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Supplementary Information

Double Hydrophosphination of Alkynes Promoted by Rhodium: the Key Role of an N-Heterocyclic Carbene Ligand

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Experimental Section

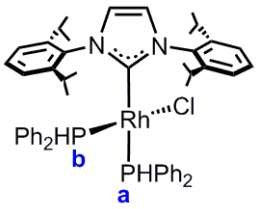
All reactions were carried out under argon atmosphere with rigorous exclusion of air. Alkynes were purchased from commercial sources and were used as received. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The organometallic catalysts $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-coe})]_2$ (**1a**),[1] $[Rh(\mu\text{-}Cl)(\eta^2\text{-coe})_2]_2$ (**1b**),[2] $RhCl(PPh_3)_3$ (**1c**),[3] $[Rh(\mu\text{-}Cl)(PCy_3)(\eta^2\text{-coe})]_2$ (**1d**),[4] were prepared following the procedures described in the literature. The diphosphines **7a**, **b**, **e** were previously reported and fully characterized.[5-8] ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300 or a Bruker Avance 500 and 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 (^{31}P), and $CFCl_3$ (^{19}F). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of $^1H\{^{31}P\}$, ^1H-^1H COSY, $^{13}C\{^1H\}$-APT, ^1H-^{13}C HSQC/HMBC, and ^1H-^{31}P HMBC experiments. High-resolution electrospray mass spectra were acquired on a Bruker Microtof-Q (ESI^+).

Table S1. Reaction of phenylacetylene with diphenylphosphine catalyzed by Rh^{I} complexes.[a]

Entry	T (°C)	Alkyne/Ph_2PH molar ratio	Catalyst[b]	Solvent	Conv. (%)[c]	**4a**/**5a**/**6a** (%)[d]	**7a** (%)[d]	**8** (%)[d]
1	25	1:1	**1a**	C_6D_6	0	---	---	---
2	50	1:1	**1a**	C_6D_6	23	4/31/45	12	9
3	80	1:1	**1a**	C_6D_6	52	1/23/32	35	9
4	80	1:1	**1a**[e]	C_6D_6	21	3/25/48	20	5
5	80	1:5[f]	**1a**	C_6D_6	>99[g]	0/17/45	14	23
6	80	5:1[h]	**1a**	C_6D_6	>99	13/17/60	10	1
7	80	1:1	**1a**	Pyr-d_5	0	---	---	---
8	80	1:1	**1a**	Acetone-d_6	19	2/23/57	9	8
9	120	0.5:1[i]	**1a**	tol-d_8	90	0/6/4	66	24
10	120	0.5:1[i]	**1a**	1.4-dioxane	90	2/9/17	47	25
11	120	0.5:1[i]	**none**	tol-d_8	44	0/88/12	0	0
12	120	0.5:1[j]	**1a**	none	91	0/6/2	57	36
13	120	Only Ph_2PH[k]	**none**	tol-d_8	0	---	---	---
14	120	Only Ph_2PH[k]	**1a**	tol-d_8	43	---	---	100
15	120	0.5:1[i]	**10**	tol-d_8	96	0/8/4	67	22
16	120	0.5:1[i]	**11**	tol-d_8	45	2/79/17	1	1

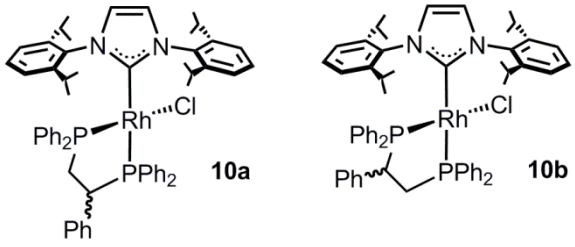
[a] Reaction conditions: 0.2 mmol of phenylacetylene, 0.2 mmol of Ph_2PH, 0.5 mL of solvent, 24 h of reaction. [b] $Rh/PHPh_2$=0.05. [c] Based on phosphine consumption, quantified by integration of the Inverse Gated Decoupled-^{31}P NMR spectra. [d] molar ratio, quantified by integration of the Inverse Gated Decoupled-^{31}P NMR spectra. [e] $Rh/PHPh_2$=0.025. [f] 0.2 mmol of phenylacetylene, 1 mmol of Ph_2PH. [g] Based on phenylacetylene consumption, quantified by integration of the ^1H-NMR spectra. [h] 1 mmol of phenylacetylene, 0.2 mmol of Ph_2PH. [i] 0.1 mmol of phenylacetylene, 0.2 mmol of Ph_2PH. [j] 0.4 mmol of phenylacetylene, 0.8 mmol of Ph_2PH and 0.02 mmol of **1a**. [k] 0.2 mmol of Ph_2PH.

***In-situ* preparation of RhCl(IPr)(PHPh$_2$)$_2$ (9)**.



A solution of **1a** (25 mg, 0.020 mmol) in C_6D_6 (0.5 mL, NMR-tube) at room temperature was treated with diphenylphosphine (16 µL, 0.092 mmol). It was immediately observed the formation of **9**. ^{1}H NMR (300 MHz, toluene-d_8, 298 K): δ 7.58 – 6.79 (H_{Ph}, 26H), 6.83 (s, 2H, =CHN), 6.39 (d, $J_{P\text{-}H}$ = 330, 1H, P_aH), 5.46 (d, $J_{P\text{-}H}$ = 331, 1H, P_bH), 4.10 (sept, $J_{H\text{-}H}$ = 7, 2H, C<u>H</u>Me$_{IPr}$), 3.24 (sept, $J_{H\text{-}H}$ = 7, 2H, C<u>H</u>Me$_{IPr}$), 1.49 (d, $J_{H\text{-}H}$ = 7, 1H, CH<u>Me</u>$_{IPr}$), 1.15 (d, $J_{H\text{-}H}$ = 7, 1H, CH<u>Me</u>$_{IPr}$), 0.99 (d, $J_{H\text{-}H}$ = 7, 1H, CH<u>Me</u>$_{IPr}$), 0.90 (d, $J_{H\text{-}H}$ = 7, 1H, CH<u>Me</u>$_{IPr}$). ^{13}C{^{1}H}-APT NMR (75.1 MHz, toluene-d_8, 298 K): δ 193.3 (ddd, $J_{C\text{-}P}$ = 123, $J_{C\text{-}Rh}$ = 47, $J_{C\text{-}P}$ = 16, Rh-C_{IPr}), 148.6 (s, $C_{q\text{-}IPr}$), 144.6 (s, $C_{q\text{-}IPr}$), 137.5 (s, C_qN), 135-122 (C_{Ph}), 28.9 (s, <u>C</u>HMe$_{IPr}$), 28.7 (s, <u>C</u>HMe$_{IPr}$), 26.2 (s, CH<u>Me</u>$_{IPr}$), 25.9 (s, CH<u>Me</u>$_{IPr}$), 23.5 (s, CH<u>Me</u>$_{IPr}$), 21.7 (s, CH<u>Me</u>$_{IPr}$). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d_8, 298 K): δ 16.4 (dd, $J_{Rh\text{-}P}$ = 189, $J_{P\text{-}P}$ = 53, P_a), 9.7 (dd, $J_{Rh\text{-}P}$ = 118, $J_{P\text{-}P}$ = 53, P_b).

Preparation of RhCl(IPr)(*rac*-Phenphos) (10a,b).

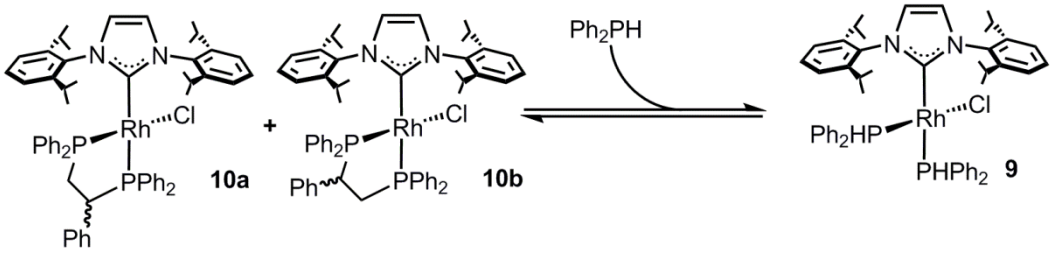


A yellow solution of **1a** (100 mg, 0.078 mmol) in toluene (10 mL) was treated with **7a** (74 mg, 0.157 mmol) and stirred at room temperature for 1 h. The solution was concentrated to ca. 1 mL and then *n*-hexane (3 mL) was added to induce the precipitation of a yellow solid which was washed with hexane (3 x 3 mL) and dried in vacuo. The compound was obtained as a diastereomer mixture of **10a**/**10b** in a 98/2 ratio. Yield: 141 mg (90%). **10a**: ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.81 – 6.76 (H_{Ph}, 31H), 4.93 (sept, $J_{H\text{-}H}$ = 7, 1H, C<u>H</u>Me$_{IPr}$), 3.85 (sept, $J_{H\text{-}H}$ = 7, 1H, C<u>H</u>Me$_{IPr}$), 3.32 (sept, $J_{H\text{-}H}$ = 7, 1H, C<u>H</u>Me$_{IPr}$), 2.74 (sept, $J_{H\text{-}H}$ = 7,

1H, C<u>H</u>Me$_{IPr}$), 3.32 (overlapped, 1H, CHP), 2.61 – 2.50 (m, 1H, CH_2P), 2.43-2.30 (m, 1H, CH_2P), 1.87 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 1.37 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 1.28 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 1.20 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 1.09 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 1.06 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 0.97 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$), 0.36 (d, J_{H-H} = 7, 3H, CH<u>Me</u>$_{IPr}$). $^{13}C\{^1H\}$-APT NMR (125 MHz, C_6D_6, 298 K): δ 195.9 (ddd, J_{C-P} = 121, J_{C-Rh} = 47, J_{C-P} = 12, Rh-C_{IPr}), 149.4 (s, C_{q-IPr}), 149.2 (s, C_{q-IPr}), 144.9 (s, C_{q-IPr}), 143.7 (s, C_{q-IPr}), 138.1 (s, C_qN), 137.5 (s, C_qN), 149.0 – 122.1 (C_{Ph}), 42.2 (dd, J_{C-P} = 19, 15, CHP), 39.5 (dd, J_{C-P} = 36, 29, CH_2-P), 29.4 (s, C<u>H</u>Me$_{IPr}$), 28.7 (s, C<u>H</u>Me$_{IPr}$), 28.6 (s, C<u>H</u>Me$_{IPr}$), 28.2 (s, C<u>H</u>Me$_{IPr}$), 27.5 (s, CH<u>Me</u>$_{IPr}$), 26.7 (s, CH<u>Me</u>$_{IPr}$), 26.1 (s, CH<u>Me</u>$_{IPr}$), 25.6 (s, CH<u>Me</u>$_{IPr}$), 24.4 (s, CH<u>Me</u>$_{IPr}$), 24.2 (s, CH<u>Me</u>$_{IPr}$), 23.8 (s, CH<u>Me</u>$_{IPr}$), 22.6 (s, CH<u>Me</u>$_{IPr}$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ 78.1 (dd, J_{Rh-P} = 122, J_{P-P} = 44, P-CH), 45.9 (dd, J_{Rh-P} = 203, J_{P-P} = 44, P-CH_2).

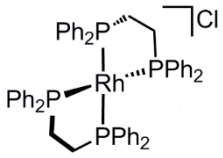
10b: $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K): δ 74.2 (dd, J_{Rh-P} = 210, J_{P-P} = 44, P-CH), 46.6 (dd, J_{Rh-P} = 122, J_{P-P} = 44, P-CH_2).

Reaction of 10 with $PHPh_2$.



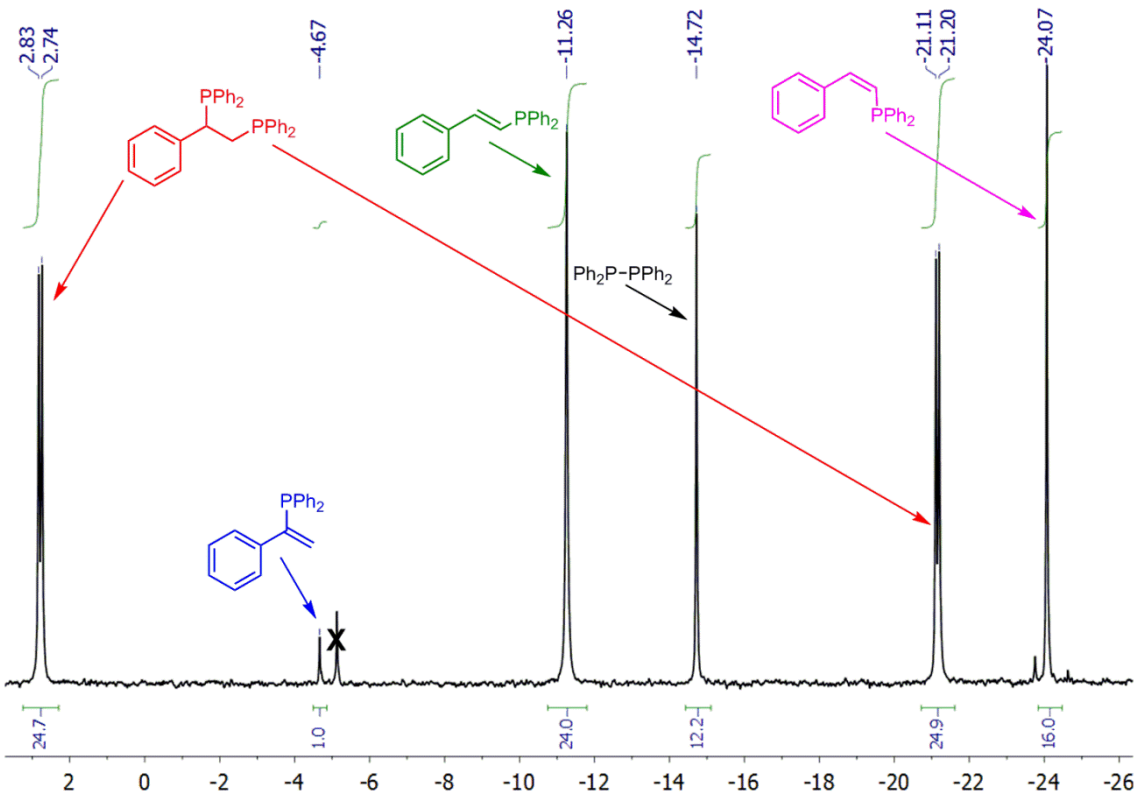
A solution of **10** (10 mg, 0.01 mmol) in C_6D_6 (0.5 mL, NMR-tube) at room temperature was treated with $PHPh_2$ (3.5 µL, 0.02 mmol). The solution was heated at 333 K (60°C) in a NMR spectrometer and the interconversion between **10a,b** and **9** quantified every 10 min by integration of the Inverse Gated Decoupled-^{31}P NMR spectra. After 5 h **10b** was totally undetectable and a **10a**:**9** molar ratio of 79:21 was measured. This value remained unchanged in the next 5 h where upon the formation of tetraphenylbiphosphine (**8**) decreases the amount of both complexes.

Preparation of [RhCl(dppe)$_2$]Cl (11).



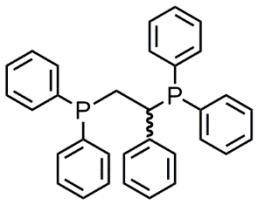
Complex **11** was prepared according to a modified literature method and its spectra were consistent with that of the published data.[9] A red solution of [RhCl(PPh_3)$_3$] (**1c**) (104 mg, 0.112 mmol) in CH_2Cl (10 mL) at room temperature was treated with {1,2-bis(diphenylphosphino)ethane} (dppe) (90 mg, 0.224 mmol) and stirred at room temperature for 1 h. The solution was concentrated to ca. 1 mL and then diethylether (3 mL) was added to induce the precipitation of a yellow solid which was washed with diethylether (3 x 3 mL) and dried in vacuo. Yield: 96 mg (92%).

Standard procedure for the catalytic hydrophosphination of alkynes. In a Young type NMR tube 0.005 mol of catalyst **1a** were dissolved in 0.4 mL of toluene + 0.1 mL of C_6D_6 and then 0.2 mmol of phosphine and 0.1 mmol of alkyne were added and the solution was heated at 120 °C. Conversion was quantified by integration of $^{31}P\{^1H\}$ NMR spectra. Inverse Gated Decoupling was employed to obtain ^1H decoupled NMR spectra of ^{31}P nuclei without signal enhancement by nuclear Overhauser effects (NOE). To observe all components in the sample, a full spectrum was recorded with 256 scans using a 200 ppm spectral width, 101K data points, 0.99-s acquisition time, a relaxation delay of 5 s, and a 30° pulse width. A typical example of $^{31}P\{^1H\}$ NMR spectra corresponding to the hydrophosphination of phenylacetylene (entry 3, Table S1) is shown below (peak marked with X correspond to PPh_3, an impurity already present in the commercial Ph_2PH).



Reaction of phenylacetylene and diphenylphosphine.

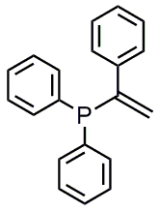
Preparation of (1-phenylethane-1,2-diyl)bis(diphenylphosphine) (*rac*-Phenphos) (7a).



In a schlenk tube 64 mg of **1a** (0.05 mmol) in 10 mL of toluene was treated with 110 µL of phenylacetylene (1 mmol), 350 µL of Ph_2PH (2 mmol) and magnetically stirred for 24 h at 120 °C. At the end of the reaction, the volatiles were removed in vacuo. The residue was dissolved in 10 mL of dichloromethane and filtered through a short column (5 cm) of silica. The resulted solution was concentrated to ca. 1 mL and then methanol (10 mL) was added to induce the precipitation of a fluffy off-white solid which was washed with methanol (3 x 10 mL) cold hexane (3 x 2 mL) and dried in vacuo. Yield: 195 mg (41%). The NMR spectrum was consistent with that of the published data.[5] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.67 – 6.91 (25H, CH_{Ph}), 3.77 – 3.66 (m, 1H, CHP), 2.89 – 2.77 (m, 2H, CH_2P). $^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298

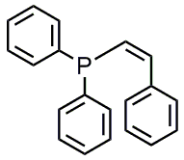
K): δ 141.0 – 126.3 (C_{Ph}), 42.3 (dd, $J_{C\text{-}P}$ = 16, 15, CHP), 32.9 (dd, $J_{C\text{-}P}$ = 22, 17, CH_2P). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ 2.8 (d, $J_{P\text{-}P}$ = 18, CHP), -21.2 (d, $J_{P\text{-}P}$ = 18, CH_2P).

diphenyl(1-phenylvinyl)phosphine (4a)



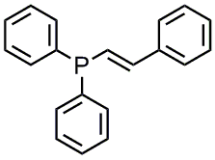
The NMR spectrum was consistent with that of the published data.[10] ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.49 – 7.24 (15H, CH_{Ph}), 6.00 (dd, 1H, $J_{H\text{-}P}$ = 13, $J_{H\text{-}H}$ = 1, $=CH_{(trans\text{-}P)}$), 5.15 (dd, 1H, $J_{H\text{-}P}$ = 6, $J_{H\text{-}H}$ = 1, $=CH_{(cis\text{-}P)}$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -4.7 (s).

(Z)-diphenyl(styryl)phosphine (5a)



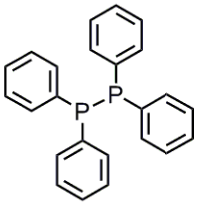
The NMR spectrum was consistent with that of the published data.[10] ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.52 – 7.30 (15H, CH_{Ph}), 7.28 (overlapped, 1H, =CHP), 6.50 (dd, 1H, $J_{H\text{-}H}$ = 13, $J_{H\text{-}P}$ = 3, =CHPh). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -24.1 (s).

(E)-diphenyl(styryl)phosphine (6a)



The NMR spectrum was consistent with that of the published data.[10] ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.61 – 7.28 (15H, CH_{Ph}), 7.49 (overlapped, 1H, =CHP), 6.95 (overlapped, 1H, =CHPh). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -11.3 (s).

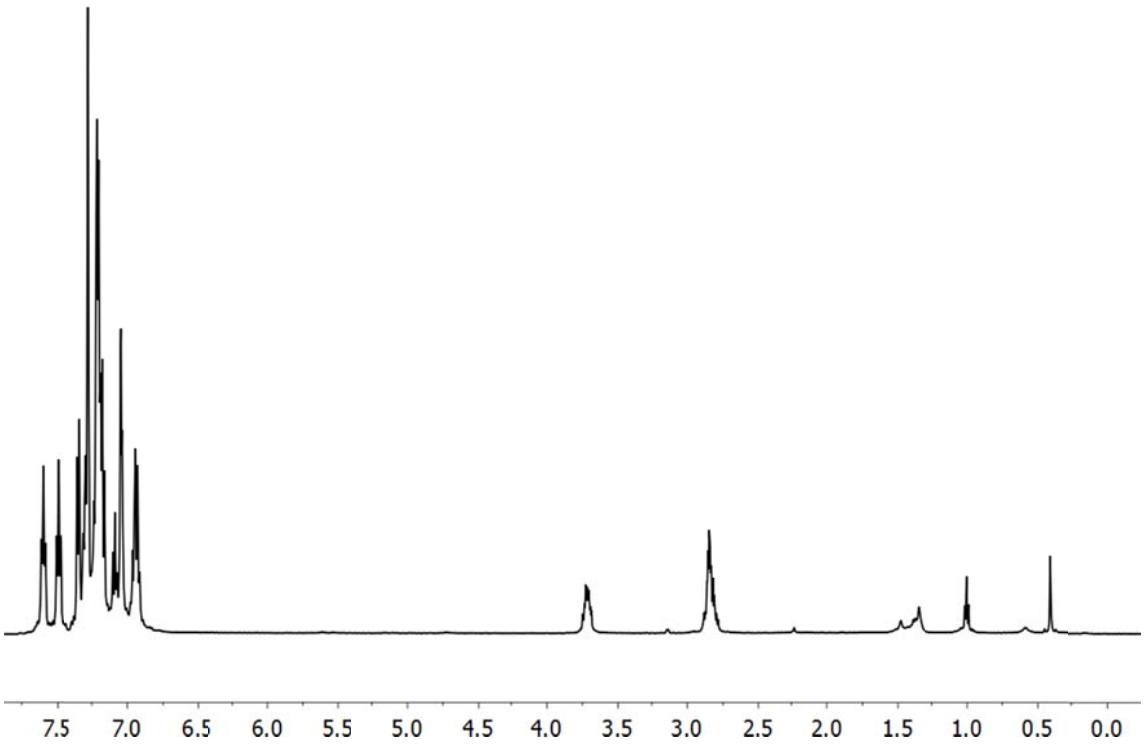
tetraphenylbiphosphine (8)



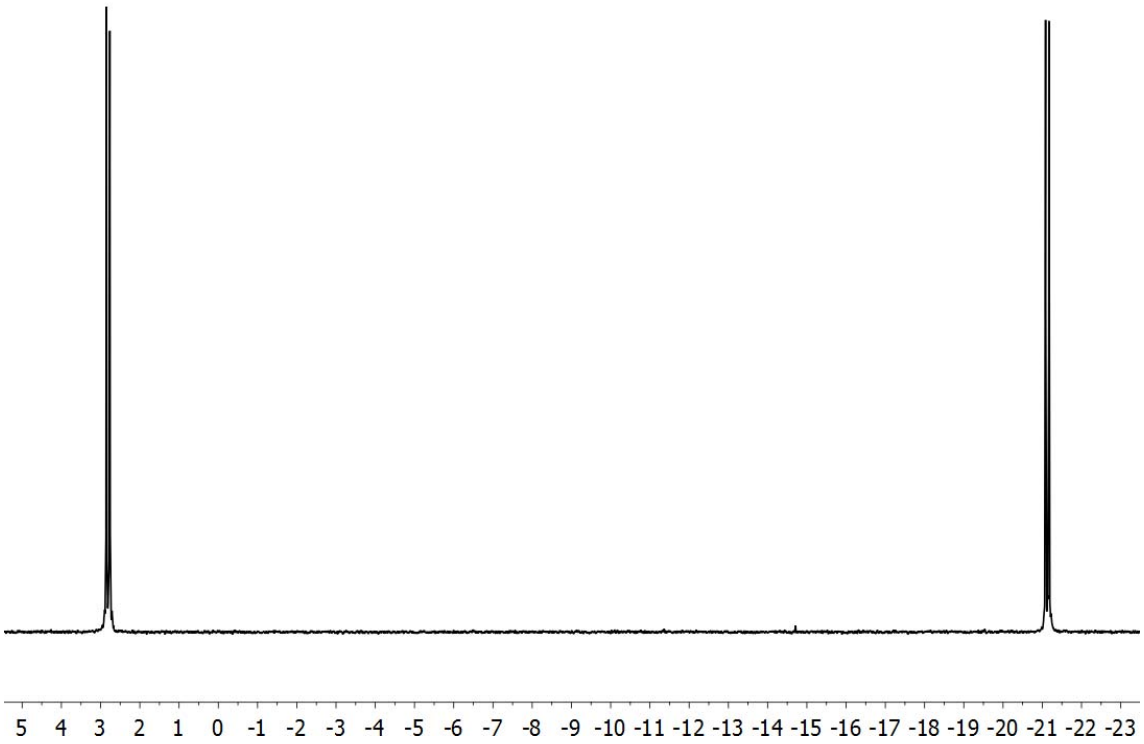
The NMR spectrum was consistent with that of the published data.[11] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.42 – 7.01 (20H, CH_{Ph}). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): -14.7 (s).

