# Catalytic Synthesis of Methylmalonate Salt from Ethylene and Carbon Dioxide through Photo-induced Activation and Photoredox-catalyzed Reduction of Nickelalactones

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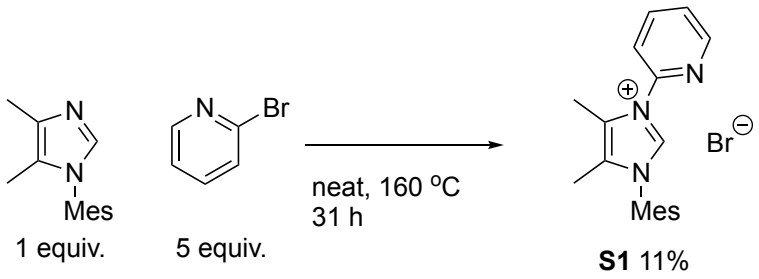
## General methods

$^{1}H$, $^{13}C$, $^{31}P$ NMR spectra were recorded on a JEOL ECZ-500 (500 MHz for $^{1}H$, 125 MHz for $^{13}C$ and 202 MHz for $^{31}P$), a JEOL ECX-500 (500 MHz for $^{1}H$, 125 MHz for $^{13}C$ and 202 MHz for $^{31}P$) or a JEOL ECS-400 (400 MHz for $^{1}H$, 100 MHz for $^{13}C$ and 160 MHz for $^{31}P$) in $CDCl_3$, $CD_2Cl_2$, $C_6D_6$, $D_2O$ or THF-$d_8$. Chemical shifts are expressed in parts per million (ppm) using residual solvent signals for $^{1}H$ (7.26 ppm for $CDCl_3$, 5.32 ppm for $CD_2Cl_2$, 7.15 for $C_6D_6$, 4.79 for $D_2O$, and 1.73 ppm for THF-$d_8$) and the solvent signal for $^{13}C$ (77.16 ppm for $CDCl_3$, 53.84 ppm for $CD_2Cl_2$, 128.06 for $C_6D_6$, and 25.31 ppm for THF-$d_8$) as internal standards, and 85% $H_3PO_4$ aq. as an external standard for $^{31}P$. IR spectra were recorded on a Cary 630 (Agilent Technologies) spectrometer. Mass spectra were recorded on a Bruker micrOTOF–QII (ESI-mass) mass spectrometer. Crystal data were collected by a Rigaku XtaLAB Synergy R-DW system. Photoirradiation was conducted by using Relyon Twin LED Light with sockets of 365, 395 or 425 nm light or an USHIO Optical Modulex OPM2-502XQ Hg lamp without optical filter, in a water bath (for the reactions at room temperature) or in an oil bath (for the reactions with heating). Silica Gel 60 (Kanto Chemical Co., Inc.) was used for flash column chromatography. Merck Kieselgel 60 F254 (0.25 mm thickness, coated on glass 20×20 $cm^2$) plate was used for analytical thin layer chromatography (TLC). Dehydrated THF, $Et_2O$, *n*-hexane and toluene were purchased from Kanto Chemicals and purified by solvent purification system of Glass-Contour. Dehydrated $CH_2Cl_2$ and DMA (*N,N*-dimethylacetamide) were purchased from Kanto Chemicals. $CH_2Cl_2$ was degassed by three freeze-pump-thaw cycles and DMA was degassed by Ar bubbling. Benzene-$d_6$ and THF-$d_8$ were purchased from Kanto Chemicals, and dried and degassed by benzophenone ketyl. $CD_2Cl_2$ was dried over 4 Å molecular sieves and degassed by three freeze-pump-thaw cycles. Other deuterated solvents were purchased from Kanto Chemicals and used as received. DIPEA (*N,N*-diisopropylethylamine) was purchased from TCI, distilled, dried over 4 Å molecular sieves and degassed by three freeze-pump-thaw cycles. Ethylene/$CO_2$ (1 : 1) cylinder was purchased from Kayama Sanso. Other reagents were purchased from TCI, Kanto Chemicals, Aldrich, or Fujifilm Wako Chemicals and used as received. 5-membered nickelalactone bearing dcype **2**[1] (dcype = 1,2-bis(dicyclohexylphosphino)ethane) and 4-membered nickelalactone bearing dcype **7**[2] were prepared according to the literature procedure. NMR spectra of nickelalactones bearing an NHC-P ligand were collected quickly after preparing an NMR sample (within 1 day) in thoroughly dried and degassed THF-$d_8$ since isomerization to their geometrical isomers slowly takes place at room temperature and a small amount of water facilitates the isomerization. The effect of water in isomerization of nickelalactone was described in our previous report.[3] Diisopropylphosphonylmethanol[4] was prepared by the same method reported for the synthesis of Di-*tert*-butylphosphonylmethanol[5], and the spectral data was matched with the literature report of Diisopropylphosphonylmethanol prepared by another method. **Ni(NHC$^{Me}$-P$^{Cy}$)(cod)** (starting material of **4**/**4'**) was prepared by our previously reported method.[3] Data of X-ray single crystal analysis of **8** is available on the Cambridge Crystallographic Data Centre (CCDC deposition numbers is 2121037).

## Synthesis of NHC-P nickel complexes

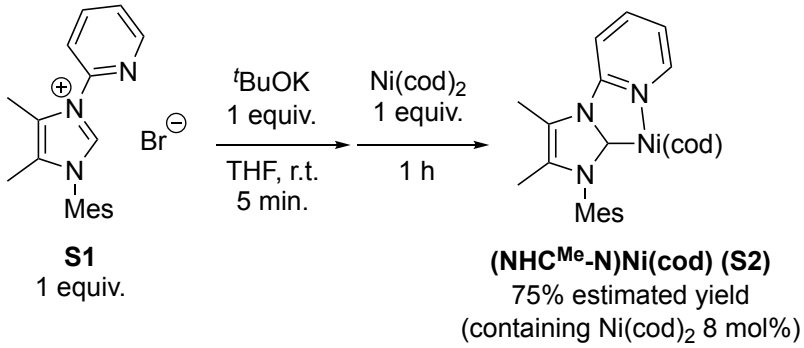
### 1-(2-pyridyl)-3-mesityl-4,5-dimethylimidazolium bromide (S1)




To a test tube were added 1-mesityl-4,5-dimethylimidazole (0.600 g, 2.80 mmol)[6] and 2-bromopyridine (2.23 g, 14.1 mmol), and the mixture was heated at 160 °C for 31 h. To the mixture was added $Et_2O$ and the resulting solid was collected by filtration and washed with $Et_2O$ to give **S1** as a brown solid (117 mg, 0.31 mmol, 11% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 2.04 (s, 3H), 2.15 (s, 6H), 2.36 (s, 3H), 2.57 (s, 3H), 7.05 (s, 2H), 7.51 (dd, *J* = 5.0, 8.0 Hz, 1H), 8.13 (dt, *J* = 1.5, 7.5 Hz, 1H), 8.59 (d, *J* = 5.0 Hz, 1H), 8.89 (d, *J* = 8.0 Hz, 1H), 10.6 (s, 1H).
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 8.4, 11.0, 18.1, 21.3, 121.1, 125.6, 127.8, 128.1, 128.7, 130.1, 134.9, 136.1, 140.8, 141.5, 147.2, 148.9.
IR (ATR): 3075, 2995, 2980, 2917, 2857, 2756, 1589, 1528, 1476, 1437, 1325, 1288, 1232, 1042, 995, 915, 863, 814, 792, 762, 747, 669 $cm^{-1}$
HRMS (ESI): *m/z* Calcd. for $C_{19}H_{22}N_3^+$ : 292.1808, Found: 292.1810.

### Synthesis of (NHC$^{Me}$-N)Ni(cod) (S2)

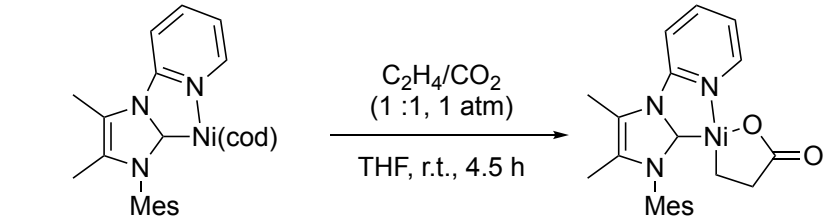



In an Ar filled glove box, to a 20 mL vial with a magnetic stirring bar were added **S1** (100 mg, 0.269 mmol) and THF (4.0 mL). To the solution was added a solution of $^t$BuOK (33.2 mg, 0.296 mmol) in THF (1.0 mL) and the resulting solution was stirred for 5 minutes at room temperature to generate NHC carbene. In another 30 mL round bottomed flask, a solution of $Ni(cod)_2$ (74.0 mg, 0.269 mmol) in THF (6 mL) was prepared and the solution of the NHC carbene was added dropwise to the solution of $Ni(cod)_2$ with washing with 1 mL of THF. After the mixture was stirred for 1 h, the solvent was evaporated and the resulting solid was dissolved in a mixture of hexane and $Et_2O$ (c.a. 1 : 1), and the remaining solids were removed by filtration. The solvent was evaporated to give **S2** as a purple solid (98.0 mg,

containing 8 mol% of $Ni(cod)_2$ judging from $^1H$ NMR. Estimated amount and yield of **S2** were 0.20 mmol and 75%, respectively). The resulting mixture was used in the next step without further purification. For NMR analyses, pure sample of **S2** was prepared by recrystalization from hexane at –30 °C.

$^1H$ NMR ($C_6D_6$, 500 MHz): δ = 1.57 (s, 3H), 1.82-1.94 (m, 4H), 1.94 (s, 3H), 2.12 (s, 6H), 2.20 (s, 3H), 2.34-2.43 (m, 2H), 2.90-3.00 (m, 2H), 3.92-4.02 (m, 2H), 4.36-4.48 (m, 2H), 6.64 (t, *J* = 6.5 Hz, 1H), 6.92 (s, 2H), 7.08 (t, *J* = 8.5 Hz, 1H), 9.76 (d, *J* = 5.0 Hz, 1H). (One aromatic proton is missing probably due to overlapping with $C_6D_5H$).
$^{13}C$ NMR ($C_6D_6$, 125 MHz): δ = 8.9, 12.6, 18.1, 21.2, 32.0, 32.8, 76.9, 80.1, 111.6, 118.5, 118.6, 126.8, 127.2, 129.1, 137.1, 137.3, 138.1, 146.4, 151.6, 200.8.

**Synthesis of (NHC-N)Ni_lac (2)**

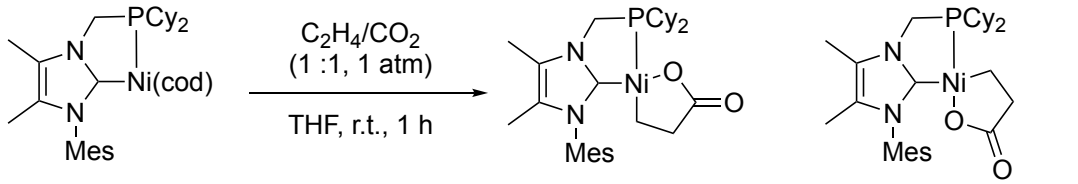



**(NHC$^{Me}$-N)Ni(cod) (S2)**
(containing $Ni(cod)_2$ 8 mol%)

**(NHC$^{Me}$-N)Ni_lac (3)**
64% estimated yield

In an Ar filled glovebox, to a Schlenk tube equipped with a J. Young valve were added **S2** (41.5 mg, containing 8 mol% of $Ni(cod)_2$, estimated amount of **S2** was 0.086 mmol) and THF (3.0 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1 : 1). After the mixture was stirred for 4.5 h, the solvent was evaporated, and the resulting solid was re-dissolved in THF and filtered to remove solids. After evaporation of the solvent, the resulting solid was washed with $Et_2O$ to give **3** as a yellow solid (23.1 mg, 0.0547 mmol, estimated yield was 64%). Concerning the geometry on the Ni atom, we assume the isomer indicated in the scheme (Carbene carbon is located *trans* to the oxygen atom of the lactone moiety) is generated by the similarity of NMR chemical shifts of the lactone part with **1** ($^1H$ NMR chemical shifts of NiC$\underline{H_2}$ (**3** : 0.36, **1** : 0.36) and $^{13}C$ NMR chemical shift of NiO$\underline{C}$O (**3** : 178.3, **1** : 177.8)).
$^1H$ NMR (THF-$d_8$, 500 MHz): δ = 0.36 (t, *J* = 7.5 Hz, 2H), 1.68 (t, *J* = 7.5 Hz, 2H), 1.76 (s, 3H), 2.08 (s, 6H), 2.34 (s, 3H), 2.59 (s, 3H), 7.02 (s, 2H), 7.38 (t, *J* = 6.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 7.0 Hz, 1H), 9.00 (d, *J* = 4.5 Hz, 1H).
$^{13}C$ NMR (THF-$d_8$, 125 MHz): δ = 0.6, 8.4, 11.8, 17.9, 21.2, 39.0, 111.6, 122.6, 123.8, 129.2, 129.9, 134.7, 135.8, 140.0, 140.2, 149.8, 151.9, 178.3, 185.4.
IR (ATR): 3124, 2920, 1633, 1605, 1569, 1489, 1472, 1446, 1402, 1375, 1327, 1318, 1302, 1262, 1224, 1202, 1154 913, 846, 766 $cm^{-1}$
HRMS (ESI): *m/z* Calcd. for $C_{22}H_{25}N_3NiO_2 + H^+$: 422.1373, Found: 422.1387.

**Synthesis of a mixture of (NHC$^{Me}$-P$^{Cy}$)Ni_lac 4 and 4'**




**(NHC$^{Me}$-P$^{Cy}$)Ni(cod)** **(NHC$^{Me}$-P$^{Cy}$)Ni_lac (4)** **(NHC$^{Me}$-P$^{Cy}$)Ni_lac (4')**

total 83%, **4** : **4'** = 90 : 10

In an Ar-filled glovebox, to a Schlenk tube equipped with a J. Young valve were added **(NHC$^{Me}$-P$^{Cy}$)Ni(cod)**[3] (30.4 mg, 0.0514 mmol) and THF (3.0 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1:1). After the mixture was stirred for 1 h, the solvent was evaporated. The resulting solid was washed with $Et_2O$ to give a mixture of **4** and **4'** as a yellow solid (23.6 mg, 0.0425 mmol, 83% yield, **4** : **4'** = 90 : 10 by $^{31}$P NMR). **4** and **4'** were assigned by the similarity of the $^{1}$H, $^{13}$C and $^{31}$P NMR spectra with those of **1** and **1'**, which had been characterized by X-ray and NMR analysis in our previous report.[3]

**Spectral data of 4**

$^{1}$H NMR (THF-$d_8$, 500 MHz): δ = 0.29 (q, $J$ = 8.0 Hz, 2H, NiC$\underline{H_2}$), 1.26-1.44 (m, 6H), 1.48-1.66 (m, 6H), 1.60 (s, 3H), 1.66-1.88 (m, 8H), 2.00-2.12 (m, 2H), 2.03 (s, 6H), 2.18-2.28 (m, 2H), 2.21 (s, 3H), 2.31 (s, 3H), 3.90 (d, $J$ = 4.0 Hz, 2H, PC$\underline{H_2}$N), 6.95 (s, 2H, mesityl group).

$^{13}$C NMR (THF-$d_8$, 125 MHz): δ = 8.6, 8.8, 9.2, 9.8, 18.3, 21.1, 27.1, 27.5-27.9 (overlapped signals), 29.0 (d, $J$ = 6.0 Hz), 29.2, 32.4 (d, $J$ = 12.0 Hz), 37.0 (d, $J$ = 4.8 Hz), 39.7 (d, $J$ = 21.5 Hz), 125.5, 125.6, 127.0, 129.6, 136.0, 139.1, 174.3 (d, $J$ = 6.0 Hz), 189.3 (d, $J$ = 19.1 Hz).

$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 50.5

IR (ATR): 2919, 2848, 1612, 1490, 1443, 1374, 1333, 1247, 1005, 911, 854, 744 cm$^{-1}$

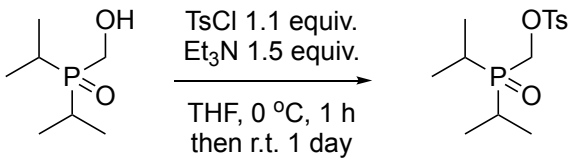
HRMS (ESI): *m/z* Calcd. for $C_{30}H_{45}N_2NiO_2P + H^+$: 555.2645, Found: 555.2642.

**Selected NMR signals of 4'**

$^{1}$H NMR (THF-$d_8$, 500 MHz): 0.22 (q, $J$ = 8.0 Hz, 2H, NiC$\underline{H_2}$), 3.97 (d, $J$ = 6.5 Hz, 2H, PC$\underline{H_2}$N), 6.84 (s, 2H, mesityl group).

$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 68.4

**Synthesis of diisopropylphosphinoylmethyl tosylate (S3)**




1 equiv. **S3** 37%

To a two-necked, round-bottomed flask were added diisopropylphosphonylmethanol[4] (1.39 g, 8.47 mmol), triethylamine (1.8 mL, 13 mmol) and THF (23 mL). The solution was cooled with an ice/water bath and a solution of *p*-toluenesulfonyl chloride (1.78 g, 9.34 mmol) in THF (5.3 mL) was added dropwise to the solution over 15 minutes. After the mixture was stirred at the same temperature for 1 h, the stirring was continued for 1 day at room temperature. Water (18 mL) was added to the mixture and the organic components were extracted three times with EtOAc, and washed with water and brine. After dried over $Na_2SO_4$, the solvent was evaporated and the resulting mixture was purified by silica gel column chromatography ($CH_2Cl_2$ : MeOH = 19 : 1) to give **S3** as a yellow oil (0.999 g, 3.14 mmol, 37% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.15 (dd, *J* = 7.0, 16.0 Hz, 6H), 1.23 (dd, *J* = 7.0, 16.0 Hz, 6H), 2.11-2.22 (m, 2H), 2.47 (s, 3H), 4.20 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H).

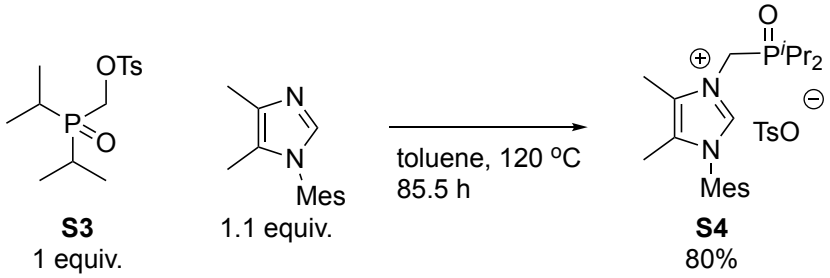
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 14.9, 15.6, 21.9, 24.4 (d, *J* = 62.5 Hz), 60.3 (d, *J* = 66.3 Hz), 128.4, 130.3, 131.2, 146.0.

$^{31}$P NMR ($CDCl_3$, 200 MHz): δ = 55.2

IR (ATR): 3420, 2965, 2933, 2876, 1733, 1595, 1463,1429, 1364, 1306, 1174, 1152, 1094, 1042, 1025, 990, 930, 887, 816, 753, 680, 662 $cm^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{14}H_{23}O_4PS + H^+$: 319.1127, Found: 319.1130.

**Synthesis of 1-(diisopropylphosphinoylmethyl)-3-mesityl-4,5-dimethylimidazolium tosylate (S4)**




**S3** 1 equiv. | 1.1 equiv. | **S4** 80%

To a test tube were added 1-mesityl-4,5-dimethylimidazole (0.492 g, 2.30 mmol), **S3** (0.662 g, 2.08 mmol) and toluene (1.7 mL), and the mixture was heated at 120 °C for 85.5 h. After evaporation of the solvent, $Et_2O$ was added. The resulting solid was collected by filtration and washed with $Et_2O$. The resulting solid was purified by silica gel column chromatography (EtOAc 100%, then $CH_2Cl_2$ : MeOH = 9 : 1) to give **S4** as a dark oil (886.5 mg, 1.66 mmol, 80% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.18-1.36 (m, 12H), 1.93 (s, 3H), 1.96, (s, 6H), 2.24-2.40 (m, 2H), 2.32 (s, 3H), 2.35 (s, 3H), 2.54 (s, 3H), 5.21 (d, *J* = 4.0 Hz, 2H), 7.00 (s, 2H), 7.08 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 9.68 (s, 1H),

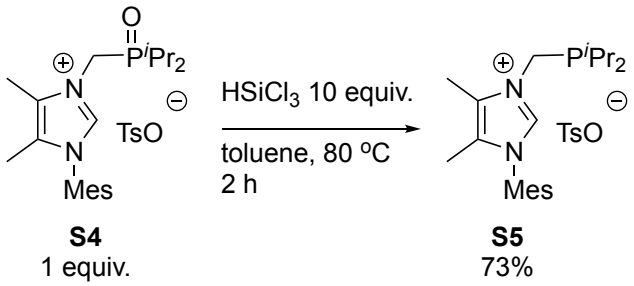
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 8.5, 9.7, 15.6 (d, *J* = 2.5 Hz), 15.8 (d, *J* = 2.5 Hz), 17.6, 21.3, 21.4, 25.9 (d, *J* = 64.6 Hz), 42.5 (d, *J* = 52.8 Hz), 126.1, 126.9, 128.6, 129.0, 129.6, 130.0, 135.0, 136.9, 139.5, 141.4, 143.3.

$^{31}$P NMR ($CDCl_3$, 200 MHz): δ = 54.1

IR (ATR): 3459, 2967, 2932, 2876, 1551, 1459, 1215, 1187, 1148, 1120, 1034, 1012, 885, 816, 711, 680 $cm^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{21}H_{34}N_2OP^+$: 361.2403, Found: 361.2403.

**Synthesis of 1-(diisopropylphosphinomethyl)-3-mesityl-4,5-dimethyl imidazolium tosylate (S5)**




**S4**
1 equiv.

**S5**
73%

Under a $N_2$ atmosphere, to a well-dried 50 mL two-necked, round-bottomed flask were added **S4** (0.881 g, 1.65 mmol), toluene (11 mL) and trichlorosilane (1.7 mL, 17 mmol). After the mixture was stirred at 80 °C for 2 h, the volatile components were removed under vacuum. To the mixture was added degassed water and the organic components were extracted three times with degassed $CH_2Cl_2$ under $N_2$. The combined organic extracts were dried over $Na_2SO_4$. The flask was brought into a $N_2$ filled glove box, and the extracts were filtered through a celite short pad. Evaporation of the solvent gave **S5** as a beige solid (0.619 g, 1.20 mmol, 73% yield).

$^1$H NMR ($C_6D_6$, 500 MHz): δ = 1.02-1.14 (m, 6H), 1.16-1.26 (m, 6H), 1.26 (s, 3H), 1.87 (s, 6H), 2.00 (s, 3H), 2.03 (s, 3H), 2.11 (s, 3H), 2.27-2.42 (m, 2H), 5,17 (s, 2H), 6.61 (s, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 10.6 (s, 1H).

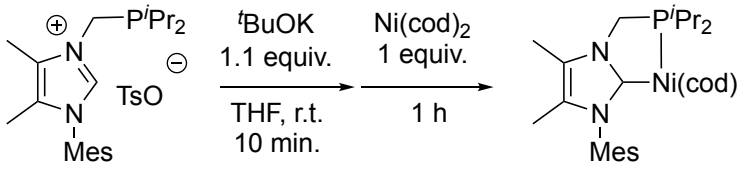
$^{13}$C NMR ($C_6D_6$, 125 MHz): δ = 7.8, 9.9 (d, *J* = 10.8 Hz), 17.6, 19.5 (d, *J* = 9.5 Hz), 20.0 (d, *J* = 13.1 Hz), 21.1, 21.2, 23.6 (d, *J* = 10.8 Hz), 44.2 (d, *J* = 20.4 Hz), 126.8, 126.9, 128.3, 128.4, 128.7, 129.86, 129.95, 135.5, 137.7 (d, *J* = 4.8 Hz), 140.3, 147.2.

$^{31}$P NMR ($C_6D_6$, 200 MHz): δ = 5.9

IR (ATR): 3099, 2948, 2920, 2863, 1634, 1606, 1541, 1457, 1443, 1211, 1189, 1150, 1116, 1031, 1010, 867, 850, 814, 798, 677 cm$^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{21}H_{34}N_2P^+$: 345.2454, Found: 345.2458.

**Synthesis of [Ni(NHC$^{Me}$-P$^{iPr}$)(cod)] (S6)**




**S5**
1 equiv.

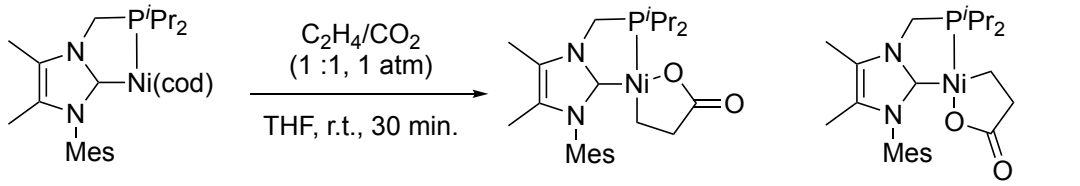
**(NHC$^{Me}$-P$^{iPr}$)Ni(cod) (S6)**
39%

In an Ar-filled glove box, to a 20 mL vial with a magnetic stirring bar were added **S5** (100 mg, 0.194 mmol) and THF (3.0 mL). To the solution was added $^t$BuOK (23.9 mg, 0.213 mmol) and the resulting solution was stirred for 10 minutes at room temperature to generate NHC carbene. In another 50 mL round bottomed flask, a solution of Ni(cod)$_2$ (52.8 mg, 0.192 mmol) in THF (4 mL) was prepared and the solution of the NHC carbene was added dropwise to the

solution of $Ni(cod)_2$ over 10 minutes. After the mixture was stirred for 1 h, the solvent was evaporated and the resulting solid was dissolved in hexane. The remaining solids were removed by filtration. The solvent was evaporated and the resulting solid was purified by recrystalization from hexane at –30 °C to give **S6** as a brown solid (38.9 mg, 0.0761 mmol, 39% yield).

$^1$H NMR ($C_6D_6$, 500 MHz): δ = 1.02 (dd, J = 6.5, 12.0 Hz, 6H), 1.09 (dd, J = 6.5, 13 Hz, 6H), 1.43 (s, 3H), 1.75 (s. 3H), 1.76-1.84 (m, 2H), 1.92-2.00 (m, 2H), 2.06 (s, 6H), 2.16 (s, 3H), 2.16-2.24 (m, 2H), 2.36-2.44 (m, 2H), 2.54-2.62 (m, 2H), 3.27 (d, J = 3.5 Hz, 2H), 4.24-4.34 (m, 2H), 4.50-4.60 (m, 2H), 6.85 (s, 2H).
$^{13}$C NMR ($C_6D_6$, 125 MHz): δ = 9.2, 10.3, 18.3, 18.5 (d, *J* = 2.4 Hz), 18.9 (d, *J* = 7.3 Hz), 21.2, 25.4 (d, *J* = 7.1 Hz), 31.7 (d, *J* = 7.3 Hz), 33.2, 43.2 (d, *J* = 15.5 Hz), 74.6 (d, *J* = 3.6 Hz), 77.2 (d, *J* = 12 Hz), 121.6, (d, *J* = 4.8 Hz), 123.2, 129.1, 137.0, 137.5, 137.9, 201.7.
$^{31}$P NMR ($C_6D_6$, 200 MHz): δ = 63.0.

### Synthesis of a mixture of (NHC$^{Me}$-P$^{iPr}$)Ni_lac 5 and 5'




**(NHC$^{Me}$-P$^{iPr}$)Ni(cod) (S6)** **(NHC$^{Me}$-P$^{iPr}$)Ni_lac (5)** **(NHC$^{Me}$-P$^{iPr}$)Ni_lac (5')**

total 74%, **5** : **5'** = 95 : 5

In an Ar-filled glovebox, to a Schlenk tube equipped with a J. Young valve were added **S6** (30.8 mg, 0.0602 mmol) and THF (3.1 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1:1). After the mixture was stirred for 30 minutes, the solvent was evaporated. The resulting solid was washed with $Et_2O$ to give a mixture of **5** and **5'** as a yellow solid (21.3 mg, 0.0448 mmol, 74% yield, **5** : **5'** = 95 : 5 by $^{31}$P NMR). **5** and **5'** were assigned by the similarity of the $^1$H and $^{13}$C NMR spectra with those of **1** and **1'**, which had been characterized by X-ray and NMR analysis in our previous report.[3]

**Spectral data of 5**

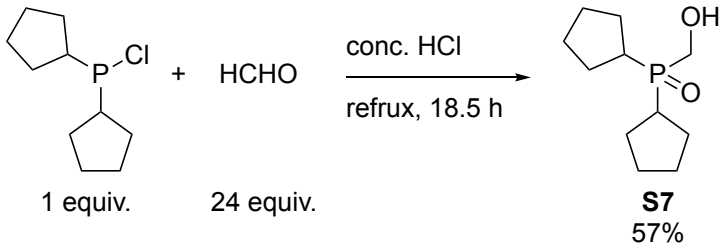
$^1$H NMR (THF-$d_8$, 500 MHz): δ = 0.31 (q, *J* = 7.0 Hz, 2H, NiC*H*$_2$), 1.22 (dd, *J* = 10.0, 15.0 Hz, 6H), 1.37 (dd, *J* = 10.0, 15.0 Hz, 6H), 1.54 (q, *J* = 7.5 Hz, 2H), 1.62 (s, 3H), 2.04 (s, 6H), 2.22 (s, 3H), 2.20-2.30 (m, 2H), 2.31 (s, 3H), 3.89 (d, *J* = 4.0 Hz, 2H, PC*H*$_2$N), 6.96 (s, 2H, mesityl group).
$^{13}$C NMR (THF-$d_8$, 125 MHz): δ =8.8, 9.4, 9.8, 18.4 (d, *J* = 18.0 Hz), 18.8 (d, *J* = 7.1 Hz), 21.1, 23.2 (d, *J* = 12.0 Hz), 37.0 (d, *J* = 4.8 Hz), 39.6 (d, *J* = 20.4 Hz), 125.58, 125.64, 127.0, 129.7, 136.0, 139.1, 174.4 (d, *J* = 5.9 Hz), 189.2 (d, *J* = 19.1 Hz) (One aliphatic carbon is missing probably due to overlapping).
$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 59.0
IR (ATR): 2948, 2920, 2887, 1629, 1489, 1459, 1437, 1372, 1303, 1249, 1230, 1029, 903, 882, 863, 660 cm$^{-1}$
HRMS (ESI): *m/z* Calcd. for $C_{24}H_{37}N_2NiO_2P + H^+$: 475.2019, Found: 475.2028.

