5 Appendix of Chapter 3

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5.1.1 Synthesis of complexes

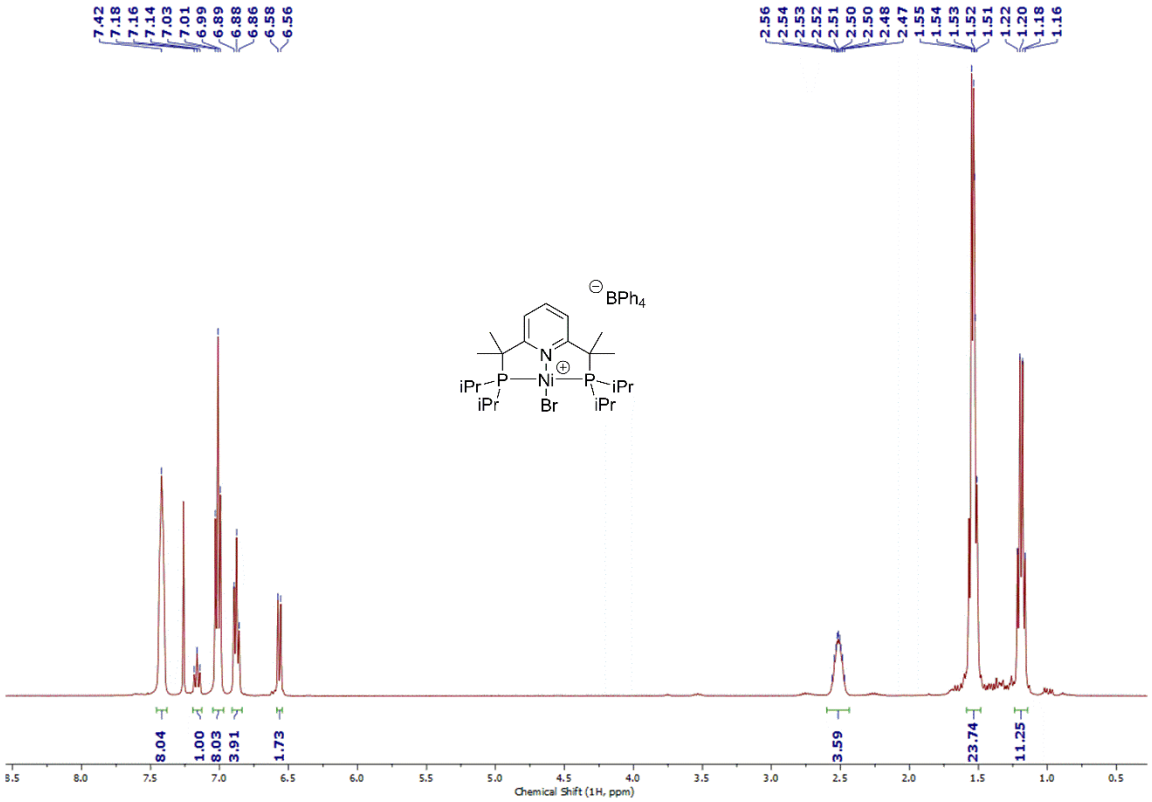


Figure 5. 1 ^{1}H NMR spectrum of **3.24** (400 MHz, $CDCl_3$).

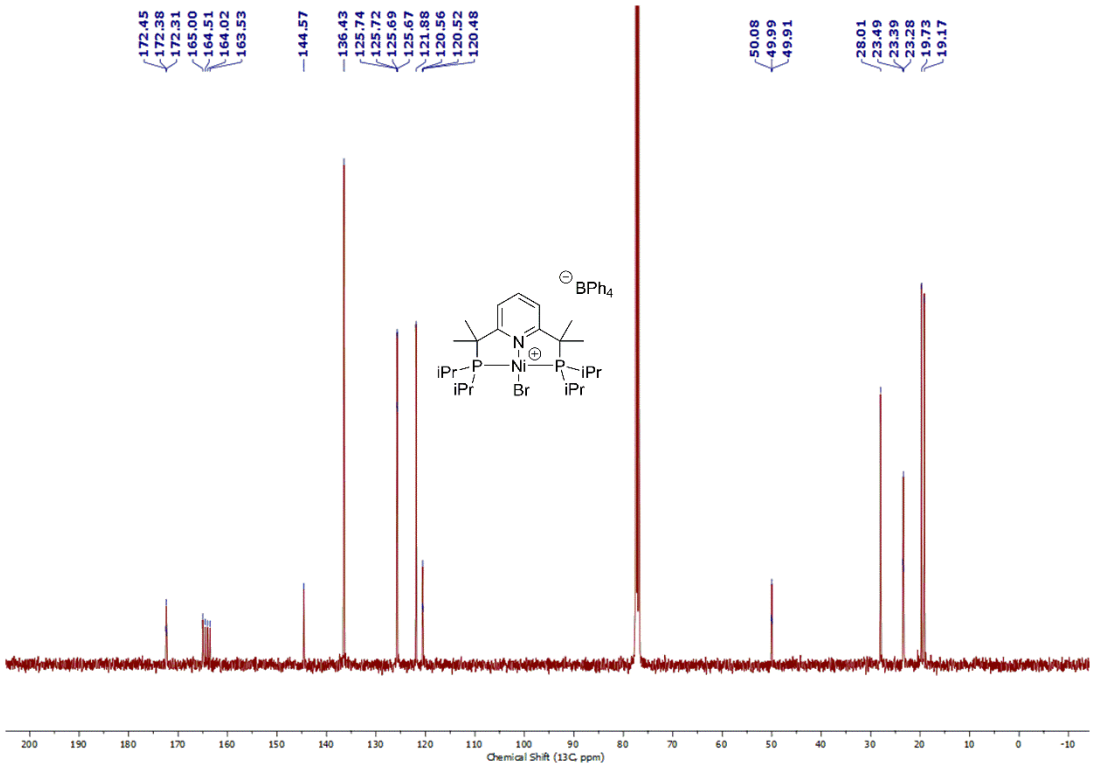


Figure 5. 2 $^{13}C\{^{1}H\}$ NMR spectrum of **3.24** (101 MHz, $CDCl_3$).

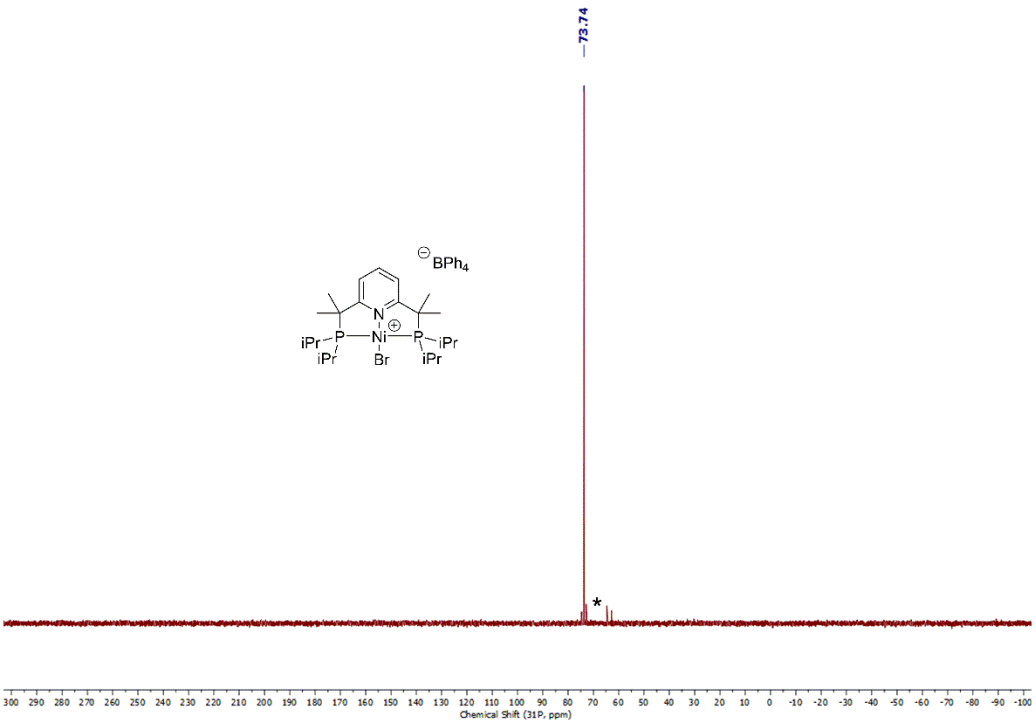


Figure 5. 3 $^{31}P\{^{1}H\}$ NMR spectrum of **3.24** (162 MHz, $CDCl_3$). Asterisk(*) marks trace of an unidentified unsymmetrical species.

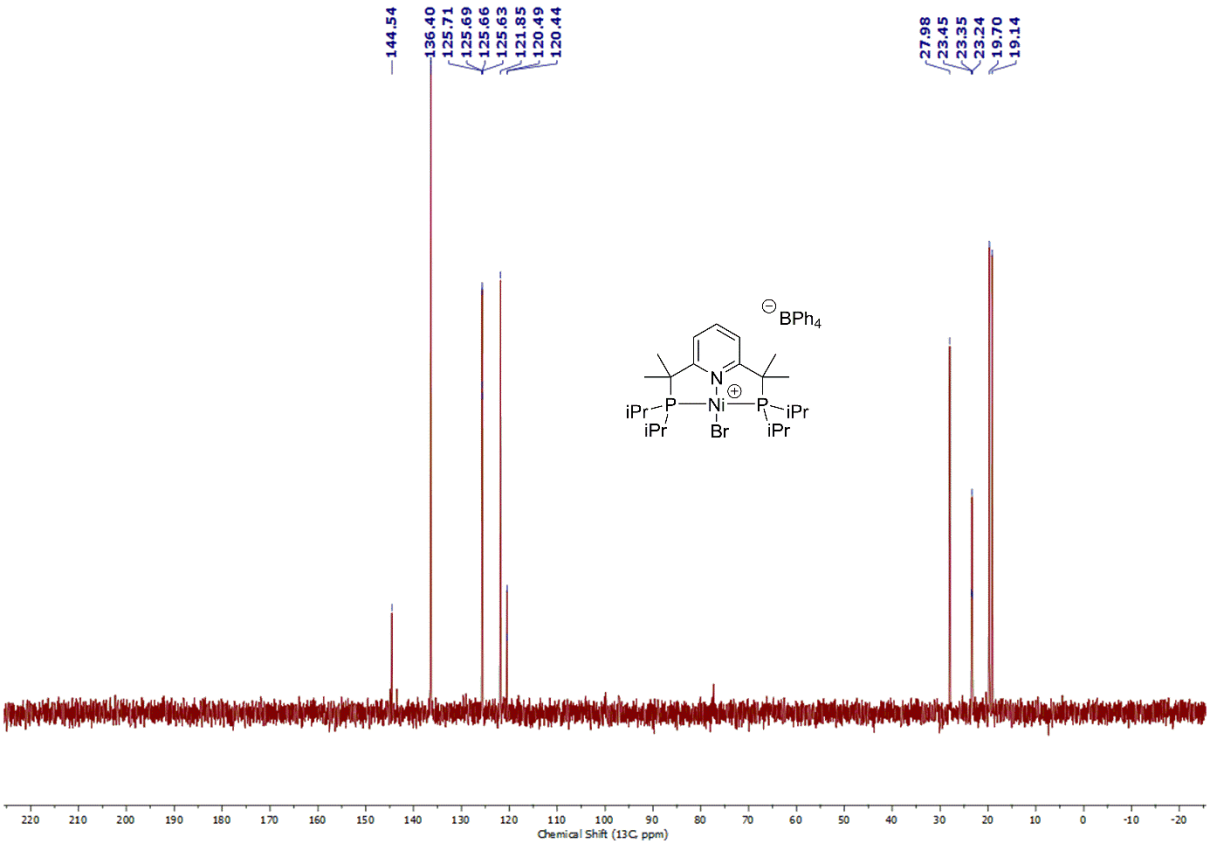


Figure 5. 4 DEPT-135 NMR spectrum of **3.24** (162 MHz, $CDCl_3$).

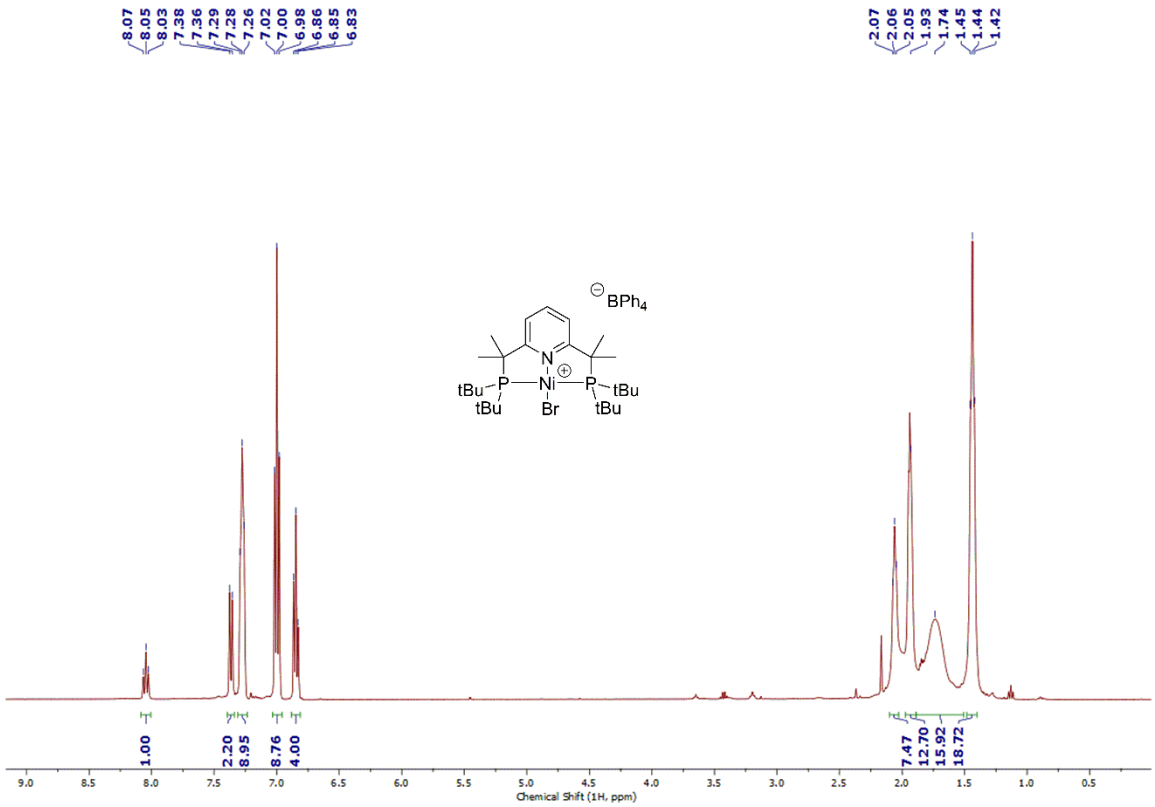


Figure 5. 5 ^{1}H NMR spectrum of **3.25** (400 MHz, CD_3CN).

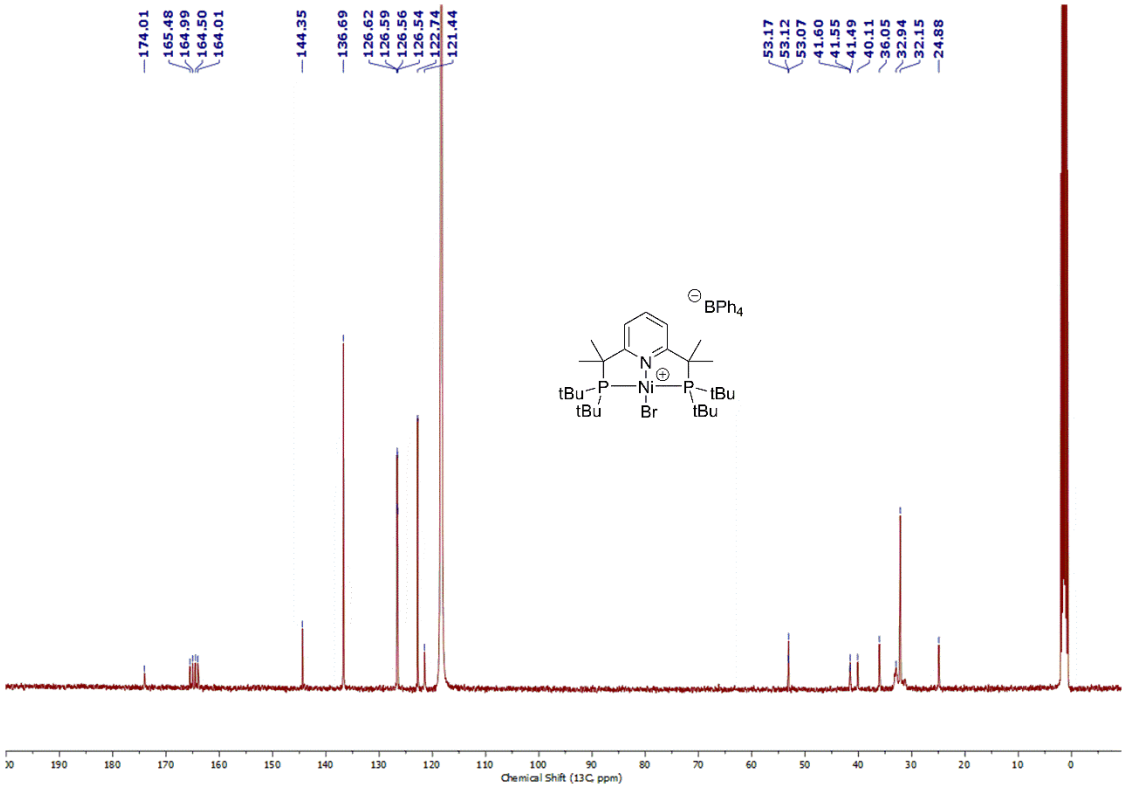


Figure 5. 6 $^{13}C\{^{1}H\}$ NMR spectrum of **3.25** (101 MHz, CD_3CN).

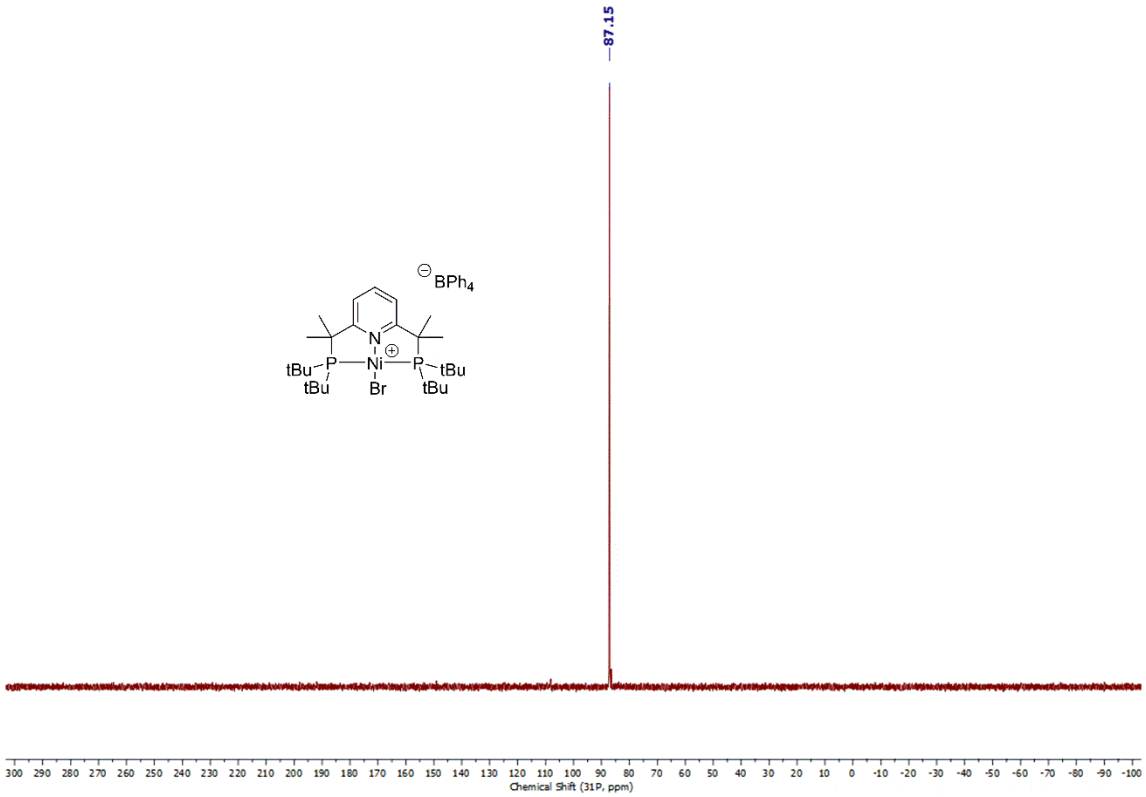


Figure 5. 7 $^{31}P\{^{1}H\}$ NMR spectrum of **3.25** (162 MHz, CD_3CN)

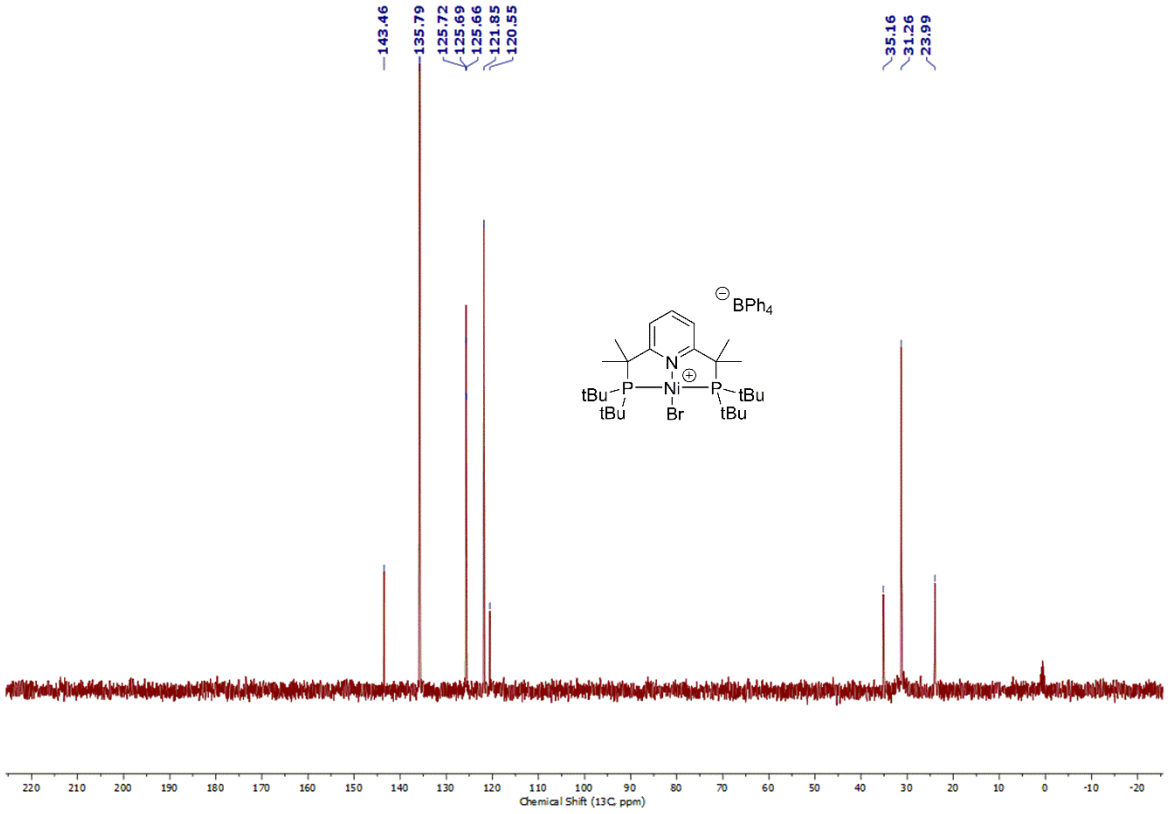


Figure 5. 8 DEPT-135 NMR spectrum of **3.25** (101 MHz, CD_3CN).

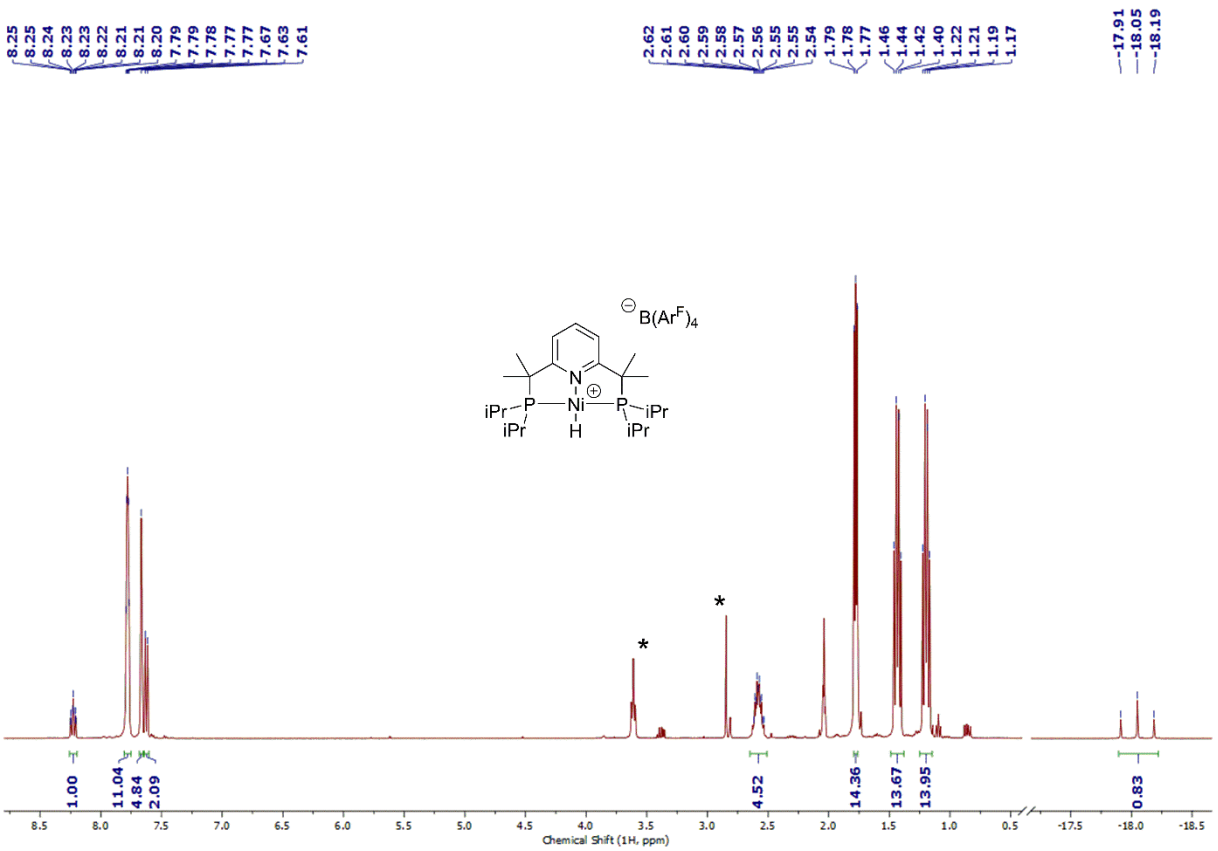


Figure 5. 9 ^{1}H NMR spectrum of **3.26** (400 MHz, acetone-d_6). Asterisks (*) marks traces of DCM and water.

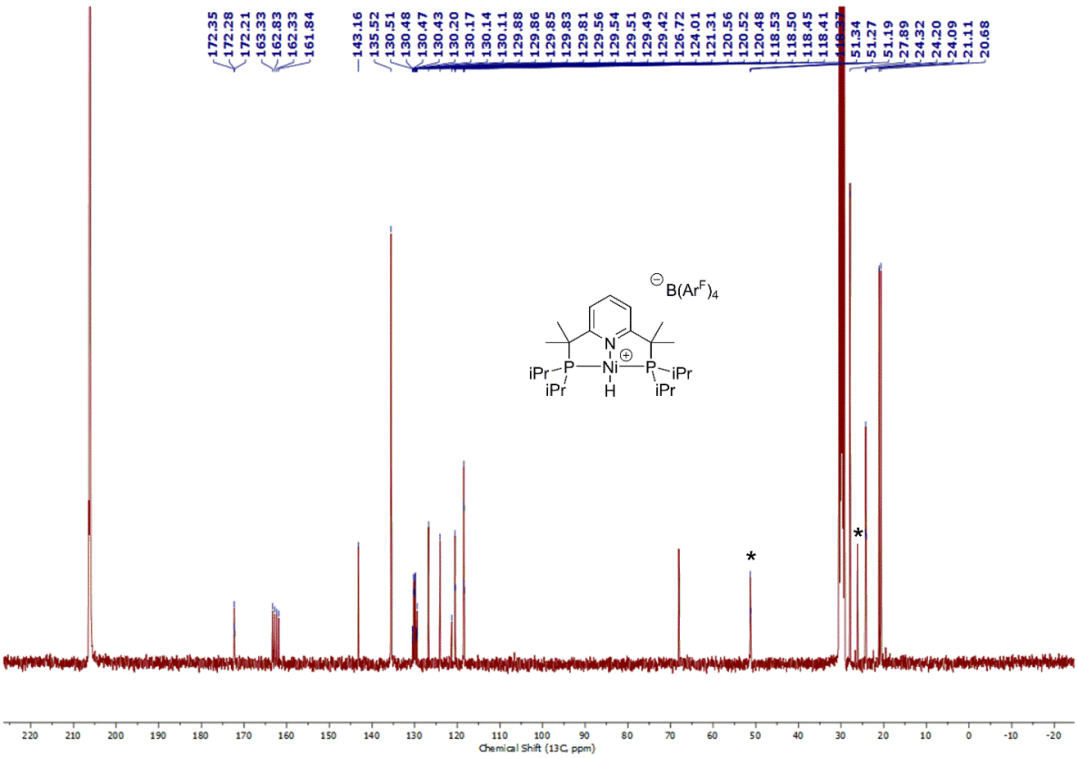


Figure 5. 10 ^{13}C{^{1}H} NMR spectrum of **3.26** (101 MHz, acetone-d_6). Asterisk (*) marks trace of DCM and THF

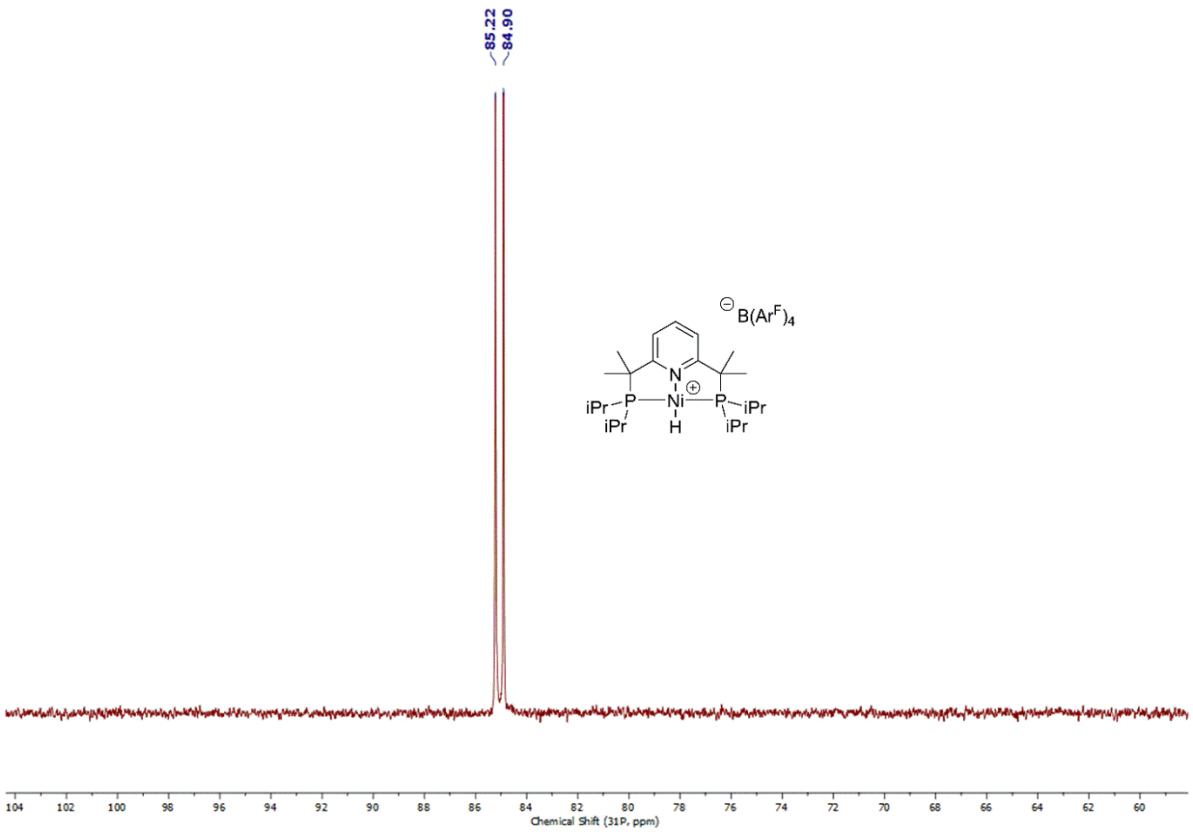


Figure 5. 11 $^{31}P\{^{1}H\}$ NMR spectrum of **3.26** (162 MHz, acetone-d_6).

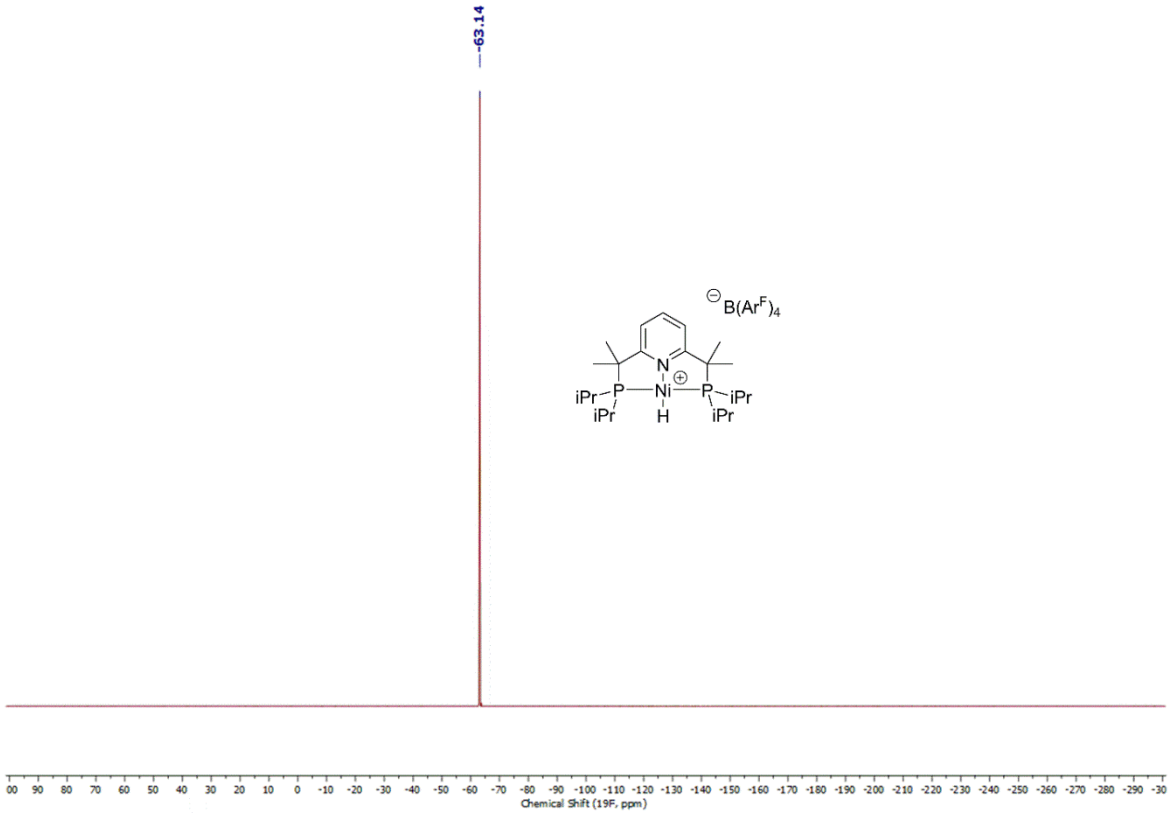


Figure 5. 12 ^{19}F NMR spectrum of **3.26** (376.2 MHz, acetone-d_6)

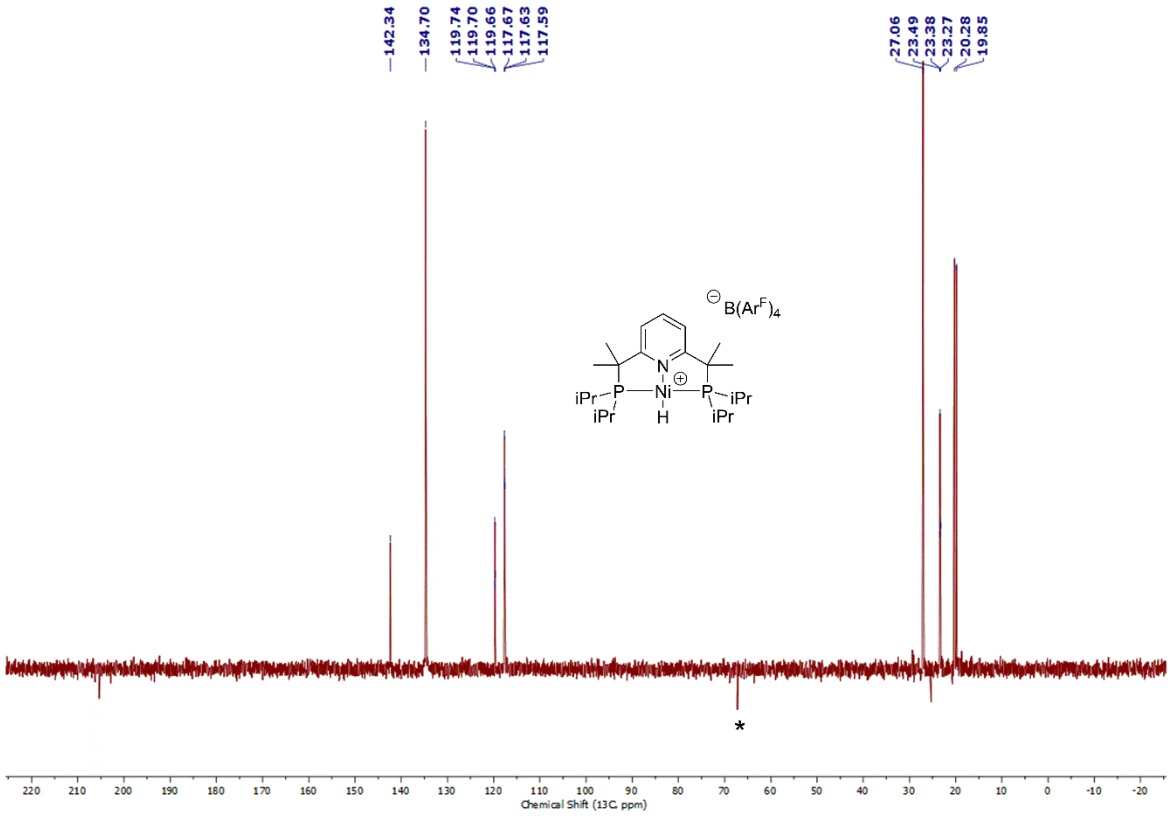
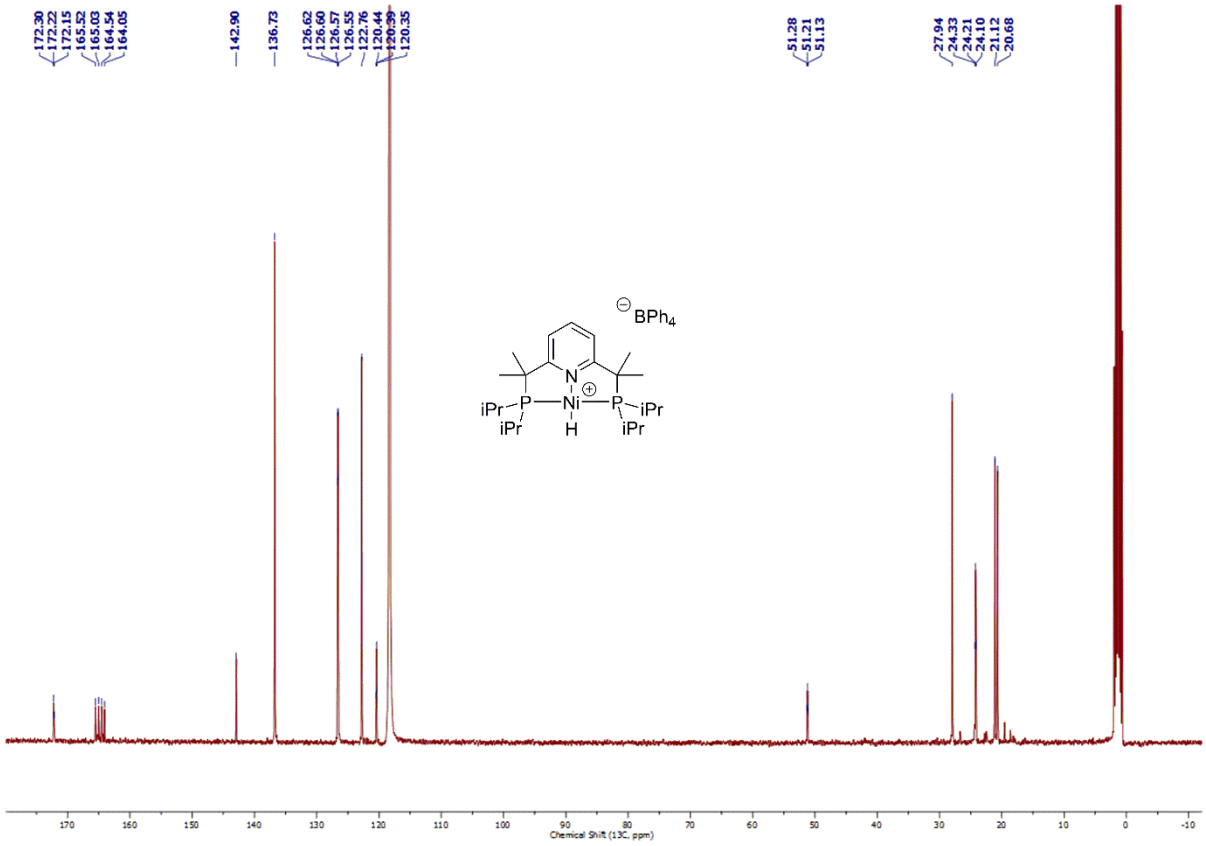


Figure 5. 13 DEPT-135 NMR spectrum of **3.26** (101 MHz, acetone-d_6). Asterisk(*) marks traces of DCM



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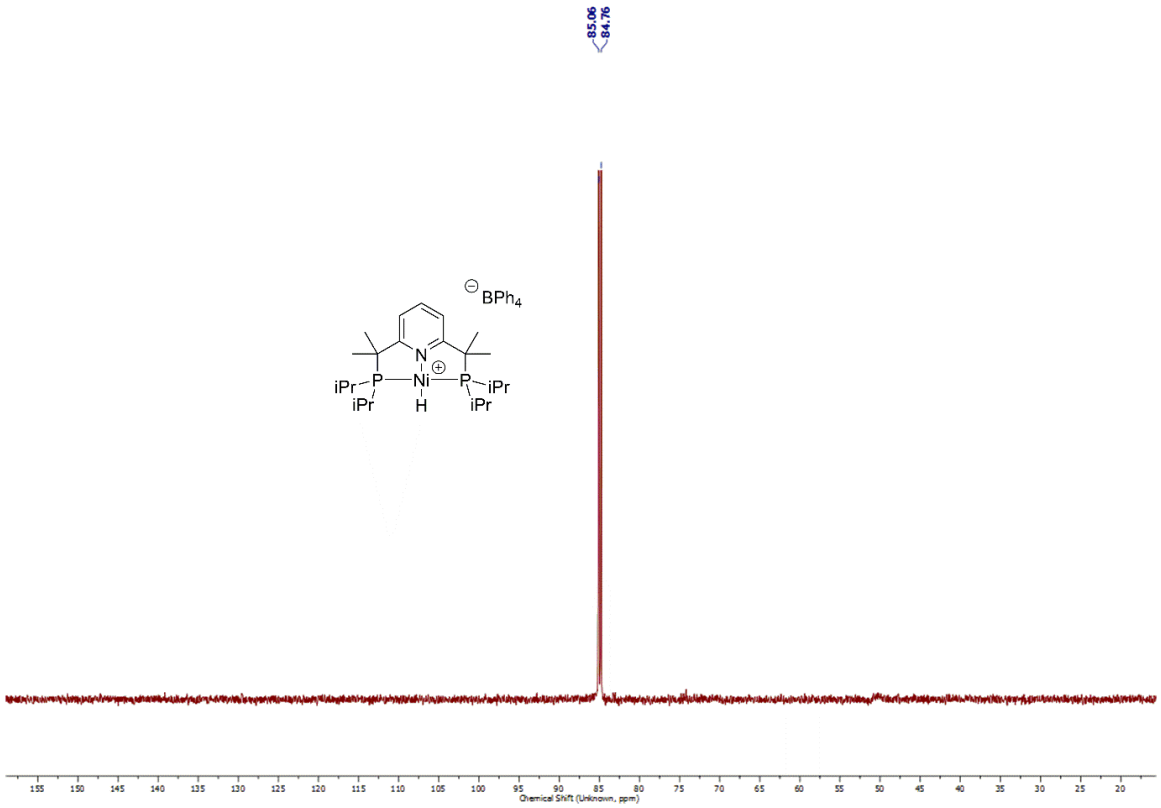


Figure 5. 15 $^{31}P\{^{1}H\}$ NMR spectrum of **3.27** (162 MHz, CD_3CN). The doublet arises from incomplete decoupling from Ni-H. **.**

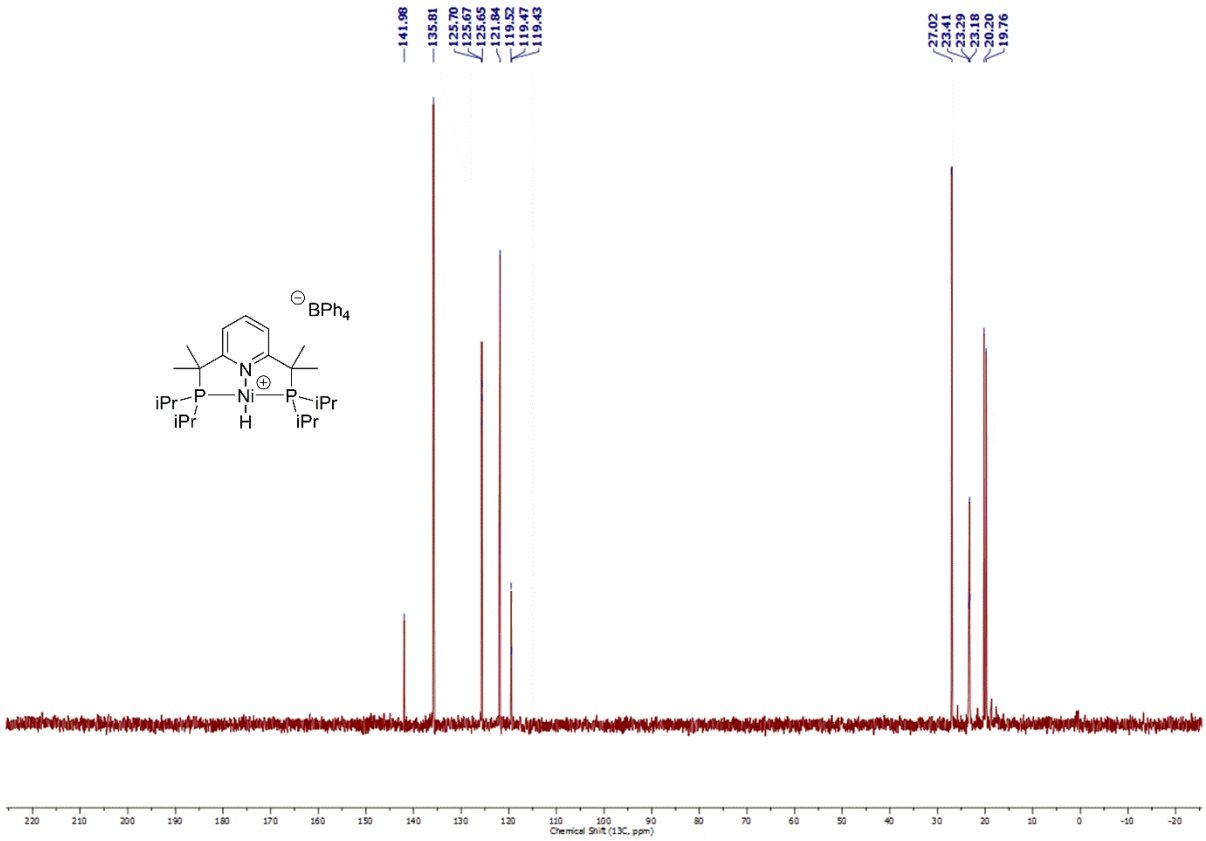
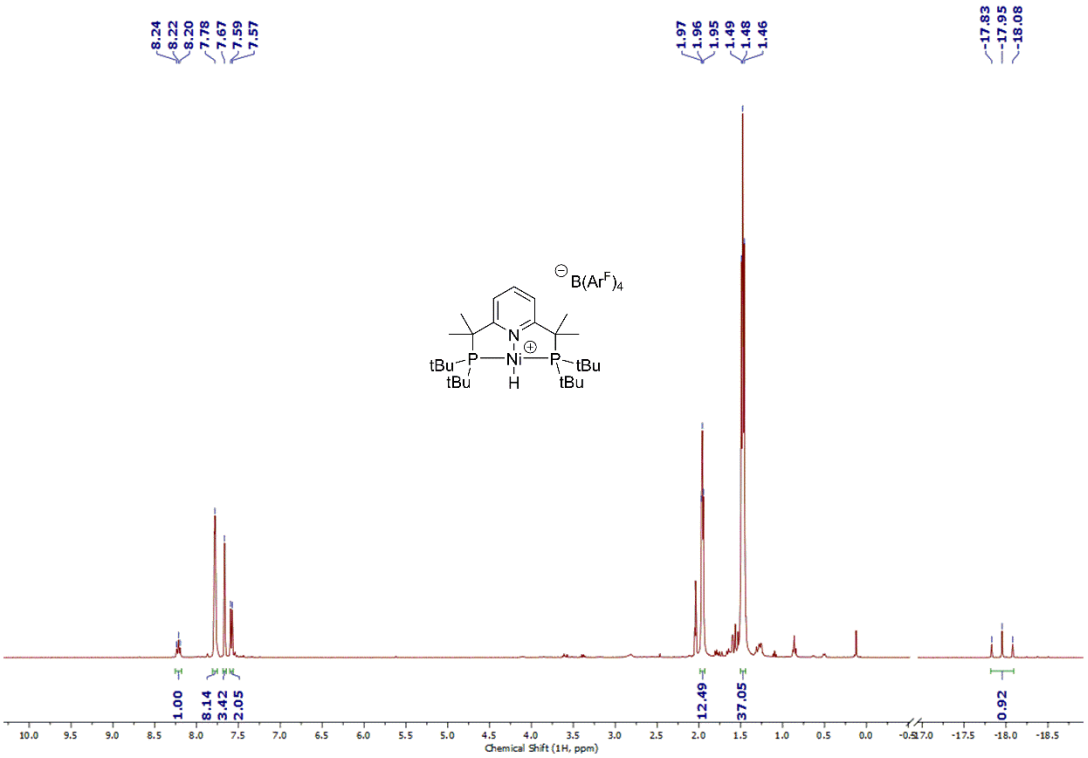


Figure 5. 16 DEPT-135 NMR spectrum of **3.27** (101 MHz, CD_3CN)



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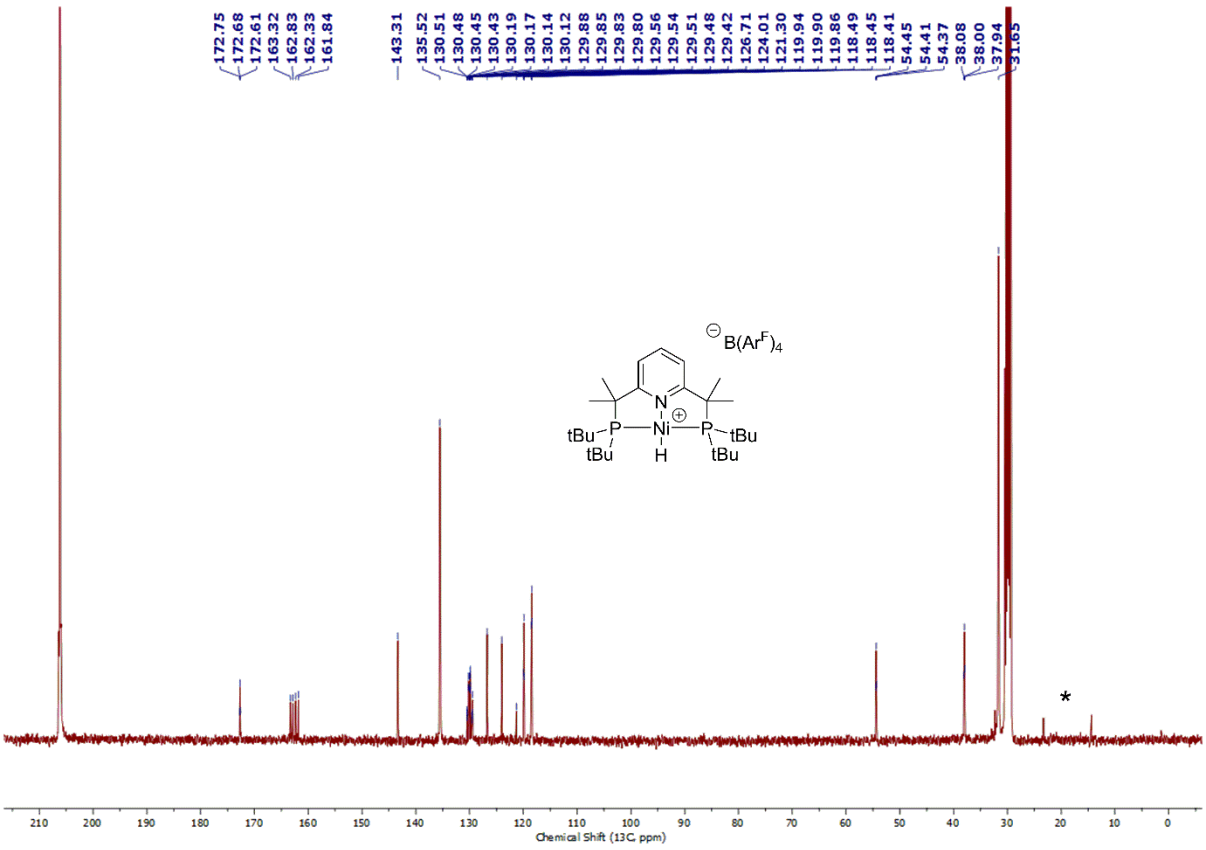


Figure 5. 18 ^{13}C{^{1}H} NMR spectrum of **3.28** (101 MHz, acetone-d_6). Asterisk(*) marks traces of solvents

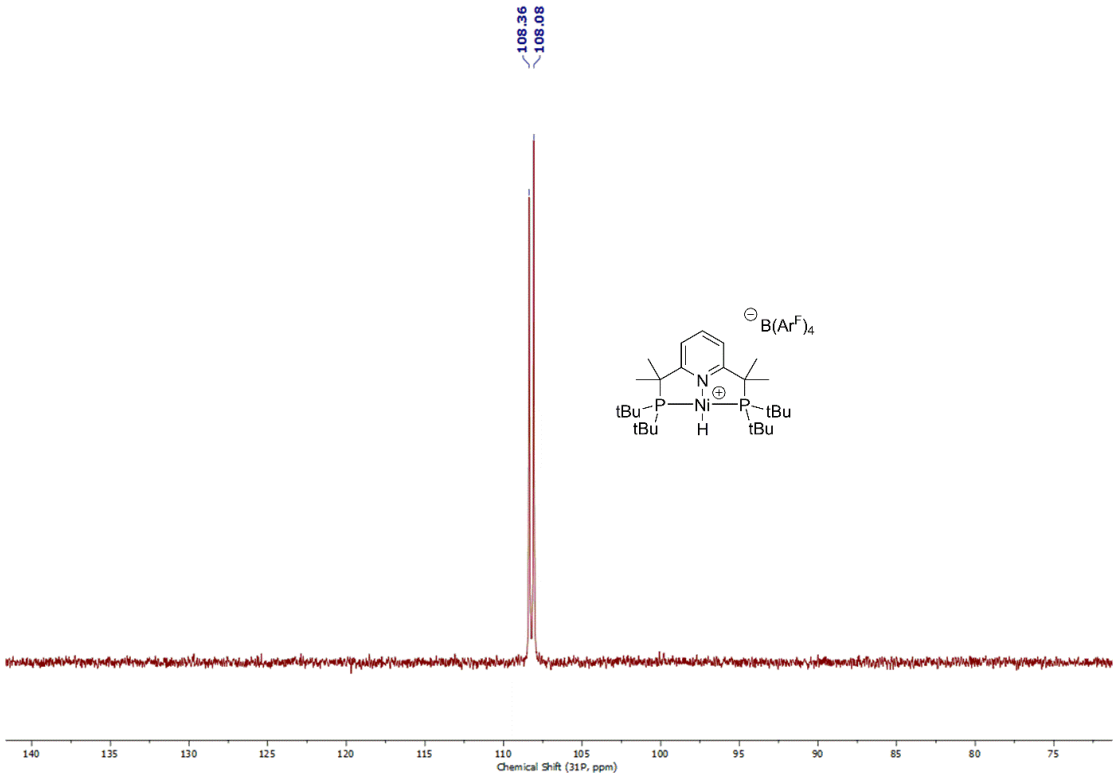


Figure 5. 19 $^{31}P\{^{1}H\}$ NMR spectrum of **3.28** (162 MHz, acetone-d_6). The doublet arises from incomplete decoupling from Ni-H

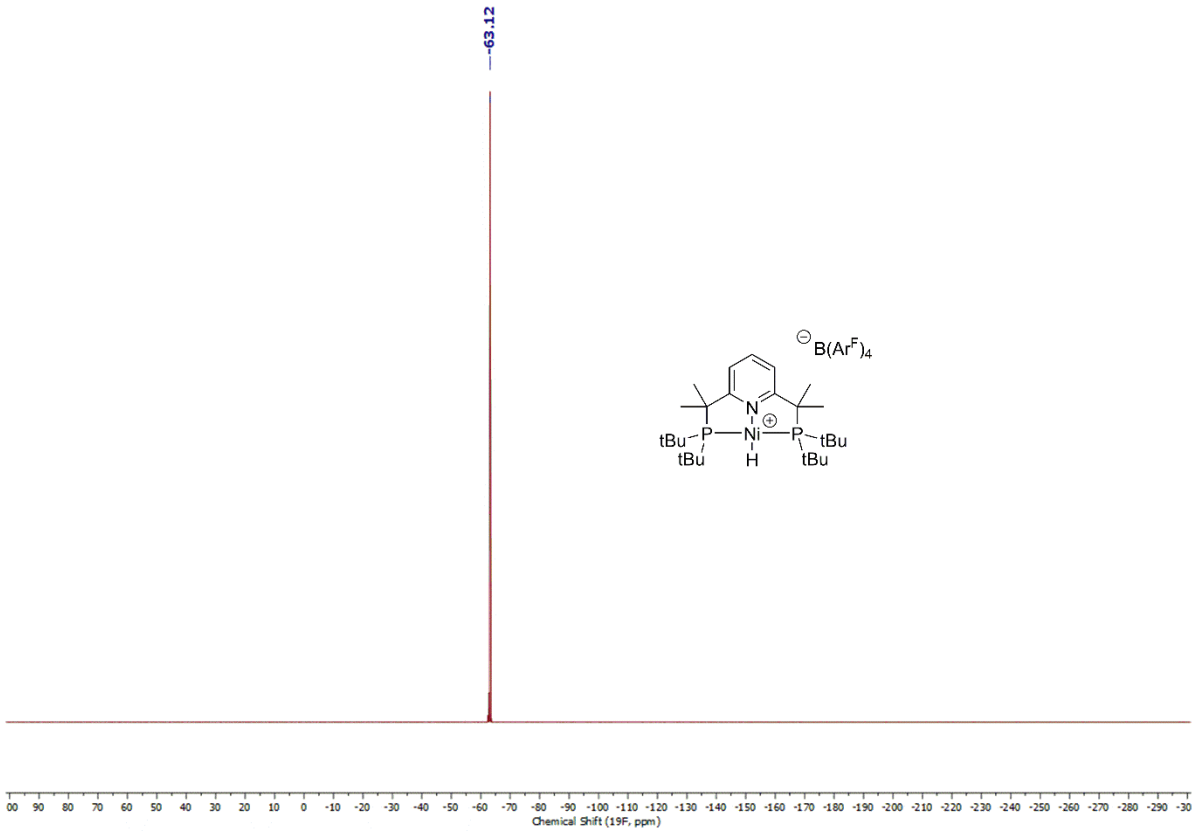


Figure 5. 20 ^{19}F NMR spectrum of **3.28** (376.2 MHz, acetone-d_6)

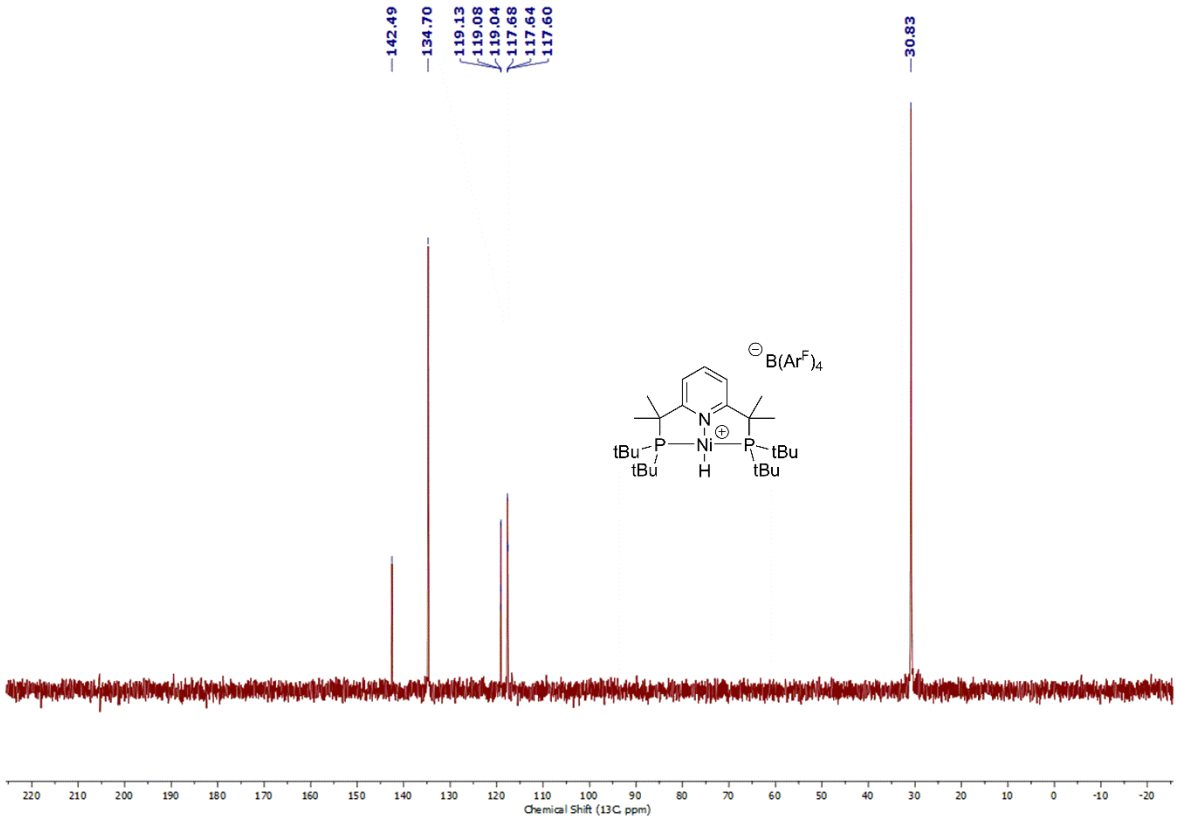


Figure 5. 21 DEPT-135 NMR spectrum of **3.28** (101 MHz, acetone-d_6)

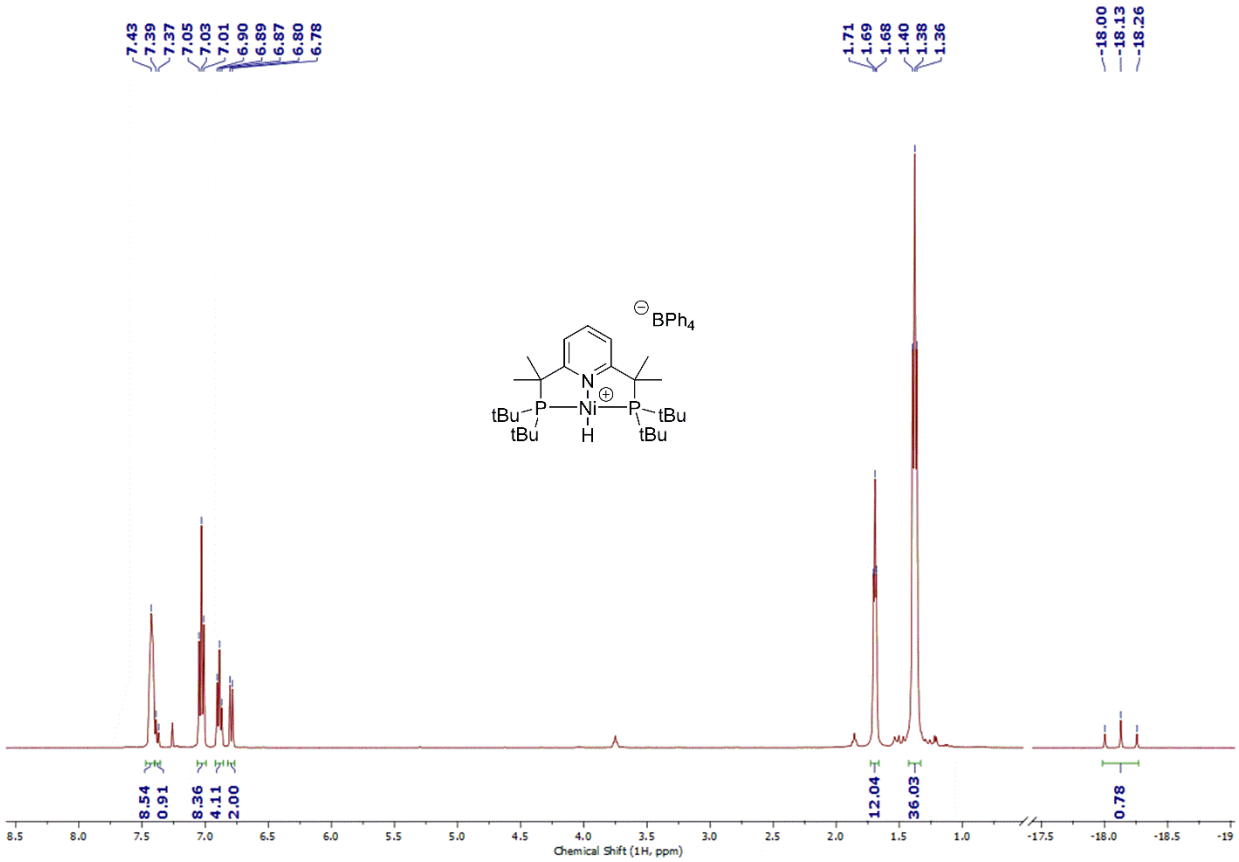


Figure 5. 22 ^{1}H NMR spectrum of **3.29** (400 MHz,$CDCl_3$).

