Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Manganese-catalysed dehydrogenative oxidation of glycerol to lactic acid

Chen-Qiang Deng, [a] Jin Deng*[a] and Yao Fu*[a,b]

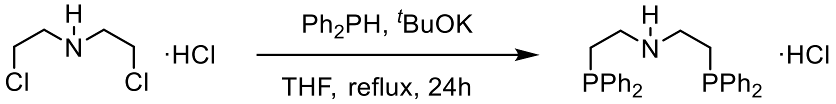
[a] Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory of Biomass Clean Energy, Center for Excellence in Molecular Synthesis of CAS, Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China;
[b] Institute of Energy, Hefei Comprehensive National Science Center, Hefei 230031, People's Republic of China
E-mail for J. Deng: dengjin@ustc.edu.cn
E-mail for Y. Fu: fuyao@ustc.edu.cn

I. General Information

All reactions were carried out under argon atmosphere using Schlenk techniques. All solvents were reagent grade or better. Pentacarbonylbromomanganese ($Mn(CO)_5Br$) was purchased from Alfa Aesar. Manganese chloride ($MnCl_2$), Cobaltous chloride ($CoCl_2$), and Potassium diphenylphosphide (0.5 mmol/L in THF) were purchased from Energy Chemical Co., Ltd. Bis[(2-diipropylphosphino)ethyl]amine, Bis(2-[dicyclohexylphosphaneyl)ethyl]amine (10 wt.% in THF), and 2,6-Bis[(diphenylphosphaneyl)methyl]pyridine ligands were purchased from Sinoco Technology Co., Ltd and used without further purification. Deuterated solvents were ordered from Cambridge Isotope Laboratories. Glyceraldehyde and dihydroxyacetone were purchased from Adamas Reagent Co., Ltd. Other reagents were ordered from commercial sources with >95% purity and used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on the Bruker AVANCE NEO 400 MHz spectrometer at ambient temperature. Chemical shifts (δ) for ^1H and ^{13}C-NMR spectra are given in ppm relative to tetramethyl silane (TMS).

II. Ligand Synthesis

Synthesis of Bis(2-(diphenylphosphino)ethyl)amine hydrochloride[1]

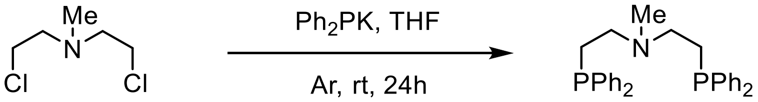


A solution of 16 mmol of Ph_2PH (2.96 g) in 50 mL of THF was added to the three-necked flask. 25 mmol of potassium tert-butoxide (2.8 g) was added at 0 °C and stirred for 10 min. Then 8 mmol of dichloroethylenediamine hydrochloride (1.43 g) was added to the above flask. The reaction mixture was stirred at 65°C for 24 hours under argon atmosphere. Upon completion, 50 mL of n-hexane was added and then washed with 10% aqueous NaOH and saturated brine. The organic layer was separated, and 2 mol/L hydrochloric acid solution was added. The crude product was obtained by filtration. The crude product was recrystallized with hot acetonitrile to afford pure the desired product (2.51g, 71% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 10.20 – 9.81 (m, 2H), 7.47 – 7.26 (m, 20H), 2.92 (dp, *J* = 14.7, 5.1 Hz, 4H), 2.65 – 2.44 (m, 4H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -20.90.

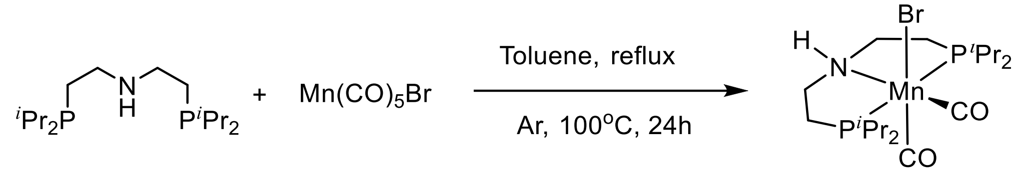
Synthesis of 2-(diphenylphosphaneyl)-N-(2-(diphenylphosphaneyl)ethyl)-N-methylethan-1-amine



A solution of 10 mmol of Ph_2PK (20 mL, 0.5 mol/L in THF) was added a 100 mL Schlenk flask. After cooling to 0 °C, a solution of 5 mmol of 2-chloro-N-(2-chloroethyl)-N-methylethan-1-amine in 10 mL of THF were added dropwise under constant stirring. The reaction mixture could be allowed to reach room temperature and then stirred overnight under an argon atmosphere. Upon completion, 10 mL of degassed water were added. The organic phase was separated and then dried over magnesium sulfate. The solvent was removed in vacuum to give a colorless oil liquid (1.48 g, 65% yield, 90 % purity according to ^{31}P NMR). The ligand was used without further purification.

III. Manganese complexes Synthesis

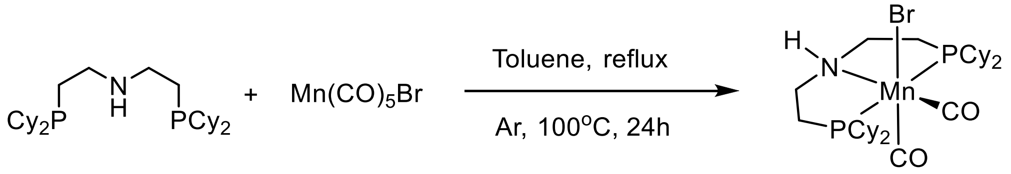
Synthesis of Mn(CO)2(Br)[HN(C2H4PiPr2)2] (Mn-1)[2]



0.31 mmol of $Mn(CO)_5Br$ was added to a 25 mL Schlenk flask containing 5 mL toluene. Then, a solution of Bis(2-(diisopropylphosphaneyl)ethyl)amine (0.33 mmol, 10 wt.% in THF) was added to the above mixture. After stirring at room temperature for 10 min, the reaction mixture was heated to 100°C and then refluxed for 24 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with n-hexane. The residue was dried in vacuo to afford **Mn-1** complex as a yellow powder (135.0 mg, 88% yield).

^{1}H NMR (400 MHz, Benzene-*d*$_6$) δ 3.26 (s, 2H), 2.87 (s, 1H), 2.51 (s, 2H), 2.21 (s, 2H), 1.96 (s, 2H), 1.67 (s, 2H), 1.51 (s, 6H), 1.27 (d, J = 39.5 Hz, 14H), 1.07 (s, 6H).
^{31}P NMR (162 MHz, Benzene-*d*$_6$) δ 81.25.

Synthesis of $Mn(CO)_2(Br)[HN(C_2H_4PCy_2)_2]$ (Mn-2)[2]

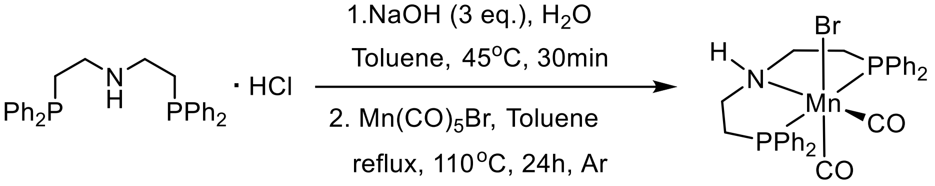


0.30 mmol of $Mn(CO)_5Br$ was added to a 25 mL Schlenk flask containing 10 mL toluene. Then, 0.33 mmol Bis(2-(dicyclohexylphosphaneyl)ethyl)amine was added to the above mixture. After stirring at room temperature for 10 min, the reaction mixture was heated to 100°C and then refluxed for 24 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with n-hexane. The residue was dried in vacuo to afford **Mn-2** complex as a yellow powder (181.0 mg, 92% yield).

^{1}H NMR (400 MHz, Benzene-*d*$_6$) δ 3.02 (s, 3H), 2.75 (s, 4H), 1.86 (m, 33H), 1.30 (m, 13H).

^{31}P NMR (162 MHz, Benzene-*d*$_6$) δ 73.09.