**Selected NMR signals of 5'**

$^1$H NMR (THF-$d_8$, 500 MHz): 0.24 (q, $J$ = 8.0 Hz, 2H, NiC$\underline{H_2}$), 3.95 (d, $J$ = 5.5 Hz, 2H, PC$\underline{H_2}$N), 6.85 (s, 2H, mesityl group).

$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 77.3

### Synthesis of dicyclopentylphosphinoylmethanol (S7)




To a 100 mL two-necked, round-bottomed flask were added chlorodicyclopentylphosphine (2.27 g, 11.1 mmol) and concentrated hydrochloric acid (22 mL), followed by aqueous solution of formaldehyde (37 wt% in water, 22 ml, 270 mmol). The resulting mixture was refluxed for 18.5 h. The resulting solution was neutralized with solid NaOH and $NaHCO_3$, and the organic components were extracted three times with $CHCl_3$ and dried over $Na_2SO_4$. After evaporation of the solvent, hexane was added to the resulting oil to give **S7** as a white solid (1.38 g, 6.38 mmol, 57% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.56-1.70 (m, 4H), 1.68-2.00 (m, 12H), 2.13-2.25 (m, 2H), 4.02 (s, 2H).

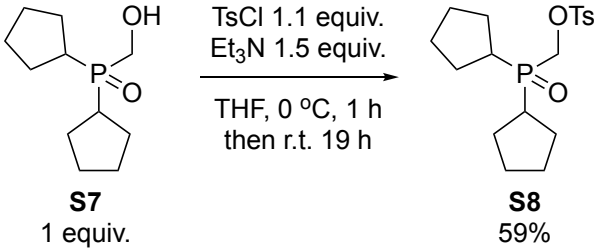
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ =26.3-26.7 (overlapped signals for cyclopentyl groups), 35.4 (d, $J$ = 65.9 Hz), 57.9 (d, $J$ = 75.4 Hz).

$^{31}$P NMR ($CDCl_3$, 200 MHz): δ = 54.8

IR (ATR): 3125, 2945, 2909, 2865, 2816, 1450, 1422, 1185, 1124, 1049, 904, 863, 792, 718 cm$^{-1}$

Anal. Calcd for $C_{11}H_{21}O_2P$: C, 61.09; H, 9.79; Found: C, 61.08; H, 9.87.

### Synthesis of dicyclopentylphosphinoylmethyl tosylate (S8)

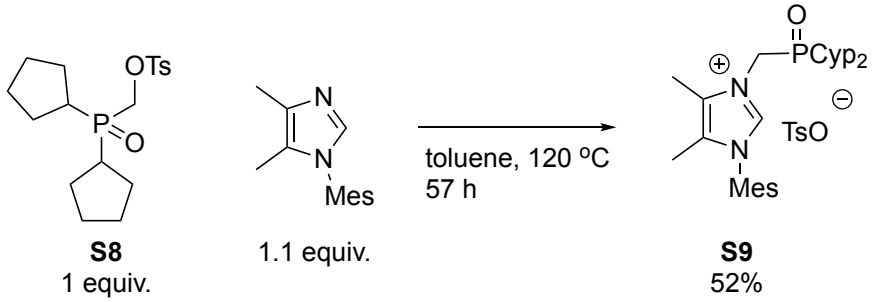



To a 100 mL two-necked, round-bottomed flask were added **S7** (70.6 mg, 0.326 mmol), triethylamine (68 μL, 0.49 mmol) and THF (1 mL). The solution was cooled with an ice/water bath and a solution of *p*-toluenesulfonyl chloride (68.6 mg, 0.359 mmol) in THF (0.3 mL) was added dropwise to the solution over 10 minutes. After the mixture was stirred at the same temperature for 1 h, the stirring was continued for 19 hours at room temperature. Water (1 mL) was

added to the mixture and the organic components were extracted three times with EtOAc, and washed with water and brine. After the extracts were dried over $Na_2SO_4$, the solvent was evaporated and the resulting mixture was purified by silica gel column chromatography ($CH_2Cl_2$ : MeOH = 19 : 1) to give **S8** as a yellow oil (71.3 mg, 0.192 mmol, 59% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ = 1.50-1.96 (m, 16H), 2.08-2.20 (m, 2H), 2.48 (s, 3H), 4.16 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H).
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 21.9, 25.8, 26.1 (d, *J* = 10.8 Hz), 26.3, 26.8 (d, *J* = 10.8 Hz), 35.8 (d, *J* = 69.4 Hz), 62.7 (d, *J* = 70.6 Hz), 128.4, 130.3, 131.3, 145.9.
$^{31}$P NMR ($CDCl_3$, 200 MHz): δ = 50.8.
IR (ATR): 2950, 2866, 1595, 1493, 1448, 1429, 1400, 1366, 1299, 1187, 1172, 1094, 990, 906, 814, 751, 662 $cm^{-1}$
HRMS (ESI): *m/z* Calcd. for $C_{18}H_{27}O_4PS + H^+$: 371.1440, Found: 371.1443.

**Synthesis of 1-(dicyclopentylphosphinoylmethyl)-3-mesityl-4,5-dimethyimidazolium tosylate (S9)**

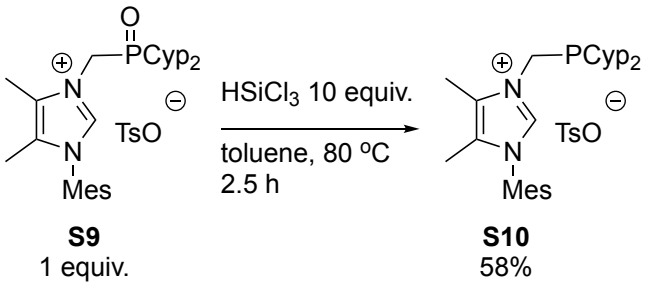



**S8** 1 equiv. | 1.1 equiv. | **S9** 52%

To a test tube were added 1-mesityl-4,5-dimethylimidazole (0.274 g, 1.28 mmol), **S8** (0.430 g, 1.16 mmol) and toluene (0.95 mL), and the mixture was heated at 120 °C for 57 h. After evaporation of the solvent, $Et_2O$ was added and the resulting solid was collected by filtration and washed with $Et_2O$. The resulting solid was purified by silica gel column chromatography ($CH_2Cl_2$ 100%, then $CH_2Cl_2$ : MeOH = 9 : 1) to give **S9** as a beige solid (0.350 g, 0.599 mmol, 52% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ =1.52-1.96 (m, 16H), 1.94 (s, 3H), 1.97 (s, 6H), 2.32 (s, 3H), 2.35 (s, 3H), 2.36-2.46 (m, 2H), 2.56 (s, 3H), 5.15 (d, *J* = 4.5 Hz, 2H), 7.01 (s, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 9.72 (s, 1H).
$^{13}$C NMR ($CDCl_3$, 125 MHz): δ = 8.5, 9.7, 17.7, 21.3, 21.5, 26.2-27.0 (overlapped signals for cyclopentyl groups), 27.1, 37.1 (d, *J* = 67.0 Hz), 45.5 (d, *J* = 57.4 Hz), 126.1, 127.0, 128.7, 129.0, 129.6, 130.1, 134.9, 137.0, 139.8, 141.5, 142.8.
$^{31}$P NMR ($CDCl_3$, 200 MHz): δ = 51.8.
IR (ATR): 3107, 3034, 2950, 2866, 1629, 1605, 1545, 1448, 1400, 1381, 1223, 1182, 1116, 1034, 1012, 824, 714, 678 $cm^{-1}$
HRMS (ESI): *m/z* Calcd. for $C_{25}H_{37}N_2OP^+$: 413.2716, Found: 413.2721.

**Synthesis of 1-(dicyclopentylphosphinomethyl)-3-mesityl-4,5-dimethyimidazolium tosylate (S10)**




**S9**
1 equiv.

**S10**
58%

Under a $N_2$ atmosphere, to a well-dried 30 mL two-necked, round-bottomed flask were added **S9** (0.332 g, 0.568 mmol), toluene (4 mL) and trichlorosilane (0.57 mL, 5.6 mmol). After stirring the mixture at 80 °C for 2.5 h, the volatile components were removed under vacuum. To the mixture was added degassed water and organic components were extracted three times with degassed $CH_2Cl_2$ under $N_2$. The combined organic extracts were dried over $Na_2SO_4$. The flask was brought into a $N_2$-filled glovebox, and the mixture was filtered through a celite short pad. Evaporation of the solvent gave **S10** as a white solid (0.1861 g, 0.327 mmol, 58% yield).

$^1$H NMR ($C_6D_6$, 500 MHz): δ = 1.16 (s, 3H), 1.18-1.64 (m, 12H), 1.78-1.88 (m, 2H), 1.85 (s, 9H), 1.96 (s, 3H), 2.00 (s, 3H), 2.02-2.10 (m, 2H), 2.18-2.30 (m, 2H), 5.07 (s, 2H), 6.56, (s, 2H), 6.86, (d, *J* = 8.0 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 10.9 (s, 1H).

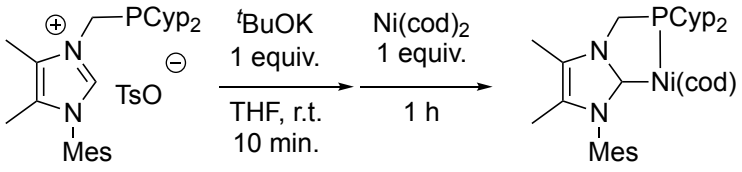
$^{13}$C NMR ($C_6D_6$, 125 MHz): δ = 7.6, 9.8 (d, *J* = 12 Hz), 17.6, 21.1, 21.2, 26.4 (d, *J* = 7.3 Hz), 26.6 (d, *J* = 7.3 Hz), 30.1 (d, *J* = 14.4 Hz), 31.7 (d, *J* = 16.8 Hz), 36.2 (d, *J* = 10.8 Hz), 47.2 (d, *J* = 19.1 Hz), 126.3, 126.9, 128.3, 128.4, 129.9, 135.5, 137.7, 138.3, 140.3, 147.2 (One aromatic carbon is missing due to overlapping).

$^{31}$P NMR ($C_6D_6$, 200 MHz): δ = –1.4

IR (ATR): 3103, 3032, 2948, 2863, 1627, 1608, 1541, 1489, 1448, 1224, 1183, 1153, 1116, 1034, 1012, 861, 814, 798, 677 cm$^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{25}H_{37}N_2P^+$: 397.2767, Found: 397.2770.

**Synthesis of [Ni(NHC$^{Me}$-P$^{Cyp}$)(cod)] (S11)**




**S10**
1 equiv.

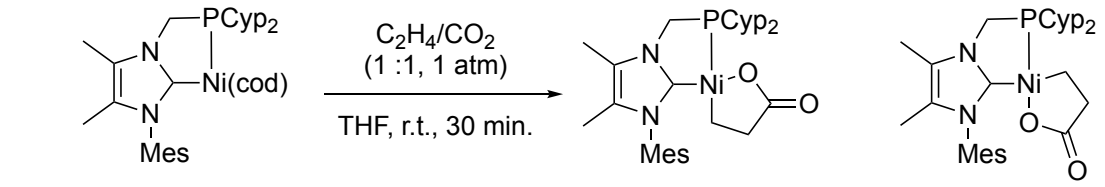
**(NHC$^{Me}$-P$^{Cyp}$)Ni(cod) (S11)**
97% estimated yield
(containing $Ni(cod)_2$ 4 mol%)

In an Ar-filled glove box, to a 20 mL vial with a magnetic stirring bar were added **S10** (86.0 mg, 0.151 mmol) and THF (2.0 mL). To the solution was added a solution of $^t$BuOK (17.0 mg, 0.152 mmol) in THF (1.0 mL) and the resulting solution was stirred for 10 minutes at room temperature to generate NHC carbene. In another 30 mL round bottomed

flask, a solution of $Ni(cod)_2$ (41.6 mg, 0.151 mmol) in THF (4 mL) was prepared and the solution of the NHC carbene was added dropwise to the solution of $Ni(cod)_2$ over 10 minutes. After the mixture was stirred for 1 h, solvent was evaporated and the resulting solid was dissolved in hexane and the remaining solids were removed by filtration. The solvent was evaporated to give **S11** as a yellow solid (84.1 mg, containing 4 mol% of $Ni(cod)_2$ judging from $^1$H NMR. Estimated amount and yield of **S11** were 0.15 mmol and 97%, respectively). The resulting mixture was used in the next step without further purification. For NMR analyses, pure sample of **S11** was prepared by recrystalization from hexane at –30 °C.

$^1$H NMR ($C_6D_6$, 500 MHz): δ = 1.42-1.88 (m, 18H), 1.46 (s, 3H), 1.78 (s, 3H), 2.04-2.24 (m, 4H), 2.10 (s, 6H), 2.17 (s, 3H), 2.34-2.46 (m, 2H), 2.50-2.60 (m, 2H), 3.34 (d, *J* = 3.5 Hz, 2H), 4.26-4.34 (m, 2H), 4.52-4.62 (m, 2H), 6.87 (s, 2H).
$^{13}$C NMR ($C_6D_6$, 125 MHz): δ = 9.2, 10.4, 18.4, 21.2, 27.0 (d, *J* = 7.1 Hz), 27.3 (d, *J* = 8.4 Hz), 29.5-29.9 (overlapped), 31.6 (d, *J* = 6.0 Hz), 33.4, 38.9 (d, *J* = 8.4 Hz), 46.1 (d, *J* = 17.9 Hz), 74.1 (d, *J* = 3.6 Hz), 77.0 (d, *J* = 13.1 Hz), 121.7(d, *J* = 4.8 Hz), 123.1, 129.1, 137.1, 137.5, 137.9, 201.7.
$^{31}$P NMR ($C_6D_6$, 200 MHz): δ = 58.1

**Synthesis of a mixture of (NHC$^{Me}$-P$^{Cyp}$)Ni_lac 6 and 6'**




**(NHC$^{Me}$-P$^{Cyp}$)Ni(cod) (S11)**
(containing $Ni(cod)_2$ 4 mol%)

**(NHC$^{Me}$-P$^{Cyp}$)Ni_lac (6)** **(NHC$^{Me}$-P$^{Cyp}$)Ni_lac (6')**

total 84%, **6** : **6'** = 95 : 5

In an Ar-filled glovebox, to a Schlenk tube equipped with a J. Young valve were added **S11** (34.3 mg, containing 4 mol% of $Ni(cod)_2$. Estimated amount of **S11** was 0.060 mmol) and THF (3.4 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1:1). After the mixture was stirred for 30 minutes, the solvent was evaporated. The resulting solid was washed with $Et_2O$ to give a mixture of **6** and **6'** as a yellow solid (26.6 mg, 0.0504 mmol, estimated yield was 84%, **6** : **6'** = 95 : 5 by $^{31}$P NMR). **6** and **6'** were assigned by the similarity of the $^1$H, $^{13}$C and $^{31}$P NMR spectra with those of **1** and **1'**, which had been characterized by X-ray and NMR analysis in our previous report.[3]

**Spectral data of 6**

$^1$H NMR (THF-$d_8$, 500 MHz): δ = 0.29 (q, *J* = 7.0 Hz, 2H, NiC$\underline{H_2}$), 1.53 (q, *J* = 7.5 Hz, 2H), 1.56-1.66 (m, 4H), 1.62 (s, 3H), 1.70-2.04 (m, 12H), 2.05 (s, 6H), 2.20 (s, 3H), 2.25-2.38 (m, 2H), 2.31 (s, 3H), 3.92 (d, *J* = 3.5 Hz, 2H, PC$\underline{H_2}$N), 6.95 (s, 2H, mesityl group).
$^{13}$C NMR (THF-$d_8$, 125 MHz): δ = 8.7, 8.8, 9.3, 9.8, 18.3, 21.1, 27.0-27.6 (overlapped signals for cyclopentyl groups), 29.8 (d, *J* = 8.8 Hz), 30.2 (d, *J* = 2.5 Hz), 35.1 (d, *J* = 13.8 Hz), 37.0 (d, *J* = 5.0 Hz), 42.2 (d, *J* = 23.8 Hz), 125.6, 125.7, 127.0, 129.6, 135.9, 139.1, 174.7 (d, *J* = 5.0 Hz), 189.1 (d, *J* = 21.3 Hz).

$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 51.2.

IR (ATR): 2952, 2917, 2889, 2865, 1620, 1489, 1437, 1372, 1321, 1239, 1204, 908, 850, cm$^{-1}$

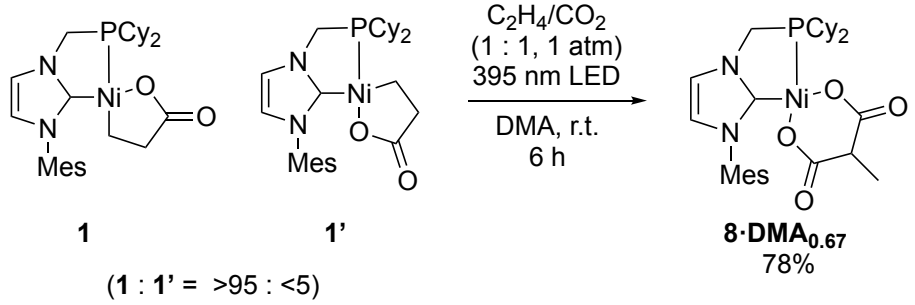
HRMS (ESI): *m/z* Calcd. for $C_{28}H_{41}N_2NiO_2P + H^+$: 527.2332, Found: 527.2343.

**Selected NMR signals of 6'**

$^1$H NMR (THF-$d_8$, 500 MHz): δ = 3.97 (d, *J* = 6.3 Hz, 2H, PC$\underline{H_2}$N), 6.85 (s, 2H, mesityl group).

$^{31}$P NMR (THF-$d_8$, 200 MHz): δ = 68.5

### Synthesis of methylmalonate complex bearing an NHC-P ligand (8)




In an Ar-filled glovebox, to a Schlenk tube were added a mixture of **1** and **1'** (**1** : **1'** = >95 : <5, 21.5 mg, 0.0408 mmol) and DMA (1.5 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1 : 1). After stirring the mixture under irradiation with 2 sockets of 395 nm LED light for 6 h, the solvent was removed under reduced pressure. The resulting solid was purified by reprecipitation with THF and hexane, and washed with a minimum amount of THF to give **8** as a pale yellow solid (20.0 mg, containing 0.67 equiv. of DMA, 0.0318 mmol, 78% yield). A single crystal suitable for X-ray analysis was grown by DMA/hexane at room temperature. DMA was difficult to remove because it co-crystallizes with **8**.

$^1$H NMR ($CD_2Cl_2$, 500MHz): δ = 1.18 (d, *J* = 7.5 Hz, 3H), 1.26–1.52 (m, 6H), 1.56-1.99 (m, 12H), 2.01 (s, 2H, $DMA_{0.67}$), 2.02-2.20 (m, 2H), 2.09 (s, 3H), 2.15 (s, 3H), 2.31 (s, 3H), 2.34-2.42 (m, 1H), 2.48-2.58 (m, 1H), 2.87 (s, 2H, $DMA_{0.67}$), 2.97 (s, 2H, $DMA_{0.67}$), 3.28 (q, *J* = 8.0 Hz, 1H), 4.00 (d, *J* = 5.0 Hz, 2H), 6.74 (s, 1H), 6.93 (s, 1H), 6,95 (s, 1H), 7.18 (s, 1H).

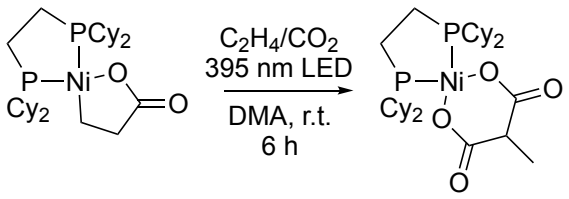
$^{13}$C NMR: ($CD_2Cl_2$, 125 MHz): δ = 15.2, 18.0, 18.2, 21.2, 21.8 (DMA), 26.2, 26.6-27.1 (overlapped signals for cyclohexyl groups), 28.28, 28.33, 28.5 (d, *J* = 3.6 Hz), 28.7, 31.5 (d, *J* = 21.5 Hz), 31.6 (d, *J* = 21.6 Hz), 35.1 (DMA), 38.2 (DMA), 42.0 (d, *J* = 31.1 Hz), 51.8, 120.4, 120.5, 127.1, 128.8, 128.9, 134.2 135.5, 139.0, 160.5 (d, *J* = 35.9 Hz), 170.5 (DMA), 174.7, 176.6.

$^{31}$P NMR ($CD_2Cl_2$, 160 MHz): δ = 69.0.

IR (ATR): 2926, 2851, 1644, 1621, 1554, 1489, 1448, 1413, 1377, 1344, 1273, 1197, 1183, 1161, 1120, 1098, 1072, 1033, 1010, 967, 936, 895, 872, 852, 775, 740, 721, 691 cm$^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{29}H_{41}N_2NiO_4P + H^+$: 571.2230, Found: 571.2240.

### Synthesis of methylmalonate complex bearing dcype ligand 9




**2** **9·THF$_{0.5}$** 17%

In an Ar-filled glovebox, to a Schlenk tube were added **2** (35.3 mg, 0.0638 mmol) and DMA (2.0 mL). The Schlenk tube was degassed by a freeze-pump-thaw cycle and filled with an atmospheric pressure of ethylene/$CO_2$ (1 : 1). After stirring the mixture under irradiation with 2 sockets of 395 nm LED light for 6 h, the solvent was removed under reduced pressure. The resulting solid was purified by reprecipitation with THF and hexane and washed with a minimum amount of THF to give **9** as a pale yellow solid (7.0 mg, containing 0.5 equiv. of THF, 0.011 mmol, 17% yield). THF could not be removed even after long time of drying under vacuum.

$^{1}$H NMR ($CD_2Cl_2$, 500MHz): δ = 1.26 (d, *J* = 7.5 Hz, 3H), 1.26–2.16 (m, 44H), 1.82 (m, 2H, $THF_{0.5}$), 2.32-2.40 (m, 2H), 2.48-2.56 (m, 2H), 3.36 (q, *J* = 7.0 Hz, 1H), 3.68 (m, 2H, $THF_{0.5}$).

$^{13}$C NMR: ($CD_2Cl_2$, 125 MHz): δ = 15.1, 20.6 (t, *J* = 20.4 Hz), 26.0 (THF), 26.3, 27.0-27.2 (m), 27.2-27.5 (m), 28.7, 29.2, 29.7 (d, *J* = 10.8 Hz), 33.9 (t, *J* = 9.5 Hz), 34.3 (t, *J* = 10.8 Hz) 51.8, 68.2 (THF), 176.2.

$^{31}$P NMR ($CD_2Cl_2$, 160 MHz): δ = 79.1.

IR (ATR): 2924, 2850, 1649, 1623, 1444, 1374, 1344, 1269, 1202, 1180, 1115, 1066, 1005, 893, 870, 850, 824, 800, 747, 719, 678, 656 cm$^{-1}$

HRMS (ESI): *m/z* Calcd. for $C_{30}H_{53}NiO_4P_2 + H^+$: 597.2767, Found: 597.2787.

## General procedure for the synthesis of sodium methylmalonate

In an Ar-filled glovebox, to a test tube equipped with a stirring bar were added nickel complex, ligand, photosensitizer, additive, sacrificial reductant and solvent (1.0 mL). The test tube was closed with three-way stop cock and atmospheric pressure of ethylene and $CO_2$ (1 : 1) was introduced by two freeze-pump-thaw cycles. Then the mixture was subjected to the desired reaction conditions. Under air, the mixture was transferred to a separatory funnel and added with 5% NaOH aq. (2 mL). The water layer was washed with c.a. 5 mL of $Et_2O$ (When NMP or DMPU was used as a solvent, the water layer was further washed 4 times with c.a. 5 mL of $CH_2Cl_2$) and evaporated under reduced pressure. To the resulting solid was added sodium 3-(trimethylsilyl)-1-propanesulfonate (~11 mg) as internal standard and $D_2O$ (2.0 mL), and submitted for $^1$H NMR experiment after filtration through cotton plug. The turnover numbers (TON) of sodium methylmalonate and sodium propionate were determined by the integral ratios of signal of $SiMe_3$ group of sodium 3-(trimethylsilyl)-1-propanesulfonate and signals of $CH_3$ group of sodium methylmalonate ($\delta$ = 1.1 ppm, d, $J$ = 7 Hz) and that of sodium propionate ($\delta$ = 0.9 ppm, t, $J$ = 8 Hz).

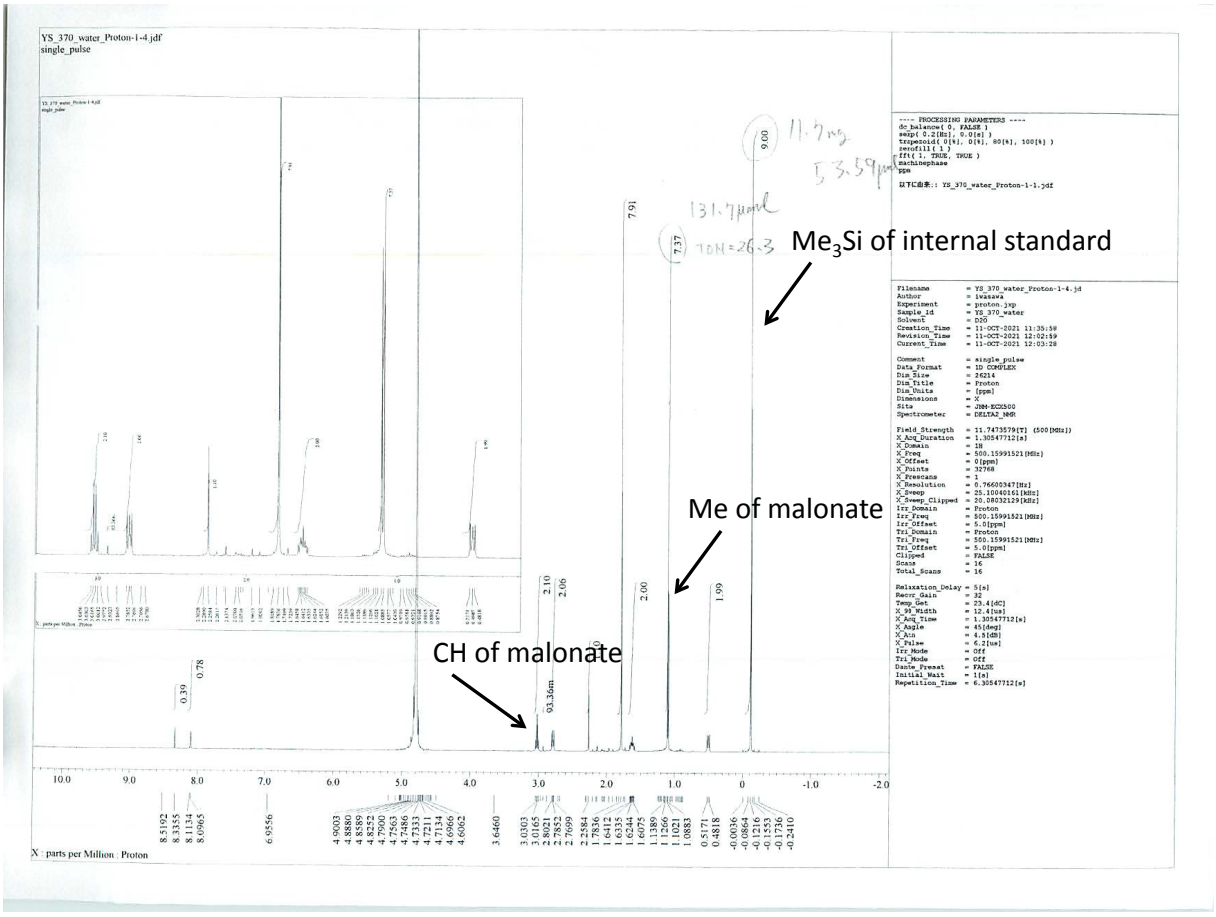
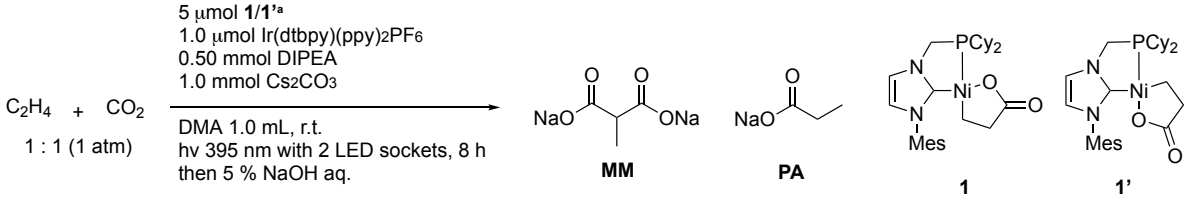



**Figure S1.** Representative $^1$H NMR spectrum of synthesis of methylmalonate salt.

## Control experiments

Control experiments were performed in the absence of each component as indicated below. In every case, methylmalonate salt was not obtained catalytically.

**Table S1.** Control experiments

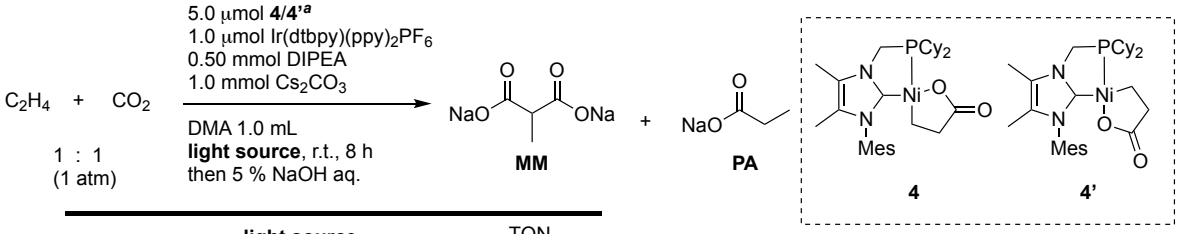



| entry | condition | TON | |
|---|---|---|---|
| | | **MM** | **PA** |
| 1 | | 8.1 | 0 |
| 2 | without **1/1'** | 0 | 0 |
| 3 | without Ir | 0.9 | 0 |
| 4 | without DIPEA | 1.1 | 0 |
| 5 | Under dark | 0 | 0 |

[a] **1** : **1'** = 95 : 5 for entry 1 and >95 : <5 for entries 2-5

## Screening of reaction conditions

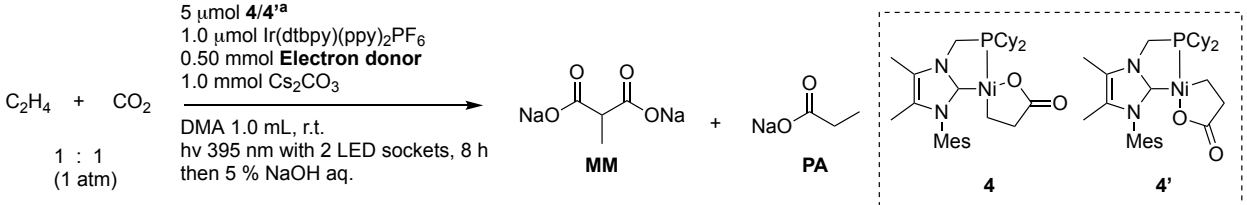
**Table S2. Screening of light sources**



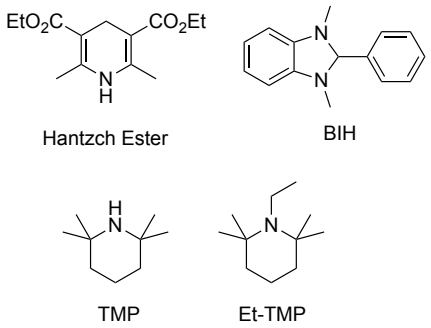

| Entry | **light source (number of socket)** | TON | |
|---|---|---|---|
| | | **MM** | **PA** |
| 1 | 395 nm × 2 | 8.2 | 0 |
| 2 | 365 nm × 2 | 8.0 | 0 |
| 3 | 365 nm × 2 and 425 nm × 2 | 8.7 | 0 |
| 4 | Hg lamp (without optical filter | 3.5 | 2.5 |
| 5[b] | 395 nm × 2 | 6.6 | 0 |

[a]Ratio was not determined. [b]70 °C.