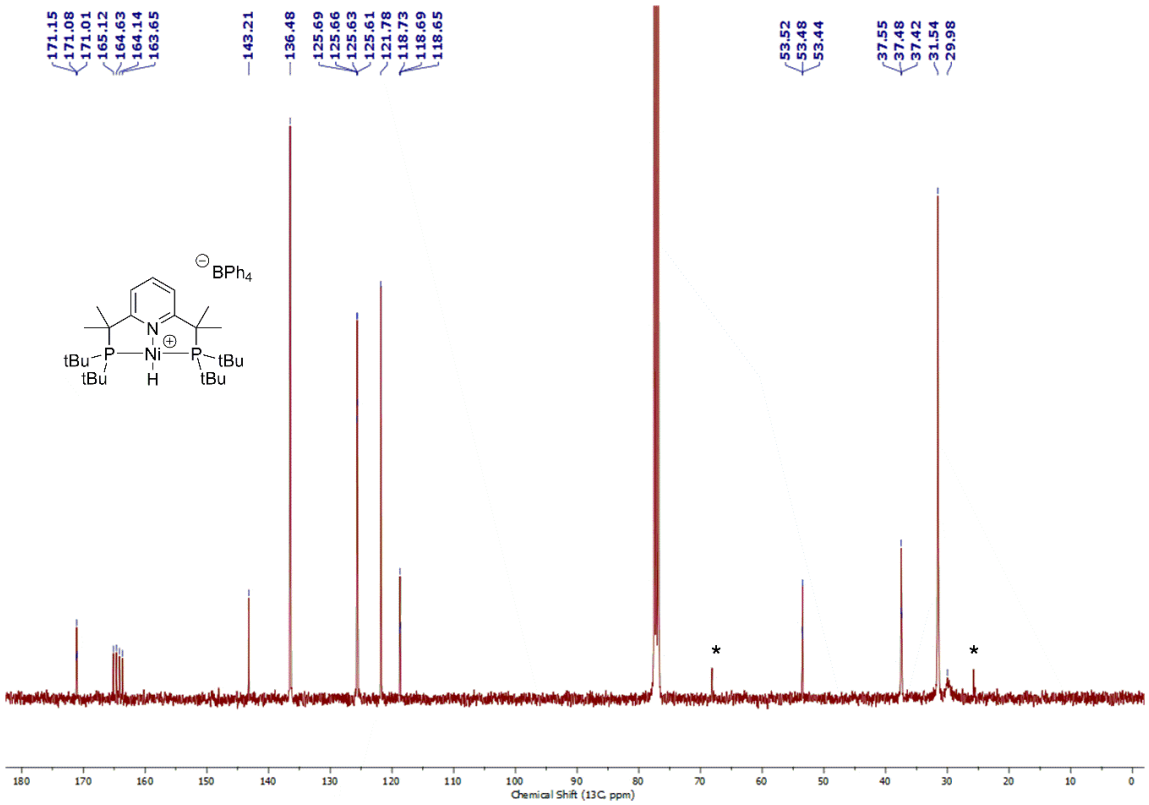


Figure 5. 23 $^{13}C\{^{1}H\}$ NMR spectrum of **3.29** (101 MHz,$CDCl_3$). Asterisk (*) marks traces of THF.

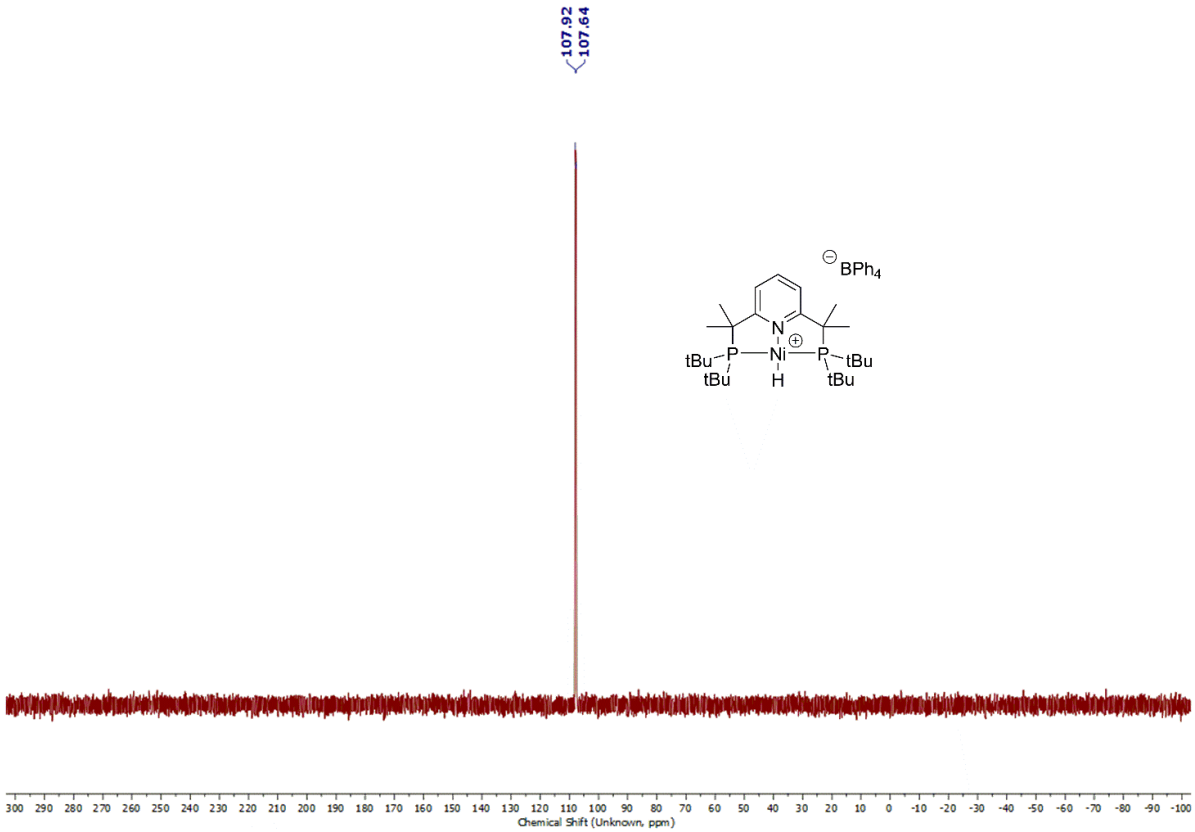


Figure 5. 24 $^{31}P\{^{1}H\}$ NMR spectrum of **3.29** (162 MHz,$CDCl_3$). The doublet arises from incomplete decoupling from Ni-H.

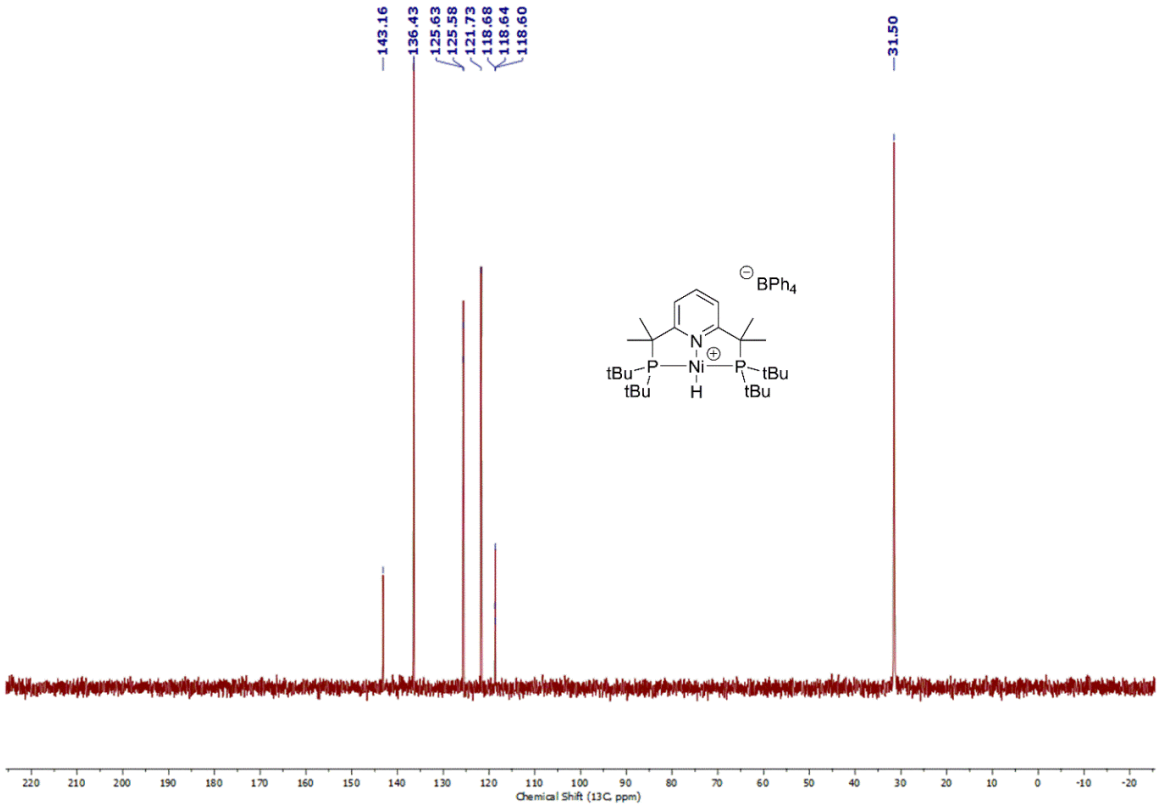


Figure 5. 25 DEPT-135 NMR spectrum of **3.29** (101 MHz,$CDCl_3$).

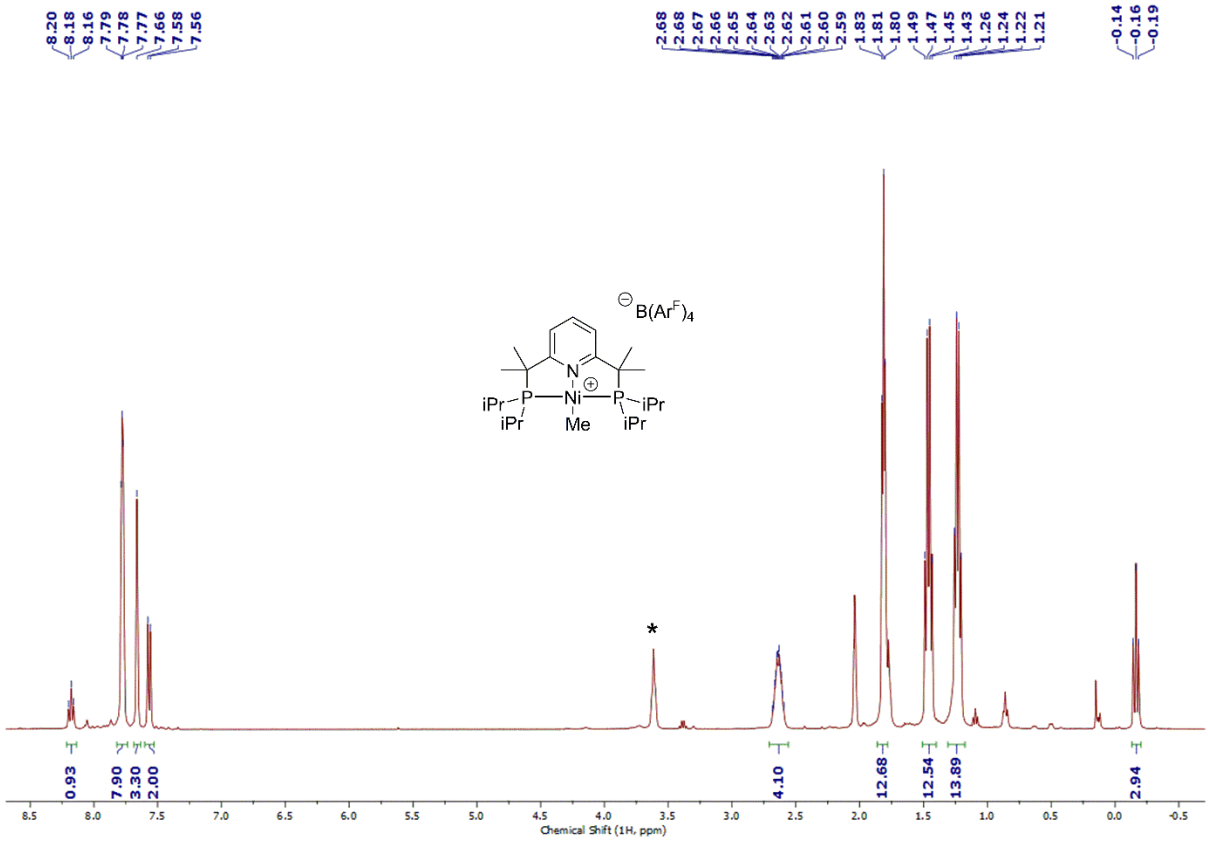


Figure 5. 26 ^{1}H NMR spectrum of **3.30** (400 MHz, acetone-d_6). Asterisk(*) marks trace THF.

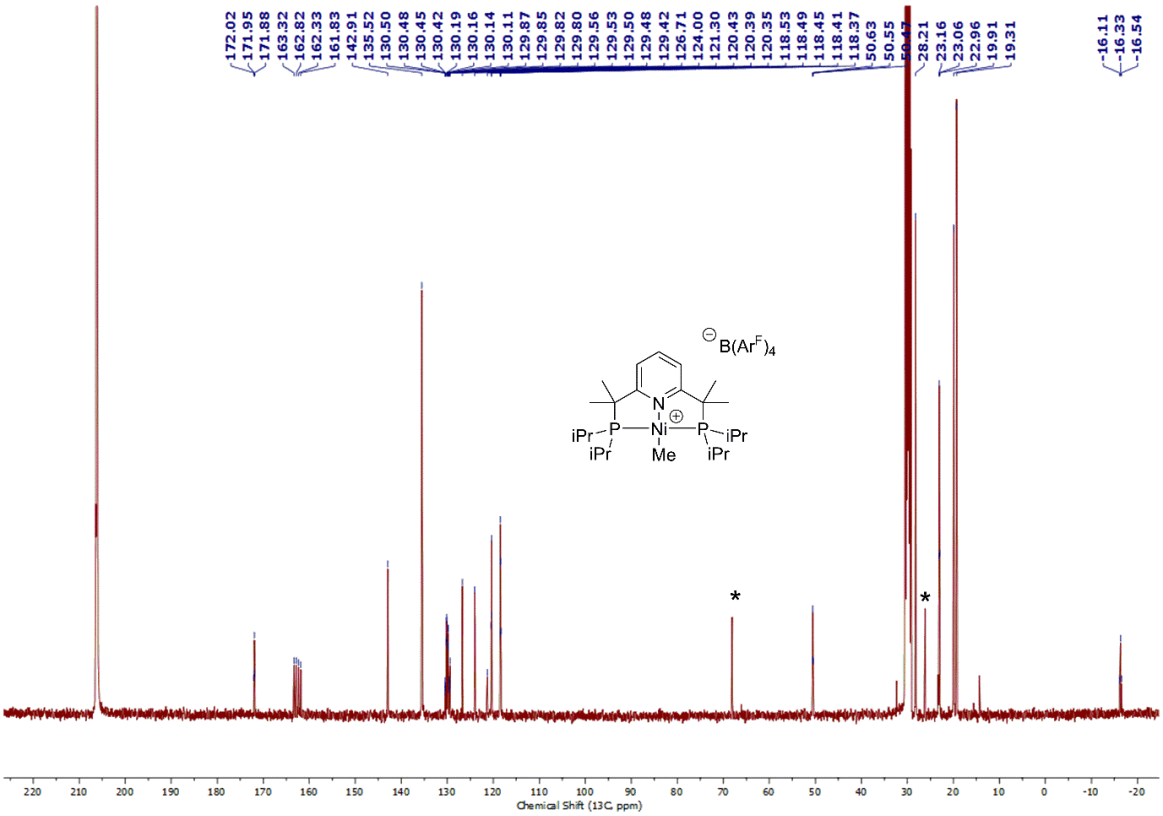


Figure 5. 27 $^{13}C\{^{1}H\}$ NMR spectrum of **3.30** (101 MHz, acetone-d_6). Asterisk (*) marks traces THF

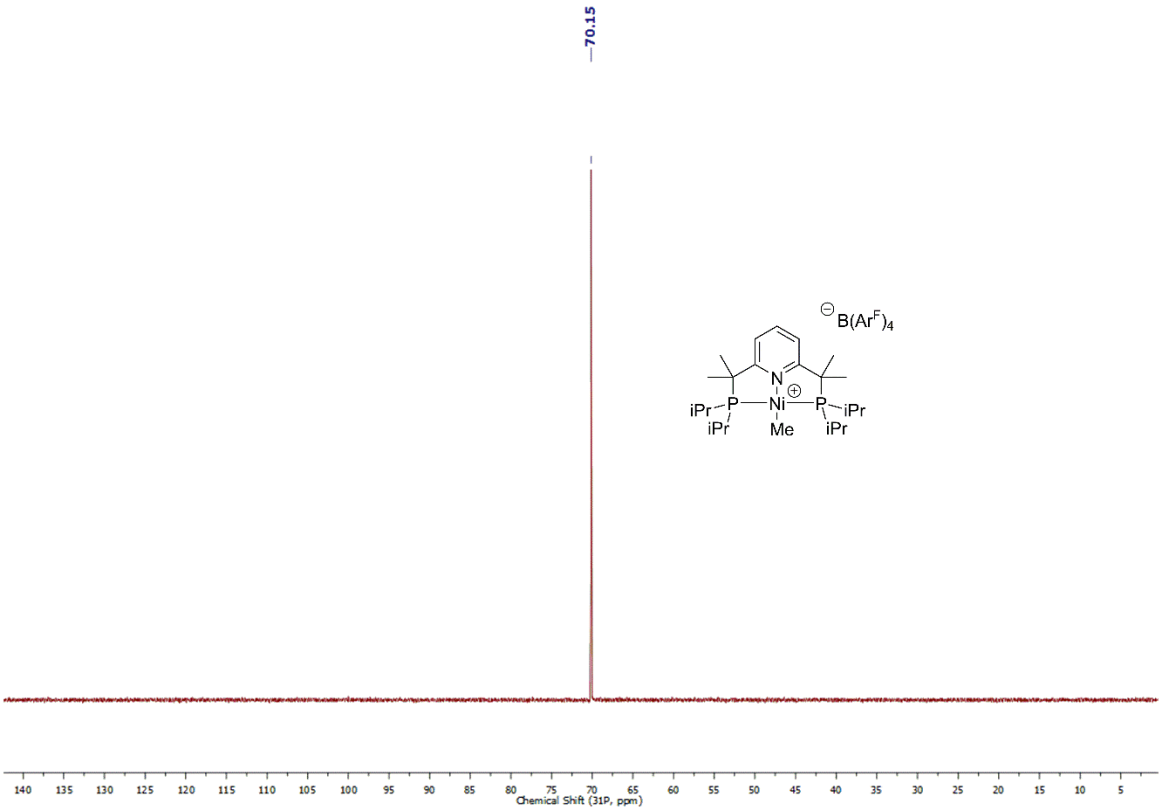


Figure 5. 28 $^{31}P\{^{1}H\}$ NMR spectrum of **3.30** (162 MHz, acetone-d_6)

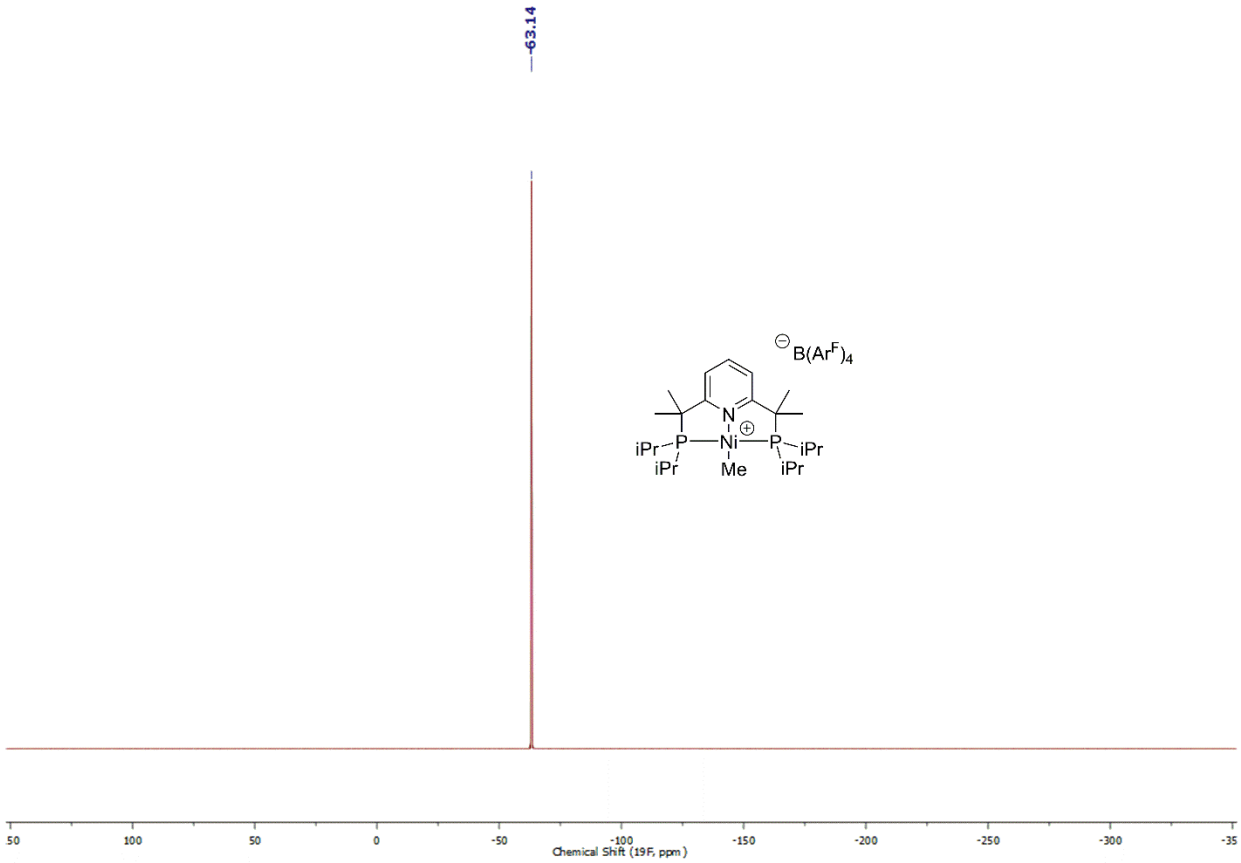


Figure 5. 29 ^{19}F NMR spectrum of **3.30** (376.2 MHz, acetone-d_6)

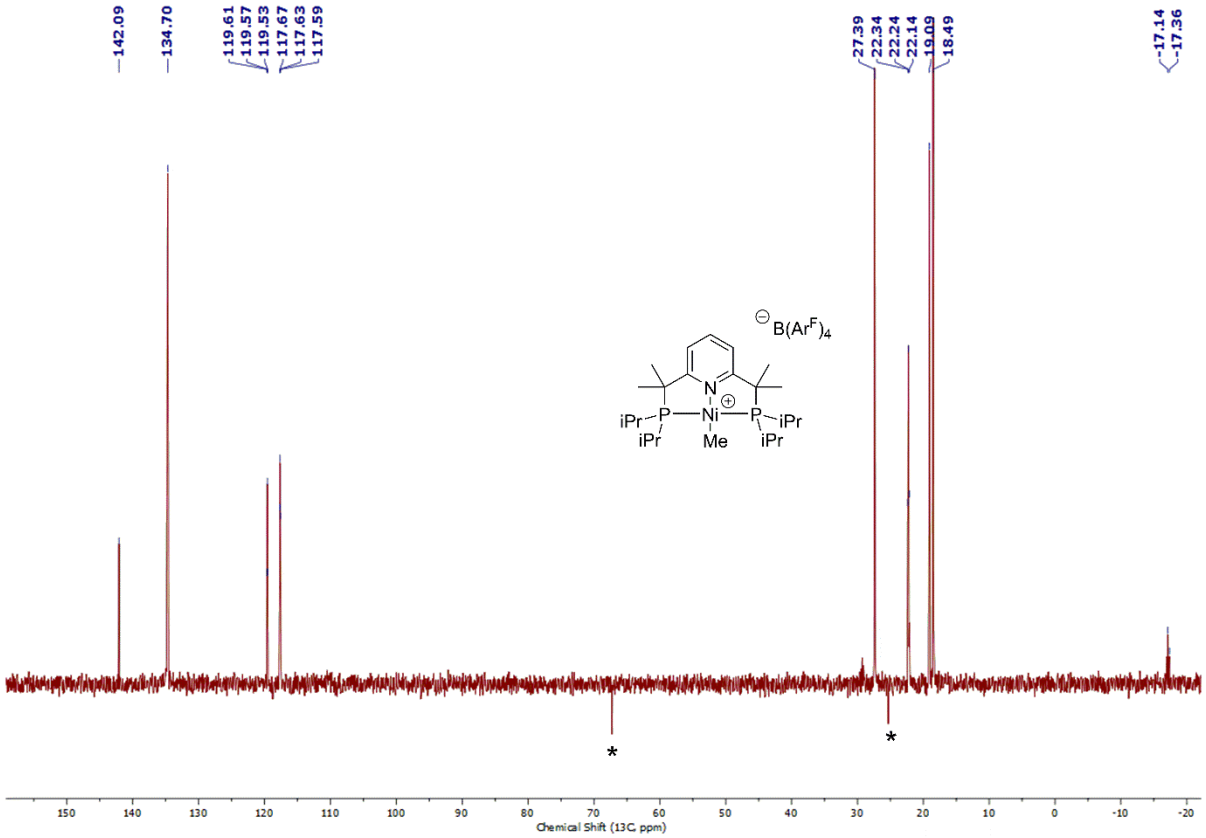


Figure 5. 30 DEPT-135 NMR spectrum of **3.30** (101 MHz, acetone-d_6). Asterisk(*) marks traces of DCM

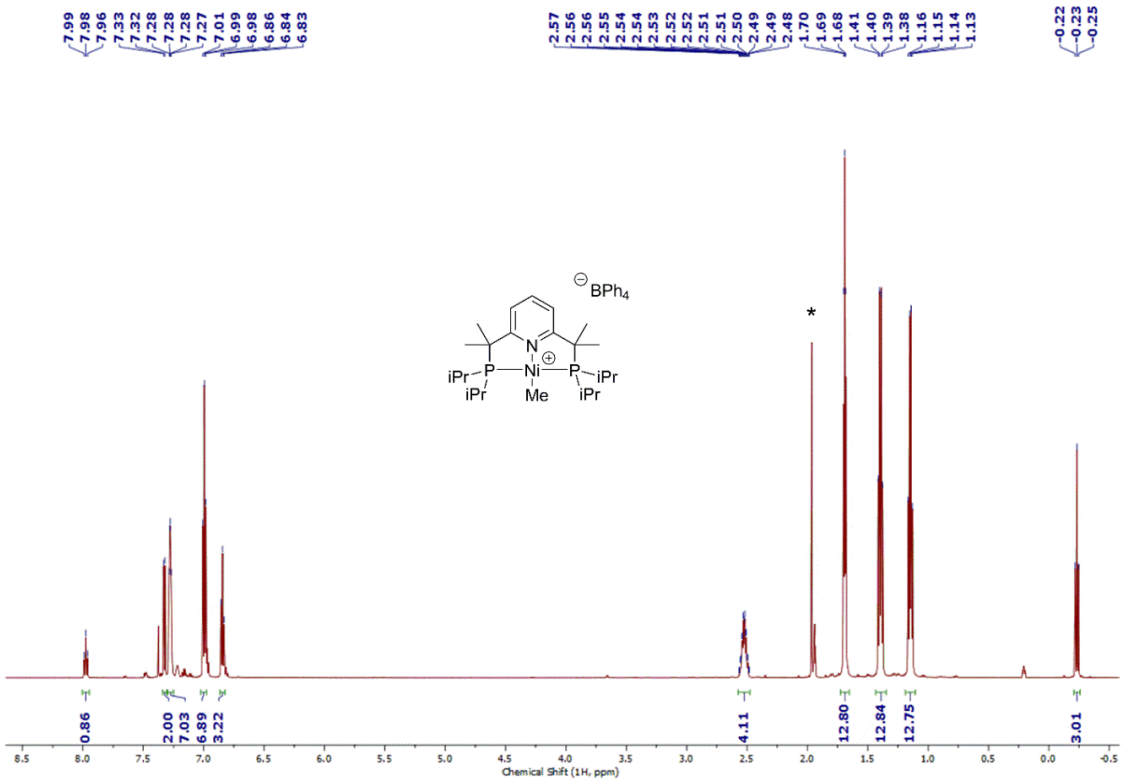


Figure 5. 31 ^{1}H NMR spectrum of **3.31** (600 MHz, CD_3CN). Asterisk (*) marks trace of CH_3CN

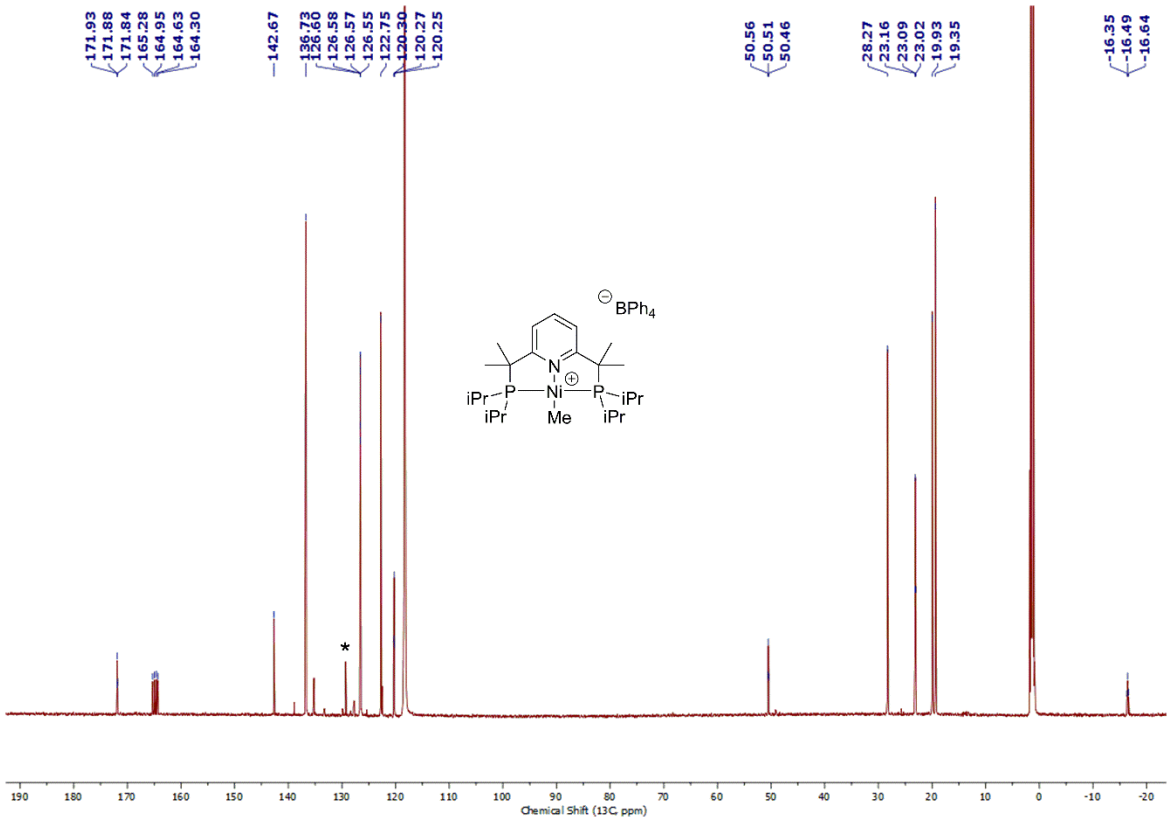


Figure 5. 32 $^{13}C\{^{1}H\}$ NMR spectrum of **3.31** (151 MHz, CD_3CN). Asterisk (*) marks trace of C_6H_6

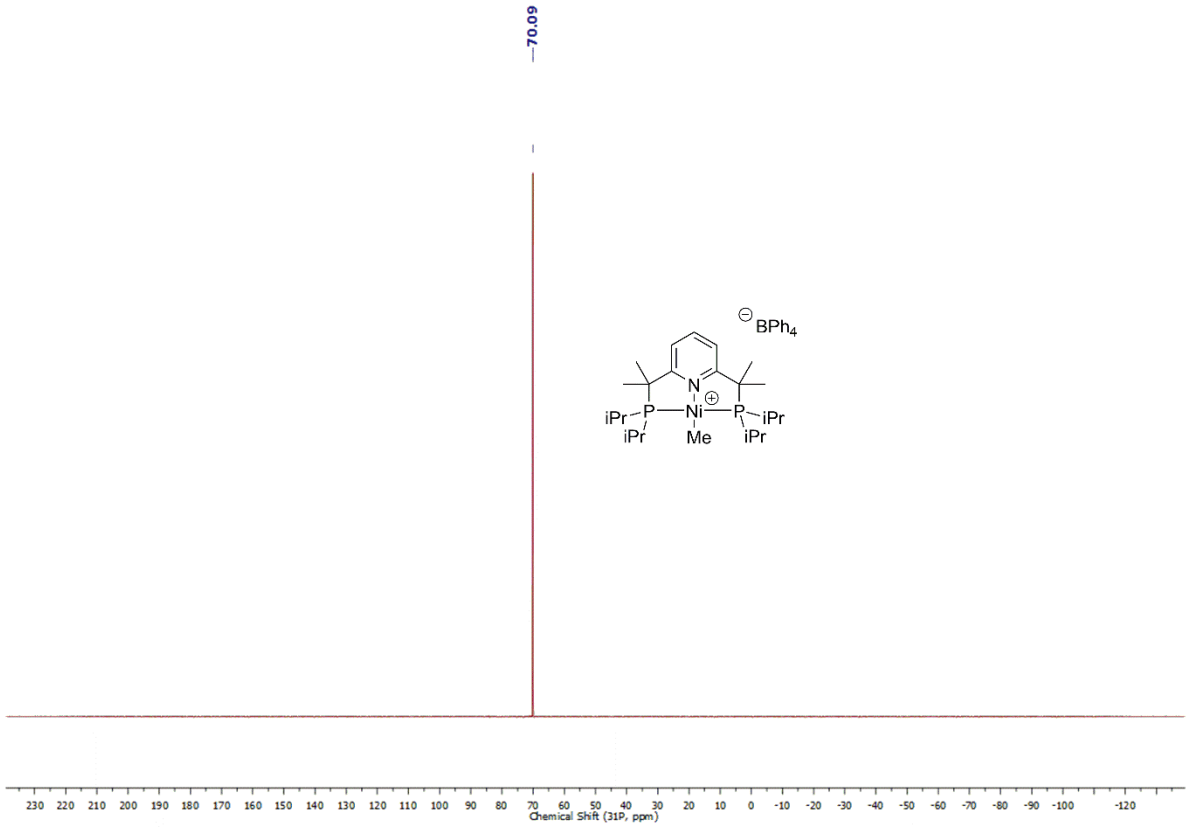


Figure 5. 33 $^{31}P\{^{1}H\}$ NMR spectrum of **3.31** (292 MHz, CD_3CN)

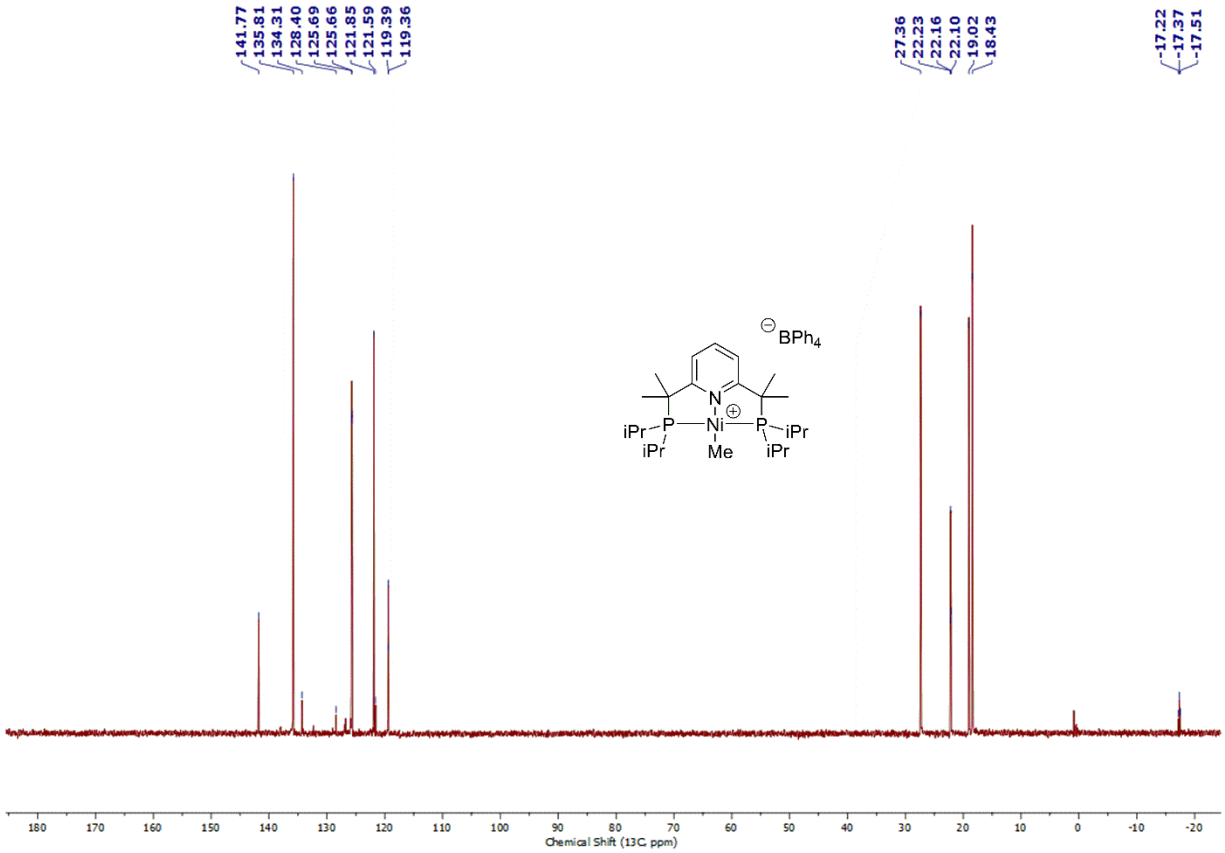


Figure 5. 34 DEPT-135 NMR spectrum of **3.31** (151 MHz, CD_3CN)

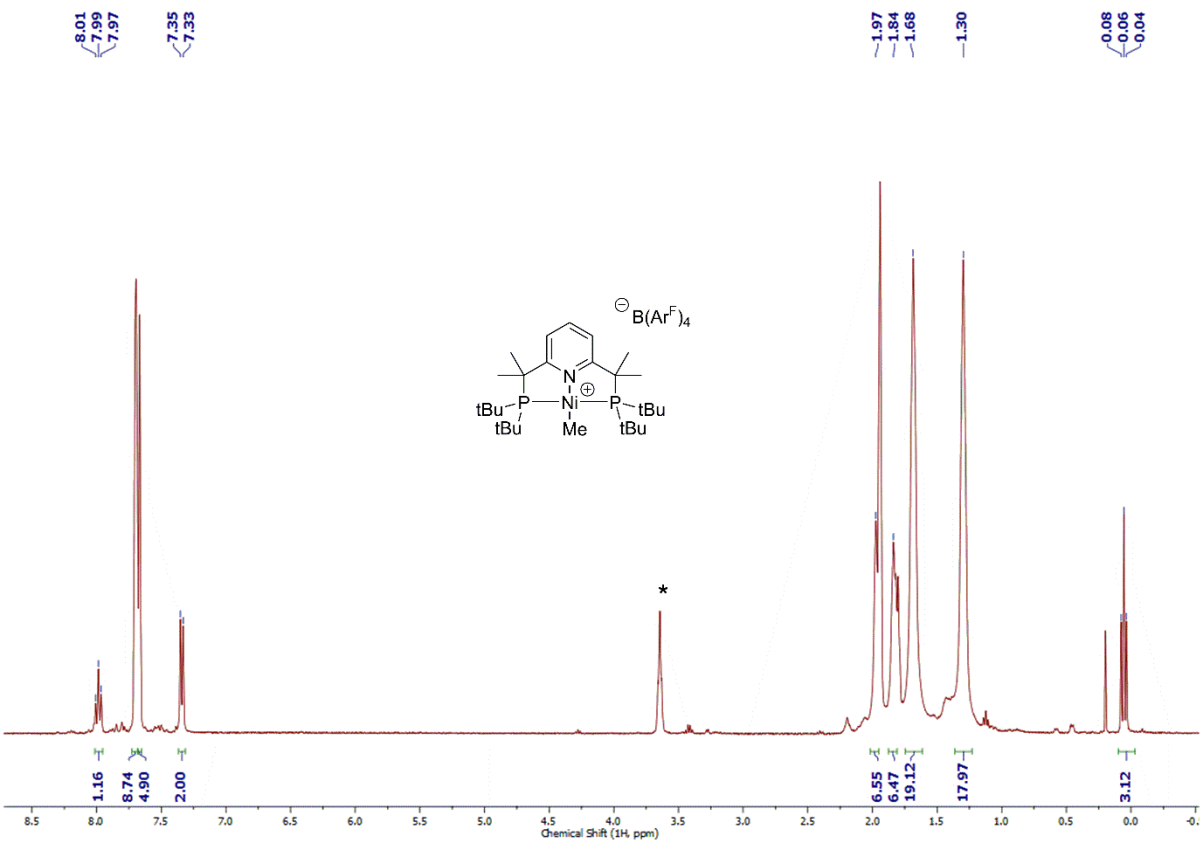


Figure 5. 35 ^{1}H NMR spectrum of **3.32** (400 MHz, CD_3CN). * Traces of THF

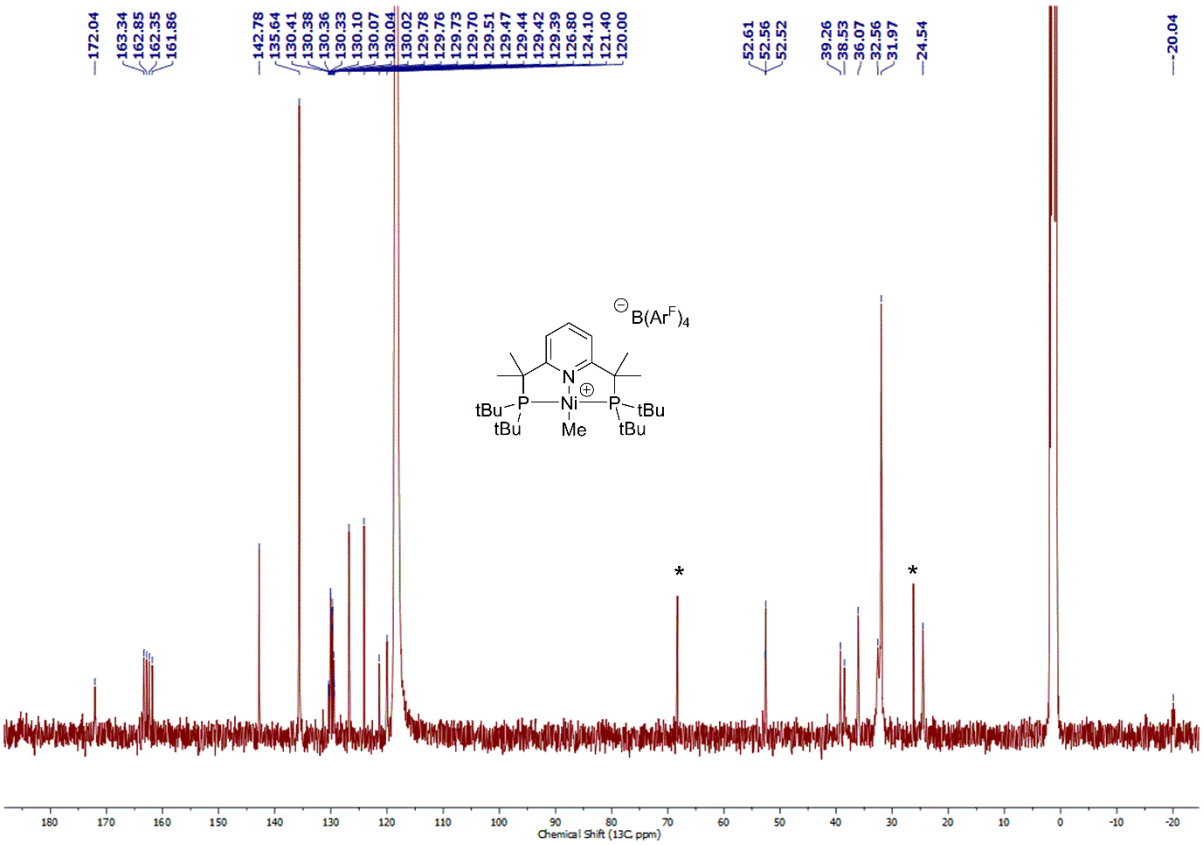


Figure 5. 36 $^{13}C\{^{1}H\}$ NMR spectrum of **3.32** (101 MHz, CD_3CN). * Traces of THF

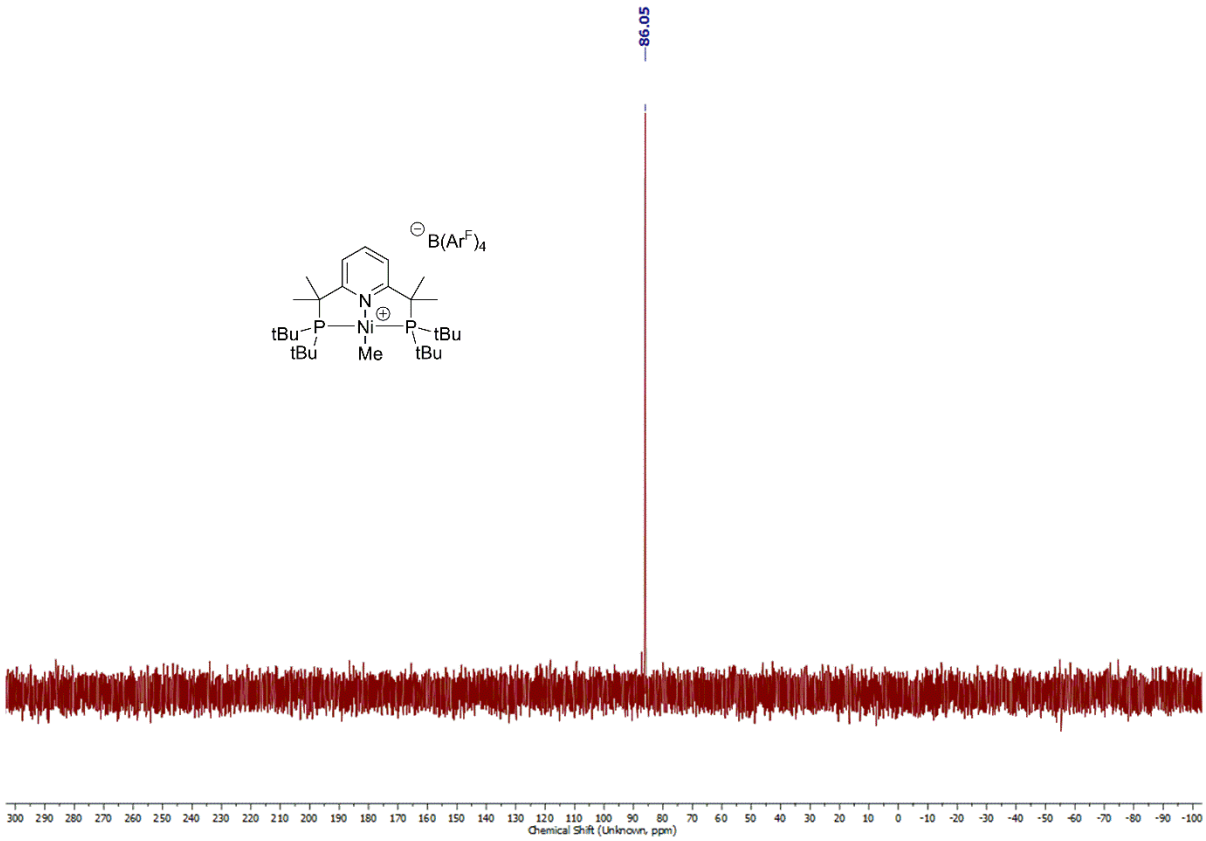


Figure 5. 37 $^{31}P\{^{1}H\}$ NMR spectrum of **3.32** (162 MHz, CD_3CN).

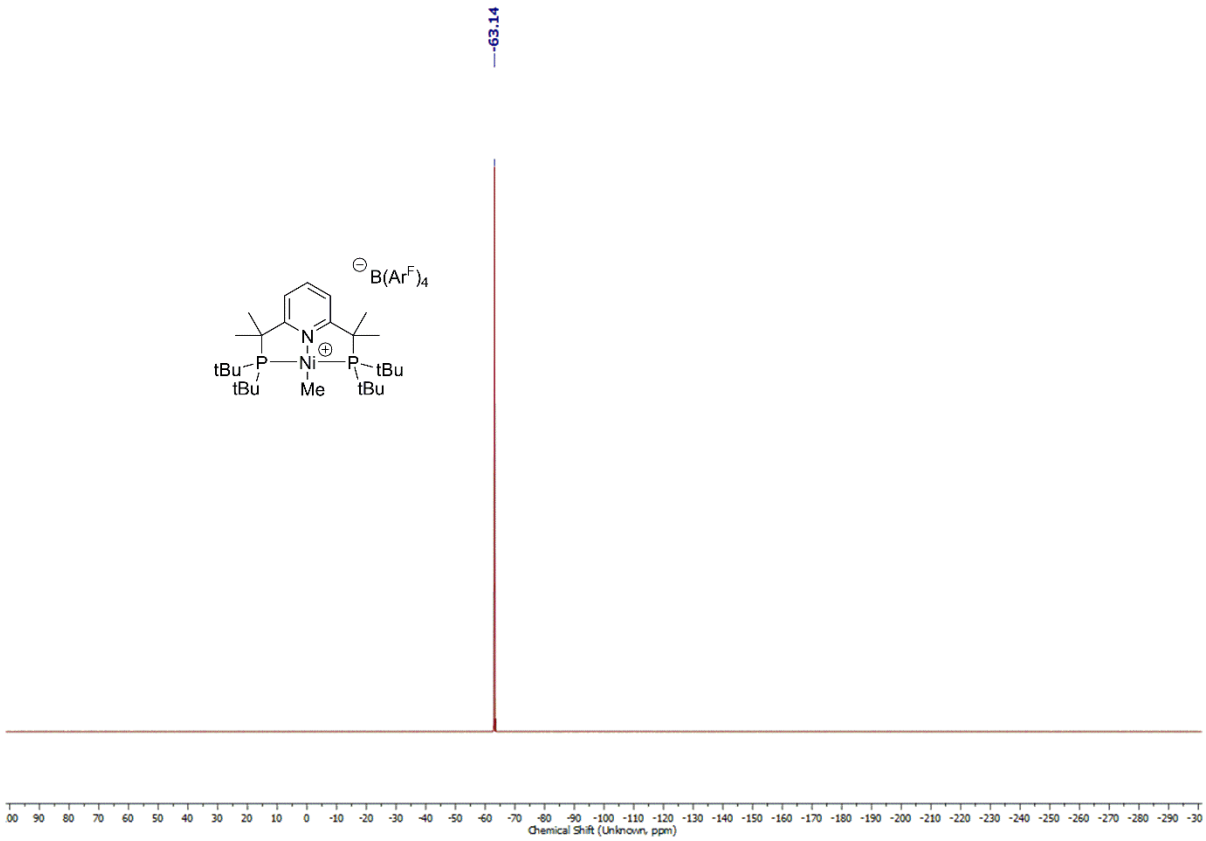


Figure 5. 38 ^{19}F NMR spectrum of **3.32** (396 MHz, CD_3CN).

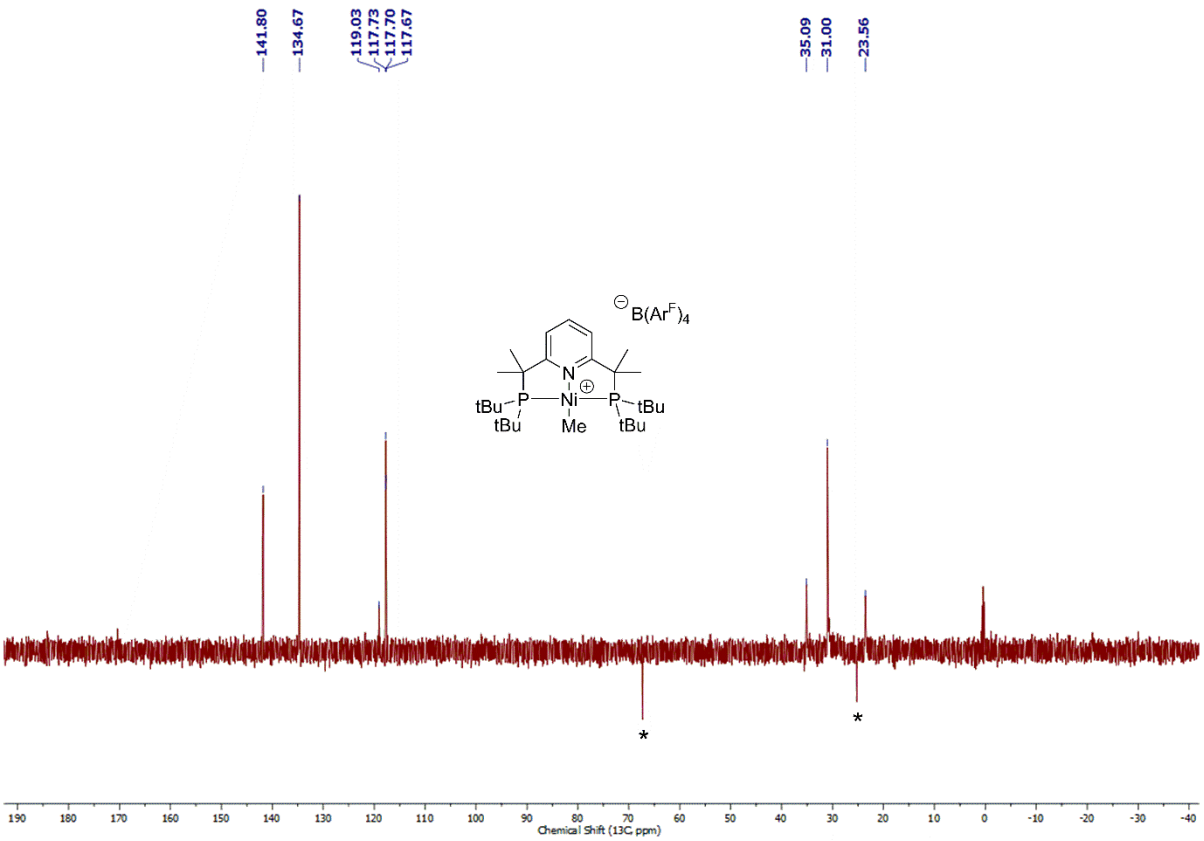


Figure 5. 39 DEPT-135 NMR spectrum of **3.32** (126 MHz, CD_3CN). *Traces of THF

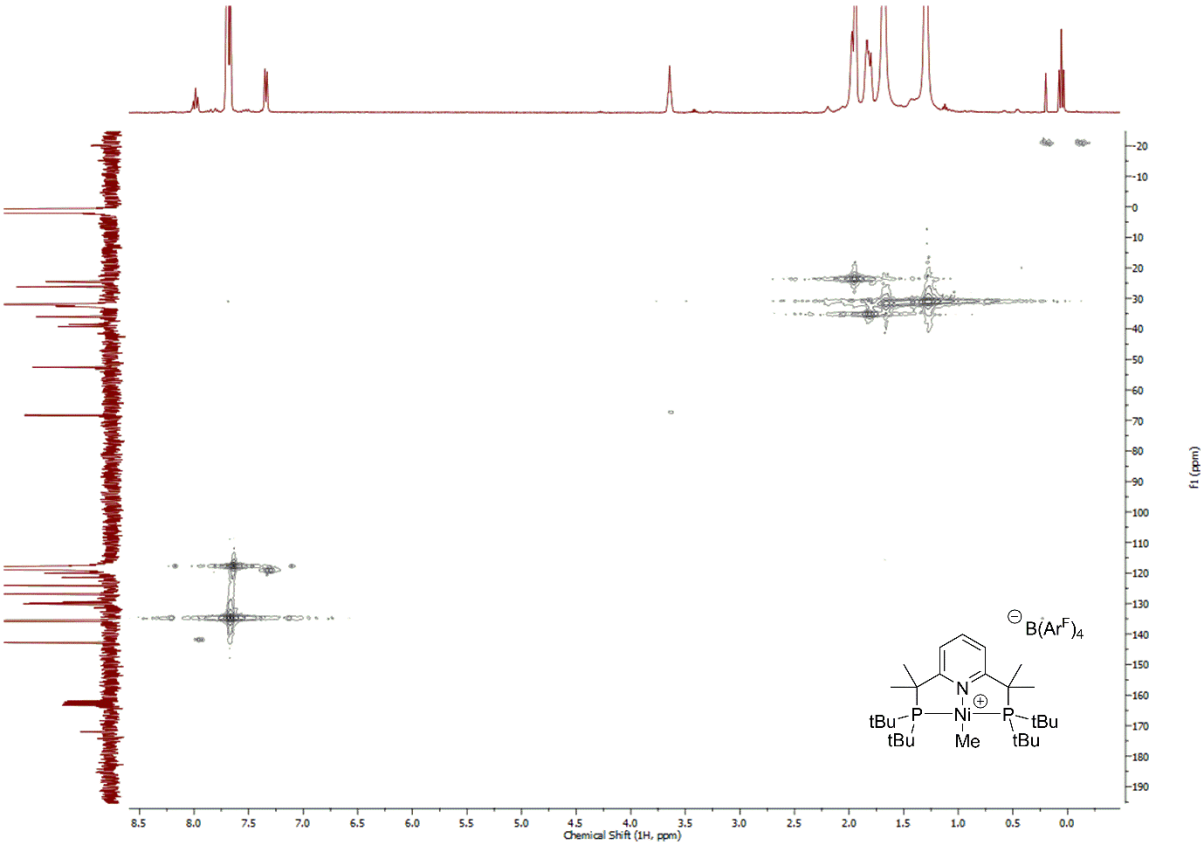


Figure 5. 40 ^{1}H-^{13}C HMQC NMR spectrum of **3.32** (CD_3CN).