NMR spectra of 7a

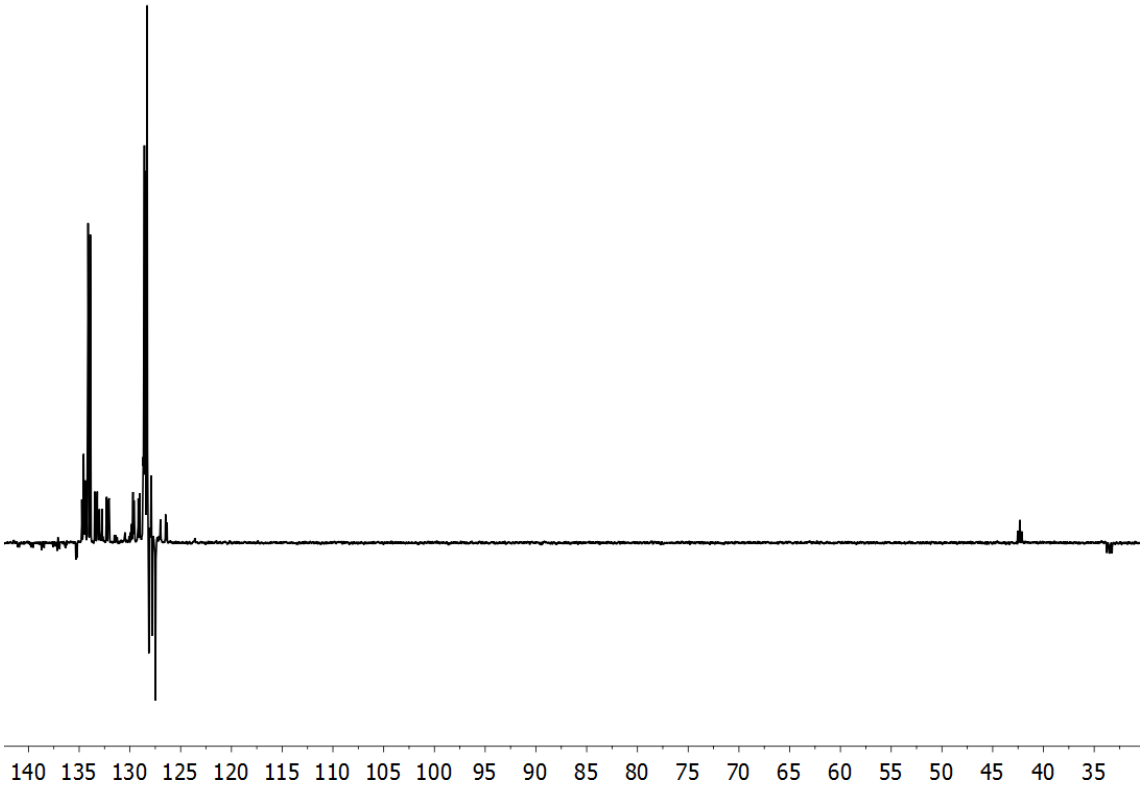
^{1}H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

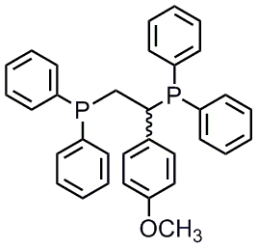


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



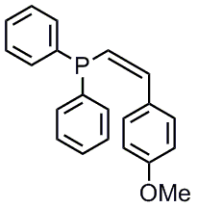
Reaction of 4-methoxyphenylacetylene and diphenylphosphine.

(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7b)



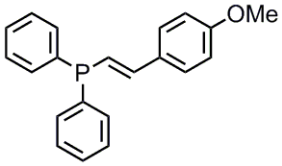
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.68 – 6.63 (24H, CH_{Ph}), 3.74 – 3.67 (m, 1H, CHP), 3.27 (s, 3H, OMe), 2.86 – 2.84 (m, 2H, CH_2P), 2.83 – 2.75 (m, 2H, CH_2P). ^{13}C{^{1}H}-APT NMR (75 MHz, C_6D_6, 298 K): δ 158.6 (d, $J_{C\text{-}P}$ = 2, $\underline{C}_qOCH_3$), 140.1 – 113.7 (C_{Ph}), 54.5 (s, OCH_3), 41.5 (dd, $J_{C\text{-}P}$ = 16, 15, CHP), 33.9 (dd, $J_{C\text{-}P}$ = 23, 17, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ 1.8 (d, $J_{P\text{-}P}$ = 17, CHP), -21.2 (d, $J_{P\text{-}P}$ = 17, CH_2P).

(Z)-(4-methoxystyryl)diphenylphosphine (5b)



^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.48 – 7.25 (14H, CH_{Ph}), 7.30 (overlapped, 1H, =CHP), 6.43 (dd, 1H, $J_{H\text{-}H}$ = 13, $J_{H\text{-}P}$ = 3, =CHPh), 3.41 (s, 3H, OMe). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -23.6 (s).

(E)-(4-methoxystyryl)diphenylphosphine (6b)

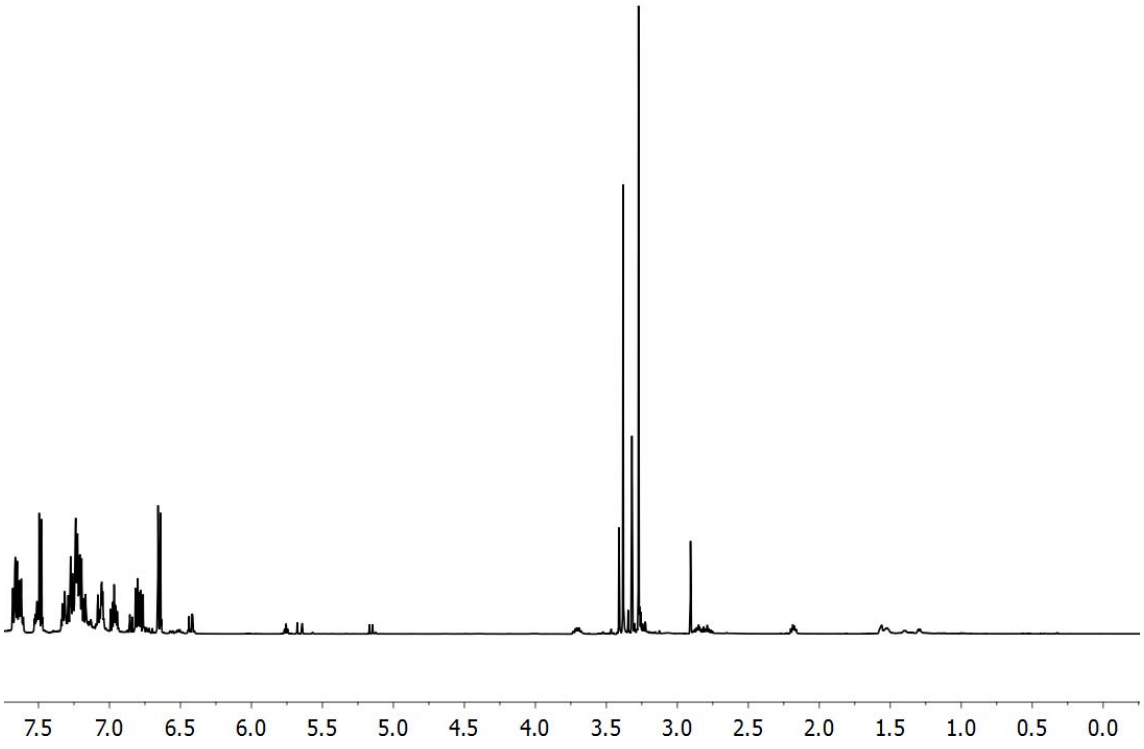


^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.69 – 7.20 (14H, CH_{Ph}), 7.23 (overlapped, 1H, =CHP), 6.97 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 6, =CHPh), 3.32 (s, 3H, OMe). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -11.2 (s).

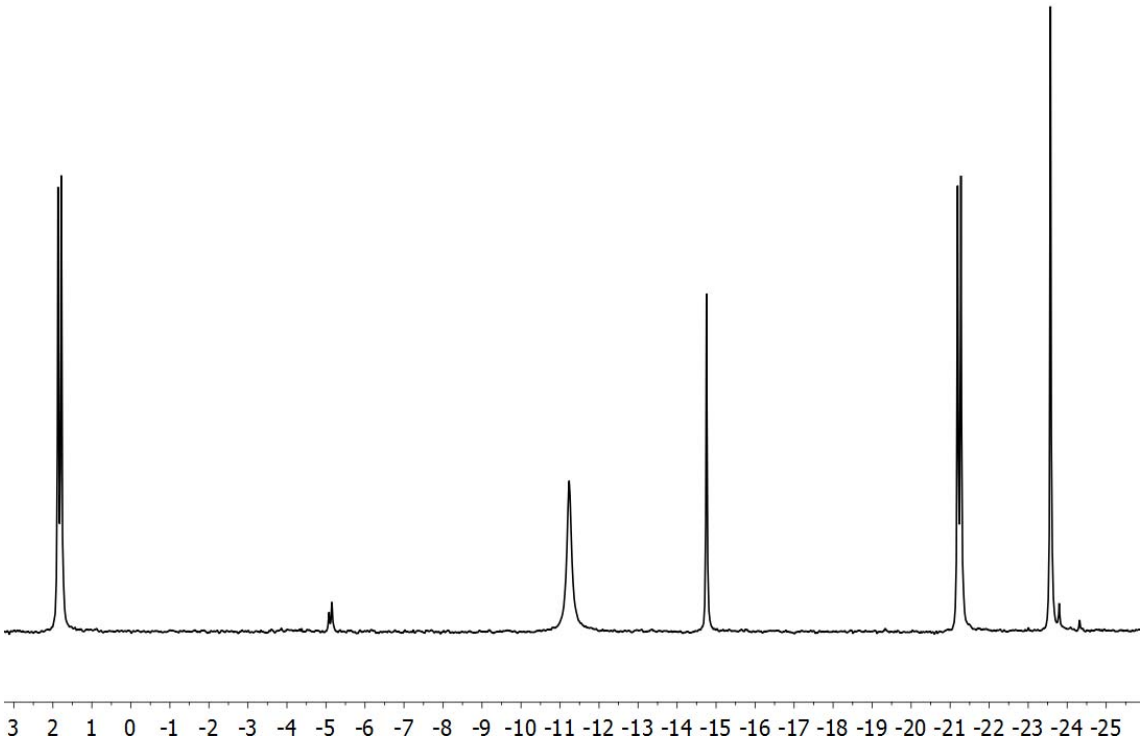
NMR spectra of the reaction crude.

Reaction conditions: 4-methoxyphenylacetylene (0.2 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 48 h at 80 °C.

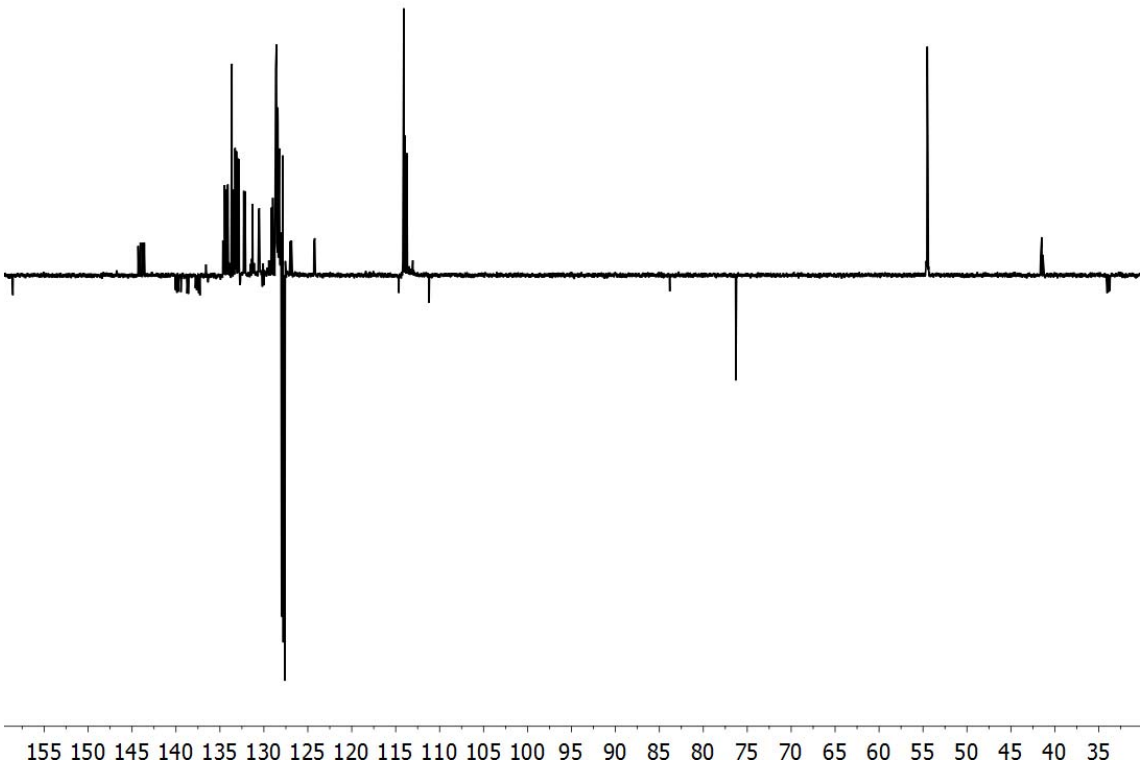
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

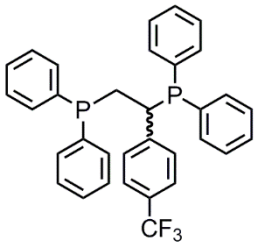


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



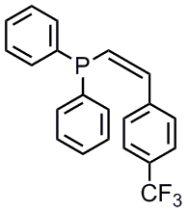
Reaction of 4-trifluoromethylphenylacetylene and diphenylphosphine.

(1-(4-(trifluoromethyl)phenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7c)



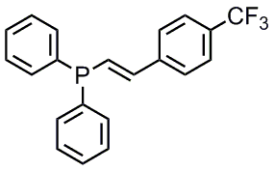
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.63 – 6.81 (24H, CH_{Ph}), 3.74 – 3.68 (m, 1H, CHP), 2.8 – 2.78 (m, 2H, CH_2P), 2.76 – 2.69 (m, 2H, CH_2P). $^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K): δ 142.4 – 114.9 (C_{Ph}), 42.5 (dd, $J_{C\text{-}P}$ = 17, 16, CHP), 32.9 (dd, $J_{C\text{-}P}$ = 21, 18, CH_2P). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ 4.2 (d, $J_{P\text{-}P}$ = 17, CHP), -20.1 (d, $J_{P\text{-}P}$ = 17, CH_2P). ^{19}F NMR (228 MHz, C_6D_6, 298 K): δ -62.1 (s, CF_3).

(Z)-diphenyl(4-(trifluoromethyl)styryl)phosphine (5c)



^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.54 – 7.07 (14H, CH_{Ph}), 7.10 (overlapped, 1H, =CHP), 6.57 (dd, 1H, $J_{H\text{-}H}$ = 13, $J_{H\text{-}P}$ = 2, =CHPh). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -24.1 (s). ^{19}F NMR (228 MHz, C_6D_6, 298 K): δ -62.0 (s, CF_3).

(E)-diphenyl(4-(trifluoromethyl)styryl)phosphine (6c)

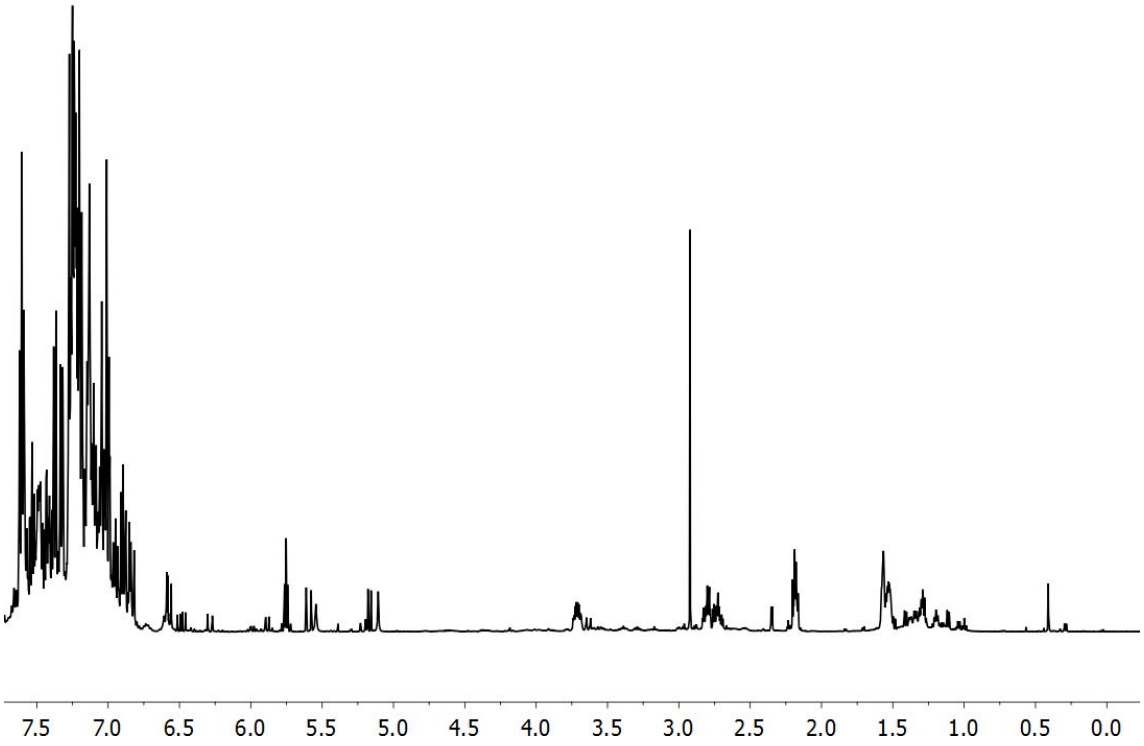


^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.62 – 7.24 (14H, CH_{Ph}), 7.03 (overlapped, 1H, =CHP), 6.85 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 11, =CHPh). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -10.8 (s). ^{19}F NMR (228 MHz, C_6D_6, 298 K): δ -61.7 (s, CF_3).

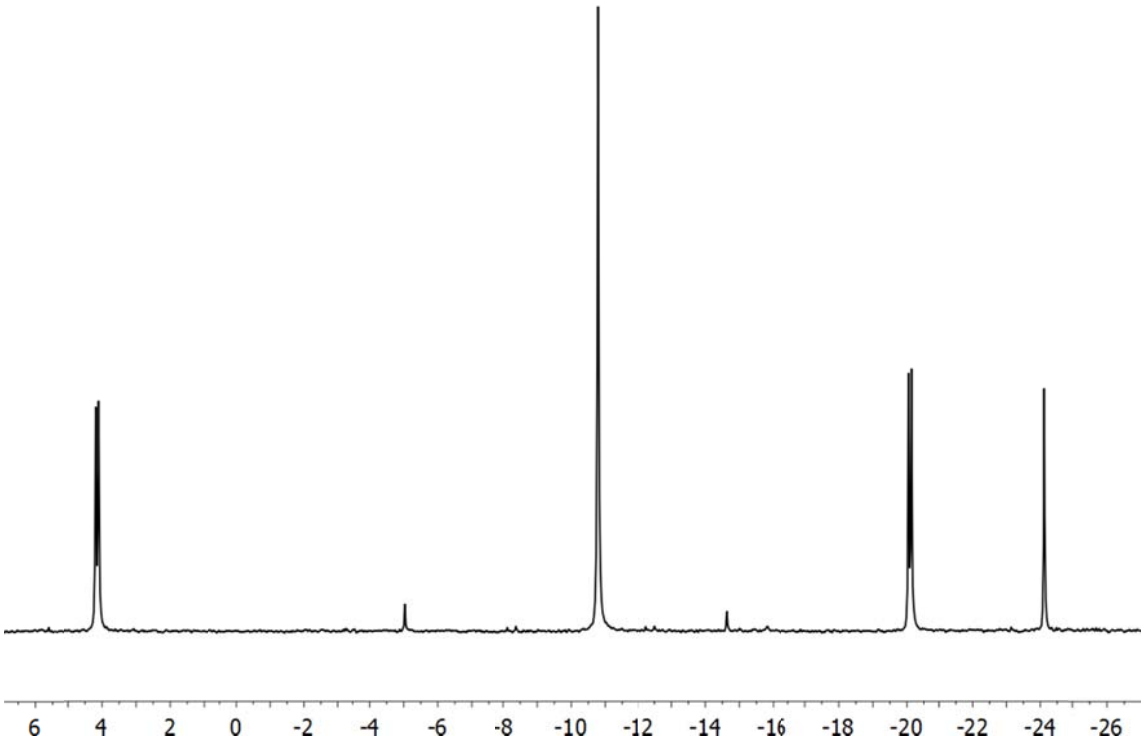
NMR spectra of the reaction crude.

Reaction conditions: 4-trifluoromethylphenylacetylene (0.2 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 48 h at 80 °C.

