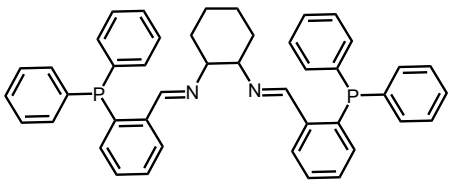
Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


# Supplementary Information

## Contents

# NMR spectrum of ligands and catalysts




**L1**

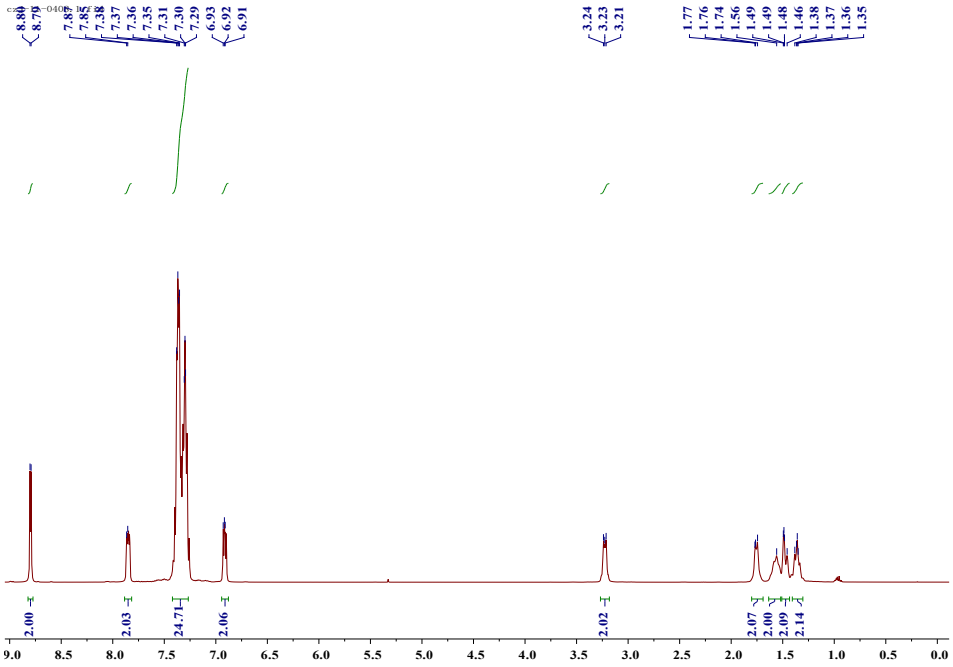



**Figure S1**. $^{1}H$ NMR of **L1**, $CDCl_3$

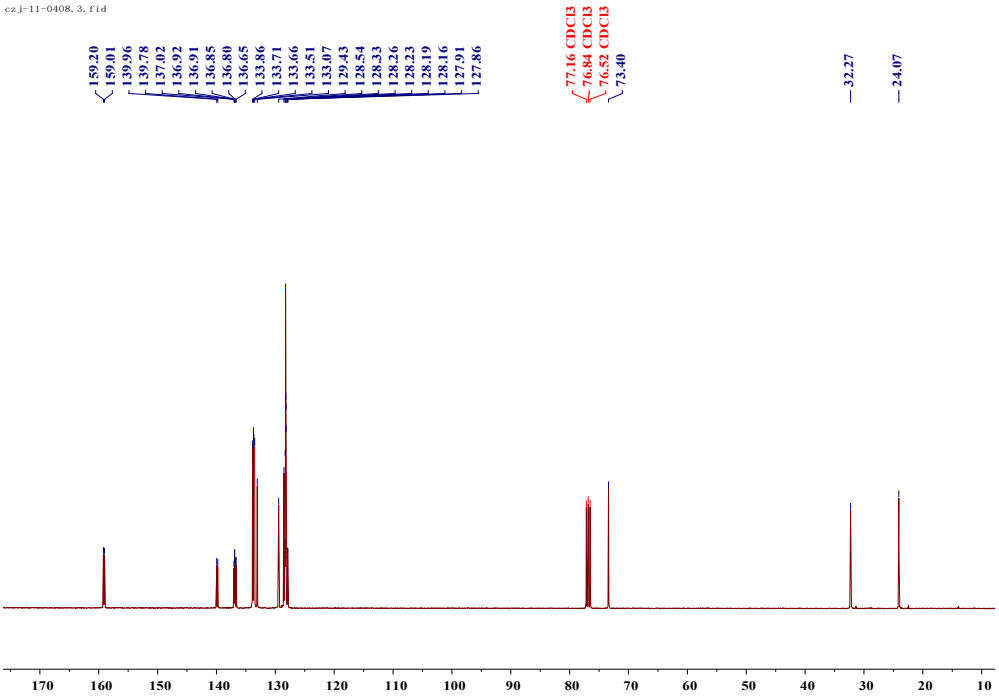



**Figure S2.** $^{13}C$ NMR of **L1**, $CDCl_3$

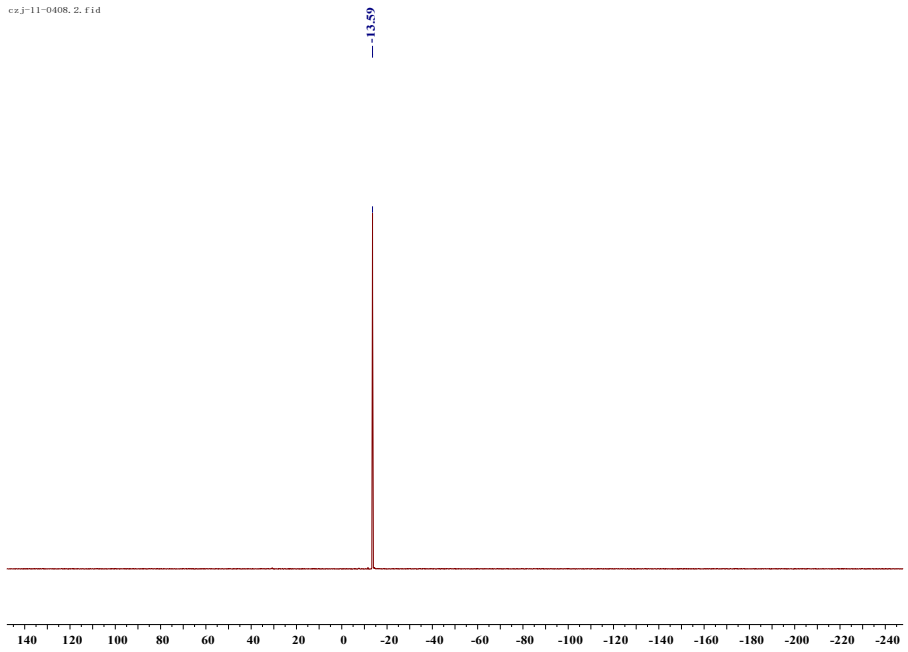
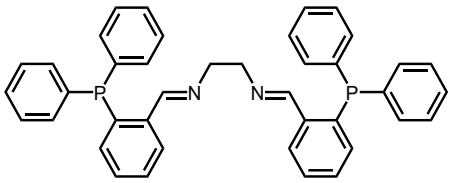