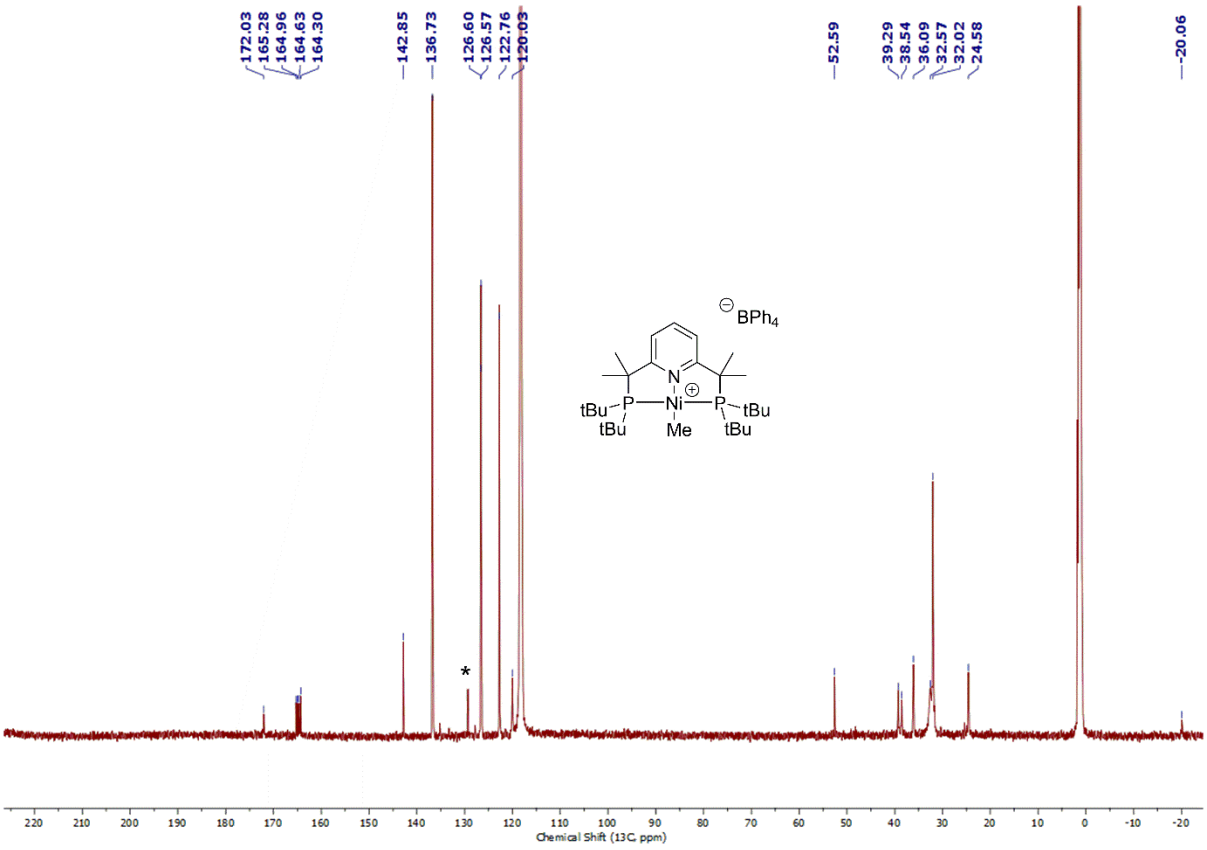


Figure 5. 41 $^{13}C\{^{1}H\}$ NMR spectrum of **3.33** (151 MHz, CD_3CN). Asterisk (*) marks traces of C_6H_6

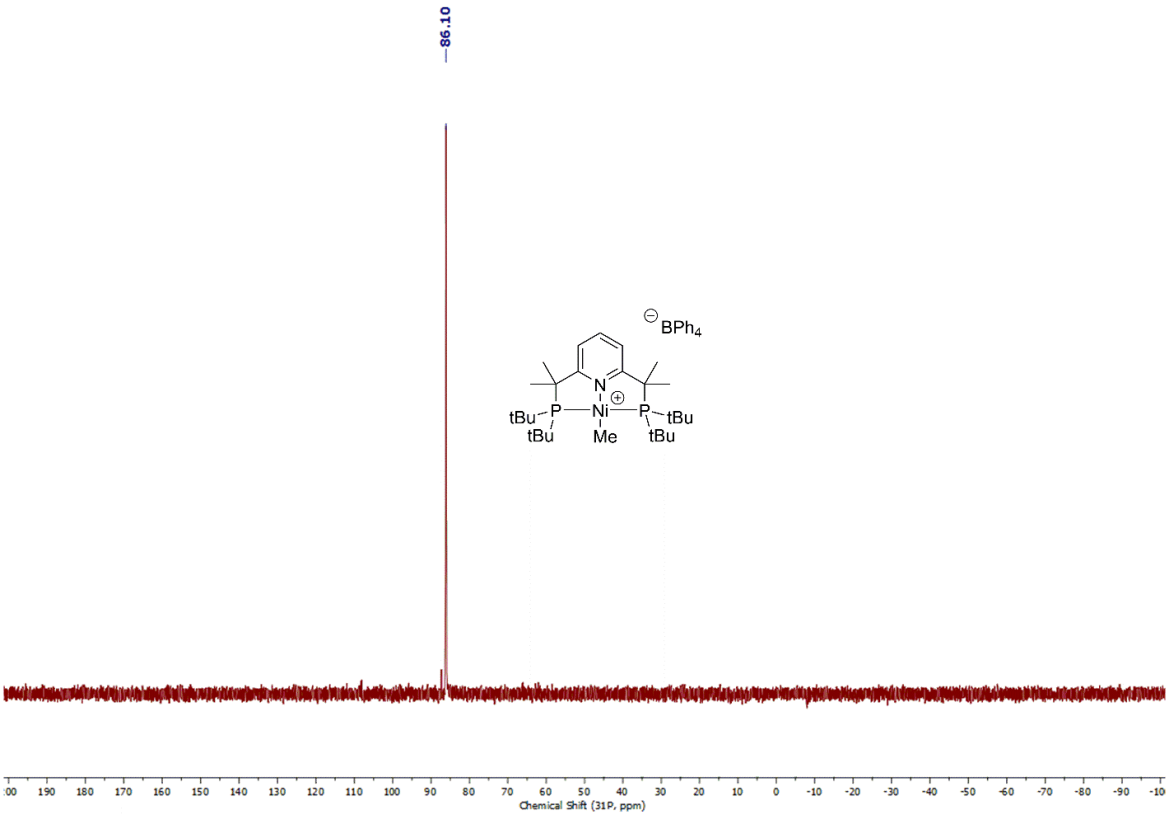


Figure 5. 42 $^{31}P\{^{1}H\}$ NMR spectrum of **3.33** (292 MHz, CD_3CN).

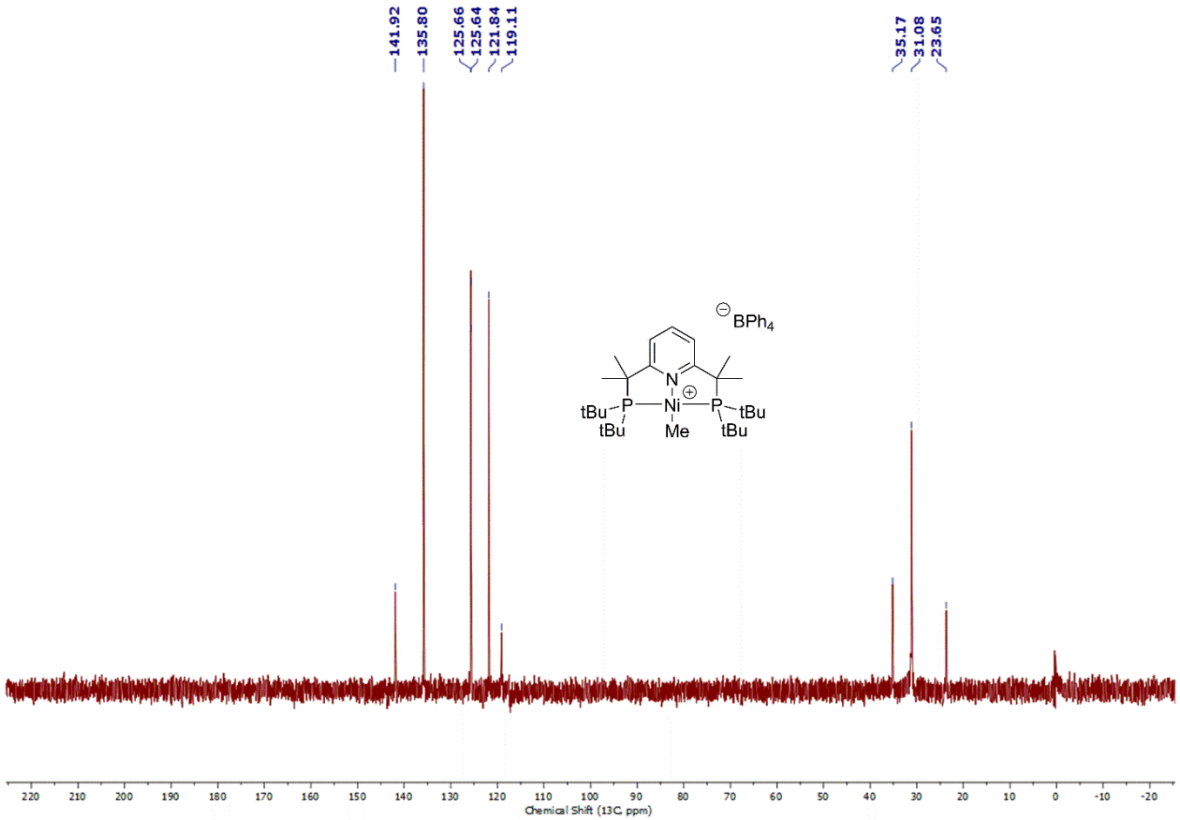


Figure 5. 43 DEPT-135 NMR spectrum of **3.33** (151 MHz, CD_3CN).

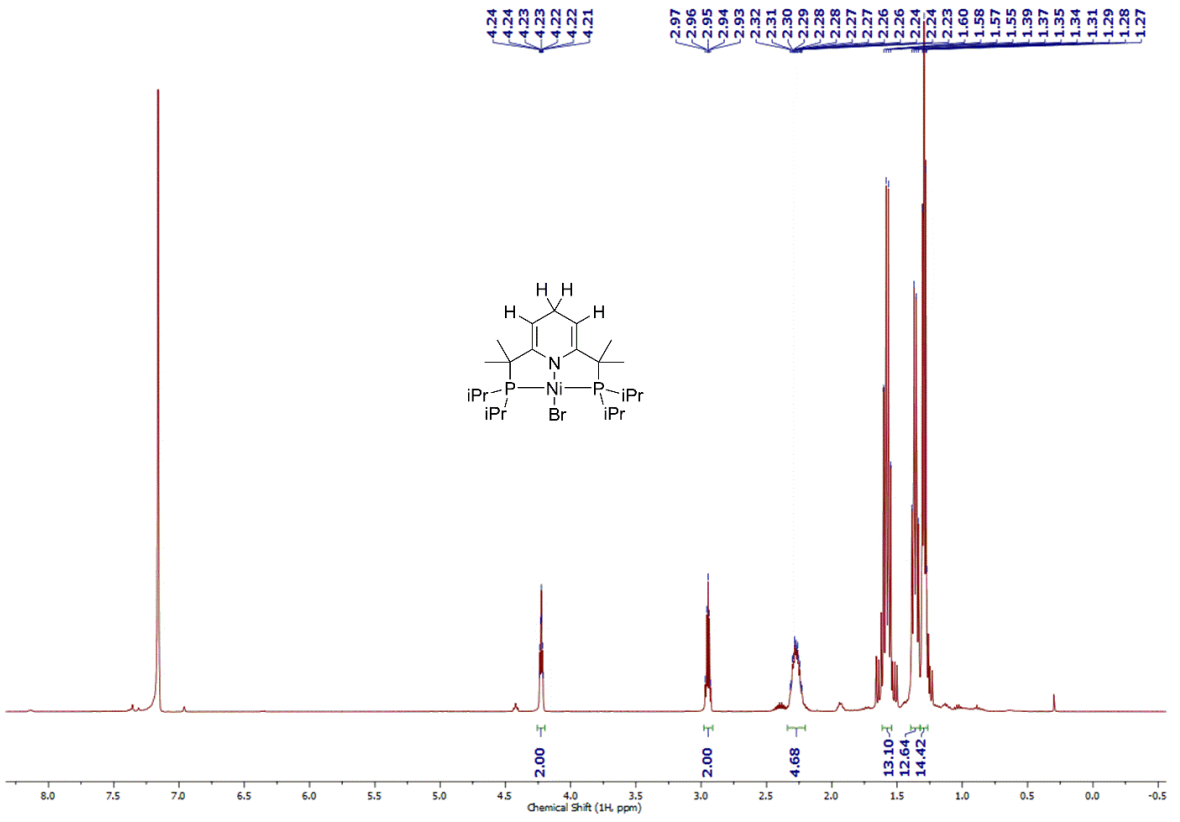


Figure 5. 44 ^1H NMR spectrum of **3.34** obtained by the reaction of **3.24** with 1 equiv of $LiBEt_3H$ (400 MHz, C_6D_6)

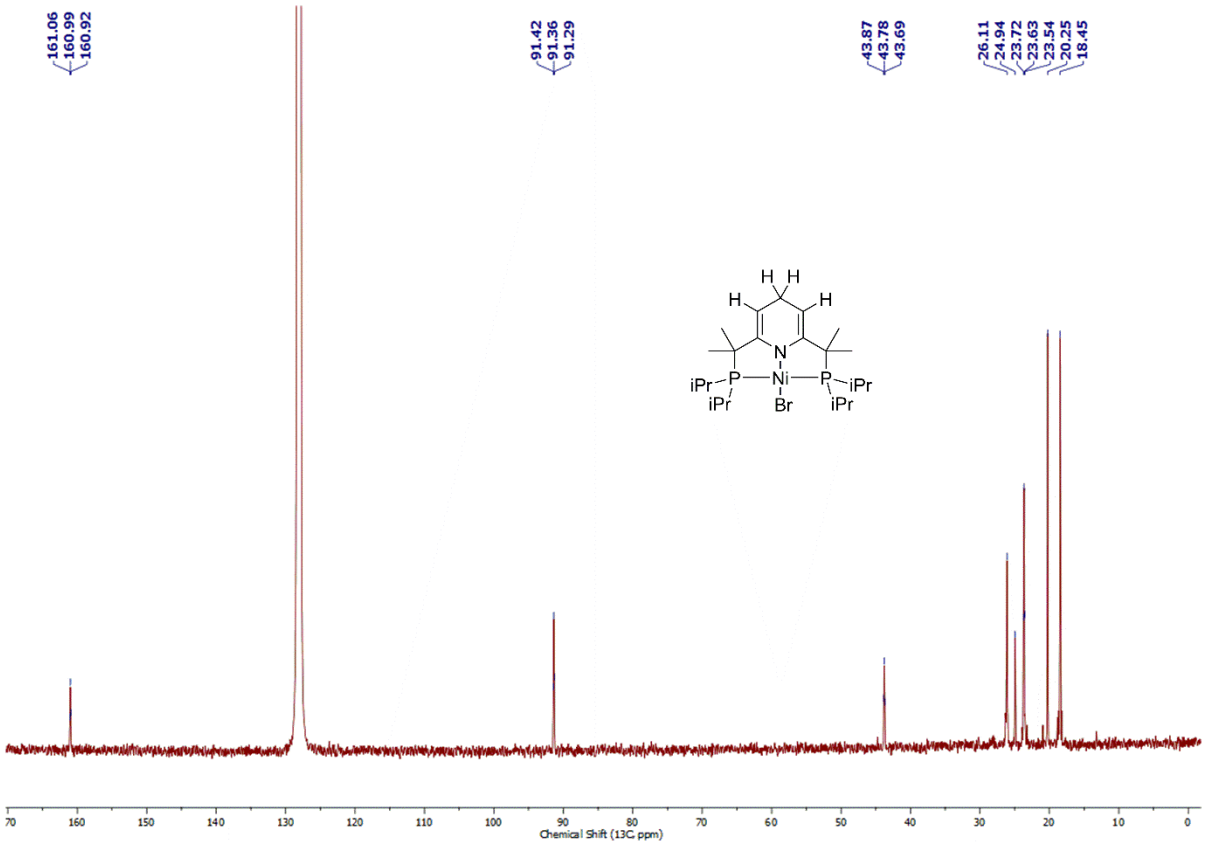


Figure 5. 45 $^{13}C\{^{1}H\}$ NMR spectrum of **3.34** obtained by the reaction of **3.24** with 1 equiv of $LiBEt_3H$(101 MHz, C_6D_6)

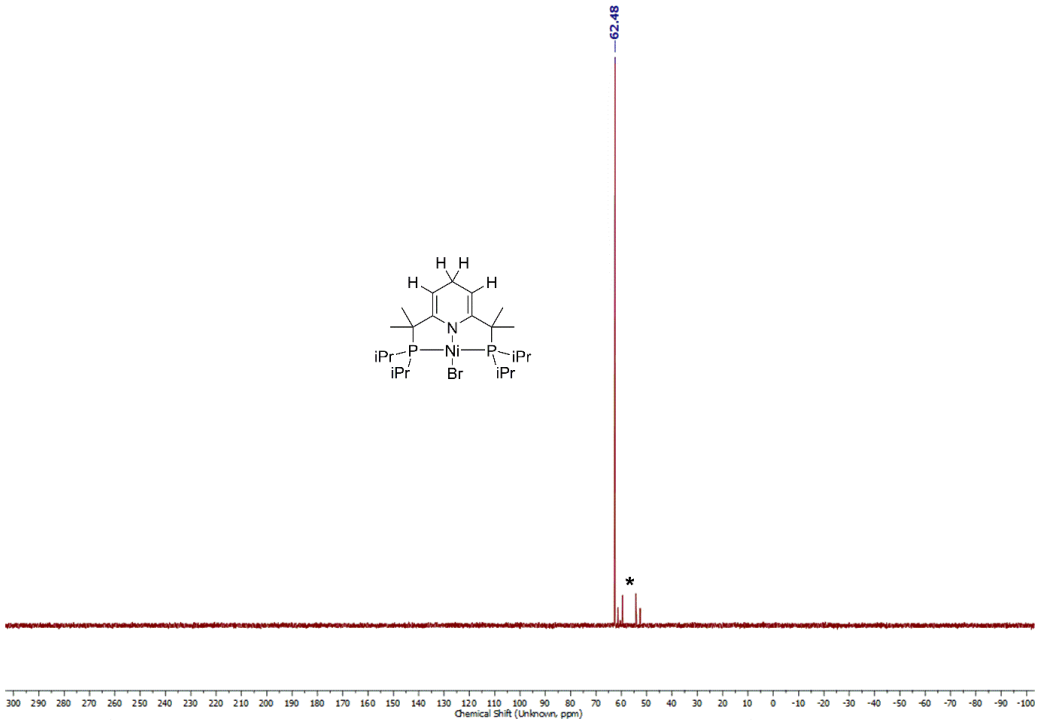


Figure 5. 46 $^{31}P\{^{1}H\}$ NMR spectrum of **3.34** obtained by the reaction of **3.24** with 1 equiv of $LiBEt_3H$ (162 MHz, C_6D_6). * Trace of unidentified unsymmetrical species

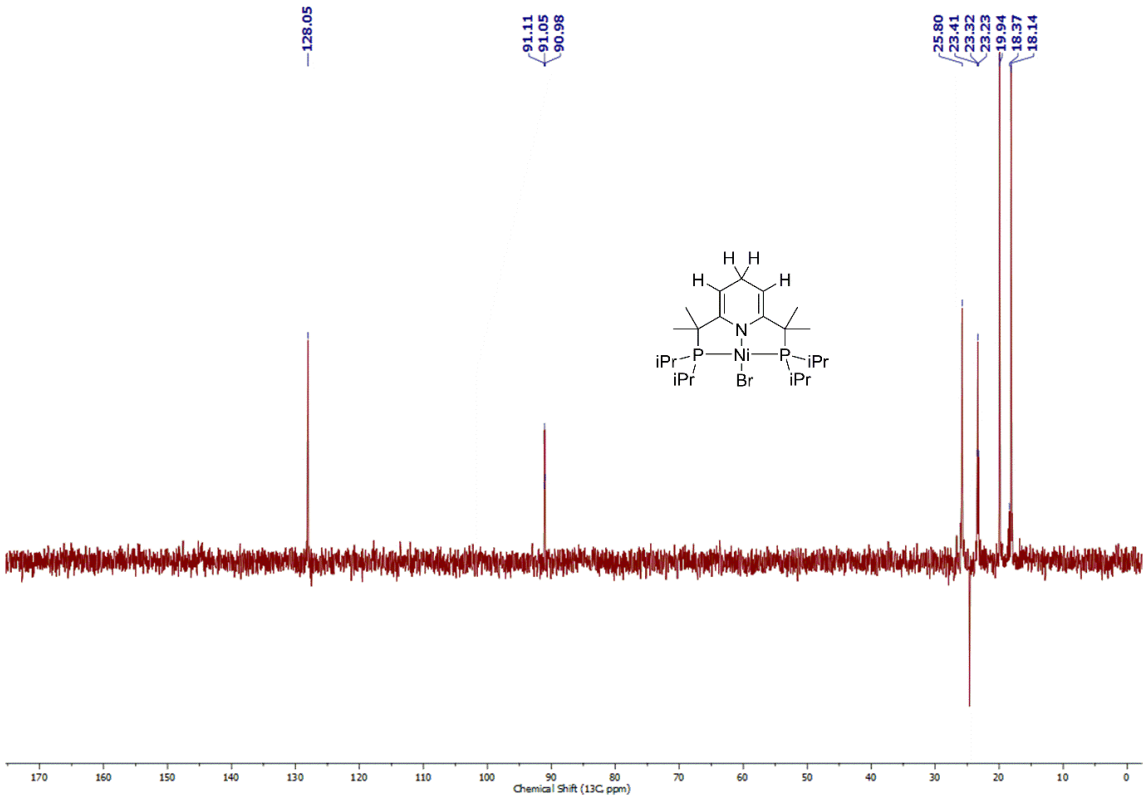


Figure 5. 47 DEPT-135 NMR spectrum of **3.34** obtained by the reaction of **3.24** with 1 equiv of $LiBEt_3H$ (101 MHz, C_6D_6)

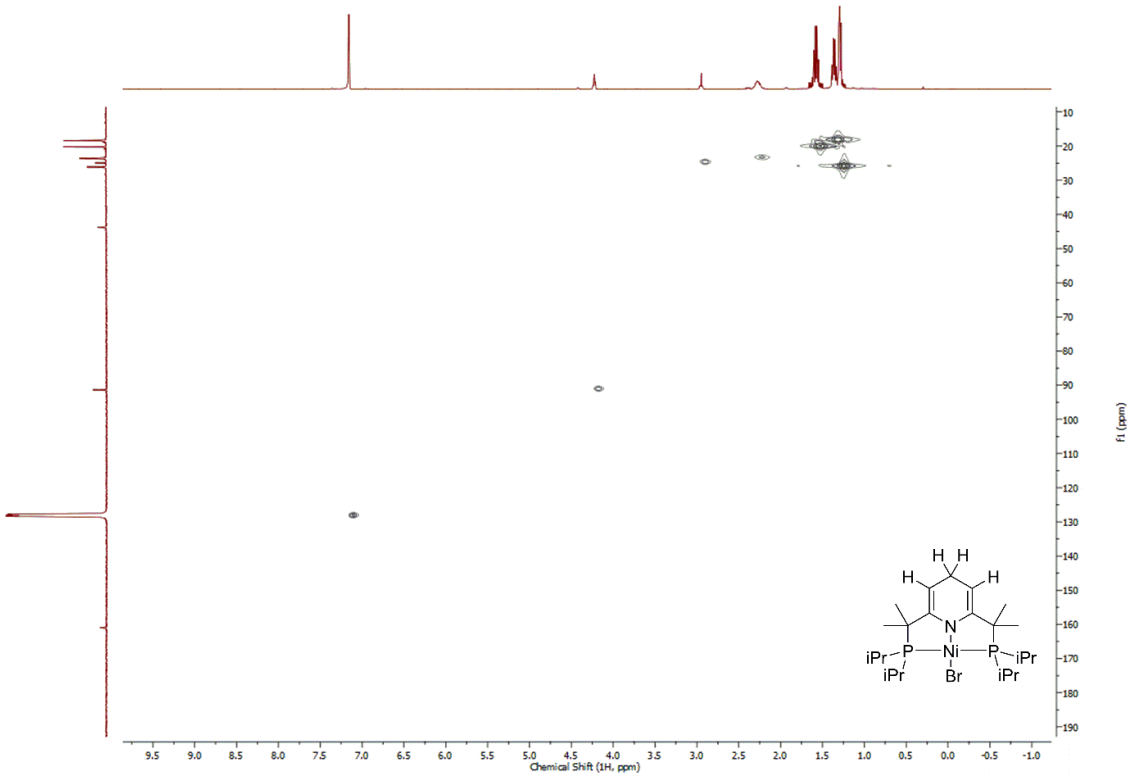


Figure 5. 48 HMQC NMR spectrum of **3.34** obtained by the reaction of **3.24** with 1 equiv of $LiBEt_3H$ (C_6D_6)

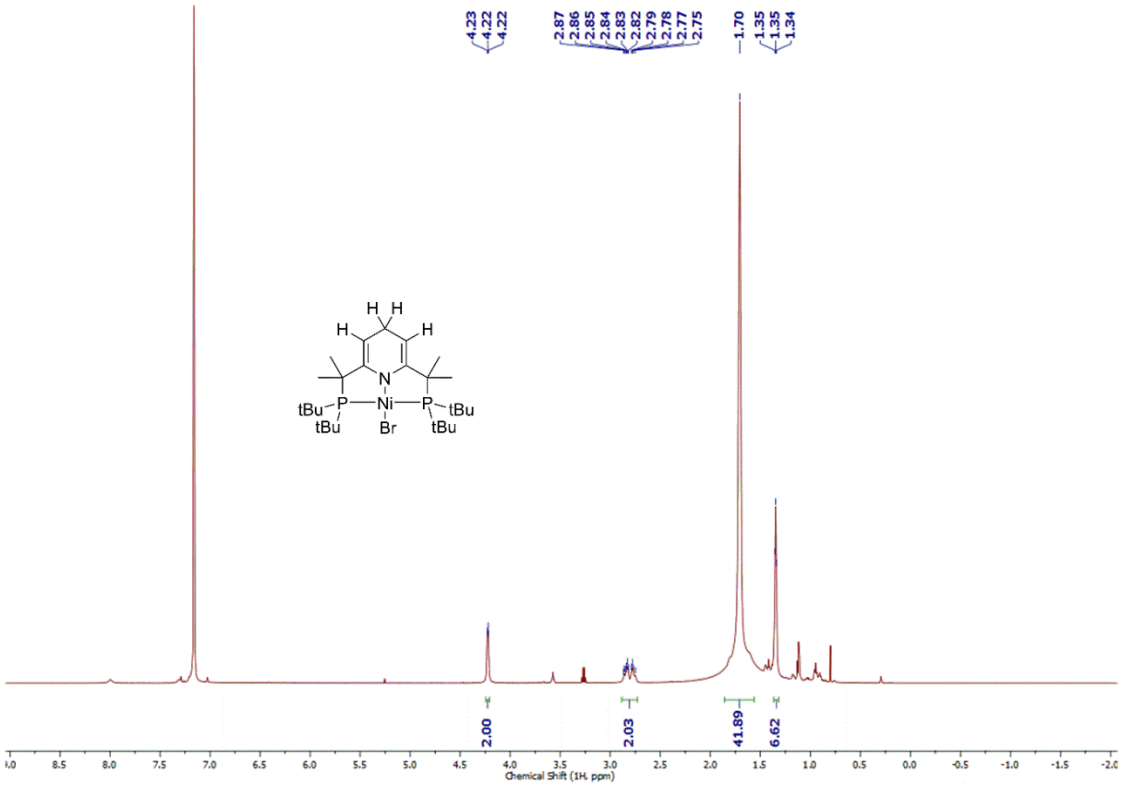


Figure 5. 49 ^{1}H NMR spectrum of **3.35** obtained by the reaction of **3.25** with 0.8 equiv of $LiBEt_3H$ (600 MHz, C_6D_6)

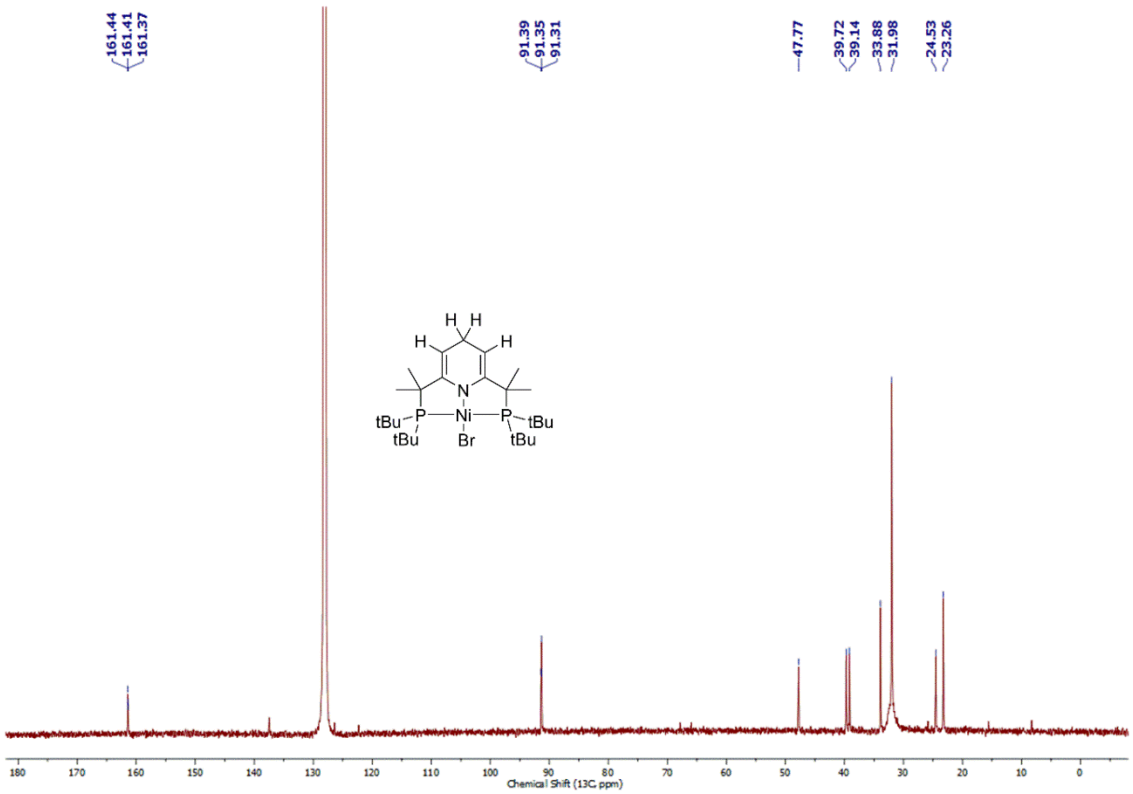


Figure 5. 50 $^{13}C\{^{1}H\}$ NMR spectrum of **3.35** obtained by the reaction of **3.25** with 0.8 equiv of $LiBEt_3H$ (151 MHz, C_6D_6)

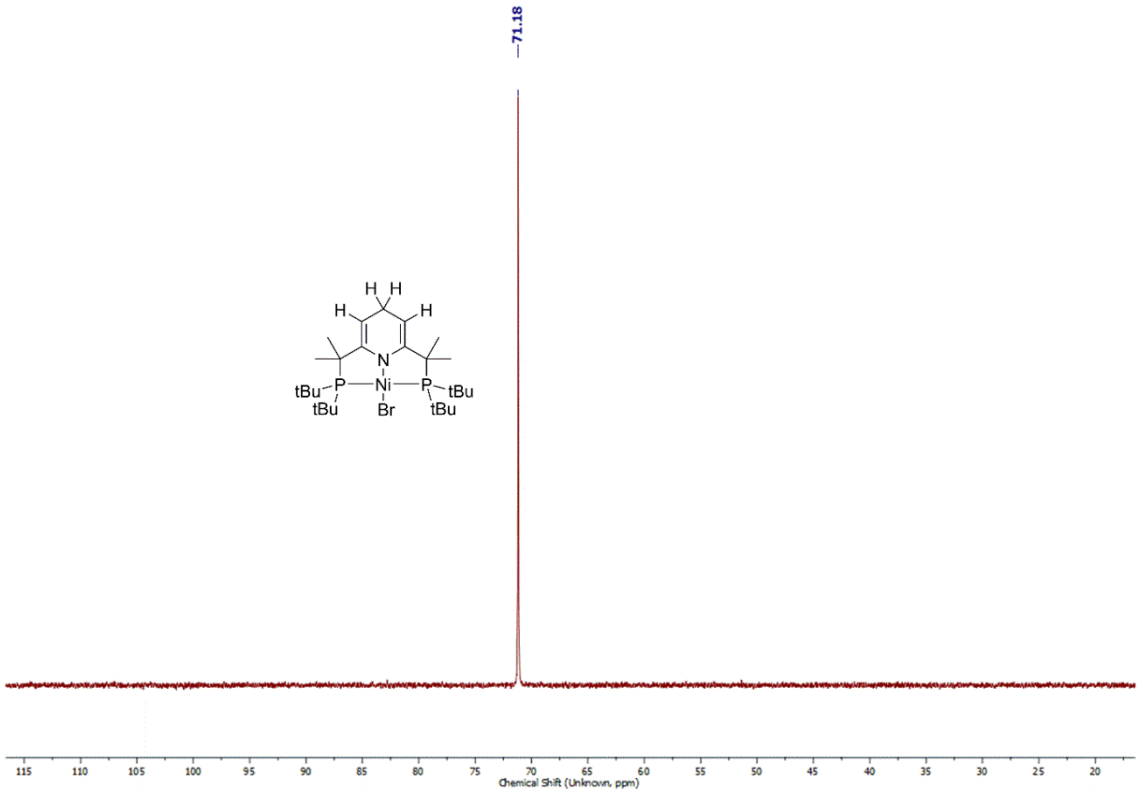


Figure 5. 51 $^{31}P\{^{1}H\}$ NMR spectrum of **3.35** obtained by the reaction of **3.25** with 0.8 equiv of $LiBEt_3H$ (243 MHz, C_6D_6)

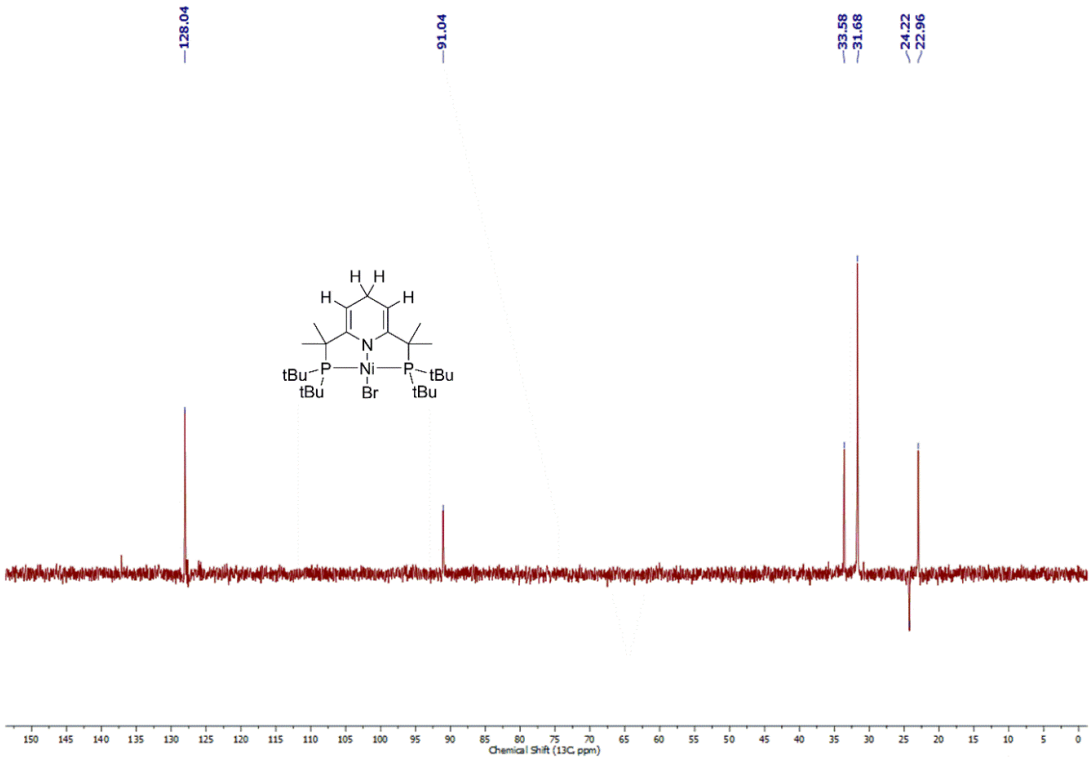


Figure 5. 52 DEPT-135 NMR spectrum of **3.35** obtained by the reaction of **3.25** with 0.8 equiv. of $LiBEt_3H$ (151 MHz, C_6D_6).

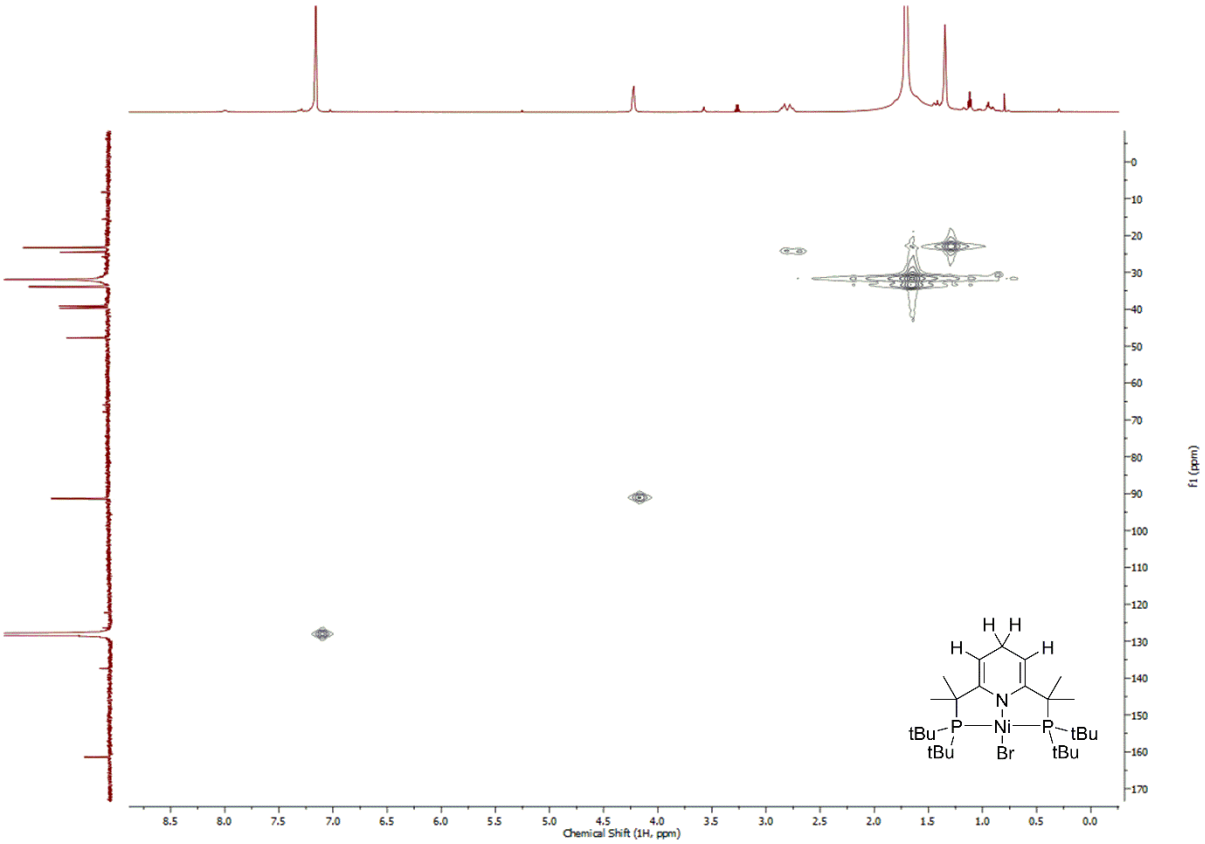


Figure 5. 53 HMQC NMR spectrum of **3.35** obtained by the reaction of **3.25** with 0.8 equiv. of $LiBEt_3H$ (C_6D_6)

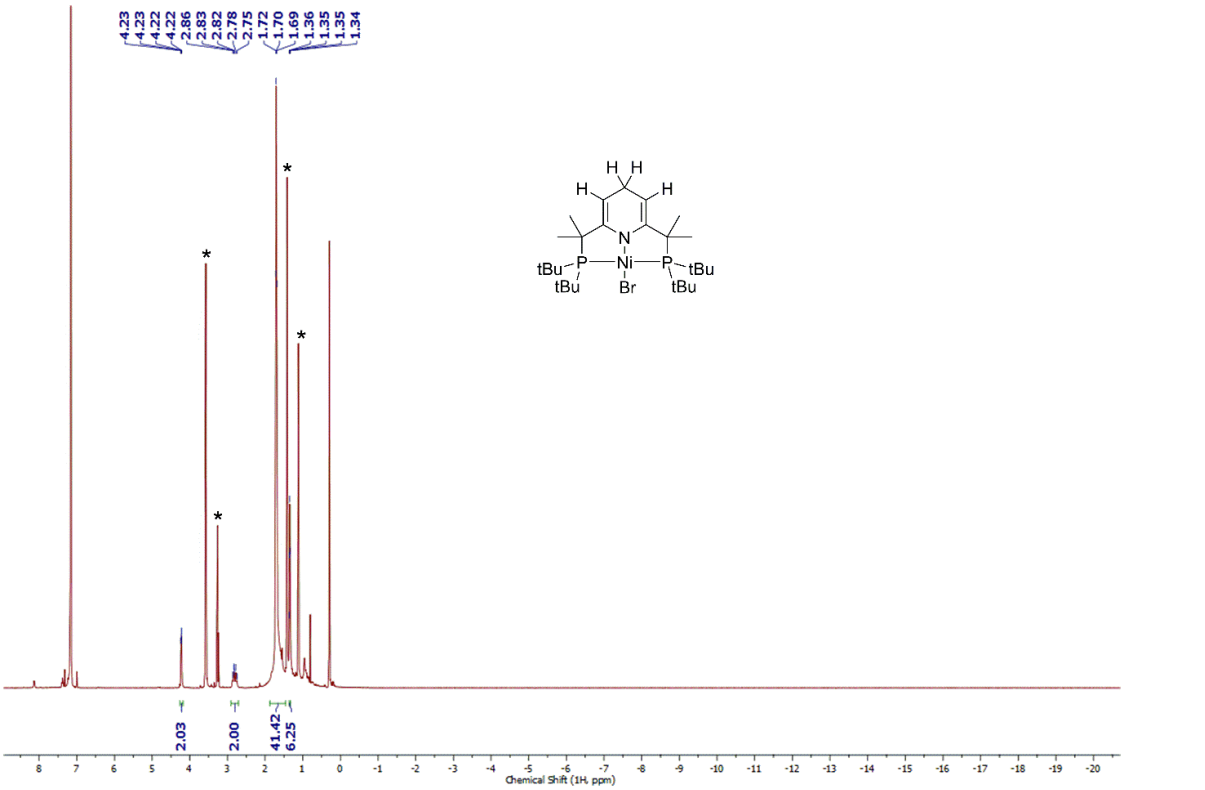


Figure 5. 54 ^1H NMR spectrum of **3.35** obtained by the reaction of **3.25** with 1 equiv. of $LiBEt_3H$ (400 MHz, C_6D_6). *Peaks of THF and diethyl ether.

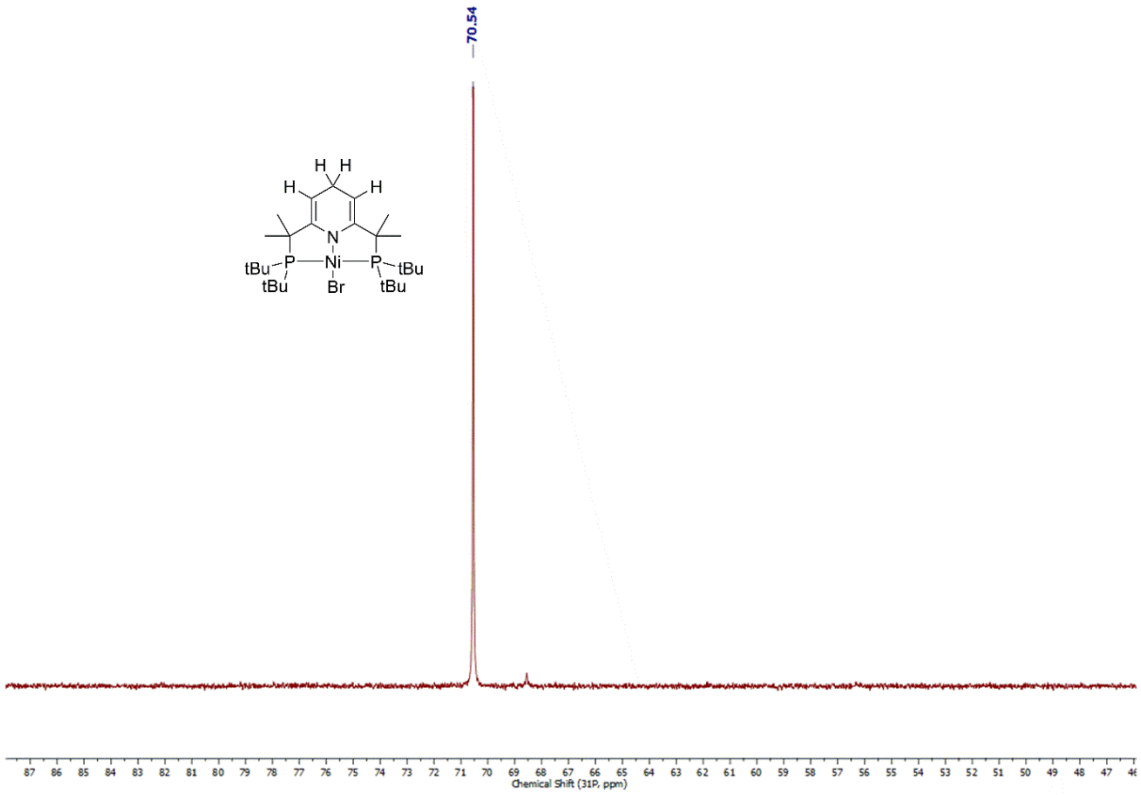


Figure 5. 55 $^{31}P\{^{1}H\}$ NMR spectrum of **3.35** obtained by the reaction of **3.25** with 1 equiv of $LiBEt_3H$ (162 MHz, C_6D_6).

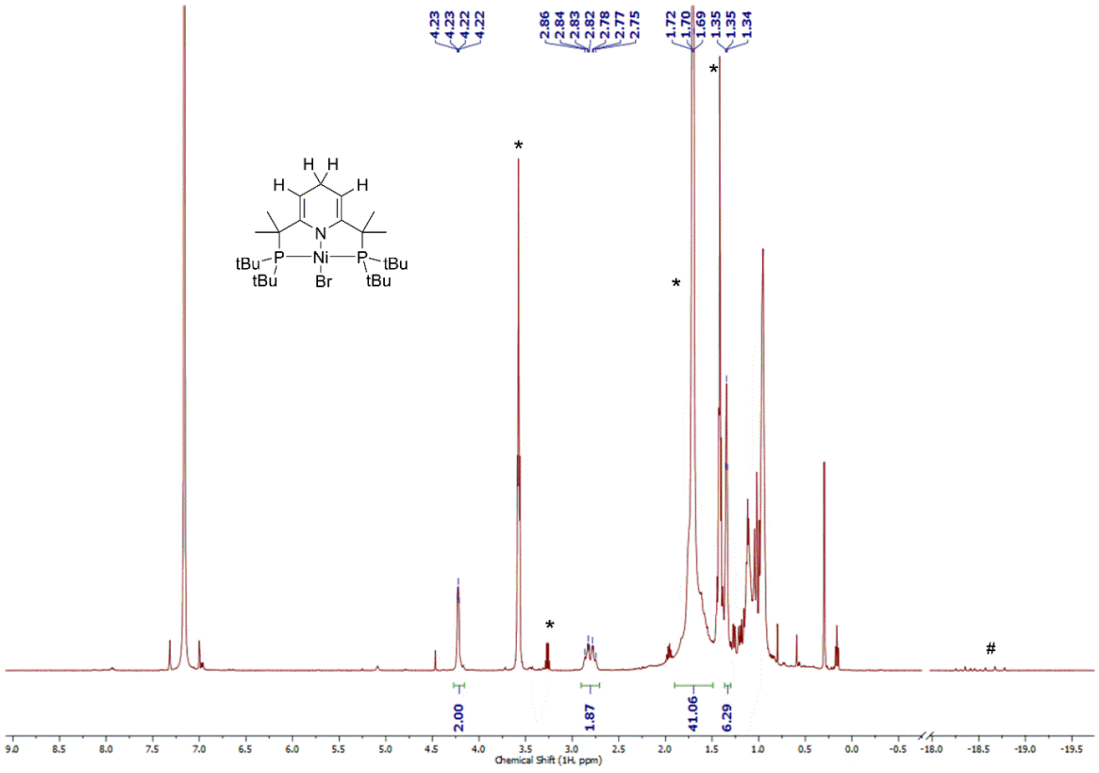


Figure 5. 56 ^{1}H NMR spectrum of the reaction mixture after treatment of **3.25** with 2 equiv of $LiBEt_3H$ (400 MHz, C_6D_6). *Peaks of THF and Et_2O. # Peaks of minor hydride products

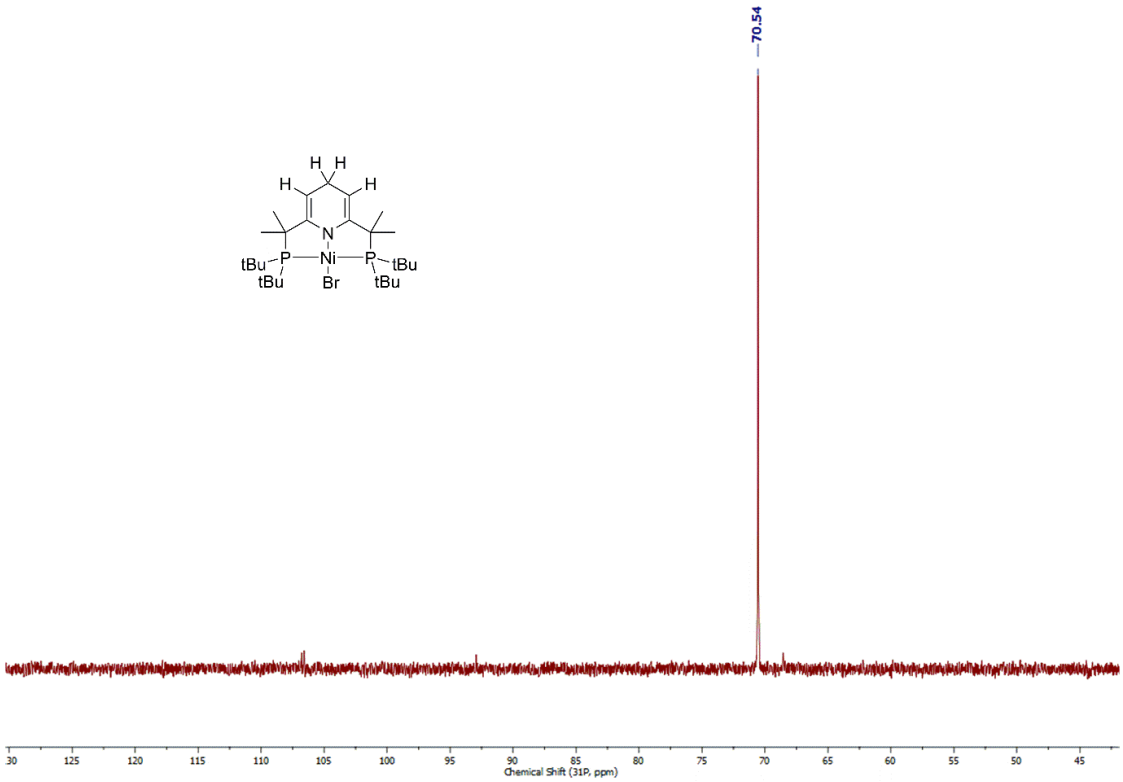


Figure 5. 57 $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture after treatment of **3.25** with 2 equiv of $LiBEt_3H$ (162 MHz, C_6D_6).

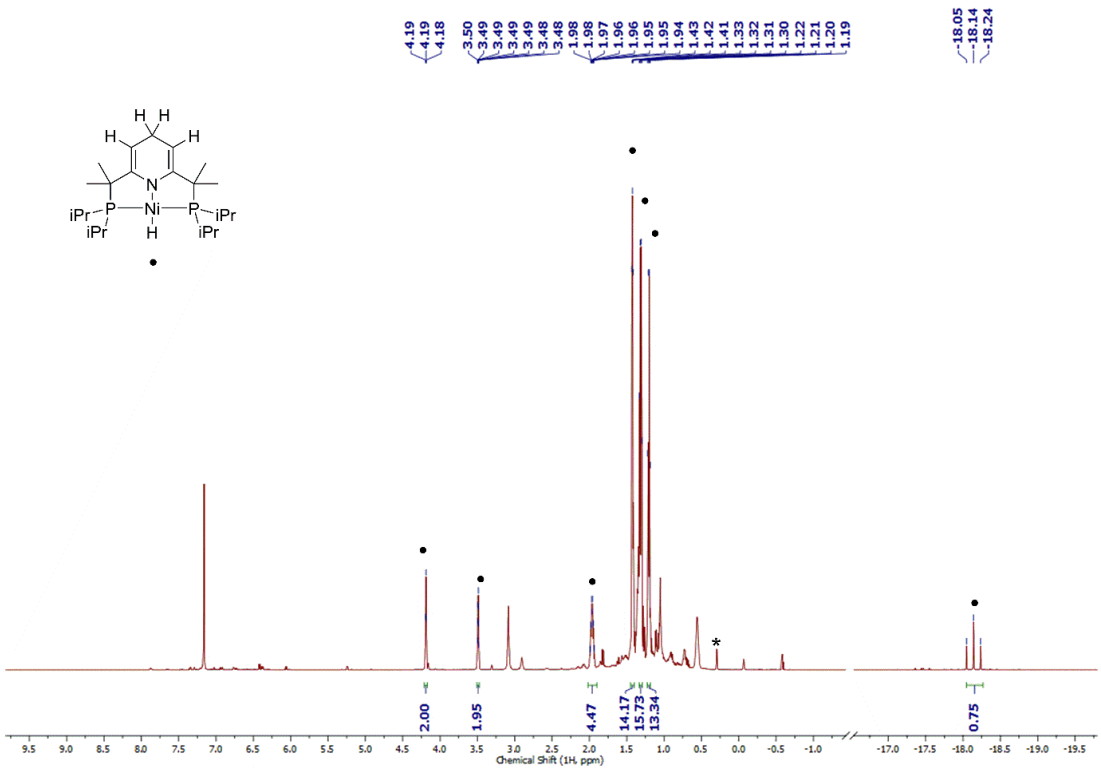


Figure 5. 58 ^{1}H NMR spectrum of the reaction mixture obtained by treatment of **3.24** with 2 equiv of $LiBEt_3H$ (600 MHz, C_6D_6). • Peaks of the major complex 3.36. *Trace silicon grease.

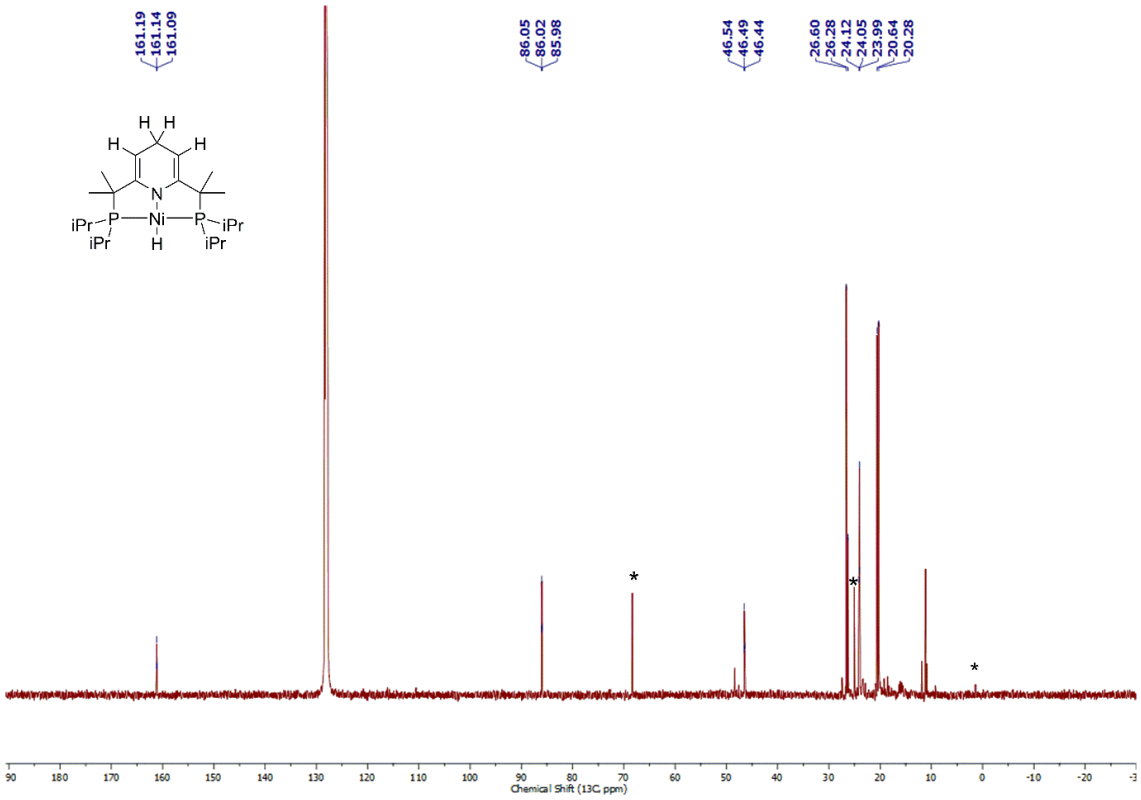


Figure 5. 59 $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture obtained by treatment of **3.24** with 2 equiv of $LiBEt_3H$ (151 MHz, C_6D_6). •Peaks of major complex **3.36**. *Traces of silicon grease and THF

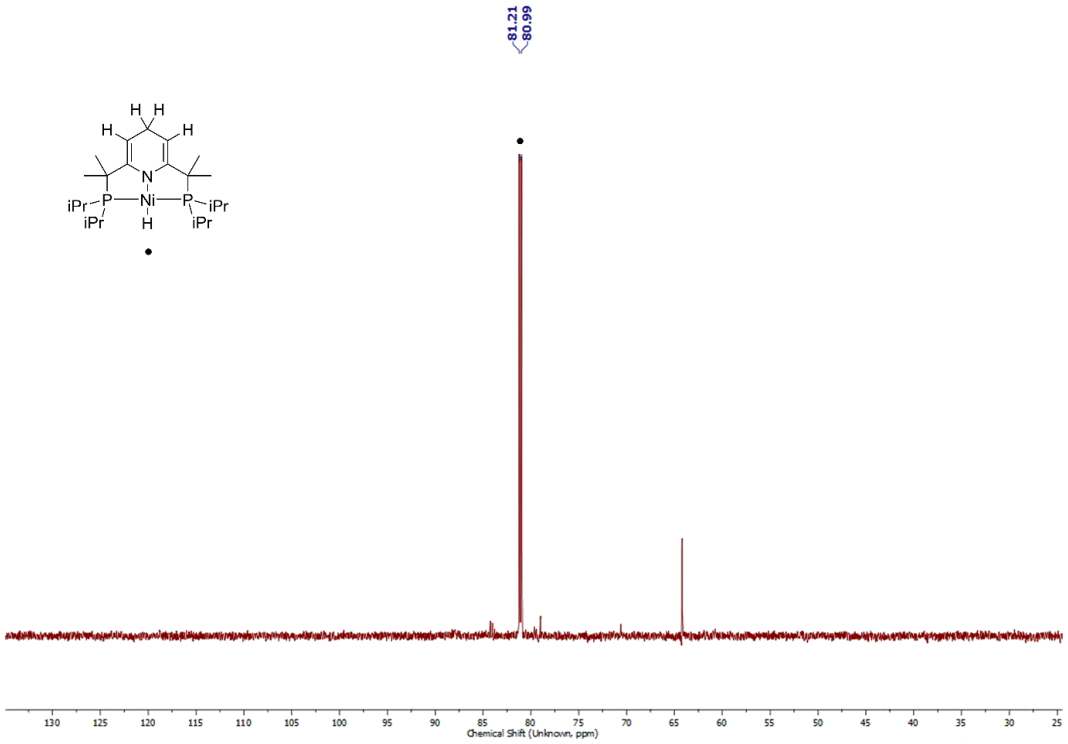


Figure 5. 60 $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture obtained by treatment of **3.24** with 2 equiv of $LiBEt_3H$ (243 MHz, C_6D_6). • Peak of major complex **3.36**. The doublet arises from incomplete decoupling from Ni-H.

