Supporting Information For:

Synthesis of Unsymmetrical 5,6-POCOP´-Type Pincer Complexes of Nickel (II): Impact of Nickelacycle Size on Structures and Spectroscopic Properties

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Table 1. ^{1}H NMR chemical shifts for all complexes

Comp.	2xCH_3 (dd) ($^{3}J_{HH}$ $^{3}J_{HP}$)	2xCH_3 (dd) ($^{3}J_{HH}$ $^{3}J_{HP}$)	2xCH_3 (dd) ($^{3}J_{HH}$ $^{3}J_{HP}$)	2xCH_3 (dd) ($^{3}J_{HH}$ $^{3}J_{HP}$)	2xCH (m)	2xCH (m)	OCH_2Ar (d) ($^{3}J_{HP}$)	ArH^3 (d) ($^{3}J_{HH}$)	ArH^4 (t) ($^{3}J_{HH}$ $^{4}J_{HH}$)	ArH^5 (d) ($^{3}J_{HH}$ $^{4}J_{HH}$)
ligand	0.91 (7, 2)	1.00 (7, 2)	1.10 (7, 2)	1.14 (7, 2)	1.76 (m)		4.72 (8)	6.82 (6)	6.90 (m)	
1	1.09 (7, 13)	1.16 (7, 14)	1.42 (7, 2)	1.46 (7, 2)	2.42 (m)		4.60 (17)	6.43 (6)	6.88 (m)	
2	0.96 (7, 13)	1.21 (7, 12)	1.37 (7, 17)	1.74 (7, 19)	2.02 (m)	2.90 (m)	4.54 (17)	6.35 (8)	6.74 (m)	
3	0.92 (7, 13)	1.05 (7, 12)	1.36 (7, 18)	1.55 (7, 19)	2.09 (m)	2.58 (m)	4.44 (17)	6.28 (7)	6.61 (7)	6.70 (7, 1)
4b	1.11 (7, 14)	1.30 (7, 14)	1.38 (7, 6)	1.43 (vt, 7)	1.97 (m)	2.30 (m)	4.89 (17)	6.79 (7)	6.87 (7)	7.02 (7)
5	1.21 (m)		1.40 (7, 16)	1.48 (7,16)	2.43 (m)		4.75 (15)	6.53 (7)	6.97 (7)	7.07 (8)
6	1.11 (7, 13)	1.16 (7, 19)	1.20 (7, 18)	1.25 (7, 19)	2.15 (m)		4.76 (16)	6.59 (8)	7.00 (7, 2)	8 (7)

Table 2. ^{13}C NMR chemical shifts for aliphatic carbons all complexes

Comp.	2xCH_3 (s)	2xCH_3 (s)	2xCH_3 (d) ($^{3}J_{CP}$)	2xCH_3 (d) ($^{3}J_{CP}$)	1xCH (d) ($^{1}J_{CP}$)	1xCH (d) ($^{1}J_{CP}$)	1xCH (d) ($^{1}J_{CP}$)	1xCH (d) ($^{1}J_{CP}$)	CH_2 (s)
ligand	17.81 (20)	17.53 (20)	16.92 (20)	16.82 (20)	28.13 (24) dd		28.31 (24) dd		74.03
1	17.10 d (15)		18.34 (4)	19.15 (5)	28.06 (24, 3)		28.47 (20, 3)		76.10
2	16.69	17.30	18.15 (6)	19.83 (7)	27.08 (21)		29.75 (16)		76.99
3	16.29	16.69	17.63 s	17.69 s	27.28 s		28.47 br		76.53 br
4b	17.54	18.39	19.06 (7)	20.68 (8)	27.93 (23)		30.60 (18, 3)		77.48
5	14.47	15.49 d (5)	16.68 (5)		25.68 (22)		26.67 (26)		72.59
6	16.87	17.01	17.78	18.83	27.44 dd (12, 3)		27.65 dd (12, 3)		75.12

