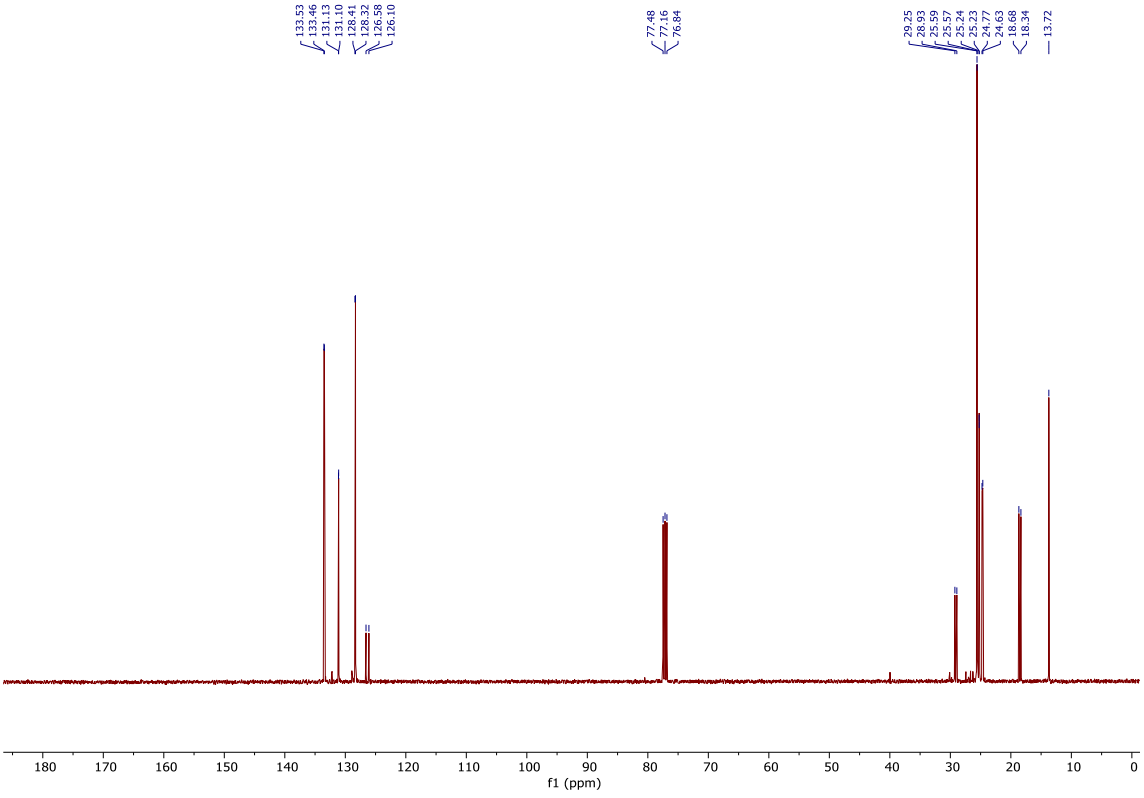
tert-Butylbutylphenylphosphine borane adduct (**2r**) – ^{1}H NMR spectrum ($CDCl_3$)



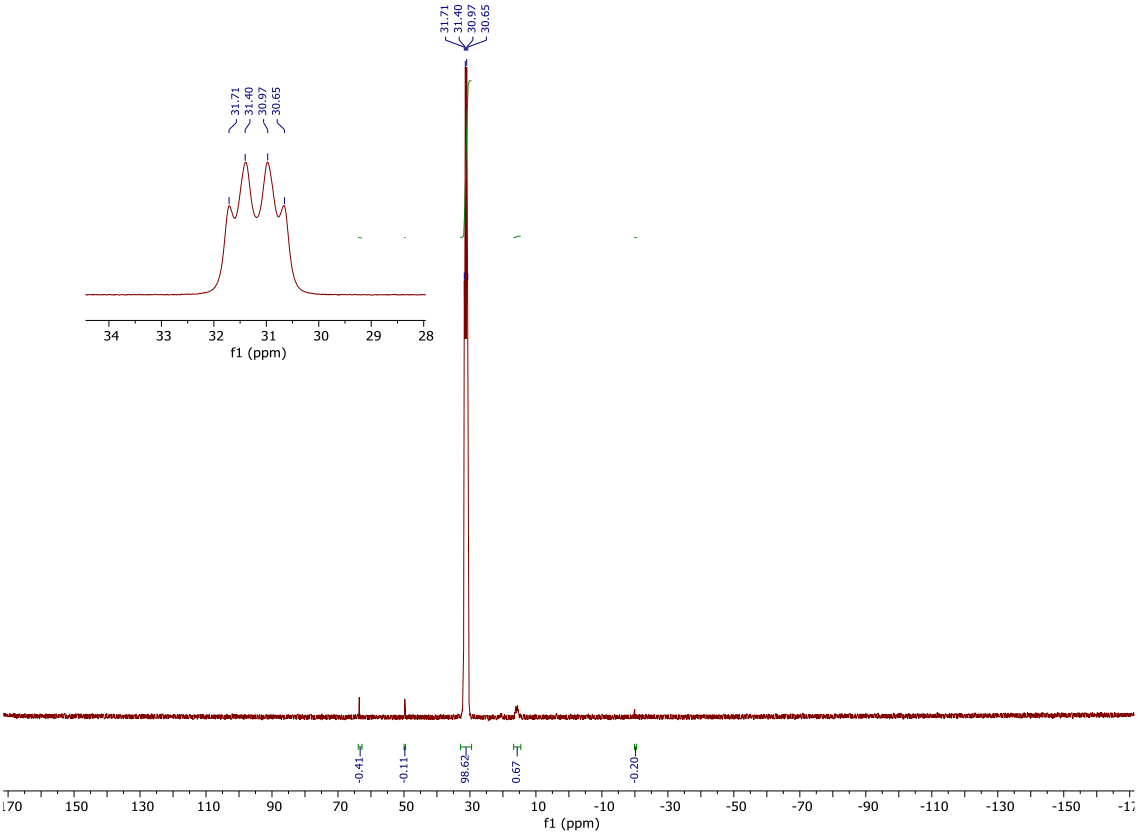
tert-Butylbutylphenylphosphine borane adduct (**2r**) – ^{11}B NMR spectrum ($CDCl_3$)



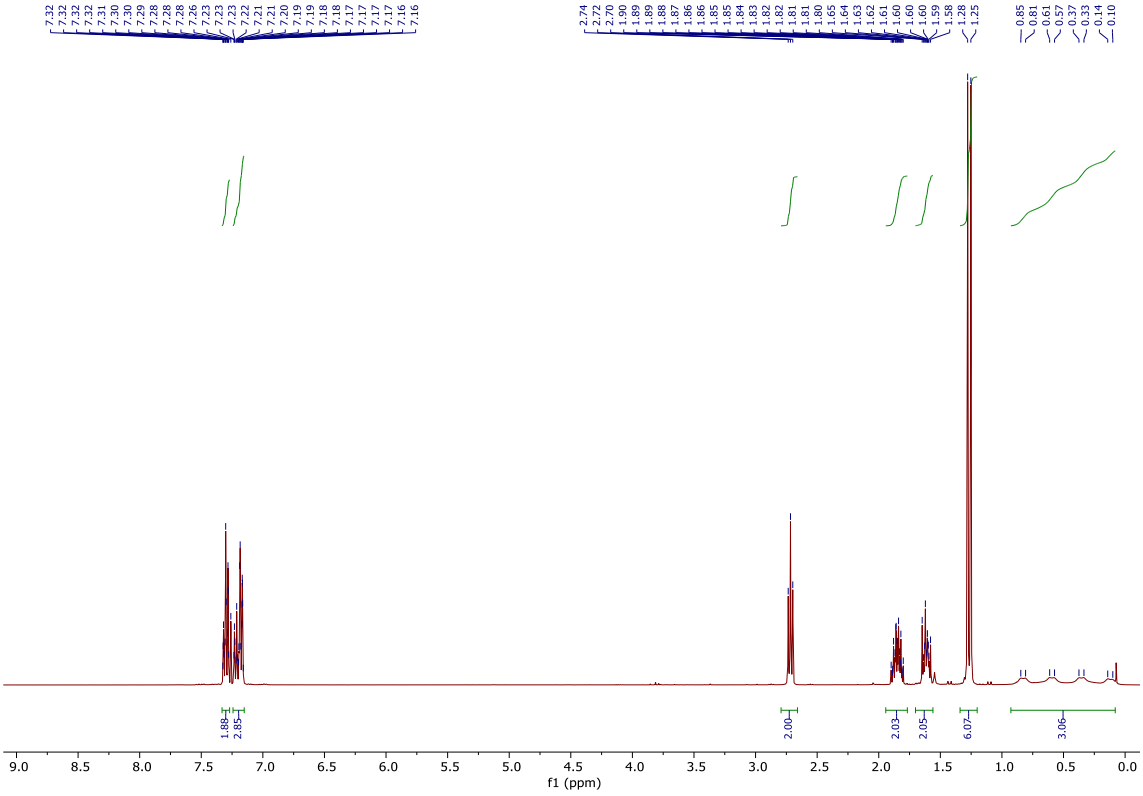
tert-Butylbutylphenylphosphine borane adduct (**2r**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



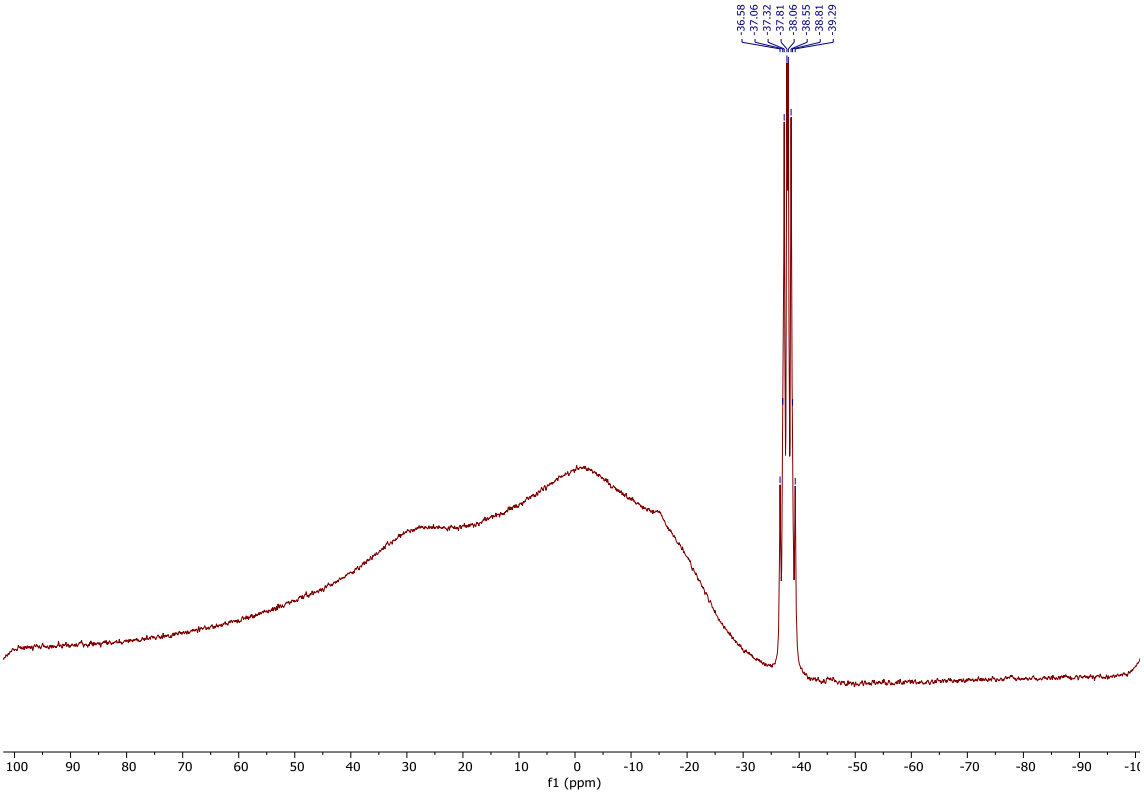
tert-Butylbutylphenylphosphine borane adduct (**2r**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



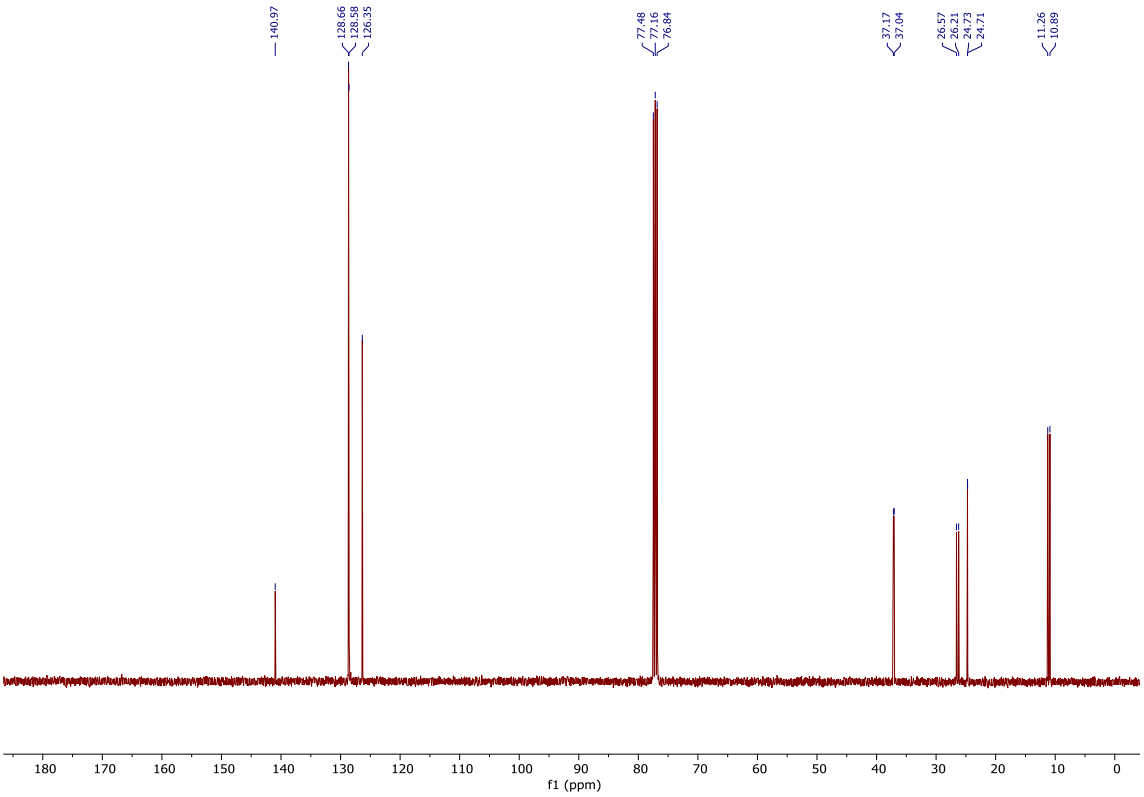
Dimethyl(3-phenylpropyl)phosphine borane adduct (**2s**) – ^{1}H NMR spectrum ($CDCl_3$)



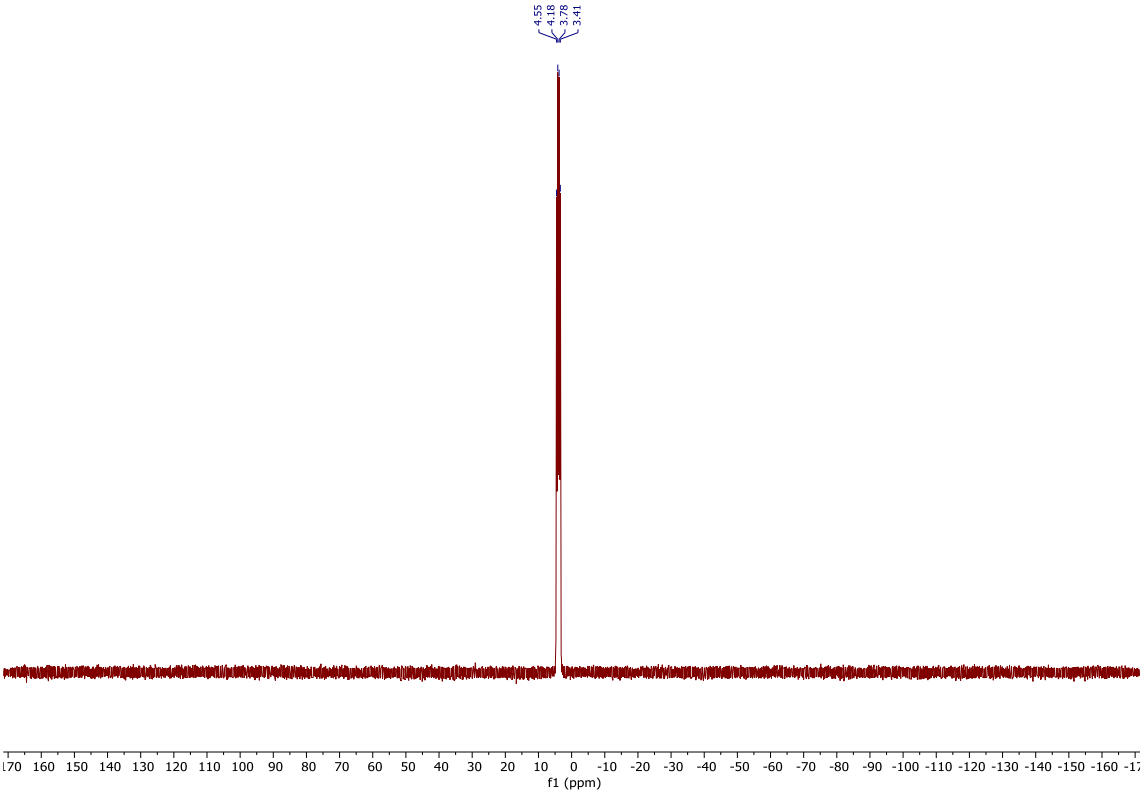
Dimethyl(3-phenylpropyl)phosphine borane adduct (**2s**) – ^{11}B NMR spectrum ($CDCl_3$)



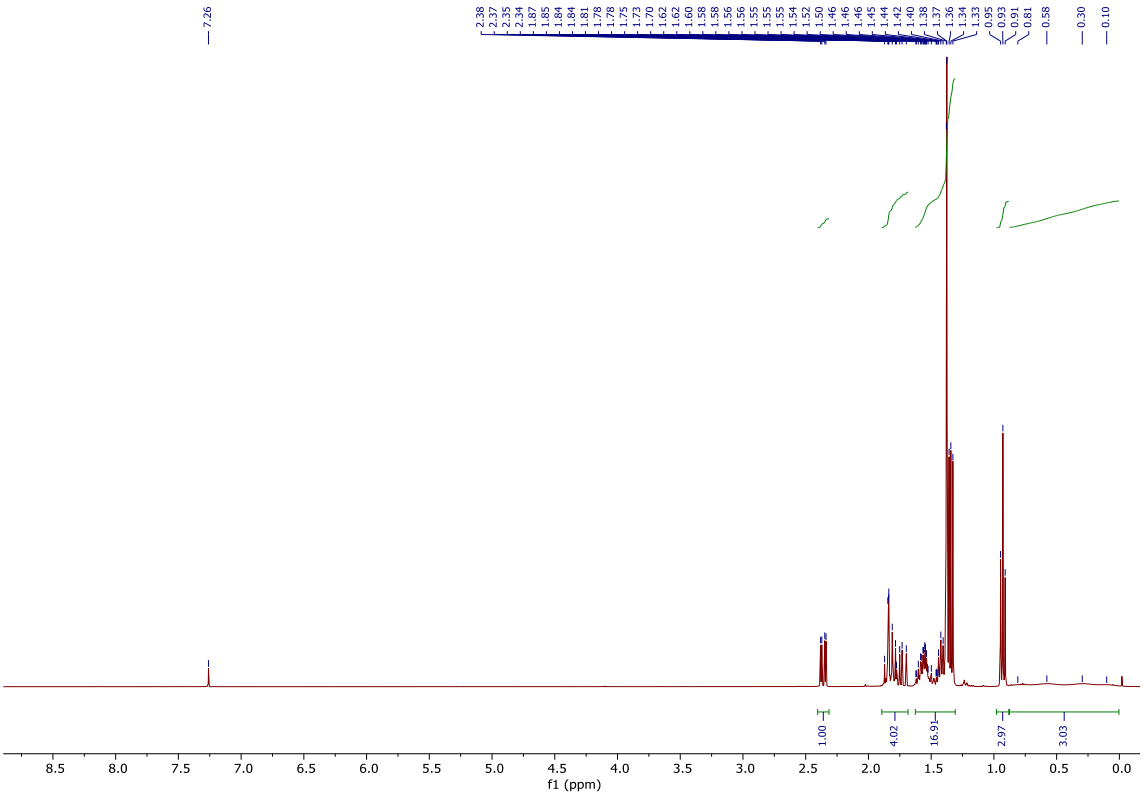
Dimethyl(3-phenylpropyl)phosphine borane adduct (**2s**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



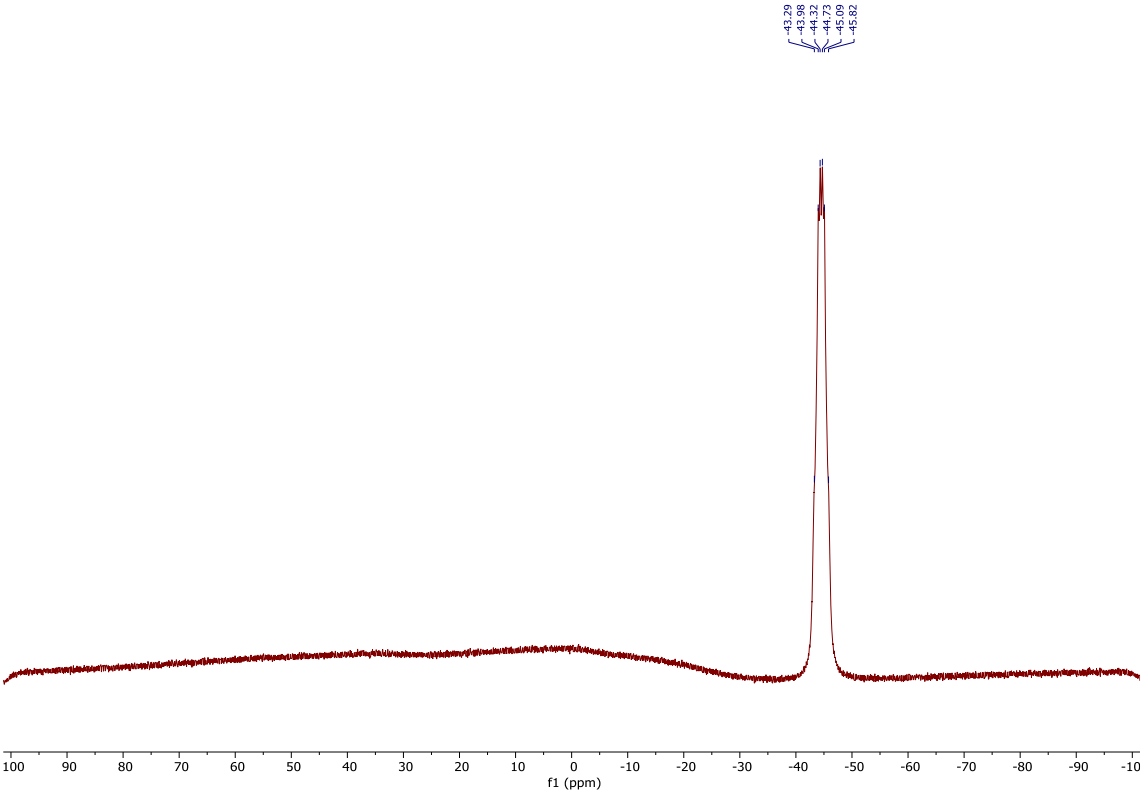
Dimethyl(3-phenylpropyl)phosphine borane adduct (**2s**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



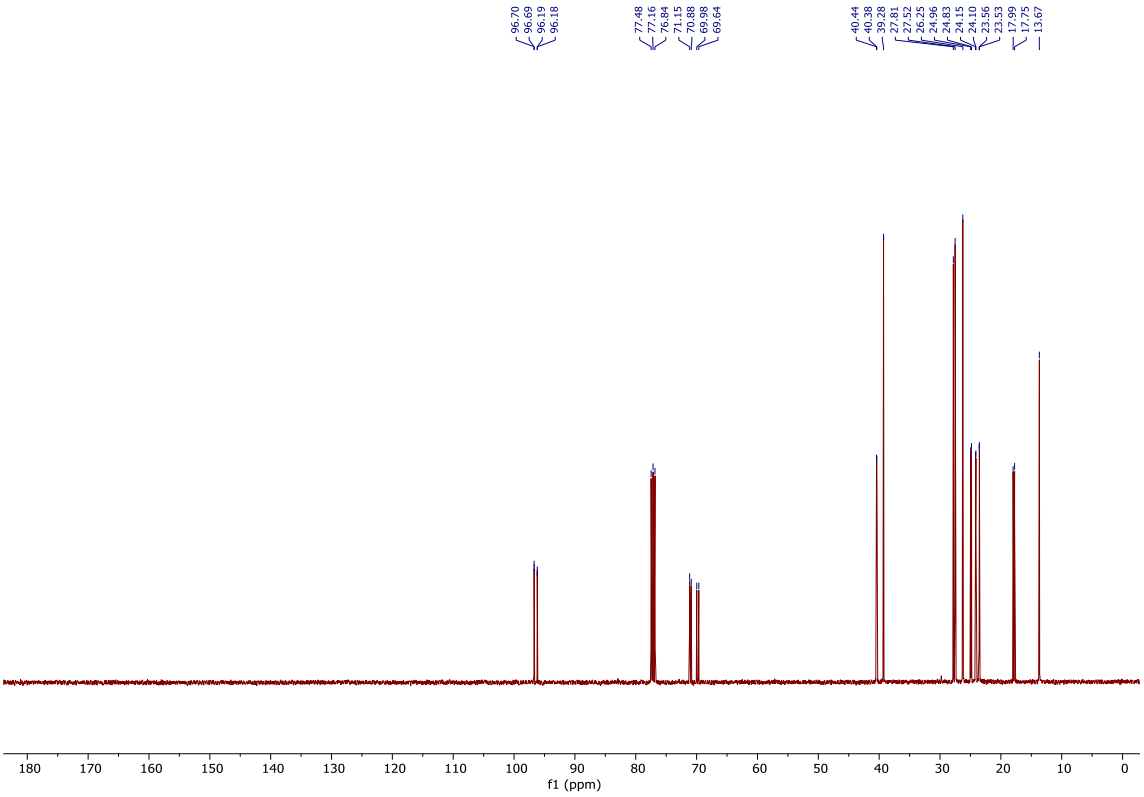
Phosphine borane adduct **2t** – ^{1}H NMR spectrum ($CDCl_3$)



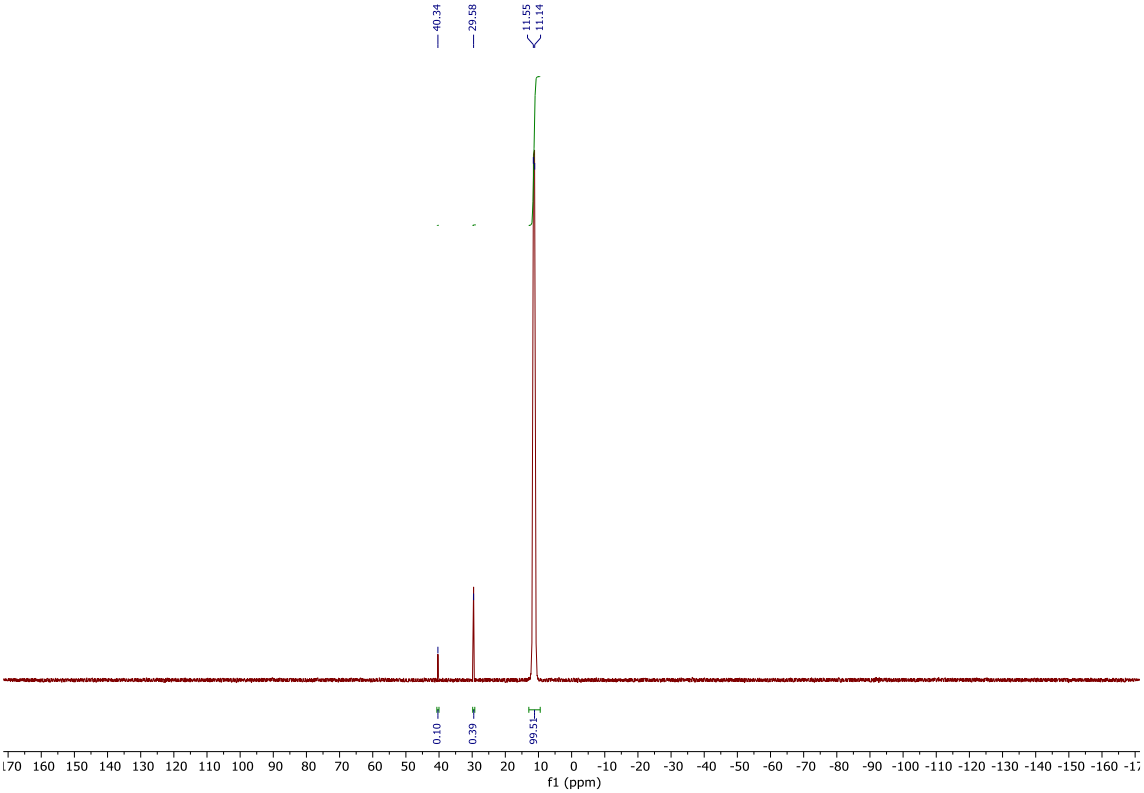
Phosphine borane adduct **2t** – ^{11}B NMR spectrum ($CDCl_3$)