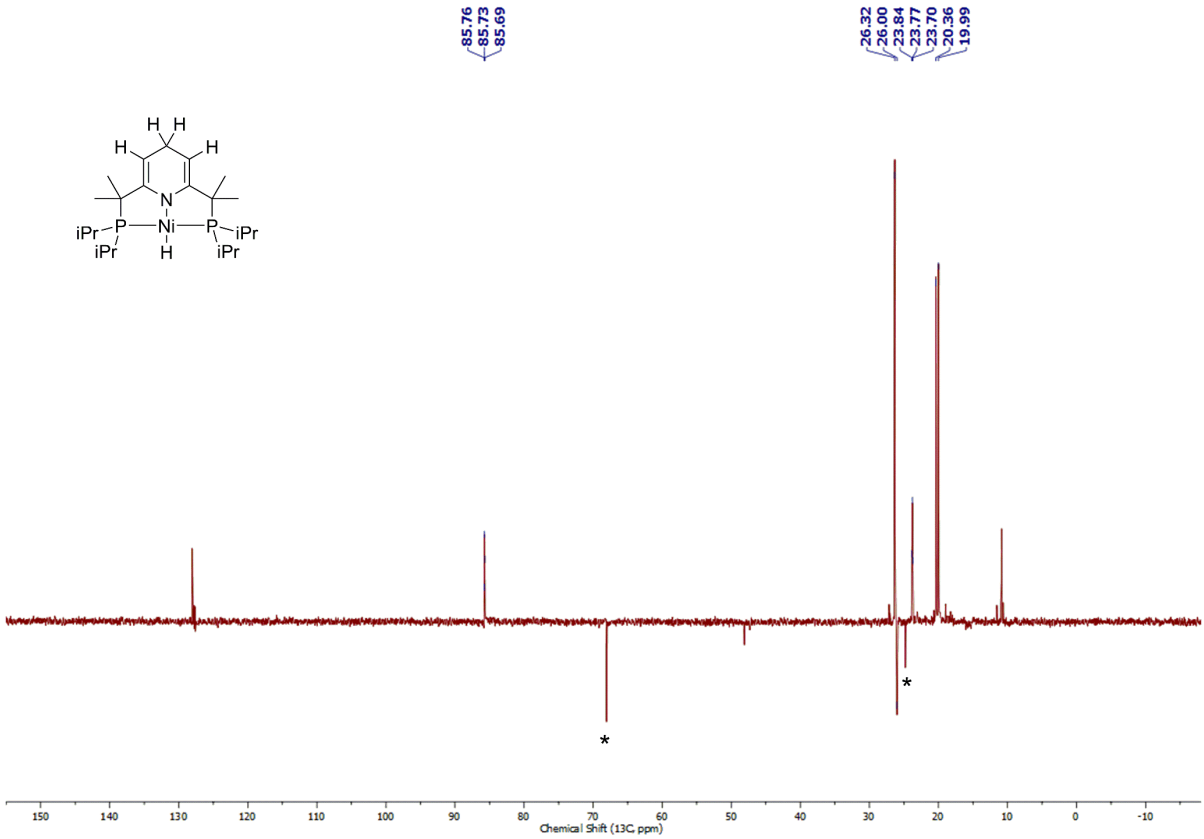


Figure 5. 61 DEPT-135 NMR spectrum of the reaction mixture obtained by treatment of 3.24 with 2 equiv of $LiBEt_3H$ (151 MHz, C_6D_6). * Peaks of THF

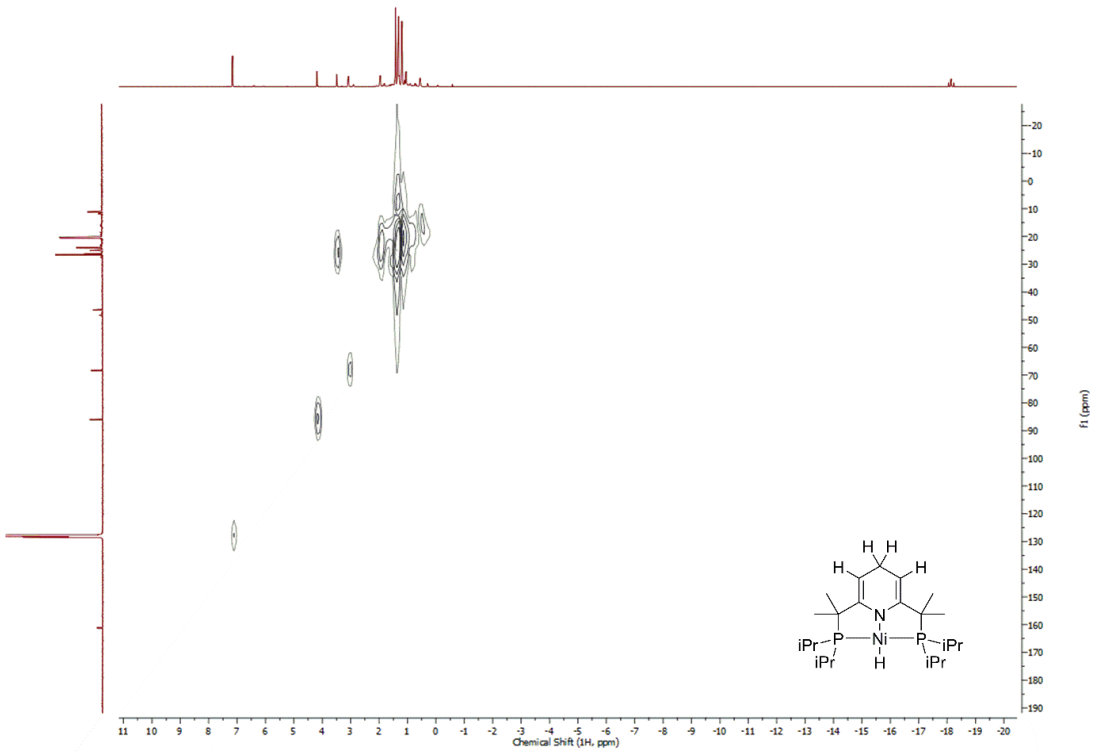


Figure 5. 62 ^{1}H-^{13}C HMQC NMR spectrum of the reaction mixture obtained by treatment of **3.24** with 2 equiv of $LiBEt_3H$ (C_6D_6).

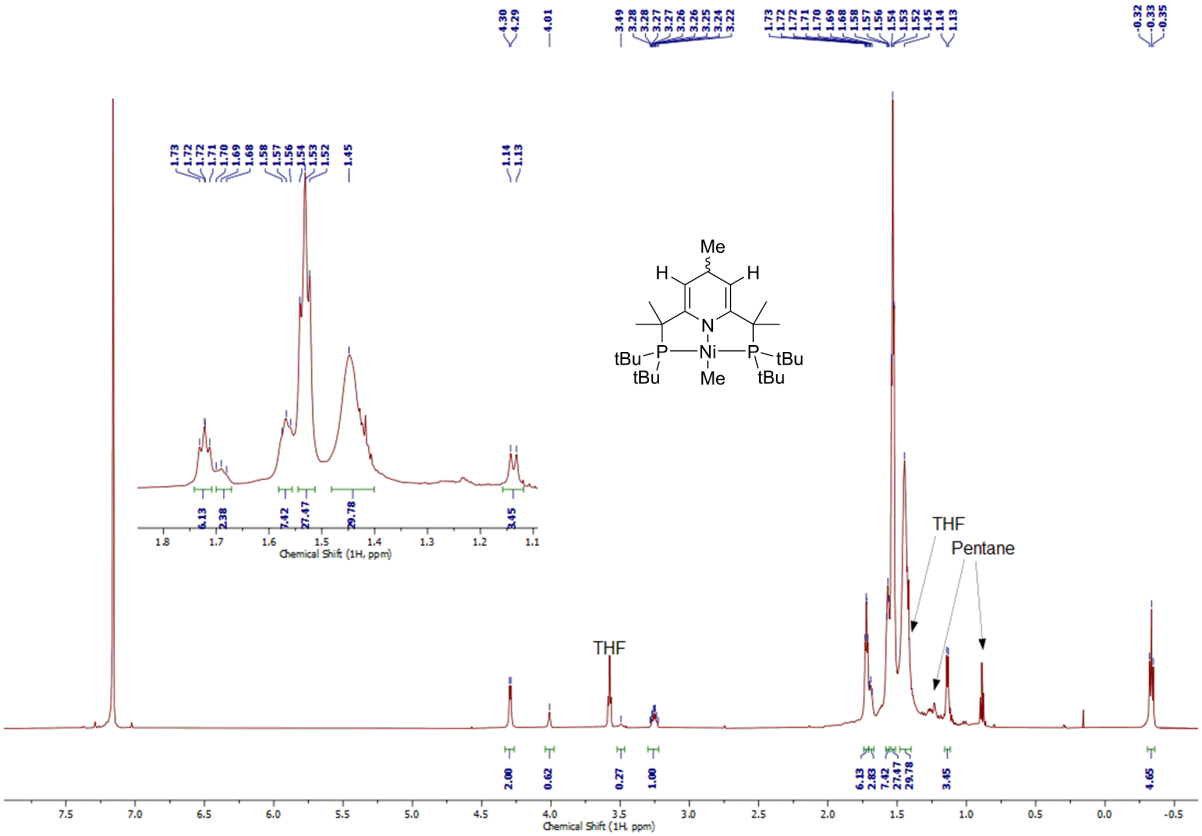


Figure 5. 63 ^{1}H NMR spectrum of **3.37** (400 MHz, C_6D_6). *Impurities of starting complex.

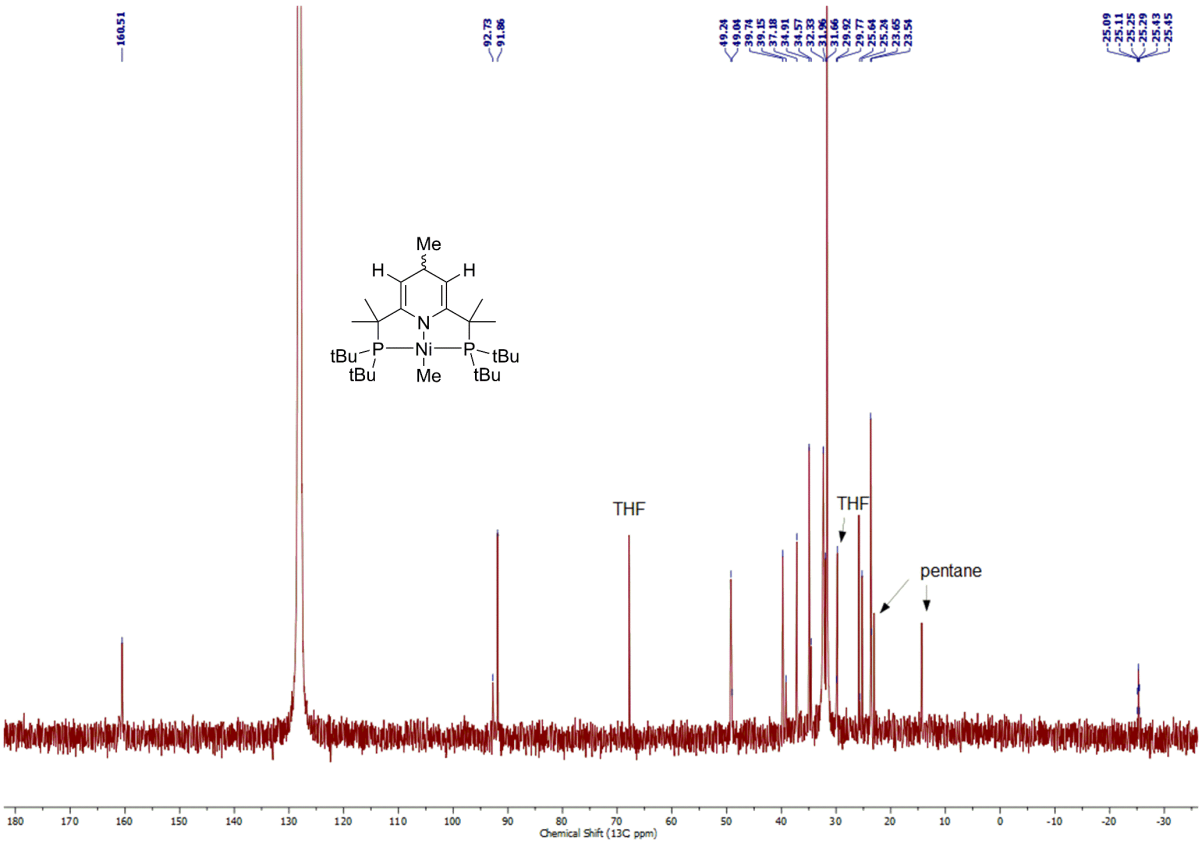


Figure 5. 64 ^{13}C{^{1}H} NMR spectrum of **3.37** (101 MHz, C_6D_6).

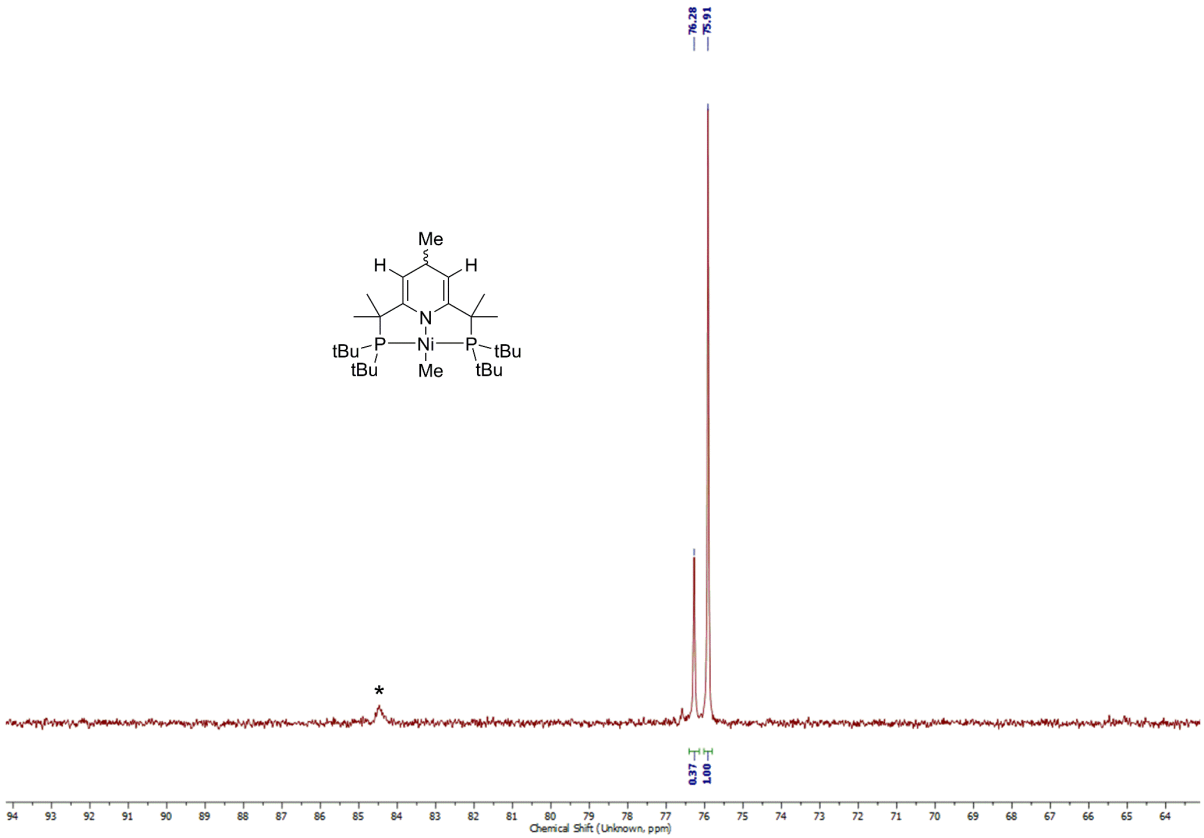


Figure 5. 65 $^{31}P\{^{1}H\}$ NMR spectrum of **3.37** (162 MHz, C_6D_6). * Trace impurities of unidentified complex

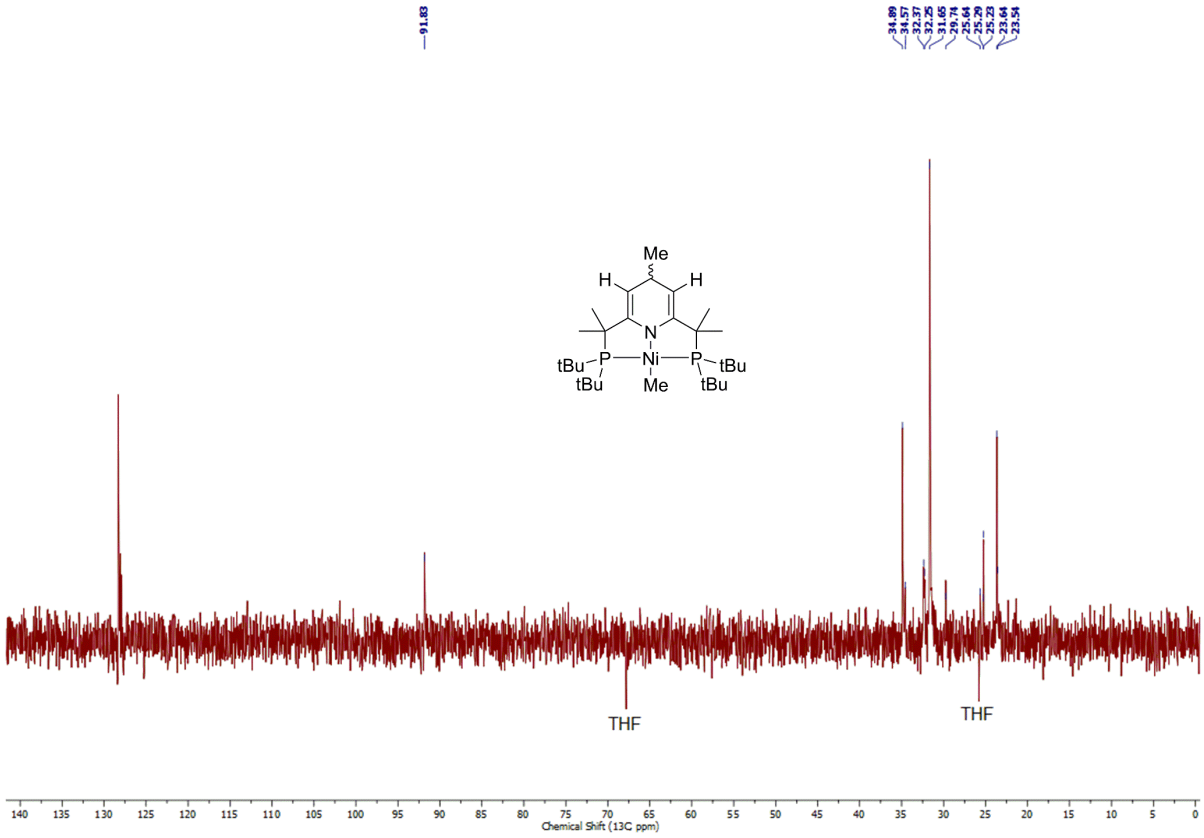


Figure 5. 66 DEPT-135 NMR spectrum of **3.37** (101 MHz, C_6D_6)

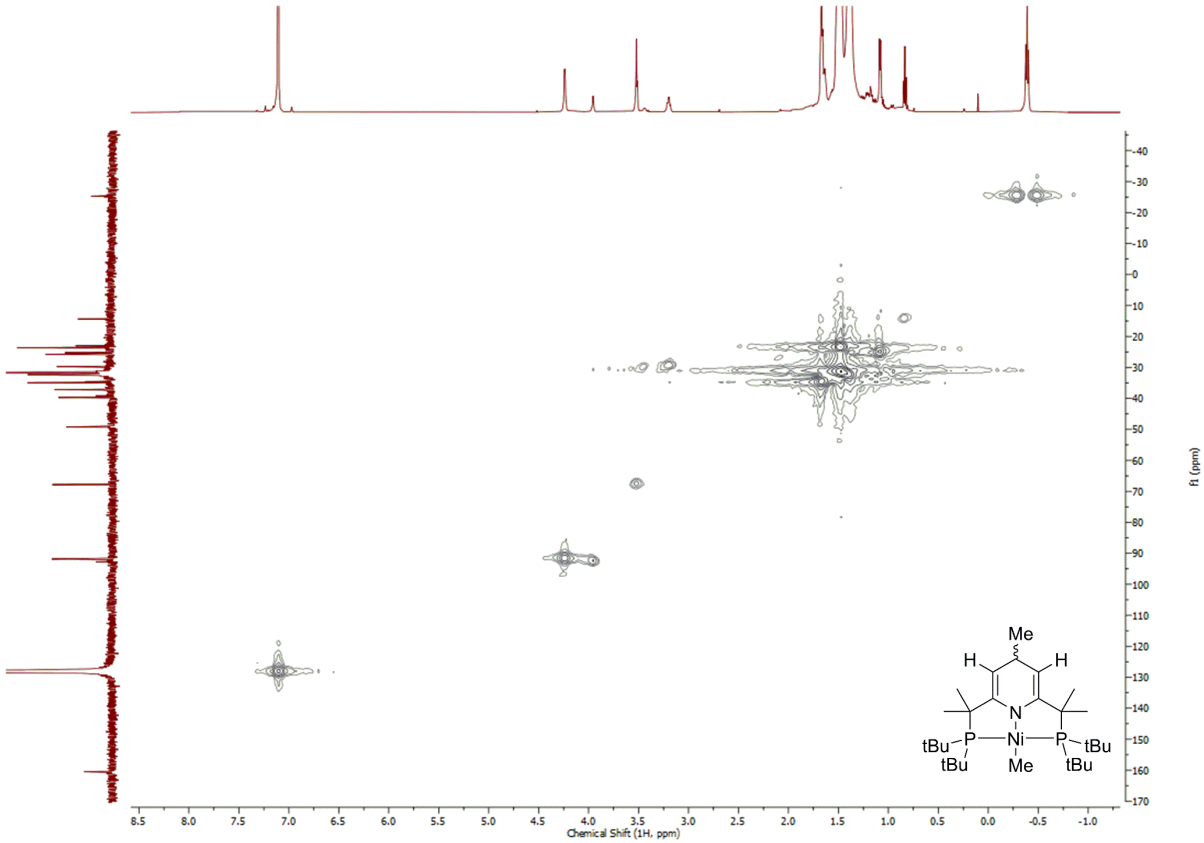


Figure 5. 67 ^{1}H-^{13}C HMQC NMR spectrum of **3.37** (C_6D_6)

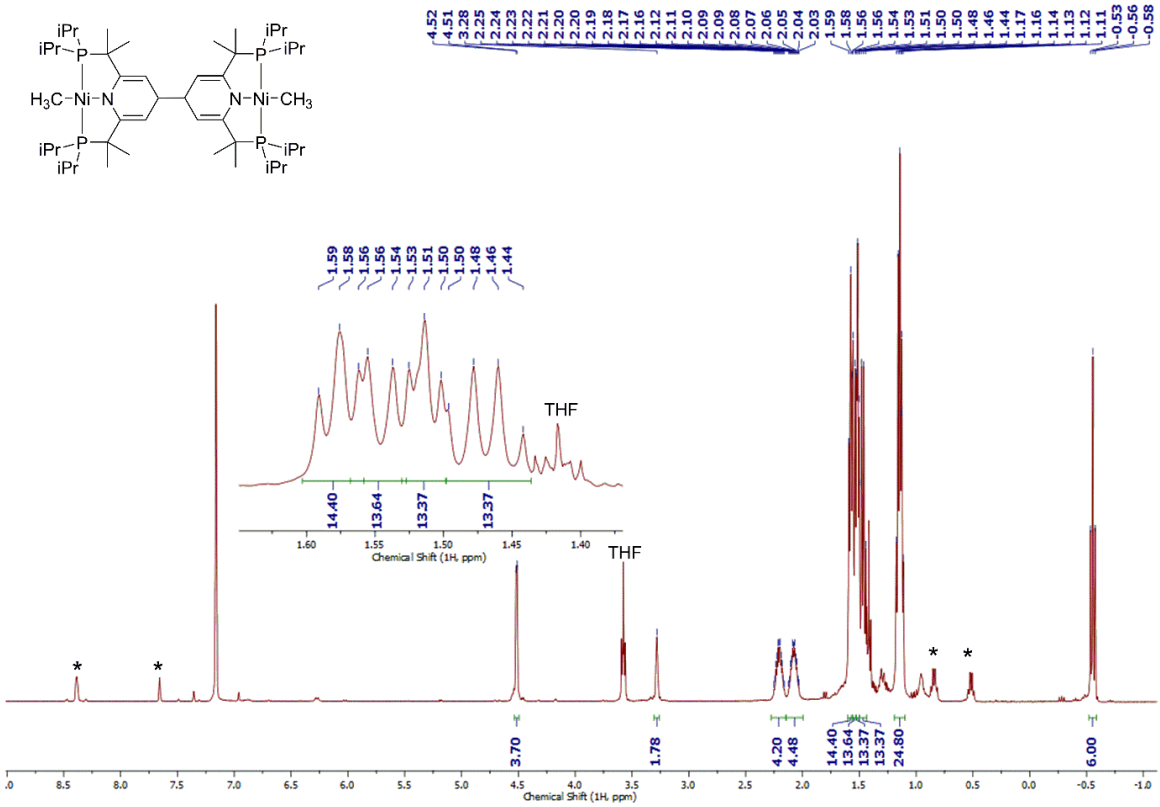


Figure 5. 68 ^{1}H NMR spectrum of **3.38** (400 MHz, C_6D_6). *Impurities of starting complex.

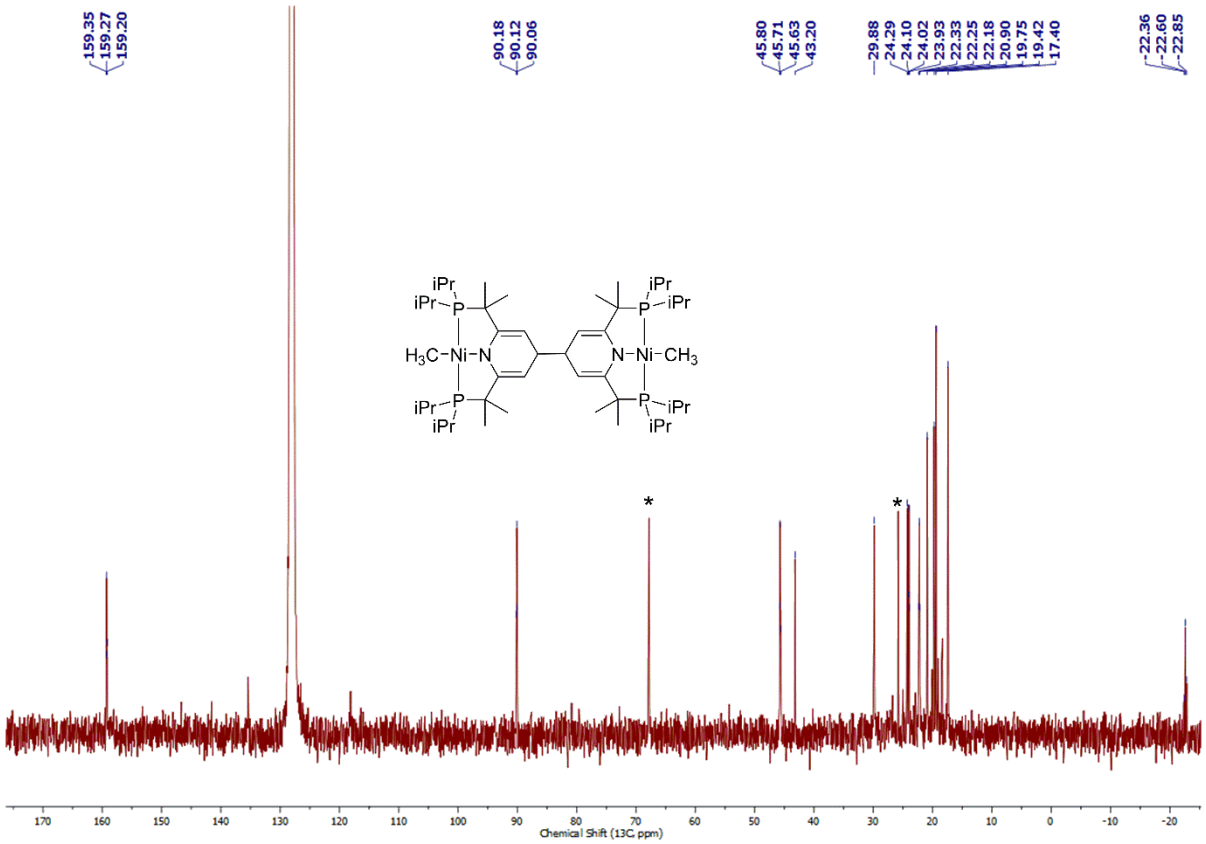


Figure 5. 69 $^{13}C\{^{1}H\}$ NMR spectrum of **3.38** (101 MHz, C_6D_6). *Traces of THF

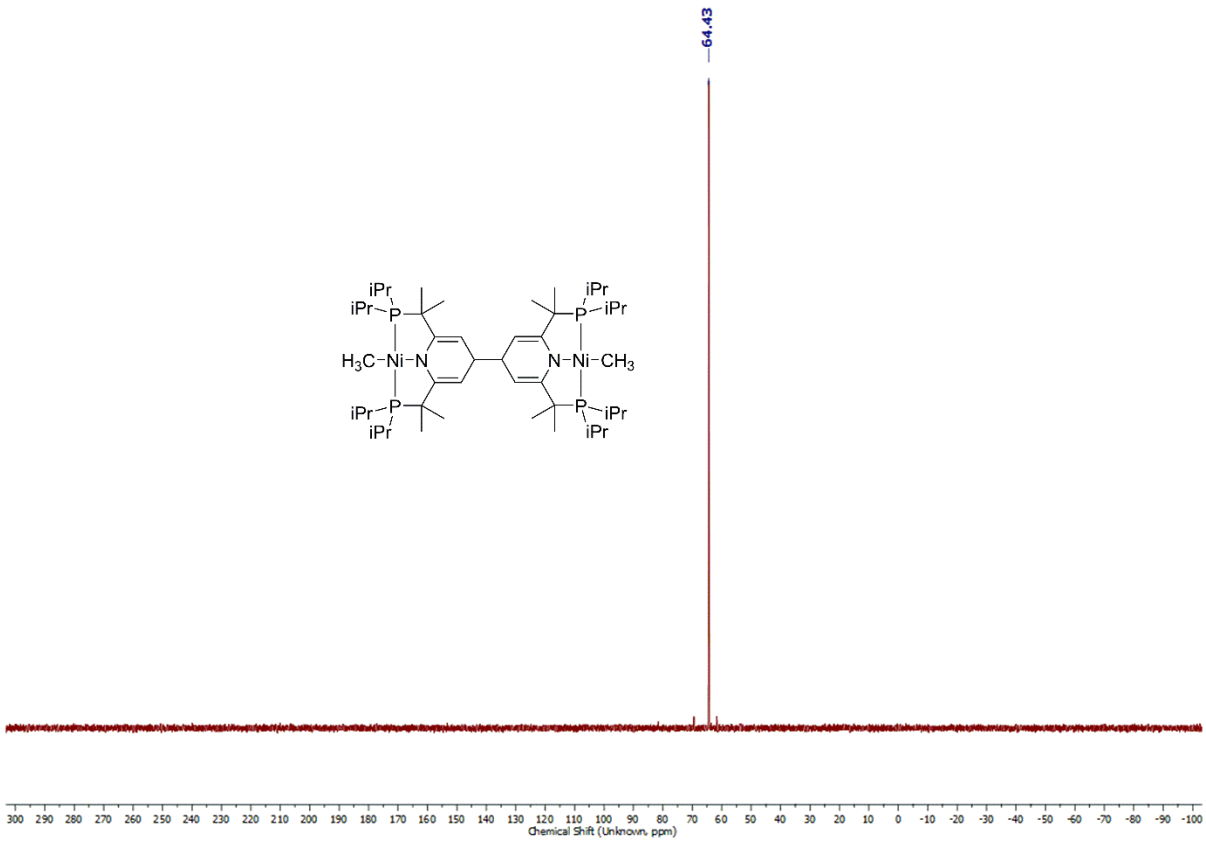


Figure 5. 70 $^{31}P\{^{1}H\}$ NMR spectrum of **3.38** (162 MHz, C_6D_6)

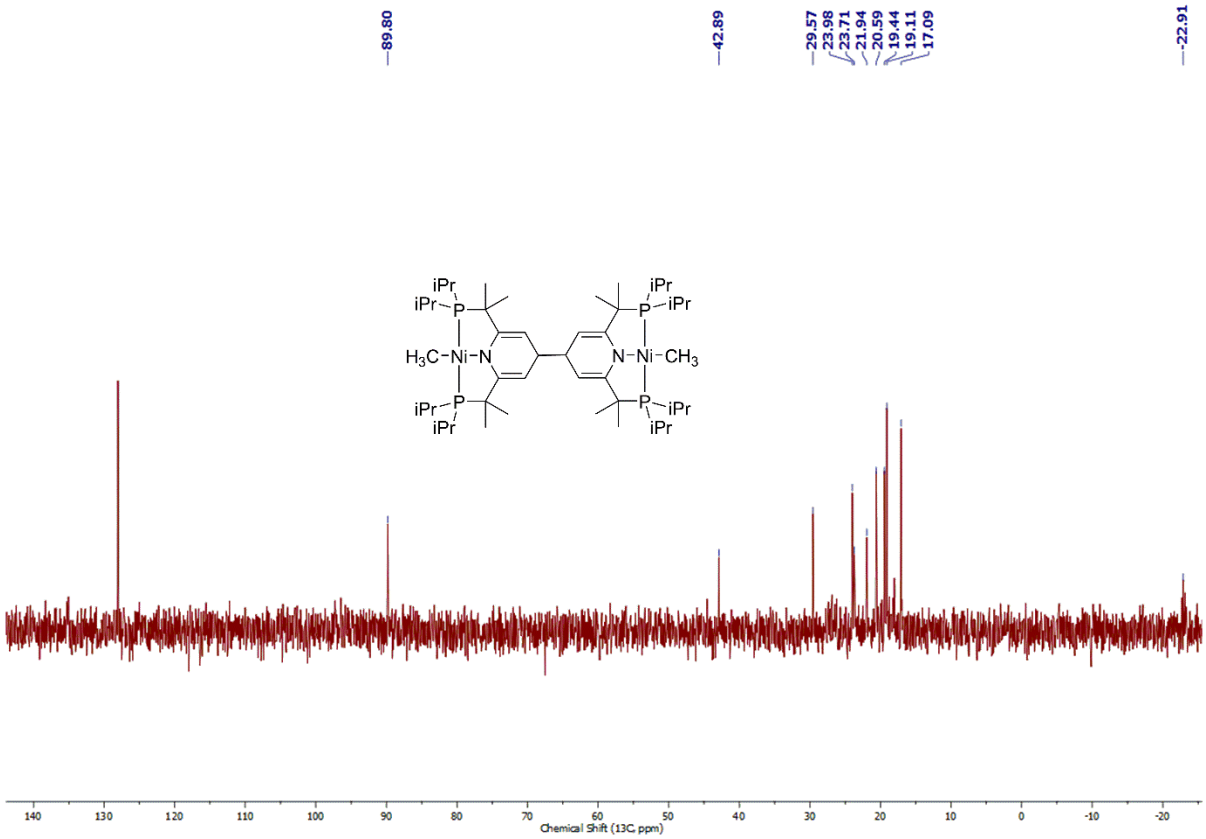


Figure 5. 71 DEPT-135 NMR spectrum of **3.38** (101 MHz, C_6D_6)

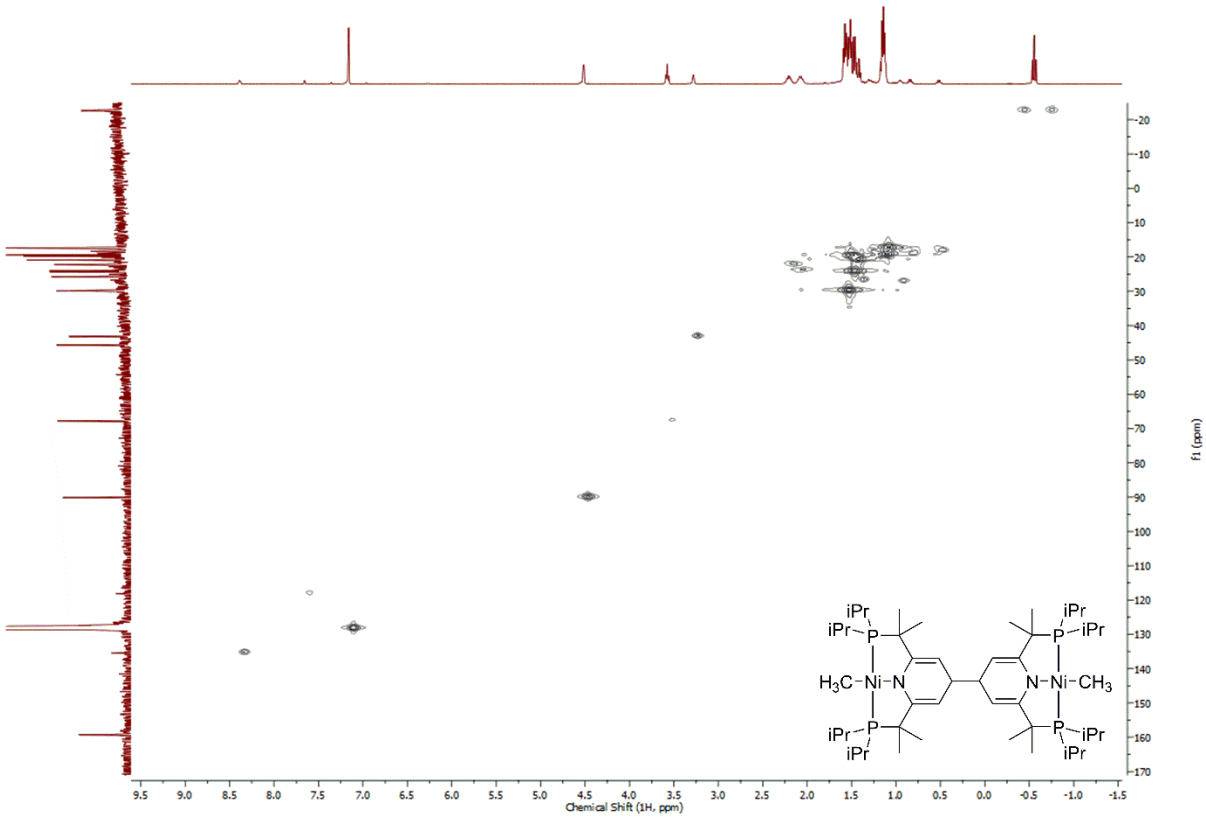


Figure 5. 72 ^{1}H-^{13}C HMQC NMR spectrum of **3.38** (C_6D_6)

5.1.2 Small molecule reactivity

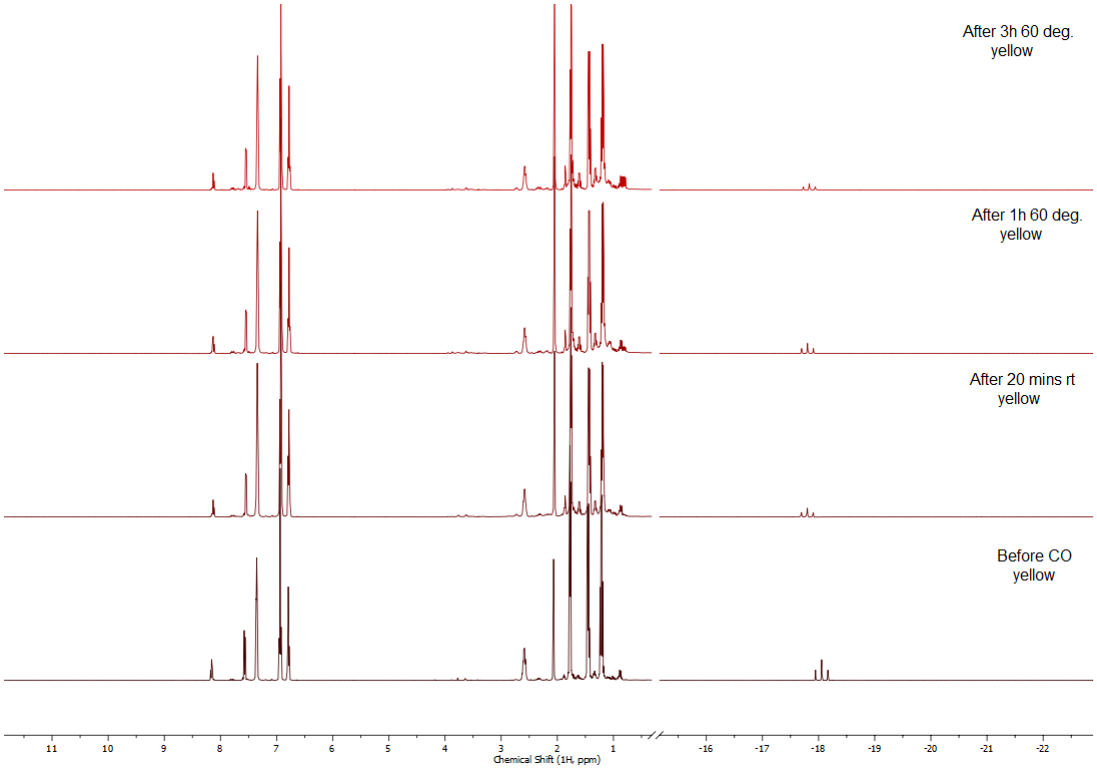


Figure 5. 73 Stacked ^{1}H NMR spectra of the reaction of **3.27** with CO up to 3 hours at 60 °C (500 MHz, acetone-d_6).

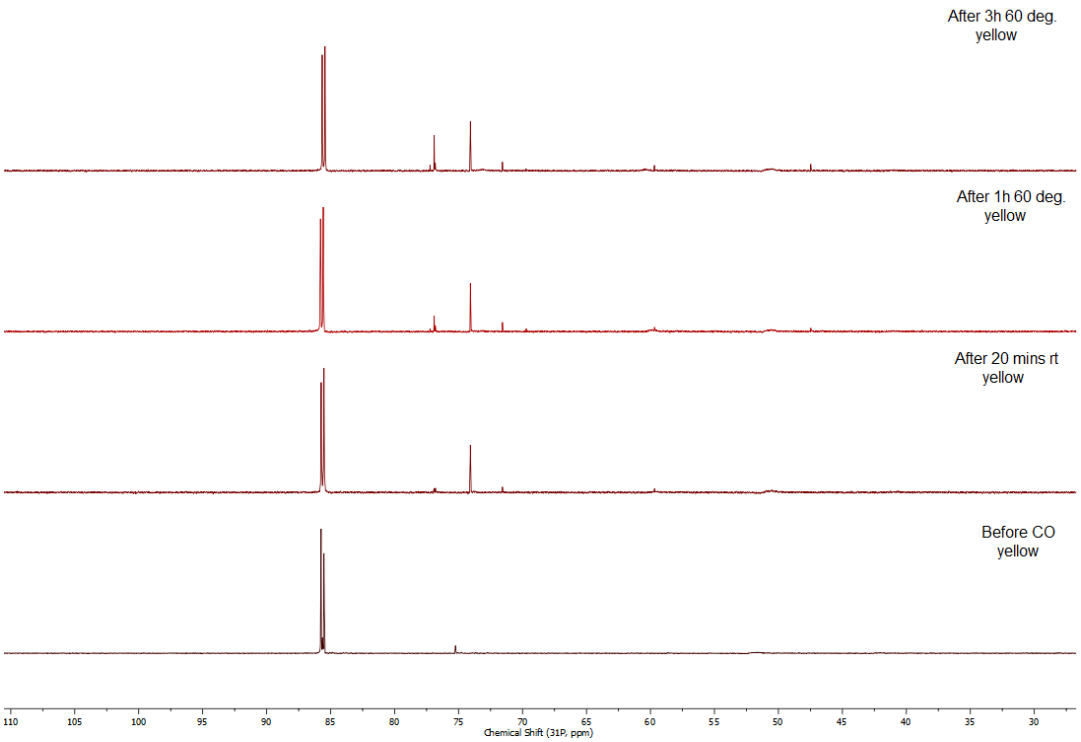


Figure 5. 74 Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **3.27** with CO up to 3 hours at 60 °C (202 MHz, acetone-d_6).

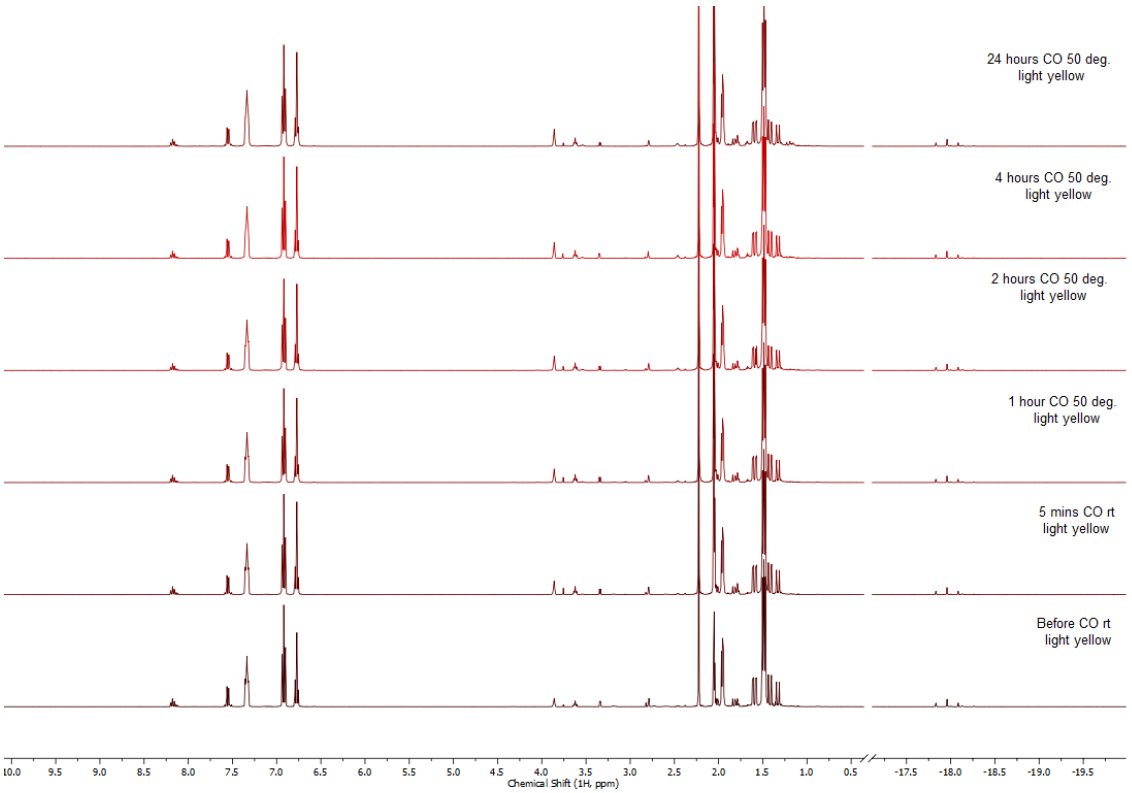


Figure 5. 75 Stacked ^{1}H NMR spectra of the reaction of **3.29** with CO up to 24 hours at 50 °C (400 MHz, acetone-d_6).

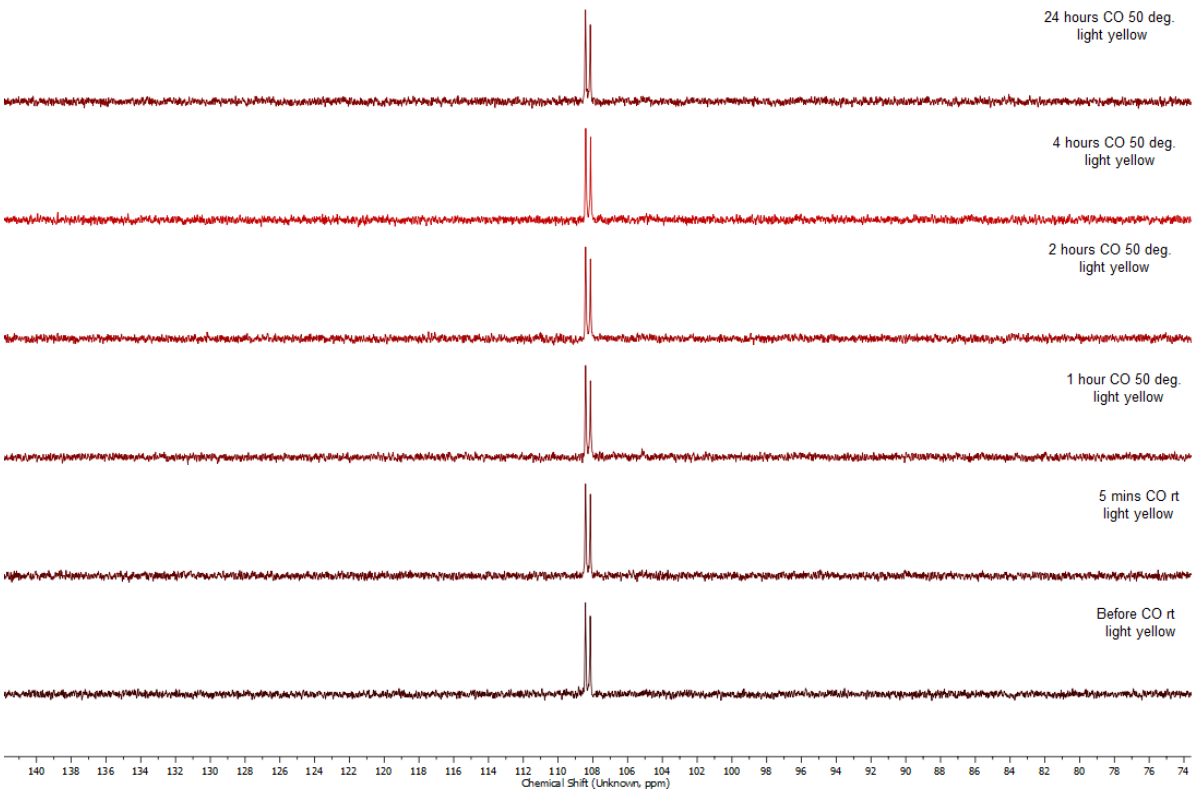


Figure 5. 76 Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **3.29** with CO up to 24 hours at 50 °C (400 MHz, acetone-d_6).

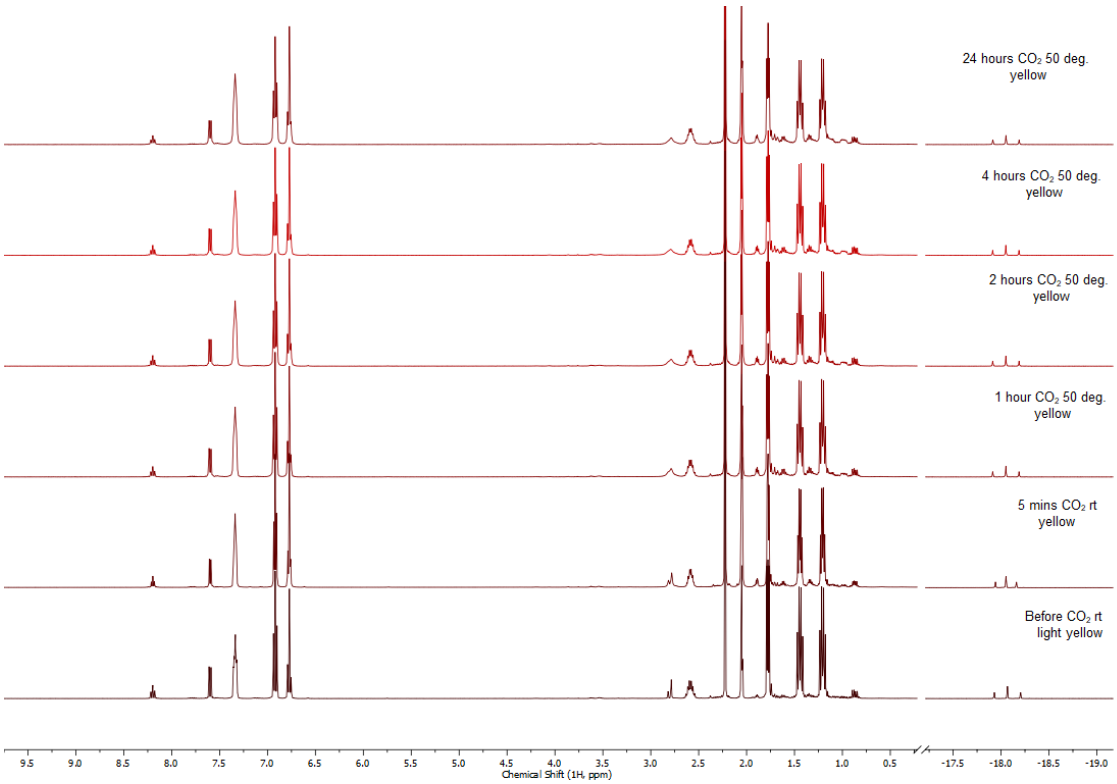


Figure 5. 77 Stacked ^{1}H NMR spectra of the reaction of **3.27** with CO_2 up to 24 hours at 50 °C (400 MHz, acetone-d_6).

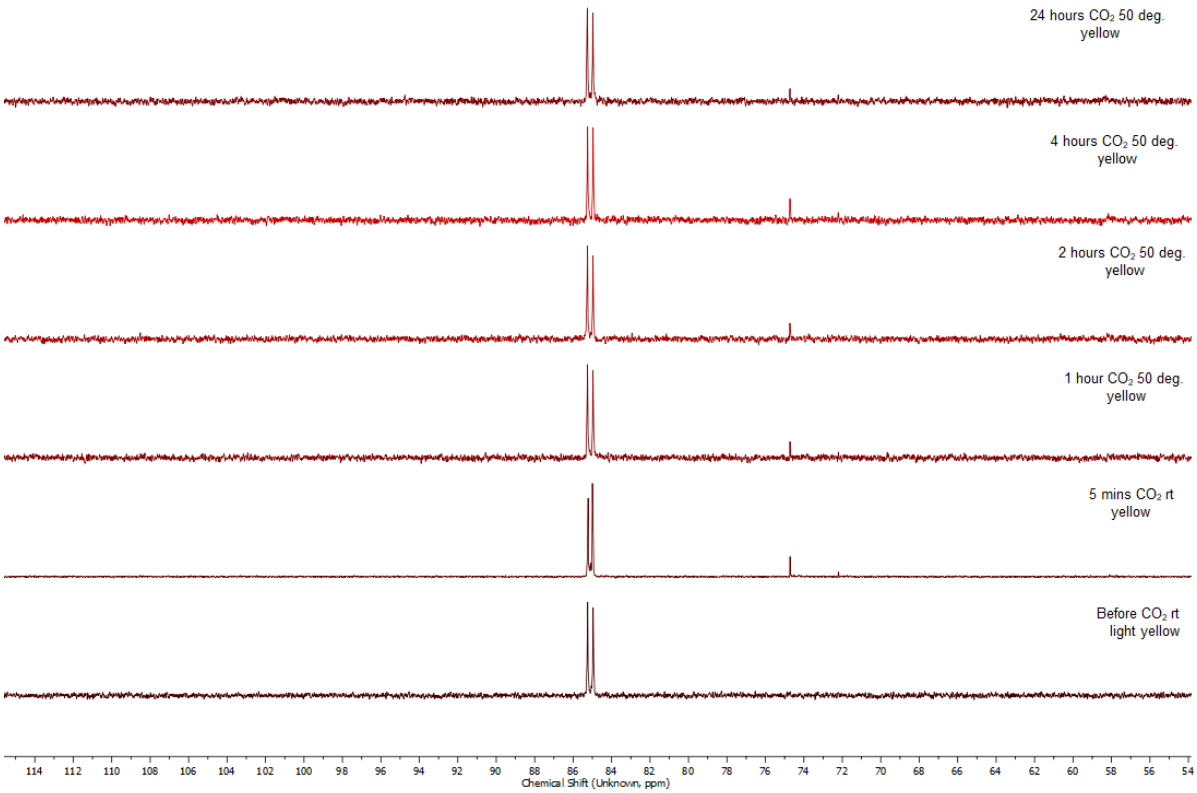


Figure 5. 78 Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **3.27** with CO_2 up to 24 hours at 50 °C (400 MHz, acetone-d_6).

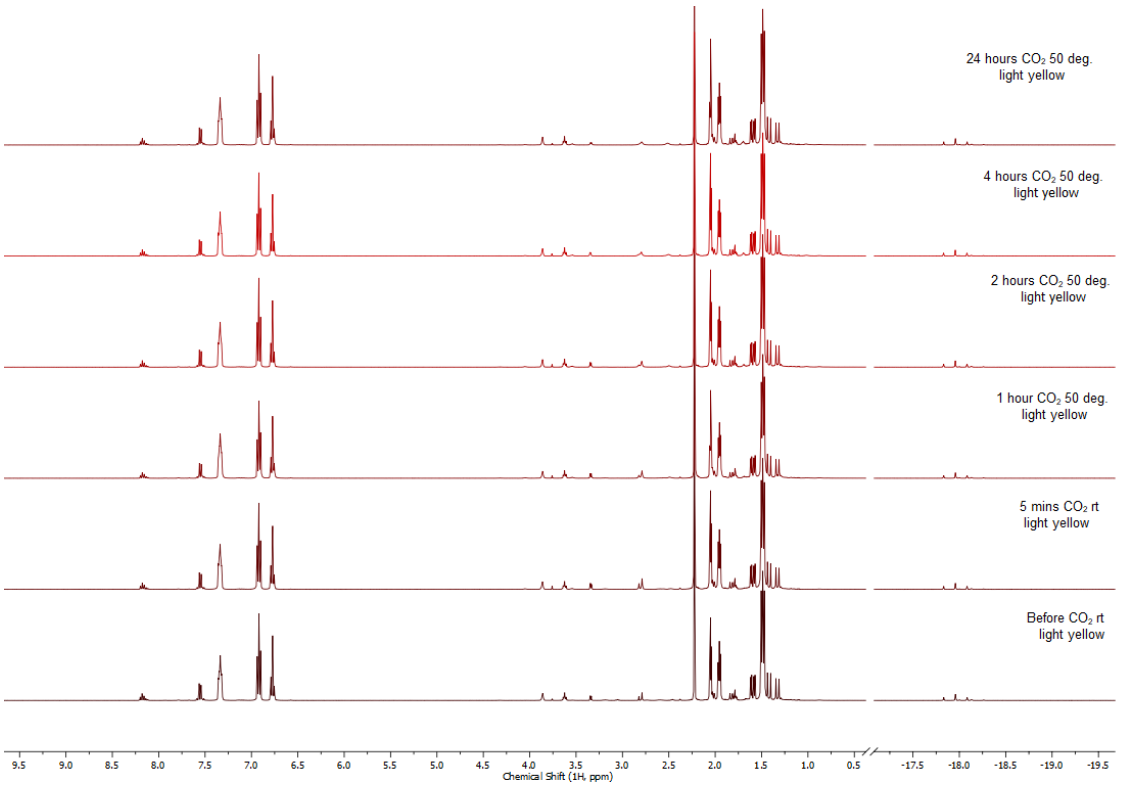


Figure 5. 79 Stacked ^{1}H NMR spectra of the reaction of **3.29** with CO_2 up to 24 hours at 50 °C (400 MHz, acetone-d_6).

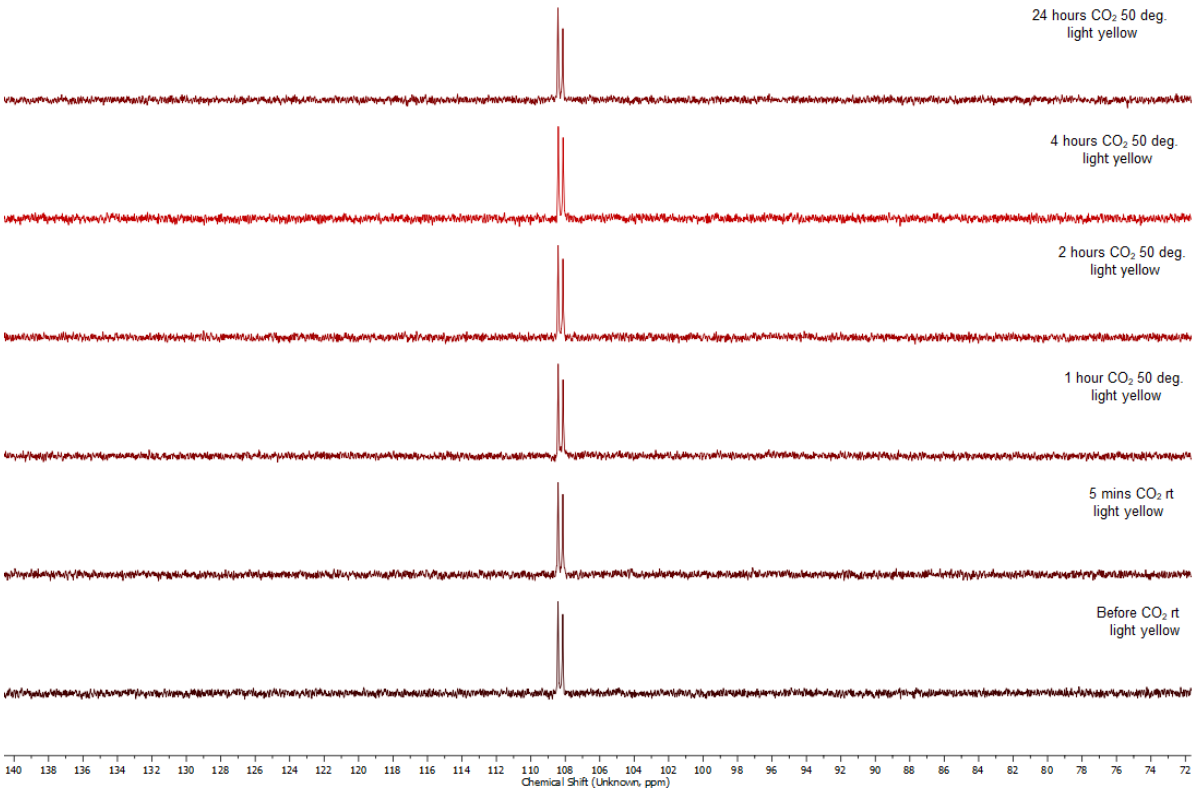


Figure 5. 80 Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **3.29** with CO_2 up to 24 hours at 50 °C (400 MHz, acetone-d_6).