Table 3. ^{13}C NMR chemical shifts for Aromatic ring for all complexes

Comp.	ArC^1 (dd) ($^2J_{CP}$)	ArC^2 (dd) ($^2J_{CP}$ $^3J_{CP}$)	ArC^3 (d) ($^3J_{CP}$)	ArC^4 (s)	ArC^5 (s)	ArC^6 (dd) ($^3J_{CP}$)
ligand	159.70 (9)	120.52 (2)	141.45 (8)	114.66 (6)	129.30	141.45 (8)
1	132.03 (42)	170.07 (17, 2)	111.63 (13)	127.17	120.89	142.15 (12)
2	142.11	170.24 (15)	111.93 (11)	127.46	121.30	142.63 (12)
3	136.47 (42)	169.65 (17, 2)	112.00 (13)	128.80	121.39	141.51 (12)
4b	133.96 (29)	169.39 (17)	112.78 (10)	128.31	122.15	143.49 (14)
5	136.21 (19)	167.71 (18)	108.15 (13)	124.10	117.61	139.74 (12)
6	142.40 pst. (20.4)	169.20 (18, 6)	110.47 (13)	125.74	119.56	143.05 (10)

Table 4. ^{31}P{^{1}H} NMR chemical shifts for all complexes

Compound	δ for ArO-*P* (multicplicity, $^2J_{pp}$ in Hz)	δ for ArCH$_2$O-*P* (multicplicity, $^2J_{pp}$ in Hz)
POCHOP´	154 (s)	147 (s)
1	187 (d, 283)	155 (d, 283)
2	189 (d, 302)	148 (d, 302)
3	189 (d, 285)	148 (d, 285)
4b	194 (d, 260)	152 (d, 260)
5	187 (d, 323)	160 (d, 323)
6	187 (d, 323)	160 (d, 323)

Table 5. Crystal Data Collection and Refinement Parameters for Complexes 1-6.

	1	**2**	**4b**	**5**	**6**
Chem. Formula	$C_{19}H_{33}O_2P_2Br_1Ni$	$C_{26}H_{40}O_5P_2S_1Ni$	$C_{57}H_{56}O_2P_2N_1B_1Ni$	$C_{22}H_{36}O_2P_2Ni$	$C_{20}H_{36}O_2P_2Ni$
Cryst. colour	yellow	yellow	yellow	yellow	yellow
Fw	494.01	585.29	833.05	450.15	429.14
T (K)	150	150	150	150	150
λ (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
Space Group	P-1	P21/c	Pbca	P-1	P-1
A (Å)	8.3325(2)	8.4032(3)	19.7665(4)	8.0421(7)	8.3833(2)
B (Å)	10.9016(2)	16.9796(7)	17.7155(4)	16.7084(15)	10.8596(2)
C(Å)	12.7875(3)	21.3710(8)	23.8071(6)	17.4737(16)	12.7379(3)
α (deg)	102.314(1)	90	90	90.814(4)	102.681(1)
β (deg)	94.699(1)	105.376(2)	90	90.648(4)	94.204(1)
γ (deg)	91.958(1)	90	90	97.959(4)	92.443(1)
Z	2	4	4	2	2
V(Å^3)	1129.45(4)	2940.1(2)	8336.6(3)	2324.9(4)	1126.26(4)
ρ_{calcd}	1.453	1.322	1.327	1.295	1.265
μ (cm^{-1})	47.20	29.08	17.14	26.03	26.55
θ range (deg)	4.16-67.42	3.37-67.95	3.71-67.92	2.53-68.00	3.57-67.96
R1 [a] [I>2σ]	0.0320	0.0300	0.0371	0.0506	0.0407
wR2[b] [I > 2σ(I)]	0.0853	0.0836	0.0979	0.1318	0.1124
R1[all data]	0.0340	0.0318	0.0380	0.0527	0.0412
WR2[all data]	0.0867	0.0846	0.0985	0.1335	0.1130
GOF	1.048	1.048	1.104	1.048	1.029

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

Table 6. Selected Bond Distances (Å) and Angles (deg) for Complexes 1-6.