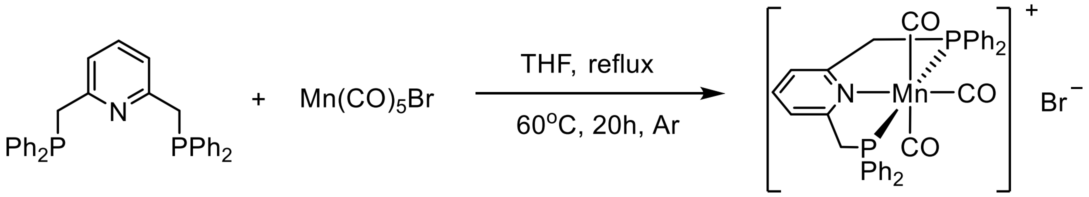
Synthesis of $Mn(CO)_2(Br)[HN(C_2H_4PPh_2)_2]$ (Mn-3)[3]



A suspension of 0.85 mmol of ^{Ph}PNP • HCl ligand in 8 mL toluene was added to a solution of 2.4 mmol NaOH in 2 mL water. The reaction mixture was stirred at 45°C for 30 minutes. The organic phase was separated and washed 3 times with water. The solvent was removed by in vacuo to yield ^{Ph}PNP free ligand as a colorless oil. 0.80 mmol of $Mn(CO)_5Br$ was added to a 50 mL Schlenk flask containing 15 mL toluene. Then, 0.82 mmol Bis(2-(diphenylphosphaneyl)ethyl)amine was added to the above mixture. After stirring at room temperature for 10 min, the reaction mixture was heated to 110°C and then refluxed for 24 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with n-hexane. The residue was dried in vacuo to afford **Mn-3** complex as a yellow powder (475.1 mg, 94% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90 (s, 4H), 7.58 (d, $J = 5.2$ Hz, 4H), 7.35 (ddd, $J = 25.0, 16.4, 6.3$ Hz, 12H), 3.67 (s, 2H), 3.52 (s, 1H), 3.27 (s, 2H), 2.76 (s, 2H), 2.42 (s, 2H).
^{31}P NMR (162 MHz, CD_2Cl_2) δ 69.64.

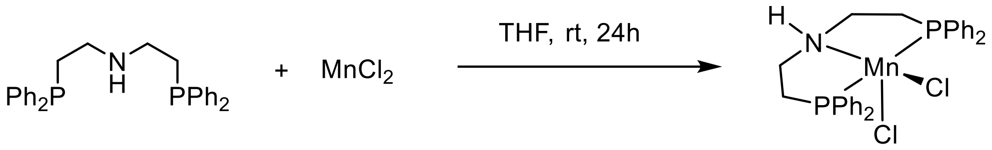
Synthesis of $Mn(Ph_2PCH_2)_2(C_5H_3N)(CO)_3Br$ (Mn-4)[4]



0.99 mol of 2,6-Bis((diphenylphosphaneyl)methyl)pyridine and 0.9 mmol of $Mn(CO)_5Br$ were added to a 50 ml Schlenk flask. 20 mL THF was then added to the above mixture. The reaction mixture was heated to 60°C and then refluxed for 20 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with n-hexane and dichloromethane. The residue was dried in vacuo to afford **Mn-2** complex as a yellow powder (568.3 mg, 91% yield).

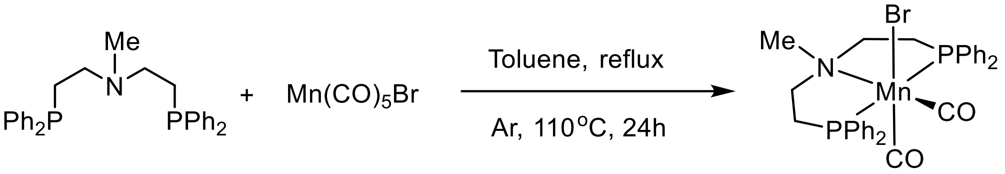
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.15 (s, 2H), 7.47 (d, J = 59.6 Hz, 21H), 4.95 – 4.31 (m, 4H).
^{31}P NMR (162 MHz, CD_2Cl_2) δ 69.38.

Synthesis of $Mn(Cl_2)[HN(C_2H_4PPh_2)_2]$ (Mn-5)[2b]



0.3 mol of 2,6-Bis((diphenylphosphaneyl)methyl)pyridine and 0.33 mmol of $MnCl_2$ were added to a 25 ml Schlenk flask. Then, 7 mL THF was added to the above mixture. The reaction mixture was stirred at room temperature for 24 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with Et_2O. The residue was dried in vacuo to afford **Mn-5** complex as a white powder (144.1 mg, 85% yield).

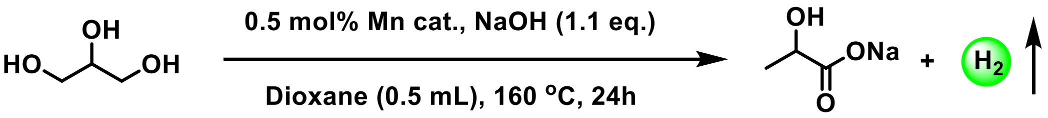
Synthesis of $Mn(CO)_2(Br)[MeN(C_2H_4PPh_2)_2]$ (Mn-7)[5]



0.30 mmol of $Mn(CO)_5Br$ was added to a 25 mL Schlenk flask containing 10 mL toluene. Then, 0.33 mmol 2-(diphenylphosphaneyl)-N-(2-(diphenylphosphaneyl)ethyl)-N-methylethan-1-amine was added to the above mixture. After stirring at room temperature for 10 min, the reaction mixture was heated to 100 °C and then refluxed for 24 hours under argon atmosphere. The volatiles were removed in vacuo and the residue was washed with n-hexane. The residue was dried in vacuo to afford **Mn-2** complex as a yellow powder (170.4 mg, 88% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (s, 8H), 7.39 (d, *J* = 30.1 Hz, 12H), 3.71 (s, 2H), 3.15 (s, 2H), 2.94 (s, 2H), 2.63 (s, 3H).
^{31}P NMR (162 MHz, CD_2Cl_2) δ 69.03.

IV. General procedure for Mn-catalyzed conversion of glycerol to lactic acid



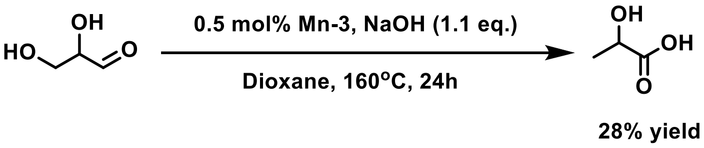
A 25 mL pressure-resistant Schlenk tube was charged with a stirring bar, 5 mmol glycerol, 0.5 mol% Mn catalyst, 5.5 mmol NaOH, and 0.5 mL Dioxane were added. The reaction mixture was placed in a preheated oil bath at 160 ^{o}C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled and the gas was released carefully. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard.

V. Poisoning experiments with mercury and triphenylphosphine

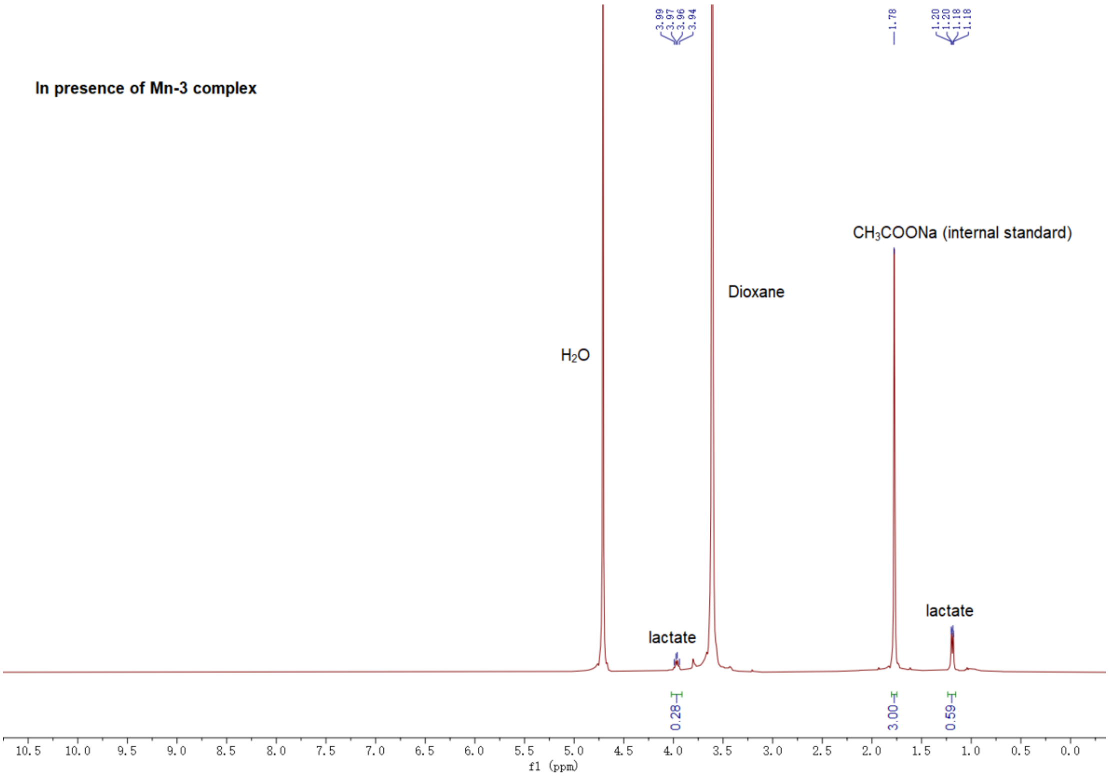
A 25 mL pressure-resistant Schlenk tube was charged with a stirring bar, glycerol (5 mmol), **Mn-3** (0.025 mmol), NaOH (5.5 mmol), Dioxane (0.5 mL) and a drop of mercury or triphenylphosphine (equivalents respect to **Mn-3**) under an argon atmosphere. The sealed Schlenk tube was taken out of the glove box and heated at 160 ^{o}C for 24 h. Upon completion, the reaction was quenched by adding 5 mL of water. The yield of sodium lactate was determined by ^{1}H NMR with sodium acetate as the internal standard.