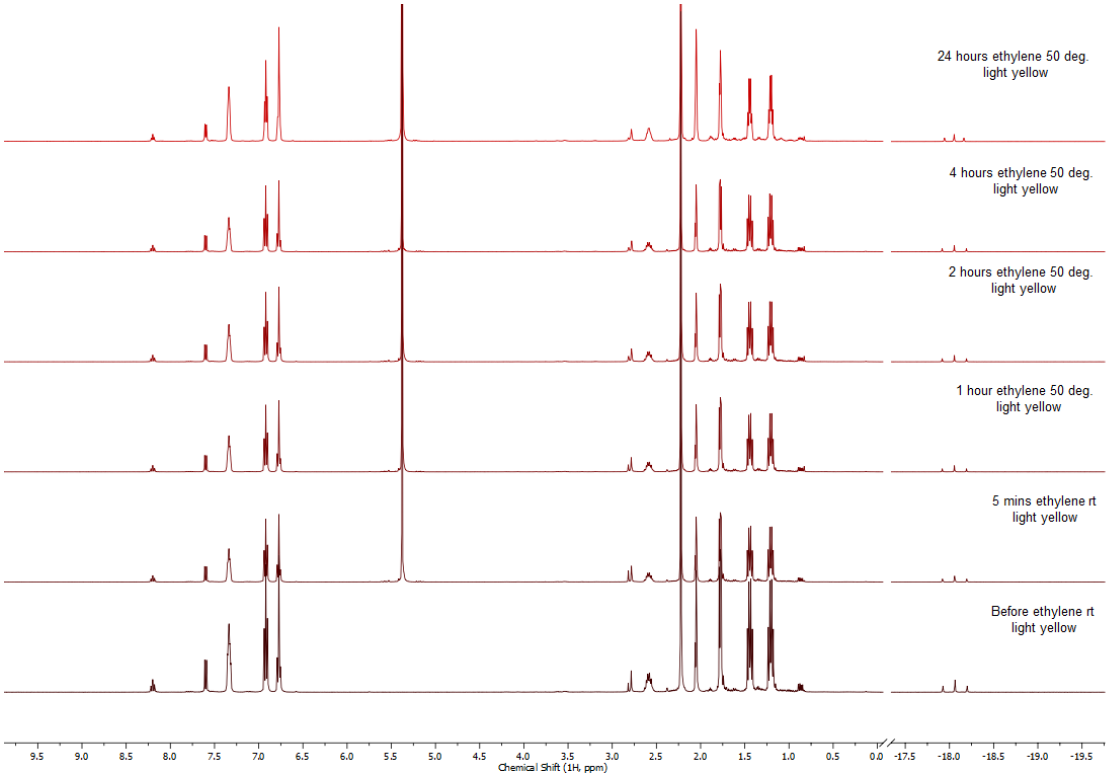


Figure 5. 81 Stacked ^{1}H NMR spectra of the reaction of **3.27** with ethylene up to 24 hours at 50 °C (400 MHz, acetone-d_6).

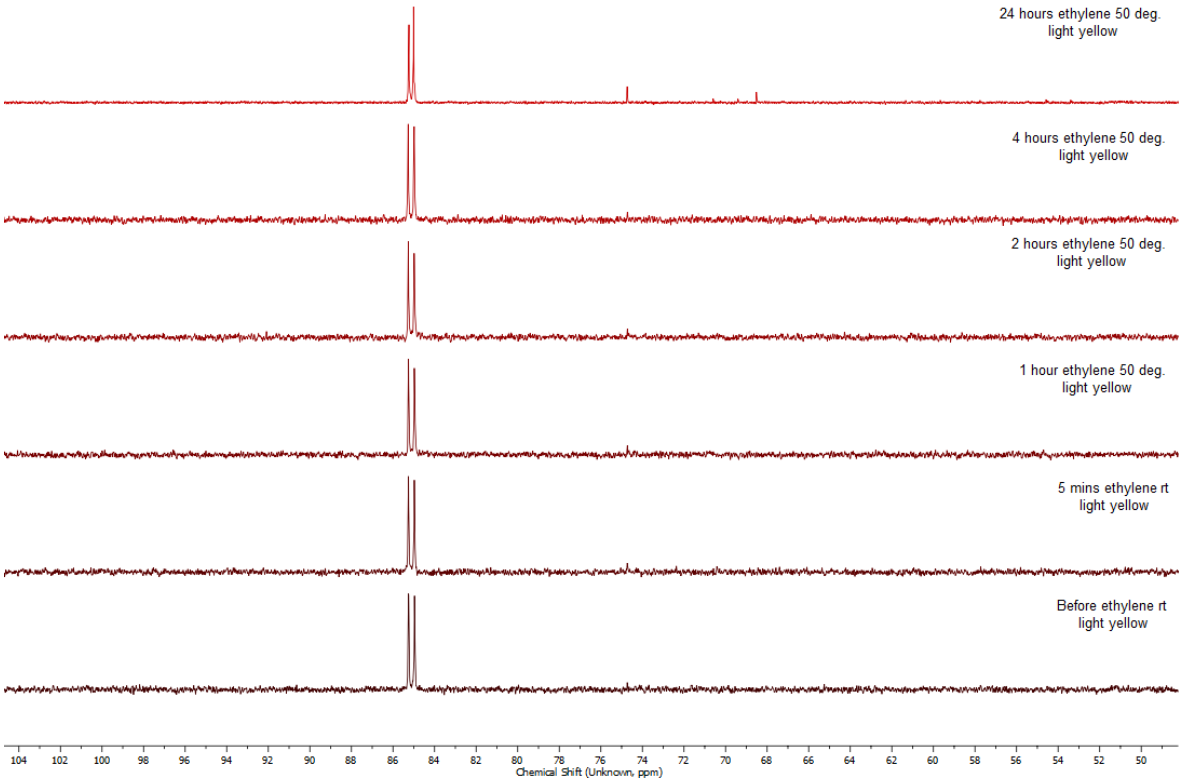


Figure 5. 82 Stacked ^{31}P{^{1}H} NMR spectra of the reaction of **3.27** with ethylene up to 24 hours at 50 °C (400 MHz, acetone-d_6).

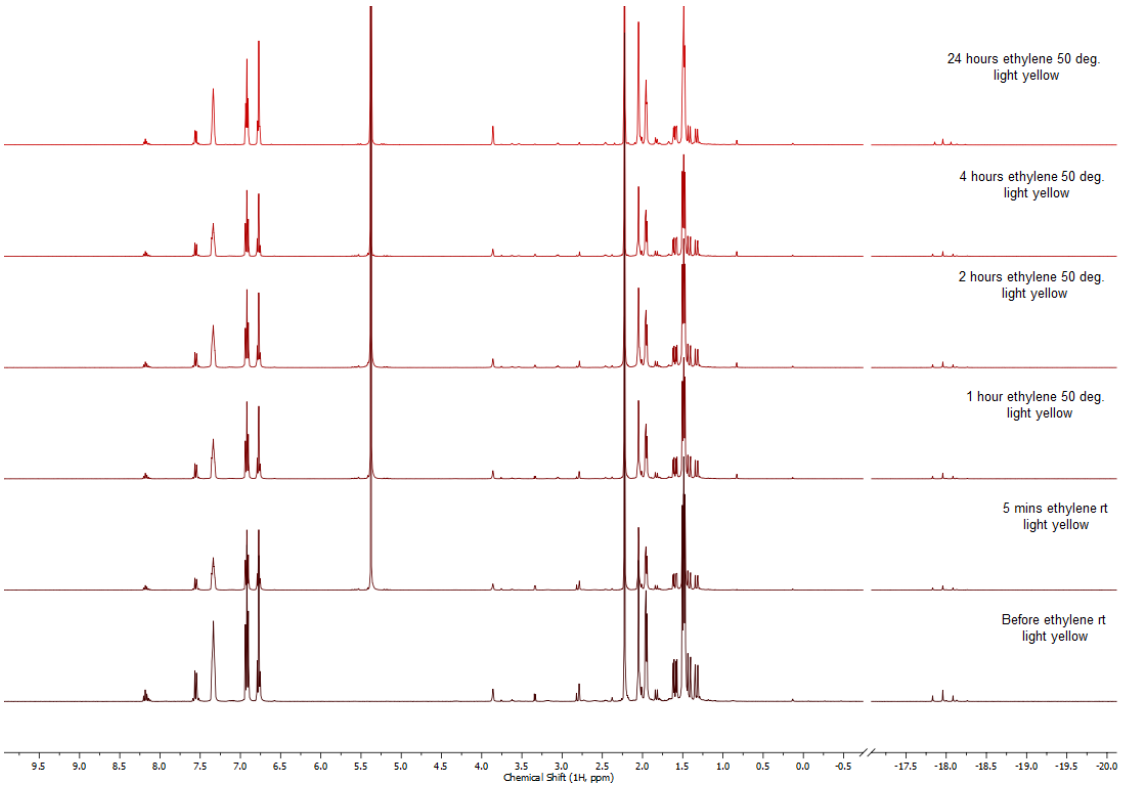


Figure 5. 83 Stacked ^{1}H NMR spectra of the reaction of **3.29** with ethylene up to 24 hours at 50 °C (400 MHz, acetone-d_6).

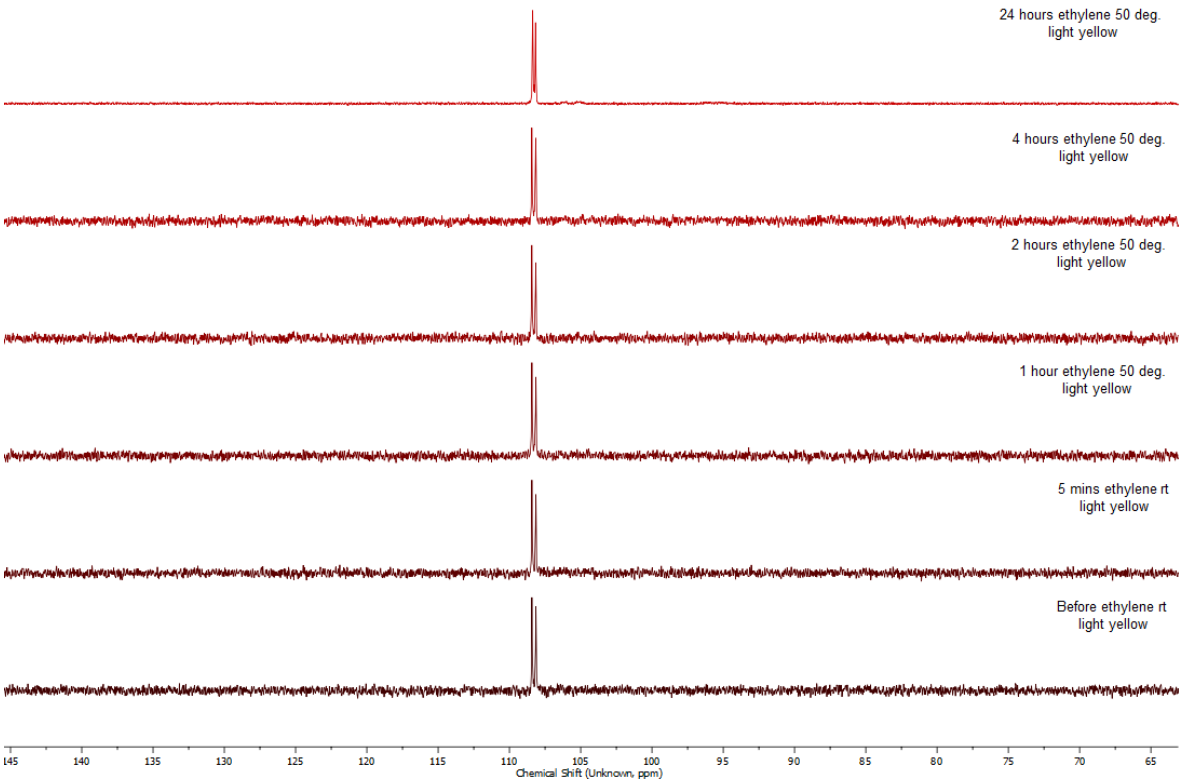


Figure 5. 84 Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **3.29** with ethylene up to 24 hours at 50 °C (400 MHz, acetone-d_6).

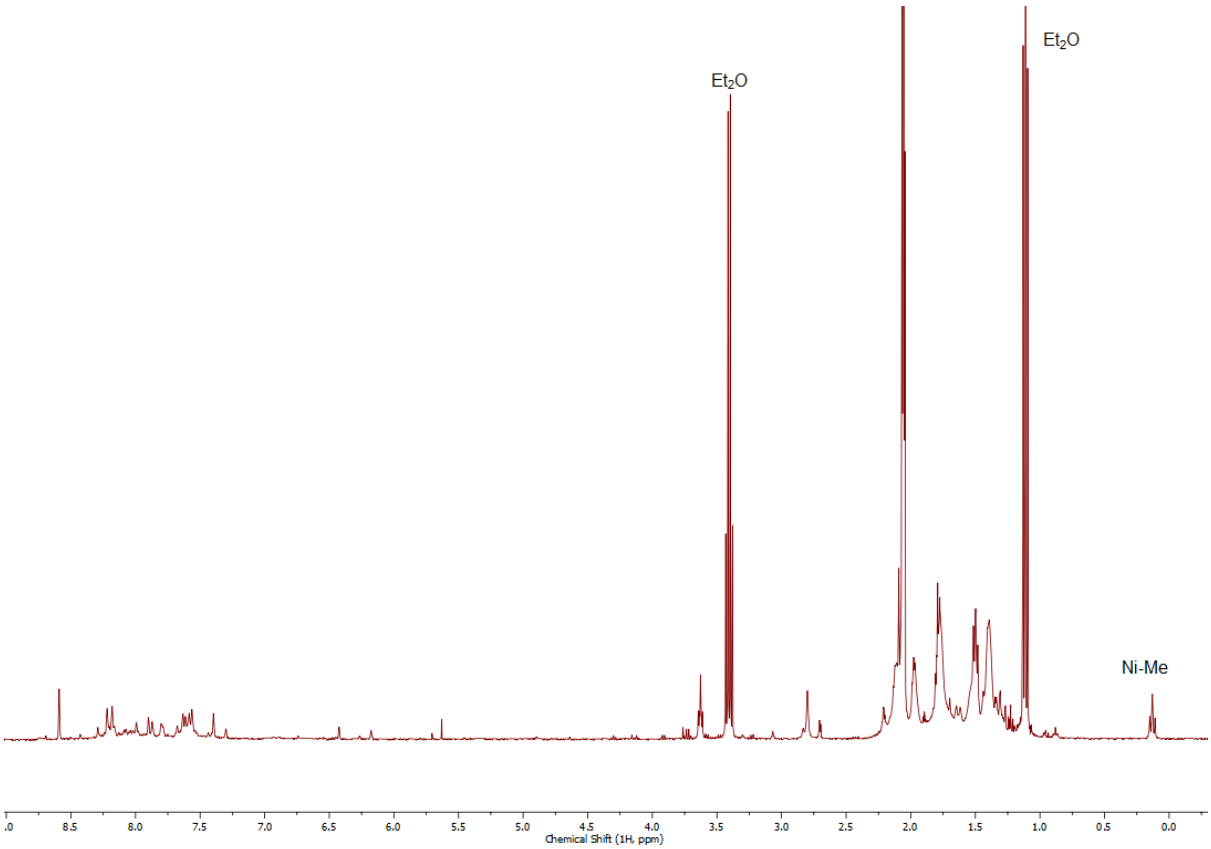


Figure 5. 85 ^{1}H NMR spectra of the reaction of **3.32** under UV irradiation for 1.5h (400 MHz, acetone-d_6)

5.2 UV-VIS analysis

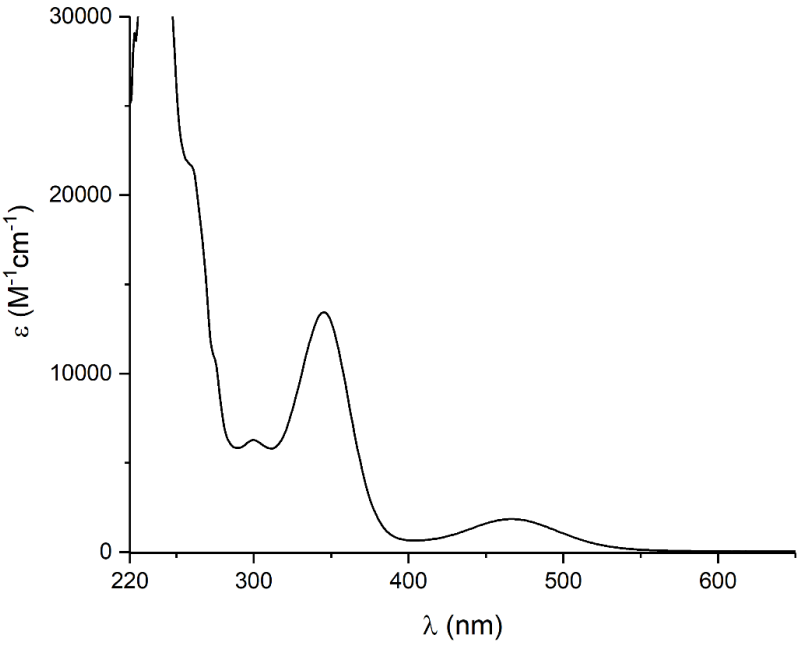


Figure 5. 86 UV-vis spectrum of **3.24**

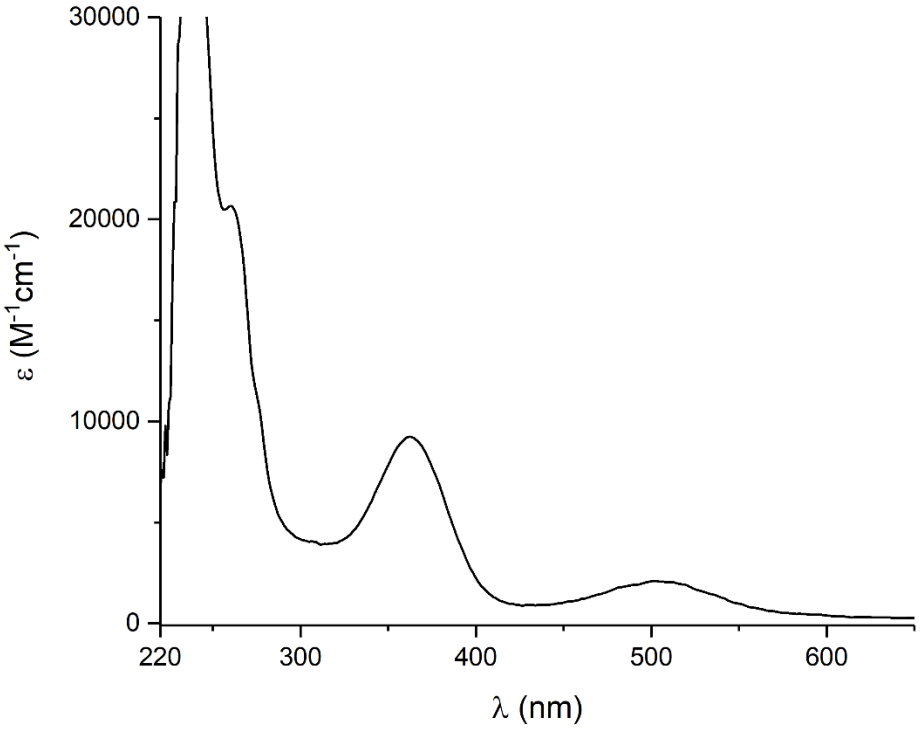


Figure 5. 87 UV-vis spectrum of **3.25**

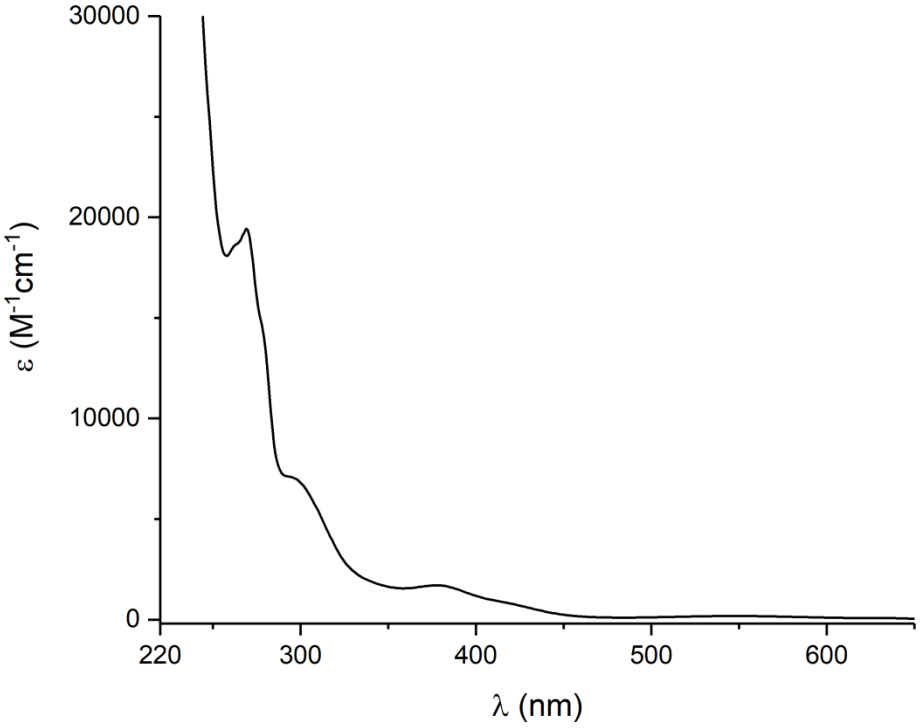


Figure 5. 88 UV-vis spectrum of **3.26**

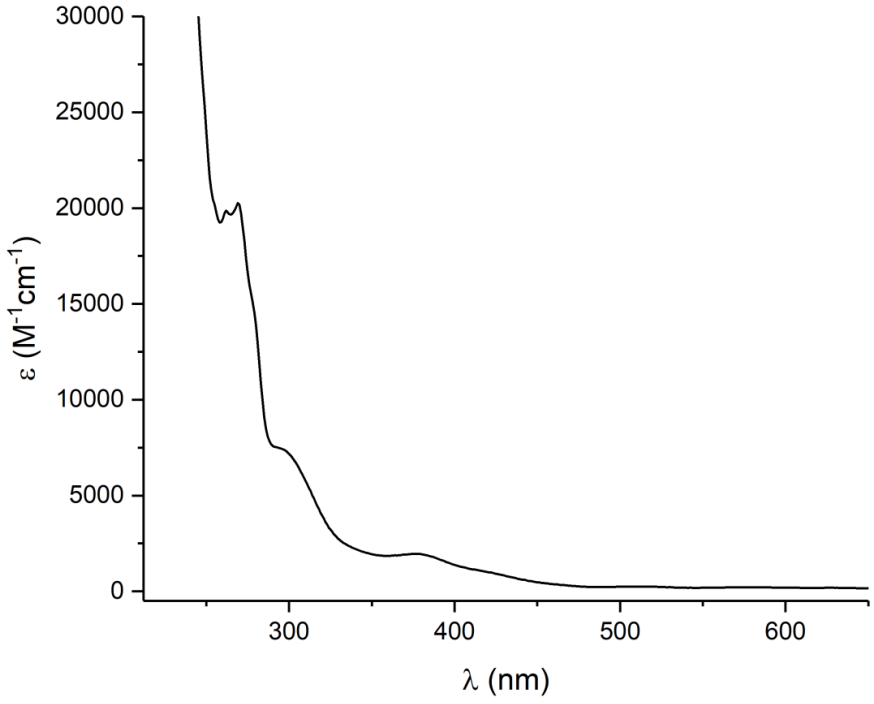


Figure 5. 89 UV-vis spectrum of **3.26** after bubbling O_2 for 5 seconds**.**

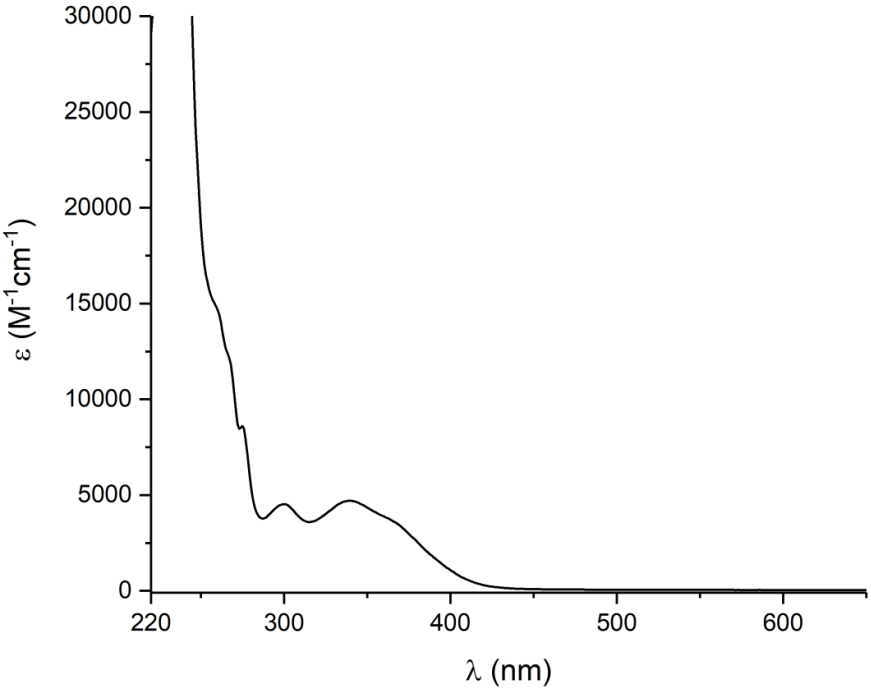


Figure 5. 90 UV-vis spectrum of **3.27**

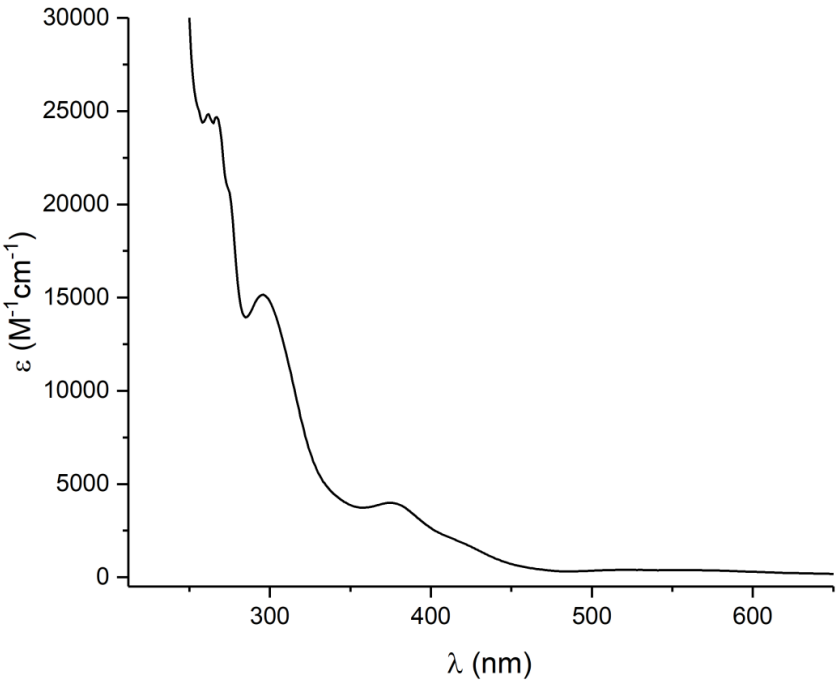


Figure 5. 91 UV-vis spectrum of **3.27** after bubbling O_2 for 5 seconds.

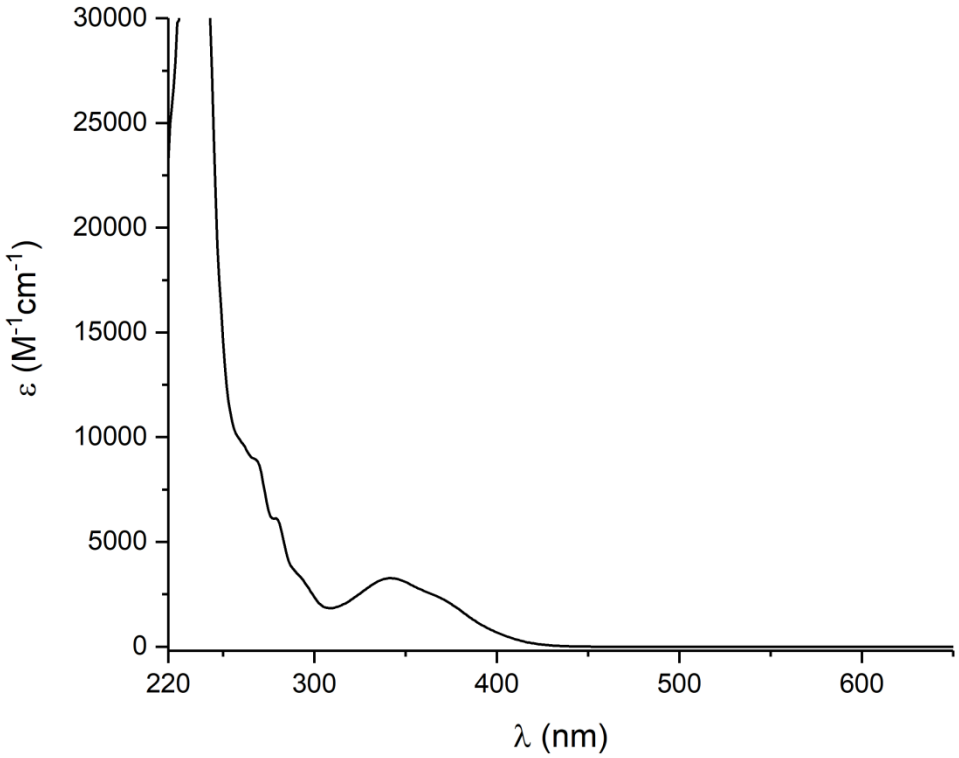


Figure 5. 92 UV-vis spectrum of **3.28**

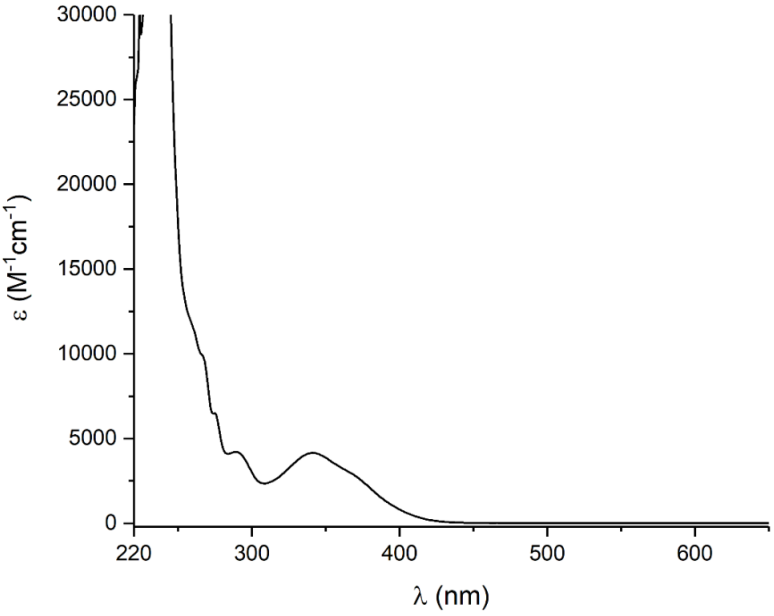


Figure 5. 93 UV-vis spectrum of **3.29**

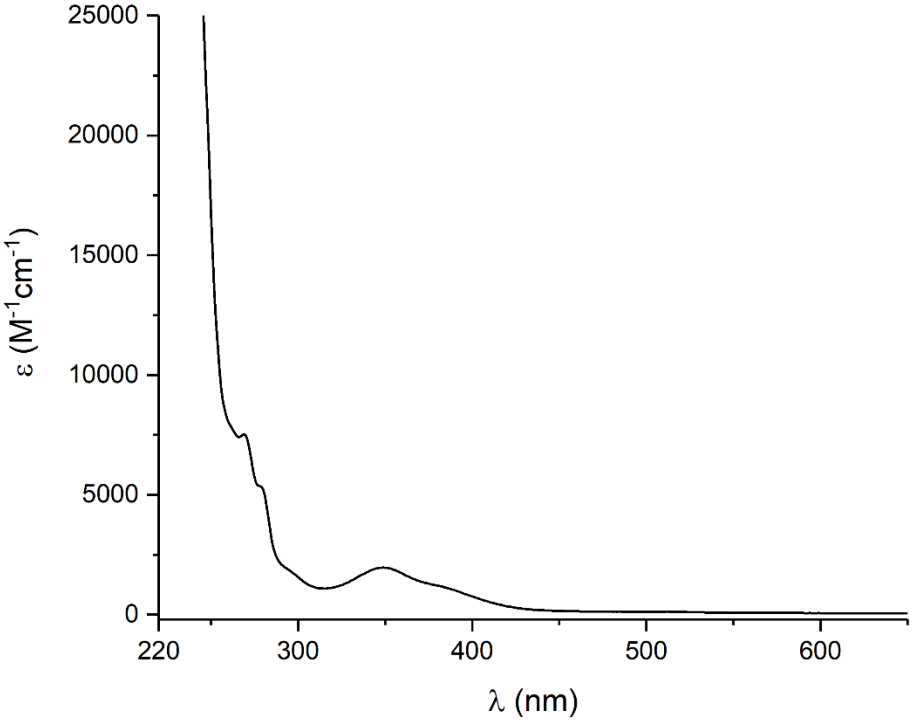


Figure 5. 94 UV-vis spectrum of **3.30**

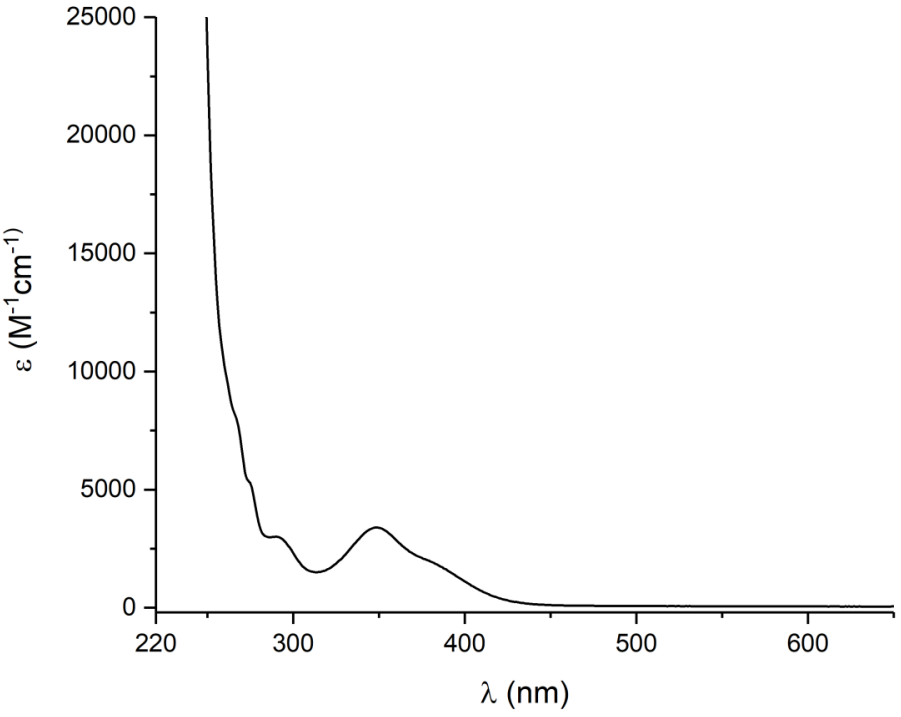


Figure 5. 95 UV-vis spectrum of **3.31**

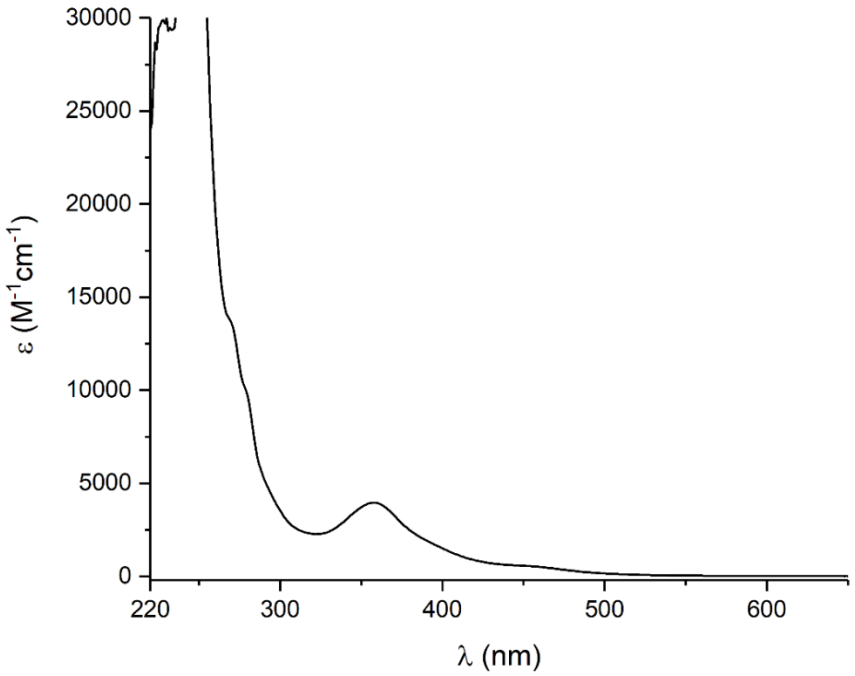


Figure 5. 96 UV-vis spectrum of **3.32**

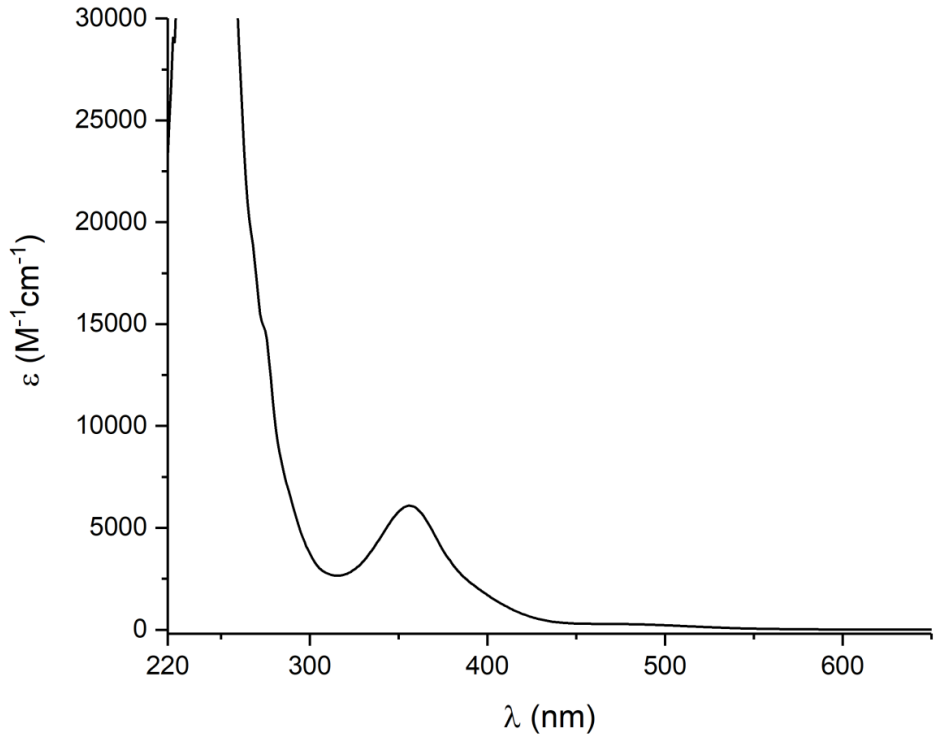


Figure 5. 97 UV-vis spectrum of **3.33**

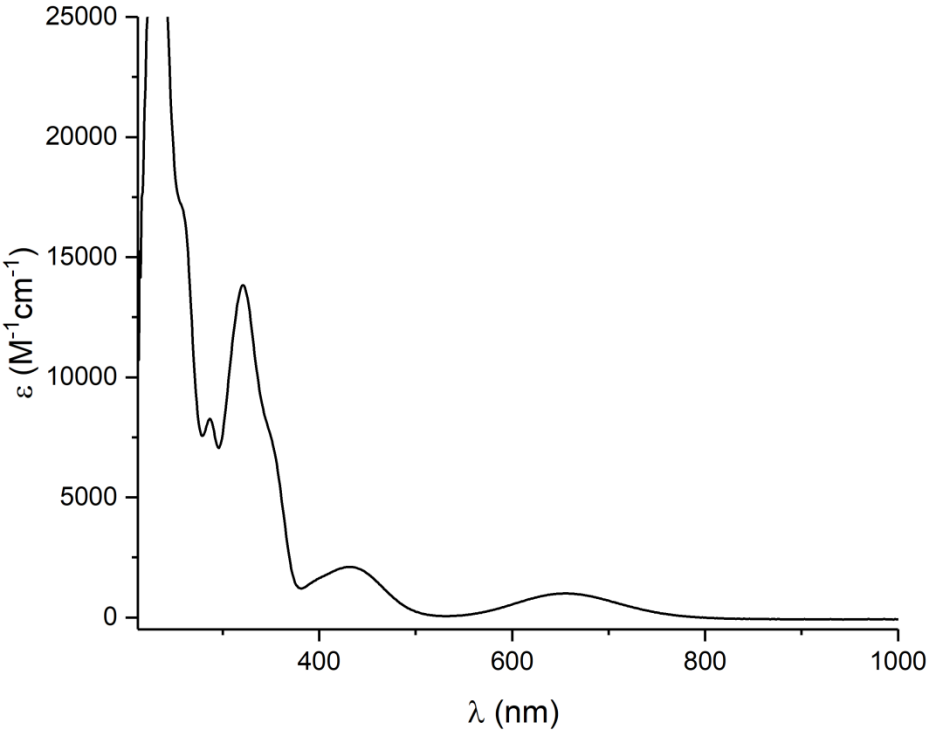


Figure 5. 98 UV-vis spectrum **of 3.34**

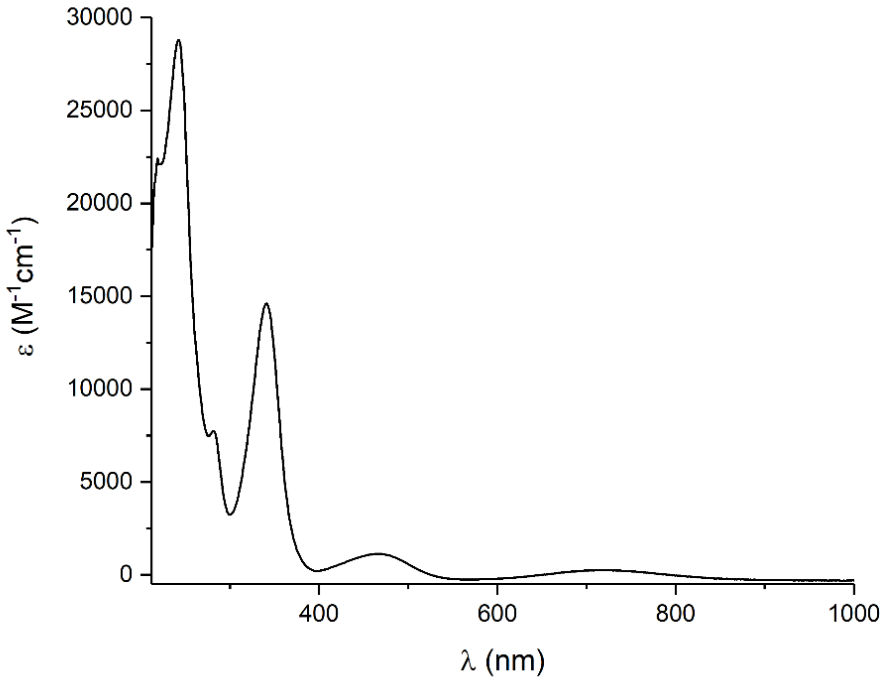


Figure 5. 99 UV-vis spectrum of **3.35**

5.3 IR analysis

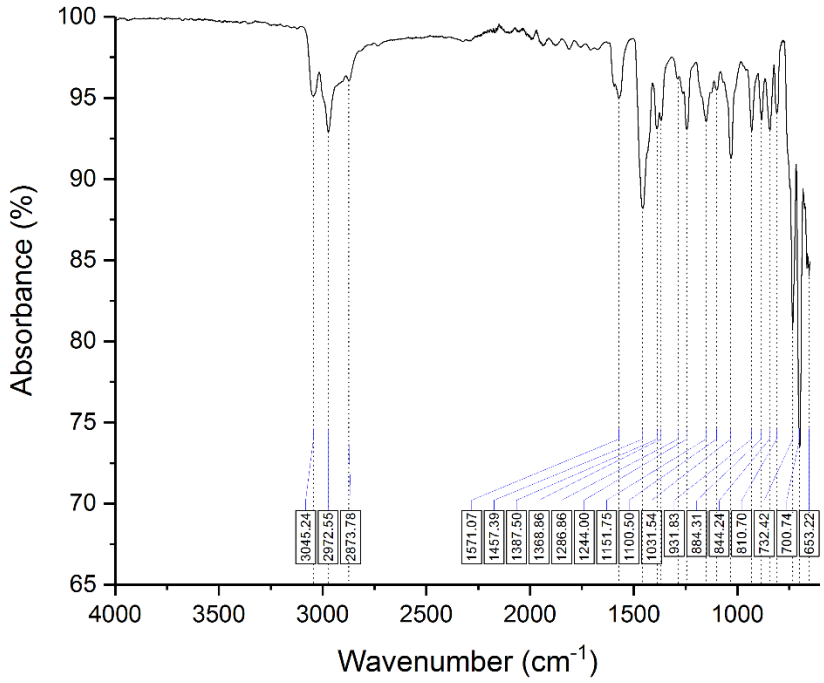


Figure 5. 100 IR spectrum of **3.24**

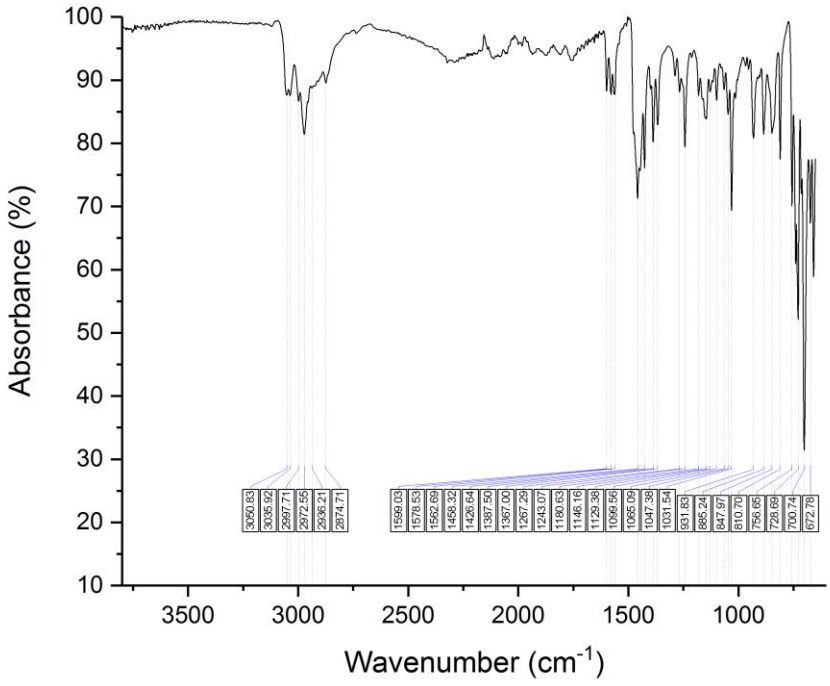


Figure 5. 101 IR spectrum of **3.25**

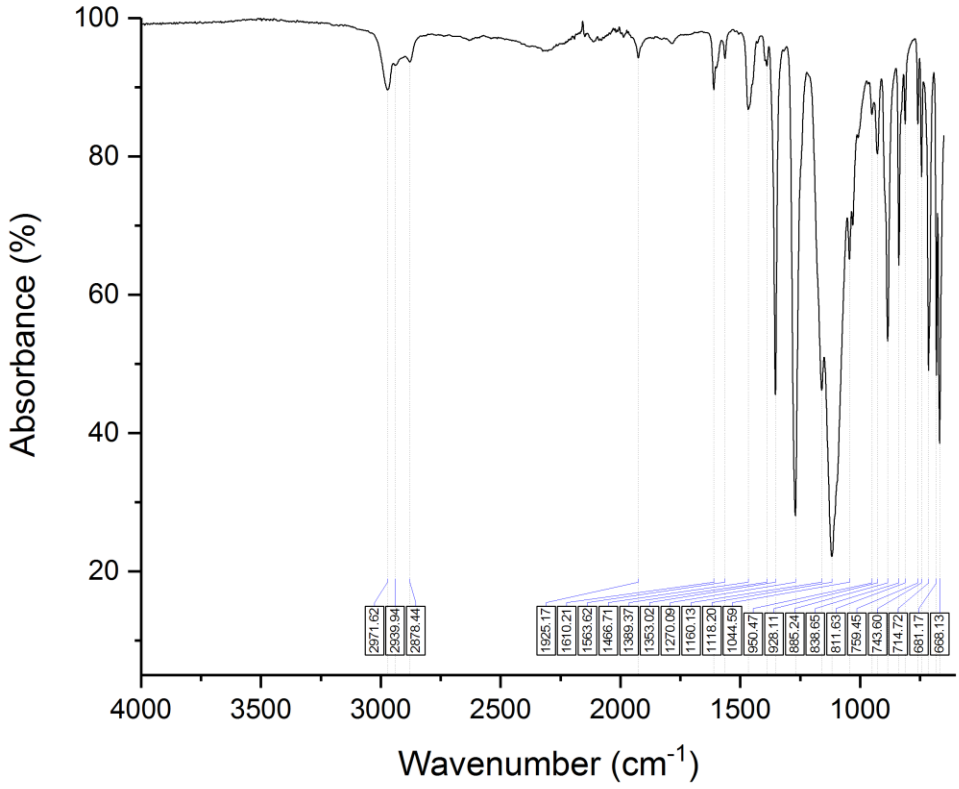


Figure 5. 102 IR spectrum of **3.26**

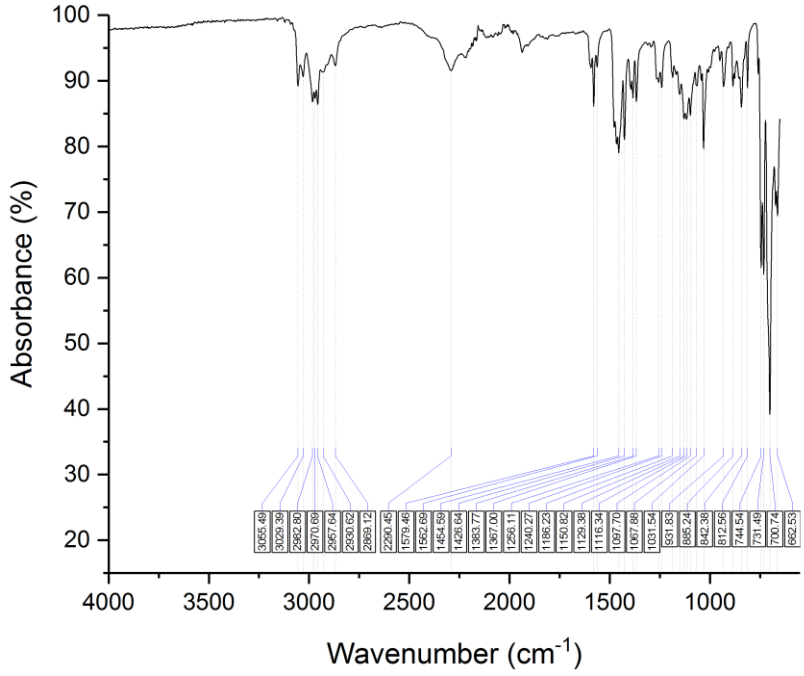


Figure 5. 103 IR spectrum of **3.27**

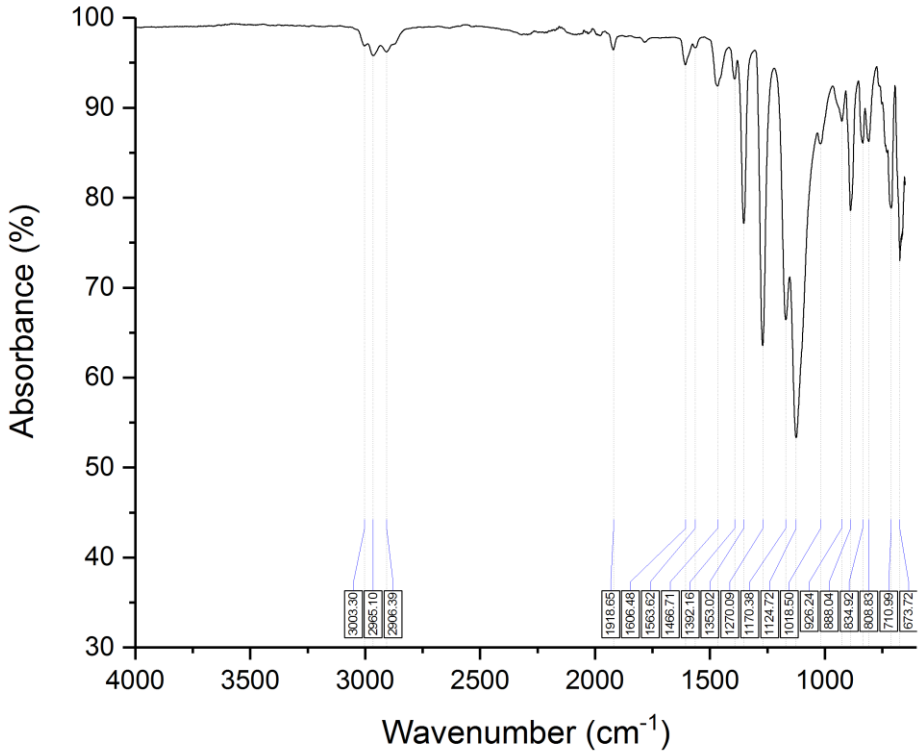


Figure 5. 104 IR spectrum of **3.28**

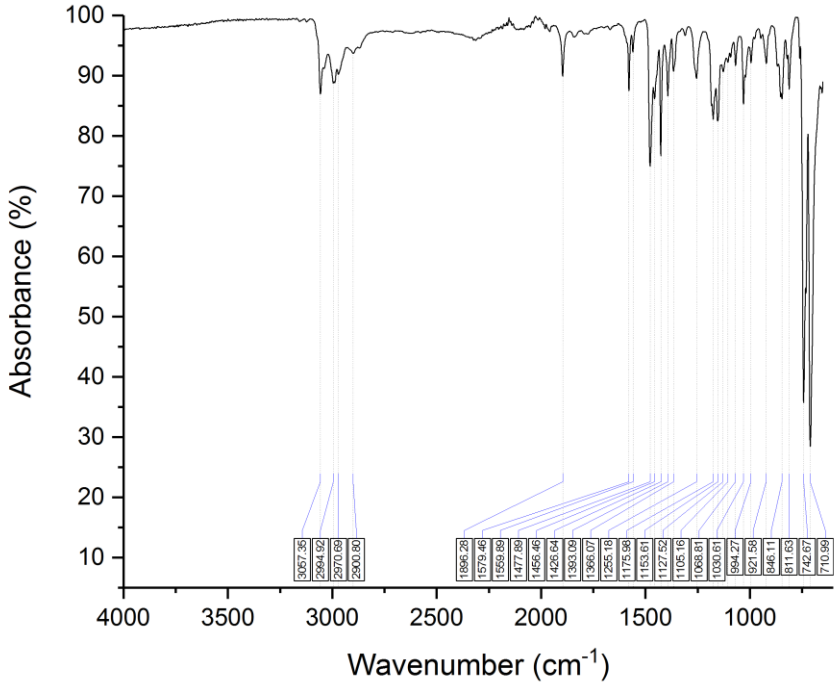


Figure 5. 105 IR spectrum of **3.29**

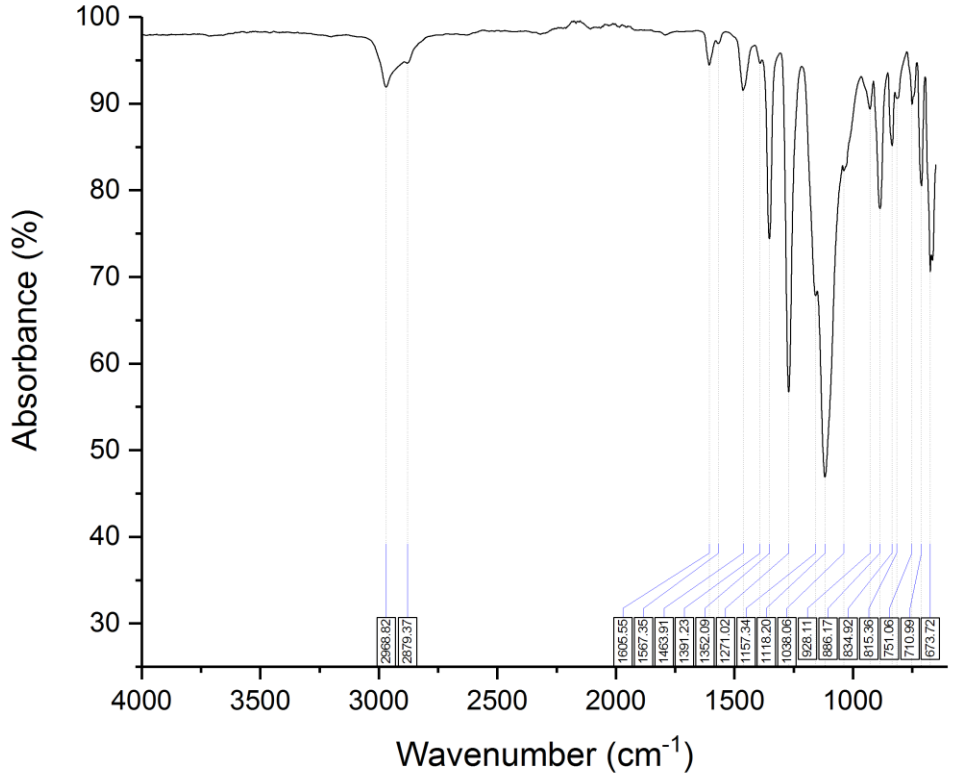


Figure 5. 106 IR spectrum of **3.30**

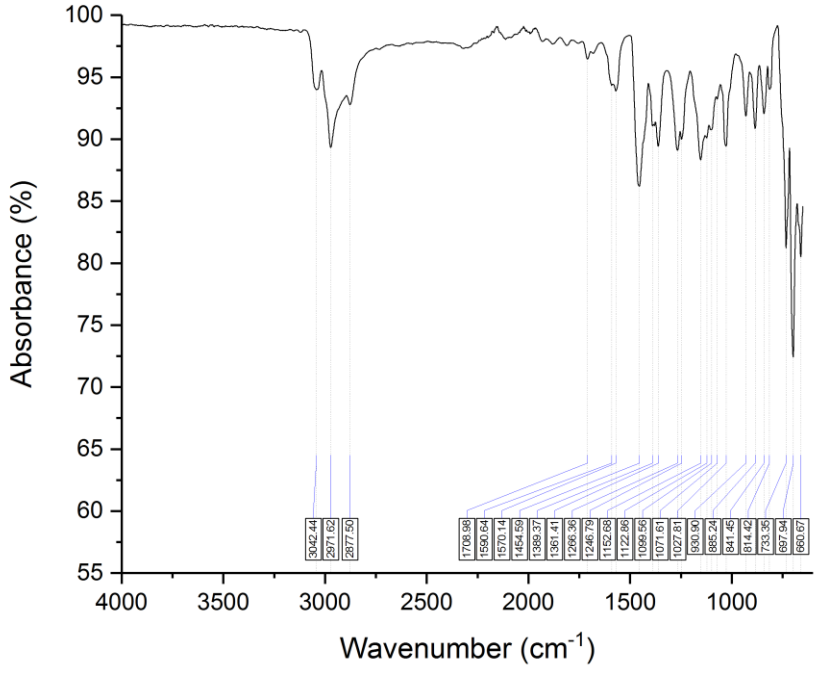


Figure 5. 107 IR spectrum of **3.31**

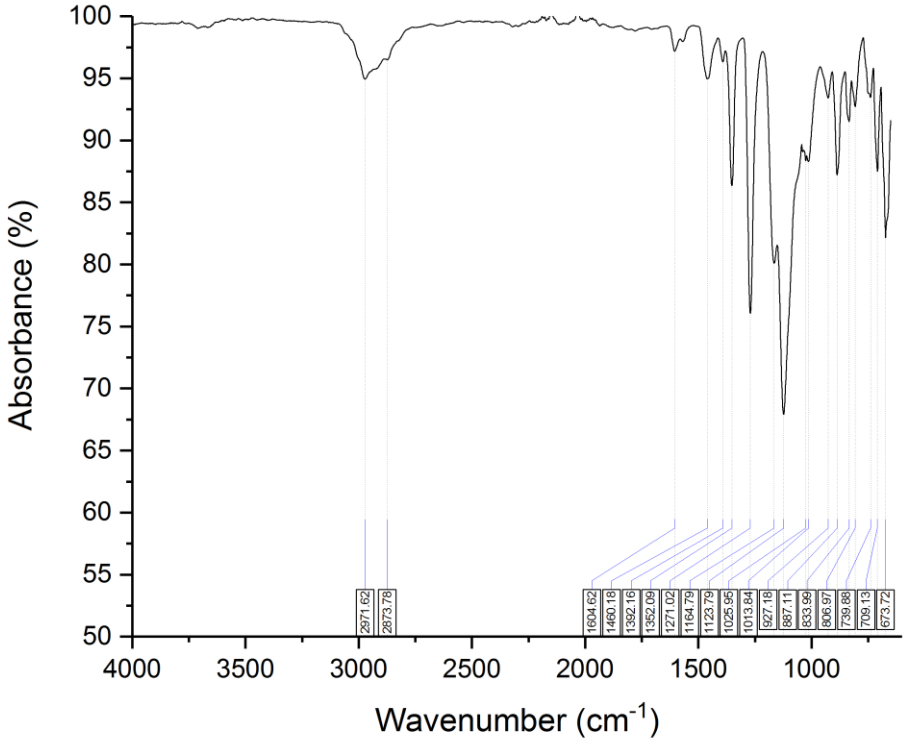


Figure 5. 108 IR spectrum of **3.32**

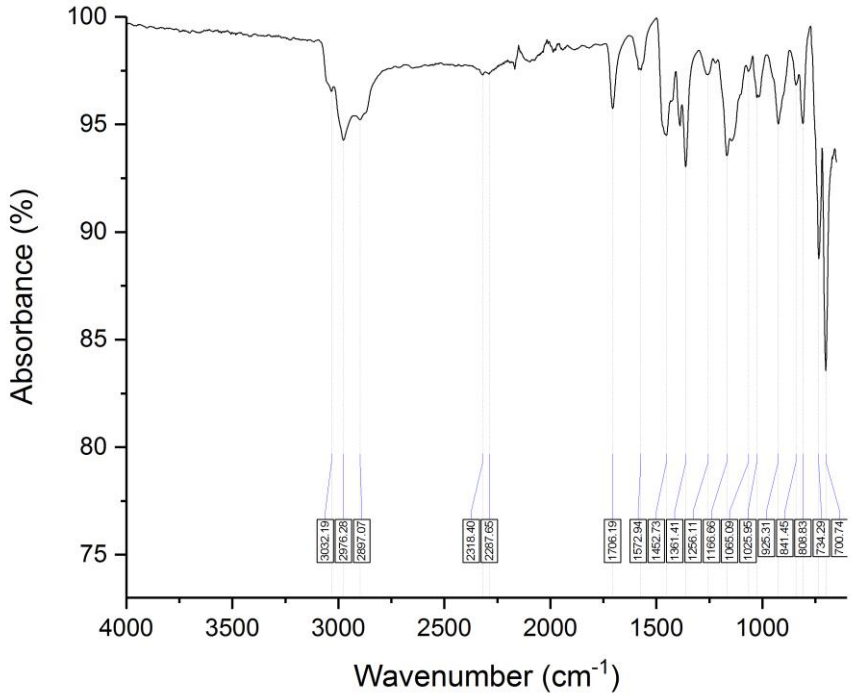


Figure 5. 109 IR spectrum of **3.33**

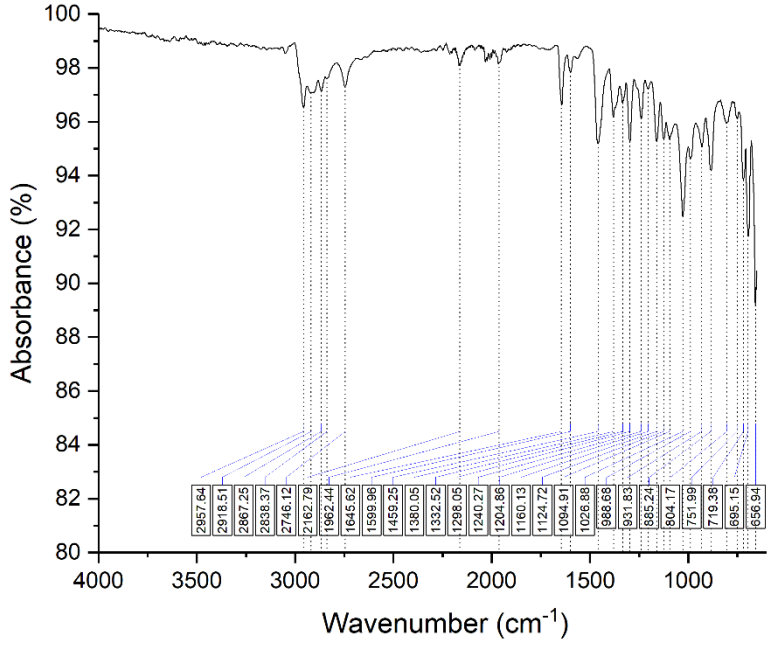


Figure 5. 110 IR spectrum of **3.34**

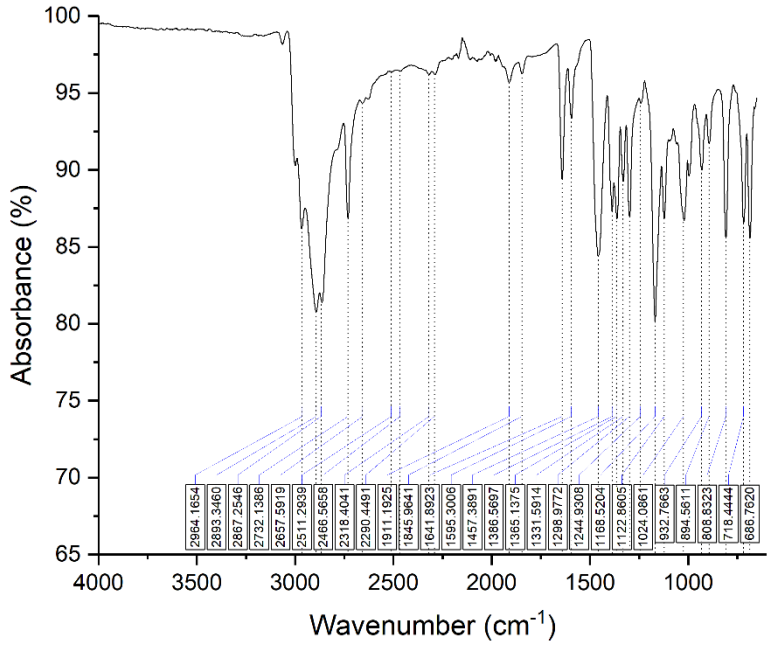


Figure 5. 111 IR spectrum of **3.35**

5.4 EPR analysis

Table 5. 1 Parameters used for EPR experiments

Reactions	Temperature (K)	Solvent	Frequency (MHz)
3.26 + O_2	84	acetone-d_6	9077.956
3.26 + O_2 + DMPO	298	acetone-d_6	9085.676
3.30 + UV	93	acetone-d_6	9079.659
3.32 + UV	93	acetone-d_6	9084.559
3.30 + UV + DMPO	298	acetone-d_6	9115.252
3.32 + UV + DMPO	298	acetone-d_6	9090.782
3.30 + UV + ^{n}Bu$_4$NCl	93	acetone-d_6	9079.490
3.30 + UV + ^{n}Bu$_4$NBr	95	acetone-d_6	9077.678
3.26 + 1 equiv KC_8	94	Me-THF	9078.274
3.29 + 1 equiv KC_8	93.5	30% acetone-d_6 / 70% Me-THF	9074.871
3.33 + 1 equiv. KC_8	92	50% acetone-d_6 / 50% Me-THF	9078.290

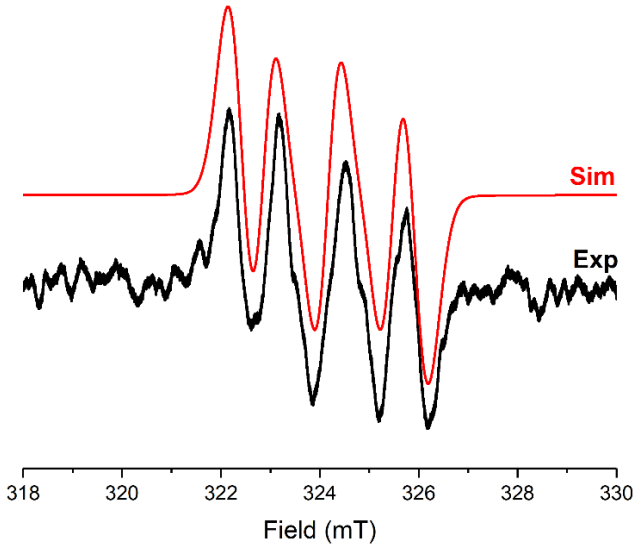


Figure 5. 112 Experimental (black line) and simulated (red line) EPR spectrum of complex **3.26** with O_2 for 30s with excess DMPO at 298K. Simulated parameters: g = 2.0025, a_H = 13.2 G, a_N = 8.11 G.