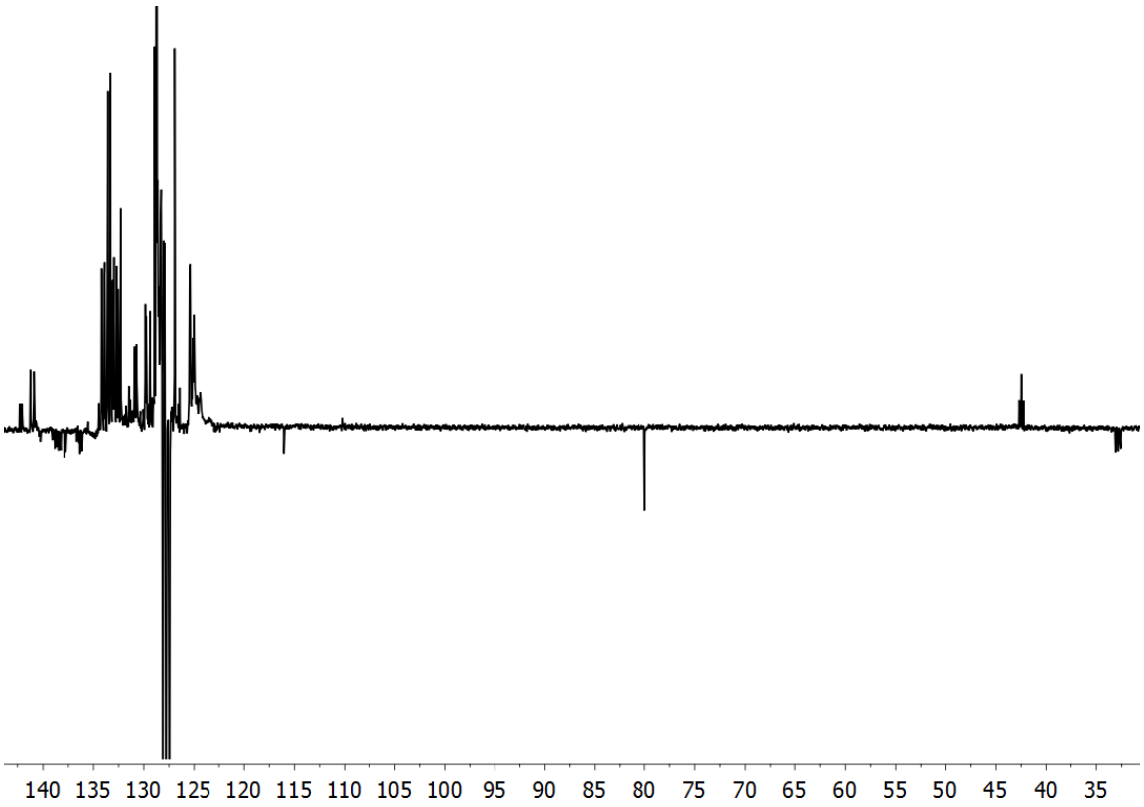
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

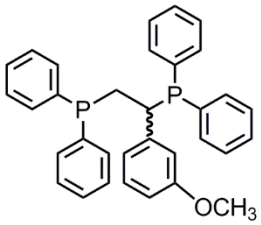


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



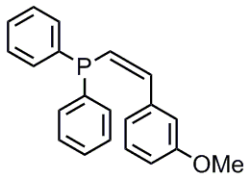
Reaction of 3-methoxyphenylacetylene and diphenylphosphine.

(1-(3-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7d)



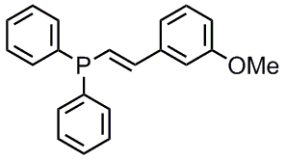
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.71 – 6.68 (24H, CH_{Ph}), 3.77 – 3.65 (m, 1H, CHP), 3.38 (s, 3H, OMe), 2.88 – 2.81 (m, 2H, CH_2P). ^{13}C{^{1}H}-APT NMR (75 MHz, C_6D_6, 298 K): δ 159.9 (s, $\underline{C}_qOCH_3$), 140.8 – 133.5 (C_{Ph}), 54.4 (s, OCH_3), 42.5 (dd, J_{C-P} = 16, 15, CHP), 33.5 (dd, J_{C-P} = 22, 17, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ 2.5 (d, J_{P-P} = 18, CHP), -20.9 (d, J_{P-P} = 18, CH_2P).

(Z)-(3-methoxystyryl)diphenylphosphine (5d)



^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.60 – 7.13 (14H, CH_{Ph}), 7.29 (overlapped, 1H, =CHP), 6.52 (dd, 1H, J_{H-H} = 13, J_{H-P} = 2, =CHPh), 3.40 (s, 3H, OMe). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -23.2 (s).

(E)-(3-methoxystyryl)diphenylphosphine (6d)

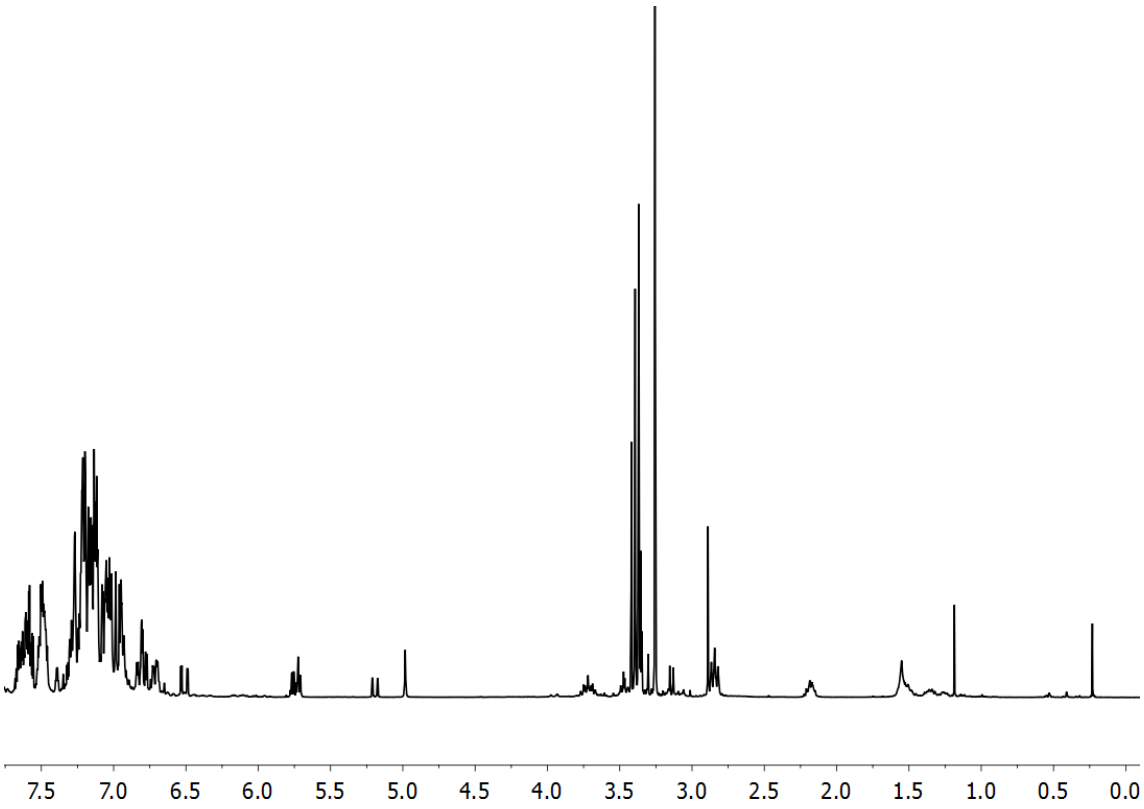


^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.65 – 7.22 (14H, CH_{Ph}), 7.13 (overlapped, 1H, =CHP), 6.83 (overlapped, 1H, =CHPh), 3.43 (s, 3H, OMe). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -11.3 (s).

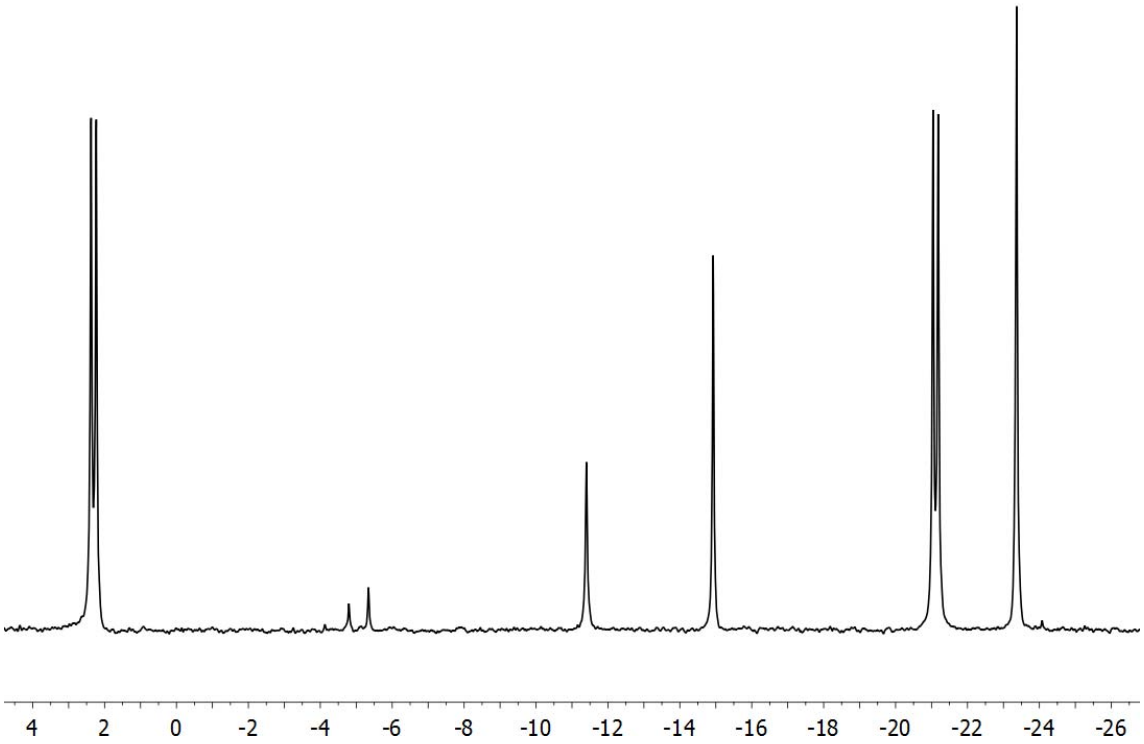
NMR spectra of the reaction crude.

Reaction conditions: 1-ethynyl-3-methoxybenzene (0.2 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 72 h at 80 °C.

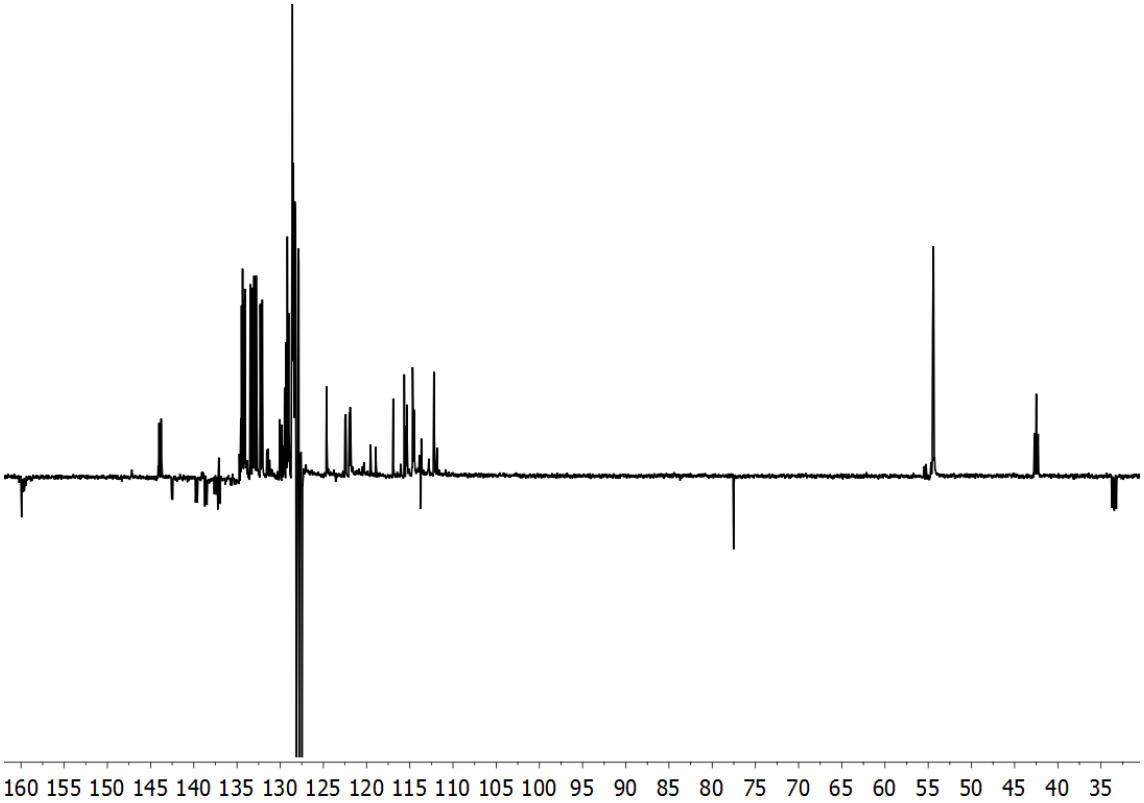
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

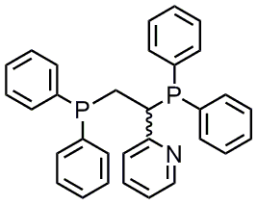


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



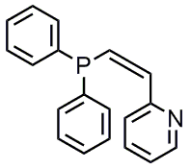
Reaction of 2-ethynylpyridine and diphenylphosphine.

2-(1,2-bis(diphenylphosphanyl)ethyl)pyridine (7e)



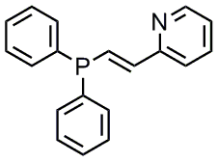
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.48 – 8.44 (m, 1H, $H_{2\text{-py}}$), 7.58 – 6.77 (23H, CH_{Ph}), 3.93 – 3.83 (m, 1H, CH_2P), 3.47 – 3.35 (m, 1H, CHP), 2.75 – 2.66 (m, 1H, CH_2P). ^{13}C{^{1}H}-APT NMR (75 MHz, C_6D_6, 298 K): δ 160.8 (dd, $J_{C\text{-}P}$ = 6, 2, $C_{q\text{-py}}$), 149.5 (s, $C_{2\text{-py}}$), 139.7 – 127.8 (C_{Ph}+C_{Py}), 124.6 (d, $J_{C\text{-}P}$ = 5, C_{py}), 121.0 (d, $J_{C\text{-}P}$ = 2, C_{py}), 44.7 (t, $J_{C\text{-}P}$ = 16, CHP), 32.1 (dd, $J_{C\text{-}P}$ = 22, 17, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ 3.4 (d, $J_{P\text{-}P}$ = 21, CHP), -19.9 (d, $J_{P\text{-}P}$ = 21, CH_2P).

(Z)-2-(2-(diphenylphosphanyl)vinyl)pyridine (5e)



The NMR spectrum was consistent with that of the published data.[12] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.43 – 8.42 (m, 1H, $H_{2\text{-py}}$), 7.66 – 6.55 (13H, CH_{Ph}), 7.67 (overlapped, 1H, =CH), 7.22 (overlapped, 1H, =CH). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -15.0 (s).

(E)-2-(2-(diphenylphosphanyl)vinyl)pyridine (6e)

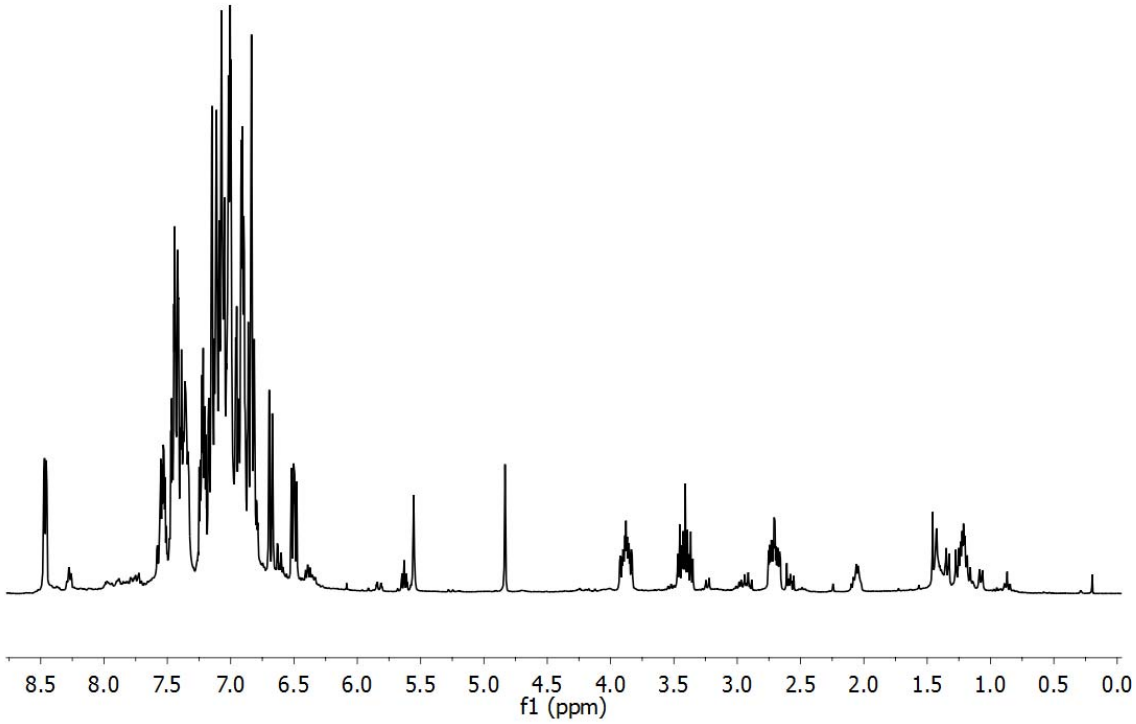


The NMR spectrum was consistent with that of the published data.[12] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.45 – 8.43 (m, 1H, $H_{2\text{-py}}$), 7.69 – 6.63 (13H, CH_{Ph}), 8.10 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 13, =CH), 7.08 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 11, =CH). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -11.8 (s).

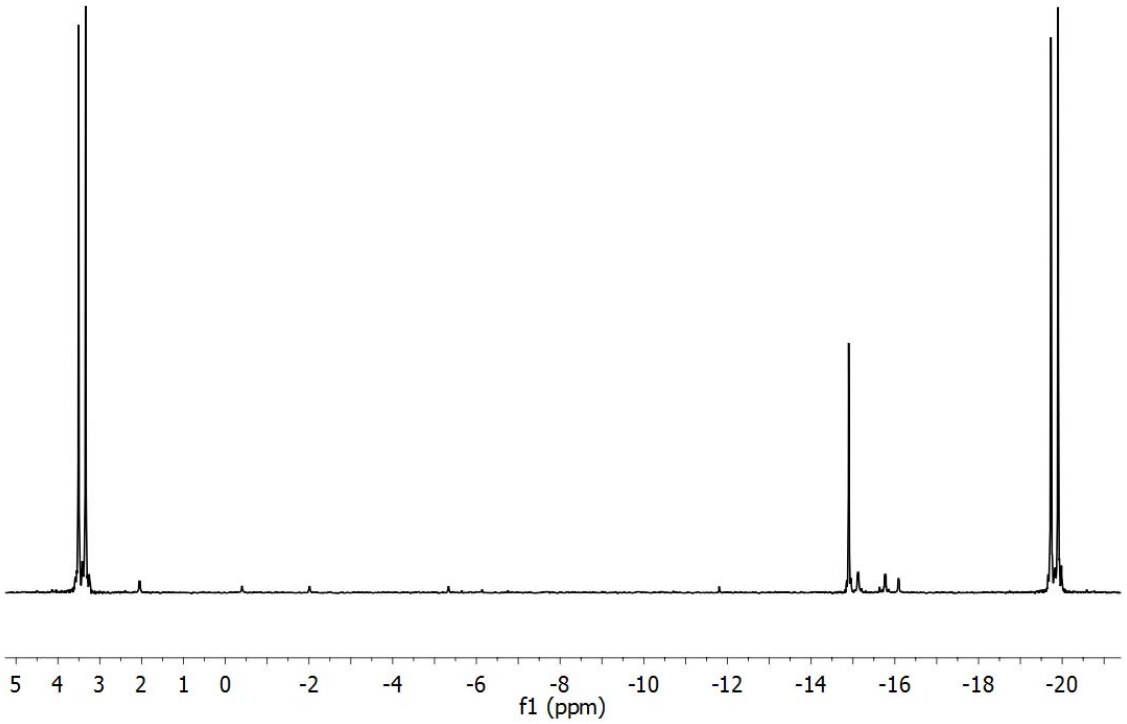
NMR spectra of the reaction crude.

Reaction conditions: 2-ethynylpyridine (0.2 mmol), Ph_2PH (0.4 mmol), **1a** (0.005 mmol), of C_6D_6 (0.5 mL), 72 h at 80 °C.

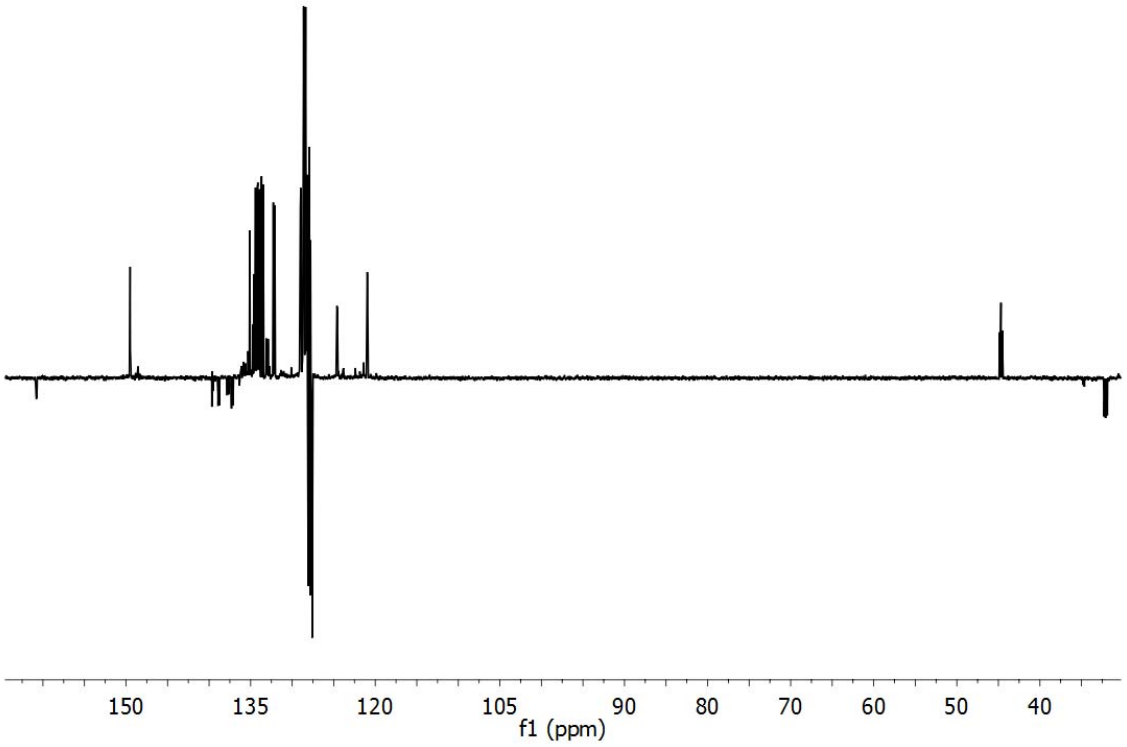
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

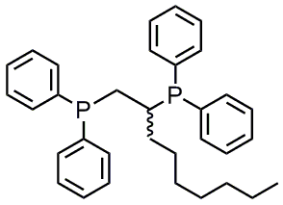


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



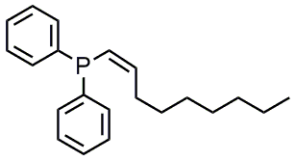
Reaction of 1-nonine and diphenylphosphine.

nonane-1,2-diylbis(diphenylphosphine) (7f)



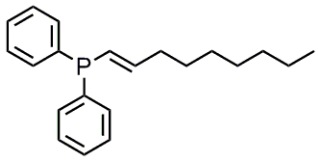
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.54 – 6.86 (20H, CH_{Ph}), 2.69 – 2.58 (m, 1H, CHP), 2.57 – 2.50 (m, 1H, CH_2P), 2.31 – 2.21 (m, 1H, CH_2P), 2.19 - 1.06 (12H, CH_2), 0.96 (t, J_{H-H} = 7, 3H, CH_3). $^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K): δ 139.4 – 128.4 (C_{Ph}), 33.0 (dd, J_{C-P}= 15, 12, CHP), δ 31.2 (dd, J_{C-P} = 14, 10, $CH_2(C_3)$), 30.9 (dd, J_{C-P} = 17, 15, CH_2P), δ 27.1 (dd, J_{C-P} = 10, 2, $CH_2(C_4)$), 32.2 – 23.1 ($CH_2(C_5$-$C_8)$), 14.0 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -3.7 (d, J_{P-P} = 22, CHP), -20.4 (d, J_{P-P} = 22, CH_2P).