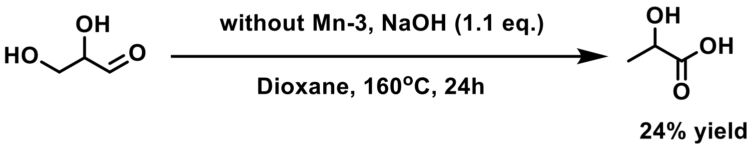
Entry	additives	Yield	TON
1	a drop of Hg	96%	192
2	0.0125 mmol PPh_3	95%	190
3	0.025 mmol PPh_3	95%	190

VI. Control and Mechanistic Experiments

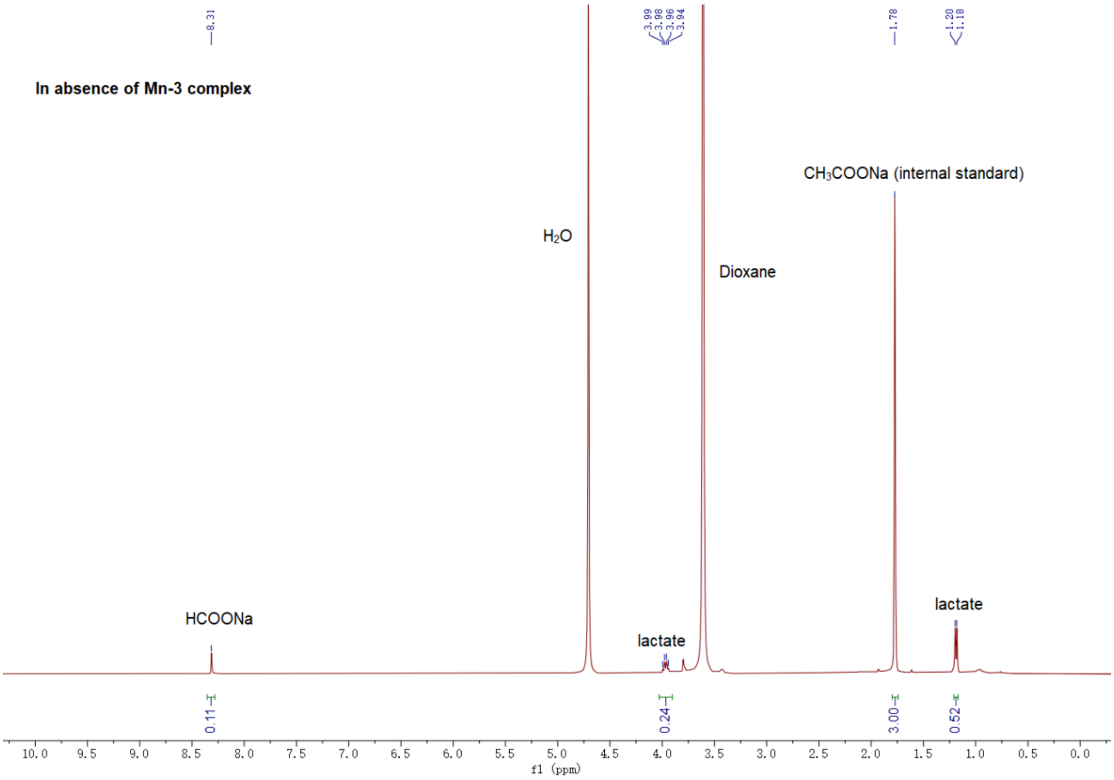


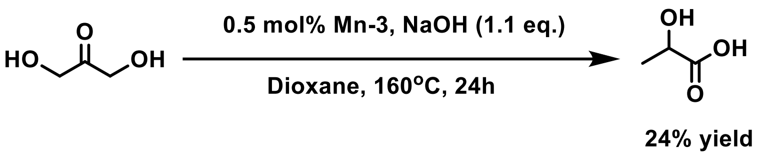
In a glove box, 5 mmol glyceraldehyde, 0.5 mol% **Mn-3** catalyst, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled and the gas was released carefully. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. 28% yield of sodium lactate was detected in the reaction.



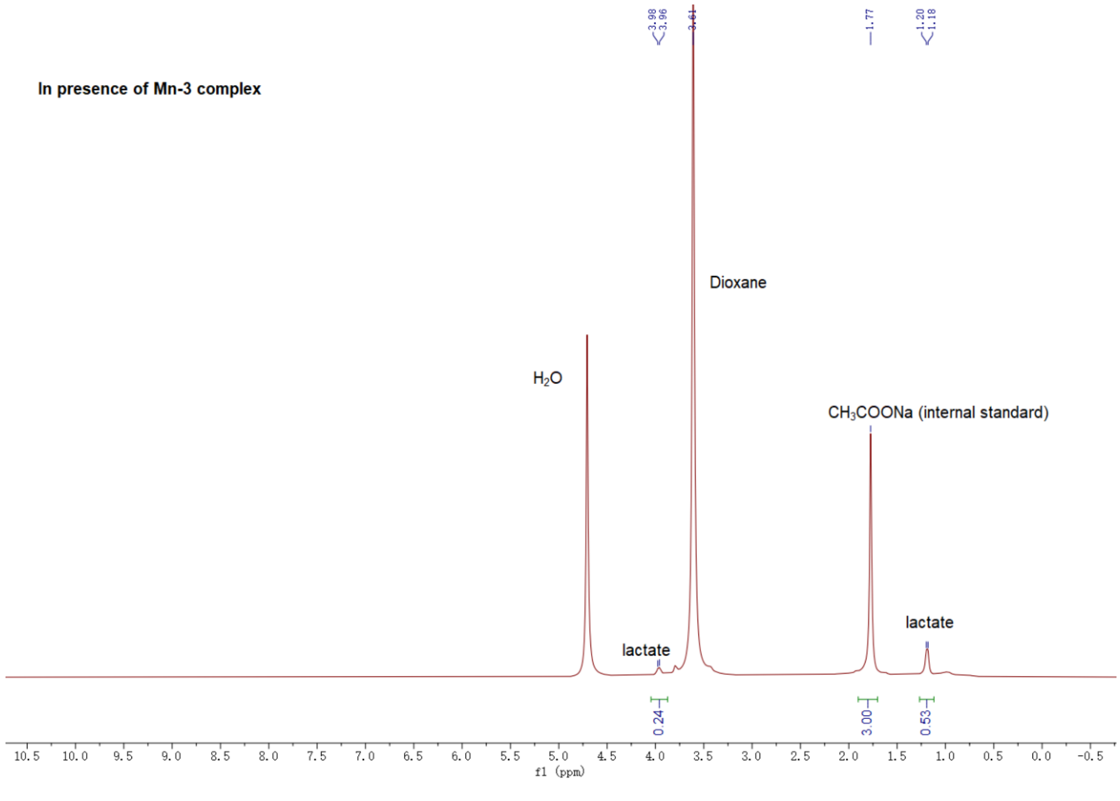


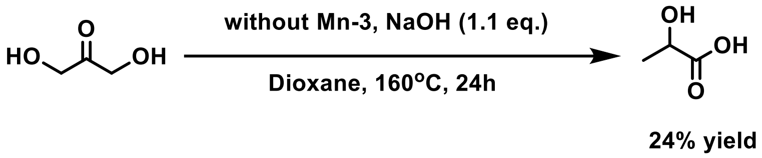
In a glove box, 5 mmol glyceraldehyde, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled and the gas was released carefully. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. 24% yield of sodium lactate was detected in the reaction. Meanwhile, it was found that an 11% yield of sodium formate was observed. We speculated that the formation of sodium formate was via sodium hydroxide to attack the C=O bond of glyceraldehyde, followed by cleavage of the C-C bond.