**Figure S3**. $^{31}P$ NMR of **L1**, $CDCl_3$




**L2**

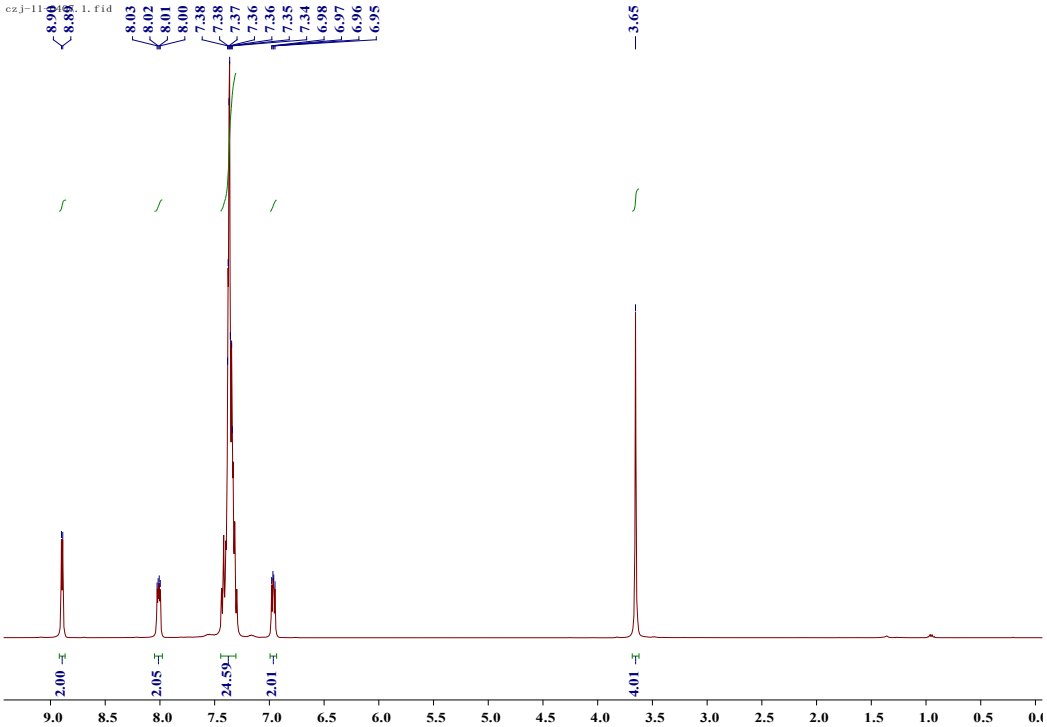



**Figure S4.** $^{1}H$ NMR of **L2**, $CDCl_3$

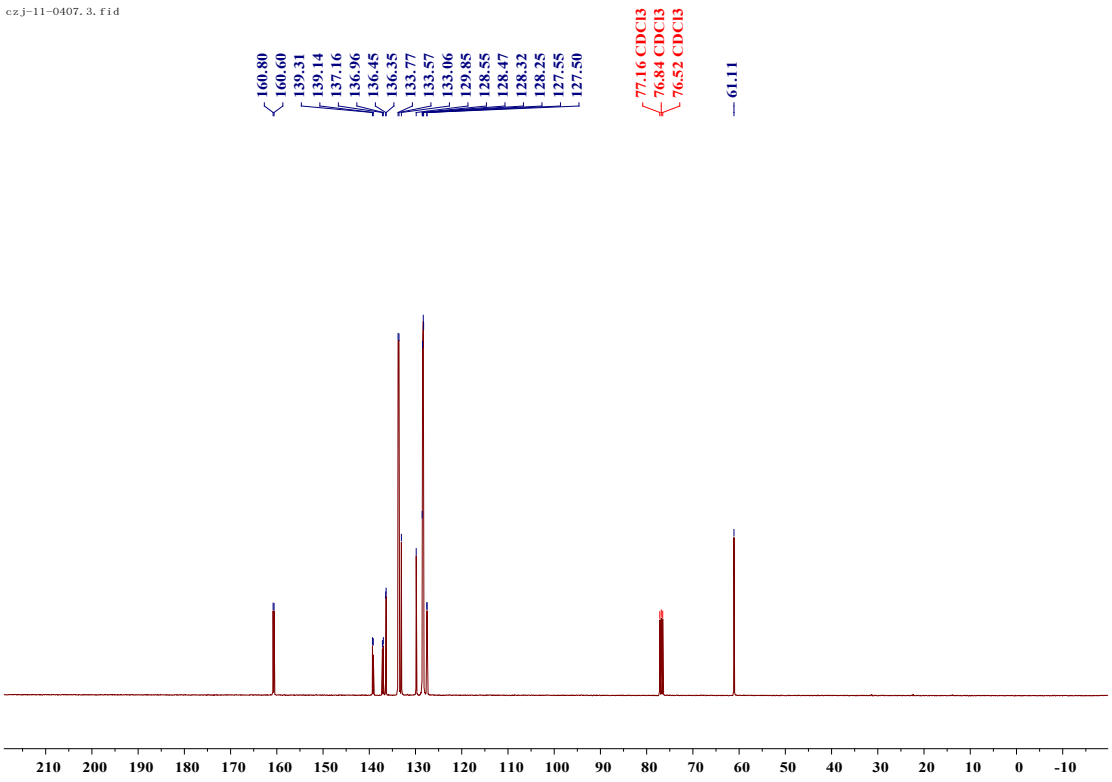



**Figure S5.** $^{13}C$ NMR of **L2**, $CDCl_3$

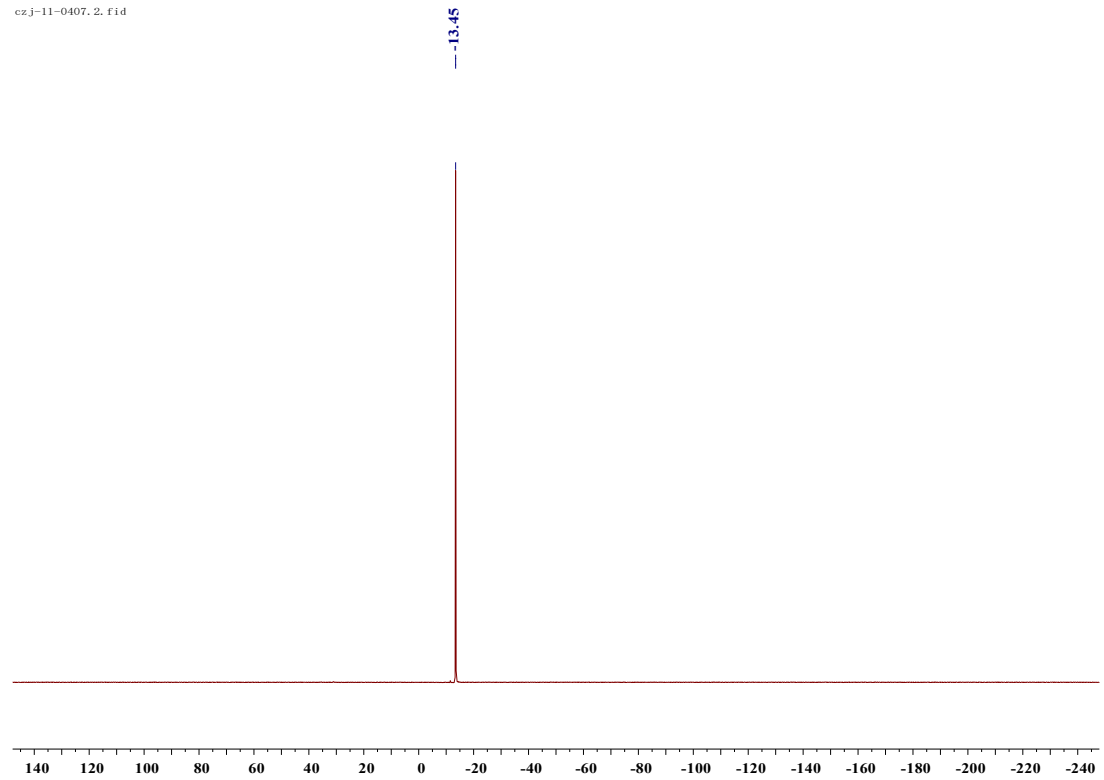



**Figure S6.** $^{31}P$ NMR of **L2**, $CDCl_3$

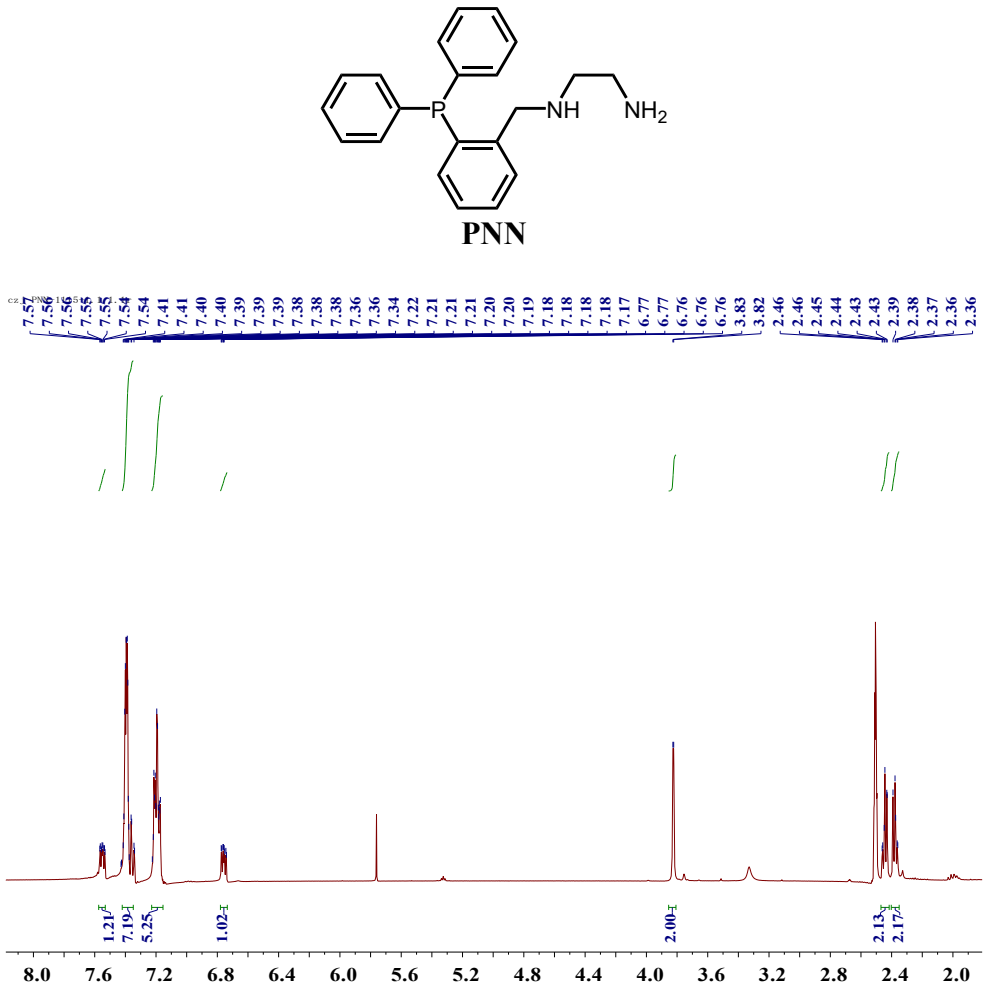



**Figure S7.** $^{1}$H NMR of **PNN**, DMSO-d6

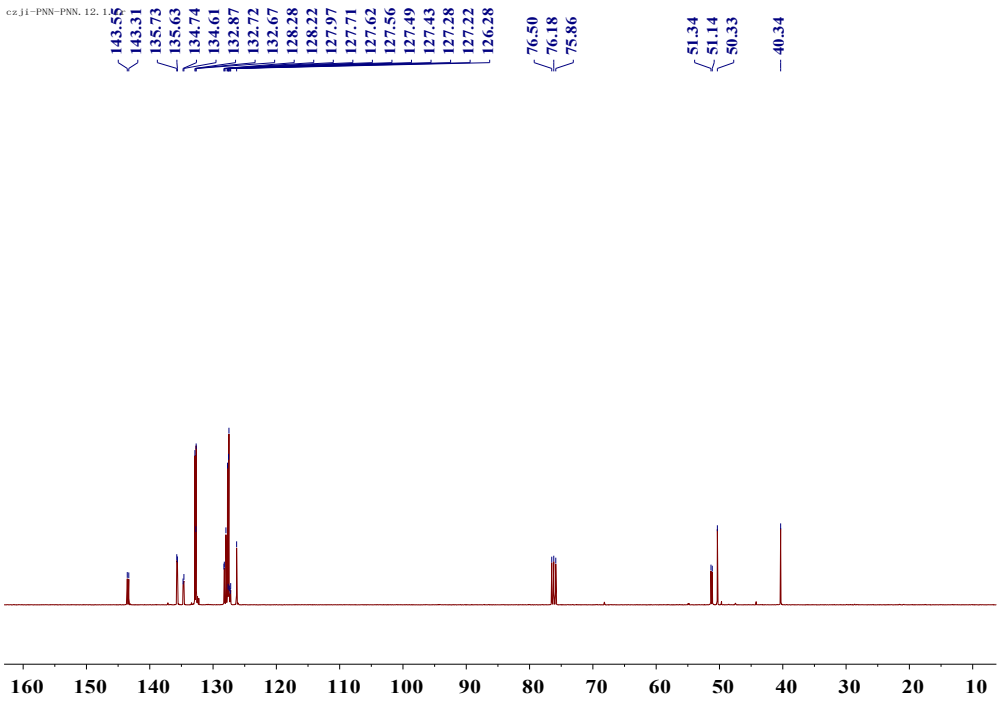



**Figure S8.** $^{13}$C NMR of **PNN**, $CDCl_3$

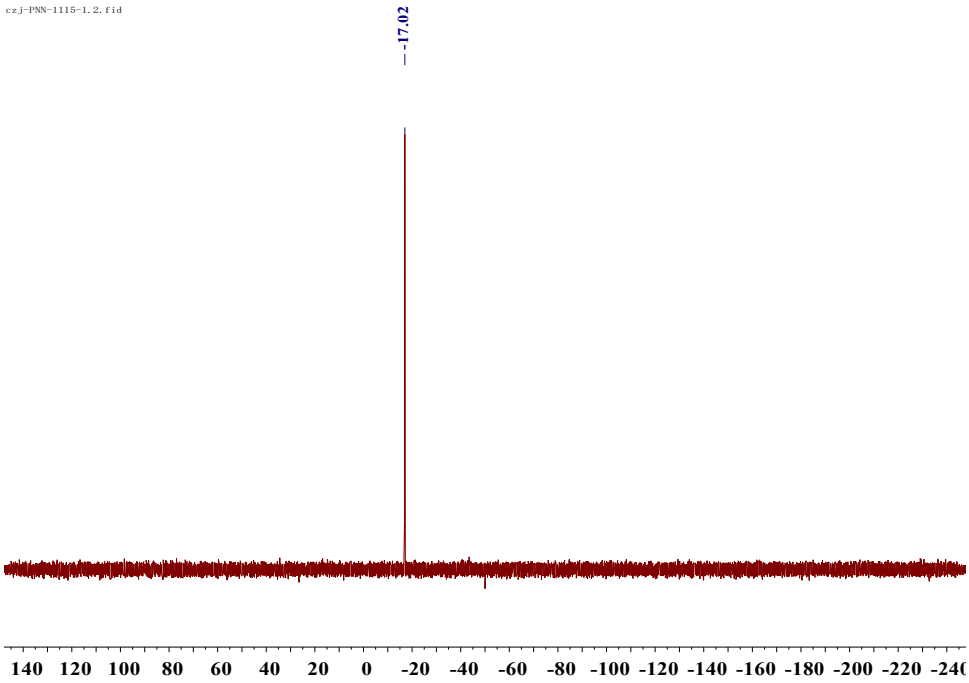
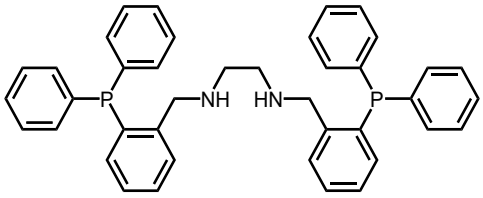



**Figure S9.** $^{31}P$ NMR of **PNN**, DMSO-d6




**L4**

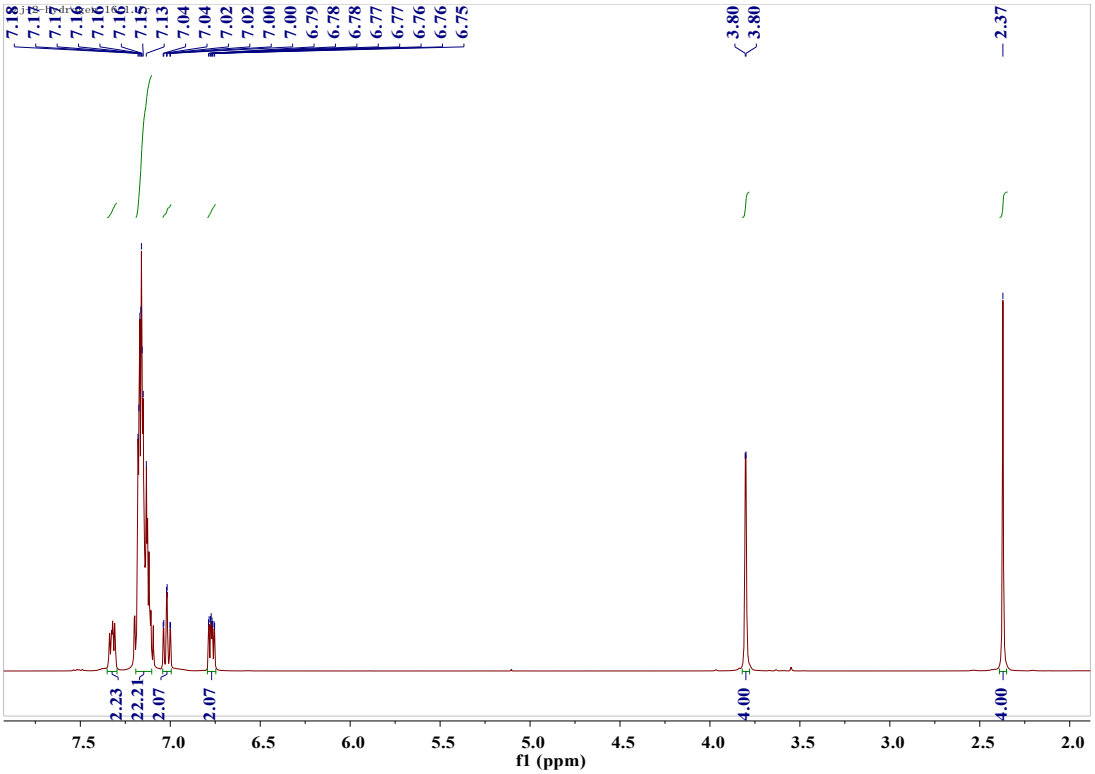



**Figure S10.** $^{1}H$ NMR of **L4**, $CDCl_3$

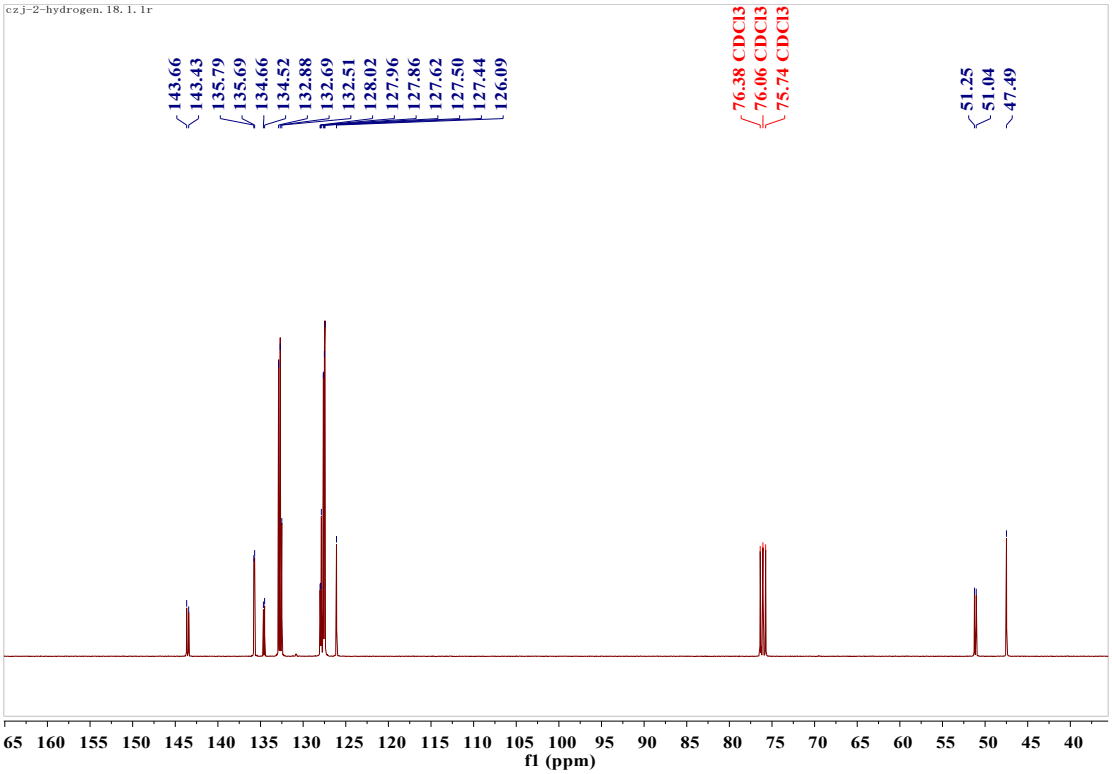



**Figure S11.** $^{13}C$ NMR of **L4**, $CDCl_3$

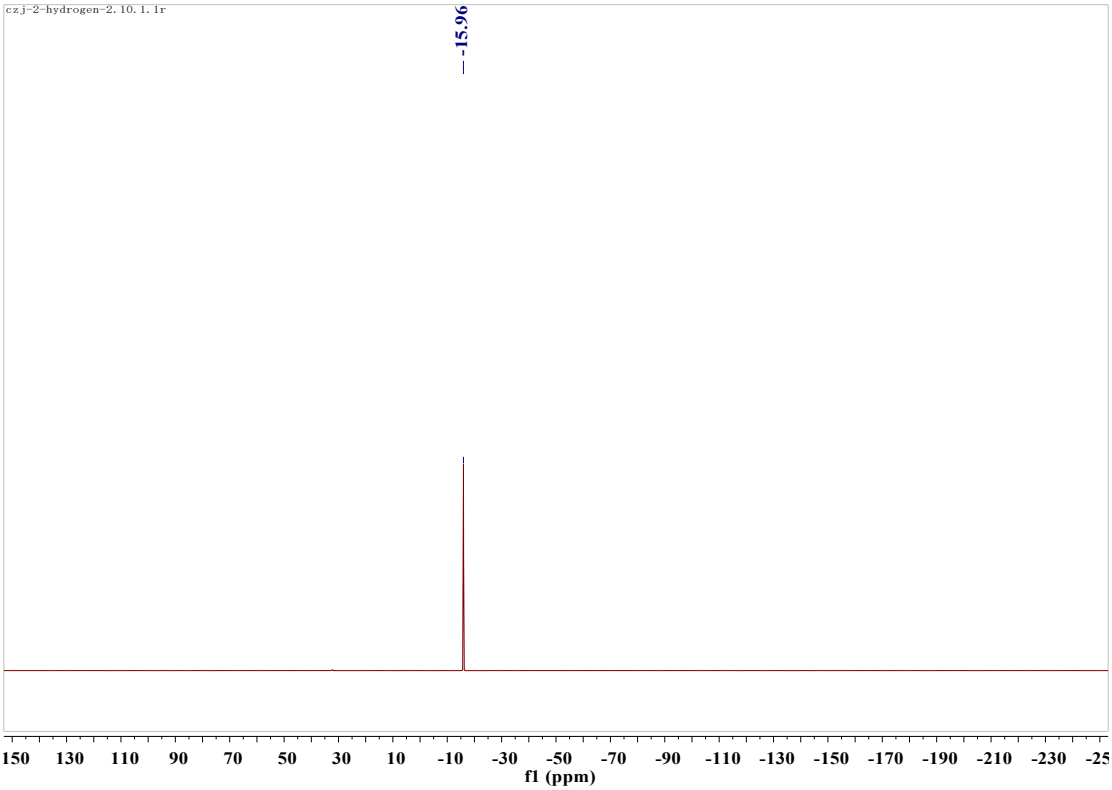
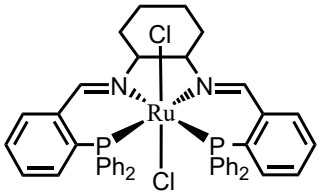



