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Recycling of Homogeneous Catalysts in Reactive Ionic Liquid – Solvent-Free Aminofunctionalizations of Alkenes

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Electronic Supplementary Information

Table of Content

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1. Experimental results

1.1. Hydroamination of β-farnesene with dimcarb

Table 1: Results of the hydroamination of β-farnesene with dimcarb using the DPPB-ligand

Run #	$Y_{hydroamination}$ [%]	c(P) [ppm]	Leaching P [%]	c(Pd) [ppm]	Leaching Pd [%]
0	81	5[a]	0.3	205	34.7
1	59	4[a]	0.2	67	11.3
2	39	4[a]	0.2	33	5.6
3	15	5[a]	0.3	7	1.1
4	6	4[a]	0.2	5	0.8

Reaction conditions: Precursor=$Pd(tfa)_2$, 0.1 mol% based on β-farnesene, ligand=1,4-*bis*(diphenylphosphino)butane, metal/ligand=1/4, $n_{dimcarb}$=45 mmol, $n_{\beta\text{-farnesene}}$=15 mmol, T=100 °C, t=3 h, 500 rpm, yields (Y) given in % based on β-farnesene and determined by GC-FID using decane as internal standard.
Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol), phase separation under schlenk technique, addition of 15 mmol β-farnesene, restarting of the reaction.
Leaching is given in concentration (in ppm) in the product phase and relatively to the initially employed amount of the respective element (in %)
[a]: value is below limit of quantification for phosphorous (6 ppm)

Table 2: Results of the hydroamination of β-farnesene with dimcarb using the DPPBTS-ligand

Run #	**$Y_{hydroamination}$ [%]**	**c(P) [ppm]**	**Leaching P [%]**	**c(Pd) [ppm]**	**Leaching Pd [%]**
0	68	2[a]	< 0.1	3	0.1
1	86	2[a]	< 0.1	14	0.6
2	86	2[a]	< 0.1	3	0.1
3	88	2[a]	< 0.1	2[b]	< 0.1
4	91	2[a]	< 0.1	2[b]	< 0.1
5	92	2[a]	< 0.1	3	0.1
6	89	2[a]	< 0.1	2[b]	< 0.1
7	90	2[a]	< 0.1	1[b]	< 0.1
8	84	2[a]	< 0.1	2[b]	< 0.1
9	64	1[a]	< 0.1	12	0.7
10	28	2[a]	< 0.1	26	1.7
11	9	n.d.	-/-	n.d.	-/-
12	0	n.d.	-/-	n.d.	-/-

Reaction conditions: Precursor=$Pd(tfa)_2$, 0.1 mol% based on β-farnesene, ligand=1,4-*bis*(diphenylphosphino)butane-*tetra*-sulfonate, metal/ligand=1/4, $n_{dimcarb}$=45 mmol, $n_{\beta\text{-farnesene}}$=15 mmol, *T*=100 °C, *t*=3 h, 500 rpm, yields (Y) given in % based on β-farnesene and determined by GC-FID using decane as internal standard.

Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol), phase separation under schlenk technique, addition of 15 mmol β-farnesene, restarting of the reaction.

Leaching is given in concentration (in ppm) in the product phase and relatively to the initially employed amount of the respective element (in %)

[a]: value is below limit of quantification for phosphorous (6 ppm)

[b]: value is below limit of quantification for palladium (3 ppm)

1.2. Hydroamination of β-myrcene with dimcarb

Table 3: Results of the hydroamination of β-myrcene with dimcarb

Run #	$Y_{\text{hydroamination}}$ [%]	c(P) [ppm]	Leaching P [%]	c(Pd) [ppm]	Leaching Pd [%]
0	58	4[a]	0.2	< 1[b]	< 0.1
1	83	4[a]	0.2	< 1[b]	< 0.1
2	77	3[a]	0.2	2[b]	0.4
3	60	3[a]	0.2	3	0.5
4	64	3[a]	0.3	11	2.1

Reaction conditions: Precursor=Pd(tfa)$_2$, 0.1 mol% based on β-myrcene, ligand=1,4-*bis*(diphenylphosphino)butane-*tetra*-sulfonate, metal/ligand=1/4, n_{dimcarb}=45 mmol, $n_{\beta\text{-myrcene}}$=15 mmol, T=100 °C, t=3 h, 500 rpm, yields (Y) given in % based on β-myrcene and determined by GC-FID using dodecane as internal standard.
Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol), phase separation under schlenk technique, addition of 15 mmol β-myrcene, restarting of the reaction.
Leaching is given in concentration (in ppm) in the product phase and relatively to the initially employed amount of the respective element (in %)
[a]: value is below limit of quantification for phosphorous (6 ppm)
[b]: value is below limit of quantification for palladium (3 ppm)

1.3. Hydroamination isoprene with dimcarb

Table 4: Results of the hydroamination isoprene with dimcarb

Run #	$Y_{\text{hydroamination}}$ [%]	c(P) [ppm]	Leaching P [%]	c(Pd) [ppm]	Leaching Pd [%]
0	39	4[a]	0.3	< 1[b]	< 0.1
1	69	3[a]	0.3	< 1[b]	< 0.1
2	77	5[a]	0.6	< 1[b]	< 0.1
3	67	5[a]	0.4	< 1[b]	< 0.1
4	93	4[a]	0.5	< 1[b]	< 0.1

Reaction conditions: Precursor=Pd(tfa)$_2$, 0.1 mol% based on isoprene, ligand=1,4-*bis*(diphenylphosphino)butane-*tetra*-sulfonate, metal/ligand=1/4, n_{dimcarb}=45 mmol, $n_{isoprene}$=15 mmol, *T*=100 °C, *t*=3 h, 500 rpm, yields (Y) given in % based on isoprene and determined by GC-FID using dodecane as internal standard.
Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol), phase separation under schlenk technique, addition of 15 mmol isoprene, restarting of the reaction.
Leaching is given in concentration (in ppm) in the product phase and relatively to the initially employed amount of the respective element (in %)
[a]: value is below limit of quantification for phosphorous (6 ppm)
[b]: value is below limit of quantification for palladium (3 ppm)

1.4. Telomerization of 1,3-butadiene with dimcarb

Table 5: Results of the telomerization of 1,3-butadiene with dimcarb

Run #	**$Y_{\text{telomerization}}$ [%]**	**c(P) [ppm]**	**Leaching P [%]**	**c(Pd) [ppm]**	**Leaching Pd [%]**
0	83	5[a]	0.18	1[b]	< 0.1
1	90	4[a]	0.14	2[b]	< 0.1
2	93	4[a]	0.14	2[b]	< 0.1
3	91	3[a]	0.1	2[b]	< 0.1
4	87	4[a]	0.18	2[b]	< 0.1
5	91	4[a]	0.14	1[b]	< 0.1
6	89	4[a]	0.14	1[b]	< 0.1
7	90	4[a]	0.14	< 1[b]	< 0.1
8	90	4[a]	0.14	1[b]	< 0.1
9	91	5[a]	0.18	< 1[b]	< 0.1
10	91	6[a]	0.21	< 1[b]	< 0.1
11	89	5[a]	0.18	< 1[b]	< 0.1
12	87	4[a]	0.14	< 1[b]	< 0.1
13	93	5[a]	0.18	< 1[b]	< 0.1

Run #	$Y_{telomerization}$ [%]	c(P) [ppm]	Leaching P [%]	c(Pd) [ppm]	Leaching Pd [%]
14	90	4[a]	0.14	1[b]	< 0.1
15	89	4[a]	0.14	1[b]	< 0.1
16	90	3[a]	0.1	1[b]	< 0.1
17	91	4[a]	0.14	1[b]	< 0.1
18	89	4[a]	0.14	< 1[b]	< 0.1
19	92	3[a]	0.1	1[b]	< 0.1
20	91	4[a]	0.14	1[b]	< 0.1
21	91	4[a]	0.14	1[b]	< 0.1
22	92	4[a]	0.14	1[b]	< 0.1
23	91	4[a]	0.14	1[b]	< 0.1
24	91	4[a]	0.14	1[b]	< 0.1
25	90	4[a]	0.14	1[b]	< 0.1
26	92	10	0.35	< 1[b]	< 0.1
27	90	4[a]	0.14	< 1[b]	< 0.1
28	93	4[a]	0.14	1[b]	< 0.1
29	89	4[a]	0.14	1[b]	< 0.1
30	90	5[a]	0.18	1[b]	< 0.1

Reaction conditions: Precursor=Pd(acac)$_2$, 0.03 mol% based on 1,3-butadiene, ligand=TPPTS (=triphenylphosphine-*tri*-sulfonate), metal/ligand=1/4, n_{dimcarb}=30 mmol, $n_{\text{1,3-butadiene}}$=38 mmol, T=80 °C, t =2 h, 500 rpm, yields (Y) given in % based on 1,3-butadiene and determined by GC-FID using dibutyl ether as internal standard.

Recycling conditions: Extraction of the product with cyclohexane (2x2 mL), dimcarb was refilled to 30 mmol (addition of 11 mmol), addition of 38 mmol 1,3-butadiene, restarting of the reaction.