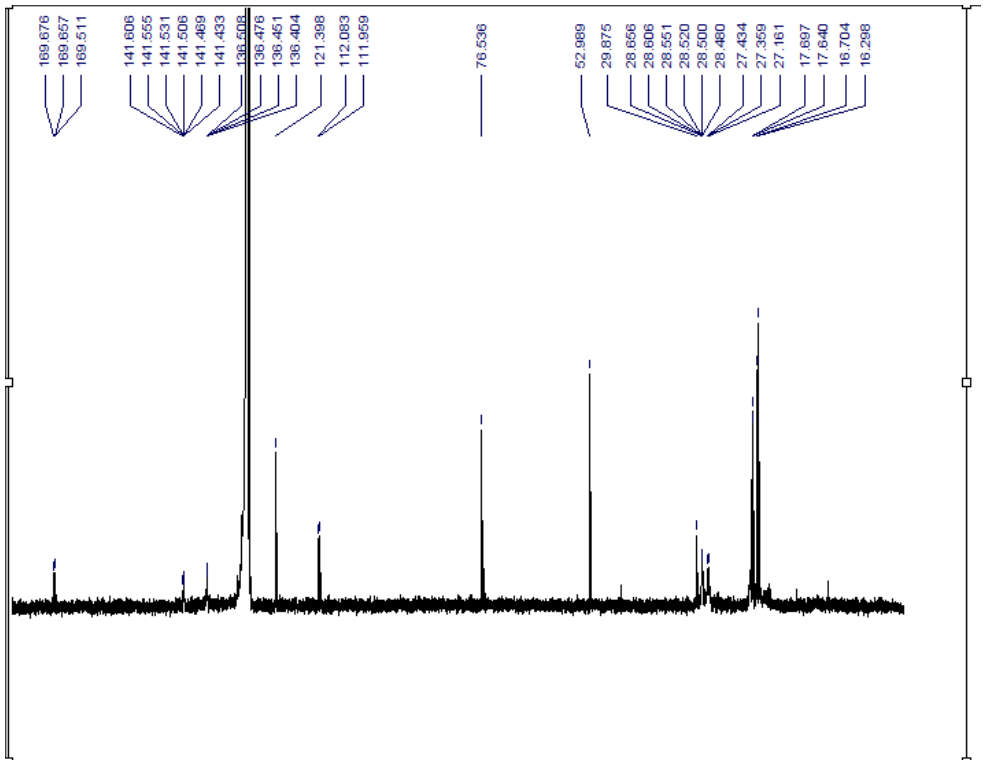
	1	**2**	**4b**	**5**[†]	**6**
Ni-C(1)	1.920(2)	1.916(2)	1.919(2)	1.936(3)	1.947(2)
Ni-P(1)	2.1443(7)	2.1684(5)	2.1559(5)	2.1267(8)	2.1177(6)
Ni-P(2)	2.1744(7)	2.1924(5)	2.1921(5)	2.1283(8)	2.1355(5)
Ni-X/L	2.3372(4)	1.937(1)	1.881(1)	1.9100(3)	2.065(2)
P(1)-Ni-P(2)	169.26(3)	169.19(2)	169.30(2)	170.26(4)	168.14(3)
P(1)-Ni-X	91.15(2)	94.39(4)	93.71(5)	92.24(9)	92.19(5)
P(2)-Ni-X	92.24(2)	88.55(4)	92.82(5)	91.28(9)	91.89(5)
P(1)-Ni-C(1)	83.39(6)	83.95(5)	81.56(5)	85.39(10)	83.03(6)
P(2)-Ni-C(1)	93.06(6)	92.92(5)	91.86(5)	93.76(10)	92.78(6)
C(1)-Ni-X	174.53(6)	178.26(6)	175.27(7)	176.57(13)	175.22(8)
Twist angle[‡]	21	16	25	9	22
Tetrahedral distortion[*]	0.197	0.280	0.000	0.124	0.213

[†]All the values cited for this complex represent averages of the corresponding values in two independent molecules.

