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Aminoazine-Based Unsymmetric Multidentate Ligands in Mn(II & I) Complexes and Application in Hydrophosphination Reactions

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Contents

1.0 Experimental Section

1.1 Chemistry

The reagents and chemicals required for the study were procured, and all reagents were used as received unless otherwise noted. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) on silica gel aluminum plates, with visualization under UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, with TMS as an internal standard. The ^{1}H NMR and ^{13}C NMR spectra were recorded in CD_2Cl_2 and, for a few compounds, in DMSO-*d6* at 2.50 ppm and 39.51 ppm, respectively. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz). The abbreviations used to characterize the signals are as follows: s = singlet, m = multiplet, d = doublet, br. s. = broad singlet, dd = doublet of doublets, t = triplet, and coupling constant in Hz. Infrared spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer, either as thin films on KBr plates. High-resolution mass spectra (HRMS) were recorded using the ESI-TOF method.

1.2 Computational Methods

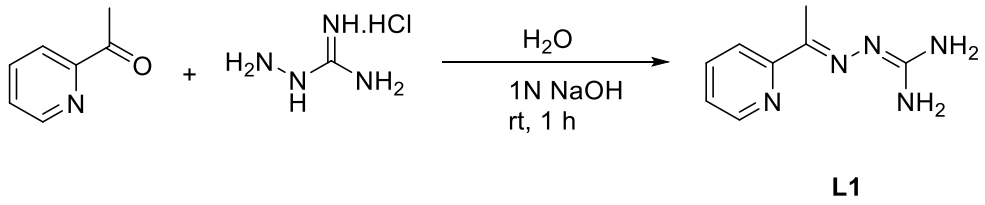
The quantum chemical calculations were carried out using the Gaussian 16 program.[1] Geometries of C, H, N, O, and P were optimized using the PBE0-PBE1 functional[2] and the def2-TZVP[3] basis set, whereas for Manganese, Lanl2dz[4]. Solvent effects were considered implicitly using the SMD[5] method with toluene as solvent. The nature of each stationary point was confirmed by frequency calculations (no imaginary frequencies for minima and one for transition state structures). The frequency calculations were carried out on all the structures to verify the character of the stationary points (minima v/s saddle points).

2.0 General Procedures of Synthesis

Synthesis of 4-pyridyl-4-methyl-1,1-diaminoazine (L1):

Through a single-step process, a non-palindromic NNN-pincer ligand was successfully synthesized using a combination of 2-acetylpyridylcarboxaldehyde (0.5g, 4.13 mmol) and aminoguanidine hydrochloride (0.455g, 4.13 mmol) in water (5 mL) at room temperature with the aid of 1N NaOH solution (1 mL). The resulting ligand, 4-pyridyl-4-methyl-1,1-

diaminoazine (**L1**), was isolated as a light brown solid in an 85% yield, following a cost-effective and environmentally friendly procedure (Scheme 1). The chemical structure of the ligand was confirmed through various spectroscopic techniques, including ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry. Notably, the ^{1}H NMR spectrum displayed distinct peaks for the methyl and –NH2 groups, further validating the successful synthesis of the ligand (**L1**).

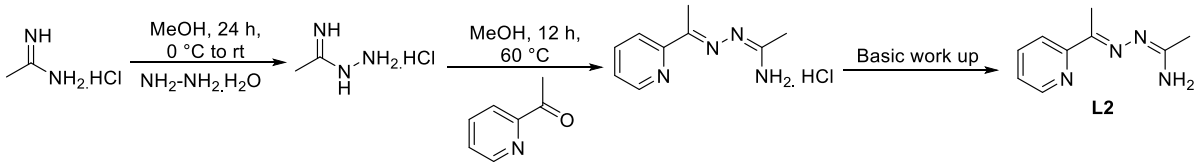


L1

Scheme S1. Synthesis of non-palindromic NNN-pincer ligand (**L1**).

Synthesis of 4-pyridyl-1, 4-dimethylaminoazine (L2):

A solution of acetamidine hydrochloride (1.0g, 10 mmol) in MeOH (10 ml) was cooled in an ice bath, and then hydrazine hydrate (0.530g, 0.52 ml, 10 mmol) was added, the mixture was stirred for 24 h, giving rise to an intense red solution. The solution was then concentrated in a vacuum, giving rise to red coloured acetamidrazone hydrochloride (hygroscopic in nature). The acetamidrazone (0.939g, 12.86 mmol) was then reacted with 2-acetylpyridine (1.71g, 14.14 mmol) in MeOH, refluxed at 60 °C for 12 h. The solution was concentrated, and the greenish solid was neutralised with saturated sodium carbonate solution by performing DCM/Water workup to yield the desired ligand (**L2**) (Scheme 2).



L2

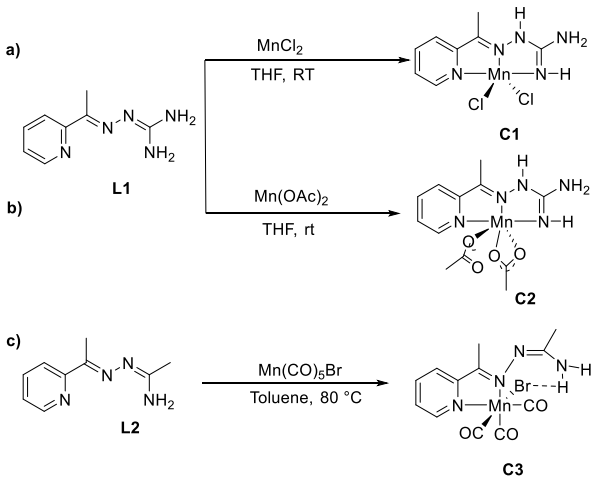
Scheme S2. Synthesis of non-palindromic NNN-pincer ligand (**L2**).

General Procedure for the synthesis of complex C1, C2, and C3

The synthesis of pincer complexes **C1** and **C2** was performed in a single step. In a 50 mL RBF, pyridyl azine **L1** (1 mmol) and anhydrous $MnCl_2$ (1 mmol) were added in dry THF (10 mL) at room temperature. The resulting reaction mixture was stirred at room temperature for 12 hours, affording a light brown precipitate of complex C1 in 90% yield (Scheme S1a). X-ray diffraction analysis revealed **C1** as a pentacoordinated complex with a trigonal bipyramidal geometry and a 15-electron count, indicating stronger bonding of the guanidine portion than of the pyridine ring.

Similarly, the synthesis of complex **C2** was carried out using the above-mentioned procedure with manganese acetate as a precursor and characterized with X-ray crystallography, a hexa-coordinated complex with octahedral geometry and a 17-electron count.

In a 50 ml Schlenk flask, **L2** (0.35 g, 2 mmol), $Mn(CO)_5Br$ (0.537 g, 1.92 mmol), and 10 ml dry toluene were mixed under an argon atmosphere. The reaction mixture was stirred at 80 ℃ for 12 h. A light-yellow precipitate was formed, which was washed with 50 ml (2x20 ml and 1x10 ml) of dry hexane and decanted using a cannula. The solid was then dried under vacuum to obtain the desired complex C3. Yield 90%. The crystals suitable for X-ray diffraction were obtained from a methanol-diethyl ether solvent system (slow diffusion technique). The solid-state structure shows that **C3** is a hexa-coordinated complex with octahedral geometry, and it is an 18-electron complex. The nitrogen from the guanidine portion do not form a bond with the central metal atom, hence serves as a bidendate ligand under given reaction conditions as shown below (Scheme S3).

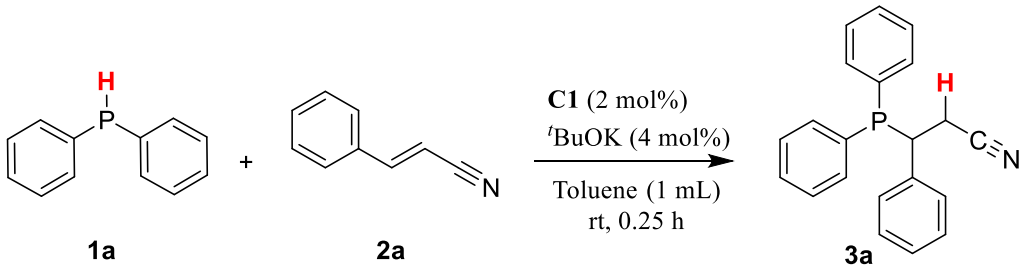


Scheme S3. Synthesis of **C1**, **C2** -Mn(II) and **C3** -Mn(I) aminoazine complexes. All these reactions were performed under inert conditions

General procedure for the hydrophosphination of alkenes:

In toluene (1 ml), complex **C1** (2 mol%, 3 mg), and *t*-BuOK (4 mol%, 2.3 mg) were added. The reaction mixture was stirred for 5 minutes, turning light greenish. Subsequently, cinnamonitrile (0.5 mmol, 64 mg) was added to the mixture, resulting in a deep red colour change, followed by the addition of diphenylphosphine (0.5 mmol, 93 mg). The reaction was carried out at room temperature under an argon atmosphere for one hour and monitored using $^{31}P\{^{1}H\}$ NMR. Upon completion of the reaction, the mixture was diluted with 10 times its volume of dry hexane, leading to the precipitation of the product. The mixture was then filtered through a silica pad in a glass pipette saturated with hexane to separate unreacted starting

materials. The silica bed was washed with additional hexane (3 mL), followed by passing dichloromethane through the silica bed. The resulting solution was collected in a second vial for further processing. The solvent was evaporated under reduced pressure, and the pure product was utilized for further analysis.



Scheme S1: Synthesis of 3-(diphenylphosphaneyl)-3-phenylpropanenitrile using complex **C1**.

Control experiments:

1. **In the absence of base**: In this experiment, no catalysis was observed, which shows that base is important for hydrophosphination reactions.
2. **In the presence of reducing agent (Sodium borohydride)**: It was believed that $NaBH_4$ shall reduce Mn(II) to Mn(I), which would help in catalysis and the scope of the reaction. However, there was no reaction. This experiment further adds to the importance of the base in the reaction.
3. **Addition of PPH_3 to the optimised reaction condition:** Most of the catalysts for the hydrophosphination reactions are phosphorus-based complexes. Hence, it seems that phosphine is necessary for such reactions. 1 equivalent of PPh_3 was added to the optimised condition; however, no significant improvement was observed.
4. **In the presence of base only**: In this experiment, no catalysis was observed, which shows that the manganese complex is important for hydrophosphination reactions.
5. **Sequence of addition after catalyst activation**: Addition of Cinnamonitrile before the diphenylphosphine would slow down the reaction rate. Hence, it is believed that coordination of diphenylphosphine to manganese accelerates the reaction, as it acts as a phosphide donor.

3.0 Spectral Data:

1,1-diaminopyridylazine (L1):

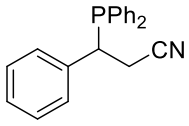
^{1}H NMR (300 MHz, DMSO-*d6*) δ 8.49-8.48 (d, J = 8.0 Hz, 1H), 8.23-8.21 (d, J = 8.0 Hz, 1H), 7.68-7.65 (t, J = 7.6 Hz, 1H), 7.22-7.19 (t, J = 7.2 Hz, 1H), 6.03 (brs, 2H), 5.68 (brs, 2H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d6*); δ 160.81, 148.98, 148.59, 135.93, 122.38, 120.00, 12.85; IR (KBr, cm^{-1}): 3458 (NH), 1659 (C=N), 1609 (C=N). HRMS (EI-TOF) calcd for $C_8H_{12}N_5$ $[M+H]^+$: 178.1087, found 178.1088.

(Pyridin-2-yl-ethylidene)acetohydrazonamide (L2):

^{1}H NMR (300 MHz, DMSO-*d6*) *δ:* 8.56-8.55 (d, J = 8.0 Hz, 1H), 8.33-8.30 (d, J = 8.0 Hz, 1H), 7.77-7.74 (t, J = 7.6 Hz, 1H), 7.35-7.31 (t, J = 7.2 Hz, 1H), 6.6 (brs, 2H), 2.27 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d6*); δ 163.24, 158.86, 153.35, 148.67, 136.78, 125.25, 121.86, 16.32, 14.02; IR (KBr, cm^{-1}): 3458 (NH), 1659 (C=N), 1609 (C=N). HRMS (EI-TOF) calcd for $C_8H_{12}N_5$ $[M+H]^+$: 176.2230, found 176.2231.

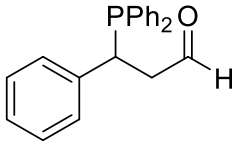
Spectral data of hydrophosphination products:

1. **3-(diphenylphosphaneyl)-3-phenylpropanenitrile**[6]



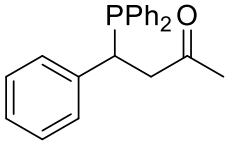
^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.66 – 7.63 (m, 2H), 7.47 – 7.45 (m, 3H), 7.31 – 7.29 (m, 4H), 7.26 – 7.16 (m, 6H), 3.79 – 3.75 (m, 1H), 2.75 – 2.68 (m, 1H), 2.66 – 2.60 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 134.4 (d, J = 21.4 Hz), 133.5 (d, J = 19.0 Hz), 130.5, 129.5, 129.4 (d, J = 3.2 Hz), 129.2, 129.2, 128.6 (d, J = 6.9 Hz), 127.9, 42.0 (d, J = 15.5 Hz), 23.2 (d, J = 23.0 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ = -1.95 (s). HRMS (ESI) calcd for $[C_{21}H_{18}NP]^+$: 315.12 $[M]^+$; found: 315.13.

2. **3-(diphenylphosphaneyl)-3-phenylpropanal**[6]



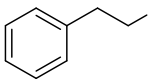
^{1}H NMR (300 MHz, CD_2Cl_2) δ = 9.54 – 9.52 (m, 1H), 7.66 – 7.61 (m, 2H), 7.43 – 7.42 (m, 3H), 7.24 – 7.12 (m, 10H), 4.14 – 4.09 (m, 1H), 3.05 – 2.96 (m, 1H), 2.70 – 2.62 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 200.7 (d, J = 12.6 Hz), 140.7 (d, J = 8.7 Hz), 136.5 (d, J = 17.1 Hz), 134.4 (d, J = 20.9 Hz), 133.7 (d, J = 19.0 Hz), 130.0, 129.4 (d, J = 7.7 Hz), 129.2 (d, J = 7.8 Hz), 128.8, 128.5 (d, J = 6.8 Hz), 127.0 (d, J = 2.2 Hz), 47.7 (d, J = 20.4 Hz), 39.0 (d, J = 14.0 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ = -0.60. HRMS (ESI) calcd for $[C_{21}H_{19}OP]^+$: 318.12 $[M]^+$; found: 318.13.

3. **4-(diphenylphosphaneyl)-4-phenylbutan-2-one**[6]



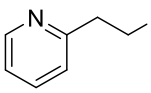
^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.67 – 7.62 (m, 2H), 7.44 – 7.41 (m, 3H), 7.24 – 7.09 (m, 10H), 4.13 – 4.09 (m, 1H), 3.09 – 3.03 (m, 1H), 2.67 – 2.62 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 206.6, 141.2 (d, J = 8.6 Hz), 136.7 (d, J = 16.6 Hz), 134.3 (d, J = 23.5 Hz), 133.6 (d, J = 16.6 Hz), 129.9, 129.3 (d, J = 8.1 Hz), 129.0 (t, J = 7.0 Hz), 128.5, 128.3 (d, J = 6.9 Hz), 126.6, 47.3 (d, J = 21.2 Hz), 136.7 (d, J = 16.6 Hz), 39.8 (d, J = 11.6 Hz), 30.8. ^{31}P NMR (121MHz, CD_2Cl_2) δ = -0.97 (s). HRMS (ESI) calcd for $[C_{22}H_{21}OP]^+$: 332.13 $[M]^+$; found: 332.13.

4. Phenethyldiphenylphosphane[6]



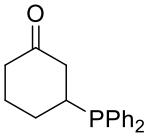
^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.39 – 7.31 (m, 4H), 7.29 – 7.21 (m, 6H), 7.20 – 7.14 (m, 2H), 7.10 – 7.04 (m, 3H), 2.66 – 2.58 (m, 2H), 2.30 – 2.24 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 143.17 (d, J = 12.8 Hz), 139.2 (d, J = 13.8 Hz), 134.3 (d, J = 16.8 Hz), 133.1 (d, J = 18.7 Hz), 128.9 (d, J = 10.0 Hz), 128.8 (d, J = 5.3 Hz), 128.6, 126.4, 32.54 (d, J = 18.1 Hz), 30.45 (d, J = 13.0 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ = -16.2 (s). HRMS (ESI) calcd for $[C_{20}H_{19}P]^+$: 290.12 $[M]^+$; found: 290.13.

5. 2-(2-(diphenylphosphaneyl)ethyl)pyridine[6]



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 8.51 – 8.49 (m, 1H), 7.59 – 7.56 (m, 4H), 7.49 – 7.46 (m, 6H), 7.38 – 7.32 (m, 6H), 7.13 – 7.09 (m, 2H), 2.90 – 2.85 (m, 2H), 2.52 – 2.49 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 149.6, 139.2, 136.5, 133.1 (d, J = 18.5 Hz), 122.9, 121.5, 34.8 (d, J = 18.3 Hz), 28.2 (d, J = 13.9 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ = -15.89 (s). HRMS (ESI) calcd for $[C_{19}H_{18}NP]^+$: 291.12 $[M]^+$; found: 291.13.

6. 3-(diphenylphosphaneyl)cyclohexan-1-one[6]



^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.52 – 7.45 (m, 4H), 7.40 – 7.31 (m, 6H), 2.72 – 2.62z (m, 1H), 2.37 – 2.29 (m, 1H), 2.27 – 2.21 (m, 1H), 2.18 2.10 (m, 1H), 1.90 – 1.84 (m, 1H), 1.80 – 1.68 (m, 1H), 1.62 – 1.51 (m, 1H), 1.5 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 210.0 (d, J = 12.0 Hz), 136.7 (d, J = 14.6 Hz), 136.1 (d, J = 14.3 Hz), 133.9 (m), 129.5 (d, J = 15.5 Hz), 128.9 (d, J = 7.1 Hz), 44.5 (d, J = 14.8 Hz), 36.3 (d, J = 12.6 Hz), 31.5, 28.5 (d, J = 16.3 Hz), 27.1 (d, J = 12.5 Hz). ^{31}P NMR (121 MHz, CD_2Cl_2) δ = -4.1 (s). HRMS (ESI) calcd for $[C_{18}H_{19}OP]^+$: 282.12 $[M]^+$; found: 282.13

4.0 UV and IR spectra of the complexes C1, and C2

UV-Spectrum of complexes shows a weak band at 420 nm, which corresponds to the Metal-Ligand transfer process (though weak in **C1** and **C2**). This study reveals that amino-azine ligands are weak field ligands; thus, the gap between t2g and e.g., energy levels stays less than the pairing energy. Thus, electrons do not prefer pairing. This makes the complexes **C1** and **C2** d^5 high-spin complexes. Hence, the expected magnetic moment for **C1** and **C2** is μeff ≈ 5.29 (Bm). It is also known that Mn (II) complexes with Schiff bases prefer to be d^5 high-spin complexes.

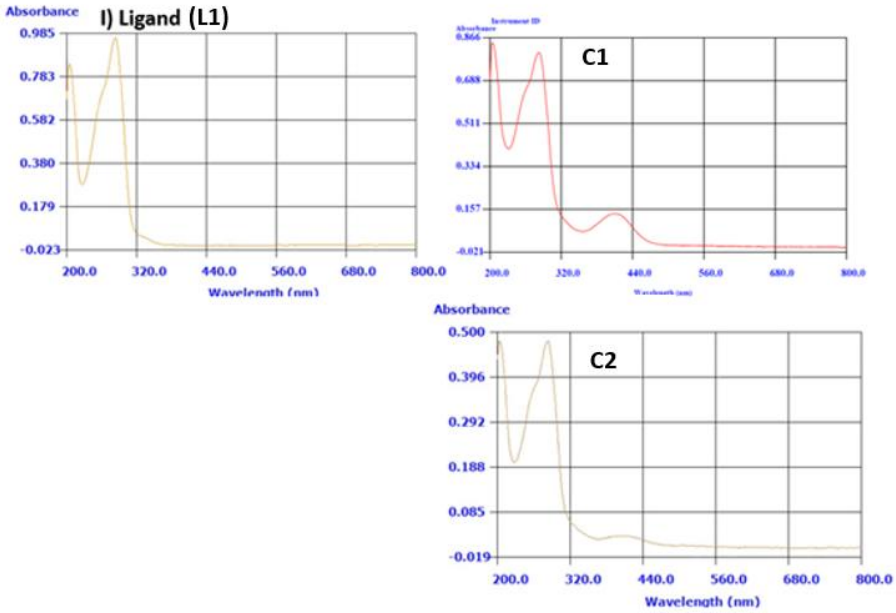


Figure S1: UV spectra of azine ligand (**L1**) and its complexes **C1** and **C2**.