**Figure S12.** $^{31}P$ NMR of **L4**, $CDCl_3$




**1**

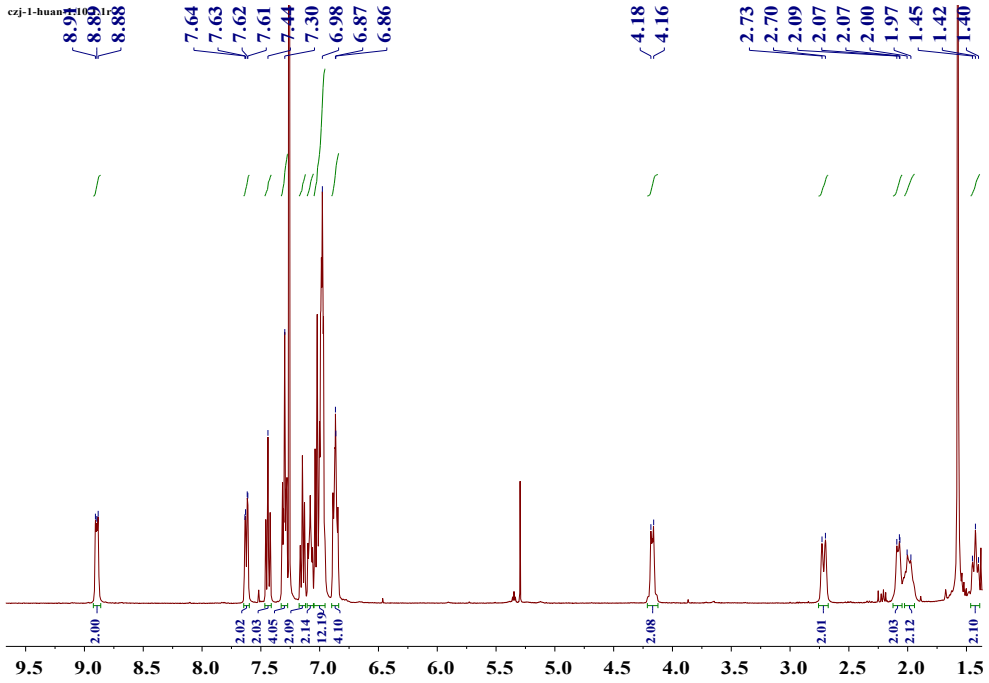



**Figure S13.** $^{1}$H NMR of **1**, $CDCl_3$

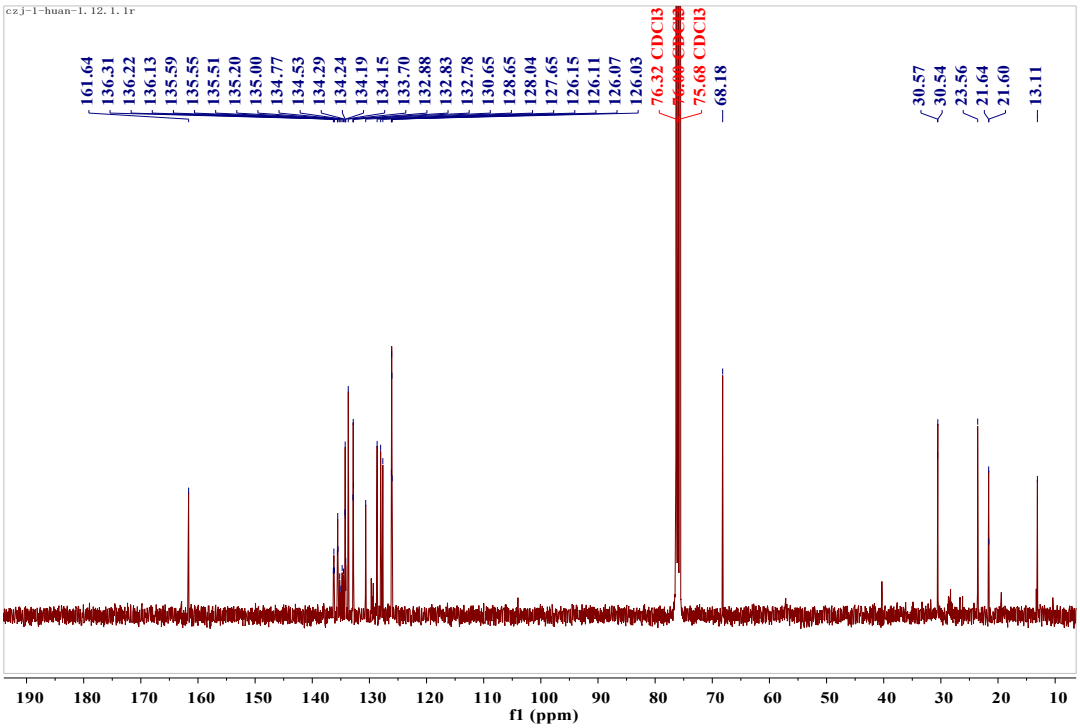



**Figure S14**. $^{13}$C NMR of **1**, $CDCl_3$

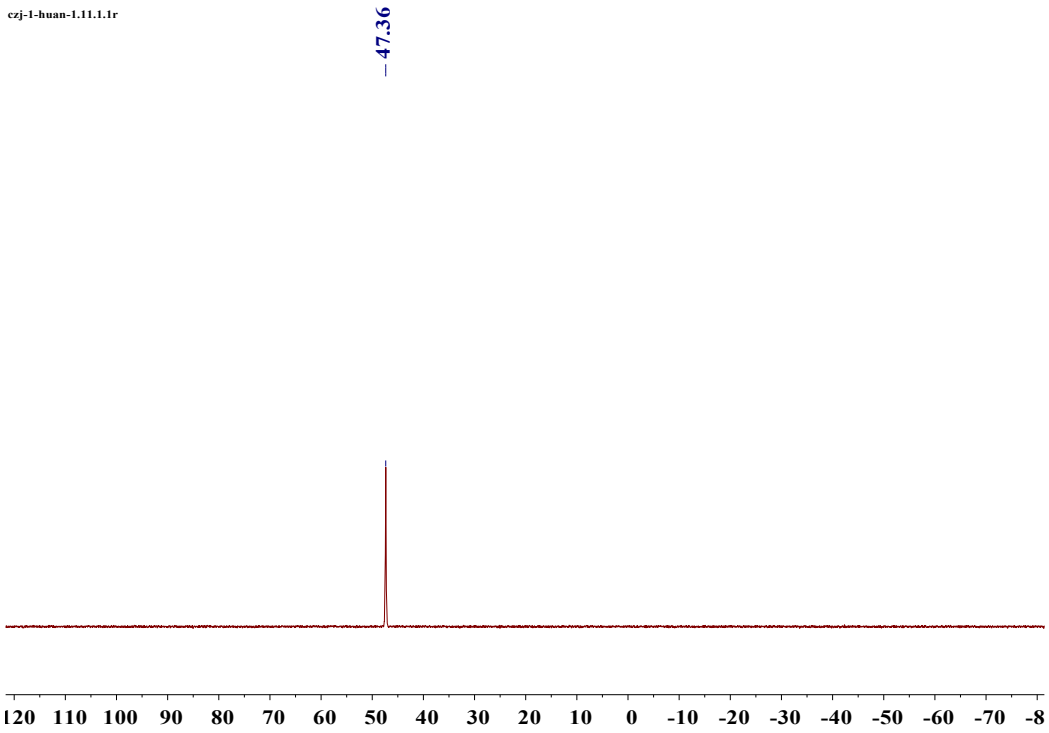
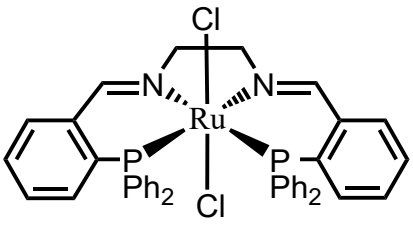



**Figure S15**. $^{31}P$ NMR of **1**, $CDCl_3$




**2**

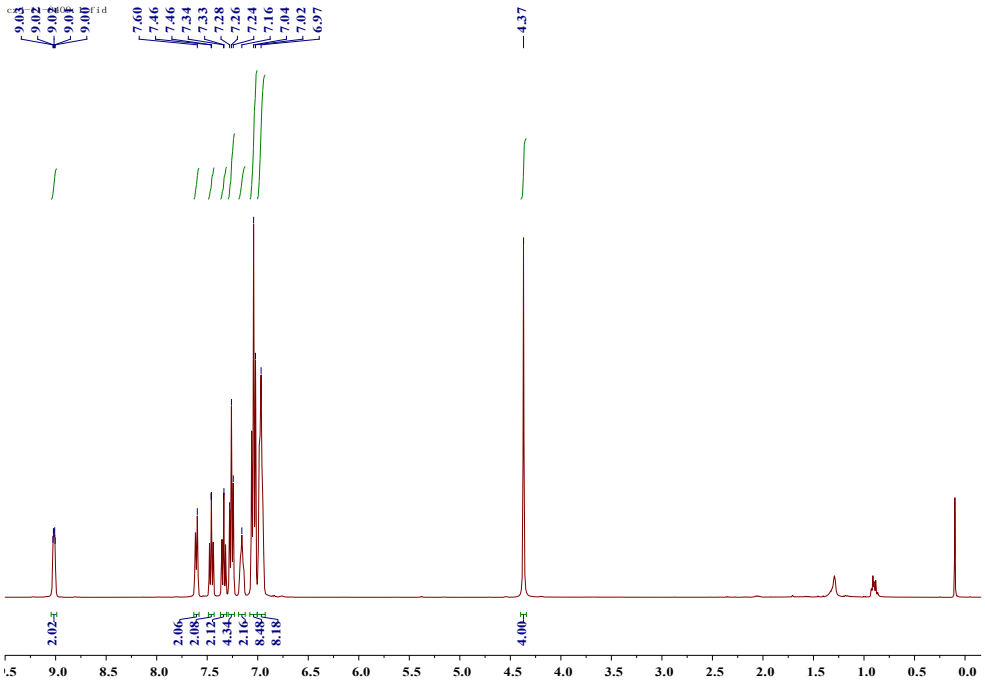



**Figure S16.** $^{1}H$ NMR of **2**, $CDCl_3$

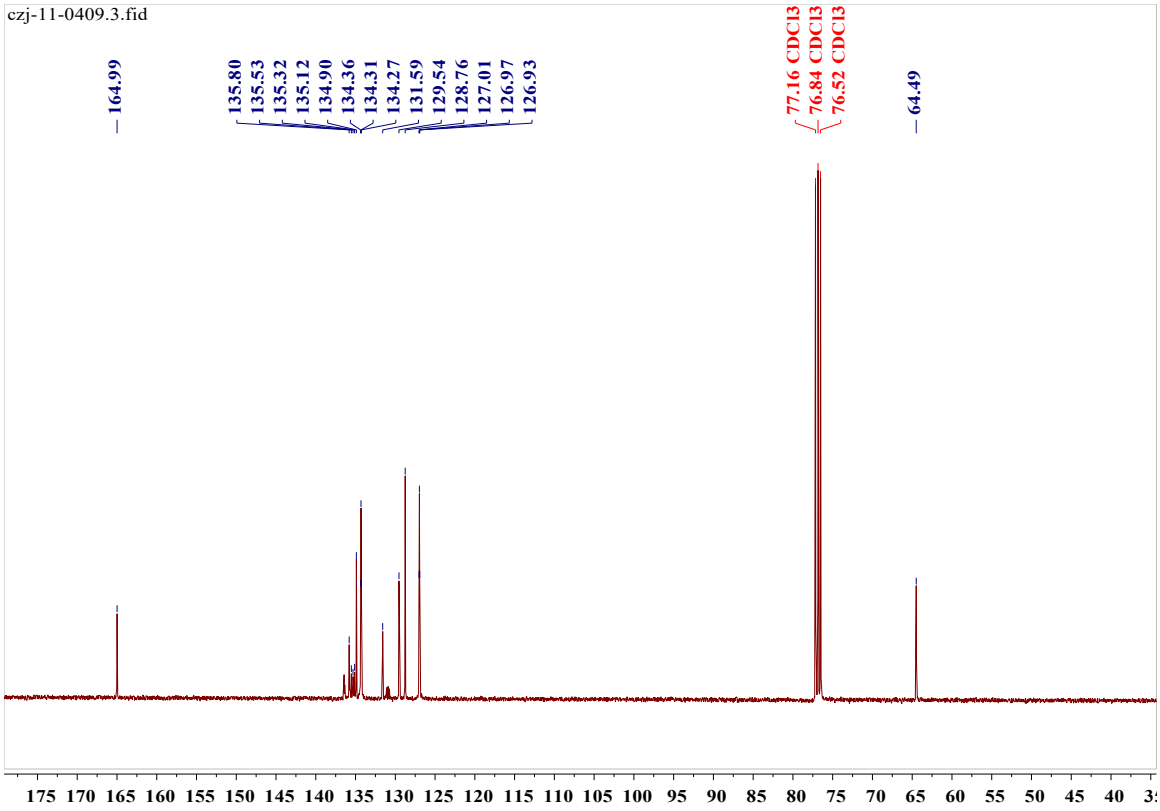



**Figure S17**. $^{13}C$ NMR of **2**, $CDCl_3$

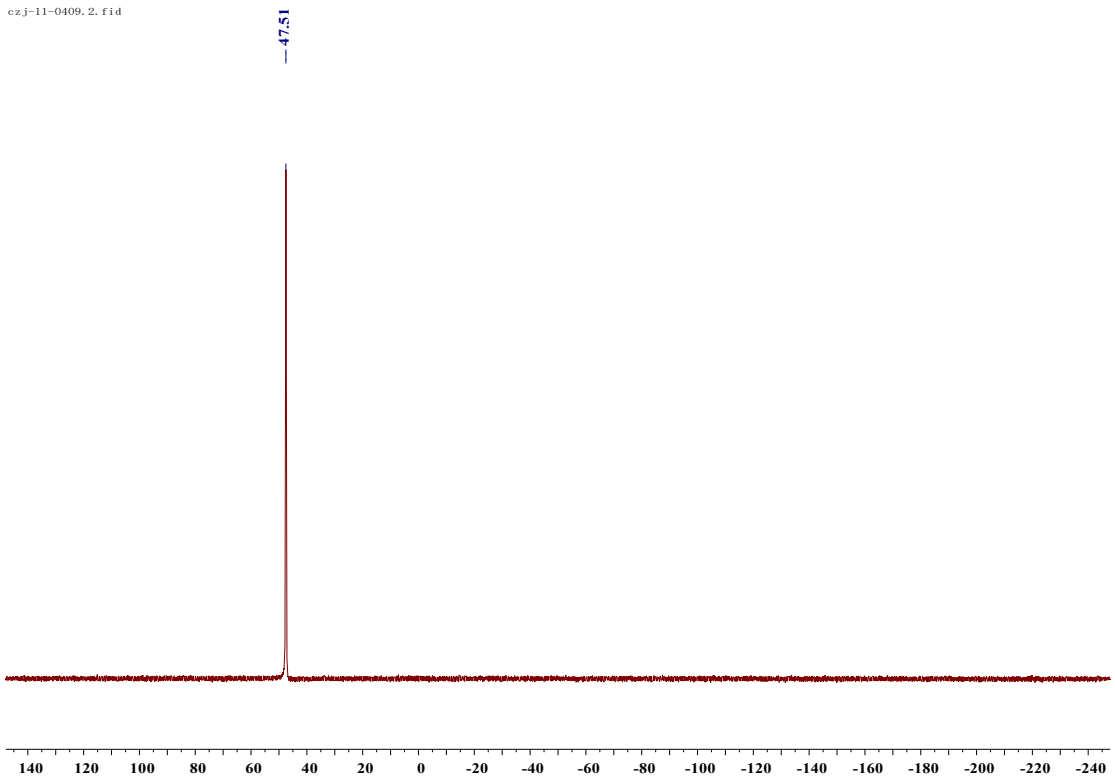
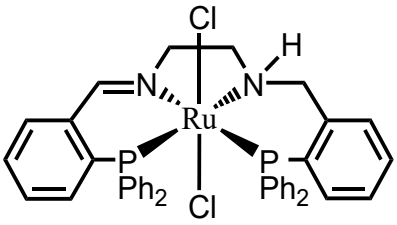



**Figure S18**. $^{31}P$ NMR of **2**, $CDCl_3$




**3**

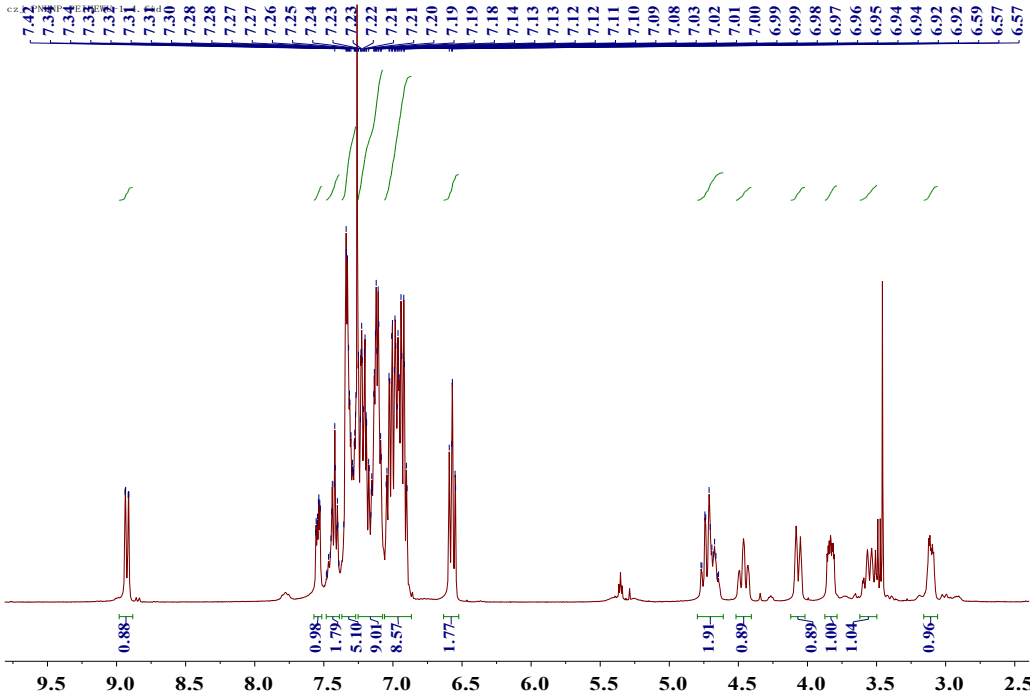



**Figure S19**. $^{1}$H NMR of **3**, $CDCl_3$

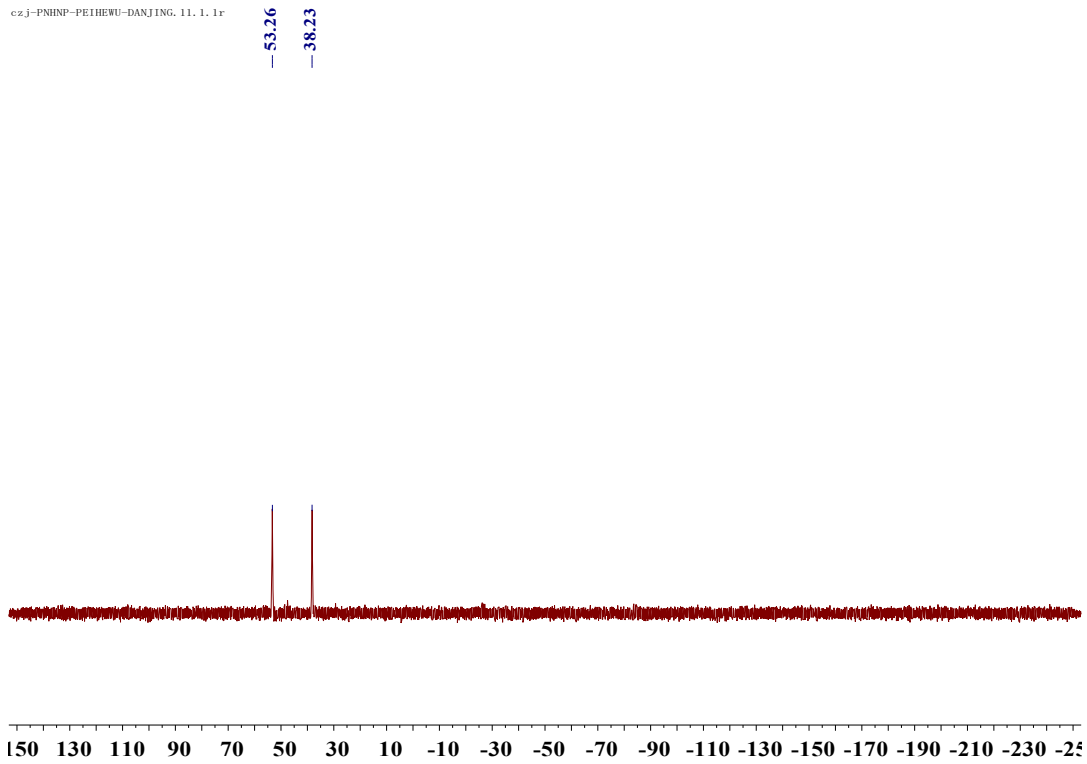
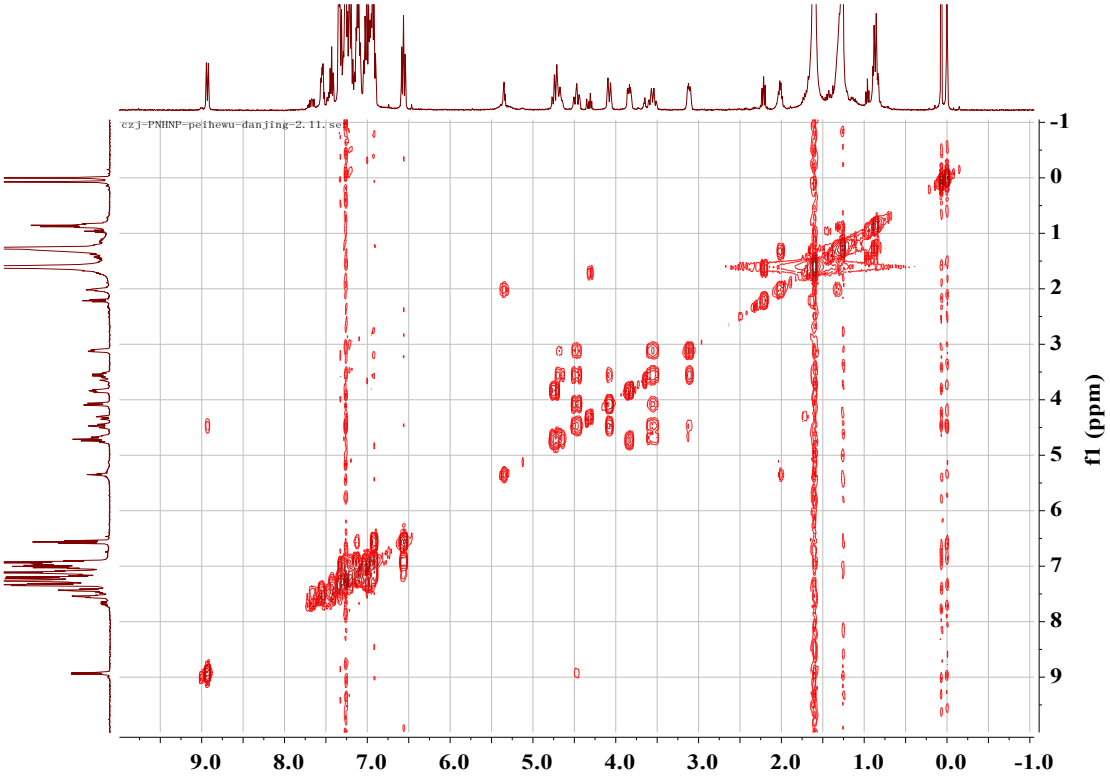



**Figure S20**. $^{31}P$ NMR of **3**, $CDCl_3$

(a) $^{1}H$-$^{1}H$ 2D-nosy




(b) 1H-1H 2D-nosy partial enlarged view.