Leaching is given in concentration (in ppm) in the product phase and relatively to the initially employed amount of the respective element (in %)

[a]: value is below limit of quantification for phosphorous (6 ppm)

[b]: value is below limit of quantification for palladium (3 ppm)

1.5. Hydroaminomethylation of 1-dodecene with dimcarb

1.5.1. Reaction parameters

Table 6: Parameter screening for the hydroaminomethylation of 1-dodecene with dimcarb

Entry	**$X_{1\text{-dodecene}}$ [%]**	**Y_{HAM} [%]**	**S_{HAM} [%]**
1[a]	51	1	1
2[b]	60	19	42
3[c]	83	25	39
4[d]	55	40	87

Reaction conditions: Precursor=$[Rh(cod)Cl]_2$, 0.1 mol% based on 1-dodecene, ligand=sulfo-XantPhos, metal/ligand=1/4, $n_{dimcarb}$=30 mmol, $n_{1\text{-}dodecene}$=15 mmol, T=140 °C, t=4 h, p_{syngas}=50 bar, p_{CO}/p_{H2}=1/1; 500 rpm, Conversion (X) and yields (Y) are given in % based on 1-dodecene and determined by GC-FID using dibutyl ether as internal standard. Selectivity (S) was calculated as moles of products per converted mole of 1-dodecene
[a]: 0.05 mol% $[Rh(cod)Cl]_2$
[b]: 0.2 mol% $[Rh(cod)Cl]_2$
[c]: p_{syngas}=70 bar
[d]: p_{CO}/p_{H2}=1/2.5

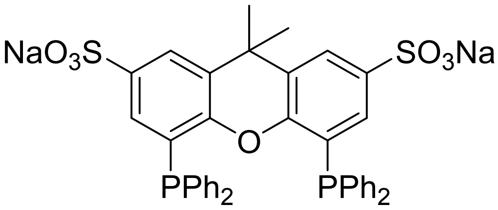


Figure 1: The sulfo-XantPhos ligand

1.5.2. Recycling experiments

Table 7: Results of the recycling experiments of the hydroaminomethylation of 1-dodecene with dimcarb

Run #	**Y_{HAM} [%]**	**c(P) [ppm]**	**c(Rh) [ppm]**
0	41	7	< 1[a]
1	35	7	< 1[a]

2	33	6	< 1[a]
3	31	6	1[a]
4	29	8	< 1[a]
5	23	8	< 1[a]

Reaction conditions: Precursor=$[Rh(cod)Cl]_2$, 0.1 mol% based on 1-dodecene, ligand=sulfo-XantPhos, metal/ligand=1/4, n_{dimcarb}=30 mmol, $n_{\textit{1-dodecene}}$=15 mmol, T=140 °C, t=4 h, p_{syngas}=50 bar, $p_{\text{CO}}/p_{\text{H2}}$=1/2.5; 500 rpm, Conversion (X) and yields (Y) are given in % based on 1-dodecene and determined by GC-FID using dibutyl ether as internal standard.

Recycling conditions: Dimcarb was refilled to 45 mmol (addition of 7.5 mmol), phase separation under schlenk technique, addition of 15 mmol 1-dodecene, restarting of the reaction.

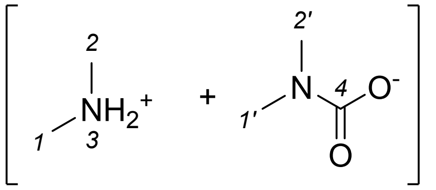
Leaching is given in concentration (in ppm) in the product phase.

[a]: value is below limit of quantification for rhodium (3 ppm)

2. Product Characterization & Analytics

2.1. Reactive Ionic Liquid

2.1.1. Dimethylammonium dimethylcarbamate (dimcarb)

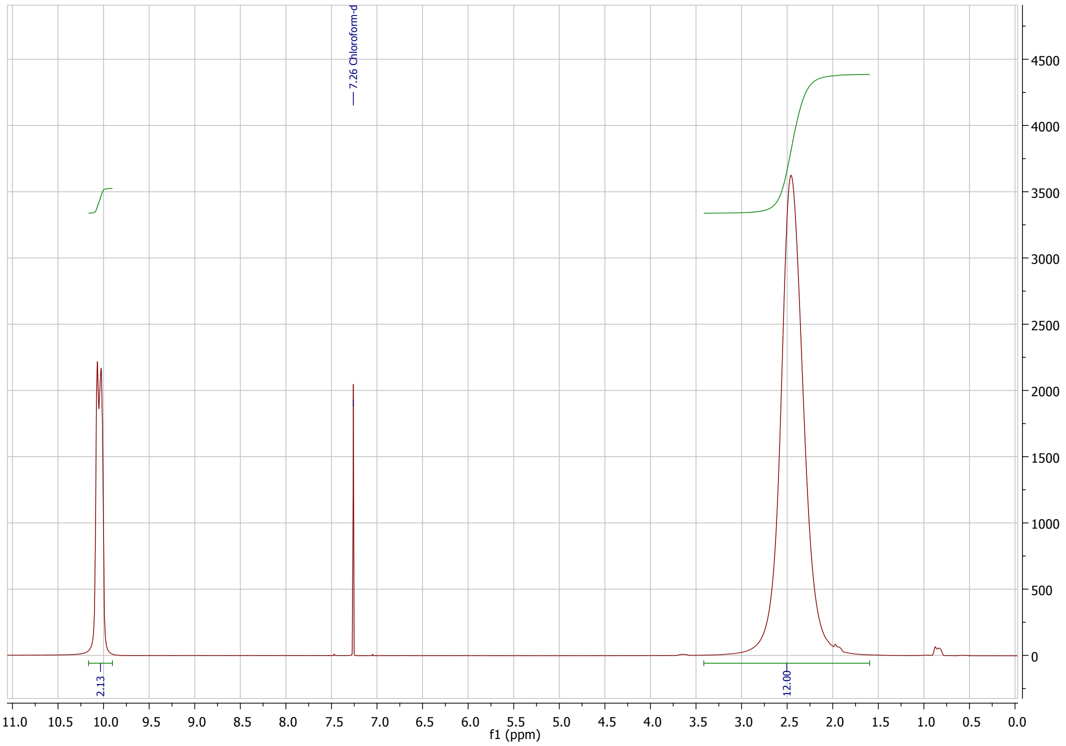


Chemical Formula: $C_5H_{14}N_2O_2$
Exact Mass: 134.1

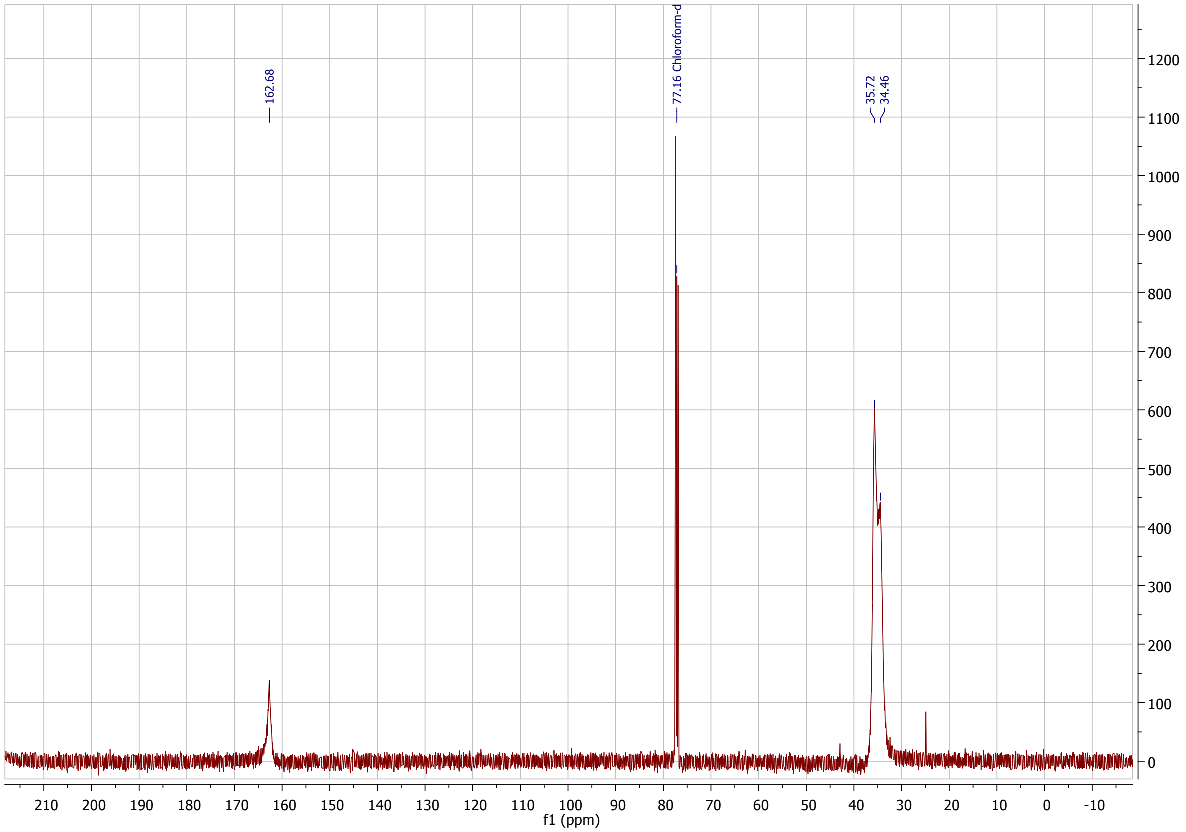
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 10.05 (m, 2H (*3*)), 2.22 (s, 12H (*1, 1′, 2, 2′*)).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 162.68 (*4*), 35.72 (*1, 1′*), 34.46 (*2, 2′*).