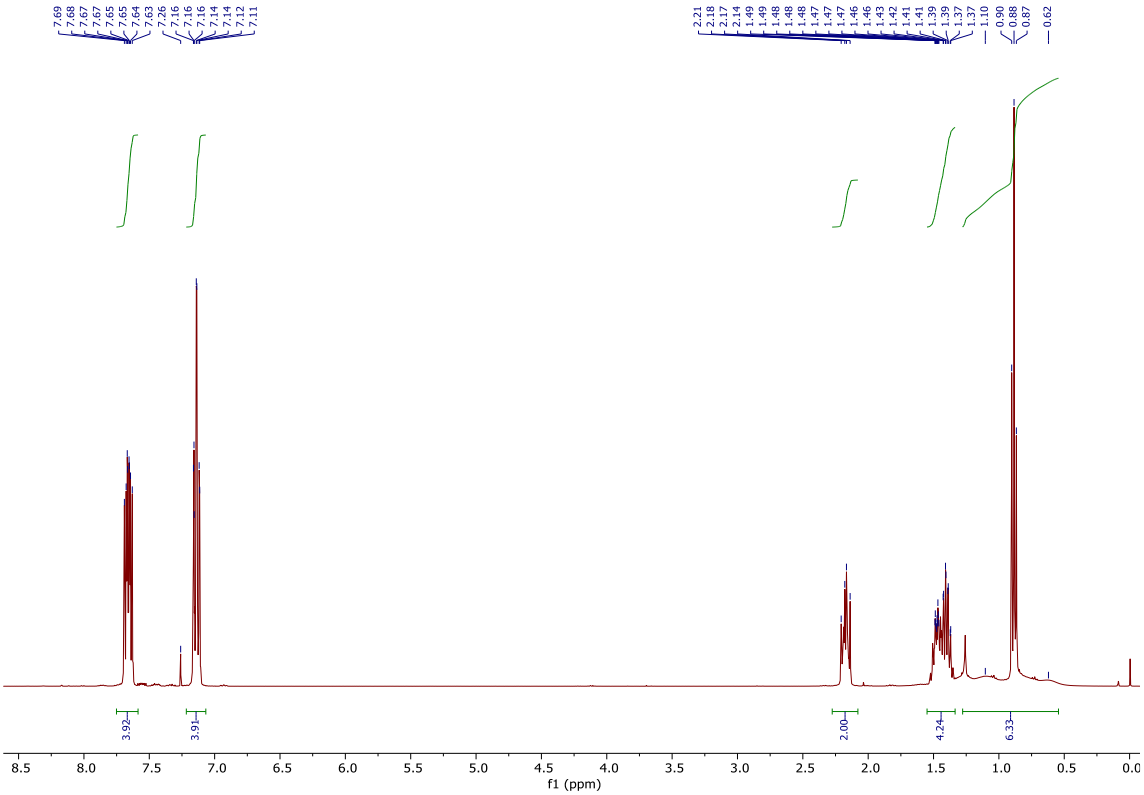
Phosphine borane adduct **2t** – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



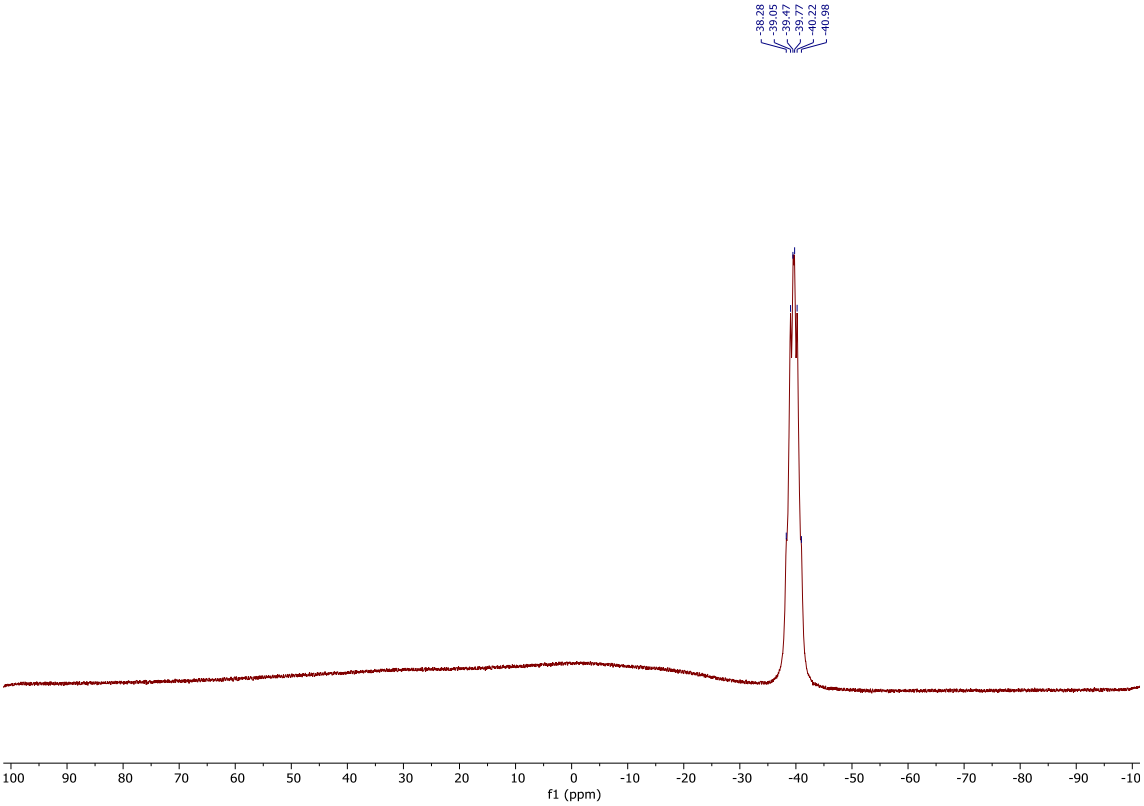
Phosphine borane adduct **2t** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



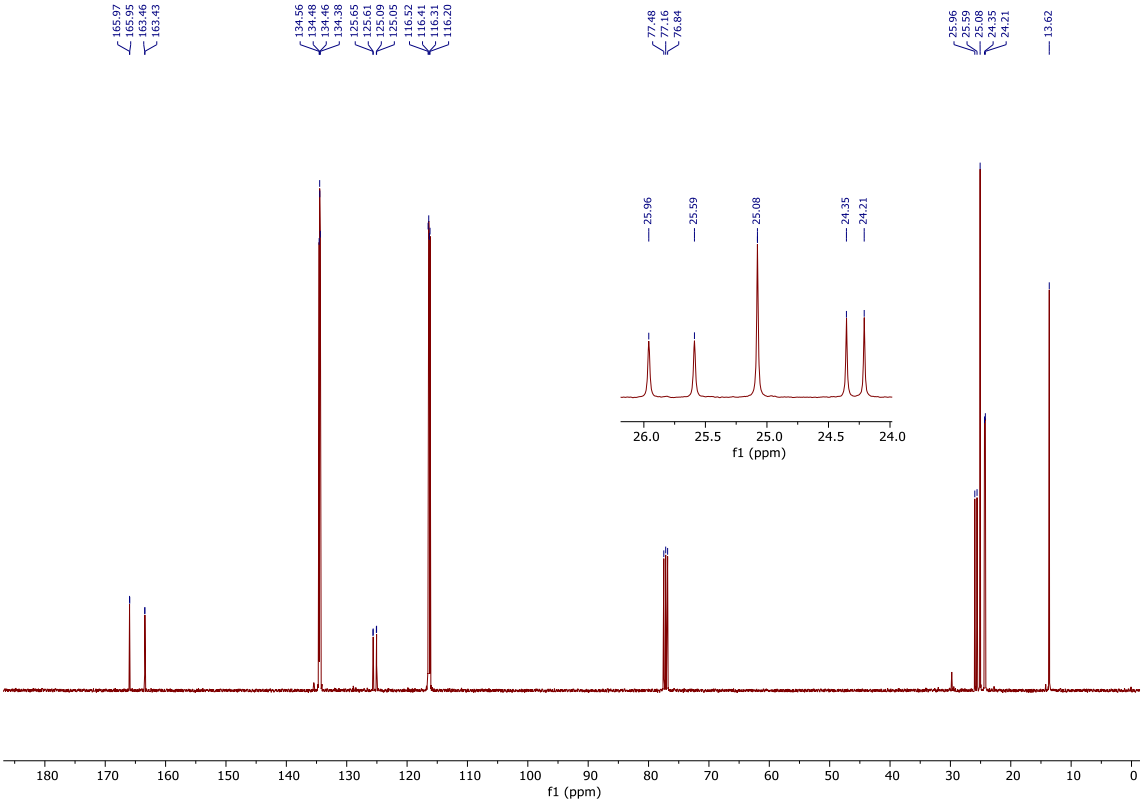
Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**) – ^{1}H NMR spectrum ($CDCl_3$)



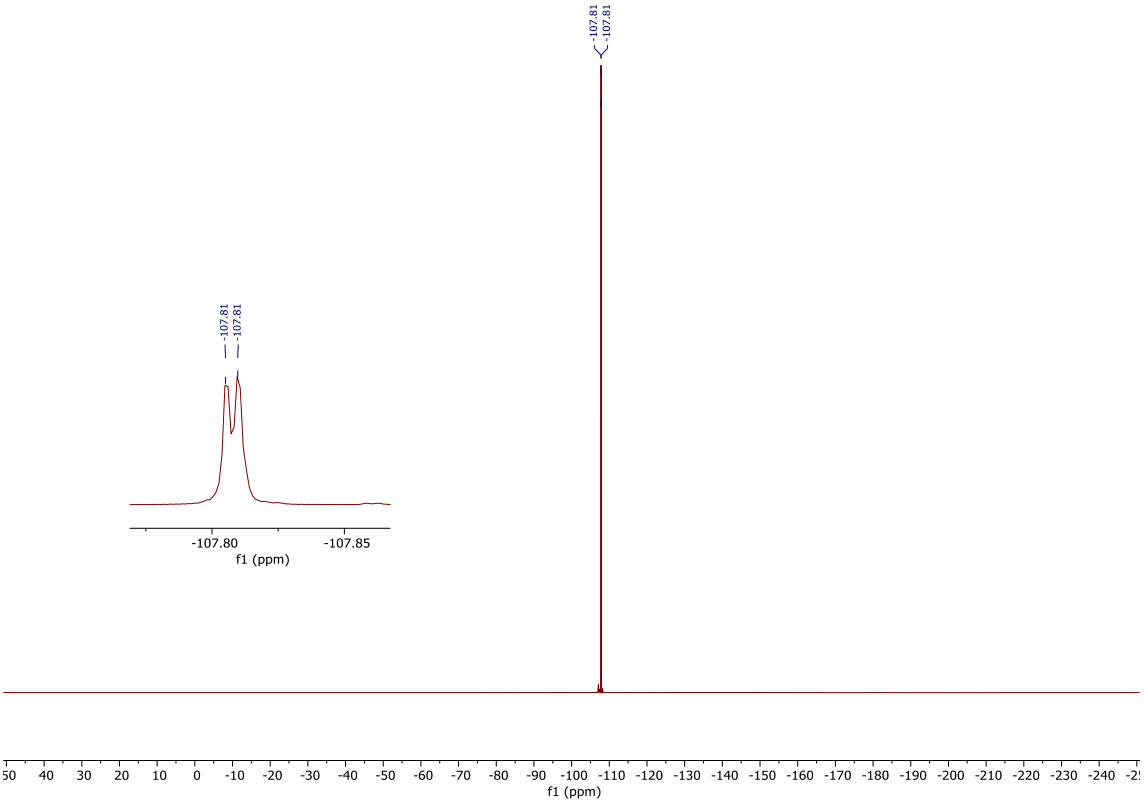
Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**) – ^{11}B NMR spectrum ($CDCl_3$)



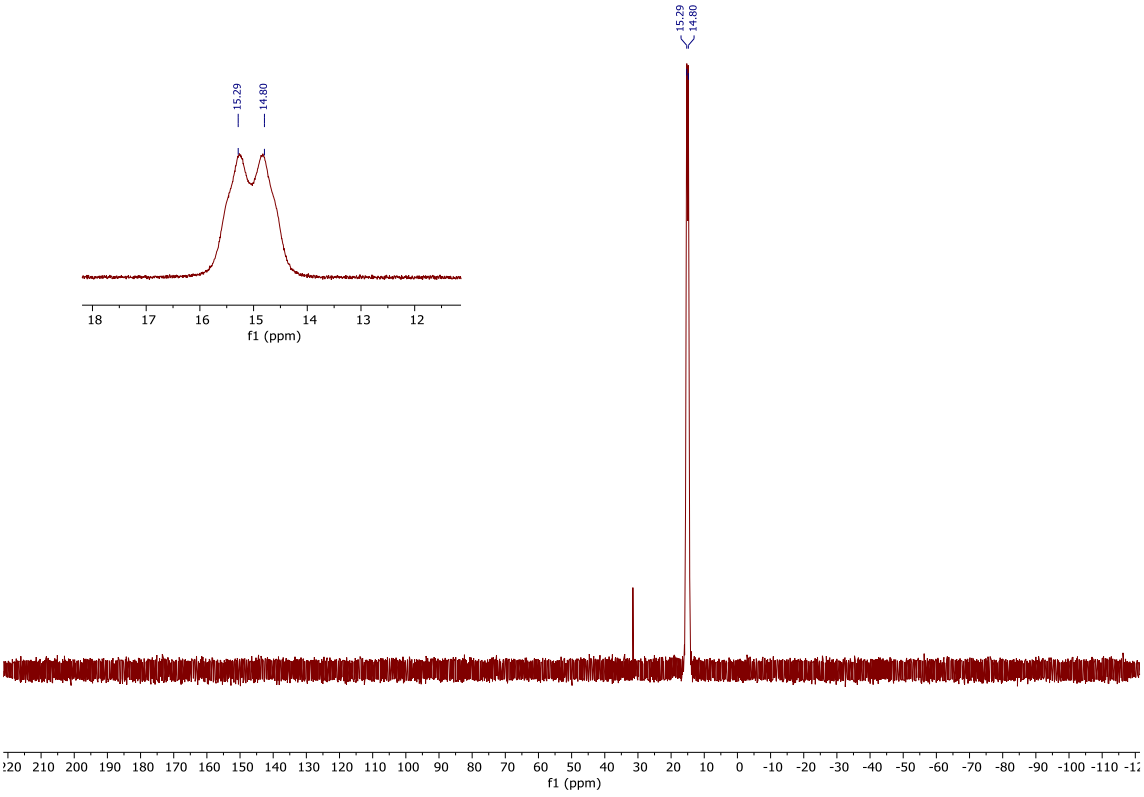
Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



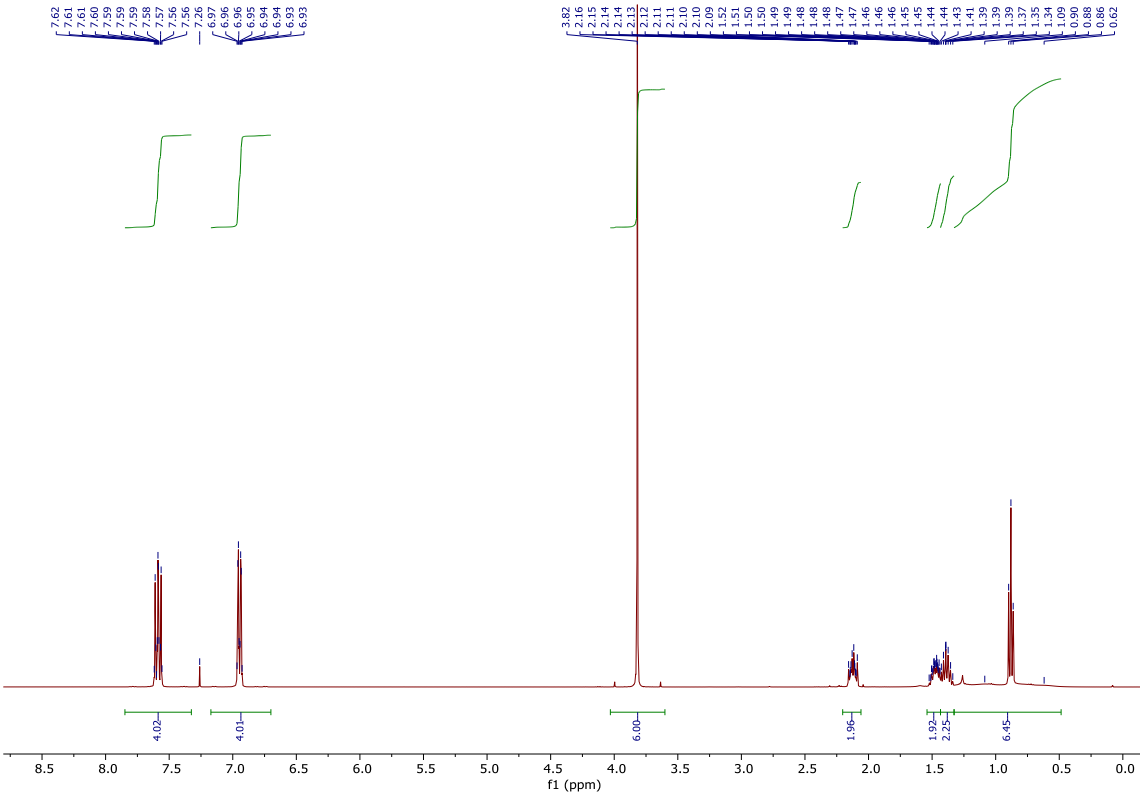
Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



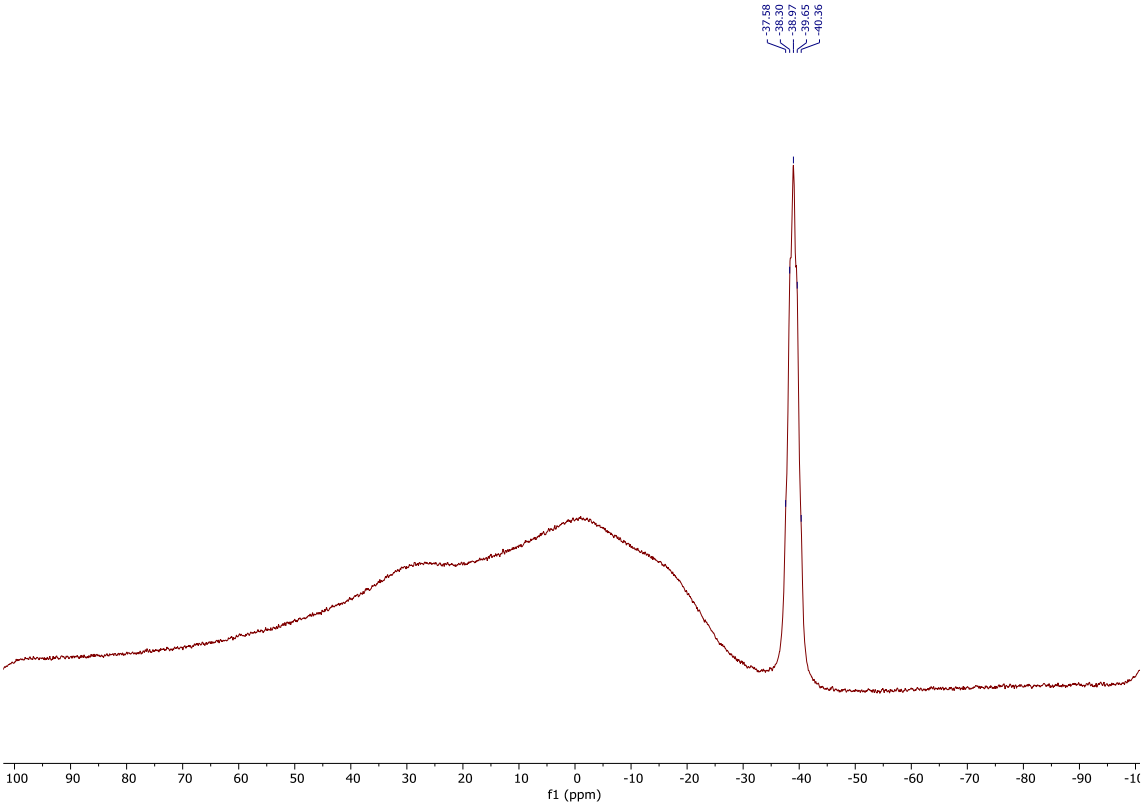
Butylbis(4-fluorophenyl)phosphine borane adduct (**2u**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



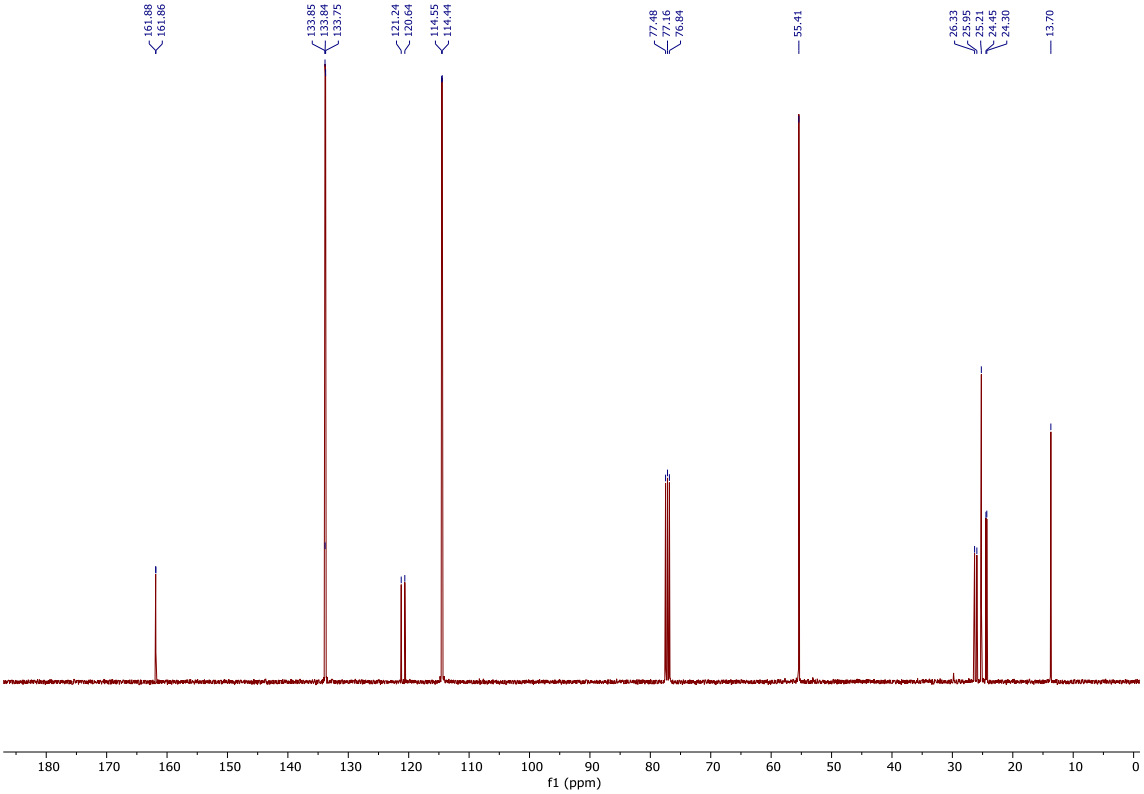
Butylbis(4-methoxyphenyl)phosphine borane adduct (**2v**) – ^{1}H NMR spectrum ($CDCl_3$)



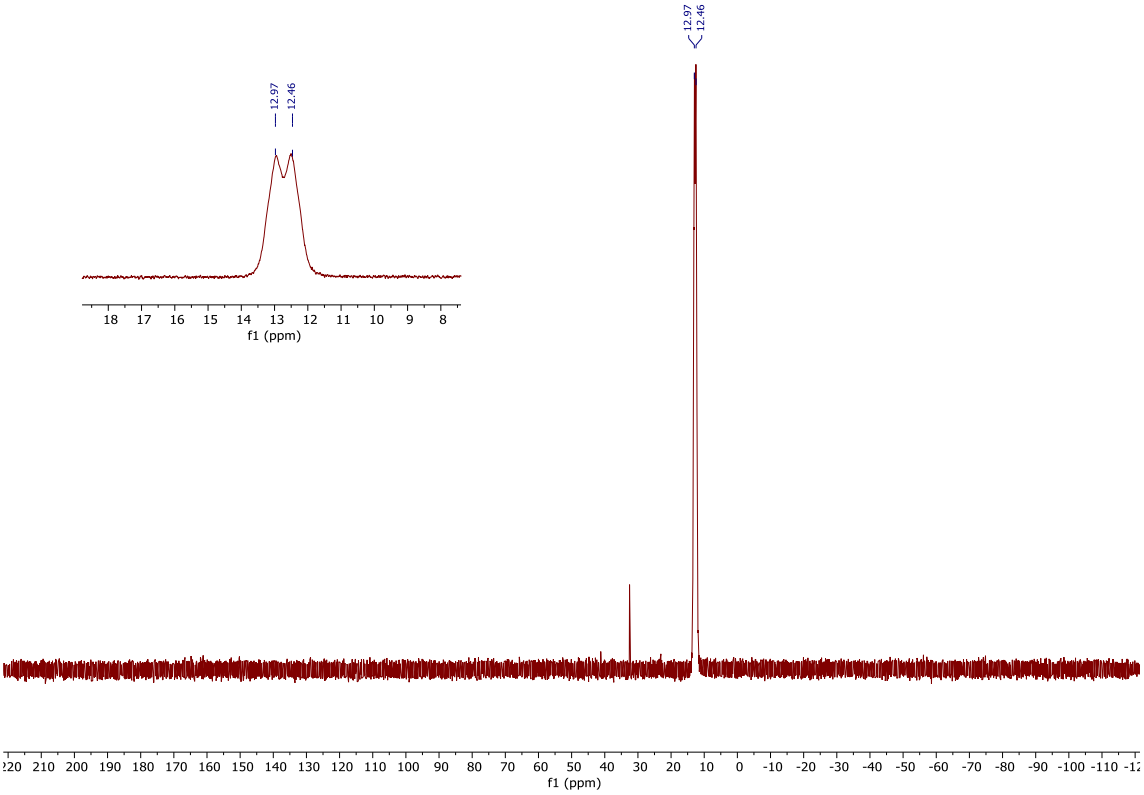
Butylbis(4-methoxyphenyl)phosphine borane adduct (**2v**) – ^{11}B NMR spectrum ($CDCl_3$)



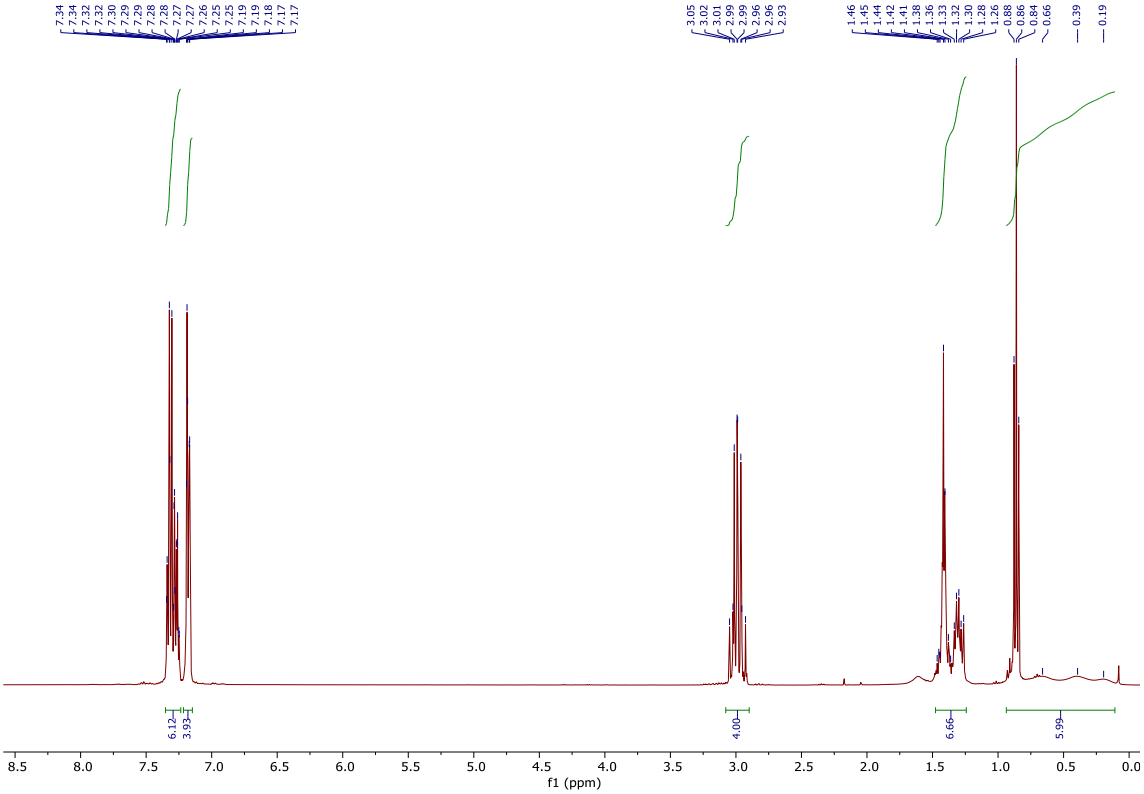
Butylbis(4-methoxyphenyl)phosphine borane adduct (**2v**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