**Table S3. Screening of electron donors**

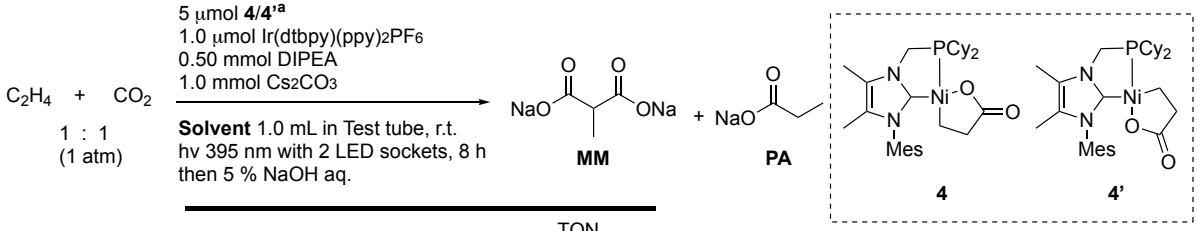



| Entry | Electron donor | TON | |
|---|---|---|---|
| | | MM | PA |
| 1 | DIPEA | 8.2 | 0 |
| 2 | $Cy_2NMe$ | 2.0 | 0 |
| 3 | $Et_3N$ | 7.3 | 0 |
| 4 | Hantzch Ester | 0 | 0.2 |
| 5 | BIH | 6.5 | 0 |
| 6 | TMP | 1.0 | 0 |
| 7 | Et-TMP | 8.9 | 0 |
| 8[b] | Zn | 1.1 | trace |




[a]Ratio was not determined. [b]Without $Ir(dtbpy)(ppy)_2PF_6$

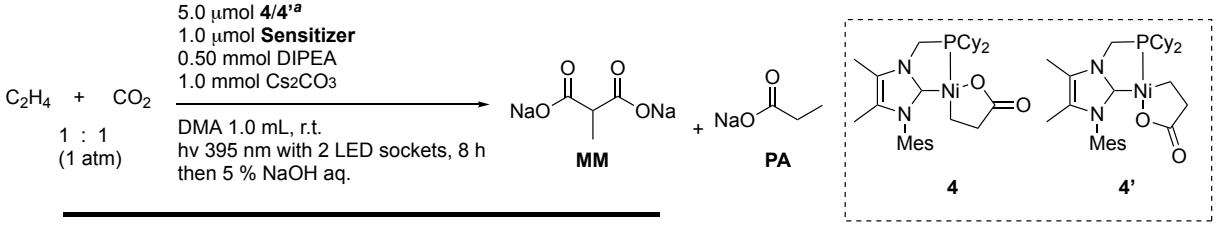
**Table S4. Screening of solvents**




| Entry | Solvent | TON | |
|---|---|---|---|
| | | MM | PA |
| 1 | DMA | 8.2 | 0 |
| 2 | DME | 0.4 | 0 |
| 3 | DMSO | < 2.0 | 0 |
| 4 | NMP | 6.9 | 0 |
| 5 | MeCN | 3.6 | 0.5 |
| 6 | DMPU | 4.3 | 0.2 |
| 7 | Propylene Carbonate | 4.5 | 0 |

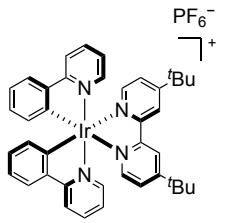
[a]Ratio was not determined.

**Table S5. Screening of photo sensitizer**

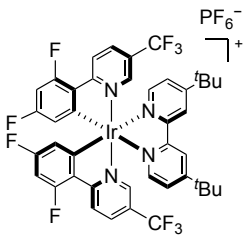



| Entry | Sensitizer | TON | |
|---|---|---|---|
| | | MM | P |
| 1 | $Ir(dtbpy)(ppy)_2PF_6$ | 8.2 | 0 |
| 2 | $Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$ | 7.6 | 0 |
| 3 | $Ir(dF(CF_3)ppy)_2(bpy)PF_6$ | 7.0 | 0 |
| 4 | $Ir(ppy)_3$ | 1.2 | 0 |
| 5 | $Ru(dmbpy)_3(PF_6)_2$ | 4.9 | 0 |
| 6 | 4CzIPN | 6.6 | 1.0 |
| 7 | 4DPAIPN | 6.2 | 3.1 |

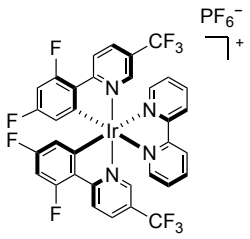
[a]Ratio was not determined.



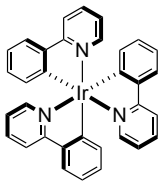

$Ir(dtbpy)(ppy)_2PF_6$



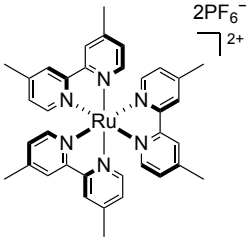

$Ir(dF(CF_3)ppy)_2(dtbpy)PF_6$



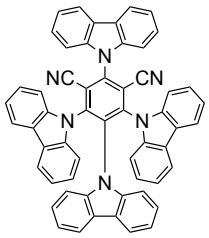

$Ir(dF(CF_3)ppy)_2(bpy)PF_6$



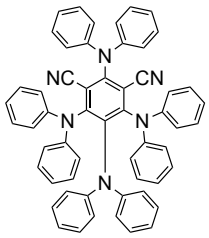

$Ir(ppy)_3$




$Ru(dmbpy)_3(PF_6)_2$

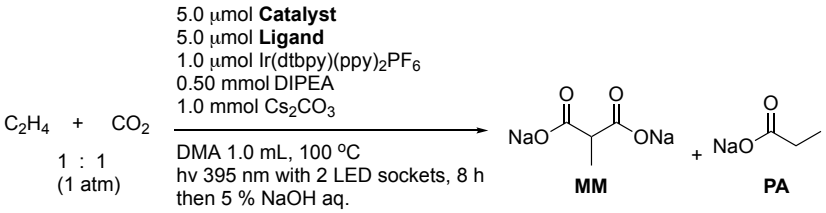



4CzIPN

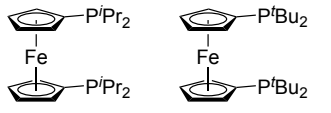


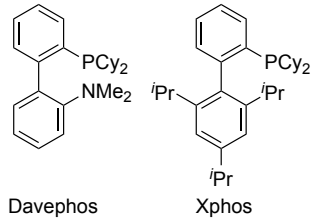

4DPAIPN

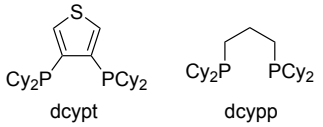
**Table S6. Screening of metal precursors and phosphine ligands**

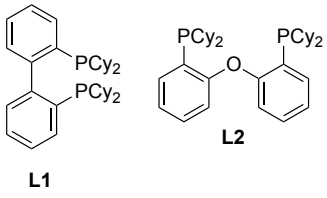



| Entry | Catalyst | Ligand | TON | |
|---|---|---|---|---|
| | | | MM | PA |
| 1 | $Ni(glyme)Cl_2$ | dcype | 6.3 | 0 |
| 2 | $Ni(glyme)Br_2$ | dcype | 8.7 | 0 |
| 3 | $Ni(OTf)_2$ | dcype | 6.0 | 0 |
| 4 | $Ni(acac)_2$ | dcype | 3.4 | 0 |
| 5 | $Pd(OAc)_2$ | dcype | 0 | 0 |
| 6 | $PdBr_2$ | dcype | 0 | trace |
| 7 | $PtBr_2$ | dcype | 0 | 0 |
| 8 | $(DMSO)_4RuCl_2$ | dcype (10.0 μmol) | 0 | 1.6 |
| 9 | $Ni(glyme)Cl_2$ | $PCy_3$ (10.0 μmol) | 0 | 0.7 |
| 10 | $Ni(glyme)Br_2$ | - | 0 | 0 |
| 11 | $Ni(glyme)Br_2$ | dippf | 0 | 0 |
| 12 | $Ni(glyme)Br_2$ | dtbpf | 0 | trace |
| 13 | $Ni(glyme)Br_2$ | Davephos (10.0 μmol) | 0 | 0 |
| 14 | $Ni(glyme)Br_2$ | Xphos (10.0 μmol) | 0 | 0 |
| 15 | $Ni(glyme)Br_2$ | dcypt | 4.0 | 0 |
| 16 | $Ni(glyme)Br_2$ | **L1** | 0 | 0.4 |
| 17 | $Ni(glyme)Br_2$ | **L2** | 0 | 0 |
| 18 | $Ni(glyme)Br_2$ | dcypp (7.5 μmol) | 1.3 | 0 |
| 19 | $Ni(glyme)Br_2$ | dcype (7.5 μmol) | 10.7 | 0 |
| 20 | $Ni(glyme)Br_2$ | dcype (15 μmol) | 10.9 | 0 |
| 21 | $Ni(glyme)Br_2$ (10 μmol) | dcype (15 μmol) | 12.0 | 0 |



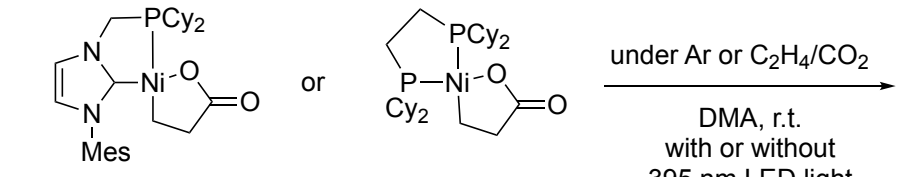



## NMR experiments for the investigation of the stoichiometric reactivity of the nickelalactones

### General procedure of NMR experiment using 1 or 2 (Figure 2, main text)

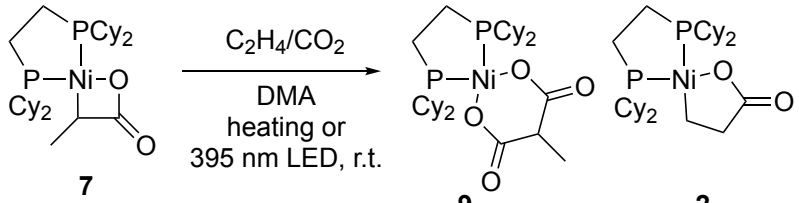



**1**
(containing 5% of **1'**)

**2**

Under an Ar atmosphere, to an NMR tube equipped with a J. Young valve were added a mixture of **1** and **1'** (**1** : **1'** = 95 : 5, 1.3 mg, 2.5 μmol in total) or **2** (1.4 mg, 2.5 μmol), capillary tube containing benzene-$d_6$ solution of $P(OPh)_3$ as an internal standard and DMA (0.5 mL). The initial ratio of the total amount of **1** and **1'** or **2** and the internal standard was determined by $^{31}P$ NMR analysis. If needed, an atmospheric pressure of ethylene and $CO_2$ (1:1) was introduced by a freeze-pump-thaw cycle. Then the mixture was subjected to the desired reaction conditions and the reaction progress was followed by $^{31}P$ NMR analysis.

### NMR experiment using 7 (Table 2, main text)




**7**
(containing 10% of **2**)

**9**

**2**

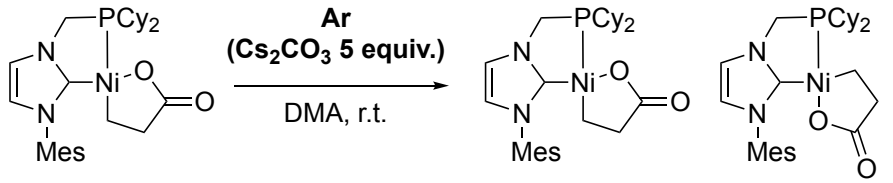
Under an Ar atmosphere, to an NMR tube equipped with a J. Young valve were added a mixture of **7** and **2** (**7** : **2** = 90 : 10, 1.4 mg, 2.5 μmol in total), capillary tube containing benzene-$d_6$ solution of $P(OPh)_3$ as an internal standard and DMA (0.5 mL). The initial ratio of the total amount of **7** and **2** and the internal standard was determined by $^{31}P$ NMR analysis. An atmospheric pressure of ethylene and $CO_2$ (1 : 1) was introduced by a freeze-pump-thaw cycle. Then the mixture was subjected to the desired reaction conditions and the reaction progress was followed by $^{31}P$ NMR analysis.

## NMR experiments to test the effect of Cs cation

In our system, the TON of methylmalonate salt was improved by using $Cs_2CO_3$ as an additive. Although we have obtained experimental supports that the isomerization of 5-membered nickelalactones to 4-membered ones and the conversion to methylmalonate complexes were accelerated by the photoirradiation, possibilities that Cs cation is more crucial than photoirradiation in these elementary step were still remained. To test the possibilities, we conducted following NMR experiments.

### The effect of Cs cation on the isomerization of 5-membered nickelalactones

NHC-P nickelalactone (**1**) was treated under Ar atmoshere with 5 equivalents of $Cs_2CO_3$ in the dark and the reaction progress was followed. However, the isomerization to **1'** proceeded similar rate to the case without $Cs_2CO_3$.

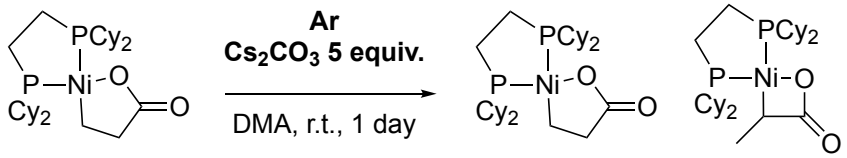



**1** (containing 5% of **1'**) → **1** + **1'**

yields were determined by $^{31}P$ NMR

| | with $Cs_2CO_3$ | | without $Cs_2CO_3$ | |
|---|---|---|---|---|
| | **1** | **1'** | **1** | **1'** |
| 1 h | 95% | 5% | 95% | 5% |
| 1 day | 70% | 25% | 60% | 35% |
| 3 days | 50% | 50% | 40% | 45% |

Nickelalactone bearing dcype (**2**) was treated under Ar atmoshere with 5 equivalents $Cs_2CO_3$ in the dark and the isomerization to **7** was monitored. In this case, isomerization to 4-membered nickelalactone did not proceed at all after 1 day.



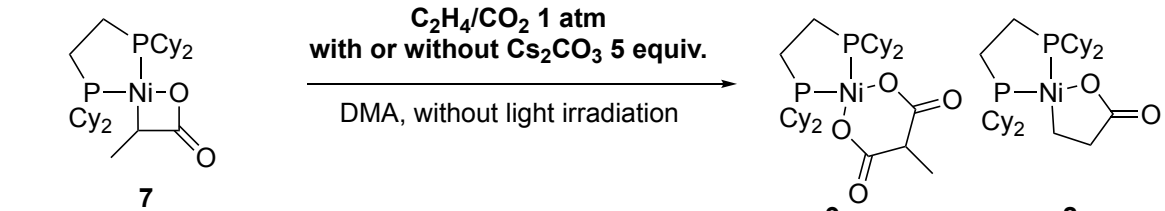

**2** → **2** (100%) + **7** (0%)

These results suggested that $Cs_2CO_3$ is not effective for the acceleration of isomerization of 5-membered nickelalactone to 4-membered ones.

**The effect of Cs cation on the insertion of $CO_2$ to 4-membered nickelalactone**

4-membered nickelalactone **7** was treated under ethylene/$CO_2$ (1:1) atmosphere in the presence of 5 equivalents of $Cs_2CO_3$ at room temperature and then 100 °C in the dark. Reactivity of 4-membered nickelalactone **7** *at room temperature* under ethylene/$CO_2$ (1:1) atmosphere in the absence of of $Cs_2CO_3$ was also tested (**7** contained 5% of **2** was usesd).

After 1 day at room temperature, total 75% of nickelalactones (60% of 4-membered (**7**) and 15% of 5-membered (**2**) nickelalactone) remained and 10% of malonate complex was generated accompanied by the formation of several unknown species. Even after heating at 100 °C for 1 hour, still 50% of nickelalactones (15% of 4-membered (**7**) and 35% of 5-membered (**2**) nickelalactone) remained and only 5% of malonate complex was observed. Since close to full consumption (95%) of nickelalactones (5% of **2** remained) and 85% yield of malonate complex **9** was achieved by the irradiation of 395 nm LED light at room temperature for 10 minutes (Table 2, in the main text), photoirradiation is confirmed to be more crucial to the insertion of second molecule of $CO_2$ than $Cs_2CO_3$. Although small amount of malonate complex **9** was generated at room temperature, it was also observed in the absence of $Cs_2CO_3$ at room temperature after 6 h. It also denies the participation of Cs cation to the formation of **9**.



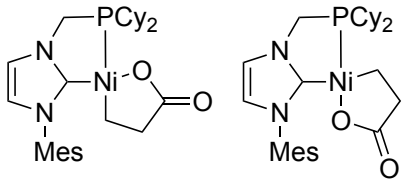

**7** (containing 5~10% of **2**) → **9** + **2**

| $Cs_2CO_3$ | conditions | results[a] |
|---|---|---|
| ○ | r.t. 1 day[b] | **7** 60%, **9** 10%, **2** 15% + multiple compounds |
| | r.t. 1 day then 100 °C, 1 h[b] | **7** 15%, **9** 5%, **2** 35% + multiple compounds |
| × | r.t. 6 h[c] | **7** 85%, **9** 10%, **2** 5% |

[a]Yields were calculated based on the sum of initial amount of **7** and **2** determined by $^{31}P$ NMR. [b]Starting from **7** containing 5% of **2**. [c]Starting from **7** containing 10% of **2**

## Previously reported NMR data of 1 and 1'[3]

Previously we reported $^{1}H$, $^{31}P$, and $^{13}C$ NMR spectra of almost pure **1** (**1** : **1'** = 97 : 3) and a mixture of **1** and **1'** (**1** : **1'** = 60 : 40). Also, we confirmed the structures of these two isomers by X-ray single crystal analysis (CCDC deposition numbers are **1**: 1945817 and **1'**: 1903155).




**1** **1'**

**NMR data of 1 (picked from 97 : 3 mixture of 1 and 1')**

$^{1}H$ NMR (THF-$d_8$, 500 MHz): δ = 0.36 (q, *J* = 7.0 Hz, 2H, NiC$\underline{H_2}$), 1.20-1.42 (m, 8H), 1.44-1.65 (m, 6H), 1.65-1.91 (m, 6H) 1.94-2.24 (m, 4H), 2.14 (s, 6H), 2.30 (s, 3H), 4.08 (d, *J* = 4.0 Hz, 2H, PC$\underline{H_2}$N), 6.83 (s, 1H), 6.94 (s, 2H, mesityl group), 7.30 (s, 1H)

$^{13}C$ NMR (THF-$d_8$, 125 MHz): δ = 9.1, 9.6, 18.5, 21.1, 27.1, 27.3-28.1 (overlapped signals for Cy groups), 28.8-29.4 (overlapped signals for Cy groups), 32.4 (d, *J* = 12.0 Hz), 37.1 (d, *J* = 5.9), 42.2 (d, *J* = 20.3 Hz), 121.3, 125.4, 129.0, 135.4, 137.9, 139.1, 177.8, 188.9 (d, *J* = 19.3 Hz)

$^{31}P$ NMR (THF-$d_8$, 160 MHz): δ = 52.0 (s)

**NMR data of 1' (picked from 60 : 40 mixture of 1 and 1')**

$^{1}H$ NMR (THF-$d_8$, 500 MHz): δ = 0.26 (q, *J* = 8.0 Hz, 2H, NiC$\underline{H_2}$), 1.20-2.23 (m, 24H, signals for Cy groups and α-proton of carbonyl were overlapped with those of **1** and solvent), 2.02 (s, 6H), 2.27 (s, 3H), 4.14 (d, *J* = 5.0 Hz, 2H, PC$\underline{H_2}$N), 6.80-6.85 (m, 3H, overlapped signals for mesityl and backbone of NHC moiety), 7.33 (s, 1H)

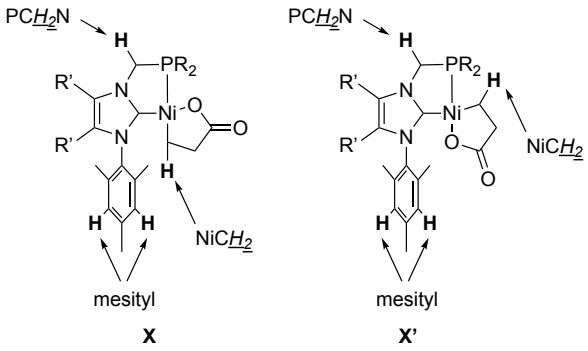
$^{13}C$ NMR (THF-$d_8$, 125 MHz): δ = 5.3, 5.5, 18.3, 21.5, 26.4, 27.3-28.1 (overlapped signals for Cy groups), 28.8 (d, *J* = 2.0 Hz), 28.9-29.2 (overlapped signals for Cy groups), 29.4, 33.4 (d, *J* = 25.1 Hz), 37.9, 45.3 (d, *J* = 26.4 Hz), 119.7 (d, *J* = 6.0 Hz), 125.0, 135.4, 137.2 (two aromatic carbons are missing probably due to overlapping with those of **1**), 187.2, 187.9 (d, *J* = 10.8 Hz).

$^{31}P$ NMR (THF-$d_8$, 160 MHz): δ = 69.1 (s)

## Comparison of $^{1}$H and $^{31}$P NMR chemical shifts of geometrical isomers of nickelalactones

On the basis of spectral data of **1**/**1'**, newly synthesized nickelalactones **4**/**4'**, **5**/**5'** and **6**/**6'** were chracterized. On $^{1}$H NMR, signals for mesityl, PC$\underline{H_2}$N and NiC$\underline{H_2}$ of any **X** and **X'** were separately observed (except NiC$\underline{H_2}$ of **6** and **6'**), and the chemical shifts of those of **4**/**4'**, **5**/**5'** and **6**/**6'** were similar to those of **1**/**1'** (Table S7). Furthermore, in all the cases, the chemical shifts of PC$\underline{H_2}$N of **X'** were 0.05~0.07 ppm down field compared to **X** and those of mesityl and NiC$\underline{H_2}$ of **X'** were 0.11 ppm and 0.07 ~ 0.1 ppm (except **6** and **6'**) high field compared to **X**. $^{31}$P NMR chemical shifts of **X'** were 17.3~18.3 ppm down field compared to **X**. Those similarities reasonably supported our assignment of **4**/**4'**, **5**/**5'** and **6**/**6'**.

**Table S7. Comparison of selected $^{1}$H and $^{31}$P NMR chemical shifts of geometrical isomers of nickelalactones**




| | | R = Cy, R' = H | | R = Cy, R' = Me | | R = $^{i}$Pr, R' = Me | | R = Cyp, R' = Me | |
|---|---|---|---|---|---|---|---|---|---|
| Assingments | | **1** | **1'** | **4** | **4'** | **5** | **5'** | **6** | **6'** |
| $^{1}$H NMR | NiC$\underline{H_2}$ | 0.36 | 0.26 | 0.29 | 0.22 | 0.31 | 0.24 | 0.29[b] | 0.29[b] |
| | PC$\underline{H_2}$N | 4.08 | 4.14 | 3.90 | 3.97 | 3.89 | 3.95 | 3.92 | 3.97 |
| | mesityl | 6.94 | 6.80-6.85[a] | 6.95 | 6.84 | 6.96 | 6.85 | 6.95 | 6.85 |
| $^{31}$P NMR | | 52.0 | 69.1 | 50.5 | 68.4 | 59.0 | 77.3 | 51.2 | 68.5 |

[a]Overlapped with other signals. [b]Signals for **6** and **6'** were overlapped

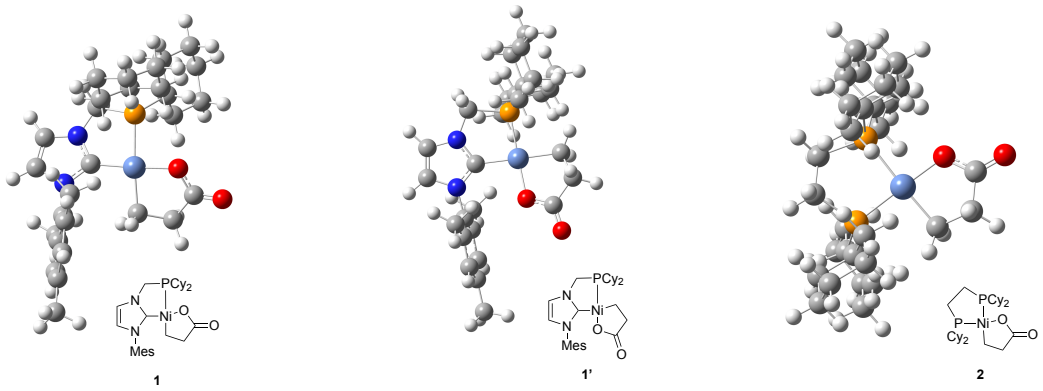
## DFT analysis

All calculations were performed with Gaussian 16 program,[7] by using B3LYP[8] method with 6-31+G*[9] basis set for all atoms. Solvent effect in DMA by CPCM model was applied for all calculations.

### Comparison of Ni-O bond lengths and relative energies of nickelalactones 1, 1', 2 and excited triplet states of them.

For **1** and **1'**, 4 isomers of triplet state existed because the plane of P-Ni-$C_{carbene}$ and $O_{lactone}$-Ni-$C_{lactone}$ are perpendicular to each other in the excited state.

a) Ground states ($S_0$) of **1, 1'** and **2**.




b) Triplet states ($T_1$) **1**, **1'** and **2**

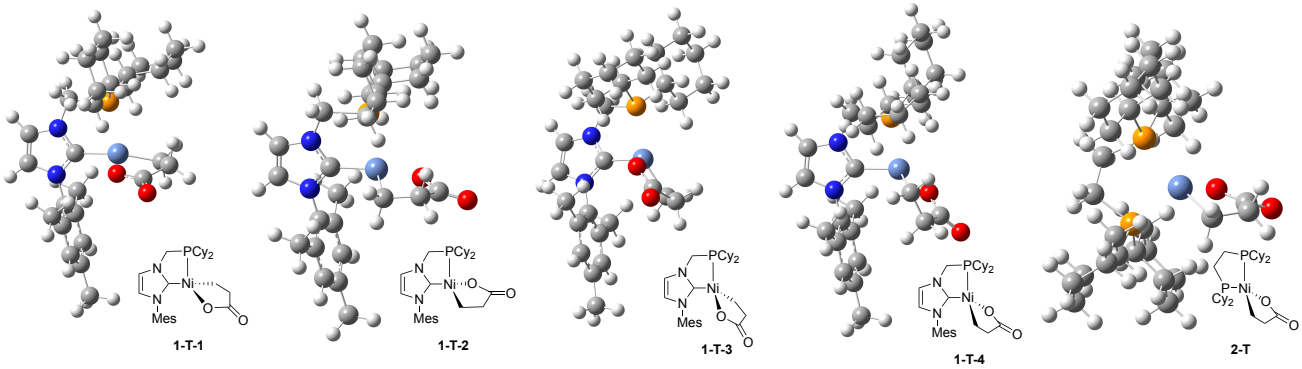



**Figure S2.** Optimized structures of a) ground states ($S_0$) of **1**, **1'** and **2**, and b) triplet states ($T_1$) of **1**, **1'** and **2**.

**Table S8.** Summary of Ni-O bond lengths and relative free energies of singlet ($S_0$) and triplet ($T_1$) states of **1**, **1'** and **2**.

| | 1 | 1' | 1-T-1 | 1-T-2 | 1-T-3 | 1-T-4 | 2 | 2-T |
|---|---|---|---|---|---|---|---|---|
| bond length of Ni-O (Å) | 1.87483 | 1.87573 | 1.97059 | 1.94787 | 1.95997 | 1.9464 | 1.87989 | 1.96409 |
| Relative free energy (kcal/mol) | 1.4 | 0 | 15.8 | 13.2 | 16.4 | 13.9 | 0 | 15.6 |

**DFT analysis for the insertion of $CO_2$ to 4-membered nickelalactones to form methylmalonate complexes**

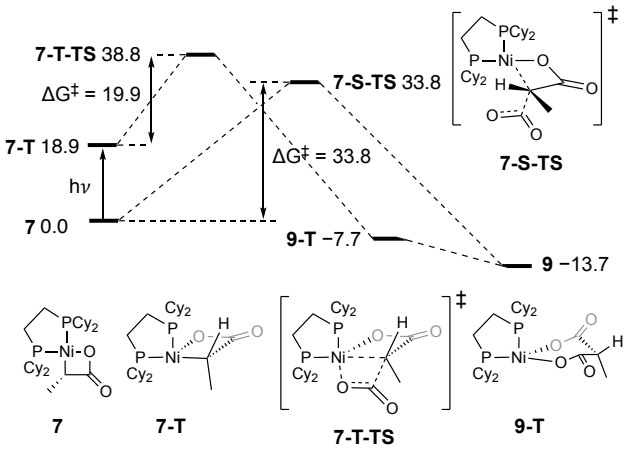



**Figure S3.** DFT analysis for the reaction of 4-membered nickelalactone bearing dcype **7** with $CO_2$ at excited triplet state and singlet ground state (Relative energies are described in kcal/mol).

**DFT analysis for the evaluation of the energies required for structural change to form transition states at singlet and triplet states.**

From both of the transition state structures of **7-S-TS** and **7-T-TS**, the $CO_2$ molecules were deleted and frequency calculations without structural optimizations were conducted for the resulting structures (**7-S-TS − $CO_2$** and **7-T-TS − $CO_2$**). The free energy of **7-S-TS − $CO_2$** relative to **7** was 19.9 kcal/mol and that of **7-T-TS − $CO_2$** relative to **7-T** was 8.5 kcal/mol, respectively. Therefore, the energy required for the structural change of **7-T** to form the corresponding transition sate is 11.4 kcal/mol less than that of **7-T**.