2.1.1.1. ^{1}H-NMR Spectrum

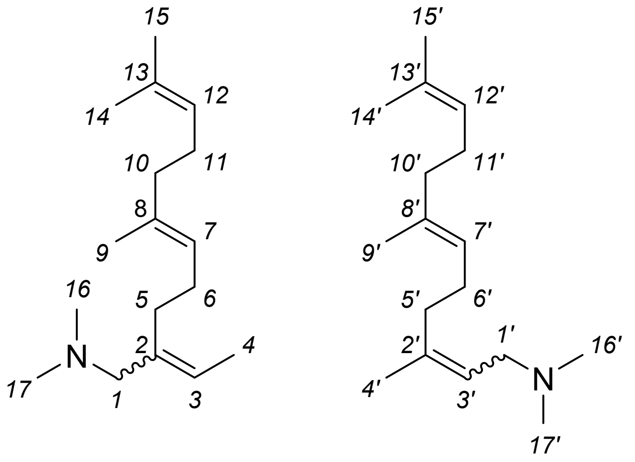


2.1.1.2. ^{13}C-NMR Spectrum



2.2. Hydroamination products with dimcarb

2.2.1. Dimethyl farnesylamines



Chemical Formula: $C_{17}H_{31}N$
Exact Mass: 249.2

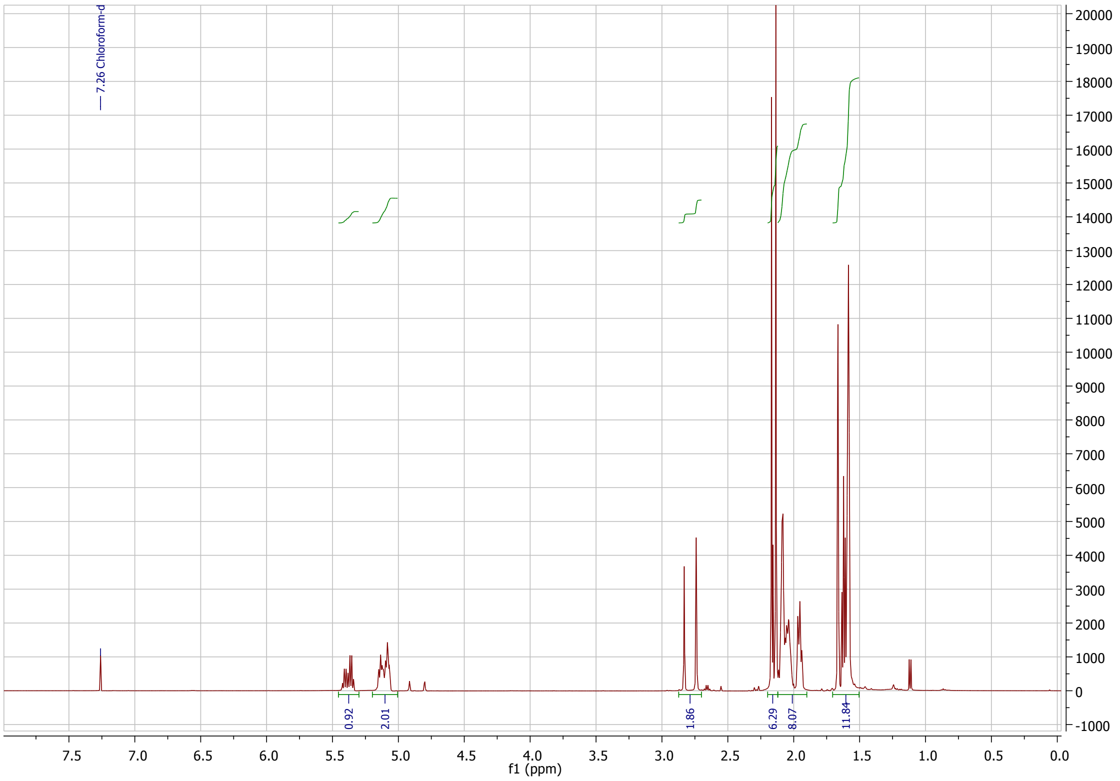
^{1}**H NMR** (500 MHz, $CDCl_3$) δ [ppm] = 5.45 – 5.30 (m, 1H (*3, 3’*)), 5.20 – 5.01 (m, 2H (*7, 7’, 12, 12’*)), 2.87 – 2.70 (m, 2H (*1, 1’*)), 2.20 – 2.12 (m, 6H (*16, 16’, 17, 17’*)), 2.12 – 1.90 (m, 8H (*5, 5’, 6, 6’, 10, 10’, 11, 11’*)), 1.70 – 1.50 (m, 12H (*4, 4’, 9, 9’, 14, 14’, 15, 15’*).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ [ppm] = 137.81 (*2, 2’*), 135.09 (*8, 8’*), 131.38 (*13, 13’*), 124.51 (*7, 7’*), 122.51 (*12, 12’*), 66.63 (*3, 3’*), 57.97 (*1, 1’*), 45.54 (*16, 16’*), 45.51 (*17, 17’*), 39.86 (*11, 11’*), 35.84 (*5, 5’*), 28.44 (*10, 10’*), 26.53 (*6, 6’*), 25.82 (*15, 15’*), 17.79 (*4, 4’*), 16.09 (*14, 14’*), 13.29 (*9, 9’*).

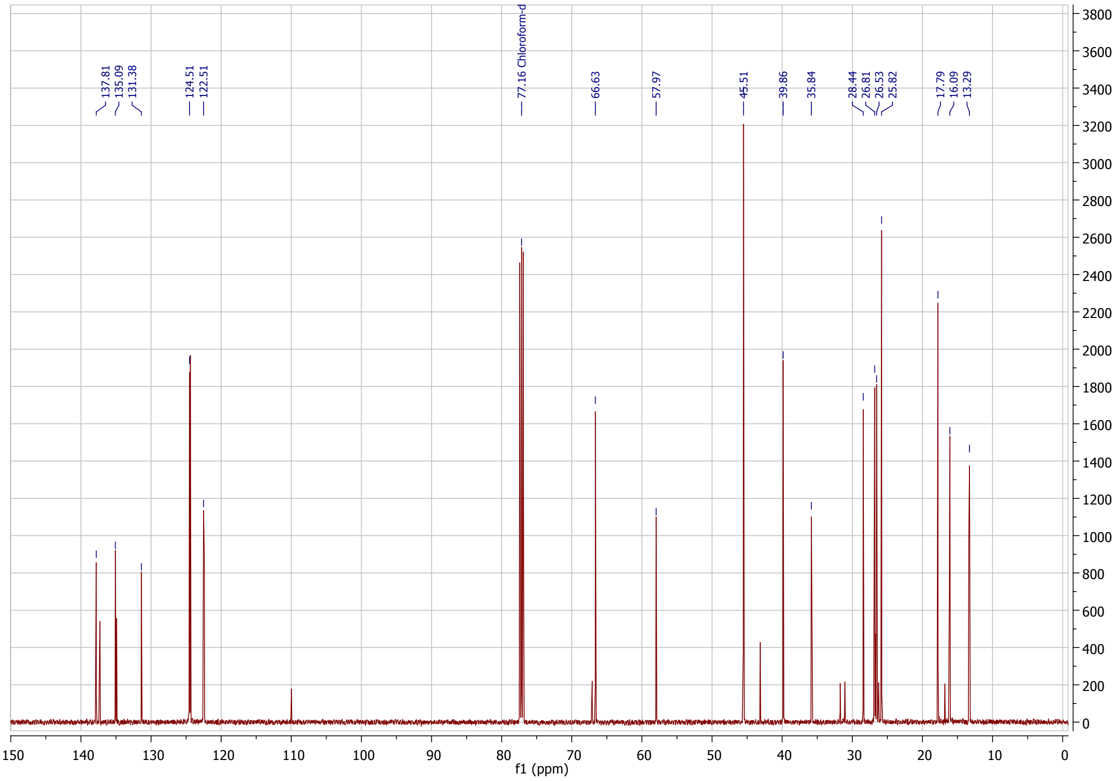
EI-MS (m/z) = 249 $[M]^+$ (13%), 180 (15), 161 (3), 133 (11), 120 (6), 112 (100), 98 (22), 93 (27), 81 (17), 69 (64), 58 (72), 44 (31).