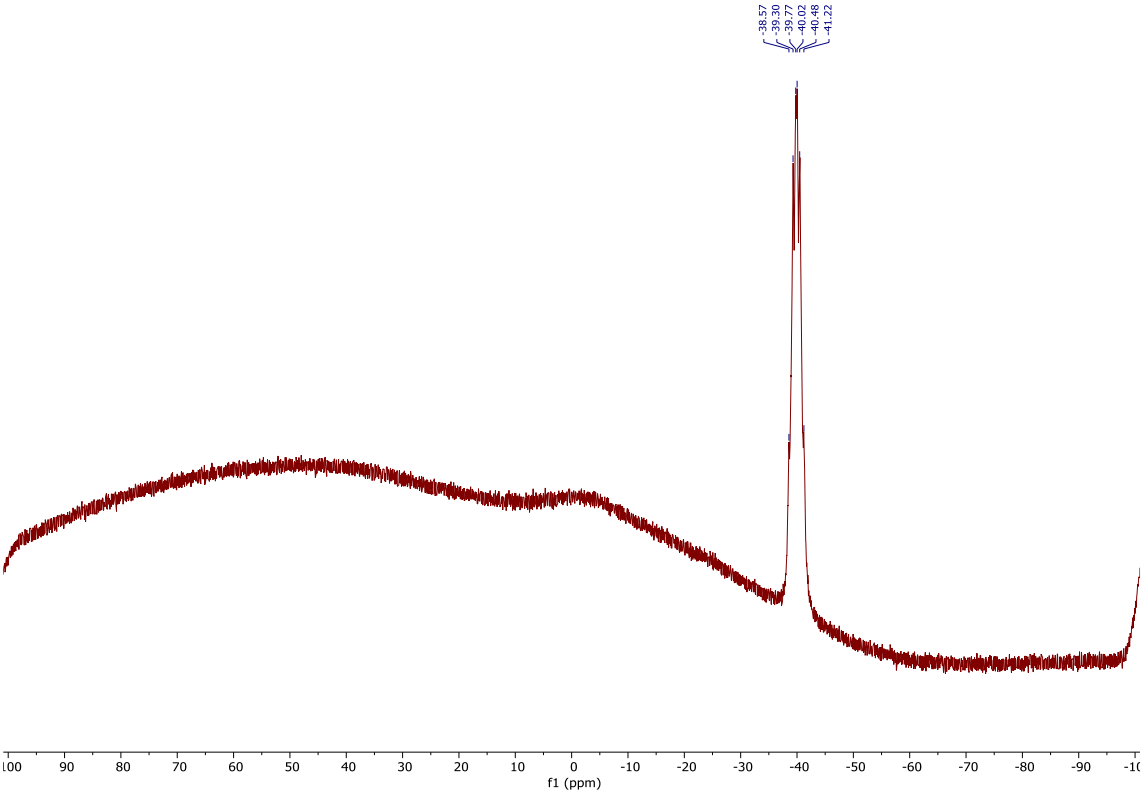
Butylbis(4-methoxyphenyl)phosphine borane adduct (**2v**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



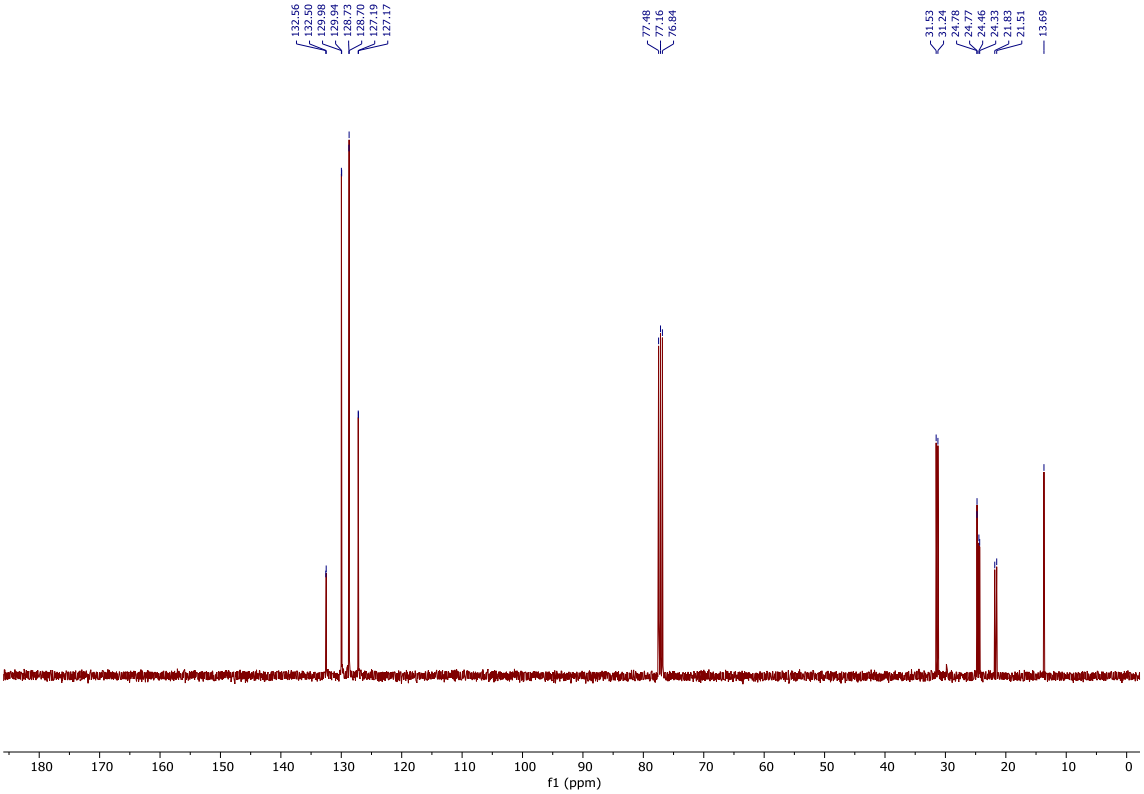
Dibenzylbutylphosphine borane adduct (**2w**) – ^{1}H NMR spectrum ($CDCl_3$)



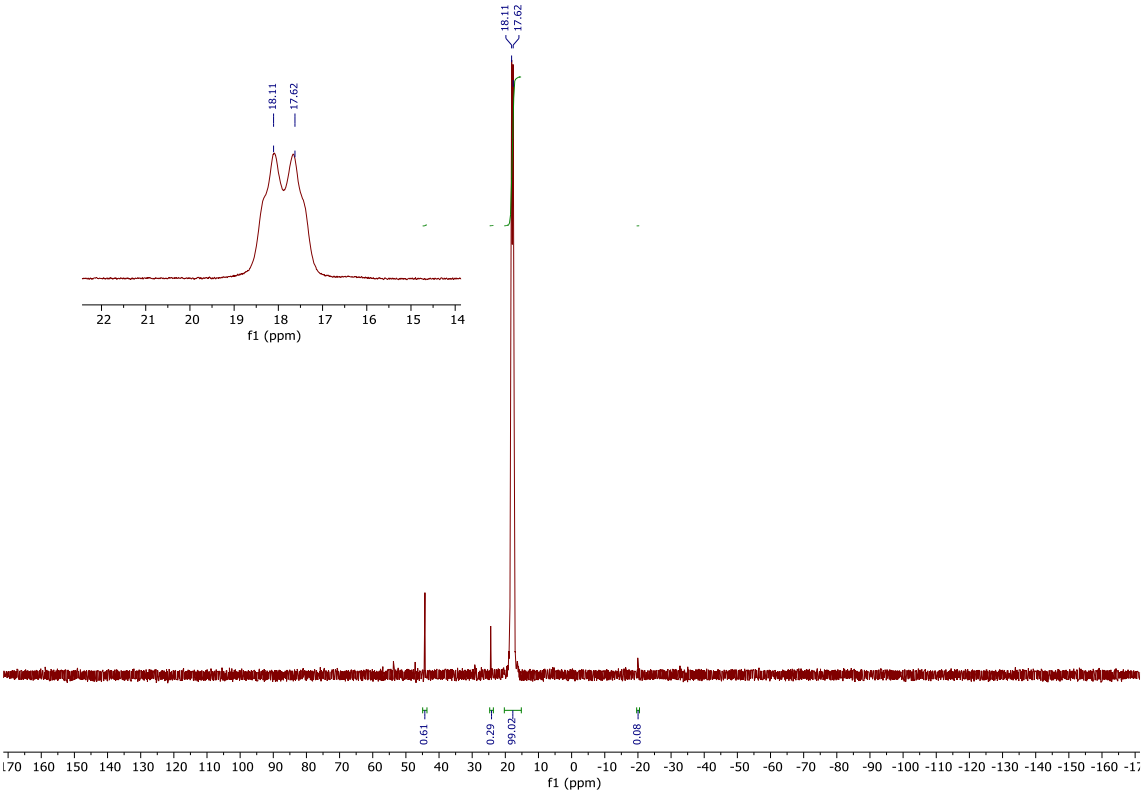
Dibenzylbutylphosphine borane adduct (**2w**) – ^{11}B NMR spectrum ($CDCl_3$)



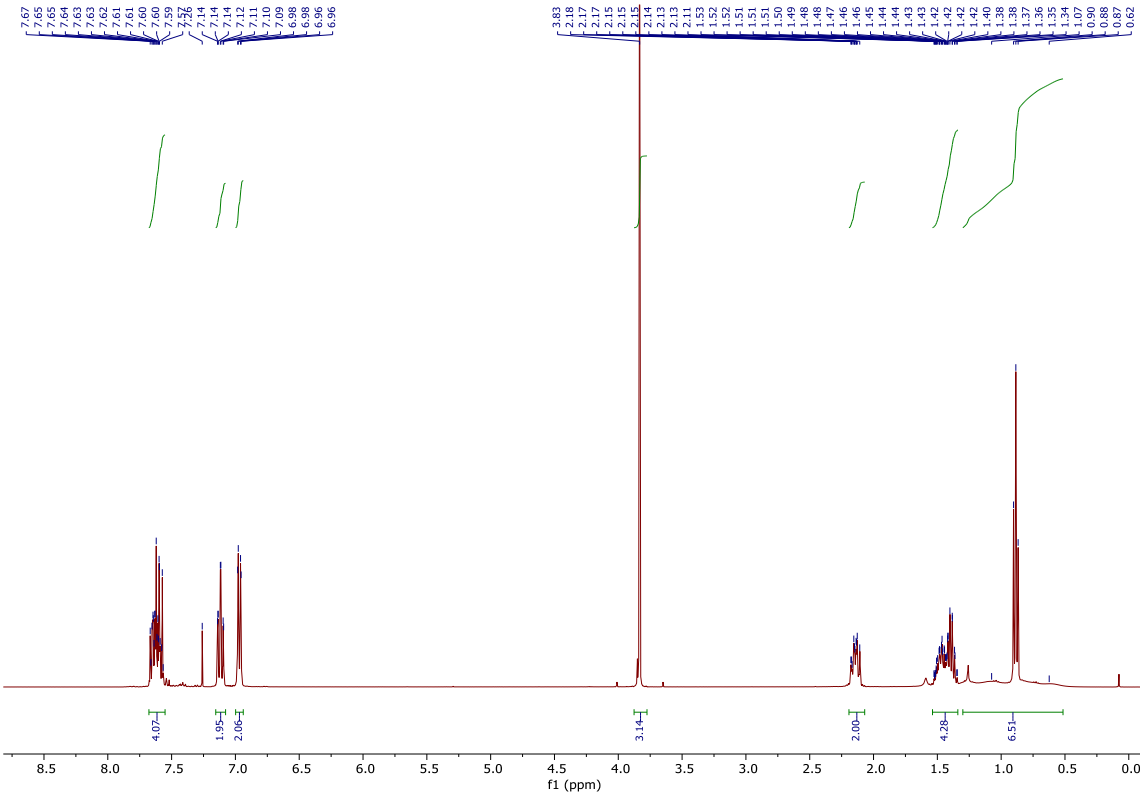
Dibenzylbutylphosphine borane adduct (**2w**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



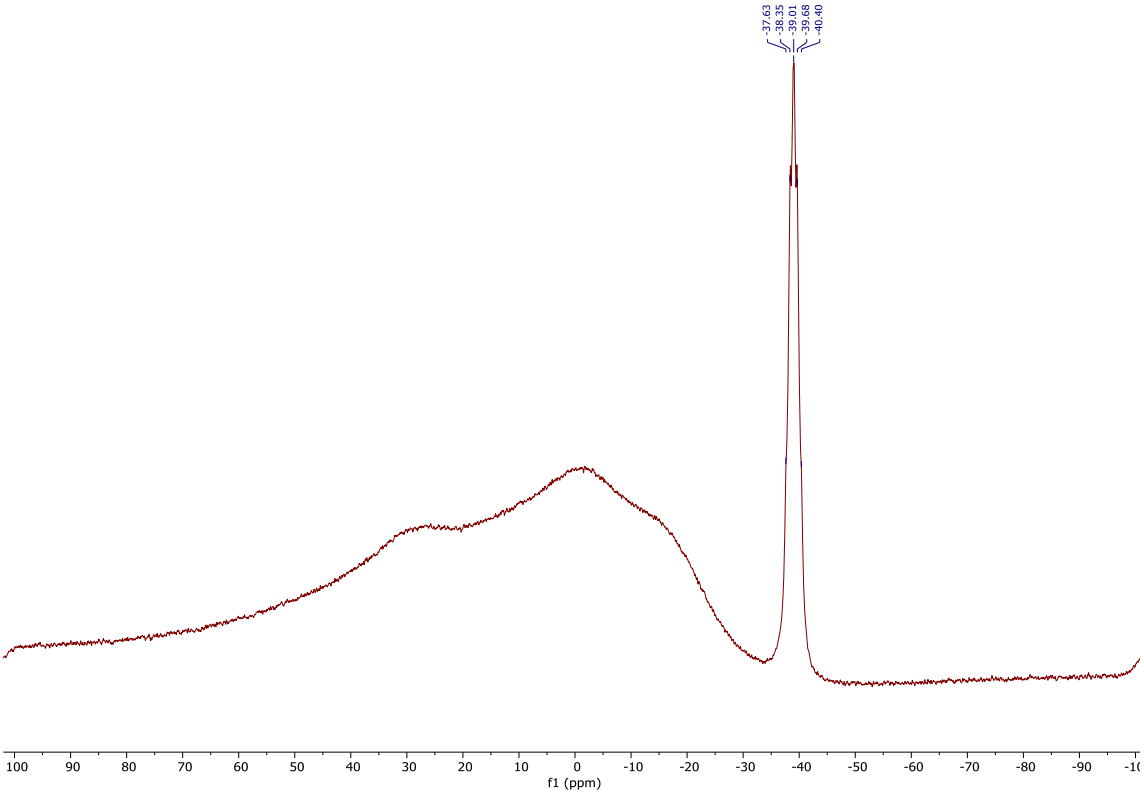
Dibenzylbutylphosphine borane adduct (**2w**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



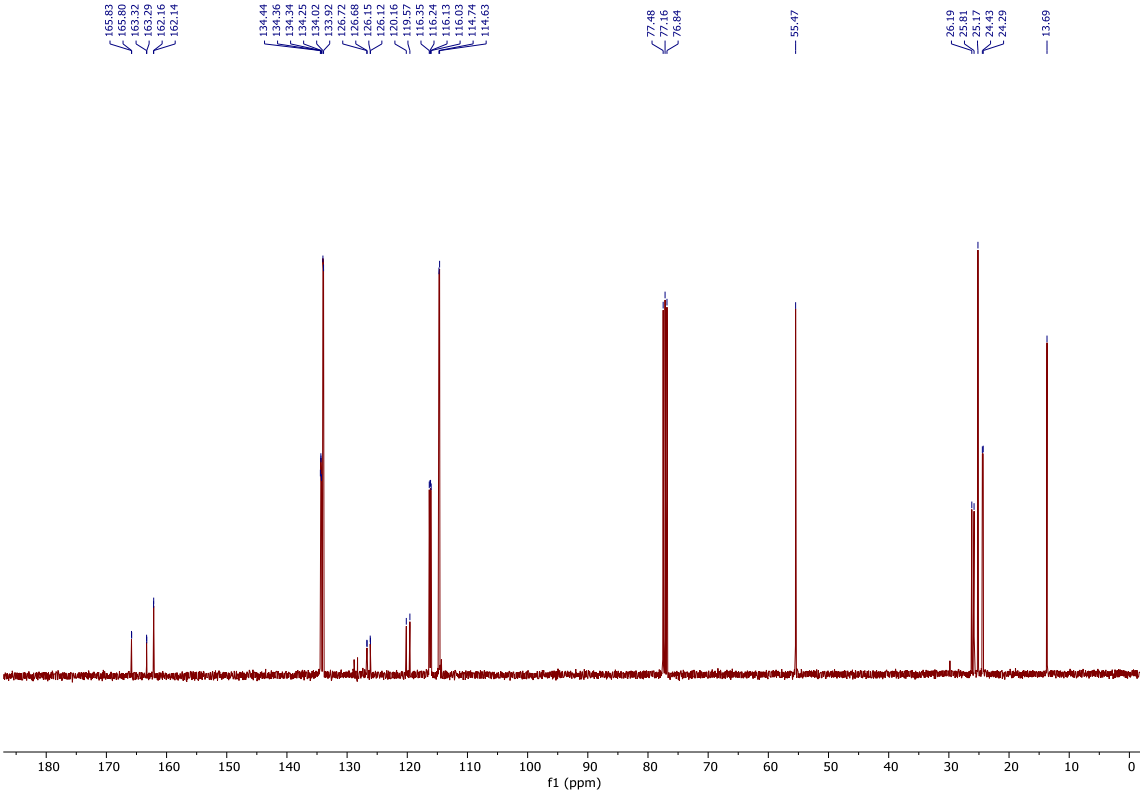
Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (**2x**) – ^{1}H NMR spectrum ($CDCl_3$)



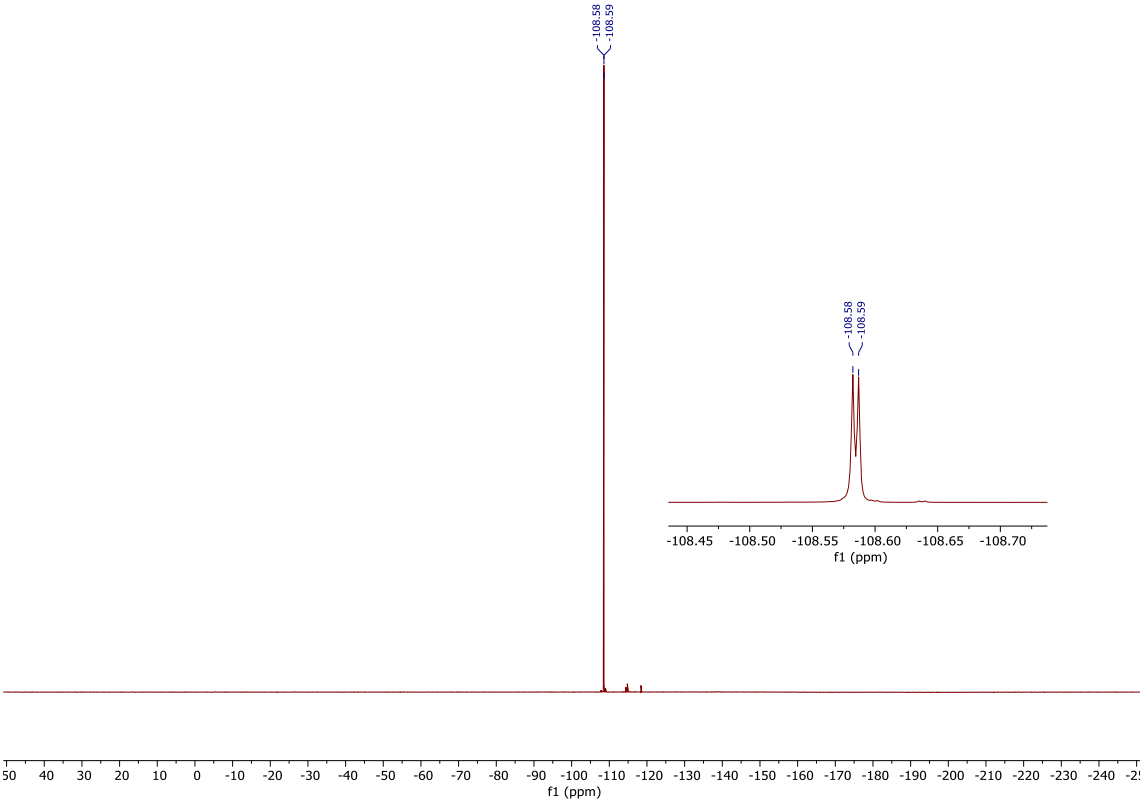
Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (**2x**) – ^{11}B NMR spectrum ($CDCl_3$)



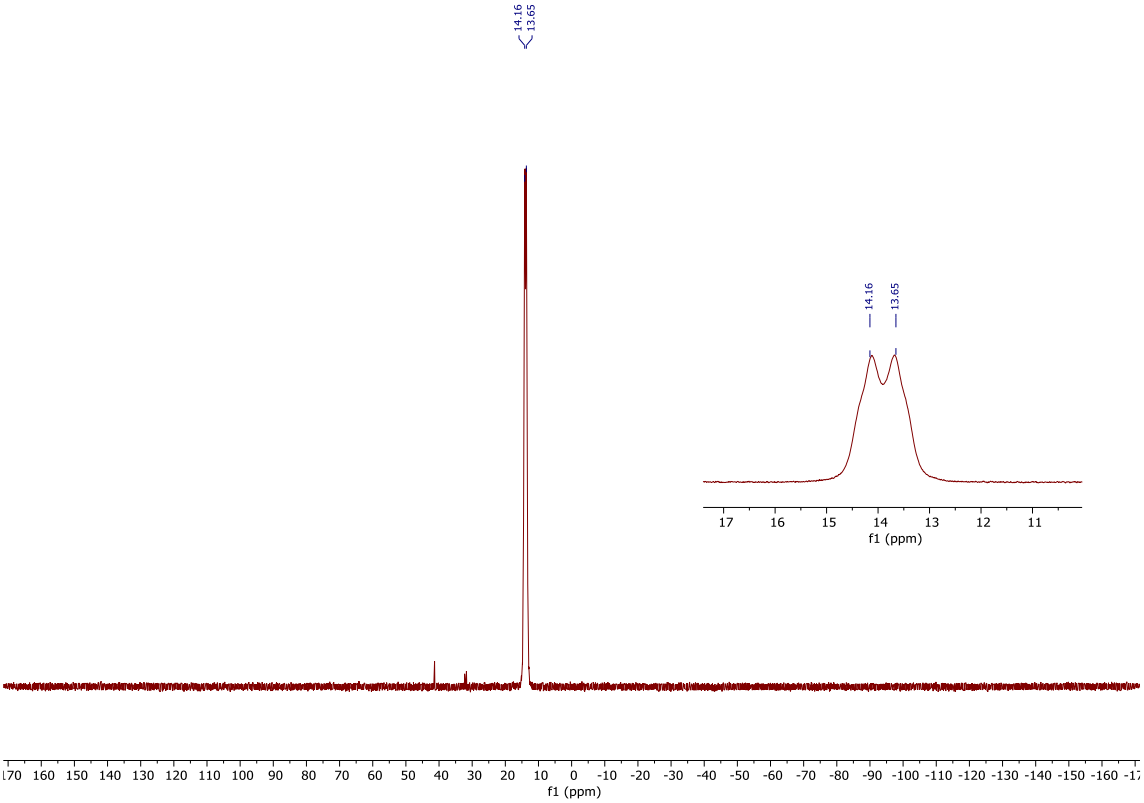
Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (**2x**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



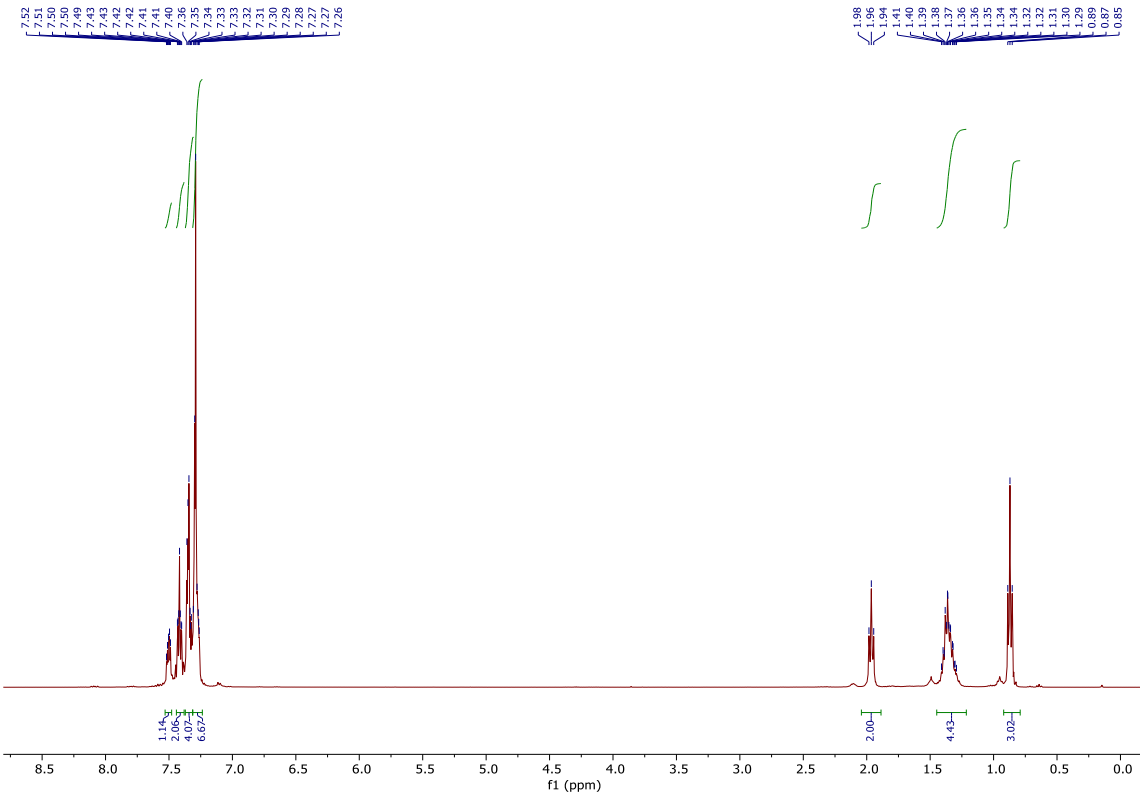
Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (**2x**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



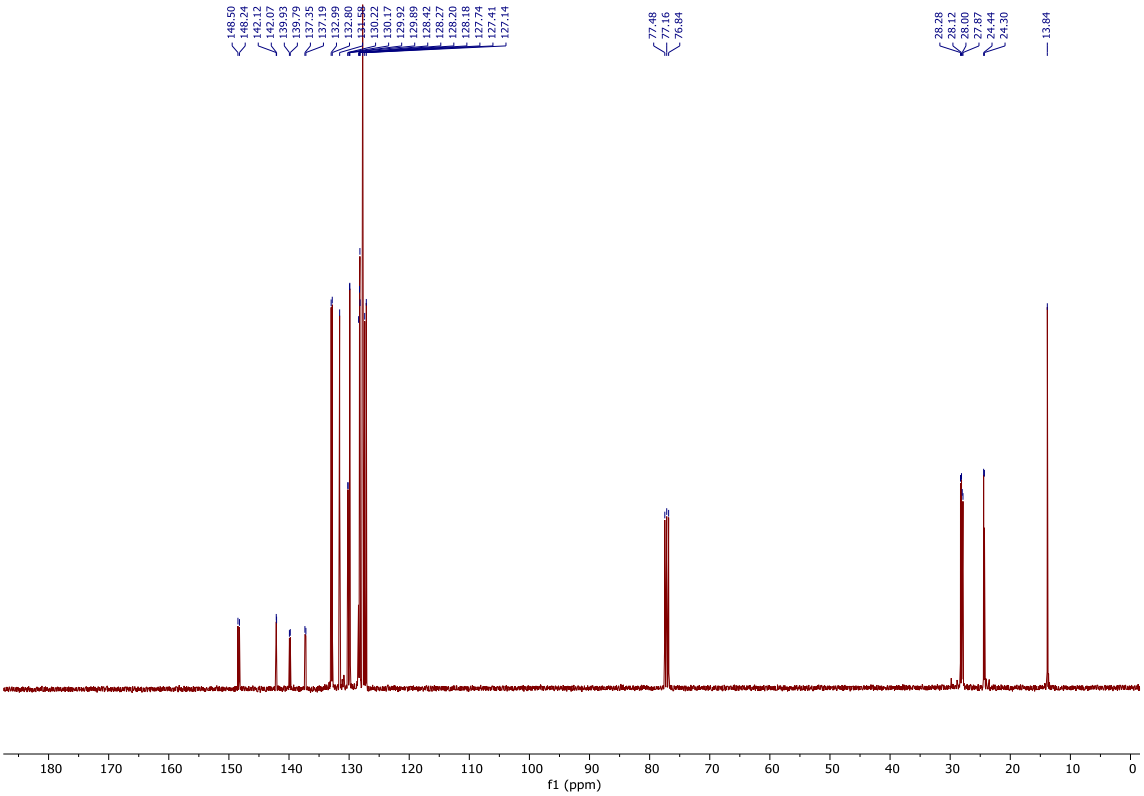
Butyl(4-fluorophenyl)(4-methoxyphenyl)phosphine borane adduct (**2x**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