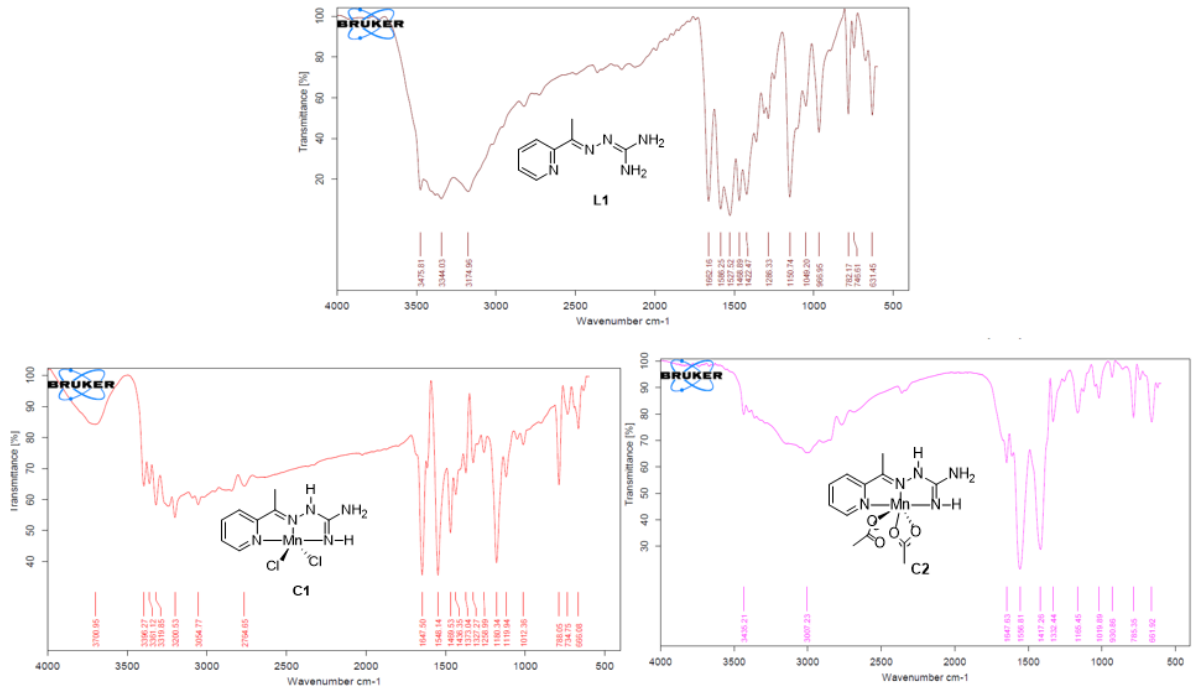


Figure S2: IR-spectra of ligand **L1** and its complex **C1**.

5.0 Crystal Structures details of Complex C1, C2, and C3

X-ray diffraction experiments were performed on a Rigaku XtaLAB Synergy-S diffractometer, equipped with a HyPix-6000HE hybrid photon counting detector, using a microfocus tube (Cu, λ = 1.54184 Å). Suitable crystals were covered with polybutene oil, selected using a microscope using polarized light, transferred on a MiTeGen MicroMount and mounted under a cold nitrogen stream. Data-sets were collected at 100 K. The data collection and reduction were performed using the Rigaku CrysAlisPro Software.[7] Structure solution and refinement were performed with SHELXT[8] and SHELXL,[9] respectively, embedded in Olex2.[10] All atoms heavier than hydrogen were refined with anisotropic displacement parameters, while hydrogen atoms attached to carbon atoms were placed at calculated positions and were refined according to the riding model. All hydrogen atoms attached to the nitrogen atoms were found in the Difference Fourier Map and refined freely.

5.1 Crystal Structures details of Complex C1

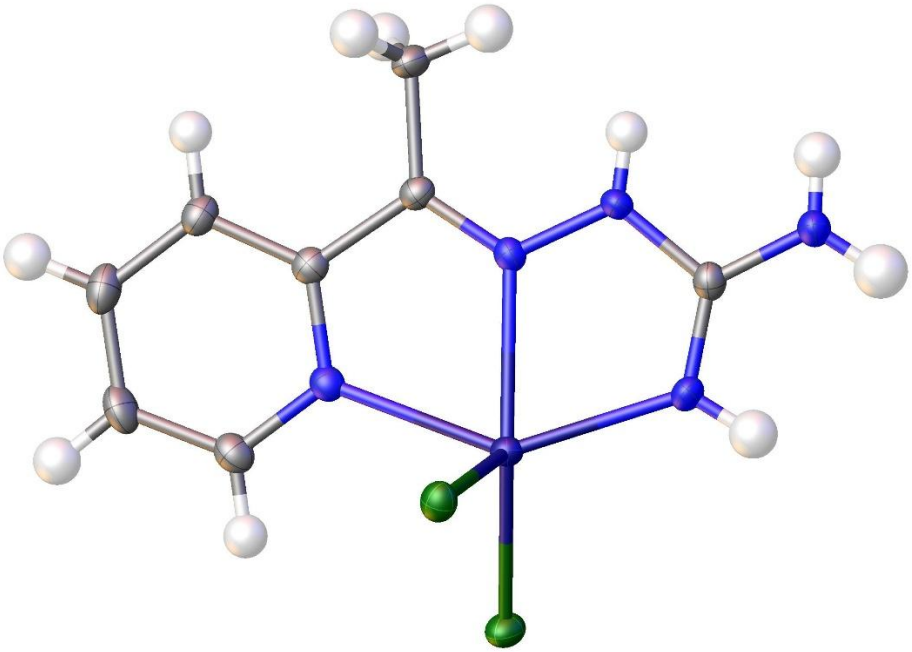


*Figure S3: Molecular structure of complex **1** with displacement ellipsoids drawn at 50 % probability level. (C in grey, H in white, N in blue, Mn in dark blue, Cl in green). All hydrogen atoms attached to the nitrogen atoms were found in the Difference Fourier Map and refined freely.*

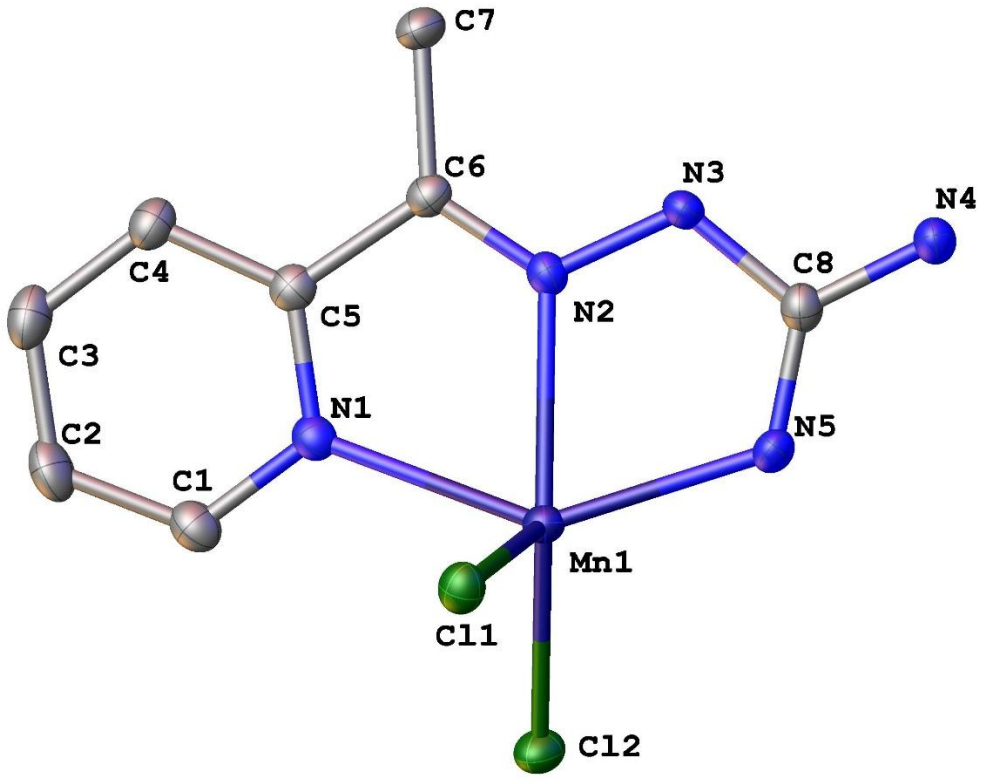


*Figure S4: Molecular structure of complex **1** with displacement ellipsoids drawn at 50 % probability level. H atoms are omitted for clarity (C in grey, N in blue, Mn in dark blue, Cl in green).*

Table 1. Crystal data and structure refinement for **C1** (CCDC 2348863).

Identification code	AA-3-2_auto
Empirical formula	$C_8H_{11}Cl_2MnN_5$
Formula weight	303.06
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.62890(10)
b/Å	15.5631(2)
c/Å	11.48390(10)
α/°	90
β/°	92.2570(10)
γ/°	90
Volume/Å^3	1183.83(3)
Z	4
ρ_{calc}g/cm^3	1.700
μ/mm^{-1}	13.067
F(000)	612.0
Crystal size/mm^3	0.226 × 0.115 × 0.084
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.576 to 153.59
Index ranges	$-8 \le h \le 8$, $-18 \le k \le 19$, $-14 \le l \le 13$
Reflections collected	14177
Independent reflections	2382 [R_{int} = 0.0336, R_{sigma} = 0.0212]
Data/restraints/parameters	2382/0/162
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0224, wR_2 = 0.0586
Final R indexes [all data]	R_1 = 0.0239, wR_2 = 0.0593
Largest diff. peak/hole / e Å^{-3}	0.36/-0.29

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for AA-3-2_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	2935.7(4)	6397.1(2)	6756.1(2)	15.81(9)
Cl1	4124.6(6)	6450.0(2)	8770.1(3)	20.93(10)
Cl2	542.5(6)	5268.6(2)	6646.6(4)	22.09(11)
N1	711(2)	7501.0(9)	6950.8(12)	17.8(3)
N2	4028(2)	7574.2(9)	5846.5(11)	16.9(3)
N3	5743(2)	7460.5(9)	5253.3(12)	19.0(3)
N4	8064(2)	6535.1(11)	4554.4(14)	23.8(3)
N5	5444(2)	6030.6(9)	5720.6(13)	20.5(3)
C1	-981(3)	7441.7(12)	7547.7(15)	22.3(3)
C2	-2134(3)	8152.6(13)	7816.8(16)	26.1(4)
C3	-1532(3)	8954.6(12)	7455.4(16)	25.9(4)
C4	204(3)	9026.1(11)	6822.6(15)	21.1(3)
C5	1292(2)	8286.6(11)	6589.3(14)	18.0(3)
C6	3165(2)	8309.9(10)	5922.3(14)	17.0(3)
C7	3876(3)	9131.6(10)	5409.0(16)	21.6(3)
C8	6428(2)	6627.0(11)	5186.6(14)	18.8(3)

Table 3. Bond Lengths for AA-3-2_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	Cl1	2.4153(4)	N3	C8	1.378(2)
Mn1	Cl2	2.3668(4)	N4	C8	1.337(2)
Mn1	N1	2.2810(14)	N5	C8	1.302(2)
Mn1	N2	2.2430(14)	C1	C2	1.387(3)
Mn1	N5	2.1587(15)	C2	C3	1.379(3)
N1	C1	1.340(2)	C3	C4	1.389(3)
N1	C5	1.352(2)	C4	C5	1.390(2)
N2	N3	1.3595(19)	C5	C6	1.485(2)
N2	C6	1.285(2)	C6	C7	1.492(2)

Table 4. Bond Angles for AA-3-2_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	Mn1	Cl1	105.598(16)	N2	N3	C8	115.74(14)
N1	Mn1	Cl1	93.91(4)	C8	N5	Mn1	118.83(12)
N1	Mn1	Cl2	97.44(4)	N1	C1	C2	122.59(17)
N2	Mn1	Cl1	108.60(4)	C3	C2	C1	119.12(17)
N2	Mn1	Cl2	144.04(4)	C2	C3	C4	119.02(17)
N2	Mn1	N1	69.66(5)	C3	C4	C5	118.77(17)
N5	Mn1	Cl1	107.89(4)	N1	C5	C4	122.22(16)
N5	Mn1	Cl2	107.69(4)	N1	C5	C6	115.76(14)
N5	Mn1	N1	140.18(5)	C4	C5	C6	122.01(15)
N5	Mn1	N2	71.91(5)	N2	C6	C5	113.40(14)
C1	N1	Mn1	123.74(12)	N2	C6	C7	126.04(15)
C1	N1	C5	118.27(15)	C5	C6	C7	120.56(14)
C5	N1	Mn1	117.25(11)	N4	C8	N3	114.04(15)
N3	N2	Mn1	114.76(10)	N5	C8	N3	118.23(15)
C6	N2	Mn1	122.92(11)	N5	C8	N4	127.73(16)
C6	N2	N3	122.24(14)				

5.2 Crystal Structures details of Complex C2

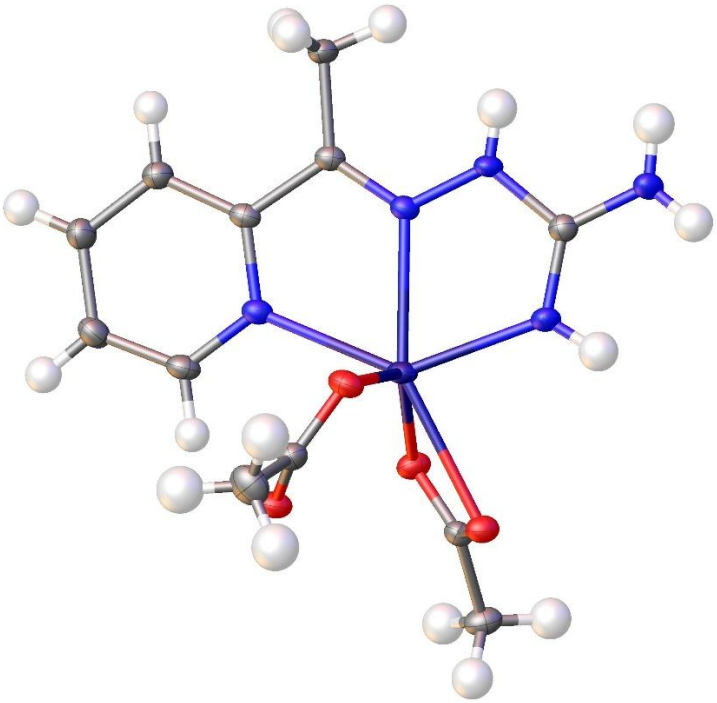


*Figure S5: Molecular structure of complex **2** with displacement ellipsoids drawn at 50 % probability level. (C in grey, H in white, N in blue, Mn in dark blue, Cl in green). All hydrogen atoms attached to the nitrogen atoms were found in the Difference Fourier Map and refined freely.*

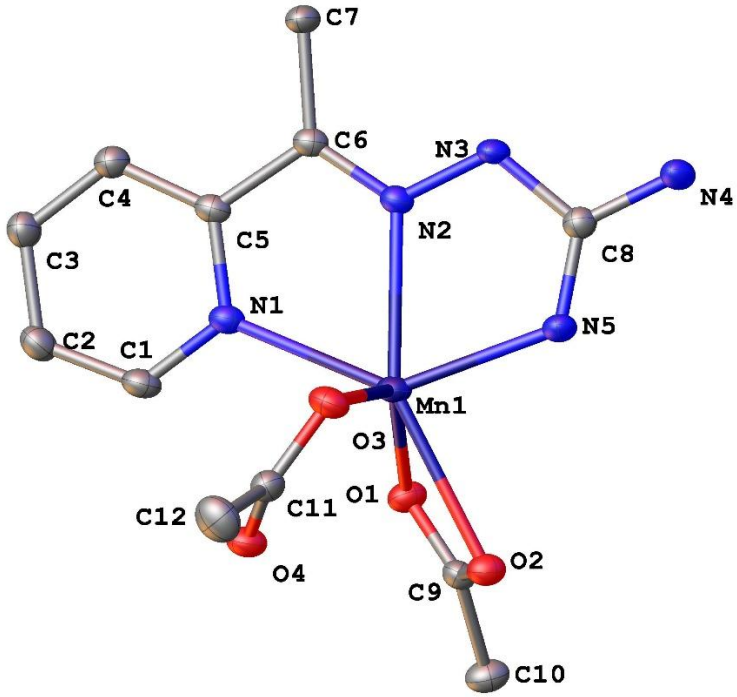


*Figure S6: Molecular structure of complex **2** with displacement ellipsoids drawn at 50 % probability level. H atoms are omitted for clarity (C in grey, N in blue, Mn in dark blue, Cl in green).*

Table 5. Crystal data and structure refinement for **C2** (CCDC 2348644).

Identification code	aa310_auto
Empirical formula	$C_{12}H_{17}MnN_5O_4$
Formula weight	350.24
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	8.3343(3)
b/Å	8.4136(3)
c/Å	12.5945(4)
α/°	73.241(3)
β/°	83.832(3)
γ/°	60.862(3)
Volume/Å^3	738.05(5)
Z	2
ρ_{calc}g/cm^3	1.576
μ/mm^{-1}	7.526
F(000)	362.0
Crystal size/mm^3	0.16 × 0.12 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.336 to 160.038
Index ranges	$-10 \leq h \leq 8$, $-10 \leq k \leq 10$, $-16 \leq l \leq 16$
Reflections collected	21434
Independent reflections	3124 [R_{int} = 0.0406, R_{sigma} = 0.0244]
Data/restraints/parameters	3124/0/218
Goodness-of-fit on F^2	1.126
Final R indexes [I>=2σ (I)]	R_1 = 0.0284, wR_2 = 0.0797
Final R indexes [all data]	R_1 = 0.0299, wR_2 = 0.0805
Largest diff. peak/hole / e Å^{-3}	0.36/-0.44

Table 6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for aa310_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	6881.0(3)	3712.5(4)	7688.4(2)	17.44(10)
O1	6725.0(17)	6492.1(17)	7081.7(10)	21.0(3)
O2	7643.3(17)	5183.6(17)	8847.3(10)	20.6(2)
O3	8936.2(17)	926.4(17)	8425.1(11)	22.9(3)
O4	10625.4(17)	2313.2(18)	7706.7(10)	22.8(3)
N1	7569.7(19)	3257.7(19)	5906.8(12)	18.1(3)
N2	4818.2(19)	3105.7(19)	7007.4(11)	16.9(3)
N3	3461(2)	3093(2)	7700.3(12)	18.5(3)
N4	1838(2)	3984(2)	9201.9(13)	23.5(3)
N5	4598(2)	4136(2)	8782.6(12)	20.7(3)
C1	8970(2)	3399(2)	5344.0(15)	21.1(3)
C2	9514(2)	2952(3)	4342.3(15)	23.3(4)
C3	8542(2)	2321(3)	3900.4(15)	22.7(4)
C4	7071(2)	2187(2)	4464.8(14)	20.5(3)
C5	6615(2)	2661(2)	5467.3(13)	17.0(3)
C6	5063(2)	2561(2)	6120.8(13)	16.8(3)
C7	3989(2)	1792(3)	5759.8(14)	20.7(3)
C8	3324(2)	3766(2)	8601.0(14)	18.1(3)
C9	7262(2)	6526(2)	7977.9(14)	17.9(3)
C10	7444(3)	8217(2)	7995.9(15)	24.1(4)
C11	10472(2)	894(2)	8279.4(14)	20.3(3)
C12	12169(3)	-909(3)	8811.0(18)	31.6(4)

Table 7. Bond Lengths for aa310_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.1828(12)	N2	C6	1.286(2)
Mn1	O2	2.4642(12)	N3	C8	1.378(2)
Mn1	O3	2.1135(13)	N4	C8	1.341(2)
Mn1	N1	2.3485(14)	N5	C8	1.301(2)
Mn1	N2	2.3187(14)	C1	C2	1.387(3)
Mn1	N5	2.1690(15)	C2	C3	1.391(3)
O1	C9	1.271(2)	C3	C4	1.387(3)
O2	C9	1.260(2)	C4	C5	1.392(2)
O3	C11	1.261(2)	C5	C6	1.481(2)
O4	C11	1.263(2)	C6	C7	1.498(2)
N1	C1	1.337(2)	C9	C10	1.509(2)
N1	C5	1.355(2)	C11	C12	1.510(2)
N2	N3	1.355(2)			