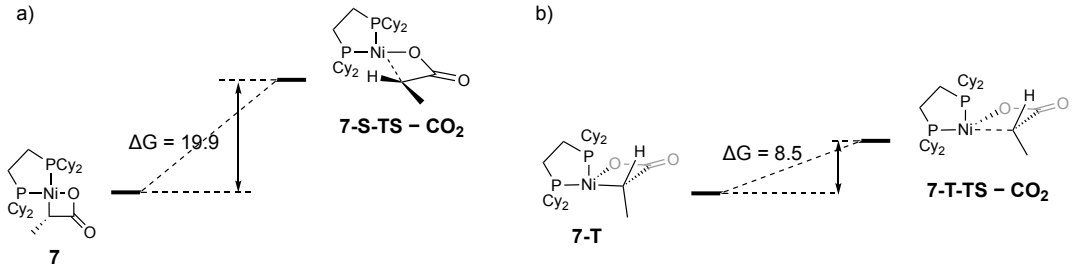



**Figure S4.** DFT analysis for the evaluation of the energies required for the structural change to form the transition states at a) singlet ground state and b) excited triplet state (Relative energies are described in kcal/mol).

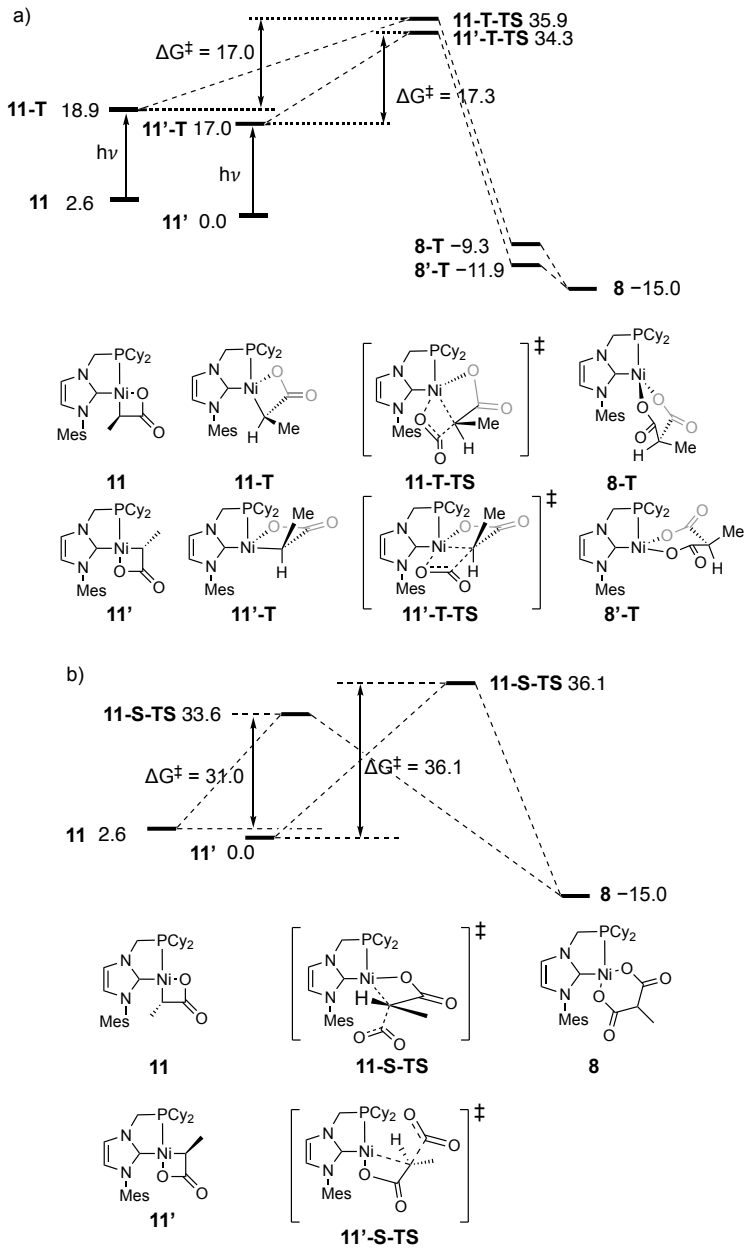



**Figure S5.** DFT analysis for the reaction of 4-membered nickelalactones bearing an NHC-P ligand **11** and **11'** with $CO_2$ at a) excited triplet states and b) singlet ground states (Relative energies are described in kcal/mol).

## Table S9. Crystal data and structure refinement for (NHC-P)Ni malonate complex 8

| | **8 • DMA** |
|---|---|
| Empirical formula | $C_{33}H_{50}N_3NiO_5P$ |
| Formula weight | 658.44 |
| Temperature (K) | 123 |
| Wavelength (Å) | 0.71075 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | $a$ = 16.5365(9) Å |
| | $b$ = 15.9821(6) Å |
| | $c$ = 12.9995(6) Å |
| | $\alpha = 90°$ |
| | $\beta = 97.271(5)°$ |
| | $\gamma = 90°$ |
| Volume (Å$^3$) | 3408.0(3) |
| $Z$ | 4 |
| Density (calculated) | 1.283 |
| Absorption coefficient | 1.605 |
| $F$(000) | 1408.0 |
| Crystal size (mm$^3$) | 0.263 × 0.041 × 0.023 |
| 2θ range for data collection | 7.724° to 136.492° |
| Index ranges | $-19 \le h \le 19$, $-19 \le k \le$ |
| | $15$, $-15 \le l \le 15$ |
| Reflections collected | 21916 |
| Independent reflections | 6223 |
| Data / restraints / parameters | 6223/0/395 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final $R$ indices [$I$>2sigma($I$)] | $R_1$ = 0.0608 |
| | $wR_2$ = 0.1585 |
| Final $R$ indices (all data) | $R_1$ = 0.0849 |
| | $wR_2$ = 0.1731 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.65/-0.45 |