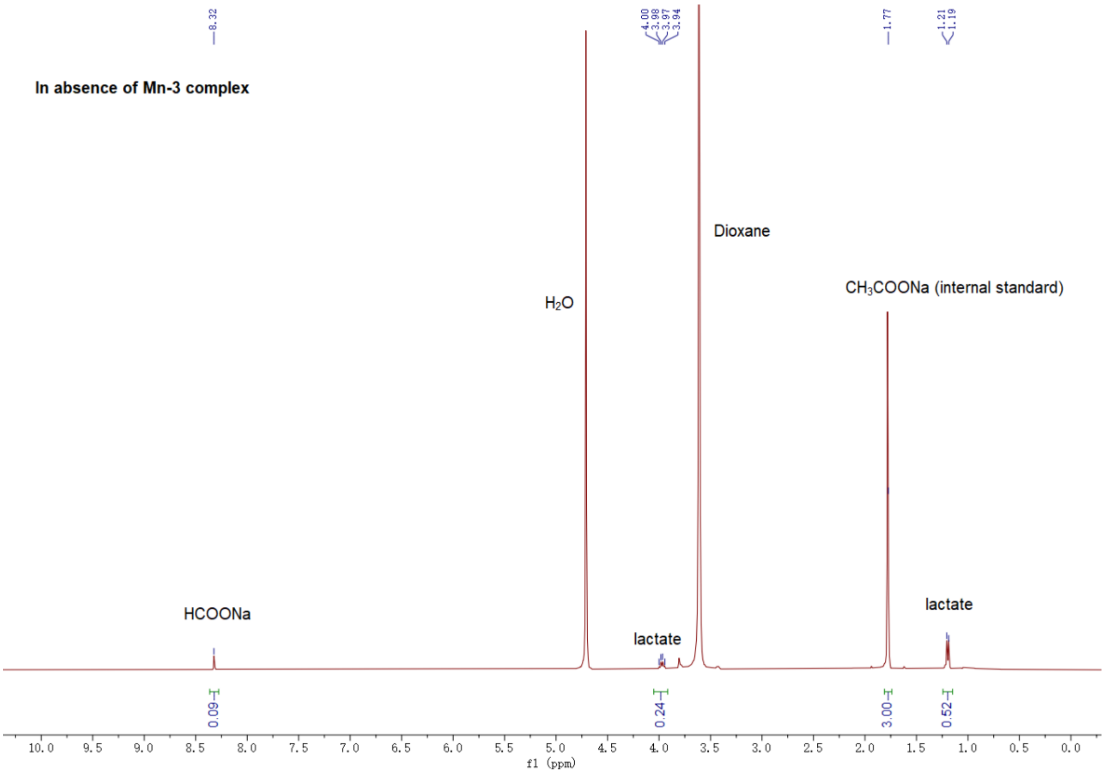


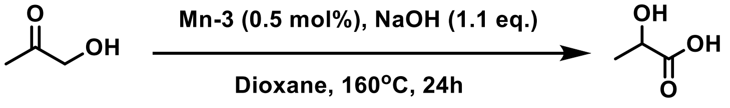
In a glove box, 5 mmol dihydroxyacetone, 0.5 mol% **Mn-3** catalyst, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled and the gas was released carefully. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. A 24% yield of sodium lactate was observed and sodium formate was not detected. This result was similar to that of glyceraldehyde in presence of Mn-3.



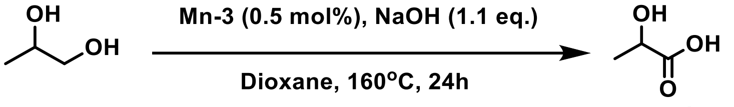


In a glove box, 5 mmol dihydroxyacetone, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled and the gas was released carefully. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. This result was similar to that of glyceraldehyde in absence of Mn-3.



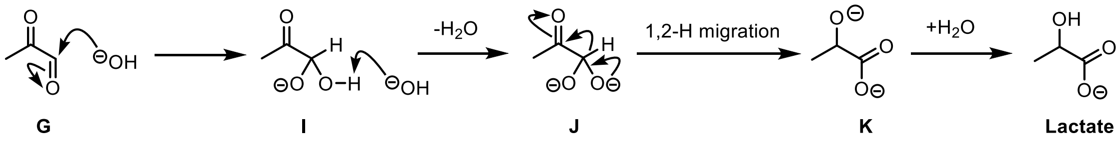


In a glove box, 5 mmol acetol, 0.5 mol% **Mn-3** catalyst, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. The formation of sodium lactate was not detected.



In a glove box, 5 mmol 1,2-propanediol, 0.5 mol% **Mn-3** catalyst, 5.5 mmol NaOH, and 0.5 mL Dioxane were added to a 25 mL pressure-resistant Schlenk tube. The reaction mixture was placed in a preheated oil bath at 160 °C for 24 hours under argon atmosphere. Upon completion, the Schlenk tube was cooled. The reaction was quenched by adding 5 mL of water. The lactate yield was determined by ^{1}H NMR with sodium acetate as an internal standard. The formation of sodium lactate was not detected.

Scheme S1. A possible reaction mechanism for the conversion of pyruvaldehyde to lactate.



The sodium hydroxide first attacked the aldehyde group of pyruvaldehyde **G** to form a tetrahedral intermediate **I**, which then abstracted protons by the base to give a double anion **J**. Next, it underwent 1,2-hydrogen migration to afford intermediate **K**. Finally, the lactate was obtained by protonation.

VII. Identification of reactive intermediates

In the glove box, 0.0316 mmol (20 mg) of **Mn-3** was added and dissolved in 1.0 mL of tetrahydrofuran (THF) in Young-NMR tube. After testing ^{31}P NMR on a Bruker Avance 600 (150 MHz), the tube was retrieved. Then, NaOH (100 eq.) was added to the above Young-NMR tube in the glove box. The solution changed from yellow to bright red after stirring at room temperature for 60 min. The mixture was determined by ^{31}P NMR. Next, upon addition of glycerol to the mixture, the solution immediately turned from bright red to yellow. The ^{31}P NMR spectra of these mixtures were provided as shown in **Figure S1**.