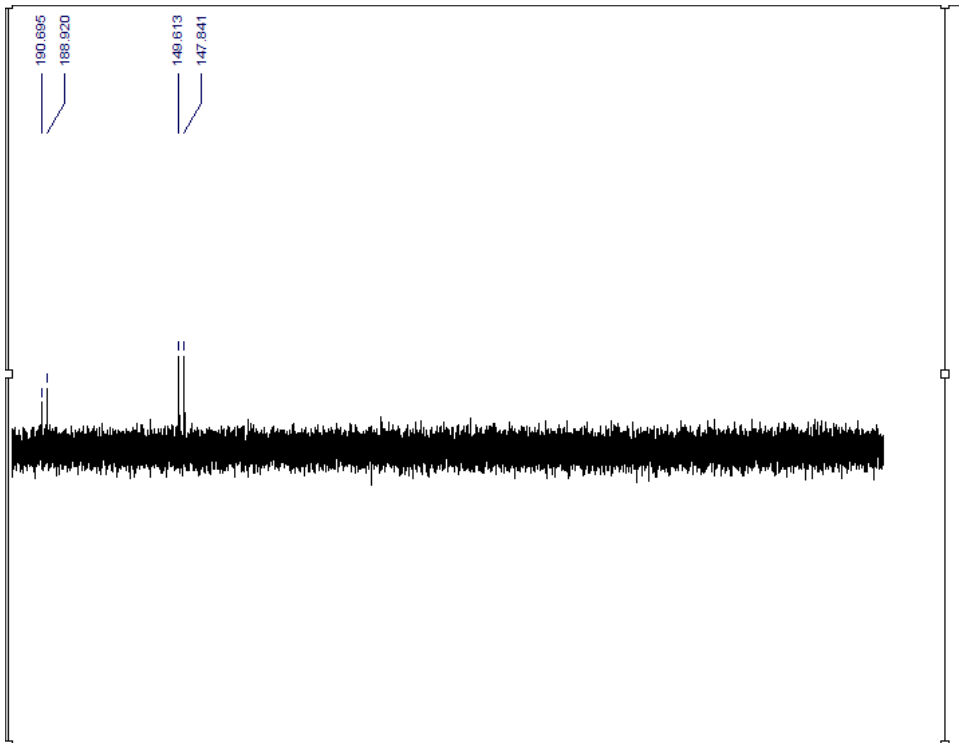
[‡] Twist angle is defined as the angle between the (mean) planes encompassing the benzenic moiety of the 5,6-POCOP′ ligand (C(1)-C(6)) and the atoms P(1), C(1), and P(2).

[*] Distance of Ni from the plane defined by the atoms P(1), C(1), and P(2).

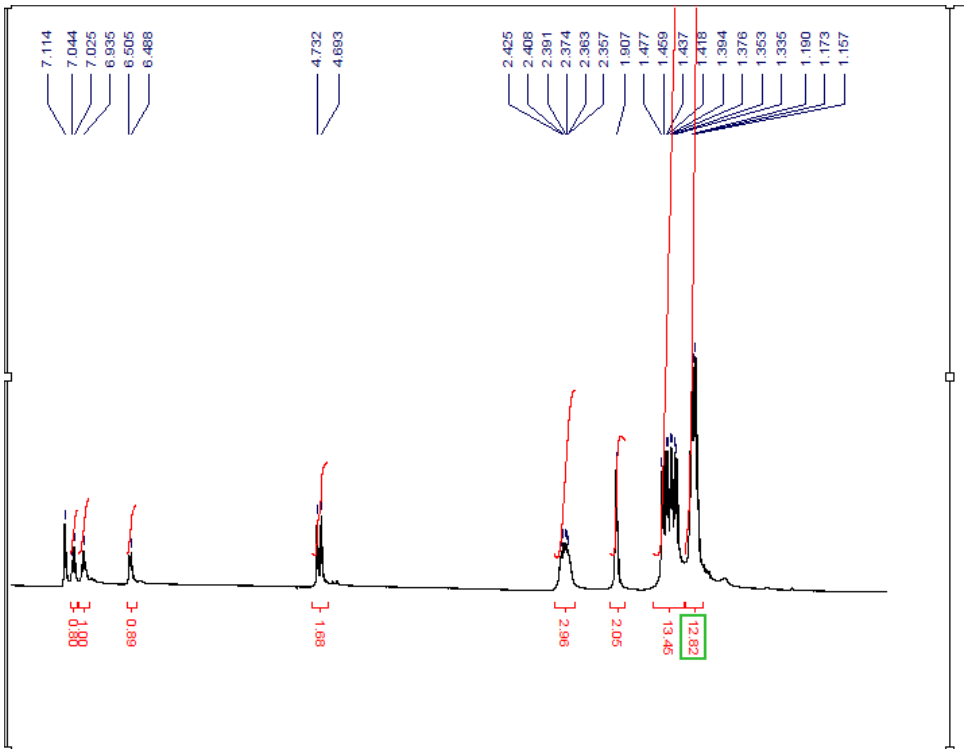
Complex 3 : $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6)