Table 8 .Bond Angles for aa310_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Mn1	O2	56.35(4)	C6	N2	N3	121.33(14)
O1	Mn1	N1	90.24(5)	N2	N3	C8	115.10(14)
O1	Mn1	N2	120.30(5)	C8	N5	Mn1	120.70(12)
O3	Mn1	O1	136.14(5)	N1	C1	C2	123.83(16)
O3	Mn1	O2	95.24(5)	C1	C2	C3	117.89(16)
O3	Mn1	N1	91.35(5)	C4	C3	C2	119.14(16)
O3	Mn1	N2	100.50(5)	C3	C4	C5	119.41(16)
O3	Mn1	N5	104.12(5)	N1	C5	C4	121.65(15)
N1	Mn1	O2	136.26(5)	N1	C5	C6	115.56(14)
N2	Mn1	O2	151.46(5)	C4	C5	C6	122.79(15)
N2	Mn1	N1	67.34(5)	N2	C6	C5	113.90(14)
N5	Mn1	O1	104.35(5)	N2	C6	C7	125.64(15)
N5	Mn1	O2	83.07(5)	C5	C6	C7	120.40(14)
N5	Mn1	N1	136.67(5)	N4	C8	N3	114.81(15)
N5	Mn1	N2	70.11(5)	N5	C8	N3	118.51(15)
C9	O1	Mn1	97.39(10)	N5	C8	N4	126.68(16)
C9	O2	Mn1	84.77(9)	O1	C9	C10	118.99(15)
C11	O3	Mn1	107.74(11)	O2	C9	O1	121.47(15)
C1	N1	Mn1	122.93(11)	O2	C9	C10	119.54(15)
C1	N1	C5	118.08(14)	O3	C11	O4	122.13(16)
C5	N1	Mn1	118.72(11)	O3	C11	C12	118.32(16)
N3	N2	Mn1	114.62(10)	O4	C11	C12	119.55(16)
C6	N2	Mn1	123.36(11)				

5.3 Crystal Structures details of Complex C3

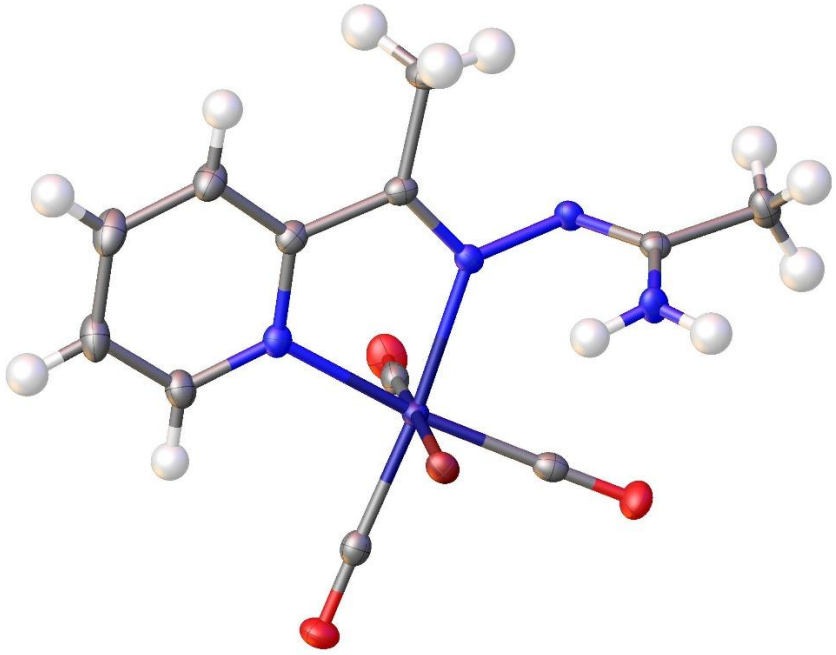


*Figure S7: Molecular structure of complex **3** with displacement ellipsoids drawn at 50 % probability level. (C in grey, H in white, N in blue, Mn in dark blue, Cl in green). All hydrogen atoms attached to the nitrogen atoms were found in the Difference Fourier Map and refined freely.*

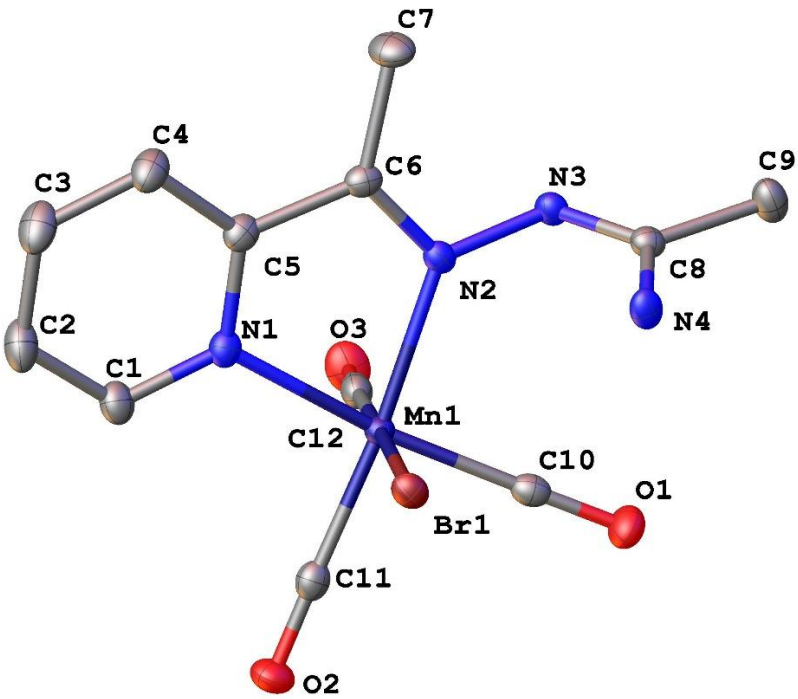


*Figure S8: Molecular structure of complex **3** with displacement ellipsoids drawn at 50 % probability level. H atoms are omitted for clarity (C in grey, N in blue, Mn in dark blue, Cl in green).*

Table 9. Crystal data and structure refinement for **C3** (CCDC 2348861).

Identification code	AA2-130_auto
Empirical formula	$C_{12}H_{12}BrMnN_4O_3$
Formula weight	395.11
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.51700(10)
b/Å	9.98160(10)
c/Å	14.63770(10)
α/°	90
β/°	90.8590(10)
γ/°	90
Volume/Å^3	1536.44(2)
Z	4
ρ_{calc}g/cm^3	1.708
μ/mm^{-1}	10.177
F(000)	784.0
Crystal size/mm^3	0.18 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.284 to 160.232
Index ranges	$-12 \leq h \leq 13$, $-12 \leq k \leq 12$, $-18 \leq l \leq 17$
Reflections collected	16918
Independent reflections	3368 [R_{int} = 0.0322, R_{sigma} = 0.0251]
Data/restraints/parameters	3368/0/200
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0230, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0237, wR_2 = 0.0598
Largest diff. peak/hole / e Å^{-3}	0.39/-0.52

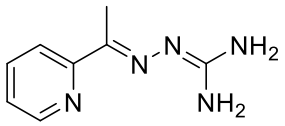
Table 10. Bond Lengths for AA2-130_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Mn1	2.5354(3)	N2	N3	1.413(2)
Mn1	N1	2.0458(15)	N2	C6	1.291(2)
Mn1	N2	2.0411(14)	N3	C8	1.301(2)
Mn1	C10	1.8167(19)	N4	C8	1.337(2)
Mn1	C11	1.8201(18)	C1	C2	1.390(3)
Mn1	C12	1.806(2)	C2	C3	1.386(3)
O1	C10	1.146(2)	C3	C4	1.388(3)
O2	C11	1.146(2)	C4	C5	1.385(3)
O3	C12	1.142(2)	C5	C6	1.473(2)
N1	C1	1.337(2)	C6	C7	1.498(2)
N1	C5	1.358(2)	C8	C9	1.498(3)

Table 11. Bond Angles for AA2-130_auto.

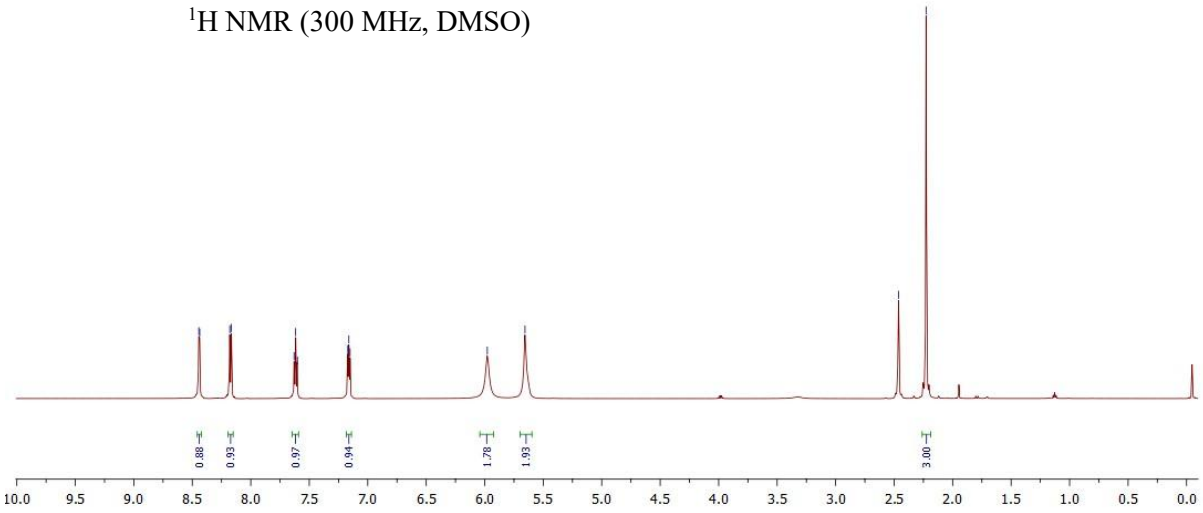
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mn1	Br1	82.95(4)	C6	N2	Mn1	118.16(12)
N2	Mn1	Br1	90.67(4)	C6	N2	N3	117.08(14)
N2	Mn1	N1	77.81(6)	C8	N3	N2	114.91(14)
C10	Mn1	Br1	89.95(6)	N1	C1	C2	122.70(18)
C10	Mn1	N1	169.71(7)	C3	C2	C1	118.99(18)
C10	Mn1	N2	94.91(7)	C2	C3	C4	118.74(18)
C10	Mn1	C11	90.34(8)	C5	C4	C3	119.20(18)
C11	Mn1	Br1	88.44(6)	N1	C5	C4	122.13(17)
C11	Mn1	N1	96.87(7)	N1	C5	C6	114.40(15)
C11	Mn1	N2	174.67(7)	C4	C5	C6	123.46(16)
C12	Mn1	Br1	178.69(6)	N2	C6	C5	114.18(15)
C12	Mn1	N1	97.15(7)	N2	C6	C7	124.59(17)
C12	Mn1	N2	90.63(7)	C5	C6	C7	121.23(16)
C12	Mn1	C10	90.12(8)	N3	C8	N4	125.27(17)
C12	Mn1	C11	90.25(8)	N3	C8	C9	117.23(16)
C1	N1	Mn1	126.24(13)	N4	C8	C9	117.49(16)
C1	N1	C5	118.23(16)	O1	C10	Mn1	179.49(16)
C5	N1	Mn1	114.96(12)	O2	C11	Mn1	178.65(17)
N3	N2	Mn1	123.84(11)	O3	C12	Mn1	176.78(17)

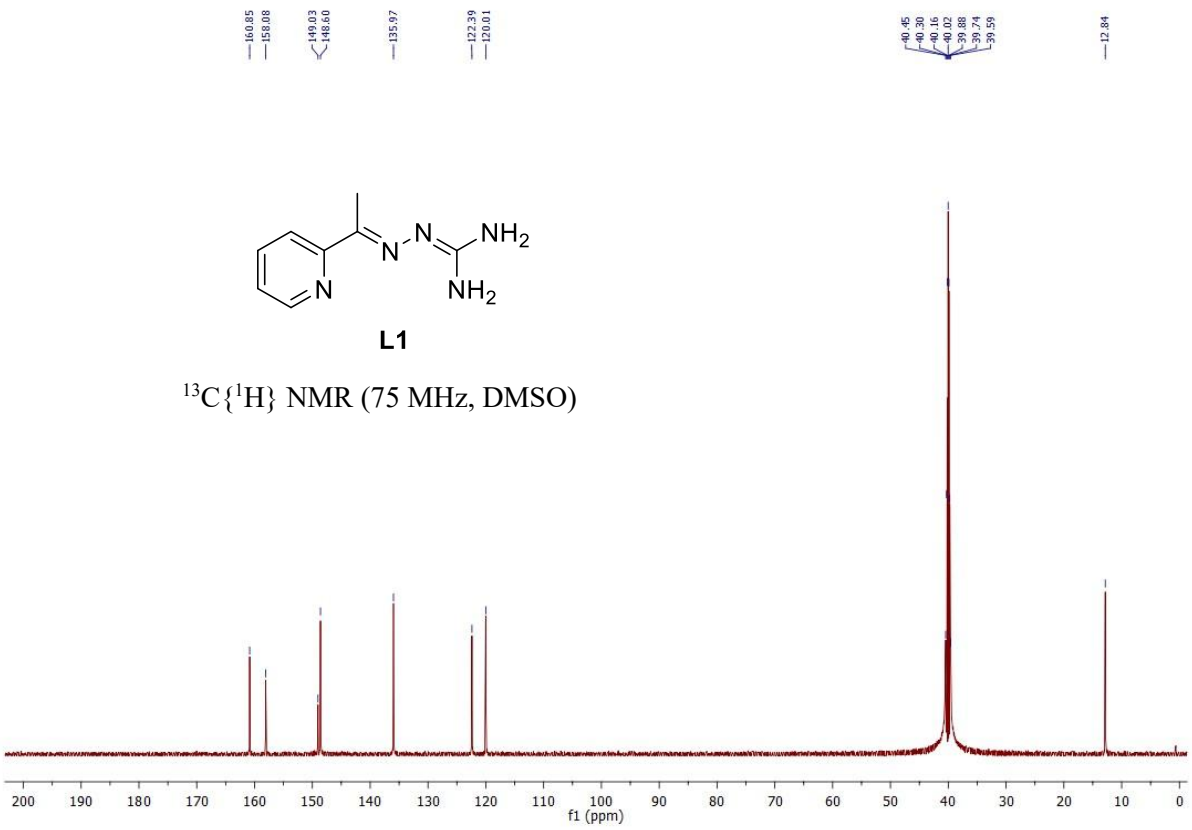
6.0 ^{1}H and ^{13}C NMR spectra of synthesized compounds:



L1

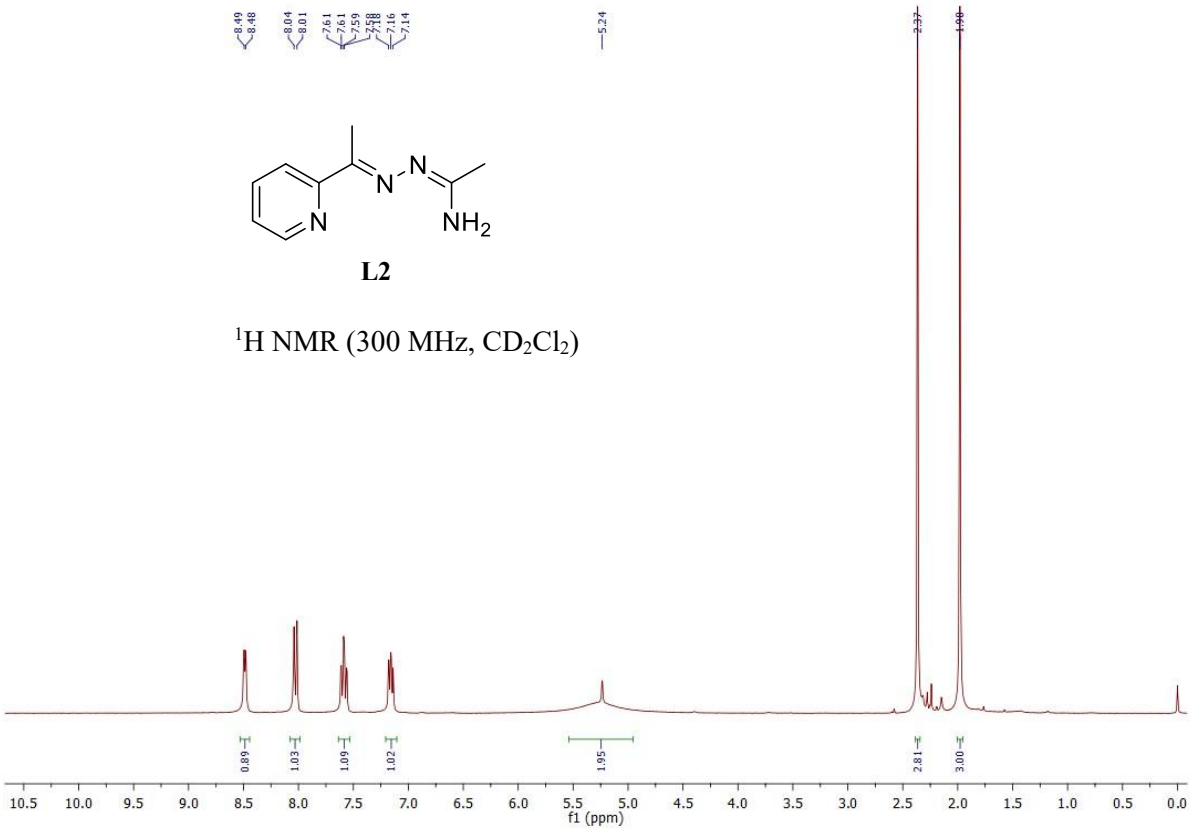
^{1}H NMR (300 MHz, DMSO)





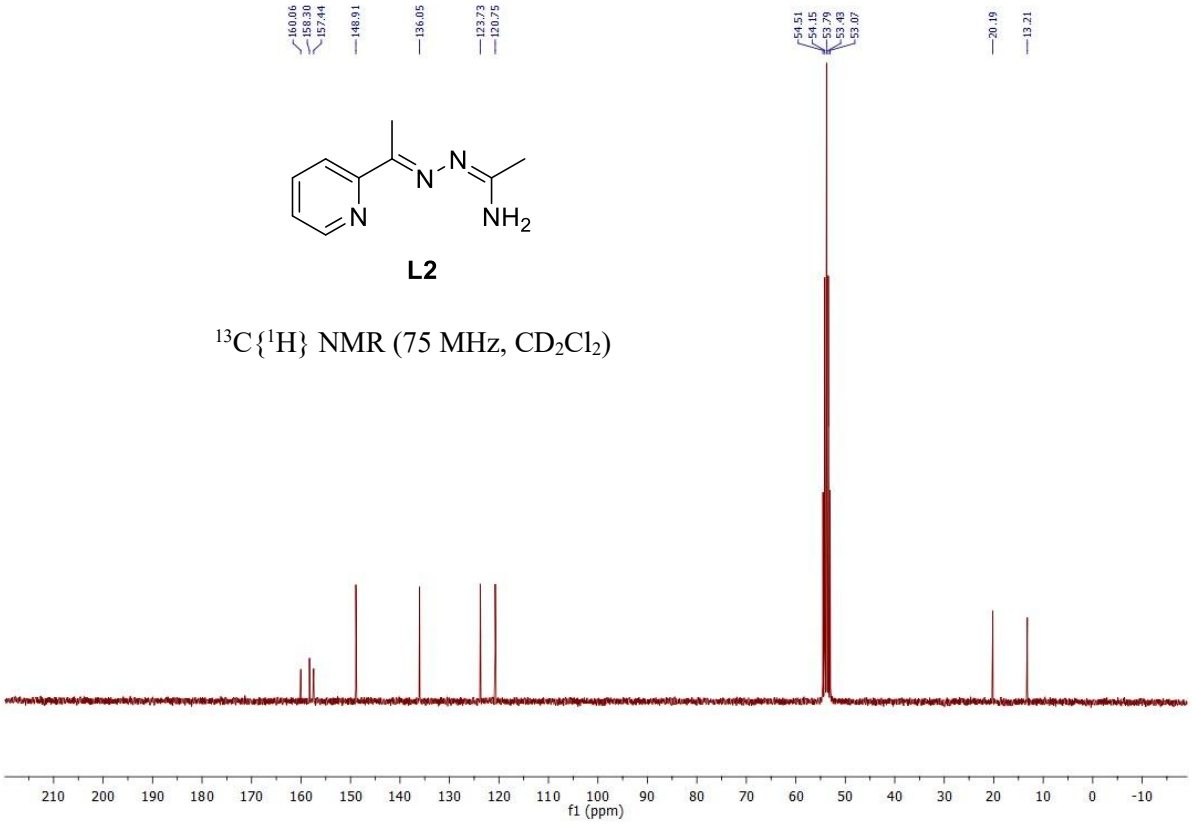
L1

$^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO)