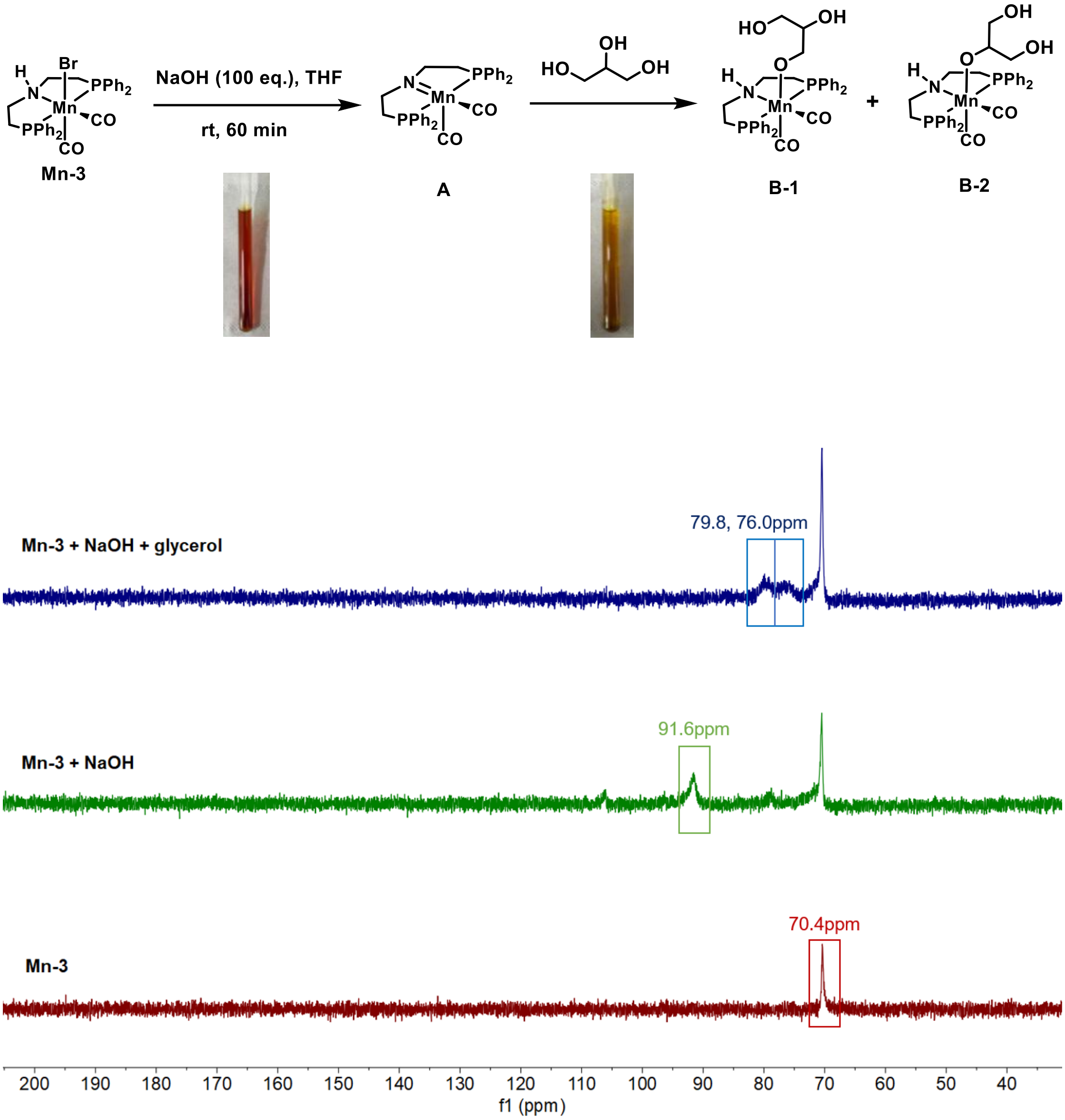
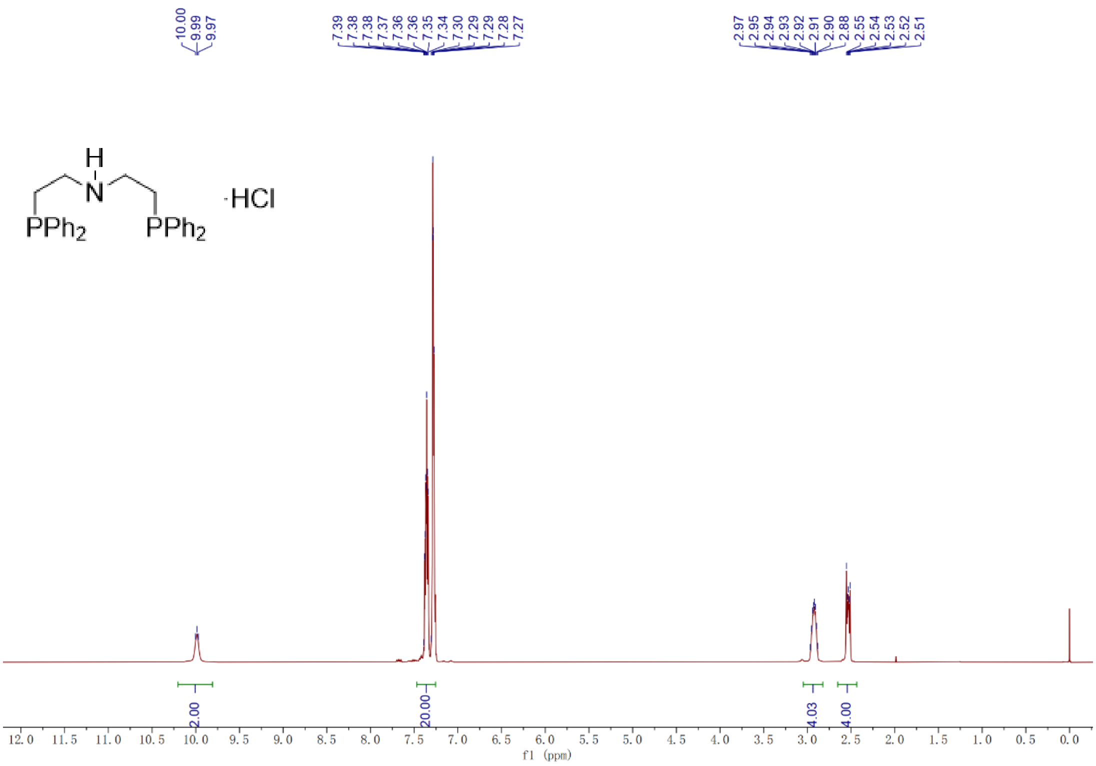
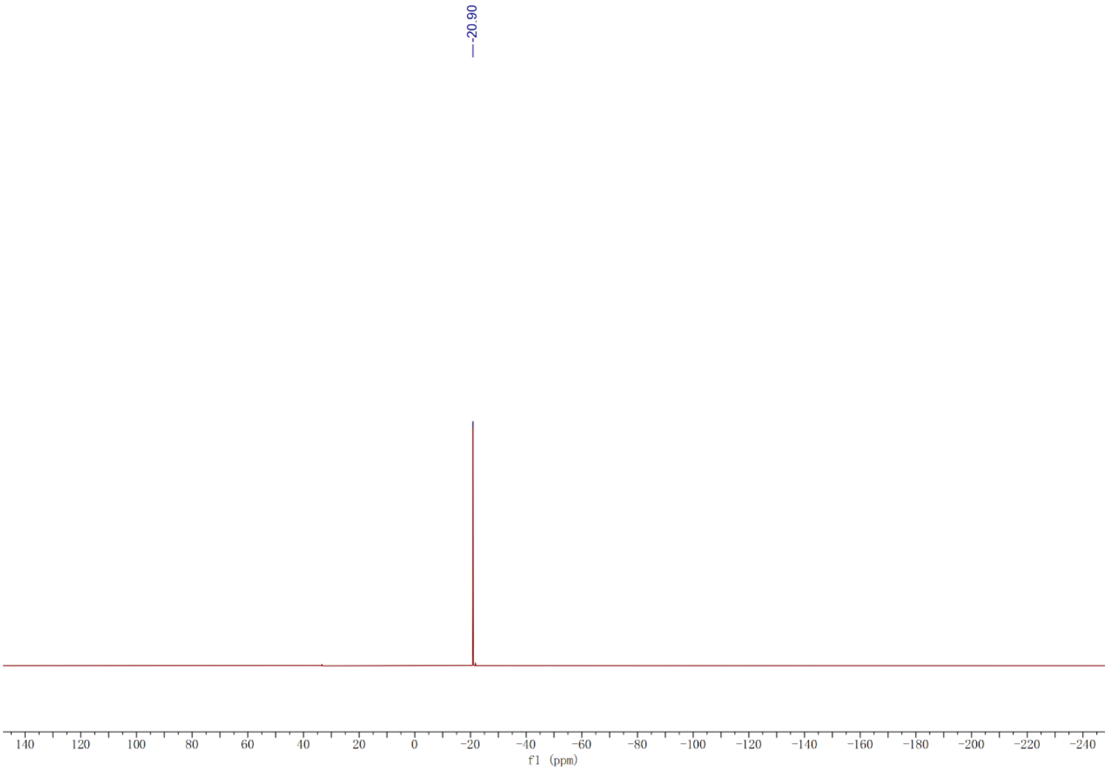
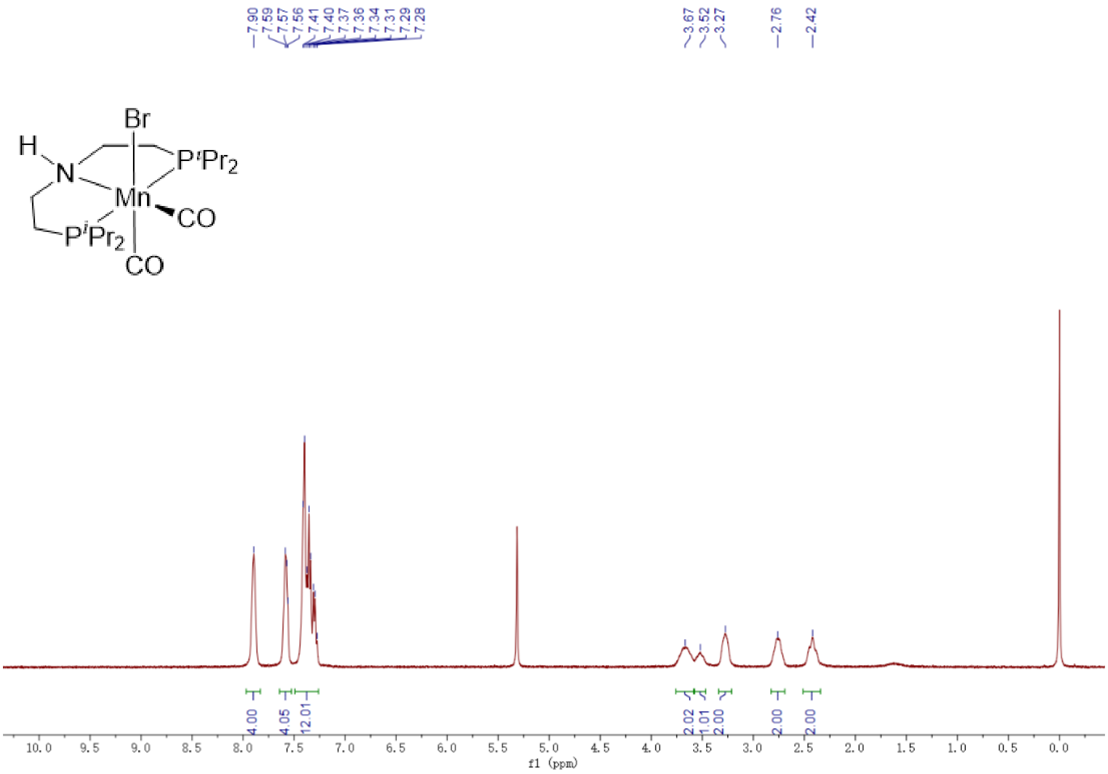


Figure S1. Identification of manganese species by using in situ ^{31}P NMR.