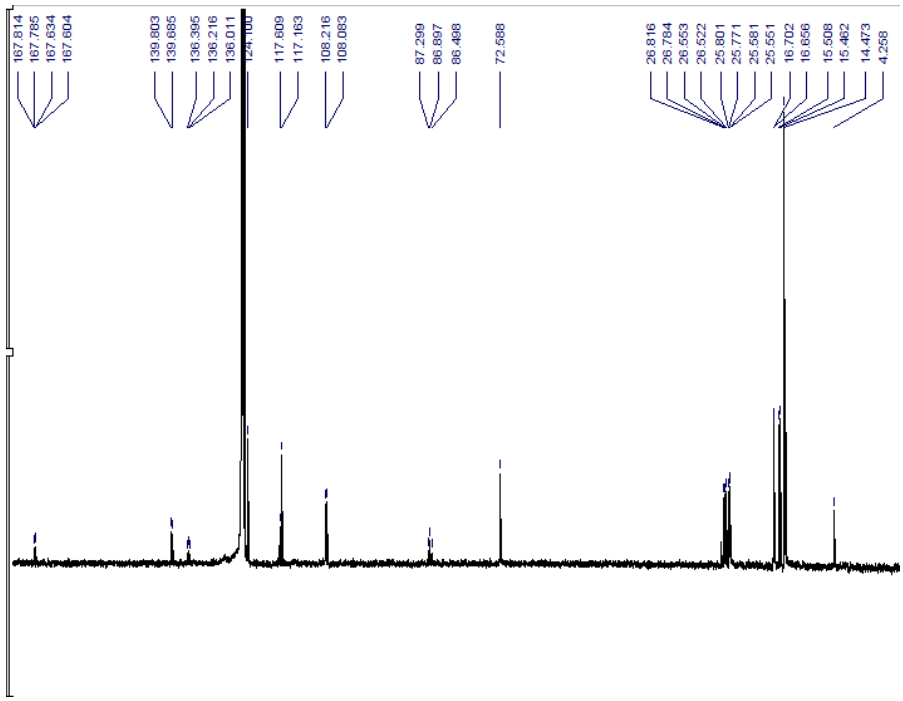
Complex 3 : $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6)



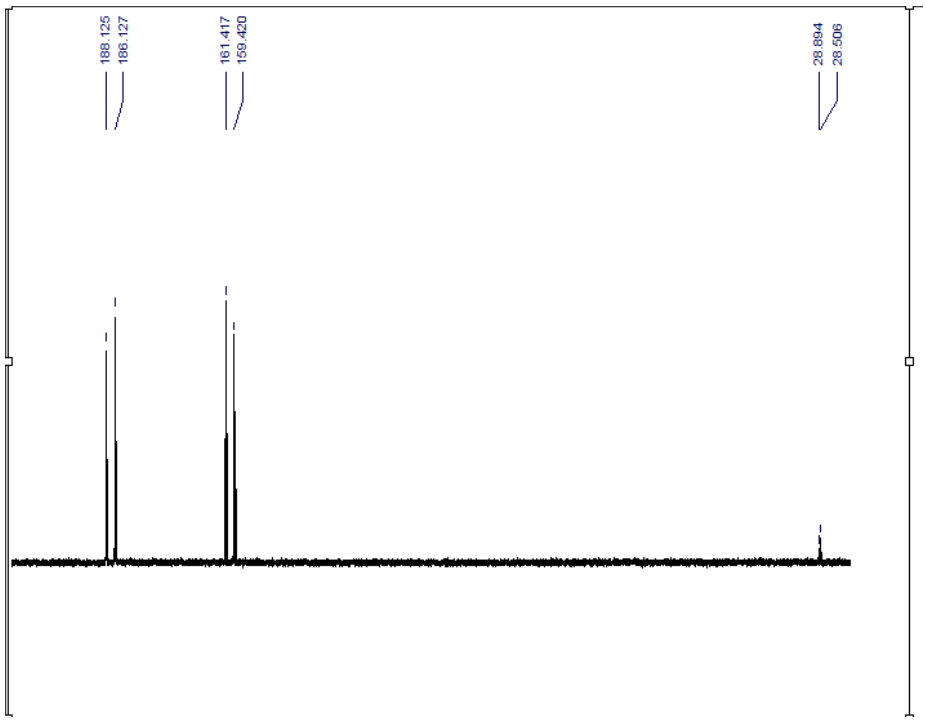
Complex 5: ^{1}H NMR (400 MHz, C_6D_6)