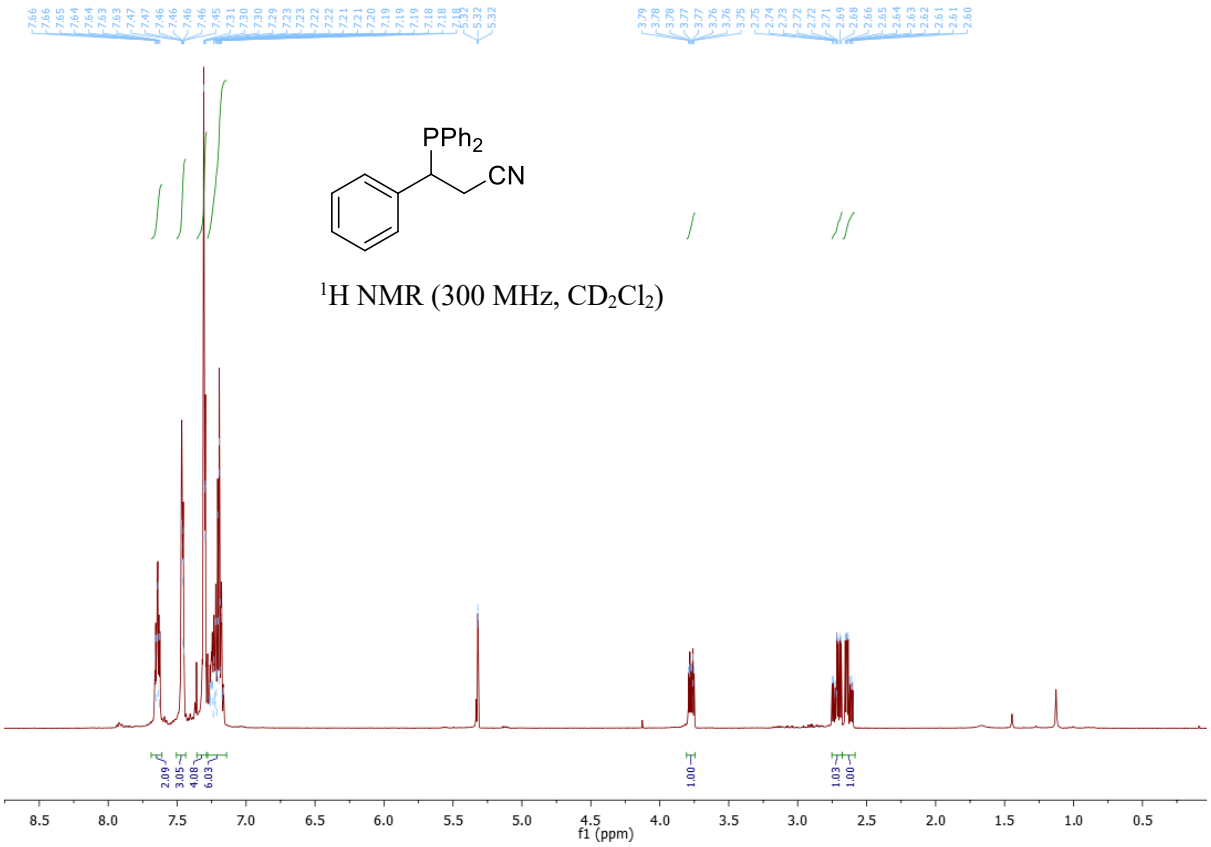
L2

^{1}H NMR (300 MHz, CD_2Cl_2)

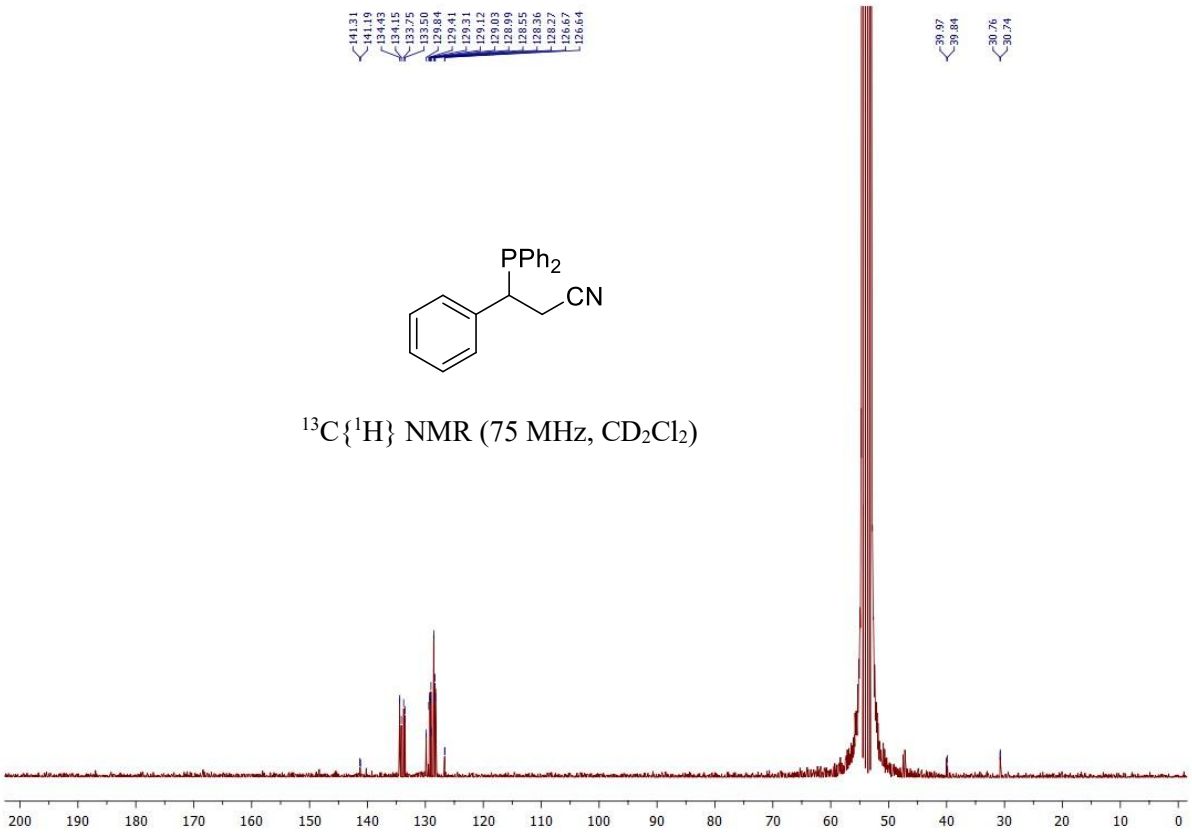


L2

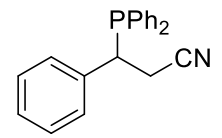
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)



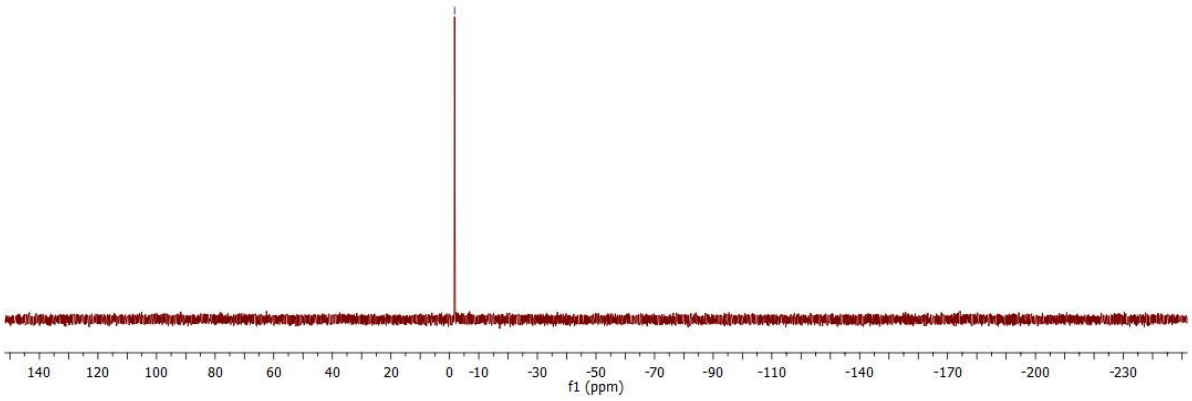
^{1}H NMR (300 MHz, CD_2Cl_2)

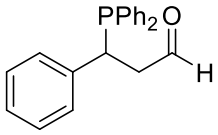


$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

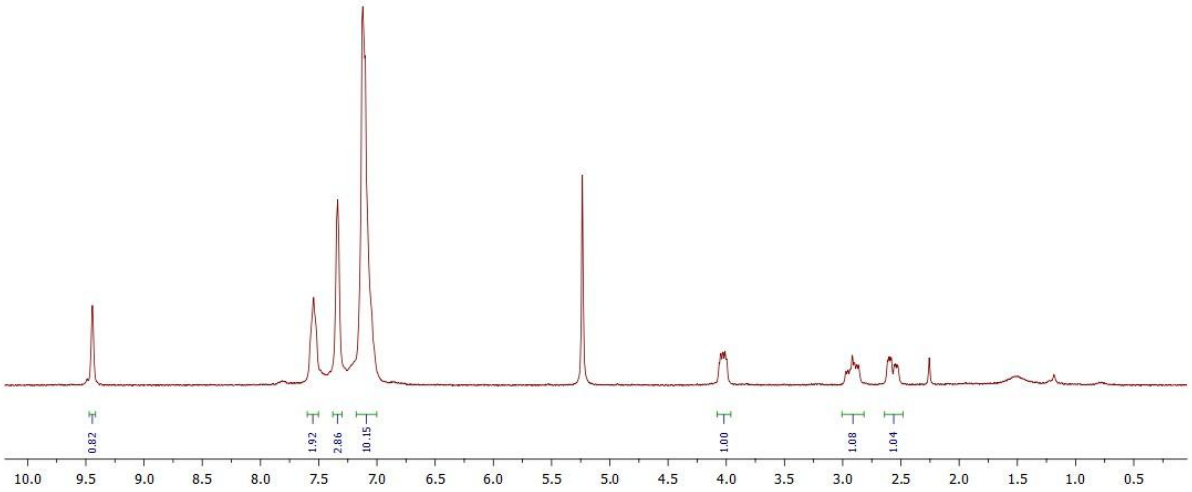


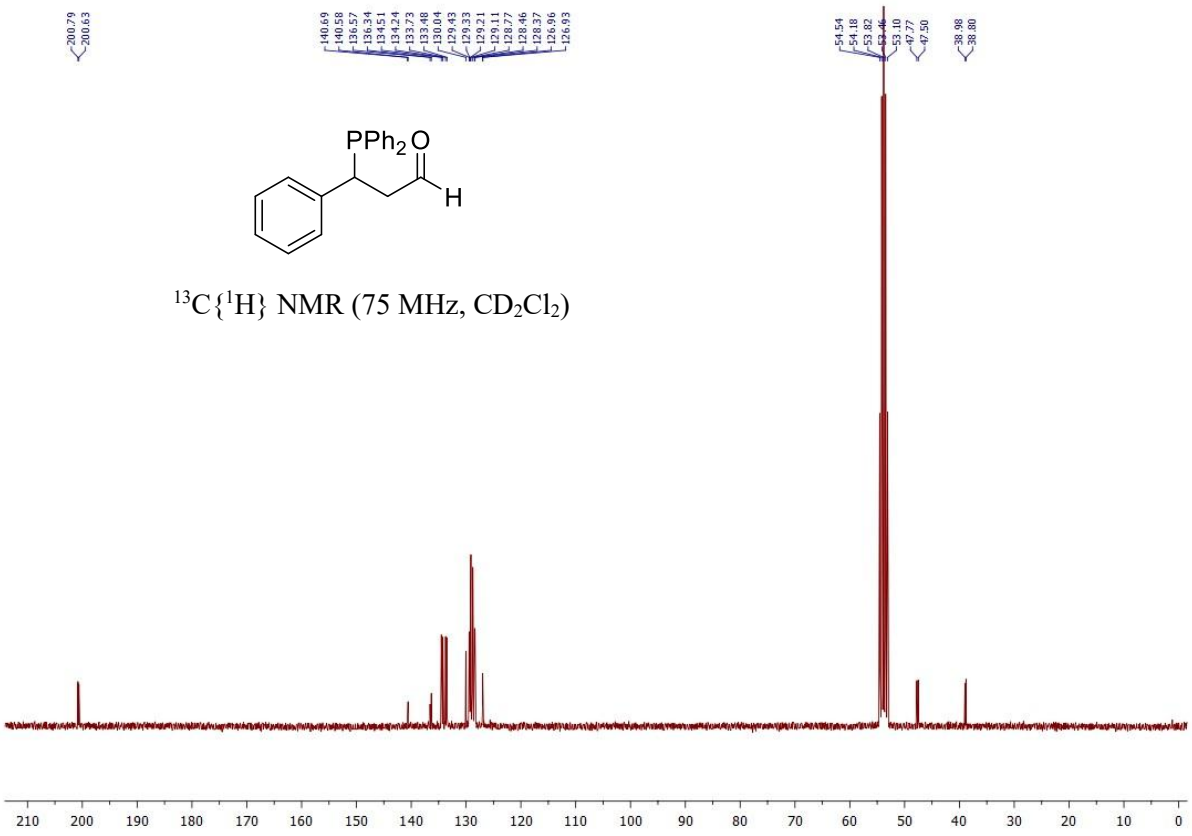
$^{31}P\{^{1}H\}$ NMR (121MHz, CD_2Cl_2)



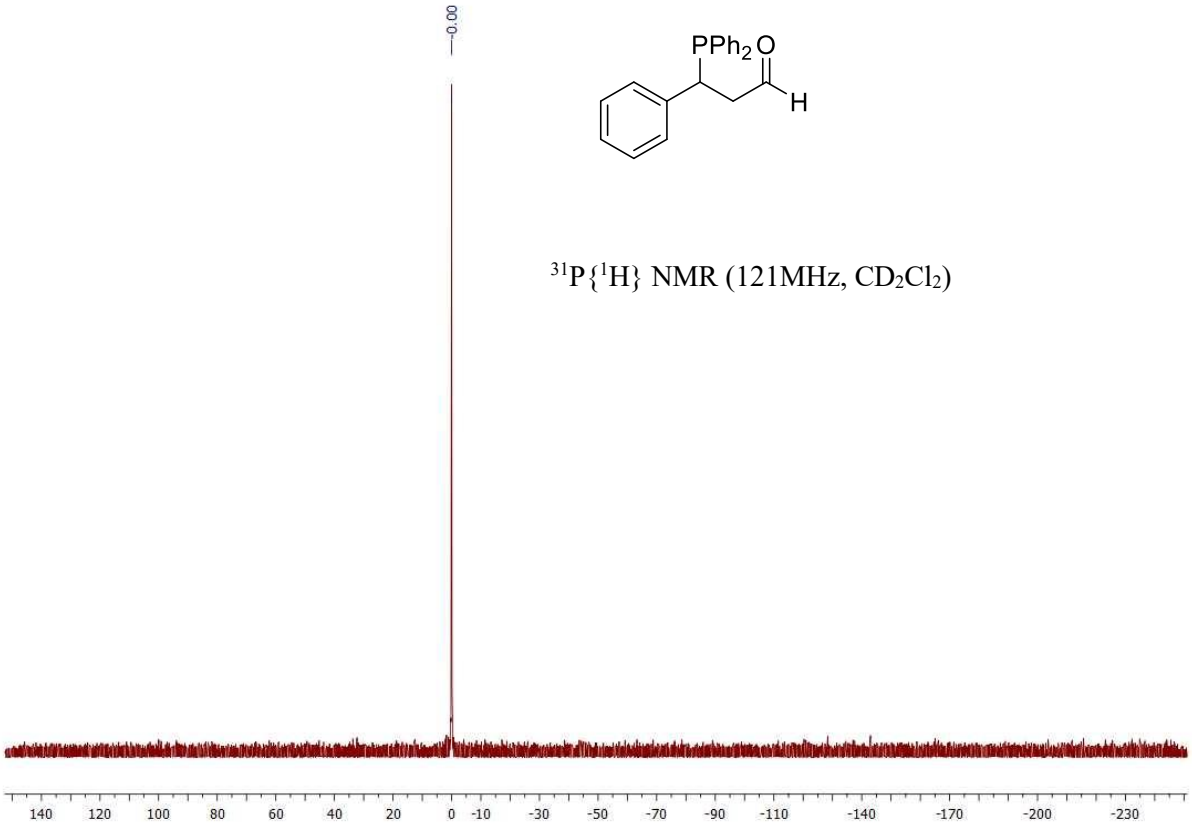


^{1}H NMR (300 MHz, CD_2Cl_2)

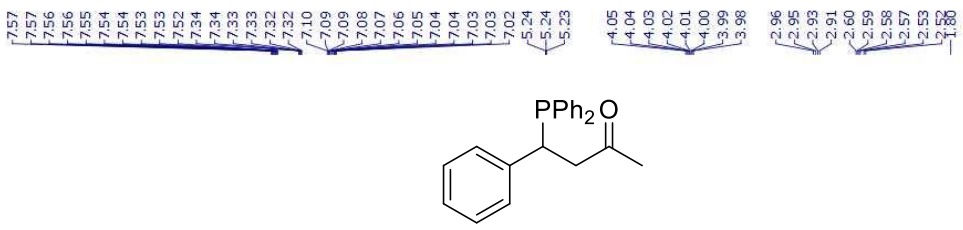




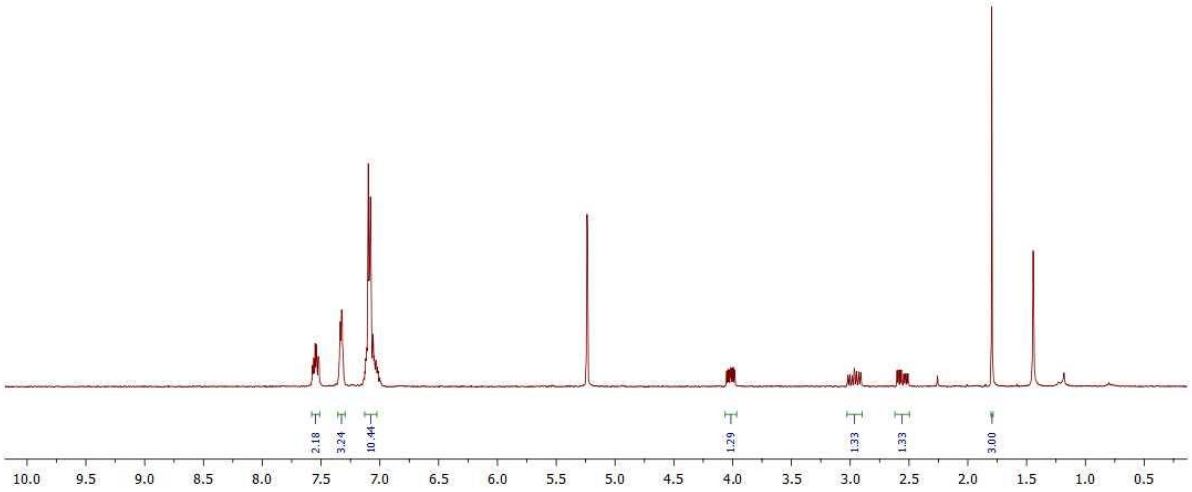
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