VIII. NMR spectrum



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7.59
7.57
7.56
7.41
7.40
7.37
7.36
7.34
7.31
7.29
7.28
3.67
3.52
3.27
2.76
2.42
Br
H
N
Mn
P^{i}Pr$_2$
P^{i}Pr$_2$
CO
CO
4.00
4.05
12.01
2.02
1.01
2.00
2.00
2.00
10.0
9.5
9.0
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2.0
1.5
1.0
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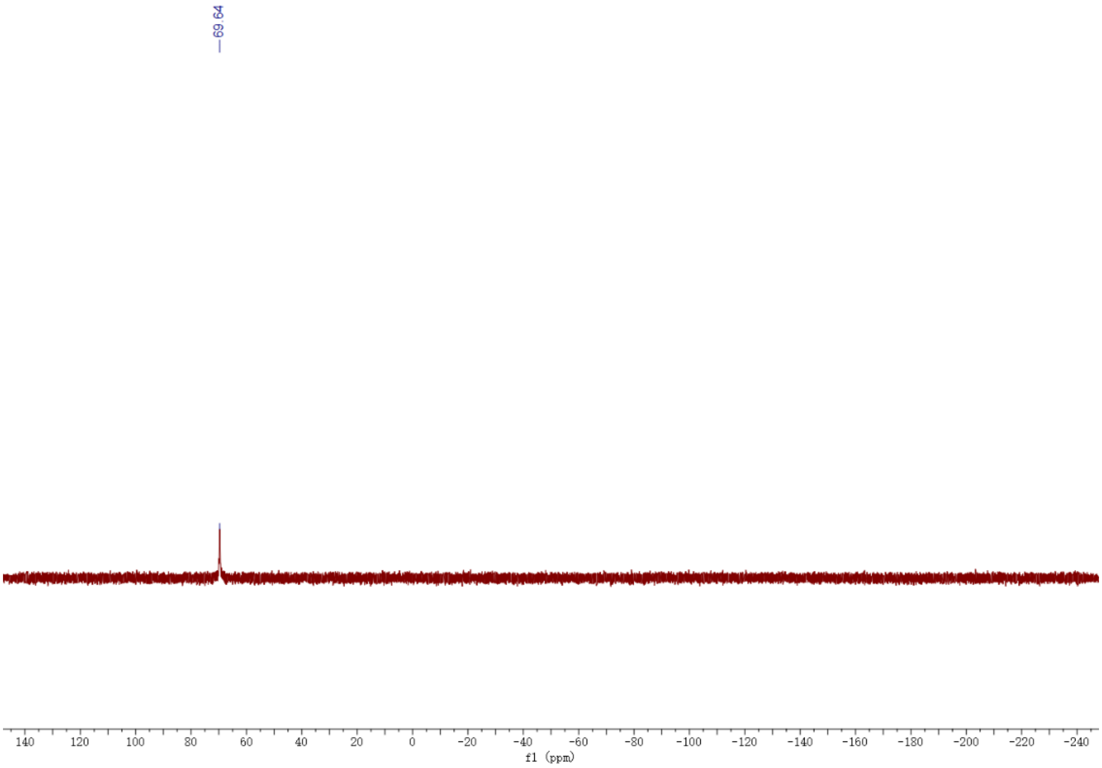
0.0
f1 (ppm)


69.64
140
120
100
80
60
40
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-60
-80
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-140
-160
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-200
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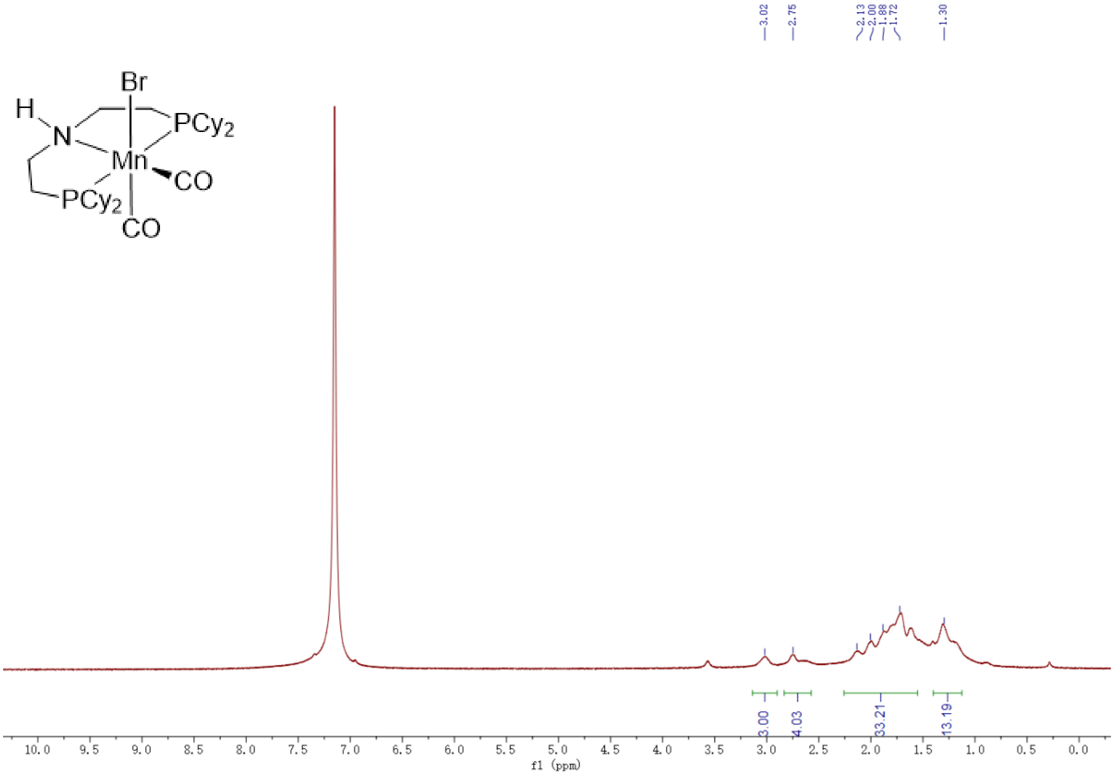
-240
f1 (ppm)



3.02
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1.72
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Br
H
N
Mn
PCy2
PCy2
CO
CO
3.00
4.03
33.21
13.19
10.0
9.5
9.0
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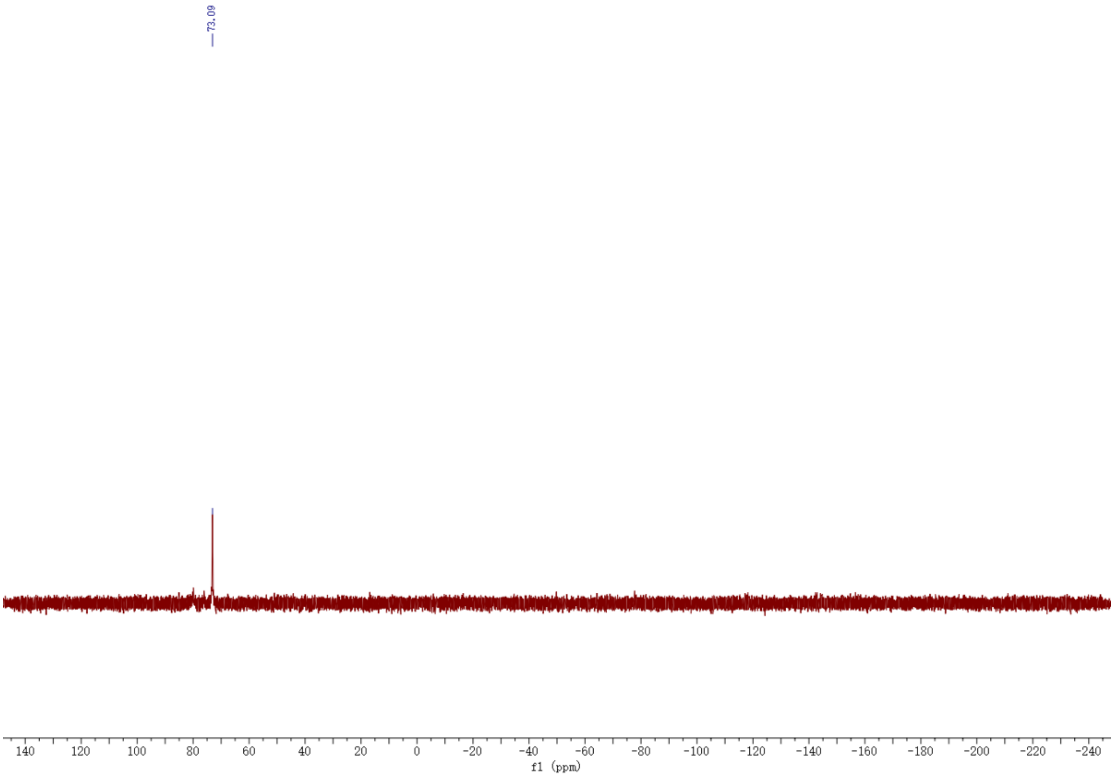
f1 (ppm)