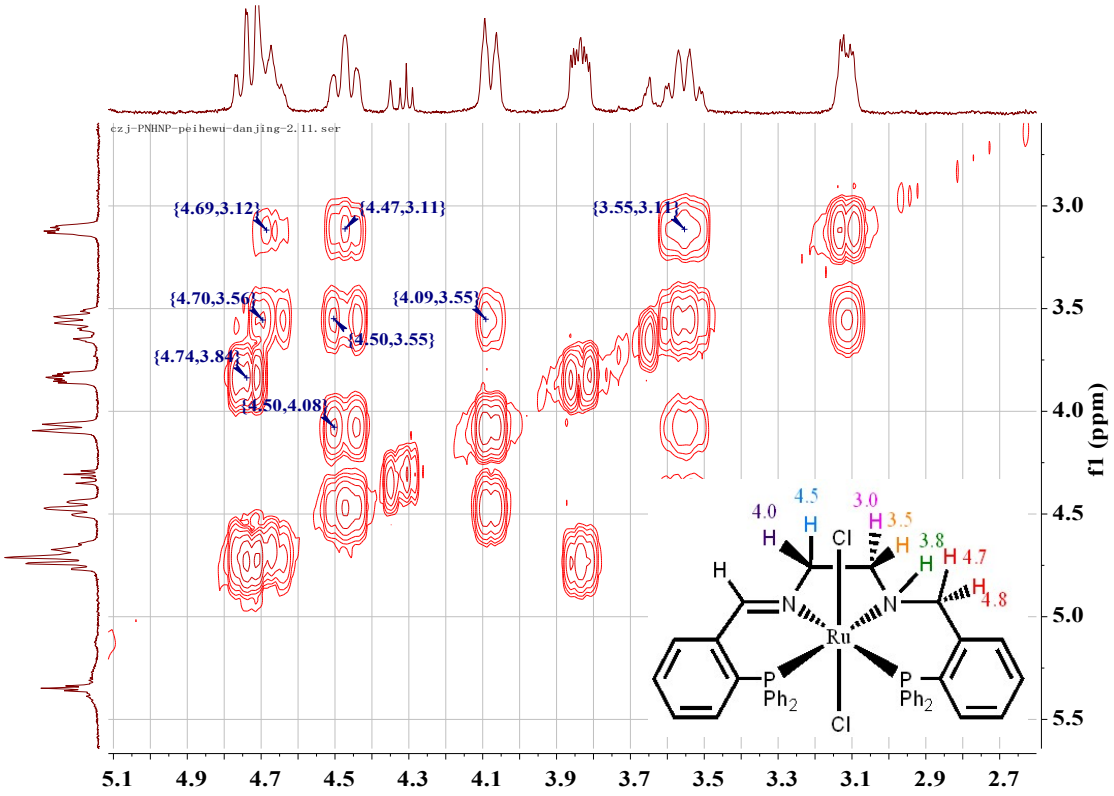
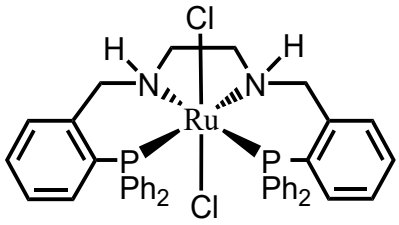



**Figure S21.** $^{1}$H-$^{1}$H 2D-nosy spectrum of **3**.




**4**

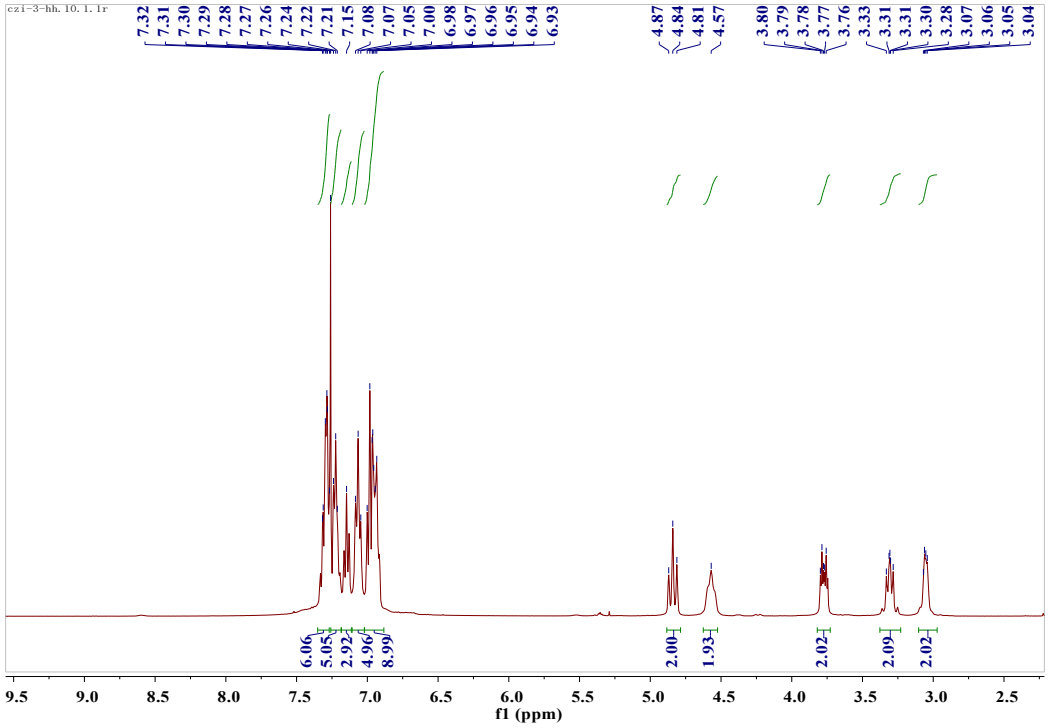



**Figure S22**. $^{1}$H NMR of **4**, $CDCl_3$

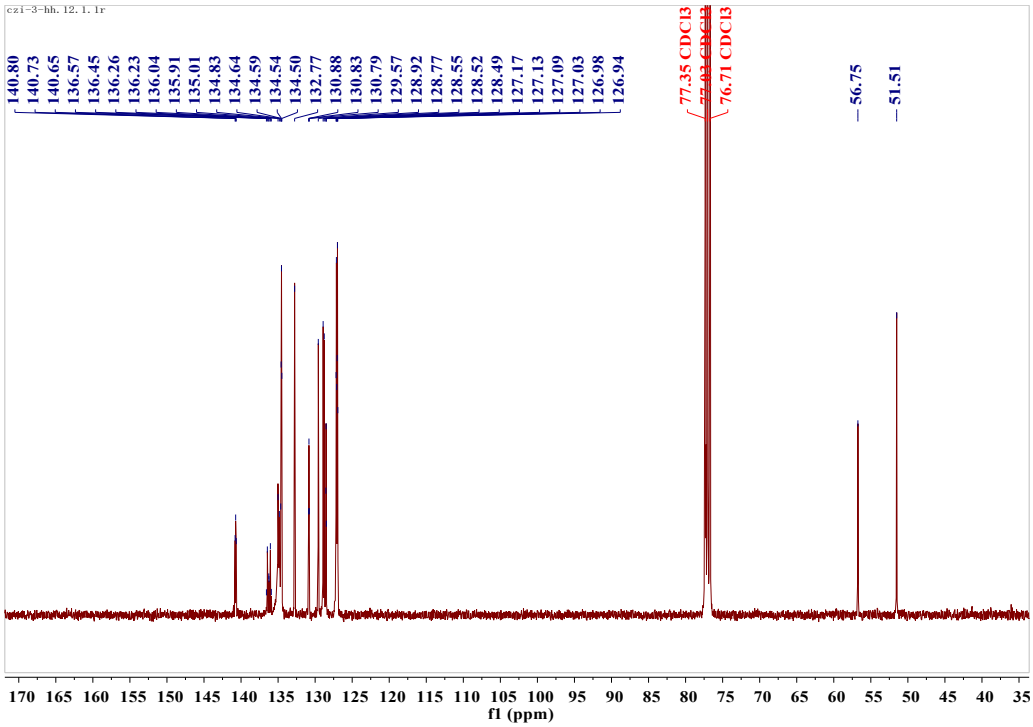



**Figure S23**. $^{13}$C NMR of **4**, $CDCl_3$

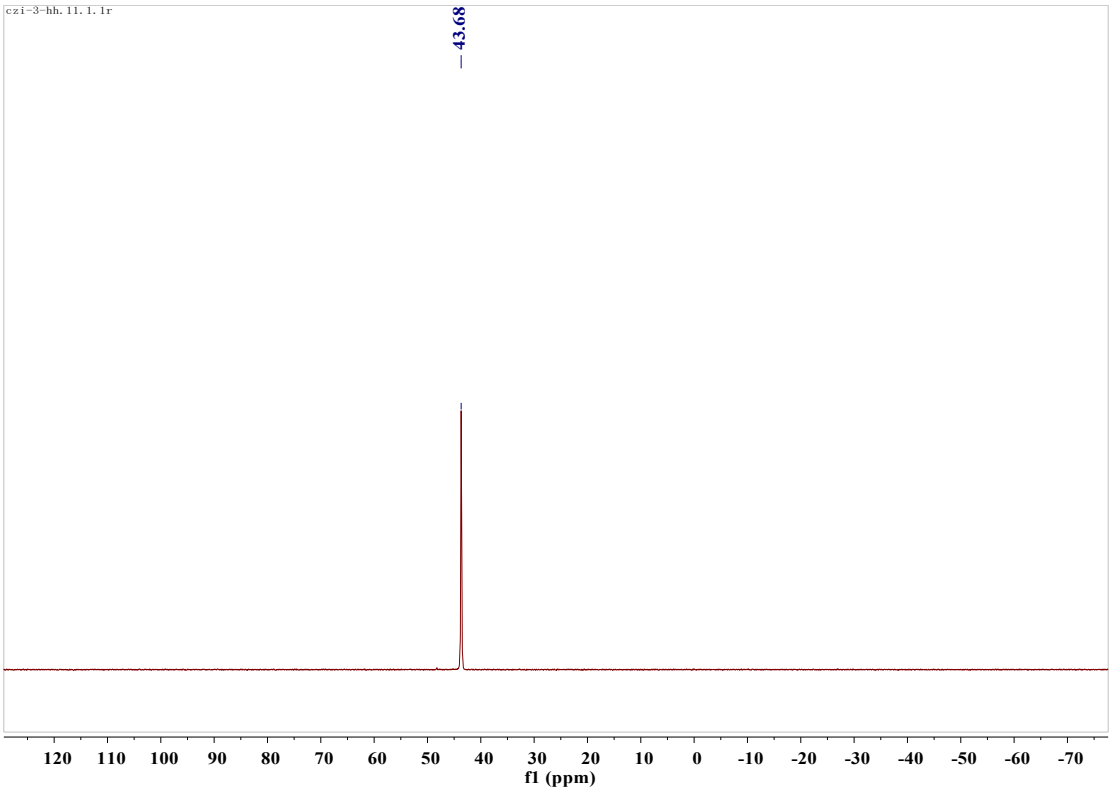



**Figure S24**. $^{31}P$ NMR of **4**, $CDCl_3$.

# Supplementary Figures

***Report***

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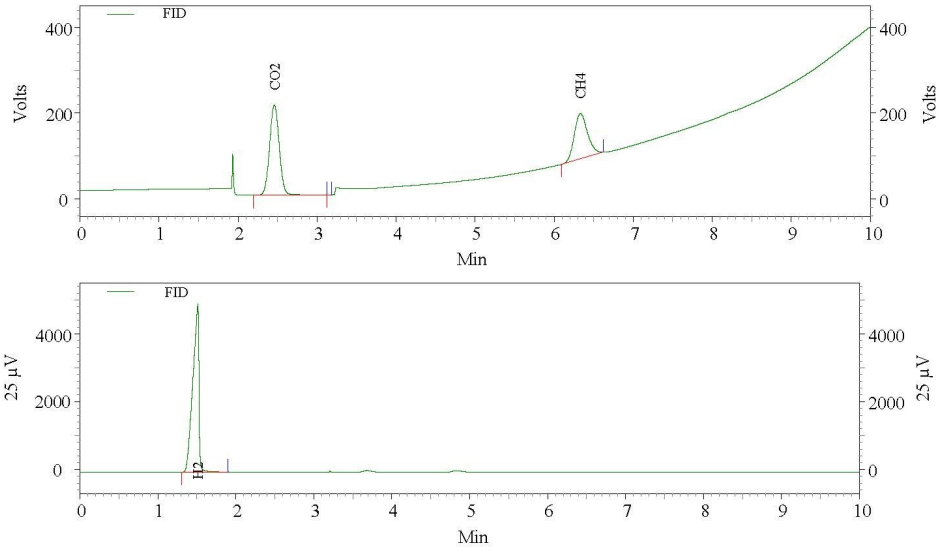
**Data File:** D:\Data\Result\czj\czj-1-8bi1-yea-11.rslt\czj-1-8bi1-yea-11.dat zhijian
**User:** chen
**Acquisition:** 2021/1/8 17:20:27 (GMT +08:00)
**Print time:** 2021/1/8 17:32:45 (GMT +08:00)




| FID reault | peak#name | retation time | Area | Amount / % |
|---|---|---|---|---|
| 1 | CO2 | 2.460 | 13599098 | **0.021** |
| 3 | CH4 | 6.333 | 9454863 | **0.014** |
| | CO | | | **0.000 BDL** |
| Aggregate | | | 23053961 | **0.036** |

| FID reault | peak#name | retation time | Area | Amount / % |
|---|---|---|---|---|
| 1 | H2 | 1.510 | 204959613 | **12.669** |
| Aggregate | | | 204959613 | **12.669** |

**Figure S25**. GC data for APRM reaction uisng 8 ml MeOH, 2 ml $H_2O$, and 4 µmol **2**. $T_{set}$ = 120 °C, 5 hours.

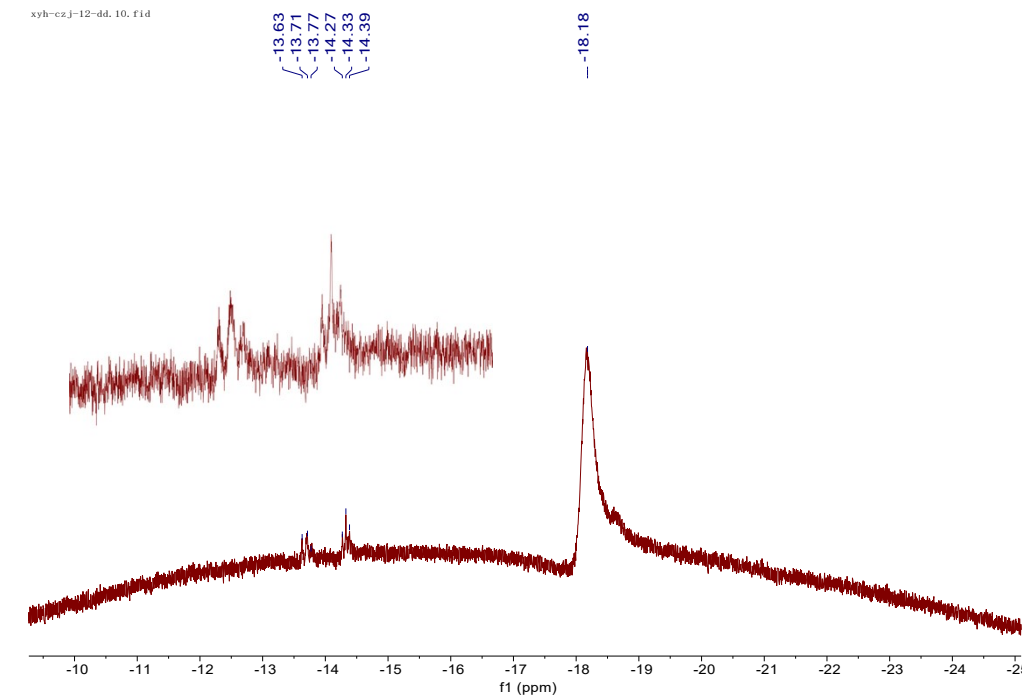



**Figure S26**. $^{1}$H NMR ($d^{6}$-DMSO) of the reaction mixture. Reaction condition: $CH_3OH/H_2O$ (8:2 *v*/*v*, 3mL), KOH (8 M), triglyme (1 mL), **2** (10 μmol) for 1 hour. Inset: Magnified chemical-shift window between −15 ppm and −13 ppm.