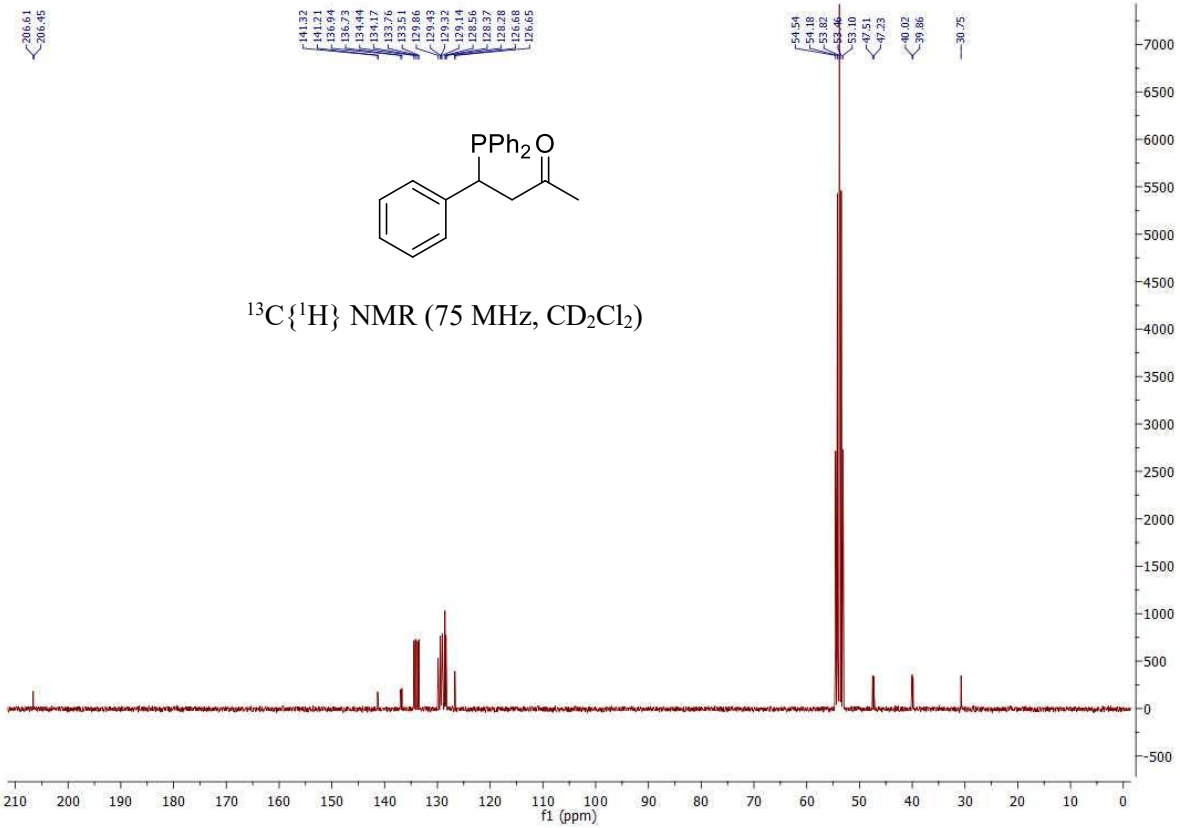


$^{31}P\{^{1}H\}$ NMR (121MHz, CD_2Cl_2)

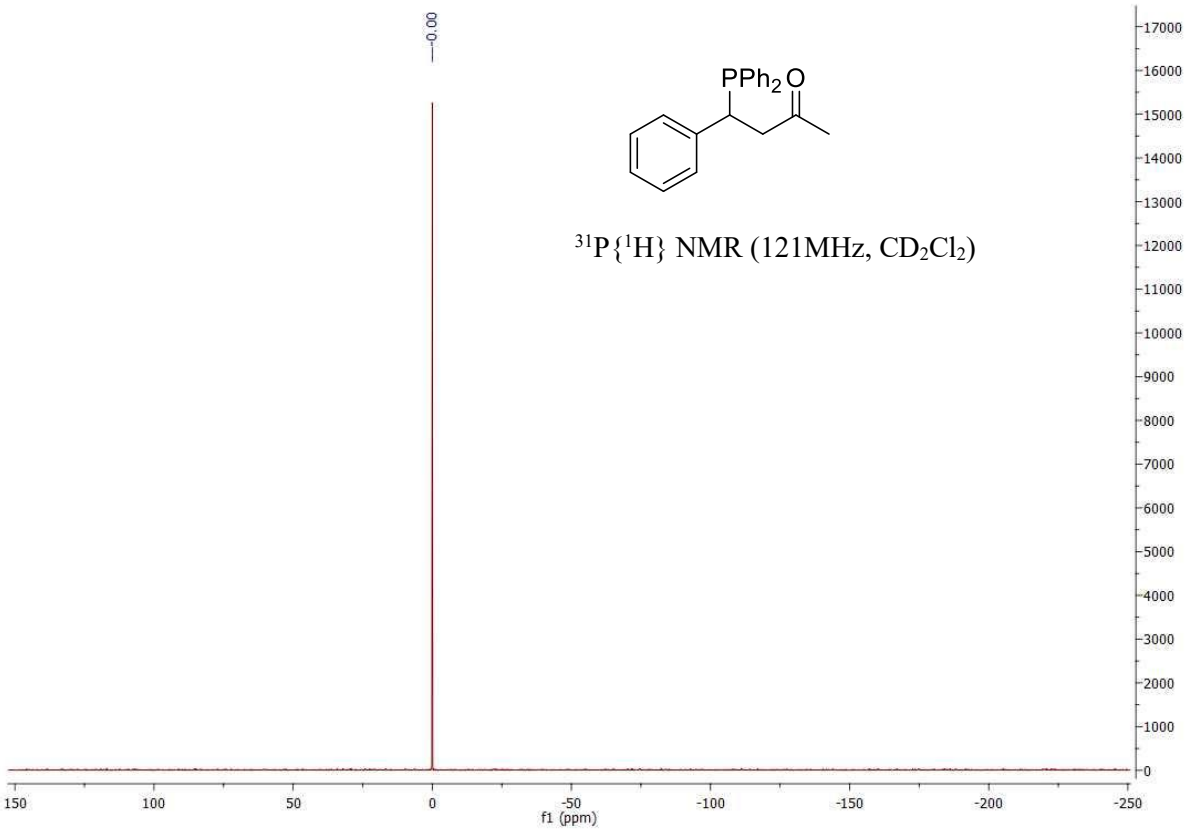


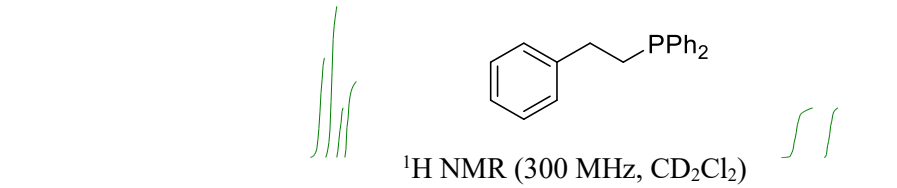
^{1}H NMR (300 MHz, CD_2Cl_2)



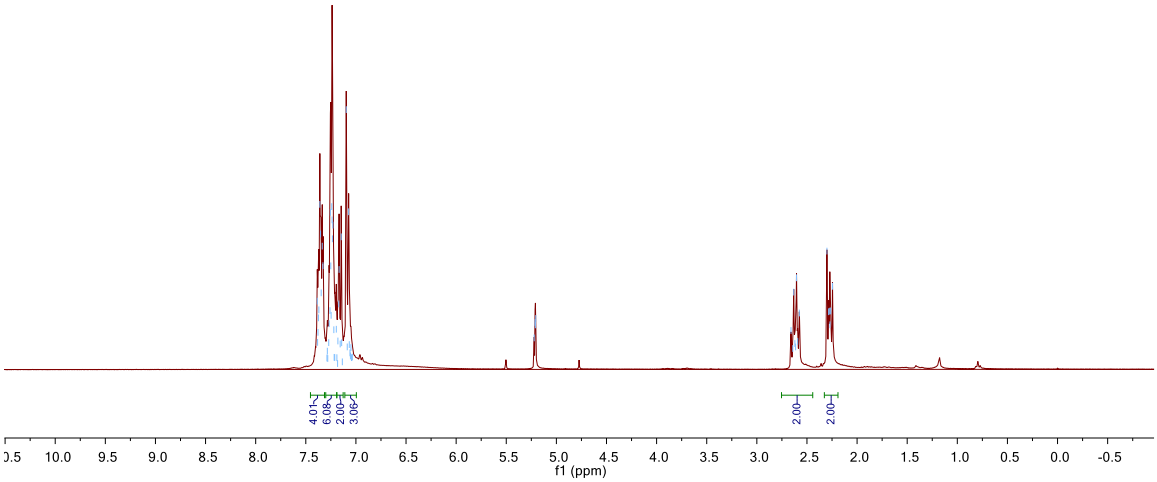


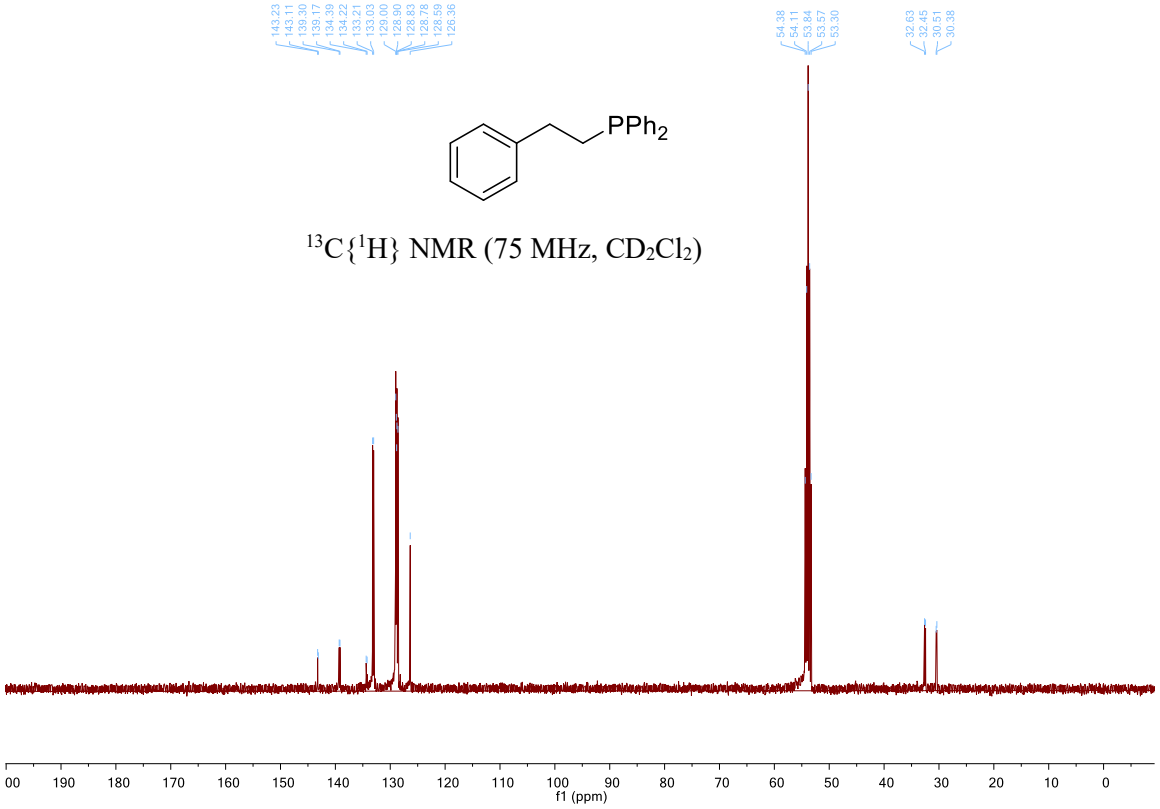
^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2)



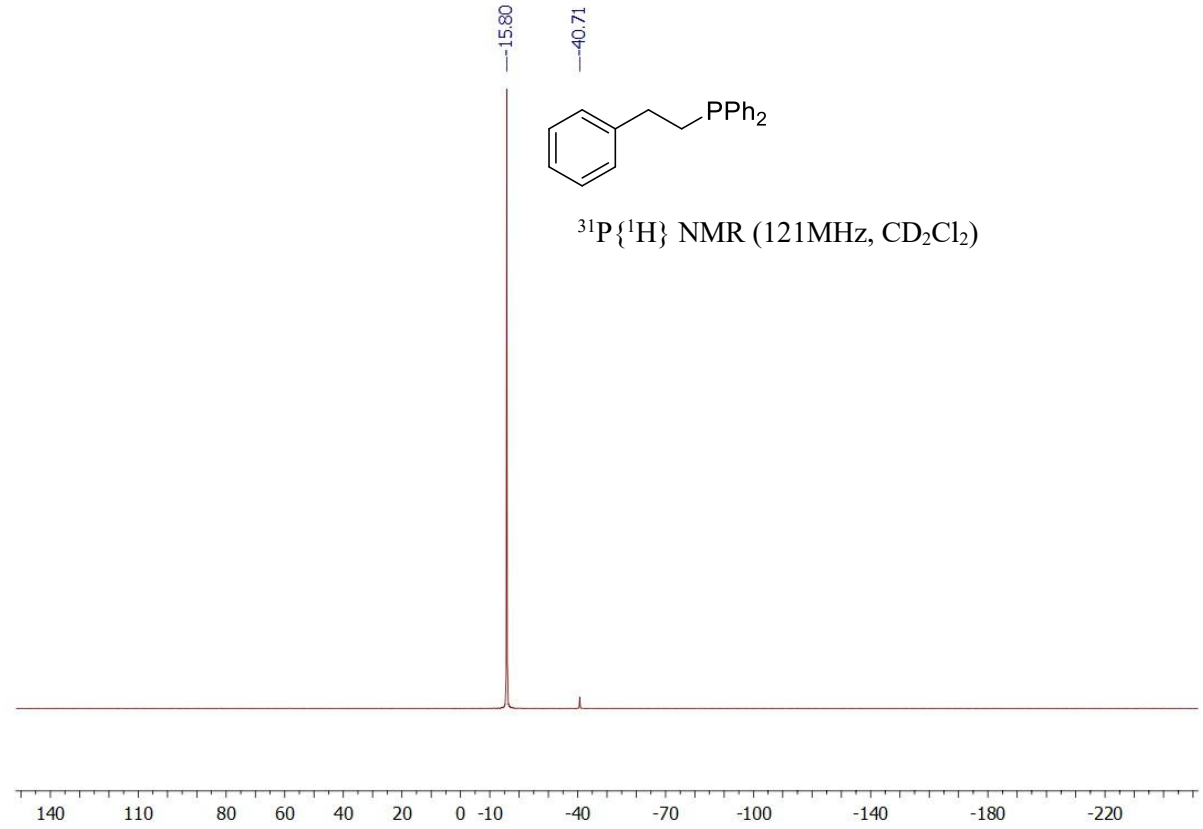


^{1}H NMR (300 MHz, CD_2Cl_2)

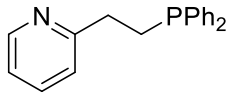




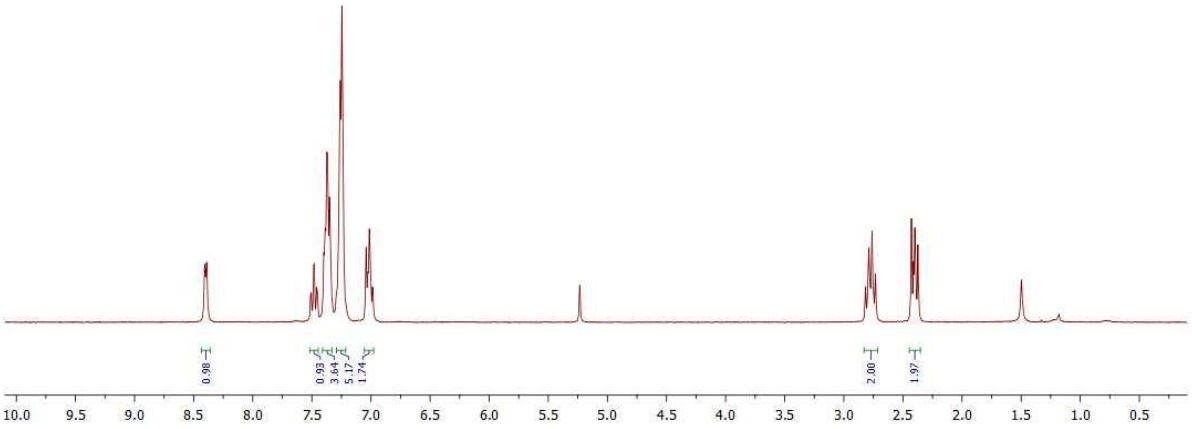
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)



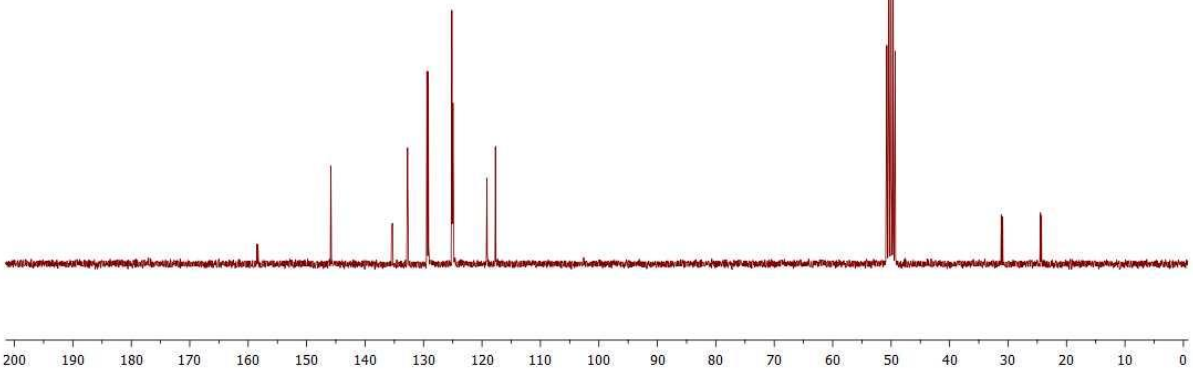
$^{31}P\{^{1}H\}$ NMR (121MHz, CD_2Cl_2)

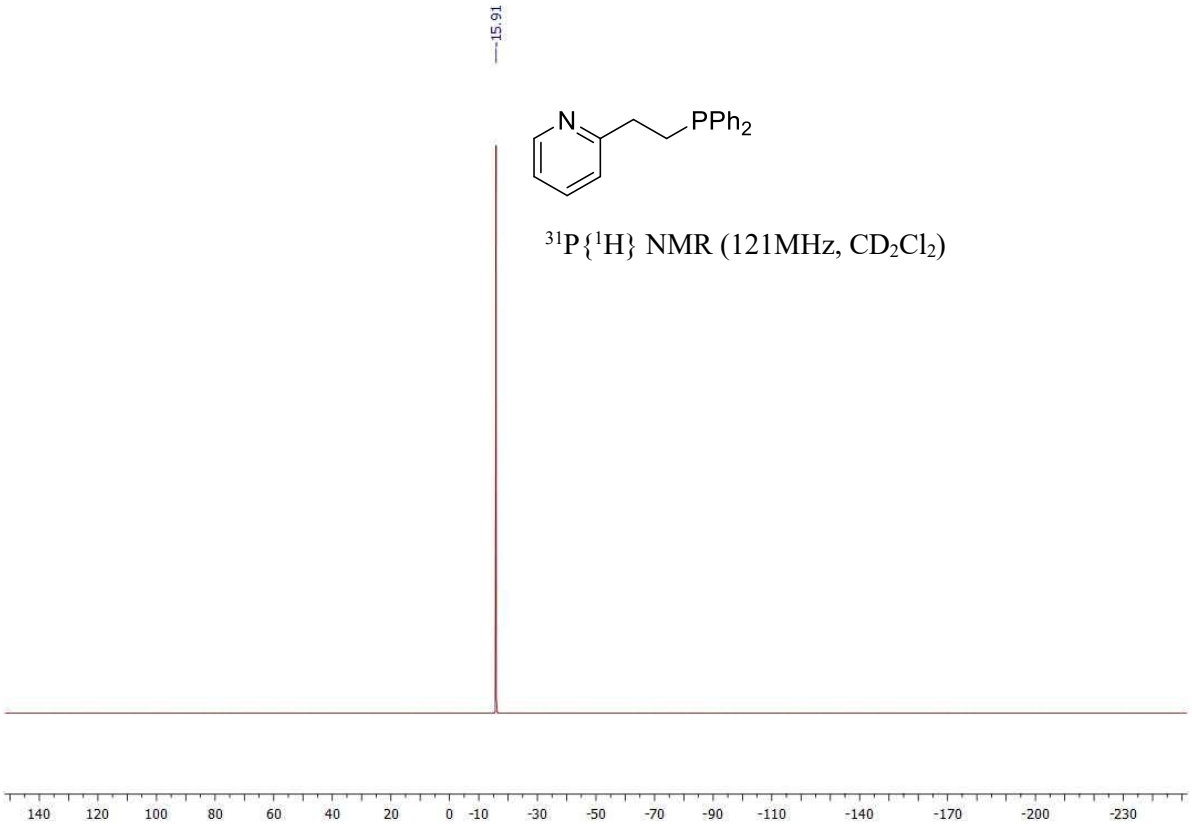


^{1}H NMR (300 MHz, CD_2Cl_2)