HRMS $[M+H]^+$ calculated: 250.25293
measured: 250.25286

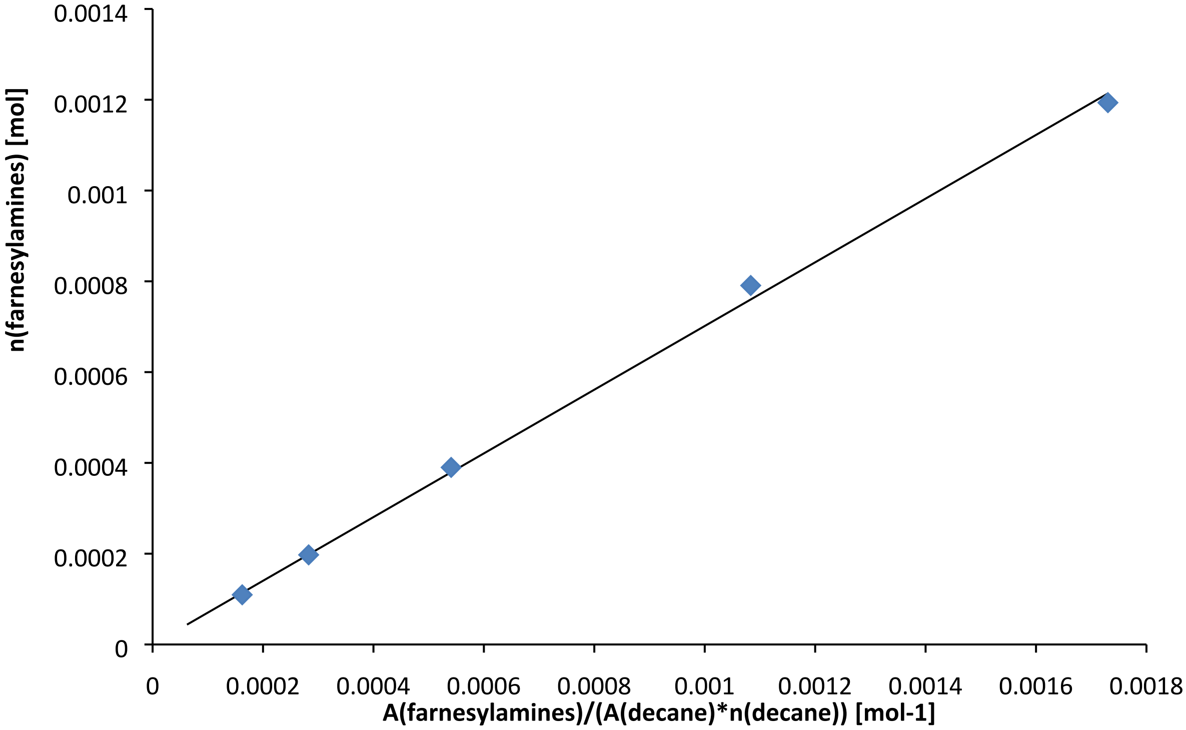
2.2.1.1. ^{1}H-NMR Spectrum



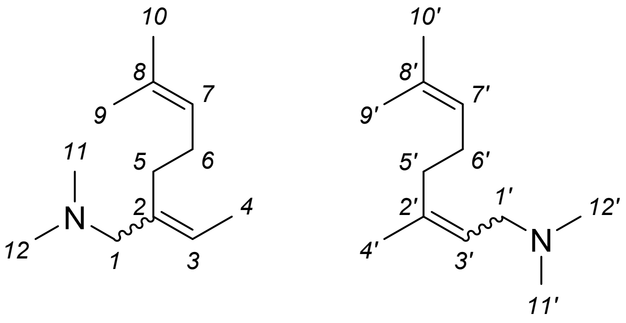
2.2.1.2. ^{13}C-NMR Spectrum



2.2.1.3. Calibration Line



2.2.2. Dimethyl myrcenylamines



Chemical Formula: $C_{12}H_{23}N$
Exact Mass: 181.2

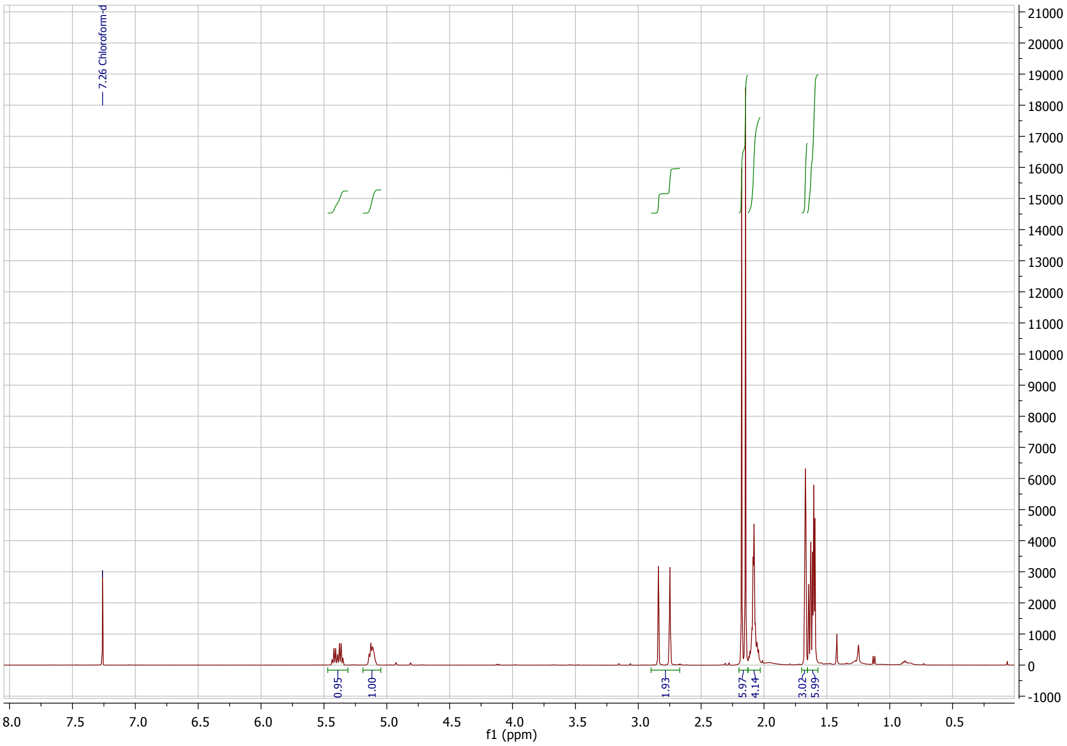
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 5.47 – 5.31 (m, 1H (*3, 3’*)), 5.19 – 5.05 (m, 1H (*7, 7’*)), 2.90 – 2.67 (m, 2H (*1, 1’*)), 2.20 – 2.13 (m, 6H (*11, 11’, 12, 12’*)), 2.13 – 2.03 (m, 4H (*5, 5’, 6, 6’*)), 1.67 (s, 3H (*4, 4’*)), 1.65 – 1.57 (m, 6H (*9, 9’ 10 ,10’*)).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 137.78 (*2, 2’*), 131.55 (*8, 8’*), 124.60 (*7, 7’*), 122.43 (*3, 3’*), 57.97 (*1, 1’*), 45.56 (*11, 11’*), 45.53 (*12, 12’*), 35.89 (*5, 5’*), 28.51 (*6, 6’*), 25.87 (*10, 10’*), 17.79 (*4, 4’*), 13.28 (*9, 9’*).

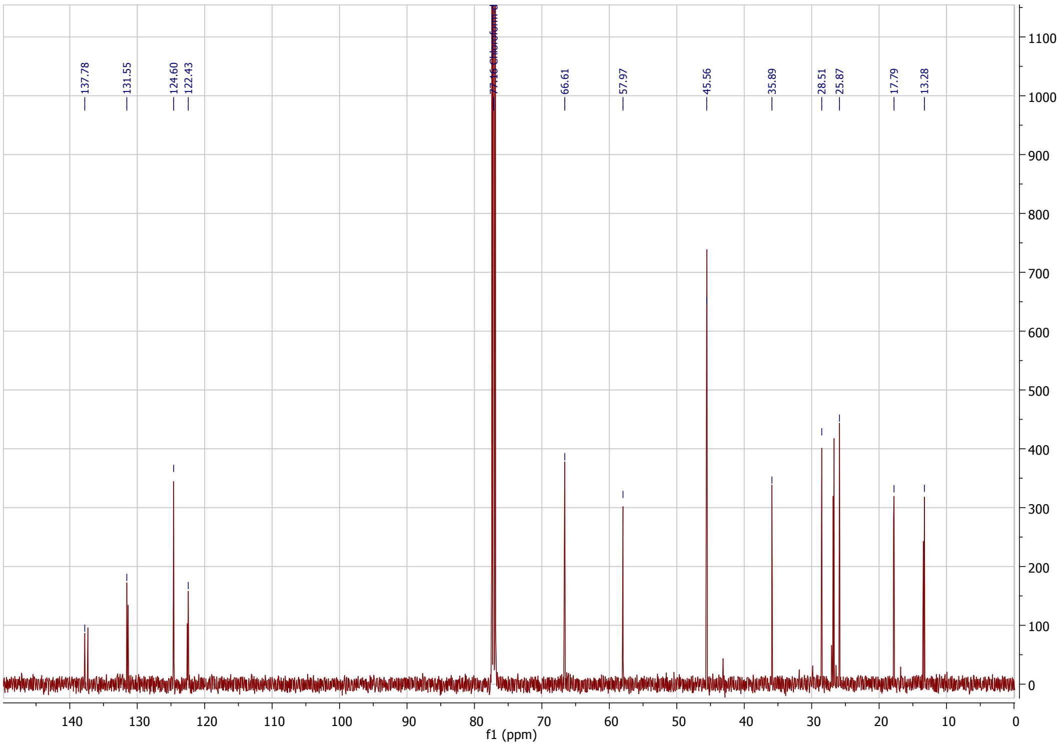
EI-MS (m/z) = 181 [M]$^+$ (6%), 166 (31), 124 (3), 112 (15), 110 (31), 107 (8), 98 (3), 96 (11), 95 (4), 94 (4), 93 (16), 91 (6), 82 (20), 81 (5), 79 (5), 77 (7), 71 (5), 69 (15), 67 (12), 58 (100), 55 (5), 53 (10).