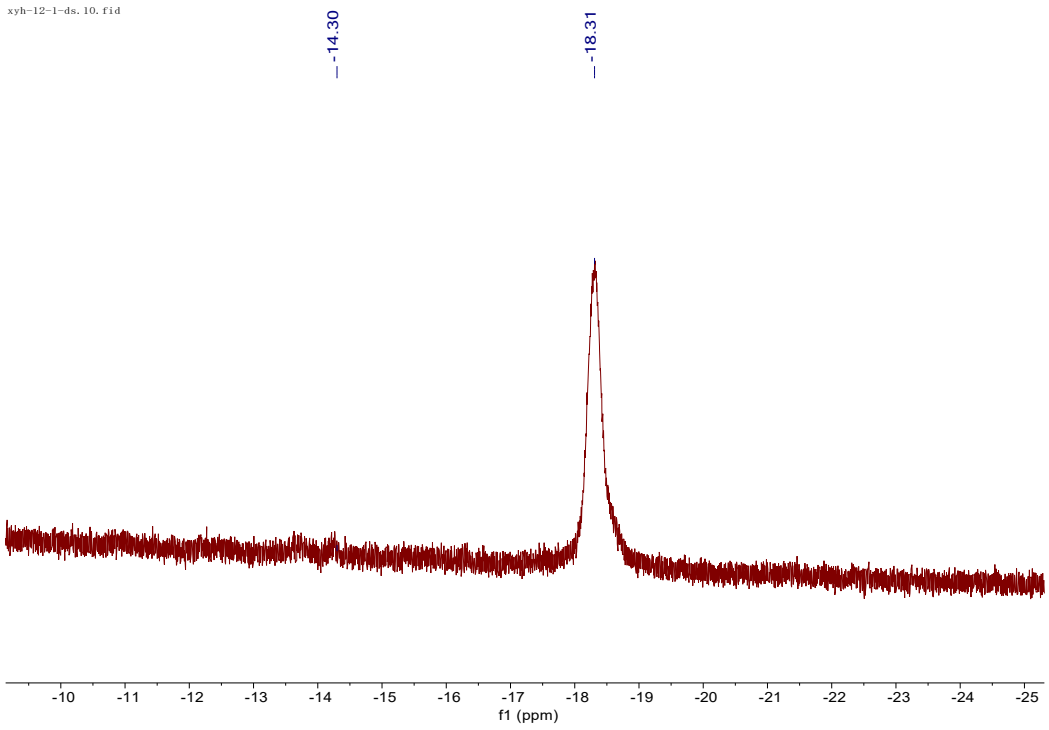



**Figure S27**. $^{1}$H NMR ($d^{6}$-DMSO) of the reaction mixture. Reaction condition: $CH_3OH/H_2O$ (8:2 *v*/*v*, 3mL), KOH (8 M), triglyme (1 mL), **3** (10 μmol) for 1 hour.

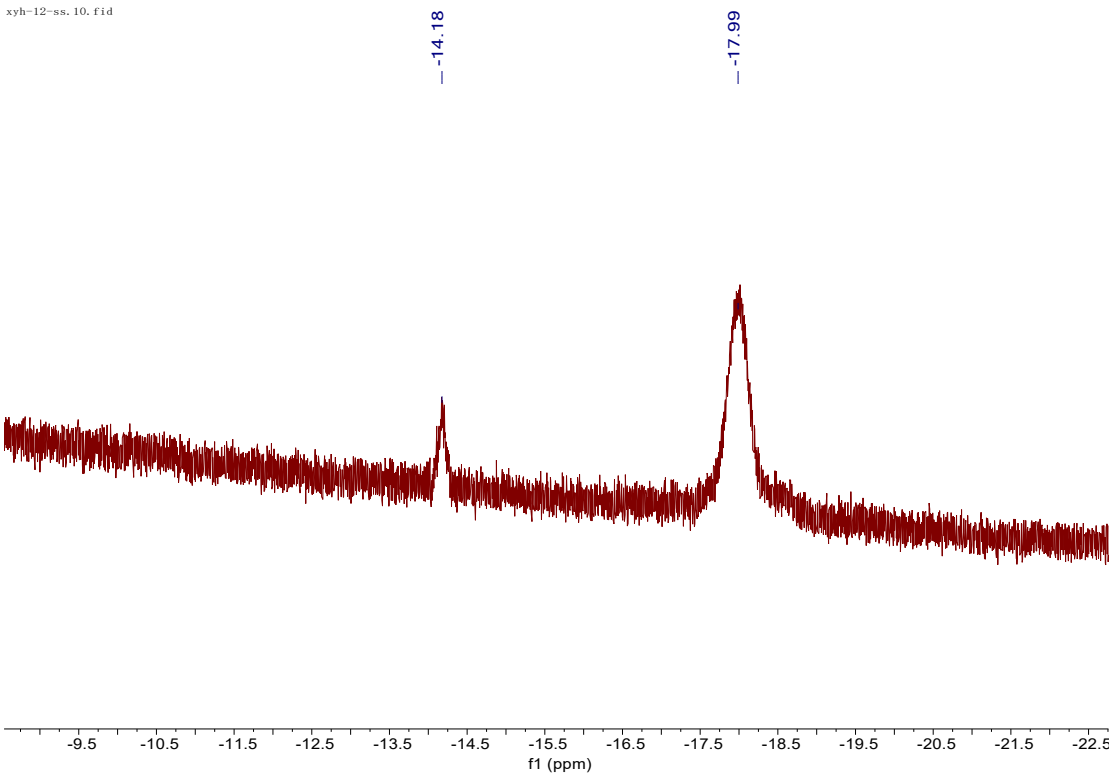



**Figure S28**. $^{1}$H NMR ($d^{6}$-DMSO) of the reaction mixture. Reaction condition: $CH_3OH/H_2O$ (8:2 *v*/*v*, 3mL), KOH (8 M), triglyme (1 mL), **4** (10 μmol) for 1 hour.

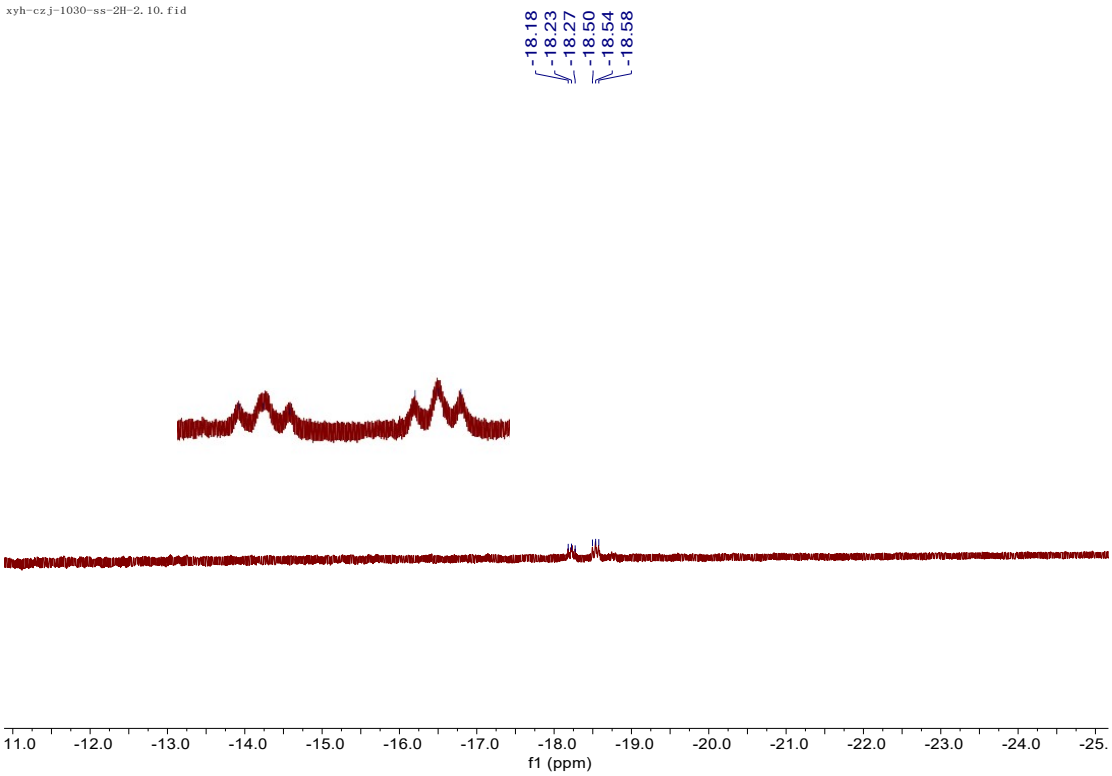



**Figure S29**. $^{1}$H NMR ($d^{6}$-DMSO) of the reaction mixture for 2 hours with **4** (10 μmol) and 2 equivalent $NaBEt_3H$ in 1 mL of triglymeat 80 °C. Inset: Magnified chemical-shift window between −19 ppm and −18 ppm.

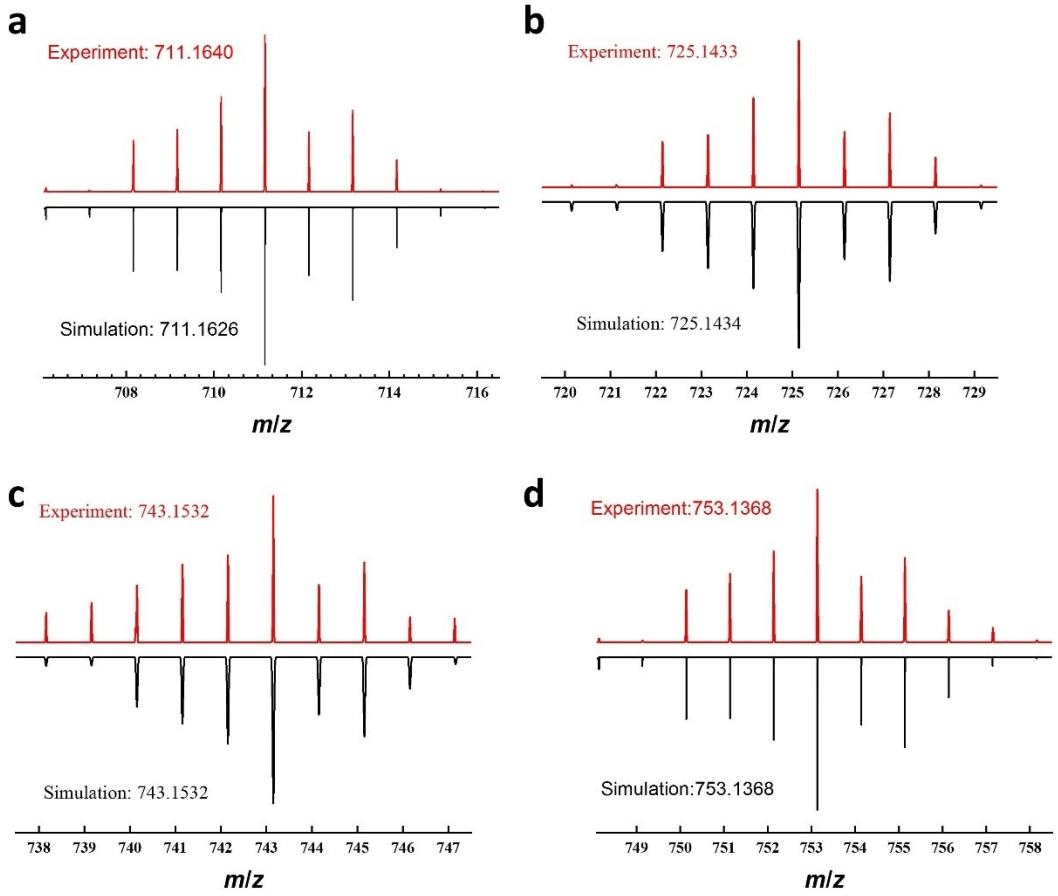



**Figure S30**. The found intermediates in HRESI-MS of the reaction solution using **2**, together with the simulated plots.

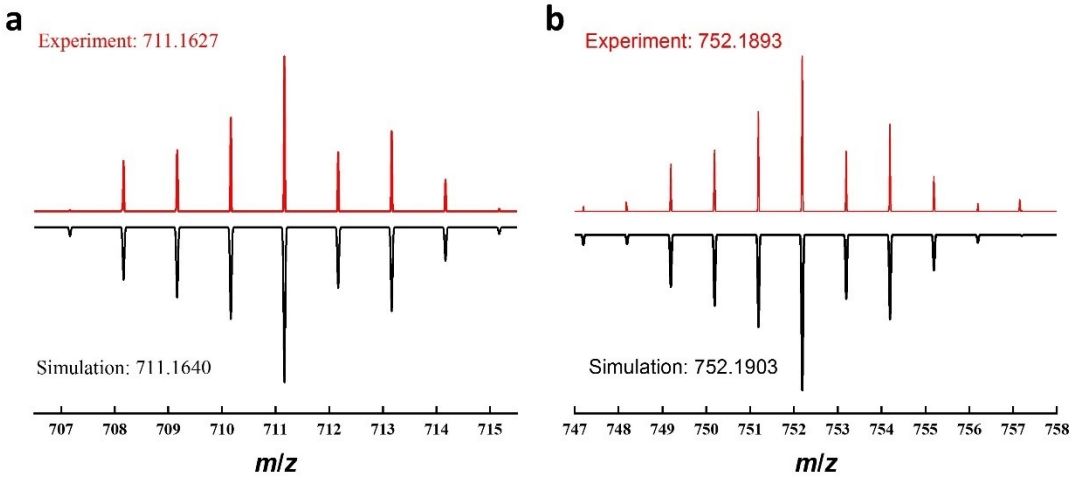



**Figure S31**. The found intermediates in HRESI-MS of the reaction solution using **3**,

together with the simulated plots.

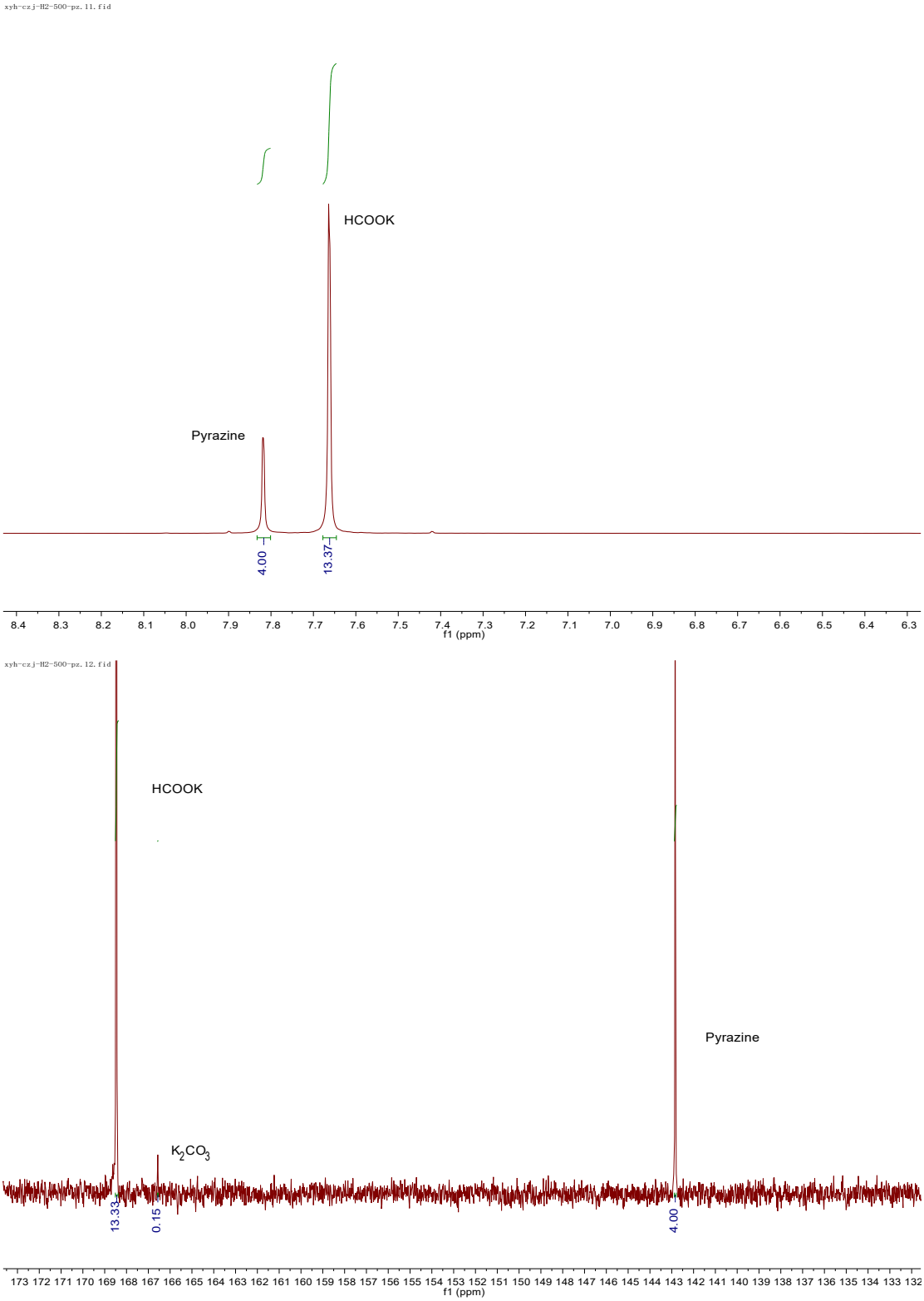



**Figure S32** The quantitative $^{1}H$ NMR and quantitative $^{13}C$ NMR of reaction mixture. $CH_3OH/H_2O$ (8:2 *v*/*v*, 10mL), 8 M KOH, 500 mL $H_2$ generated, entry 1 in Table S3.