73.09
140
120
100
80
60
40
20
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-80
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-120
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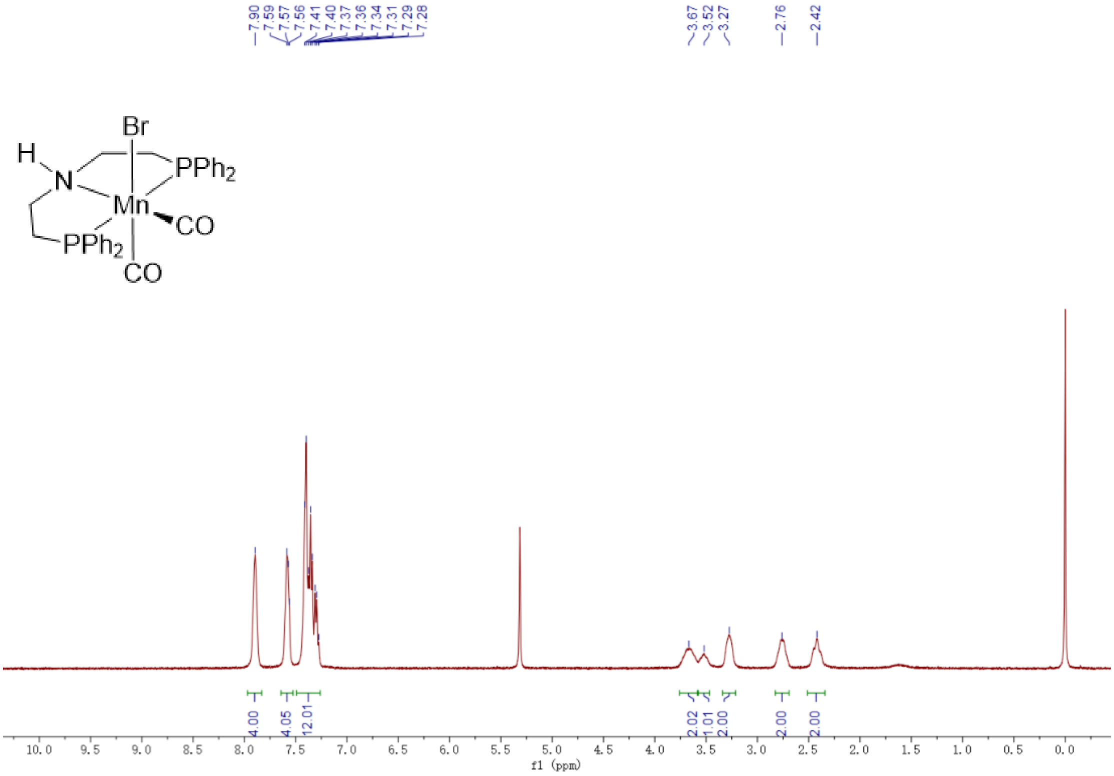
-220
-240
f1 (ppm)