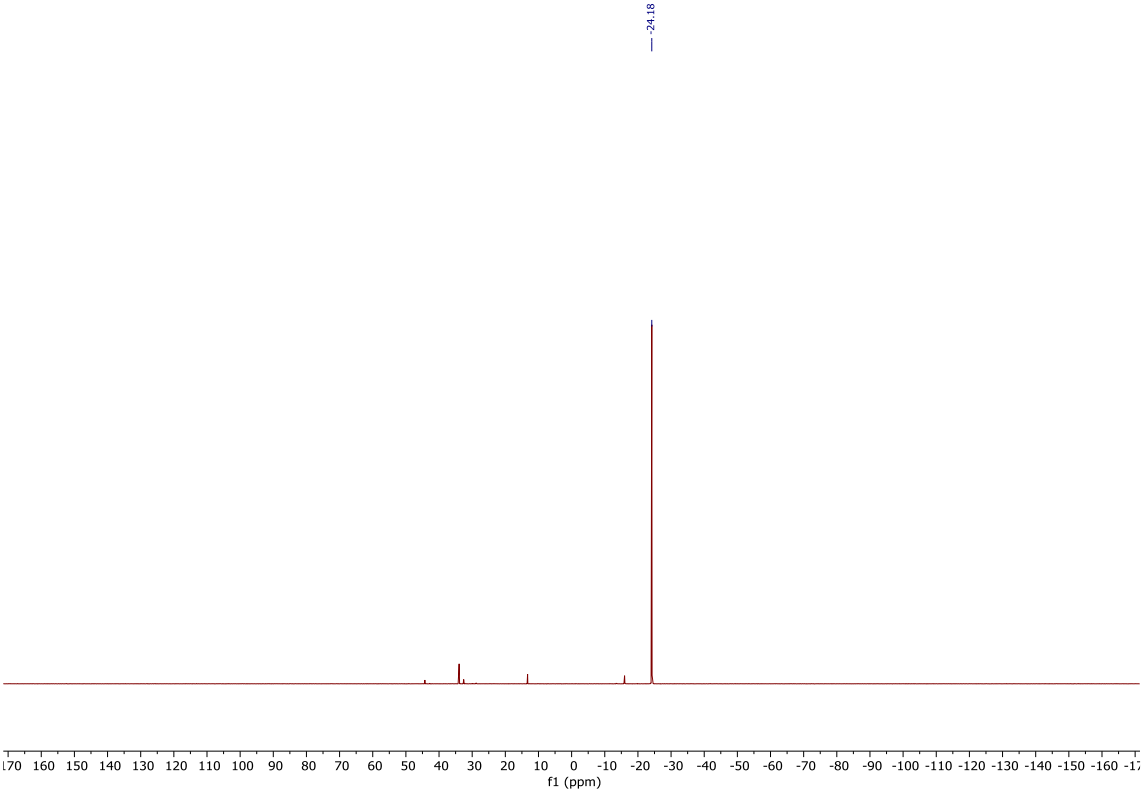
[1,1'-Biphenyl]-2-yl(butyl)(phenyl)phosphine (**2z**) – ^{1}H NMR spectrum ($CDCl_3$)



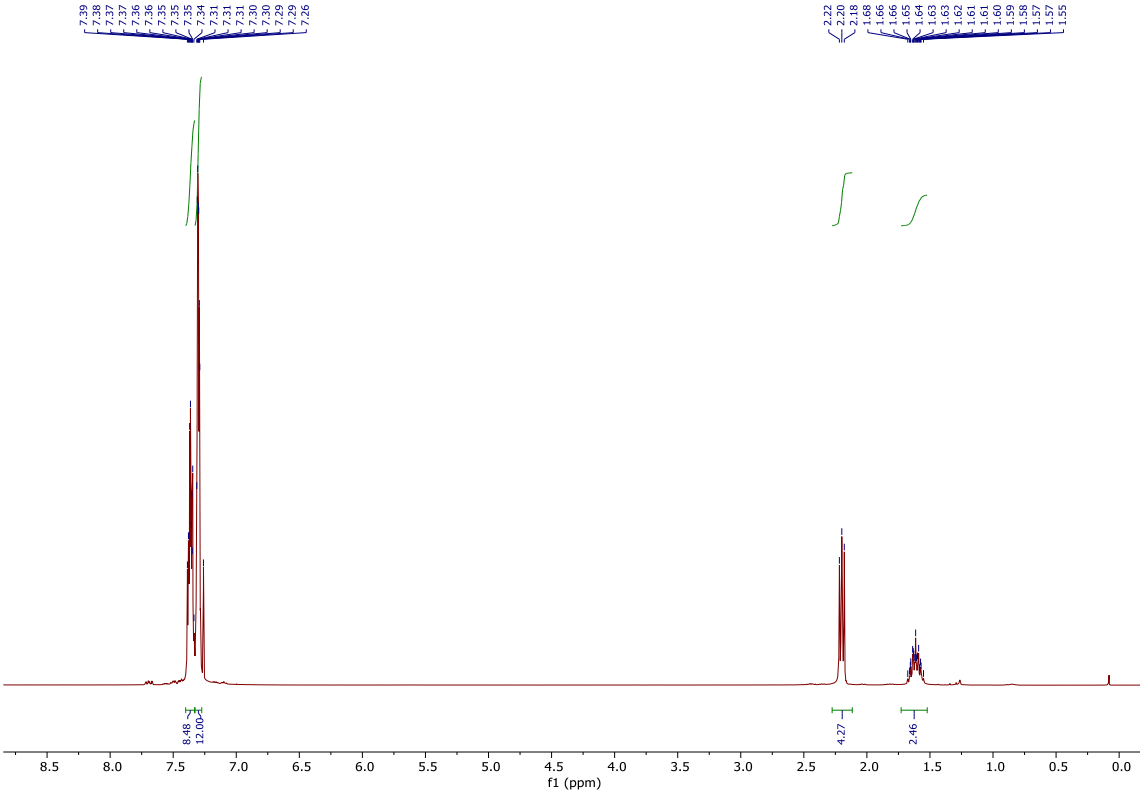
[1,1'-Biphenyl]-2-yl(butyl)(phenyl)phosphine (**2z**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



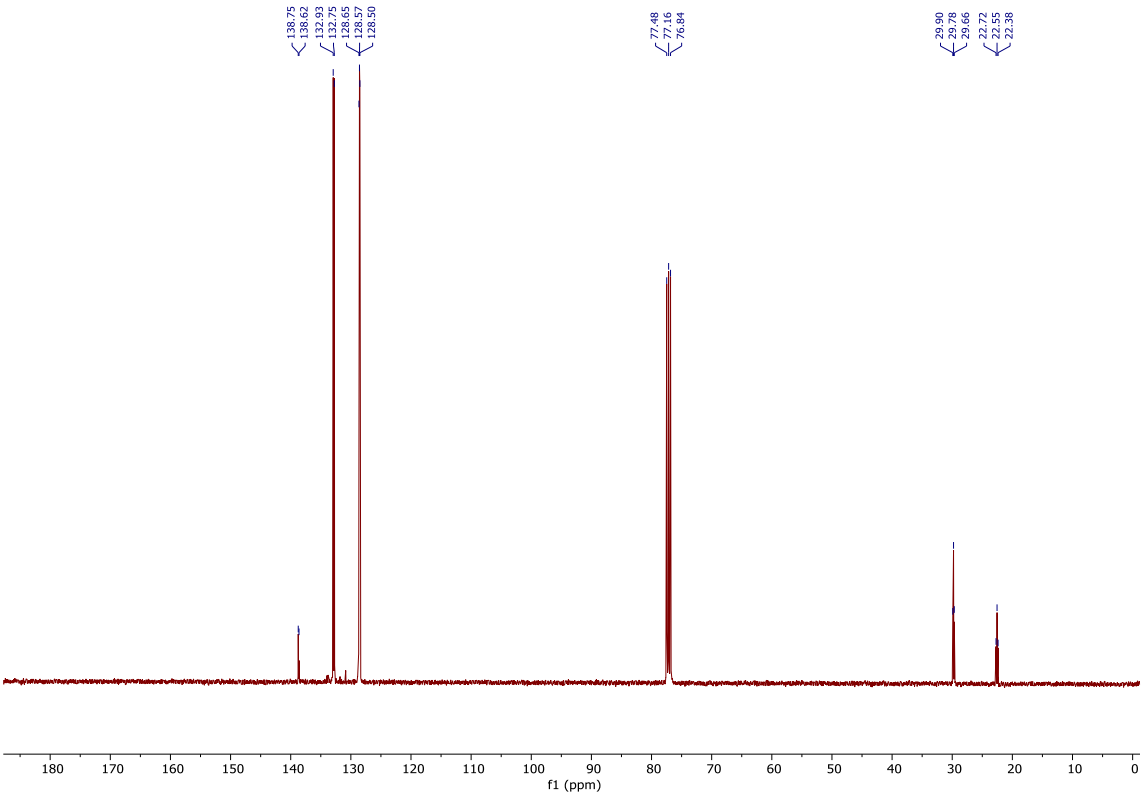
[1,1'-Biphenyl]-2-yl(butyl)(phenyl)phosphine (**2z**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



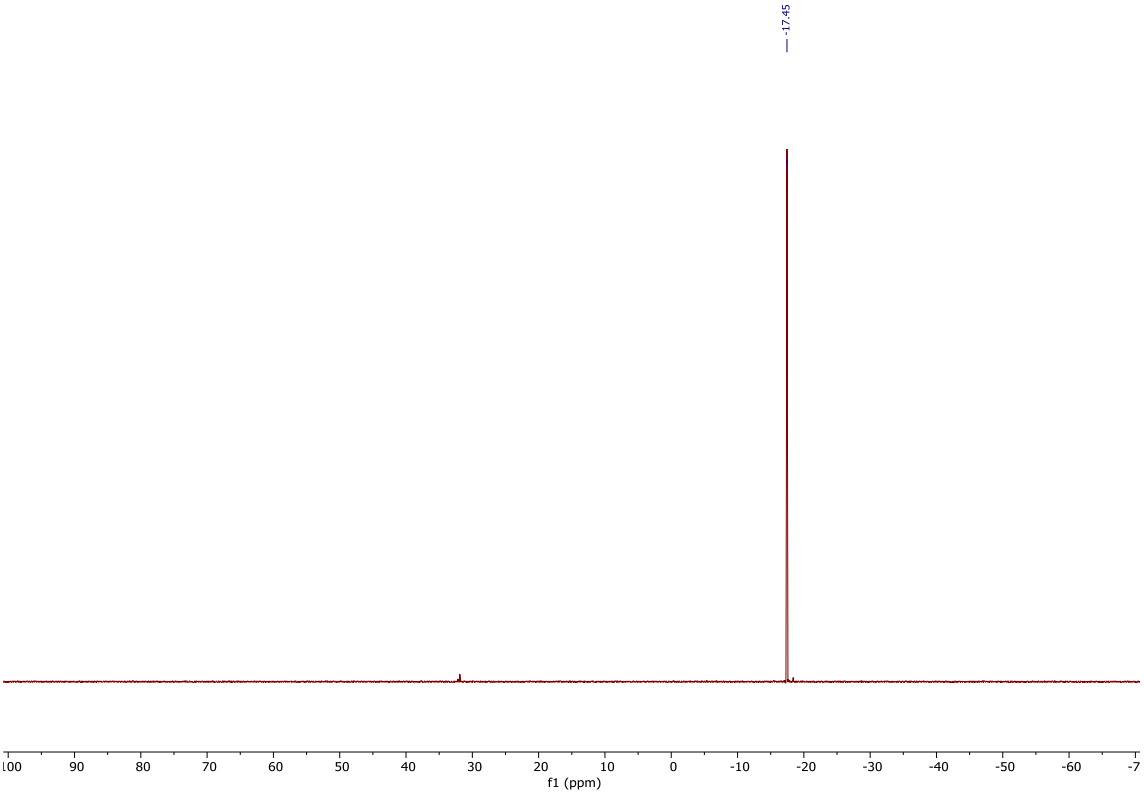
DPPP (**5**) – ^{1}H NMR spectrum ($CDCl_3$)



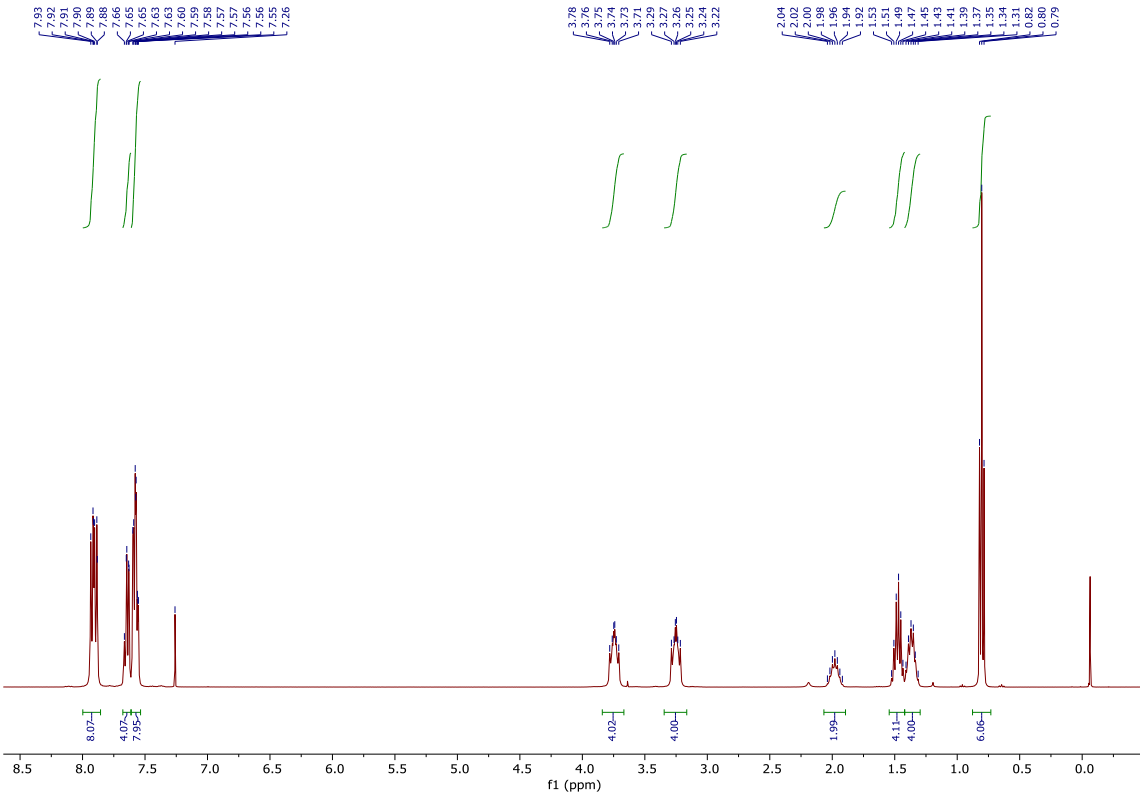
DPPP (**5**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



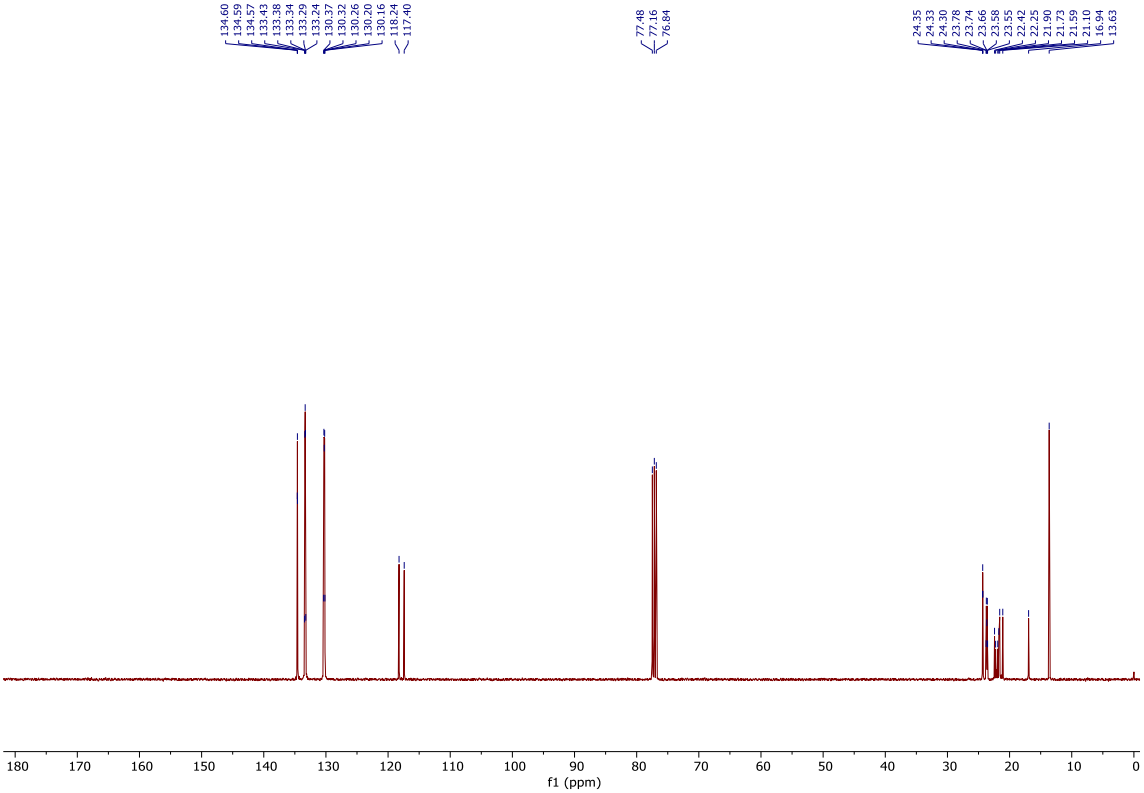
DPPP (**5**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



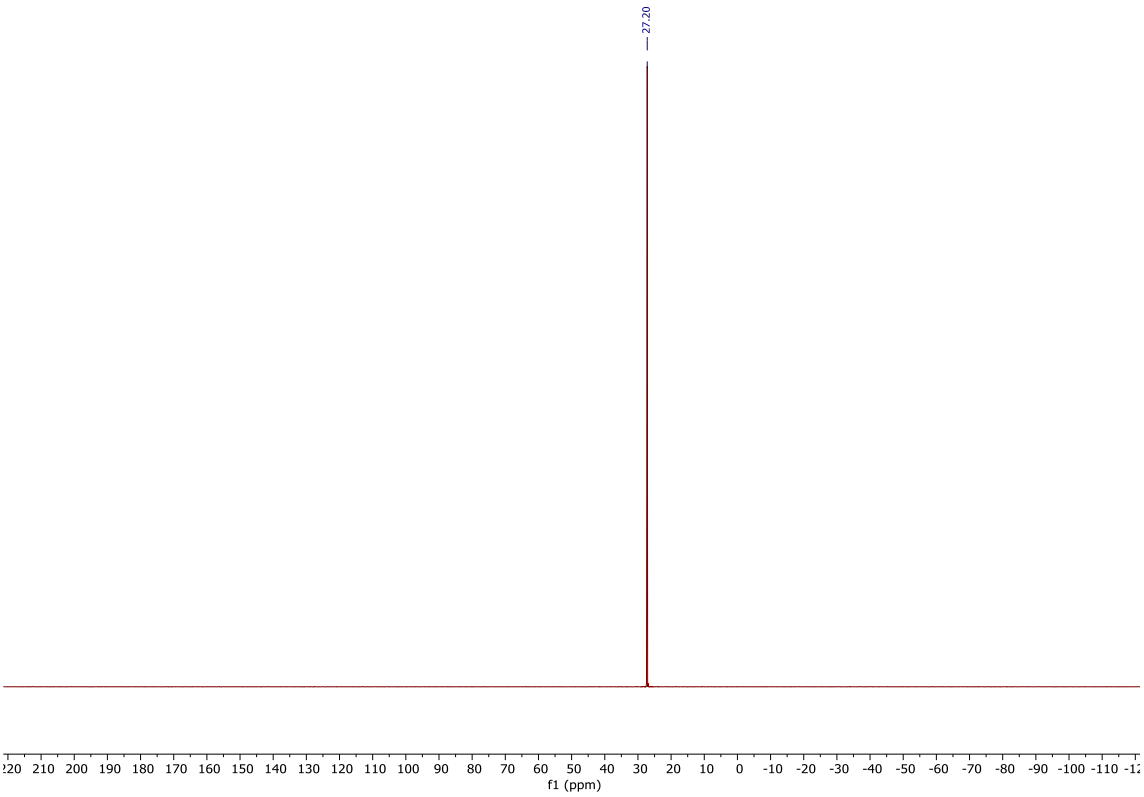
Bisphosphonium salt **6** – ^{1}H NMR spectrum ($CDCl_3$)



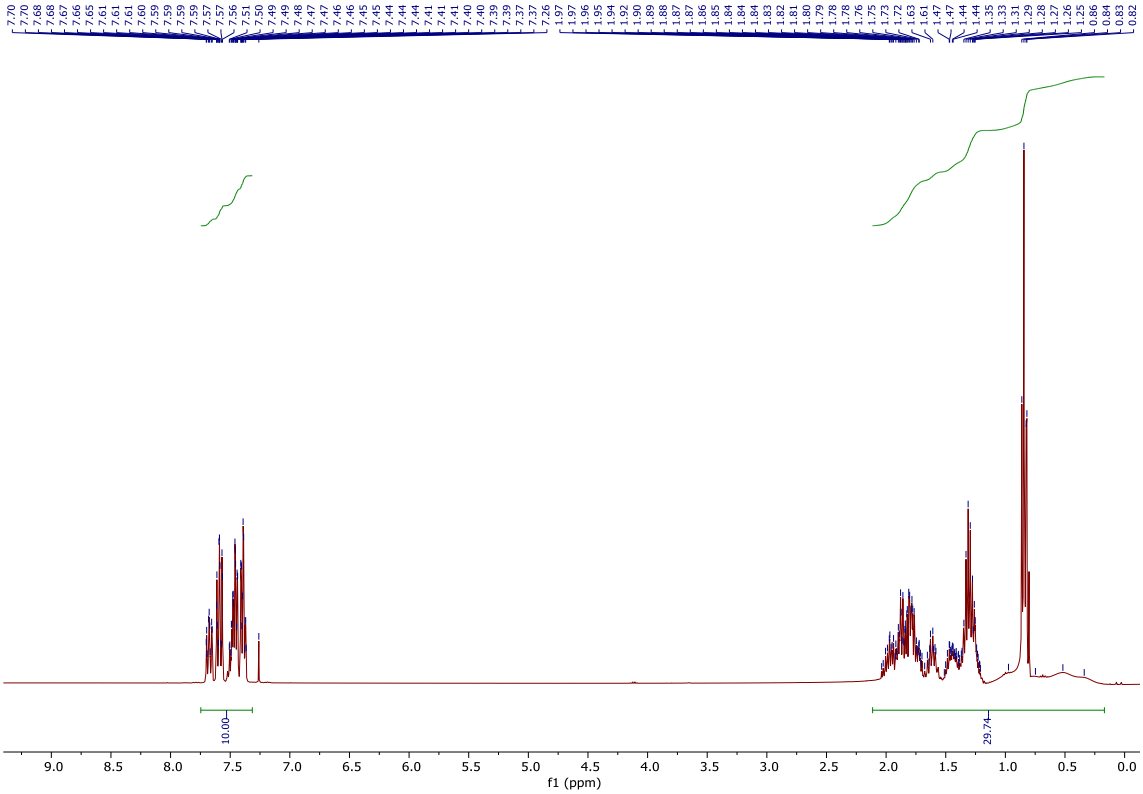
Bisphosphonium salt **6** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



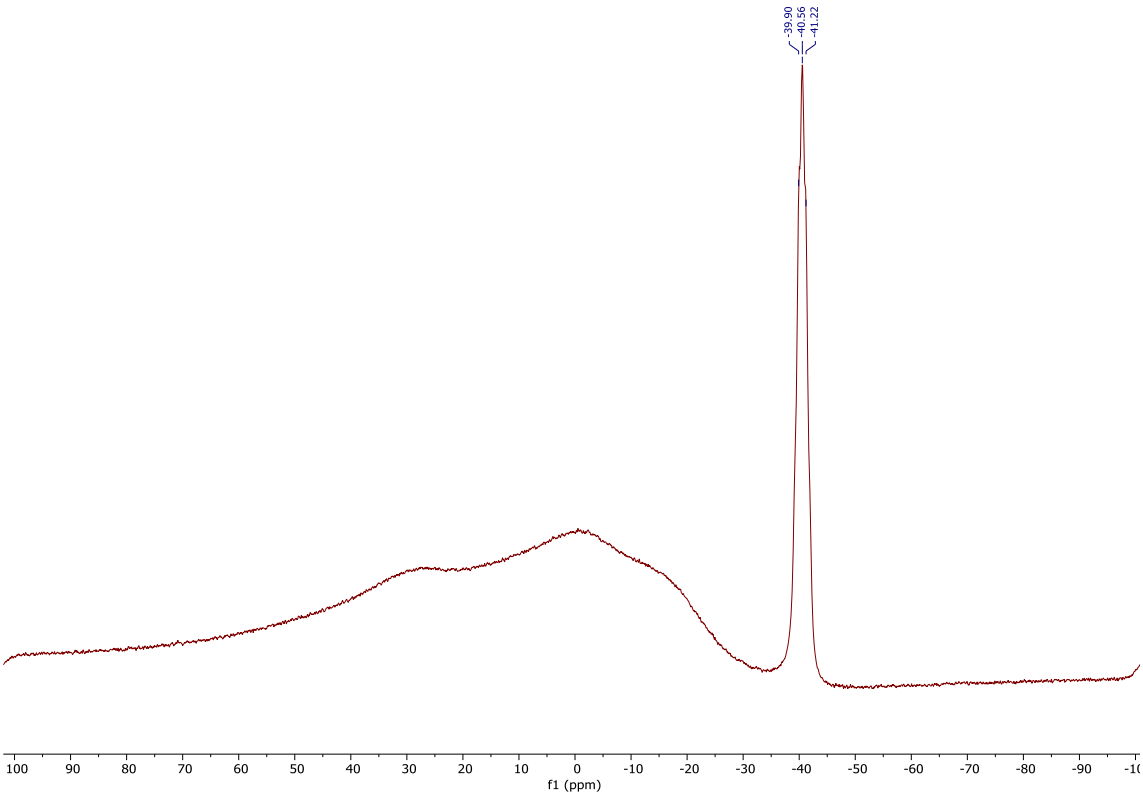
Bisphosphonium salt **6** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



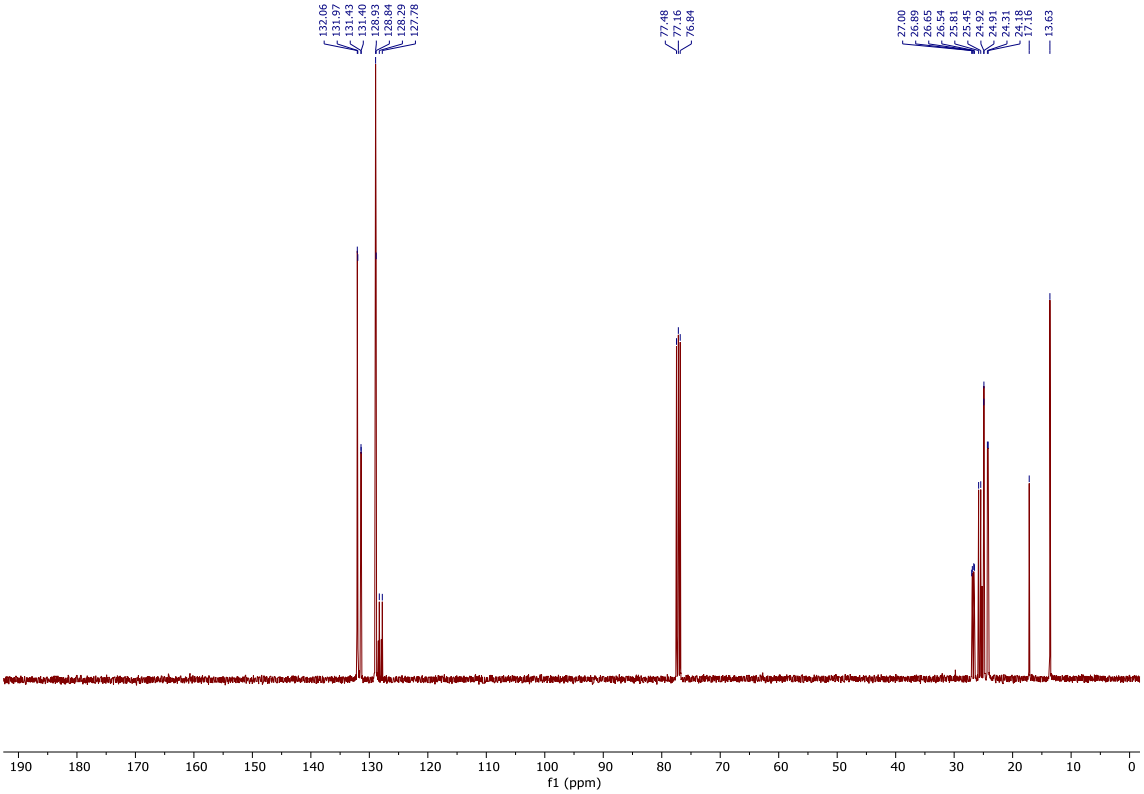
1,3-Bis(butyl(phenyl)phosphino)propane di-borane adduct (**7**) – ^{1}H NMR spectrum ($CDCl_3$)