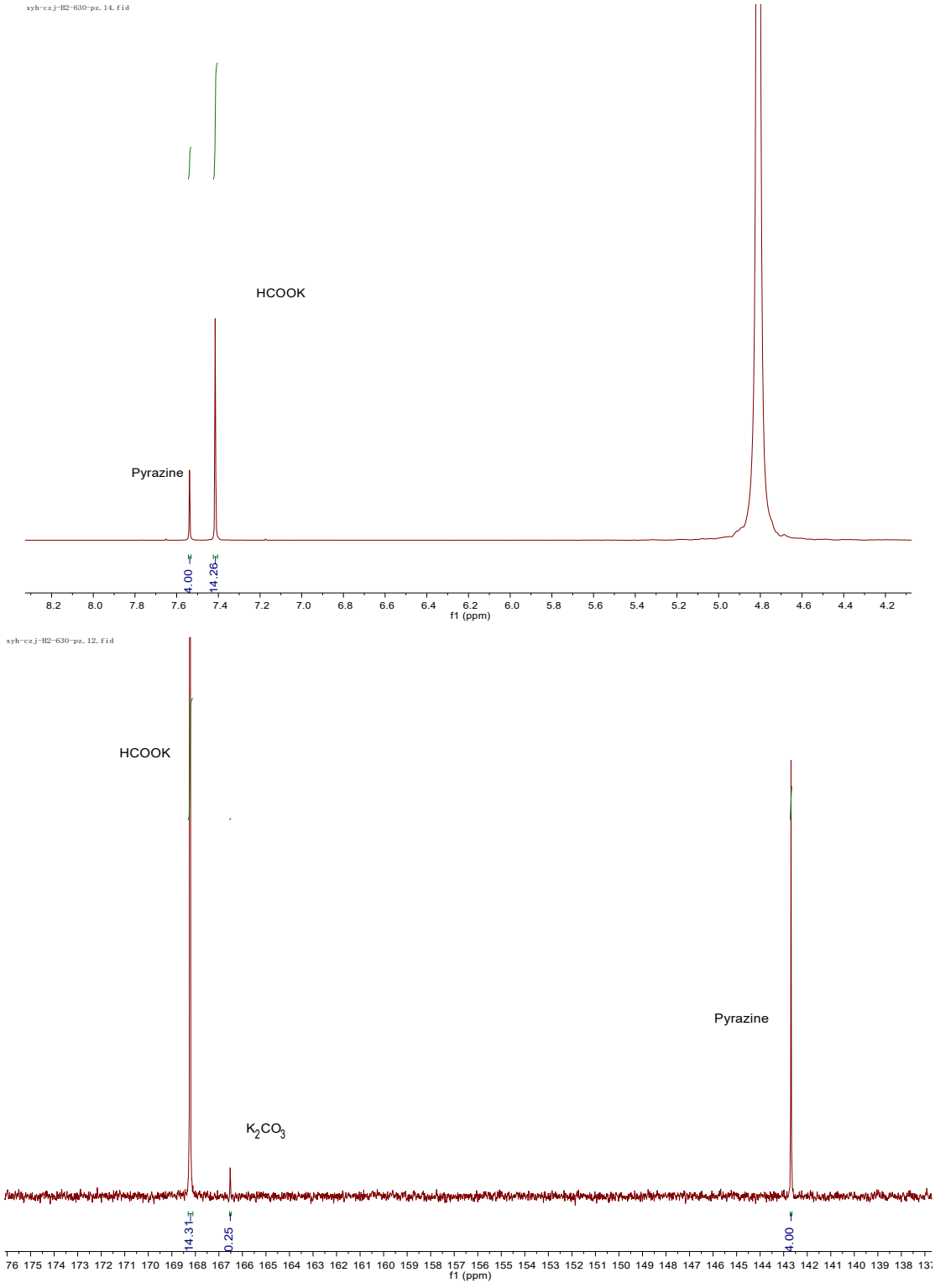



**Figure S33**. The quantitative $^{1}H$ NMR and quantitative $^{13}C$ NMR of reaction mixture. $CH_3OH/H_2O$ (8:2 *v*/*v*, 10mL), 8 M KOH, 630 mL $H_2$ generated, entry 2 in Table S3.

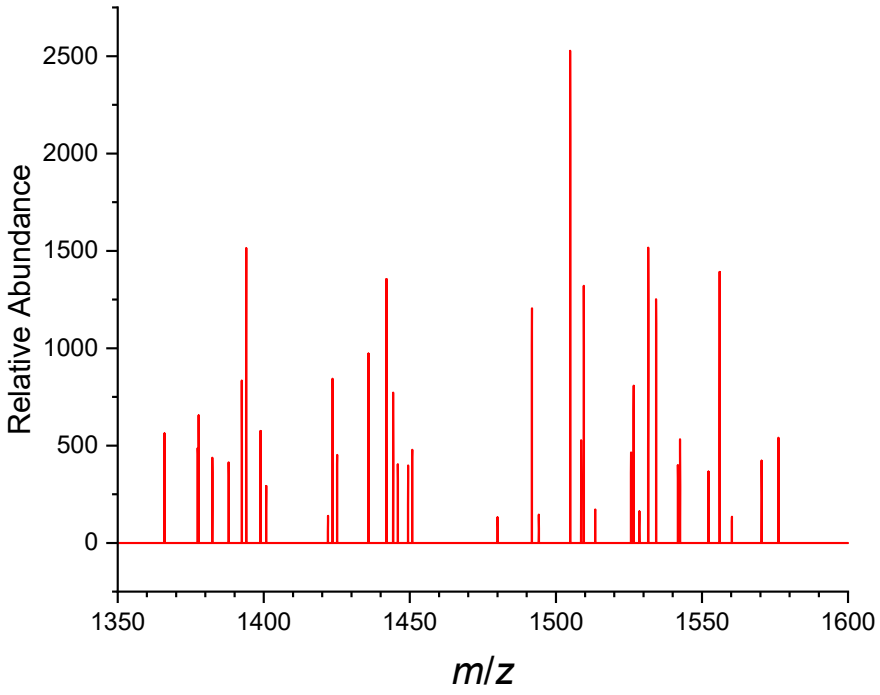



**Figure S34**. HRESI-MS of the reaction solution (1 h) using **2** in the range of 1350-1600 for m/z.

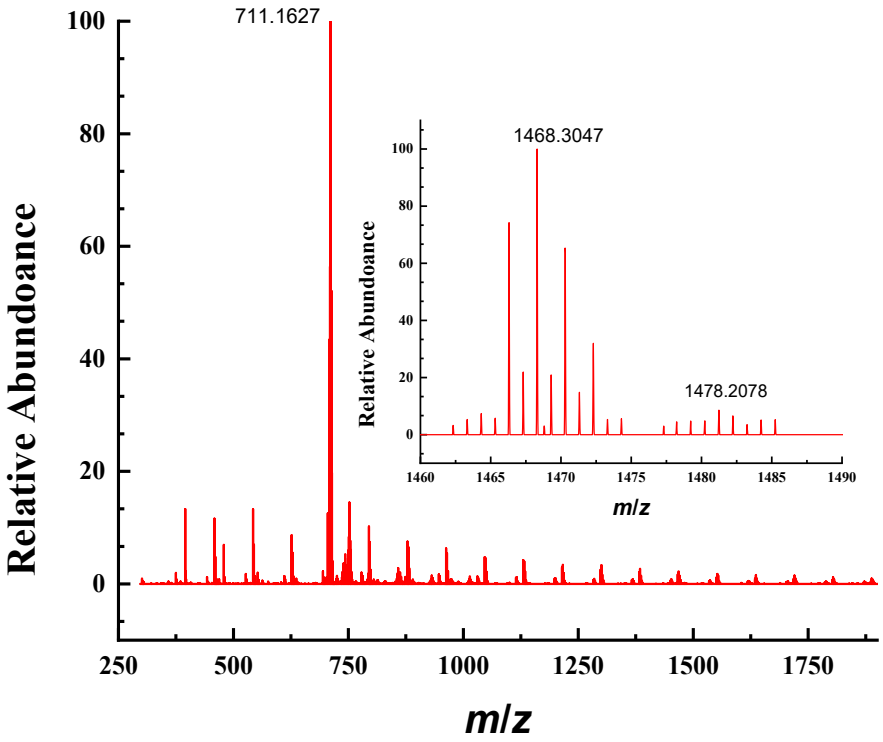



**Figure S35**. HRESI-MS of the reaction solution using **3** in the *m*/*z* range of 250-1900 (10 min). Insert: the partial magnified view in the indicated *m*/*z* range.

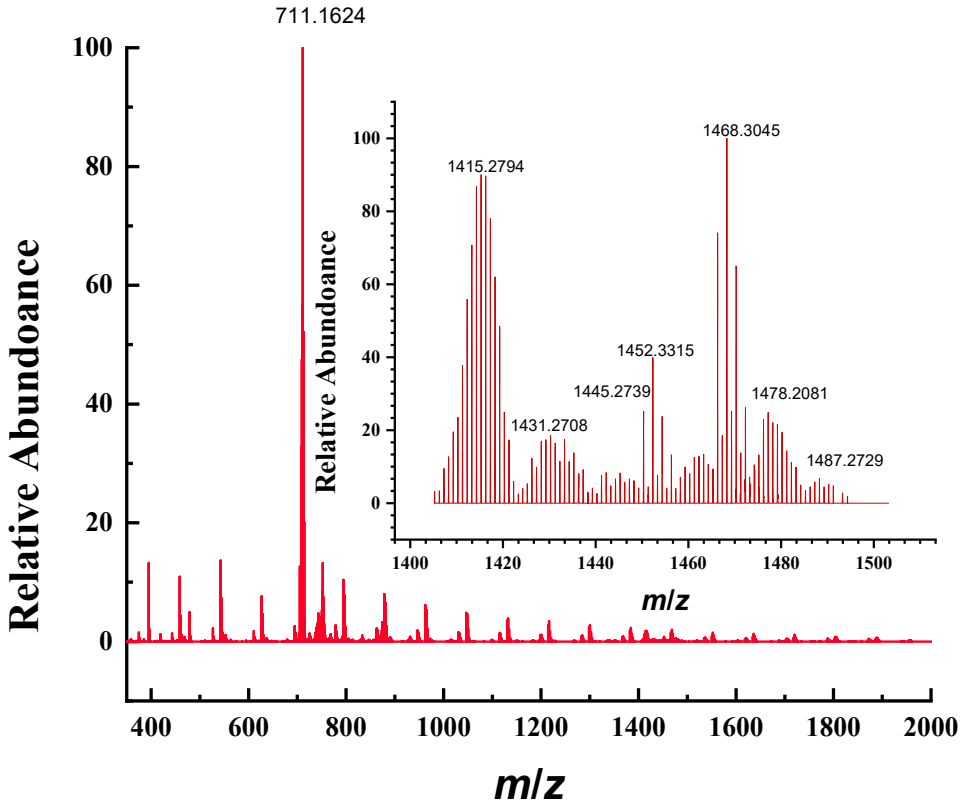



**Figure S36**. HRESI-MS of the reaction solution using **4** in the *m*/*z* range of 400-2000 (10 min). Insert: the partial magnified view in the indicated *m*/*z* range.

## Supplementary Tables

**Table S1.** Selection of different bases for APRM reaction catalysed by **2**.

| entry | Base | Inner *T* / °C | TON | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1h | 2h | 3h | 4h | 5h |
| 1 | 0.12 mol EtONa | 103 | 21 | - | - | - | - |
| 2 | 0.05 mol $^{t}$BuOK | 88 | 10 | 41 | 72 | 93 | 109 |
| 3 | 8 M HCOOK | 84 | 59 | 78 | 98 | 105 | 121 |
| 4 | 8 M HCOONa | 103 | 8 | 27 | - | - | - |
| 5 | 8 M NaOH | 100 | 129 | 191 | 227 | 253 | 279 |
| 6 | 8 M KOH | 112 | 1066 | 1558 | 1884 | 2138 | 2319 |
| 7 | 0.05 mol $Et_3N$ | 76 | 50 | - | - | - | - |

[a] Reaction conditions: MeOH/$H_2O$ = 8:2 (10 mL), triglyme (5 mL), catalyst (4 μmol), 5 hours, $T_{Set}$ = 120 °C.

**Table S2.** Dehydrogenation of ethanol, glycol and formic catalyzed by **2**.

| Entry | | TON | |
|---|---|---|---|
| 1 | 5072 (1 h) | 9196 (3 h) | 12907 (5 h) |
| 2 | 2686 (20 min) | 5134 (40 min) | 6706 (1 h) |
| 3 | 401 (1 h) | 746 (3 h) | 1136 (5 h) |
| 4 | 878 (1 h) | 4070 (3 h) | 4473 (5 h) |

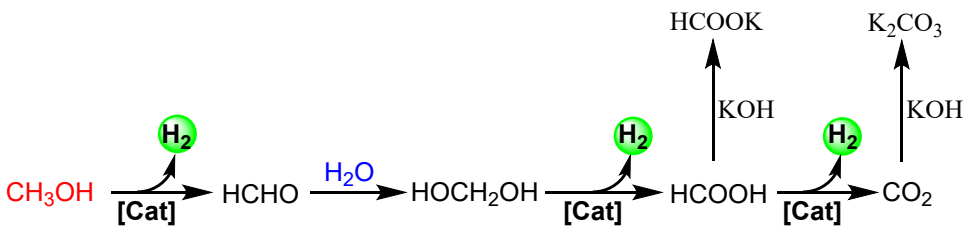
[a] Reaction condition: (1) 8 ml EtOH, 2 ml $H_2O$, 5 ml triglyme, 8M KOH, 1 μmol catalyst, 100 °C; (2) 8 ml EtOH, 2 ml $H_2O$, 5 ml triglyme, 8M KOH, 4 μmol catalyst, 120 °C; (3) 8 ml glycol, 2 ml $H_2O$, 5 ml triglyme, 8M KOH, 4 μmol catalyst, 120 °C; (4) 8 ml HCOOH, 20 ml triethylamine, 2 ml triglyme, 1 μmol catalyst, 120 °C.

**Table S3.** Comparison of hydrogen generation calculated from HCOOK and $K_2CO_3$ production with it from quantitative $^1$H NMR and quantitative $^{13}$C NMR through two independent experiments.

| Entry | $V(H_2)$/mL | $H_2$ generation calculated from HCOOK/mL | $H_2$ generation calculated from $K_2CO_3$ /mL | Deviation[c] |
|---|---|---|---|---|
| 1 | 500 | 491[a] | 8.29[b] | 0.142% |
| | | 493[b] | 8.29[b] | 0.258% |
| 2 | 630 | 618[a] | 16.3[b] | 0.682% |
| | | 621[b] | 16.3[b] | 1.16% |

Reaction conditions: $CH_3OH/H_2O$ (8:2 *v*/*v*, 10mL), KOH (8 M ). a. quantitative $^1$H NMR; b. quantitative $^{13}$C NMR; c. the deviation was calculated by the differences between the amount of $H_2$ measured by using a gas burette and the combined volume calculated based on the amount of HCOOK and $K_2CO_3$.

**Scheme S1**. Aqueous-phase methanol reforming (APRM) process in the presence of KOH.



## Crystallography Information

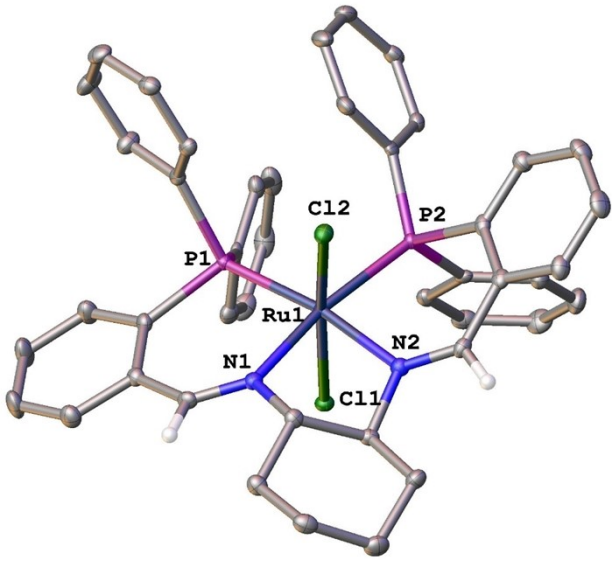



**Figure S30.** ORTEP diagrams of the molecular structures of **1**. Ellipsoids are set at 50% probability.

**Table S3. Crystal data and structure refinement for 1.**

| Identification code | **1** |
|---|---|
| Empirical formula | $C_{45}H_{42}Cl_4N_2P_2Ru$ |
| Formula weight | 915.62 |
| Temperature/K | 101.84 |
| Crystal system | triclinic |
| Space group | *P*-1 |
| *a*/Å | 10.7329(4) |
| *b*/Å | 12.9445(5) |
| *c*/Å | 14.7579(5) |
| *α*/° | 93.7350(10) |
| *β*/° | 98.0700(10) |
| *γ*/° | 91.9380(10) |
| Volume/Å$^3$ | 2023.81(13) |
| *Z* | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.503 |
| $\mu$/mm$^{-1}$ | 0.766 |
| *F*(000) | 936.0 |
| Crystal size/mm$^3$ | 0.17 × 0.13 × 0.08 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 4.86 to 50.02 |

| | |
|---|---|
| Index ranges | $-12 \le h \le 12$, $-15 \le k \le 15$, $-17 \le l \le 17$ |
| Reflections collected | 24441 |
| Independent reflections | 7126 [$R_{int}$ = 0.0449, $R_{sigma}$ = 0.0421] |
| Data/restraints/parameters | 7126/65/514 |
| Goodness-of-fit on $F^2$ | 1.048 |
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0477, $wR_2$ = 0.1194 |
| Final R indexes [all data] | $R_1$ = 0.0535, $wR_2$ = 0.1238 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.07/-1.70 |

**Table S4. Bond Lengths for 1.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ru1 | Cl1 | 2.4019(9) | C17 | C18 | 1.377(6) |
| Ru1 | Cl2 | 2.4532(10) | C18 | C19 | 1.404(6) |
| Ru1 | P1 | 2.3130(10) | C19 | C20 | 1.464(6) |
| Ru1 | P2 | 2.2880(11) | C21 | C22 | 1.526(6) |
| Ru1 | N1 | 2.096(3) | C21 | C26 | 1.544(6) |
| Ru1 | N2 | 2.103(3) | C22 | C23 | 1.524(6) |
| P1 | C1 | 1.848(4) | C23 | C24 | 1.519(6) |
| P1 | C7 | 1.838(4) | C24 | C25 | 1.525(6) |
| P1 | C14 | 1.846(4) | C25 | C26 | 1.528(5) |
| P2 | C33 | 1.839(4) | C27 | C28 | 1.467(6) |
| P2 | C34 | 1.844(4) | C28 | C29 | 1.403(6) |
| P2 | C40 | 1.840(4) | C28 | C33 | 1.413(6) |
| N1 | C20 | 1.282(5) | C29 | C30 | 1.387(6) |
| N1 | C21 | 1.490(5) | C30 | C31 | 1.380(7) |
| N2 | C26 | 1.488(5) | C31 | C32 | 1.395(6) |
| N2 | C27 | 1.281(5) | C32 | C33 | 1.388(6) |
| C1 | C2 | 1.397(6) | C34 | C35 | 1.395(6) |
| C1 | C6 | 1.403(6) | C34 | C39 | 1.401(6) |
| C2 | C3 | 1.392(6) | C35 | C36 | 1.389(6) |
| C3 | C4 | 1.382(6) | C36 | C37 | 1.384(7) |
| C4 | C5 | 1.390(6) | C37 | C38 | 1.391(7) |
| C5 | C6 | 1.387(6) | C38 | C39 | 1.386(6) |
| C7 | C8 | 1.395(6) | C40 | C41 | 1.398(6) |
| C7 | C13 | 1.399(6) | C40 | C45 | 1.395(6) |
| C8 | C9 | 1.392(6) | C41 | C42 | 1.393(6) |
| C9 | C10 | 1.381(7) | C42 | C43 | 1.384(6) |
| C10 | C11 | 1.384(7) | C43 | C44 | 1.389(7) |
| C11 | C13 | 1.396(6) | C44 | C45 | 1.392(6) |

| | | | | | |
|---|---|---|---|---|---|
| C14 | C15 | 1.400(6) | Cl1S | C1S | 1.56(3) |
| C14 | C19 | 1.407(6) | Cl2S | C1S | 2.12(3) |
| C15 | C16 | 1.383(6) | Cl3S | C2S | 1.54(3) |
| C16 | C17 | 1.386(7) | Cl4S | C2S | 1.94(3) |