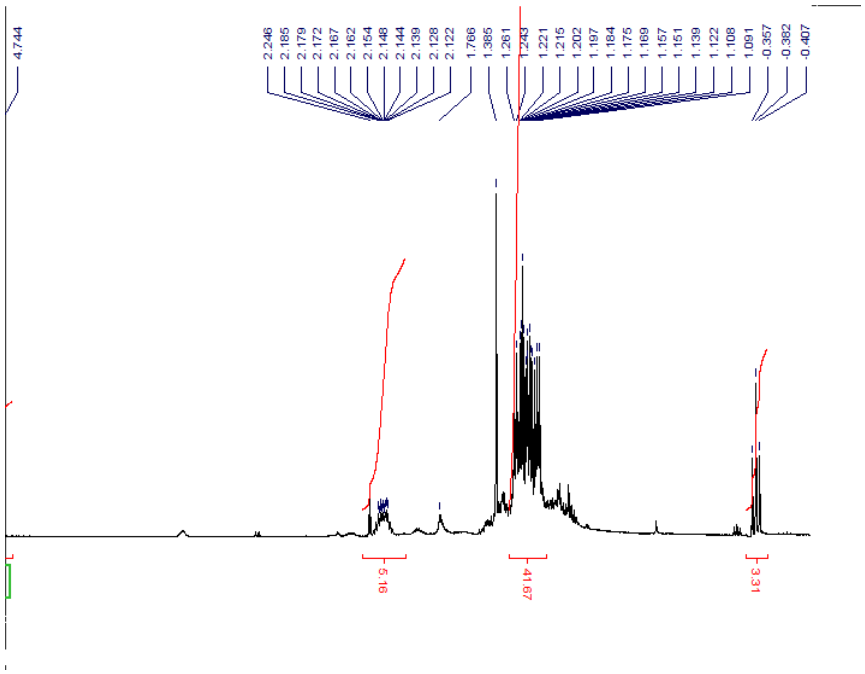
Complex 5: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6)



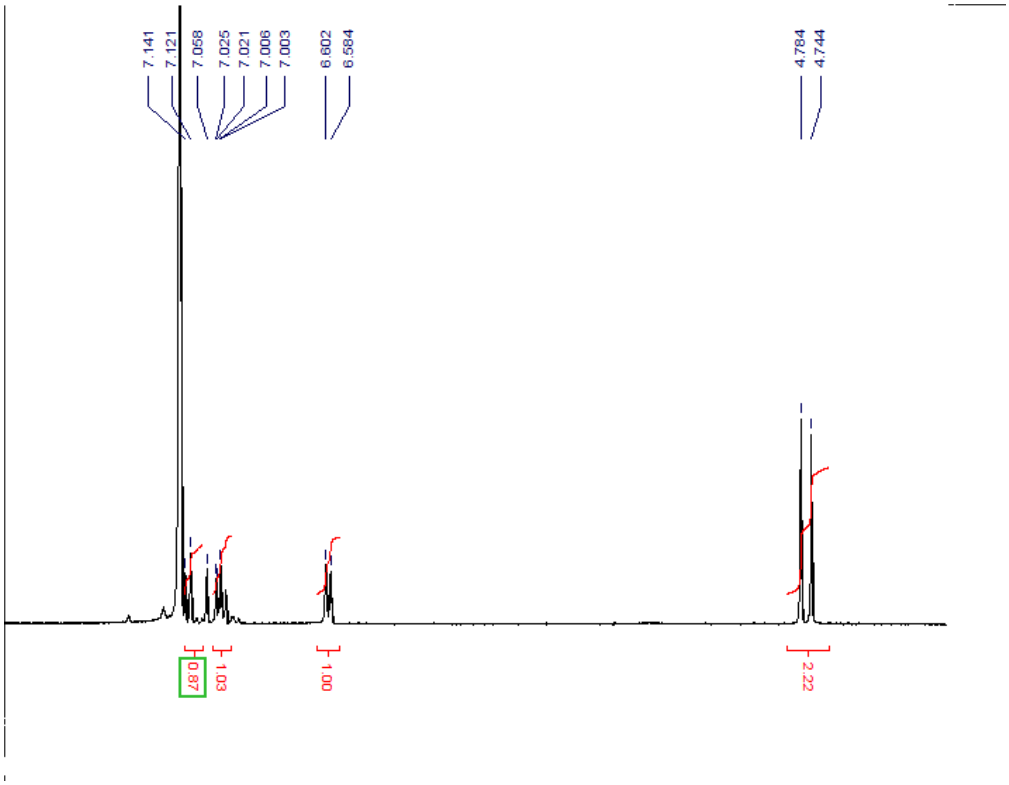
Complex 5: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6)