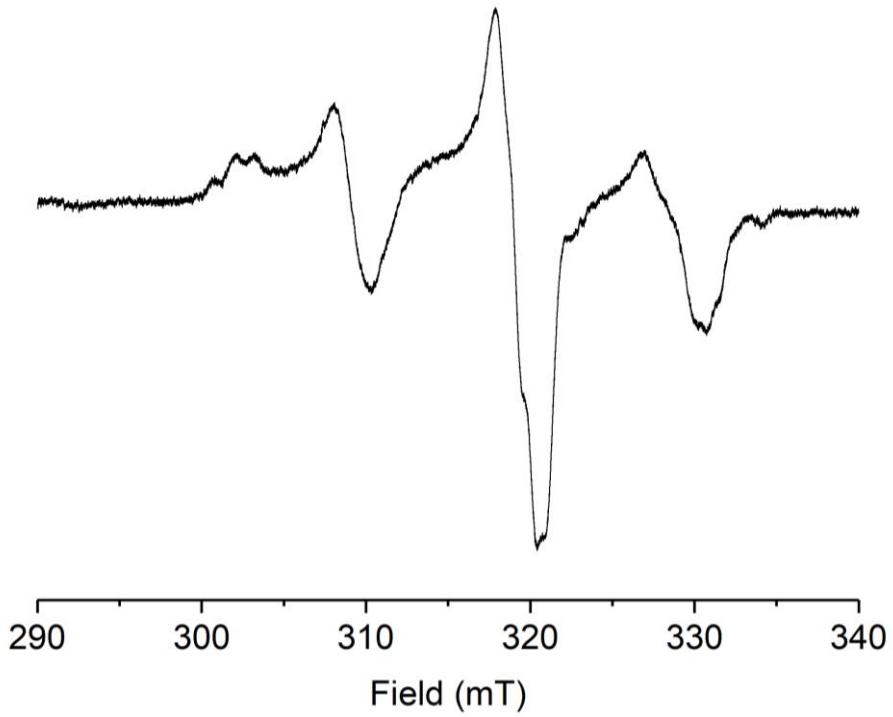


Figure 5. 113 EPR spectrum of complex **3.32** after UV irradiation for 3.5h at 298K.

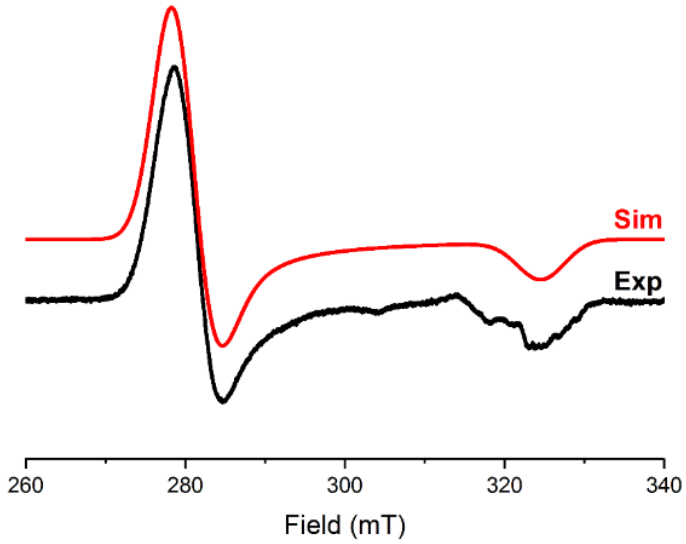


Figure 5. 114 Experimental (black line) and simulated (red line) EPR spectrum of complex **3.30** with 1 equivalent of $^{n}Bu_4NCl$ under UV irradiation for 1 h at 93K in frozen acetone-d_6.

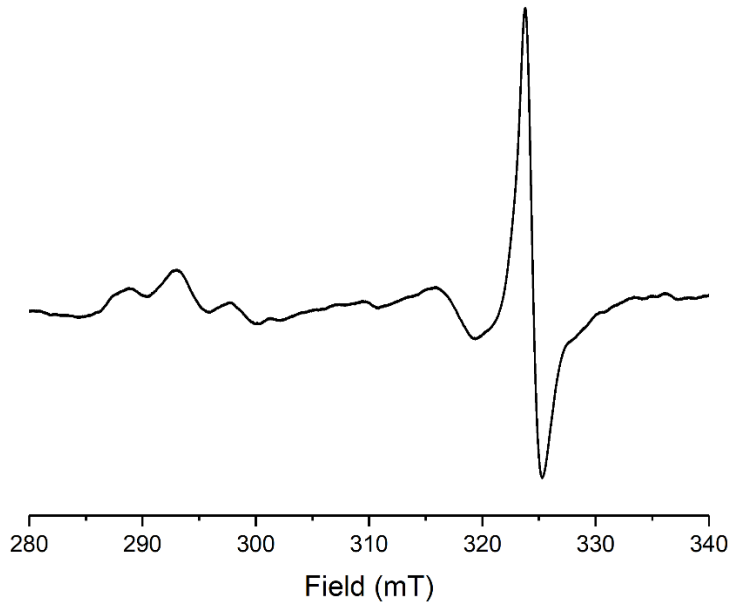


Figure 5. 115 EPR spectrum of the reaction mixture after treatment of complex **3.26** with 1 equiv of KC_8 after 5 minutes at 94 K in frozen 2-methyltetrahydrofuran.

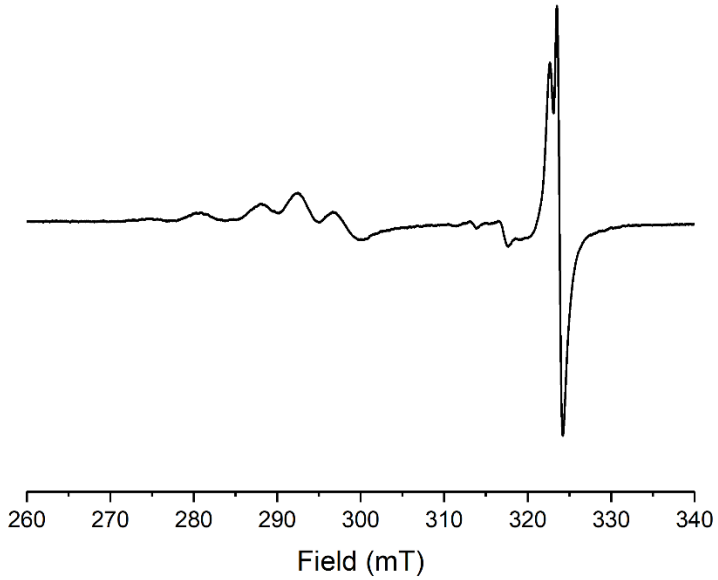


Figure 5. 116 Experimental EPR spectrum of the reaction mixture after treatment of **3.29** with 1 equiv of KC_8 after 5 minutes at 93.5K in a frozen mixture of 30% acetone-d_6 and 70% 2-methyltetrahydrofuran.

5.5 LC-ESI-MS analysis

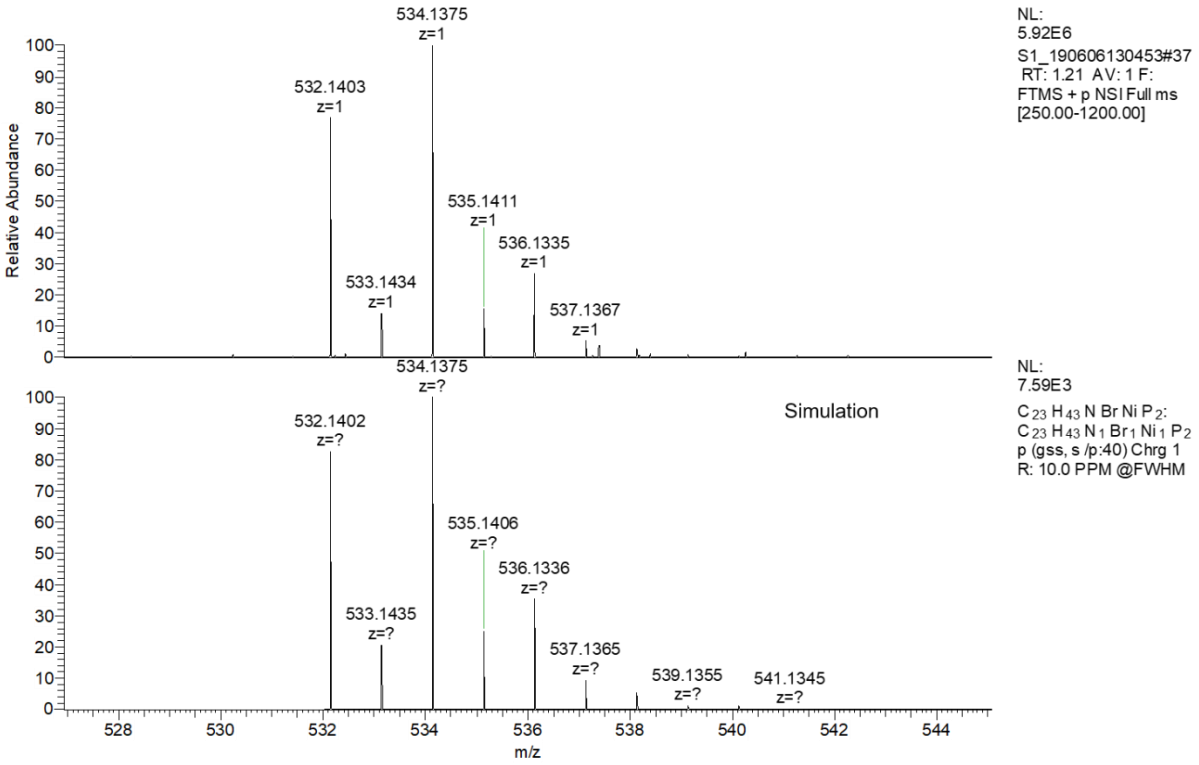


Figure 5. 117 ESI-HRMS analysis of complex **3.24** in positive mode

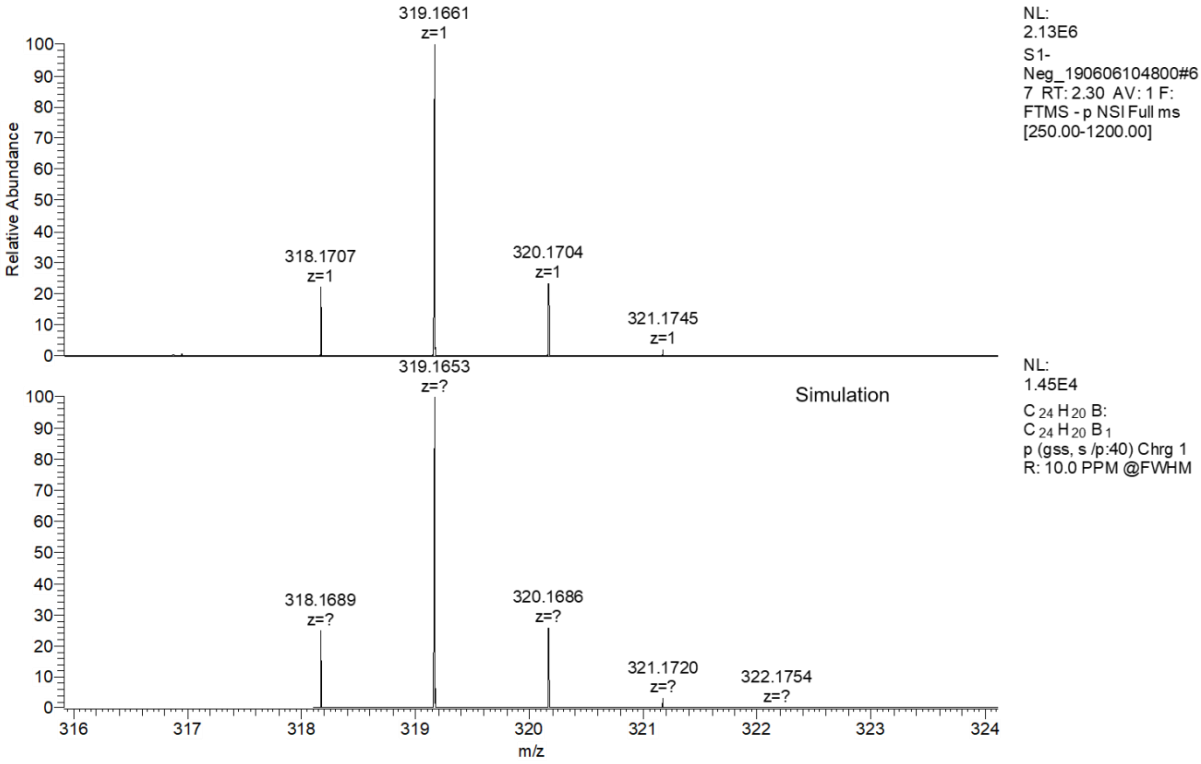


Figure 5. 118 ESI-HRMS analysis of complex **3.24** in negative mode

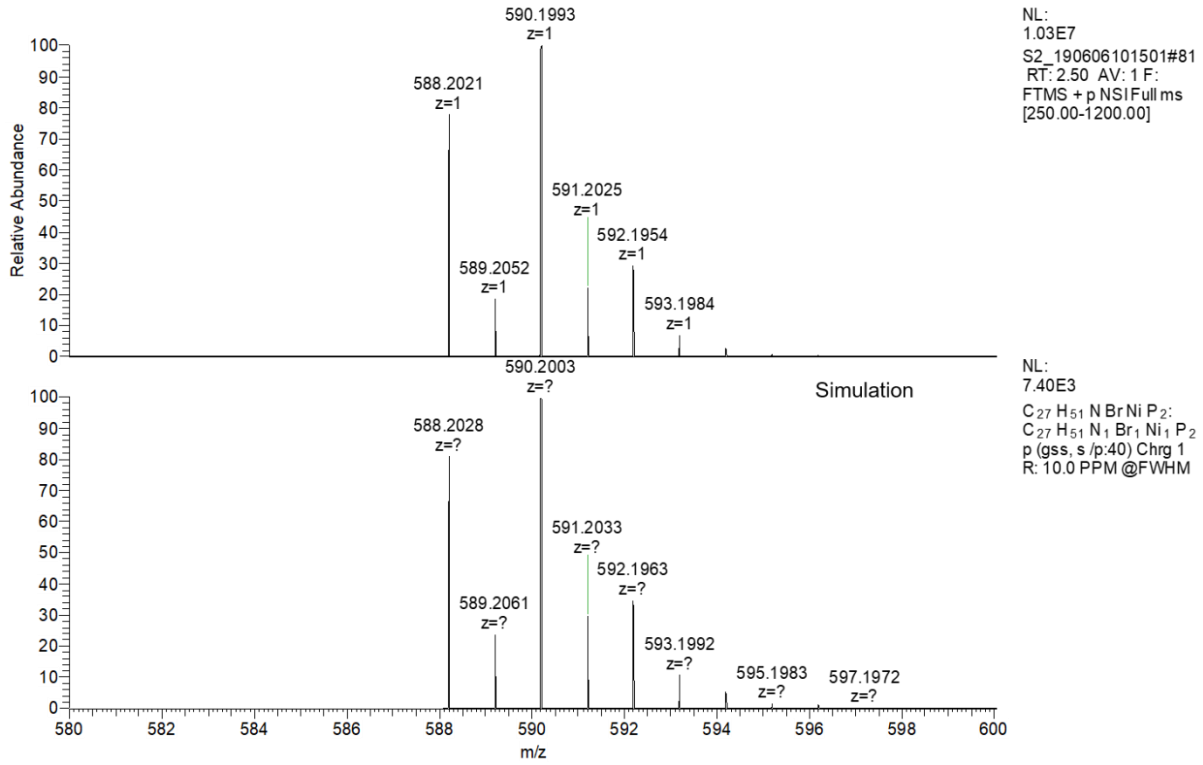


Figure 5. 119 ESI-HRMS analysis of complex **3.25** in positive mode

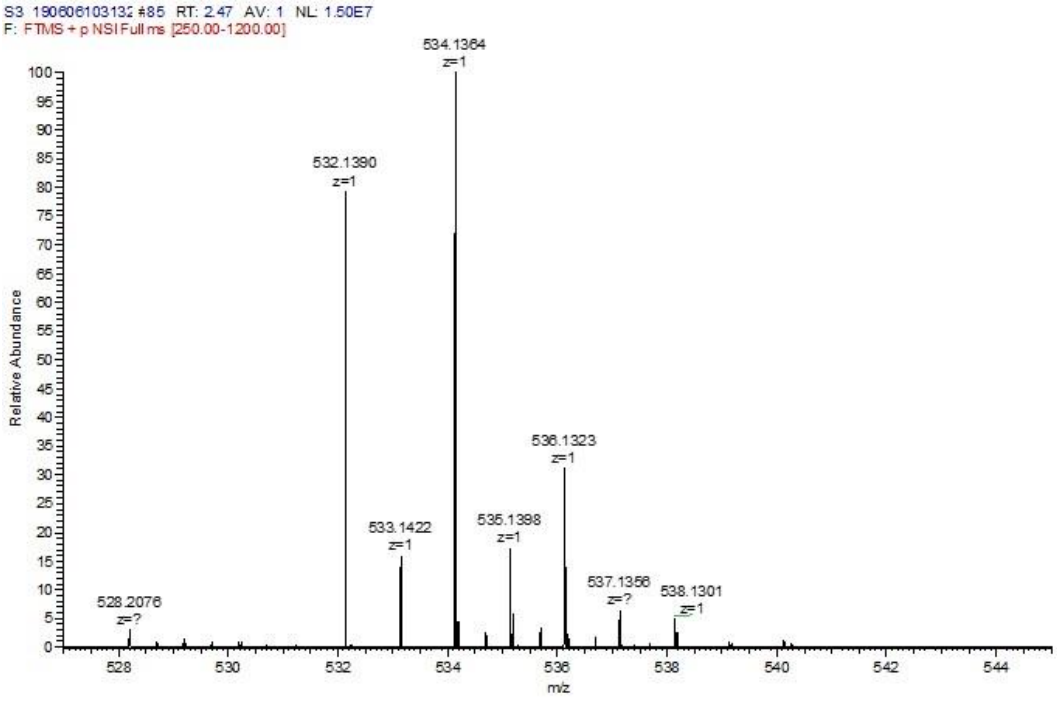


Figure 5. 120 ESI-HRMS analysis of complex **3.25** in negative mode

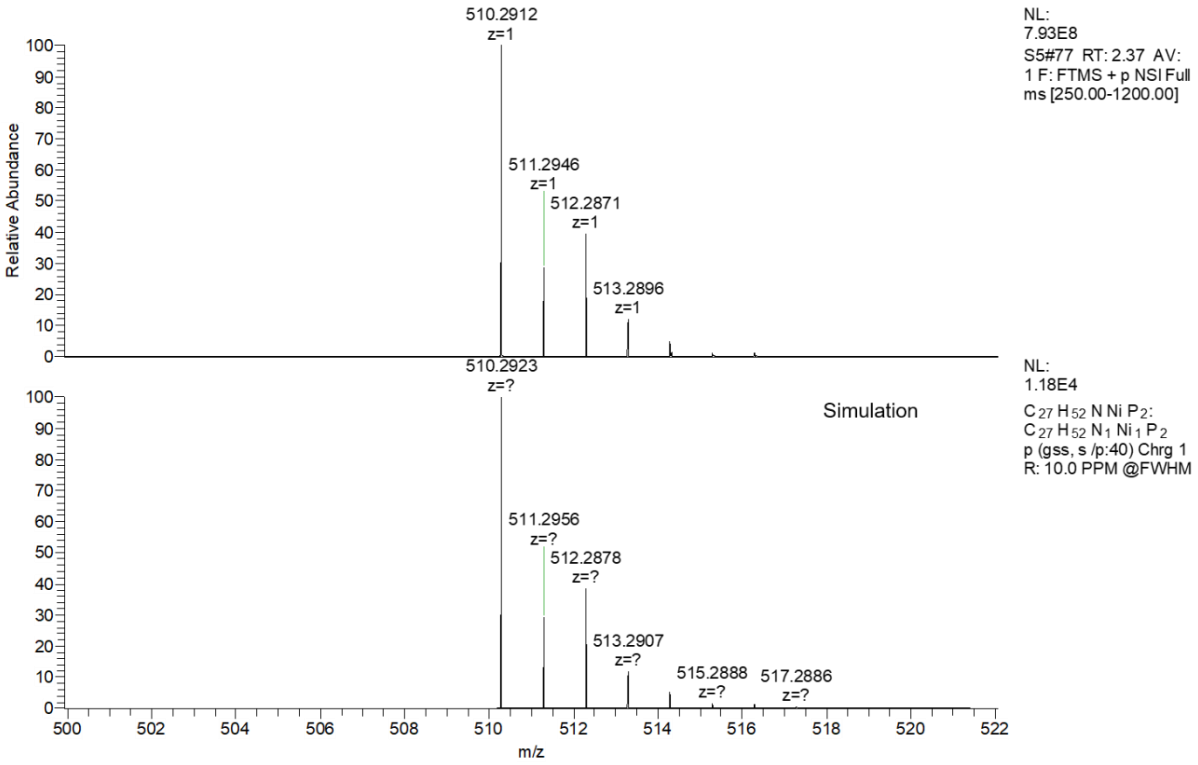


Figure 5. 121 ESI-HRMS analysis of complex **3.28** in positive mode

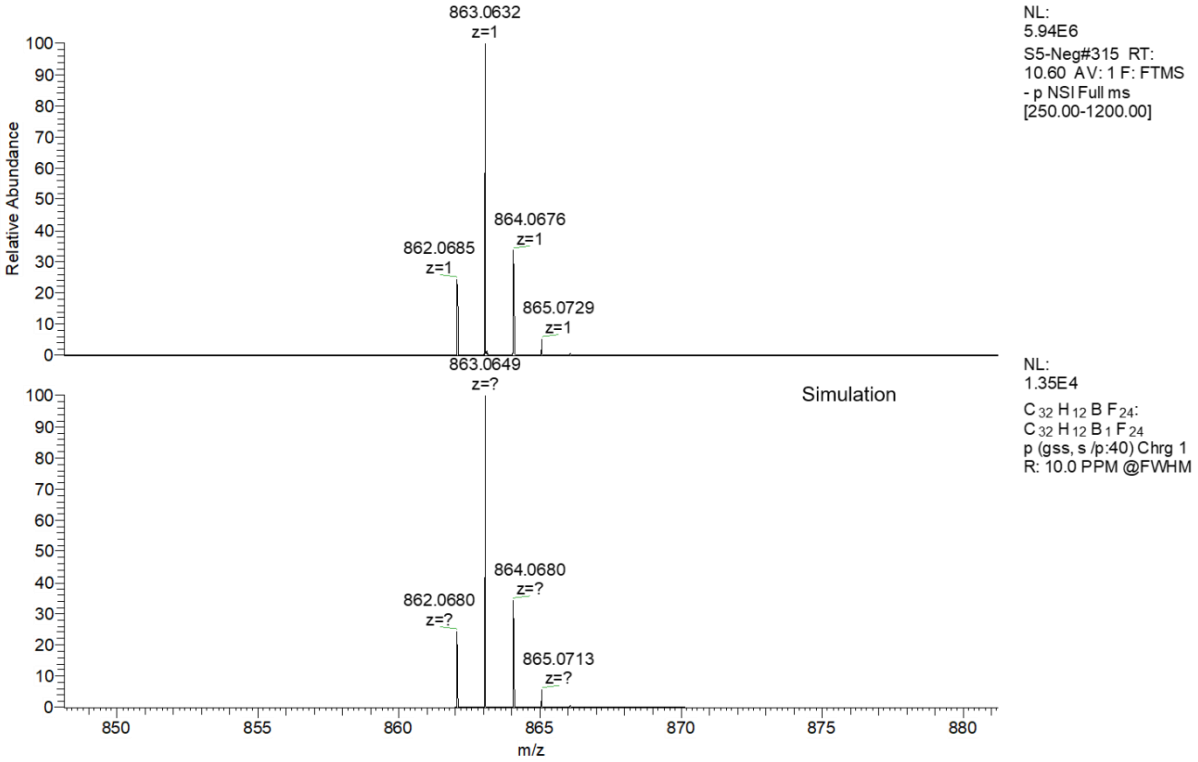


Figure 5. 122 ESI-HRMS analysis of complex **3.28** in negative mode

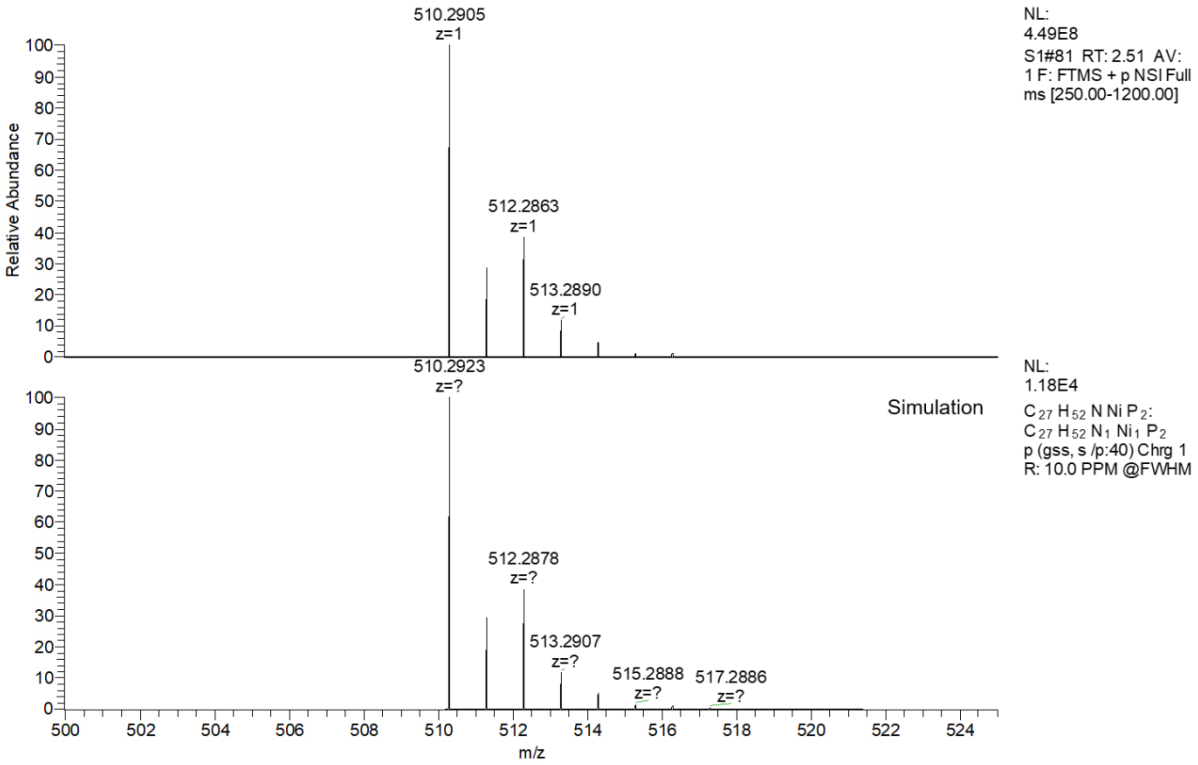


Figure 5. 123 ESI-HRMS analysis of complex **3.29** in positive mode

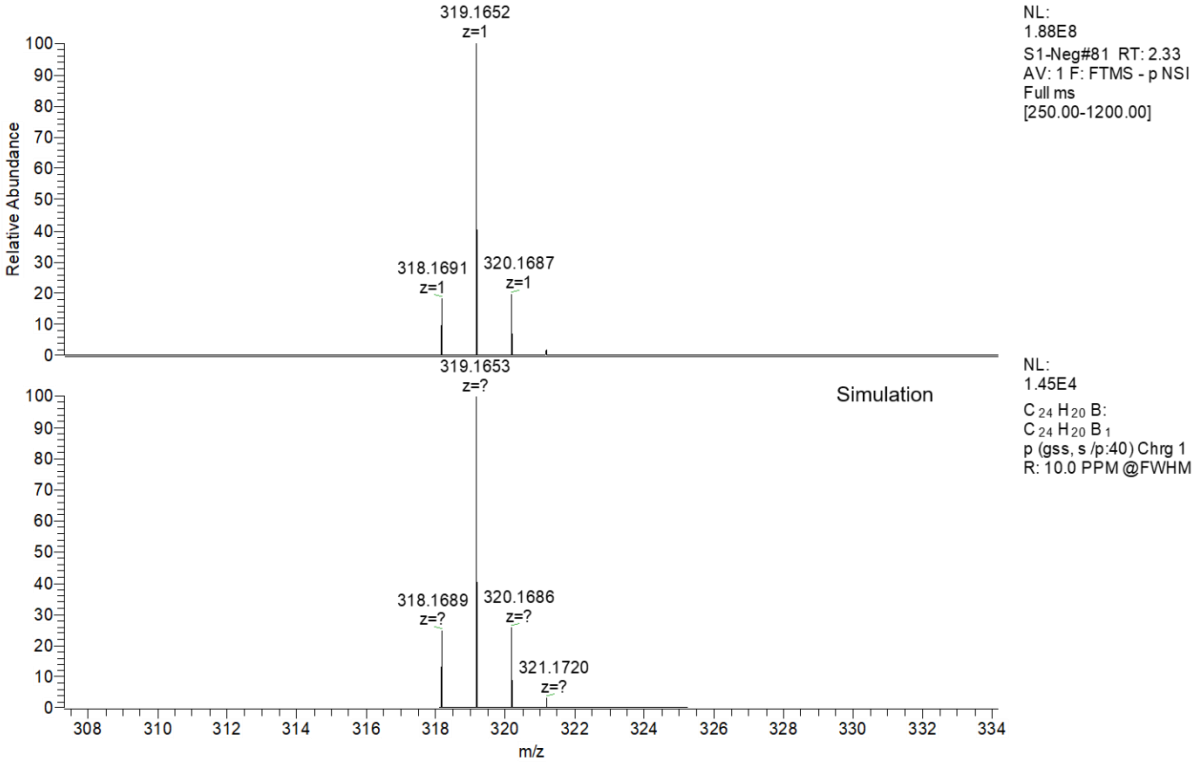


Figure 5. 124 ESI-HRMS analysis of complex **3.29** in negative mode

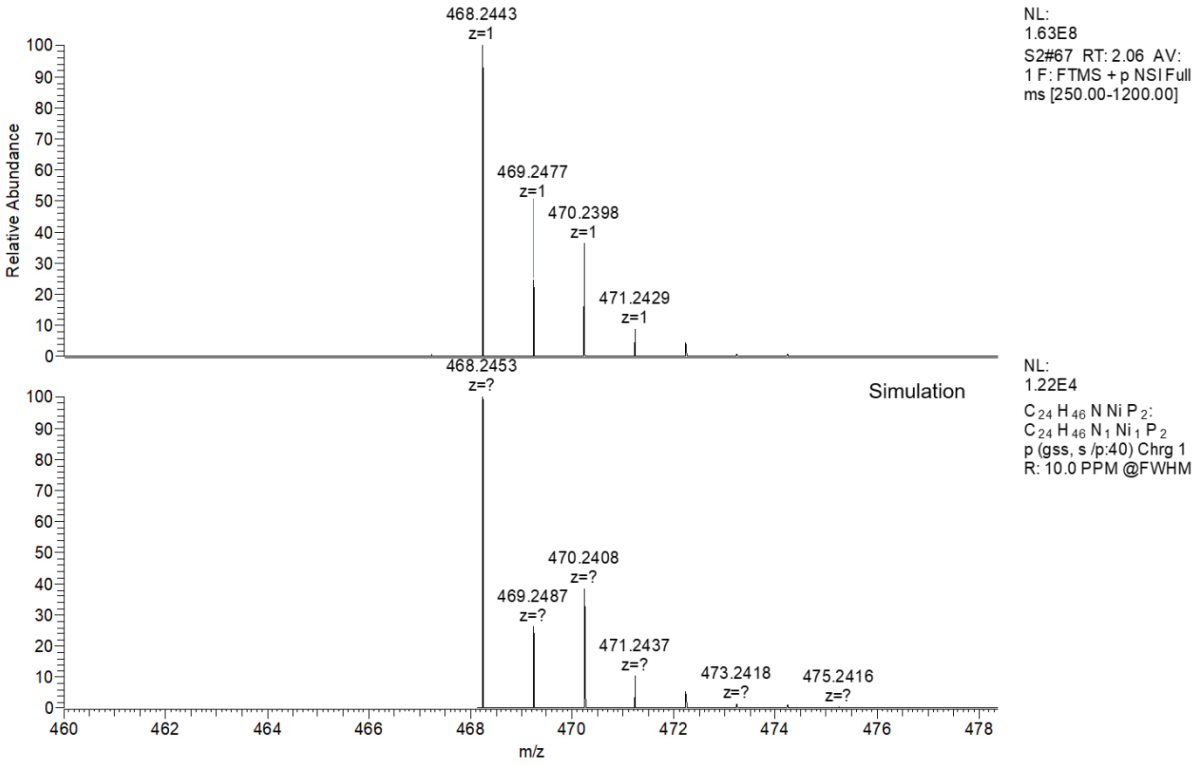


Figure 5. 125 ESI-HRMS analysis of complex **3.30** in positive mode

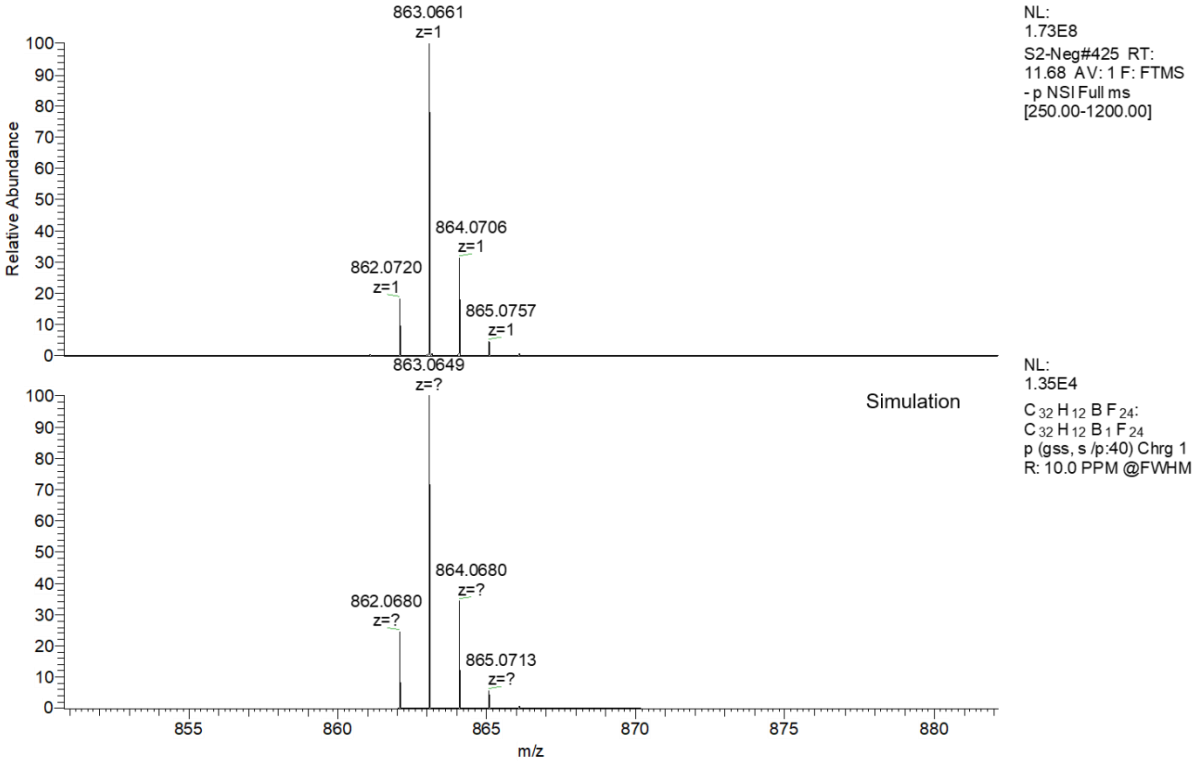


Figure 5. 126 ESI-HRMS analysis of complex **3.30** in negative mode

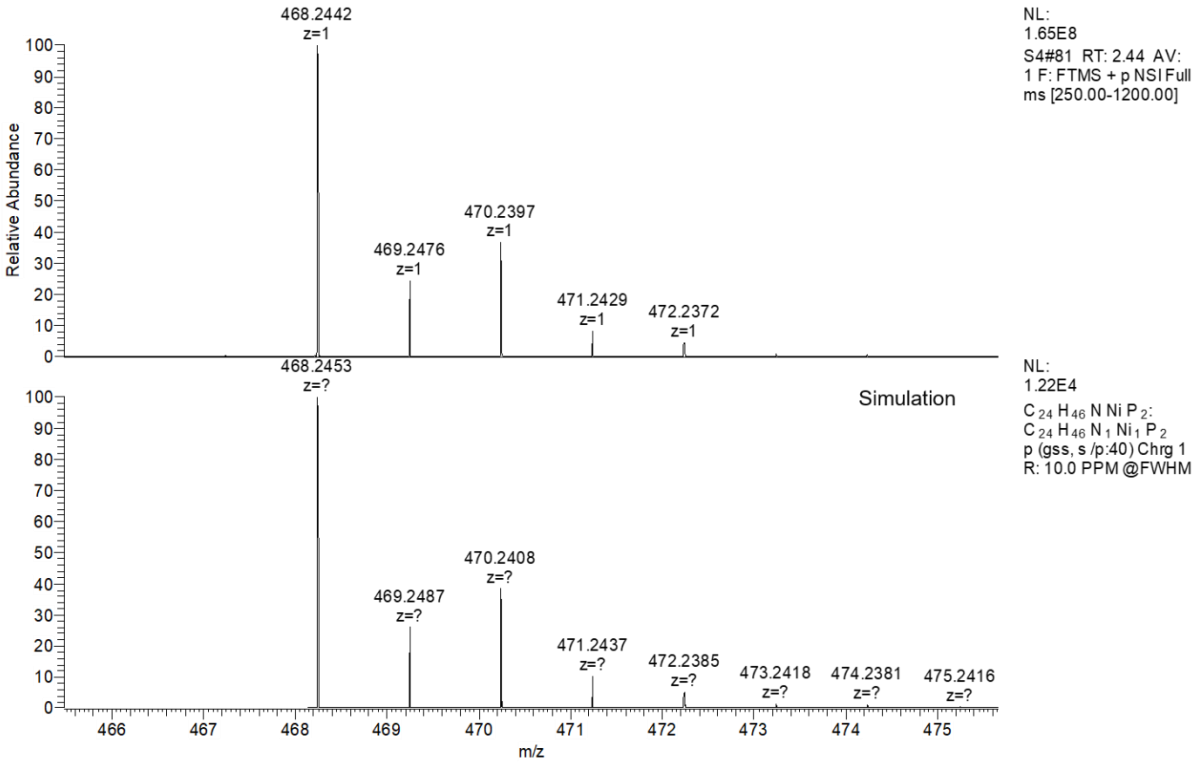


Figure 5. 127 ESI-HRMS analysis of complex **3.31** in positive mode

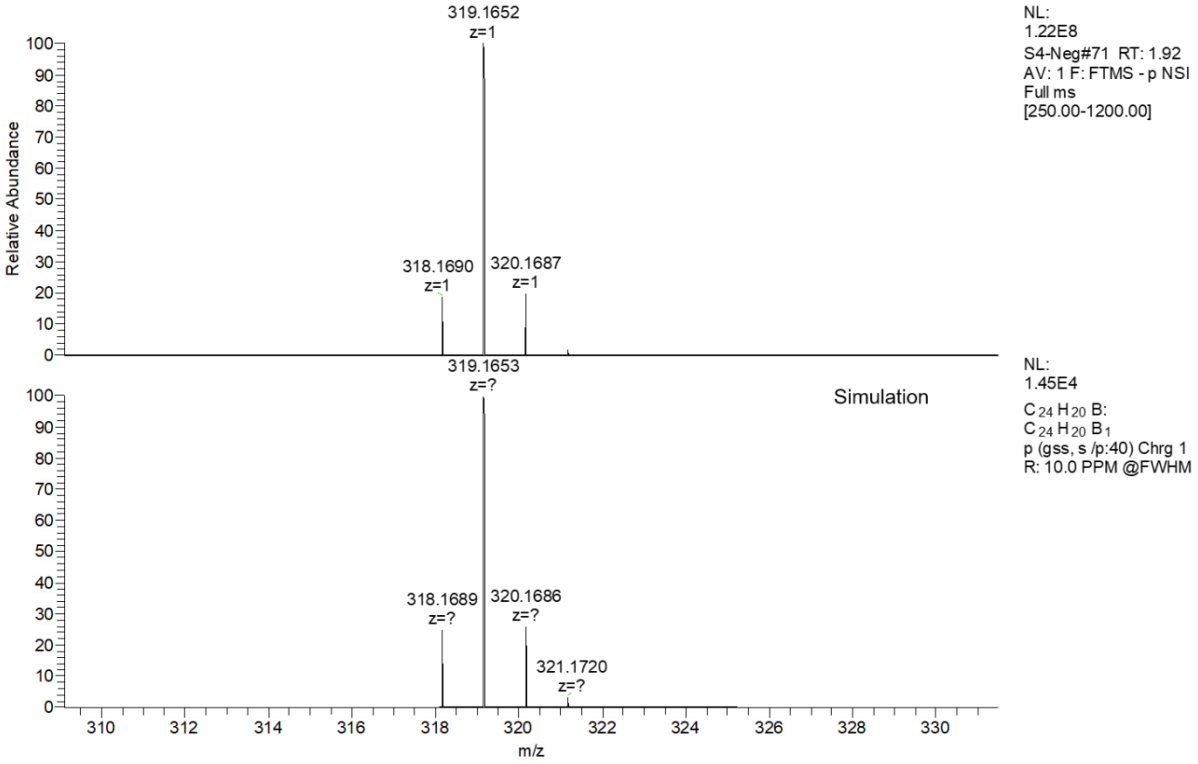


Figure 5. 128 ESI-HRMS analysis of complex **3.31** in negative mode

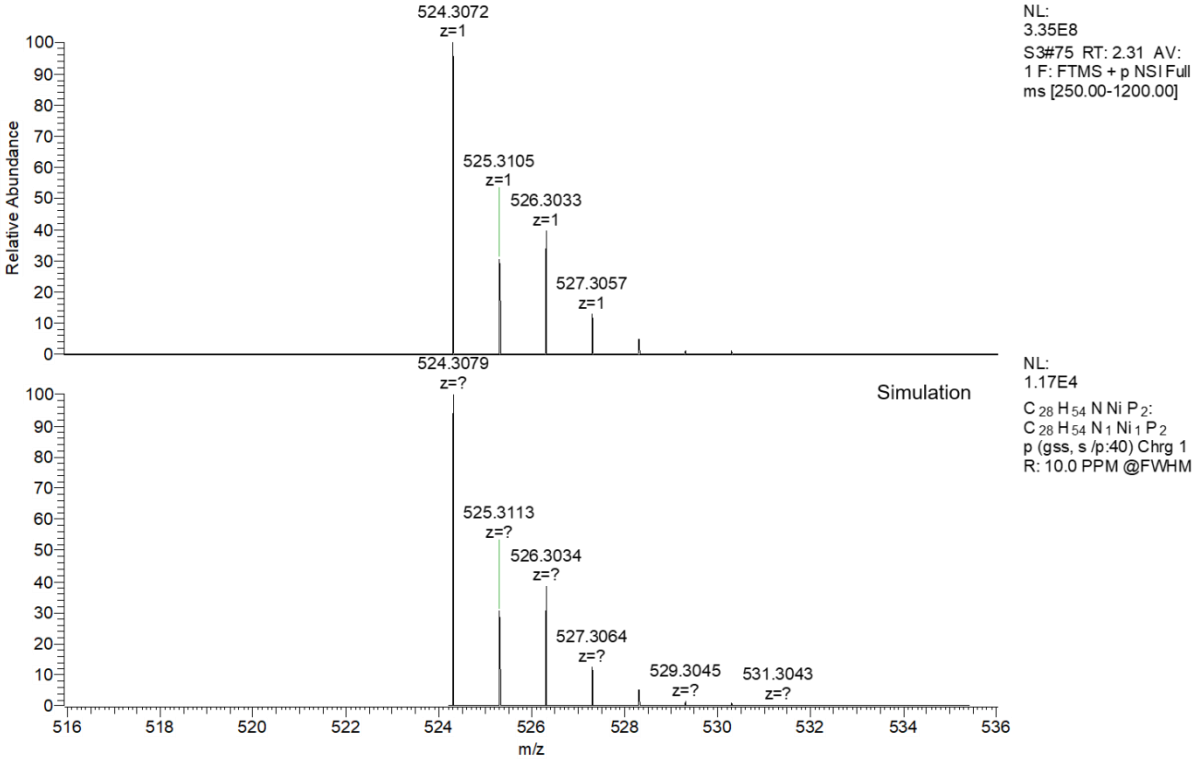


Figure 5. 129 ESI-HRMS analysis of complex **3.32** in positive mode.