**Table S5. Bond Angles for 1.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Cl1 | Ru1 | Cl2 | 168.14(3) | C15 | C14 | C19 | 117.7(4) |
| P1 | Ru1 | Cl1 | 86.64(3) | C19 | C14 | P1 | 122.5(3) |
| P1 | Ru1 | Cl2 | 102.81(4) | C16 | C15 | C14 | 122.2(4) |
| P2 | Ru1 | Cl1 | 95.61(4) | C15 | C16 | C17 | 120.2(4) |
| P2 | Ru1 | Cl2 | 90.14(4) | C18 | C17 | C16 | 118.6(4) |
| P2 | Ru1 | P1 | 98.43(4) | C17 | C18 | C19 | 122.4(4) |
| N1 | Ru1 | Cl1 | 84.71(9) | C14 | C19 | C20 | 128.0(4) |
| N1 | Ru1 | Cl2 | 87.79(9) | C18 | C19 | C14 | 119.0(4) |
| N1 | Ru1 | P1 | 91.87(9) | C18 | C19 | C20 | 113.0(4) |
| N1 | Ru1 | P2 | 169.69(10) | N1 | C20 | C19 | 130.1(4) |
| N1 | Ru1 | N2 | 80.61(13) | N1 | C21 | C22 | 115.6(3) |
| N2 | Ru1 | Cl1 | 88.17(9) | N1 | C21 | C26 | 106.4(3) |
| N2 | Ru1 | Cl2 | 81.54(9) | C22 | C21 | C26 | 111.5(3) |
| N2 | Ru1 | P1 | 171.23(9) | C23 | C22 | C21 | 111.9(3) |
| N2 | Ru1 | P2 | 89.10(10) | C24 | C23 | C22 | 110.3(3) |
| C1 | P1 | Ru1 | 124.19(14) | C23 | C24 | C25 | 110.1(4) |
| C7 | P1 | Ru1 | 116.26(13) | C24 | C25 | C26 | 112.0(3) |
| C7 | P1 | C1 | 101.89(19) | N2 | C26 | C21 | 105.5(3) |
| C7 | P1 | C14 | 100.25(18) | N2 | C26 | C25 | 116.0(3) |
| C14 | P1 | Ru1 | 112.10(13) | C25 | C26 | C21 | 111.9(3) |
| C14 | P1 | C1 | 98.33(18) | N2 | C27 | C28 | 128.7(4) |
| C33 | P2 | Ru1 | 109.72(14) | C29 | C28 | C27 | 114.1(4) |
| C33 | P2 | C34 | 101.10(18) | C29 | C28 | C33 | 118.7(4) |
| C33 | P2 | C40 | 102.34(18) | C33 | C28 | C27 | 127.2(4) |
| C34 | P2 | Ru1 | 120.09(13) | C30 | C29 | C28 | 121.2(4) |
| C40 | P2 | Ru1 | 120.17(14) | C31 | C30 | C29 | 119.9(4) |
| C40 | P2 | C34 | 100.53(18) | C30 | C31 | C32 | 119.6(4) |
| C20 | N1 | Ru1 | 131.6(3) | C33 | C32 | C31 | 121.4(4) |
| C20 | N1 | C21 | 117.2(3) | C28 | C33 | P2 | 120.5(3) |
| C21 | N1 | Ru1 | 111.0(2) | C32 | C33 | P2 | 120.3(3) |
| C26 | N2 | Ru1 | 109.8(2) | C32 | C33 | C28 | 119.1(4) |
| C27 | N2 | Ru1 | 130.4(3) | C35 | C34 | P2 | 123.2(3) |
| C27 | N2 | C26 | 119.1(3) | C35 | C34 | C39 | 118.8(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2 | C1 | P1 | 119.0(3) | C39 | C34 | P2 | 117.9(3) |
| C2 | C1 | C6 | 118.2(4) | C36 | C35 | C34 | 120.5(4) |
| C6 | C1 | P1 | 122.7(3) | C37 | C36 | C35 | 120.5(4) |
| C3 | C2 | C1 | 120.7(4) | C36 | C37 | C38 | 119.3(4) |
| C4 | C3 | C2 | 120.6(4) | C39 | C38 | C37 | 120.6(4) |
| C3 | C4 | C5 | 119.4(4) | C38 | C39 | C34 | 120.3(4) |
| C6 | C5 | C4 | 120.4(4) | C41 | C40 | P2 | 123.1(3) |
| C5 | C6 | C1 | 120.8(4) | C45 | C40 | P2 | 117.8(3) |
| C8 | C7 | P1 | 120.6(3) | C45 | C40 | C41 | 119.1(4) |
| C8 | C7 | C13 | 118.8(4) | C42 | C41 | C40 | 120.2(4) |
| C13 | C7 | P1 | 120.5(3) | C43 | C42 | C41 | 120.2(4) |
| C9 | C8 | C7 | 120.3(4) | C42 | C43 | C44 | 120.1(4) |
| C10 | C9 | C8 | 120.5(4) | C43 | C44 | C45 | 120.0(4) |
| C9 | C10 | C11 | 119.7(4) | C44 | C45 | C40 | 120.4(4) |
| C10 | C11 | C13 | 120.4(4) | Cl1S | C1S | Cl2S | 94.6(14) |
| C11 | C13 | C7 | 120.2(4) | Cl3S | C2S | Cl4S | 109.1(16) |
| C15 | C14 | P1 | 119.6(3) | | | | |

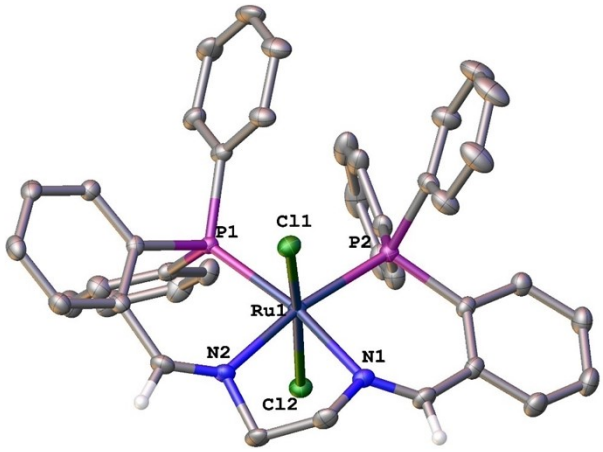



**Figure S31.** ORTEP diagrams of the molecular structures of **2**. Ellipsoids are set at 50% probability.

**Table S6. Crystal data and structure refinement for 2.**

| Identification code | **2** |
|---|---|
| Empirical formula | $C_{45}H_{48}Cl_2N_2O_2P_2Ru$ |
| Formula weight | 882.76 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| *a*/Å | 13.2836(6) |
| *b*/Å | 10.3229(5) |

| | |
|---|---|
| $c$/Å | 29.8771(14) |
| $\alpha$/° | 90 |
| $\beta$/° | 91.870(2) |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 4094.7(3) |
| $Z$ | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.432 |
| $\mu$/mm$^{-1}$ | 0.632 |
| $F$(000) | 1824.0 |
| Crystal size/mm$^3$ | 0.15 × 0.14 × 0.1 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 4.174 to 51.996 |
| Index ranges | $-16 \le h \le 16$, $-12 \le k \le 12$, $-35 \le l \le 36$ |
| Reflections collected | 42943 |
| Independent reflections | 8043 [$R_{int}$ = 0.0876, $R_{sigma}$ = 0.0566] |
| Data/restraints/parameters | 8043/0/491 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0397, $wR_2$ = 0.1009 |
| Final R indexes [all data] | $R_1$ = 0.0467, $wR_2$ = 0.1056 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.26/-0.95 |

**Table S7. Bond Lengths for 2.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ru1 | Cl1 | 2.4179(7) | C14 | C15 | 1.379(4) |
| Ru1 | Cl2 | 2.4076(7) | C15 | C16 | 1.390(5) |
| Ru1 | P1 | 2.2885(7) | C16 | C17 | 1.381(4) |
| Ru1 | P2 | 2.2882(7) | C17 | C18 | 1.404(4) |
| Ru1 | N1 | 2.093(2) | C18 | C19 | 1.462(4) |
| Ru1 | N2 | 2.096(2) | C20 | C21 | 1.512(4) |
| P1 | C6 | 1.843(3) | C22 | C23 | 1.466(4) |
| P1 | C12 | 1.839(3) | C23 | C24 | 1.404(4) |
| P1 | C13 | 1.845(3) | C23 | C28 | 1.409(4) |
| P2 | C28 | 1.838(3) | C24 | C25 | 1.383(4) |
| P2 | C29 | 1.845(3) | C25 | C26 | 1.382(4) |
| P2 | C35 | 1.840(3) | C26 | C27 | 1.390(4) |
| N1 | C21 | 1.475(3) | C27 | C28 | 1.395(4) |
| N1 | C22 | 1.278(4) | C29 | C30 | 1.398(4) |
| N2 | C19 | 1.275(4) | C29 | C34 | 1.397(4) |
| N2 | C20 | 1.479(3) | C30 | C31 | 1.392(4) |
| C1 | C2 | 1.387(4) | C31 | C32 | 1.386(5) |

| | | | | | |
|---|---|---|---|---|---|
| C1 | C6 | 1.412(4) | C32 | C33 | 1.383(5) |
| C2 | C3 | 1.380(5) | C33 | C34 | 1.392(4) |
| C3 | C4 | 1.376(5) | C35 | C36 | 1.394(4) |
| C4 | C5 | 1.404(5) | C35 | C40 | 1.394(4) |
| C5 | C6 | 1.384(4) | C36 | C37 | 1.397(4) |
| C7 | C8 | 1.390(5) | C37 | C38 | 1.376(5) |
| C7 | C12 | 1.398(4) | C38 | C39 | 1.393(5) |
| C8 | C9 | 1.372(5) | C39 | C40 | 1.387(4) |
| C9 | C10 | 1.393(5) | O1S | C3S | 1.477(5) |
| C10 | C11 | 1.388(4) | O1S | C4S | 1.434(6) |
| C11 | C12 | 1.401(4) | C2S | C3S | 1.468(8) |
| C13 | C14 | 1.399(4) | C4S | C5S | 1.390(8) |
| C13 | C18 | 1.411(4) | O2S | C1S | 1.391(6) |

**Table S8. Bond Angles for 2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Cl2 | Ru1 | Cl1 | 170.67(2) | C7 | C12 | P1 | 123.1(2) |
| P1 | Ru1 | Cl1 | 98.17(2) | C7 | C12 | C11 | 118.6(3) |
| P1 | Ru1 | Cl2 | 89.05(2) | C11 | C12 | P1 | 117.9(2) |
| P2 | Ru1 | Cl1 | 89.40(2) | C14 | C13 | P1 | 118.4(2) |
| P2 | Ru1 | Cl2 | 95.09(3) | C14 | C13 | C18 | 117.9(3) |
| P2 | Ru1 | P1 | 100.68(3) | C18 | C13 | P1 | 123.5(2) |
| N1 | Ru1 | Cl1 | 84.08(7) | C15 | C14 | C13 | 122.4(3) |
| N1 | Ru1 | Cl2 | 87.87(7) | C14 | C15 | C16 | 119.4(3) |
| N1 | Ru1 | P1 | 170.68(7) | C17 | C16 | C15 | 119.8(3) |
| N1 | Ru1 | P2 | 88.36(7) | C16 | C17 | C18 | 121.2(3) |
| N1 | Ru1 | N2 | 81.17(9) | C13 | C18 | C19 | 126.4(3) |
| N2 | Ru1 | Cl1 | 89.25(6) | C17 | C18 | C13 | 119.3(3) |
| N2 | Ru1 | Cl2 | 84.84(6) | C17 | C18 | C19 | 114.3(3) |
| N2 | Ru1 | P1 | 89.80(6) | N2 | C19 | C18 | 128.7(3) |
| N2 | Ru1 | P2 | 169.52(6) | N2 | C20 | C21 | 107.0(2) |
| C6 | P1 | Ru1 | 118.69(9) | N1 | C21 | C20 | 107.0(2) |
| C6 | P1 | C13 | 96.17(13) | N1 | C22 | C23 | 128.0(3) |
| C12 | P1 | Ru1 | 117.03(9) | C24 | C23 | C22 | 114.3(2) |
| C12 | P1 | C6 | 108.99(13) | C24 | C23 | C28 | 119.1(3) |
| C12 | P1 | C13 | 99.84(13) | C28 | C23 | C22 | 126.5(2) |
| C13 | P1 | Ru1 | 112.57(9) | C25 | C24 | C23 | 121.5(3) |
| C28 | P2 | Ru1 | 111.14(9) | C26 | C25 | C24 | 119.4(3) |
| C28 | P2 | C29 | 102.05(12) | C25 | C26 | C27 | 120.0(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C28 | P2 | C35 | 101.08(12) | C26 | C27 | C28 | 121.6(3) |
| C29 | P2 | Ru1 | 119.51(10) | C23 | C28 | P2 | 121.2(2) |
| C35 | P2 | Ru1 | 118.88(9) | C27 | C28 | P2 | 120.2(2) |
| C35 | P2 | C29 | 101.44(13) | C27 | C28 | C23 | 118.4(2) |
| C21 | N1 | Ru1 | 109.34(16) | C30 | C29 | P2 | 117.7(2) |
| C22 | N1 | Ru1 | 133.25(19) | C34 | C29 | P2 | 123.1(2) |
| C22 | N1 | C21 | 116.8(2) | C34 | C29 | C30 | 119.2(3) |
| C19 | N2 | Ru1 | 133.2(2) | C31 | C30 | C29 | 120.0(3) |
| C19 | N2 | C20 | 116.5(2) | C32 | C31 | C30 | 120.4(3) |
| C20 | N2 | Ru1 | 109.27(17) | C33 | C32 | C31 | 119.9(3) |
| C2 | C1 | C6 | 121.5(3) | C32 | C33 | C34 | 120.3(3) |
| C3 | C2 | C1 | 119.3(3) | C33 | C34 | C29 | 120.1(3) |
| C4 | C3 | C2 | 120.4(3) | C36 | C35 | P2 | 123.4(2) |
| C3 | C4 | C5 | 120.5(3) | C40 | C35 | P2 | 118.1(2) |
| C6 | C5 | C4 | 120.2(3) | C40 | C35 | C36 | 118.3(3) |
| C1 | C6 | P1 | 113.2(2) | C35 | C36 | C37 | 120.8(3) |
| C5 | C6 | P1 | 128.7(2) | C38 | C37 | C36 | 120.1(3) |
| C5 | C6 | C1 | 118.0(3) | C37 | C38 | C39 | 119.7(3) |
| C8 | C7 | C12 | 120.1(3) | C40 | C39 | C38 | 120.1(3) |
| C9 | C8 | C7 | 120.8(3) | C39 | C40 | C35 | 120.9(3) |
| C8 | C9 | C10 | 120.0(3) | C4S | O1S | C3S | 109.4(4) |
| C11 | C10 | C9 | 119.7(3) | C2S | C3S | O1S | 109.5(4) |
| C10 | C11 | C12 | 120.8(3) | C5S | C4S | O1S | 113.0(5) |

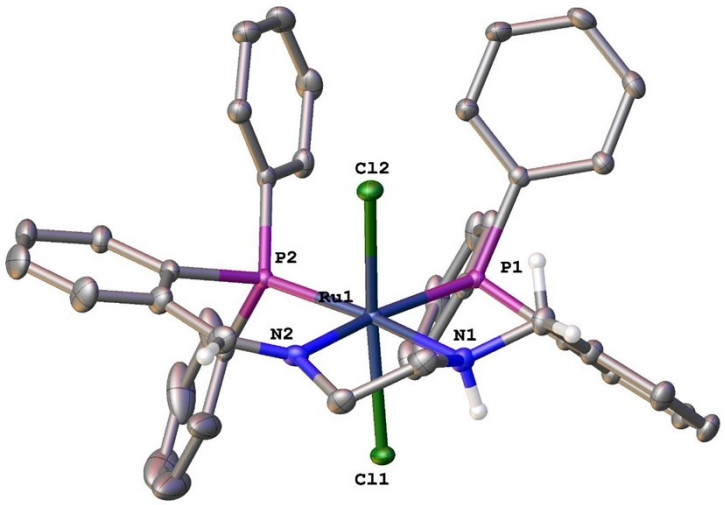



**Figure S32.** ORTEP diagrams of the molecular structures of **3**. Ellipsoids are set at 50% probability.

**Table S9. Crystal data and structure refinement for 3.**

| Identification code | **3** |
|---|---|
| Empirical formula | $C_{42.96}H_{43.23}Cl_{2.69}N_2O_{0.65}P_2Ru$ |
| Formula weight | 856.48 |
| Temperature/K | 100.02 |
| Crystal system | monoclinic |
| Space group | *C*2/c |
| *a*/Å | 39.124(3) |
| *b*/Å | 10.1523(8) |
| *c*/Å | 24.618(2) |
| *α*/° | 90 |
| *β*/° | 123.769(2) |
| *γ*/° | 90 |
| Volume/Å$^3$ | 8128.5(11) |
| *Z* | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.400 |
| $\mu$/mm$^{-1}$ | 0.676 |
| *F*(000) | 3520.0 |
| Crystal size/mm$^3$ | 0.38 × 0.26 × 0.2 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| 2*Θ* range for data collection/° | 4.202 to 55.132 |
| Index ranges | $-45 \le h \le 50$, $-12 \le k \le 13$, $-32 \le l \le 32$ |
| Reflections collected | 35457 |
| Independent reflections | 9176 [$R_{int}$ = 0.0582, $R_{sigma}$ = 0.0507] |
| Data/restraints/parameters | 9176/28/499 |
| Goodness-of-fit on $F^2$ | 1.067 |
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0427, $wR_2$ = 0.1103 |
| Final R indexes [all data] | $R_1$ = 0.0431, $wR_2$ = 0.1107 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.54/-0.89 |