## NMR spectra

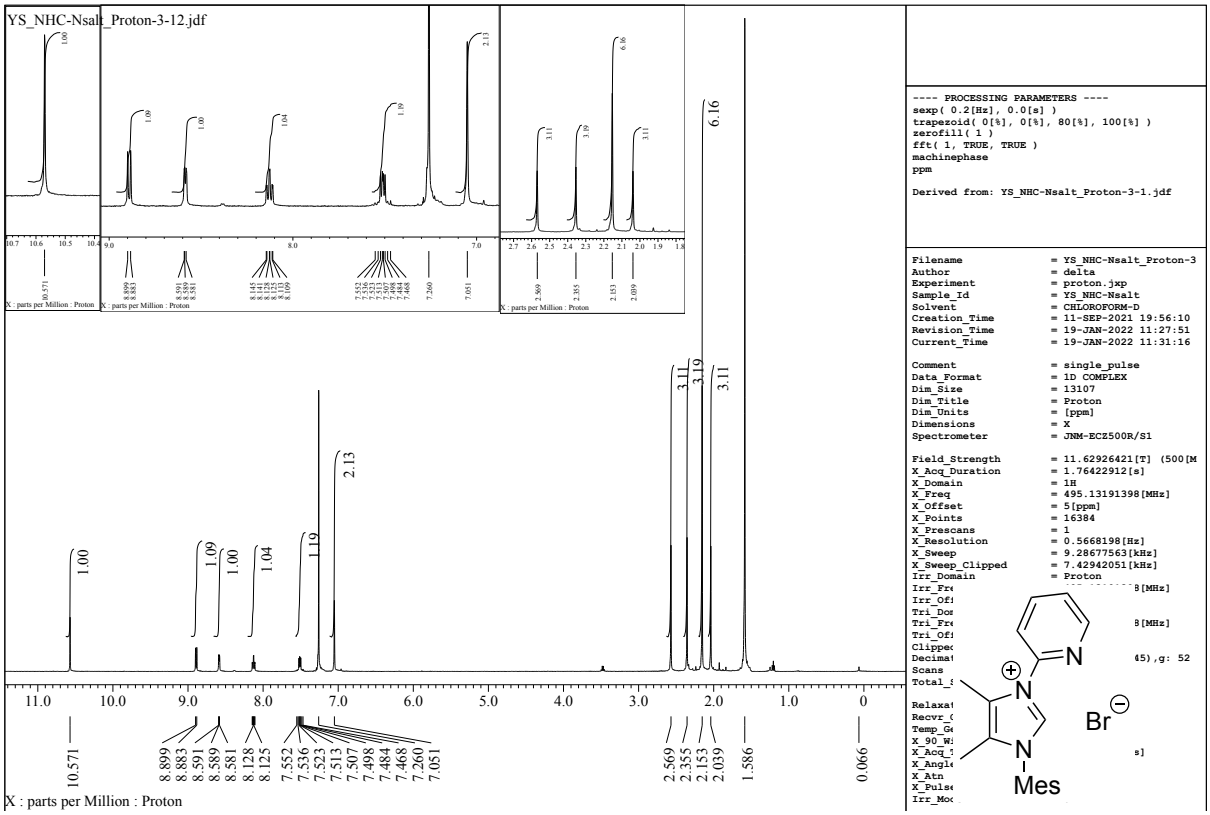



**Figure S6.** $^{1}$H NMR spectrum of **S1**.

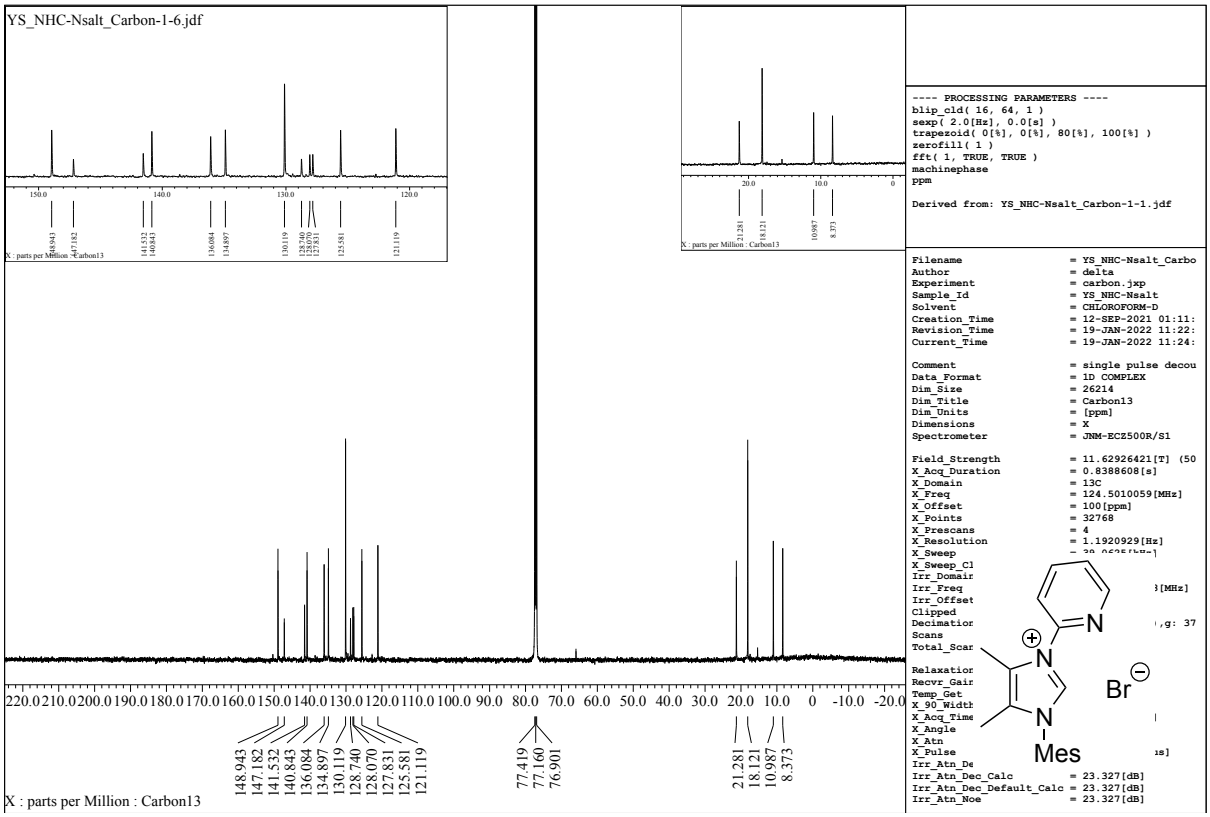



**Figure S7.** $^{13}$C NMR spectrum of **S1**.

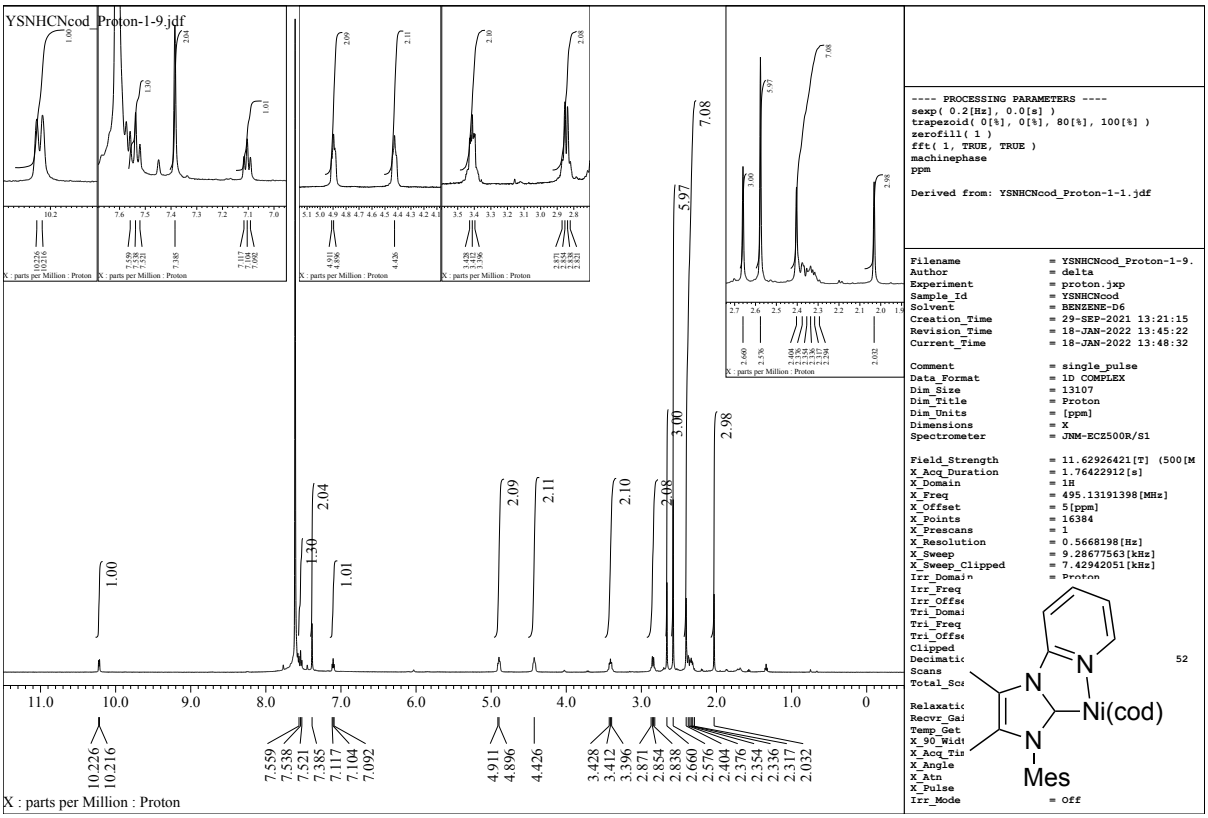



**Figure S8.** $^{1}$H NMR spectrum of **S2**.

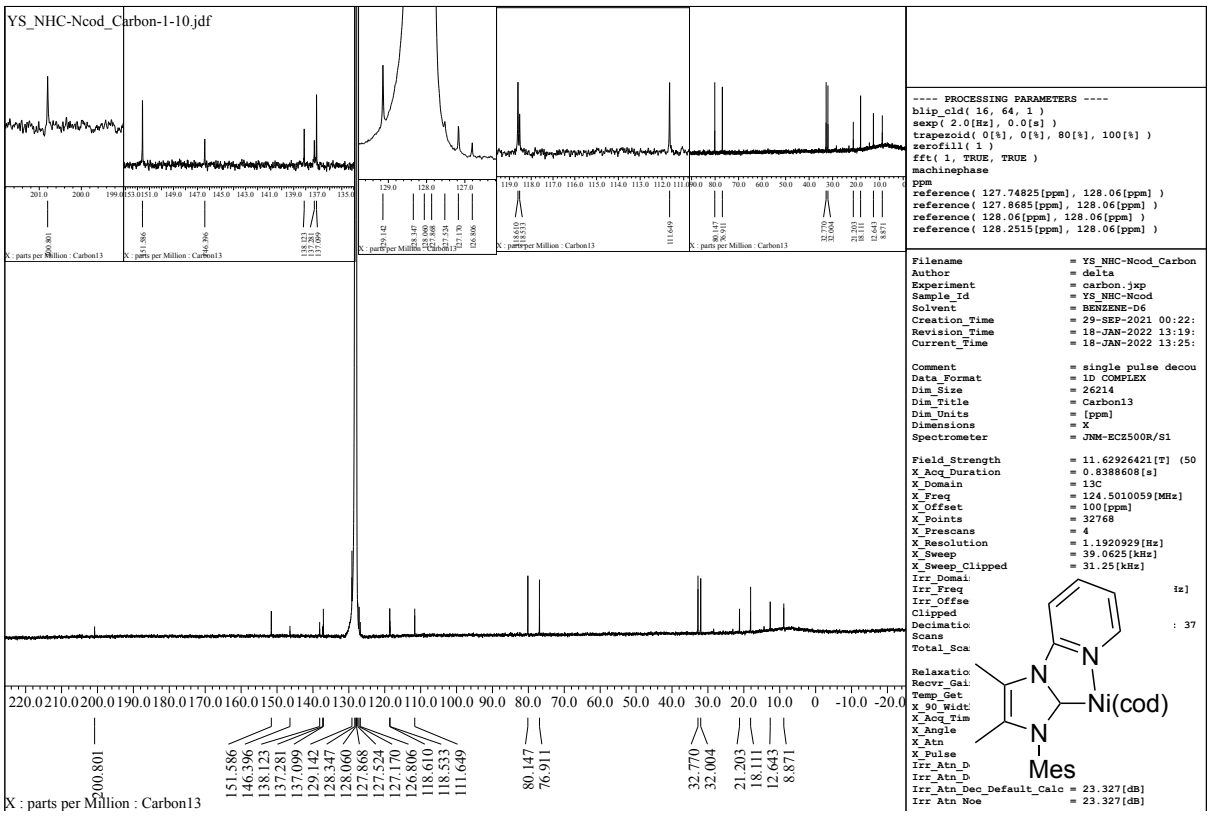



**Figure S9.** $^{13}$C NMR spectrum of **S2**.

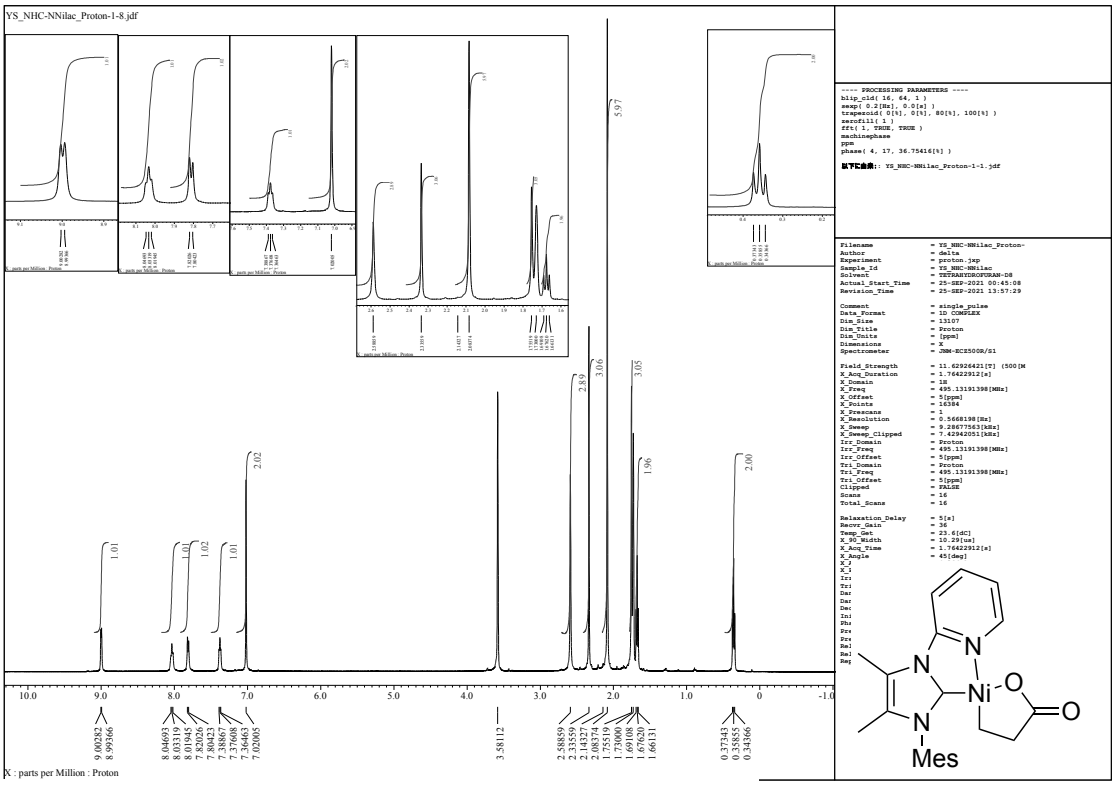



**Figure S10.** $^{1}$H NMR spectrum of **3**.

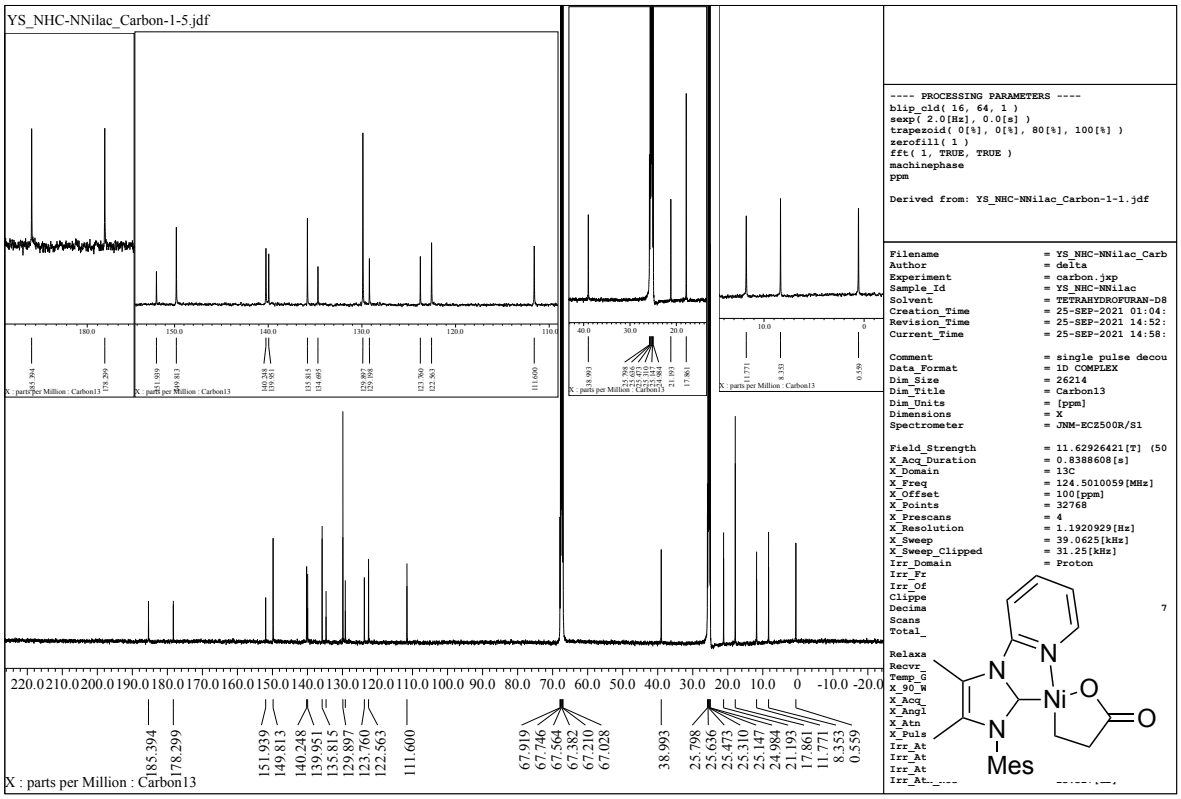



**Figure S11.** $^{13}$C NMR spectrum of **3**

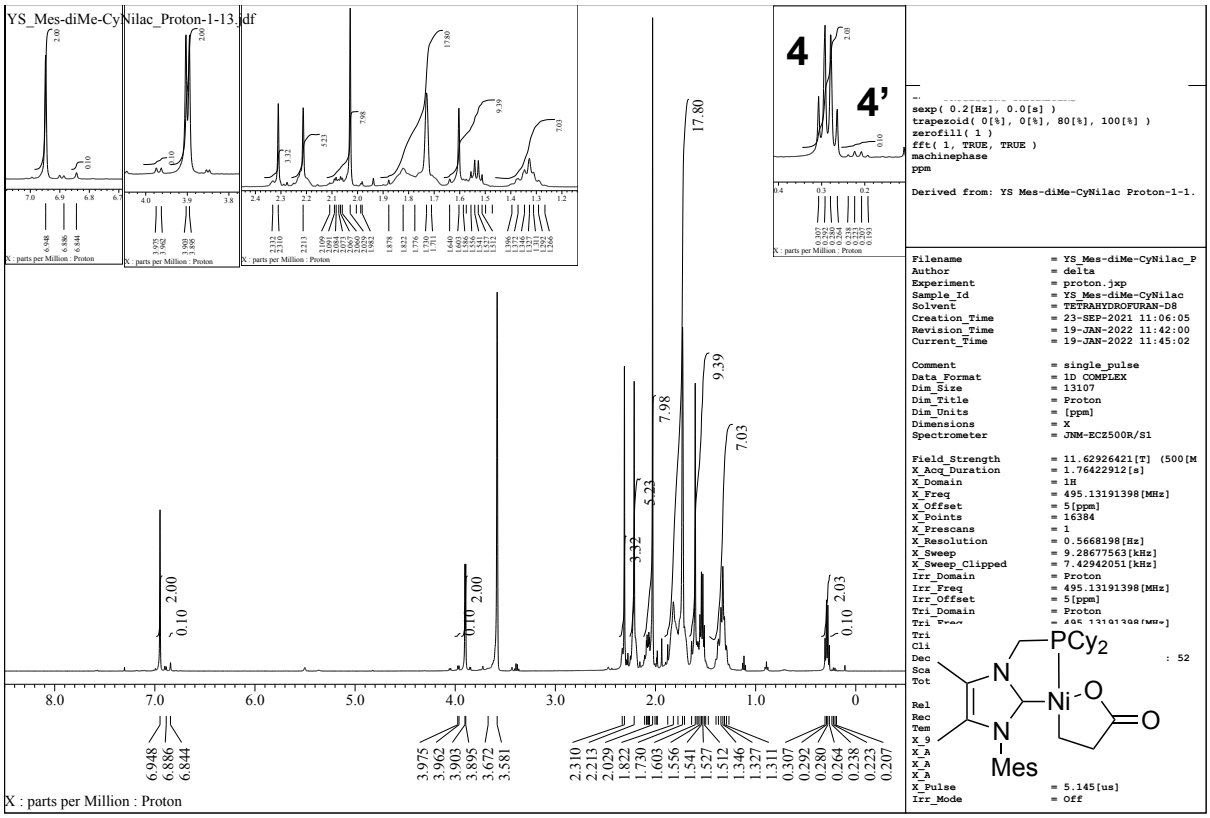



**Figure S12.** $^{1}$H NMR spectrum of **4** (with 10% of **4'**).

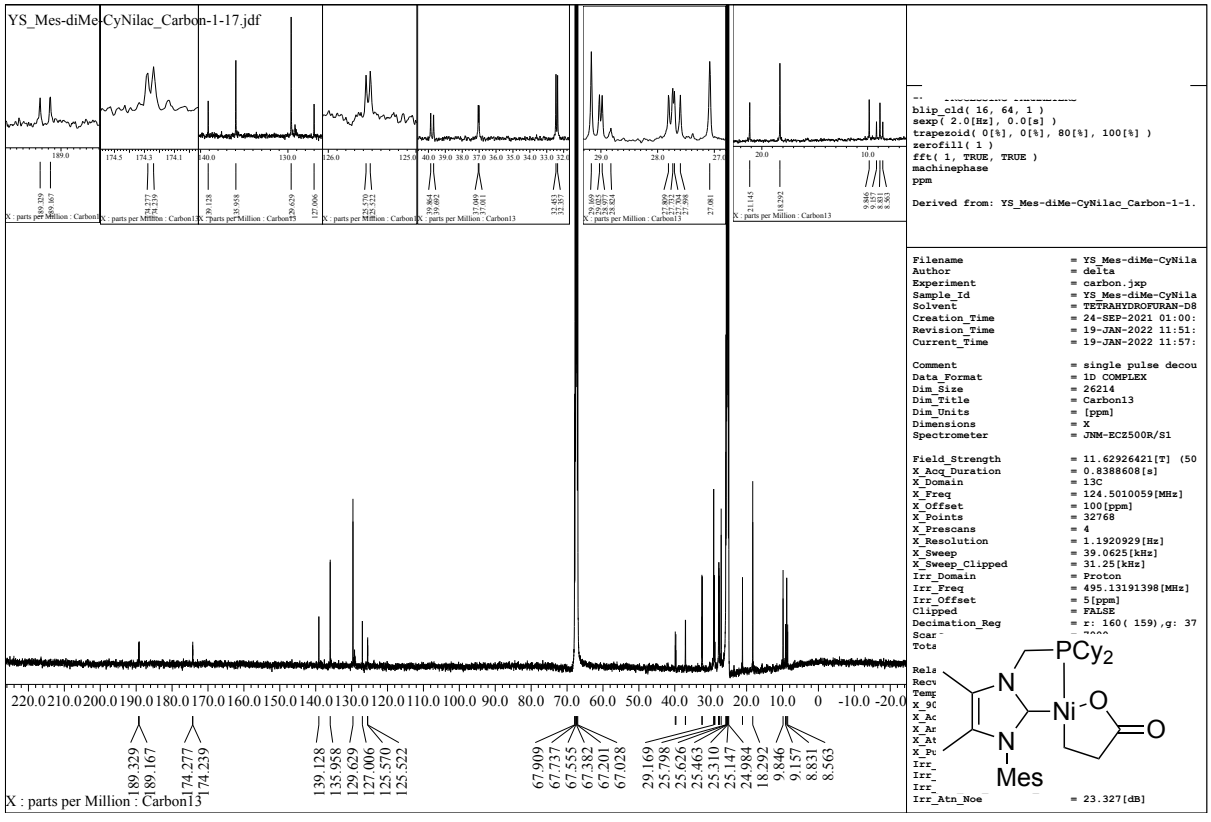



**Figure S13.** $^{13}$C NMR spectrum of **4** (with 10% of **4'**).

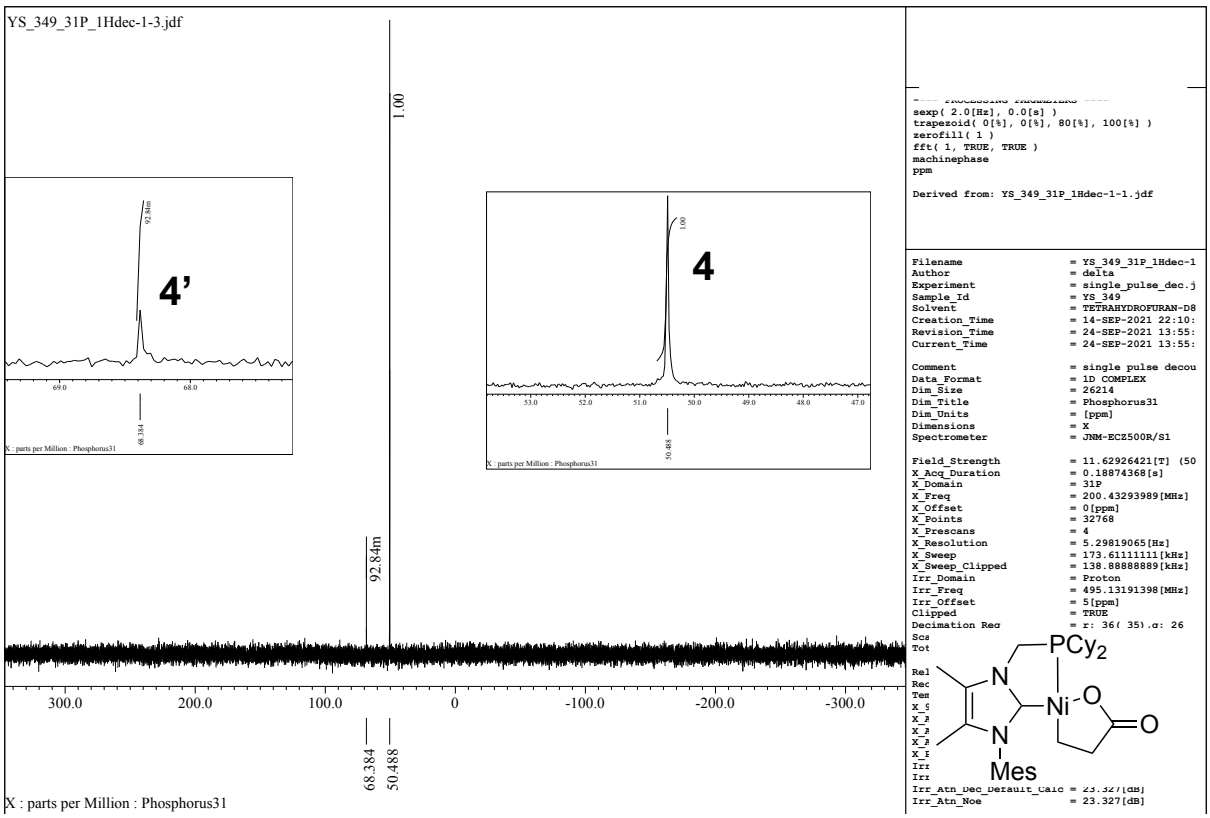



**Figure S14.** $^{31}$P NMR spectrum of **4**.

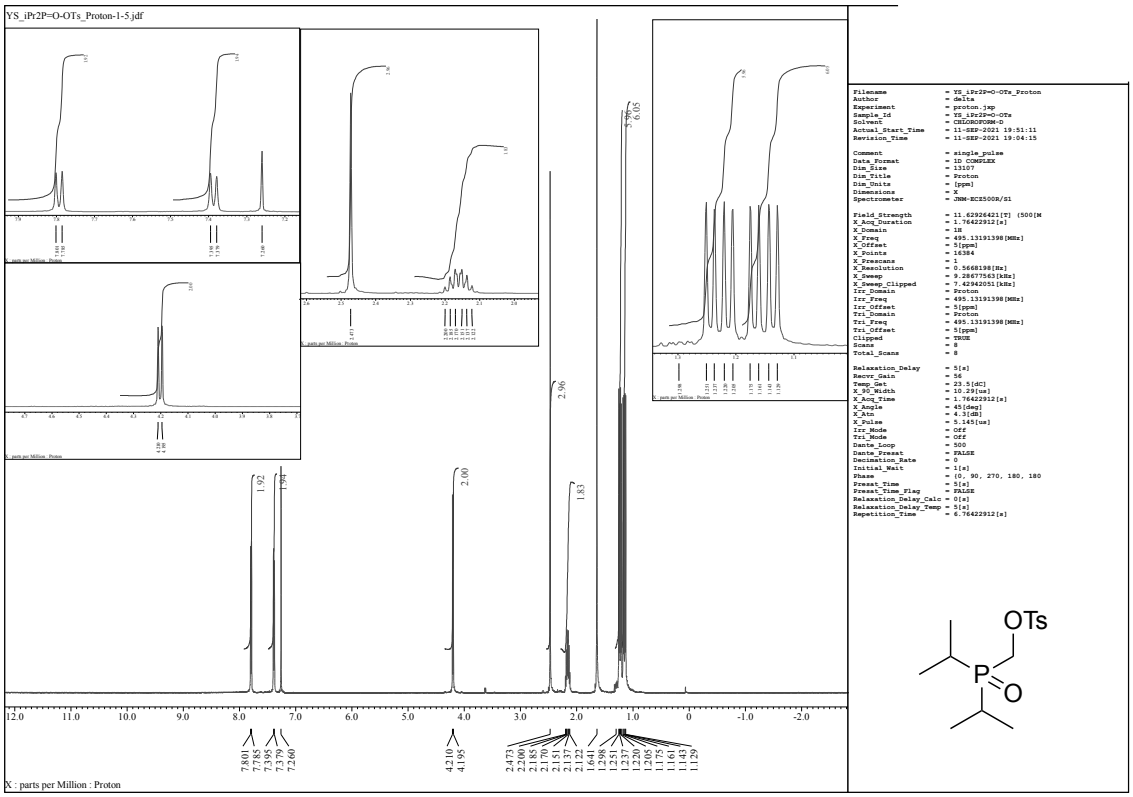



**Figure S15.** $^{1}$H NMR spectrum of **S3**.

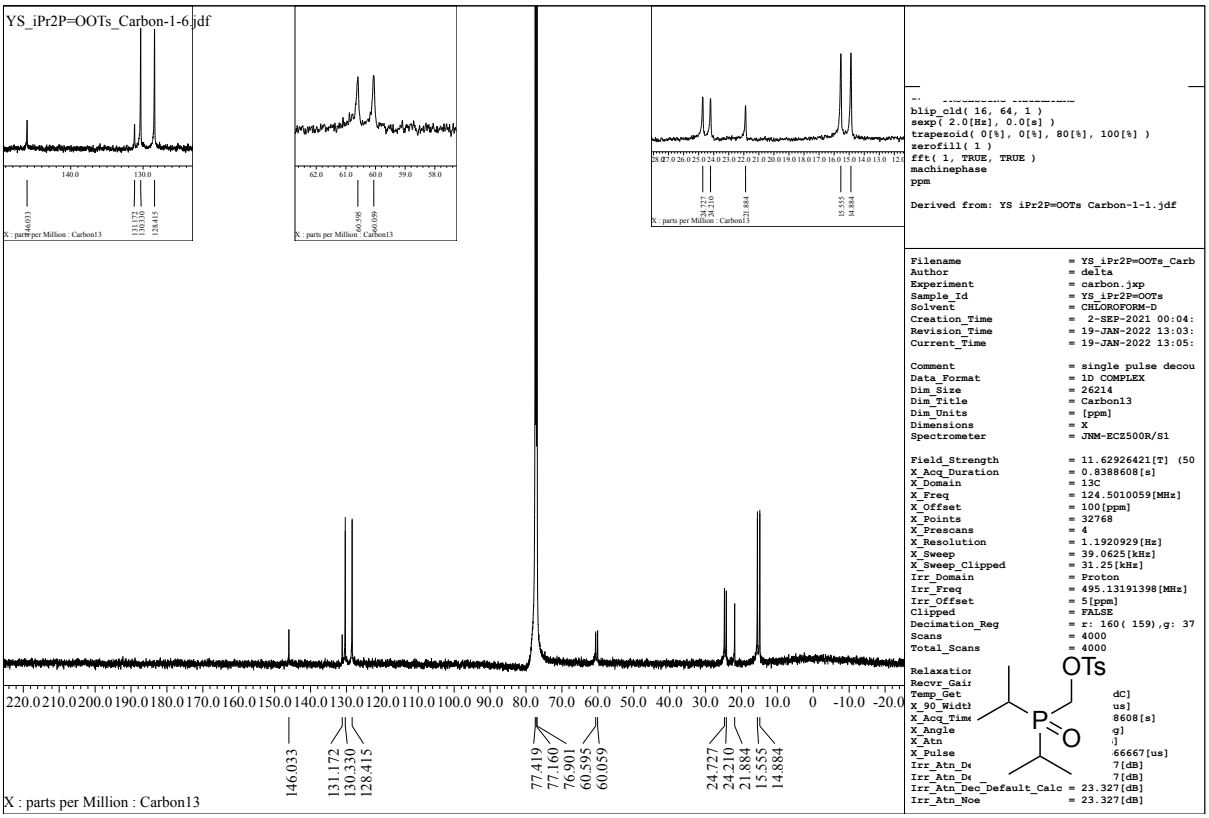



**Figure S16.** $^{13}$C NMR spectrum of **S3**.

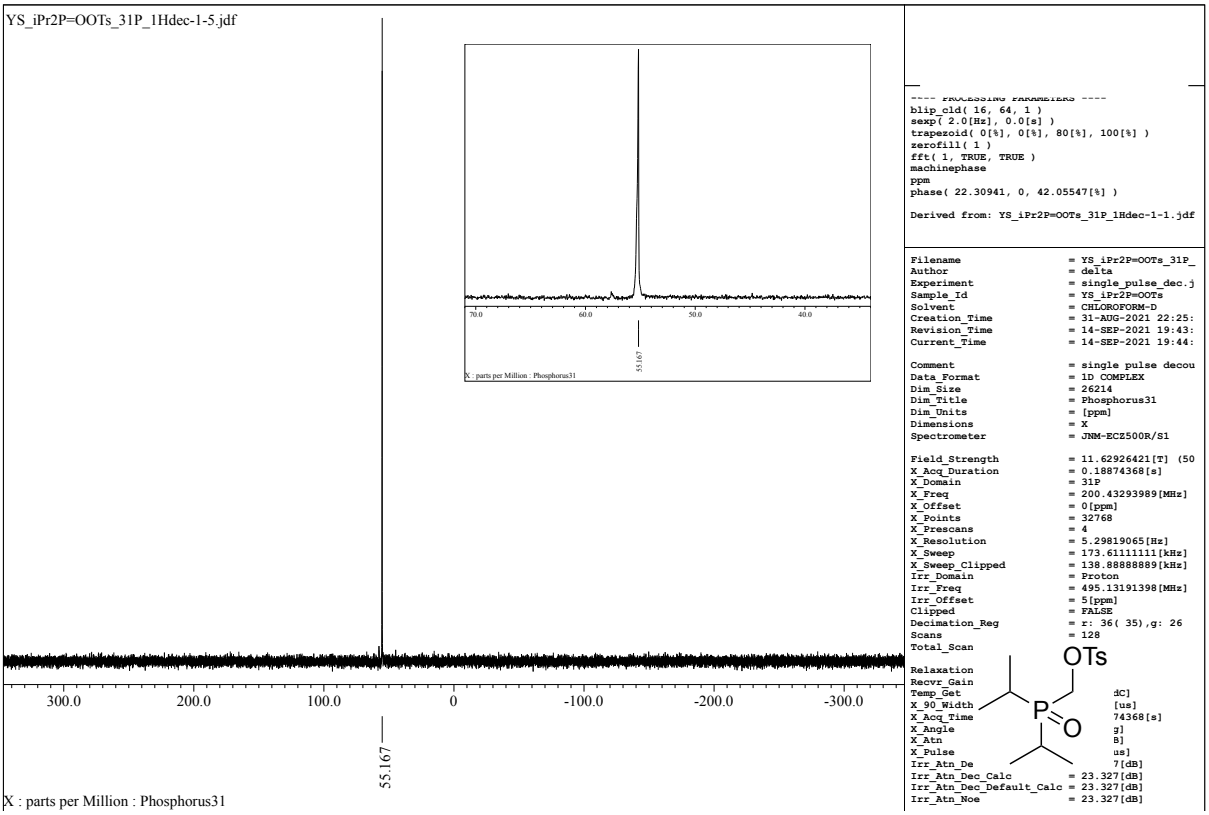