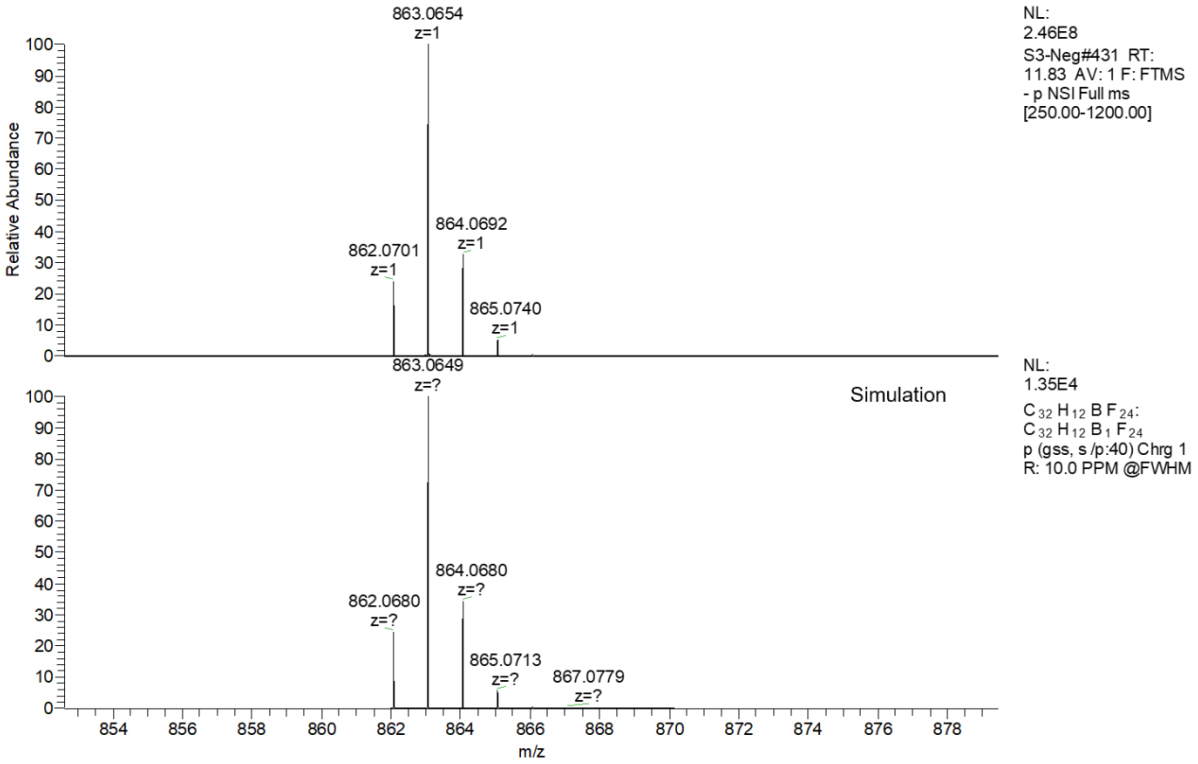


Figure 5. 130 ESI-HRMS analysis of complex **3.32** in negative mode

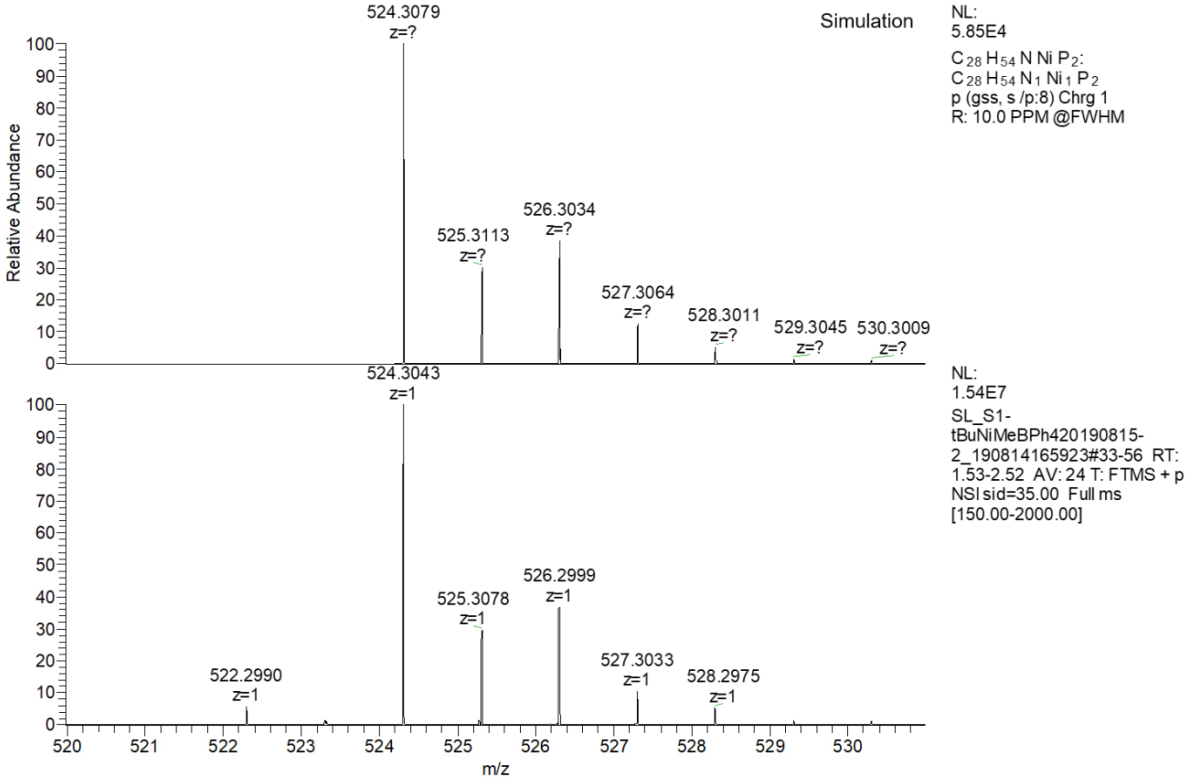


Figure 5. 131 ESI-HRMS analysis of complex **3.33** in positive mode

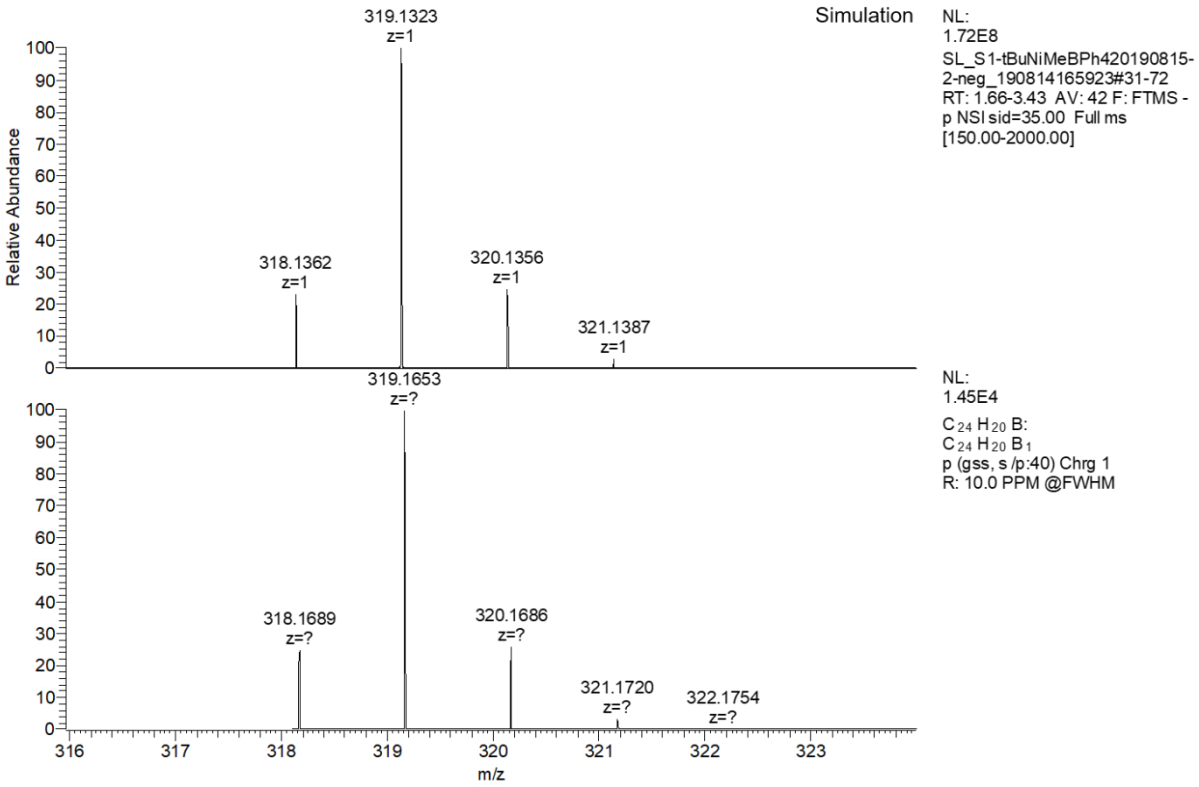


Figure 5. 132 ESI-HRMS analysis of complex **3.33** in negative mode

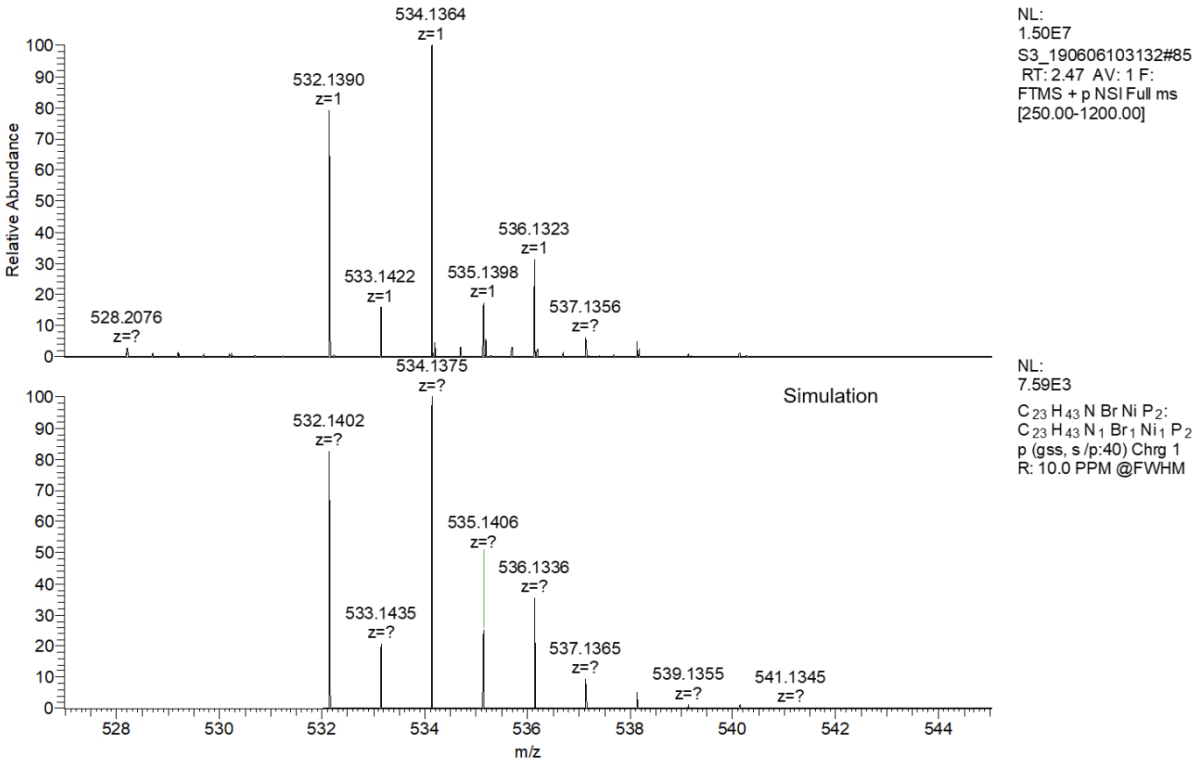


Figure 5. 133 ESI-HRMS analysis of complex **3.34** in positive mode

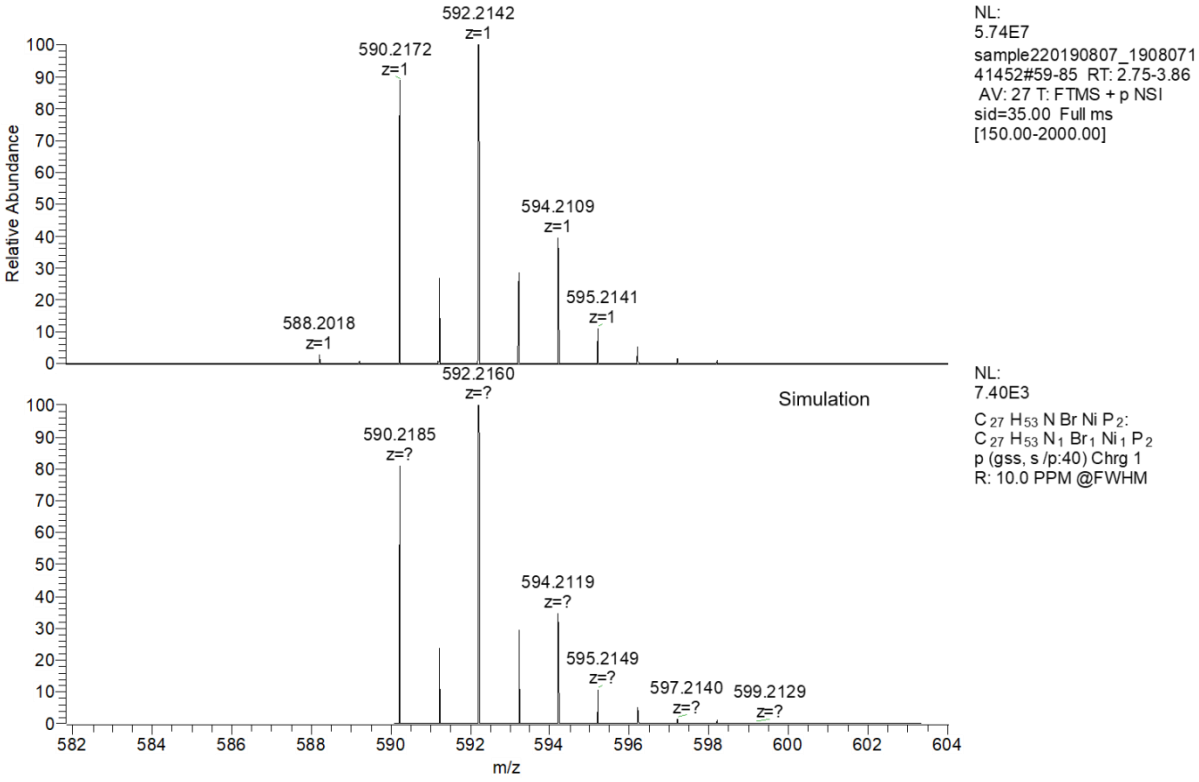


Figure 5. 134 ESI-HRMS analysis of complex **3.35** in positive mode

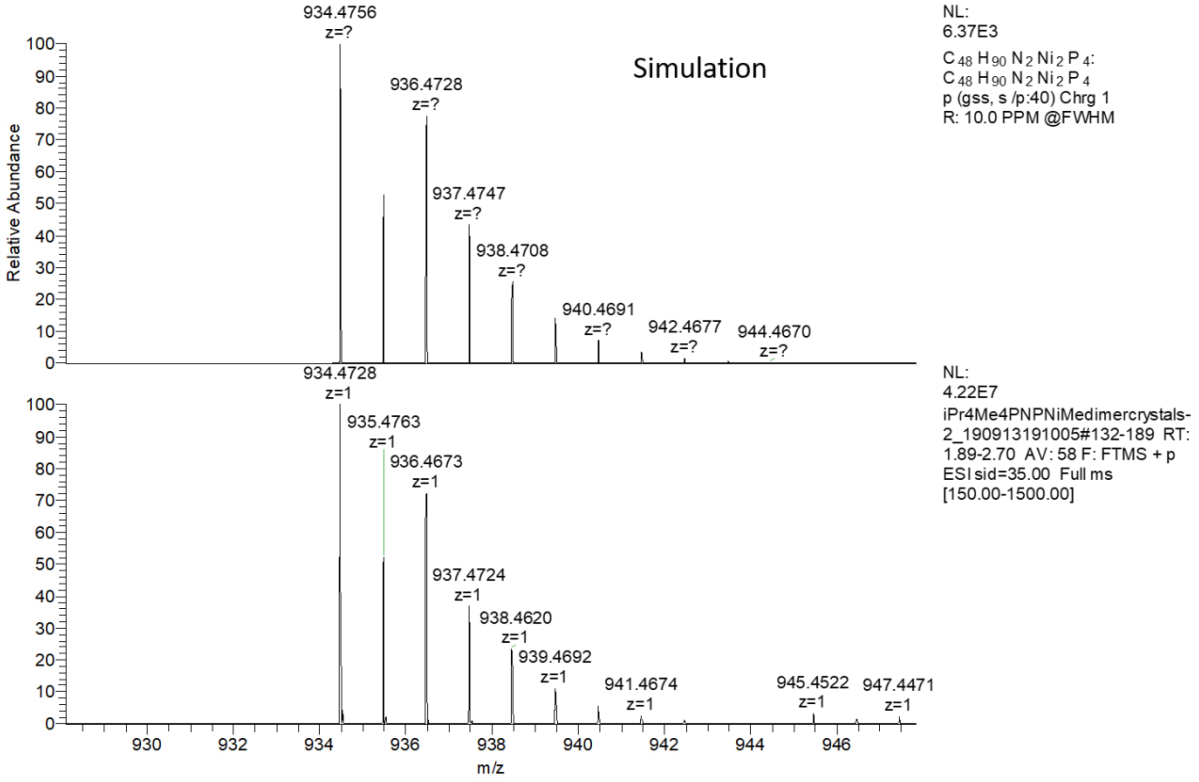


Figure 5. 135 ESI-HRMS analysis of complex **3.36** in positive mode

5.6 Electrochemical analysis

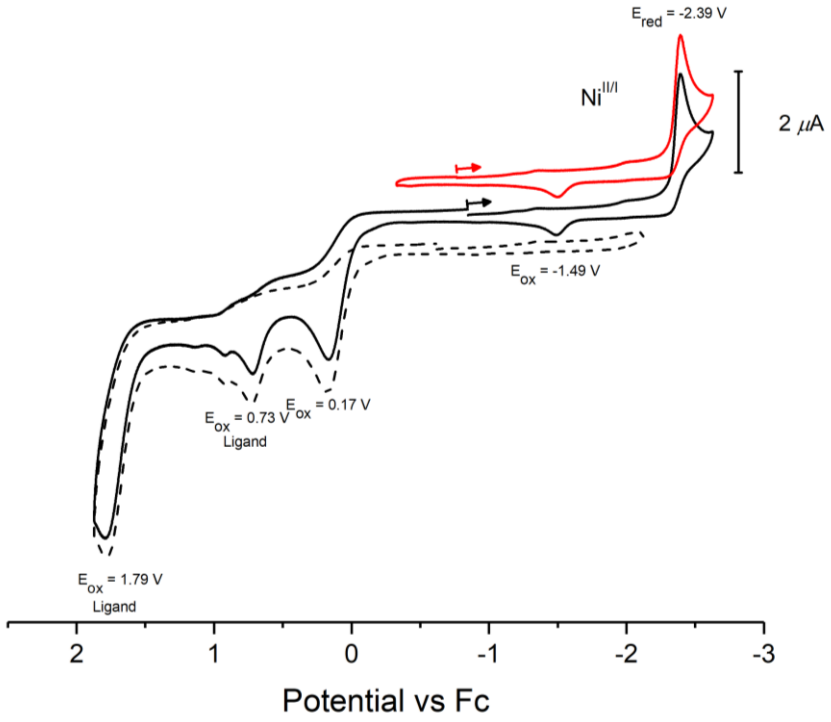


Figure 5. 136 Full cyclic voltammogram of complex **3.26.** Red trace is a CV recorded in a shorter range to estimate reversibility of Ni^{II}/Ni^{I} wave; the curve was translated upwards in the vertical direction for clarity. The dashed trace is recorded until just before the Ni^{II}/Ni^{I} wave to show that reverse oxidation wave at -1.49V corresponds to the oxidation of the Ni^{I} species and not from another species in solution.

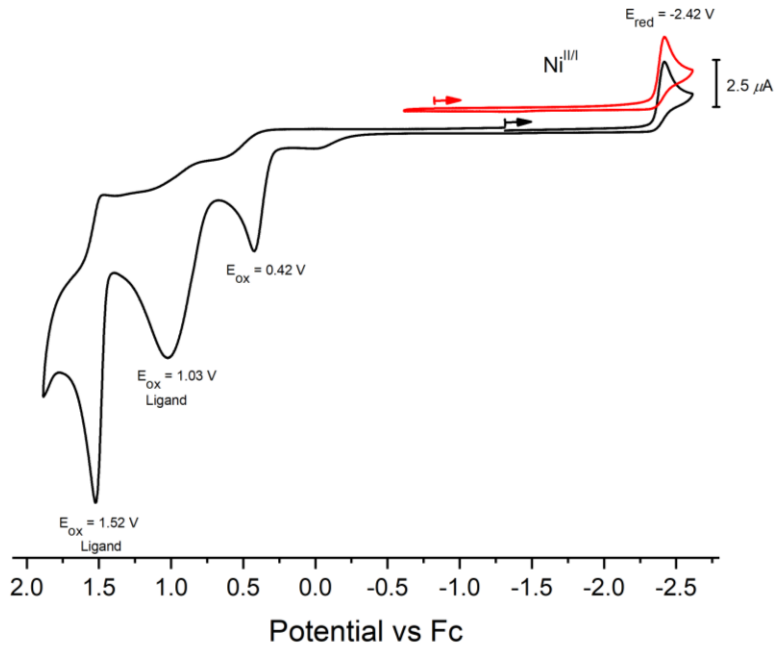


Figure 5. 137 Full cyclic voltammogram of complex **3.29.** Red trace is a CV recorded in a shorter range to estimate reversibility of Ni^{II}/Ni^{I} wave; the curve was translated upwards in the vertical direction for clarity

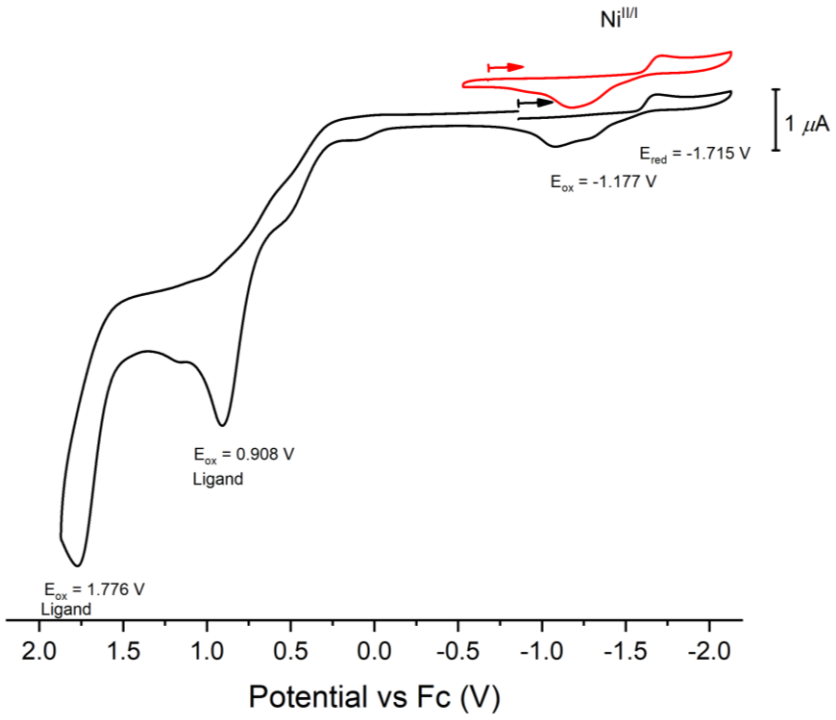


Figure 5. 138 Full cyclic voltammogram of complex **3.30**. Red trace is a CV recorded in a shorter range to estimate reversibility of Ni^{II}/Ni^{I} wave; the curve was translated upwards in the vertical direction for clarity.

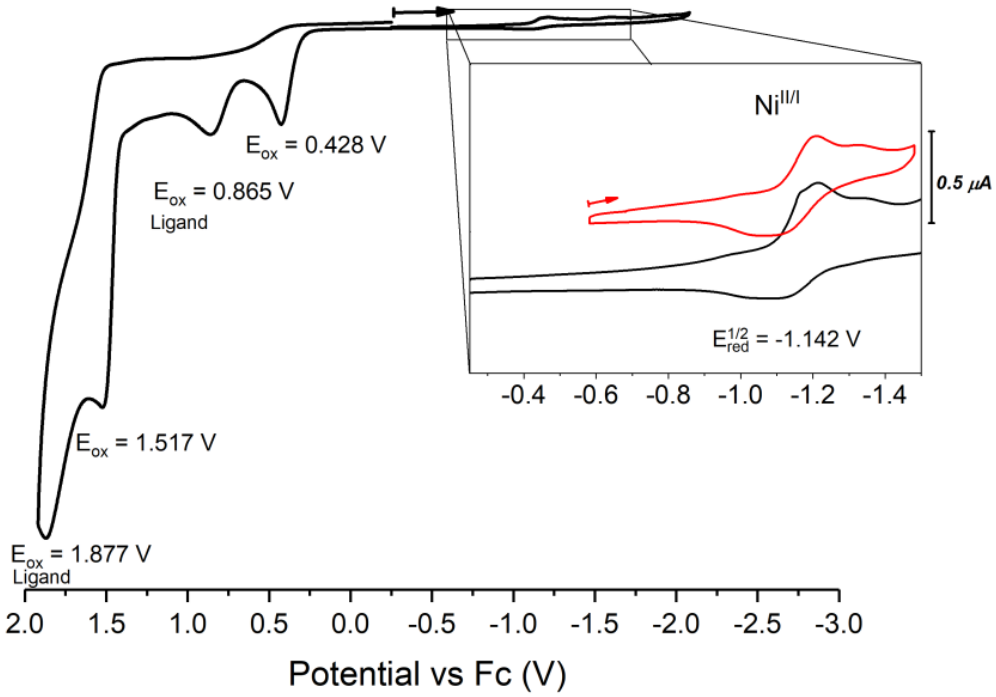
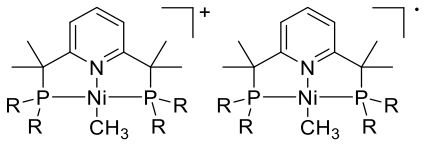


Figure 5. 139 Full cyclic voltammogram of complex **3.33.** Red trace is a CV recorded in a shorter range to estimate reversibility of Ni^{II}/Ni^{I} wave; the curve was translated upwards in the vertical direction for clarity.

5.7 Computational details

Table 5. 2 Bond distances [Å] and angles [deg] for optimized cationic and radical geometries of **[iPrNiMe]+/•** and **[tBuNiMe]+/•**. The atom numbering corresponds to that of Figure 3.3 in the main thesis



R = ^{i}Pr **[iPrNiMe]$^{+}$** R = ^{i}Pr **[iPrNiMe]$^{\bullet}$**
R = ^{t}Bu **[tBuNiMe]$^{+}$** R = ^{t}Bu **[tBuNiMe]$^{\bullet}$**

.Complex	Ni1–N1	Ni1–X	Ni1–P1	Ni1–P2	∠ P1–Ni1–P2	∠ N1–Ni1–X	τ_4'[a]	τ_4
[iPrNiMe]$^{+}$	2.022	1.953	2.225	2.232	170.89	177.78	0.06	0.08
[iPrNiMe]$^{\bullet}$	1.966	1.972	2.213	2.218	168.94	177.76	0.06	0.09
[tBuNiMe]$^{+}$	2.029	1.952	2.278	2.289	169.95	178.73	0.05	0.08
[tBuNiMe]$^{\bullet}$	1.973	1.972	2.269	2.277	168.19	177.94	0.07	0.10

Geometries were calculated using the unrestricted B3LYP/6-311++G** basis set for C, H, N, P atoms and LANL2DZ electron-core potential basis for Ni.

Table 5. 3 LCAO-MO analysis of the HOMO for all complexes (highest contributions are shown) using Chemissian

Complex	Highest contributors to the HOMO (coefficient)			
[iPrNiMe]$^{+}$	Ni –3d_{z2} (0.78)	P - 1p_y (0.49)	C – 5s (0.42)	Ni – 3p_y (0.41)
[iPrNiMe]$^{\bullet}$	Ni – 3d_{z2} (0.79)	Ni – 3p_y (0.53)	P – 3p_y (0.49)	C – 5s (-0.43)
[tBuNiMe]$^{+}$	Ni – 3d_{z2} (0.79)	C – 5s (0.51)	C – 5s (-0.50)	C – 5s (0.47)
[tBuNiMe]$^{\bullet}$	Ni – 3d_{z2} (0.80)	C – 5s (0.56)	C – 5s (0.50)	C – 4p_x (0.50)

LCAO-MO analysis was done using the unrestricted B3LYP/6-311++G** basis set for C, H, N, P atoms and LANL2DZ electron-core potential basis for Ni.

Table 5. 4 LCAO-MO analysis of the SOMO for all complexes (highest contributions are shown) using Chemissian

Complex	Highest contributors to the SOMO (coefficient)			
[iPrNiMe]$^{\bullet}$	C – 5s (1.88)	C – 5s (-1.64)	P – 1p_y (-1.52)	C – 4p_x (1.15)
[tBuNiMe]$^{\bullet}$	C – 5s (1.59)	C – 5s (-1.48)	C – 4p_z (-0.80)	C – 5s (0.80)

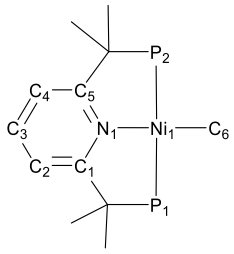
LCAO-MO analysis was done using the unrestricted B3LYP/6-311++G** basis set for C, H, N, P atoms and LANL2DZ electron-core potential basis for Ni.

Table 5. 5 LCAO-MO analysis of the LUMO for all complexes (highest contributions are shown) using Chemissian

Complex	Highest contributors to the LUMO (coefficient)			
$[iPrNiMe]^+$	C – 5s (1.37)	C – 5s (-1.19)	P – $1p_y$ (-1.14)	P – $1p_y$ (0.88)
$[iPrNiMe]^\bullet$	Ni – $3p_y$ (4.79)	P – $1p_y$ (-2.81)	P – 7s (4.31)	Ni – 3s (2.43)
$[tBuNiMe]^+$	C – 5s (1.38)	C – 5s (-1.26)	C – 5s (-0.78)	P – 7s (0.76)
$[tBuNiMe]^\bullet$	Ni – $3p_y$ (3.29)	P – $1p_y$ (-2.08)	P – $1p_y$ (-1.91)	C – 5s (-1.59)

LCAO-MO analysis was done using the unrestricted B3LYP/6-311++G** basis set for C, H, N, P atoms and LANL2DZ electron-core potential basis for Ni.

Table 5. 6 Selected spin densities with summed hydrogens (Mulliken) for optimized complexes **[iPrNiMe]•** and **[tBuNiMe]•**



atom	[5]•	[6]•
Ni1	0.000	-0.050
N1	0.340	0.343
P1	0.032	-0.033
P2	0.028	-0.027
C1	0.152	0.185
C2	-0.109	-0.118
C3	0.492	0.466
C4	-0.114	-0.121
C5	0.168	0.212
C6	-0.013	-0.014

Mulliken analysis was done using the unrestricted B3LYP/6-311++G** basis set for C, H, N, P atoms and LANL2DZ electron-core potential basis for Ni.

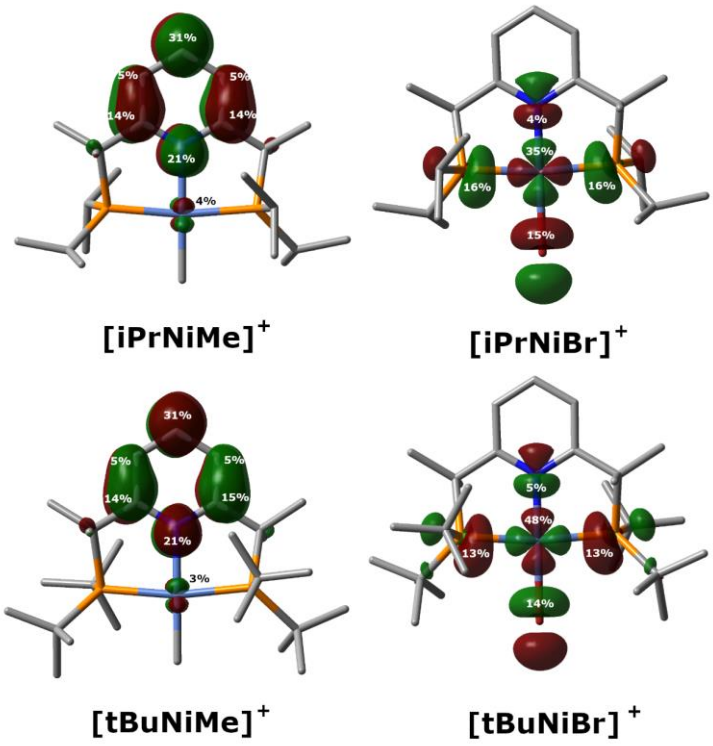


Figure 5. 140 Comparison of the LUMO orbitals between bromo and methyl containing complexes. The percentage contribution of each atom to the LUMO is written on the orbital representation directly. DFT optimized geometries, B3LYP, 6-311++G**/lanl2dz(Ni), alpha orbital representations, isovalue = 0.04.

5.7.1 Copy of XYZ coordinates file of DFT-optimized structures

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[iPrNiBr]+ cationic iPr4Me4PNPNiBr ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni,Br 1 1 with polarization, in vacuuo

Br	0.00000000	2.73363600	0.00000000
C	-3.32731900	1.49151600	0.70449100
H	-3.09326900	2.36800500	0.09195600
C	-2.91094700	1.85242100	2.14066600
H	-3.23350600	1.10757900	2.86811600
H	-3.39093700	2.79686600	2.41096400
H	-1.83491800	1.99943700	2.23043000
C	-4.83757700	1.22020300	0.60708700
H	-5.17348200	1.01646900	-0.41144600
H	-5.37849600	2.10457600	0.95524300
H	-5.14524500	0.38759300	1.24414600
C	-2.91626600	1.57472000	-2.54654300
H	-3.63399200	2.22711400	-2.04786900
H	-3.23084400	1.48498800	-3.58985000
H	-1.94123100	2.06635000	-2.52902700
H	2.43236400	-0.81577900	3.79720800
Ni	0.00000000	0.36588200	0.00000000
P	2.23294400	0.23079900	0.15105300
P	-2.23294400	0.23079900	-0.15105300
N	0.00000000	-1.59466100	0.00000000
C	1.16123700	-2.28087700	-0.21130500
C	1.17607600	-3.67347200	-0.19985400
H	2.10303900	-4.20348500	-0.36245700
C	0.00000000	-4.37797300	0.00000000
H	0.00000000	-5.46177700	0.00000000
C	-1.17607600	-3.67347200	0.19985500
H	-2.10304000	-4.20348500	0.36245800

C	-1.16123700	-2.28087600	0.21130600
C	2.43995900	-1.51654300	-0.56676300
C	3.71382800	-2.23086700	-0.06832200
H	4.58809400	-1.59981500	-0.22857000
H	3.89130300	-3.15236300	-0.62864400
H	3.66726700	-2.48366800	0.99171100
C	2.49130700	-1.43847100	-2.11639200
H	1.66731100	-0.85609800	-2.53184400
H	2.43242600	-2.44873300	-2.53004800
H	3.43115600	-0.99974600	-2.45024300
C	-2.43995900	-1.51654200	0.56676400
C	-2.49130600	-1.43846900	2.11639300
H	-1.66731100	-0.85609700	2.53184500
H	-2.43242500	-2.44873100	2.53004900
H	-3.43115600	-0.99974500	2.45024300
C	-3.71382800	-2.23086700	0.06832300
H	-4.58809400	-1.59981500	0.22857200
H	-3.89130200	-3.15236300	0.62864600
H	-3.66726800	-2.48366800	-0.99171000
C	2.85501200	0.16927400	1.92259100
C	1.99988000	-0.76395100	2.79444400
H	0.98099800	-0.38123600	2.89406300
H	1.94492400	-1.78426500	2.41016000
H	1.94123200	2.06635200	2.52902600
H	1.83491600	1.99943700	-2.23043000
C	-2.85501100	0.16927300	-1.92259100
H	-3.87122100	-0.23435300	-1.87432700
C	-1.99987900	-0.76395300	-2.79444400
H	-0.98099700	-0.38123800	-2.89406200
H	-2.43236400	-0.81578100	-3.79720800

H	-1.94492400	-1.78426700	-2.41015900
H	3.23084500	1.48499000	3.58984900
H	3.87122100	-0.23435200	1.87432700
C	2.91626700	1.57472100	2.54654200
H	3.63399300	2.22711500	2.04786800
C	3.32731800	1.49151500	-0.70449200
H	3.09327000	2.36800500	-0.09195800
C	2.91094500	1.85242000	-2.14066700
H	3.23350300	1.10757800	-2.86811700
H	3.39093600	2.79686500	-2.41096600
C	4.83757700	1.22020300	-0.60708900
H	5.17348200	1.01646800	0.41144400
H	5.37849500	2.10457500	-0.95524600
H	5.14524400	0.38759100	-1.24414800

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[tBuNiBr]+ cationic tBu4Me4PNPNiBr ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni,Br 1 1 with polarization, in vacuuo

Br	0.00000000	2.68169400	0.00000100
Ni	0.00000000	0.31025100	0.00000000
P	-2.29627600	0.14365500	-0.02100000
P	2.29627500	0.14365600	0.02100000
N	0.00000000	-1.65594800	0.00000000
C	-1.12782600	-2.34229800	0.33931000
C	-1.14434200	-3.73520800	0.33389900
H	-2.04496500	-4.26621000	0.60206700
C	0.00000100	-4.43963700	-0.00000100
H	0.00000100	-5.52348000	-0.00000100
C	1.14434300	-3.73520800	-0.33390000
H	2.04496600	-4.26620900	-0.60206900
C	1.12782700	-2.34229800	-0.33931100
C	-2.35094500	-1.57373800	0.84072000

C	-3.65763800	-2.37191900	0.64239700
H	-4.52380500	-1.75740700	0.87234300
H	-3.69365000	-3.22410700	1.32655800
H	-3.77182500	-2.75143600	-0.37238300
C	-2.12297000	-1.40257500	2.36974700
H	-1.26776700	-0.76440700	2.59530900
H	-1.93531100	-2.38623400	2.80879100
H	-3.00452500	-0.99091300	2.85752900
C	2.35094600	-1.57373600	-0.84072100
C	2.12297000	-1.40257200	-2.36974700
H	1.26776700	-0.76440300	-2.59530800
H	1.93531100	-2.38623100	-2.80879300
H	3.00452500	-0.99090900	-2.85752900
C	3.65763900	-2.37191700	-0.64239800
H	4.52380500	-1.75740400	-0.87234500
H	3.69365100	-3.22410500	-1.32656000
H	3.77182600	-2.75143500	0.37238100
C	-3.44354100	1.38503100	0.94073900
C	-4.81379900	0.78502700	1.32071400
H	-5.37255300	0.40535000	0.46582200
H	-5.41287000	1.58478700	1.76740000
H	-4.73844600	-0.00368000	2.06957400
C	-2.74032500	1.85735600	2.23373100
H	-2.60587800	1.06410300	2.96559900
H	-3.37906000	2.61503300	2.69837100
H	-1.77675100	2.31899600	2.02875700
C	-3.68889000	2.63657800	0.06852800
H	-2.76040700	3.10341100	-0.25505000
H	-4.22799800	3.36409200	0.68284100
H	-4.31283000	2.43124500	-0.80033900

C	-2.88573600	-0.06511400	-1.85206100
C	-4.41237100	-0.19565400	-2.02278900
H	-4.82734200	-1.05556400	-1.49694400
H	-4.62590000	-0.33349900	-3.08773500
H	-4.95054300	0.69571500	-1.70451600
C	-2.21850600	-1.31325300	-2.46731000
H	-1.13014200	-1.26049300	-2.42829900
H	-2.50419600	-1.36134400	-3.52237400
H	-2.53770400	-2.24803400	-2.00659800
C	-2.38239400	1.15412900	-2.65812900
H	-2.83164700	2.09327700	-2.34399200
H	-2.64406000	0.99918200	-3.70964400
H	-1.29929000	1.26641600	-2.59160500
C	2.88573600	-0.06511500	1.85206200
C	2.21850400	-1.31325300	2.46731000
H	1.13014000	-1.26049100	2.42829900
H	2.50419400	-1.36134500	3.52237400
H	2.53770000	-2.24803400	2.00659700
C	4.41237100	-0.19565700	2.02278900
H	4.82734000	-1.05556700	1.49694300
H	4.62589900	-0.33350500	3.08773600
H	4.95054400	0.69571100	1.70451900
C	2.38239600	1.15412800	2.65813000
H	2.83164900	2.09327600	2.34399400
H	2.64406200	0.99918100	3.70964400
H	1.29929200	1.26641600	2.59160700
C	3.44354100	1.38503200	-0.94074000
C	4.81379700	0.78502700	-1.32071600
H	5.37255300	0.40535100	-0.46582500
H	5.41286800	1.58478600	-1.76740500

H	4.73844300	-0.00368100	-2.06957500
C	3.68889100	2.63657900	-0.06852900
H	2.76040900	3.10341200	0.25504900
H	4.22799900	3.36409200	-0.68284300
H	4.31283200	2.43124500	0.80033800
C	2.74032300	1.85735600	-2.23373100
H	2.60587700	1.06410400	-2.96559800
H	3.37905700	2.61503400	-2.69837100
H	1.77674900	2.31899500	-2.02875600

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Complex [iPrNiMe]+ iPrPNPMe4NiMe cationic ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni 1 1 with polarization, in vacuuo

Ni	0.00447459	-0.70047949	-0.01945144
P	2.21554357	-0.52802433	0.15369924
P	-2.21656581	-0.52150651	-0.14982080
N	0.00775193	1.32160734	-0.00402257
C	1.16483432	2.00236631	-0.22380545
C	1.18488557	3.39603456	-0.22634729
H	2.11036947	3.92656295	-0.39693674
C	0.00797452	4.10117328	-0.02782388
H	0.00783660	5.18500395	-0.03815733
C	-1.16886762	3.39965890	0.18502480
H	-2.09394429	3.93333334	0.34752758
C	-1.14879630	2.00635092	0.20745521
C	2.43871976	1.22101415	-0.57117725
C	2.49341679	1.13045229	-2.11962430
H	3.43001728	0.68190181	-2.45048694
H	2.44298951	2.13754232	-2.54221829
H	1.66369864	0.55240075	-2.53015695
C	3.71553535	1.93176017	-0.07552855
H	3.66897518	2.19059255	0.98303683

H	3.89467884	2.85108333	-0.63903444
H	4.58920657	1.29938995	-0.23184026
C	-2.41852689	1.22976506	0.57853239
C	-3.70308092	1.94287013	0.10765343
H	-3.67723237	2.20162035	-0.95164497
H	-3.86936266	2.86238189	0.67485126
H	-4.57464361	1.31183054	0.28146621
C	-2.44402089	1.14545330	2.12820481
H	-3.37740123	0.70517656	2.47852966
H	-2.37878444	2.15418186	2.54489045
H	-1.61092923	0.56368397	2.52589449
C	3.35402269	-1.77270046	-0.67631351
H	3.16152376	-2.64469491	-0.04231514
C	2.93345797	-2.17642768	-2.10035749
H	1.85840308	-2.33467768	-2.18390708
H	3.42793378	-3.11631373	-2.36086262
H	3.23344079	-1.43896478	-2.84480664
C	4.85938243	-1.47036809	-0.60228399
H	5.14221508	-0.64675811	-1.26171255
H	5.41773160	-2.35043863	-0.93399773
H	5.19933063	-1.23369801	0.40781491
C	2.84191304	-0.44754291	1.92593772
H	3.86561197	-0.06370627	1.87904498
C	2.87523971	-1.84340080	2.57267680
H	1.88495225	-2.30579966	2.57873226
H	3.20212422	-1.74872338	3.61179891
H	3.56939852	-2.52492042	2.07899660
C	2.00068035	0.50965803	2.78507631
H	1.96741761	1.52650349	2.39039142
H	2.42737235	0.56278364	3.79047283

H	0.97317953	0.14941202	2.87921159
C	-2.90037782	-0.43826666	-1.90026703
H	-3.91217809	-0.02911536	-1.82263369
C	-2.06280436	0.49567326	-2.78853095
H	-1.99586558	1.51307066	-2.39914919
H	-2.51670950	0.55473969	-3.78160917
H	-1.04636065	0.11266486	-2.91027298
C	-2.99164140	-1.83499583	-2.53880837
H	-2.01537004	-2.32405721	-2.57901573
H	-3.35282929	-1.73527726	-3.56602935
H	-3.68436257	-2.49677300	-2.01718658
C	-3.32340885	-1.76602562	0.72117536
H	-3.12454990	-2.64564638	0.09887447
C	-2.87709884	-2.13456687	2.14804623
H	-1.79408771	-2.23105584	2.23450876
H	-3.31886398	-3.09731278	2.41936465
H	-3.21616304	-1.40710983	2.88537384
C	-4.83422259	-1.48818925	0.66597044
H	-5.11750329	-0.65284668	1.31035758
H	-5.37450221	-2.36773489	1.02779156
H	-5.19403858	-1.27988130	-0.34337605
C	-0.00092001	-2.65184179	-0.10998429
H	-0.13380283	-2.91201547	-1.16621106
H	-0.82386281	-3.09430748	0.45248513
H	0.92294623	-3.11632114	0.23736017

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Complex [iPrNiMe]• iPrPNPMe4NiMe radical ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni 0 2 with polarization, in vacuuo

Ni	0.00337210	-0.71280335	-0.02252167
P	-2.20073070	-0.49622006	-0.14448950
P	2.19971823	-0.50559326	0.15013931

N	0.00958232	1.25328425	-0.00511650
C	-1.16418193	2.00502795	0.21665517
C	-1.17149571	3.37708707	0.18976840
H	-2.09989329	3.90514856	0.36917765
C	0.00920651	4.12067191	-0.03481216
H	0.00899978	5.20183450	-0.04729476
C	1.19126755	3.37238089	-0.23793485
H	2.12051634	3.89658332	-0.42432091
C	1.18442407	2.00021331	-0.23419131
C	-2.41669463	1.22537061	0.62793957
C	-2.41247943	1.08885658	2.17326630
H	-3.31868879	0.60474179	2.54413954
H	-2.36546887	2.09120539	2.60632912
H	-1.54487478	0.53065608	2.52947897
C	-3.72615843	1.92272925	0.21065703
H	-3.74456682	2.17117374	-0.85131067
H	-3.85227980	2.85481570	0.76801938
H	-4.59427440	1.30100833	0.43702538
C	2.44317687	1.21374339	-0.61556538
C	3.74472344	1.90695638	-0.16678747
H	3.73999411	2.15034478	0.89648199
H	3.88411714	2.84168302	-0.71638154
H	4.61700973	1.28571454	-0.37688632
C	2.47440491	1.07258017	-2.16020370
H	3.38228012	0.57456674	-2.50836046
H	2.45122611	2.07367631	-2.59802865
H	1.60749575	0.52474192	-2.53446273
C	-3.31788232	-1.78228235	0.66309516
H	-3.10191582	-2.64423893	0.02248867
C	-2.89206858	-2.18872711	2.08577191

H	-1.80900903	-2.27114026	2.18211034
H	-3.32646413	-3.16430927	2.32679205
H	-3.24735966	-1.48138075	2.83554530
C	-4.83117641	-1.52155232	0.59951751
H	-5.12778442	-0.70881694	1.26656316
H	-5.37062435	-2.41787869	0.92373966
H	-5.17865764	-1.27757816	-0.40650935
C	-2.88454649	-0.37632636	-1.89654929
H	-3.90124503	0.02050055	-1.80992330
C	-2.95806130	-1.75112674	-2.58169242
H	-1.97612302	-2.22965607	-2.61914850
H	-3.30381026	-1.62338935	-3.61241260
H	-3.65114896	-2.43627185	-2.08980140
C	-2.05546066	0.59520621	-2.75230737
H	-1.96730172	1.58578753	-2.30468932
H	-2.52407315	0.70367587	-3.73599880
H	-1.04310354	0.21214606	-2.90021766
C	2.82447655	-0.39163367	1.92501047
H	3.85496590	-0.02526228	1.87185615
C	1.99700105	0.60584884	2.75148318
H	1.94859533	1.59678552	2.29902184
H	2.43903861	0.70503243	3.74837007
H	0.97081818	0.25107421	2.86999376
C	2.83121929	-1.76609988	2.61541647
H	1.83528032	-2.21697774	2.60770525
H	3.13342776	-1.64545376	3.66054138
H	3.52771928	-2.47057017	2.15656861
C	3.34760107	-1.79103431	-0.61562484
H	3.14644771	-2.64204407	0.04341835
C	2.93741062	-2.24297623	-2.02790736

H	1.86317647	-2.40836089	-2.10448708
H	3.44016139	-3.18689193	-2.26265358
H	3.22931562	-1.52120012	-2.79132457
C	4.85499582	-1.49946944	-0.54647912
H	5.14398614	-0.70390616	-1.23705580
H	5.41334927	-2.39600441	-0.83608434
H	5.18811240	-1.21687174	0.45442260
C	-0.00775748	-2.68288917	-0.11699221
H	-0.82395958	-3.13953480	0.44857646
H	0.91764108	-3.15722566	0.22159512
H	-0.14902182	-2.96055869	-1.17013562

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Complex [tBuNiMe]+ cationic tBuPNPMe4NiMe ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni 1 1 with polarization, in vacuuo

H	2.49042874	1.08581995	3.53314937
Ni	0.00671715	-0.59680299	0.00099535
P	2.27550779	-0.39337066	0.02452875
P	-2.27367600	-0.40022842	-0.01693863
N	-0.00373538	1.43236871	0.00126360
C	0.00839390	-2.54794397	-0.04176465
H	-0.29139703	-2.85944777	-1.04710543
H	-0.70263723	-2.96628595	0.66754236
H	0.97585510	-2.99125233	0.17642738
C	-1.13265581	2.11402315	0.32818788
C	1.12212047	2.11650221	-0.33038198
C	-2.35220794	1.33149845	0.82572867
C	-2.89488179	-0.20363444	-1.84392250
C	2.34271235	1.33556687	-0.82964866
C	2.88586640	-0.19189470	1.84861124
C	3.43768356	-1.62030987	-0.94139507
C	2.11077432	1.16895966	-2.35833151

H	2.97917899	0.73574257	-2.85127179
H	1.94462927	2.15624964	-2.79803224
H	1.23791050	0.55291116	-2.57822470
C	-3.41857321	-1.62983208	0.95820664
C	-0.00928854	4.21225950	-0.00624364
H	-0.01125224	5.29618413	-0.00923275
C	-2.13619572	1.17724311	2.35774192
H	-3.02646613	0.78234648	2.84432634
H	-1.94204534	2.16412459	2.78664274
H	-1.28857890	0.53392152	2.59664912
C	-1.15747759	3.50777262	0.31820978
H	-2.06141557	4.03960084	0.57469732
C	4.41037018	-0.04220920	2.01919035
H	4.96421514	-0.91580806	1.67891209
H	4.62764086	0.07682060	3.08582658
H	4.80832256	0.83525853	1.50985249
C	3.65203143	2.12788801	-0.62835397
H	3.76386688	2.50568502	0.38748627
H	3.69010755	2.98271082	-1.30920635
H	4.51882417	1.51421731	-0.85764322
C	-4.82113073	-1.08248176	1.29513064
H	-4.78928164	-0.26172047	2.01208834
H	-5.39419686	-1.88808159	1.76588956
H	-5.38089949	-0.75866894	0.41906939
C	1.14160955	3.51037648	-0.32758731
H	2.04276788	4.04484410	-0.58791903
C	3.75269038	-2.86212743	-0.07552192
H	4.38664810	-2.63489937	0.77991583
H	2.86108514	-3.37725446	0.27848925
C	2.20358105	1.04106783	2.47803041

H	2.50877556	1.98301779	2.02240383
H	1.11611616	0.97389880	2.43679374
C	-2.25413377	1.05613907	-2.46485939
H	-2.59755562	1.98589074	-2.01260879
H	-2.53300927	1.09109680	-3.52250872
H	-1.16530063	1.02946172	-2.41529961
C	2.69736277	-2.12226101	-2.20222852
H	1.76010645	-2.61716164	-1.95603046
H	3.33850727	-2.85481595	-2.70270401
H	2.49170176	-1.33312886	-2.92209433
C	-4.42383841	-0.10754547	-2.01179311
H	-4.93843843	-1.02048501	-1.71411925
H	-4.64413836	0.04958015	-3.07283740
H	-4.86048484	0.72803914	-1.46494932
C	-3.66759036	2.11221374	0.61643421
H	-3.78674683	2.48059638	-0.40165828
H	-3.71315389	2.97186813	1.29075324
H	-4.52757717	1.49087410	0.85305111
C	4.78667105	-1.00677609	-1.37188431
H	4.67787536	-0.21721977	-2.11485893
H	5.38325247	-1.79711450	-1.83867146
H	5.36621767	-0.61990026	-0.53369812
C	-2.74126961	-2.03670223	2.28973082
H	-1.70353040	-2.34004335	2.16638632
H	-3.28832561	-2.89120778	2.69958534
H	-2.77789560	-1.24897615	3.03835343
C	-3.59305159	-2.91148920	0.11118000
H	-4.19614410	-2.74510638	-0.78031946
H	-4.12263952	-3.64928649	0.72133307
H	-2.64359842	-3.35504758	-0.18643329

C	2.39677629	-1.42473151	2.64361195
H	1.31587712	-1.55268546	2.55856627
H	2.63698017	-1.27286259	3.70068932
H	2.87302683	-2.35275560	2.33404044
C	-2.37042233	-1.40692171	-2.66033926
H	-1.28108502	-1.46216229	-2.63446318
H	-2.67454983	-1.27410715	-3.70346774
H	-2.76667720	-2.36368491	-2.32630749
H	4.30413600	-3.56960165	-0.70225413

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Complex [tBuNiMe]• radical tBuPNPMe4NiMe ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni 0 2 with polarization, in vacuuo

H	2.45995009	1.16943792	3.50337221
Ni	0.00392307	-0.60811843	0.00438996
P	2.26071436	-0.37260412	0.02121585
P	-2.26080081	-0.37608853	-0.00654411
N	-0.00730448	1.36490774	-0.02485227
C	-0.00111302	-2.57993433	-0.03554375
H	-0.29956554	-2.91025047	-1.03804214
H	-0.70729528	-3.01503757	0.67189012
H	0.96476132	-3.03264041	0.18203384
C	-1.14594205	2.11761710	0.32411867
C	1.14053532	2.11146219	-0.35927251
C	-2.35662672	1.34112620	0.84645011
C	-2.87789163	-0.18301190	-1.83847907
C	2.34369830	1.32543849	-0.88092727
C	2.87327710	-0.13757740	1.84443327
C	3.43173340	-1.64201096	-0.88578984
C	2.10824005	1.10310124	-2.40090189
H	2.95256749	0.61832549	-2.89343356
H	1.97202625	2.08394617	-2.86342801

H	1.20704362	0.51787395	-2.58967218
C	-3.41584818	-1.62951967	0.93277768
C	0.00512495	4.23262598	-0.01098188
H	0.00909444	5.31391813	-0.00777083
C	-2.15017206	1.16403472	2.37632739
H	-3.02281617	0.72896998	2.86604112
H	-1.98798222	2.15499184	2.80719007
H	-1.27568164	0.55305486	2.60471765
C	-1.15003758	3.48984162	0.32019485
H	-2.05238413	4.01968412	0.59660342
C	4.39838491	-0.00054555	2.01935541
H	4.94588269	-0.89278121	1.71657958
H	4.61272348	0.16165152	3.08203875
H	4.80502430	0.85137448	1.47405985
C	3.66606463	2.10149962	-0.71598758
H	3.80466132	2.47342965	0.29873975
H	3.67249054	2.96705967	-1.38433501
H	4.52837290	1.49439236	-0.98259793
C	-4.82476393	-1.10012449	1.27254794
H	-4.79726764	-0.28664425	1.99767505
H	-5.39731996	-1.91564183	1.72993179
H	-5.38008080	-0.76367666	0.39799754
C	1.15474400	3.48407205	-0.34454150
H	2.06084696	4.00988347	-0.61556588
C	3.73867631	-2.86115804	0.01372165
H	4.37493528	-2.61289097	0.86218289
H	2.84085076	-3.35168246	0.38622990
C	2.20603191	1.12112765	2.43844104
H	2.54500956	2.04480593	1.97220048
H	1.12079837	1.08637103	2.34733785

C	-2.25463450	1.09200832	-2.44643795
H	-2.63495234	2.01035756	-2.00284001
H	-2.49841910	1.11137489	-3.51465027
H	-1.17015001	1.10146454	-2.34322058
C	2.69978096	-2.18253481	-2.13602642
H	1.76414141	-2.67317885	-1.87663435
H	3.34696291	-2.92320225	-2.61971194
H	2.48711640	-1.40899328	-2.87066937
C	-4.40664533	-0.10775353	-2.01849930
H	-4.91307715	-1.03178283	-1.73833689
H	-4.62204158	0.06582936	-3.07911237
H	-4.85495397	0.71349218	-1.45874752
C	-3.68223104	2.10457890	0.64614103
H	-3.81912738	2.44547495	-0.37917751
H	-3.70034753	2.98908566	1.28891816
H	-4.54132812	1.49772961	0.92637291
C	4.78689488	-1.05497124	-1.33398680
H	4.67968982	-0.29288256	-2.10517763
H	5.38531478	-1.86498646	-1.76678626
H	5.36075397	-0.63283889	-0.50868556
C	-2.74625473	-2.05133052	2.26370302
H	-1.70657085	-2.34522829	2.13612051
H	-3.29217491	-2.91241899	2.66483792
H	-2.78473934	-1.26738828	3.01632191
C	-3.57975655	-2.90555733	0.07620542
H	-4.17603739	-2.73346042	-0.81929849
H	-4.10932426	-3.65424966	0.67542800
H	-2.62387564	-3.33607351	-0.21938630
C	2.36510703	-1.34064044	2.67116326
H	1.28387997	-1.45632725	2.57222304

H	2.59341364	-1.16013699	3.72755983
H	2.83204553	-2.28403323	2.39295951
C	-2.32838602	-1.37029134	-2.66081482
H	-1.23917509	-1.41027919	-2.61149665
H	-2.61537676	-1.22934555	-3.70895775
H	-2.71590592	-2.33663232	-2.34216282
H	4.28225277	-3.59537828	-0.59103592

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[iPrNi]+ cationic radical iPr4Me4PNPNi ub3lyp/6-311++g(d,p) PCHN Lanl2dz Ni 1 2 with polarization, in vacuuo

Ni	-0.00000019	-0.78805274	0.00000828
P	-2.25609611	-0.64364978	-0.16677651
P	2.25609637	-0.64364811	0.16678552
N	-0.00000097	1.25097067	-0.00000814
C	-1.15596208	1.91351702	0.23562345
C	-1.17979612	3.30804916	0.22382163
H	-2.09943178	3.84653180	0.40123668
C	0.00000289	4.00566077	-0.00001017
H	0.00000448	5.08968558	-0.00001074
C	1.17980024	3.30804548	-0.22384119
H	2.09943735	3.84652547	-0.40125663
C	1.15596232	1.91351375	-0.23564099
C	-2.40577730	1.10079654	0.62679149
C	-2.35616074	0.94549786	2.17034968
H	-3.25873219	0.46307506	2.54593140
H	-2.29393231	1.93443848	2.63279960
H	-1.48920830	0.36814309	2.49693038
C	-3.70970491	1.82975214	0.24534513
H	-3.73572653	2.12168703	-0.80543015
H	-3.84147120	2.73247022	0.84783148
H	-4.57509775	1.19801242	0.44282104

C	2.40577382	1.10078746	-0.62680762
C	3.70970493	1.82974660	-0.24538078
H	3.73573510	2.12169487	0.80539060
H	3.84146722	2.73245685	-0.84787980
H	4.57509557	1.19800346	-0.44285537
C	2.35614567	0.94546802	-2.17036332
H	3.25871408	0.46303968	-2.54594524
H	2.29391420	1.93440254	-2.63282589
H	1.48919052	0.36810929	-2.49692957
C	-3.37229519	-1.88937769	0.69653470
H	-3.31155555	-2.71039365	-0.02658337
C	-2.77531137	-2.43374908	2.00553035
H	-1.72397211	-2.70782493	1.88822353
H	-3.32151126	-3.33332667	2.30289935
H	-2.85144915	-1.72201774	2.82829645
C	-4.85533860	-1.52143426	0.85134454
H	-5.00952741	-0.74963305	1.60854651
H	-5.41483234	-2.40344470	1.17616638
H	-5.30508961	-1.17942409	-0.08331631
C	-2.99205697	-0.48525444	-1.89084608
H	-4.00414535	-0.08579392	-1.77376392
C	-3.08804157	-1.85610082	-2.58239586
H	-2.11211895	-2.34780783	-2.63653165
H	-3.44372861	-1.71897064	-3.60722854
H	-3.78635107	-2.53358398	-2.08897746
C	-2.17818383	0.48674767	-2.75986631
H	-2.10304389	1.48721637	-2.33068325
H	-2.65459975	0.58524798	-3.73918421
H	-1.16383931	0.11200635	-2.92126792
C	2.99206879	-0.48522900	1.89084791

H	4.00415622	-0.08576975	1.77375340
C	2.17820030	0.48678564	2.75985850
H	2.10305889	1.48724829	2.33066153
H	2.65462086	0.58529968	3.73917277
H	1.16385634	0.11204702	2.92127015
C	3.08805778	-1.85606544	2.58241652
H	2.11213598	-2.34777284	2.63656342
H	3.44374896	-1.71892046	3.60724579
H	3.78636605	-2.53355459	2.08900466
C	3.37228758	-1.88938930	-0.69651669
H	3.31154920	-2.71039681	0.02661109
C	2.77529568	-2.43377360	-2.00550326
H	1.72395638	-2.70784573	-1.88818793
H	3.32149194	-3.33335569	-2.30286535
H	2.85143081	-1.72205128	-2.82827743
C	4.85533121	-1.52145179	-0.85133822
H	5.00951825	-0.74965947	-1.60854962
H	5.41482091	-2.40346738	-1.17615299
H	5.30508791	-1.17943227	0.08331649

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[iPrNiMe]+ cationic iPr4Me4PNPNiMe ub3lyp/6-311g(d,p) CHNP, lanl2dz Ni 1 1 without polarization, with SMD(THF) for comparison with CO complexes

Ni	0.00353000	-0.69502000	-0.03507700
P	2.21557100	-0.52758000	0.15358400
P	-2.21819700	-0.51311800	-0.15375000
N	0.01194800	1.32501900	-0.00817800
C	1.17282600	2.00585400	-0.21025300
C	1.19490900	3.39901200	-0.21677800
H	2.12492600	3.92524900	-0.37585400
C	0.01684200	4.10632000	-0.03948600
H	0.01848500	5.19021700	-0.05337600

C	-1.16341800	3.40738200	0.15789500
H	-2.09082400	3.94083500	0.30708900
C	-1.14591700	2.01456400	0.18439000
C	2.45856000	1.23207200	-0.52545900
C	2.57850000	1.17031900	-2.06942500
H	3.52761700	0.72172300	-2.36368200
H	2.55267800	2.18742400	-2.47085200
H	1.76344100	0.60676200	-2.52738200
C	3.71326800	1.93307000	0.03461400
H	3.61935200	2.17599800	1.09375700
H	3.91264400	2.86050200	-0.50915100
H	4.59078400	1.29982100	-0.09376600
C	-2.42766300	1.24966500	0.53360100
C	-3.69391200	1.95745400	0.00993600
H	-3.62836300	2.20026300	-1.05156500
H	-3.87175800	2.88569500	0.55968700
H	-4.57102400	1.32875900	0.16415400
C	-2.50243300	1.19389600	2.08084700
H	-3.44365300	0.74914000	2.40433900
H	-2.46159600	2.21294400	2.47613300
H	-1.67584100	0.63063700	2.51736500
C	3.36830500	-1.75425000	-0.68063000
H	3.18151300	-2.63612600	-0.05995100
C	2.96540000	-2.14193900	-2.11296300
H	1.89214800	-2.30773300	-2.21257700
H	3.47175100	-3.07526900	-2.37866100
H	3.26589800	-1.39006300	-2.84310200
C	4.86809500	-1.43598500	-0.59391200
H	5.14091600	-0.60064600	-1.24291600
H	5.43683500	-2.30916000	-0.92981300

H	5.19501600	-1.20420200	0.42176100
C	2.79481300	-0.49541400	1.94259400
H	3.81958900	-0.11237100	1.93629300
C	2.80789700	-1.90438100	2.55724500
H	1.81086300	-2.35356400	2.55137900
H	3.13228600	-1.83268600	3.59999500
H	3.49434700	-2.58470400	2.05003200
C	1.92532500	0.43783000	2.79755900
H	1.94016200	1.47294600	2.45237600
H	2.29632600	0.43106300	3.82724000
H	0.88588900	0.09958000	2.81399500
C	-2.89706500	-0.48471500	-1.90560600
H	-3.90005600	-0.05278200	-1.85012200
C	-2.03071100	0.39504000	-2.81864600
H	-1.96380600	1.42874800	-2.47452300
H	-2.46471000	0.41110300	-3.82331700
H	-1.01546800	-0.00279700	-2.89889600
C	-3.01675600	-1.90021600	-2.49294700
H	-2.05177400	-2.41342200	-2.50960900
H	-3.37033100	-1.82565100	-3.52600100
H	-3.72815300	-2.52525900	-1.95032400
C	-3.31451700	-1.73952100	0.75048700
H	-3.14195700	-2.62712900	0.13312000
C	-2.83828800	-2.09734600	2.16849500
H	-1.75372900	-2.20500800	2.22830800
H	-3.28467400	-3.05355000	2.45892000
H	-3.14939800	-1.35658600	2.90526600
C	-4.82047200	-1.44172100	0.72600700
H	-5.07509100	-0.59093500	1.36234000
H	-5.36295700	-2.31132800	1.11125500

H	-5.19495400	-1.24190800	-0.28004500
C	-0.00739900	-2.64740400	-0.15543600
H	-0.11855800	-2.88587500	-1.22042300
H	-0.84513000	-3.10167900	0.37850300
H	0.91013000	-3.12059500	0.20169400

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[iPrNiMe]CO-up after optimization iPr4Me4PNPNiMe + CO up ub3lyp/6-311g(d,p) PCHNO Lanl2dz Ni 1 1 no polarization, with SMD(THF)

Ni	-0.00261000	0.33370600	0.33749700
P	-2.18619800	-0.06622600	0.45179700
P	2.21864400	0.40908700	0.13192100
N	0.13319400	-1.51157900	-0.46690000
C	-0.98211300	-2.14531000	-0.92158700
C	-0.90006100	-3.40493500	-1.51204900
H	-1.79364000	-3.89468100	-1.87187700
C	0.33437000	-4.01695200	-1.65797200
H	0.41336100	-4.99189500	-2.12495400
C	1.46697300	-3.36508800	-1.19602100
H	2.43713300	-3.83065600	-1.29087800
C	1.34695900	-2.11624900	-0.59065000
C	-2.33628400	-1.42644800	-0.87083400
C	-2.54454100	-0.77333000	-2.26138600
H	-3.53358900	-0.31993800	-2.33183800
H	-2.47783200	-1.54728500	-3.03129900
H	-1.79072300	-0.01483700	-2.48060900
C	-3.50344500	-2.40021500	-0.60900400
H	-3.33372900	-3.03021500	0.26530900
H	-3.66082400	-3.05428900	-1.47031800
H	-4.43218400	-1.84876300	-0.45958700
C	2.58245500	-1.45764900	0.03451700
C	3.87436400	-1.78469500	-0.73971200

H	3.79070300	-1.56775000	-1.80565200
H	4.13323300	-2.84092700	-0.62972500
H	4.71091600	-1.21277100	-0.33820000
C	2.71087700	-2.03418000	1.46809600
H	3.62896700	-1.68721700	1.94308800
H	2.75705100	-3.12533700	1.41025100
H	1.86140200	-1.76661600	2.09917800
C	-3.41970400	1.31849700	0.16300100
H	-3.25689300	1.90679500	1.07153100
C	-3.06730300	2.23879100	-1.01771700
H	-1.99606500	2.43273900	-1.08328100
H	-3.57372300	3.19953600	-0.88216700
H	-3.39885400	1.82656000	-1.97112900
C	-4.89873500	0.90896300	0.13549600
H	-5.14712900	0.35007300	-0.76962200
H	-5.51950800	1.81090600	0.14301600
H	-5.18558500	0.30763000	1.00069300
C	-2.71635800	-0.83291800	2.08142900
H	-3.70476900	-1.27157500	1.91830400
C	-2.83293200	0.22576600	3.18953700
H	-1.88020400	0.73530600	3.35849100
H	-3.11457900	-0.26898700	4.12423000
H	-3.59344700	0.97913100	2.97780000
C	-1.74730200	-1.94143200	2.51961300
H	-1.65661400	-2.74654300	1.78831200
H	-2.10665200	-2.38526300	3.45329300
H	-0.74827600	-1.53726800	2.70397700
C	2.82049600	1.15099900	-1.48691600
H	3.85196000	0.81359900	-1.62313500
C	1.97559000	0.65201400	-2.66846100

H	1.98508500	-0.43472900	-2.77085500
H	2.36998800	1.07328800	-3.59850900
H	0.93586700	0.97558400	-2.56931900
C	2.81640500	2.68743200	-1.45010300
H	1.81185300	3.08424600	-1.28046000
H	3.15846600	3.06399800	-2.41925300
H	3.48245700	3.09636100	-0.68860600
C	3.26031100	1.24836600	1.44941300
H	2.98884700	2.29246900	1.26098500
C	2.83290200	0.94311300	2.89548900
H	1.74835700	0.91395100	3.01379900
H	3.21736700	1.73172100	3.55001100
H	3.23982200	-0.00293400	3.25322400
C	4.78130100	1.12277100	1.28326900
H	5.12736700	0.11160500	1.50914800
H	5.27542300	1.80183200	1.98575400
H	5.12173700	1.38529400	0.27969600
C	-0.13657200	2.15145700	1.04998200
H	-1.08977300	2.37149800	1.53605700
H	-0.02912100	2.83049700	0.19547000
H	0.65940600	2.38085100	1.76221000
C	-0.66918600	4.97420200	-1.74044600
O	-1.16498300	5.80769500	-1.16648000

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[iPrNiMe]CO-down after optimization iPr4Me4PNPNiMe + CO down ub3lyp/6-311g(d,p) PCHNO Lanl2dz Ni 1 1 no polarization, with SMD(THF)

Ni	0.00851100	-0.65023300	-0.20566700
P	-2.24205500	-0.46767700	0.03083600
P	2.20972600	-0.44606600	0.30128500
N	0.02523700	1.39353600	-0.09128300
C	-1.14360900	2.07867500	0.04718000

C	-1.19631000	3.45026900	-0.18394300
H	-2.13155200	3.98367300	-0.09442500
C	-0.03309100	4.13608500	-0.50502000
H	-0.05949700	5.20309500	-0.69397700
C	1.16548800	3.44462500	-0.54956600
H	2.08729600	3.96705400	-0.76300500
C	1.17715100	2.06574600	-0.33380600
C	-2.36025000	1.34321400	0.62018700
C	-2.19518400	1.40998700	2.16183800
H	-3.07086800	0.99814000	2.66376900
H	-2.10237400	2.45833000	2.45991600
H	-1.30756000	0.88266300	2.50705600
C	-3.70221000	2.01653200	0.27030300
H	-3.82431300	2.20467800	-0.79604000
H	-3.79312000	2.97193400	0.79387600
H	-4.53311400	1.39410300	0.60413100
C	2.51432300	1.31141200	-0.39967300
C	3.61454100	2.07639000	0.37232100
H	3.31873500	2.32422200	1.39209400
H	3.86034900	3.00916000	-0.14171100
H	4.53111600	1.48737500	0.41199600
C	2.94584000	1.23477000	-1.88520600
H	3.93348400	0.78375300	-1.98088100
H	3.00747600	2.24991300	-2.28707800
H	2.23982200	0.67740300	-2.50151000
C	-3.09033900	-1.63040300	1.24548200
H	-3.00083600	-2.57375800	0.69675700
C	-2.34420300	-1.83165400	2.57537900
H	-1.26302800	-1.87465700	2.44366300
H	-2.66426600	-2.78027400	3.01749300