7.90
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7.57
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7.41
7.40
7.37
7.36
7.34
7.31
7.29
7.28
3.67
3.52
3.27
2.76
2.42
Br
H
N
PPh2
Mn
CO
PPh2
CO
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4.05
12.01
2.02
1.01
2.00
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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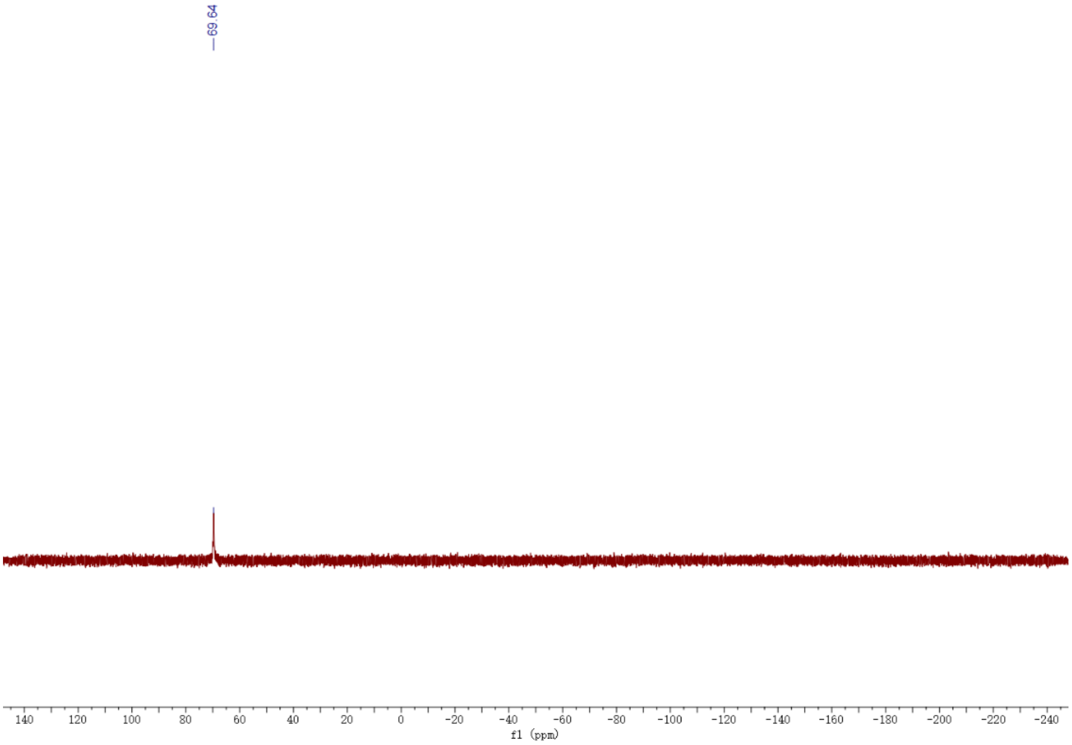
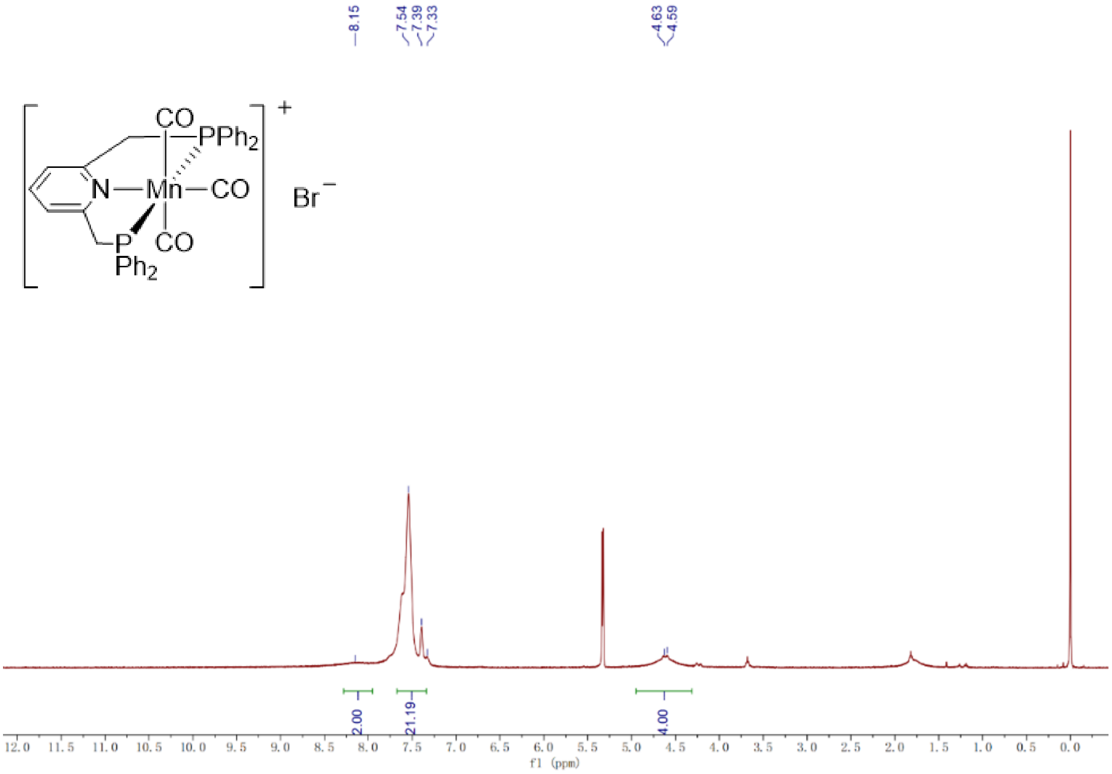
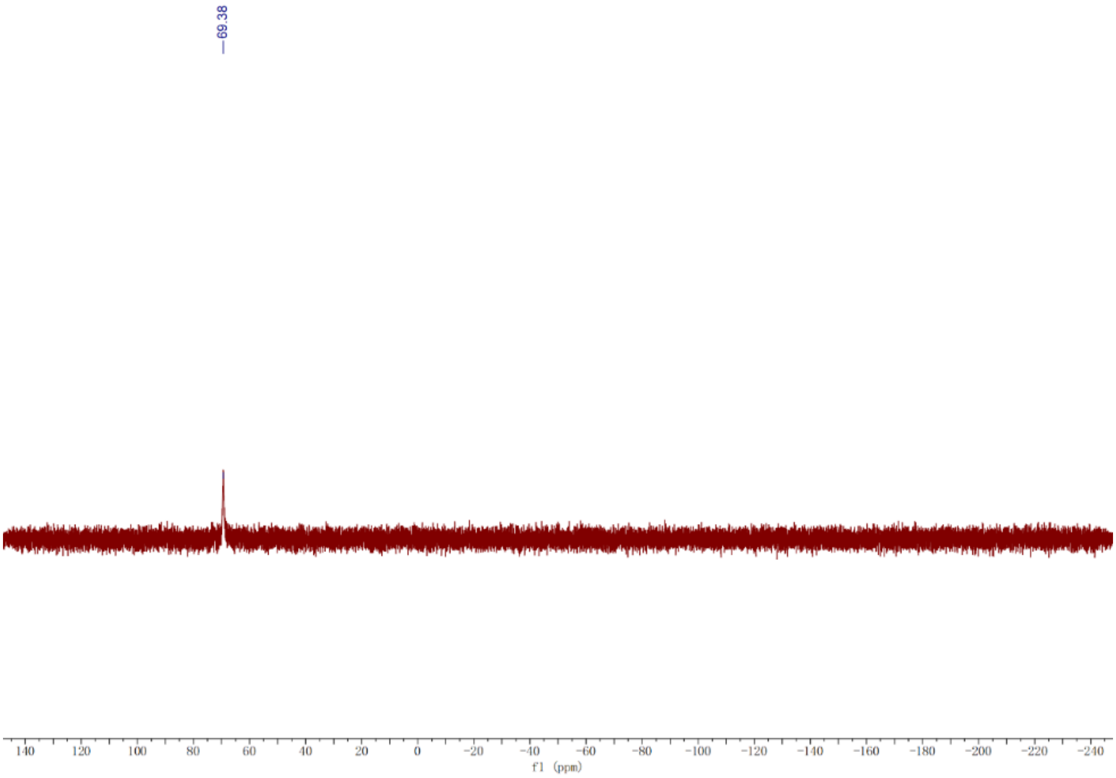
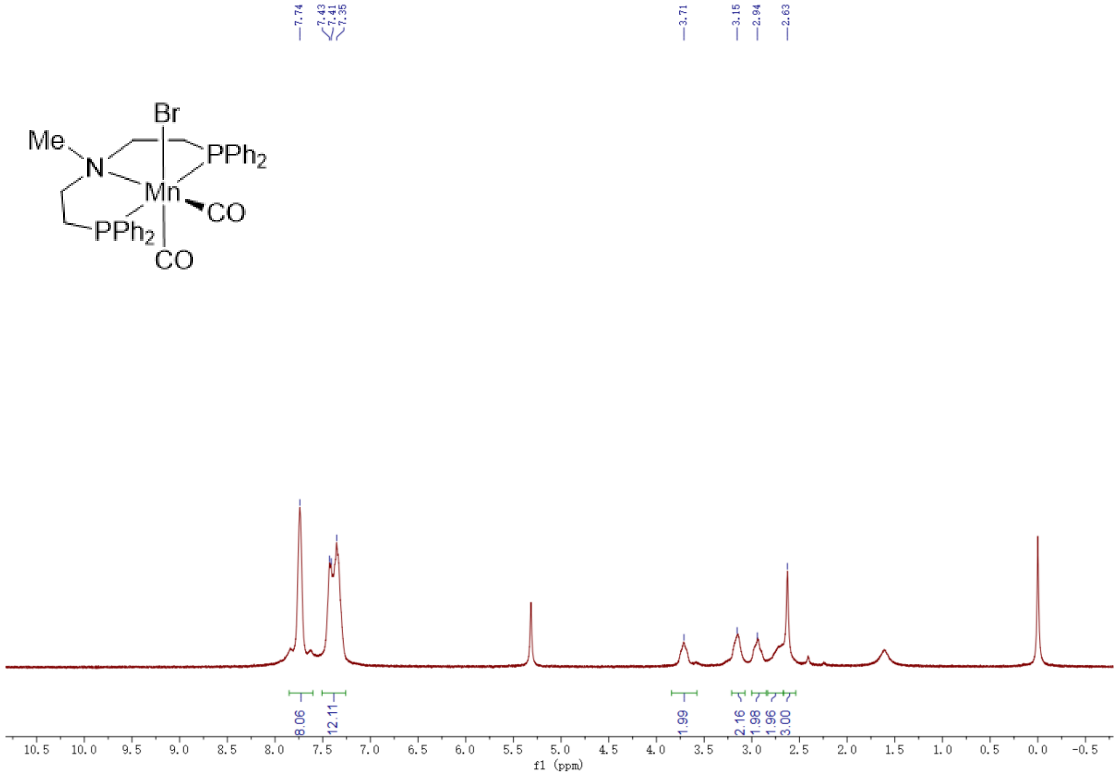
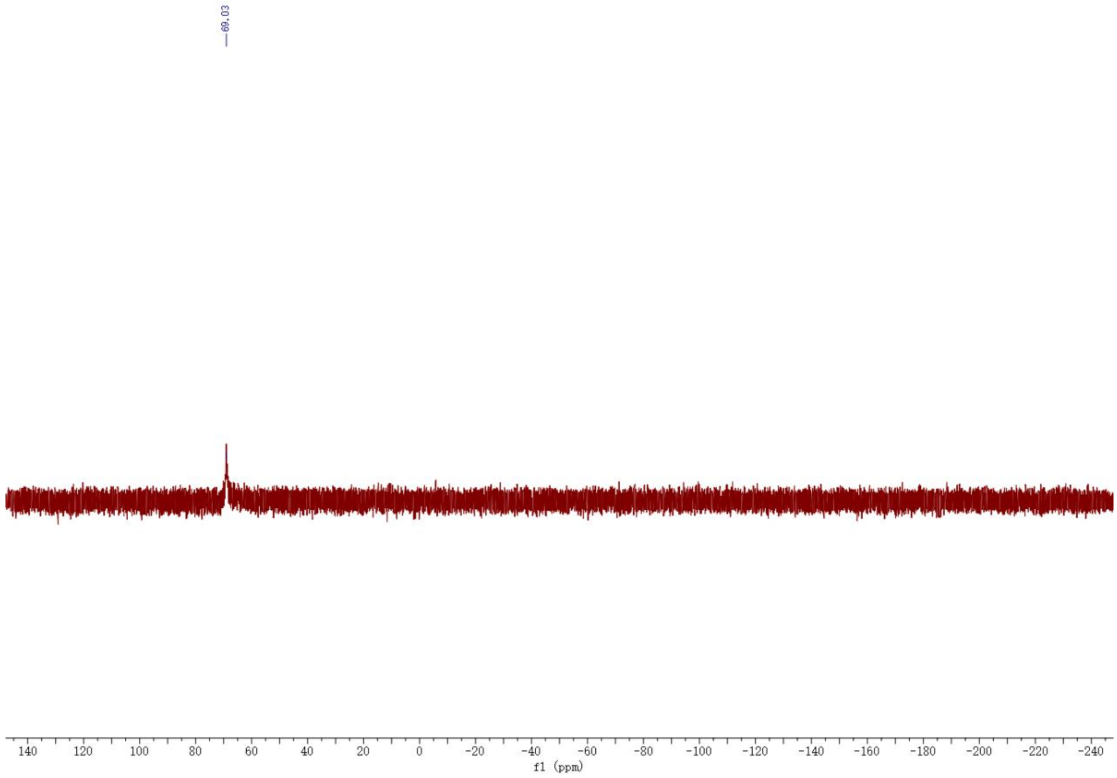
f1 (ppm)


69.64
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


8.15
7.54
7.39
7.33
4.63
4.59
CO
PPh2
N
Mn
CO
Br−
P
CO
Ph2
+
2.00
21.19
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


69.38
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)


7.74
7.43
7.41
7.35
3.71
3.15
2.94
2.63
Br
Me
N
PPh2
Mn
CO
PPh2
CO
8.06
12.11
1.99
2.16
1.98
1.96
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


69.03
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

VIII. References

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