(Z)-non-1-en-1-yldiphenylphosphine (5f)



^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.64 – 7.30 (10H, CH_{Ph}), 6.26 (overlapped, 1H, =CH), 6.18 (overlapped, 1H, =CH), 2.07 (overlapped, 2H, C$\underline{H}_2$CH), 1.62-0.90 (overlapped, 13H, $(CH_2)_5CH_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -29.8 (s).

(E)-non-1-en-1-yldiphenylphosphine (6f)

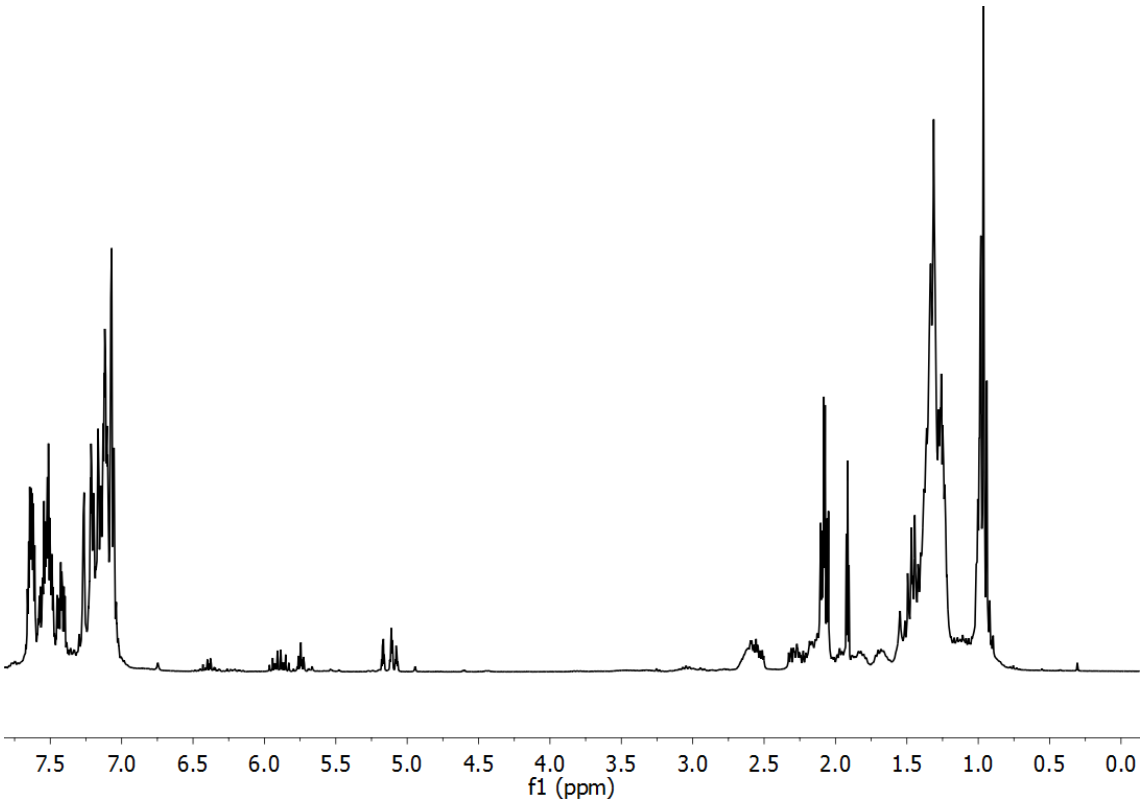


^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.65 – 7.22 (10H, CH_{Ph}), 6.37 (overlapped, 1H, =CH), 6.33 (overlapped, 1H, =CH), 2.51 (overlapped, 2H, C$\underline{H}_2$CH), 1.71-0.89 (overlapped, 13H, (C$\underline{H}_2)_5$C$\underline{H}_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ -13.4 (s).

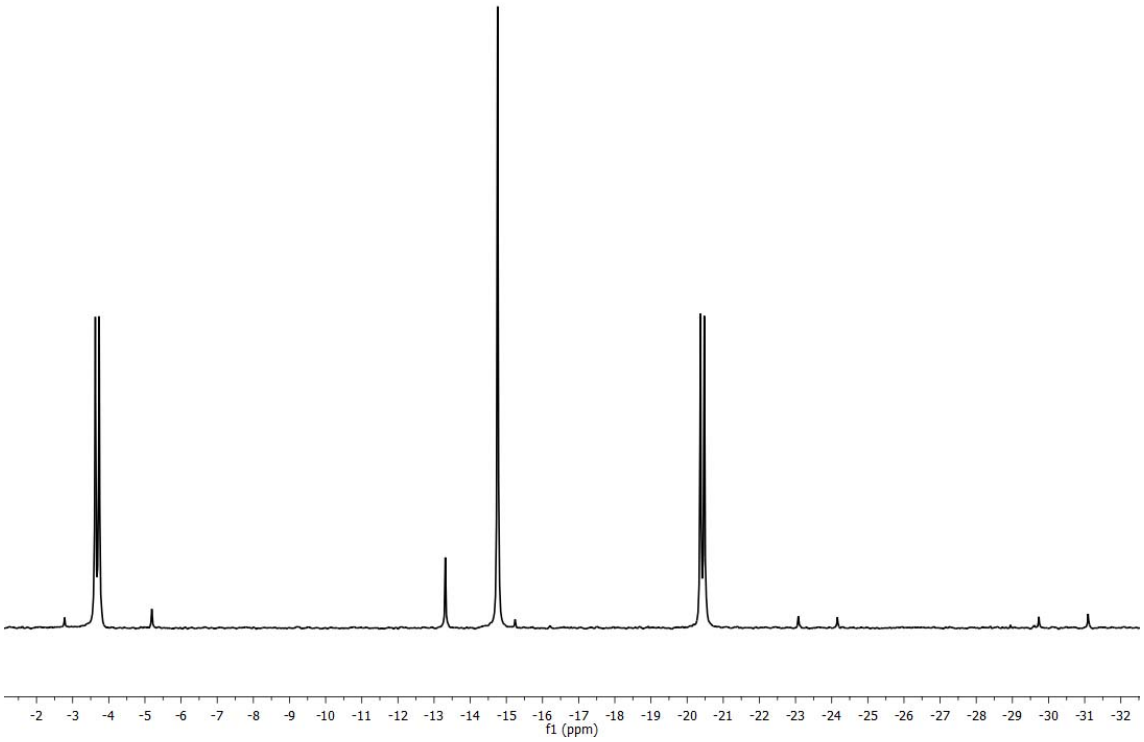
NMR spectra of the reaction crude.

Reaction conditions: 1-nonyne (0.2 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 48 h at 80 °C.

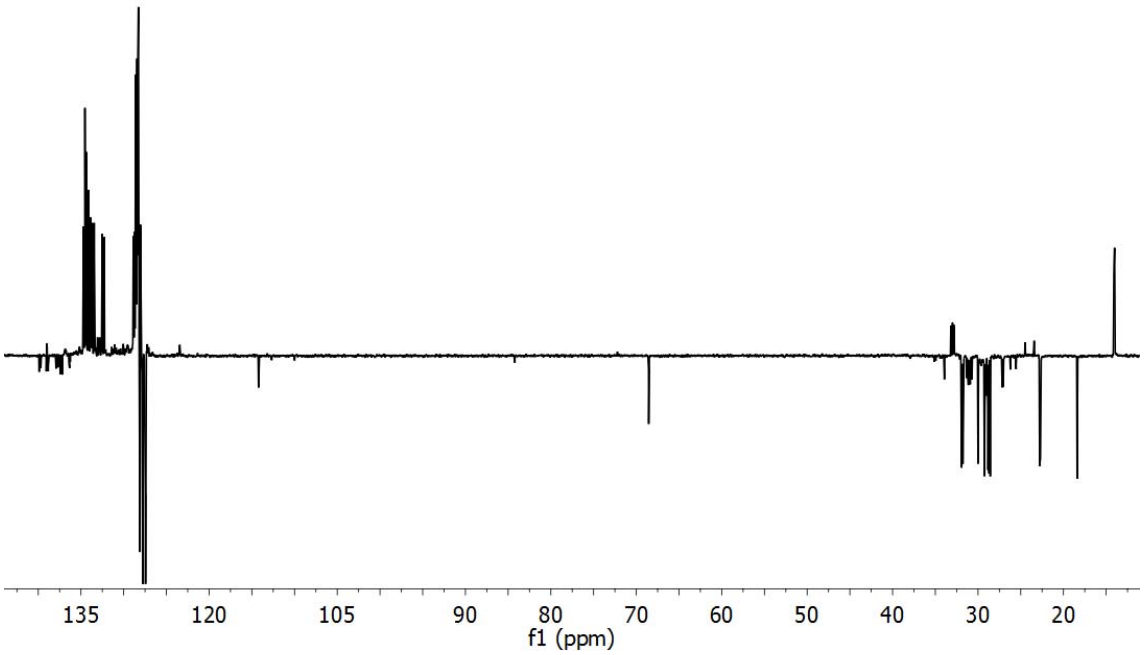
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

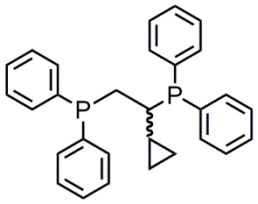


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



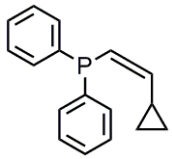
Reaction of cyclopropylacetylene and diphenylphosphine.

(1-cyclopropylethane-1,2-diyl)bis(diphenylphosphine) (7g)



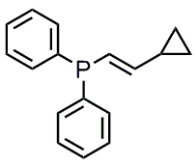
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.66 – 6.87 (20H, CH_{Ph}), 2.74 – 2.64 (m, 1H, CH_2P), 2.48 – 2.37 (m, 1H, CH_2P), 2.08 – 1.96 (m, 1H, CHP), 0.96 – 0.84 (m, 1H, CH), 0.72 – 0.62 (m, 1H, CH_2), 0.62 – 0.52 (m, 1H, CH_2), 0.42 – 0.29 (m, 1H, CH_2), 0.10 – 0.01 (m, 1H, CH_2). ^{13}C{^{1}H}-APT NMR (75 MHz, C_6D_6, 298 K): δ 139.3 – 128.2 (C_{Ph}), 38.9 (dd, J_{C-P} = 16, 12, CHP), 33.2 (dd, J_{C-P} = 19, 15, CH_2P), 15.2 (dd, J_{C-P} = 19, 5, CH), 7.5 (dd, J_{C-P} = 13, 8, CH_2), 5.9 (dd, J_{C-P} = 5, 3, CH_2). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ 0.3 (d, J_{P-P} = 23, CHP), -18.6 (d, J_{P-P} = 23, CH_2P).

(Z)-(2-cyclopropylvinyl)diphenylphosphine (5g)



^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.71 – 7.19 (10H, CH_{Ph}), 6.20 (dd, 1H, J_{H-H} = 12, J_{H-P} = 3, CHP), 5.61 (overlapped, 1H, =CH), 2.38 (overlapped, 1H, C<u>H</u>C_2H_4), 0.65 (overlapped, 2H, CH_2), 0.35 (overlapped, 2H, CH_2). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -29.3 (s).

(E)-(2-cyclopropylvinyl)diphenylphosphine (6g)

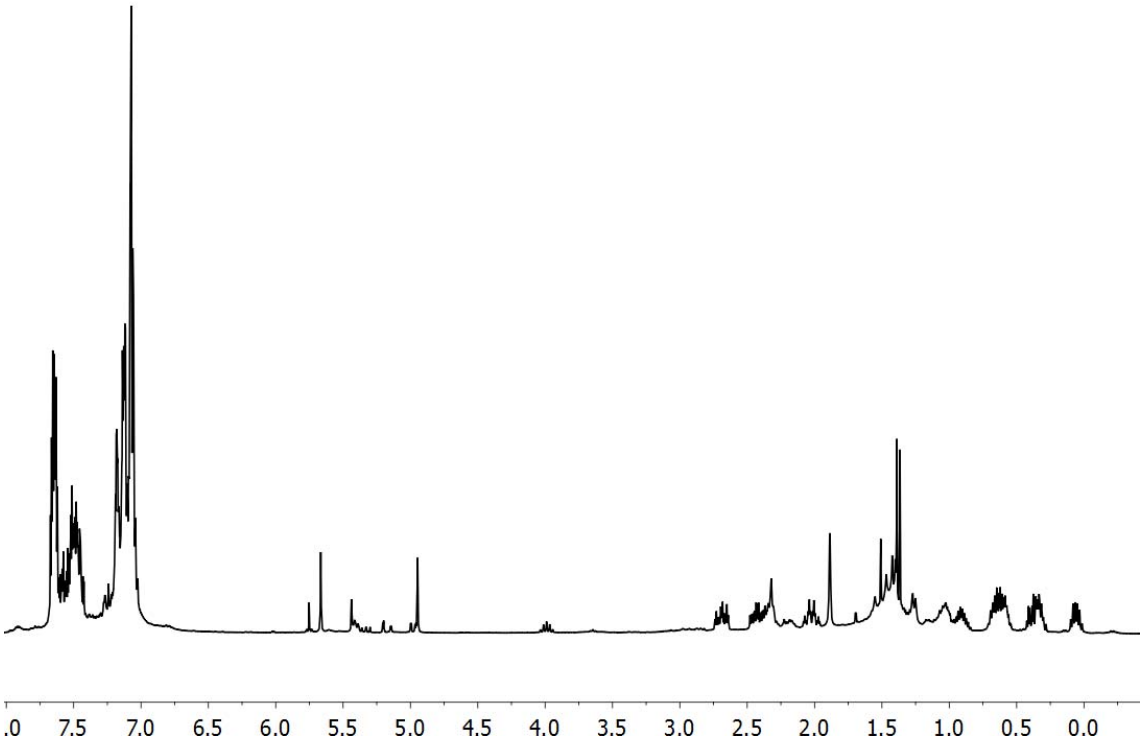


^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.66 – 7.08 (10H, CH_{Ph}), 6.40 (dd, 1H, J_{H-H} = 16, J_{H-P} = 2, =CHP), 5.88 (overlapped, 1H, =CH), 1.43 (overlapped, 1H, C<u>H</u>C_2H_4), 0.59 (overlapped, 2H, CH_2), 0.34 (overlapped, 2H, CH_2). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -13.1 (s).

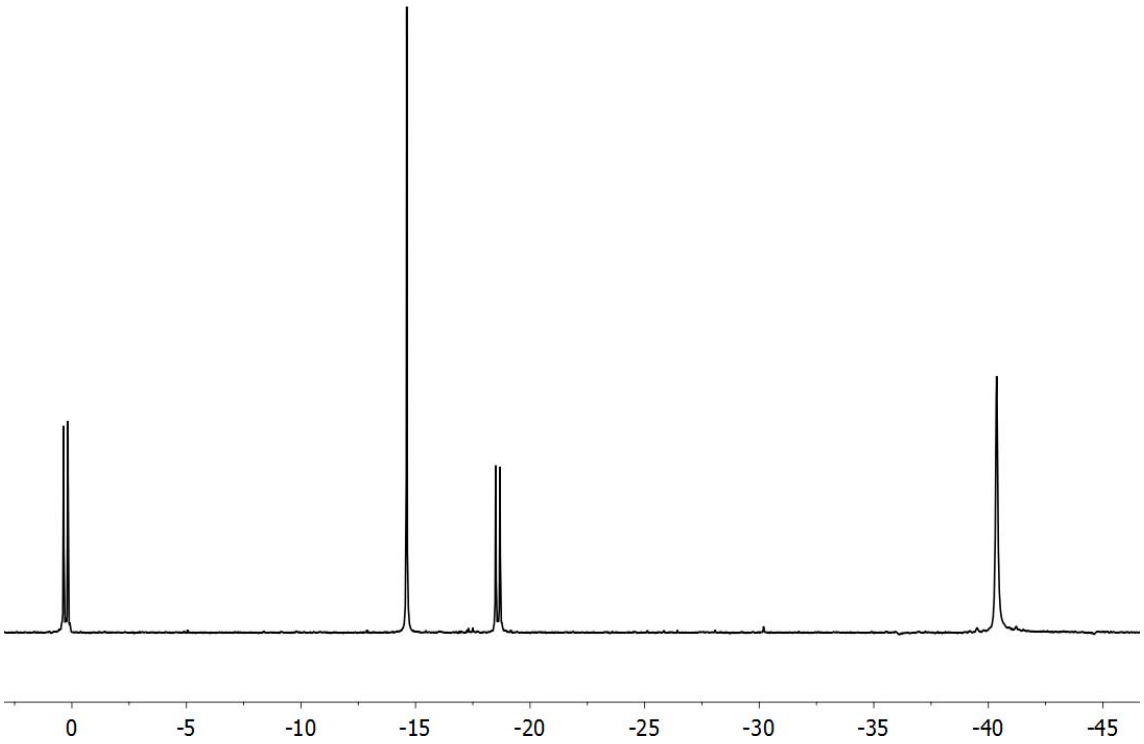
NMR spectra of the reaction crude.

Reaction conditions: cyclopropylacetylene (0.2 mmol), Ph_2PH (0.4 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 72 h at 80 °C.

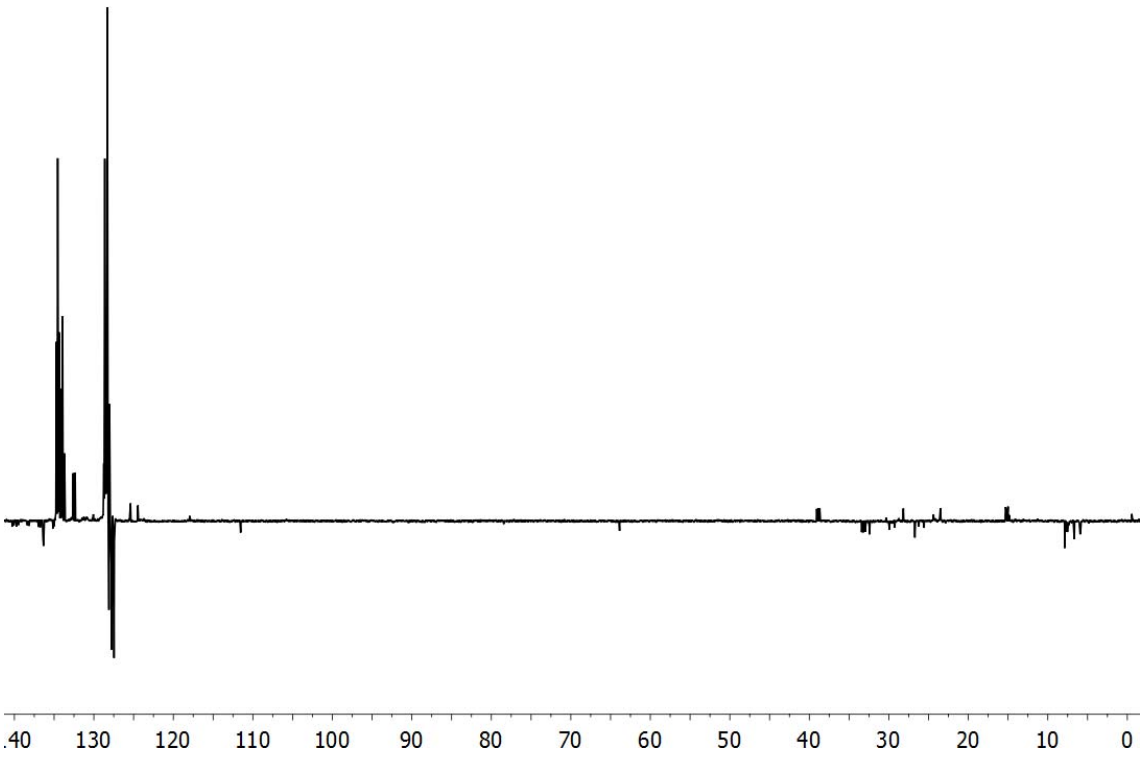
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

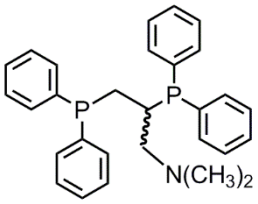


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



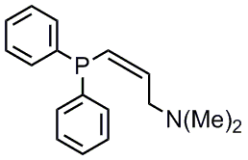
Reaction of 3-dimethylamino-1-propyne and diphenylphosphine.

2,3-bis(diphenylphosphanyl)-N,N-dimethylpropan-1-amine (7i)



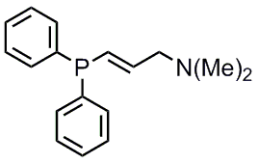
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.73 – 7.02 (20H, CH_{Ph}), 2.87 – 2.78 (m, 1H, CHP), 2.78 – 2.69 (m, 1H, CH_2N), 2.62 – 2.54 (m, 2H, CH_2P), 2.54 – 2.48 (m, 1H, CH_2N), 2.13 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -4.67 (d, $J_{P\text{-}P}$ = 35, CHP), -18.83 (d, $J_{P\text{-}P}$ = 35, CH_2P). ^{13}C{^{1}H}-APT NMR (75 MHz, C_6D_6, 298 K): δ 140.3 – 132.5 (C_{Ph}), 61.5 (dd, $J_{C\text{-}P}$ = 15, 7, CH_2N), 45.5 (s, CH_3N), 32.7 (dd, $J_{C\text{-}P}$ = 16, 12, CHP), 30.2 (dd, $J_{C\text{-}P}$ = 17, 12, CH_2P). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -4.7 (d, $J_{P\text{-}P}$ = 35, CHP), -18.8 (d, $J_{P\text{-}P}$ = 35, CH_2P).

(Z)-3-(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (5i)



The NMR spectrum was consistent with that of the published data.[10] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.40 – 7.00 (10H, CH_{Ph}), 6.52 – 6.30 (overlapped, m, 2H, P<u>H</u>C=C<u>H</u>C), 2.90 – 2.78 (m, 2H, CH_2N), 2.12 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -30.0 (s).