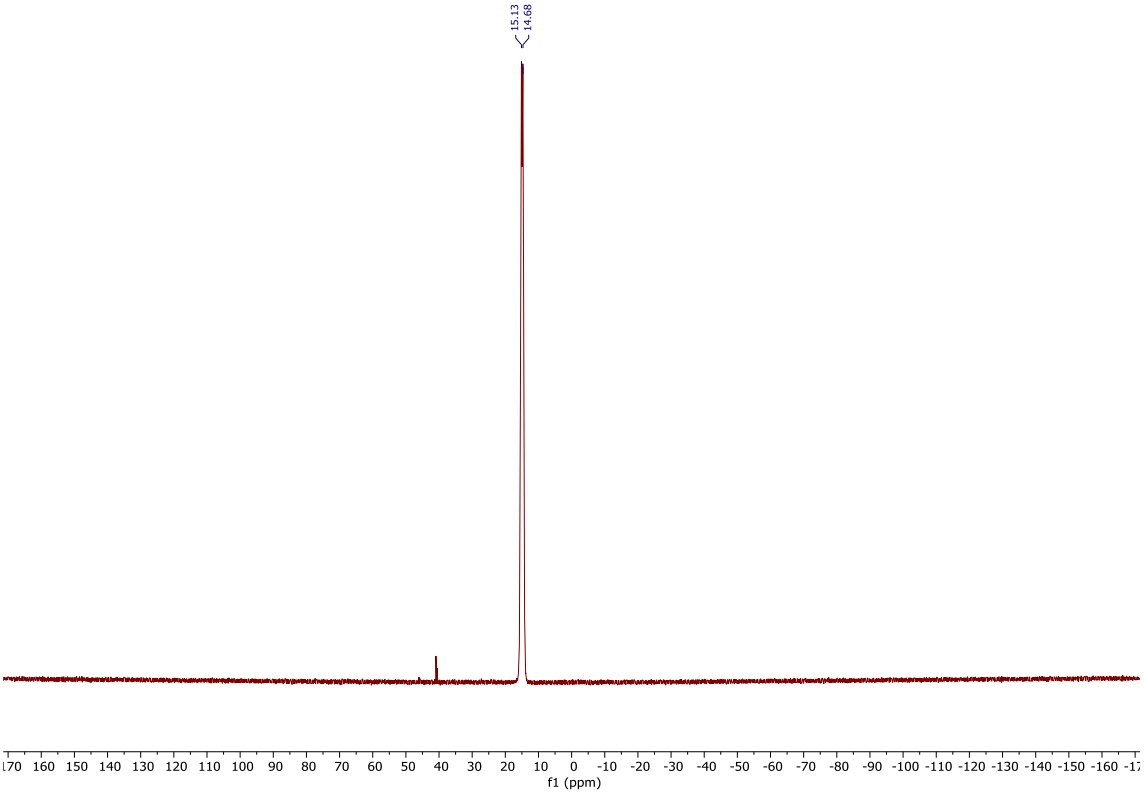
1,3-Bis(butyl(phenyl)phosphino)propane di-borane adduct (**7**) – ^{11}B NMR spectrum ($CDCl_3$)



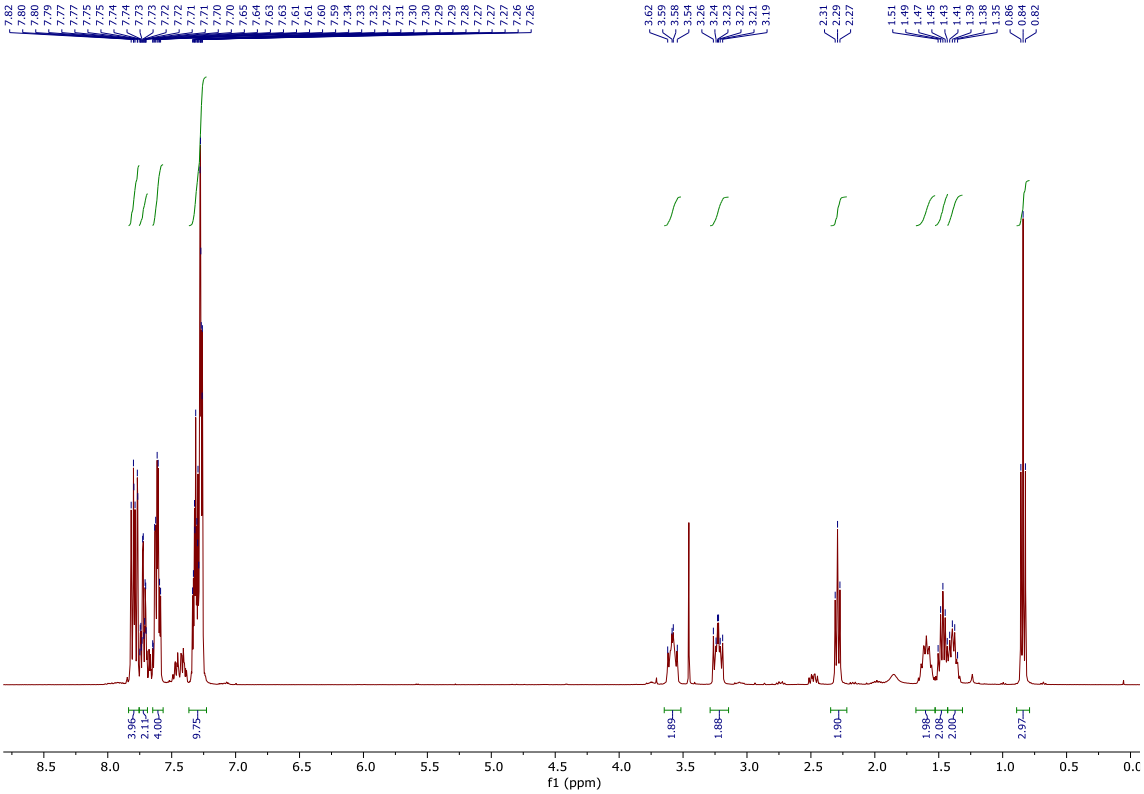
1,3-Bis(butyl(phenyl)phosphino)propane di-borane adduct (**7**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



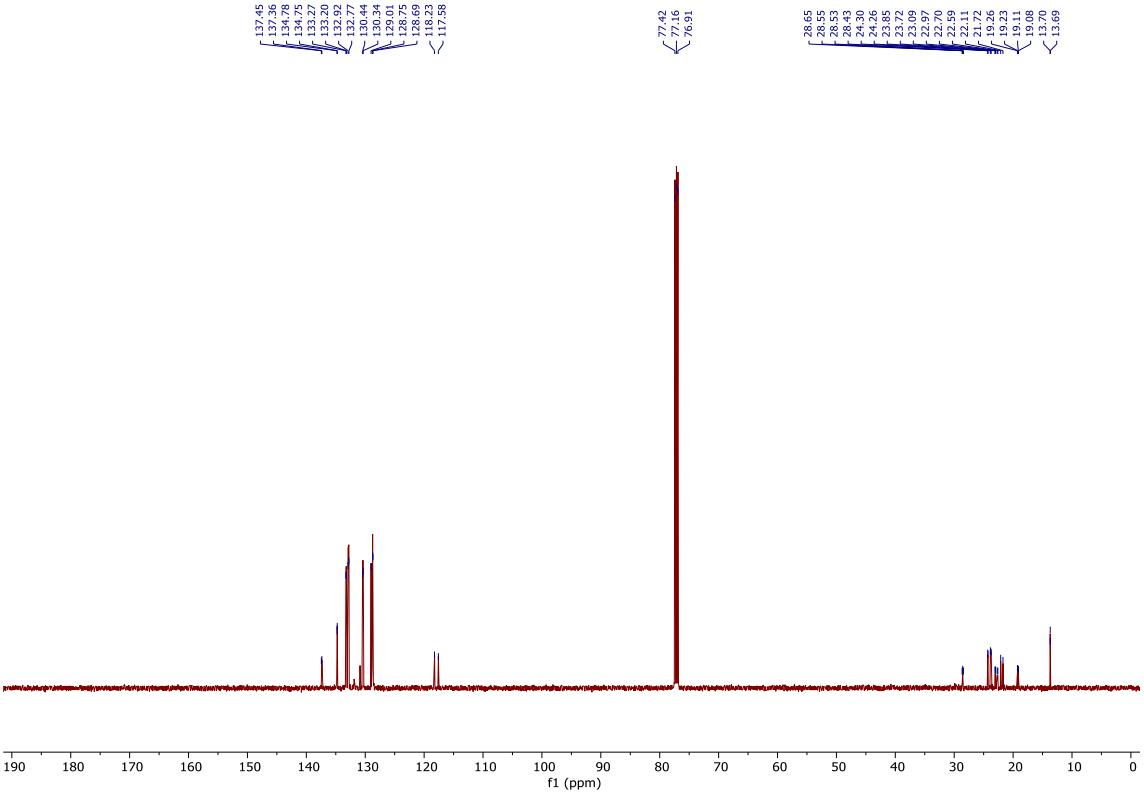
1,3-Bis(butyl(phenyl)phosphino)propane di-borane adduct (**7**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



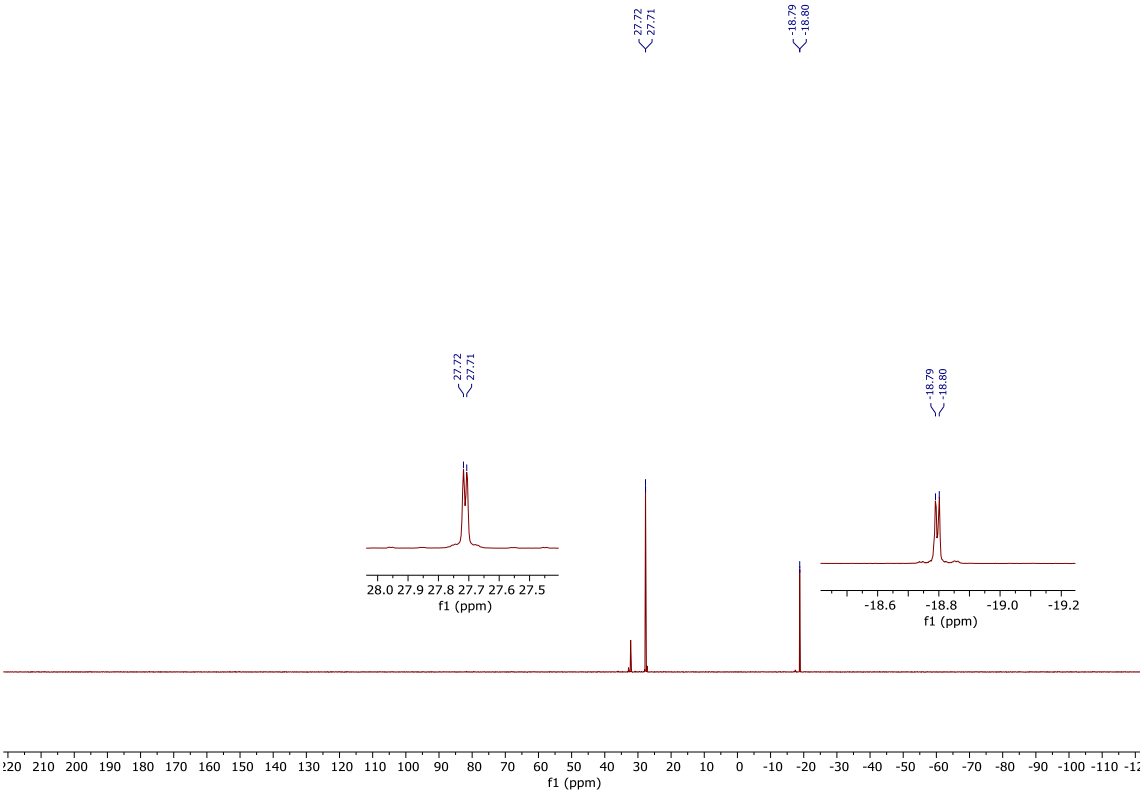
Monophosphonium salt **8** – ^{1}H NMR spectrum ($CDCl_3$)



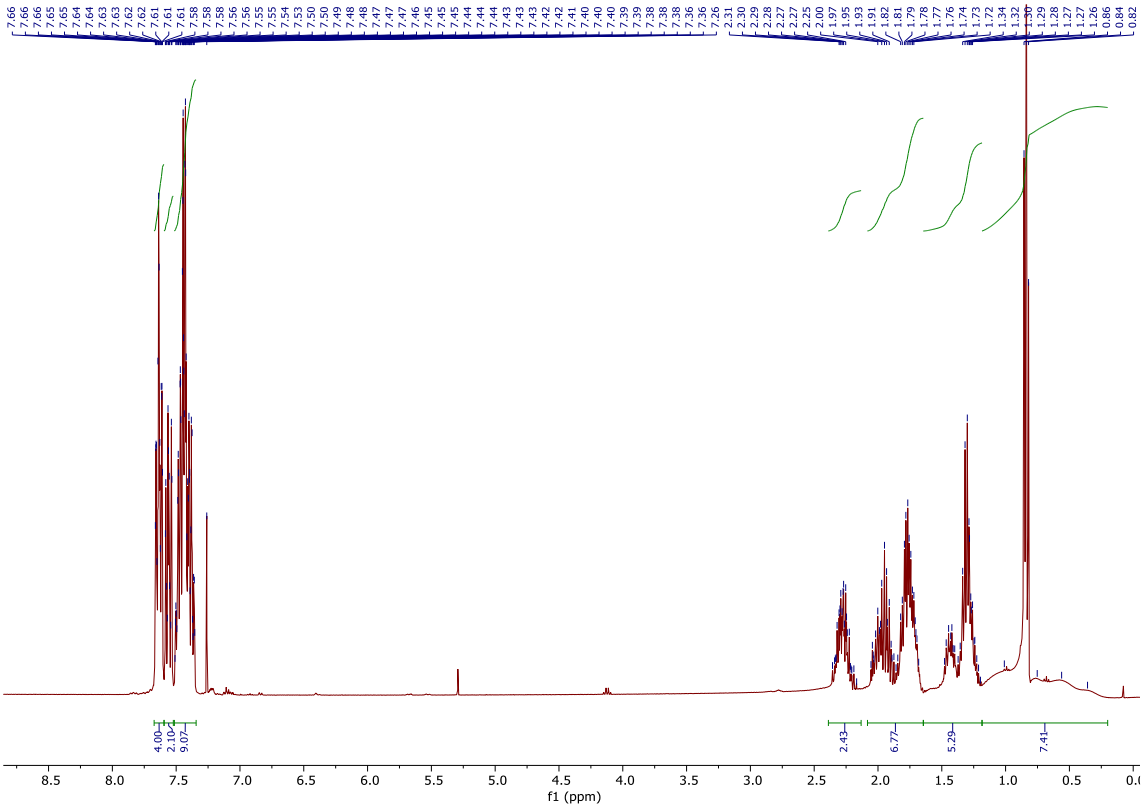
Monophosphonium salt **8** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



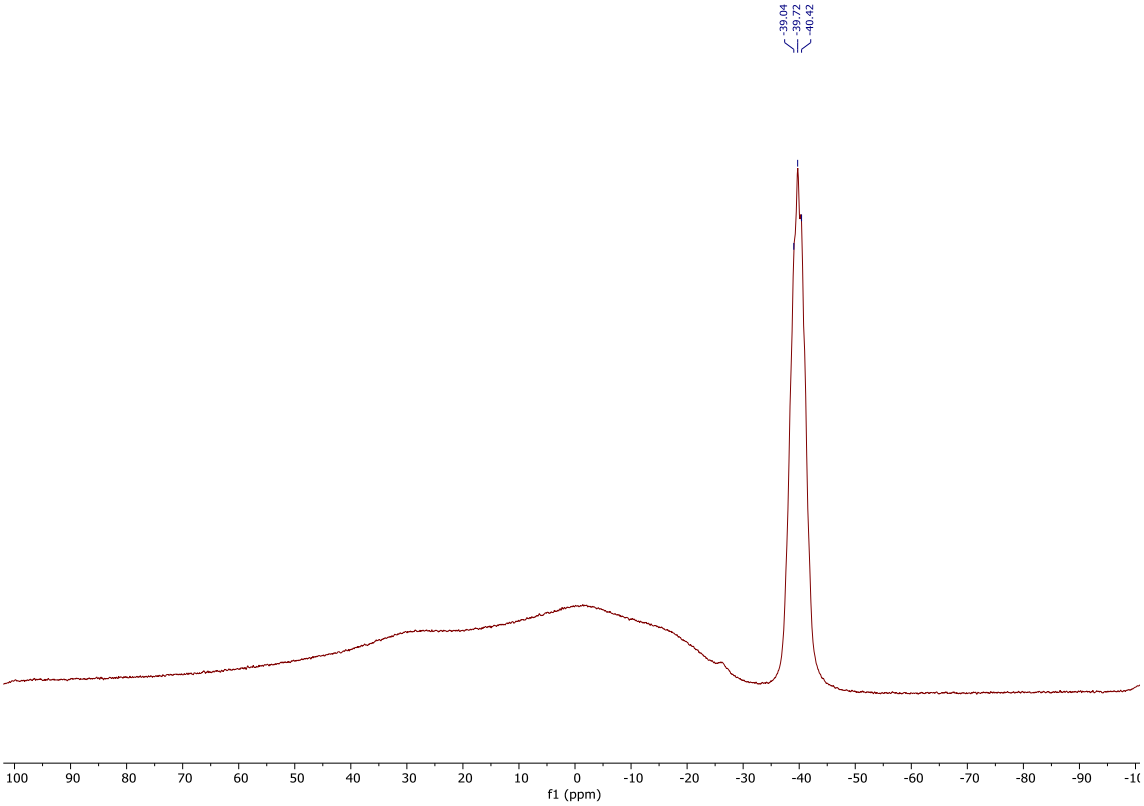
Monophosphonium salt **8** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



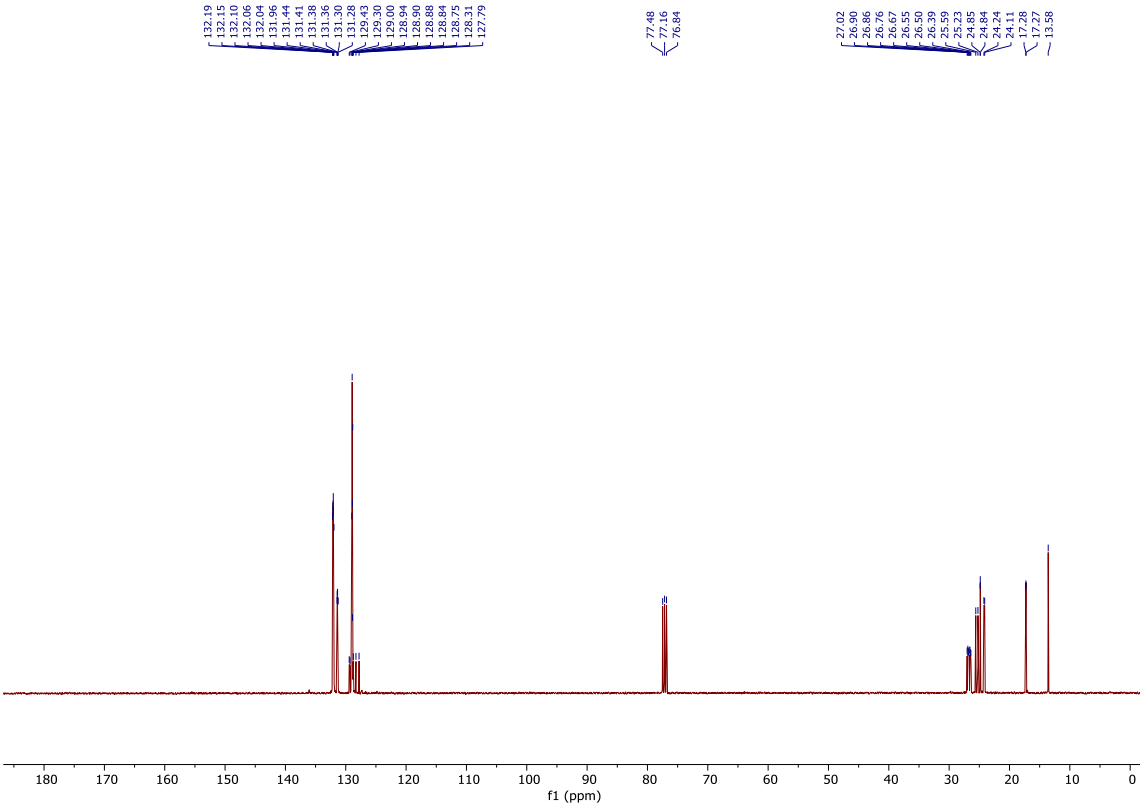
Bisphosphine di-borane adduct **9** – ^{1}H NMR spectrum ($CDCl_3$)



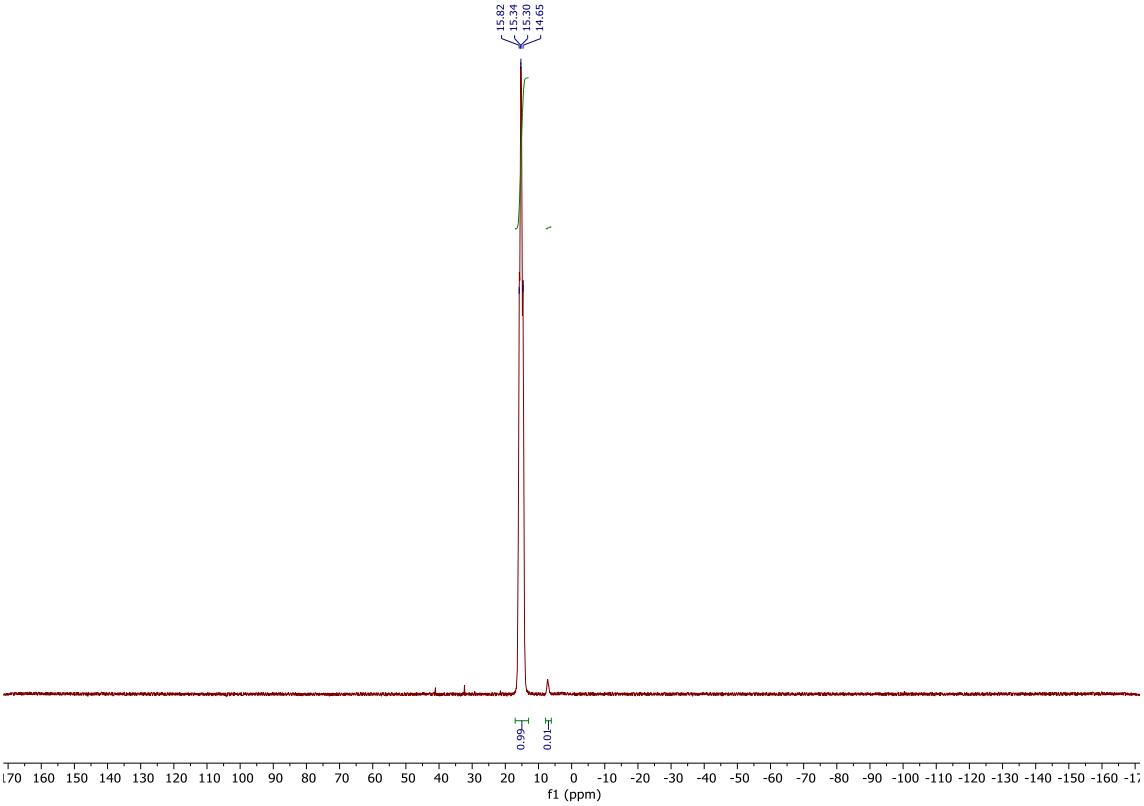
Bisphosphine di-borane adduct **9** – ^{11}B NMR spectrum ($CDCl_3$)



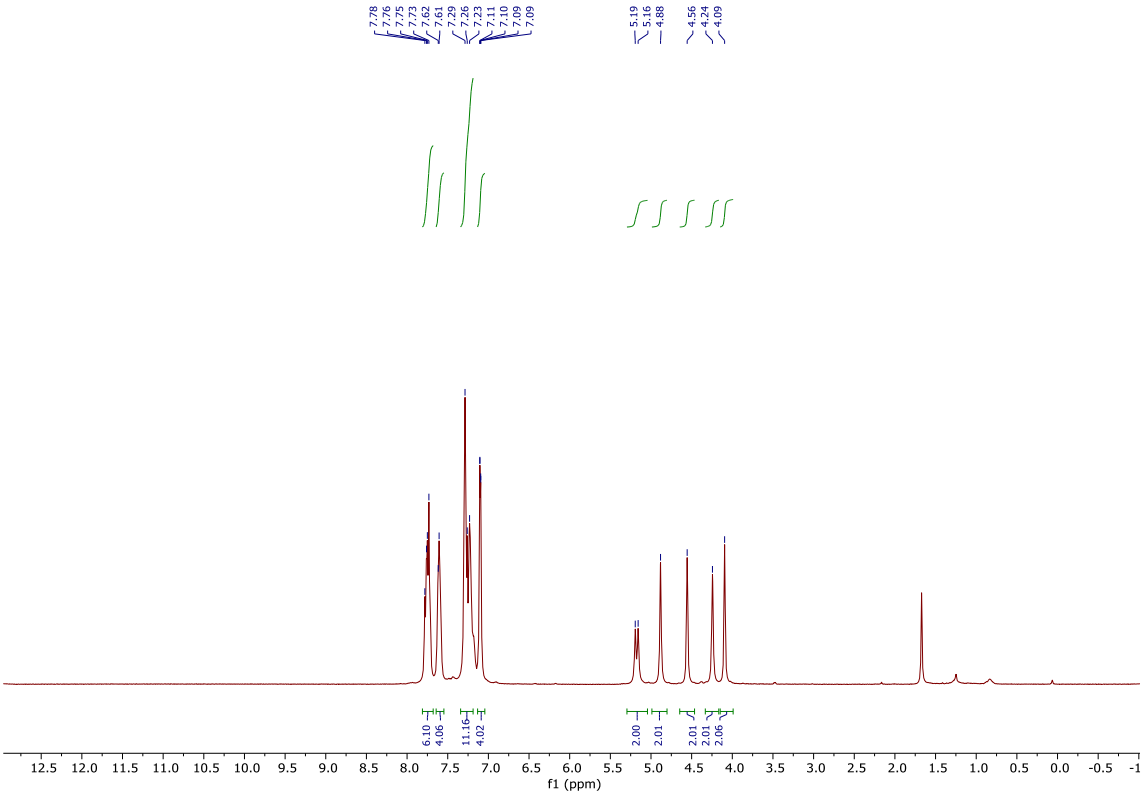
Bisphosphine di-borane adduct **9** – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