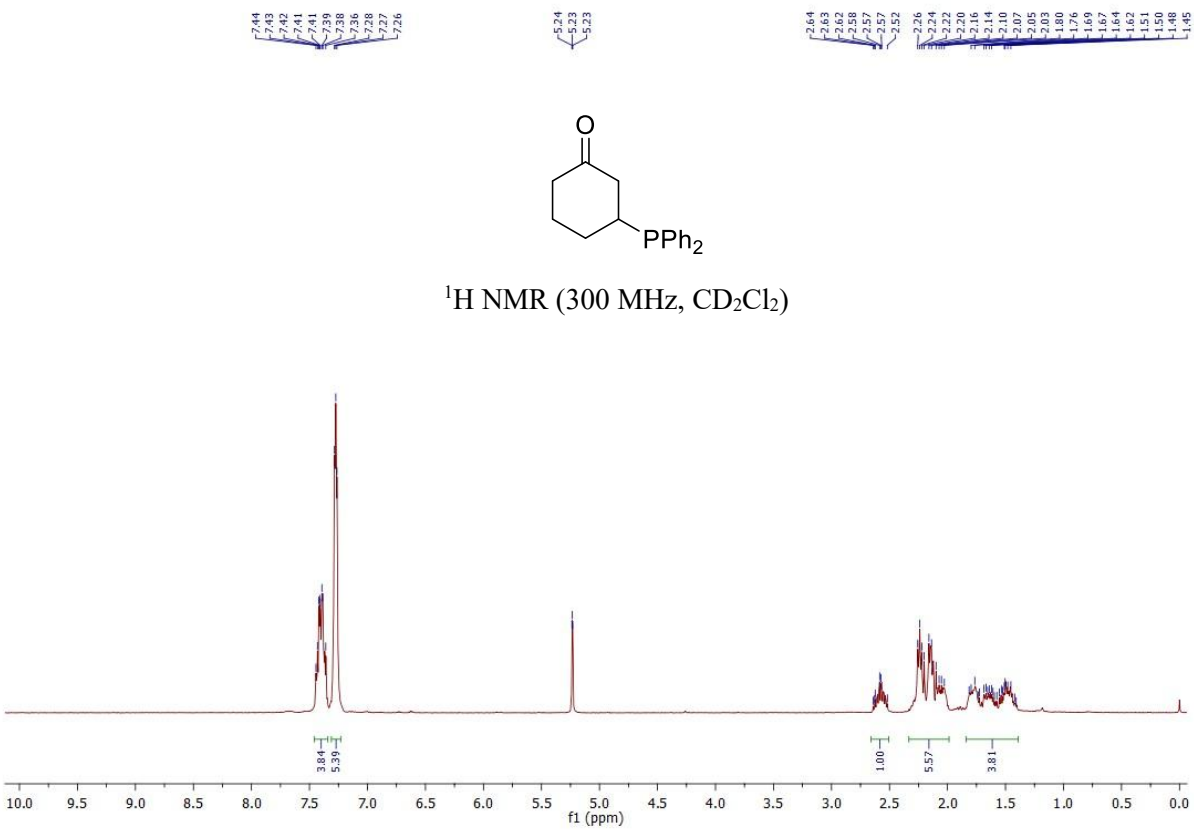


^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2)

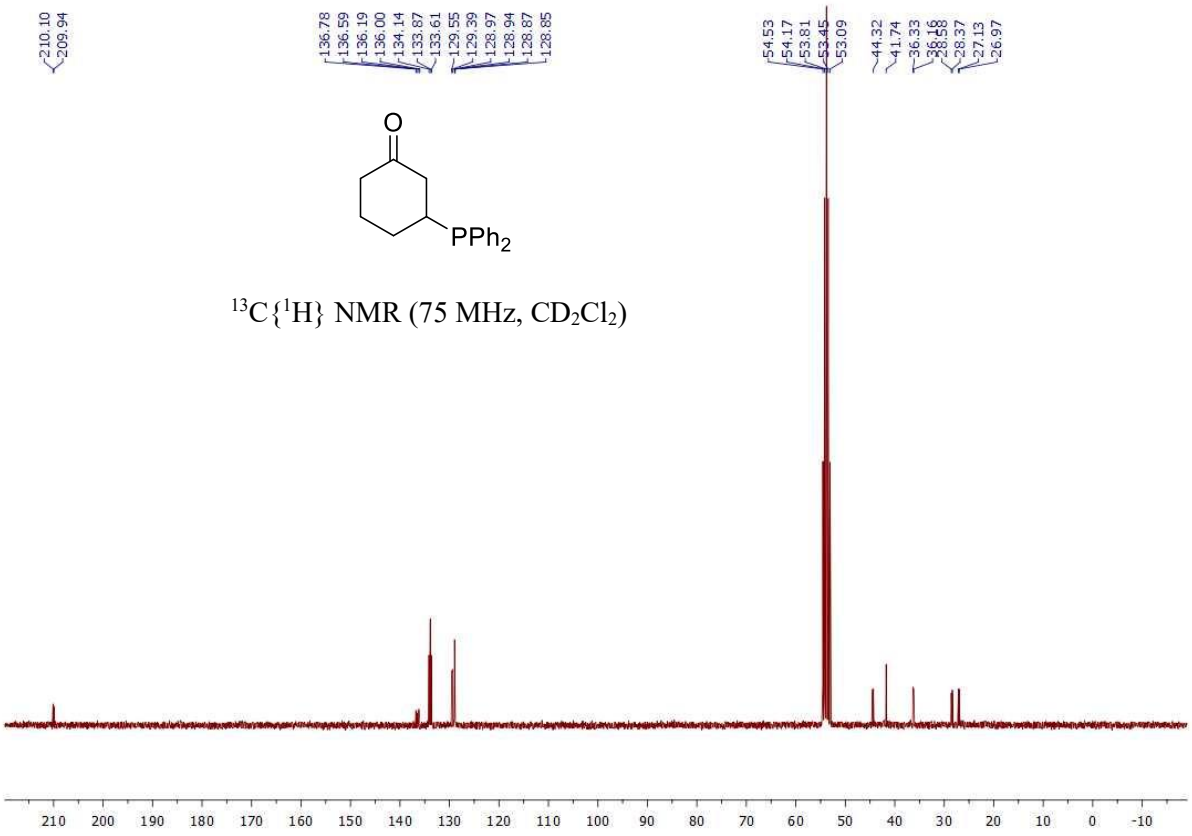




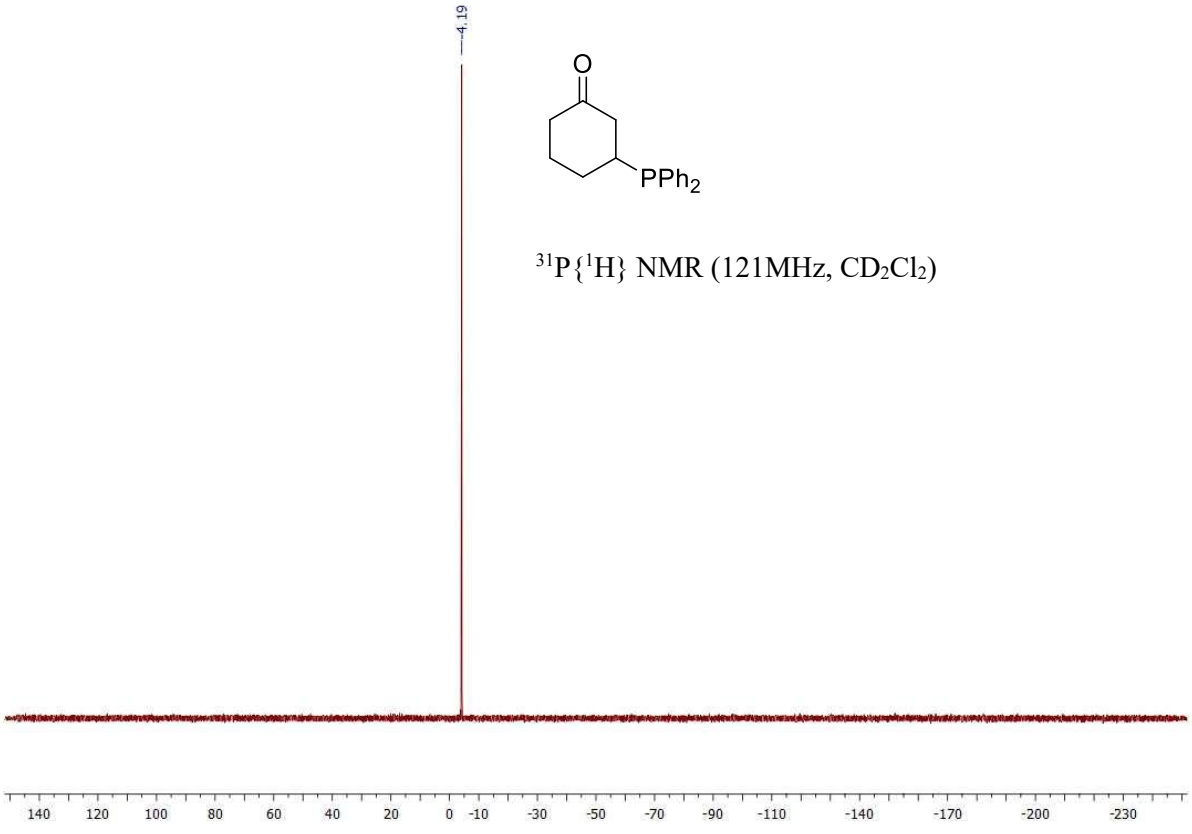
$^{31}P\{^{1}H\}$ NMR (121MHz, CD_2Cl_2)



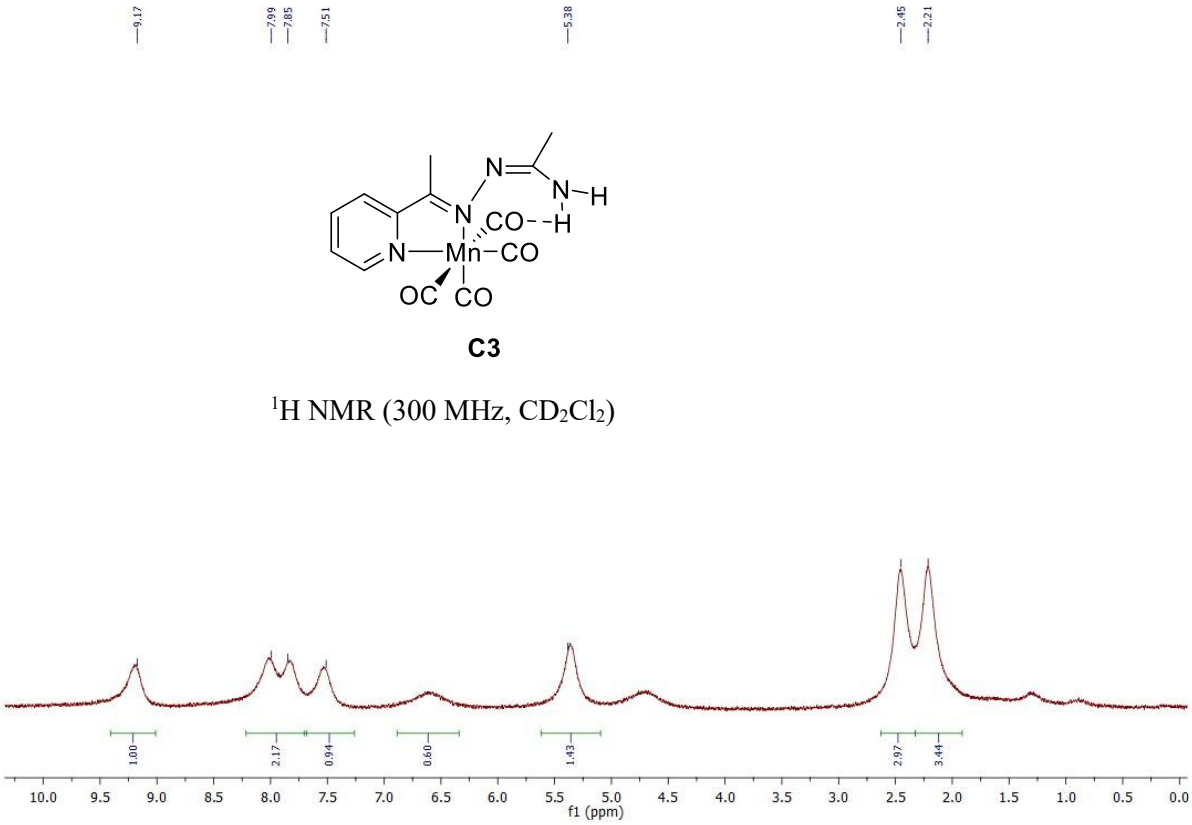
^{1}H NMR (300 MHz, CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

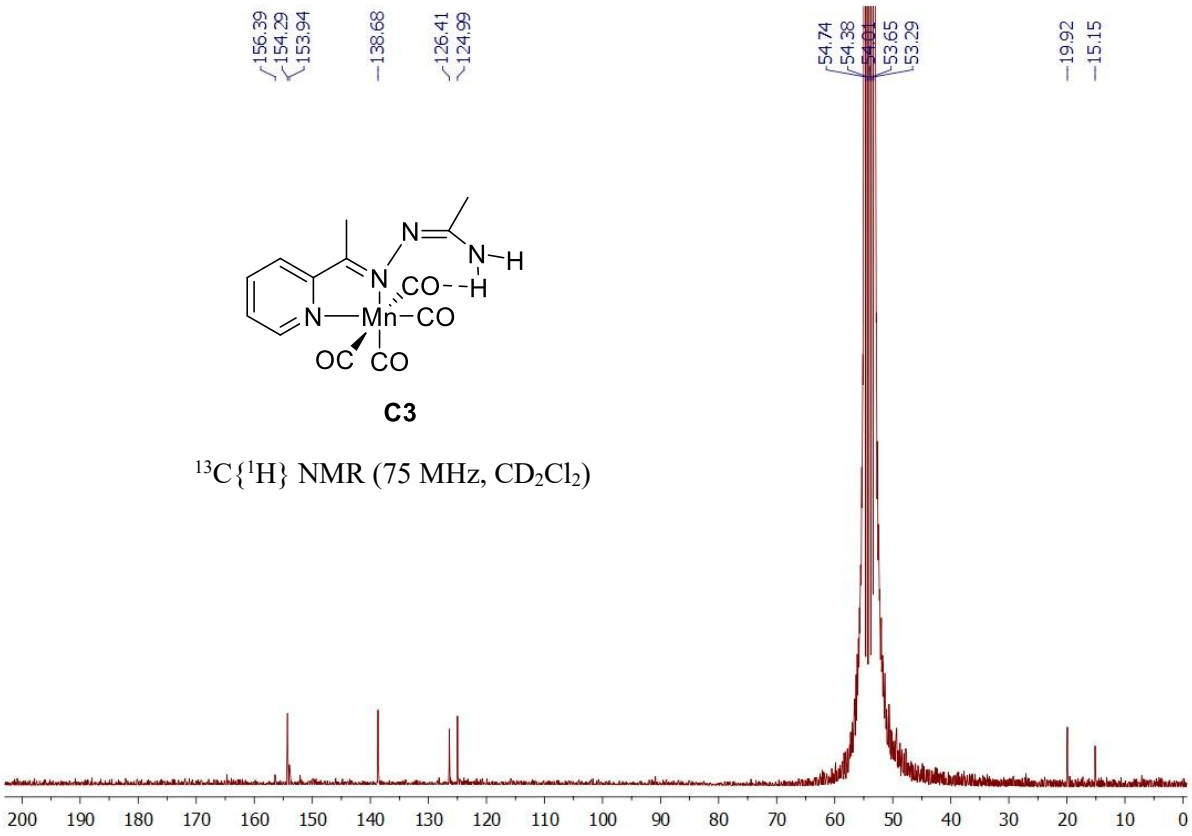


$^{31}P\{^{1}H\}$ NMR (121MHz, CD_2Cl_2)



C3

^{1}H NMR (300 MHz, CD_2Cl_2)

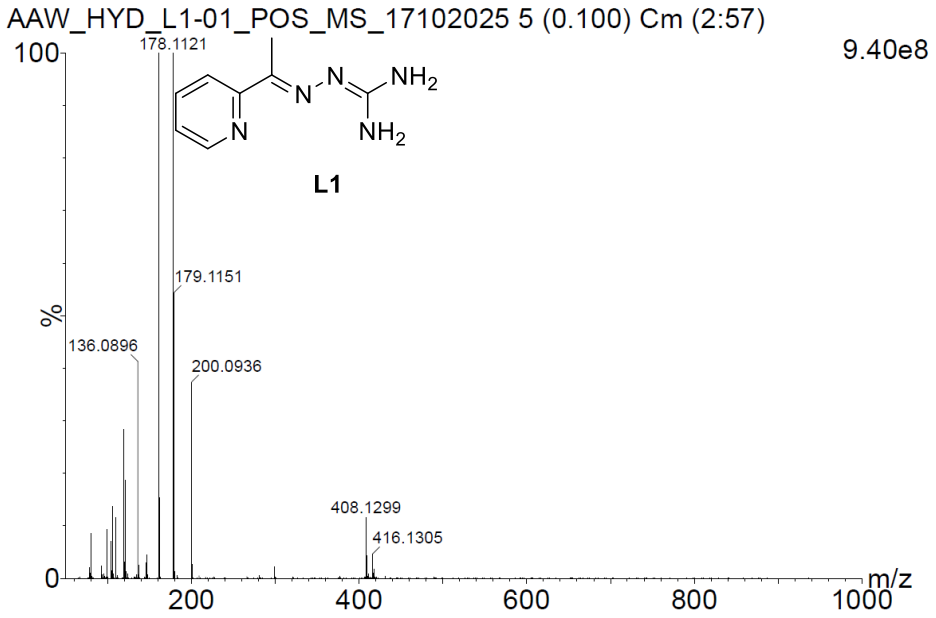


C3

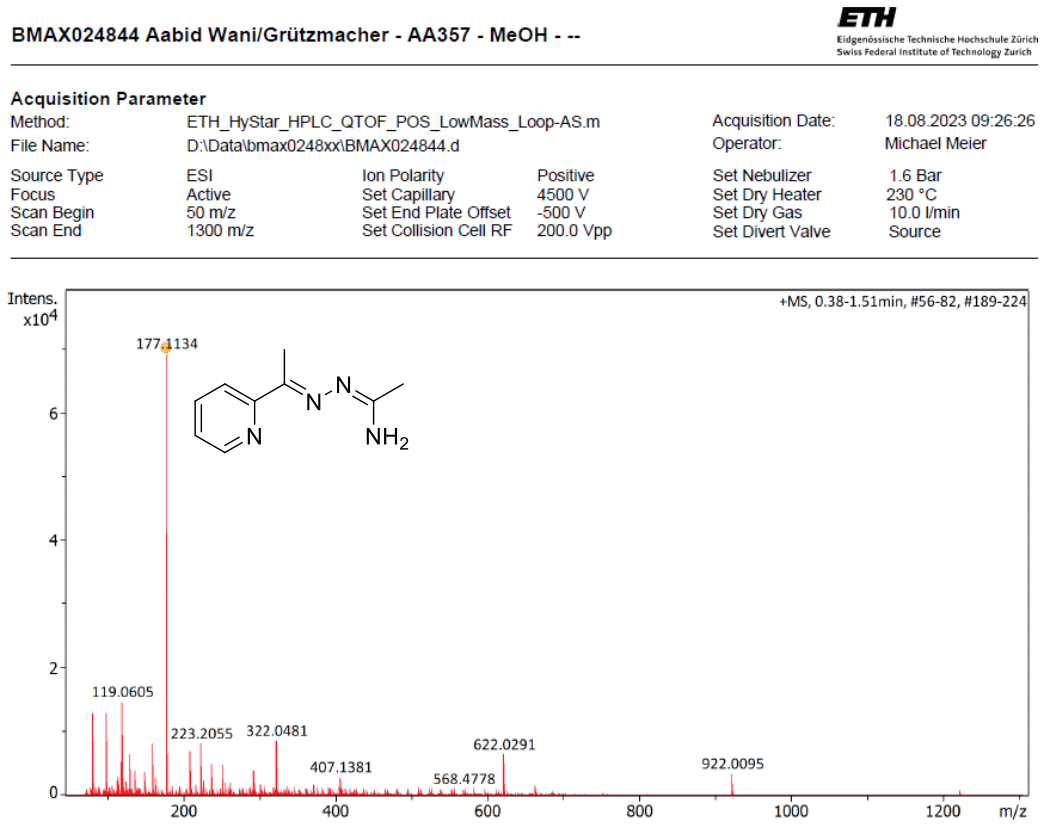
$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2)

Mass-spectrum of ligands:

L1:

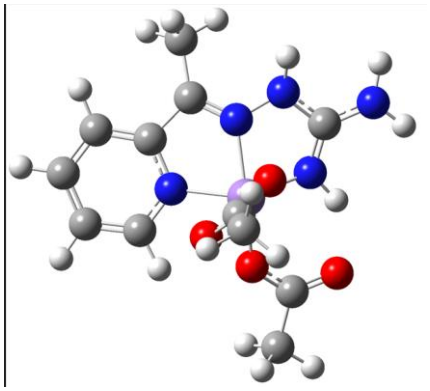


L2:



7.0 The 3D structures and coordinates of the optimized reactant, intermediates, and products

St-1



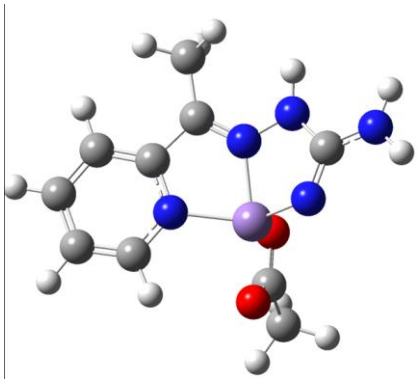
Energy= -1144.962547 Hartree

1 1

C	-3.83996500	-1.81335200	-0.63190200
C	-2.74443000	-2.65874900	-0.61028700
C	-1.47886500	-2.12067000	-0.44742300
C	-2.34803400	0.02463900	-0.36776400
C	-3.64083100	-0.44756900	-0.50951900
H	-4.84166000	-2.21108700	-0.74208100
H	-2.85682000	-3.73090000	-0.70499700
H	-0.58627100	-2.73044200	-0.39825500
H	-4.47379500	0.24352700	-0.52476700
C	-1.96051400	1.43018000	-0.33367400
N	-0.69482200	1.53098900	-0.13884100
N	-0.00173200	2.68304500	-0.32433800
C	1.27645100	2.43425000	-0.73750300
N	2.08676400	3.45905100	-0.97796900
H	1.76399600	4.41158300	-0.95876300
H	3.03270900	3.28552100	-1.27417700
N	1.54965000	1.16875500	-0.86480400
H	2.44874000	0.83072900	-1.21462600
N	-1.28848000	-0.81108500	-0.32938900
C	-2.86897700	2.56490500	-0.61112400
H	-3.71408900	2.25262000	-1.22330100
H	-3.26513400	2.97884000	0.32171600
H	-2.33659900	3.36125400	-1.13672600
O	1.41068000	-1.55229800	-0.46408800
C	2.58073100	-1.69234900	-1.03182300
C	2.93575200	-3.12594500	-1.30777500
H	3.93383900	-3.19853500	-1.73500800
H	2.88107400	-3.70547200	-0.38362700
H	2.20783200	-3.55374200	-2.00202200
O	3.33929800	-0.78002400	-1.32617900
Mn	0.45868400	-0.03165500	0.12815700
O	0.07415600	-1.16110900	1.84235000
C	0.53066600	-0.20338100	2.50194300
O	0.78591900	0.84823300	1.82209400
C	0.81044900	-0.26271300	3.95632400
H	1.88188700	-0.43500000	4.09514300

H	0.56130900	0.68608400	4.43247700
H	0.26120700	-1.08116800	4.41864100
H	-0.31999500	3.55839700	0.06358600

St-2

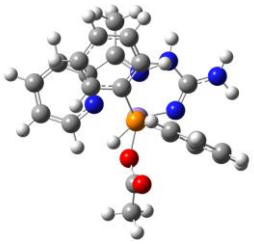


Energy= -916.039985 Hartree

1 1

C	-3.95185400	-0.66611700	-0.16066900
C	-3.61627500	0.47877500	-0.86411500
C	-2.27980800	0.80453200	-1.01147000
C	-1.62660400	-1.08948800	0.15823600
C	-2.94444400	-1.46469000	0.35582600
H	-4.99026600	-0.93912600	-0.01561500
H	-4.37351900	1.12464100	-1.28896300
H	-1.96648100	1.70133900	-1.53182800
H	-3.17799400	-2.36817100	0.90399500
C	-0.45923000	-1.86053800	0.56831100
N	0.61830900	-1.23426800	0.24658900
N	1.86840600	-1.72003100	0.36945500
C	2.69975400	-1.01410000	-0.48232100
N	3.96858700	-1.39861100	-0.58545300
H	4.37062500	-2.09329600	0.02096700
H	4.58442300	-0.86854900	-1.17996300
N	2.14673300	-0.01820800	-1.11237900
N	-1.30800000	0.04775500	-0.50293100
C	-0.51794300	-3.19944500	1.20044300
H	-0.42296400	-3.12022300	2.28785400
H	-1.46355200	-3.69269100	0.97948700
H	0.27943400	-3.85340800	0.83913000
O	0.27213200	2.51078400	-0.56183700
C	0.48461100	2.52584500	0.68933600
C	0.50576600	3.78256900	1.46957000
H	0.30797500	3.58959500	2.52272900
H	1.50587700	4.21831000	1.37747500
H	-0.20911900	4.49574800	1.06014700
O	0.70022300	1.39598300	1.23601700
Mn	0.59721800	0.54859500	-0.49817000
H	2.02417300	-2.68368600	0.63955000

St-3



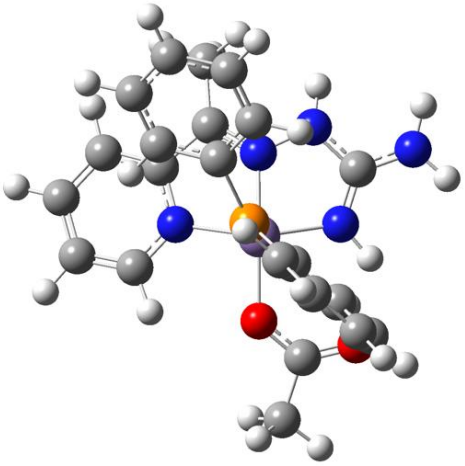
Energy= -1720.626700 Hartree

1 1

C	4.57677200	-0.96310700	-1.23457300
C	3.74295200	-1.98028100	-1.66632300
C	2.47987500	-2.09344800	-1.11298800
C	2.85027800	-0.26742400	0.25796400
C	4.12521500	-0.09491500	-0.25484500
H	5.57084900	-0.84837900	-1.65004400
H	4.05812700	-2.68729500	-2.42236100
H	1.79001600	-2.87067400	-1.41321900
H	4.75547000	0.70401700	0.11309800
C	2.28365300	0.51130000	1.34978000
N	1.08766400	0.11927900	1.61126200
N	0.37758400	0.54139100	2.68106000
C	-0.58788200	-0.42291300	2.96147000
N	-1.31099300	-0.25487500	4.07642500
H	-1.33178300	0.63252600	4.55053400
H	-2.07231700	-0.89217700	4.24244900
N	-0.68380500	-1.39337600	2.11986100
N	2.03413900	-1.25313900	-0.17854800
C	3.03924400	1.54911300	2.09231600
H	3.75353200	1.09473200	2.78619700
H	3.60330400	2.17517000	1.39933000
H	2.37868900	2.20897100	2.65493400
O	-0.26770000	-2.84727800	-0.35832400
C	-1.28153900	-3.09035600	-1.15322200
C	-1.47960100	-4.55005200	-1.44352200
H	-2.34600200	-4.69586600	-2.08515400
H	-0.58925500	-4.95644900	-1.92986500
H	-1.61208000	-5.09721600	-0.50740900
O	-1.99046400	-2.22398600	-1.62872600
Mn	0.18139500	-1.32482800	0.57398200
P	-0.72144900	0.25010300	-0.80281700
C	-2.47471500	0.68315400	-0.62831000
C	-2.99020000	1.76719400	-1.33795900
C	-3.31973600	-0.08079500	0.17026300
C	-4.33614400	2.08225900	-1.24367200
H	-2.34261200	2.36881400	-1.96563600
C	-4.66476100	0.24191800	0.26554900
H	-2.92530900	-0.93482000	0.70695200
C	-5.17428200	1.32148900	-0.44033000
H	-4.73123600	2.92277700	-1.80272600
H	-5.31803800	-0.36051300	0.88651100
H	-6.22760600	1.56863300	-0.36900000
C	0.14721300	1.84094400	-0.93122400
C	-0.04901300	2.85834600	0.00254500
C	1.06122500	2.03387100	-1.96551200

C	0.65425500	4.04782000	-0.10230500
H	-0.76858800	2.72696600	0.80394900
C	1.76890600	3.22364700	-2.06484200
H	1.21150500	1.25616000	-2.70785700
C	1.56582800	4.23172800	-1.13436100
H	0.48320100	4.84018000	0.61801200
H	2.46936400	3.36751600	-2.87985700
H	2.10748400	5.16703900	-1.21936100
H	0.87148100	1.01304000	3.43020100
H	-0.59339800	-0.17582400	-2.13639800

St-4



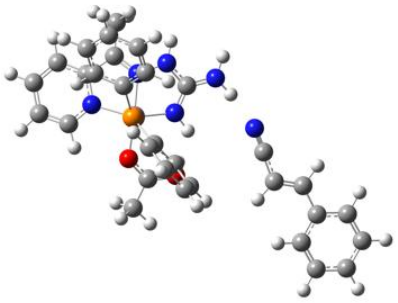
Energy= -1720.647516 Hartree

1 1

C	4.04550700	-1.57966000	-2.24122000
C	2.86632900	-2.02010300	-2.82003500
C	1.68233300	-1.88161800	-2.11701500
C	2.78725500	-0.90597600	-0.32700100
C	4.00751200	-1.01858800	-0.97569000
H	4.98804900	-1.67667100	-2.76650800
H	2.85406200	-2.46623400	-3.80614600
H	0.72933600	-2.20761500	-2.51503400
H	4.91455400	-0.68120500	-0.49191700
C	2.61328300	-0.41325000	1.03554700
N	1.37344300	-0.49504400	1.38987100
N	0.94224200	-0.29366800	2.66243600
C	-0.21997100	-0.98775700	2.91816900
N	-0.64623400	-1.03642400	4.17858300
H	-0.21268200	-0.49207200	4.90517700
H	-1.53290200	-1.46689900	4.38182700
N	-0.77530100	-1.53884100	1.88237500
N	1.63869600	-1.33164300	-0.90578700
C	3.73331400	0.03369200	1.90286900
H	4.19914200	-0.81174700	2.42019200
H	4.50570700	0.52207300	1.30808600
H	3.40520400	0.76086800	2.64806400
O	-1.06255500	-2.31624800	-0.84231500
C	-2.09494700	-3.02566900	-0.50541400
C	-2.52712200	-4.00558800	-1.56416800
H	-3.36165600	-4.60989200	-1.21386400

H	-2.82302900	-3.45960300	-2.46357400
H	-1.69049800	-4.65179700	-1.83945700
O	-2.70467700	-2.93879200	0.55737300
Mn	0.01641900	-1.11666500	0.19223900
P	-0.55031000	0.79512200	-0.39796100
C	-2.26856100	1.28983400	-0.54311600
C	-2.63467800	2.51786200	-1.10484100
C	-3.26832300	0.39344400	-0.15070400
C	-3.97227900	2.84300900	-1.25500000
H	-1.87454700	3.21766100	-1.43126000
C	-4.60286900	0.72712700	-0.30677600
H	-3.00205800	-0.56839600	0.27376200
C	-4.95905000	1.95185100	-0.85508700
H	-4.24526000	3.79690400	-1.69197000
H	-5.36818100	0.02465600	0.00345000
H	-6.00504700	2.21059800	-0.97480600
C	0.44555000	2.29481300	-0.32253100
C	0.11918600	3.35215900	0.53183800
C	1.60918200	2.37557500	-1.08973000
C	0.94195200	4.46327200	0.61318900
H	-0.78339800	3.30468100	1.13106100
C	2.42805500	3.49205600	-1.00776400
H	1.86172200	1.56861900	-1.76840100
C	2.09684200	4.53555200	-0.15572100
H	0.67978800	5.27887800	1.27768600
H	3.32165500	3.55079900	-1.61905600
H	2.73439000	5.41040500	-0.09565700
H	1.62824800	-0.17958500	3.39594900
H	-1.64147800	-2.06719600	1.96419400

St-5



Energy= -2122.110598 Hartree

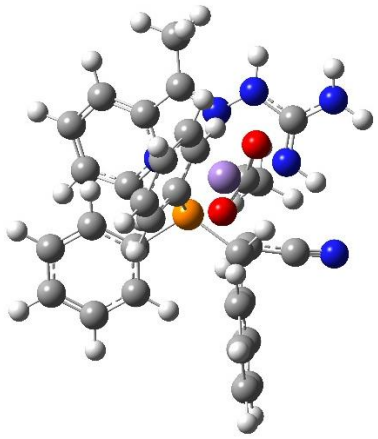
1 1

C	5.27702500	-3.29299500	-1.72616500
C	4.38795600	-2.86457200	-2.69907000
C	3.26699900	-2.15216500	-2.31269000
C	3.86756900	-2.29599800	-0.07537700
C	5.01283700	-3.01008600	-0.39684200
H	6.16721000	-3.84773000	-1.99790200
H	4.55657600	-3.07022400	-3.74825600
H	2.53698500	-1.78509800	-3.02378500
H	5.68658000	-3.34800800	0.37939000
C	3.41214200	-1.99770200	1.27638000
N	2.29932500	-1.34188000	1.24479000

N	1.55424100	-1.09982800	2.35108700
C	0.21567400	-0.97495600	2.03817200
N	-0.65647800	-0.90197400	3.02885700
H	-0.35759800	-0.89495500	3.98919800
H	-1.65264900	-0.79816900	2.82069200
N	-0.04367600	-0.94459500	0.75874100
N	3.01672200	-1.86269700	-1.03785800
C	4.06610300	-2.45462200	2.52720600
H	3.47597300	-3.23908900	3.01461800
H	5.05636400	-2.86180300	2.33901100
H	4.17820600	-1.62449300	3.23071200
O	0.48920100	-0.94827900	-2.04408900
C	-0.78288600	-0.88941000	-2.28653200
C	-1.13856400	-1.20530100	-3.71685400
H	-2.21689000	-1.18114300	-3.86247900
H	-0.66386200	-0.47686800	-4.37901900
H	-0.75090800	-2.18971400	-3.98938600
O	-1.65305200	-0.60183800	-1.46989500
Mn	1.46318400	-0.83495000	-0.39576900
P	2.29193600	1.07864000	-0.38583200
C	1.32656300	2.53761100	-0.79165700
C	1.93687600	3.78255400	-0.97884900
C	-0.04966500	2.41319600	-1.00534100
C	1.18151100	4.87859200	-1.36016300
H	3.00495500	3.89396100	-0.83262300
C	-0.79625000	3.51498300	-1.38865900
H	-0.53742500	1.45369000	-0.87208900
C	-0.18572000	4.74911400	-1.56480400
H	1.66511600	5.83843100	-1.50317700
H	-1.86330200	3.40680100	-1.54781400
H	-0.77361000	5.61001300	-1.86275700
C	3.73262700	1.63249100	0.54612900
C	3.62306500	2.54438800	1.60017300
C	4.98434800	1.09364100	0.24197500
C	4.74308600	2.90544300	2.33058100
H	2.65760500	2.97389300	1.84425800
C	6.10386800	1.46081100	0.97394600
H	5.08217000	0.39789300	-0.58425400
C	5.98475900	2.36515900	2.01922600
H	4.64805200	3.61481300	3.14516500
H	7.07358000	1.04780400	0.71954400
H	6.86078600	2.65606800	2.58799300
H	1.83037500	-1.52076000	3.22871700
H	-1.00339000	-0.84207800	0.43895800
C	-10.55849400	-0.03076300	-0.55115100
C	-9.40778000	-0.03878100	-1.33251000
C	-8.16501000	-0.15825000	-0.74173900
C	-8.04944400	-0.27271200	0.64844700
C	-9.21468100	-0.26340300	1.42124500
C	-10.45964300	-0.14293200	0.82737000
H	-11.53107100	0.06427300	-1.02047700
H	-9.48464700	0.04895000	-2.41014500
H	-7.27980800	-0.16167800	-1.36717300
H	-9.13499100	-0.35039600	2.50006400
H	-11.35343700	-0.13697700	1.44045100

C	-6.77663600	-0.40007300	1.33379100
C	-5.55464700	-0.41843100	0.77509300
C	-4.39404200	-0.54452300	1.56816600
N	-3.43310600	-0.64578500	2.19677400
H	-6.83786800	-0.48805000	2.41524100
H	-5.38337500	-0.33881300	-0.29280300

St-6



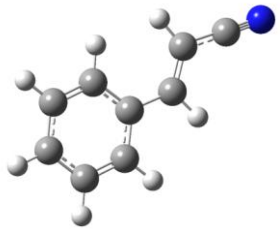
Energy: -2122.097612 Hartree

1 1

C	3.33063600	3.24613600	-1.64100800
C	2.49078900	2.59393100	-2.52156500
C	1.87534200	1.41961100	-2.11456700
C	2.88914900	1.52047300	-0.04708200
C	3.53075900	2.70242900	-0.38192500
H	3.83209100	4.16351800	-1.92505500
H	2.30624700	2.97435400	-3.51773900
H	1.22347000	0.87155500	-2.77986200
H	4.18492500	3.19303500	0.32533400
C	3.05184600	0.84021300	1.23650600
N	2.30936900	-0.20455000	1.33823800
N	2.37190500	-1.00133000	2.42907500
C	1.72901600	-2.20931100	2.24870600
N	1.92980700	-3.13741900	3.19403400
H	2.34185100	-2.89918100	4.07971400
H	1.43956500	-4.01399700	3.13447900
N	1.00448000	-2.30486500	1.19191900
H	0.56024400	-3.20607100	1.05879100
N	2.06807700	0.88744300	-0.91314800
C	4.00406700	1.25590300	2.29764700
H	4.83901000	0.54774100	2.35620000
H	4.42710800	2.23993200	2.11594900
H	3.50966800	1.27653800	3.27366100
O	1.55314700	-1.36807200	-2.19145900
C	2.62886100	-1.96451500	-1.89235900
C	3.43165600	-2.66865900	-2.92854600
H	3.30161200	-2.20068000	-3.90394000
H	4.48439600	-2.69048500	-2.64871000
H	3.07297300	-3.70011800	-2.99571600
O	2.95708600	-1.95343400	-0.68052400
Mn	1.23672400	-0.87149700	-0.23713100

P	-0.73593700	0.36892100	0.27724100
C	-1.24419900	1.15395800	1.84279200
C	-2.39798600	1.93997500	1.89800500
C	-0.52886800	0.92489900	3.01589500
C	-2.82283500	2.47887800	3.10146700
H	-2.96871600	2.13180200	0.99729100
C	-0.95618100	1.46683500	4.21989800
H	0.36863100	0.32065600	2.99600300
C	-2.10292000	2.24438500	4.26506700
H	-3.72200500	3.08382600	3.12897700
H	-0.39052800	1.28066500	5.12606500
H	-2.43563600	2.66919400	5.20529700
C	-1.24812500	1.58862300	-0.96994900
C	-1.92744200	1.24606400	-2.13722200
C	-0.86958800	2.92052600	-0.77973500
C	-2.22801500	2.21252300	-3.08710900
H	-2.24997600	0.22839500	-2.30728000
C	-1.17438300	3.88319400	-1.72761600
H	-0.34482200	3.21614500	0.12229500
C	-1.85394200	3.53167500	-2.88600200
H	-2.76883600	1.92900200	-3.98287500
H	-0.88230800	4.91350900	-1.55834200
H	-2.09710200	4.28623400	-3.62540600
C	-5.84591600	-1.59280400	-0.77595800
C	-4.91405100	-1.96298700	-1.73258100
C	-3.55604900	-1.83500900	-1.47422700
C	-3.10754800	-1.33599800	-0.25465900
C	-4.05447000	-0.98612000	0.70830000
C	-5.40993000	-1.10625100	0.44910500
H	-6.90620900	-1.69334800	-0.97813500
H	-5.24203400	-2.36171900	-2.68605300
H	-2.84368700	-2.14557100	-2.23074400
H	-3.72474100	-0.62284400	1.67573600
H	-6.12938000	-0.82780900	1.21117400
C	-1.64446100	-1.21716400	0.06735000
H	-1.46492500	-1.67878900	1.04487900
C	-0.58734100	-1.74245600	-0.89860300
H	-0.70577900	-1.34128500	-1.90297900
C	-0.45563800	-3.16169200	-0.96711000
N	-0.30790800	-4.30796700	-0.93565900
H	3.20049800	-0.96132600	3.00777600

Cinnamonitrile



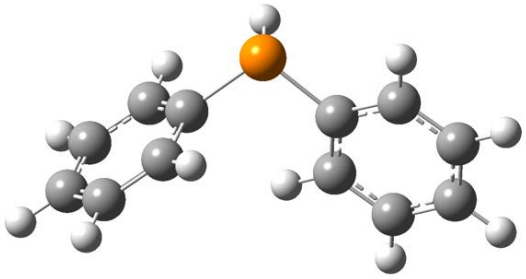
Energy= -401.464294 Hartree

0 1

C	-3.12785200	0.19197700	0.00034800

C	-2.27125100	1.28763000	-0.00014000
C	-0.90222000	1.10223000	-0.00051300
C	-0.35947800	-0.18746900	-0.00041700
C	-1.23238200	-1.27874200	-0.00002700
C	-2.60485500	-1.09195600	0.00041600
H	-4.20139500	0.34310600	0.00062600
H	-2.67751700	2.29275000	-0.00026900
H	-0.24975000	1.96796300	-0.00095100
H	-0.82252100	-2.28352700	-0.00000700
H	-3.26671400	-1.95049700	0.00076800
C	1.07103900	-0.44835500	-0.00067300
C	2.05105700	0.46777700	0.00066000
C	3.41729600	0.09776100	0.00032700
N	4.53736300	-0.17883000	0.00000100
H	1.35552900	-1.49707600	-0.00202000
H	1.85271000	1.53397400	0.00195500