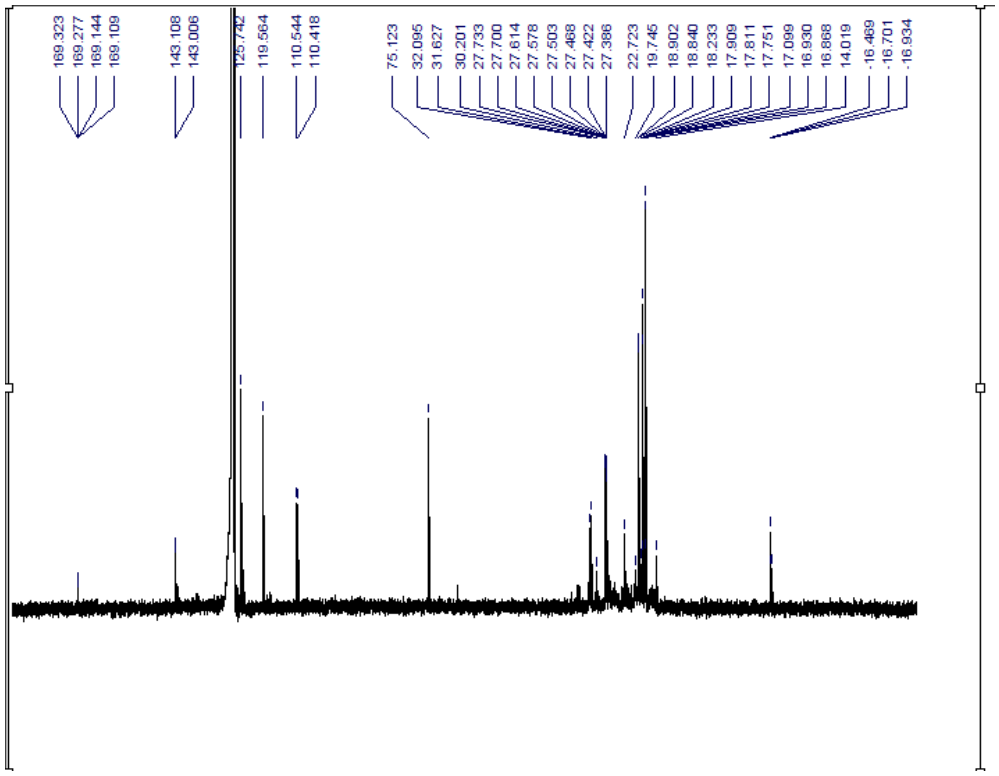
Complex 6: aliphatic region of ^{1}H NMR (400 MHz, C_6D_6)



Complex 6: vinylic/aromatic region of ^{1}H NMR (400 MHz, C_6D_6)



Complex 6: $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6)



Complex 6: $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6)