(E)-3-(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (6i)

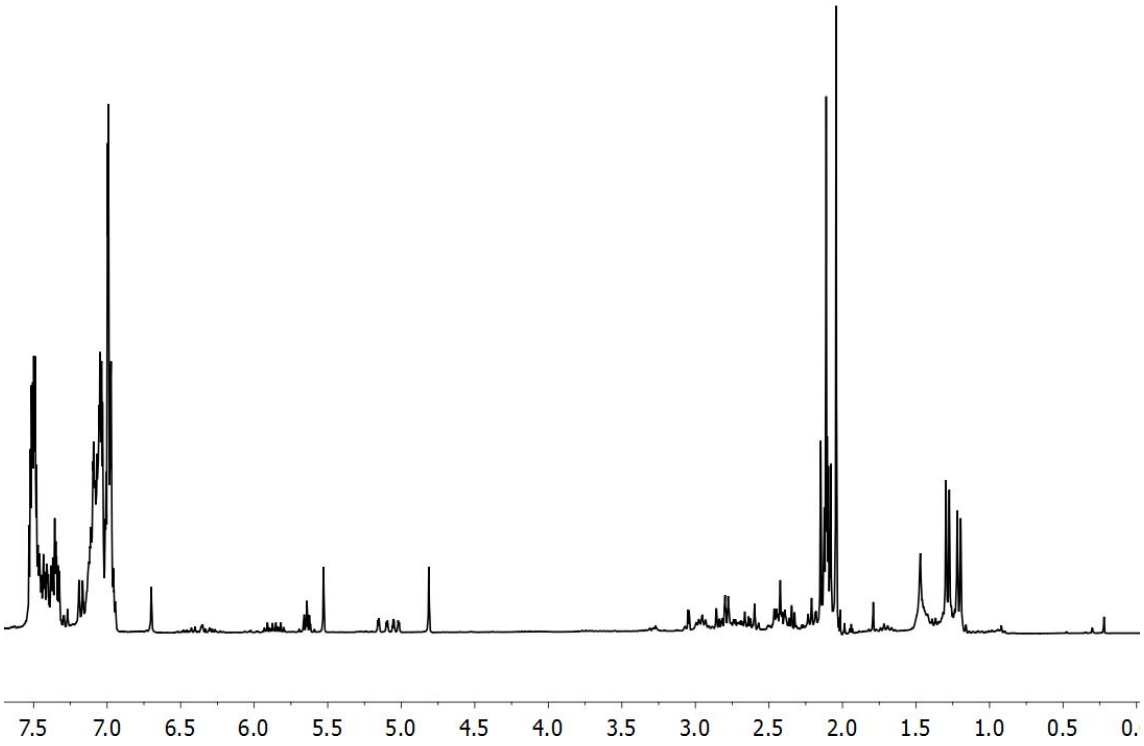


The NMR spectrum was consistent with that of the published data.[10] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.57 – 6.93 (10H, CH_{Ph}), 6.49 – 6.23 (overlapped, m, 2H, P<u>H</u>C=C<u>H</u>C), 2.79 – 2.64 (m, 2H, CH_2N), 2.14 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ -13.8 (s).

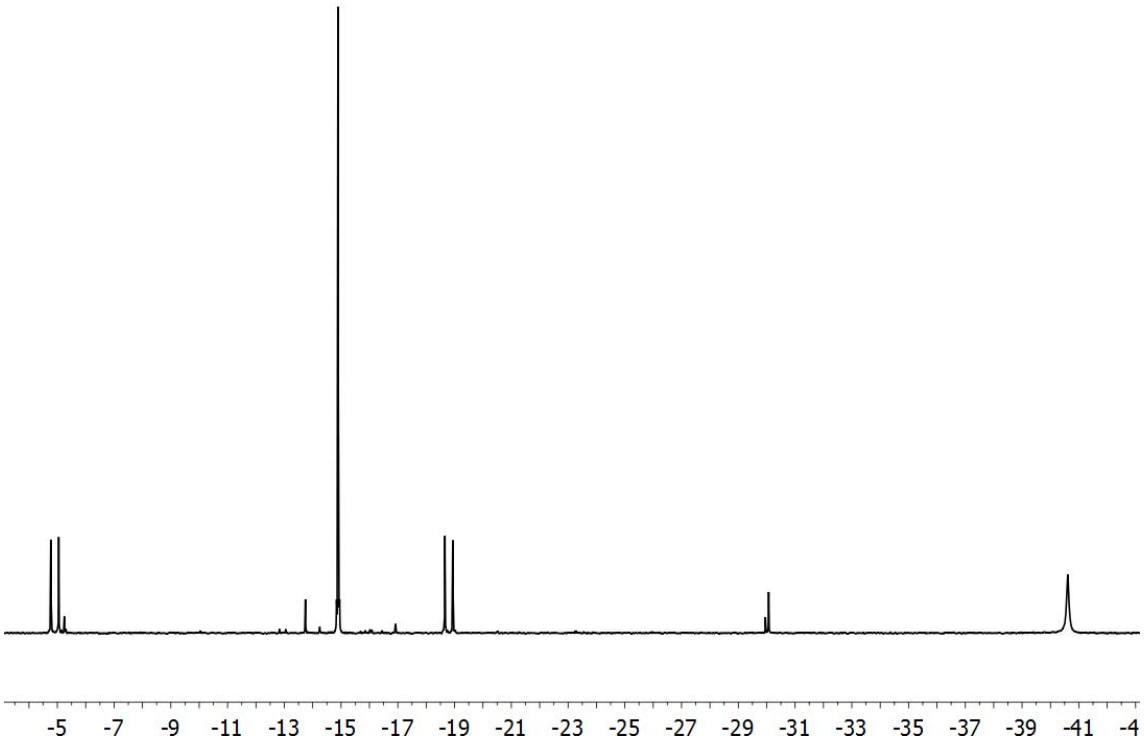
NMR spectra of the reaction crude.

Reaction conditions: 3-dimethylamino-1-propyne (0.1 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 24 h at 120 °C.

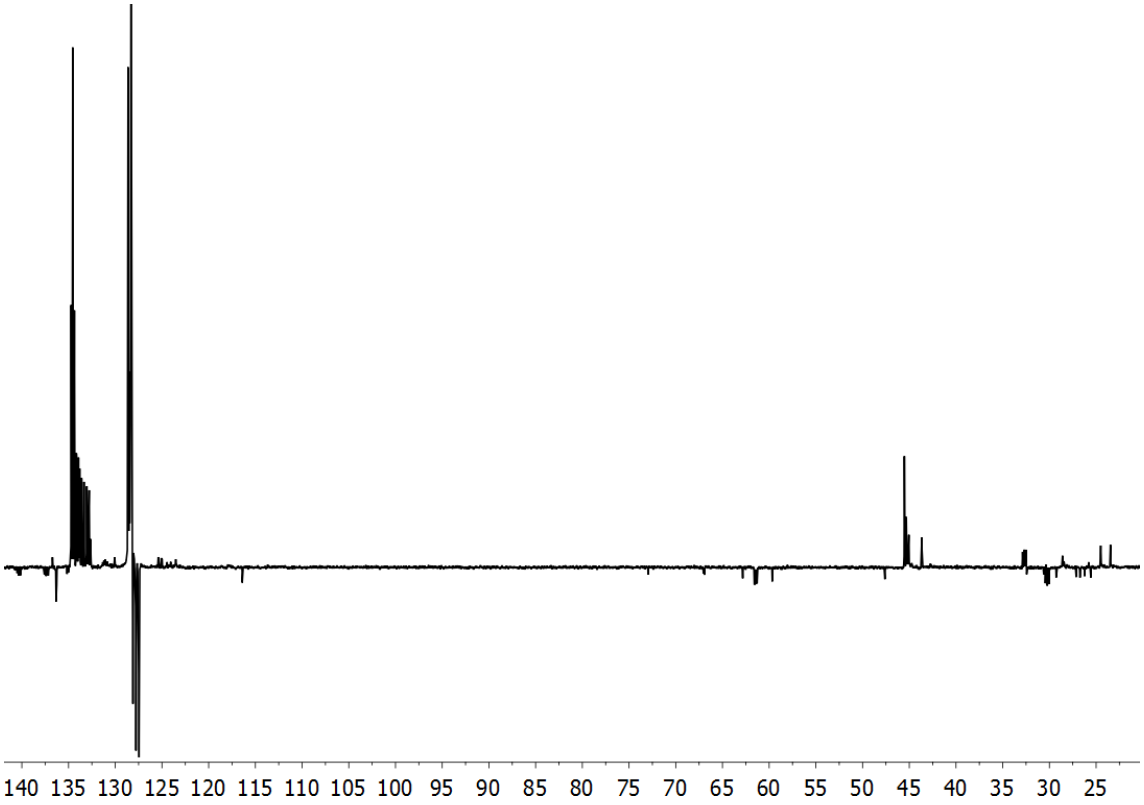
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K)

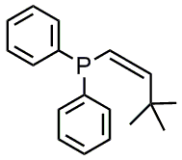


$^{13}C\{^{1}H\}$-APT NMR (75 MHz, C_6D_6, 298 K)



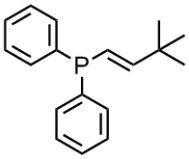
Reaction of 3,3-Dimethyl-1-butyne and diphenylphosphine.

(Z)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine (5h)



The NMR spectrum was consistent with that of the published data.[13] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.68 – 6.92 (10H, CH_{Ph}), 6.45 (dd, 1H, $J_{H\text{-}H}$ = 28, $J_{H\text{-}P}$ = 13, CHC), 6.21 (dd, 1H, $J_{H\text{-}H}$ = 13, $J_{H\text{-}P}$ = 4, CHP), 1.37 (s, 9H, $C(CH_3)_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ -29.0 (s).

(E)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine (6h)

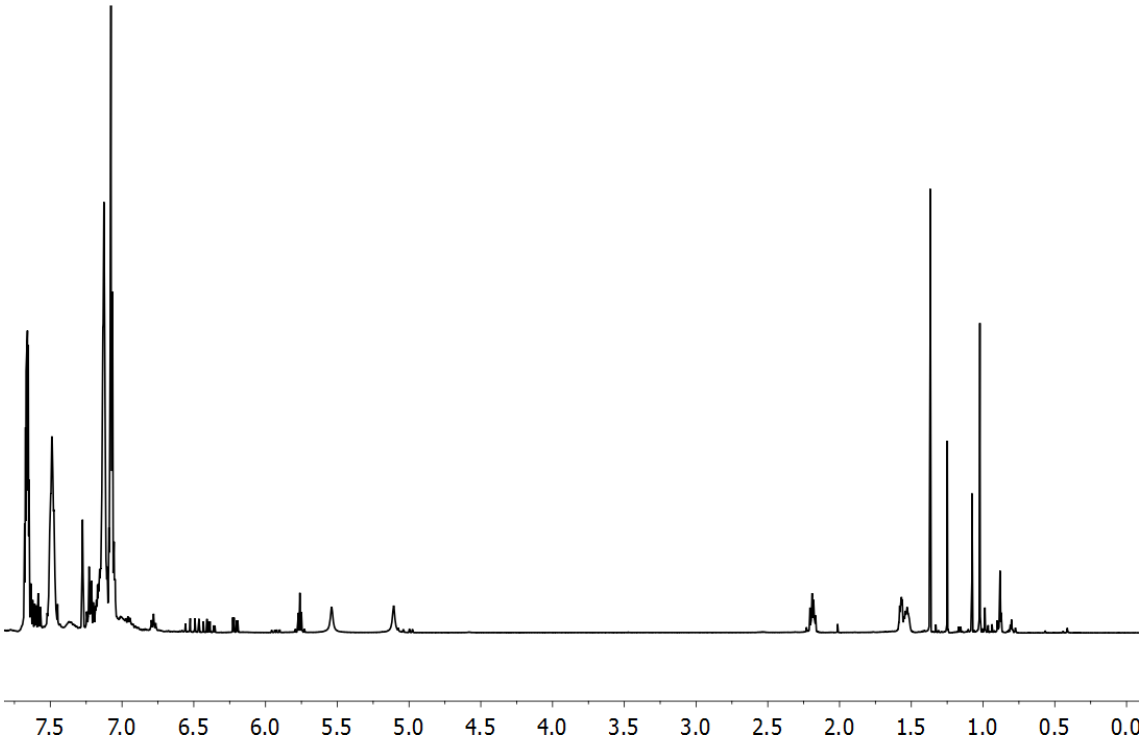


The NMR spectrum was consistent with that of the published data.[13] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.71 – 6.89 (10H, CH_{Ph}), 6.52 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 16, CHC), 6.37 (dd, 1H, $J_{H\text{-}H}$ = 17, $J_{H\text{-}P}$ = 4, CHP), 1.02 (s, 9H, $C(CH_3)_3$). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ -13.3 (s).

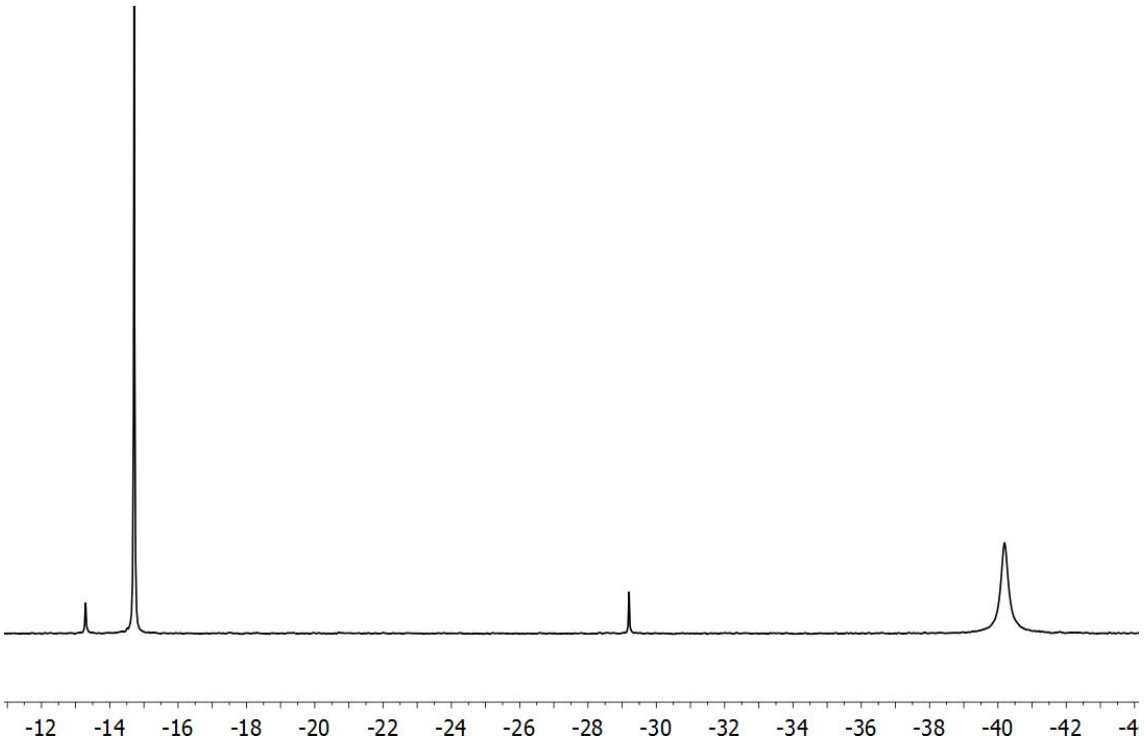
NMR spectra of the reaction crude.

Reaction conditions: 3,3-Dimethyl-1-butyne (0.2 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), C_6D_6 (0.5 mL), 24 h at 80 °C.

^1H NMR (300 MHz, C_6D_6, 298 K)

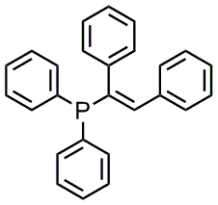


$^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K)



Reaction of diphenylacetylene and diphenylphosphine.

(E)-(1,2-diphenylvinyl)diphenylphosphine (6j)

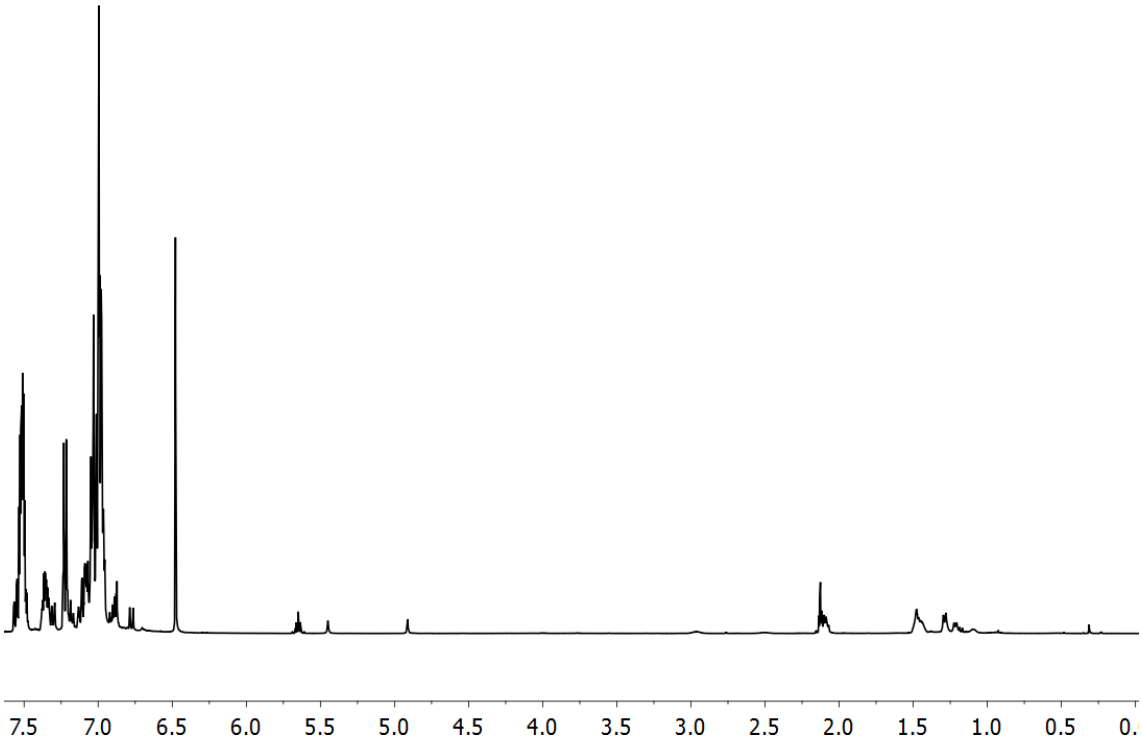


The NMR spectrum was consistent with that of the published data.[12] ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.57 – 6.87 (20H, CH_{Ph}) 6.78 (d, 1H, $J_{H\text{-}P}$ = 9, =CH),. $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6, 298 K): δ 9.1 (s).

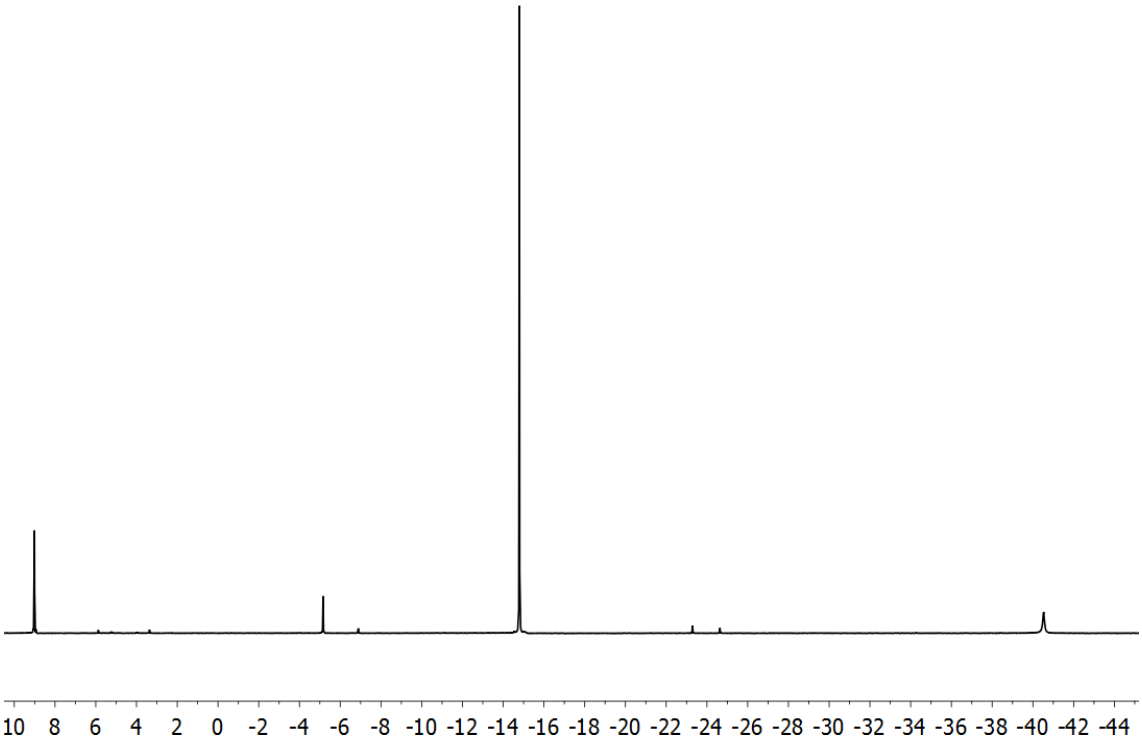
NMR spectra of the reaction crude.

Reaction conditions: diphenylacetylene (0.1 mmol), Ph_2PH (0.2 mmol), **1a** (0.005 mmol), of tol-d_8 (0.5 mL), 24 h at 120 °C.

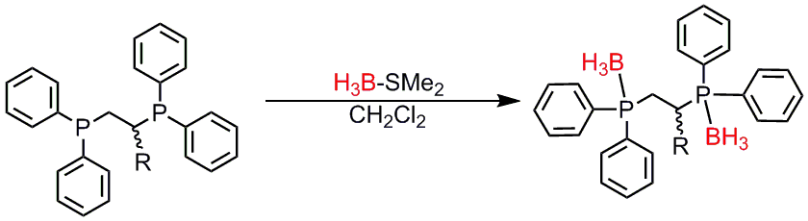
^1H NMR (300 MHz, C_6D_6, 298 K)



$^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 298 K)

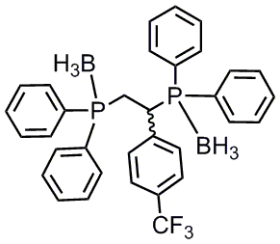


Preparation and isolation of diphosphine-borane adducts.



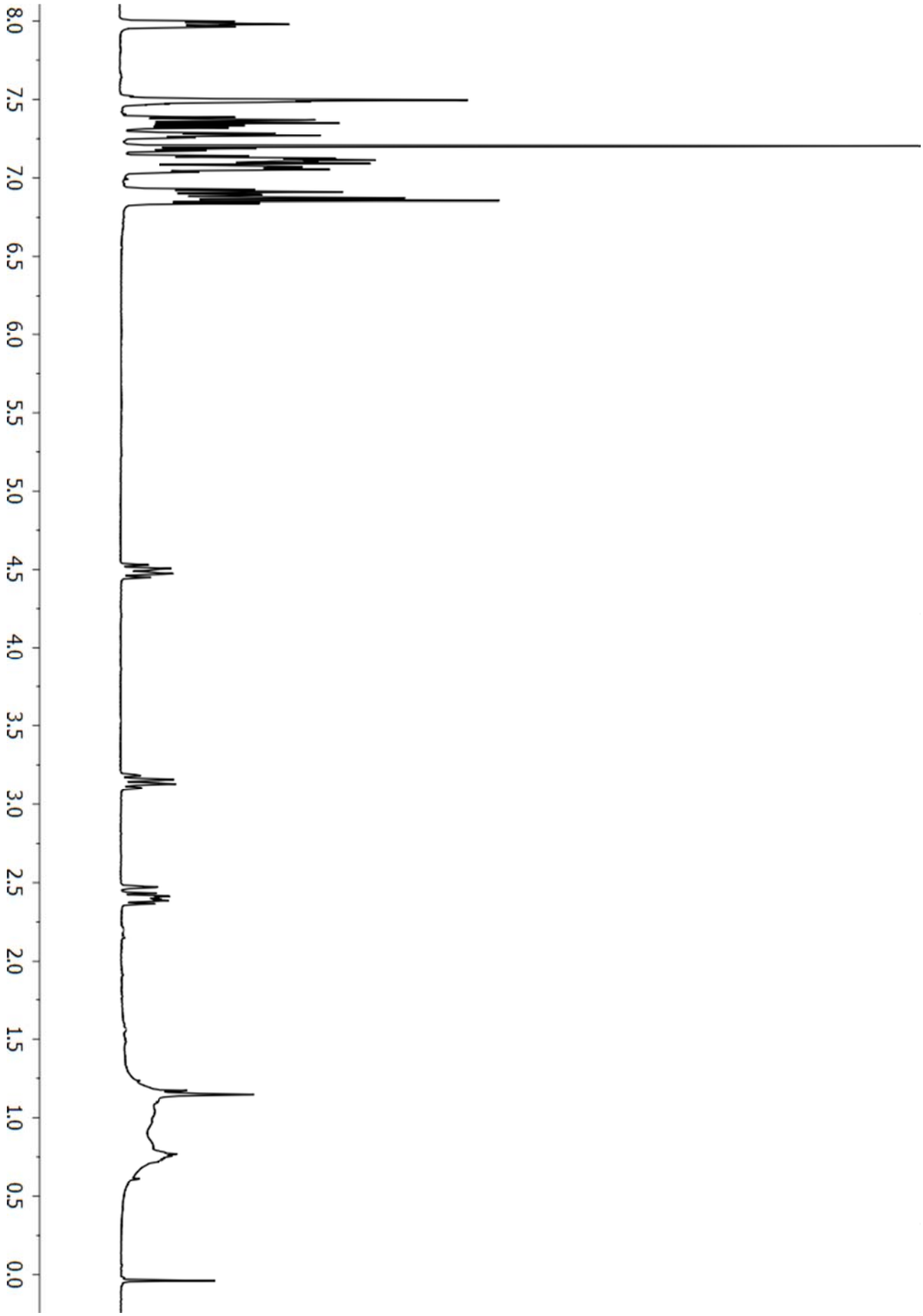
In a Young type NMR tube 0.005 mol of catalyst **1a** were dissolved in 0.5 mL of toluene and then 0.2 mmol (35 µL) of Ph_2PH and 0.1 mmol of the corresponding alkyne were added and the solution was heated at 120 °C for 24 h. At the end of the reaction, the volatiles were removed in vacuo. The residue was dissolved in 1 mL of dichloromethane and filtered through a short pad of silica (2 cm). The resulted solution was treated with 0.32 mmol (30 µL) of BH_3-SMe_2 in a schlenk tube and the mixture magnetically stirred for 1h at room temperature. After the elimination of volatiles in vacuo the samples were dissolved in 2 mL of CH_3CN and then purified by HPLC operating in reverse phase. Samples were injected and eluted at 30ºC with a mixture of acetonitrile:water (80:20) pumped at a flow rate of 15 mL/min. The elimination of volatiles in vacuo provides the diphosphine-borane adducts that were isolated as solids and characterized by NMR.