**Figure S17.** $^{31}$P NMR spectrum of **S3**.

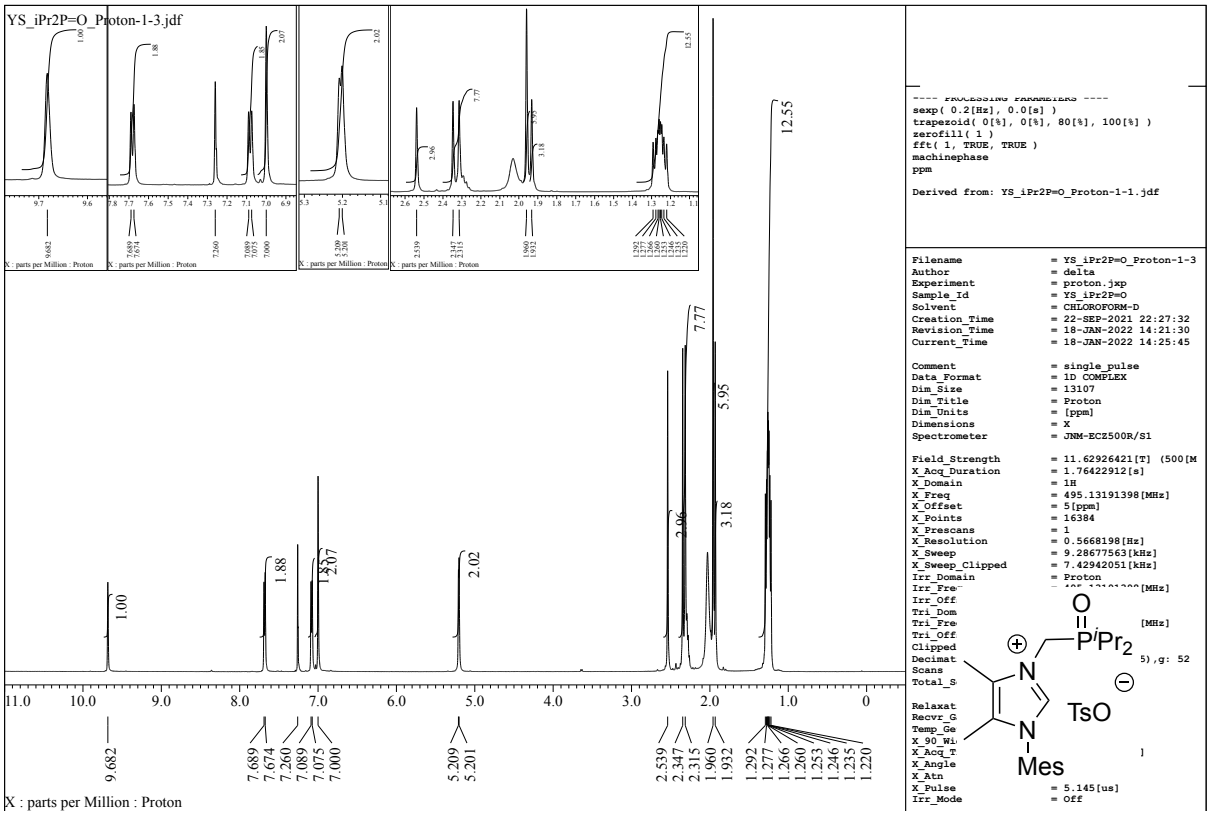



**Figure S18.** $^{1}$H NMR spectrum of **S4**.

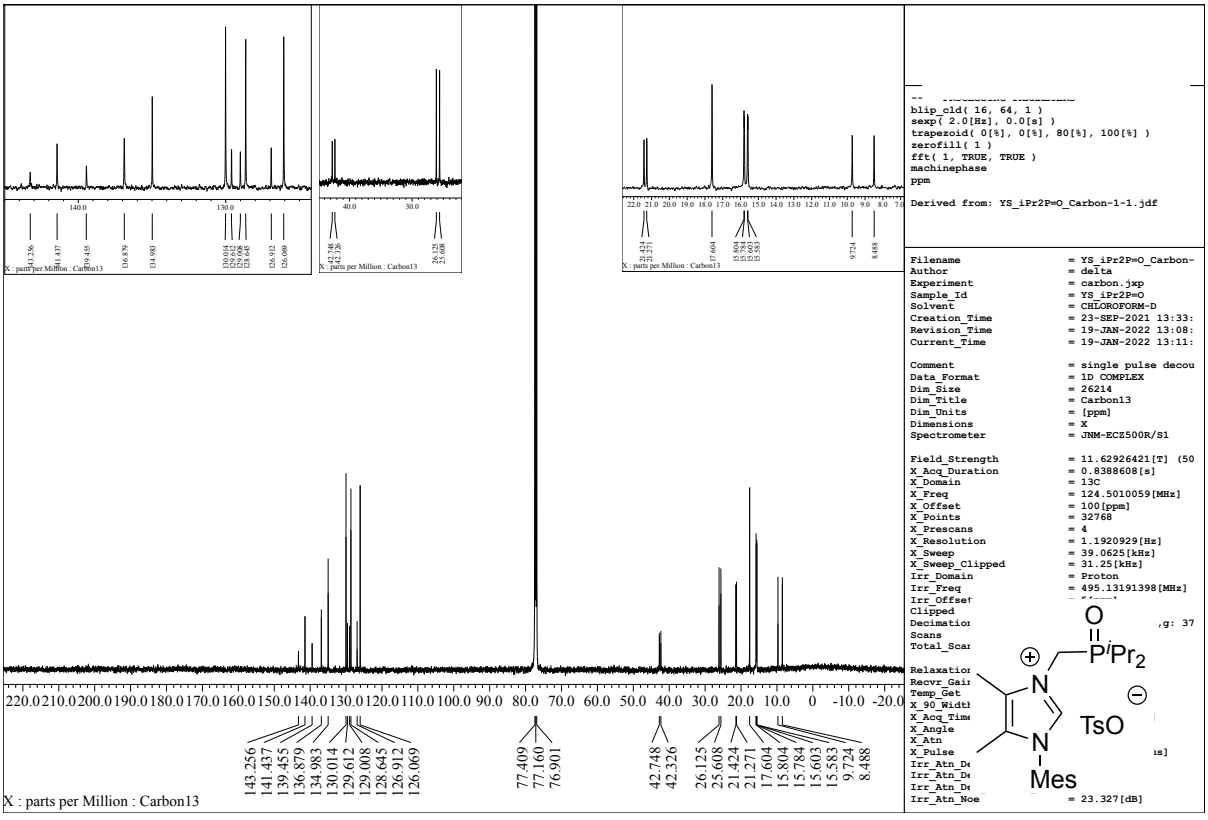



**Figure S19.** $^{13}$C NMR spectrum of **S4**.

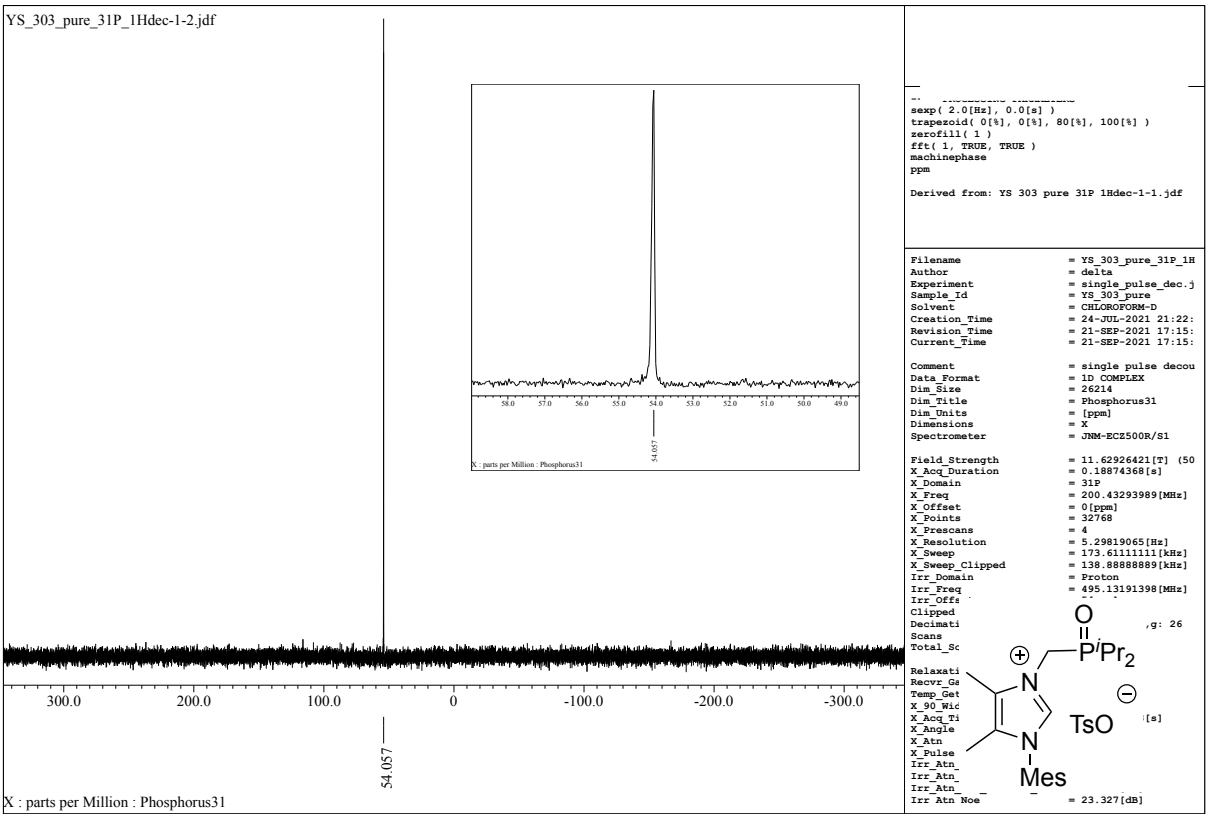



**Figure S20.** $^{31}$P NMR spectrum of **S4**.

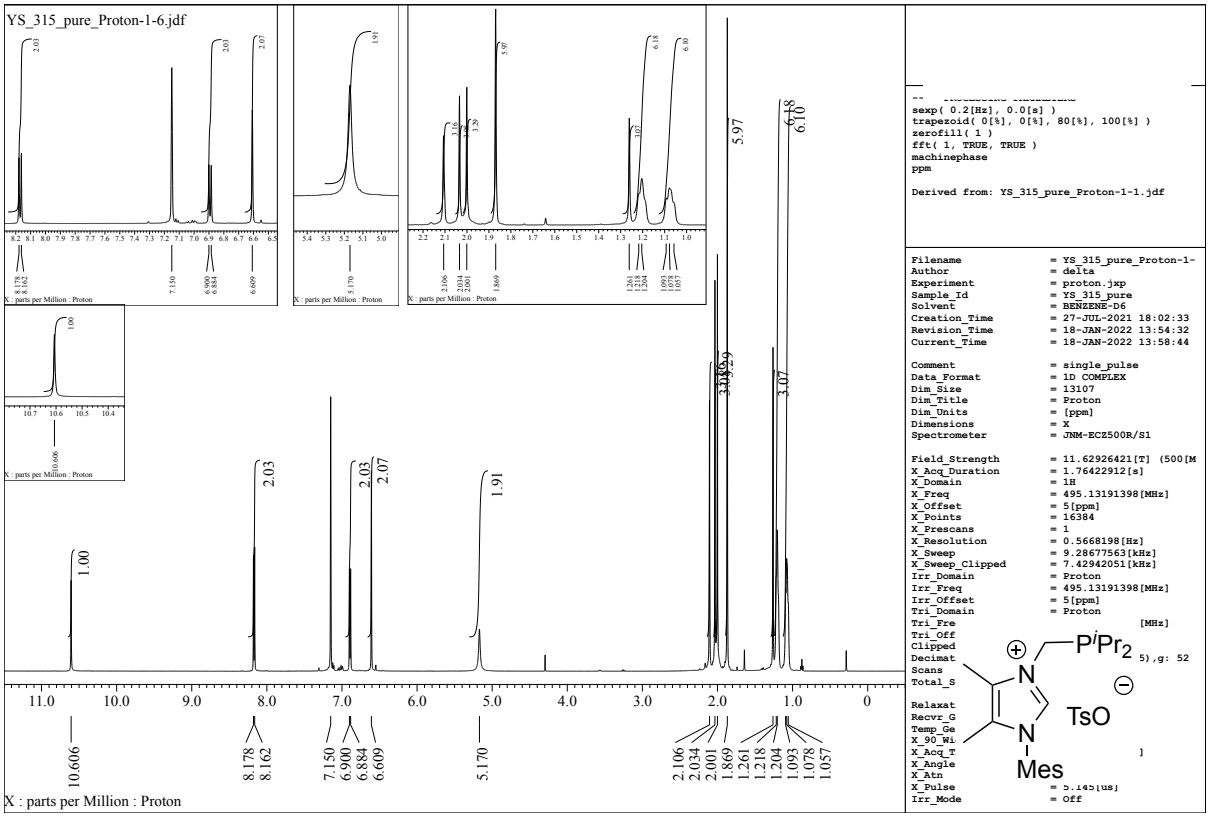



**Figure S21.** $^{1}$H NMR spectrum of **S5**.

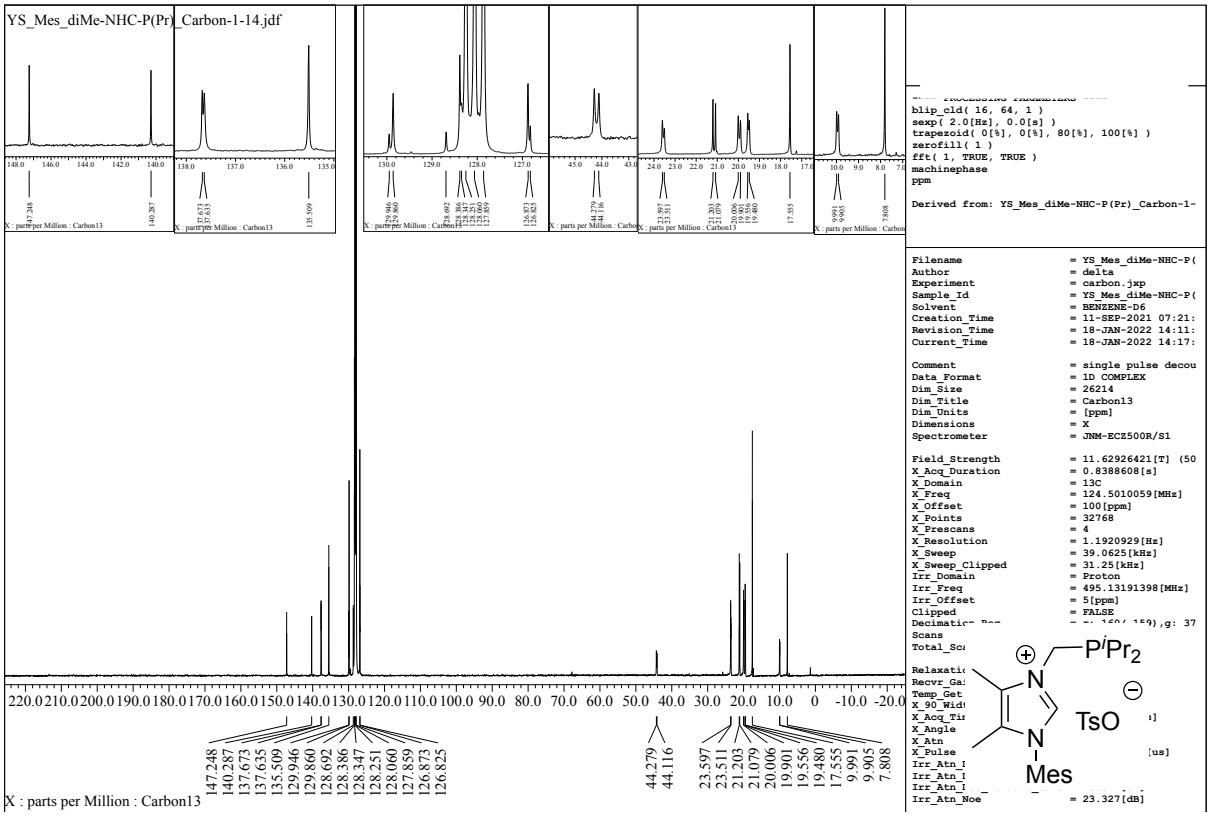



**Figure S22.** $^{13}$C NMR spectrum of **S5**.

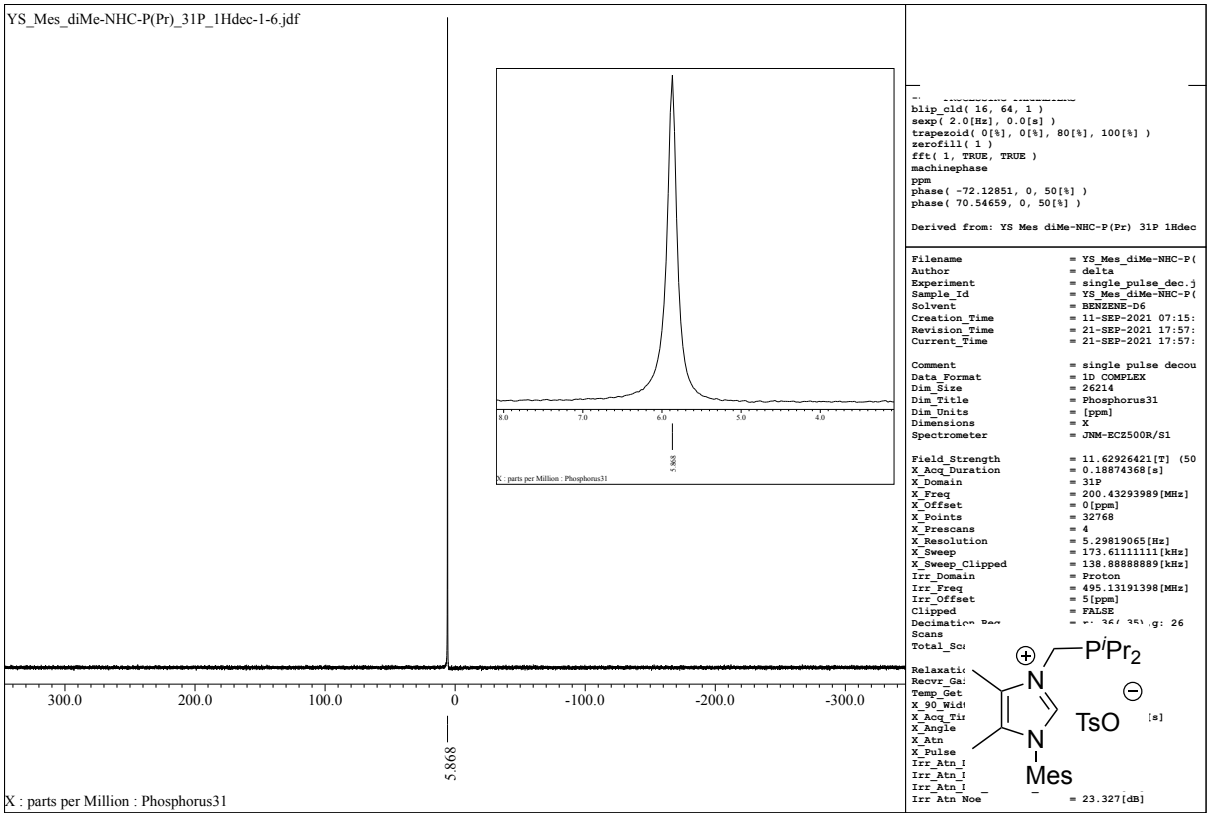



**Figure S23.** $^{31}$P NMR spectrum of **S5**.

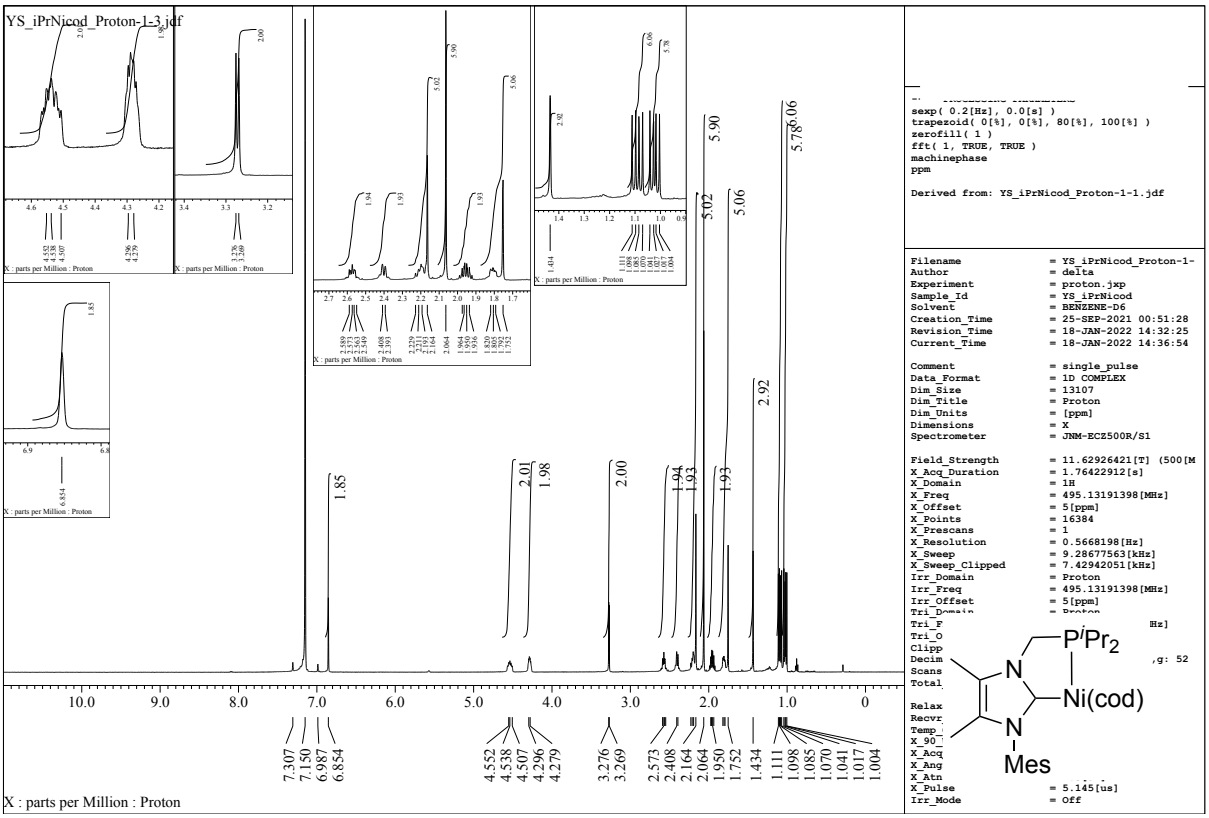



**Figure S24.** $^1$H NMR spectrum of **S6**.

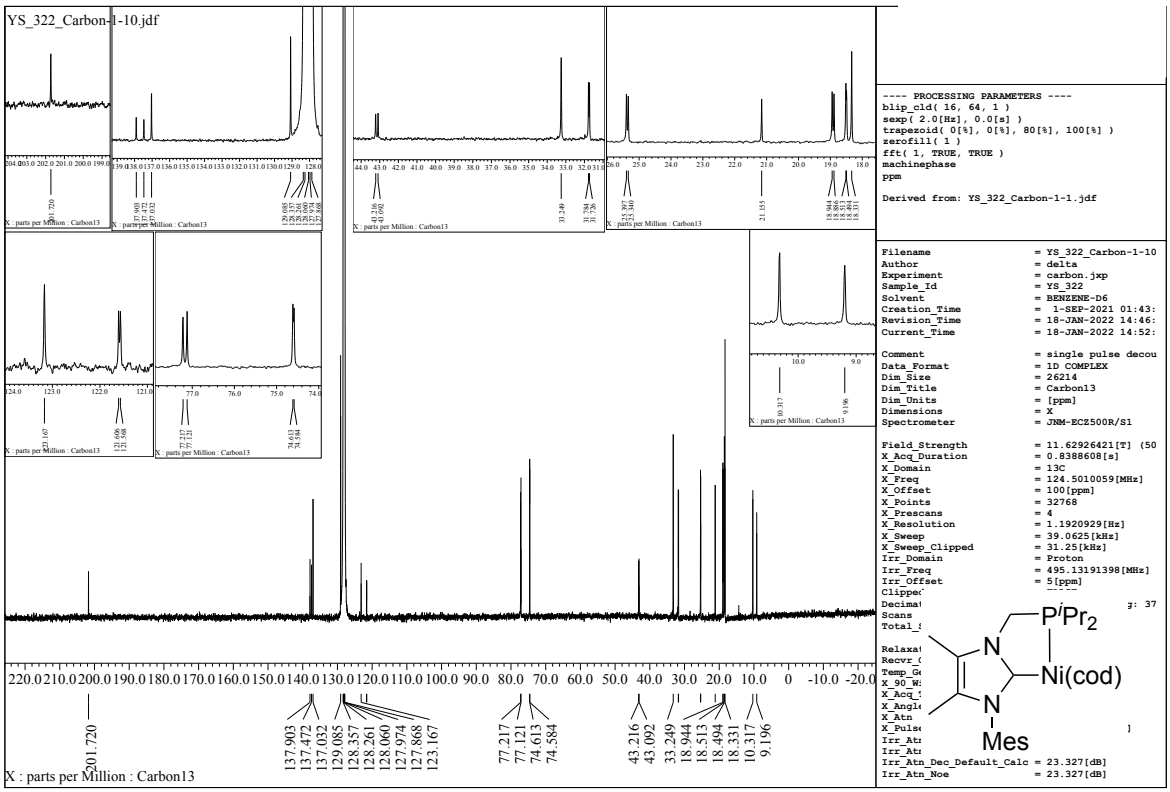



**Figure S25.** $^{13}$C NMR spectrum of **S6**.

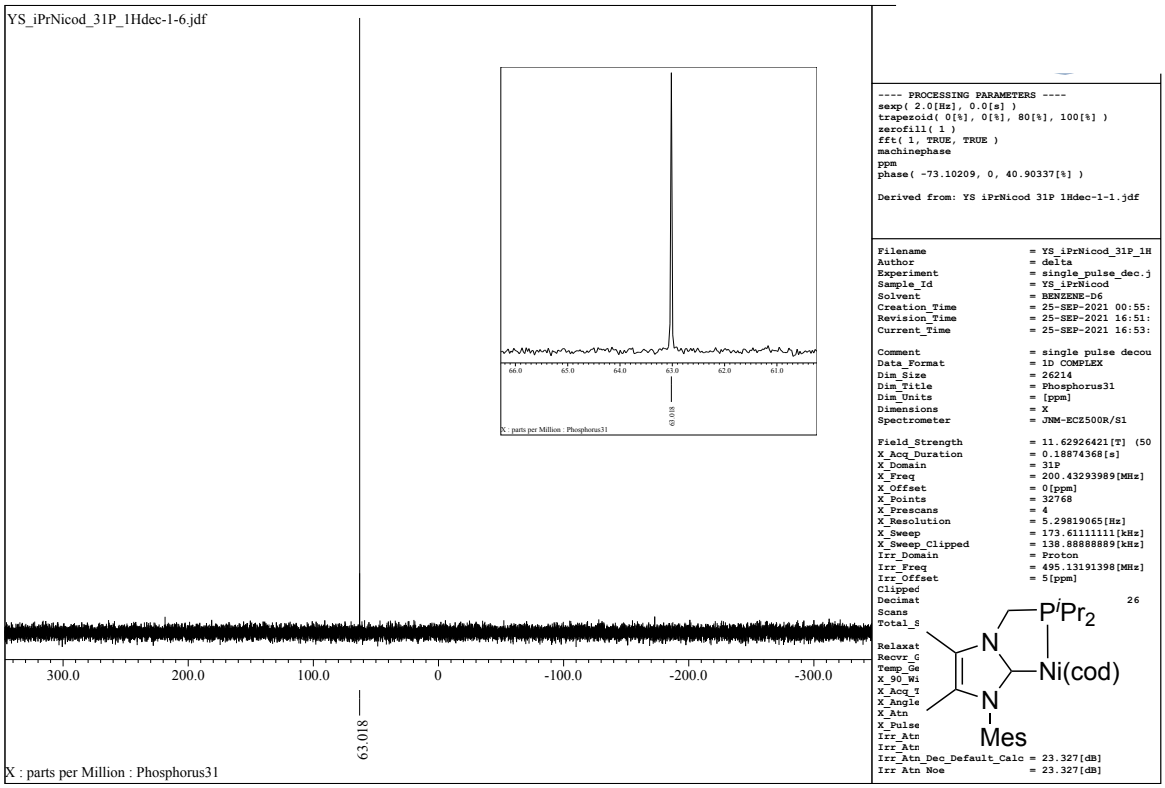



**Figure S26.** $^{31}$P NMR spectrum of **S6**.

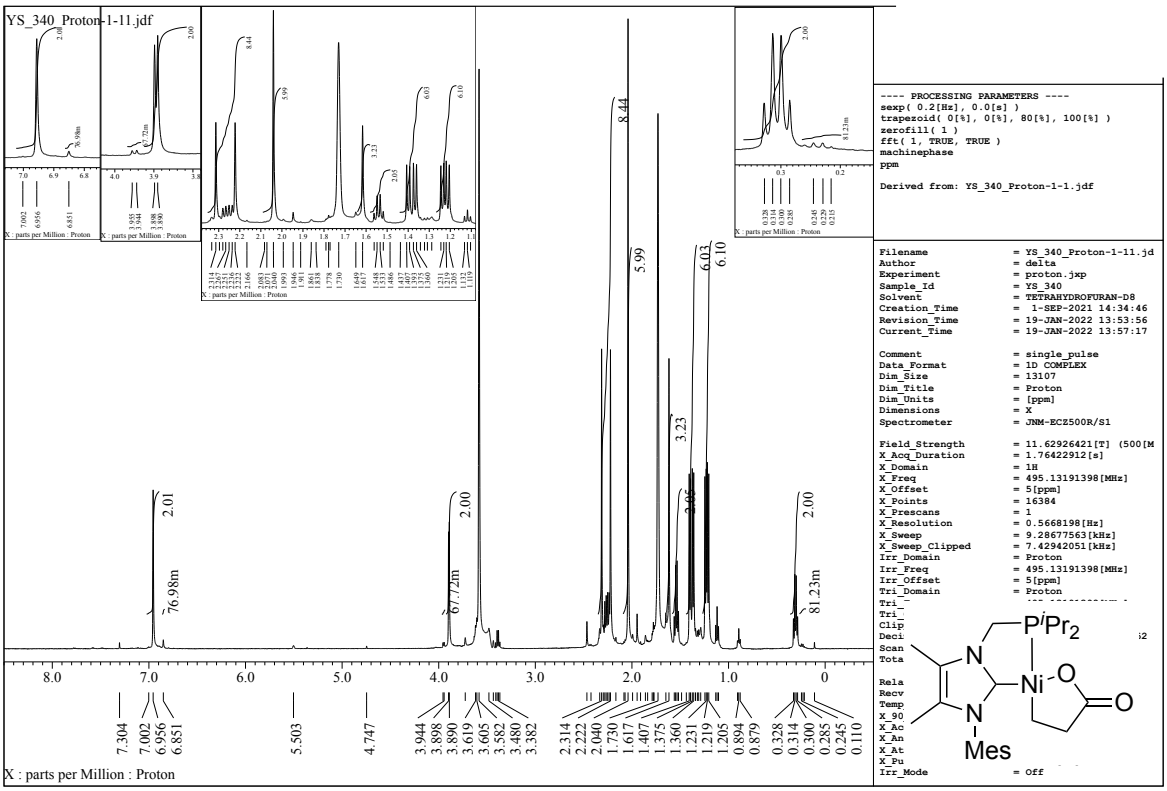



**Figure S27.** $^{1}$H NMR spectrum of **5**.

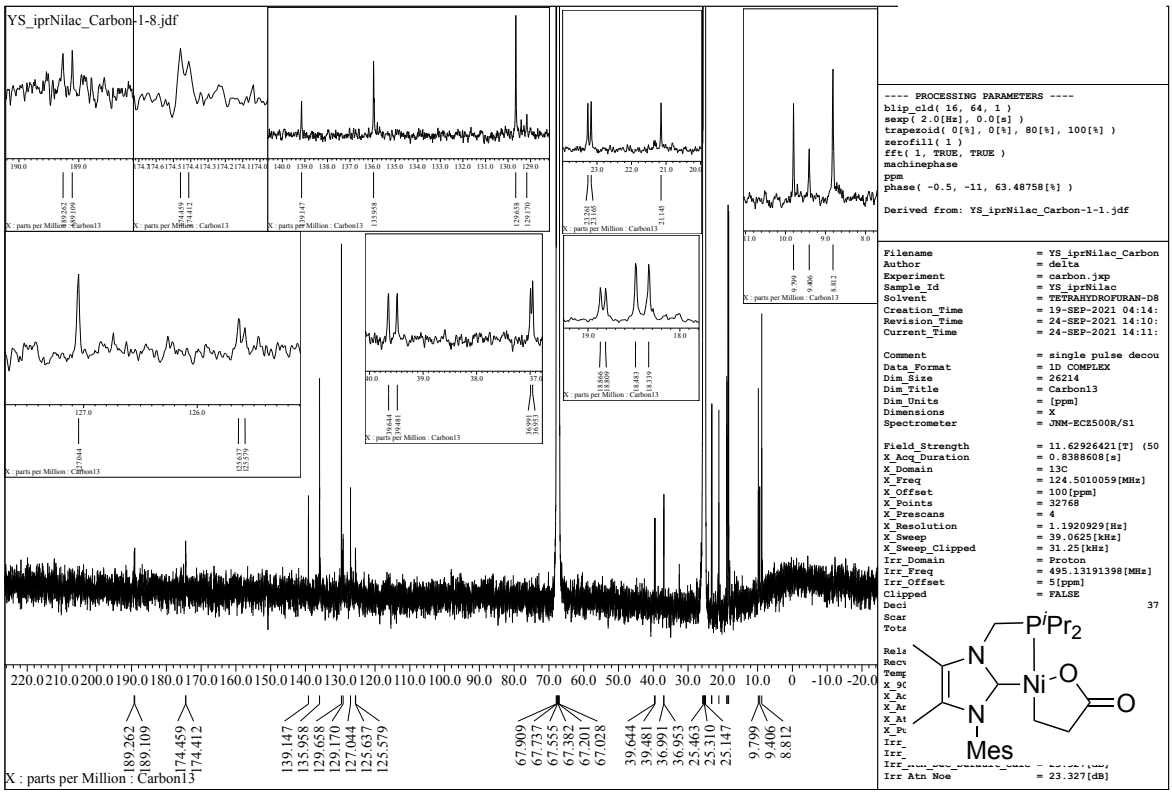



**Figure S28.** $^{13}$C NMR spectrum of **5**.

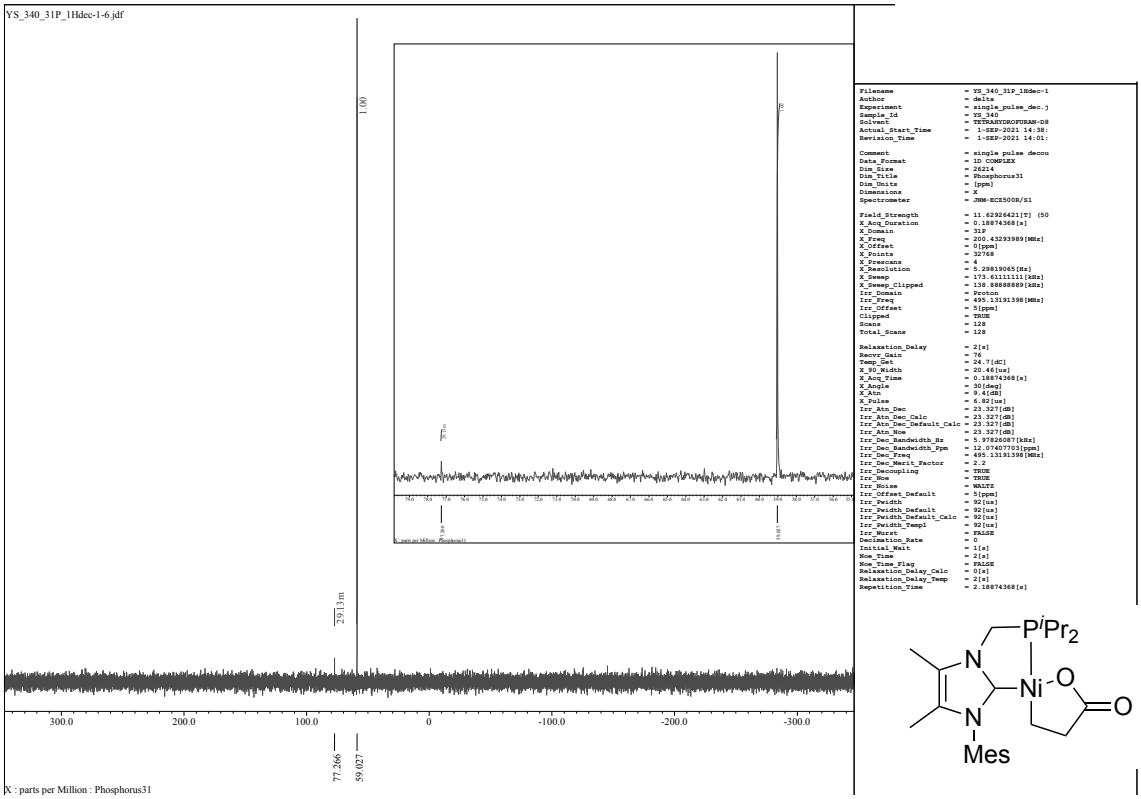



**Figure S29.** $^{31}$P NMR spectrum of **5**.

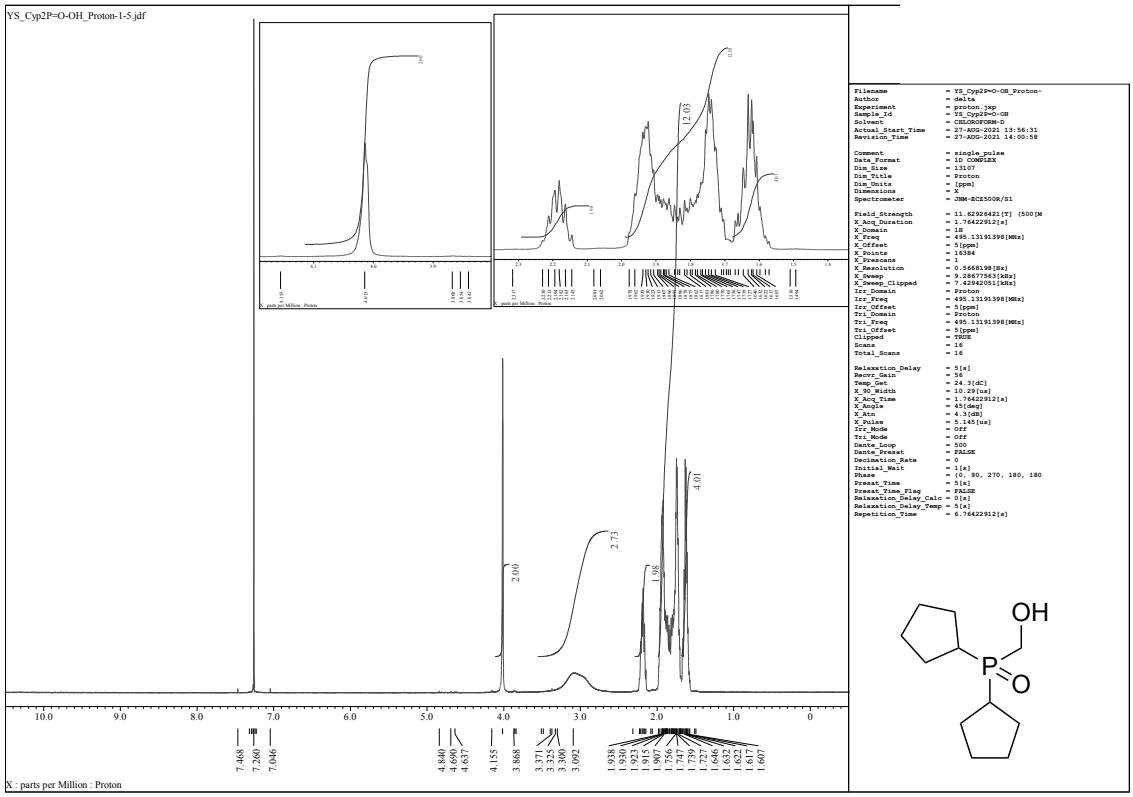