HRMS: [M+H]$^+$ (calculated) = 182.19033
(measured) = 182.19021

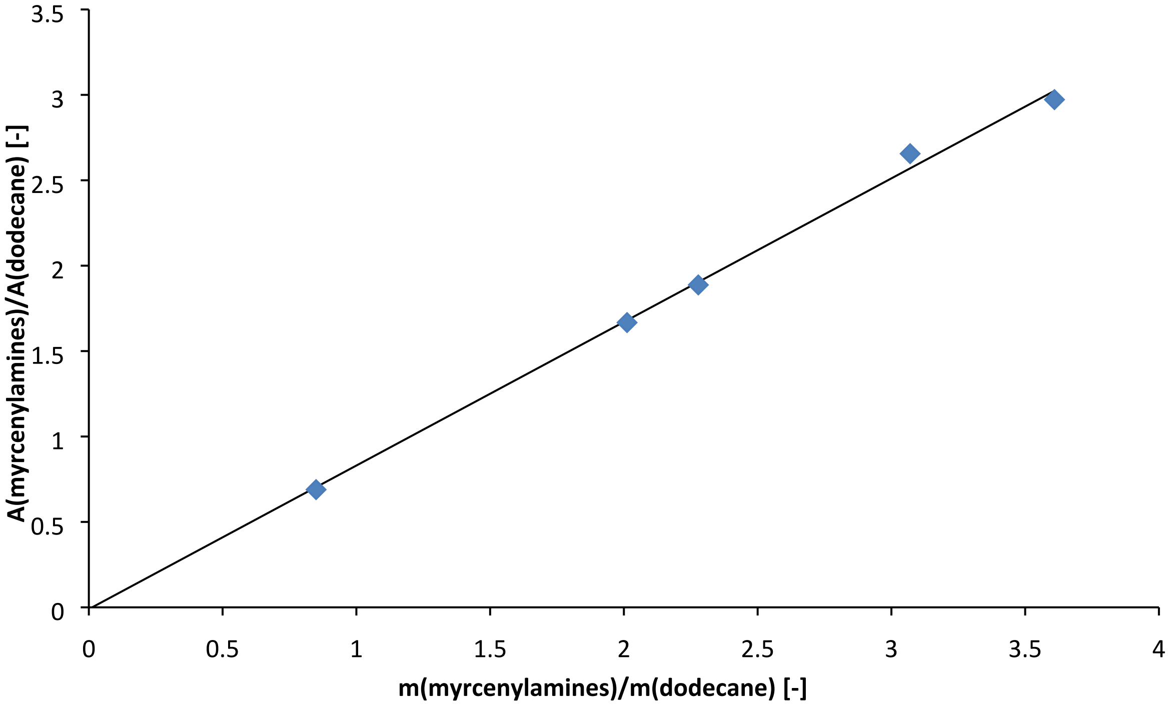
2.2.2.1. ^{1}H-NMR Spectrum



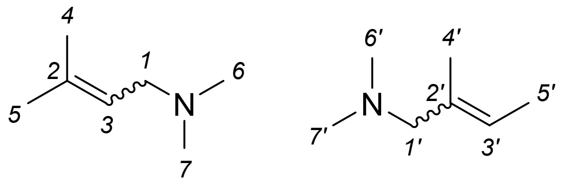
2.2.2.2. ^{13}C-NMR Spectrum



2.2.2.3. Calibration line



2.2.3. Dimethyl isoprenylamines



Chemical Formula: $C_7H_{15}N$
Exact Mass: 113.1

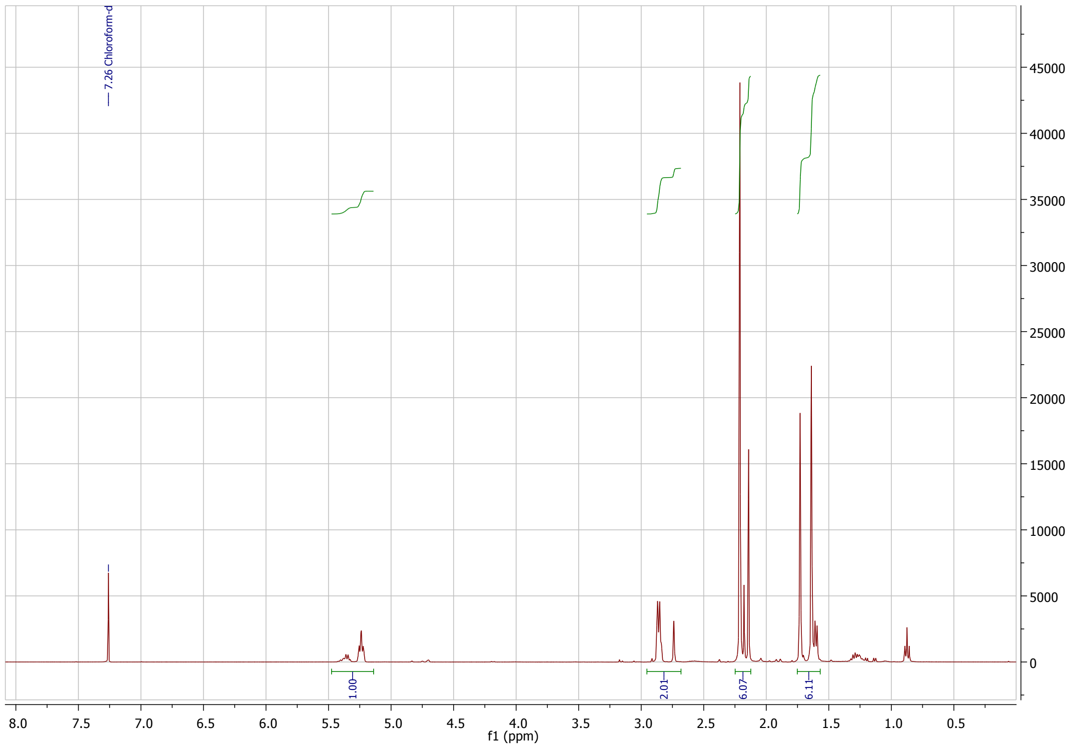
^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 5.48 – 5.14 (m, 1H (*3, 3′*)), 2.95 – 2.68 (m, 2H (*1, 1′*)), 2.19 (m, 6H (*6, 6′, 7, 7′*)), 1.75 – 1.57 (m, 6H (*4, 4′, 5, 5′*)).

^{13}C NMR (100 MHz, $CDCl_3$) δ [ppm] = 133.91 (*2, 2′*), 121.87 (*3, 3′*), 57.22 (*1, 1′*), 45.39 (*6, 6′*), 45.33 (*7, 7′*), 26.03 (*4, 4′*), 18.09 (*5, 5′*).

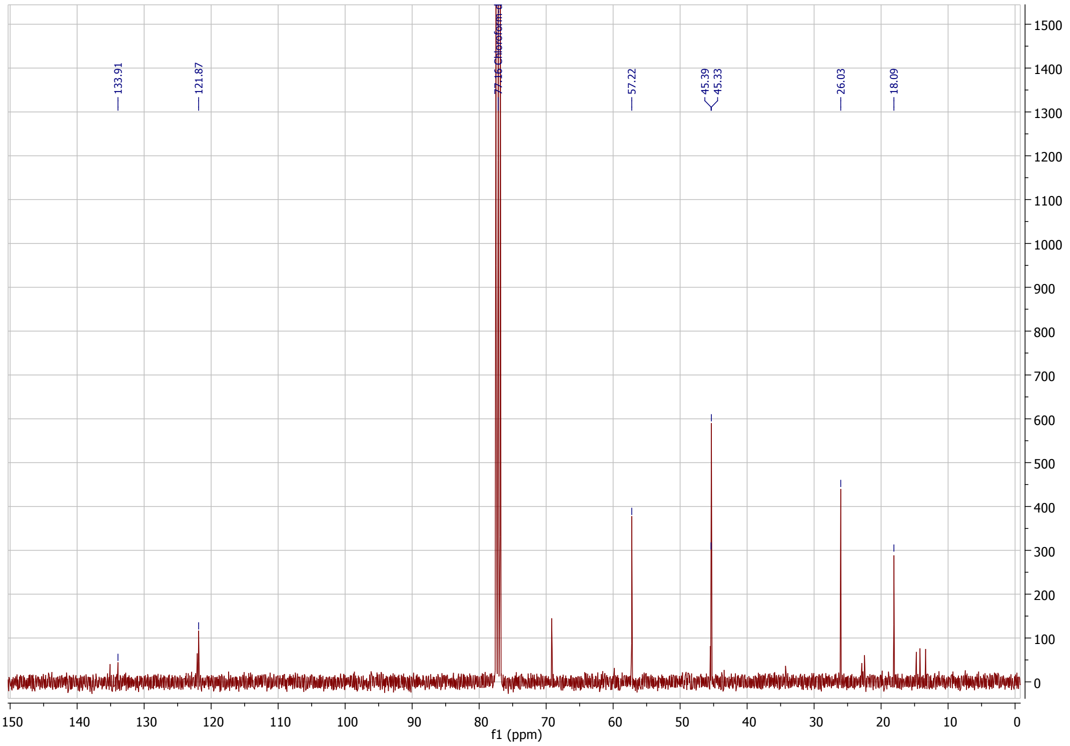
EI-MS (m/z) = 113 $[M]^+$ (39%), 112 (45), 99 (5), 98 (78), 96 (8), 83 (4), 82 (16), 80 (3), 71 (3), 70 (10), 69 (26), 68 (6), 67 (9), 59 (3), 58 (100), 57 (7), 56 (8), 55 (8), 54 (4), 53 (12), 51 (5).