(1-(4-(trifluoromethyl)phenyl)ethane-1,2-diyl)bis(diphenylphosphine)-bis(borane) (7c-BH_3)

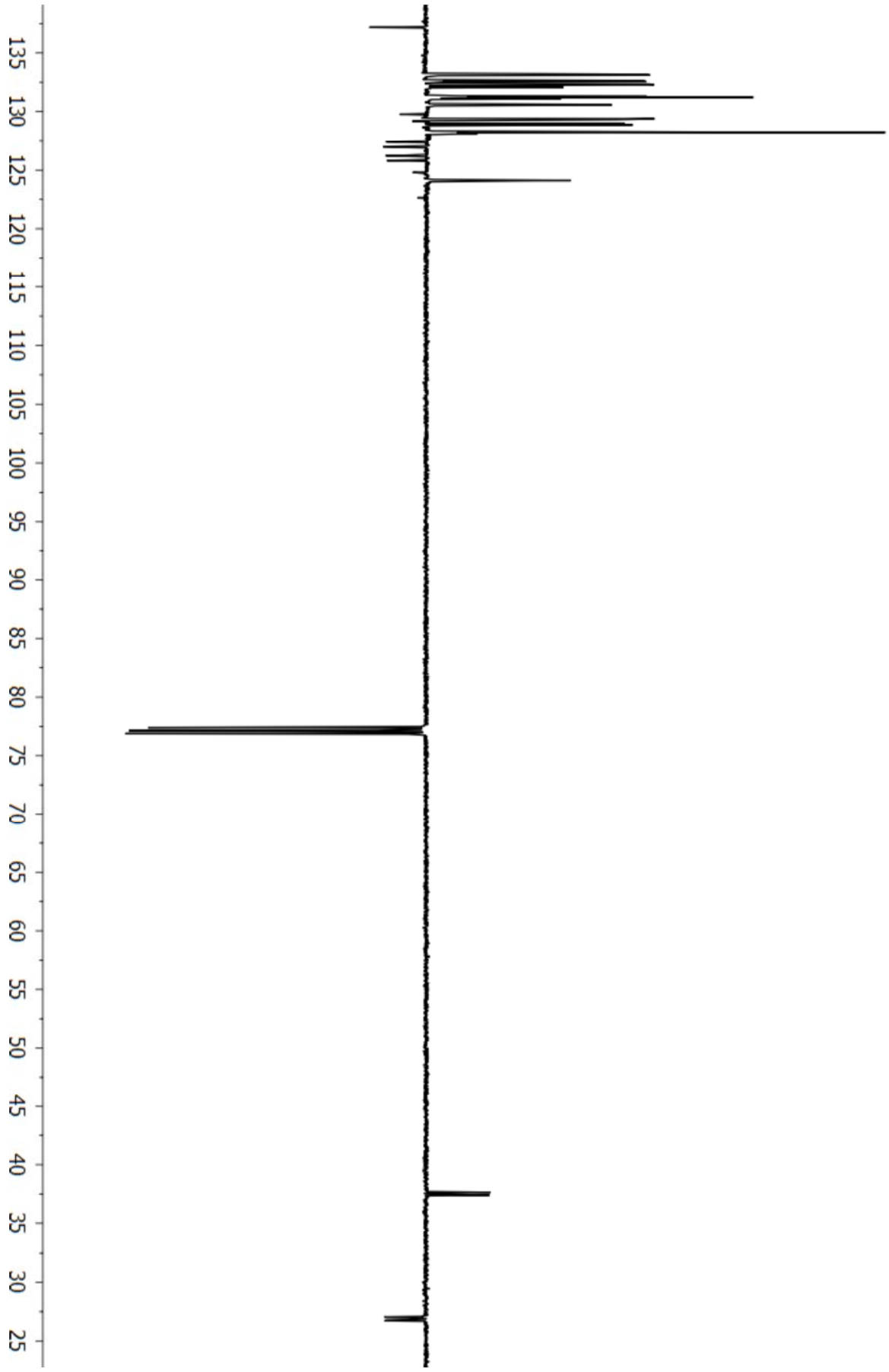


Yield: 20 mg (35%), off yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.05 – 6.86 (m, 24H, CH_{Ph}), 4.57 – 4.47 (m, 1H, CHP), 3.24 – 3.13 (m, 1H, CH_2P), 2.55 – 2.44 (m, 1H, CH_2P), 1.28 – 0.66 (br, 6H, BH_3). $^{13}C\{^{1}H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K): δ 137.2 – 123.3 (C_{Ph}), 125.9 (q, J_{C-F} = 272 Hz, CF_3), 37.5 (d, J_{C-P} = 30 Hz, CHP), 26.9 (dd, J_{C-P} = 34, 5 Hz, CH_2P). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 25.0 (br, CHP), 17.0 (br, CH_2P). $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 298 K): δ -42.1 (br, BH_3), -40.3 (br, BH_3). HRMS (ESI) m/z calcd for $C_{33}H_{33}B_2F_3P_2$ ($M + Na^+$) 593.2099 found 593.2070

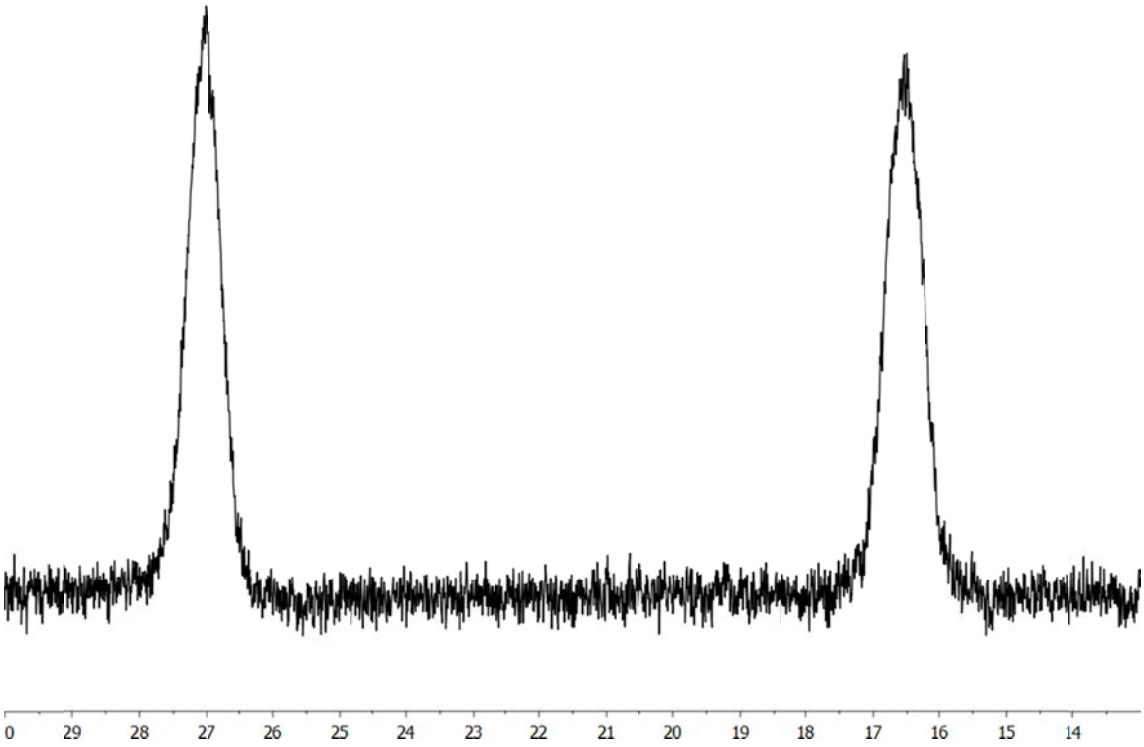
7c-BH_3: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



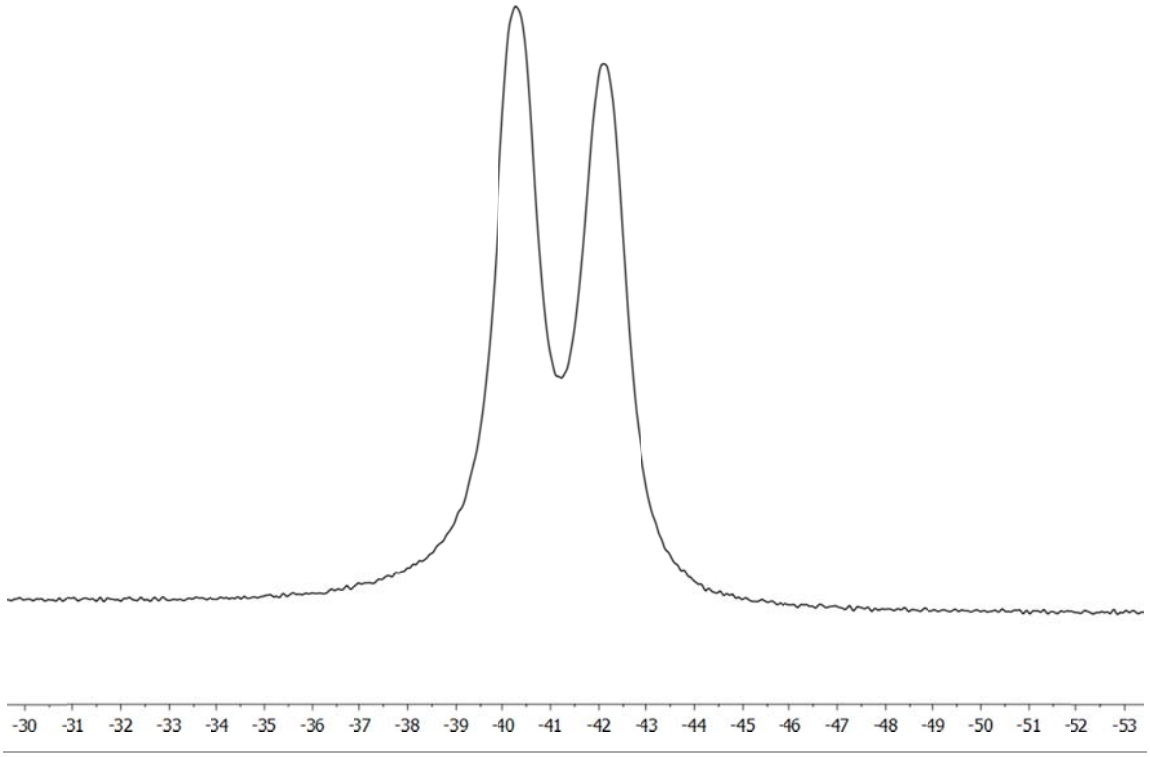
7c-BH_3: $^{13}C\{^1H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K)



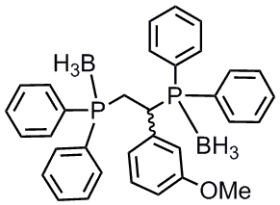
7c-BH_3: $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K)



7c-BH_3: $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 298 K)

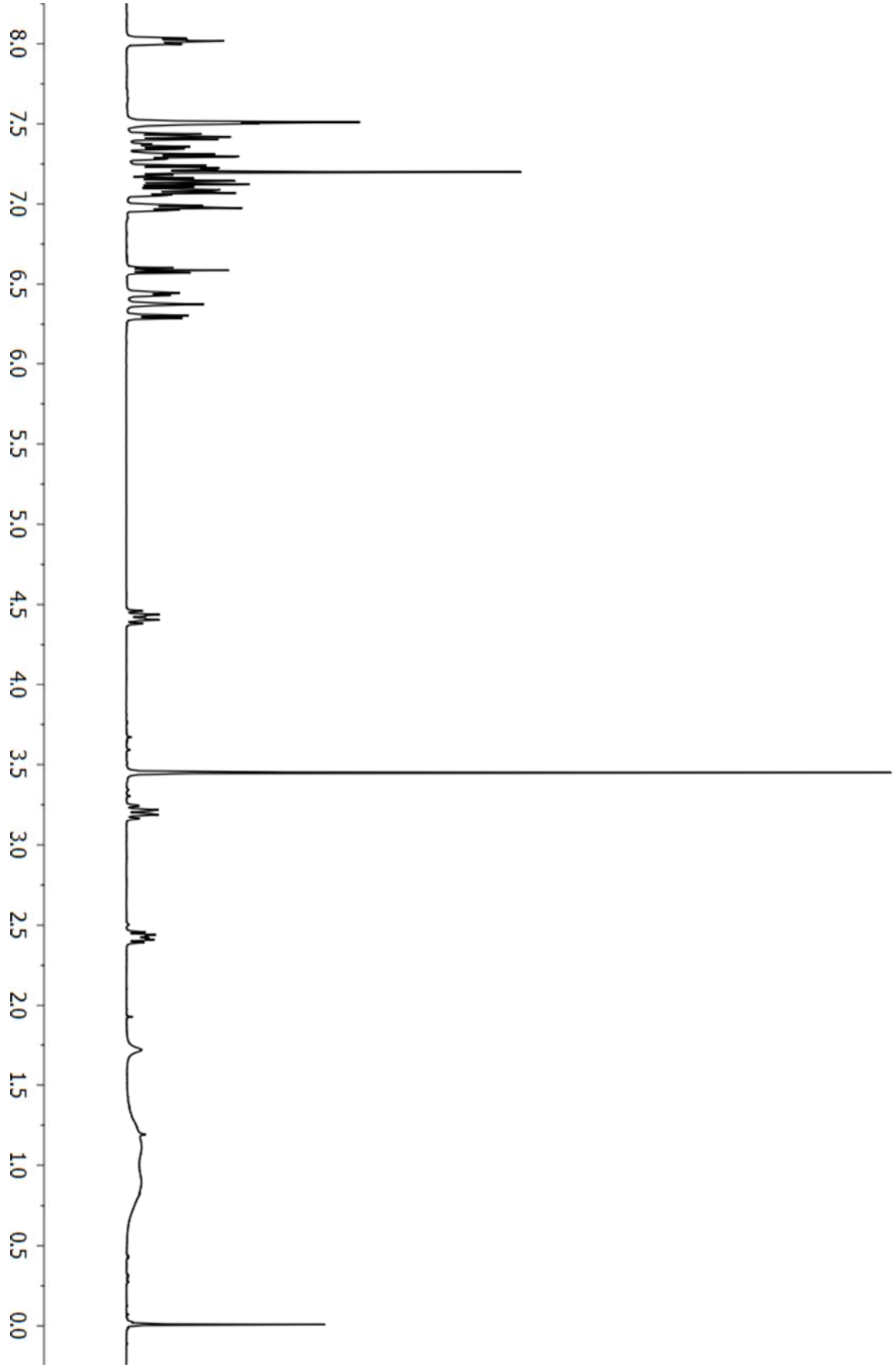


(1-(3-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine)-bis(borane) (7d-BH_3)

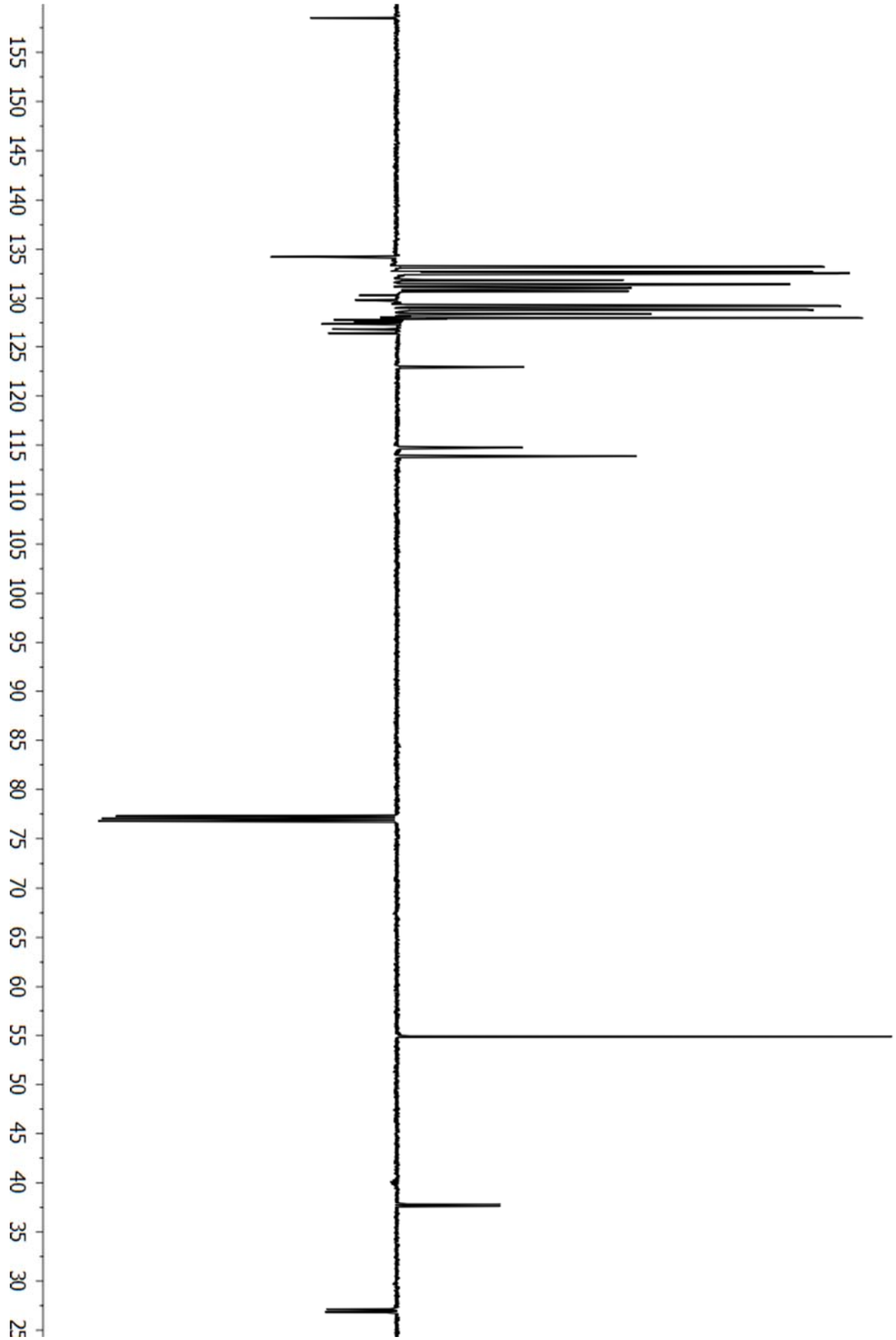


Yield: 22 mg (42%), off white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.05 – 6.26 (m, 24H, CH_{Ph}), 4.46 – 4.37 (m, 1H, CHP), 3.45 (s, 3H, OMe), 3.25 – 3.15 (m, 1H, CH_2P), 2.47 – 2.37 (m, 1H, CH_2P), 1.28 – 0.64 (br, 6H, BH_3). $^{13}C\{^{1}H\}$-APT NMR (126 MHz, $CDCl_3$): δ 135.8 – 111.9 (C_{Ph}), 54.9 (s, OCH_3), 37.8 (dd, $J_{C\text{-}P}$ = 30, 2 Hz, CHP), 27.0 (dd, $J_{C\text{-}P}$ = 34, 6 Hz, CH_2P). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 26.6 (br, CHP), 16.7 (br, CH_2P). $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 298 K): δ -41.6 (br, BH_3), -40.2 (br, BH_3). HRMS (ESI) m/z calcd for $C_{33}H_{36}B_2OP_2$ ($M + Na^+$) 555.2331 found 555.2312

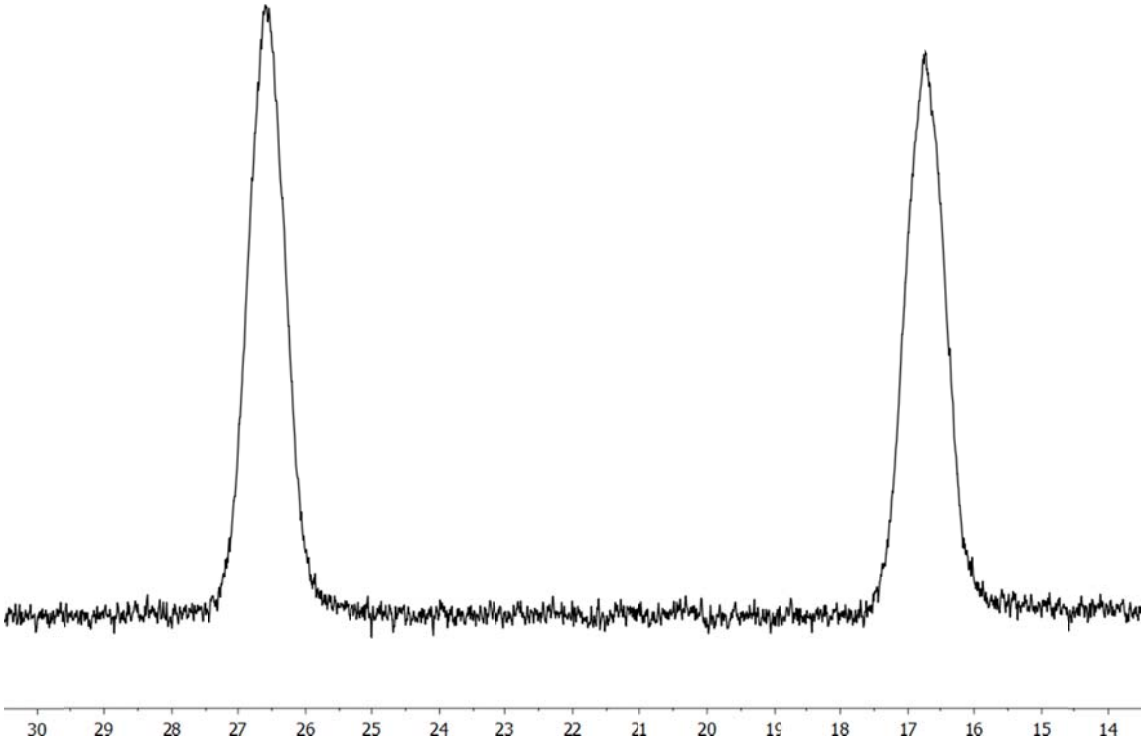
7d-BH_3: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