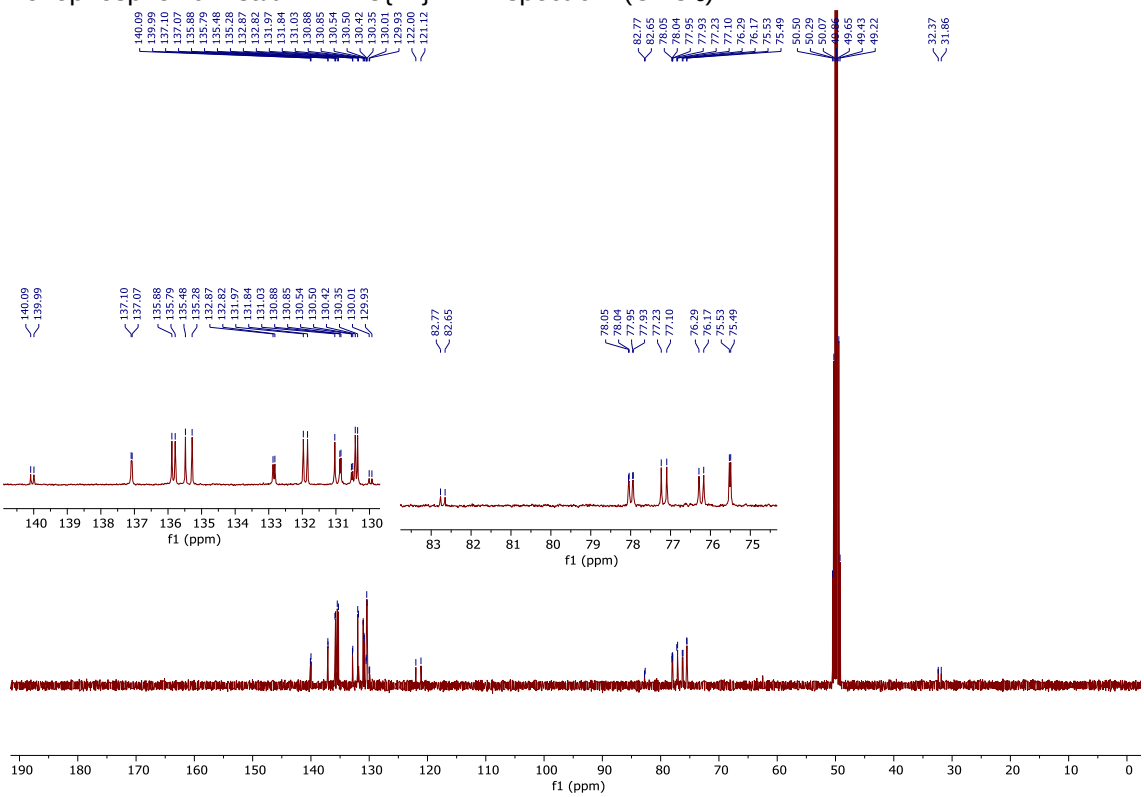
Bisphosphine di-borane adduct **9** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



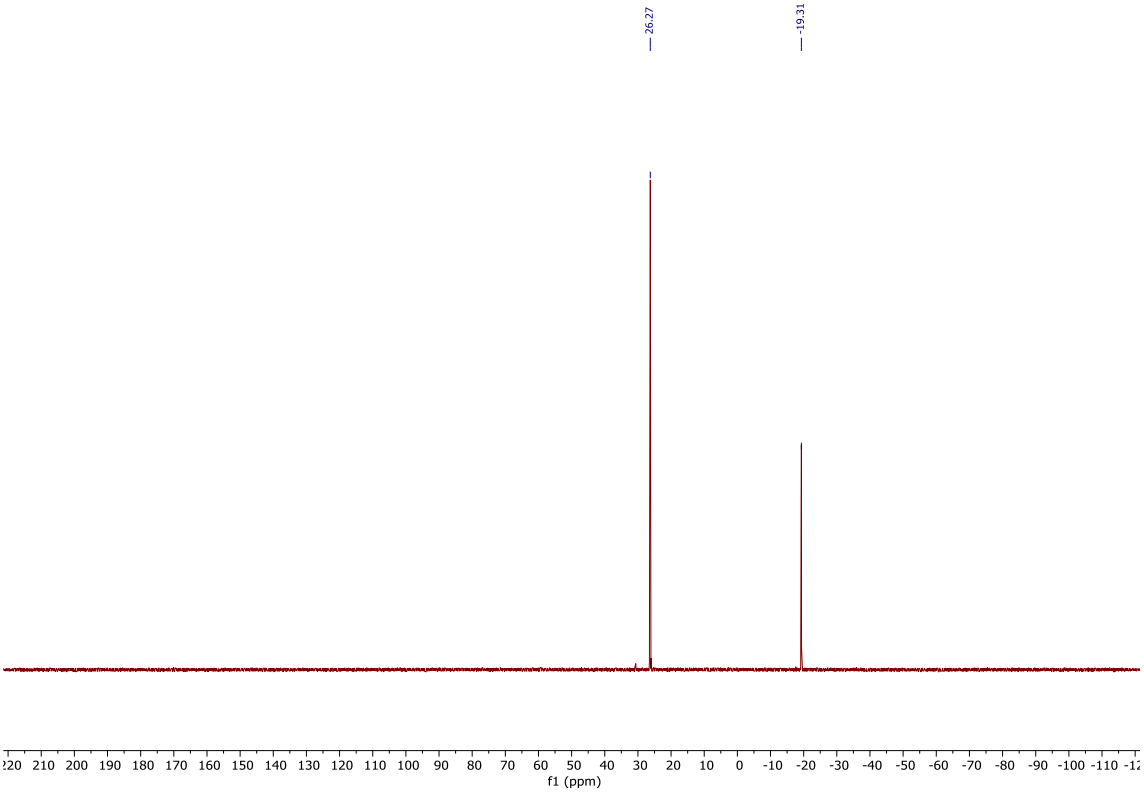
Monophosphonium salt **12** – ^{1}H NMR spectrum ($CDCl_3$)



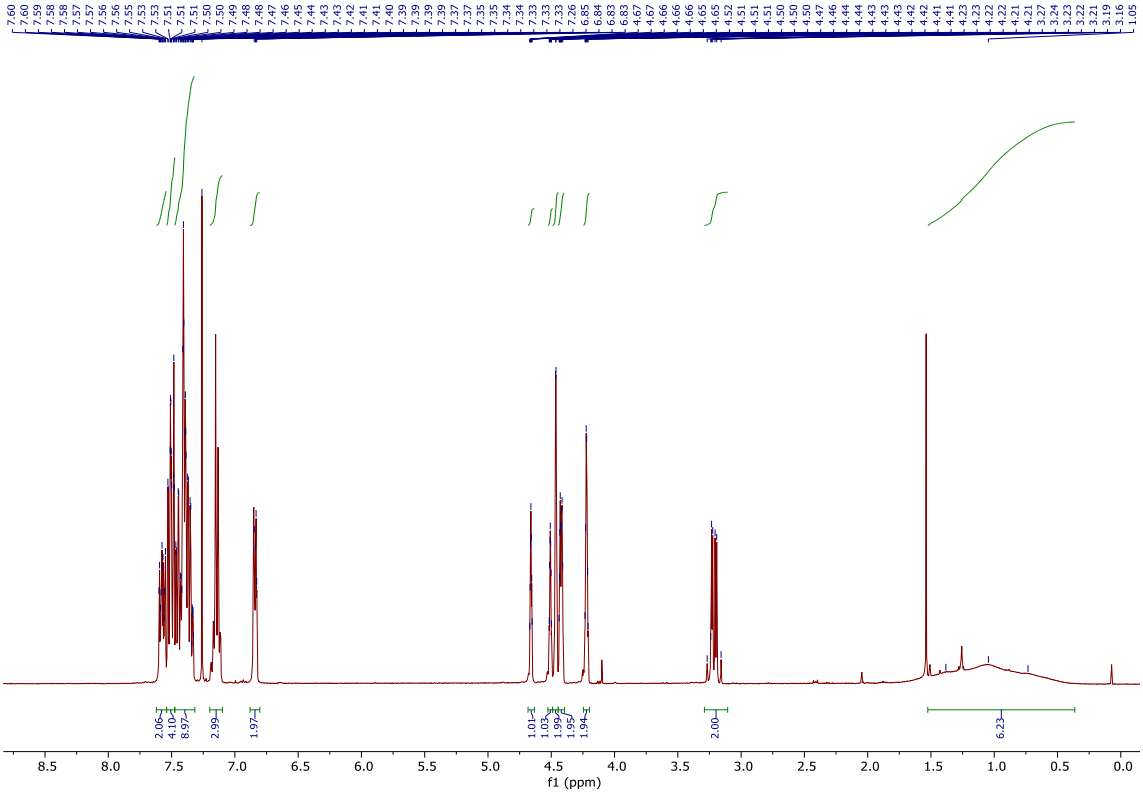
Monophosphonium salt **12** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



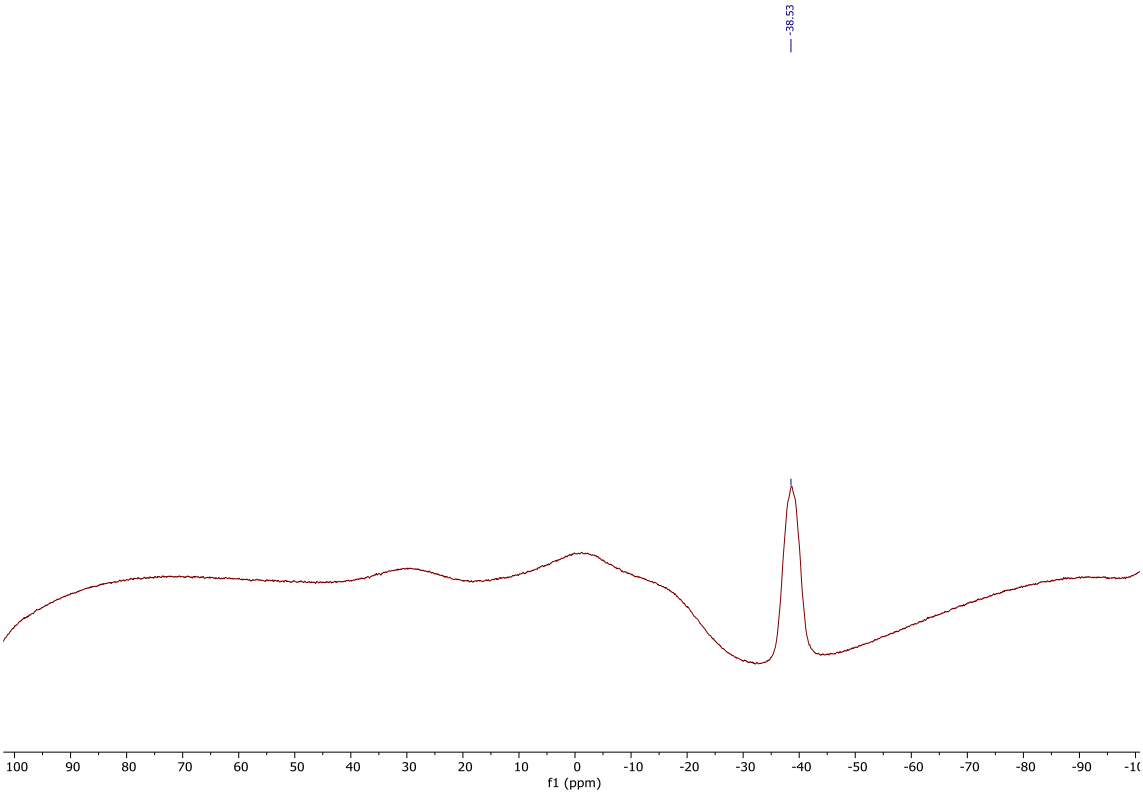
Monophosphonium salt **12** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



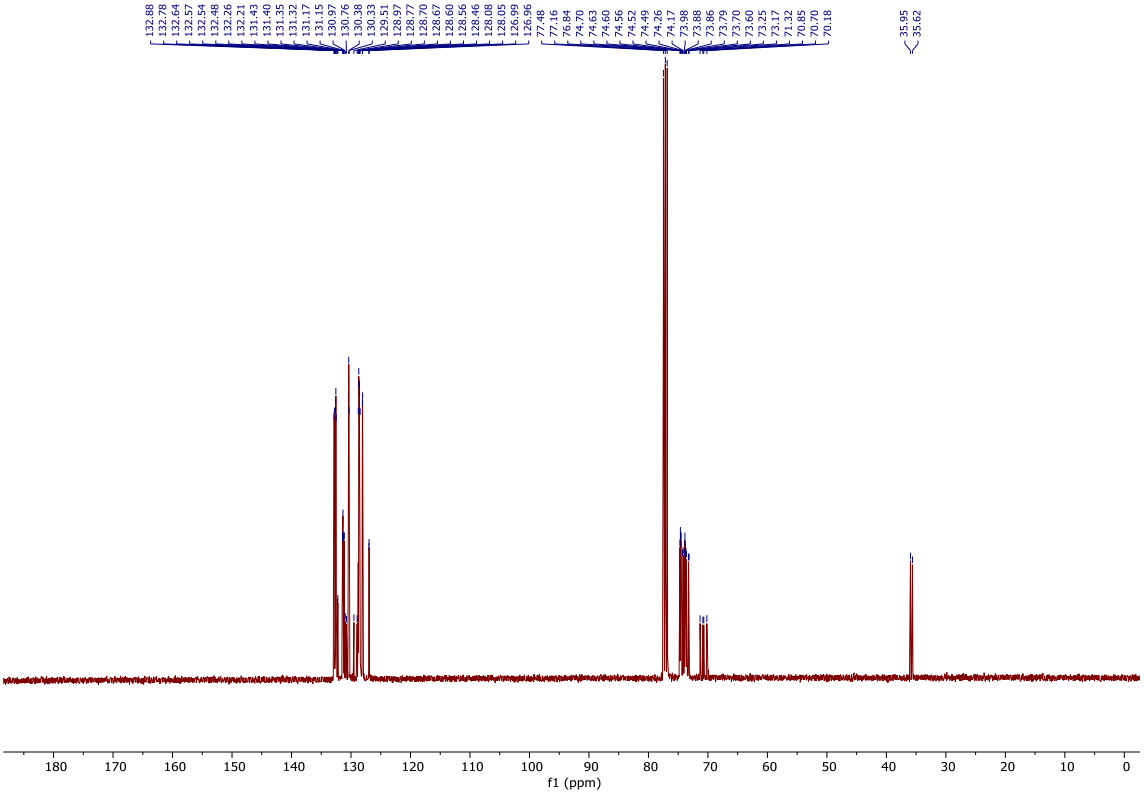
Bisphosphine di-borane adduct **13** – ^{1}H NMR spectrum ($CDCl_3$)



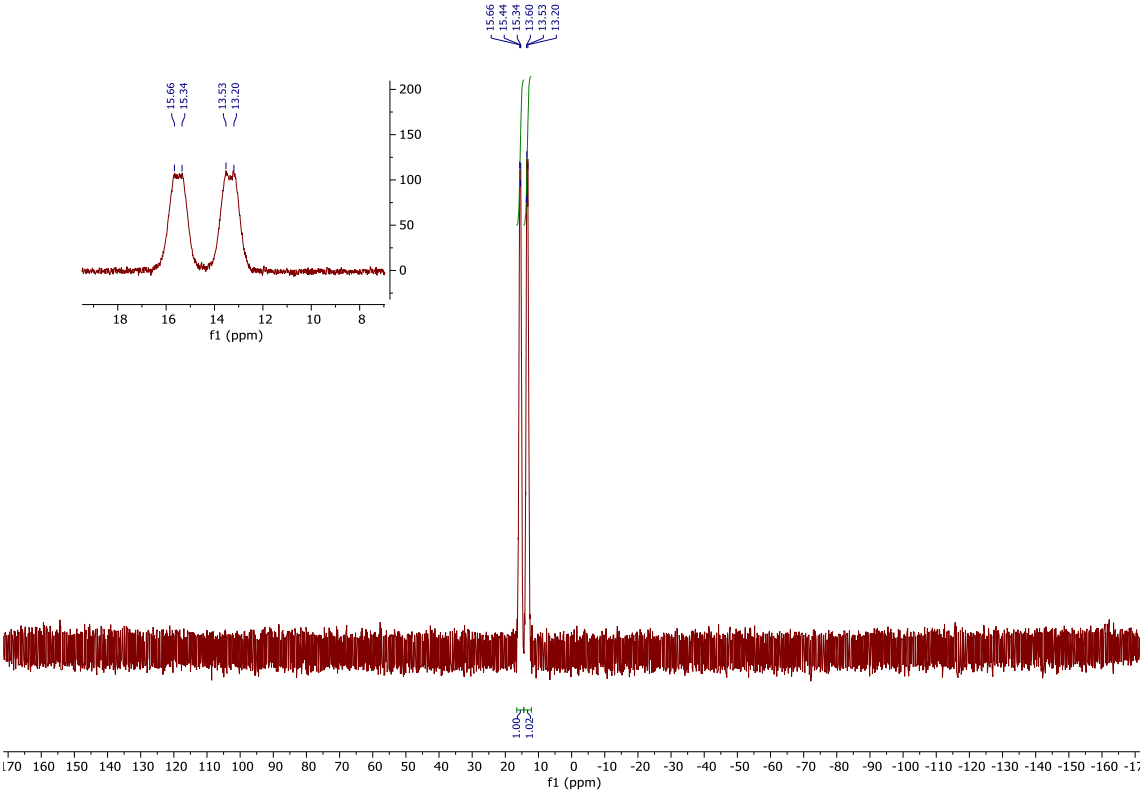
Bisphosphine di-borane adduct **13** – ^{11}B NMR spectrum ($CDCl_3$)



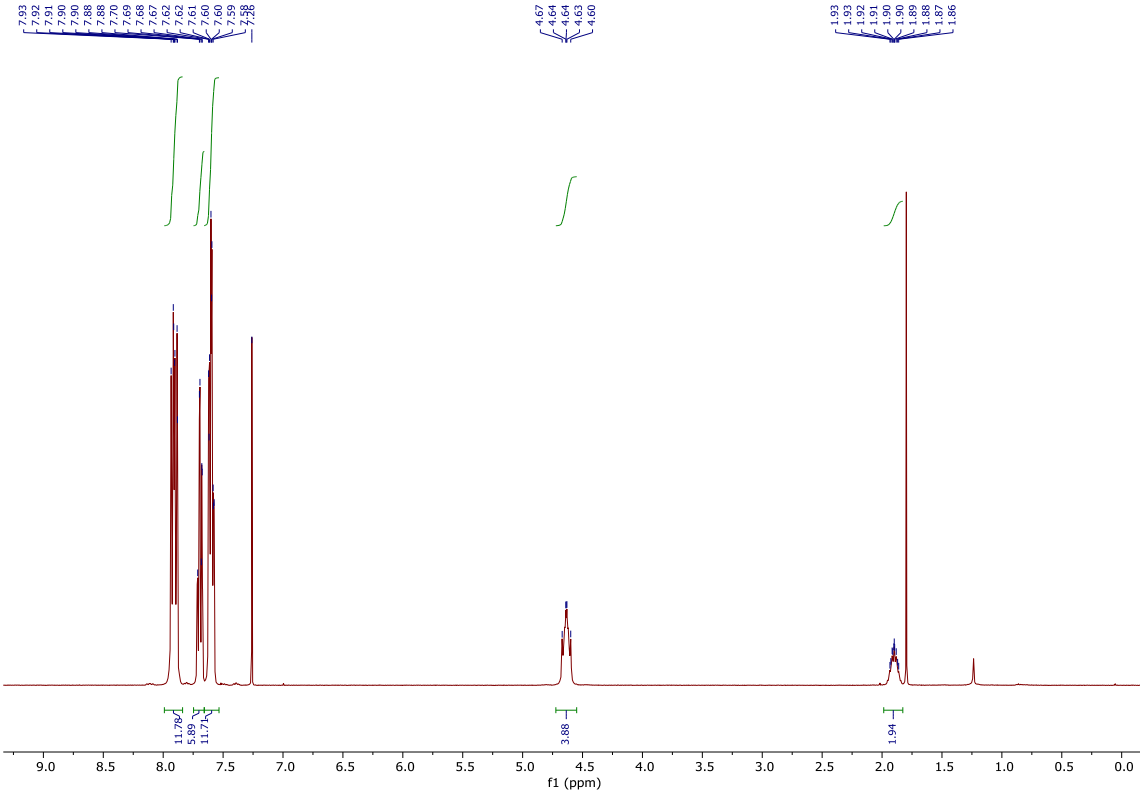
Bisphosphine di-borane adduct **13** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



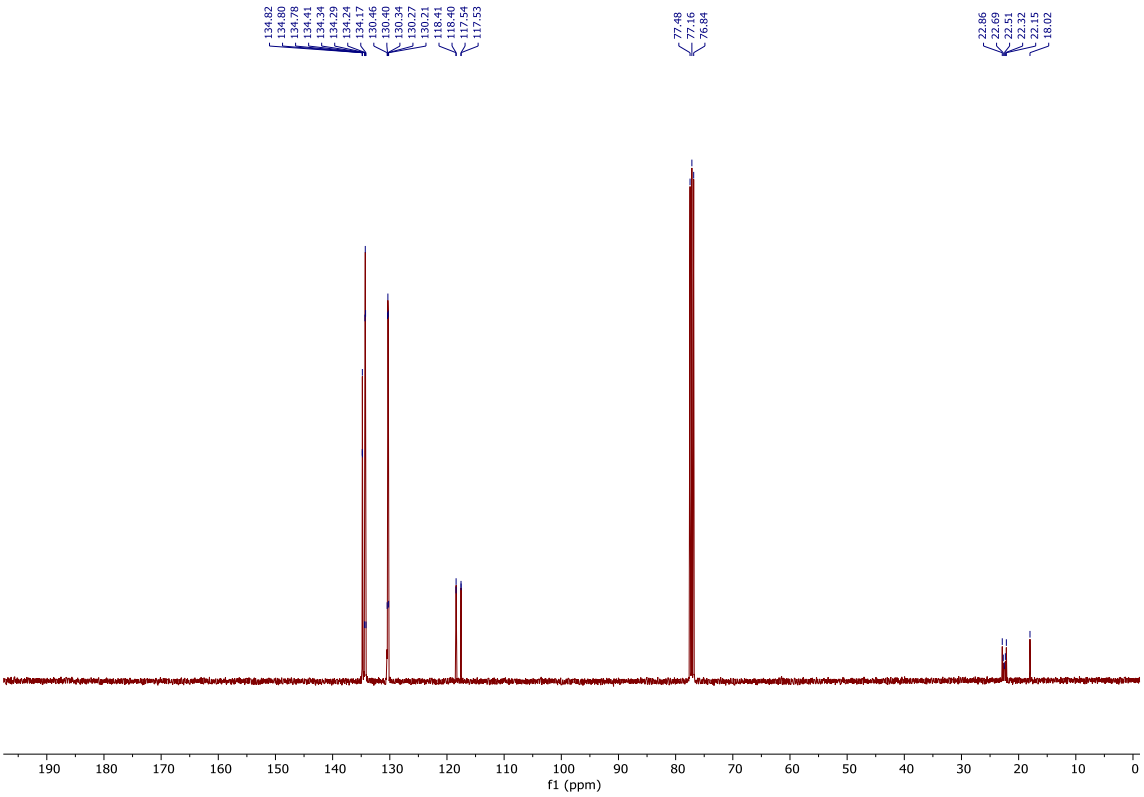
Bisphosphine di-borane adduct **13** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



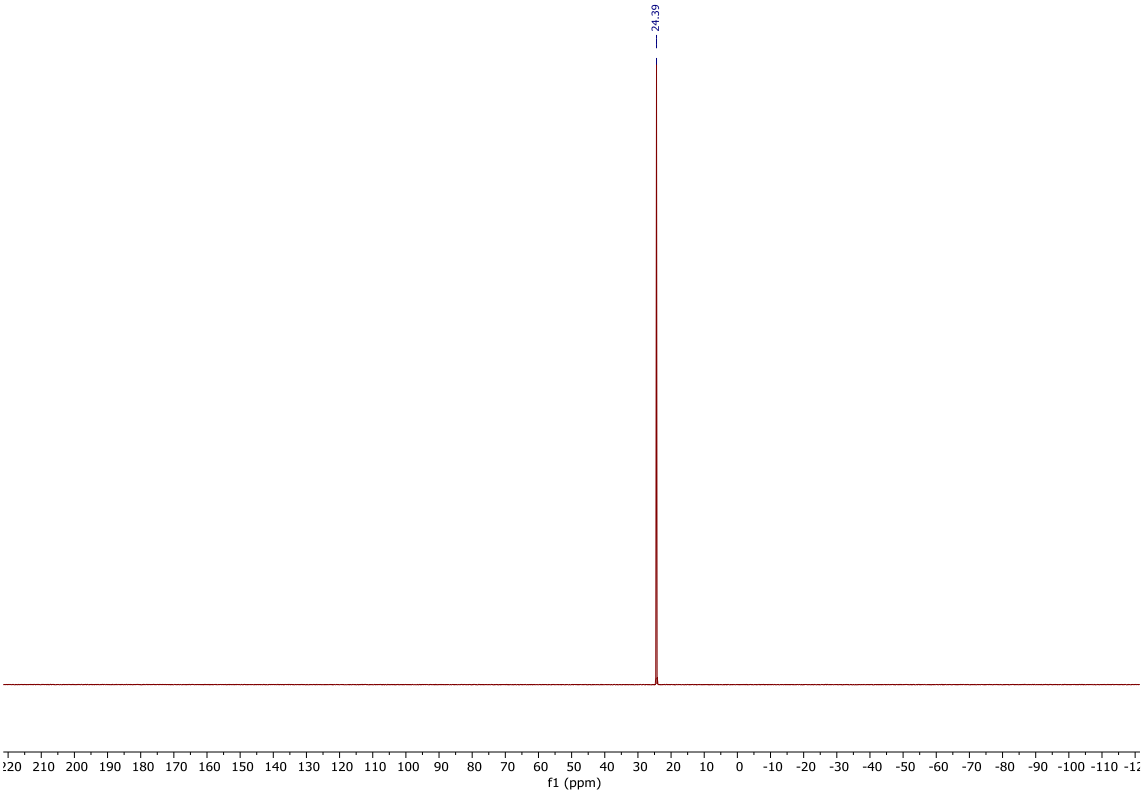
Monophosphonium salt **15** – ^{1}H NMR spectrum ($CDCl_3$)



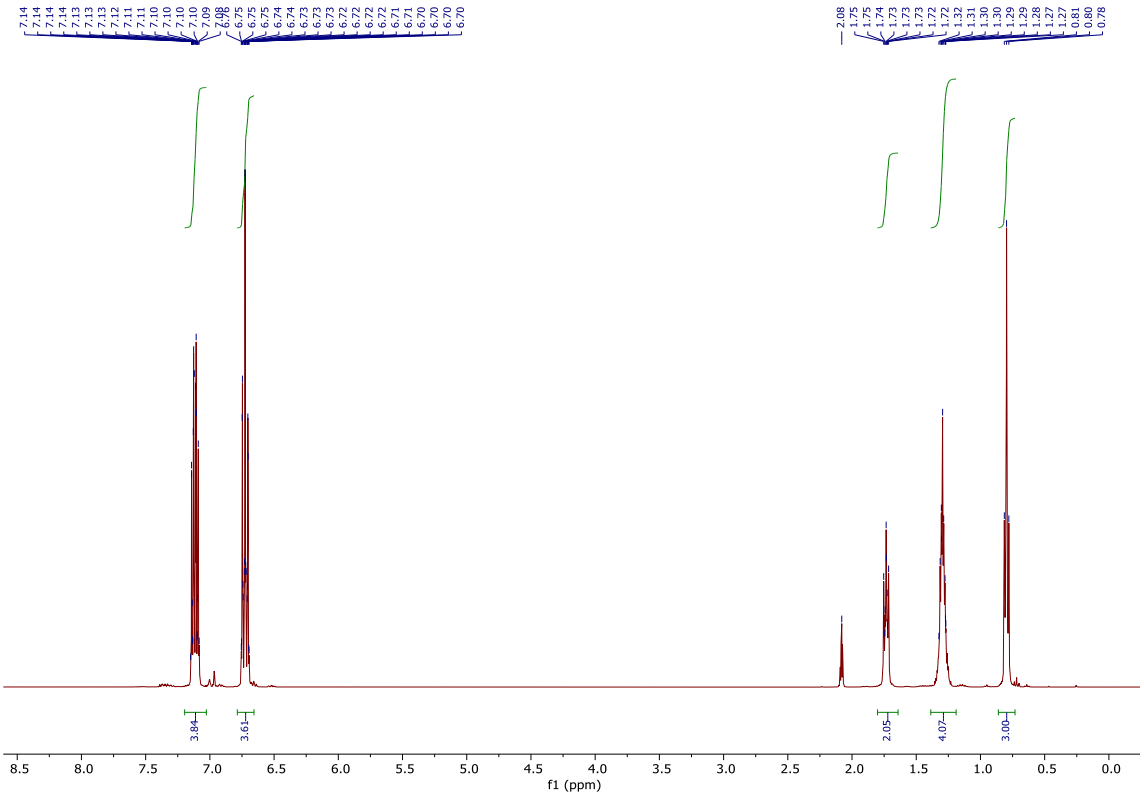
Monophosphonium salt **15** – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