DiphenylPhosphine

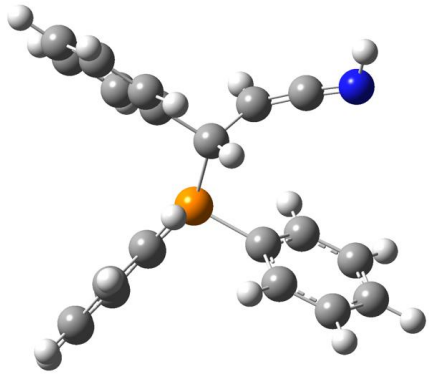


Energy= -804.591193 Hartree

0 1

C	3.67774600	-1.22675300	0.00701500
C	3.78942400	0.09602700	0.40715400
C	2.67908800	0.92816400	0.36872000
C	1.45009900	0.45387800	-0.08651800
C	1.34779400	-0.87863600	-0.48268300
C	2.45370200	-1.71301300	-0.43379700
H	4.54137300	-1.88161900	0.04386900
H	4.73996900	0.48061900	0.76028000
H	2.76528300	1.95865900	0.69916400
H	0.39614600	-1.26814700	-0.82748200
H	2.36056600	-2.74831300	-0.74369800
P	0.05563000	1.64979700	-0.12875400
H	0.01272200	1.85076300	-1.53306600
C	-1.42196800	0.58372100	-0.02613600
C	-1.81372300	0.10271800	1.22463200
C	-2.21414300	0.28749800	-1.13454800
C	-2.95461000	-0.67179200	1.35910900
H	-1.21928000	0.33866200	2.10198700
C	-3.36642600	-0.47439700	-0.99716600
H	-1.92708500	0.65354200	-2.11469300
C	-3.73633200	-0.95988900	0.24801700
H	-3.24110900	-1.04353300	2.33681600
H	-3.97285300	-0.69416000	-1.86914900
H	-4.63408600	-1.55858900	0.35447600

3a'



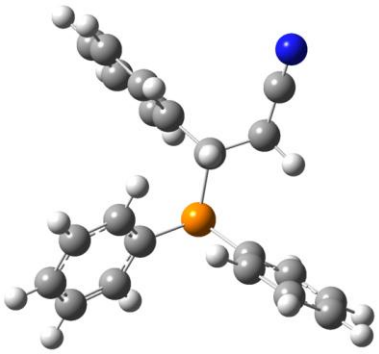
Energy= -1206.022892 Hartree

0 1

C	-3.90038300	-1.32169800	1.28442800
C	-2.51656100	-1.27336800	1.21310500
C	-1.86894800	-1.21053100	-0.01934900
C	-2.64342900	-1.19932500	-1.17601900
C	-4.02803100	-1.24830000	-1.10756500
C	-4.66210200	-1.30888500	0.12445700
H	-4.38645000	-1.36770500	2.25287200
H	-1.93204200	-1.27812300	2.12744000
H	-2.15457700	-1.15732300	-2.14453300
H	-4.61268800	-1.23841200	-2.02106700
H	-5.74428300	-1.34523700	0.18105100
C	-0.36116200	-1.18942300	-0.11625900
C	0.23346400	-2.50999900	0.30065200
H	0.02177300	-2.89013600	1.29515500
C	0.96632400	-3.25290100	-0.48656200
N	1.74482500	-3.88777400	-1.17837500
P	0.37006100	0.14913800	0.99321900
C	-0.28303200	1.70460900	0.28237000
C	-0.31531500	2.80463600	1.14081700
C	-0.74427500	1.86819700	-1.02328800
C	-0.77565700	4.03744000	0.70395600
H	0.02277400	2.68861400	2.16596000
C	-1.21830200	3.09731700	-1.45863700
H	-0.73900600	1.03377300	-1.71445400
C	-1.23136600	4.18552800	-0.59799700
H	-0.78812700	4.88098100	1.38542400
H	-1.57901000	3.20471200	-2.47591300
H	-1.60220700	5.14543400	-0.94008400
C	2.11347400	0.15013200	0.42468300
C	3.01245600	-0.64824400	1.13357300
C	2.59154700	0.90151000	-0.64795500
C	4.34722800	-0.71625100	0.76393800
H	2.66152400	-1.21942800	1.98683600
C	3.92935300	0.84418100	-1.01013300
H	1.91782800	1.54636400	-1.20086600
C	4.80908800	0.03136300	-0.30939200
H	5.02928300	-1.34858900	1.32160200
H	4.28572300	1.43836400	-1.84477000
H	5.85431700	-0.01332200	-0.59490600

H	-0.07424200	-0.98969500	-1.15145200
H	1.32849300	-4.58886000	-1.79088200

3a



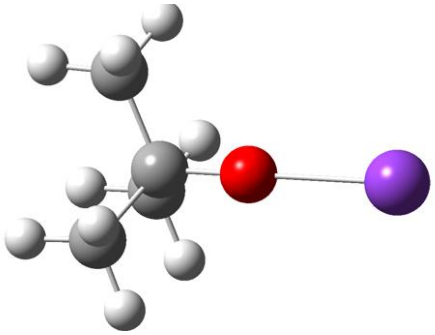
Energy= -1206.057822 Hartree

0 1

C	3.94515200	-0.26536400	-1.49407500
C	2.60340100	-0.57346100	-1.33232400
C	2.03646700	-0.64098500	-0.06028000
C	2.84958800	-0.39705200	1.04309200
C	4.19271900	-0.08978900	0.88352800
C	4.74468600	-0.02103000	-0.38652900
H	4.36760800	-0.21446200	-2.49154900
H	1.98711600	-0.75557600	-2.20686100
H	2.42875700	-0.46025400	2.04157300
H	4.80953800	0.09270100	1.75650100
H	5.79416500	0.21985100	-0.51353800
C	0.58498800	-1.00531600	0.13108200
C	0.31434600	-2.48442600	-0.20422200
H	0.62149900	-2.70988700	-1.22938900
C	1.01604800	-3.38648700	0.69335400
N	1.56102100	-4.09239100	1.41920400
P	-0.52279500	0.04132600	-0.96284200
C	-0.36581300	1.71498200	-0.24105000
C	-0.81346600	2.76350000	-1.04718100
C	0.15147900	2.01808000	1.01702900
C	-0.76852100	4.07458800	-0.60057800
H	-1.19967000	2.54631700	-2.03846200
C	0.21041200	3.33206800	1.45963200
H	0.52127600	1.23258700	1.66451200
C	-0.25338700	4.36234400	0.65543200
H	-1.12607500	4.87432700	-1.23972000
H	0.62200400	3.55003300	2.43910300
H	-0.20650500	5.38813000	1.00375400
C	-2.18247900	-0.47816500	-0.37121800
C	-2.96424500	-1.23616500	-1.24279700
C	-2.69525900	-0.16278900	0.88715100
C	-4.22181100	-1.68443500	-0.86169200
H	-2.58345700	-1.47141700	-2.23182700
C	-3.95210900	-0.60600800	1.26718600
H	-2.11454900	0.44532600	1.57239300
C	-4.71664500	-1.37020400	0.39456500
H	-4.81725100	-2.27321100	-1.55071600

H	-4.33947500	-0.35143000	2.24770400
H	-5.70074200	-1.71386800	0.69349600
H	-0.75418400	-2.70639500	-0.12795600
H	0.31144000	-0.84925300	1.17854900

^{t}BuOK

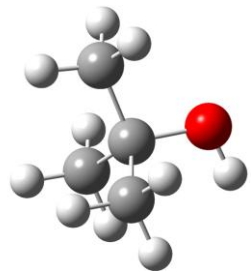


Energy= -832.579172 Hartree

0 1

C	-1.07576700	-0.00001100	0.00003300
C	-1.61679900	-0.67662200	-1.27106200
H	-1.25201300	-0.14371600	-2.15489500
H	-1.24839100	-1.70606500	-1.32434400
H	-2.71218200	-0.70160800	-1.31363600
C	-1.61768200	-0.76204200	1.22135400
H	-1.25128000	-1.79338200	1.20339900
H	-1.25145600	-0.29223900	2.13972100
H	-2.71307600	-0.78786600	1.26269200
O	0.29004100	-0.00033900	0.00056400
K	2.57241200	-0.00014700	0.00001900
C	-1.61612800	1.43923900	0.04916400
H	-2.71146800	1.48915100	0.05214200
H	-1.24795000	1.93918600	0.95069900
H	-1.25007900	1.99867400	-0.81758200

^{t}BuOH



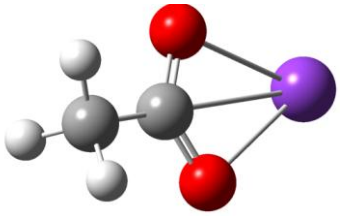
Energy= -233.386007 Hartree

0 1

C	-0.00157800	0.01737800	-0.00000000
C	-1.51395100	0.13846900	0.00000000
H	-1.85269000	0.68198700	0.88511400
H	-1.85269000	0.68198700	-0.88511400
H	-1.98218700	-0.84823000	0.00000000
C	0.48356400	-0.69955700	-1.25251200
H	0.15763800	-0.16463400	-2.14765800
H	1.57689400	-0.75683300	-1.26759100

H	0.09751500	-1.72115200	-1.30097700
O	0.48356400	1.36268000	-0.00000000
C	0.48356400	-0.69955700	1.25251200
H	0.09751500	-1.72115200	1.30097700
H	1.57689400	-0.75683300	1.26759100
H	0.15763800	-0.16463400	2.14765800
H	1.44536000	1.32765000	-0.00000000

Pot. acetate



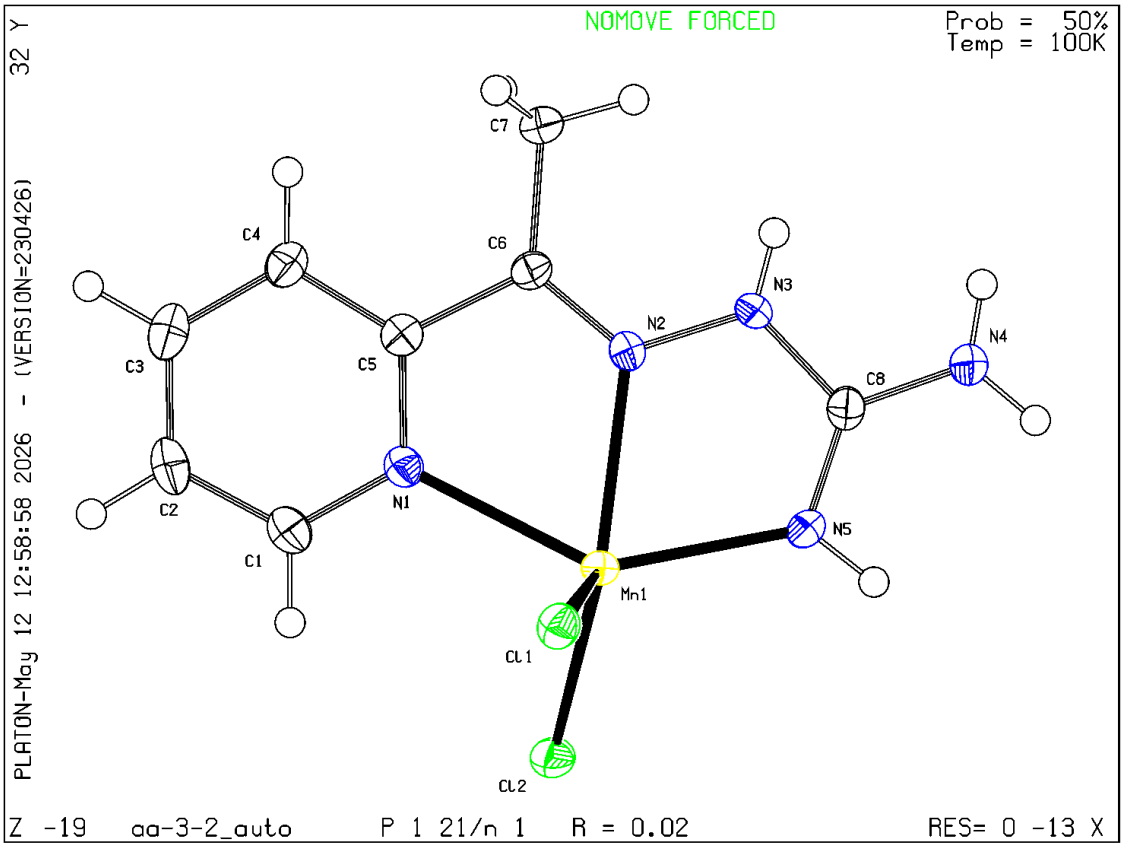
Energy= -828.139132 Hartree

0 1

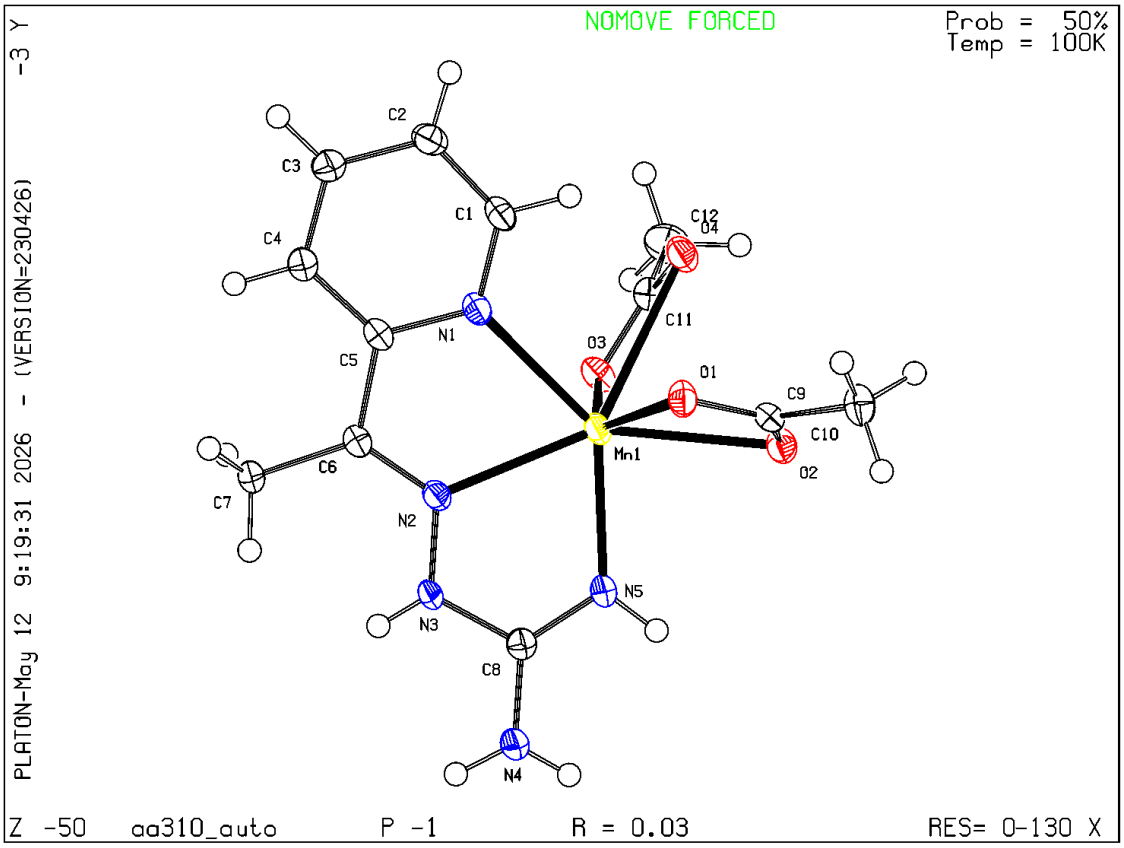
C	0.98419100	0.00088900	-0.01444300
C	2.50185600	-0.00022800	0.00508700
H	2.89889100	-0.88321600	-0.49729100
H	2.90203700	0.90811400	-0.44658700
H	2.83501400	-0.03225300	1.04736800
O	0.40039400	1.11609100	-0.00849500
O	0.40088500	-1.11470800	-0.00853200
K	-1.89276100	-0.00040400	0.00467700

8. ORTEP diagrams:

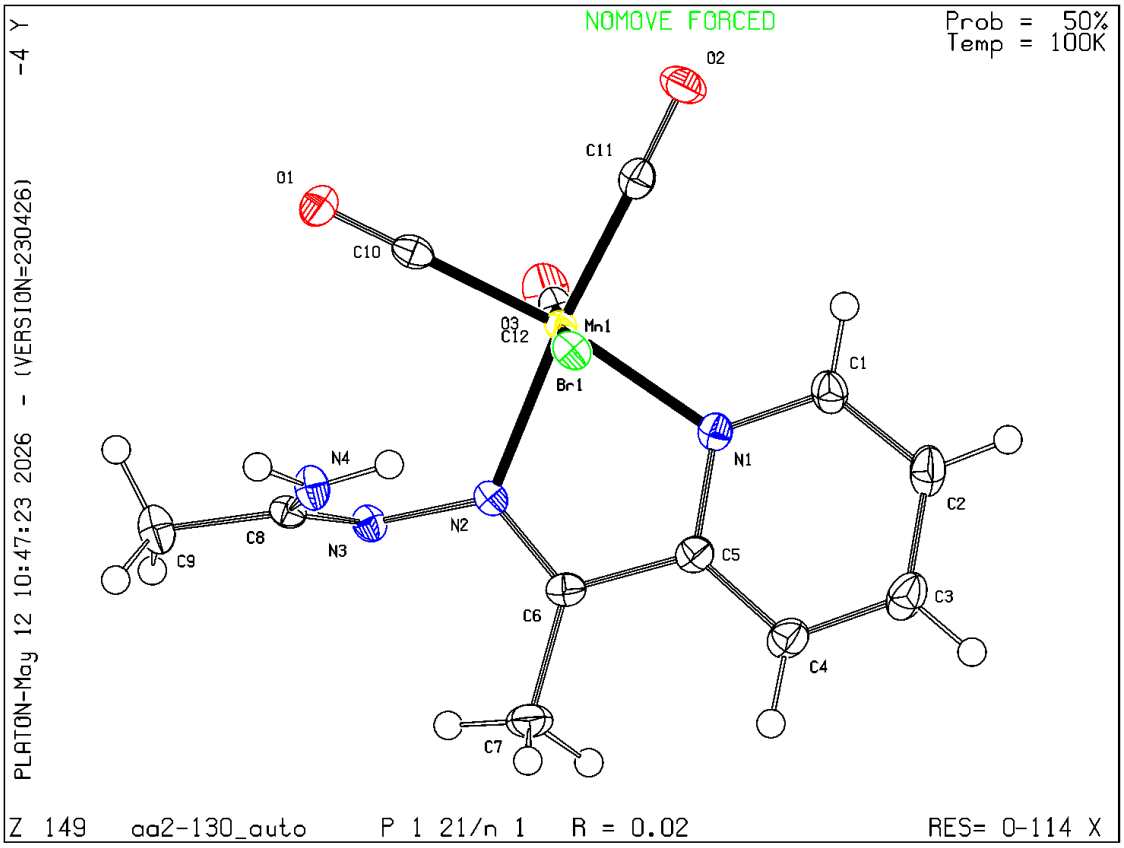
C1



C2


NOMOVE FORCED
Prob = 50%
Temp = 100K
-3 Y
PLATON-May 12 9:19:31 2026 - (VERSION=230426)
C2
C3
C1
C12
O4
C4
C11
N1
O3
C5
O1
C9
C10
Mn1
O2
C6
C7
N2
N5
N3
C8
N4
Z -50 aa310_auto P -1 R = 0.03 RES= 0-130 X

C3



9.0 References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, **2016.**

2. a) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465; b) C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
3. a) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065; b) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
4. a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299–310; b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284–298; c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283.
5. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys. B*, 2009, **113**, 6378–6396.
6. A. A. Wani, J. J. G. Carballo, H. Jayaprakash, M. Wörle, A. Widera, A. Togni and H. Grützmacher, *Chem. Eur. J.*, 2024, **30**, e202303848.
7. CrysAlisPro 1.171.44.140a (Rigaku Oxford Diffraction, 2026)
8. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
9. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.
10. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.