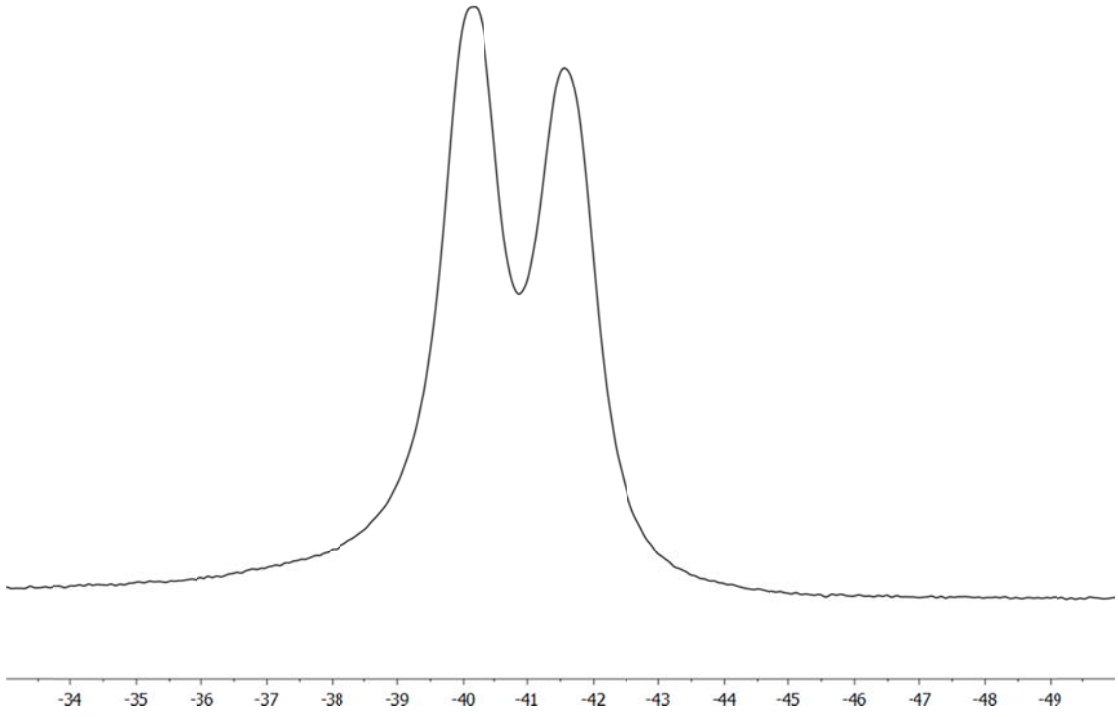
7d-BH_3: $^{13}C\{^1H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K)



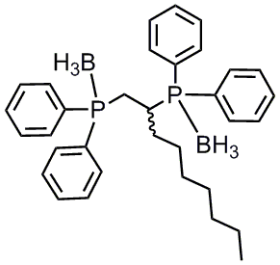
7d-BH_3: $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K)



7d-BH_3: $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 298 K)

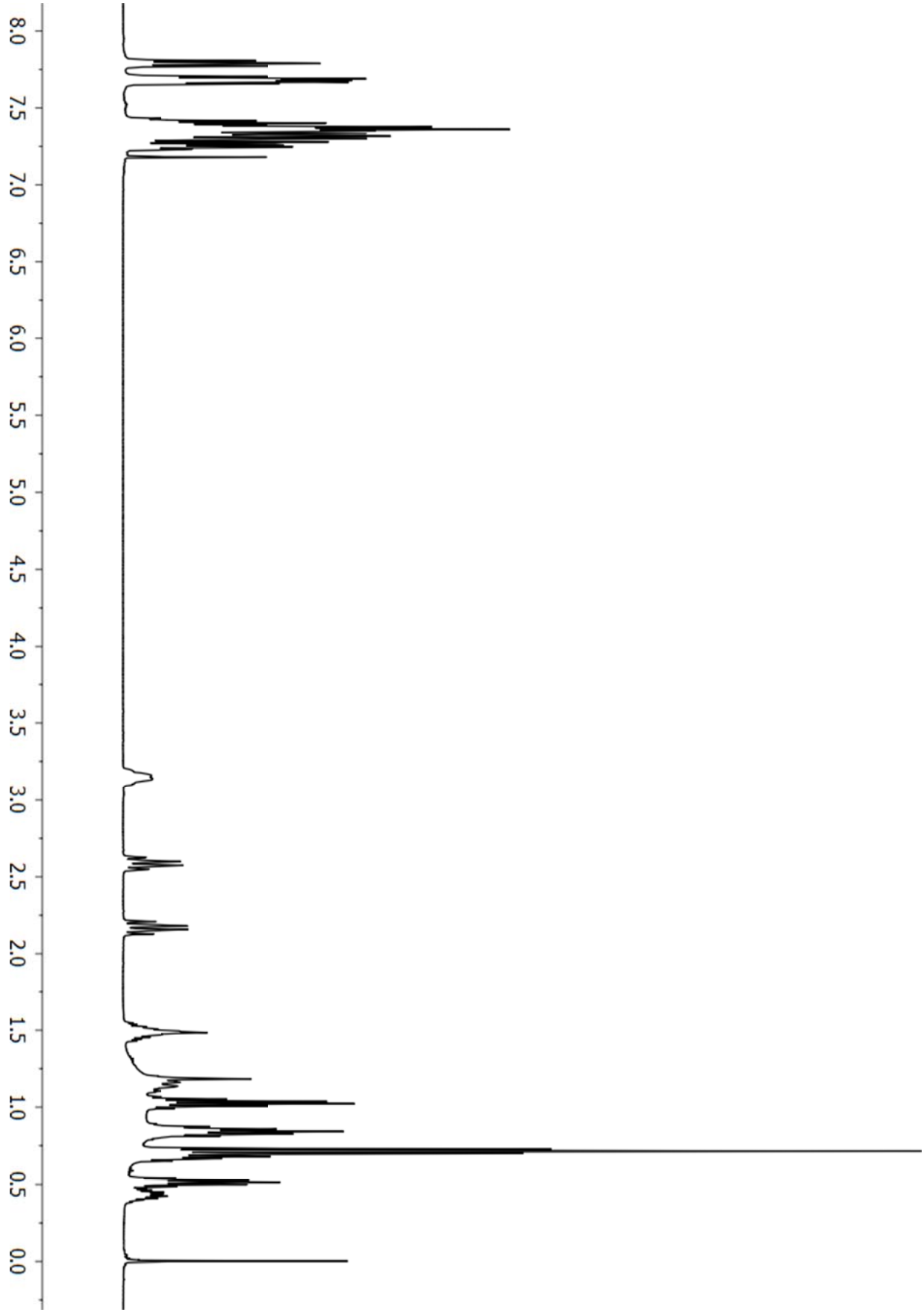


(nonane-1,2-diylbis(diphenylphosphine))-bis(borane) (7f-BH_3)

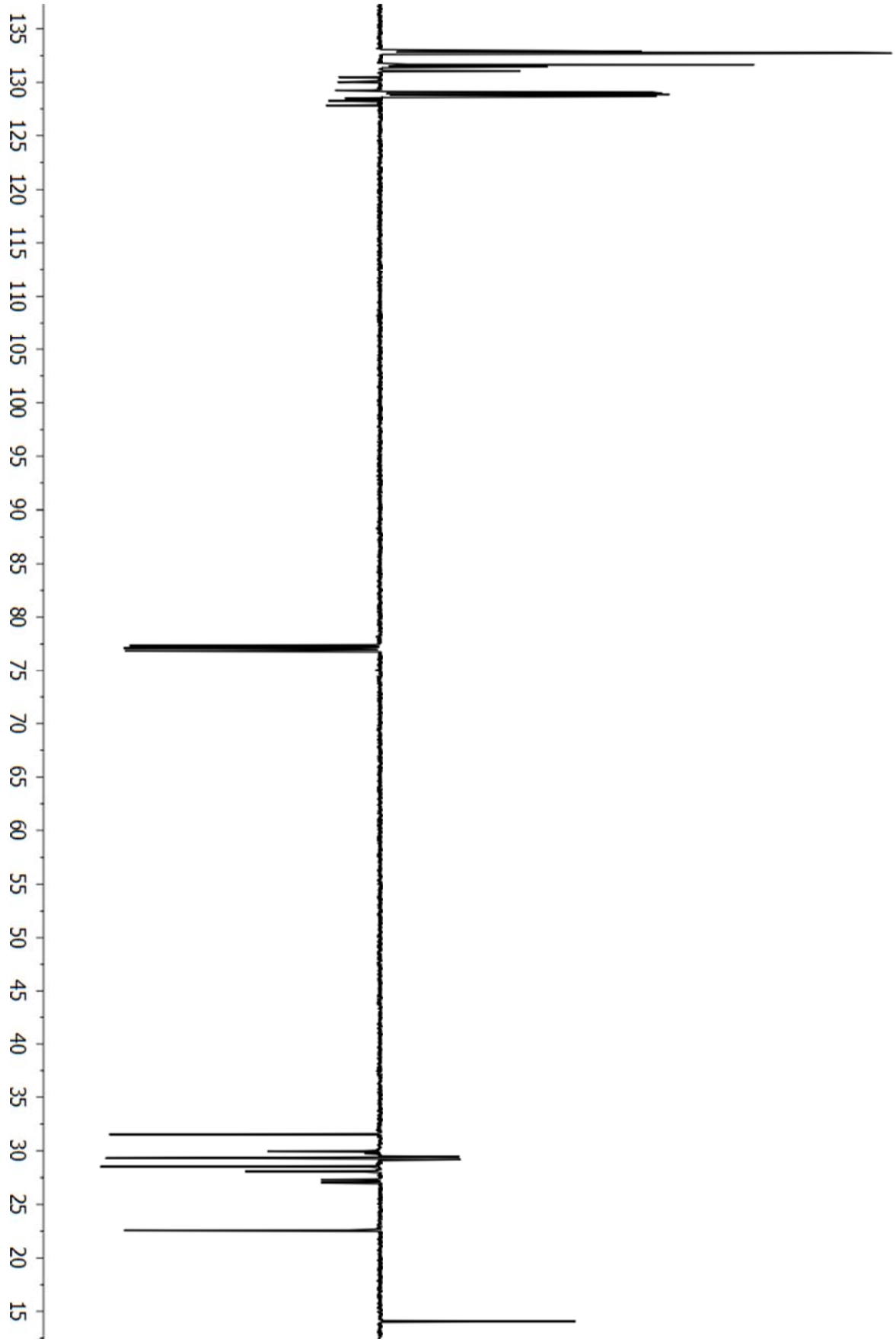


Yield: 22 mg (42%), brown waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.85 – 7.18 (m, 20H, CH_{Ph}), 3.21 – 3.08(m, 1H, CHP), 2.65 – 2.54 (m, 1H, CH_2P), 2.21 – 2.11 (m, 1H, CH_2P), 1.60 - 0.37 (m, 12H, CH_2), 1.22-0.91 (br, 6H, BH_3), 0.75 (t, J_{H-H} = 7 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K): δ 133.0 – 127.7 (C_{Ph}), 29.9 (d, J_{C-P} = 2 Hz, $CH_2(C_3)$), 29.3 (dd, J_{C-P}= 33, 2 Hz, CHP), 28.1 (d, J_{C-P} = 3 Hz, $CH_2(C_4)$), 27.2 (dd, J_{C-P} = 33, 5 Hz, CH_2P), 31.5 – 22.5 (all s, $CH_2(C_5$-$C_8)$), 14.1 (s, CH_3). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 25.0 (br, CHP), 17.0 (br, CH_2P). $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 298 K): δ -42.1 (br, BH_3), -39.6 (br, BH_3). HRMS (ESI) m/z calcd for $C_{33}H_{44}B_2P_2$ ($M + Na^+$) 523.3020 found 523.3005

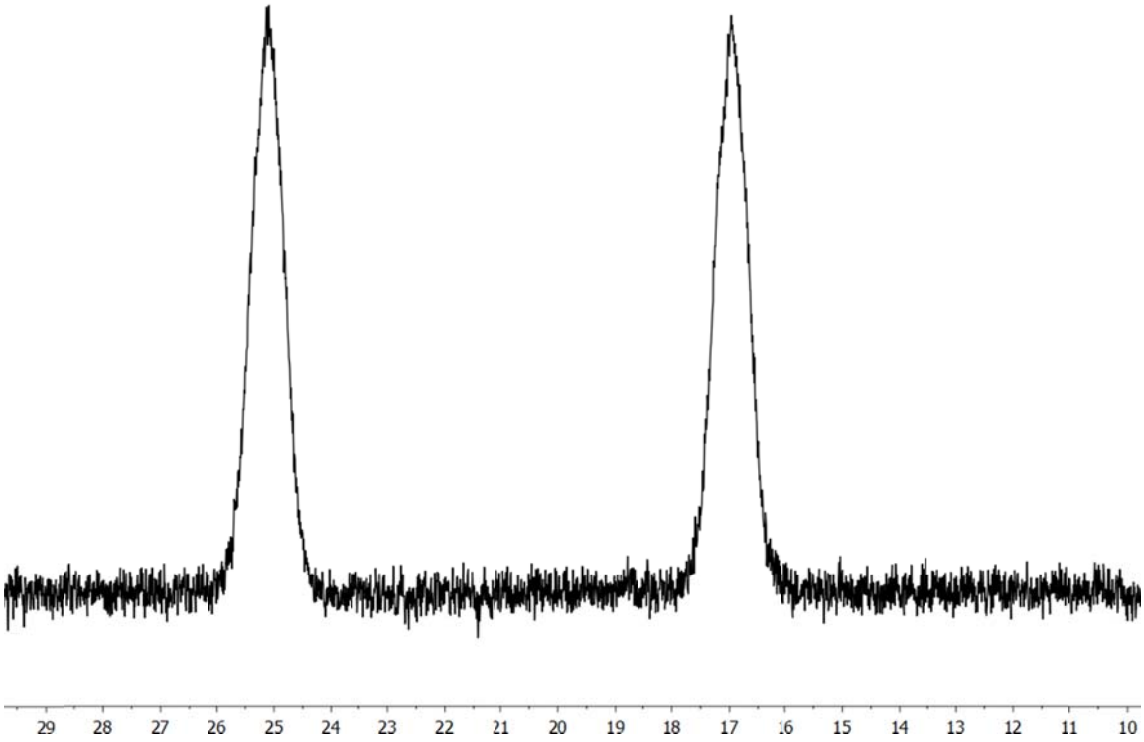
7f-BH_3: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



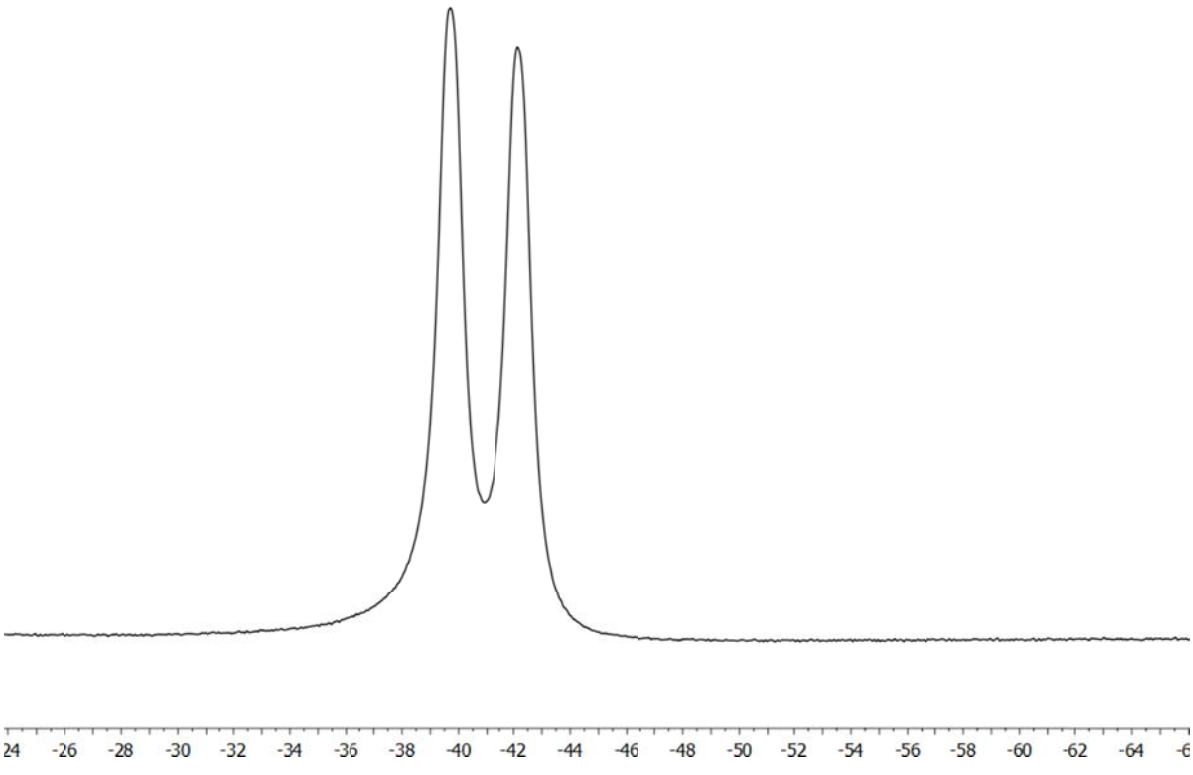
7f-BH_3: $^{13}C\{^1H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K)



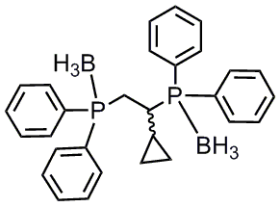
7f-BH_3: $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K)



7f-BH_3: $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 298 K)

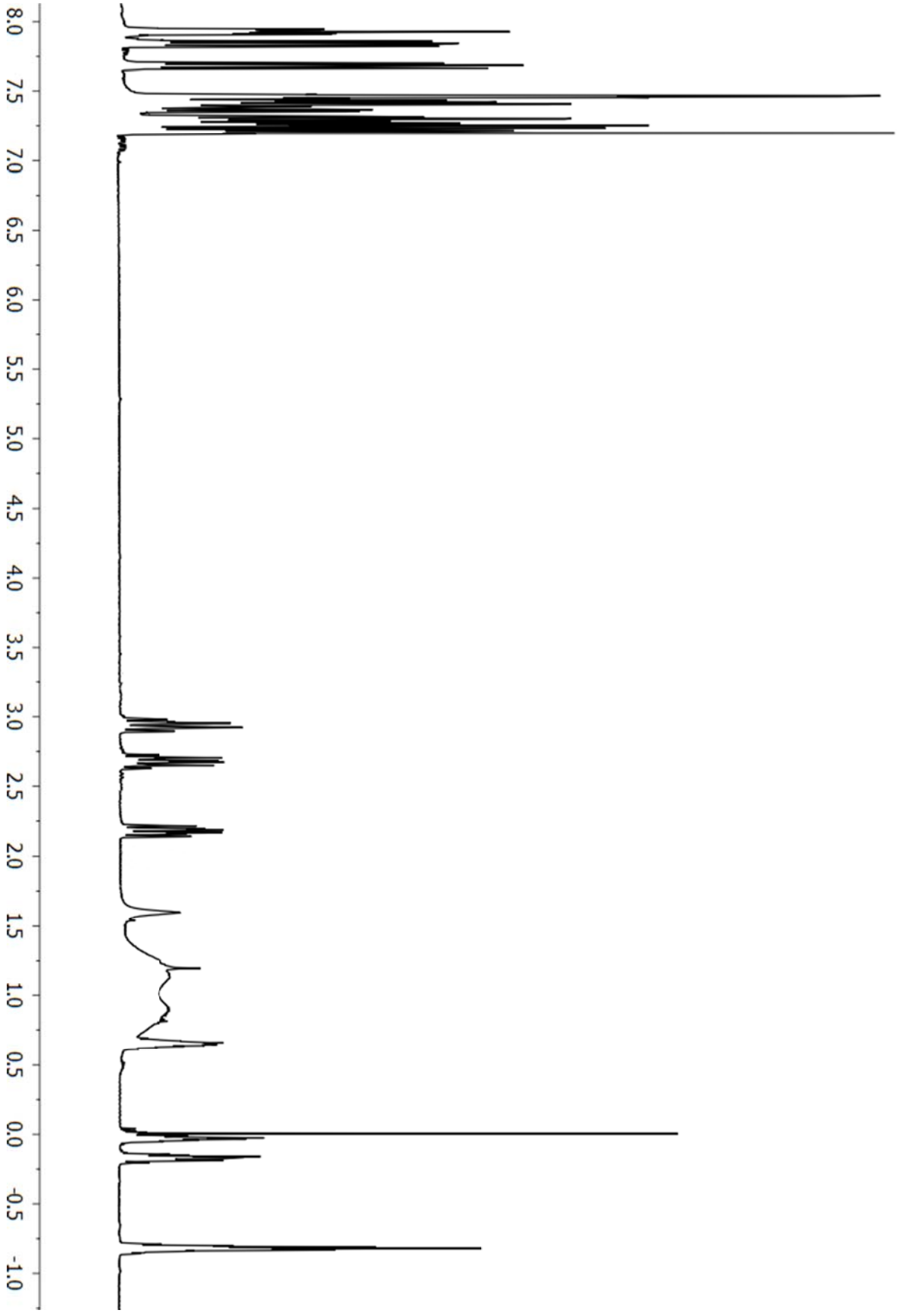


(1-cyclopropylethane-1,2-diyl)bis(diphenylphosphine))-bis(borane) (7g-BH_3)