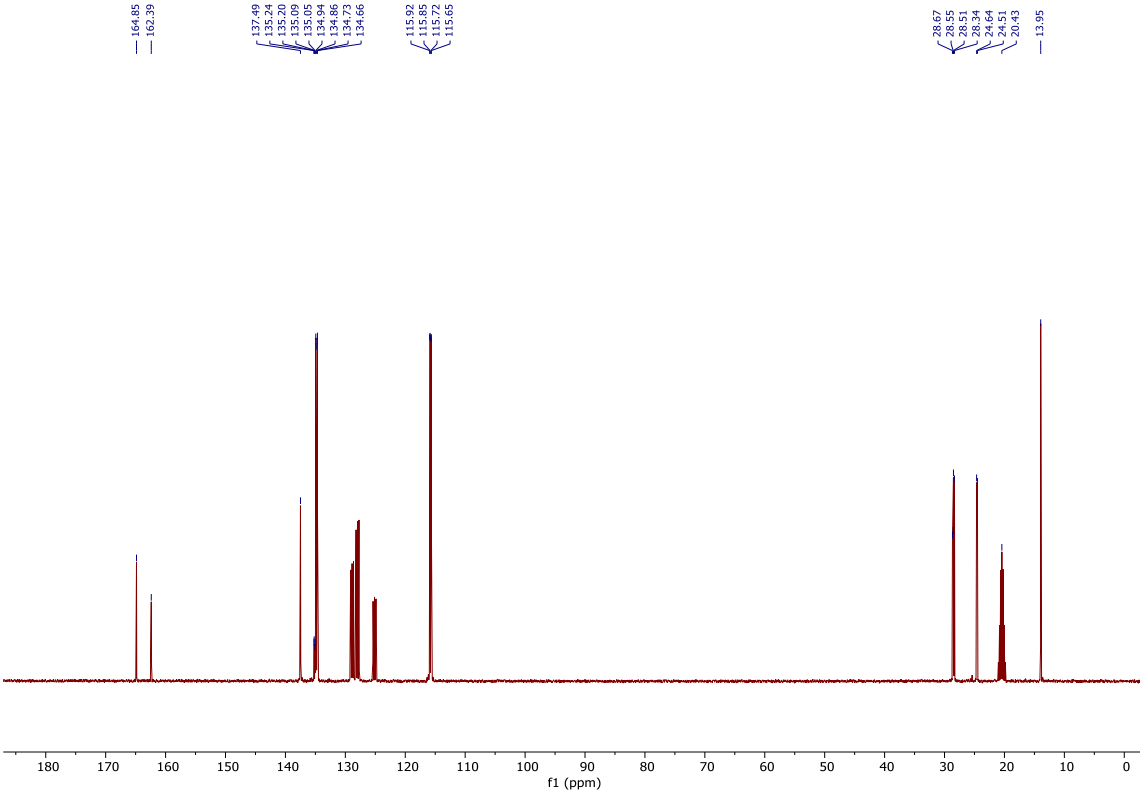
Monophosphonium salt **15** – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



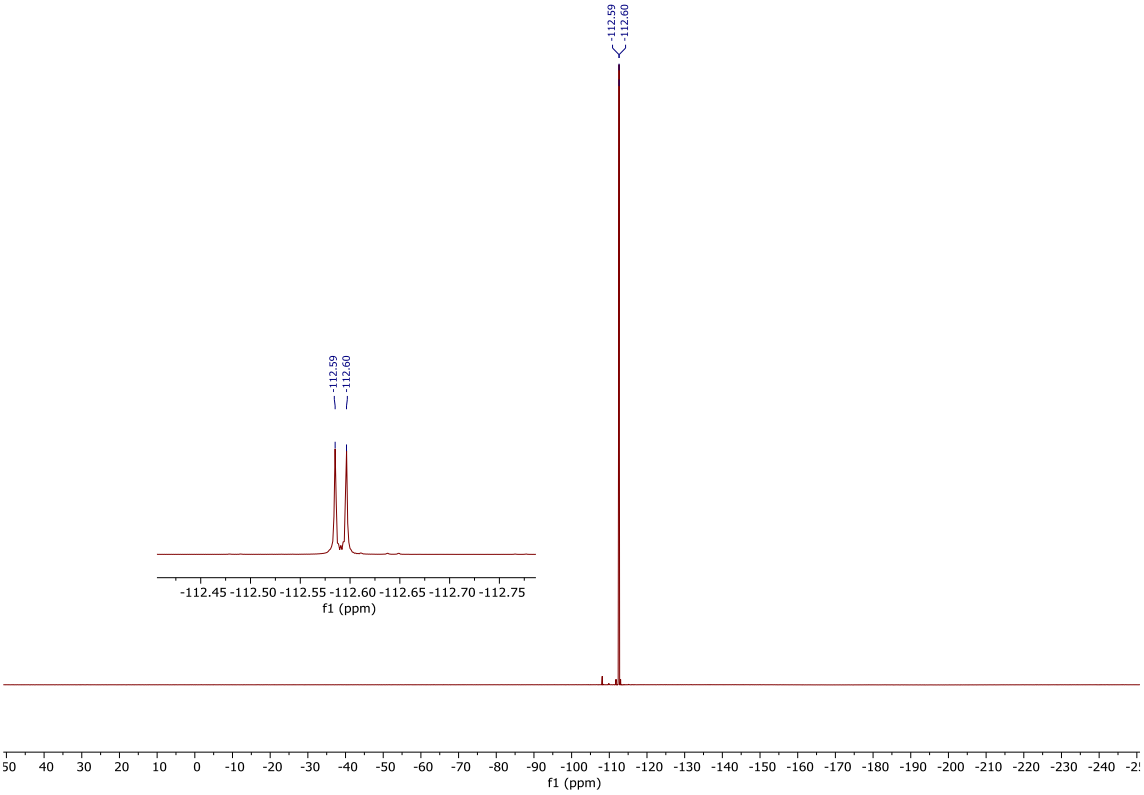
Butylbis(4-fluorophenyl)phosphine (**16**) – ^{1}H NMR spectrum (tol-d_8)



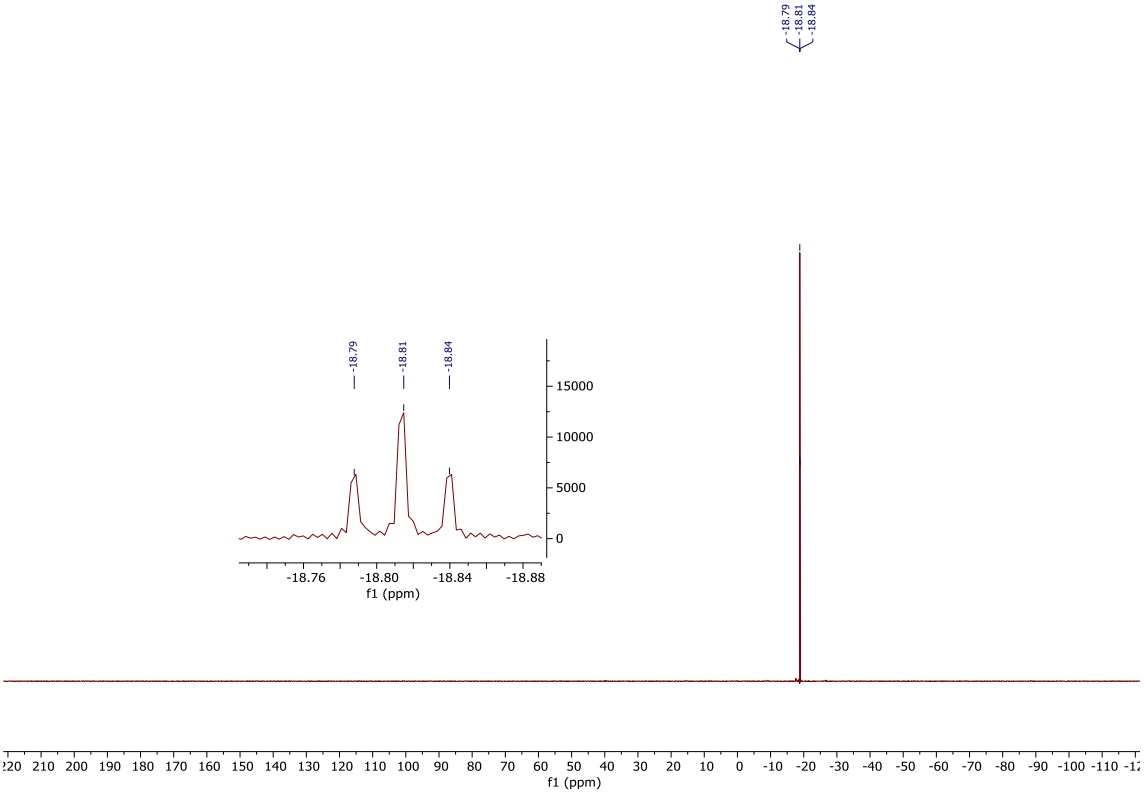
Butylbis(4-fluorophenyl)phosphine (**16**) – $^{13}C\{^{1}H\}$ NMR spectrum (tol-d_8)



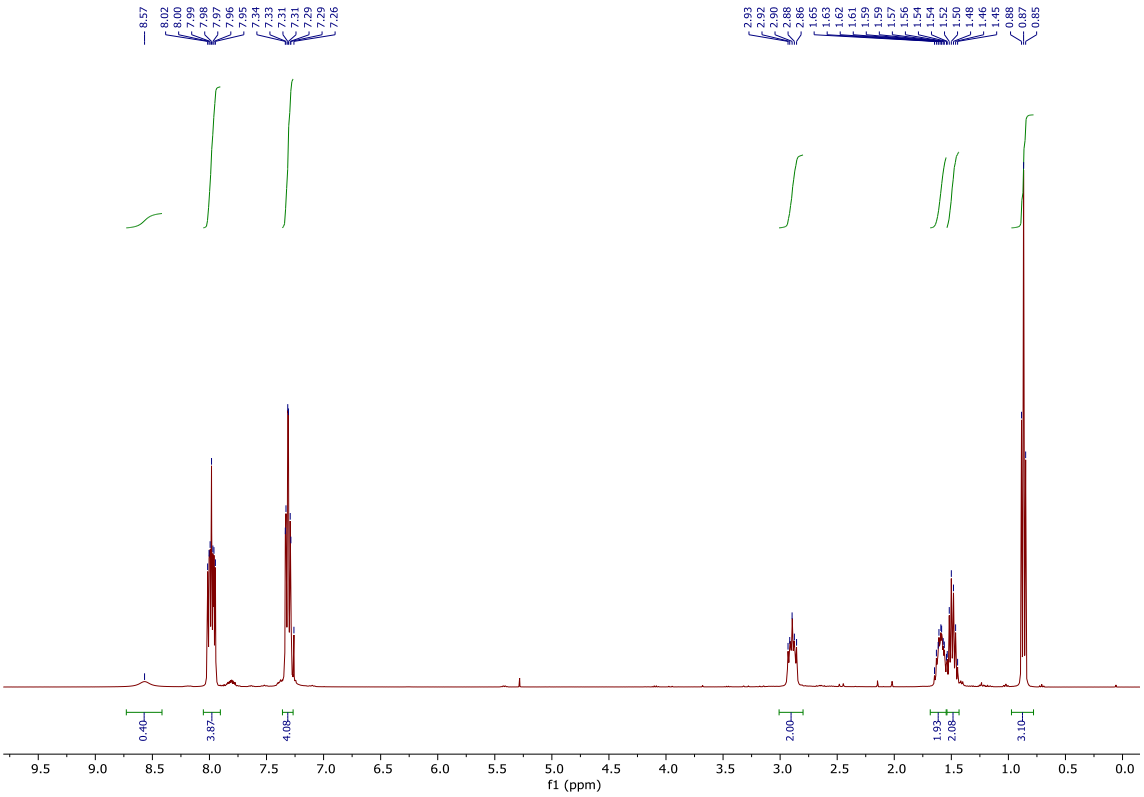
Butylbis(4-fluorophenyl)phosphine (**16**) – $^{19}F\{^{1}H\}$ NMR spectrum (tol-d_8)



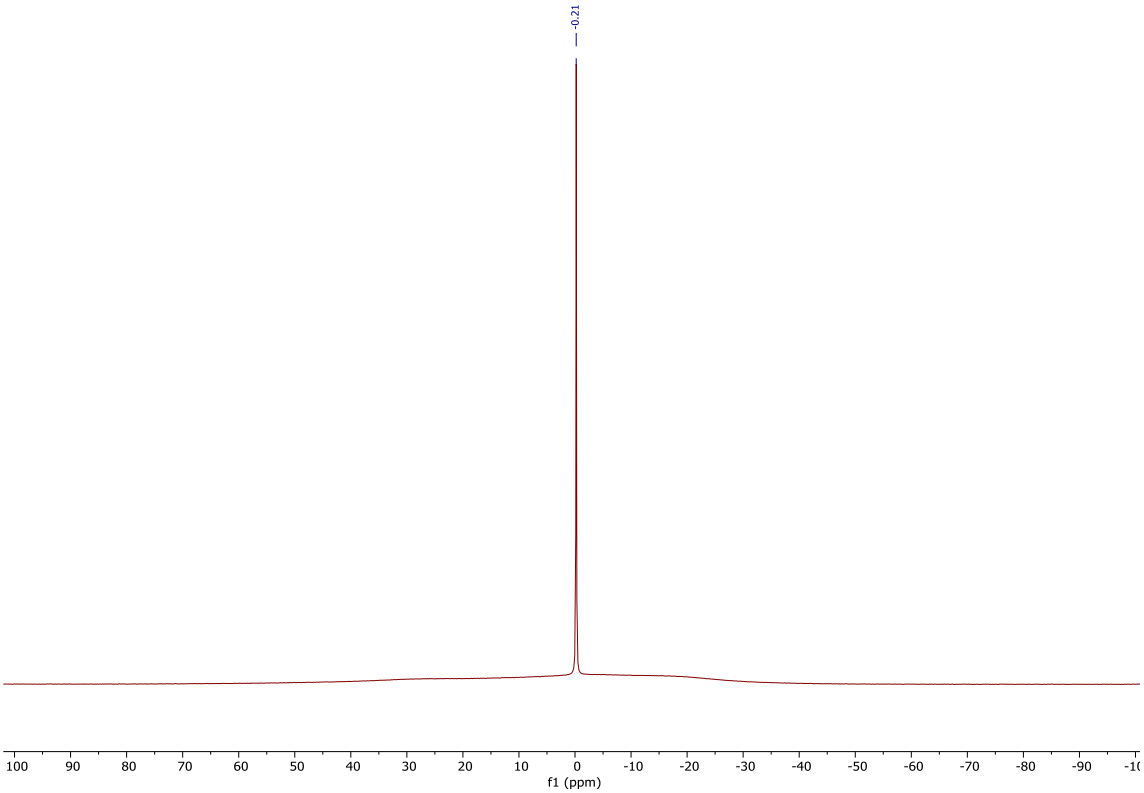
Butylbis(4-fluorophenyl)phosphine (**16**) – $^{31}P\{^{1}H\}$ NMR spectrum (tol-d_8)



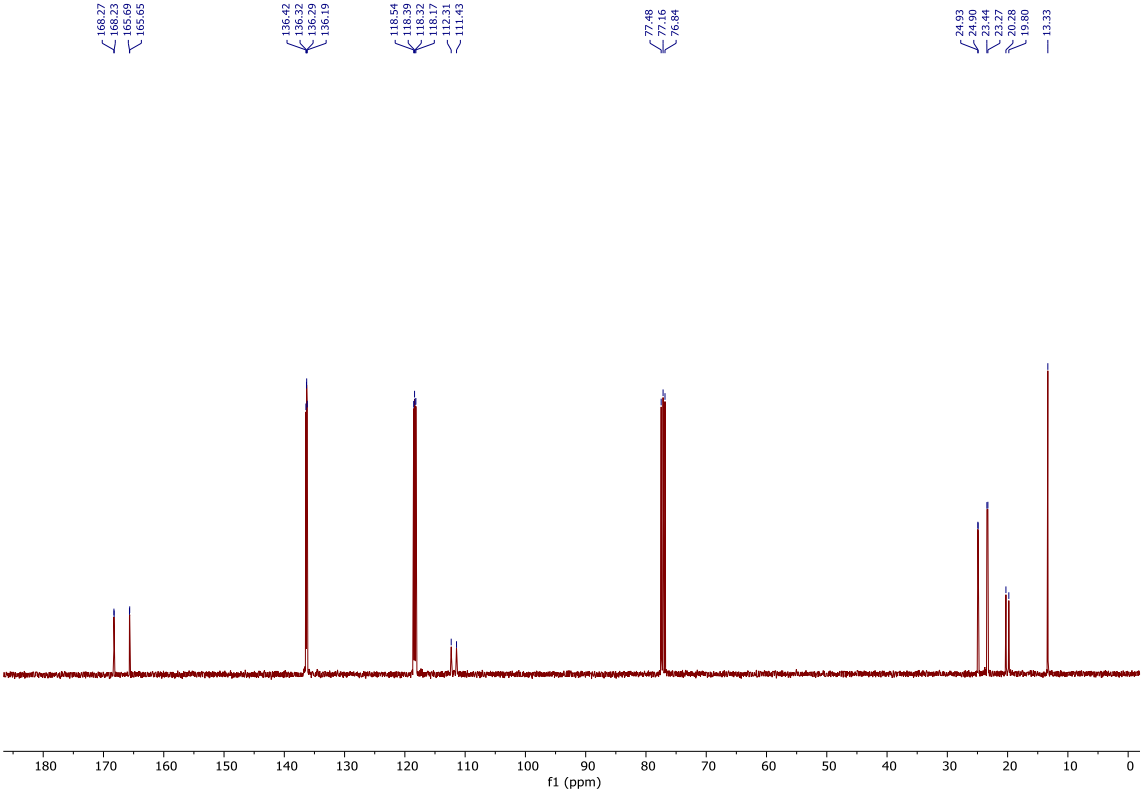
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – ^{1}H NMR spectrum ($CDCl_3$)



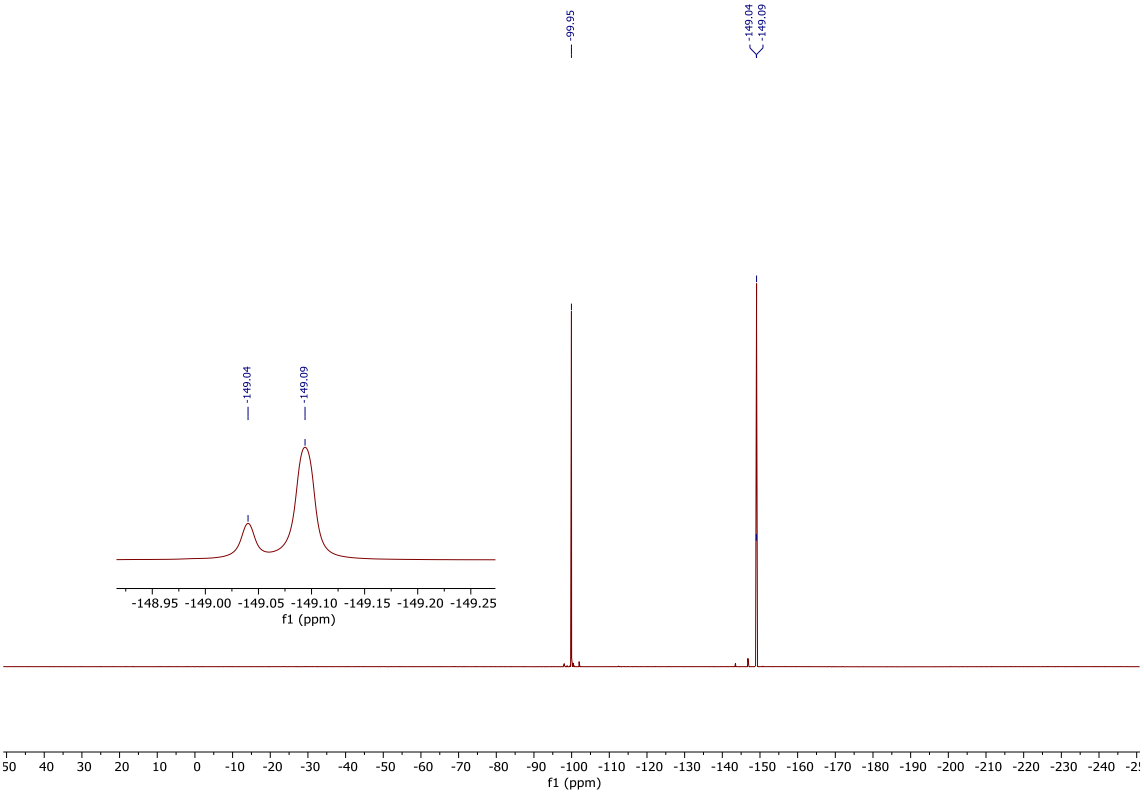
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – ^{11}B NMR spectrum ($CDCl_3$)



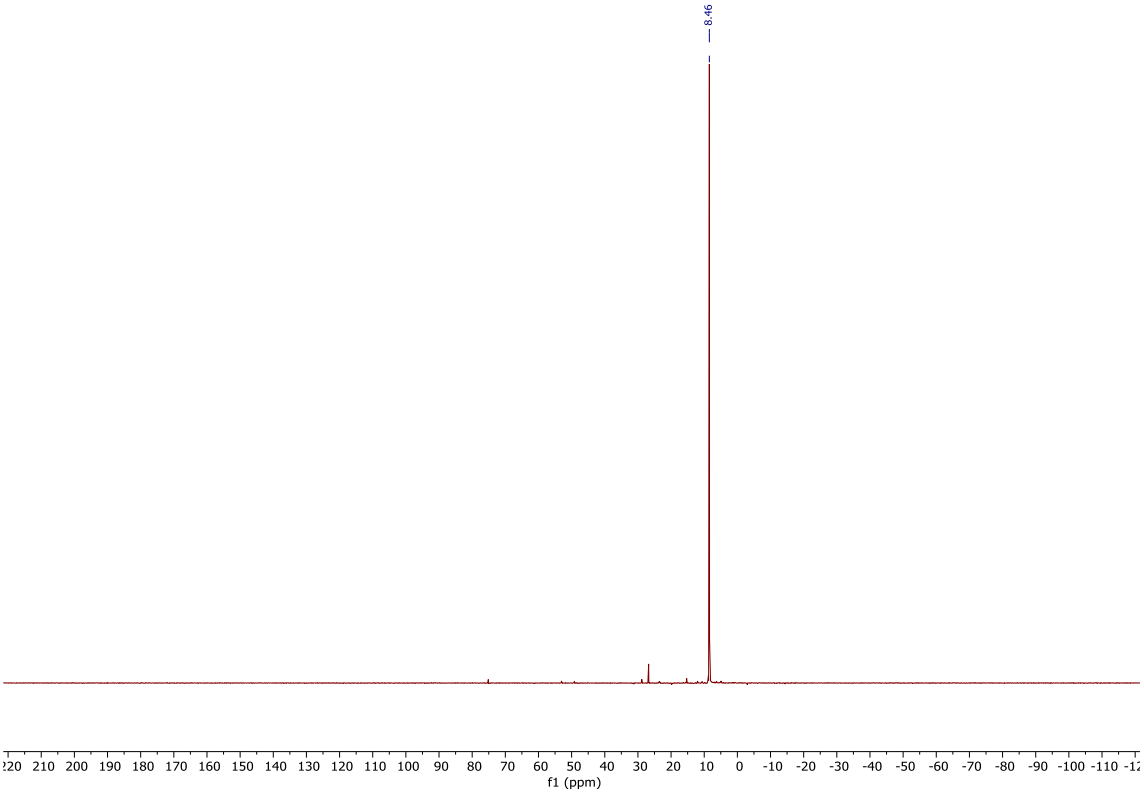
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



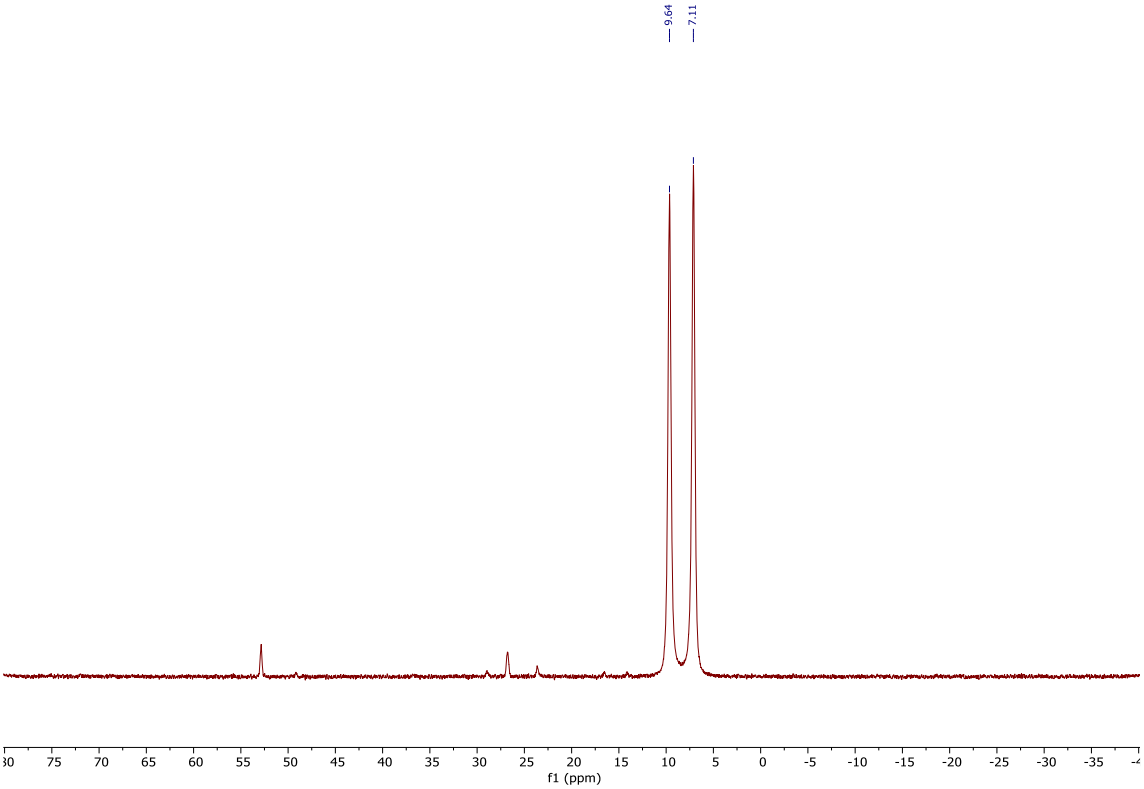
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



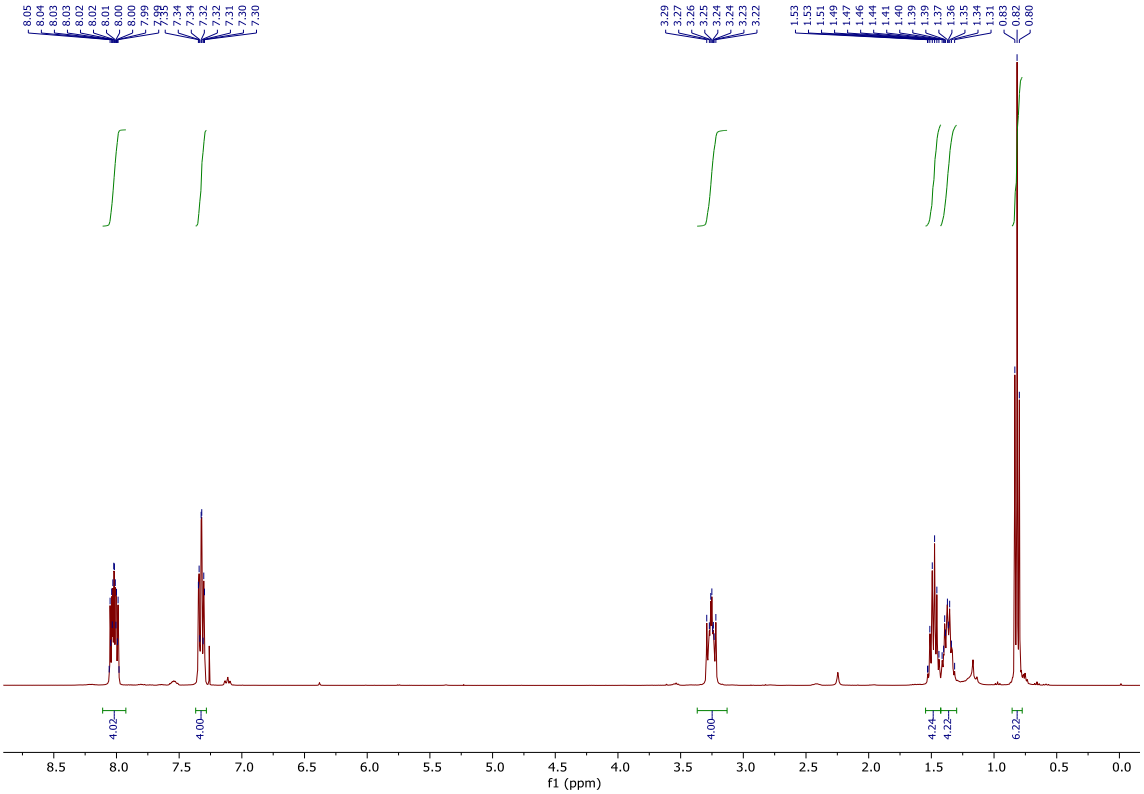
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