**Table S10. Bond Lengths for 3.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ru1 | Cl1 | 2.4210(6) | C15 | C16 | 1.380(4) |
| Ru1 | Cl2 | 2.4078(6) | C16 | C17 | 1.390(4) |
| Ru1 | P1 | 2.3117(6) | C17 | C18 | 1.396(3) |
| Ru1 | P2 | 2.2657(6) | C18 | C19 | 1.508(3) |
| Ru1 | N1 | 2.178(2) | C20 | C21 | 1.512(4) |
| Ru1 | N2 | 2.087(2) | C22 | C23 | 1.459(4) |
| P1 | C1 | 1.833(2) | C23 | C24 | 1.404(4) |

| | | | | | |
|---|---|---|---|---|---|
| P1 | C7 | 1.835(2) | C23 | C28 | 1.411(4) |
| P1 | C13 | 1.838(2) | C24 | C25 | 1.380(4) |
| P2 | C28 | 1.841(2) | C25 | C26 | 1.383(4) |
| P2 | C29 | 1.836(2) | C26 | C27 | 1.389(4) |
| P2 | C35 | 1.839(3) | C27 | C28 | 1.401(3) |
| N1 | C19 | 1.479(3) | C29 | C30 | 1.399(3) |
| N1 | C20 | 1.482(3) | C29 | C34 | 1.403(3) |
| N2 | C21 | 1.476(3) | C30 | C31 | 1.396(4) |
| N2 | C22 | 1.276(3) | C31 | C32 | 1.383(4) |
| C1 | C2 | 1.400(3) | C32 | C33 | 1.383(4) |
| C1 | C6 | 1.400(3) | C33 | C34 | 1.398(4) |
| C2 | C3 | 1.390(4) | C35 | C36 | 1.380(4) |
| C3 | C4 | 1.389(5) | C35 | C40 | 1.411(4) |
| C4 | C5 | 1.388(5) | C36 | C37 | 1.419(5) |
| C5 | C6 | 1.389(4) | C37 | C38 | 1.395(8) |
| C7 | C8 | 1.395(3) | C38 | C39 | 1.386(7) |
| C7 | C12 | 1.400(3) | C39 | C40 | 1.388(5) |
| C8 | C9 | 1.391(3) | Cl1S | C5S | 1.750(15) |
| C9 | C10 | 1.377(4) | Cl2S | C5S | 1.959(17) |
| C10 | C11 | 1.384(4) | O1S | C2S | 1.442(9) |
| C11 | C12 | 1.390(3) | O1S | C3S | 1.305(7) |
| C13 | C14 | 1.395(3) | C1S | C2S | 1.422(9) |
| C13 | C18 | 1.405(3) | C3S | C4S | 1.589(9) |
| C14 | C15 | 1.396(3) | | | |

**Table S11. Bond Angles for 3.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Cl2 | Ru1 | Cl1 | 168.30(2) | C10 | C11 | C12 | 121.2(2) |
| P1 | Ru1 | Cl1 | 90.44(2) | C11 | C12 | C7 | 119.7(2) |
| P1 | Ru1 | Cl2 | 94.38(2) | C14 | C13 | P1 | 121.79(18) |
| P2 | Ru1 | Cl1 | 98.14(2) | C14 | C13 | C18 | 119.2(2) |
| P2 | Ru1 | Cl2 | 91.56(2) | C18 | C13 | P1 | 118.96(18) |
| P2 | Ru1 | P1 | 99.72(2) | C13 | C14 | C15 | 120.9(2) |
| N1 | Ru1 | Cl1 | 81.39(6) | C16 | C15 | C14 | 120.0(2) |
| N1 | Ru1 | Cl2 | 88.09(6) | C15 | C16 | C17 | 119.6(2) |
| N1 | Ru1 | P1 | 88.34(6) | C16 | C17 | C18 | 121.4(2) |
| N1 | Ru1 | P2 | 171.93(6) | C13 | C18 | C19 | 121.8(2) |
| N2 | Ru1 | Cl1 | 89.63(6) | C17 | C18 | C13 | 119.1(2) |
| N2 | Ru1 | Cl2 | 83.60(6) | C17 | C18 | C19 | 119.1(2) |
| N2 | Ru1 | P1 | 168.99(6) | N1 | C19 | C18 | 109.2(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N2 | Ru1 | P2 | 91.16(6) | N1 | C20 | C21 | 106.8(2) |
| N2 | Ru1 | N1 | 80.79(8) | N2 | C21 | C20 | 109.29(19) |
| C1 | P1 | Ru1 | 120.54(8) | N2 | C22 | C23 | 128.6(2) |
| C1 | P1 | C7 | 100.70(11) | C24 | C23 | C22 | 114.1(2) |
| C1 | P1 | C13 | 102.72(11) | C24 | C23 | C28 | 119.1(2) |
| C7 | P1 | Ru1 | 119.45(8) | C28 | C23 | C22 | 126.7(2) |
| C7 | P1 | C13 | 100.18(10) | C25 | C24 | C23 | 121.9(3) |
| C13 | P1 | Ru1 | 110.27(8) | C24 | C25 | C26 | 119.2(3) |
| C28 | P2 | Ru1 | 113.33(8) | C25 | C26 | C27 | 119.9(3) |
| C29 | P2 | Ru1 | 117.87(8) | C26 | C27 | C28 | 122.0(3) |
| C29 | P2 | C28 | 100.22(11) | C23 | C28 | P2 | 123.78(19) |
| C29 | P2 | C35 | 106.83(12) | C27 | C28 | P2 | 118.29(19) |
| C35 | P2 | Ru1 | 118.94(9) | C27 | C28 | C23 | 117.9(2) |
| C35 | P2 | C28 | 96.03(11) | C30 | C29 | P2 | 118.86(18) |
| C19 | N1 | Ru1 | 118.57(15) | C30 | C29 | C34 | 118.4(2) |
| C19 | N1 | C20 | 113.91(19) | C34 | C29 | P2 | 122.34(19) |
| C20 | N1 | Ru1 | 106.93(15) | C31 | C30 | C29 | 121.0(2) |
| C21 | N2 | Ru1 | 110.61(15) | C32 | C31 | C30 | 119.8(3) |
| C22 | N2 | Ru1 | 133.20(18) | C31 | C32 | C33 | 120.2(2) |
| C22 | N2 | C21 | 115.6(2) | C32 | C33 | C34 | 120.4(3) |
| C2 | C1 | P1 | 118.55(19) | C33 | C34 | C29 | 120.2(3) |
| C6 | C1 | P1 | 122.47(19) | C36 | C35 | P2 | 126.6(2) |
| C6 | C1 | C2 | 118.9(2) | C36 | C35 | C40 | 119.4(3) |
| C3 | C2 | C1 | 120.4(3) | C40 | C35 | P2 | 114.0(2) |
| C4 | C3 | C2 | 120.2(3) | C35 | C36 | C37 | 119.4(4) |
| C5 | C4 | C3 | 119.9(3) | C38 | C37 | C36 | 120.2(4) |
| C4 | C5 | C6 | 120.2(3) | C39 | C38 | C37 | 120.3(3) |
| C5 | C6 | C1 | 120.4(3) | C38 | C39 | C40 | 119.4(4) |
| C8 | C7 | P1 | 122.34(18) | C39 | C40 | C35 | 121.2(4) |
| C8 | C7 | C12 | 118.6(2) | Cl1S | C5S | Cl2S | 95.4(7) |
| C12 | C7 | P1 | 118.81(17) | C3S | O1S | C2S | 106.5(6) |
| C9 | C8 | C7 | 121.0(2) | C1S | C2S | O1S | 101.2(6) |
| C10 | C9 | C8 | 120.1(2) | O1S | C3S | C4S | 103.3(5) |
| C9 | C10 | C11 | 119.5(2) | | | | |

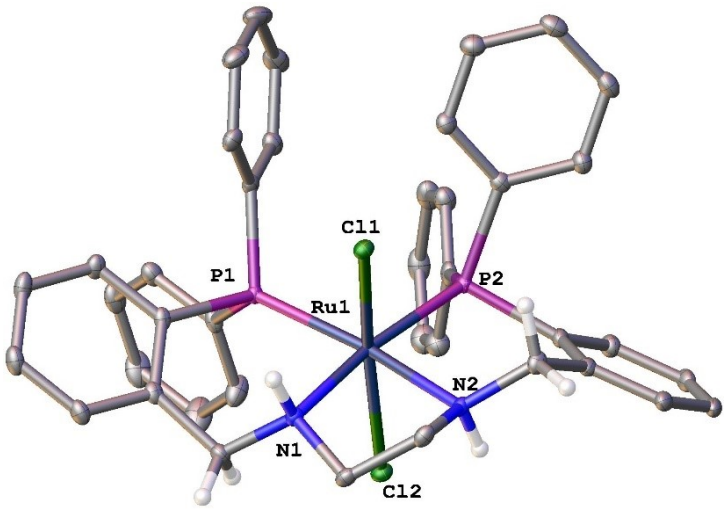



**Figure S33.** ORTEP diagrams of the molecular structures of **4**. Ellipsoids are set at 50% probability.

**Table S12. Crystal data and structure refinement for 4.**

| Identification code | **4** |
|---|---|
| Empirical formula | $C_{41}H_{40}Cl_4N_2P_2Ru$ |
| Formula weight | 865.56 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a$/Å | 10.7044(4) |
| $b$/Å | 15.6123(6) |
| $c$/Å | 23.0008(10) |
| $\alpha$/° | 90 |
| $\beta$/° | 95.634(2) |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 3825.3(3) |
| $Z$ | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.503 |
| $\mu$/mm$^{-1}$ | 0.806 |
| $F$(000) | 1768.0 |
| Crystal size/mm$^3$ | 0.18 × 0.09 × 0.08 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 4.372 to 55.058 |
| Index ranges | $-13 \le h \le 13$, $-20 \le k \le 19$, $-29 \le l \le 29$ |
| Reflections collected | 37085 |
| Independent reflections | 8795 [$R_{int}$ = 0.0404, $R_{sigma}$ = 0.0342] |
| Data/restraints/parameters | 8795/0/451 |
| Goodness-of-fit on $F^2$ | 1.025 |

| | |
|---|---|
| Final R indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0236, $wR_2$ = 0.0613 |
| Final R indexes [all data] | $R_1$ = 0.0249, $wR_2$ = 0.0623 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.37/-0.53 |

**Table S13. Bond Lengths for 4.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ru1 | Cl1 | 2.4032(3) | C13 | C18 | 1.407(2) |
| Ru1 | Cl2 | 2.4422(3) | C14 | C15 | 1.390(2) |
| Ru1 | P1 | 2.2936(4) | C15 | C16 | 1.389(2) |
| Ru1 | P2 | 2.2937(4) | C16 | C17 | 1.383(2) |
| Ru1 | N1 | 2.1517(12) | C17 | C18 | 1.405(2) |
| Ru1 | N2 | 2.1610(12) | C18 | C19 | 1.507(2) |
| P1 | C1 | 1.8329(15) | C20 | C21 | 1.516(2) |
| P1 | C7 | 1.8520(15) | C22 | C23 | 1.515(2) |
| P1 | C13 | 1.8612(15) | C23 | C24 | 1.397(2) |
| P2 | C28 | 1.8458(15) | C23 | C28 | 1.411(2) |
| P2 | C29 | 1.8518(16) | C24 | C25 | 1.396(2) |
| P2 | C35 | 1.8401(15) | C25 | C26 | 1.387(2) |
| N1 | C19 | 1.4811(18) | C26 | C27 | 1.392(2) |
| N1 | C20 | 1.4918(18) | C27 | C28 | 1.399(2) |
| N2 | C21 | 1.4870(18) | C29 | C30 | 1.402(2) |
| N2 | C22 | 1.4824(19) | C29 | C34 | 1.398(2) |
| C1 | C2 | 1.400(2) | C30 | C31 | 1.394(2) |
| C1 | C6 | 1.403(2) | C31 | C32 | 1.388(2) |
| C2 | C3 | 1.388(2) | C32 | C33 | 1.391(2) |
| C3 | C4 | 1.392(3) | C33 | C34 | 1.396(2) |
| C4 | C5 | 1.389(3) | C35 | C36 | 1.396(2) |
| C5 | C6 | 1.391(2) | C35 | C40 | 1.405(2) |
| C7 | C8 | 1.405(2) | C36 | C37 | 1.397(2) |
| C7 | C12 | 1.390(2) | C37 | C38 | 1.388(3) |
| C8 | C9 | 1.389(2) | C38 | C39 | 1.385(3) |
| C9 | C10 | 1.390(3) | C39 | C40 | 1.393(2) |
| C10 | C11 | 1.384(3) | Cl1S | C1S | 1.767(2) |
| C11 | C12 | 1.401(2) | Cl2S | C1S | 1.7667(18) |
| C13 | C14 | 1.407(2) | | | |

**Table S14. Bond Angles for 4.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Cl1 | Ru1 | Cl2 | 164.959(12) | C8 | C9 | C10 | 120.01(15) |
| P1 | Ru1 | Cl1 | 90.295(13) | C11 | C10 | C9 | 119.80(15) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| P1 | Ru1 | Cl2 | 101.097(13) | C10 | C11 | C12 | 120.38(17) |
| A | Ru1 | P2 | 99.544(13) | C7 | C12 | C11 | 120.30(16) |
| P2 | Ru1 | Cl1 | 95.069(13) | C14 | C13 | P1 | 120.60(11) |
| P2 | Ru1 | Cl2 | 92.706(13) | C18 | C13 | P1 | 121.09(11) |
| N1 | Ru1 | Cl1 | 83.72(3) | C18 | C13 | C14 | 118.06(13) |
| N1 | Ru1 | Cl2 | 86.47(3) | C15 | C14 | C13 | 121.91(14) |
| N1 | Ru1 | P1 | 89.98(3) | C16 | C15 | C14 | 119.66(14) |
| N1 | Ru1 | P2 | 170.42(3) | C17 | C16 | C15 | 119.36(14) |
| N1 | Ru1 | N2 | 80.54(5) | C16 | C17 | C18 | 121.75(14) |
| N2 | Ru1 | Cl1 | 86.66(3) | C13 | C18 | C19 | 123.96(13) |
| N2 | Ru1 | Cl2 | 80.49(3) | C17 | C18 | C13 | 119.25(13) |
| N2 | Ru1 | P1 | 170.30(3) | C17 | C18 | C19 | 116.79(13) |
| N2 | Ru1 | P2 | 89.91(3) | N1 | C19 | C18 | 111.54(12) |
| C1 | P1 | Ru1 | 116.20(5) | N1 | C20 | C21 | 107.64(12) |
| C1 | P1 | C7 | 100.54(7) | N2 | C21 | C20 | 106.86(11) |
| C1 | P1 | C13 | 102.01(7) | N2 | C22 | C23 | 109.48(11) |
| C7 | P1 | Ru1 | 125.55(5) | C24 | C23 | C22 | 118.04(13) |
| C7 | P1 | C13 | 96.06(6) | C24 | C23 | C28 | 119.18(14) |
| C13 | P1 | Ru1 | 112.52(5) | C28 | C23 | C22 | 122.77(13) |
| C28 | P2 | Ru1 | 110.36(5) | C25 | C24 | C23 | 121.26(14) |
| C28 | P2 | C29 | 98.50(7) | C26 | C25 | C24 | 119.61(14) |
| C29 | P2 | Ru1 | 121.70(5) | C25 | C26 | C27 | 119.66(14) |
| C35 | P2 | Ru1 | 118.68(5) | C26 | C27 | C28 | 121.51(14) |
| C35 | P2 | C28 | 102.46(7) | C23 | C28 | P2 | 119.49(11) |
| C35 | P2 | C29 | 101.83(7) | C27 | C28 | P2 | 121.54(11) |
| C19 | N1 | Ru1 | 117.52(9) | C27 | C28 | C23 | 118.76(13) |
| C19 | N1 | C20 | 111.68(11) | C30 | C29 | P2 | 121.42(12) |
| C20 | N1 | Ru1 | 108.31(8) | C34 | C29 | P2 | 120.19(11) |
| C21 | N2 | Ru1 | 107.69(8) | C34 | C29 | C30 | 118.35(14) |
| C22 | N2 | Ru1 | 118.01(9) | C31 | C30 | C29 | 120.98(14) |
| C22 | N2 | C21 | 113.36(11) | C32 | C31 | C30 | 120.07(15) |
| C2 | C1 | P1 | 120.34(11) | C31 | C32 | C33 | 119.57(15) |
| C2 | C1 | C6 | 118.73(14) | C32 | C33 | C34 | 120.50(15) |
| C6 | C1 | P1 | 120.68(11) | C33 | C34 | C29 | 120.51(14) |
| C3 | C2 | C1 | 120.47(14) | C36 | C35 | P2 | 123.02(12) |
| C2 | C3 | C4 | 120.35(15) | C36 | C35 | C40 | 118.65(14) |
| C5 | C4 | C3 | 119.79(15) | C40 | C35 | P2 | 118.28(11) |
| C4 | C5 | C6 | 120.11(15) | C35 | C36 | C37 | 120.55(15) |
| C5 | C6 | C1 | 120.55(14) | C38 | C37 | C36 | 120.21(15) |
| C8 | C7 | P1 | 120.31(11) | C39 | C38 | C37 | 119.70(14) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | C7 | P1 | 120.53(12) | C38 | C39 | C40 | 120.49(16) |
| C12 | C7 | C8 | 118.73(14) | C39 | C40 | C35 | 120.35(15) |
| C9 | C8 | C7 | 120.76(15) | Cl2S | C1S | Cl1S | 112.13(10) |