**Figure S30.** $^{1}$H NMR spectrum of **S7**.

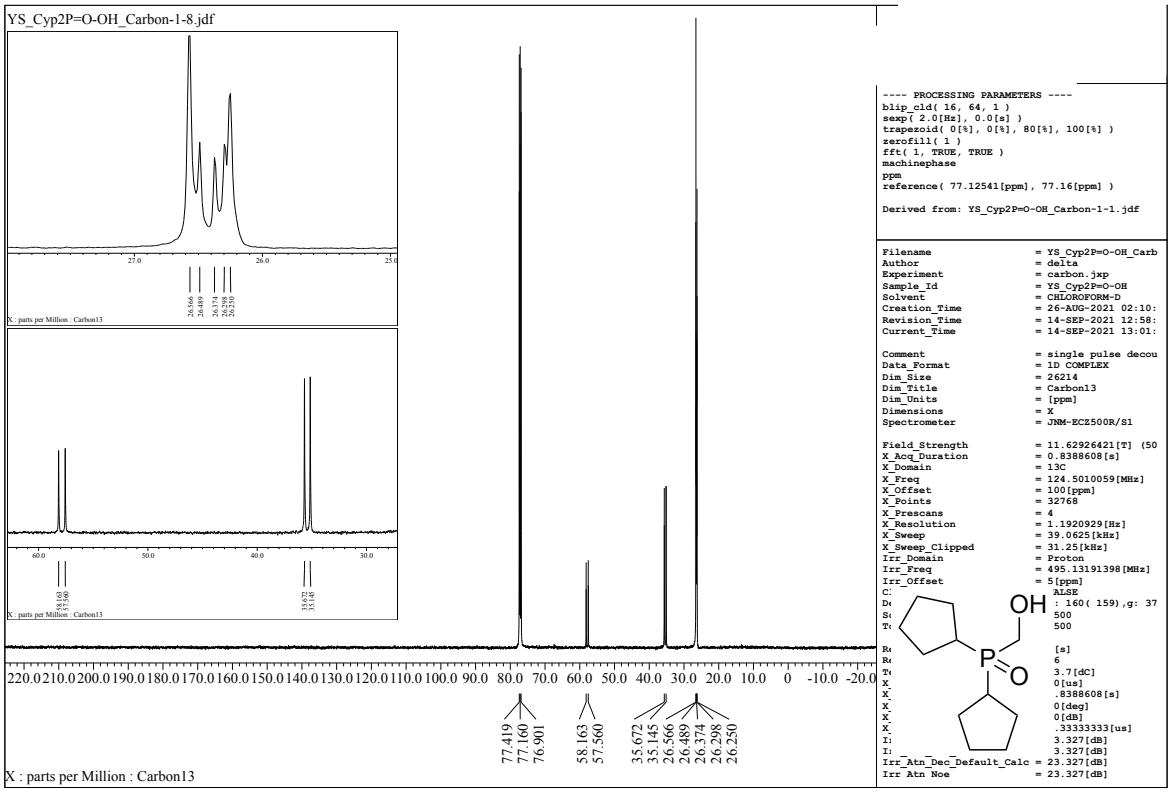



**Figure S31.** $^{13}$C NMR spectrum of **S7**.

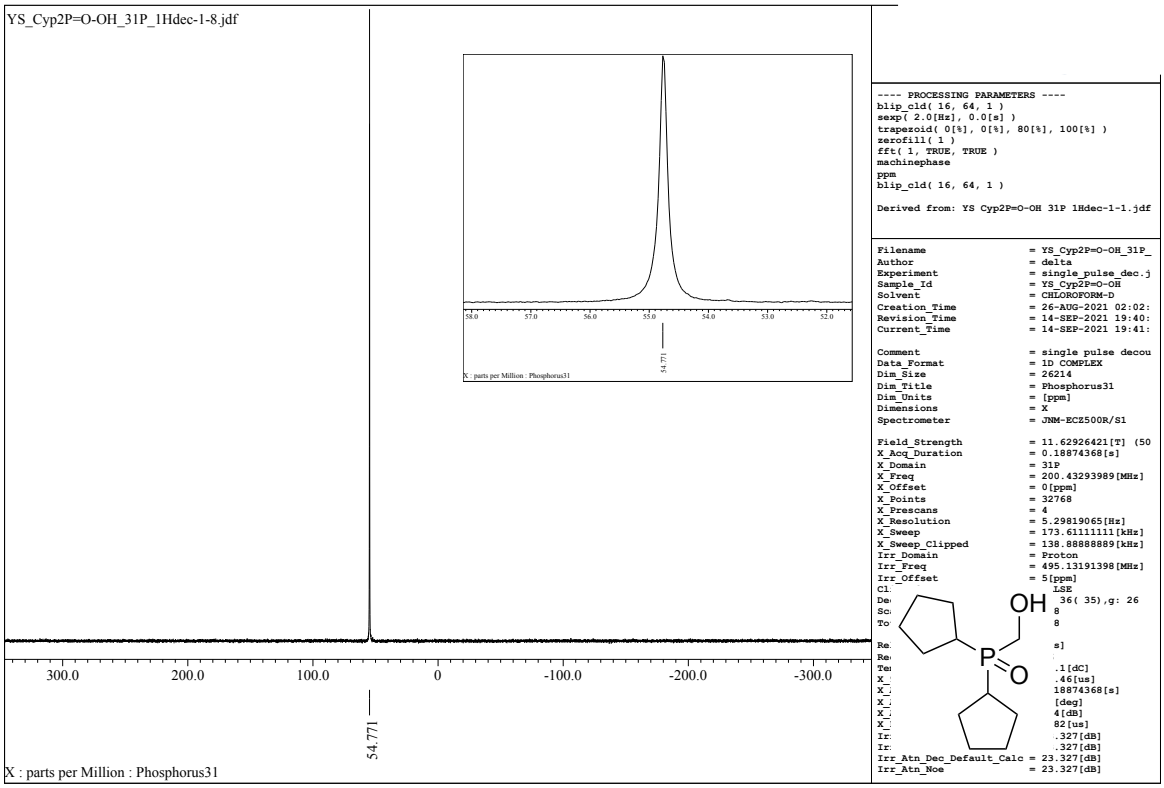



**Figure S32.** $^{31}$P NMR spectrum of **S7**.

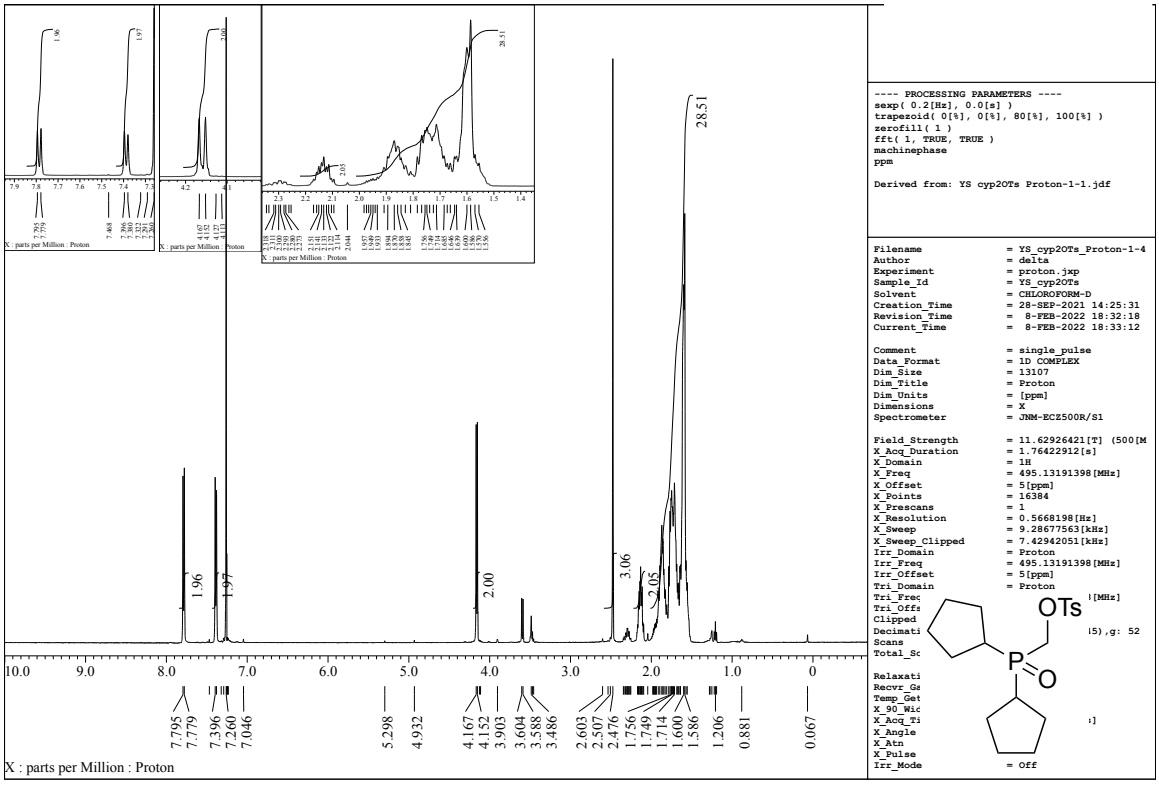



**Figure S33.** $^{1}$H NMR spectrum of **S8**.

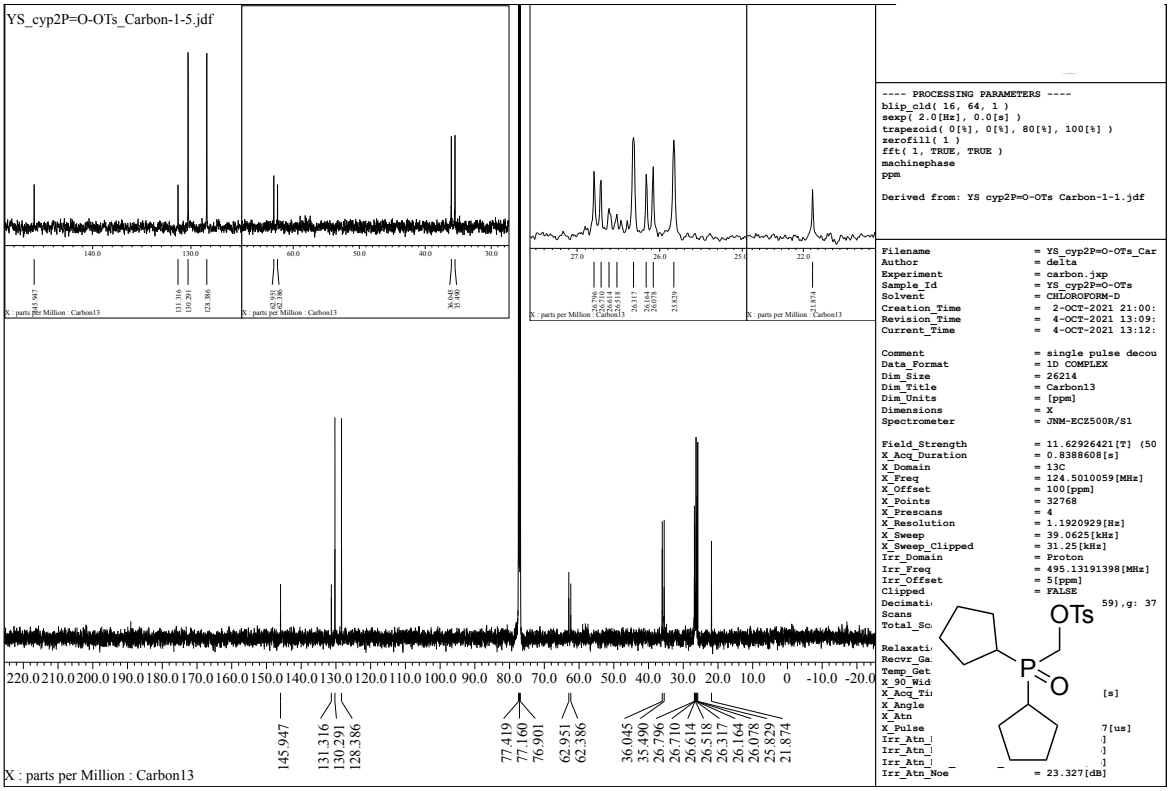



**Figure S34.** $^{13}$C NMR spectrum of **S8**.

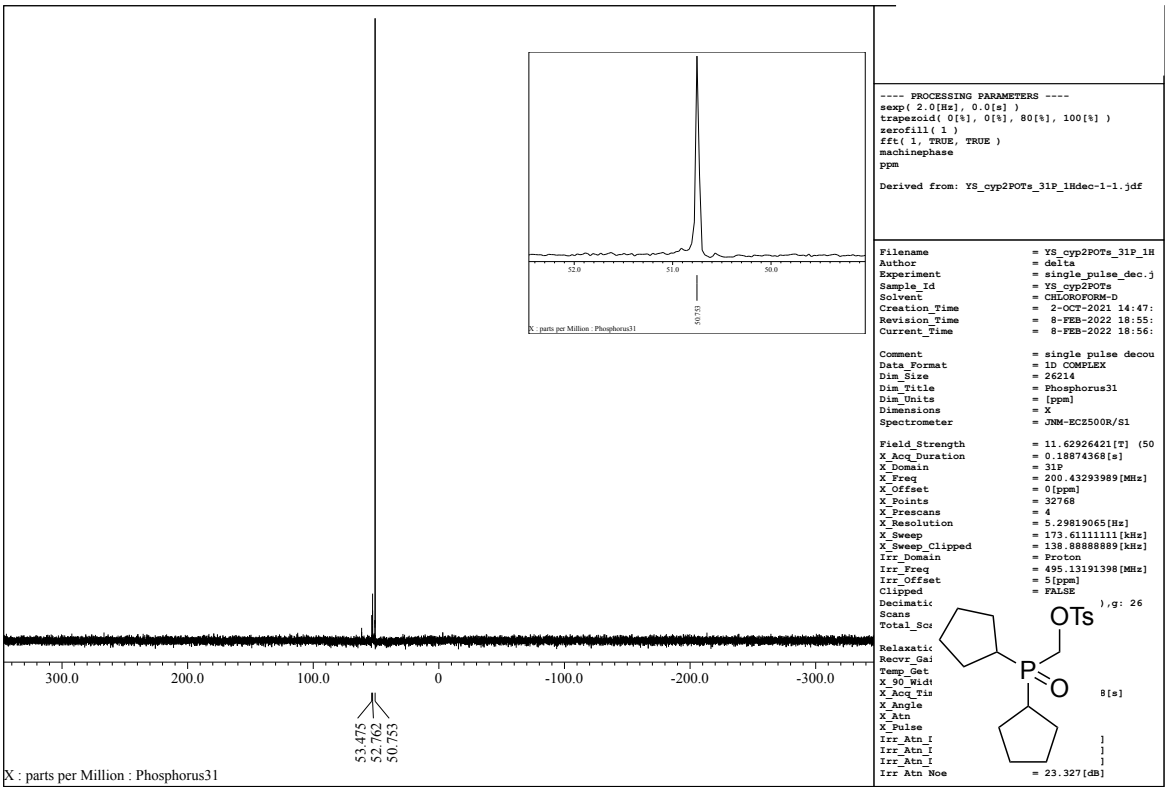



**Figure S35.** $^{31}$P NMR spectrum of **S8**.

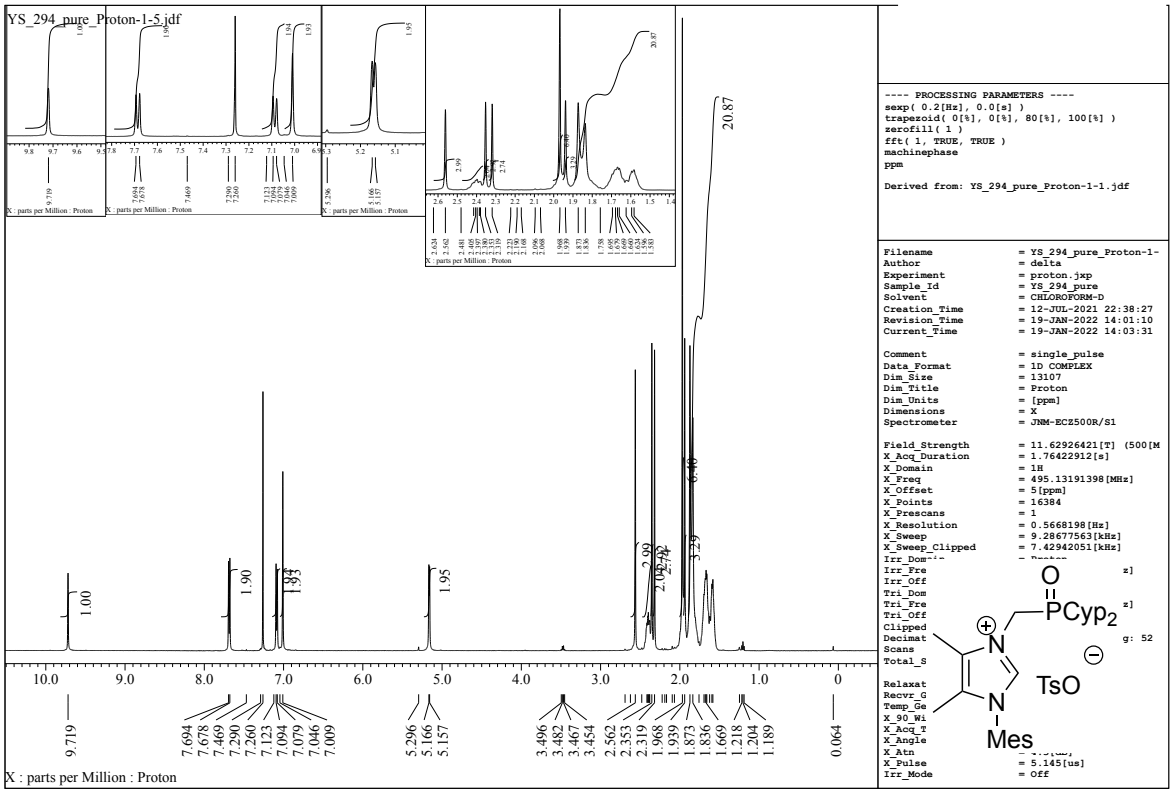



**Figure S36.** $^{1}$H NMR spectrum of **S9**.

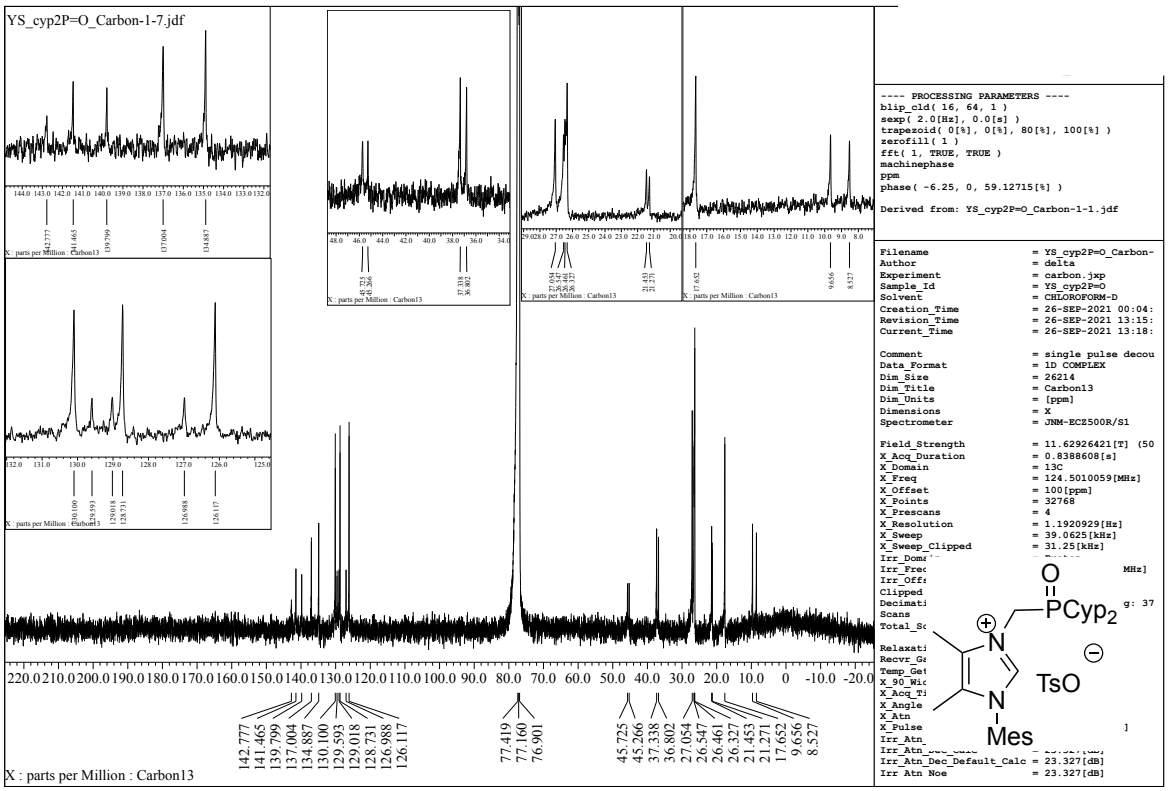



**Figure S37.** $^{13}$C NMR spectrum of **S9**.

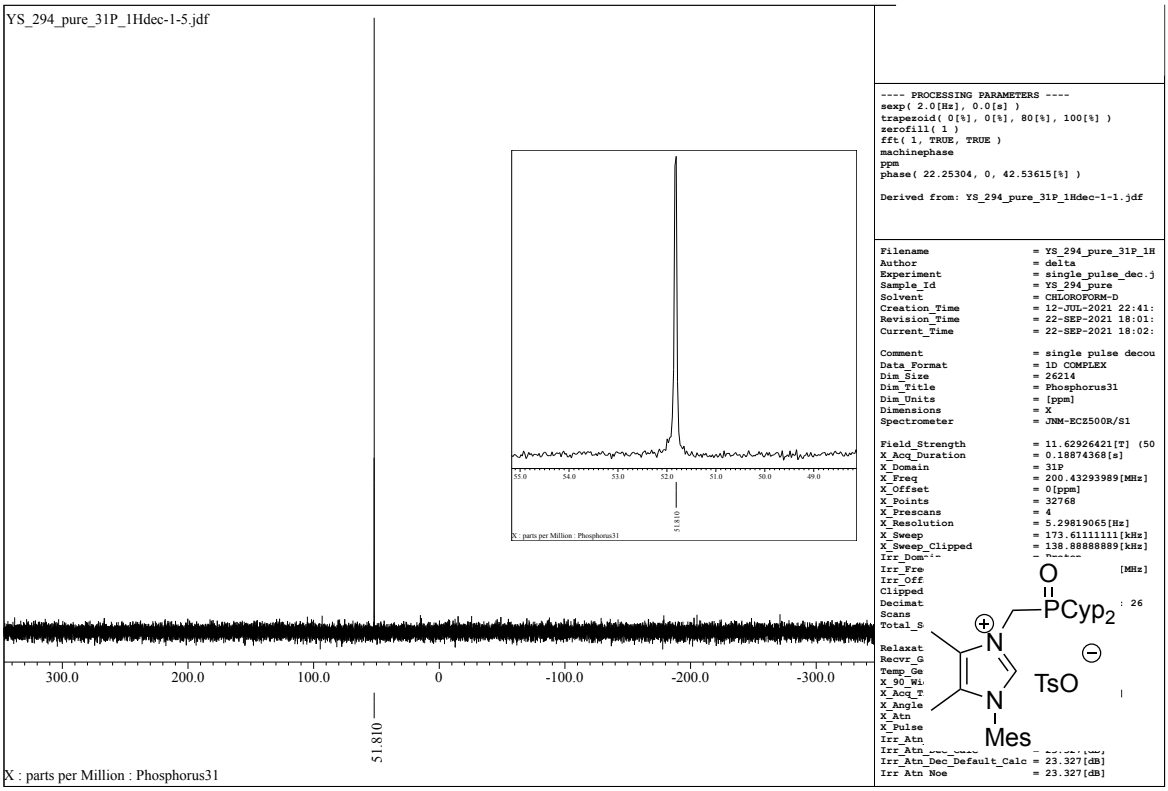



**Figure S38.** $^{31}$P NMR spectrum of **S9**.

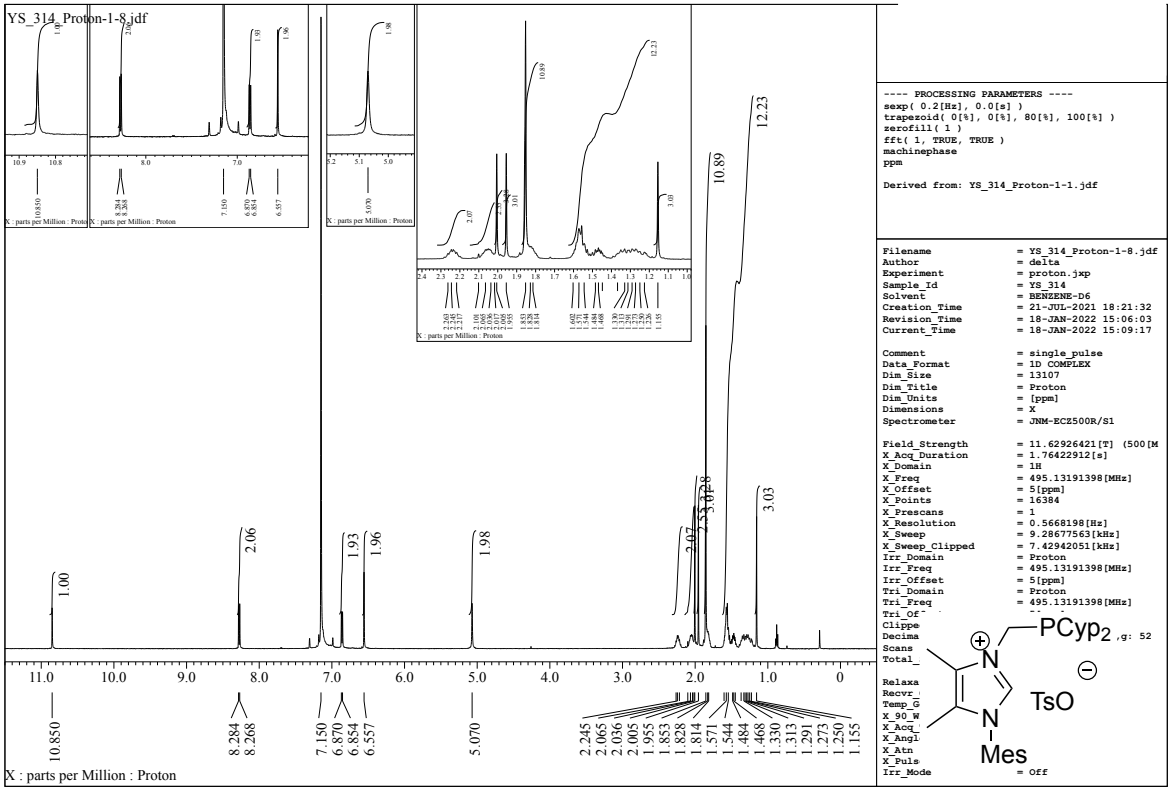



**Figure S39.** $^{1}$H NMR spectrum of **S10**.

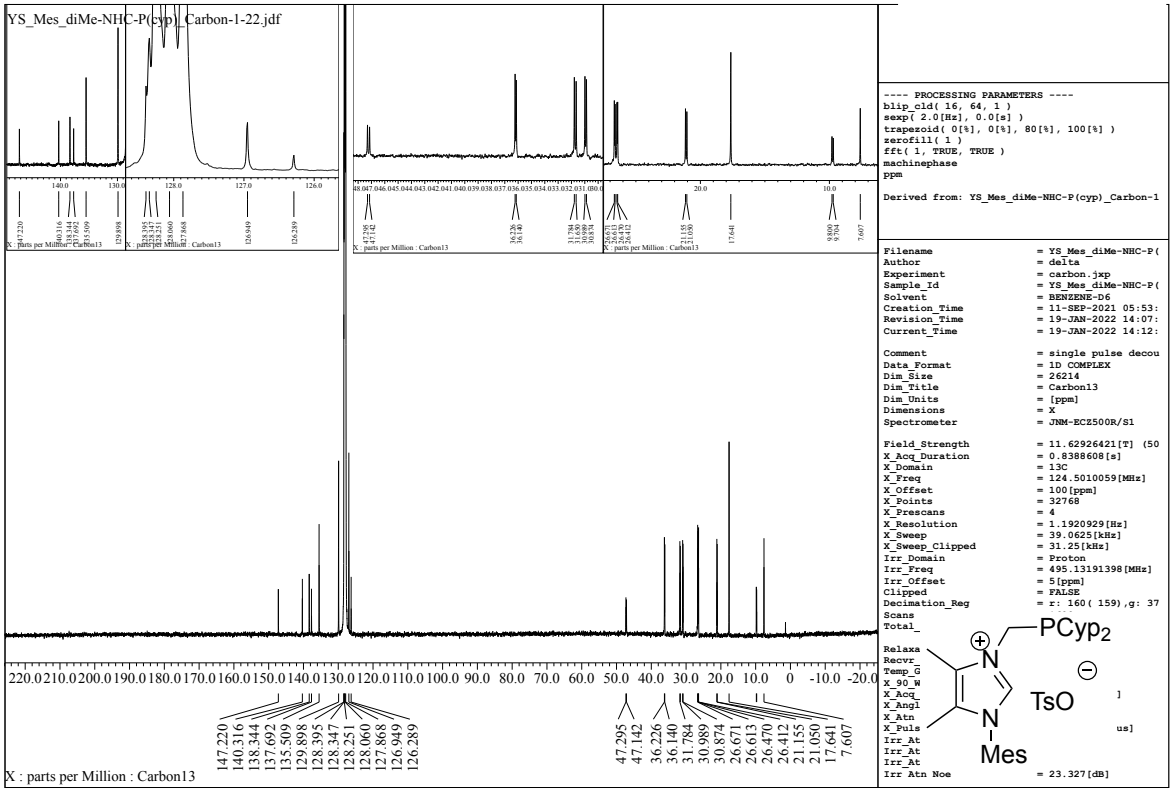



**Figure S40.** $^{13}$C NMR spectrum of **S10**.

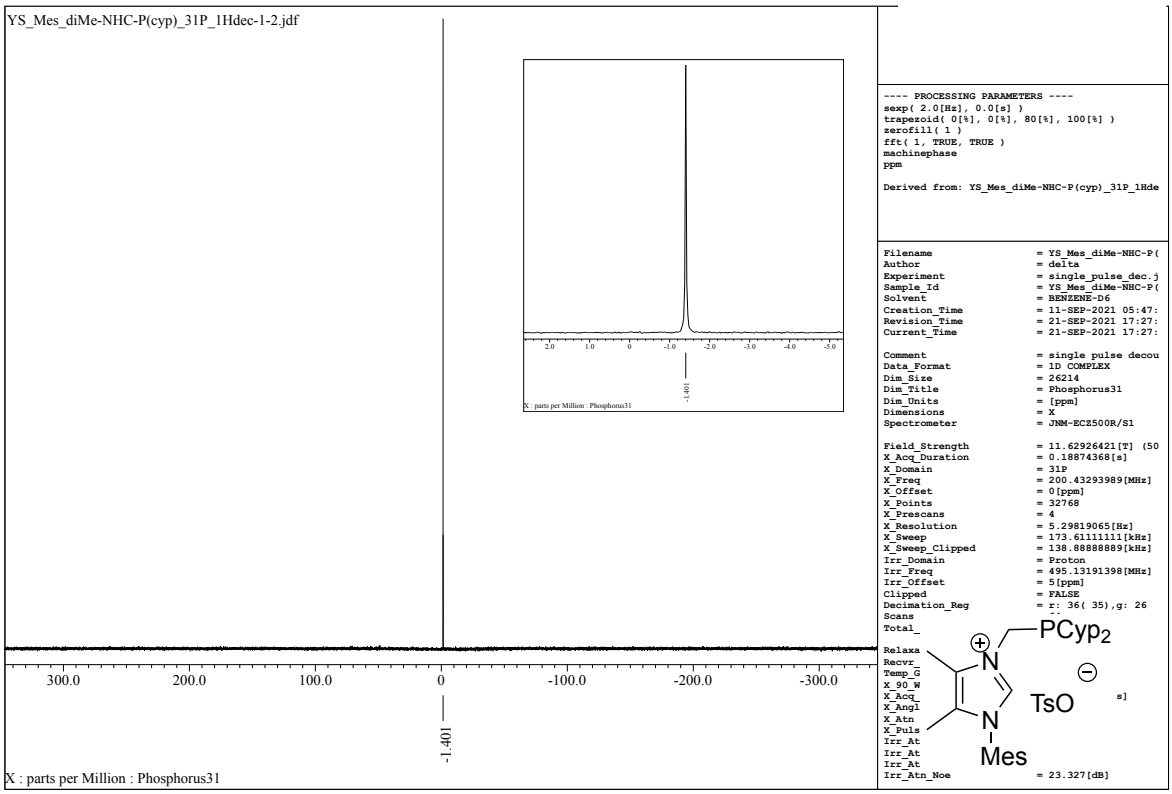



**Figure S41.** $^{31}$P NMR spectrum of **S10**.

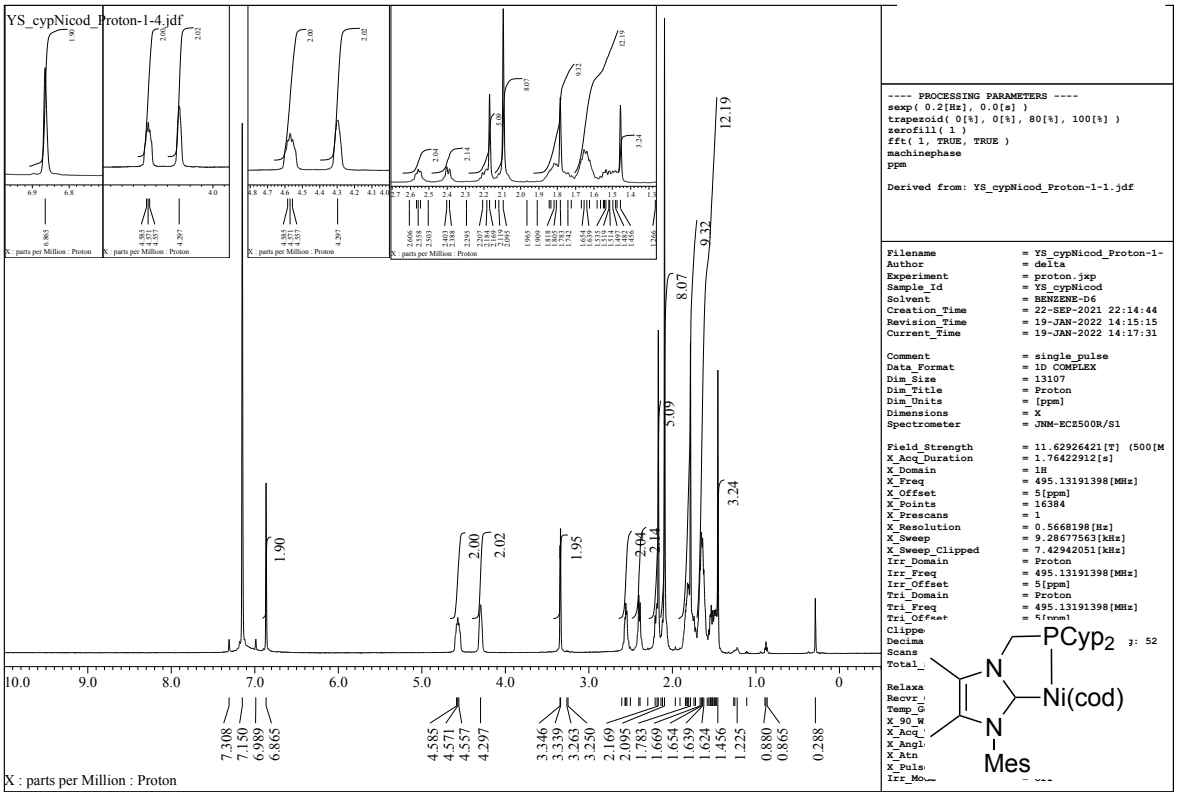