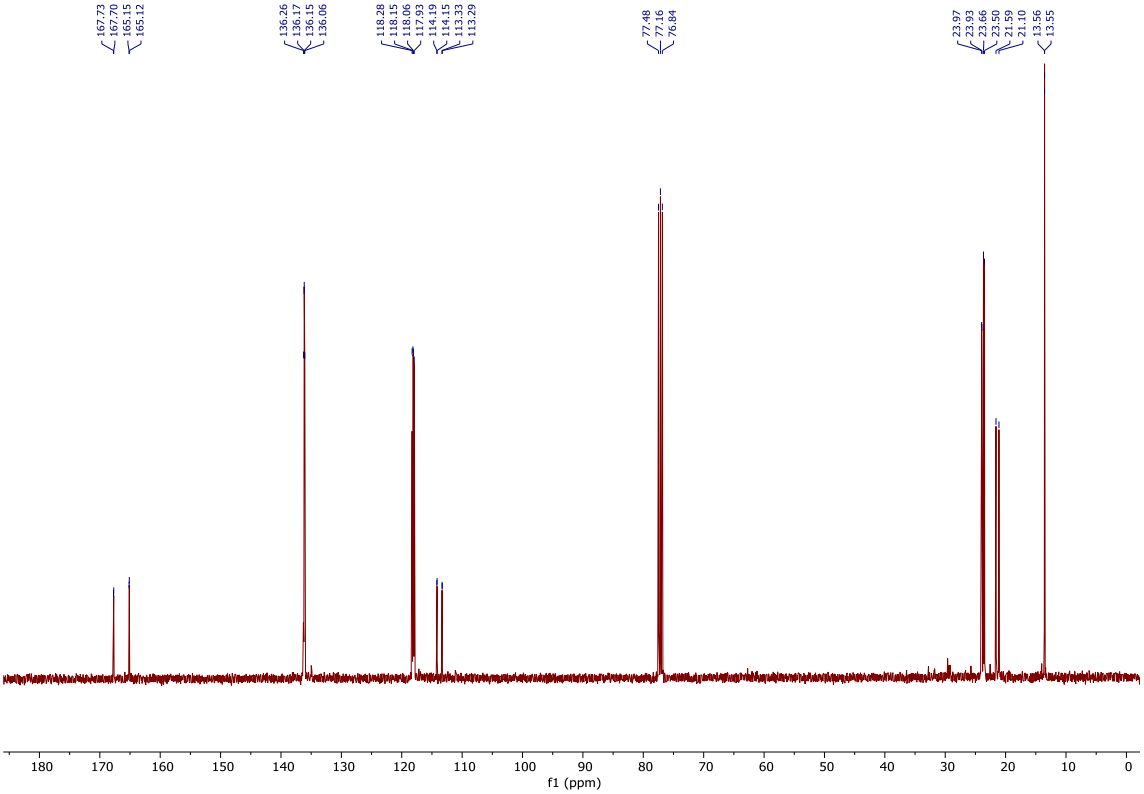
Butylbis(4-fluorophenyl)phosphonium tetrafluoroborate (**17**) – $^{31}P\{/\}$ NMR spectrum ($CDCl_3$)



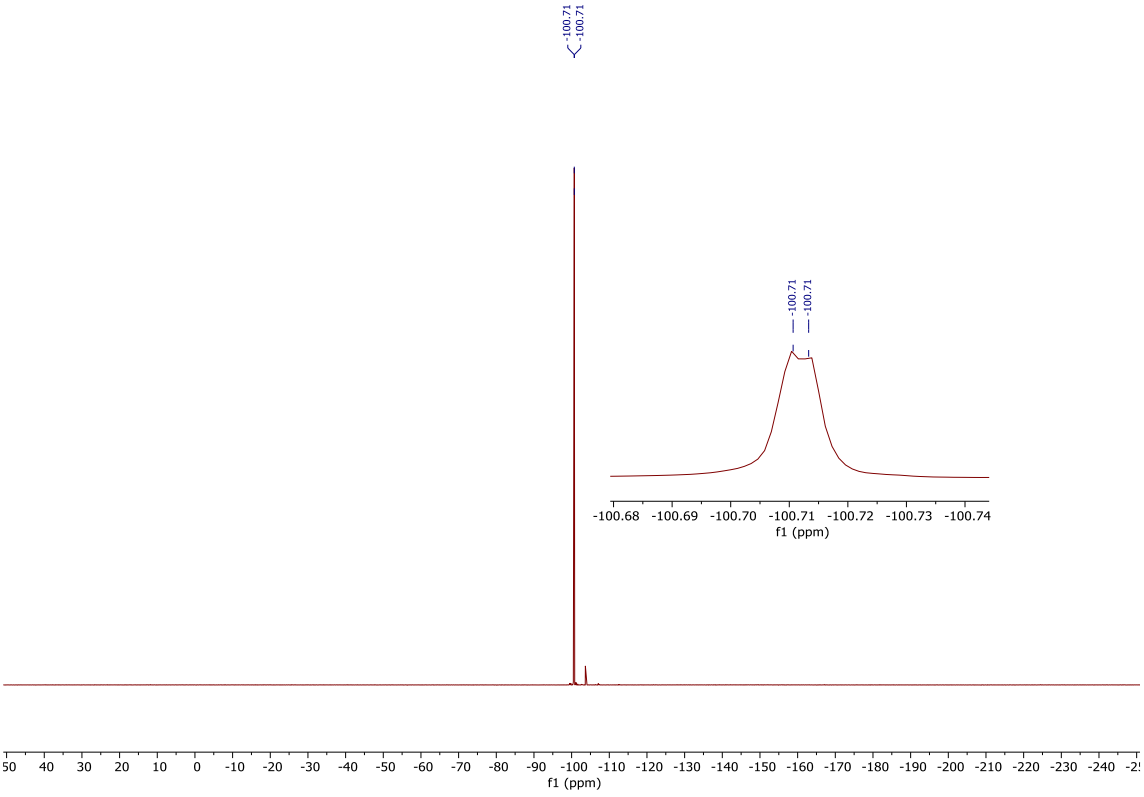
Dibutylbis(4-fluorophenyl)phosphonium bromide (**18**) – ^{1}H NMR spectrum ($CDCl_3$)



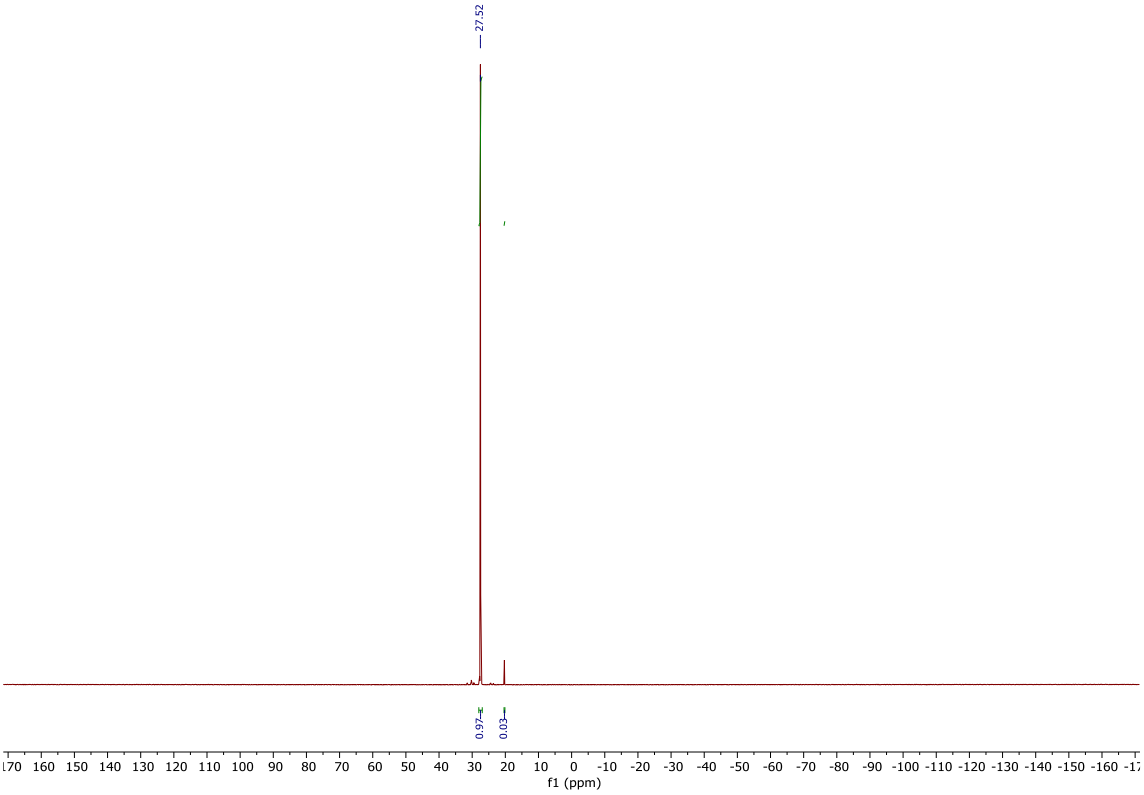
Dibutylbis(4-fluorophenyl)phosphonium bromide (**18**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



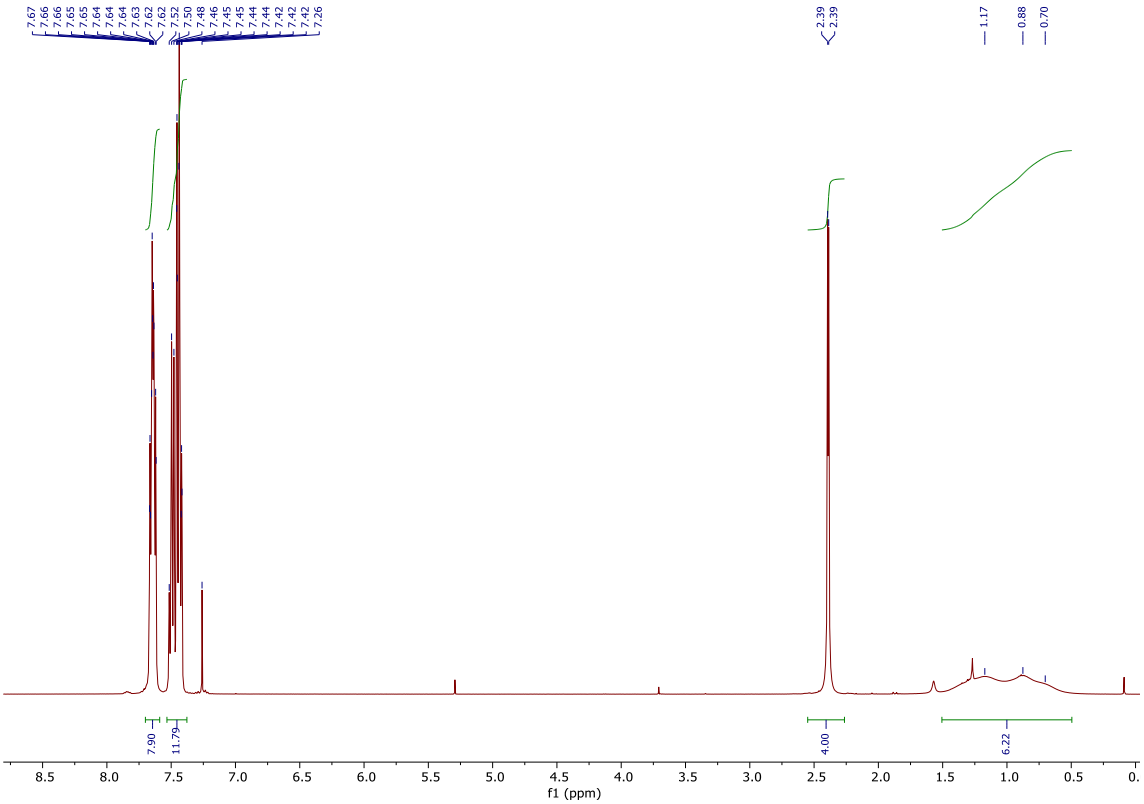
Dibutylbis(4-fluorophenyl)phosphonium bromide (**18**) – $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$)



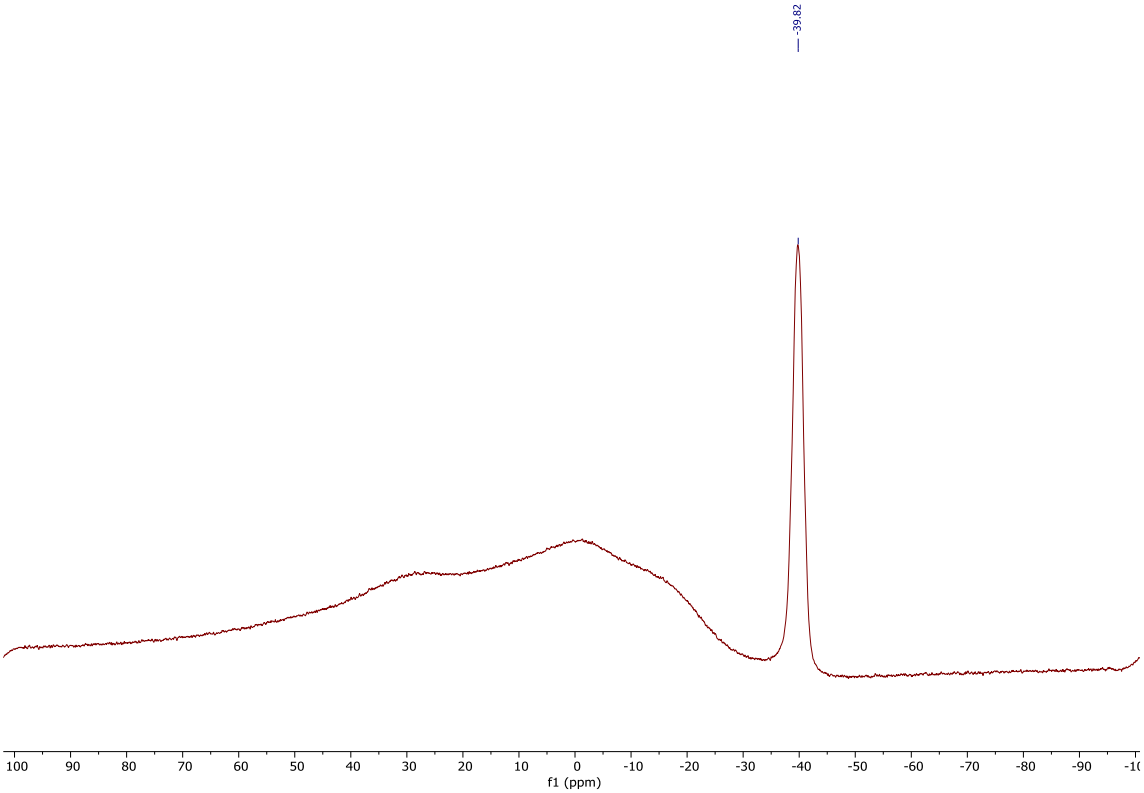
Dibutylbis(4-fluorophenyl)phosphonium bromide (**18**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



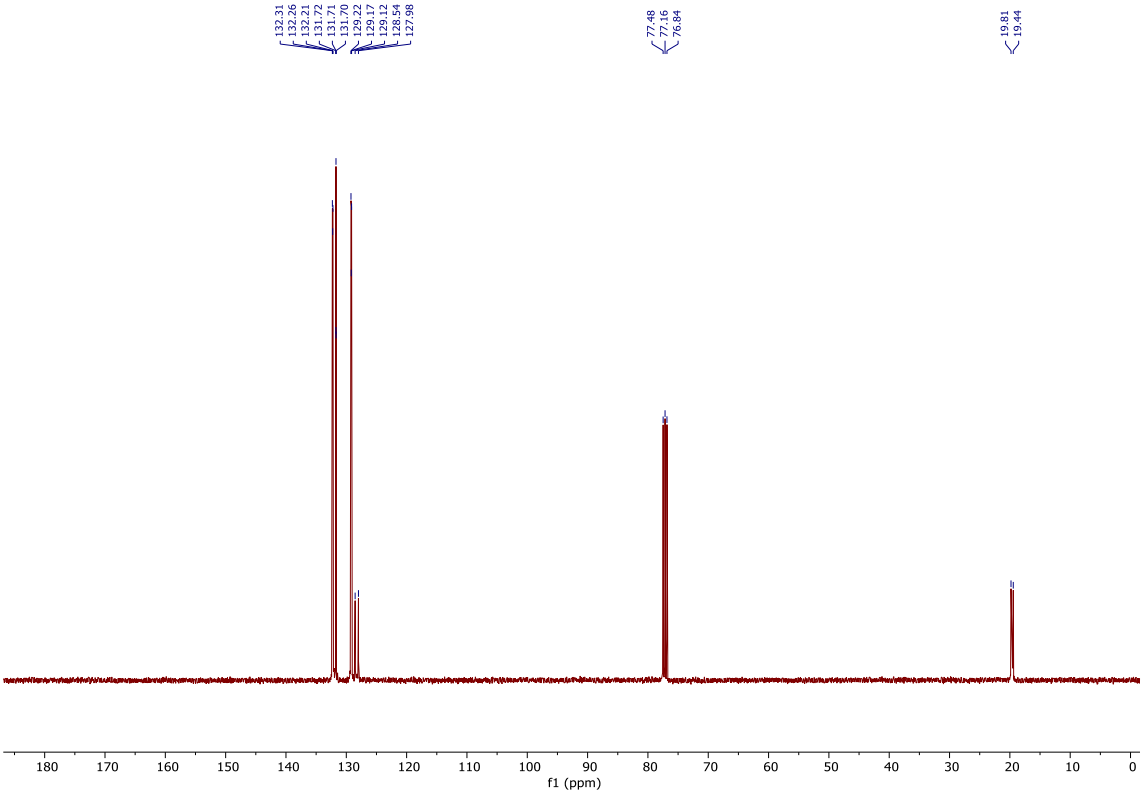
1,2-Bis(diphenylphosphino)ethane di-borane adduct (**19**) – ^{1}H NMR spectrum ($CDCl_3$)



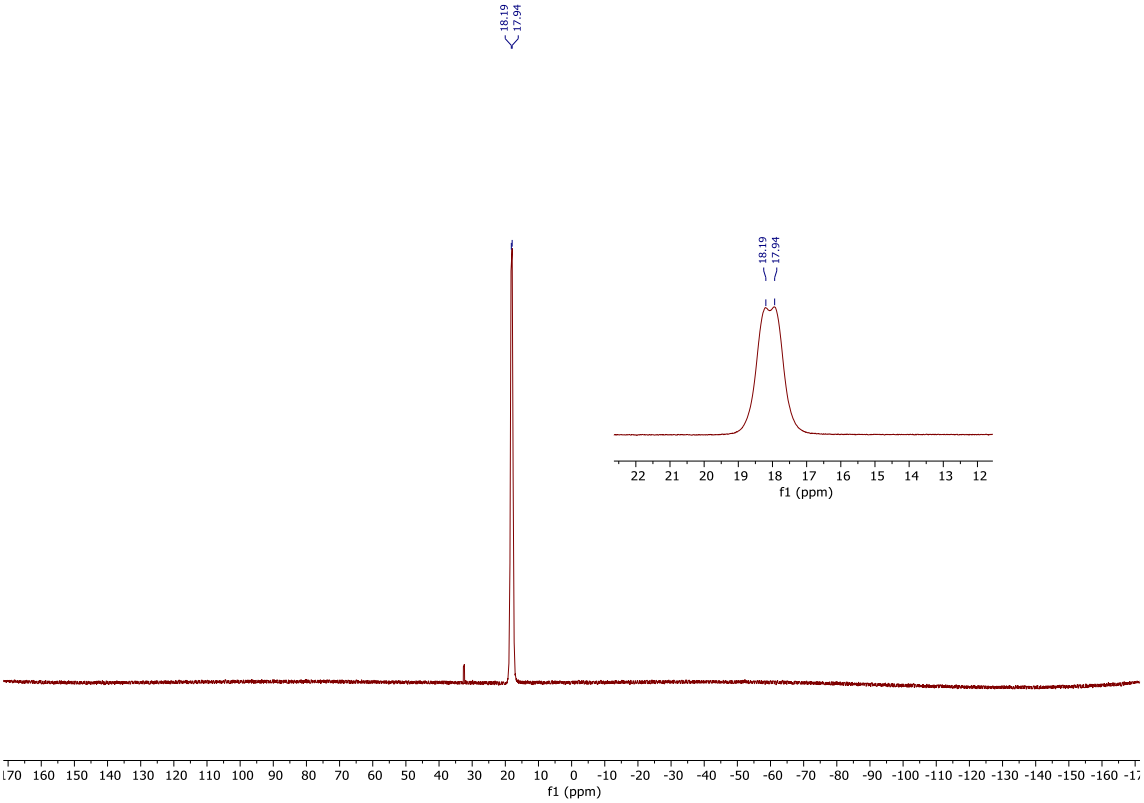
1,2-Bis(diphenylphosphino)ethane di-borane adduct (**19**) – ^{11}B NMR spectrum ($CDCl_3$)



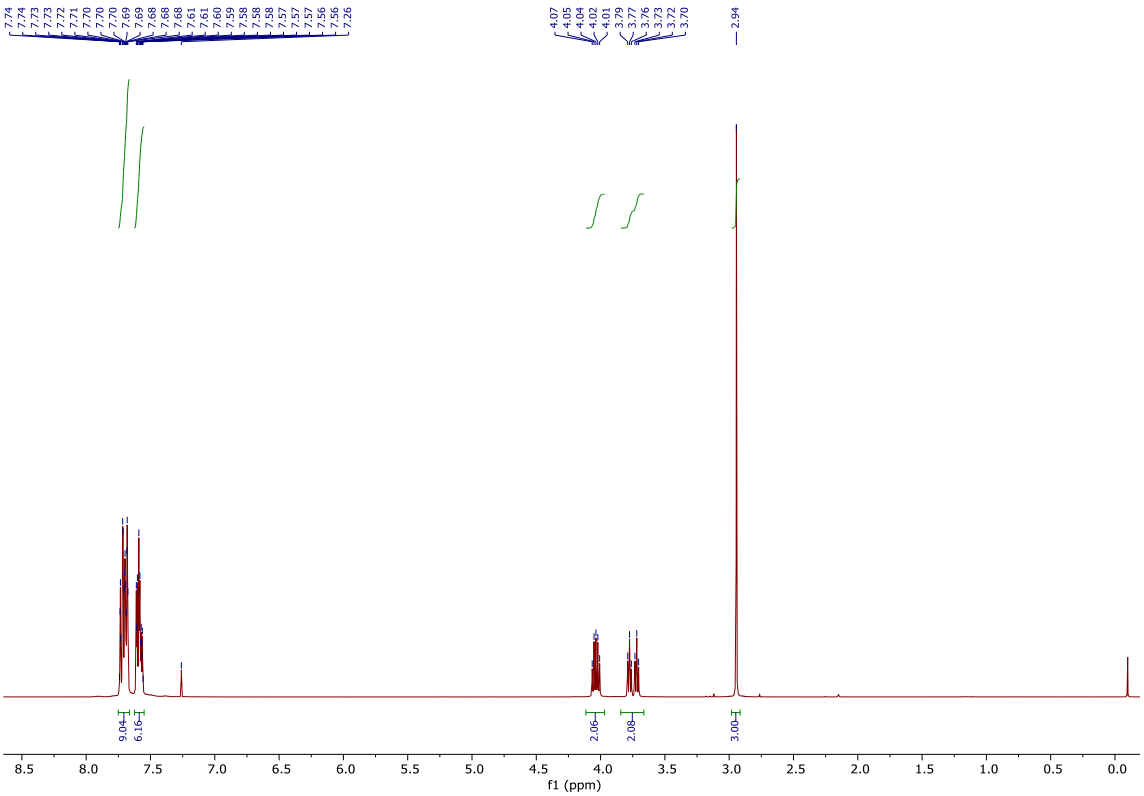
1,2-Bis(diphenylphosphino)ethane di-borane adduct (**19**) – $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$)



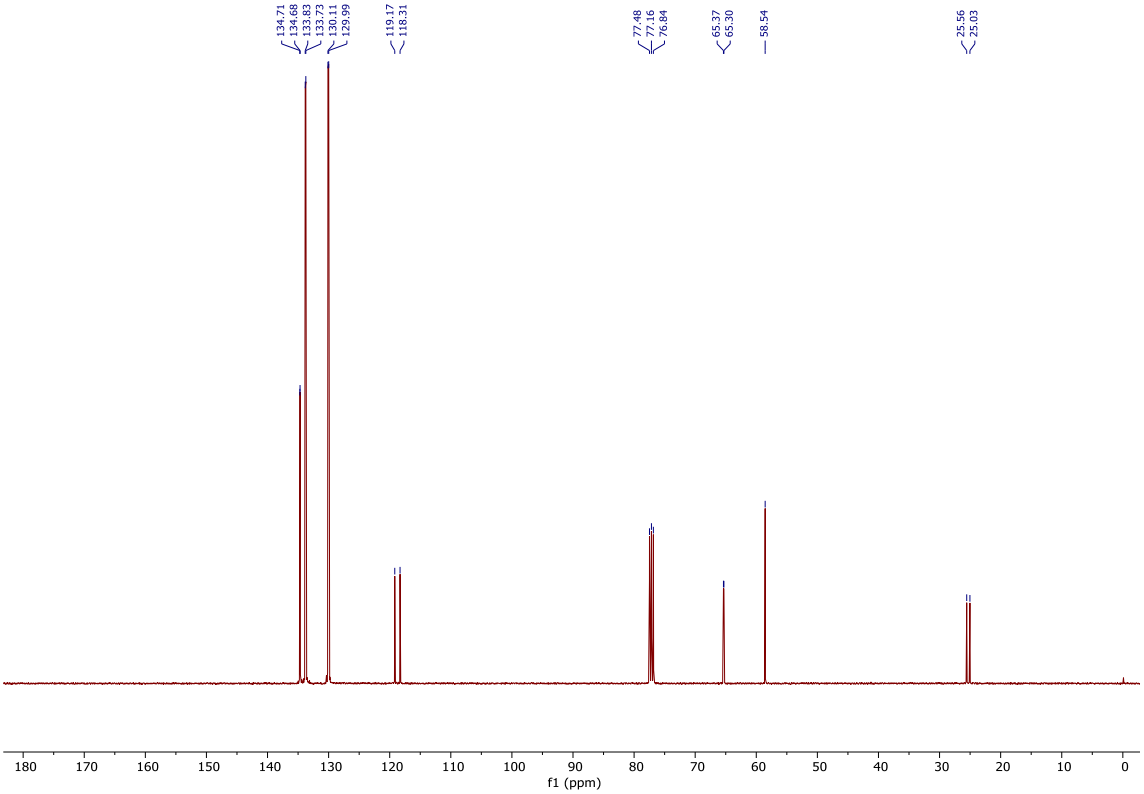
1,2-Bis(diphenylphosphino)ethane di-borane adduct (**19**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



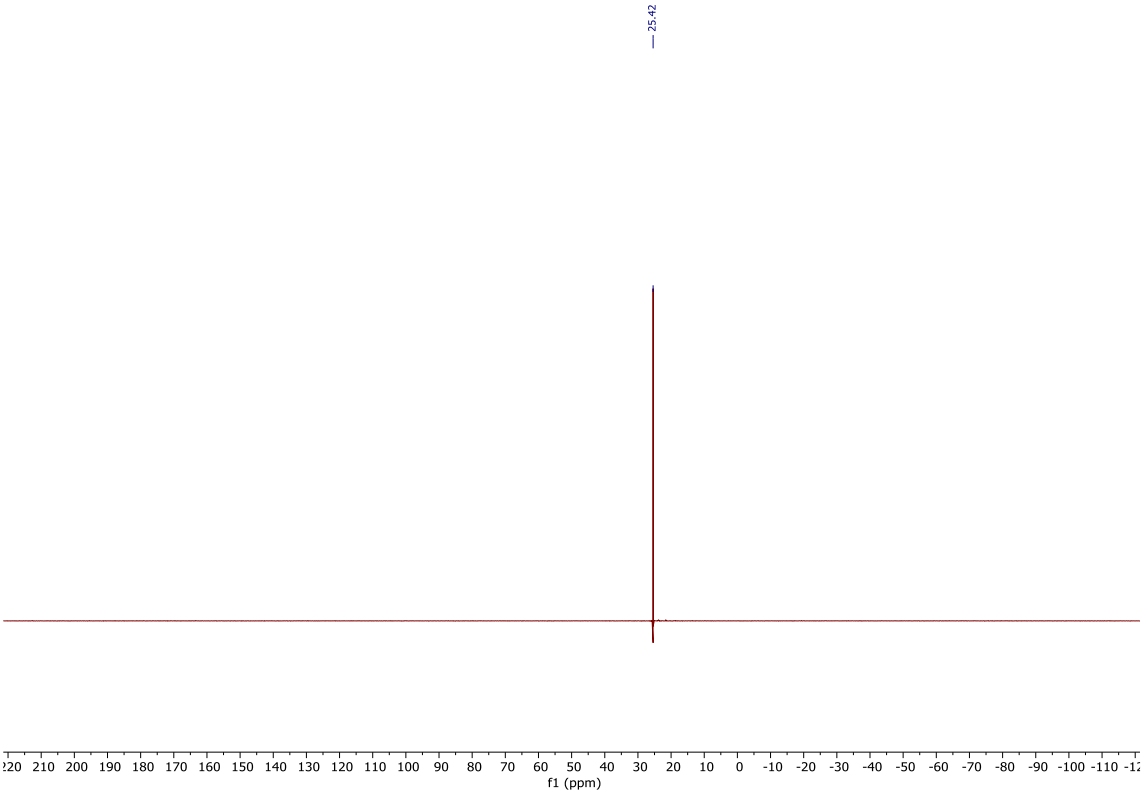
(2-Methoxyethyl)triphenylphosphonium bromide (**S13**) – ^{1}H NMR spectrum ($CDCl_3$)



(2-Methoxyethyl)triphenylphosphonium bromide (**S13**) – $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$)



(2-Methoxyethyl)triphenylphosphonium bromide (**S13**) – $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$)



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