HRMS: $[M+H]^+$ (calculated) = 114.12773
(measured) = 114.12736

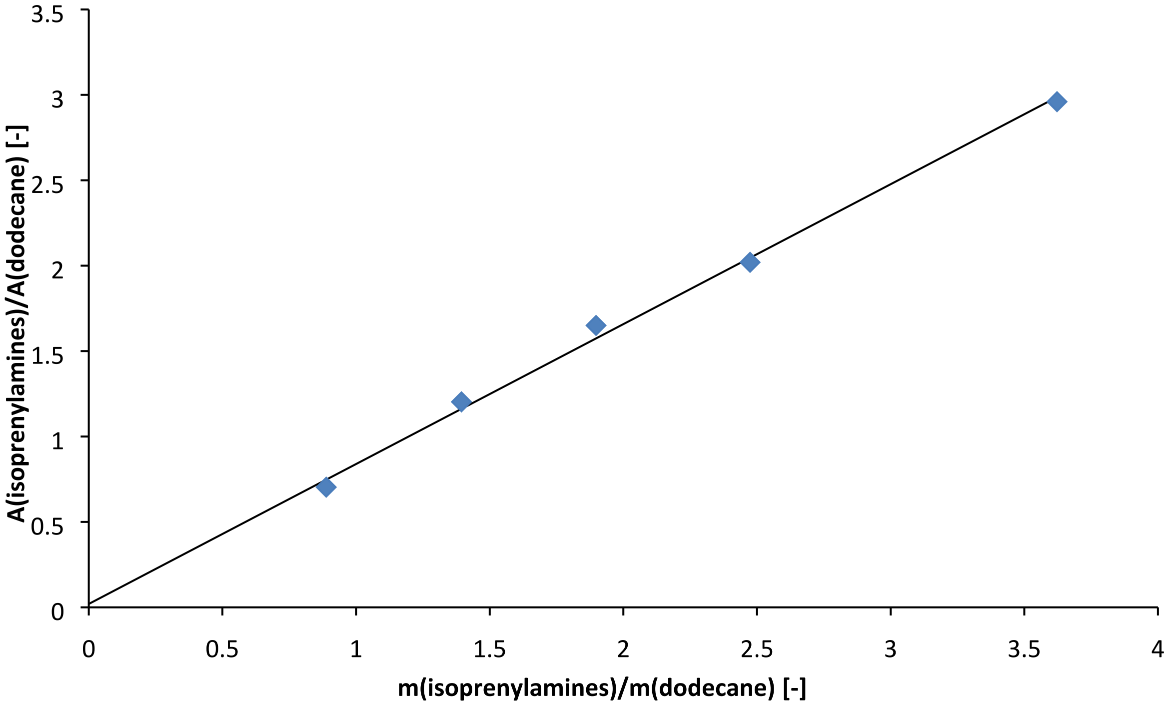
2.2.3.1. ^{1}H NMR Spectrum



2.2.3.2. ^{13}C NMR Spectrum

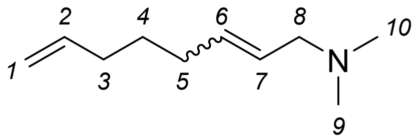


2.2.3.1. Calibration line



2.3. Telomerization products with dimcarb

2.3.1. Dimethyl octadienylamines



Chemical Formula: $C_{10}H_{19}N$
Exact Mass: 153.2

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 5.81 – 5.62 (m, 1H (*2*)), 5.62 – 5.29 (m, 2H (*6, 7*)), 4.95 – 4.78 (m, 2H (*1*)), 3.00 – 2.50 (m, 2H (*8*)), 2.33 – 2.03 (m, 6H (*9, 10*)), 1.96 (m, 4H (*3, 5*)), 1.44 – 1.34 (m, 2H (*4*)).

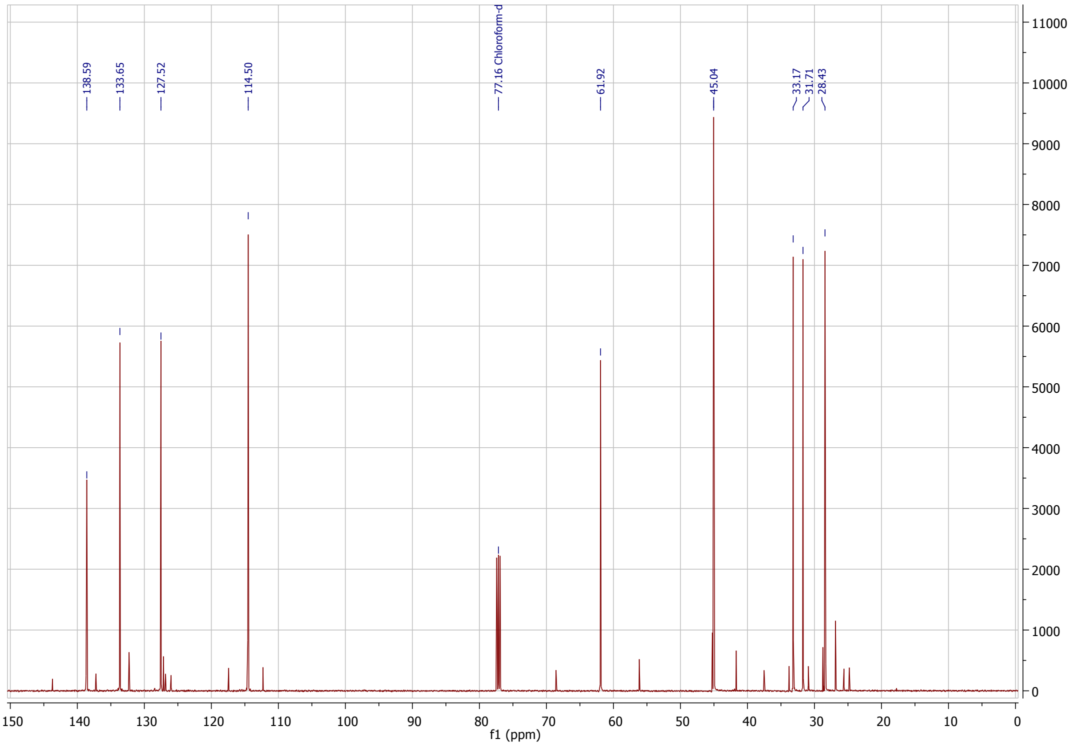
^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 138.59 (*2*), 133.65 (*6*), 127.52 (*7*), 114.50 (*1*), 61.92 (*8*), 45.04 (*9, 10*), 33.17 (*3*), 31.71 (*5*), 28.43 (*5*).

EI-MS (m/z): 153 $[M]^+$ (8%), 138 (5), 110 (24), 98 (16), 84 (34), 67 (17), 58 (100), 45 (24).

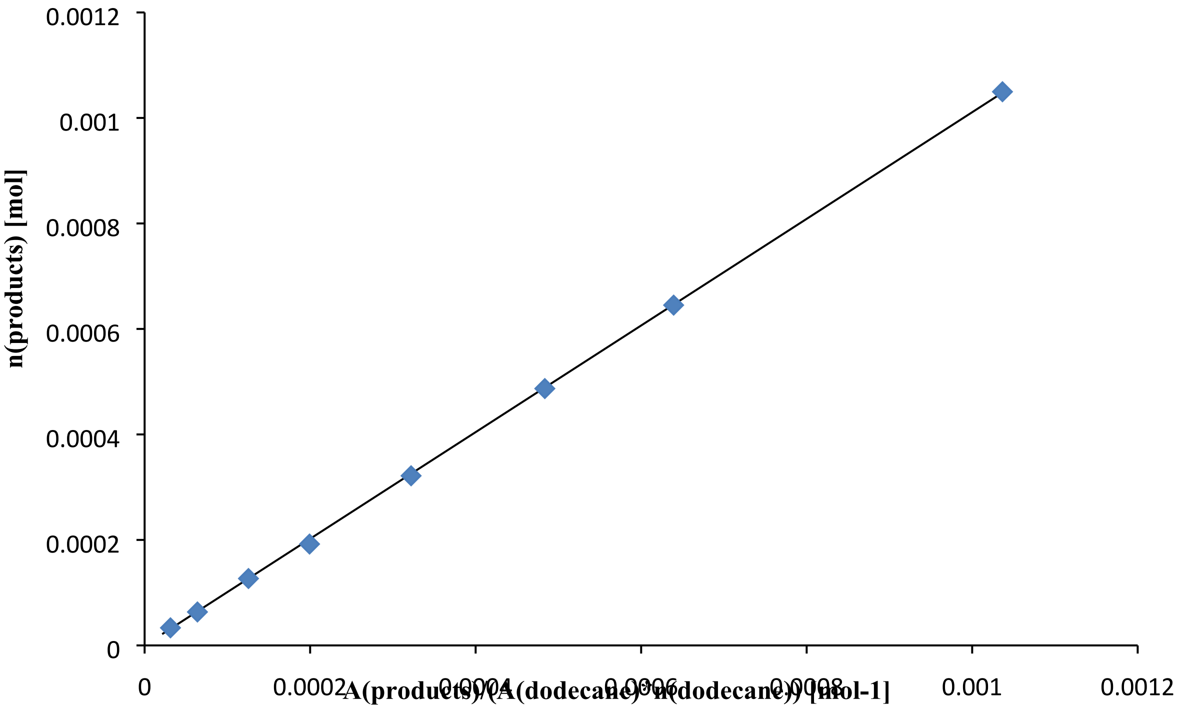
HRMS $[M+H]^+$	calculated:	154.15903
	measured:	154.15865