H	-2.57063700	-1.04451800	3.29495800
C	-4.58372600	-1.37144500	1.49485300
H	-4.74360100	-0.44925300	2.05842600
H	-4.99097800	-2.19384300	2.09210700
H	-5.16838600	-1.31828700	0.57481500
C	-3.35549600	-0.56474900	-1.49058500
H	-4.32607300	-0.19681600	-1.14742000
C	-3.54013400	-2.00970700	-1.98012600
H	-2.58862200	-2.46867600	-2.25918100
H	-4.17461800	-2.00367200	-2.87204300
H	-4.02487300	-2.65026100	-1.24169100
C	-2.90009600	0.33170600	-2.65295300
H	-2.65143400	1.34970200	-2.35125700
H	-3.71203500	0.39600800	-3.38424900
H	-2.03465100	-0.08210800	-3.17045900
C	2.58674500	-0.35012700	2.14586400
H	3.58323600	0.09221400	2.22640800
C	1.59630800	0.54128100	2.90545000
H	1.47264700	1.52986100	2.46125500
H	1.95602100	0.68161000	3.92970700
H	0.61404400	0.06823900	2.96382700
C	2.62635100	-1.74455600	2.79183000
H	1.68840200	-2.28521100	2.63961600
H	2.76967300	-1.62999600	3.87078900
H	3.44361600	-2.36447900	2.42081200
C	3.52688000	-1.65058500	-0.30415500
H	3.28424200	-2.52047200	0.31473200
C	3.39443400	-2.11418500	-1.76191000
H	2.39987400	-2.49527100	-1.98605900
H	4.10166500	-2.93333200	-1.92726200

H	3.63336100	-1.32883600	-2.47903200
C	4.97533000	-1.24482300	0.01022000
H	5.30428600	-0.41072900	-0.61381800
H	5.63411500	-2.09281500	-0.20267100
H	5.12442000	-0.97038800	1.05573900
C	-0.01426000	-2.62181000	-0.06078200
H	-0.13599400	-2.90254300	0.98793900
H	0.91266200	-3.06256400	-0.43184500
H	-0.84611000	-3.04107000	-0.63155200
C	0.18792900	-0.88987700	-2.36492700
O	0.22168500	-1.67275100	-3.18980000

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[iPrNiMe]CO-bipy after optimization iPr4Me4PNPNiMe + CO bipyramidal ub3lyp/6-311g(d,p) PCHNO Lanl2dz Ni 1 1 no polarization, with SMD(THF)

Ni	0.00851200	-0.65023700	-0.20566100
P	-2.24205500	-0.46767900	0.03083600
P	2.20972800	-0.44606400	0.30128500
N	0.02523600	1.39353400	-0.09128200
C	-1.14361000	2.07867300	0.04718500
C	-1.19631200	3.45026800	-0.18393600
H	-2.13155300	3.98367100	-0.09441400
C	-0.03309400	4.13608400	-0.50501700
H	-0.05950100	5.20309400	-0.69397300
C	1.16548500	3.44462400	-0.54956800
H	2.08729100	3.96705300	-0.76301000
C	1.17714900	2.06574500	-0.33380800
C	-2.36025100	1.34321100	0.62019100
C	-2.19518400	1.40997700	2.16184200
H	-3.07087100	0.99813400	2.66377200
H	-2.10236800	2.45831800	2.45992500
H	-1.30756300	0.88264600	2.50705800

C	-3.70221000	2.01653100	0.27030900
H	-3.82431100	2.20468400	-0.79603200
H	-3.79312100	2.97193000	0.79388800
H	-4.53311500	1.39410000	0.60413100
C	2.51432200	1.31141200	-0.39967700
C	3.61454100	2.07639300	0.37231100
H	3.31873800	2.32422700	1.39208500
H	3.86034800	3.00916100	-0.14172300
H	4.53111700	1.48737800	0.41198500
C	2.94583500	1.23476800	-1.88521200
H	3.93347900	0.78375100	-1.98088800
H	3.00746800	2.24990900	-2.28708600
H	2.23981500	0.67739900	-2.50151300
C	-3.09035600	-1.63040600	1.24546900
H	-3.00085400	-2.57375900	0.69673900
C	-2.34423500	-1.83166900	2.57537200
H	-1.26305900	-1.87468300	2.44366800
H	-2.66431300	-2.78028800	3.01747900
H	-2.57066900	-1.04453300	3.29495200
C	-4.58374400	-1.37144300	1.49482800
H	-4.74361900	-0.44925600	2.05841100
H	-4.99100700	-2.19384400	2.09206900
H	-5.16839600	-1.31827000	0.57478600
C	-3.35548500	-0.56473900	-1.49059500
H	-4.32606500	-0.19681000	-1.14743300
C	-3.54011900	-2.00969300	-1.98014800
H	-2.58860400	-2.46866000	-2.25919700
H	-4.17459500	-2.00365100	-2.87207200
H	-4.02486500	-2.65025300	-1.24172300
C	-2.90007900	0.33172500	-2.65295200

H	-2.65142300	1.34972000	-2.35124800
H	-3.71201100	0.39602800	-3.38425500
H	-2.03462800	-0.08208200	-3.17045400
C	2.58675000	-0.35012000	2.14586400
H	3.58323900	0.09222400	2.22640500
C	1.59631100	0.54128900	2.90544800
H	1.47264800	1.52986600	2.46125000
H	1.95602400	0.68162100	3.92970400
H	0.61404900	0.06824400	2.96382600
C	2.62635900	-1.74454600	2.79183400
H	1.68841100	-2.28520400	2.63962200
H	2.76968200	-1.62998300	3.87079200
H	3.44362500	-2.36447000	2.42081700
C	3.52688400	-1.65058300	-0.30415200
H	3.28424800	-2.52046800	0.31473800
C	3.39443600	-2.11418900	-1.76190600
H	2.39987800	-2.49528100	-1.98605000
H	4.10167100	-2.93333200	-1.92725700
H	3.63335700	-1.32884000	-2.47903100
C	4.97533300	-1.24481700	0.01021900
H	5.30428700	-0.41072600	-0.61382300
H	5.63411900	-2.09280900	-0.20266700
H	5.12442300	-0.97037600	1.05573700
C	-0.01425300	-2.62181200	-0.06076100
H	-0.13596200	-2.90253600	0.98796500
H	0.91266100	-3.06256700	-0.43184200
H	-0.84611500	-3.04108100	-0.63150800
C	0.18793000	-0.88988700	-2.36491700
O	0.22169000	-1.67276500	-3.18978600

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[tBuNiMe]+ cationic tBu4Me4PNPNiMe ub3lyp/6-311g(d,p) CHNP, lanl2dz Ni 1 1 without polarization, with SMD(THF) for comparison with CO complexes

H	2.43160100	1.11343200	3.52580400
Ni	0.00432100	-0.60613600	-0.01119100
P	2.27928700	-0.39227200	0.02360000
P	-2.27755100	-0.39547400	-0.01706000
N	0.00039500	1.42136500	-0.00181400
C	0.00097800	-2.55816700	-0.09716600
H	-0.18979600	-2.82929400	-1.14127200
H	-0.78244000	-3.00691500	0.51143300
H	0.94463700	-3.00885700	0.20547100
C	-1.12293700	2.10450000	0.33935200
C	1.12059200	2.10519400	-0.35078900
C	-2.33545700	1.32133400	0.84993100
C	-2.88961500	-0.18030800	-1.84299900
C	2.33800900	1.32257500	-0.85298100
C	2.85917100	-0.16599900	1.85553400
C	3.46057500	-1.62638500	-0.90755700
C	2.09205900	1.13458700	-2.37561900
H	2.96114100	0.70363600	-2.87073900
H	1.91425900	2.11667900	-2.82327900
H	1.22038600	0.51002600	-2.57814700
C	-3.43160400	-1.63112100	0.94289800
C	-0.00644100	4.20038900	-0.01924800
H	-0.00913700	5.28442500	-0.02669800
C	-2.08686300	1.13912700	2.37240800
H	-2.96534100	0.73050200	2.86944300
H	-1.88745000	2.12027200	2.81288300
H	-1.22998100	0.49609100	2.57931300
C	-1.14918100	3.49764100	0.32671500
H	-2.04895800	4.02931300	0.59740500

C	4.37672800	0.00890800	2.04731000
H	4.94835100	-0.85379500	1.70799000
H	4.57389600	0.12668000	3.11898800
H	4.76237700	0.89732500	1.54708100
C	3.64468800	2.12045300	-0.67092200
H	3.76370600	2.50207500	0.34314200
H	3.66606400	2.97298100	-1.35549700
H	4.51066200	1.50879700	-0.90821400
C	-4.81522200	-1.06394300	1.31673200
H	-4.75137500	-0.25184600	2.04081700
H	-5.39153300	-1.86853800	1.78736700
H	-5.38439700	-0.71856400	0.45424800
C	1.13977500	3.49877000	-0.35564900
H	2.03675300	4.03161600	-0.63288700
C	3.76949100	-2.85411800	-0.02231000
H	4.41379800	-2.61412100	0.82237100
H	2.87380400	-3.34923200	0.35087700
C	2.14988700	1.05807800	2.46900200
H	2.44263700	2.00071800	2.00629300
H	1.06417500	0.97026200	2.42256700
C	-2.22718500	1.06941300	-2.45758500
H	-2.56321500	2.00242600	-2.00574500
H	-2.50019000	1.10589600	-3.51747800
H	-1.13886500	1.02696900	-2.40102800
C	2.74334400	-2.15101300	-2.17110900
H	1.82703900	-2.68572800	-1.92828900
H	3.41720400	-2.85606400	-2.66986800
H	2.50562600	-1.36860600	-2.88910000
C	-4.41466600	-0.05862800	-2.01423400
H	-4.94403500	-0.96180100	-1.71214500

H	-4.62715100	0.09941200	-3.07773900
H	-4.83388700	0.78730500	-1.46936800
C	-3.64849400	2.10976400	0.67325500
H	-3.78241200	2.48365200	-0.34168000
H	-3.67074100	2.96625800	1.35275300
H	-4.50605700	1.49089700	0.92309400
C	4.80934600	-1.01186400	-1.33054500
H	4.69902700	-0.24315000	-2.09486000
H	5.42023500	-1.81061600	-1.76547500
H	5.36780700	-0.59438400	-0.49263300
C	-2.73759100	-2.07766800	2.25057900
H	-1.71218100	-2.40987400	2.09651900
H	-3.30208100	-2.92192100	2.66017200
H	-2.73152300	-1.29799600	3.00906500
C	-3.65475700	-2.88916000	0.07410000
H	-4.28407300	-2.68699600	-0.79227400
H	-4.17773800	-3.63038000	0.68732700
H	-2.72439200	-3.34294900	-0.26696900
C	2.37982100	-1.40054000	2.65093500
H	1.30246000	-1.54807900	2.54926500
H	2.59855900	-1.23238700	3.71101100
H	2.88000700	-2.32094900	2.35581400
C	-2.38092800	-1.38883200	-2.65939800
H	-1.29295600	-1.46395900	-2.62261300
H	-2.67326000	-1.24210000	-3.70480800
H	-2.79963700	-2.33928900	-2.33313500
H	4.30767300	-3.57871700	-0.64246200

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[tBuNiMe]CO-up tBu4Me4PNPNiMe cationic CO up ub3lyp/6-311g(d,p) CHNPO lanl2dz Ni 1 1 no polarization, with SMD(THF)

Ni	-0.03090400	0.07688700	-0.56773900

P	2.24728800	-0.14601800	-0.43541600
P	-2.30272100	0.06227800	-0.36256200
N	-0.05027700	-1.13995300	1.05249400
C	-0.00913900	1.20404000	-2.16373900
H	-0.95147800	1.71545600	-2.35201500
H	0.20257100	0.55335300	-3.01911900
H	0.76951100	1.96485000	-2.12287300
C	-1.19656200	-1.77708000	1.40655400
C	1.07652100	-1.33195100	1.78596100
C	-2.42090300	-1.66040900	0.49385600
C	-2.82582100	1.41531200	0.91110200
C	2.32600300	-0.51277000	1.45232400
C	2.78221600	-1.75169400	-1.38073900
C	3.45259700	1.32118900	-0.84922500
C	2.16336700	0.80941500	2.24974500
H	3.07619600	1.40165400	2.21659100
H	1.96981400	0.56218600	3.29741600
H	1.33120900	1.41354500	1.88549700
C	-3.49691900	0.09034900	-1.90273600
C	-0.09106900	-2.81873200	3.26775800
H	-0.10718400	-3.47322200	4.13176200
C	-2.23630200	-2.77769100	-0.57087400
H	-3.11977400	-2.87976000	-1.19926400
H	-2.08989200	-3.73001200	-0.05314900
H	-1.36689100	-2.60315900	-1.20702400
C	-1.23986900	-2.61217000	2.52147500
H	-2.15764400	-3.11022400	2.79505400
C	4.29679800	-2.02533800	-1.40556500
H	4.85150800	-1.26087300	-1.94900100
H	4.46389500	-2.97581800	-1.92502100

H	4.72494300	-2.12124300	-0.40759200
C	3.61836600	-1.20102500	1.93759600
H	3.69569900	-2.23689300	1.60877700
H	3.66428000	-1.19119300	3.03020900
H	4.49569700	-0.66537500	1.58370900
C	-4.86174900	-0.58084700	-1.65203600
H	-4.78077200	-1.65461000	-1.48431400
H	-5.47201500	-0.44260700	-2.55130300
H	-5.40602800	-0.13620400	-0.81878100
C	1.07836500	-2.17768700	2.89365700
H	1.98134700	-2.32313300	3.46716100
C	3.63986800	1.40411200	-2.38050700
H	4.22368600	0.57271900	-2.77403700
H	2.69610700	1.45703000	-2.92348900
C	-2.09922400	1.15749100	2.24676100
H	-2.41430600	0.23551900	2.73581800
H	-2.33888600	1.98369400	2.92446800
H	-1.01575200	1.13493900	2.12454300
C	2.82574500	2.65550300	-0.38134200
H	1.80215800	2.79156400	-0.72675200
H	3.42555100	3.47230800	-0.79657100
H	2.83673000	2.76745900	0.70047300
C	-4.33779300	1.50600600	1.18909800
H	-4.91529700	1.77983900	0.30664700
H	-4.50100600	2.29040800	1.93690800
H	-4.74595300	0.58006700	1.59397200
C	-3.73109800	-1.93579200	1.26108700
H	-3.80910500	-1.35104300	2.17777700
H	-3.79385300	-2.99420200	1.52920300
H	-4.59898800	-1.71859700	0.64423100

C	4.84860500	1.21084200	-0.20460500
H	4.81256100	1.29350700	0.88194900
H	5.45340100	2.04860800	-0.56953700
H	5.37200100	0.29301000	-0.46946600
C	-2.80696200	-0.62403900	-3.08490100
H	-1.87878800	-0.13360300	-3.37313600
H	-3.48496500	-0.58189800	-3.94440400
H	-2.59696300	-1.67380600	-2.89040400
C	-3.77341000	1.54183900	-2.35170800
H	-4.38096500	2.09693900	-1.63802400
H	-4.33903200	1.49248400	-3.28817400
H	-2.86570500	2.10989700	-2.55267100
C	2.26193900	-1.64878900	-2.83050200
H	1.17830500	-1.52426300	-2.85458900
H	2.50483300	-2.58285300	-3.34865900
H	2.71224100	-0.83479700	-3.39601200
C	-2.31708600	2.77686300	0.38731000
H	-1.24059000	2.75688700	0.20392600
H	-2.51393800	3.53500500	1.15302700
H	-2.81399400	3.09689400	-0.52642000
H	4.19751400	2.32091000	-2.59913500
C	0.69758100	6.43997400	1.63253200
O	0.67587900	5.33412900	1.84995100
C	2.07455400	-2.96826900	-0.74986500
H	2.41041200	-3.18537300	0.26396000
H	0.99012000	-2.85238800	-0.74114800
H	2.30746900	-3.84560300	-1.36253900

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[tBuNiMe]CO-down tBu4Me4PNPNiMe cationic ub3lyp/6-311g(d,p) CHNPO lanl2dz Ni 1 1 no polarization, with SMD(THF)

H	-3.21936200	0.92615600	-3.36708700

Ni	0.01194700	-0.57005600	-0.22586200
P	-2.32219500	-0.34581600	0.10676700
P	2.30438600	-0.33334700	0.14480800
N	0.05330800	1.47261100	-0.11141700
C	0.01259100	-2.53675600	-0.16436000
H	0.09991500	-2.86603700	0.87305600
H	0.84890500	-2.95116100	-0.72504200
H	-0.90922500	-2.93848200	-0.58567200
C	1.17844000	2.14901600	-0.45682500
C	-1.08615900	2.16105100	0.17346100
C	2.49473600	1.39516100	-0.70980200
C	2.65028700	-0.10217400	2.04685700
C	-2.23893700	1.42293400	0.86801800
C	-3.34206700	-0.21123100	-1.54323700
C	-3.26305900	-1.51844400	1.34677600
C	-1.80933800	1.33241600	2.35877300
H	-2.63359400	0.99441700	2.98438900
H	-1.52545600	2.33131400	2.70210100
H	-0.96156300	0.66884900	2.51109100
C	3.63339000	-1.55714000	-0.58237500
C	-0.02540800	4.22912900	-0.43538300
H	-0.06304100	5.30153900	-0.58867700
C	2.64942700	1.28263300	-2.25001400
H	3.60579400	0.83914600	-2.52457200
H	2.63048900	2.29443800	-2.66456200
H	1.84668000	0.72159400	-2.72375600
C	1.15514600	3.53321700	-0.62778200
H	2.05235500	4.05954200	-0.91896900
C	-4.85560800	0.03885200	-1.38561000
H	-5.36194500	-0.78232700	-0.87883500

H	-5.28768400	0.11052600	-2.39056900
H	-5.08963700	0.96535100	-0.86519700
C	-3.55424900	2.22592700	0.83867800
H	-3.83929800	2.54935800	-0.16071800
H	-3.45493400	3.11822300	1.46320600
H	-4.37070300	1.64117900	1.25611800
C	5.05436600	-0.96609300	-0.68222300
H	5.11895900	-0.16156300	-1.41539200
H	5.72418600	-1.76375700	-1.02257500
H	5.43987300	-0.60159900	0.26765400
C	-1.15174500	3.53980300	-0.01186800
H	-2.06597700	4.07699800	0.18908900
C	-3.67511300	-2.81353700	0.61445300
H	-4.49238000	-2.65223100	-0.08664600
H	-2.84676900	-3.28787900	0.08774800
C	-2.74979700	0.94587400	-2.37830000
H	-2.95254900	1.92627800	-1.94674500
H	-1.67285200	0.85709700	-2.52612600
C	1.96814500	1.17881000	2.56529700
H	2.45731400	2.09176500	2.22993200
H	2.02159900	1.16716700	3.65912000
H	0.92043500	1.23039200	2.28792200
C	-2.31534000	-1.93295800	2.49270900
H	-1.42763700	-2.44452900	2.12537600
H	-2.85764600	-2.63476700	3.13570000
H	-2.00284500	-1.09872100	3.11687300
C	4.13627200	-0.03143900	2.44893100
H	4.67839200	-0.95536500	2.25427100
H	4.18143000	0.14503100	3.52951700
H	4.66362200	0.79032700	1.96421600

C	3.71686800	2.20870800	-0.21825700
H	3.60874800	2.58009800	0.79812900
H	3.87926200	3.06967900	-0.87165200
H	4.62015300	1.60452100	-0.26584600
C	-4.53654600	-0.90847300	1.96666400
H	-4.32803100	-0.06865900	2.62902100
H	-5.01719800	-1.68360700	2.57413800
H	-5.25994000	-0.58699800	1.21924000
C	3.21603700	-2.01727400	-1.99503400
H	2.27956300	-2.57072600	-1.98865100
H	3.99108400	-2.69793900	-2.36352100
H	3.13568700	-1.20347600	-2.71166600
C	3.68931200	-2.82689100	0.29561200
H	4.13221400	-2.65202700	1.27483900
H	4.32389200	-3.55693500	-0.21800500
H	2.70944900	-3.28567700	0.43133100
C	-3.17691200	-1.52570300	-2.34421100
H	-2.17100000	-1.93604800	-2.30667400
H	-3.41550300	-1.32633400	-3.39379400
H	-3.85994300	-2.29989200	-2.00005400
C	1.98188300	-1.28671100	2.77838600
H	0.90489400	-1.30390600	2.60437400
H	2.14674500	-1.16390100	3.85420200
H	2.38859300	-2.25522200	2.49314600
H	-4.03123700	-3.52249200	1.36911200
C	0.09599000	-0.81085100	-2.45290400
O	0.14393600	-1.56939100	-3.29775800

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[tBuNiMe]CO-bipy tBu4Me4PNPNiMe cationic ub3lyp/6-311g(d,p) CHNPO lanl2dz Ni 1 1 no polarization, with SMD(THF)

H	2.02159900	1.16716200	3.65912400

Ni	0.01195000	-0.57005700	-0.22585300
P	2.30438600	-0.33334600	0.14480900
P	-2.32219500	-0.34581600	0.10676600
N	0.05330800	1.47261100	-0.11141200
C	0.01259000	-2.53675400	-0.16437300
H	-0.90922300	-2.93847400	-0.58569900
H	0.09989900	-2.86605000	0.87304000
H	0.84890900	-2.95115800	-0.72505000
C	-1.08616000	2.16105000	0.17346300
C	1.17843900	2.14901700	-0.45682100
C	-2.23893900	1.42293200	0.86802000
C	-3.34206800	-0.21123000	-1.54323700
C	2.49473600	1.39516200	-0.70979700
C	2.65028500	-0.10217700	2.04685900
C	3.63339000	-1.55713800	-0.58237500
C	2.64943100	1.28263800	-2.25000900
H	3.60580000	0.83915500	-2.52456500
H	2.63049100	2.29444400	-2.66455500
H	1.84668700	0.72159800	-2.72375400
C	-3.26305800	-1.51844600	1.34677500
C	-0.02541200	4.22912700	-0.43538600
H	-0.06304800	5.30153700	-0.58868300
C	-1.80934000	1.33241400	2.35877500
H	-2.63359700	0.99441200	2.98439000
H	-1.52546100	2.33131200	2.70210400
H	-0.96156400	0.66884800	2.51109300
C	-1.15174900	3.53980100	-0.01187000
H	-2.06598200	4.07699500	0.18908400
C	4.13627100	-0.03144300	2.44893400
H	4.67839000	-0.95537000	2.25427400

H	4.18142800	0.14502800	3.52951900
H	4.66362100	0.79032200	1.96421700
C	3.71686900	2.20870800	-0.21824900
H	3.60874700	2.58009900	0.79813700
H	3.87926500	3.06967900	-0.87164400
H	4.62015300	1.60451900	-0.26583600
C	-4.53654600	-0.90847800	1.96666300
H	-4.32803300	-0.06866400	2.62902100
H	-5.01719900	-1.68361300	2.57413500
H	-5.25994000	-0.58700100	1.21923900
C	1.15514200	3.53321700	-0.62778200
H	2.05235000	4.05954300	-0.91897000
C	3.68930900	-2.82689200	0.29560800
H	4.13221100	-2.65203200	1.27483600
H	2.70944500	-3.28567600	0.43132600
C	1.96814500	1.17880700	2.56530100
H	2.45731400	2.09176200	2.22993800
H	0.92043400	1.23039000	2.28792700
C	-2.74980000	0.94587800	-2.37829700
H	-2.95255600	1.92628000	-1.94674300
H	-3.21936200	0.92615800	-3.36708500
H	-1.67285400	0.85710400	-2.52612000
C	3.21604000	-2.01726700	-1.99503600
H	2.27956200	-2.57071300	-1.98865900
H	3.99108400	-2.69793600	-2.36352200
H	3.13569900	-1.20346600	-2.71166600
C	-4.85560900	0.03884800	-1.38560900
H	-5.36194300	-0.78233600	-0.87883900
H	-5.28768500	0.11052800	-2.39056800
H	-5.08964200	0.96534200	-0.86518900

C	-3.55425100	2.22592500	0.83868000
H	-3.83930300	2.54935200	-0.16071700
H	-3.45493300	3.11822400	1.46320500
H	-4.37070400	1.64117900	1.25612500
C	5.05436700	-0.96609100	-0.68221800
H	5.11896100	-0.16155900	-1.41538400
H	5.72418700	-1.76375400	-1.02257000
H	5.43987200	-0.60160100	0.26766100
C	-2.31534000	-1.93296000	2.49270900
H	-1.42763500	-2.44452800	2.12537600
H	-2.85764500	-2.63477100	3.13569700
H	-2.00284700	-1.09872300	3.11687400
C	-3.67511100	-2.81353900	0.61445100
H	-4.49237700	-2.65223300	-0.08664900
H	-4.03123500	-3.52249500	1.36910900
H	-2.84676600	-3.28788000	0.08774700
C	1.98188000	-1.28671500	2.77838500
H	0.90489100	-1.30390800	2.60437300
H	2.14674200	-1.16390700	3.85420200
H	2.38858900	-2.25522600	2.49314300
C	-3.17690800	-1.52570000	-2.34421300
H	-2.17099000	-1.93603200	-2.30668900
H	-3.41551300	-1.32633100	-3.39379300
H	-3.85992500	-2.29989700	-2.00005000
H	4.32388700	-3.55693600	-0.21801100
C	0.09598800	-0.81084100	-2.45293400
O	0.14395100	-1.56938400	-3.29778400

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Complex 3.25 up up complex tBu4Me4PNPNiBr no counterion cationic ub3lyp/6-311++d(d,p) CHNP lanl2dz Ni,Br 1 1 in vacuuo

Br	-0.00000100	-2.64600200	0.09417300

Ni	0.00000200	-0.28424700	-0.16830200
P	2.30795500	-0.14206600	-0.02499500
P	-2.30795600	-0.14206700	-0.02508400
N	0.00000600	1.67865900	-0.34672100
C	-1.17655100	2.36208500	-0.29630700
C	2.27988600	1.57495700	-2.30570400
H	3.17071200	1.17166900	-2.78259200
H	2.14150300	2.59394700	-2.67792900
H	1.41637000	0.98501400	-2.61205700
C	-2.27979500	1.57495400	-2.30579500
H	-1.41626700	0.98501000	-2.61211200
H	-2.14139600	2.59394400	-2.67801500
H	-3.17060200	1.17166700	-2.78272000
C	3.68814500	-2.64621400	-0.23496900
H	4.31285500	-2.48885800	0.64355100
H	4.22741300	-3.33782100	-0.88963700
H	2.76034600	-3.13039600	0.06309900
C	2.36868900	-1.31681000	2.56787900
H	1.28732000	-1.43165600	2.50681300
H	2.64230400	-1.21648300	3.62306800
H	2.81884700	-2.23505200	2.19871900
C	-1.19536500	3.72345100	-0.00393200
H	-2.13415200	4.25186700	0.06429800
C	1.17656000	2.36208600	-0.29626000
C	-2.43612800	1.62886400	-0.75644500
C	-0.00000600	4.40072700	0.18566700
H	-0.00001100	5.45533800	0.43595100
C	-3.68813500	-2.64621500	-0.23510900
H	-2.76034800	-3.13039800	0.06299500
H	-4.22737900	-3.33782300	-0.88979700

H	-4.31287800	-2.48885700	0.64338600
C	3.44320300	-1.34891800	-1.03666900
C	1.19536200	3.72345300	-0.00388400
H	2.13414600	4.25186800	0.06438300
C	2.16833700	1.15229800	2.49585900
H	2.51015500	2.11543900	2.11895400
H	2.39671900	1.12602200	3.56554400
H	1.08251600	1.10696000	2.39722900
C	2.86099300	-0.05352900	1.82823100
C	-3.72873600	2.40697000	-0.44584300
H	-4.60365700	1.82561900	-0.72652000
H	-3.76336500	3.32896900	-1.03339800
H	-3.82569200	2.67540700	0.60490100
C	4.38559200	0.07418700	2.02476400
H	4.92594300	-0.80450400	1.67525100
H	4.58301400	0.16288600	3.09808000
H	4.81208300	0.95422400	1.54503300
C	-3.44316100	-1.34892100	-1.03680200
C	-2.36878100	-1.31680600	2.56778700
H	-2.81891900	-2.23505000	2.19861000
H	-2.64243900	-1.21648000	3.62296500
H	-1.28740900	-1.43164600	2.50676500
C	2.43615600	1.62886600	-0.75634800
C	-2.16843700	1.15230300	2.49577000
H	-1.08261200	1.10697500	2.39717300
H	-2.39685200	1.12602400	3.56544800
H	-2.51025100	2.11544200	2.11885600
C	-2.86106300	-0.05352800	1.82812000
C	-2.70753400	-1.74564000	-2.33632800
H	-2.54471100	-0.90871400	-3.01238800

H	-3.33068000	-2.47183200	-2.86773900
H	-1.75081000	-2.22163000	-2.12505500
C	3.72875100	2.40697200	-0.44569200
H	3.82566300	2.67540900	0.60505600
H	3.76340300	3.32897200	-1.03324500
H	4.60368400	1.82562200	-0.72633400
C	4.81661100	-0.74321000	-1.39293700
H	4.74780100	0.09784900	-2.08181900
H	5.40168100	-1.51770000	-1.89878300
H	5.38604600	-0.43187600	-0.51744300
C	2.70762800	-1.74563600	-2.33622500
H	1.75089600	-2.22162900	-2.12499000
H	3.33079600	-2.47182600	-2.86761300
H	2.54483000	-0.90871000	-3.01229100
C	-4.81655500	-0.74321300	-1.39312500
H	-5.38602600	-0.43188000	-0.51765500
H	-5.40160500	-1.51770400	-1.89899600
H	-4.74771700	0.09784500	-2.08200400
C	-4.38567000	0.07418300	2.02459900
H	-4.81214600	0.95421700	1.54485100
H	-4.58313000	0.16288400	3.09790700
H	-4.92600700	-0.80451100	1.67507000

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Complex 3.25 up down complex tBu4Me4PNPNiBr no counterion cationic ub3lyp/6-311++d(d,p) CHNP lanl2dz Ni,Br 1 1 in vacuuo

Br	0.00000000	2.68169400	0.00000100
Ni	0.00000000	0.31025100	0.00000000
P	-2.29627600	0.14365500	-0.02100000
P	2.29627500	0.14365600	0.02100000
N	0.00000000	-1.65594800	0.00000000
C	-1.12782600	-2.34229800	0.33931000

C	-1.14434200	-3.73520800	0.33389900
H	-2.04496500	-4.26621000	0.60206700
C	0.00000100	-4.43963700	-0.00000100
H	0.00000100	-5.52348000	-0.00000100
C	1.14434300	-3.73520800	-0.33390000
H	2.04496600	-4.26620900	-0.60206900
C	1.12782700	-2.34229800	-0.33931100
C	-2.35094500	-1.57373800	0.84072000
C	-3.65763800	-2.37191900	0.64239700
H	-4.52380500	-1.75740700	0.87234300
H	-3.69365000	-3.22410700	1.32655800
H	-3.77182500	-2.75143600	-0.37238300
C	-2.12297000	-1.40257500	2.36974700
H	-1.26776700	-0.76440700	2.59530900
H	-1.93531100	-2.38623400	2.80879100
H	-3.00452500	-0.99091300	2.85752900
C	2.35094600	-1.57373600	-0.84072100
C	2.12297000	-1.40257200	-2.36974700
H	1.26776700	-0.76440300	-2.59530800
H	1.93531100	-2.38623100	-2.80879300
H	3.00452500	-0.99090900	-2.85752900
C	3.65763900	-2.37191700	-0.64239800
H	4.52380500	-1.75740400	-0.87234500
H	3.69365100	-3.22410500	-1.32656000
H	3.77182600	-2.75143500	0.37238100
C	-3.44354100	1.38503100	0.94073900
C	-4.81379900	0.78502700	1.32071400
H	-5.37255300	0.40535000	0.46582200
H	-5.41287000	1.58478700	1.76740000
H	-4.73844600	-0.00368000	2.06957400

C	-2.74032500	1.85735600	2.23373100
H	-2.60587800	1.06410300	2.96559900
H	-3.37906000	2.61503300	2.69837100
H	-1.77675100	2.31899600	2.02875700
C	-3.68889000	2.63657800	0.06852800
H	-2.76040700	3.10341100	-0.25505000
H	-4.22799800	3.36409200	0.68284100
H	-4.31283000	2.43124500	-0.80033900
C	-2.88573600	-0.06511400	-1.85206100
C	-4.41237100	-0.19565400	-2.02278900
H	-4.82734200	-1.05556400	-1.49694400
H	-4.62590000	-0.33349900	-3.08773500
H	-4.95054300	0.69571500	-1.70451600
C	-2.21850600	-1.31325300	-2.46731000
H	-1.13014200	-1.26049300	-2.42829900
H	-2.50419600	-1.36134400	-3.52237400
H	-2.53770400	-2.24803400	-2.00659800
C	-2.38239400	1.15412900	-2.65812900
H	-2.83164700	2.09327700	-2.34399200
H	-2.64406000	0.99918200	-3.70964400
H	-1.29929000	1.26641600	-2.59160500
C	2.88573600	-0.06511500	1.85206200
C	2.21850400	-1.31325300	2.46731000
H	1.13014000	-1.26049100	2.42829900
H	2.50419400	-1.36134500	3.52237400
H	2.53770000	-2.24803400	2.00659700
C	4.41237100	-0.19565700	2.02278900
H	4.82734000	-1.05556700	1.49694300
H	4.62589900	-0.33350500	3.08773600
H	4.95054400	0.69571100	1.70451900

C	2.38239600	1.15412800	2.65813000
H	2.83164900	2.09327600	2.34399400
H	2.64406200	0.99918100	3.70964400
H	1.29929200	1.26641600	2.59160700
C	3.44354100	1.38503200	-0.94074000
C	4.81379700	0.78502700	-1.32071600
H	5.37255300	0.40535100	-0.46582500
H	5.41286800	1.58478600	-1.76740500
H	4.73844300	-0.00368100	-2.06957500
C	3.68889100	2.63657900	-0.06852900
H	2.76040900	3.10341200	0.25504900
H	4.22799900	3.36409200	-0.68284300
H	4.31283200	2.43124500	0.80033800
C	2.74032300	1.85735600	-2.23373100
H	2.60587700	1.06410400	-2.96559800
H	3.37905700	2.61503400	-2.69837100
H	1.77674900	2.31899500	-2.

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Complex iPrNiBrdearo neutral ub3lyp/6-311++d(d,p) CHNP lanl2dz Ni,Br 0 1 in vacuuo

Br	0.00000134	-2.75165811	0.41318138
Ni	0.00000004	-0.36297693	0.00986774
P	-2.23806135	-0.20384102	-0.02647904
P	2.23806121	-0.20383836	-0.02647894
N	-0.00000106	1.53117895	-0.26809179
C	1.18868974	2.26920016	-0.13482497
C	-1.18869275	2.26919868	-0.13482465
C	-3.08122832	-0.22576535	1.65782627
H	-4.05554003	0.25216444	1.51427263
C	3.18638895	-1.47159818	-1.03836324
H	3.06459221	-2.35422942	-0.40322667

C	-2.42921383	1.56432179	-0.69599243
C	-1.22922839	3.52820033	0.34311848
H	-2.16169272	4.07765172	0.34165237
C	2.42921172	1.56432464	-0.69599252
C	-3.18638657	-1.47160187	-1.03836440
H	-3.06458792	-2.35423352	-0.40322877
C	3.31472545	-1.64761615	2.19521139
H	2.37892037	-2.20340714	2.28163089
H	3.76169392	-1.57865413	3.19220292
H	3.99819138	-2.22800853	1.57287655
C	1.22922380	3.52820198	0.34311790
H	2.16168737	4.07765464	0.34165154
C	3.08122763	-0.22576134	1.65782668
H	4.05553535	0.25217720	1.51427497
C	-2.51954833	-1.81986382	-2.37885171
H	-2.63739109	-1.03046608	-3.12190343
H	-2.98553114	-2.72426453	-2.78320281
H	-1.45675704	-2.02687005	-2.24950261
C	-3.31471374	-1.64762008	2.19521658
H	-3.99817575	-2.22802036	1.57288488
H	-3.76168139	-1.57865805	3.19220848
H	-2.37890391	-2.20340300	2.28163698
C	-2.31429917	1.55485530	-2.23971664
H	-1.41621550	1.03676101	-2.57553437
H	-2.25258512	2.59049134	-2.58576198
H	-3.18696945	1.09450237	-2.70746270
C	2.51955101	-1.81986282	-2.37885002
H	1.45676011	-2.02687072	-2.24950052
H	2.98553528	-2.72426321	-2.78320020
H	2.63739232	-1.03046574	-3.12190268

C	4.68859250	-1.19568679	-1.20570979
H	4.87343943	-0.35506208	-1.87875940
H	5.17296994	-2.07386202	-1.64512081
H	5.18946011	-0.98682676	-0.25767195
C	2.27523503	0.59900753	2.67511440
H	2.09727786	1.62276217	2.34365885
H	2.81702566	0.63599278	3.62572149
H	1.30431729	0.13269308	2.86012523
C	-2.27524291	0.59901453	2.67511077
H	-1.30432149	0.13270871	2.86012404
H	-2.81703425	0.63599961	3.62571747
H	-2.09729404	1.62276916	2.34365066
C	-0.00000265	4.22121385	0.87142038
H	-0.00000343	5.27796870	0.57233961
H	-0.00000238	4.24328254	1.97733287
C	-3.75414845	2.23932857	-0.30770055
H	-4.60851071	1.65133416	-0.64816808
H	-3.82703889	3.21974595	-0.78705237
H	-3.84763039	2.39111154	0.76813634
C	-4.68859079	-1.19569348	-1.20571051
H	-5.18945869	-0.98683501	-0.25767249
H	-5.17296648	-2.07386945	-1.64512197
H	-4.87343957	-0.35506875	-1.87875956
C	2.31429740	1.55485771	-2.23971669
H	3.18696854	1.09450606	-2.70746242
H	2.25258183	2.59049358	-2.58576226
H	1.41621465	1.03676192	-2.57553456
C	3.75414570	2.23933267	-0.30770052
H	3.84762792	2.39111469	0.76813648
H	3.82703479	3.21975058	-0.78705147

H	4.60850852	1.65133961	-0.64816894

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Complex tBuNiBrdearo neutral ub3lyp/6-311++d(d,p) CHNP lanl2dz Ni,Br 0 1 in vacuuo

Br	-0.00000300	-2.70655020	0.33711903
Ni	0.00000000	-0.30446302	-0.06065400
P	2.30080018	-0.11612901	-0.05142500
P	-2.30080118	-0.11612501	-0.05142500
N	0.00000100	1.58684912	-0.36019603
C	1.18459609	2.33858618	-0.32683002
C	1.22352710	3.63521528	0.03683800
H	2.14318416	4.19887332	-0.04464800
C	0.00000300	4.34042533	0.55927504
H	0.00000400	5.39171343	0.24536302
H	0.00000200	4.37428534	1.66575313
C	-1.22352109	3.63521728	0.03683600
H	-2.14317716	4.19887732	-0.04465100
C	-1.18459209	2.33858818	-0.32683103
C	2.40650819	1.60951813	-0.89137707
C	3.72144428	2.38232218	-0.69025905
H	3.88737130	2.67542721	0.34530903
H	3.69986128	3.29757625	-1.28927310
H	4.57985035	1.80183214	-1.02433608
C	2.16292617	1.48034111	-2.41841818
H	3.00851223	1.03311608	-2.94110623
H	2.02088016	2.48956319	-2.81490421
H	1.26281610	0.90894707	-2.63890520
C	-2.40650519	1.60952212	-0.89137907
C	-2.16291917	1.48034311	-2.41841918
H	-1.26280810	0.90895007	-2.63890320
H	-2.02087215	2.48956419	-2.81490622

H	-3.00850323	1.03311708	-2.94110923
C	-3.72144028	2.38232718	-0.69026605
H	-4.57984735	1.80183714	-1.02434208
H	-3.69985628	3.29757925	-1.28928310
H	-3.88736930	2.67543621	0.34530003
C	2.97222822	0.03299300	1.75890513
C	2.32732018	1.26412310	2.42893418
H	2.65916420	2.20906517	2.00531615
H	2.59957820	1.25393310	3.49001927
H	1.23838410	1.23574709	2.36411918
C	4.50553734	0.15547801	1.86446714
H	5.02172239	-0.74064506	1.51939912
H	4.76862936	0.29017902	2.91984522
H	4.90162938	1.01127508	1.31908610
C	2.51383019	-1.19741309	2.57247020
H	1.42949411	-1.30230210	2.57084420
H	2.84410021	-1.05911408	3.60810228
H	2.93277722	-2.13479516	2.21469917
C	3.36884726	-1.39561511	-1.05046908
C	4.72246436	-0.83109606	-1.52925312
H	4.61358535	-0.01365300	-2.24069317
H	5.26227640	-1.63409313	-2.04362016
H	5.35384339	-0.49137504	-0.70766605
C	3.65603928	-2.65914420	-0.21109202
H	4.33924333	-2.46860919	0.61673105
H	4.14300332	-3.38994026	-0.86631107
H	2.74336721	-3.11271924	0.17164201
C	2.54842419	-1.84879914	-2.27928417
H	1.60857412	-2.30975118	-1.97667615
H	3.13268024	-2.59916520	-2.82398121

H	2.33366618	-1.03778208	-2.97252623
C	-3.36885026	-1.39561111	-1.05046708
C	-4.72246736	-0.83109006	-1.52925012
H	-5.35384540	-0.49137004	-0.70766105
H	-5.26228040	-1.63408713	-2.04361616
H	-4.61358935	-0.01364600	-2.24068817
C	-3.65604328	-2.65913720	-0.21108802
H	-2.74337121	-3.11271324	0.17164601
H	-4.14300732	-3.38993426	-0.86630507
H	-4.33924633	-2.46860019	0.61673405
C	-2.54842920	-1.84879714	-2.27928417
H	-2.33367218	-1.03778008	-2.97252723
H	-3.13268724	-2.59916320	-2.82397922
H	-1.60858012	-2.30975018	-1.97667715
C	-2.97222822	0.03299400	1.75890513
C	-2.32732018	1.26412310	2.42893718
H	-1.23838310	1.23574709	2.36412118
H	-2.59957620	1.25392910	3.49002227
H	-2.65916420	2.20906617	2.00532315
C	-4.50553634	0.15547701	1.86446814
H	-4.90163037	1.01127607	1.31908910
H	-4.76862936	0.29017502	2.91984622
H	-5.02172139	-0.74064506	1.51939612
C	-2.51382919	-1.19741409	2.57246620
H	-2.93277522	-2.13479516	2.21469217
H	-2.84409921	-1.05911908	3.60809828
H	-1.42949311	-1.30230310	2.57084020

5.8 X-ray diffraction analysis

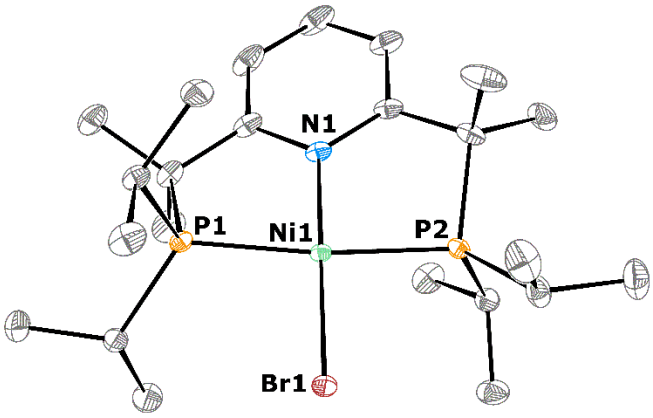

Figure 5. 141 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.24**. Hydrogen atoms as well as counterion and solvent molecules are omitted for clarity

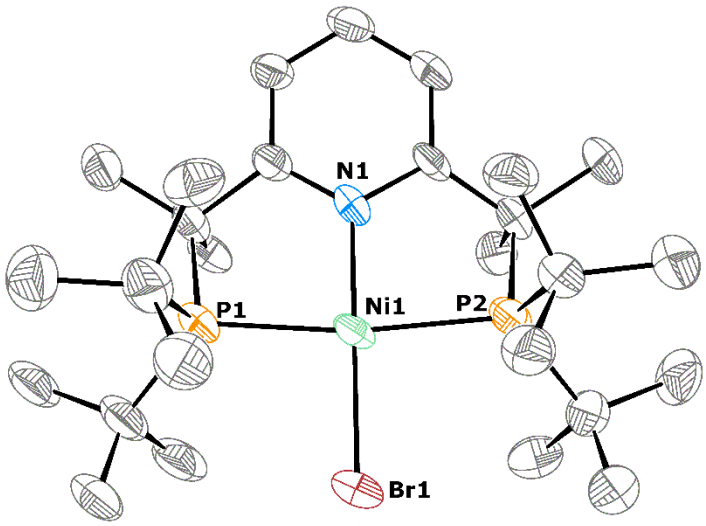

Figure 5. 142 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.25** from measurement done on Cu source. Only the major disordered component is shown. Hydrogen atoms as well as counterion and solvent molecules are omitted for clarity**.**

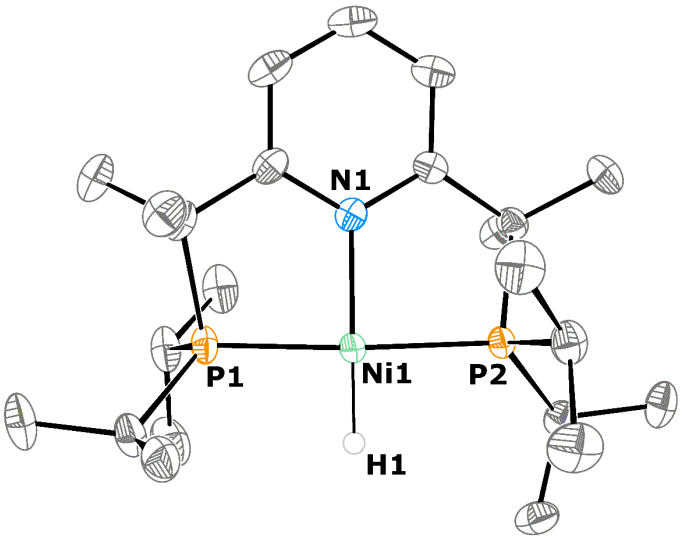

Figure 5. 143 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.27.** Hydrogen atoms, except for the hydrogen on the nickel center, as well as counterion and solvent molecules are omitted for clarity.

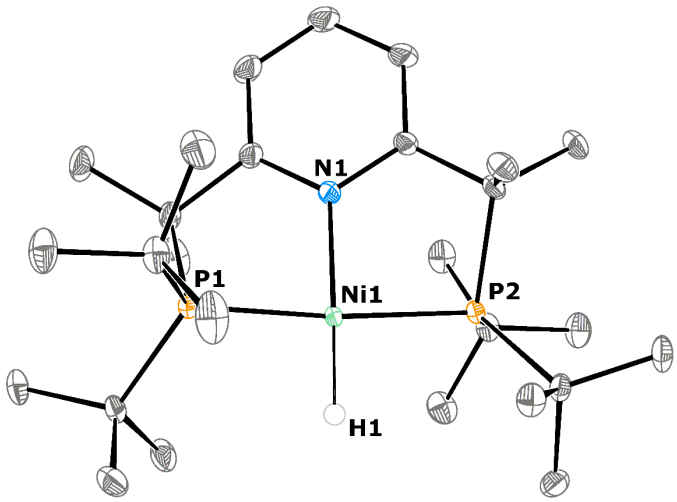

Figure 5. 144 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.29**. Hydrogen atoms, except for the hydrogen on the nickel center, as well as counterion and solvent molecules are omitted for clarity.

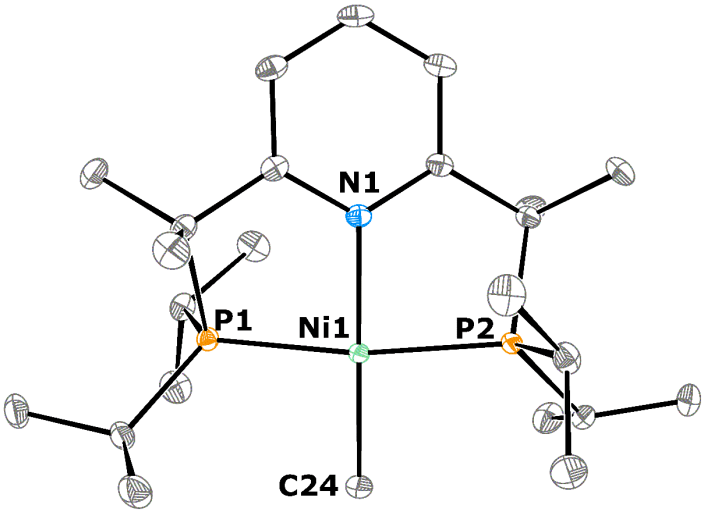

Figure 5. 145 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.31.** Hydrogen atoms as well as counterion and solvent molecules are omitted for clarity.

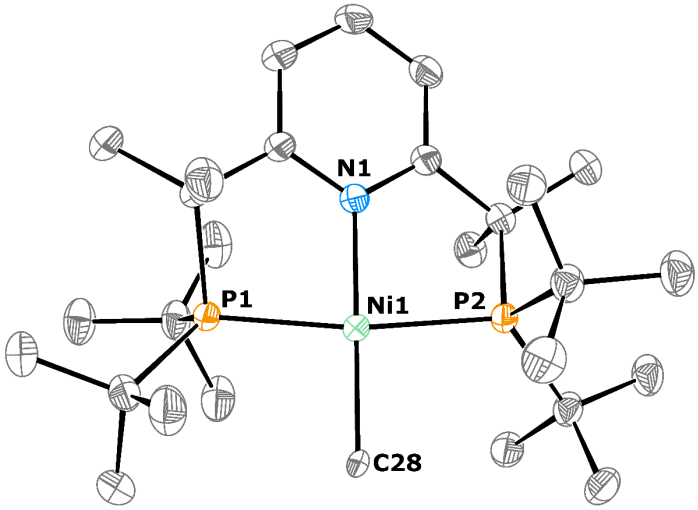

Figure 5. 146 ORTEP diagram showing 50% probability anisotropic displacement ellipsoids of non-hydrogen atoms for complex **3.33.** Hydrogen atoms as well as counterion and solvent molecules are omitted for clarity.

Table 5. 7 Crystal Data, Collection, and Refinement Parameters for complexes **3.24-3.26**

	3.24	**3.25 (Cu source)**	**3.26**
Identification code	JK227	JK329	JK313
Empirical formula	$C_{49}H_{66}BBrN_2NiP_2$	$C_{51}H_{71}BBrNNiP_2$	$C_{62}H_{64}BF_{24}NNiP_2$
Formula weight	894.4	909.45	1410.6
Temperature	100(2) K	101(2) K	93(2) K
Wavelength	0.71073 Å	1.54184 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	*Pbca*
Unit cell dimensions	a = 11.82732(15) Å	a = 16.6303(4) Å	a = 25.6658(3) Å
	b = 13.41875(17) Å	b = 16.7388(5) Å	b = 18.46458(18) Å
	c = 14.59047(19) Å	c = 17.0700(4) Å	c = 26.7911(3) Å
Volume	2277.40(5) $Å^3$	4678.0(2) $Å^3$	12696.6(2) $Å^3$
Z	2	4	8
Density (calculated)	1.304 Mg/m^3	1.291 Mg/m^3	1.476 Mg/m^3
Absorption coefficient	1.409 mm^{-1}	2.494 mm^{-1}	0.467 mm^{-1}
F(000)	944	1928	5776
Crystal size	0.239 x 0.136 x 0.077 mm^3	0.093 x 0.047 x 0.036 mm^3	0.213 x 0.194 x 0.162 mm^3
Theta range for data collection	2.196 to 32.180°.	3.727 to 75.745°.	2.198 to 31.498°.
Index ranges	-17<=h<=17, -19<=k<=19, -21<=l<=20	-20<=h<=19, -20<=k<=20, 20<=l<=21	--37<=h<=37, -27<=k<=27, -39<=l<=39
Reflections collected	66758	94546	443198
Independent reflections	14563 [R(int) = 0.0609]	9537 [R(int) = 0.0786]	21079 [R(int) = 0.0307]
Completeness	99.80%	99.80%	99.90%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.432	0.975 and 0.871	1.000 and 0.484
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14563 / 0 / 518	9537 / 2624 / 854	21079 / 477 / 988
Goodness-of-fit on F^2	1.033	1.079	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0751	R1 = 0.1090, wR2 = 0.2456	R1 = 0.0357, wR2 = 0.0922
R indices (all data)	R1 = 0.0441, wR2 = 0.0786	R1 = 0.1160, wR2 = 0.2493	R1 = 0.0448, wR2 = 0.0980
Largest diff. peak and hole	0.839 and -0.539 $e.Å^{-3}$	2.411 and -1.364 $e.Å^{-3}$	0.697 and -0.628 $e.Å^{-3}$

Table 5. 8 Crystal Data, Collection, and Refinement Parameters for complexes **3.27-3.29**

	3.27	**3.28**	**3.29**
Identification code	JK423	jk673_sq	JK327
Empirical formula	C47 H64 B N Ni P2	$C_{60.33}H_{67.33}BF_{24}NNiO_{0.33}P_2$	$C_{51}H_{72}BNNiP_2$
Formula weight	774.45	1399.27	830.55
Temperature	93(2) K	96(2) K	100(2) K
Wavelength	1.54184 Å	1.54184 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$I2/a$	$P2_1/n$
Unit cell dimensions	a = 10.90555(8) Å	a = 26.56323(16) Å	a = 16.94511(19) Å
	b = 12.82042(10) Å	b = 19.25607(10) Å	b = 14.40719(15) Å
	c = 31.1054(2) Å	c = 39.5263(2) Å	c = 19.4041(2) Å
Volume	4304.95(6) $Å^3$	19911.6(2) $Å^3$	4569.73(9) $Å^3$
Z	4	12	4
Density (calculated)	1.195 Mg/m^3	1.400 Mg/m^3	1.207 Mg/m^3
Absorption coefficient	1.580 mm^{-1}	1.823 mm^{-1}	0.529 mm^{-1}
F(000)	1664	8616	1792
Crystal size	0.065 x 0.038 x 0.023 mm^3	0.220 x 0.052 x 0.034 mm^3	0.168 x 0.108 x 0.099 mm^3
Theta range for data collection	3.735 to 68.245°.	2.560 to 73.249°.	2.334 to 32.370°.
Index ranges	-13<=h<=13, -15<=k<=14, -36<=l<=37	-32<=h<=32, -23<=k<=15, 49<=l<=49	--25<=h<=25, -21<=k<=21, -28<=l<=28
Reflections collected	42922	197074	123829
Independent reflections	7880 [R(int) = 0.0333]	19936 [R(int) = 0.0904]	15370 [R(int) = 0.0364]
Completeness	99.8 %	99.90%	99.90%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.906	1.000 and 0.583	1.000 and 0.704
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7880 / 0 / 485	19936 / 880 / 1535	15370 / 0 / 525
Goodness-of-fit on F^2	1.053	1.028	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0864	R1 = 0.0574, wR2 = 0.1638	R1 = 0.0295, wR2 = 0.0757
R indices (all data)	R1 = 0.0356, wR2 = 0.0889	R1 = 0.0618, wR2 = 0.1681	R1 = 0.0362, wR2 = 0.0781
Largest diff. peak and hole	0.384 and -0.293 e.$Å^{-3}$	1.111 and -0.548 e.$Å^{-3}$	0.466 and -0.263 e.$Å^{-3}$

Table 5. 9 Crystal Data, Collection, and Refinement Parameters for complexes **3.30**-**3.32**

	3.30	**3.31**	**3.32**
Identification code	JK396	JK695	JK669
Empirical formula	$C_{56}H_{58}BF_{24}NNiP_2$	$C_{48}H_{66}BNNiP_2$	$C_{60}H_{66}BF_{24}NNiP_2$
Formula weight	1332.49	788.47	1388.59
Temperature	93(2) K	95(2) K	96(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 17.61800(15) Å	a = 10.43115(16) Å	a = 17.1879(3) Å
	b = 17.47387(13) Å	b = 13.90761(19) Å	b = 19.0336(3) Å
	c = 20.75109(18) Å	c = 30.4008(4) Å	c = 19.8584(4) Å
Volume	5997.62(9) $Å^3$	4396.36(11) $Å^3$	6280.7(2) $Å^3$
Z	4	4	4
Density (calculated)	1.476 Mg/m^3	1.191 Mg/m^3	1.469 Mg/m^3
Absorption coefficient	0.489 mm^{-1}	0.547 mm^{-1}	0.470 mm^{-1}
F(000)	2720	1696	2848
Crystal size	0.205 x 0.169 x 0.097 mm^3	0.278 x 0.220 x 0.158 mm^3	0.126 x 0.110 x 0.075 mm^3
Theta range for data collection	2.331 to 32.361°.	2.446 to 32.362°.	2.106 to 27.449°.
Index ranges	-26<=h<=26, -26<=k<=25, -31<=l<=31	-14<=h<=15, -19<=k<=20, 45<=l<=42	--22<=h<=22, -24<=k<=24, -25<=l<=25
Reflections collected	353329	97103	125669
Independent reflections	20726 [R(int) = 0.0418]	14563 [R(int) = 0.0330]	14357 [R(int) = 0.0478]
Completeness	99.90%	99.90%	99.90%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.578	1.000 and 0.387	1.000 and 0.770
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	20726 / 244 / 836	14563 / 0 / 492	14357 / 81 / 847
Goodness-of-fit on F^2	1.035	1.026	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0883	R1 = 0.0303, wR2 = 0.0761	R1 = 0.0371, wR2 = 0.0909
R indices (all data)	R1 = 0.0423, wR2 = 0.0917	R1 = 0.0368, wR2 = 0.0786	R1 = 0.0482, wR2 = 0.0964
Largest diff. peak and hole	0.761 and -0.619 e.$Å^{-3}$	0.456 and -0.347 e.$Å^{-3}$	0.761 and -0.519 e.$Å^{-3}$

Table 5. 10 Crystal Data, Collection, and Refinement Parameters for complexes **3.33-3.35**

	3.33	**3.34**	**3.35**
Identification code	JK335	JK660	JK212
Empirical formula	$C_{52}H_{74}BNNiP_2$	$C_{23}H_{44}BrNNiP_2$	$C_{27}H_{52.33}Br_{0.67}NNiP_2$
Formula weight	844.58	535.15	565.22
Temperature	93(2) K	99(2) K	100(2) K
Wavelength	1.54184 Å	1.54184 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a = 16.83437(13) Å	a = 18.33845(6) Å	a = 12.2202(2) Å
	b = 14.65048(9) Å	b = 8.69143(4) Å	b = 15.1220(2) Å
	c = 19.51631(15) Å	c = 33.33541(11) Å	c = 16.6774(3) Å
Volume	4629.38(6) $Å^3$	5301.38(3) $Å^3$	2888.01(9) $Å^3$
Z	4	8	4
Density (calculated)	1.212 Mg/m^3	1.341 Mg/m^3	1.300 Mg/m^3
Absorption coefficient	1.508 mm^{-1}	4.012 mm^{-1}	1.725 mm^{-1}
F(000)	1824	2256	1211
Crystal size	0.115 x 0.045 x 0.041 mm^3	0.188 x 0.056 x 0.033 mm^3	0.208 x 0.182 x 0.097 mm^3
Theta range for data collection	3.078 to 70.509°.	2.657 to 69.147°.	2.592 to 29.986°.
Index ranges	-20<=h<=20, -17<=k<=17, -23<=l<=23	-22<=h<=22, -10<=k<=10, 40<=l<=40	--16<=h<=17, -21<=k<=20, -23<=l<=22
Reflections collected	65611	115393	66054
Independent reflections	8766 [R(int) = 0.0460]	9907 [R(int) = 0.0328]	7806 [R(int) = 0.0418]
Completeness	99.70%	100.00%	99.90%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.763	1.000 and 0.665	1.000 and 0.597
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8766 / 0 / 531	9907 / 169 / 588	7806 / 1 / 310
Goodness-of-fit on F^2	1.04	1.042	1.06
Final R indices [I>2sigma(I)]	R1 = 0.0412, wR2 = 0.1103	R1 = 0.0286, wR2 = 0.0757	R1 = 0.0285, wR2 = 0.0658
R indices (all data)	R1 = 0.0449, wR2 = 0.1146	R1 = 0.0299, wR2 = 0.0767	R1 = 0.0341, wR2 = 0.0673
Largest diff. peak and hole	0.928 and -0.361 e.$Å^{-3}$	1.181 and -0.416 e.$Å^{-3}$	0.468 and -0.379 e.$Å^{-3}$

Table 5. 11 Crystal Data, Collection, and Refinement Parameters for complex **3.37** and **3.25** (Mo)

	3.37	**3.25 (Mo source)**
Identification code	JK417_sq	BJK002
Empirical formula	$C_{48}H_{92}N_2Ni_2P_4$	$C_{51}H_{71}BBrNNiP_2$
Formula weight	938.53	909.45
Temperature	93(2) K	100(2) K
Wavelength	1.54184 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a = 8.27611(14) Å	a = 16.6161(9) Å
	b = 11.24869(17) Å	b = 16.7035(11) Å
	c = 16.3269(3) Å	c = 17.0546(11) Å
Volume	1395.67(4) $Å^3$	4659.1(5) $Å^3$
Z	1	4
Density (calculated)	1.117 Mg/m^3	1.297 Mg/m^3
Absorption coefficient	2.132 mm^{-1}	1.378 mm^{-1}
F(000)	510	1928
Crystal size	0.059 x 0.040 x 0.032 mm^3	0.039 x 0.038 x 0.028 mm^3
Theta range for data collection	2.883 to 70.748°.	2.246 to 25.349°.
Index ranges	-9<=h<=5, -13<=k<=13, -19<=l<=19	-20<=h<=20, -20<=k<=20, -20<=l<=20
Reflections collected	15463	171541
Independent reflections	5128 [R(int) = 0.0312]	8510 [R(int) = 0.0938]
Completeness	97.60%	99.90%
Absorption correction	Gaussian	Semi-empirical from equivalents
Max. and min. transmission	0.994 and 0.929	0.6088 and 0.5216
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5128 / 0 / 266	8510 / 2630 / 854
Goodness-of-fit on F^2	1.024	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1171	R1 = 0.0701, wR2 = 0.1729
R indices (all data)	R1 = 0.0478, wR2 = 0.1209	R1 = 0.0769, wR2 = 0.1763
Largest diff. peak and hole	1.020 and -0.374 $e.Å^{-3}$	0.501 and -0.917 $e.Å^{-3}$

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