**Figure S42.** $^{1}$H NMR spectrum of **S11**.

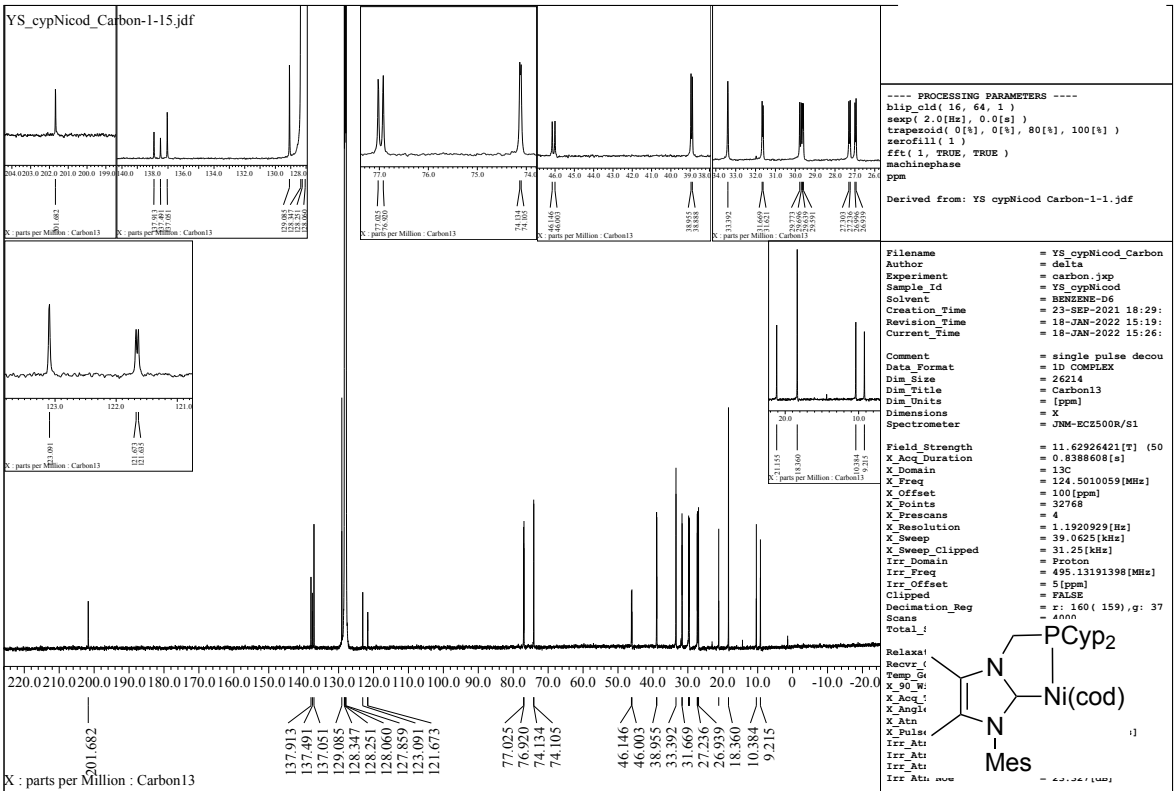



**Figure S43.** $^{13}$C NMR spectrum of **S11**.

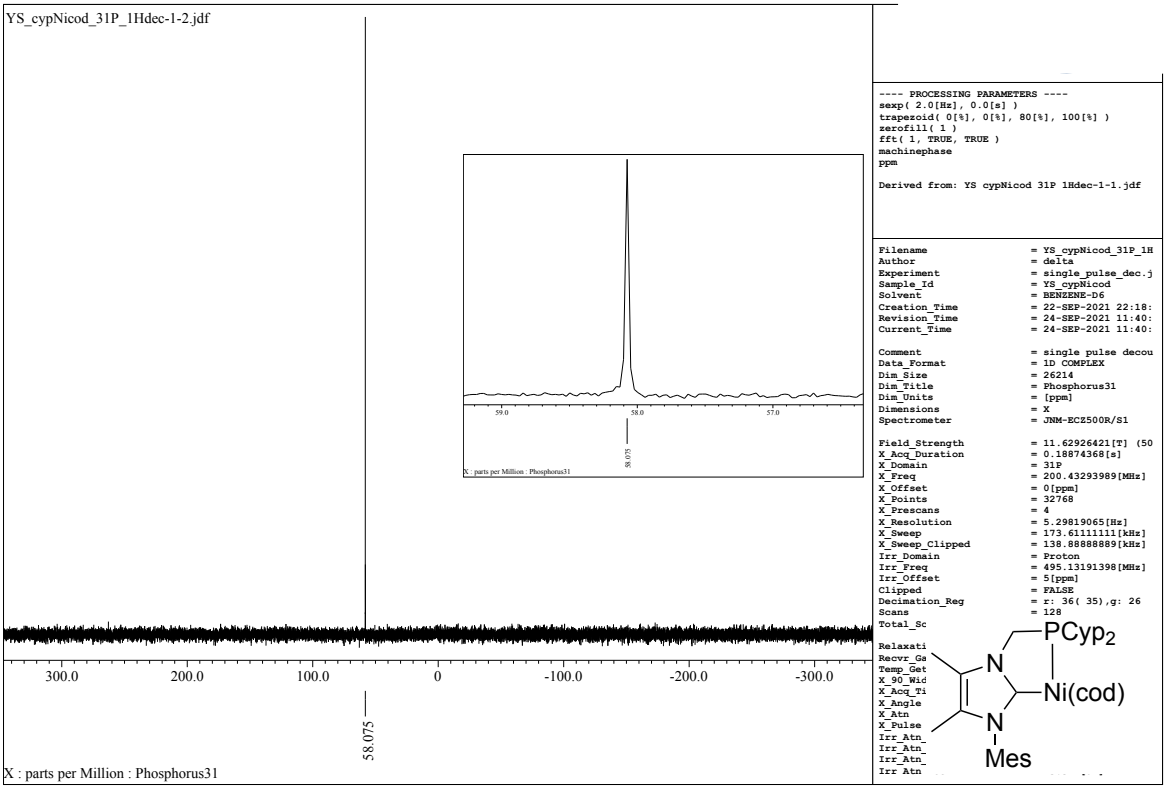



**Figure S44.** $^{31}$P NMR spectrum of **S11**.

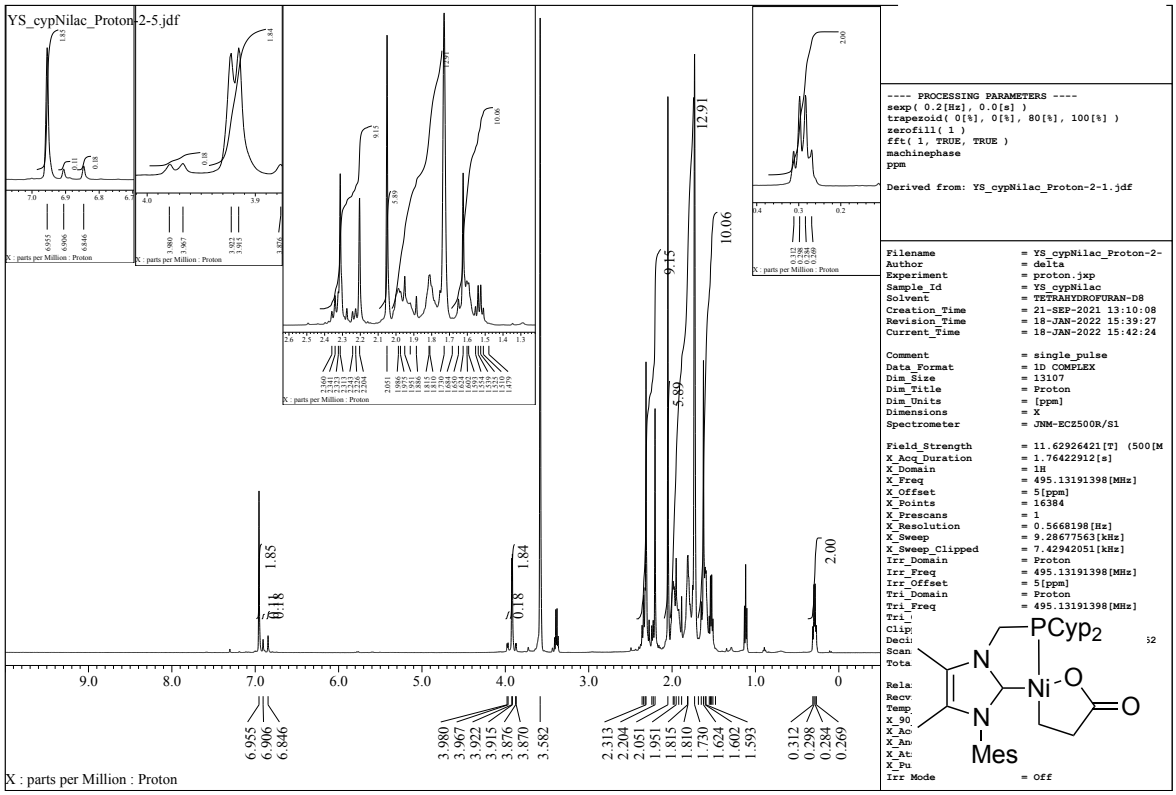



**Figure S45.** $^{1}$H NMR spectrum of **6**.

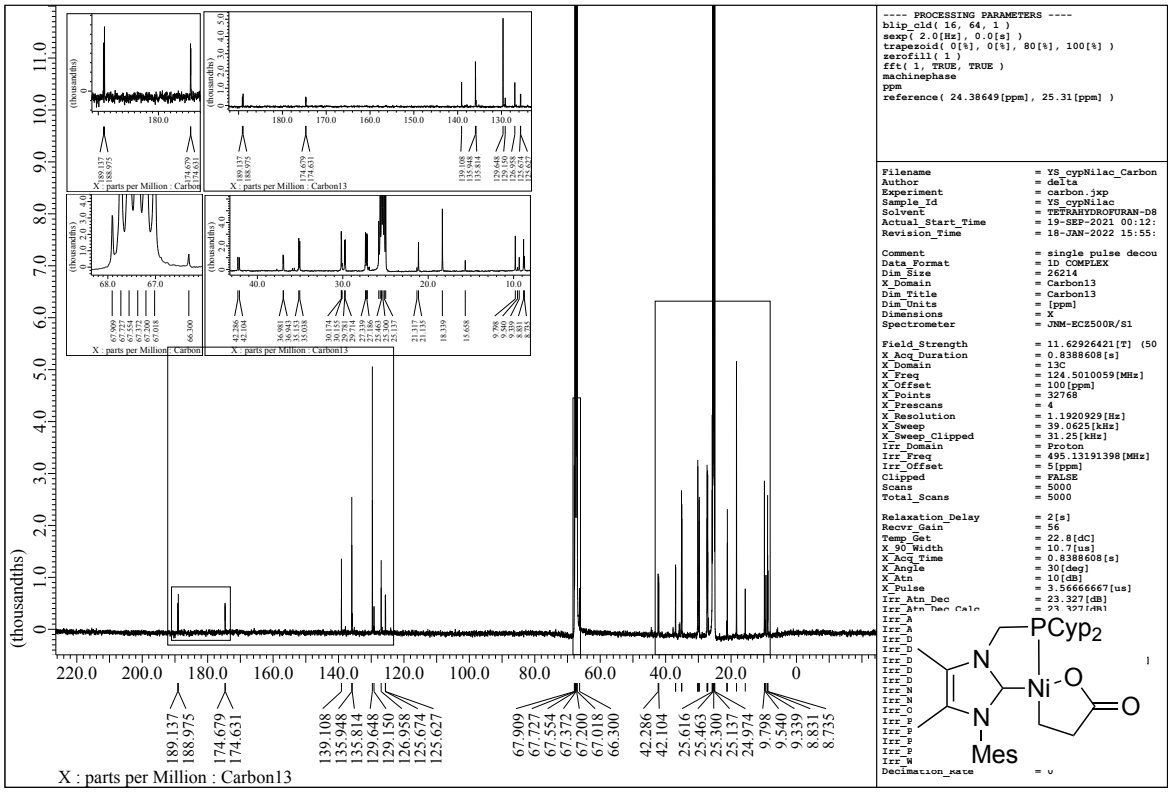



**Figure S46.** $^{13}$C NMR spectrum of **6**.

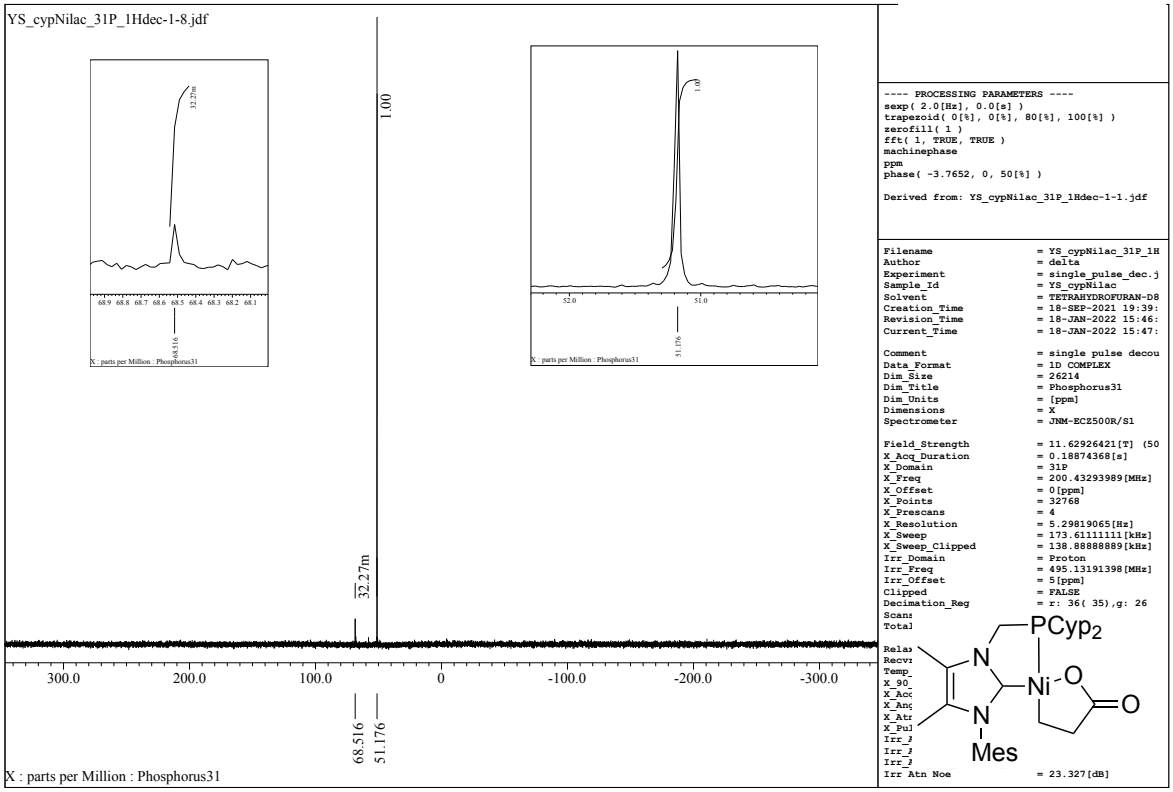



**Figure S47.** $^{31}$P NMR spectrum of **6**.

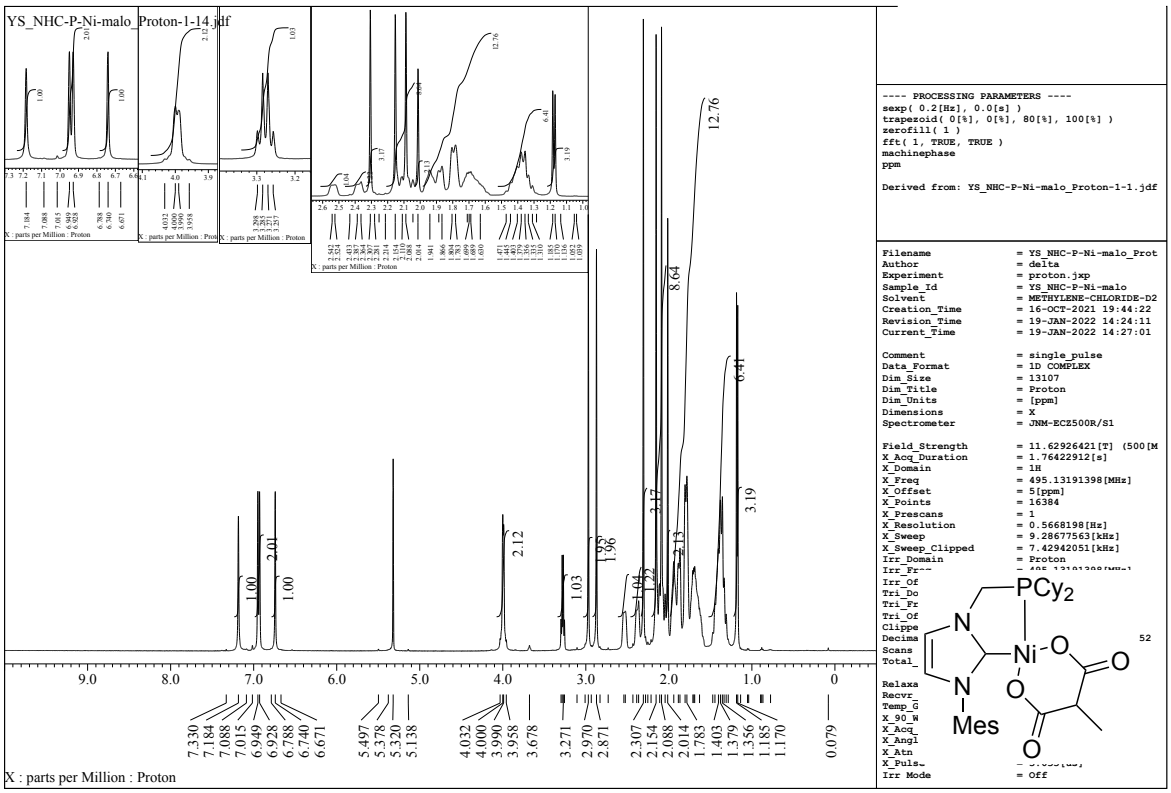



**Figure S48.** $^{1}$H NMR spectrum of **8**.

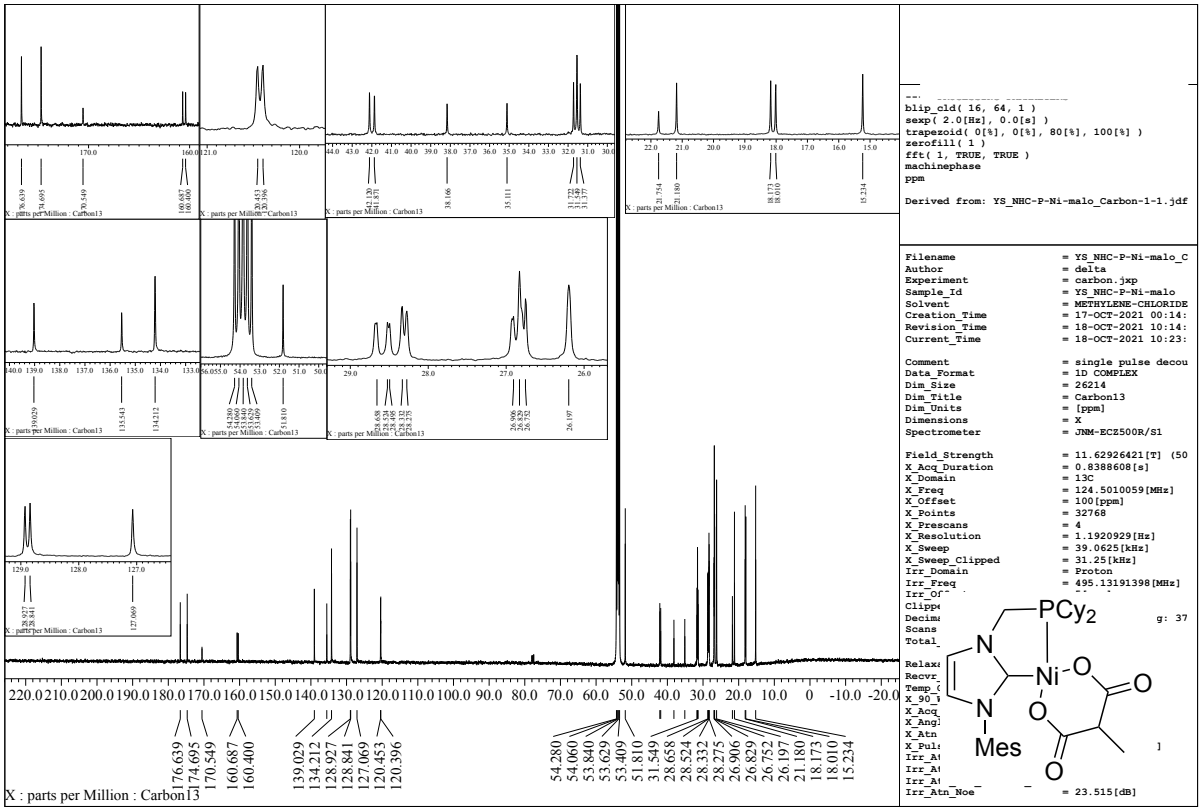



**Figure S49.** $^{13}$C NMR spectrum of **8**.

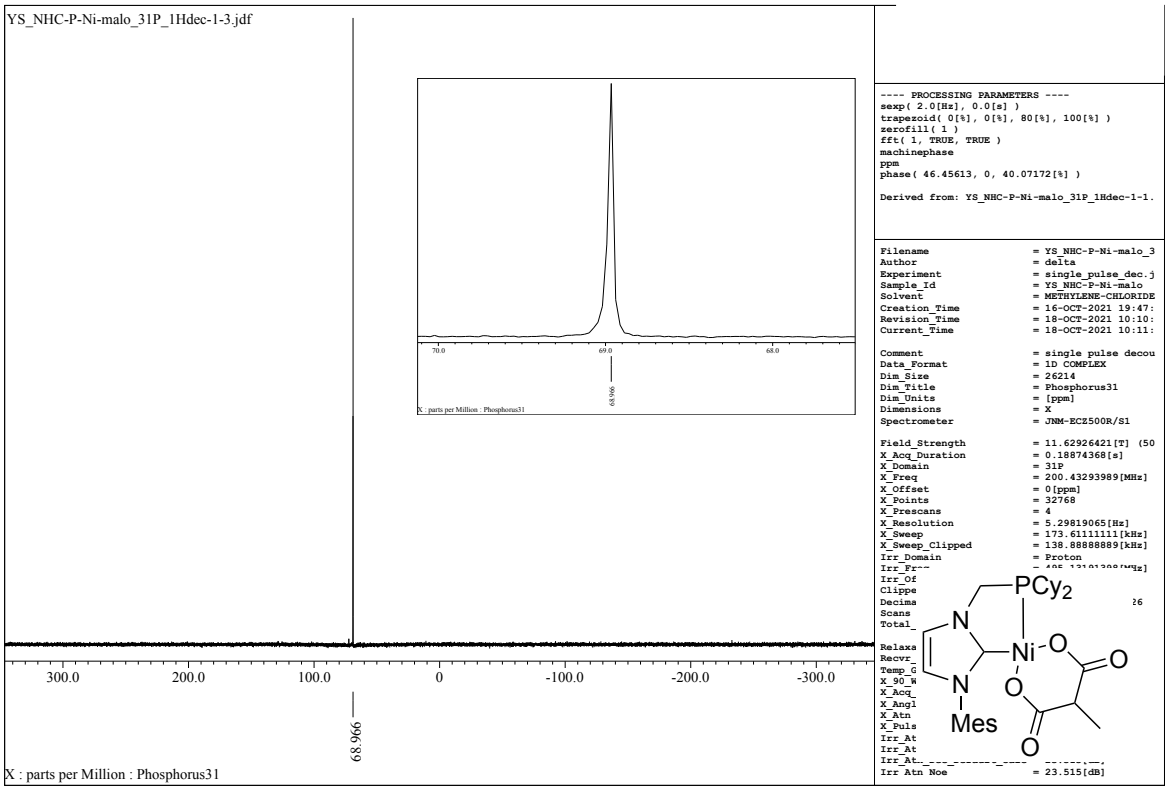



**Figure S50.** $^{31}$P NMR spectrum of **8**.

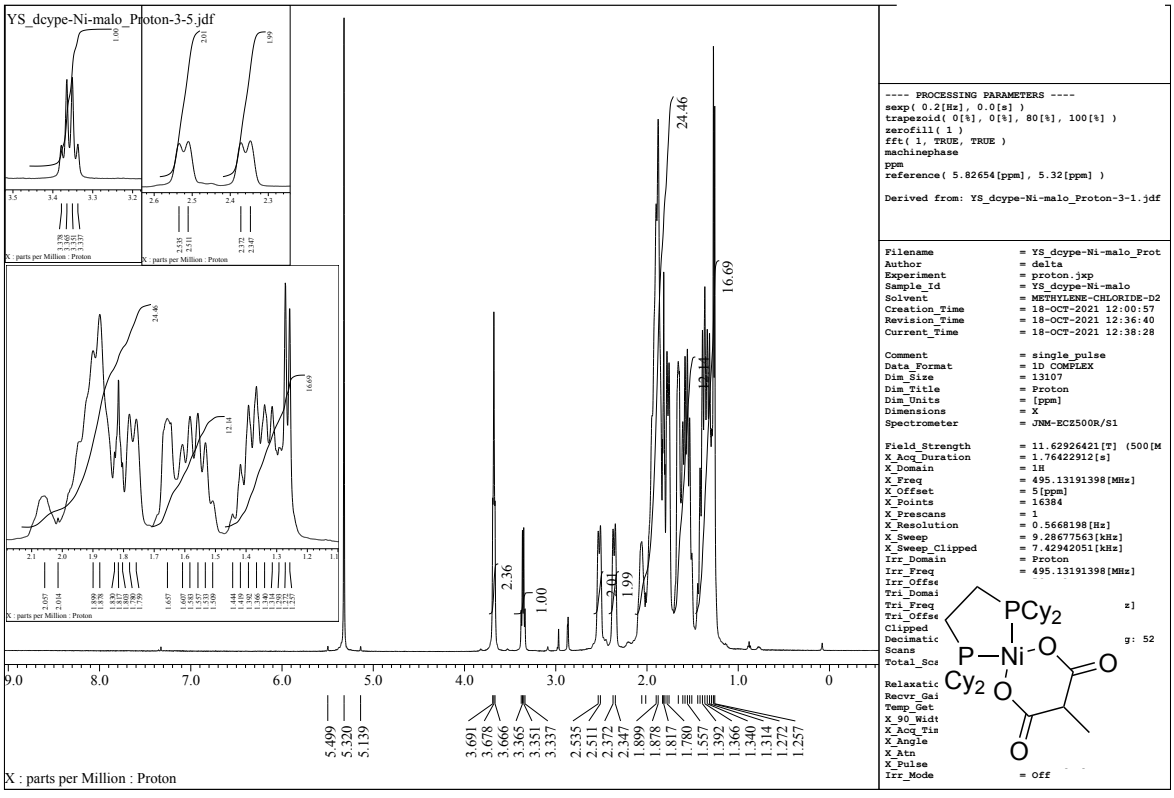



**Figure S51.** $^{1}$H NMR spectrum of **9**.

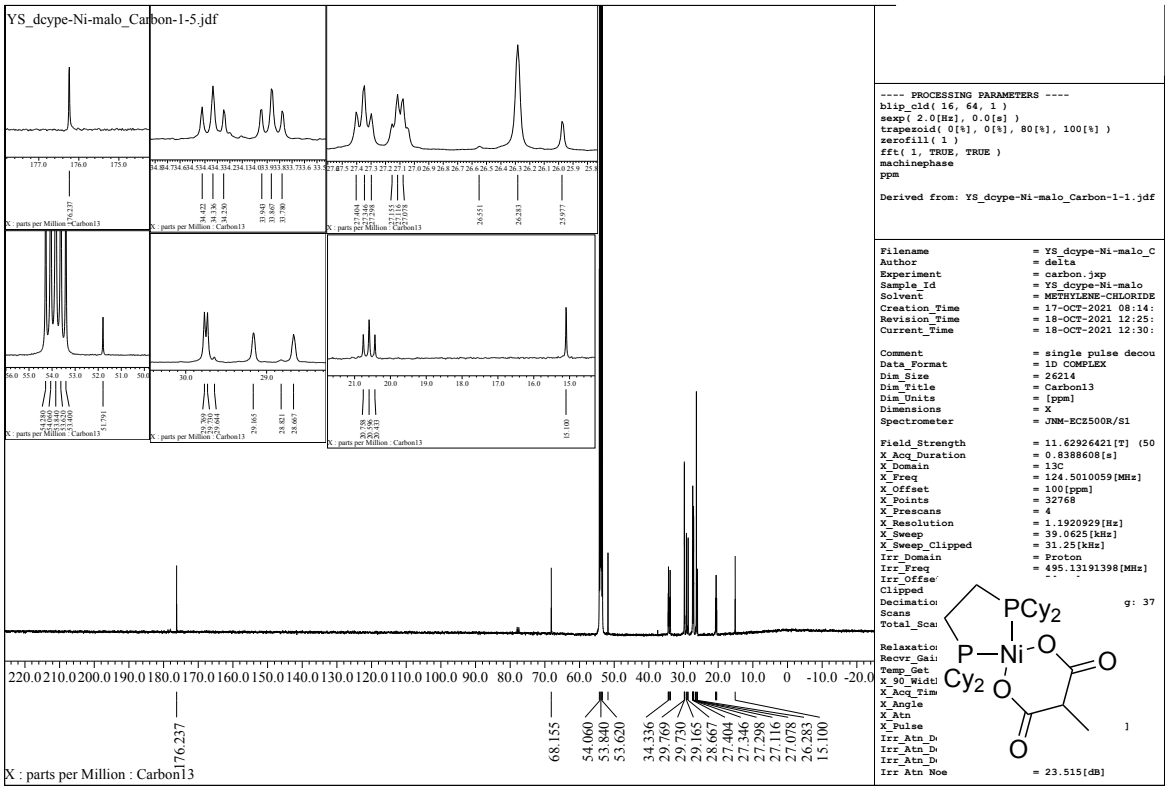



**Figure S52.** $^{13}$C NMR spectrum of **9**.

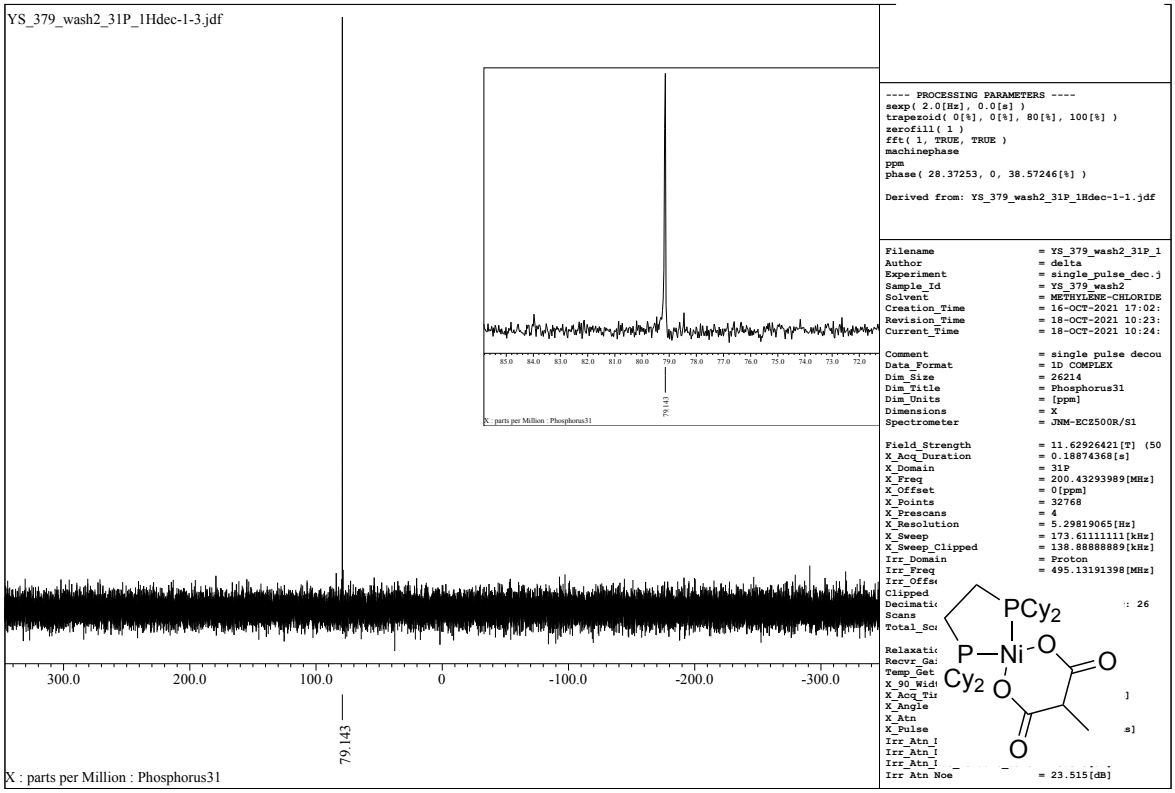



**Figure S53.** $^{31}$P NMR spectrum of **9**.

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