2.3.1.1. ^{1}H-NMR Spectrum

2.3.1.2. ^{13}C-NMR Spectrum

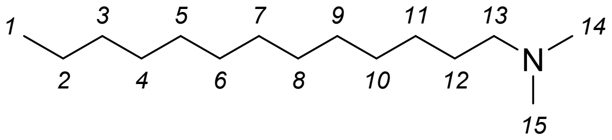


2.3.1.3. Calibration line



2.4. Hydroaminomethylation products

2.4.1. Dimethyl tridecylamine



Chemical Formula: $C_{15}H_{33}N$
Exact Mass: 227.3

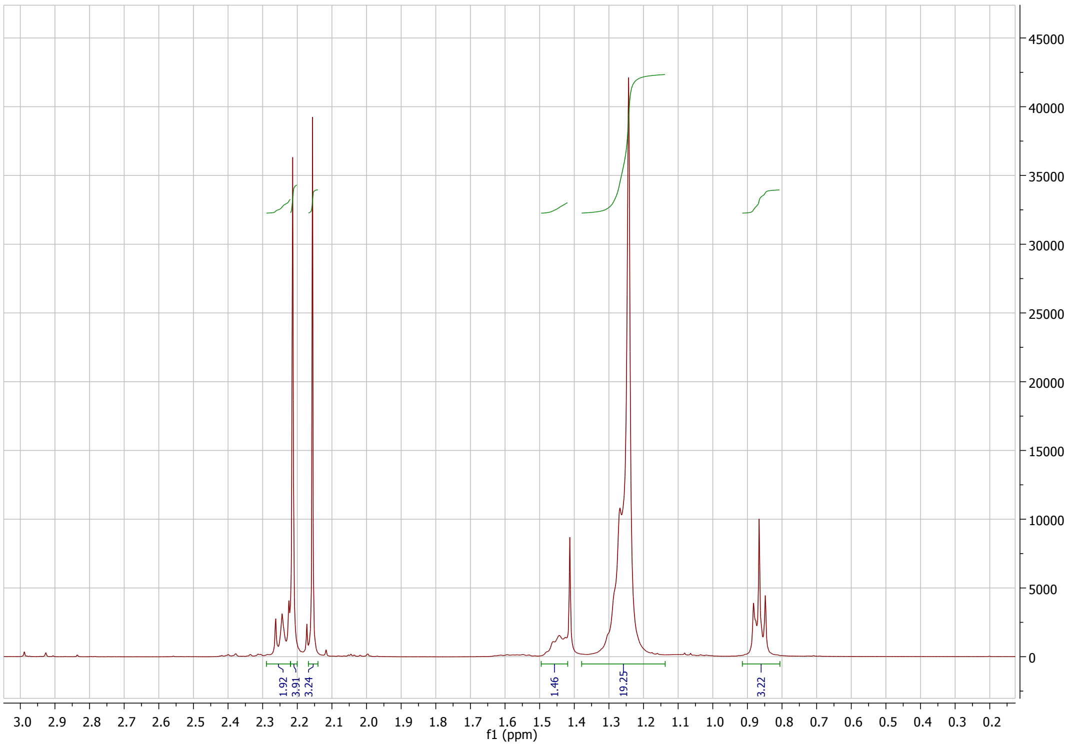
^{1}H NMR (400 MHz, $CDCl_3$) *δ* [ppm] = 2.29 – 2.22 (m, 2H (*13*)), 2.21 (s, 3H (*14*)), 2.16 (s, 3H (*14*)), 1.44 (m, 2H (*15*)), 1.26 (d, 22H (*2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12*)), 0.87 (t, *J* = 6.8 Hz, 3H (*1*)).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* [ppm] = 60.33 (*13*), 45.82 (*14, 15*), 32.37, 31.36, 30.13, 30.11, 30.09, 30.08, 30.07, 28.09, 27.96, 27.36, (*3, 4, 5, 6, 7, 8, 9, 10, 11, 12*) 23.14 (*2*), 14.56 (*1*).

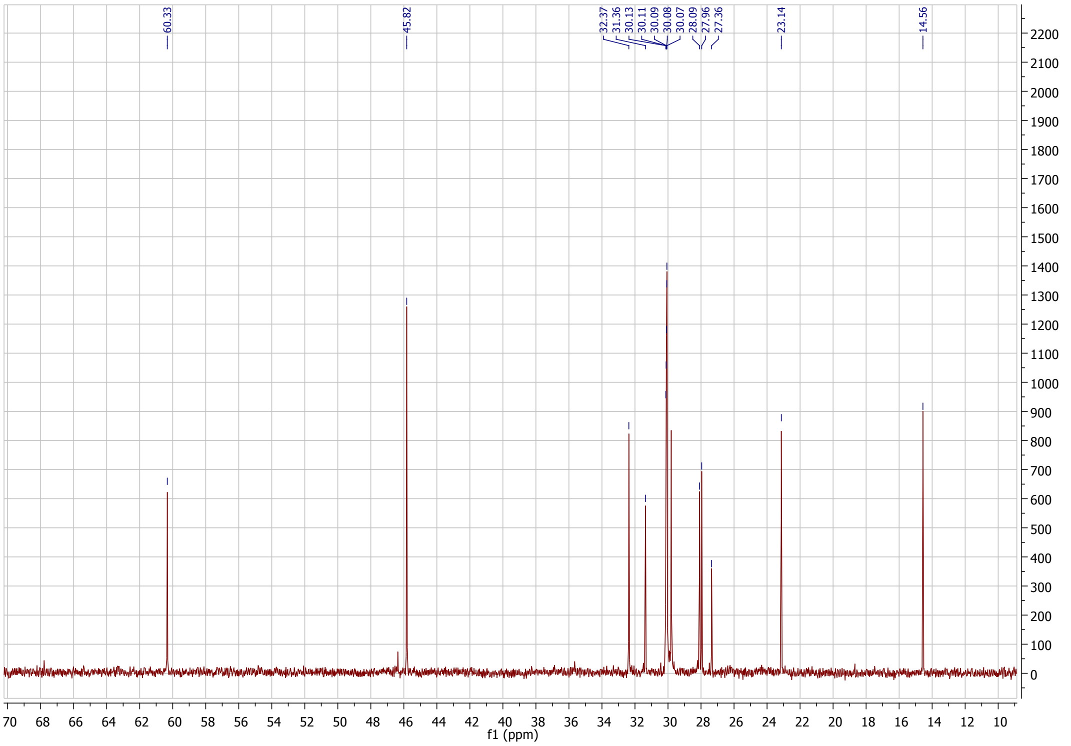
EI-MS (m/z): 227 $[M]^+$ (7%), 114 (1), 84 (3), 71 (1), 58 (100)