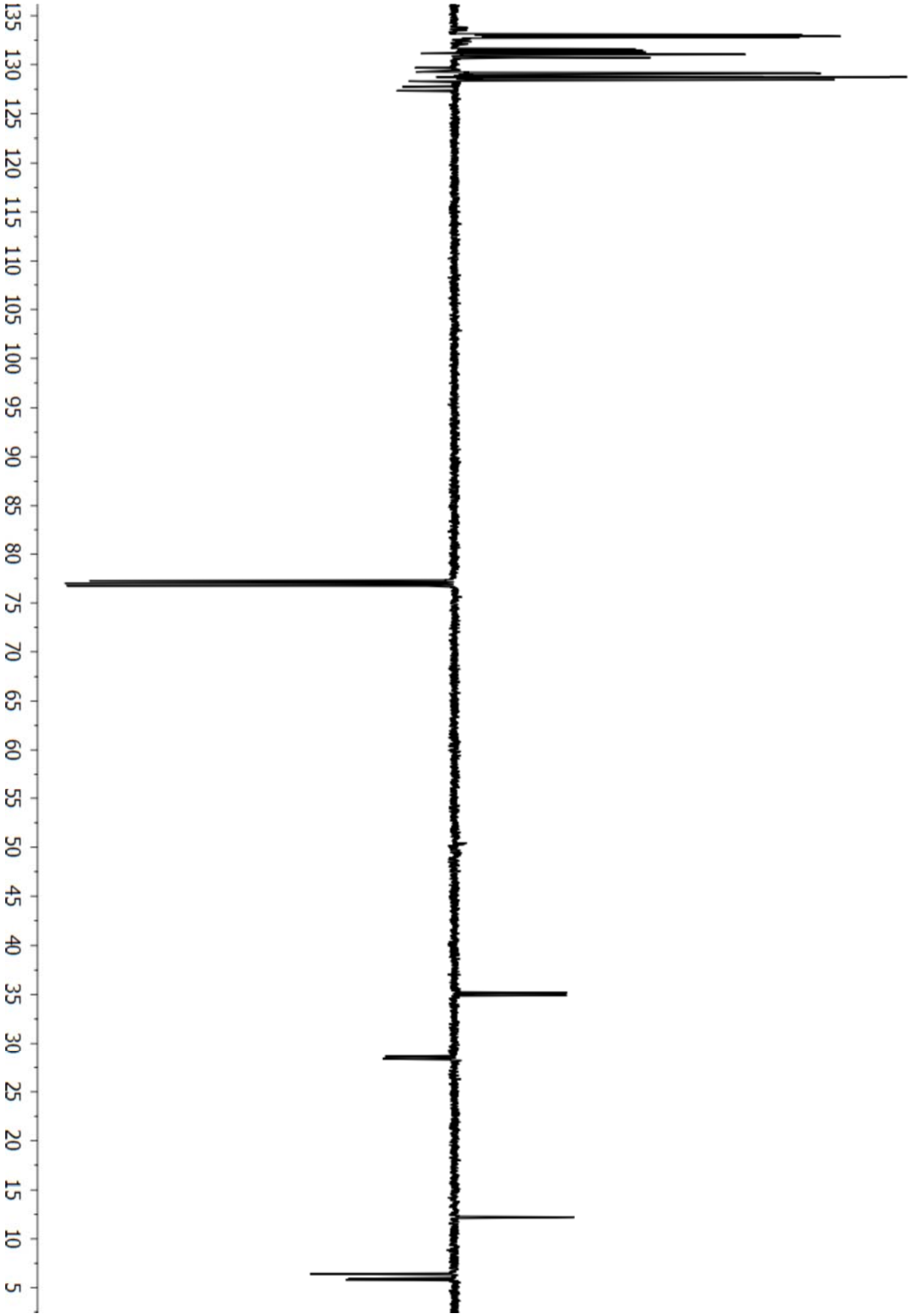


Yield: 13 mg (28%), off white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.95 – 7.19 (m, 20H, CH_{Ph}), 2.99 – 2.89 (m, 1H, CH_2P), 2.75 – 2.63 (m, 1H, CHP), 2.25 – 2.14 (m, 1H, CH_2P), 0.69 – 0.61 (m, 1H, CH), 0.01 – (-0.06) (m, 1H, CH_2), (-0.12) – (-0.20) (m, 1H, CH_2), (-0.78) – (-0.86) (m, 2H, CH_2). $^{13}C\{^{1}H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K): δ 133.3 – 126.9 (C_{Ph}), 35.1 (d, $J_{C\text{-}P}$ = 34 Hz, CHP), 28.5 (dd, $J_{C\text{-}P}$ = 33, 7 Hz, CH_2P), 12.2 (d, $J_{C\text{-}P}$ = 4 Hz, CH), 6.4 (dd, $J_{C\text{-}P}$ = 2 Hz, CH_2), 5.9 (dd, $J_{C\text{-}P}$ = 13 Hz, CH_2). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K): δ 24.8 (br, CHP), 16.5 (br, CH_2P). $^{11}B\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 298 K): δ -42.6 (br, BH_3), -39.8 (br, BH_3). HRMS (ESI) m/z calcd for $C_{29}H_{34}B_2P_2$ ($M + Na^+$) 489.2224 found 489.2213

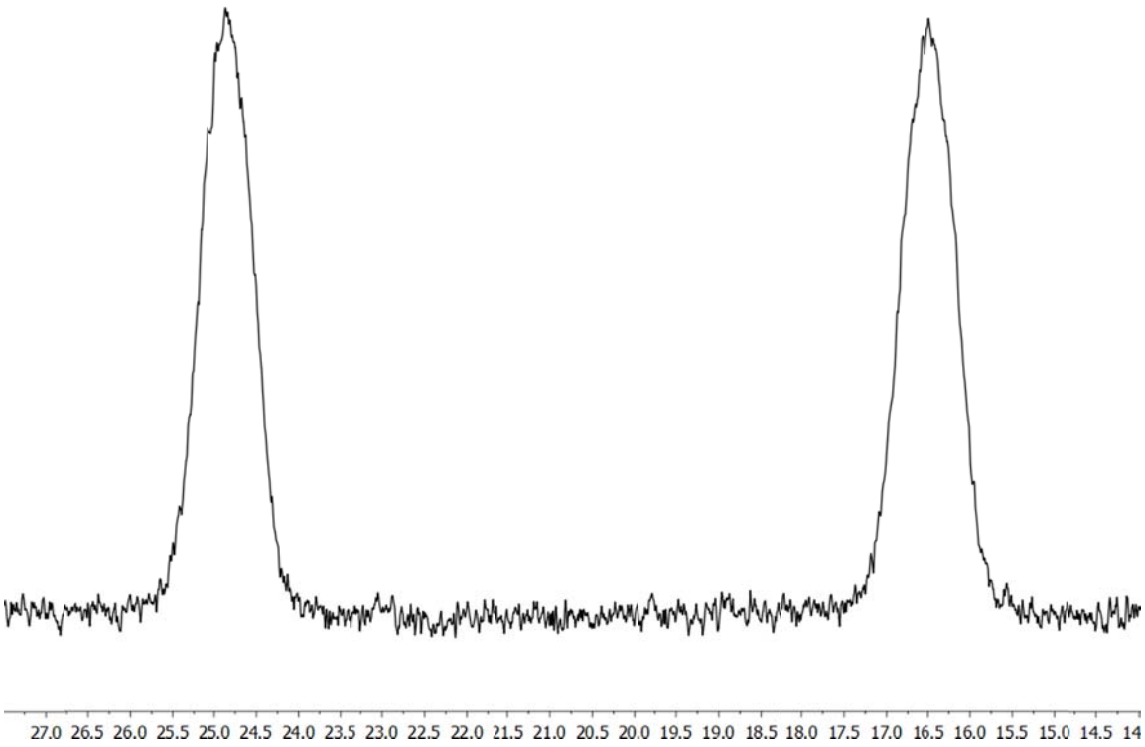
7g-BH_3: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



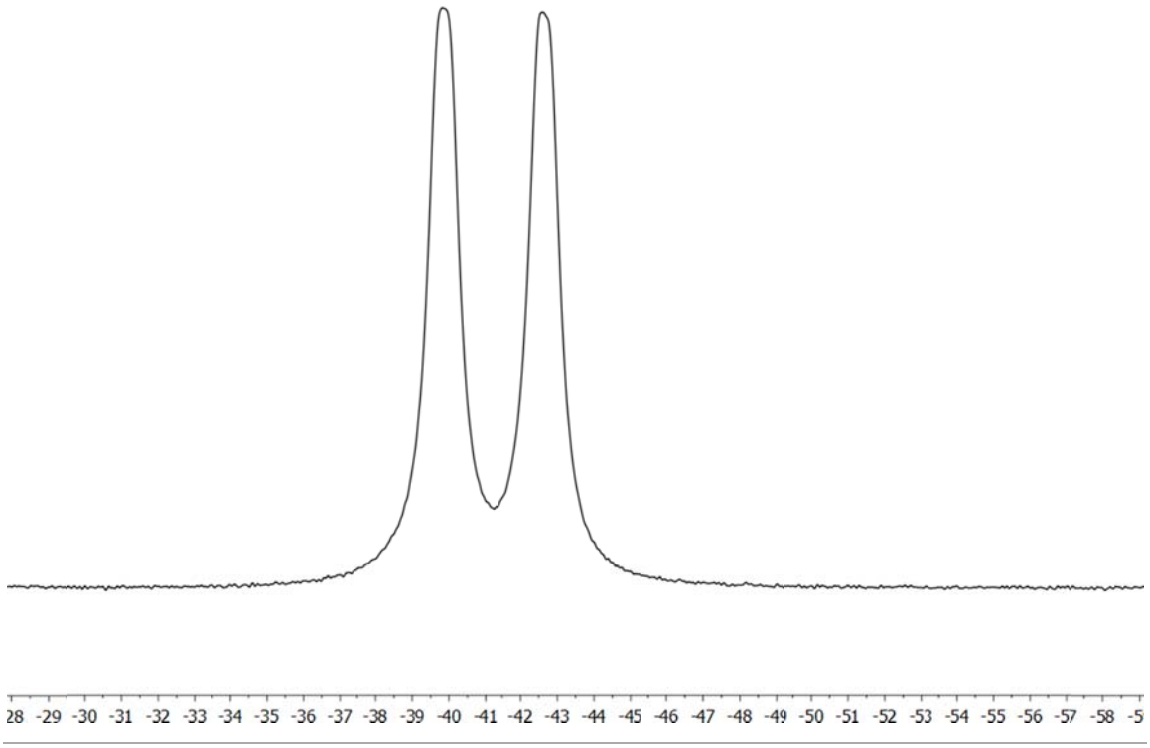
7g-BH_3: $^{13}C\{^1H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K)



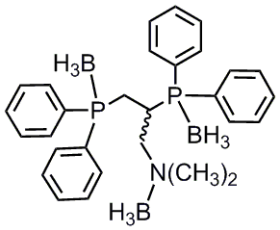
7g-BH$_3$: $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K)



7g-BH$_3$: $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 298 K)

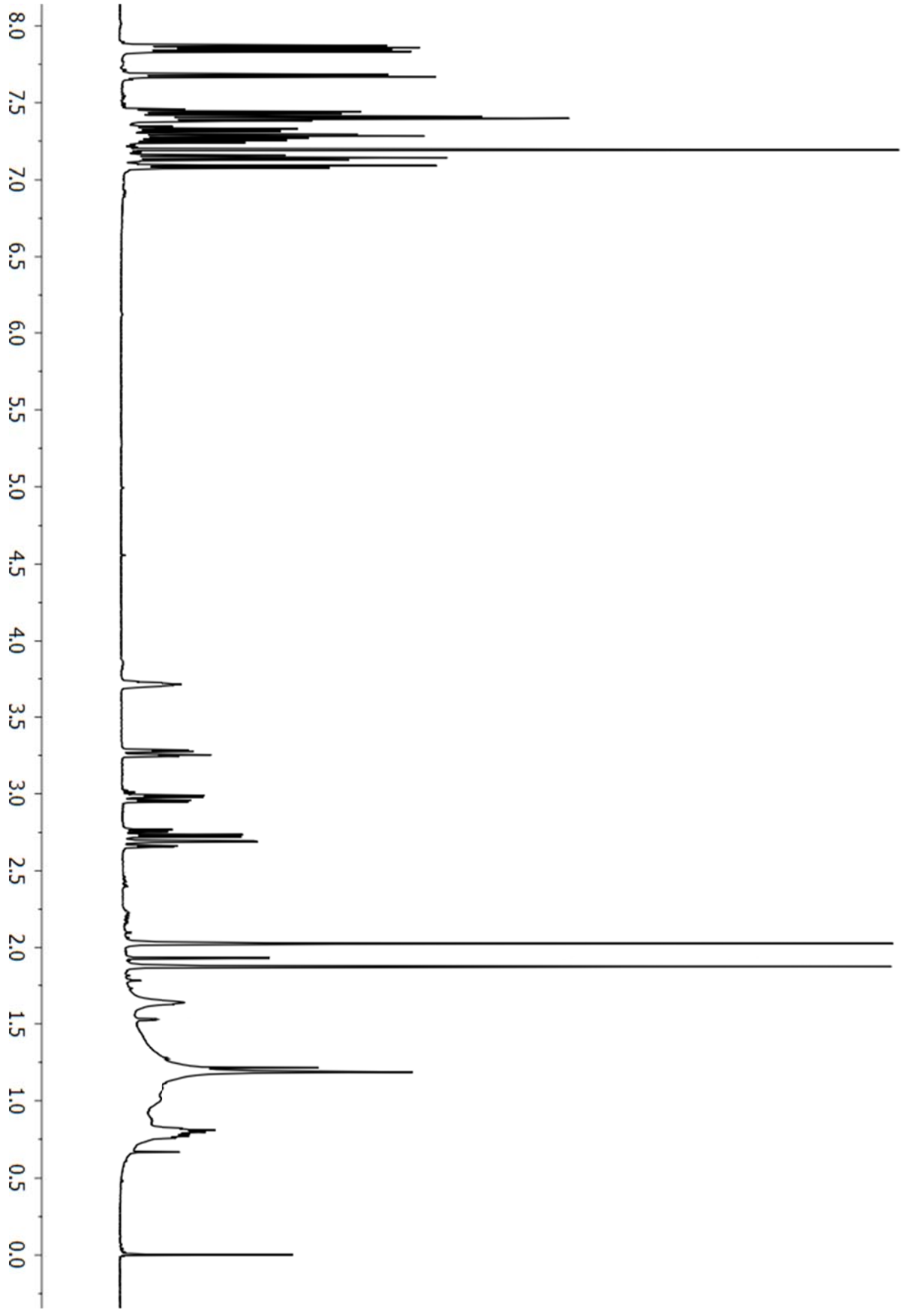


(2,3-bis(diphenylphosphanyl)-N,N-dimethylpropan-1-amine)-tris(borane) (7i-BH_3)

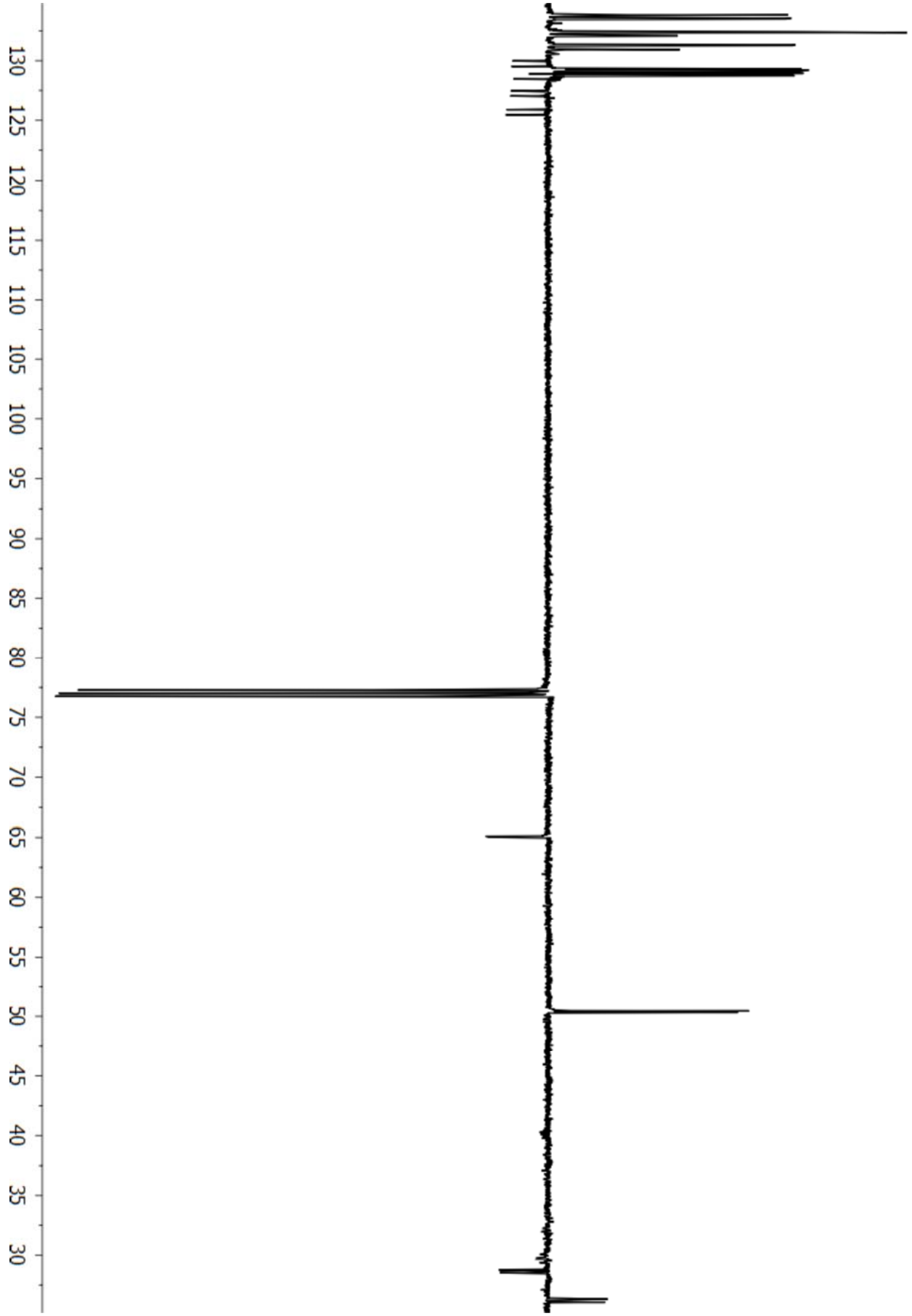


Yield: 13 mg (26%), off white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.91 – 7.05 (m, 20H, CH_{Ph}), 3.77 – 3.65 (m, 1H, CHP), 3.32 – 3.23 (m, 1H, CH_2N), 3.03 – 2.93 (m, 1H, CH_2N), 2.81 – 2.62 (m, 2H, CH_2P), 2.0 (s, 3H, CH_3), 1.9 (s, 3H, CH_3). ^{13}C{^{1}H}-APT NMR (126 MHz, $CDCl_3$, 298 K): δ 134.4 – 125.0 (C_{Ph}), 65.0 (dd, $J_{C\text{-}P}$ = 9, 3 Hz, CH_2N), 50.5 (s, CH_3N), 50.4 (s, CH_3N), 28.6 (dd, $J_{C\text{-}P}$ = 32, 5 Hz, CH_2P), 26.2 (dd, $J_{C\text{-}P}$ = 32, 2 Hz, CHP). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 298 K): δ 29.4 (s, CHP), 16.7 (s, CH_2P). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 298 K): δ -8.2 (br, N-BH_3), -42.5 (br, P-BH_3), -39.8 (br, P-BH_3). HRMS (ESI) m/z calcd for $C_{29}H_{40}B_3NP_2$ ($M + Na^+$) 520.2822 found 520.2807

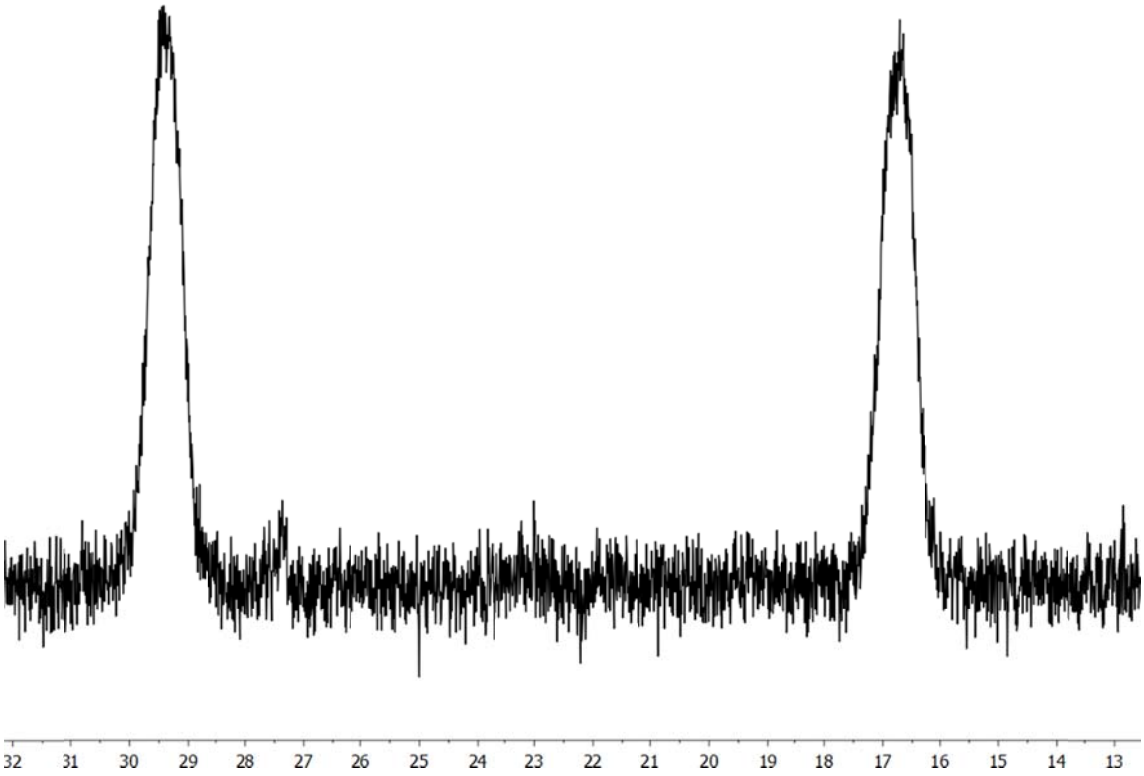
7i-BH_3: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K)



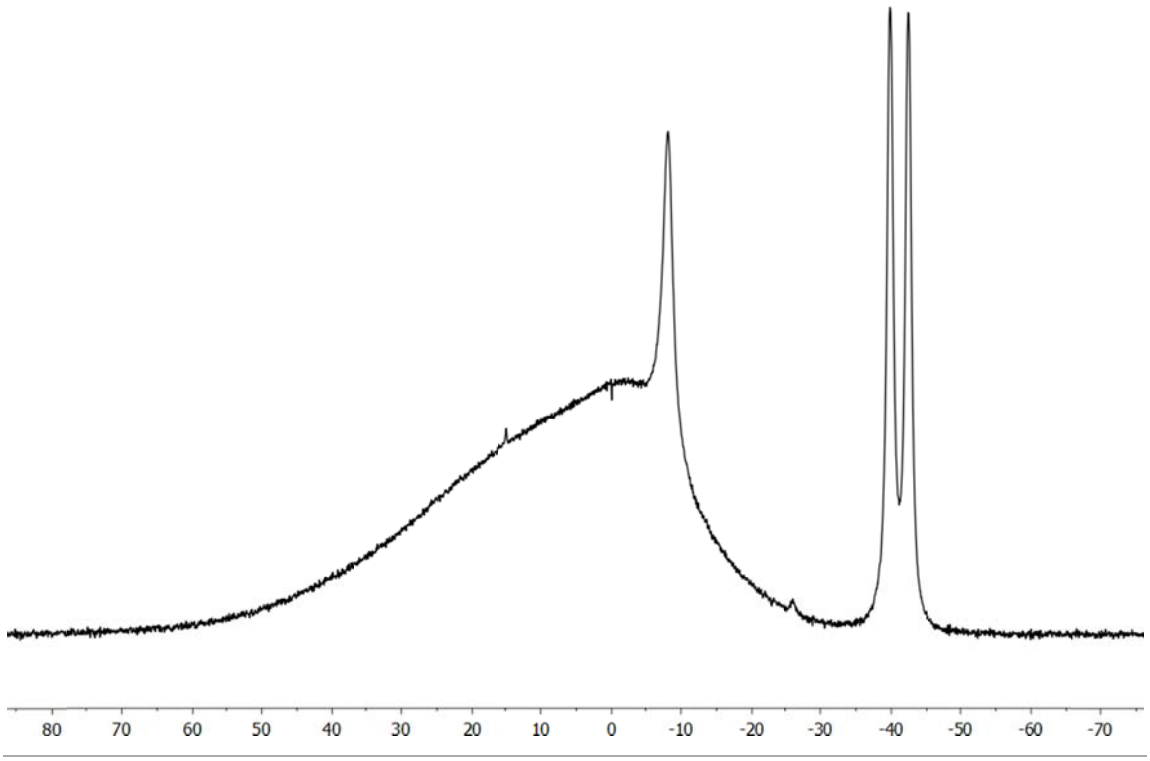
7i-BH_3: $^{13}C\{^1H\}$-APT NMR (126 MHz, $CDCl_3$, 298 K)



7i-BH_3: $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 298 K)



7i-BH_3: $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 298 K)



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