HRMS $[M+H]^+$	calculated:	228.26858
	measured:	228.26831

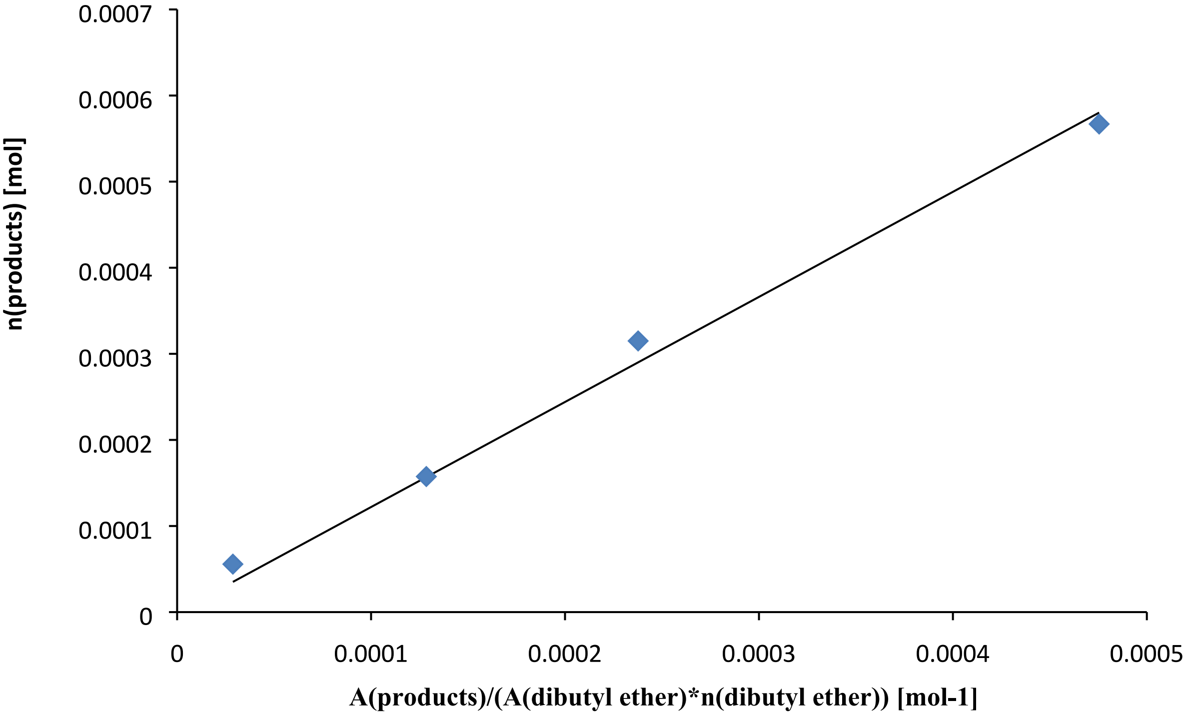
2.4.1.1. ^{1}H-NMR spectrum



2.4.1.2. ^{13}C-NMR spectrum



2.4.1.3. Calibration line



2.5. Ligand Oxidation

2.5.1. DPPBTS

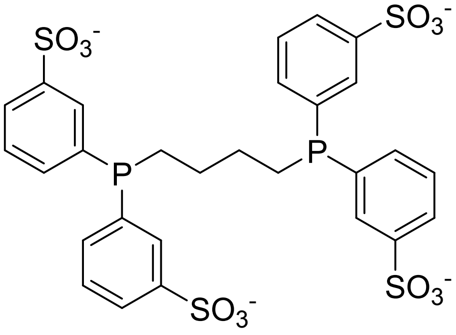


Figure 2: Structure of the DPPBTS-ligand

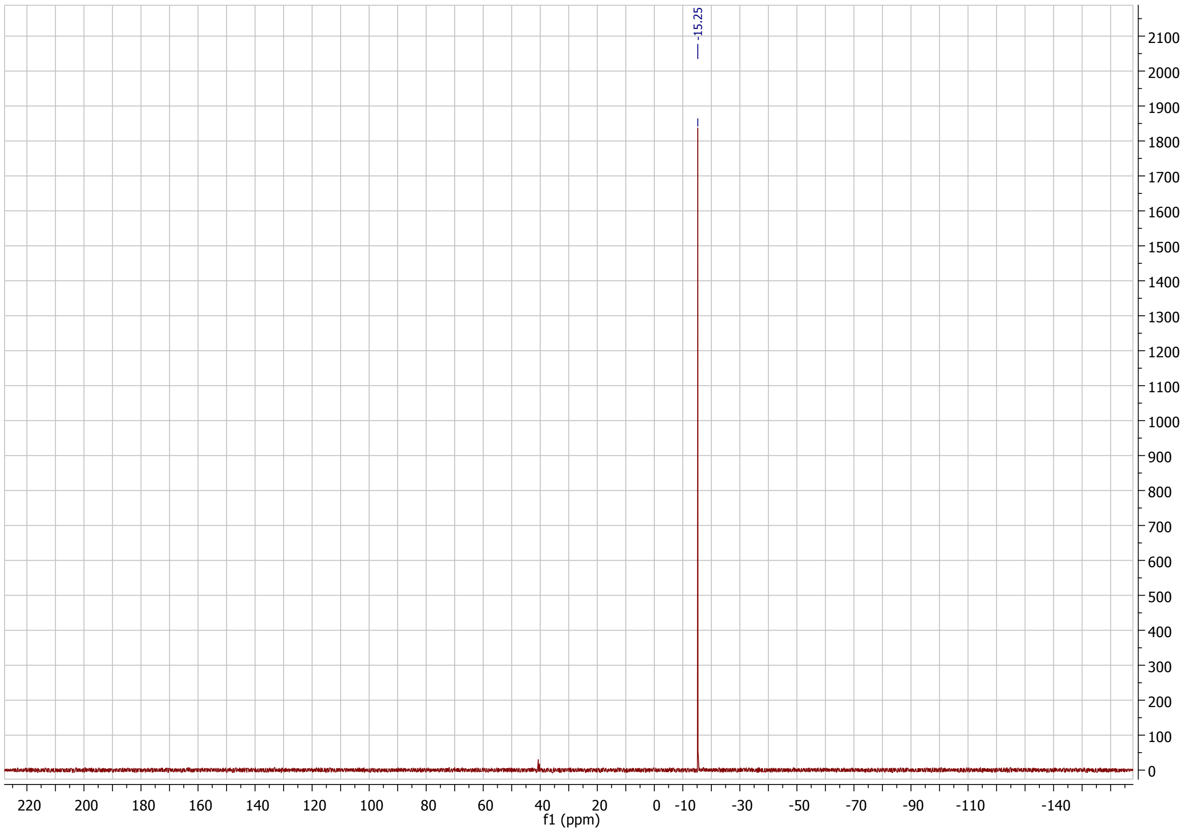


Figure 3: ^{31}P-NMR of the pure ligand in D_2O.
Chemical Shift of the phosphorous(III) atom is **-15.25**

2.5.2. DPPBTS-oxide

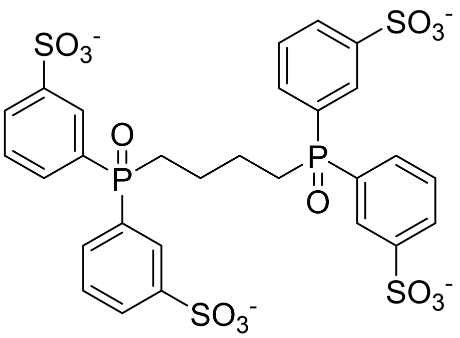


Figure 4: Structure of the oxidized DPPBTS-ligand

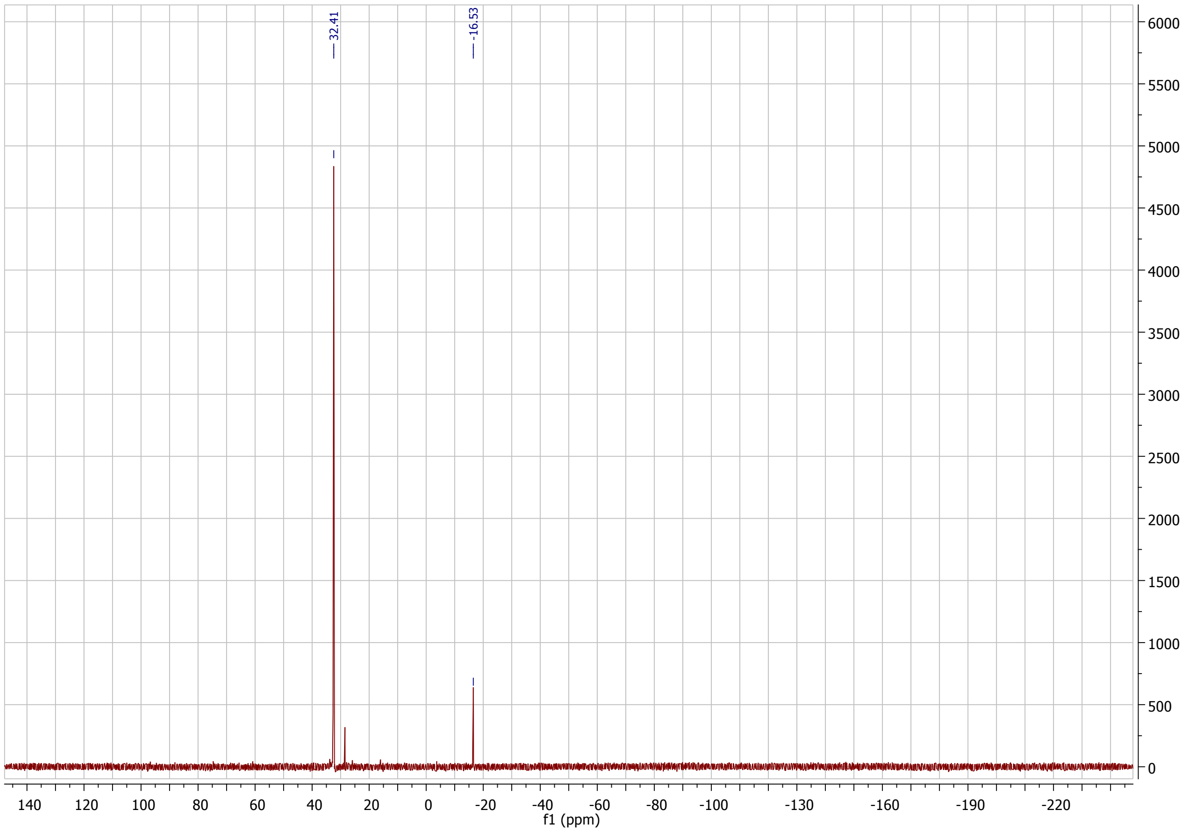


Figure 5: ^{31}P-NMR of the oxidized ligand after the 8th recycling run.
Chemical shift of the phosphorous(V) atom is **+32.41**

2.6. ICP-OES analytics

The content of phosphorous and palladium in the product phases were determined via ICP-OES (Iris Intrepid by *Thermo Elemental*). For this, 0.23 g of a sample was measured out in a Teflon cup and 2.5 mL nitric acid (65%) and 4 mL sulfuric acid (96%) were added. The digestion process was conducted in a *CEM* MARS 6 Digestion / Extraction System microwave. Upon completion of the digestion process, the samples were treated with 2 ml pure water (purified with PURELAB® flex 3 Water System, *ELGA LabWater*) and 1 mL of H_2O_2 (*Fisher Scientific*, optima grade, phosphorous free). The prepared samples were allowed to rest for twelve hours before measurement. All contents of phosphorous and palladium given in the tables were collected by double determination.

2.7. GC-FID and GC-MS analytics

Routine gas chromatographic analyses were performed on an *Agilent 7890B* instrument equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m, diameter 0.32 mm, film thickness 0.25 µm) connected to an auto sampler (*7693*) and an injector (*G4513A*). GC-MS analyses of the products were carried using an Agilent *5977A MSD* (70 eV) on the same device. For both GC-FID and GC-MS the following heat ramp was used with a split ratio of 50:1.

Table 8: Heat ramp for GC measurements

	heating rate / °C min^{-1}	Temperature / °C	hold time / min
Start	-/-	40	3
Ramp 1	7.5	150	0
Ramp 2	40	320	8